Supporting Information

Photoredox-Catalyzed Amidyl Radical Insertion to Bicyclo[1.1.0]butanes

Chetan C. Chintawar[1,2], Ranjini Laskar[1,2], Debanjan Rana[1], Felix Schäfer[1], Nele Van Wyngaerden[1], Subhabrata Dutta[1], Constantin G. Daniliuc[1], and Frank Glorius[1,]*

[1]Organisch-Chemisches Institut, Universität Münster, Münster, Germany.

[2]These authors contributed equally.

*Correspondence to: glorius@uni-muenster.de

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1. General information

1.1 Materials, reagents, and solvents

Unless otherwise stated, reactions were carried out in oven-dried glassware under argon, using standard Schlenk techniques. Given reaction temperatures are the ones of the heating/cooling media and the reactions were stirred using PTFE-coated magnetic stirring bars. Removal of solvents was achieved by rotary evaporation under reduced pressure, using a water bath at 40 °C.

Thioxanthone was purchased from Fluorochem and used as received. Other employed photocatalysts: Ir(*d*F(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$, *fac*-Ir(ppy)$_3$, Ir(ppy)$_2$(dtbbpy)PF$_6$, Ru(bpy)$_3$(PF$_6$)$_2$, (Mes-Acr)BF$_4$, and (Mes-Acr)ClO$_4$ were prepared following literature procedures. Commercially available chemicals were purchased from commercial suppliers and were used without further purification, unless otherwise stated.

The following solvents were purchased from ACROS Organics, Fischer Scientific, and Sigma-Aldrich (HPLC grade), dried using a solvent purification system (SPS) with activated alumina columns – custom-built by the “Feinmechanische Werkstatt des Organisch-Chemischen Instituts, WWU Münster” – and collected under positive argon pressure: dichloromethane (CH$_2$Cl$_2$), acetonitrile (MeCN), tetrahydrofuran (THF), diethyl ether (Et$_2$O), *N*,*N*-dimethylformamide (DMF), toluene, and methanol (MeOH). Other dry solvents were bought from ACROS Organics (ACROS ExtraDry solvents with ACROSeal® cap), stored over 3 or 4 Å molecular sieves, and collected under positive argon pressure.

Solvents such as ^{n}Pentane, CH$_2$Cl$_2$, and ethyl acetate (EtOAc) used for column chromatography, extractions, etc., were purchased of technical grade and purified by atmospheric pressure distillation.

1.2 Analytical techniques

NMR spectra were recorded at room temperature in deuterated solvents using Bruker Avance II 400, Bruker Avance Neo 400, Agilent DD2 500, or Agilent DD2 600 spectrometers. Deuterated solvents were purchased from Eurisotop and Sigma-Aldrich (CDCl$_3$, deuteration > 99.8%). ^{1}H and ^{13}C chemicals shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS, $\delta = 0.00$ ppm) and were internally referenced to residual solvent signals (CDCl$_3$: 7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C; CD$_3$OD: 3.34 ppm for ^{1}H, 49.83 ppm for ^{13}C; or (CD$_3$)$_2$SO: 2.50 ppm for ^{1}H, 39.52 ppm for ^{13}C). Coupling constants (J) are reported in

Hertz (Hz) and the following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

High-resolution mass spectra (HRMS) were obtained by the mass spectrometry service of the Organisch-Chemisches Institut, Westfälische Wilhelms Universität Münster, using 4 electrospray ionisation (ESI) on a MicroToF spectrometer (Bruker Daltonics) or on an LTQ Orbitap LTQ XL (Thermo-Fisher Scientific).

1.3 Purification techniques

Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F254 pre-coated aluminium sheets and were visualized using UV light (254 nm) and/or staining with basic aq. $KMnO_4$ solution. Flash column chromatography was carried out manually using standard techniques with silica gel (Thermo Scientific, 0.035-0.070 mm, 60 Å) under a slight positive pressure, eluting with the specified solvent system as mentioned.

1.4 Photochemical set-up

All photochemical reactions, unless otherwise stated, were performed in 10 mL Schlenk tubes under an argon atmosphere. The reactions were carried out in a commercial Hepatochem EvoluChem™ PhotoRedOx Box Duo device and irradiated with two EvoluChem™ blue LEDs (either HCK1012-01-008 LEDs: 30 W, λ_{max} = 450 nm; HCK1012-01-010 LEDs: 18 W, λ_{max} = 405 nm; or HCK1012-01006 LEDs: 30 W, λ_{max} = 365 nm). The reaction temperature in this setup was measured to be between 30–35 °C.

Figure S1. Hepatochem EvoluChem™ PhotoRedOx Box Duo with irradiation by EvoluChem™ HCK1012-01-008 blue LEDs (30 W, λ_{max} = 450 nm).

2. Synthesis of starting materials

2.1 Synthesis of bicyclo[1.1.0]butanes

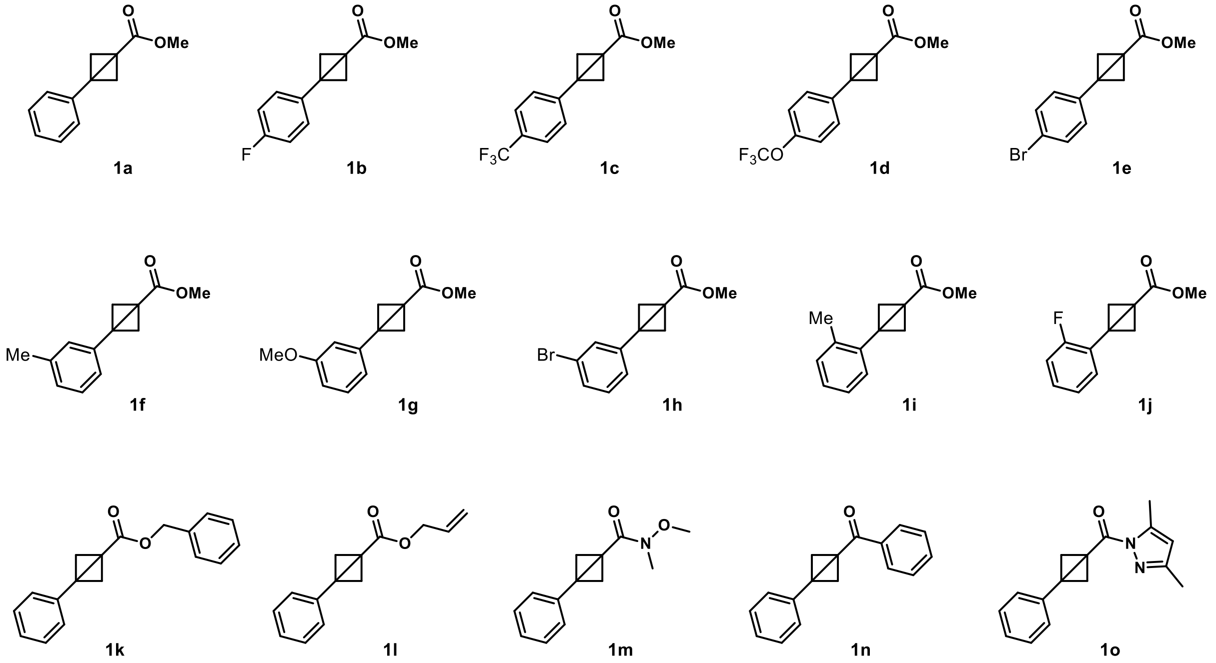

Figure S2. Bicyclo[1.1.0]butanes utilized in this study.

All the bicyclo[1.1.0]butanes are known in the literature and prepared according to the literature known procedures.[1]

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1. (a) Yu, T.; Yang, J.; Wang, Z.; Ding, Z.; Xu, M.; Wen, J.; Xu, L.; Li, P. Selective $[2\sigma + 2\sigma]$ Cycloaddition Enabled by Boronyl Radical Catalysis: Synthesis of Highly Substituted Bicyclo[3.1.1]heptanes. *J. Am. Chem. Soc.* **2023**, *145*, 4304–431. (b) Liang, Y.; Paulus, F.; Daniliuc, C. G.; Glorius, F. Catalytic Formal $[2\pi+2\sigma]$ Cycloaddition of Aldehydes with Bicyclobutanes: Expedient Access to Polysubstituted 2-Oxabicyclo[2.1.1]hexanes. *Angew. Chem., Int. Ed.* **2023**, *62*, e2023050. (c) Livingstone, K.; Siebold, K.; Meyer, S.; Martín-Heras, V.; Daniliuc, C. G. Gilmour, R. Skeletal Ring Contractions via I(I)/I(III) Catalysis: Stereoselective Synthesis of *cis*-α,α-Difluorocyclopropanes. *ACS Catal.* **2022**, *12*, 14507–14516. (d) Liang, Y.; Kleinmans, R.; Daniliuc, C. G.; Glorius, F. Synthesis of Polysubstituted 2-Oxabicyclo[2.1.1]hexanes via Visible-Light-Induced Energy Transfer. *J. Am. Chem. Soc.* **2022**, *144*, 20207–20213.

2.2 Synthesis of amidyl radical precursors

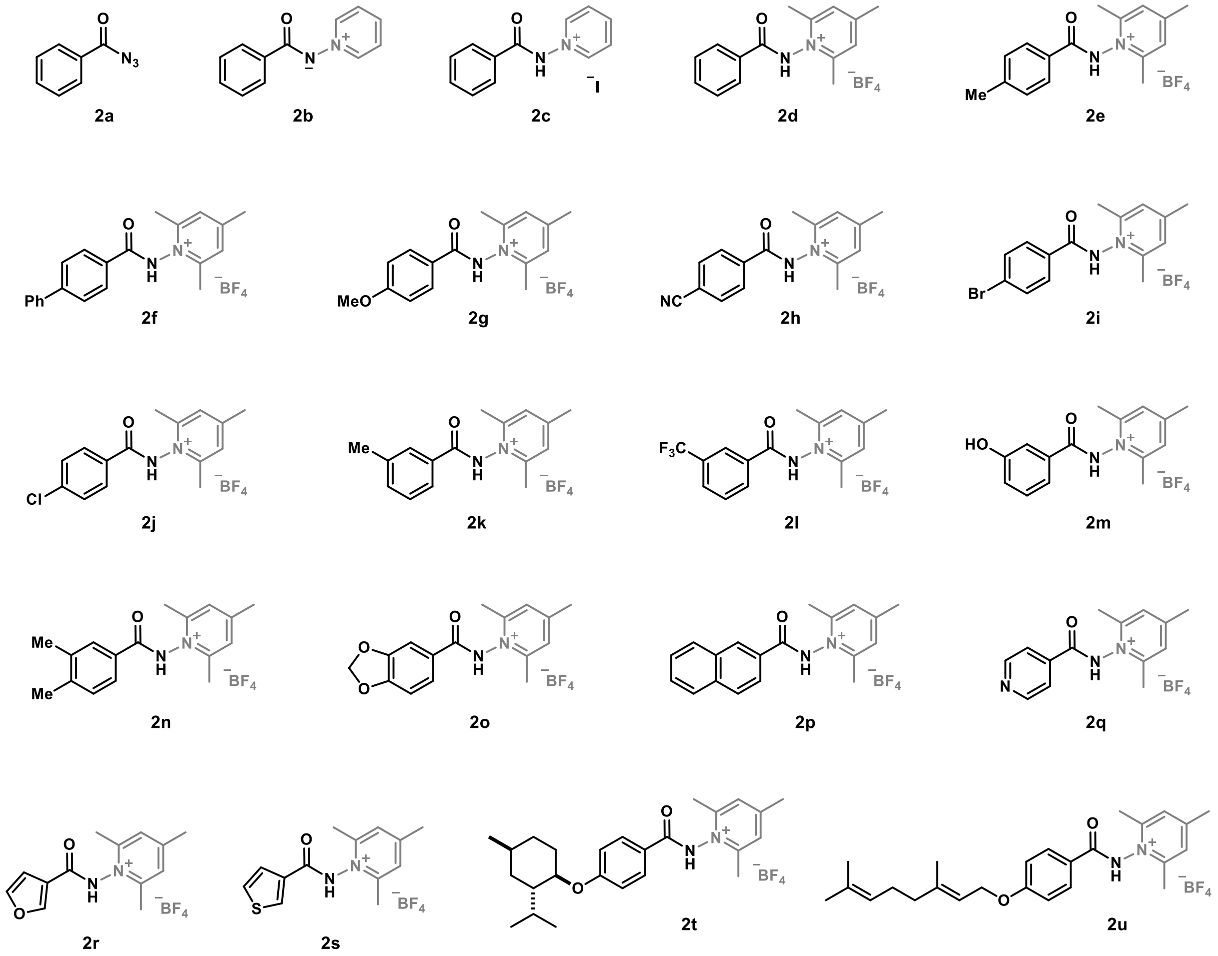

Figure S3. Amidyl radical precursors utilized in this study.

Compounds **2a**–**2e**, **2g**, **2i**, **2j**, **2n**, and **2r** are known in the literature and prepared according to the literature known procedures.[2] Compounds **2f**, **2h**, **2k-2m**, **2o**–**2q**, and **2s**–**2u** are not known

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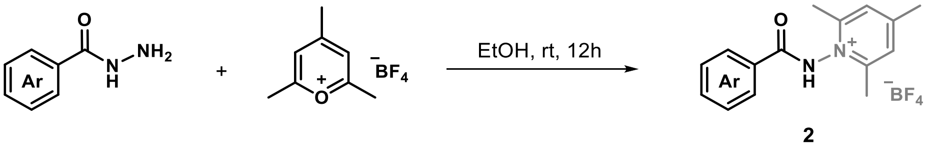
[2] (a) Wang, Y.-Z.; Lin, W.-J.; Liu, H.-C.; Yu, W. Visible-Light-Promoted Radical Amidoarylation of Arylacrylamides towards Amidated Oxindoles. *Org. Chem. Front.* **2022**, *9*, 2164–2168. (b) Wang, Y.-Z.; Liang, P.-Y.; Liu, H.-C.; Lin, W.-J.; Zhou, P.-P.; Yu, W. Visible-Light-Driven [3 + 2]/[4 + 2] Annulation Reactions of Alkenes with *N*-Aminopyridinium Salts. *Org. Lett.* **2022**, *24*, 6037–6042. (c) Chatzopouloua, E.; Davies, P. W. Highly Regioselective Synthesis of 2,4,5-(Hetero)Aryl Substituted Oxazoles By Intermolecular [3+2]-Cycloaddition of Unsymmetrical Internal Alkynes. *Chem. Commun.* **2013**, *49*, 8617–8619. (d) Wijeratne, N. R.; Wenthold, P. G. Structure and Reactivity of Benzoylnitrene Radical Anion in the Gas Phase. *J. Org. Chem.* **2007**, *72*, 9518–9522. (e) Epsztajn, J.; Lunt, E.; Katritzky, A. R. *N*-Oxides and Related Compounds: Some Reactions of 1-Aminopyridinium Salts. *Tetrahedron* **1970**, *26*, 1665–1673.

in the literature but these were also prepared by following the literature known procedure (**GP1**).

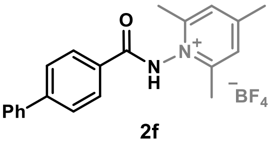
General procedure for the synthesis of *N*-amidocollidinium tetrafluoroborate derivatives (GP1):



An oven-dried Schlenk tube, equipped with a magnetic stir bar, was charged with pyrylium salt (2.0 mmol, 1.0 equiv), acyl hydrazine (2.0 mmol, 1.0 equiv), and ethanol (4 mL, 0.5 M). The resulting reaction mixture was stirred for 12 h at room temperature. After this time, the reaction mixture was cooled 0 °C and pentane (10 mL) was added in order to precipitate the product. The precipitate was collected and washed with Et_2O (10 mL) to afford the desired *N*-amidocollidinium tetrafluoroborate salt **2**.

Characterization data of newly synthesized N-amidocollidinium tetrafluoroborate salts:

1-([1,1'-biphenyl]-4-carboxamido)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate (2f):



2f

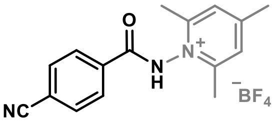
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2f** as a yellow solid (630 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (s, 1H), 8.23 – 8.14 (m, 2H), 7.84 – 7.76 (m, 2H), 7.70 – 7.61 (m, 2H), 7.54 – 7.47 (m, 4H), 7.47 – 7.41 (m, 1H), 2.76 (s, 6H), 2.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.01, 160.01, 157.95, 146.90, 139.23, 128.92, 128.51, 128.41, 127.76, 127.44, 127.15, 126.86, 22.03, 19.46.

HRMS (ESI): *m*/*z* calculated for $C_{21}H_{21}N_2O$ $(M)^+$: 317.16484, found: 317.16459.

1-(4-Cyanobenzamido)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate (2h):



2h

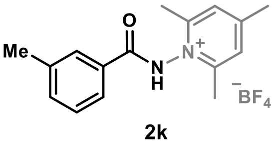
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2h** as an orange solid (444 mg, 63% yield).

^{1}H NMR (400 MHz, CDCl3) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.54 (s, 2H), 2.73 (s, 6H), 2.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.09, 160.73, 157.92, 133.22, 132.44, 128.98, 127.92, 117.85, 117.59, 22.42, 19.75.

HRMS (ESI): *m*/*z* calculated for $C_{16}H_{16}N_3O$ $(M)^+$: 266.12879, found: 266.12880.

2,4,6-Trimethyl-1-(3-methylbenzamido)pyridin-1-ium tetrafluoroborate (2k):



2k

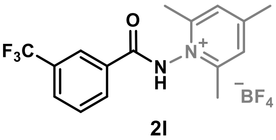
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2k** as a pink solid (517 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (bs, 1H), 7.94 – 7.87 (m, 2H), 7.54 – 7.42 (m, 4H), 2.74 (s, 6H), 2.63 (s, 3H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.75, 160.16, 158.31, 139.65, 135.20, 129.43, 128.75, 128.60, 127.70, 125.29, 22.35, 21.47, 19.79.

HRMS (ESI): *m*/*z* calculated for $C_{16}H_{19}N_2O$ $(M)^+$: 255.14919, found: 255.14897.

2,4,6-Trimethyl-1-(3-(trifluoromethyl)benzamido)pyridin-1-ium tetrafluoroborate (2l):



2l

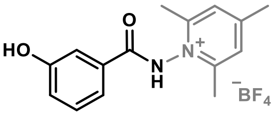
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2l** as a white solid (554 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.29 (m, 2H), 7.95 (d, *J* = 7.1 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.54 (s, 2H), 2.74 (s, 6H), 2.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.00, 160.34, 157.74, 130.49 (q, *J* = 3.8 Hz), 130.44, 130.07, 129.26, 127.57, 125.80 (q, *J* = 3.8 Hz), 22.08, 19.43.

HRMS (ESI): *m*/*z* calculated for $C_{16}H_{16}F_3N_2O$ $(M)^+$: 309.12092, found: 309.12063.

1-(3-Hydroxybenzamido)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate (2m):



2m

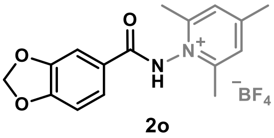
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2m** as an off-white solid (521 mg, 76% yield).

^{1}H NMR (400 MHz, CD_3OD) δ 7.88 (d, *J* = 1.4 Hz, 2H), 7.52 – 7.38 (m, 3H), 7.14 (ddd, *J* = 7.9, 2.5, 1.2 Hz, 1H), 2.70 (s, 6H), 2.67 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 166.75, 162.59, 159.31, 158.10, 132.16, 131.23, 129.16, 121.71, 119.49, 115.57, 21.78, 19.04.

HRMS (ESI): *m*/*z* calculated for $C_{15}H_{17}N_2O_2$ $(M)^+$: 257.12845, found: 257.12817.

1-(Benzo[d][1,3]dioxole-5-carboxamido)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate (2o):



2o

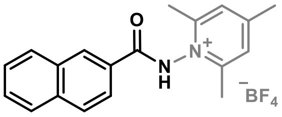
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2o** as a yellow solid (535 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 7.72 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.51 (d, *J* = 9.7 Hz, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.09 (s, 2H), 2.72 (s, 6H), 2.62 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.52, 159.84, 158.02, 152.59, 148.47, 127.36, 123.73, 122.18, 108.67, 108.05, 102.08, 22.02, 19.45.

HRMS (ESI): *m*/*z* calculated for $C_{16}H_{17}N_2O_3$ $(M)^+$: 285.12337, found: 285.12302.

1-(2-Naphthamido)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate (2p):



2p

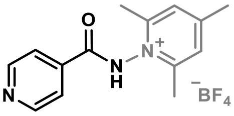
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2p** as a light-brown solid (604 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (s, 1H), 8.77 – 8.71 (m, 1H), 8.14 – 8.05 (m, 2H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.57 (m, 2H), 7.53 (s, 2H), 2.78 (s, 6H), 2.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.70, 160.28, 158.35, 136.09, 132.70, 130.03, 129.50, 129.34, 127.93, 127.77, 127.54, 125.64, 123.40, 22.37, 19.83.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{19}N_2O$ $(M)^+$: 291.14919, found: 291.14893.

1-(Isonicotinamido)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate (2q):



2q

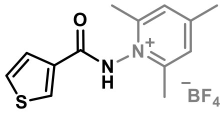
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2q** as a pink solid (448 mg, 68% yield).

^{1}H NMR (400 MHz, CD_3OD) δ 8.95 – 8.89 (m, 2H), 8.61 – 8.55 (m, 2H), 7.62 (s, 2H), 2.56 (s, 6H), 2.55 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 165.85, 155.07, 153.83, 128.02, 126.58, 21.15, 19.17.

HRMS (ESI): *m*/*z* calculated for $C_{14}H_{16}N_3O$ $(M)^+$: 242.12879, found: 242.12871.

2,4,6-Trimethyl-1-(thiophene-3-carboxamido)pyridin-1-ium tetrafluoroborate (2s):



2s

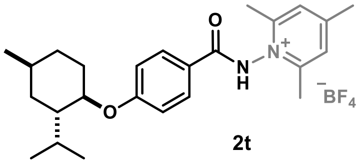
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2s** as a light-brown solid (460 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.74 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.51 (s, 2H), 7.24 (dd, *J* = 5.0, 3.9 Hz, 1H), 2.75 (s, 6H), 2.63 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.72, 159.77, 158.76, 134.63, 132.50, 129.55, 128.02, 22.68, 20.11.

HRMS (ESI): *m*/*z* calculated for $C_{13}H_{15}N_2OS$ $(M)^+$: 247.08996, found: 247.08971.

1-(4-((-2-Isopropyl-4-methylcyclohexyl)oxy)benzamido)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate (2t):



2t

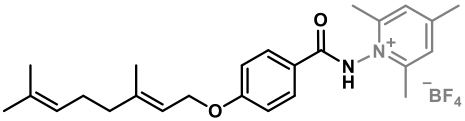
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2t** as an off-white solid (626 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 8.17 – 7.98 (m, 2H), 7.49 (s, 2H), 7.09 – 6.95 (m, 2H), 4.17 (td, *J* = 10.6, 4.1 Hz, 1H), 2.72 (s, 6H), 2.62 (s, 3H), 2.21 – 2.06 (m, 2H), 1.82 – 1.69 (m, 2H), 1.62 – 1.45 (m, 2H), 1.18 – 1.01 (m, 2H), 1.00 – 0.86 (m, 7H), 0.80 – 0.72 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.01, 163.53, 160.17, 158.30, 158.28, 130.54, 127.68, 120.10, 115.83, 78.00, 47.97, 40.04, 34.50, 31.49, 26.39, 23.93, 22.26, 22.18, 20.75, 19.68, 16.79.

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{35}N_2O_2$ $(M)^+$: 395.26930, found: 395.26893.

(*E*)-1-(4-((3,7-Dimethylocta-2,6-dien-1-yl)oxy)benzamido)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate (2u):



2u

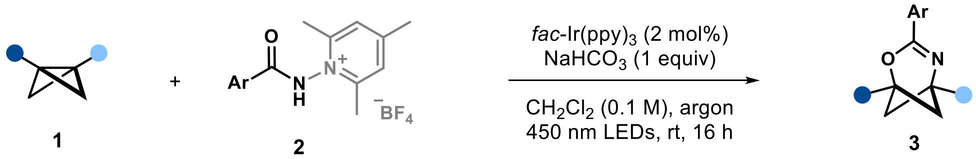
The title compound was prepared by following the general procedure **GP1** using respective acyl hydrazine and pyrilium tetrafluoroborate. Recrystallization of the crude residue with Et_2O (10 mL) afforded the product **2u** as a yellow solid (585 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.19 (s, 1H), 8.05 (d, *J* = 8.9 Hz, 2H), 7.53 (s, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 5.47 (td, *J* = 6.3, 3.3 Hz, 1H), 5.16 – 5.01 (m, 1H), 4.63 (d, *J* = 6.5 Hz, 2H), 2.69 (s, 6H), 2.59 (s, 3H), 2.18 – 2.02 (m, 4H), 1.75 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.01, 163.80, 160.35, 158.11, 142.37, 132.03, 130.35, 127.74, 123.78, 120.56, 118.64, 115.36, 65.42, 39.63, 26.36, 25.78, 22.18, 19.56, 17.82, 16.86.

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{33}N_2O_2$ $(M)^+$: 393.25365, found: 393.25351.

3. General procedure for amidyl radical insertion to BCBs (GP2)

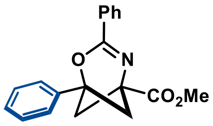


An oven-dried Schlenk tube, equipped with a magnetic stir bar, was charged with BCB **1** (0.2 mmol, 1.0 equiv), *N*-amidocollidinium tetrafluoroborate **2** (0.4 mmol, 2.0 equiv), $NaHCO_3$ (0.2 mmol, 1.0 equiv), and *fac*-Ir(ppy)$_3$ (0.004 mmol, 2 mol%) under air. The tube was evacuated and back-filled with argon three times, and then dry dichloromethane (0.1 M) was added under argon counter-flow. The tube was then sealed with a screw-cap, and the resulting reaction mixture was vigorously stirred under the irradiation at 450 nm for 16 h. After this time, the solvent was removed under reduced pressure and the product was purified by silica gel column chromatography, using pentane/EtOAc as eluent, to afford the desired 2-oxa-4-azabicyclo[3.1.1]hept-3-ene product **3**.

4. Substrate scope

Characterization data of 2-oxa-4-azabicyclo[3.1.1]hept-3-enes (3):

Methyl 3-phenyl-1-(*p*-tolyl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3a):



3a

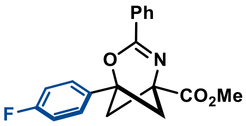
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3a** as a white solid (41.7 mg, 68% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12 – 8.02 (m, 2H), 7.58 – 7.52 (m, 2H), 7.51 – 7.44 (m, 3H), 7.45 – 7.37 (m, 3H), 3.90 (s, 3H), 2.88 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.00 (dd, *J* = 6.8, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 172.30, 158.18, 138.91, 131.59, 131.13, 128.82, 128.73, 128.15, 127.32, 125.28, 83.98, 59.47, 52.67, 38.84.

HRMS (ESI): *m/z* calculated for $C_{19}H_{17}NO_3$ (M + Na)$^+$: 330.11006, found: 330.10979.

Methyl 1-(4-fluorophenyl)-3-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3b):



3b

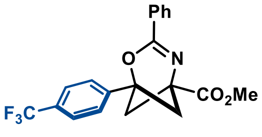
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3b** as an off-white solid (39.6 mg, 61% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 – 7.99 (m, 2H), 7.55 – 7.43 (m, 3H), 7.43 – 7.36 (m, 2H), 7.20 – 7.11 (m, 2H), 3.90 (s, 3H), 2.84 (dd, *J* = 6.8, 2.4 Hz, 2H), 1.99 (dd, *J* = 6.8, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.28, 163.02 (d, *J* = 248.0 Hz), 158.23, 135.01 (d, *J* = 3.2 Hz), 131.57, 131.32, 128.30, 127.41, 127.33, 115.83 (d, *J* = 21.6 Hz), 83.63, 59.49, 52.81, 38.95.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{16}FNO_3$ $(M + Na)^+$: 348.10064, found: 348.10030.

Methyl 3-phenyl-1-(4-(trifluoromethyl)phenyl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3c):



3c

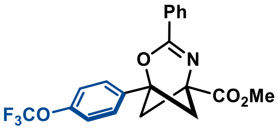
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3c** as an off-white solid (40.5 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.45 – 7.38 (m, 2H), 3.91 (s, 3H), 2.90 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.02 (dd, *J* = 6.8, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, CDCl3) δ 172.13, 157.97, 142.70, 131.48, 131.43, 129.03, 128.38, 127.43, 127.16, 126.70, 125.94 (q, *J* = 3.8 Hz), 125.90, 83.51, 59.51, 52.91, 39.10.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{16}F_3NO_3$ $(M + Na)^+$: 398.09745, found: 398.09669.

Methyl 3-phenyl-1-(4-(trifluoromethoxy)phenyl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3d):



3d

The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column

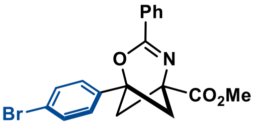
chromatography (eluent: ^{n}Pentane/EtOAc = 85:15) afforded the product **3d** as an off-white solid (40.6 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.62 – 7.54 (m, 2H), 7.52 – 7.45 (m, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 3.90 (s, 3H), 2.87 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.00 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.20, 158.10, 149.58, 137.70, 131.50, 131.40, 128.34, 127.42, 127.11, 120.59 (q, *J* = 257.4 Hz), 121.35, 83.48, 59.49, 52.86, 39.03.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{16}F_3NO_4$ $(M + Na)^+$: 414.09236, found: 414.09284.

Methyl 1-(4-bromophenyl)-3-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3e):



3e

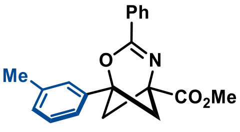
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3e** as a white solid (42.3 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.64 – 7.57 (m, 2H), 7.50 – 7.45 (m, 1H), 7.43 – 7.36 (m, 4H), 3.90 (s, 3H), 2.89 – 2.79 (m, 2H), 2.02 – 1.93 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.20, 158.08, 138.01, 132.04, 131.50, 131.37, 128.32, 127.40, 127.16, 123.06, 83.60, 59.46, 52.83, 38.93.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{16}BrNO_3$ $(M + Na)^+$: 408.02058, found: 408.02058.

Methyl 3-phenyl-1-(m-tolyl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3f):



3f

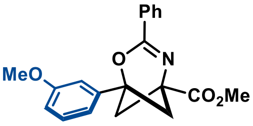
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3f** as a white solid (40.4 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.31 (m, 5H), 7.25 – 7.19 (m, 2H), 3.90 (s, 3H), 2.86 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.43 (s, 3H), 1.99 (dd, *J* = 6.8, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, CDCl3) δ 172.48, 158.38, 138.99, 138.62, 131.77, 131.24, 129.71, 128.78, 128.27, 127.47, 126.09, 122.49, 84.16, 59.62, 52.79, 38.92, 21.68.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{19}NO_3$ $(M + Na)^+$: 344.12571, found: 344.12561.

Methyl 1-(3-methoxyphenyl)-3-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3g):



3g

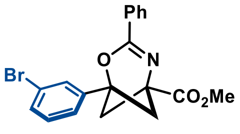
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 85:15) afforded the product **3g** as an off-white solid (41.1 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.50 – 7.44 (m, 1H), 7.44 – 7.36 (m, 3H), 7.15 – 7.09 (m, 1H), 7.09 – 7.05 (m, 1H), 6.95 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.86 (dd, *J* = 6.8, 2.4 Hz, 2H), 1.99 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.40, 160.08, 158.27, 140.60, 131.69, 131.27, 130.00, 128.29, 127.45, 117.67, 114.10, 111.45, 84.00, 59.55, 55.53, 52.80, 39.02.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{19}NO_4$ $(M + Na)^+$: 360.12063, found: 360.12036.

Methyl 1-(3-bromophenyl)-3-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3h):



3h

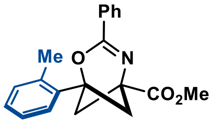
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3h** as a white solid (52.0 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.69 (t, *J* = 1.8 Hz, 1H), 7.56 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 3.90 (s, 3H), 2.86 (dd, *J* = 6.8, 2.4 Hz, 2H), 1.99 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.25, 158.15, 141.30, 132.17, 131.57, 131.50, 130.59, 128.84, 128.44, 127.54, 124.17, 123.15, 83.50, 59.59, 52.96, 39.13.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{16}BrNO_3$ $(M - H)^+$: 384.02298, found: 384.02355.

Methyl 3-phenyl-1-(o-tolyl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3i):



3i

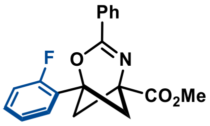
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3i** as a white solid (39.8 mg, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.94 (m, 2H), 7.47 – 7.42 (m, 1H), 7.40 – 7.32 (m, 3H), 7.30 – 7.24 (m, 3H), 3.90 (s, 3H), 2.88 (dd, *J* = 6.7, 2.4 Hz, 2H), 2.47 (s, 3H), 2.21 (dd, *J* = 6.7, 2.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.37, 158.52, 137.77, 136.14, 131.71, 131.53, 131.19, 129.47, 128.25, 127.39, 127.05, 126.16, 85.02, 59.58, 52.75, 38.07, 19.88.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{19}NO_3$ $(M + Na)^+$: 344.12571, found: 344.12440.

Methyl 1-(2-fluorophenyl)-3-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3j):



3j

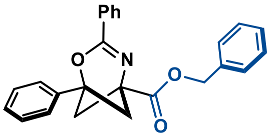
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3j** as a white solid (33.8 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.94 (m, 2H), 7.49 – 7.33 (m, 5H), 7.26 – 7.20 (m, 1H), 7.19 – 7.10 (m, 1H), 3.89 (s, 3H), 2.95 (dd, *J* = 6.9, 2.4 Hz, 1H), 2.15 (dt, *J* = 7.0, 2.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.21, 161.44 (d, *J* = 250.7 Hz), 158.15, 131.65, 131.23, 131.14, 128.25, 128.20, 127.47, 125.72 (d, *J* = 13.0 Hz), 124.45 (d, *J* = 3.6 Hz), 116.43 (d, *J* = 21.2 Hz), 81.79, 60.30, 52.78, 38.26, 38.24.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{16}FNO_3$ $(M + Na)^+$: 348.10064, found: 348.10194.

Benzyl 1,3-diphenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3k):



3k

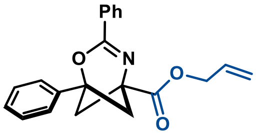
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 85:15) afforded the product **3k** as an off-white solid (36.8 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.00 (m, 2H), 7.58 – 7.29 (m, 13H), 5.34 (s, 2H), 2.91 – 2.82 (m, 2H), 2.13 – 1.93 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.63, 158.18, 139.03, 135.99, 131.75, 131.23, 128.96, 128.85, 128.73, 128.41, 128.39, 128.32, 128.26, 127.45, 125.46, 84.01, 67.10, 59.69, 38.85.

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{21}NO_3$ $(M + Na)^+$: 406.14136, found: 406.13925.

Allyl 1,3-diphenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3l):



3l

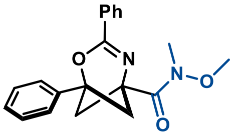
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 85:15) afforded the product **3l** as an off-white solid (39.9 mg, 60% yield).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 2H), 7.59 – 7.52 (m, 2H), 7.52 – 7.36 (m, 6H), 6.03 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.42 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.30 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.80 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.89 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.02 (dd, *J* = 6.8, 2.4 Hz, 2H).

^{13}**C NMR** (100 MHz, $CDCl_3$) δ 171.50, 158.14, 139.03, 132.08, 131.72, 131.20, 128.93, 128.83, 128.23, 127.42, 125.41, 118.74, 83.99, 66.09, 59.61, 38.87.

HRMS (ESI): *m*/*z* calculated for $C_{21}H_{19}NO_3$ $(M + Na)^+$: 356.12571, found: 356.12529.

N-methoxy-*N*-methyl-1,3-diphenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxamide (3m):



3m

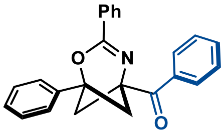
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 70:30) afforded the product **3m** as an off-white solid (40.3 mg, 60% yield).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 2H), 7.57 – 7.50 (m, 2H), 7.47 (t, *J* = 7.2 Hz, 3H), 7.44 – 7.36 (m, 3H), 3.90 (s, 3H), 3.33 (s, 3H), 2.81 – 2.64 (m, 2H), 2.10 – 1.94 (m, 2H).

^{13}**C NMR** (100 MHz, $CDCl_3$) δ 172.90, 156.89, 139.43, 132.13, 130.98, 128.76, 128.68, 128.30, 127.10, 125.38, 83.67, 61.95, 60.86, 38.33, 36.69.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{20}N_2O_3$ $(M + Na)^+$: 359.13661, found: 359.13583.

(1,3-Diphenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3n):



3n

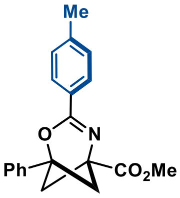
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3n** as an off-white solid (47.3 mg, 67% yield).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.29 – 8.18 (m, 2H), 8.10 – 8.01 (m, 2H), 7.64 – 7.55 (m, 3H), 7.54 – 7.37 (m, 8H), 2.91 (dd, *J* = 6.9, 2.4 Hz, 2H), 2.09 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}**C NMR** (100 MHz, $CDCl_3$) δ 198.29, 157.27, 139.33, 134.90, 133.29, 131.99, 131.22, 130.26, 128.87, 128.46, 128.37, 127.34, 125.45, 83.94, 64.70, 39.00.

HRMS (ESI): *m*/*z* calculated for $C_{24}H_{19}NO_2$ $(M + Na)^+$: 376.13080, found: 376.13045.

Methyl 1-phenyl-3-(p-tolyl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3o):



3o

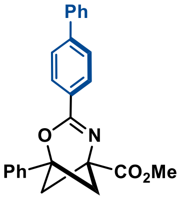
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3o** as a white solid (41.7 mg, 65% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 – 7.89 (m, 2H), 7.55 (dt, *J* = 6.2, 1.4 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.92 – 2.82 (m, 2H), 2.39 (s, 3H), 2.05 – 1.95 (m, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 172.82, 158.71, 141.87, 139.45, 129.30, 129.26, 129.21, 129.15, 127.72, 125.73, 84.27, 59.85, 53.09, 39.35, 21.97.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{19}NO_3$ $(M + Na)^+$: 344.12571, found: 344.12563.

Methyl 3-([1,1'-biphenyl]-4-yl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3p):



3p

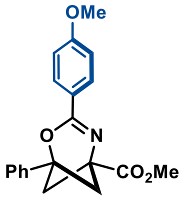
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3p** as a yellow solid (44.4 mg, 58% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 – 8.10 (m, 2H), 7.67 – 7.60 (m, 4H), 7.57 (dt, *J* = 6.3, 1.4 Hz, 2H), 7.53 – 7.41 (m, 5H), 7.40 – 7.34 (m, 1H), 3.92 (s, 3H), 2.90 (dd, *J* = 6.9, 2.4 Hz, 2H), 2.03 (dd, *J* = 6.8, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 172.42, 158.16, 143.96, 140.47, 139.03, 130.57, 128.98, 128.87, 127.93, 127.31, 126.95, 125.43, 84.15, 59.65, 52.80, 38.99.

HRMS (ESI): *m*/*z* calculated for $C_{25}H_{21}NO_3$ $(M + Na)^+$: 406.14136, found: 406.14063.

Methyl 3-(4-methoxyphenyl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3q):



3q

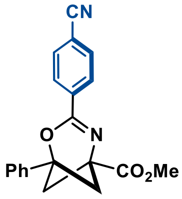
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: *ⁿ*Pentane/EtOAc = 90:10) afforded the product **3q** as an off-white solid (41.8 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.57 – 7.51 (m, 2H), 7.51 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 6.93 – 6.86 (m, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 2.86 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.00 (dd, *J* = 6.8, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.54, 162.13, 158.10, 139.17, 129.14, 128.88, 128.82, 125.40, 124.26, 113.57, 83.91, 59.50, 55.47, 52.76, 39.14.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{19}NO_4$ $(M + Na)^+$: 360.12063, found: 360.11961.

Methyl 3-(4-cyanophenyl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3r):



3r

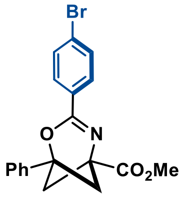
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: *ⁿ*Pentane/EtOAc = 85:15) afforded the product **3r** as a white solid (46.5 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.12 (m, 2H), 7.74 – 7.64 (m, 2H), 7.56 – 7.41 (m, 5H), 3.90 (s, 3H), 2.91 (dd, *J* = 6.9, 2.4 Hz, 2H), 2.00 (dd, *J* = 7.0, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.90, 156.83, 138.39, 135.75, 132.13, 129.26, 128.98, 128.03, 125.42, 118.54, 114.73, 84.88, 59.81, 52.89, 38.62.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{16}N_2O_3$ $(M + Na)^+$: 355.10531, found: 355.10497.

Methyl 3-(4-bromophenyl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3s):



3s

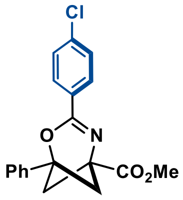
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3s** as a white solid (52.2 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.57 – 7.46 (m, 6H), 7.45 – 7.40 (m, 1H), 3.89 (s, 3H), 2.88 (dd, *J* = 6.9, 2.4 Hz, 2H), 1.99 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.85, 157.24, 138.41, 131.17, 130.30, 128.73, 128.70, 128.56, 125.64, 125.07, 84.05, 59.28, 52.48, 38.45.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{16}BrNO_3$ $(M – H)^+$: 384.02298, found: 384.02342.

Methyl 3-(4-chlorophenyl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3t):



3t

The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column

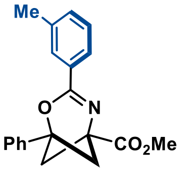
chromatography (eluent: ^{n}Pentane/EtOAc = 85:15) afforded the product **3t** as a white solid (40.9 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.55 – 7.45 (m, 4H), 7.46 – 7.40 (m, 1H), 7.40 – 7.33 (m, 2H), 3.89 (s, 3H), 2.88 (dd, *J* = 6.9, 2.4 Hz, 2H), 1.99 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.20, 157.48, 138.76, 137.46, 130.18, 129.05, 128.88, 128.82, 128.53, 125.40, 84.36, 59.60, 52.80, 38.83.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{16}ClNO_3$ $(M + Na)^+$: 364.07109, found: 364.06850.

Methyl 1-phenyl-3-(m-tolyl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3u):



3u

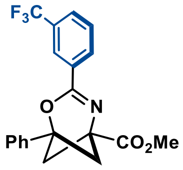
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3u** as a white solid (35.3 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.1 Hz, 1H), 7.84 (ddd, *J* = 5.8, 3.7, 2.0 Hz, 1H), 7.55 (dt, *J* = 6.3, 1.4 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.40 (m, 1H), 7.33 – 7.25 (m, 2H), 3.90 (s, 3H), 2.87 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.39 (s, 3H), 2.00 (dd, *J* = 6.8, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.43, 158.50, 139.05, 138.02, 132.06, 131.58, 128.93, 128.85, 128.18, 128.00, 125.43, 124.53, 84.04, 59.56, 52.79, 38.91, 21.44.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{19}NO_3$ $(M + Na)^+$: 344.12571, found: 344.12382.

Methyl 1-phenyl-3-(3-(trifluoromethyl)phenyl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3v):



3v

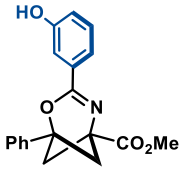
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 85:15) afforded the product **3v** as a white solid (49.5 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.24 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.56 – 7.48 (m, 5H), 7.47 – 7.41 (m, 1H), 3.91 (s, 3H), 2.90 (dd, *J* = 6.9, 2.4 Hz, 2H), 2.01 (dd, *J* = 7.0, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.09, 157.15, 138.58, 132.56, 130.92 (q, *J* = 32.6 Hz), 130.68, 129.17, 128.96, 128.86, 127.81 (q, *J* = 3.8 Hz), 125.45, 124.37 (q, *J* = 3.8 Hz), 124.01 (q, *J* = 272.4 Hz), 84.68, 59.69, 52.85, 38.73.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{16}F_3NO_3$ $(M + Na)^+$: 398.09745, found: 398.09653.

Methyl 3-(3-hydroxyphenyl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3w):



3w

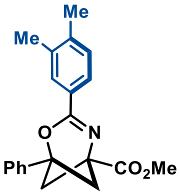
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 75:25) afforded the product **3w** as a white solid (27.1 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.50 – 7.45 (m, 2H), 7.44 – 7.39 (m, 1H), 7.29 – 7.23 (m, 1H), 6.96 (ddd, *J* = 8.1, 2.7, 1.0 Hz, 1H), 3.88 (s, 3H), 2.87 (dd, *J* = 6.9, 2.4 Hz, 2H), 1.99 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 172.37, 158.29, 155.91, 138.89, 133.08, 129.64, 129.01, 128.87, 125.42, 119.75, 118.59, 114.29, 84.23, 59.57, 52.81, 38.89.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{17}NO_4$ (M + Na)$^+$: 346.10498, found: 346.10485.

Methyl 3-(3,4-dimethylphenyl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3x):



3x

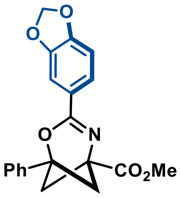
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3x** as a white solid (36.2 mg, 54% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.77 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.52 – 7.44 (m, 2H), 7.45 – 7.38 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 3.90 (s, 3H), 2.91 – 2.81 (m, 2H), 2.30 (s, 6H), 2.04 – 1.93 (m, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 172.46, 158.50, 140.19, 139.11, 136.53, 129.50, 129.17, 128.84, 128.78, 128.43, 125.38, 124.85, 83.85, 59.48, 52.71, 38.95, 19.93, 19.71.

HRMS (ESI): *m*/*z* calculated for $C_{21}H_{21}NO_3$ (M + Na)$^+$: 358.14136, found: 358.14072.

Methyl 3-(benzo[d][1,3]dioxol-5-yl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3y):



3y

The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column

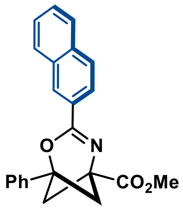
chromatography (eluent: ^{n}Pentane/EtOAc = 85:15) afforded the product **3y** as a white solid (37.9 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.54 – 7.50 (m, 3H), 7.50 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.00 (s, 2H), 3.89 (s, 3H), 2.86 (dd, *J* = 6.8, 2.4 Hz, 2H), 1.98 (dd, *J* = 6.8, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.45, 157.81, 150.27, 147.76, 139.03, 128.94, 128.85, 125.87, 125.40, 122.30, 107.97, 107.83, 101.63, 84.10, 59.52, 52.78, 39.06.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{17}NO_5$ $(M + Na)^+$: 374.09989, found: 374.09875.

Methyl 3-(naphthalen-2-yl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3z):



3z

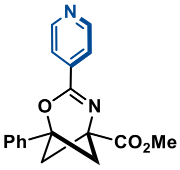
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3z** as a white solid (48.5 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.8 Hz, 1H), 8.17 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.92 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.86 (dd, *J* = 8.2, 3.1 Hz, 2H), 7.60 (dt, *J* = 6.2, 1.4 Hz, 2H), 7.56 – 7.42 (m, 5H), 3.93 (s, 3H), 2.92 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.07 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.43, 158.46, 139.04, 134.86, 132.81, 129.10, 129.03, 129.01, 128.91, 128.01, 127.86, 127.68, 127.44, 126.51, 125.53, 124.30, 84.26, 59.74, 52.85, 38.98.

HRMS (ESI): *m*/*z* calculated for $C_{23}H_{19}NO_3$ $(M + Na)^+$: 380.12571, found: 380.12574.

Methyl 1-phenyl-3-(pyridin-4-yl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3aa):



3aa

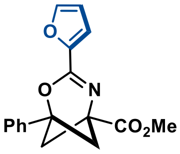
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 80:20) afforded the product **3aa** as a white solid (34.5 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 – 8.62 (m, 2H), 7.97 – 7.81 (m, 2H), 7.57 – 7.38 (m, 5H), 3.90 (s, 3H), 2.91 (dd, *J* = 7.0, 2.4 Hz, 2H), 1.99 (dd, *J* = 7.0, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.87, 156.75, 150.30, 139.05, 138.37, 129.24, 128.97, 125.41, 121.25, 84.84, 59.80, 52.89, 38.54.

HRMS (ESI): *m*/*z* calculated for $C_{18}H_{16}N_2O_3$ $(M + H)^+$: 309.12337, found: 309.12407.

Methyl 3-(furan-2-yl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3ab):



3ab

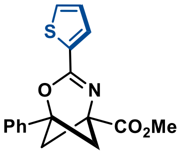
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3ab** as a white solid (30.3 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 1H), 7.52 – 7.44 (m, 4H), 7.44 – 7.39 (m, 1H), 6.97 (d, *J* = 3.4 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.89 (s, 3H), 2.89 (dd, *J* = 6.9, 2.4 Hz, 2H), 2.05 (dd, *J* = 7.0, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.09, 151.94, 145.77, 145.11, 138.54, 129.11, 128.89, 125.46, 113.26, 111.50, 84.82, 59.58, 52.89, 39.07.

HRMS (ESI): *m*/*z* calculated for $C_{17}H_{15}NO_4$ $(M + Na)^+$: 320.08933, found: 320.08855.

Methyl 1-phenyl-3-(thiophen-2-yl)-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3ac):



3ac

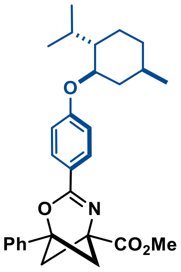
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3ac** as a white solid (44.4 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.55 – 7.39 (m, 6H), 7.05 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.88 (s, 3H), 2.89 (dd, *J* = 6.9, 2.4 Hz, 2H), 2.05 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.12, 155.19, 138.73, 135.35, 129.36, 129.26, 129.00, 128.84, 127.48, 125.39, 84.67, 59.64, 52.81, 39.31.

HRMS (ESI): *m*/*z* calculated for $C_{17}H_{15}NO_3S$ $(M + Na)^+$: 336.06649, found: 336.06459.

Methyl 3-(4-((-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3ad):



3ad

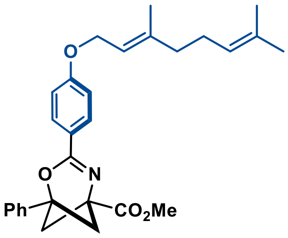
The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3ad** as an off-white solid (51.6 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.58 – 7.50 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.37 (m, 1H), 6.92 – 6.84 (m, 2H), 4.14 – 4.06 (m, 1H), 3.89 (s, 3H), 2.92 – 2.79 (m, 2H), 2.23 – 2.08 (m, 2H), 2.02 – 1.93 (m, 2H), 1.77 – 1.66 (m, 2H), 1.57 – 1.40 (m, 2H), 1.14 – 0.97 (m, 3H), 0.92 (dd, *J* = 6.8, 1.8 Hz, 6H), 0.74 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.56, 161.13, 158.12, 139.21, 129.18, 128.82, 128.78, 125.35, 123.81, 115.10, 83.80, 77.71, 59.48, 52.71, 48.16, 40.33, 39.20, 34.56, 31.51, 26.23, 23.84, 22.23, 20.80, 16.67.

HRMS (ESI): *m*/*z* calculated for $C_{29}H_{35}NO_4$ $(M + Na)^+$: 484.24583, found: 484.24559.

Methyl (*E*)-3-(4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)phenyl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (3ae):



3ae

The title compound was prepared by following the general procedure **GP2** using respective BCB **1** and *N*-amidocollidinium tetrafluoroborate **2**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 90:10) afforded the product **3ae** as an off-white solid (48.6 mg, 53% yield).

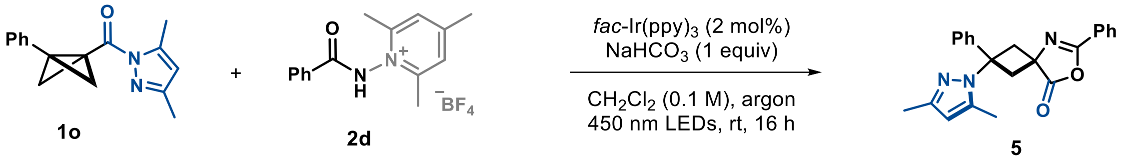
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.57 – 7.51 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.38 (m, 1H), 6.94 – 6.87 (m, 2H), 5.48 (tq, *J* = 6.6, 1.3 Hz, 1H), 5.09 (ddt, *J* = 6.7, 5.3, 1.6 Hz, 1H), 4.58 (d, *J* = 6.0 Hz, 2H), 3.89 (s, 3H), 2.86 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.15 – 2.04 (m, 4H), 1.99 (dd, *J* = 6.8, 2.4 Hz, 2H), 1.74 (s, 3H), 1.68 (s, 3H), 1.60 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.58, 161.49, 158.18, 141.67, 139.20, 132.00, 129.10, 128.88, 128.83, 125.41, 124.10, 123.90, 119.25, 114.35, 83.91, 65.12, 59.52, 52.78, 39.68, 39.18, 26.44, 25.82, 17.85, 16.86.

HRMS (ESI): *m*/*z* calculated for $C_{29}H_{33}NO_4$ $(M + Na)^+$: 482.23018, found: 482.23062.

4.1 Unusual observation

2-(3,5-dimethyl-1H-pyrazol-1-yl)-2,6-diphenyl-7-oxa-5-azaspiro[3.4]oct-5-en-8-one (5):



The title compound was prepared by following the general procedure **GP2** using BCB **1o** and *N*-amidocollidinium tetrafluoroborate **2d**. Purification by silica gel column chromatography (eluent: ^{n}Pentane/EtOAc = 75:25) afforded the product **5** as a white solid (34.9 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.00 (m, 2H), 7.62 – 7.55 (m, 1H), 7.54 – 7.46 (m, 2H), 7.39 – 7.33 (m, 2H), 7.31 – 7.25 (m, 3H), 5.93 (s, 1H), 4.11 – 3.85 (m, 2H), 3.32 – 3.18 (m, 2H), 2.31 (s, 3H), 1.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.71, 160.98, 146.90, 144.62, 139.26, 133.04, 128.94, 128.68, 128.22, 127.59, 125.89, 125.59, 107.64, 62.86, 60.32, 44.95, 13.84, 12.21.

HRMS (ESI): *m*/*z* calculated for $C_{23}H_{21}N_3O_2$ $(M + Na)^+$: 394.15260, found: 394.15261.

4.2 Limitations

Following products could not be obtained when the respective substrates were treated under the standard reaction conditions.

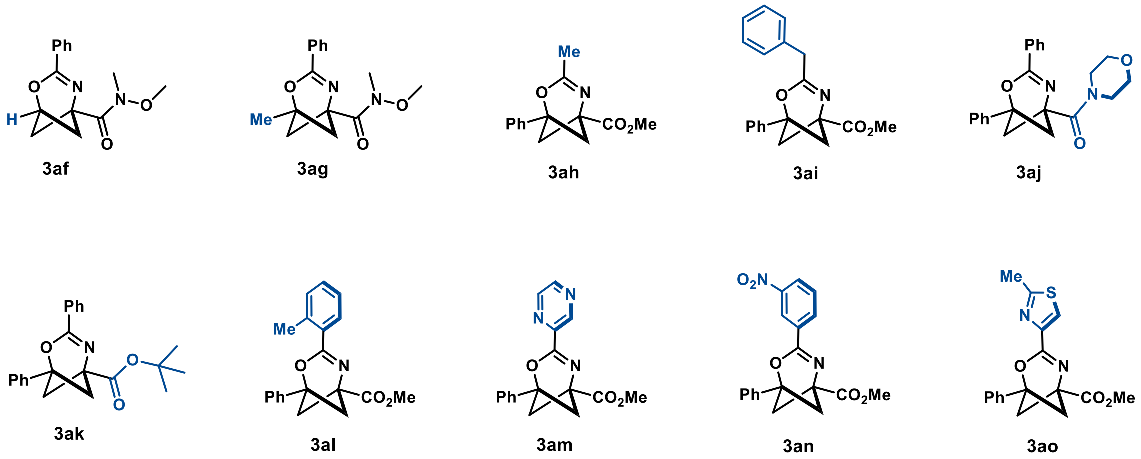


Figure S4. Unsuccessful attempts

5. Sensitivity assessment

A reaction conditions-based sensitivity assessment was conducted in a similar manner as reported by Glorius and co-workers.[3] General procedure (**GP2**) was followed by using BCB **1a** and *N*-amidocollidinium tetrafluoroborate **2d** as starting materials. Following deviations in the standard reaction conditions, mentioned in **Table S1**, were considered to carry out this experiment. The deviations in the yield of product **3a** was determined by ^{1}H NMR of the crude reaction mixture using CH_2Br_2 as an internal standard.

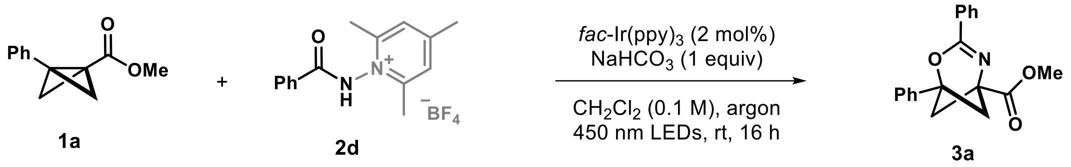


Table S1. Reaction conditions-based sensitivity assessment: Reaction conditions and results.

Entry	**Parameter**	**Deviation from standard conditions**	**% Yield**[a]	**% Deviation in yield**
1	High *c*	−10% DCM	66%	−2%
2	Low *c*	+10% DCM	68%	0%
3	H_2O	+20 µL H_2O	33%	−35%
4	High O_2	+20 mL air	29%	−39%
5	Low O_2	Freeze-pump-thaw (3x)	67%	−1%
6	High *T*	Reaction stirred w/o fan	68%	0%
7	Low *T*	Jacketed Schlenk tube with still water	66%	−2%
8	High *I*	2 cm away from light source	71%	+3%
9	Low *I*	32 cm away from light source	63%	−5%

[a] Determined by ^{1}H NMR of the crude reaction mixture by using CH_2Br_2 as an internal standard.

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[3] Pitzer, L.; Schäfers, F.; Glorius, F. Rapid Assessment of the Reaction-Condition-Based Sensitivity of Chemical Transformations. *Angew. Chem., Int. Ed.* **2019**, *58*, 8572–8576.

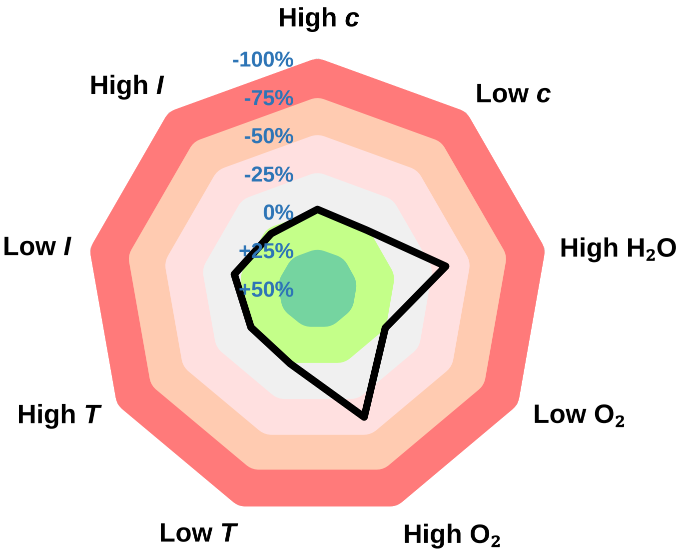


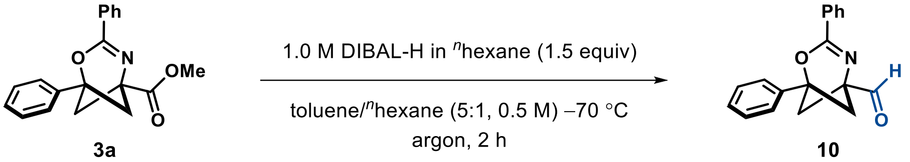
Figure S5. Sensitivity assessment radar diagram

6. Gram-scale reaction

An oven-dried 100 mL Schlenk tube, equipped with a magnetic stir bar, was charged with BCB **1a** (188 mg, 1.0 mmol, 1.0 equiv), *N*-amidocollidinium tetrafluoroborate **2d** (656 mg, 2.0 mmol, 2.0 equiv), $NaHCO_3$ (84 mg, 1.0 mmol, 1.0 equiv), and *fac*-Ir(ppy)$_3$ (13 mg, 0.02 mmol, 2 mol%) under air. The tube was evacuated and back-filled with argon three times, and then dry dichloromethane (10 mL, 0.1 M) was added under argon counter-flow. The tube was then sealed with a screw-cap, and placed in-between two 30 W 450 nm LEDs (each at a distance of 5 cm), and irradiated for 16 h, cooling the reaction vessel with a fan. After this time, the solvent was removed under reduced pressure and the product was purified by silica gel column chromatography (eluent: pentane/EtOAc = 90:10) to afford the desired 2-oxa-4-azabicyclo[3.1.1]hept-3-ene product **3a** as a colourless solid (129 mg, 42% yield).

7. Product diversification

Procedure for the synthesis of 1,3-Diphenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carbaldehyde (10):



The title compound was prepared by following the modified literature procedure.[4] A solution of 1.0 M DIBAL-H in ^{n}hexane (150 µL, 0.15 mmol, 1.5 equiv) was added dropwise to a stirred and cooled solution of **3a** (30.7 mg, 0.1 mmol, 1.0 equiv) in toluene/^{n}hexane (170 µL:30 µL, 0.5 M) at –70 °C under argon and reaction was stirred at the same for 2 h. Subsequently, MeOH (20 µL) was added and the reaction mixture was stirred at the same temperature for 30 minutes. The mixture was then quenched by the addition of EtOAc (100 µL) and sat. aq. Na.K tartarate solution (0.5 mL). The cooling bath was then removed and the mixture was allowed to warm to room temperature. The organic layer was extracted with EtOAc (3 × 2 mL) and the combined organic extracts were concentrated *in vacuo*. The resultant residue was purified by silica gel column chromatography (eluent: pentane/EtOAc = 80:20) to afford **10** as a colourless solid (23.2 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.12 – 8.04 (m, 2H), 7.58 – 7.40 (m, 8H), 2.76 (dd, *J* = 6.6, 2.3 Hz, 2H), 1.88 (dd, *J* = 6.7, 2.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.64, 158.69, 138.93, 131.68, 131.40, 129.02, 128.88, 128.45, 127.25, 125.39, 83.73, 63.80, 37.85.

HRMS (ESI): *m*/*z* calculated for $C_{18}H_{15}NO_2$ $(M + Na)^+$: 300.09950, found: 300.09953.

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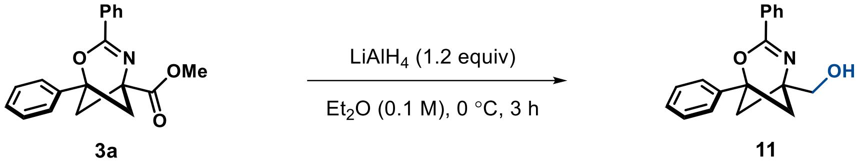
[4] Mori, K.; Funaki, Y. Synthesis of (4E, 8E, 2S, 3R, 2′R)-N-2′-Hydroxyhexadecanoyl-1-O-β-D-glucopyranosyl-9-methyl-4,8-sphingadienine, the Fruiting-Inducing Cerebroside in a Basidiomycete Schizophyllum Commune. *Tetrahedron* **1985**, *41*, 2379–2386.

Procedure for synthesis of (1,3-Diphenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-en-5-yl)metanol (11):



The title compound was prepared by following the modified literature procedure.[5] To a solution of **3a** (30.7 mg, 0.1 mmol, 1.0 equiv) in Et_2O (1 mL, 0.1 M) was added $LiAlH_4$ (45.5 mg, 0.12 mmol, 1.2 equiv) in small portions at 0 °C. The mixture was stirred for 3 h at 0 °C. After this time, the reaction was quenched with water (100 µL) and the organic layer was extracted with EtOAc (3 × 2 mL). The combined organic extracts were concentrated *in vacuo*. The resultant residue was purified by silica gel column chromatography (eluent: pentane/EtOAc = 70:30) to afford **11** as a colourless solid (22.0 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 2H), 7.57 – 7.50 (m, 2H), 7.50 – 7.44 (m, 3H), 7.44 – 7.36 (m, 3H), 3.90 (s, 2H), 2.66 (bs, 1H), 2.35 (dd, *J* = 6.9, 2.5 Hz, 2H), 1.82 (dd, *J* = 6.9, 2.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.33, 139.72, 132.03, 131.05, 128.75, 128.67, 128.32, 127.18, 125.51, 84.25, 67.63, 59.48, 37.03.

HRMS (ESI): *m*/*z* calculated for $C_{18}H_{17}NO_2$ $(M + Na)^+$: 302.11515, found: 302.11511.

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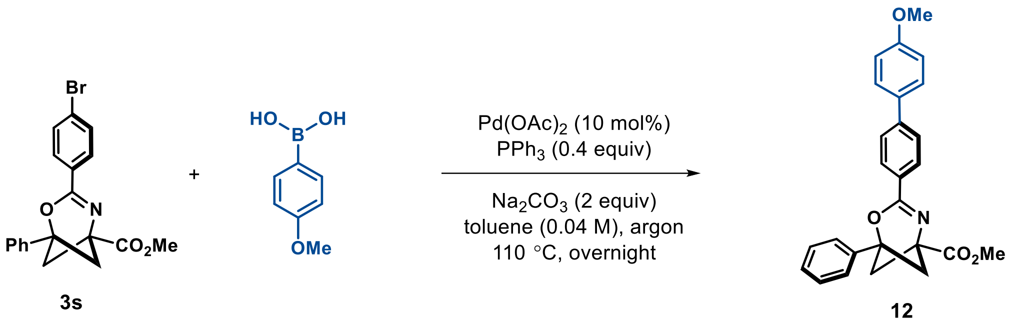
[5] Aït-Haddou, H.; Hoarau, O.; Cramailére, D.; Pezet, F.; Daran, J.-C.; Balavoine, G. G. A. New Dihydroxy Bis(Oxazoline) Ligands for the Palladium-Catalyzed Asymmetric Allylic Alkylation: Experimental Investigations of the Origin of the Reversal of the Enantioselectivity. *Chem. Eur. J.* **2004**, *10*, 699–707.

