ヨウ化テトラフルオロポリスチレン誘導体の合成と不均一系求核触媒反応への応用：４−アミノピリジンペンダント型高分子触媒の開発

堀　達暁

博士（理学）

総合研究大学院大学

物理科学研究科

機能分子科学専攻

2023 年度

目次

謝辞

本研究を遂行するにあたり、終始丁寧なご指導とご鞭撻を賜りました分子科学研究所　兼総合研究大学院大学　椴山　儀恵　准教授に厚く御礼申し上げます。

同研究室で研究を進めていくにあたり、様々なご助言をいただきました　大塚　尚哉　助教に深く感謝致します。

また、本研究の進行にあたり、直接丁寧にご指導していただきました　藤波　武　博士に深く感謝致します。

煩雑な事務手続きを快く引き受けていただき、常に研究生活を支えていただきました事務職員牛田　妃菜乃　様に深く感謝致します。

同期に配属され日々互いに切磋琢磨した菅原　湧斗氏に深く感謝いたします。
さらに、ともに研究に励み、様々な面でお世話になりました大石　峻也氏、加藤　雅之氏、西岡　雪奈氏、原田　晋子氏、丸山　莉央氏、柿沼　秀哉氏、MOUD ARIS, Muhammad Zhafran Bin 氏、大田　陽野氏、渡辺　葉子氏、JONGWOHAN, Chanantida 氏、小谷　駿輔氏、杉浦　聡氏、泉関　督人氏、桝井　悠氏、重光　麻衣氏、CHAIBUTH, Pawittra 氏に深く感謝致します。

また、元素分析を行っていただきました分子科学研究所機器センターの皆様に深く感謝いたします。さらに詳しい元素分析をしていただきました京都大学大学院薬学研究科有機微量元素分析総合施設の皆様に深く感謝いたします。

固体 DNP-NMR を測定して、有益なご助言をいただきました、産業技術総合研究所　触媒化学融合研究センター　田中　真司　主任研究員に深く感謝いたします。

サンプルを提供していただきました、岐阜医療科学大学　萬代　大樹　准教授　に深く感謝いたします。

ご多忙のところ、本博士論文の審査員を務めていただきました、名城大学　松儀　真人　教授、分子科学研究所　魚住　泰広　教授、山本　浩史　教授、西村　勝之　准教授　に深く御礼申し上げます。

最後に、今日まで著者を育てていただき、経済的な支援をいただきました両親に心より感謝いたします。

研究業績

学術論文

（１）Tatsuaki Hori, Shuya Kakinuma, Naoya Ohtsuka, Takeshi Fujinami, Toshiyasu, Suzuki, and Norie Momiyama* “Synthesis of Halogen Bond Donor Site-Introduced Functional Monomers via Wittig Reaction of Perfluorohalogenated Benzaldehydes: Toward Digitalization as Reliable Strategy in Small Molecule Synthesis” Synlett accepted (Special Issue Dedicated to Prof. Hisashi Yamamoto, invitation only). DOI: 10.1055/a-2118-6813

（２）Tatsuaki Hori, Taku Watanabe, Katsunori Yamanishi, Shinji Tanaka, Kazuhiko Sato, Yumiko Nakajima, Takeshi Fujinami, Naoya Ohtsuka, Toshiyasu Suzuki, and Norie Momiyama* “Halogen Bond Enabling Heterogeneous Nucleophilic Catalysis in Water” 執筆中

ポスター発表

（１）堀　達暁、椴山　儀恵「ハロゲン結合を鍵とする高分子固定化求核触媒の開発」第 22 回ヨウ素学会シンポジウム、ポスター番号 45、千葉、千葉大学、2019 年 8 月 30 日

（２）Tatsuaki Hori, Katsunori Yamanishi, Taku Watanabe, Takeshi Fujinami, Norie Momiyama, Development of Polymer-Immobilized Nucleophilic Catalyst via Halogen Bond, International Joint Symposium on Organic Synthesis ISONIS-12, ISMMS-5, ICAMS-2 and ICSFC, Poster No. 7, Awaji, Awaji Yumebutai International Conference Center, Nov. 21~23, 2019

（３）Tatsuaki Hori, Takeshi Fujinami, Naoya Ohtsuka, Norie Momiyama, Development of DMAP-Pendant Polymer Catalysts via Halogen Bond, 5th International Symposium on Halogen Bonding (ISXB5), Poster No. 13, Kisarazu, Kazusa Arc, Nov. 6~10, 2022

口頭発表

（１）堀　達暁、藤波　武、椴山　儀恵「ハロゲン結合を鍵とする高分子固定化求核触媒の開発」日本化学会第 100 春季年会、講演番号 3F5-09、野田、東京理科大学理工学部、2020 年 3 月 24 日

（２）堀　達暁、藤波　武、椴山　儀恵「ハロゲン結合を鍵とする高分子固定化 DMAP 触媒の合成とベンゾフラノンのアシル基転移反応への応用」日本化学会第 101 春季年会、講演番号 A11-1am-07、オンライン開催、2021 年 3 月 19 日

（３）堀　達暁、藤波　武、大塚　尚哉、椴山　儀恵「ハロゲン結合を鍵とする DMAP ペンダント型ポリマーによるアズラクトンの ppm レベルアシル基転移反応」日本化学会第 102 春季年会、講演番号 K4-3vn-12、オンライン開催、2022 年 3 月 25 日

第１章

序論

1−1．4-ジメチルアミノピリジン（DMAP）の高分子固定化

有機触媒は、金属元素を含まない、炭素、酸素、窒素などの典型元素から構成され、有機分子変換反応を促進することから、環境調和性に優れた触媒として、現在広く知られている[1]。有機触媒の中でも、4-ジメチルアミノピリジン（DMAP）を代表とする求核触媒は、アシル化など多くの有機反応に利用され[2]、均一系触媒反応から不均一系触媒反応に至るまで、様々な触媒が開発されてきた[3]。

これまでに報告された DMAP 誘導体の高分子固定化触媒を示す（**Figure 1-1**）。Klotz らは、市販のポリエチレンイミンを 3-[methyl(pyridin-4-yl)amino]propanoic acid とカップリングすることで、DMAP 誘導体を側鎖にもつイミン（**1**, **2**）を合成した[4]。また、この DMAP 誘導体が、パラニトロフェニルエステルの加水分解を効率的に進行させることを見出した。1981 年に Shinkai らは、クロロメチルポリスチレン樹脂から 3〜4 段階で調製したポリスチレン固定化 DMAP 誘導体（**3**, **4**）を用いることによって、過剰量のメタノール、化学量論量の DCC 存在下、アシル化反応が良好な収率で進行することを見出した[5]。1982 年に Tomoi らは、4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine、スチレン、ジビニルベンゼンとの共重合で合成した DMAP 誘導体（PS-DMAP: **5**, **6**）を報告した[6]。PS-DMAP（**5**, **6**）の触媒活性は、リナロールのアセチル化反応において比較され、DMAP に及ばないことが明らかになっている[7]。また、2012 年に O'Reilly らは、DMAP 置換スチレンを合成し、可逆的付加開裂連鎖移動（RAFT）重合により、水中でミセル状の高分子固定化触媒（**7**）を開発した[8]。高分子固定化触媒（**7**）は、DMAP では達成できない水中でのアルコールのアシル化に有効であることが見出された。

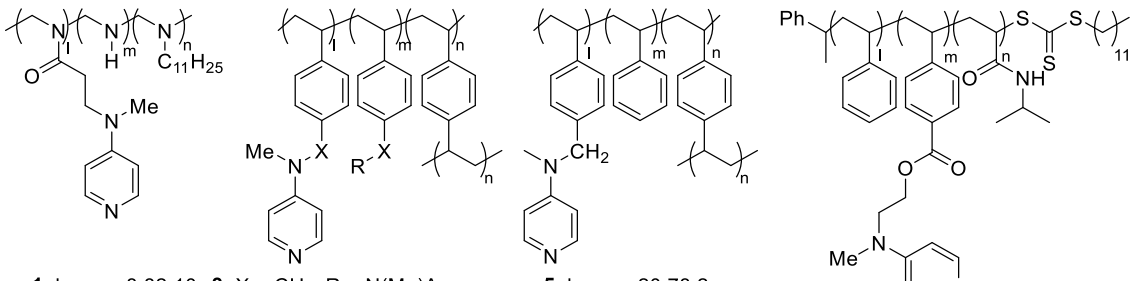


Figure 1-1. Examples of Polymer-Immobilized DMAP Derivatives

高分子固定化 DMAP 触媒は、DMAP を触媒とする均一系反応と比較して、触媒活性が低下する。これは、触媒母骨格と高分子担体の側鎖とが共有結合により連結されていることに起因している。特に、高分子側鎖の *N*-ベンジル基が、DMAP の *N*-メチル基と比べて高い電子求引性を有し、ピリジニウム中間体が不安定化されるためと考えられている[9]。求核触媒の高分子固定化における触媒活性の向上に向けて、従来の高分子固定化に代わる新たな方法論の確立が望まれる。

1–2. ハロゲン結合を利用する高分子

1–2–1. ハロゲン結合

共有結合での連結に代わる新たな方法として、ハロゲン結合[10]に着目した(**Figure 1-2**)。ハロゲン結合とは、電子不足環境下のハロゲン原子(ハロゲン結合供与体)とルイス塩基やアニオン(ハロゲン結合受容体)との間に生じる非共有結合性相互作用である。水素結合と同様に方向性を有し、ハロゲン結合供与体と受容体の組み合わせによっては、水素結合よりも強いことが報告されている。例えば、水二分子間の水素結合は−4.80 kcal/mol[11]であるのに対し、ペンタフルオロヨードベンゼンとピリジンとのハロゲン結合は−5.59 kcal/mol[12]である。

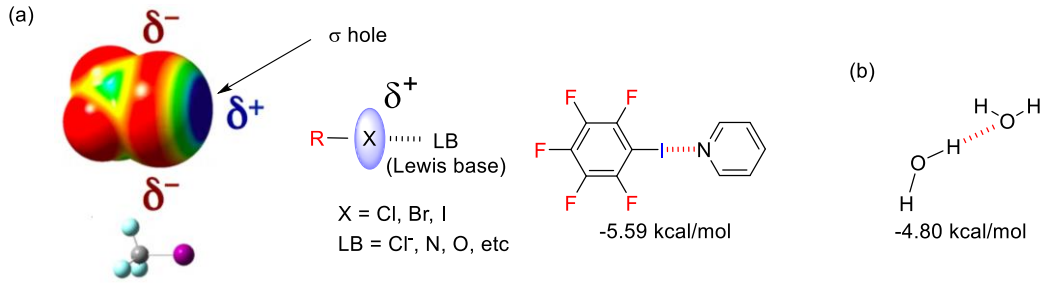


Figure 1-2. (a) Electrostatic Potential Map of CF_3I as Example of Halogen Bonding, and (b) Dimer of H_2O as Example of Hydrogen Bonding

1–2–2. ハロゲン結合を活用する高分子の先行例

2000 年に入り、ハロゲン結合は、超分子形成を基盤とする機能性分子の開発に応用され、盛んに研究されてきた[13]。一方、高分子化学分野におけるハロゲン結合の活用は、近年、報告され始めているものの、有機低分子系に比べて報告例は限られる[14]。ハロゲン結合供与部位が導入された高分子について、ハロゲン結合供与部位の種類ごとに示す。

テトラフルオロヨードベンゼン類は、高分子中のハロゲン結合供与部位として最も多く用いられている（**Figure 1-3**）。2005 年に Takeuchi らは、ペルフルオロヨードベンゼンを側鎖に持つ鋳型高分子（**8**）が含窒素化合物の認識に有効であることを示した（**Figure 1-3a**）[15]。Taylor らは、ペルフルオロヨードベンゼンを側鎖に有する様々なハロゲン結合供与体高分子（**9**, **10**, **11**, **12**）を合成し、ハロゲン結合受容体高分子と溶液中で自己集合すること[16]や、親水性溶媒中でミセルを形成することを見出した（**Figure 1-3b**）[17]。Das らは、テトラフルオロヨードフェニル PEG（**13**）を活用して、pH 応答性ミセルの開発に成功した（**Figure 1-3c**）[18]。

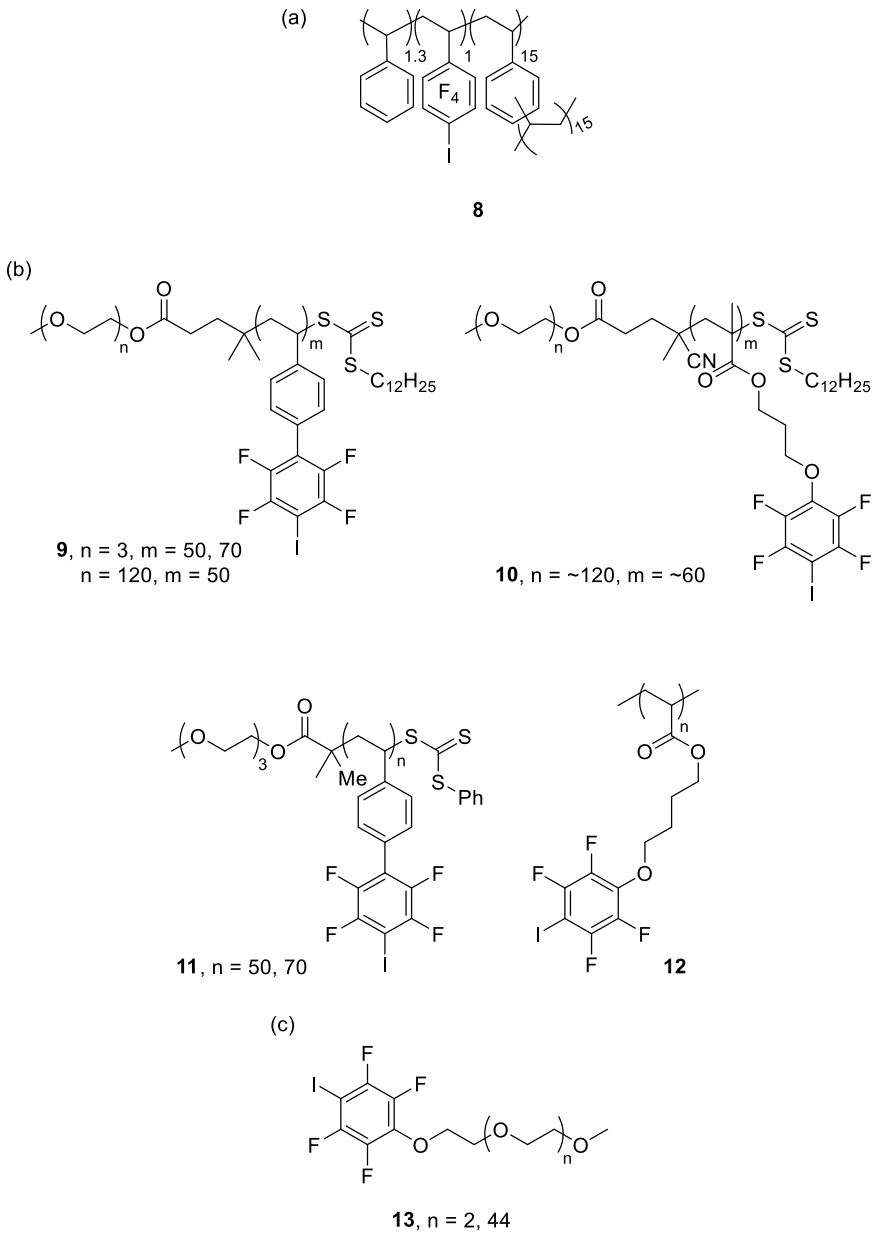


Figure 1-3. Examples of Polymer with Perfluoroiodobenzene

ハロゲン結合供与能の向上を目的として、ヨウ素化された複素五員環化合物をハロゲン結合供与部位として導入する高分子も報告されている（**Figure 1-4**）。Hager・Schubert らは、2 点型のハロゲン結合供与体を側鎖に持つポリメタクリル酸エステル（**14**, **15**）とハロゲン結合受容体を側鎖に持つポリメタクリル酸エステルとを組み合わせ、自己修復機能を有する機能性高分子材料の開発に成功した（**Figure 1-4a**）[19]。2021 年に Huber らは、均一系触媒反応で高い触媒活性を示すビスヨードトリアゾリルピリジニウムをポリスチレンに固定化した高分子触媒（**16**）を開発し、不均一系ハロゲン結合有機触媒反応を達成した（**Figure 1-4b**）[20]。ハロゲン結合を活用する高分子触媒は、これまでに Huber らの一例のみである。

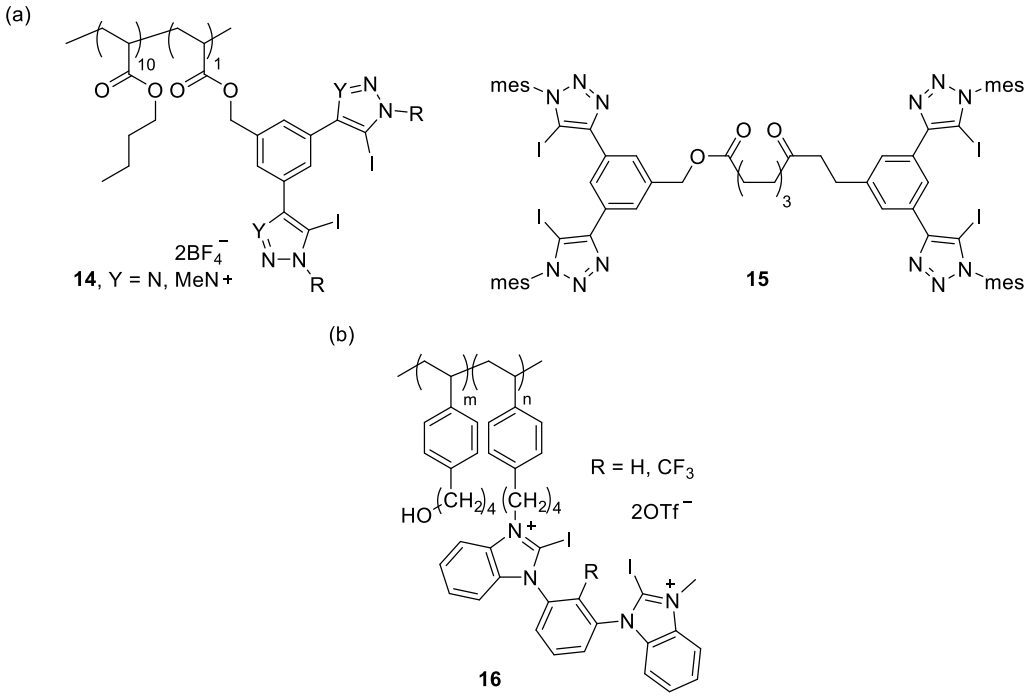


Figure 1-4. Examples of Polymer with Bidentate Halogen Bond Donor

また、Goroff らは、ポリヨードジアセチレン及びポリブロモジアセチレン（**17**, **18**）を合成し、ビスピリジルオキサルアミド及びビスニトリルオキサルアミドとの共結晶化に成功した（**Figure 1-5**）[21]。高分子中のヨウ素が、アルキンの sp 混成炭素に起因する電子求引性により、ハロゲン結合供与部位として機能することを示した。

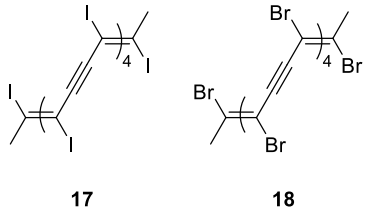


Figure 1-5. Examples of Poly Halo Acetylene

1–3．本研究
「テトラフルオロポリスチレン誘導体の合成と不均一系求核触媒反応への応用：4-アミノピリジンペンダント型高分子触媒の開発」

1–3–1．設計指針

本研究では、共有結合による求核触媒の高分子固定を非共有結合性相互作用のハロゲン結合に代替した「DMAP ペンダント型高分子触媒系」を開発することで、求核触媒の高分子固定における触媒活性低下の課題解決と不均一系求核触媒反応の効率化を目指した。

設計指針を以下に記す（**Figure 1-6**）。テトラフルオロポリスチレン誘導体のハロゲン結合供与部位は、非共有結合性の相互作用であるハロゲン結合を介して求核触媒 DMAP と相互作用することが可能である。ヨウ化テトラフルオロベンゼンと DMAP との間に働くハロゲン結合は、C_6F_5I…ピリジンの間に働くハロゲン結合と同程度の弱い非共有結合性相互作用に分類される。そのため、DMAP は求核性を損なうことなく、ハロゲン結合を介して高分子鎖近傍に存在しながら、求核触媒として機能できるのではないかと考えた。さらに、高分子鎖による疎水性や凝集性を活用することで、これまでの高分子固定化求核触媒の課題であった触媒活性低下の問題を解決でき、不均一系触媒反応における効率性を獲得できるのではないかと期待した。本研究で開発する触媒は、ハロゲン結合によって DMAP が高分子鎖にぶら下がるように見えることから、DMAP ペンダント型高分子触媒と名付けた。

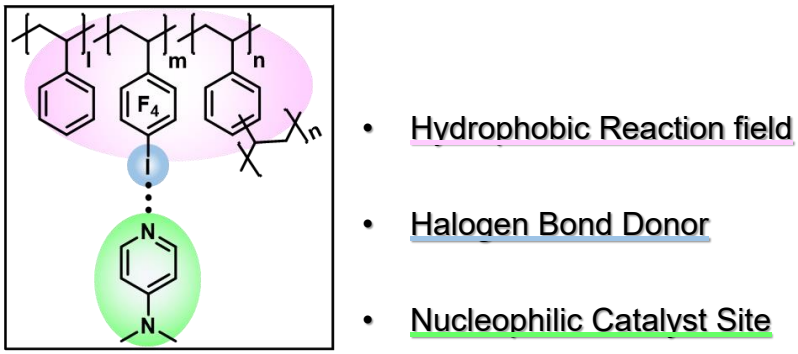
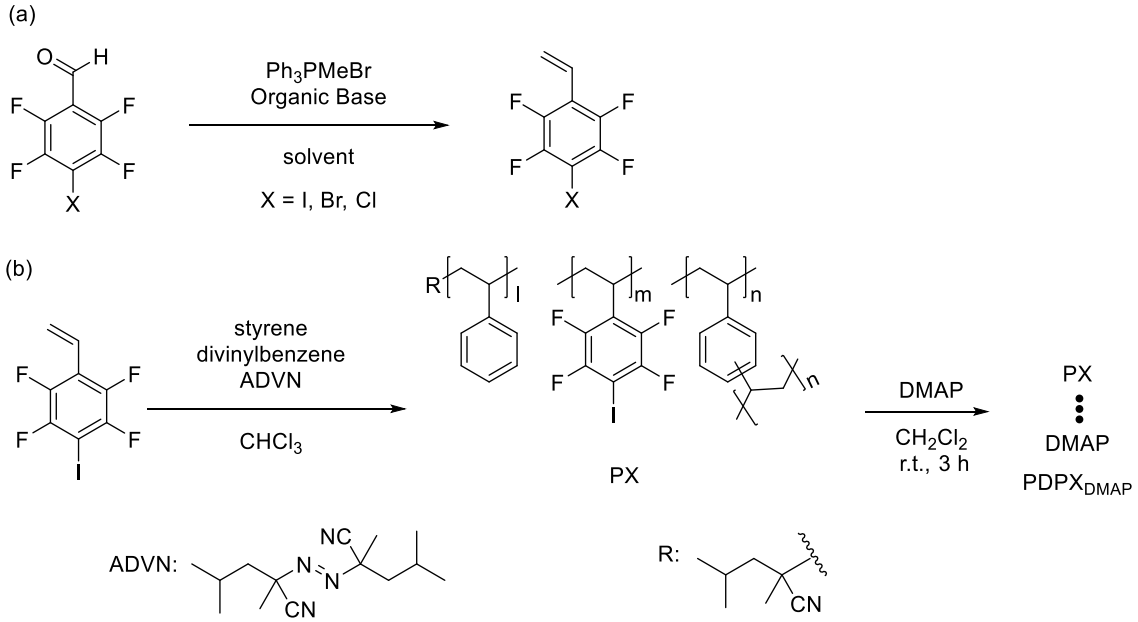


Figure 1-6. Design Concept for Catalysis with 4-Dimethylaminopyridine-Penant Polymer *via* Halogen Bond as Key Interaction

1–3–2．合成法の確立

はじめに、機能性モノマーとなるハロゲン化テトラフルオロスチレン（TFXS）の合成および精製方法を検討した（**Scheme 1-1**）。次に、機能性モノマーとして高純度のヨウ化テトラフルオロスチレン（TFIS）を用いて、架橋剤としてスチレンおよびジビニルベンゼンを選択し、竹内らの報告を参考に[15]、ラジカル重合により得られるハロゲン結合供与部位導入型高分子（PX）を

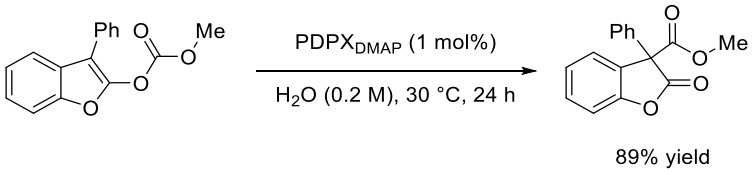
合成した。特に、高分子中のテトラフルオロヨードベンゼン部位の含有量が理論値と近い値になる手法を確立した。続いて、得られた高分子と DMAP から DMAP ペンダント型高分子触媒（$PDPX_{DMAP}$）を調製した後、その組成を微量元素分析により評価することで、DMAP の正確な含有量を算出することに成功した。以上の DMAP ペンダント型高分子触媒の合成および組成評価に関する実験結果については第二章で述べる。



Scheme 1-1. Preparation of DMAP-Pendant Polymer Catalyst

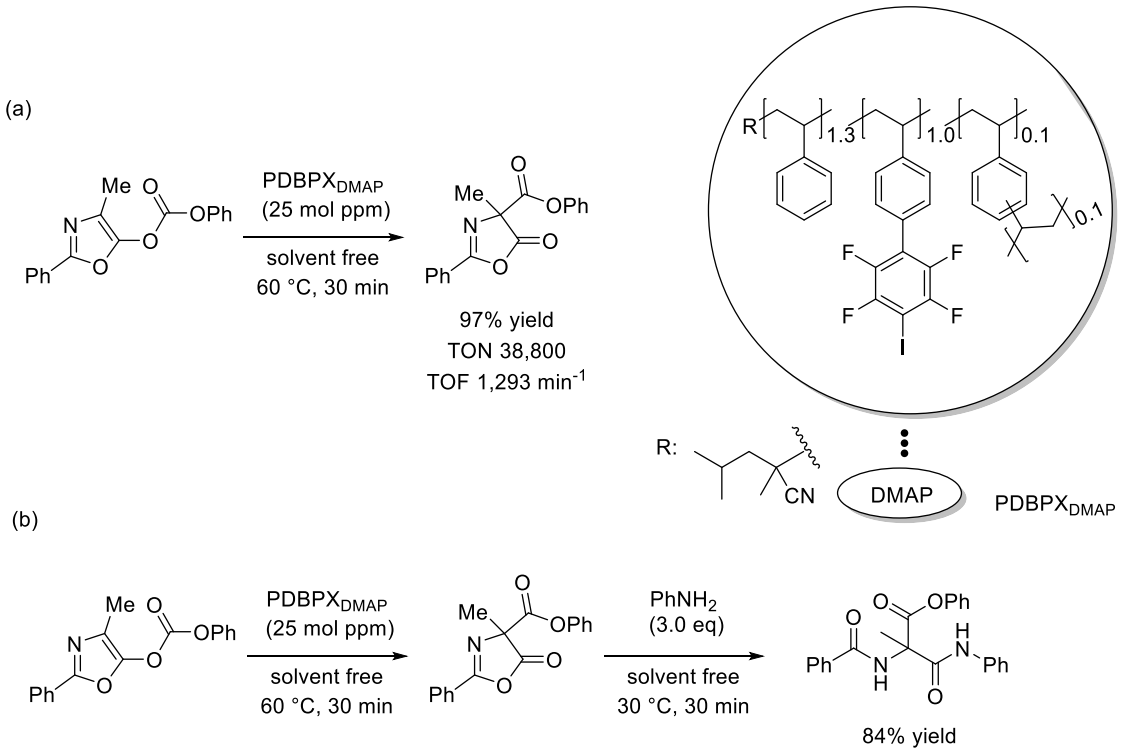
1–3–3. *O*–アシル化エノラートの転位反応における触媒機能開拓

開発した DMAP ペンダント型高分子触媒の機能を開拓するため、不均一系求核触媒反応として、水中でのベンゾフラノンのアシル基転位反応を検討した（**Scheme 1-2**）。まず、ジビニルベンゼンの当量が異なる $PDPX_{DMAP}$ を用いて、本反応に最適な架橋剤の当量を調査した。その結果、TFIS に対して 15 当量のジビニルベンゼンを用いて合成した PX と DMAP から調製した $PDPX_{DMAP}$ が、最も高い収率で目的生成物を与えることを見出した。DMAP 単体や市販で入手可能なポリスチレン触媒 PS_{DMAP} では反応は進行せず、目的生成物の収率は 10%以下であった。本触媒は様々な置換基を有する *O*-アシルベンゾフラノンに適用可能であり、対応する転位生成物を良好な収率で与えた。初期検討や基質一般性、高分子触媒の再利用、反応機構を第三章で述べる。



Scheme 1-2. Rearrangement Reaction of *O*-Acyl Benzofuranone

開発した DMAP ペンダント型高分子触媒の有用性を拡張するため、無溶媒でのアズラクトンのアシル基転位反応を検討した(**Scheme 1-3a**)。ベンゾフラノンのアシル基転位反応同様、ジビニルベンゼンの当量がそれぞれ異なる $PDPX_{DMAP}$ を調製して反応に適用した結果、TFIS に対して 0.1 または 0.01 当量のジビニルベンゼン由来の $PDPX_{DMAP}$ が、最も高い反応効率で目的生成物を与え、25 mol ppm の触媒量で、高収率、高い TON、TOF を示すことを見出した(97% 収率、TON 38,800、TOF 1,293 min^{-1})。一方、市販の PS_{DMAP} を用いた場合の収率は、$PDPX_{DMAP}$ に遠く及ばなかった。また、実用性の観点から、TFIS に代わりビフェニル型の機能性モノマーを選択し、ハロゲン結合供与部位導入型 DMAP 高分子触媒($PDBPX_{DMAP}$)を合成して検討を行った。その結果、$PDBPX_{DMAP}$ の触媒活性は $PDPX_{DMAP}$ と大きな差異は無く、$PDBPX_{DMAP}$ が広い基質適用範囲を示すことを見出した。さらに、無溶媒でのアシル化アズラクトンの触媒反応の有用性を確立するため、転位生成物に対しアミンを加えるワンポット開環反応を行い、四置換アミノ酸誘導体の合成を試みた(**Scheme 1-3b**)。本システムは不斉触媒反応にも適用可能であった。反応条件の最適化、基質適用範囲の検討、アミノ酸誘導体合成への応用、アズラクトンの不斉アシル基転位反応の実験結果を第四章で述べる。



Scheme 1-3. Rearrangement Reaction of *O*-Acyl Azlactone

最後に、第 5 章において本学位研究を総括し、本研究の展望を述べる。

引用文献

[1] For reviews, see: (a) Melchiorre, P.; Marigo, M.; Carlone, A.; Bartoli, G. Asymmetric Aminocatalysis—Gold Rush in Organic Chemistry. *Angew. Chem. Int. Ed.* **2008**, *47*, 6138–6171. (b) Bertelsen, S.; Jørgensen, K. A. Organocatalysis—After the Gold Rush. *Chem. Soc. Rev.* **2009**, *38*, 2178–2189. (c) Scheffler, U.; Mahrwald, R. Recent Advances in Organocatalytic Methods for Asymmetric C-C Bond Formation. *Chem. Eur. J.* **2013**, *19*, 14346–14396. (d) Han, B.; He, X. H.; Liu, Y. Q.; He, G.; Peng, C.; Li, J. L. Asymmetric Organocatalysis: An Enabling Technology for Medicinal Chemistry. *Chem. Soc. Rev.* **2021**, *50*, 1522–1586.

[2] For reviews, see: (a) Wurz, R. P. Chiral Dialkylaminopyridine Catalysts in Asymmetric Synthesis. *Chem. Rev.* **2007**, 107, 5570–5595. (b) Müller, C. E.; Schreiner, P. R. Organocatalytic Enantioselective Acyl Transfer onto Racemic as well as *meso* Alcohols, Amines, and Thiols. *Angew. Chem. Int. Ed.* **2011**, *50*, 6012–6042. (c) Furuta, T.; Kawabata, T. *In Asymmetric Organocatalysis 1: Lewis Base and Acid Catalysts* ed. by List, B. Georg Thieme Verlag KG, Stuttgart·New York: 2012. (d) Mandai, H.; Fujii, K.; Suga, S. Recent Topics in Enantioselective Acyl Transfer Reactions with Dialkylaminopyridine-Based Nucleophilic Catalysts. *Tetrahedron Lett.* **2018**, *59*, 1787–1803.

[3] For examples, see: (a) Ruble, J. C.; Fu, G. C. Enantioselective Construction of Quaternary Stereocenters: Rearrangements of *O*-Acylated Azlactones Catalyzed by a Planar-Chiral Derivative of 4-(Pyrrolidino)pyridine. *J. Am. Chem. Soc.* **1998**, *120*, 11532–11533. (b) Shaw, S. A.; Aleman, P.; Christy, J.; Kampf, J. W.; Va, P.; Vedejs, E. Enantioselective TADMAP-Catalyzed Carboxyl Migration Reactions for the Synthesis of Stereogenic Quaternary Carbon. *J. Am. Chem. Soc.* **2006**, *128*, 925–934. (c) Mandai, H.; Fujii, K.; Yasuhara, H.; Abe, K.; Mitsudo, K.; Korenaga, T.; Suga, S. Enantioselective Acyl Transfer Catalysis by a Combination of Common Catalytic Motifs and Electrostatic Interactions. *Nat. Commun.* **2016**, *7*, 11297.

[4] (a) Hierl, M. A.; Gamson, E. P.; Klotz, I. M. Nucleophilic Catalysis by Polyethylenimines with Covalently Attached 4-Dialkylaminopyridine. *J. Am. Chem. Soc.* **1979**, *101*, 6020–6022. (b) Delaney, E. J.; Wood, L. E.; Klotz, I. M. Poly(ethylenimines) with Alternative (Alkylamino)pyridines as Nucleophilic Catalysts. *J. Am. Chem. Soc.* **1982**, *104*, 799–807.

[5] Shinkai, S.; Tsuji, H.; Hara, Y.; Manabe, O. Polymer-Bound "Dimethylaminopyridine" as a Catalyst for Facile Ester Synthesis. *Bull. Chem. Soc. Jpn*. **1981**, *54*, 631–632.

[6] Takeda, K. Polystyrene-bound dimethylaminopyridines (PS-DMAP) in e-EROS Encyclopedia of Reagents for Organic Synthesis

[7] Tomoi, M.; Akada, Y.; Kakiuchi, H. Polymer-Supported Bases, 1. Synthesis and Catalytic Activity of Polymer-Bound 4-(*N* -benzyl-*N* -methylamino)pyridine. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 537–542.

[8] Cotanda, P.; Lu, A.; Patterson, J. P.; Petzetakis, N.; O'Reilly, R. K. Functionalized Organocatalytic Nanoreactors: Hydrophobic Pockets for Acylation Reactions in Water. *Macromolecules* **2012**, *45*, 2377–2384.

[9] Benaglia, M.; Puglisi, A.; Cozzi, F. Polymer-Supported Organic Catalysts. *Chem. Rev.* **2003**, *103*, 3401–3430.

[10] For books and reviews, see: (a) Halogen Bonding I/II: Impact on Materials Chemistry and Life Sciences, ed. by Metrangolo, P.; Resnati, G. Springer Cham, New York, **2015**. (b) Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. The Halogen Bond. *Chem. Rev.* **2016**, *116*, 2478–2601. (c) Costa, P. J. The Halogen Bond: Nature and Applications. *Phys. Sci. Rev.* **2017**, *2*, 2017.

[11] Tsuzuki, S.; Wakisaka, A.; Ono, T.; Sonoda, T. Magnitude and Origin of the Attraction and Directionality of the Halogen Bonds of the Complexes of C_6F_5X and C_6H_5X (X=I, Br, Cl and F) with Pyridine. *Chem. Eur. J.* **2012**, *18*, 951–960.

[12] Tuzuki, S.; Lüthi, H. P. Interaction Energies of van der Waals and Hydrogen Bonded Systems Calculated Using Density Functional Theory: Assessing the PW91 Mode. *J. Chem. Phys.* **2001**, *114*, 3949–3957.

[13] Gilday, L. C.; Robinson, S. W.; Barendt, T. A.; Langton, M. J.; Mullaney, B. R.; Beer, P. D. Halogen Bonding in Supramolecular Chemistry. *Chem. Rev.* **2015**, *115*, 7118–7195.

[14] For reviews, see: a) Biswas, S.; Das, A. Recent Developments in Polymeric Assemblies and Functional Materials by Halogen Bonding. *ChemNanoMat* **2021**, *7*, 748–772. b) Kampes, R.; Zechel, S.; Hager, M. D.; Schubert, U. S. Halogen Bonding in Polymer Science: towards New Smart Materials. *Chem. Sci.* **2021**, *12*, 9275–9286.

[15] Takeuchi, T.; Minato, Y.; Takase, M.; Shinmori, H. Molecularly Imprinted Polymers with Halogen Bonding-based Molecular Recognition Sites. *Tetrahedron Lett.* **2005**, *46*, 9025–9027.

[16] (a) Vanderkooy, A.; Taylor, M. S. Solution-Phase Self-Assembly of Complementary Halogen Bonding Polymers. *J. Am. Chem. Soc.* **2015**, *137*, 5080–5086. (b) Vanderkooy, A.; Pfefferkorn, P.; Taylor, M. S. Self-Assembly of Polymer Nanostructures through Halogen Bonding Interactions of an Iodoperfluoroarene-Functionalized Polystyrene Derivative. *Macromolecules* **2017**, *50*, 3807–3817.

[17] Vanderkooy, A.; Taylor, M. S. Exploring the Construction of Multicompartmental Micelles by Halogen Bonding of Complementary Macromolecules. *Faraday Discuss.* **2017**, *203*, 285–299.

[18] (a) Jamadar, A.; Das, A. A pH-Responsive Graftable Supramolecular Polymer with Tailorable Surface Functionality by Orthogonal Halogen Bonding and Hydrogen Bonding. *Polym. Chem.* **2020**, *11*, 385–392. (b) Jamadar, A.; Karan, C. K.; Roy, L.; Das, A. Structurally Tunable pH-Responsive Luminescent Assemblies from Halogen Bonded Supra-π-amphiphiles. *Langmuir* **2020**, *36*, 3089–3095.

[19] (a) Tepper, R.; Bode, S.; Geitner, R.; Jager, M.; Gorls, H.; Vitz, J.; Dietzek, B.; Schmitt, M.; Popp, J.; Hager, M. D.; Schubert, U. S. Polymeric Halogen-Bond-Based Donor Systems Showing Self-Healing Behavior in Thin Films. *Angew. Chem. Int. Ed.* **2017**, *56*, 4047–4051. (b) Dahlke, J.; Tepper, R.; Geitner, R.; Zechel, S.; Vitz, J.; Kampes, R.; Popp, J.; Hager, M. D.; Schubert, U. S. A Healing Ionomer Crosslinked by a Bis-Bidentate Halogen Bond Linker: a Route to Hard and Healable

Coatings. *Polym. Chem.* **2018**, *9*, 2193–2197.

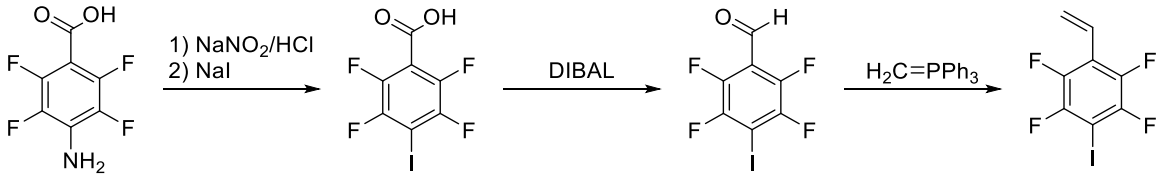
[20] Papagna, R.; Kutzinski, D.; Huber, S. M. Polymer-Bound Halogen Bonding Organocatalysis. *Eur. J. Org. Chem.* **2022**, doi.org/10.1002/ejoc.202200852

[21] (a) Goroff, N. S.; Curtis, S. M.; Webb, J. A.; Fowler, F. W.; Lauher, J. W. Designed Cocrystals Based on the Pyridine−Iodoalkyne Halogen Bond. *Org. Lett.* **2005***, 7,* 1891–1893. (b) Sun, A.; Lauher, J. W.; Goroff, N. S. Preparation of Poly(diiododiacetylene), an Ordered Conjugated Polymer of Carbon and Iodine. *Science* **2006**, *312*, 1030–1034. (c) Wilhelm, C.; Boyd, S. A.; Chawda, S.; Fowler, F. W.; Goroff, N. S.; Halada, G. P.; Grey, C. P.; Lauher, J. W.; Luo, L.; Martin, C. D.; Parise, J. B.; Tarabrella, C.; Webb, J. A. Pressure-Induced Polymerization of Diiodobutadiyne in Assembled Cocrystals. *J. Am. Chem. Soc.* **2008**, *130*, 4415–4420. (d) Jin, H.; Plonka, A. M.; Parise, J. B.; Goroff, N. S. Pressure Induced Topochemical Polymerization of Diiodobutadiyne: a Single-Crystal-to-Single-Crystal Transformation. *CrystEngComm* **2013**, *15*, 3106–3110. (e) Jin, H.; Young, C. N.; Halada, G. P.; Phillips, B. L.; Goroff, N. S. Synthesis of the Stable Ordered Conjugated Polymer Poly(dibromodiacetylene) from an Explosive Monomer. *Angew. Chem. Int. Ed.* **2015**, *54*, 14690–14695.

第２章
DMAP ペンダント型高分子触媒の合成

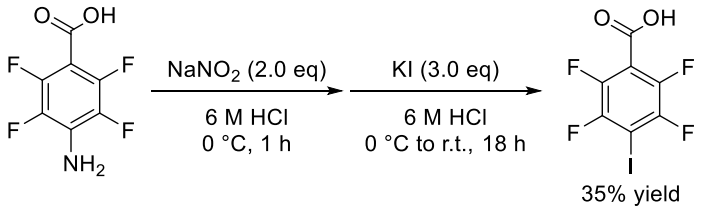
2−1．機能性モノマーの合成報告例

Takeuchi らは、ハロゲン結合を活用した分子鋳型高分子の合成と分子認識機能に関する論文において、機能性モノマーであるヨウ化テトラフルオロスチレンの合成方法を報告した（**Scheme 2-1**）[1]。Takeuchi らの報告では、市販の 4-アミノ-2,3,5,6-テトラフルオロ安息香酸を出発原料に用い、Sandmeyer 反応によるヨウ素化、続く水素化ジイソブチルアルミニウム（DIBAL）による還元反応により、2,3,5,6-テトラフルオロ-4-ヨードベンズアルデヒドを合成した後、Wittig 反応でヨウ化テトラフルオロスチレンの合成を行ったと記されている。しかし、各反応における反応条件や実験方法、さらに Wittig 反応で用いた塩基について、詳細は記載されていない。



Scheme 2-1. Synthesis of 2,3,5,6-Tetrafluoro-4-iodostylene Reported by Takeuchi

当グループの山西（当時、博士研究員）は、Takeuchi らの報告を参考にヨウ化テトラフルオロ安息香酸の合成を試みた（**Scheme 2-2**）。その結果、目的とするヨウ化テトラフルオロ安息香酸は得られたものの、収率は 35%であった。

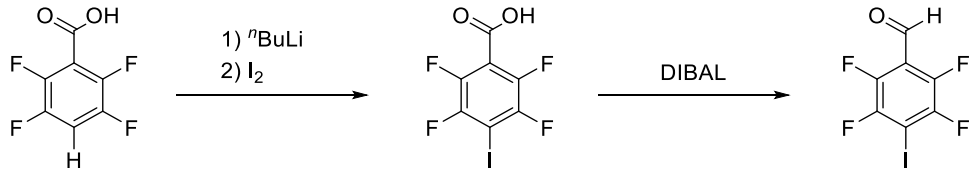


Scheme 2-2. Synthesis of 2,3,5,6-Tetrafluoro-4-iodobenzoic Acid in Our Group

2–2. ハロゲン化テトラフルオロベンズアルデヒドの合成

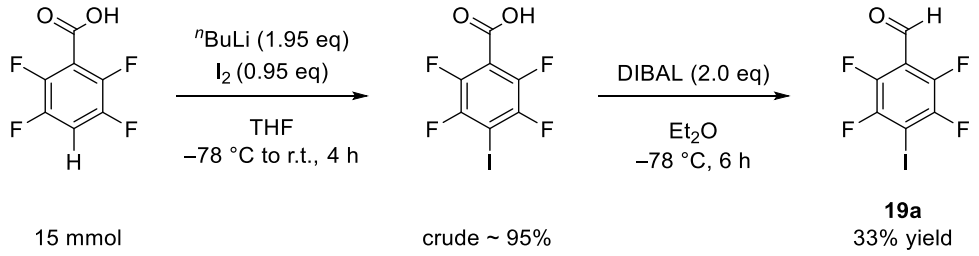
2–2–1. ヨウ化テトラフルオロベンズアルデヒドの合成

当グループの山西(当時、博士研究員)は、機能性モノマーの合成に向けて、ヨウ化テトラフルオロ安息香酸の合成反応を改良した(**Scheme 2-3**)[2]。改良合成法では、市販の 2,3,5,6-テトラフルオロ安息香酸を出発原料に用い、リチオ化と続くヨウ素化でヨウ化テトラフルオロ安息香酸を合成する。得られたヨウ化テトラフルオロ安息香酸に対し、DIBAL による還元反応を行うことで、ヨウ化テトラフルオロベンズアルデヒドが得られる。



Scheme 2-3. Synthetic Route of 2,3,5,6-Tetrafluoro-4-iodobenzaldehyde

はじめに、山西が開発した合成法に基づき、ヨウ化テトラフルオロ安息香酸およびヨウ化テトラフルオロベンズアルデヒドを合成した(**Scheme 2-4**)。市販で入手可能なテトラフルオロ安息香酸を出発原料として、THF 溶媒中、*n*-BuLi、分子ヨウ素を作用させ、−78 ℃から室温に昇温しながら 4 時間撹拌した。その結果、目的とするヨウ素化体が良好な粗収率で得られた。続いて、ジエチルエーテル中、得られたヨウ素化体に DIBAL を作用させ、−78 ℃で 6 時間撹拌することで、目的とするアルデヒドを 30%程度の単離収率で得た。得られたヨウ化テトラフルオロベンズアルデヒドの純度は、NMR および元素分析(**Table 2-1**)で決定した。計算値と実測値は良い一致を示し、改良合成法により、テトラフルオロ安息香酸からアルデヒド **19a** を問題なく合成できることがわかった。



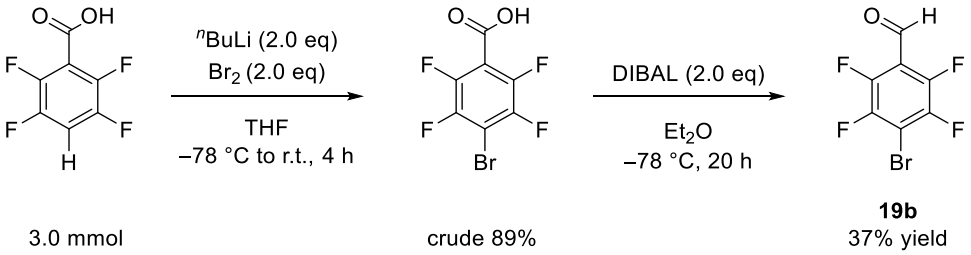
Scheme 2-4. Synthesis of 2,3,5,6-Tetrafluoro-4-iodobenzaldehyde (**19a**)

Table 2-1. Elemental Analysis of 2,3,5,6-Tetrafluoro-4-iodobenzaldehyde (**19a**)

C_7HF_4IO	H (%)	C (%)	F (%)	I (%)
found	0.38	27.63	25.07	41.70
calcd.	0.33	27.66	25.00	41.75

2-2-2. 臭化テトラフルオロベンズアルデヒドの合成

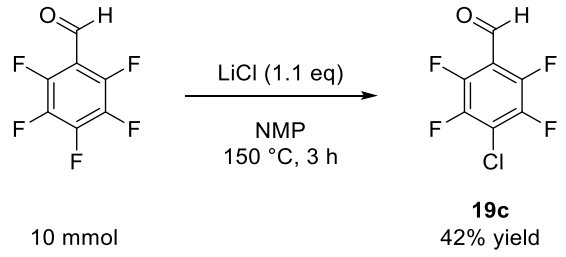
臭化テトラフルオロベンズアルデヒド(**19b**)は、分子ヨウ素の代わりに臭素を用い、2-2-1と同様の反応経路で合成した(**Scheme 2-5**)。その結果、臭化テトラフルオロ安息香酸が良好な粗収率で得られ、目的とするアルデヒドの単離収率は 37%であった。



Scheme 2-5. Synthesis of 4-Bromo-2,3,5,6-tetrafluorobenzaldehyde (**19b**)

2-2-3. 塩化テトラフルオロベンズアルデヒドの合成

塩化テトラフルオロベンズアルデヒド(**19c**)は、文献[3]に基づいて合成した(**Scheme 2-6**)。市販で入手可能なペンタフルオロベンズアルデヒドに対して、塩化リチウムを作用させ、NMP溶媒中、150 ℃で 3 時間撹拌することで、目的とする **19c** が 42%の単離収率で得られた。



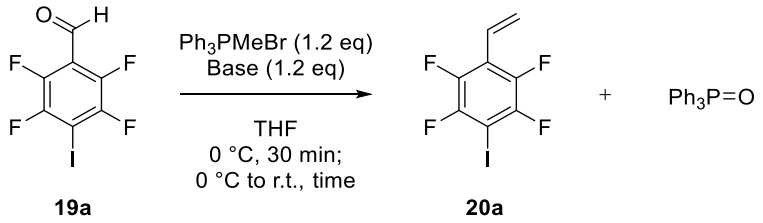
Scheme 2-6. Synthesis of 4-Chloro-2,3,5,6-tetrafluorobenzaldehyde (**19c**)

2-3. Wittig 反応によるハロゲン化テトラフルオロスチレンの合成

2-3-1. 初期検討

ヨウ化テトラフルオロスチレン **20a** を合成するため、Wittig 反応の代表的な有機金属塩基や無機塩基である *n*-BuLi、*t*-BuOK、NaH、K_2CO_3 を用いて検討を行った（**Table 2-2**）。*n*-BuLi では、反応時間 2 時間と 22 時間で検討を行ったが、どちらの反応時間においても反応副生成物であるトリフェニルホスフィンオキシドが中程度の収率で得られた。しかし、目的生成物であるスチレン **20a** の収率は 30%程度で、同定不明の反応副生成物が確認された（entries 1, 2）。*t*-BuOK の場合は、反応時間の伸長に伴いトリフェニルホスフィンオキシドの生成と Wittig 反応の進行が認められたが、**20a** の収率は 10%未満であった。**20a** が得られた後に、同定不明の反応副生成物へと変換されていることが示唆された。一方、NaH や K_2CO_3 では、目的生成物 **20a** の収率は 10%未満で、原料 **19a** が回収された（entries 3-8）。

Table 2-2. Screening of Organometallic Base and Inorganic Base in Wittig Reaction of **19a**[a]



19a **20a**

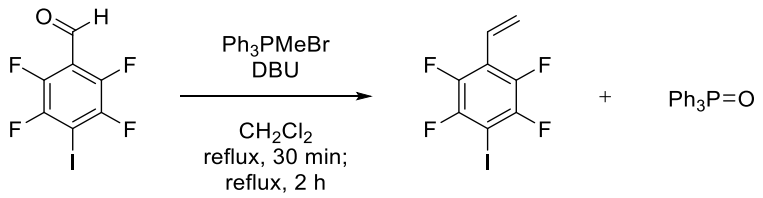
Entry	Base	time (h)	Yield (%)	
			20a[b]	$Ph_3P=O$[c]
1	*n*-BuLi	2	31	64
2	*n*-BuLi	24	34	71
3	*t*-BuOK	2	2	28
4	*t*-BuOK	24	7	51
5	NaH	2	<1	2
6	NaH	24	2	4
7	K_2CO_3	2	<1	6
8	K_2CO_3	24	<1	10

[a] Reactions were performed using **19a** (0.5 mmol), Ph_3PMeBr (0.6 mmol), base (0.6 mmol) in THF (6.5 mL). [b] Determined by ^{19}F nuclear magnetic resonance spectroscopy using α,α,α-trifluorotoluene as a standard. [c] Determined by ^{31}P nuclear magnetic resonance spectroscopy using Ph_3P as an internal standard.

2-3-2. 有機塩基および反応条件の最適化

1,8-diazabicyclo[5.4.0]undec-7-ene（DBU）は、4-ニトロベンズアルデヒドを用いる Wittig 反応の塩基として有効であることが報告されている[4]。C_6F_5 基は、ニトロ基と同様に強力な電子求引基であることから、DBU による Wittig 反応を行うことで **20a** を合成することにした。検討は、ジクロロメタン溶媒中、還流条件下、反応時間 2 時間で行った（**Table 2-3**）。臭化メチルトリフェニルホスホニウムと DBU をそれぞれ 1.2 当量用いた場合、目的生成物である **20a** およびトリフェニルホスフィンオキシドは低収率であったが、同定不明の副生成物が抑制されることがわかった（entry 1）。さらに、臭化メチルトリフェニルホスホニウムと DBU の当量を検討したが、**20a** およびトリフェニルホスフィンオキシドの収率は十分に向上しなかった（entries 2-4）。

Table 2-3. Screening of Equivalents of Ph_3PMeBr and DBU in Wittig Reaction of **19a**[a]



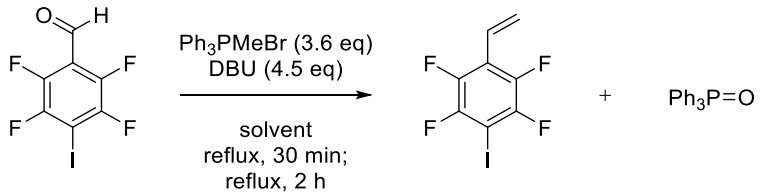
19a **20a**

Entry	Ph_3PMeBr (Equiv.)	DBU (Equiv.)	Yield (%)	
			20a[b]	$Ph_3P=O$[c]
1	1.2	1.2	7	10
2	1.2	1.5	8	12
3	2.4	3.0	12	17
4	3.6	4.5	11	24

[a] Reactions were performed using **19a** (0.5 mmol), Ph_3PMeBr, DBU for 2 h in CH_2Cl_2 (6.5 mL). "Reflux" in dichloromethane as solvent indicates to set up the temperature controller of hotplate stirrer at 55 °C. [b] Determined by ^{19}F nuclear magnetic resonance spectroscopy using α,α,α-trifluorotoluene as an internal standard. [c] Determined by ^{31}P nuclear magnetic resonance spectroscopy using Ph_3P as an internal standard.

次に、トリフェニルホスフィンオキシドの収率が最も高かった、臭化メチルトリフェニルホスホニウムを 3.6 当量、DBU を 4.5 当量の条件で反応溶媒を検討した（**Table 2-4**）。まず、還流条件下、ジクロロメタン、THF、アセトニトリル、トルエン中で反応を行ったところ、THF が最も良い結果を与えた（entries 1-4）。4 種類のエーテル系溶媒、ジエチルエーテル、*tert*-ブチルメチルエーテル、1,2-ジメトキシエタン（glyme）、1,4-ジオキサンを検討したが、スチレン **20a** の収率は THF を用いた entry 2 に及ばなかった（entries 5-8）。

Table 2-4. Screening of Solvent in Wittig Reaction of **19a**[a]



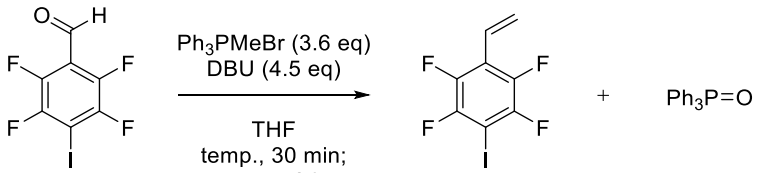
19a **20a**

Entry	solvent	/	Setup temp. (°C)[b]	Yield (%)	
				20a[c]	$Ph_3P=O$[d]
1	CH_2Cl_2	/	55	11	24
2	THF	/	80	35	71
3	MeCN	/	95	<1	17
4	toluene	/	125	9	23
5	Et_2O	/	45	29	37
6	*t*-BuOMe	/	65	25	31
7	glyme	/	95	21	59
8	1,4-dioxane	/	115	11	76

[a] Reactions were performed using **19a** (0.5 mmol), Ph_3PMeBr (1.8 mmol), DBU (2.3 mmol) for 2 h in solvent (6.5 mL). [b] Reaction temperature was set up based on the temperature controller of hotplate stirrer. [c] Determined by ^{19}F nuclear magnetic resonance spectroscopy using α,α,α-trifluorotoluene as an internal standard. [d] Determined by ^{31}P nuclear magnetic resonance spectroscopy using Ph_3P as an internal standard.

最適溶媒を THF として、反応温度を検討した（**Table 2-5**)。80、70、60 °C では、スチレン **20a** の収率に顕著な変化はなく、35~37%であった（entries 1-3)。反応温度を 50、40 °C と下げるにつれて、収率が低下した（entries 4, 5)。

Table 2-5. Screening of Rection Temperature in Wittig Reaction of **19a**[a]



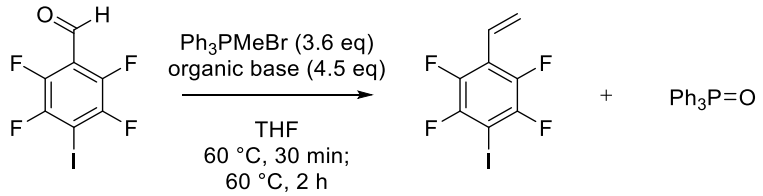
19a **20a**

Entry	Setup temp. (°C)[b]	Yield (%)	
		20a[c]	$Ph_3P=O$[d]
1	80	35	71
2	70	36	65
3	60	37	61
4	50	32	44
5	40	26	44

[a] Reactions were performed using **19a** (0.5 mmol), Ph_3PMeBr (1.8 mmol), DBU (2.3 mmol) for 2 h in THF (6.5 mL). [b] Reaction temperature was set up based on the temperature controller of hotplate stirrer. [c] Determined by ^{19}F nuclear magnetic resonance spectroscopy using α,α,α-trifluorotoluene as an internal standard. [d] Determined by ^{31}P nuclear magnetic resonance spectroscopy using Ph_3P as an internal standard.

反応温度を 60 °C とし、pK_{BH} を参考に種々の有機塩基を検討した（**Table 2-6**）。DBU より塩基性度の高い、TBD、MTBD、DBN を試した（entry 1-3）。MTBD は、目的生成物のスチレン（**20a**）を、DBU 存在下の場合と同程度の収率で与えた。一方、TBD と DBN を用いた場合は、**20a** が得られたものの、DBU 存在下の場合の半分以下の収率であった。DBU より塩基性度の低い、TMG、ピペリジン、キヌクリジン、*i*-Pr_2EtN、Et_3N、DABCO の場合は、TMG のみが **20a** を与えた（entries 5-10）。検討した有機塩基の中で、TMG の場合に最も良好な収率が得られた。

Table 2-6. Screening of Organic Base in Wittig Reaction of **19a**[a]



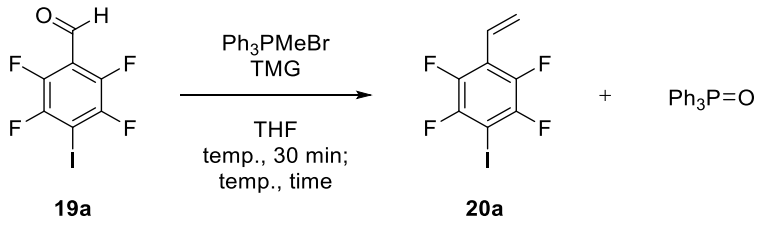
19a **20a**

Entry	Organic Base	/	pK_{BH}[b]	Yield (%)	
				20a[c]	$Ph_3P=O$[d]
1	TBD	/	20.1	8	33
2	MTBD	/	18.0	36	56
3	DBN	/	17.2	15	16
4	DBU	/	16.9	37	61
5	TMG	/	15.5	43	52
6	Piperidine	/	14.3	<1	<1
7	Quinuclidine	/	13.1	<5	<1
8	*i*-Pr_2EtN	/	12.7	<1	<1
9	Et_3N	/	12.5	<5	<1
10	DABCO	/	11.7	<1	<1

[a] Reactions were performed using **19a** (0.5 mmol), Ph_3PMeBr (1.8 mmol), organic base (2.3 mmol) for 2 h in THF (6.5 mL). [b] *Eur. J. Org. Chem.* **2019**, *40*, 6735–6748. [c] Determined by ^{19}F nuclear magnetic resonance spectroscopy using α,α,α-trifluorotoluene as an internal standard. [d] Determined by ^{31}P nuclear magnetic resonance spectroscopy using Ph_3P as an internal standard. MTBD = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene. DBN = 1,5-diazabicyclo[4.3.0]non-5-ene. TMG = 1,1,3,3-tetramethylguanidine.

続いて、**Table 2-6** の結果に基づき、THF 溶媒中、有機塩基として TMG を用い、反応条件を検討した（**Table 2-7**）。2 時間の反応時間で反応温度 60 °C と 80 °C で検討したところ、スチレン **20a**、トリフェニルホスフィンオキシドの収率はいずれも 80 °C の方が高かった（entries 1, 2）。反応温度を 80 °C に変えて、反応時間 4 時間、6 時間、24 時間で検討を行うと、6 時間で **20a** の収率は 53%、トリフェニルホスフィンオキシドの収率は 82%に達し、その後、収率に大きな変化は見られなかった（entries 3-5）。したがって、entry 4 の反応条件を最適条件とし、以後の検討を行った。

Table 2-7. Optimization for Wittig Reaction of **19a**[a]



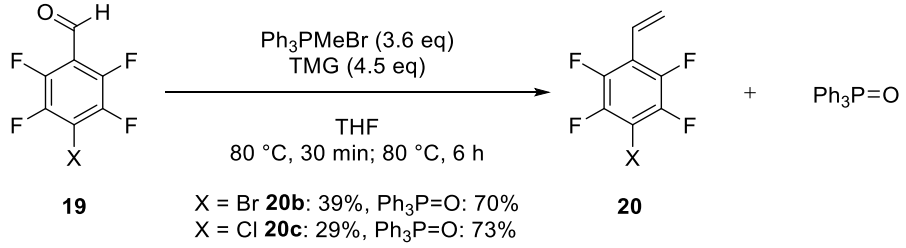
19a **20a**

Entry	temp. (°C)[b]	time (h)	Yield (%)	
			20a[c]	$Ph_3P=O$[d]
1	60	2	43	52
2	80	2	46	64
3	80	4	51	69
4	80	6	53	82
5	80	24	54	80

[a] Reactions were performed using **19a** (0.5 mmol), Ph_3PMeBr (1.8 mmol), DBU (2.3 mmol) in THF (6.5 mL). [b] The reaction temperature was set up based on the temperature controller of hotplate stirrer. [c] Determined by ^{19}F nuclear magnetic resonance spectroscopy using α,α,α-trifluorotoluene as an internal standard. [d] Determined by ^{31}P nuclear magnetic resonance spectroscopy using Ph_3P as an internal standard.

2–3–3．臭化/塩化テトラフルオロスチレン合成への応用

臭化テトラフルオロスチレン **20b** や塩素化テトラフルオロスチレン **20c** の合成を試みた（**Scheme 2-5**）。検討は、合成した臭化テトラフルオロベンズアルデヒド **19b** や塩化テトラフルオロベンズアルデヒド **19c** を用い、**20a** の合成反応で最適化した反応条件下で行った。その結果、**20a** と比較して、**20b** や **20c** の収率は低下したものの、有機塩基 TMG の有効性が確かめられた。しかし、どちらの場合もトリフェニルホスフィンオキシドが良好な収率で得られていたことから、低収率の原因は、生成物であるスチレンの安定性に起因するものであると推察された。



19 **20**

Scheme 2-7. Synthesis of 2,3,5,6-Tetrafluoro-4-halostyrene

2−3−4．精製方法の検討

ヨウ化テトラフルオロスチレン **20a** の単離精製を試みた。その結果、シリカゲルクロマトグラフィーの展開溶媒であるヘキサン中で分解することが明らかになった。展開溶媒をヘキサンからペンタンに変えたところ、目的生成物の分解は抑制された。最終的に分取 HPLC で精製することによって、ペンタンが 10%程度含まれるものの、高純度の **20a** を 9%収率で得ることに成功した。

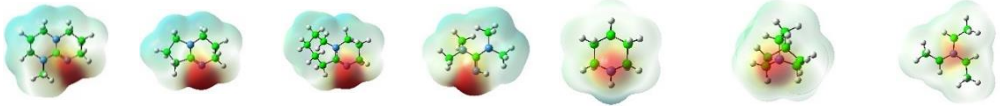
2−3−5．有機塩基を用いる Wittig 反応の考察

密度汎関数理論（DFT）計算の結果をもとに、有機塩基を用いる Wittig 反応を考察し、ハロゲン化テトラフルオロスチレン（TFXS）の生成に重要な因子を明らかにすることにした。DFT 計算は、マテリアル先端リサーチインフラの有機合成 DX 量子化学計算の一環として実施し、鈴木敏泰リーダーが担当した。

まず、静電ポテンシャルマップにより、Wittig 反応に用いた有機塩基の正および負電荷の領域を可視化した（**Table 2-8**、最上段 MEP）。静電ポテンシャルマップの赤色は負電荷の領域を、水色は正電荷の領域を示している。Wittig 反応が進行した MTBD、DBN、DBU、TMG では、イリドの生成に関与する塩基性窒素上が濃い赤色となったのに対し、反応が進行しなかったピペリジン、キヌクリジン、トリエチルアミンでは薄い赤色となった。MTBD、DBN、DBU、TMG は、ピペリジン、キヌクリジン、トリエチルアミンに比べ、負電荷を十分に有することが示唆された。

次に、イリドの生成に関与する窒素原子上のポテンシャルエネルギー（$V_{s,min}$）と NBO 電荷を算出して、有機塩基の活性を定量的に評価した（**Table 2-8**、中段および下段）。その結果、TFXS の生成には $V_{s,min}$ と NBO がそれぞれ−175 kJ/mol、−0.60 a.u.必要であることが示された。しかし、各々の有機塩基の pK_{BH} や $V_{s,min}$、NBO と収率に明確な相関は見出せず、TMG が TBD や MTBD、DBN、DBU と比較して有意な結果を説明することはできなかった。

Table 2-8. Molecular electrostatic potential maps, $V_{s,min}$, and NBO charges[a]

MEPs							
Organic base	MTBD	DBN	DBU	TMG	Piperidine	Quinuclidine	NEt_3
$V_{s,min}$ (kJ/mol)	–176	–200	–197	–187	–132	–140	–118
NBO (a.u.)	–0.67	–0.64	–0.64	–0.84	–0.73	–0.58	–0.60

[a] DFT calculations were performed at the SMD(THF)/M06-2X-D3/6-311+G(d,p) level at 333K.

有機塩基を用いる Wittig 反応の考察を深めるため、相関分析を行った。相関分析は、ヒートマップの作成と相関係数の絶対値(|r|)をもとに、スチレン **20a** の収率に対する重要因子を評価した[5]。相関分析にあたり、反応に関する指標、有機塩基の求核部位に関する指標、有機塩基の構造に関する指標の３つに分類して、Wittig 反応を記述した(**Table 2-9**)。また、今回の相関分析では、機械学習手法による反応記述子を用いず、実験担当者が理解できる記述子の範囲に留めた。相関係数の評価は、$0.9 < |r| < 1.0$ の場合に相関が非常に高い、$0.7 < |r| < 0.9$ の場合に相関が高い、$0.5 < |r| < 0.7$ の場合に相関がある、$0.3 < |r| < 0.5$ の場合に相関が低い、$|r| < 0.3$ の場合は相関が弱いもしくは相関がないとして、定量的に判断した。

Table 2-9. Classifications of the Descriptors Used in the Correlation Analysis of the Organic Base-Mediated Wittig Reaction of **19a**

Category	Descriptor	Physical meaning
Reaction	yield (%) of $Ph_3P=O$	Yield of triphenylphosphine oxide
	UDR-Pro	Undesired Reaction Product[a]
	temp. (°C)	Reaction temperature
	time (h)	Reaction time
	SVI-PC5[13,14]	Reaction solvent index
Nucleophilic Site	pK_{B-H}	Basicity of organic base
	$V_{s,min}$ (kJ/mol)	Electrostatic potential energy[b]
	NBO (a.u.)	NBO charge[b]
	delta G (kcal/mol)	ΔG: Gibbs free energy[c]
	Mayer-N	[d]
Structure	NXBA	Number of halogen bond acceptors
	Cyclic/Acyclic	Structure of the organic base[e]
	NRing	Number of rings in the organic base
	Ring Size of N	[f]
	Ring Size of S	[g]

[a] Calculated according to the following equation: UDR-Pro (%) = 100 - (recovery yield of **20a** (%) + yield of **19a** (%)). [b] For nitrogen atom as the active center. [c] For the protonation of an organic base. [d] Mayr's nucleophilicity parameters. [e] Equal to 1 if the structure is cyclic; equal to 0 if the structure is acyclic. [f] Size of the ring the basicity center; "0" if the active center is out of the ring. [g] Size of the ring that is out of the basicity center, "0" if the organic base is without ring structure or no ring structure in the out of the active center.

相関分析の結果、**20a** の収率は、トリフェニルホスフィンオキシドの収率に相関が高いことが明らかになった(|r|: 0.88)(**Figure 2-1a**)。この結果は、生成物であるスチレン **20a** の取り扱いが難しく、Wittig 反応の進行を生成物で判断することが困難な場合、反応の進行を **20a** と共に得られるトリフェニルホスフィンオキシドの生成をもとに判断してよいことを示している。**20a** の収率に対する５つの反応に関する指標の相関係数は、相関が高い順に、yields (%) of $Ph_3P=O$（|r|: 0.88）> time (h)（|r|: 0.44）> SVI-PC5（|r|: 0.23）> UDR-Pro（|r|: 0.12）> temp. (°C)（|r|: 0.06)であった(**Figure 2-1b**)。反応時間や反応温度は目的物 **20a** の収率と相関が低く、反応時間の延長や反応温度の昇温は、必ずしも好ましい結果を与えないということが示唆された。有機塩基の求核部位に関する指標の中では、求核性パラメータ(Mayr-N)が **20a** の収率に対し負の相関を示した(|r|: 0.75)。この結果は、有機塩基による求核攻撃によって **19a** または **20a** の分解が始まり、有機塩基の求核性が高い程 **20a** の収率が低下することを合理的に説明できる。良

好な収率を達成するには、有機塩基の低い求核性が 2 番目に大事であることが示された。実際に、TMG の求核性は 11.4 であるのに対し、DBN の場合は 16.6 と見積もられた。$V_{s,\min}$ と NBO は、**20a** の収率に中程度の相関を示しており（|r|: 0.64 for NBO, |r|: 0.41 for $V_{s,\min}$）（**Figure 2-1a**）、イリド生成に適度な塩基性度が重要であるといえる。さらに、ハロゲン結合受容体の数（NXBA）が **20a** の収率に正の相関を示した（|r|: 0.73, **Figure 2-1b**）。ハロゲン結合受容体の数（NXBA）が 3 番目に重要な因子であることが明らかになった。**20a** と有機塩基がハロゲン結合を介して錯形成することで、反応系中における **20a** の安定化に寄与していると考えられる。

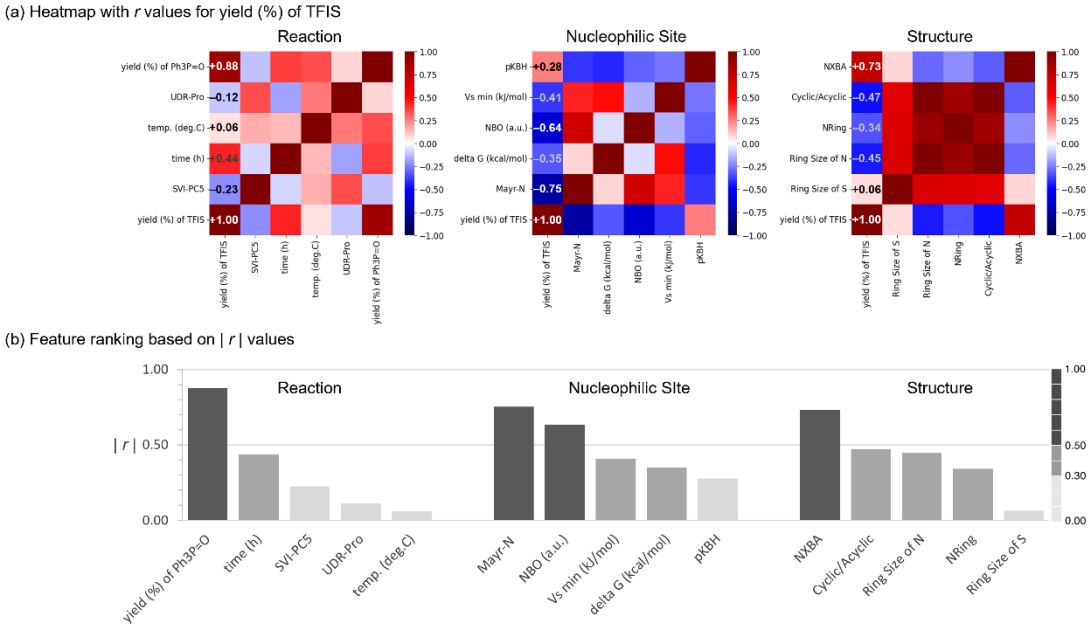
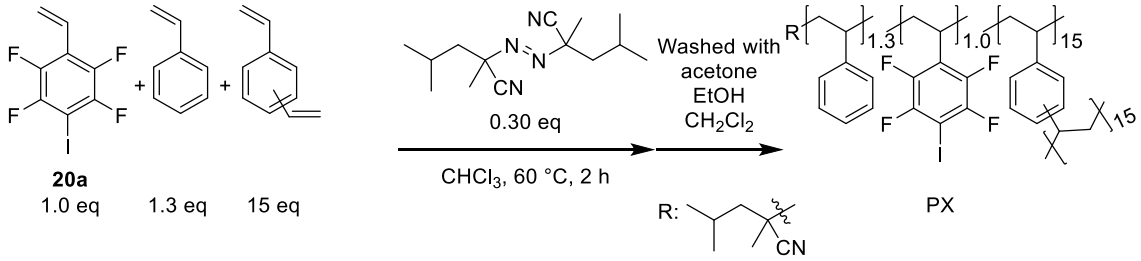


Figure 2-1. Correlation analysis. (a) Heatmap with *r* values for the yield (%) of TFIS (b) Feature ranking based on the |*r*| values.

2–4. ハロゲン結合供与部位を有する高分子の合成

高純度の **20a** を用いて高分子合成を行った。架橋剤としてジビニルベンゼンを使用し、その当量がそれぞれ異なる 4 種類の高分子を合成した。はじめに、**20a** に対して 15 当量のジビニルベンゼンを用いて合成した結果を以下に示す。**20a** に対して、1.33 当量のスチレン、15 当量のジビニルベンゼンを用い、重合開始剤 ADVN 存在下、クロロホルム溶媒中、60 ℃、2 時間、撹拌した（**Scheme 2-8**）。得られた高分子をアセトン、エタノール、ジクロロメタンを用いて洗浄し、未反応のスチレン、ADVN を取り除いた。続いて、すり潰すことで、白色の粉末を得た。得られた高分子組成を元素分析により評価した（**Table 2-10**）。ヨウ化テトラフルオロスチレン由来のフッ素とヨウ素が検出された。また、実測値と計算値に大きな差はなかった。尚、本手法により合成した高分子を、polymer with halogen (X)-bond donor site と命名し、PX と表記する。



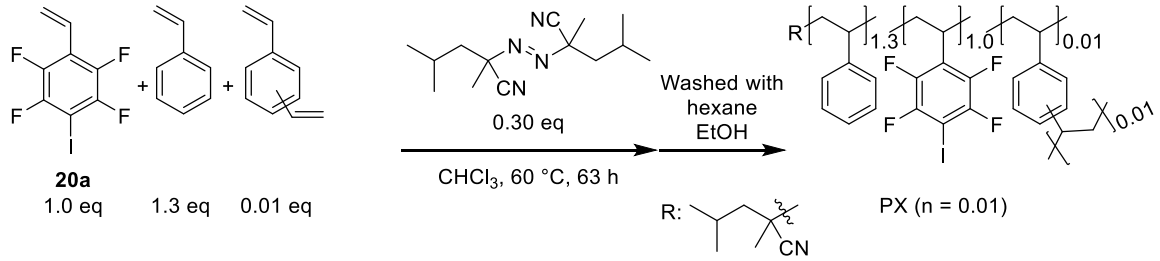
Scheme 2-8. Synthesis of PX (n = 15)

Table 2-10. Elemental Analysis of PX (n = 15)

$C_{170.7}H_{167.2}N_{0.3}F_4I$	H (%)	C (%)	N (%)	F (%)	I (%)
found	7.04	85.37	0.27	2.70	4.18
calcd.	6.95	84.52	0.17	3.13	5.23
			Content of $[C_6F_4I]$[a]	0.355 mmol/g (F based)	0.329 mmol/g (I based)

[a](Content of $[C_6F_4I]$ in PX) mmol/g = (mole of used TFIS) mmol / (theoretical weight of PX) g

ジビニルベンゼン 15 当量で確立した方法をもとに、ジビニルベンゼン 0.01 当量、0.1 当量、1.0 当量の場合も同様に、高分子を合成した(**Scheme 2-9~11**, **Table 2-11~13**)。ジビニルベンゼン 0.01 当量、0.1 当量を用いて重合反応を行った場合、反応溶液が固体になるまでそれぞれ 63 時間、17 時間か必要であった。また、ジクロロメタンやアセトンに可溶のため、ヘキサンとエタノールで洗浄した。ジビニルベンゼン 1.0 当量の場合は、15 当量と同様に 2 時間で固体になり、アセトン、ジクロロメタン、エタノールで洗浄を行った。

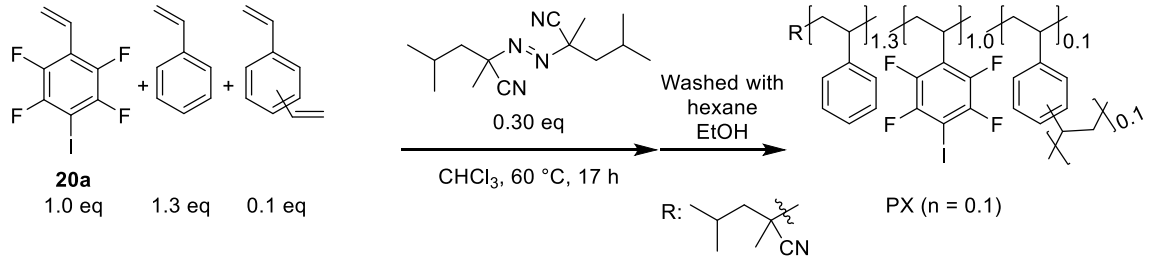


Scheme 2-9. Synthesis of PX (n = 0.01)

Table 2-11. Elemental Analysis of PX (n = 0.01)

$C_{18.7}H_{13.7}N_{0.3}F_4I$	H (%)	C (%)	N (%)	F (%)	I (%)
found	4.04	50.94	1.35	15.59	24.51
calcd.	3.13	50.94	0.30	17.20	28.72
			Content of $[C_6F_4I]$[a]	2.05 mmol/g (F based)	1.93 mmol/g (I based)

[a] (Content of $[C_6F_4I]$ in PX) mmol/g = (mole of used TFIS) mmol / (theoretical weight of PX) g

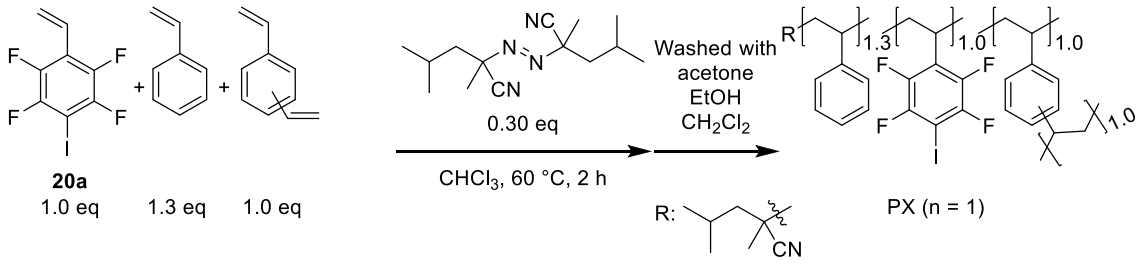


Scheme 2-10. Synthesis of PX (n = 0.1)

Table 2-12. Elemental Analysis of PX (n = 0.1)

$C_{19.6}H_{14.6}N_{0.3}F_4I$	H (%)	C (%)	N (%)	F (%)	I (%)
found	4.38	55.80	1.40	14.02	23.77
calcd.	3.25	52.01	0.50	16.76	27.98
			Content of $[C_6F_4I]$[a]	1.84 mmol/g (F based)	1.88 mmol/g (I based)

[a] (Content of $[C_6F_4I]$ in PX) mmol/g = (mole of used TFIS) mmol / (theoretical weight of PX) g



Scheme 2-11. Synthesis of PX (n =1)

Table 2-13. Elemental Analysis of PX (n = 1)

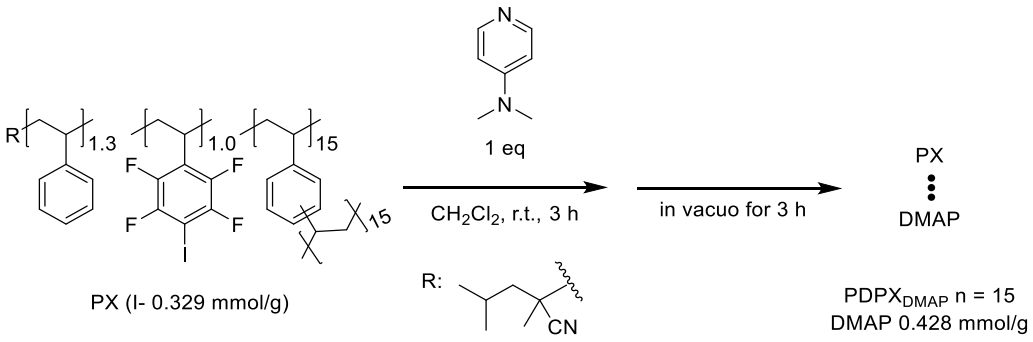
$C_{28.6}H_{23.6}N_{0.3}F_4I$	H (%)	C (%)	N (%)	F (%)	I (%)
found	4.34	60.12	0.41	12.96	21.15
calcd.	4.18	60.27	0.30	13.32	22.24
			Content of $[C_6F_4I]$[a]	1.71 mmol/g (F based)	1.67 mmol/g (I based)

[a] (Content of $[C_6F_4I]$ in PX) mmol/g = (mole of used TFIS) mmol / (theoretical weight of PX) g

2−5. 高分子触媒の調製と表面分析

2-5-1. 高分子触媒の調製

得られた 4 種類の高分子 PX 中のヨウ素に対して、ジクロロメタン溶媒中、1 当量の DMAP を加え室温で 3 時間攪拌することで、DMAP ペンダント型高分子触媒（$PDPX_{DMAP}$）を調製した。$PDPX_{DMAP}$ の結果を以下に示す（**Scheme 2-12~15**）。元素分析の結果（**Table 2-14~17**）から、高分子中の DMAP の含有量はそれぞれ 0.428、1.47、1.48、1.44 mmol/g と計算された[6]。

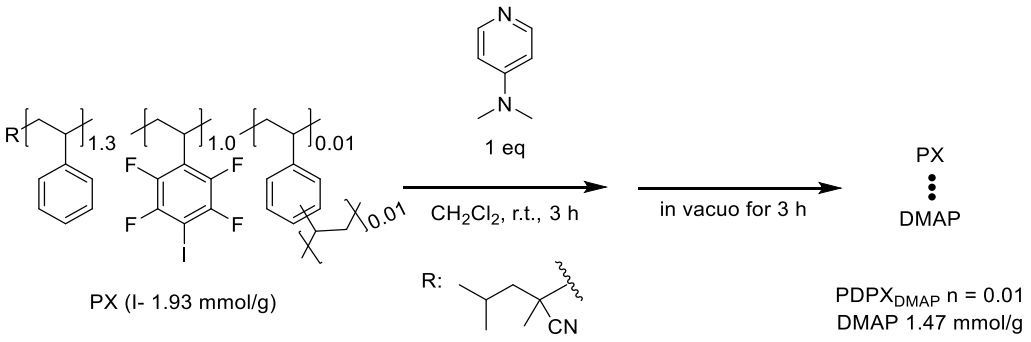


Scheme 2-12. Preparation of $PDPX_{DMAP}$ (n = 15)

Table 2-14. Elemental Analysis of and $PDPX_{DMAP}$ (n = 15)

$C_{175.64}H_{173.64}N_{2.3}F_4I$	H (%)	C (%)	N (%)
found	6.11	83.51	1.47
calcd.	6.96	83.86	1.11

(Content of [DMAP] in $PDPX_{DMAP}$) mmol/g = (mole of DMAP calculated by elemental analysis) mmol / (obtained weight of $PDPX_{DMAP}$) g

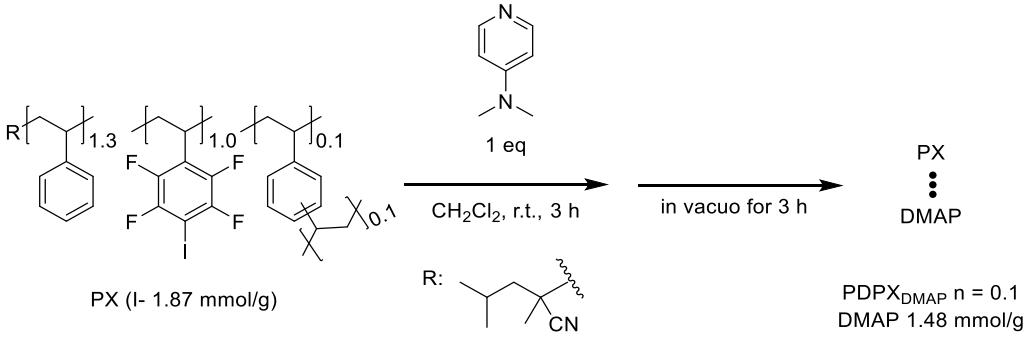


Scheme 2-13. Preparation of $PDPX_{DMAP}$ (n = 0.01)

Table 2-15. Elemental Analysis of and $PDPX_{DMAP}$ (n = 0.01)

$C_{25.7}H_{23.7}N_{2.3}F_4I$	H (%)	C (%)	N (%)
found	4.80	56.61	5.47
calcd.	4.21	54.41	5.67

(Content of [DMAP] in $PDPX_{DMAP}$) mmol/g = (mole of DMAP calculated by elemental analysis) mmol / (obtained weight of $PDPX_{DMAP}$) g

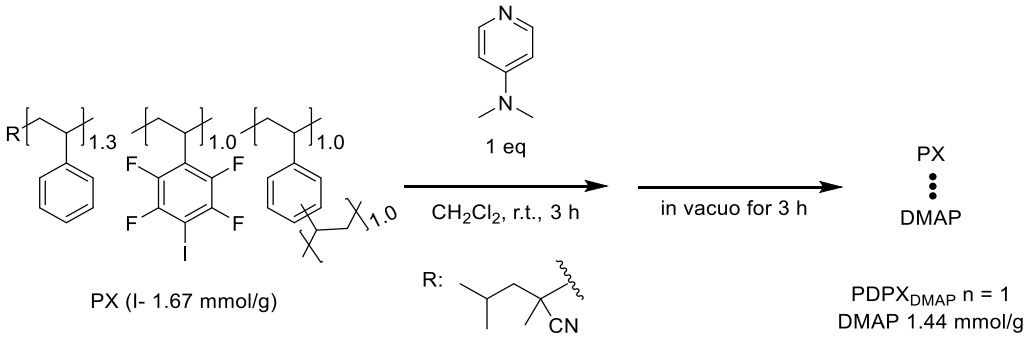


Scheme 2-14. Preparation of $PDPX_{DMAP}$ (n = 0.1)

Table 2-16. Elemental Analysis of and $PDPX_{DMAP}$ (n = 0.1)

$C_{.26.6}H_{24.6}N_{2.3}F_4I$	H (%)	C (%)	N (%)
found	5.08	58.01	5.53
calcd.	4.28	55.17	5.56

(Content of [DMAP] in $PDPX_{DMAP}$) mmol/g = (mole of DMAP calculated by elemental analysis) mmol / (obtained weight of $PDPX_{DMAP}$) g



Scheme 2-15. Preparation of $PDPX_{DMAP}$ (n = 1)

Table 2-17. Elemental Analysis of and $PDPX_{DMAP}$ (n = 1)

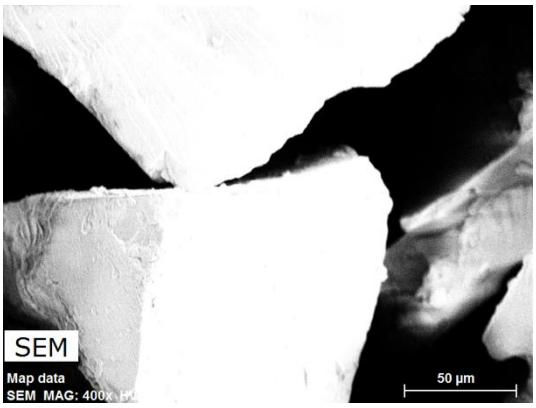
$C_{.35.6}H_{33.6}N_{2.3}F_4I$	H (%)	C (%)	N (%)
found	5.14	61.42	4.46
calcd.	4.86	61.41	4.62

(Content of [DMAP] in $PDPX_{DMAP}$) mmol/g = (mole of DMAP calculated by elemental analysis) mmol / (obtained weight of $PDPX_{DMAP}$) g

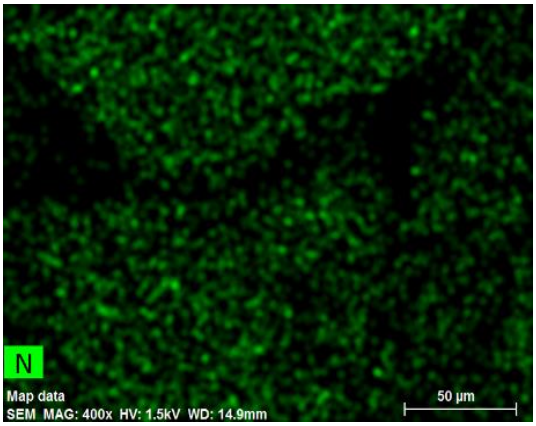
2-5-2. 高分子担体の表面観察および元素マッピング

走査電子顕微鏡（SEM）測定およびエネルギー分散型 X 線分析（EDS）により、高分子担体 PX の表面観察および元素マッピングを行った（**Figure 2-2~4**）。PX の粒径は、試料ごと粒子の大きさにばらつきがあり、50~400 μm 程度であった。また、全ての PX でフッ素が満遍なく見られた。表面の観察および元素分析マッピングから、ヨウ化テトラフルオロベンゼン部位は、高分子中に偏在することなく含まれていることが示唆された。窒素は、EDS の感度の観点から正確に含有量を測定することはできなかった。

(a)



(b)



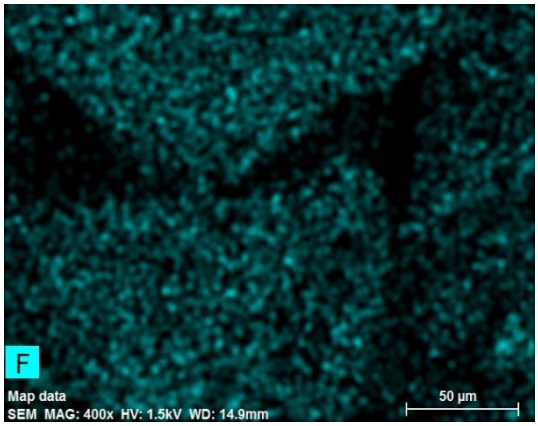
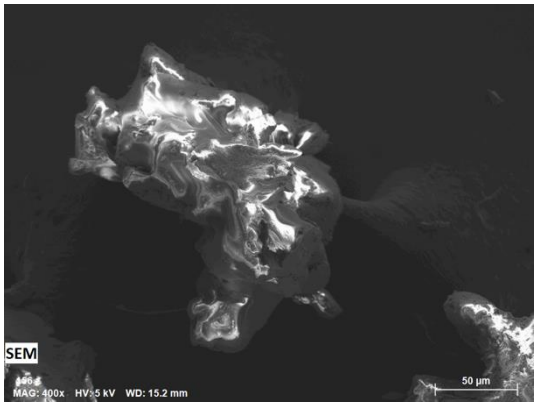


Figure 2-2. (a) SEM image and (b) elementary mapping for PX (n = 15) showing a 50 µm scale for each.

(a)



(b)

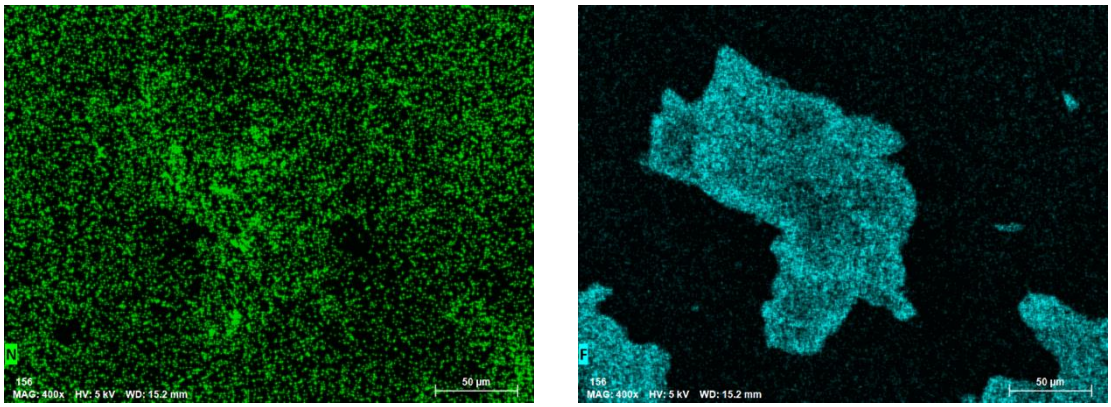
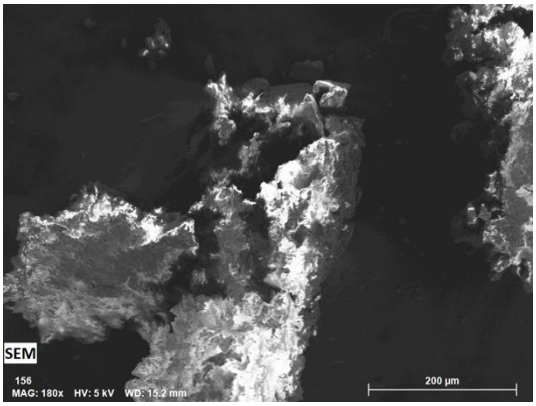


Figure 2-3. (a) SEM image and (b) elementary mapping for PX (n = 0.01) showing a 200 µm scale for each.

(a)



(b)

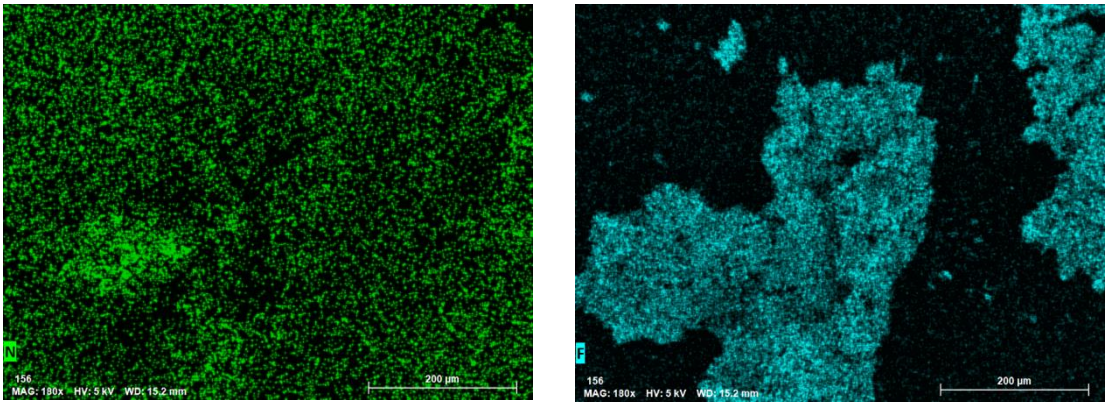
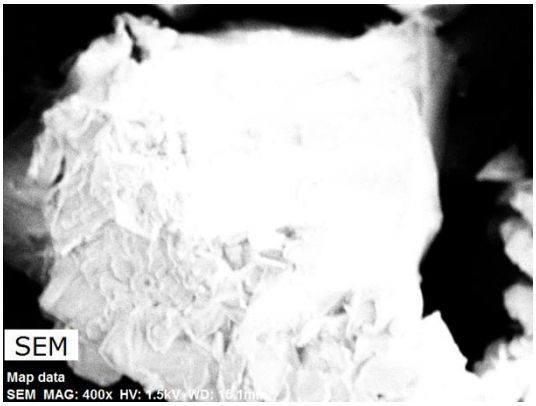


Figure 2-4. (a) SEM image and (b) elementary mapping for PX (n = 1) showing a 200 µm scale for each.

2-5-3. 高分子触媒の表面観察および元素マッピング

高分子触媒 PX_{DMAP} の表面観察および元素マッピングも同様に SEM 及び EDS で行った（**Figure 2-5~7**）。PX と比較して、表面形態に大きな違いは見られなかった。また、DMAP を PX に加えることによって、**2-5-1** で述べたように窒素の含有量は増えているが、視覚的な違いは見られなかった。

(a)



(b)

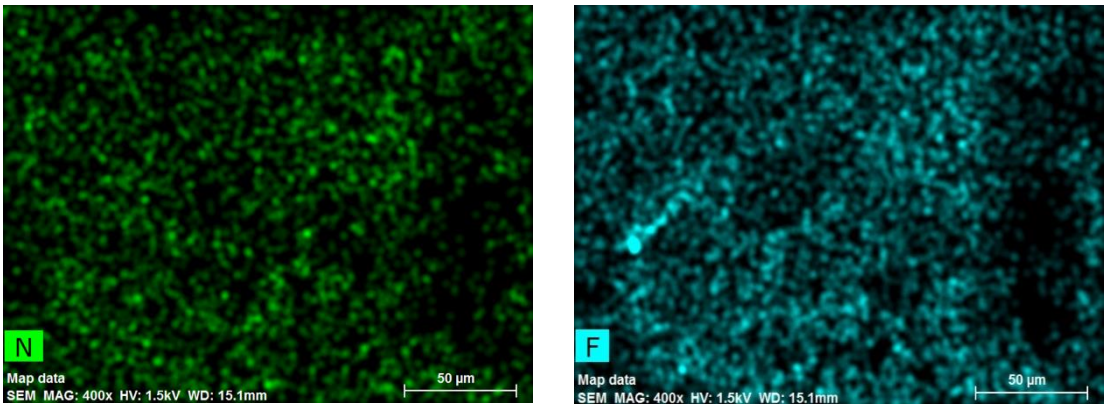
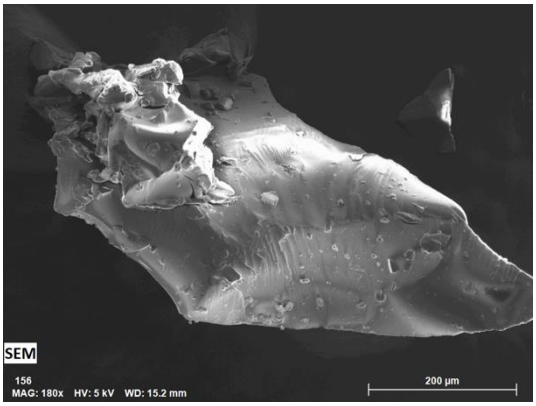
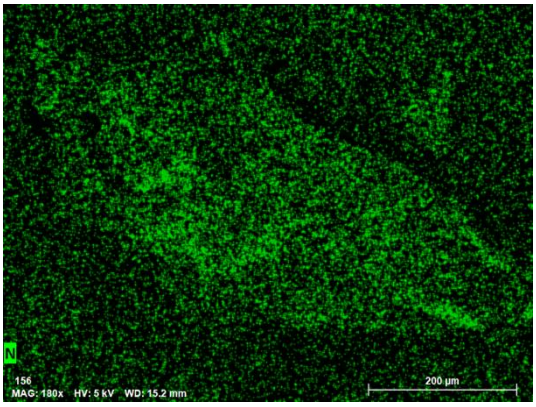


Figure 2-5. (a) SEM image and (b) elementary mapping for $PDPX_{DMAP}$ (n = 15) showing a 50 µm scale for each.

(a)



(b)



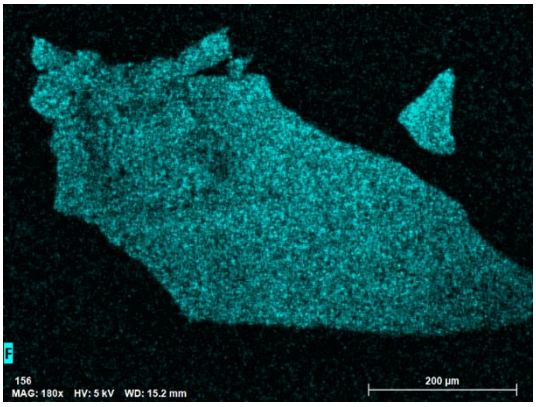
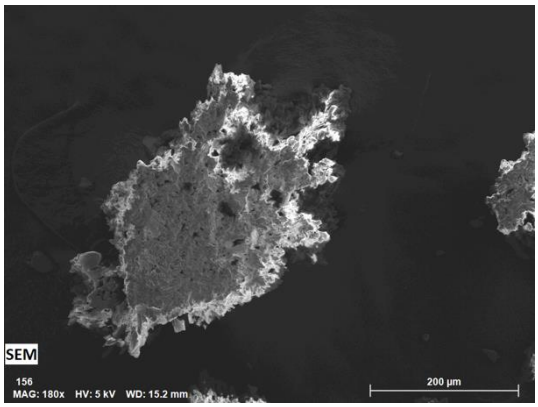


Figure 2-6. (a) SEM image and (b) elementary mapping for $PDPX_{DMAP}$ (n = 0.01) showing a 200 µm scale for each.

(a)



(b)

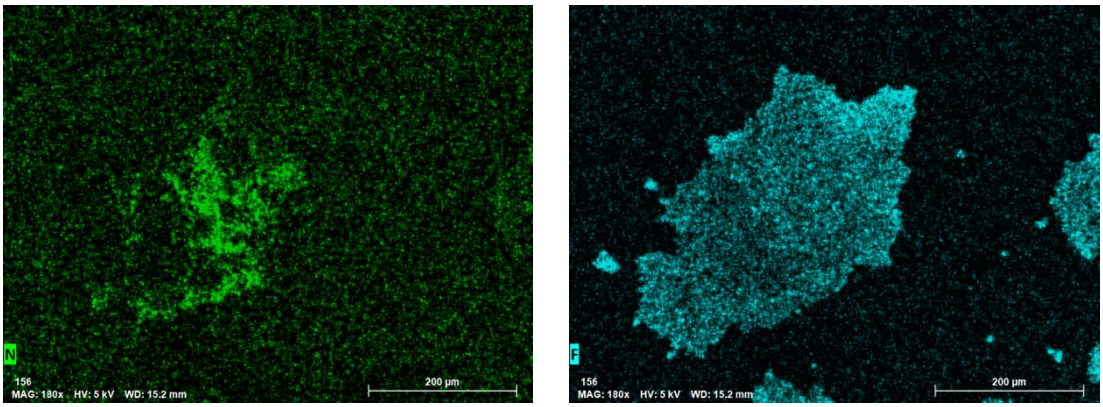


Figure 2-7. (a) SEM image and (b) elementary mapping for $PDPX_{DMAP}$ (n = 1) showing a 200 µm scale for each.

