Supplementary Information-Experimental Details

Access to Arynes from Arenes via Formal Dehydrogenation: Increased Efficiency and Scope, Synthetic Applications and Mechanistic Analysis

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[1]These authors contributed equally

General considerations:

Materials: Commercially available reagents and solvents were used without further purification unless otherwise stated. 1d-TT,[1] 1l-TT,[2] 1m-TT,[3] 1n-TT,[3] 1o-TT,[4] 1p-TT,[1] 1v-IMes,[5] 2j,[6] 1x,[7] and thianthrene *S*-oxide (TTO)[1] were prepared by literature procedure.

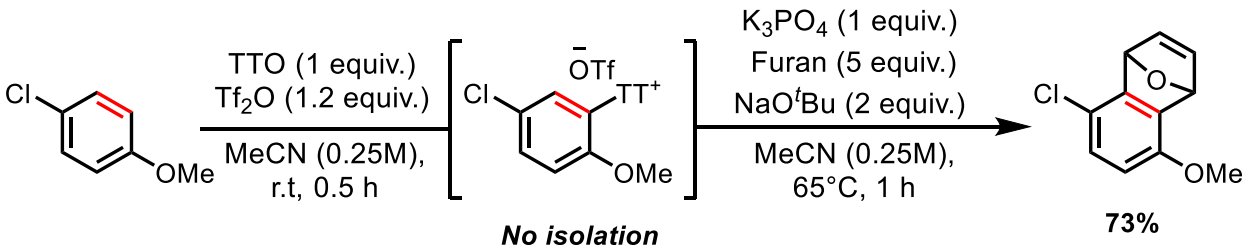
Experimental methods: Reactions performed above ambient room temperature were done so in an oil bath or aluminum block heated externally. Reactions performed below ambient room temperature were done so in an ice bath. Crude reaction mixtures were analyzed by ^{1}H NMR spectroscopy or thin-layer chromatography (TLC) on Selecto Scientific Flexible TLC plates (silica gel 60 Å F-254) and visualized by UV irradiation or iodine stain. Crude material was purified by flash column chromatography on SilicaFlash P60 silica gel, unless otherwise stated. NMR yields for optimization experiments were obtained by integration of peaks known for the analyte molecules. For optimization experiments, these integrations are compared to the integration of peaks belonging to internal standard (1,3,5-trimethoxybenzene). ^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} spectra were recorded in $CDCl_3$, DMSO-d_6, or CD_3CN with tetramethylsilane as an internal standard on a Bruker Avance II 400 MHz; the following notation is used: br – broad, s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, dd – doublet of doublets, dt – doublet of triplets, and ddd – doublet of doublet of doublets. FTIR spectra were recorded on Thermo Scientific Nicolet iS5 Infra-red spectrometer. High resolution mass spectrometry (HRMS) data were recorded on Thermo Scientific Q-exactive mass spectrometer by electrospray ionization with an Orbitrap mass-analyzer (ESIOrbitrap). Melting points were recorded on Mel-Temp (Thermo scientific) and are reported as uncorrected.

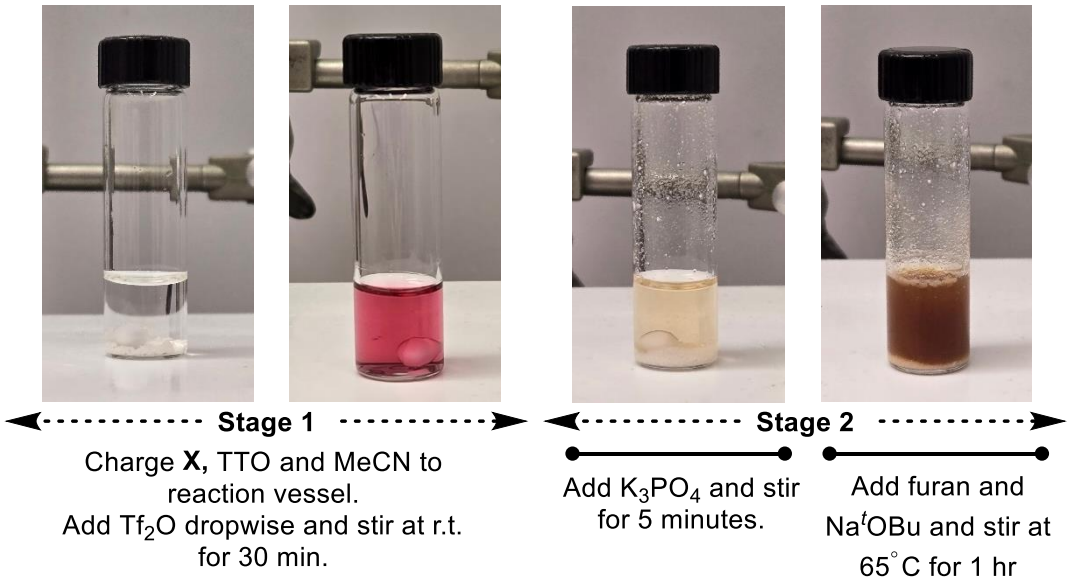
Computational methods: Compounds were optimized using M06-2x[8] with the triple-zeta Def2-tzvpp[9] basis set, an ultrafine grid, and with SMD[10] solvation in toluene (ε=2.3741). Intermediate structures were confirmed to have no negative values in frequency calculations, and transition states had only one negative frequency value, with said value corresponding to the relevant reaction. Geometry optimizations and frequency calculations were all conducted using Gaussian09.[11] Full reaction coordinate diagrams are given in section S120-125. Kinetic isotope effects were calculated using frequency values from the optimized geometries of the reactants and transition states of each reaction step using Kinisot[12], with cclib[13] for file conversions. The combined KIE for the thianthrenium multi-step aryne extrusion was calculated using the formula (SF1):

$$KIE_{calc} = \frac{KIE_2 + KIE_1 e^{-\frac{\Delta\Delta G^{\ddagger}}{RT}}}{1 + e^{-\frac{\Delta\Delta G^{\ddagger}}{RT}}} \quad \text{(SF1)}$$

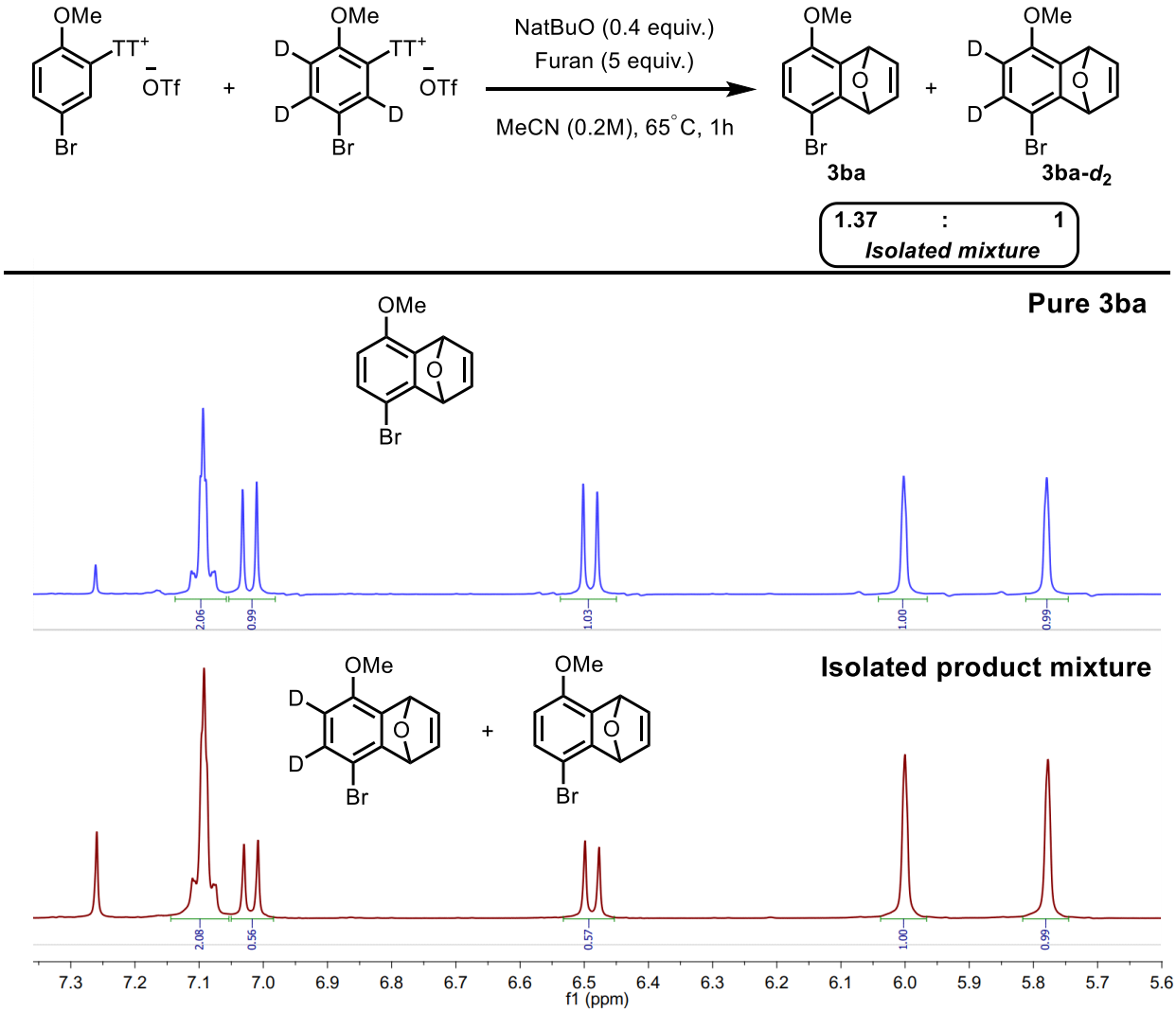
in which $\Delta\Delta G^{\ddagger}$ the difference in energy between $\Delta G^{\ddagger}_1$ and $\Delta G^{\ddagger}_2$ when both $\Delta G^{\ddagger}_1$ and $\Delta G^{\ddagger}_2$ are the energy difference between reactants and the transition state for their respective reaction steps.[14,15] All optimized geometries are available in formaldehydrogenation.xyz

1. Pictorial example of a thianthrenium mediated one-pot formal dehydrogenation:



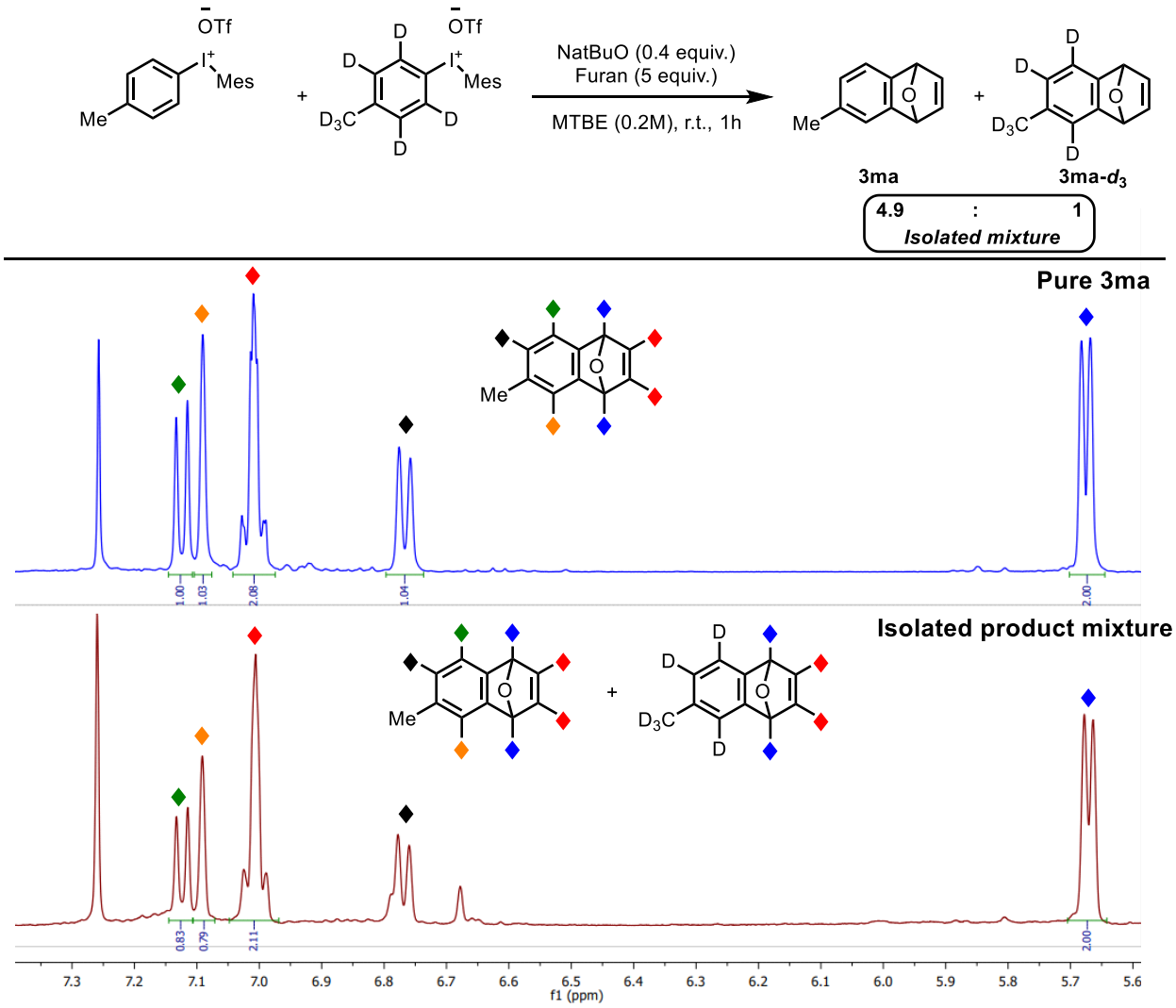


2. Aryl thianthrenium derived aryne DKIE with NaO^{t}Bu:



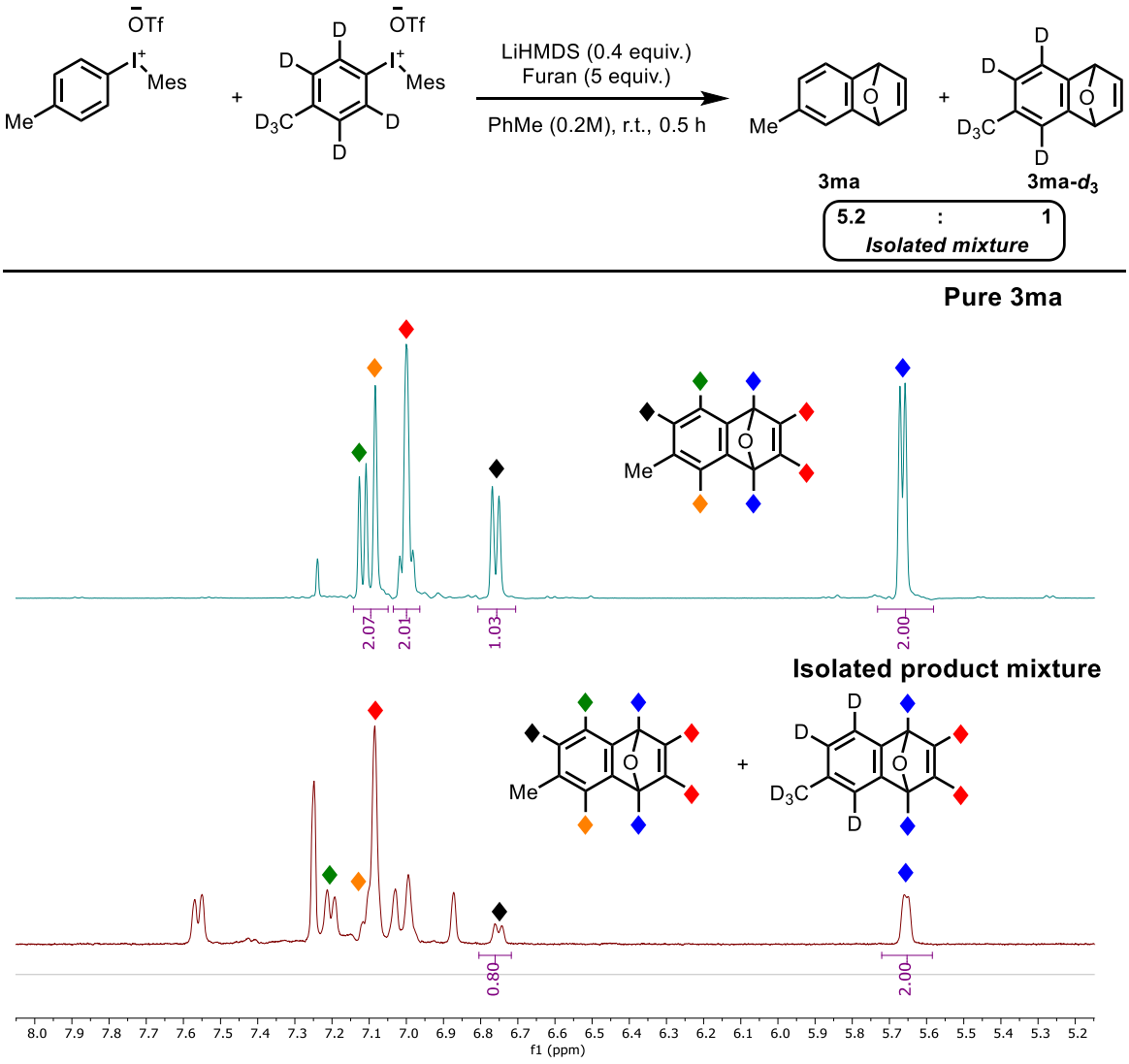
An 8 mL vial was charged with **1b**-TT (0.25 mmol), **1b**-TT-d_3 (0.25 mmol), acetonitrile (0.2M, 2.5 mL), furan (5 equiv.) and a magnetic stir bar. NaO^{t}Bu (0.2 mmol, 19.2 mg, 0.4 eq (relative to total molar quantity thianthrenium salt in reaction.)) was added in one portion. The vial was then placed on a heating block and heated at 65˚C for 1 hour. The reaction was quenched with DI water (3 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic layer was dried over sodium sulfate, concentrated under reduced pressure and the resulting residue was purified via silica chromatography with EtOAc/hexanes as the solvent system.

3. Diaryliodonium derived aryne DKIE with NaO^{t}Bu:



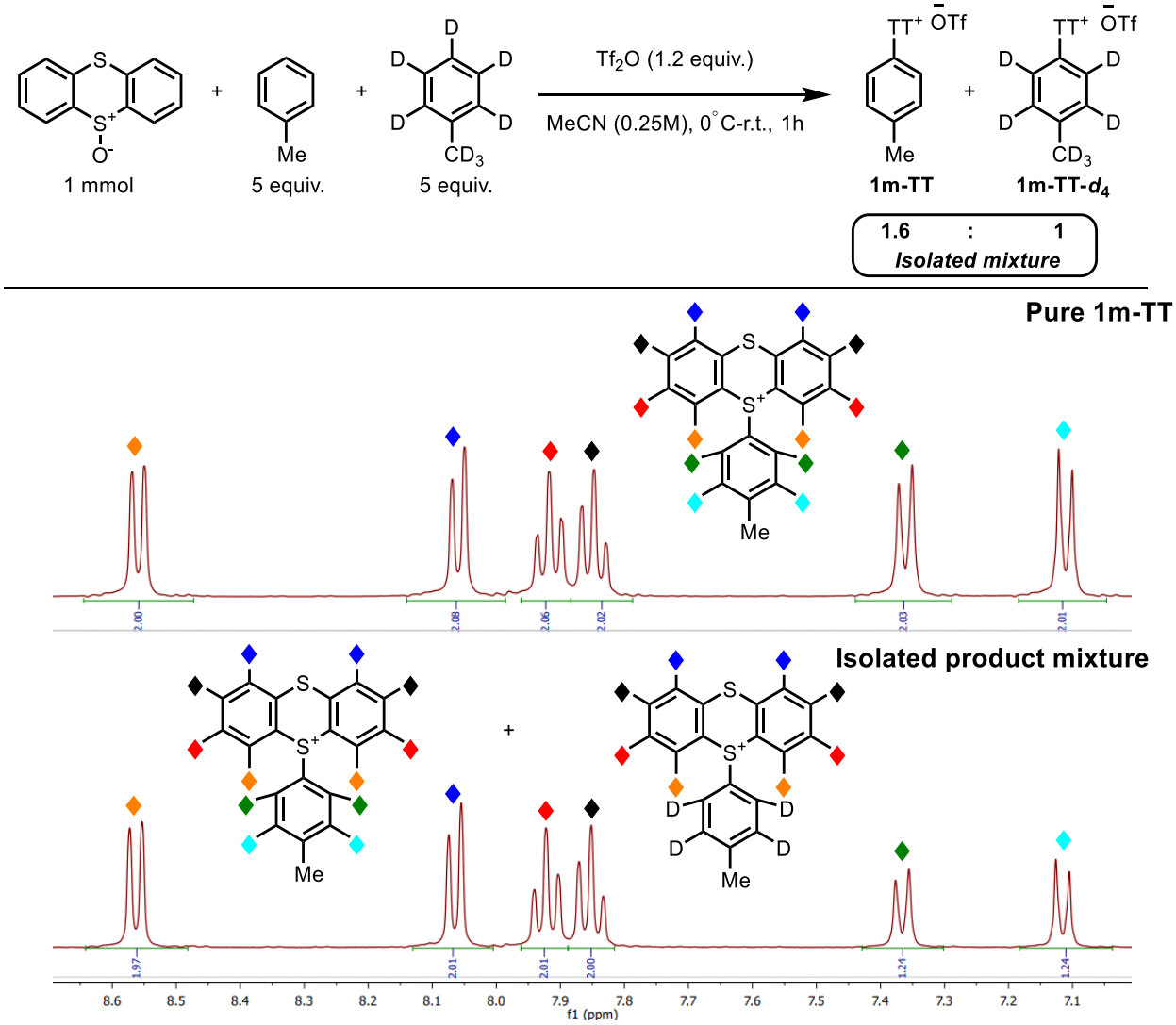
An 8 mL vial was charged with **1n**-IMes (0.50 mmol), **1n**-IMes-d_7 (0.50 mmol), MTBE (0.2M, 5 mL), furan (5 equiv.) and a magnetic stir bar. NaO^{t}Bu (0.4 mmol, 38.4 mg, 0.4 equiv. (relative to total molar quantity iodonium salt in reaction.)) was added in one portion. The vial was then stirred at room temperature for 1 hour. The reaction was quenched with DI water (3 mL) and extracted with ethyl acetate (3 x 8 mL). The combined organic layer was dried over sodium sulfate, concentrated under reduced pressure and the resulting residue was purified via silica chromatography with EtOAc/hexanes as the solvent system.

4. Iodonium derived aryne DKIE with LiHMDS:



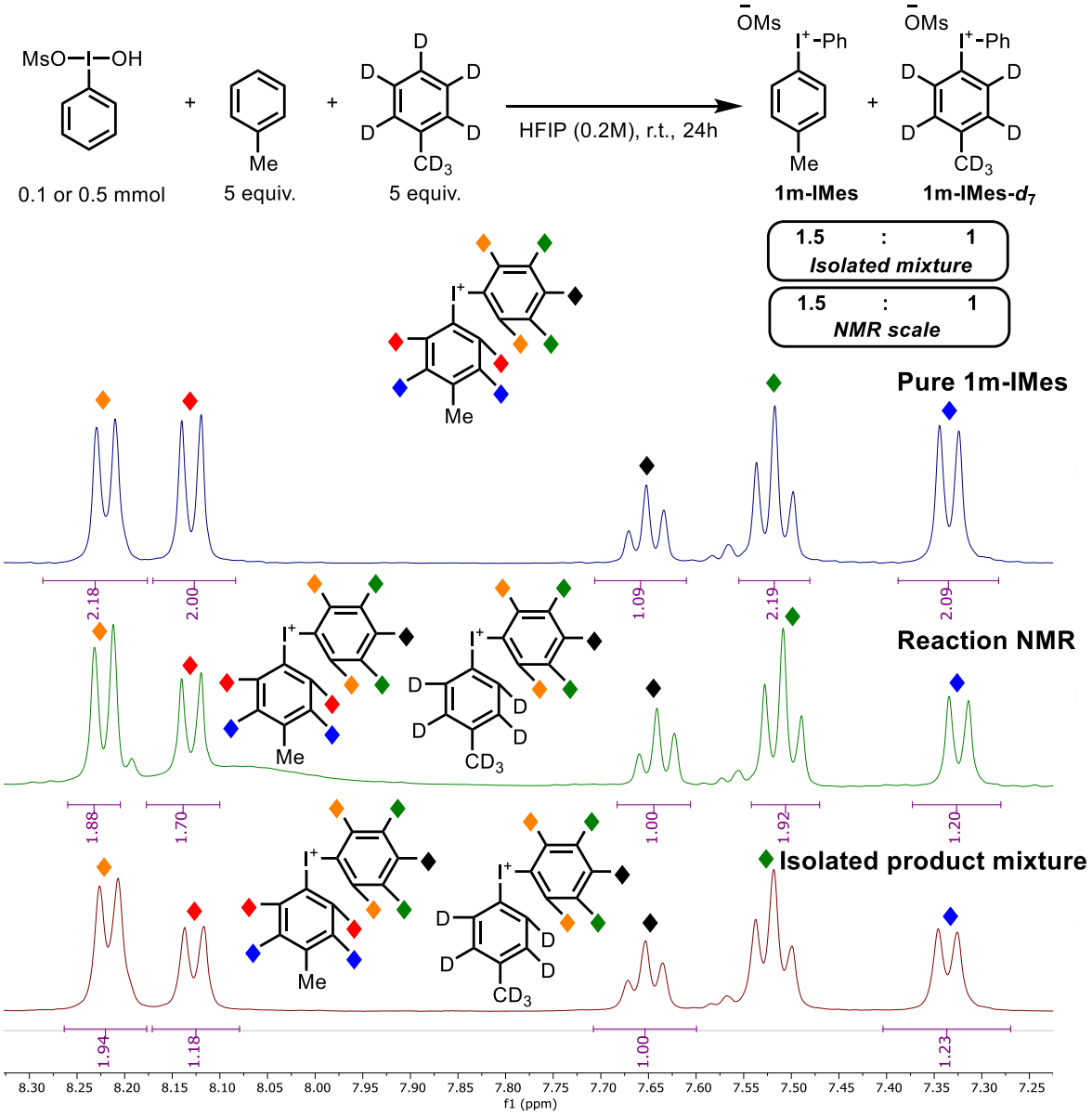
A 4 mL vial was charged with **1n**-IMes (0.05 mmol), **1n**-IMes-d_7 (0.05 mmol), PhMe (0.2M, 0.5 mL), furan (5 equiv.) and a magnetic stir bar. 1M LiHMDS in PhMe (0.04 mmol, 0.4 equiv. (relative to total molar quantity iodonium salt in reaction.)) was added in one portion. The vial was then stirred at room temperature for 0.5 hours. The reaction was quenched with DI water (2 mL) and extracted with ethyl acetate (3 x 3 mL). The combined organic layer was dried over sodium sulfate, concentrated under reduced pressure and the resulting residue was analyzed via ^{1}HNMR.

5. Toluene thianthrenation DKIE:



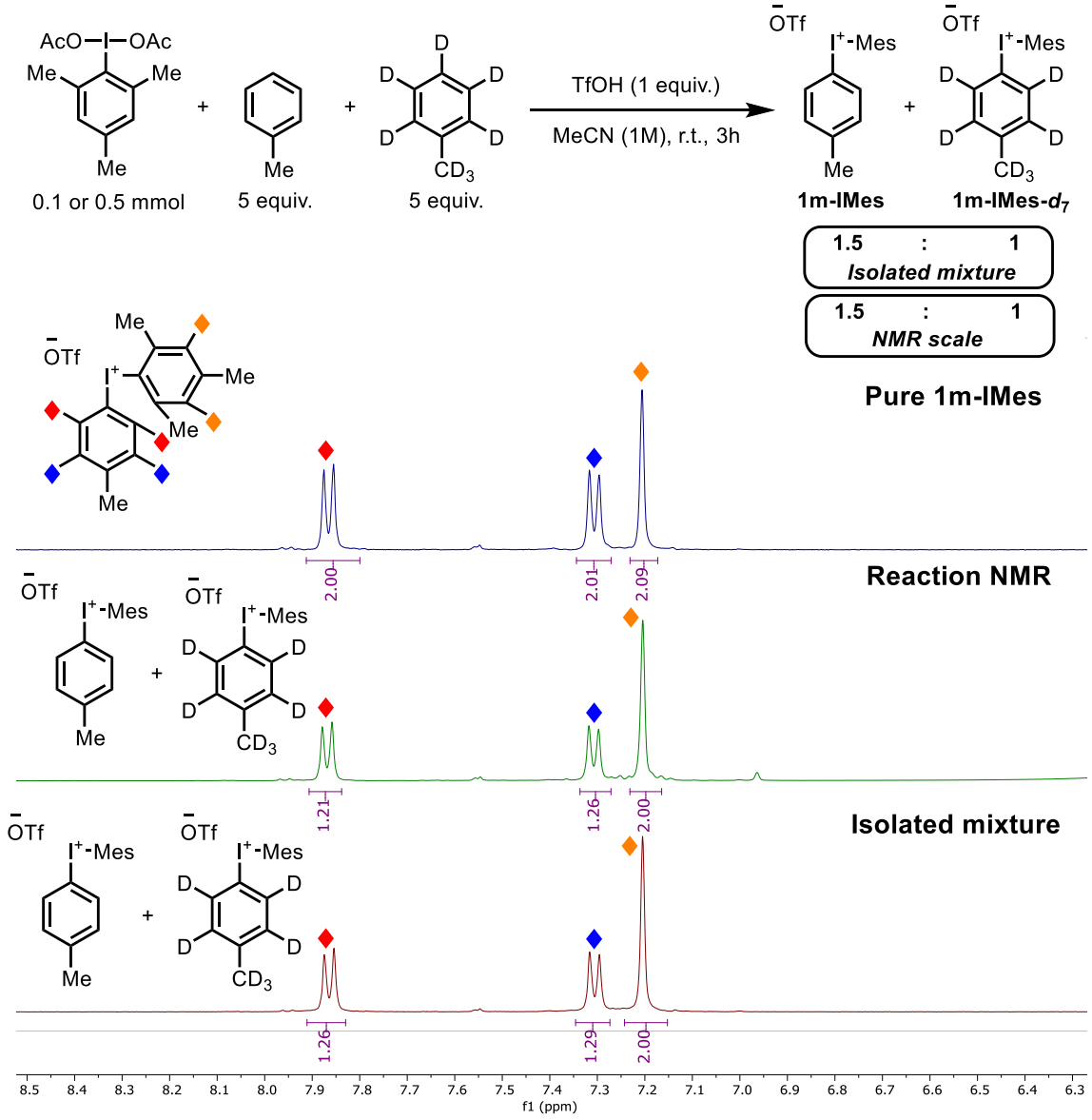
An 8 mL vial was charged with TTO (1 mmol), PhMe (5 equiv.), PhMe-d_8 (5 equiv.), acetonitrile (0.25M, 4 mL) and a magnetic stir bar. The vial was placed in an ice bath and Tf_2O (1.2 equiv.) was added dropwise over the course of 10 seconds with vigorous stirring. The reaction was allowed to come to room temperature over the course of 1 hour. The reaction was quenched with methanol (~1 mL) which dissipated the deep purple color of the reaction. The mixture was then added dropwise to a 100 mL round bottom flask containing 60 mL of diethyl ether while stirring. The resulting precipitate was then collected via vacuum filtration and analyzed via ^{1}HNMR.

6. Toluene iodonium installation with HMIB DKIE:



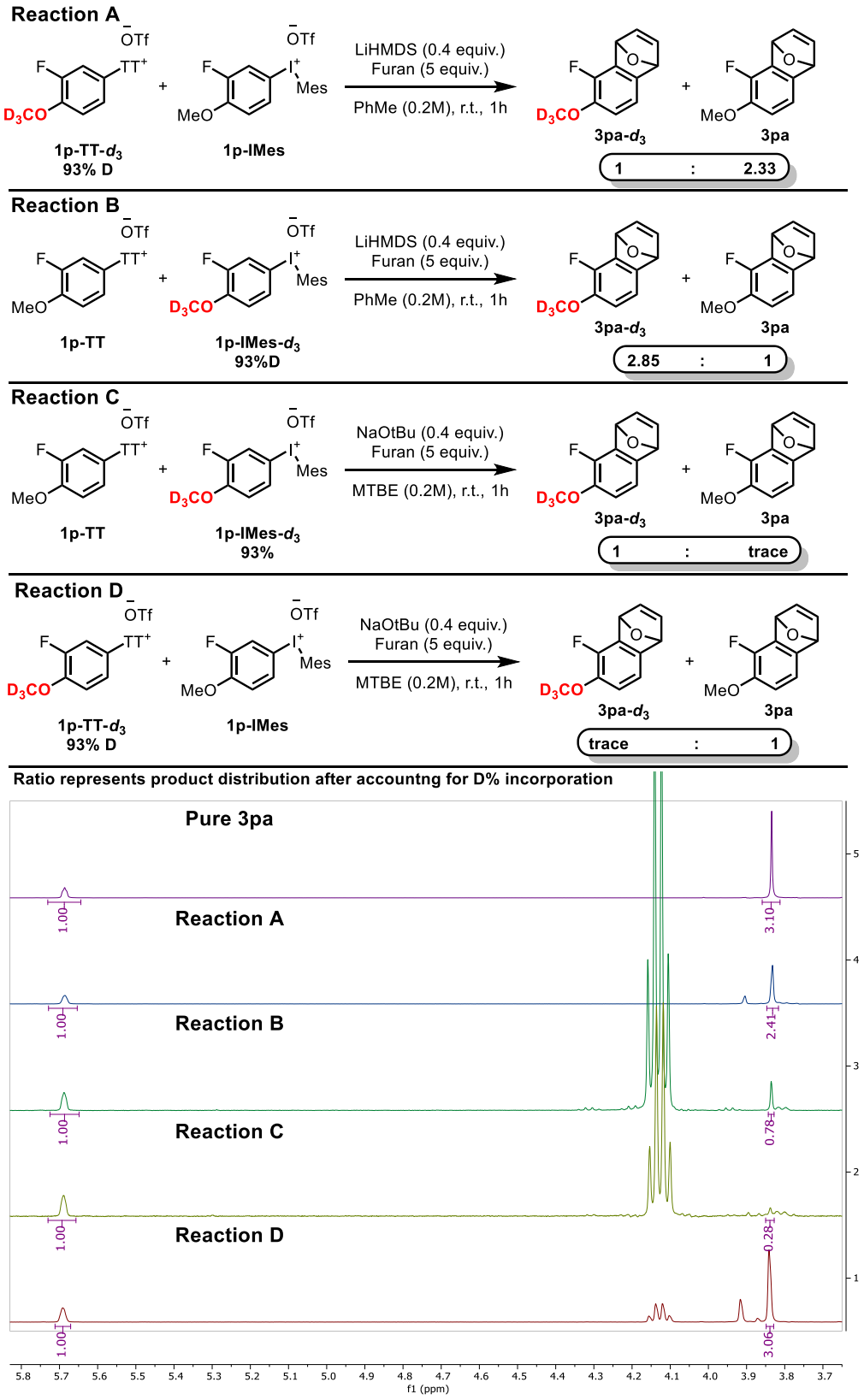
A 4 or 8 mL vial was charged with hydroxy(mesyloxy)iodo benzene (0.1 mmol or 0.5 mmol), PhMe (5 equiv.), PhMe-d_8 (5 equiv.), hexafluoroisopropanol (0.2M, 0.5 mL or 2.5 mL) and a magnetic stir bar. The mixture was stirred at room temperature for 24 hours. **For the 0.5 mmol reaction:** The mixture was then added dropwise to a 100 mL round bottom flask containing 60 mL of diethyl ether while stirring. The resulting precipitate was then collected via vacuum filtration and analyzed via ^{1}HNMR. **For the 0.1 mmol reaction:** The reaction was concentrated under reduced pressure and the residue was analyzed via ^{1}HNMR.

7. Toluene iodonium installation with MesI(OAc)$_2$ DKIE:

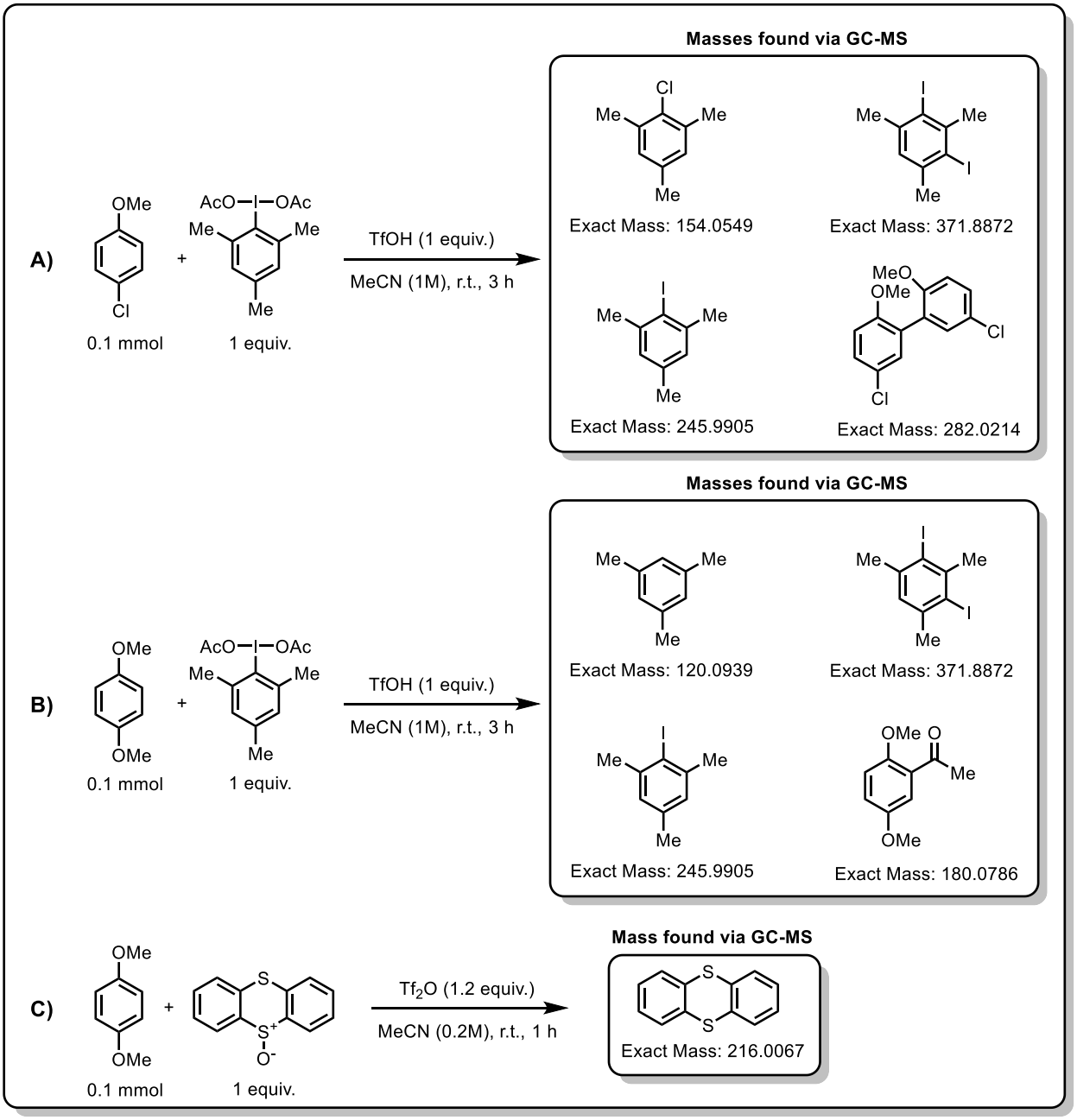


A 4 or 8 mL vial was charged with iodomesitylene diacetate (0.1 mmol or 0.5 mmol), PhMe (5 equiv.), PhMe-d_8 (5 equiv.), acetonitrile (1M, 0.1 mL or 0.5 mL) and a magnetic stir bar. Trifluoromethanesulfonic acid (1 equiv.) was added dropwise over 10 seconds to the mixture with vigorous stirring. The reaction was then stirred at room temperature for 3 hours. **For the 0.5 mmol reaction:** The mixture was then added dropwise to a 100 mL round bottom flask containing 60 mL of diethyl ether while stirring. The resulting precipitate was then collected via vacuum filtration and analyzed via ^{1}HNMR. **For the 0.1 mmol reaction:** The reaction was concentrated under reduced pressure and the residue was analyzed via ^{1}HNMR.

8. Leaving group competition experiments:

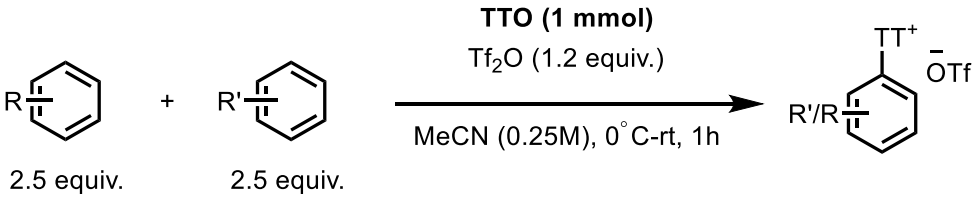


9. Identification of challenging reaction byproducts via GC-MS:

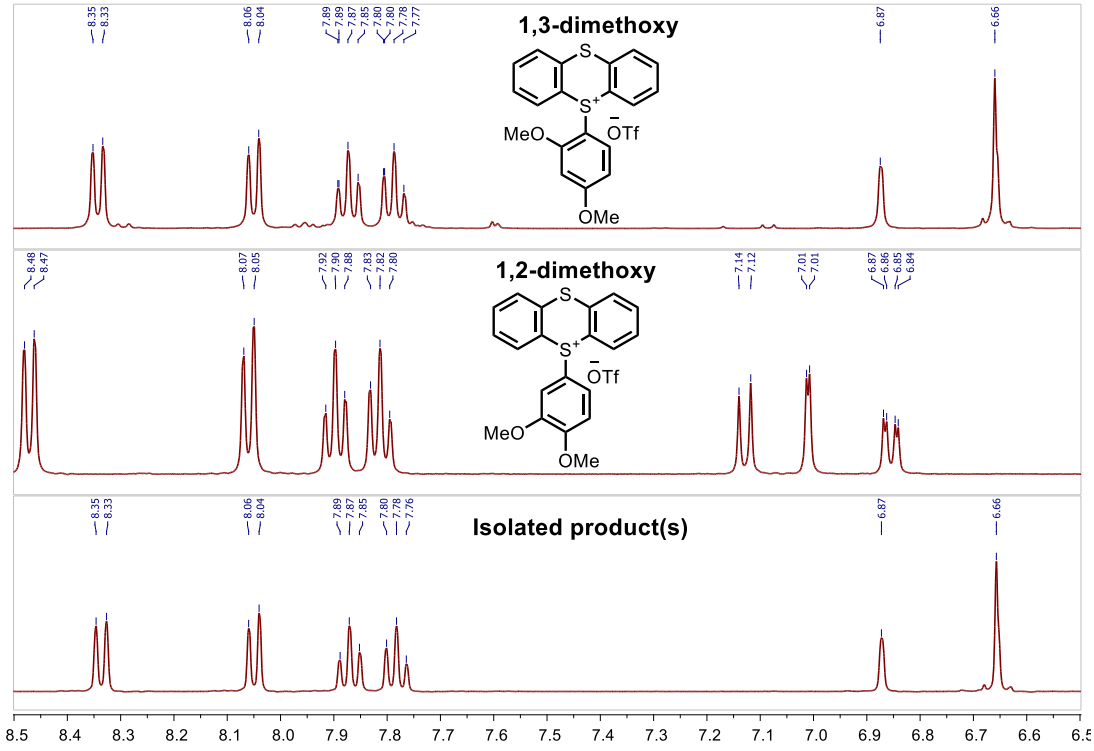


Reactions A-C were conducted at 0.1 mmol scale in accordance with general procedures E and A respectively. After the allotted time and aliquot of each reaction was analyzed via GC-MS.