Procedure for Synthesis of Methyl 3-(4'-methoxy-[1,1'-biphenyl]-4-yl)-1-phenyl-2-oxa-4-azabicyclo[3.1.1]hept-3-ene-5-carboxylate (12):



The title compound was prepared by following the modified literature procedure.[6] An oven-dried Schlenk tube, equipped with a magnetic stir bar, was charged with **3s** (38.6 mg, 0.1 mmol, 1 equiv), (4-methoxyphenyl)boronic acid (22.8 mg, 0.15 mmol, 1.5 equiv), PPh_3 (10.5 mg, 0.04 mmol, 0.4 equiv), and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 10 mol%) under air. The tube was evacuated and back-filled with argon three times, and then degassed anhydrous toluene (2.5 mL, 0.04 M) and Na_2CO_3 (21.2 mg, 0.2 mmol, 2 equiv, as 1.0 M aq. solution) was added, and the tube was sealed with a screw-cap. The resulting mixture was refluxed overnight at 110 °C before addition of water (1 mL). The organic layer was extracted with Et_2O (3 × 5 mL) and the combined organic extracts were concentrated *in vacuo*. The resultant residue was purified by silica gel column chromatography (eluent: pentane/EtOAc = 80:20) to afford **12** as a yellow solid (25.2 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 2H), 7.63 – 7.54 (m, 6H), 7.53 – 7.46 (m, 2H), 7.46 – 7.40 (m, 1H), 7.03 – 6.96 (m, 2H), 3.91 (s, 3H), 3.85 (s, 3H), 2.90 (dd, *J* = 6.8, 2.4 Hz, 2H), 2.02 (dd, *J* = 6.9, 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.44, 159.72, 158.21, 143.54, 139.06, 132.92, 129.92, 128.94, 128.85, 128.35, 127.91, 126.40, 125.42, 114.43, 84.08, 59.63, 55.49, 52.79, 39.01.

HRMS (ESI): *m*/*z* calculated for $C_{26}H_{23}NO_4$ $(M + Na)^+$: 436.15193, found: 436.15178.

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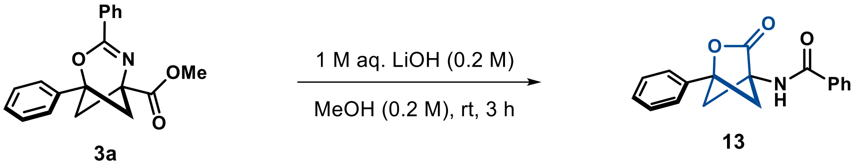
[6] Gilbert, A.; Bertrand, X.; Paquin, J.-F. Silver-Promoted Synthesis of 5-[(Pentafluorosulfanyl)methyl]-2-oxazolines. *Org. Lett.* **2018**, *20*, 7257–7260.

Procedure for the synthesis of *N*-(-3-oxo-1-phenyl-2-oxabicyclo[2.1.1]hexan-4-yl)benzamide (13):



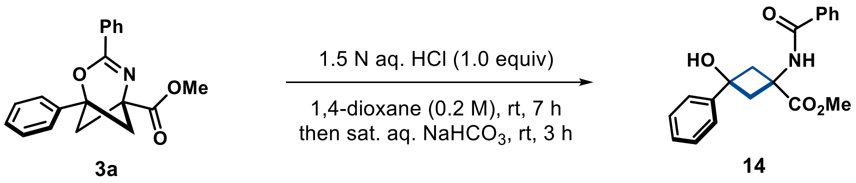
An oven-dried Schlenk tube, equipped with a magnetic stir bar, was charged with **3a** (30.7 mg, 0.1 mmol, 1 equiv) and methanol (0.5 mL, 0.2 M). To this solution, 1.0 M aqueous solution of LiOH (0.5 mL, 0.2 M) was added at room temperature and the reaction mixture was allowed to stir at the same temperature for 3 h. The reaction mixture was cooled to 0 °C, and acidified to pH = 2 by using conc. aqueous HCl solution. After removing MeOH *in vacuo*, the resulting aqueous layer was extracted with EtOAc (3 × 2 mL). The solvent was removed *in vacuo* and the resultant residue was purified by silica gel column chromatography (eluent: pentane/EtOAc = 80:20) to afford **13** as a colourless solid (15.8 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.60 – 7.53 (m, 1H), 7.53 – 7.38 (m, 7H), 7.10 (s, 1H), 3.80 (dd, *J* = 5.0, 2.1 Hz, 2H), 2.93 (dd, *J* = 5.0, 2.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.85, 167.87, 133.39, 133.16, 132.50, 129.58, 128.95, 128.92, 127.23, 126.30, 86.58, 59.72, 55.19.

HRMS (ESI): *m*/*z* calculated for $C_{18}H_{15}NO_3$ $(M + Na)^+$: 316.09441, found: 316.09441.

Procedure for synthesis of Methyl-1-benzamido-3-hydroxy-3-phenylcyclobutane-1-carboxylate (14):



The title compound was prepared by following the modified literature procedure.[7] To a solution of **3a** (30.7 mg, 0.1 mmol, 1 equiv) in 1,4-dioxane (0.5 mL, 0.2 M) was added 1.5 N aq. HCl

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7. Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. Asymmetric Synthesis of β-Hydroxy-α-alkylamino Acids by Asymmetric Aldol Reaction of α-Isocyanocarboxylates Catalyzed by Chiral Ferrocenylphosphine-Gold(I) Complexes. *Tetrahedron* **1988**, *44*, 5253–5262.

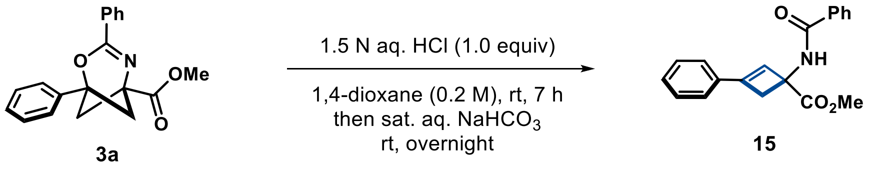
solution (80 µL, 0.1 mmol, 1 equiv) and the reaction mixture was stirred at room temperature for 7 h. After this time, sat. aq. $NaHCO_3$ solution (100 µL) was added and the mixture was stirred for 3 h. The organic layer was extracted with EtOAc (3 × 2 mL) and the combined organic extracts were concentrated *in vacuo*. The resultant residue was purified by silica gel column chromatography (eluent: pentane/EtOAc = 60:40) to afford **14** as a colourless solid (15.6 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 2H), 7.72 – 7.62 (m, 3H), 7.59 – 7.53 (m, 1H), 7.52 – 7.45 (m, 2H), 7.43 – 7.36 (m, 2H), 7.33 – 7.27 (m, 1H), 6.20 (s, 1H), 3.84 (s, 3H), 3.52 – 3.41 (m, 2H), 3.23 – 3.12 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.94, 167.27, 145.27, 134.19, 132.25, 128.92, 128.38, 127.31, 127.20, 125.39, 71.14, 53.49, 52.92, 48.17.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{19}NO_4$ $(M + Na)^+$: 348.12063, found: 348.12024.

Procedure for synthesis of Methyl-1-benzamido-3-phenylcyclobut-2-ene-1-carboxylate (15):



To a solution of **3a** (30.7 mg, 0.1 mmol, 1 equiv) in 1,4-dioxane (0.5 mL, 0.2 M) was added 1.5 N aq. HCl solution (80 µL, 0.1 mmol, 1 equiv) and the reaction mixture was stirred at room temperature for 7 h. After this time, sat. aq. $NaHCO_3$ solution (100 µL) was added and the mixture was stirred for overnight. The organic layer was extracted with EtOAc (3 × 2 mL) and the combined organic extracts were concentrated *in vacuo*. The resultant residue was purified by silica gel column chromatography (eluent: pentane/EtOAc = 70:30) to afford **15** as a colourless solid (15.9 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.55 – 7.49 (m, 1H), 7.47 – 7.41 (m, 4H), 7.41 – 7.32 (m, 3H), 7.00 (s, 1H), 6.50 (s, 1H), 3.78 (s, 3H), 3.69 (d, *J* = 13.0 Hz, 1H), 3.04 (d, *J* = 13.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.53, 167.57, 150.55, 133.76, 133.05, 132.00, 129.48, 128.75, 128.67, 127.29, 125.62, 124.79, 59.45, 52.95, 40.64.

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{17}NO_3$ $(M + Na)^+$: 330.11006, found: 330.11006.

8. Mechanistic studies

8.1 UV-Vis absorption spectroscopy

UV/Vis absorption spectra were recorded on a JASCO V-730 spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in Starna® fluorescence quartz cuvettes (type: 29-F, chamber volume = 1.400 mL, H × W × D = 48 mm × 12.5 mm × 12.5 mm, path length = 10 mm). The following parameters were set prior to the measurements: response time = 0.05 sec, data interval = 0.5 nm, scan speed = 1000 nm/min.

UV-Vis absorption spectroscopy studies suggest that only *fac*-Ir(ppy)$_3$ photocatalyst shows efficient absorption at 450 nm.

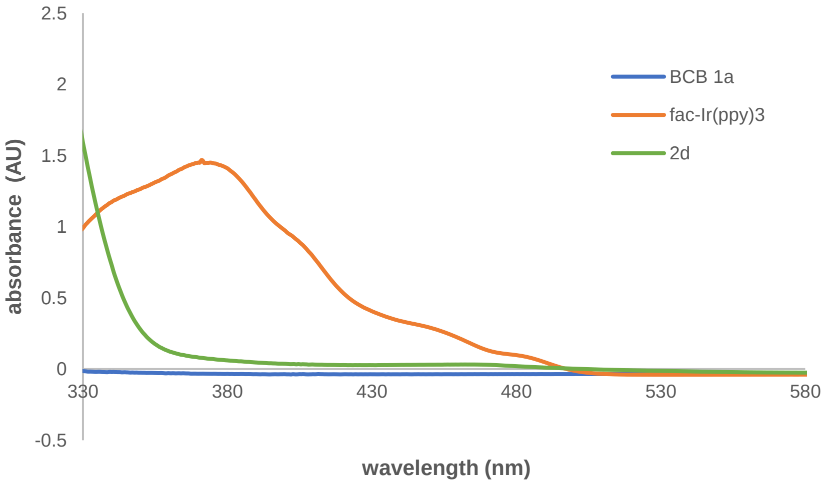


Figure S6. UV-Vis absorption spectra of BCB **1a** (10 mM), *fac*-Ir(ppy)$_3$ (0.1 mM), and *N*-amidocollidinium tetrafluoroborate **2d** (10 mM) in MeCN.

8.2 Stern-Volmer luminescence quenching studies

Stern-Volmer luminescence quenching studies were performed using a JASCO FP-8300 spectrofluorometer using Starna® fluorescence quartz cuvettes (type: 29-F, chamber volume = 1.400 mL, H × W × D = 48 mm × 12.5 mm × 12.5 mm, path length = 10 mm). The following parameters were set: data interval = 0.5 nm, scan-speed = 500 nm/min, excitation wavelength λ_{ex} = 350 nm, luminescence measurement window λ = 430–630 nm (λ_{max} = 512 nm). All samples used in the luminescence quenching experiments were prepared in an argon-filled glovebox with degassed and dry DCM. Stock solutions of potential quenchers (1 mM each) and the photocatalyst *fac*-Ir(ppy)$_3$ (0.1 mM) were initially prepared. Stern-Volmer luminescence quenching studies were performed using a stock solution of the photocatalyst and variable concentrations of the potential quenchers at rt under an argon atmosphere. The samples were prepared by dilution in the 1.4 mL quartz cuvettes inside the argon-filled glovebox. The solutions were irradiated at 350 nm and the luminescence was measured in the range of λ = 430–630 nm (λ_{max} = 512 nm). The ratio of I_0/I was plotted as a function of the quencher concentration (I_0 = emission intensity of the photocatalyst at the specified wavelength; I = observed emission intensity of the photocatalyst with added quencher).

Stern-Volmer luminescence quenching studies show that only *N*-amidocollidinium tetrafluoroborate **2d** quenches the fluorescence of the excited photocatalyst.

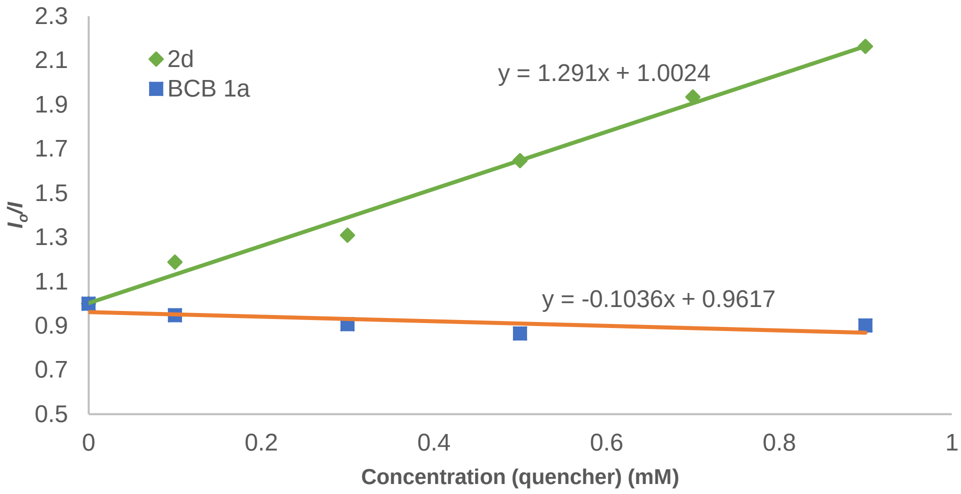


Figure S7. Stern-Volmer luminescence quenching plot.

8.3 Quantum yield determination

Measurement of the photon flux:

A 3 W blue LED (λ_{max} = 416 nm) was used for the quantum yield measurement. The photon flux of the utilized blue LED was determined by following a literature procedure.[8]

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[8] Cismesia, M. A.; Yoon, T. P. Characterizing Chain Processes in Visible Light Photoredox Catalysis. *Chem. Sci.* **2015**, *6*, 5426–5434.

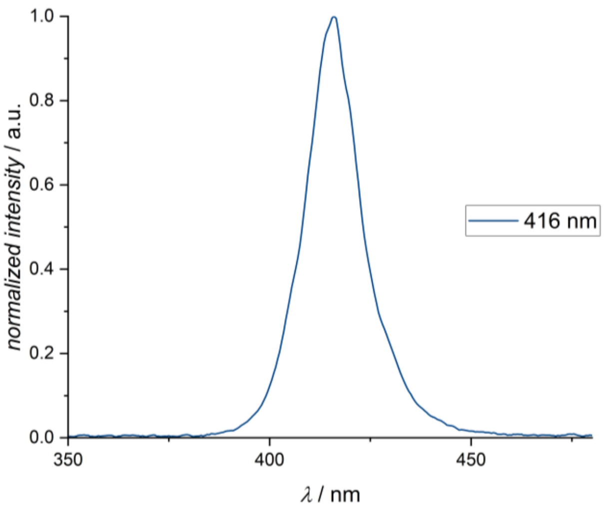

Figure S8. Emission spectrum of the used 3 W blue LED (λ_{max} = 416 nm).

A solution (10 mL, 0.15 M) of potassium ferrioxalate hydrate (737 mg, 1.50 mmol) in aq. H_2SO_4 (50 mM) and a solution (20 mL, 5.0 mM) of 1,10-phenanthroline monohydrate (20 mg, 0.10 mmol) and sodium acetate (4.50 g) in aq. H_2SO_4 (500 mM) were prepared and kept in the dark. All following steps were conducted in the dark as well.

Six Schlenk tubes were charged with the prepared potassium ferrioxalate solution (1.0 mL) and three of these tubes were successively irradiated with the described blue LED for 60 s at a distance of 5 cm, while three tubes were left in the dark. Then, to all six Schlenk tubes was added the prepared phenanthroline solution (175 µL each) and the reaction mixtures were stirred for 60 mins. For all six solutions, the absorbance at 510 nm was measured and the difference between the average absorbance of the three irradiated samples and the average absorbance of the three control samples was determined ($\Delta A_{510\text{ nm}}$ = 2.225).

The formed amount of Fe(II) was calculated based on the Lambert–Beer law (equation 1) with V = 1.175 mL, l = 1.0 cm, and ε = 11100 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.[9]

$$n_{Fe(II)} = \frac{V \cdot \Delta A_{510\text{ nm}}}{l \cdot \varepsilon} \qquad (1)$$

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[9] (a) Hatchard, C. G.; Parker C. A. A New Sensitive Chemical Actinometer - II. Potassium Ferrioxalate as a Standard Chemical Actinometer. *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.* **1956**, *235*, 518–536. (b) Chen, J.; Dvornikov, A. S.; Rentzepis, P. M. Comment on "New insight into photochemistry of ferrioxalate". *J. Phys. Chem. A* **2009**, *113*, 8818–8819.

The fraction of light which was absorbed by the actinometer at λ = 416 nm (f) was determined with equation 2 with the absorbance of the ferrioxalate stock solution at λ = 416 nm being $A_{416\text{ nm}}$ >3 (f >0.999).

$$f = 1 - 10^{-A_{416\text{ nm}}} \tag{2}$$

The photon flux ϕ_q was finally determined using equation 3 with ϕ_F = 1.12 (at λ = 416 nm) and t = 60 s, giving $\phi_\text{q} = 3.505 \cdot 10^{-9}$ mol·s^{-1}.[10]

$$\phi_\text{q} = \frac{n_{Fe(II)}}{\phi_\text{F} \cdot t \cdot f} \tag{3}$$

Determination of the quantum yield for the formation of the product 3a:

An oven-dried 10 mL Schlenk tube, equipped with a magnetic stir bar, was charged with *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol, 2 mol%), BCB **1a** (18.82 mg, 0.1 mmol, 1.0 equiv), collidinium salt **2d** (65.62 mg, 0.2 mmol, 2.0 equiv), and NaHCO$_3$ (8.40 mg, 0.1 mmol, 1 equiv). The tube was evacuated and backfilled with argon three times before the addition of dry dichloromethane (1.0 mL, 0.1 M) under the argon counterflow. The reaction mixture was then irradiated at 416 nm for 7200 s. After this time, the solvent was removed *in vacuo* and the resultant residue was dissolved in CDCl$_3$ (0.5 mL). To this solution 1,2-dibromomethane (0.1 mmol, 1 equiv) was added as an internal standard and the sample was analyzed by ^{1}H NMR spectroscopy. The NMR yield of the desired product **3a** was determined to be 2.066% (average of three reactions).

The quantum yield of the reaction was determined by using equation 4, considering the value photon flux ($\phi_\text{q} = 3.505 \cdot 10^{-9}$ mol·s^{-1}), the irradiation time (t = 7200 s), and the fraction of light absorbed by the reaction mixture (f_R = 0.999; determined according to equation 2 with $A_{416\text{ nm}}$ = >3).

$$\phi = \frac{n_\text{product}}{\phi_q \cdot t \cdot f_\text{R}} \tag{4}$$

The determined quantum yield was ϕ = 0.08.

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[10] Wegner, E. E.; Adamson, A. W. Photochemistry of Complex Ions. III. Absolute Quantum Yields for the Photolysis of Some Aqueous Chromium(III) Complexes. Chemical Actinometry in the Long Wavelength Visible Region. *J. Am. Chem. Soc.* **1966**, *88*, 394–404.

8.4 Cyclic voltammetry analysis

The cyclic voltammograms (CVs) were recorded with a standard three-electrode cell set-up (reference electrode: Ag/AgCl (sat. aq. KCl), working electrode: 3 mm glassy carbon disc electrode, and counter electrode: platinum wire) on CHI600e electrochemical workstation (CH Instruments, Austin, Texas, USA). All the measurements were done at room temperature. All the samples were prepared in degassed MeCN (50 mM) along with tetrabutylammonium-hexafluorophosphate $^{n}Bu_4NPF_6$ as electrolyte.

Setup: As electrolyte a 0.10 M solution of $^{n}Bu_4NPF_6$ in MeCN was prepared, which was degassed inside the set-up (4 mL of the electrolyte solution was used per measurement) by bubbling argon through it. After measuring a blanc CV, the substance (40 µL of a 0.10 M solution in MeCN) was added, and the CV was recorded. The redox potentials were converted to the saturated calomel electrode (SCE) scale by subtracting 45 mV (0.045 V).

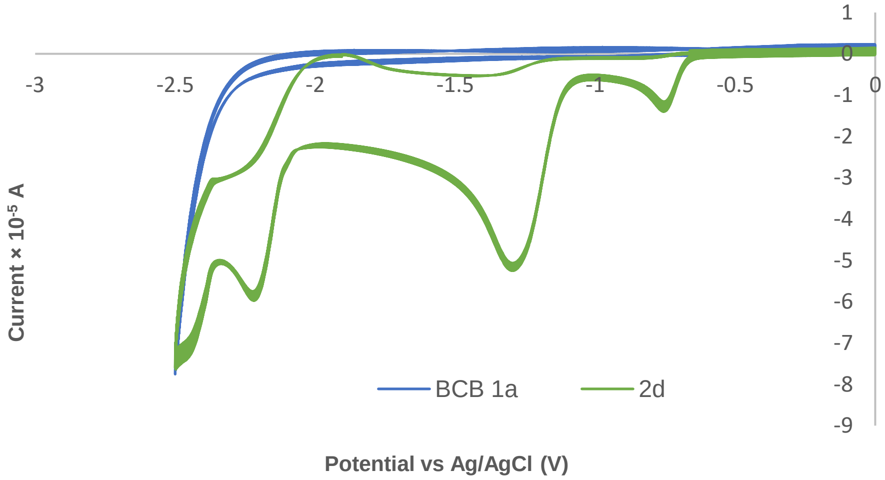


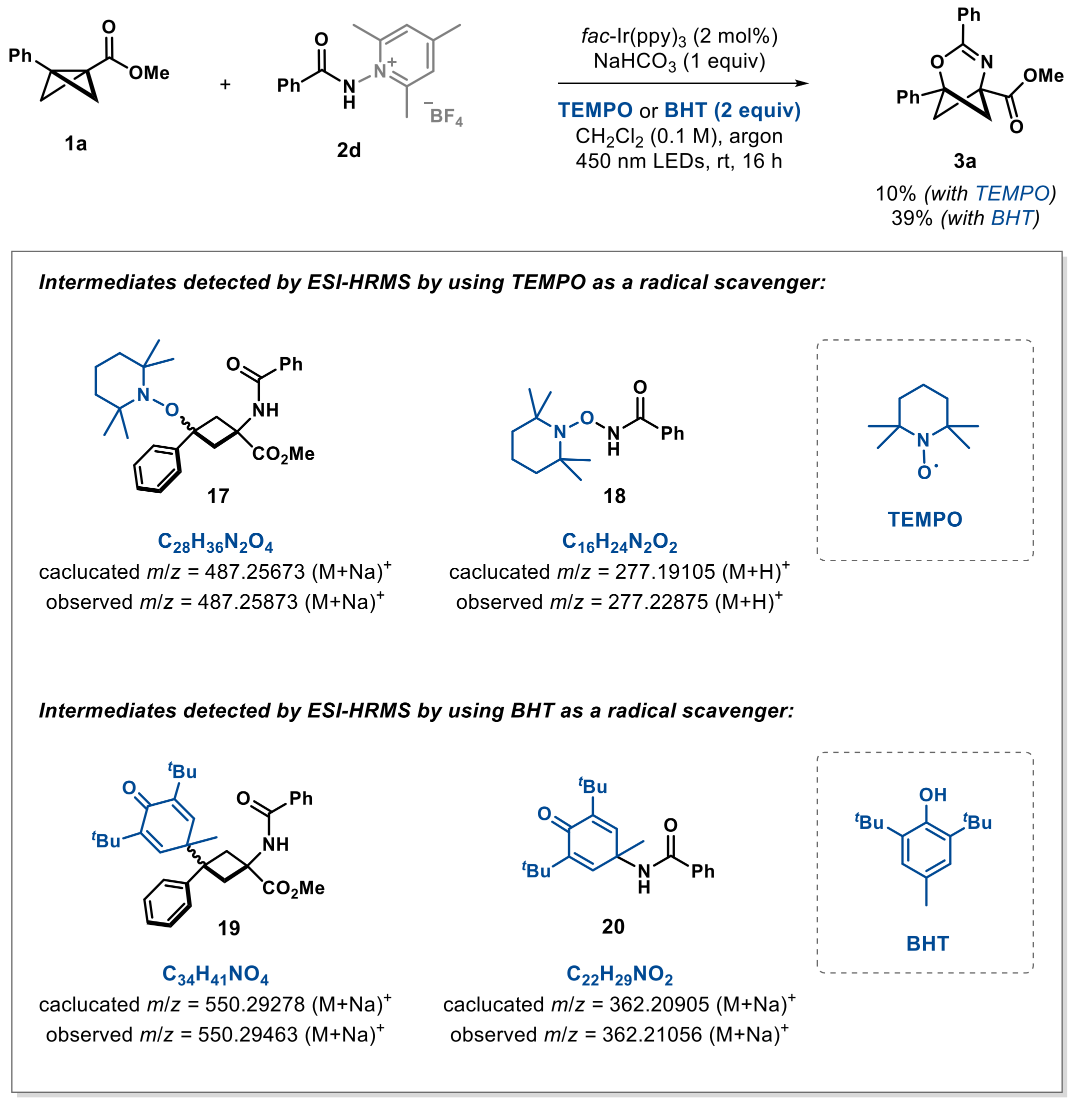
Figure S9. Cyclic voltammogram of **1a** and **2d**.

8.5 Intermediates trapping experiments

To investigate the intermediacy of radicals and/or cation in the current reaction, different radical trapping experiments were performed.

Radical trapping experiments:

An oven-dried Schlenk tube, equipped with a magnetic stir bar, was charged with BCB **1a** (18.8 mg, 0.1 mmol, 1.0 equiv), *N*-amidocollidinium tetrafluoroborate **2d** (65.6 mg, 0.2 mmol, 2.0 equiv), $NaHCO_3$ (8.4 mg, 0.1 mmol, 1.0 equiv), and *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol, 2 mol%) under air. To this mixture was added a radical scavenger i.e. either TEMPO (31.2 mg, 0.2 mmol, 2 equiv) or BHT (44.0 mg, 0.2 mmol, 2 equiv). The tube was evacuated and back-filled with argon three times, and then dry dichloromethane (0.1 M) was added under argon counter-flow. The tube was then sealed with a screw-cap, and the resulting reaction mixture was vigorously stirred under the irradiation at 450 nm for 16 h. After this time, the solvent was removed under reduced pressure and ^{1}H NMR of the crude reaction mixture was recorded by using CH_2Br_2 (7.0 μL, 0.1 mmol, 1.0 equiv) as an internal standard to assess the formation of product **3a**. Further, the crude reaction mixture was analyzed by ESI-HRMS to check the intermediates formed during the reaction.



Intermediates detected by ESI-HRMS by using TEMPO as a radical scavenger:

17

$C_{28}H_{36}N_2O_4$

caclucated *m/z* = 487.25673 $(M+Na)^+$

observed *m/z* = 487.25873 $(M+Na)^+$

18

$C_{16}H_{24}N_2O_2$

caclucated *m/z* = 277.19105 $(M+H)^+$

observed *m/z* = 277.22875 $(M+H)^+$

Intermediates detected by ESI-HRMS by using BHT as a radical scavenger:

19

$C_{34}H_{41}NO_4$

caclucated *m/z* = 550.29278 $(M+Na)^+$

observed *m/z* = 550.29463 $(M+Na)^+$

20

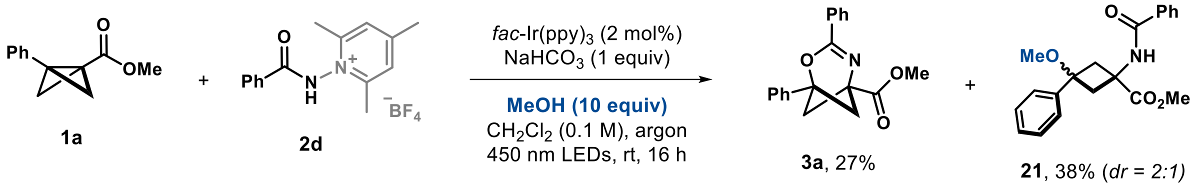
$C_{22}H_{29}NO_2$

caclucated *m/z* = 362.20905 $(M+Na)^+$

observed *m/z* = 362.21056 $(M+Na)^+$

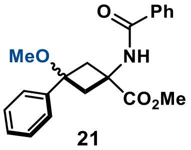
Figure S10. Intermediates detected during radical trapping experiments.

Cation trapping experiment:



An oven-dried Schlenk tube, equipped with a magnetic stir bar, was charged with BCB **1a** (18.8 mg, 0.1 mmol, 1.0 equiv), *N*-amidocollidinium tetrafluoroborate **2d** (65.6 mg, 0.2 mmol, 2.0 equiv), $NaHCO_3$ (8.4 mg, 0.1 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol, 2 mol%), and MeOH (32 mg, 1.0 mmol, 10 equiv) under air. The tube was evacuated and back-filled with argon three times, and then dry dichloromethane (0.1 M) was added under argon counter-flow. The tube was then sealed with a screw-cap, and the resulting reaction mixture was vigorously stirred under the irradiation at 450 nm for 16 h. After this time, the solvent was removed under reduced pressure and ^{1}H NMR of the crude reaction mixture was recorded by using CH_2Br_2 (7.0 µL, 0.1 mmol, 1.0 equiv) as an internal standard to assess the formation of **3a**. Further, the solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: pentane/EtOAc = 80:20) to afford the methanol-trapped product **21** in as a colourless solid (12.9 mg, 38% yield, dr = 2:1).

Characterization data for 21:



21

Data for major isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 2H), 7.56 – 7.50 (m, 1H), 7.46 (tt, *J* = 6.6, 1.6 Hz, 2H), 7.39 (dtd, *J* = 7.3, 6.4, 1.5 Hz, 4H), 7.34 – 7.28 (m, 1H), 7.01 (s, 1H), 3.68 (s, 3H), 3.33 – 3.23 (m, 2H), 2.95 (s, 3H), 2.75 – 2.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.08, 167.29, 141.46, 133.76, 131.99, 128.74, 128.51, 127.92, 127.32, 126.38, 78.27, 53.78, 52.80, 50.75, 41.76.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{21}NO_4$ $(M + Na)^+$: 362.13628, found: 362.13587.

Data for minor isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 5H), 7.40 – 7.28 (m, 5H), 6.30 (s, 1H), 3.80 (s, 3H), 3.27 – 3.18 (m, 2H), 2.96 (s, 3H), 2.92 – 2.86 (m, 2H).

^{13}C NMR (125 MHz, cdcl$_3$) δ 172.87, 167.60, 142.07, 133.80, 131.91, 128.67, 128.63, 127.98, 127.14, 126.98, 77.02, 53.04, 52.36, 50.80, 42.25.

HRMS (ESI): *m*/*z* calculated for $C_{20}H_{21}NO_4$ $(M + Na)^+$: 362.13628, found: 362.13619.

9. X-ray crystallographic information

X-Ray diffraction:

Data sets for compounds **3a**, **3i**, **5** and **13** were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: *APEX4* Version 2021.4-0[11] (Bruker AXS Inc., **2021**); cell refinement: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); data reduction: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); absorption correction, *SADABS* Version 2016/2 (Bruker AXS Inc., **2021**); structure solution *SHELXT*-Version 2018-3[12] (Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3–8); structure refinement *SHELXL*- Version 2018-3[13] (Sheldrick, G. M. *Acta Cryst.* **2015**, *C71* (1), 3–8) and graphics, *XP*[14] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: For compounds **3i** and **13** parts of the corresponding molecule were found disordered over two or three positions in the asymmetrical unit. Several restraints (SADI, SAME, ISOR, SUMP and SIMU) were used in order to improve refinement stability.

X-ray crystal structure analysis of 3a (glo10469):

A colourless, prism-like specimen of $C_{19}H_{17}NO_3$, approximate dimensions 0.047 mm x 0.049 mm x 0.097 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1308 frames were collected. The total exposure time was 20.55 hours. The frames were integrated with the Bruker SAINT software package using a wide-

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[11] Bruker AXS (**2021**) *APEX4 Version 2021.4-0, SAINT Version 8.40B* and *SADABS Bruker AXS area detector scaling and absorption correction Version 2016/2*, Bruker AXS Inc., Madison, Wisconsin, USA.

[12] Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015**, *A71*, 3–8.

[13] Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.

[14] Bruker AXS (**1998**) *XP – Interactive molecular graphics, Version 5.1*, Bruker AXS Inc., Madison, Wisconsin, USA.

frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 27918 reflections to a maximum θ angle of 66.77° (0.84 Å resolution), of which 2680 were independent (average redundancy 10.417, completeness = 99.7%, R_{int} = 18.29%, R_{sig} = 7.34%) and 1654 (61.72%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.9686(5) Å, b = 7.9220(3) Å, c = 15.6150(5) Å, β = 109.532(3)°, volume = 1511.93(10) $Å^3$, are based upon the refinement of the XYZ-centroids of 1897 reflections above 20 σ(I) with 7.232° < 2θ < 126.9°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.864. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9320 and 0.9660. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{19}H_{17}NO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 210 variables converged at R1 = 5.78%, for the observed data and wR2 = 16.38% for all data. The goodness-of-fit was 1.024. The largest peak in the final difference electron density synthesis was 0.270 $e^-/Å^3$ and the largest hole was -0.291 $e^-/Å^3$ with an RMS deviation of 0.069 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.350 g/cm^3 and F(000), 648 e^-. **CCDC Nr.: 2312457**.

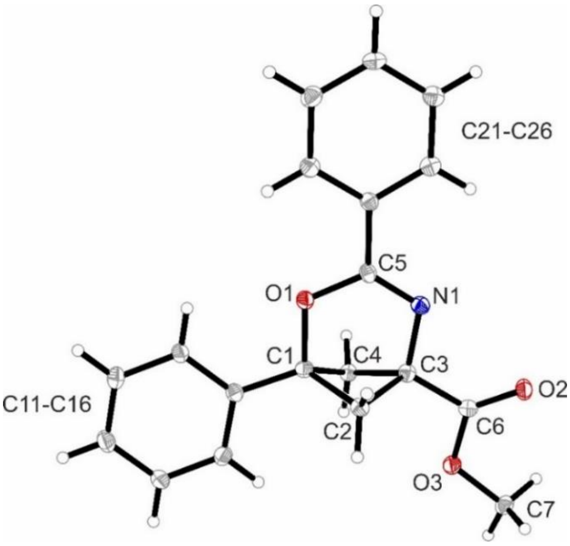


Figure S11. Crystal structure of compound **3a** (CCDC Nr.: 2312458). Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 3i (glo10542):

A colourless, prism-like specimen of $C_{20}H_{19}NO_3$, approximate dimensions 0.110 mm x 0.125 mm x 0.149 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1111 frames were collected. The total exposure time was 14.41 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 26014 reflections to a maximum θ angle of 66.49° (0.84 Å resolution), of which 2883 were independent (average redundancy 9.023, completeness = 99.6%, R_{int} = 6.91%, R_{sig} = 3.10%) and 2244 (77.84%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.3579(3) Å, b = 8.8707(3) Å, c = 19.9456(7) Å, β = 98.973(2)°, volume = 1635.44(10) $Å^3$, are based upon the refinement of the XYZ-centroids of 8587 reflections above 20 σ(I) with 8.977° < 2θ < 132.9°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.858. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9020 and 0.9260. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{20}H_{19}NO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 296 variables converged at R1 = 4.10%, for the observed data and wR2 = 10.25% for all data. The goodness-of-fit was 1.024. The largest peak in the final difference electron density synthesis was 0.221 $e^-/Å^3$ and the largest hole was -0.196 $e^-/Å^3$ with an RMS deviation of 0.041 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.305 g/cm^3 and F(000), 680 e^-. **CCDC Nr.: 2312458**.

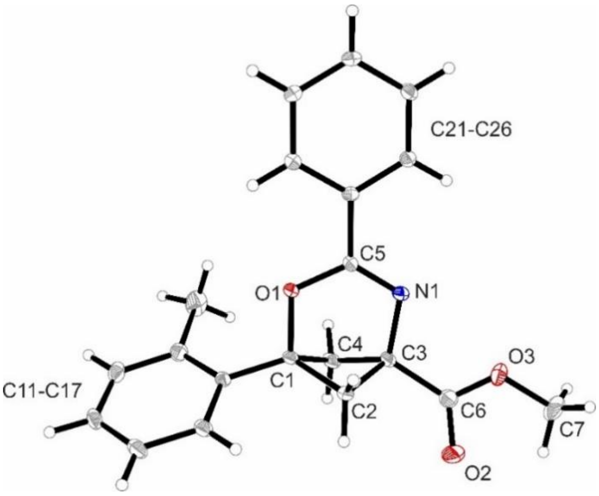


Figure S12. Crystal structure of compound **3i** (CCDC Nr.: 2312458). Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 5 (glo10491):

A colourless, prism-like specimen of $C_{23}H_{21}N_3O_2$, approximate dimensions 0.122 mm x 0.128 mm x 0.139 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1431 frames were collected. The total exposure time was 17.04 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 38609 reflections to a maximum θ angle of 66.72° (0.84 Å resolution), of which 3381 were independent (average redundancy 11.419, completeness = 99.5%, R_{int} = 6.06%, R_{sig} = 2.61%) and 2949 (87.22%) were greater than $2\sigma(F^2)$. The final cell constants of a = 24.4635(4) Å, b = 7.09950(10) Å, c = 25.1731(6) Å, β = 119.0020(10)°, volume = 3823.79(13) $Å^3$, are based upon the refinement of the XYZ-centroids of 9846 reflections above 20 $\sigma(I)$ with 13.14° < 2θ < 133.3°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.901. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9120 and 0.9230. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 1 2/c 1, with Z = 8 for the formula unit, $C_{23}H_{21}N_3O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 255 variables converged at R1 = 3.75%, for the observed data and wR2 = 9.07% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 0.274 $e^-/Å^3$ and the largest hole was -0.308 $e^-/Å^3$ with an RMS deviation of 0.043 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.290 g/cm^3 and F(000), 1568 e^-. **CCDC Nr.: 2312459**.

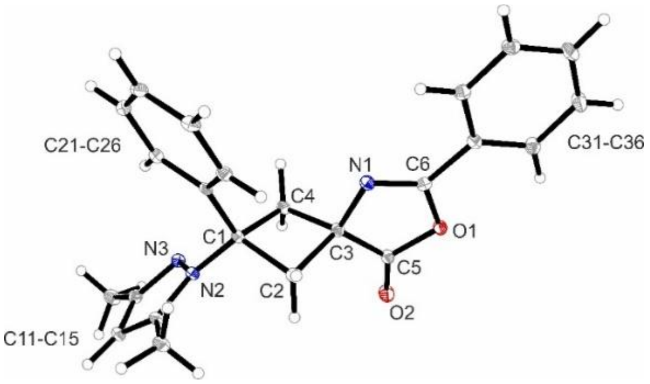


Figure S13. Crystal structure of compound **5** (CCDC Nr.: 2312459).
Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 13 (glo10534):

A colorless, plate-like specimen of $C_{18}H_{15}NO_3$, approximate dimensions 0.035 mm x 0.103 mm x 0.183 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1173 frames were collected. The total exposure time was 13.97 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 24069 reflections to a maximum θ angle of 66.69° (0.84 Å resolution), of which 2526 were independent (average redundancy 9.529, completeness = 99.9%, R_{int} = 13.12%, R_{sig} = 5.02%) and 1886 (74.66%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.3200(2) Å, b = 14.5593(3) Å, c = 10.6845(2) Å, volume = 1449.81(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 3985 reflections above 20 σ(I) with $6.070° < 2\theta < 132.3°$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.893. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8750 and 0.9740. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Pca*2_1, with Z = 4 for the formula unit, $C_{18}H_{15}NO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 313 variables converged at R1 = 4.53%, for the observed data and wR2 = 10.65% for all data. The goodness-of-fit was 1.086. The largest peak in the final difference electron density synthesis was 0.168 $e^-/Å^3$ and the largest hole was -0.167 $e^-/Å^3$ with an RMS deviation of 0.043 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.344 g/cm^3 and F(000), 616 e^-. **CCDC Nr.: 2312460**.

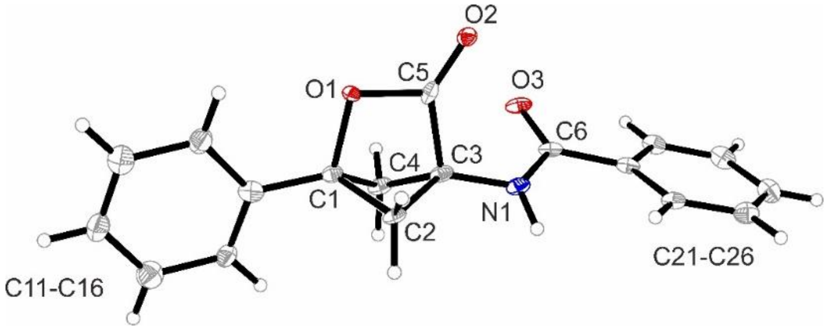
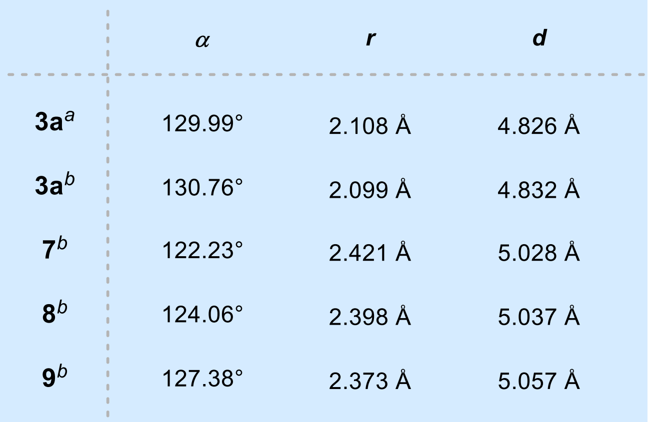


Figure S14. Crystal structure of compound **13** (CCDC Nr.: 2312460). Thermal ellipsoids are shown at 30% probability.

10. Exit vectors analysis

Geometry optimization of 2-oxa-4-azabicyclo[3.1.1]hept-3-ene **3a**, benzene **7**, pyridine **8**, and pyrimidine **9** derivatives were performed using the CAM-B3LYP range-separated hybrid functional[15] on a recontracted Ahlrichs double-ζ-basis (def2-SVP)[16] applying the CPCM continuum solvation model for dichloromethane[17] and a Grimme D3 atom-pairwise dispersion correction.[18] The corresponding α, r and d values were then determined from the optimized geometries using 3D-molecule visualization tools.

Table S2. Comparison of exit vectors of 2-oxa-4-azabicyclo[3.1.1]hept-3-ene **3a** with related benzene **7**, pyridine **8**, and pyrimidine **9** derivatives.



	α	*r*	*d*
3a[a]	129.99°	2.108 Å	4.826 Å
3a[b]	130.76°	2.099 Å	4.832 Å
7[b]	122.23°	2.421 Å	5.028 Å
8[b]	124.06°	2.398 Å	5.037 Å
9[b]	127.38°	2.373 Å	5.057 Å

[a]Values obtained from X-ray crystal structure. [b]Calculated values.

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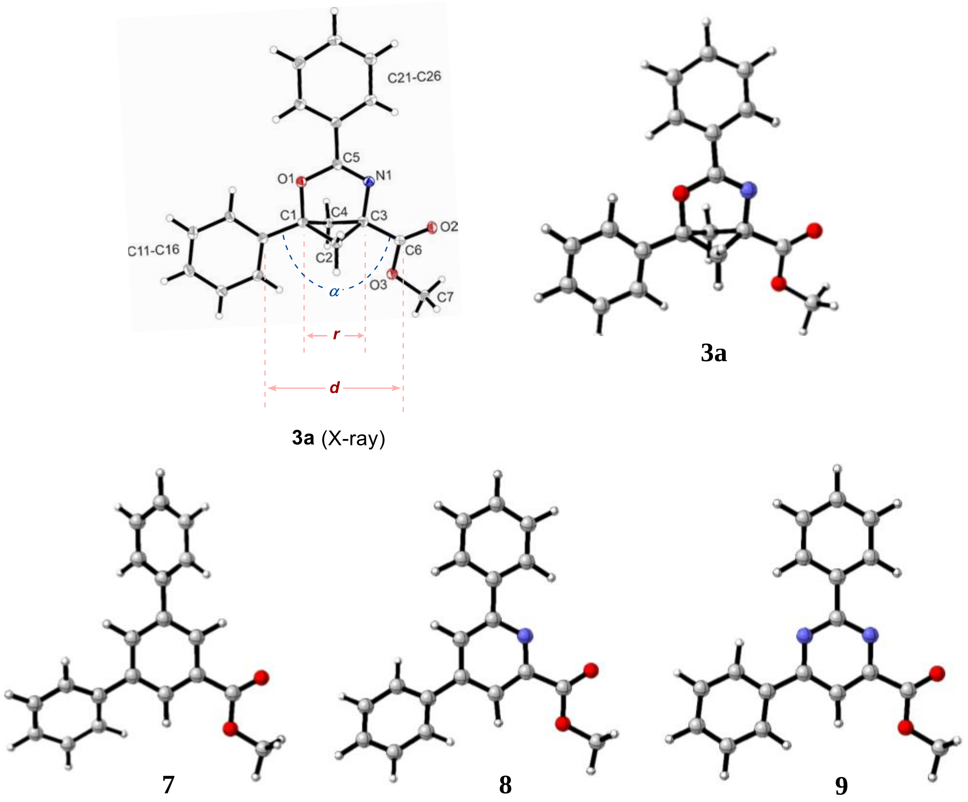
15. Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.

16. Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and assessment of Accuracy. *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297–3305.

17. (a) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* **1998**, *102*, 1995–2001. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, Structures, and Electronic Properties of Molecules in Solution with the C-PCM Solvation Model. *J. Comput. Chem.* **2003**, 24, 669–681.

18. (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *Chem. Phys.* **2010**, 132, 154104. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, 32, 1456–1465.



3a (X-ray)

3a

7

8

9

Figure S15. X-ray crystal structure of **3a** and optimized geometries of **3a**, **7**, **8**, and **9** for the comparison of their exit vectors.

Cartesian coordinates:

7
38

O	0.49574968	4.17036943	-0.3642268
C	-0.4026372	3.36476631	-0.2935493
O	-1.6880163	3.70959526	-0.3141056
C	-1.9761396	5.09963102	-0.4251365
C	-0.1989178	1.89286816	-0.1734005
C	-1.2737649	1.00976825	-0.0774824
C	-1.0474304	-0.3645789	0.03874841
C	-2.1843847	-1.316347	0.14284663
C	-3.3463305	-0.9672713	0.84377029
C	-4.4095064	-1.8590083	0.95139886

C	-4.3317581	-3.1178471	0.35893922
C	-3.182754	-3.4761695	-0.3433833
C	-2.1197447	-2.5839884	-0.4505354
C	0.27347025	-0.8249546	0.05422779
C	1.36447674	0.04648348	-0.0395152
C	2.75713862	-0.4721562	-0.0058835
C	3.08983857	-1.5883216	0.77311446
C	4.39374546	-2.0741347	0.80342403
C	5.39185421	-1.4519356	0.0564712
C	5.07432227	-0.3405266	-0.7218464
C	3.77011002	0.14457391	-0.7520805
C	1.1105265	1.4151478	-0.1546548
H	-1.5423493	5.65216485	0.41989628
H	-3.0676655	5.18853006	-0.4172322
H	-1.5680043	5.5042621	-1.3618204
H	-2.2898832	1.40042974	-0.1094998
H	-3.4113996	0.00851459	1.32894944
H	-5.3028221	-1.5697722	1.50943052
H	-5.1653308	-3.8183297	0.44420044
H	-3.1145195	-4.4576112	-0.8178007
H	-1.2333591	-2.8704119	-1.0199659
H	0.45837203	-1.8960868	0.14458135
H	2.32259339	-2.0725738	1.38016225
H	4.63289452	-2.9417485	1.42228781
H	6.41521041	-1.832597	0.08126472
H	5.84755716	0.15048028	-1.3168387
H	3.53081104	1.00498996	-1.3799526
H	1.92799731	2.13379551	-0.2148731

8

37

O	-1.9809211	3.64558243	0.18799823

C	-0.8525112	3.22797891	0.23284728
O	0.21803873	4.01020845	0.34728043
C	-0.0200646	5.41272484	0.41866312
C	-0.4823504	1.77130702	0.16777897
C	0.84510865	1.35948279	0.21019469
C	1.1227139	-0.0102034	0.14142453
C	2.51777652	-0.515525	0.17384793
C	3.50124644	0.14910552	0.91760611
C	4.80925623	-0.3248607	0.94864455
C	5.1575578	-1.468034	0.2319618
C	4.18803023	-2.1357778	-0.513333
C	2.87911346	-1.6645424	-0.5411731
C	0.03759798	-0.879754	0.03584827
C	-1.2703416	-0.3781649	-0.0043907
C	-2.4616042	-1.266908	-0.1269445
C	-2.3551133	-2.6630327	-0.1429887
C	-3.4895386	-3.4604357	-0.265899
C	-4.750064	-2.8774525	-0.3748753
C	-4.8677982	-1.4885473	-0.3578552
C	-3.7349188	-0.6922835	-0.2343185
N	-1.5048745	0.9313949	0.06239991
H	-0.653575	5.65162827	1.28403939
H	0.96173278	5.88622875	0.52358616
H	-0.5179024	5.76534187	-0.4953855
H	1.6404617	2.09884489	0.27761886
H	3.23774744	1.03656211	1.49610346
H	5.56082895	0.2008837	1.5413571
H	6.18479879	-1.8381252	0.25331576
H	4.45327539	-3.0281104	-1.0842395
H	2.13412026	-2.1855895	-1.1451775
H	0.21392943	-1.9528422	-0.0021005
H	-1.3827693	-3.1485231	-0.0567705

H	-3.3853467	-4.5475114	-0.2760773
H	-5.6390454	-3.504323	-0.4726999
H	-5.8512549	-1.0209358	-0.4423136
H	-3.8148904	0.39444805	-0.2195345

9

36

O	-3.1927182	-2.7068766	-0.6865892
C	-1.9914714	-2.747	-0.7237672
O	-1.2877025	-3.8471535	-0.9594375
C	-2.0268158	-5.0474258	-1.1752439
C	-1.1017527	-1.5483882	-0.504748
C	0.28073012	-1.6490897	-0.5374987
C	1.00298891	-0.4700761	-0.3069956
C	2.48734385	-0.437611	-0.3050576
C	3.15495787	0.6449423	0.28078223
C	4.54432273	0.69189894	0.29932755
C	5.28697048	-0.3381336	-0.2759964
C	4.63180252	-1.4157129	-0.8683951
C	3.24143973	-1.4675438	-0.880512
N	0.35871067	0.67042259	-0.0658755
C	-0.9749523	0.6738058	-0.0580145
C	-1.6699098	1.96156729	0.2034041
C	-0.9401167	3.13625901	0.41590263
C	-1.5983981	4.33746923	0.65825304
C	-2.9914823	4.3785353	0.69098722
C	-3.7245929	3.21162024	0.47962919
C	-3.0683525	2.00983012	0.23715583
N	-1.7292651	-0.4025732	-0.2720871
H	-1.2874662	-5.8348761	-1.3538537
H	-2.6878302	-4.9379509	-2.0458712
H	-2.6342998	-5.2855799	-0.2913053

H	0.7610811	-2.6068416	-0.7179045
H	2.56697267	1.44673918	0.72740051
H	5.05197314	1.53862	0.76612486
H	6.37841262	-0.3000278	-0.2641917
H	5.20684185	-2.2223344	-1.3277001
H	2.74733219	-2.3135828	-1.35979
H	0.14852862	3.09668059	0.38679227
H	-1.0200815	5.24923824	0.82218742
H	-3.5071293	5.32248381	0.88118868
H	-4.8160942	3.23840723	0.50401251
H	-3.6299175	1.09065776	0.07048675

11. DFT Calculations

Methods and general considerations:

All computations were done using ORCA 5.0.3 software package.[19] Geometry optimization of all relevant stationary points was performed using the CAM-B3LYP range-separated hybrid functional[15] on a recontracted Ahlrichs double-ζ-basis (def2-SVP)[16] applying the CPCM continuum solvation model for dichloromethane[17] and a Grimme D3 atom-pairwise dispersion correction.[18] For Iridium complexes, the Ir atom was described using the def2-ECP pseudopotential.[20] All optimized geometries were confirmed to be local minima on the respective potential energy surface by the absence of imaginary frequencies, as obtained from the vibrational frequency calculations at the same level of theory. In most cases, conformational search was performed[21] and the lowest energy conformer was pre-optimized using the semi-empirical GFN2-xTB algorithm.[22]

Relaxed surface scan and Nudged elastic band calculations were performed to identify transition state geometries.[23] Transition states were characterized by one negative eigenvalue of the Hessian and the analysis of the corresponding eigenvector vibration. Intrinsic reaction coordinate (IRC) calculations were carried out to confirm the transition states are connected to the correct minima.

The electronic energy of the previously optimized geometries was then refined through an additional single point calculation on the CAM-B3LYP / def2-TZVPP level,[16] with the CPCM continuum solvation model for dichloromethane and a Grimme D3 atom-pairwise dispersion correction. The reported Gibbs free energies at 298 K were obtained as the sum of the electronic energies and the corresponding free energy corrections (ZPVE, thermal corrections, enthalpy correction, entropic corrections), as obtained from the frequency calculation. CYLview20 was used to visualize the optimized structures.[24]

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20. Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta.* **1990**, *77*, 123–141.
21. Wang, S.; Witek, J.; Landrum, G. A.; Riniker, S. *J. Chem. Inf. Model.* **2020**, *60*, 2044.
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23. Ásgeirsson, V.; Birgisson, B. O.; Bjornsson, R.; Becker, U.; Neese, F.; Riplinger, C.; Jónsson, H. *J. Chem. Theory Comput.* **2021**, *17*, 4929–4945.
24. Legault, C. Y., *CYLview20*. Université de Sherbrooke, **2020** (http://www.cylview.org).

Results and discussion:

Upon irradiation, the excited photocatalyst ^{3}Ir(III) reduces **2d** to form **2d'**. The subsequent *N*–*N* bond cleavage of **2d**' (through a kinetic barrier of $\Delta G^{\ddagger} = 11.6$ kcal/mol for **TS-2d'**) leads to the formation of *N*-centered amidyl radical **Int-1** and 2,4,6-collidine **2da**.

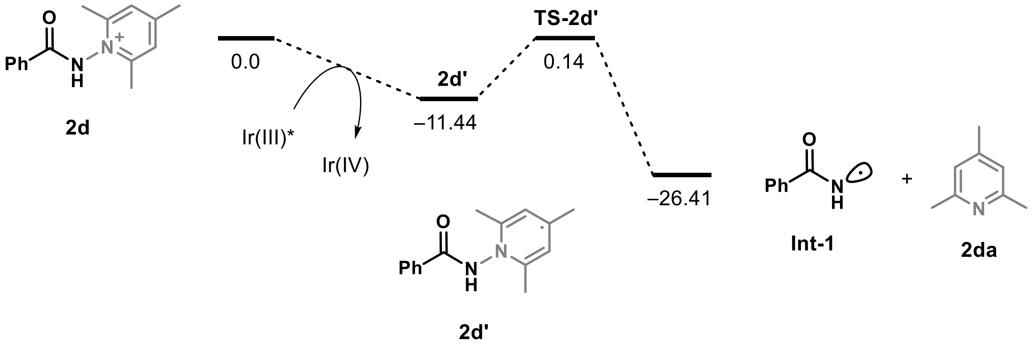
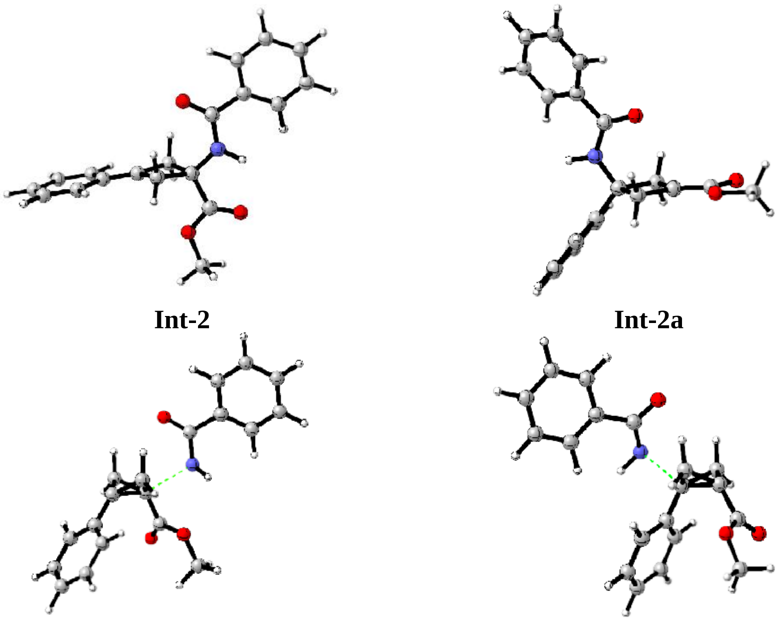


Figure S16. Generation of amidyl radical from *N*-amidocollidinium salt.

We conducted DFT calculations to rationalize the regioselectivity of the *N*-centered amidyl radical addition to the BCB **1a**. It was found that the addition of amidyl radical across the inter-bridgehead C1–C3 σ-bond of BCB proceeds through a lower kinetic barrier of 14.4 kcal/mol ($\Delta G^{\ddagger}_{\text{TS-1}}$) to form **Int-2** as compared to 16.5 kcal/ mol ($\Delta G^{\ddagger}_{\text{TS-1a}}$) for the generation of **Int-2a**. Moreover, **Int-2** is also thermodynamically more stable than **Int-2a** ($\Delta\Delta G_{\text{Int2/Int-2a}} = -6.8$ kcal/mol). **Int-2** can subsequently undergo exergonic SET with oxidized photocatalyst i.e. Ir(IV) to form stabilized benzylic carbocation **Int-3** and regenerate Ir(III) photocatalyst.

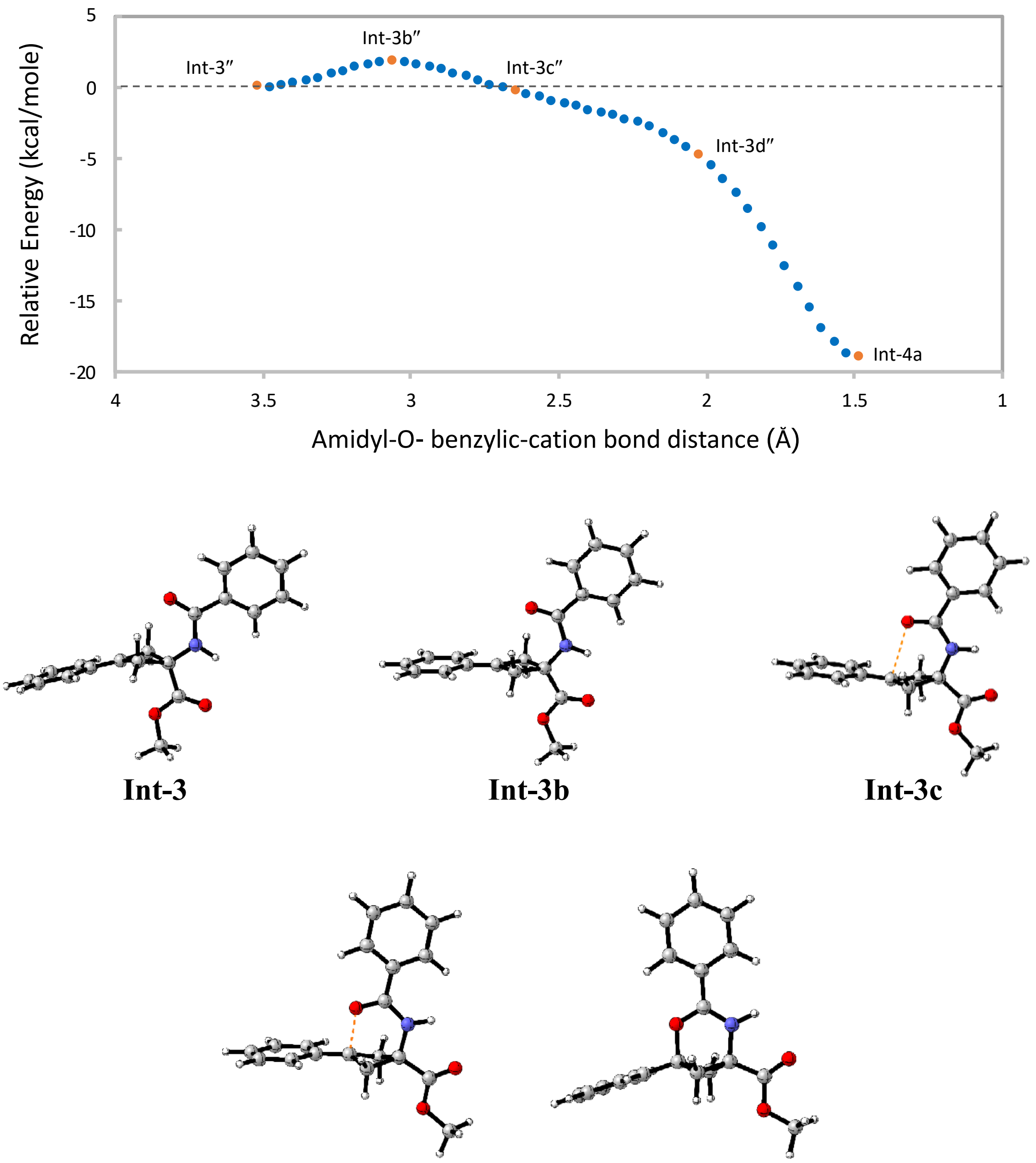


Int-2 **Int-2a**

TS-1 **TS-1a**

Figure S17. Intermediates and transition state geometries involved in the regioselectivity determining amidyl radical addition to BCB.

Next, the potential energy surface of the cyclization process from the cationic intermediate **Int-3** to form **Int-4a** was investigated using relaxed surface scan (**Figure S17**). It can be observed that the cyclization process is exothermic and proceeds through an early kinetic barrier between **Int-3** and **Int-3c**. This shallow kinetic barrier ($\Delta E_{\text{Int-3b/Int-3}}$ = 1.87 kcal/mol) is associated with the conformational transition of **Int-3** to form **Int-3c**. Harmonic vibrational frequency analysis of the geometry corresponding to the energy maximum (**Int-3b**) revealed a bending interaction of the amidyl-carbonyl moiety over the cyclobutane ring towards the benzylic carbocation and a simultaneous flattening of the cyclobutane ring. The actual ring-closing bond formation between the amidyl oxygen atom and the benzylic carbocation occurs further downhill. From **Int-3c**, the cyclization to form **Int-4a** is essentially barrier-less.

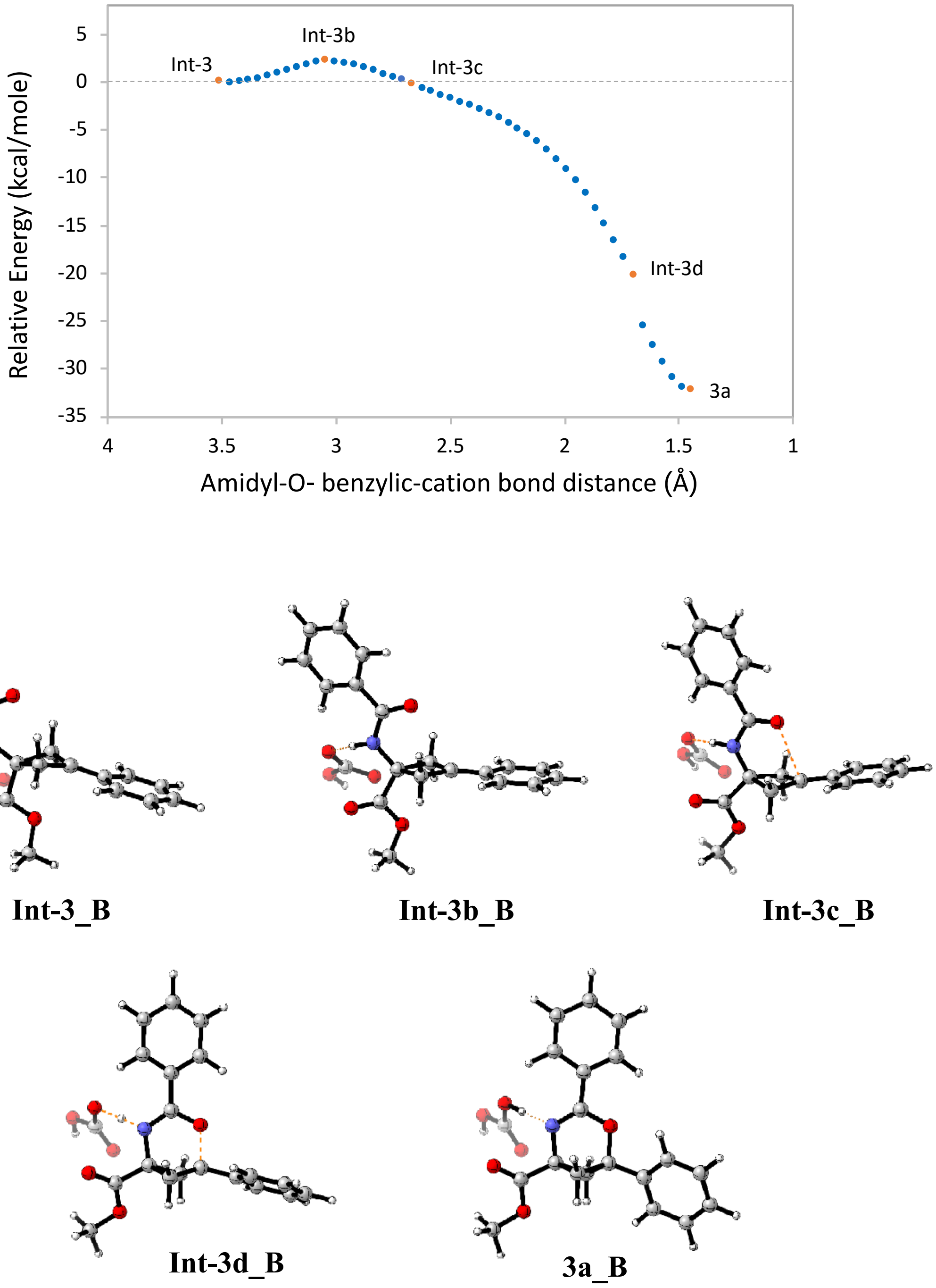


Int-3 **Int-3b** **Int-3c**

Int-3d **Int-4a**

Figure S18. Relaxed surface scan for amidyl-*O*-benzylic-carbocation bond formation between 3.52 Å to 1.48 Å.

The cyclization step was also investigated by considering the presence of the bicarbonate base ($NaHCO_3$). In this case the reaction proceeds through a simultaneous deprotonation-cyclization step. Consistent with our observation as before, the reaction energy profile is exothermic and shows an early kinetic barrier ($\Delta E_{\text{Int-3b\_B/Int-3\_B}}$ = 2.21 kcal/mol) associated with the conformational transition from **Int-3_B** to **Int-3c_B**. Notably, from **Int-3c_B** the energetic pathway takes a downhill trajectory leading to the formation of **3a_B**. The bicarbonate-mediated proton abstraction and cyclization from **Int-3c_B** was found to be barrier-less.