2−6. 高分子触媒の DNP ^{15}N NMR 測定

高分子担体と DMAP との分子間相互作用を確かめるため、$PDPX_{DMAP}$ の NMR 測定を行った。15 当量のジビニルベンゼンを用いて合成した $PDPX_{DMAP}$ (n = 15)はあらゆる有機溶媒に不溶なため、固体 NMR を検討した。固体 NMR は溶液 NMR よりも感度が低く、分解能が悪いことが知られている。特に、$PDPX_{DMAP}$ (n = 15)の窒素の組成比は 1.47%に過ぎず、DNP ^{15}N CPMAS を利用することにした[7]。DNP ^{15}N CPMAS は、動的核偏極を利用する固体 NMR である。近年、固体 NMR の感度の問題を解決する手法として発展を遂げている。

測定は、$PDPX_{DMAP}$ (n = 15)と DMAP、さらに比較として、DMAP 窒素とヨウ素部位がハロゲン結合を形成するヨウ化テトラフルオロビフェニル/DMAP の DNP ^{15}N NMR 測定を、産業技術総合研究所触媒化学融合研究センターの田中真司博士の協力のもと共同研究として実施した(**Figure 2-8**)。

ヨウ化テトラフルオロビフェニル/DMAP の場合、260 ppm 付近のピリジン窒素に由来するピークが DMAP のピークと比較して数 ppm 高磁場シフトした。一方、$PDPX_{DMAP}$(n = 15)の場合、このピリジン窒素に由来するピークは数 ppm 低磁場シフトした。また、60 ppm 付近のジメチルアミノ基由来のピークは高磁場シフトした。$PDPX_{DMAP}$(n＝15)は、ヨウ化テトラフルオロビフェニル/DMAP と異なる化学シフト変化を示したことから、$PDPX_{DMAP}$(n＝15)中の DMAP は、高分子中でスチレンやジビニルベンゼンに起因する非共有結合性の相互作用の影響も受けながら存在していることが示唆された。4-PhC_6F_4I···DMAP の固体状態とは異なる分子配列の可能性も考えられる。

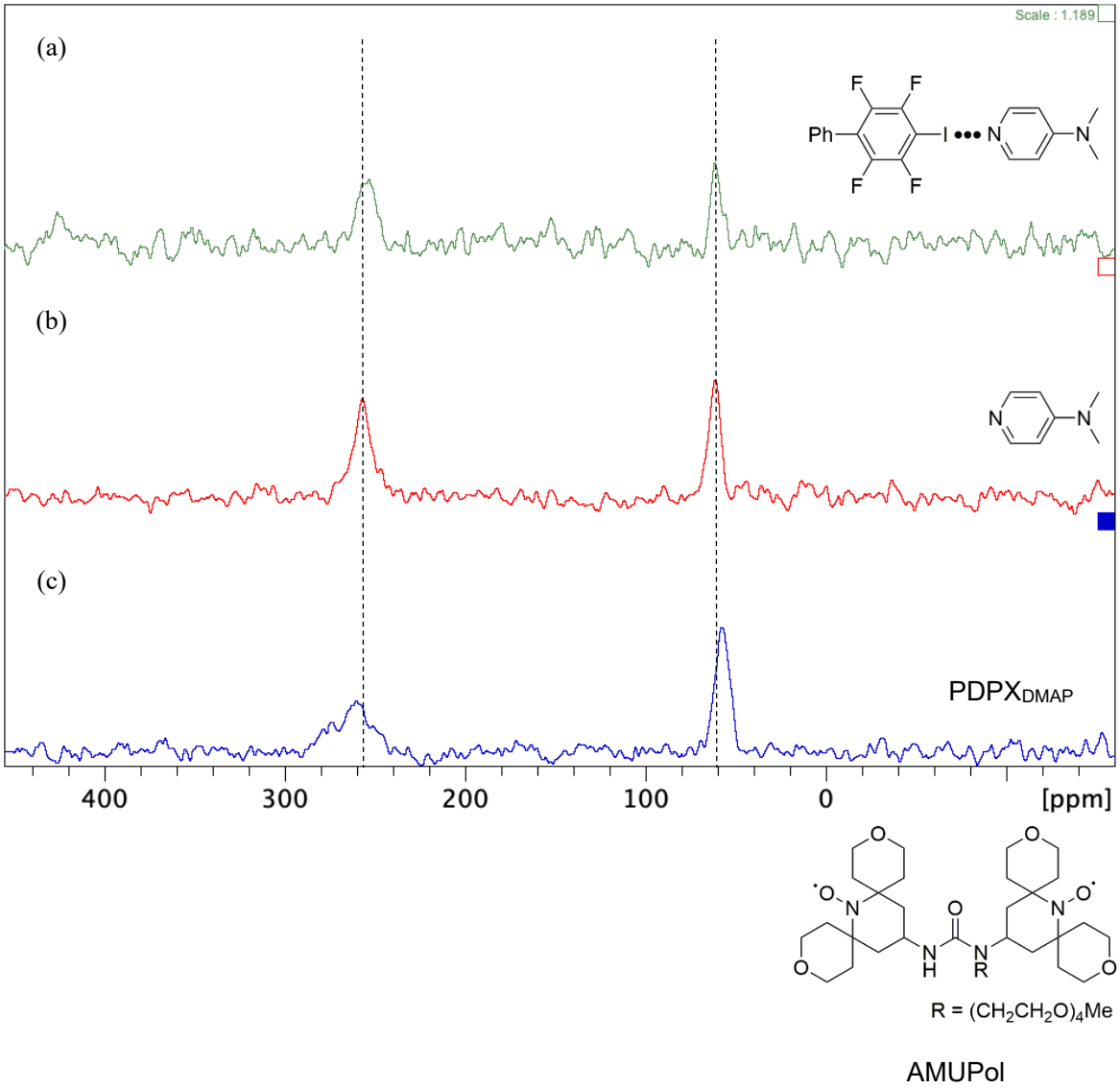


Figure 2-8. DNP ^{15}N NMR (41 MHz, 103−105 K, 3.2 mm, 10 kHz).
(a) Tetrafuluoroiodobiphenyl/DMAP in AMUPol/DMSO d_6, (b) DMAP in AMUPol/DMSO d_6, and (c) $PDPX_{DMAP}$ in AMUPol/DMSO d_6.

2–7. まとめ

第 2 章をまとめる。市販で入手可能なテトラフルオロ安息香酸からヨウ化テトラフルオロスチレン(TFIS)を合成するための合成手法を確立した。特に、ヨウ化テトラフルオロベンズアルデヒドの Wittig 反応を開発し、検討した種々の有機塩基の中で、TMG を用いた場合に、最も高い収率で TFIS が得られることを見出した。また、相関分析により、Wittig 反応に有効な有機塩基として、1)イリド生成に適当な負電荷を有すること、2)アルデヒド **19** およびスチレン **20** の分解を促進しない低求核性であること、3)生成物のスチレン **20** と錯形成可能なハロゲン結合受容能を有すること、これら 3 つの要素が重要であることを示した。スチレン **20** の精製では、展開溶媒としてペンタンを用いることで、目的生成物の分解を抑制できることを見出し、高純度の TFIS を得ることに成功した。さらに、高純度の TFIS を用いることによって、テトラフルオロヨードベンゼン部位を十分に有する高分子を得ることに成功し、1 当量の DMAP を加え、目的とする高分子触媒を調製する方法を確立した。最後に、DNP ^{15}N NMR 測定により、得られた高分子 DMAP 体が、ポリ C_6F_4I スチレンのヨウ素部位と DMAP 芳香環窒素とのハロゲン結合ではなく、炭化水素系スチレンやジビニルベンゼンと芳香環との非共有結合性相互作用により複合体を形成している可能性が示された。

引用文献

[1] Takeuchi, T.; Minato, Y.; Takase, M.; Shinmori, H. Molecularly Imprinted Polymers with Halogen Bonding-based Molecular Recognition Sites. *Tetrahedron Lett.* **2005**, *46*, 9025–9027.

[2] Dumele, O.; Trapp, N.; Diederich, F. Halogen Bonding Molecular Capsules. *Angew. Chem. Int. Ed.* **2015**, *54*, 12339–12344.

[3] (a) Mariaca, P.; Labat, G.; Behrnd, N.-R.; Bonin, M.; Helbling, F.; Eggli, P.; Couderc, G.; Neels, A.; Stoeckli-Evans, H.; Hulliger, J. Preparation of Donor–Acceptor Substituted Fluorostilbenes and Crystal Chemistry of Fluorinated (*E*)-4-(4-halogeno-styryl)-benzonitriles. *J. Fluorine Chem.* **2009**, *130*, 175–196. (b) Senaweera, S.; Weaver, J. D. S_NAr Catalysis Enhanced by an Aromatic Donor–Acceptor Interaction; Facile Access to Chlorinated Polyfluoroarenes. *Chem. Commun.* **2017**, *53*, 7545−7548.

[4] Okuma, K.; Sakai, O.; Shioji, K. Wittig Reaction by Using DBU as a Base. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1675–1676.

[5] http://www.datachemicallab.com

[6] (Content of [DMAP] in $PDPX_{DMAP}$) mmol/g = (mole of DMAP calculated by elemental analysis) mmol / (obtained weight of $PDPX_{DMAP}$) g

[7] Ni, Q. Z.; Daviso, E.; Can, T. V.; Markhasin, E.; Jawla, S. K.; Swager, T. M.; Temkin, R. J.; Herzfeld, J.; Griffin, R. G. Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy. *Acc. Chem. Res.* **2013**, *46*, 1933−1941.

実験項

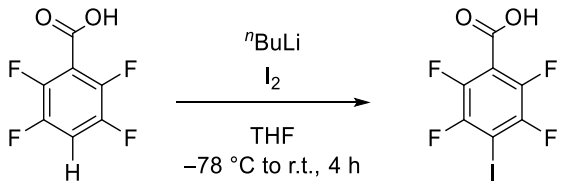
1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of standard grade nitrogen gas (oxygen <10 ppm) in flame-dried glassware with magnetic stirring. Anhydrous THF, CH_2Cl_2, toluene and diethyl ether (Et_2O) were supplied from Kanto Chemical Co., Inc. as "Dehydrated solvent system". Other reagents were purchased from commercial suppliers and used without further purification. Purification of reaction products was carried out by column chromatography on silica gel 60 (spherical, neutral, 100-210 μm; KANTO and Merck). Analytical thin layer chromatography (TLC) was performed on E. Merck precoated (0.25 mm) silica gel 60-F254 plates. Visualization was accomplished with UV light and phosphomolybdic acid solution in ethanol by heating.^{1}H NMR spectra were recorded on a JEOL ECS-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: referenced to TMS 0.00 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL ECS-400 (100 MHz) spectrometer with complete proton decoupling or fluorine decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). ^{19}F NMR spectra were recorded on a JEOL ECS-400 (376 MHz) spectrometer. Chemical shifts are reported in ppm from α,α,α-trifluorotoluene as the external standard (–63.72 ppm). DNP solid-state ^{15}N NMR measurements were performed with a Bruker Avance NEO 400 MHz/263 GHz 9.4 T DNP system. AMUPol was purchased from a commercial source, and used as a polarizing agent. Incipient wetness impregnation of AMUPol in DMSO-d6 was used to prepare the samples for DNP experiments. The impregnated samples were packed into sapphire rotors and sealed with teflon insert and zirconia cap under an inert atmosphere, and the sample was frozen at ca. 100 K inside the precooled low temperature 3.2 mm MAS probe head. The sweep coil of the main magnetic field was set so that microwave irradiation occurred at the 1 H positive DNP enhancement maximum of the nitroxide biradicals. Standard ramped cross polarization (CP) was used to transfer polarization from the 1 H nuclei to the nucleus of interest (^{15}N). CP contact time was 3000- 9000 Ps. SPINAL-64 1 H heteronuclear decoupling was applied during acquisition. The DNP enhanced solid-state ^{15}N NMR spectra were typically acquired with a recycle delay 2.4-3.3 s and 16384 scans with a sample spinning frequency of 10 kHz and a sample temperature of 103-105 K. ^{15}N chemical shifts were referenced to liq. NH_3 at 0 ppm using $^{15}NH_4Cl$ as an external standard (39.3 ppm). High-performance liquid chromatography (HPLC) was performed on a Jasco HPLC-2000 system equipped with a

variable wavelength detector using YMC-Pack SIL-06 column from YMC. Elemental analysis of H, C, and N was performed on J-SCIENCE LAB MICRO CORDER JM10 at the Instrument Center, Institute for Molecular Science. Elemental analysis of F, I, and Cl in addition to H, C, and N was performed on XS-2100H at Organic Elemental Microanalysis Center, Kyoto University. SEM images were obtained using Hitachi High-Tech SU6600 and EDS mapping were measured using BrukerAXS QUANTAX XFlash 5060FQ and XFlash6|10. Infrared (IR) spectra were recorded on a Jasco FT/IR-460plus spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 instrument (double-focusing magnetic sector mass analyzer: EB) using fast atom bombardment (FAB) as the ionization method and 3-nitrobenzyl alcohol as the matrix at the Instrument Center of the Institute for Molecular Science.

2. Preparation of DMAP-pendant XB polymers

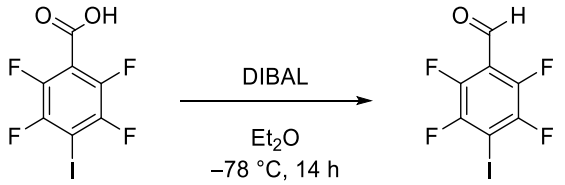
Synthesis of 2,3,5,6-tetrafluoro-4-iodobenzoic acid (S1)



S1

The **S1** was synthesized according to literature procedure.[S1] To a solution of 2,3,5,6-tetrafluorobenzoic acid (2.91 g, 15.0 mmol, 1.0 equiv.) in THF (300 mL) was added *n*-BuLi (1.6 M in hexane, 18.3 mL, 29.3 mmol, 2.0 equiv.) dropwise over 15 min at –78 ºC under nitrogen atmosphere, then the mixture was stirred at –78 ºC for 1 h. A solution of iodine (3.70 g, 14.3 mmol, 0.95 equiv.) in THF (20 mL) was then slowly added to the reaction mixture. The mixture was allowed to slowly warm up to room temperature and stirred for 4 h. 2M HCl aq. (19 mL) was added to the mixture and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with sat. $Na_2S_2O_3$ aq. (50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure after filtration to afford **S1** as a white solid (4.56 g, 14.3 mmol, 95% yield). The **S1** was used in the next reaction without further purification.

Synthesis of 2,3,5,6-tetrafluoro-4-iodobenzaldehyde (19a)



S1 **19a**

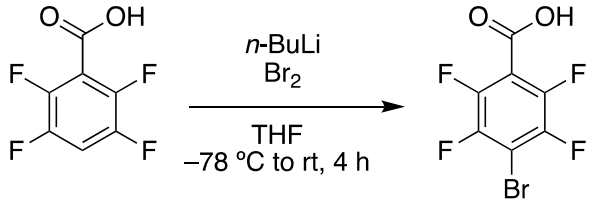
The **19a** was synthesized according to literature procedure.[S2] To a solution of 2,3,5,6-tetrafluoro-4-iodobenzoic acid **S1** (4.64 g, 14.5 mmol, 1.0 equiv.) in diethyl ether (180 mL) was added DIBAL (1.0 M in *n*-hexane, 28.4 mL, 29.0 mmol, 2.0 equiv.) dropwise over 15 min at –78 °C under nitrogen atmosphere, then the mixture was stirred at –78 ºC for 14 h. Methanol (22.7 mL) was added to the mixture, and the mixture was allowed to warm to room temperature. Then 30% Rochelle's salt aq. (28.4 mL), celite (30 g), and sea sand (50 g) were added to the mixture, and the mixture was further stirred at room temperature for 1.5 h. The resulting suspension was filtered by celite and washed with diethyl ether (50 mL). A filtrate was extracted with diethyl ether (3 × 50 mL). The combined

organic layers were washed with sat. Rochelle's salt aq. (20 mL, 15 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The obtained crude product was purified by silica gel chromatography (hexane/ethyl acetate = 30:1 to 8:1) to afford **19a** (1.36 g, 4.50 mmol, 31%) as a white solid.

Rf = 0.42 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.32 (s, 1H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –118.18- –118.24 (m, 2F), –143.56- –143.65 (m, 2F). elemental analysis calcd. (%) for C_7HF_4IO: C 27.66, H 0.33, F 25.00, I 41.75; found: C 27.63, H 0.38, F 25.07, I 41.70.

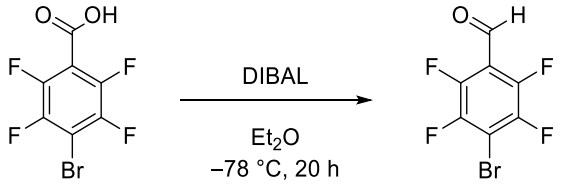
Synthesis of 4-bromo-2,3,5,6-tetrafluorobenzoic acid (S2)



S2

The **S2** was synthesized according to **Synthesis of 2,3,5,6-tetrafluoro-4-iodobenzoic acid (S1)**. To a solution of 2,3,5,6-tetrafluorobenzoic acid (584 mg, 3.01 mmol, 1.0 equiv) in THF (64 mL) was added *n*-BuLi (1.59 M in hexane, 3.80 mL, 6.04 mmol, 2.0 equiv) dropwise over 15 min at –78 ºC under nitrogen atmosphere, then the mixture was stirred at –78 ºC for 1 h. Bromine (310 μL, 6.10 mmol, 2.0 equiv.) was then added to the reaction mixture. The mixture was allowed to slowly warm up to room temperature and stirred for 4 h. 2M HCl aq. (4 mL) was added to the mixture and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with sat. $Na_2S_2O_3$ aq. (50 mL) and brine (50 mL), and concentrated under reduced pressure after filtration. The obtained residue was dissolved in CH_2Cl_2 (40 mL) then the solution was back-extracted with 5% NaOH aq. (4 × 25 mL). The aqueous layer was acidified with 2M-HCl aq. (100 mL), then extracted with CH_2Cl_2 (4 × 25 mL). The combined organic layers were washed with H_2O (15 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure after filtration to afford **S2** as a white solid (728 mg, 2.67 mmol, 89% yield). The **S2** was used in the next reaction without further purification.

Synthesis of 4-bromo-2,3,5,6-tetrafluorobenzaldehyde (19b)[S3]



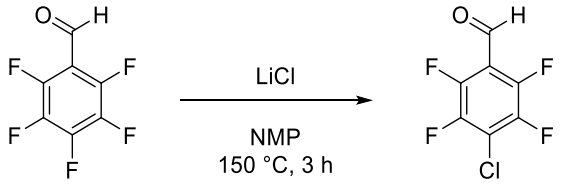
S2 **19b**

The **19b** was synthesized according to **Synthesis of 2,3,5,6-tetrafluoro-4-iodobenzaldehyde (19a)** using 4-bromo-2,3,5,6-tetrafluorobenzoic acid (**S2**) (728 mg, 2.67 mmol, 1.0 equiv.) to afford **19b** as a white solid (286 mg, 1.11 mmol, 37%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H).

^{19}F NMR (375 MHz, $CDCl_3$) δ –131.3- –131.4 (m, 2F), –141.0- –141.1 (m, 2F).

Synthesis of 4-chloro-2,3,5,6-tetrafluorobenzaldehyde (19c)



19c

The **19c** was synthesized according to literature procedure.[S4]

A 100 mL three neck flask equipped with a magnetic stirring bar and a septum was charged with LiCl (466 mg, 11.0 mmol, 1.1 equiv.). The flask was flame-dried under vacuo then backfilled with nitrogen gas after cooling to room temperature. *N*-methylpyrrolidone (15 mL) and pentafluorobenzaldehyde (1.25 mL, 10.0 mmol, 1.0 equiv.) were added to the flask. The resulting suspension was warmed up to 150 ºC and stirred for 3 h. After cooling to room temperature, the mixture was poured into ice-water (50 mL) then extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The obtained crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 10:1) to afford **19c** as a pale-yellow solid (1.52 g, 7.10 mmol, 71% yield, 89% purity). The **19c** was further purified by washing with a little amount of hexane to afford 99% purity of **19c** as a white solid (891 mg, 4.20 mmol, 42% yield).

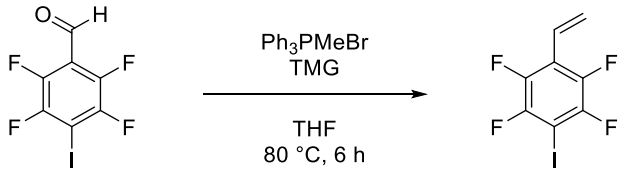
Rf = 0.20 (hexane/ethyl acetate = 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –138.8- –138.9 (m, 2F), –144.1- –144.2 (m, 2F).

Synthesis of 1-ethenyl-2,3,5,6-tetrafluoro-4-iodobenzene (20a)

General procedure for Wittig reaction:

Synthesis of 2,3,5,6-tetrafluoro-4-iodostyrene (20a)



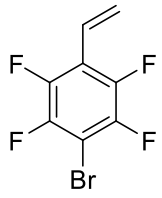
19a **20a**

To a solution of methyltriphenylphosphonium bromide (0.643 g, 1.80 mmol, 3.6 equiv.) in THF (5 mL) was added 1,1,3,3-tetramethylguanidine (282 µL, 2.25 mmol, 4.5 equiv.) and the reaction mixture was stirred at 80 ºC for 30 min. Then a solution of 2,3,5,6-tetrafluoro-4-iodobenzaldehyde **19a** (0.152 g, 0.50 mmol, 1.0 equiv.) in THF (1.5 mL) was added to the mixture. The mixture was stirred for 6 h. H_2O (10 mL) was added to the mixture and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$. Small aliquots from the organic layers were analyzed by ^{19}F NMR using α,α,α-trifluorotoluene as a standard (53% NMR yield). The organic layers were concentrated under reduced pressure to afford crude of **20a** as colorless oil. *Due to the stability of the product, the **20a** was characterized as a mixture.*

Rf = 0.53 (hexane)

^1H NMR ($CDCl_3$, 400 MHz) δ 6.69 (dd, 1H, *J* = 11.9, 6.2 Hz), 6.15 (d, 1H, *J* = 18.1 Hz), 5.76 (d, *J* = 11.9 Hz, 1H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –121.65- –121.74 (m, 2F), –141.56- –141.66 (m, 2F). ^{13}C NMR {^{19}F} ($CDCl_3$, 100 MHz) δ147.2, 144.0 (d, *J* = 4.9 Hz), 124.3 (t, *J* = 160 Hz), 122.3 (dd, *J* = 163, 2.9 Hz), 117.6-117.3 (m), 70.3. IR (ATR) 1471, 1416, 1259, 1101, 983, 953, 794.

4-bromo-2,3,5,6-tetrafluorostyrene (20b)



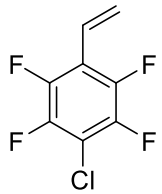
20b

The **20b** was synthesized according to General Procedure using **19b** (128 mg, 0.500 mmol, 1.0 equiv.) to afford **20b** in 39% NMR yield. *Due to the stability of the product, the **20b** was characterized as a mixture and full data could not be collected.*

Rf = 0.58 (hexane)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.67 (dd, 1H, *J* = 11.9, 18.1 Hz), 6.14 (d, 1H, *J* = 17.9 Hz), 5.76 (d, 1H, *J* = 11.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –134.43- –134.50 (m, 2F), –142.10- –142.18 (m, 2F). ^{13}C NMR {^{19}F} ($CDCl_3$, 100 MHz) δ 144.9, 144.7, 124.3 (dt, *J* = 160, 1.9 Hz), 122.0 (ddd, *J* = 162, 3.8, 2.8 Hz), 116.5-116.1 (m), 98.2. IR (ATR) 1481, 1457, 1421, 1398, 1267, 1122, 1072, 988, 957, 820, 741, 704.

4-chloro-2,3,5,6-tetrafluorostyrene (20c)



20c

The **20c** was synthesized according to General Procedure using **19c** (106 mg, 0.500 mmol, 1.0 equiv.) to afford **20c** in 29% NMR yield. *Due to the stability of the product, the **20c** was characterized as a mixture and full date could not be collected.*

Rf = 0.60 (hexane)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.67 (dd, 1H, *J* = 11.5, 18.6 Hz), 6.12 (d, 1H, *J* = 18.6 Hz), 5.76 (d, 1H, *J* = 12.6 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –142.11- –142.19 (m, 2F), –142.65- –142.71 (m, 2F). ^{13}C NMR {^{19}F} ($CDCl_3$, 100 MHz) δ 144.7, 144.1, 124.3 (t, *J* = 161 Hz), 121.8 (ddd, *J* = 162, 2.8, 1.9 Hz), 115.7-115.3 (m), 110.7. IR (ATR) 1485, 1465, 1425, 1402, 1279, 1108, 1000, 989, 961, 939, 901, 859.

Calculation of yield for 20a.

After the finish of reaction in 0.50 mmol scale, 1.0 equivalent of α,α,α-trifluorotoluene as internal standard was added to organic extract. 500 μL of the organic extract was transferred to NMR tube, then ^{19}F NMR was measured without lock and shim. The yield of **20a** was determined by ^{19}F NMR based on integration ratios of two fluorines at either the *ortho* or *meta* position of **20a** comparing with those of CF_3 group in α,α,α-trifluorotoluene as an internal standard.

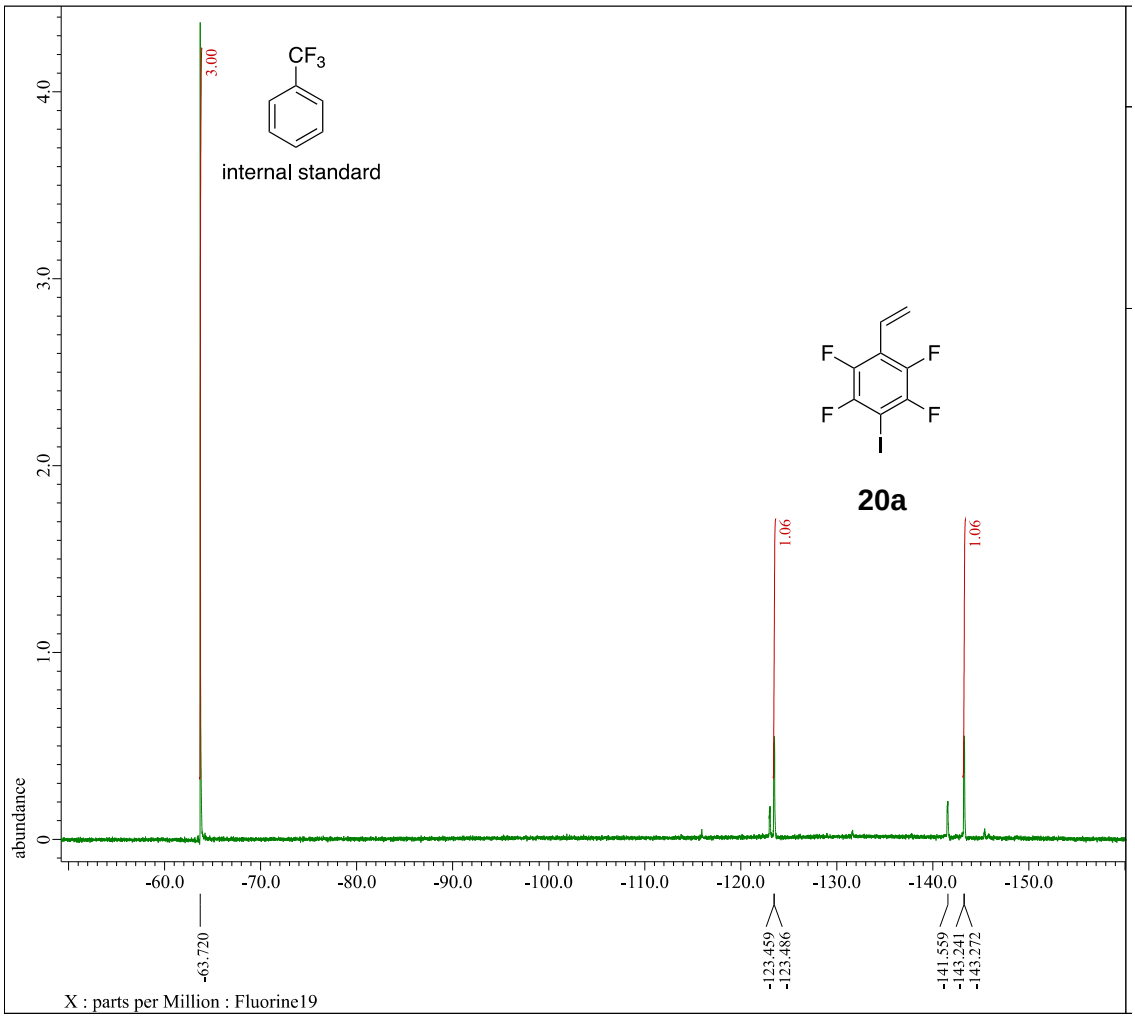


Figure S1. ^{19}F NMR spectra (CH_2Cl_2/THF) for crude product with α,α,α-trifluorotoluene as an internal standard.

Calculation of yield for $Ph_3P=O$.

After the finish of reaction in 0.50 mmol scale, 1.0 equivalent of Ph_3P as an internal standard was added to organic extract. 500 μL of the organic extract was transferred to NMR tube, then ^{31}P NMR was measured without lock and shim. The yield of $Ph_3P=O$ was determined by ^{31}P NMR based on integration ratios of phosphorous atom in $Ph_3P=O$ comparing with that in Ph_3P as an internal standard.

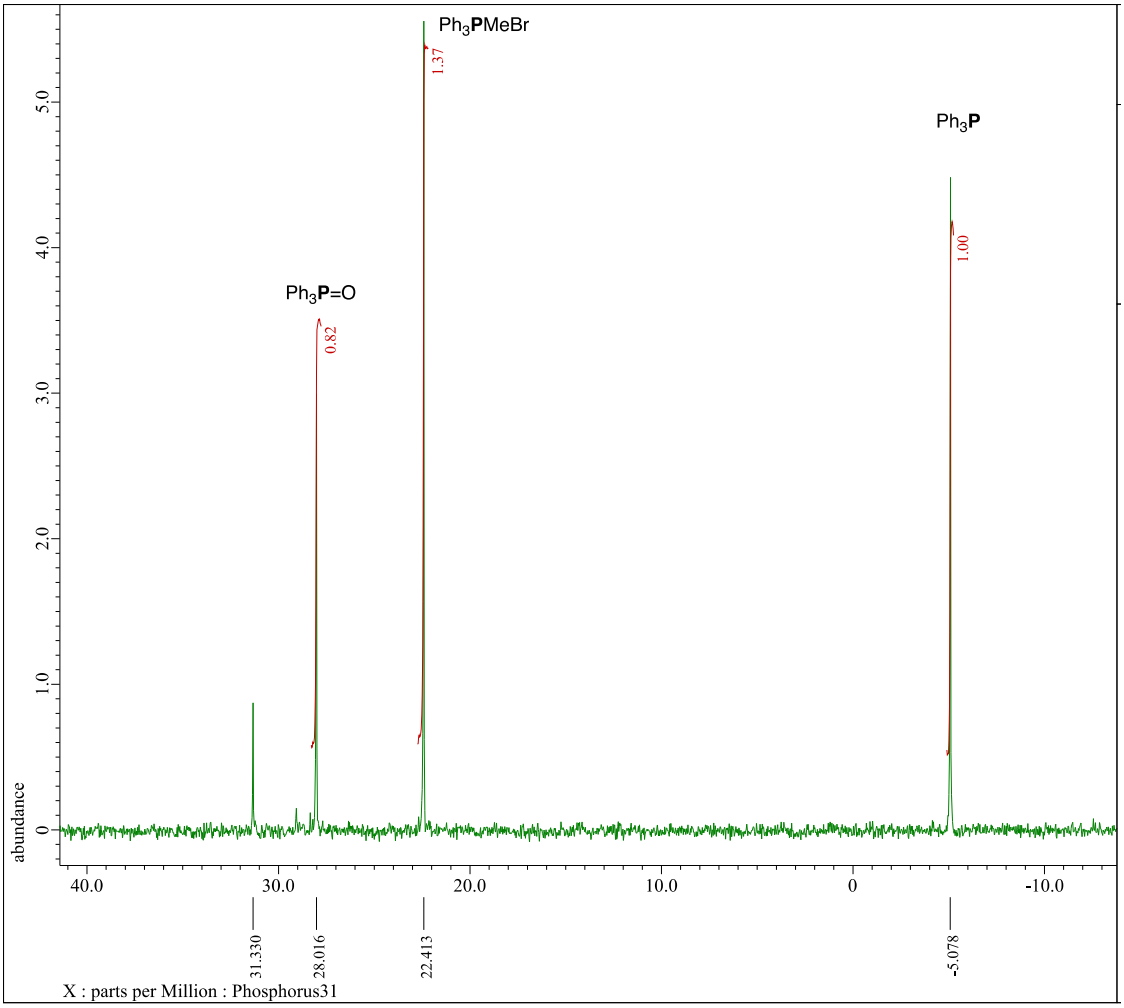


Figure S2. ^{31}P NMR spectra (CH_2Cl_2/THF) for crude product with Ph_3P as an internal standard.

DFT Calculations

Computational analysis by DFT

All molecular geometries were optimized by the M06-2X functional with Grimme's D3 dispersion correction[S5] using the 6-311+G(d,p) basis set. The SMD solvation model[S6] was used with the solvents indicated. The stationary geometries were checked by the vibration analyses after the geometry optimization procedures. The stationary geometries and their energies were refined using Gaussian 16 software package.[S7]

Computational details

The table shows total energy *E*, enthalpy *H*, and Gibbs free energy *G* (hartree) at the SMD/M06-2X-D3/6-311+G(d,p) level.

Table S4. Organic bases

compound	solvent	temp. (°C)	*E*	*H*	*G*
MTBD	THF	60	-478.0685409	-477.820122	-477.874209
DBN	THF	60	-383.4162621	-383.216875	-383.264765
DBU	THF	40	-462.0245018	-461.765565	-461.814401
DBU	THF	60	-462.0245018	-461.764137	-461.817565
DBU	THF	80	-462.0245018	-461.762611	-461.820816
DBU	CH_2Cl_2	55	-462.0271203	-461.767163	-461.819432
DBU	MeCN	95	-462.0265648	-461.763596	-461.825434
DBU	toluene	125	-462.0220921	-461.756142	-461.825920
DBU	Et_2O	45	-462.0242003	-461.764818	-461.814828
DBU	1,4-dioxane	115	-462.0179106	-461.752743	-461.819820
TMG	THF	60	-362.5440492	-362.341413	-362.394088
TMG	THF	80	-362.5440492	-362.340084	-362.397289
piperidine	THF	60	-251.8589684	-251.691224	-251.731886
quinuclidine	THF	60	-329.2536598	-329.048446	-329.092528
Et_3N	THF	60	-292.3478434	-292.128626	-292.180267

Table S5. (Organic base)·HBr salts

compound	solvent	temp. (°C)	*E*	*H*	*G*
MTBD·HBr	THF	60	-3052.9024750	-3052.635936	-3052.698567
DBN·HBr	THF	60	-2958.2499495	-2958.033479	-2958.091369
DBU·HBr	THF	40	-3036.8606171	-3036.584522	-3036.642610
DBU·HBr	THF	60	-3036.8606171	-3036.582886	-3036.646370
DBU·HBr	THF	80	-3036.8606171	-3036.581151	-3036.650232
DBU·HBr	CH_2Cl_2	55	-3036.8639084	-3036.586625	-3036.648763
DBU·HBr	MeCN	95	-3036.8654663	-3036.584698	-3036.658308
DBU·HBr	toluene	125	-3036.8508323	-3036.567264	-3036.650314
DBU·HBr	Et_2O	45	-3036.8576031	-3036.581161	-3036.640606

DBU·HBr	1,4-Dioxane	115	-3036.8452591	-3036.562597	-3036.641936
TMG·HBr	THF	60	-2937.3741575	-2937.154729	-2937.217686
TMG·HBr	THF	80	-2937.3741575	-2937.153162	-2937.221512
piperidine·HBr	THF	60	-2826.6854590	-2826.500219	-2826.550472
quinuclidine·HBr	THF	60	-2904.0849020	-2903.862007	-2903.915777
Et_3N·HBr	THF	60	-2867.1788689	-2866.941629	-2867.001054

Table S6. HBr

compound	solvent	temp. (°C)	*E*	*H*	*G*
HBr	THF	40	-2574.7712306	-2574.761714	-2574.785546
HBr	THF	60	-2574.7712306	-2574.761493	-2574.787075
HBr	THF	80	-2574.7712306	-2574.761271	-2574.788617
HBr	CH_2Cl_2	55	-2574.7716789	-2574.761997	-2574.787141
HBr	MeCN	95	-2574.7712393	-2574.761118	-2574.789796
HBr	toluene	125	-2574.7712645	-2574.760778	-2574.792136
HBr	Et_2O	45	-2574.7714449	-2574.761869	-2574.786137
HBr	1,4-Dioxane	115	-2574.7703863	-2574.760006	-2574.790467

Correlation analyses

Preparation of data sets

Data sets were prepared as csv. file using bellow descriptors.

Table S7. Descriptors for correlation analyses

Category	Descriptor	Physical meaning	Reference
Reaction	yield (%) of TFIS	Yield of 2,3,5,6-tetrafluoro-4-iodostyrene **2a**	
	yield (%) of $Ph_3P=O$	Yield of triphenylphosphine oxide	
	UDR-Pro	Undesired Reaction Product: 0: Not observed. -1:observed	
	temp. (deg C)	Reaction temperature	
	time (h)	Reaction time	
Basicity	pK_{BH}	Basicity of organic base.	Ref.S8
	Vs,min (kJ/mol)	Electrostatic potential energy for nitrogen atom center	
	NBO (a.u.)	NBO charge for nitrogen atom center	
	delta G (kcal/mol)	ΔG: Gibbs free energy for nitrogen atom center	
	Mayer-N	Nucleophilicity of organic base	Ref. S9
	Volume	Volume of organic base	

	Surface	Surface area of organic base	
	HBD	Number of hydrogen-bond door centers connected to or conjugated with the bacisity center.	Ref. S8
Structure	NXBA	Number of Halogen bond acceptor in organic base	
	Cyclic/Acyclic	Type of structure for organic base (Equal to 1 if the structure is cyclic; equal to 0 if the structure is acyclic)	
	NRing	Number of ring in organic base	
	Ring Size of N	Size of the ring containing the basicity center (“0” if the center is not part of a ring)	
	Ring Size of S	Size of the ring that is out of the basicity center (“0” if the organic base is without ring structure or no ring structure in the out of active center)	
Solvent	SVI-Et(30)	Solvent index: polarity index based on molar absorption energy (kcal/mol)	Ref. S10
	SVI-n	Solvent index: Reflective index	Ref. S11
	SVI-epsilon	Solvent index: dielectric constant	
	SVI-mu	Solvent index: dipole moment	
	SVI-pi*	Solvent index: polarity index based on solvatochromism	
	SVI-PC1	Principal components which are reported in ACS solvent selection tool	Ref. S12
	SVI-PC2		
	SVI-PC3		
	SVI-PC4		
	SVI-PC5		
	SVI-DN	Solvent index: Number of Electron pair Donor	Ref. S13
	SVI-AN	Solvent index: Number of Electron pair Acceptor	
	SVI-dD	Solvent index: The energy from dispersion forces between molecules	Ref. S14
	SVI-dP	Solvent index: The energy from dipolar intermolecular forces between molecules	
	SVI-dH	The energy from hydrogen bonds between molecules	

Missing values

Some missing values such as $pK_{B\text{-}H}$ of DBU in CH_2Cl_2, toluene, diethyl ether, MTBE, glyme, and 1,4-dioxane, $pK_{B\text{-}H}$ of DMAP, NMI, *N*-methylpyrrolidine in THF, Mayer-N of MTBD, TMG, DABCO, DIPEA, NMO and TBD, ΔG of DBU in MTBE and glyme, NBO of DBU in MTBE and glyme, Vs,min of DBU in MTBE and glyme, SVI-pi* of MTBE, SVI-DN of MTBE, and SVI-AN of MTBE, were complemented by Datachemical LAB[S15] using VBGMR as prediction model.

Heatmaps

Correlation analyses were performed by Datachemical LAB[S15] using the prepared data sets.

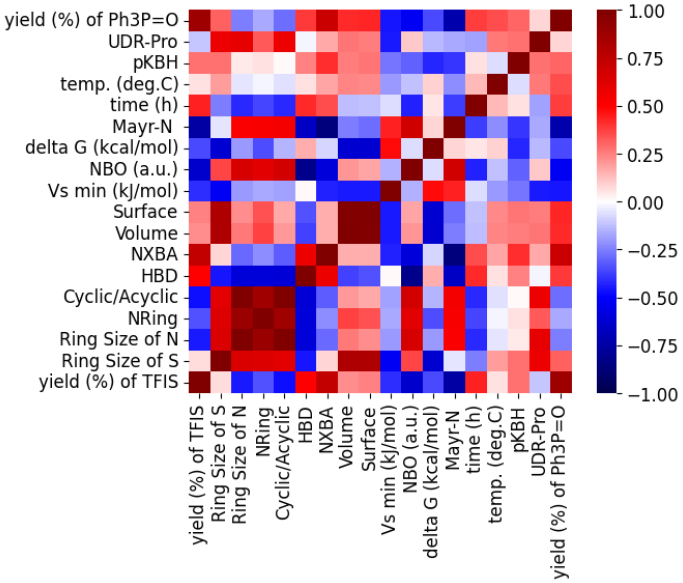


Figure S3. Heatmap for reaction, basicity, and structure.

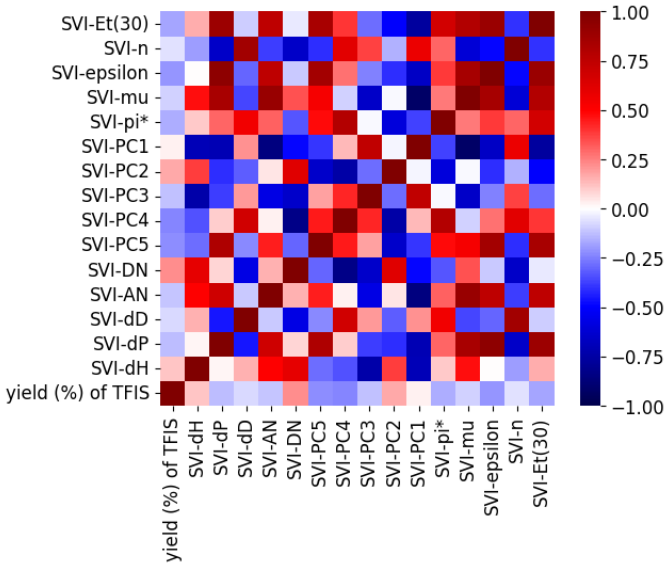


Figure S4. Heatmap for solvent index.

Table S6. Absolute value of coefficients |*r*| between yield of TFIS and other descriptors

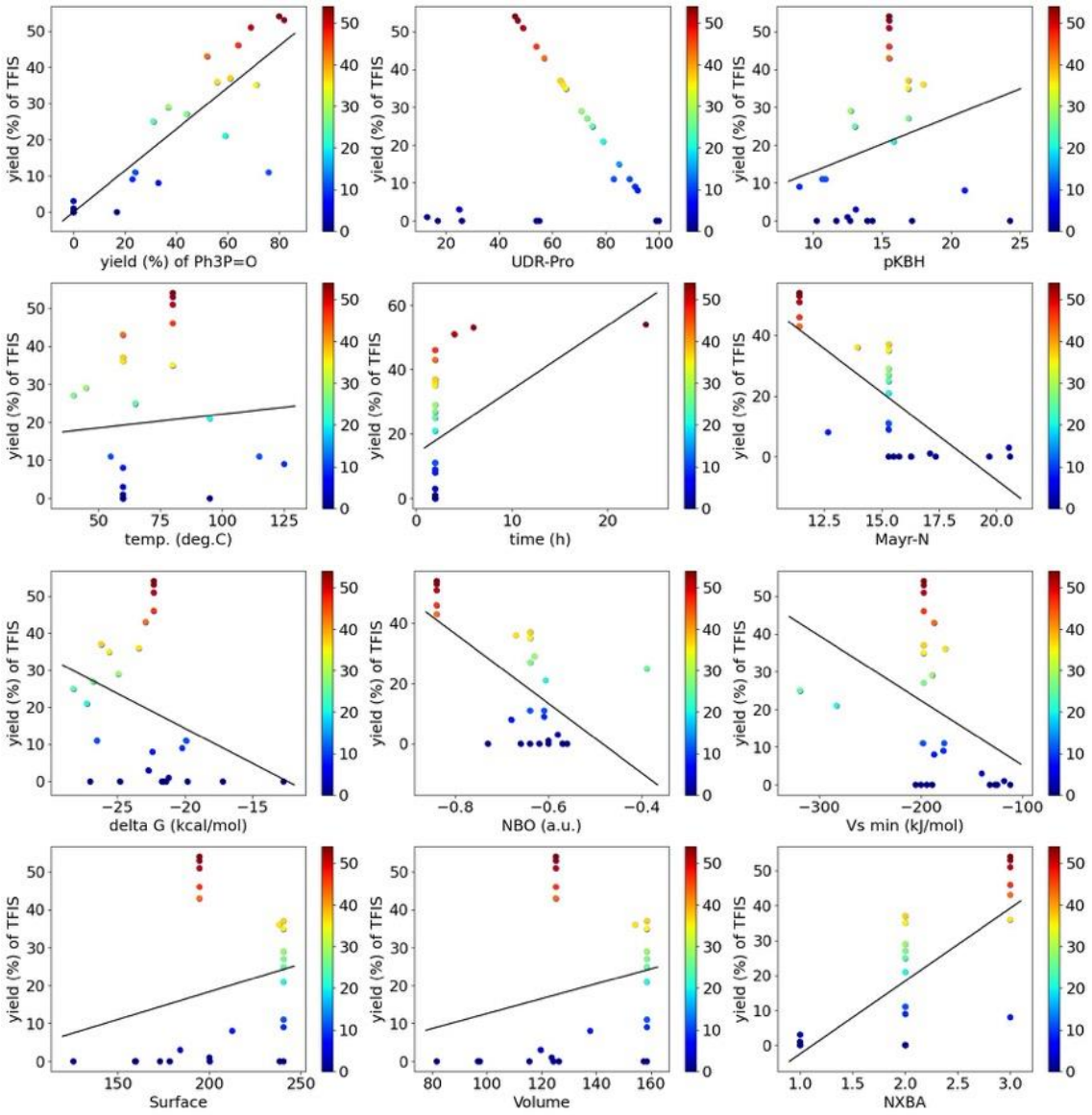
a) |*r*| with reaction, basicity, and structure

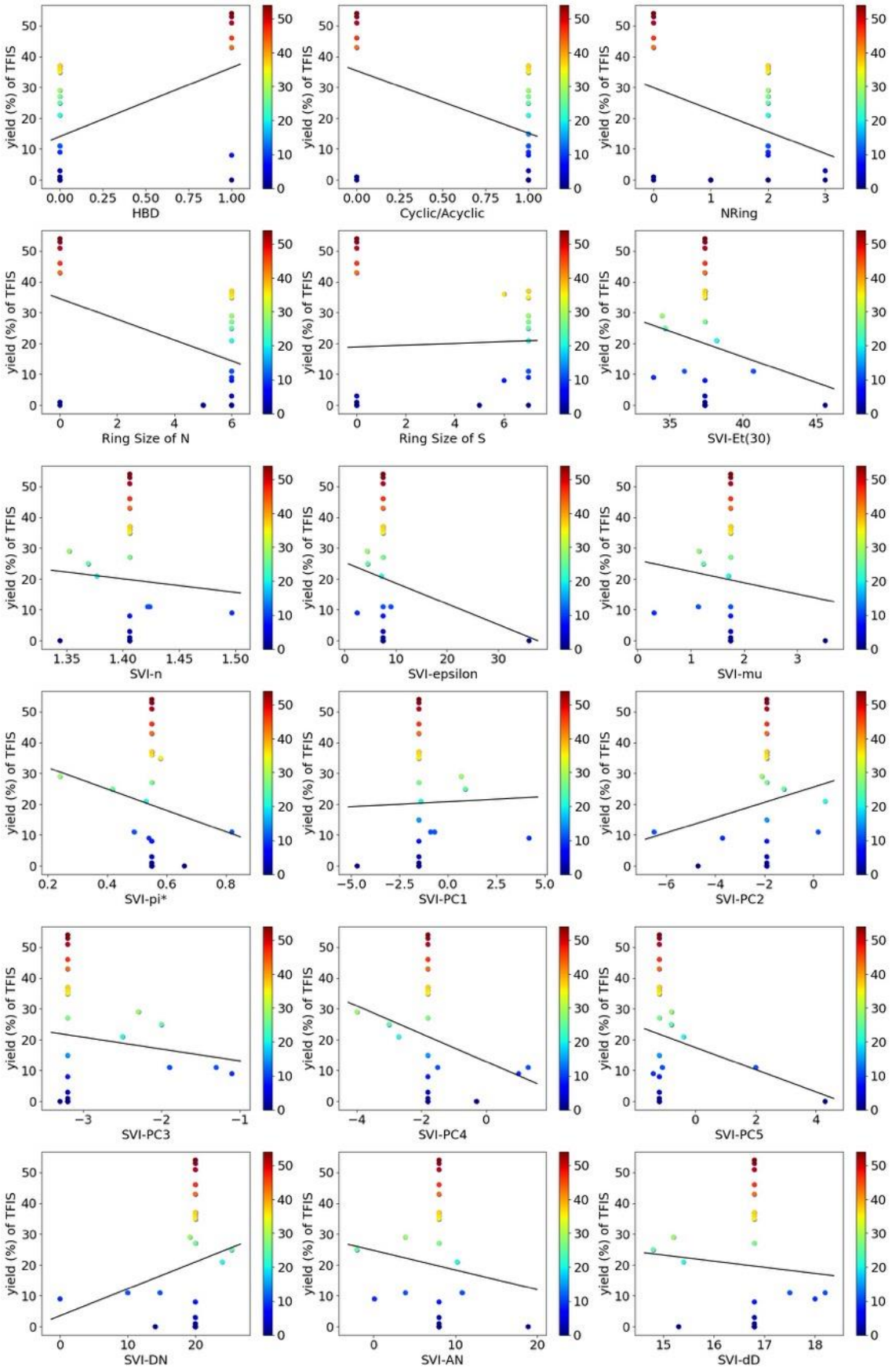
yield (%) of Ph3P=O	0.87851602
Mayr-N	0.75498824
NXBA	0.73258635
NBO (a.u.)	0.63623788
HBD	0.50353021
Cyclic/Acyclic	0.47202832
Ring Size of N	0.44661906
time (h)	0.43708529
Vs min (kJ/mol)	0.40885252
delta G (kcal/mol)	0.3517582
NRing	0.34331351
pKBH	0.27723438
Surface	0.24364337
Volume	0.22430024
UDR-Pro	0.11519679
Ring Size of S	0.06486573
temp. (deg.C)	0.0602195

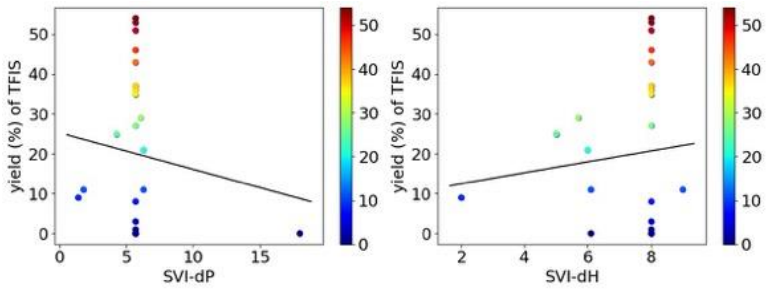
b) |*r*| with solvent index

SVI-PC4	0.23832203
SVI-PC5	0.22652904
SVI-DN	0.22047459
SVI-epsilon	0.20423598
SVI-Et(30)	0.17919842
SVI-PC2	0.16431018
SVI-pi*	0.15798741
SVI-dP	0.13012447
SVI-PC3	0.1247082
SVI-dH	0.11489653
SVI-AN	0.11364303
SVI-mu	0.08929459
SVI-dD	0.0718004
SVI-n	0.05710998
SVI-PC1	0.02393466

Scatter plots between yield of TFIS and other descriptors




yield (%) of TFIS
HBD
Cyclic/Acyclic
NRing
Ring Size of N
Ring Size of S
SVI-Et(30)
SVI-n
SVI-epsilon
SVI-mu
SVI-pi*
SVI-PC1
SVI-PC2
SVI-PC3
SVI-PC4
SVI-PC5
SVI-DN
SVI-AN
SVI-dD


yield (%) of TFIS
SVI-dP
yield (%) of TFIS
SVI-dH

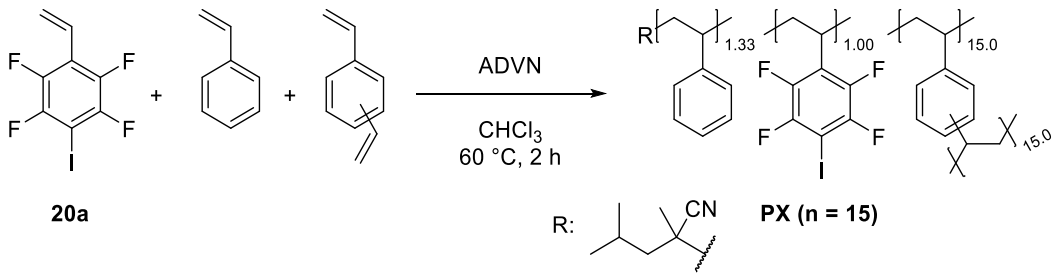
3. Preparation of DMAP-pendant XB polymers

Isolation of 2,3,5,6-tetrafluoro-4-iodostyrene 20a for polymerization

To a solution of methyltriphenylphosphonium bromide (5.36 g, 15.0 mmol, 3.0 equiv.) in CH_2Cl_2 (52 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (2.27 mL, 15.2 mmol, 3.0 equiv.) and the reaction mixture was stirred at reflux condition for 30 min. Then a solution of 2,3,5,6-tetrafluoro-4-iodobenzaldehyde **19a** (1.52 g, 5.00 mmol, 1.0 equiv.) in CH_2Cl_2 (12 mL) was added to the mixture and the mixture was stirred at reflux for 3 h. After cooling to room temperature, the reaction mixture was washed with H_2O (30 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure after filtration. The obtained crude product was through the short-plug silica gel column chromatography (pentane/CH_2Cl_2 = 4:1 as eluent), then purified by silica gel column chromatography (pentane 100% as eluent) followed by preparative HPLC (YMC-Pack SIL-06, pentane 100%, 5 mL/min) to afford 1-ethenyl-2,3,5,6-tetrafluoro-4-iodobenzene **20a** (140 mg, 0.464 mmol, 9% yield) as colorless oil. *Due to the stability, the **20a** was obtained as mixture with pentane.*
Rf = 0.53 (pentane)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.69 (dd, 1H, *J* = 11.9, 6.2 Hz), 6.15 (d, 1H, *J* = 18.1 Hz), 5.76 (d, 1H, *J* = 11.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –121.65—121.74 (m, 2F), –141.56—141.66 (m, 2F). ^{13}C NMR {^{19}F} ($CDCl_3$, 100 MHz) δ 147.24 (dd, *J* = 229, 15 Hz), 144.11 (dd, *J* = 239, 15 Hz), 124.40 (t, *J* = 160 Hz), 122.41 (d, *J* = 166 Hz), 117.51 (t, *J* = 13 Hz), 70.40 (s). IR (ATR) 1471, 1416, 1259, 1101, 983, 953, 794. HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd
for $C_8H_3F_4I$ 301.9216, found 301.9223.

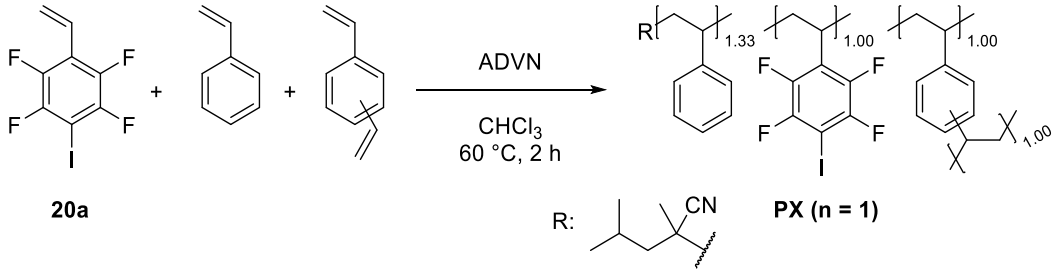
Synthesis of Polymer with XB Donor Site (PX) (n = 15)



To a solution of 2,3,5,6-tetrafluoro-4-iodostyrene **20a** (188 mg, 0.335 mmol, 1.0 equiv., 10% pentane contained) in $CHCl_3$ (1.68 mL) was added styrene (51 μL, 0.446 mmol, 1.3 equiv.), and divinylbenzene (710 μL, 5.03 mmol, 15.0 equiv.) at room temperature. The reaction mixture was degassed by Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (24.9 mg,

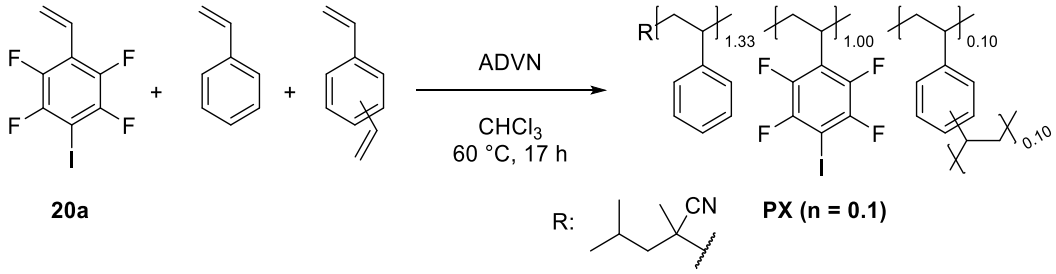
0.101 mmol, 0.3 equiv.) was added to the mixture, and the reaction mixture was stirred at 60 ºC for 2 h. The resulting suspension was transferred to mortar while washing with acetone (8 mL) then the suspension was ground and filtered. The residue was washed with acetone (2 mL), EtOH (2 mL), and CH_2Cl_2 (2 mL), then dried under vacuo to afford **PX** as a white solid (674 mg, 84% yield, [-C_6F_4I]: 0.343 mmol/g). elemental analysis calcd (%) for $C_{170.74}H_{167.24}N_{0.3}F_4I$: C 84.52, H 6.95, N 0.17, F 3.13, I 5.23, found: C 85.26, H 7.26, N 0.25, F 2.72, I 4.35.

Synthesis of PX (n = 1)



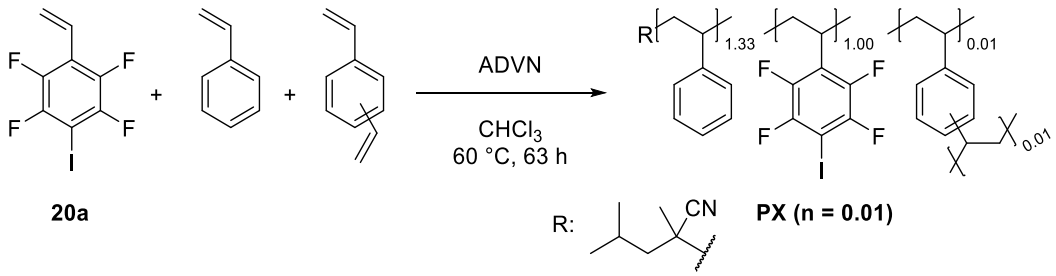
To a solution of 2,3,5,6-tetrafluoro-4-iodostyrene **20a** (297 mg, 0.794 mmol, 1.0 equiv., 20% pentane contained) in $CHCl_3$ (830 μL) was added styrene (120 μL, 1.06 mmol, 1.3 equiv.), and divinylbenzene (110 μL, 0.794 mmol, 1.0 equiv.) at room temperature. The reaction mixture was degassed by Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (59.1 mg, 0.238 mmol, 0.30 equiv.) was added to the mixture, and the reaction mixture was stirred at 60 ºC for 2 h. The resulting suspension was transferred to mortar while washing with acetone (3 mL) then the suspension was ground and filtered. The residue was washed with acetone (2 mL), EtOH (2 mL), and CH_2Cl_2 (2 mL), then dried under vacuo to afford **PX (n = 1)** as a white solid (275 mg, 61% yield, [-C_6F_4I]: 1.67 mmol/g). elemental analysis calcd (%) for $C_{28.64}H_{23.64}N_{0.3}F_4I$: C 60.27, H 4.18, N 0.30, F 13.32, I 22.24, found: C 60.12, H 4.34, N 0.41, F 12.96, I 21.15.

Synthesis of PX (n = 0.1)



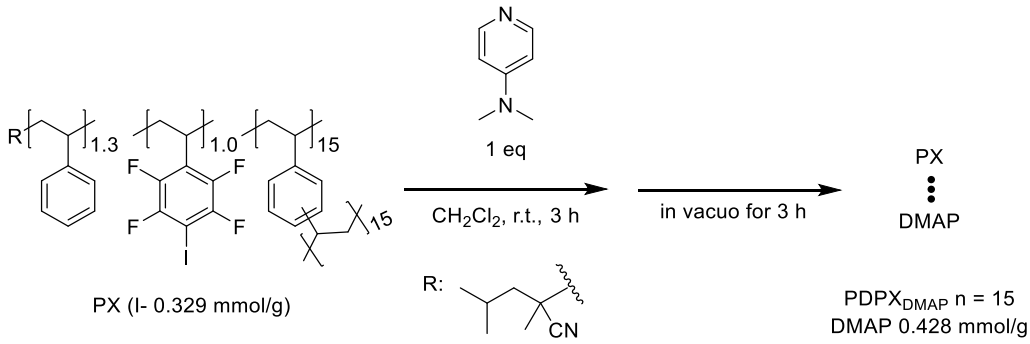
To a solution of 2,3,5,6-tetrafluoro-4-iodostyrene **20a** (350 mg, 1.16 mmol, 1.0 equiv., 6% pentane contained) in $CHCl_3$ (0.81 mL) was added styrene (180 μL, 1.54 mmol, 1.3 equiv.), and divinylbenzene (16 μL, 0.116 μmol, 0.1 equiv.) at room temperature. The reaction mixture was degassed by Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (86.4mg, 0.348 mmol, 0.30 equiv.) was added to the mixture, and the reaction mixture was stirred at 60 ºC for 17 h. The resulting suspension was transferred to mortar while washing with hexane (8 mL) then the suspension was ground and filtered. The residue was washed with hexane (2 mL) and EtOH (2 mL), then dried under vacuo to afford **PX (n = 0.1)** as a yellow solid (417 mg, 79% yield, [-C_6F_4I]: 1.88 mmol/g). elemental analysis calcd (%) for $C_{19.64}H_{14.64}N_{0.3}F_4I$: C 52.01, H 3.25, N 0.50, F 16.76, I 27.98, found: C 55.80, H 4.38, N 1.40, F 14.02, I 23.77.

Synthesis of PX (n = 0.01)



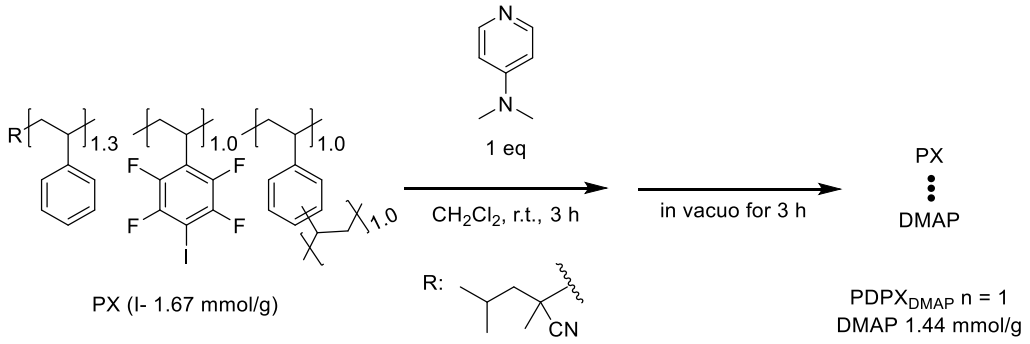
To a solution of 2,3,5,6-tetrafluoro-4-iodostyrene **20a** (1.04 g, 3.25 mmol, 1.0 equiv., 6% pentane contained) in $CHCl_3$ (1.68 mL) was added styrene (500 μL, 4.33 mmol, 1.3 equiv.), and divinylbenzene (5 μL, 32.5 μmol, 0.01 equiv.) at room temperature. The reaction mixture was degassed by Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (242 mg, 0.976 mmol, 0.30 equiv.) was added to the mixture, and the reaction mixture was stirred at 60 ºC for 63 h. The resulting suspension was transferred to mortar while washing with hexane (8 mL) then the suspension was ground and filtered. The residue was washed with hexane (2 mL) and EtOH (2 mL), then dried under vacuo to afford **PX (n = 0.01)** as a yellow solid (817 mg, 57% yield, [-C_6F_4I]: 1.93 mmol/g). elemental analysis calcd (%) for $C_{18.74}H_{13.74}N_{0.3}F_4I$: C 50.94, H 3.13, N 0.30, F 17.20, I 28.72, found: C 50.94, H 4.04, N 1.35, F 15.59, I 24.51.

Preparation of $PDPX_{DMAP}$ (n = 15)



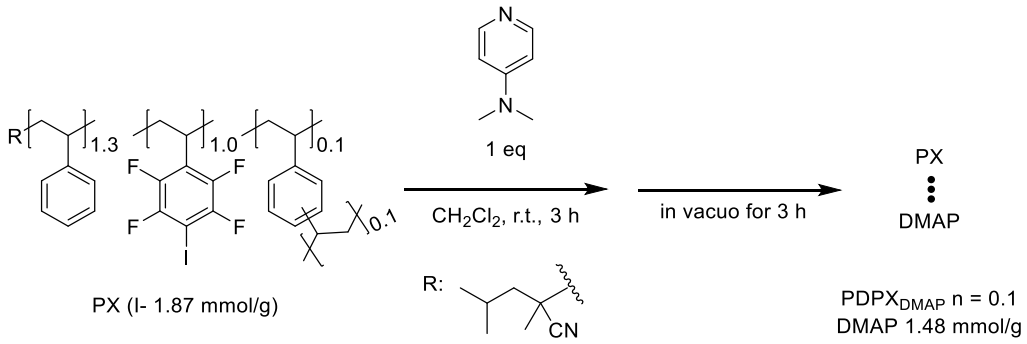
To a suspension of **PX (n = 15)** (460 mg, [-C_6F_4I]: 0.343 mmol/g) in CH_2Cl_2 (3 mL) was added DMAP (19.3 mg, 0.158 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h then concentrated under reduced pressure to afford **$PDPX_{DMAP}$ (n = 15)** as a white solid (474 mg, [DMAP]: 0.393 mmol/g). elemental analysis calcd (%) for $C_{177.74}H_{177.24}N_{2.3}F_4I$: C 83.86, H 6.96, N 1.11, found: C 84.32, H 7.15, N 0.25.

Preparation of $PDPX_{DMAP}$ (n = 1)



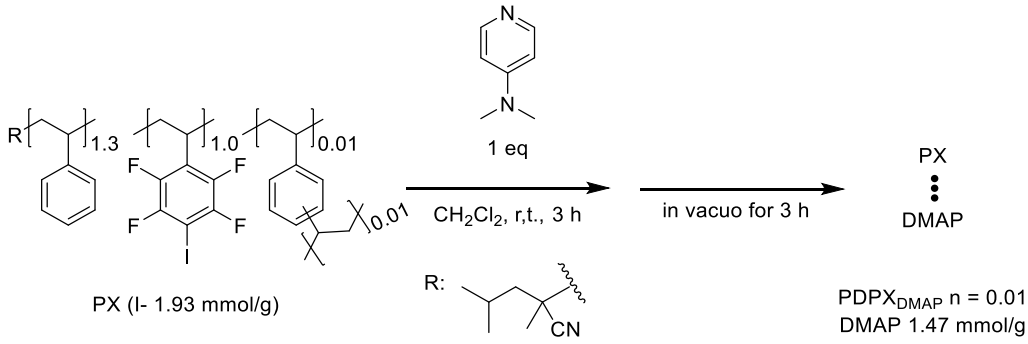
To a suspension of **PX (n = 1)** (100 mg, [-C_6F_4I]: 1.67 mmol/g) in CH_2Cl_2 (2 mL) was added DMAP (20.4 mg, 0.167 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure to afford **$PDPX_{DMAP}$ (n = 1)** as a white solid (75.0 mg, [DMAP]: 1.44 mmol/g). elemental analysis calcd (%) for $C_{35.64}H_{33.64}N_{2.3}F_4I$: C 61.41, H 4.86, N 4.62, found: C 61.42, H 5.14, N 4.46.

Preparation of $PDPX_{DMAP}$ (n = 0.1)



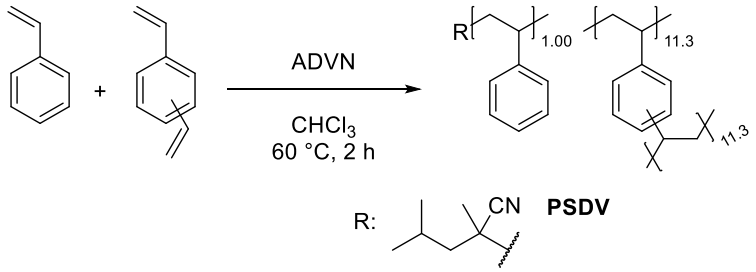
To a solution of **PX (n = 0.1)** (100 mg, [-C_6F_4I]: 1.87 mmol/g) in CH_2Cl_2 (2 mL) was added DMAP (20.8 mg, 0.187 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure to afford **$PDPX_{DMAP}$ (n = 0.1)** as a yellow solid (56.6 mg, [DMAP]: 1.48 mmol/g). elemental analysis calcd (%) for $C_{26.64}H_{24.64}N_{2.3}F_4I$: C 55.17, H 4.28, N 5.56, found: C 58.01, H 5.08, N 5.53.

Preparation of $PDPX_{DMAP}$ (n = 0.01)



To a solution of **PX (n = 0.01)** (100 mg, [-C_6F_4I]: 1.93 mmol/g) in CH_2Cl_2 (2 mL) was added DMAP (23.6 mg, 0.193 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure to afford **$PDPX_{DMAP}$ (n = 0.01)** as a yellow solid (53.6 mg, [DMAP]: 1.47 mmol/g). elemental analysis calcd (%) for for $C_{25.74}H_{23.74}N_{2.3}F_4I$: C 54.41, H 4.21, N 5.67, found: C 56.61, H 4.80, N 5.47.

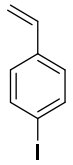
Synthesis of PSDV



To a solution of styrene (30 μL, 0.260 mmol, 1.0 equiv.) in $CHCl_3$ (980 μL) was added divinylbenzene (410 μL, 2.93 mmol, 11.3 equiv.) at room temperature. The reaction mixture was degassed by Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (14.5 mg, 0.0585 mmol, 0.23 equiv.) was added, and the reaction mixture was stirred at 60 ºC for 2 h. The resulting suspension was transferred to mortar while washing with acetone (8 mL) then the suspension was ground and filtered. The residue was washed with acetone (2 mL), EtOH (2 mL), and CH_2Cl_2 (2 mL), then dried under vacuo to afford **PSDV** as a white solid (293 mg).

Synthesis of PS[C_6H_4I]DV

1-ethenyl-4-iodobenzene (S3)



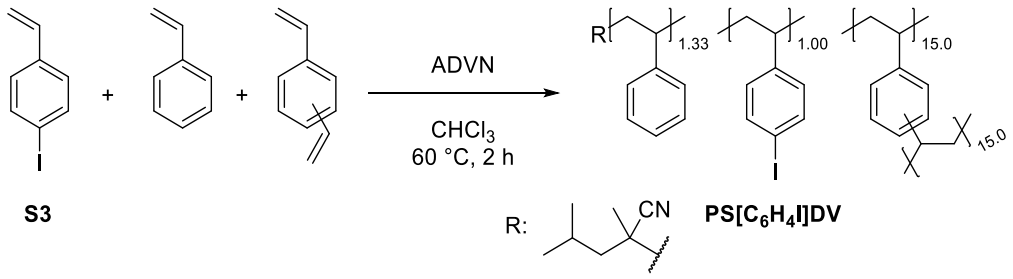
S3

S3 was prepared according to the literature.[S16]

Rf = 0.91 (hexane/ethyl acetate = 1:1)

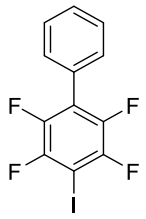
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67-7.63 (m, 2H), 7.16-7.12 (m, 2H), 6.64 (dd, 1H, *J* = 17.6, 10.8 Hz), 5.75 (dd, 1H, *J* = 17.6, 0.8 Hz), 5.27 (dd, 1H, *J* = 10.8, 0.8 Hz).

Spectral data are in agreement with the literature.[S17]



To a solution of 1-ethenyl-4-iodobenzene **S3** (33.2 mg, 0.144 mmol, 1.0 equiv.) in $CHCl_3$ (0.72 mL) at room temperature was added styrene (22 μL, 0.192 mmol, 1.3 equiv.) and divinylbenzene (300 μL, 2.16 mmol, 15.0 equiv.). The reaction mixture was degassed by Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (10.7 mg, 43.2 μmol, 0.3 equiv.) was added, and the reaction mixture was stirred at 60 ºC for 2 h. The resulting suspension was transferred to mortar while washing with acetone (8 mL) then the suspension was ground and filtered. The residue was washed with acetone (2 mL), EtOH (2 mL), and CH_2Cl_2 (2 mL), then dried under vacuo to afford **PS[C_6H_4I]DV** as white solid (299 mg, [C_6H_4I]: 0.410 mmol/g). elemental analysis calcd (%) for $C_{168.64}H_{167.64}N_{0.3}I$: C 87.07, H 7.27, N 0.20, I 5.46, found: C 87.17, H 7.50, N 0.17, I 5.20.

2,3,5,6-tetrafluoro-4-iodo-1,1'-biphenyl (S4)



S4

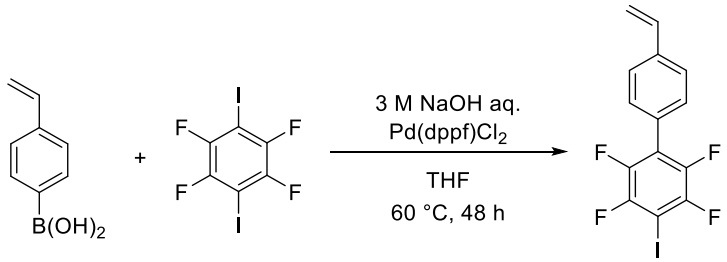
S4 was prepared and characterized according to the literature.[S18]

Rf = 0.33 (cyclohexane)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (t, 2H, *J* = 4.9 Hz), 7.53-7.46 (m, 3H), ^{19}F NMR ($CDCl_3$, 376 MHz) δ –120.41- –121.14 (m, 2F), –141.12- –141.92 (m, 2F).

Synthesis of BPX (n = 0.1)

Synthesis of 4′-ethenyl-2,3,5,6-tetrafluoro-4-iodo-1,1′-biphenyl (28)



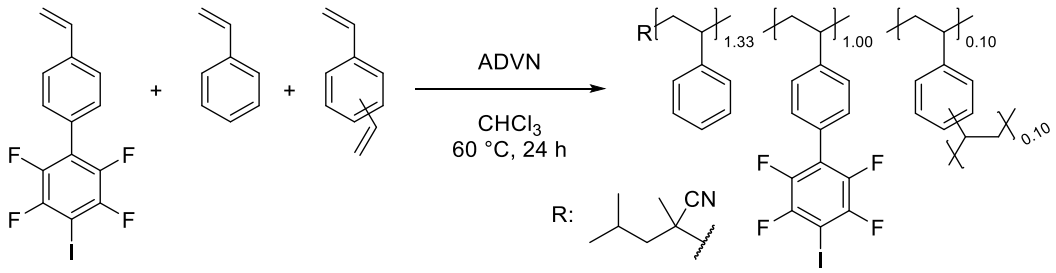
28

To a 500-mL flame-dried three-necked flask was charged 4-vinylphenylboronic acid (1.47 g, 10.0 mmol, 1.0 equiv.), tetrafluoro-1,4-diiodobenzene (4.01 g, 10.0 mmol, 1.0 eq), and $Pd(dppf)Cl_2$ (118 mg, 0.145 mmol, 0.015 equiv.). The flask was evacuated and refilled with nitrogen 3 times. 200 mL

of dry THF was added to the solid starting materials. After stirring for 5 min to this was added 1.24 mL of a 3 M aqueous solution of sodium hydroxide (30.0 mmol, 3.0 equiv) which had been previously degassed with a stream of argon. The mixture was heated and stirred at 60 °C for 48 hours. The reaction mixture was through the short-plug silica gel column chromatography (THF/hexane = 1:1 as eluent), then purified by silica gel column chromatography (hexane/CH_2Cl_2 = 10:1) to afford 4′-ethenyl-2,3,5,6-tetrafluoro-4-iodo-1,1′-biphenyl **28** (2.00 g, 5.29 mmol, 53% yield) as a white solid. Spectral data are in agreement with the literature.[S19]

Rf = 0.40 (hexane)

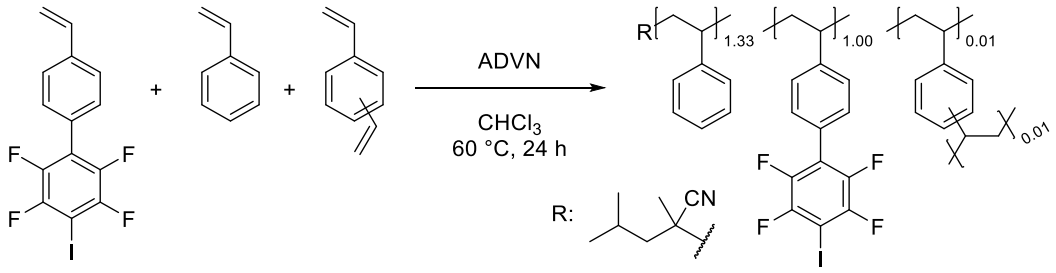
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55-7.52 (m, 2H), 7.44-7.42 (m, 2H), 6.77 (dd, 1H, *J* = 17.6, 10.9 Hz), 5.85 (dd, 1H, *J* = 17.6, 0.8 Hz), 5.36 (dd, 1H, *J* = 10.9, 0.8 Hz) ^{19}F NMR ($CDCl_3$, 376 MHz) δ –121.9- –122.0 (m, 2F), –142.6- –142.7 (m, 2F).



28 **BPX (n = 0.1)**

To a solution of 4′-ethenyl-2,3,5,6-tetrafluoro-4-iodo-1,1′-biphenyl **28** (378 mg, 1.00 mmol, 1.0 equiv.) in $CHCl_3$ (1.4 mL) was added styrene (150 μL, 1.33 mmol, 1.3 equiv.), and divinylbenzene (14 μL, 0.10 mmol, 0.1 equiv.) at room temperature. The reaction mixture was degassed by Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (74.5 mg, 0.30 mmol, 0.30 equiv.) was added to the mixture, and the reaction mixture was stirred at 60 ºC for 24 h. The resulting suspension was transferred to mortar while washing with hexane (8 mL) then the suspension was ground and filtered. The residue was washed with hexane (2 mL) and EtOH (2 mL), then dried under vacuo to afford **BPX (n = 0.1)** as a yellow solid (302 mg, 57% yield, [-C_6F_4I]: 1.59 mmol/g). elemental analysis calcd (%) for $C_{25.64}H_{18.64}N_{0.3}F_4I$: C 58.14, H 3.55, N 1.40, F 14.35, I 23.96, found: C 60.25, H 4.25, N 1.29, F 12.20, I 20.10.

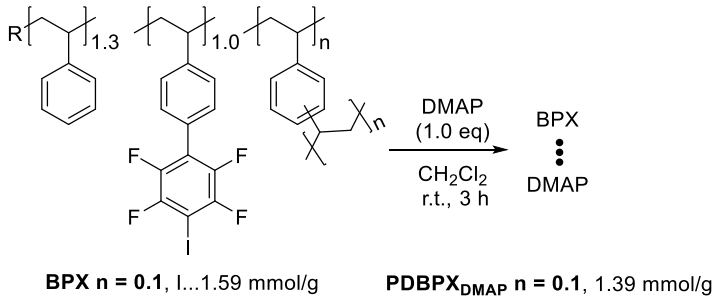
Synthesis of BPX (n = 0.01)



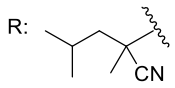
28 **BPX (n = 0.01)**

To a solution of 4′-ethenyl-2,3,5,6-tetrafluoro-4-iodo-1,1′-biphenyl **28** (378 mg, 1.00 mmol, 1.0 equiv.) in $CHCl_3$ (0.70 mL) was added styrene (150 μL, 1.33 mmol, 1.3 equiv.), and divinylbenzene (1.4 μL, 0.01 mmol, 0.01 equiv.) at room temperature. The reaction mixture was degassed by Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (74.5 mg, 0.30 mmol, 0.30 equiv.) was added to the mixture, and the reaction mixture was stirred at 60 ºC for 24 h. The resulting suspension was transferred to mortar while washing with hexane (8 mL) then the suspension was ground and filtered. The residue was washed with hexane (2 mL) and EtOH (2 mL), then dried under vacuo to afford **BPX (n = 0.01)** as a yellow solid (359 mg, 69% yield, [-C_6F_4I]: 1.63 mmol/g). elemental analysis calcd (%) for $C_{24.74}H_{17.74}N_{0.3}F_4I$: C 57.37, H 3.45, N 1.35, F 14.67, I 24.50, found: C 60.22, H 4.22, N 1.18, F 12.46, I 20.70.

Preparation of $PDBPX_{DMAP}$ (n = 0.1)

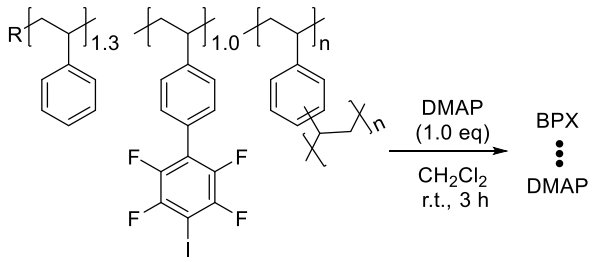


BPX n = 0.1, I...1.59 mmol/g **$PDBPX_{DMAP}$ n = 0.1**, 1.39 mmol/g

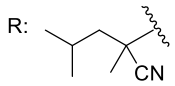


To a solution of **BPX (n = 0.1)** (100 mg, [-C_6F_4I]: 1.59 mmol/g) in CH_2Cl_2 (2 mL) was added DMAP (19.4 mg, 0.159 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure to afford **$PDBPX_{DMAP}$ (n = 0.1)** as a yellow solid (59.6 mg, [DMAP]: 1.39 mmol/g). elemental analysis calcd (%) for $C_{32.64}H_{28.64}N_{2.3}F_4I$: C 59.76, H 4.40, N 6.10, found: C 62.00, H 5.07, N 4.48.

Preparation of $PDBPX_{DMAP}$ (n = 0.01)



BPX n = 0.01, I...1.63 mmol/g **$PDBPX_{DMAP}$ n = 0.01**, 1.30 mmol/g



To a solution of **BPX (n = 0.01)** (92.0 mg, [-C_6F_4I]: 1.63 mmol/g) in CH_2Cl_2 (2 mL) was added DMAP (18.3 mg, 0.150 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure to afford **$PDBPX_{DMAP}$ (n = 0.01)** as a yellow solid (59.0 mg, [DMAP]: 1.30 mmol/g). elemental analysis calcd (%) for $C_{31.74}H_{27.74}N_{2.3}F_4I$: C 59.17, H 4.34, N 6.18, found: C 61.67, H 4.98, N 4.81.

4. References

[S1] Biot, N.; Bonifazi, D. *Chem. Eur. J.* **2020**, *26*, 2904−2913.

[S2] Dumele, O.; Trapp, N.; Diederich, F. *Angew. Chem. Int. Ed.* **2015**, *54*, 12339−12344.

[S3] Koehne, I.; Lik, A.; Gerstel, M.; Bruhn, C.; Reithmaier, J. P.; Benyoucef, M.; Pietschnig, R. *Dalton Trans.* **2020**, *49*, 16683−16692.

[S4] (a) Mariaca, P.; Labat, G.; Behrnd, N.-R.; Bonin, M.; Helbling, F.; Eggli, P.; Couderc, G.; Neels, A.; Stoeckli-Evans, H.; Hulliger, J. *J. Fluorine Chem.* **2009**, *130*, 175−196. (b) Senaweera, S.; Weaver, J. D. *Chem. Commun.* **2017**, *53*, 7545−7548.

[S5] Grimme, S.; Antony, J.; Ehrlich S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

[S6] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378 − 6396.

[S7] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J.V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[S8] Tshepelevitsh, S.; Kütt, A.; Lõkov, M.; Kaljirand, I.; Saame, J.; Heering, A.; Plieger, P. G.; Vianello, R.; Leito, I. *Eut. J. Org. Chem.* **2019**, *2019*, 6735.

[S9] Mayr's database: https://www.cup.lmu.de/oc/mayr/reaktionsdatenbank2/

[S10] Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

[S11] a) Laurence, C.; Nicolet, P.; Dalati, T. *J. Phys. Chem.* **1994**, *98*, 5807. b) Spingler, B.; Schnidrig, S.; Todorova, T.; Wild, F. *CrystEngComm* **2012**, *14*, 751.

[S12] a) Diorazio, L. J.; Hose, D. R. J.; Adlington, N. K. *Org. Process Res. Des.* **2016**, *20*, 760. b) ACS solvent selection tool: https://www.acs.org/greenchemistry/research-innovation/tools-for-green-chemistry/solvent-selection-tool.html

[S13] a) Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* **1975**, *106*, 1235. b) Gutmann, V. Coord. *Chem. Rev.* **1976**, *18*, 225. c) Marcus, Y. J. *Solution Chem.* **1984**, *13*, 599.

[S14] Takebayashi, Y.; Morii, N.; Sue, K.; Furuya, T.; Yoda, S.; Ikemizu, D.; Taka, H. *Ind. Eng. Chem. Res.* **2015**, *54*, 8801. b) Ruwoldt, J.; Tanase-Opedal, M.; Syverud, K. *ACS Omega* **2022**, *7*, 46371.

[S15] Datachemical LAB: https://www.datachemicallab.com/

[S16] Cao, H.; Jiang, H.; Feng, H.; Kwan, J. M. C.; Liu, X.; Wu, J. *J. Am. Chem. Soc.* **2018**, *140*, 16360−16367.

[S17] Thiebes, C.; Prakash, G. K. S.; Petasis, N. A.; Olah, G. A. *Synlett* **1998**, 141−142.

[S18] Sapegin, A.; Krasavin, M. *Tetrahedron Lett.* **2018**, *59*, 1948−1951.

[S19] Vanderkooy, A.; Pfefferkorn, P.; Taylor, M. S. *Macromolecules* **2017**, *50*, 3807−3817.

第３章
O-アシル化ベンゾフラノンの転位反応における触媒機能開拓

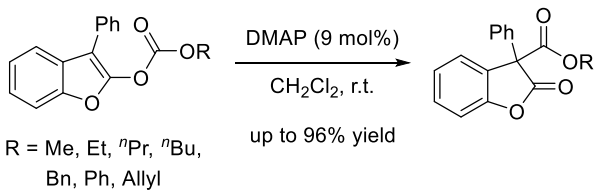
3–1. 高分子触媒による水溶媒中での有機分子変換

有機化合物を合成する際、通常、有機溶媒を用いて行う。有機溶媒は、生物や環境にとって有害であることが多く、それに代わる環境にやさしい溶媒が求められている。その中で、「水」は最も身近で無害かつ低コストの溶媒であるが、多くの有機分子は水に溶けない。そのため、水中での有機分子変換を実現する方法論の開発が進められてきた。

魚住らは、両親媒性高分子に遷移金属を固定化し、水中での鈴木・宮浦クロスカップリングや Heck 反応、不斉アリル置換反応など様々な触媒的有機分子変換を達成した[1]。高分子マトリクスを反応場とすることで、水溶媒中での効率的な反応を実現している。高分子固定化有機分子触媒による水中での有機分子変換も報告されている。2006 年に Pericàs らは、ポリスチレン固定化ヒドロキシプロリンを合成し、水中での不斉アルドール反応を報告した[2]。また、2010 年に Hansen らは、様々なプロリン誘導体をポリアクリル酸エステルに固定化し、水中での不斉アルドール反応を報告した[3]。2012 年から 2013 年にかけて、O'Reilly らは、高分子固定化ミセル触媒を開発し、DMAP や L-プロリンを固定化した触媒を使って、水中での不斉アルドール反応やアルコールのアシル化反応を報告した[4]。

3–2. *O*-アシル化ベンゾフラノンの転位反応

求核触媒によるベンゾフラノンのアシル基転位反応は、1986 年に Black らにより報告されて以来、ベンゾフラノン骨格の３位に４置換炭素を構築できる手法として知られている[5]（**Scheme 3-1**）。生成した 3,3'-二置換ベンゾフラノンは様々な天然化合物骨格にみられる[6]。均一系触媒反応による、高効率的・高立体選択的アシル基転位反応は数多く知られているものの[7]、不均一系触媒反応は一例に限られる[8]。また、水を溶媒とする報告はない。



Scheme 3-1. Acyl Rearrangement Reaction of *O*-Acyl Benzofuranone

3–3. 高分子触媒による水中での *O*-アシル化ベンゾフラノンの転位反応

3-3-1. 高分子触媒反応場のデザイン

本研究では、開発した $PDPX_{DMAP}$ の触媒機能を開拓するため、水中でのベンゾフラノンのアシル基転位反応を検討することにした。具体的には、高分子鎖を疎水性反応場として、テトラフルオロヨードベンゼンに由来するハロゲン結合供与部位を反応基質の捕捉部位として、*O*-アシルエノラートの電子不足なカルボニル酸素を結合受容体部位として、不均一系求核触媒反応の促進に活用することにした。高分子側鎖の C_6F_4I 部位と *O*-アシルエノラートのカルボニル酸素が、水分子に働く水素結合よりも強いハロゲン結合を形成できれば[9]、反応基質である *O*-アシルエノラートは、水中で高分子鎖近傍に凝集することができる。この性質により、効率的な水中の触媒反応が可能になると考えた（**Figure 3-1**）。

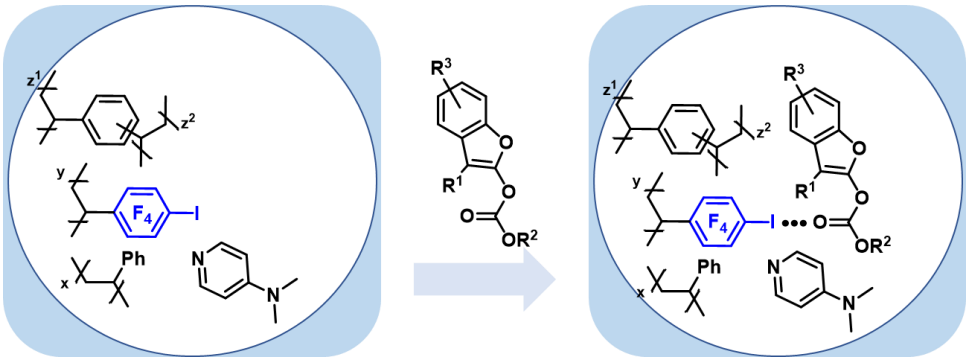


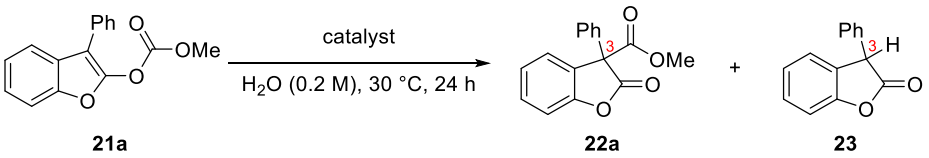
Figure 3-1. Working Hypothesis in Polymer Catalysis
Black three dots represent the halogen bonding.

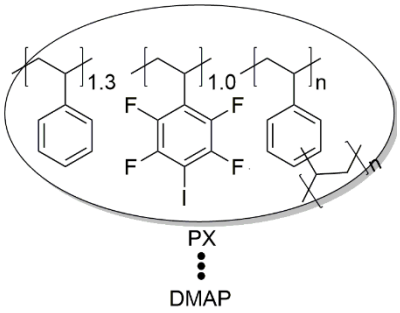
3-3-2. 初期検討

はじめに、ジビニルベンゼン（DVB）の当量比が収率に与える影響を調べた。検討は、ベンゾフラノンの *O*-アシルエノラート **21a** を用い、1 mol%の $PDPX_{DMAP}$ を用いて、水中、30 ℃、24 時間、撹拌して行った（**Table 3-1**）。その結果、$PDPX_{DMAP}$（n = 15）を用いた場合、目的生成物 **22a** は 89%収率で得られたのに対し（entry 1）、DVB を 1、0.1、0.01 当量用いた $PDPX_{DMAP}$ (n = 1)、$PDPX_{DMAP}$ (n = 0.1)、$PDPX_{DMAP}$ (n = 0.01)では、収率が低下した（entries 2~4）。これらの検討から、DVB の含有量が多くなるほど、より疎水性の反応場が構築され、反応は、高分子表面もしくは近傍で進行していると考えられる。

最も良い結果を与えた $PDPX_{DMAP}$（n = 15）を用いて、次に触媒量の低減を試みた。0.5 mol%の触媒量で 3-アシル化ベンゾフラノン **22a** は良好な収率で得られ、0.2 mol%の触媒量では中程度の収率であった（entries 5, 6）。

Table 3-1. Rearrangement Reaction of *O*-Acyl Benzofuranones with $PDPX_{DMAP}$[a]





$PDPX_{DMAP}$ (n = 15, 1, 0.1, 0.01)

entry	Catalyst[b]	(mol%)	yield[b] (%)		scale (mmol)
			3-acyl	3-H	
1	$PDPX_{DMAP}$ (n = 15)	1	89	2	0.2
2	$PDPX_{DMAP}$ (n = 1)	1	66	8	0.2
3	$PDPX_{DMAP}$ (n = 0.1)	1	50	10	0.2
4	$PDPX_{DMAP}$ (n = 0.01)	1	50	11	0.2
5	$PDPX_{DMAP}$ (n = 15)	0.5	83	5	0.2
6	$PDPX_{DMAP}$ (n = 15)	0.2	65	3	0.2

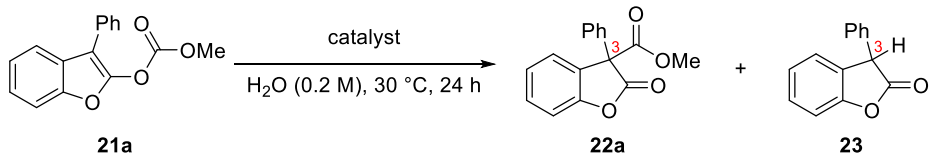
[a] The reactions were performed using **21a** (0.2 mmol) and catalyst at 30 °C for 24 h in H_2O (1.0 mL).
[b] Isolated yield.

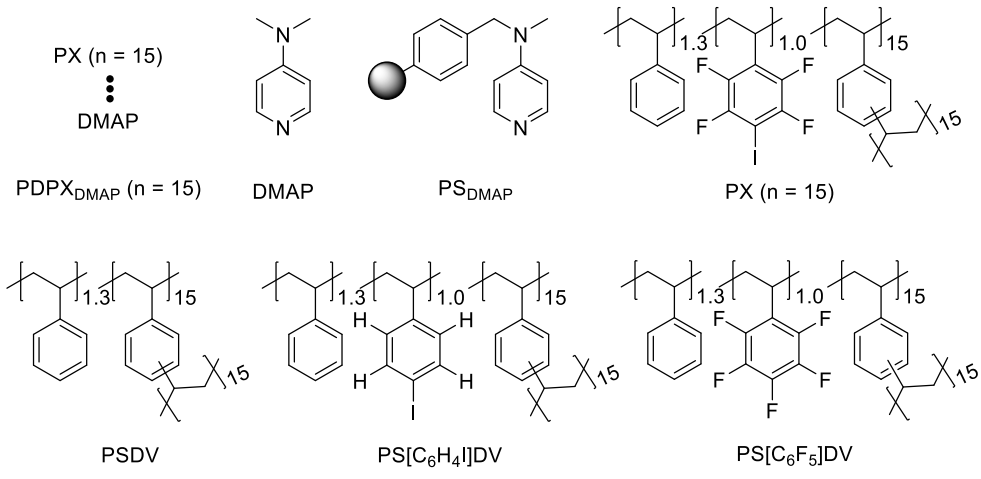
3-3-3. 対照実験

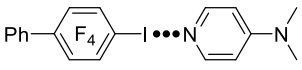
$PDPX_{DMAP}$の有効性を検証するため、DMAP のみ、市販で入手可能な高分子触媒 PS_{DMAP}、合成した高分子 PX を用いて対照実験を行った（**Table 3-2**）。DMAP や PS_{DMAP} をそれぞれ 1 mol%ずつ用いた場合、目的生成物 **22a** は 10%未満に留まり、$PDPX_{DMAP}$の場合に比べ、収率が極端に低下した（entries 1~3）。また、PX のみでは、反応は全く進行しなかった（entry 4）。15 当量の DVB から合成した PX（1 mol%）と DMAP（1 mol%）を加えると、20%程度の目的生成物 **22a** と 10%程度の 3 位のプロトン化体 **23** が得られた（entry 5）。テトラフルオロヨードベンゼンユニットの含まれていない PSDV と PLM[C_6H_4I]、PLM[C_6F_5]を用いた場合、目的生成物 **22a** は得られたが、収率は $PDPX_{DMAP}$ の場合に比べ極端に低下した（entries 6~8）。4-フェニルテトラフルオロヨードベンゼンと DMAP の複合体を 1 mol%用いると、中程度の収率に留まった（entry 9）。以上の結果から、高分子鎖が疎水性の反応場を創り出し、ハロゲン結合供与部位が効率的な転

位反応の進行に寄与していると考えられる。

Table 3-2. Rearrangement Reaction of *O*-Acyl Benzofuranones with Several Catalysts[a]



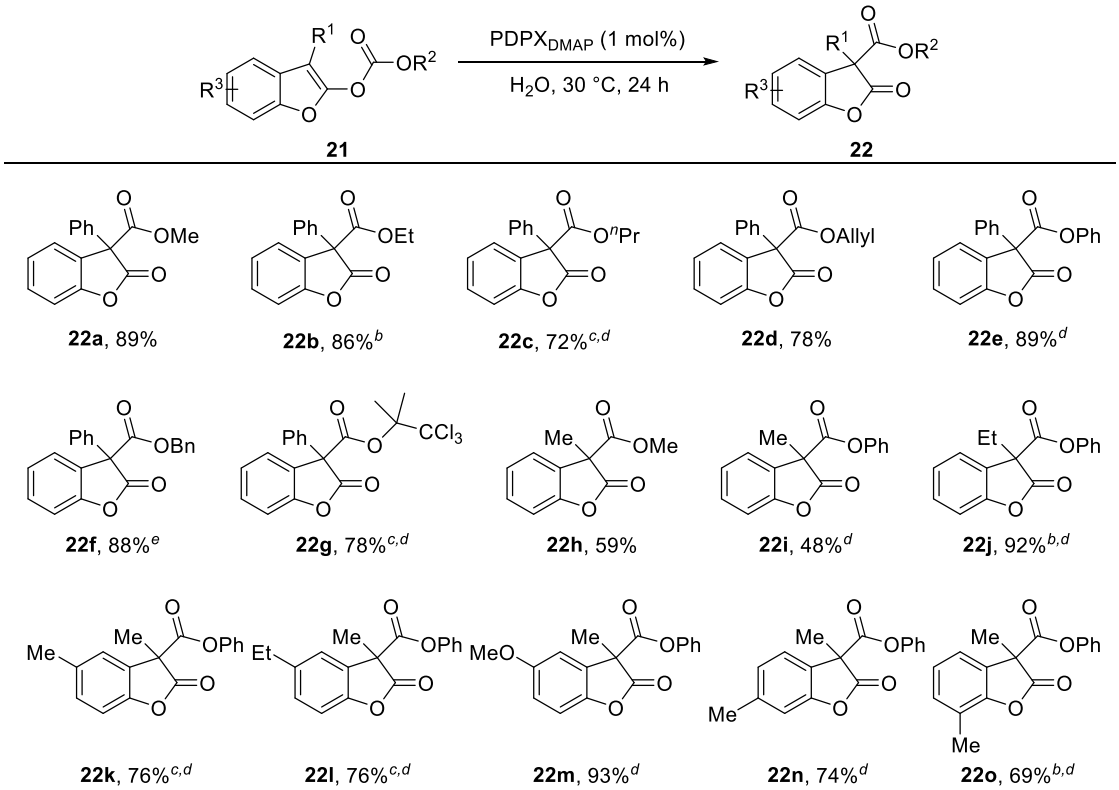


entry	catalyst	(mol%)	yield[b] (%)		scale
			3-acyl	3-H	(mmol)
1	$PDPX_{DMAP}$ (n = 15)	1	89	2	0.2
2	DMAP	1	8	<1	1
3	PS_{DMAP}[c]	1	4	0	0.2
4	PX (n = 15)	1[d]	0	0	0.2
5	PX (n = 15) + DMAP	1[d] + 1	23	12	1
6	PSDV+ DMAP	1[e] + 1	6	0	1
7	$PS[C_6H_4I]DV$ + DMAP	1[f] + 1	11	<1	1
8	$PS[C_6F_5]DV$ + DMAP	1[g] + 1	23	<1	1
9		1	41	17	1

[a] The reactions were performed using **21a** and catalyst at 30 °C for 24 h in H_2O. [b] Isolated yield. [c] 0.3 mmol/g. [d] Based on $[C_6F_4I]$ of PX. [e] PSDV amount is same as PX amount (**Table 3-1** entry 9). [f] $PS[C_6H_4I]DV$ is based on $[C_6H_4I]$. [g] $PS[C_6F_5]DV$ is based on $[C_6F_5]$.

3-3-4. 基質一般性

3−3−2 および 3−3−3 の検討結果から、1 mol%の $PDPX_{DMAP}$（n = 15）存在下、30℃、24 時間を最適条件とし、基質一般性の検討を行った（**Scheme 3-2**）。その結果、**21a**、**21d**、**21e**、**21h**、**21i**、**21l**、**21m**、**21n** の場合は、完全水中で対応する *C*-アシルベンゾフラノン **22** が中程度から良好な収率で得られた。一方、**21b**、**21c**、**21f**、**21g**、**21j**、**21k** の場合、完全水中では低収率に留まった。これらの基質に対しては、1,4-ジオキサンや THF、エタノールを 1 当量加えることで、対応する目的生成物 **22** を良好な収率で得ることができた。3-メチルベンゾフラノン **21h** や **21i** の場合、目的生成物 **22h** や **22i** の収率は中程度であった。



Scheme 3-2. Substrate Scope[a]

[a] **3** (0.2 mmol) and $PDPX_{DMAP}$ (1.0 mol%) were stirred in H_2O (1.0 mL) at 30 ℃. Isolated yield. [b] 1,4-Dioxane (1.0 eq) was added. [c] THF (1.0 eq) was added. [d] Obtained as a mixture with 3-*H*-benzofuranones. [e] EtOH (1.0 eq) was added.