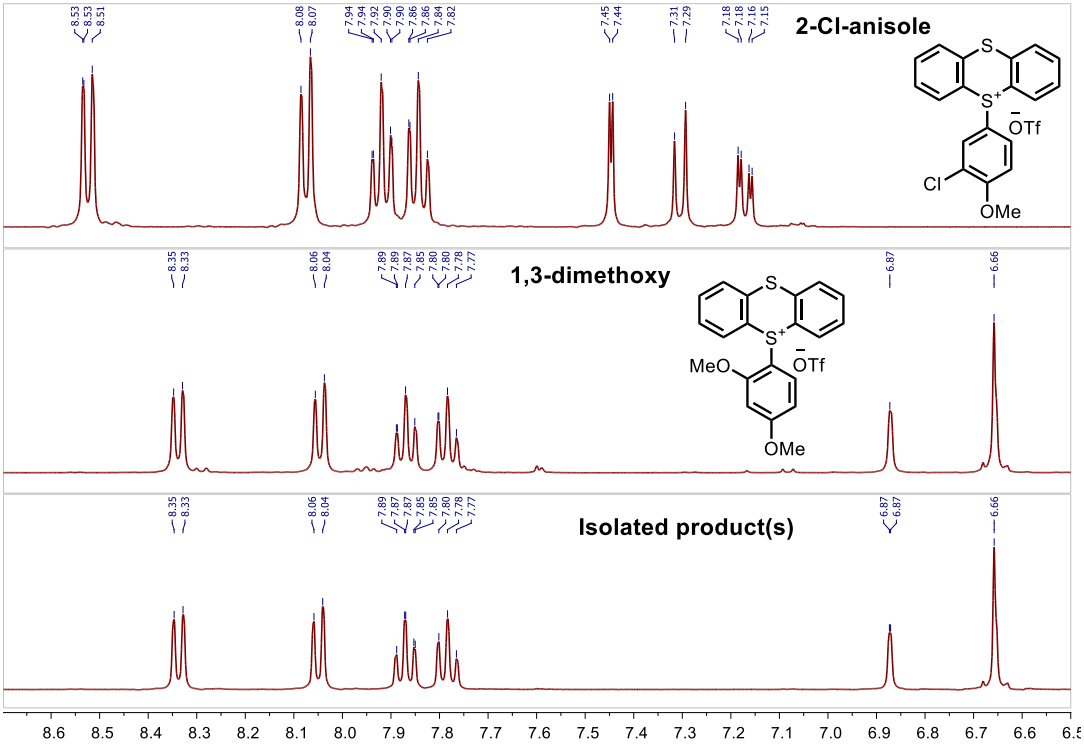
10. Arene thianthrenation competition reactions



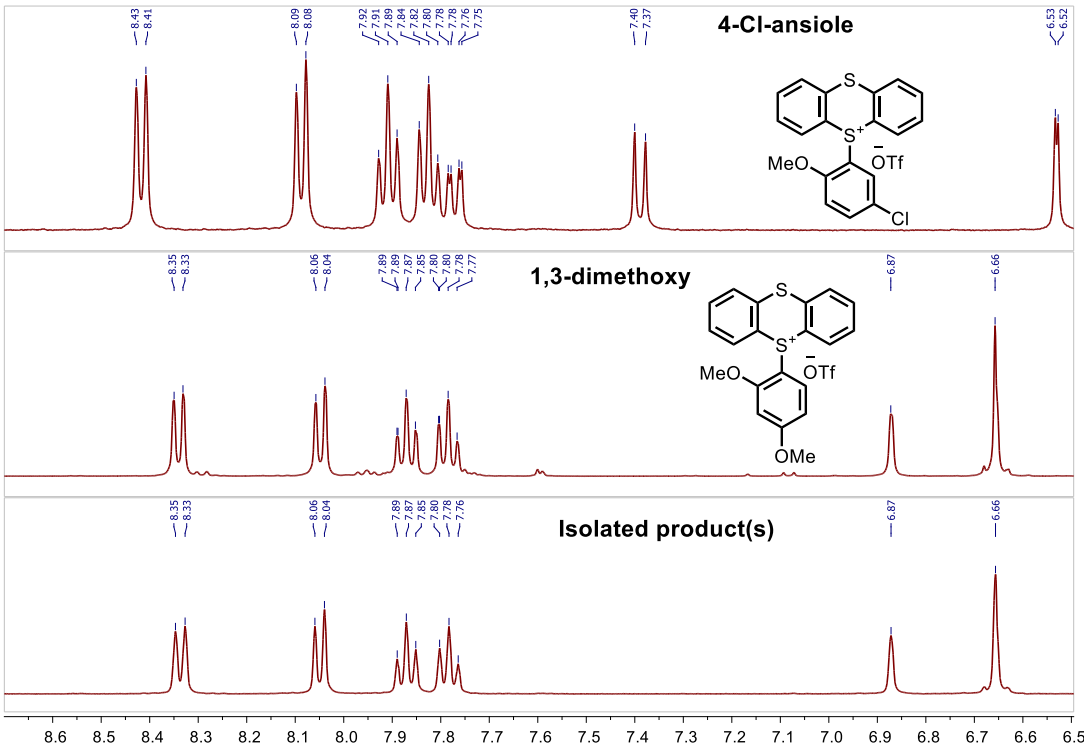
To an 8 mL vial was added thianthrene *S*-oxide (0.2323 g, 1 mmol), acetonitrile (4 mL), two arenes (2.5 mmol each) and a magnetic stir bar. The mixture was placed on ice with stirring and Tf_2O (0.2020 mL, 1.2 mmol, 1.2 equiv.) was added dropwise. The reaction was then removed from ice and stirred at room temperature for 1 hour. The reaction was then quenched with MeOH (1 mL) and the entire mixture was added to a stirring round bottom flask of diethyl ether (150 mL). The resulting solid was filtered via vacuum filtration and analyzed via ^{1}HNMR. The spectra shown below are of pure aryl thianthrenium salts stacked against spectra of the recovered solids.



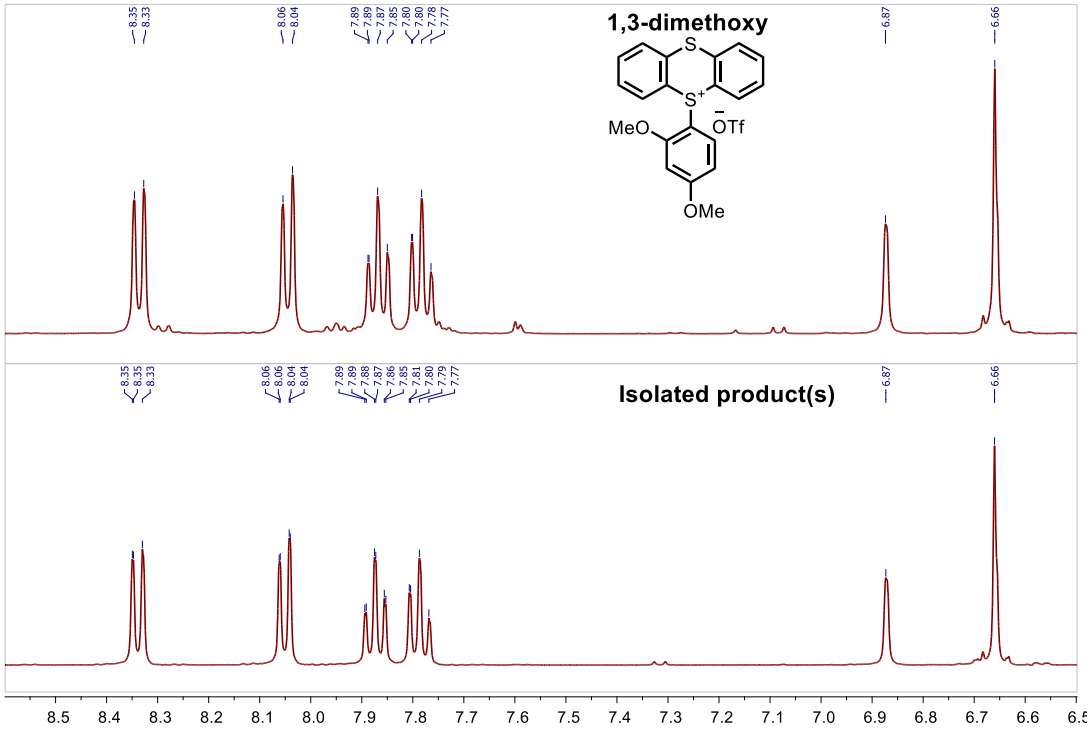
1,3-dimethoxybenzene vs. 1,2-dimethoxybenzene



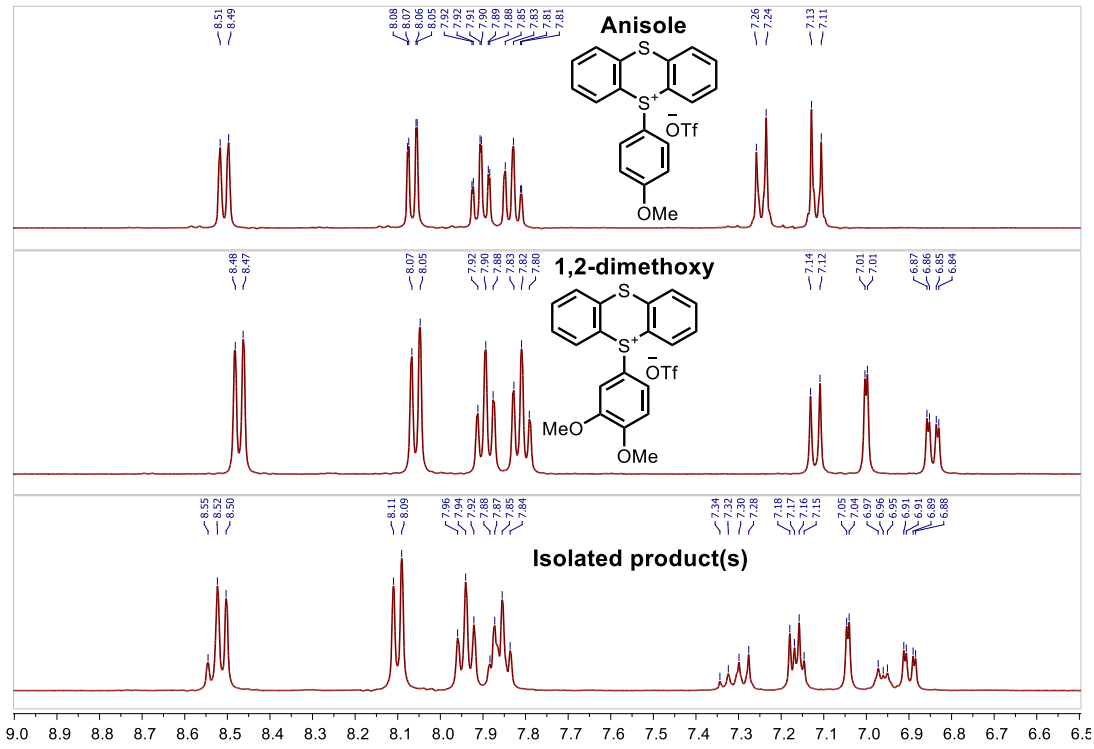
1,3-dimethoxybenzene vs. 2-Cl-ansiole



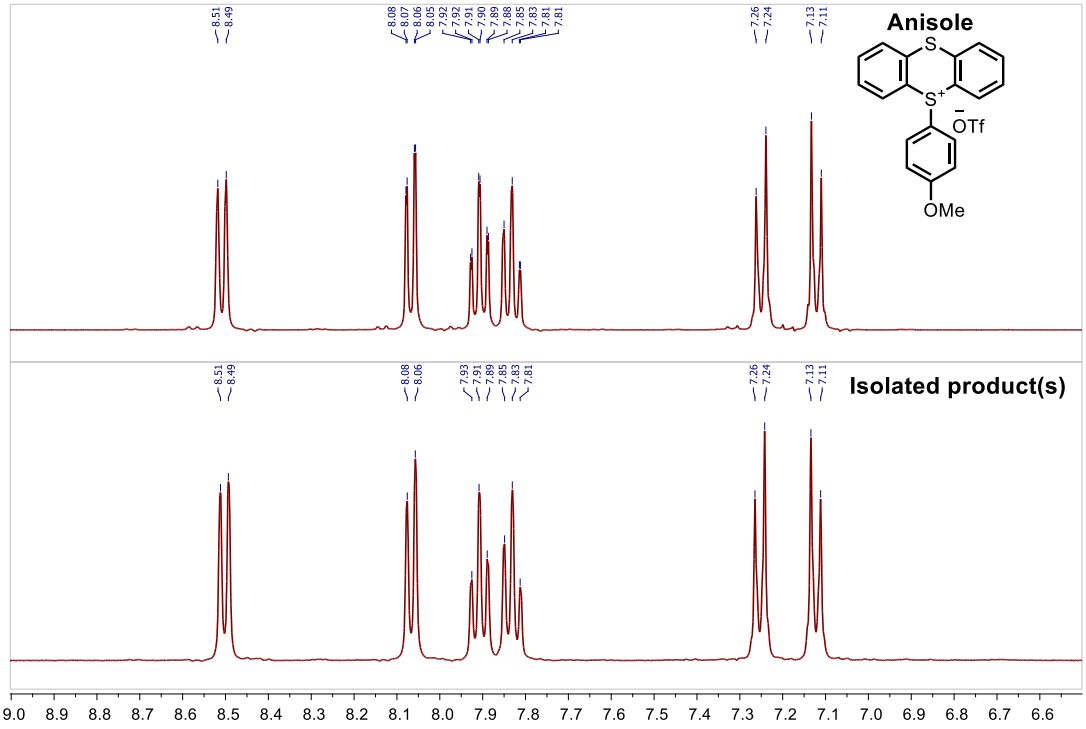
1,3-dimethoxybenzene vs. 4-Cl-anisole



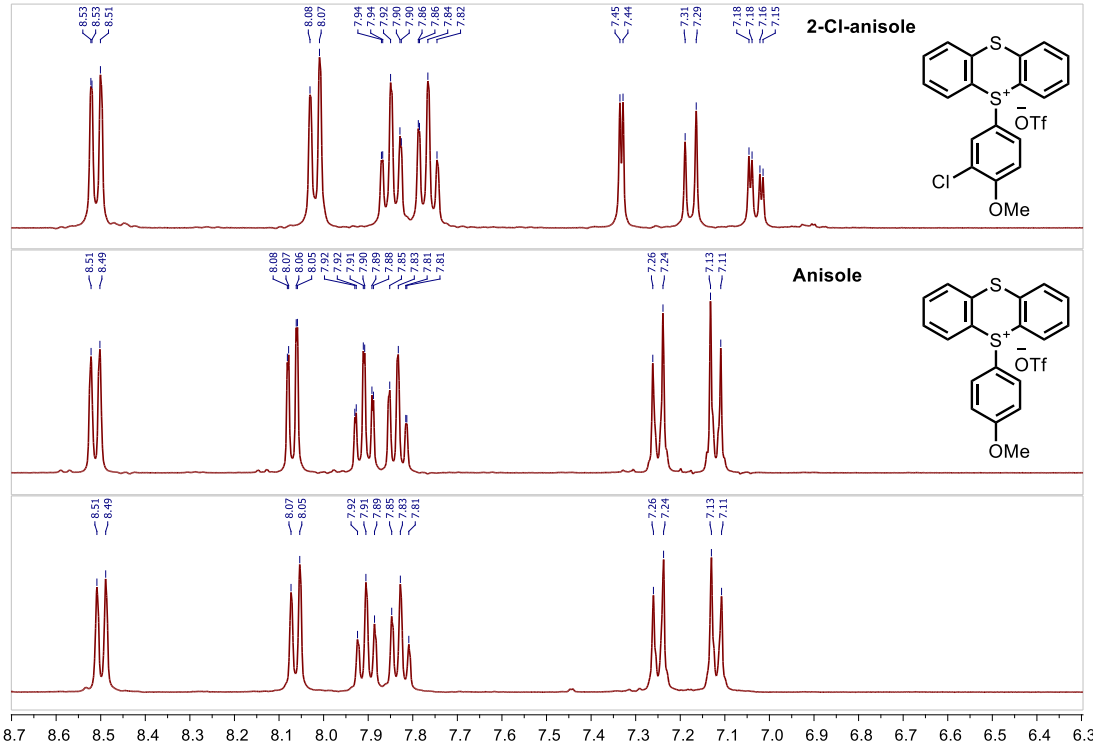
1,3-dimethoxybenzene vs. 1,4-dimethoxybenzene (unable to synthesize standard)



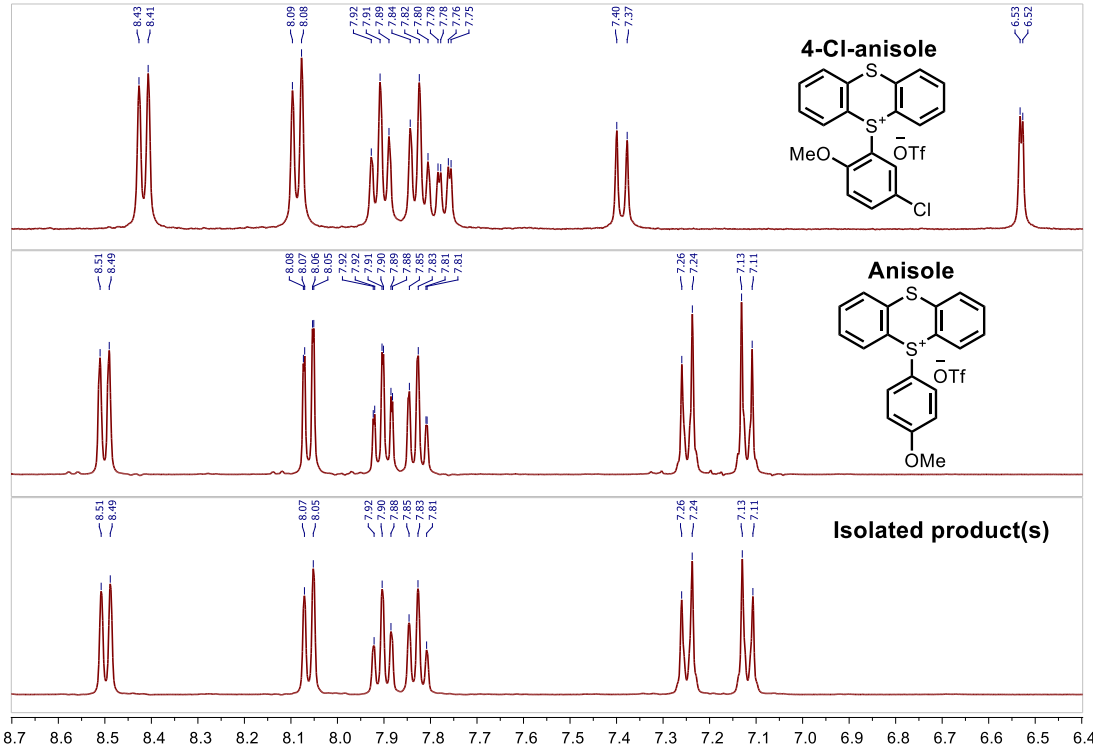
1,2-dimethoxybenzene vs. anisole



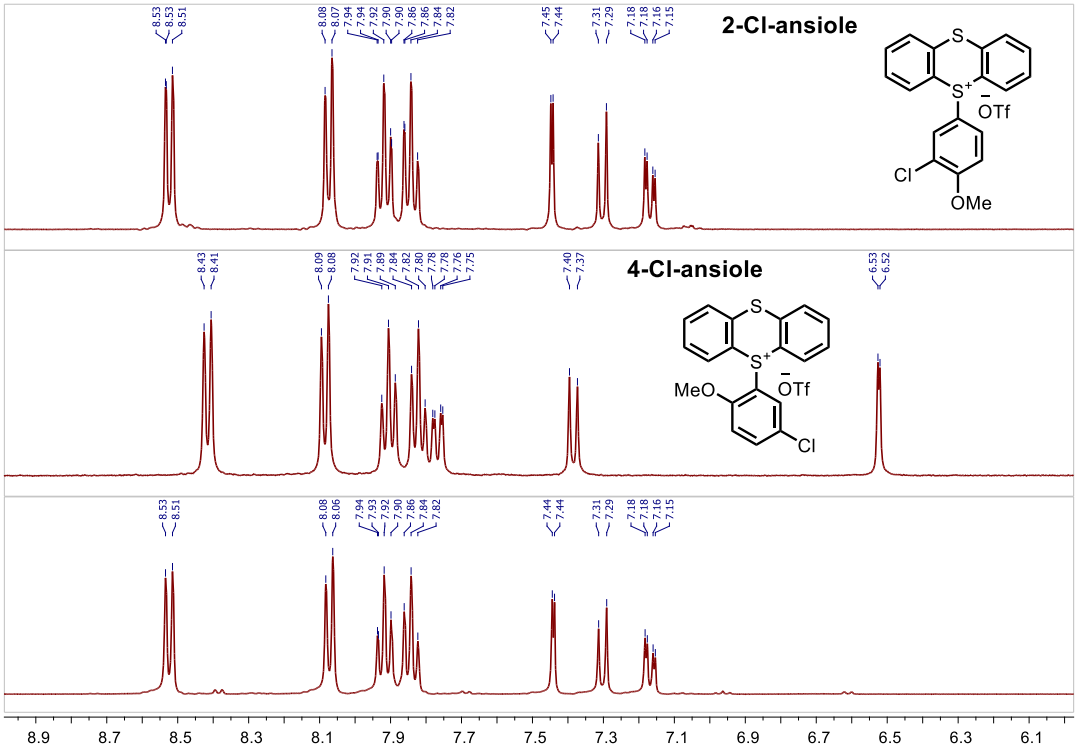
1,4-dimethoxybenzene (unable to synthesize standard) vs. anisole



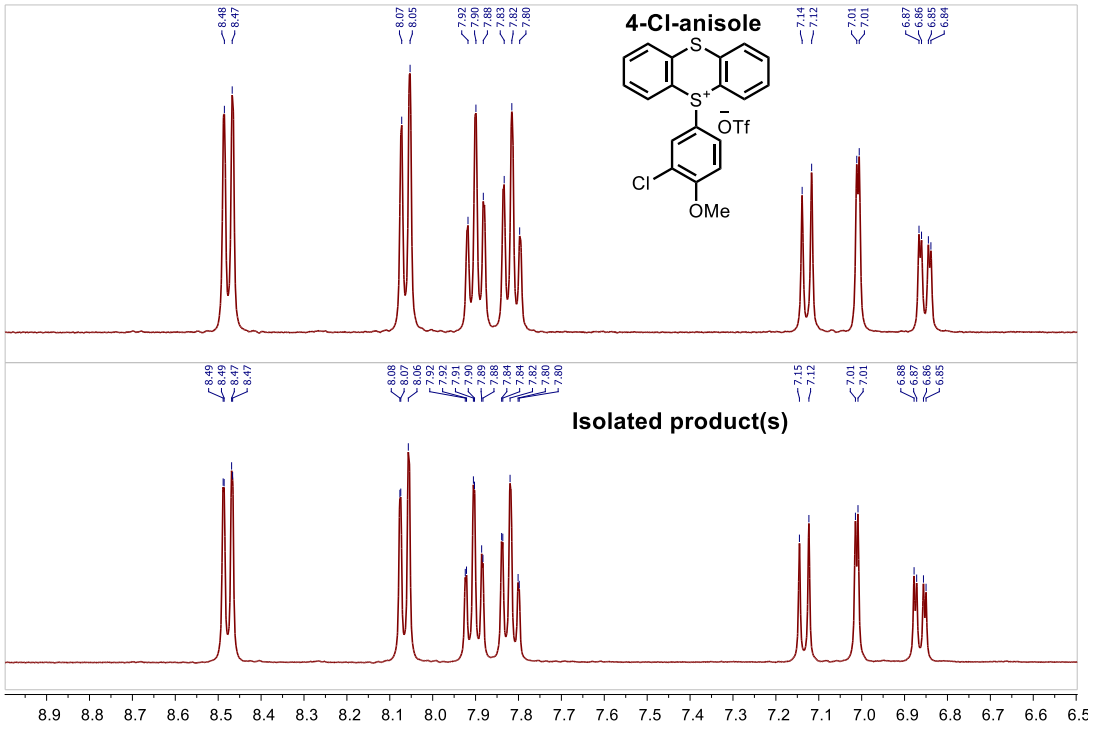
2-Cl-ansiole vs. anisole



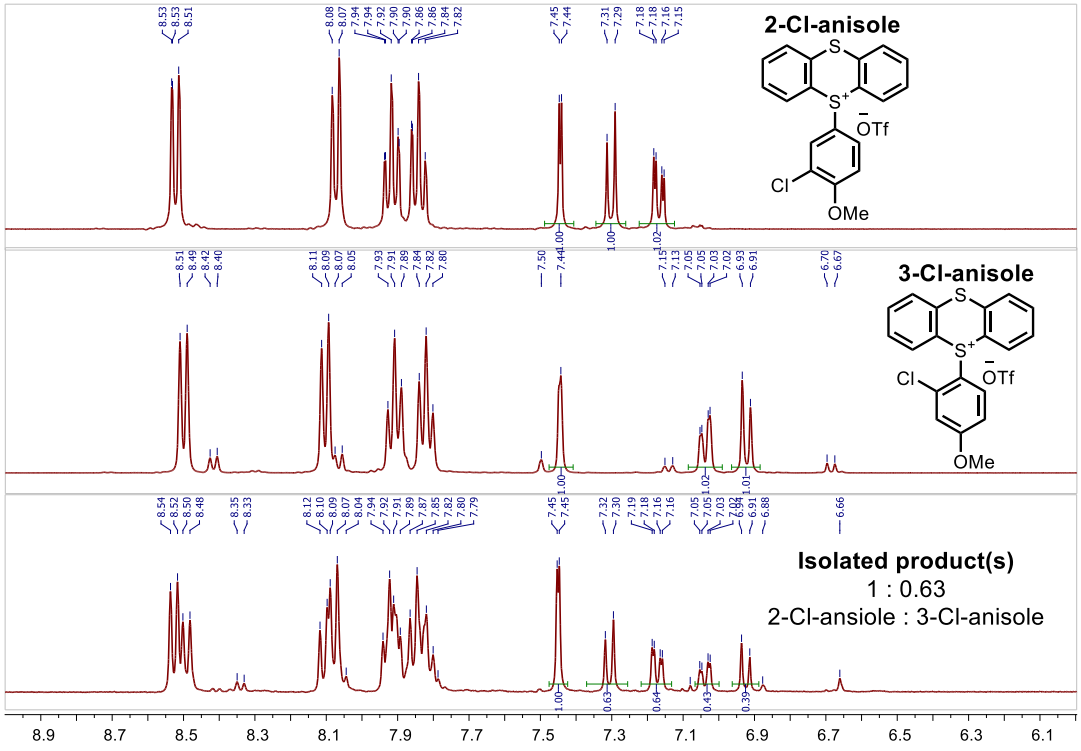
Anisole vs. 4-Cl-anisole



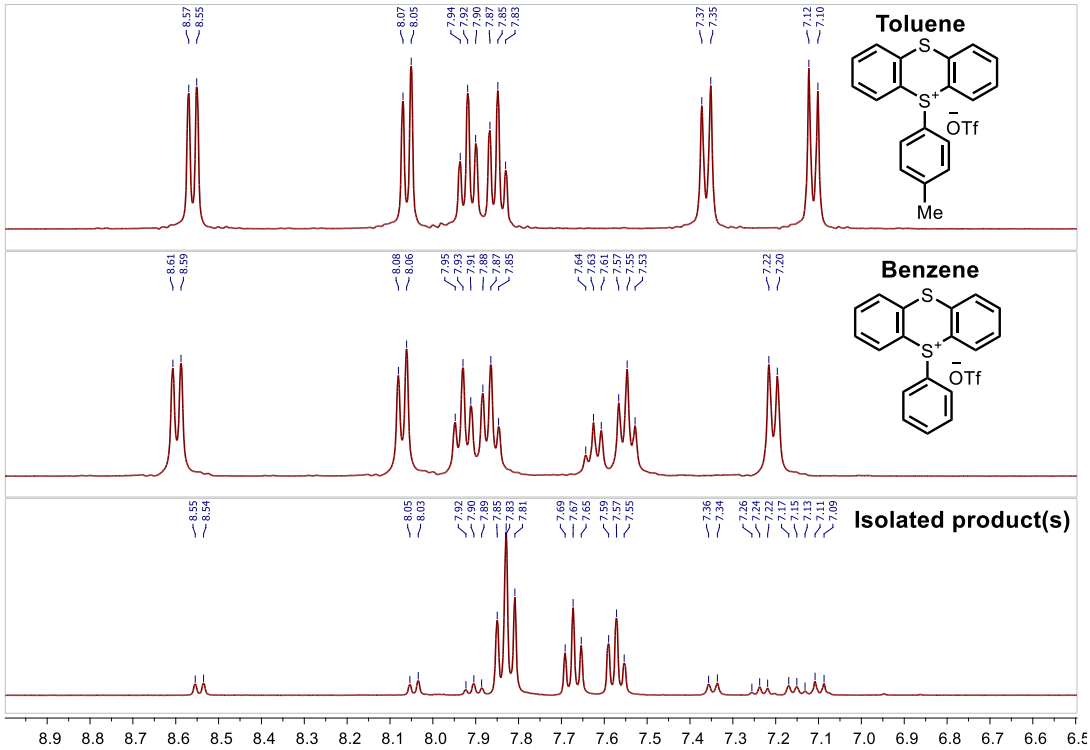
2-Cl-anisole vs. 4-Cl-anisole



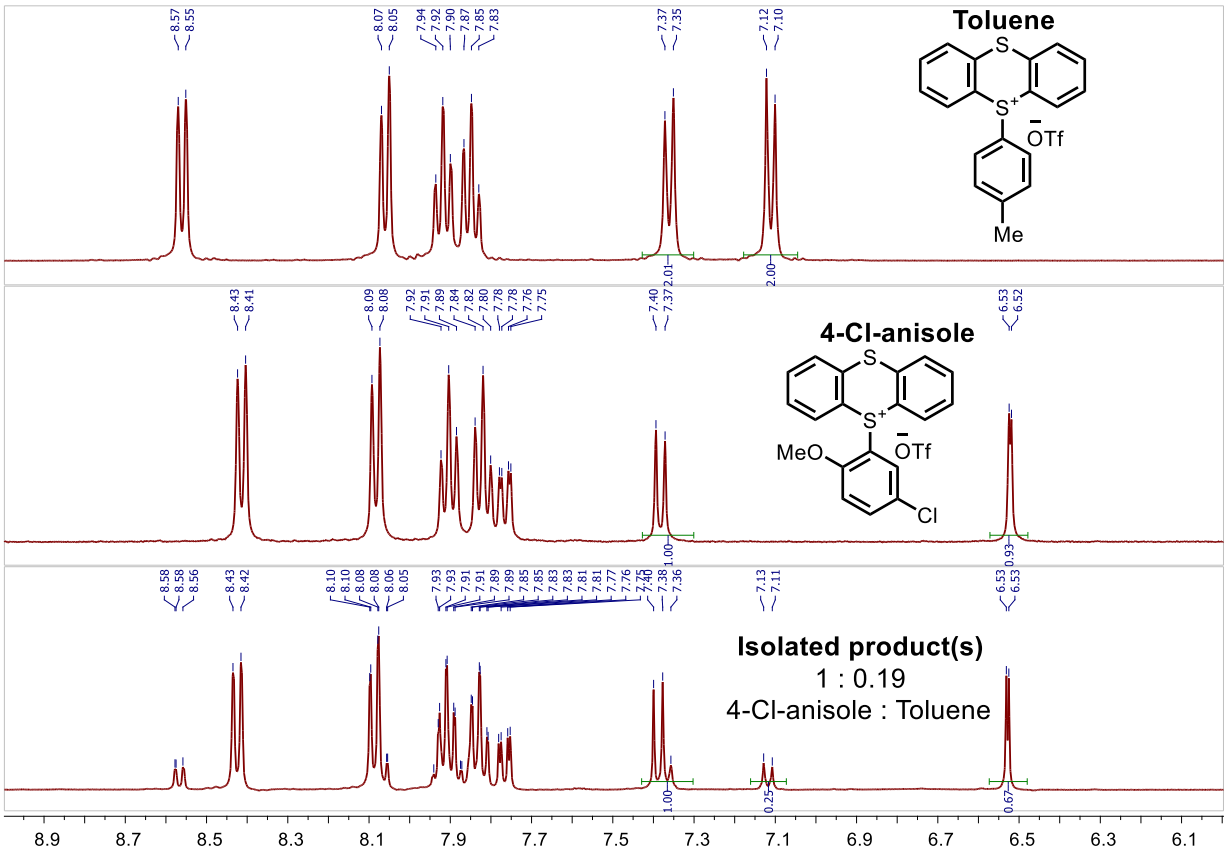
2-Cl-anisole vs. 1,4-dimethoxybenzene (unable to synthesize standard)



3-Cl-anisole vs. 2-Cl-anisole

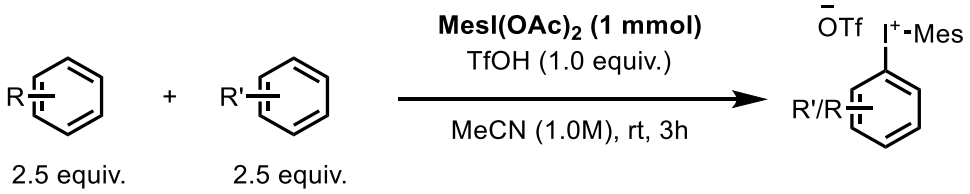


Toluene vs. Benzene

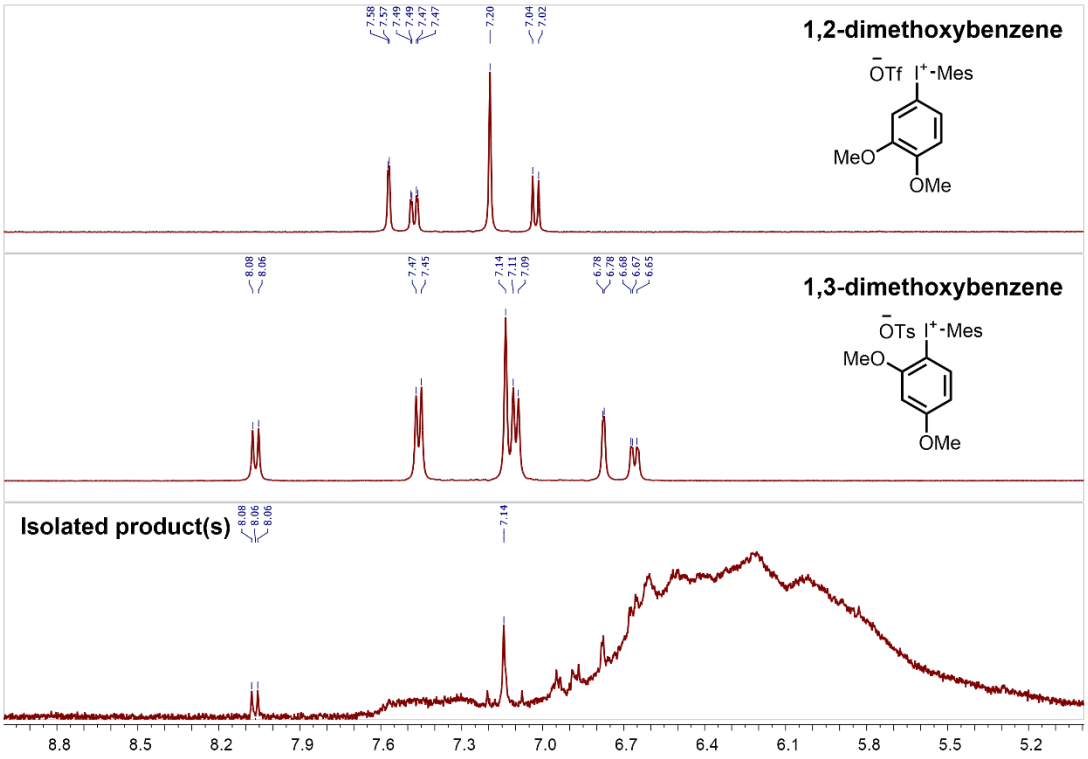


Toluene vs. 4-Cl-anisole

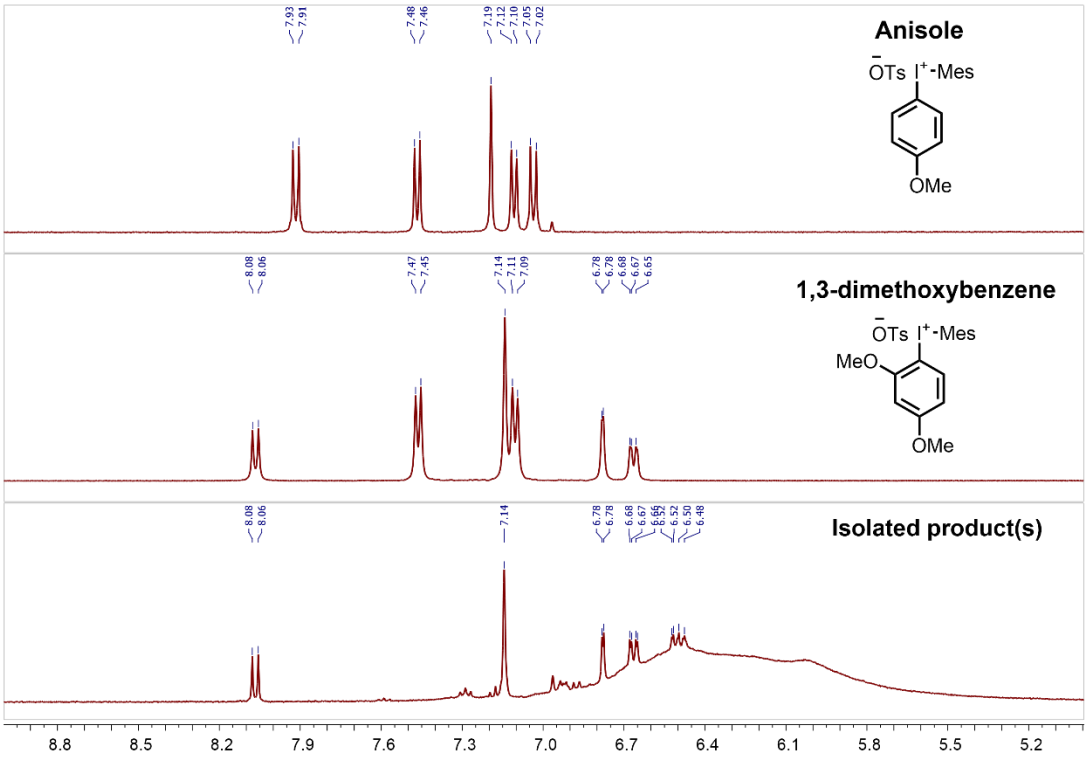
11. Arene iodination competition reactions



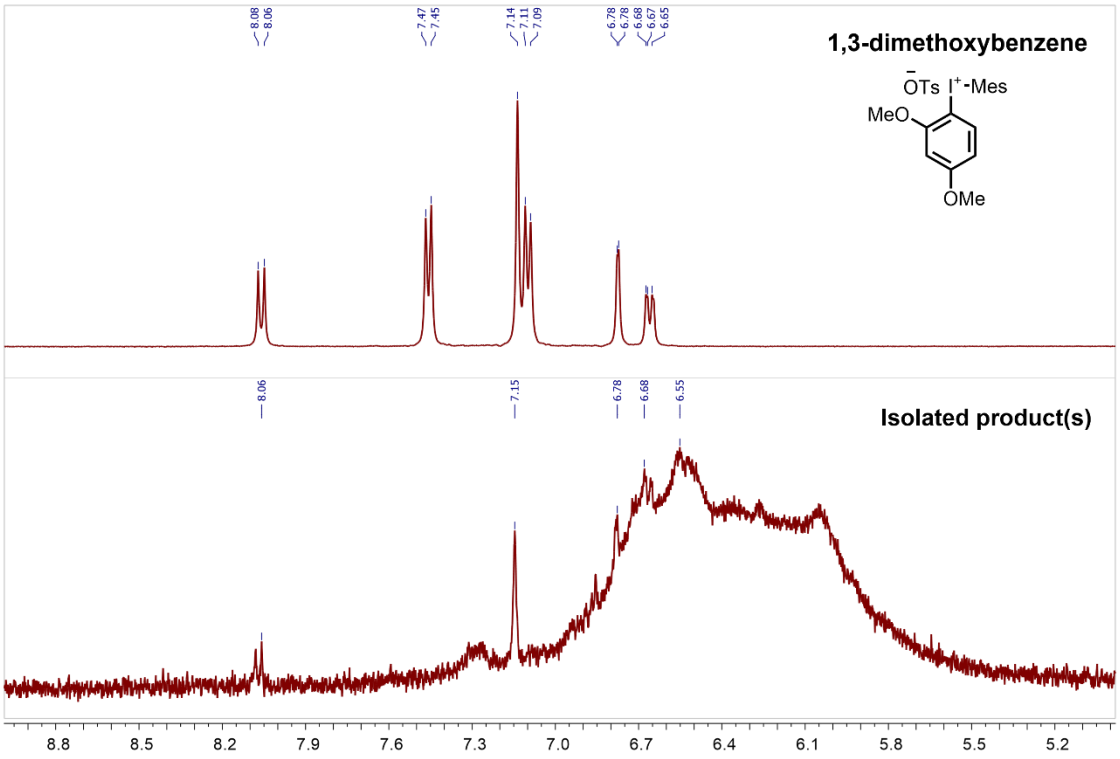
To an 8 mL vial was added iodomesitylene diacetate (0.3642 g, 1 mmol), acetonitrile (1 mL), two arenes (2.5 mmol each) and a magnetic stir bar. The mixture was placed on ice with stirring and trifluoromethanesulfonic acid (0.0885 mL, 1 mmol, 1 equiv.) was added dropwise. The reaction was then removed from ice and stirred at room temperature for 3 hours. The reaction was then added to a stirring round bottom flask of diethyl ether (150 mL). The resulting solid was filtered via vacuum filtration and analyzed via ^{1}HNMR. The spectra shown below are of pure diaryliodonium salts stacked against spectra of the recovered solids.