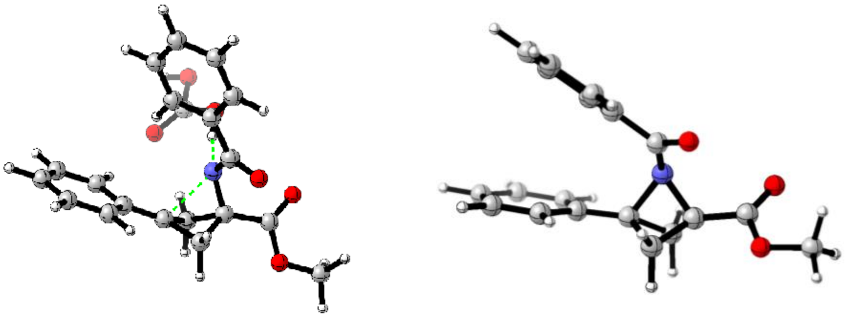


Int-3_B **Int-3b_B** **Int-3c_B**

Int-3d_B **3a_B**

Figure S19. Relaxed Surface Scan for amidyl-*O*-benzylic-carbocation bond formation between 3.50 Å to 1.44 Å in the presence of bicarbonate base ($NaHCO_3$).

On the other hand, the alternative pathway involving bicarbonate-mediated deprotonation and direct amidyl-nitrogen attack on the benzylic cation, leading to **3a'**, was found to be endergonic ($\Delta G_{3a'/Int\text{-}3} = 1.0$ kcal/mol). Furthermore, the formation of **3a'** is also associated with an elevated kinetic barrier ($\Delta G^{\ddagger}_{TS\text{-}2'} = 14.2$ kcal/mol) due to the induction of high strain.



TS2’ 3a’

Figure S20. Transition state and product **3a’** geometry.

Summary of energies:

Name	Electronic energy	ZPVE	Thermal correction	Enthalpy correction	Entropy correction
Int-2	-1015.18909	0.3325	0.02026963	0.00094421	-0.0692419
Int-2a	-1015.17931	0.3324	0.01954462	0.00094421	-0.0674034
1a	-614.845523	0.2134	0.01231273	0.00094421	-0.051518
Int-1	-400.248064	0.1145	0.00734175	0.00094421	-0.0407186
2d	-766.333432	0.2944	0.01697166	0.00094421	-0.0610762
2d’	-766.443763	0.2908	0.01737164	0.00094421	-0.0627379
2da	-366.191883	0.1714	0.00969812	0.00094421	-0.0453987
^{3}Ir(III)	-1540.38136	0.4831	0.02883502	0.00094421	-0.0853457
Ir(IV)	-1540.28956	0.4877	0.0284894	0.00094421	-0.084488
Ir(III)	-1540.4824	0.4872	0.0282071	0.00094421	-0.0831846
Int-3_B	-1279.62608	0.3622	0.02488676	0.00094421	-0.0779474
3a_B	-1279.66842	0.3658	0.02386311	0.00094421	-0.0762903
B	-264.590035	0.027	0.00346323	0.00094421	-0.0301241
BH	-265.057857	0.04	0.00368176	0.00094421	-0.0304897

Int-3	-1015.0135	0.3338	0.02018811	0.00094421	-0.0682414
Int-4a	-1015.04017	0.3377	0.01895908	0.00094421	-0.0655043
3a	-1014.59333	0.3244	0.0187622	0.00094421	-0.0655705
3a’	-1014.54749	0.3231	0.01933935	0.00094421	-0.0660653
TS-2d’	-766.423607	0.2887	0.01717303	0.00094421	-0.0621387
TS-1	-1015.09344	0.3288	0.02080354	0.00094421	-0.0706468
TS-1a	-1015.09035	0.3292	0.02066309	0.00094421	-0.0705914
TS-2’	-1279.60273	0.3615	0.02426281	0.00094421	-0.0767322

Cartesian coordinates:

2d

35

C	-0.9844296	-0.2433432	-2.3993543
C	-1.7316622	-0.1519214	-1.1142432
N	-1.0602127	0.25099269	0.00412818
N	0.28454183	0.52543353	-0.1124687
C	1.18524814	-0.4976652	0.10313853
C	2.62006091	-0.1457423	-0.0730897
C	3.56204329	-1.0038748	0.5029272
C	4.91976788	-0.7431104	0.3641823
C	5.34386678	0.37029852	-0.3604837
C	4.40899187	1.22153092	-0.9464887
C	3.04861178	0.96686585	-0.8046044
O	0.79240658	-1.6009446	0.42037307
C	-1.6402051	0.34203749	1.23659647
C	-0.7997314	0.76438393	2.39127439
C	-2.9809943	0.03493028	1.34896617

C	-3.7264836	-0.3704502	0.23798779
C	-5.1828454	-0.6764847	0.35851218
C	-3.0716474	-0.4592551	-0.9938552
H	-0.4939285	0.71028229	-2.6389128
H	-1.6752572	-0.5082989	-3.2070104
H	-0.2032411	-1.015295	-2.3345026
H	0.5387738	1.50131687	-0.2369341
H	3.21133286	-1.8736691	1.05996331
H	5.6521409	-1.4119111	0.82033297
H	6.4108981	0.57313817	-0.474128
H	4.74022015	2.08599503	-1.5248445
H	2.33285463	1.62997578	-1.2935206
H	-1.4230083	0.84408528	3.28844706
H	-0.3202089	1.73438001	2.19864264
H	-0.006427	0.02543893	2.57665716
H	-3.4482957	0.10783264	2.33122601
H	-5.4988287	-1.4136334	-0.3910404
H	-5.4330981	-1.0389942	1.36396665
H	-5.7601309	0.24637006	0.18315353
H	-3.6111534	-0.7807146	-1.8850545

2d’

35

C	-1.044296	-0.0993332	-2.4382603
C	-1.8113812	-0.0836948	-1.1567856
N	-1.1205252	0.34573789	-0.0027557
N	0.23258861	0.53438615	-0.0768045
C	1.1002684	-0.5051429	0.10574534
C	2.54811111	-0.1741791	-0.0747472
C	3.48152514	-0.9699056	0.59533096

C	4.84222898	-0.7227633	0.45454449
C	5.2804159	0.31204757	-0.3715012
C	4.35490366	1.09741689	-1.0553826
C	2.99125959	0.85771191	-0.9075856
O	0.71555831	-1.6203538	0.40638851
C	-1.7458508	0.33082629	1.26591933
C	-0.9135687	0.73170364	2.43857303
C	-3.0631876	-0.0273353	1.33755111
C	-3.8202944	-0.4121787	0.20251606
C	-5.2605024	-0.8181449	0.29495221
C	-3.1233371	-0.4322362	-1.0413229
H	-0.5979104	0.88354474	-2.6587148
H	-1.712758	-0.3711698	-3.2645482
H	-0.2185972	-0.8287763	-2.410892
H	0.5666987	1.48315881	-0.2132982
H	3.12097328	-1.7831395	1.22697671
H	5.56633648	-1.3421791	0.98780035
H	6.34941655	0.50320959	-0.4878533
H	4.69552985	1.89837417	-1.7145376
H	2.2787595	1.46467914	-1.4693673
H	-1.5348643	0.74583591	3.34288329
H	-0.4698894	1.73191222	2.30688535
H	-0.0818947	0.02815441	2.60606662
H	-3.536793	-0.0114666	2.32230031
H	-5.4071115	-1.892193	0.07937228
H	-5.6631225	-0.6292604	1.30084927
H	-5.8900728	-0.2678495	-0.4252337
H	-3.6464869	-0.7371974	-1.9509143

TS-2d'

Imaginary frequency = -665.58 cm^{-1}

35

C	-1.8624247	0.57720808	-2.8535067
C	-2.1022555	0.29338331	-1.4054128
N	-1.2738322	0.91250802	-0.5085067
N	0.3872867	0.69971741	-0.9603238
C	1.00345486	-0.3537738	-0.3712333
C	2.47871712	-0.2178087	-0.0877146
C	3.04576633	-1.1126844	0.8242079
C	4.40063336	-1.04412	1.12991341
C	5.20652015	-0.0882296	0.51244752
C	4.65217735	0.79563889	-0.4114178
C	3.29357783	0.73238778	-0.7107648
O	0.40725053	-1.3842694	-0.0787478
C	-1.4779141	0.75401411	0.83286281
C	-0.5714401	1.50929567	1.75350047
C	-2.4870283	-0.0747088	1.29509716
C	-3.3242986	-0.7595469	0.40939242
C	-4.3897806	-1.6964406	0.89557012
C	-3.1135576	-0.535179	-0.9599548
H	-1.8667422	1.66212983	-3.0414656
H	-2.6310788	0.1042772	-3.4775331
H	-0.8729972	0.20424394	-3.1557328
H	0.82994443	1.6109087	-0.8841411
H	2.40027518	-1.8596956	1.28796323
H	4.83248015	-1.7408844	1.8516523
H	6.27174555	-0.0357499	0.74828088
H	5.28251787	1.53674845	-0.9074078
H	2.87639979	1.41740958	-1.4514393

H	-1.0030744	1.56614743	2.76093178
H	-0.3958925	2.5289629	1.38049732
H	0.41070267	1.01534629	1.83870054
H	-2.6381402	-0.1621599	2.37341067
H	-4.0059422	-2.7287448	0.95429195
H	-4.7381721	-1.4194954	1.90073697
H	-5.2528548	-1.7090819	0.21435643
H	-3.7720237	-0.9977545	-1.6985111

2da

20

C	3.044163	0.21727812	0.26008944
C	1.54782285	0.13754682	0.13864902
N	0.87206864	1.28003593	0.29435225
C	-0.4597865	1.26741543	0.20018006
C	-1.1644917	2.58116065	0.39563557
C	-1.1717764	0.09403577	-0.057932
C	-0.4877036	-1.1095657	-0.2258778
C	-1.2133512	-2.3879585	-0.5336186
C	0.90358147	-1.0727945	-0.1199933
H	3.44526301	0.94369948	-0.462653
H	3.32549826	0.57327888	1.26303889
H	3.52114491	-0.7559756	0.08562714
H	-1.0320442	2.93349644	1.43054895
H	-2.2400072	2.50241696	0.18996691
H	-0.7291044	3.34686971	-0.2631789
H	-2.2614063	0.12364432	-0.1257984
H	-1.2259018	-2.5679497	-1.6208011
H	-0.7184476	-3.2508262	-0.0660094
H	-2.2566749	-2.3497326	-0.1915743

H	1.49053213	-1.9863531	-0.2377403

Int-1

15

N	2.63725467	1.33057504	0.13886573
C	2.08314229	0.08726797	-0.0882328
C	0.60498387	-0.0249817	-0.0075945
C	-0.1906333	1.08202681	0.30469629
C	-1.5745374	0.94795337	0.3565737
C	-2.1644888	-0.2888376	0.10039006
C	-1.3724607	-1.3952681	-0.210423
C	0.00946488	-1.2639984	-0.2653401
O	2.82021458	-0.8762113	-0.2543331
H	3.50349648	1.41787818	-0.4102105
H	0.28193613	2.04309633	0.51209712
H	-2.1962767	1.81122187	0.60184888
H	-3.250988	-0.3927222	0.14300798
H	-1.8375445	-2.3623366	-0.4117336
H	0.64641644	-2.1156636	-0.5096221

1a

26

O	2.52185845	-0.5457091	0.83694347
C	2.01779242	-0.4366971	-0.2574517
O	2.17652222	0.63528324	-1.0374192
C	2.96698526	1.69483373	-0.5090546
C	1.12521021	-1.4269494	-0.8612587
C	0.1948421	-1.2864445	-2.0234956
C	-0.3760142	-1.3877014	-0.6493441
C	0.42976651	-2.5387943	-0.1472231

C	-1.15169	-0.3961053	0.11452971
C	-1.5902062	0.79026939	-0.4885573
C	-2.2813261	1.74604837	0.24945579
C	-2.5550488	1.53065844	1.59904115
C	-2.1370847	0.34676264	2.20310926
C	-1.4439375	-0.6102177	1.46759832
H	2.97250108	2.48276404	-1.269871
H	3.99218258	1.35189943	-0.3114502
H	2.53221295	2.07382486	0.42636919
H	0.16026341	-0.3099884	-2.5122933
H	0.09505682	-2.1449804	-2.6996279
H	0.59363809	-2.6012825	0.93194284
H	0.35052234	-3.5052886	-0.6603829
H	-1.3933754	0.96685285	-1.5470774
H	-2.6136085	2.66609194	-0.2363884
H	-3.1003246	2.2803718	2.17616419
H	-2.3557178	0.16278399	3.25725401
H	-1.1310006	-1.538276	1.94847774

Int-2

41

N	4.30264238	2.05696969	-3.7436976
C	3.08332582	1.51184568	-3.9426765
C	2.56375395	1.54094506	-5.3519735
C	3.37983593	1.74708238	-6.4686641
C	2.82868753	1.75639561	-7.7471729
C	1.4602144	1.55865339	-7.9204024
C	0.64360265	1.34141323	-6.8113622
C	1.19499644	1.32697964	-5.5349481
O	2.42066533	1.02599525	-3.0328008

H	4.45774918	1.88028121	-6.3577963
H	3.47406713	1.91413128	-8.6136328
H	1.02946014	1.56879724	-8.9239941
H	-0.4285585	1.18139473	-6.9433956
H	0.57444894	1.15067468	-4.6555575
H	8.73816637	3.51774274	-0.7283983
H	4.58478459	3.71907647	-0.9083701
C	8.30602787	3.52061452	-1.7342983
H	3.6836179	3.12340541	1.4998255
H	3.63127505	2.59325161	3.91452592
O	7.03211456	2.88756808	-1.6200348
C	4.22075777	2.73839653	-1.2523024
H	8.18876552	4.55047818	-2.0977377
C	4.06023935	2.16168279	1.85528988
H	3.13925737	2.80044836	-1.4445522
C	4.03104117	1.86246249	3.20754276
H	8.94888252	2.96271122	-2.42855
C	6.30929521	2.78492308	-2.7216156
C	4.97272124	2.10993302	-2.4747312
C	4.61297461	1.52809748	-0.4579454
C	4.57616518	1.22915202	0.91419658
C	4.50969273	0.6324983	3.67420454
H	4.48402576	0.40207251	4.74121055
O	6.66867255	3.18782742	-3.8025907
C	5.12878211	0.78536418	-1.6550794
C	5.05666509	-0.0140998	1.40884791
H	4.43905488	0.00949798	-2.0191502
C	5.02042516	-0.3003395	2.76378206
H	6.14576925	0.36704987	-1.599572
H	5.45587969	-0.7480013	0.70519445

H	5.3940008	-1.2620057	3.12342252
H	4.79025435	2.51949294	-4.5040001

Int-2a

41

N	2.94869785	-0.3011791	0.4455934
C	2.37143028	-0.671827	-0.7203001
C	1.12526311	-1.5016523	-0.6062833
C	0.83195704	-2.2871327	0.51253095
C	-0.3354113	-3.04525	0.54913153
C	-1.216788	-3.0234711	-0.5297718
C	-0.9234448	-2.2500401	-1.6524358
C	0.24640514	-1.4993952	-1.6927368
O	2.8207052	-0.3479177	-1.8130199
H	1.52328005	-2.3334979	1.35644863
H	-0.5541762	-3.6617647	1.42344632
H	-2.1336158	-3.6162348	-0.4979013
H	-1.6097761	-2.234673	-2.5017148
H	0.49789594	-0.896898	-2.5667197
H	5.81619883	4.37252215	-4.0371924
H	4.44497097	2.71673484	0.27873987
C	6.27330617	3.39901367	-3.8274061
H	3.44043206	2.52468229	2.24387847
H	3.81345516	2.67486243	4.68270622
O	5.60930614	2.88119853	-2.683918
C	4.17755676	1.81273195	-0.2908282
H	6.1465966	2.72949692	-4.6905176
C	3.9835796	1.72721451	2.75482637
H	3.25487519	2.01376851	-0.8534099
C	4.19056252	1.81126096	4.13050418

H	7.34905652	3.52080242	-3.6340981
C	6.01829043	1.67576103	-2.2504394
C	5.29034593	1.23374209	-1.0944197
C	4.16840988	0.48734822	0.54969555
C	4.46222675	0.63398527	2.02958553
C	4.87463893	0.79846491	4.79815509
H	5.03995399	0.86529263	5.8756548
O	6.90860062	1.04377352	-2.7920111
C	5.36314696	-0.0367669	-0.3225269
C	5.13908165	-0.3825864	2.70982445
H	5.1563147	-0.9466141	-0.9040329
C	5.34629868	-0.3016453	4.08409366
H	6.3008103	-0.1845457	0.2367321
H	5.50847907	-1.250292	2.15885362
H	5.88010754	-1.1025908	4.60021256
H	2.46274572	-0.5010021	1.31077041

TS-1

Imaginary frequency = -270.35 cm^{-1}

41

N	0.34044297	-0.5807928	-1.939763
C	-0.9157051	-0.9252889	-2.3661612
C	-1.5176471	-0.1231777	-3.4901934
C	-0.8313803	0.90847442	-4.1393381
C	-1.4410168	1.61216439	-5.1742988
C	-2.7379551	1.28982522	-5.5690681
C	-3.4237191	0.25620348	-4.9314526
C	-2.813953	-0.4493497	-3.9005343
O	-1.5145451	-1.8849358	-1.8996704
H	0.19056856	1.16255263	-3.8521181

H	-0.8981919	2.41500143	-5.6772411
H	-3.215665	1.84441073	-6.379823
H	-4.4389119	-0.000366	-5.2416769
H	-3.3318396	-1.2637053	-3.3923377
H	2.75268991	2.86431518	0.16583965
H	-0.8762414	0.99853587	1.06163761
C	2.95503992	1.80100398	0.33238591
H	-0.4332965	1.3491439	3.17806331
H	0.65411439	1.88123511	5.32906258
O	1.69424157	1.13929268	0.26456387
C	-0.9208296	-0.0712777	0.84473558
H	3.63391896	1.41686163	-0.4413035
C	0.14654137	0.58120189	3.69199443
H	-1.8204628	-0.3964587	0.30753167
C	0.75566039	0.87980048	4.9055052
H	3.41475829	1.651769	1.31899539
C	1.70464469	-0.1829076	0.45305345
C	0.35030171	-0.7500318	0.41480791
C	-0.3318649	-1.0110771	1.82902926
C	0.27064191	-0.6980899	3.12835639
C	1.48891357	-0.0940675	5.58266101
H	1.96398629	0.14165595	6.53731339
O	2.70969898	-0.8242447	0.64590994
C	0.0203373	-2.1236335	0.91195884
C	1.00173784	-1.6729893	3.82246893
H	-0.7860911	-2.616863	0.35860324
C	1.60536837	-1.3719028	5.0386725
H	0.86093863	-2.7648645	1.18911384
H	1.09130072	-2.6785938	3.40949872
H	2.17048625	-2.1429877	5.56646046

H	0.47298346	0.43415807	-1.8932431

TS-1a

Imaginary frequency = -412.82 cm^{-1}

41

N	-0.8834441	-1.6219121	-0.8610456
C	-1.9297123	-0.9915705	-1.461381
C	-3.184899	-0.7451464	-0.6711536
C	-3.1945907	-0.6547395	0.72456487
C	-4.3822953	-0.3941447	1.40271716
C	-5.5696053	-0.2305771	0.69269195
C	-5.5666255	-0.3176379	-0.6997089
C	-4.3791498	-0.5667707	-1.3771943
O	-1.8728142	-0.6637362	-2.6459547
H	-2.2718743	-0.7658115	1.29796693
H	-4.3784667	-0.316327	2.4917992
H	-6.5017899	-0.0316571	1.22599546
H	-6.4960233	-0.1879322	-1.2582389
H	-4.356404	-0.6268166	-2.4662029
H	3.63461837	3.90443495	0.59176915
H	0.25907421	1.94874266	-0.5539703
C	3.96413243	3.02700686	0.02546487
H	0.3826649	1.06460737	1.43633901
H	1.3024034	0.48775837	3.65416402
O	2.79734082	2.49006645	-0.5917152
C	0.33999191	1.17712552	-1.3225406
H	4.70219082	3.3180436	-0.734455
C	1.06682888	0.22015458	1.53210137
H	-0.4856381	1.15005538	-2.0439826
C	1.58139512	-0.1082157	2.78264918

H	4.41624918	2.2859997	0.69938664
C	2.96486183	1.39620781	-1.3314622
C	1.689176	0.87802394	-1.8473149
C	0.87973664	-0.1772204	-0.9293568
C	1.41518398	-0.5296835	0.40116489
C	2.44415331	-1.1931029	2.92407573
H	2.84567464	-1.4510016	3.90624801
O	4.03520105	0.86911023	-1.5272599
C	1.49593284	-0.5266778	-2.2605777
C	2.26902556	-1.6282366	0.55453033
H	0.76638498	-0.7226169	-3.0533582
C	2.78235799	-1.9534099	1.80610089
H	2.38090885	-1.1675701	-2.2693932
H	2.52732239	-2.2397258	-0.3111103
H	3.44976349	-2.8115852	1.90873597
H	-0.939241	-1.5935115	0.15891076

^{3}Ir(III)

61

C	3.4095899	-0.2479924	2.76927464
C	4.09233107	-1.3564388	2.26438701
C	3.57610591	-2.0273122	1.16416351
C	2.38324257	-1.5981738	0.56638994
C	1.67551064	-0.4768771	1.06637214
C	2.22389922	0.18043588	2.17919779
C	1.80101231	-2.2799629	-0.6021179
C	2.33885534	-3.4134591	-1.2217763
C	1.69494117	-3.969688	-2.3161781
C	0.51581277	-3.3905191	-2.7824553
C	0.03512858	-2.2691974	-2.1267054

N	0.6609287	-1.7315989	-1.075153
C	-3.3010286	-2.7672538	2.30344503
C	-2.0071825	-2.7317148	2.82789036
C	-1.0224927	-1.9520398	2.22587676
C	-1.2885155	-1.1794881	1.08550989
C	-2.6063372	-1.2337835	0.5652514
C	-3.5968561	-2.017413	1.17273001
C	-2.8748972	-0.423346	-0.636391
N	-1.8157118	0.26914713	-1.1134629
C	-1.9344631	1.04087525	-2.1987827
C	-3.1295981	1.16974937	-2.8857826
C	-4.2368911	0.46467583	-2.4151451
C	-4.1098237	-0.3332087	-1.288313
C	-0.4009417	1.63849027	1.10462557
C	-1.2188261	1.77154121	2.24087888
C	-1.4030126	2.98722641	2.88230086
C	-0.7463847	4.14829745	2.37471706
C	0.06000274	4.09923581	1.26861156
C	0.26711	2.85740191	0.58124398
C	1.05619888	2.71523997	-0.5711658
C	1.76102242	3.76770089	-1.2409225
C	2.51641594	3.49999235	-2.3481485
C	2.59872916	2.1635718	-2.8312625
C	1.88953641	1.17673729	-2.1597399
N	1.13767751	1.41561867	-1.0894435
Ir	-0.0074868	0.02260386	0.05742204
H	3.80737952	0.28820887	3.63498623
H	5.02154446	-1.6943495	2.72760164
H	4.11169858	-2.8927647	0.76969957
H	1.70412691	1.04503456	2.59727327

H	3.25891271	-3.8566524	-0.8437463
H	2.1101919	-4.8535147	-2.8047361
H	-0.0241513	-3.7962687	-3.6382727
H	-0.8820174	-1.7743953	-2.451146
H	-4.0744832	-3.3770807	2.774837
H	-1.7663603	-3.3187087	3.71829016
H	-0.0203207	-1.9358005	2.66024843
H	-4.6092751	-2.0461068	0.76539513
H	-1.0318332	1.56744437	-2.5145682
H	-3.1883895	1.8090503	-3.7669558
H	-5.1986499	0.53808741	-2.9269236
H	-4.9675581	-0.8869697	-0.9097031
H	-1.7142435	0.88139709	2.63301822
H	-2.0375362	3.06541673	3.76682825
H	-0.8913951	5.10452802	2.88508063
H	0.54406539	5.00969321	0.91327501
H	1.68574843	4.78576604	-0.8585504
H	3.05235886	4.30328194	-2.857818
H	3.19523134	1.9062226	-3.7062588
H	1.92135567	0.13940553	-2.5031918

Ir(III)

61

C	3.376347	-0.299131	2.80769
C	4.065078	-1.408031	2.309438
C	3.56761	-2.067997	1.193853
C	2.389327	-1.625996	0.576161
C	1.671464	-0.50325	1.06584
C	2.205758	0.140084	2.195763
C	1.821728	-2.296723	-0.605373

C	2.362548	-3.427718	-1.228229
C	1.733352	-3.971352	-2.337401
C	0.564812	-3.381096	-2.816735
C	0.079699	-2.263405	-2.157624
N	0.689793	-1.737583	-1.090322
C	-3.268234	-2.770385	2.321224
C	-1.96043	-2.755115	2.812427
C	-0.979924	-1.987337	2.190331
C	-1.258399	-1.201691	1.058412
C	-2.592865	-1.235974	0.575332
C	-3.579506	-2.008894	1.202847
C	-2.879061	-0.408161	-0.608104
N	-1.818207	0.272228	-1.098534
C	-1.957739	1.060105	-2.169918
C	-3.16698	1.216025	-2.827333
C	-4.274211	0.523237	-2.33981
C	-4.129399	-0.290019	-1.226596
C	-0.404951	1.670291	1.066294
C	-1.223379	1.806445	2.20108
C	-1.426506	3.037133	2.818807
C	-0.816398	4.190794	2.319917
C	-0.00342	4.095131	1.198696
C	0.202169	2.855974	0.576392
C	1.062075	2.704669	-0.609043
C	1.748038	3.746267	-1.244969
C	2.529655	3.478707	-2.35807
C	2.621965	2.169571	-2.828244
C	1.919561	1.182781	-2.155893
N	1.162202	1.442567	-1.084871
Ir	0.009246	-0.012937	0.022736

H	3.75981	0.228078	3.685724
H	4.982888	-1.753864	2.789573
H	4.106011	-2.934651	0.80481
H	1.686705	1.007515	2.6096
H	3.274649	-3.878784	-0.839918
H	2.151464	-4.853237	-2.827148
H	0.03571	-3.776362	-3.684291
H	-0.830613	-1.759993	-2.488771
H	-4.038332	-3.372165	2.80832
H	-1.705297	-3.350841	3.693242
H	0.032593	-1.990771	2.599795
H	-4.601963	-2.019318	0.81992
H	-1.059543	1.581493	-2.505905
H	-3.235356	1.867756	-3.698801
H	-5.247256	0.618288	-2.826071
H	-4.985394	-0.835092	-0.831433
H	-1.711109	0.92135	2.615096
H	-2.068975	3.101494	3.701456
H	-0.974694	5.157003	2.8035
H	0.473126	4.996955	0.80903
H	1.665291	4.763512	-0.86486
H	3.066161	4.287688	-2.858086
H	3.226368	1.913673	-3.698852
H	1.95494	0.141058	-2.480096

Ir(IV)

61

C	3.38579359	-0.2578864	2.84176569
C	4.02061446	-1.4246284	2.40170315
C	3.52506214	-2.128671	1.30498751

C	2.38656689	-1.6769343	0.64345557
C	1.71483045	-0.4909163	1.08356484
C	2.25418382	0.20536457	2.18920425
C	1.81529301	-2.365468	-0.5271754
C	2.30591418	-3.5481904	-1.0802256
C	1.66484398	-4.1022133	-2.1807344
C	0.54538657	-3.4671429	-2.7106924
C	0.10957573	-2.2921649	-2.115509
N	0.73190876	-1.7617333	-1.0611927
C	-3.2205533	-2.8316981	2.17766503
C	-1.9195919	-2.8442326	2.67936588
C	-0.9308156	-2.0516812	2.10094672
C	-1.2205661	-1.2226668	1.00990345
C	-2.5388085	-1.2191407	0.50827241
C	-3.527014	-2.0200311	1.09387147
C	-2.8064569	-0.3451884	-0.644677
N	-1.7380411	0.34832012	-1.0971437
C	-1.8650163	1.17854986	-2.138979
C	-3.0682161	1.36141246	-2.7982885
C	-4.181108	0.65395319	-2.349102
C	-4.0492283	-0.2025596	-1.2670726
C	-0.3408155	1.66937092	1.11746325
C	-1.1074551	1.75712466	2.28370355
C	-1.3413847	2.9856158	2.89778516
C	-0.8164065	4.15989588	2.35567292
C	-0.0565578	4.09967546	1.19517954
C	0.18219263	2.86619919	0.57561703
C	0.97991555	2.73505431	-0.6528885
C	1.57927862	3.79303207	-1.3426764
C	2.31062452	3.53726716	-2.4918523

C	2.44326689	2.22527584	-2.9488999
C	1.82680259	1.21825686	-2.2304622
N	1.11679715	1.47037062	-1.1212712
Ir	0.10708461	-0.004546	0.06267506
H	3.78303843	0.28583004	3.7012983
H	4.91216605	-1.7883254	2.91637678
H	4.04168242	-3.030966	0.97544656
H	1.76011016	1.11062519	2.54299023
H	3.18134769	-4.033693	-0.6513597
H	2.03824747	-5.0280579	-2.6224079
H	0.01259529	-3.8708307	-3.5719386
H	-0.7625721	-1.7534177	-2.4906285
H	-3.9944111	-3.4540384	2.63079053
H	-1.6698572	-3.4784114	3.53335768
H	0.07720961	-2.0740513	2.51704555
H	-4.5456285	-2.0131997	0.70341346
H	-0.9691327	1.71162258	-2.4568407
H	-3.1255972	2.04589197	-3.6447553
H	-5.148977	0.77038895	-2.8404926
H	-4.9088715	-0.7613491	-0.9009039
H	-1.5252553	0.85138967	2.72699225
H	-1.9400749	3.02891419	3.81100307
H	-1.0000027	5.12141912	2.83878451
H	0.35090026	5.02073794	0.77515611
H	1.46873541	4.81281061	-0.9772897
H	2.77968437	4.36072953	-3.0339508
H	3.01440168	1.98546985	-3.8457539
H	1.89236111	0.17346572	-2.5382852

Int-3_B

46

O	7.12013751	1.9183388	-3.7875756
C	6.414294	2.14527265	-2.8434671
O	6.85612983	2.54063017	-1.6517069
C	8.24063467	2.85442745	-1.5486653
C	4.92235693	1.85569101	-2.7833204
N	4.39107048	1.79072917	-4.1082548
C	3.1560144	1.30866098	-4.3649314
C	2.66403491	1.35509086	-5.7833722
C	3.29606773	2.07351435	-6.804042
C	2.76793528	2.05566985	-8.093113
C	1.61695234	1.3233251	-8.3758397
C	0.98196895	0.61079308	-7.3594474
C	1.50192128	0.63117199	-6.0705747
O	2.44713882	0.80841815	-3.4870984
C	4.19556081	2.71983475	-1.7136696
C	4.46643288	1.63917988	-0.7420916
C	4.55559701	1.60460329	0.65527717
C	4.88486949	0.39759577	1.32107883
C	4.93803275	0.36812264	2.70076508
C	4.67232027	1.53471331	3.42667117
C	4.35156758	2.73646087	2.78588
C	4.2928162	2.7771055	1.40651932
C	4.72674014	0.6463369	-1.7966277
H	8.42245853	3.10690512	-0.4985782
H	8.47049185	3.71426514	-2.1927461
H	8.85700551	1.99663591	-1.8495174
H	4.87411375	2.43015069	-4.7810297
H	4.18624513	2.66912286	-6.5995534

H	3.26263709	2.62302714	-8.884463
H	1.21133113	1.30978977	-9.390061
H	0.07753731	0.03718222	-7.5732626
H	1.01748853	0.08449894	-5.261106
H	3.11375726	2.70822921	-1.9368758
H	4.53810664	3.7420403	-1.5224901
H	5.09195605	-0.5015827	0.73856948
H	5.18756114	-0.5560081	3.22374089
H	4.71885131	1.50694686	4.51784463
H	4.15144043	3.63321459	3.37369773
H	4.04755727	3.70454904	0.88641516
H	3.7534977	0.19128098	-2.0652324
H	5.49690869	-0.1239779	-1.6609475
O	5.54251227	3.81203737	-5.5690945
C	5.90373841	4.65719354	-4.724441
O	5.78364191	4.61432223	-3.4864712
O	6.51958927	5.76232084	-5.2544003
H	6.75146854	6.32964949	-4.5049816

3a_B

46

O	1.71249738	3.78433294	-0.4421593
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O	-0.507908	4.02779352	-0.52745
C	-0.3641432	5.4457231	-0.5488149
C	0.35774161	1.82761991	-0.3693385
N	-1.0251027	1.42930806	-0.5567178
C	-1.221723	0.16700275	-0.4761366
C	-2.556303	-0.4514785	-0.5959156
C	-3.6002096	0.25120183	-1.2068311

C	-4.8639738	-0.3206443	-1.2966459
C	-5.0925564	-1.595899	-0.7806684
C	-4.0526007	-2.3008935	-0.1775173
C	-2.7857934	-1.7336204	-0.0867522
O	-0.2319436	-0.7006259	-0.2435977
C	0.90401041	1.09670226	0.89104173
C	1.07319542	-0.1161609	-0.0467204
C	2.05383939	-1.2106185	0.24637565
C	1.66492259	-2.5500998	0.30613376
C	2.60171399	-3.5419226	0.59220077
C	3.93360708	-3.2071361	0.81838071
C	4.32819951	-1.8711028	0.75531009
C	3.39467353	-0.8802313	0.47128246
C	1.28513273	0.89772358	-1.1885042
H	-1.3801716	5.85376762	-0.5564813
H	0.18311405	5.76206469	-1.4473462
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H	-2.2051184	2.37443034	0.12023148
H	-3.4129985	1.24404857	-1.6167489
H	-5.6755481	0.22979534	-1.77661
H	-6.0864227	-2.0431304	-0.8513999
H	-4.229645	-3.2991932	0.22757629
H	-1.9702812	-2.2773182	0.39068635
H	0.21175555	1.00188194	1.73716696
H	1.87795414	1.49648335	1.19362238
H	0.62432266	-2.8177634	0.12771036
H	2.2836747	-4.5857662	0.63863121
H	4.66565151	-3.9855679	1.04399862
H	5.37110888	-1.5979461	0.92956135
H	3.71633236	0.16267327	0.42572039

H	0.95605049	0.60615177	-2.1951111
H	2.31071613	1.28161707	-1.1947826
O	-2.2105859	1.52597734	2.33668893
C	-2.9619082	2.35650305	1.87248273
O	-2.9390719	2.8306778	0.65370501
O	-3.9507227	2.9204578	2.56832451
H	-3.9295175	2.5490762	3.46471204

B

5

O	-0.7538088	0.62035719	0.01626688
C	0.64650133	0.64635224	0.01308024
O	1.14810297	1.13241258	-1.0078035
O	1.1871115	0.17963147	1.03250463
H	-0.993697	0.22583652	0.86582176

BH

6

O	-0.6908984	0.62143832	-0.0288055
C	0.63249893	0.70568302	-0.0376014
O	1.30009982	1.10140683	-0.9583417
O	1.10386291	0.28481818	1.12831462
H	-1.0202234	0.93212783	-0.8877983
H	2.07235015	0.35296583	1.10667229

Int-3

41

O	6.62876651	3.12973866	-3.6148963
C	6.17307186	2.69879346	-2.5882353
O	6.77415388	2.73700364	-1.413104
C	8.07485682	3.33215835	-1.3503811

C	4.80891715	2.03435615	-2.4808597
N	4.22202707	2.02151898	-3.7794194
C	2.99900715	1.50211174	-4.0468429
C	2.5380259	1.55810764	-5.4686447
C	3.40586228	1.75800544	-6.5473204
C	2.90752719	1.79462759	-7.8462159
C	1.54269582	1.63223983	-8.0764298
C	0.67521215	1.42266287	-7.0052603
C	1.17232725	1.38001145	-5.7078456
O	2.29953031	1.01934648	-3.1613632
C	4.00093511	2.61350109	-1.2714398
C	4.51553356	1.48462147	-0.4663947
C	4.67611479	1.27750985	0.90230281
C	5.26275897	0.07318608	1.37479258
C	5.39531805	-0.1376019	2.7315207
C	4.95279559	0.84286604	3.62796288
C	4.37537218	2.03807318	3.18214923
C	4.236615	2.26125852	1.82795916
C	4.90115179	0.70408547	-1.6638278
H	8.38782336	3.26465256	-0.3038721
H	8.024014	4.38076459	-1.6712683
H	8.77061858	2.78227834	-1.9975443
H	4.76005829	2.49102028	-4.5014432
H	4.4813822	1.86344057	-6.3918592
H	3.59081563	1.94624195	-8.6840635
H	1.15398722	1.66454531	-9.0965209
H	-0.3939307	1.2911181	-7.1834739
H	0.50993899	1.21094131	-4.8581292
H	2.9304845	2.42200539	-1.4664748
H	4.15077974	3.64483919	-0.9277965

H	5.60324701	-0.6781525	0.66026078
H	5.84289599	-1.0587918	3.10651498
H	5.06318836	0.67257687	4.70147914
H	4.04175401	2.78582505	3.9026163
H	3.79188464	3.18778254	1.46104011
H	4.04186539	0.06980885	-1.9444418
H	5.82481642	0.11178124	-1.65219

Int-4a

41

O	-1.7663225	2.40736758	2.64645711
C	-0.622415	2.09280371	2.43078253
O	0.4306356	2.52350126	3.08902214
C	0.20036986	3.44966811	4.15722766
C	-0.2326863	1.12920495	1.3403947
N	-1.433645	0.70361406	0.63179572
C	-1.2961066	-0.1375584	-0.3583884
C	-2.393072	-0.6559756	-1.1717448
C	-2.1159952	-1.6599049	-2.1097042
C	-3.1416109	-2.1716437	-2.8929165
C	-4.4392811	-1.6837557	-2.7474758
C	-4.7164657	-0.6813555	-1.8177723
C	-3.6982069	-0.1654942	-1.0287056
O	-0.0957113	-0.5498173	-0.6441155
C	0.60676866	-0.1389007	1.63540803
C	1.0370693	-0.0414454	0.16481359
C	2.27662487	-0.656062	-0.3909146
C	2.58953344	-0.4616847	-1.7401888
C	3.74775276	-1.0144437	-2.2739702
C	4.60236	-1.7622638	-1.4631684

C	4.29340576	-1.9567637	-0.120002
C	3.13054296	-1.4063122	0.41651711
C	0.83486646	1.48124299	0.27790754
H	1.18571428	3.68404868	4.57140154
H	-0.4407367	2.99092804	4.92141519
H	-0.2816467	4.35706495	3.77022779
H	-2.3328809	1.07140301	0.94415984
H	-1.0982556	-2.0353972	-2.215289
H	-2.9280304	-2.9555992	-3.6212373
H	-5.2438004	-2.0866093	-3.3661822
H	-5.731965	-0.2971858	-1.7097031
H	-3.930578	0.62598135	-0.3146585
H	0.07214291	-1.0383352	1.96647518
H	1.44059797	0.10099401	2.30291223
H	1.91877	0.12267963	-2.3741705
H	3.98791042	-0.8608821	-3.3279559
H	5.51315983	-2.1948562	-1.8825964
H	4.95883503	-2.5427021	0.51703912
H	2.8936513	-1.566382	1.46996653
H	0.50741017	2.03421451	-0.6119235
H	1.71123065	1.94663366	0.74100987

3a

40

O	-0.8265087	4.01430748	-0.0594437
C	0.11802571	3.27390321	0.02791667
O	1.37539742	3.69957945	0.15618889
C	1.57459207	5.1094697	0.19208219
C	0.06553607	1.76635294	0.01052149
C	0.98845793	0.99458786	-0.9731744

C	0.95473696	-0.13374	0.07951872
C	0.78527061	0.97556147	1.13910294
C	2.05108405	-1.1527192	0.17045265
C	3.37258681	-0.7215517	0.33073713
C	4.41226962	-1.6415675	0.41172798
C	4.14536048	-3.0081092	0.3344171
C	2.83304722	-3.4435616	0.17489647
C	1.7903007	-2.5219857	0.09215503
O	-0.3065437	-0.8102132	-0.0464828
C	-1.3786244	0.0058063	-0.1450198
C	-2.6654939	-0.7122582	-0.2809188
C	-2.7173422	-2.1087172	-0.2501659
C	-3.9391219	-2.7638415	-0.3809763
C	-5.1121507	-2.0305885	-0.5434942
C	-5.0631373	-0.6363756	-0.5744104
C	-3.8460795	0.02074101	-0.443491
N	-1.2865161	1.27438176	-0.1250547
H	1.04923937	5.55019818	1.05076603
H	1.20134934	5.57483079	-0.7306303
H	2.65435473	5.26579331	0.2871286
H	0.5855608	0.77214897	-1.9704713
H	1.98332846	1.4476563	-1.0344338
H	1.74769366	1.42791106	1.39905606
H	0.19898535	0.73518421	2.03627998
H	3.59647253	0.34574245	0.39364906
H	5.43824565	-1.2886144	0.53648146
H	4.96126776	-3.7313091	0.39886496
H	2.61401638	-4.5118461	0.11338082
H	0.76536187	-2.867522	-0.0349883
H	-1.798042	-2.6799013	-0.1217534
H	-3.9741558	-3.8549917	-0.3558916
H	-6.0694101	-2.5463506	-0.6467848

H	-5.9811941	-0.0590181	-0.702204
H	-3.7882913	1.10942593	-0.4660348

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40

O	0.92103601	4.09005283	0.76800924
C	0.22433007	3.61614844	-0.0923842
O	-0.0760348	4.21828669	-1.2350317
C	0.49229467	5.50950593	-1.4446079
C	-0.4481173	2.28323292	0.0204498
N	0.31587922	1.08290473	0.46117069
C	1.42270244	0.6799375	-0.2511937
C	1.82696136	-0.7441839	-0.0781319
C	2.53278066	-1.3624602	-1.1139651
C	2.89787548	-2.7000035	-1.0079282
C	2.57632565	-3.4200792	0.14262015
C	1.89417385	-2.7997653	1.18818122
C	1.51788219	-1.4649771	1.07860074
O	2.05317872	1.46224312	-0.9464507
C	-1.1675334	1.43346754	-1.0491232
C	-1.1344255	0.59076448	0.25211616
C	-1.5532562	-0.8149989	0.46863845
C	-1.945638	-1.2454943	1.73803829
C	-2.2779768	-2.5796913	1.95437297
C	-2.2227575	-3.4915262	0.90132733
C	-1.8439084	-3.0644126	-0.3702793
C	-1.5127586	-1.7301038	-0.5859703
C	-1.5451938	1.86329922	1.02728786
H	1.58915124	5.44600305	-1.453021

H	0.12326432	5.85311309	-2.4166073
H	0.17978471	6.20091421	-0.6500075
H	2.77985163	-0.7826668	-2.0048877
H	3.43594099	-3.1848116	-1.8251465
H	2.86490923	-4.4702322	0.2266151
H	1.65228865	-3.3594558	2.09397163
H	0.98904141	-0.9732679	1.8945066
H	-0.5479003	1.08609206	-1.8851002
H	-2.1566316	1.78000283	-1.3763594
H	-1.9802092	-0.5315404	2.5637495
H	-2.5803447	-2.9107282	2.95013335
H	-2.4792604	-4.5393411	1.07207179
H	-1.8034597	-3.7755731	-1.1979291
H	-1.2063844	-1.3972897	-1.5797963
H	-1.2525449	1.90444972	2.08296333
H	-2.5553268	2.24219485	0.8320971

TS-2’

Imaginary frequency = -258.01 cm^{-1}

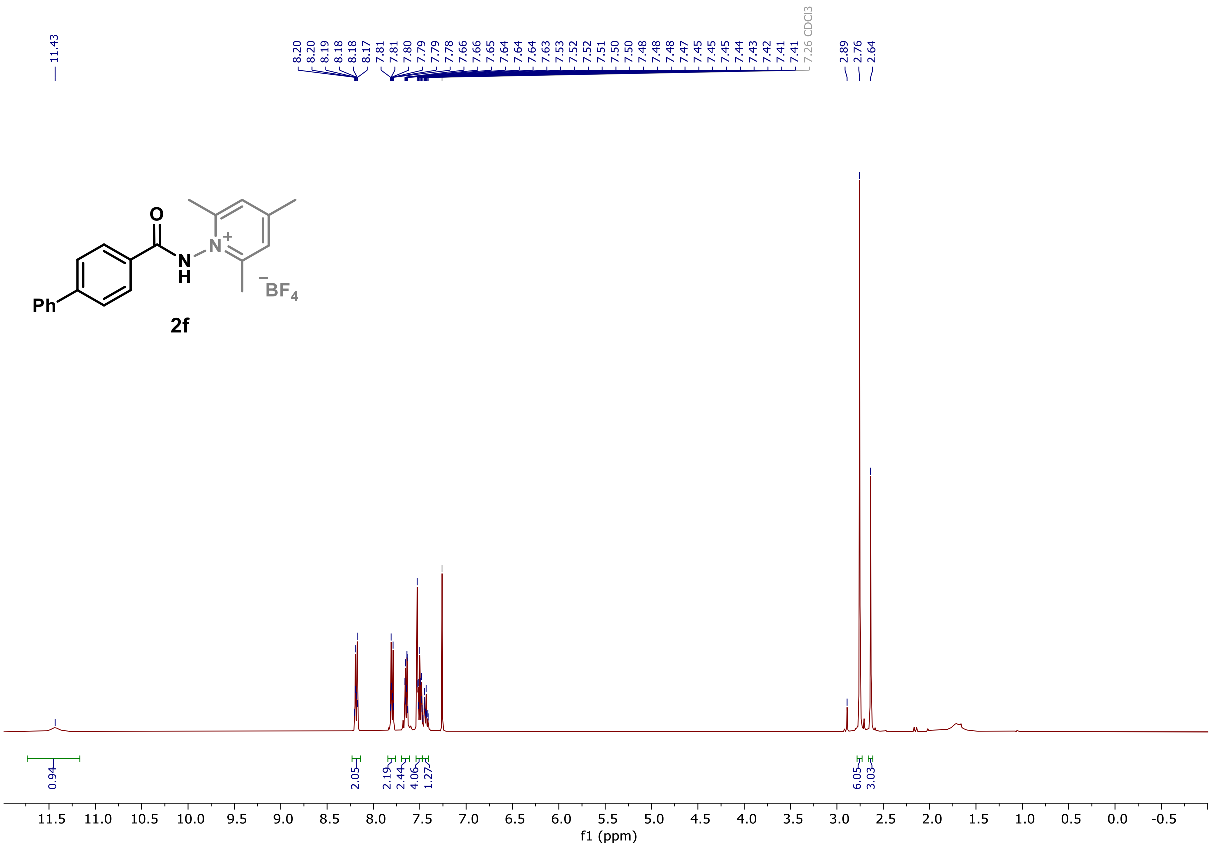
46

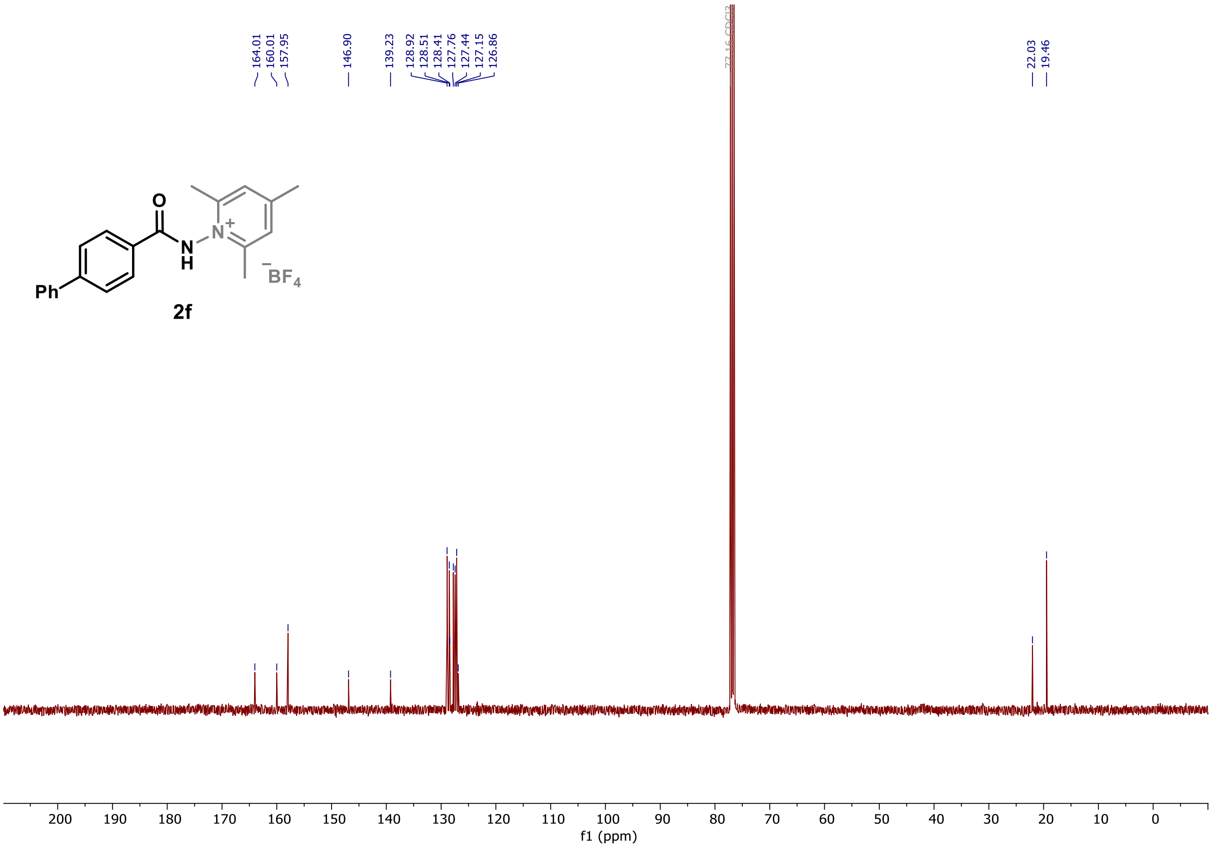
O	3.32958765	0.30348825	-1.9027725
C	3.19353303	0.76197523	-0.7978801
O	4.09732094	1.51577441	-0.1825008
C	5.2994405	1.78954799	-0.8995314
C	1.99611363	0.50782156	0.07678646
N	0.75280664	0.12838999	-0.5814248
C	0.14616133	1.10781774	-1.3092831
C	-1.2546353	0.80331	-1.7444512
C	-1.8512775	1.61761989	-2.7105979
C	-3.1567638	1.37561102	-3.124789

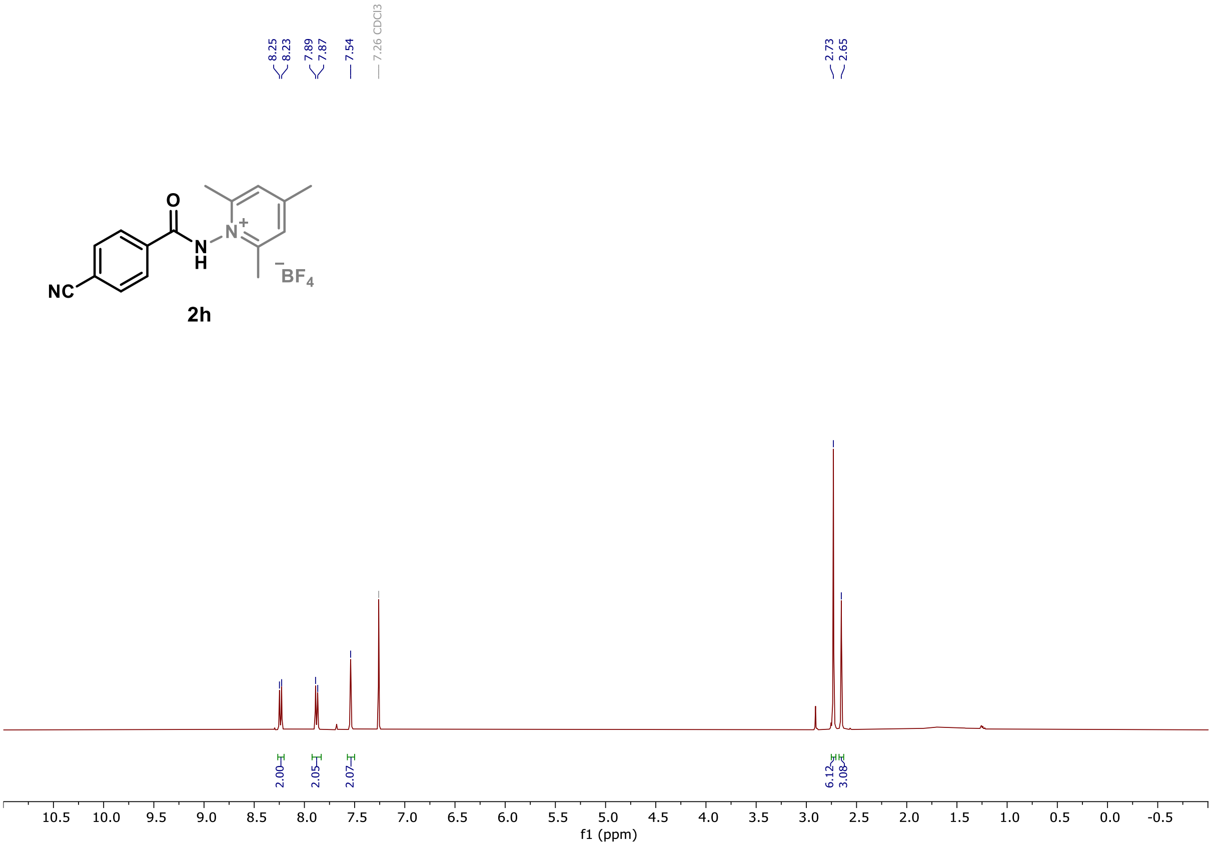
C	-3.8801377	0.32243109	-2.5651519
C	-3.2951095	-0.4855559	-1.5912674
C	-1.9855718	-0.2492598	-1.1834963
O	0.68256	2.17866621	-1.5909071
C	1.48167152	1.50406684	1.14673766
C	0.79657738	0.24092876	1.57162859
C	-0.443172	-0.0309522	2.21767568
C	-0.8415925	-1.3602848	2.46022592
C	-2.051833	-1.607335	3.0889181
C	-2.8665719	-0.5406834	3.47616316
C	-2.4830416	0.78000414	3.23151103
C	-1.2779369	1.03779416	2.5980368
C	1.98186049	-0.5890864	1.17750237
H	5.91925081	2.40299243	-0.2372027
H	5.07586688	2.33550124	-1.8263504
H	5.81826354	0.85433765	-1.1512972
H	0.67869553	-1.27116	-1.2274158
H	-1.2711842	2.44151461	-3.128904
H	-3.6148829	2.01054359	-3.8862636
H	-4.9061351	0.1324442	-2.888564
H	-3.8627045	-1.3053503	-1.1458749
H	-1.5267685	-0.8776435	-0.4202323
H	0.88977931	2.35826965	0.80384429
H	2.24689253	1.80579127	1.87679465
H	-0.2150329	-2.1814142	2.11057113
H	-2.3715339	-2.6340798	3.27486596
H	-3.8194316	-0.7417619	3.97102761
H	-3.1318605	1.60389181	3.53308481
H	-0.9683597	2.06409235	2.39373938
H	1.81087646	-1.6242183	0.86619873

H	2.79461289	-0.4890728	1.9123499
O	0.61810078	-2.1570897	-1.7894424
C	0.45859494	-3.2120476	-1.0523428
O	0.41286835	-3.2506498	0.16444185
O	0.35011191	-4.3096721	-1.8055778
H	0.24399043	-5.0673086	-1.2085825

12. NMR spectra



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8.23
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7.87
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N
H
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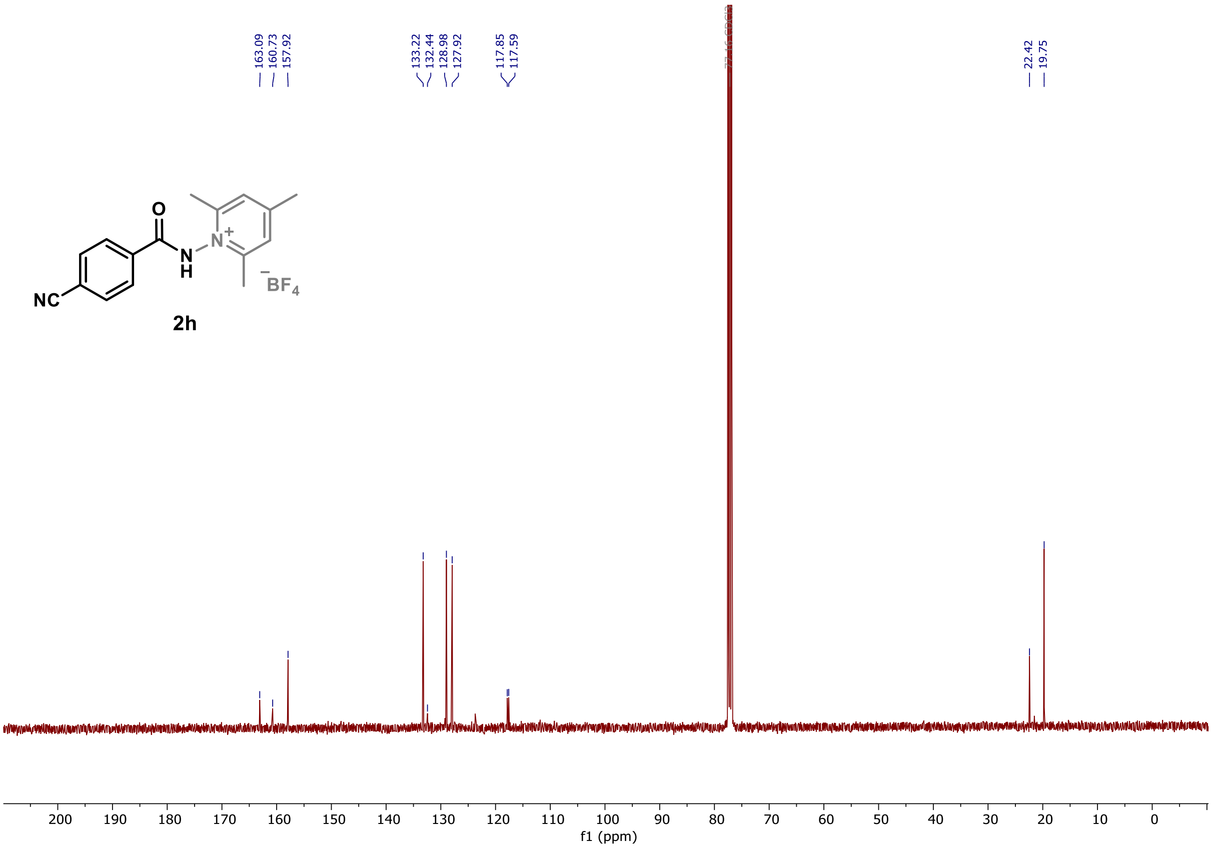
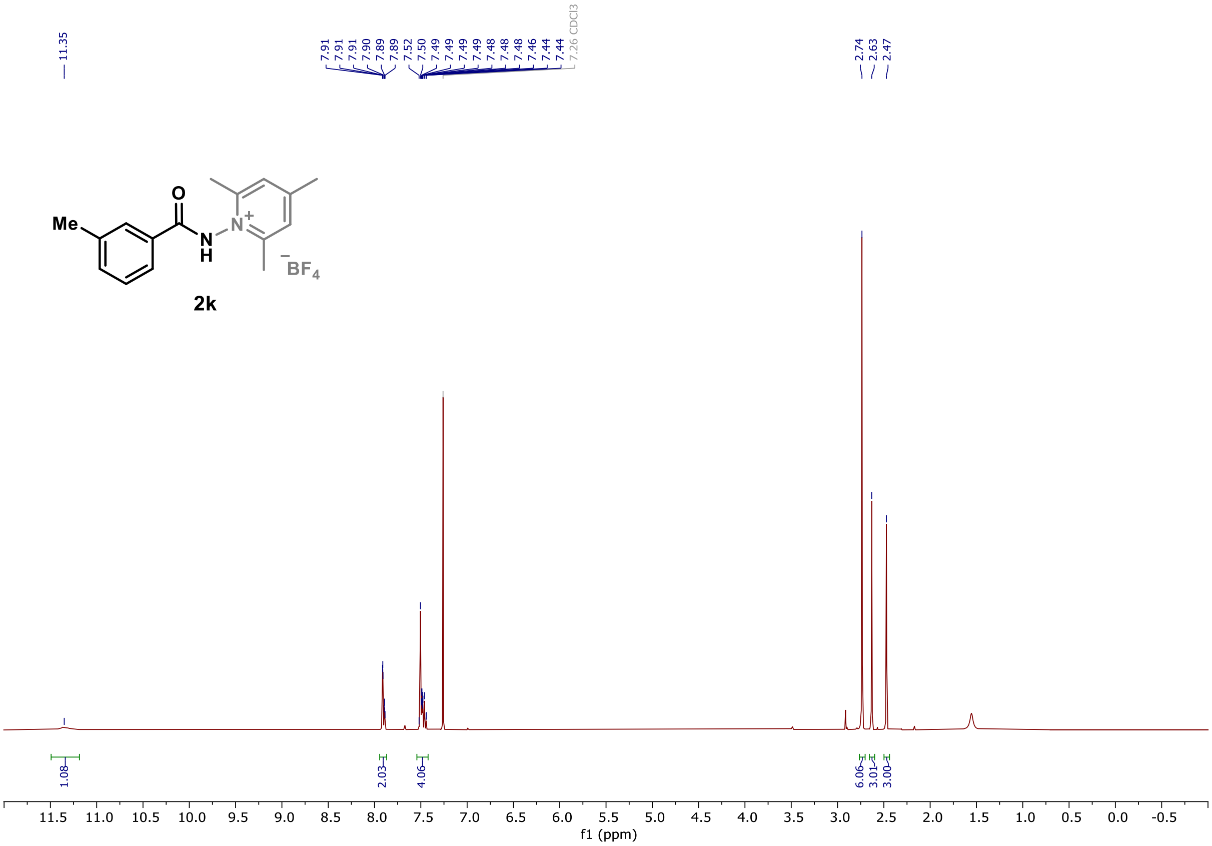
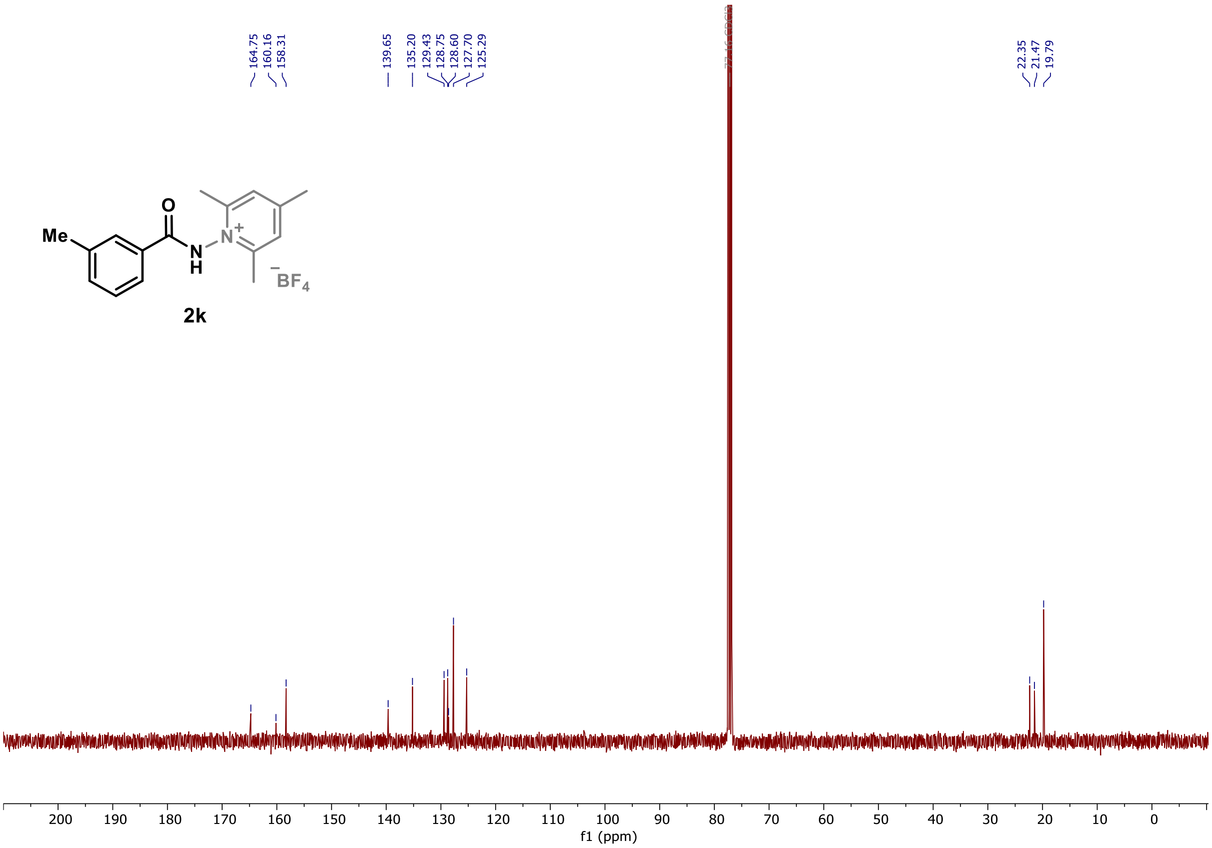
2.00
2.05
2.07
6.12
3.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