3–4. 想定される反応機構

Figure 3-2 に想定される反応機構を示す。まず、ハロゲン結合や高分子鎖に由来する非共有結合性の分子間相互作用を介して、DMAP と反応基質とが互いに高分子鎖表面で接近する。次に、求核攻撃と続くアシル基転位反応が進行し、*C*-アシルベンゾフラノンを与える。最後に、転位生成物が高分子表面から解離して、次の触媒サイクルが起こる。**Table 3–2** で述べたように、あらかじめ調製した $PDPX_{DMAP}$ を用いる場合（entry 1）が、DMAP と PX をそれぞれ別々に加える場合（entry 5）よりも、良好な収率が得られたことから、水中において、DMAP と反応基質が高分子鎖近傍に凝集する過程が律速段階であると考えられる。

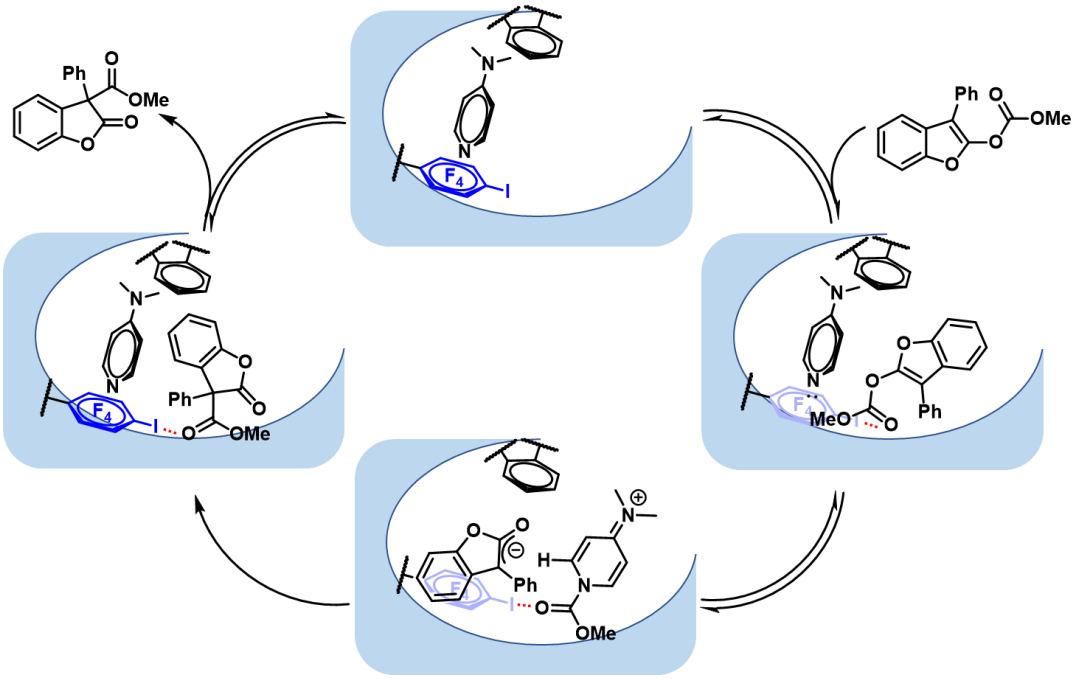


Figure 3-2. Proposed Reaction Mechanism

3–5. 高分子触媒の再利用

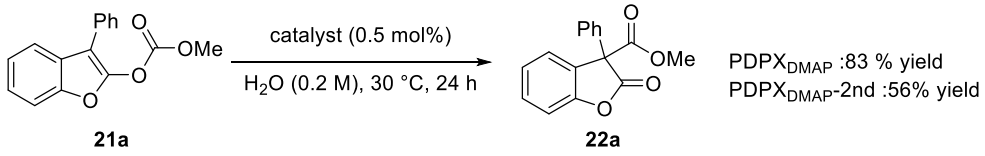
触媒の回収と再利用は、高分子固定化触媒の特長である。そこで、本研究においても、$PDPX_{DMAP}$ の再利用性を調べ、有用性の向上を目指した。まず、水中のベンゾフラノンのアシル基転位反応後、$PDPX_{DMAP}$ を濾別し、アセトン、ジクロロメタン、エタノールで洗浄した。さらに、真空乾燥を行い、得られた $PDPX_{DMAP}$ を用いて、水溶媒中、ベンゾフラノンのアシル基転位反応を行った。その結果、反応は全く進行しなかった。$PDPX_{DMAP}$ を洗浄した際に DMAP も洗い流されたと考え、元素分析を行った（**Table 3-5**）。窒素の元素分析値から、洗浄後の触媒には、ADVN 由来の 0.21%を差し引いた 0.17%に相当する DMAP もしくは DMAP 誘導体が残

存していたが、大半の DMAP は洗い流されていることがわかった。回収した $PDPX_{DMAP}$ を用いた場合、反応は全く進行しなかったことから、高分子中に残存している窒素由来の分子は、反応後のクエンチで使用した塩酸水溶液によって生成した DMAP 塩酸塩ではないかと考えられる。

そこで、回収した高分子に 1 当量の DMAP を加えて触媒を調製した（$PDPX_{DMAP}$-2nd）。0.5 mol%の $PDPX_{DMAP}$-2nd 存在下、水中、30 ℃、24 時間で、ベンゾフラノンのアシル基転位反応を行った（**Scheme 3-3**）。その結果、目的生成物 **22a** の収率は 56%に低下した。この結果は、DMAP 塩酸塩が高分子中のペルフルオロヨードベンゼン付近を占拠して、露出しているヨウ素が少なくなったためと推察している。

Table 3-5. Elemental Analysis of PX, $PDPX_{DMAP}$, and Used $PDPX_{DMAP}$

	H (%)	C (%)	N (%)
PX	7.15	84.93	0.21
$PDPX_{DMAP}$	7.15	84.32	1.32
Used $PDPX_{DMAP}$	7.04	84.47	0.38

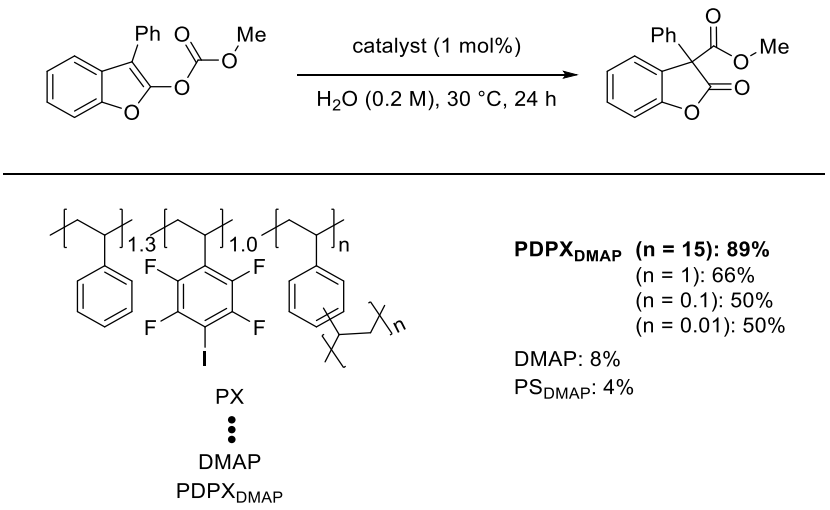


Scheme 3-3. Comparison of $PDPX_{DMAP}$ and $PDPX_{DMAP}$-2nd

3−6. まとめ

第 3 章では、$PDPX_{DMAP}$ を不均一系触媒として用いるベンゾフラノンのアシル基転位反応について述べた（**Scheme 3-4**）。本研究では、特に、テトラフルオロヨードスチレンに対してそれぞれ 0.01、0.1、1、15 当量の DVB から成る PX が、水中での不均一系触媒反応に与える影響を調べながら、$PDPX_{DMAP}$ の水中での触媒機能を見出した。その結果、15 当量の DVB から合成した $PDPX_{DMAP}$ が 0.01、0.1、1 当量のものより高収率で目的生成物を与えることを明らかにした。また、DMAP 単体や市販で入手可能なポリスチレン触媒 PS_{DMAP} を用いて対照実験を行い、$PDPX_{DMAP}$ の有用性を示した。DMAP 単体やポリスチレン触媒 PS_{DMAP} では、目的生成物の収率が 10%以下となることを明らかにした。開発した $PDPX_{DMAP}$ (n = 15) は様々な置換基を有する *O*-アシルベンゾフラノンに適用可能であり、対応する転位生成物を良好または高

収率で与えることを見出した。高分子触媒としての再利用はできなかったが、本研究は、ハロゲン結合供与部位を有する高分子を水中での不均一系触媒反応に用いた初めての例である。



Scheme 3-4. Representative results for acyl rearrangement reaction of benzofuranones in H_2O catalyzed by $PDPX_{DMAP}$

引用文献

[1] For examples, see: (a) Uozumi, Y.; Danjo, H.; Hayashi, T. New Amphiphilic Palladium-Phosphine Complexes Bound to Solid Supports: Preparation and Use for Catalytic Allylic Substitution in Aqueous Media. *Tetrahedron Lett.* **1997**, *38*, 3557–3560. (b) Uozumi, Y.; Danjo, H.; Hayashi, T. Cross-Coupling of Aryl Halides and Allyl Acetates with Arylboron Reagents in Water Using an Amphiphilic Resin-Supported Palladium Catalyst. *J. Org. Chem.* **1999**, *64*, 3384–3388. (c) Uozumi, Y.; Watanabe, T. Green Catalysis: Hydroxycarbonylation of Aryl Halides in Water Catalyzed by an Amphiphilic Resin-Supported Phosphine−Palladium Complex. *J. Org. Chem.* **1999**, *64*, 6921–6923. (d) Uozumi, Y.; Shibatomi, K. Catalytic Asymmetric Allylic Alkylation in Water with a Recyclable Amphiphilic Resin-Supported P,N-Chelating Palladium Complex. *J. Am. Chem. Soc.* **2001**, *123*, 2919–2920.

[2] Font, D.; Jimeno, C.; Pericàs, M. A. Polystyrene-Supported Hydroxyproline: An Insoluble, Recyclable Organocatalyst for the Asymmetric Aldol Reaction in Water. *Org. Lett.* **2006**, *8*, 4653–4655.

[3] Kristensen, T. E.; Vestli, K.; Jakobsen, M. G.; Hansen, F. K.; Hansen, T. A General Approach for Preparation of Polymer-Supported Chiral Organocatalysts via Acrylic Copolymerization. *J. Org. Chem.* **2010**, *75*, 1620–1629.

[4] (a) Cotanda, P.; Lu, A.; Patterson, J. P.; Petzetakis, N.; O'Reilly, R. K. Functionalized Organocatalytic Nanoreactors: Hydrophobic Pockets for Acylation Reactions in Water *Macromolecules* **2012**, *45*, 2377–2384. (b) Zayas, H. A.; Lu A.; Valade, D.; Amir, F.; Jia, Z.; O'Reilly, R. K.; Monteiro, M. J. Thermoresponsive Polymer-Supported L-Proline Micelle Catalysts for the Direct Asymmetric Aldol Reaction in Water. *ACS Macro Lett.* **2013**, *2*, 327–331.

[5] (a) Black, T. H.; Arrivo, S. M.; Schumm, J. S.; Knobeloch, J. M. A novel Oxygen-to-Carbon Ester Migration Catalysed by 4-(*N*,*N*-dimethylamino)-pyridine in the Benzofuranone Ring System. *J. Chem. Soc., Chem. Commun.* **1986**, 1524–1525. (b) Black, T. H.; Arrivo, S. M.; Schumm, J. S.; Knobeloch, J. M. 4-(Dimethylamino)pyridine as a Catalyst for Carbon Acylation. 2. Control of Carbon vs. Oxygen Acylation in Benzofuranones. *J. Org. Chem.* **1987**, *52*, 5425–5430.

[6] (a) Vedejs, E.; Zajac, M. A. Synthesis of the Diazonamide A Macrocyclic Core via a Dieckmann-Type Cyclization. *Org. Lett.* **2001**, *3*, 2451–2454. (b) Sontag, B.; Rüth, M.; Spiteller, P.; Arnold, N.; Steglich, W.; Reichert, M.; Bringmann, G. Chromogenic Meroterpenoids from the Mushrooms Russula *ochroleuc*a and R. *viscida*. *Eur. J. Org. Chem.* **2006**, 1023–1033. (c) Li, Y.; Li, X.; Cheng, J. P. Catalytic Asymmetric Synthesis of Chiral Benzofuranones. *Adv. Synth. Catal.* **2014**, *356*, 1172−1198.

[7] For examples, see: (a) Hills, I. D.; Fu, G. C. Catalytic Enantioselective Synthesis of Oxindoles and Benzofuranones That Bear a Quaternary Stereocenter. *Angew. Chem. Int. Ed.* **2003**, *42*, 3921–3924. (b) Shaw, S. A.; Aleman, P.; Christy, J.; Kampf, J. W.; Va, P.; Vedejs, E. Enantioselective TADMAP-Catalyzed Carboxyl Migration Reactions for the Synthesis of Stereogenic Quaternary Carbon. *J. Am.*

Chem. Soc. **2006**, *128*, 925−934. (c) Fujii, K.; Mitsudo, K.; Mandai, H.; Korenaga, T.; Suga, S. Enantioselective Acyl Migration Reactions of Furanyl Carbonates with Chiral DMAP Derivatives. *Chem. Eur. J.* **2019**, *25*, 2208−2212.

[8] Yamamoto, T.; Murakami, R.; Suginome, M. Single-Handed Helical Poly(quinoxaline-2,3-diyl)s Bearing Achiral 4-Aminopyrid-3-yl Pendants as Highly Enantioselective, Reusable Chiral Nucleophilic Organocatalysts in the Steglich Reaction. *J. Am. Chem. Soc.* **2017**, *139*, 2557–2560.

[9] (a) Tsuzuki, S.; Wakisaka, A.; Ono, T.; Sonoda, T. Magnitude and Origin of the Attraction and Directionality of the Halogen Bonds of the Complexes of C_6F_5X and C_6H_5X (X=I, Br, Cl and F) with Pyridine. *Chem. Eur. J.* **2012**, *18*, 951–960. (b) Tuzuki, S.; Lüthi, H. P. Interaction Energies of van der Waals and Hydrogen Bonded Systems Calculated Using Density Functional Theory: Assessing the PW91 Mode. *J. Chem. Phys.* **2001**, *114*, 3949–3957.

実験項

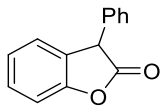
1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of standard grade nitrogen gas (oxygen <10 ppm) in flame-dried glassware with magnetic stirring. ^{1}H NMR spectra were recorded on a JEOL ECS-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: referenced to TMS 0.00 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL ECS-400 (100 MHz) spectrometer with complete proton decoupling or fluorine decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). ^{19}F NMR spectra were recorded on a JEOL ECS-400 (376 MHz) spectrometer. Chemical shifts are reported in ppm from α,α,α-trifluorotoluene as the external standard (–63.72 ppm). High-performance liquid chromatography (HPLC) was performed on a Jasco HPLC-2000 system equipped with a variable wavelength detector using YMC-Pack SIL-06 column from YMC. Elemental analysis of H, C, and N was performed on J-SCIENCE LAB MICRO CORDER JM10 at the Instrument Center, Institute for Molecular Science. Elemental analysis of F, I, and Cl in addition to H, C, and N was performed on XS-2100H at Organic Elemental Microanalysis Center, Kyoto University. SEM images were obtained using Hitachi High-Tech SU6600 and EDS mapping were measured using BrukerAXS QUANTAX XFlash 5060FQ and Xflash6|10. Infrared (IR) spectra were recorded on a Jasco FT/IR-460plus spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 instrument (double-focusing magnetic sector mass analyzer: EB) using fast atom bombardment (FAB) as the ionization method and 3-nitrobenzyl alcohol as the matrix at the Instrument Center of the Institute for Molecular Science.

Purification of reaction products was carried out by flash column chromatography using silica gel 60 N (Merck: 0.040-0.063 mm). Dichloromethane (CH_2Cl_2), diethyl ether (Et_2O) and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were supplied from FUJIFILM Wako Pure Chemical Corporation. As dehydrated solvents. Other reagents were used without further purification.

2. Synthesis of *O*-acylated benzofuranones

3-Phenylbenzofuran-2(3*H*)-one (23)



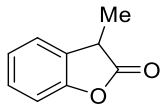
23

23 was synthesized and characterized according to the literature.[S1]

Rf = 0.41 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.19 (m, 9H), 4.91 (s, 1H).

3-Methylbenzofuran-2(3*H*)-one (S5)



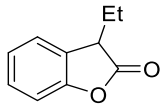
S5

S5 was synthesized and characterized according to the literature.[S2]

Rf =0.41 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.22 (m, 2H), 7.17-7.05 (m, 2H), 3.72 (q, 1H, J = 7.5 Hz), 1.57 (d, 3H, J = 7.6 Hz).

3-Ethylbenzofuran-2(3*H*)-one (S6)



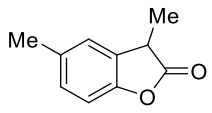
S6

S6 was synthesized and characterized according to the literature.[S2]

Rf = 0.44 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.25 (m, 2H), 7.20-7.08 (m, 2H), 3.71 (t, 1H, J = 5.7 Hz), 2.13-2.00 (m, 2H), 0.97 (t, 3H, J = 7.4 Hz).

3,5-Dimethylbenzofuran-2(3*H*)-one (S7)



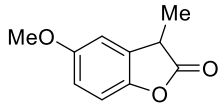
S7

S7 was synthesized and characterized according to the literature.[S2]

Rf = 0.29 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.13-7.04 (m, 2H), 7.01-6.94 (m, 1H), 3.69 (q, 1H, *J* = 7.5 Hz), 2. 35 (s, 3H), 1.55 (d, 3H, *J* = 7.7 Hz).

5-Methoxy-3-methylbenzofuran-2(3*H*)-one (S8)



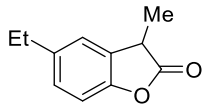
S8

S8 was synthesized and characterized according to the literature.[S2]

Rf = 0.19 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09-6.96 (m, 1H), 6.86-6.70 (m, 2H), 3.80 (s, 3H), 3.72 (q, 1H, *J* = 7.4 Hz), 1.57 (d, 3H, *J* = 7.6 Hz).

5-Ethyl-3-methylbenzofuran-2(3*H*)-one (S9)



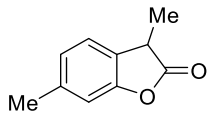
S9

S9 was synthesized and characterized according to the literature.[S2]

Rf = 0.20 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.11-7.08 (m, 1H), 7.03-6.98 (m, 2H), 3.70 (q, 1H, *J* = 7.5 Hz), 2.64 (q, 2H, *J* = 7.6 Hz), 1.56 (d, 3H, *J* = 7.6 Hz), 1.23 (t, 3H, *J* = 7.6 Hz).

3,6-Dimethylbenzofuran-2(3*H*)-one (S10)



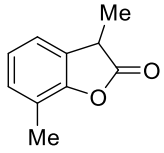
S10

S10 was synthesized and characterized according to the literature.[S2]

Rf = 0.35 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15-7.10 (m, 1H), 6.99-6.88 (m, 2H), 3.67 (q, 1H, *J* = 7.5 Hz), 2. 37 (s, 3H), 1.54 (d, 3H, *J* = 7.6 Hz).

3,7-Dimethylbenzofuran-2(3*H*)-one (S11)



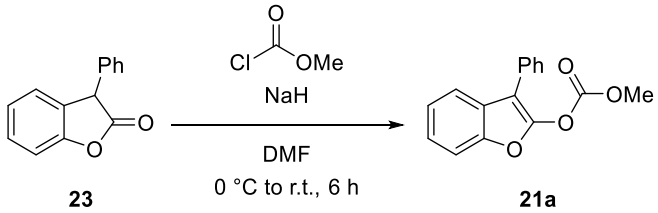
S11

S11 was synthesized and characterized according to the literature.[S2]

Rf = 0.19 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15-7.00 (m, 3H), 3.72 (q, 1H, *J* = 7.6 Hz), 2.32 (s, 3H), 1.56 (d, 3H, *J* = 7.6 Hz).

Synthesis of methyl 3-phenylbenzofur-2-yl carbonates (21a)

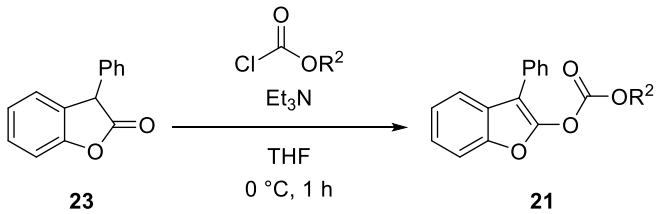


To a 50-mL flame-dried two-necked flask was charged sodium hydride (60% dispersion in oil, 536 mg, 13.4 mmol, 1.4 equiv.) that was washed with 5 mL of hexane three times. DMF (10 mL) was added to the flask under nitrogen atmosphere. To the suspension was added **23** (2.09 g, 9.94 mmol, 1.0 equiv.), then the mixture was stirred at 0 ºC for 1.5 h. Methyl chloroformate (840 μL, 10.9 mmol, 1.1 equiv.) was added over a period of several minutes to the mixture. The reaction mixture was stirred at room temperature for 6 h, then poured into H_2O (30 mL), and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with H_2O (3 x 30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The obtained crude product was purified by silica gel column chromatography (hexane/diethyl ether = 40:1 to 10:1 as eluent) to afford **21a** (2.36 g, 8.85 mmol, 89% yield) as colorless oil. Spectral data are in agreement with the literature.[S3a]

Rf = 0.18 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00-7.20 (m, 9H), 3.80 (s, 3H).

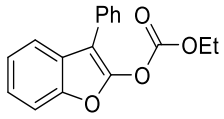
General procedure for synthesis of *O*-acylated benzofuranones 21



23 **21**

To a solution of **23** (2.00 mmol, 1.0 equiv.) in THF (7 mL) was added triethylamine (420 μL, 3.00 mmol, 1.5 equiv.) and chloroformate (290 μL, 3.00 mmol, 1.5 equiv.) at 0 °C under nitrogen atmosphere. The mixture was stirred at 0 °C for 1 h and then diluted with Et_2O (5 mL) and quenched with 0.1 M HCl (2 mL). The organic layer was separated and the aqueous layer extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The residual crude product was purified by silica gel column chromatography (hexane/diethyl ether = 30:1 as eluent) to afford *O*-acylated benzofuranone **21**.

Ethyl 3-phenylbenzofur-2-yl carbonate (21b)



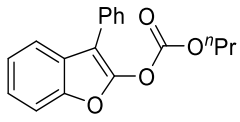
21b

General procedure was followed using **23** (421 mg, 2.00 mmol, 1.0 equiv.), ethyl chloroformate (290 μL, 3.00 mmol, 1.5 equiv.), triethylamine (420 μL, 3.00 mmol, 1.5 equiv.), and THF (7 mL) to afford **21b** as colorless oil (538 mg, 1.91 mmol, 95%). Spectral data are in agreement with the literature.[S3a]

Rf = 0.15 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78-7.12 (m, 9H), 4.25 (q, 2H, *J* = 7.1 Hz), 1.28 (t, 3H, *J* = 7.3 Hz).

Propyl 3-phenylbenzofur-2-yl carbonate (21c)



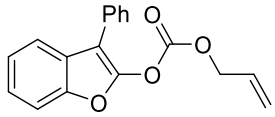
21c

General procedure was followed using **23** (298 mg, 1.42 mmol, 1.0 equiv.), *n*-propyl chloroformate (240 μL, 2.13 mmol, 1.5 equiv.), triethylamine (420 μL, 3.00 mmol, 1.5 equiv.), and THF (5 mL) to afford **21c** as colorless oil (398 mg, 1.34 mmol, 95%). Spectral data are in agreement with the literature.[S3a]

Rf = 0.28 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05-7.19 (m, 9H), 4.18 (t, 2H, *J* = 6.6 Hz), 1.15 (m, 2H), 0.83 (t, 3H, *J* = 7.6 Hz).

2-Propenyl 3-phenylbenzofur-2-yl carbonate (21d)



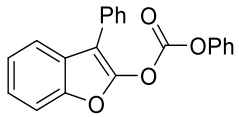
21d

General procedure was followed using **23** (421 mg, 2.00 mmol, 1.0 equiv.), allyl chloroformate (320 μL, 3.00 mmol, 1.5 equiv.), triethylamine (420 μL, 3.00 mmol, 1.5 equiv.), and THF (7 mL) to afford **21d** as colorless oil (559 mg, 1.90 mmol, 95%). Spectral data are in agreement with the literature.[10a]

Rf = 0.27 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09-7.18 (m, 9H), 5.81 (m, 1H), 5.28 (m, 2H), 4.61 (br, 2H).

Phenyl 3-phenylbenzofur-2-yl carbonate (21e)



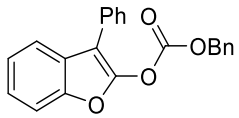
21e

General procedure was followed using **23** (421 mg, 2.00 mmol, 1.0 equiv.), phenyl chloroformate (250 μL, 3.00 mmol, 1.5 equiv.), triethylamine (420 μL, 3.00 mmol, 1.5 equiv.), and THF (7 mL) to afford **21e** as colorless oil (660 mg, 2.00 mmol, >99%). Spectral data are in agreement with the literature.[10a]

Rf = 0.23 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.00-7.50 (m, 14H).

Benzyl 3-phenylbenzofur-2-yl carbonate (21f)



21f

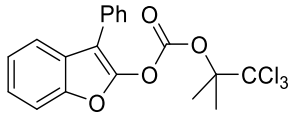
General procedure was followed using **23** (421 mg, 2.00 mmol, 1.0 equiv.), benzyl chloroformate (430 μL, 3.00 mmol, 1.5 equiv.), triethylamine (420 μL, 3.00 mmol, 1.5 equiv.), and THF (7 mL) to afford **21f** as colorless oil (598 mg, 1.74 mmol, 87%). Spectral data are in agreement with the

literature.[S3a]

Rf = 0.24 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00-7.20 (m, 14H), 4.95 (s, 2H).

2,2,2-Trichloro-1,1-dimethylethyl 3-phenylbenzofur-2-yl carbonate (21g)



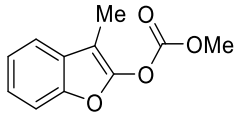
21g

21g was synthesized and characterized according to the literature.[S3b]

Rf = 0.34 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, 1H, *J* = 7.5 Hz), 7.55 (d, 2H, *J* = 7.7 Hz), 7.40 (m, 3H), 7.26 (m, 3H), 1.85 (s, 6H).

Methyl 3-methylbenzofur-2-yl carbonate (21h)



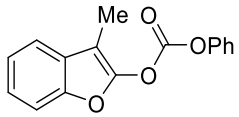
21h

21h was synthesized and characterized according to the literature.[S3c]

Rf = 0.37 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42-7.35 (m, 1H), 7.33-7.27 (m, 1H), 7.24-7.12 (m, 2H), 3.89 (s, 3H), 2.05 (s, 3H)

Phenyl 3-methylbenzofur-2-yl carbonate (21i)



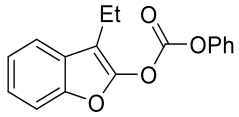
21i

21i was synthesized and characterized according to the literature. [S3d]

Rf = 0.50 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48-7.39 (m, 4H), 7.31-7.22 (m, 5H), 2.18 (s, 3H).

Phenyl 3-ethylbenzofur-2-yl carbonate (21j)



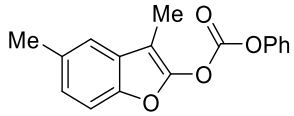
21j

21j was synthesized and characterized according to the literature.[S3d]

Rf = 0.25 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.51 (m, 2H), 7.45-7.40 (m, 3H), 7.32-7.25 (m, 4H), 2.68 (q, 2H, *J* = 7.2 Hz), 1.32 (t, 3H, *J* = 7.6 Hz).

Phenyl 3,5-dimethylbenzofur-2-yl carbonate (21k)



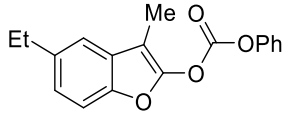
21k

21k was synthesized and characterized according to the literature.[S3e]

Rf = 0.25 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.41 (t, 2H, *J* = 8.0 Hz), 7.32-7.25 (m, 5H), 7.10-7.08 (m, 1H), 2.45 (s, 3H), 2.17 (s, 3H).

Phenyl 5-ethyl-3-methylbenzofur-2-yl carbonate (21l)



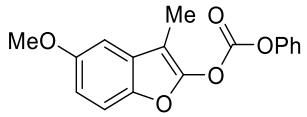
21l

21l was synthesized and characterized according to the literature.[S3e]

Rf = 0.26 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.39 (m, 2H), 7.33-7.27 (m, 5H), 7.14-7.10 (m, 1H), 2.73 (q, 2H, *J* = 7.2 Hz), 2.17 (s, 3H), 1.28 (t, 3H, *J* = 7.6 Hz).

Phenyl 5-methoxy-3-methylbenzofur-2-yl carbonate (21m)



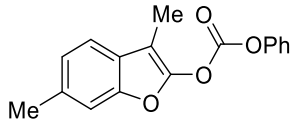
21m

21m was synthesized and characterized according to the literature.[S3e]

Rf = 0.18 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (t, 2H, *J* = 7.6 Hz), 7.30 (d, 4H, *J* = 9.2 Hz), 6.94-6.86 (m, 2H), 3.86 (s, 3H), 2.17 (s, 3H).

Phenyl 3,6-dimethylbenzofur-2-yl carbonate (21n)



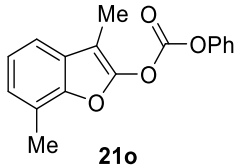
21n

21n was synthesized and characterized according to the literature.[S3e]

Rf = 0.26 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.41 (m, 2H), 7.35 (d, 1H, *J* = 8.4 Hz), 7.32-7.21 (m, 4H), 7.09-7.07 (m, 1H), 2.46 (s, 3H), 2.17 (s, 3H).

Phenyl 3,7-dimethylbenzofur-2-yl carbonate (21o)



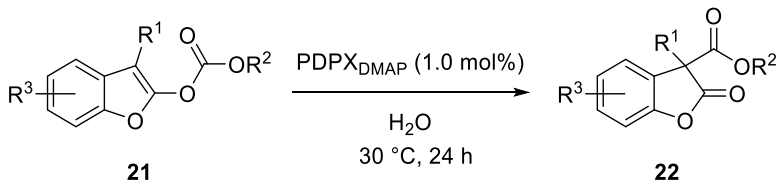
21o

21o was synthesized and characterized according to the literature.[S3e]

Rf = 0.33 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.26 (m, 6H), 7.17 (t, 1H, *J* = 7.2 Hz), 7.10-7.08 (m, 1H), 2.49 (s, 3H), 2.18 (s, 3H).

3. $PDPX_{DMAP}$ catalyzed acyl rearrangement reaction of benzofuranones

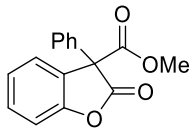


21 **22**

General Procedure A: for liquid starting material: To a mixture of *O*-acylated benzofuranone **21** (0.200 mmol, 1.0 equiv.) in H_2O (1 mL) was added $PDPX_{DMAP}$ ([DMAP]: 0.393 mmol/g, 5.2 mg, 0.002 mmol, 1.0 mol%) and the reaction mixture was stirred at 30 ºC for 24 h. The reaction mixture was quenched with 2 M HCl (1 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with 2 M HCl (2 mL), sat. $NaHCO_3$ aq. (2 mL), and brine, dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The residual crude product was purified by silica gel column chromatography (hexane/diethyl ether = 19:1 to 7:1 as eluent) to afford desired product **22**.

General Procedure B: for solid starting material: To a mixture of *O*-acylated benzofuranone **21** (0.200 mmol, 1.0 equiv.), and corresponding organic solvent (0.200 mmol, 1.0 equiv.) in H_2O (1 mL) was added $PDPX_{DMAP}$ ([DMAP]: 0.393 mmol/g, 5.2 mg, 0.002 mmol, 1.0 mol%) and the reaction mixture was stirred at 30 ºC for 24 h. The reaction mixture was quenched with 2 M HCl (1 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with 2 M HCl (2 mL), sat. $NaHCO_3$ aq. (2 mL), and brine, dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The residual crude product was purified by silica gel column chromatography (hexane/diethyl ether = 19:1 to 7:1 as eluent) to afford desired product **22**.

Methyl 2,3-dihydro-2-oxo-3-phenyl-3-benzofurancarboxylate (22a)[S3a]



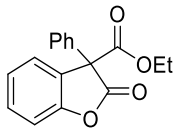
22a

General Procedure A was followed using **21a** (59.7 mg, 0.22 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.507 mmol/g, 4.4 mg, 0.002 mmol, 1.0 mol%) and H_2O (1 mL) to afford **22a** as colorless oil (53.4 mg, 0.20 mmol, 89% yield).

Rf = 0.26 (hexane/diethyl ether = 7:3)

^1H NMR ($CDCl_3$, 400 MHz) δ 7.53-7.44 (m, 2 H), 7.38-7.21 (m, 7 H), 3.80 (s, 3 H).

Ethyl 2,3-dihydro-2-oxo-3-phenyl-3-benzofurancarboxylate (22b)[S3a]



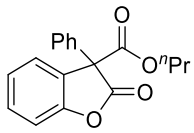
22b

General Procedure B was followed using **21b** (63.7 mg, 0.23 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.393 mmol/g, 5.8 mg, 0.002 mmol, 1.0 mol%), H_2O (1 mL), and 1,4-dioxane (19.3 μL, 0.23 mmol, 1.0 equiv.) to afford **22b** as a white solid (55.1 mg, 0.20 mmol, 86% yield).

Rf = 0.16 (hexane/diethyl ether = 7:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.46 (m, 2 H), 7.37-7.21 (m, 7 H), 4.32-4.20 (m, 2 H), 1.23 (t, 3H, *J* = 7.2 Hz).

Propyl 2,3-dihydro-2-oxo-3-phenyl-3-benzofurancarboxylate (22c)[S3a]



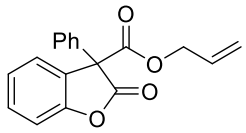
22c

General Procedure B was followed using **21c** (62.6 mg, 0.211 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.189 mmol/g, 11.2 mg, 0.002 mmol, 1.0 mol%), H_2O (1 mL), and THF (17.5 μL, 0.20 mmol, 1.0 equiv.) to afford **22c** as a white solid (47.3 mg, 0.169 mmol, 72% yield).

Rf = 0.16 (hexane/diethyl ether = 7:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.21 (m, 9H), 4.22-4.12 (m, 2H), 1.64-1.55 (m, 2H), 0.82 (t, 3H, *J* = 7.5 Hz).

2-Propenyl 2,3-dihydro-2-oxo-3-phenyl-3-benzofurancarboxylate (22d)[S3a]



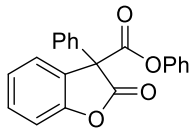
22d

General Procedure A was followed using **21d** (60.0 mg, 0.20 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.393 mmol/g, 5.2 mg, 0.002 mmol, 1.0 mol%), and H_2O (1 mL) to afford **22d** as colorless oil (46.7 mg, 0.16 mmol, 78% yield).

Rf = 0.19 (hexane/diethyl ether = 19:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51-7.24 (m, 9 H), 5.86-5.79 (m, 1 H), 5.22-5.19 (m, 2 H), 4.71-4.66 (m, 2 H).

Phenyl 2,3-dihydro-2-oxo-3-phenyl-3-benzofurancarboxylate (22e)[S3a]



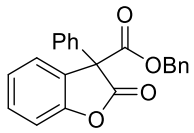
22e

General Procedure A was followed using **21e** (63.5 mg, 0.19 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.393 mmol/g, 4.9 mg, 0.002 mmol, 1.0 mol%), and H_2O (1 mL) to afford **22e** as colorless oil (56.3 mg, 0.17 mmol, 89% yield).

Rf = 0.16 (hexane/diethyl ether = 7:1)

^1H NMR ($CDCl_3$, 400 MHz) δ 7.64 (dd, 1H, *J* = 6.4, 1.1 Hz), 7.54-7.20 (m, 11H), 7.03-7.00 (m, 2 H)

Benzyl 2,3-dihydro-2-oxo-3-phenyl-3-benzofurancarboxylate (22f)[S3a]



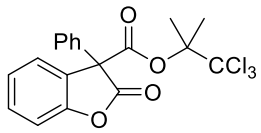
22f

General Procedure B was followed using **21f** (68.0 mg, 0.20 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.393 mmol/g, 5.0 mg, 0.002 mmol, 1.0 mol%), H_2O (1 mL), and ethanol (11.5 µL, 0.20 mmol, 1.0 equiv.) to afford **22f** as a yellow solid (63.8 mg, 0.19 mmol, 88% yield).

Rf = 0.16 (hexane/diethyl ether = 7:1)

^1H NMR ($CDCl_3$, 400 MHz) δ 7.47-7.19 (m, 14 H), 5.22 (dd, 2 H, *J* = 12.4, 5.3 Hz).

2,2,2-Trichloro-1,1-dimethylethyl 2,3-dihydro-2-oxo-3-phenyl-3-benzofurancarboxylate (22g)[S3b]



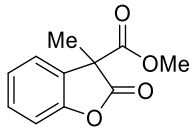
22g

General Procedure B was followed using **21g** (85.8 mg, 0.21 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.189 mmol/g, 11.0 mg, 0.002 mmol, 1.0 mol%), H_2O (1.1 mL), and THF (16.9 µL, 0.21 mmol 1.0 equiv.) to afford **22g** as a white solid (67.9 mg, 0.17 mmol, 78% yield).

Rf = 0.14 (hexane/diethyl ether = 19:1)

^1H NMR ($CDCl_3$, 400 MHz) δ 7.59 (dd, 1H, *J* = 6.2, 1.4 Hz), 7.48-7.35 (m, 6H), 7.31-7.20 (m, 2H), 1.92 (s, 3H), 1.80 (s, 3H).

Methyl 2,3-dihydro-2-oxo-3-methyl-3-benzofurancarboxylate (22h)[S3c]



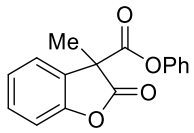
22h

General Procedure A was followed using **21h** (56.3 mg, 0.27 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.393 mmol/g, 7.0 mg, 0.003 mmol, 1.0 mol%), and H_2O (1.4 mL) to afford **22h** as colorless oil (33.1 mg, 0.16 mmol, 59% yield).

Rf = 0.16 (hexane/diethyl ether = 7:1)

^1H NMR ($CDCl_3$, 400 MHz) δ 7.37 (ddd, 1H, *J* = 6.6, 1.4, 0.9 Hz), 7.30 (dd, 1H, *J* = 6.2, 1.4 Hz), 7.20-7.15 (m, 2H), 3.72 (s, 3H), 1.79 (s, 3H).

Phenyl 2,3-dihydro-2-oxo-3-methyl-3-benzofurancarboxylate (22i)[S3d]



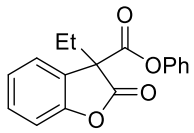
22i

General Procedure A was followed using **21i** (51.3 mg, 0.19 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.393 mmol/g, 4.9 mg, 0.002 mmol, 1.0 mol%), and H_2O (1 mL) to afford **22i** as colorless oil (30.8 mg, 0.092 mmol, 48% yield).

Rf = 0.21 (hexane/diethyl ether = 7:1)

^1H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.20 (m, 7H), 6.99-6.96 (m, 2H), 1.89 (s, 3H).

Phenyl 2,3-dihydro-2-oxo-3-ethyl-3-benzofurancarboxylate (22j)[S3d]



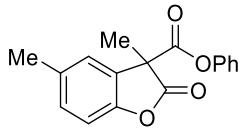
22j

General Procedure B was followed using **21j** (53.3 mg, 0.19 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.507 mmol/g, 3.7 mg, 0.002 mmol, 1.0 mol%), H_2O (1 mL), and 1,4-dioxane (16.2 μL, 0.19 mmol, 1.0 equiv.) to afford **22j** as colorless oil (52.0 mg, 0.17 mmol, 92% yield). mixture with 3-ethylbenzofuran-2(3*H*)-one (**S6**) (5%).

Rf = 0.15 (hexane/diethyl ether = 7:1)

^1H NMR ($CDCl_3$, 400 MHz) δ 7.44-7.20 (m, 7H), 7.00-6.98 (m, 2H), 2.54-2.35 (m, 2H), 0.86 (t, 3H, *J* = 7.4 Hz).

Phenyl 2,3-dihydro-3,5-dimethyl-2-oxo-3-benzofurancarboxylate (22k)[S3e]



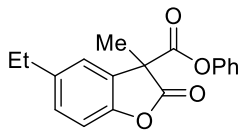
22k

General Procedure B was followed using **21k** (55.8 mg, 0.20 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.178 mmol/g, 11.1 mg, 0.002 mmol, 1.0 mol%), H_2O (1 mL) and THF (16.0 μL, 0.20 mmol, 1,0 equiv.) to afford **22k** as a white solid (44.6 mg, 0.15 mmol, 76% yield). mixture with 3,5-dimethylbenzofuran-2(3*H*)-one (**S7**) (13%).

Rf = 0.23 (hexane/diethyl ether = 7:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.31 (m, 2H), 7.26-7.19 (m, 3H), 7.10-7.06 (m, 1H), 7.00-6.98 (m, 2H), 2.39 (s, 3H), 1.86 (s, 3H).

Phenyl 5-ethyl-2,3-dihydro-3-methyl-2-oxo-3-benzofurancarboxylate (22l)[S3e]



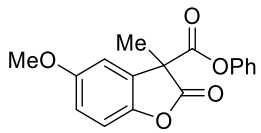
22l

General Procedure B was followed using **21l** (58.1 mg, 0.20 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.178 mmol/g, 11.0 mg, 0.002 mmol, 1.0 mol%), H_2O (1 mL) and THF (15.9 μL, 0.20 mmol, 1,0 equiv.) to afford **22l** as colorless oil (47.0 mg, 0.15 mmol, 76% yield).

Rf = 0.14 (hexane/diethyl ether = 7:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (t, 2H, *J* = 7.8 Hz), 7.26-7.21 (m, 3H), 7.11 (dd, 1H, *J* = 7.6 Hz), 7.00-6.96 (m, 2H), 2.68 (q, 2H, *J* = 7.6 Hz), 1.87 (s, 3H), 1.26 (t, 3H, *J* = 7.7 Hz).

Phenyl 2,3-dihydro-5-methoxy-3-methyl-2-oxo-3-benzofurancarboxylate (22m)[S3e]



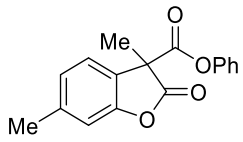
22m

General Procedure A was followed using **21m** (59.5 mg, 0.20 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.507 mmol/g, 3.9 mg, 0.002 mmol, 1.0 mol%), and H_2O (1 mL) to afford **22m** as a white solid (57.3 mg, 0.19 mmol, 93% yield).

Rf = 0.081 (hexane/diethyl ether = 7:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (t, 2H, *J* = 7.9 Hz), 7.23 (t, 1H, *J* = 7.4 Hz), 7.13 (dd, 1H, *J* = 4.8, 2.3 Hz), 6.99 (d, 2H, *J* = 8.2 Hz), 6.93-6.90 (m, 2H), 3.82 (s, 3H), 1.87 (s, 3H).

Phenyl 2,3-dihydro-3,6-dimethyl-2-oxo-3-benzofurancarboxylate (22n)[S3e]



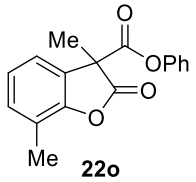
22n

General Procedure A was followed using **21n** (56.5 mg, 0.20 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.178 mmol/g, 11.3 mg, 0.002 mmol, 1.0 mol%), and H_2O (1 mL) to afford **22n** as yellow oil (50.5 mg, 0.18 mmol, 74% yield).

Rf = 0.29 (hexane/diethyl ether = 7:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.21 (m, 4H), 7.05-6.95 (m, 4H), 2.42 (s, 3H), 1.86 (s, 3H).

Phenyl 2,3-dihydro-3,7-dimethyl-2-oxo-3-benzofurancarboxylate (22o)[S3e]



22o

General Procedure B was followed using **21o** (56.2 mg, 0.20 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.507 mmol/g, 3.9 mg, 0.002 mmol, 1.0 mol%), H_2O (1 mL), and 1,4-dioxane (17.0 μL, 0.20 mmol, 1,0 equiv) to afford **22o** as colorless oil (41.7 mg, 0.14 mmol, 69% yield). mixuture with 3,7-dimethylbenzofuran-2(3*H*)-one (**S11**) (8%).

Rf = 0.29 (hexane/diethyl ether = 7:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.31 (t, 2H, *J* = 7.9 Hz), 7.24-7.20 (m, 3H), 7.15-7.11 (m, 1H), 7.00-6.96 (d, 2H, *J* = 8.5 Hz), 2.38 (s, 3H), 1.87 (s, 3H).

4. Catalyst reuse

A mixture of *O*-acylated benzofuranone (**21a**, 55.1 mg, 0.200 mmol, 1.0 equiv.), $PDPX_{DMAP}$ ([DMAP]: 0.393 mmol/g, 2.6 mg, 0.001 mmol, 0.5 mol%), and H_2O (1 mL) was stirred at 30 ºC for 24 h. The reaction mixture was quenched with 2 M HCl (1 mL). $PDPX_{DMAP}$ was filtrated and washed with acetone (2 mL), CH_2Cl_2 (2 mL), and EtOH (2 mL). The residue was corrected and dried under vacuo to afford a recovered-PDPX. To a suspension of recovered PDPX (49.8 mg, [-C_6F_4I]: 0.329 mmol/g) in CH_2Cl_2 (2 mL) was added DMAP (2.0 mg, 0.0164 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h then concentrated under reduced pressure to afford **$PDPX_{DMAP}$-2nd** as a white solid (40.1 mg, [DMAP]: 0.446 mmol/g). elemental analysis calcd (%) for $C_{177.74}H_{177.24}N_{2.3}F_4I$: C 83.86, H 6.96, N 1.11, found: C 82.93, H 7.14, N 1.51. A mixture of **21a** (72.4 mg, 0.270 mmol, 1.0 equiv.), **$PDPX_{DMAP}$-2nd** ([DMAP]: 0.446 mmol/g, 2.9 mg, 0.0013 mmol, 0.5 mol%), and H_2O (1.3 mL) was stirred at 30 ºC for 24 h. The reaction mixture was quenched with 2 M HCl (1 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with 2 M HCl (2 mL), sat. $NaHCO_3$ aq. (2 mL), and brine, dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The residual crude product was purified by silica gel column chromatography (hexane/diethyl ether = 19:1 to 7:1 as eluent) to afford **22a** as colorless oil (40.5 mg, 0.151 mmol, 56%).

5. References

[S1] Padwa, A.; Dehm, D.; Oine, T.; Lee, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 1837–1845.

[S2] Zhang, Z.; Zhang, W. *Chem. Commun.* **2017**, *53*, 1381−1384.

[S3] (a) Black, T. H.; Arrivo, S. M.; Schumm, J. S.; Knobeloch, J. M. *J. Org. Chem.* **1987**, *52*, 5425–5430. (b) Hills, I. D.; Fu, G. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 3921–3924. (c) Cruchter, T.; Medvedev, M. G.; Shen, X.; Mietke, T.; Harms, K.; Marsch, M.; Meggers, E. *ACS Catal.* **2017**, *7*, 5151−5162. (d) Shaw, S. A.; Aleman, P.; Christy, J.; Kampf, J. W.; Va, P.; Vedejs, E. *J. Am. Chem. Soc.* **2006**, *128*, 925−934. (e) Wang, M.; Zhang, Z.; Liu, S.; Xie, F.; Zhang, W. *Chem. Commun.* **2014**, *50*, 1227−1230.

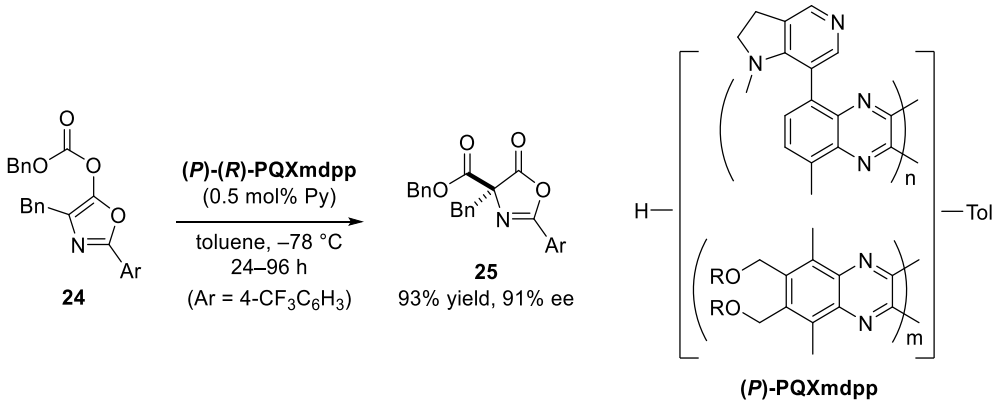
第４章
O-アシル化アズラクトンの転位反応における触媒機能開拓

4–1．無溶媒での有機分子変換

複雑な天然・非天然化合物の合成が可能になった昨今、合成反応の効率性に加え、環境にやさしい合成法が求められている。化学プロセスの環境調和性を定量評価する指標として、1992 年、Sheldon によって E 値が提唱された[1]。E 値とは、廃棄物の重量を生成物の重量で割った値である。E 値が小さいほど環境調和性が高いと評価でき、廃棄物が生じなければ E 値は「０」となる。一般的な医薬品の合成プロセスにおいて、E 値は 100 以上と推定されている。E 値に最も大きく影響を与えるのが有機溶媒であり、無溶媒反応の開発は、環境調和性の向上に繋がる重要な課題である[2]。無溶媒反応には、コストの削減、消費エネルギーの節約、反応時間の短縮、反応容器や資本投資の縮小といったメリットがある。これまでに無溶媒での高分子化[3]、ラジカル付加[4]、イオン液体反応[5]、固体反応[2b,6]、光化学反応[7]、エナンチオ選択的反応[8]が達成されている。また、近年、無溶媒反応の一種である、メカノケミストリー[9]にも注目が集まっている。

4–2．*O*-アシル化アズラクトンの転位反応

DMAP ペンダント型高分子触媒 $PDPX_{DMAP}$ の有用性を拡張するため、ベンゾフラノンの窒素類縁体であるアズラクトンのアシル基転位反応[10]に着目した。転位生成物はアミノ酸の前駆体となり、様々な非天然アミノ酸の合成が可能である[11]。高効率的・高立体選択的均一系求核触媒は報告されているものの[12]、不均一系触媒反応においては杉野目らの一例のみである[13]。杉野目らは、4-アミノピリジル基を側鎖に持つ、らせん状のポリキノキサリン（**PQXmdpp**）を開発し、アズラクトンの高効率的・エナンチオ選択的アシル基転位反応を達成した（**Scheme 4-1**）。



Scheme 4-1. Chiral Poly(quinoxaline-2,3-diyl)s bearing 4-aminopyridid-3-yl Pendant Catalyzed Asymmetric Steglich Rearrangement of Benzyl 4-benzyl-2-(4-trifluoromethylphenyl)-oxazol-5-yl carbonate **24**

4–3. 高分子触媒による無溶媒での *O*-アシル化アズラクトンの転位反応

4-3-1. 無溶媒系高分子反応場への展開

第３章で述べたとおり、*O*-アシルベンゾフラノンの転位反応は、高分子鎖近傍で進行していることが示唆された。開発した DMAP ペンダント型高分子触媒は、ヨウ素が反応基質の相互作用部位として機能していると推察される。また、用いる架橋剤の当量により、高分子鎖の性質を変化させることも可能である。反応基質を取り込みやすいように高分子鎖の性質を変えることで、高分子鎖が触媒活性中心と反応基質との媒体となり、迅速な無溶媒反応が実現できるのではないかと考えた(**Figure 4-1**)。

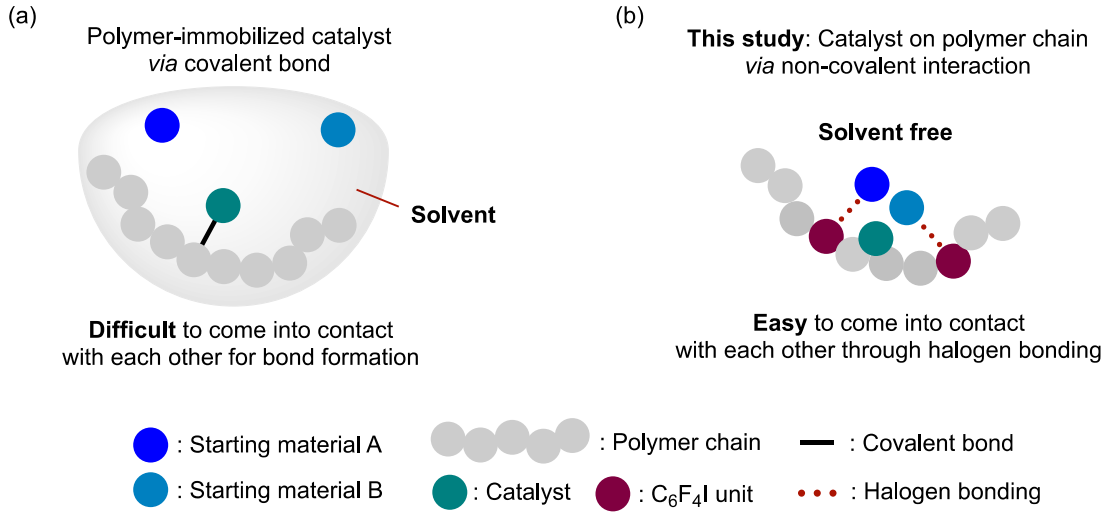
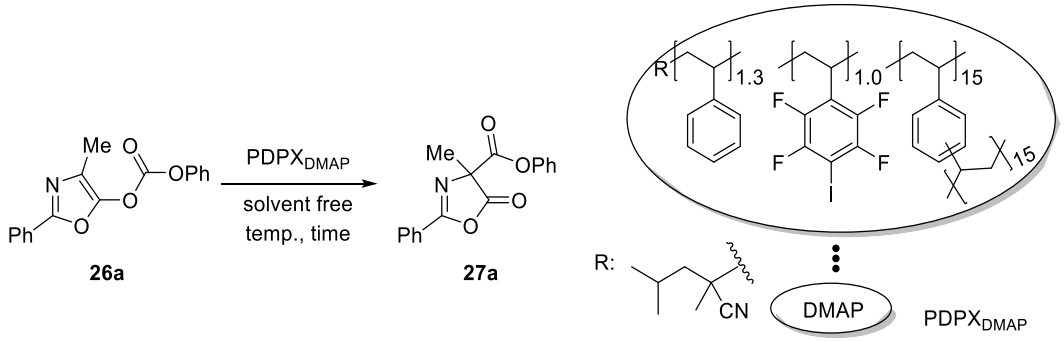


Figure 4-1 (a) Conventional Heterogeneous Reaction in Solvent (b) This Study: PDPX-Mediated Heterogeneous Reaction without Solvent

4-3-2. 初期検討

初期検討は、ベンゾフラノンのアシル基転位反応の結果をもとに、ジビニルベンゼン 15 当量から成る $PDPX_{DMAP}$(n = 15)存在下、*O*-アシルアズラクトン(**26a**)を用い、反応温度 30 ℃で撹拌して行った(**Table 4-1**)。尚、転位生成物 **27a** は、シリカゲルによるカラム精製において分解したため、NMR 測定により収率を算出した。1 mol%の $PDPX_{DMAP}$ 存在下で 10 分間撹拌した場合、91%収率で目的生成物を与えた(entry 1)。触媒量 0.1 mol%の場合、反応時間 30 分で転位生成物が良好な収率で得られた(entry 2)。0.05 mol%(500 mol ppm)の場合、反応時間 30 分で収率は 17%にとどまった(entry 3)。そこで、40 ℃、50 ℃、60 ℃で反応温度の検討を行った。その結果、収率が向上し、反応温度 60 ℃の場合は 91%収率で目的生成物が得られた(entries 4~6)。反応温度を 60 ℃、触媒量 250 mol ppm、100 mol ppm で検討を行ったところ、反応時間 30 分で転位生成物がそれぞれ高収率で得られた(entries 7, 8)。50 mol ppm の場合、反応時間 30 分では 12%収率であったが(entry 9)、45 分後に定量的に得られた(entries 10, 11)。25 mol ppm の場合も、30 分後の収率は 6%であったものの(entry 12)、反応時間を延ばすと収率が向上し(entries 13, 14)、70 分後には 96%(entry 15)、90 分後には 99%以上の高収率で目的生成物が得られた(entry 16)。TON、TOF はそれぞれ最大で 40,000、549 mn^{-1} に達した。

Table 4-1. Acyl Rearrangement Reaction of Azlactones[a]



entry	catalyst loading (mol ppm)	temp. (℃)	time (min)	yield[b] (%)	TON	TOF (min^{-1})
1	10,000 = 1 mol%	30	10	91	91	9
2	1,000 = 0.1 mol%	30	30	89	890	30
3	500 = 0.05 mol%	30	30	17	340	11
4	500	40	30	59	1,180	39
5	500	50	30	82	1,640	55
6	500	60	30	91	1,820	61
7	250	60	30	94	3,760	125
8	100	60	30	96	9,600	320
9	50	60	30	12	2,400	80

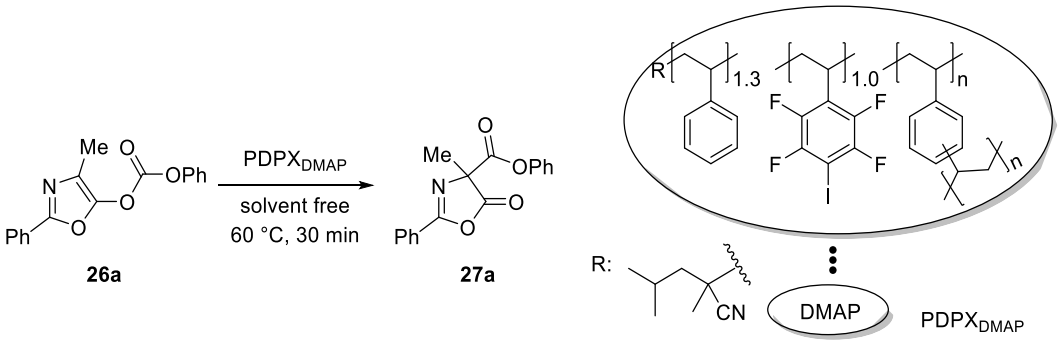
10	50	60	45	99	19,800	440
11	50	60	60	99	19,800	330
12	25	60	30	6	2,400	80
13	25	60	45	23	9,200	204
14	25	60	60	78	31,200	520
15	25	60	70	96	38,400	549
16	25	60	90	>99	40,000	444

[a] Reactions were performed using **26a** and $PDPX_{DMAP}$.

[b] Yields were determined by ^1H NMR.

次に、架橋剤であるジビニルベンゼンの当量を変えて高分子を合成し、架橋剤の当量が反応収率に及ぼす影響を調べた(**Table 4-2**)。検討は、25 mol ppm の $PDPX_{DMAP}$ 存在下、反応時間 30 分で行った。比較のため、Table 4-1, entry 12, n=15 の検討結果を Table 4-2, entry 1 に示した。n = 15 の $PDPX_{DMAP}$ の場合、収率はわずか 6%であったが(entry 1)、n = 1 では 35%(entry 2)、n = 0.1 では 97%(entry 3)、n = 0.01 では 91%であった(entry 4)。これらの結果から、ジビニルベンゼンの当量は反応性に大きな影響を及ぼし、n = 0.1 の場合に最も高い収率、TON、TOF を与えることがわかった。この時、TON は 38,800、TOF は 1,293 min^{-1} であった。触媒量の更なる低減を目指し、触媒量 20 mol ppm の $PDPX_{DMAP}$ n = 0.1 を用いて検討を行った(entry 5)。この場合、実験の再現性に乏しい結果となったため、以降の検討を 25 mol ppm で行うことにした。

Table 4-2. Acyl Rearrangement Reaction of Azlactones: Examination of DVB[a]



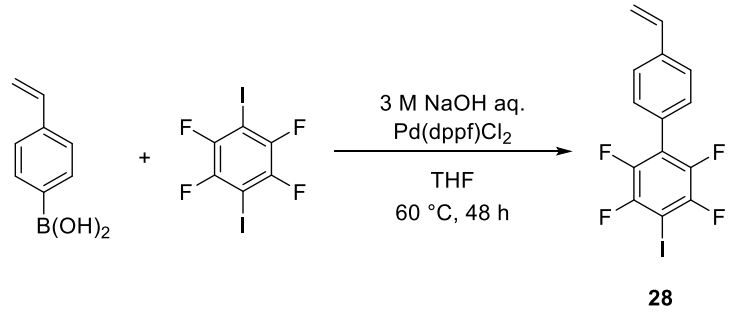
entry	catalyst loading (mol ppm)	n	yield[b] (%)	TON	TOF (min^{-1})
1	25	15	6	2,400	80
2	25	1	35	14,000	467
3	25	0.1	97	38,800	1,293
4	25	0.01	91	36,400	1,213
5	20	0.1	45~89	22,500~44,500	750~1,483

[a] Reactions were performed using **26a** and $PDPX_{DMAP}$ at 60 °C for 30 min.
[b] Yields were determined by ^{1}H NMR.

4-3-3. ハロゲン結合供与部位の改良

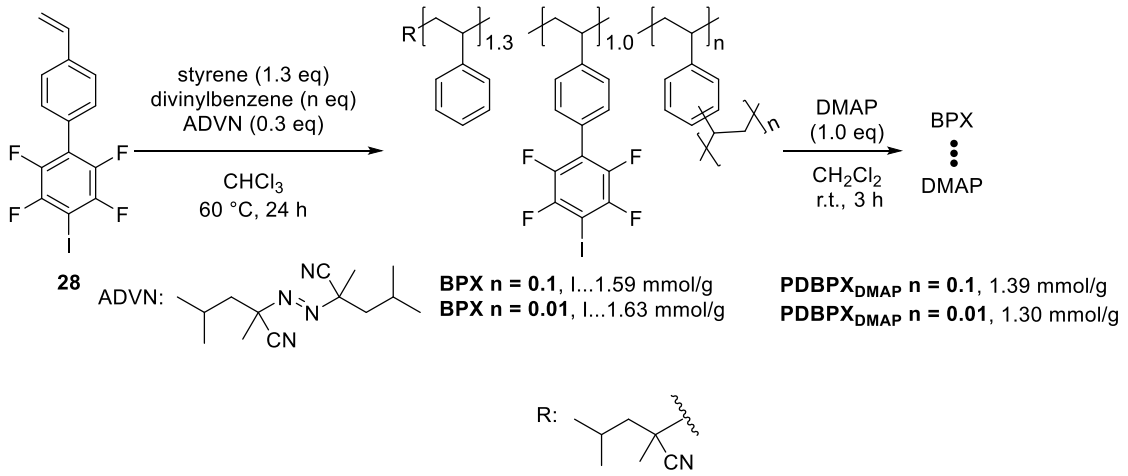
初期検討により、開発した $PDPX_{DMAP}$ が、アズラクトンの無溶媒系アシル基転位反応に対して優れた触媒機能を有することがわかった。一方で、高分子合成に用いる機能性モノマーTFIS は、市販の 2,3,5,6-テトラフルオロ安息香酸から 3 工程をかけて合成しなければならず、純度の高い TFIS を得るためには、分取 HPLC による精製も必要である。そこで、TFIS よりも簡便に合成可能な機能性モノマーとして、ヨウ化テトラフルオロビフェニルスチレン(**28**)に着目した。ヨウ化テトラフルオロビフェニルスチレン[14]は、ヨウ化ペルフルオロアレーンを置換基にもつポリスチレンの原料に用いられている。

まず、Taylor の報告を参考にヨウ化テトラフルオロビフェニルスチレン(**28**)の合成を行った(**Scheme 4-2**)。市販の 4−ビニルフェニルボロン酸とテトラフルオロ 1,4-ジヨードベンゼンとの鈴木−宮浦クロスカップリングを行い、得られた粗生成物をシリカゲルカラムクロマトグラフィーにより単離精製した。その結果、目的とする **28** が 53%収率で得られた。



Scheme 4-2. Synthesis of 4′-Ethenyl-2,3,5,6-tetrafluoro-4-iodo-1,1′-biphenyl (**28**)

次に、$PDPX_{DMAP}$ と同じ手順で高分子合成を行った(**Scheme 4-3**)。**28** に対して、1.3 当量のスチレン、0.1 または、0.01 当量のジビニルベンゼンを用い、重合開始剤 ADVN 存在下、クロロホルム溶媒中、60 ℃、24 時間、撹拌した。得られた高分子をヘキサン、エタノールを用いて洗浄し、未反応のスチレン、ADVN を取り除いた。続いて、すり潰すことで、白色の粉末(BPX)を得た。得られた 2 種類の高分子 BPX 中のヨウ素に対して、ジクロロメタン溶媒中、1 当量の DMAP を加え室温で 3 時間撹拌することで、DMAP ペンダント型高分子触媒を調製した。尚、本手法により合成した高分子 DMAP 触媒を、Pendant biphenyl polymer with halogen (X)-bond donor $_{DMAP}$ と命名し、$PDBPX_{DMAP}$ と表記する。

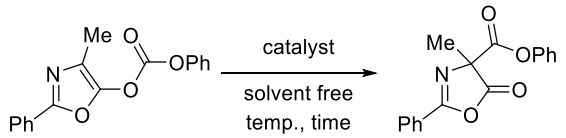


Scheme 4-3. Preparation of $PDBPX_{DMAP}$

4-3-4. 改良高分子触媒による検討

はじめに、$PDPX_{DMAP}$ n = 0.1 と $PDBPX_{DMAP}$ n = 0.1 の触媒活性を比較した。検討は、Table 4-2 の実験結果を参考に、触媒量 25 mol ppm、反応時間 30 分で行った。比較のため、Table 4-2, entry 3, n=0.1 の検討結果を Table 4-3, entry 1 に示した。$PDBPX_{DMAP}$ は、$PDPX_{DMAP}$ と同等の収率を与え、高い触媒活性を発現することがわかった(entry 2)。また、市販の高分子 DMAP 触媒である PS_{DMAP} と比較したところ、PS_{DMAP} は触媒量 100 mol ppm、反応温度 60 ℃、反応時間 30 分の条件でも反応は全く進行しなかった。$PDBPX_{DMAP}$ n = 0.1 が良好な触媒活性を有することが明らかになったため、$PDBPX_{DMAP}$ n = 0.1 を用い、以降の検討を行うことにした。

Table 4-3. Comparison of Catalyst in Acyl Rearrangement Reaction of Azlactones[a]



26a **27a**

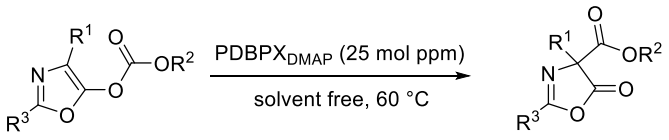
entry	catalyst	catalyst loading (mol ppm)	temp. (℃)	time (min)	yield[b] (%)	TON	TOF (min^{-1})
1	$PDPX_{DMAP}$ n = 0.1	25	60	30	97	38,800	1,293
2	$PDBPX_{DMAP}$ n = 0.1	25	60	30	97	38,800	1,293
3	PS_{DMAP}	100	60	30	<1	–	–

[a] Reactions were performed using **26a** and catalyst at 60 °C for 30 min.

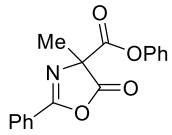
[b] Yields were determined by ^{1}H NMR.

4-3-4. 基質一般性

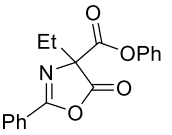
25 mol ppm の $PDBPX_{DMAP}$ n = 0.1 存在下、反応温度 60 ℃で、基質一般性を調査した（**Scheme 4-4**）。R^1 がメチル基、エチル基、*n*-プロピル基の場合や、R^2 のベンゼン環上に電子求引性置換基を有する場合、R^3 のベンゼン環上に電子求引性置換基または、メチル基を有する場合、30分の反応時間で転位生成物が良好な収率で得られた。一方、R^1に長鎖のアルキル基やベンゼン環をもつ場合や、R^2、R^3 のベンゼン環上に電子供与性基が置換された反応基質では、反応時間を伸長することにより、良好な収率で転位生成物が得られた。いずれの場合も、様々な置換基を有する *O*-アシルアズラクトンに対して、高い TON を示した。４位にイソプロピル基が置換した反応基質に対して、反応は遅く（**27d**）、また副生成物として 2-アシル化体も得られた（**27d'**）。



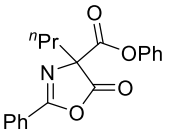
26 **27**



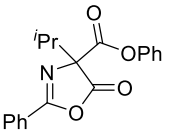
27a, 96% (30 min)
TON 38,400
TOF 1,280 min^{-1}



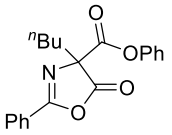
27b, 92% (30 min)
TON 36,800
TOF 1,227 min^{-1}



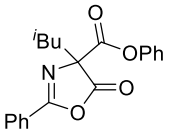
27c, 96% (30 min)
TON 38,400
TOF 1,280 min^{-1}



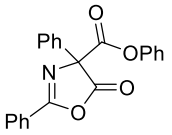
27d^{b}, 45% (42 h)
TON 4,500
TOF 2 min^{-1}



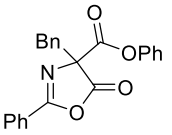
27e, 94% (48 h)
TON 37,600
TOF 13 min^{-1}



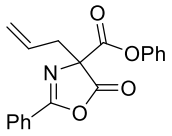
27f, 99% (3 h)
TON 39,600
TOF 220 min^{-1}



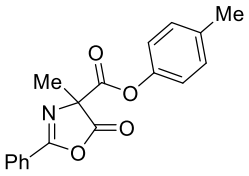
27g, 97% (8 h)
TON 38,800
TOF 81 min^{-1}



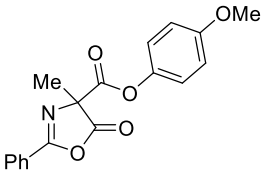
27h, 94% (4.5 h)
TON 37,600
TOF 139 min^{-1}



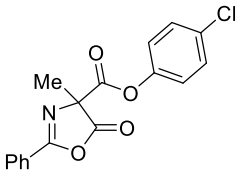
27i, 87% (15.5 h)
TON 34,800
TOF 37 min^{-1}



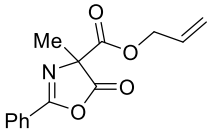
27j, 96% (45 min)
TON 38,400
TOF 853 min^{-1}



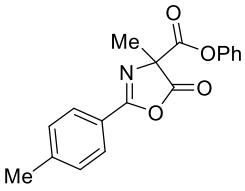
27k, 90% (75 min)
TON 36,000
TOF 480 min^{-1}



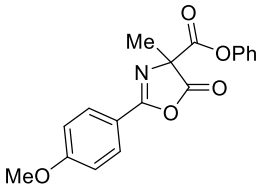
27l, 92% (30 min)
TON 36,800
TOF 1,227 min^{-1}



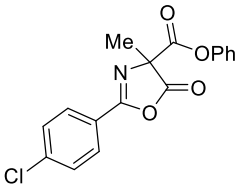
27m, 91% (1 h)
TON 36,400
TOF 607 min^{-1}



27n^{c}, 94% (30 min)
TON 18,800
TOF 627 min^{-1}



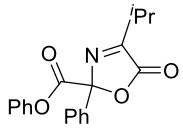
27o, 96% (1.5 h)
TON 38,400
TOF 427 min^{-1}



27p^{c}, 96% (30 min)
TON 19,200
TOF 640 min^{-1}

Scheme 4-4. Substrate Scope[a]

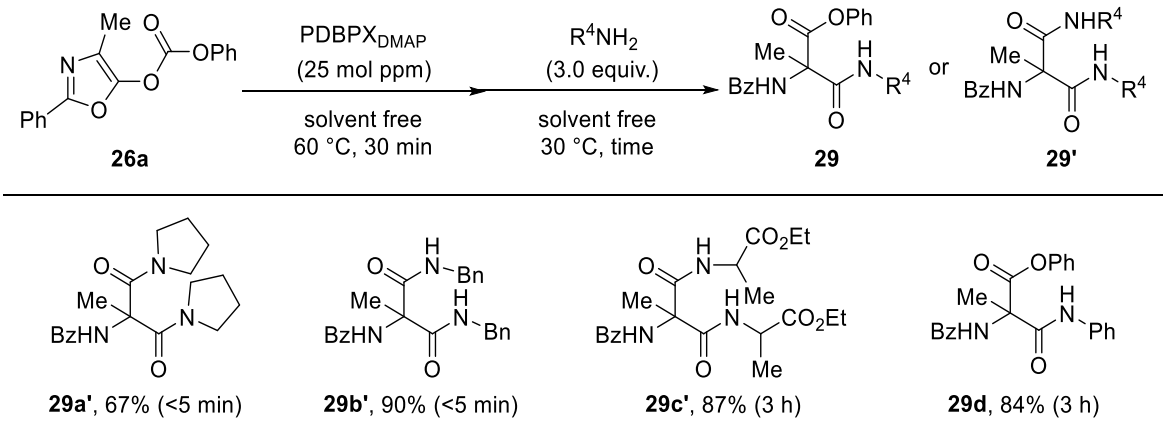
[a] Reactions were performed using **26** and PDBPX$_{DMAP}$ (25 mol ppm) at 60 °C. Yields were determined by ^{1}H NMR. [b] PDBPX$_{DMAP}$ 100 mol ppm. Regioisomer **27d'** was obtained in 36% yield. [c] PDBPX$_{DMAP}$ 50 mol ppm.



27d'

4–4. ワンポットアミノ酸誘導体の合成

アズラクトンのアシル基転位反応生成物は、４置換不斉炭素を有するアミノ酸誘導体を合成するうえで、有用な前駆体である。そこで、アズラクトンのアシル基転位反応とアミンによる開環反応の連続反応によるアミノ酸誘導体の合成を試みた(**Scheme 4-5**)。検討は、*O*-アシルアズラクトン **26a** に対して、25 mol ppm の $PDBPX_{DMAP}$ を用い、60 ℃で 30 分間撹拌した後に、反応温度を 30 ℃に下げ、3 当量のアミンを加え、さらに撹拌することで行った。その結果、求核剤としてピロリジン、ベンジルアミン、アラニンエチルエステルを用いると、目的とする **29** は得られず、エステル交換した **29'**が得られた(**29a'**, **29b'**, **29c'**)。加えるアミンを 1 当量に減らした場合は、**29** は得られたものの低収率に留まった。一方、求核剤としてアニリンを加えた場合、**29d'**は全く観られず、目的とするアミノ酸誘導体 **29d** が良好な収率で得られた。



Scheme 4-5. Synthesis of Amino Acid Derivatives in One-pot[a][b]

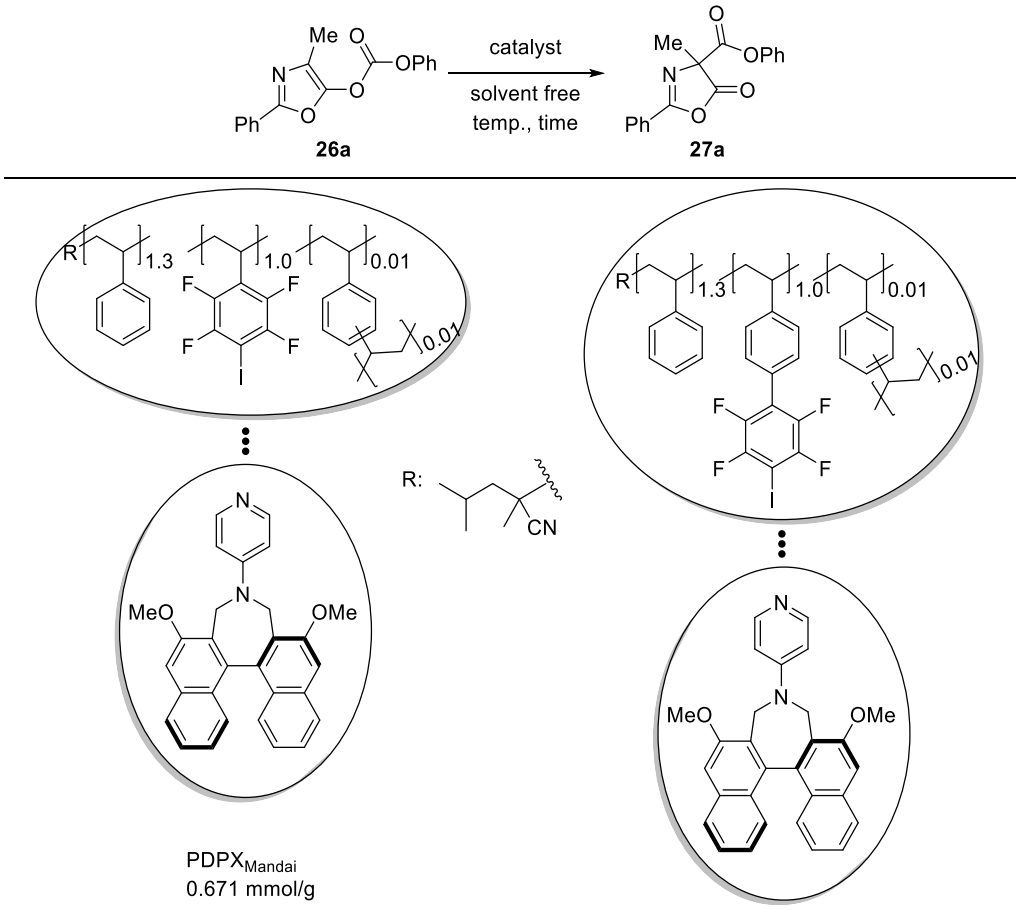
[a] Reactions were performed using **26a** and $PDBPX_{DMAP}$ (25 mol ppm) at 60 °C for 30 min. Then the reaction mixture was added to amine (3.0 eq) and stirred at 30 °C. [b] Isolated yield.

4–5. *O*-アシル化アズラクトンの不斉転位反応

本触媒反応系の利点の一つは、開発したハロゲン結合供与部位を有する高分子と既存の求核触媒を混ぜるだけで、不均一系求核触媒を調製することができる点である。そこで、均一系触媒反応で報告されているキラル求核触媒[12c]を用い、ペンダント型高分子触媒を調製することで、不均一系不斉触媒反応へと展開することにした。キラル求核触媒は、Mandai と Suga により開発された(*S*)-2,6-Dimethoxy-4-(pyridin-4-yl)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine を用いた。尚、本研究は、ナノプラットテクノロジーフォーム「分子・物質合成プラットフォーム支援事業」の支援のもと、岐阜医療科学大学萬代先生と共同研究として実施した。

検討は、得られた高分子触媒 $PDPX_{Mandai}$ および $PDBPX_{Mandai}$ を用い、$PDPX_{DMAP}$ で良い結果を示した触媒量 25 mol ppm、反応温度 60 ℃、反応時間 30 分の条件で行った(**Table 4-5**)。その結果、反応は円滑に進行し、53%のエナンチオ選択性で転位生成物 **27a** が得られた(entry 1)。次に、50 ℃や 30 ℃で反応を行った場合、エナンチオ選択性はわずかに向上した(entries 2, 3)。$PDBPX_{Mandai}$ を用いても、エナンチオ選択性は変化しなかった(entry 4)。高分子鎖は、不斉環境の構築に影響を与えないことが示唆された。

Table 4-5. Asymmetric Acyl Rearrangement Reaction of Azlactones[a]

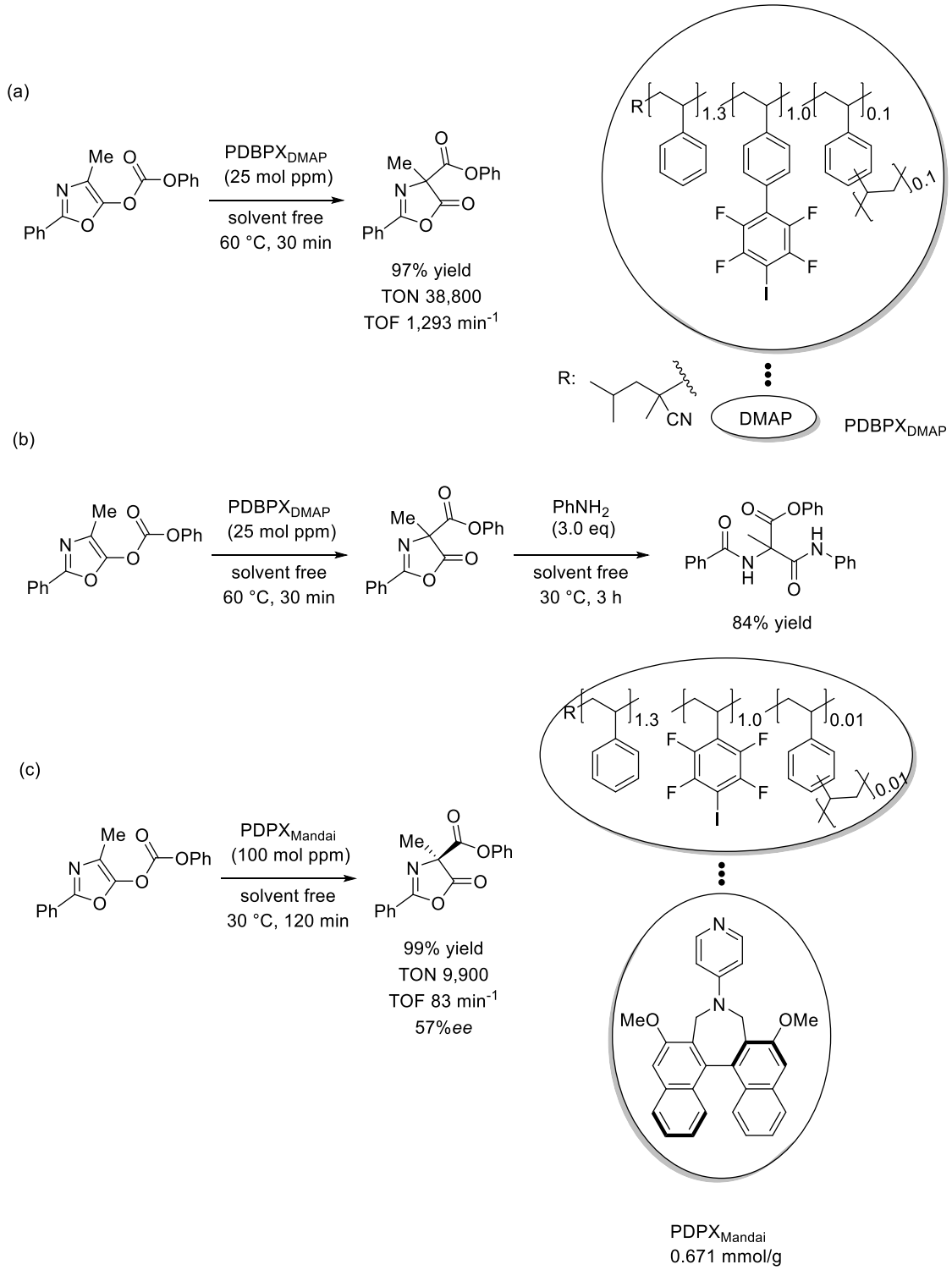


entry	catalyst	(mol ppm)	temp. (℃)	time (min)	yield[b] (%)	TON	TOF (min^{-1})	ee[c] (%)
1	$PDPX_{mandai}$	(25)	60	30	95	38,000	1,267	53
2	$PDPX_{mandai}$	(50)	50	70	94	37,600	537	55
3	$PDPX_{mandai}$	(100)	30	120	99	9,900	83	57
4	$PDBPX_{mandai}$	(100)	30	240	>99	10,000	42	57

[a] Reactions were performed using **26a** and catalyst. [b] Yields were determined by ^{1}H NMR. [c] Ee was determined by HPLC.

4−6. まとめ

第 4 章では、DMAP ペンダント型高分子触媒 $PDPX_{DMAP}$ や $PDBPX_{DMAP}$ を用いる無溶媒でのアズラクトンのアシル基転位反応の開発について述べた(**Scheme 4-6a**)。0.1 もしくは 0.01 当量のジビニルベンゼンから合成した $PDPX_{DMAP}$ や $PDBPX_{DMAP}$ が高い触媒活性を有し、ppm レベルの触媒量でアズラクトンのアシル基転位生成物を与えることを見出した。さらに、開発した無溶媒不均一系触媒反応は、広範な基質適用範囲を示した。また、生成した *C*-アシルアズラクトンにアニリンを加えることで、4 置換 α-アミノ酸誘導体の合成に成功した(**Scheme 4-6b**)。不斉触媒反応への展開においては、中程度のエナンチオ選択性の獲得に成功した(**Scheme 4-6c**)。



Scheme 4-6. Representative Results for Rearrangement Reaction of *O*-Acyl Azlactones

引用文献

[1] Sheldon, R. A. “Organic synthesis; past, present and future”, Chem. Ind. (London), 1992, 903−906.

[2] (a) Metzger, J. O. Solvent-Free Organic Syntheses. *Angew. Chem. Int. Ed.* **1998**, *37*, 2975−2978. (b) Tanaka, K.; Toda, F. Solvent-Free Organic Synthesis. *Chem. Rev.* **2000***, 100,* 1025−1074.

[3] (a) Fortenberry, D. I.; Pojman, J. A. Solvent-Free Synthesis of Polyacrylamide by Frontal Polymerization. *J. Polym. Sci. Part A: Polym. Chem*. **2000**, *38*, 1129–1135. (b) Wang, Y.; Teng, X.; Wang, J. -S.; Yang, H. Solvent-Free Atom Transfer Radical Polymerization in the Synthesis of Fe_2O_3@Polystyrene Core−Shell Nanoparticles. *Nano Lett.* **2003**, *3*, 789−793. (c) Mahapatro, A.; Kumar, A.; Kalra, B.; Gross, R. A. Solvent-Free Adipic Acid/1,8-Octanediol Condensation Polymerizations Catalyzed by Candida antartica Lipase B. *Macromolecules* **2004**, *37*, 35−40. (d) Chmura, A. J.; Davidson, M. G.; Frankis, C. J.; Jones, M. D.; Lunn, M. D. Highly Active and Stereoselective Zirconium and Hafnium Alkoxide Initiators for Solvent-Free Ring-Opening Polymerization of *rac*-Lactide. *Chem. Commun*. **2008**, 1293–1295.

[4] (a) Metzger, J. O.; Mahler, R. Radical Additions of Activated Haloalkanes to Alkenes Initiated by Electron Transfer from Copper in Solvent-Free Systems. *Angew. Chem., Int. Ed.* **1995**, *34*, 902–904. (b) Metzger, J. O.; Mahler, R.; Francke, G. Radical Additions of Alkyl 2-Haloalkanoates and 2-Haloalkanenitriles to Alkenes Initiated by Electron Transfer from Copper in Solvent-Free Systems. *Liebigs Ann. Recl.I* **1997**, 2303–2313. (c) Biermann, U.; Metzger, J. O. Catalytic C,C-Bond Forming Additions to Unsaturated Fatty Compounds. *Top. Catal.* **2004**, *27*, 119–130.

[5] (a) Peng, J.; Deng, Y. Ionic Liquids Catalyzed Biginelli Reaction under Solvent-Free Conditions. *Tetrahedron Lett.* **2001**, *42*, 5917–5919. (b) Huang, J.; Jiang, T.; Gao, H.; Han, B.; Liu, Z.; Wu, W.; Chang, Y.; Zhao, G. Pd Nanoparticles Immobilized on Molecular Sieves by Ionic Liquids: Heterogeneous Catalysts for Solvent-Free Hydrogenation. *Angew. Chem., Int. Ed.* **2004**, *43*, 1397–1399. (c) Ji, S. J.; Jiang, Z. Q.; Lu, J.; Loh, T. P. Facile Ionic Liquids-Promoted One-Pot Synthesis of Polyhydroquinoline Derivatives under Solvent Free Conditions. *Synlett* **2004**, 831–835.

[6] (a) Schaak, R. E.; Mallouk, T. E. Perovskites by Design: A Toolbox of Solid-State Reactions. *Chem. Mater.* **2002**, *14*, 1455–1471. (b) Kaupp, G. Organic Solid-State Reactions with 100% Yield. *Top Curr Chem* **2005**, 25*4*, 95**–**183. (c) Biradha, K.; Santra, R. Crystal Engineering of Topochemical Solid State Reactions. *Chem. Soc. Rev.* **2013***, 42,* 950–967.

[7] (a) Feng, Y.; Liang, H.; Yang, Z.; Yuan, T.; Luo, Y.; Li, P.; Yang, Z.; Zhang, C. A Solvent-Free and Scalable Method To Prepare Soybean-Oil-Based Polyols by Thiol−Ene Photo-Click Reaction and Biobased Polyurethanes Therefrom. *ACS Sustainable Chem. Eng.* **2017**, *5*, 7365–7373. (b) Ghosh, A.; Nakanishi, T. Frontiers of Solvent-Free Functional Molecular Liquids. *Chem. Commun.* **2017**, *53*, 10344**–**10357. (c) Honda, S.; Toyota, T. Photo-Triggered Solvent-Free Metamorphosis of Polymeric Materials. *Nat. Commun.* **2017***, 8,* 502.

[8] Walsh, P. J.; Li, H.; Anaya, C.; de Parrodi, C. A.; A Green Chemistry Approach to Asymmetric Catalysis: Solvent-Free and Highly Concentrated Reactions. *Chem. Rev.* **2007***, 107,* 2503−2545.

[9] (a) Friščić, T.; Mottillo, C.; Titi, H. M. Mechanochemistry for Synthesis. *Angew. Chem. Int. Ed.* **2020**, *59*, 1018−1029. (b) Cuccu, F.; De Luca, L.; Delogu, F.; Colacino, E.; Solin, N.; Mocci, R.; Porcheddu, A. Mechanochemistry: New Tools to Navigate the Uncharted Territory of "Impossible" Reactions. *ChemSusChem* **2022***, 15,* e202200362.

[10] (a) Steglich, W.; Höfle, G. 5-Acyloxyoxazoles and their Rearrangement to 4-Acyloxazol-5-ones. *Angew. Chem. Int. Ed.* **1968**, *7*, 61. (b) Steglich, W.; Höfle, G. *N,N*-Dimethyl-4-pyridinamine, a Very Effective Acylation Catalyst. *Angew. Chem. Int. Ed.* **1969**, *8*, 981.

[11] (a) Obrecht, D.; Bohdal, U.; Broger, C.; Bur, D.; Lehmann, C.; Ruffieux, R; Schönholzer, P.; Müller, K. L-Phenylalanine Cyclohexylamide: A Simple and Convenient Auxiliary for the Synthesis of Optically Pure α,α-Disubstituted (*R*)- and (*S*)-Amino Acids *Helv. Chim. Acta* **1995**, *78*, 563−580. (b) Obrecht, D.; Abrecht, C.; Altorfer, M.; Bohdal, U.; Grieder, A.; Kleber, M.; Pfyffer, P.; Müller, K. Synthesis, Conformational Properties, and Synthetic Applications of Novel Optically Pure α,α-Disubstituted (*R*)- and (*S*)-Glycines ('α-Chimeras') Combining Side Chains of Asp, Glu, Leu, Phe, Ser, and Val. *Helv. Chim. Acta* **1996**, *79*, 1315−1337.

[12] (a) Ruble, J. C.; Fu, G. C. Enantioselective Construction of Quaternary Stereocenters: Rearrangements of *O*-Acylated Azlactones Catalyzed by a Planar-Chiral Derivative of 4-(Pyrrolidino)pyridine. *J. Am. Chem. Soc.* **1998**, *120*, 11532−11533. (b) Shaw, S. A.; Aleman, P.; Christy, J.; Kampf, J. W.; Va, P.; Vedejs, E. Enantioselective TADMAP-Catalyzed Carboxyl Migration Reactions for the Synthesis of Stereogenic Quaternary Carbon. *J. Am. Chem. Soc.* **2006**, *128*, 925−934. (c) Mandai, H.; Fujii, K.; Yasuhara, H.; Abe, K.; Mitsudo, K.; Korenaga, T.; Suga, S. Enantioselective Acyl Transfer Catalysis by a Combination of Common Catalytic Motifs and Electrostatic Interactions. *Angew. Chem. Int. Ed. Nat. Commun.* **2016**, *7*, 11297.

[13] Yamamoto, T.; Murakami, R.; Suginome, M. Single-Handed Helical Poly(quinoxaline-2,3-diyl)s Bearing Achiral 4-Aminopyrid-3-yl Pendants as Highly Enantioselective, Reusable Chiral Nucleophilic Organocatalysts in the Steglich Reaction. *J. Am. Chem. Soc.* **2017**, *139*, 2557–2560.

[14] Vanderkooy, A.; Pfefferkorn, P.; Taylor, M. S. Self-Assembly of Polymer Nanostructures through Halogen Bonding Interactions of an Iodoperfluoroarene-Functionalized Polystyrene Derivative. *Macromolecules* **2017**, *50*, 3807–3817.

実験項

1. General information

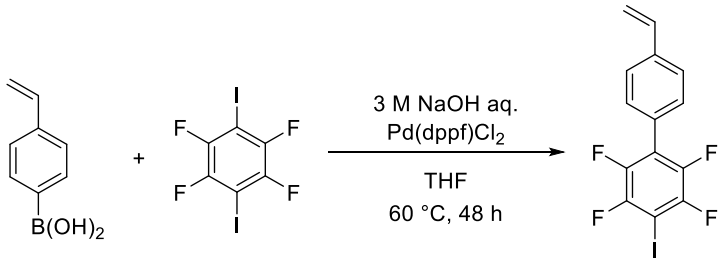
Unless otherwise noted, all reactions were carried out under an atmosphere of standard grade nitrogen gas (oxygen <10 ppm) in flame-dried glassware with magnetic stirring. ^{1}H NMR spectra were recorded on a JEOL ECS-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: referenced to TMS 0.00 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL ECS-400 (100 MHz) spectrometer with complete proton decoupling or fluorine decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). ^{19}F NMR spectra were recorded on a JEOL ECS-400 (376 MHz) spectrometer. Chemical shifts are reported in ppm from α,α,α-trifluorotoluene as the external standard (–63.72 ppm). High-performance liquid chromatography (HPLC) was performed on a Jasco HPLC-2000 system equipped with a variable wavelength detector using YMC-Pack SIL-06 column from YMC. Elemental analysis of H, C, and N was performed on J-SCIENCE LAB MICRO CORDER JM10 at the Instrument Center, Institute for Molecular Science. Elemental analysis of F, I, and Cl in addition to H, C, and N was performed on XS-2100H at Organic Elemental Microanalysis Center, Kyoto University. SEM images were obtained using Hitachi High-Tech SU6600 and EDS mapping were measured using BrukerAXS QUANTAX XFlash 5060FQ and XFlash6|10. Infrared (IR) spectra were recorded on a Jasco FT/IR-460plus spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 instrument (double-focusing magnetic sector mass analyzer: EB) using fast atom bombardment (FAB) as the ionization method and 3-nitrobenzyl alcohol as the matrix at the Instrument Center of the Institute for Molecular Science.

Purification of reaction products was carried out by flash column chromatography using silica gel 60 N (Merck: 0.040-0.063 mm). Dichloromethane (CH_2Cl_2), diethyl ether (Et_2O) and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were supplied from FUJIFILM Wako Pure Chemical Corporation. as dehydrated solvents. Other reagents were used without further purification.

2. Preparation of DMAP-pendant XB polymers

Synthesis of BPX (n = 0.1)

Synthesis of 4′-ethenyl-2,3,5,6-tetrafluoro-4-iodo-1,1′-biphenyl (28)

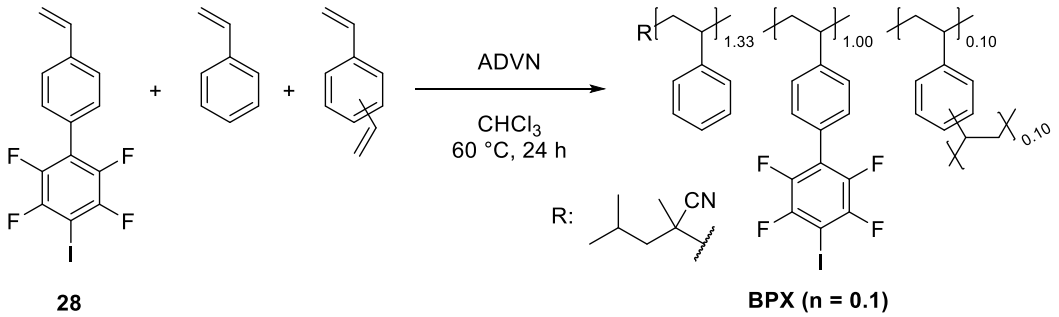


28

To a 500-mL flame-dried three-necked flask was charged 4-vinylphenylboronic acid (1.47 g, 10.0 mmol, 1.0 equiv.), tetrafluoro-1,4-diiodobenzene (4.01 g, 10.0 mmol, 1.0 eq), and $Pd(dppf)Cl_2$ (118 mg, 0.145 mmol, 0.015 equiv.). The flask was evacuated and refilled with nitrogen 3 times. 200 mL of dry THF was added to the solid starting materials. After stirring for 5 min to this was added 1.24 mL of a 3 M aqueous solution of sodium hydroxide (30.0 mmol, 3.0 equiv) which had been previously degassed with a stream of argon. The mixture was heated and stirred at 60 °C for 48 hours. The reaction mixture was filtered through the short-plug silica gel column chromatography (THF/hexane = 1:1 as eluent), then purified by silica gel column chromatography (hexane/CH_2Cl_2 = 10:1) to afford 4′-ethenyl-2,3,5,6-tetrafluoro-4-iodo-1,1′-biphenyl **28** (2.00 g, 5.29 mmol, 53% yield) as a white solid. Spectral data are in agreement with the literature.[S11]

Rf = 0.40 (hexane)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55-7.52 (m, 2H), 7.44-7.42 (m, 2H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.85 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.36 (dd, *J* = 10.9, 0.8 Hz, 1H) ^{19}F NMR ($CDCl_3$, 376 MHz) δ –121.9-–122.0 (m, 2F), –142.6-–142.7 (m, 2F).

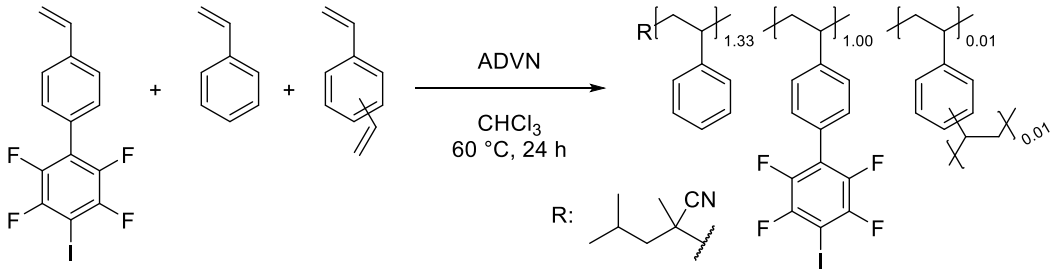


28 **BPX (n = 0.1)**

To a solution of 4′-ethenyl-2,3,5,6-tetrafluoro-4-iodo-1,1′-biphenyl **28** (378 mg, 1.00 mmol, 1.0 equiv.) in $CHCl_3$ (1.4 mL) was added styrene (150 μL, 1.33 mmol, 1.3 equiv.), and divinylbenzene (14 μL, 0.10 mmol, 0.1 equiv.) at room temperature. The reaction mixture was degassed by

Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (74.5 mg, 0.30 mmol, 0.30 equiv.) was added to the mixture, and the reaction mixture was stirred at 60 ºC for 24 h. After the cooling to room temperature, the solvent was removed under vacuo. The residue was transferred to mortar while washing with hexane (8 mL) then the suspension was ground and filtered. The residue was washed with hexane (2 mL) and EtOH (2 mL), then dried under vacuo to afford **BPX (n = 0.1)** as a yellow solid (302 mg, 57% yield, [-C_6F_4I]: 1.59 mmol/g). elemental analysis calcd (%) for $C_{25.64}H_{18.64}N_{0.3}F_4I$: C 58.14, H 3.55, N 1.40, F 14.35, I 23.96, found: C 60.25, H 4.25, N 1.29, F 12.20, I 20.10.

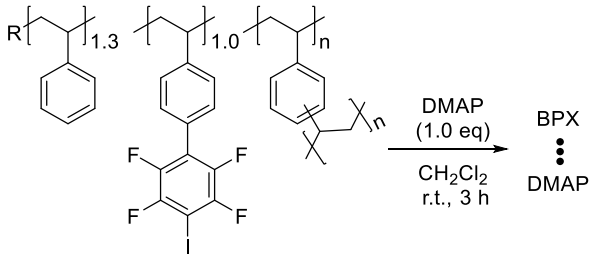
Synthesis of BPX (n = 0.01)



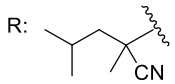
28 **BPX (n = 0.01)**

To a solution of 4′-ethenyl-2,3,5,6-tetrafluoro-4-iodo-1,1′-biphenyl **28** (378 mg, 1.00 mmol, 1.0 equiv.) in $CHCl_3$ (0.70 mL) was added styrene (150 μL, 1.33 mmol, 1.3 equiv.), and divinylbenzene (1.4 μL, 0.01 mmol, 0.01 equiv.) at room temperature. The reaction mixture was degassed by Freeze-Pump-Thaw (4 cycle). Then 2,2'-azobis(2,4-dimethylvaleronitrile) (74.5 mg, 0.30 mmol, 0.30 equiv.) was added to the mixture, and the reaction mixture was stirred at 60 ºC for 24 h. After the cooling to room temperature, the solvent was removed under vacuo. The residue was transferred to mortar while washing with hexane (8 mL) then the suspension was ground and filtered. The residue was washed with hexane (2 mL) and EtOH (2 mL), then dried under vacuo to afford **BPX (n = 0.01)** as a yellow solid (359 mg, 69% yield, [-C_6F_4I]: 1.63 mmol/g). elemental analysis calcd (%) for $C_{24.74}H_{17.74}N_{0.3}F_4I$: C 57.37, H 3.45, N 1.35, F 14.67, I 24.50, found: C 60.22, H 4.22, N 1.18, F 12.46, I 20.70.

Preparation of $PDBPX_{DMAP}$ (n = 0.1)

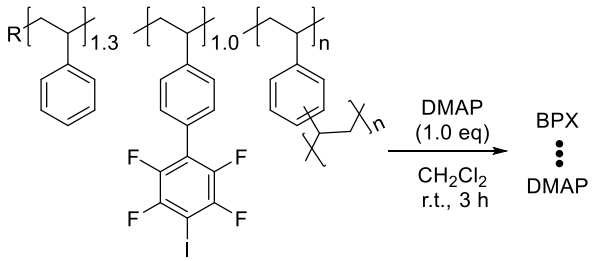


BPX n = 0.1, I...1.59 mmol/g **PDBPX$_{DMAP}$ n = 0.1**, 1.39 mmol/g

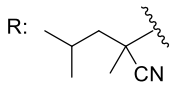


To a solution of **BPX (n = 0.1)** (100 mg, [-C_6F_4I]: 1.59 mmol/g) in CH_2Cl_2 (2 mL) was added DMAP (19.4 mg, 0.159 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure to afford **PDBPX$_{DMAP}$ (n = 0.1)** as a yellow solid (59.6 mg, [DMAP]: 1.39 mmol/g). elemental analysis calcd (%) for $C_{32.64}H_{28.64}N_{2.3}F_4I$: C 59.76, H 4.40, N 6.10, found: C 62.00, H 5.07, N 4.48.

Preparation of PDBPX$_{DMAP}$ (n = 0.01)



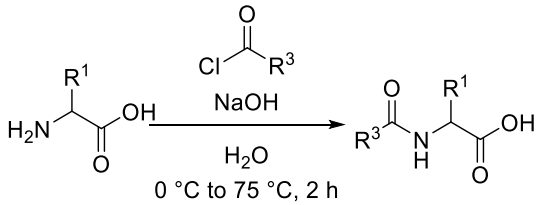
BPX n = 0.01, I...1.63 mmol/g **PDBPX$_{DMAP}$ n = 0.01**, 1.30 mmol/g



To a solution of **BPX (n = 0.01)** (92.0 mg, [-C_6F_4I]: 1.63 mmol/g) in CH_2Cl_2 (2 mL) was added DMAP (18.3 mg, 0.150 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure to afford **PDBPX$_{DMAP}$ (n = 0.01)** as a yellow solid (59.0 mg, [DMAP]: 1.30 mmol/g). elemental analysis calcd (%) for $C_{31.74}H_{27.74}N_{2.3}F_4I$: C 59.17, H 4.34, N 6.18, found: C 61.67, H 4.98, N 4.81.

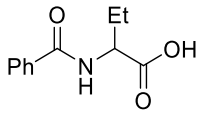
3. Synthesis of *N*-acyl aminoacids

General procedure:



To a solution of NaOH (1.68 g, 42.0 mmol, 2.1 equiv.) and amino acid (20.0 mmol, 1.0 equiv.) in H_2O (40.0 mL) at 0 ºC was added acyl chloride (22.0 mmol, 1.1 equiv.). The reaction mixture was warmed to 75 ºC and stirred for 2 h. The reaction mixture was cooled to 0 ºC and acidified with 2 M HCl (20 mL). The resulting suspension was filtered. The residue was washed with H_2O (100 mL) then dried under vacuo to afford *N*-protected amino acid as a white solid. The obtained product was used in the next step without further purification.

2-(Phenylcarbamoyl)butanoic acid (S12)[S12a]



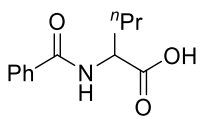
S12

General procedure was followed using DL-2-aminobutyric acid (2.06 g, 20.0 mmol, 1.0 equiv.), benzoyl chloride (2.54 mL, 22.0 mmol, 1.1 equiv.), sodium hydroxide (1.76 g, 44.0 mmol, 2.2 equiv.), and H_2O (40 mL) to afford 2-(phenylcarbamoyl)butanoic acid (**S12**) as a white solid.

Rf = 0.39 (CH_2Cl_2/MeOH = 9:1)

^{1}H NMR (MeOH d_4, 400 MHz) δ 7.86 (d, 2H, *J* = 7.3 Hz), 7.56 (t, 1H, *J* = 7.3 Hz), 7.44 (t, 2H, *J* = 7.3 Hz), 4.48 (q, 1H, *J* = 6.5 Hz), 2.07 (dq, 1H, *J* = 14.3, 6.9 Hz), 1.80 (dq, 1H, *J* = 14.3, 7.1 Hz), 1.03 (t, 3H, *J* = 7.4 Hz).

2-(Phenylcarbamoyl)pentanoic acid (S13)[S12b, S12c, S12d, S12e]



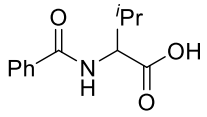
S13

General procedure was followed using DL-norvaline (2.34 g, 20.0 mmol, 1.0 equiv.), benzoyl chloride (2.54 mL, 22.0 mmol, 1.1 equiv.), sodium hydroxide (1.76 g, 44.0 mmol, 2.2 equiv.), and H_2O (40 mL) to afford 2-(phenylcarbamoyl)pentanoic acid (**S13**) as a white solid.

Rf = 0.21 (CH_2Cl_2/MeOH = 9:1)

^{1}H NMR (DMSO d_6, 400 MHz) δ 8.56 (d, 1H, *J* = 7.8 Hz), 7.90-7.87 (m, 2H), 7.56-7.46 (m, 3H), 4.38 (q, 1H, *J* = 7.5 Hz), 1.78 (q, 2H, *J* = 8.1 Hz), 1.50-1.29 (m, 2H), 0.90 (t, 3H, *J* = 7.2 Hz).

3-Methyl-2-(phenylcarbamoyl)butanoic acid (S14)[S12a]



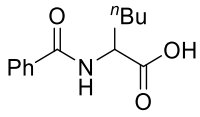
S14

General procedure was followed using DL-valine (5.86 g, 50.0 mmol, 1.0 equiv.), benzoyl chloride (6.34 mL, 55.0 mmol, 1.1 equiv.), sodium hydroxide (4.40 g, 110 mmol, 2.0 equiv.), and H_2O (100 mL) to afford 3-methyl-2-(phenylcarbamoyl)butanoic acid (**S14**) as a white solid.

Rf = 0.51 (CH_2Cl_2/MeOH = 9:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, 1H, *J* = 8.3 Hz), 7.80 (d, 2H, *J* = 7.2 Hz), 7.52 (t, 1H, *J* = 7.2 Hz), 7.47 (t, 2H, *J* = 7.2 Hz), 4.78 (dd, 1H, *J* = 8.3, 4.8 Hz), 2.41-2.30 (m, 1H), 1.05 (d, 3H, *J* = 7.1 Hz), 1.03 (d, 3H, *J* = 7.1 Hz).