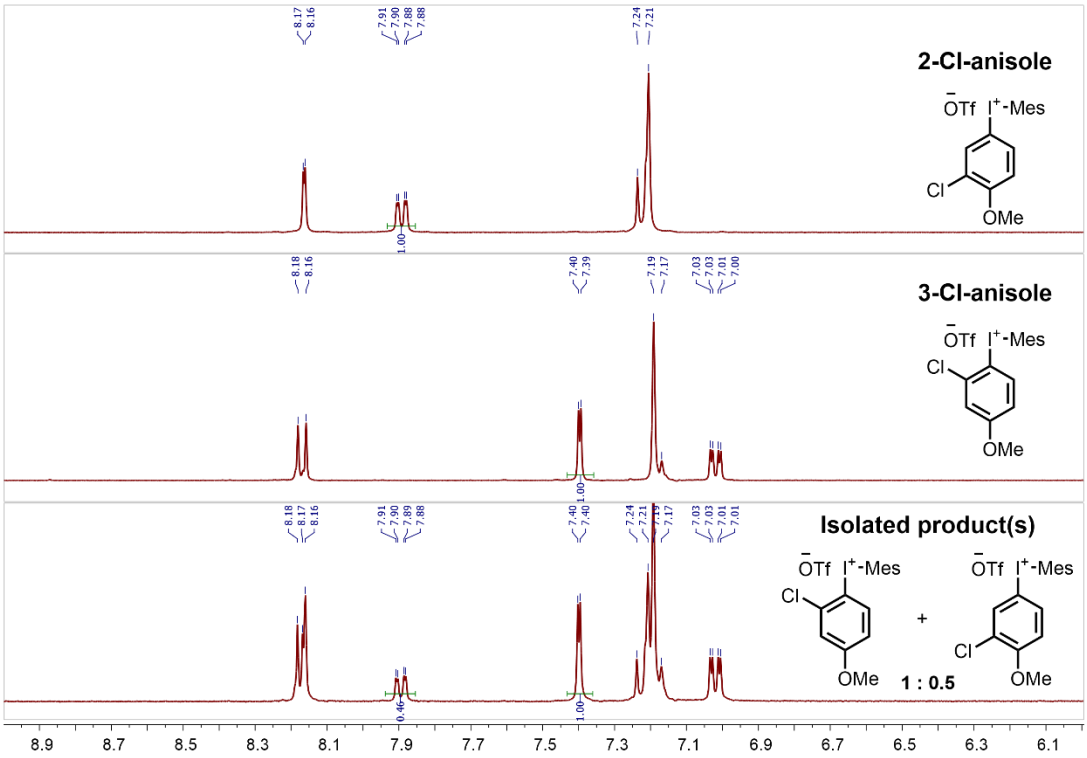
1,2-dimethoxybenzene vs. 1,3-dimethoxybenzene



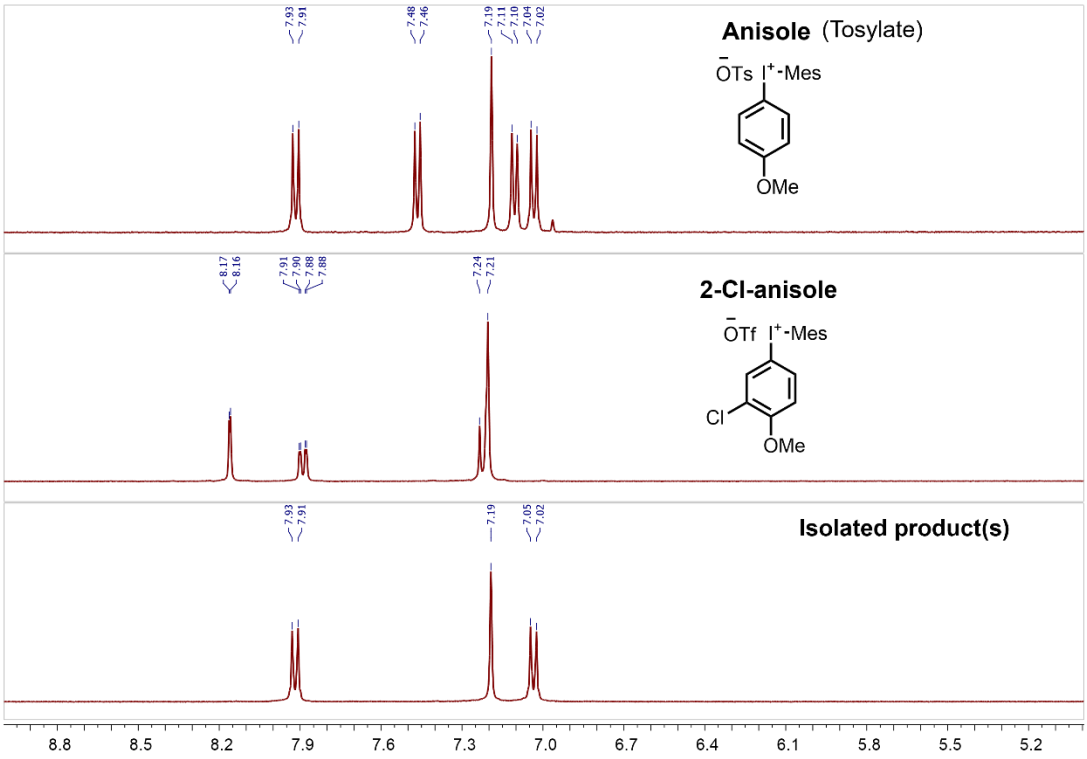
Anisole vs. 1,3-dimethoxybenzene



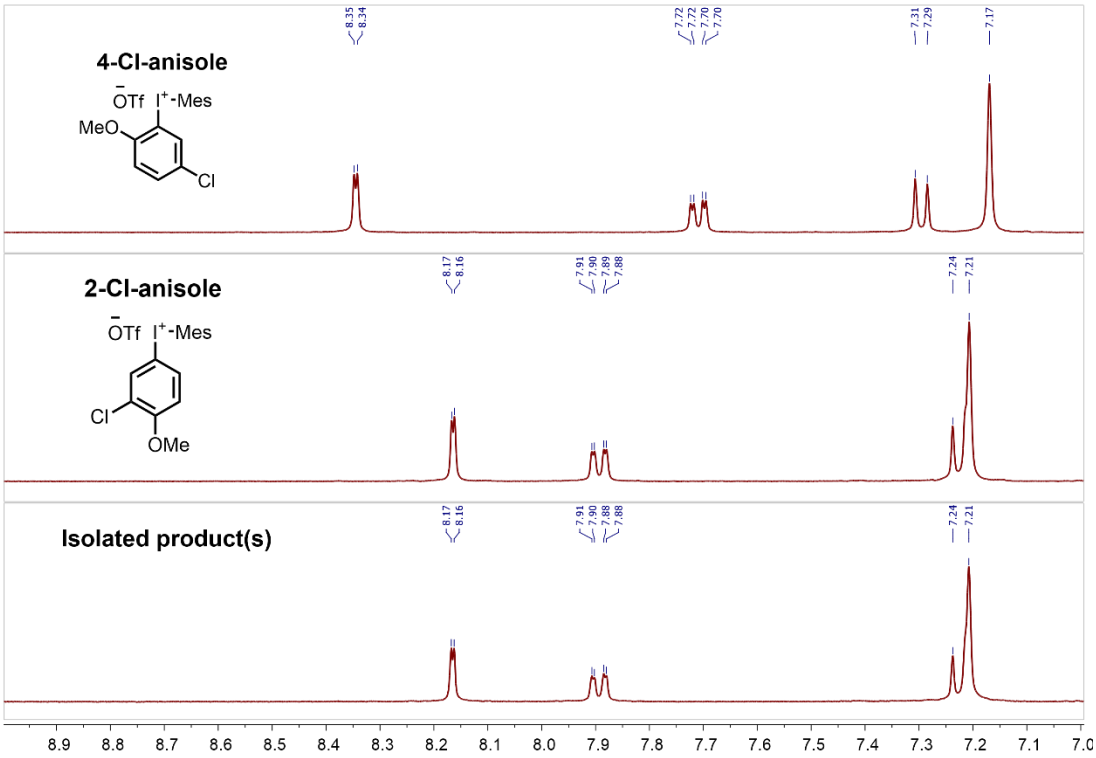
1,3-dimethoxybenzene vs. 1,4-dimethoxybenzene (unable to synthesize standard)



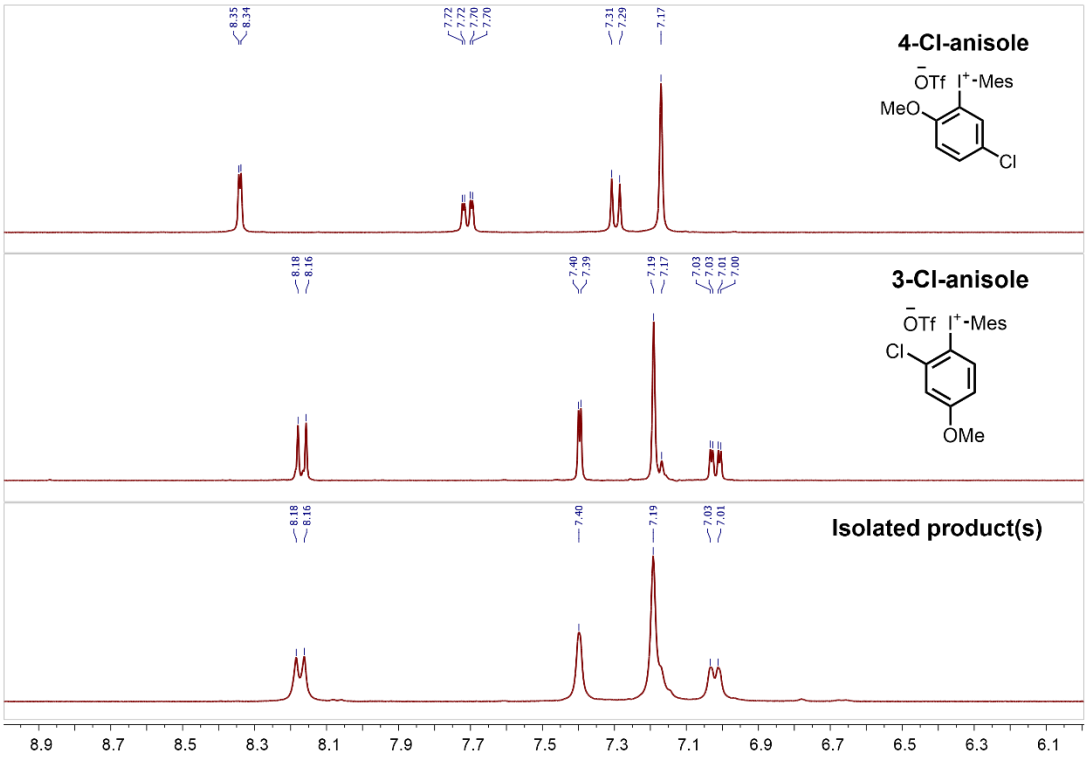
2-Cl-anisole vs. 3-Cl-anisole



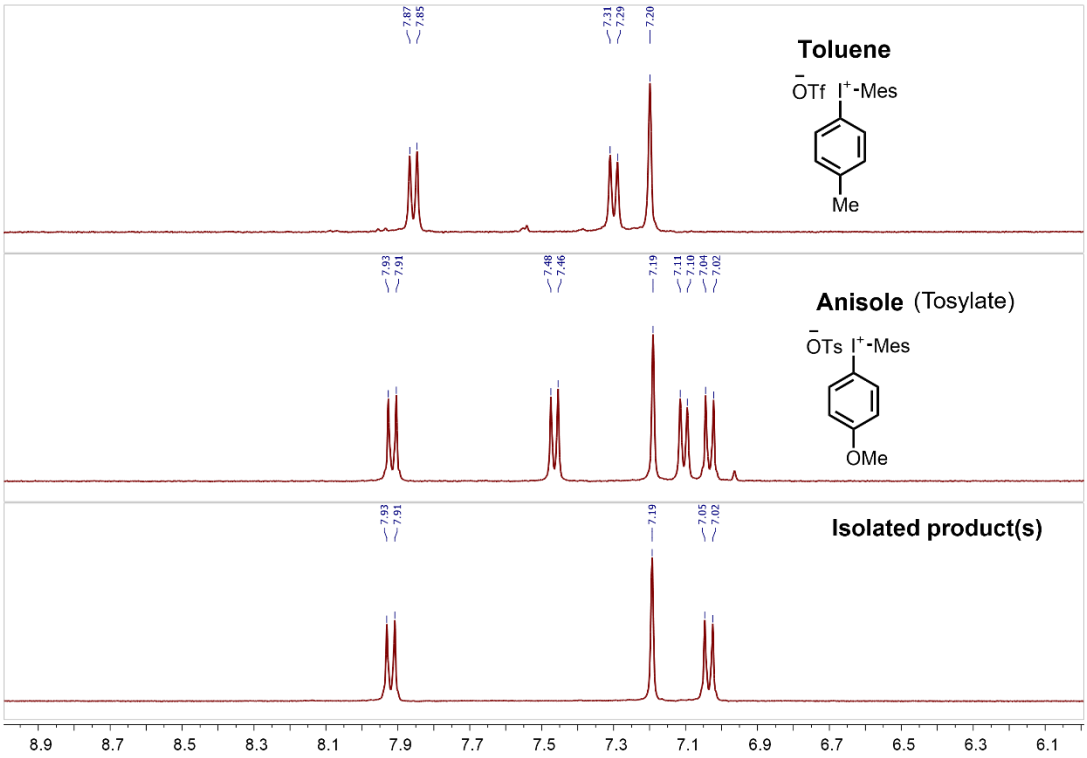
Anisole vs. 2-Cl-anisole



4-Cl-anisole vs. 2-Cl-anisole



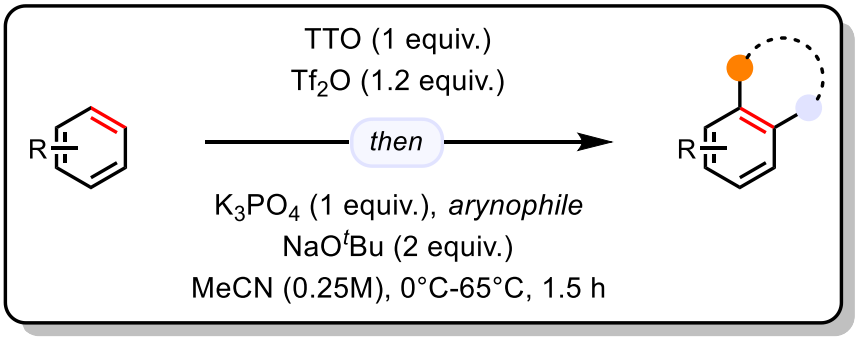
4-Cl-anisole vs. 3-Cl-anisole



Toluene vs. Anisole

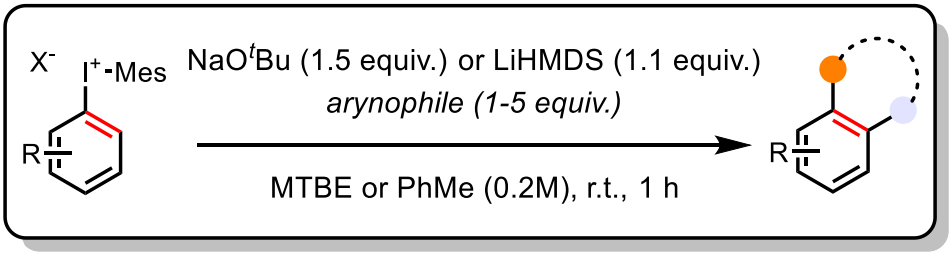
Syntheses and characterization:

General procedure A:



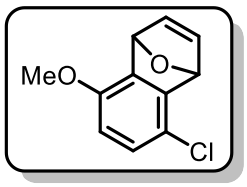
An appropriately sized reaction vessel was charged with thianthrene *S*-oxide (1 equiv.), desired arene (1 equiv.), acetonitrile (0.25M) and a magnetic stir bar. Trifluoromethanesulfonic anhydride (1.2 equiv.) was added to the stirring reaction mixture held at 0°C. The vial was capped and allowed to come to room temperature over the course of 30 minutes (by this time the deep purple color may have faded). Potassium phosphate tribasic is added to the reaction mixture in one portion and stirred vigorously for 5-10 minutes (this often results in a mild exotherm and color change). To this mixture is added arynophile (1-5 equiv.) and sodium *tert*-butoxide (2 equiv.). The vial is capped and heated to 65°C with stirring for 1 hour. The reaction is quenched with DI water and the biphasic mixture is separated. The aqueous layer is extracted with ethyl acetate (3 × 10 mL), the combined organic phases are dried with anhydrous sodium sulfate concentrated under reduced pressure and the crude residue is purified by flash column chromatography on silica gel with ethyl acetate/hexanes as the eluent.

General procedure B:



For sodium *tert*-butoxide reactions: An appropriately sized reaction vessel was charged with iodonium salt (1 equiv.) followed by addition of a magnetic stir bar, MTBE (0.2 M) and furan (5 equiv.). NaO^{t}Bu (1.5 equiv.) was added in one portion with constant stirring. **For LiHMDS reactions:** An appropriately sized reaction vessel was charged with iodonium salt (1 equiv.) followed by addition of a magnetic stir bar, PhMe (0.2 M including PhMe from LiHMDS solution) and furan (5 equiv.). LiHMDS 1M in PhMe (1.1 equiv.) was added in one portion with constant stirring. The reaction was then sealed with a cap and allowed to proceed for one hour at room temperature. Upon completion, the reaction was quenched with saturated ammonium chloride (*ca.* 4 ml) followed by extraction with EtOAc (3 x 10 ml). The combined organic phases are dried with anhydrous sodium sulfate concentrated under reduced pressure and the crude residue is purified by flash column chromatography on silica gel with ethyl acetate/hexanes as the eluent.

Compound 3aa

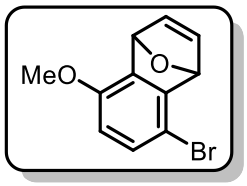


Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 73% (0.0762 g, 0.37 mmol) as a white solid was obtained. Spectra data consistent with previous reports.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 – 7.03 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.53 (d, *J* = 8.7 Hz, 1H), 5.96 (s, 1H), 5.85 (s, 1H), 3.80 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 151.8, 149.3, 143.5, 142.5, 137.7, 127.3, 119.0, 112.4, 81.7, 81.0, 56.2 ppm.

Compound 3ba

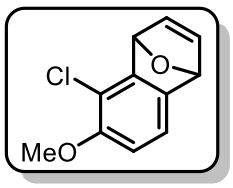


Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 83% (0.0910 g, 0.42 mmol) as a white solid was obtained. Spectra data consistent with previous reports.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 – 7.05 (m, 2H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.49 (d, *J* = 8.7 Hz, 1H), 6.00 (s, 1H), 5.78 (s, 1H), 3.80 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 152.3, 151.8, 143.6, 142.6, 138.0, 129.9, 112.8, 106.1, 83.2, 81.2, 56.1 ppm.

Compound 3ca

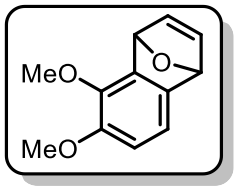


Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 83% (0.0865 g, 0.42 mmol) as a white solid was obtained. Spectra data consistent with previous reports.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 – 6.99 (m, 3H), 6.44 (d, *J* = 7.7 Hz, 1H), 5.86 (s, 1H), 5.71 (s, 1H), 3.85 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 153.1, 149.3, 144.0, 142.1, 141.8, 118.5, 116.9, 107.2, 82.9, 81.7, 56.7 ppm.

Compound 3da

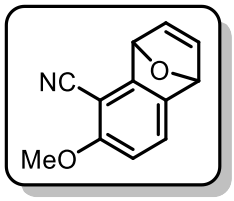


Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 76% (0.0771 g, 0.38 mmol) as a white solid was obtained. Spectra data consistent with previous reports.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01 (s, 2H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 7.5 Hz, 1H), 6.05 (s, 1H), 5.65 (s, 1H), 3.94 (s, 3H), 3.81 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 149.9, 144.0, 143.2, 141.9, 141.5, 136.7, 114.5, 107.4, 82.1, 81.3, 60.6, 56.4 ppm.

Compound 3ea



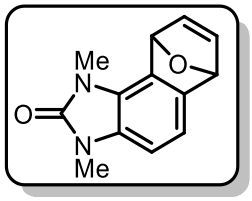
Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 60% (0.0594 g, 0.30 mmol) as a white solid was obtained.

R_f: 0.09 in 10% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 18.3, 5.5 Hz, 2H), 6.46 (d, *J* = 8.0 Hz, 1H), 5.88 (s, 1H), 5.73 (s, 1H), 3.87 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.9, 157.0, 144.4, 141.7, 141.6, 124.3, 114.5, 106.0, 97.2, 82.4, 81.8, 56.6 ppm.

Compound 3fa



Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 67% (0.0768 g, 0.34 mmol) as white solid was obtained.

R_f: 0.16 in 50% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 – 6.97 (m, 3H), 6.49 (d, *J* = 7.5 Hz, 1H), 6.08 (s, 1H), 5.76 (d, *J* = 0.9 Hz, 1H), 3.52 (s, 3H), 3.35 (s, 3H) ppm.

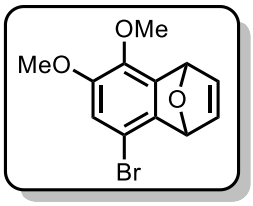
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 154.9, 143.8, 142.8, 142.1, 129.2, 128.4, 124.7, 113.6, 102.6, 82.4, 80.2, 28.8, 27.6 ppm.

FTIR: 2933, 1668, 1486, 1244, 1149, 1031, 861, 821, 636 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}N_2O_2$ 229.0972 found: 229.0977

Melting point: 68.8-75.4 °C

Compound 3ga

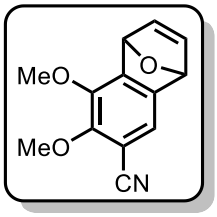


Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 56% (0.0793 g, 0.28 mmol) as a white solid was obtained. **Note: This product was isolated with a 5% TTO impurity that was unable to be separated.** Spectra data consistent with previous reports.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (dd, *J* = 5.5, 1.5 Hz, 1H), 7.02 (dd, *J* = 5.5, 1.4 Hz, 1H), 6.49 (s, 1H), 6.08 (s, 1H), 5.72 (s, 1H), 3.90 (s, 3H), 3.80 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 151.1, 143.4, 142.6, 142.3, 141.6, 138.9, 110.9, 106.6, 82.7, 82.2, 60.7, 56.6 ppm.

Compound 3ha



Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 67% (0.0779 g, 0.34 mmol) as white solid was obtained.

R_f: 0.06 in 10% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.08 – 6.98 (m, 3H), 6.03 (s, 1H), 5.68 (s, 1H), 3.98 (s, 3H), 3.95 (s, 3H) ppm.

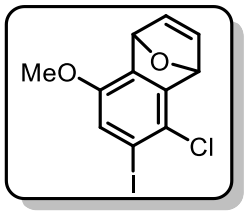
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 154.3, 147.2, 145.8, 143.7, 143.3, 141.7, 117.6, 116.6, 103.2, 81.9, 81.2, 62.1, 60.8 ppm.

FTIR: 2987, 2946, 2843, 2221, 1578, 1464, 1400, 1233, 1033, 862, 774, 648, 455 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}NO_3$ 230.0812 found: 230.0810

Melting point: 74.7-77.7 °C

Compound 3ia

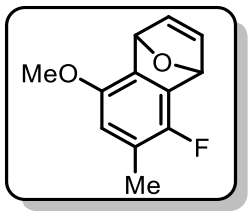


Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 85% (0.1427 g, 0.43 mmol) as a white solid was obtained. Spectra data consistent with previous reports.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14 – 7.02 (m, 3H), 5.93 (s, 1H), 5.83 (s, 1H), 3.80 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 151.8, 150.3, 143.8, 142.3, 138.9, 123.6, 122.6, 95.2, 83.2, 81.3, 56.3 ppm.

Compound 3ja



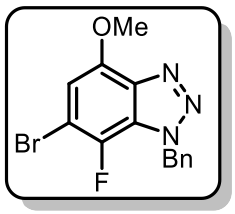
Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 76% (0.0784 g, 0.38 mmol) as a white solid was obtained. Spectra data consistent with previous reports.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.08 (dd, *J* = 5.5, 1.6 Hz, 1H), 7.03 (dd, *J* = 5.6, 1.6 Hz, 1H), 6.39 (d, *J* = 5.0 Hz, 1H), 5.91 (s, 2H), 3.78 (s, 3H), 2.21 (d, *J* = 1.4 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 151.1, 148.7, 143.5, 142.4, 135.4 (d, *J* = 23.4 Hz), 135.1 (d, *J* = 3.7 Hz), 124.7 (d, *J* = 19.8 Hz), 113.7 (d, *J* = 3.3 Hz), 80.6, 79.9, 56.5, 14.9 (d, *J* = 2.9 Hz) ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = -134.5

Compound 3kb



Prepared according to the general procedure A on a 0.5 mmol scale using benzyl azide (0.1875 mL, 1.5 mmol, 3 equiv.) as the arynophile. An isolated yield of 70% (0.1177 g, 0.35 mmol) was obtained as a 1.4:1 mixture of regioisomers presenting as a white solid.

R_f: 0.19 in 10% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) **(Major isomer)** δ = 7.38 – 7.25 (m, 8H) (Overlap with minor isomer), 6.78 (d, *J* = 4.3 Hz, 1H), 5.95 (s, 2H), 3.93 (s, 3H) ppm.

^{1}H NMR (400 MHz, $CDCl_3$) **(Minor isomer)** δ = 7.38 – 7.25 (m, 14H) (Overlap with major isomer), 6.70 (d, *J* = 4.3 Hz, 1H), 5.86 (s, 2H), 4.05 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) **(Major isomer)** δ = 144.57 (d, *J* = 251.1 Hz), 141.94 (d, *J* = 3.4 Hz), 135.79 (s), 135.04 (s), 129.08 (s), 128.90 (s), 128.47 (s), 127.85 (s), 110.17 (s), 101.64 (d, *J* = 19.8 Hz), 56.56 (s), 53.75 (s) ppm.

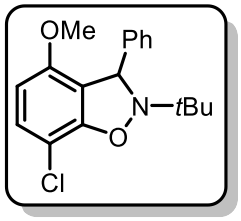
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = -127.7, -134.1 ppm.

FTIR: 2943, 1602, 1514, 1203, 1079, 810, 698 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}BrFN_3O$ 336.0142 found: 336.0143

Melting point: 129.4-148.5 °C

Compound 3ac



Prepared according to the general procedure A on a 0.5 mmol scale using N-tert-Butyl-α-phenylnitrone (0.0886 g, 0.50 mmol, 1.0 equiv.) as the arynophile. An isolated yield of 44% (0.0697 g, 0.22 mmol) as a white solid was obtained.

R_f: 0.58 in 10% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (dd, *J* = 11.8, 4.6 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.30 (d, *J* = 8.7 Hz, 1H), 5.66 (s, 1H), 3.64 (s, 3H), 1.18 (s, 9H) ppm.

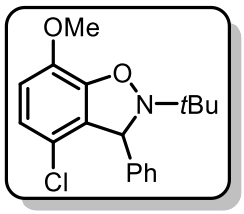
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 154.4, 154.1, 142.6, 130.0, 128.4, 127.6, 127.4, 118.1, 105.3, 104.8, 66.0, 61.7, 55.8, 25.4 ppm.

FTIR: 3081, 2288, 1561, 1460, 1380, 1257, 1155, 1028, 635, 465 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}ClNO$ 318.1255 found: 318.1247

Melting point: 148.9-151.6 °C

Compound 3ac'



Prepared according to the general procedure A on a 0.5 mmol scale using N-tert-Butyl-α-phenylnitrone (0.0886 g, 0.50 mmol, 1.0 equiv.) as the arynophile. An isolated yield of 29% (0.0466 g, 0.15 mmol) as a white solid was obtained.

R_f: 0.50 in 10% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.21 (m, 5H), 6.76 – 6.69 (m, 2H), 5.60 (s, 1H), 3.90 (s, 3H), 1.19 (s, 9H) ppm.

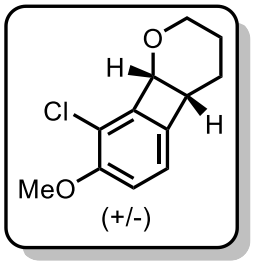
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 147.2, 141.8, 141.8, 128.6, 128.2, 127.7, 121.7, 120.9, 114.2, 67.3, 61.8, 56.8, 25.5 ppm.

FTIR: 3082, 2285, 1558, 1460, 1379, 1250, 1153, 1028, 635, 465 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}ClNO$ 318.1255 found: 318.1252

Melting point: 121.6-125.5 °C

Compound 3cd



Prepared according to the general procedure A on a 0.5 mmol scale using 3,4-dihydropyran (0.2281 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 52% (0.0584 g, 0.26 mmol) as a white solid was obtained.

R_f: 0.48 in 10% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.13 (d, *J* = 4.9 Hz, 1H), 3.88 (s, 3H), 3.78 (t, *J* = 7.2 Hz, 2H), 3.59 (q, *J* = 5.2 Hz, 1H), 2.22 – 2.06 (m, 1H), 1.95 – 1.80 (m, 1H), 1.63 – 1.49 (m, 1H), 1.47 – 1.32 (m, 1H) ppm.

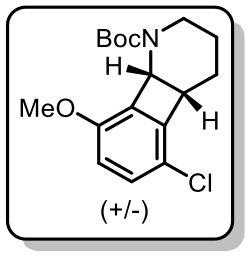
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 154.7, 144.6, 140.3, 122.1, 117.5, 114.4, 72.1, 62.1, 56.6, 41.9, 23.2, 19.5 ppm.

FTIR: 2936, 2868, 1463, 1434, 1260, 1056, 805, 642 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}ClO_2$ 225.0677 found: 225.0672

Melting point: 37.1-39.9 °C

Compound 3ae



Prepared according to the general procedure A on a 0.5 mmol scale using tert-butyl 3,4-dihydropyridine-1(2H)-carboxylate (0.458 g, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 44% (0.0712 g, 0.22 mmol) as a white solid was obtained.

R_f: 0.44 in 10% EtOAc in hexanes

^{1}H NMR (400 MHz, 333K, CD_3CN) δ 7.15 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 1H), 5.75 (s, 1H), 4.00 (s, 1H), 3.81 (s, 3H), 3.72 – 3.58 (m, 1H), 3.18 (s, 1H), 2.13 (d, *J* = 13.9 Hz, 1H), 1.92 – 1.81 (m, 1H), 1.67 – 1.55 (m, 1H), 1.47 (s, 10H), 1.36 – 1.19 (m, 1H) ppm.

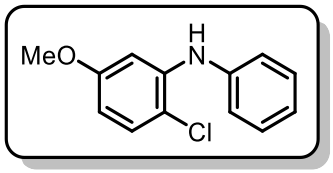
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 155.6 (d, *J* = 80.8 Hz), 154.0 (d, *J* = 8.3 Hz), 143.8 (d, *J* = 13.5 Hz), 131.4 (d, *J* = 25.4 Hz), 130.3 (d, *J* = 11.8 Hz), 119.2 (d, *J* = 16.0 Hz), 116.7 (d, *J* = 91.3 Hz), 80.2 (d, *J* = 14.2 Hz), 57.1 (d, *J* = 35.4 Hz), 53.1 (d, *J* = 68.0 Hz), 44.0, 41.5 (d, *J* = 95.4 Hz), 28.5 (d, *J* = 4.2 Hz), 22.9 (d, *J* = 6.8 Hz), 17.5 (d, *J* = 13.2 Hz) ppm. Rotamers responsible for signal splitting.

FTIR: 2936, 1681, 1577, 1476, 1409, 1262, 1158, 1102, 810 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H\text{-}Boc]^+$ Calcd for $C_{12}H_{15}ClNO$ 224.0837 found: 224.0843

Melting point: 68.6-72.8 °C

Compound 3af



Prepared according to the general procedure A on a 7 mmol scale using aniline (3.165 mL, 35.0 mmol, 5 equiv.) as the arynophile. An isolated yield of 81% (1.31 g, 5.67 mmol) was obtained as a 10:1 mixture of regioisomers presenting as a yellow oil. Spectra data consistent with previous reports.[1]

^{1}H NMR (400 MHz, $CDCl_3$) **(Major isomer)** δ = 7.25 (t, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 2.8 Hz, 1H), 6.29 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.02 (s, 1H), 3.64 (s, 3H) ppm.

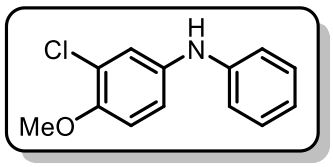
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) **(Major isomer)** δ = 159.3, 141.4, 141.2, 130.1, 129.6, 123.0, 120.7, 113.3, 105.8, 101.4, 55.6 ppm.

FTIR: 2948, 2230, 1602, 1463, 1343, 1271, 1055, 864, 806, 715 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}NO_2$ 200.0706 found: 200.0711

Melting point: 63.6-66.7 °C

Compound 3bf

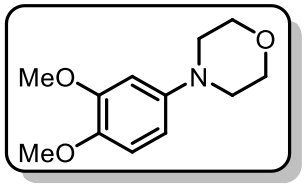


Prepared according to the general procedure A on a 0.5 mmol scale using aniline (0.2261 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 70% (0.0815 g, 0.35 mmol) as an orange solid was obtained. Spectra data consistent with previous reports.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.19 (m, 2H), 7.16 (d, *J* = 2.6 Hz, 1H), 7.00 – 6.82 (m, 5H), 3.87 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 150.5, 144.1, 136.9, 129.6, 123.1, 122.1, 120.6, 119.2, 116.7, 113.3, 56.7 ppm.

Compound 3dg

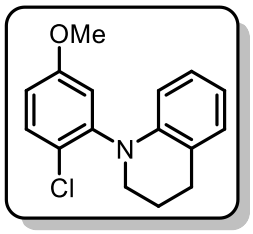


Prepared according to the general procedure A on a 0.5 mmol scale using morpholine (0.2156 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 59% (0.0656 g, 0.30 mmol) as a clear colorless oil was obtained. Spectra data consistent with previous reports.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.80 (d, *J* = 8.7 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.45 (dd, *J* = 8.7, 2.7 Hz, 1H), 3.90 – 3.85 (m, 7H), 3.84 (s, 3H), 3.11 – 3.04 (m, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 149.7, 146.3, 143.9, 112.2, 107.8, 102.6, 67.1, 56.4, 56.0, 51.1 ppm.

Compound 3ah



Prepared according to the general procedure A on a 0.5 mmol scale using tetrahydroquinoline (0.3141 mL, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 67% (0.0920 g, 0.34 mmol) was obtained as a 8.1:1 mixture of regioisomers presenting as an clear colorless oil.

R_f: 0.59 in 10% EtOAc in hexanes

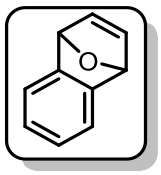
^{1}H NMR (400 MHz, $CDCl_3$) **(Major isomer)** δ = 7.38 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 2.8 Hz, 1H), 6.78 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.20 (d, *J* = 8.2 Hz, 1H), 3.77 (s, 3H), 3.55 (s, 2H), 2.89 (t, *J* = 6.4 Hz, 2H), 2.15 – 2.04 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) **(Major isomer)** δ = 159.6, 145.4, 144.3, 131.3, 129.5, 126.8, 125.1, 122.4, 117.5, 115.4, 113.9, 113.6, 55.8, 50.5, 28.0, 22.3 ppm.

FTIR: 2931, 2835, 1590, 1490, 1441, 1300, 1024, 743 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}ClNO$ 274.0993 found: 274.0994

Compound 3la

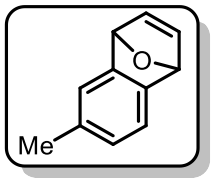


Prepared according to the general procedure B on a 0.43 mmol scale using furan (0.1564 mL, 2.15 mmol, 5 equiv.) as the arynophile with the following modification: LiHMDS in toluene (1M) was used being sure to maintain a starting concentration of 0.2M. The reaction was also allowed to proceed for 24 hours prior to quenching. An isolated yield of 66% (0.041 g, 0.28 mmol) as a white solid was obtained. Spectra data consistent with previous reports.[18]

^{1}H NMR (400 MHz, CDCl3) δ = 7.26-7.24 (m, 2H), 7.03 (s, 2H), 6.98-6.96 (m, 2H), 5.72 (s, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 149.0, 143.0, 125.0, 120.3, 82.3 ppm.

Compound 3ma

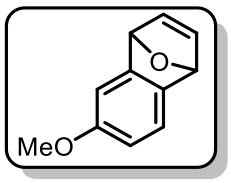


Prepared according to the general procedure B on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile in 78% (0.062 g, 0.39 mmol) yield as a clear oil was obtained. Spectra data consistent with previous reports.[19]

^{1}H NMR (400 MHz, CDCl3) δ = 7.12 (d, *J* = 7.2 Hz, 1H), 7.08 (s, 1H), 7.02-6.98 (m, 2H), 6.76 (d, *J* = 7.2 Hz, 1H), 5.67 (s, 1H), 5.66 (s, 1H), 2.29 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 149.4, 146.1, 143.3, 142.8, 134.8, 125.0, 121.6, 120.0, 82.3, 82.2, 21.3 ppm.

Compound 3na

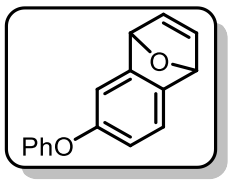


Prepared according to the general procedure B on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile in 71% (0.062 g, 0.36 mmol) yield as a clear oil was obtained. Spectra data consistent with previous reports.[5]

^{1}H NMR (400 MHz, CDCl3) δ = 7.12 (d, *J* = 7.8 Hz, 1H), 7.03-6.98 (m, 2H), 6.82 (s, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 5.67 (s, 1H), 5.66 (s, 1H), 3.77 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 157.5, 151.0, 143.5, 142.2, 140.4, 120.4, 109.7, 107.2, 82.4, 82.0, 55.6 ppm.

Compound 3pa



Prepared according to the general procedure B on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile in 94% (0.111 g, 0.47 mmol) yield as a white solid was obtained.

R_f = 0.47 in 20% EtOAc in Hexanes

^{1}H NMR (400 MHz, CDCl3) δ = 7.31 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.10-6.96 (m, 6H), 6.58 (d, *J* = 7.7 Hz, 1H), 5.73 (s, 1H), 5.66 (s, 1H) ppm.

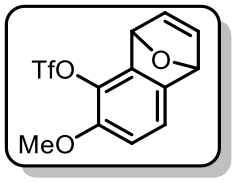
^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 157.5, 154.7, 151.4, 143.5, 143.4, 142.5, 129.7, 123.1, 120.7, 118.7, 114.3, 113.1, 82.4, 82.1 ppm.

FTIR: 3008, 2970, 2843, 1585, 1488, 1344, 1272, 1056, 1015, 691 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}O_2$ 237.0910 found: 237.0908

Melting point: 103-106 °C

Compound 3qa



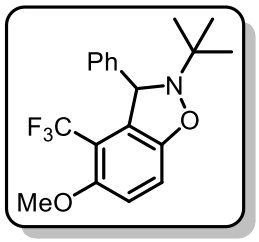
Prepared according to the general procedure B on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile in 76% (0.120 g, 0.38 mmol) yield as a white solid was obtained. Spectra data consistent with previous reports.[20]

^{1}H NMR (400 MHz, CDCl3) δ = 7.11 (d, *J* = 7.7 Hz, 1H), 7.07-7.01 (m, 2H), 6.54 (d, *J* = 7.7 Hz, 1H), 5.88 (s, 1H), 5.81 (s, 1H), 3.85 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 149.1, 143.5, 142.8(3), 142.8(0), 141.8, 132.9, 119.5, 118.7 (q, *J* = 320.3 Hz), 108.3, 82.4, 80.7, 56.5 ppm.

^{19}F{^{1}H} NMR (376 MHz, CDCl3) δ = -73.6 ppm.

Compound 3rc



Prepared according to the general procedure B on a 0.47 mmol scale using N-tert-Butyl-α-phenylnitrone (0.125 g, 0.71 mmol, 1.5 equiv.) as the arynophile in 85% (0.140 g, 0.40 mmol) yield as a white solid was obtained.

R_f = 0.63 in 20% EtOAc in Hexanes

^{1}H NMR (400 MHz, CDCl3) δ = 7.29-7.21 (m, overlaps with solvent residual signal, 3H), 7.05 (d, J = 7.3 Hz, 2H), 7.00 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 9.0 Hz, 1H), 5.71 (s, 1H), 3.85 (s, 3H), 1.17 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 153.0, 152.8 (m), 142.2, 128.6, 128.2 (m), 127.6, 127.2, 123.4 (q, J = 273.8 Hz), 114.7 (q, J = 32.0 Hz), 113.7, 110.2, 66.53 (m), 61.5, 57.1, 25.5 ppm.

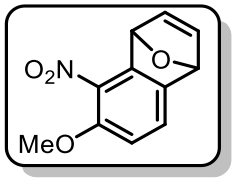
^{19}F{^{1}H} NMR (376 MHz, CDCl3) δ = -58.2 ppm.

FTIR: 2970, 2970, 2866, 1617, 1477, 1455, 1325, 1290, 1128, 1059, 1014, 811, 714 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}F_3NO_2$ 352.1519 found: 352.1515

Melting point: 139-142 °C

Compound 3sa



Prepared according to the general procedure B on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile in 80% (0.086 g, 0.4 mmol) yield as a yellow solid was obtained.

R_f = 0.13 in 20% EtOAc in Hexanes

^{1}H NMR (400 MHz, CDCl3) δ = 7.29 (d, *J* = 7.9 Hz, 1H), 7.13-7.10 (m, 2H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.01 (s, 1H), 5.75 (s, 1H), 3.89 (s, 3H) ppm.

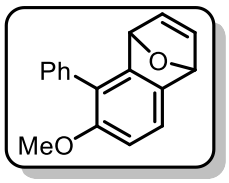
^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 150.1, 148.3, 144.4, 142.4, 141.7, 135.3, 123.7, 108.6, 82.5, 82.1, 57.0 ppm.

FTIR: 2939, 1624, 1590, 1270, 1358, 1012, 868, 833, 816, 705, 651 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}NO_4$ 220.0604 found: 220.0602

Melting point: 70-73 °C

Compound 3ta



Prepared according to the general procedure B on a 0.43 mmol scale using furan (0.1564 mL, 2.15 mmol, 5 equiv.) as the arynophile in 93% (0.100 g, 0.40 mmol) yield as a white solid was obtained containing a 1:6 mixture of regioisomers.

R_f = 0.38 (two poorly resolved spots) in 20% EtOAc:Hexanes

^{1}H NMR (400 MHz, CDCl3) δ = 7.43 (t, *J* = 7.8 Hz, 2H), 7.37-7.31 (m, 3H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.08-7.04 (m, 2H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.71 (s, 1H), 5.53 (s, 1H), 3.73 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 154.4, 149.7, 143.5, 142.2, 140.1, 135.7, 129.9, 128.1, 127.3, 119.4, 105.7, 82.4, 82.0, 56.0 ppm.

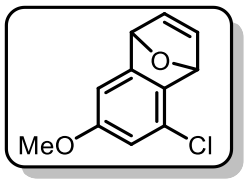
*note – 1 resonance in the ^{13}C spectrum could not be assigned due to peak overlap and the presence of the regioisomer

FTIR: 3017, 2974, 1607, 1436, 1404, 1345, 1276, 1209, 1155, 1134, 1087, 1048, 1031, 992, 884, 830, 698, 641, 606, 574 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}O_2$ 251.1067 found: 251.1060

Melting point: 160-165 °C

Compound 3ua



Prepared according to the general procedure B on a 0.53 mmol scale using furan (0.1927 mL, 2.65 mmol, 5 equiv.) as the arynophile in 97% (0.111 g, 0.52 mmol) yield as a clear oil was obtained containing a 1:0.12 mixture of regioisomers.

R_f = 0.33 in 20% EtOAc in Hexanes

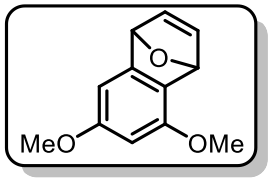
^{1}H NMR (400 MHz, CDCl3) δ = 7.07-7.05 (m, 1H), 7.00-6.99 (m, 1H), 6.78 (d, *J* = 1.3 Hz, 1H), 6.37 (d, *J* = 1.7 Hz, 1H), 5.82 (s, 1H), 5.68 (s, 1H), 3.75 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 158.6, 152.5, 142.9, 142.4, 138.5, 126.1, 108.6, 108.1, 83.0, 81.0, 55.9 ppm.

FT-IR 3087, 3011, 2940, 2835, 1631, 1588, 1463, 1400, 1353, 1249, 1222, 1179, 1030,841, 807, 651, 613 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}ClO_2$ 209.0364 found: 209.0368

Compound 3oa

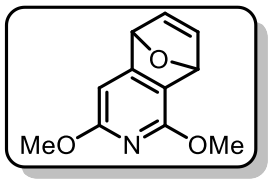


Prepared according to the general procedure B on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile in 65% (0.067 g, 0.33 mmol) yield as a yellow solid was obtained. Spectra data consistent with previous reports.[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.06 (dd, *J* = 5.5, 1.6 Hz, 1H), 6.98 (dd, *J* = 5.5, 1.7 Hz, 1H), 6.60 (d, *J* = 1.5 Hz, 1H), 6.10 (d, *J* = 1.7 Hz, 1H), 5.92 (s, 1H), 5.64 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 159.6, 153.3, 153.0, 143.7, 142.2, 126.7, 101.9, 95.8, 82.8, 80.3, 56.0, 55.8 ppm.

Compound 3va



Prepared according to the general procedure B on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile in 80% (0.082 g, 0.40 mmol) yield as a white solid was obtained.

R_f: 0.34 in 10% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (dd, *J* = 5.5, 1.6 Hz, 1H), 6.91 (dd, *J* = 5.5, 1.7 Hz, 1H), 6.40 (s, 1H), 5.83 (s, 1H), 5.62 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H) ppm.

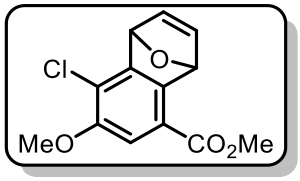
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 165.6, 161.7, 154.2, 143.9, 140.8, 119.0, 97.5, 82.2, 79.4, 53.9, 53.3 ppm.

FTIR: 2945, 2857, 1637, 1596, 1445, 1358, 993, 829, 710, 655, cm^{-1}

HRMS (ESI-Orbitrap) m/z: [M+H]+ Calcd for $C_{11}H_{12}NO_3$ 206.0812 found: 206.0809

Melting point: 72.1-74.8 °C

Compound 3wa



Prepared according to the general procedure B on a 0.4 mmol scale using furan (0.1454 mL, 2.0 mmol, 5 equiv.) as the arynophile in 61% (0.065 g, 0.24 mmol) yield as a white solid was obtained.

R_f = 0.33 in 20% EtOAc in Hexanes

^{1}H NMR (400 MHz, CDCl3) δ = 7.08 (br, 2H), 6.45 (s, 1H), 6.05 (s, 1H), 5.84 (s, 1H), 3.92 (s, 3H), 3.83 (s, 3H) ppm.

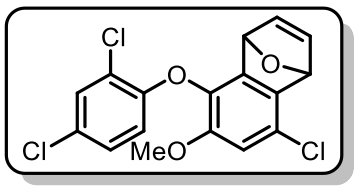
^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 165.1, 157.1, 155.8, 143.2, 142.3, 139.1, 129.3, 107.9, 83.9, 80.8, 56.8, 52.2 ppm.

FTIR: 2971, 1725, 1594, 1459, 1429, 1348, 1255, 1187, 1111, 1058, 1025, 892, 711 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}ClO_4$ 267.0419 found: 267.0409

Melting point: 96-99 °C

Compound 3xa



Prepared according to the general procedure A on a 1.0 mmol scale using furan (0.3636 mL, 5.0 mmol, 5 equiv.) as the arynophile. An isolated yield of 81% (0.300 g, 0.81 mmol) as a white solid was obtained.

R_f: 0.47 in 10% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 2.3 Hz, 1H), 7.14 – 7.04 (m, 2H), 6.84 (dd, *J* = 5.5, 1.4 Hz, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 6.47 (s, 1H), 5.82 (s, 1H), 5.57 (s, 1H), 3.74 (s, 3H) ppm.

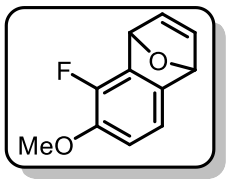
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 152.7, 150.9, 143.2, 142.7, 142.0, 139.9, 137.2, 130.5, 128.1, 127.9, 124.1, 122.2, 117.2, 109.3, 81.4, 80.9, 56.8 ppm.

FTIR: 2934, 1683, 1474, 1262, 1239, 862, 809, 744 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{17}H_{12}Cl_3O_3$ 368.9847 found: 368.9838

Melting point: 127.8-136.4 °C

Compound 3za



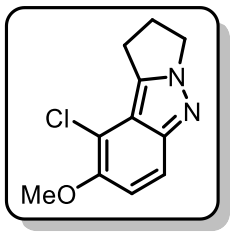
Prepared according to the general procedure B on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile in 96% (0.094 g, 0.48 mmol) yield as a white solid was obtained. Spectra data consistent with previous reports.[1]

^{1}H NMR (400 MHz, CDCl3) δ = 7.04-7.00 (m, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.5-6.46 (m, 1H), 5.95 (s, 1H), 5.68 (s, 1H), 3.83 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ = 146.6, (d, *J* = 248.7 Hz), 146.5 (d, *J* = 12.6 Hz), 143.4, 142.4 (d, *J* = 3.2 Hz), 141.8, 134.6 (d, *J* = 18.0 Hz), 115.5 (d, *J* = 3.7 Hz), 108.7, 82.3, 79.6, 56.6 ppm.

^{19}F{^{1}H} NMR (376 MHz, CDCl3) δ = -141.4 ppm.

Additional compound



Prepared according to the general procedure A on a 0.5 mmol scale using 5,6-dihydro-4H-pyrrolo[1,2-c][1,2,3]oxadiazol-2-ium-3-olate (0.3153 mg, 2.5 mmol, 5 equiv.) as the arynophile. An isolated yield of 29% (0.0328 g, 0.15 mmol) was obtained as a 1.3:1 mixture of regioisomers presenting as an orange solid.

R*f*: 0.28 in 50% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) **(Major isomer)** δ = 7.54 (d, *J* = 9.3 Hz, 1H), 7.12 (d, *J* = 9.3 Hz, 1H), 4.42 (t, *J* = 7.4 Hz, 2H), 3.94 (s, 3H), 3.38 (t, *J* = 7.3 Hz, 2H), 2.83 – 2.70 (m, 4H) (Overlap with minor isomer) ppm.

^{1}H NMR (400 MHz, $CDCl_3$) **(Minor isomer)** δ = 7.47 (d, *J* = 9.0 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 4.46 (t, *J* = 7.4 Hz, 2H), 3.98 (s, 3H), 3.19 (t, *J* = 7.3 Hz, 2H), 2.83 – 2.71 (m, 5H) (Overlap with minor isomer) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) **(Major isomer)** δ = 152.9, 148.8, 138.6, 119.2, 117.3, 117.0, 110.6, 58.4, 49.1, 26.0, 23.9 ppm.

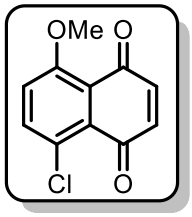
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) **(Minor isomer)** δ = 151.9, 150.4, 140.4, 116.6, 113.3, 111.2, 107.6, 57.6, 49.3, 25.8, 23.3 ppm.

FTIR: 2938, 1631, 1523, 1435, 1252, 1080, 797, 606 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}ClN_2O$ 223.0633 found: 223.0640

Melting point: 120.7-125.6 °C

Compound 4



Prepared according to the general procedure A on a 1.0 mmol scale using 2,5-bis-TBDMS furan (**2j**) (985.8 mg, 3 mmol, 3 equiv.). At the end of the formal dehydrogenation sequence the reaction was allowed to cool to room temperature before TFA (1 mL, 13 mmol, 26 equiv.) was added in one portion. The mixture was stirred for 5 minutes before quenching with water. The mixture was extracted with ethyl acetate (3 x 10 mL) and the combined organic layer was dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by silica flash column chromatography using 0-20% ethyl acetate in hexanes as eluent. An isolated yield of 60% (0.0665 g, 0.3 mmol) as yellow solid was obtained.

R_f: 0.09 in 20% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 9.1 Hz, 1H), 7.25 (d, *J* = 9.9 Hz, 1H), 6.91 – 6.78 (m, 2H), 4.00 (s, 3H) ppm.