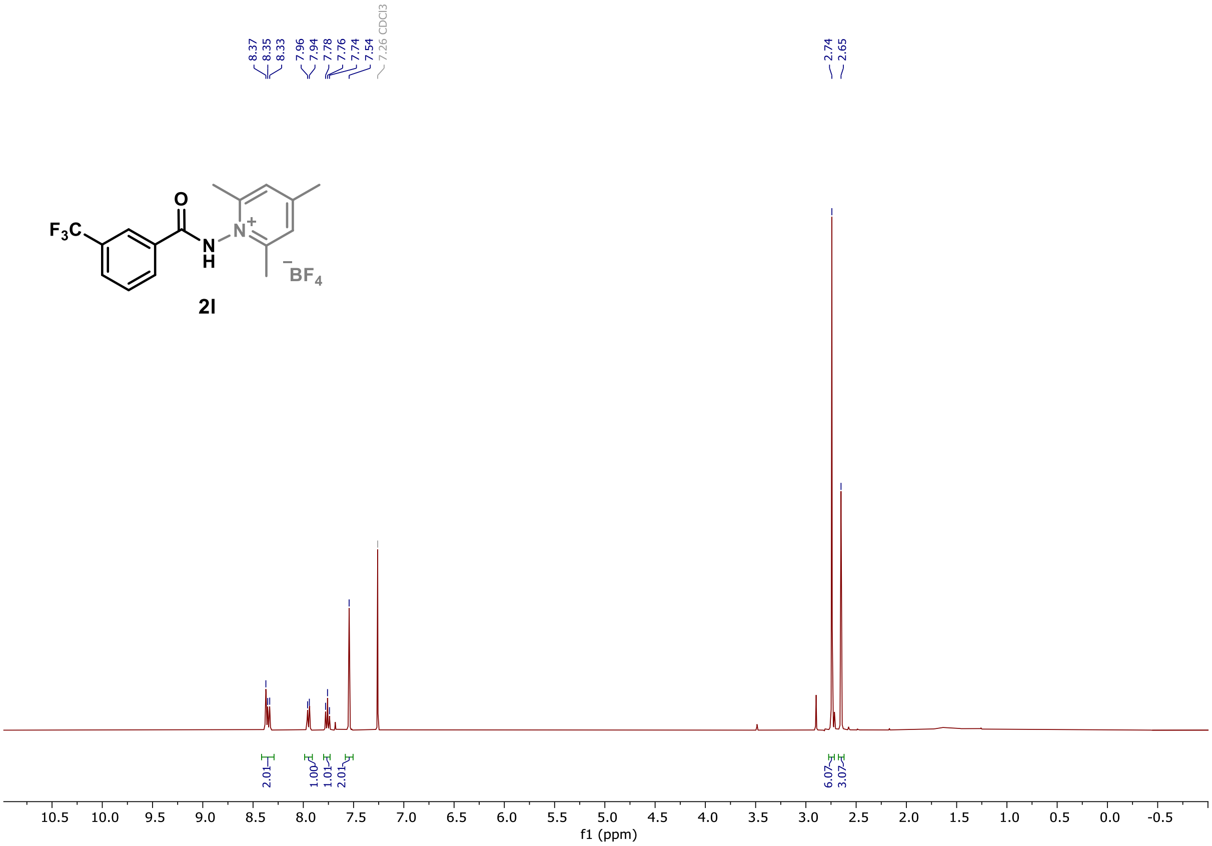
2h

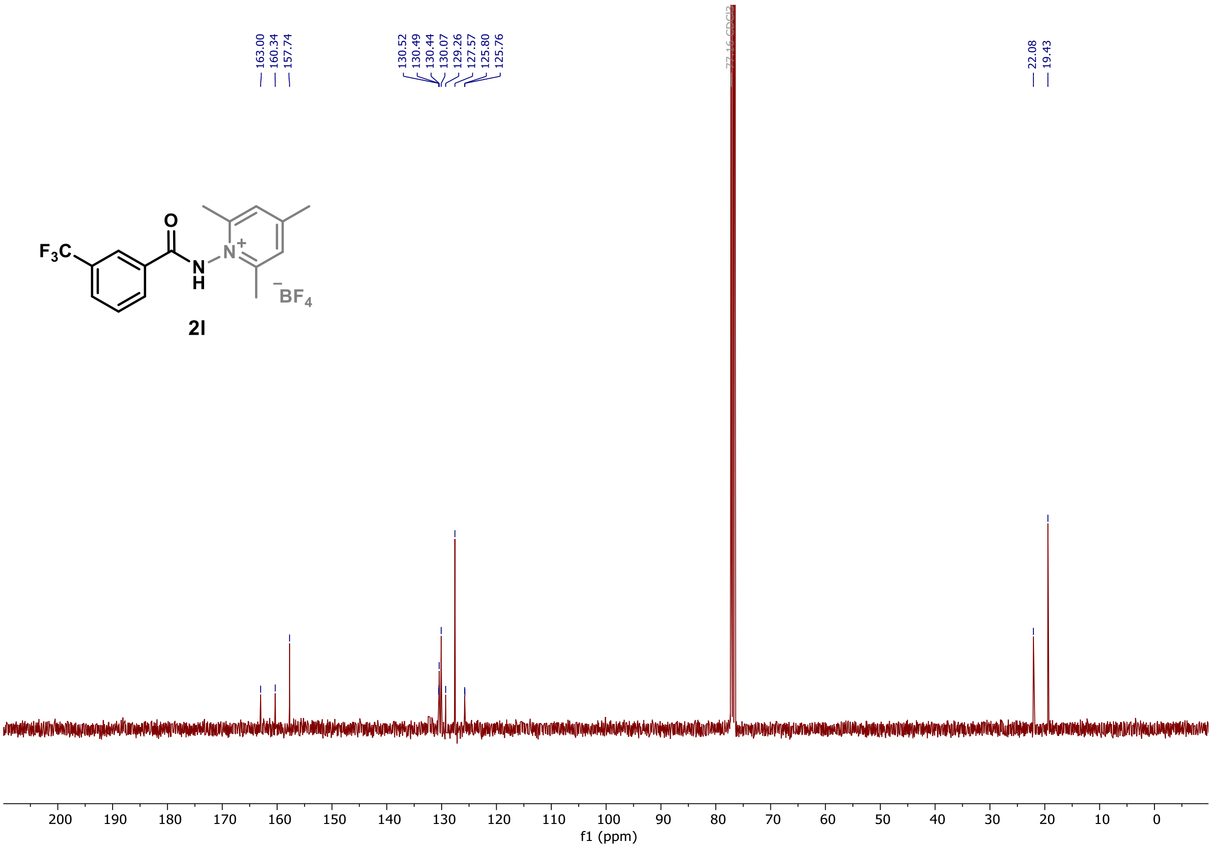

163.09
160.73
157.92
133.22
132.44
128.98
127.92
117.85
117.59
22.42
19.75
O
N
H
N+
NC
−BF4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

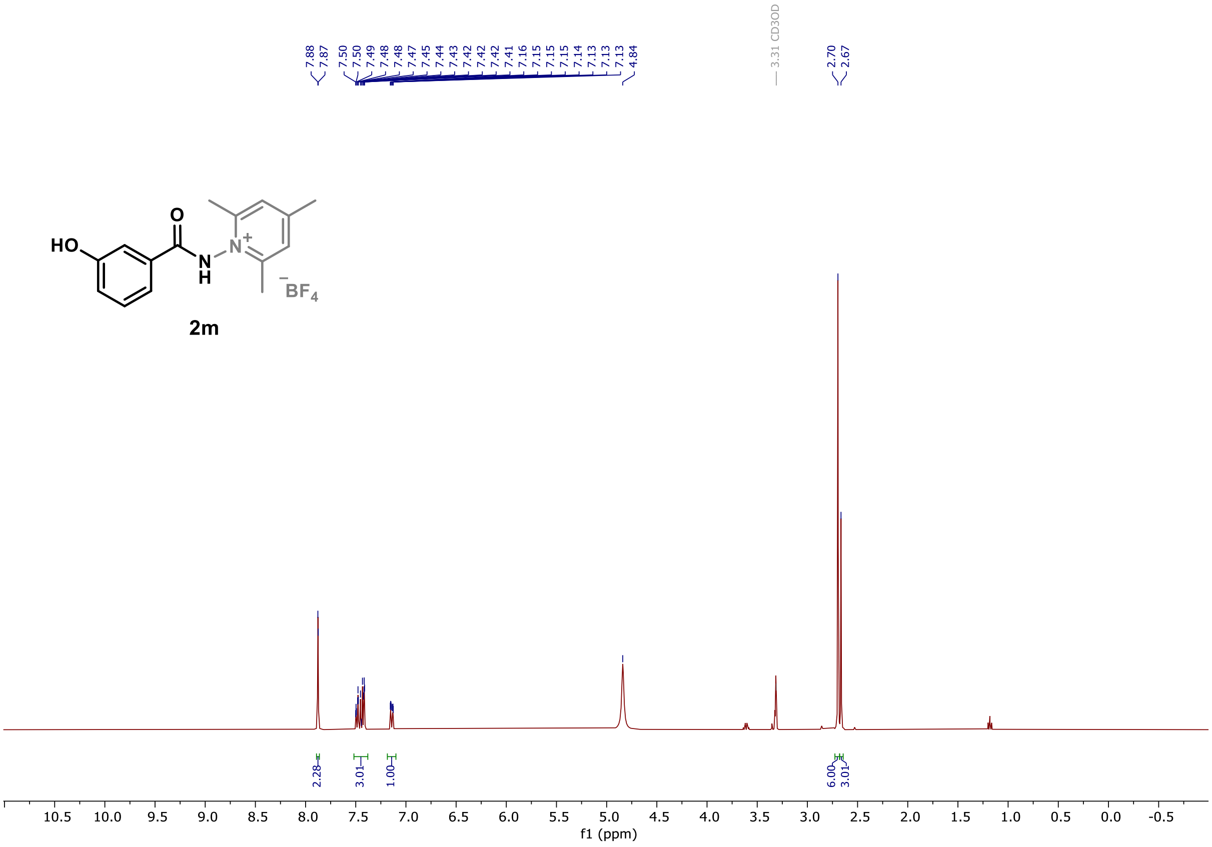
2h

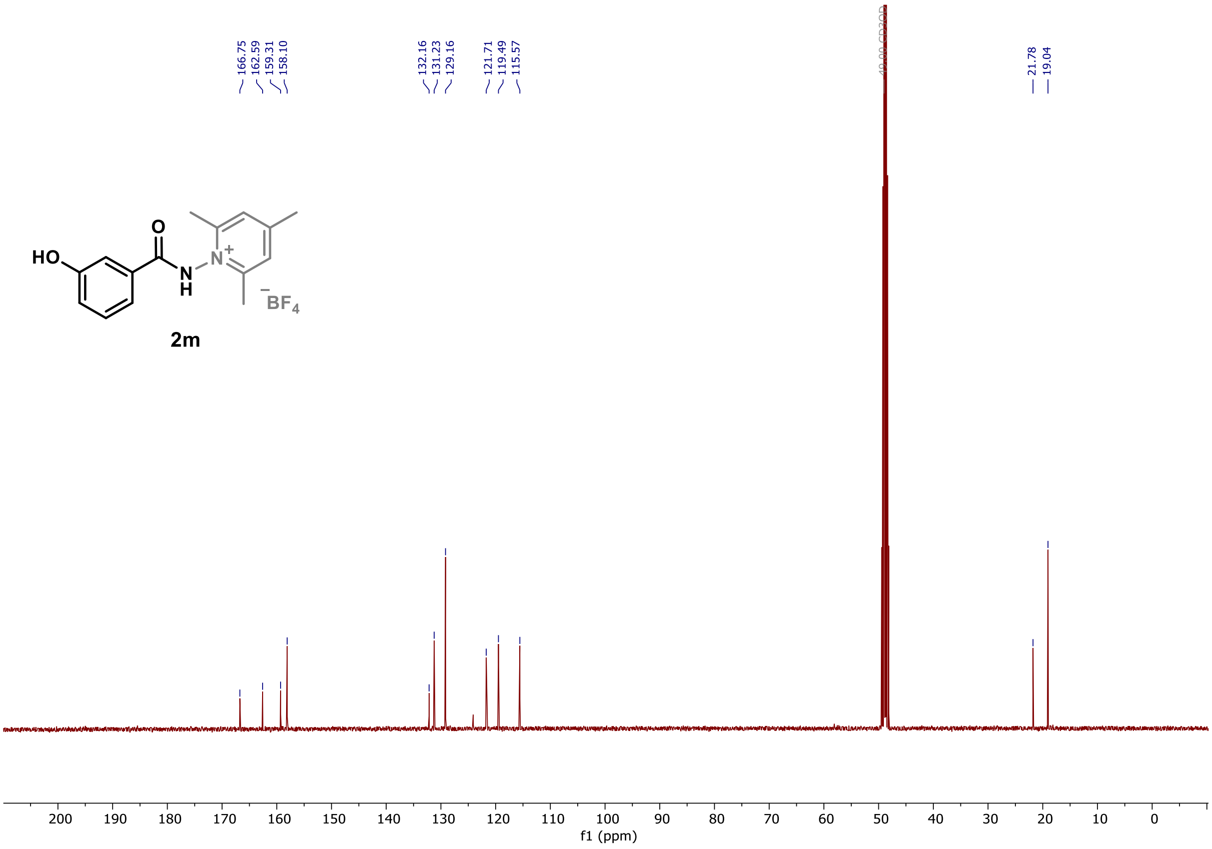

11.35
7.91
7.91
7.91
7.90
7.89
7.89
7.52
7.50
7.49
7.49
7.49
7.49
7.48
7.48
7.46
7.44
7.44
7.26 CDCl3
2.74
2.63
2.47
Me
O
N
H
N+
−BF4
2k
1.08
2.03
4.06
6.06
3.01
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

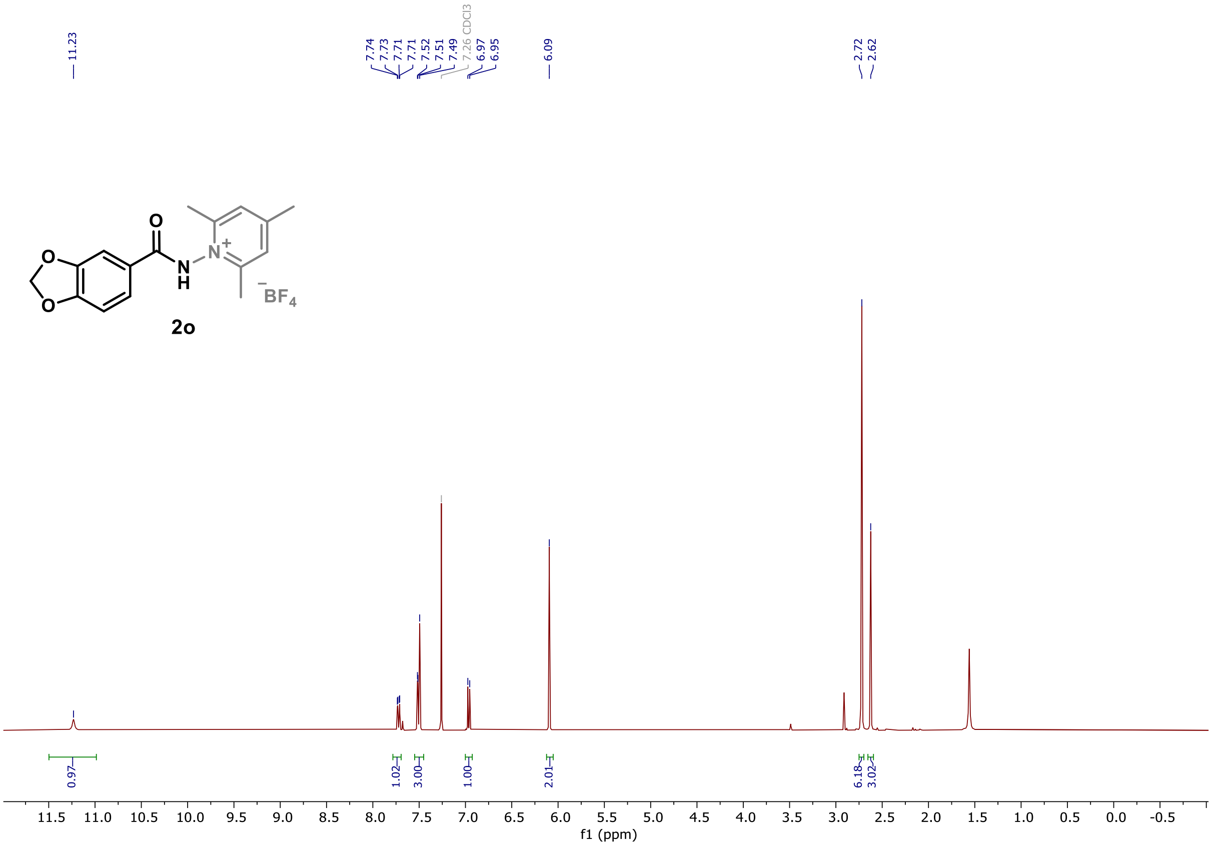

164.75
160.16
158.31
139.65
135.20
129.43
128.75
128.60
127.70
125.29
77.16 CDCl3
22.35
21.47
19.79
Me
O
N
H
N+
−BF4
2k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

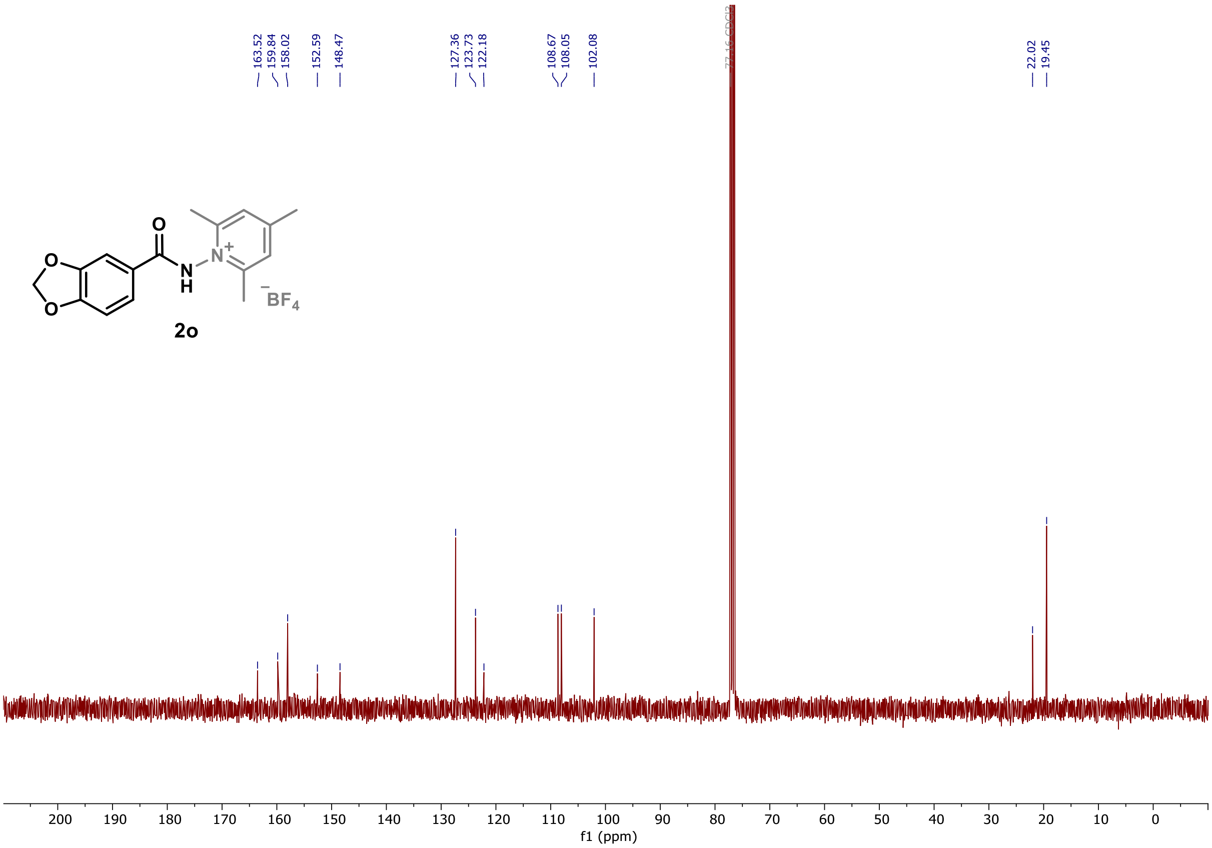

8.37
8.35
8.33
7.96
7.94
7.78
7.76
7.74
7.54
7.26 CDCl3
2.74
2.65
F3C
O
N
H
N+
−BF4
2l
2.01
1.00
1.01
2.01
6.07
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

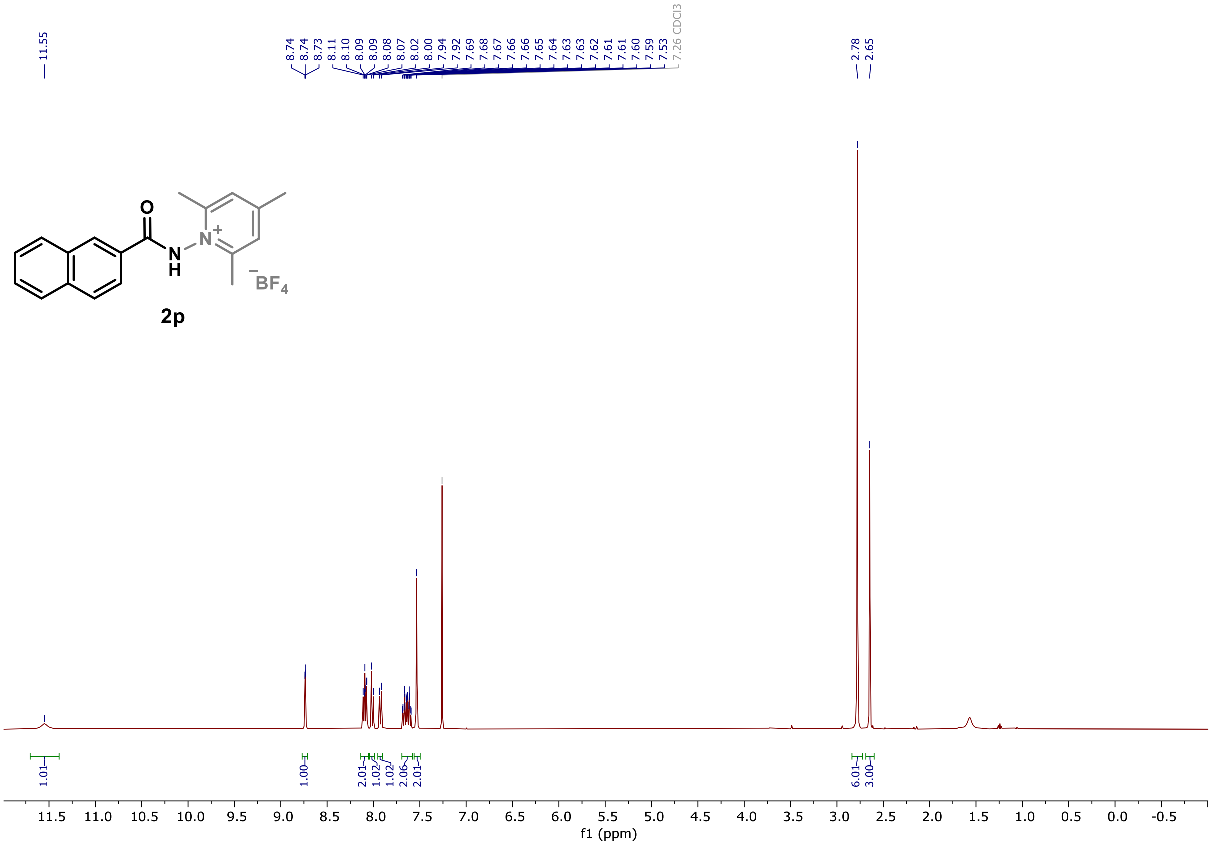

163.00
160.34
157.74
130.52
130.49
130.44
130.07
129.26
127.57
125.80
125.76
77.16 CDCl3
22.08
19.43
F3C
O
N
H
N+
−BF4
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.88
7.87
7.50
7.50
7.49
7.48
7.48
7.47
7.45
7.44
7.43
7.42
7.42
7.42
7.41
7.16
7.15
7.15
7.15
7.14
7.13
7.13
7.13
4.84
3.31 CD3OD
2.70
2.67
HO
O
N
H
N+
−BF4
2m
2.28
3.01
1.00
6.00
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

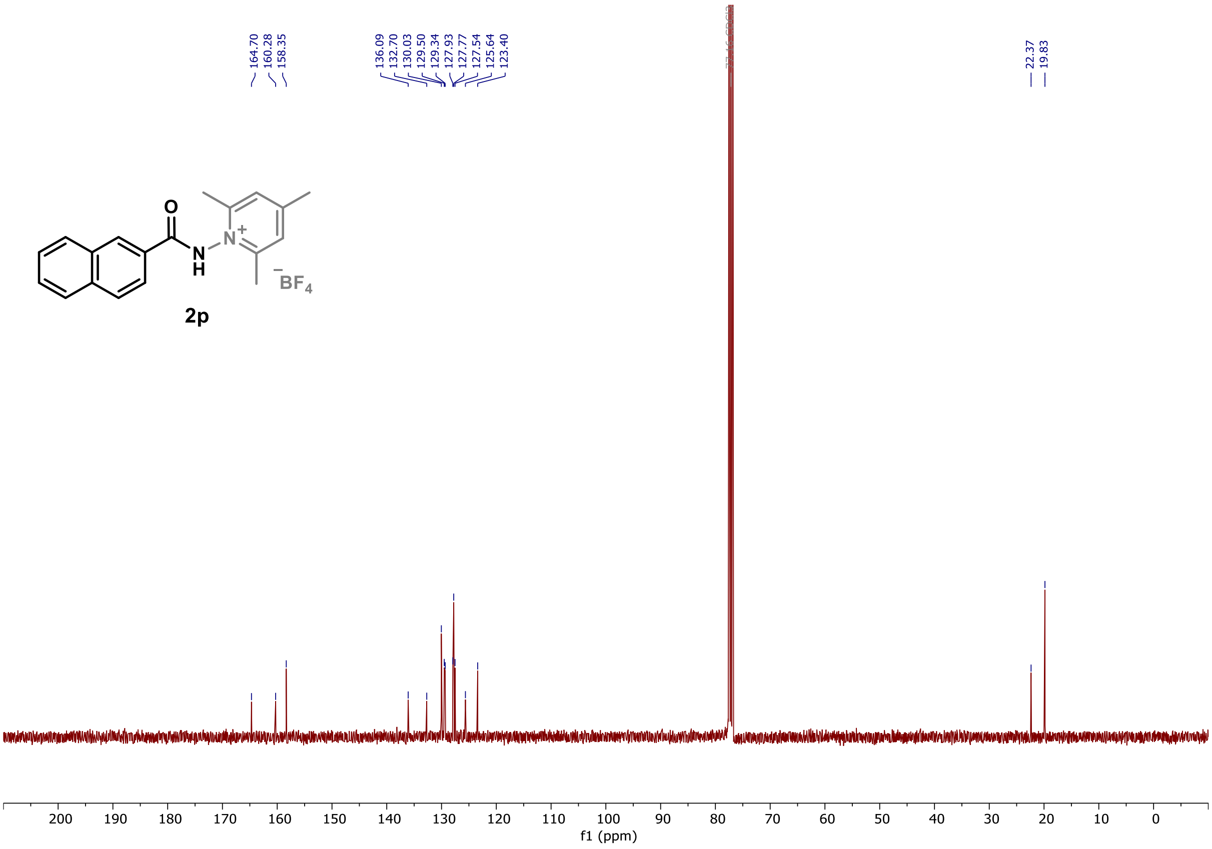

166.75
162.59
159.31
158.10
132.16
131.23
129.16
121.71
119.49
115.57
49.00 CD3OD
21.78
19.04
HO
O
N
H
N+
−BF4
2m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.23
7.74
7.73
7.71
7.71
7.52
7.51
7.49
7.26 CDCl3
6.97
6.95
6.09
2.72
2.62
O
N
H
N+
BF4
2o
0.97
1.02
3.00
1.00
2.01
6.18
3.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

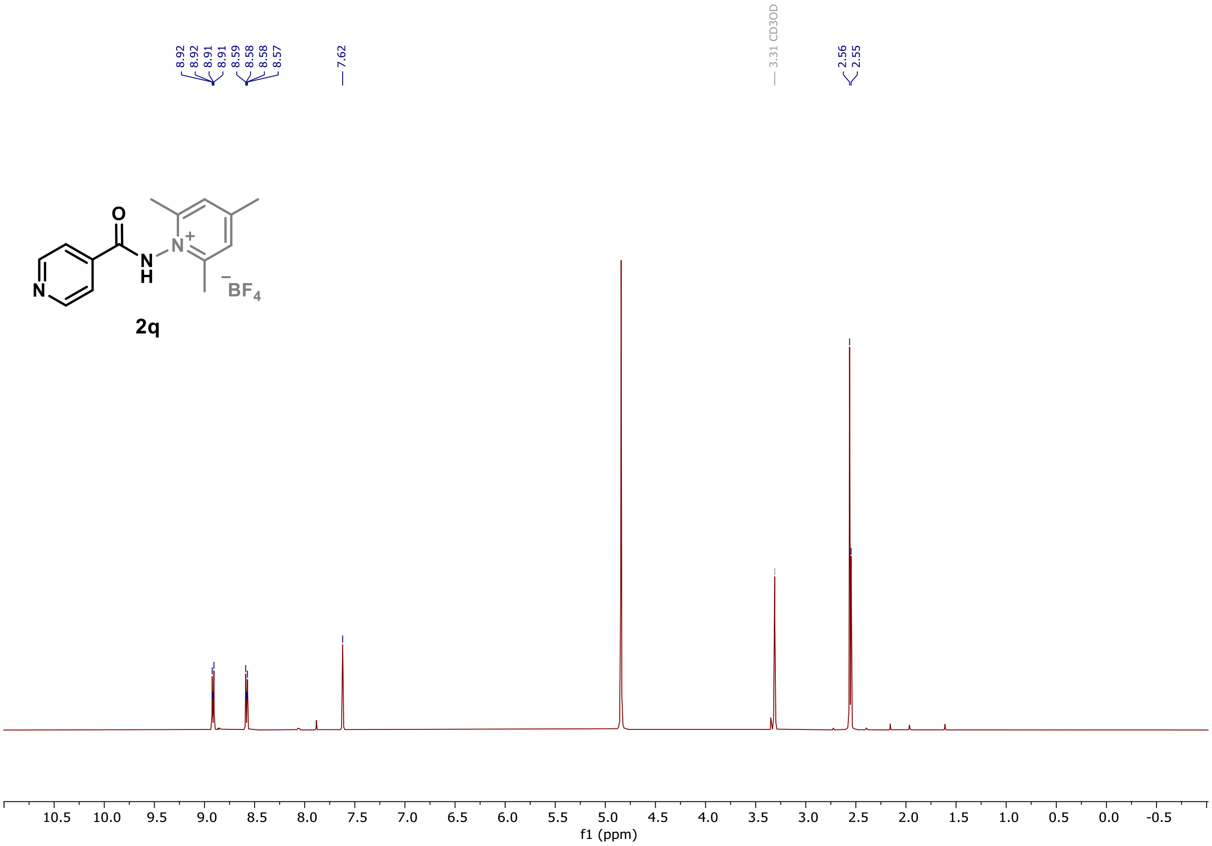

163.52
159.84
158.02
152.59
148.47
127.36
123.73
122.18
108.67
108.05
102.08
77.16 CDCl3
22.02
19.45
O
N
H
N+
BF4
2o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

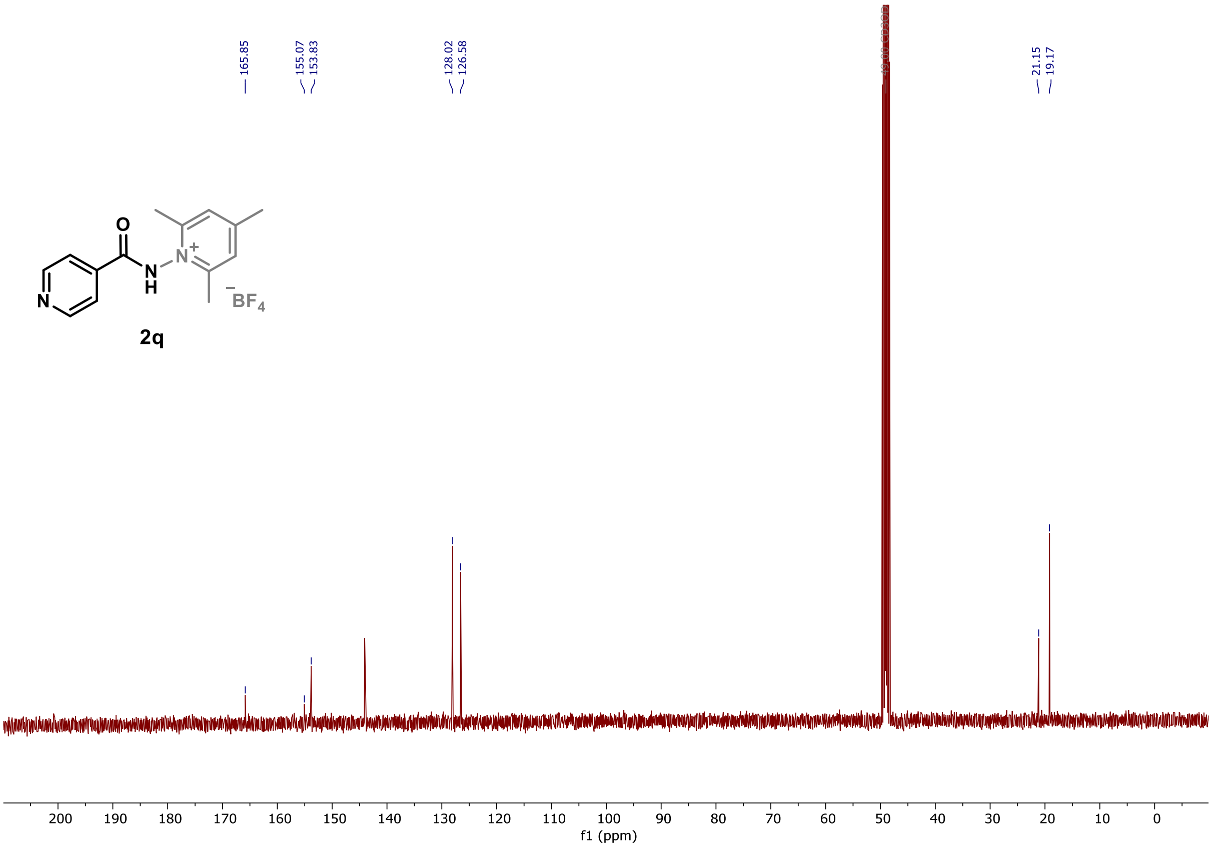

11.55
8.74
8.74
8.73
8.11
8.10
8.09
8.09
8.08
8.07
8.02
8.00
7.94
7.92
7.69
7.68
7.67
7.66
7.66
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.60
7.59
7.53
7.26 CDCl3
2.78
2.65
O
N
H
N
+
$^{-}BF_4$
1.01
1.00
2.01
1.02
1.02
2.06
2.01
6.01
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

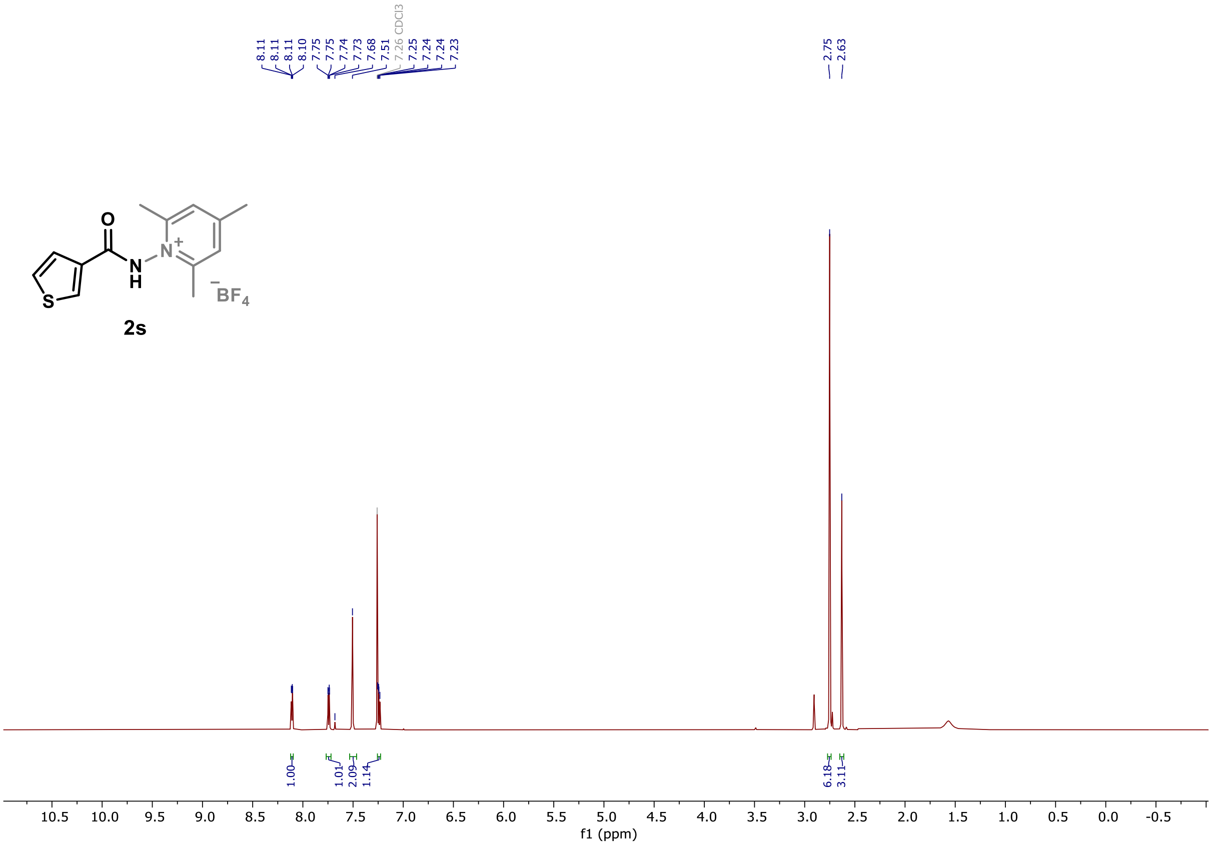
2p

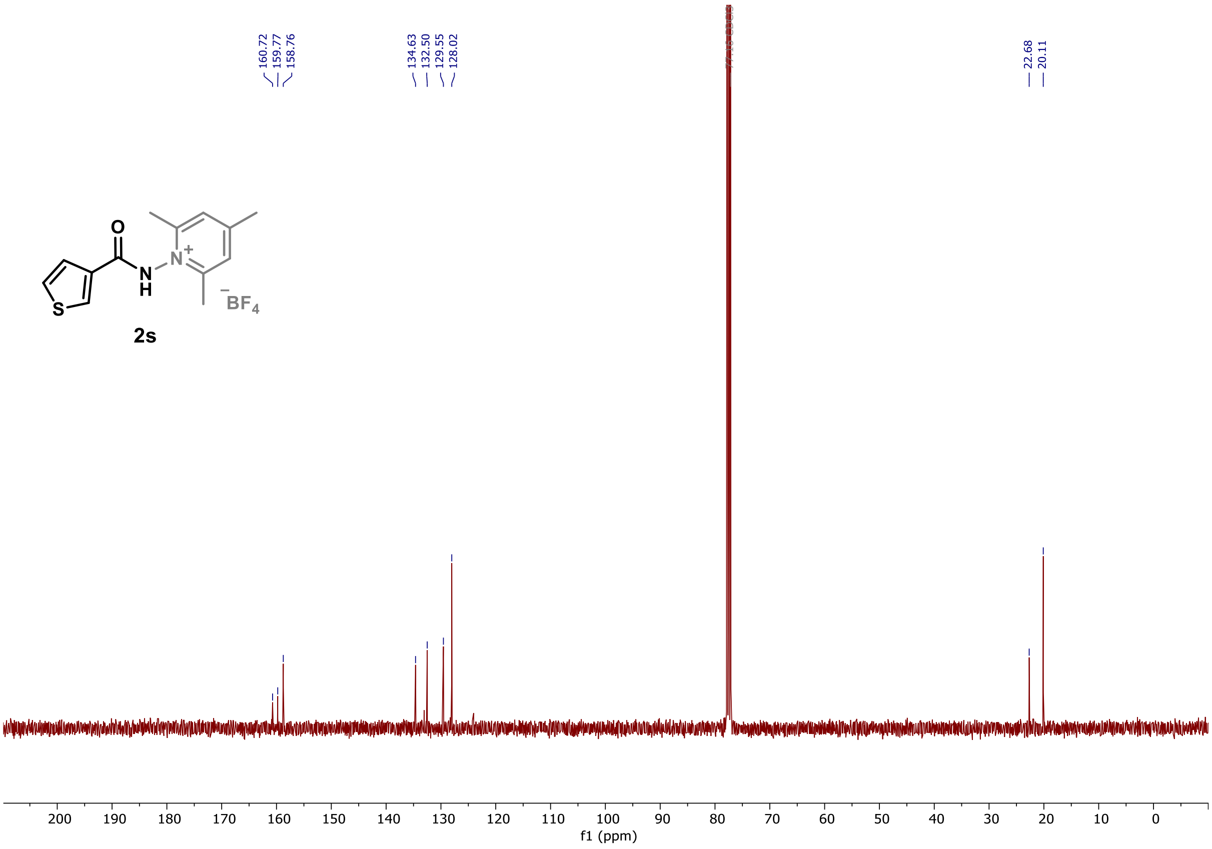

164.70
160.28
158.35
136.09
132.70
130.03
129.50
129.34
127.93
127.77
127.54
125.64
123.40
22.37
19.83
O
N
H
N
+
$^{-}BF_4$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

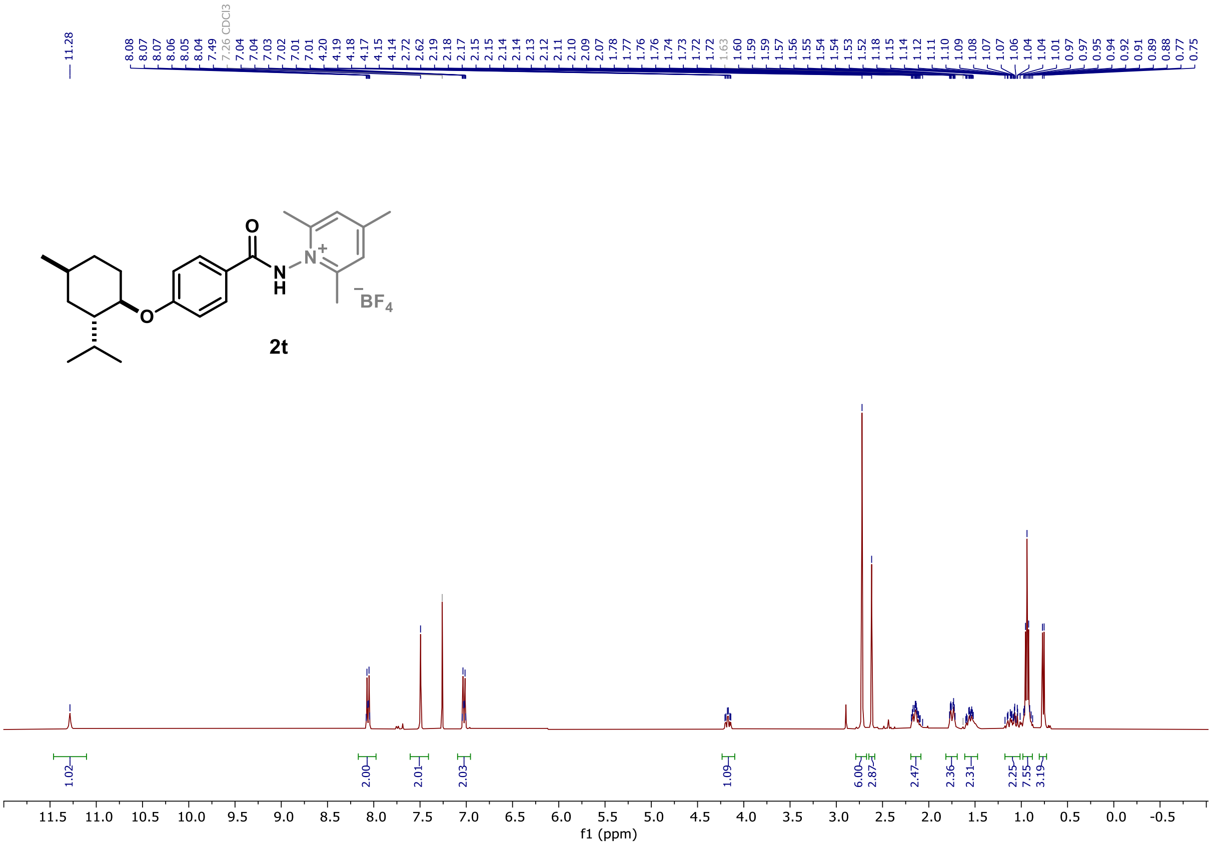
2p


8.92
8.92
8.91
8.91
8.59
8.58
8.58
8.57
7.62
3.31 CD3OD
2.56
2.55
O
N
H
N
+
N
−
BF4
2q
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

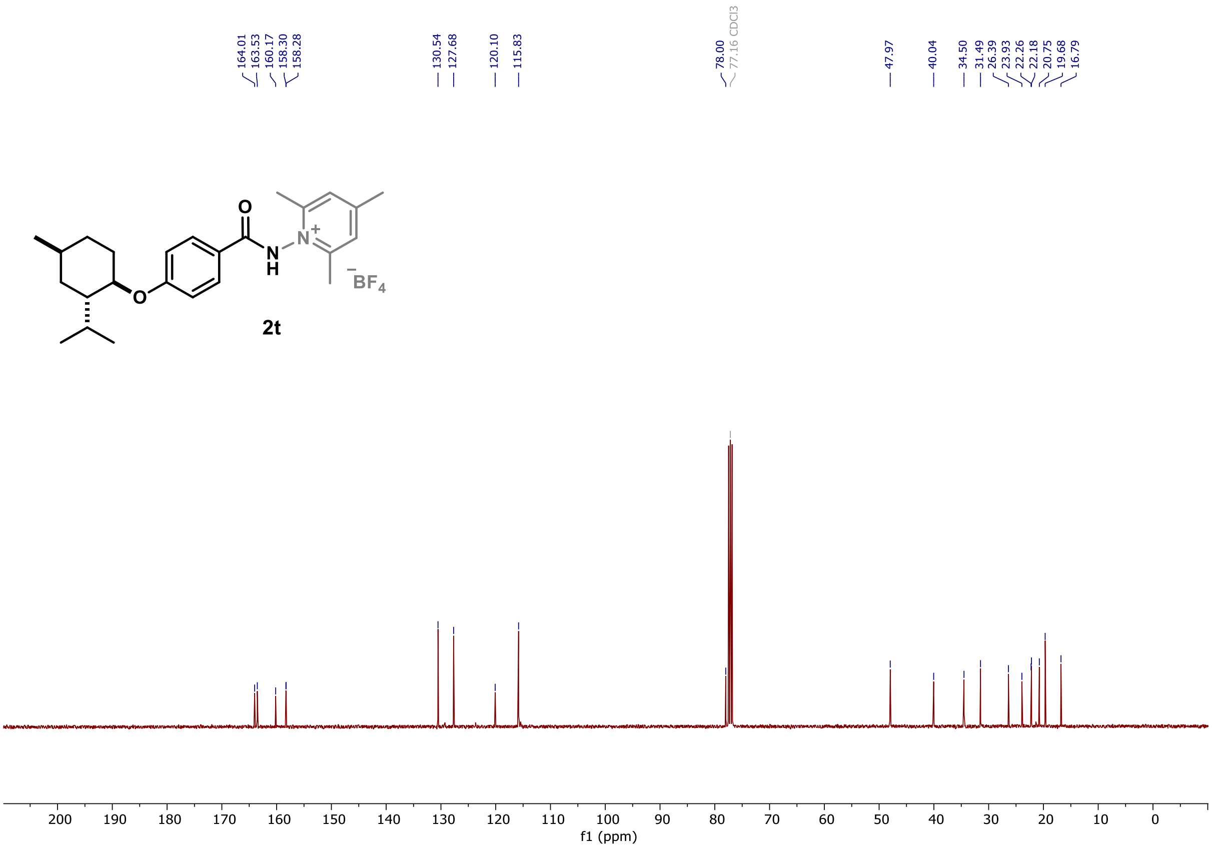

165.85
155.07
153.83
128.02
126.58
21.15
19.17
O
N
H
N
+
N
−
BF4
2q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.11
8.11
8.11
8.10
7.75
7.75
7.74
7.73
7.68
7.51
7.26 CDCl3
7.25
7.24
7.24
7.23
2.75
2.63
O
N
H
N+
S
BF4
2s
1.00
1.01
2.09
1.14
6.18
3.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

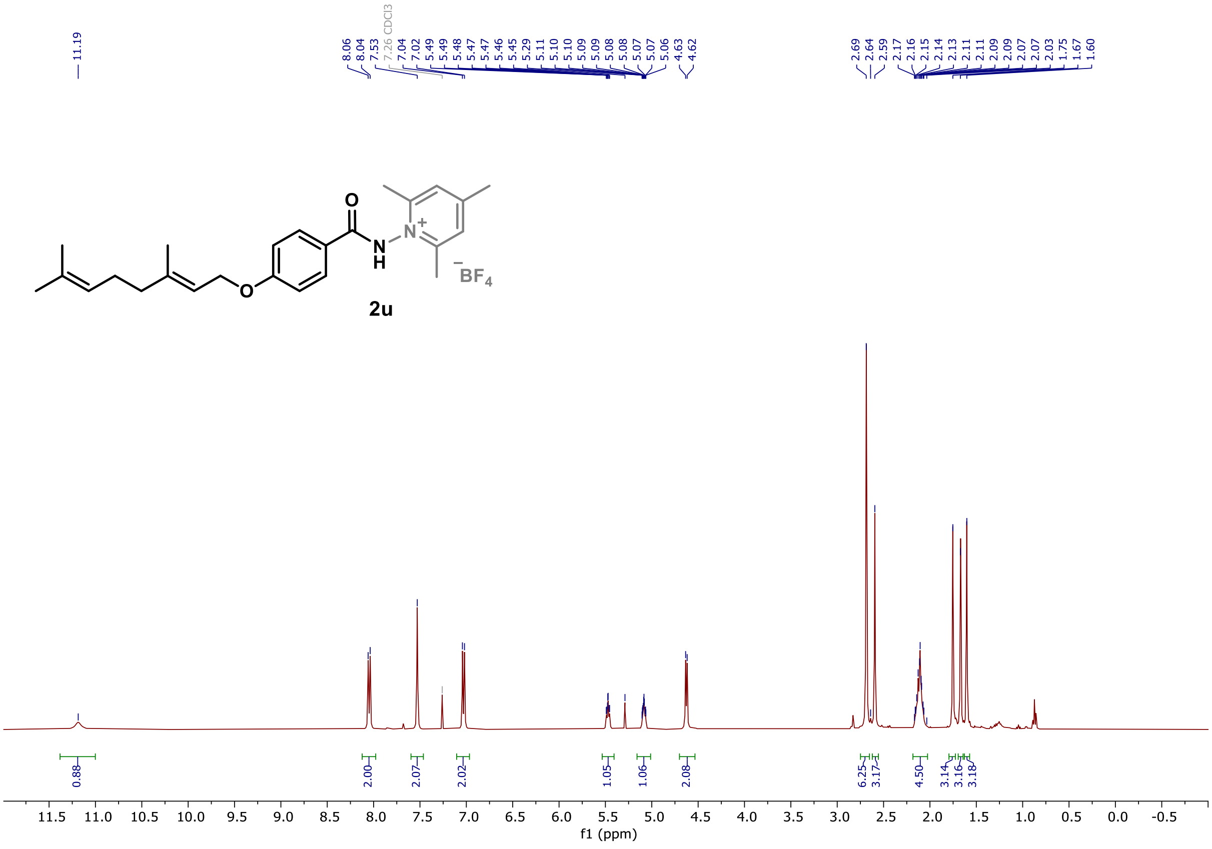

160.72
159.77
158.76
134.63
132.50
129.55
128.02
22.68
20.11
O
N
H
N+
S
BF4
2s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

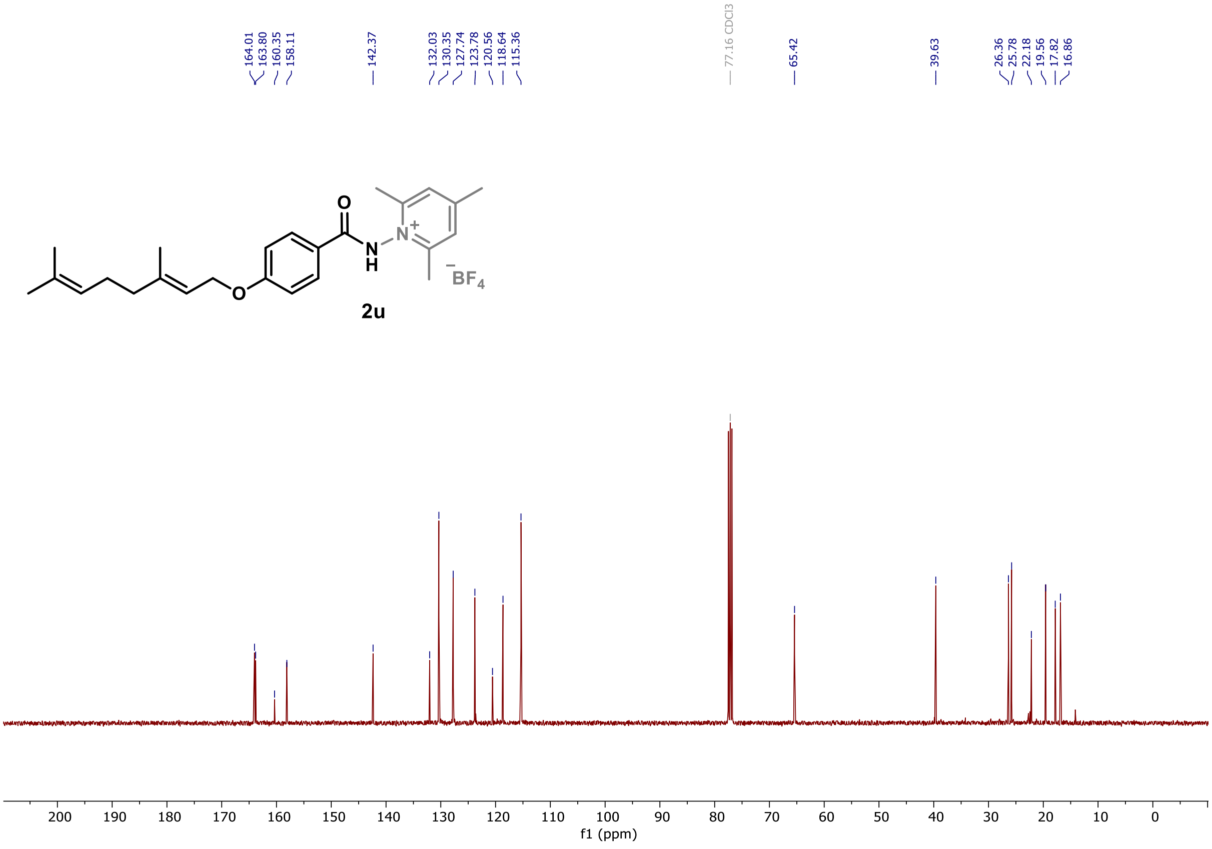

11.28
8.08
8.07
8.07
8.06
8.05
8.04
7.49
7.26 CDCl3
7.04
7.04
7.03
7.02
7.01
7.01
4.20
4.19
4.18
4.17
4.15
4.14
2.72
2.62
2.19
2.18
2.17
2.15
2.15
2.14
2.14
2.13
2.12
2.11
2.10
2.09
2.07
1.78
1.77
1.76
1.76
1.74
1.73
1.72
1.72
1.63
1.60
1.59
1.59
1.57
1.56
1.55
1.54
1.54
1.53
1.52
1.18
1.15
1.14
1.12
1.11
1.10
1.09
1.08
1.07
1.07
1.06
1.04
1.04
1.01
0.97
0.97
0.95
0.94
0.92
0.91
0.89
0.88
0.77
0.75
O
N
H
N+
−BF4
1.02
2.00
2.01
2.03
1.09
6.00
2.87
2.47
2.36
2.31
2.25
7.55
3.19
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

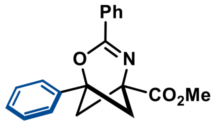
2t


164.01
163.53
160.17
158.30
158.28
130.54
127.68
120.10
115.83
78.00
77.16 CDCl3
47.97
40.04
34.50
31.49
26.39
23.93
22.26
22.18
20.75
19.68
16.79
O
N
H
N+
−BF4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

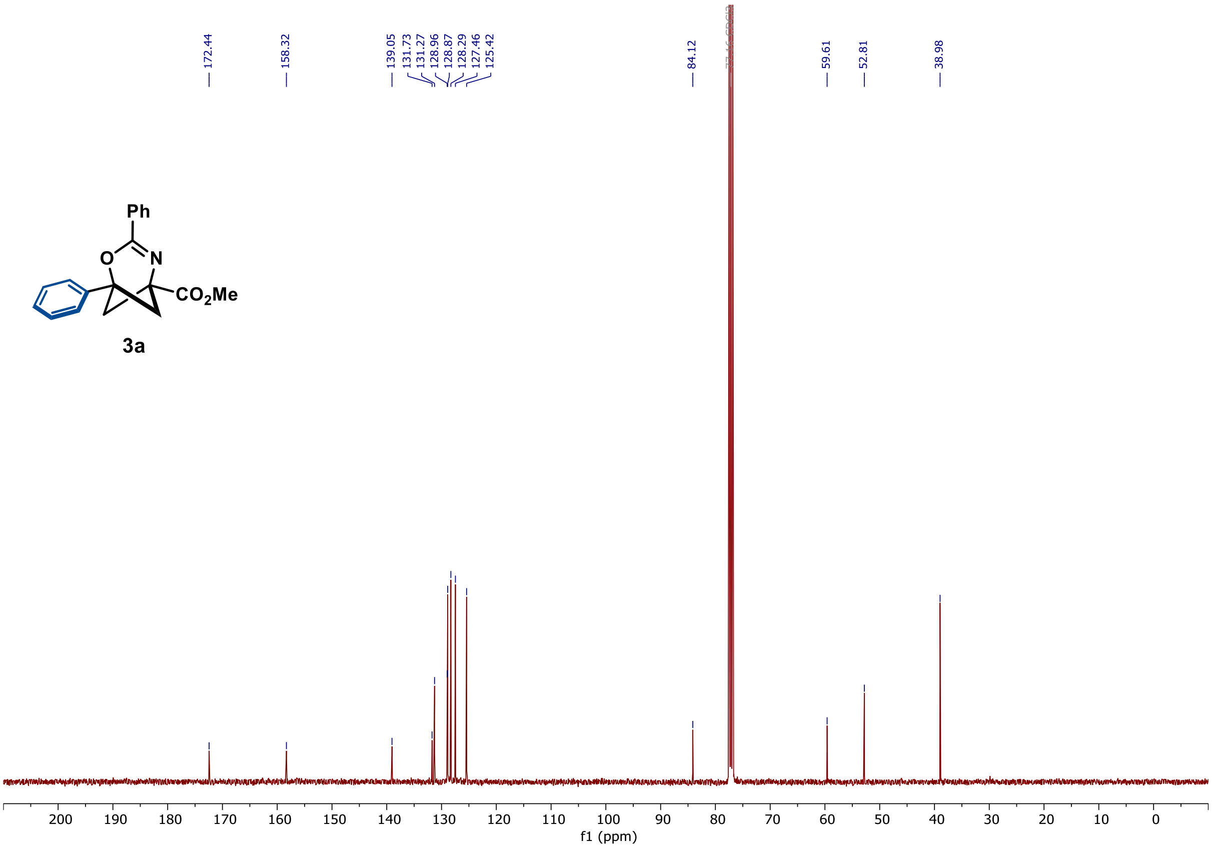
2t

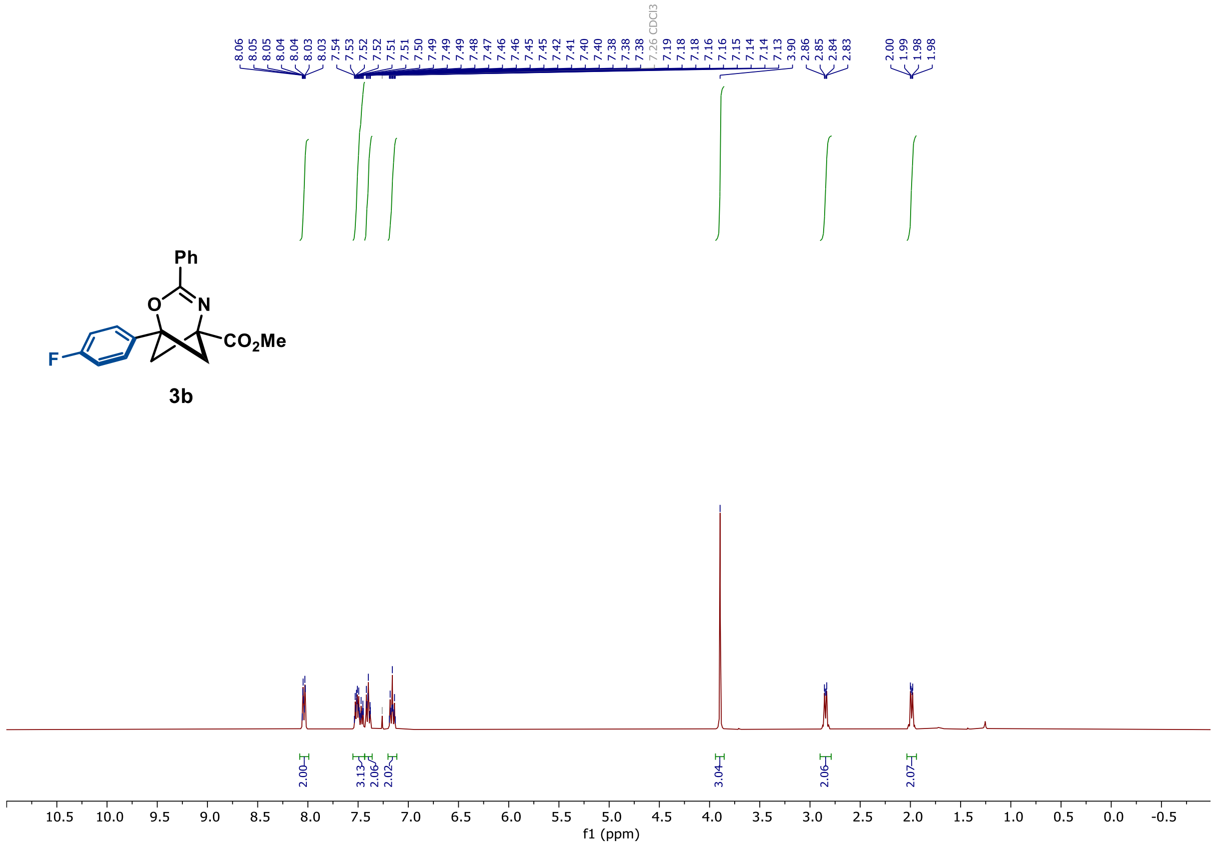

11.19
8.06
8.04
7.53
7.26 CDCl3
7.04
7.02
5.49
5.49
5.48
5.47
5.47
5.46
5.45
5.29
5.11
5.10
5.10
5.09
5.09
5.08
5.08
5.07
5.07
5.06
4.63
4.62
2.69
2.64
2.59
2.17
2.16
2.15
2.14
2.13
2.11
2.11
2.09
2.07
2.07
2.03
1.75
1.67
1.60
O
N
N+
H
BF4
2u
0.88
2.00
2.07
2.02
1.05
1.06
2.08
6.25
3.17
4.50
3.14
3.16
3.18
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

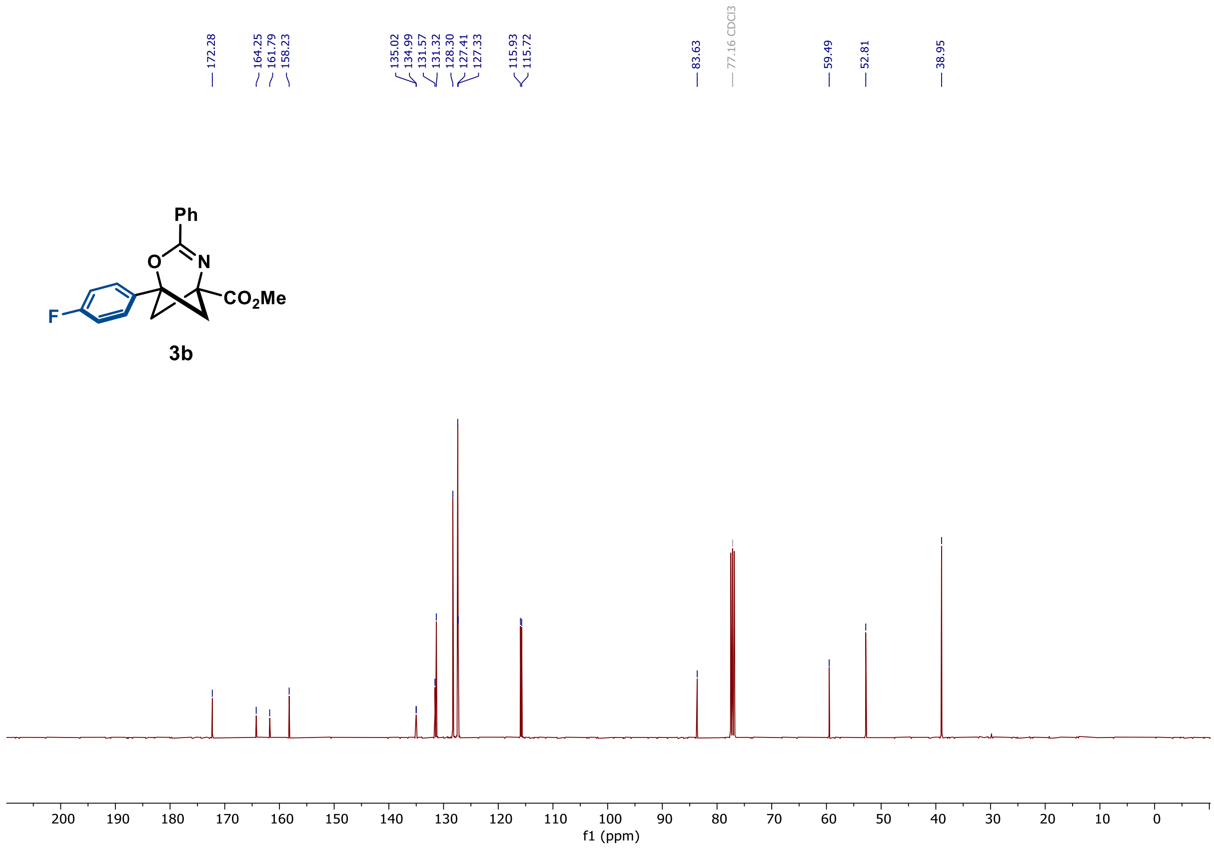

164.01
163.80
160.35
158.11
142.37
132.03
130.35
127.74
123.78
120.56
118.64
115.36
77.16 CDCl3
65.42
39.63
26.36
25.78
22.18
19.56
17.82
16.86
O
N
N+
H
BF4
2u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