2-(Phenylcarbamoyl)hexanoic acid (S15)[S12f]



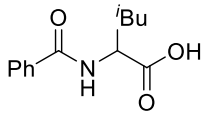
S15

General procedure was followed using DL-norleucine (6.56 g, 50.0 mmol, 1.0 equiv.), benzoyl chloride (6.34 mL, 55.0 mmol, 1.1 equiv.), sodium hydroxide (4.40 g, 110 mmol, 2.0 equiv.), and H_2O (100 mL) to afford 2-(phenylcarbamoyl)hexanoic acid (**S15**) as a white solid.

Rf = 0.32 (CH_2Cl_2/MeOH = 9:1)

^{1}H NMR (DMSO d_6, 400 MHz) δ 8.58 (d, 1H, *J* = 7.8 Hz), 7.89 (d, 2H, *J* = 6.9 Hz), 7.54-7.46 (m, 3H), 4.38-4.32 (m, 1H), 1.81-1.78 (m, 2H), 1.32-1.29 (m, 4H), 0.87 (t, 3H, *J* = 7.1 Hz).

4-Methyl-2-(phenylcarbamoyl)pentanoic acid (S16)[S12a]



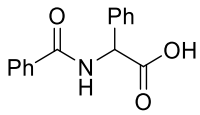
S16

General procedure was followed using DL-isoleucine (6.56 g, 50.0 mmol, 1.0 equiv.), benzoyl chloride (6.34 mL, 55.0 mmol, 1.1 equiv.), sodium hydroxide (4.40 g, 110 mmol, 2.0 equiv.), and H_2O (100 mL) to afford 4-methyl-2-(phenylcarbamoyl)pentanoic acid (**S16**) as a white solid.

Rf = 0.42 (CH_2Cl_2/MeOH = 9:1)

^{1}H NMR (MeOH d_4, 400 MHz) δ 7.86 (d, 2H, *J* = 7.0 Hz), 7.52 (t, 1H, *J* = 7.4 Hz), 7.44 (dd, 2H, *J* = 7.4, 7.0 Hz), 4.69 (dd, 1H, *J* = 10.0, 4.6 Hz), 1.88-1.69 (m, 3H), 0.99 (d, 3H, *J* = 6.2 Hz), 0.97 (d, 3H, *J* = 6.2 Hz).

2-Phenyl-2-(phenylcarbamoyl)acetic acid (S17)[S12a]



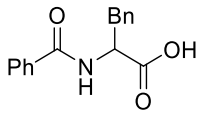
S17

General procedure was followed using DL-2-phenylglycine (7.56 g, 50.0 mmol, 1.0 equiv.), benzoyl chloride (6.34 mL, 55.0 mmol, 1.1 equiv.), sodium hydroxide (4.40 g, 110 mmol, 2.0 equiv.), and H_2O (100 mL) to afford 2-phenyl-2-(phenylcarbamoyl)acetic acid (**S17**) as a white solid.

Rf = 0.17 (CH_2Cl_2/MeOH = 7:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.60 (s, 1H), 7.92 (d, 2H, *J* = 7.3 Hz), 7.88-7.78 (m, 2H), 7.60-7.33 (m, 9H), 5.78 (s, 1H).

3-Phenyl-2-(phenylcarbamoyl)propanoic acid (S18)[S12a]



S18

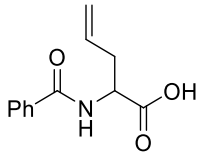
General procedure was followed using DL-phenylalanine (8.04 g, 48.7 mmol, 1.0 equiv.), 4-methyl chloroformate (6.17 mL, 53.5 mmol, 1.1 equiv.), sodium hydroxide (4.40 g, 110 mmol,

2.3 equiv.), and H_2O (100 mL) to afford 3-phenyl-2-(phenylcarbamoyl)propanoic acid (**S18**) as a white solid.

Rf = 0.20 (CH_2Cl_2/MeOH = 9:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71-7.16 (m, 10H), 6.70 (d, 1H, *J* = 7.3 Hz), 5.08 (dt, 1H, *J* = 7.3, 5.6 Hz), 3.37 (dd, 1H, *J* = 13.9, 5.6 Hz), 3.26 (dd, 1H, *J* = 13.9, 5.6 Hz).

2-(Phenylcarbamoyl)-4-pentenoic acid (S19)[S12h]



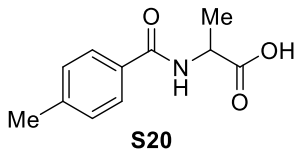
S19

General procedure was followed using DL-2-allylglycine (2.30 g, 20.0 mmol, 1.0 equiv.), benzoyl chloride (2.54 mL, 22.0 mmol, 1.1 equiv.), sodium hydroxide (1.76 g, 44.0 mmol, 2.0 equiv.), and H_2O (40 mL) to afford 2-(phenylcarbamoyl)-4-pentenoic acid (**S19**) as a white solid.

Rf = 0.29 (CH_2Cl_2/MeOH = 9:1)

^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.54 (d, 1H, *J* = 7.8 Hz), 7.79 (d, 2H, *J* = 7.1 Hz), 7.49-7.35 (m, 3H), 5.88-5.78 (m, 1H), 4.98 (dd, 2H, *J* = 25.4, 15.3 Hz), 4.48-4.42 (m, 1H), 2.64-2.53 (m, 1H).

2-[(4-Methylphenyl)carbamoyl]propanoic acid (S20)[S12i]



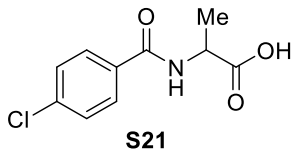
S20

General procedure was followed using DL-alanine (4.45 g, 50.0 mmol, 1.0 equiv.), 4-methylbenzoyl chloride (7.50 mL, 55.0 mmol, 1.1 equiv.), sodium hydroxide (4.40 g, 110 mmol, 2.2 equiv.), and H_2O (100 mL) to afford 2-[(4-methylphenyl)carbamoyl]propanoic acid (**S2**) as a white solid.

Rf = 0.31 (CH_2Cl_2/MeOH = 9:1)

^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.58 (d, 1H, *J* = 7.1 Hz), 7.84-7.78 (m, 2H), 7.31-7.27 (m, 2H), 4.43-4.36 (m, 1H), 2.36 (s, 3H), 1.38 (d, 3H, *J* = 7.3 Hz).

2-[(4-Chlorophenyl)carbamoyl]propanoic acid (S21)[S12j]



S21

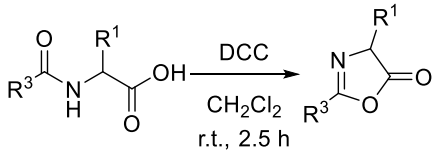
General procedure was followed using DL-alanine (4.45 g, 50.0 mmol, 1.0 equiv.), 4-chlorobenzoyl chloride (7.03 mL, 55.0 mmol, 1.1 equiv.), sodium hydroxide (4.40 g, 110 mmol, 2.2 equiv.), and H_2O (100 mL) to afford 2-[(4-chlorophenyl)carbamoyl]propanoic acid (**S21**) as a white solid.

Rf = 0.22 (CH_2Cl_2/MeOH = 7:1)

^{1}H NMR (DMSO d_6, 400 MHz) δ 8.78 (d, 1H, *J* = 7.1 Hz), 7.95-7.90 (m, 2H), 7.58-7.55 (m, 2H), 4.41 (q, 1H, *J* = 7.3 Hz), 3.44 (d, 3H, *J* = 7.6 Hz).

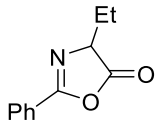
4. Synthesis of azlactones

General Procedure:



To a solution of *N*-protected amino acid (20.0 mmol, 1.0 equiv.) in CH_2Cl_2 (40 mL) was added DCC (4.13 g, 20.0 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 2.5 h. The resulting suspension was filtered by celite then the residue was washed with diethyl ether (25 mL). The filtrate was concentrated under reduced pressure to afford an azlactone as a crude product. The crude product was used in next step without further purification.

4-Ethyl-2-phenyloxazol-5(4*H*)-one (S22)[S12h]



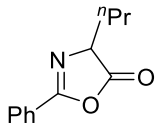
S22

General procedure was followed using **S12** (8.29 g, 40.0 mmol, 1.0 equiv.), DCC (8.26 g, 40.0 mmol, 1.0 equiv.), and dichloromethane (80 mL) to afford 2-phenyl-4-ethyloxazolone (**S22**) as a white solid.

Rf = 0.35 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, 2H, *J* = 7.1 Hz), 7.58 (t, 1H, *J* = 7.3 Hz), 7.49 (t, 2H, *J* = 7.8 Hz), 4.40 (t, 1H, *J* = 6.1 Hz), 2.14-1.90 (m, 2H), 1.06 (t, 3H, *J* = 7.6 Hz).

2-Phenyl-4-propyloxazol-5(4*H*)-one (S23)[S12k]



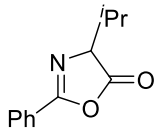
S23

General procedure was followed using **S13** (3.79 g, 11.7 mmol, 1.0 equiv.), DCC (2.42 g, 11.7 mmol, 1.0 equiv.), and dichloromethane (23 mL) to afford 2-phenyl-4-propyloxazolone (**S23**) as a white solid.

Rf = 0.35 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, 2H, *J* = 7.6 Hz), 7.65-7.47 (m, 3H), 7.49 (t, 2H, *J* = 7.8 Hz), 4.42 (dd, 1H, *J* = 5.7, 1.4 Hz), 1.59-1.43 (m, 2H), 1.37-1.21 (m, 2H), 0.99 (t, 3H, *J* = 7.3 Hz).

4-Isopropyl-2-phenyloxazol-5(4*H*)-one (S24)[S12g]



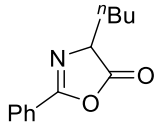
S24

General procedure was followed using **S14** (4.43 g, 20.0 mmol, 1.0 equiv.), DCC (4.13 g, 20.0 mmol, 1.0 equiv.), and dichloromethane (40 mL) to afford 4-isopropyl-2-phenyloxazolone (**S24**) as a white solid.

Rf = 0.44 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, 2H, *J* = 7.3 Hz), 7.58 (t, 1H, *J* = 7.6 Hz), 7.49 (t, 2H, *J* = 7.6 Hz), 4.30 (d, 1H, *J* = 4.6 Hz), 2.45-2.34 (m, 1H), 1.15 (d, 3H, *J* = 6.9 Hz), 1.02 (d, 3H, *J* = 6.9 Hz).

4-Butyl-2-phenyloxazol-5(4*H*)-one (S25)[S12l]



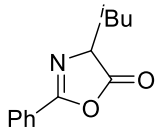
S25

General procedure was followed using **S15** (4.71 g, 20.0 mmol, 1.0 equiv.), DCC (4.13 g, 20.0 mmol, 1.0 equiv.), and dichloromethane (40 mL) to afford 4-butyl-2-phenyloxazolone (**S25**) as a white solid.

Rf = 0.41 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, 2H, *J* = 7.3 Hz), 7.60-7.47 (m, 3H), 4.42 (t, 1H, *J* = 6.9 Hz), 2.08-1.84 (m, 2H), 1.53-1.34 (m, 4H), 0.92 (t, 3H, *J* = 7.1 Hz).

4-Isobutyl-2-phenyloxazol-5(4*H*)-one (S26) [S12g]



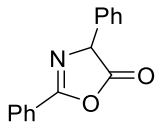
S26

General procedure was followed using **S16** (3.57 g, 15.2 mmol, 1.0 equiv.), DCC (3.13 g, 15.2 mmol, 1.0 equiv.), and dichloromethane (30 mL) to afford 4-isobutyl-2-phenyloxazolone (**S26**) as a white solid.

Rf = 0.49 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, 2H, *J* = 7.3 Hz), 7.59-7.47 (m, 3H), 4.42 (dd, 1H, *J* = 5.7, 3.2 Hz), 2.12-1.65 (m, 3H), 1.02 (dd, 6H, *J* = 6.6, 3.0 Hz).

2,4-Diphenyloxazol-5(4*H*)-one (S27)[S12m]



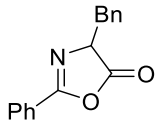
S27

General procedure was followed using **S17** (5.10 g, 20.0 mmol, 1.0 equiv.), DCC (4.13 g, 20.0 mmol, 1.0 equiv.), and dichloromethane (40 mL) to afford 2,4-diphenyloxazolone (**S27**) as a white solid.

Rf = 0.47 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, 2H, *J* = 7.3 Hz), 7.64-7.36 (m, 8H), 5.53 (s, 1H).

4-Benzyl-2-phenyloxazol-5(4*H*)-one (S28)[S12g]



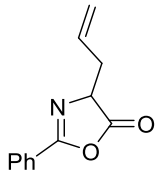
S28

General procedure was followed using **S18** (10.8 g, 40.0 mmol, 1.0 equiv.), DCC (8.26 g, 40.0 mmol, 1.0 equiv.), and dichloromethane (80 mL) to afford 4-benzyl-2-phenyloxazolone (**S28**) as a white solid.

Rf = 0.42 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94-7.90 (m, 2H), 7.58-7.52 (m, 1H), 7.48-7.42 (m, 2H), 7.28-7.18 (m, 5H), 4.70 (dd, 1H, *J* = 6.7, 4.9 Hz), 3.38 (dd, 1H, *J* = 13.9, 4.9 Hz), 3.19 (dd, 1H, *J* = 14.0, 6.7 Hz).

2-Phenyloxazol-4-(2-propenyl)-5(4*H*)-one (S29)[S12m]



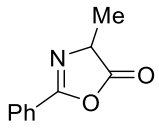
S29

General procedure was followed using **S19** (2.45 g, 11.2 mmol, 1.0 equiv.), DCC (2.31 g, 11.2 mmol, 1.0 equiv.), and dichloromethane (22 mL) to afford 4-allyl-2-phenyloxazolone (**S29**) as a white solid.

Rf = 0.51 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01-8.00 (m, 2H), 7.60-7.47 (m, 3H), 5.85-5.75 (m, 1H), 5.28-5.16 (m, 2H), 4.51 (t, 1H, *J* = 5.7 Hz), 2.86-2.79 (m, 1H), 2.69-2.62 (m, 1H).

4-Methyl-2-phenyloxazol-5(4*H*)-one (S30)[S12m]



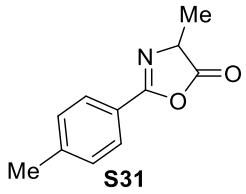
S30

General procedure was followed using benzoyl DL-alanine (3.86 g, 20.0 mmol, 1.0 equiv.), DCC (4.13 g, 20.0 mmol, 1.0 equiv.), and dichloromethane (40 mL) to afford 4-methyl-2-phenyloxazolone (**S30**) as a white solid.

Rf = 0.14 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, 2H, *J* = 7.6 Hz), 7.60-7.46 (m, 3H), 4.46 (q, 1H, *J* = 7.6 Hz), 1.60 (d, 3H, *J* = 7.6 Hz).

2-(4-Methylphenyl)-4-methyloxazol-5(4*H*)-one (S31)[S12k]



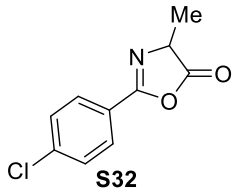
S31

General procedure was followed using **S20** (2.36 g, 11.4 mmol, 1.0 equiv.), DCC (2.35 g, 11.4 mmol, 1.0 equiv.), and dichloromethane (23 mL) to afford 2-(4-methylphenyl)-4-methyloxazolone (**S31**) as a white solid.

Rf = 0.43 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (d, 2H, *J* = 8.2 Hz), 7.28 (t, 3H, *J* = 8.0 Hz), 4.44 (q, 1H, *J* = 7.6 Hz), 2.43 (s, 3H), 1.59 (d, 3H, *J* = 7.6 Hz).

2-(4-Chlorophenyl)-4-methyloxazol-5(4*H*)-one (S32)[S12l]



S32

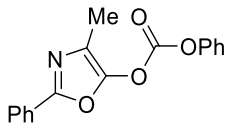
General procedure was followed using **S21** (4.15 g, 20.0 mmol, 1.0 equiv.), DCC (4.13 g, 20.0 mmol, 1.0 equiv.), and dichloromethane (40 mL) to afford 2-(4-chlorophenyl)-4-methyloxazolone (**S32**) as a white solid.

Rf = 0.38 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95-7.92 (m, 2H), 7.49-7.46 (m, 2H), 4.45 (q, 1H, *J* = 7.6 Hz), 1.59 (d, 3H, *J* = 7.6 Hz).

5. Synthesis of *O*-acylated azlactones 26

Phenyl 4-methyl-2-phenyloxazol-5-yl carbonate (26a)



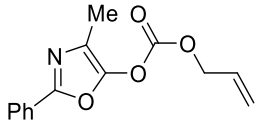
26a

26a was synthesized and characterized according to the literature.[S12l]

Rf = 0.19 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (m, 2H), 7.49-7.46 (m, 5H), 7.35-7.30 (m, 3H), 2.26 (s, 3H).

2-Propenyl 4-methyl-2-phenyloxazol-5-yl carbonate (26m)



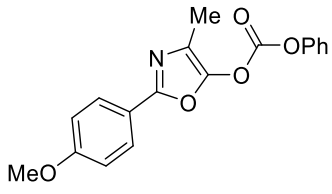
26m

26m was synthesized and characterized according to the literature.[S12m]

Rf = 0.23 (hexane/ethyl acetate = 8:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95-7.92 (m, 2H), 7.43-7.40 (m, 3H), 6.03-5.96 (m, 1H), 5.46 (dd, 1H, *J* = 16.0, 1.0 Hz), 5.38 (dd, 1H, *J* = 10.8, 1.0 Hz), 4.79 (d, 2H, *J* = 6.0 Hz), 2.14 (s, 3H).

Phenyl 2-(4-methoxyphenyl)-4-methyloxazol-5-yl carbonate (26o)



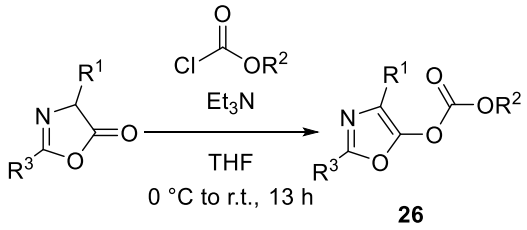
26o

26o was synthesized and characterized according to the literature.[S12n]

Rf = 0.51 (hexane/ethyl acetate = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, 2H, *J* = 8.8 Hz), 7.46-7.43 (m, 2H), 7.33-7.29 (m, 3H), 6.95 (d, 2H, *J* = 8.8 Hz), 3.85 (s, 3H), 2.19 (s, 3H).

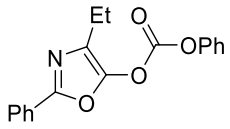
General procedure for *O*-acylated azlactones 26



26

To a solution of azlactone (20.0 mmol, 1.0 equiv.) and triethylamine (22.0 mmol, 1.1 equiv.) in THF (17.5 mL) at 0 ºC was added chloroformate (21.0 mmol, 1.1 equiv.). The reaction mixture was warmed to room temperature and stirred for 13 h. The reaction mixture was quenched with H_2O (20 mL) and extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with 2 M HCl aq. (10 mL), sat. $NaHCO_3$ aq. (10 mL), and brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The residue was purified by silica gel column chromatography (hexane/ethyl acetate/CH_2Cl_2 = 8:2:1 as eluent) to afford *O*-acylated azlactone **26**.

Phenyl 4-ethyl-2-phenyloxazol-5-yl carbonate (26b)



26b

General procedure was followed using **S22** (7.56 g, 40.0 mmol, 1.0 equiv.), phenyl chloroformate (5.30 mL, 42.0 mmol, 1.1 equiv.), triethylamine (6.10 mL, 44.0 mmol, 1.1 equiv.), and THF (35 mL) to afford **26b** as a white solid (1.01 g, 25.1 mmol, 63%).

Rf = 0.43 (hexane/ethyl acetate = 4:1)

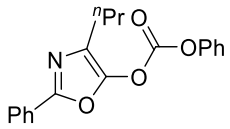
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04-7.93 (m, 2H), 7.51-7.38 (m, 5H), 7.34-7.25 (m, 3H), 2.59 (q, 2H, *J* = 7.6 Hz), 1.30 (t, 3H, *J* = 7.7 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.2, 150.8, 150.4, 145.2, 130.4, 129.9, 128.8, 127.2, 127.0, 126.1, 126.0, 120.6, 18.6, 12.5.

IR (ATR) 3065, 2977, 2934, 2876, 1789, 1666, 1593, 1552, 1496, 1447, 1335, 1227, 1192, 1173, 1083, 1067, 997, 939, 869.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}NO_4$ 310.1074, found 310.1076.

Phenyl 2-phenyl-4-propyloxazol-5-yl carbonate (26c)



26c

General procedure was followed using **S23** (2.38 g, 11.7 mmol, 1.0 equiv.), phenyl chloroformate (1.55 mL, 12.3 mmol, 1.1 equiv.), triethylamine (1.79 mL, 12.9 mmol, 1.1 equiv.), and THF (10 mL) to afford **26c** as a white solid (4.62 g, 12.4 mmol, 31%).

Rf = 0.53 (hexane/ethyl acetate = 4:1)

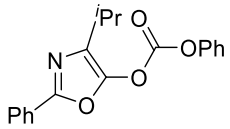
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06-7.89 (m, 2H), 7.53-7.38 (m, 5H), 7.37-7.27 (m, 3H), 2.53 (t, 2H, *J* = 7.6 Hz), 1.75 (td, 2H, *J* = 7.4 Hz), 1.00 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.0, 150.7, 150.2, 145.6, 130.3, 129.8, 128.7, 127.1, 126.8, 125.9, 124.7, 120.5, 26.9, 21.2, 13.8.

IR (ATR) 3069, 2962, 2933, 2873, 1799, 1662, 1591, 1554, 1492, 1449, 1263, 1210, 1186, 1085, 1068, 985, 940.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}NO_4$ 324.1230, found 324.1241.

Phenyl 4-isopropyl-2-phenyloxazol-5-yl carbonate (26d)



26d

General procedure was followed using **S24** (4.06 g, 20.0 mmol, 1.0 equiv.), phenyl chloroformate (2.65 mL, 21.0 mmol, 1.1 equiv.), triethylamine (3.05 mL, 22.0 mmol, 1.1 equiv.), and THF (18 mL) to afford **26d** as a white solid (5.00 g, 15.5 mmol, 77%).

Rf = 0.58 (hexane/ethyl acetate = 4:1)

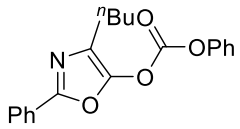
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02-7.92 (m, 2H), 7.48-7.39 (m, 5H), 7.35-7.26 (m, 3H), 3.03-2.86 (m, 1H), 1.33 (d, 6H, *J* = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.9, 150.7, 150.4, 144.1, 130.2, 129.8, 128.7, 127.2, 126.8, 126.7 126.0, 120.5, 25.5, 21.0.

IR (ATR) 3066, 2967, 2933, 2873, 1795, 1654, 1591, 1556, 1485, 1457, 1449, 1207, 1186, 1105, 1068, 1024, 1005, 985, 940, 864.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}NO_4$ 324.1230, found 324.1238.

Phenyl 4-butyl-2-phenyloxazol-5-yl carbonate (26e)



26e

General procedure was followed using **S25** (4.34 g, 20.0 mmol, 1.0 equiv.), phenyl chloroformate (2.65 mL, 21.0 mmol, 1.1 equiv.), triethylamine (3.05 mL, 22.0 mmol, 1.1 equiv.), and THF (18 mL) to afford **26e** as a white solid (5.54 g, 16.4 mmol, 82%).

Rf = 0.41 (hexane/ethyl acetate = 4:1)

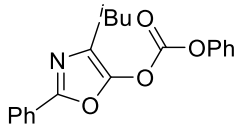
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05-7.91 (m, 2H), 7.52-7.38 (m, 5H), 7.38-7.26 (m, 3H), 2.55 (t, 2H, *J* = 7.6 Hz), 1.88-1.60 (m, 2H), 1.42 (td, 2H, *J* = 7.4 Hz), 1.03-0.88 (m, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 150.7, 150.2, 145.4, 130.3, 129.7, 128.7, 127.1, 126.8, 125.9, 124.9, 120.5, 30.0, 24.6, 22.3, 13.8.

IR (ATR) 3068, 2957, 2931, 2861, 1800, 1717, 1645, 1592, 1526, 1488, 1206, 1182, 1088, 1070, 1025, 984, 870.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}NO_4$ 338.1387, found 338.1400.

Phenyl 4-isobutyl-2-phenyloxazol-5-yl carbonate (26f)



26f

General procedure was followed using **S26** (3.15 g, 14.5 mmol, 1.0 equiv.), phenyl chloroformate (2.02 mL, 16.0 mmol, 1.1 equiv.), triethylamine (2.32 mL, 16.7 mmol, 1.1 equiv.), and THF (13 mL) to afford **26f** as a white solid (2.20 g, 6.52 mmol, 31%).

Rf = 0.54 (hexane/ethyl acetate = 4:1)

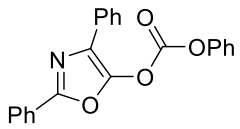
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05-7.93 (m, 2H), 7.51-7.39 (m, 5H), 7.34-7.25 (m, 3H), 2.42 (d, 2H, *J* = 7.1 Hz), 2.19-2.03 (m, 1H), 1.00 (d, 6H, *J* = 6.6 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.0, 150.7, 150.2, 146.1, 130.3, 129.7, 128.7, 127.1, 126.8, 125.9, 124.1, 120.4, 33.8, 27.6, 22.3.

IR (ATR) 3061, 2954, 2926, 2867, 1790, 1666, 1552, 1482, 1285, 1223, 1188, 1174, 1071, 987, 939, 874.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}NO_4$ 338.1387, found 338.1400.

Phenyl 2-phenyl-4-phenyloxazol-5-yl carbonate (26g)



26g

General procedure was followed using **S27** (4.74 g, 20.0 mmol, 1.0 equiv.), phenyl chloroformate (2.65 mL, 21.0 mmol, 1.1 equiv.), triethylamine (3.05 mL, 22.0 mmol, 1.1 equiv.), and THF (18 mL) to afford **26g** as a white solid (0.626 g, 1.75 mmol, 9%).

Rf = 0.51 (hexane/ethyl acetate = 4:1)

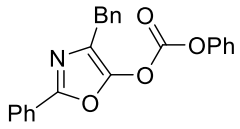
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09-8.07 (m, 1H), 7.89 (d, 1H, *J* = 7.1 Hz), 7.50-7.29 (m, 13H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 150.68, 149.7, 145.0, 130.6, 129.8, 129.7, 128.8, 128.8, 128.1, 126.9, 126.9, 126.2, 126.0, 123.8, 120.5.

IR (ATR) 1789, 1495, 1240, 1217, 1197, 980, 784, 761, 724, 712, 687.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{22}H_{16}NO_4$ 358.1079, found 358.1079.

Phenyl 4-benzyl-2-phenyloxazol-5-yl carbonate (26h)



26h

General procedure was followed using **S28** (10.1 g, 40.0 mmol, 1.0 equiv.), phenyl chloroformate (5.30 mL, 42.0 mmol, 1.1 equiv.), triethylamine (6.10 mL, 44.0 mmol, 1.1 equiv.), and THF (35 mL) to afford **26h** as a white solid (4.62 g, 12.4 mmol, 31%).

Rf = 0.50 (hexane/ethyl acetate = 4:1)

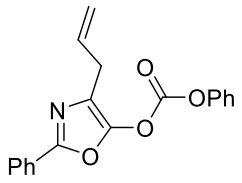
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03-7.90 (m, 2H), 7.45-7.12 (m, 13H), 3.94 (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.2, 150.6, 149.8, 145.9, 137.2, 130.4, 129.6, 128.9, 128.7, 128.5, 126.9, 126.8, 126.6, 126.0, 123.7, 120.4, 31.7.

IR (ATR) 3065, 3028, 2976, 2918, 1798, 1661, 1556, 1541, 1491, 1455, 1208, 1192, 1170, 1118, 1067, 1024, 1004, 985, 941, 873.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}NO_4$ 372.1230, found 372.1242.

Phenyl 2-phenyl-4-(2-propenyl)oxazol-5-yl carbonate (26i)



26i

General procedure was followed using **S29** (2.25 g, 11.2 mmol, 1.0 equiv.), phenyl chloroformate (1.48 mL, 11.8 mmol, 1.1 equiv.), triethylamine (1.71 mL, 12.3 mmol, 1.1 equiv.), and THF (9.9 mL) to afford **26i** as a white solid (1.13 g, 3.52 mmol, 31%).

Rf = 0.59 (hexane/ethyl acetate = 4:1)

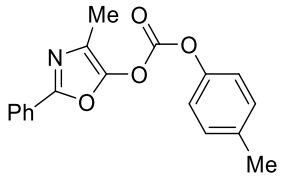
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05-7.87 (m, 2H), 7.52-7.38 (m, 5H), 7.37-7.24 (m, 3H), 6.12-5.93 (m, 1H), 5.40-4.98 (m, 2H), 3.36 (dt, 2H, J = 6.6, 1.5 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.2, 150.7, 150.0, 145.9, 133.3, 130.4, 129.7, 128.7, 126.9, 126.0, 122.7, 120.5, 117.2, 29.7.

IR (ATR) 3080, 3018, 2979, 2959, 1779, 1666, 1592, 1552, 1481, 1447, 1275, 1230, 1174, 1094, 1072, 998, 911.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}NO_4$ 322.1074, found 322.1077.

4-Methylphenyl 4-methyl-2-phenyloxazol-5-yl carbonate (26j)



26j

General procedure was followed using **S30** (3.50 g, 20.0 mmol, 1.0 equiv.), 4-methylphenyl carbonate (2.91 mL, 21.0 mmol, 1.1 equiv.), triethylamine (3.05 mL, 22.0 mmol, 1.1 equiv.), and THF (17.5 mL) to afford **26j** as a white solid (3.90 g, 12.6 mmol, 63%).

Rf = 0.22 (hexane/dichloromethane = 1:1)

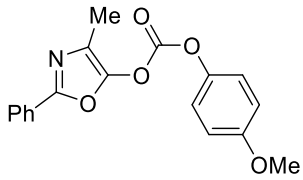
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07-7.87 (m, 2H), 7.44-7.42 (m, 3H), 7.24-7.07 (m, 4H), 2.36 (s, 3H), 2.20 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.9, 150.2, 148.6, 145.8, 136.6, 130.3, 130.2, 128.7, 127.0, 125.9, 120.6, 120.1, 20.8, 10.4.

IR (ATR) 3051, 2962, 2924, 2861, 1782, 1667, 1551, 1508, 1479, 1446, 1248, 1229, 1193, 1171, 1150, 1079, 999, 940, 880, 821.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}NO_4$ 310.1074, found 310.1070.

4-Methoxyphenyl 4-methyl-2-phenyloxazol-5-yl carbonate (26k)



26k

General procedure was followed using **S30** (3.50 g, 20.0 mmol, 1.0 equiv.), 4-methoxyphenyl carbonate (3.11 mL, 21.0 mmol, 1.1 equiv.), triethylamine (3.05 mL, 22.0 mmol, 1.1 equiv.), and THF (17.5 mL) to afford **26k** as a white solid (1.29 g, 3.97 mmol, 20%).

Rf = 0.36 (hexane/dichloromethane = 1:1)

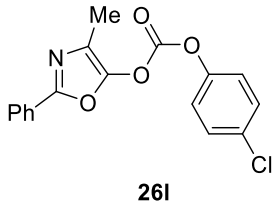
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07-7.89 (m, 2H), 7.44-7.42 (m, 3H), 7.21 (dd, 2H, *J* = 6.8, 2.4 Hz), 6.92 (dd, 2H, *J* = 6.9, 2.3 Hz), 3.80 (s, 3H), 2.20 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.9, 154.9, 150.4, 145.8, 144.3, 130.3, 128.7, 127.0, 125.8, 121.4, 120.6, 114.6, 55.6, 10.4.

IR (ATR) 3064, 2956, 2932, 2837, 1794, 1667, 1597, 1553, 1505, 1210, 1187, 1175, 1068, 1027, 991, 831.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}NO_5$ 326.1023, found 326.1034.

4-Chlorophenyl 4-methyl-2-phenyloxazol-5-yl carbonate (26l)



26l

General procedure was followed using **S30** (3.50 g, 20.0 mmol, 1.0 equiv.), 4-chlorophenyl carbonate (2.89 mL, 21.0 mmol, 1.1 equiv.), triethylamine (3.05 mL, 22.0 mmol, 1.1 equiv.), and THF (28.5 mL) to afford **26l** as a white solid (1.85 g, 5.62 mmol, 28%).

Rf = 0.42 (hexane/dichloromethane = 1:1)

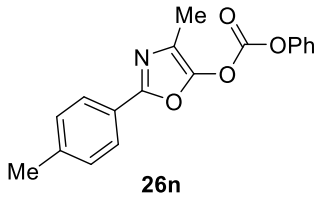
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07-7.87 (m, 2H), 7.50-7.35 (m, 5H), 7.31-7.18 (m, 2H), 2.21 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.0, 149.8, 149.1, 145.5, 132.4, 130.4, 129.8, 128.8, 126.9, 125.9, 121.9, 120.7, 10.4.

IR (ATR) 3013, 3061, 2977, 2933, 1787, 1719, 1669, 1554, 1487, 1448, 1253, 1229, 1202, 1090, 1002, 939, 876, 828.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}ClNO_4$ 330.0528, found 330.0534.

Phenyl 4-methyl-2-(4-methylphenyl)oxazol-5-yl carbonate (26n)



26n

General procedure was followed using **S31** (3.78 g, 20.0 mmol, 1.0 equiv.), phenyl chloroformate (2.91 mL, 21.0 mmol, 1.1 equiv.), triethylamine (3.05 mL, 22.0 mmol, 1.1 equiv.), and THF (17.5 mL) to afford **26n** as a white solid (3.14 g, 10.2 mmol, 51%).

Rf = 0.46 (hexane/ethyl acetate = 4:1)

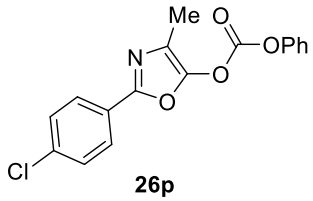
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, 2H, *J* = 8.2 Hz), 7.43 (d, 2H, *J* = 7.3 Hz), 7.33-7.12 (m, 5H), 2.39 (s, 3H), 2.20 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.2, 150.7, 150.1, 145.5, 140.7, 129.8, 129.5, 126.8, 125.9, 124.3, 120.5, 120.4, 21.5, 10.4.

IR (ATR) 3034, 2955, 2922, 2857, 1785, 1666, 1592, 1497, 1247, 1222, 1196, 1179, 1076, 1005, 939, 899, 867, 819.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}NO_4$ 310.1074, found 310.1074.

Phenyl 2-(4-chlorophenyl)-4-methyloxazol-5-yl carbonate (26p)



26p

General procedure was followed using **S32** (4.18 g, 20.0 mmol, 1.0 equiv.), phenyl chloroformate (2.91 mL, 21.0 mmol, 1.1 equiv.), triethylamine (3.05 mL, 22.0 mmol, 1.1 equiv.), and THF (17.5 mL) to afford **26p** as a white solid (2.03 g, 6.16 mmol, 31%).

Rf = 0.49 (hexane/ethyl acetate = 4:1)

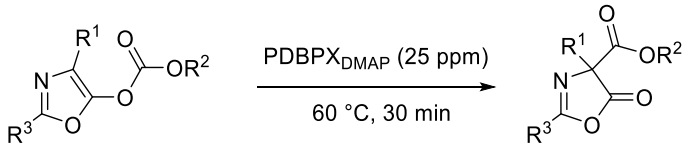
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94-7.86 (m, 2H), 7.50-7.37 (m, 4H), 7.37-7.27 (m, 3H), 2.20 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.0, 150.7, 150.0, 145.8, 136.5, 129.8, 129.1, 127.1, 126.9, 125.5, 120.9, 120.5, 10.4.

IR (ATR) 3093, 3065, 2964, 2925, 1782, 1666, 1603, 1547, 1495, 1482, 1458, 1402, 1252, 1226, 1195, 1172, 1090, 1072, 1006, 939, 833.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}ClNO_4$ 330.0528, found 330.0532.

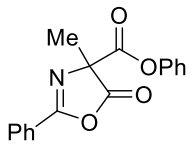
6. PDBPX$_{DMAP}$ catalyzed acyl rearrangement reaction of azlactones



26 **27**

General Procedure: *O*-acylated azlactone **26** (1.96 mmol, 1.0 equiv.) and PDBPX$_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0348 mg, 0.0491 μmol, 25 ppm) were charged to flask and the mixture was stirred at 60 ºC for 30 min. After cooling to 0 ºC, the mixture was treated with H_2O (4.0 mL), stirred at 0 ºC for a few minutes, then treated with 0.1 M HCl (10 μL), stirred at 0 ºC for a few minutes, and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure after filtration. Yields were determined by ^{1}H NMR without purification.

Phenyl 4,5-dihydro-4-methyl-5-oxo-2-phenyl-4-oxazolecarboxylate (27a)[S12l]



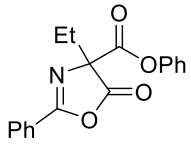
27a

General procedure was followed using **26a** (1.17 g, 3.97 mmol, 1.0 equiv.) and PDBPX$_{DMAP}$ ([DMAP]: 1.14 mmol/g, 0.087 mg, 0.099 μmol, 25 ppm) for 30 min afforded **27a** as a white solid (96% yield, TON 38,400, TOF 1,280 /min).

Rf = 0.67 (dichloromethane/diethyl ether = 50:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.11 (d, 2H, *J* = 8.0 Hz), 7.66 (t, 1H, *J* = 7.0 Hz), 7.56 (t, 2H, *J* = 8.0 Hz), 7.40 (t, 2H, *J* = 5.0 Hz), 7.21 (t, 1H, *J* = 7.5 Hz), 7.09 (d, 2H, *J* = 7.6 Hz), 1.88 (s, 3H).

Phenyl 4-ethyl-4,5-dihydro-5-oxo-2-phenyl-4-oxazolecarboxylate (27b)



27b

General procedure was followed using **26b** (686 mg, 2.22 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0393 mg, 0.0554 μmol, 25 ppm) for 30 min afforded **27b** as colorless oil (92% yield, TON 36,800, TOF 1,227 /min).

Rf = 0.73 (dichloromethane/diethyl ether = 50:1)

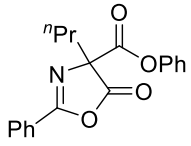
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19-8.02 (m, 2H), 7.69-7.57 (m, 1H), 7.51 (t, 2H, *J* = 7.7 Hz), 7.41-7.30 (m, 2H), 7.24-7.21 (m, 1H), 7.15-7.03 (m, 2 H), 2.53-2.31 (m, 2H), 1.01 (t, 3H, *J* = 7.6 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.9, 164.3, 163.6, 150.1, 133.4, 129.4, 128.9, 128.3, 126.4, 121.0, 77.2, 27.8, 7.6.

IR (ATR) 3060, 2977, 2937, 1818, 1765, 1648, 1590, 1491, 1451, 1321, 1293, 1186, 1039, 1021, 929, 883, 843.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}NO_4$ 310.1074, found 310.1076.

Phenyl 4,5-dihydro-5-oxo-2-phenyl-4-propyl-4-oxazolecarboxylate (27c)



27c

General procedure was followed using **26c** (336 mg, 1.04 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0184 mg, 0.0259 μmol, 25 ppm) for 30 min afforded **27c** as colorless oil (96% yield, TON 38,400, TOF 1,280 /min).

Rf = 0.82 (dichloromethane/diethyl ether = 50:1)

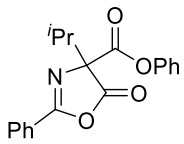
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19-8.08 (m, 2H), 7.88-7.79 (m, 1H), 7.70-7.06 (m, 7H), 2.54-2.20 (m, 2H), 1.63-1.19 (m, 2H), 1.11-0.86 (m, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.9, 164.3, 163.6, 150.1, 133.5, 129.5, 128.3, 126.5, 124.9, 121.0, 66.8, 36.3, 16.8, 13.7.

IR (ATR) 3060, 2964, 2933, 2875, 1821, 1768, 1648, 1482, 1451, 1321, 1294, 1185, 1159, 1107, 1042, 1023, 956, 887, 840.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}NO_4$ 324.1230, found 324.1230.

Phenyl 4,5-dihydro-4-isopropyl-5-oxo-2-phenyl-4-oxazolecarboxylate (27d)



27d

General procedure was followed using **26d** (625 mg, 1.93 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.137 mg, 0.193 μmol, 100 ppm) for 42 h afforded **27d** (45% yield, TON 4,500, TOF 2 /min) as colorless oil.

It was difficult to separate the isomers. Products were analyzed as a mixture.

Rf = 0.76 (dichloromethane/diethyl ether = 50:1)

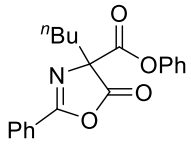
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13-8.10 (m, 1H), 7.82-7.01 (m, 9H), 3.18-3.03 (m, 0.4H), 3.03-2.84 (m, 0.6H), 1.38 (q, 2H, *J* = 6.6 Hz), 1.20 (d, 2H, *J* = 6.9 Hz), 1.08 (d, 2H, *J* = 6.9 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.2, 169.7, 164.2, 164.0, 163.8, 163.1, 150.22, 150.15, 134.2, 133.3, 130.0, 129.5, 128.8, 128.6, 128.3, 126.9, 126.5, 126.4, 125.0, 121.1, 120.7, 80.4, 34.8, 28.5, 19.0, 18.9, 17.2, 16.3.

IR (ATR) 3061, 2971, 2936, 2877, 1818, 1794, 1764, 1649, 1591, 1491, 1451, 1321, 1294, 1186, 1115, 1059, 1024, 967, 884, 843.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}NO_4$ 324.1230, found 324.1242.

Phenyl 4-buthyl-4,5-dihydro-5-oxo-2-phenyl-4-oxazolecarboxylate (27e)



27e

General procedure was followed using **26e** (437 mg, 1.30 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0231 mg, 0.0326 μmol, 25 ppm) for 48 h afforded **27e** as colorless oil (94% yield, TON 37,600, TOF 13 /min).

Rf = 0.56 (hexane/ethyl acetate = 7:3)

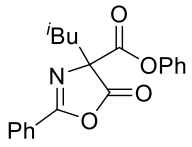
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15-8.03 (m, 2H), 7.67-7.58 (m, 1H), 7.56-7.49 (m, 2H), 7.40-7.30 (m, 2H), 7.28-7.19 (m, 1H), 7.14-7.05 (m, 2H), 2.57-2.22 (m, 2H), 1.55-1.17 (m, 4H), 0.91 (t, 3H, J = 7.1 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.1, 164.4, 163.5, 150.2, 133.4, 129.5, 128.9, 128.3, 126.5, 125.1, 121.0, 76.8, 34.1, 25.4, 22.4, 13.7.

IR (ATR) 3060, 2957, 2931, 2862, 1748, 1638, 1529, 1487, 1224, 1180, 1159, 1127, 1071, 1024, 1001, 913.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}NO_4$ 338.1387, found 338.1382.

Phenyl 4,5-dihydro-4-isobuthyl-5-oxo-2-phenyl-4-oxazolecarboxylate (27f)



27f

General procedure was followed using **26f** (605 mg, 1.79 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0318 mg, 0.0448 μmol, 25 ppm) for 3 h afforded **27f** as colorless oil (99% yield, TON 39,600, TOF 220 /min).

Rf = 0.88 (dichloromethane/diethyl ether = 50:1)

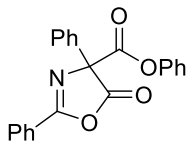
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, 1H, J = 7.3 Hz), 7.95-6.98 (m, 9H), 2.53 (dd, 1H, J = 14.3, 5.8 Hz), 2.18 (q, 1H, J = 7.2 Hz), 1.93-1.68 (m, 1H), 1.10-0.90 (m, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.5, 164.5, 163.3, 150.2, 133.4, 129.5, 128.9, 218.3, 126.5, 125.1, 121.0 76.3, 42.7, 24.7, 23.7, 23.0.

IR (ATR) 3061, 2959, 2934, 2872, 1822, 1767, 1649, 1482, 1292, 1183, 1159, 1049, 1024, 967, 886.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}NO_4$ 338.1387, found 338.1385.

Phenyl 4,5-dihydro-2,4-diphenyl-5-oxo-4-oxazolecarboxylate (27g)



27g

General procedure was followed using **26g** (500 mg, 1.40 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0248 mg, 0.0350 μmol, 25 ppm) for 8 h afforded **27g** as a white solid (97% yield, TON 38,800, TOF 81 /min).

Rf = 0.21 (hexane/toluene = 1:1)

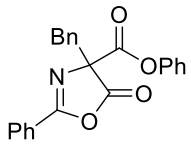
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20-8.18 (m, 2H), 7.86-7.84 (m, 2H), 7.67-7.23 (m, 9H), 7.10-7.08 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.3, 164.2, 163.8, 150.4, 133.7, 133.3, 129.5, 129.4, 129.0, 128.9, 128.6, 126.6, 126.5, 125.1, 121.0.

IR (ATR) 1820, 1752, 1655, 1492, 1226, 1185, 1141, 1052, 974, 946, 886, 735, 713, 695.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{22}H_{16}NO_4$ 358.1079, found 358.1079.

Phenyl 4-benzyl-4,5-dihydro-5-oxo-2-phenyl-4-oxazolecarboxylate (27h)



27h

General procedure was followed using **26h** (610 mg, 1.64 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0291 mg, 0.0410 μmol, 25 ppm) for 4.5 h afforded **27h** as a white solid (94% yield, TON 37,600, TOF 139 /min).

Rf = 0.76 (dichloromethane/diethyl ether = 50:1)

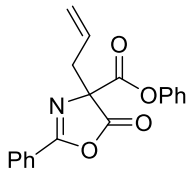
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05-7875 (m, 2H), 7.58-7.05 (m, 13H), 3.75-3.61 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.3, 164.2, 163.5, 150.3, 133.3, 132.5, 130.4, 129.5, 128.8, 128.3, 128.2, 127.7, 126.5, 124.8, 121.0, 76.7, 40.1.

IR (ATR) 3062, 3032, 934, 1821, 1764, 1648, 1491, 1452, 1321, 1292, 1184, 1094, 1056, 974, 897, 878, 846.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}NO_4$ 372.1230, found 372.1238.

Phenyl 4-allyl-4,5-dihydro-5-oxo-2-phenyl-4-oxazolecarboxylate (27i)



27i

General procedure was followed using **26i** (453 mg, 1.41 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0250 mg, 0.0353 μmol, 25 ppm) for 15.5 h afforded **27i** as colorless oil (87% yield, TON 34,800, TOF 37 /min).

Rf = 0.75 (dichloromethane/diethyl ether = 50:1)

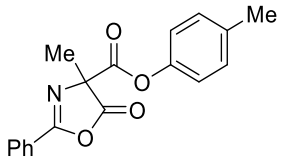
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19-8.02 (m, 2H), 7.66-7.06 (m, 8H), 5.79-5.51 (m, 1H), 5.32 (dd, 1H, *J* = 17.2, 1.1 Hz), 5.22 (dd, 1H, *J* = 10.1, 0.7 Hz), 3.30-2.93 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.4, 170.6, 167.3, 164.0, 163.7, 150.1, 133.5, 129.5, 128.9, 128.4, 127.0, 124.9, 121.0, 76.6, 38.3.

IR (ATR) 3074, 2981, 2929, 2920, 1823, 1761, 1648, 1482, 1293, 1183, 1056, 1024, 971, 929, 893, 841.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{19}H_{16}NO_4$ 322.1074, found 322.1085.

4-Methylphenyl 4,5-dihydro-4-methyl-5-oxo-2-phenyl-4-oxazolecarboxylate (27j)



27j

General procedure was followed using **26j** (760 mg, 2.46 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.33 mmol/g, 0.0462 mg, 0.0614 μmol, 25 ppm) for 45 min, afforded **27j** as colorless oil (96% yield, TON 38,400, TOF 853 /min).

Rf = 0.74 (dichloromethane/diethyl ether = 50:1)

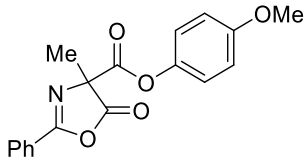
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.16-7.97 (m, 2H), 7.67-7.57 (m, 1H), 7.56-7.47 (m, 2H), 7.14 (d, 2H, *J* = 8.2 Hz), 6.97 (dt, 2H, *J* = 9.2, 2.5 Hz), 2.31 (s, 3H), 1.88 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.7, 164.7, 163.7, 147.9, 136.2, 133.5, 129.9, 128.9, 128.3, 125.0, 120.6, 72.8, 20.8, 20.4.

IR (ATR) 3065, 3034, 2939, 2868, 1830, 1766, 1646, 1506, 1450, 1321, 1161, 1091, 1006, 913, 881, 854.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}NO_4$ 310.1074, found 310.1070.

4-Methoxyphenyl 4,5-dihydro-4-methyl-5-oxo-2-phenyl-4-oxazolecarboxylate (27k)



27k

General procedure was followed using **26k** (269 mg, 0.828 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.39 mmol/g, 0.0149 mg, 0.0207 μmol, 25 ppm) for 75 min, afforded **27k** as colorless oil (90% yield, TON 36,000, TOF 480 /min).

Rf = 0.63 (dichloromethane/diethyl ether = 50:1)

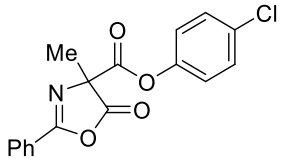
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15-8.02 (m, 2H), 7.61 (d, 1H, *J* = 7.6 Hz), 7.52 (d, 2H, *J* = 7.7 Hz), 7.01 (dd, 2H, *J* = 6.9, 2.3 Hz), 6.85 (dd, 2H, *J* = 6.6, 2.3 Hz), 3.77 (s, 3H), 1.88 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.8, 164.9, 163.6, 157.6, 143.6, 133.6, 128.9, 128.3, 125.0, 121.8, 114.4, 72.8, 55.5, 20.4.

IR (ATR) 3061, 3003, 2944, 2837, 1741, 1646, 1601, 1577, 1504, 1482, 1440, 1246, 1174, 1096, 1029, 932, 881, 812.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}NO_5$ 326.1023, found 326.1037.

4-Chlorophenyl 4,5-dihydo-4-methyl-5-oxo-2-phenyl-4-oxazolecarboxylate (27l)



27l

General procedure was followed using **26l** (530 mg, 1.61 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.33 mmol/g, 0.0303 mg, 0.0403 μmol, 25 ppm) for 75 min, afforded **27l** as colorless oil (92% yield, TON 36,800, TOF 1,227 /min).

Rf = 0.53 (dichloromethane/diethyl ether = 50:1)

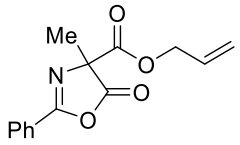
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15-8.02 (m, 2H), 7.67-7.59 (m, 1H), 7.56-7.48 (m, 2H), 7.33 (dt, 2H, *J* = 9.8, 2.7 Hz), 7.12-7.03 (m, 2H), 1.88 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.5, 164.3, 163.7, 148.5, 133.5, 129.5, 128.9, 128.3, 127.0, 124.5, 122.4, 72.8, 20.4.

IR (ATR) 3062, 3044, 2992, 2940, 1833, 1743, 1645, 1592, 1516, 1480, 1444, 1266, 1184, 1159, 1090, 1005, 932, 844.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}ClNO_4$ 330.0528, found 330.0531.

Allyl 4,5-dihydro-4-methyl-5-oxo-2-phenyl-4-oxazolecarboxylate (27m)[S12n]



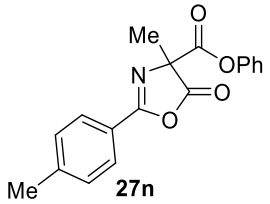
27m

General procedure was followed using **26m** (455 mg, 1.76 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.33 mmol/g, 0.0330 mg, 0.0439 μmol, 25 ppm) for 60 min afforded **27m** as colorless oil (91% yield, TON 36,400, TOF 607 /min).

Rf = 0.61 (dichloromethane/diethyl ether = 50:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (d, 2H, *J* = 8.0 Hz), 7.61 (t, 1H, *J* = 7.3 Hz), 7.50 (dd, 2H, *J* = 7.3, 8.0 Hz), 5.89-5.82 (m, 1H), 5.30 (dd, 1H, *J* = 17.5, 0.92 Hz), 5.24 (d, 1H, *J* = 10.5 Hz), 4.73-4.66 (m, 2H), 1.79 (s, 3H).

Phenyl 4,5-dihydro-4-(4-methylphenyl)-5-oxo-2-phenyl-4-oxazolecarboxylate (27n)



27n

General procedure was followed using **26n** (464 mg, 1.50 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0532 mg, 0.0750 μmol, 50 ppm) for 30 min, afforded **27n** as colorless oil (94% yield, TON 18,800, TOF 627 /min).

Rf = 0.67 (dichloromethane/diethyl ether = 50:1)

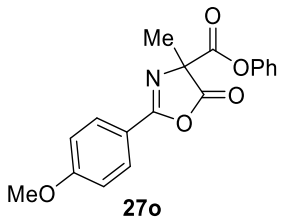
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (dd, 2H, *J* = 9.2, 2.5 Hz), 7.38-7.06 (m, 7H), 2.43 (s, 3H), 1.88 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.7, 164.6, 163.8, 150.1, 129.6, 129.5, 128.3, 126.5, 122.2, 121.0, 72.8, 21.7, 20.4.

IR (ATR) 3043, 2992, 2938, 2922, 1828, 1767, 1644, 1612, 1489, 1445, 1291, 1182, 1159, 1089, 1005, 923, 902, 880, 828.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}NO_4$ 310.1074, found 310.1082.

Phenyl 4,5-dihydro-4-(4-methoxyphenyl)-5-oxo-2-phenyl-4-oxazolecarboxylate (27o)[S12o]



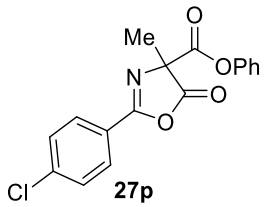
27o

General procedure was followed using **26o** (719 mg, 2.21 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0392 mg, 0.0553 μmol, 25 ppm) for 1.5 h afforded **27o** as colorless oil (96% yield, TON 38,400, TOF 427 /min).

Rf = 0.62 (dichloromethane/diethyl ether = 50:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, 2H, *J* = 8.8 Hz), 7.38-7.35 (m, 2H), 7.26-7.23 (m, 1H), 7.10 (d, 2H, *J* = 8.8 Hz), 7.01 (d, 2H, *J* = 8.8 Hz), 3.90 (s, 3H), 1.87 (s, 3H).

Phenyl 4-(4-Chlorophenyl)-4,5-dihydro-5-oxo-2-phenyl-4-oxazolecarboxylate (27p)



27p

General procedure was followed using **26p** (260 mg, 0.789 mmol, 1.0 equiv.) and $PDBPX_{DMAP}$ ([DMAP]: 1.41 mmol/g, 0.0279 mg, 0.0393 μmol, 50 ppm) for 30 min, afforded **27p** as colorless oil (96% yield, TON 19,200, TOF 640 /min).

Rf = 0.74 (dichloromethane/diethyl ether = 50:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (dd, 2H, *J* = 6.8, 1.9 Hz), 7.50 (dd, 2H, *J* = 6.8, 1.9 Hz), 7.40-7.33 (m, 2H), 7.28-7.19 (m, 1H), 7.14-7.06 (m, 2H), 1.89 (s, 3H).

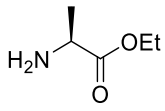
^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.3, 164.4, 162,9, 150.1, 129.6, 129.5, 129.4, 128.6, 126.6, 121.2, 121.0, 72.9, 20.4.

IR (ATR) 3060, 2992, 2938, 2853, 1833, 1764, 1645, 1593, 1515, 1480, 1444, 1404, 1275, 1184, 1159, 1088, 1004, 923, 903, 881, 841.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}ClNO_4$ 330.0528, found 330.0525.

7. $PDBPX_{DMAP}$ catalyzed acyl rearrangement reaction of azlactones followed by ring opening reaction

L-alanine ethyl ester (S33)

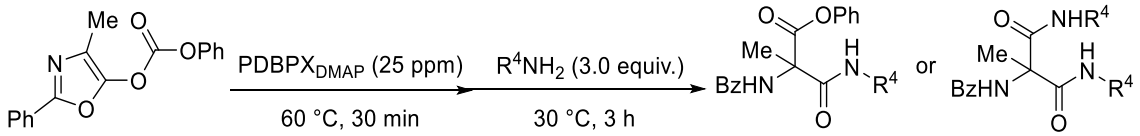


S33

S33 was prepared and characterized according to the literature.[S13]

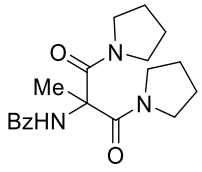
Rf = 0.35 (CH_2Cl_2/MeOH = 7:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.09 (q, 2H, *J* = 7.5 Hz), 3.45 (q, 1H, *J* = 7.2 Hz), 1.48 (s, 2H), 1.25 (d, 3H, *J* = 7.5 Hz), 1.20 (t, 3H, *J* = 7.5 Hz).



26a **29** **29'**

General Procedure for one-pot reaction: Phenyl 4-methyl-2-phenyloxazol-5-yl carbonate (**26a**) (1.00 g, 3.38 mmol, 1.0 equiv.) and PDBPX$_{DMAP}$ ([DMAP]: 1.39 mmol/g, 0.0608 mg, 0.0845 μmol, 25 ppm) were charged to flask and the mixture was stirred at 60 ºC for 30 min. After cooling to 30 ºC, corresponding primary amine (3.0 equiv.) was added to the mixture. The resulting reaction mixture was stirred at 30 ºC for 3 h. After cooling to 0 ºC, H_2O (12 mL) was added to the mixture and the mixture was stirred at 0 ºC for a few minutes, then 2 M HCl (3.5 mL) was added. After stirring at 0 ºC for a few minutes, the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10:1 to 1:1 as eluent) to afford amino acid derivative **29** or **29'**.



29a'

General procedure was followed using **26a** (880 mg, 2.97 mmol, 1.0 equiv.), PDBPX$_{DMAP}$ ([DMAP]: 1.14 mmol/g, 0.0652 mg, 0.0743 μmol, 25 ppm) for 30 min, and pyrrolidine (740 μL,

8.92 mmol, 3.0 equiv.) for a few minutes afforded **29a'** as a white solid (680 mg, 1.98 mmol, 67% yield).

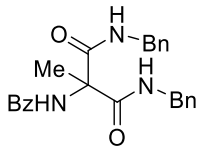
Rf = 0.35 (hexane/ethyl acetate = 1:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.41 (s, 1H), 7.88-7.86 (m, 2H), 7.57-7.52 (m, 3H), 3.68-3.45 (m, 6H), 3.29-3.23 (m, 2H), 1.88-1.73 (m, 11H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.6, 164.1, 133.8, 131.7, 128.6, 127.0, 63.1, 47.9, 46.6, 26.8, 23.3, 21.1.

IR (ATR) 3362, 1668, 1624, 1504, 1433, 950, 714, 692.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{19}H_{26}N_3O_3$ 344.1974, found 344.1961.



29b'

General procedure was followed using **26a** (700 mg, 2.36 mmol, 1.0 equiv.), $PDBPX_{DMAP}$ ([DMAP]: 1.39 mmol/g, 0.0425 mg, 0.0591 μmol, 25 ppm) for 30 min, and benzylamine (0.77 mL, 7.09 mmol, 3.0 equiv.) for a few minutes afforded **29b'** as a white solid (882 mg, 2.12 mmol, 90% yield).

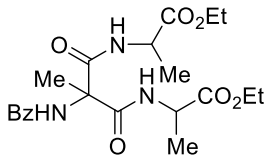
Rf = 0.33 (hexane/ethyl acetate = 1:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (s, 1H), 7.89 (d, 2H, *J* = 7.3 Hz), 7.54 (t, 1H, *J* = 7.1 Hz), 7.46 (t, 2H, *J* = 7.8 Hz), 7.33-7.22 (m, 12H), 4.54-4.42 (m, 4H), 2.00 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.0, 166.5, 137.4, 133.4, 132.2, 128.7, 128.7, 127.6, 127.3, 127.2, 63.6, 44.0, 22.5.

IR (ATR) 3305, 1653, 1539, 1498, 1470, 1430, 1263, 733, 699.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{25}H_{26}N_3O_3$ 416.1974, found 416.1964.



29c'

General procedure was followed using **26a** (1.00 g, 3.38 mmol, 1.0 equiv.), $PDBPX_{DMAP}$ ([DMAP]: 1.39 mmol/g, 0.0608 mg, 0.0845 μmol, 25 ppm) for 30 min, and L-alanine ethyl ester

S35 (1.2 mL, 10.1 mmol, 3.0 equiv.) for 3 h to afforded **29c'** as colorless oil (1.41 g, 2.94 mmol, 87% yield).

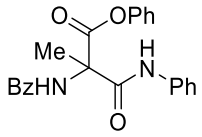
Rf = 0.22 (hexane/ethyl acetate = 3:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93-7.87 (m, 3H), 7.56-7.45 (m, 5H), 4.57-4.48 (m, 2H), 4.21-4.15 (m, 4H), 1.94 (s, 3H), 1.43 (t, 6H, *J* = 6.9 Hz), 1.26 (q, 6H, *J* = 8.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.1, 169.7, 169.3, 166.8, 133.6, 132.2, 128.8, 127.3, 63.4, 61.7, 48.9, 22.5, 18.0, 17.8, 14.1.

IR (ATR) 3329, 2984, 1736, 1664, 1506, 1475, 1377, 1202, 1156, 1052, 1020, 860, 714.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{21}H_{30}N_3O_7$ 436.2084, found 436.2074.



29d

General procedure was followed using **26a** (909 mg, 3.07 mmol, 1.0 equiv.), $PDBPX_{DMAP}$ ([DMAP]: 1.39 mmol/g, 0.0552 mg, 0.0767 μmol, 25 ppm) for 30 min, and aniline (0.84 mL, 9.21 mmol, 3.0 equiv.) for 3 h afforded **29d** as a white solid (997 mg, 2.57 mmol, 84% yield).

Rf = 0.20 (hexane/ethyl acetate = 3:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (s, 1H), 7.90 (d, 3H, *J* = 7.8 Hz), 7.57-7.52 (m, 3H), 7.48-7.44 (m, 2H), 7.36 (t, 4H, *J* = 8.2 Hz), 7.25 (m, 2H), 7.12-7.10 (m, 2H), 2.10 (s, 3H).

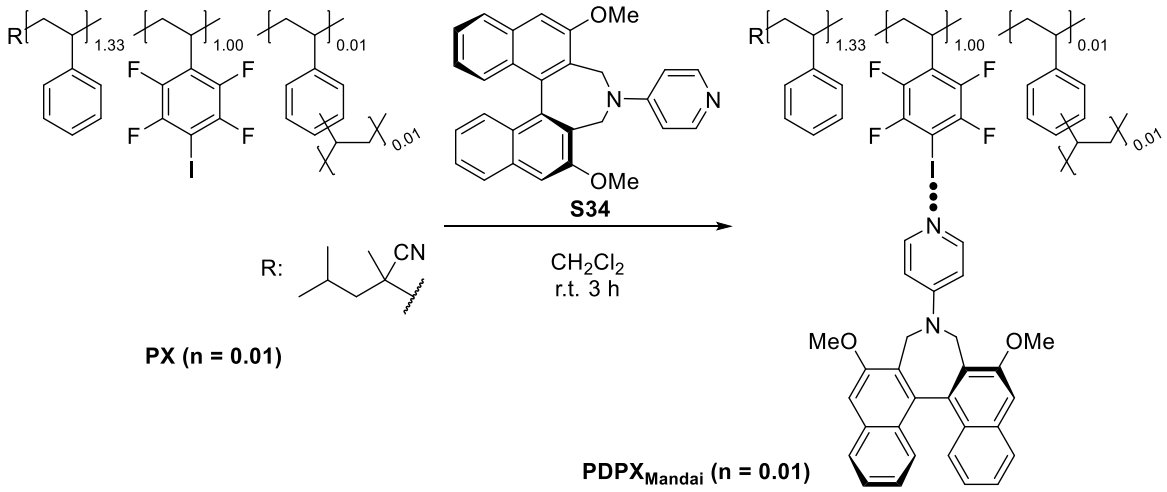
^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 167.0, 165.8, 150.6, 136.9, 133.1, 132.2, 129.5, 129.2, 128.7, 127.3, 126.4, 125.2, 121.3, 120.3, 63.6, 22.4.

IR (ATR) 2360, 1737, 1654, 1599, 1558, 1542, 1520, 1488, 1267, 1184, 1160, 1116, 760, 734, 711, 689.

HRMS (FAB/EB) *m/z* $[M+H]^+$ calcd for $C_{23}H_{21}N_2O_4$ 389.1501, found 389.1502.

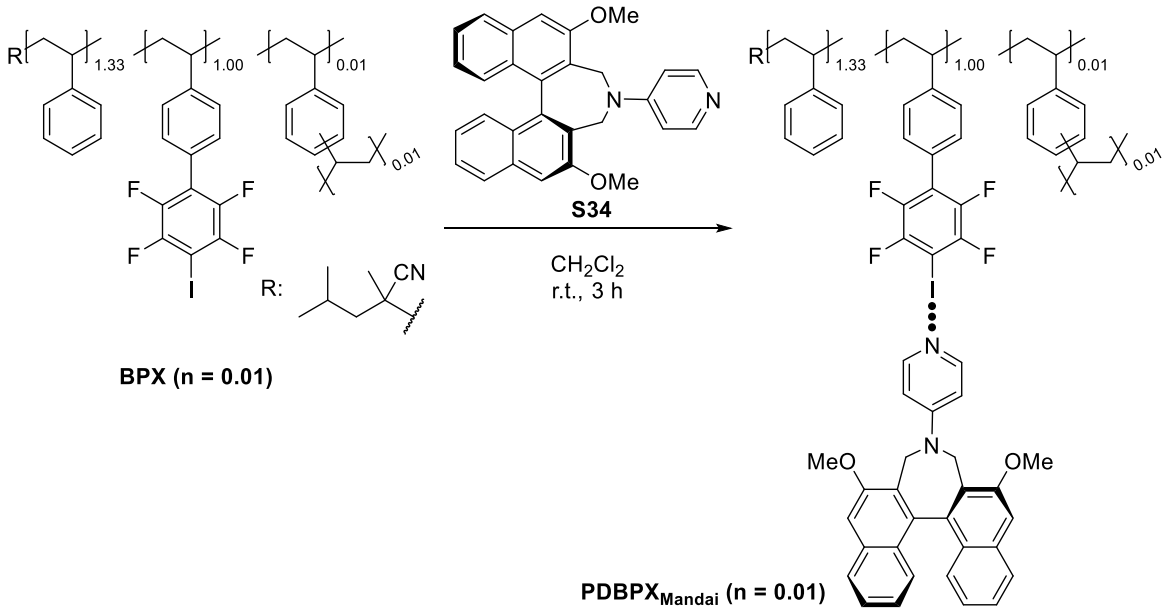
8. Asymmetric acyl rearrangement reaction of azlactones

Preparation of $PDPX_{Mandai}$ (n = 0.01)



To a solution of **PX (n = 0.01)** (60.0 mg, [-C_6F_4I]: 1.93 mmol/g) in CH_2Cl_2 (2 mL) was added **S34** (50.1 mg, 0.116 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure to afford a **$PDPX_{Mandai}$ (n = 0.01)** as a yellow solid (79.6 mg, [Mandai]: 0.657 mmol/g). elemental analysis calcd (%) for $C_{47.74}H_{37.74}N_{2.3}O_2F_4I$: C 65.58, H 4.35, N 4.56, found: C 64.02, H 4.81, N 3.24.

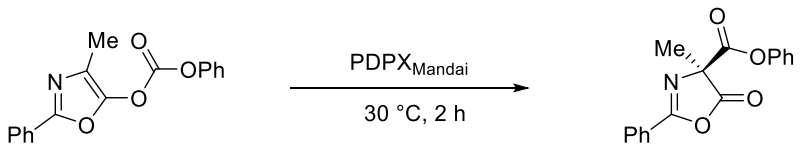
Preparation of $PDBPX_{Mandai}$ (n = 0.01)



To a solution of **BPX (n = 0.01)** (100 mg, [-C_6F_4I]: 1.63 mmol/g) in CH_2Cl_2 (2 mL) was added **S34** (43.3 mg, 0.100 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure to afford **$PDBPX_{Mandai}$ (n =**

0.01) as a yellow solid (79.6 mg, [Mandai]: 0.657 mmol/g). elemental analysis calcd (%) for $C_{53.74}H_{41.74}N_{2.3}O_2F_4I$: C 67.91, H 4.43, N 4.33, found: C 67.78, H 4.98, N 3.02.

Procedure for asymmetric acyl rearrangement reaction: synthesis of Phenyl 4-(4-Methoxyphenyl)-5-oxo-2-phenyl-4-oxazolecarboxylate (27o)[12c]



26a **27a**

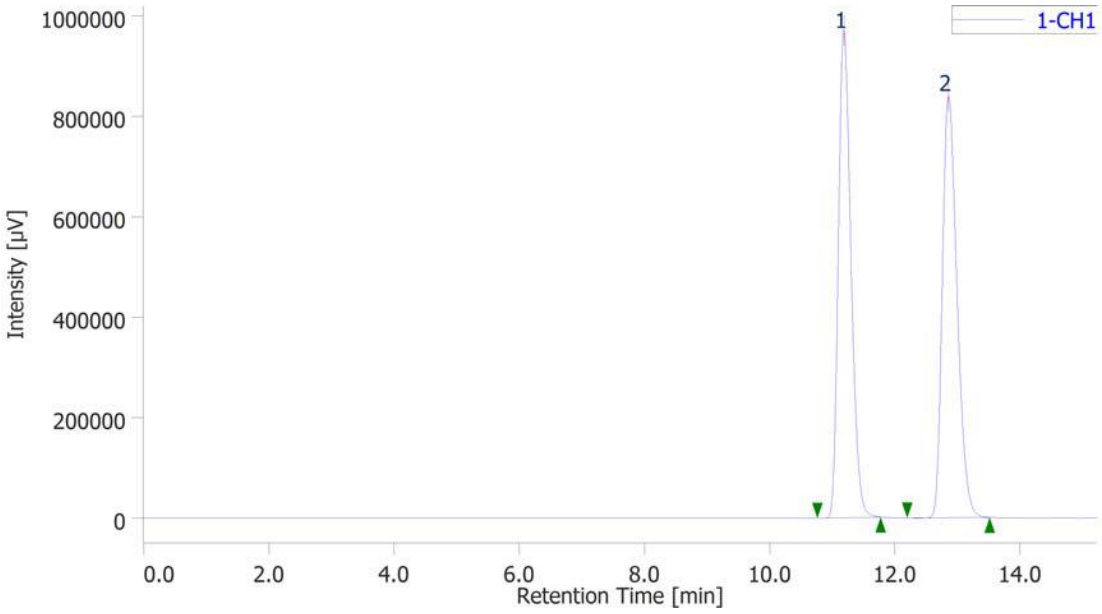
O-acylated azlactone **26a** (387 mg, 1.31 mmol, 1.0 equiv.) and PDPX$_{Mandai}$ ([Mandai Catalyst]: 0.671 mmol/g, 0.195 mg, 0.131 μmol, 100 ppm) were charged to flask and the mixture was stirred at 30 ºC for 2 h. After cooling to 0 ºC, the mixture was treated with H_2O (4.0 mL), stirred at 0 ºC for a few minutes, then treated with 0.1 M HCl (10 μL), stirred at 0 ºC for a few minutes, and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure after filtration. **27a** was afforded as colorless oil (>99% yield, TON 9,900, TOF 83 /min, 57% *ee*). Yields were determined by ^{1}H NMR and enantioselectivity was determined by chiral HPLC without further purification.

Rf = 0.67 (dichloromethane/diethyl ether = 50:1)

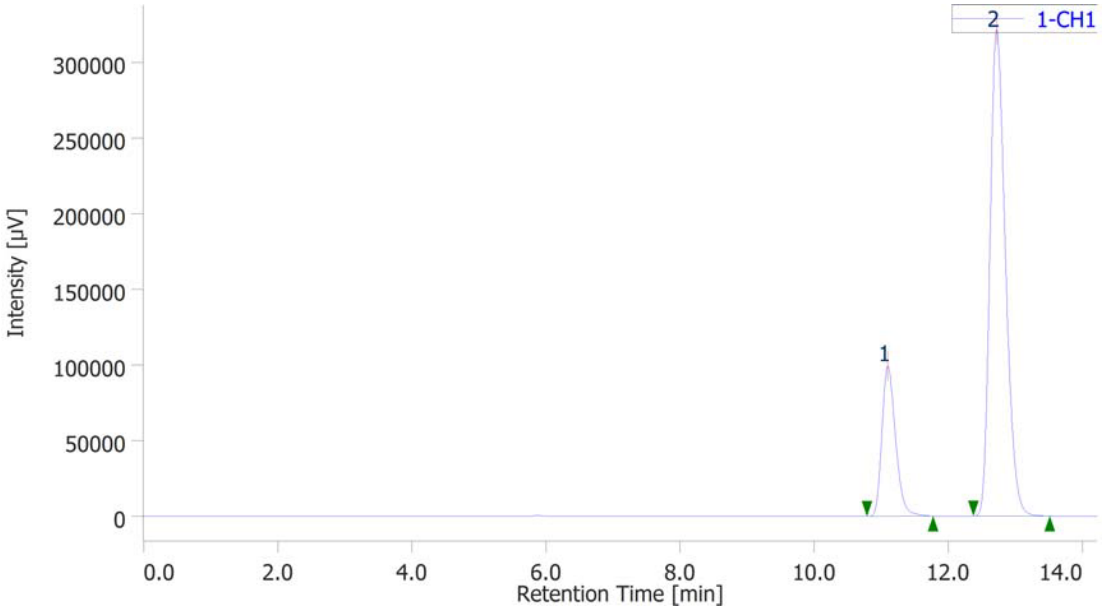
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.11 (d, 1H, *J* = 8.0 Hz), 7.66 (t, 1H, *J* = 7.0 Hz), 7.56 (t, 2H, *J* = 8.0 Hz), 7.40 (t, 2H, *J* = 5.0 Hz), 7.21 (t, 2H, *J* = 7.5 Hz), 7.09 (d, 2H, *J* = 7.6 Hz), 1.88 (s, 3H).

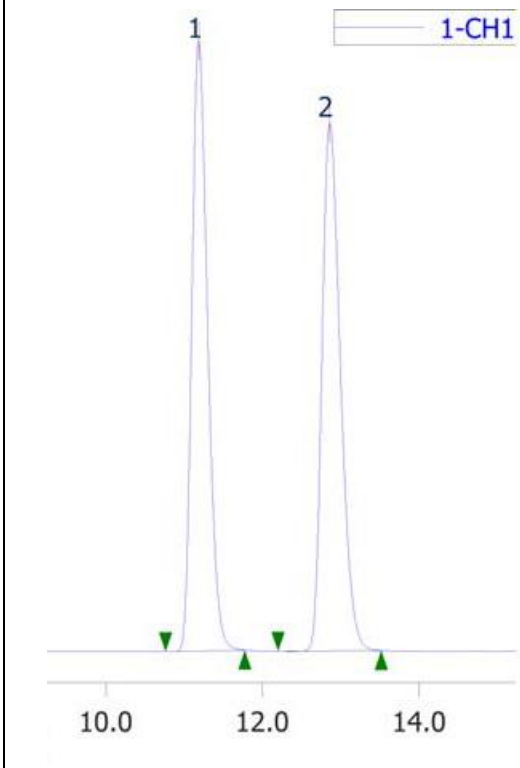
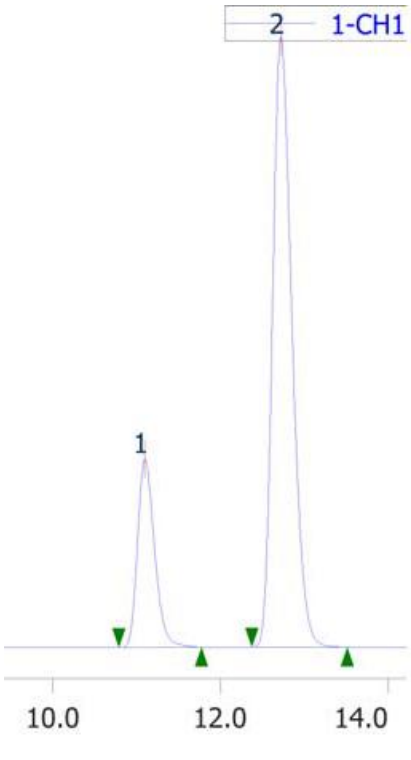
HPLC (CHIRALCEL OD-3, *n*-hexane/*i*-PrOH = 20:1 v/v, 0.525 mL min^{-1}, λ = 254 nm, 30 ºC), t_R = 11.1 min (minor), t_R = 12.7 min (major).

Racemic sample of **27a**



(*S*)-**27a**



Racemic sample of **27a**	(*S*)-**27a**
	

Peak #	**Ret. Time**	**Area**	**Area %**	**Peak #**	**Ret. Time**	**Area**	**Area %**
1	11.183	13565457	49.823	1	11.092	1402401	21.383
2	12.850	13661853	50.177	2	12.717	5155978	78.617

9. References

[S11] Vanderkooy, A.; Pfefferkorn, P.; Taylor, M. S. *Macromolecules* **2017**, *50*, 3807−3817.

[S12] (a) Almansa, R.; Collados, J. F.; Guijarro, D.; Yus, M. *Tetrahedron: Asymmetry* **2010**, *21*, 1421−1431. (b) Weber, M.; Jautze, S.; Frey, W.; Peters, R. *J. Am. Chem. Soc.* **2010**, *132*, 12222−12225. (c) Ojima, I.; Hirai, K.; Fujita, M.; Fuchikami, T. *J. Organomet. Chem.* **1985**, *279*, 203−214. (d) Otani, T. T.; Briley, R. M. *J. Pharm. Sci*. **1979**, *68*, 1366−1369. (e) Davies, T. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1157. (f) Weber, M.; Frey, W.; Peters, R. *Angew. Chem. Int. Ed.* **2013**, *52*, 13223−13227. (g) Metrano, A. J.; Miller, S. J. *J. Org. Chem.* **2014**, *79*, 1542−1554. (h) Liang, J.; Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 3154−3155. (i) Boyle, M.; Livingstone, K.; Henry. M. C.; Elwood, J. M. L.; Lopez-Fernandez, D.; Jamieson, C. *Org. Lett.* **2022**, *24*, 334−338. (j) Gledhill, A. P.; McCall, C. J.; Threadgill, M. D. *J. Org. Chem.* **1986**, *51*, 3196−3201. (k) Weber, M.; Jautze, S.; Frey, W.; Peters, R. *Chem. Eur. J.* **2012**, *18*, 14792−14804. (l) He, S.; Gu, H.; He, Y. -P.; Yang, X. *Org. Lett.* **2020**, *22*, 5633−5639. (m) Melhado, A. D.; Luparia, M.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 12638−12639. (m) Dálaigh, C. Ó.; Corr, S. A.; Gun'ko, Y.; Connon, S. J. *Angew. Chem. Int. Ed.* **2007**, *46*, 4329−4332. (n) Tokunaga, M.; Kiyosu, J.; Obora, Y.; Tsuji, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4481−4486. (o) Shaw, S. A.; Aleman, P.; Vedeys, E. *J. Am. Chem. Soc.* **2003**, *125*, 13368−13369.

[S13] Otto, K. E.; Hesse, S.; Wassermann, T. N.; Rice, C. A.; Suhm, M. A.; Stafforst, T.; Diederichsen, U. *Phys. Chem. Chem. Phys.* **2011**, *13,* 14119−14130

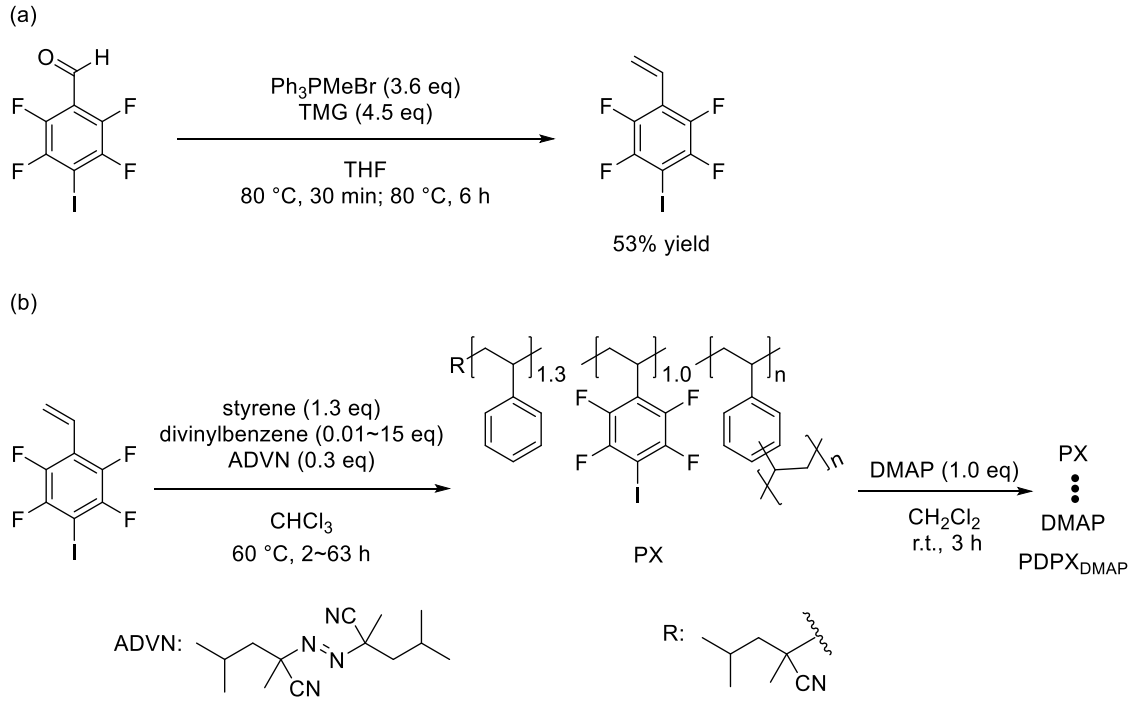
第５章
総括と展望

本学位研究では、ヨウ化テトラフルオロポリスチレン誘導体の合成法を確立し、不均一系求核触媒反応に応用した。共有結合による高分子固定化求核触媒の代替を目的として、ハロゲン結合供与部位を有する高分子を用い、4-アミノピリジンペンダント型高分子求核触媒を開発することで、効率的な不均一系求核触媒反応を達成した。本章に、本博士論文学位研究のまとめを示す。

5−1．総括

DMAP ペンダント型高分子触媒の合成（第２章）

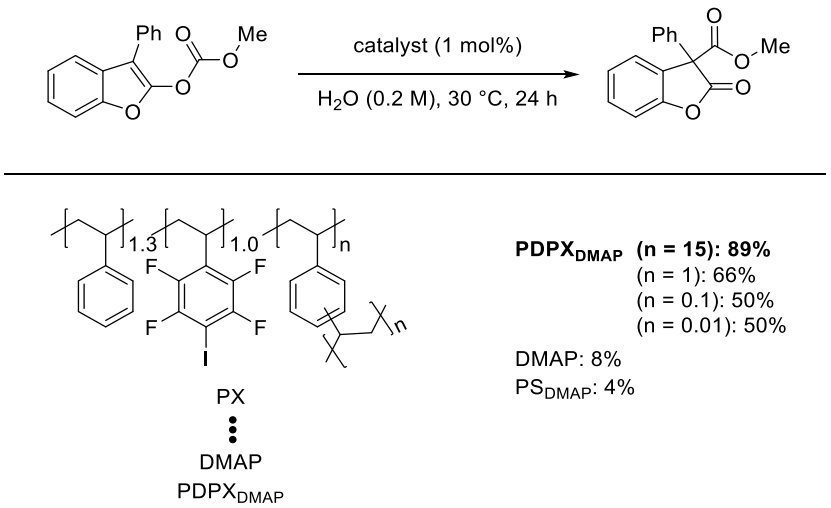
市販で入手可能なテトラフルオロ安息香酸からヨウ化テトラフルオロスチレン（TFIS）を合成するための合成手法を確立した。特に、ヨウ化テトラフルオロベンズアルデヒドの Wittig 反応を開発し、検討した種々の有機塩基の中で、TMG を用いた場合に、最も高い収率で TFIS が得られることを見出した（**Scheme 5-1a**）。また、相関分析により、Wittig 反応に有効な有機塩基として、1）イリド生成に適当な負電荷を有すること、2）アルデヒドおよびスチレンの分解を促進しない低求核性であること、3）生成物のスチレンと錯形成可能なハロゲン結合受容能を有すること、これら 3 つの要素が重要であることを示した。スチレンの精製では、展開溶媒としてペンタンを用いることで、目的生成物の分解を抑制できることを見出し、高純度の TFIS を得ることに成功した。さらに、高純度の TFIS を用いることによって、テトラフルオロヨードベンゼン部位を十分に有する高分子を得ることに成功し、１当量の DMAP を加え、目的とする高分子触媒（$PDPX_{DMAP}$）を調製する方法を確立した（**Scheme 5-1b**）。最後に、DNP ^{15}N NMR 測定により、得られた高分子 DMAP 体が、ヨウ化テトラフルオロビフェニル/DMAP と異なる化学シフト変化を示すことを見出した。



Scheme 5-1. Preparation of DMAP-Pendant Polymer Catalyst

高分子触媒による水中での *O*-アシル化ベンゾフラノンの転位反応（第３章）

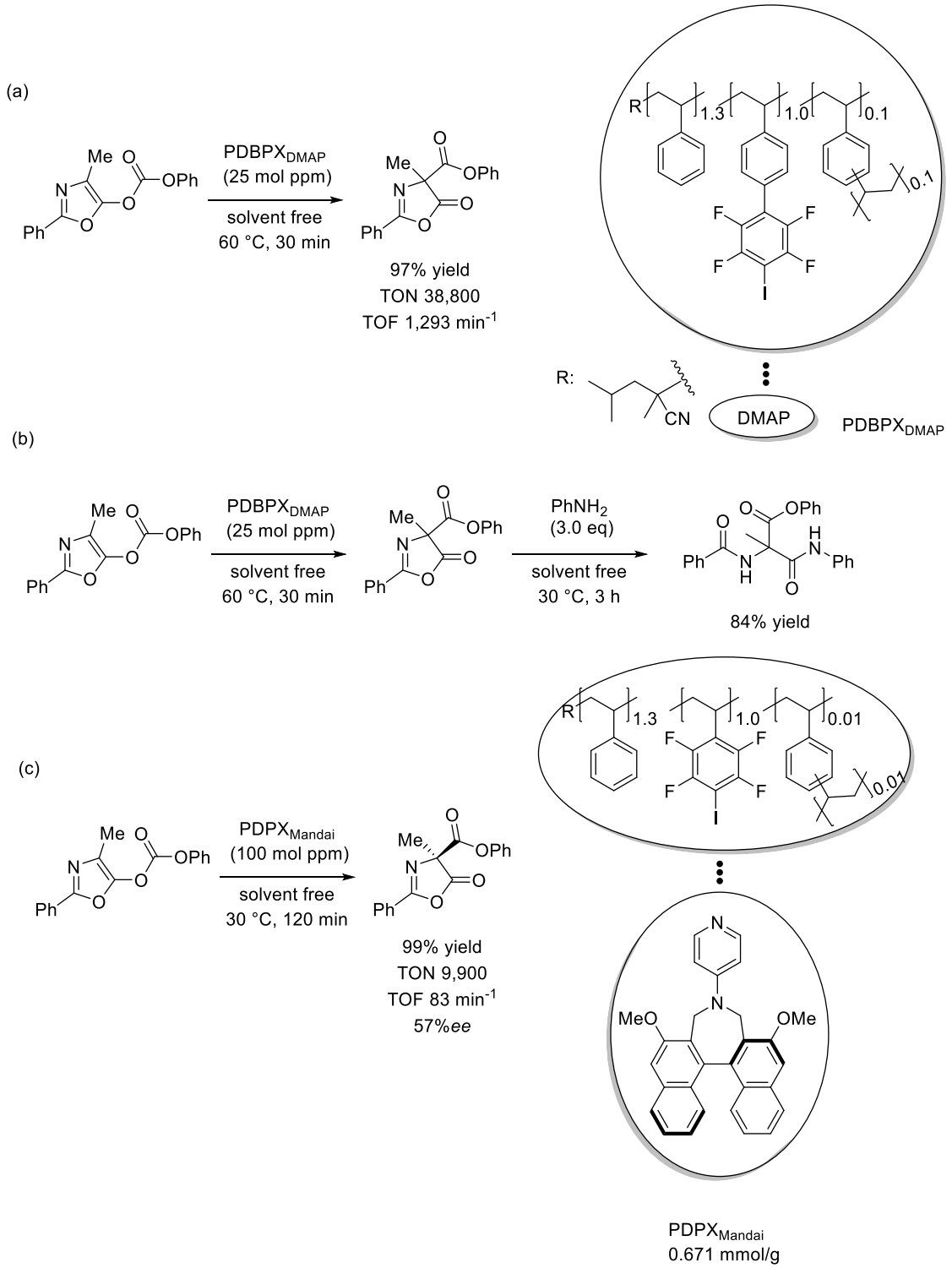
$PDPX_{DMAP}$を不均一系求核触媒として用いるベンゾフラノンのアシル基転位反応を開発した（**Scheme 5-2**）。本研究では、特に、テトラフルオロヨードスチレンに対してそれぞれ 0.01、0.1、1、15 当量の DVB から成る PX が、水中での不均一系触媒反応に与える影響を調べながら、$PDPX_{DMAP}$の水中での触媒機能を見出した。その結果、15 当量の DVB から合成した$PDPX_{DMAP}$が 0.01、0.1、1 当量の$PDPX_{DMAP}$よりも高収率で目的生成物を与えることを明らかにした。また、DMAP 単体や市販で入手可能なポリスチレン触媒 PS_{DMAP} を用いて対照実験を行い、$PDPX_{DMAP}$の有用性を示した。DMAP 単体やポリスチレン触媒 PS_{DMAP} では、目的生成物の収率が 10%以下となることを明らかにした。開発した$PDPX_{DMAP}$（n = 15）は様々な置換基を有する *O*-アシルベンゾフラノンに適用可能であり、対応する転位生成物を良好または高収率で与えることを見出した。高分子触媒としての再利用はできなかったが、本研究は、ハロゲン結合供与部位を有する高分子を水中での不均一系触媒反応に用いた初めての例である。



Scheme 5-2. Representative results for acyl rearrangement reaction of benzofuranones in H_2O catalyzed by $PDPX_{DMAP}$

高分子触媒による無溶媒での *O*-アシル化アズラクトンの転位反応（第４章）

DMAP ペンダント型高分子触媒 $PDPX_{DMAP}$ や $PDBPX_{DMAP}$ を用いる無溶媒でのアズラクトンのアシル基転位反応を開発した（**Scheme 5-3a**）。0.1 もしくは 0.01 当量のジビニルベンゼンから合成した $PDPX_{DMAP}$ や $PDBPX_{DMAP}$ が高い触媒活性を有し、ppm レベルの触媒量でアズラクトンのアシル基転位生成物を与えることを見出した。さらに、開発した無溶媒不均一系触媒反応が、広範な基質適用範囲を示すことを明らかにした。また、生成した *C*-アシルアズラクトンにアニリンを加えることで、4 置換 α-アミノ酸誘導体の合成に成功した（**Scheme 5-3b**）。不斉触媒反応への展開においては、中程度のエナンチオ選択性の獲得に成功した（**Scheme 5-3c**）。

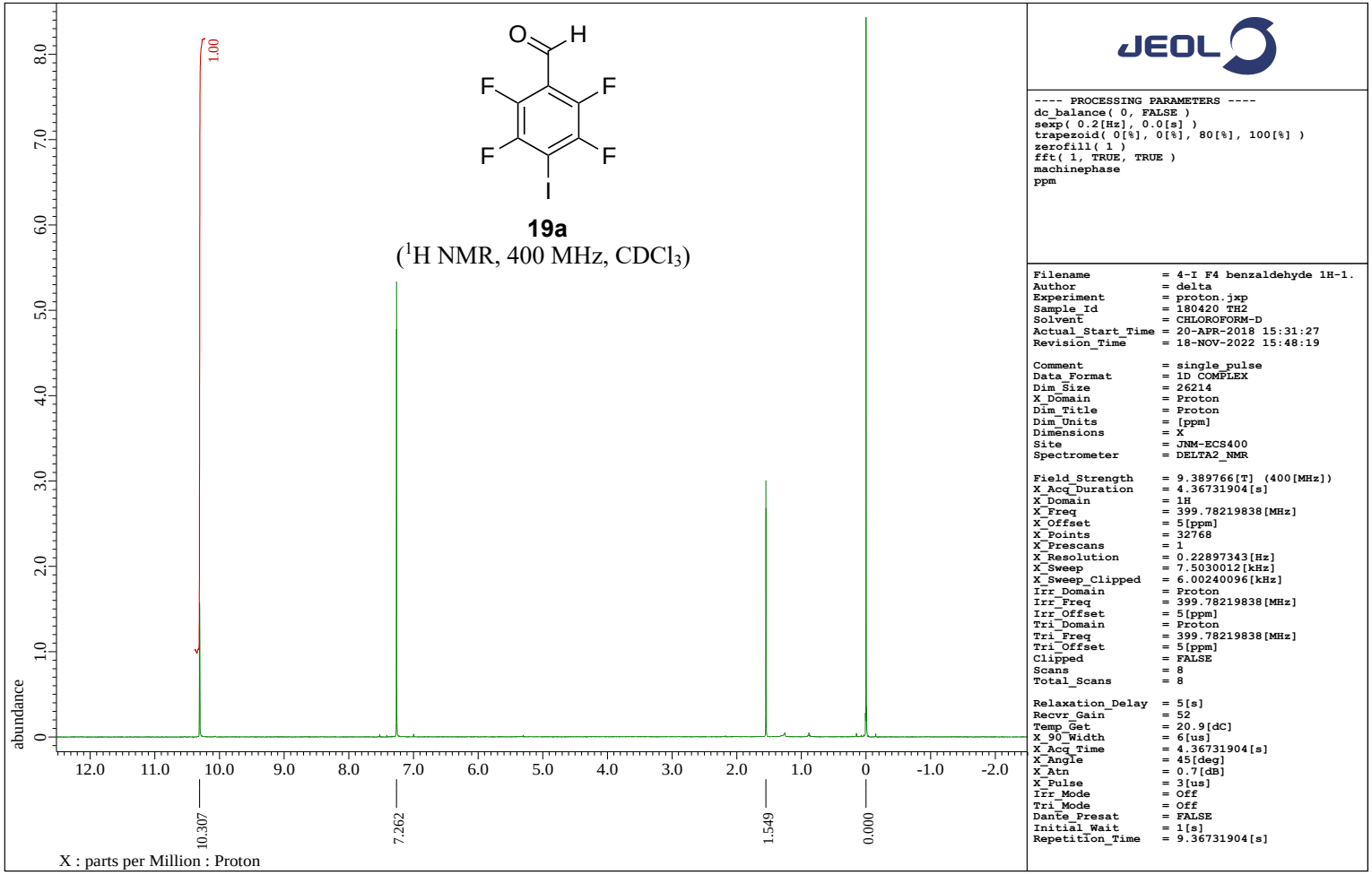


Scheme 5-3. Representative Results for Rearrangement Reaction of *O*-Acyl Azlactones

5–2. 展望

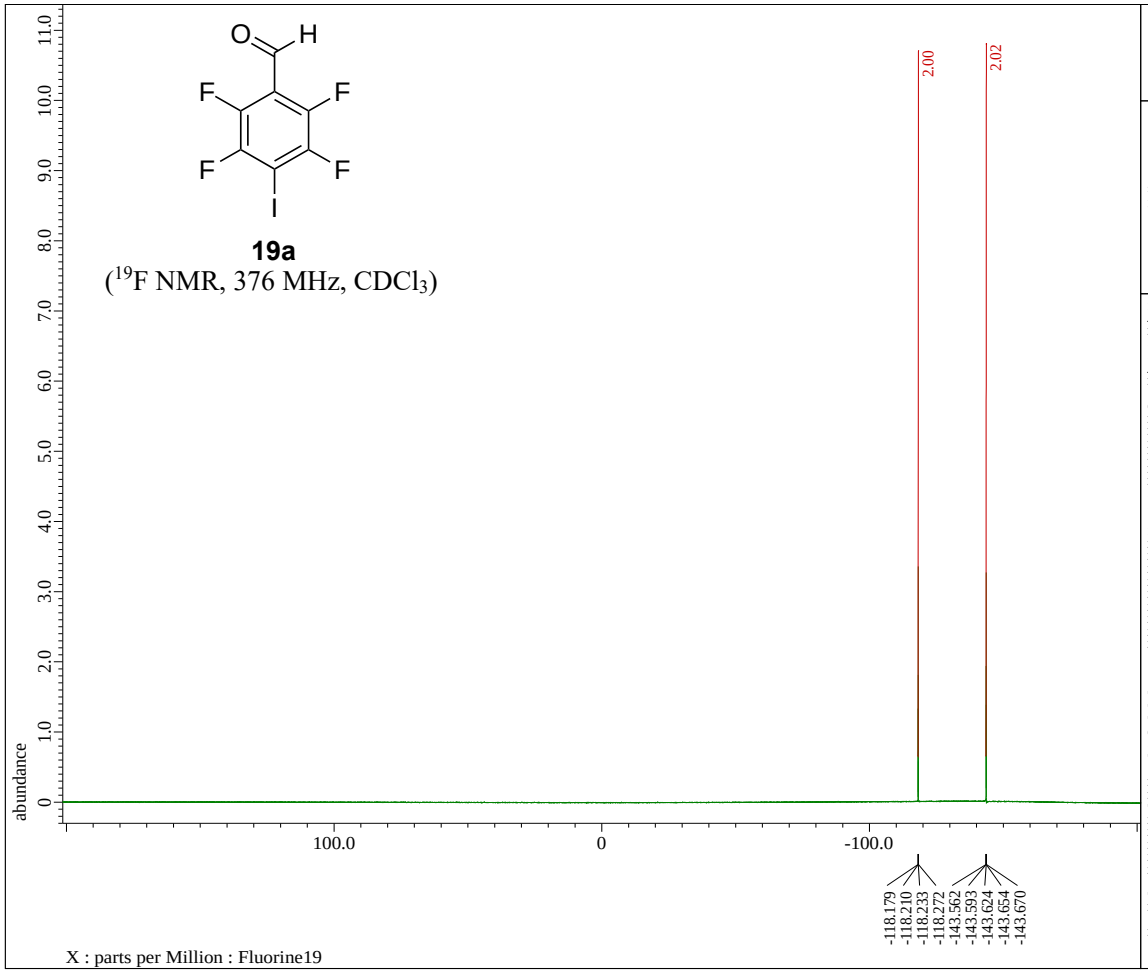
本博士論文学位研究により、これまで詳細が報告されていなかったヨウ化テトラフルオロポリスチレン誘導体の合成法を確立した。また、合成したヨウ化テトラフルオロポリスチレン誘導体を 4-アミノピリジンペンダント型高分子求核触媒として有機分子変換反応に応用し、高効率なアシル基転位反応の開発に成功した。本研究において見出された高い触媒活性は、C_6F_4I のハロゲン結合供与部位が反応基質と相互作用しているためと考えている。このような触媒反応場は、ヨウ化テトラフルオロポリスチレン誘導体を用いることで、初めて実現できる。今後、種々の不均一系求核触媒反応への応用展開が期待される。また、今回開発したペンダント型高分子触媒は、低分子系の有機触媒をそのまま用いて簡便に調製できる点に特長がある。第 4 章で述べたように、不斉触媒反応への展開も容易である。置換基の異なるキラル低分子系求核触媒を用いることで、高効率高立体選択的反応の達成が期待される。

本研究がハロゲン結合供与部位を有する機能性ポリマーの触媒反応への活用と高効率的な不均一系求核触媒反応の先駆けとなれば幸いである。



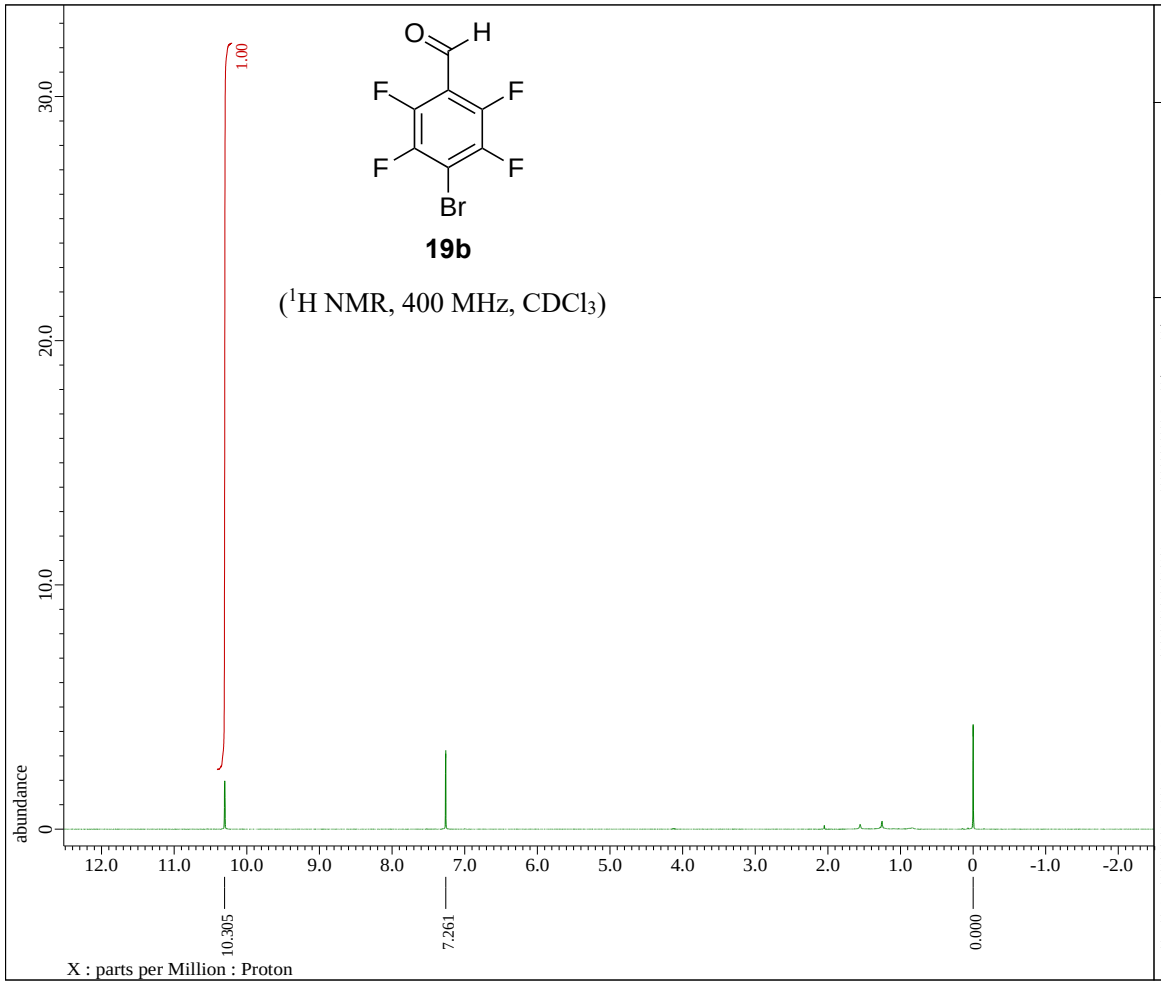

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 4-I F4 benzaldehyde 1H-1.
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 180420 TH2
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 20-APR-2018 15:31:27
Revision_Time       = 18-NOV-2022 15:48:19