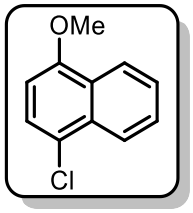
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 184.1, 183.8, 158.9, 139.1, 138.6, 137.7, 129.7, 126.0, 121.9, 118.7, 56.9 ppm.

FTIR: 3036, 1658, 1557, 1456, 1246, 1020, 831 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{11}H_8ClO_3$ 223.0156 found: 223.0156

Melting point: 144.5-147.7 °C

Compound 5

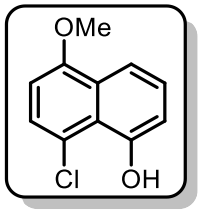


Prepared according to the general procedure A on a 0.5 mmol scale using furan (0.1818 mL, 2.5 mmol, 5 equiv.) as the arynophile. Resulting compound **3aa** was transferred to a 4 mL vial along with acetonitrile (0.5M) and sodium iodide (374.7 mg, 2.5 mmol, 5 equiv.). TMS-Cl (0.3173 mL, 2.5 mmol, 5 equiv.) was added to the mixture dropwise with stirring at room temperature and was allowed to stir for 1 hour. The reaction was quenched with 10% (w/v) aqueous sodium thiosulfate, extracted with ethyl acetate (3 x 5 mL) and the combined organic layer was dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by silica flash column chromatography using 0-10% ethyl acetate in hexanes as eluent. An isolated yield of 43% (0.0424 g, 0.22 mmol) as a clear colorless oil was obtained. Spectra data consistent with previous reports.[22]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 154.7, 131.4, 127.6, 126.7, 126.1, 125.9, 124.4, 123.3, 122.5, 103.9, 55.8 ppm.

Compound 6



Prepared according to the general procedure A on a 1 mmol scale using furan (0.3636 mL, 5.0 mmol, 5 equiv.) as the arynophile. At the end of the formal dehydrogenation sequence concentrated aqueous HCl (1 mL) was added and the reaction continued to be heated at 65°C for 30 minutes. The reaction was allowed to cool to room temperature and was then quenched with saturated aqueous sodium bicarbonate. The mixture was extracted with ethyl acetate (3 x 10 mL) and the combined organic layer was dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by silica flash column chromatography using 0-10% ethyl acetate in hexanes as eluent. An isolated yield of 66% (0.1377 g, 0.66 mmol) as yellow solid was obtained.

R_f: 0.39 in 5% EtOAc in hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 1H), 7.87 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.40 (t, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.08 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H) ppm.

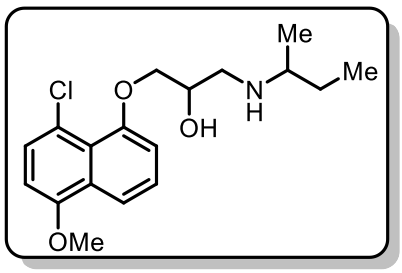
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 155.2, 152.8, 128.9, 127.2, 127.1, 120.2, 118.4, 114.8, 114.0, 103.8, 55.9 ppm.

FTIR: 3498, 2998, 1597, 1513, 1381, 1232, 1035, 800, 744 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}ClO_2$ 209.0364 found: 209.0368

Melting point: 64.2-69.4 °C

Compound 7



Prepared according to the general procedure A on a 1 mmol scale using furan (0.3636 mL, 5.0 mmol, 5 equiv.) as the arynophile. At the end of the formal dehydrogenation sequence concentrated aqueous HCl (1 mL) was added and the reaction continued to be heated at 65°C for 30 minutes. KOH flakes (280.5 mg, 5 mmol, 5 equiv.) were added to the reaction mixture followed by DMSO (4 mL) and epichlorohydrin (0.3995 mL, 5.1 mmol, 5.1 equiv.), this mixture was then stirred at room temperature for 16 hours. Sec-butylamine (1.010 mL, 10 mmol, 10 equiv.) was then added to the reaction mixture and stirred at room temperature for another 3 hours. The reaction was quenched with brine (10 mL) extracted with EtOAc (3 x 15 mL) and the combined organic layer was dried over sodium sulfate and the solvent removed under reduced pressure. The residue was purified by silica flash column chromatography using 1 : 0 : 0.3 ethyl acetate : methanol : ammonium hydroxide to 1 : 1.5 : 0.3 ethyl acetate : methanol : ammonium hydroxide as eluent. The product containing fractions were combined and the solvent was removed under reduced pressure. The resulting residue was dissolved in a

minimal amount of DCM and the product was crystallized out with n-heptane to obtain the product in a 34% yield (0.1149 g, 0.34 mmol) as a white solid.

R_f: 0.54 in 1 : 1.5 : 0.3 EtOAc : MeOH : NH_4OH

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.85 (m, 1H), 7.44 – 7.33 (m, 2H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 4.25 (s, 1H), 4.12 (s, 2H), 3.97 (s, 3H), 3.06 – 2.83 (m, 2H), 2.77 – 2.56 (m, 4H), 1.65 – 1.49 (m, 1H), 1.38 (dt, *J* = 13.4, 6.6 Hz, 1H), 1.09 (d, *J* = 5.6 Hz, 3H), 0.92 (t, *J* = 6.9 Hz, 3H) ppm.

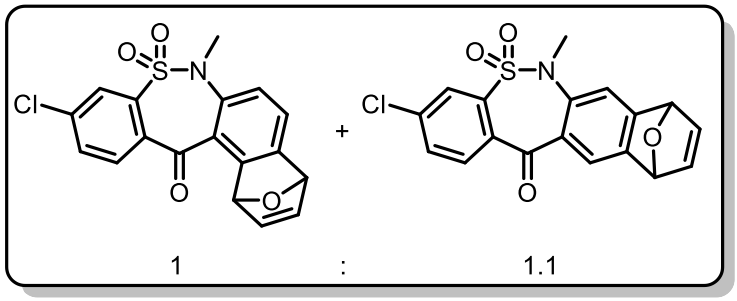
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 154.9, 154.4, 128.9, 128.5, 126.2, 123.1, 120.6, 115.4, 108.7, 104.6, 71.7, 69.0, 55.9, 55.1, 49.5, 29.4, 19.9, 10.4 ppm.

FTIR: 2960, 2931, 2359, 1594, 1510, 1370, 1350, 1265, 1246, 1064, 801, 745, 645 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}ClNO_3$ 338.1517 found: 338.1507

Melting point: 93.8 – 96.5 °C

Compound 8



Prepared according to the general procedure B on a 0.46 mmol scale using furan (0.167 mL, 2.3 mmol, 5 equiv.) as the arynophile. An isolated yield of 52% (0.089 g, 0.239 mmol) as a yellow solid was obtained as a 1:1.1 mixture of regioisomers.

R_f: 0.2 in 30% EtOAc in hexanes

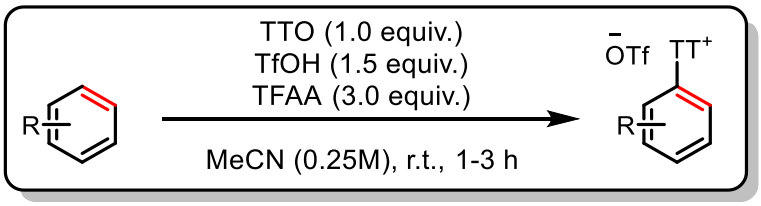
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (s, 1H), 8.01 – 7.89 (m, 4H), 7.68 (t, J = 9.8 Hz, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.29 – 7.20 (m, 3H), 7.12 – 7.04 (m, 2H), 7.04 – 6.95 (m, 2H), 6.20 (s, 1H), 5.79 (s, 1H), 5.77 (s, 1H), 5.75 (s, 1H), 3.29 (s, 3H), 3.26 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 189.0, 156.8, 146.8, 143.6, 143.6, 143.1, 141.6, 140.2, 138.9, 138.2, 134.4, 133.6, 133.44, 133.42, 128.0, 126.3, 125.7, 124.6, 122.6, 122.1, 117.5, 84.6, 82.1, 82.1, 81.6, 40.2, 39.2, 29.8 ppm.

*note – 8 resonances in the ^{13}C spectrum could not be assigned due to peak overlap and the presence of the regioisomer

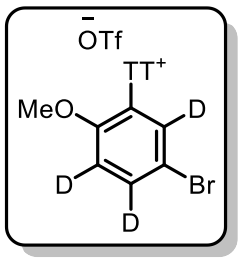
HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}ClNO_4S$ 374.0248 found: 374.0336

General procedure C:



Aryl thianthrenium triflates were prepared by known literature procedure.[23] Thianthrene S-oxide (1 equiv.), arene (1 equiv.) and acetonitrile (0.25M) were added to an appropriately sized vial, equipped with a magnetic stir bar held at 0°C. Trifluoromethanesulfonic acid (1.5 equiv.) was added in one portion, followed by one portion of trifluoroacetic anhydride (3 equiv.). The vial was capped and stirred vigorously at room temperature for 1-3 hours. Methanol was then added until the reactions dark color dissipated. The mixture was then concentrated under reduced pressure to afford an oily residue. This residue was then triturated with excess diethyl ether until precipitation ceased. The precipitate was isolated by vacuum filtration and washed by slurry filtration with diethyl ether (3 × 10 mL) to obtain thianthrenium salts in pure form.

Compound 1b-TT-d_3



Prepared according to the general procedure C on a 1.5 mmol scale using 4-bromoanisole-d_4 (0.2866 g, 1.5 mmol, 1 equiv.). An isolated yield of 79% (0.656 g, 1.19 mmol) as a white solid was obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.42 (d, *J* = 7.9 Hz, 2H), 8.09 (d, *J* = 7.9 Hz, 2H), 7.91 (t, *J* = 7.6 Hz, 2H), 7.83 (t, *J* = 7.7 Hz, 2H), 3.95 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ = 156.6, 136.1, 135.9, 134.7, 134.4, 130.3, 129.5, 128.8, 128.3, 120.71 (q, J = 322.3 Hz), 117.2, 112.0, 111.8, 57.4 ppm.

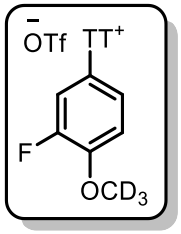
^{19}F{^{1}H} NMR (376 MHz, DMSO-d6) δ = -77.7 ppm.

FTIR: 3081, 2288, 1561, 1450, 1380, 1257, 1155, 1028, 768, 635, 465 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{11}D_3FBrOS_2$ 403.9852 found: 403.9846

Melting point: 204.0-210.7 °C

Compound 1p-TT-*d*$_3$



Prepared according to the general procedure C on a 0.4 mmol scale using 2-fluoroanisole-d_3 (0.0517 g, 0.4 mmol, 1 equiv.). An isolated yield of 89% (0.118 g, 0.35 mmol) as an off-white solid was obtained with 93% deuterium at the specific position.

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.51 (d, *J* = 7.84 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 2H), 7.92 (dt, J_1 = 7.6, J_2 = 1.1 Hz, 2H), 7.84 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 8.8 Hz, 1H), 7.30 (dd, J_1 = 10.8, J_2 = 2.5 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 3.87 (s, 0.2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ = 151.8 (d, *J* = 250.9 Hz), 151.4 (d, *J* = 10.1 Hz), 135.7, 135.5, 135.2, 130.4 (d, *J* = 57.8 Hz), 126.8 (d, *J* = 3.6 Hz), 121.1 (q, *J* = 322/3 Hz), 120.1, 116.7 (d, *J* = 22.7 Hz), 115.7 (d, *J* = 1.5 Hz), 115.2 (d, *J* = 6.9 Hz), 57.1 ppm.

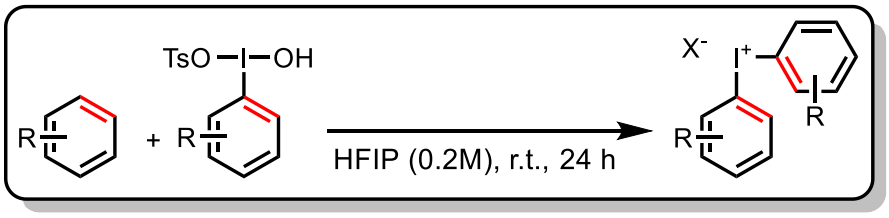
^{19}F{^{1}H} NMR (376 MHz, DMSO-d6) δ = -77.7, -130.5

FTIR: 3081, 1599, 1567, 1505, 1257, 1221, 1156, 1028, 981, 864, 765, 634 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{19}H_{11}D_3FOS_2$ 344.0653 found: 344.0649

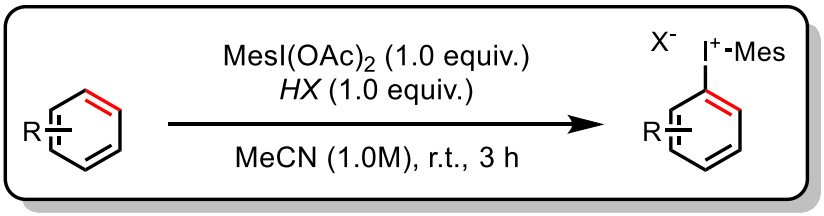
Melting point: 167-171 °C

General procedure D:



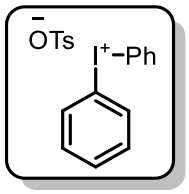
HFIP (5ml, 0.2M) was added to a 20ml screw cap vial followed by simple arene (1-3 equiv). Hydroxy(tosyloxy)iodobenzene (HTIB) (1 equiv,) was then added to this solution with constant stirring. The vial was sealed, and the reaction was allowed to progress at room temperature for 24 hours. Upon completion, the solution was concentrated under reduced pressure and the crude residue was triturated with diethyl ether (ca. 15ml). The precipitate was isolated by vacuum filtration giving analytically pure diaryliodonium salt.

General procedure E:



An appropriately sized reaction vessel was charged with iodomesitylene diacetate (1 equiv.), desired arene (1 equiv.), acetonitrile (1.0M) and a magnetic stir bar. Required acid (1 equiv.) was added to the stirring reaction mixture held at room temperature for 3 hours. The iodonium salt was triturated from the crude reaction mixture with excess diethyl ether and vacuum filtered.

Compound 1l-IPh

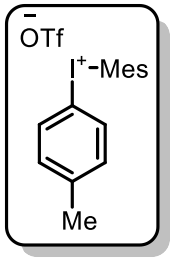


Prepared according to the general procedure D on a 1 mmol scale with HTIB. An isolated yield of 90% (0.405 g, 0.90 mmol) as an off-white solid was obtained. Spectra data consistent with previous reports.[24]

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.26 (d, *J* = 7.5 Hz, 4H), 7.67 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 4H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 2.29 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ = 145.7, 138.5, 135.7, 132.3, 132.0, 128.7, 126.1, 117.2, 21.3 ppm.

Compound 1m-IMes



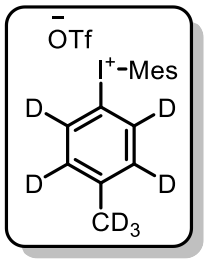
Prepared according to the general procedure E on a 1 mmol scale using toluene (0.1063 mL, 1 mmol, 1 eq). An isolated yield of 94% (0.459 g, 0.95 mmol) as a white solid was obtained. Spectra data consistent with previous reports.[5]

^{1}H NMR (400 MHz, DMSO-d6) δ = 7.88 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.21 (s, 2H), 2.33 (s, 6H), 2.26 (s, 6H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6) δ = 143.5, 142.7, 141.9, 134.9, 132.9, 130.2, 123.1, 111.2, 26.7, 21.2, 20.9 ppm.

$^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d6) δ = -77.8 ppm.

Compound 1m-IMes-*d_7*



Prepared according to the general procedure E on a 3 mmol scale using toluene-d_8 (0.1062 mL, 1 mmol, 1 equiv.). An isolated yield of 65% (0.321 g, 1.95 mmol) as white solid was obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 7.20 (s, 2H), 2.60 (s, 6H), 2,28 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6) δ = 143.4, 142.4, 141.9, 134.8-134.3 (m), 132.7-132.5 (m), 130.9-130.2 (m), 123.1, 121.2 (q, *J* = 322.2 Hz), 111.0, 26.7, 20.9, 20.9 - 20.9 (m) ppm.

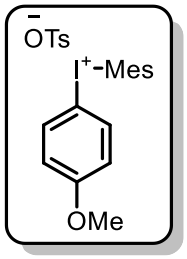
$^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d6) δ = -77.7 ppm.

FTIR: 2919, 1589, 1449, 1375, 1243, 1156, 1023, 656, 573, 443 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{16}H_{11}D_7I$ 344.0887 found: 344.0882

Melting point: 193.0-196.0 °C decomp.

Compound 1n-IMes

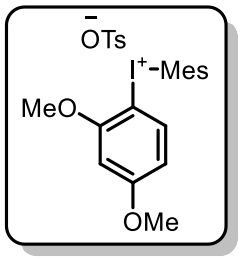


Prepared according to the general procedure E on a 1 mmol scale using anisole (0.1087 mL, 1 mmol, 1 equiv.) with the following modification: TsOH H_2O (0.1902g, 1 mmol, 1 equiv.) was used in place of trifluoromethanesulfonic acid. An isolated yield of 87% (0.4536 g, 0.87 mmol) as a white solid was obtained. Spectra data consistent with previous reports.[25]

^{1}H NMR (400 MHz, DMSO-d6) δ = 7.91 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 7.65 Hz, 2H), 7.18 (s, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.60 (s, 3H), 2.28 (s, 6H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6) δ = 162.1, 145.9, 143.2, 141.8, 138.2, 137.0, 130.1, 128.5, 126.0, 123.7, 117.9, 104.0, 56.1, 26.7, 21.3, 20.9 ppm.

Compound 1o-IMes

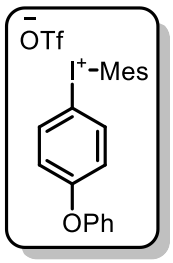


Prepared according to the general procedure E on a 2 mmol scale using 1,3-dimethoxybenzene (0.2619 mL, 2 mmol, 1 equiv.) with the following modification: *p*-toluenesulfonic acid (0.3804 g, 2 mmol, 1 equiv.) used in place of trifluoromethanesulfonic acid. An isolated yield of 82% (0.964 g, 1.74 mmol) as white solid was obtained. Spectra data consistent with previous reports.[26]

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.07 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.14 (s, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.78 (d, *J* = 2.2 Hz, 1H), 6.67 (dd, J_1 = 8.9 Hz, J_2 = 2.3 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.60 (s, 6H), 2.29 (s, 3H), 2.27 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6) δ = 164.8, 158.9, 146.0, 142.8, 142.1, 139.2, 138.1, 129.9, 128.5, 125.9, 122.6, 109.3, 100.3, 93.9, 57.3, 56.4, 26.3, 21.2, 20.9 ppm.

Compound 1p-IMes



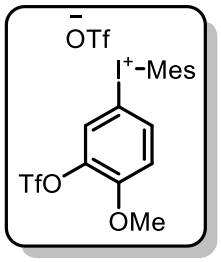
Prepared according to the general procedure E on a 1 mmol scale using diphenyl ether (0.1702 g, 1 mmol, 1 equiv.). An isolated yield of 87% (0.487 g, 0.87 mmol) as white solid was obtained. Spectra data consistent with previous reports.[27]

^{1}H NMR (400 MHz, DMSO-d6) δ = 7.99 (d, *J* = 8.5 Hz, 2H), 7.47-7.43 (m, 2H), 7.27-7.22 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 2.62 (s, 6H), 2.30 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6) δ = 160.5, 155.0, 143.5, 141.9, 137.4, 130.9, 130.2, 125.5, 123.4, 120.9, 121.2, (q, *J* = 322.4 Hz), 120.5, 106.4, 26.7, 21.0 ppm.

$^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d6) δ = -77.7 ppm.

Compound 1q-IMes



Prepared according to the general procedure E on a 0.78 mmol scale using 2-methoxyphenyl trifluoromethanesulfonate (0.1998 g, 0.78 mmol, 1 equiv.). An isolated yield of 88% (0.444 g, 0.68 mmol) as white solid was obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.29 (s, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.41 (d, *J* = 9.0 Hz, 1H), 7.22 (s, 2H), 3.94 (s, 3H), 2.61 (s, 6H), 2.30 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6) δ = 154.0, 143.7, 142.0, 138.5, 137.2, 130.2, 129.6, 123.8, 121.1 (q, *J* = 322.2 Hz), 118.6 (q, *J* = 320.6 Hz), 117.5, 102.7, 57.6, 26.7, 20.9 ppm.

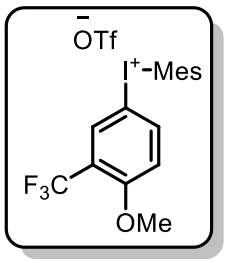
$^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d6) δ = -77.5, -77.8 ppm.

FTIR: 2969, 2939, 2865, 1589, 1492, 1425, 1242, 1210, 1165, 1055, 1018, 896, 800, 633 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{17}H_{17}F_3IO_4S$ 500.9839 found: 500.9835

Melting point: 195-198 °C

Compound 1r-IMes



Prepared according to the general procedure E on a 1 mmol scale using 1-methoxy-2-(trifluoromethyl)benzene (0.1761 g, 1 mmol, 1 equiv.). An isolated yield of 92% (0.523 g, 0.92 mmol) as white solid was obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.28 (s, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.22 (s, 2H), 3.93 (s, 3H), 2.61 (s, 6H), 2.30 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6) δ = 159.8 (m), 143.7, 142.0, 141.1, 143.5 (m), 130.3, 123.5, 122.9 (q, *J* = 273.4 Hz), 121.2 (q, *J* = 322.0 Hz), 119.6 (m), 116.9, 103.1, 57.3, 26.7, 20.9 ppm.

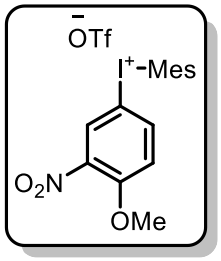
$^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d6) δ = -61.6, -77.8 ppm.

FTIR: 1579, 1573, 1492, 1320, 1412, 1220, 1166, 1082, 1020, 837, 628 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{17}H_{17}F_3IO$ 421.0271 found: 421.0262

Melting point: 246-247 °C

Compound 1s-IMes



Prepared according to the general procedure E on a 1 mmol scale using 2-nitroanisole (0.1221 mL, 1 mmol, 1 equiv.). An isolated yield of 54% (0.293 g, 0.54 mmol) as off-white solid was obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.63 (s, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.23 (s, 2H), 3.97 (s, 3H), 2.65 (s, 6H), 2.30 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6) δ = 154.5, 143.7, 142.1, 140.7, 140.6, 131.5, 130.3, 123.6, 121.2 (q, *J* =322.8 Hz), 118.1, 102.6, 57.8, 26.8, 21.0 ppm.

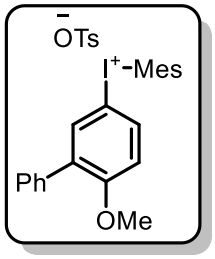
$^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d6) δ = -77.8 ppm.

FTIR: 3103, 2979, 2865, 1594, 1568, 1458, 1348, 1244, 1165, 1020, 864, 833, 630 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{16}H_{17}INO_3$ 398.0248 found: 398.0243

Melting point: 199-201 °C

Compound 1t-IMes



Prepared according to the general procedure E on a 1 mmol scale using 2-methoxy-1,1'-biphenyl (0.1842 g, 1 mmol, 1 equiv.) with the following modification: Hydroxy(tosyloxy)iodomesitylene (HTIM) (0.434g, 1 mmol, 1 equiv.) was used in place of iodomesitylene diacetate and no acid was added. An isolated yield of 66% (0.395 g, 0.66 mmol) as white solid was obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 7.92-7.90 (m, 2H), 7.47-7.40 (m, 7H), 7.21-7.19 (m, 3H), 7.10 (d, *J* = 7.7 Hz, 2H), 3.79 (s, 3H), 2.63 (s, 6H), 2.28 (s, 3H) ppm.

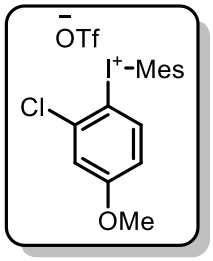
^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ = 159.0, 145.7, 143.3, 141.9, 138.3, 136.6, 136.3, 136.1, 133.3, 130.1, 129.6, 128.8, 128.6, 128.3, 125.9, 123.5, 115.6, 104.1, 56.5, 26.8, 21.2, 20.9 ppm.

FTIR: 2920, 2843, 1578, 1479, 1393, 1271, 1224, 1164, 1118, 1054, 1031, 824, 677, 566 cm^{-1}

HRMS (ESI-Orbitrap) m/z: [M-OTs]$^{+}$ Calcd for $C_{22}H_{22}IO$ 429.0710 found: 429.0713

Melting point: 214 – 216 °C

Compound 1u-IMes



Prepared according to the general procedure E on a 1 mmol scale using 3-chloroanisole (0.1225 mL, 1 mmol, 1 equiv.). An isolated yield of 89% (0.479 g, 0.89 mmol) as white solid was obtained containing a 1:0.12 mixture of isomers. When this reaction is conducted at -15 °C a ratio of 1:0.24 is obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.19 (d, *J* = 9.0 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.20 (s, 2H), 7.03 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H), 3.84 (s, 3H), 2.62 (s, 6H), 2.29 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ = 163.5, 143.5, 142.2, 140.6, 137.9, 130.3, 123.2, 116.8, 116.7, 105.9, 56.8, 26.5, 20.9 ppm.

*Note- the triflate ion ^{13}C resonance could not be unambiguously assigned due to overlap with minor isomer peaks

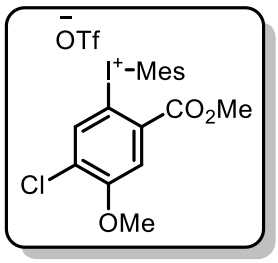
^{19}F{^{1}H} NMR (376 MHz, DMSO-d6) δ = -77.73 ppm.

FTIR: 2967, 1577, 1562, 1469, 1272, 1242, 1226, 1171, 1021, 852, 632, 573, 540 cm^{-1}

HRMS (ESI-Orbitrap) m/z: [M-OTf]$^{+}$ Calcd for $C_{16}H_{17}ClIO$ 387.0007 found: 387.0003

Melting point: 159 -161 °C

Compound 1w-IMes



Prepared according to the general procedure E on a 1 mmol scale using methyl 4-chloro-3-methoxybenzoate (0.2006 g, 1 mmol, 1 equiv.). An isolated yield of 85% (0.504 g, 0.85 mmol) as a white solid was obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.56 (s, 1H), 7.61 (s, 1H), 7.20 (s, 2H), 3.92 (s, 3H), 3.84 (s, 3H), 2.63 (s, 6H), 2.29 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ = 164.2, 161.8, 143.6, 142.3, 141.7, 141.2, 130.4, 123.0, 121.2 (q, *J* = 322.4), 115.8, 105.6, 57.6, 53.1, 26.5, 20.9 ppm.

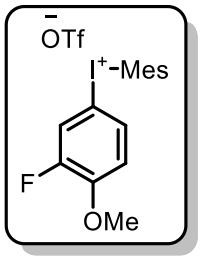
^{19}F{^{1}H} NMR (376 MHz, DMSO-d6) δ = -77.7 ppm.

FTIR: 3092, 2966, 2864, 1742, 1730, 1574, 1550, 1462, 1436, 1221, 1184, 1017, 631 cm^{-1}

HRMS (ESI-Orbitrap) m/z: [M-OTf]$^{+}$ Calcd for $C_{18}H_{19}ClIO_3$ 445.0062 found: 445.0073

Melting point: 168.2-173.9 °C

Compound 1z-IMes



Prepared according to the general procedure E on a 1 mmol scale using 2-fluoroanisole (0.1122 mL, 1 mmol, 1 equiv). An isolated yield of 73% (0.380 g, 0.73 mmol) as white powder was obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.02 (dd, J_1 = 10.3 Hz, J_2 = 1.7 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.30-7.26 (m, 1H), 7.21 (s, 2H), 3.88 (s, 3H), 2.61 (s, 6H), 2.30 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ = 152.0 (d, *J* = 251.6 Hz), 150.8 (d, *J* = 9.9 Hz), 143.6, 141.9, 132.8 (d, *J* = 4.2 Hz), 130.2, 123.6, 122.8 (d, *J* = 21.3 Hz), 121.1 (q, *J* = 322.1 Hz), 117.0, 102.0 (d, *J* = 6.7 Hz), 56.8, 26.7, 20.9 ppm.

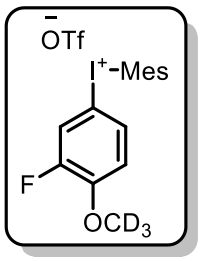
^{19}F{^{1}H} NMR (376 MHz, DMSO-d6) δ = -77.7, -130.18 ppm.

FTIR: 2985, 1594, 1582, 1500, 1444, 1313, 1268, 1243, 1159, 1021, 852, 821, 759, 631, 570, 515 cm^{-1}

HRMS (ESI-Orbitrap) m/z: [M-OTf]$^{+}$ Calcd for $C_{16}H_{17}FIO$ 371.0303 found: 371.0297

Melting point: 211-213 °C

Compound 1z-IMes-*d*$_3$



Prepared according to the general procedure E on a 0.5 mmol scale using 2-fluoroanisole-d_3 (0.0646 g, 0.5 mmol, 1 equiv). An isolated yield of 57% (0.118 g, 0.29 mmol) as off-white solid was obtained.

^{1}H NMR (400 MHz, DMSO-d6) δ = 8.02 (dd, J_1 = 10.2 Hz, J_2 = 1.8 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.27 (t, J = 8.8 Hz), 7.21 (s, 2H), 3.88 (s, 0.2H), 2.61 (s, 6H), 2.29 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, DMSO-d6) δ = 152.0 (d, J = 252.4 Hz), 150.8 (d, J = 11.7 Hz), 143.5, 141.9, 132.8 (d, J = 3.7 Hz), 130.2, 123.6, 122.8 (d, J = 21.4 Hz), 117.0 (d, J = 2.4 Hz), 102.0 (d, J = 6.8 Hz, 26.7, 20.9 ppm.

*Note- triflate ion and -C of the O-CD_3 group are not well enough resolved to unambiguously assign

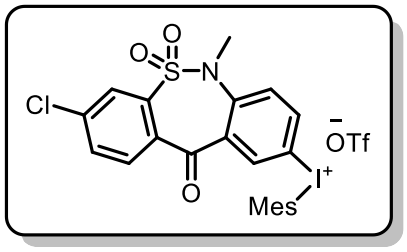
^{19}F{^{1}H} NMR (376 MHz, DMSO-d6) δ = -77.7, -130.18 ppm.

FTIR: 3081, 1599, 1567, 1505, 1450, 1323, 1257, 1221, 1156, 1028, 981, 864, 765, 634, 573, 515 cm^{-1}

HRMS (ESI-Orbitrap) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{16}H_{14}D_3FIO$ 374.0491 found: 374.0496

Melting point: 208-211 °C

Compound SI 1



Prepared according to the general procedure E on a 2 mmol scale using 3-chloro-6-methyldibenzo[c,f][1,2]thiazepin-11(6H)-one 5,5-dioxide (0.615 g, 2 mmol, 1 equiv.). An isolated crude yield of 23% (0.322 g, 0.46 mmol) as beige solid was obtained which was used without further purification.

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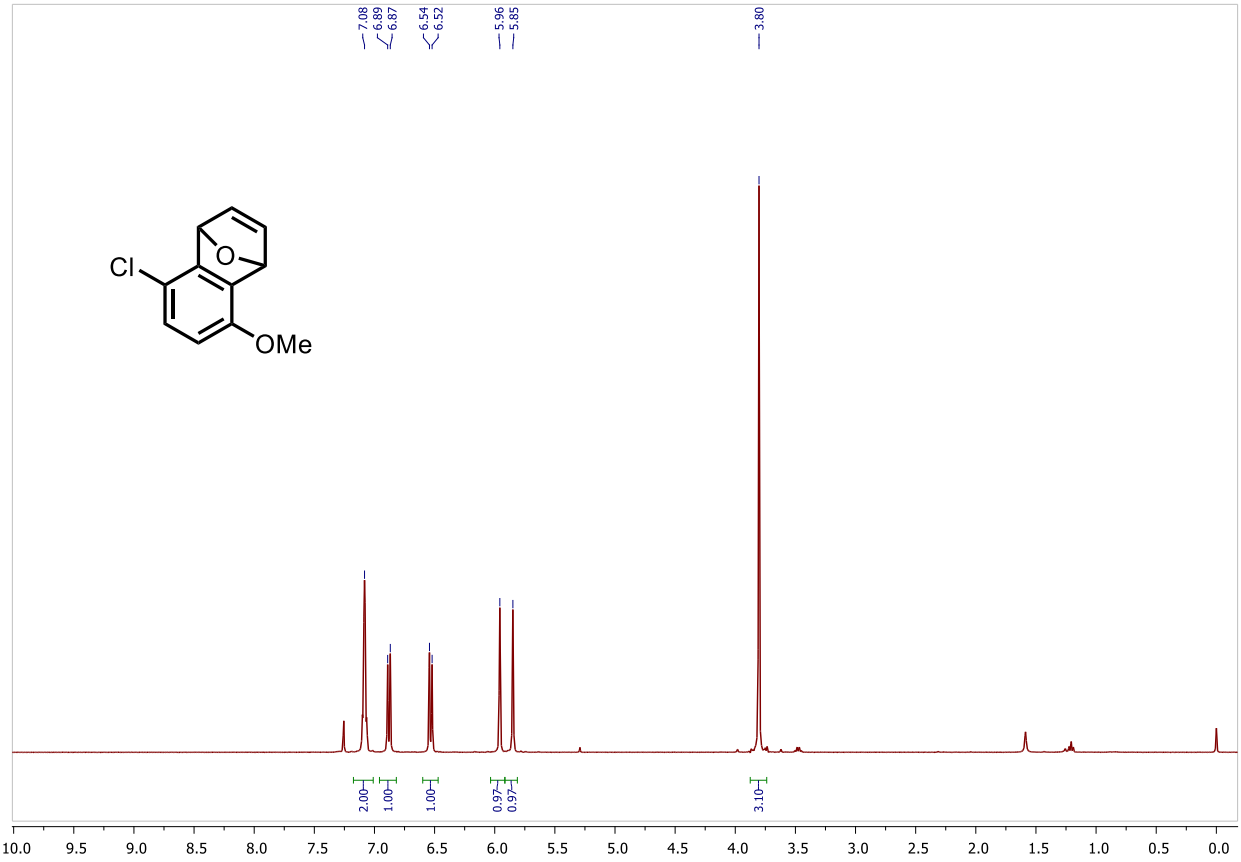
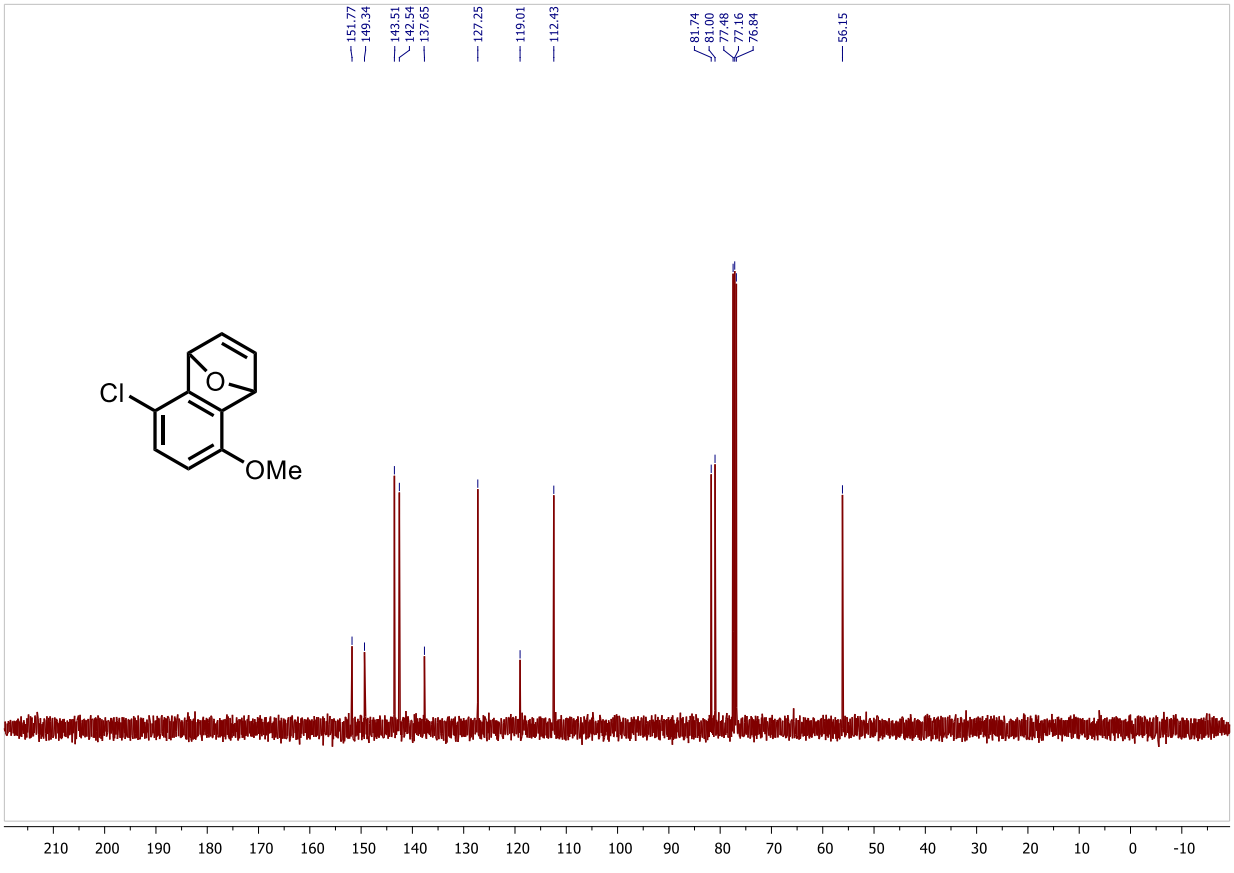
^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR Spectra:

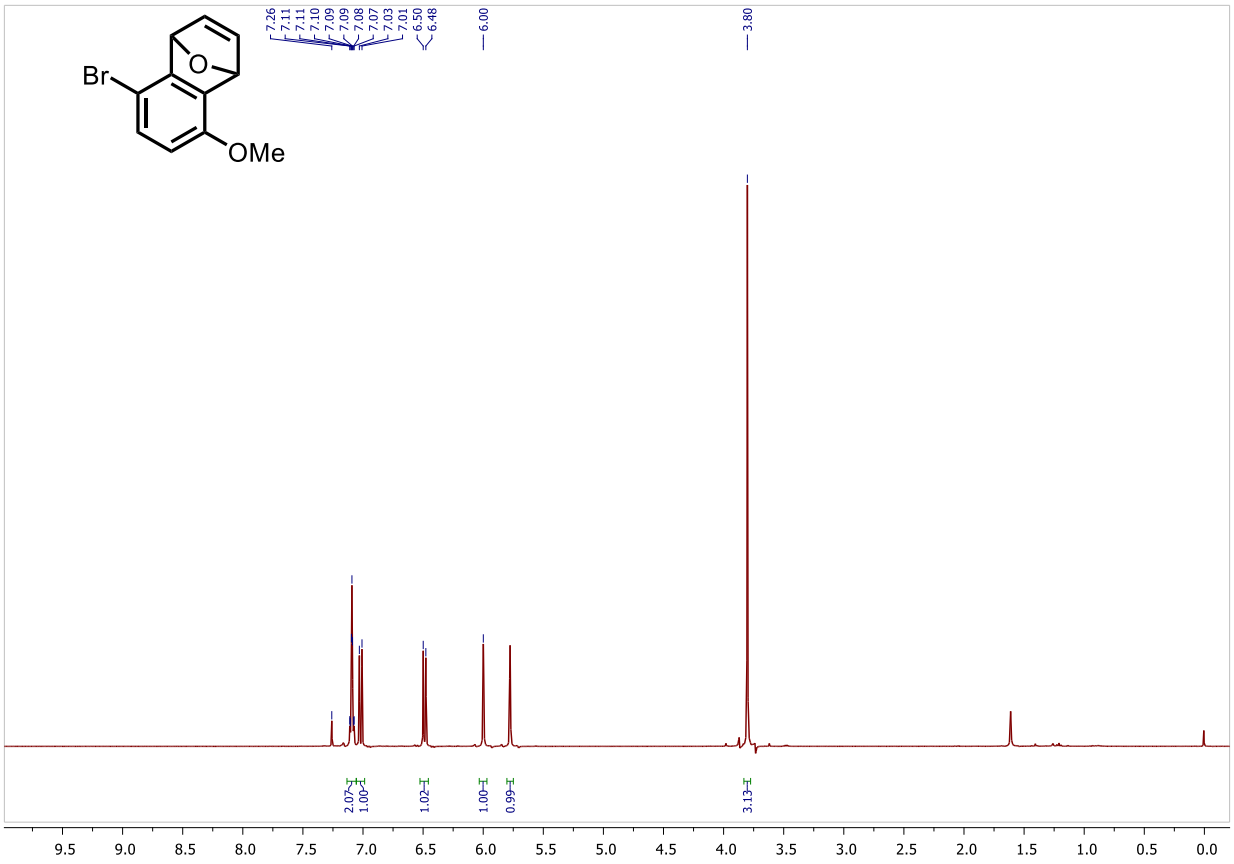
^{1}H NMR spectrum of 3aa in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



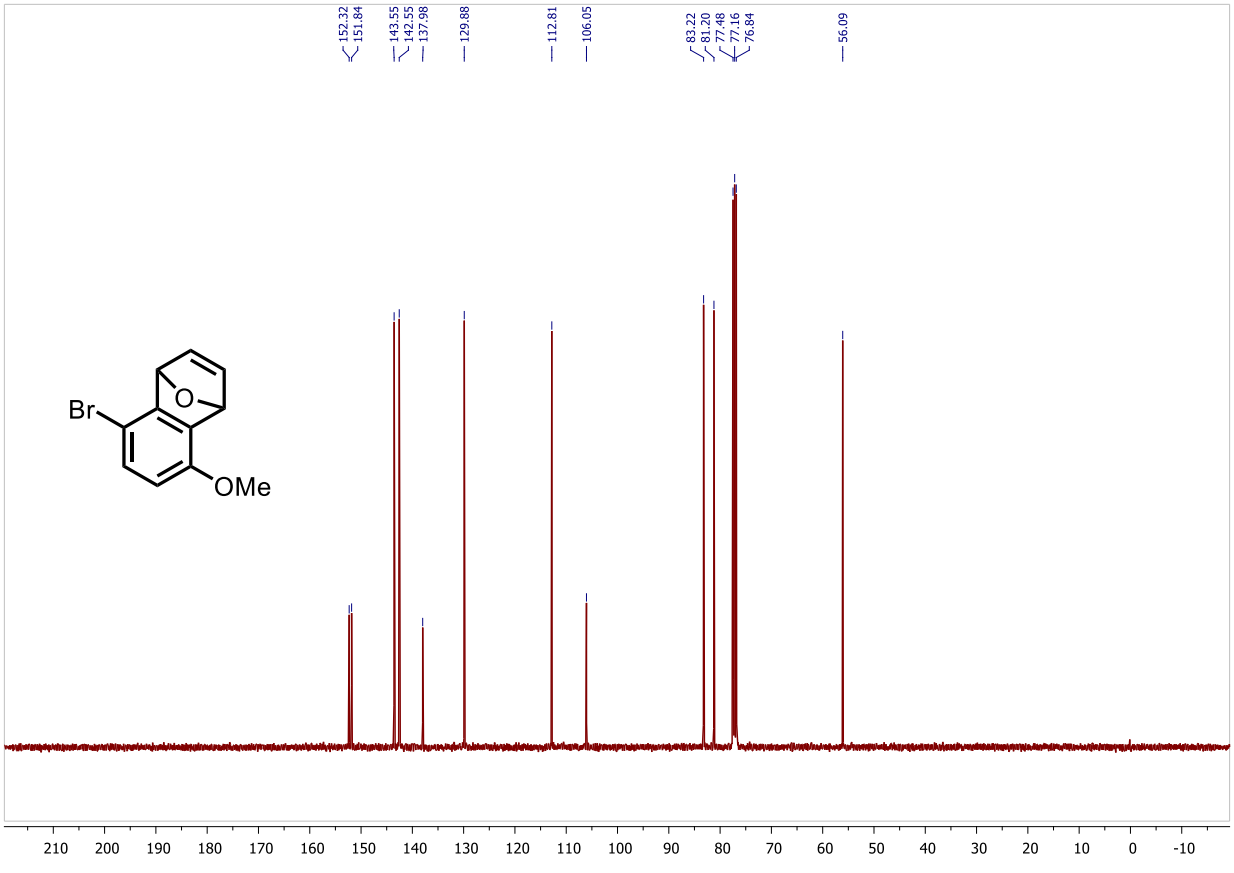
^{13}C{^{1}H} NMR spectrum of 3aa in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