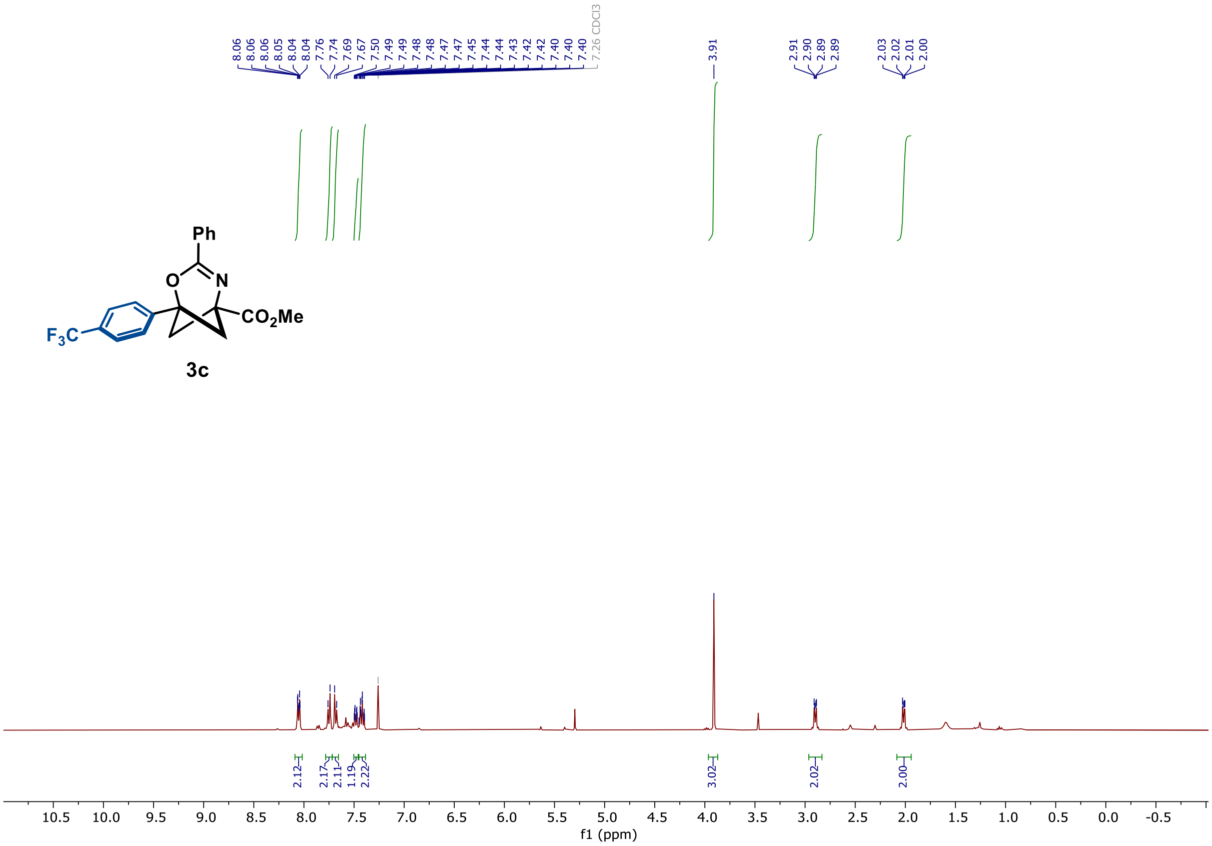

Ph
O
N
CO2Me

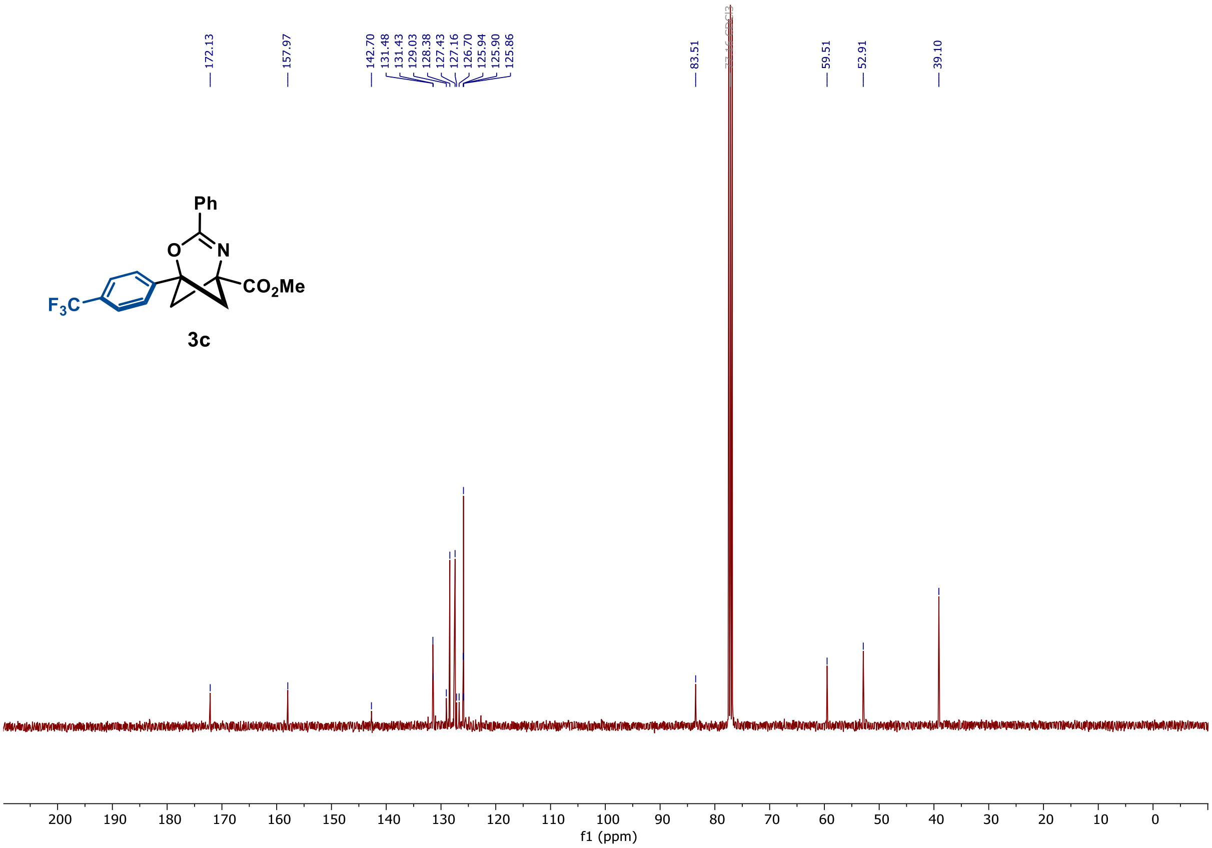
3a


172.44
158.32
139.05
131.73
131.27
128.96
128.87
128.29
127.46
125.42
84.12
77.16 CDCl3
59.61
52.81
38.98
Ph
O
N
CO2Me
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.06
8.05
8.05
8.04
8.04
8.03
8.03
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.47
7.46
7.45
7.45
7.42
7.41
7.40
7.40
7.38
7.38
7.38
7.26 CDCl3
7.19
7.18
7.18
7.16
7.16
7.15
7.14
7.14
7.13
3.90
2.86
2.85
2.84
2.83
2.00
1.99
1.98
1.98
Ph
O
N
F
CO2Me
3b
2.00
3.13
2.06
2.02
3.04
2.06
2.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


172.28
164.25
161.79
158.23
135.02
134.99
131.57
131.32
128.30
127.41
127.33
115.93
115.72
83.63
77.16 CDCl3
59.49
52.81
38.95
Ph
O
N
F
CO2Me
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.06
8.06
8.05
8.04
8.04
7.76
7.74
7.69
7.67
7.50
7.49
7.49
7.48
7.47
7.47
7.45
7.44
7.44
7.43
7.42
7.42
7.40
7.40
7.26 CDCl3
3.91
2.91
2.90
2.89
2.89
2.03
2.02
2.01
2.00
Ph
O
N
F3C
CO2Me
3c
2.12
2.17
2.11
1.19
2.22
3.02
2.02
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