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 4.36731904[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.22897343[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 52
Temp_Get            = 20.9[dC]
X_90_Width          = 6[us]
X_Acq_Time          = 4.36731904[s]
X_Angle             = 45[deg]
X_Atn               = 0.7[dB]
X_Pulse             = 3[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 9.36731904[s]
```



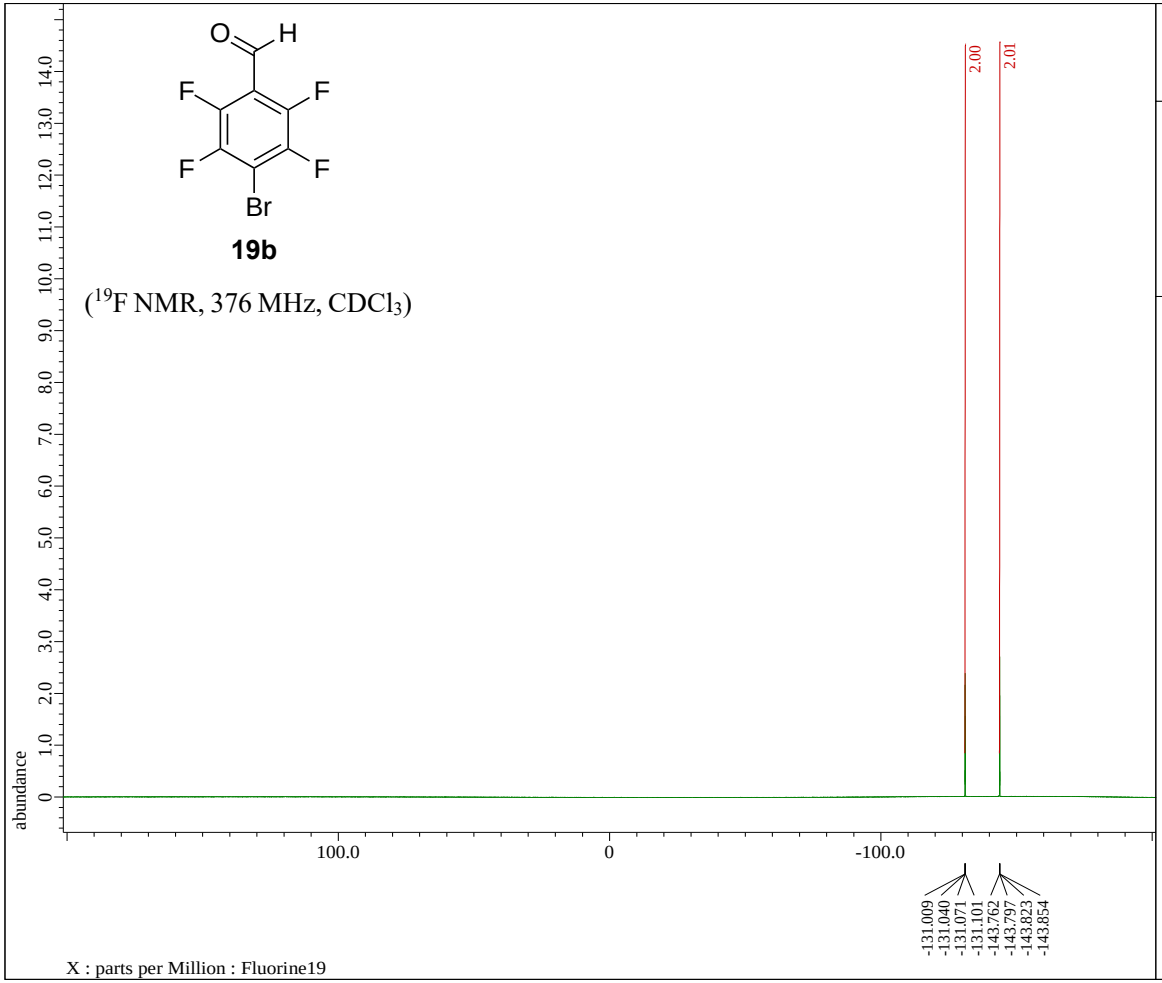

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: 4-I F4 benzaldehyde 19F.jdf
```

```
Filename            = 4-I F4 benzaldehyde 19F-1
Author              = delta
Experiment          = single_pulse.jxp
Sample_Id           = 180420_TH2
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 20-APR-2018 15:35:18
Revision_Time       = 18-NOV-2022 15:48:50

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 52429
X_Domain            = Fluori
Dim_Title           = Fluorine19
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 0.34603008[s]
X_Domain            = 19F
X_Freq              = 376.17105393[MHz]
X_Offset            = 0[ppm]
X_Points            = 65536
X_Prescans          = 1
X_Resolution        = 2.88992217[Hz]
X_Sweep             = 189.39393939[kHz]
X_Sweep_Clipped     = 151.51515152[kHz]
Irr_Domain          = Fluorine19
Irr_Freq            = 376.17105393[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Fluorine19
Tri_Freq            = 376.17105393[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 42
Temp_Get            = 21[dC]
X_90_Width          = 7.3[us]
X_Acq_Time          = 0.34603008[s]
X_Angle             = 45[deg]
X_Atn               = 2.6[dB]
X_Pulse             = 3.65[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 5.34603008[s]
```



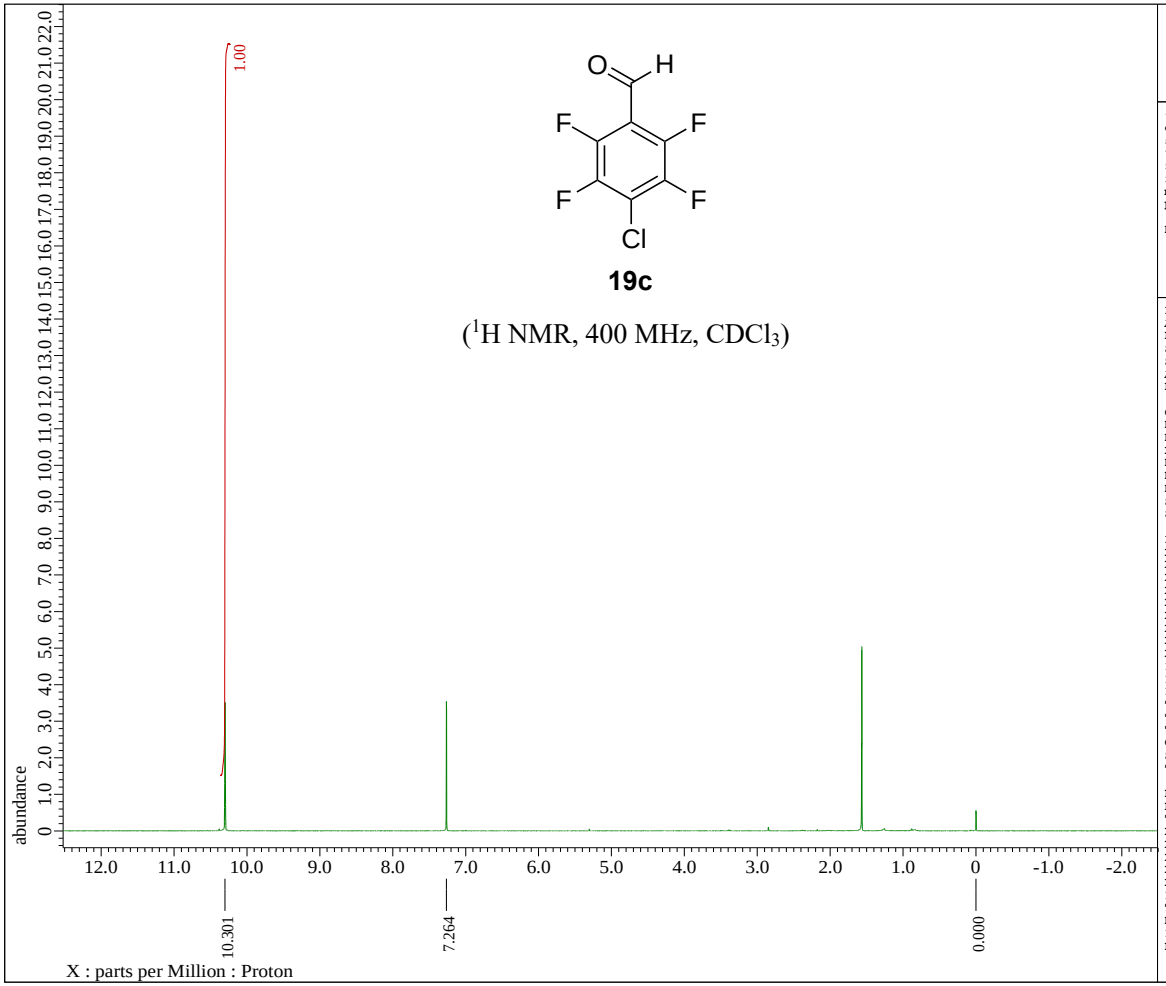

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: 4-Br F4 benzaldehyde 1H.jdf
```

```
Filename            = 4-Br F4 benzaldehyde 1H-1
Author              = delta
Experiment          = proton.jxp
Sample_Id           = SK221117_s15_pure
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 21-NOV-2022 15:29:14
Revision_Time       = 29-NOV-2022 09:49:24

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 4.36731904[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.22897343[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 52
Temp_Get            = 19.1[dC]
X_90_Width          = 6.3[us]
X_Acq_Time          = 4.36731904[s]
X_Angle             = 45[deg]
X_Atn               = 0.7[dB]
X_Pulse             = 3.15[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 9.36731904[s]
```



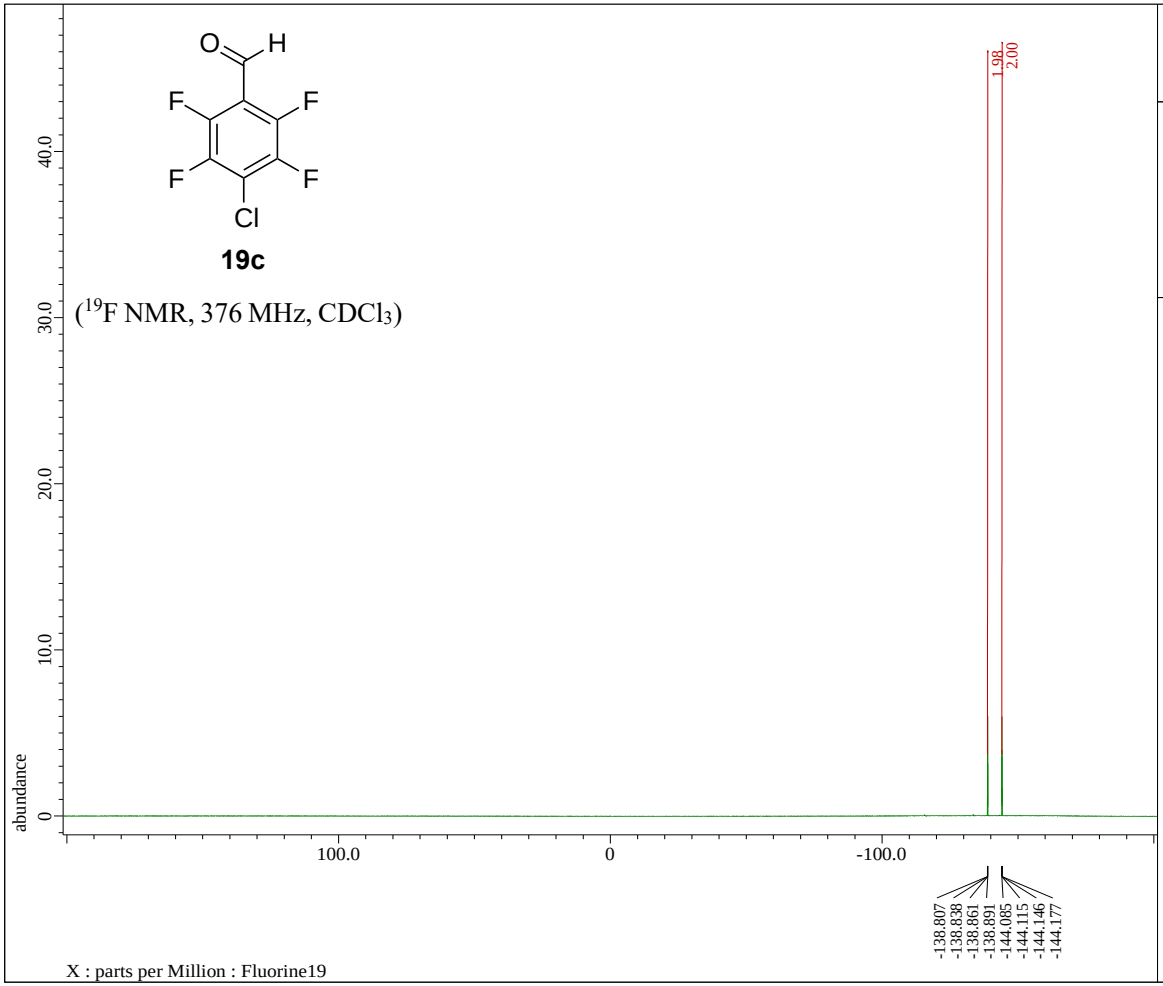

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
phase( 7.97525, 0, 50[%] )

Derived from: 4-Br F4 benzaldehyde 19F.jdf
```

```
Filename            = 4-Br F4 benzaldehyde 19F-
Author              = delta
Experiment          = single_pulse.jxp
Sample_Id           = SK221117_s15_pure
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 21-NOV-2022 15:26:06
Revision_Time       = 29-NOV-2022 09:50:00

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 52429
X_Domain            = Fluori
Dim_Title           = Fluorine19
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 0.34603008[s]
X_Domain            = 19F
X_Freq              = 376.17105393[MHz]
X_Offset            = 0[ppm]
X_Points            = 65536
X_Prescans          = 1
X_Resolution        = 2.88992217[Hz]
X_Sweep             = 189.39393939[kHz]
X_Sweep_Clipped     = 151.51515152[kHz]
Irr_Domain          = Fluorine19
Irr_Freq            = 376.17105393[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Fluorine19
Tri_Freq            = 376.17105393[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 40
Temp_Get            = 19.4[dC]
X_90_Width          = 8[us]
X_Acq_Time          = 0.34603008[s]
X_Angle             = 45[deg]
X_Atn               = 2.6[dB]
X_Pulse             = 4[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 5.34603008[s]
```



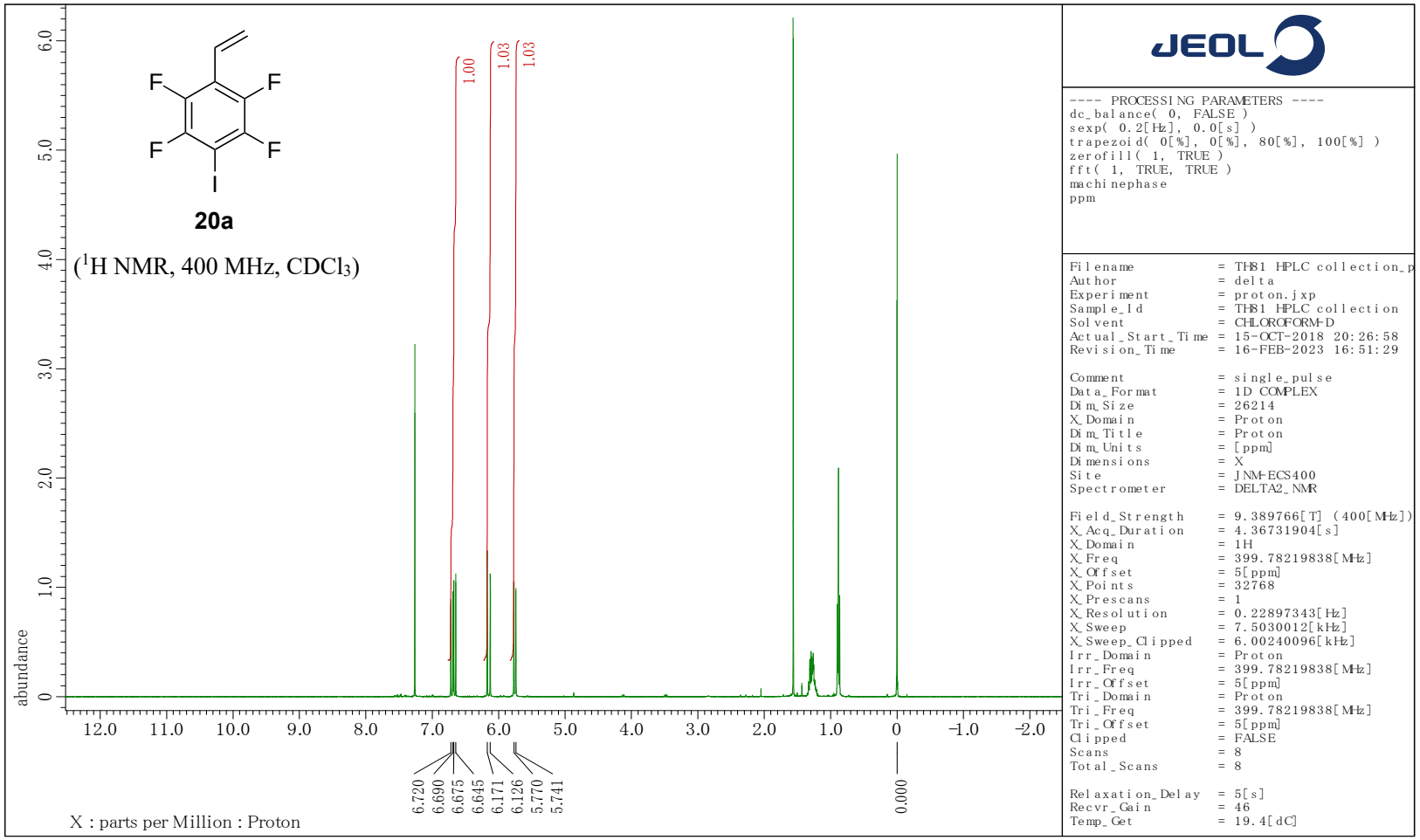

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: NO 221116 1978 wash by hexane_p
```

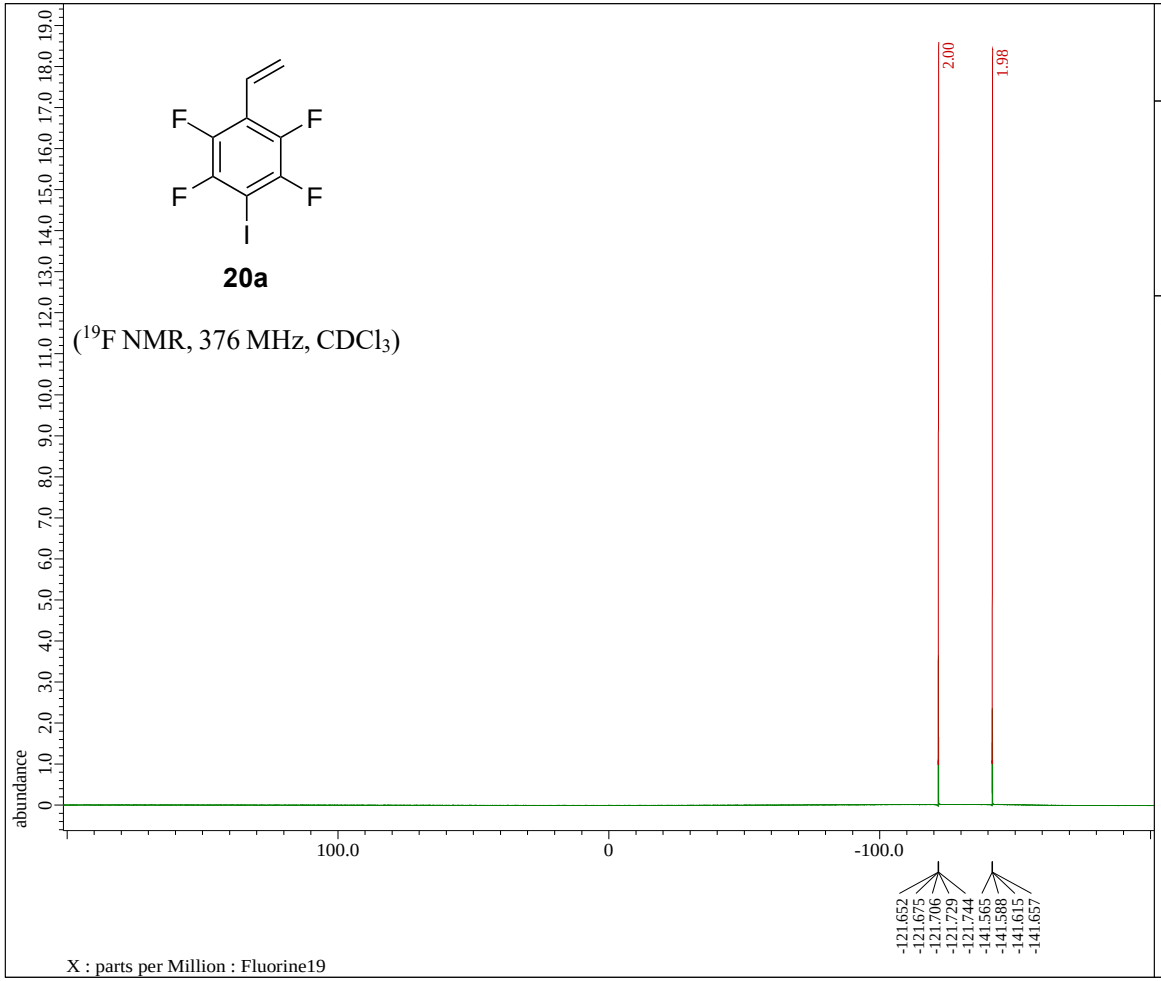
```
Filename            = NO 221116 1978 wash by he
Author              = delta
Experiment          = proton.jxp
Sample_Id           = NO 221116 1978 wash by he
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 16-NOV-2022 16:58:54
Revision_Time       = 17-NOV-2022 17:17:55

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 4.36731904[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.22897343[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 54
Temp_Get            = 19.2[dC]
X_90_Width          = 6.3[us]
X_Acq_Time          = 4.36731904[s]
X_Angle             = 45[deg]
X_Atn               = 0.7[dB]
X_Pulse             = 3.15[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 9.36731904[s]
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: NO 221116 1978 wash by hexane_1
```

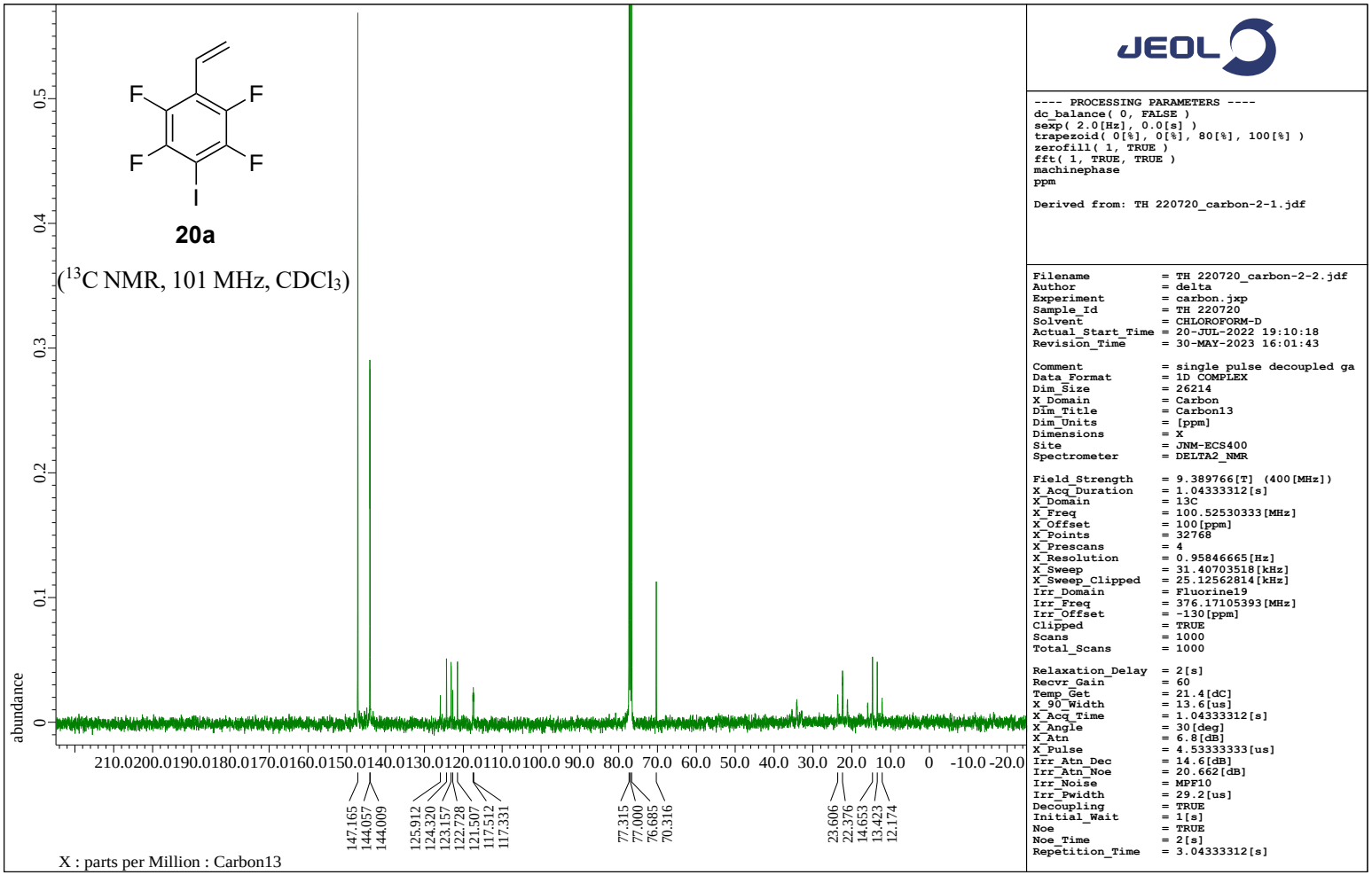
```
Filename           = NO 221116 1978 wash by he
Author             = delta
Experiment         = single_pulse.jxp
Sample_Id          = NO 221116 1978 wash by he
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 16-NOV-2022 17:02:43
Revision_Time      = 17-NOV-2022 17:15:44

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 52429
X_Domain           = Fluori
Dim_Title          = Fluorine19
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECS400
Spectrometer       = DELTA2_NMR

Field_Strength     = 9.389766[T] (400[MHz])
X_Acq_Duration     = 0.34603008[s]
X_Domain           = 19F
X_Freq             = 376.17105393[MHz]
X_Offset           = 0[ppm]
X_Points           = 65536
X_Prescans         = 1
X_Resolution       = 2.88992217[Hz]
X_Sweep            = 189.39393939[kHz]
X_Sweep_Clipped    = 151.51515152[kHz]
Irr_Domain         = Fluorine19
Irr_Freq           = 376.17105393[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = Fluorine19
Tri_Freq           = 376.17105393[MHz]
Tri_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 8
Total_Scans        = 8

Relaxation_Delay   = 5[s]
Recvr_Gain         = 42
Temp_Get           = 19.2[dC]
X_90_Width         = 8[us]
X_Acq_Time         = 0.34603008[s]
X_Angle            = 45[deg]
X_Atn              = 2.6[dB]
X_Pulse            = 4[us]
Irr_Mode           = Off
Tri_Mode           = Off
Dante_Presat       = FALSE
Initial_Wait       = 1[s]
Repetition_Time    = 5.34603008[s]
```

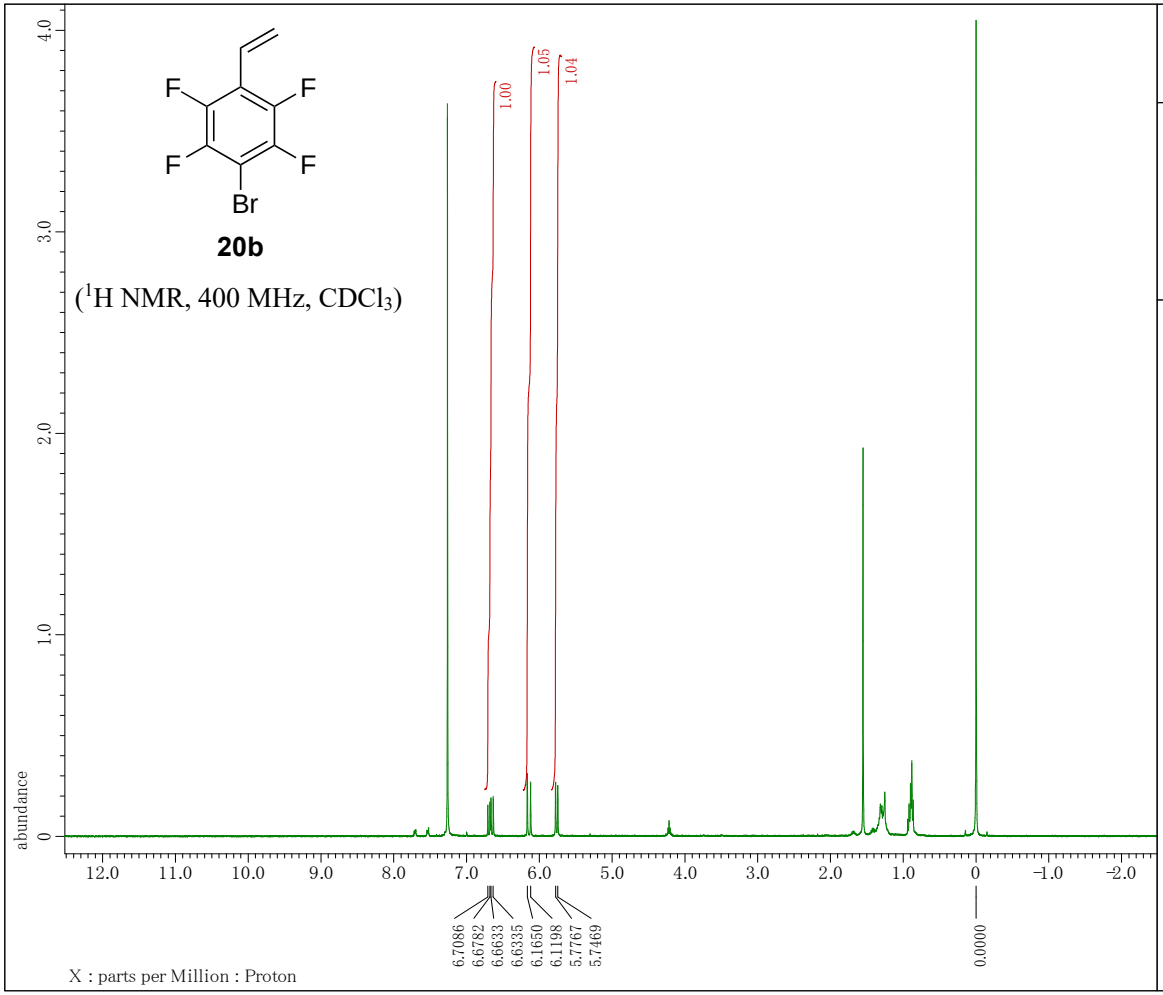

F
F
F
F
I
20a
(1H NMR, 400 MHz, CDCl3)
1.00
1.03
1.03
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
6.720
6.690
6.675
6.645
6.171
6.126
5.770
5.741
0.000
X : parts per Million : Proton
JEOL
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = THB1 HPLC collection_p
Author = delta
Experiment = proton.jxp
Sample_Id = THB1 HPLC collection
Solvent = CHLOROFORM-D
Actual_Start_Time = 15-OCT-2018 20:26:58
Revision_Time = 16-FEB-2023 16:51:29
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 46
Temp_Get = 19.4[dC]




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: TFIS 19F.jdf
```

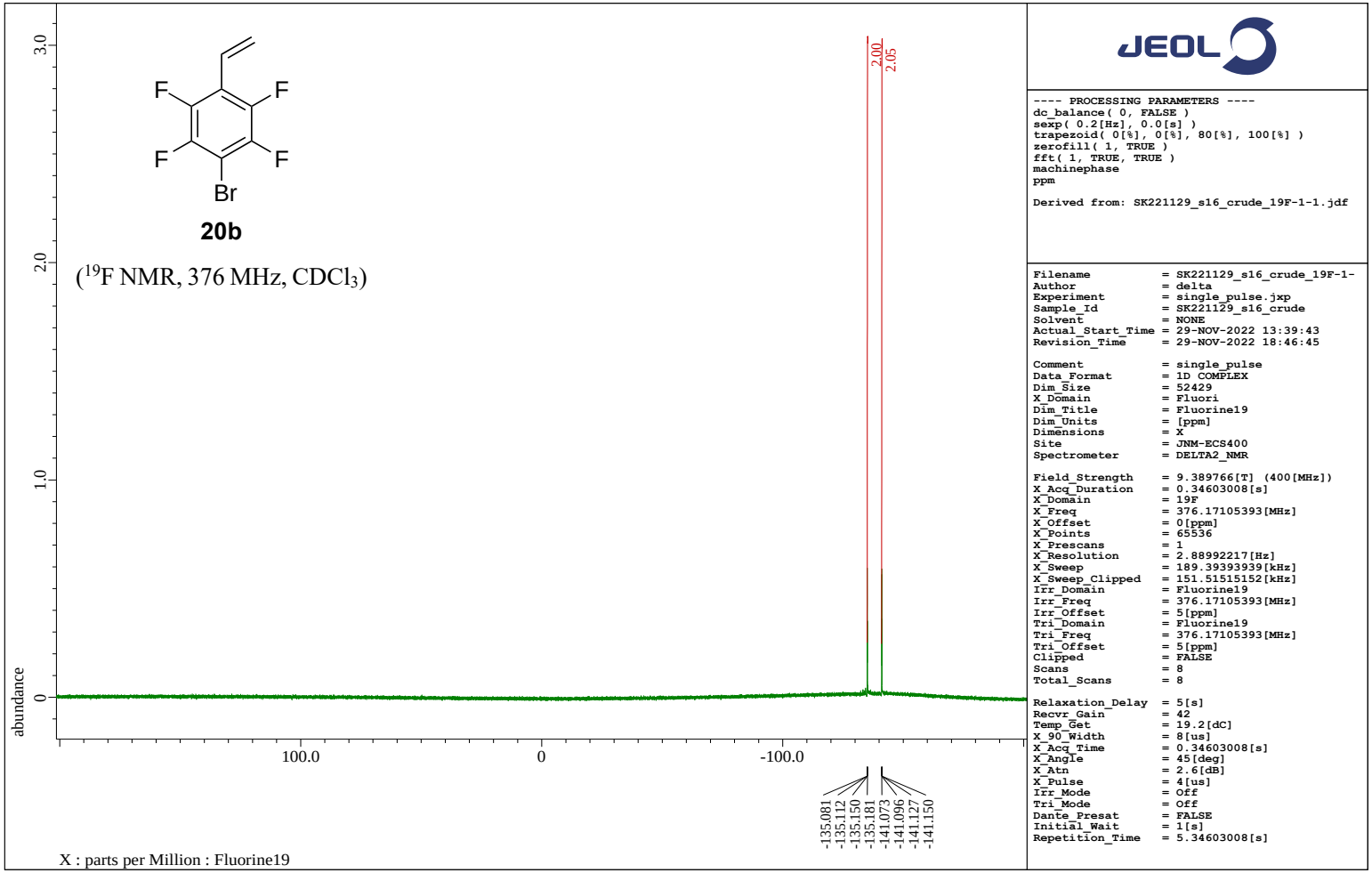
```
Filename            = TFIS 19F-1.jdf
Author              = delta
Experiment          = single_pulse.jxp
Sample_Id           = 191024 TH330
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 24-OCT-2019 16:06:27
Revision_Time       = 18-NOV-2022 15:51:23

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 52429
X_Domain            = Fluori
Dim_Title           = Fluorine19
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 0.34603008[s]
X_Domain            = 19F
X_Freq              = 376.17105393[MHz]
X_Offset            = 0[ppm]
X_Points            = 65536
X_Prescans          = 1
X_Resolution        = 2.88992217[Hz]
X_Sweep             = 189.39393939[kHz]
X_Sweep_Clipped     = 151.51515152[kHz]
Irr_Domain          = Fluorine19
Irr_Freq            = 376.17105393[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Fluorine19
Tri_Freq            = 376.17105393[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 42
Temp_Get            = 20.2[dC]
X_90_Width          = 7.3[us]
X_Acq_Time          = 0.34603008[s]
X_Angle             = 45[deg]
X_Atn               = 2.6[dB]
X_Pulse             = 3.65[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 5.34603008[s]
```

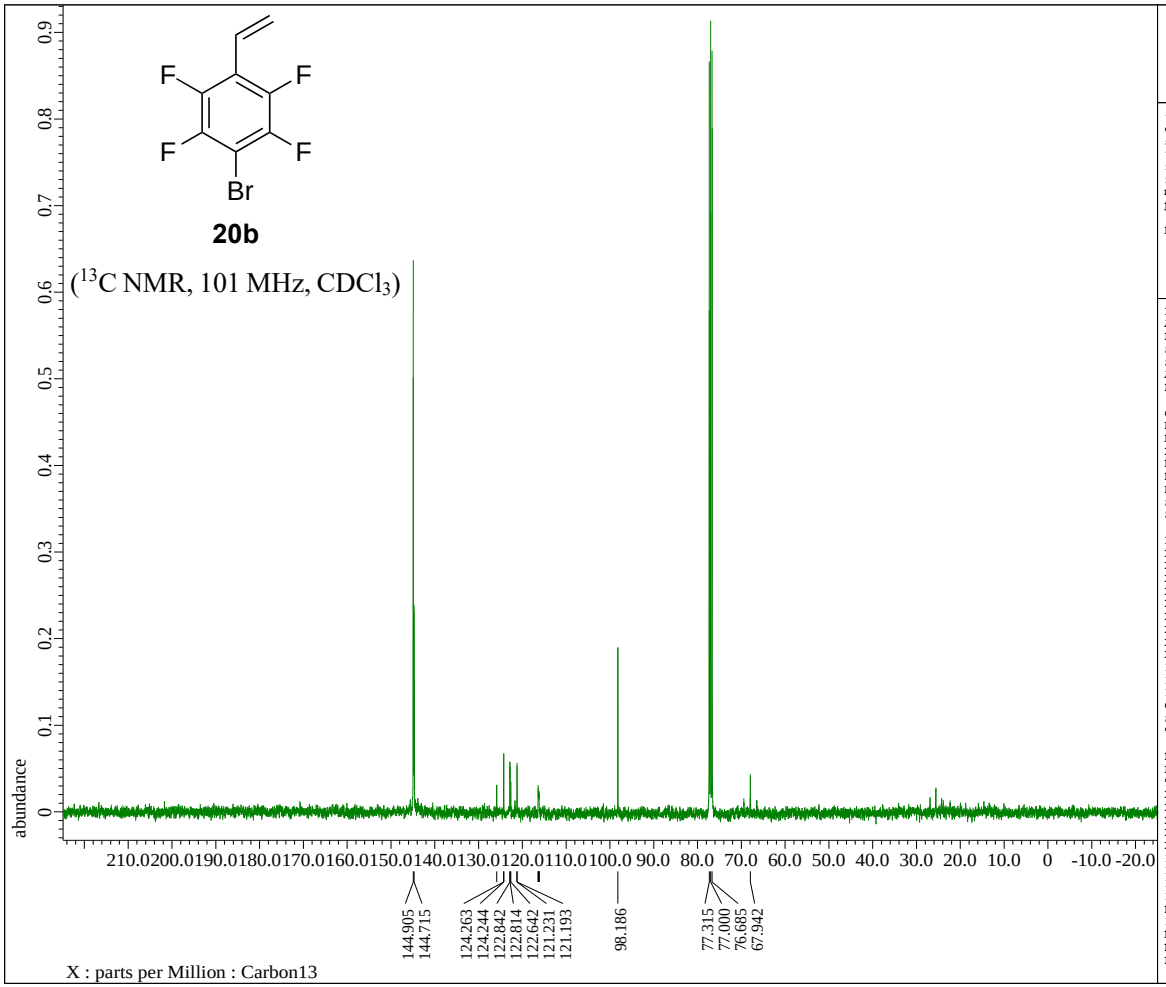

F
F
F
F
I
20a
(^{13}C NMR, 101 MHz, $CDCl_3$)
abundance
0
0.1
0.2
0.3
0.4
0.5
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
147.165
144.057
144.009
125.912
124.320
123.157
122.728
121.507
117.512
117.331
77.315
77.000
76.685
70.316
23.606
22.376
14.653
13.423
12.174
X : parts per Million : Carbon13
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Derived from: TH 220720_carbon-2-1.jdf
Filename = TH 220720_carbon-2-2.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = TH 220720
Solvent = CHLOROFORM-D
Actual_Start_Time = 20-JUL-2022 19:10:18
Revision_Time = 30-MAY-2023 16:01:43
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Fluorine19
Irr_Freq = 376.17105393[MHz]
Irr_Offset = -130[ppm]
Clipped = TRUE
Scans = 1000
Total_Scans = 1000
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.4[dC]
X_90_Width = 13.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 6.8[dB]
X_Pulse = 4.53333333[us]
Irr_Atn_Dec = 14.6[dB]
Irr_Atn_Noe = 20.662[dB]
Irr_Noise = MPF10
Irr_Pwidth = 29.2[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 3.04333312[s]




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

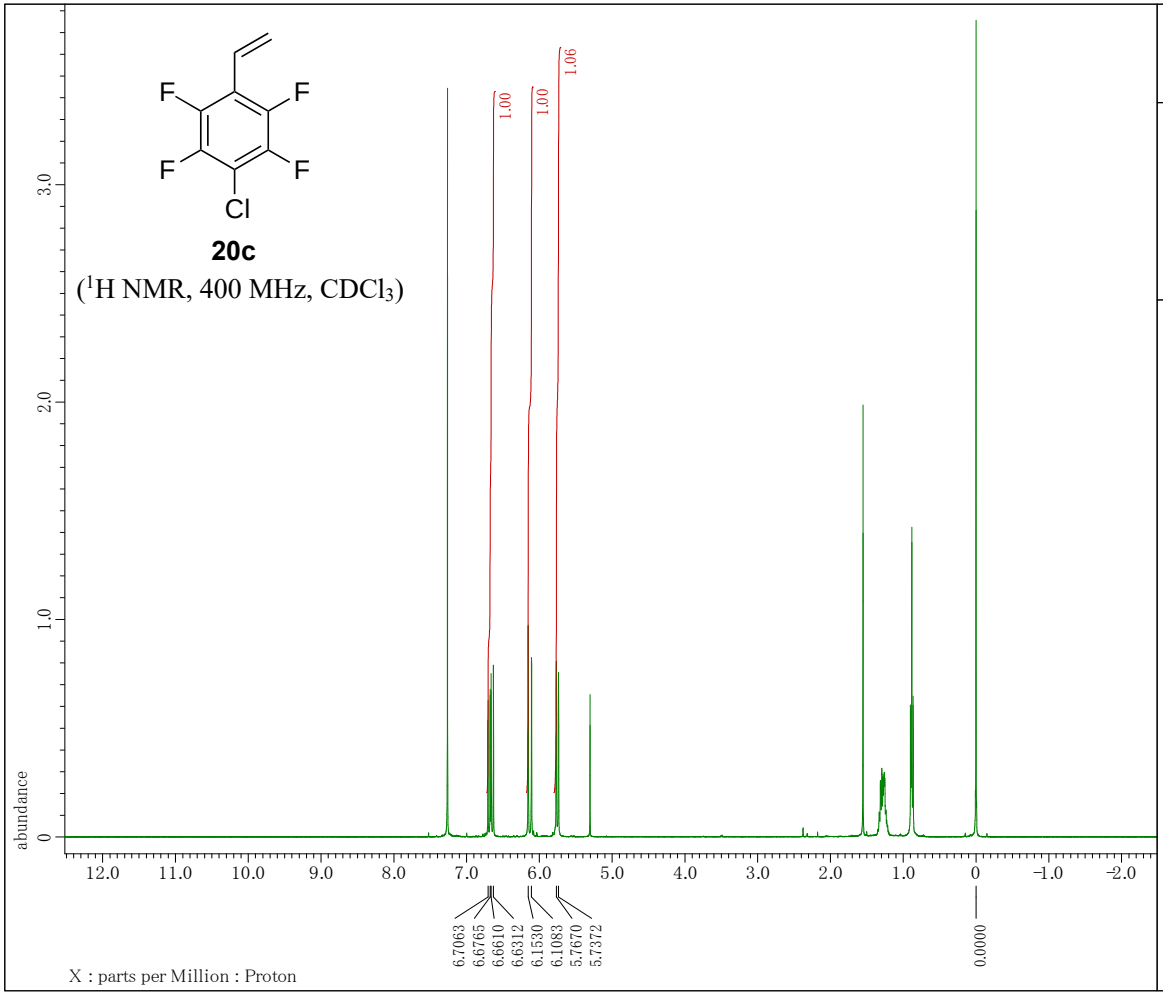
```
Filename            = 230307 C6F4Brstyrene_proto
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 230307 C6F4BrCHO
Solvent             = CHLOROFORM-D
Creation_Time       =  7-MAR-2023 14:21:56
Revision_Time       =  9-MAR-2023 09:54:27
Current_Time        =  9-MAR-2023 09:55:18

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 4.36731904[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.22897343[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 56
Temp_Get            = 18.9[dC]
X_90_Width          = 6.3[us]
X_Acq_Time          = 4.36731904[s]
X_Angle             = 45[deg]
X_Atn               = 0.7[dB]
X_Pulse             = 3.15[us]
Irr_Mode            = Off
Tri_Mode            = Off
```


F
F
F
F
Br
20b
(19F NMR, 376 MHz, CDCl3)
3.0
2.0
1.0
0
abundance
2.00
2.05
100.0
0
-100.0
-135.081
-135.112
-135.150
-135.181
-141.073
-141.096
-141.127
-141.150
X : parts per Million : Fluorine19
JEOL
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Derived from: SK221129_s16_crude_19F-1-1.jdf
Filename = SK221129_s16_crude_19F-1-
Author = delta
Experiment = single_pulse.jxp
Sample_Id = SK221129_s16_crude
Solvent = NONE
Actual_Start_Time = 29-NOV-2022 13:39:43
Revision_Time = 29-NOV-2022 18:46:45
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 52429
X_Domain = Fluori
Dim_Title = Fluorine19
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 0.34603008[s]
X_Domain = 19F
X_Freq = 376.17105393[MHz]
X_Offset = 0[ppm]
X_Points = 65536
X_Prescans = 1
X_Resolution = 2.88992217[Hz]
X_Sweep = 189.39393939[kHz]
X_Sweep_Clipped = 151.51515152[kHz]
Irr_Domain = Fluorine19
Irr_Freq = 376.17105393[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Fluorine19
Tri_Freq = 376.17105393[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 42
Temp_Get = 19.2[dC]
X_90_Width = 8[us]
X_Acq_Time = 0.34603008[s]
X_Angle = 45[deg]
X_Atn = 2.6[dB]
X_Pulse = 4[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 5.34603008[s]



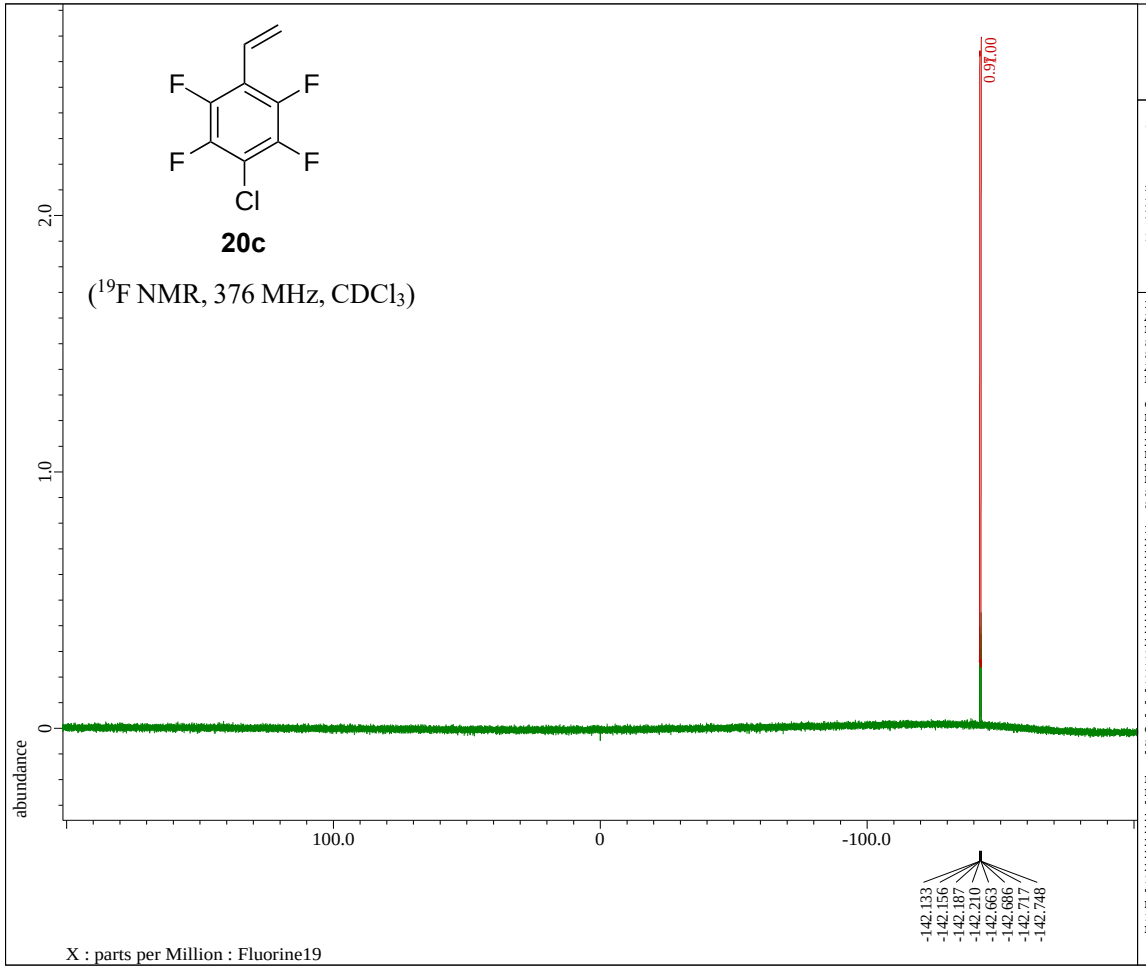

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: NO 230530 2150 TFBrS 13C_carbon
```

```
Filename            = NO 230530 2150 TFBrS 13C_
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = NO 230530 2150 TFBrS 13C
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 30-MAY-2023 15:01:07
Revision_Time       = 30-MAY-2023 15:41:21

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Fluorine19
Irr_Freq            = 376.17105393[MHz]
Irr_Offset          = -130[ppm]
Clipped             = TRUE
Scans               = 512
Total_Scans         = 512

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 19.9[dC]
X_90_Width          = 13.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
X_Atn               = 6.8[dB]
X_Pulse             = 4.53333333[us]
Irr_Atn_Dec         = 14.8[dB]
Irr_Atn_Noe         = 20.662[dB]
Irr_Noise           = MPF10
Irr_Pwidth          = 29.2[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 3.04333312[s]
```



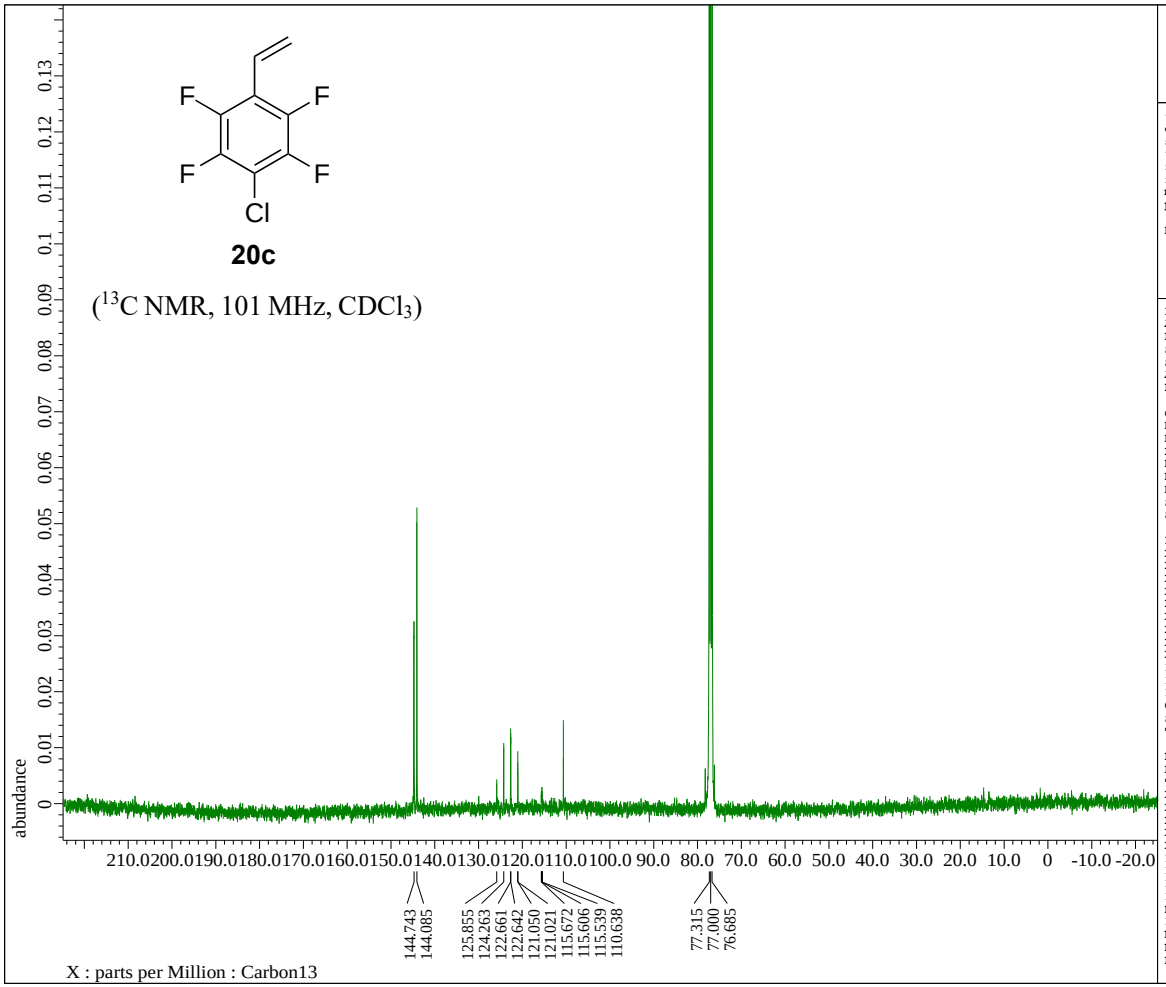

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 230308 C6F4Clstyrene_proto
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 230308 C6F4Clstyrene
Solvent             = CHLOROFORM-D
Creation_Time       =  8-MAR-2023 16:13:47
Revision_Time       =  9-MAR-2023 09:42:22
Current_Time        =  9-MAR-2023 09:42:43

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 4.36731904[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.22897343[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 46
Temp_Get            = 18.8[dC]
X_90_Width          = 6.3[us]
X_Acq_Time          = 4.36731904[s]
X_Angle             = 45[deg]
X_Atn               = 0.7[dB]
X_Pulse             = 3.15[us]
Irr_Mode            = Off
Tri_Mode            = Off
```



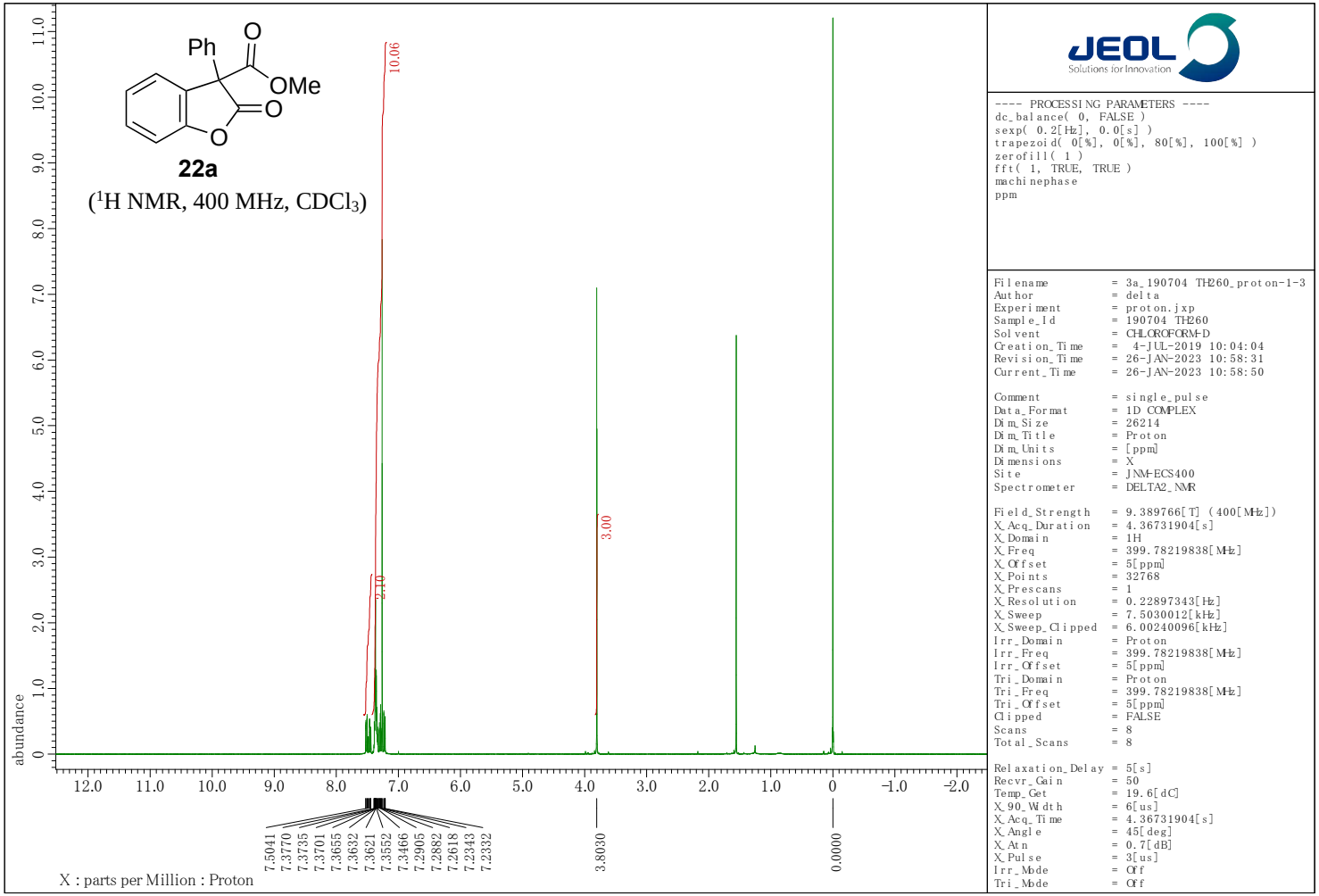

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
phase( -44.97696, 0, 50[%] )

Derived from: TFClS 19F column.jdf
```

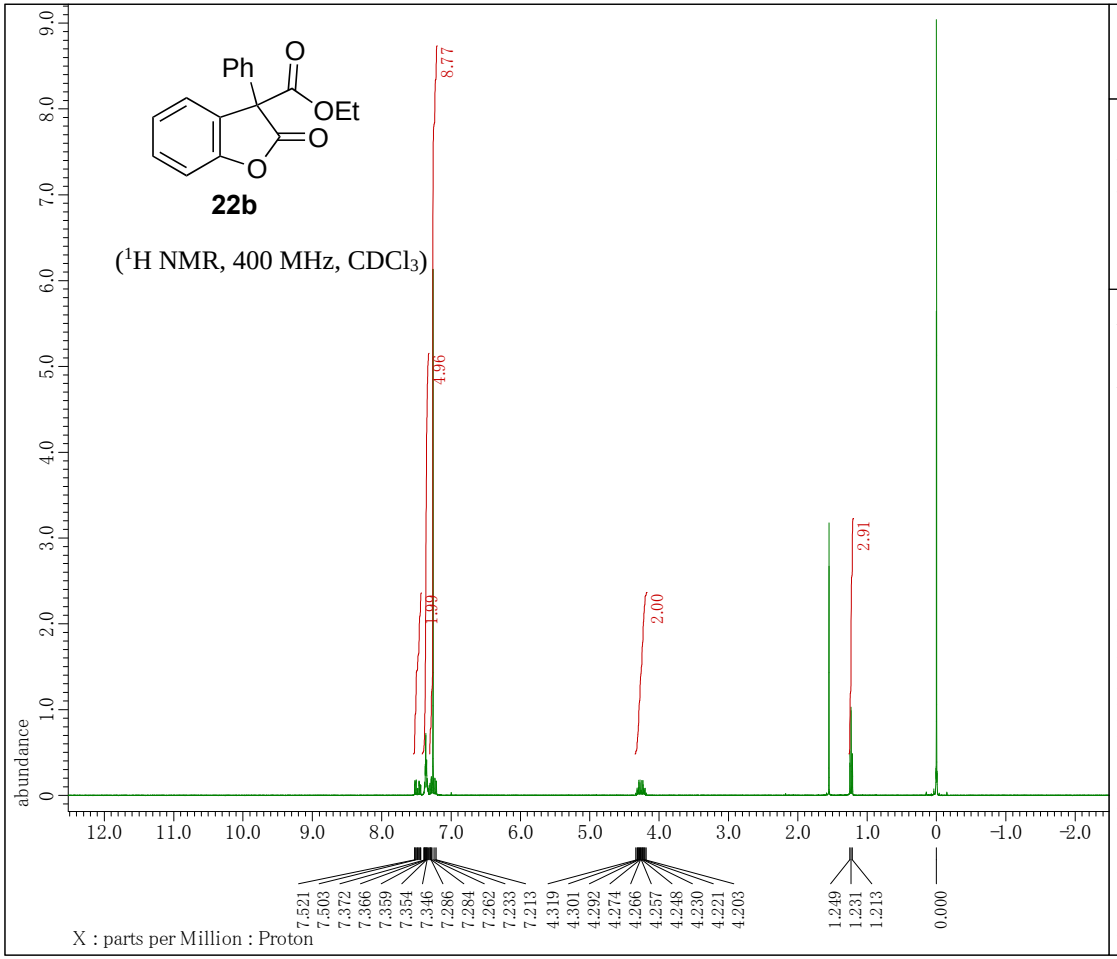
```
Filename            = TFClS 19F column-1.jdf
Author              = delta
Experiment          = single_pulse.jxp
Sample_Id           = SK221130_s18_Cl_column-He
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 30-NOV-2022 15:51:58
Revision_Time       = 30-NOV-2022 18:48:36

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 52429
X_Domain            = Fluori
Dim_Title           = Fluorine19
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 0.34603008[s]
X_Domain            = 19F
X_Freq              = 376.17105393[MHz]
X_Offset            = 0[ppm]
X_Points            = 65536
X_Prescans          = 1
X_Resolution        = 2.88992217[Hz]
X_Sweep             = 189.39393939[kHz]
X_Sweep_Clipped     = 151.51515152[kHz]
Irr_Domain          = Fluorine19
Irr_Freq            = 376.17105393[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Fluorine19
Tri_Freq            = 376.17105393[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 46
Temp_Get            = 19.4[dC]
X_90_Width          = 8[us]
X_Acq_Time          = 0.34603008[s]
X_Angle             = 45[deg]
X_Atn               = 2.6[dB]
X_Pulse             = 4[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 5.34603008[s]
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: C6F4Clstyrene 19F decoupling_ca
```

```
Filename            = C6F4Clstyrene 19F decoupl
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 230309 C6F4Clstyrene 19F
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  9-MAR-2023 19:31:18
Revision_Time       = 30-MAY-2023 16:03:09

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Fluorine19
Irr_Freq            = 376.17105393[MHz]
Irr_Offset          = -130[ppm]
Clipped             = FALSE
Scans               = 16000
Total_Scans         = 16000

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 19.5[dC]
X_90_Width          = 13.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
X_Atn               = 6.8[dB]
X_Pulse             = 4.53333333[us]
Irr_Atn_Dec         = 14.6[dB]
Irr_Atn_Noe         = 20.662[dB]
Irr_Noise           = MPF10
Irr_Pwidth          = 29.2[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 3.04333312[s]
```


Ph
O
OMe
O
O
22a
(1H NMR, 400 MHz, CDCl3)
10.06
2.10
3.00
abundance
X : parts per Million : Proton
7.5041
7.3770
7.3735
7.3701
7.3655
7.3632
7.3621
7.3552
7.3466
7.2905
7.2882
7.2618
7.2343
7.2332
3.8030
0.0000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = 3a_190704 TH260_proton-1-3
Author = delta
Experiment = proton.jxp
Sample_Id = 190704 TH260
Solvent = CHLOROFORM-D
Creation_Time = 4-JUL-2019 10:04:04
Revision_Time = 26-JAN-2023 10:58:31
Current_Time = 26-JAN-2023 10:58:50
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 50
Temp_Get = 19.6[dC]
X_90_Width = 6[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3[us]
Irr_Mode = Off
Tri_Mode = Off



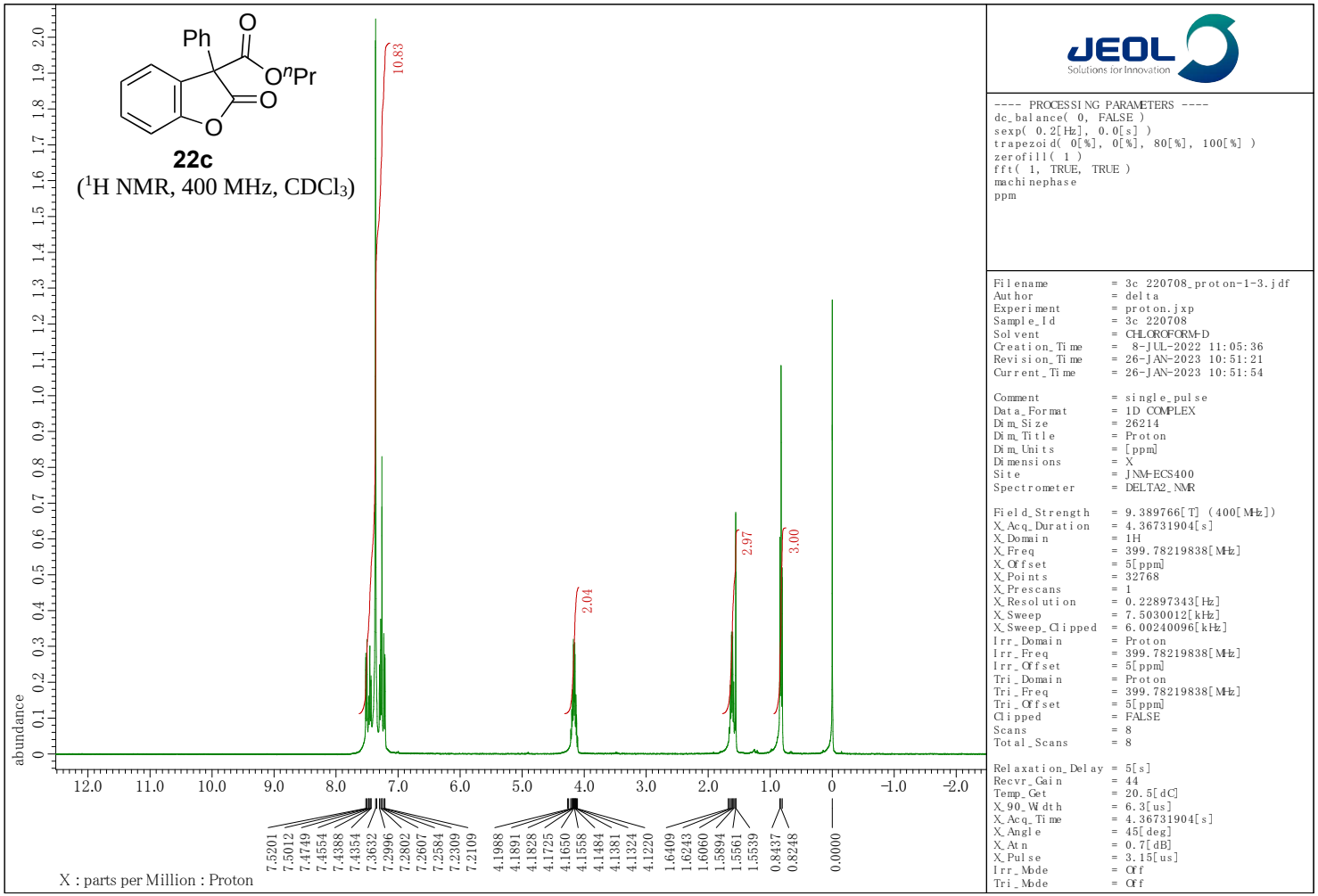
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm

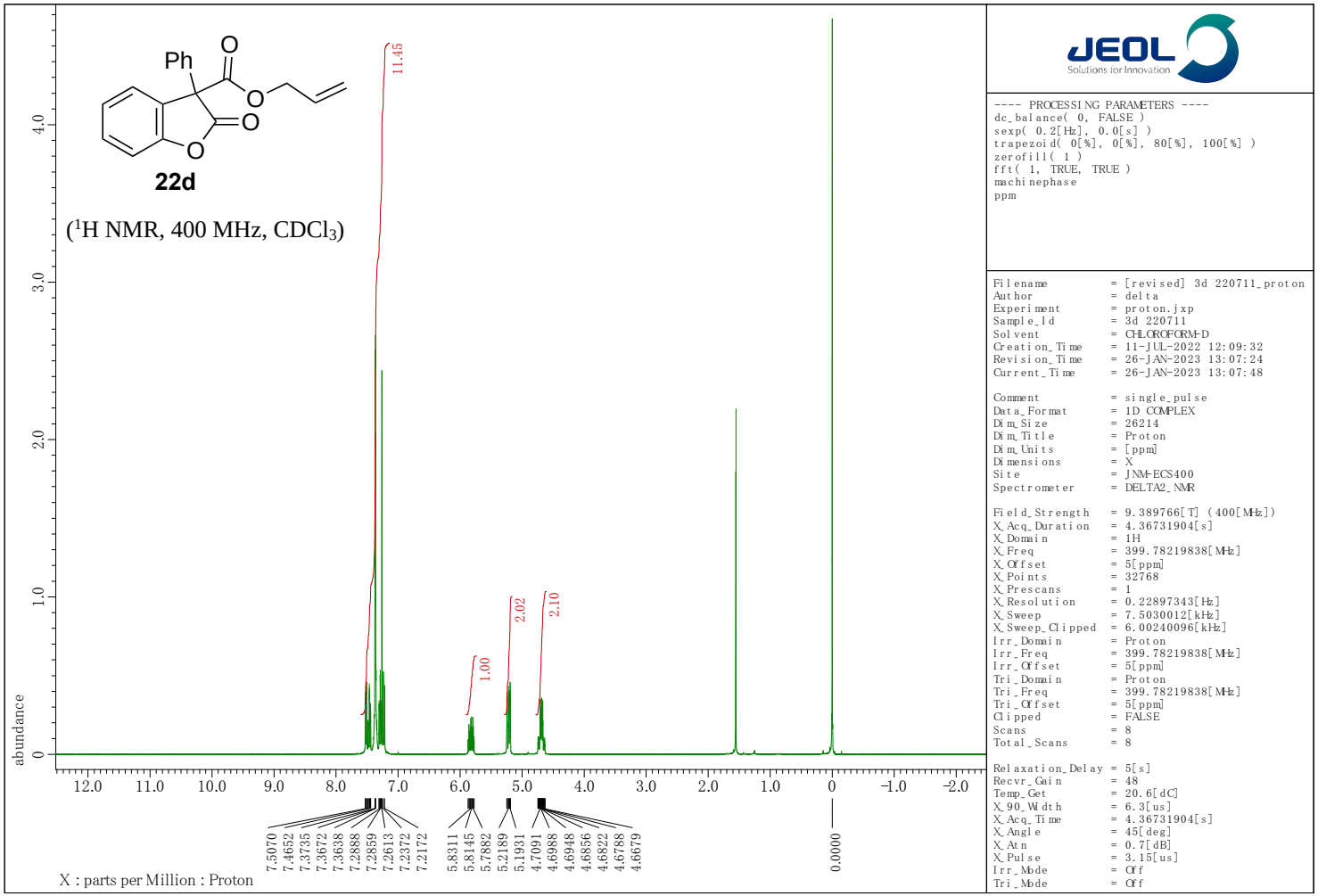
Filename = 191108 TH348_proton-1-
Author = delta
Experiment = proton.jxp
Sample_Id = 191108 TH348
Solvent = CHLOROFORM-D
Actual_Start_Time = 8-NOV-2019 12:21:49
Revision_Time = 10-FEB-2023 19:44:32

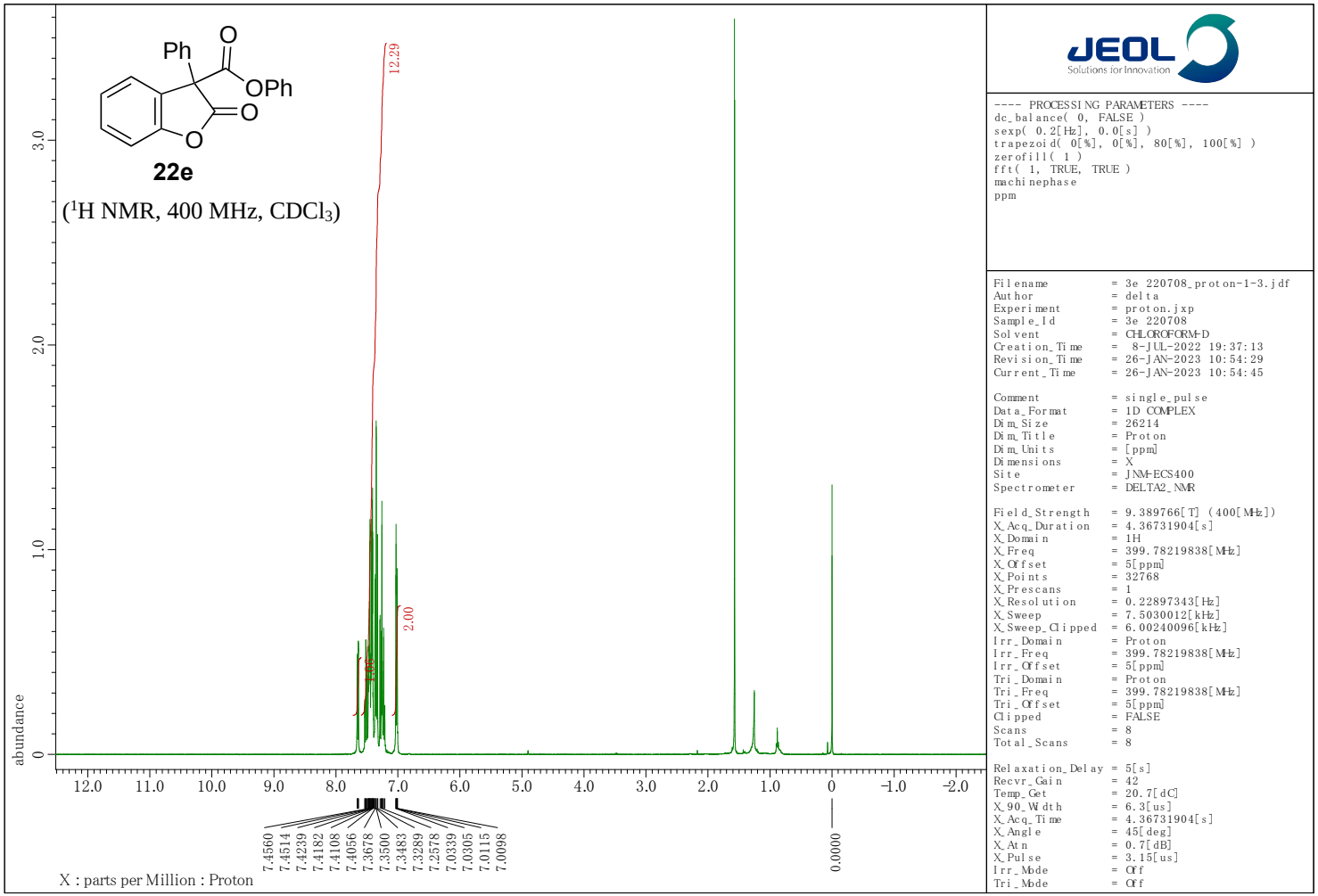
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR

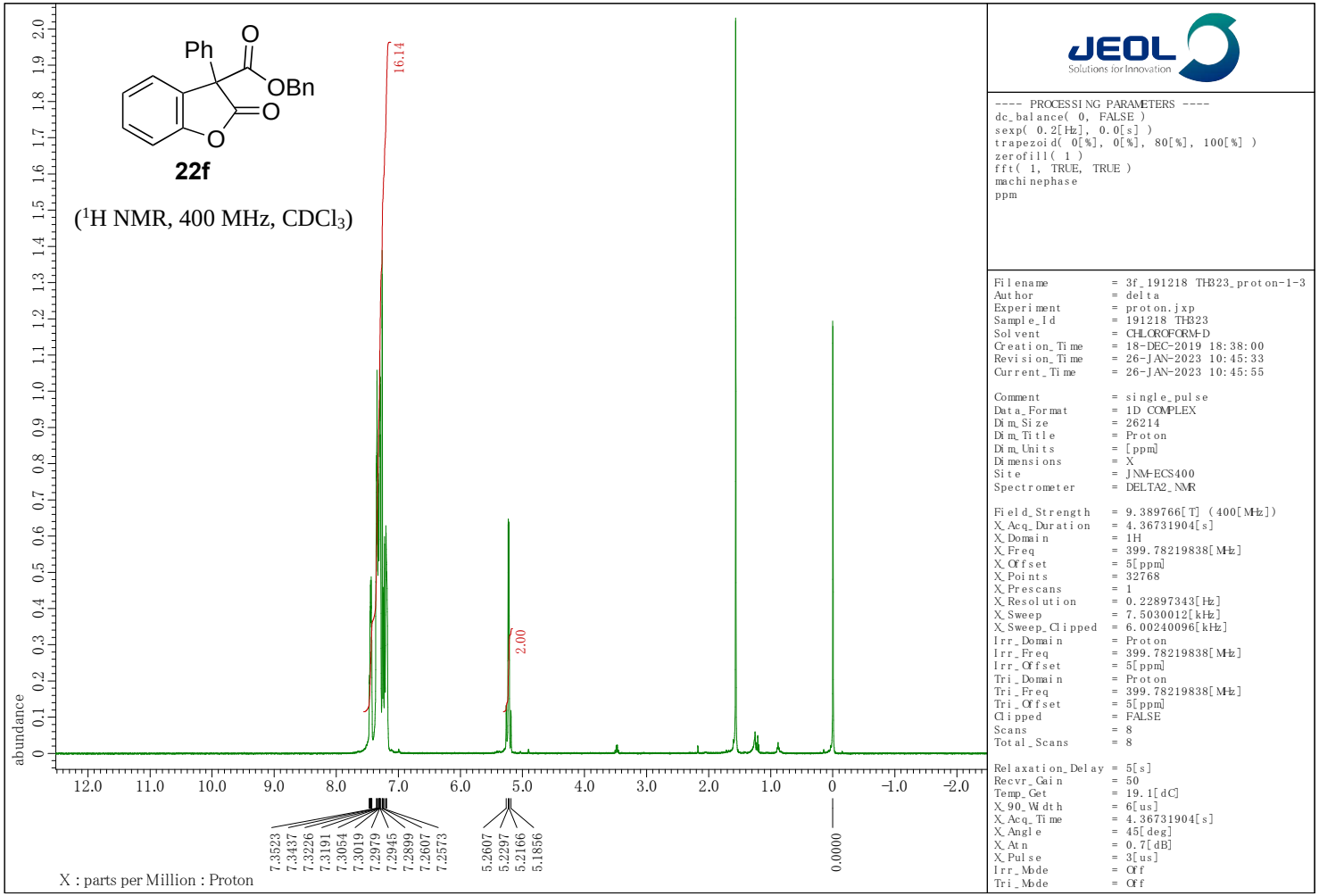
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8

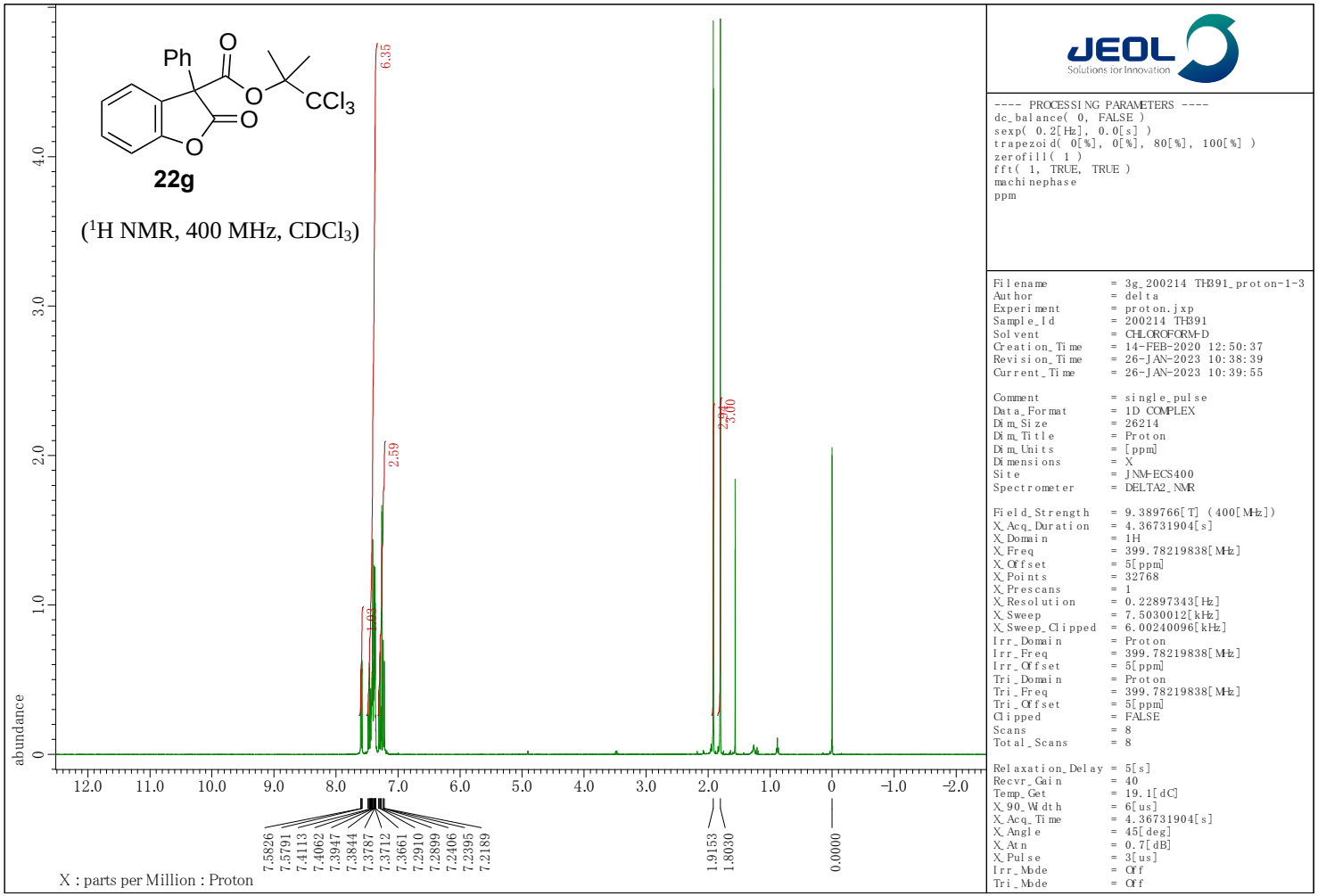
Relaxation_Delay = 5[s]
Recvr_Gain = 50
Temp_Get = 19.4[dC]

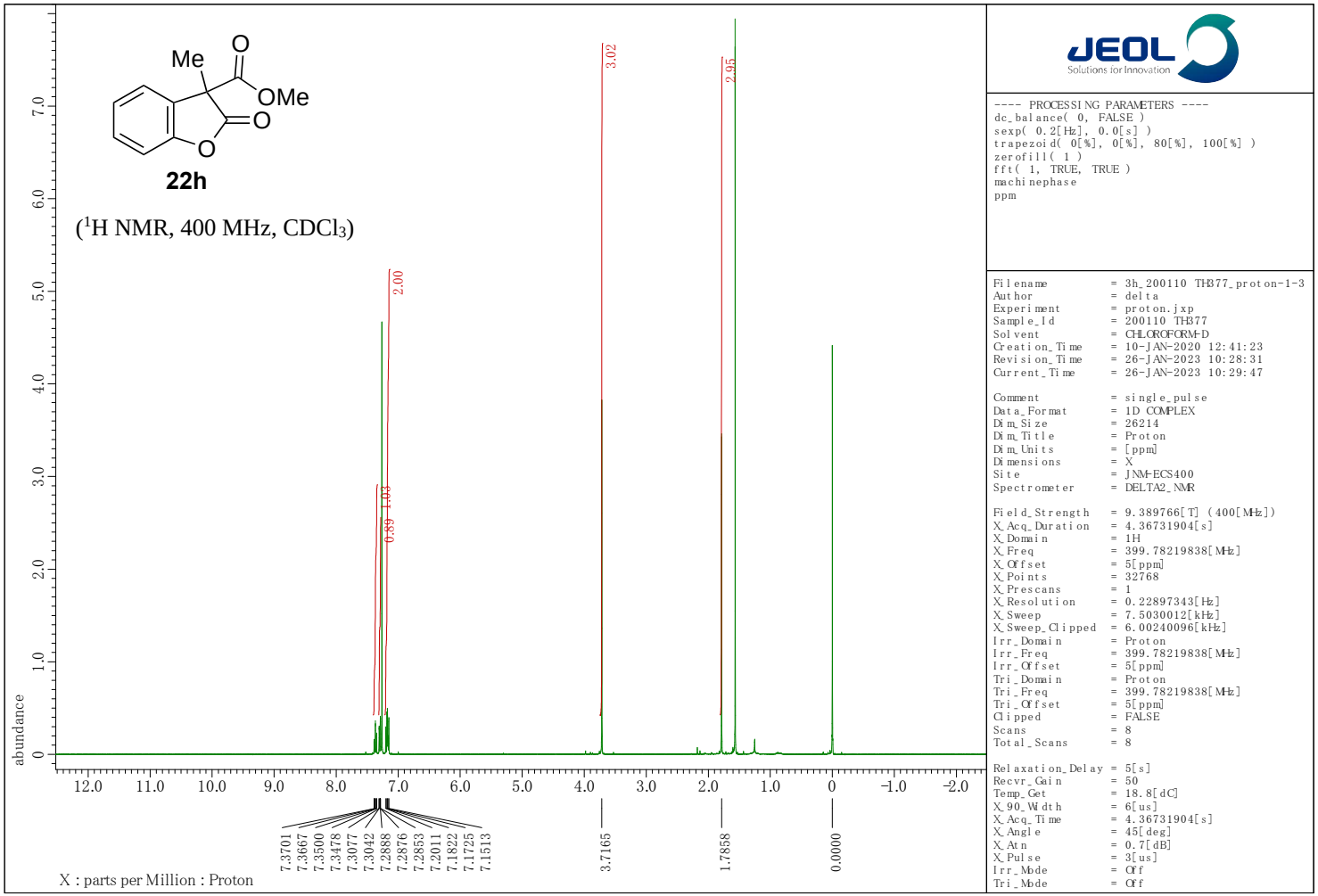

Ph
O
O
O
O
O
nPr
22c
(1H NMR, 400 MHz, CDCl3)
10.83
2.04
2.97
3.00
abundance
X : parts per Million : Proton
7.5201
7.5012
7.4749
7.4554
7.4388
7.4354
7.3632
7.2996
7.2802
7.2607
7.2584
7.2309
7.2109
4.1988
4.1891
4.1828
4.1725
4.1650
4.1558
4.1484
4.1381
4.1324
4.1220
1.6409
1.6243
1.6060
1.5894
1.5561
1.5539
0.8437
0.8248
0.0000
JEOL
Solutions for Innovation
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = 3c 220708_proton-1-3.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 3c 220708
Solvent = CHLOROFORM-D
Creation_Time = 8-JUL-2022 11:05:36
Revision_Time = 26-JAN-2023 10:51:21
Current_Time = 26-JAN-2023 10:51:54
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Get = 20.5[dC]
X_90_Width = 6.3[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3.15[us]
Irr_Mode = Off
Tri_Mode = Off

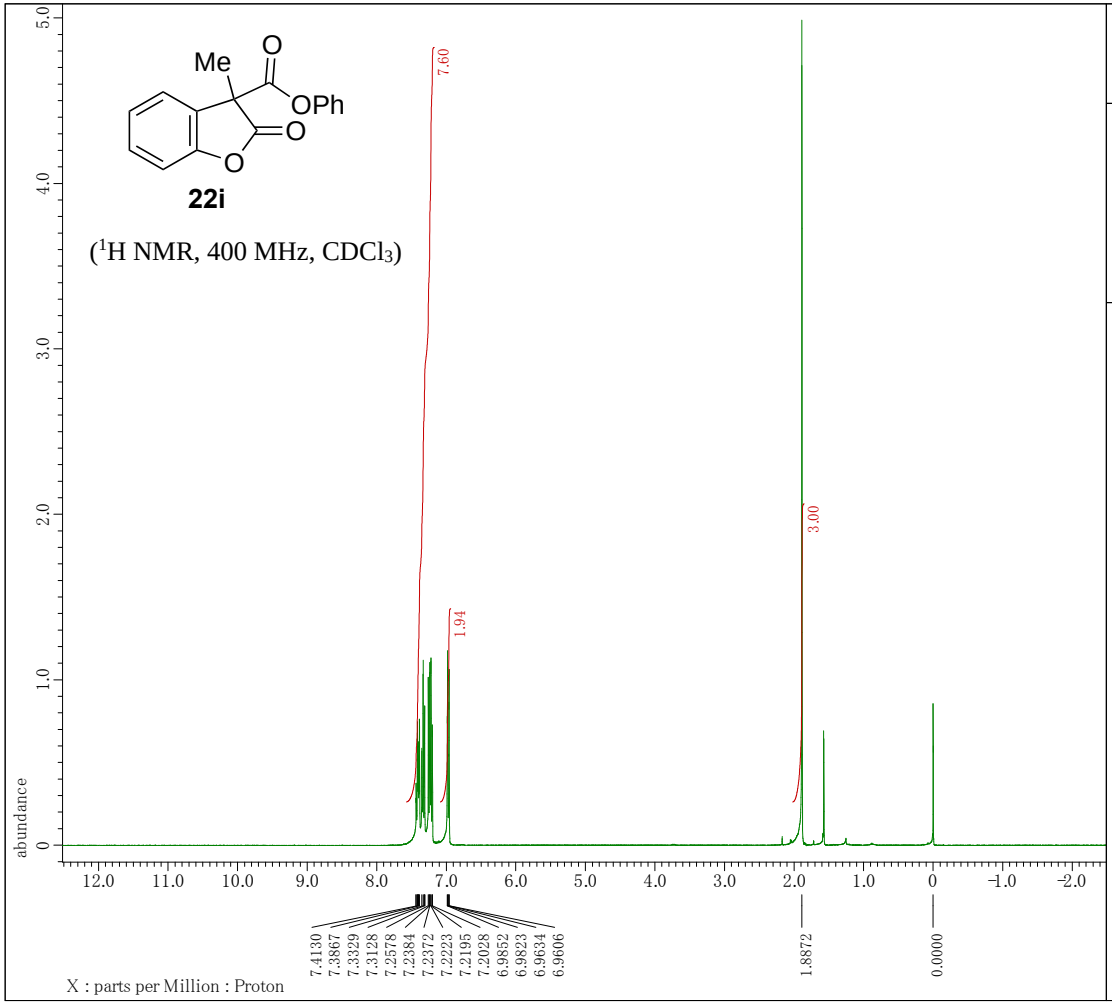

Ph
O
O
O
O
22d
(1H NMR, 400 MHz, CDCl3)
11.45
1.00
2.02
2.10
abundance
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.5070
7.4652
7.3735
7.3672
7.3638
7.2888
7.2859
7.2613
7.2372
7.2172
5.8311
5.8145
5.7882
5.2189
5.1931
4.7091
4.6988
4.6948
4.6856
4.6822
4.6788
4.6679
0.0000
X : parts per Million : Proton
JEOL
Solutions for Innovation
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = [revised] 3d 220711_proton
Author = delta
Experiment = proton.jxp
Sample_Id = 3d 220711
Solvent = CHLOROFORM-D
Creation_Time = 11-JUL-2022 12:09:32
Revision_Time = 26-JAN-2023 13:07:24
Current_Time = 26-JAN-2023 13:07:48
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 48
Temp_Get = 20.6[dC]
X_90_Width = 6.3[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3.15[us]
Irr_Mode = Off
Tri_Mode = Off


Ph
O
OPh
O
O
22e
(1H NMR, 400 MHz, CDCl3)
12.29
2.00
abundance
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.4560
7.4514
7.4239
7.4182
7.4108
7.4056
7.3678
7.3500
7.3483
7.3289
7.2578
7.0339
7.0305
7.0115
7.0098
0.0000
X : parts per Million : Proton
JEOL
Solutions for Innovation
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = 3e 220708_proton-1-3.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 3e 220708
Solvent = CHLOROFORM-D
Creation_Time = 8-JUL-2022 19:37:13
Revision_Time = 26-JAN-2023 10:54:29
Current_Time = 26-JAN-2023 10:54:45
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 42
Temp_Get = 20.7[dC]
X_90_Width = 6.3[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3.15[us]
Irr_Mode = Off
Tri_Mode = Off


Ph
O
OBn
O
O
22f
(1H NMR, 400 MHz, CDCl3)
16.14
2.00
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.3523
7.3437
7.3226
7.3191
7.3054
7.3019
7.2979
7.2945
7.2899
7.2607
7.2573
5.2607
5.2297
5.2166
5.1856
0.0000
X : parts per Million : Proton
JEOL
Solutions for Innovation
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = 3f_191218 TH323_proton-1-3
Author = delta
Experiment = proton.jxp
Sample_Id = 191218 TH323
Solvent = CHLOROFORM-D
Creation_Time = 18-DEC-2019 18:38:00
Revision_Time = 26-JAN-2023 10:45:33
Current_Time = 26-JAN-2023 10:45:55
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 50
Temp_Get = 19.1[dC]
X_90_Width = 6[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3[us]
Irr_Mode = Off
Tri_Mode = Off


Ph
O
O
O
O
CCl3
22g
(1H NMR, 400 MHz, CDCl3)
6.35
2.59
1.93
2.00
abundance
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.5826
7.5791
7.4113
7.4062
7.3947
7.3844
7.3787
7.3712
7.3661
7.2910
7.2899
7.2406
7.2395
7.2189
1.9153
1.8030
0.0000
X : parts per Million : Proton
JEOL
Solutions for Innovation
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = 3g_200214 TH391_proton-1-3
Author = delta
Experiment = proton.jxp
Sample_Id = 200214 TH391
Solvent = CHLOROFORM-D
Creation_Time = 14-FEB-2020 12:50:37
Revision_Time = 26-JAN-2023 10:38:39
Current_Time = 26-JAN-2023 10:39:55
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 40
Temp_Get = 19.1[dC]
X_90_Width = 6[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3[us]
Irr_Mode = Off
Tri_Mode = Off


Me
O
OMe
O
O
22h
(1H NMR, 400 MHz, CDCl3)
3.02
2.95
2.00
1.03
0.89
abundance
X : parts per Million : Proton
7.3701
7.3667
7.3500
7.3478
7.3077
7.3042
7.2888
7.2876
7.2853
7.2011
7.1822
7.1725
7.1513
3.7165
1.7858
0.0000
JEOL
Solutions for Innovation
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = 3h_200110 TH377_proton-1-3
Author = delta
Experiment = proton.jxp
Sample_Id = 200110 TH377
Solvent = CHLOROFORM-D
Creation_Time = 10-JAN-2020 12:41:23
Revision_Time = 26-JAN-2023 10:28:31
Current_Time = 26-JAN-2023 10:29:47
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 50
Temp_Get = 18.8[dC]
X_90_Width = 6[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3[us]
Irr_Mode = Off
Tri_Mode = Off



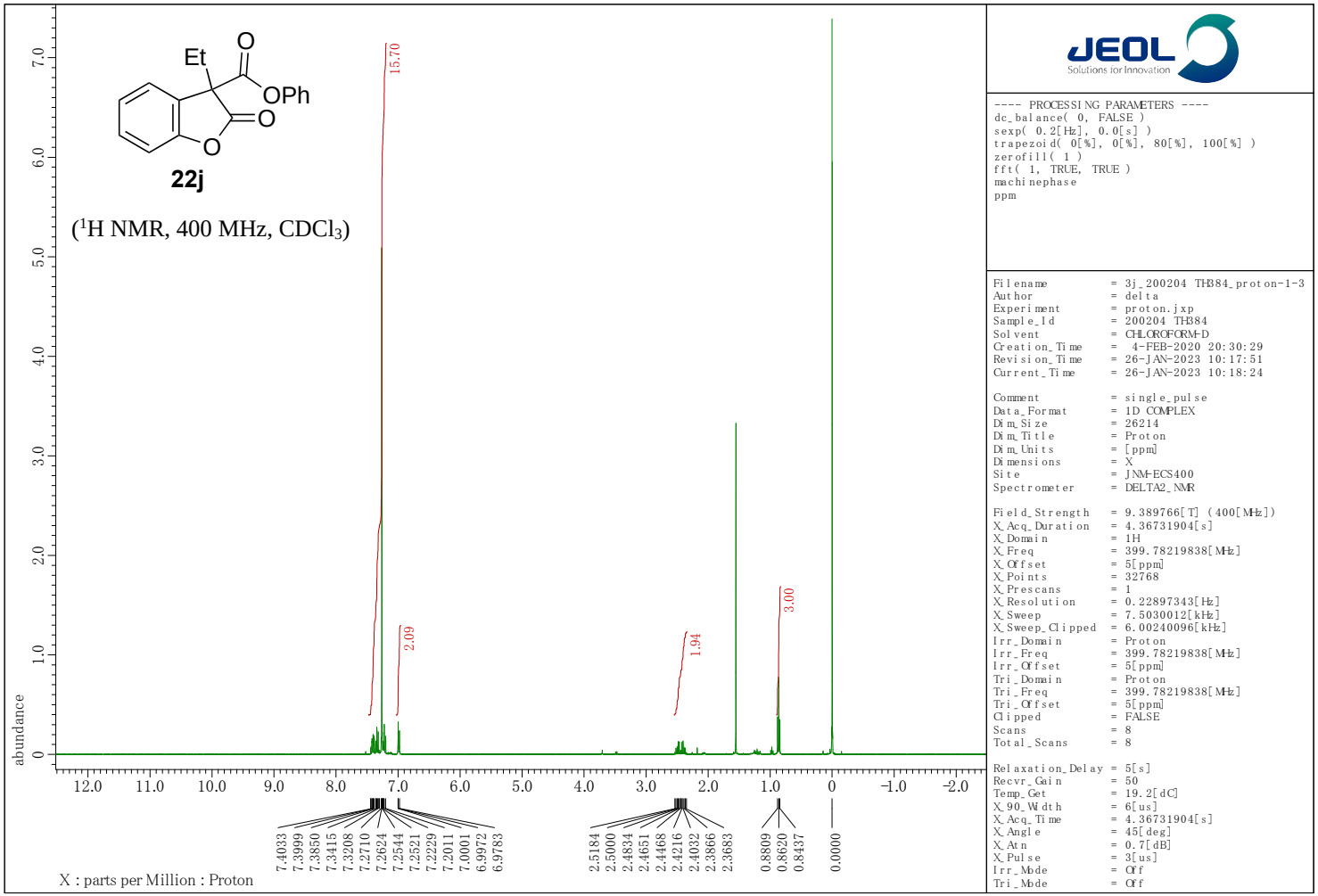
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm

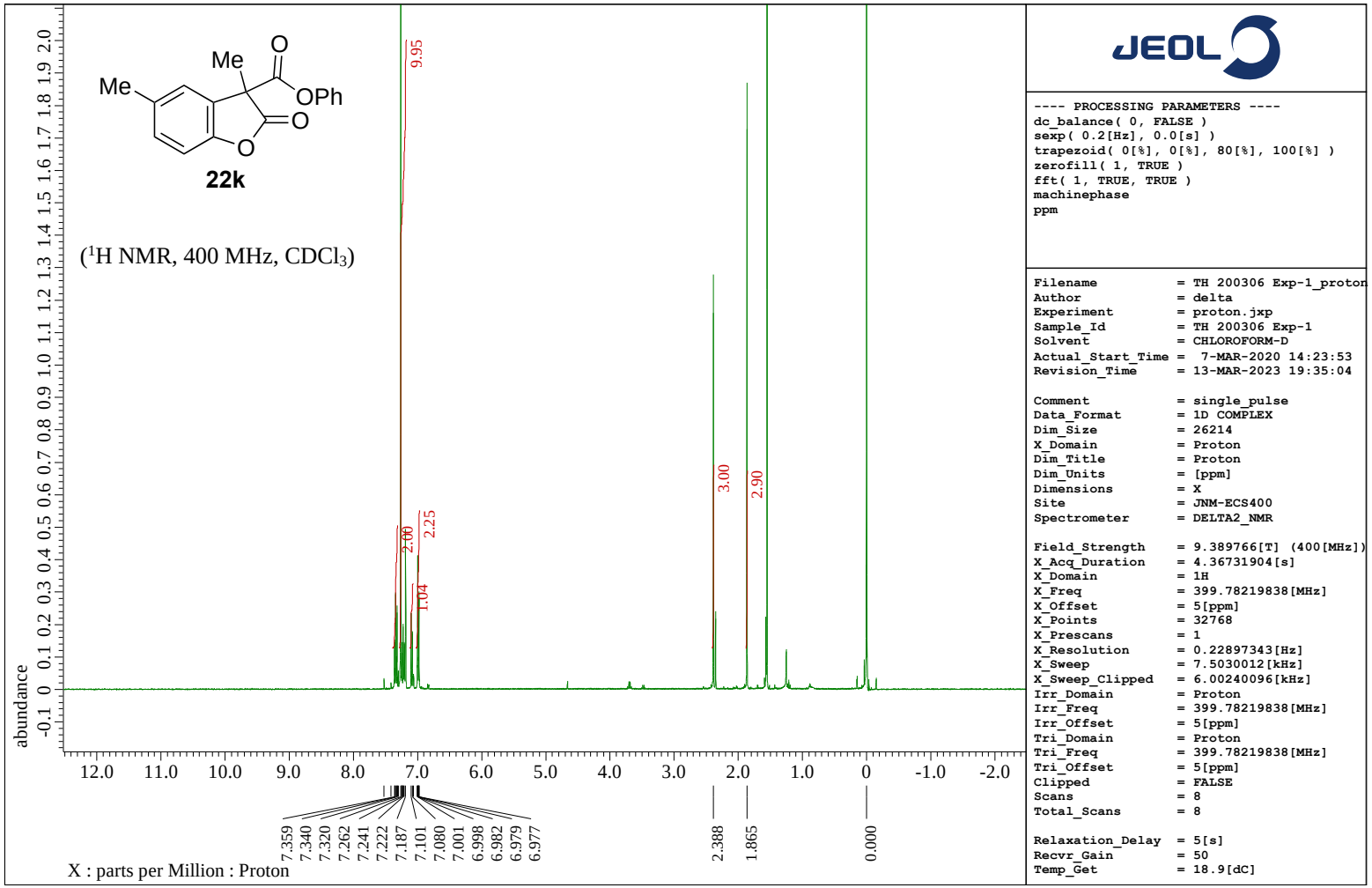
Filename = 3i 220708_proton-1-3.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 3i 220708
Solvent = CHLOROFORM-D
Creation_Time = 8-JUL-2022 10:36:22
Revision_Time = 26-JAN-2023 10:22:24
Current_Time = 26-JAN-2023 10:23:08

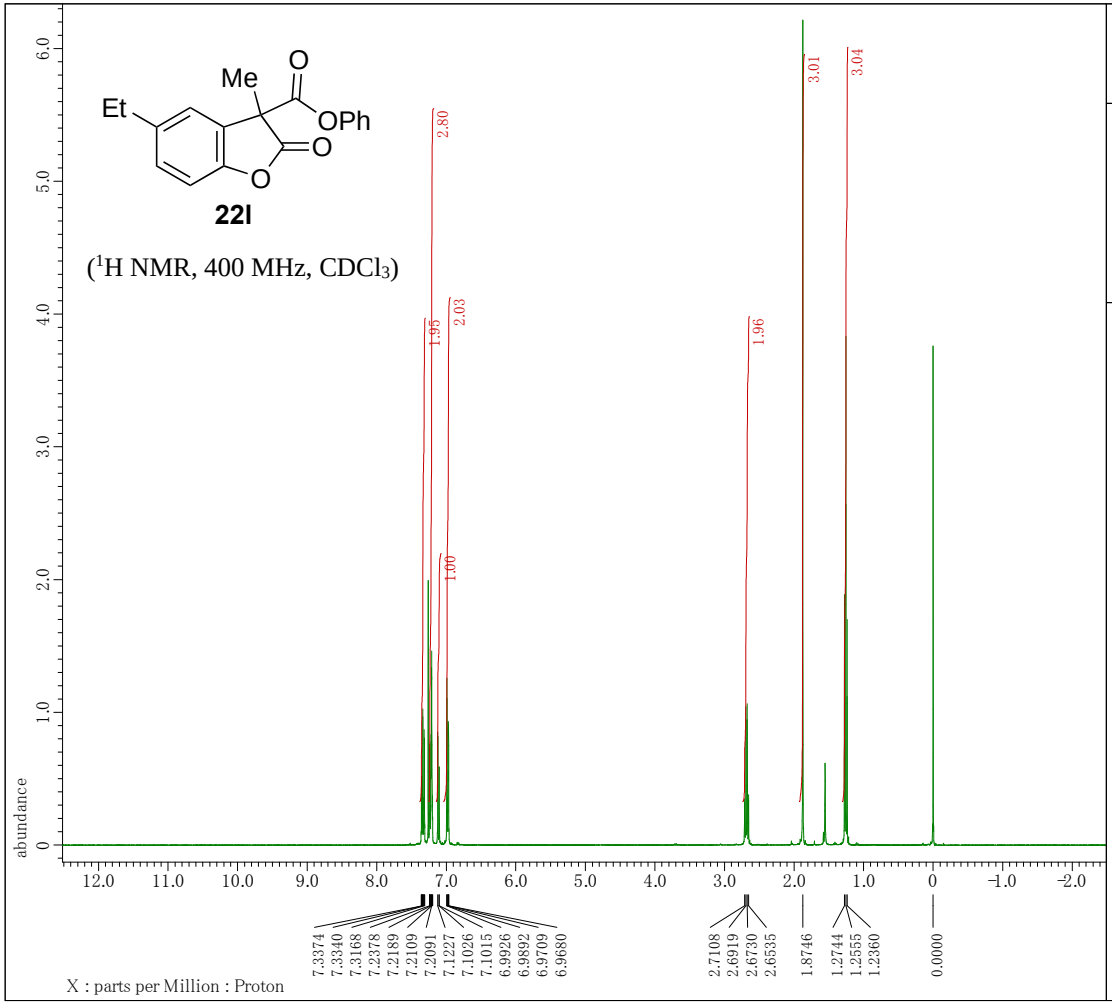
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8

Relaxation_Delay = 5[s]
Recvr_Gain = 38
Temp_Get = 20.5[dC]
X_90_Width = 6.3[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3.15[us]
Irr_Mode = Off
Tri_Mode = Off


Et
O
OPh
O
O
22j
(^{1}H NMR, 400 MHz, $CDCl_3$)
15.70
2.09
1.94
3.00
abundance
X : parts per Million : Proton
7.4033
7.3999
7.3850
7.3415
7.3208
7.2710
7.2624
7.2544
7.2521
7.2229
7.2011
7.0001
6.9972
6.9783
2.5184
2.5000
2.4834
2.4651
2.4468
2.4216
2.4032
2.3866
2.3683
0.8809
0.8620
0.8437
0.0000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = 3j_200204 TH384_proton-1-3
Author = delta
Experiment = proton.jxp
Sample_Id = 200204 TH384
Solvent = CHLOROFORM-D
Creation_Time = 4-FEB-2020 20:30:29
Revision_Time = 26-JAN-2023 10:17:51
Current_Time = 26-JAN-2023 10:18:24
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 50
Temp_Get = 19.2[dC]
X_90_Width = 6[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3[us]
Irr_Mode = Off
Tri_Mode = Off

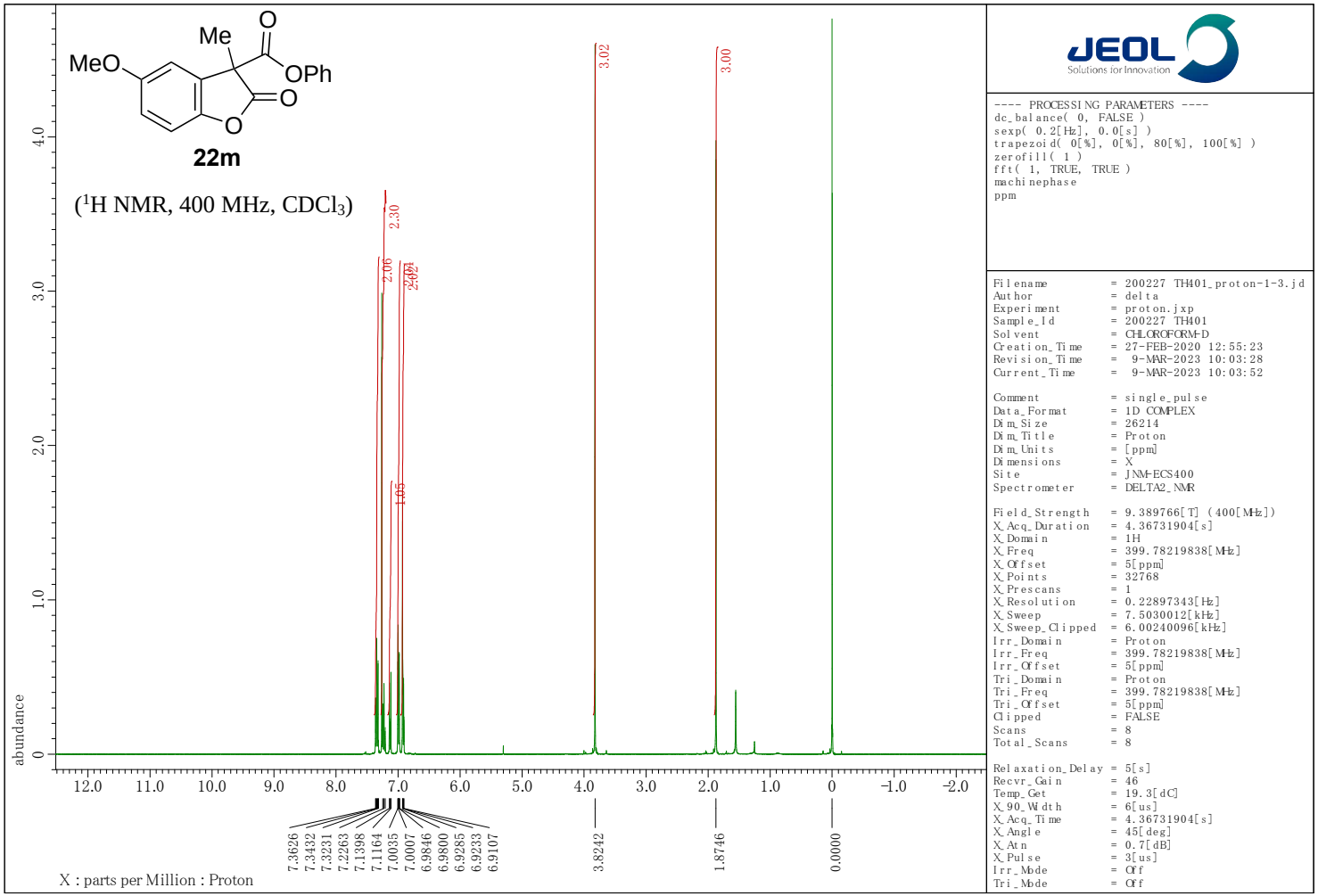

Me
Me
O
OPh
O
O
22k
(1H NMR, 400 MHz, CDCl3)
abundance
9.95
3.00
2.90
2.25
2.00
1.04
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.359 7.340 7.320 7.262 7.241 7.222 7.187 7.101 7.080 7.001 6.998 6.982 6.979 6.977
2.388 1.865 0.000
X : parts per Million : Proton
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = TH 200306 Exp-1_proton
Author = delta
Experiment = proton.jxp
Sample_Id = TH 200306 Exp-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 7-MAR-2020 14:23:53
Revision_Time = 13-MAR-2023 19:35:04
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 50
Temp_Get = 18.9[dC]

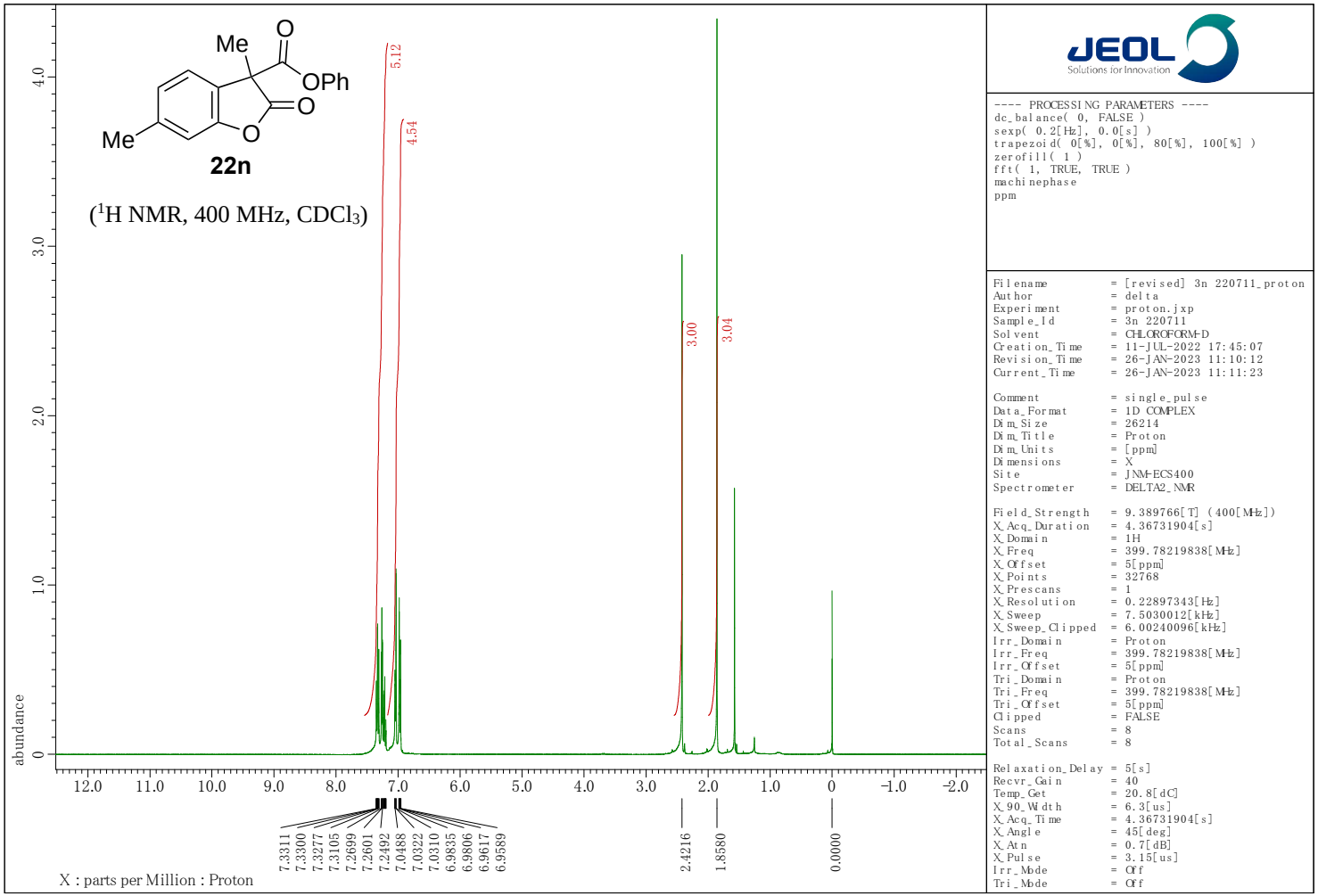


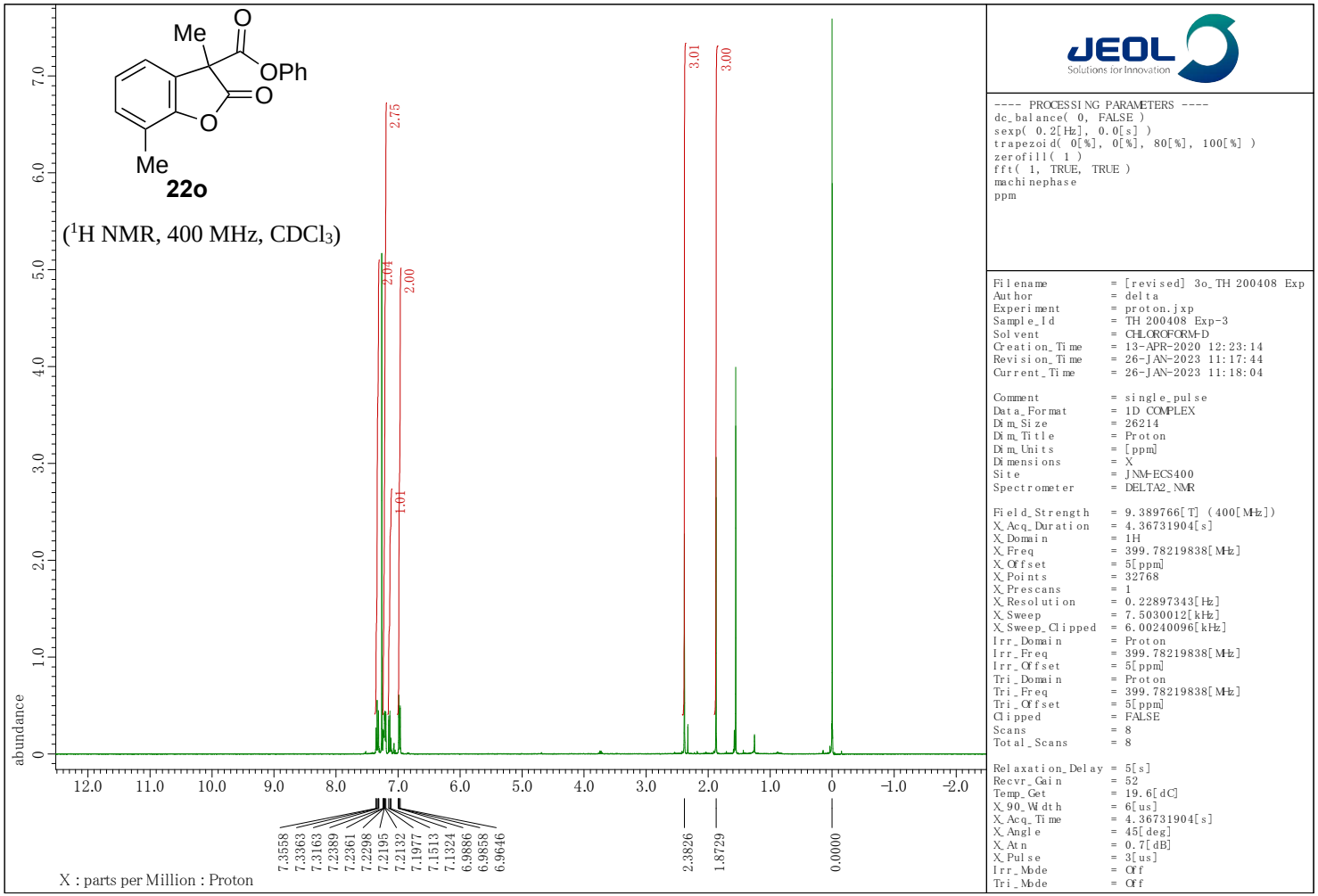
JEOL Solutions for Innovation

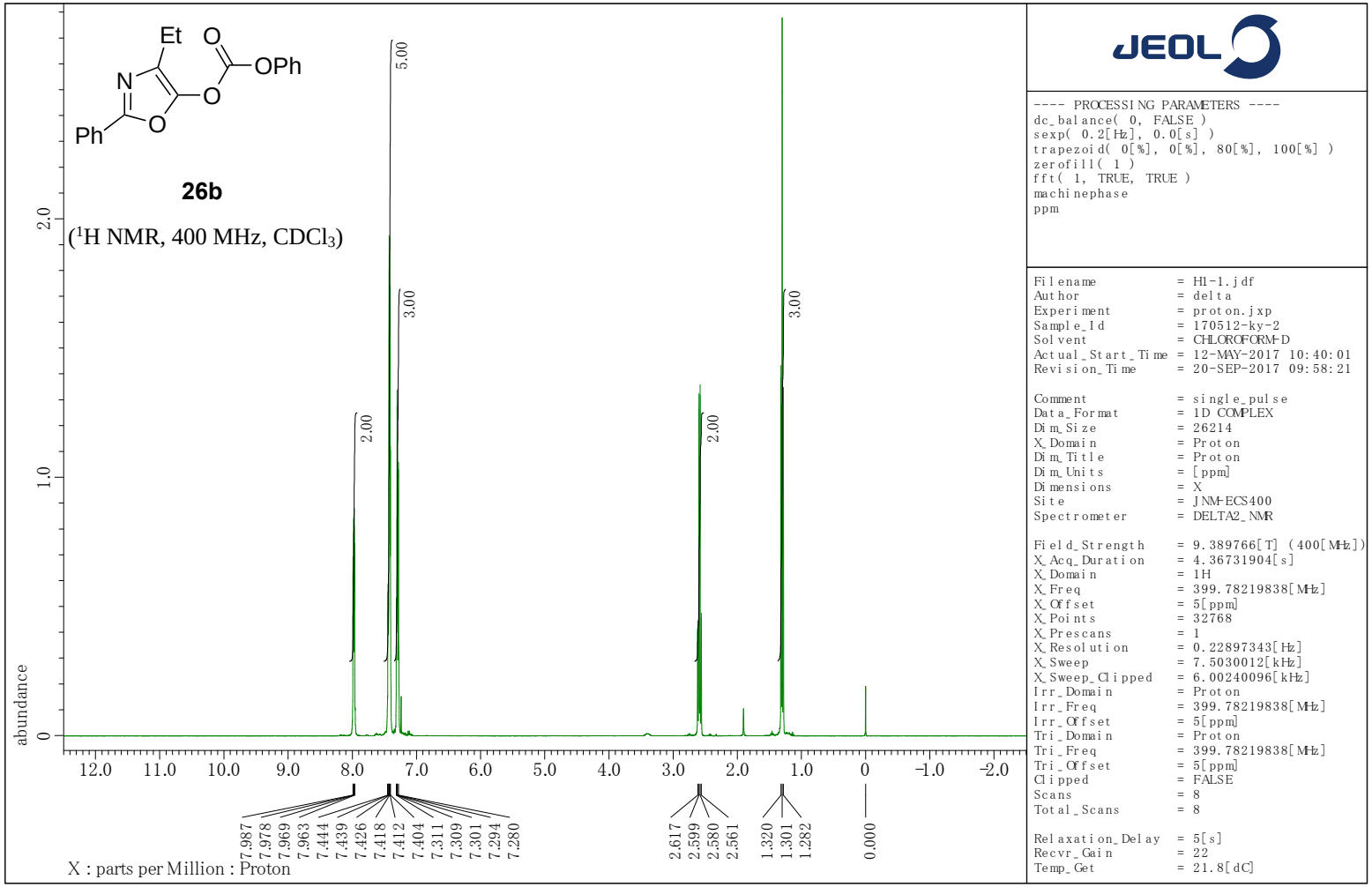
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

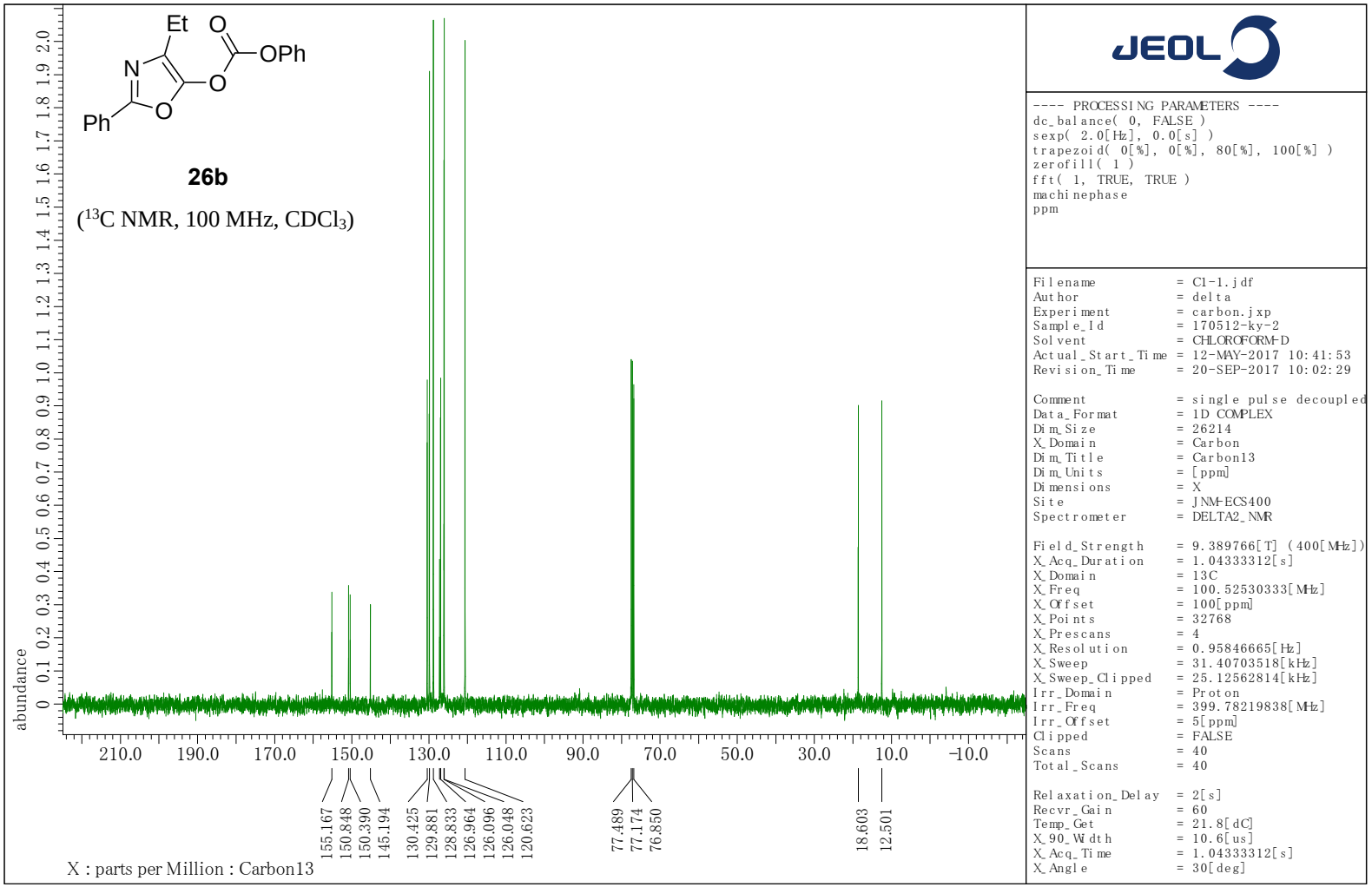
Filename	= 3l-2_proton-1-3.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 3l-2
Solvent	= CHLOROFORM-D
Creation_Time	= 6-JUL-2022 15:37:42
Revision_Time	= 26-JAN-2023 10:10:56
Current_Time	= 26-JAN-2023 10:11:56
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 44
Temp_Get	= 22.6[dC]
X_90_Width	= 6.3[us]
X_Acq_Time	= 4.36731904[s]
X_Angle	= 45[deg]
X_Atn	= 0.7[dB]
X_Pulse	= 3.15[us]
Irr_Mode	= Off
Tri_Mode	= Off


Me
O
MeO
OPh
O
O
22m
(1H NMR, 400 MHz, CDCl3)
abundance
X : parts per Million : Proton
3.02
3.00
2.30
2.06
1.85
7.3626
7.3432
7.3231
7.2263
7.1398
7.1164
7.0035
7.0007
6.9846
6.9800
6.9285
6.9233
6.9107
3.8242
1.8746
0.0000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = 200227 TH401_proton-1-3.jd
Author = delta
Experiment = proton.jxp
Sample_Id = 200227 TH401
Solvent = CHLOROFORM-D
Creation_Time = 27-FEB-2020 12:55:23
Revision_Time = 9-MAR-2023 10:03:28
Current_Time = 9-MAR-2023 10:03:52
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 46
Temp_Get = 19.3[dC]
X_90_Width = 6[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3[us]
Irr_Mode = Off
Tri_Mode = Off


Me
O
OPh
O
Me
O
22n
(1H NMR, 400 MHz, CDCl3)
5.12
4.54
3.00
3.04
abundance
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.3311
7.3300
7.3277
7.3105
7.2699
7.2601
7.2492
7.0488
7.0322
7.0310
6.9835
6.9806
6.9617
6.9589
2.4216
1.8580
0.0000
X : parts per Million : Proton
JEOL
Solutions for Innovation
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = [revised] 3n 220711_proton
Author = delta
Experiment = proton.jxp
Sample_Id = 3n 220711
Solvent = CHLOROFORM-D
Creation_Time = 11-JUL-2022 17:45:07
Revision_Time = 26-JAN-2023 11:10:12
Current_Time = 26-JAN-2023 11:11:23
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 40
Temp_Get = 20.8[dC]
X_90_Width = 6.3[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3.15[us]
Irr_Mode = Off
Tri_Mode = Off

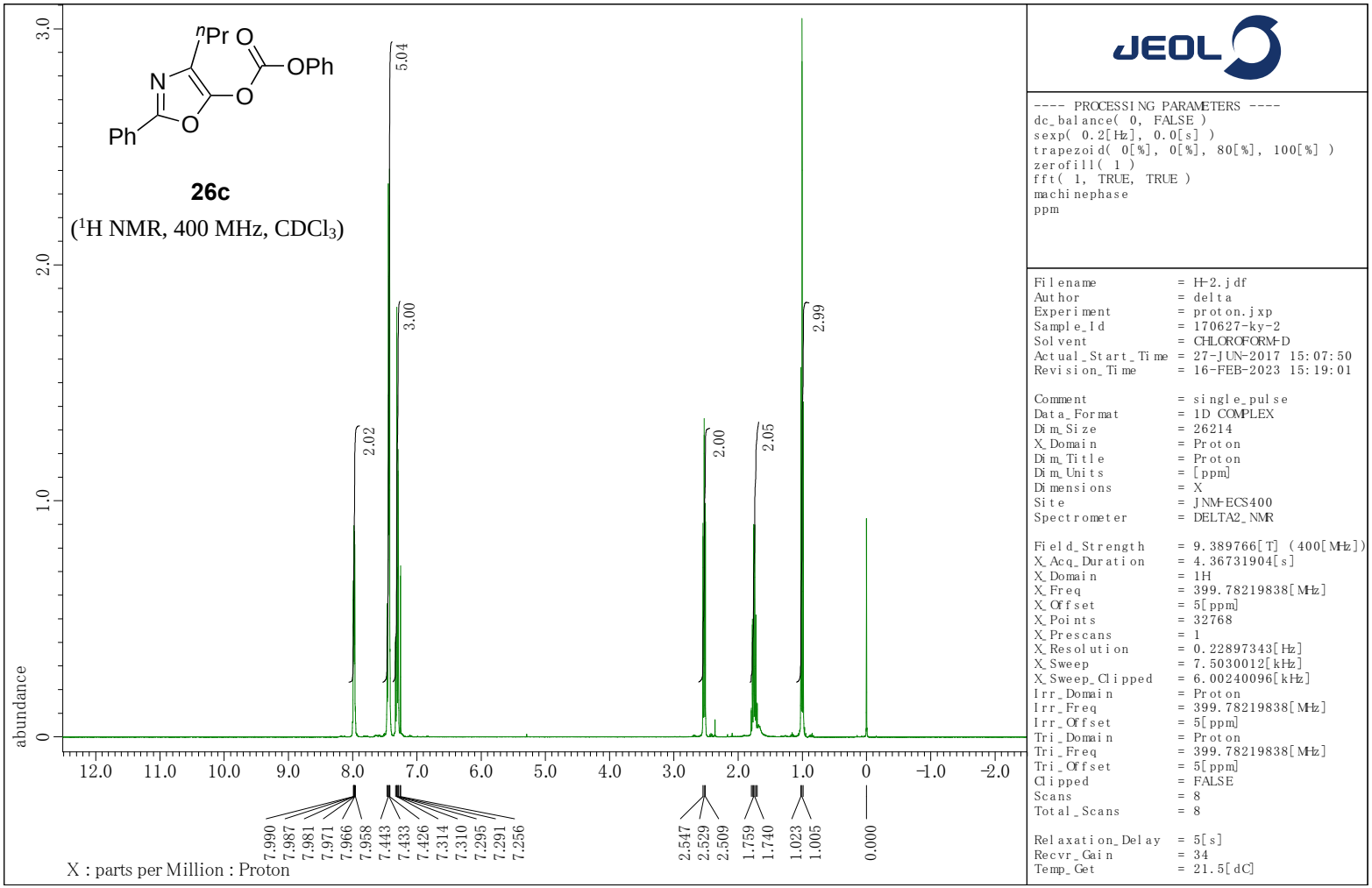

Me
O
OPh
O
O
Me
22o
(1H NMR, 400 MHz, CDCl3)
2.75
2.04
2.00
1.01
3.01
3.00
abundance
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.3558
7.3363
7.3163
7.2389
7.2361
7.2298
7.2195
7.2132
7.1977
7.1513
7.1324
6.9886
6.9858
6.9646
2.3826
1.8729
0.0000
X : parts per Million : Proton
JEOL
Solutions for Innovation
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = [revised] 3o_TH 200408 Exp
Author = delta
Experiment = proton.jxp
Sample_Id = TH 200408 Exp-3
Solvent = CHLOROFORM-D
Creation_Time = 13-APR-2020 12:23:14
Revision_Time = 26-JAN-2023 11:17:44
Current_Time = 26-JAN-2023 11:18:04
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 52
Temp_Get = 19.6[dC]
X_90_Width = 6[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3[us]
Irr_Mode = Off
Tri_Mode = Off

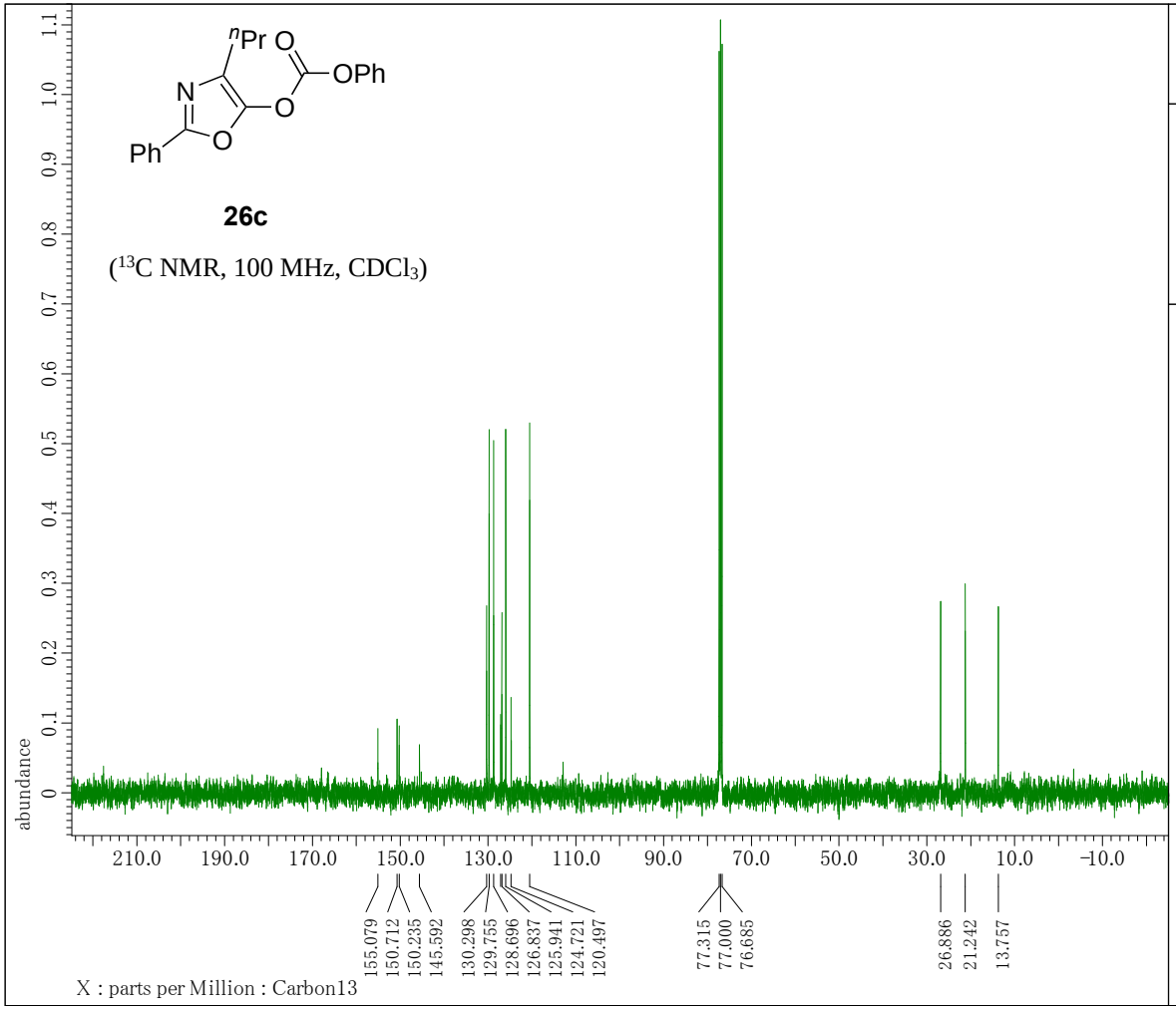

Et
O
OPh
N
O
Ph
O
26b
(1H NMR, 400 MHz, CDCl3)
abundance
2.00
5.00
3.00
2.00
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
7.987
7.978
7.969
7.963
7.444
7.439
7.426
7.418
7.412
7.404
7.311
7.309
7.301
7.294
7.280
2.617
2.599
2.580
2.561
1.320
1.301
1.282
0.000
X : parts per Million : Proton
JEOL
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H1-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170512-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 12-MAY-2017 10:40:01
Revision_Time = 20-SEP-2017 09:58:21
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 22
Temp_Get = 21.8[dC]




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = C1-1.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 170512-ky-2
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 12-MAY-2017 10:41:53
Revision_Time       = 20-SEP-2017 10:02:29

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 40
Total_Scans         = 40

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 21.8[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
```