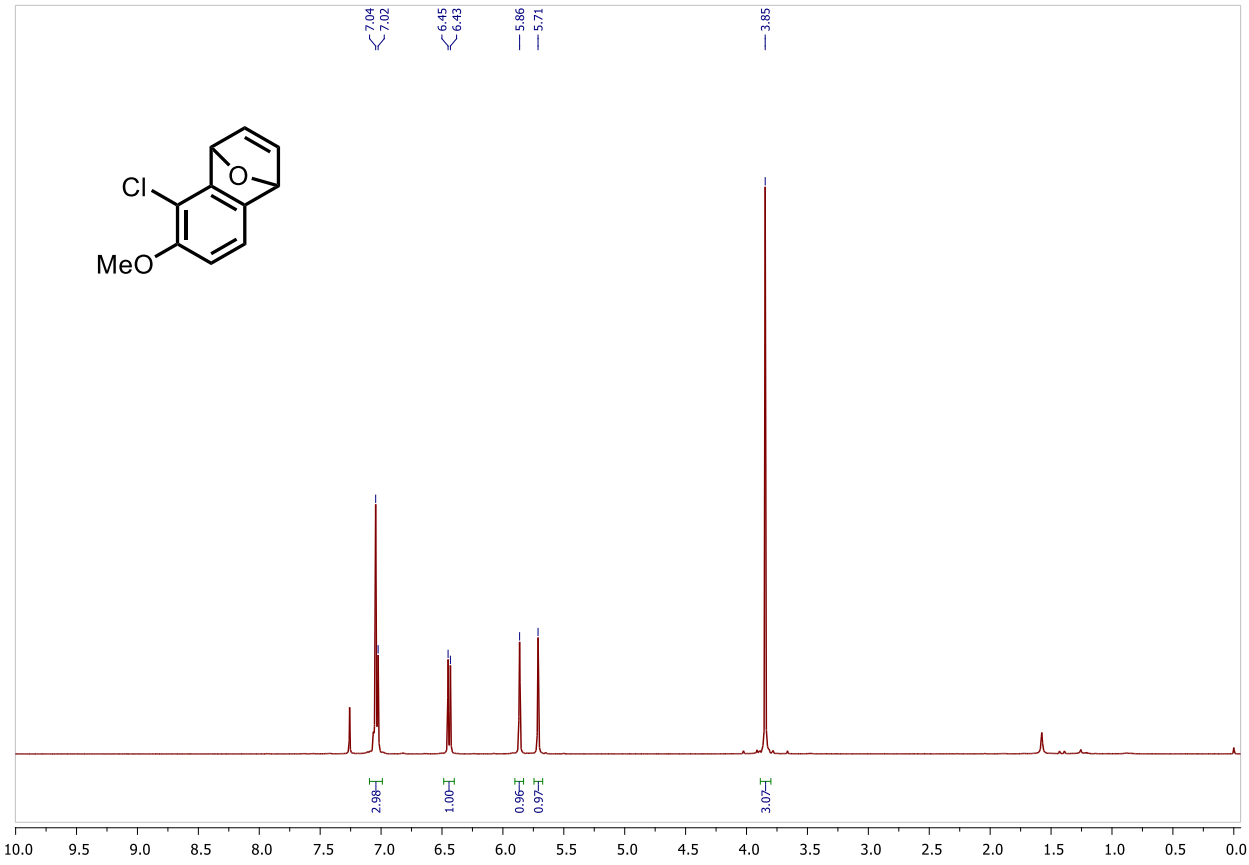
^{1}H NMR spectrum of 3ba in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



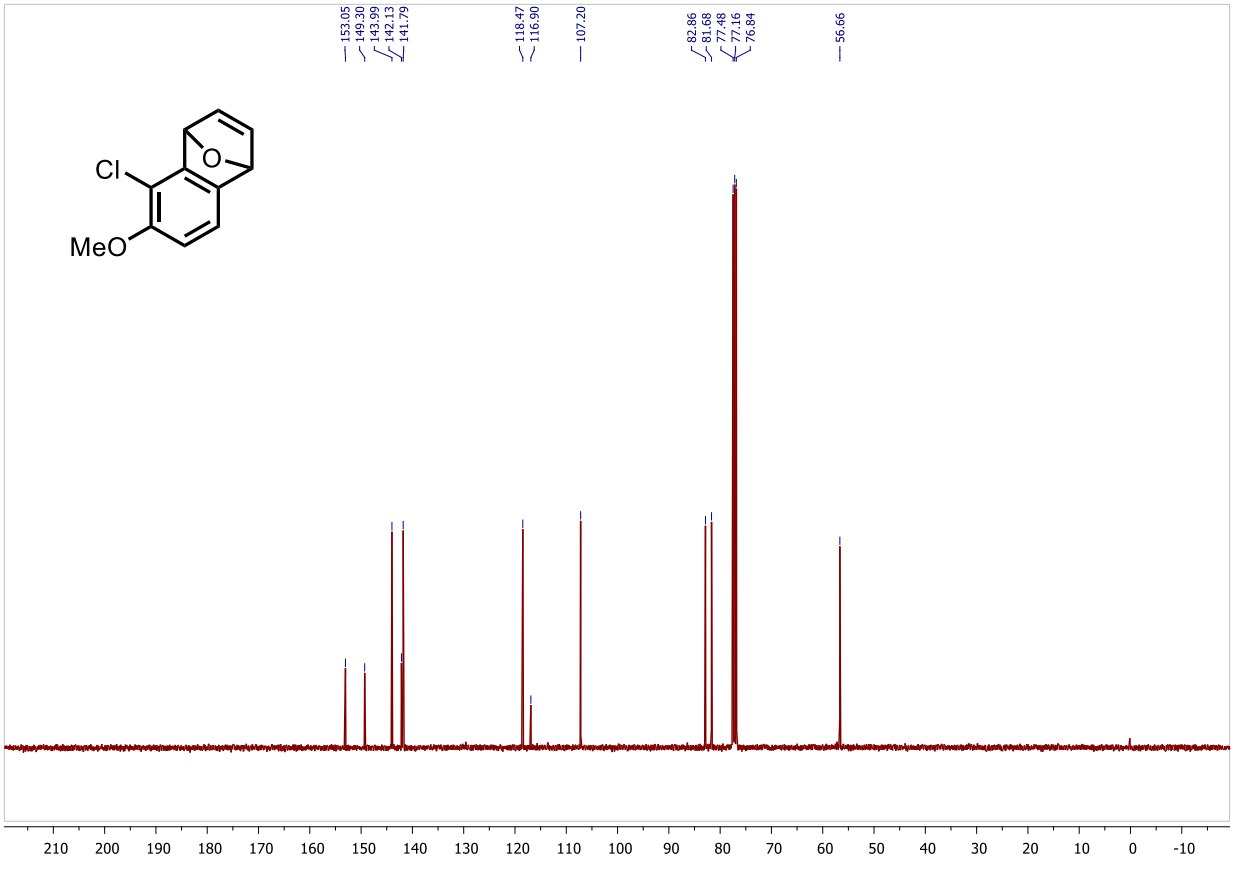
^{13}C{^{1}H} NMR spectrum of 3ba in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



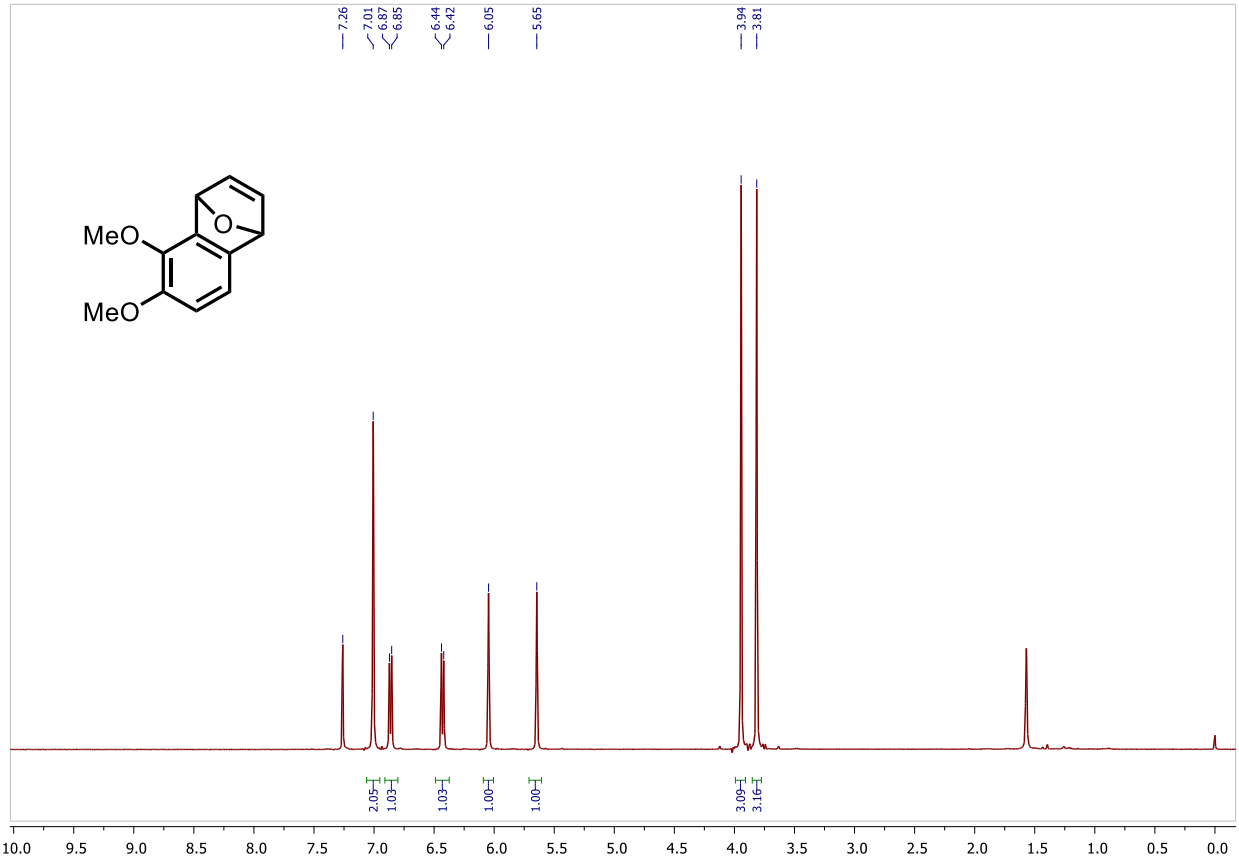
^{1}H NMR spectrum of 3ca in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



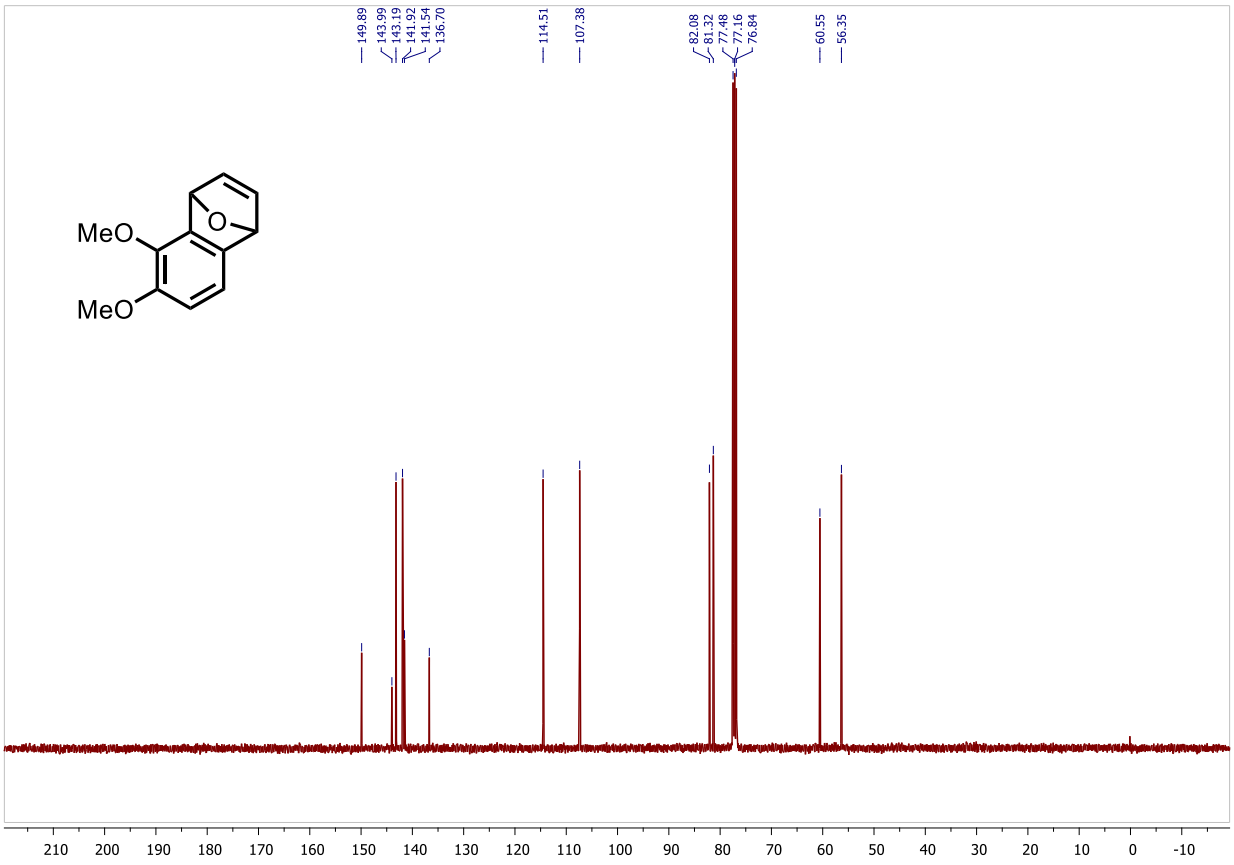
^{13}C{^{1}H} NMR spectrum of 3ca in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



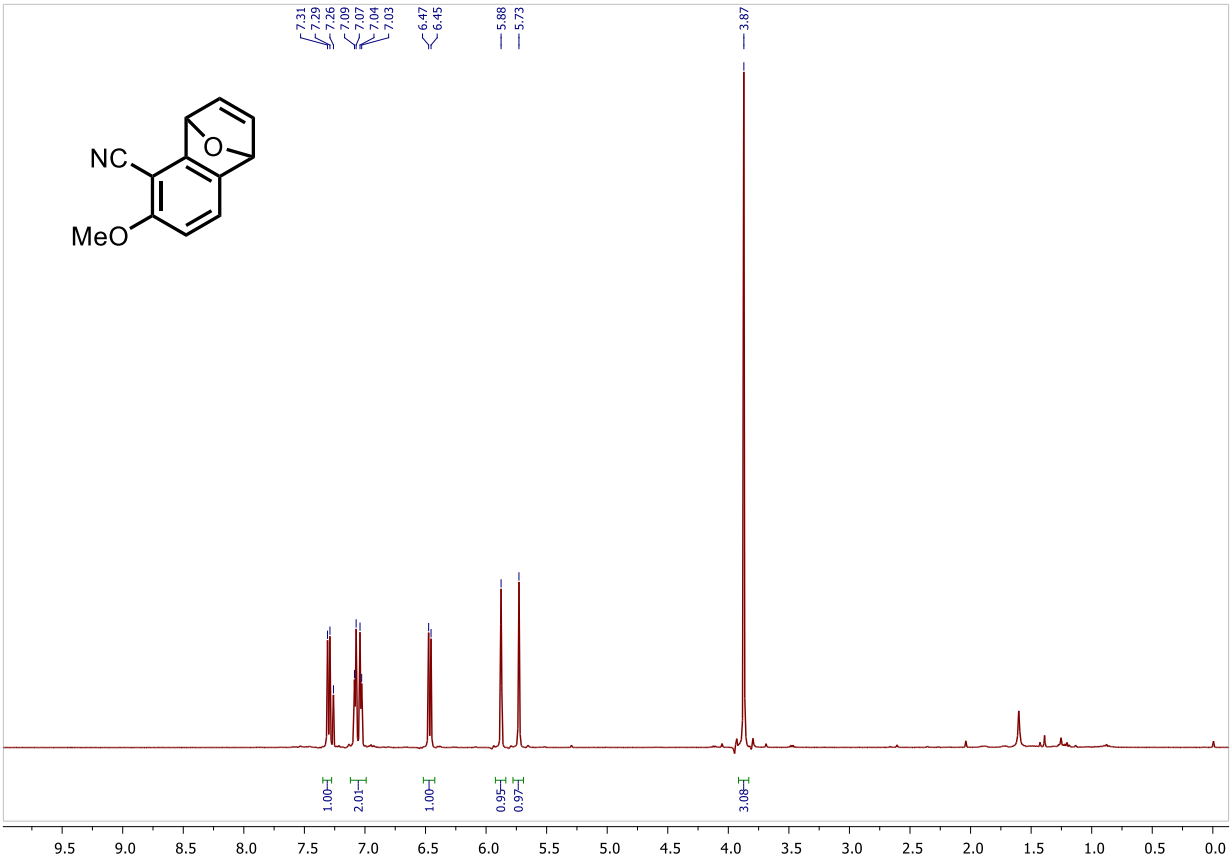
^{1}H NMR spectrum of 3da in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



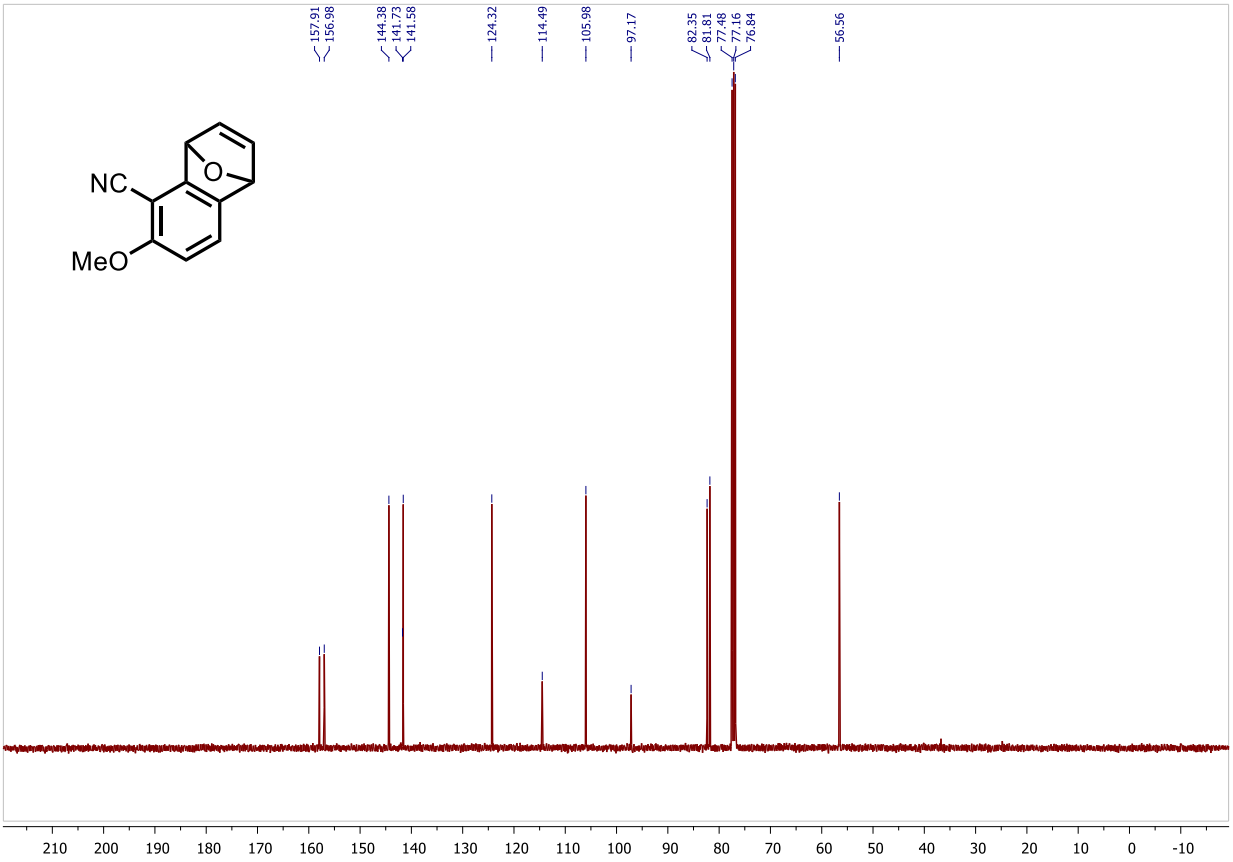
^{13}C{^{1}H} NMR spectrum of 3da in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



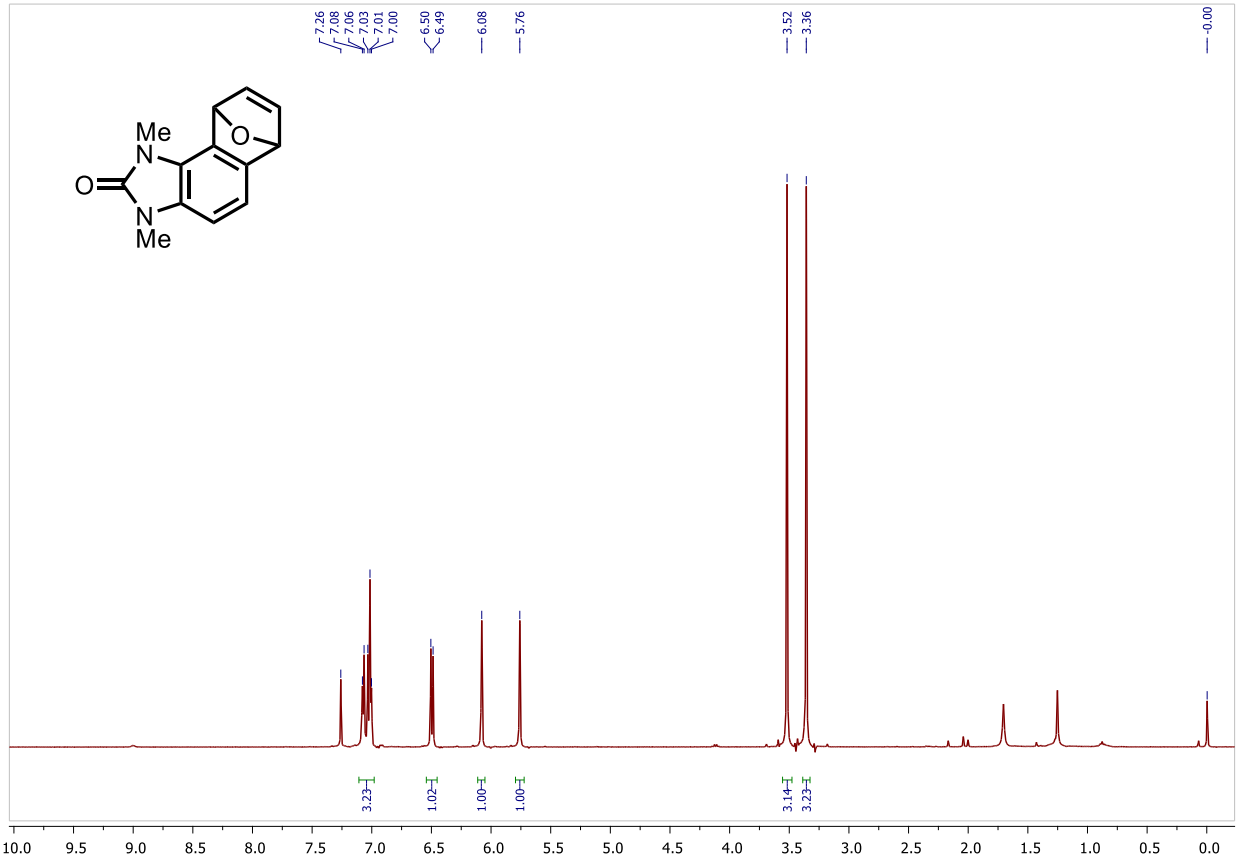
^{1}H NMR spectrum of 3ea in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



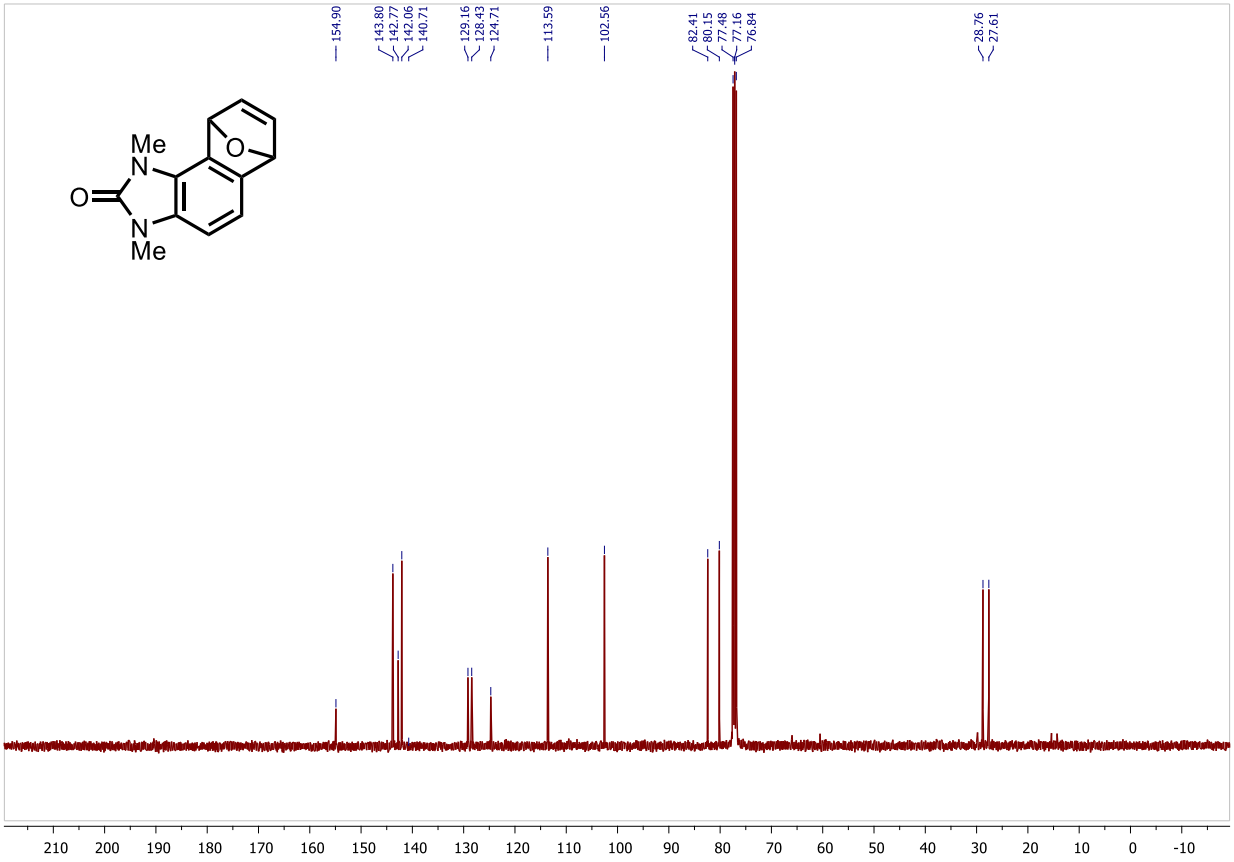
^{13}C{^{1}H} NMR spectrum of 3ea in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



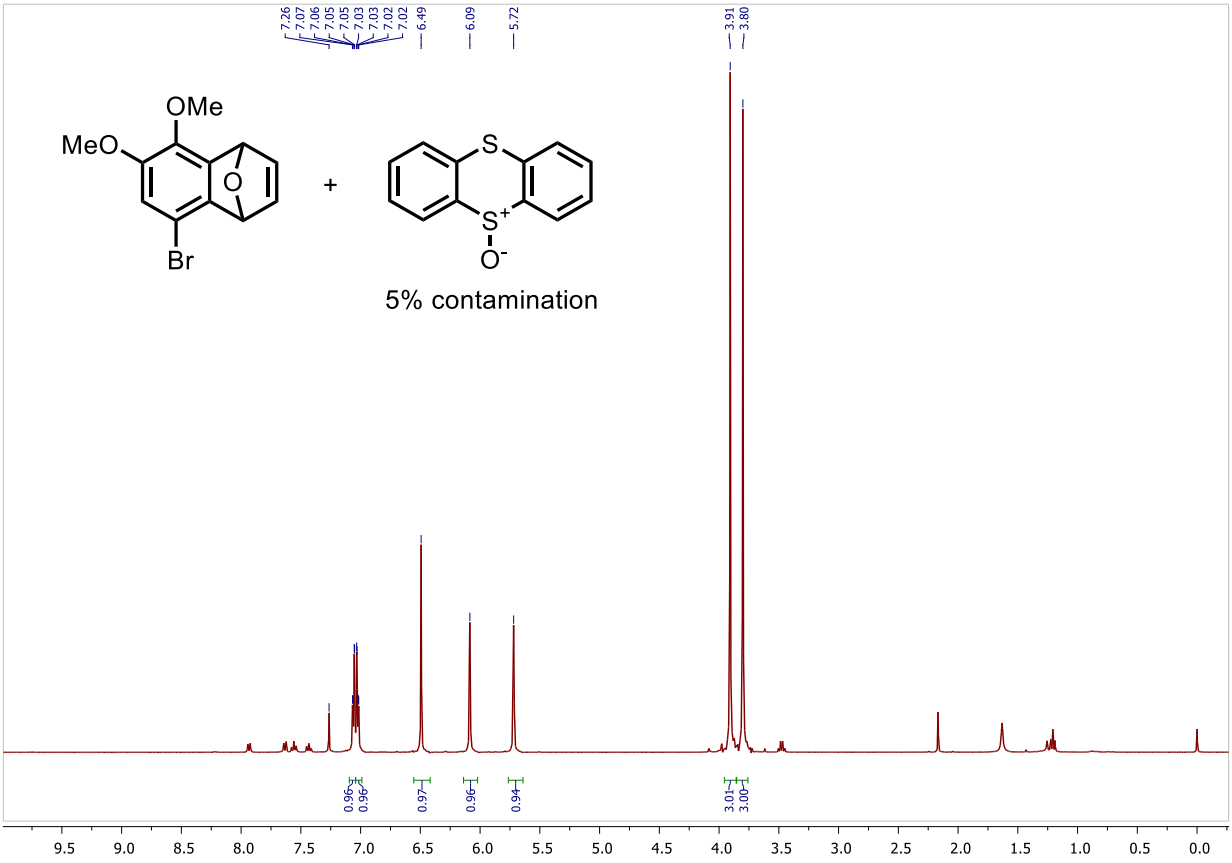
^{1}H NMR spectrum of 3fa in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



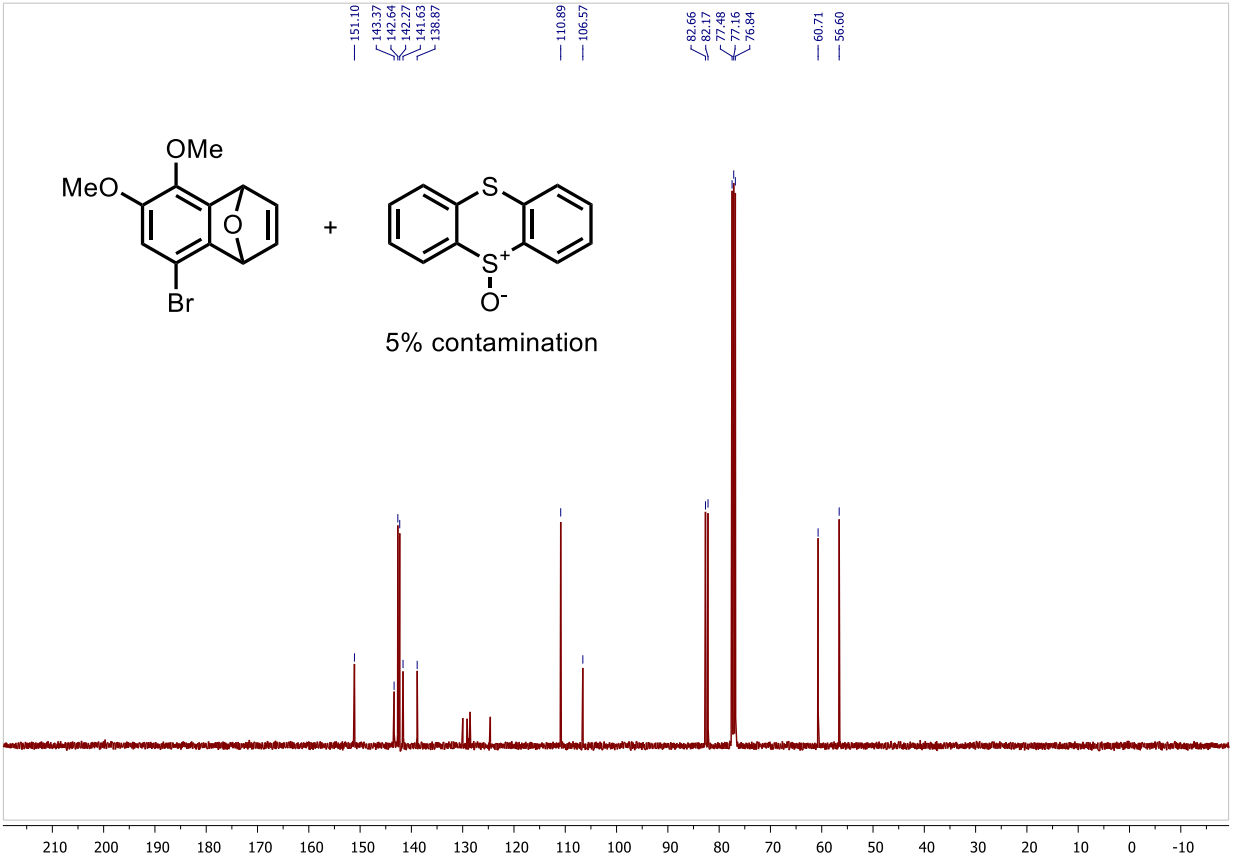
^{13}C{^{1}H} NMR spectrum of 3fa in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



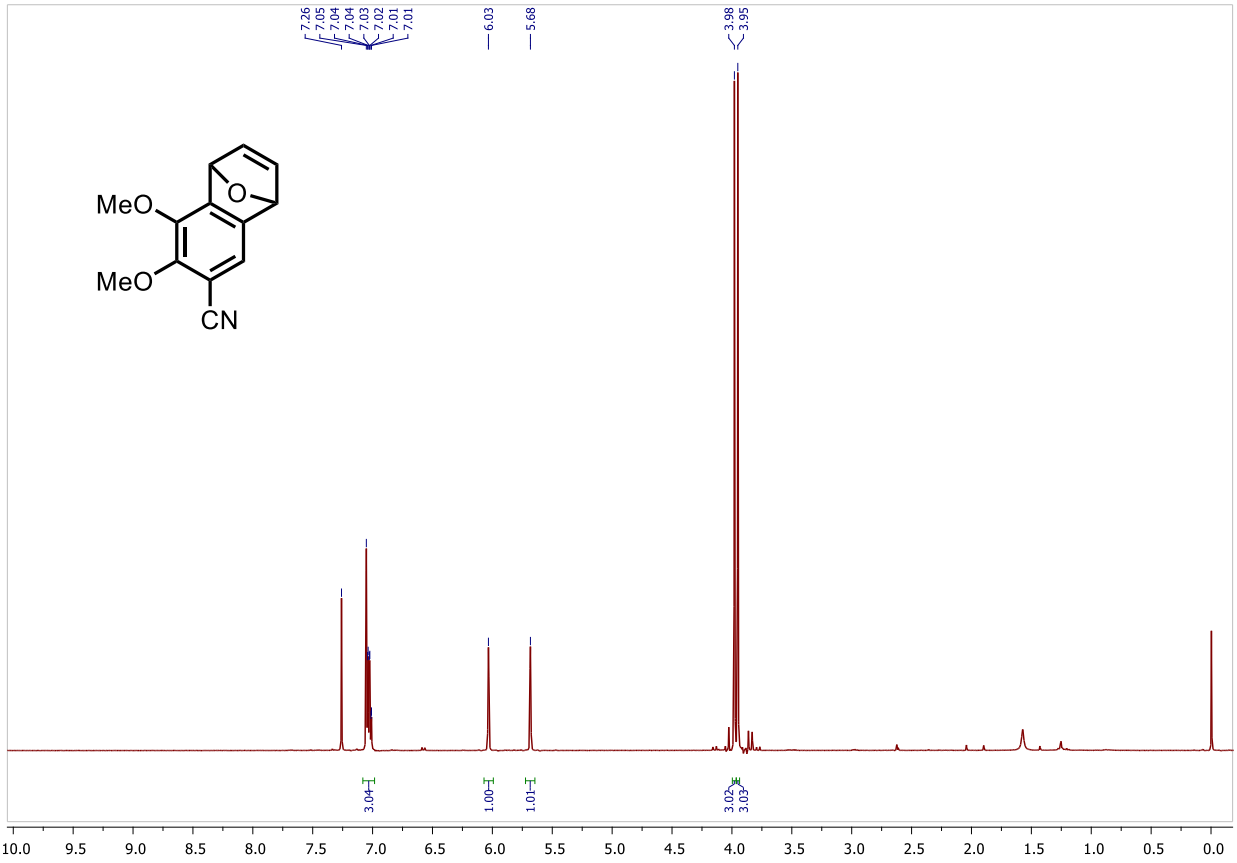
^{1}H NMR spectrum of 3ga in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



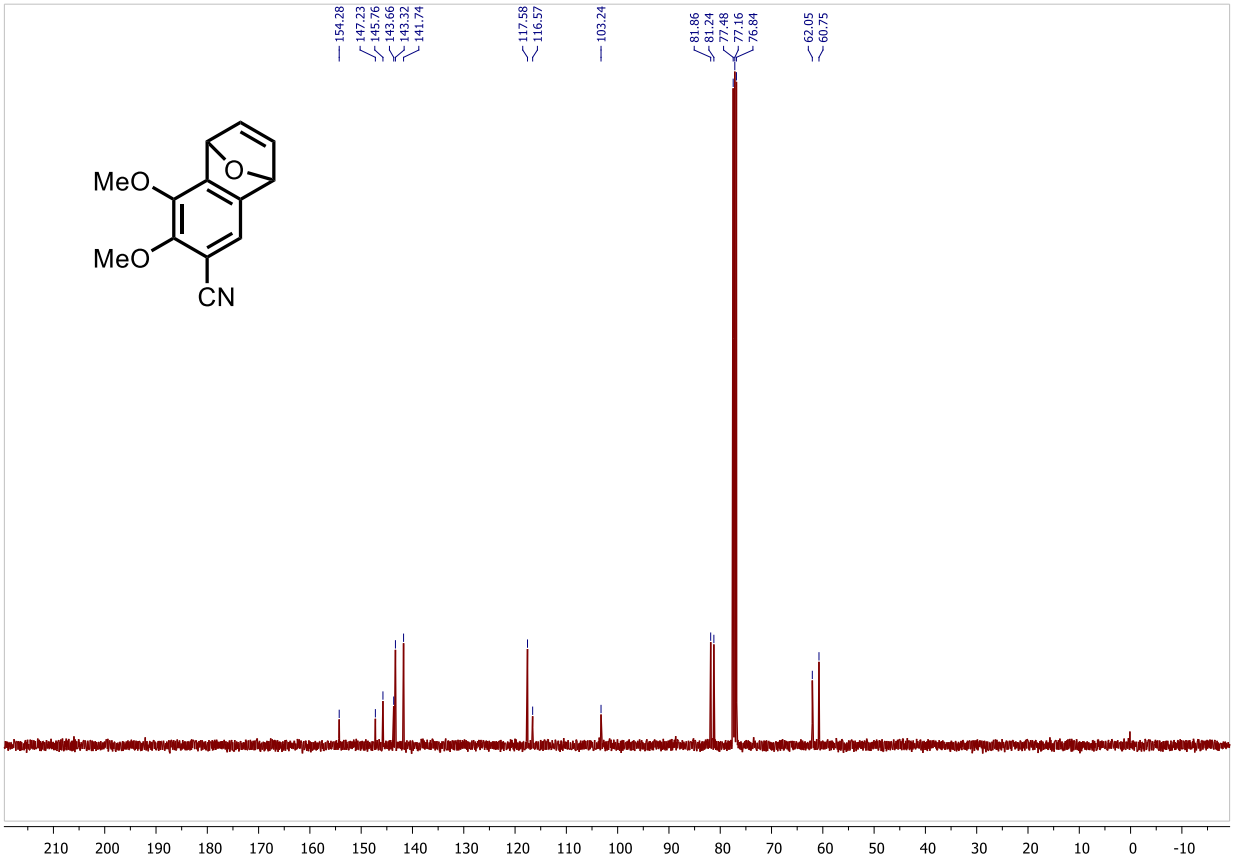
^{13}C{^{1}H} NMR spectrum of 3ga in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



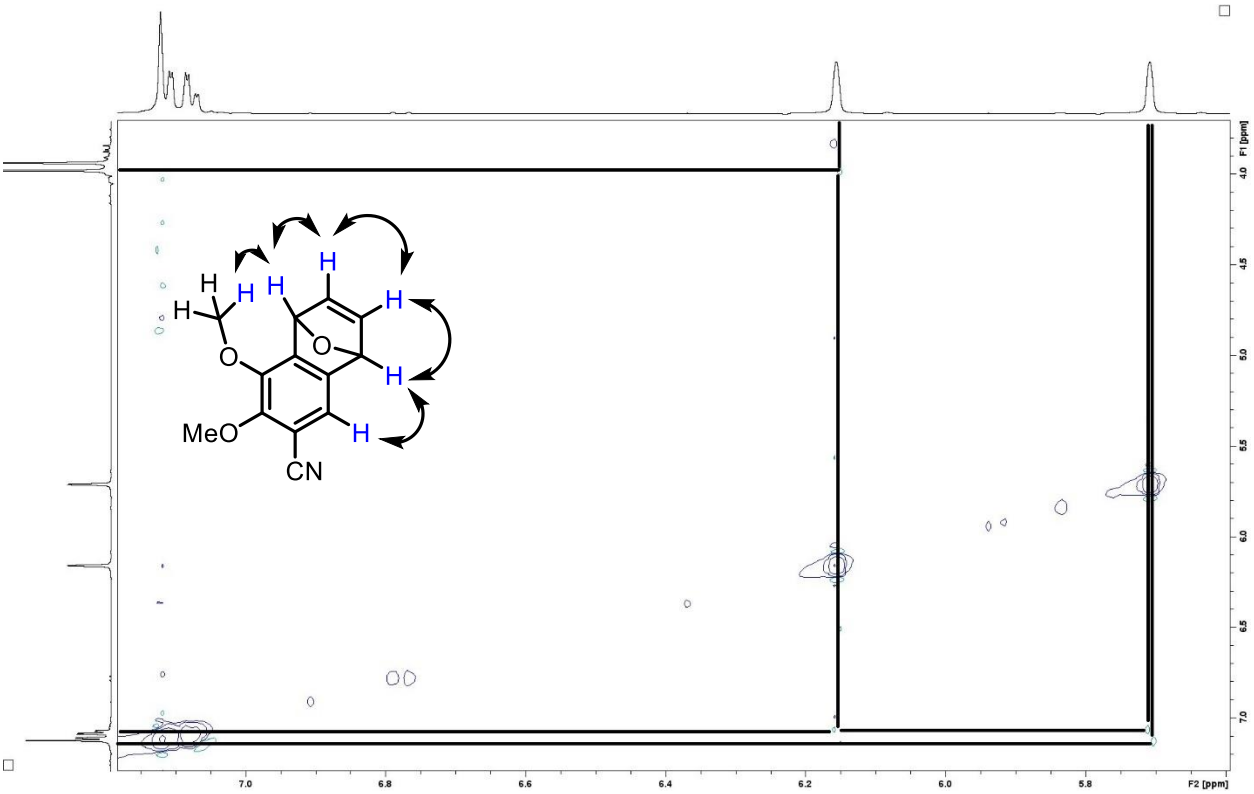
^{1}H NMR spectrum of 3ha in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



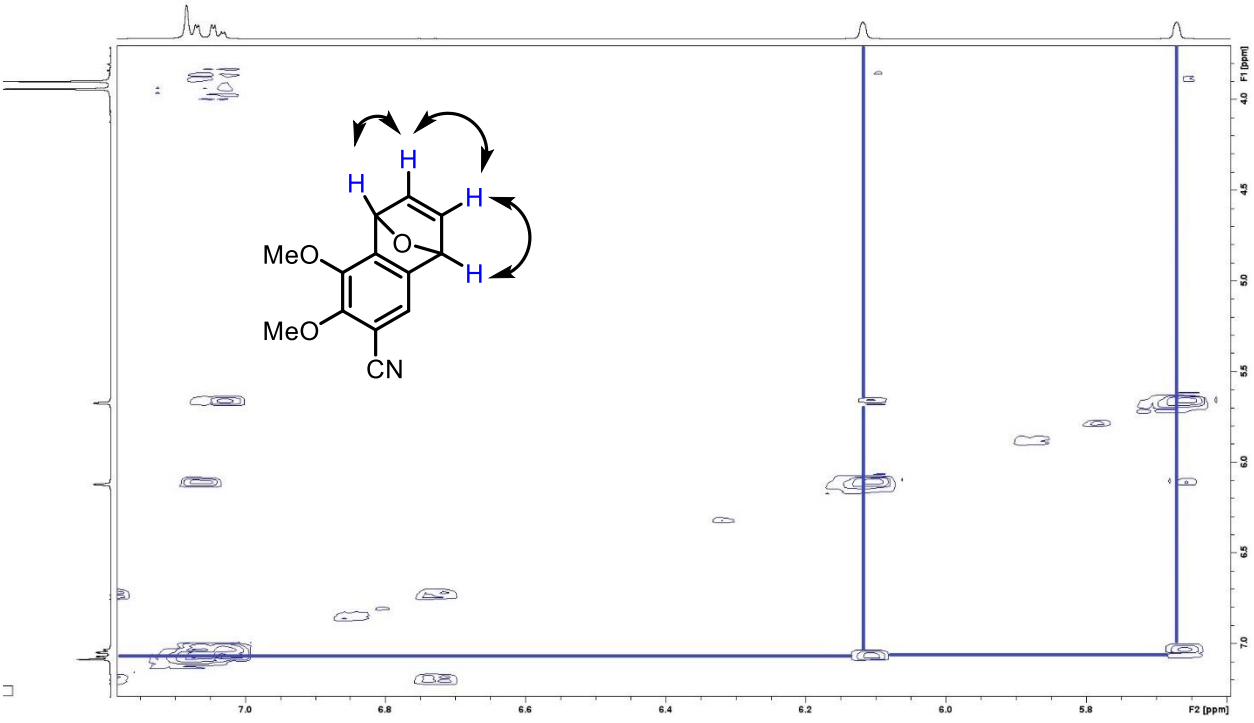
^{13}C{^{1}H} NMR spectrum of 3ha in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