172.13
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126.70
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125.90
125.86
83.51
77.16 CDCl3
59.51
52.91
39.10
Ph
O
N
F3C
CO2Me
3c
200
190
180
170
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120
110
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90
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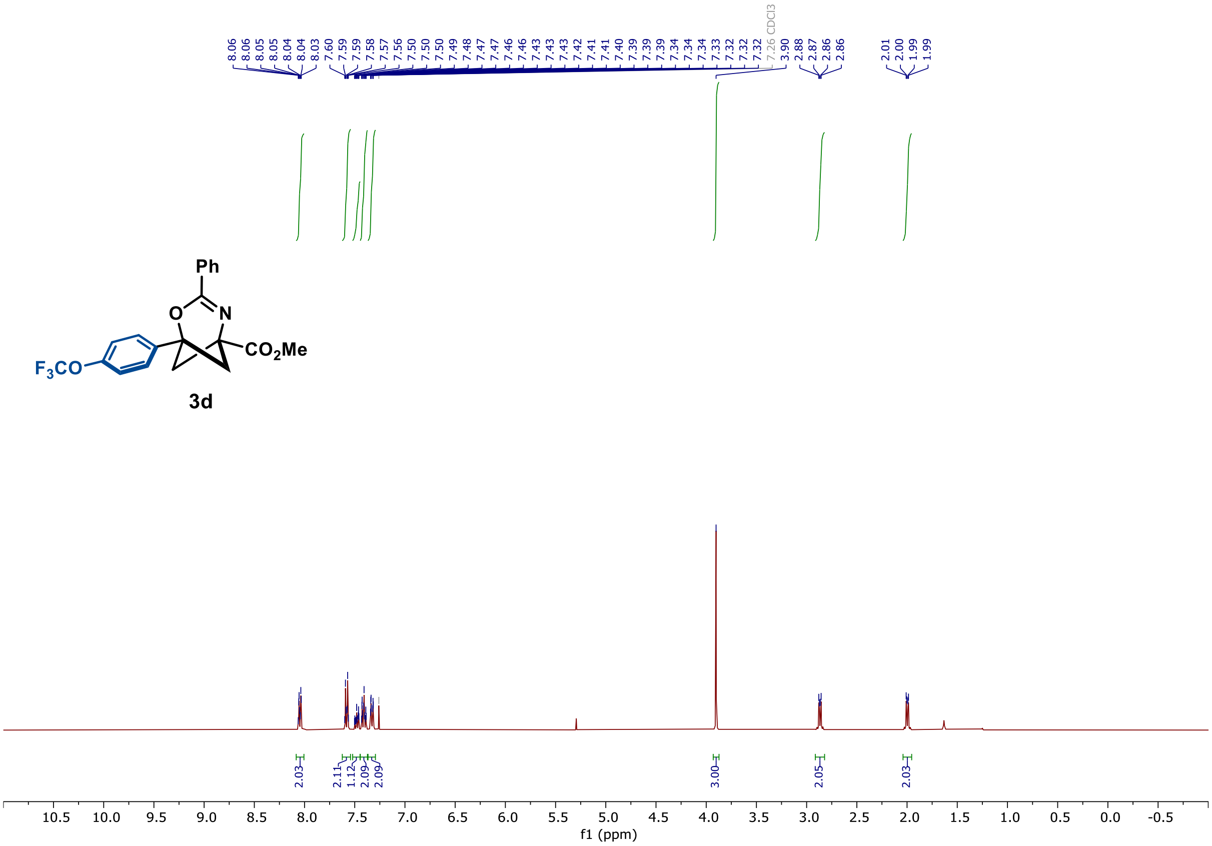
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7.57
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7.50
7.50
7.50
7.49
7.48
7.47
7.46
7.43
7.43
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7.41
7.41
7.40
7.39
7.39
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7.34
7.33
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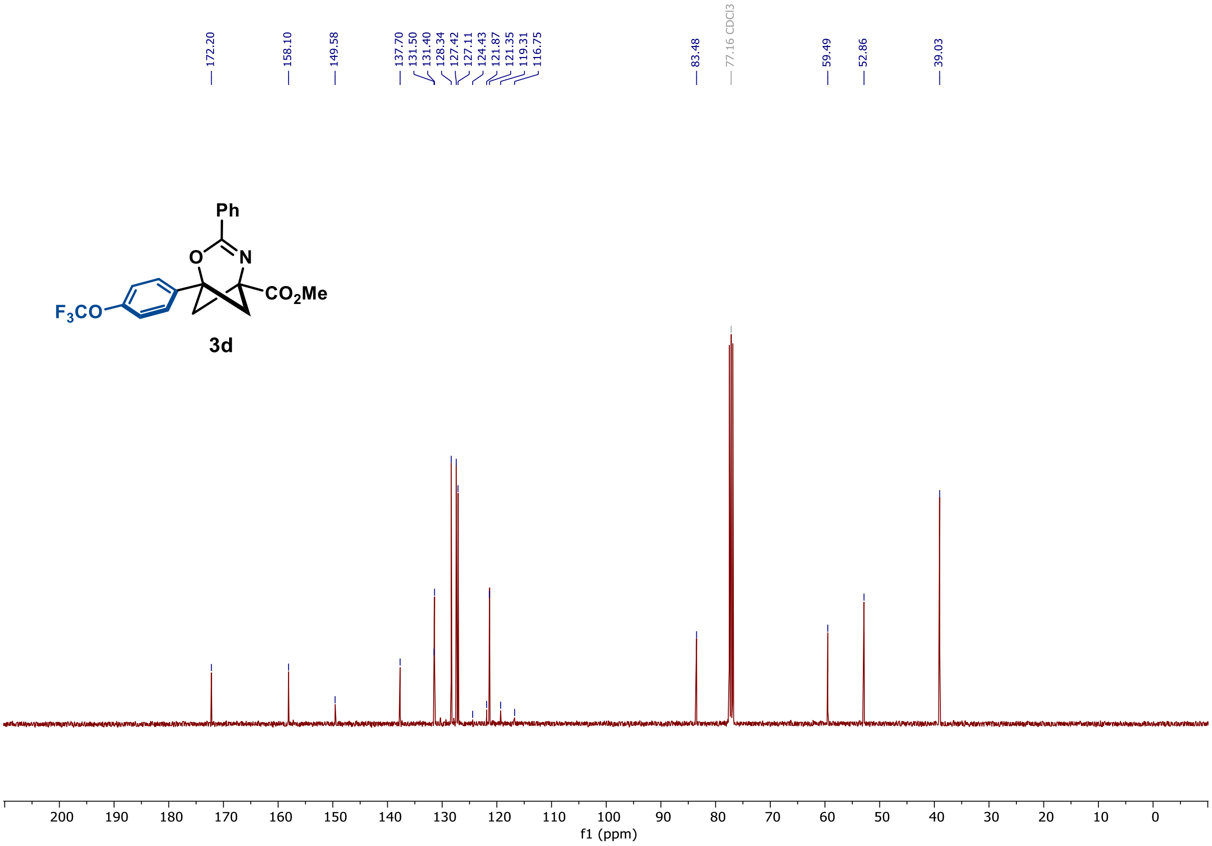
7.32
7.32
7.26 CDCl3
3.90
2.88
2.87
2.86
2.86
2.01
2.00
1.99
1.99
Ph
O
N
CO2Me
F3CO
3d
2.03
2.11
1.12
2.09
2.09
3.00
2.05
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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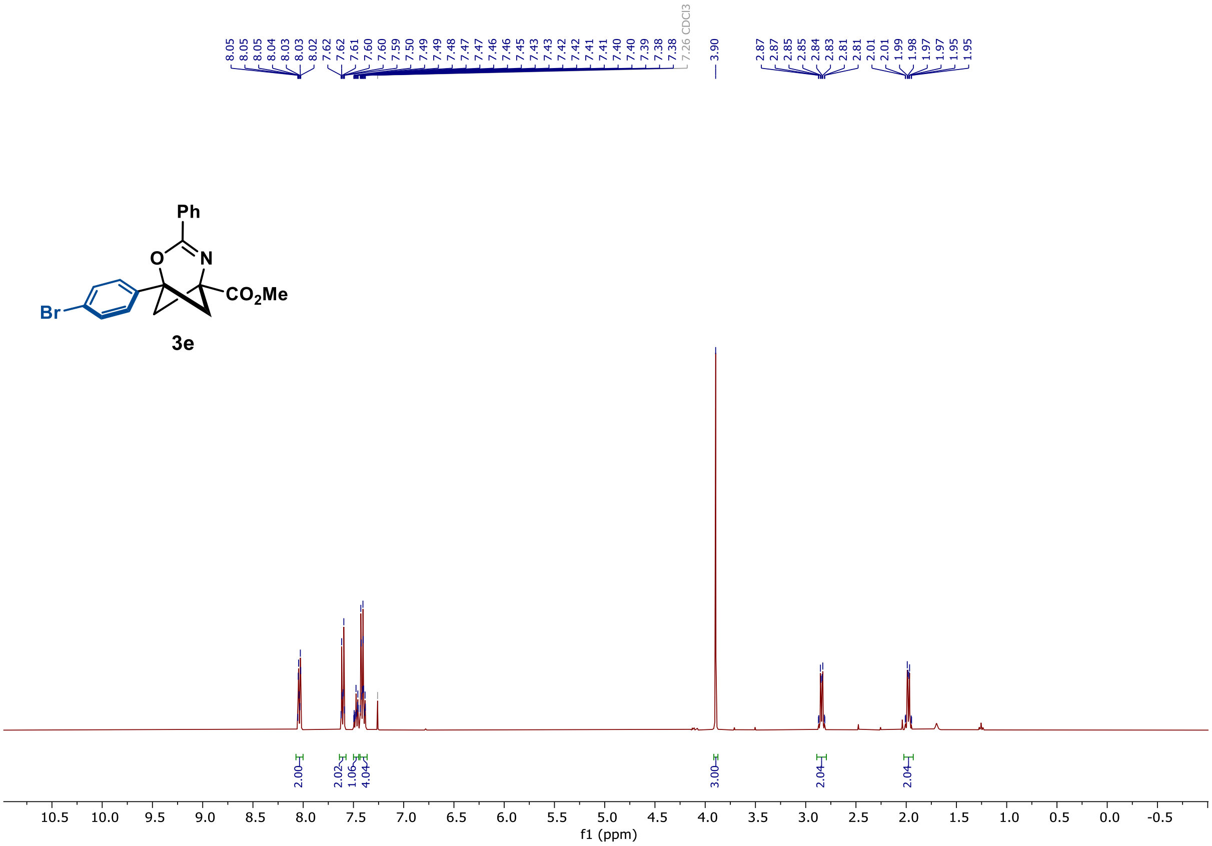
124.43
121.87
121.35
119.31
116.75
83.48
77.16 CDCl3
59.49
52.86
39.03
Ph
O
N
CO2Me
F3CO
3d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.50
7.49
7.49
7.48
7.47
7.46
7.45
7.43
7.43
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7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.26 CDCl3
3.90
2.87
2.87
2.85
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2.83
2.81
2.81
2.01
2.01
1.99
1.98
1.97
1.97
1.95
1.95
Ph
O
N
Br
CO2Me
2.00
2.02
1.06
4.04
3.00
2.04
2.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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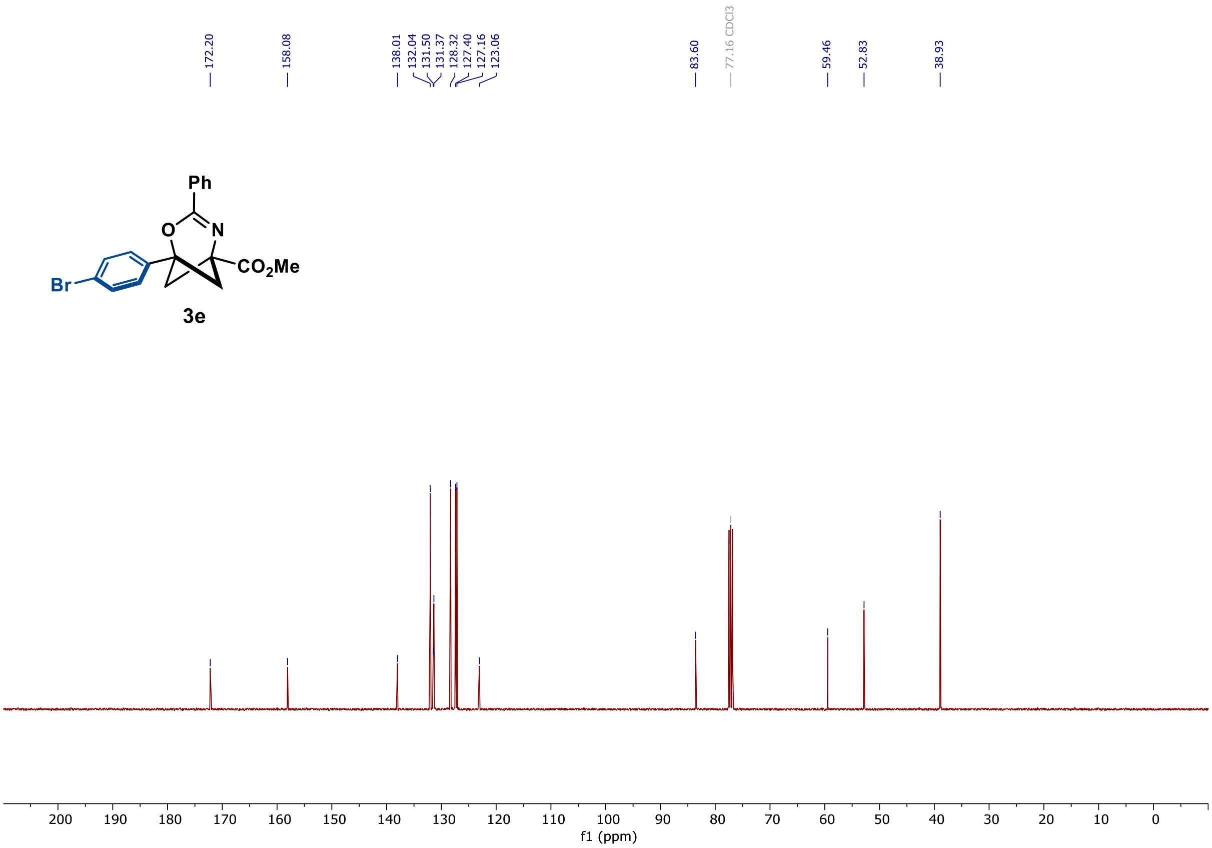
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3e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138.01
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131.37
128.32
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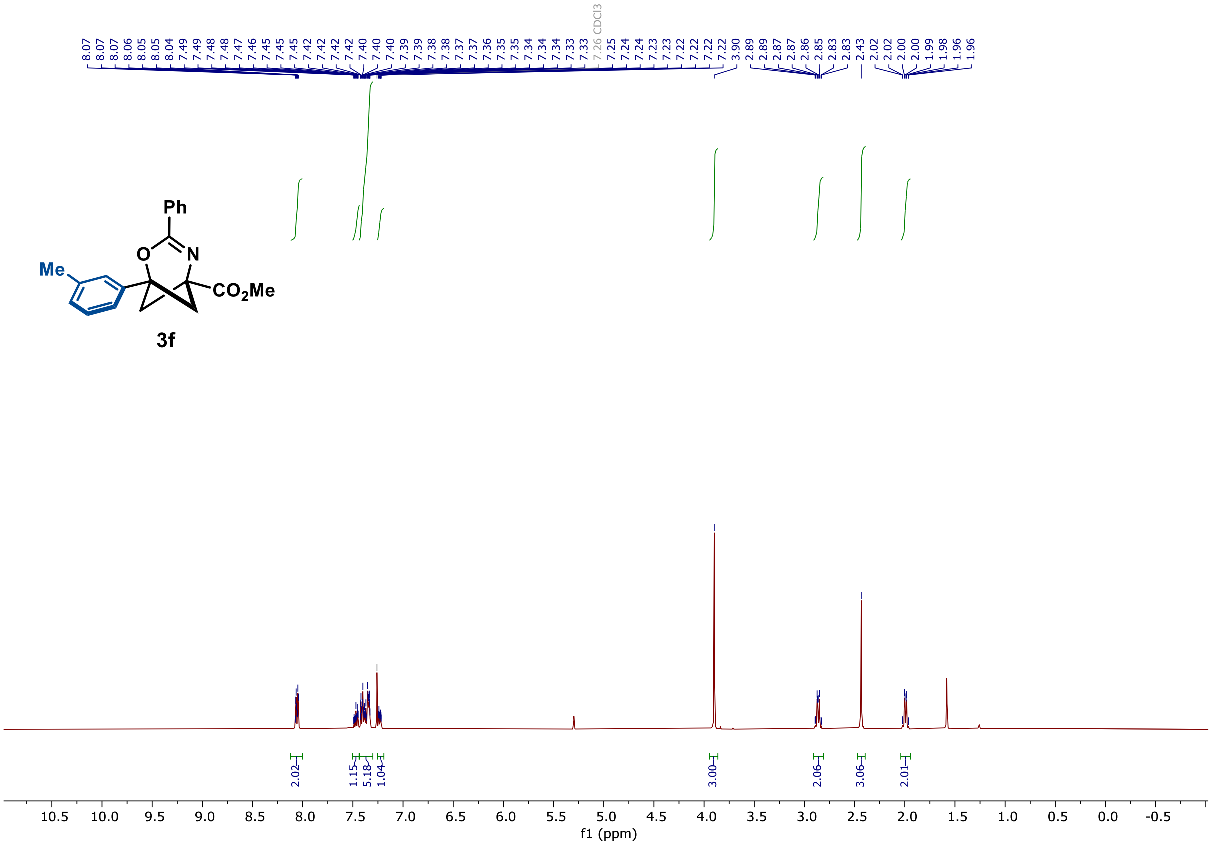
127.16
123.06
83.60
77.16 CDCl3
59.46
52.83
38.93
Ph
O
N
Br
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3e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7.35
7.34
7.34
7.34
7.33
7.33
7.26 CDCl3
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.22
7.22
3.90
2.89
2.89
2.87
2.86
2.85
2.83
2.83
2.43
2.02
2.02
2.00
1.99
1.98
1.96
1.96
Ph
O
N
Me
CO2Me
3f
2.02
1.15
5.18
1.04
3.00
2.06
3.06
2.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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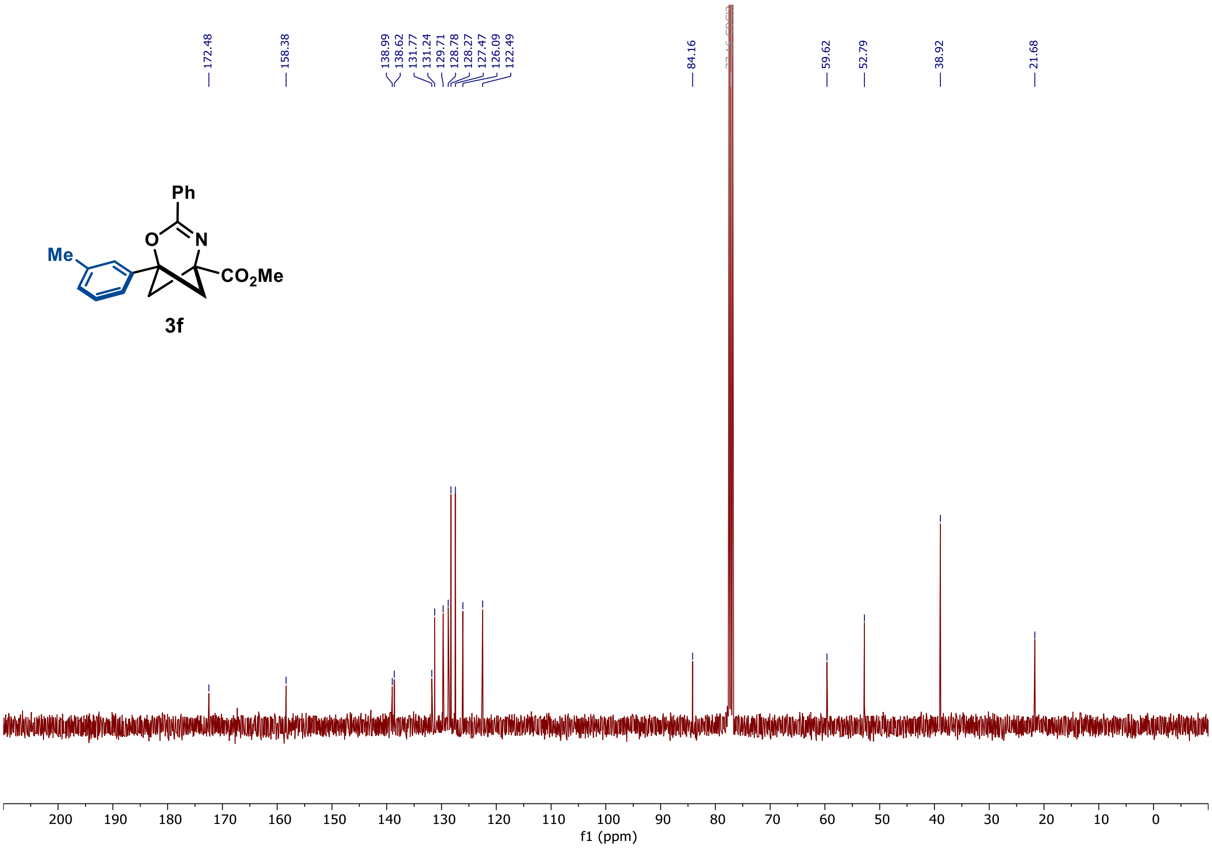
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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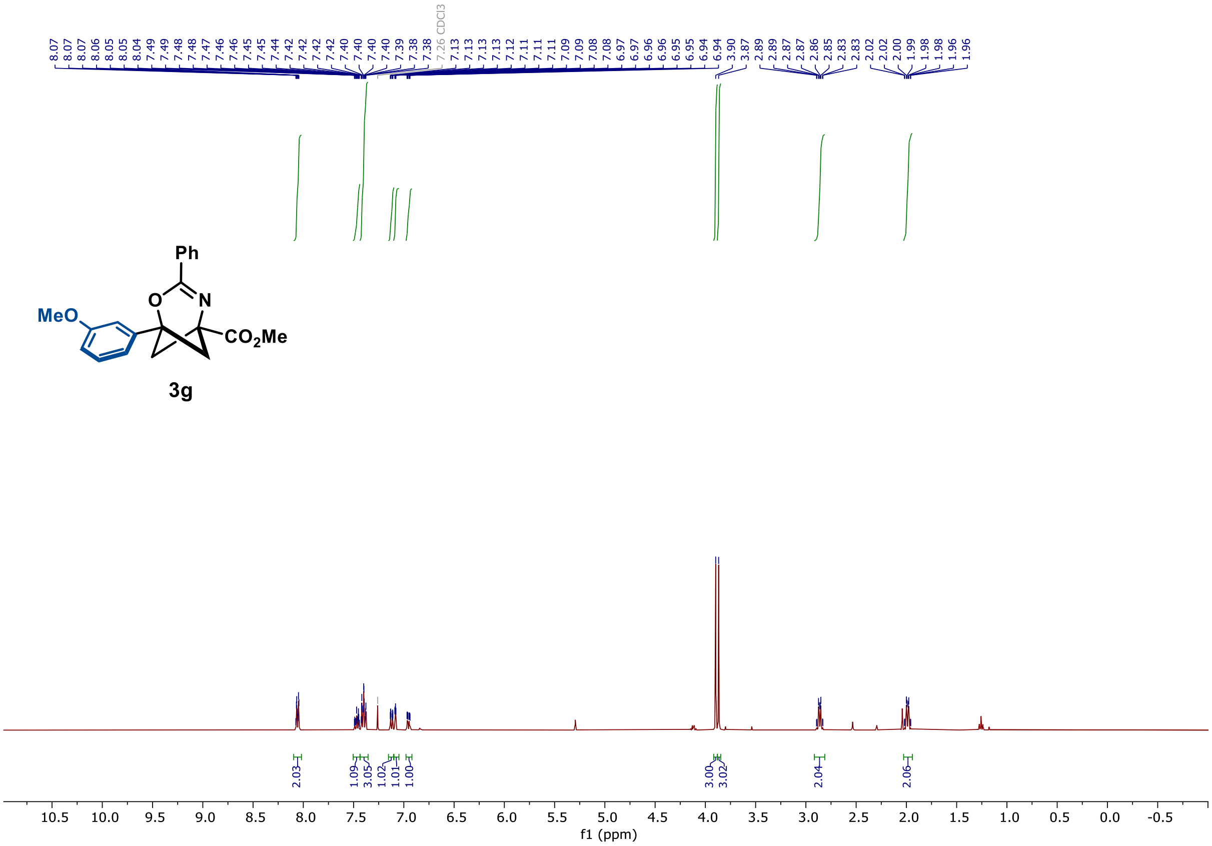
127.47
126.09
122.49
84.16
77.16 CDCl3
59.62
52.79
38.92
21.68
Ph
O
N
Me
CO2Me
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.07
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8.05
8.05
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7.48
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7.46
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7.44
7.42
7.42
7.42
7.40
7.40
7.40
7.39
7.38
7.38
7.26 CDCl3
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7.08
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6.95
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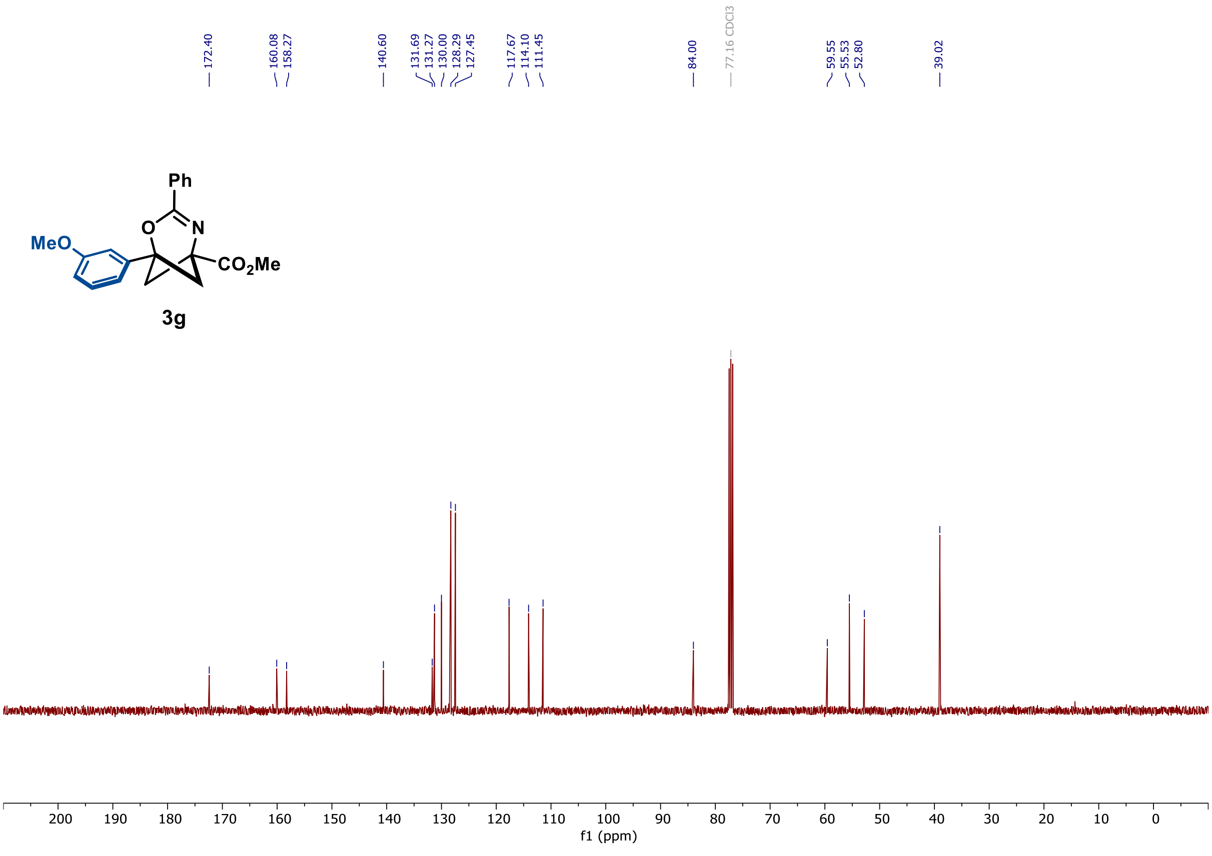
2.85
2.85
2.83
2.83
2.02
2.02
2.00
1.99
1.98
1.98
1.96
1.96
Ph
O
N
MeO
CO2Me
3g
2.03
1.09
3.05
1.02
1.01
1.00
3.00
3.02
2.04
2.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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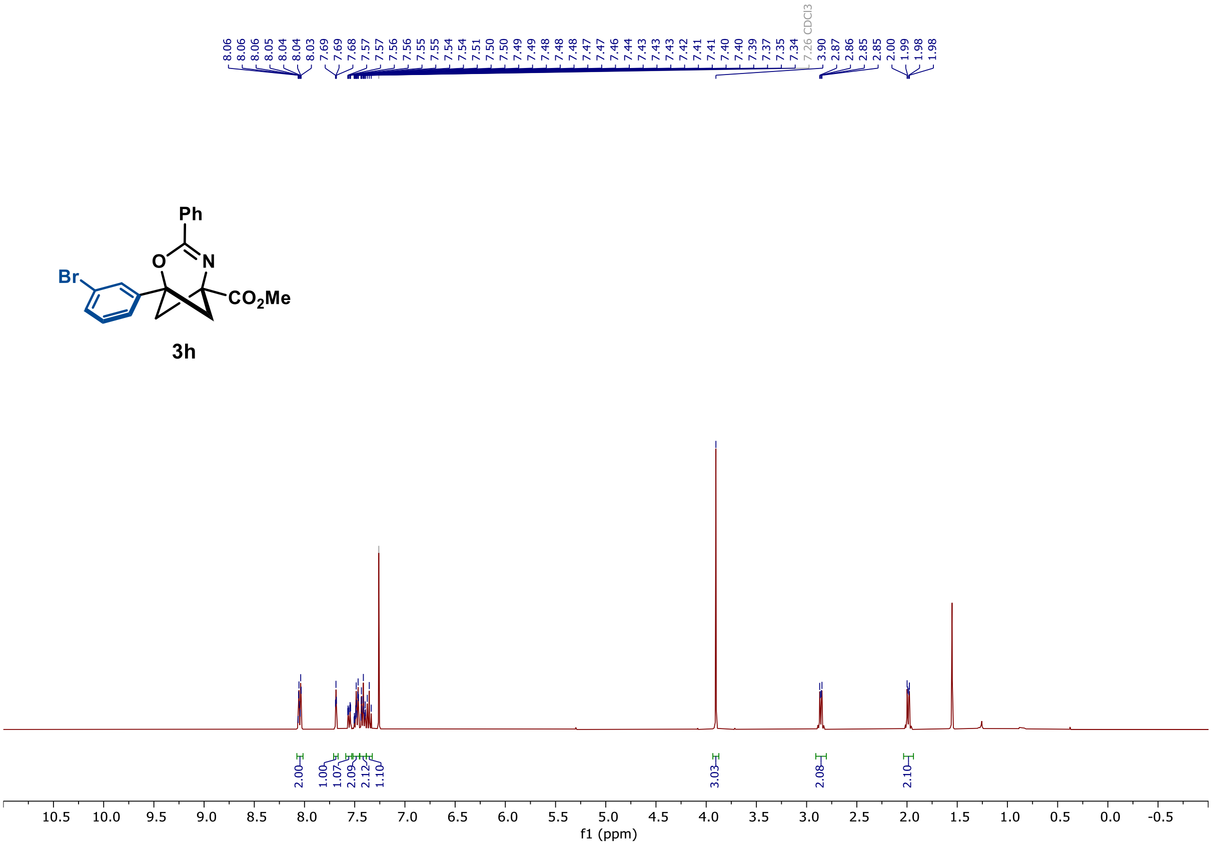
127.45
117.67
114.10
111.45
84.00
77.16 CDCl3
59.55
55.53
52.80
39.02
Ph
O
N
MeO
CO2Me
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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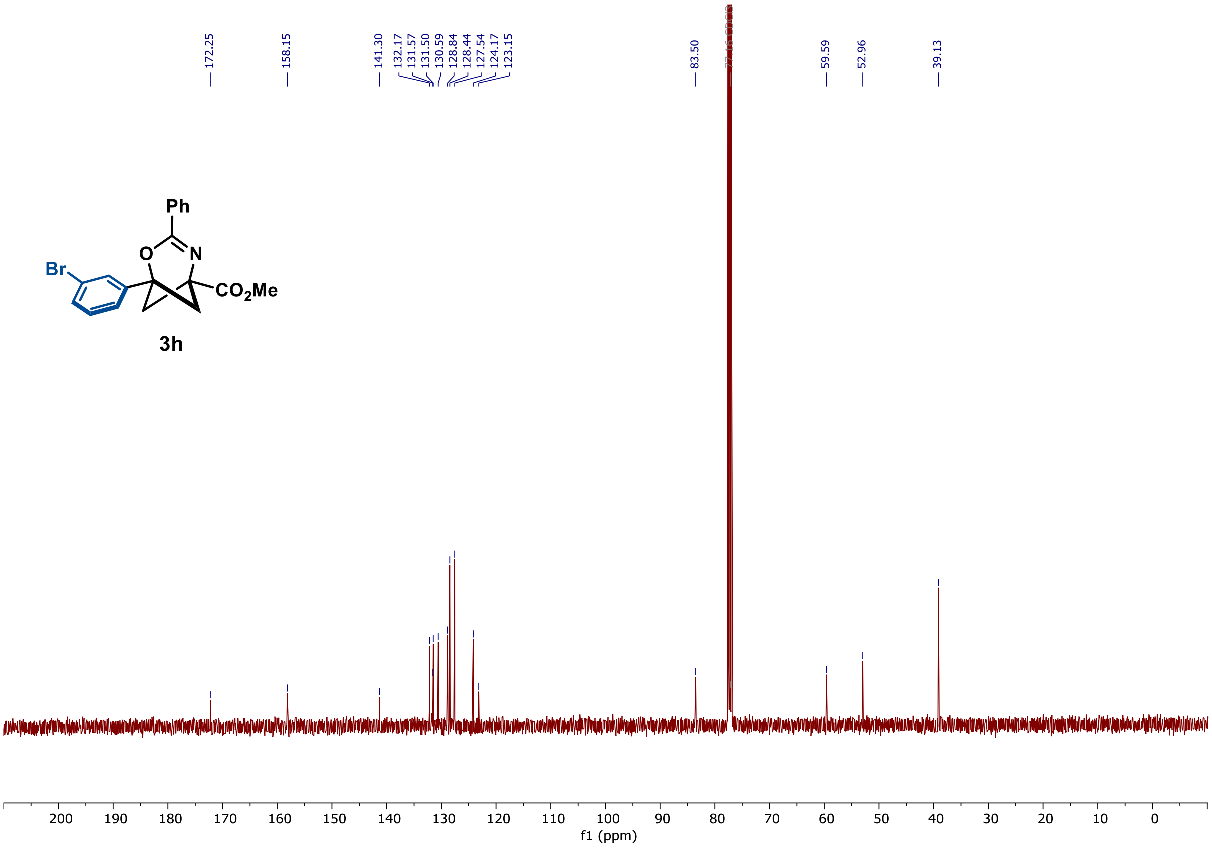
Ph
O
N
Br
CO2Me
3h
2.00
1.00
1.07
2.09
2.12
1.10
3.03
2.08
2.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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158.15
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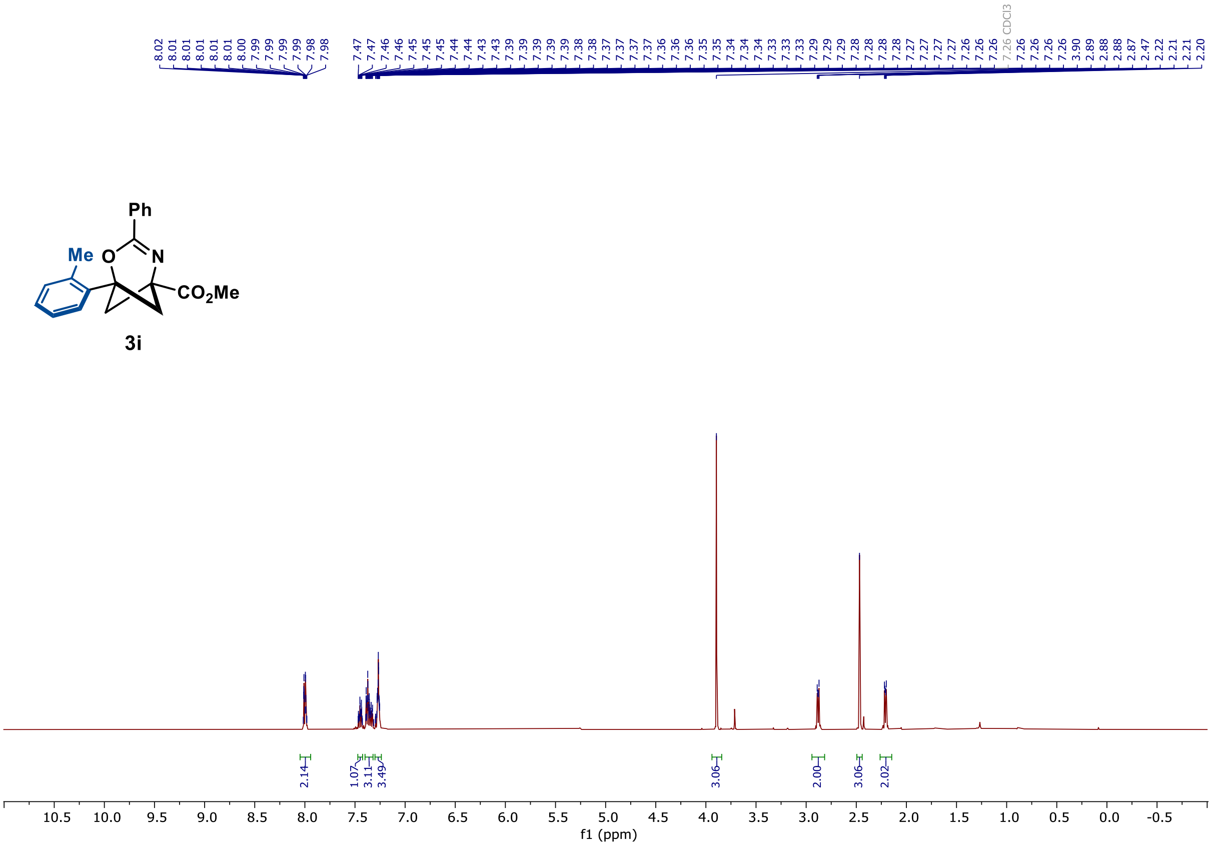
132.17 131.57 131.50 130.59 128.84 128.44 127.54 124.17 123.15
83.50
59.59
52.96
39.13
Ph
O
N
Br
CO2Me
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.00
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7.45
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7.44
7.43
7.43
7.39
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7.34
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7.33
7.33
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7.28
7.28
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7.27
7.27
7.26
7.26
7.26
7.26 CDCl3
7.26
7.26
7.26
7.26
3.90
2.89
2.88
2.87
2.47
2.22
2.21
2.21
2.20
Ph
Me
O
N
CO2Me
3i
2.14
1.07
3.11
3.49
3.06
2.00
3.06
2.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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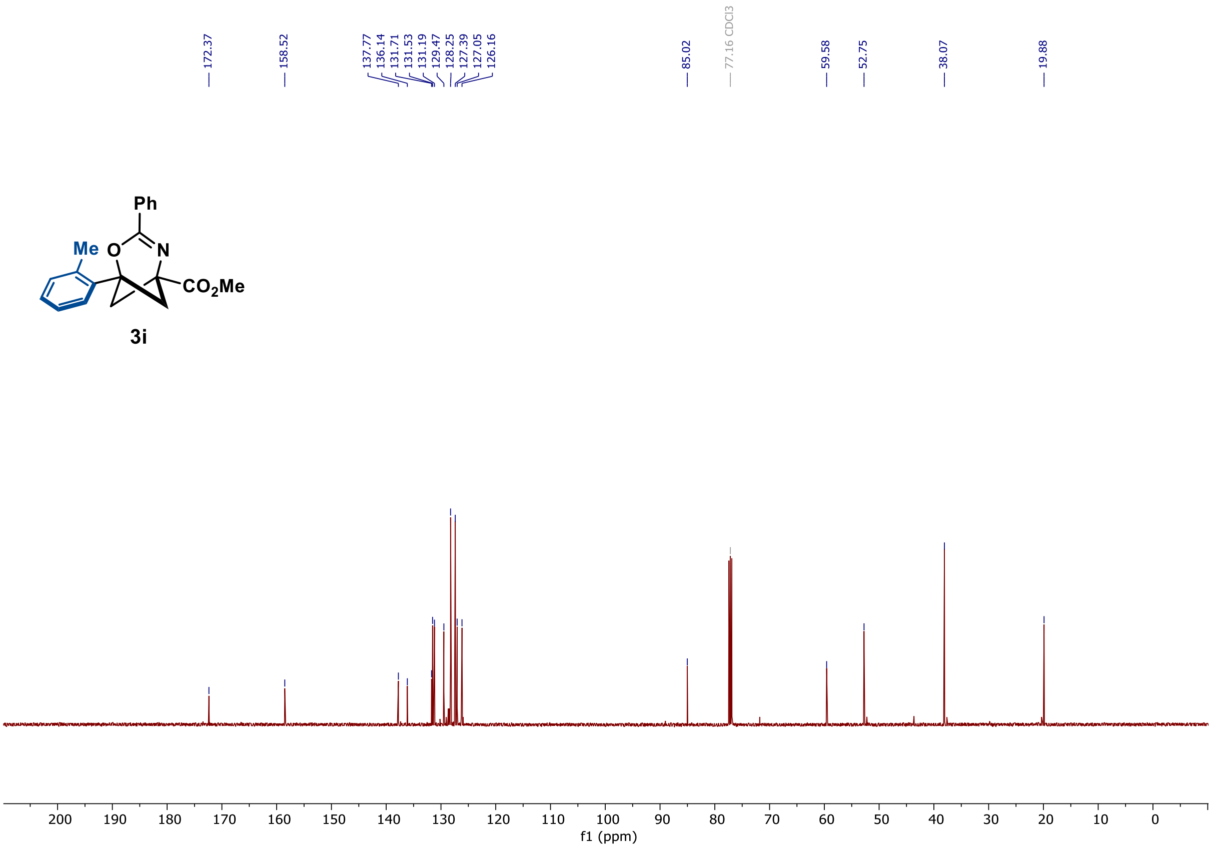
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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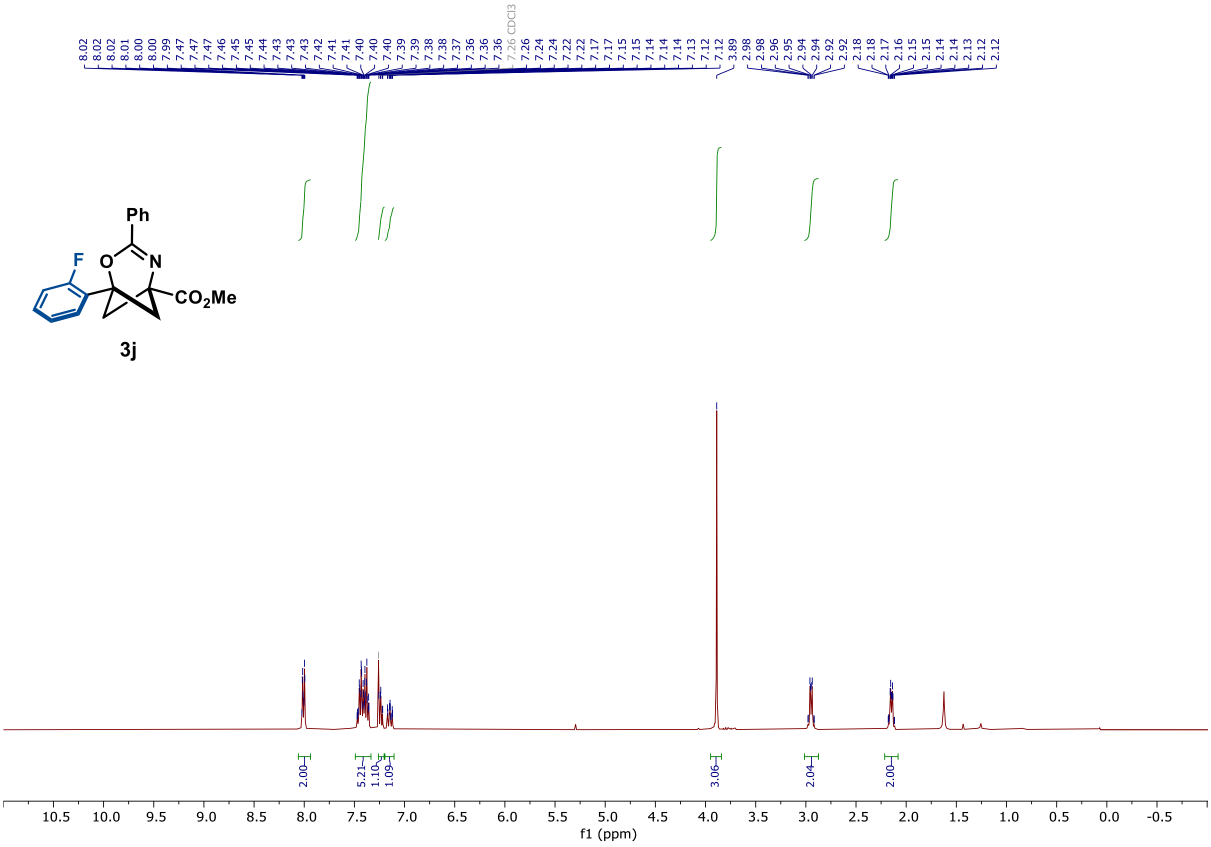
127.39
127.05
126.16
85.02
77.16 CDCl3
59.58
52.75
38.07
19.88
Ph
Me
O
N
CO2Me
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.26 CDCl3
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7.24
7.24
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7.17
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7.15
7.15
7.14
7.14
7.14
7.13
7.12
7.12
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2.98
2.96
2.95
2.94
2.94
2.92
2.92
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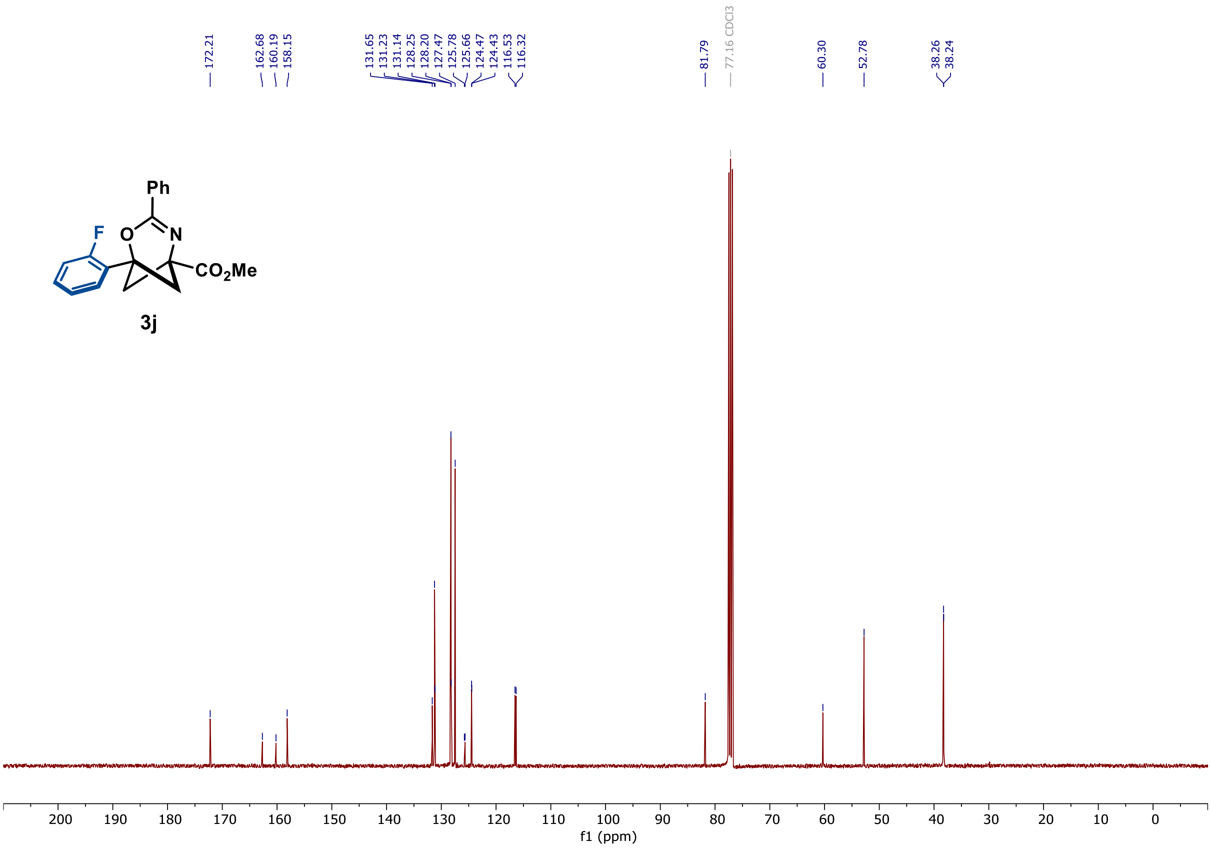
2.18
2.17
2.16
2.15
2.15
2.14
2.14
2.13
2.12
2.12
Ph
O
N
F
CO2Me
3j
2.00
5.21
1.10
1.09
3.06
2.04
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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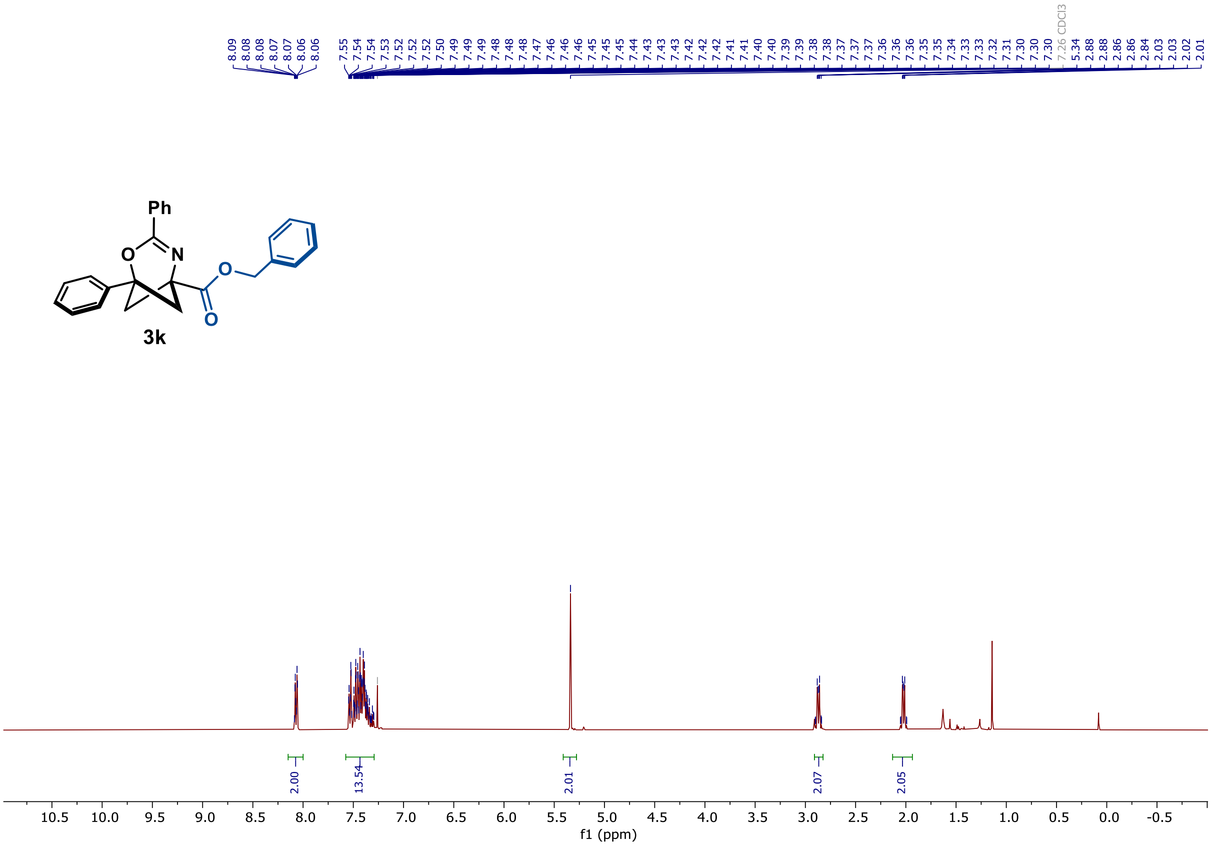
125.78
125.66
124.47
124.43
116.53
116.32
81.79
77.16 CDCl3
60.30
52.78
38.26
38.24
Ph
O
N
F
CO2Me
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.33
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7.31
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7.30
7.30
7.26 CDCl3
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2.88
2.88
2.86
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2.03
2.02
2.01
Ph
O
N
O
O
3k
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2.01
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2.05
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7.5
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6.0
5.5
5.0
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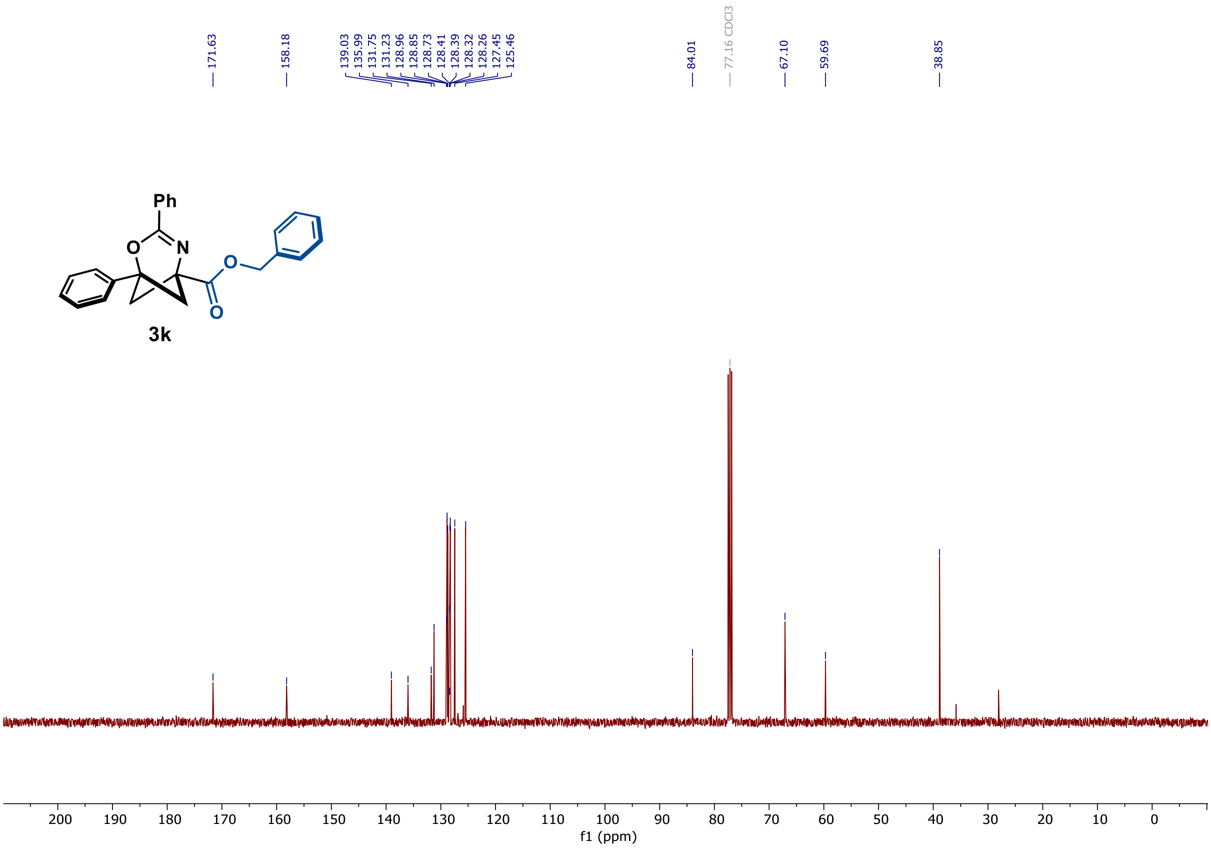
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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128.41
128.39
128.32
128.26
127.45
125.46
84.01
77.16 CDCl3
67.10
59.69
38.85
Ph
O
N
O
O
3k
200
190
180
170
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150
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120
110
100
90
80
70
60
50
40
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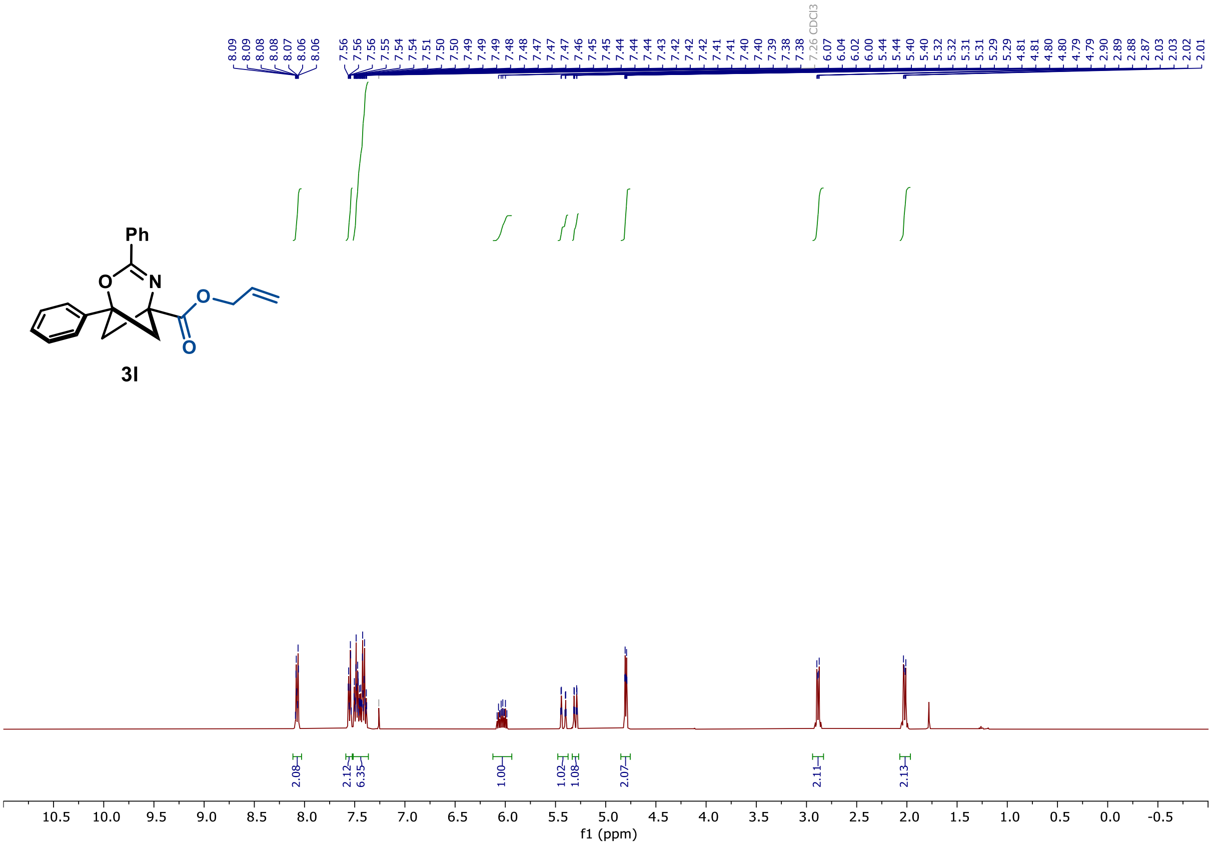
20
10
0
f1 (ppm)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7.44
7.44
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.26 CDCl3
6.07
6.04
6.02
6.00
5.44
5.44
5.40
5.40
5.32
5.32
5.31
5.29
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4.80
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2.89
2.88
2.87
2.03
2.03
2.02
2.01
Ph
O
N
O
O
3l
2.08
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1.00
1.02
1.08
2.07
2.11
2.13
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9.0
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8.0
7.5
7.0
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6.0
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5.0
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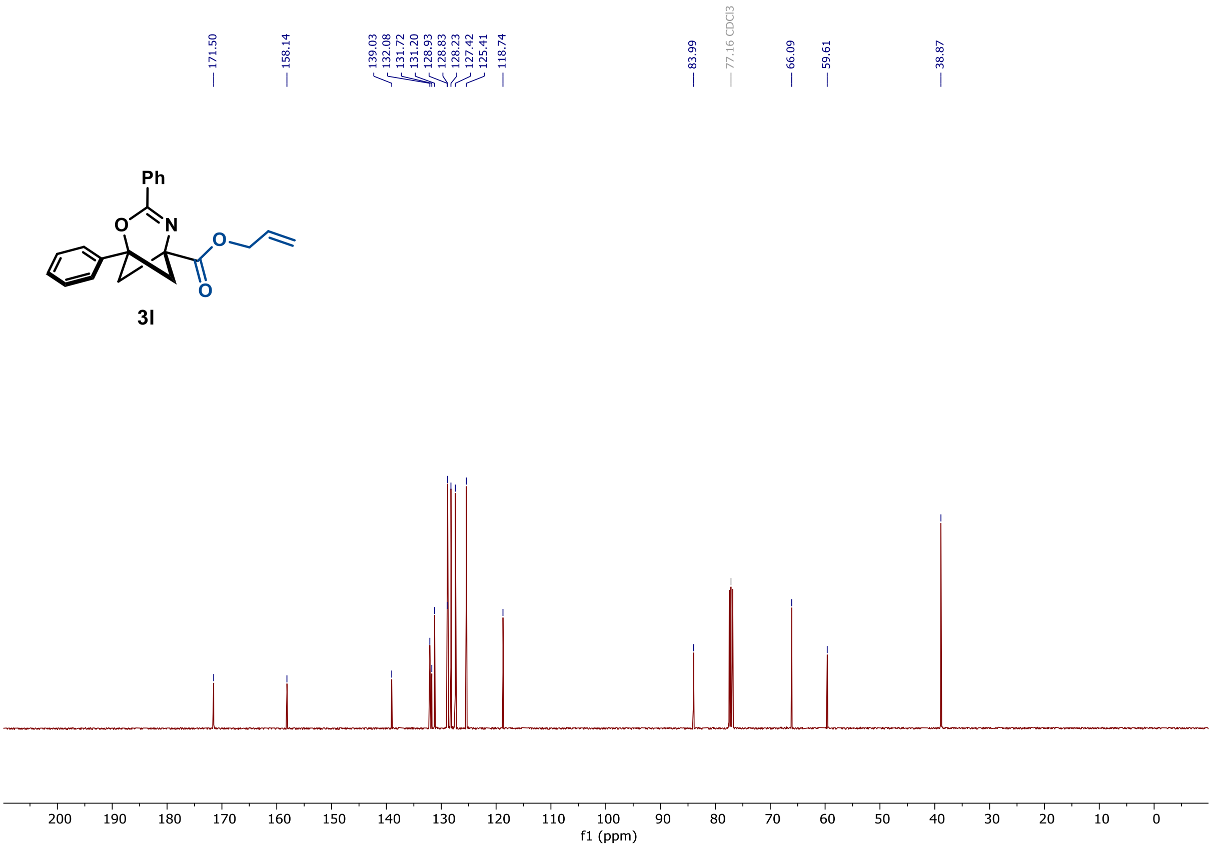
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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128.83
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127.42
125.41
118.74
83.99
77.16 CDCl3
66.09
59.61
38.87
Ph
O
N
O
O
3l
200
190
180
170
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130
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110
100
90
80
70
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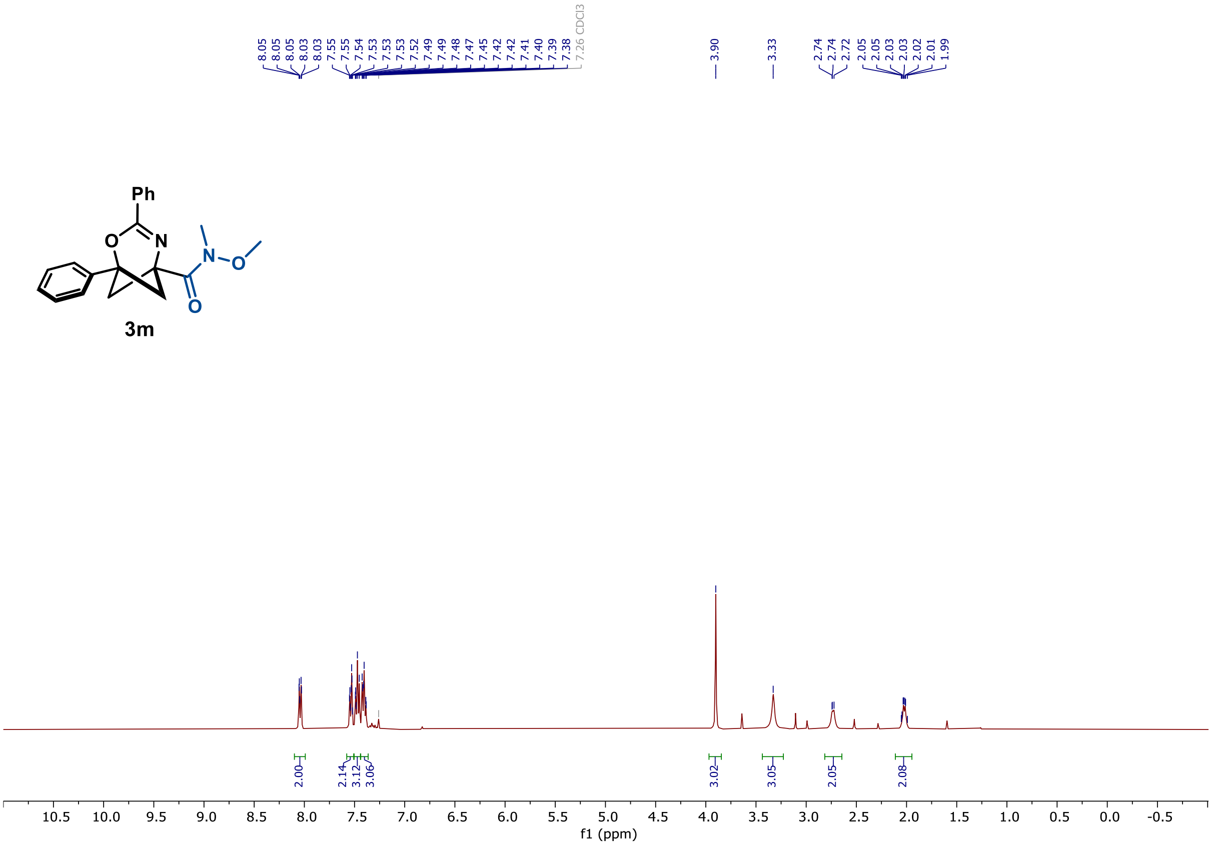
50
40
30
20
10
0
f1 (ppm)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8.05
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7.42
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7.41
7.40
7.39
7.38
7.26 CDCl3
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3.33
2.74
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2.05
2.05
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2.01
1.99
Ph
O
N
N
O
O
3m
2.00
2.14
3.12
3.06
3.02
3.05
2.05
2.08
10.5
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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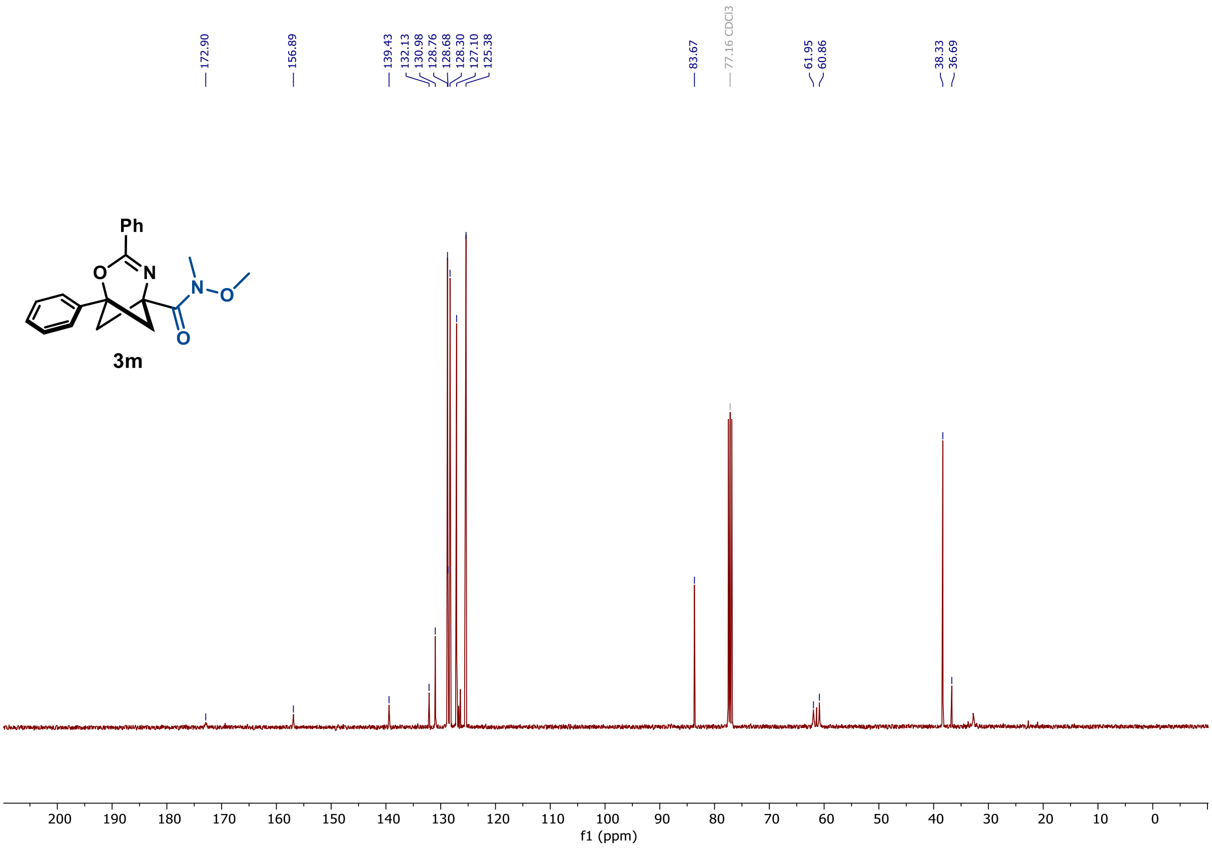
-0.5
f1 (ppm)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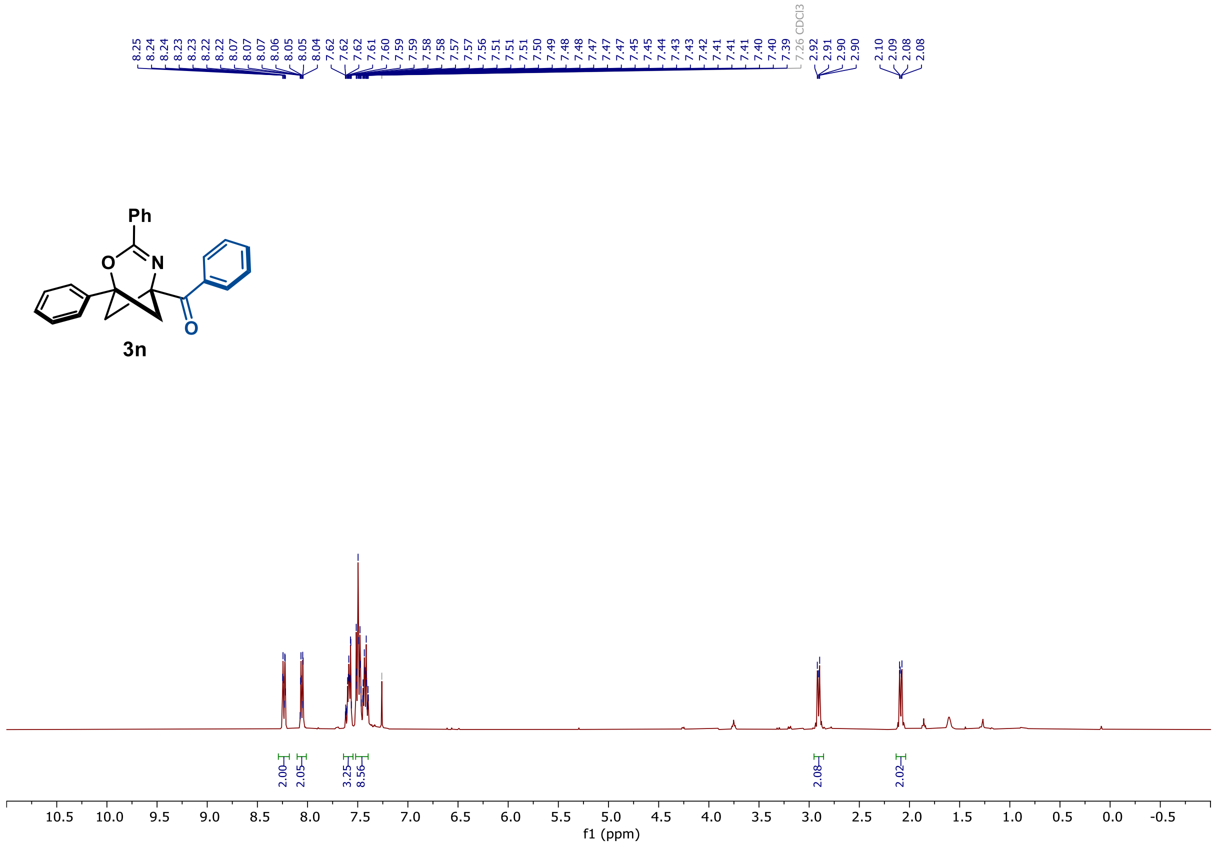
130.98
128.76
128.68
128.30
127.10
125.38
83.67
77.16 CDCl3
61.95
60.86
38.33
36.69
Ph
O
N
N
O
O
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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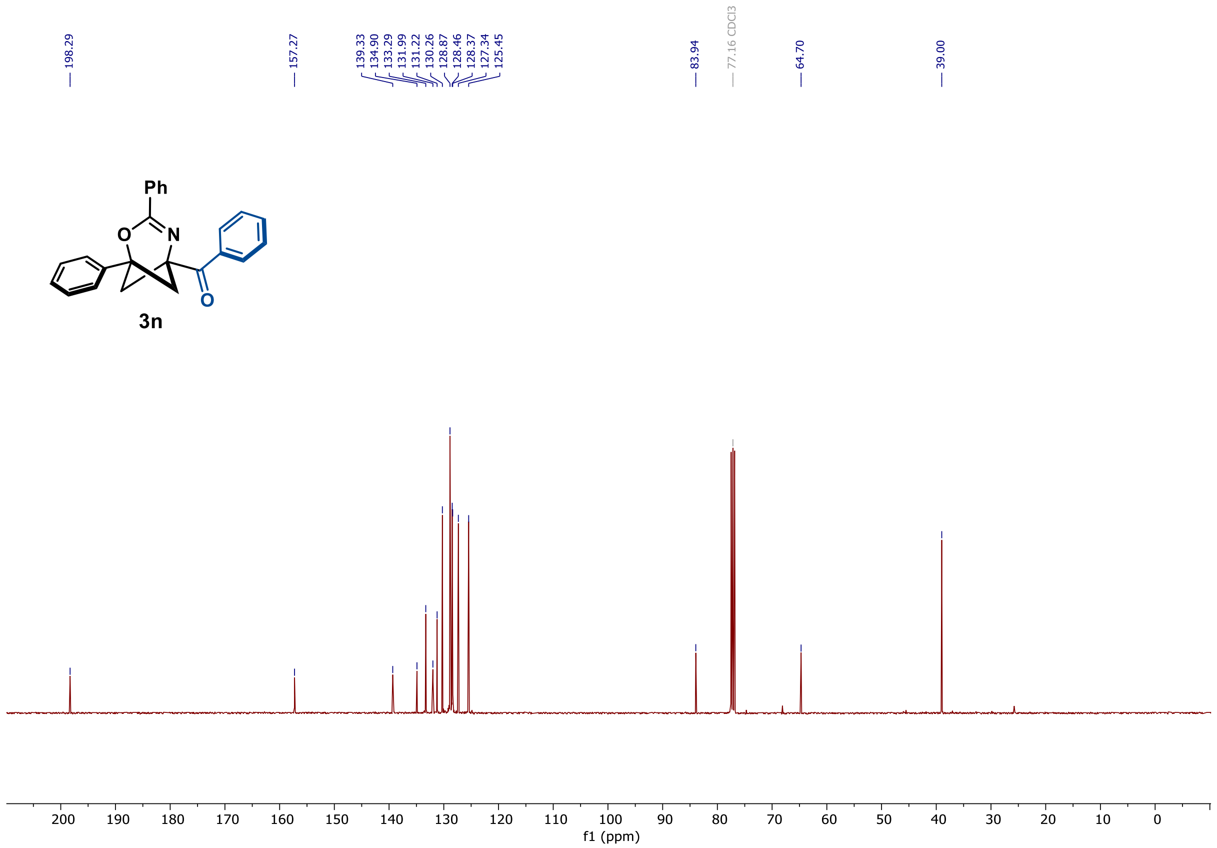
7.26 CDCl3
2.92 2.91 2.90 2.90
2.10 2.09 2.08 2.08
Ph
O
N
O
3n
2.00
2.05
3.25
8.56
2.08
2.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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83.94
77.16 CDCl3
64.70
39.00
Ph
O
N
O
3n
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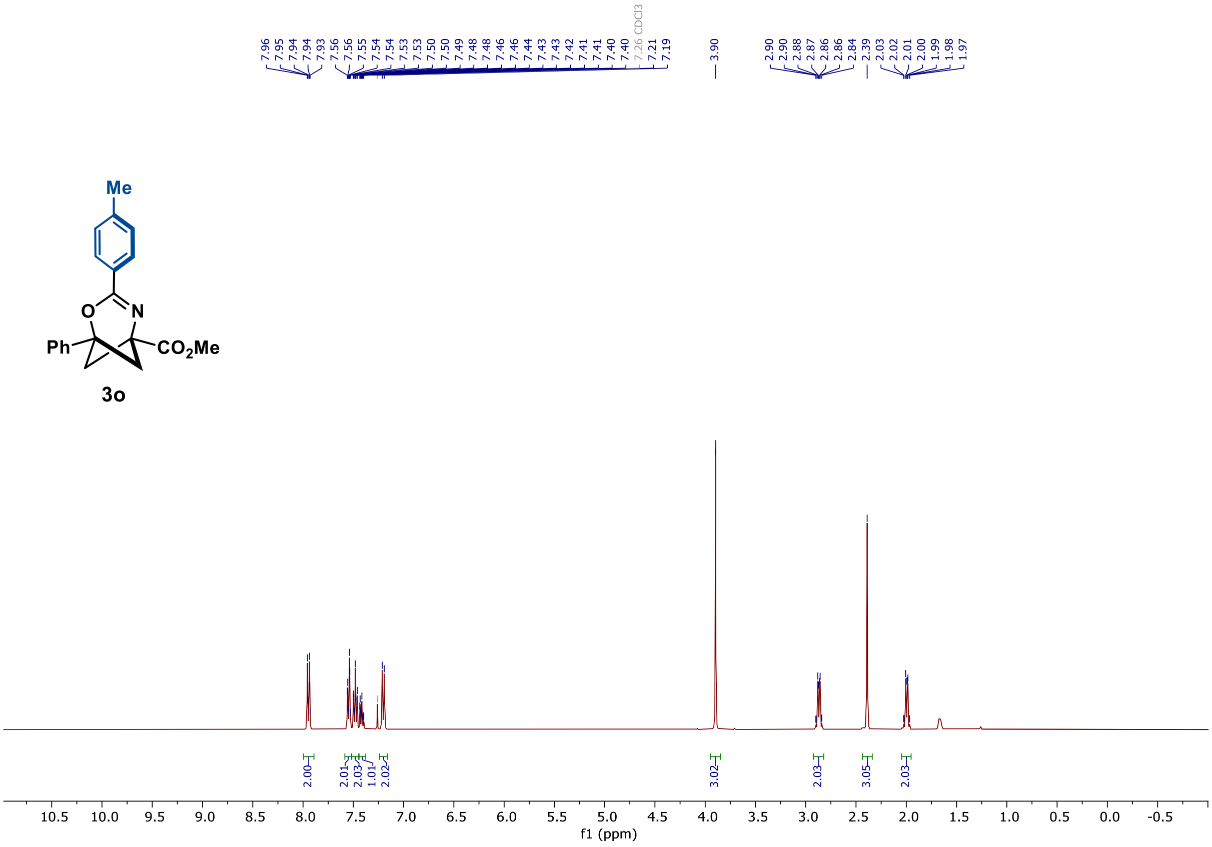
f1 (ppm)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7.53
7.50
7.50
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7.48
7.48
7.46
7.46
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.40
7.26 CDCl3
7.21
7.19
3.90
2.90
2.90
2.88
2.87
2.86
2.86
2.84
2.39
2.03
2.02
2.01
2.00
1.99
1.98
1.97
Me
O
N
Ph
CO2Me
3o
2.00
2.01
2.03
1.01
2.02
3.02
2.03
3.05
2.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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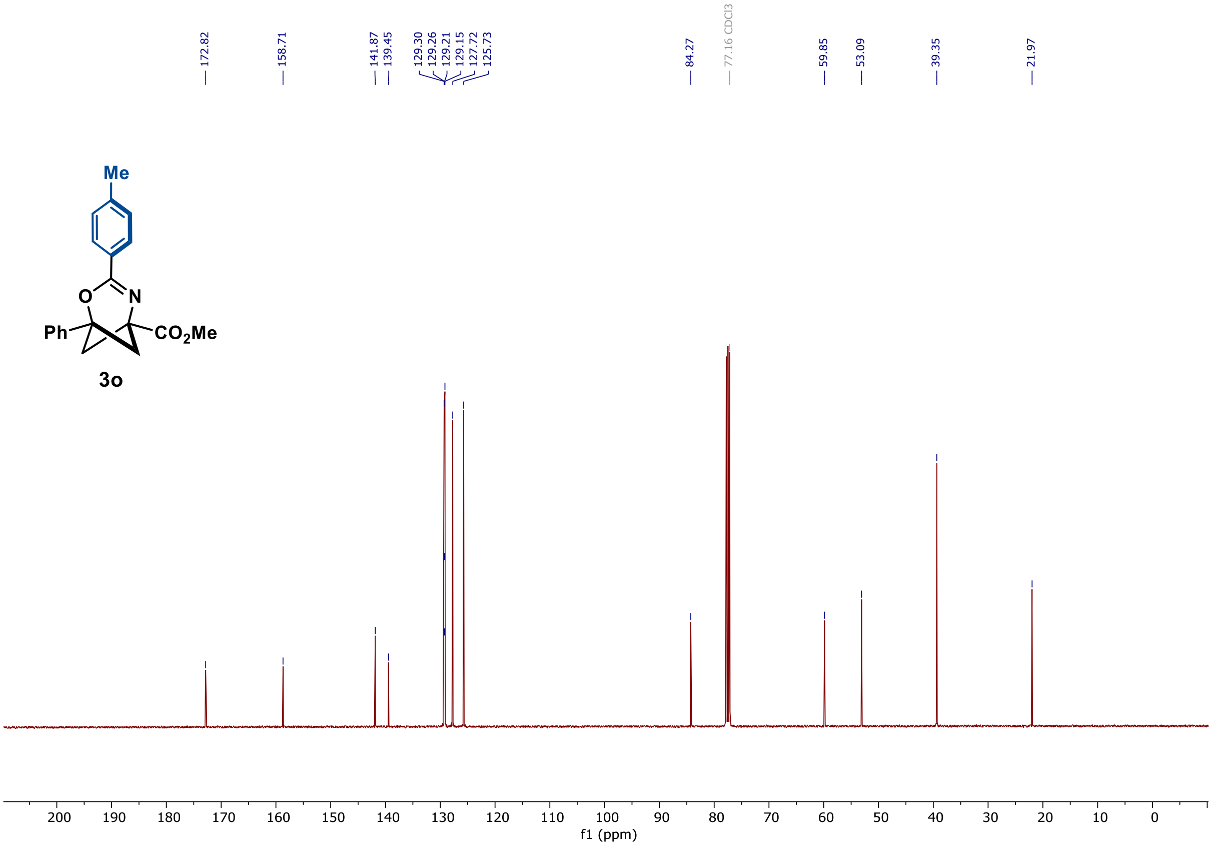
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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158.71
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127.72
125.73
84.27
77.16 CDCl3
59.85
53.09
39.35
21.97
Me
O
N
Ph
CO2Me
3o
200
190
180
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160
150
140
130
120
110
100
90
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50
40
30
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10
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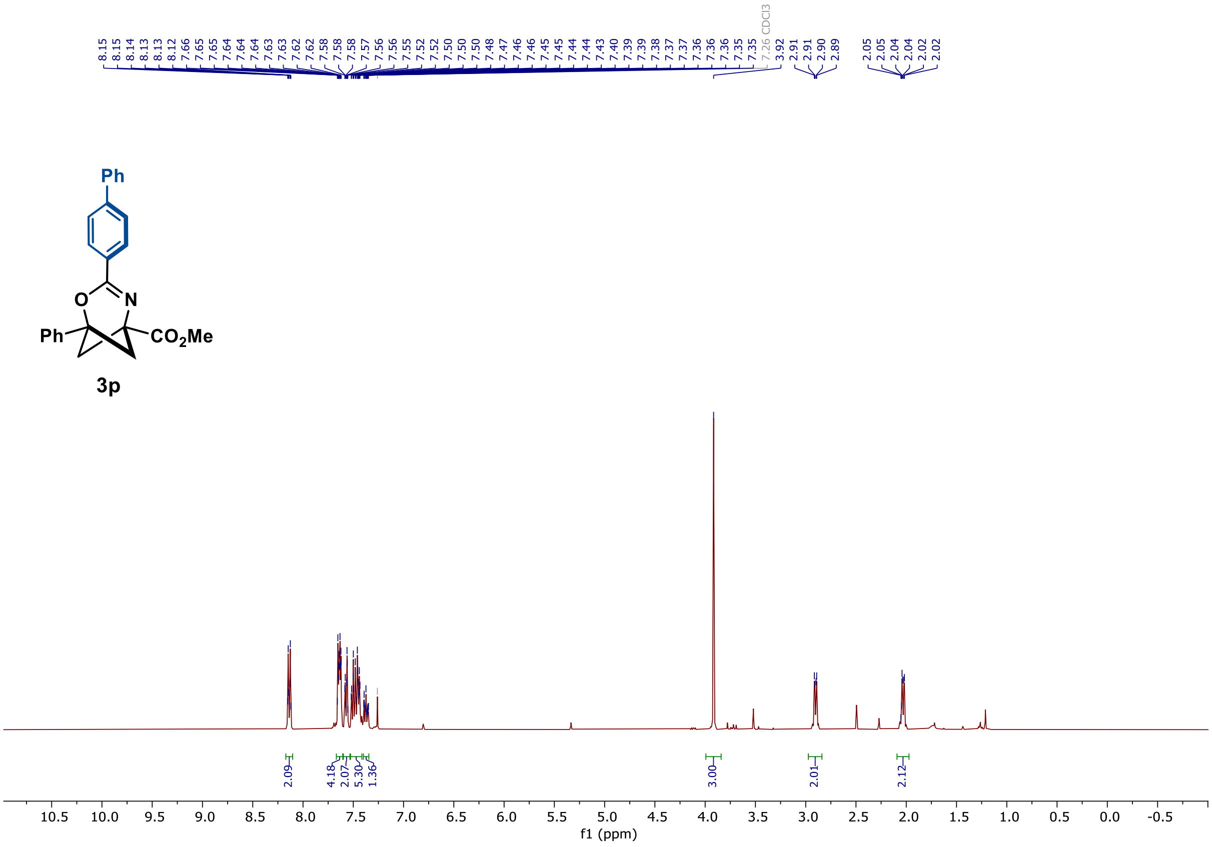
f1 (ppm)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7.62
7.62
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7.56
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7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.26 CDCl3
3.92
2.91
2.91
2.90
2.89
2.05
2.05
2.04
2.04
2.02
2.02
Ph
O
N
Ph
CO2Me
3p
2.09
4.18
2.07
5.30
1.36
3.00
2.01
2.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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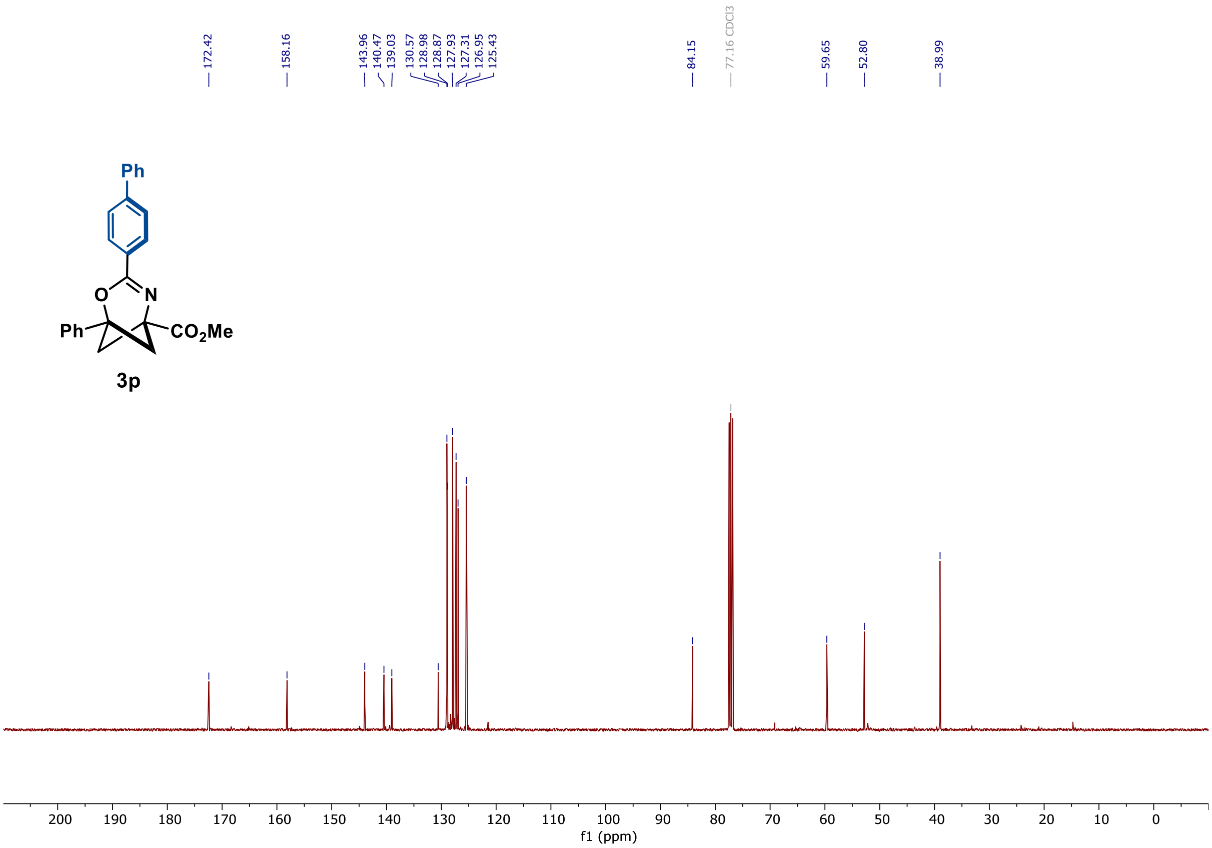
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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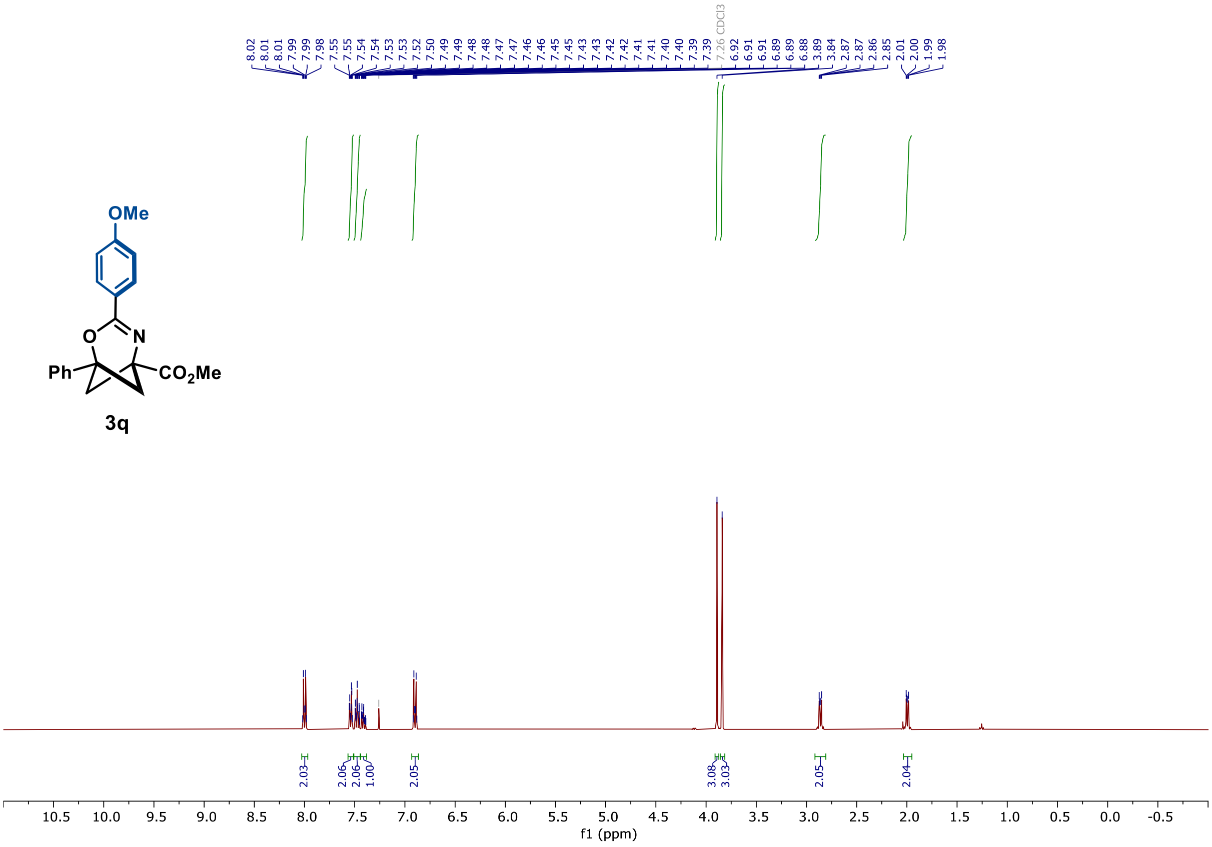
139.03
130.57
128.98
128.87
127.93
127.31
126.95
125.43
84.15
77.16 CDCl3
59.65
52.80
38.99
Ph
O
N
Ph
CO2Me
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.01
8.01
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7.98
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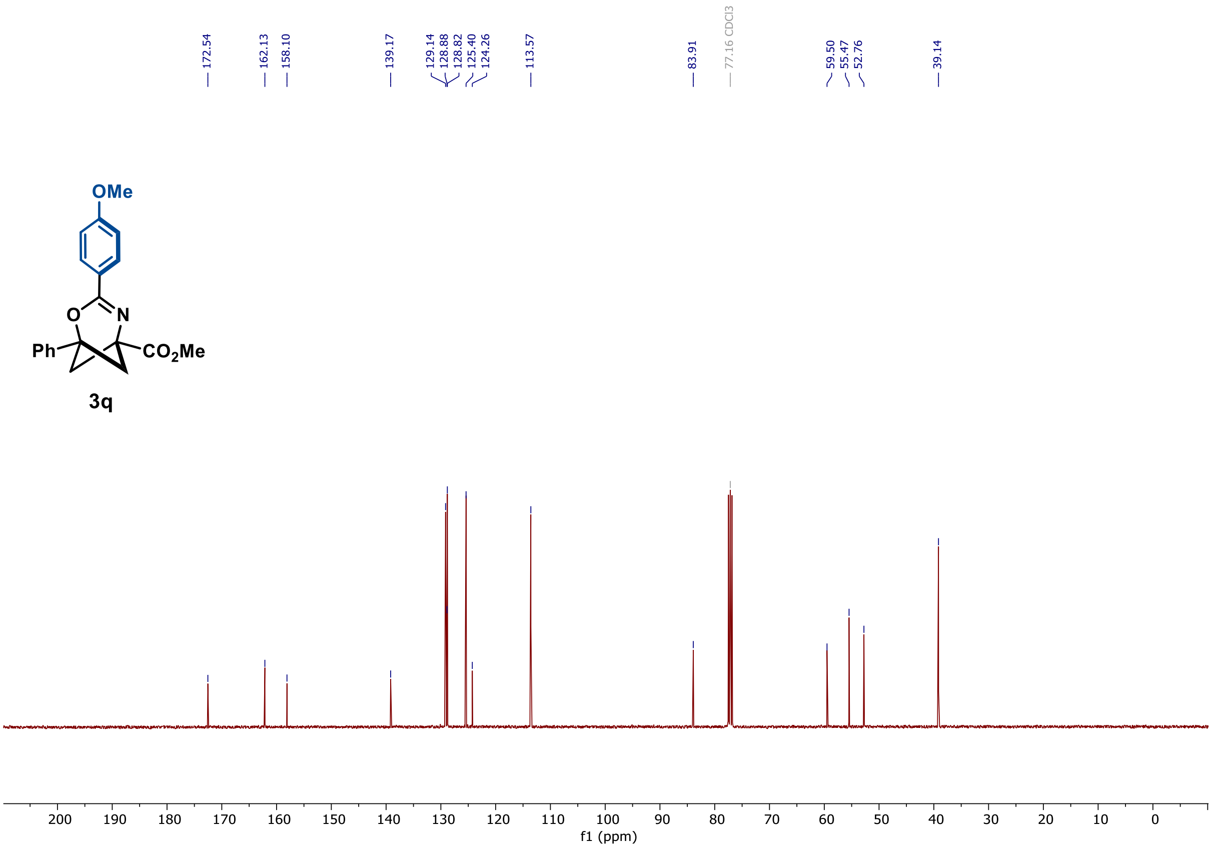
7.55
7.54
7.54
7.53
7.53
7.52
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.26 CDCl3
6.92
6.91
6.91
6.89
6.89
6.88
3.89
3.84
2.87
2.87
2.86
2.85
2.01
2.00
1.99
1.98
OMe
O
N
Ph
CO2Me
2.03
2.06
2.06
1.00
2.05
3.08
3.03
2.05
2.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3q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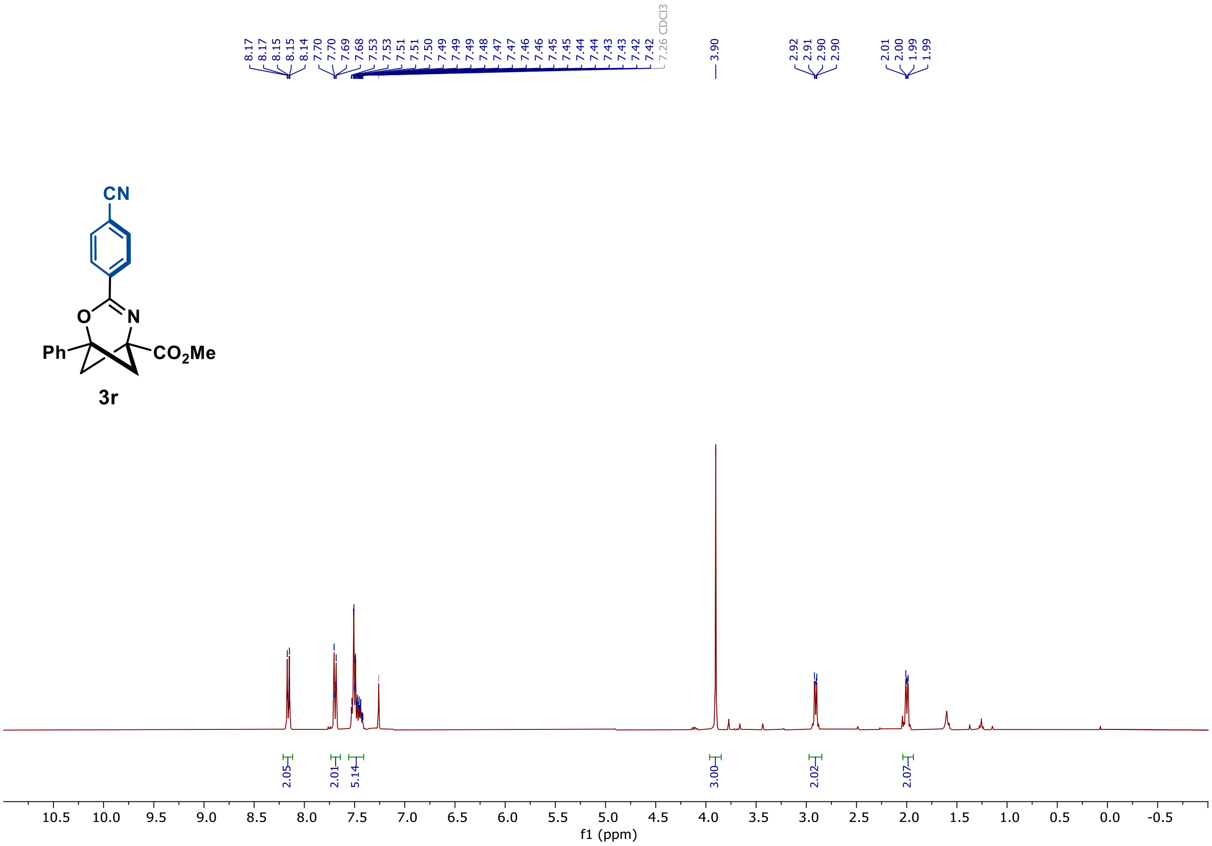
128.82
125.40
124.26
113.57
83.91
77.16 CDCl3
59.50
55.47
52.76
39.14
OMe
O
N
Ph
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3q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8.14
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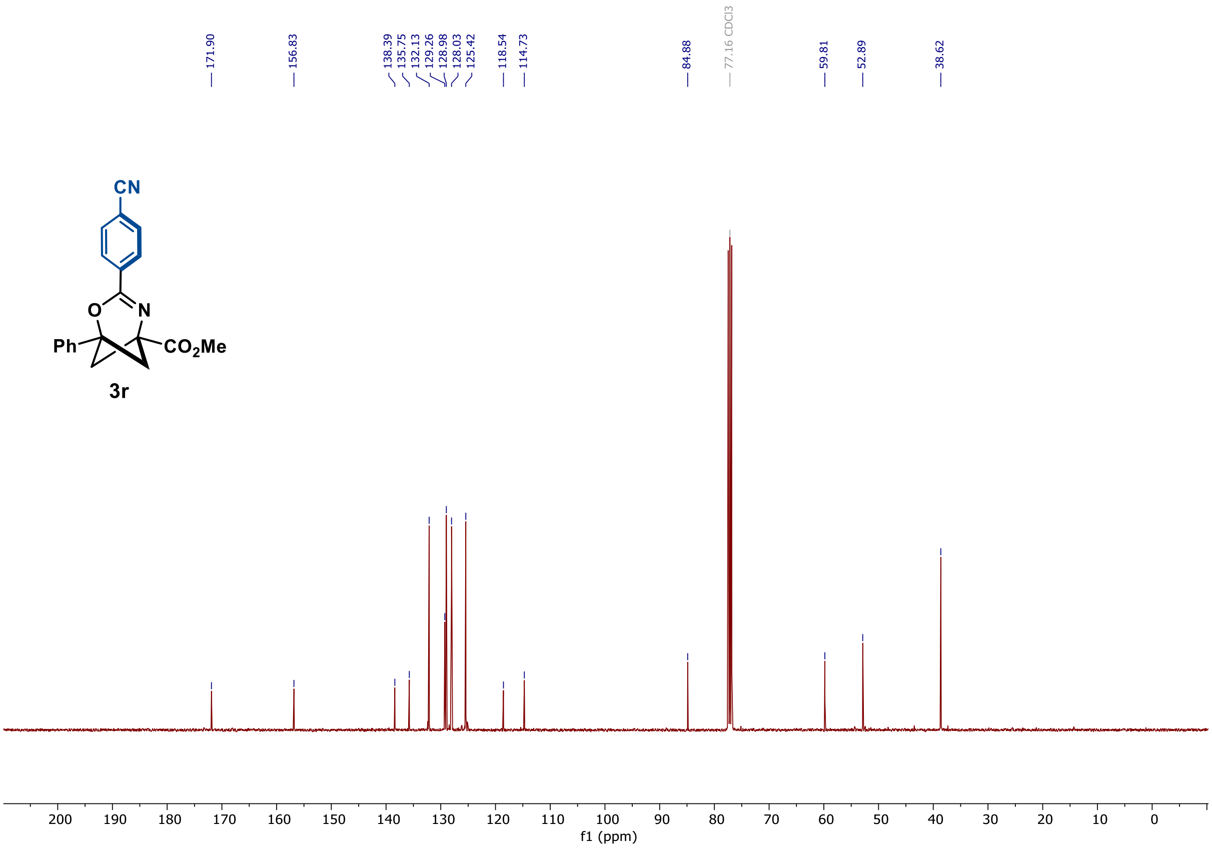
7.70
7.69
7.68
7.53
7.53
7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.26 CDCl3
3.90
2.92
2.91
2.90
2.90
2.01
2.00
1.99
1.99
CN
O
N
Ph
CO2Me
3r
2.05
2.01
5.14
3.00
2.02
2.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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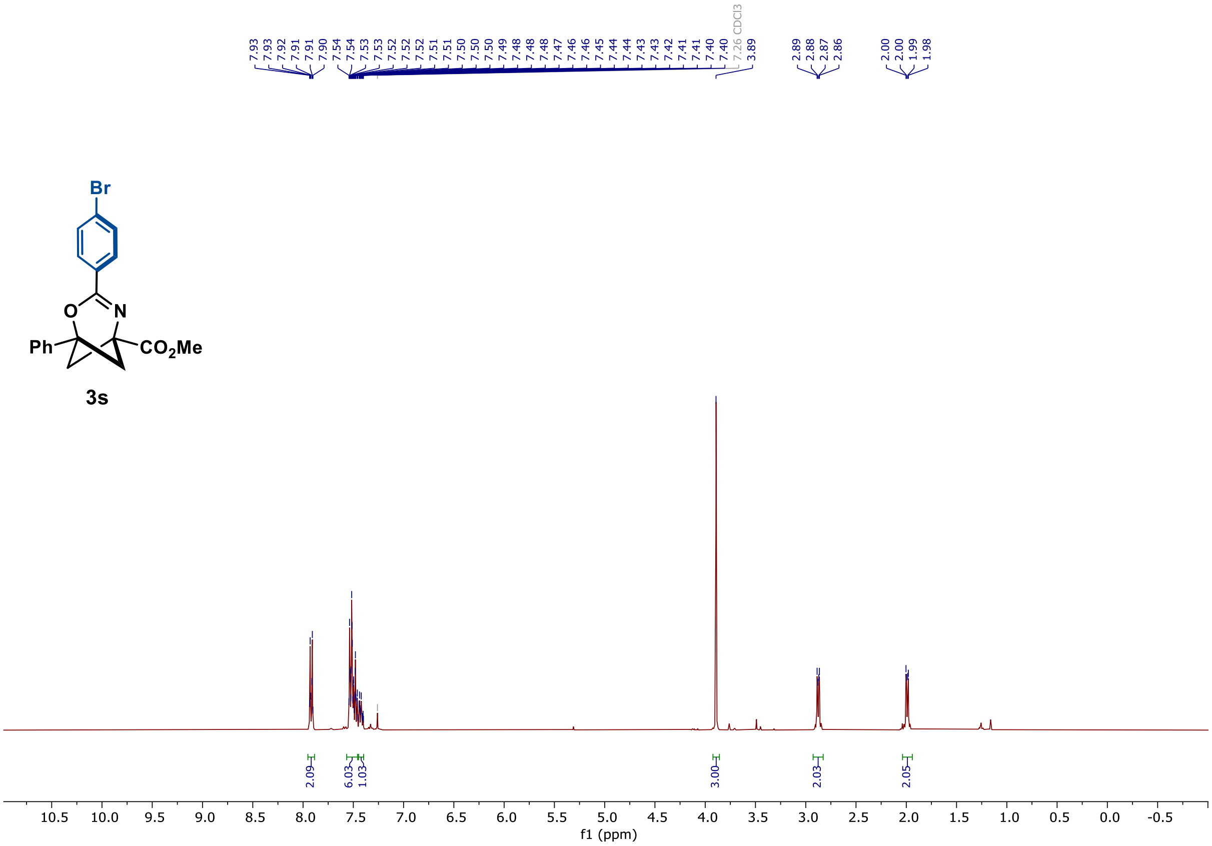
114.73
84.88
77.16 CDCl3
59.81
52.89
38.62
CN
O
N
Ph
CO2Me
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.52
7.52
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7.51
7.50
7.50
7.50
7.49
7.48
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.40
7.26 CDCl3
3.89
2.89
2.88
2.87
2.86
2.00
2.00
1.99
1.98
Br
O
N
Ph
CO2Me
2.09
6.03
1.03
3.00
2.03
2.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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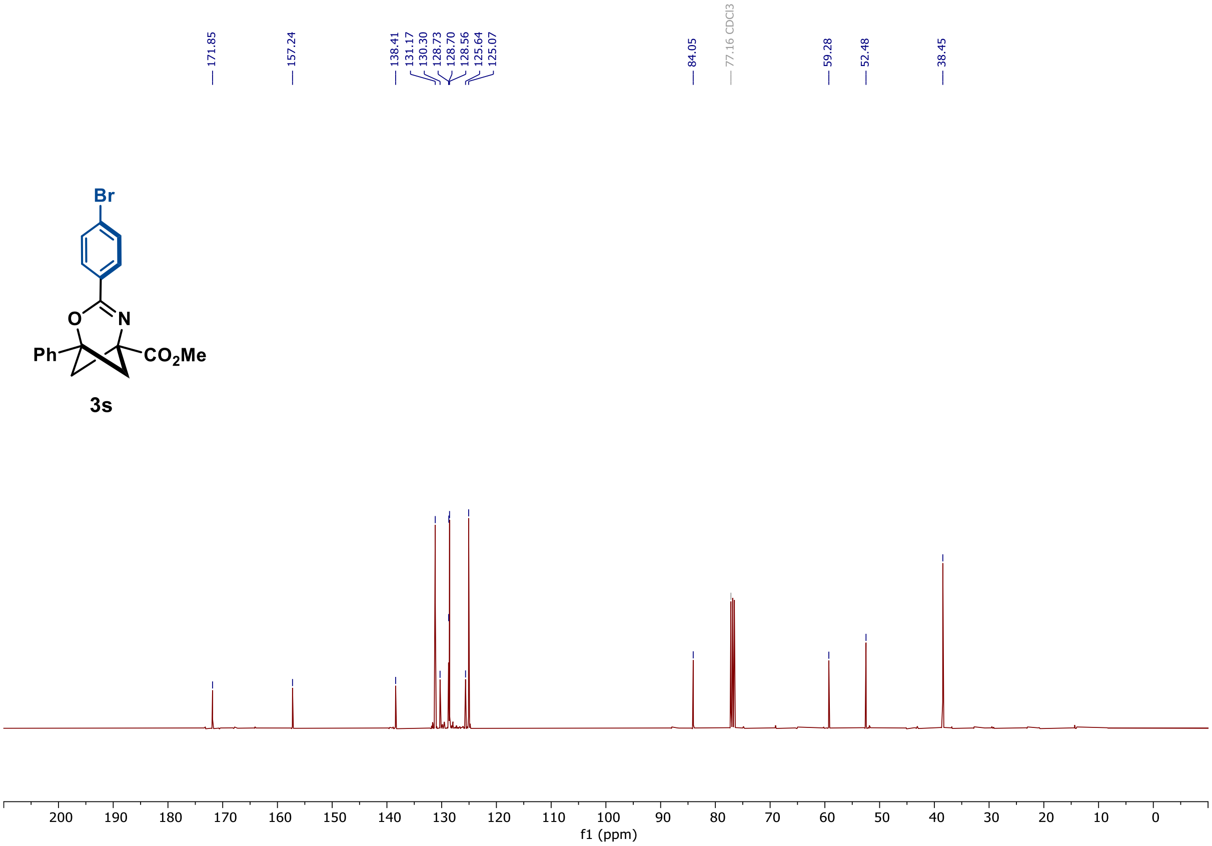
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3s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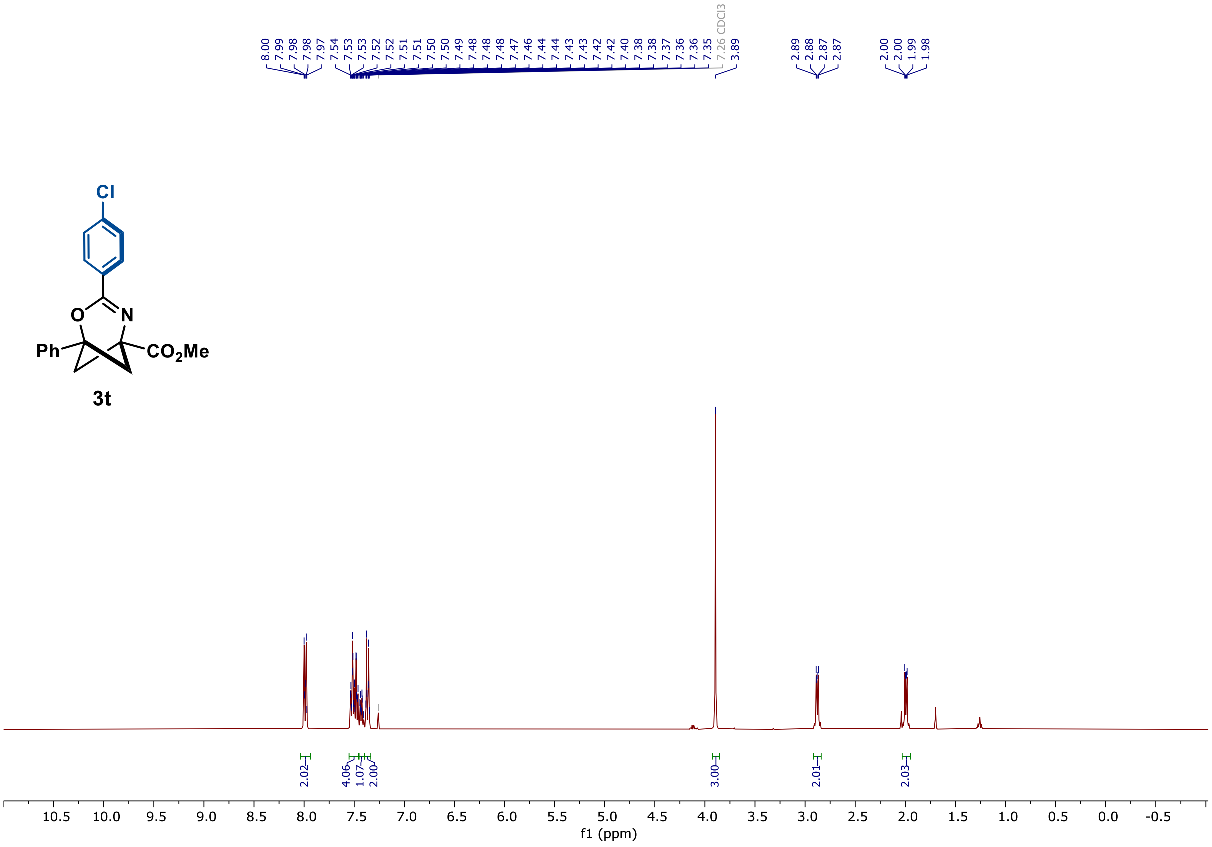
128.56
125.64
125.07
84.05
77.16 CDCl3
59.28
52.48
38.45
Br
O
N
Ph
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3s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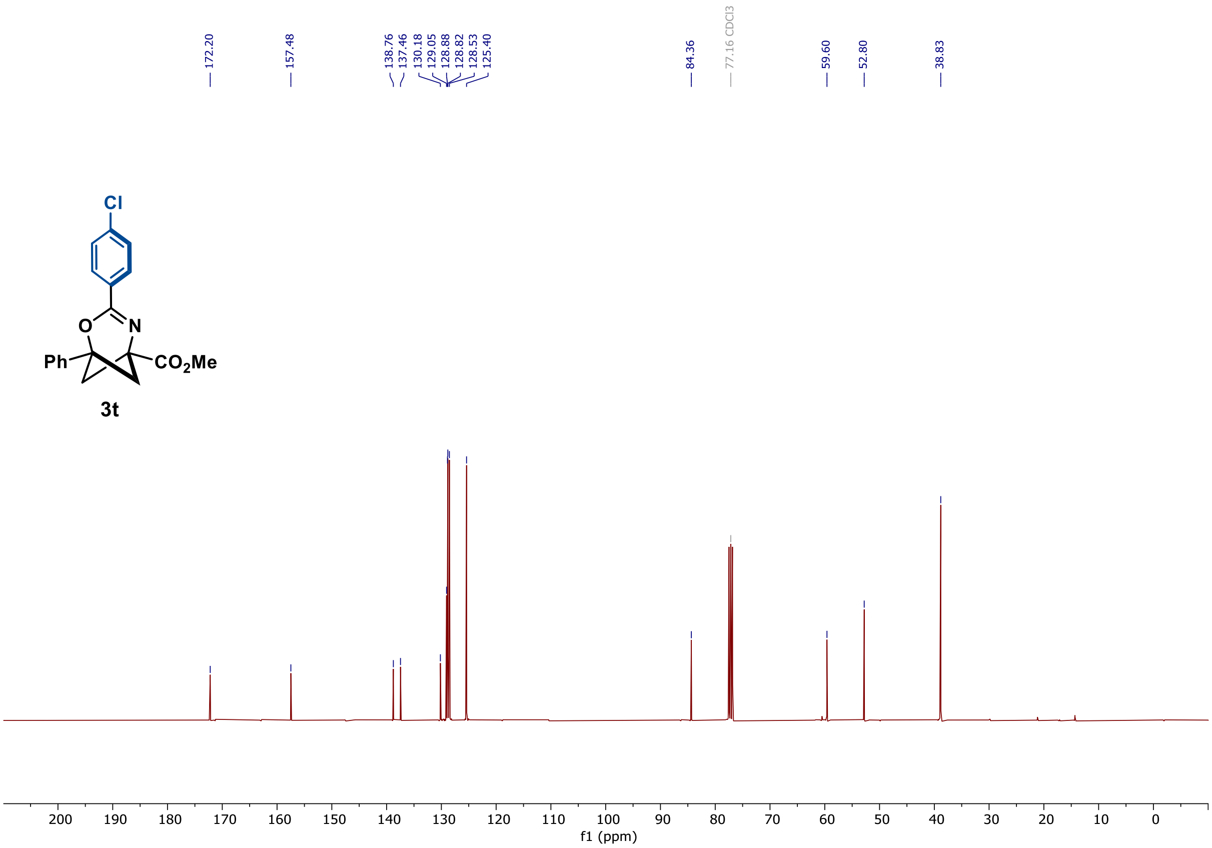
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.44
7.44
7.43
7.43
7.42
7.42
7.40
7.38
7.38
7.37
7.36
7.36
7.35
7.26 CDCl3
3.89
2.89
2.88
2.87
2.87
2.00
2.00
1.99
1.98
Cl
O
N
Ph
CO2Me
3t
2.02
4.06
1.07
2.00
3.00
2.01
2.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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125.40
84.36
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52.80
38.83
Cl
O
N
Ph
CO2Me
3t
200
190
180
170
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150
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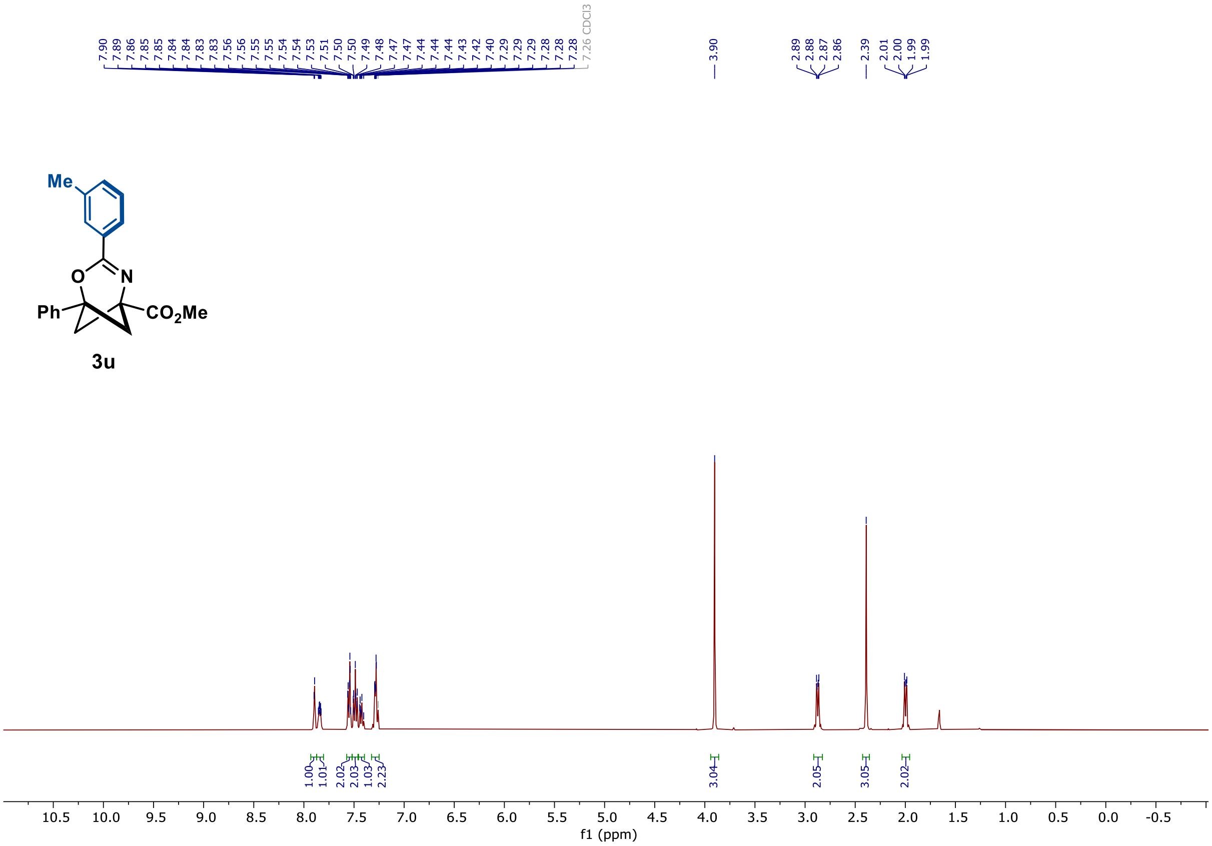
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.55
7.54
7.54
7.53
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7.50
7.50
7.49
7.48
7.47
7.47
7.44
7.44
7.43
7.42
7.40
7.29
7.29
7.29
7.28
7.28
7.26 CDCl3
3.90
2.89
2.88
2.87
2.86
2.39
2.01
2.00
1.99
1.99
Me
O
N
Ph
CO2Me
1.00
1.01
2.02
2.03
1.03
2.23
3.04
2.05
3.05
2.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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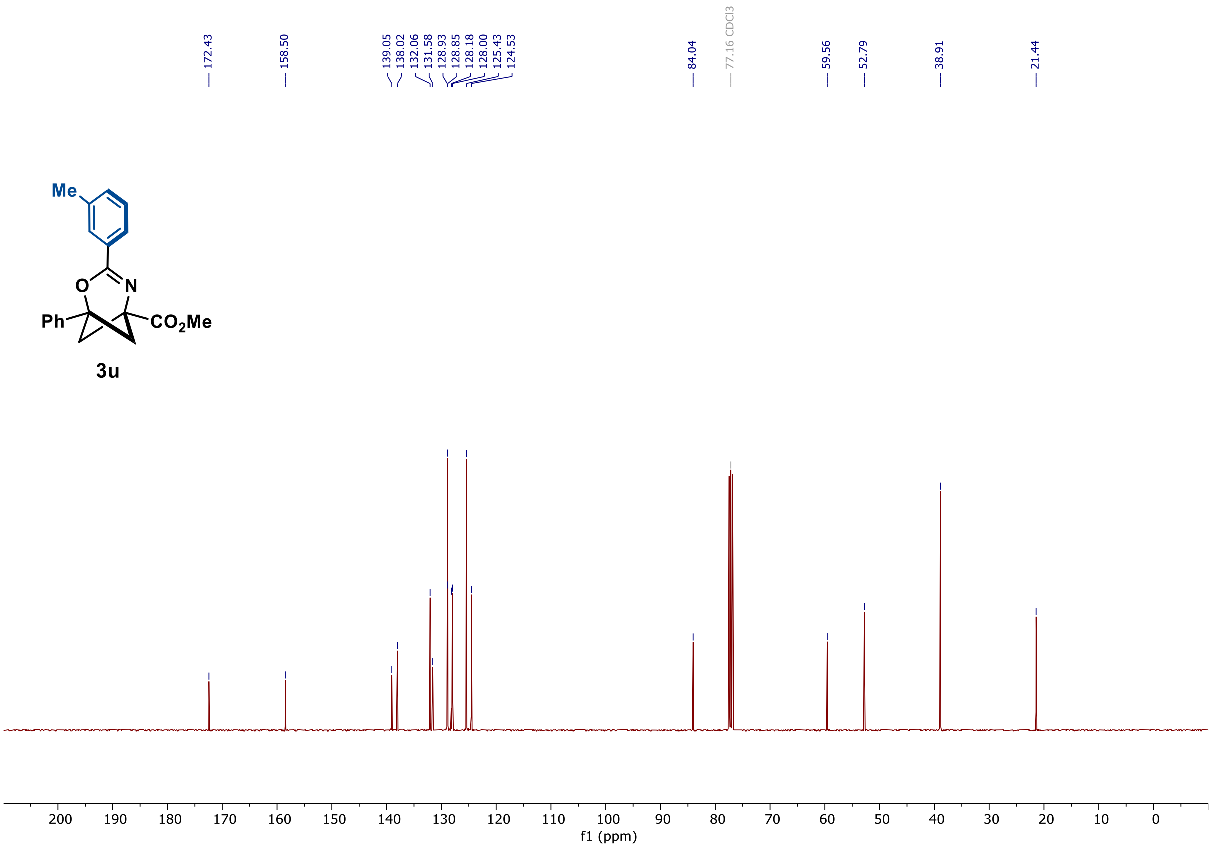
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3u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128.85
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128.00
125.43
124.53
84.04
77.16 CDCl3
59.56
52.79
38.91
21.44
Me
O
N
Ph
CO2Me
200
190
180
170
160
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140
130
120
110
100
90
80
70
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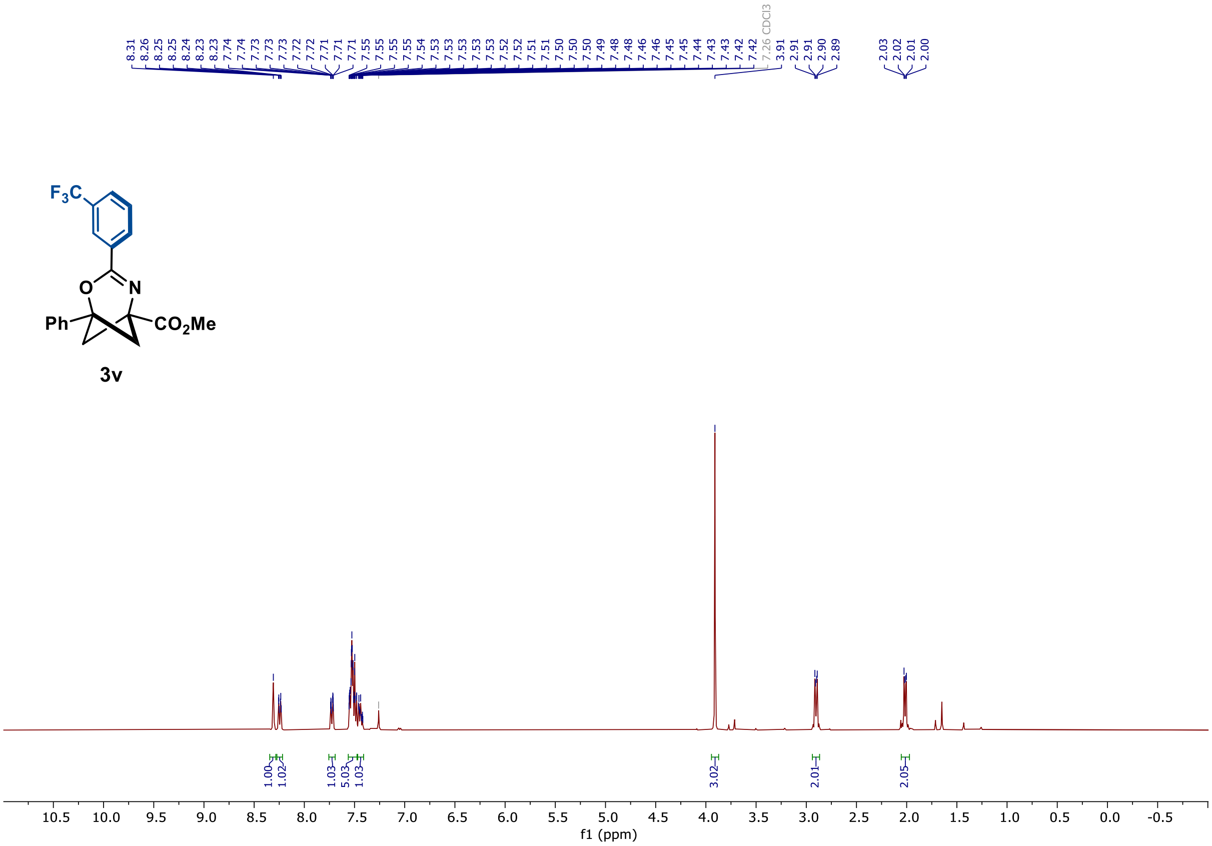
50
40
30
20
10
0
f1 (ppm)