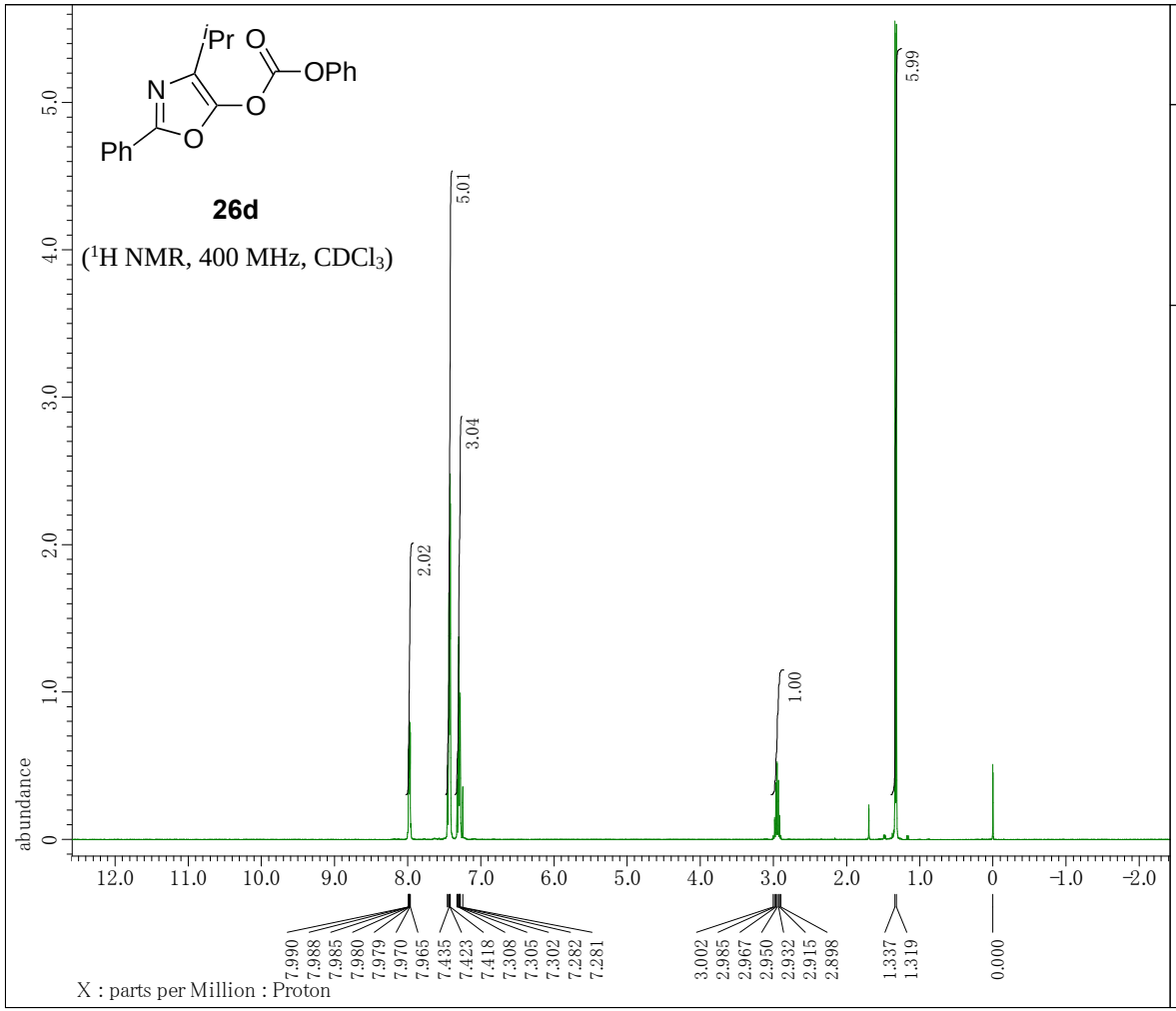

nPr
O
OPh
N
O
O
Ph
26c
(1H NMR, 400 MHz, CDCl3)
abundance
X : parts per Million : Proton
5.04
3.00
2.99
2.02
2.00
2.05
7.990
7.987
7.981
7.971
7.966
7.958
7.443
7.433
7.426
7.314
7.310
7.295
7.291
7.256
2.547
2.529
2.509
1.759
1.740
1.023
1.005
0.000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-2.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170627-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 27-JUN-2017 15:07:50
Revision_Time = 16-FEB-2023 15:19:01
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 34
Temp_Get = 21.5[dC]



JEOL

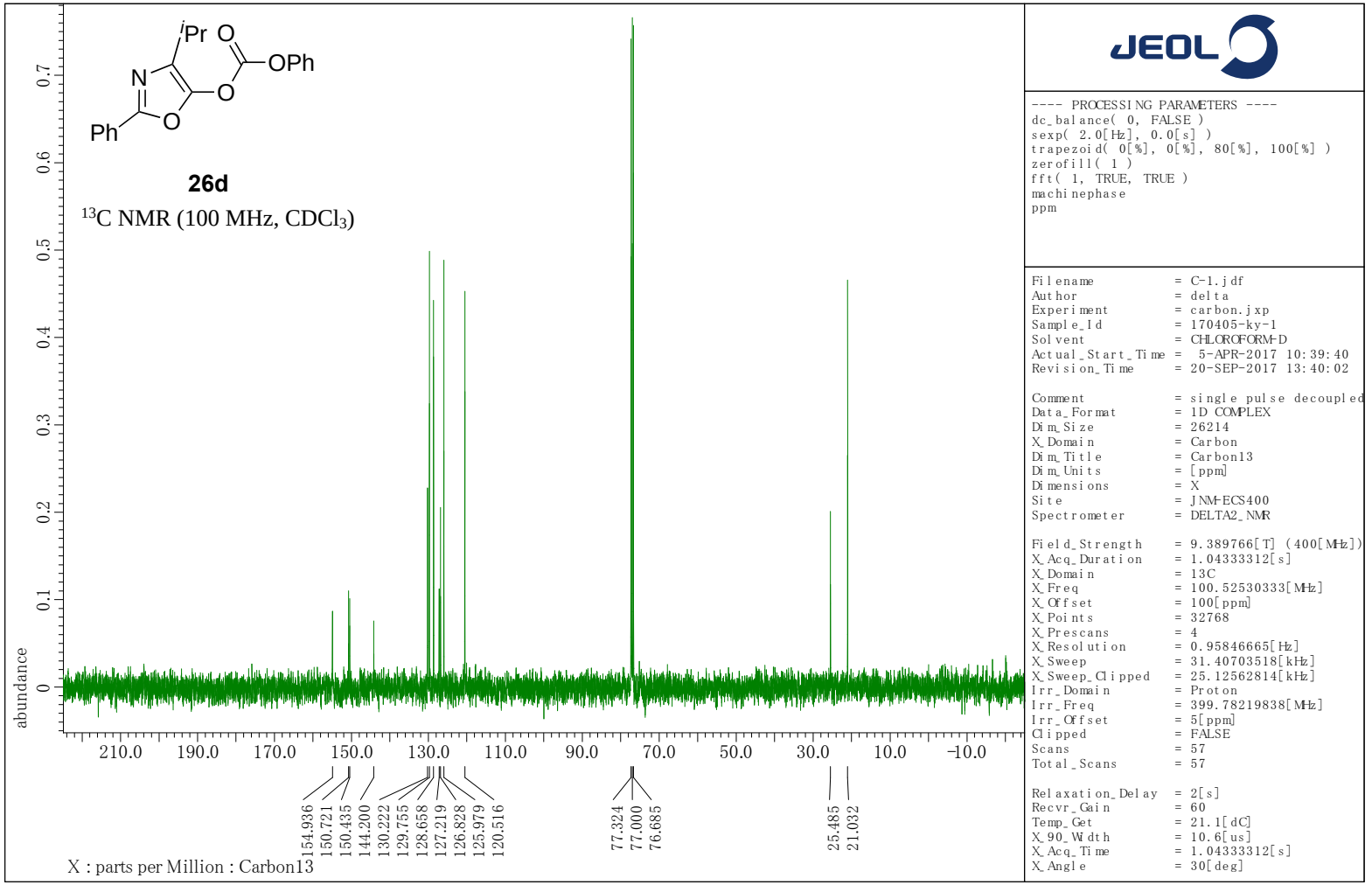
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

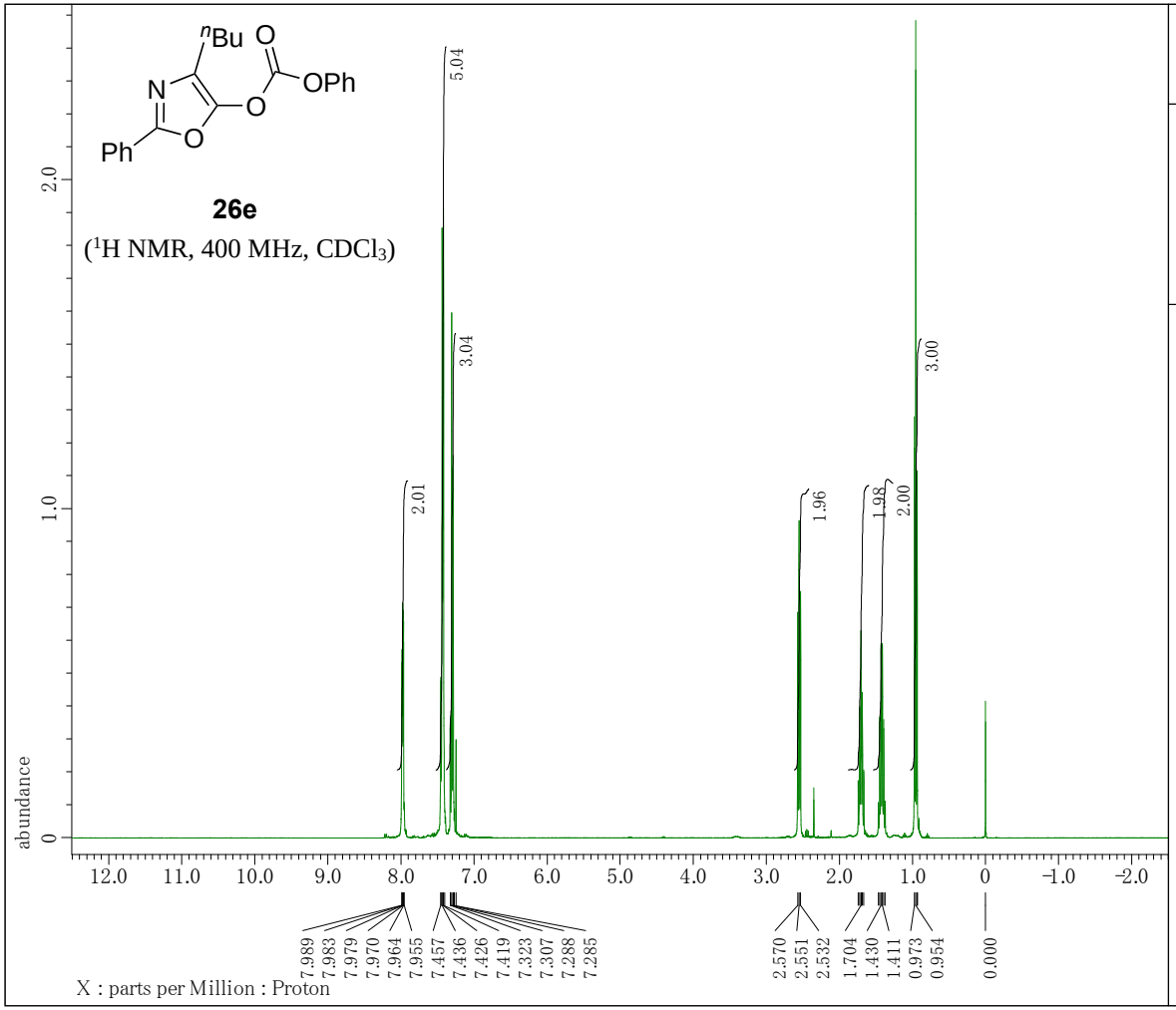
Filename	= C-1.jdf
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= 170627-ky-2
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 27-JUN-2017 15:09:42
Revision_Time	= 20-SEP-2017 10:34:30
Comment	= single pulse decoupled
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 1.04333312[s]
X_Domain	= 13C
X_Freq	= 100.52530333[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 0.95846665[Hz]
X_Sweep	= 31.40703518[kHz]
X_Sweep_Clipped	= 25.12562814[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 71
Total_Scans	= 71
Relaxation_Delay	= 2[s]
Recvr_Gain	= 60
Temp_Get	= 21.4[dC]
X_90_Width	= 10.6[us]
X_Acq_Time	= 1.04333312[s]
X_Angle	= 30[deg]




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

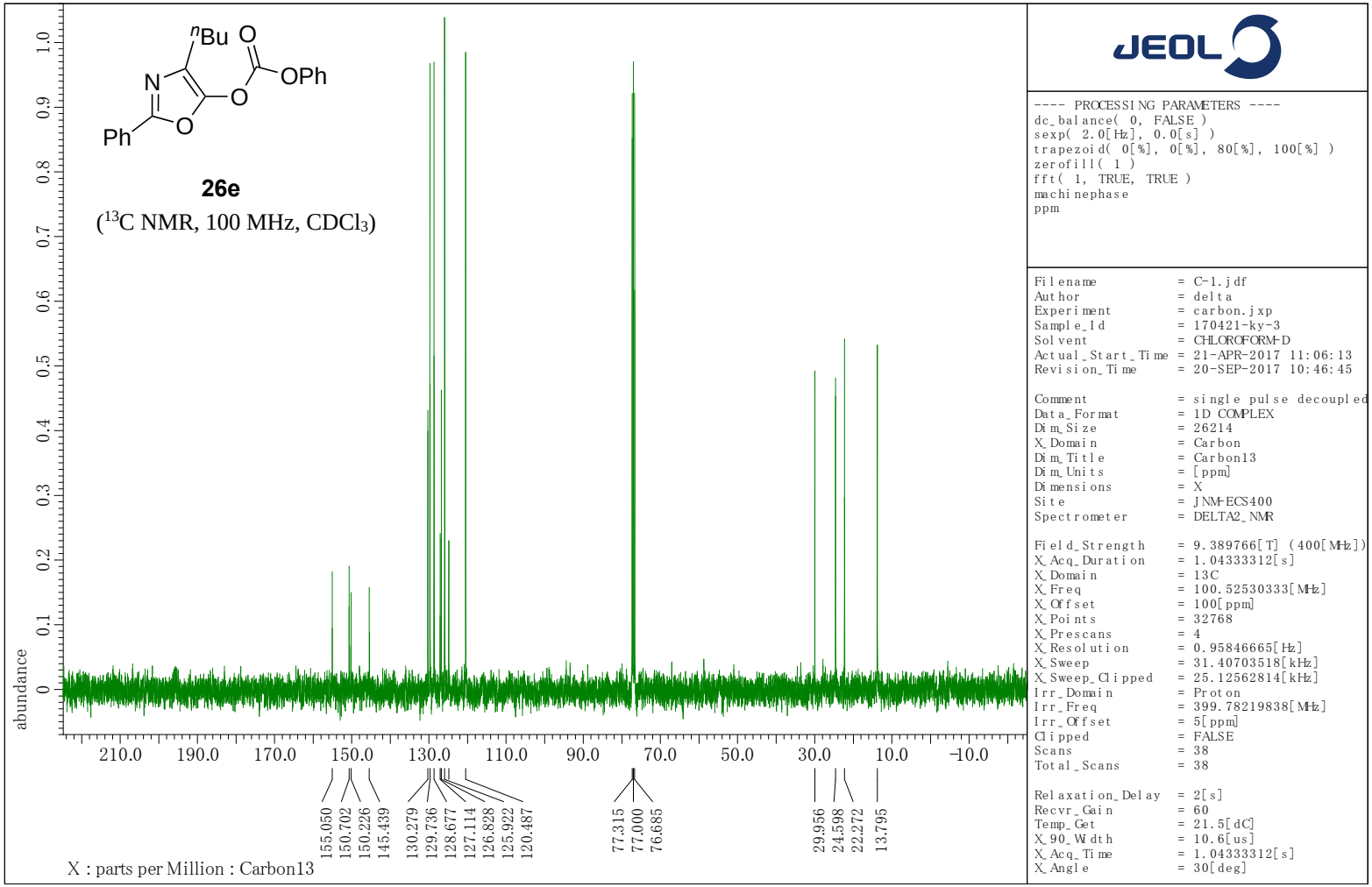
Filename	= H-1.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 170405-ky-1
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 5-APR-2017 10:37:34
Revision_Time	= 20-SEP-2017 13:35:03
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 36
Temp_Get	= 21.2[dC]


iPr
O
OPh
N
O
Ph
O
26d
13C NMR (100 MHz, CDCl3)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
210.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
154.936
150.721
150.435
144.200
130.222
129.755
128.658
127.219
126.828
125.979
120.516
77.324
77.000
76.685
25.485
21.032
X : parts per Million : Carbon13
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170405-ky-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 5-APR-2017 10:39:40
Revision_Time = 20-SEP-2017 13:40:02
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 57
Total_Scans = 57
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.1[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]



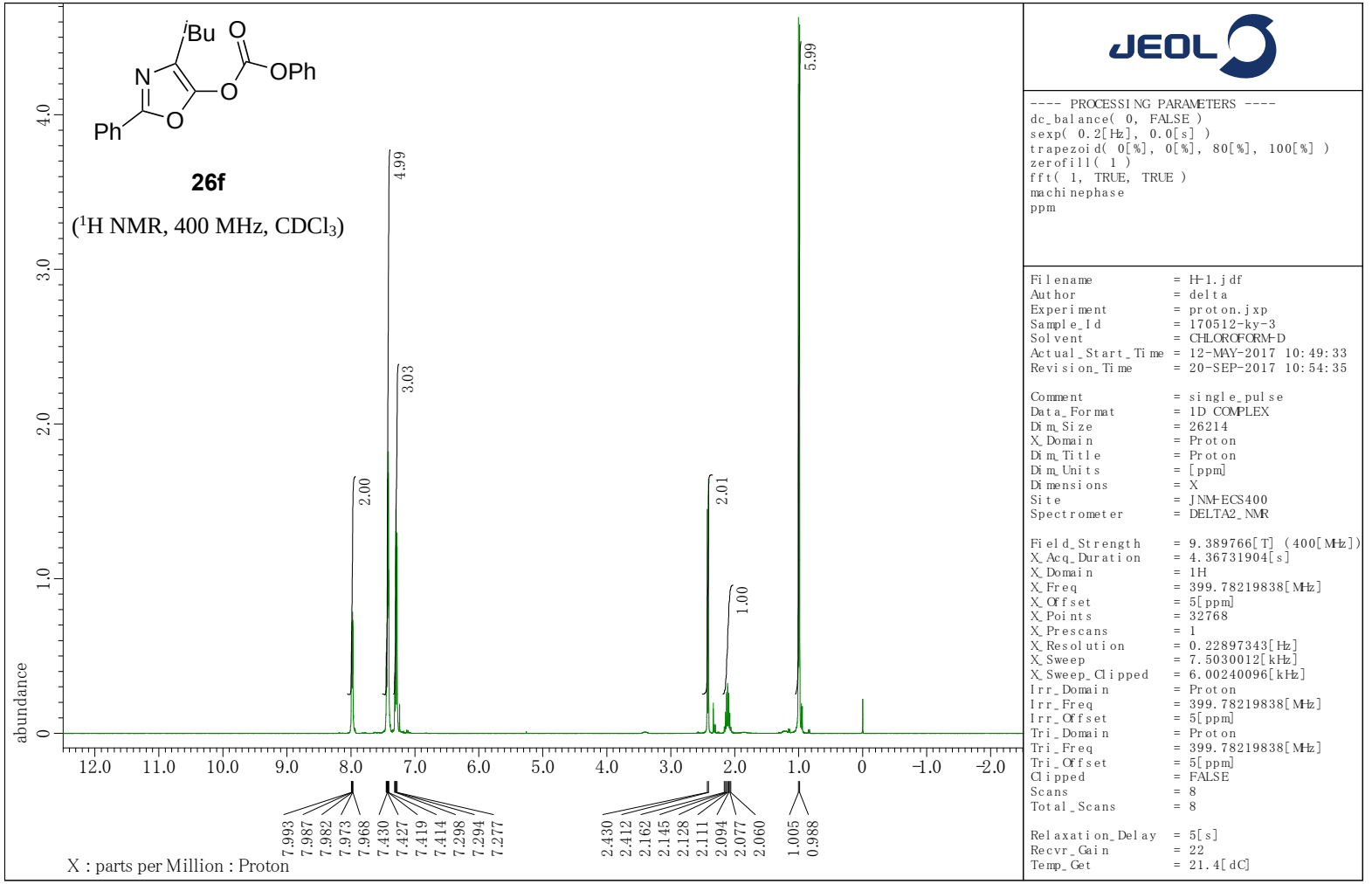
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

Filename	= H-1.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 170421-ky-3
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 21-APR-2017 11:04:22
Revision_Time	= 20-SEP-2017 10:44:25
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 28
Temp_Get	= 21.6[dC]



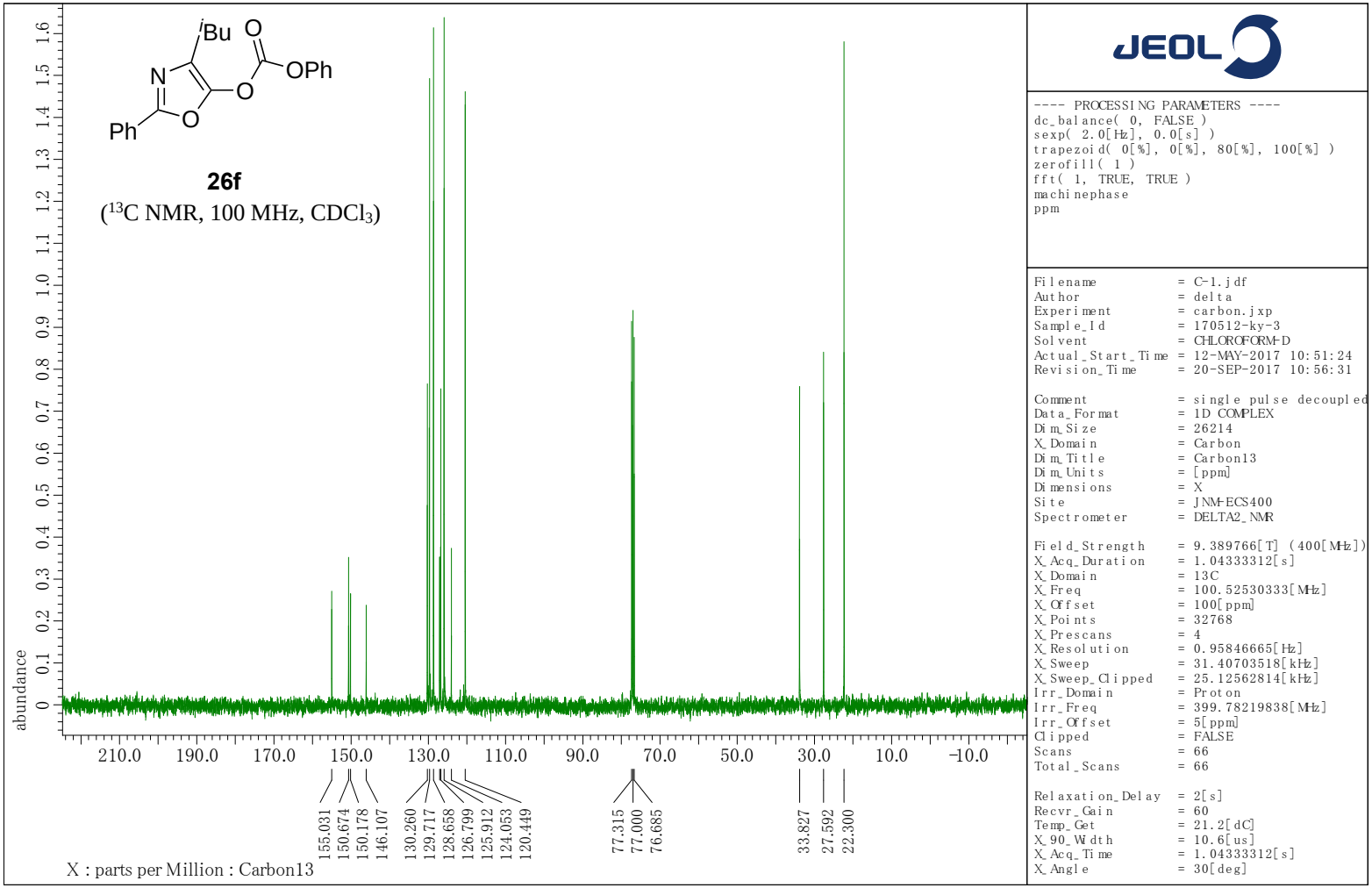

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

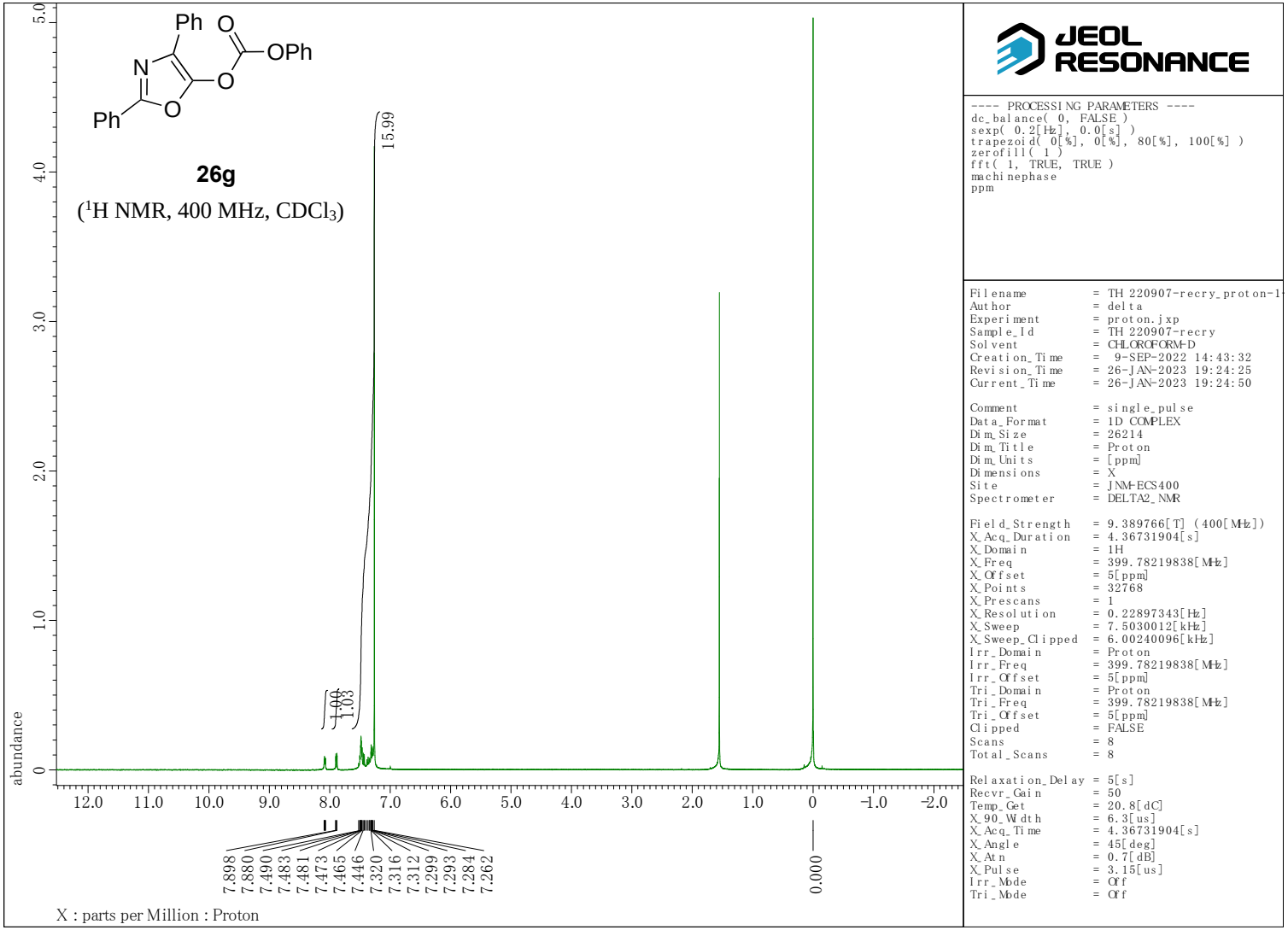
```
Filename            = C-1.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 170421-ky-3
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 21-APR-2017 11:06:13
Revision_Time       = 20-SEP-2017 10:46:45

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 38
Total_Scans         = 38

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 21.5[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
```

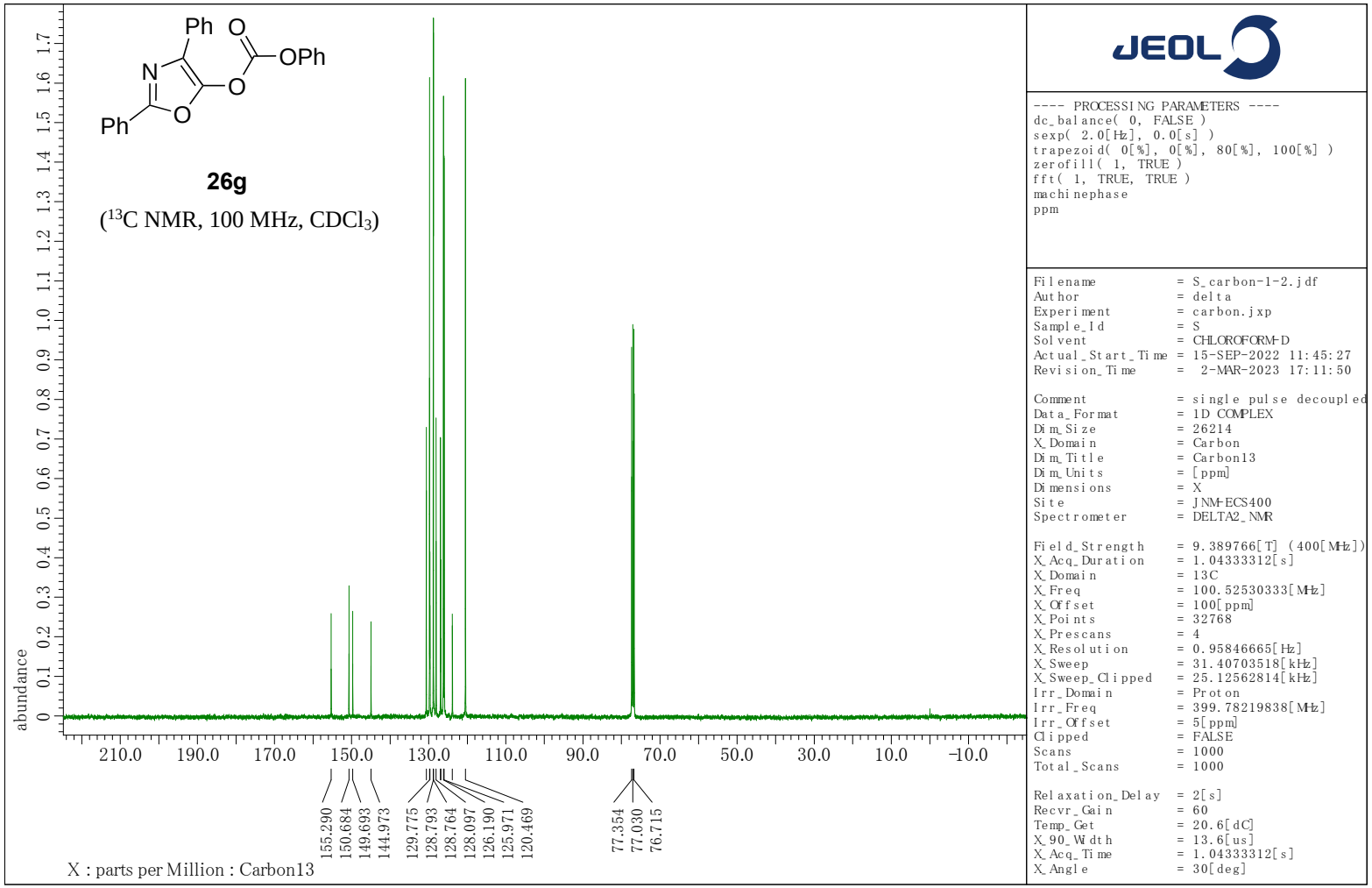



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = H-1.jdf
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 170512-ky-3
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 12-MAY-2017 10:49:33
Revision_Time       = 20-SEP-2017 10:54:35

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 4.36731904[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.22897343[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 22
Temp_Get            = 21.4[dC]
```

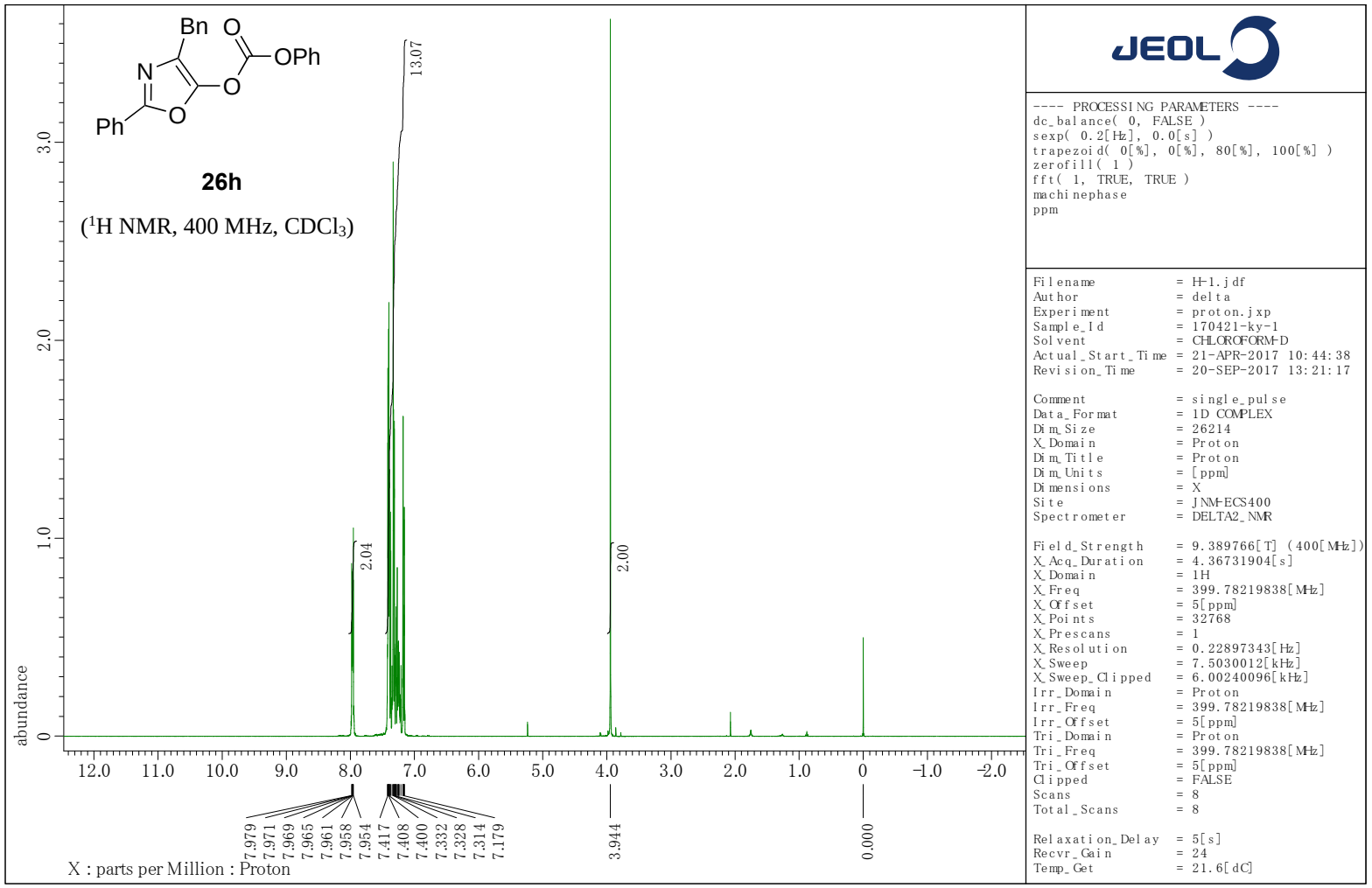

iBu
O
OPh
N
O
O
Ph
26f
(13C NMR, 100 MHz, CDCl3)
abundance
X : parts per Million : Carbon13
155.031
150.674
150.178
146.107
130.260
129.717
128.658
126.799
125.912
124.053
120.449
77.315
77.000
76.685
33.827
27.592
22.300
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170512-ky-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 12-MAY-2017 10:51:24
Revision_Time = 20-SEP-2017 10:56:31
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 66
Total_Scans = 66
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.2[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]

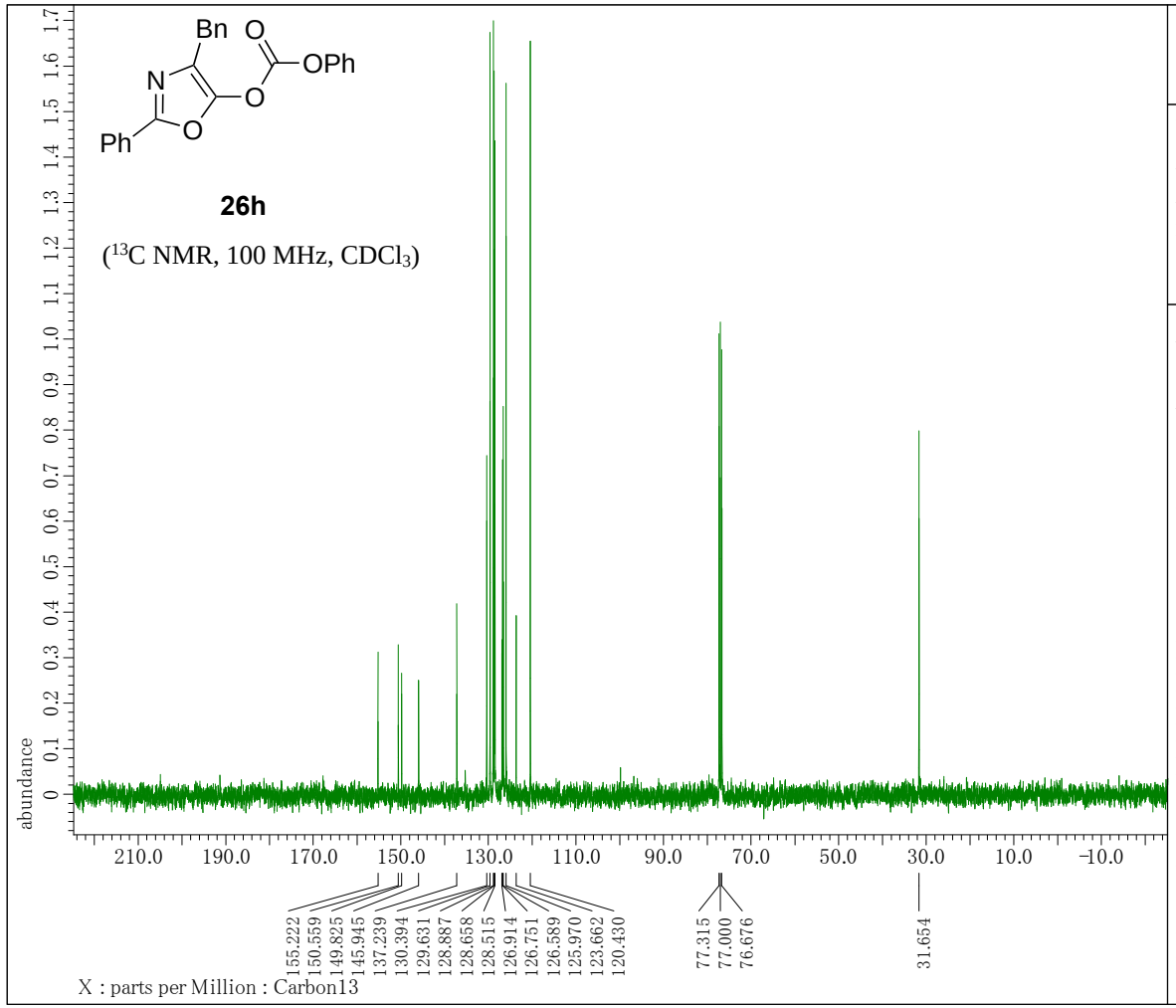

Ph
O
OPh
N
O
O
Ph
26g
(1H NMR, 400 MHz, CDCl3)
15.99
1.00
1.03
abundance
5.0
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
7.898
7.880
7.490
7.483
7.481
7.473
7.465
7.446
7.320
7.316
7.312
7.299
7.293
7.284
7.262
0.000
X : parts per Million : Proton
JEOL RESONANCE
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = TH 220907-recry_proton-1
Author = delta
Experiment = proton.jxp
Sample_Id = TH 220907-recry
Solvent = CHLOROFORM-D
Creation_Time = 9-SEP-2022 14:43:32
Revision_Time = 26-JAN-2023 19:24:25
Current_Time = 26-JAN-2023 19:24:50
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 50
Temp_Get = 20.8[dC]
X_90_Width = 6.3[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3.15[us]
Irr_Mode = Off
Tri_Mode = Off




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

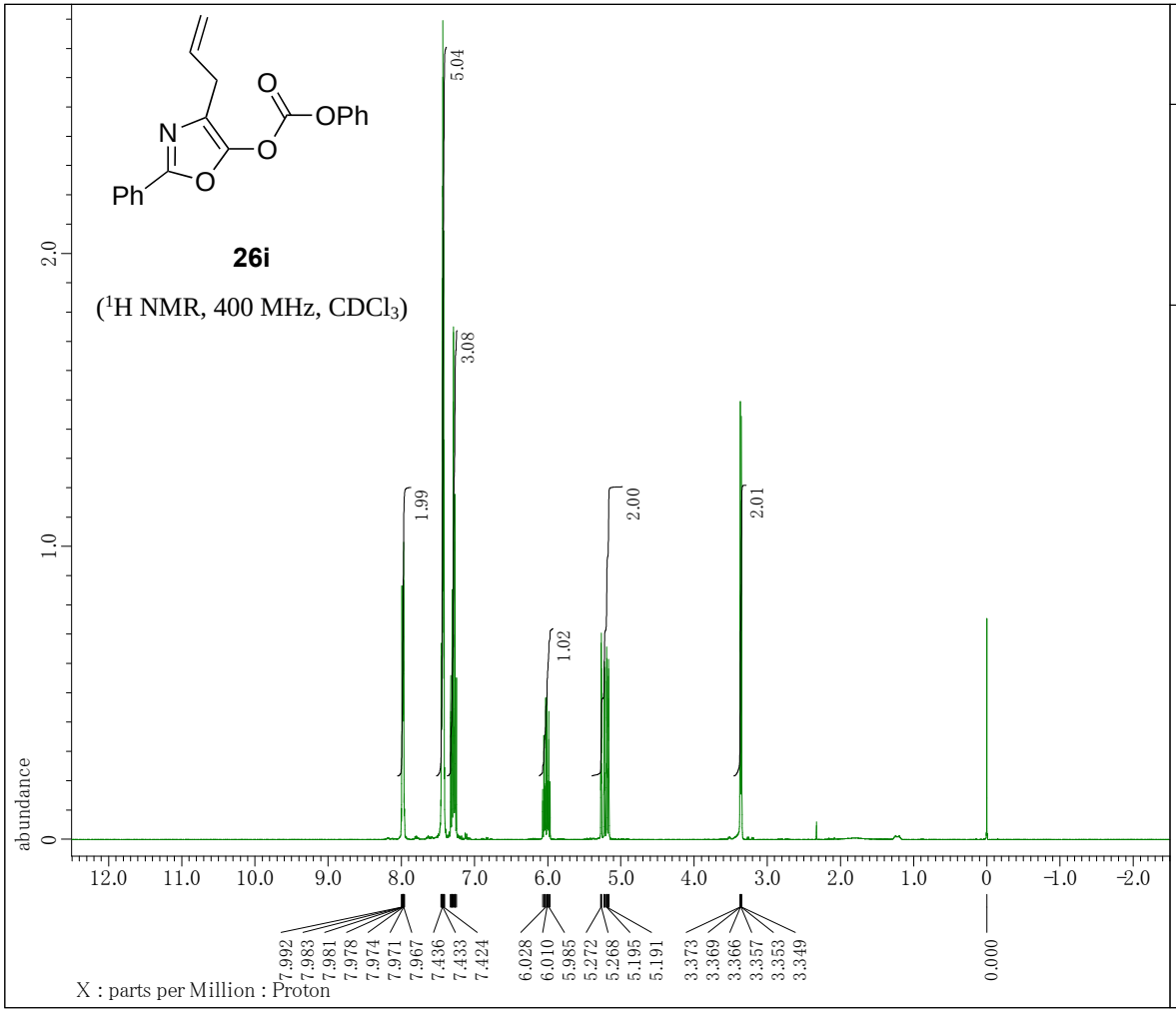
Filename	= S_carbon-1-2.jdf
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= S
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 15-SEP-2022 11:45:27
Revision_Time	= 2-MAR-2023 17:11:50
Comment	= single pulse decoupled
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 1.04333312[s]
X_Domain	= 13C
X_Freq	= 100.52530333[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 0.95846665[Hz]
X_Sweep	= 31.40703518[kHz]
X_Sweep_Clipped	= 25.12562814[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 1000
Total_Scans	= 1000
Relaxation_Delay	= 2[s]
Recvr_Gain	= 60
Temp_Get	= 20.6[dC]
X_90_Width	= 13.6[us]
X_Acq_Time	= 1.04333312[s]
X_Angle	= 30[deg]


Bn
O
OPh
N
O
O
Ph
26h
(1H NMR, 400 MHz, CDCl3)
13.07
2.04
2.00
abundance
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.979
7.971
7.969
7.965
7.961
7.958
7.954
7.417
7.408
7.400
7.332
7.328
7.314
7.179
3.944
0.000
X : parts per Million : Proton
JEOL
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170421-ky-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 21-APR-2017 10:44:38
Revision_Time = 20-SEP-2017 13:21:17
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 24
Temp_Get = 21.6[dC]




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = C-1.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 170421-ky-1
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 21-APR-2017 10:46:24
Revision_Time       = 20-SEP-2017 13:27:17

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 39
Total_Scans         = 39

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 21.4[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
```



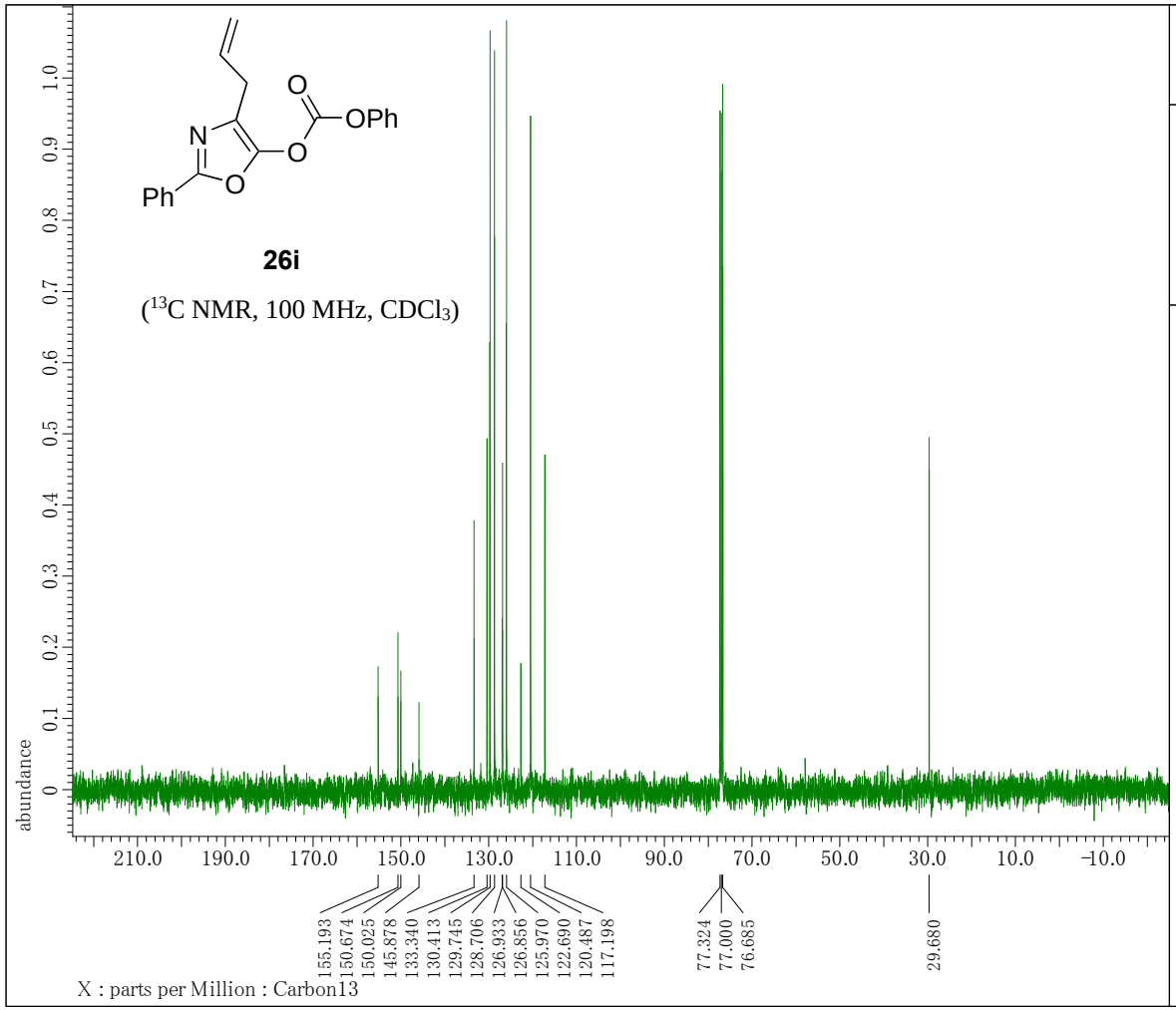
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm

Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170512-ky-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 12-MAY-2017 10:29:21
Revision_Time = 20-SEP-2017 12:43:06

Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8

Relaxation_Delay = 5[s]
Recvr_Gain = 28
Temp_Get = 21.1[dC]



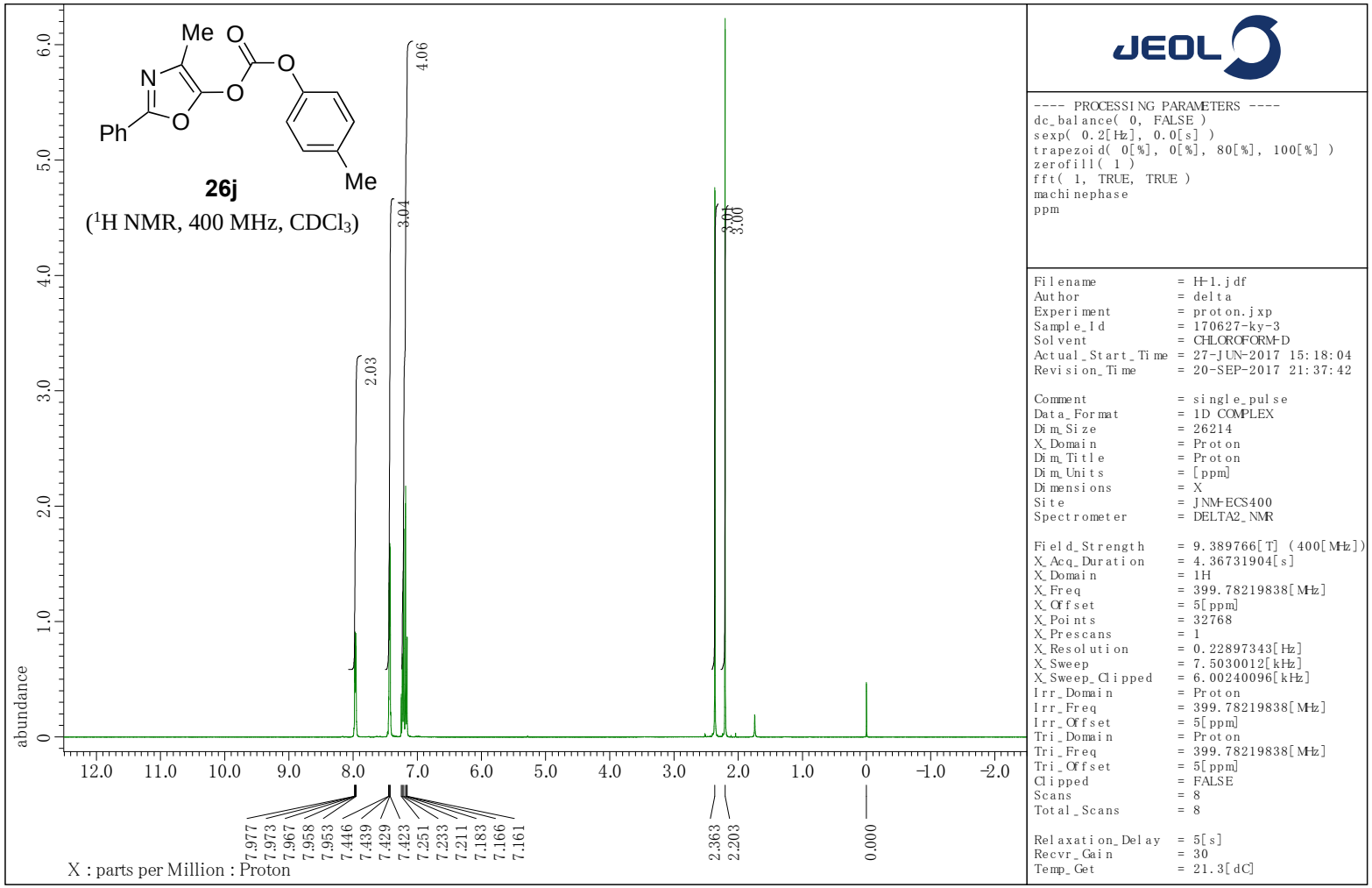
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm

Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170512-ky-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 12-MAY-2017 10:32:04
Revision_Time = 20-SEP-2017 13:13:44

Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR

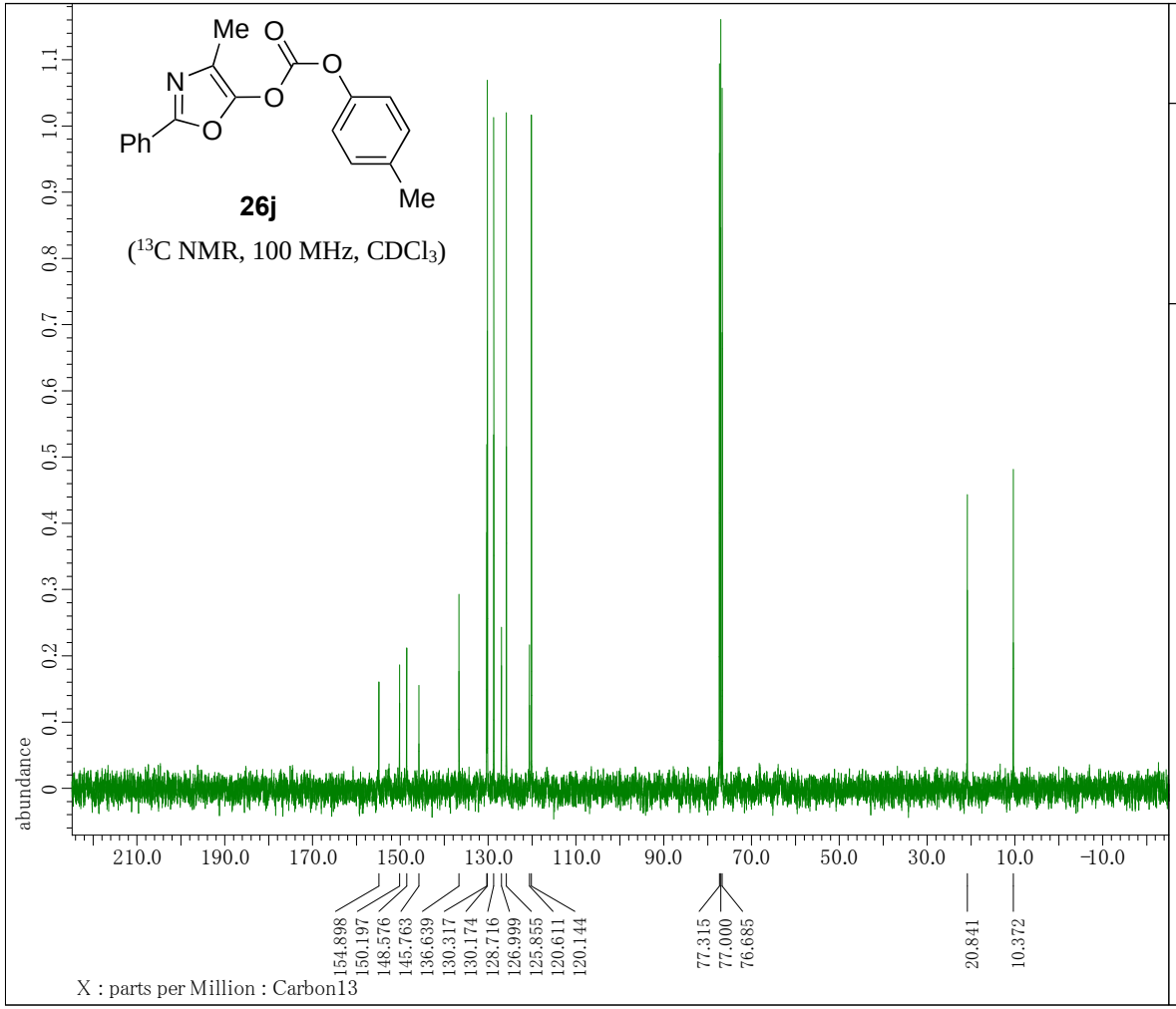
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 52
Total_Scans = 52

Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.3[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]



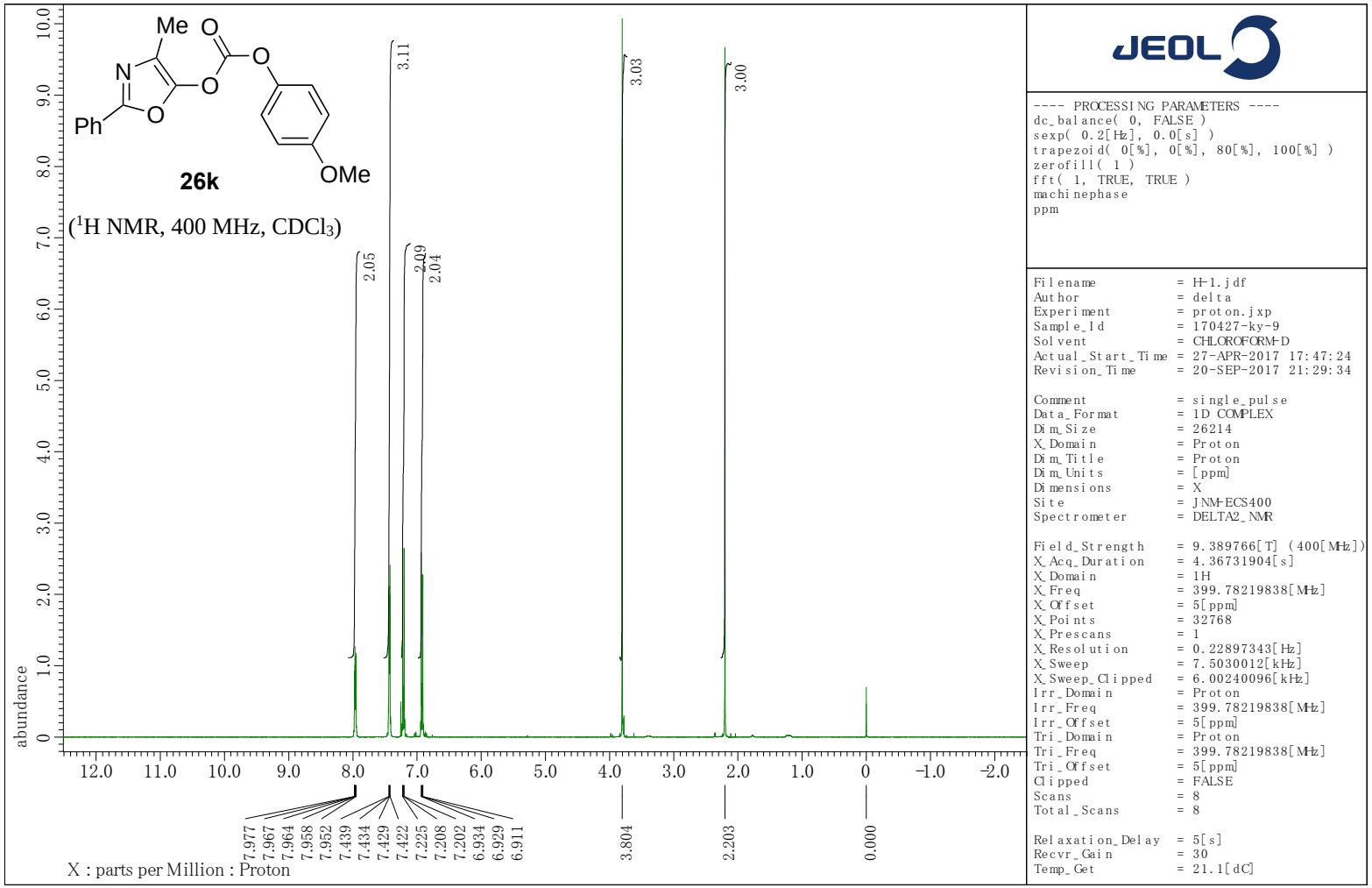

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

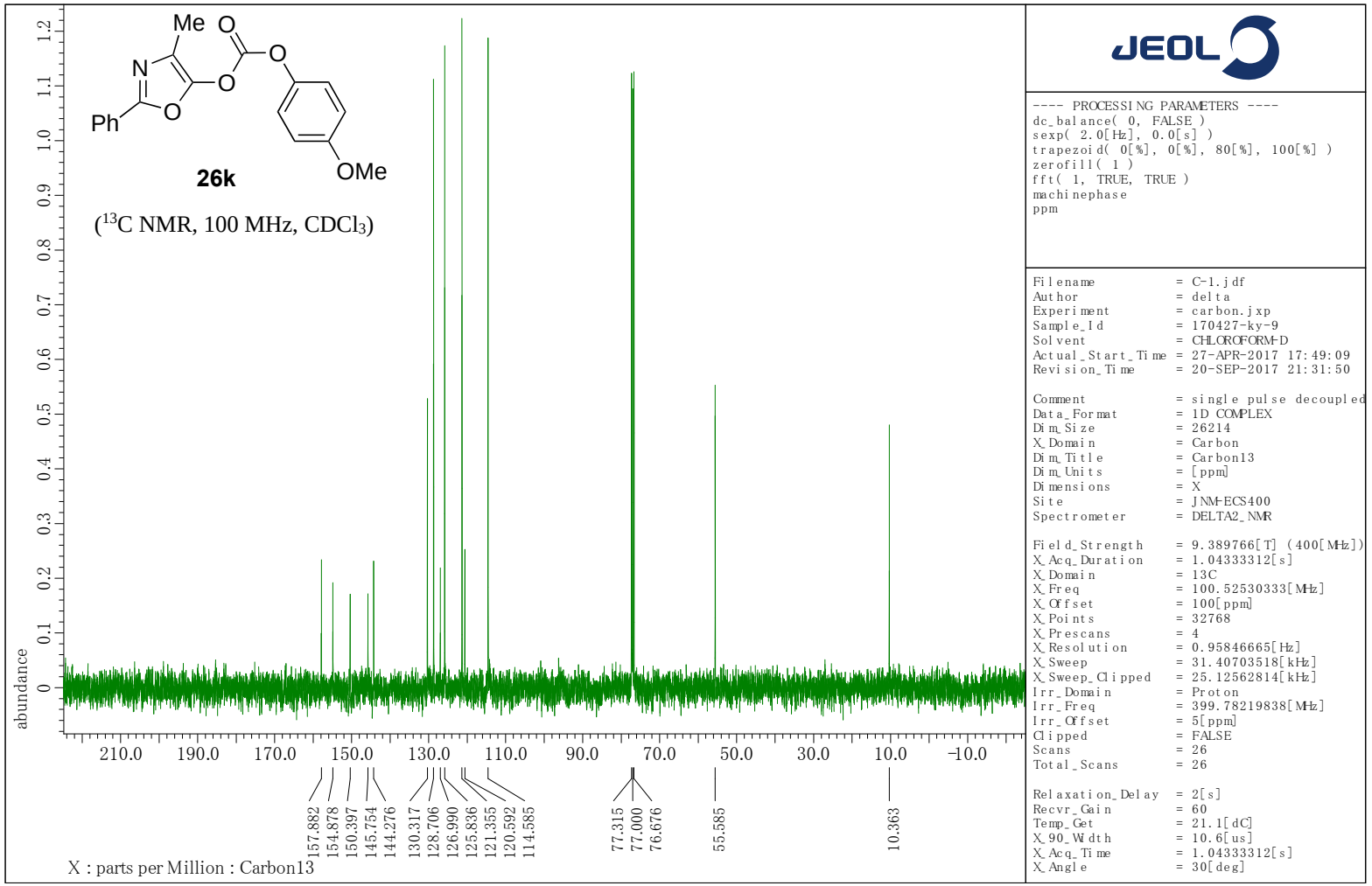
Filename	= H-1.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 170627-ky-3
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 27-JUN-2017 15:18:04
Revision_Time	= 20-SEP-2017 21:37:42
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 30
Temp_Get	= 21.3[dC]

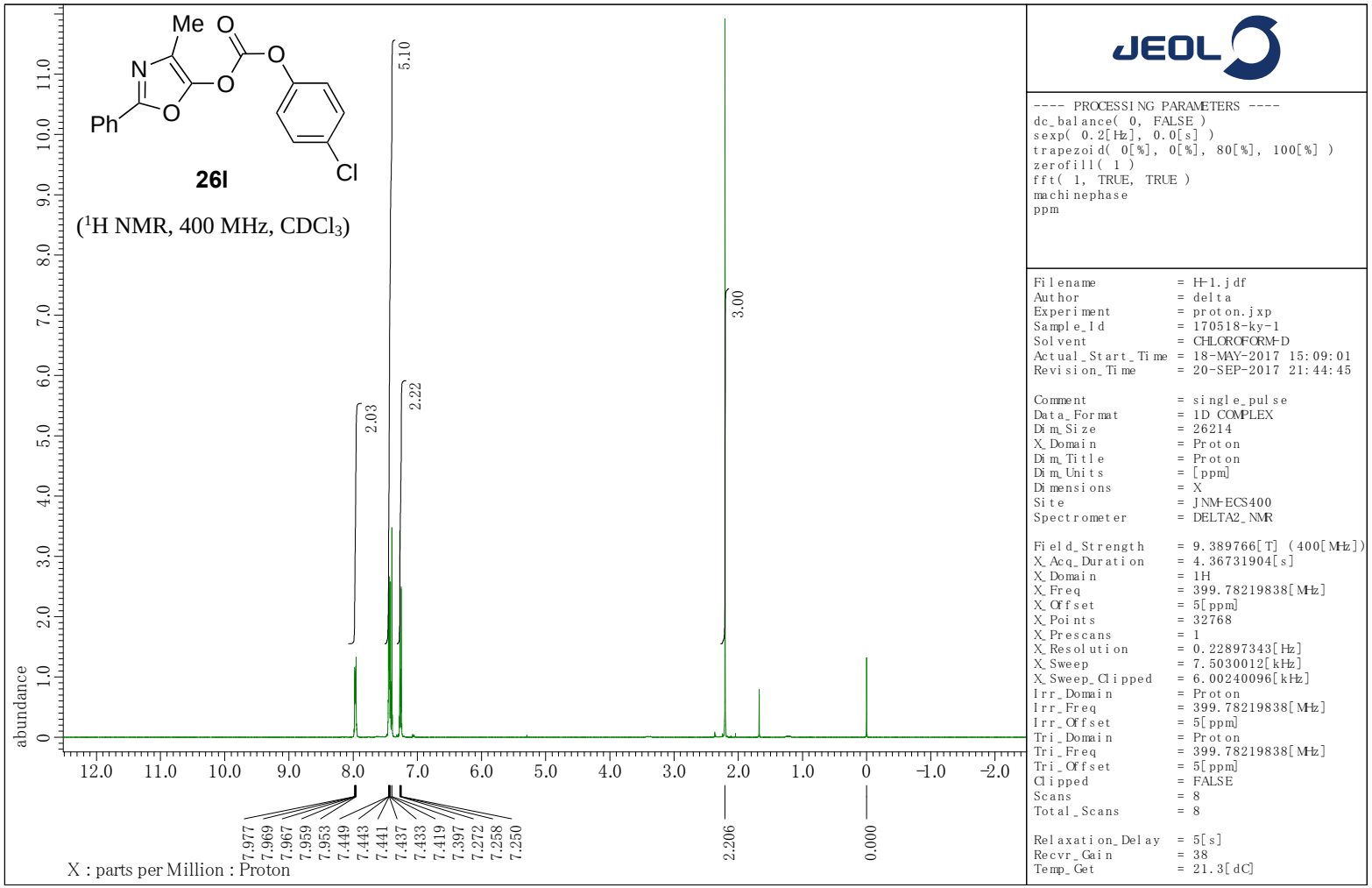


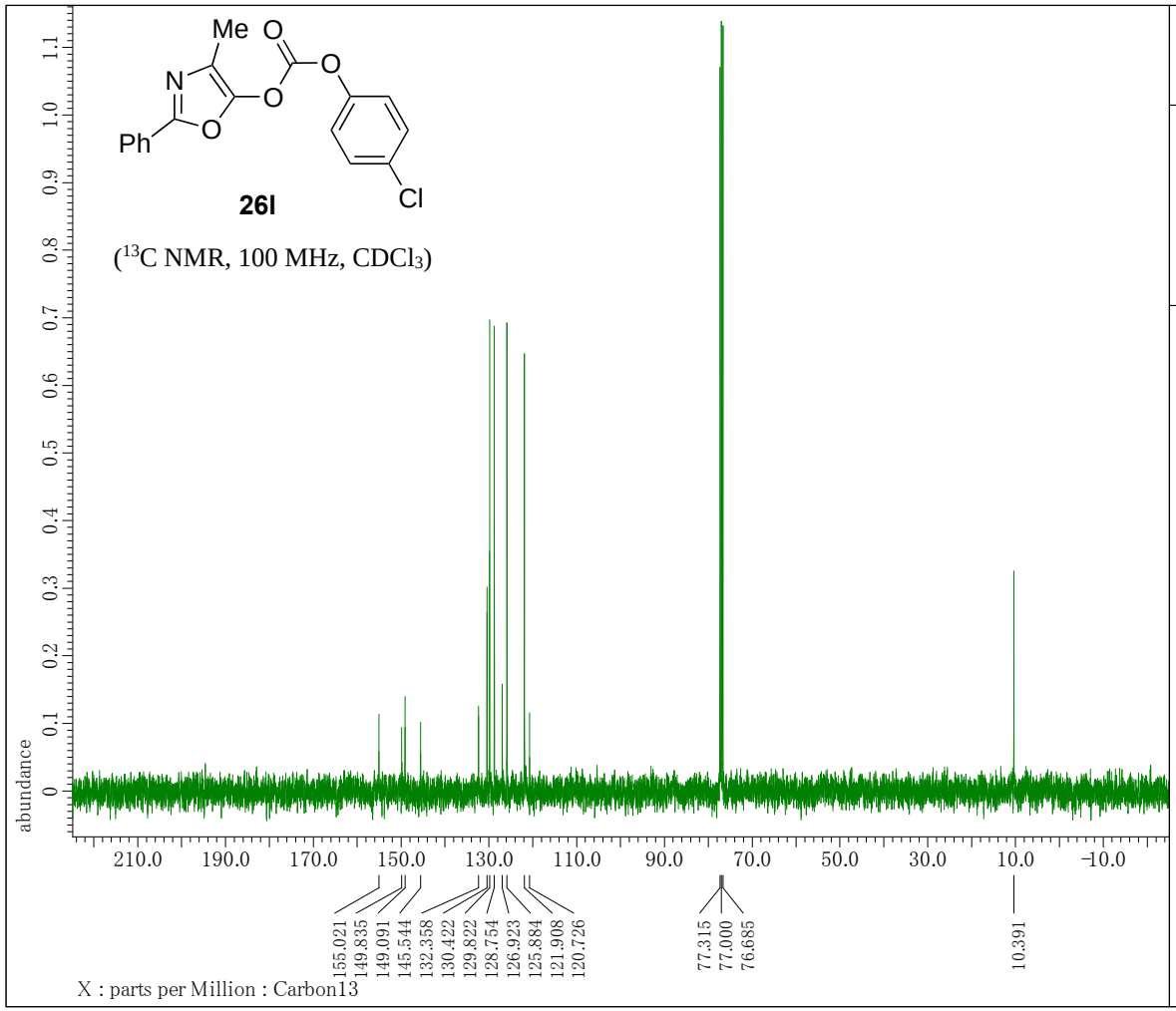

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = C-1.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 170627-ky-3
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 27-JUN-2017 15:19:55
Revision_Time       = 20-SEP-2017 21:38:55