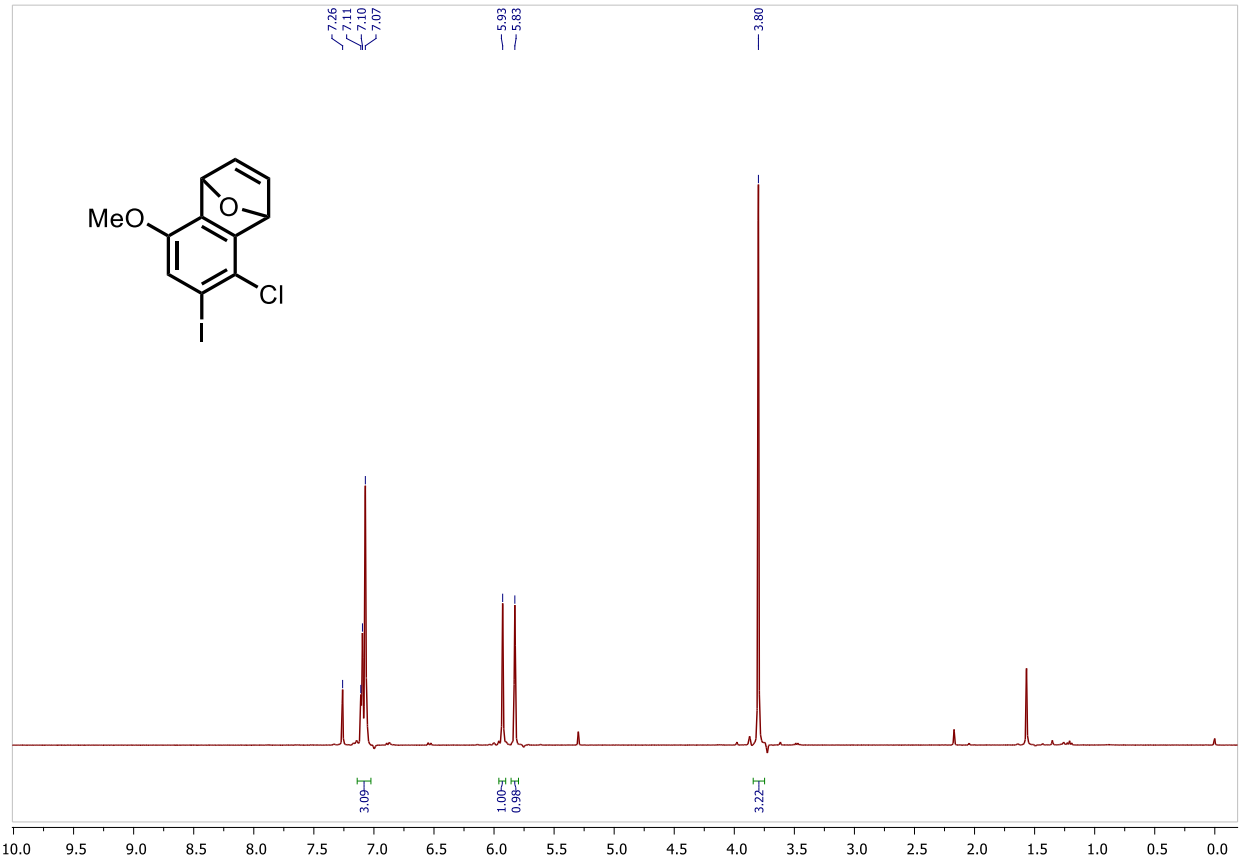
NOESY 2D NMR spectrum of 3ha in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



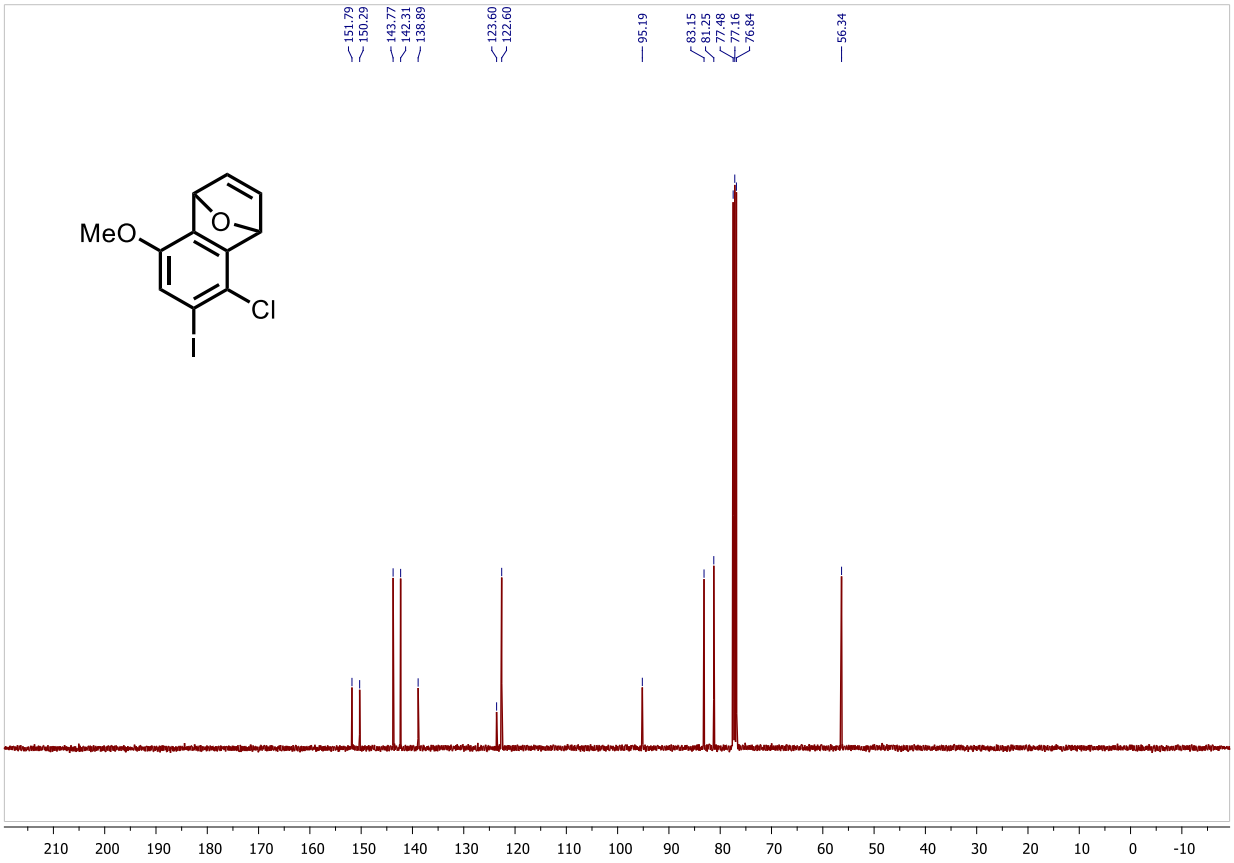
COSY 2D NMR spectrum of 3ha in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



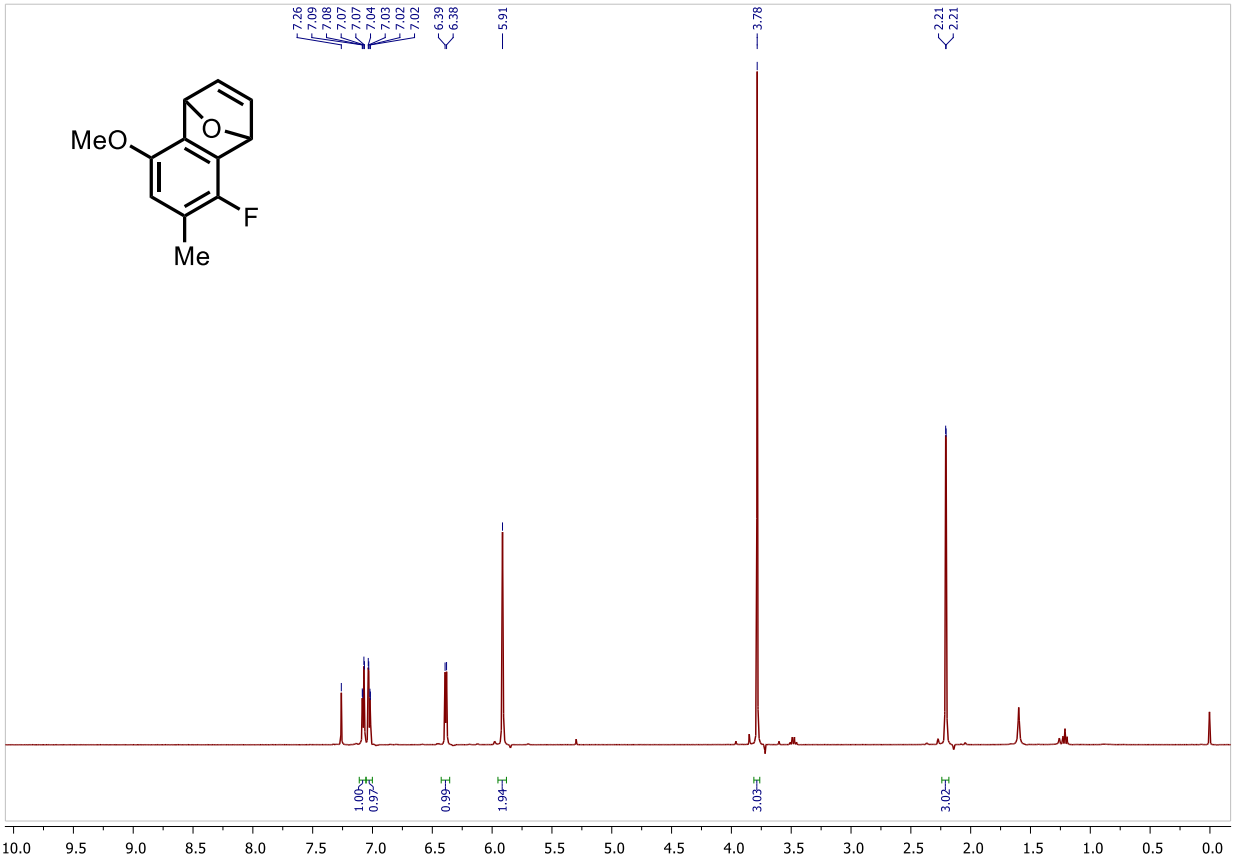
^{1}H NMR spectrum of 3ia in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



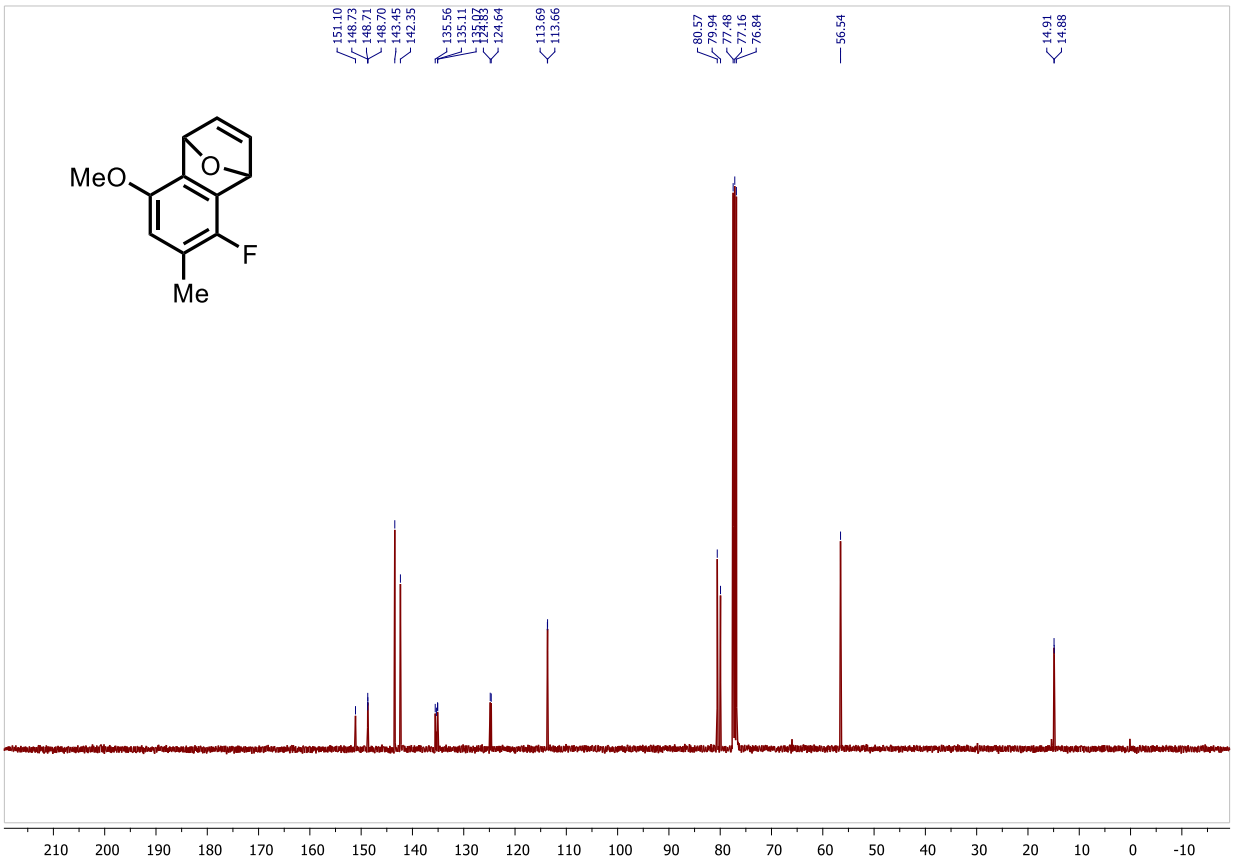
^{13}C{^{1}H} NMR spectrum of 3ia in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



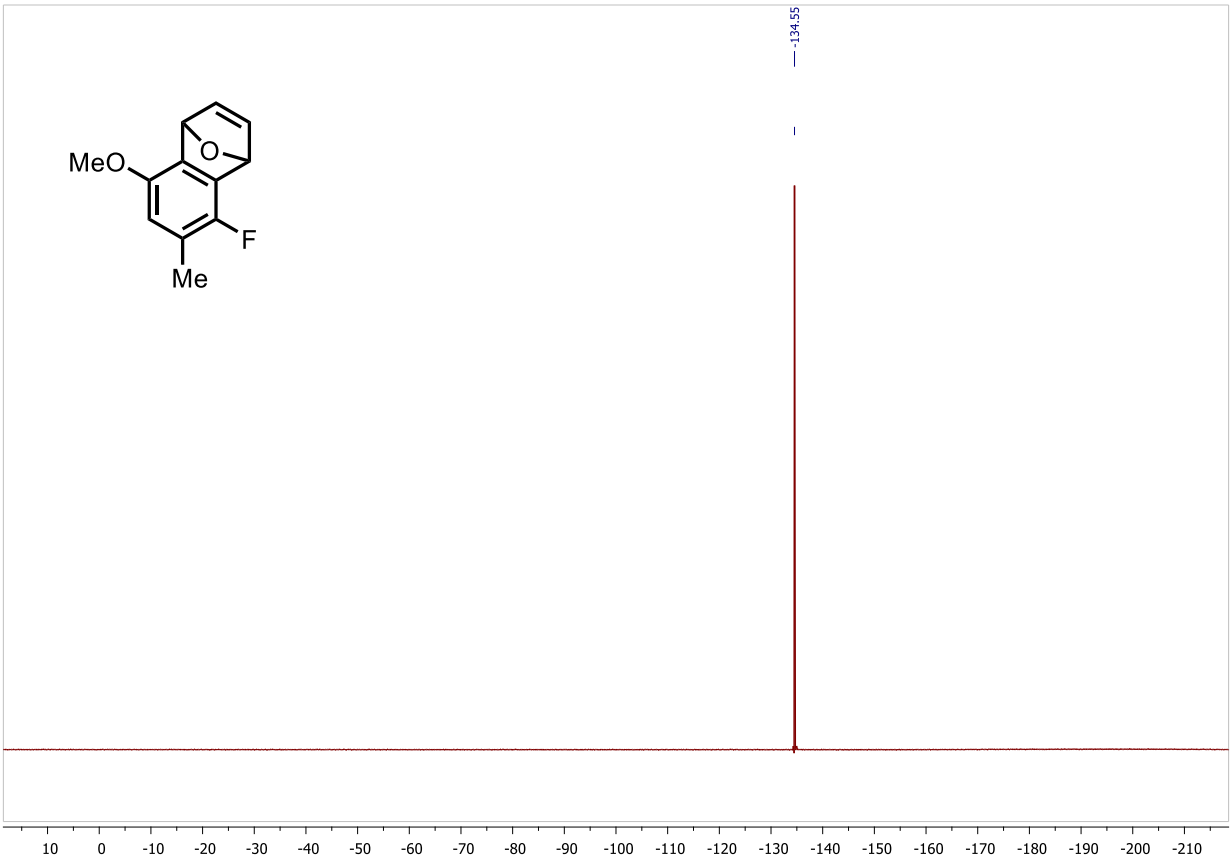
^{1}H NMR spectrum of 3ja in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



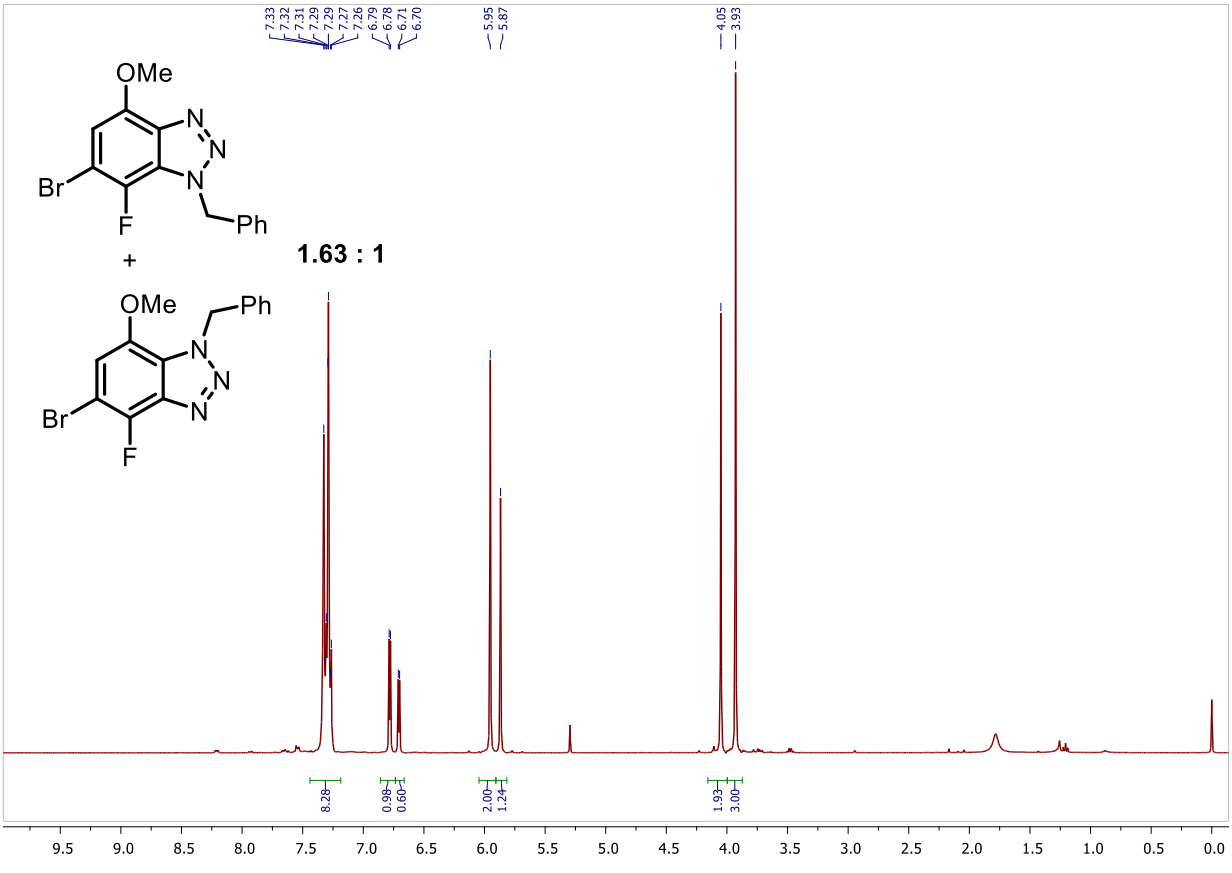
^{13}C{^{1}H} NMR spectrum of 3ja in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



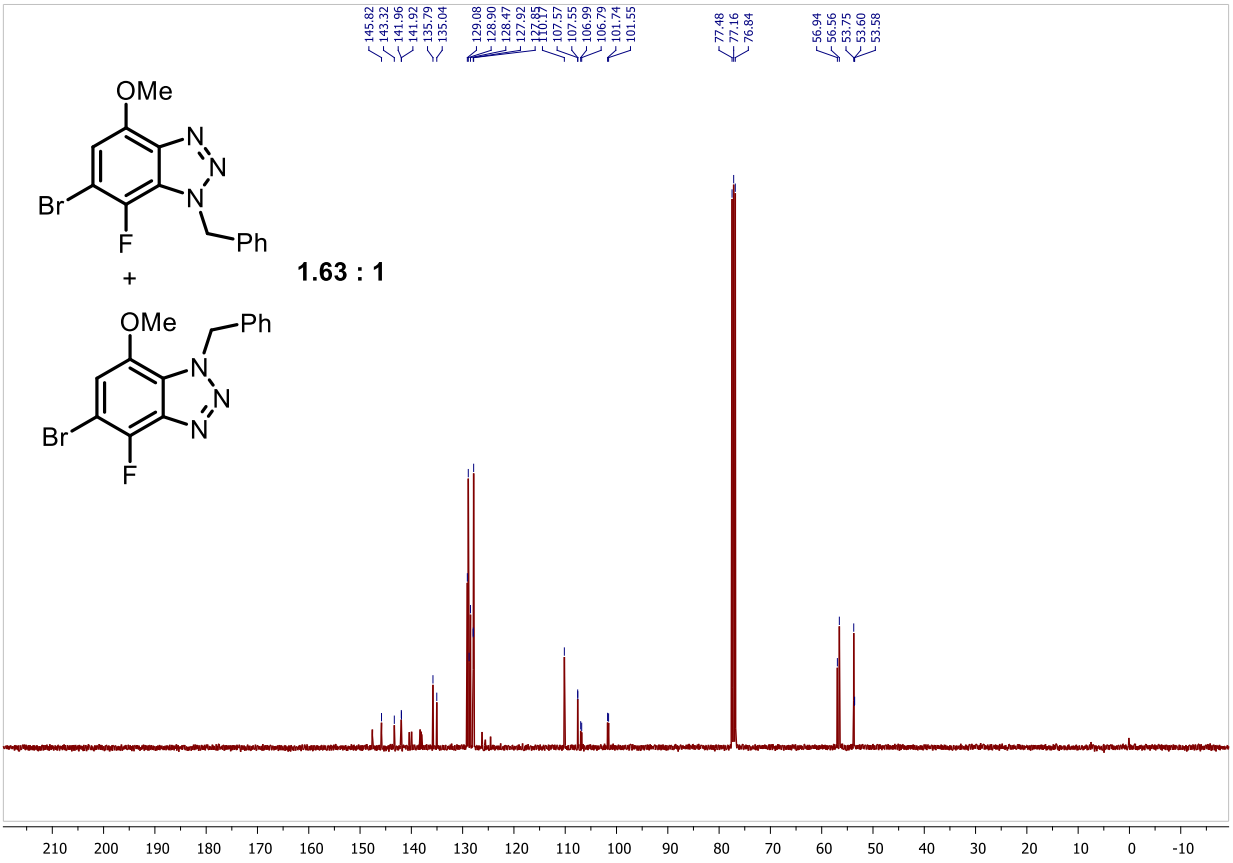
$^{19}F\{^{1}H\}$ NMR spectrum of 3ja in $CDCl_3$ with 1% v/v TMS at 376 MHz at 298 K



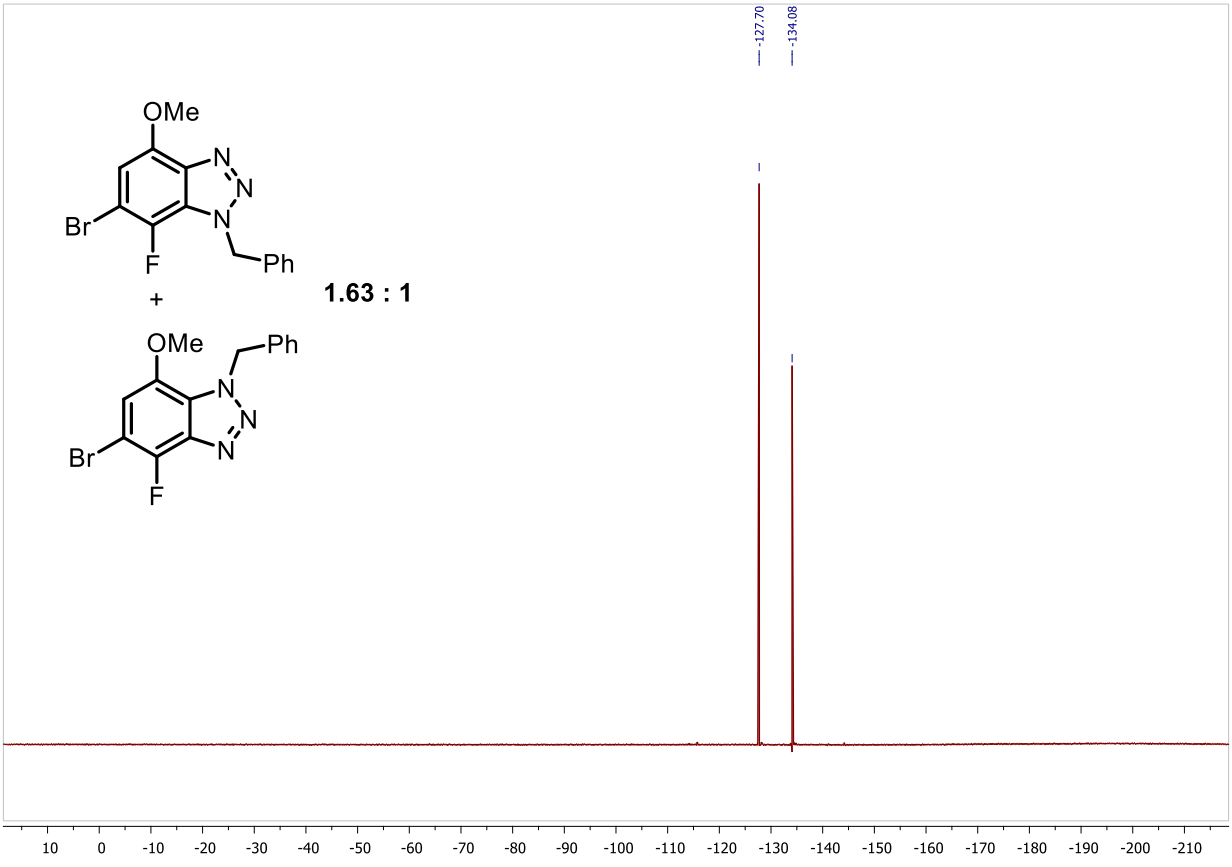
^{1}H NMR spectrum of 3kb in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



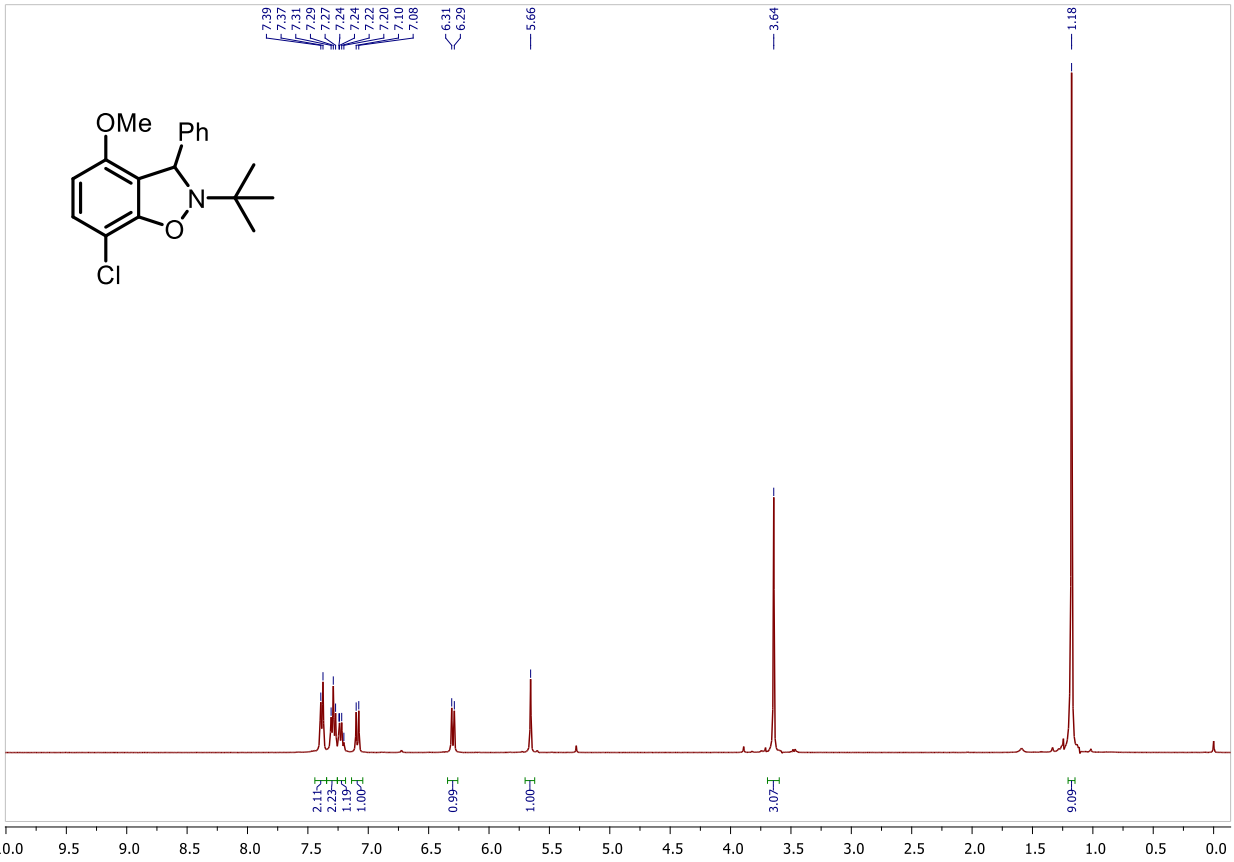
$^{13}C\{^{1}H\}$ NMR spectrum of 3kb in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



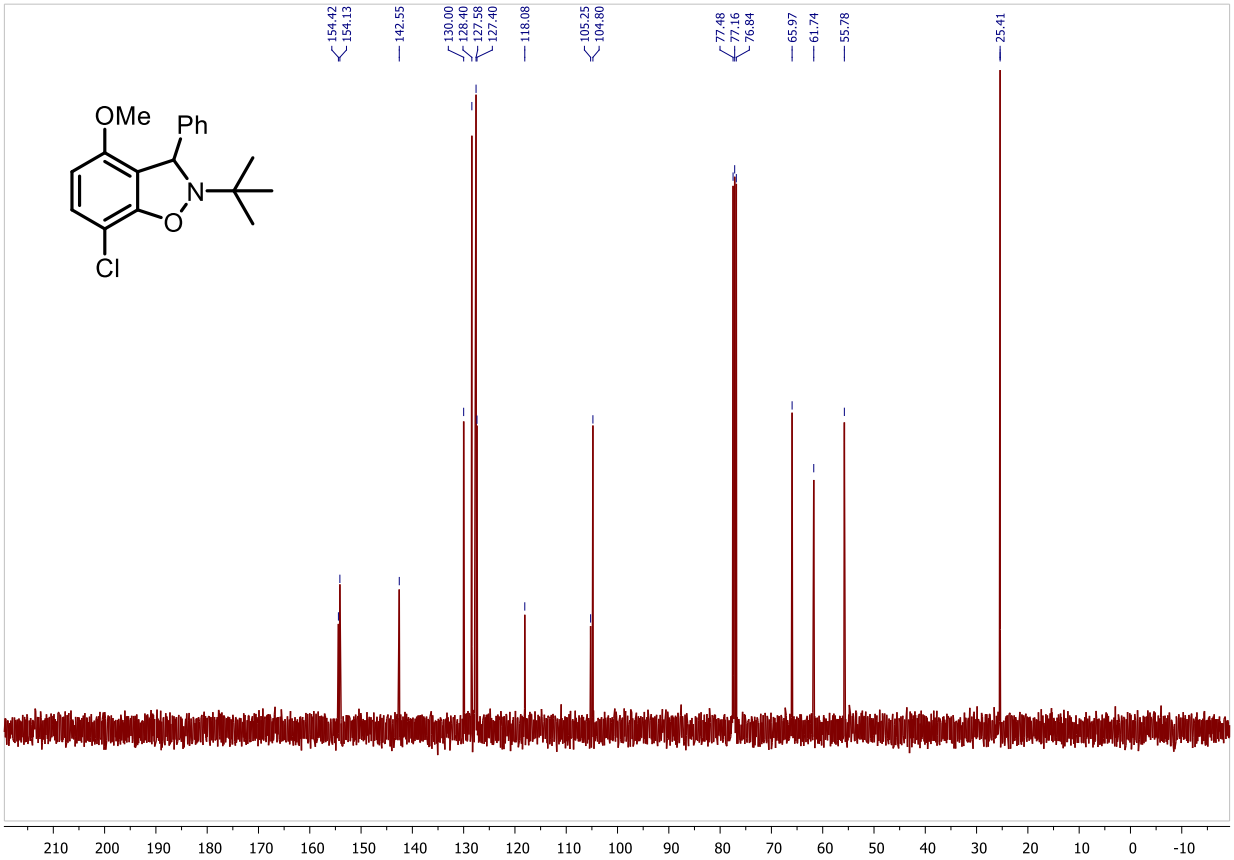
$^{19}F\{^{1}H\}$ NMR spectrum of 3kb in $CDCl_3$ with 1% v/v TMS at 376 MHz at 298 K



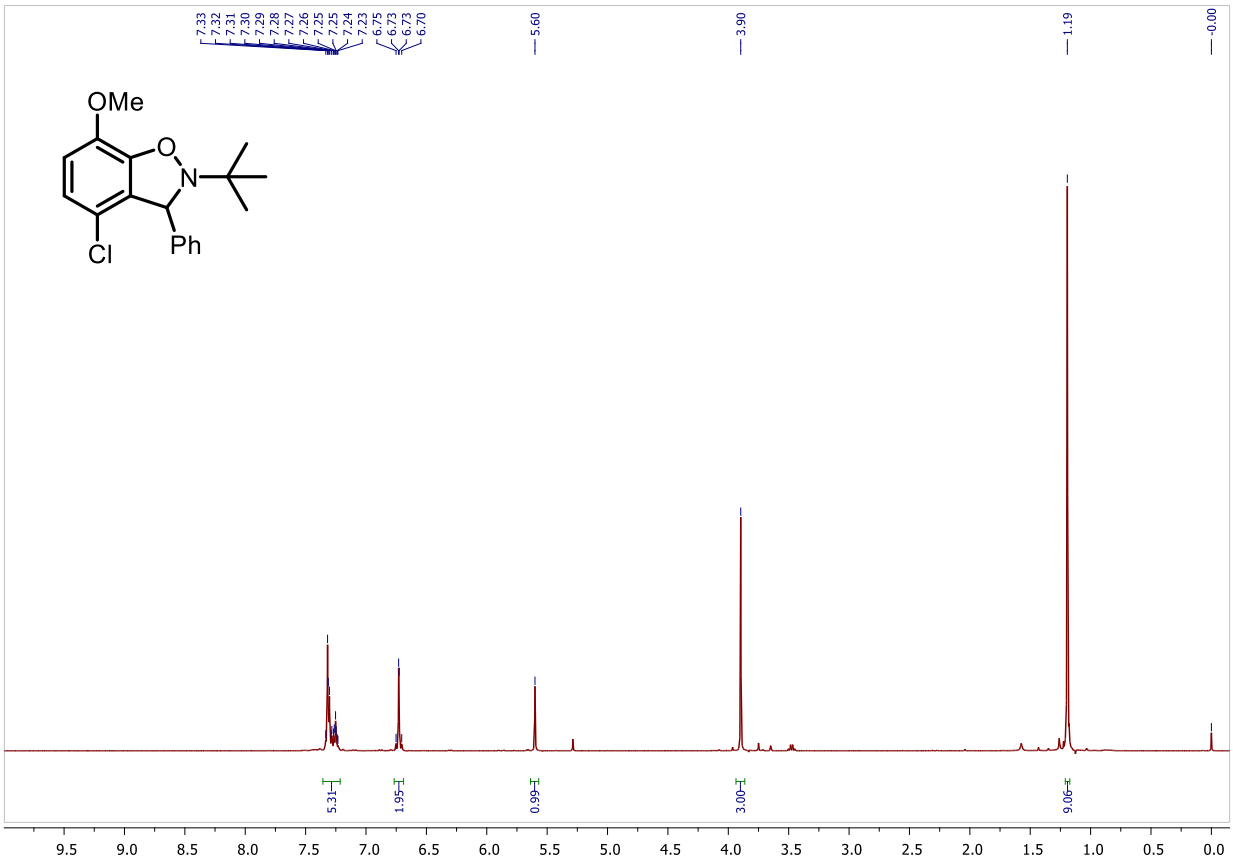
^{1}H NMR spectrum of 3ac in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



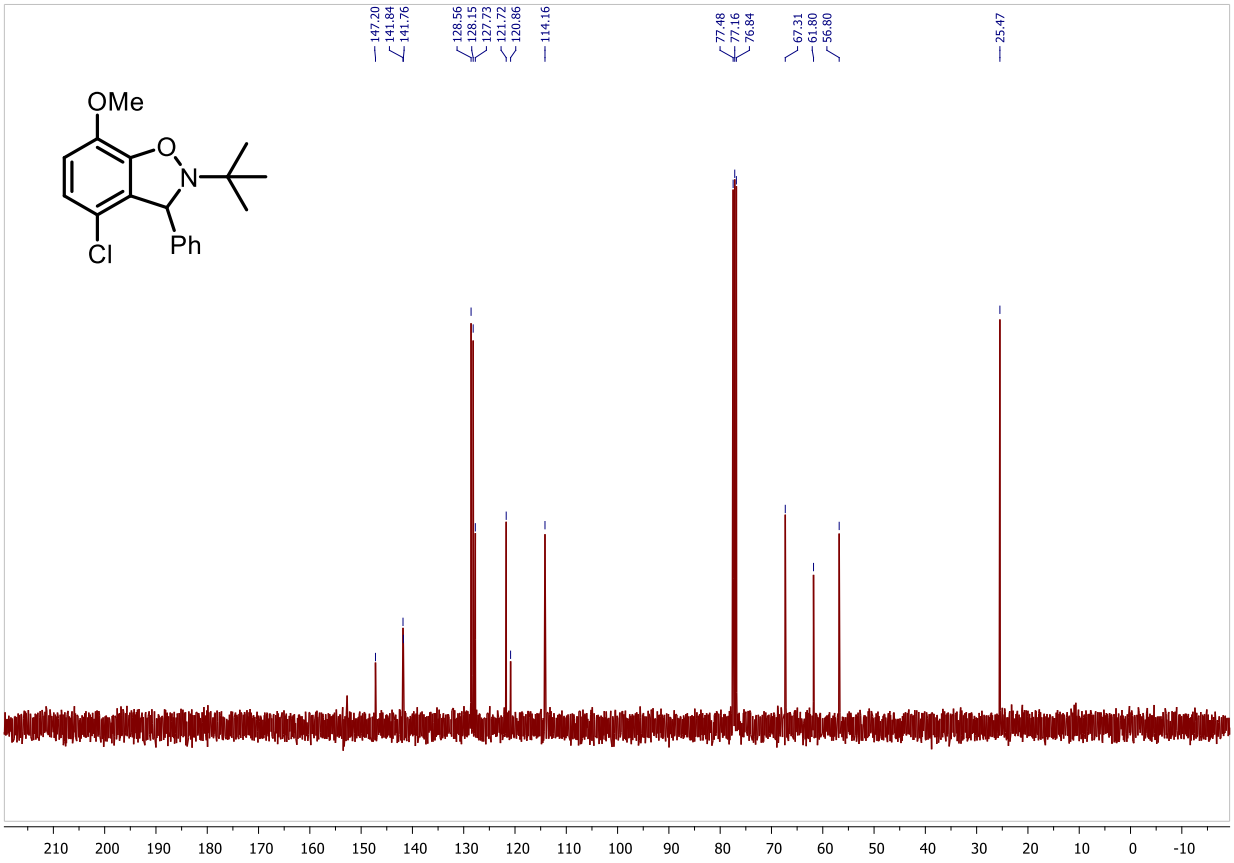
^{13}C{^{1}H} NMR spectrum of 3ac in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



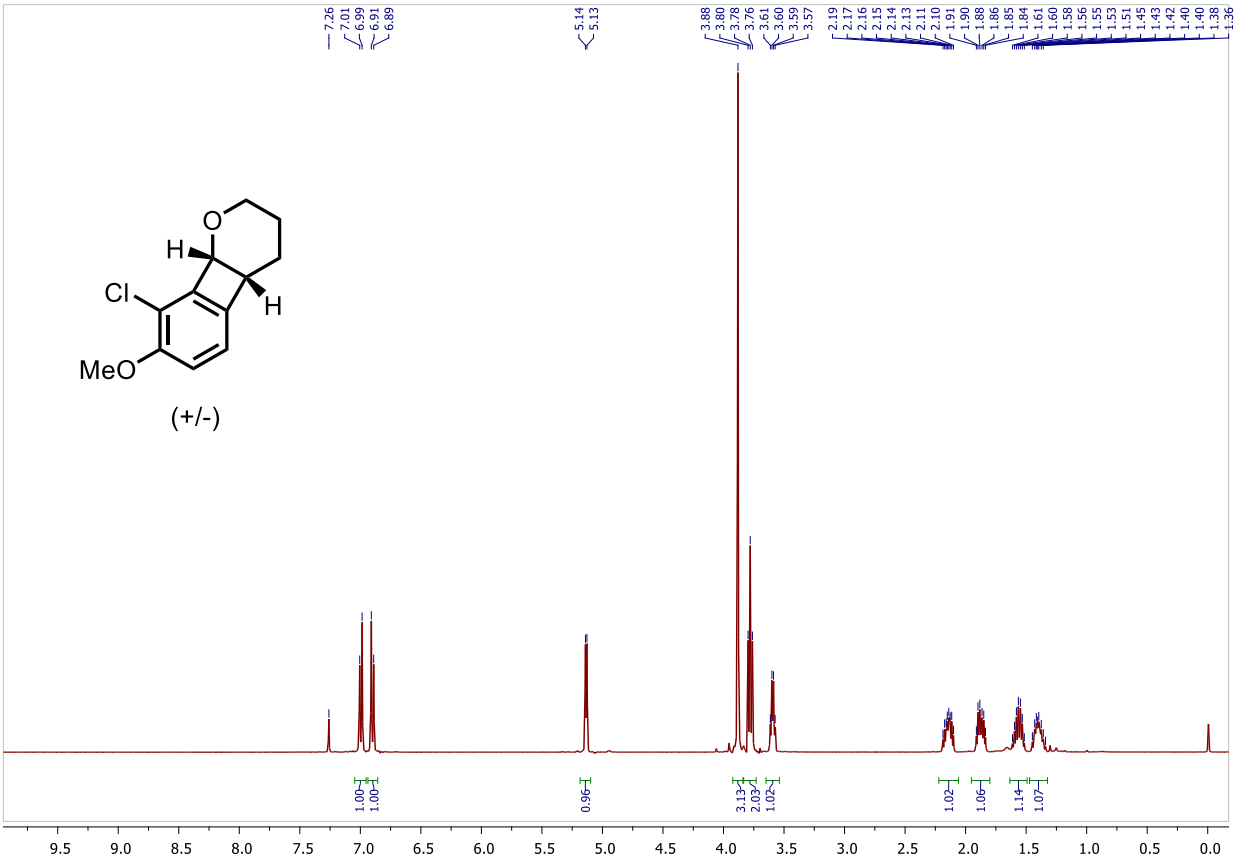
^{1}H NMR spectrum of 3ac' in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



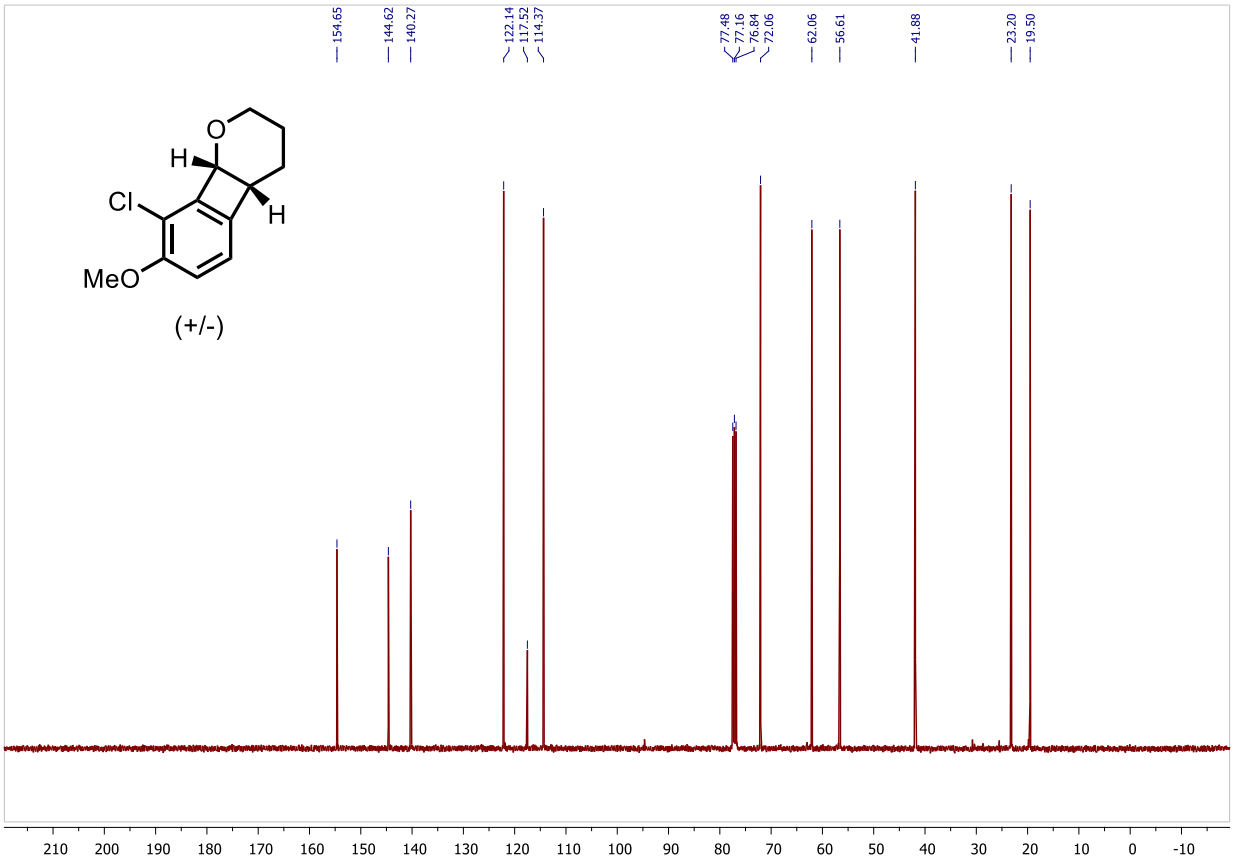
^{13}C{^{1}H} NMR spectrum of 3ac' in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