3u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7.54
7.53
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7.53
7.52
7.51
7.50
7.50
7.50
7.49
7.48
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.26 CDCl3
3.91
2.91
2.91
2.90
2.89
2.03
2.02
2.01
2.00
F3C
O
N
Ph
CO2Me
1.00
1.02
1.03
5.03
1.03
3.02
2.01
2.05
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9.0
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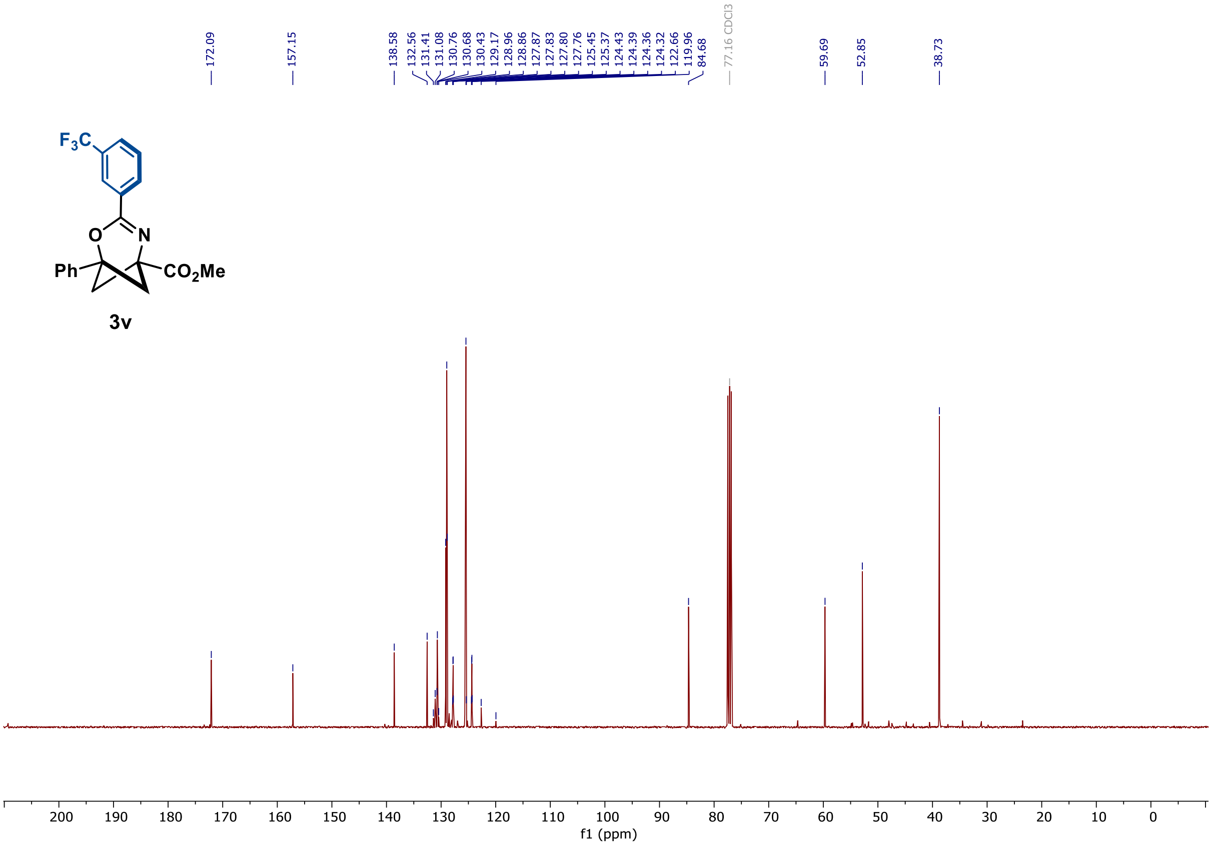
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3v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130.68
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129.17
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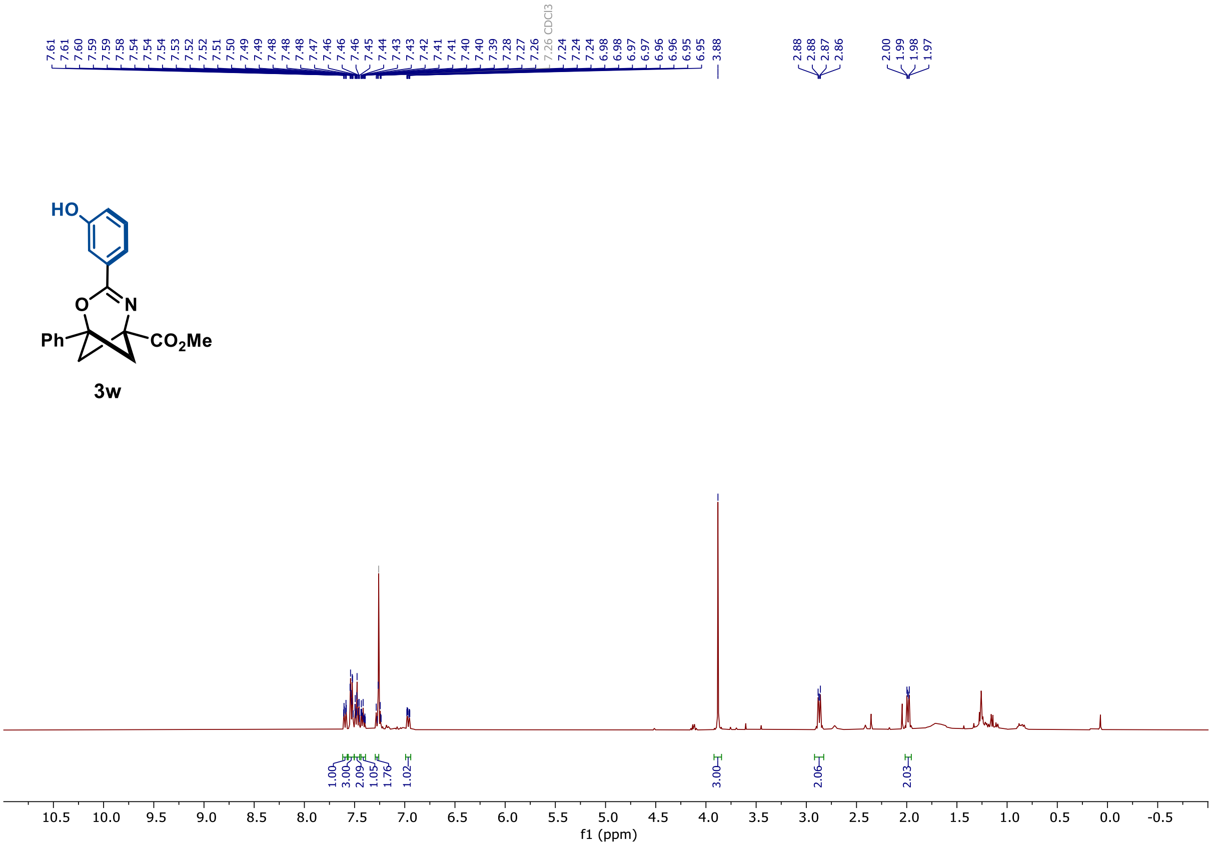
128.86
127.87
127.83
127.80
127.76
125.45
125.37
124.43
124.39
124.36
124.32
122.66
119.96
84.68
77.16 CDCl3
59.69
52.85
38.73
F3C
O
N
Ph
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3v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7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.28
7.27
7.26
7.26 CDCl3
7.24
7.24
7.24
6.98
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6.96
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6.95
6.95
3.88
2.88
2.88
2.87
2.86
2.00
1.99
1.98
1.97
HO
O
N
Ph
CO2Me
3w
1.00
3.00
2.09
1.05
1.76
1.02
3.00
2.06
2.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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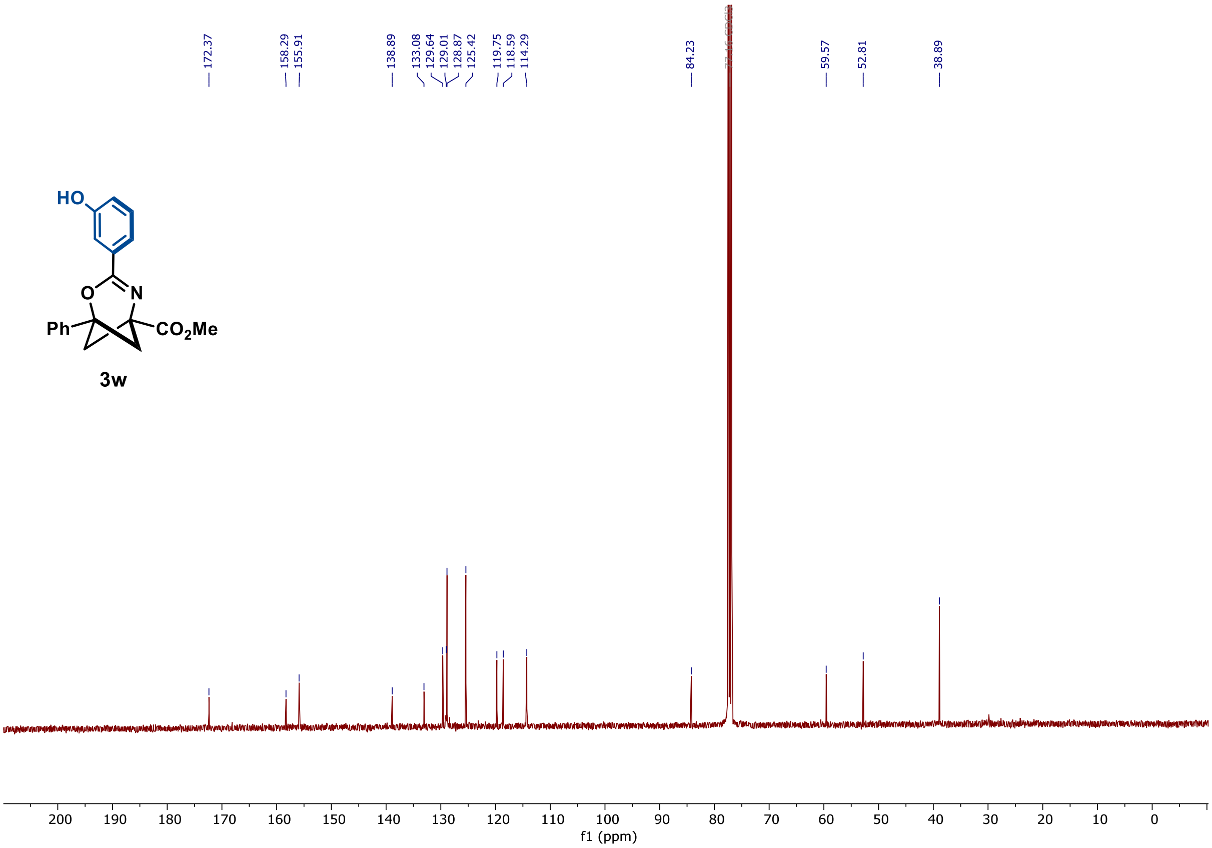
f1 (ppm)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84.23
77.16 CDCl3
59.57
52.81
38.89
HO
O
N
Ph
CO2Me
3w
200
190
180
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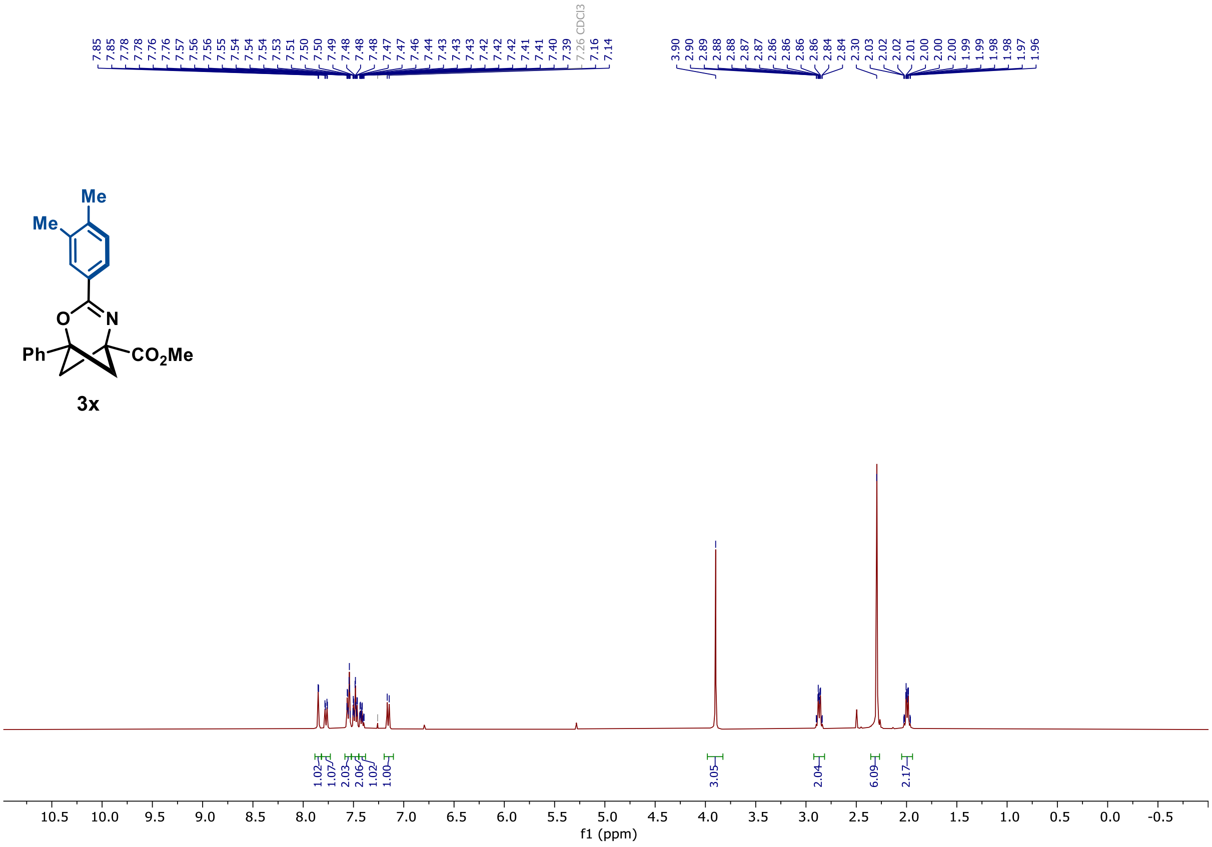
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7.41
7.40
7.39
7.26 CDCl3
7.16
7.14
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2.88
2.87
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2.86
2.86
2.86
2.86
2.84
2.84
2.30
2.03
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2.02
2.01
2.00
2.00
2.00
1.99
1.99
1.98
1.98
1.97
1.96
Me
Me
O
N
Ph
CO2Me
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1.07
2.03
2.06
1.02
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3.05
2.04
6.09
2.17
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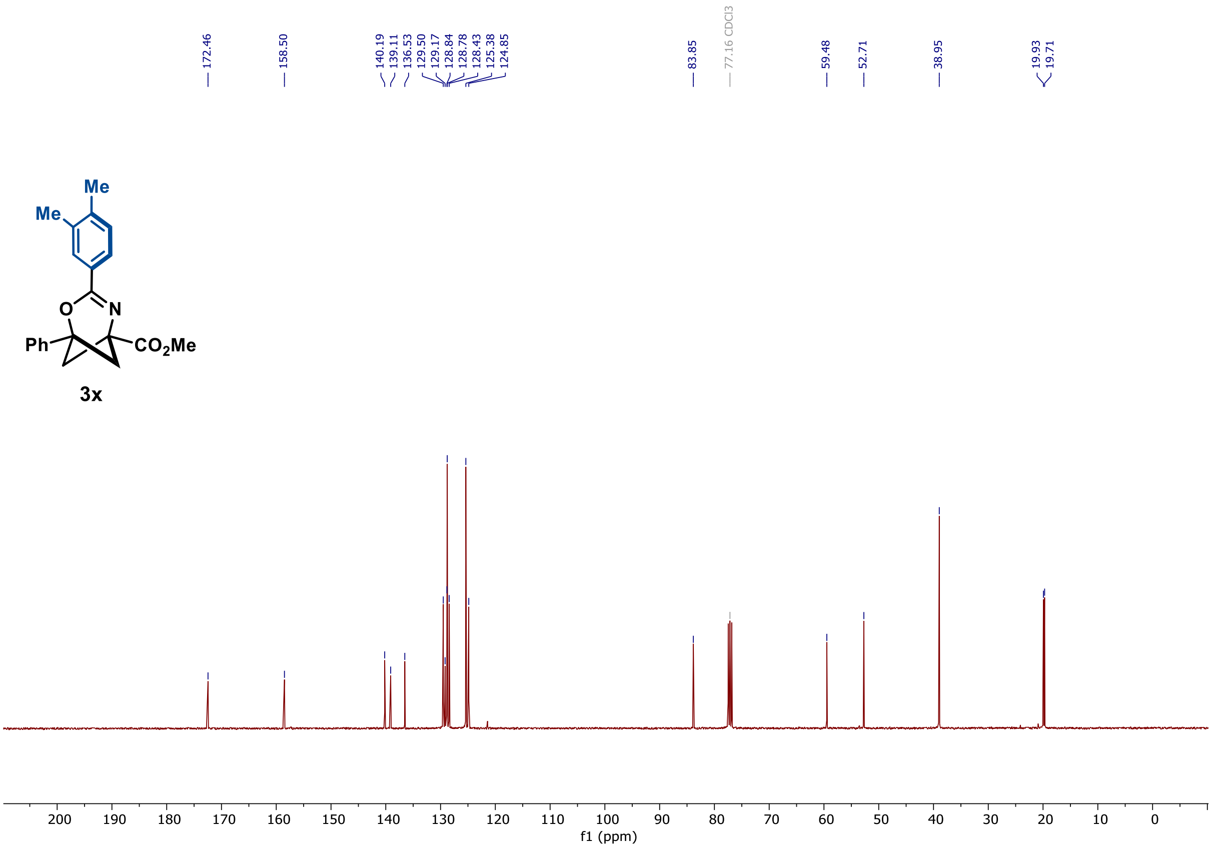
3x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128.43
125.38
124.85
83.85
77.16 CDCl3
59.48
52.71
38.95
19.93
19.71
Me
Me
O
N
Ph
CO2Me
200
190
180
170
160
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100
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80
70
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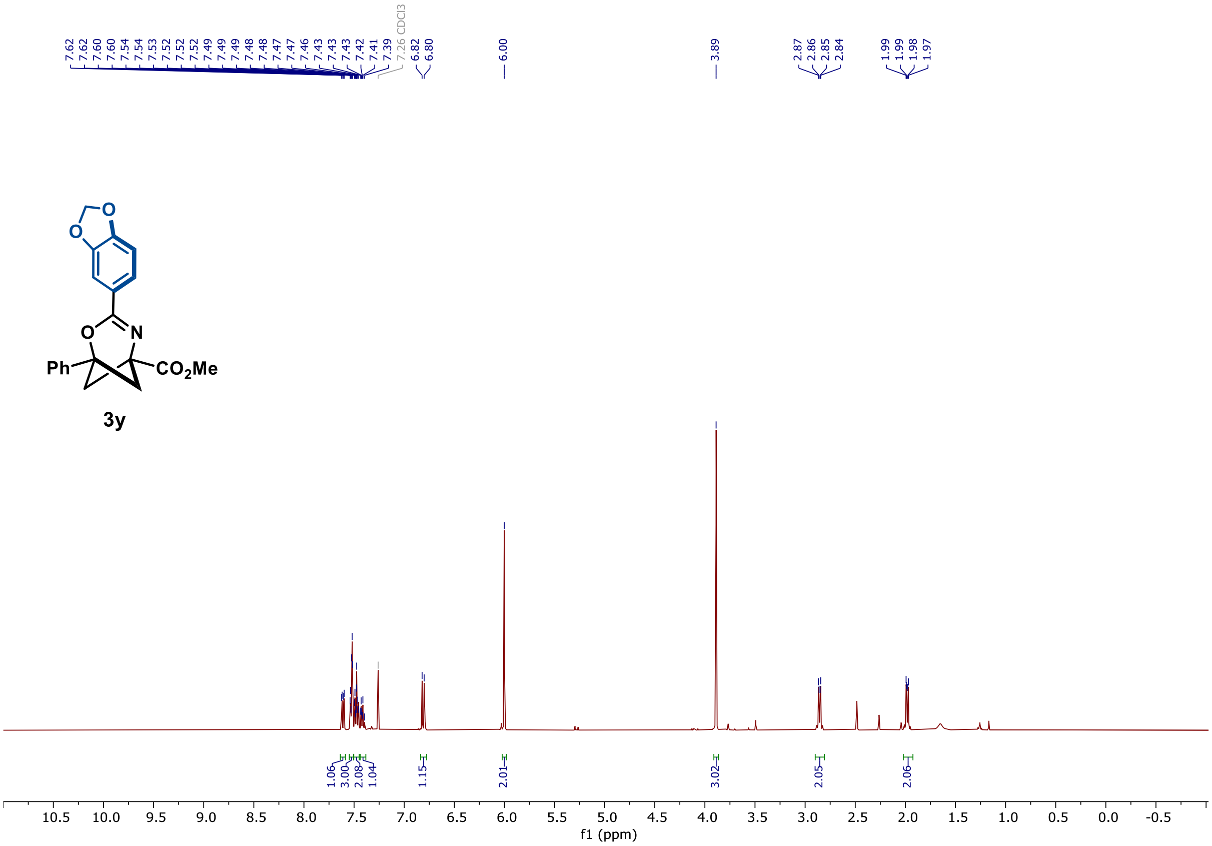
f1 (ppm)

3x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7.48
7.48
7.47
7.47
7.46
7.43
7.43
7.43
7.42
7.41
7.39
7.26 CDCl3
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6.80
6.00
3.89
2.87
2.86
2.85
2.84
1.99
1.99
1.98
1.97
O
O
O
N
Ph
CO2Me
3y
1.06
3.00
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2.01
3.02
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2.06
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5.0
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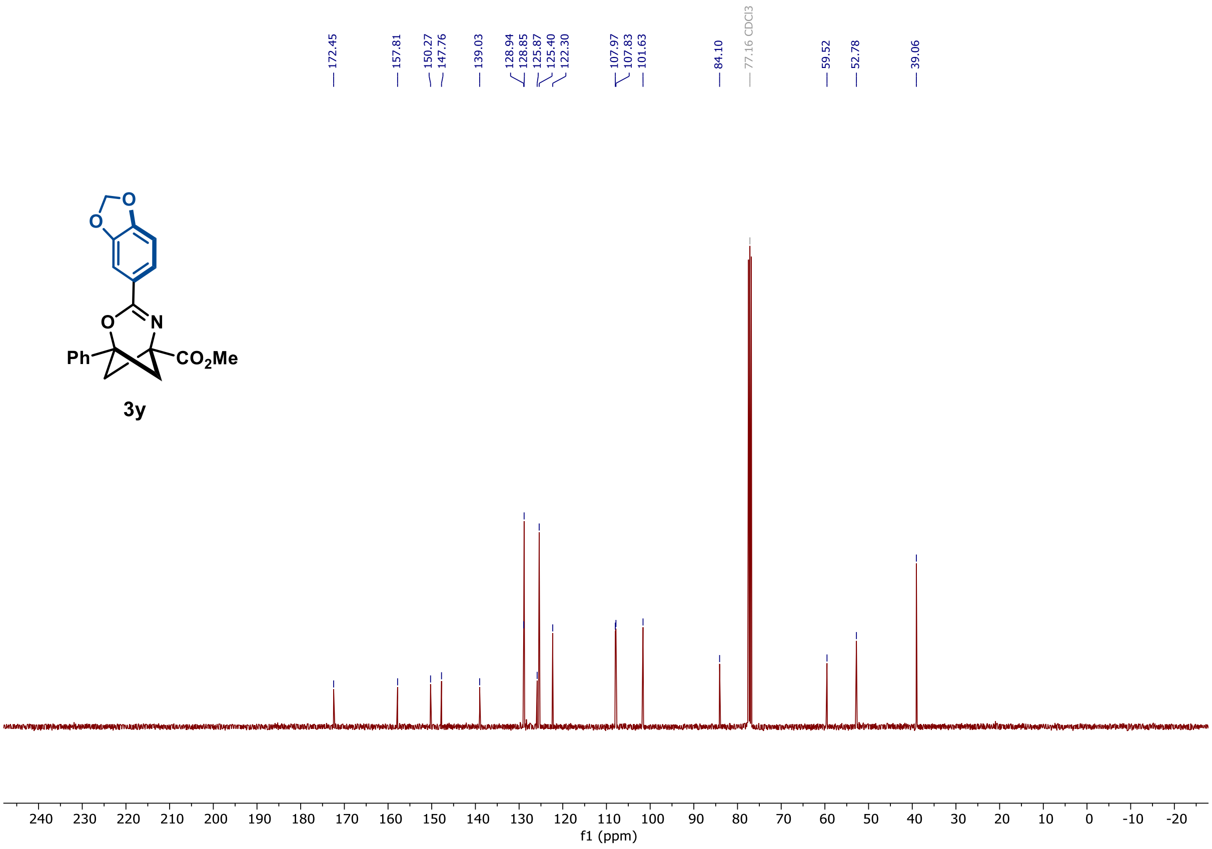
-0.5
f1 (ppm)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107.83
101.63
84.10
77.16 CDCl3
59.52
52.78
39.06
O
O
O
N
Ph
CO2Me
3y
240
230
220
210
200
190
180
170
160
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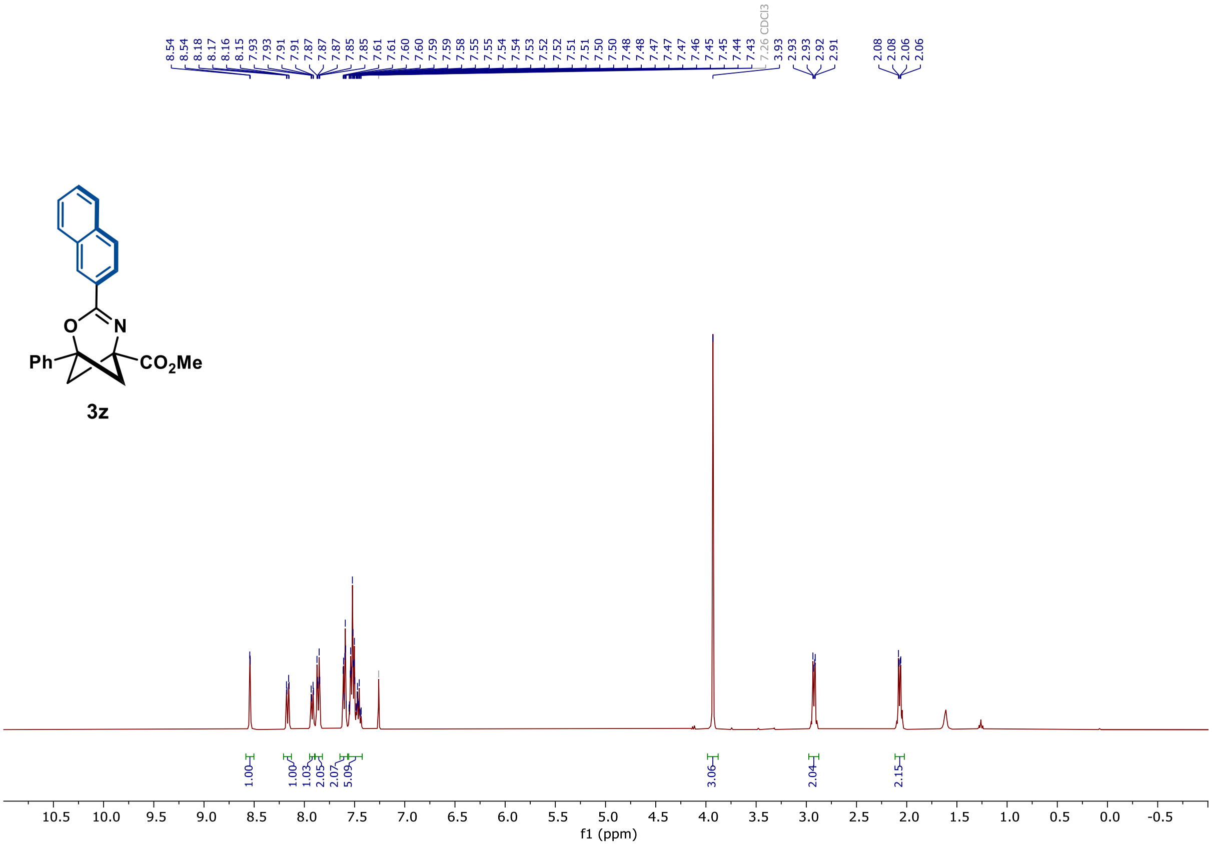
-20
f1 (ppm)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7.61
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7.59
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7.54
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7.52
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7.51
7.51
7.50
7.50
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.26 CDCl3
3.93
2.93
2.93
2.92
2.91
2.08
2.08
2.06
2.06
O
N
Ph
CO2Me
3z
1.00
1.00
1.03
2.05
2.07
5.09
3.06
2.04
2.15
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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3.0
2.5
2.0
1.5
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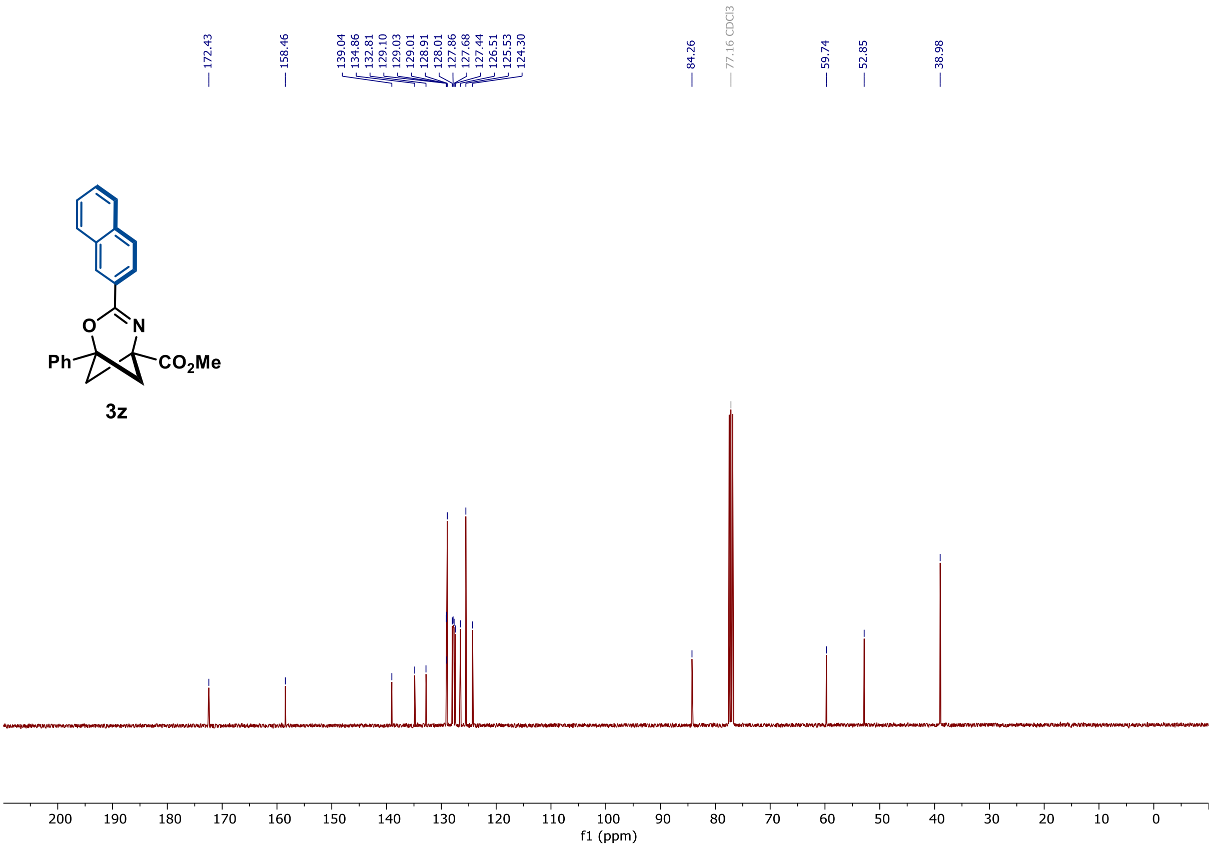
-0.5
f1 (ppm)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127.44
126.51
125.53
124.30
84.26
77.16 CDCl3
59.74
52.85
38.98
O
N
Ph
CO2Me
3z
200
190
180
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150
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130
120
110
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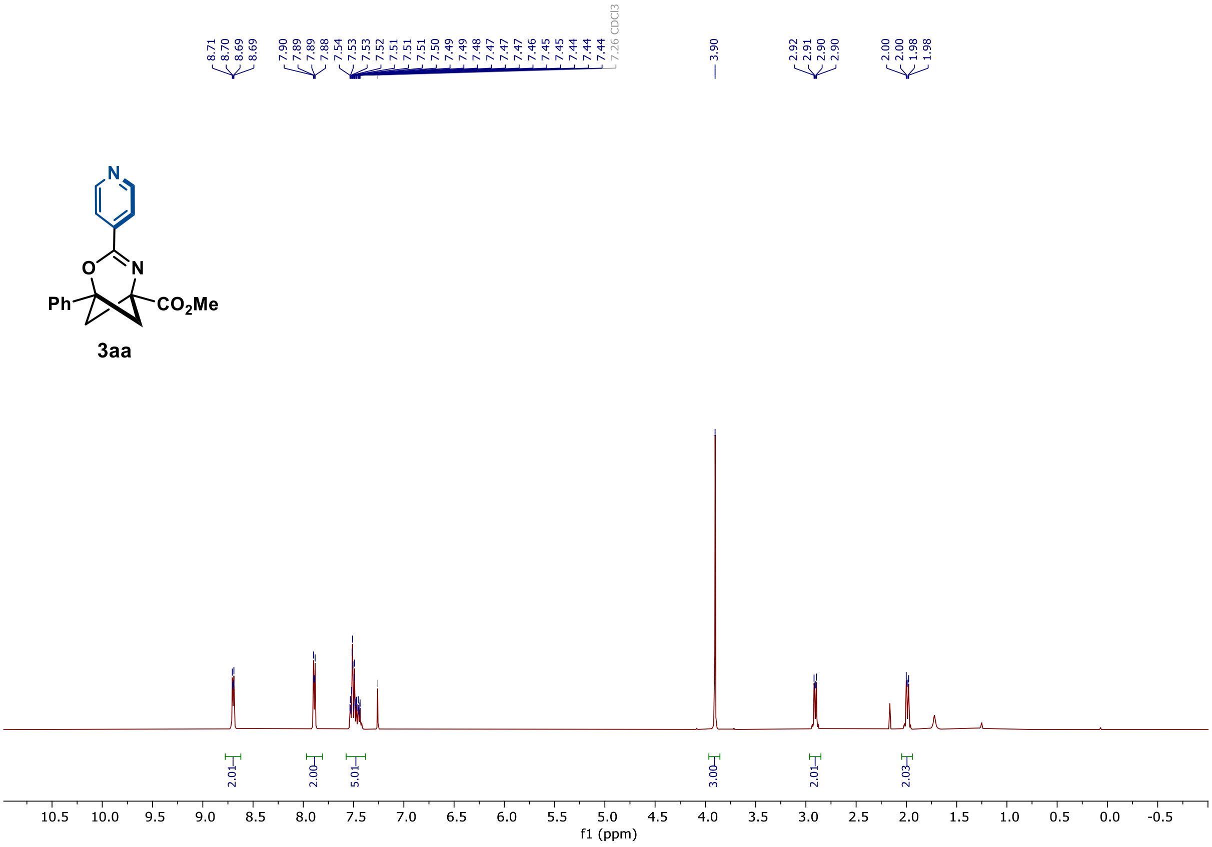
10
0
f1 (ppm)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7.45
7.45
7.44
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7.44
7.26 CDCl3
3.90
2.92
2.91
2.90
2.90
2.00
2.00
1.98
1.98
N
O
N
Ph
CO2Me
3aa
2.01
2.00
5.01
3.00
2.01
2.03
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5.0
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2.0
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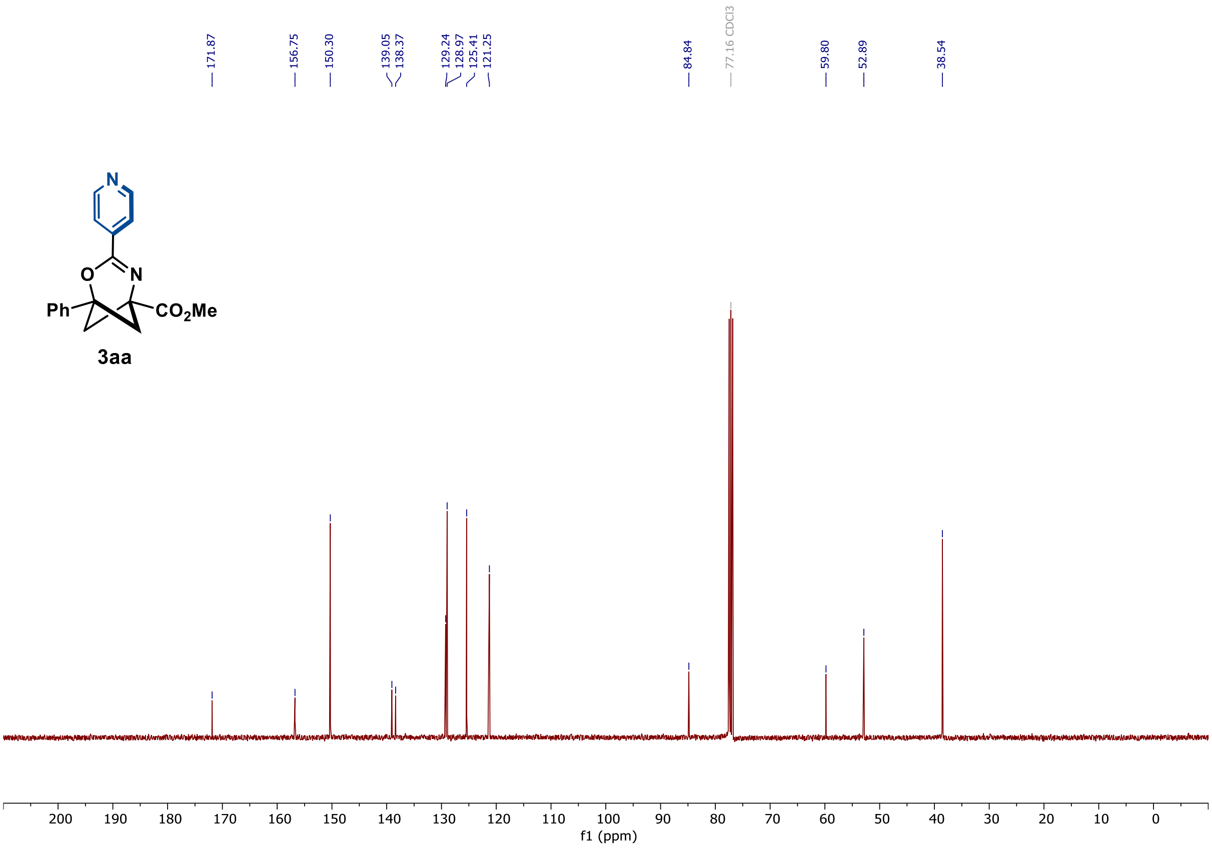
0.5
0.0
-0.5
f1 (ppm)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121.25
84.84
77.16 CDCl3
59.80
52.89
38.54
N
O
N
Ph
CO2Me
3aa
200
190
180
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130
120
110
100
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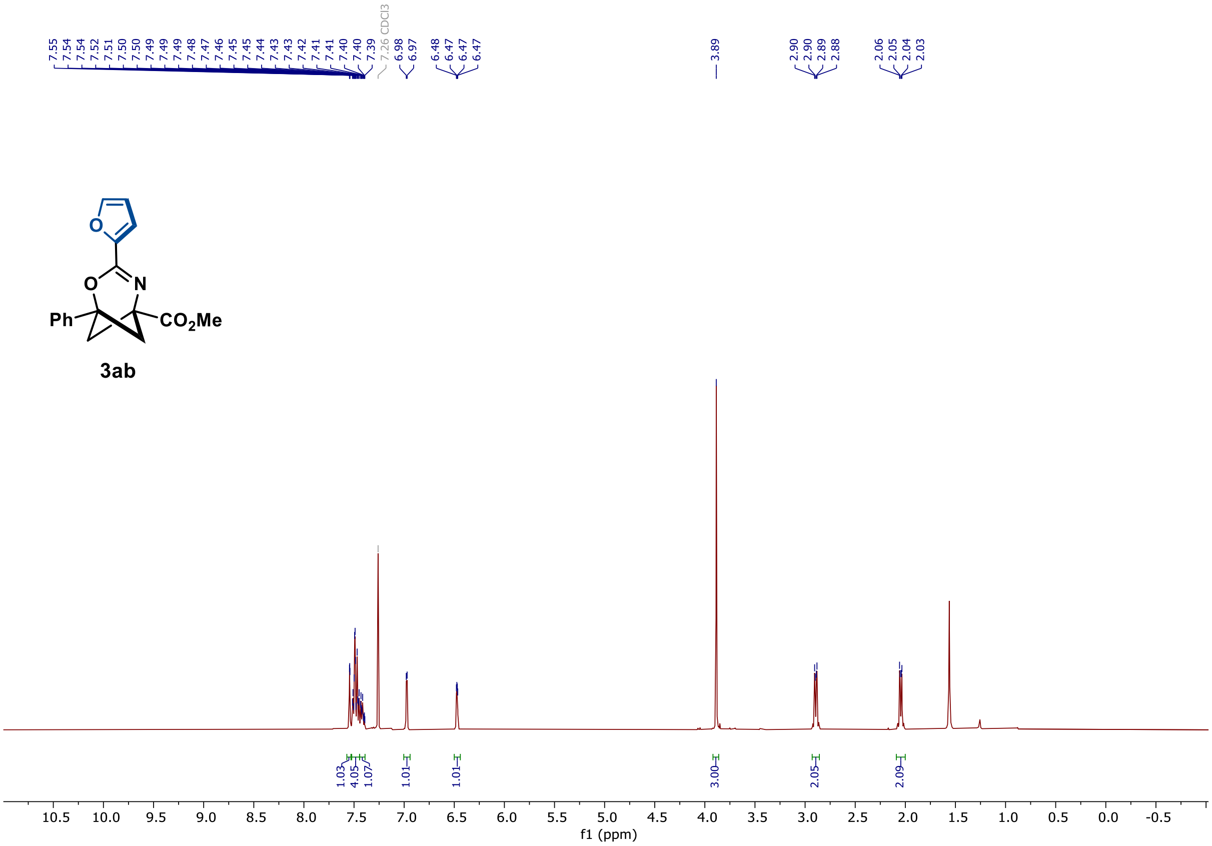
f1 (ppm)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7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.26 CDCl3
6.98
6.97
6.48
6.47
6.47
6.47
3.89
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2.89
2.88
2.06
2.05
2.04
2.03
O
O
N
Ph
CO2Me
3ab
1.03
4.05
1.07
1.01
1.01
3.00
2.05
2.09
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5.5
5.0
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2.5
2.0
1.5
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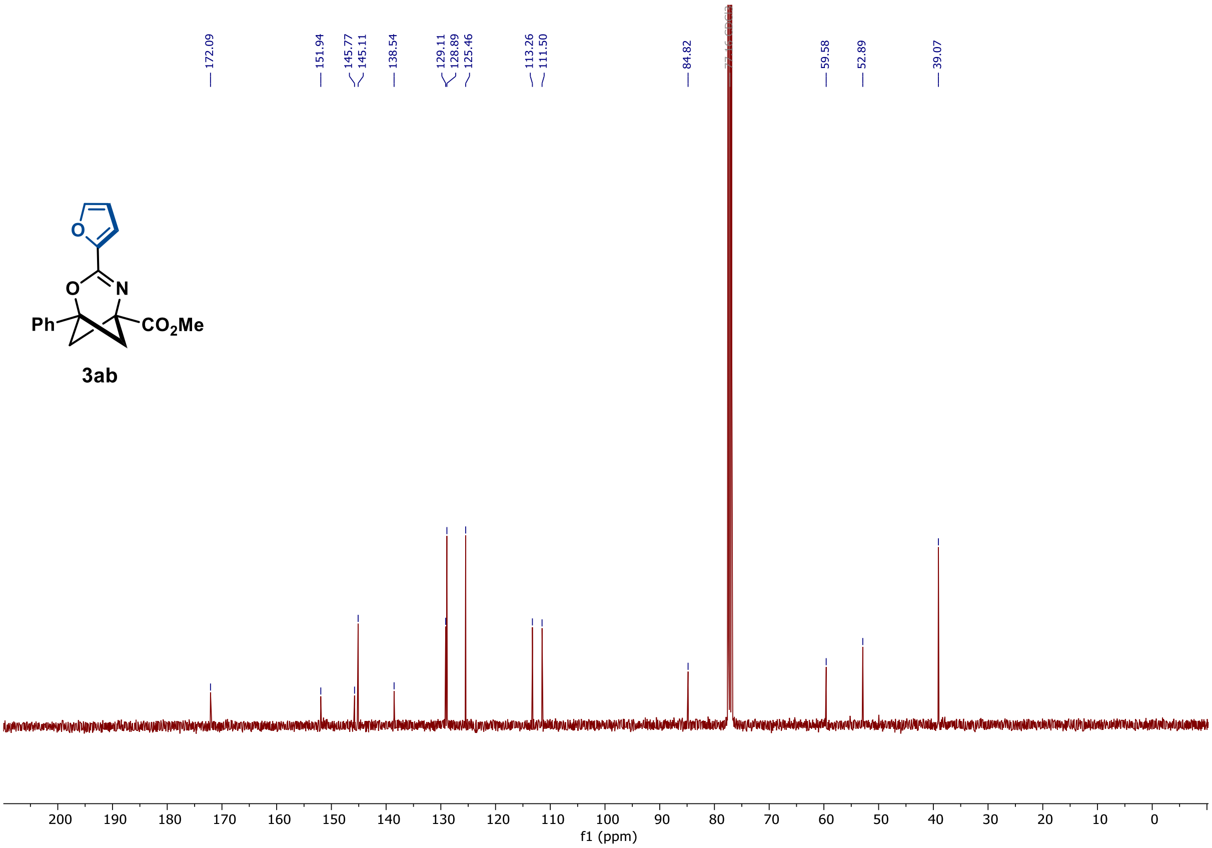
0.5
0.0
-0.5
f1 (ppm)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59.58
52.89
39.07
O
O
N
Ph
CO2Me
3ab
200
190
180
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150
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130
120
110
100
90
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70
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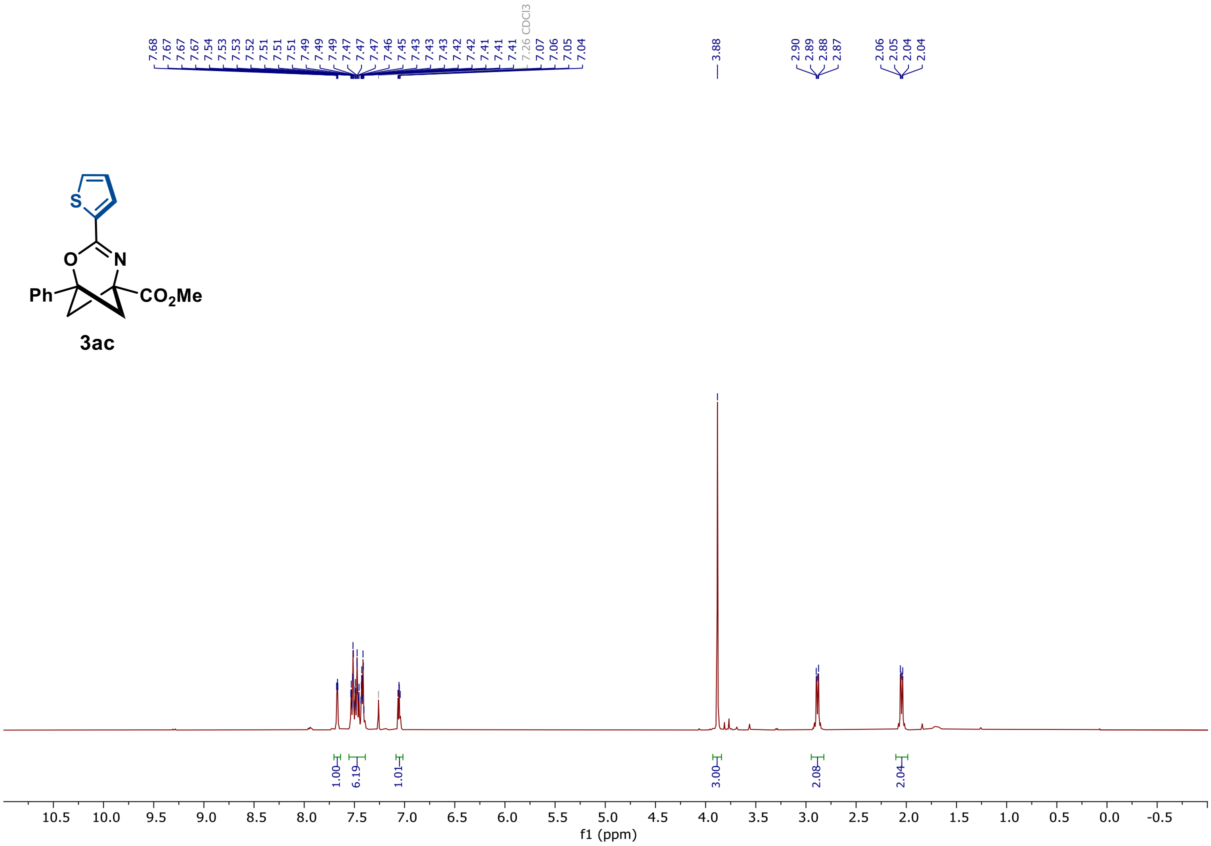
50
40
30
20
10
0
f1 (ppm)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7.47
7.47
7.46
7.45
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.26 CDCl3
7.07
7.06
7.05
7.04
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2.04
2.04
S
O
N
Ph
CO2Me
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3.00
2.08
2.04
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7.0
6.5
6.0
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5.0
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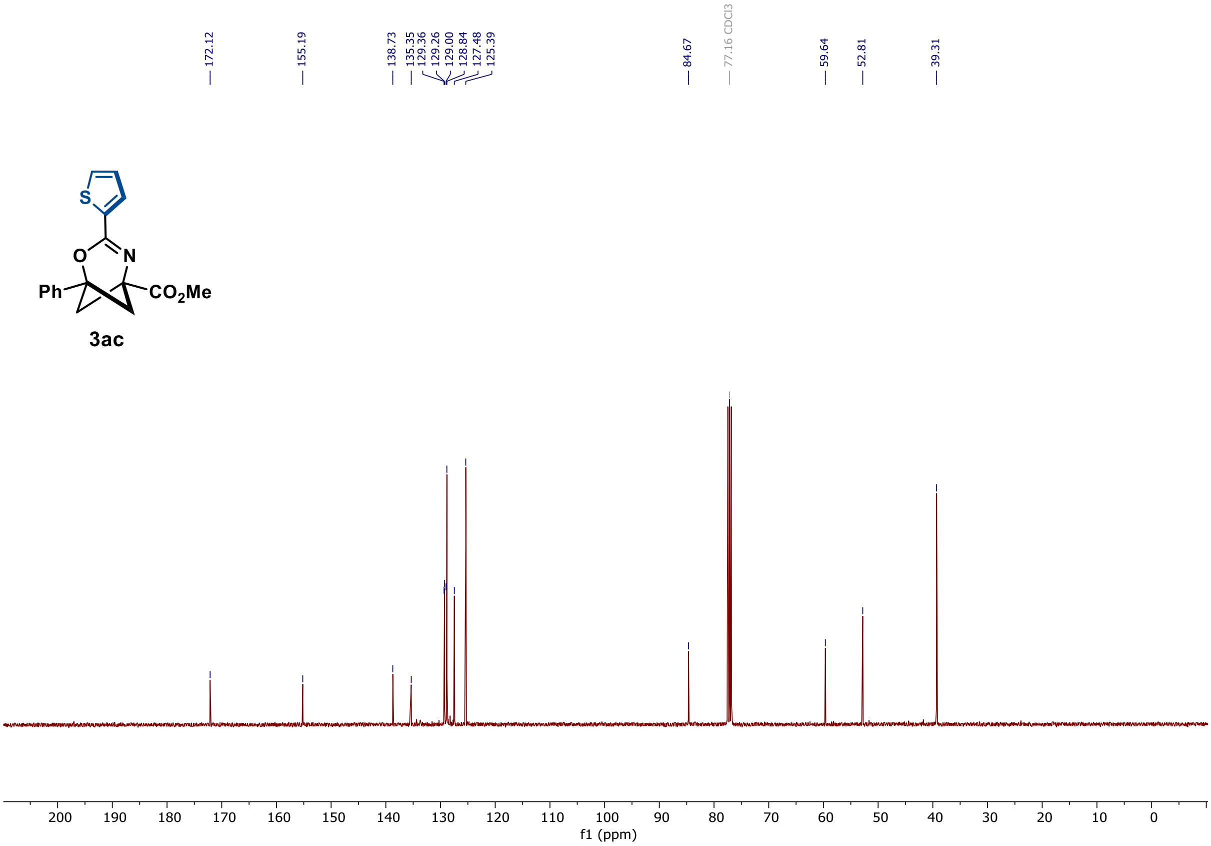
-0.5
f1 (ppm)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125.39
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52.81
39.31
S
O
N
Ph
CO2Me
3ac
200
190
180
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120
110
100
90
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70
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50
40
30
20
10
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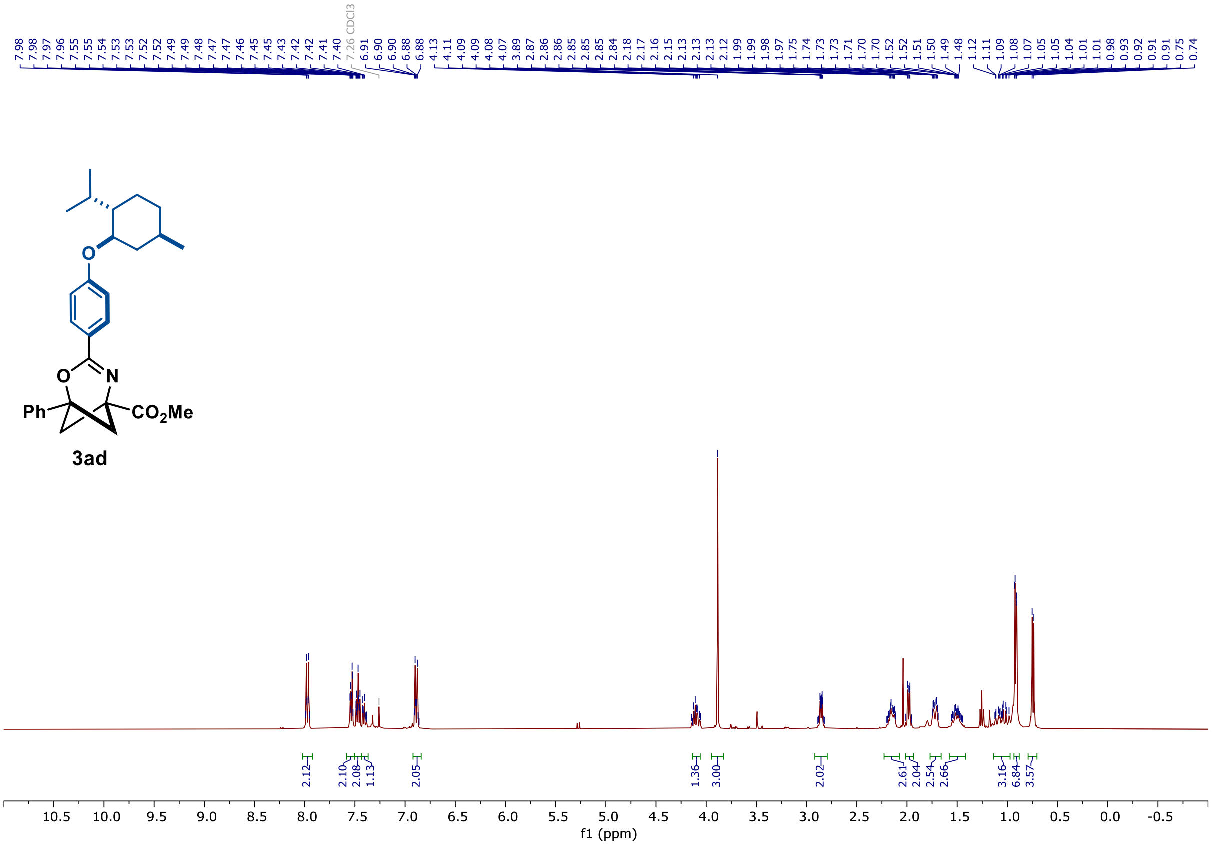
f1 (ppm)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7.47
7.46
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7.45
7.43
7.42
7.42
7.41
7.40
7.26 CDCl3
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1.01
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0.91
0.75
0.74
O
O
N
Ph
CO2Me
3ad
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2.05
1.36
3.00
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2.04
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5.0
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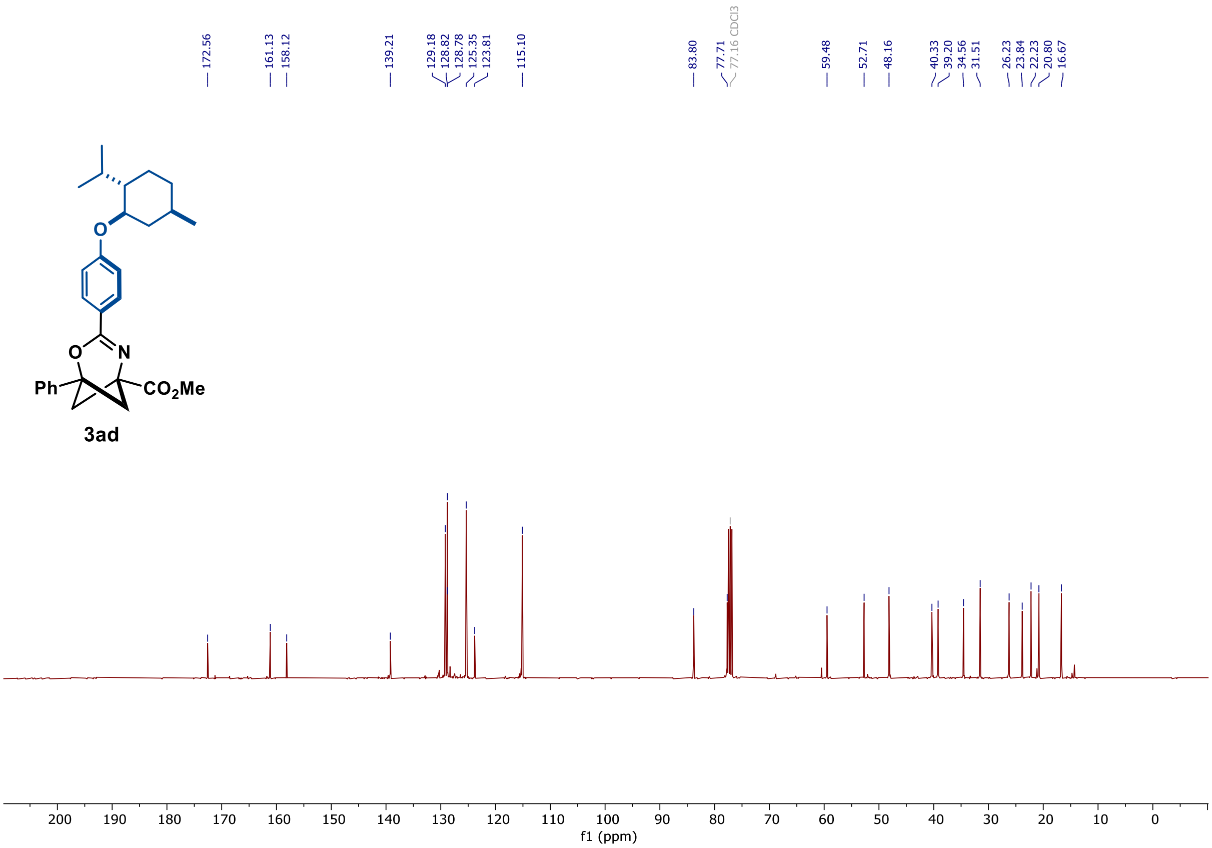
f1 (ppm)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77.71
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52.71
48.16
40.33
39.20
34.56
31.51
26.23
23.84
22.23
20.80
16.67
O
O
N
Ph
CO2Me
3ad
200
190
180
170
160
150
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130
120
110
100
90
80
70
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50
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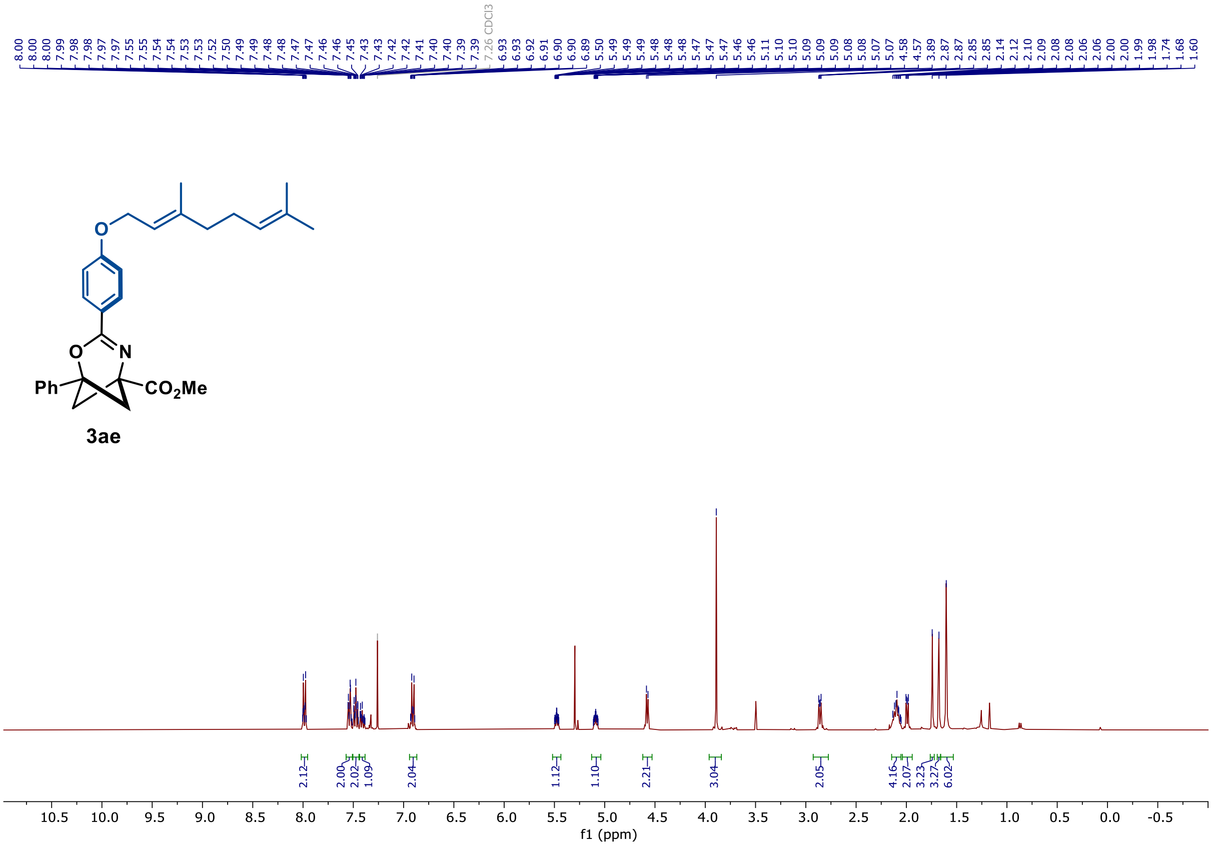
10
0
f1 (ppm)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7.42
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7.41
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7.40
7.39
7.39
7.26 CDCl3
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2.87
2.85
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O
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Ph
CO2Me
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1.12
1.10
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5.0
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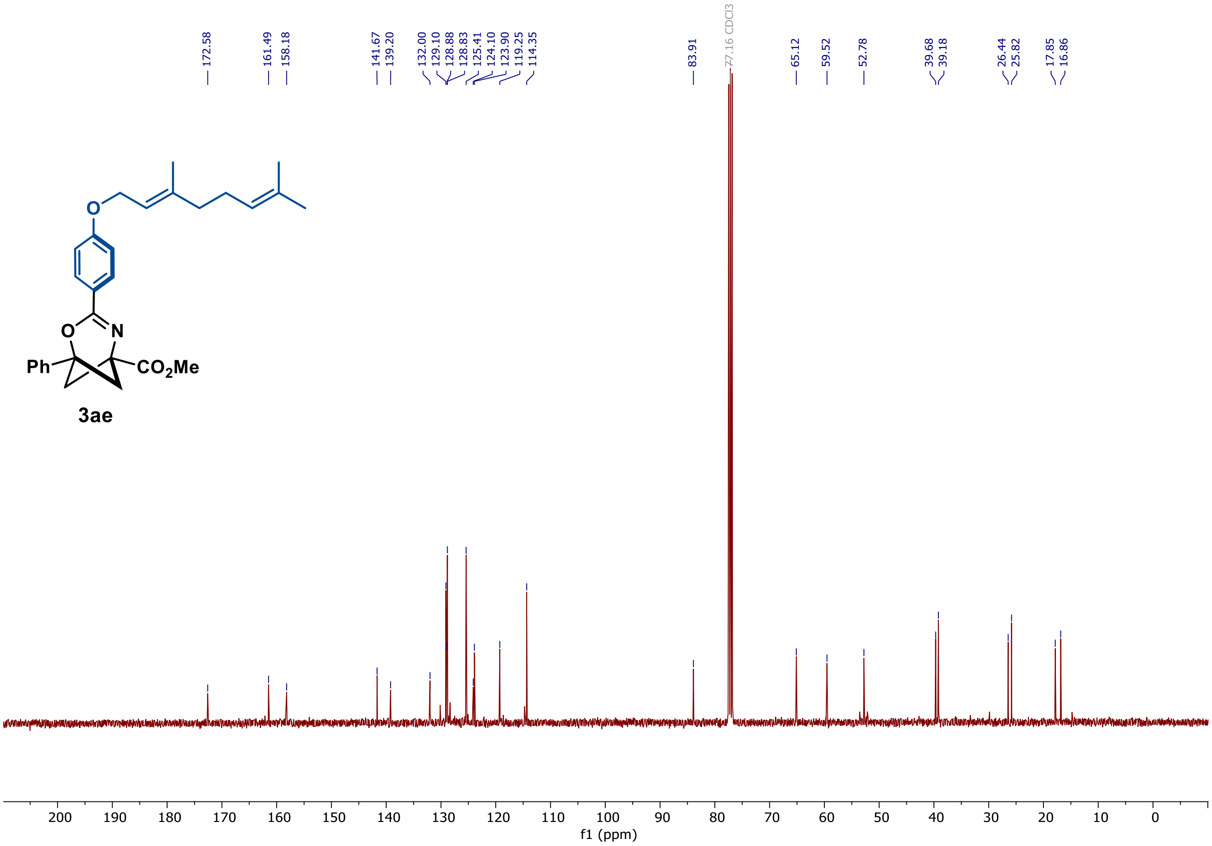
f1 (ppm)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125.41
124.10
123.90
119.25
114.35
83.91
77.16 CDCl3
65.12
59.52
52.78
39.68
39.18
26.44
25.82
17.85
16.86
O
O
N
Ph
CO2Me
3ae
200
190
180
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100
90
80
70
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50
40
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20
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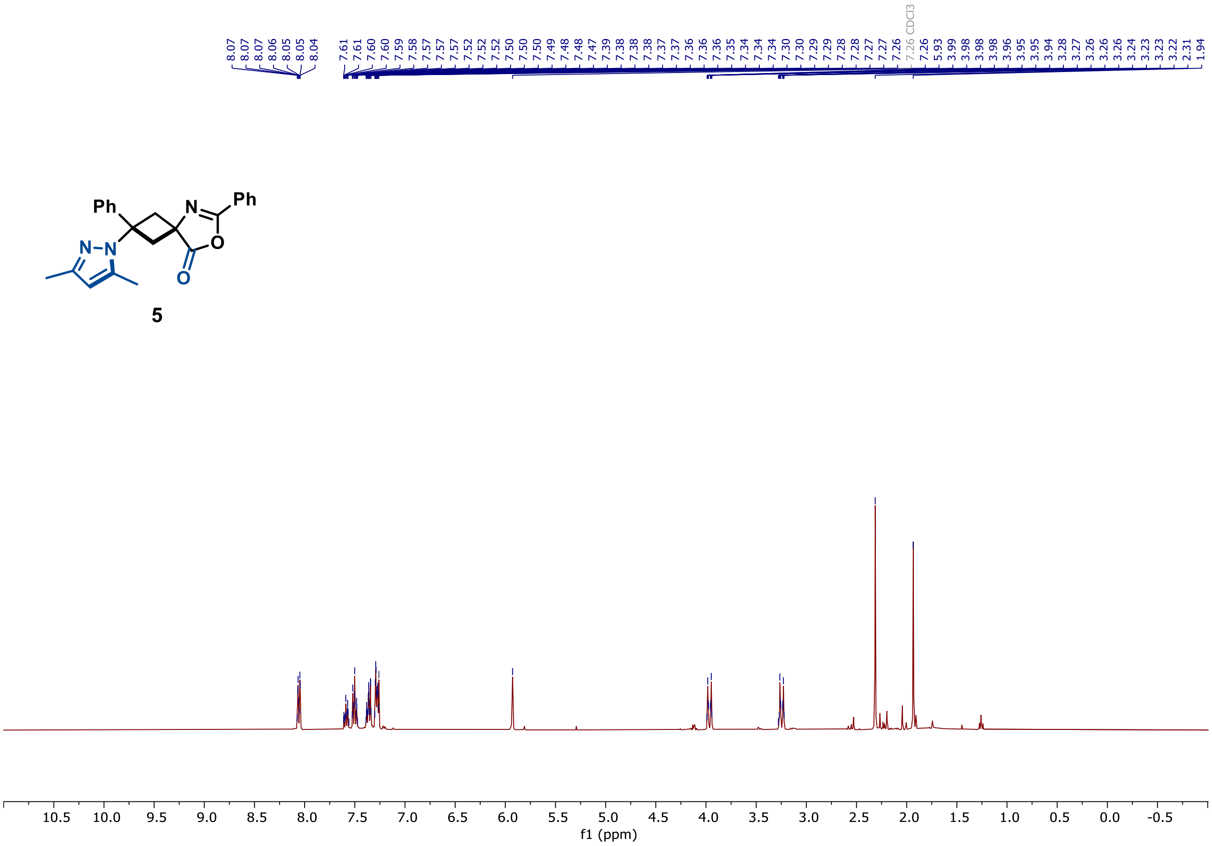
0
f1 (ppm)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3.23
3.22
2.31
1.94
Ph
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Ph
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O
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2.0
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1.0
0.5
0.0
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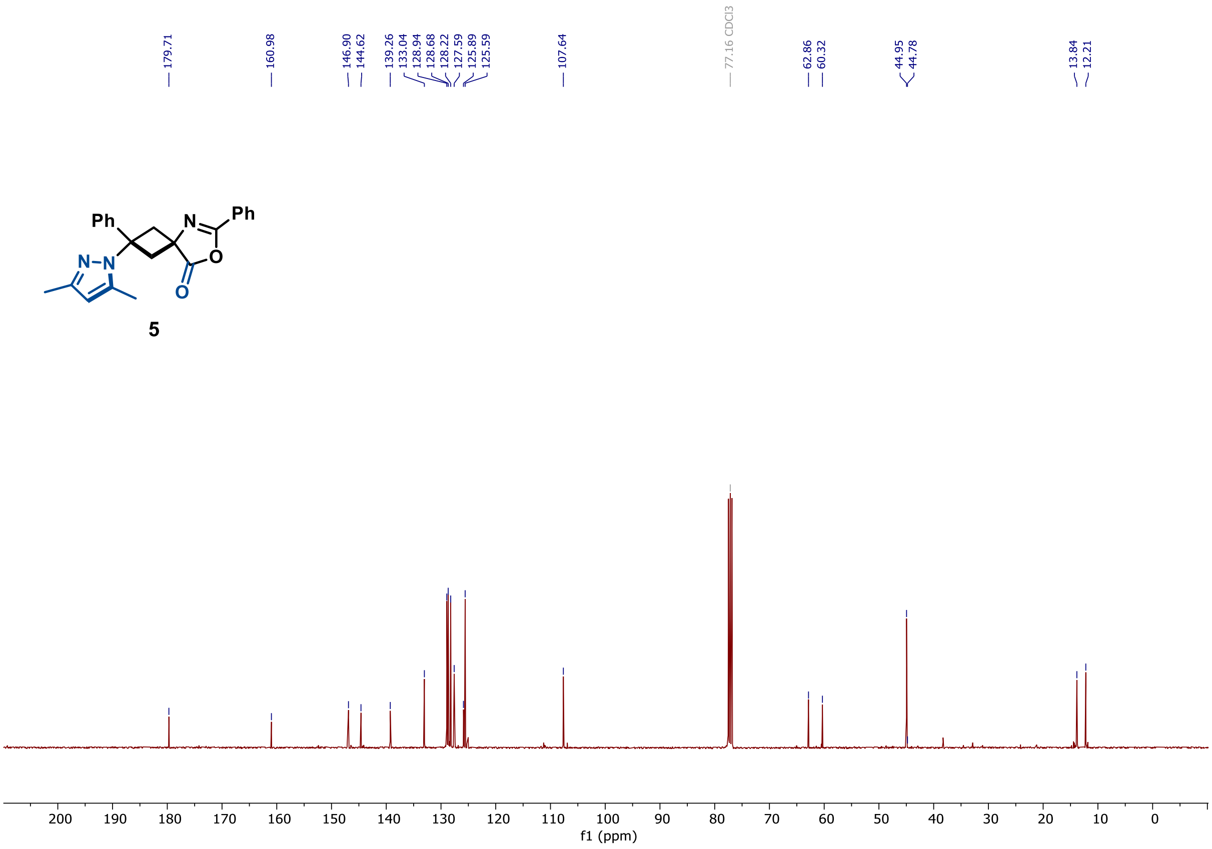
f1 (ppm)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127.59
125.89
125.59
107.64
77.16 CDCl3
62.86
60.32
44.95
44.78
13.84
12.21
Ph
N
Ph
N–N
O
O
5
200
190
180
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150
140
130
120
110
100
90
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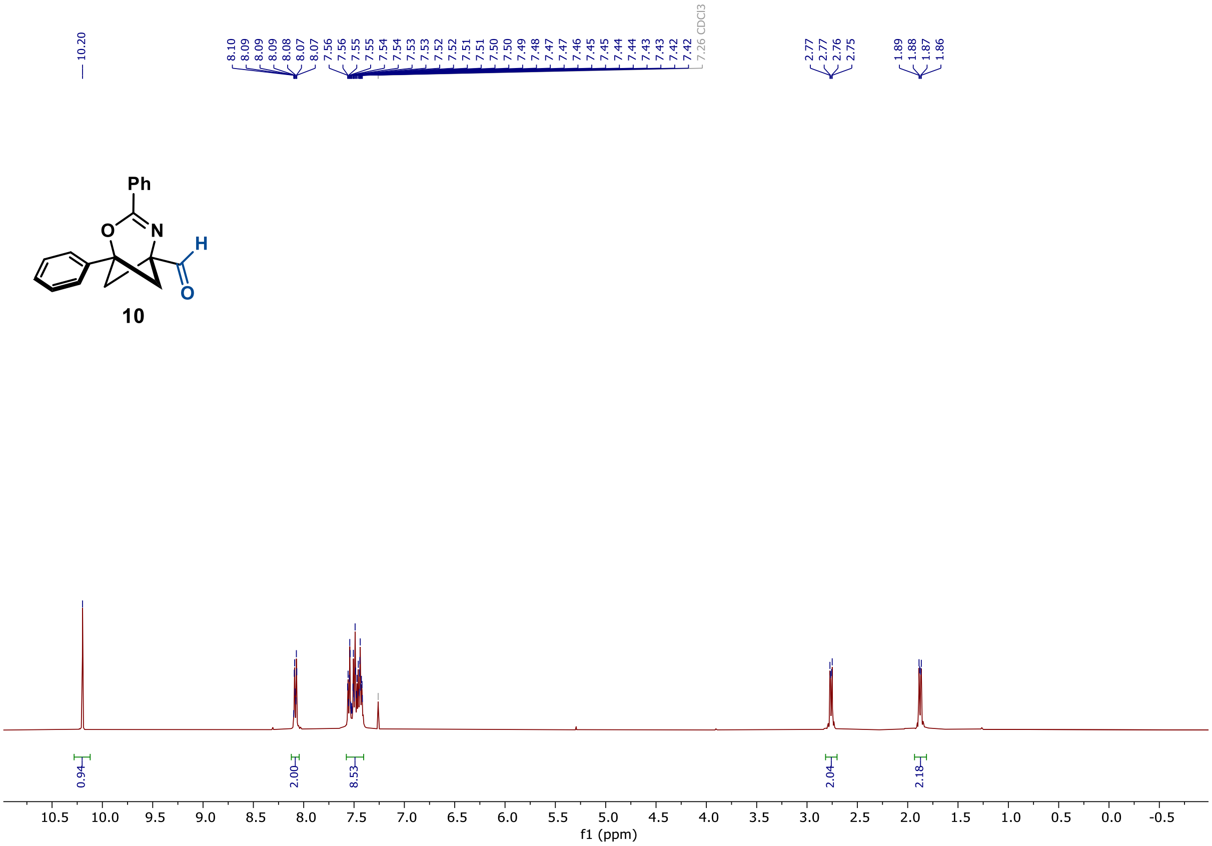
70
60
50
40
30
20
10
0
f1 (ppm)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8.09
8.08
8.07
8.07
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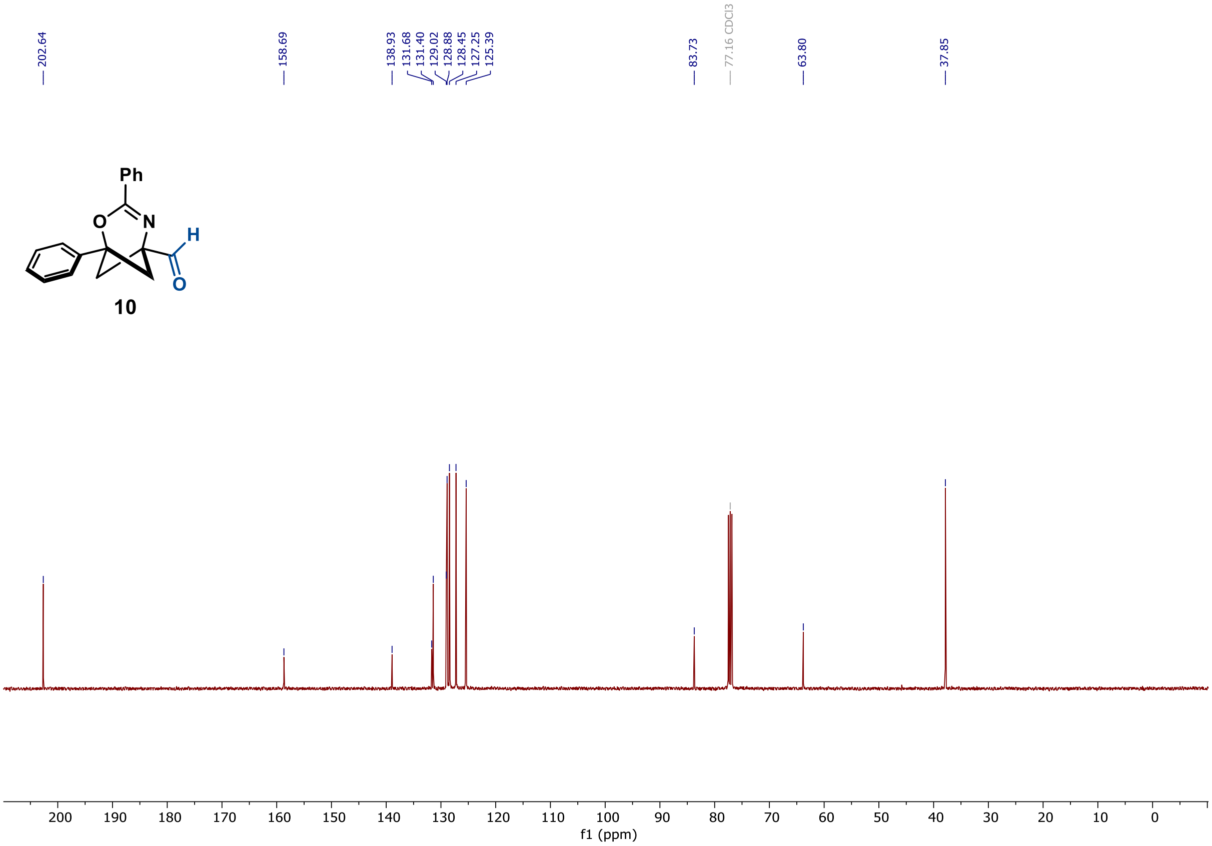
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.26 CDCl3
2.77
2.77
2.76
2.75
1.89
1.88
1.87
1.86
Ph
O
N
H
O
10
0.94
2.00
8.53
2.04
2.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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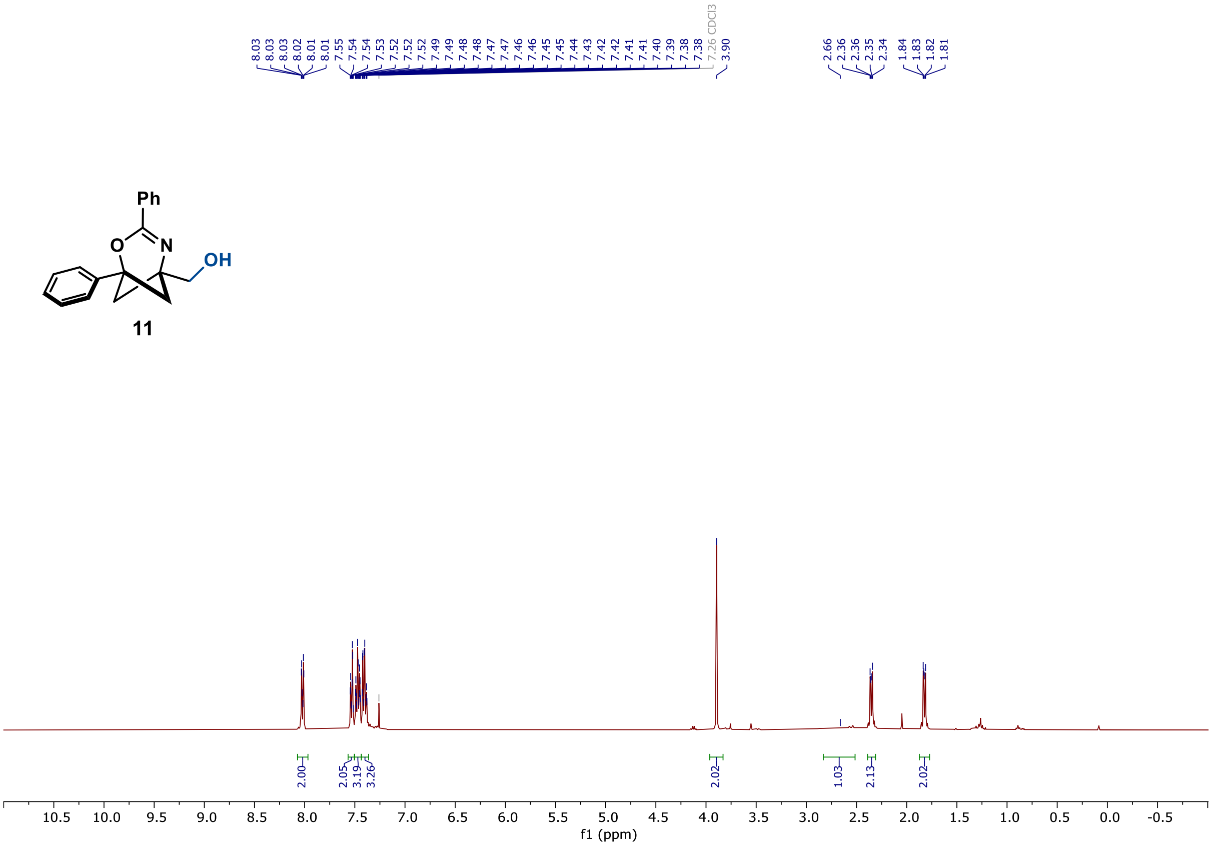
158.69
138.93
131.68
131.40
129.02
128.88
128.45
127.25
125.39
83.73
77.16 CDCl3
63.80
37.85
Ph
O
N
H
O
10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
N
OH