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 45
Total_Scans         = 45

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 21.4[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
```


Me
O
N
O
O
O
Ph
OMe
26k
(1H NMR, 400 MHz, CDCl3)
abundance
X : parts per Million : Proton
2.05
3.11
2.09
2.04
3.03
3.00
7.977
7.967
7.964
7.958
7.952
7.439
7.434
7.429
7.422
7.225
7.208
7.202
6.934
6.929
6.911
3.804
2.203
0.000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170427-ky-9
Solvent = CHLOROFORM-D
Actual_Start_Time = 27-APR-2017 17:47:24
Revision_Time = 20-SEP-2017 21:29:34
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 30
Temp_Get = 21.1[dC]

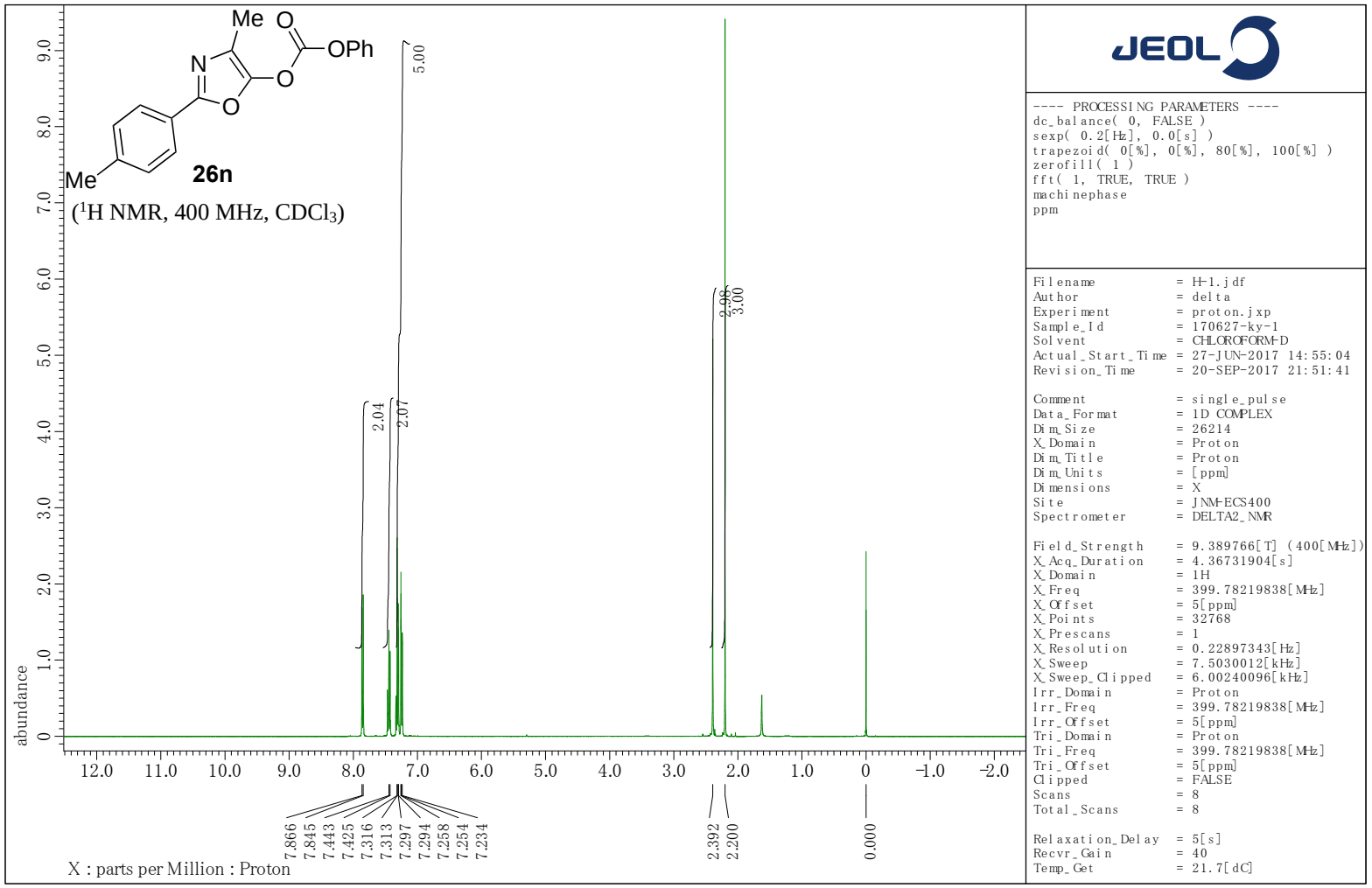

Me
O
N
O
O
Ph
O
OMe
26k
(^{13}C NMR, 100 MHz, $CDCl_3$)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
210.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
−10.0
157.882
154.878
150.397
145.754
144.276
130.317
128.706
126.990
125.836
121.355
120.592
114.585
77.315
77.000
76.676
55.585
10.363
X : parts per Million : Carbon13
JEOL
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170427-ky-9
Solvent = CHLOROFORM-D
Actual_Start_Time = 27-APR-2017 17:49:09
Revision_Time = 20-SEP-2017 21:31:50
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 26
Total_Scans = 26
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.1[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]


Me
O
N
O
O
O
Ph
Cl
26l
(1H NMR, 400 MHz, CDCl3)
5.10
3.00
2.22
2.03
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.977
7.969
7.967
7.959
7.953
7.449
7.443
7.441
7.437
7.433
7.419
7.397
7.272
7.258
7.250
2.206
0.000
X : parts per Million : Proton
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170518-ky-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 18-MAY-2017 15:09:01
Revision_Time = 20-SEP-2017 21:44:45
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 38
Temp_Get = 21.3[dC]



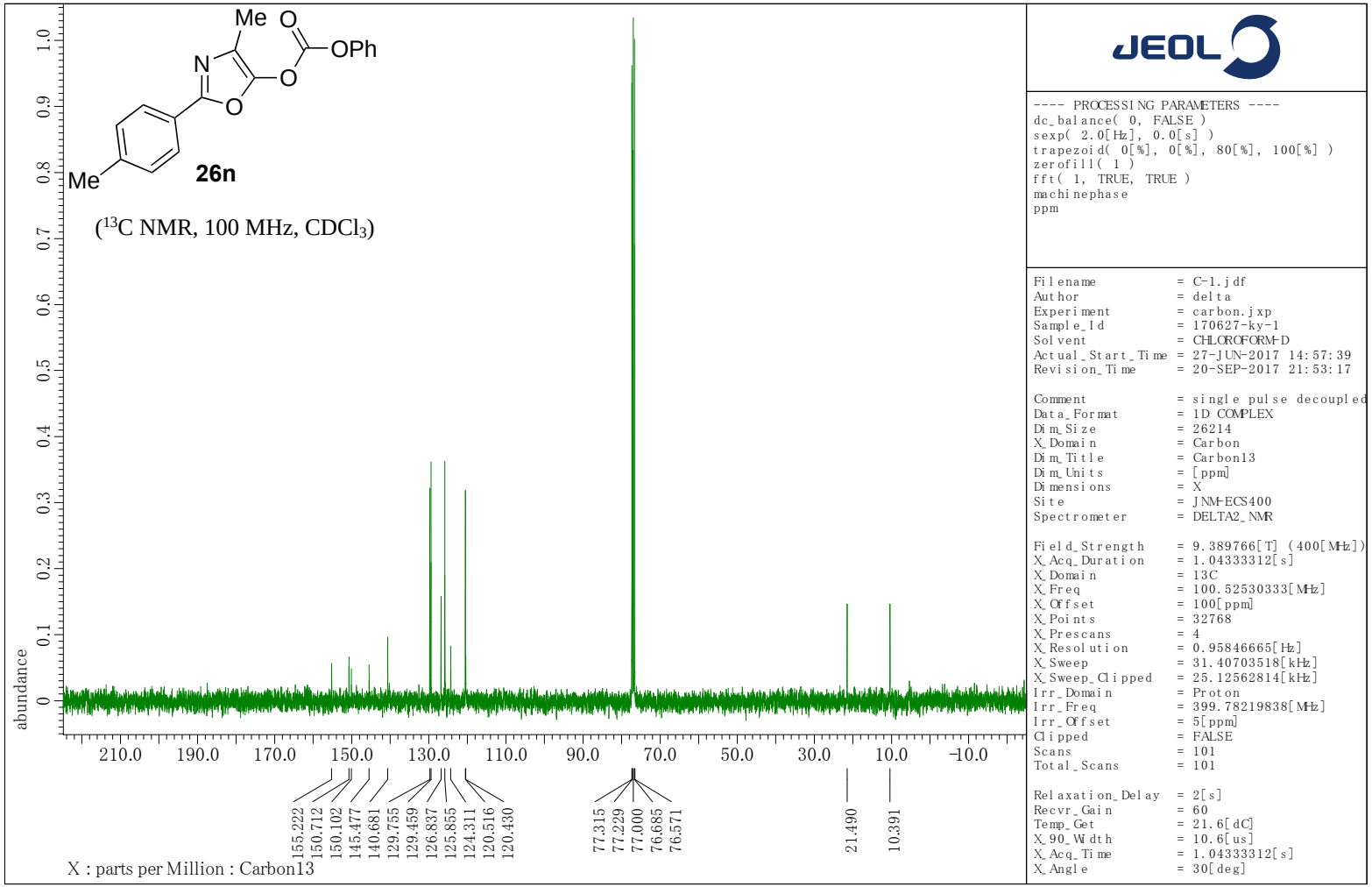
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

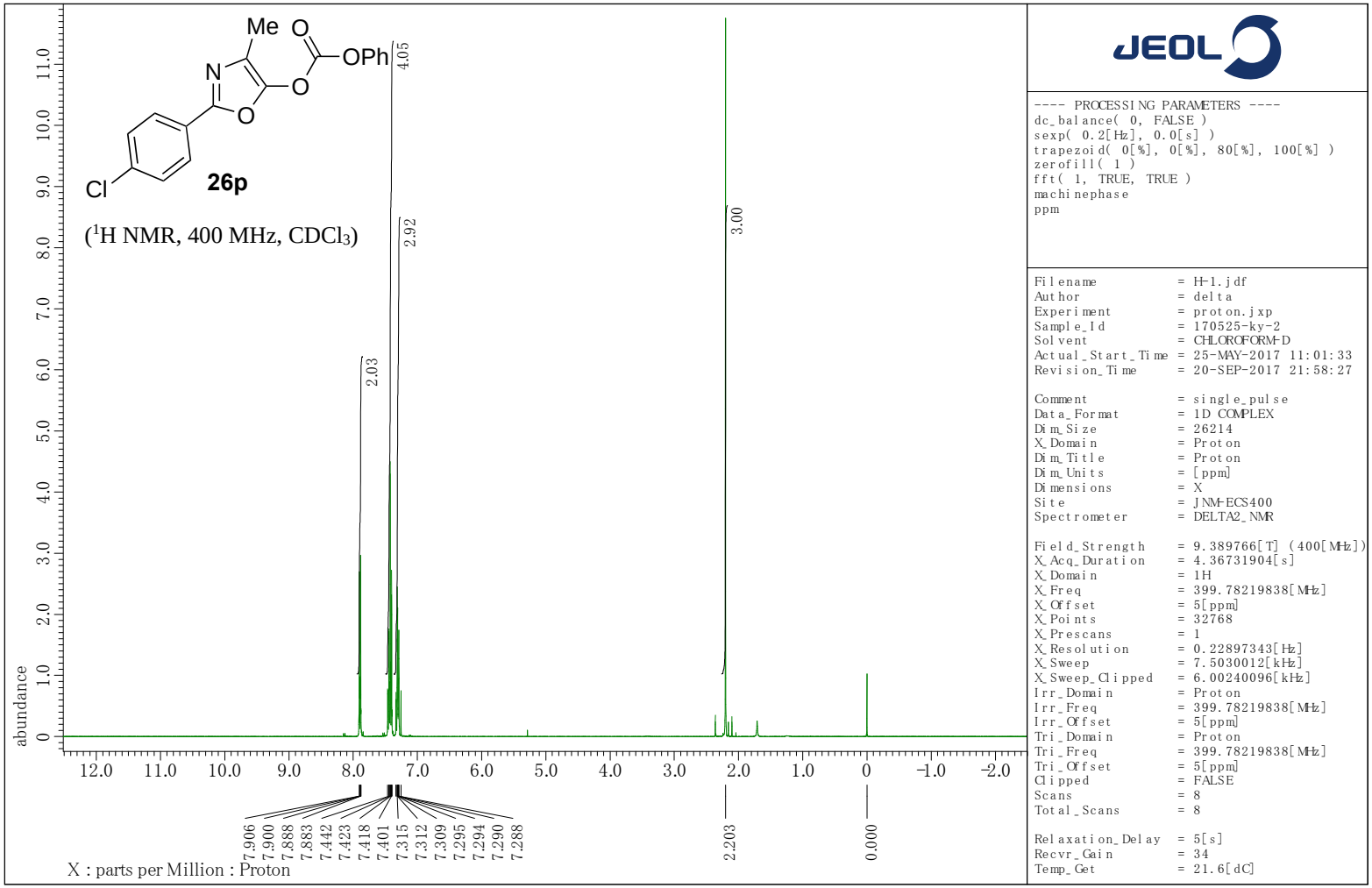
Filename	= C-1.jdf
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= 170518-ky-1
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 18-MAY-2017 15:10:53
Revision_Time	= 20-SEP-2017 21:46:02
Comment	= single pulse decoupled
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 1.04333312[s]
X_Domain	= 13C
X_Freq	= 100.52530333[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 0.95846665[Hz]
X_Sweep	= 31.40703518[kHz]
X_Sweep_Clipped	= 25.12562814[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 43
Total_Scans	= 43
Relaxation_Delay	= 2[s]
Recvr_Gain	= 60
Temp_Get	= 21.3[dC]
X_90_Width	= 10.6[us]
X_Acq_Time	= 1.04333312[s]
X_Angle	= 30[deg]

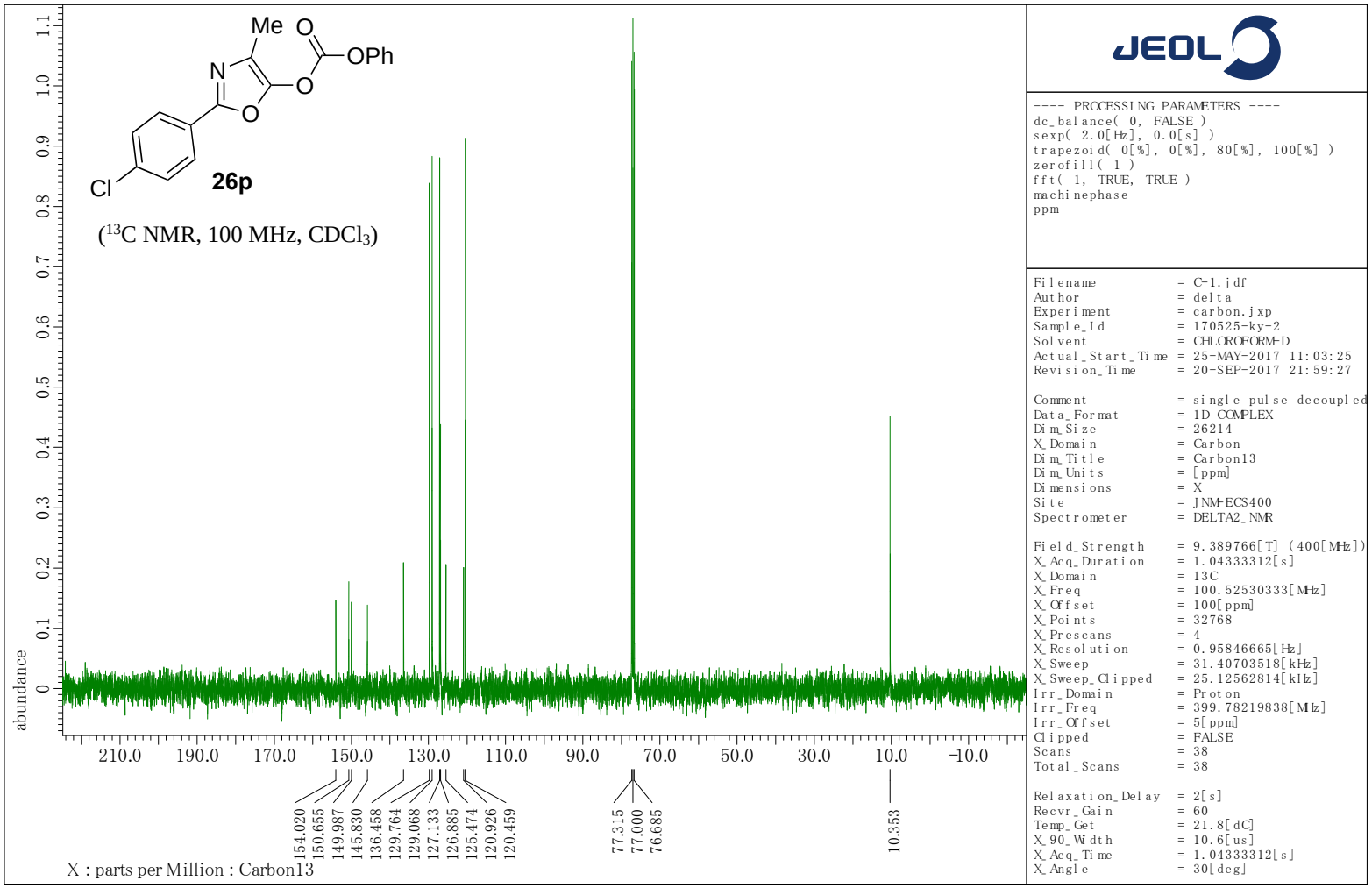


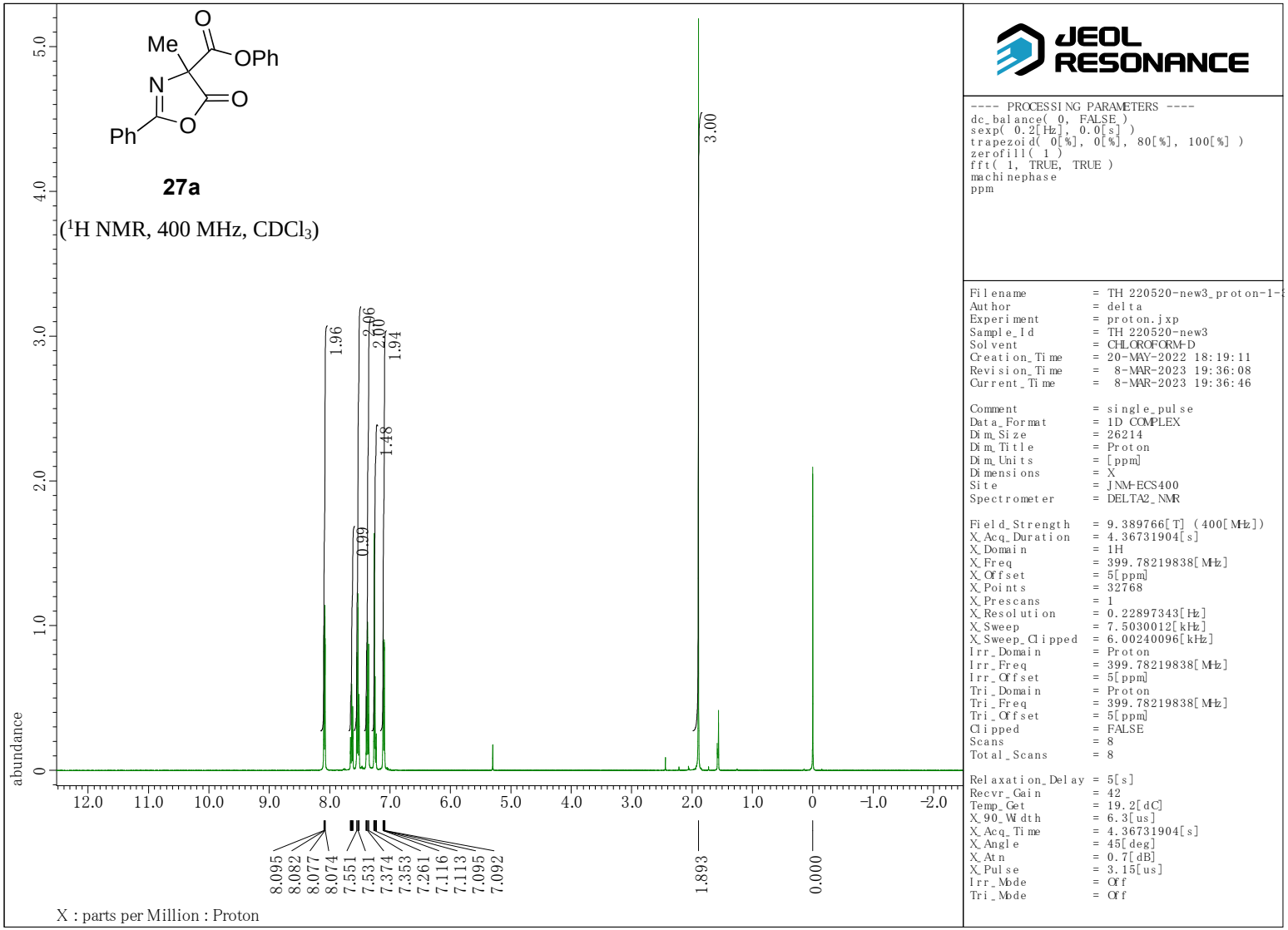
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm

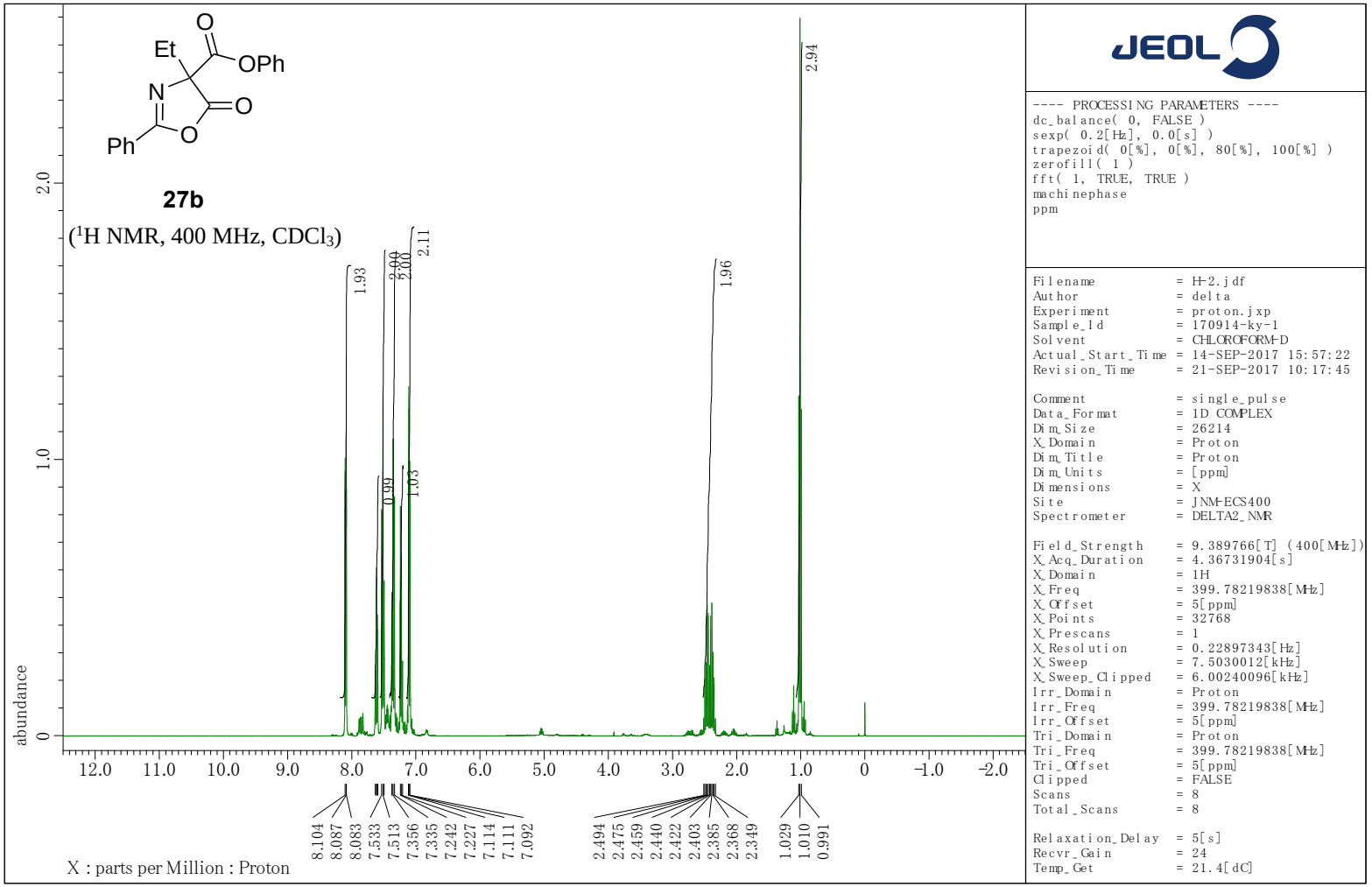
Filename	= H-1.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 170627-ky-1
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 27-JUN-2017 14:55:04
Revision_Time	= 20-SEP-2017 21:51:41
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 40
Temp_Get	= 21.7[dC]

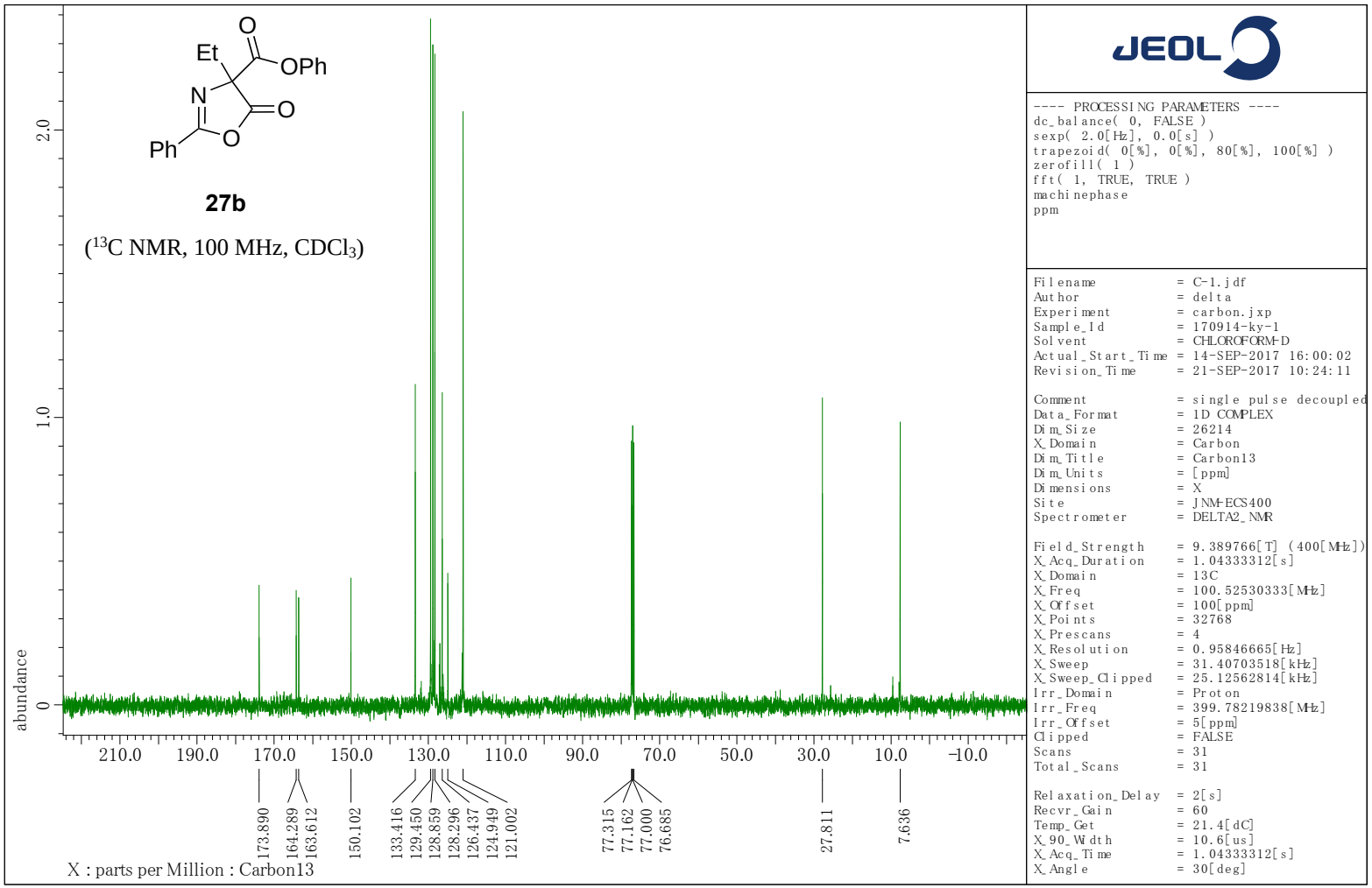

Me
O
OPh
N
O
O
Me
26n
(13C NMR, 100 MHz, CDCl3)
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
210.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
155.222
150.712
150.102
145.477
140.681
129.755
129.459
126.837
125.855
124.311
120.516
120.430
77.315
77.229
77.000
76.685
76.571
21.490
10.391
X : parts per Million : Carbon13
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170627-ky-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 27-JUN-2017 14:57:39
Revision_Time = 20-SEP-2017 21:53:17
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 101
Total_Scans = 101
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.6[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]


Me
O
OPh
N
O
O
Cl
26p
(1H NMR, 400 MHz, CDCl3)
4.05
2.92
3.00
2.03
abundance
X : parts per Million : Proton
7.906
7.900
7.888
7.883
7.442
7.423
7.418
7.401
7.315
7.312
7.309
7.295
7.294
7.290
7.288
2.203
0.000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170525-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 25-MAY-2017 11:01:33
Revision_Time = 20-SEP-2017 21:58:27
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 34
Temp_Get = 21.6[dC]


Me
O
OPh
N
O
O
Cl
26p
(^{13}C NMR, 100 MHz, $CDCl_3$)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
210.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
−10.0
154.020
150.655
149.987
145.830
136.458
129.764
129.068
127.133
126.885
125.474
120.926
120.459
77.315
77.000
76.685
10.353
X : parts per Million : Carbon13
JEOL
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170525-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 25-MAY-2017 11:03:25
Revision_Time = 20-SEP-2017 21:59:27
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 38
Total_Scans = 38
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.8[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]


Me
O
OPh
N
O
Ph
O
27a
(1H NMR, 400 MHz, CDCl3)
abundance
1.96
0.99
2.06
2.00
1.94
1.48
3.00
8.095
8.082
8.077
8.074
7.551
7.531
7.374
7.353
7.261
7.116
7.113
7.095
7.092
1.893
0.000
X : parts per Million : Proton
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = TH 220520-new3_proton-1-
Author = delta
Experiment = proton.jxp
Sample_Id = TH 220520-new3
Solvent = CHLOROFORM-D
Creation_Time = 20-MAY-2022 18:19:11
Revision_Time = 8-MAR-2023 19:36:08
Current_Time = 8-MAR-2023 19:36:46
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 42
Temp_Get = 19.2[dC]
X_90_Width = 6.3[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 0.7[dB]
X_Pulse = 3.15[us]
Irr_Mode = Off
Tri_Mode = Off

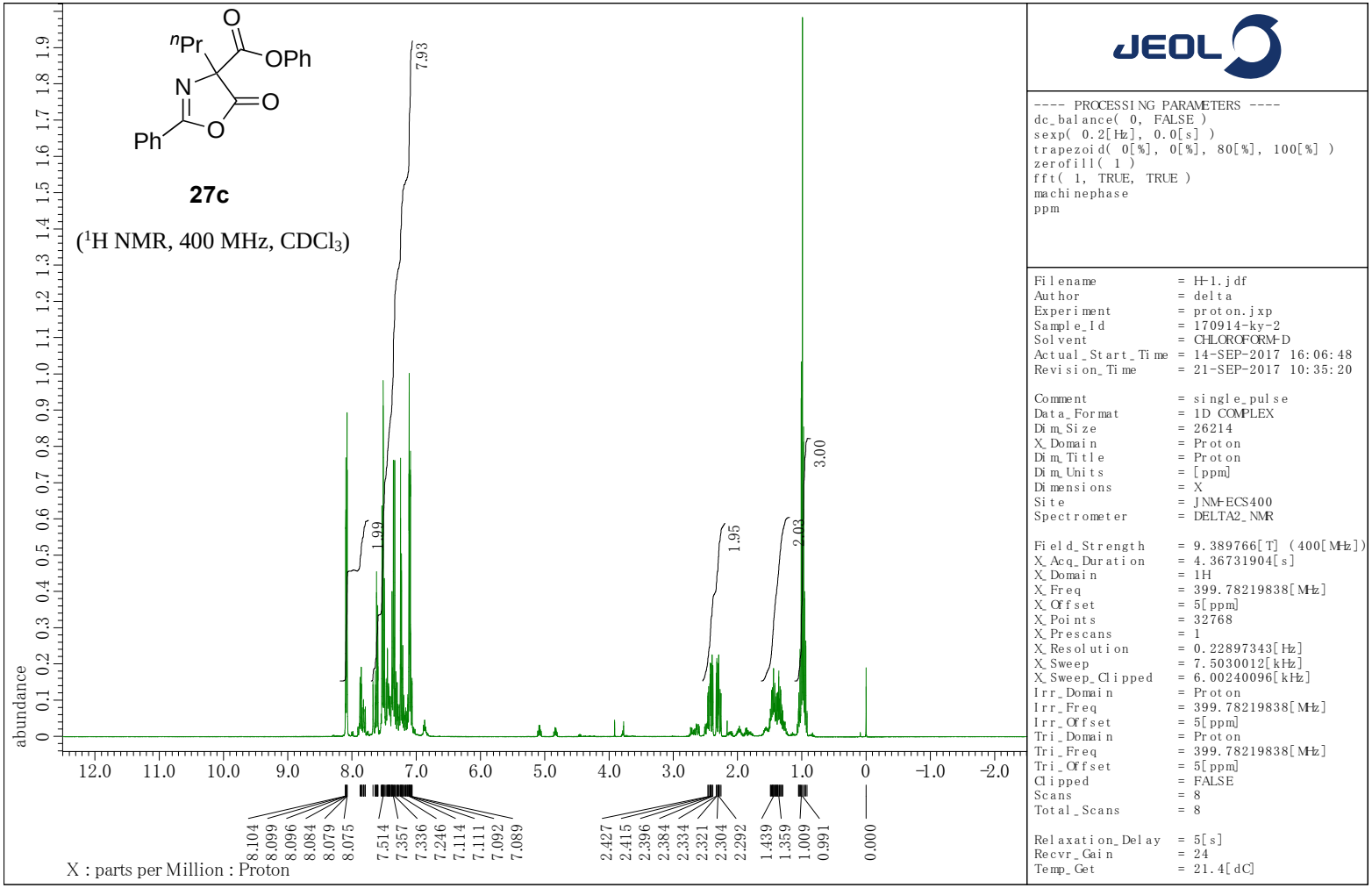

Et
OPh
N
O
O
Ph
O
27b
(1H NMR, 400 MHz, CDCl3)
abundance
2.0
1.0
0
1.93
2.00
2.00
2.11
0.99
1.03
1.96
2.94
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
8.104
8.087
8.083
7.533
7.513
7.356
7.335
7.242
7.227
7.114
7.111
7.092
2.494
2.475
2.459
2.440
2.422
2.403
2.385
2.368
2.349
1.029
1.010
0.991
X : parts per Million : Proton
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-2.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170914-ky-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 14-SEP-2017 15:57:22
Revision_Time = 21-SEP-2017 10:17:45
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 24
Temp_Get = 21.4[dC]

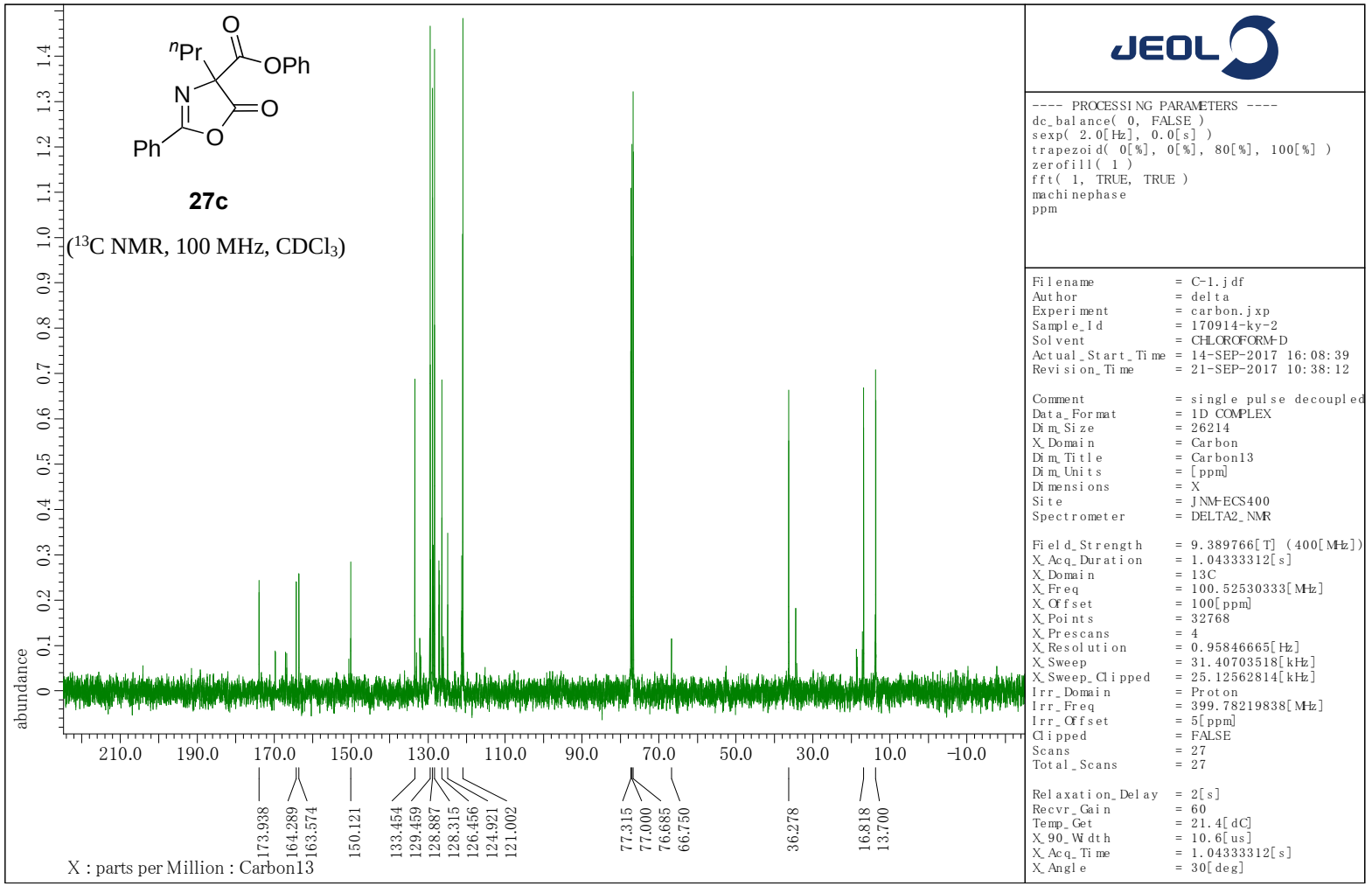


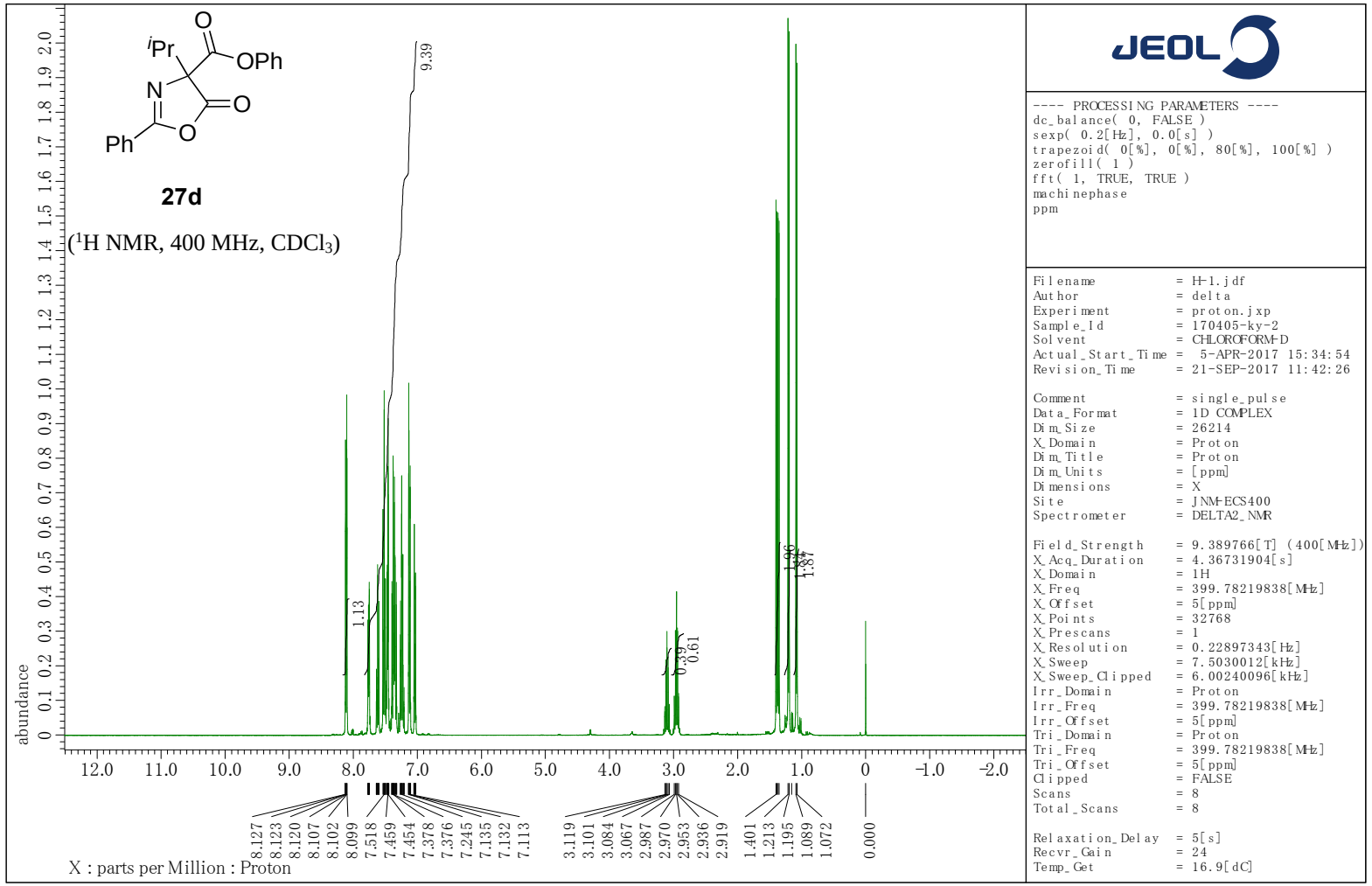
JEOL

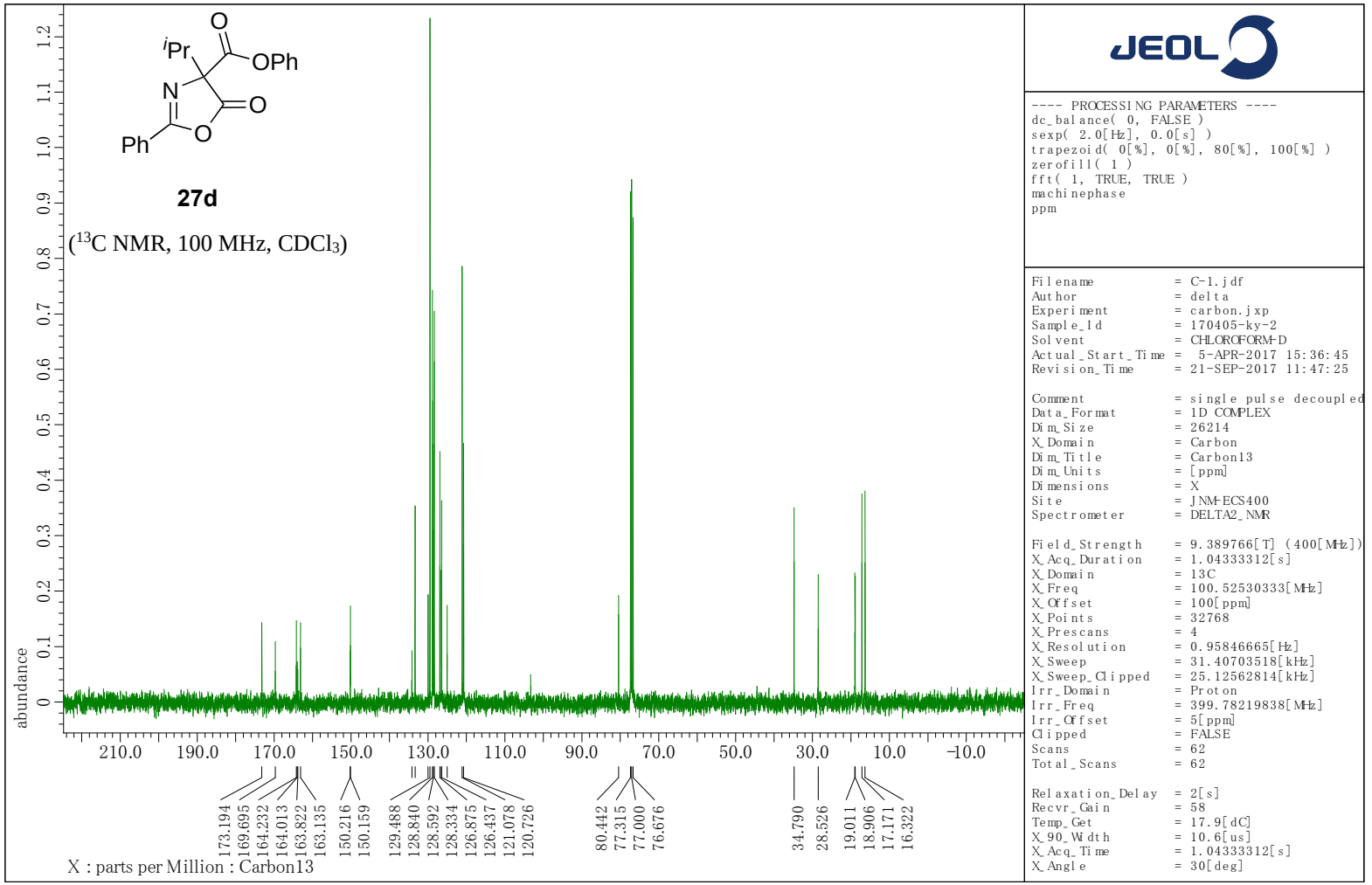
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

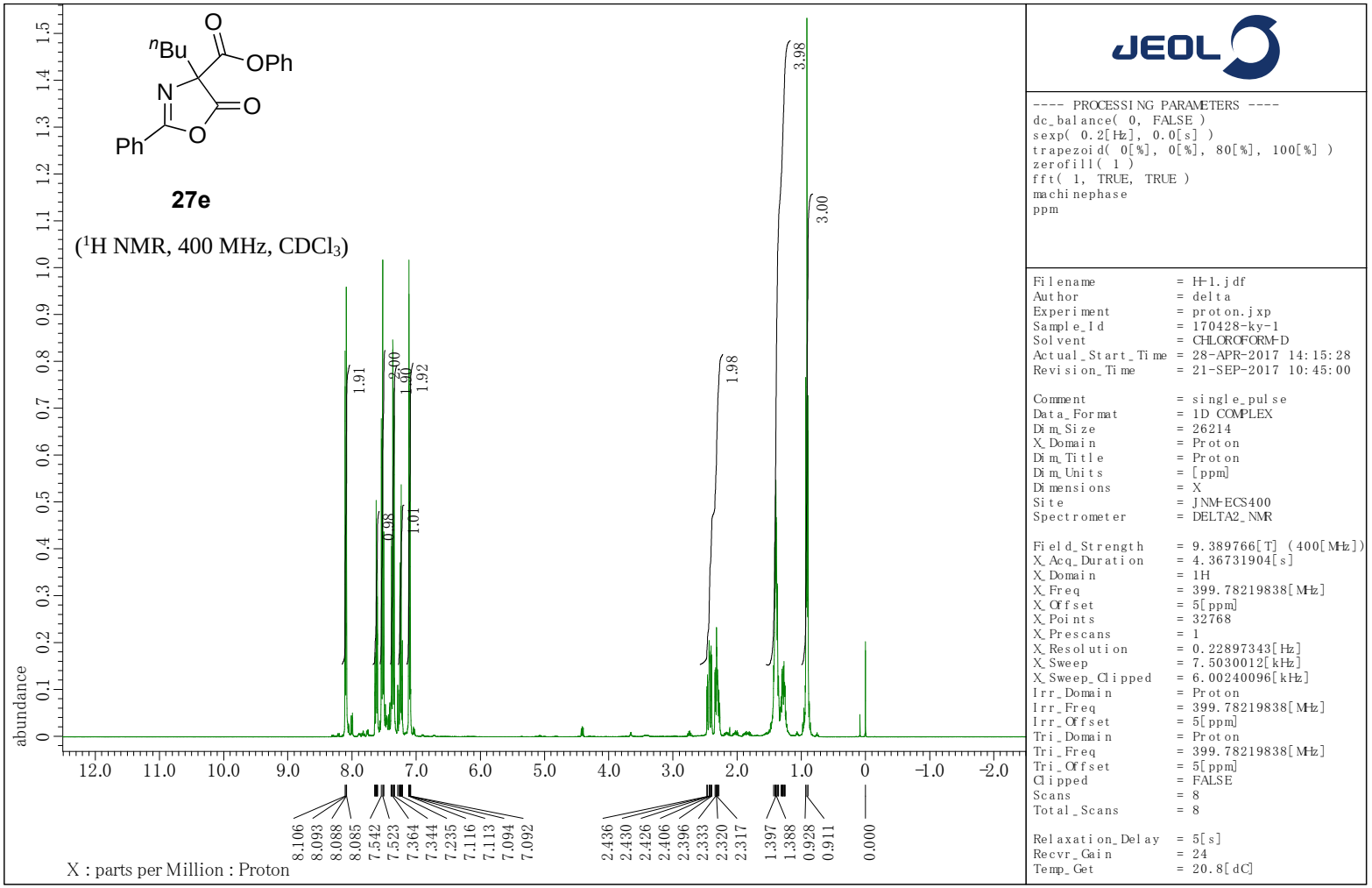
```
Filename            = C-1.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 170914-ky-1
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 14-SEP-2017 16:00:02
Revision_Time       = 21-SEP-2017 10:24:11

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 31
Total_Scans         = 31

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 21.4[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
```

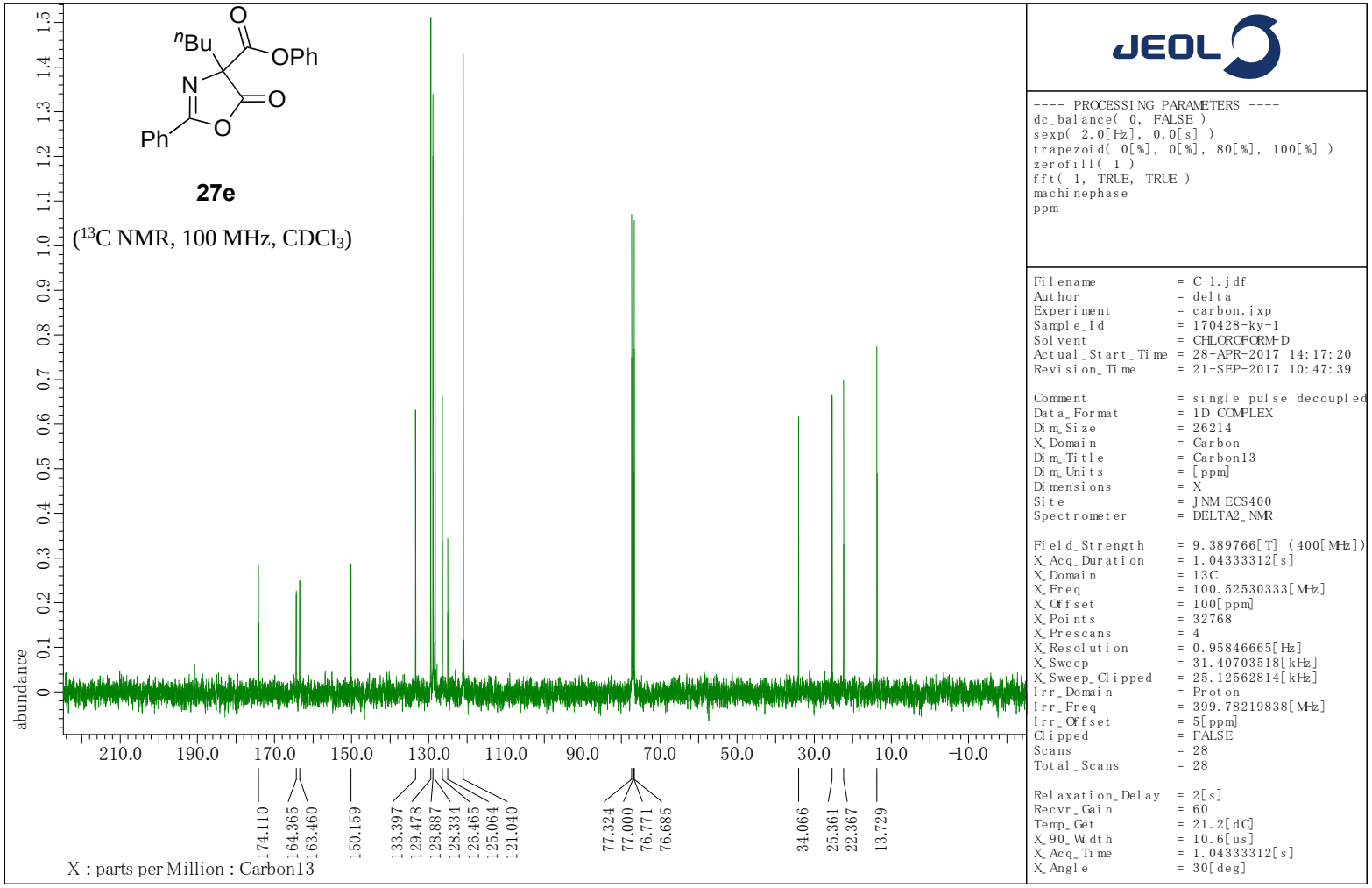

nPr
OPh
N
O
O
Ph
O
27c
(1H NMR, 400 MHz, CDCl3)
abundance
X : parts per Million : Proton
7.93
1.99
1.95
2.03
3.00
8.104
8.099
8.096
8.084
8.079
8.075
7.514
7.357
7.336
7.246
7.114
7.111
7.092
7.089
2.427
2.415
2.396
2.384
2.334
2.321
2.304
2.292
1.439
1.359
1.009
0.991
0.000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170914-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 14-SEP-2017 16:06:48
Revision_Time = 21-SEP-2017 10:35:20
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 24
Temp_Get = 21.4[dC]

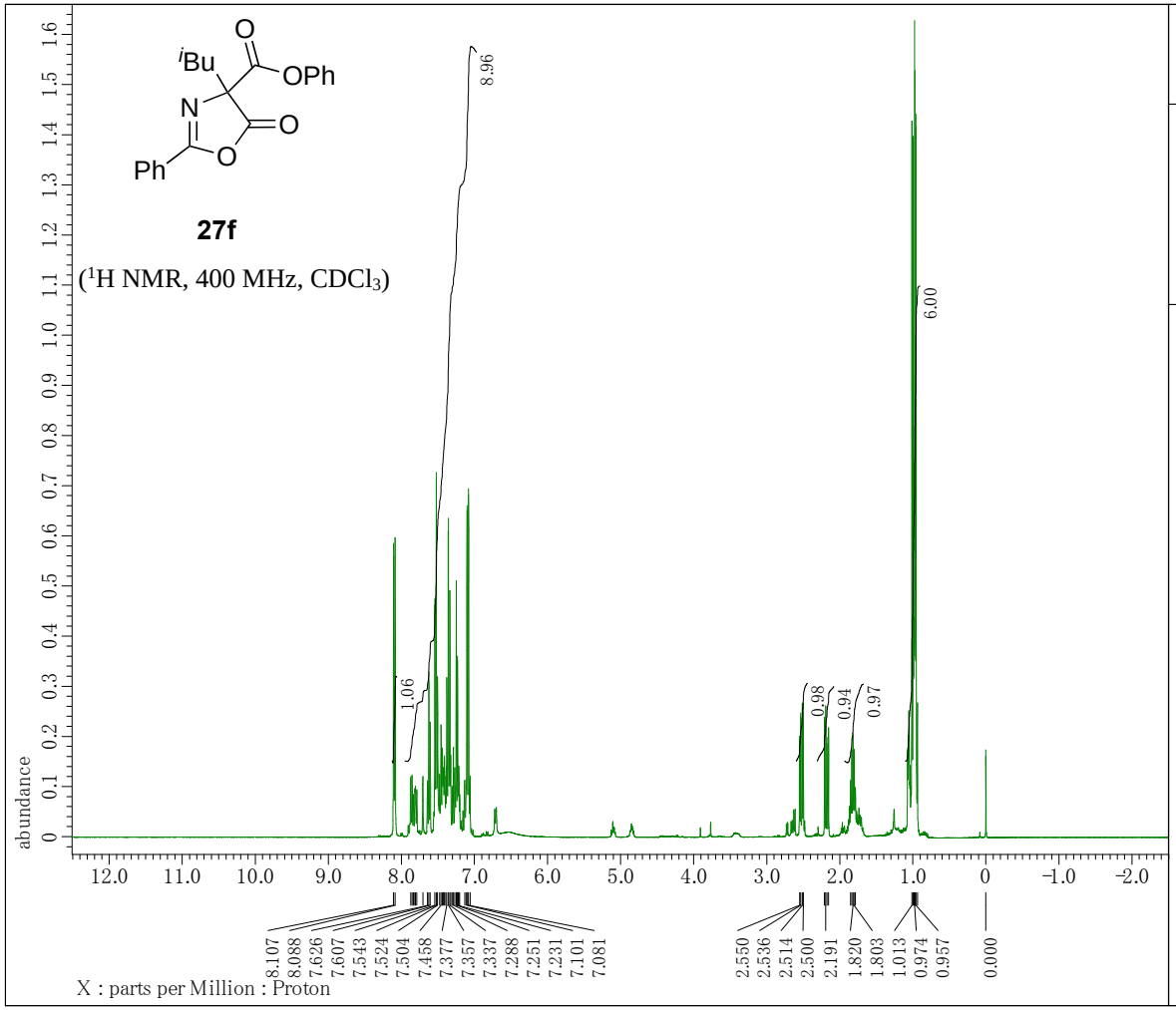

27c
(13C NMR, 100 MHz, CDCl3)
abundance
X : parts per Million : Carbon13
173.938
164.289
163.574
150.121
133.454
129.459
128.887
128.315
126.456
124.921
121.002
77.315
77.000
76.685
66.750
36.278
16.818
13.700
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170914-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 14-SEP-2017 16:08:39
Revision_Time = 21-SEP-2017 10:38:12
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 27
Total_Scans = 27
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.4[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]


27d
(1H NMR, 400 MHz, CDCl3)
X : parts per Million : Proton
abundance
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170405-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 5-APR-2017 15:34:54
Revision_Time = 21-SEP-2017 11:42:26
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 24
Temp_Get = 16.9[dC]


27d
(13C NMR, 100 MHz, CDCl3)
abundance
X : parts per Million : Carbon13
173.194
169.695
164.232
164.013
163.822
163.135
150.216
150.159
129.488
128.840
128.592
128.334
126.875
126.437
121.078
120.726
80.442
77.315
77.000
76.676
34.790
28.526
19.011
18.906
17.171
16.322
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170405-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 5-APR-2017 15:36:45
Revision_Time = 21-SEP-2017 11:47:25
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 62
Total_Scans = 62
Relaxation_Delay = 2[s]
Recvr_Gain = 58
Temp_Get = 17.9[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]

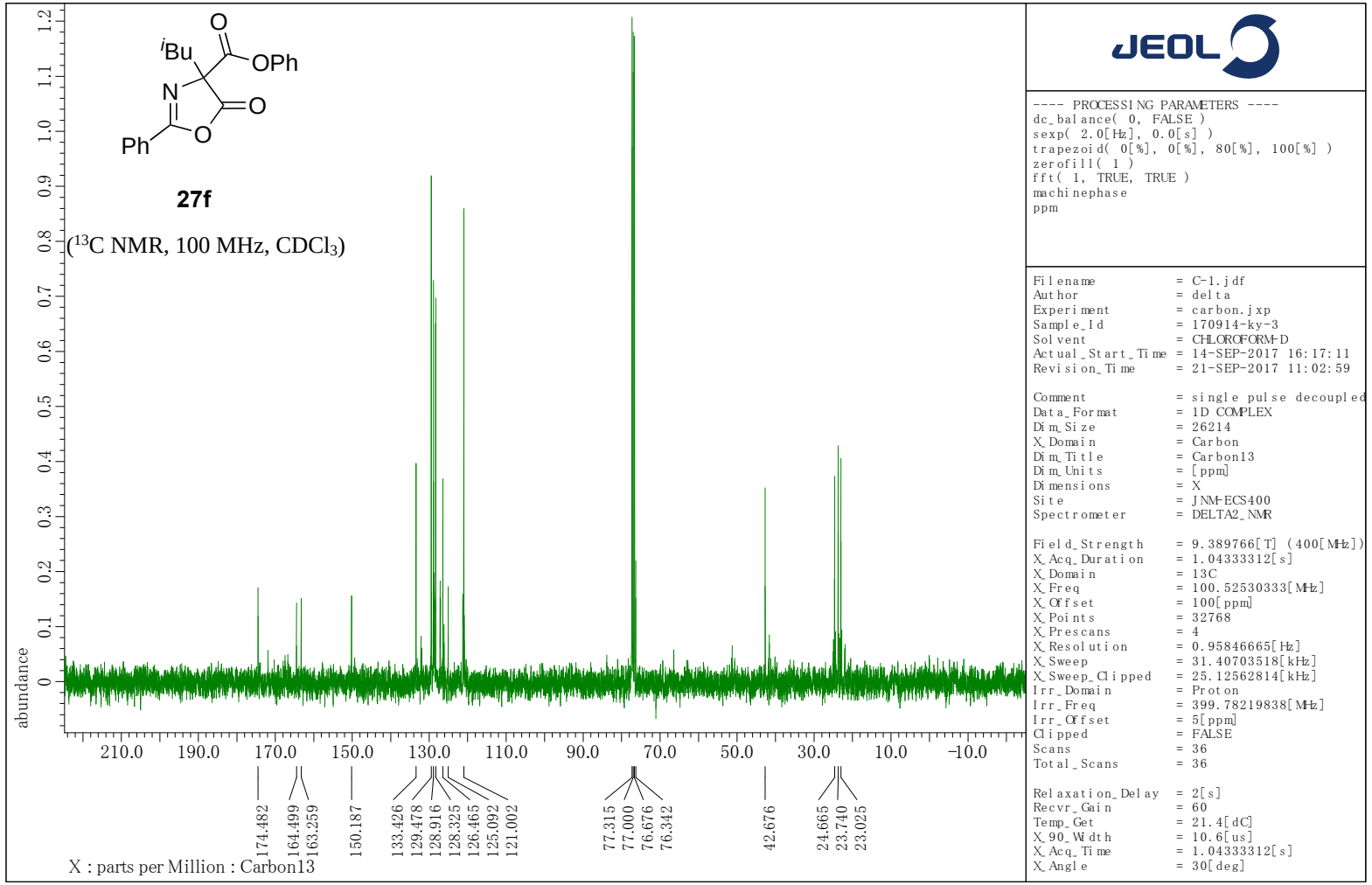

27e
(1H NMR, 400 MHz, CDCl3)
abundance
X : parts per Million : Proton
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170428-ky-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 28-APR-2017 14:15:28
Revision_Time = 21-SEP-2017 10:45:00
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 24
Temp_Get = 20.8[dC]

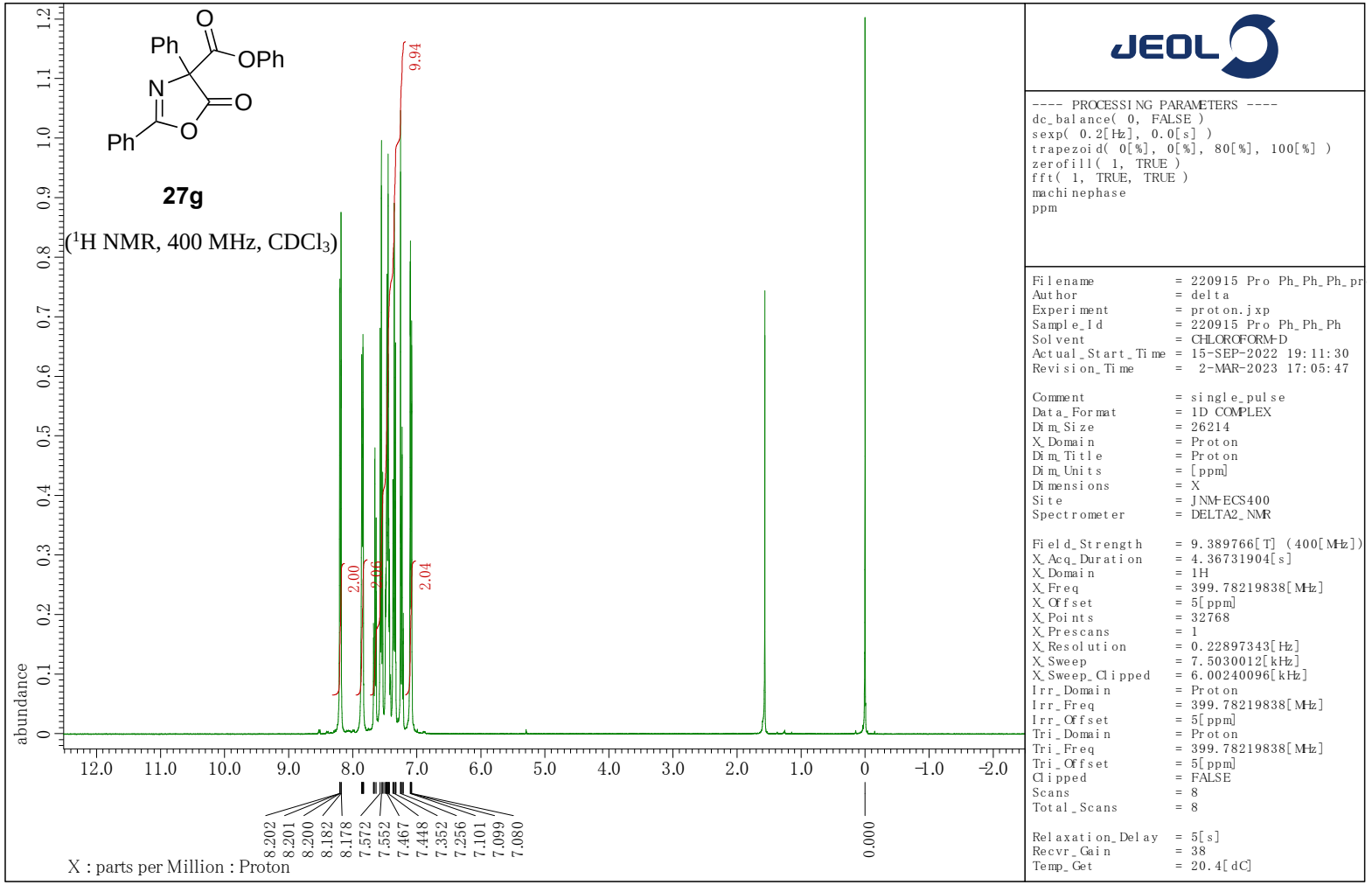

O
nBu
OPh
N
O
Ph
O
27e
(13C NMR, 100 MHz, CDCl3)
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
210.0 190.0 170.0 150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0
174.110 164.365 163.460 150.159 133.397 129.478 128.887 128.334 126.465 125.064 121.040 77.324 77.000 76.771 76.685 34.066 25.361 22.367 13.729
X : parts per Million : Carbon13
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170428-ky-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 28-APR-2017 14:17:20
Revision_Time = 21-SEP-2017 10:47:39
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 28
Total_Scans = 28
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.2[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

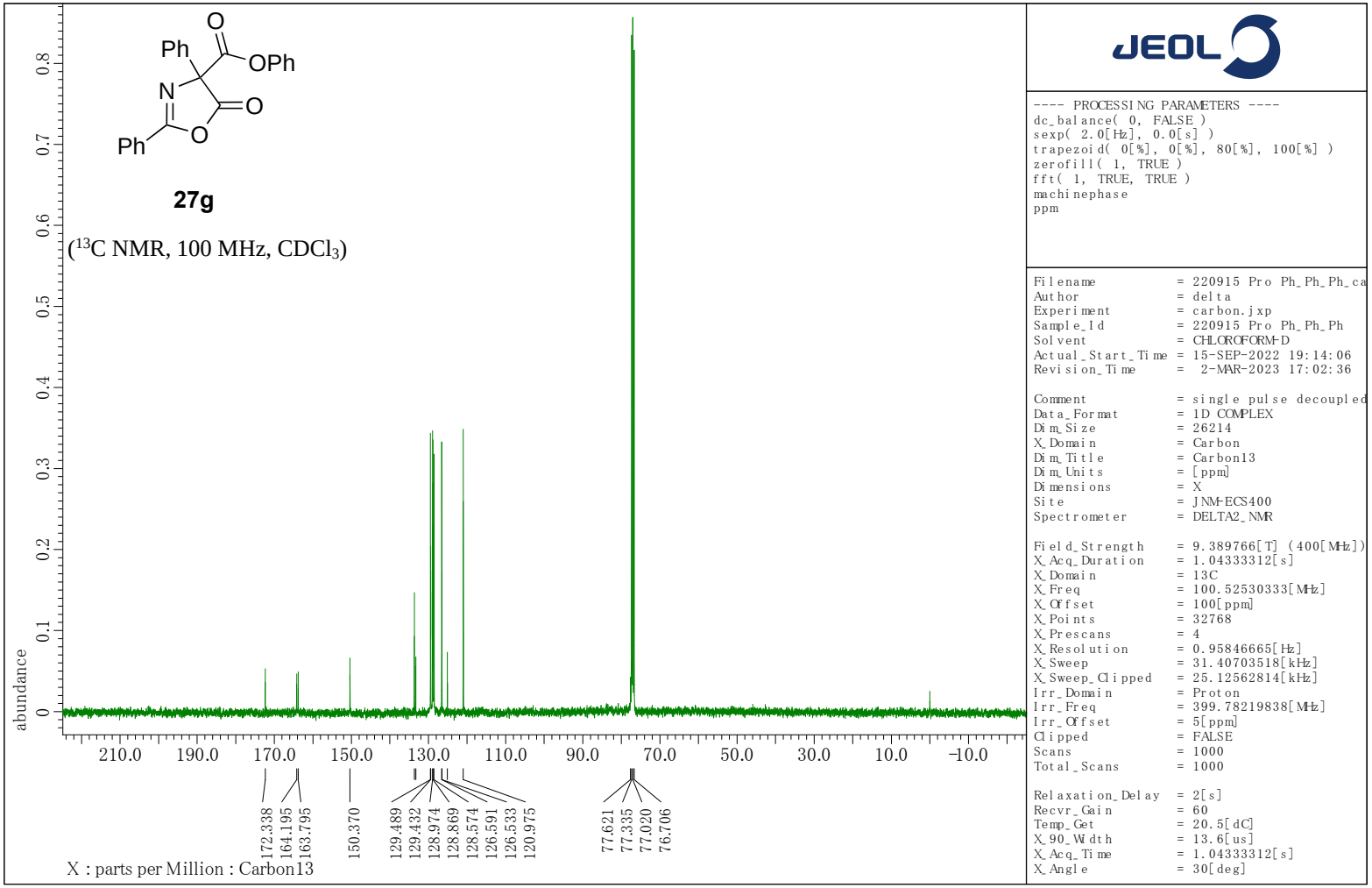
Filename	= H-1.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 170914-ky-3
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 14-SEP-2017 16:15:20
Revision_Time	= 21-SEP-2017 11:01:02
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 28
Temp_Get	= 21.4[dC]

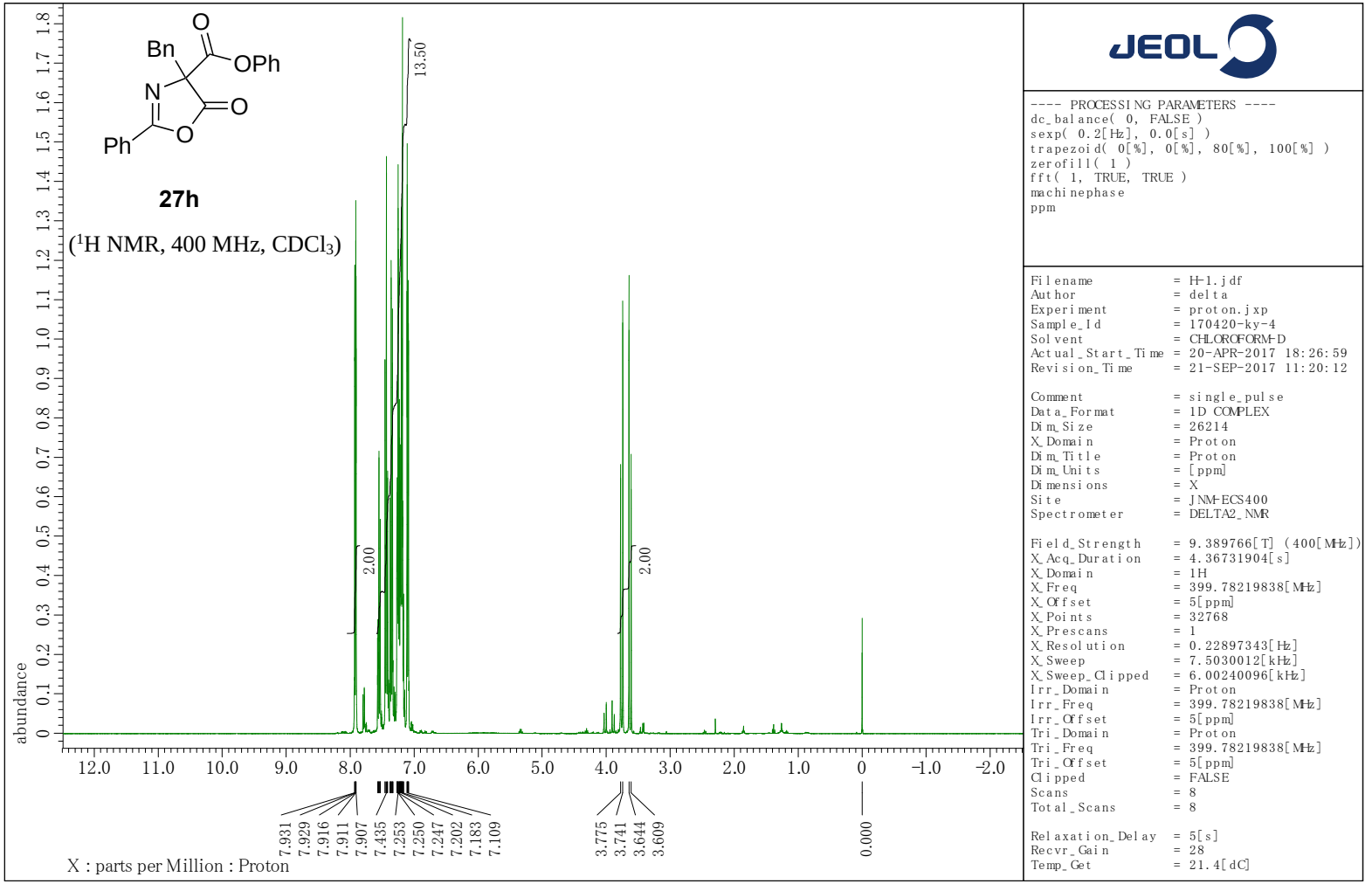

27f
(13C NMR, 100 MHz, CDCl3)
abundance
X : parts per Million : Carbon13
174.482
164.499
163.259
150.187
133.426
129.478
128.916
128.325
126.465
125.092
121.002
77.315
77.000
76.676
76.342
42.676
24.665
23.740
23.025
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170914-ky-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 14-SEP-2017 16:17:11
Revision_Time = 21-SEP-2017 11:02:59
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 36
Total_Scans = 36
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.4[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

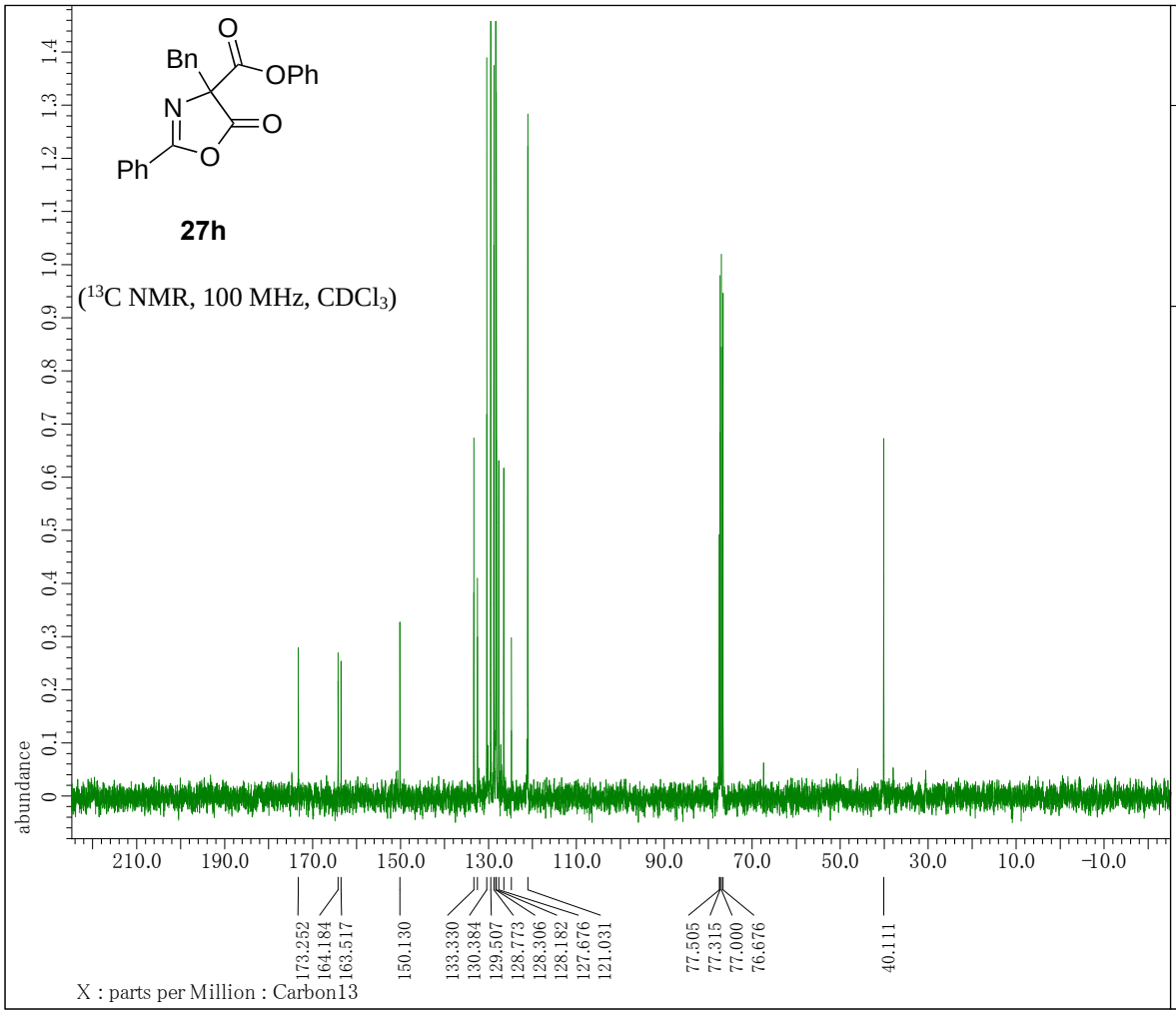
```
Filename            = 220915 Pro Ph_Ph_Ph_pr
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 220915 Pro Ph_Ph_Ph
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 15-SEP-2022 19:11:30
Revision_Time       =  2-MAR-2023 17:05:47

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 4.36731904[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.22897343[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 38
Temp_Get            = 20.4[dC]
```


Ph
O
OPh
N
O
Ph
O
27g
(13C NMR, 100 MHz, CDCl3)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
210.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
172.338
164.195
163.795
150.370
129.489
129.432
128.974
128.869
128.574
126.591
126.533
120.975
77.621
77.335
77.020
76.706
X : parts per Million : Carbon13
JEOL
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = 220915 Pro Ph_Ph_Ph_ca
Author = delta
Experiment = carbon.jxp
Sample_Id = 220915 Pro Ph_Ph_Ph
Solvent = CHLOROFORM-D
Actual_Start_Time = 15-SEP-2022 19:14:06
Revision_Time = 2-MAR-2023 17:02:36
Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1000
Total_Scans = 1000
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.5[dC]
X_90_Width = 13.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

Filename	= H-1.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 170420-ky-4
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 20-APR-2017 18:26:59
Revision_Time	= 21-SEP-2017 11:20:12
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 28
Temp_Get	= 21.4[dC]



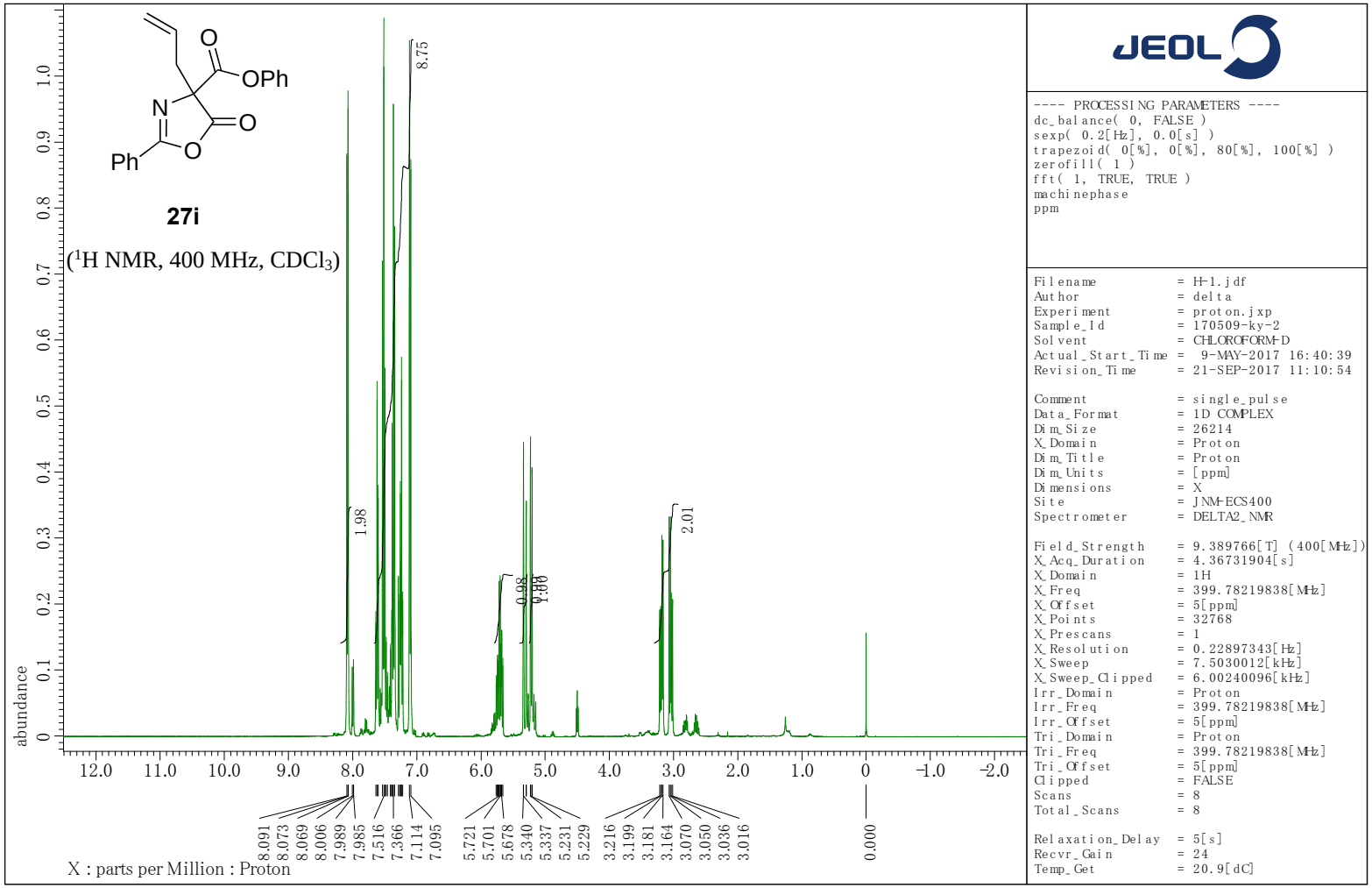
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm

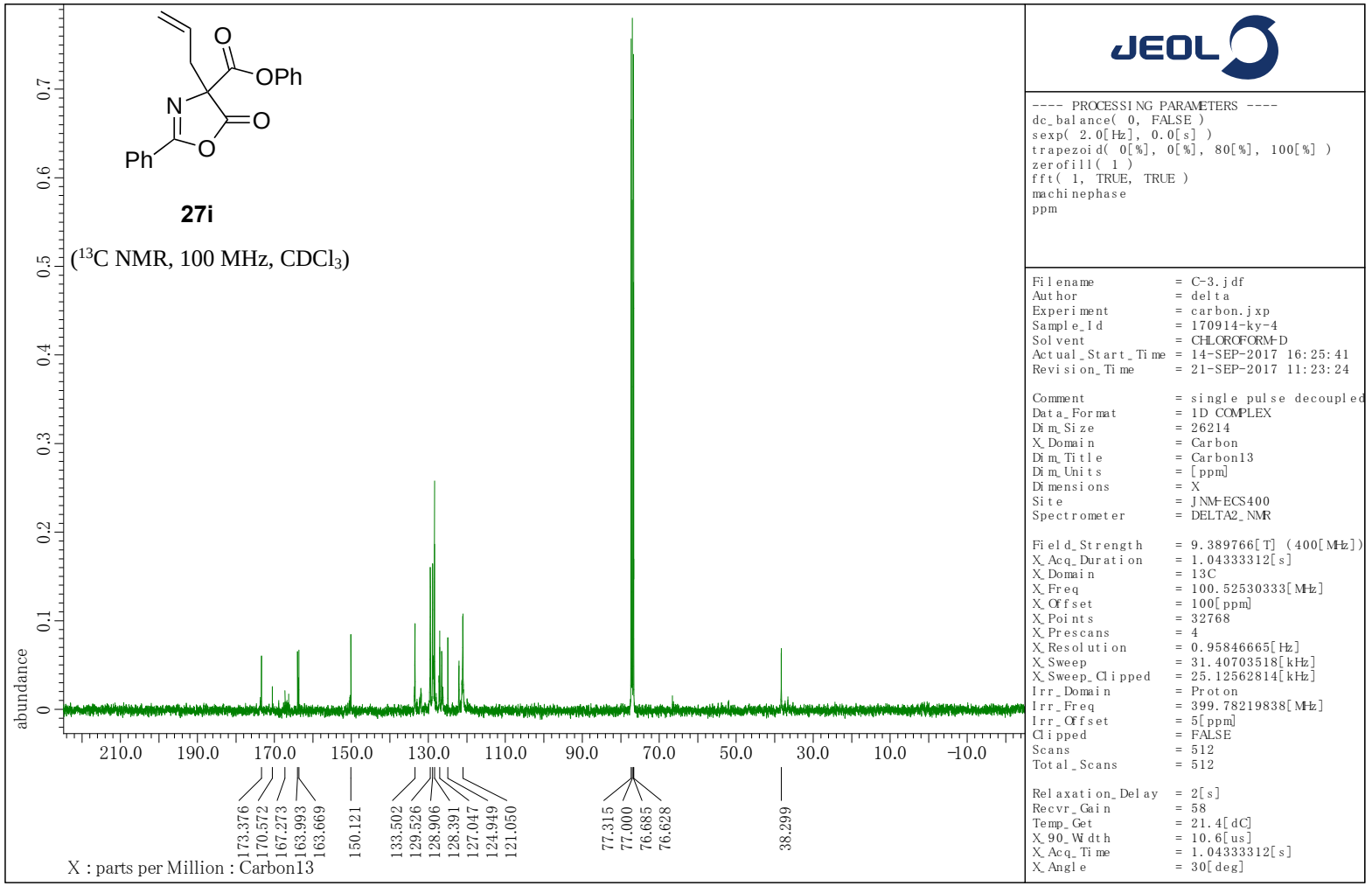
Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170420-ky-4
Solvent = CHLOROFORM-D
Actual_Start_Time = 20-APR-2017 18:28:50
Revision_Time = 21-SEP-2017 11:22:42

Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 34
Total_Scans = 34

Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.6[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]

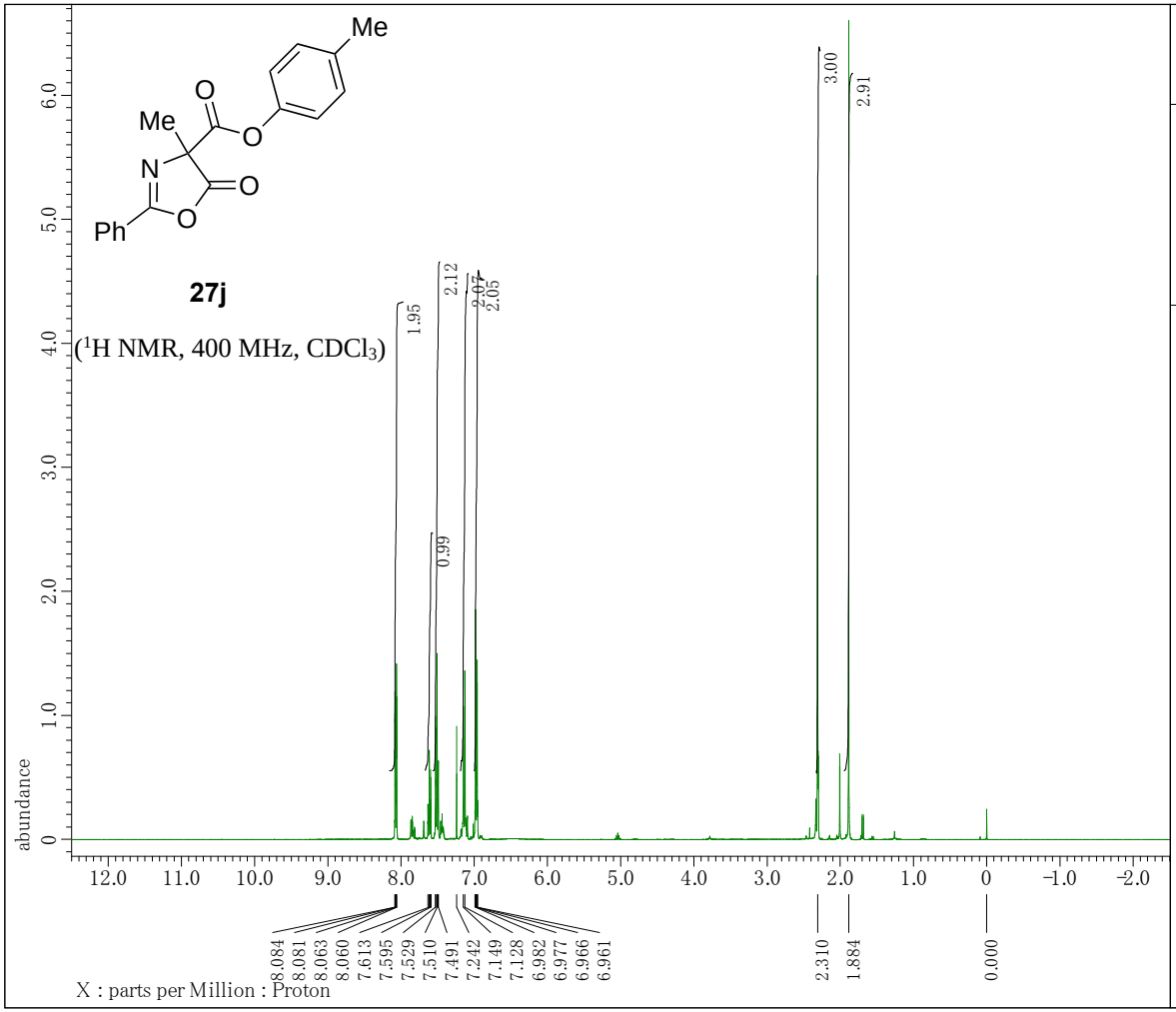

O
OPh
N
O
Ph
O
27i
(1H NMR, 400 MHz, CDCl3)
abundance
X : parts per Million : Proton
8.75
1.98
0.98
1.00
2.01
8.091
8.073
8.069
8.006
7.989
7.985
7.516
7.366
7.114
7.095
5.721
5.701
5.678
5.340
5.337
5.231
5.229
3.216
3.199
3.181
3.164
3.070
3.050
3.036
3.016
0.000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170509-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 9-MAY-2017 16:40:39
Revision_Time = 21-SEP-2017 11:10:54
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 24
Temp_Get = 20.9[dC]



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

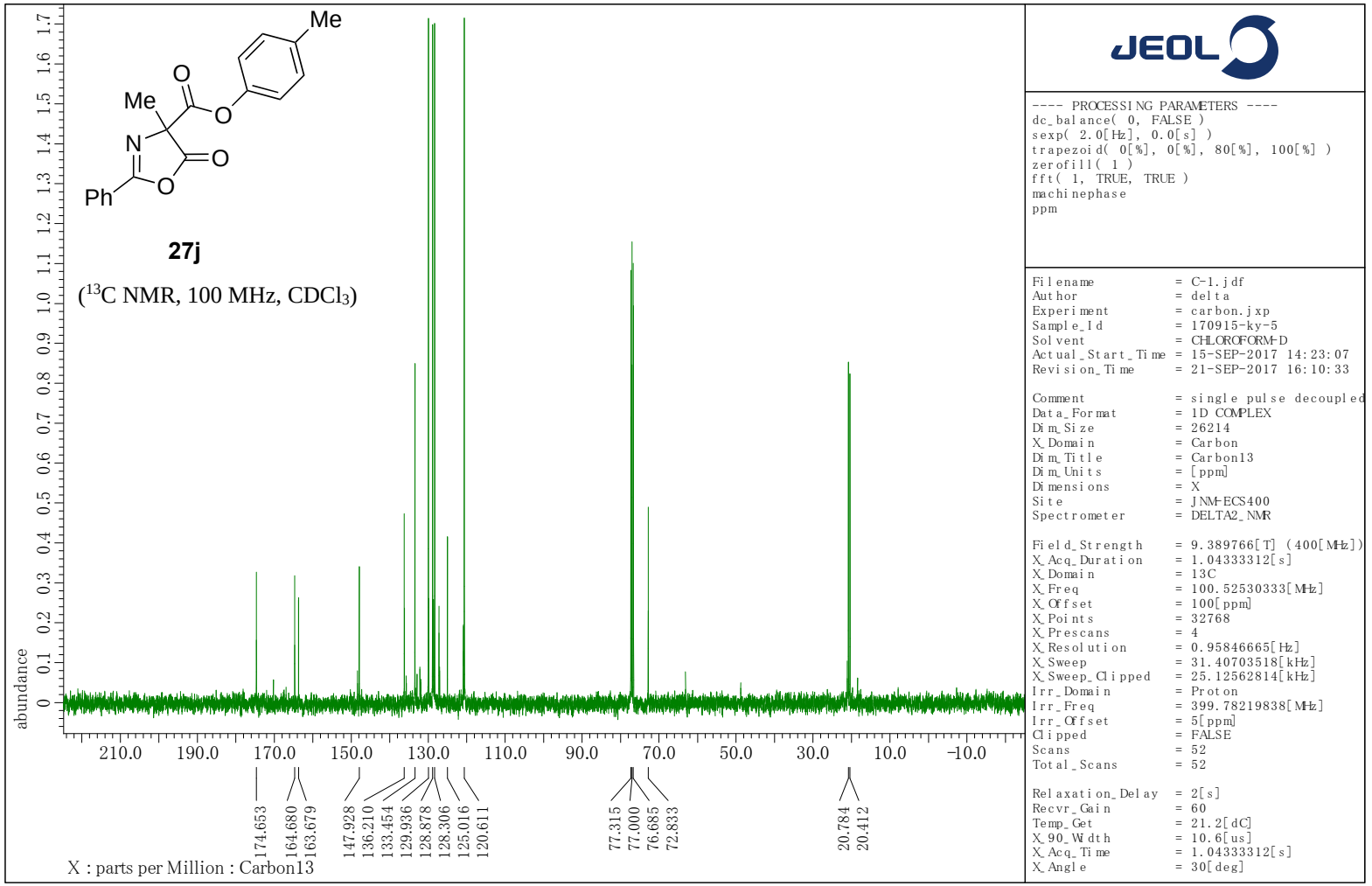
```
Filename            = C-3.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 170914-ky-4
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 14-SEP-2017 16:25:41
Revision_Time       = 21-SEP-2017 11:23:24

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 512
Total_Scans         = 512