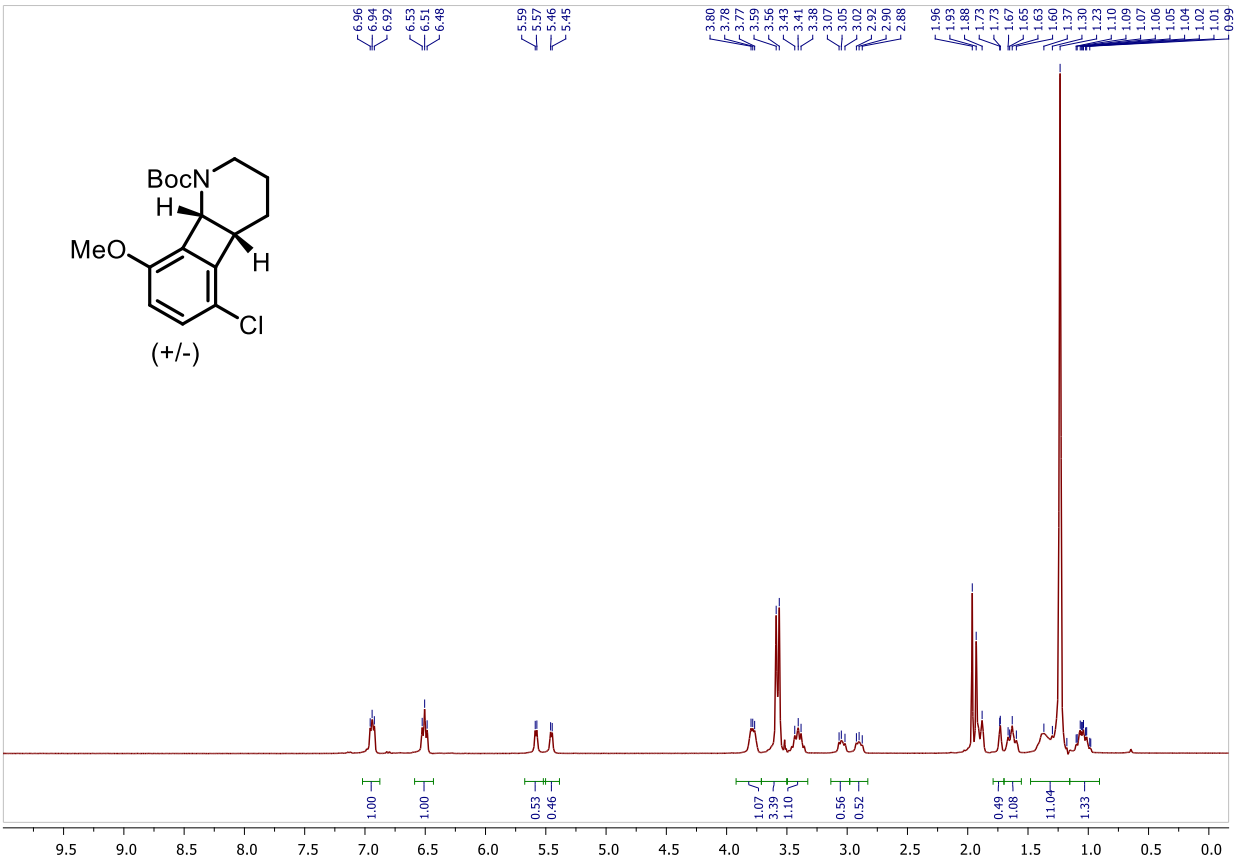
^{1}H NMR spectrum of 3cd in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



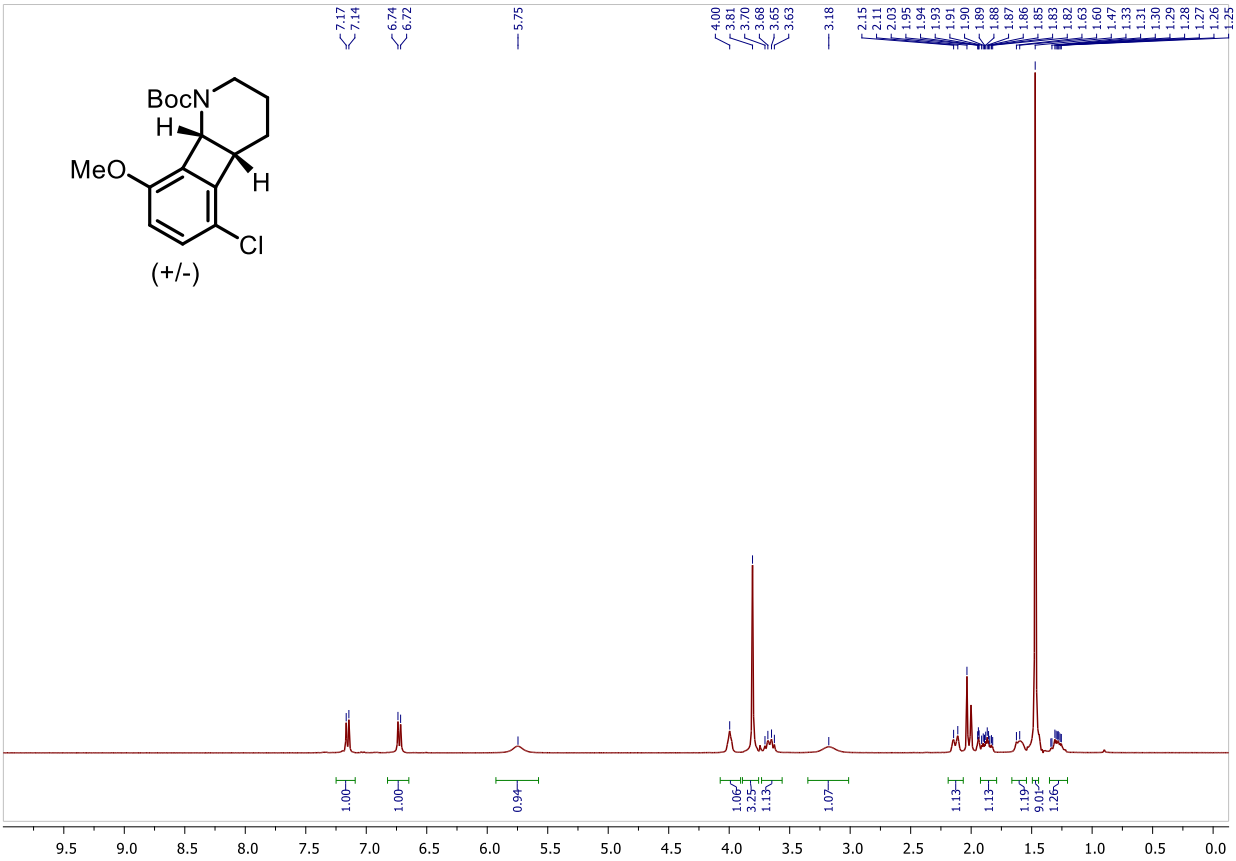
^{13}C{^{1}H} NMR spectrum of 3cd in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



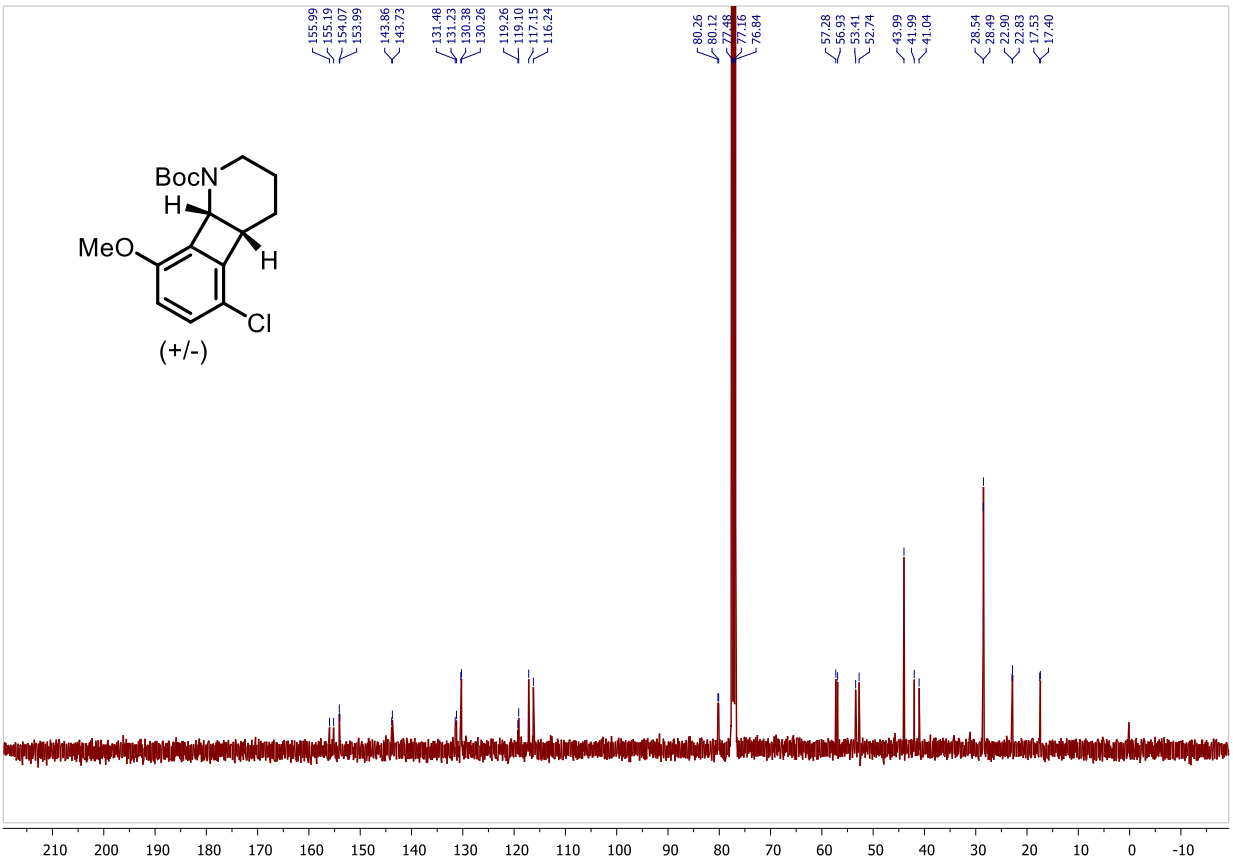
^{1}H NMR spectrum of 3ae in CD_3CN at 400 MHz at 298 K



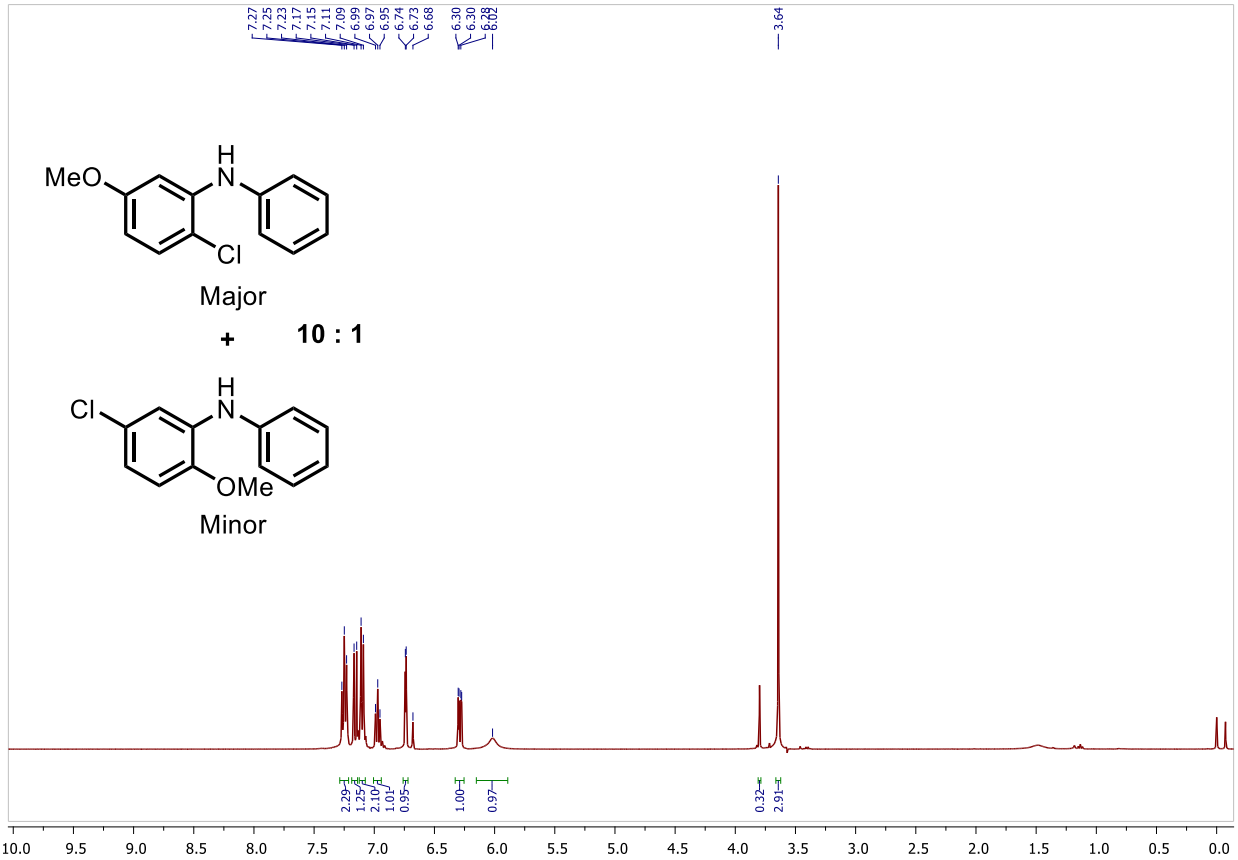
^{1}H NMR spectrum of 3ae in CD_3CN at 400 MHz at 333 K



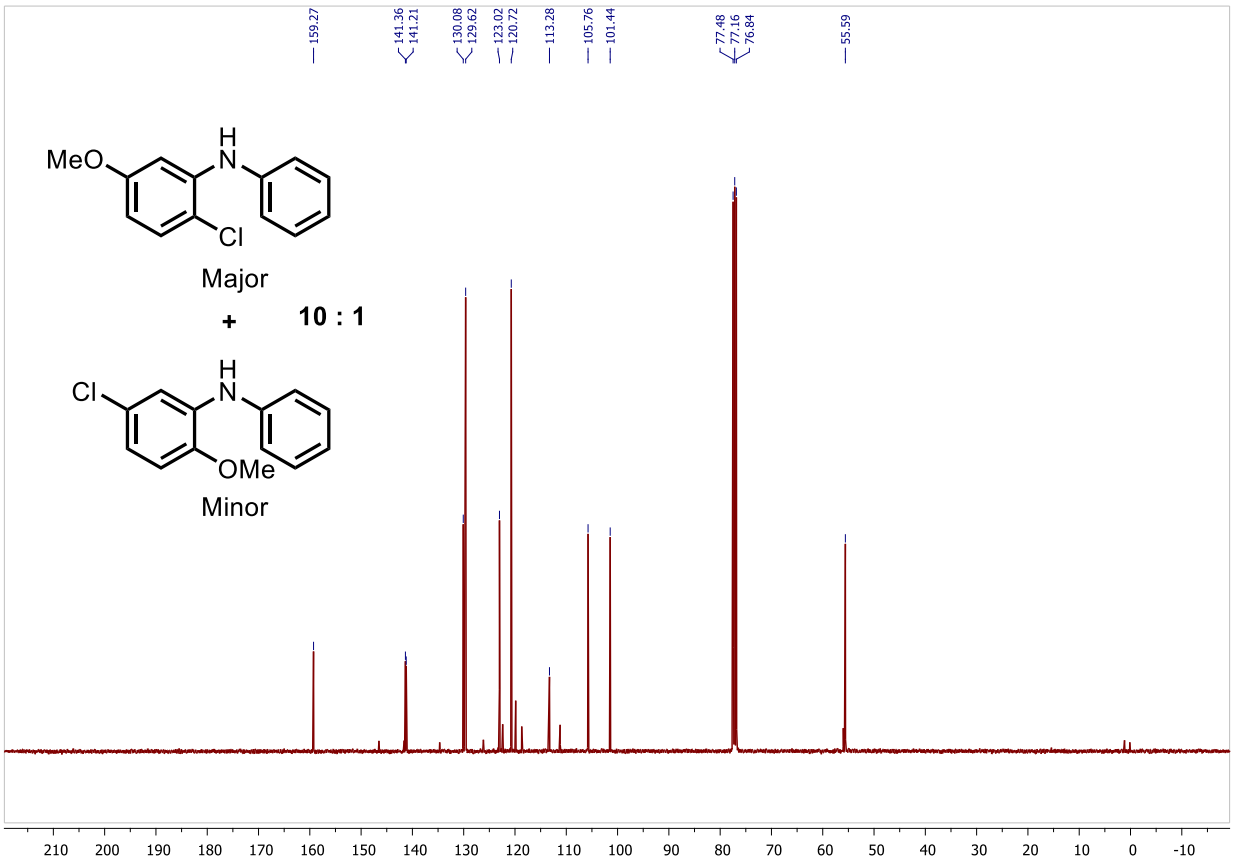
$^{13}C\{^{1}H\}$ NMR spectrum of 3ae in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



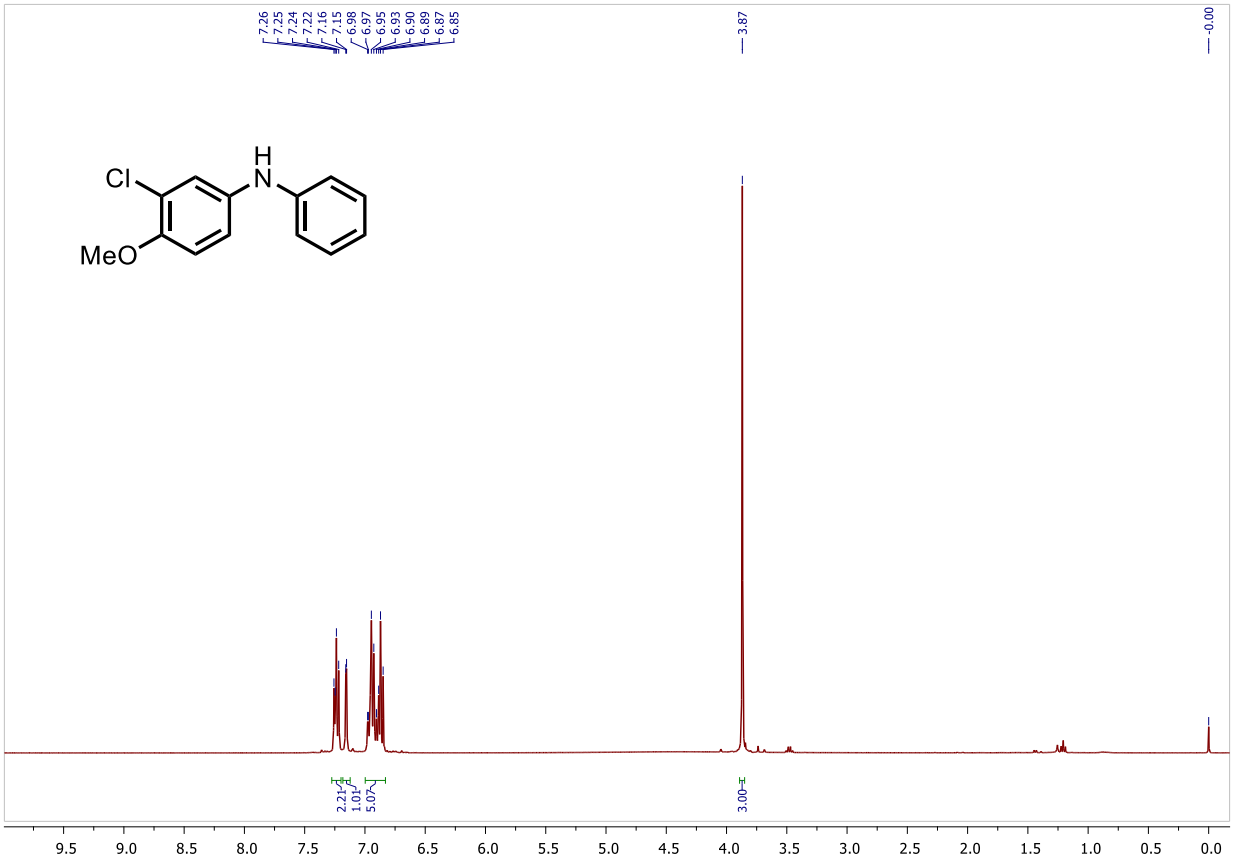
^{1}H NMR spectrum of 3af in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



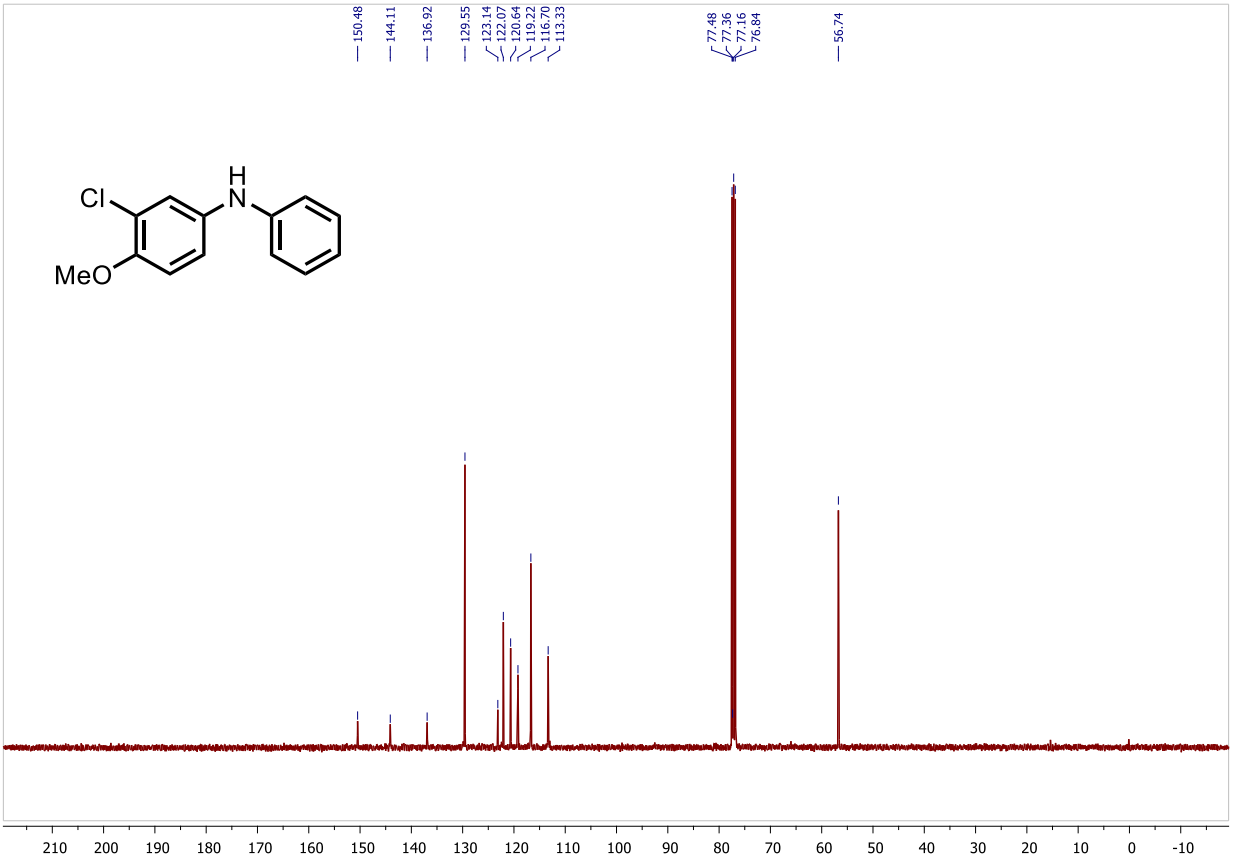
$^{13}C\{^{1}H\}$ NMR spectrum of 3af in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



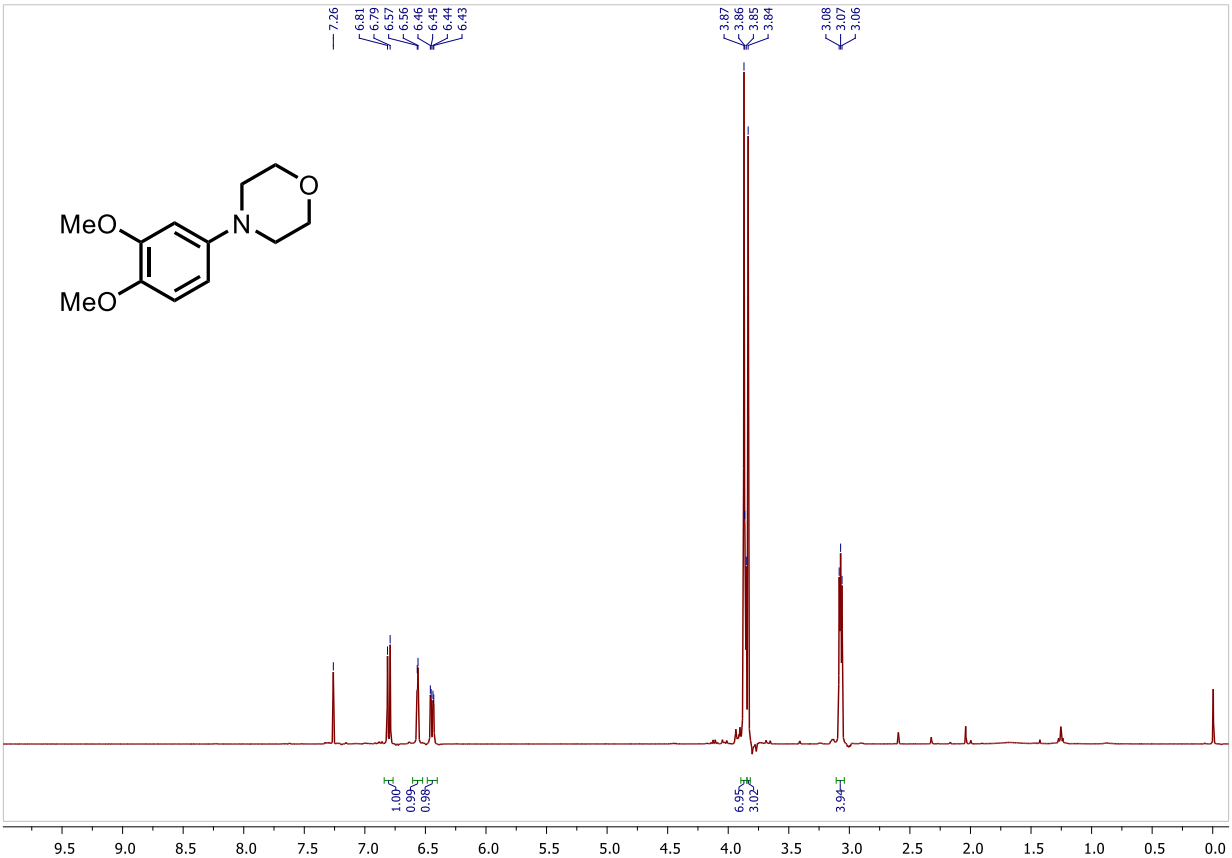
^{1}H NMR spectrum of 3bf in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



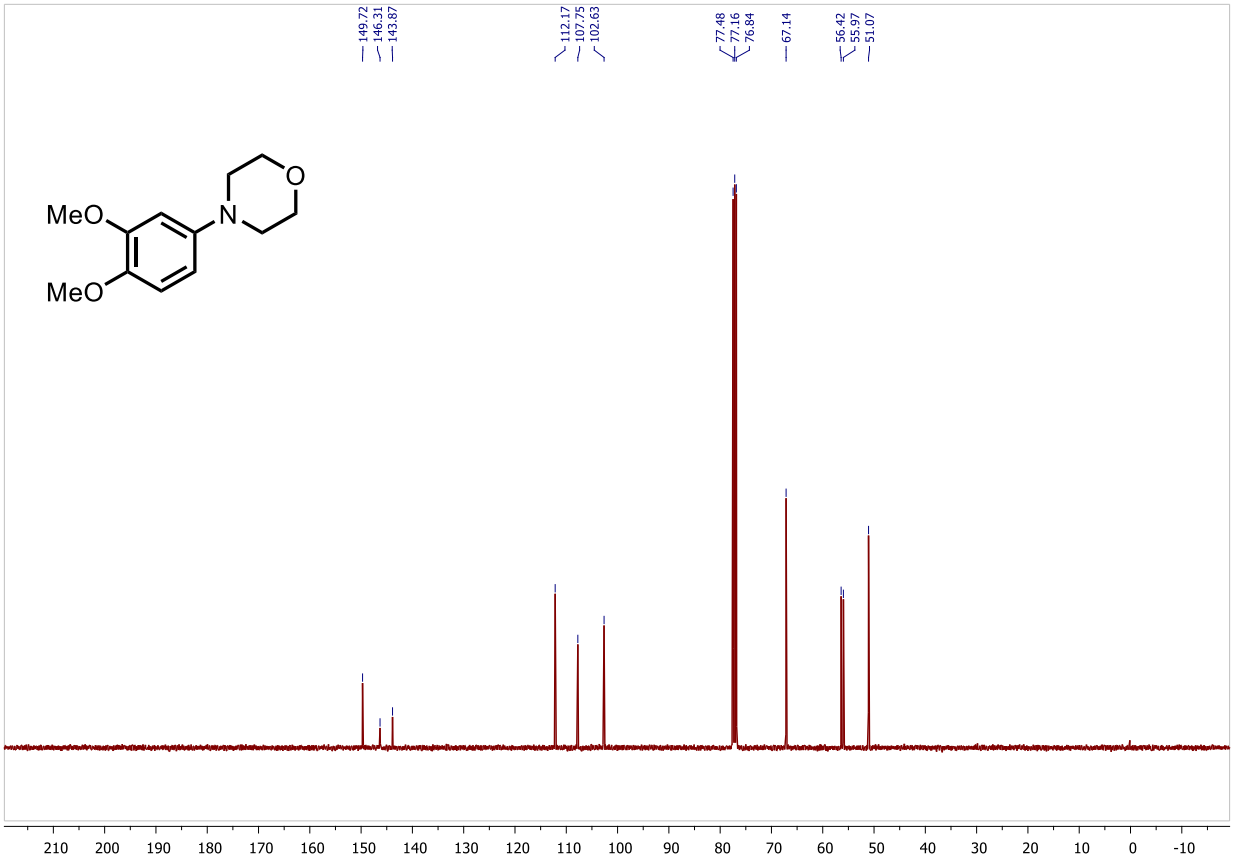
$^{13}C\{^{1}H\}$ NMR spectrum of 3bf in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



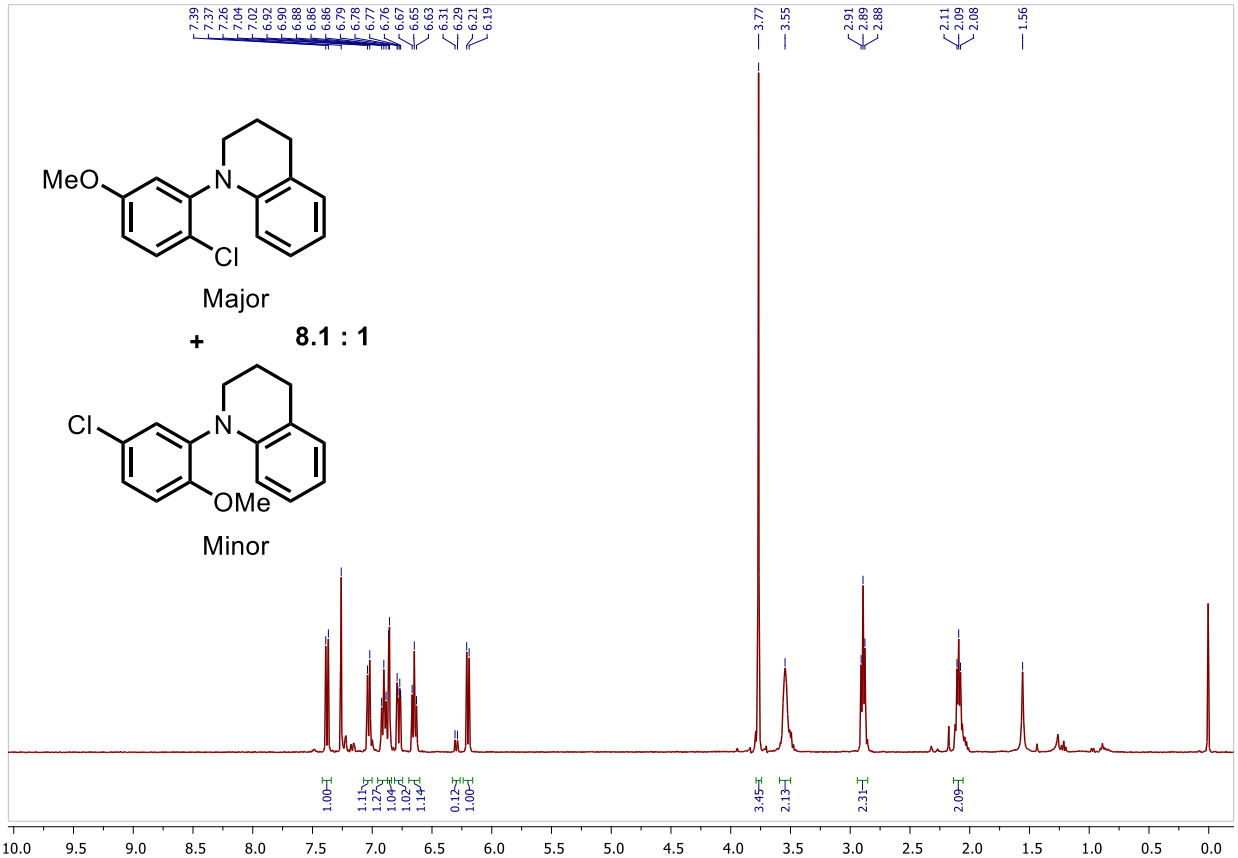
^{1}H NMR spectrum of 3dg in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



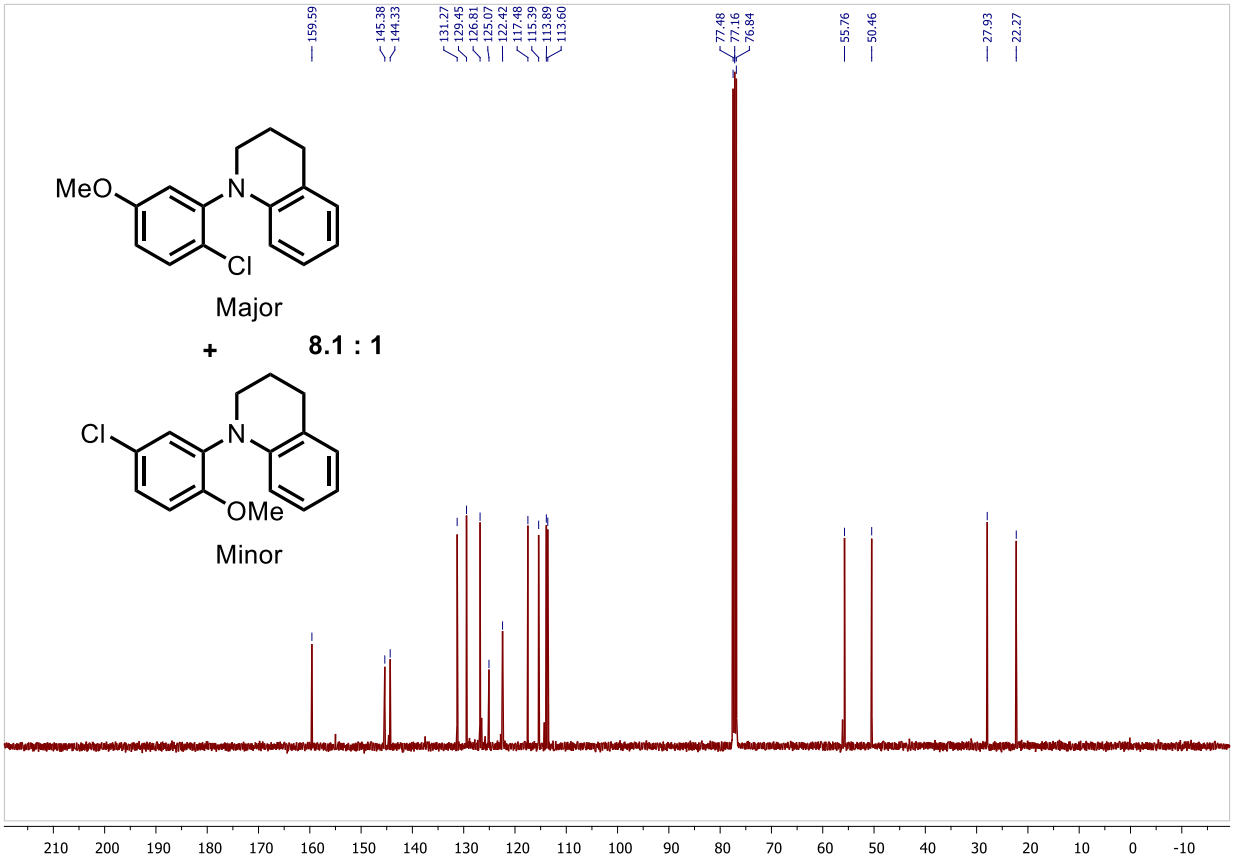
$^{13}C\{^{1}H\}$ NMR spectrum of 3dg in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



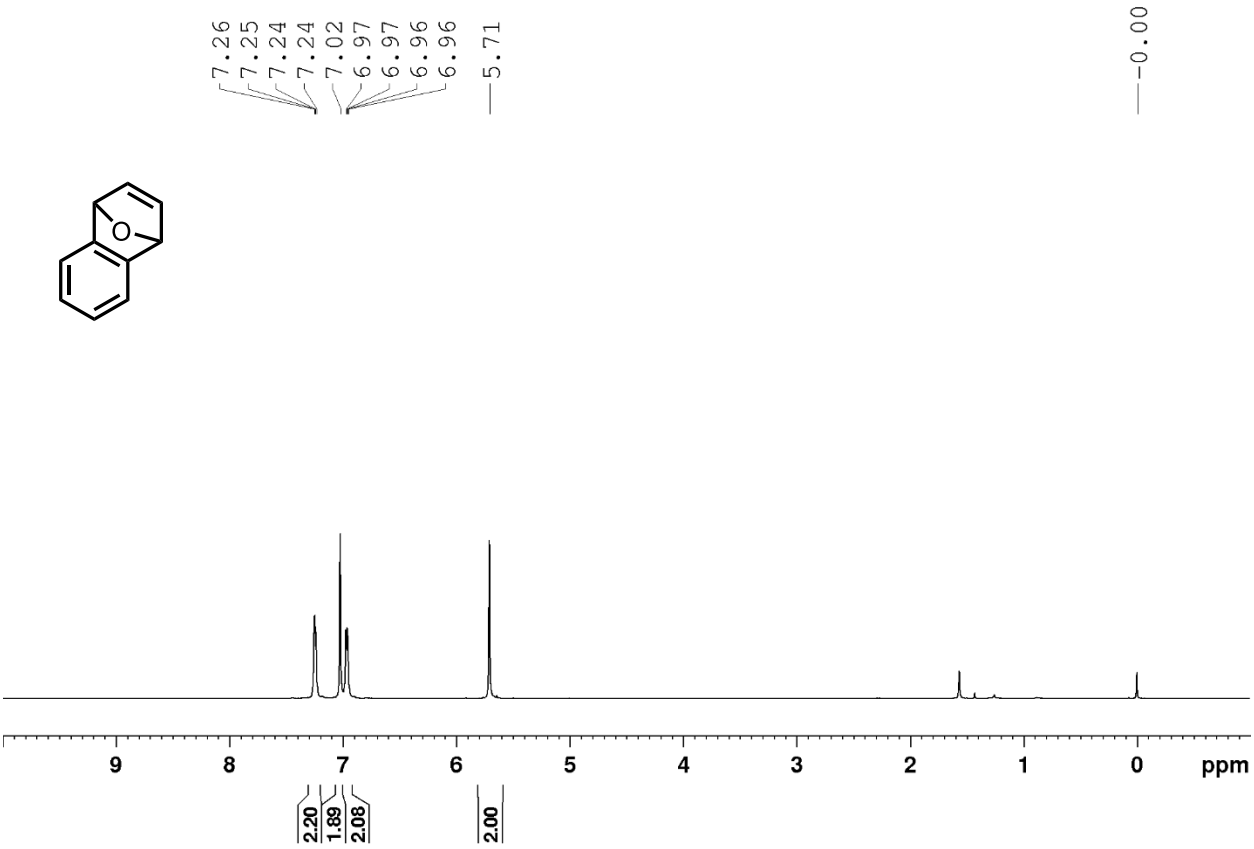
^{1}H NMR spectrum of 3ah in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



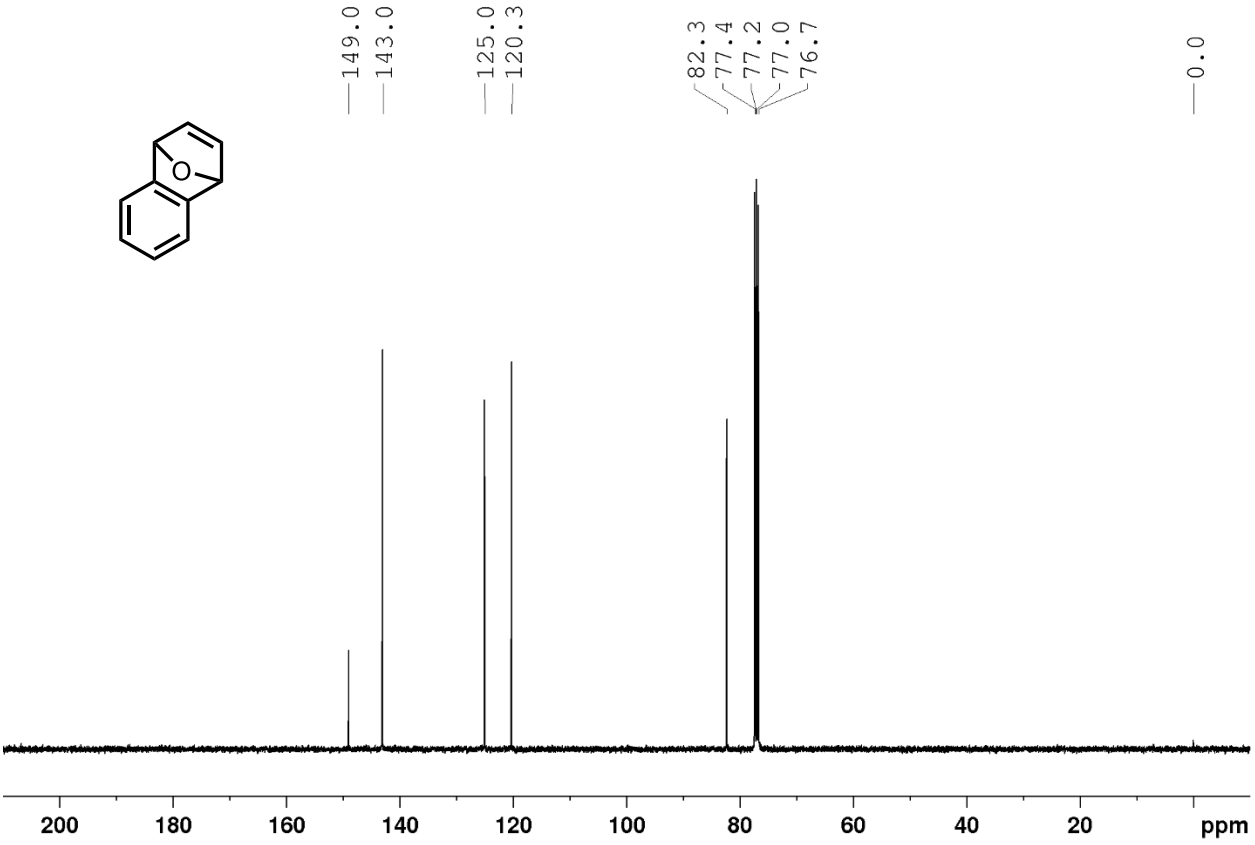
$^{13}C\{^{1}H\}$ NMR spectrum of 3ah in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