11

8.03
8.03
8.03
8.02
8.01
8.01
7.55
7.54
7.54
7.53
7.52
7.52
7.52
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.26 CDCl3
3.90
2.66
2.36
2.36
2.35
2.34
1.84
1.83
1.82
1.81
2.00
2.05
3.19
3.26
2.02
1.03
2.13
2.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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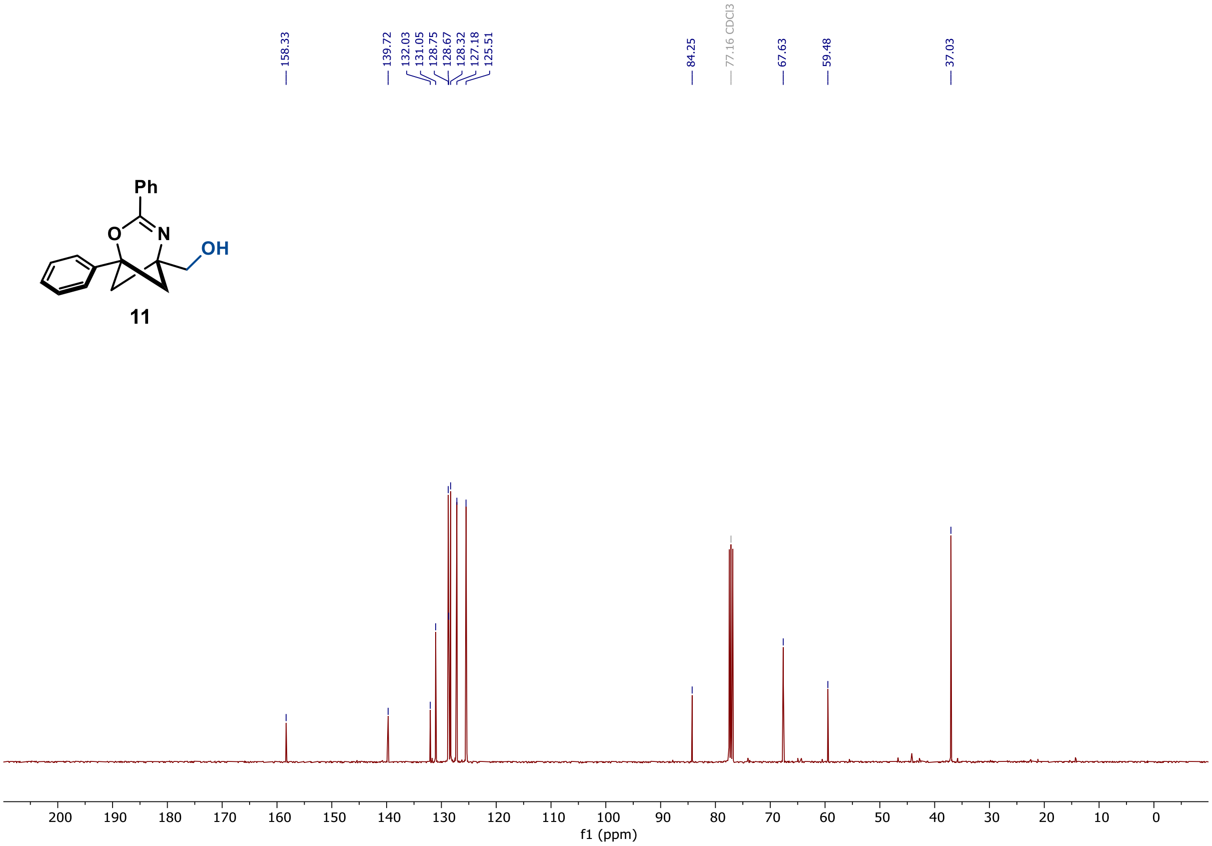
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Ph
O
N
OH

11

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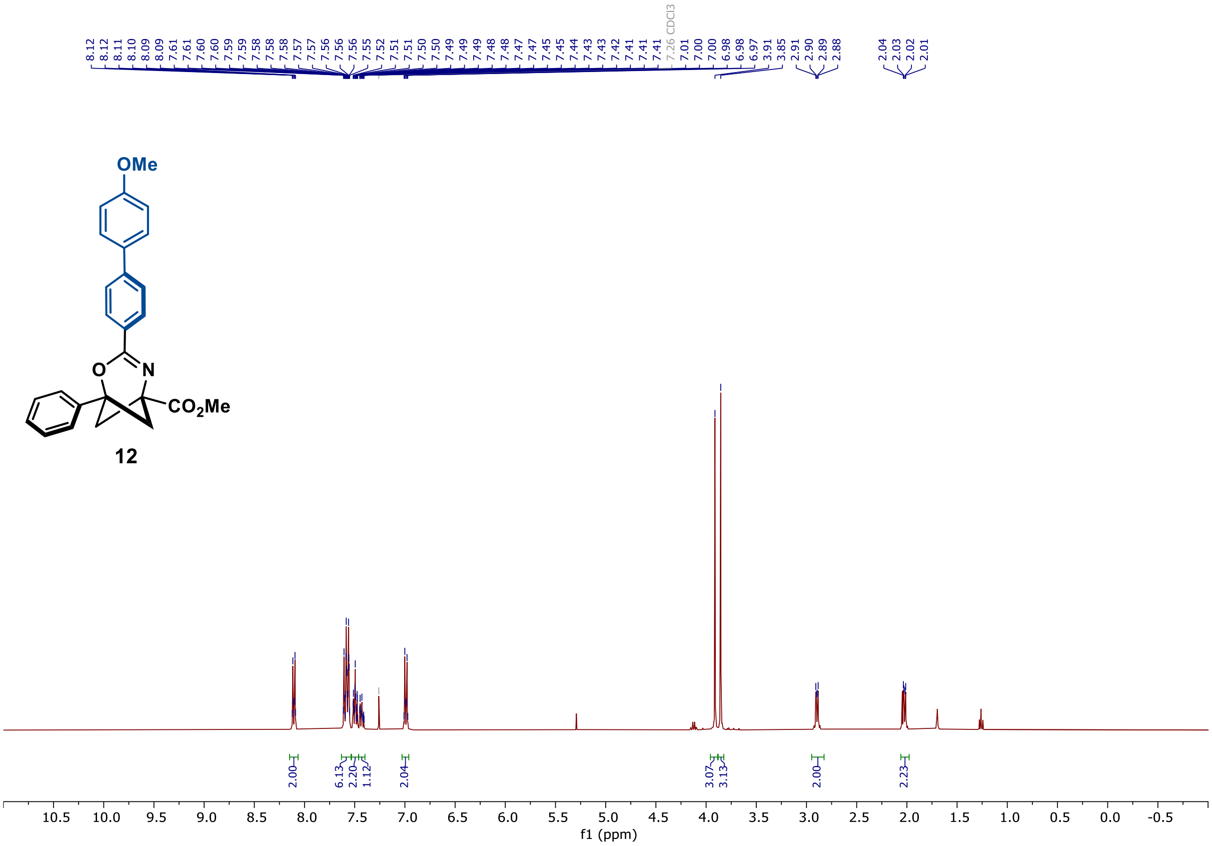
139.72
132.03
131.05
128.75
128.67
128.32
127.18
125.51
84.25
77.16 CDCl3
67.63
59.48
37.03
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.09
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7.61
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7.59
7.58
7.58
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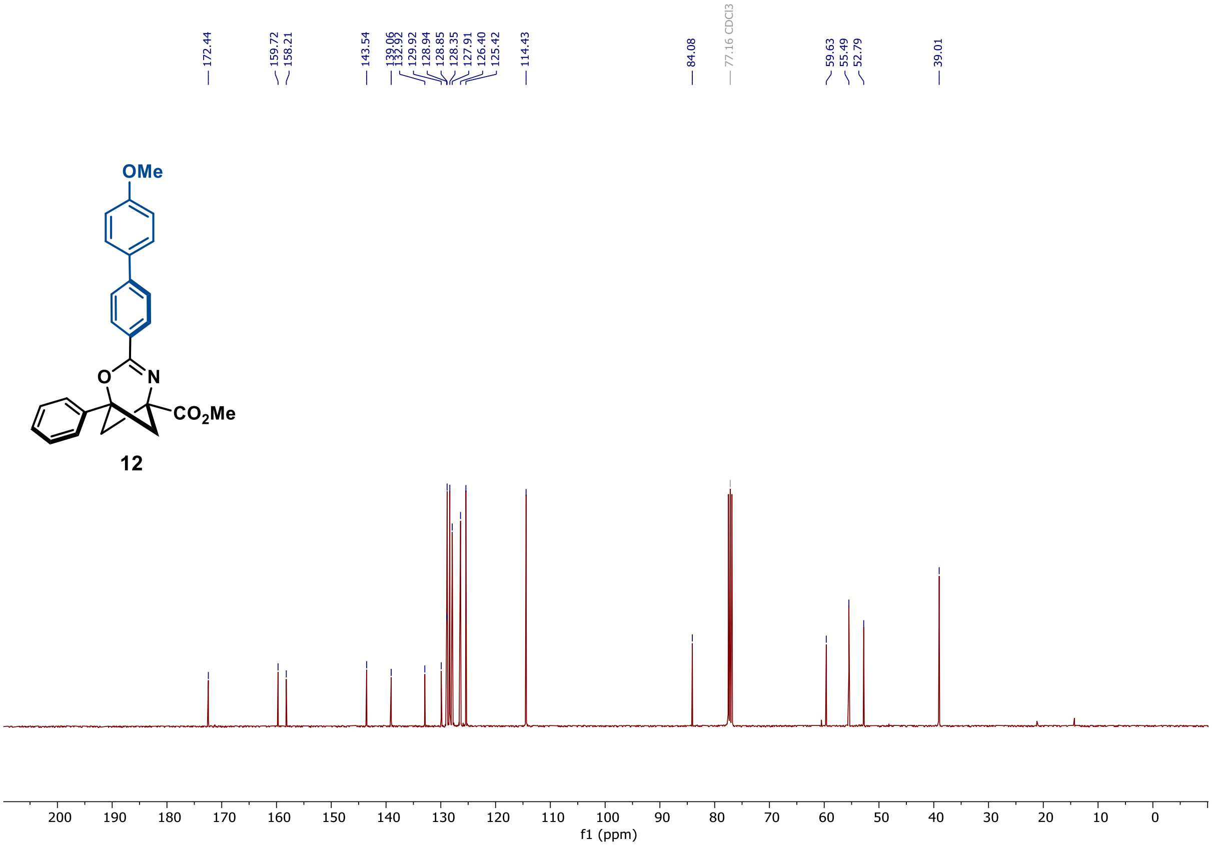
7.57
7.56
7.56
7.55
7.52
7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.47
7.47
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.26 CDCl3
7.01
7.00
6.98
6.98
6.97
3.91
3.85
2.91
2.90
2.89
2.88
2.04
2.03
2.02
2.01
OMe
O
N
CO2Me
12
2.00
6.13
2.20
1.12
2.04
3.07
3.13
2.00
2.23
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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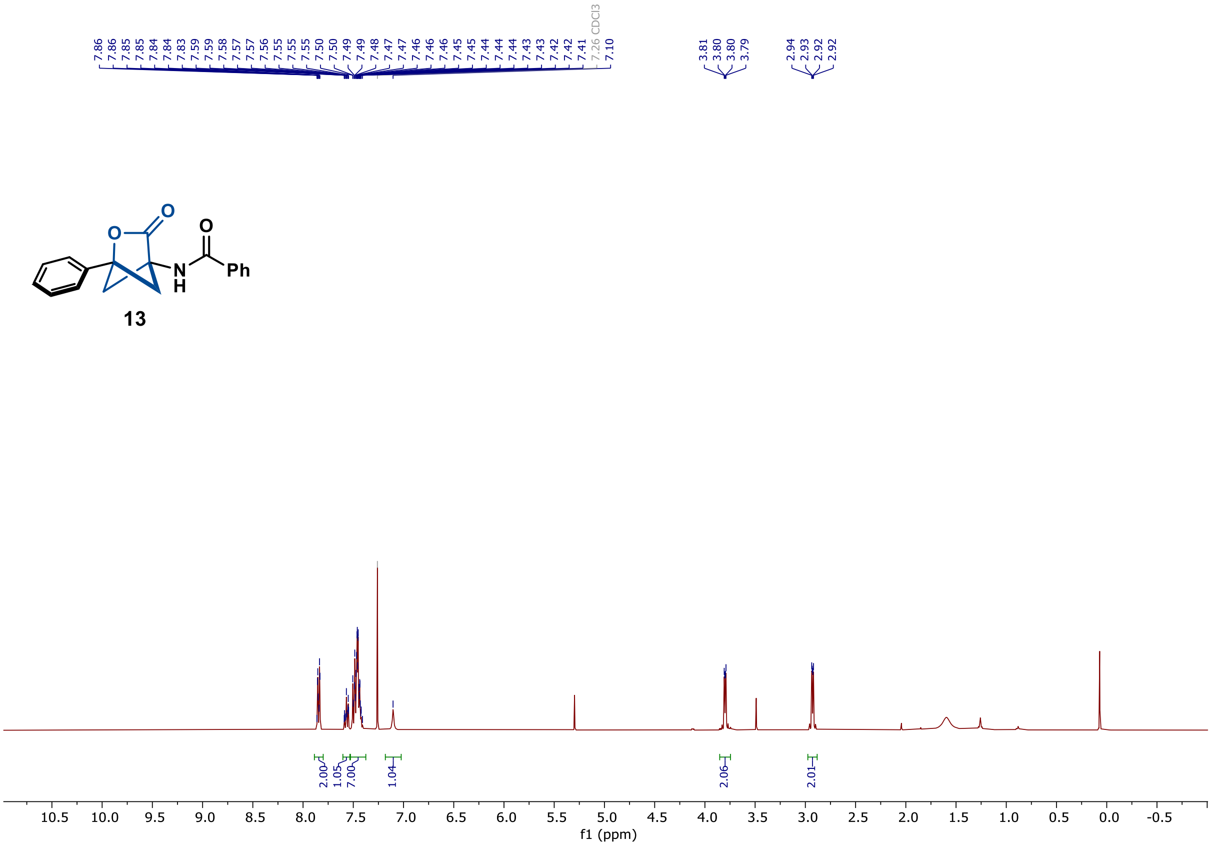
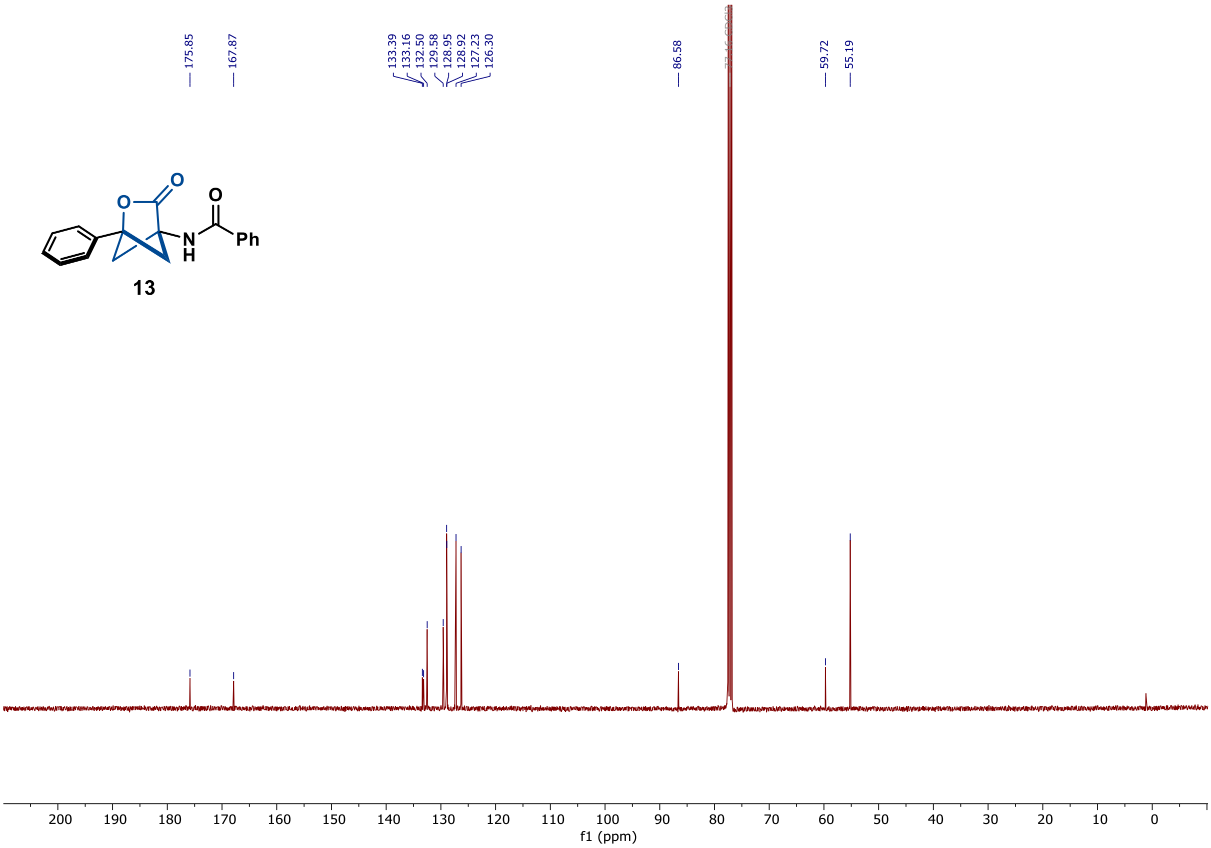
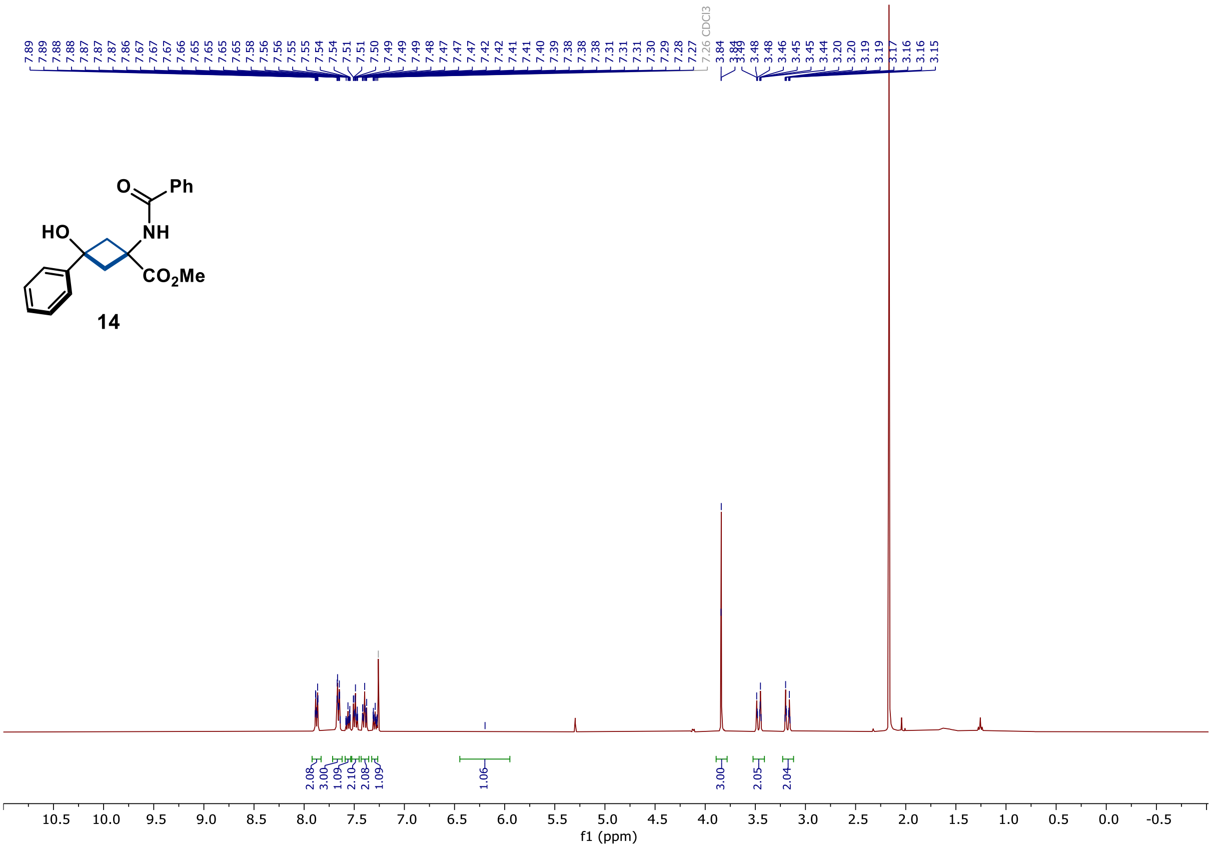
159.72
158.21
143.54
139.06
132.92
129.92
128.94
128.85
128.35
127.91
126.40
125.42
114.43
84.08
77.16 CDCl3
59.63
55.49
52.79
39.01
OMe
O
N
CO2Me
12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.86
7.86
7.85
7.85
7.84
7.84
7.83
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.55
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.26 CDCl3
7.10
3.81
3.80
3.80
3.79
2.94
2.93
2.92
2.92
O
O
N
H
Ph
2.00
1.05
7.00
1.04
2.06
2.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

13


175.85
167.87
133.39
133.16
132.50
129.58
128.95
128.92
127.23
126.30
86.58
77.16 CDCl3
59.72
55.19
O
O
N
H
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

13


7.89
7.89
7.88
7.88
7.87
7.87
7.87
7.86
7.67
7.67
7.67
7.66
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7.65
7.65
7.58
7.56
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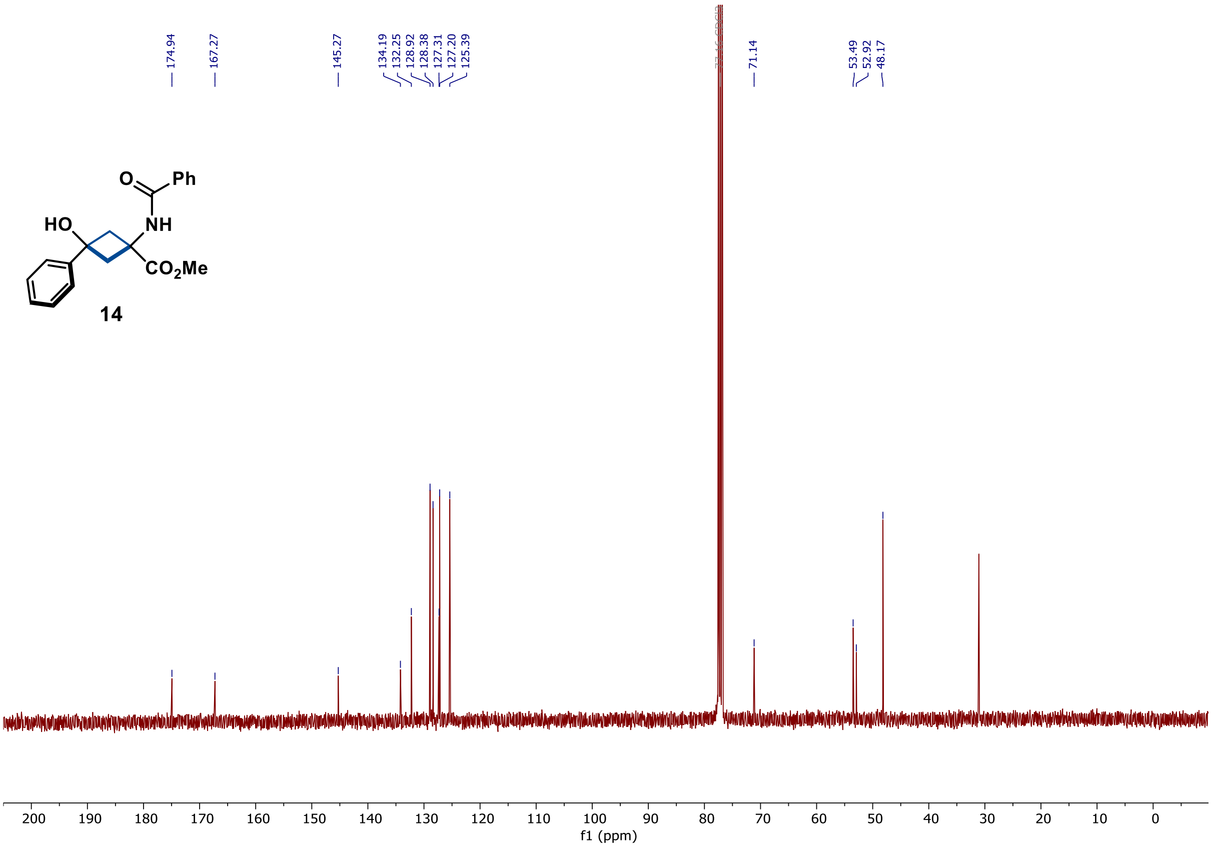
7.55
7.55
7.54
7.54
7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.47
7.47
7.47
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.38
7.31
7.31
7.31
7.30
7.29
7.28
7.27
7.26 CDCl3
3.84
3.84
3.49
3.48
3.48
3.46
3.45
3.45
3.44
3.20
3.20
3.19
3.19
3.17
3.16
3.16
3.15
O
Ph
HO
NH
CO2Me
14
2.08
3.00
1.09
2.10
2.08
1.09
1.06
3.00
2.05
2.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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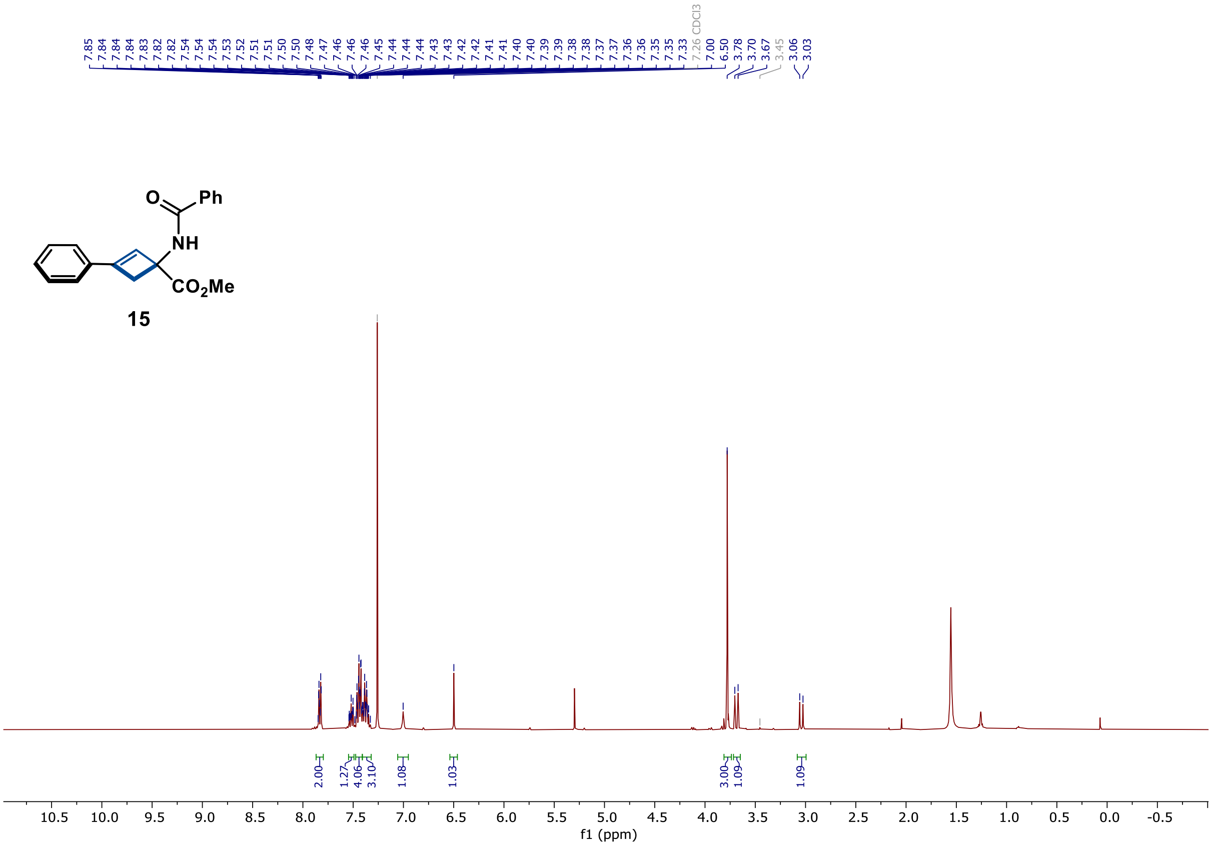
167.27
145.27
134.19
132.25
128.92
128.38
127.31
127.20
125.39
71.14
53.49
52.92
48.17
O
Ph
HO
NH
CO2Me
14
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.54
7.54
7.53
7.52
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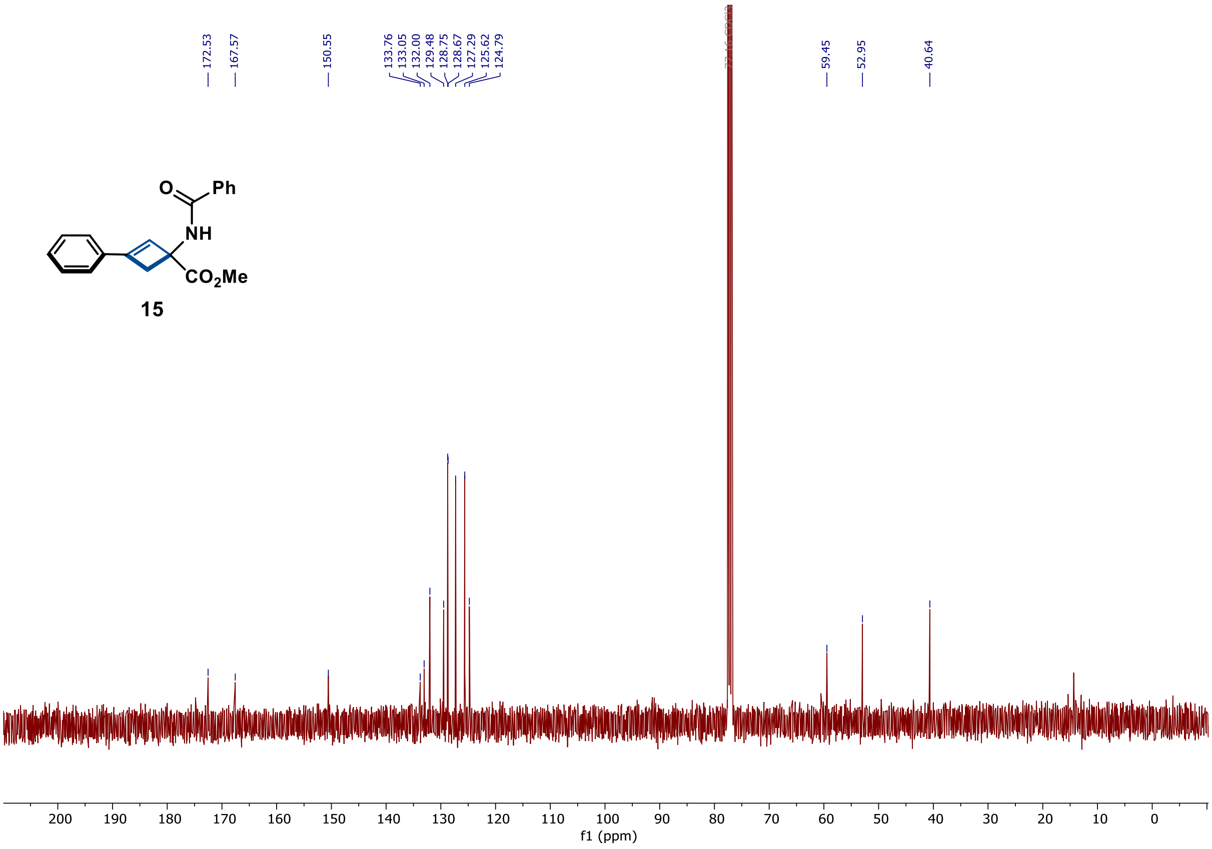
7.51
7.50
7.50
7.48
7.47
7.46
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.33
7.26 CDCl3
7.00
6.50
3.78
3.70
3.67
3.45
3.06
3.03
O
Ph
NH
CO2Me
15
2.00
1.27
4.06
3.10
1.08
1.03
3.00
1.09
1.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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167.57
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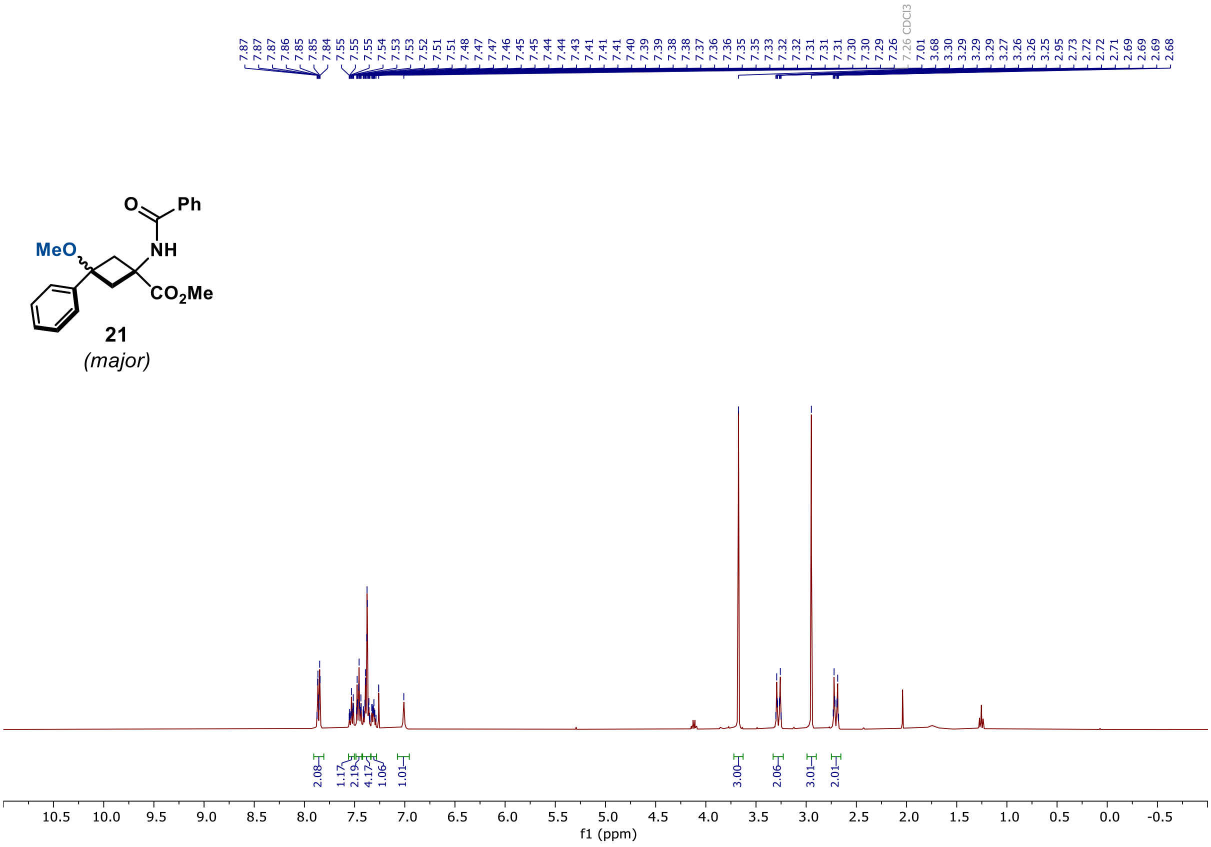
133.05
132.00
129.48
128.75
128.67
127.29
125.62
124.79
59.45
52.95
40.64
O
Ph
NH
CO2Me
15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.87
7.87
7.86
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7.55
7.54
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7.53
7.52
7.51
7.51
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.41
7.41
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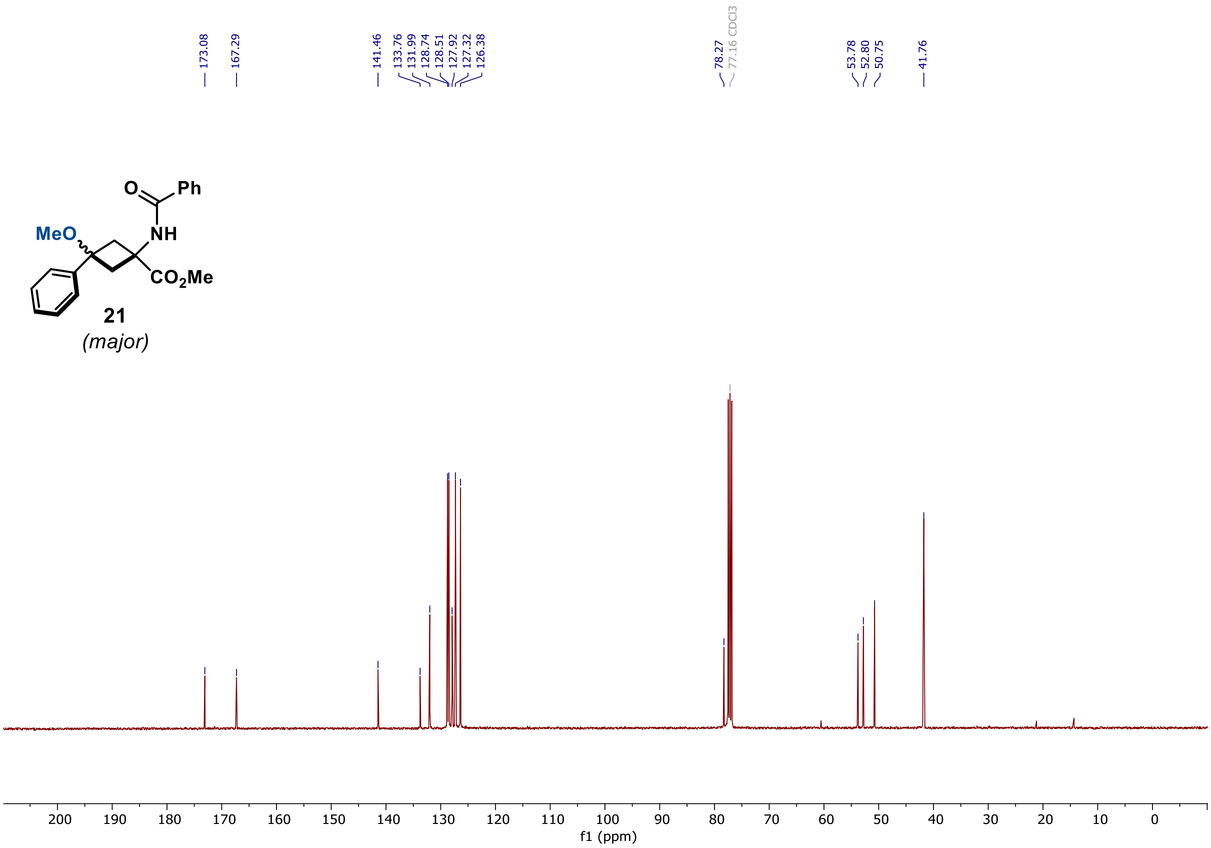
7.37
7.36
7.36
7.35
7.35
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.26
7.26 CDCl3
7.01
3.68
3.30
3.29
3.29
3.29
3.27
3.26
3.26
3.25
2.95
2.73
2.72
2.72
2.71
2.69
2.69
2.69
2.68
O
Ph
MeO
NH
CO2Me
21
(major)
2.08
1.17
2.19
4.17
1.06
1.01
3.00
2.06
3.01
2.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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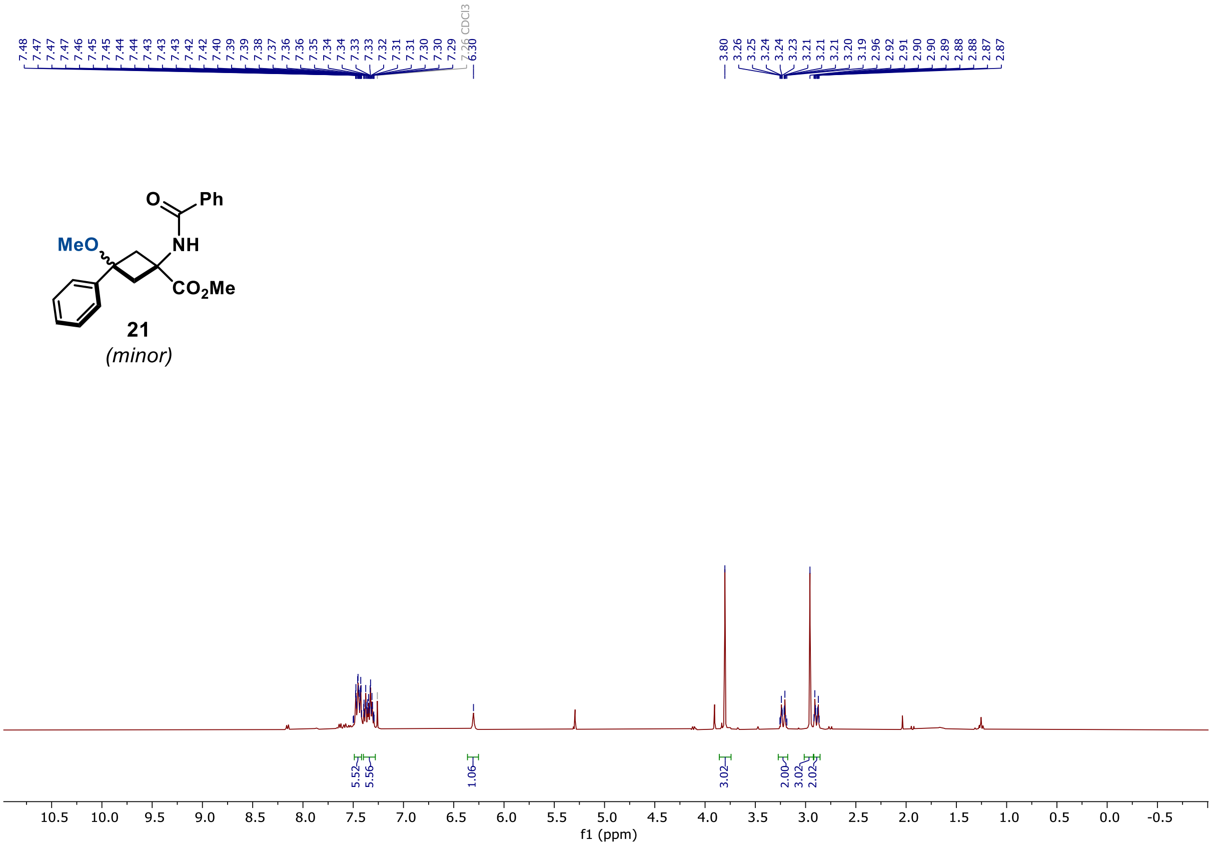
133.76
131.99
128.74
128.51
127.92
127.32
126.38
78.27
77.16 CDCl3
53.78
52.80
50.75
41.76
O
Ph
MeO
NH
CO2Me
21
(major)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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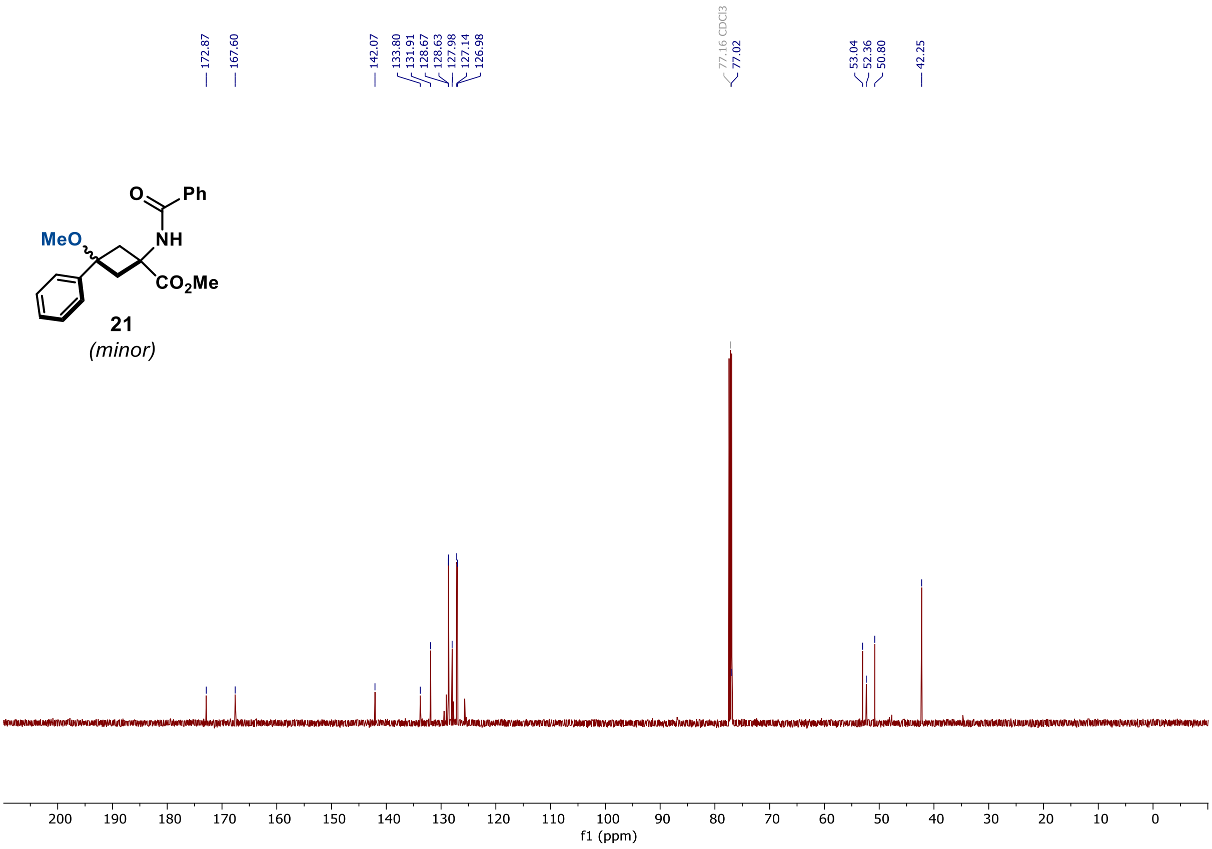
(minor)



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(minor)