Relaxation_Delay    = 2[s]
Recvr_Gain          = 58
Temp_Get            = 21.4[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
```



JEOL

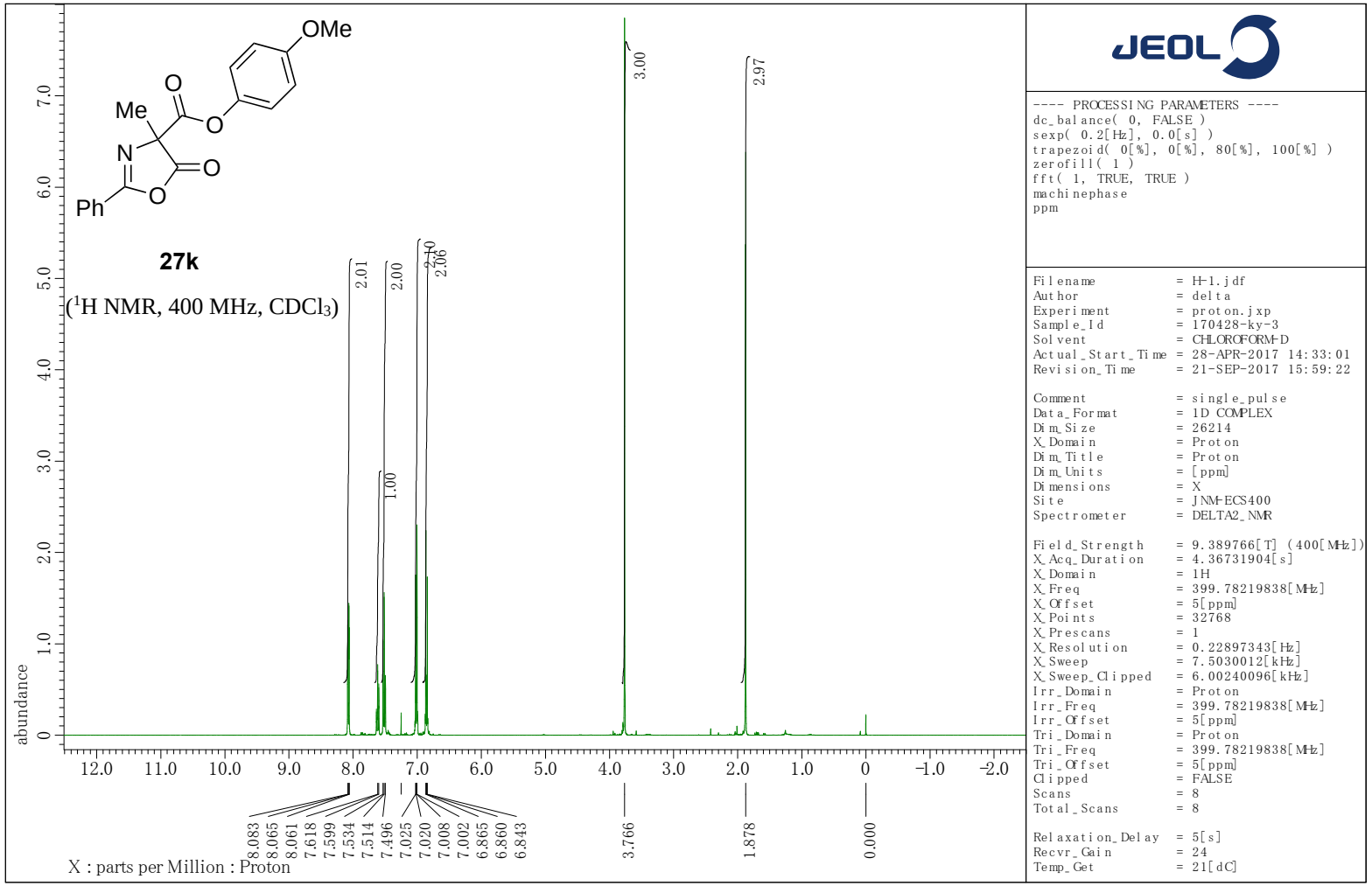
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

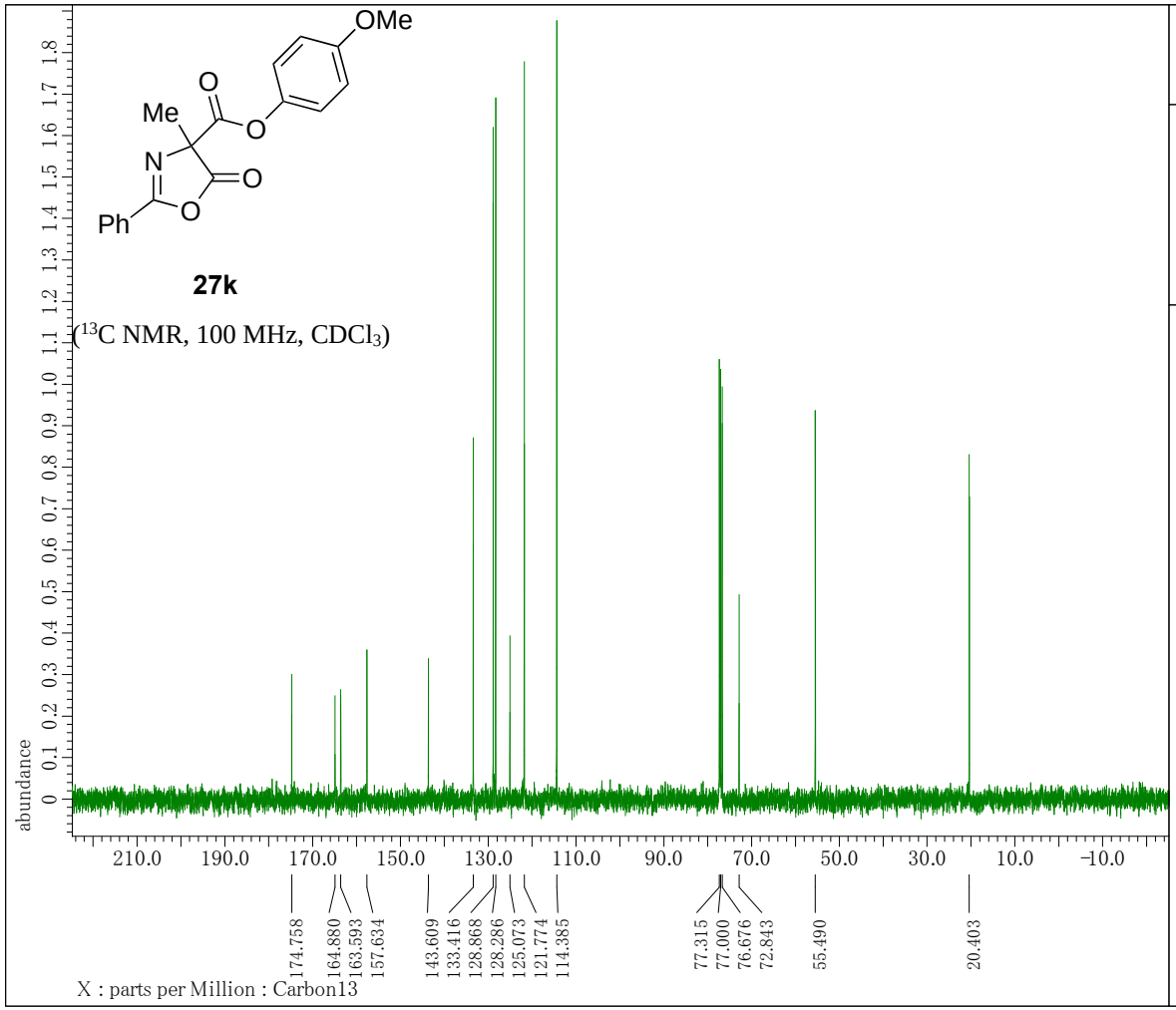
Filename	= H-1.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 170915-ky-5
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 15-SEP-2017 14:21:21
Revision_Time	= 21-SEP-2017 16:08:47
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 28
Temp_Get	= 21.2[dC]




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

Filename	= C-1.jdf
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= 170915-ky-5
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 15-SEP-2017 14:23:07
Revision_Time	= 21-SEP-2017 16:10:33
Comment	= single pulse decoupled
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 1.04333312[s]
X_Domain	= 13C
X_Freq	= 100.52530333[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 0.95846665[Hz]
X_Sweep	= 31.40703518[kHz]
X_Sweep_Clipped	= 25.12562814[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 52
Total_Scans	= 52
Relaxation_Delay	= 2[s]
Recvr_Gain	= 60
Temp_Get	= 21.2[dC]
X_90_Width	= 10.6[us]
X_Acq_Time	= 1.04333312[s]
X_Angle	= 30[deg]


OMe
O
Me
O
N
O
Ph
O
27k
(1H NMR, 400 MHz, CDCl3)
abundance
3.00
2.97
2.01
2.00
2.10
2.06
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.083
8.065
8.061
7.618
7.599
7.534
7.514
7.496
7.025
7.020
7.008
7.002
6.865
6.860
6.843
3.766
1.878
0.000
X : parts per Million : Proton
JEOL
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170428-ky-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 28-APR-2017 14:33:01
Revision_Time = 21-SEP-2017 15:59:22
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 24
Temp_Get = 21[dC]



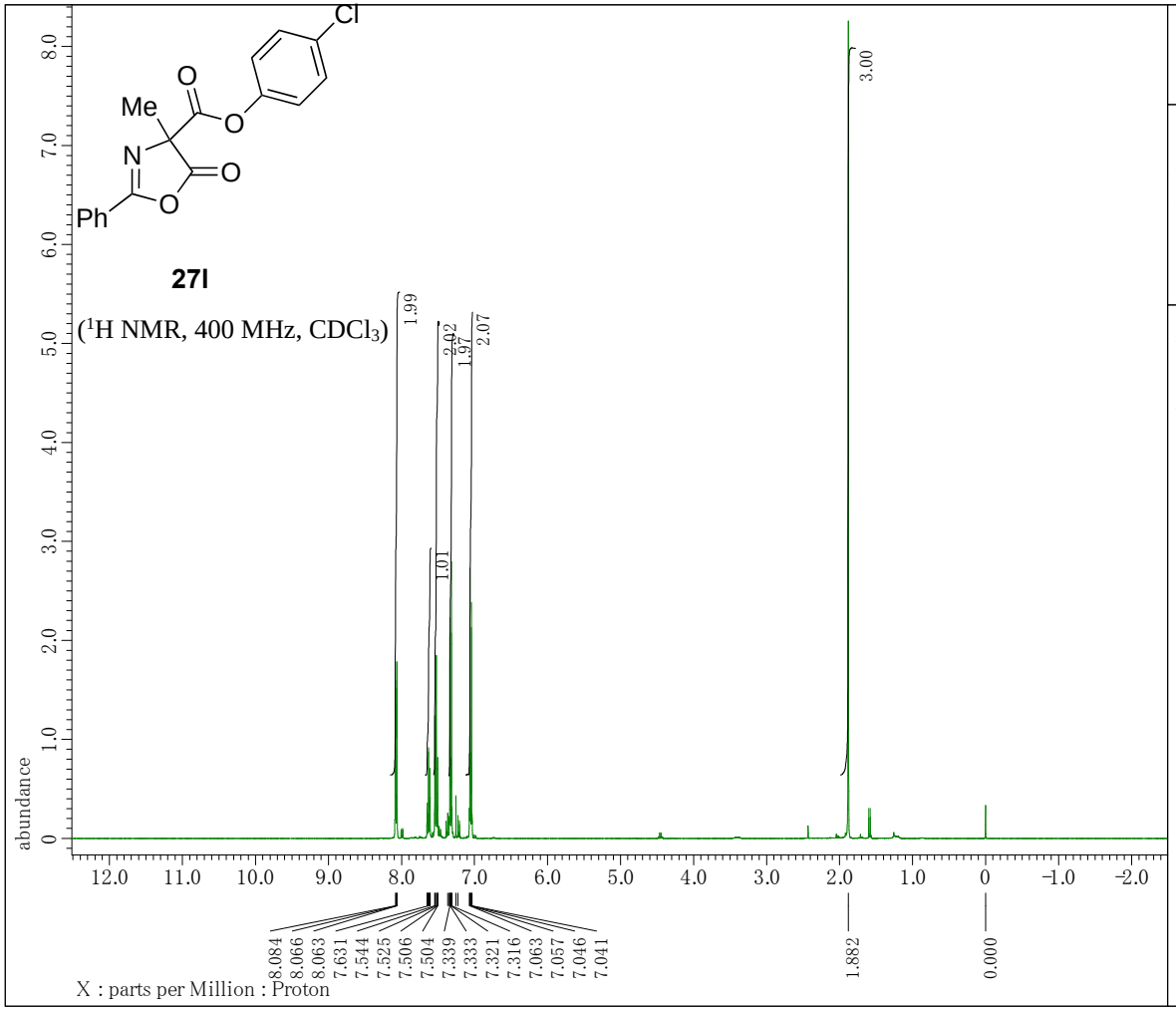
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm

Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170428-ky-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 28-APR-2017 14:34:52
Revision_Time = 21-SEP-2017 16:00:53

Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 31
Total_Scans = 31

Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.9[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]



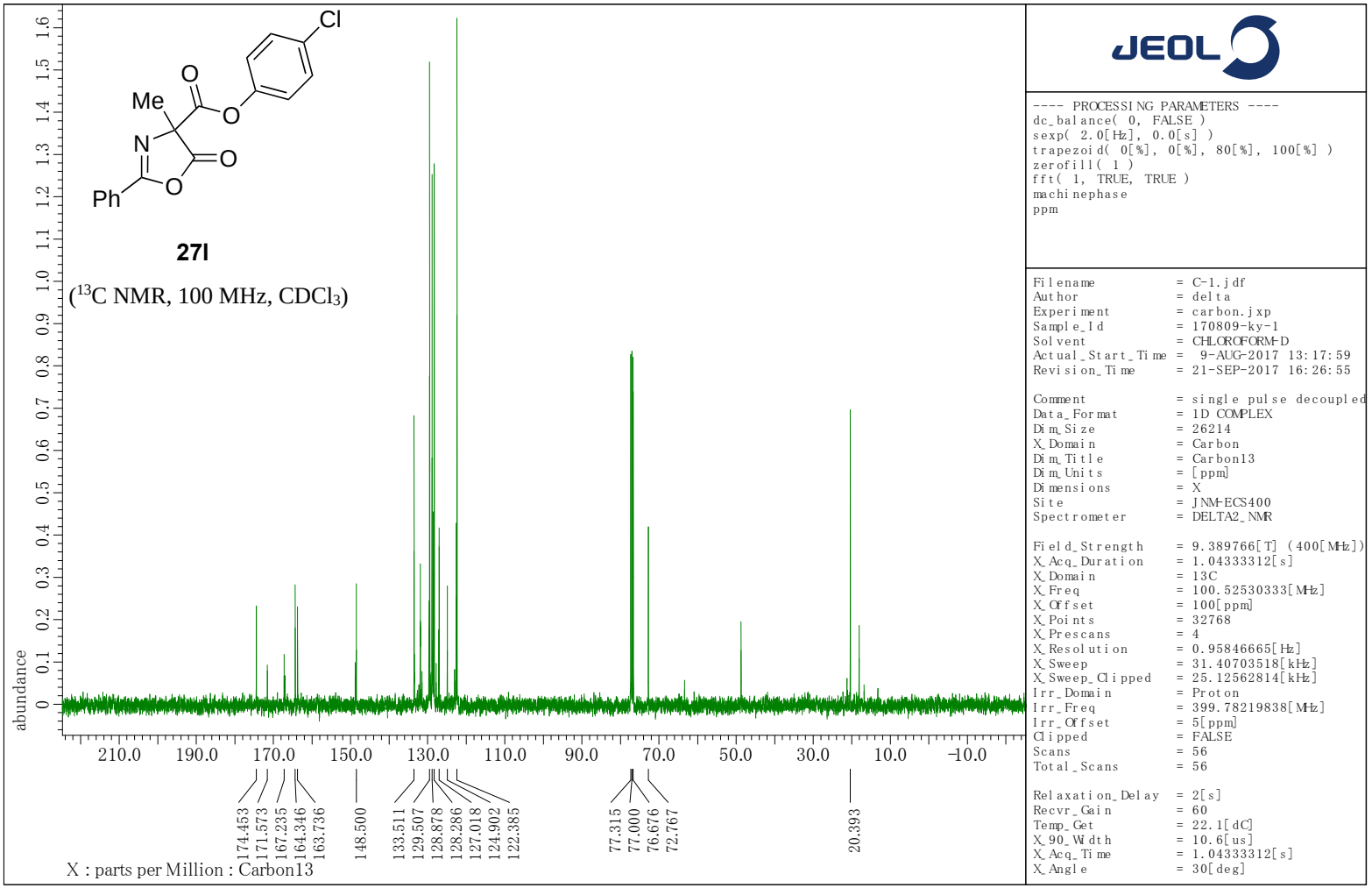
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm

Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170519-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 19-MAY-2017 12:36:35
Revision_Time = 21-SEP-2017 16:18:31

Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8

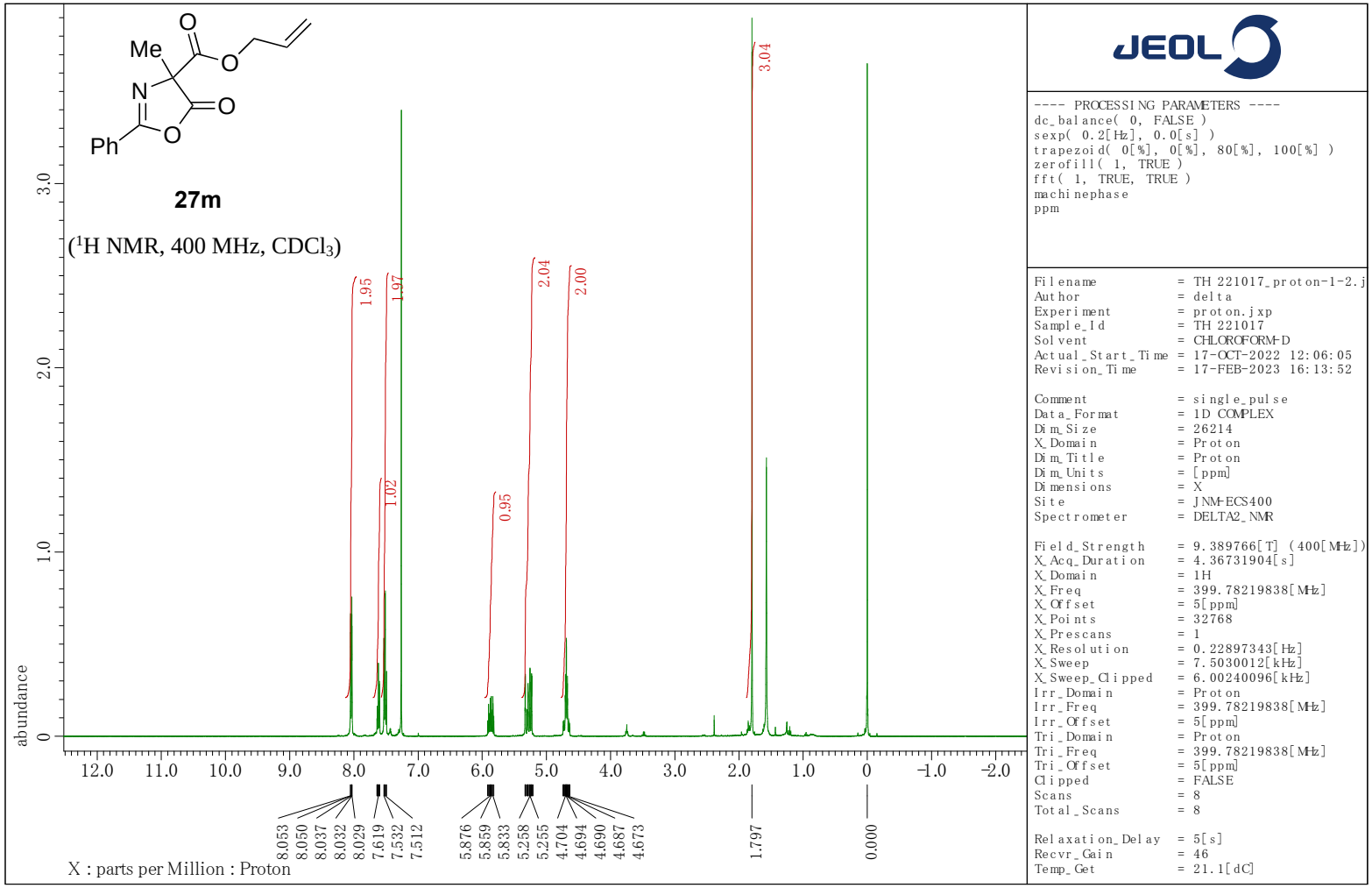
Relaxation_Delay = 5[s]
Recvr_Gain = 30
Temp_Get = 21.4[dC]



JEOL

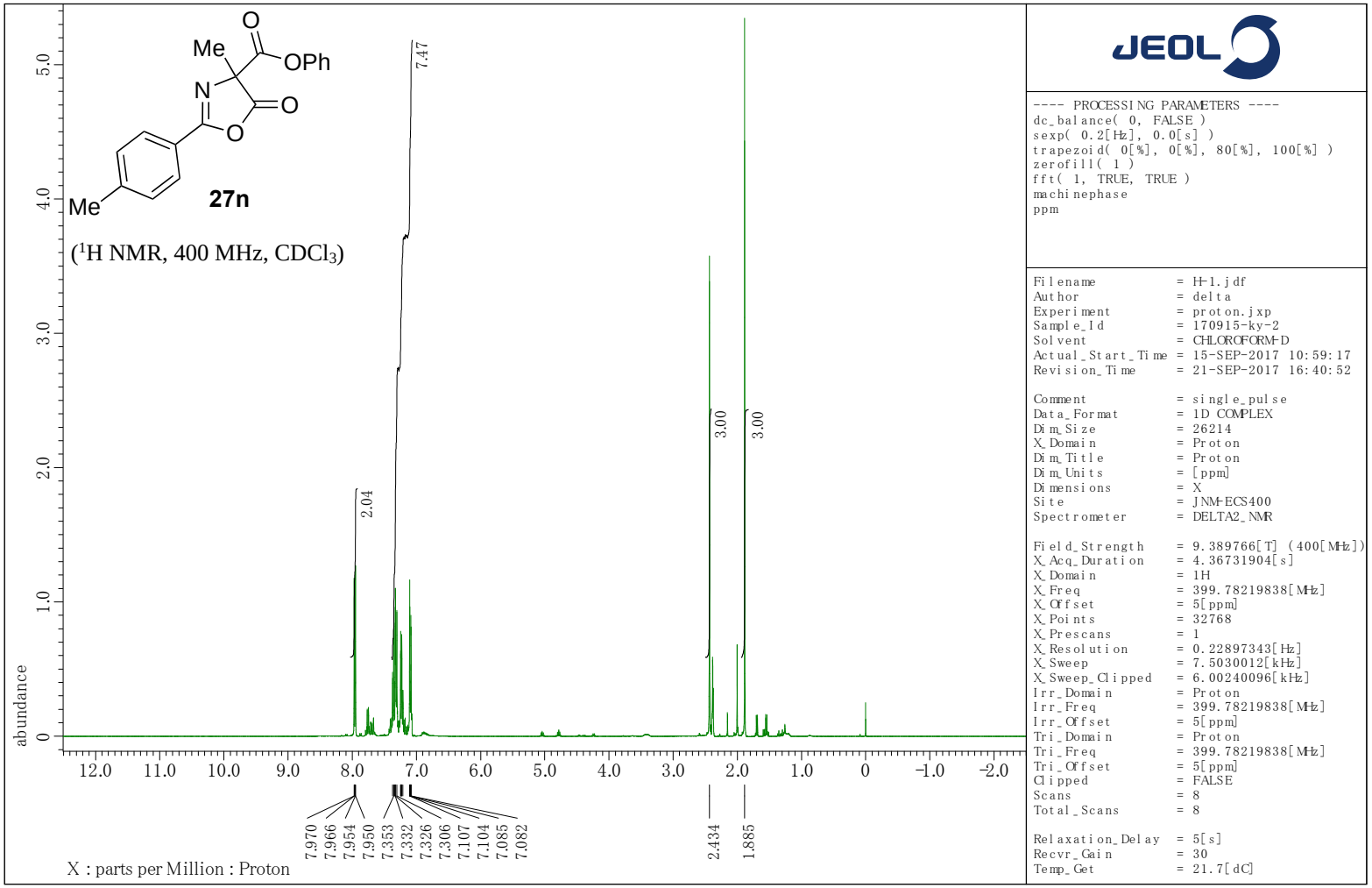
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

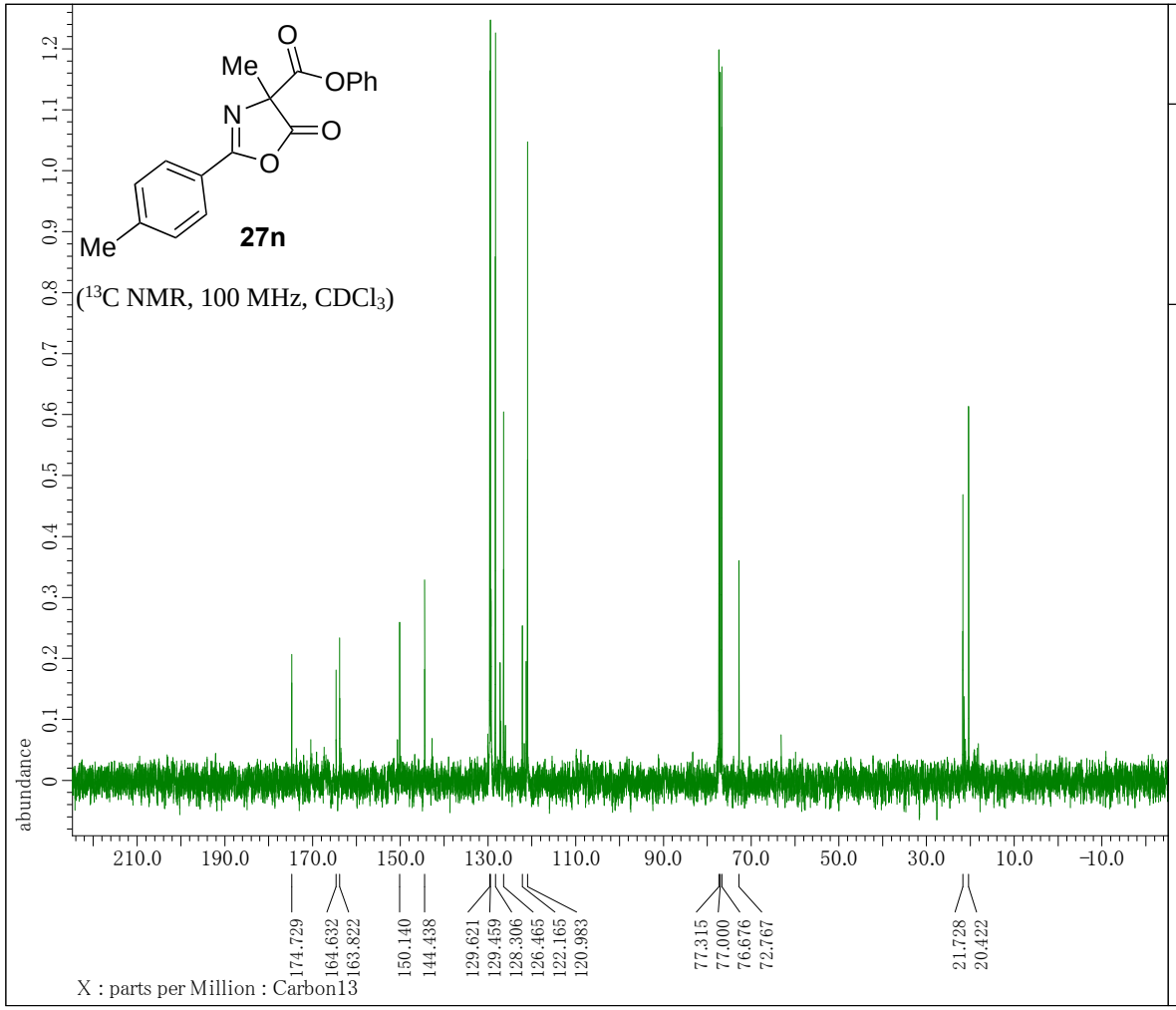
```
Filename            = C-1.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 170809-ky-1
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  9-AUG-2017 13:17:59
Revision_Time       = 21-SEP-2017 16:26:55

Comment             = single pulse decoupled
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 56
Total_Scans         = 56

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 22.1[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

Filename	= TH 221017_proton-1-2.j
Author	= delta
Experiment	= proton.jxp
Sample_Id	= TH 221017
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 17-OCT-2022 12:06:05
Revision_Time	= 17-FEB-2023 16:13:52
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 46
Temp_Get	= 21.1[dC]


Me
O
OPh
N
O
O
Me
27n
(1H NMR, 400 MHz, CDCl3)
abundance
7.47
2.04
3.00
3.00
7.970
7.966
7.954
7.950
7.353
7.332
7.326
7.306
7.107
7.104
7.085
7.082
2.434
1.885
X : parts per Million : Proton
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = H-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = 170915-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 15-SEP-2017 10:59:17
Revision_Time = 21-SEP-2017 16:40:52
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 30
Temp_Get = 21.7[dC]



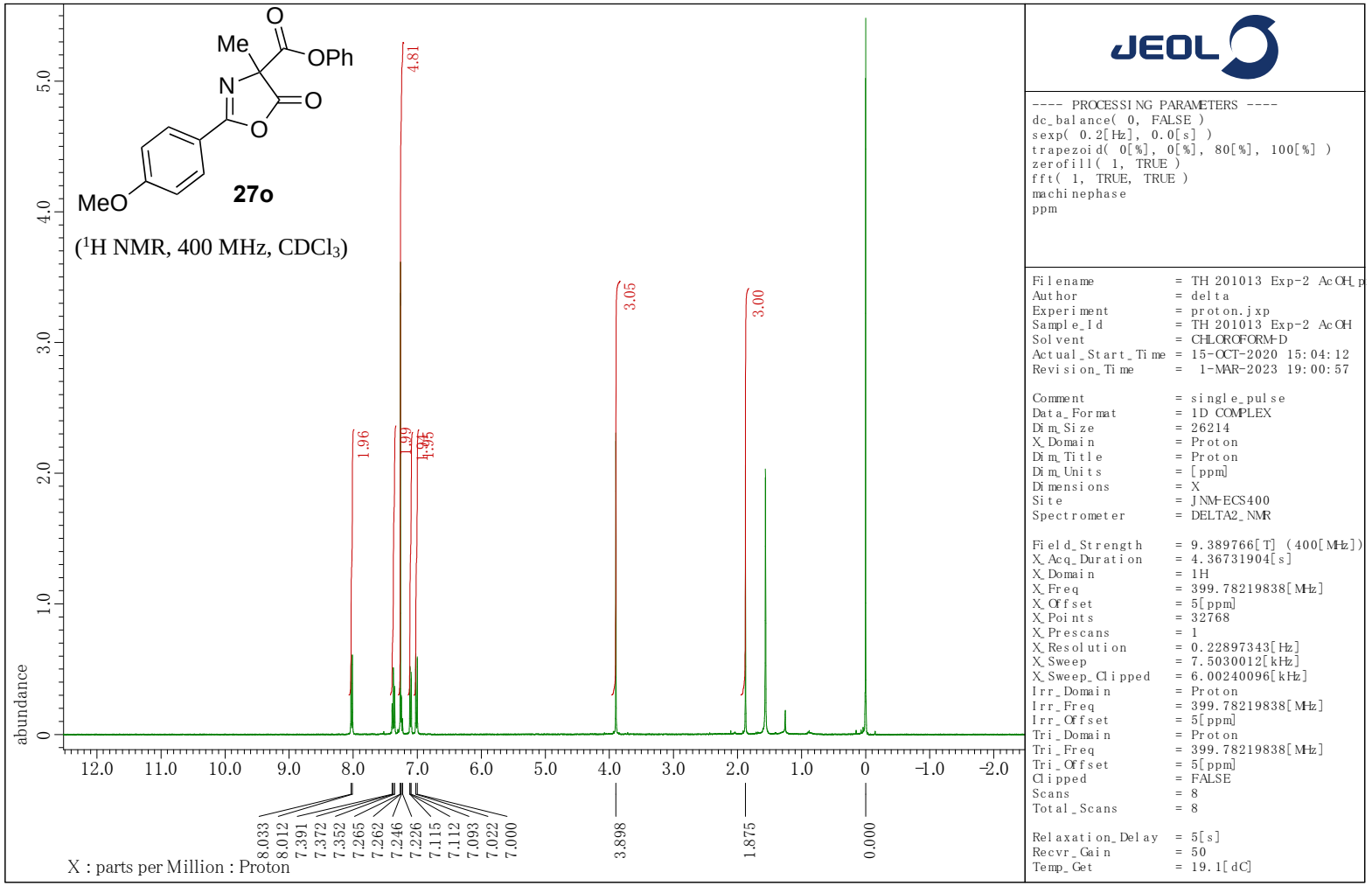
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm

Filename = C-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = 170915-ky-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 15-SEP-2017 11:01:03
Revision_Time = 21-SEP-2017 16:42:38

Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR

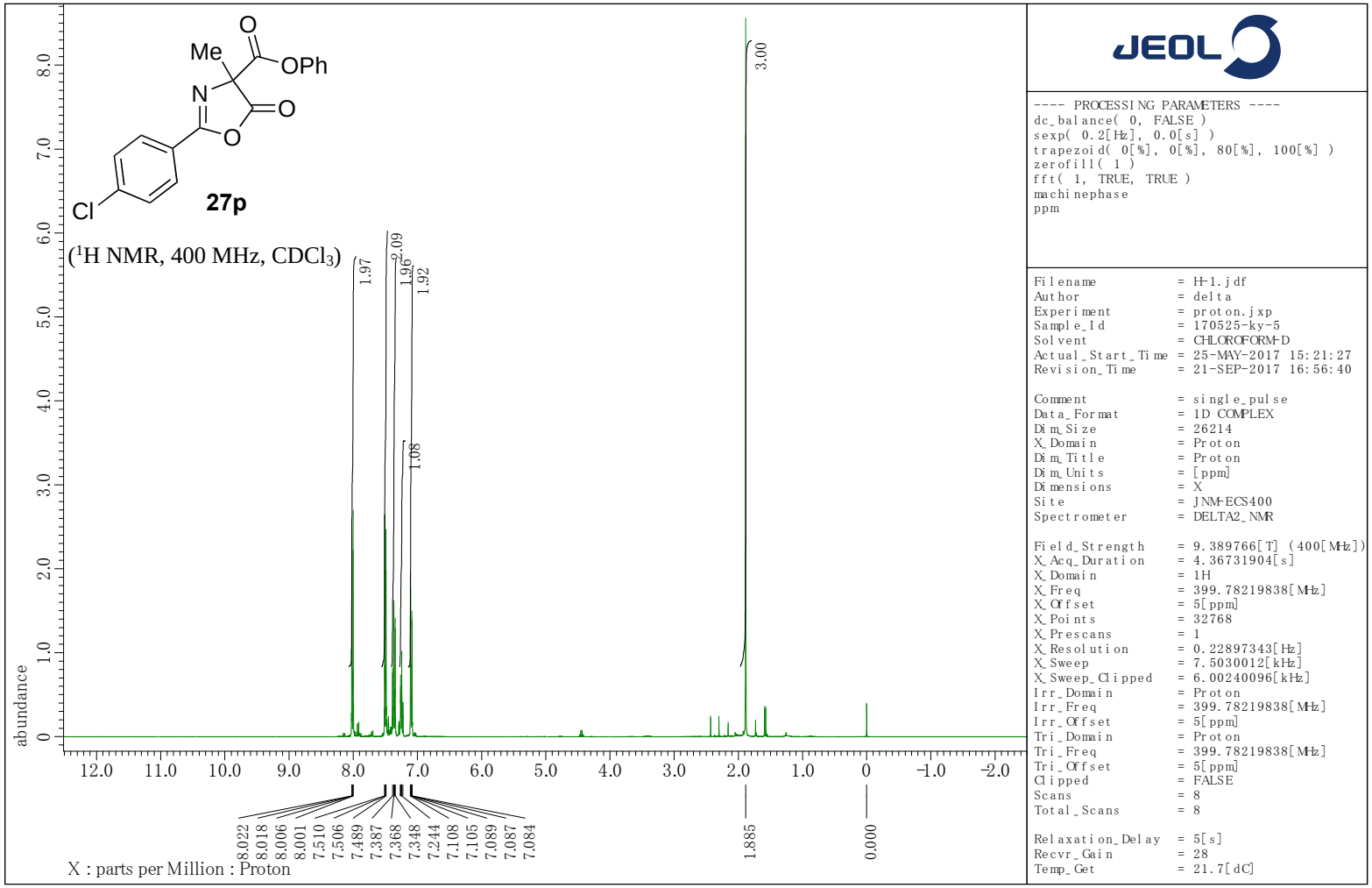
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 27
Total_Scans = 27

Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.7[dC]
X_90_Width = 10.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]



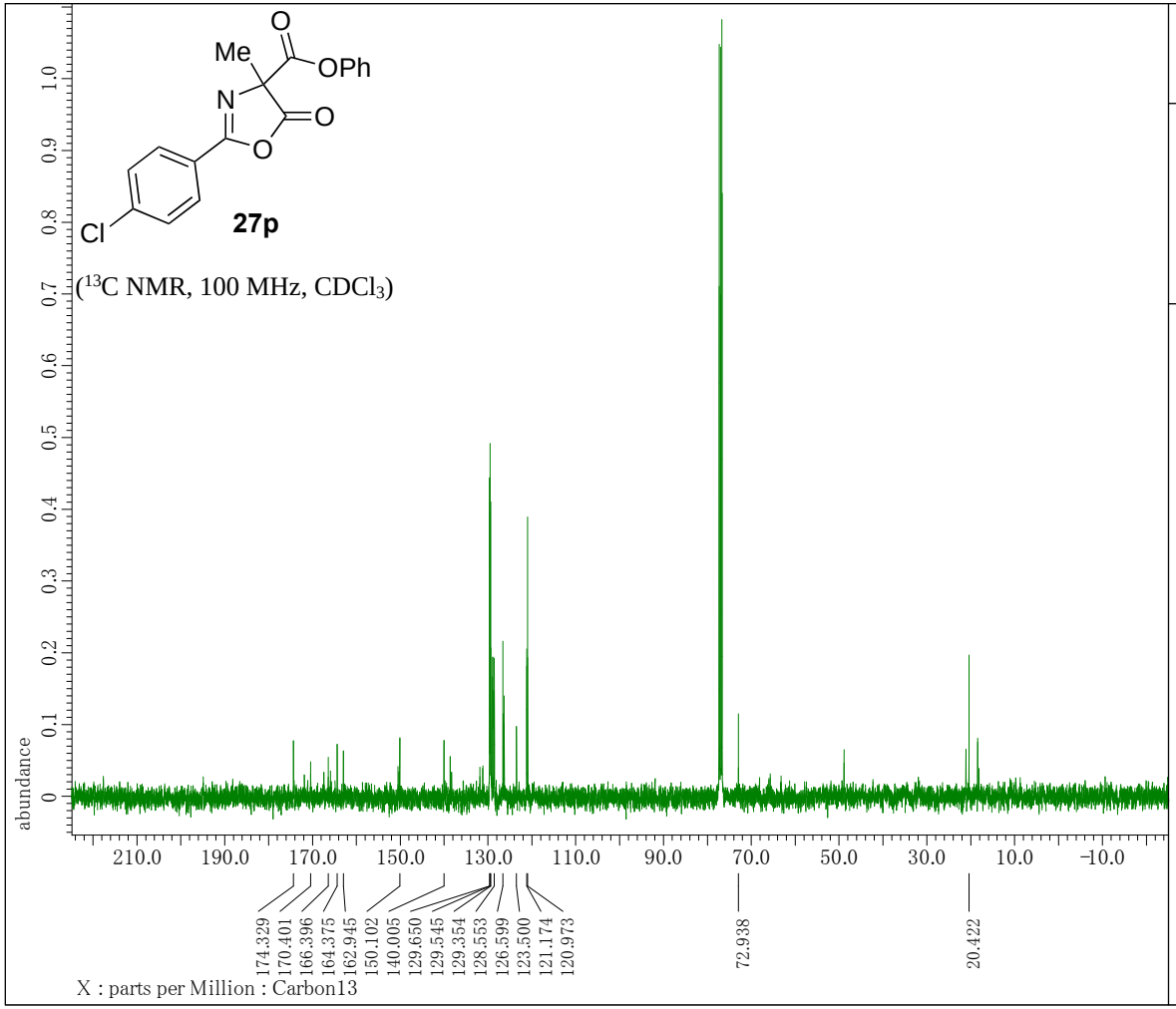

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = TH 201013 Exp-2 AcOH_p
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TH 201013 Exp-2 AcOH
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 15-OCT-2020 15:04:12
Revision_Time       =  1-MAR-2023 19:00:57

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 4.36731904[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.22897343[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 50
Temp_Get            = 19.1[dC]
```



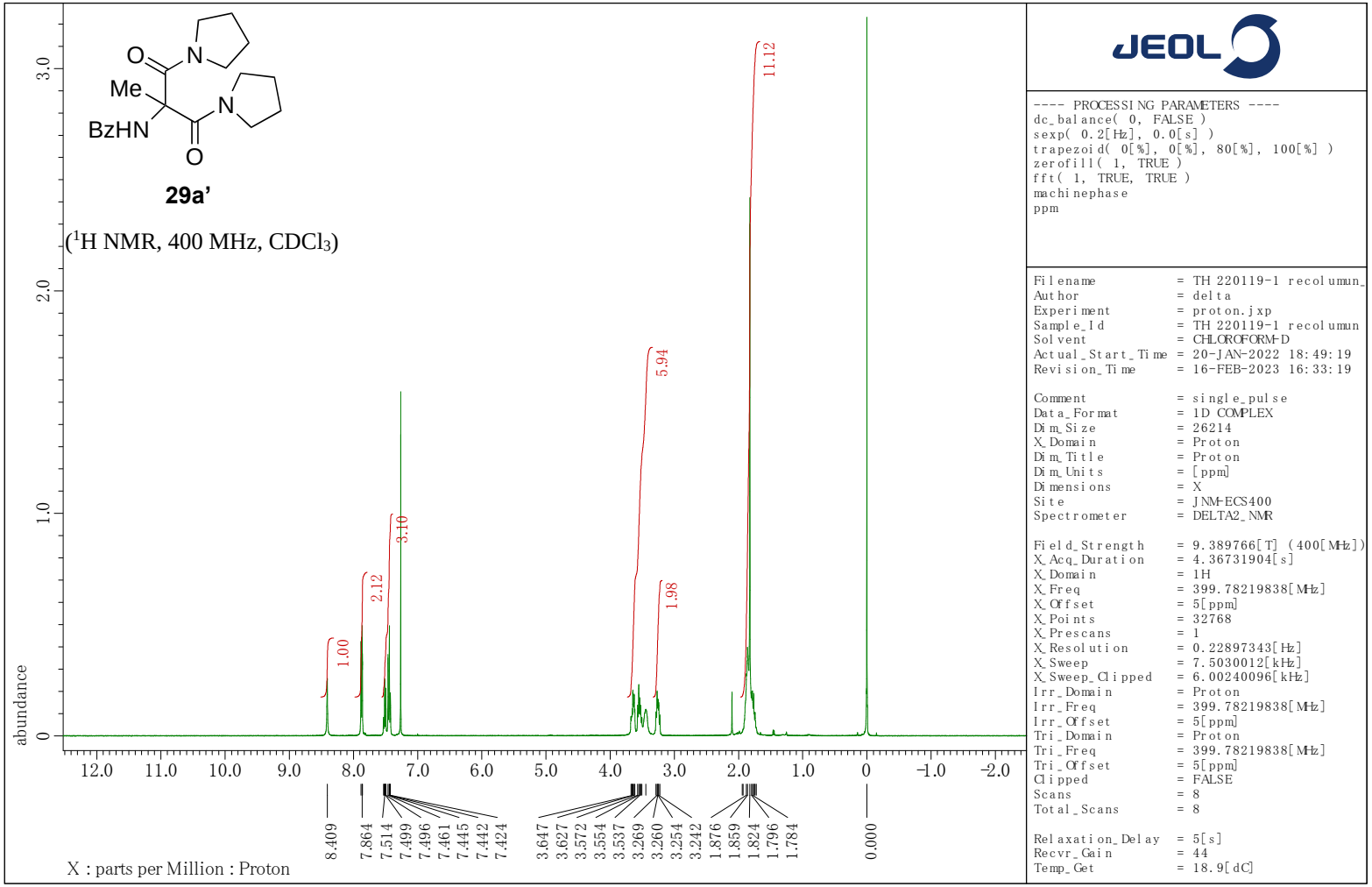

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

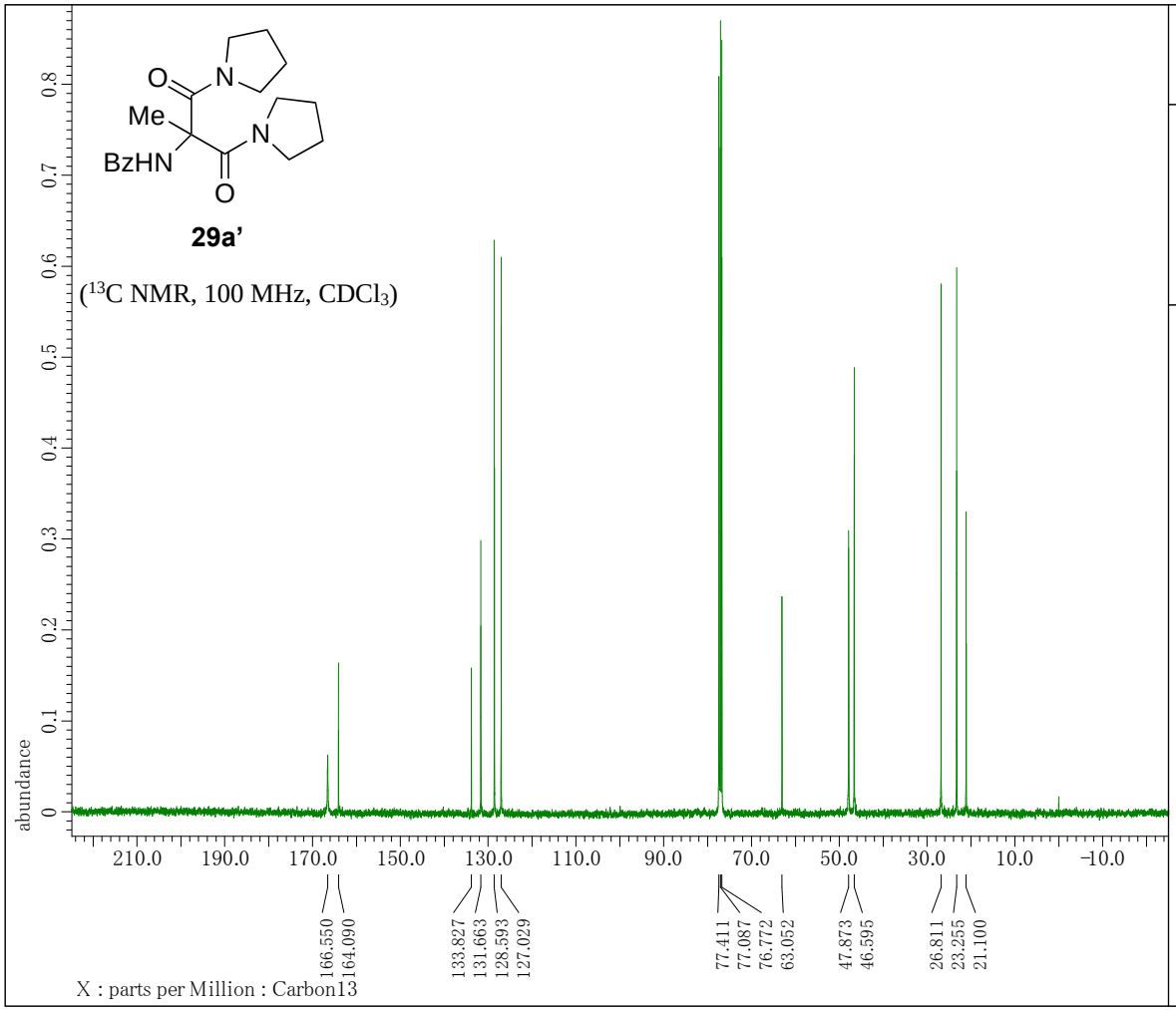
Filename	= H-1.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 170525-ky-5
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 25-MAY-2017 15:21:27
Revision_Time	= 21-SEP-2017 16:56:40
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 28
Temp_Get	= 21.7[dC]



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

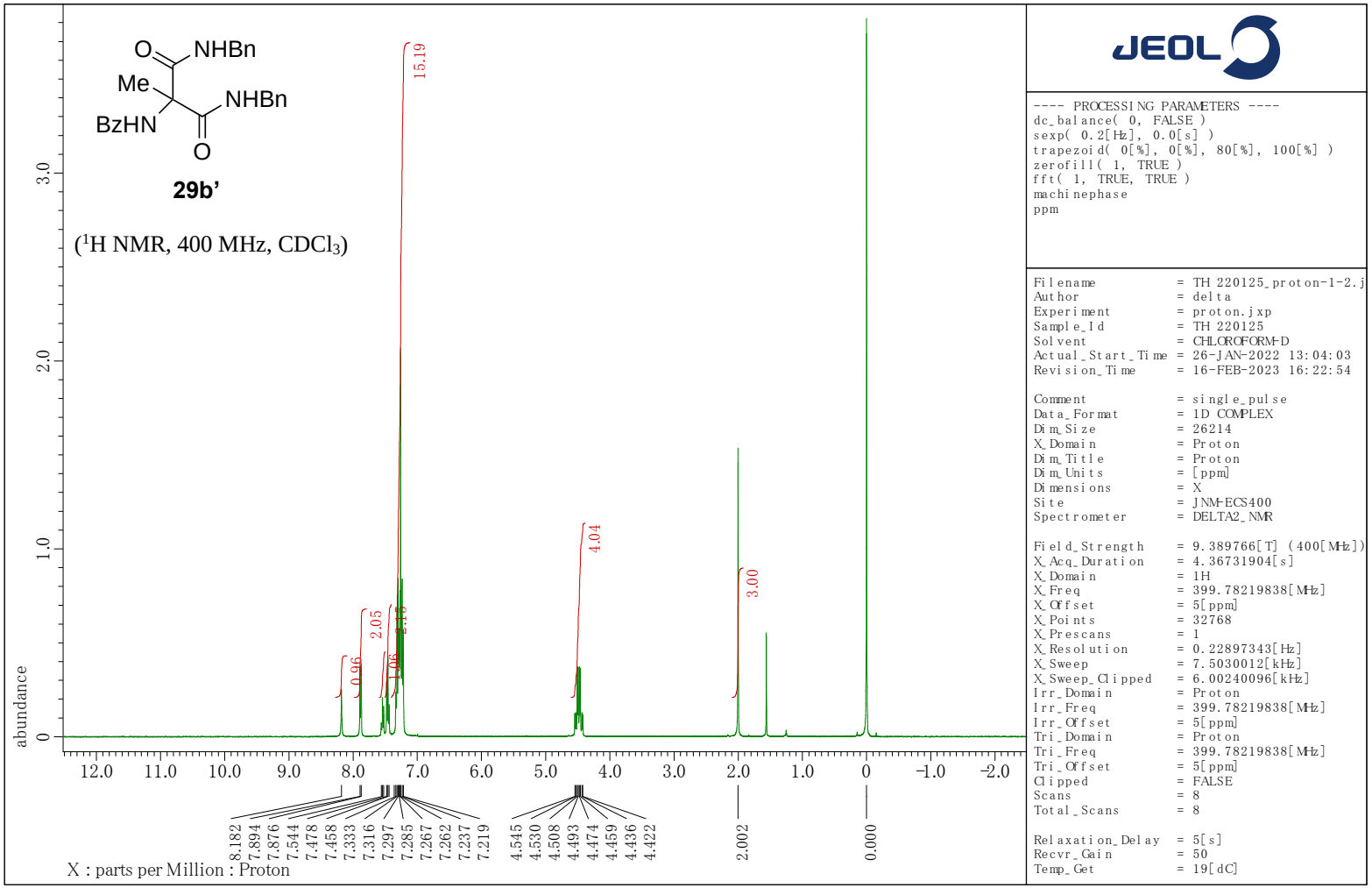
Filename	= C-1.jdf
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= 170915-ky-4
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 15-SEP-2017 14:11:01
Revision_Time	= 21-SEP-2017 17:04:29
Comment	= single pulse decoupled
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 1.04333312[s]
X_Domain	= 13C
X_Freq	= 100.52530333[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 0.95846665[Hz]
X_Sweep	= 31.40703518[kHz]
X_Sweep_Clipped	= 25.12562814[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 105
Total_Scans	= 105
Relaxation_Delay	= 2[s]
Recvr_Gain	= 60
Temp_Get	= 21.3[dC]
X_90_Width	= 10.6[us]
X_Acq_Time	= 1.04333312[s]
X_Angle	= 30[deg]

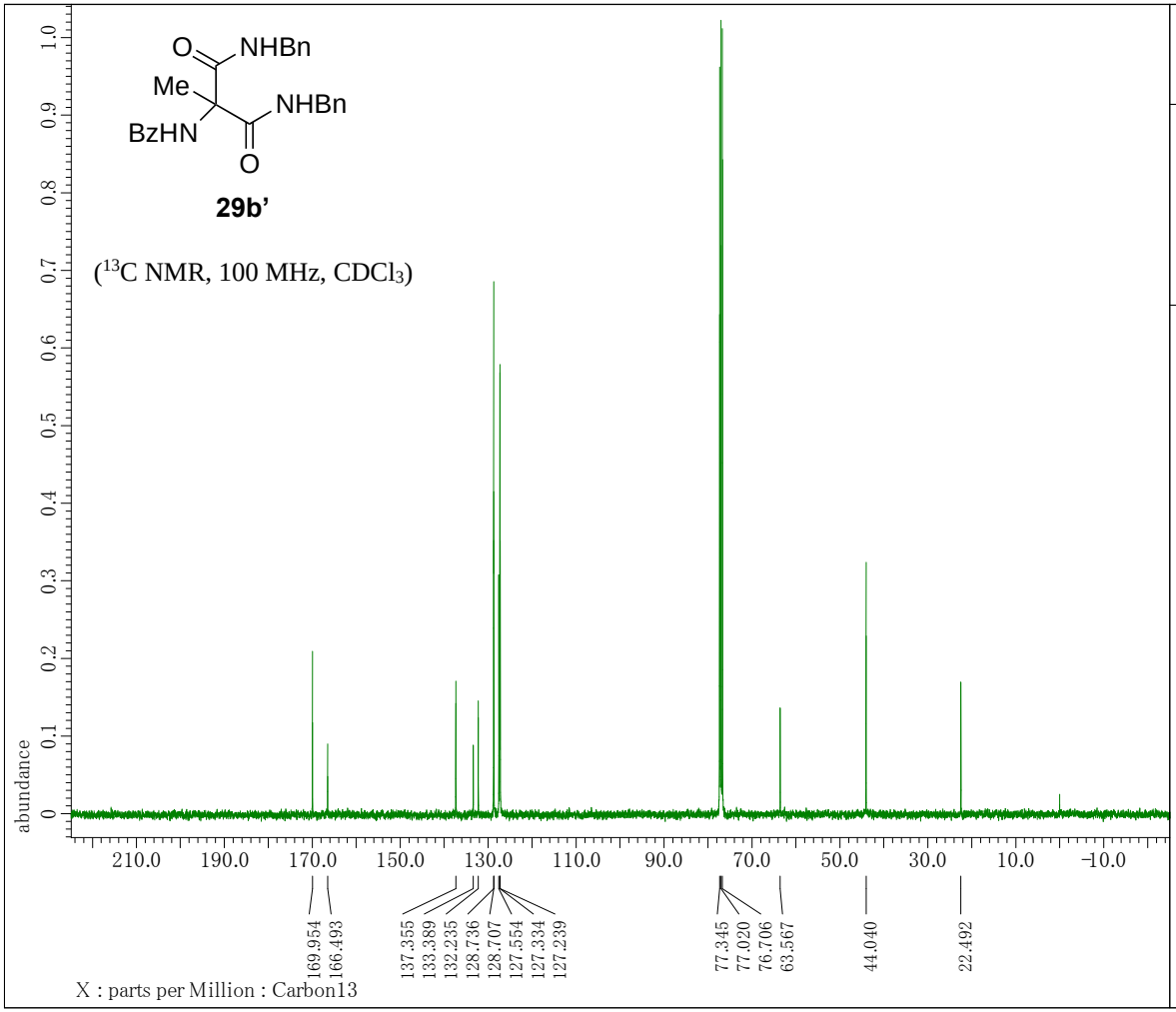

O
N
Me
BzHN
N
O
29a'
(1H NMR, 400 MHz, CDCl3)
abundance
X : parts per Million : Proton
11.12
5.94
3.10
2.12
1.98
1.00
8.409
7.864
7.514
7.499
7.496
7.461
7.445
7.442
7.424
3.647
3.627
3.572
3.554
3.537
3.269
3.260
3.254
3.242
1.876
1.859
1.824
1.796
1.784
0.000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = TH 220119-1 recolumun_
Author = delta
Experiment = proton.jxp
Sample_Id = TH 220119-1 recolumun
Solvent = CHLOROFORM-D
Actual_Start_Time = 20-JAN-2022 18:49:19
Revision_Time = 16-FEB-2023 16:33:19
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Get = 18.9[dC]



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

Filename	= Pro BzNCMeCO(Pyrorridi
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= Pro BzNCMeCO2PhCOPyror
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 7-FEB-2022 11:58:51
Revision_Time	= 16-FEB-2023 16:14:50
Comment	= single pulse decoupled
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 1.04333312[s]
X_Domain	= 13C
X_Freq	= 100.52530333[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 0.95846665[Hz]
X_Sweep	= 31.40703518[kHz]
X_Sweep_Clipped	= 25.12562814[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 1024
Total_Scans	= 1024
Relaxation_Delay	= 2[s]
Recvr_Gain	= 58
Temp_Get	= 19.4[dC]
X_90_Width	= 13.6[us]
X_Acq_Time	= 1.04333312[s]
X_Angle	= 30[deg]


O
NHBn
Me
NHBn
BzHN
O
29b'
(1H NMR, 400 MHz, CDCl3)
15.19
4.04
3.00
2.05
0.96
abundance
X : parts per Million : Proton
8.182
7.894
7.876
7.544
7.478
7.458
7.333
7.316
7.297
7.285
7.267
7.262
7.237
7.219
4.545
4.530
4.508
4.493
4.474
4.459
4.436
4.422
2.002
0.000
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = TH 220125_proton-1-2.j
Author = delta
Experiment = proton.jxp
Sample_Id = TH 220125
Solvent = CHLOROFORM-D
Actual_Start_Time = 26-JAN-2022 13:04:03
Revision_Time = 16-FEB-2023 16:22:54
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 50
Temp_Get = 19[dC]



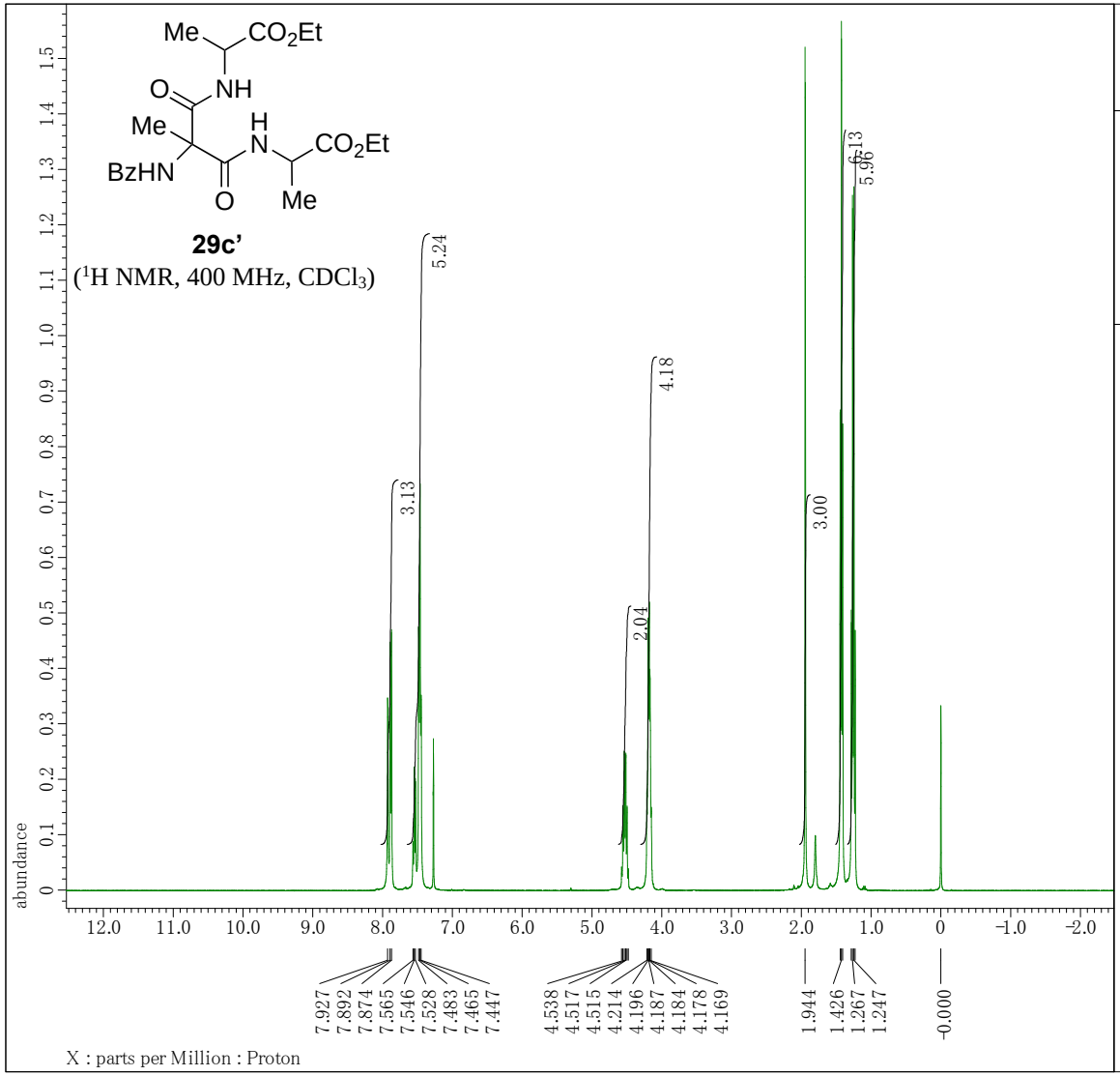
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm

Filename = Pro BzCMe(CONBn)2_carb
Author = delta
Experiment = carbon.jxp
Sample_Id = Pro BzCMe(CONBn)2
Solvent = CHLOROFORM-D
Actual_Start_Time = 7-FEB-2022 19:05:57
Revision_Time = 16-FEB-2023 16:16:31

Comment = single pulse decoupled
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR

Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1000
Total_Scans = 1000

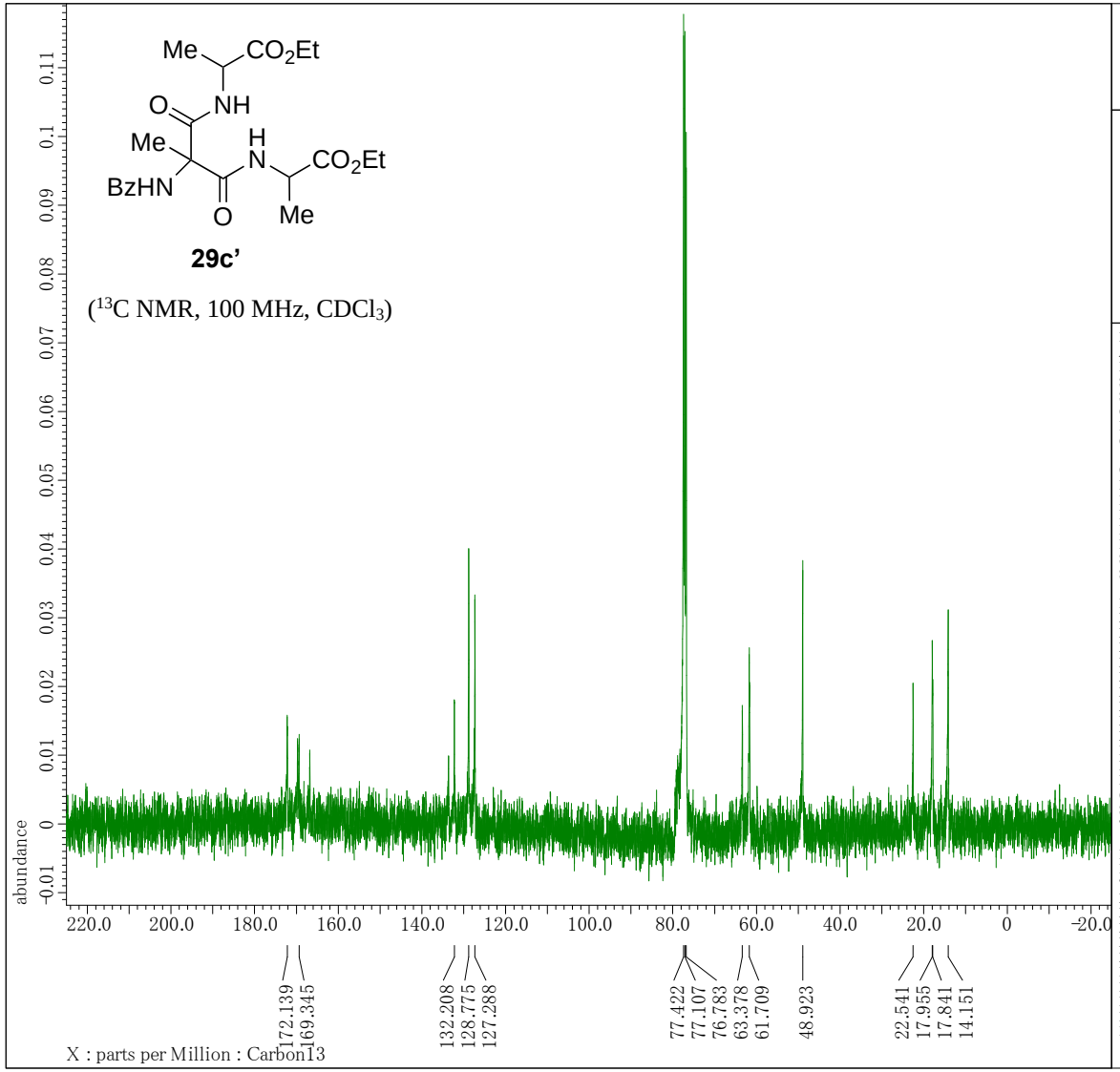
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 19[dC]
X_90_Width = 13.6[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]



JEOL RESONANCE

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

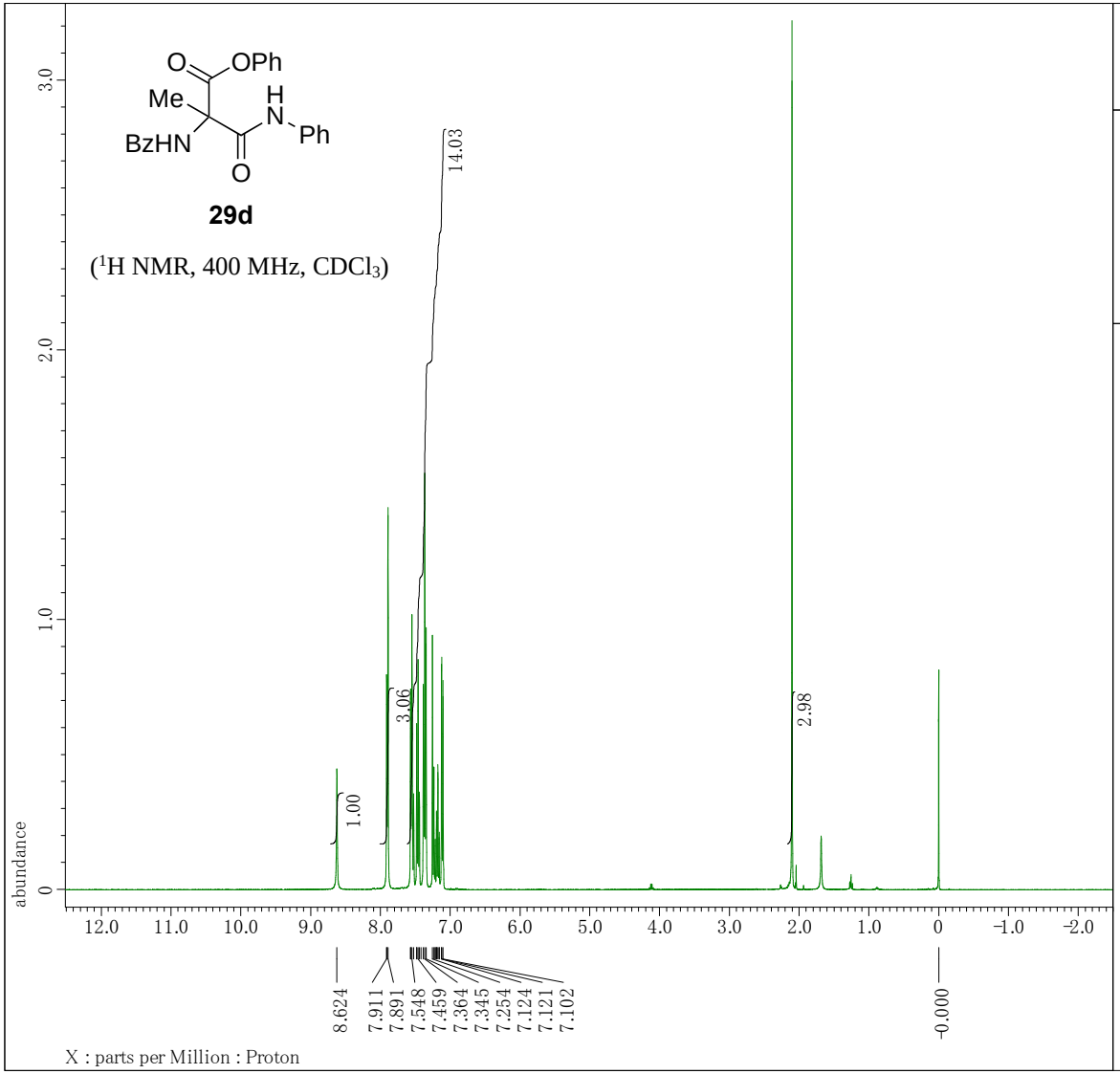
Filename	= 221130 BzNH(Me)CCONH-Ala
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 221130 BzNH(Me)CCONH-Ala
Solvent	= CHLOROFORM-D
Creation_Time	= 30-NOV-2022 14:39:20
Revision_Time	= 26-JAN-2023 18:45:06
Current_Time	= 26-JAN-2023 18:49:14
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 32
Temp_Get	= 19.2[dC]
X_90_Width	= 6.3[us]
X_Acq_Time	= 4.36731904[s]
X_Angle	= 45[deg]
X_Atn	= 0.7[dB]
X_Pulse	= 3.15[us]
Irr_Mode	= Off
Tri_Mode	= Off



JEOL RESONANCE

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

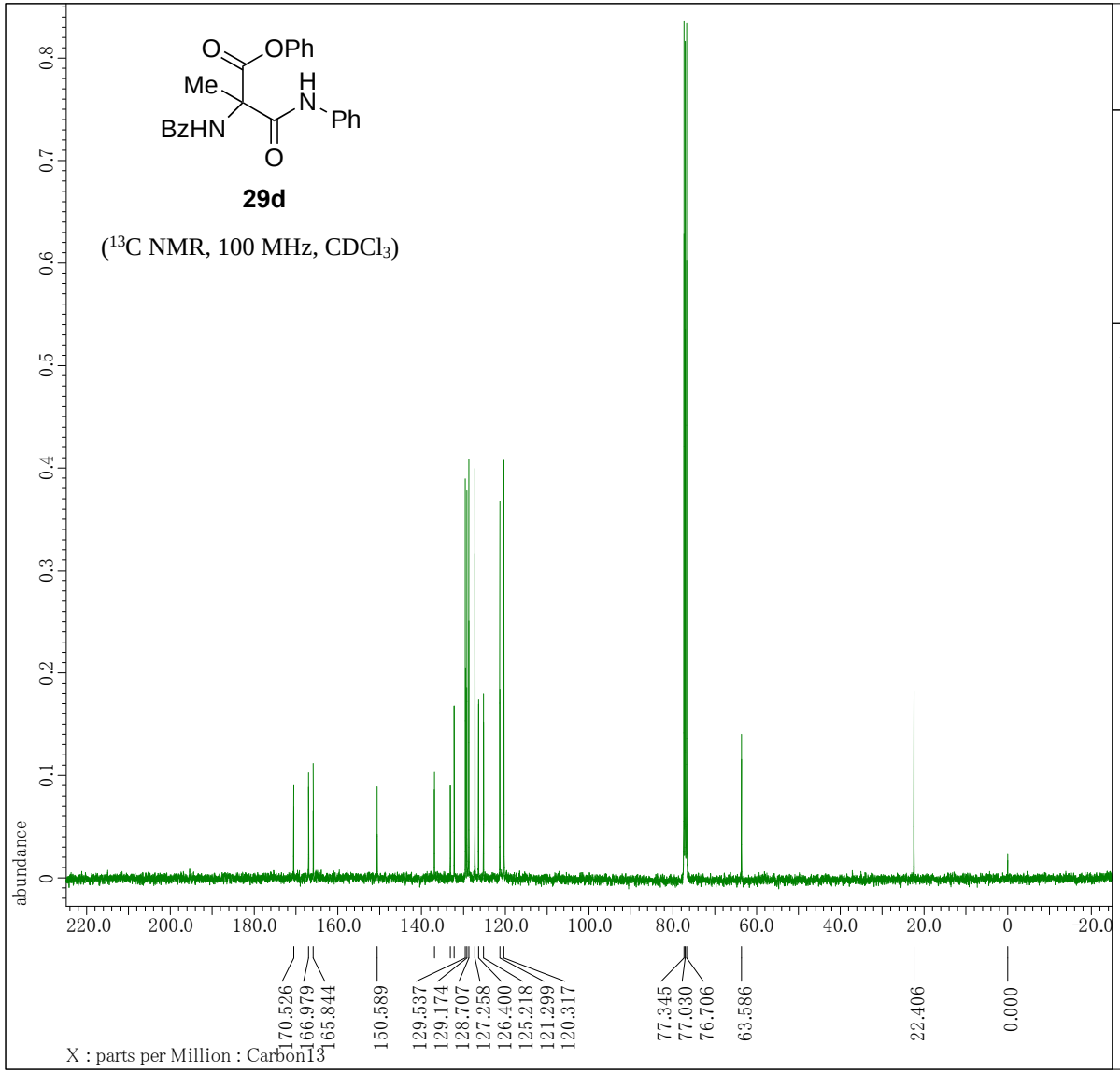
```
Filename          = 221130 BzNH(Me)CCONH-Ala
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = 221130 BzNH(Me)CCONH-Ala
Solvent           = CHLOROFORM-D
Creation_Time     = 30-NOV-2022 18:13:21
Revision_Time     = 26-JAN-2023 18:37:47
Current_Time      = 26-JAN-2023 18:38:18

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.04333312[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95846665[Hz]
X_Sweep           = 31.40703518[kHz]
X_Sweep_Clipped   = 25.12562814[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1000
Total_Scans       = 1000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 19.5[dC]
X_90_Width        = 13.6[us]
X_Acq_Time        = 1.04333312[s]
X_Angle           = 30[deg]
X_Atn             = 6.8[dB]
X_Pulse           = 4.53333333[us]
Irr_Atn_Dec       = 25.927[dB]
Irr_Atn_Noe       = 25.927[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
```



JEOL RESONANCE

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

Filename	= 221129 BzNH(Me)CO2PhCONHPh
Author	= delta
Experiment	= proton.jxp
Sample_Id	= 221129 BzNH(Me)CO2PhCONHPh
Solvent	= CHLOROFORM-D
Creation_Time	= 29-NOV-2022 17:54:10
Revision_Time	= 26-JAN-2023 18:55:07
Current_Time	= 26-JAN-2023 18:55:29
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 4.36731904[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 32768
X_Prescans	= 1
X_Resolution	= 0.22897343[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 36
Temp_Get	= 19.9[dC]
X_90_Width	= 6.3[us]
X_Acq_Time	= 4.36731904[s]
X_Angle	= 45[deg]
X_Atn	= 0.7[dB]
X_Pulse	= 3.15[us]
Irr_Mode	= Off
Tri_Mode	= Off



JEOL RESONANCE

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 221129 BzNH(Me)CO2PhCONHPh
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 221129 BzNH(Me)CO2PhCONHPh
Solvent             = CHLOROFORM-D
Creation_Time       = 29-NOV-2022 18:10:10
Revision_Time       = 26-JAN-2023 18:50:00
Current_Time        = 26-JAN-2023 18:50:25

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECS400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 1000
Total_Scans         = 1000

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 19.9[dC]
X_90_Width          = 13.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
X_Atn               = 6.8[dB]
X_Pulse             = 4.53333333[us]
Irr_Atn_Dec         = 25.927[dB]
Irr_Atn_Noe         = 25.927[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.115[ms]
Decoupling          = TRUE
```

9. Cartesian coordinates

SMD18(THF)/M06-2X-D3/6-311+G(d,p)-SDD

TBD	C	-0.061405	-0.727514	-0.035631
	N	1.155478	-1.372612	-0.214245
	C	2.409328	-0.754500	0.200280
	C	2.426446	0.675865	-0.305689
	C	1.197803	1.393990	0.222959
	N	-0.024413	0.652991	-0.083199
	N	-1.118292	-1.457098	0.070411
	C	-2.419545	-0.808732	0.179408
	C	-2.438043	0.608241	-0.379601
	C	-1.261300	1.371743	0.200500
	H	1.068152	-2.360175	-0.014334
	H	2.524530	-0.761997	1.292961
	H	3.228475	-1.333363	-0.228158
	H	2.416885	0.677991	-1.399035
	H	3.326580	1.191157	0.034220
	H	1.287672	1.538883	1.309889
	H	1.103197	2.382614	-0.232535
	H	-2.724726	-0.786907	1.233855
	H	-3.154976	-1.428857	-0.340352
	H	-3.374181	1.112234	-0.129712
	H	-2.346586	0.582219	-1.469565
	H	-1.175747	2.365146	-0.246440
	H	-1.388389	1.503530	1.285079
MTBD	C	2.007040	-1.506412	-0.292040
	C	2.332791	-0.110016	0.196553
	N	1.285120	0.822431	-0.210660
	C	-0.053497	0.477837	-0.036416
	N	-0.351941	-0.879547	-0.113837
	C	0.639719	-1.893801	0.230145
	N	-0.917025	1.424617	0.097599
	C	-2.335506	1.103661	0.187886
	C	-2.689798	-0.261040	-0.385280
	C	-1.722559	-1.277964	0.188443
	C	1.627624	2.222664	-0.026893

	H	2.756638	-2.215676	0.063929
	H	2.006260	-1.521448	-1.385327
	H	2.453692	-0.109576	1.291172
	H	3.270899	0.240120	-0.237344
	H	0.679205	-2.032792	1.321426
	H	0.307827	-2.837747	-0.208641
	H	-2.895089	1.889157	-0.327814
	H	-2.644358	1.146868	1.240368
	H	-3.718092	-0.532701	-0.136861
	H	-2.594819	-0.248695	-1.475216
	H	-1.866638	-1.368331	1.275794
	H	-1.879633	-2.266852	-0.249039
	H	1.522718	2.543531	1.017916
	H	2.664939	2.359023	-0.335443
	H	0.988491	2.853038	-0.641027
DBN	C	-0.199564	-0.735012	0.027013
	N	-0.227264	0.632734	0.009436
	N	0.832726	-1.493327	0.058036
	C	2.131506	-0.816749	0.146787
	C	2.134794	0.605709	-0.413682
	C	0.984157	1.405757	0.188915
	C	-1.563744	1.174287	0.199331
	C	-2.453264	0.026377	-0.294031
	C	-1.632090	-1.225593	0.043109
	H	2.869232	-1.424816	-0.382199
	H	2.442938	-0.795921	1.198750
	H	3.086655	1.095798	-0.199784
	H	2.010042	0.571406	-1.500124
	H	0.864694	2.368862	-0.314084
	H	1.163963	1.601758	1.254669
	H	-1.688891	2.093391	-0.377284
	H	-1.747140	1.402050	1.258290
	H	-3.437093	0.032675	0.173385
	H	-2.581759	0.109030	-1.375259
	H	-1.778024	-2.055963	-0.646741
	H	-1.853619	-1.582778	1.053423
DBU	C	-0.399604	0.779957	-0.362430

	N	-0.323718	-0.584729	-0.445636
	N	-1.477585	1.451142	-0.134876
	C	-2.702152	0.673102	0.010899
	C	-2.450338	-0.619957	0.778252
	C	-1.423437	-1.437073	0.015015
	C	0.903362	-1.287631	-0.811225
	C	1.960866	-1.310327	0.294824
	C	2.755587	-0.008392	0.385790
	C	1.909922	1.245609	0.613626
	C	0.895036	1.548091	-0.502897
	H	-3.446572	1.289885	0.518301
	H	-3.107588	0.430495	-0.981621
	H	-3.367078	-1.199732	0.901906
	H	-2.067701	-0.373145	1.773368
	H	-1.887684	-1.928247	-0.848267
	H	-1.002255	-2.220133	0.653789
	H	0.605772	-2.307472	-1.063400
	H	1.323623	-0.852905	-1.722962
	H	1.465075	-1.524798	1.248846
	H	2.652625	-2.135613	0.099504
	H	3.492954	-0.091525	1.189852
	H	3.321016	0.118704	-0.545832
	H	2.584083	2.102315	0.697998
	H	1.378746	1.172049	1.569665
	H	1.350947	1.353609	-1.479851
	H	0.617712	2.601354	-0.478841
TMG	C	-2.398071	0.548984	-0.372276
	N	-1.171717	-0.189521	-0.124589
	C	-0.006981	0.554755	-0.007916
	N	1.154368	-0.202238	0.114045
	C	2.388529	0.502159	0.409433
	C	-1.377895	-1.352177	0.734058
	N	-0.064690	1.842669	-0.007767
	C	1.357556	-1.363736	-0.748421
	H	-2.734787	1.097671	0.516623
	H	-2.252962	1.261711	-1.181852
	H	-3.173051	-0.164657	-0.658555
	H	2.245585	1.192539	1.241622

	H	3.141456	-0.231858	0.700618
	H	2.771287	1.060134	-0.457015
	H	-1.929949	-1.066957	1.639136
	H	-1.959212	-2.107104	0.198967
	H	-0.429776	-1.788903	1.037322
	H	0.865596	2.244795	-0.076923
	H	0.406668	-1.760604	-1.094876
	H	1.955406	-1.087828	-1.626526
	H	1.889178	-2.145219	-0.199631
piperidine	C	0.747395	-1.210570	0.206149
	C	-0.714513	-1.258097	-0.229077
	N	1.380336	-0.000001	-0.321053
	C	0.747396	1.210569	0.206149
	C	-0.714512	1.258097	-0.229077
	C	-1.451522	0.000001	0.236373
	H	1.289202	-2.080501	-0.171684
	H	0.791117	-1.240158	1.308618
	H	-0.754731	-1.324686	-1.321773
	H	-1.190766	-2.155378	0.175484
	H	2.365405	-0.000001	-0.077509
	H	1.289204	2.080501	-0.171684
	H	0.791118	1.240157	1.308618
	H	-1.190764	2.155379	0.175483
	H	-0.754730	1.324687	-1.321773
	H	-2.480956	0.000001	-0.131719
	H	-1.501923	0.000001	1.332208
quinuclidine	H	1.014723	-2.086630	0.509705
	H	-1.295980	-1.902641	0.861284
	H	1.202805	-1.035674	1.913119
	H	-1.088145	-0.562444	1.987590
	H	1.013482	1.482512	1.555453
	H	-1.295883	1.700368	1.212826
	H	1.208386	2.171486	-0.056033
	H	-1.081630	2.005164	-0.510328
	H	1.021636	0.603706	-2.057890
	H	-1.288204	0.202703	-2.083600
	H	1.212121	-1.136864	-1.848821

	H	-1.079552	-1.442127	-1.484432
	H	2.382759	-0.000645	0.005820
	C	1.291016	-0.000337	0.003118
	C	0.750548	-1.107306	0.920362
	C	-0.791500	-0.944349	1.007013
	C	0.752304	1.348875	0.501228
	C	-0.789183	1.346303	0.311720
	C	0.756580	-0.242131	-1.416200
	C	-0.785534	-0.401336	-1.324321
	N	-1.290272	0.000395	-0.003173
i -Pr_2EtN	N	-0.042592	0.139190	-0.147852
	C	0.237770	1.328836	0.674751
	C	0.182540	2.622495	-0.131515
	C	1.112492	-0.770507	-0.267098
	C	1.517866	-1.450703	1.046620
	C	2.301983	-0.056130	-0.906496
	C	-1.309180	-0.510343	0.237514
	C	-1.555478	-1.808605	-0.528371
	C	-2.478482	0.440325	-0.024992
	H	1.223555	1.244411	1.139258
	H	-0.471438	1.381063	1.507995
	H	0.378641	3.488585	0.508028
	H	-0.797897	2.750241	-0.596137
	H	0.930726	2.607292	-0.927911
	H	0.814962	-1.550653	-0.969842
	H	0.681216	-1.998983	1.487933
	H	2.327872	-2.163270	0.868106
	H	1.872852	-0.723022	1.782202
	H	2.006723	0.411246	-1.848993
	H	3.095731	-0.778253	-1.114553
	H	2.723028	0.714724	-0.255440
	H	-1.298780	-0.746587	1.316415
	H	-0.867049	-2.607208	-0.247041
	H	-2.568834	-2.159554	-0.320276
	H	-1.470057	-1.637352	-1.606157
	H	-2.381213	1.384426	0.513612
	H	-3.415735	-0.025427	0.290099
	H	-2.543222	0.661782	-1.094814

Et_3N	C	-0.474924	-1.308636	0.284321
	N	-0.000113	0.000282	-0.172069
	C	-0.896454	1.065502	0.284894
	C	0.340789	-2.482232	-0.246538
	C	-2.320255	0.946142	-0.246833
	C	1.370463	0.243746	0.285500
	C	1.980346	1.535420	-0.247163
	H	-1.501663	-1.428805	-0.062703
	H	-0.502043	-1.342421	1.389589
	H	-0.912867	1.104662	1.390189
	H	-0.486661	2.015039	-0.060729
	H	-0.200331	-3.413166	-0.062373
	H	1.316700	-2.572148	0.232666
	H	0.491593	-2.383693	-1.325019
	H	-2.855863	1.880296	-0.062843
	H	-2.309870	0.766353	-1.325315
	H	-2.886338	0.146008	0.232161
	H	1.987637	-0.586292	-0.059396
	H	1.412249	0.239185	1.390789
	H	3.056875	1.531742	-0.061521
	H	1.570474	2.426804	0.229883
	H	1.821119	1.614812	-1.325986
DABCO	N	-1.283848	0.001055	0.013723
	C	-0.759722	0.111108	1.383085
	C	-0.782029	-1.245325	-0.583669
	N	1.283856	-0.001100	-0.013728
	C	-0.782124	1.136111	-0.774924
	C	0.765904	1.050677	-0.901259
	C	0.768563	-1.299849	-0.471849
	C	0.789398	0.247250	1.348549
	H	-1.222891	0.975383	1.865436
	H	-1.065489	-0.783950	1.931082
	H	-1.246438	-2.090371	-0.069485
	H	-1.103702	-1.268812	-1.628124
	H	-1.261529	1.117878	-1.756760
	H	-1.086912	2.055764	-0.268669
	H	1.066020	0.803864	-1.923004

	H	1.238416	1.998387	-0.631593
	H	1.227156	-1.537478	-1.434845
	H	1.086088	-2.058346	0.248423
	H	1.104162	1.252603	1.640246
	H	1.265122	-0.464433	2.027733
DMAP	C	-1.946317	-1.132307	0.016414
	C	-0.564523	-1.198104	-0.002757
	C	0.185943	-0.000486	-0.027878
	C	-0.564749	1.197316	-0.021684
	C	-1.946516	1.131656	-0.002344
	N	-2.659936	-0.000340	0.015911
	N	1.544068	0.000518	-0.056113
	C	2.270472	-1.256407	0.005638
	C	2.266900	1.257732	0.038757
	H	-2.516543	-2.056918	0.036037
	H	-0.084203	-2.166498	0.005981
	H	-0.084298	2.165695	-0.033733
	H	-2.517012	2.056299	-0.000197
	H	2.095665	-1.779867	0.952577
	H	1.979297	-1.917255	-0.815309
	H	3.334833	-1.052491	-0.086965
	H	2.026482	1.790264	0.965513
	H	3.334697	1.051613	0.027757
	H	2.034901	1.911506	-0.807129
NMI	C	0.191294	1.083930	-0.001798
	N	1.468075	0.766914	0.002473
	C	1.500193	-0.605946	0.002605
	C	0.225210	-1.106984	-0.002019
	N	-0.602499	-0.013322	-0.006251
	C	-2.056506	-0.035593	0.004212
	H	-0.222562	2.081439	-0.004293
	H	2.430073	-1.153656	0.003755
	H	-0.163615	-2.112662	-0.004392
	H	-2.423656	-0.635886	-0.828051
	H	-2.419957	-0.451648	0.944274
	H	-2.420462	0.984825	-0.102842

N-methylpyrrolidine	N	0.709787	-0.000017	-0.372474
	C	-0.019050	1.149011	0.158860
	C	-1.491426	0.775810	-0.052957
	C	-1.491404	-0.775823	-0.053077
	C	-0.019065	-1.148990	0.158952
	C	2.114677	-0.000005	-0.015534
	H	0.193288	1.269733	1.236610
	H	0.279070	2.067773	-0.350770
	H	-1.846812	1.158215	-1.010911
	H	-2.126085	1.194299	0.728825
	H	-2.126227	-1.194474	0.728485
	H	-1.846544	-1.158075	-1.011185
	H	0.279119	-2.067817	-0.350521
	H	0.193164	-1.269554	1.236744
	H	2.604301	-0.885214	-0.428006
	H	2.261523	0.000038	1.078655
	H	2.604301	0.885173	-0.428073
TBD·HBr	C	1.336862	-2.520825	-0.493383
	C	0.483992	-2.461275	0.759451
	N	0.742020	-1.190234	1.434343
	C	0.913067	-0.045817	0.751392
	N	1.224328	-0.061538	-0.546110
	C	1.062779	-1.287879	-1.334627
	N	0.870275	1.109901	1.434859
	C	0.727697	2.398309	0.759223
	C	1.584508	2.377304	-0.492323
	C	1.200313	1.174984	-1.335299
	H	1.090826	-3.413508	-1.069485
	H	2.395316	-2.565408	-0.223932
	H	-0.577985	-2.521371	0.503089
	H	0.736945	-3.262660	1.452914
	H	0.038570	-1.300761	-1.724066
	H	1.760584	-1.223511	-2.170686
	H	1.052638	3.173776	1.452035
	H	-0.324358	2.554991	0.502364
	H	1.423874	3.288160	-1.070184
	H	2.641568	2.324007	-0.219386
	H	0.188739	1.290250	-1.740774

	H	1.901213	1.040201	-2.160618
	H	0.490950	1.044931	2.370023
	Br	-2.196364	0.109690	-0.177341
	H	0.342191	-1.083954	2.357409
MTBD·HBr	C	-1.006824	-2.460757	-1.097889
	C	-1.730607	-1.774405	0.040751
	N	-0.765034	-1.247760	1.011102
	C	0.406258	-0.733036	0.596751
	N	0.882737	-0.975494	-0.635382
	C	0.004744	-1.499346	-1.683288
	N	1.154802	-0.050298	1.484781
	C	2.282305	0.787246	1.076883
	C	3.021206	0.096342	-0.050052
	C	2.028206	-0.217373	-1.151314
	C	-1.329195	-0.802749	2.280801
	H	-1.723435	-2.754074	-1.866009
	H	-0.504011	-3.360684	-0.734225
	H	-2.340050	-0.941727	-0.327903
	H	-2.371476	-2.477618	0.572930
	H	-0.495378	-0.650972	-2.165040
	H	0.641492	-1.997481	-2.415959
	H	2.919887	0.927184	1.949511
	H	1.902066	1.758666	0.745763
	H	3.803704	0.748410	-0.439786
	H	3.486819	-0.823960	0.312189
	H	1.647495	0.705071	-1.605293
	H	2.487984	-0.829153	-1.928659
	H	-1.542142	0.271577	2.251504
	H	-2.260946	-1.341169	2.439704
	H	-0.663308	-1.039318	3.112933
	H	0.662757	0.276674	2.302520
	Br	-1.046159	1.916226	-0.437244
DBN·HBr	C	-0.909789	0.272460	-0.081282
	N	-2.224670	0.140883	-0.073546
	N	-0.084144	-0.740733	-0.113131
	C	-0.568133	-2.120670	-0.184151
	C	-1.952403	-2.212454	0.447291

	C	-2.883853	-1.158613	-0.144643
	C	-2.921643	1.430084	-0.137570
	C	-1.831453	2.419138	0.295597
	C	-0.517305	1.719672	-0.088989
	H	0.147196	-2.750996	0.343277
	H	-0.596590	-2.435135	-1.230932
	H	-2.368947	-3.205234	0.277423
	H	-1.870894	-2.056074	1.525751
	H	-3.814570	-1.094772	0.420623
	H	-3.127116	-1.383621	-1.187694
	H	-3.783403	1.414837	0.530031
	H	-3.266619	1.607135	-1.160773
	H	-1.943543	3.389539	-0.183452
	H	-1.872361	2.556276	1.376976
	H	0.319874	1.912672	0.580446
	H	-0.198036	1.971357	-1.104782
	H	0.933328	-0.540060	-0.087416
	Br	3.060310	0.077581	0.016278
DBU·HBr	C	-0.634805	0.189540	-0.408120
	N	-1.863084	0.688273	-0.394588
	N	0.421211	0.948594	-0.207686
	C	0.342844	2.382042	0.047829
	C	-0.966700	2.675250	0.759743
	C	-2.117877	2.095981	-0.044250
	C	-3.040685	-0.137676	-0.705519
	C	-3.390068	-1.130789	0.401117
	C	-2.518203	-2.385837	0.385278
	C	-1.018000	-2.129207	0.526923
	C	-0.409539	-1.282232	-0.605115
	H	1.206160	2.655177	0.654081
	H	0.401072	2.924717	-0.900005
	H	-1.108020	3.750249	0.871782
	H	-0.947768	2.224983	1.755531
	H	-2.280419	2.661666	-0.966575
	H	-3.040395	2.118701	0.537863
	H	-3.860388	0.562945	-0.862056
	H	-2.876289	-0.656171	-1.653730
	H	-3.316671	-0.620125	1.367716

	H	-4.435464	-1.423767	0.271050
	H	-2.839387	-3.053804	1.189000
	H	-2.692727	-2.919322	-0.556638
	H	-0.497060	-3.089197	0.528909
	H	-0.800566	-1.654143	1.489533
	H	-0.829245	-1.582091	-1.570372
	H	0.669110	-1.439259	-0.650844
	H	1.350347	0.494077	-0.168580
	Br	3.385972	-0.402147	0.020913
TMG·HBr	C	-0.030854	1.878926	0.683299
	N	1.114683	1.187171	0.096466
	C	1.223747	-0.147932	0.168299
	N	2.405847	-0.745910	-0.068828
	C	2.474448	-2.182813	-0.310901
	C	1.913743	1.988357	-0.827798
	N	0.159415	-0.878504	0.489604
	C	3.677928	-0.115829	0.281171
	H	-0.864389	1.940968	-0.020782
	H	-0.367371	1.358011	1.578361
	H	0.293174	2.883468	0.958103
	H	1.625908	-2.510131	-0.910627
	H	3.388146	-2.386969	-0.868950
	H	2.504179	-2.746840	0.627605
	H	1.231351	2.572056	-1.449708
	H	2.570837	2.672271	-0.285650
	H	2.508105	1.348800	-1.476260
	H	0.276637	-1.852629	0.726987
	H	3.508329	0.825936	0.797703
	H	4.219872	-0.785548	0.953177
	H	4.285419	0.060005	-0.609220
	H	-0.807839	-0.554217	0.327230
	Br	-3.019601	-0.236821	-0.112374
piperidine·HBr	C	1.083903	-1.243801	0.001518
	C	2.601436	-1.256828	0.096221
	N	0.537668	-0.000087	0.619343
	C	1.083741	1.243719	0.001552
	C	2.601271	1.256919	0.096267

	C	3.200597	0.000096	-0.536810
	H	0.624609	-2.088369	0.514213
	H	0.746777	-1.238533	-1.037402
	H	2.895116	-1.319902	1.150198
	H	2.970039	-2.158029	-0.397594
	H	-0.515965	-0.000166	0.498557
	H	0.624335	2.088207	0.514275
	H	0.746619	1.238427	-1.037369
	H	2.969769	2.158185	-0.397509
	H	2.894936	1.319988	1.150248
	H	4.285861	0.000166	-0.417879
	H	2.990047	0.000105	-1.612014
	H	0.737324	-0.000082	1.623695
	Br	-2.547395	-0.000001	-0.081123
quinuclidine·HBr	H	2.562405	1.814239	1.141931
	H	0.266227	1.997477	0.623412
	H	2.823306	2.096060	-0.580093
	H	0.559945	1.756376	-1.107163
	H	2.564563	0.080587	-2.140642
	H	0.267820	-0.456959	-2.043065
	H	2.822669	-1.552228	-1.523950
	H	0.557869	-1.835326	-0.968315
	H	2.560847	-1.895764	1.002097
	H	0.263521	-1.539021	1.414804
	H	2.819080	-0.545364	2.107801
	H	0.555001	0.080293	2.072008
	H	3.969315	-0.001146	0.002536
	C	2.879396	-0.000636	0.001424
	C	2.344670	1.432654	0.141685
	C	0.824439	1.412121	-0.106784
	C	2.345119	-0.594855	-1.310498
	C	0.824422	-0.797402	-1.170316
	C	2.342427	-0.838840	1.171375
	C	0.821944	-0.613839	1.274532
	N	0.345556	0.000576	-0.001348
	H	-0.711910	0.001003	-0.002042
	Br	-2.816973	0.000015	0.000046

i-Pr_2EtN·HBr	N	-0.882323	0.081127	0.226885
	C	-1.385380	-0.302031	1.598111
	C	-0.250556	-0.719532	2.515582
	C	-1.366297	-0.853831	-0.865626
	C	-2.862477	-0.726016	-1.101854
	C	-0.940426	-2.283088	-0.554449
	C	-1.114506	1.556470	-0.058103
	C	-0.726673	1.921813	-1.485057
	C	-0.303023	2.382002	0.935692
	H	-2.101369	-1.111904	1.482310
	H	-1.928821	0.550778	2.001513
	H	-0.660849	-0.973627	3.494911
	H	0.478972	0.083051	2.639712
	H	0.273533	-1.592083	2.120799
	H	-0.817689	-0.535113	-1.751810
	H	-3.158011	0.283741	-1.391101
	H	-3.137567	-1.399460	-1.915974
	H	-3.438298	-1.020487	-0.221086
	H	0.129422	-2.331226	-0.340304
	H	-1.135899	-2.893532	-1.438385
	H	-1.499974	-2.717098	0.276808
	H	-2.182697	1.720865	0.100730
	H	-1.383795	1.479971	-2.234352
	H	-0.795153	3.006674	-1.583839
	H	0.305539	1.624510	-1.688568
	H	-0.568654	2.181010	1.974230
	H	-0.492030	3.439509	0.744096
	H	0.764646	2.190238	0.798950
	H	0.163058	-0.038029	0.209308
	Br	2.315941	-0.239154	-0.307769
Et_3N·HBr	C	1.490826	-0.412473	1.378027
	N	1.066540	-0.000564	0.001847
	C	1.504942	1.392893	-0.327458
	C	1.095416	-1.836691	1.727304
	C	1.110177	2.411698	0.727306
	C	1.497563	-0.987785	-1.038692
	C	1.117448	-0.578221	-2.450945
	H	1.004589	0.277667	2.065319

	H	2.571773	-0.261131	1.436286
	H	2.586860	1.358899	-0.478673
	H	1.027779	1.645956	-1.272608
	H	1.257376	-1.981673	2.796768
	H	1.689022	-2.579859	1.194989
	H	0.035738	-2.005732	1.520258
	H	1.281701	3.408242	0.316825
	H	0.048492	2.324168	0.970857
	H	1.697524	2.320972	1.640955
	H	1.006322	-1.926379	-0.787544
	H	2.577029	-1.117082	-0.926888
	H	1.280559	-1.434214	-3.107940
	H	1.719656	0.249609	-2.824740
	H	0.059926	-0.307750	-2.503904
	H	0.007222	0.003600	-0.003010
	Br	-2.120445	0.002632	-0.004090
DABCO·HBr	N	2.859910	-0.001865	-0.007942
	C	2.370772	-0.382507	1.321762
	C	2.363129	1.338487	-0.337824
	N	0.342694	0.001880	0.007696
	C	2.355801	-0.959290	-0.998616
	C	0.817526	-0.837340	-1.131313
	C	0.826583	1.404407	-0.153184
	C	0.832722	-0.564063	1.298565
	H	2.853953	-1.310572	1.628668
	H	2.654782	0.401254	2.025769
	H	2.850030	2.069614	0.308125
	H	2.636252	1.558038	-1.371154
	H	2.831884	-0.764018	-1.959912
	H	2.635613	-1.962919	-0.674927
	H	0.512031	-0.331601	-2.047461
	H	0.307199	-1.798008	-1.066435
	H	0.312873	1.832509	-1.013575
	H	0.532230	1.947666	0.745113
	H	0.531313	-1.611505	1.320325
	H	0.328670	-0.030480	2.103970
	H	-0.717760	0.002460	0.013119
	Br	-2.802471	-0.000020	-0.000178

DMAP·HBr	C	-0.087464	1.168847	0.012218
	C	-1.452987	1.212794	0.011677
	C	-2.200469	-0.000091	-0.000100
	C	-1.453884	-1.213540	-0.011776
	C	-0.088320	-1.170628	-0.012035
	N	0.576084	-0.001138	0.000184
	N	-3.538928	0.000451	-0.000192
	C	-4.272951	1.261564	-0.021420
	C	-4.274017	-1.260038	0.021503
	H	0.522226	2.063383	0.023374
	H	-1.939454	2.176231	0.025404
	H	-1.941047	-2.176620	-0.025637
	H	0.520677	-2.065632	-0.023057
	H	-4.070987	1.847168	0.879609
	H	-4.002551	1.853097	-0.899759
	H	-5.336773	1.045292	-0.065877
	H	-4.004313	-1.851367	0.900197
	H	-5.337673	-1.042866	0.065553
	H	-4.072336	-1.846242	-0.879194
	H	1.627253	-0.001285	0.000179
	Br	3.764441	0.000292	-0.000032
NMI·HBr	C	-1.391025	-0.746178	0.000154
	N	-0.504389	0.238566	0.000070
	C	-1.165219	1.440499	0.000188
	C	-2.495409	1.159013	0.000189
	N	-2.611703	-0.214504	0.000096
	C	-3.870520	-0.955644	0.000071
	H	-1.172290	-1.801566	0.000133
	H	-0.640232	2.380605	0.000214
	H	-3.362038	1.798816	0.000223
	H	-4.437448	-0.697679	0.893149
	H	-4.437665	-0.697264	-0.892748
	H	-3.645692	-2.019840	-0.000206
	H	0.544676	0.109965	-0.000005
	Br	2.642753	-0.132217	-0.000158
N-methylpyrrolidine	N	-1.022259	0.731977	-0.000620

·HBr	C	-1.626835	0.051552	-1.180574
	C	-1.645034	-1.423822	-0.776238
	C	-1.654703	-1.423349	0.775353
	C	-1.626264	0.052359	1.180271
	C	-1.142909	2.201002	-0.000751
	H	-2.631595	0.460688	-1.305947
	H	-1.025856	0.273626	-2.061748
	H	-0.749147	-1.922416	-1.145482
	H	-2.514799	-1.925330	-1.198276
	H	-2.535899	-1.914364	1.185937
	H	-0.770170	-1.932930	1.156559
	H	-1.020925	0.270299	2.059474
	H	-2.628179	0.466897	1.310047
	H	-0.653857	2.592191	0.890524
	H	-2.199341	2.470331	-0.001199
	H	-0.653065	2.592119	-0.891615
	H	0.011161	0.487242	-0.000836
	Br	2.020056	-0.108247	0.000530
HBr	Br	0.000000	0.000000	0.039511
	H	0.000000	0.000000	-1.382876
TFIS	C	4.760508	-0.580134	0.231838
	C	3.850788	0.342072	-0.083119
	C	2.389704	0.182224	-0.043921
	C	1.576379	1.314559	-0.028677
	C	0.195853	1.243993	-0.007433
	C	-0.452742	0.019971	-0.007521
	C	0.334580	-1.120283	-0.030133
	C	1.715764	-1.037842	-0.048378
	F	2.395568	-2.187341	-0.092062
	F	-0.224506	-2.330972	-0.040486
	F	-0.497591	2.382213	0.014692
	F	2.136169	2.529285	-0.026667
	H	5.813416	-0.330969	0.167085
	H	4.508013	-1.577293	0.567635
	H	4.185542	1.328638	-0.385481
	I	-2.547523	-0.097102	0.019916

TFBrS	C	4.323816	-0.519547	0.242652
	C	3.402159	0.383678	-0.091318
	C	1.943868	0.199944	-0.047792
	C	1.112319	1.319155	-0.030835
	C	-0.266747	1.228226	-0.005214
	C	-0.887561	-0.011703	-0.003051
	C	-0.085339	-1.142847	-0.028956
	C	1.293465	-1.032879	-0.051241
	F	1.992209	-2.169049	-0.098774
	F	-0.631944	-2.355629	-0.039607
	F	-0.987710	2.345553	0.019404
	F	1.650991	2.541719	-0.030788
	H	5.373469	-0.258109	0.174104
	H	4.083925	-1.512833	0.598946
	H	3.721342	1.369390	-0.412561
	Br	-2.754472	-0.154456	0.030913
TFClS	C	3.845059	-0.362370	0.232540
	C	2.879795	0.494694	-0.099710
	C	1.432109	0.241502	-0.048298
	C	0.547630	1.319387	-0.028473
	C	-0.825024	1.161711	0.002225
	C	-1.384188	-0.107503	0.008308
	C	-0.528547	-1.198866	-0.020001
	C	0.842722	-1.021751	-0.047984
	F	1.595464	-2.122719	-0.099240
	F	-1.021367	-2.434336	-0.027397
	F	-1.605028	2.238528	0.029458
	F	1.026134	2.566658	-0.031022
	Cl	-3.088169	-0.321822	0.049238
	H	4.880776	-0.051858	0.157334
	H	3.654092	-1.364460	0.593939
	H	3.149843	1.493289	-0.426129

name	yield (%) of TFIS	yield (%) of Ph3P=O	Organic Base	pKBH	temp. (deg.C)	time (h)	UDR-Pro	Mayr-N
0	11	24	DBU	10.6573025	55	2	83	15.29
1	35	71	DBU	16.9	80	2	65	15.29
2	0	17	DBU	24.31	95	2	100	15.29
3	9	23	DBU	8.99183593	125	2	91	15.29
4	29	37	DBU	12.7122316	45	2	71	15.29
5	25	31	DBU	13.0328157	65	2	75	15.29
6	21	59	DBU	15.8179859	95	2	79	15.29
7	11	76	DBU	10.8803429	115	2	89	15.29
8	37	61	DBU	16.9	60	2	63	15.29
9	27	44	DBU	16.9	40	2	73	15.29
10	36	56	MTBD	18	60	2	64	13.9348139
11	15	16	DBN	17.2	60	2	85	16.28
12	37	61	DBU	16.9	60	2	63	15.29
13	43	52	TMG	15.5	60	2	57	11.4062673
14	0	0	Piperidine	14.3	60	2	99	17.35
15	3	0	Quinuclidine	13.1	60	2	25	20.54
16	1	0	Et3N	12.5	60	2	13	17.1
17	46	64	TMG	15.5	80	2	54	11.4062673
18	51	69	TMG	15.5	80	4	49	11.4062673
19	53	82	TMG	15.5	80	6	47	11.4062673
20	54	80	TMG	15.5	80	24	46	11.4062673
21	0	0	DABCO	11.7	60	2	26	19.6811049

22	0	0	DIPEA	12.7	60	2	17	16.2720408
23	8	33	TBD	21	60	2	92	12.6590042
24	0	0	DMAP	13.9312905	60	2	99	15.51
25	0	0	NMI	11.668496	60	2	55	15.7441301
26	0	0	N-Mepyrrolidine	10.2473137	60	2	54	20.59

delta G (kcal/mol)	NBO (a.u.)	Vs min (kJ/mol)	Surface	Volume	NXBA	HBD	Cyclic/Acyclic	NRing
-26.5	-0.64	-198	240.6185362	158.568	2	0	1	2
-25.6	-0.64	-197	240.6185362	158.568	2	0	1	2
-27	-0.66	-205	240.6185362	158.568	2	0	1	2
-20.2	-0.61	-178	240.6185362	158.568	2	0	1	2
-24.9	-0.63	-189	240.6185362	158.568	2	0	1	2
-28.25979554	-0.38916254	-318.9167011	240.6185362	158.568	2	0	1	2
-27.26870373	-0.606843478	-283.1995207	240.6185362	158.568	2	0	1	2
-19.9	-0.61	-177	240.6185362	158.568	2	0	1	2
-26.2	-0.64	-197	240.6185362	158.568	2	0	1	2
-26.8	-0.64	-197	240.6185362	158.568	2	0	1	2
-23.4	-0.67	-176	238.1135779	154.28	3	0	1	2
-24.8	-0.64	-200	200.262347	126.28	2	0	1	2
-26.2	-0.64	-197	240.6185362	158.568	2	0	1	2
-22.9	-0.84	-187	194.7574773	125.216	3	1	0	0
-19.8	-0.73	-132	159.4960995	96.712	1	1	1	1
-22.7	-0.58	-140	184.1903585	119.592	1	0	1	3
-21.2	-0.6	-118	200.2106681	123.768	1	0	0	0
-22.3	-0.84	-197	194.7574773	125.216	3	1	0	0
-22.3	-0.84	-197	194.7574773	125.216	3	1	0	0
-22.3	-0.84	-197	194.7574773	125.216	3	1	0	0
-22.3	-0.84	-197	194.7574773	125.216	3	1	0	0
-21.4	-0.57	-127	173.2066543	115.496	2	0	1	3

-21.6	-0.62	-112	238.479512	157.384	1	0	0	0
-22.4	-0.68	-187	212.5086809	137.776	3	1	1	2
-17.2	-0.56	-189	178.371399	124.304	2	0	1	1
-12.7	-0.57	-194	160.0939643	97.416	2	0	1	1
-21.7	-0.6	-125	125.8532292	81.56	1	0	1	1

Ring Size of N	Ring Size of S	solvent	SVI-Et(30)	SVI-n	SVI-epsilon	SVI-mu	SVI-pi*	SVI-PC1
6	7	CH2Cl2	40.7	1.424	9.02	1.14	0.82	-0.7
6	7	THF	37.4	1.406	7.47	1.75	0.58	-1.5
6	7	MeCN	45.6	1.344	36	3.53	0.66	-4.7
6	7	toluene	33.9	1.497	2.43	0.31	0.54	4.2
6	7	Et2O	34.5	1.352	4.42	1.15	0.24	0.7
6	7	t-BuOMe	34.7	1.369	4.5	1.24	0.418020504	0.9
6	7	Glyme	38.2	1.377	7.2	1.71	0.53	-1.4
6	7	1_4-Dioxane	36	1.422	7.47	1.75	0.49	-0.9
6	7	THF	37.4	1.406	7.47	1.75	0.55	-1.5
6	7	THF	37.4	1.406	7.47	1.75	0.55	-1.5
6	6	THF	37.4	1.406	7.47	1.75	0.55	-1.5
6	5	THF	37.4	1.406	7.47	1.75	0.55	-1.5
6	7	THF	37.4	1.406	7.47	1.75	0.55	-1.5
0	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
6	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
6	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
0	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
0	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
0	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
0	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
0	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
6	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5

0	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
6	6	THF	37.4	1.406	7.47	1.75	0.55	-1.5
6	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
5	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5
5	0	THF	37.4	1.406	7.47	1.75	0.55	-1.5

SVI-PC2	SVI-PC3	SVI-PC4	SVI-PC5	SVI-DN	SVI-AN	SVI-dD	SVI-dP	SVI-dH
-6.5	-1.3	1.3	2	10	3.9	18.2	6.3	6.1
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-4.7	-3.3	-0.3	4.3	14.1	18.9	15.3	18	6.1
-3.7	-1.1	1	-1.4	0	0.1	18	1.4	2
-2.1	-2.3	-4	-0.8	19.2	3.9	15.2	6.1	5.7
-1.2	-2	-3	-0.8	25.4338589	-2.038824	14.8	4.3	5
0.5	-2.5	-2.7	-0.4	24	10.2	15.4	6.3	6
0.2	-1.9	-1.5	-1.1	14.8	10.8	17.5	1.8	9
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8

-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8
-1.9	-3.2	-1.8	-1.2	20	8	16.8	5.7	8