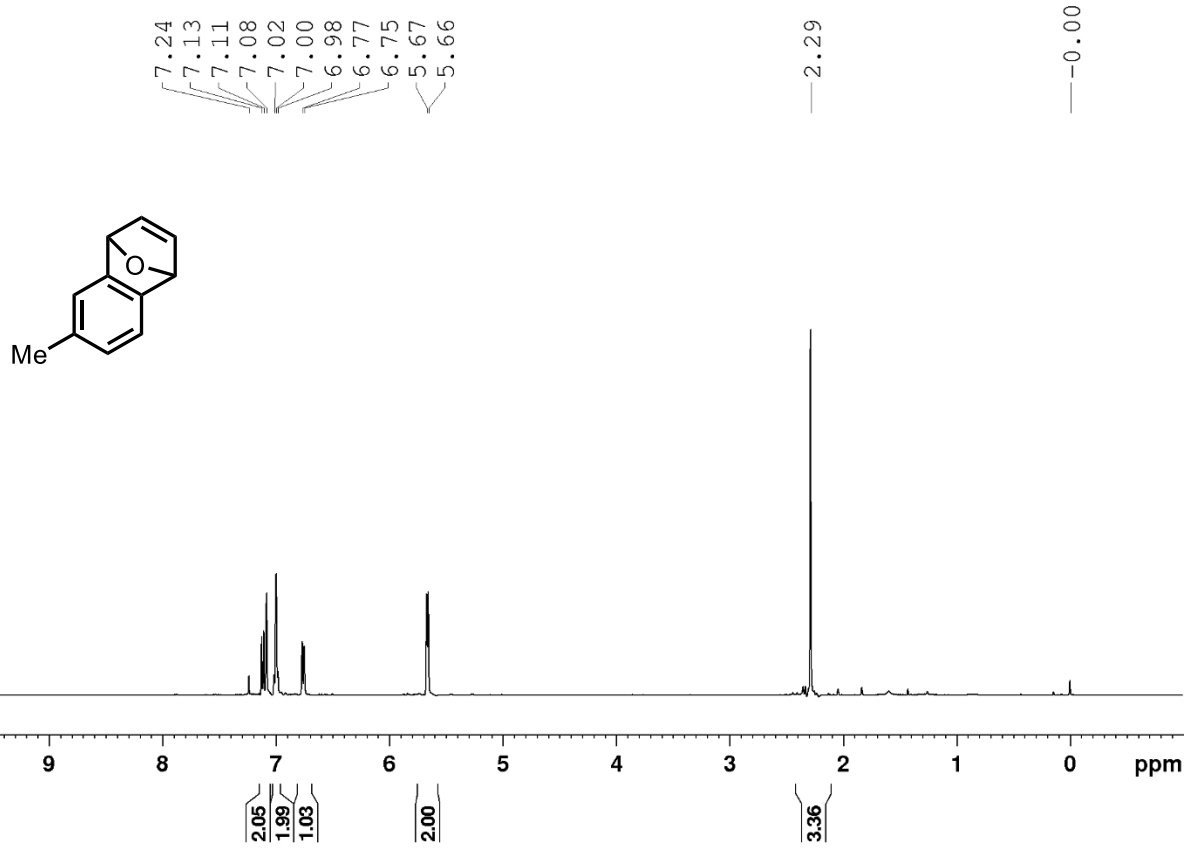
^{1}H NMR spectrum of 3la in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



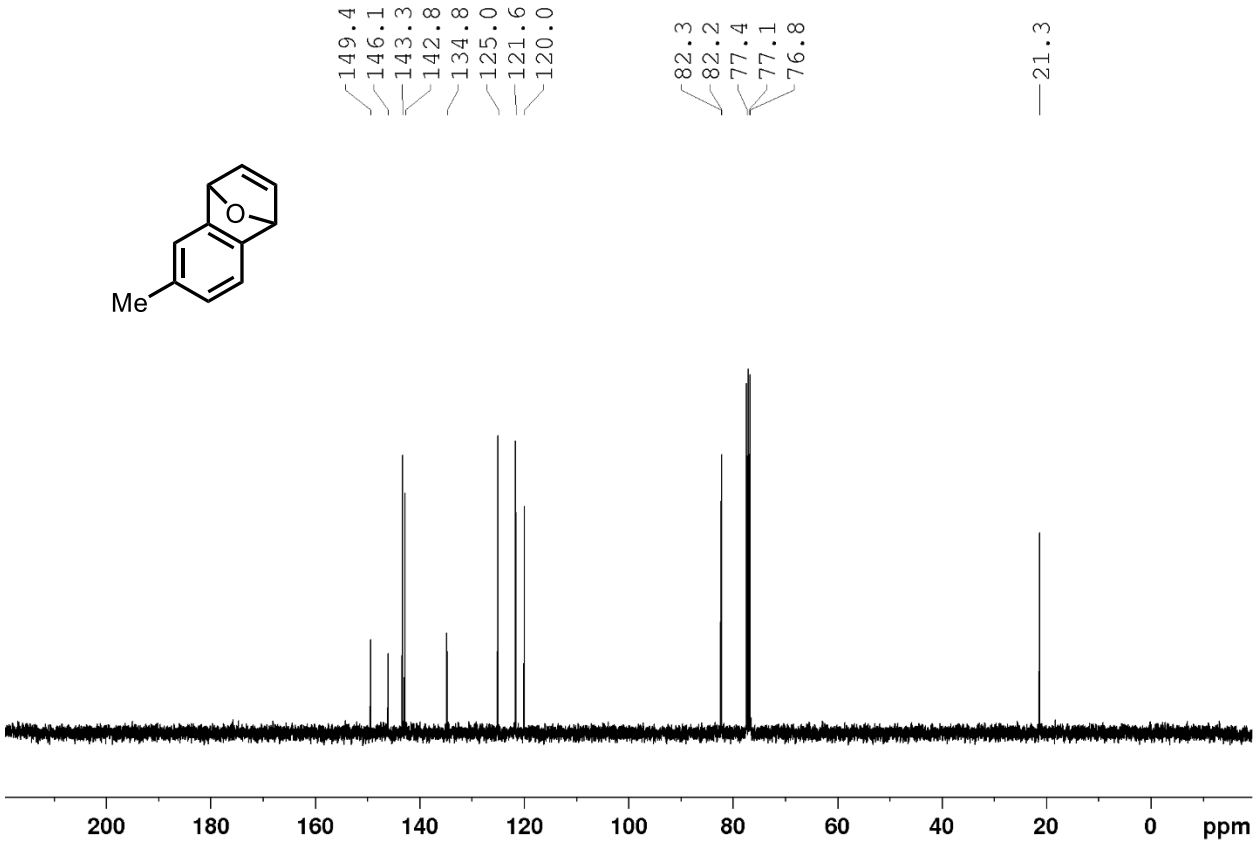
$^{13}C\{^{1}H\}$ NMR spectrum of 3la in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



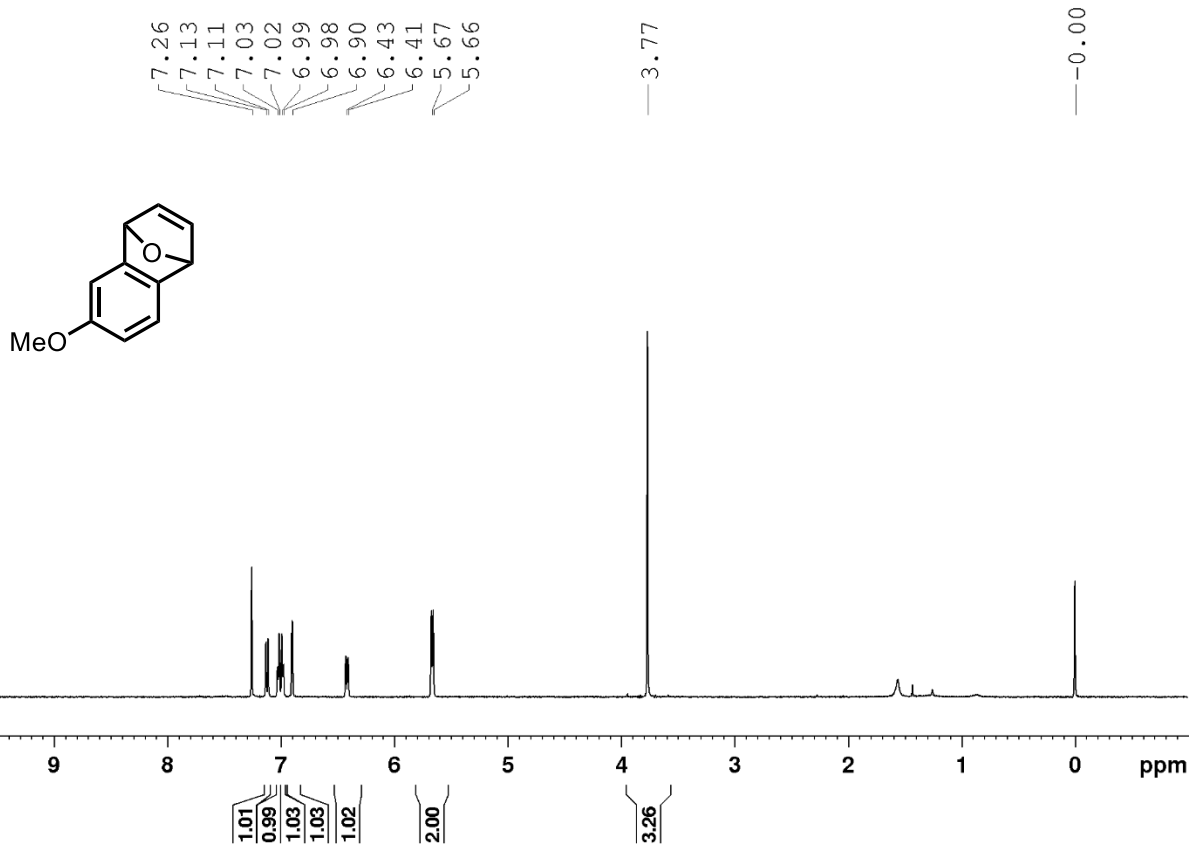
^{1}H NMR spectrum of 3ma in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



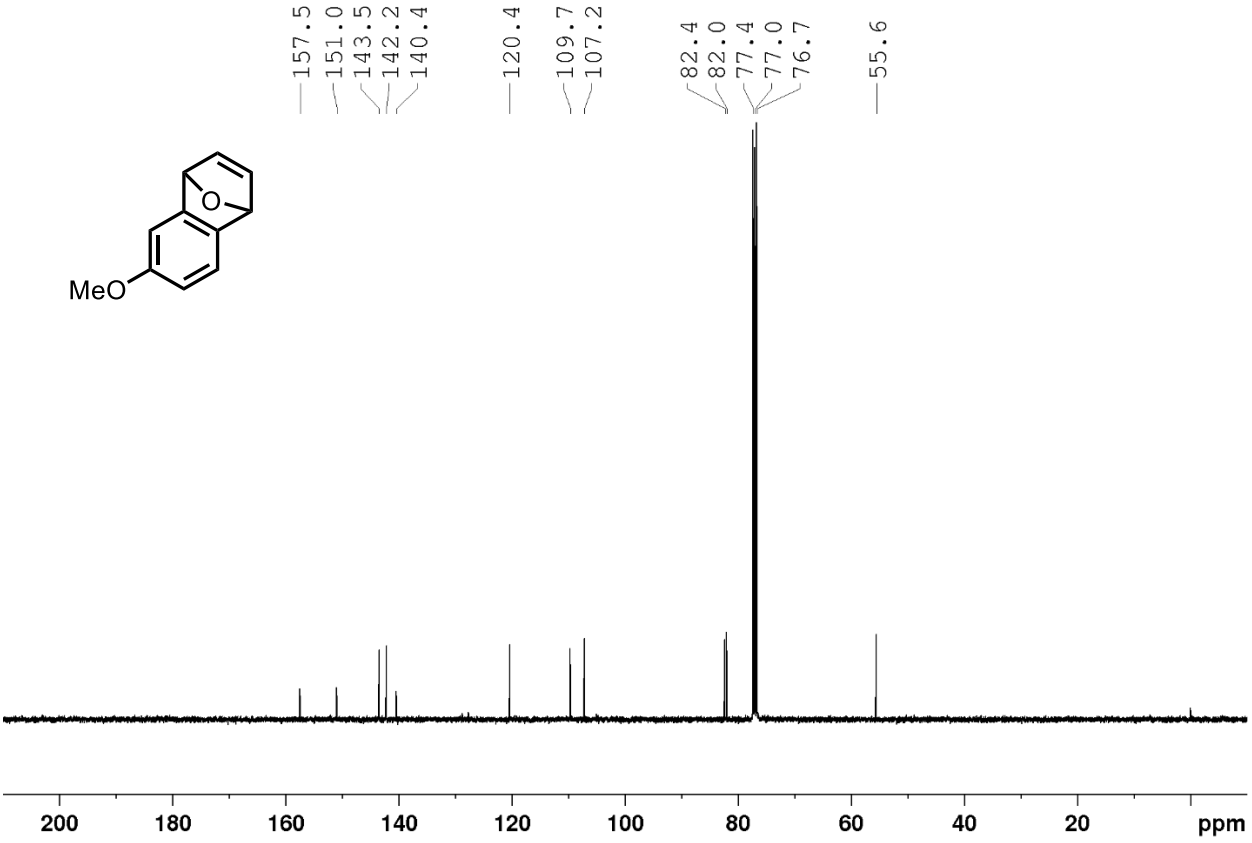
$^{13}C\{^{1}H\}$ NMR spectrum of 3ma in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



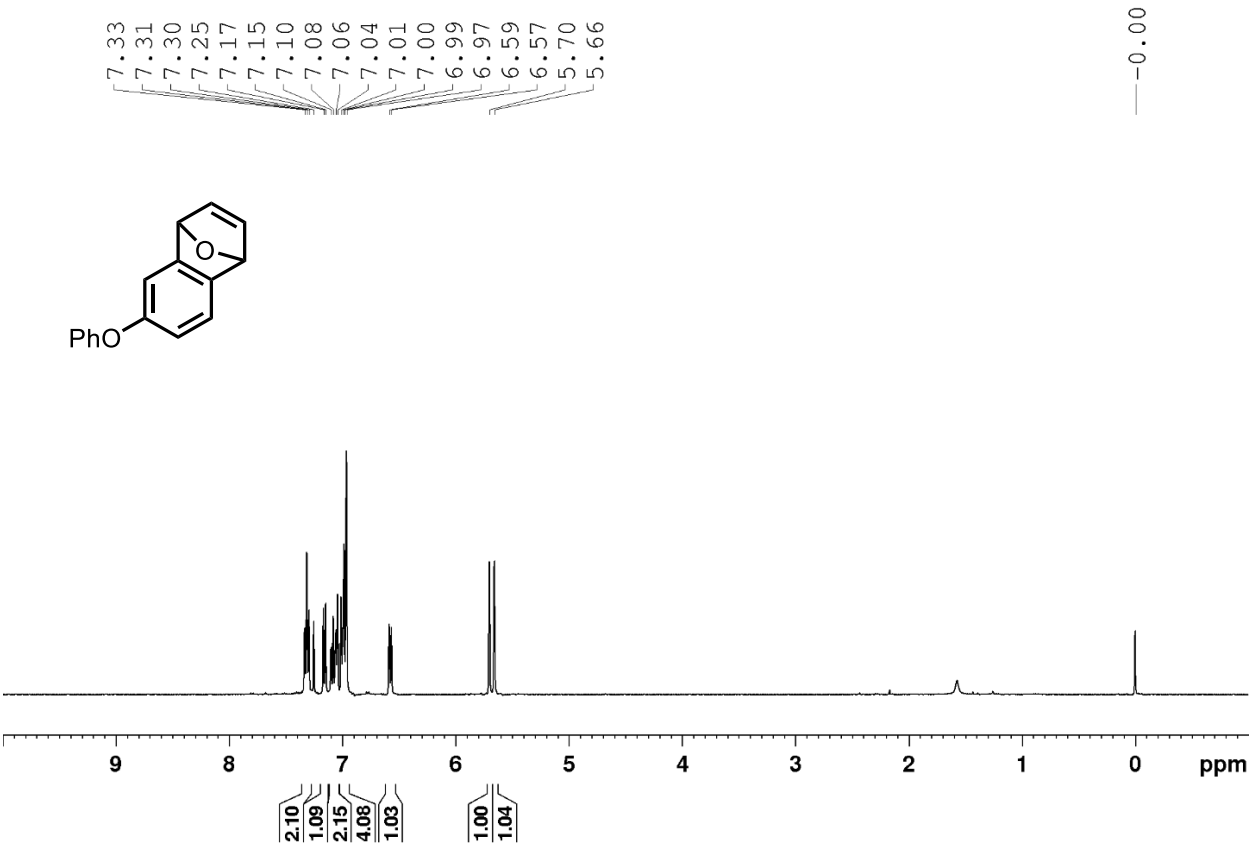
^{1}H NMR spectrum of 3na in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



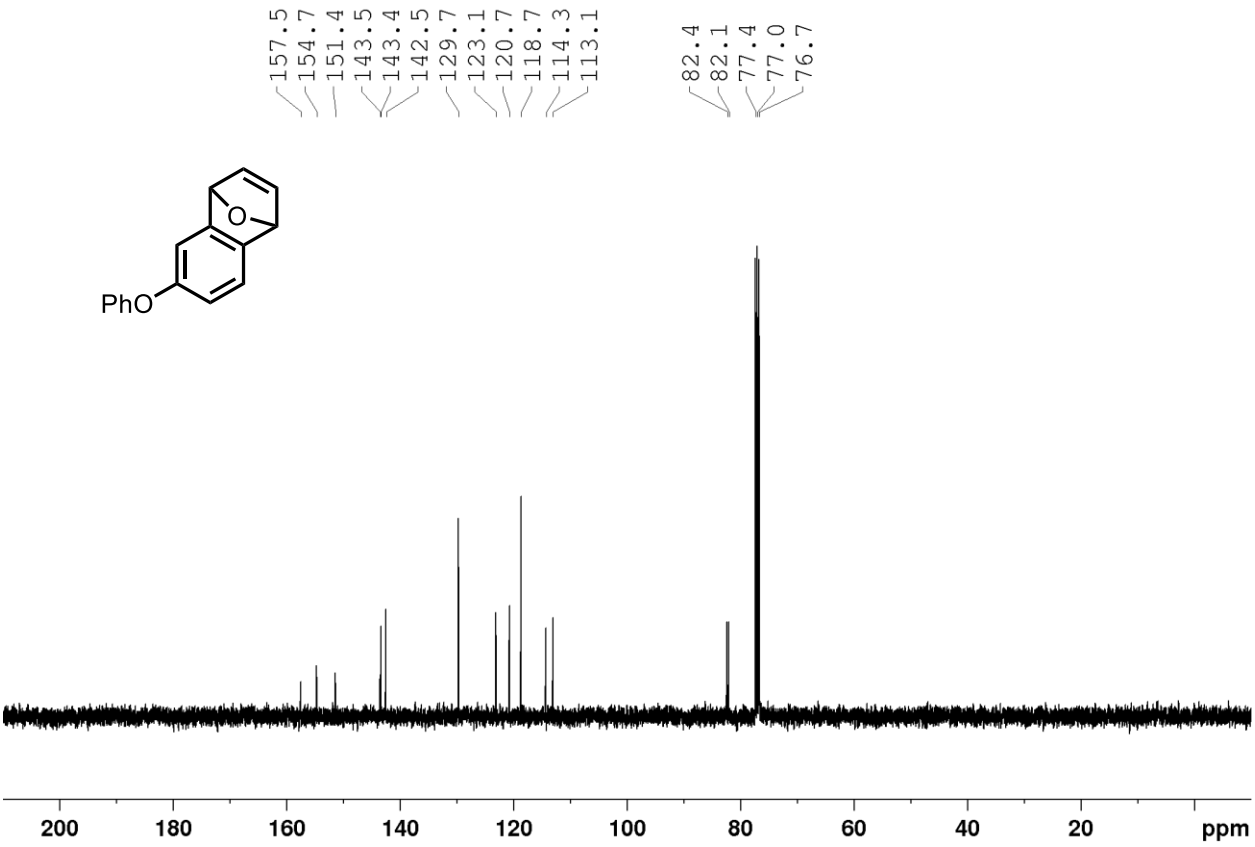
$^{13}C\{^{1}H\}$ NMR spectrum of 3na in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



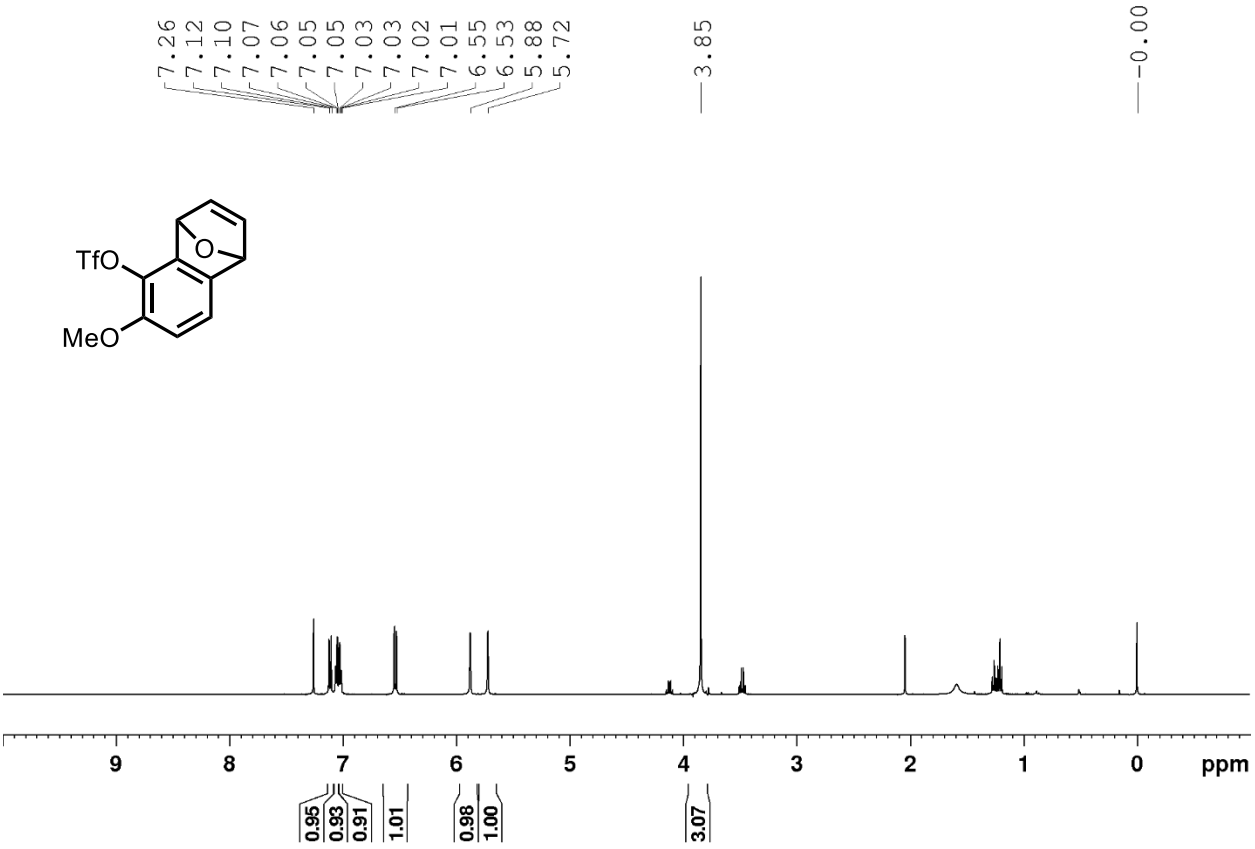
^{1}H NMR spectrum of 3pa in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



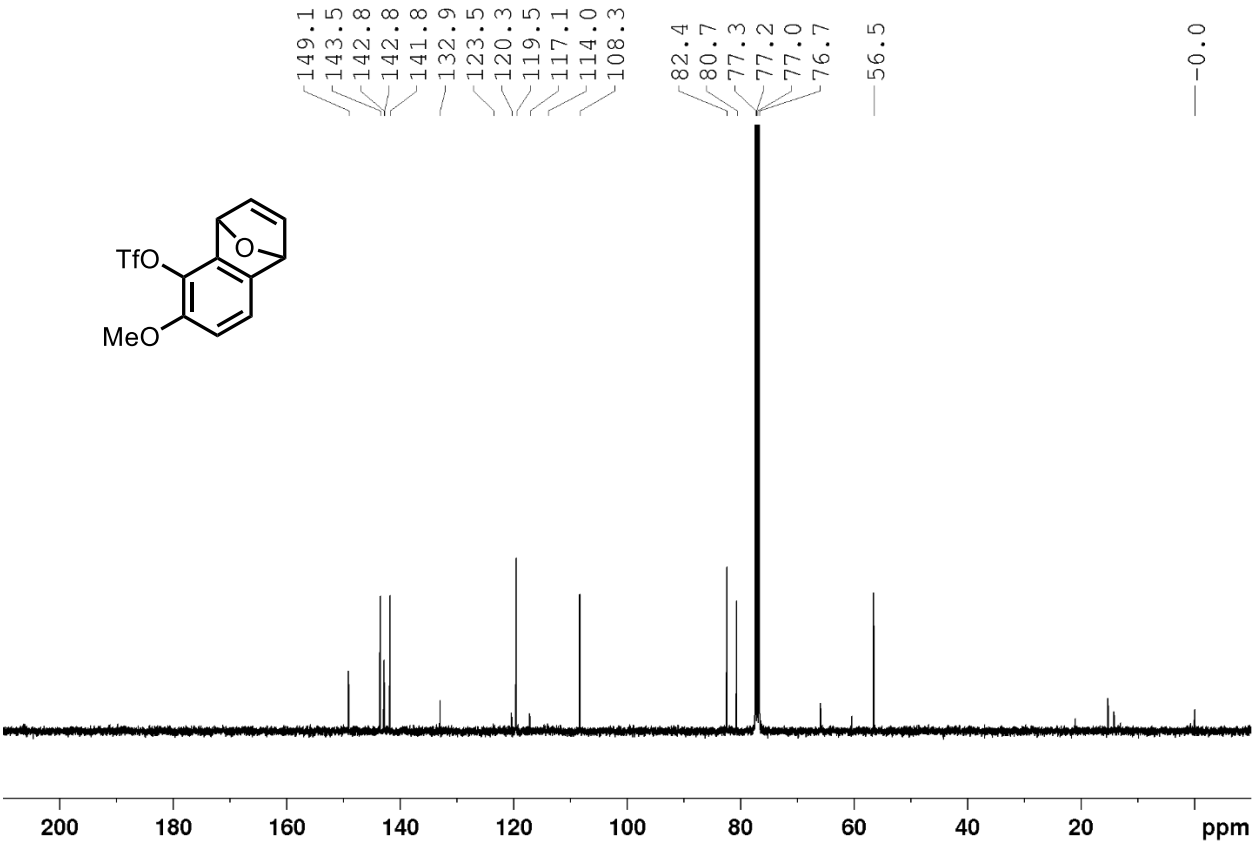
$^{13}C\{^{1}H\}$ NMR spectrum of 3pa in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



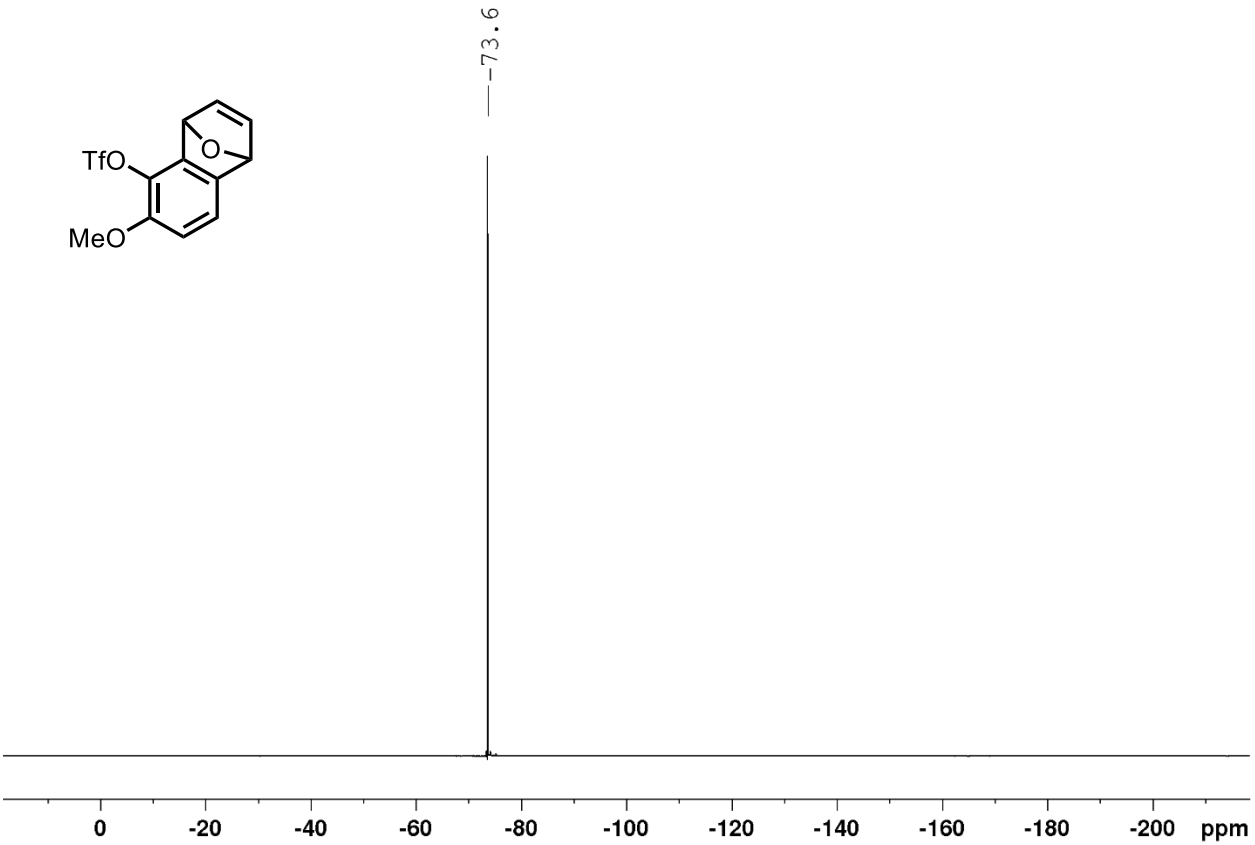
^{1}H NMR spectrum of 3qa in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



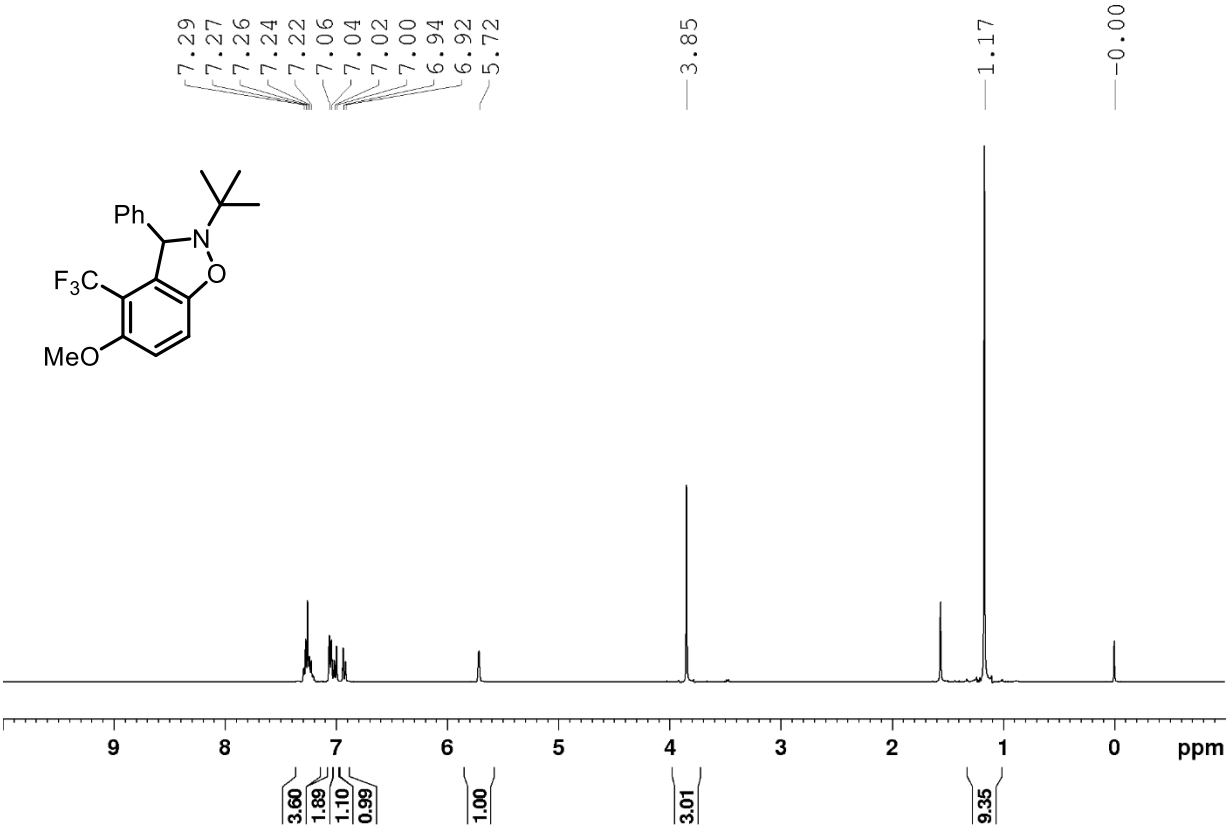
$^{13}C\{^{1}H\}$ NMR spectrum of 3qa in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



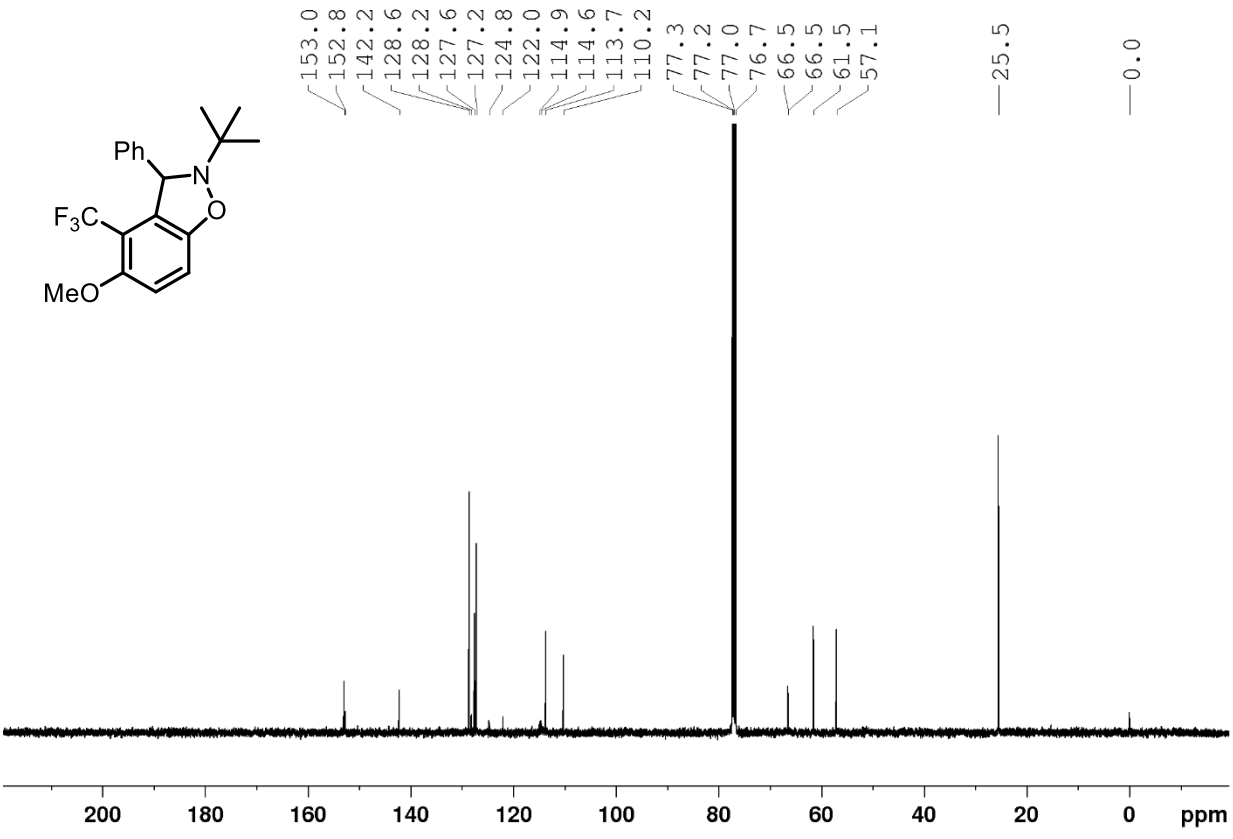
$^{19}F\{^{1}H\}$ NMR spectrum of 3qa in $CDCl_3$ with 1% v/v TMS at 376 MHz at 298



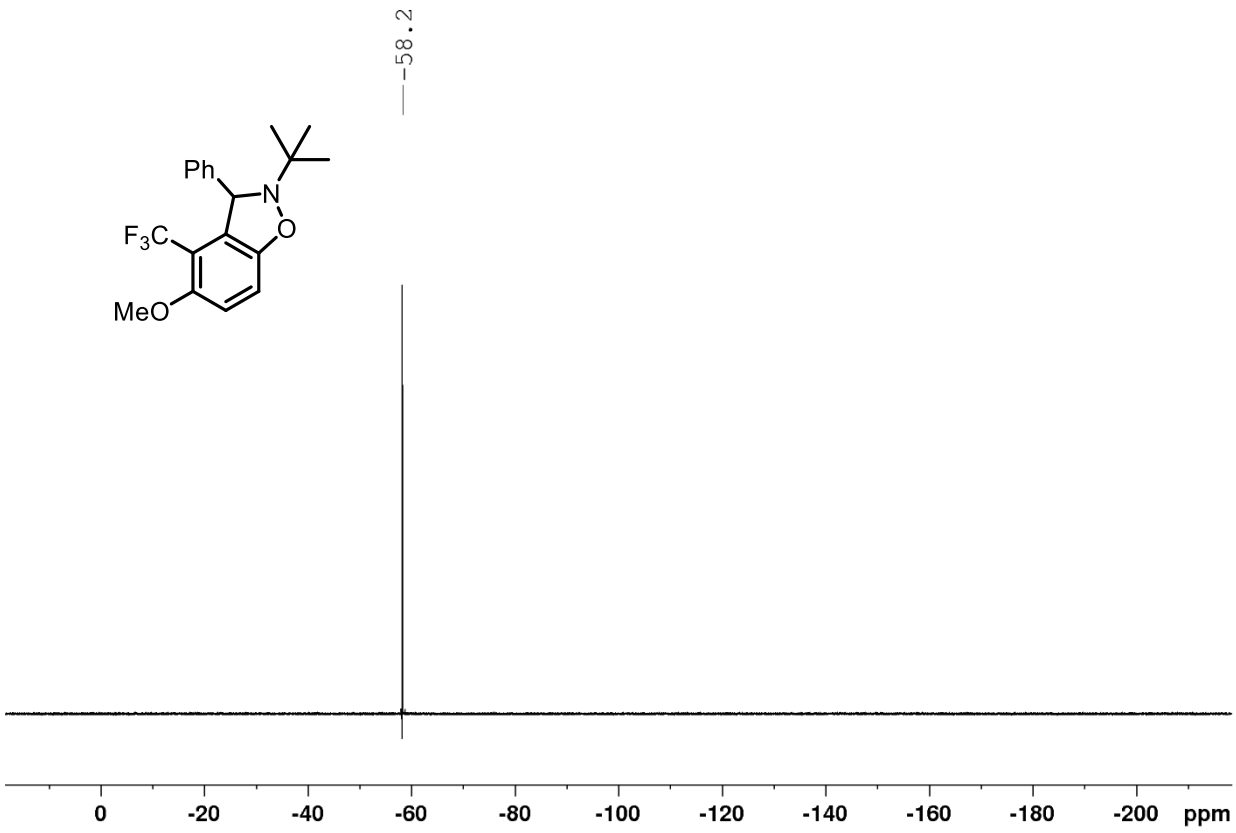
^{1}H NMR spectrum of 3rc in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



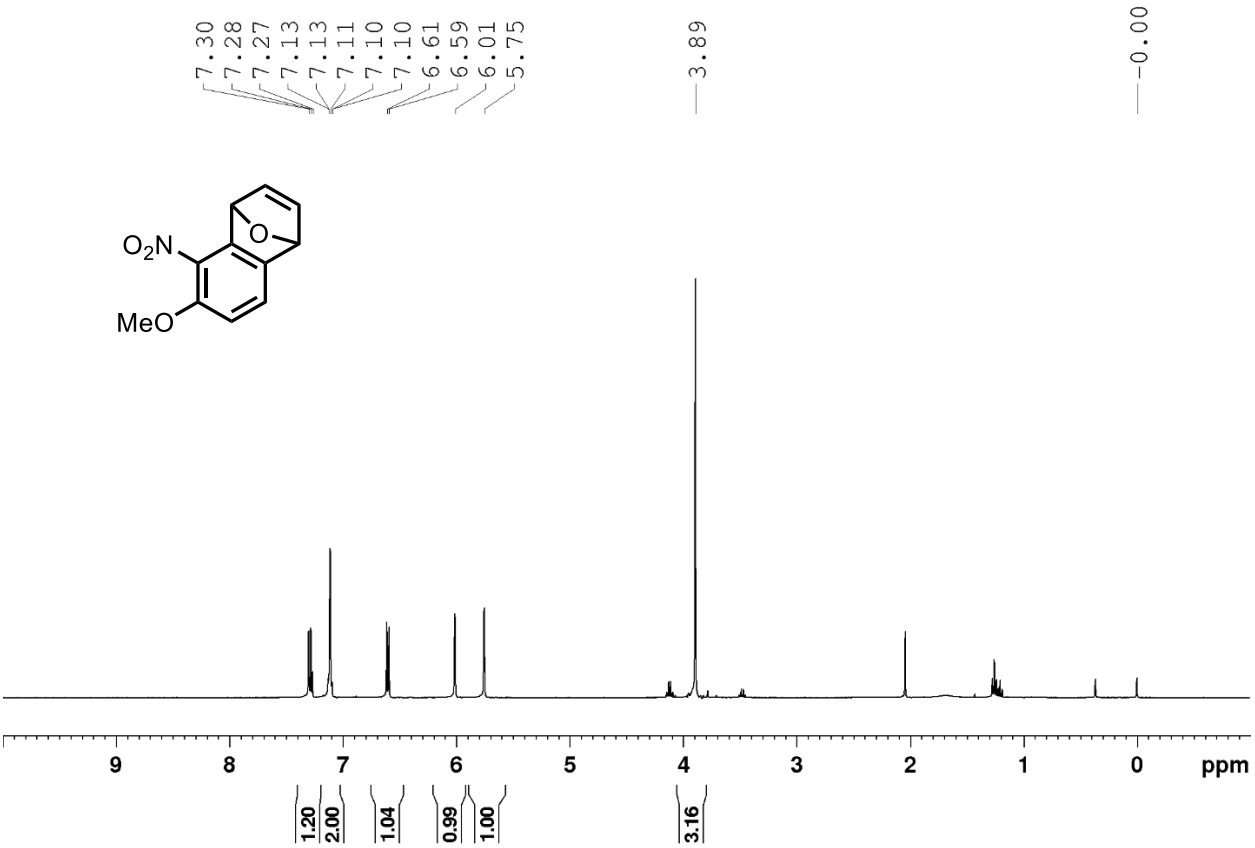
^{13}C{^{1}H} NMR spectrum of 3rc in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



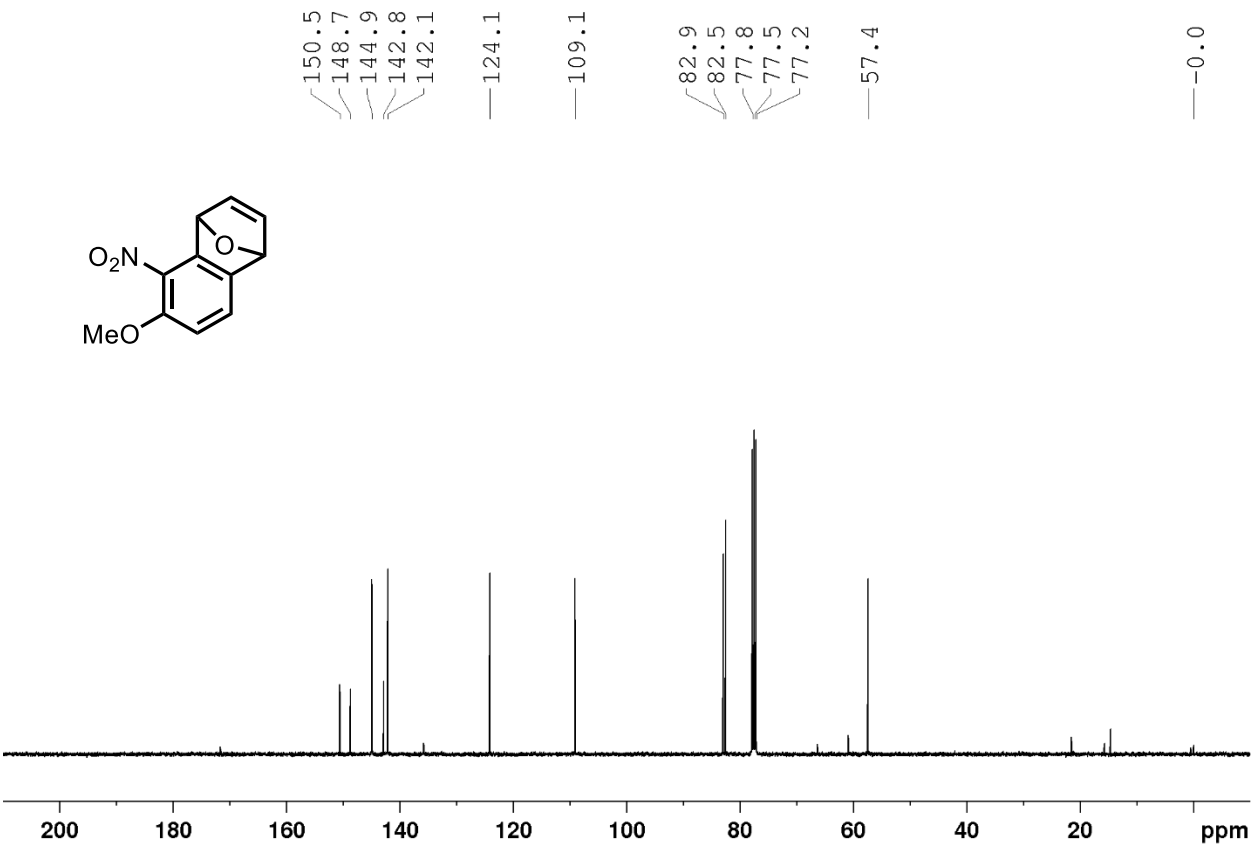
$^{19}F\{^{1}H\}$ NMR spectrum of 3qa in $CDCl_3$ with 1% v/v TMS at 376 MHz at 298 K



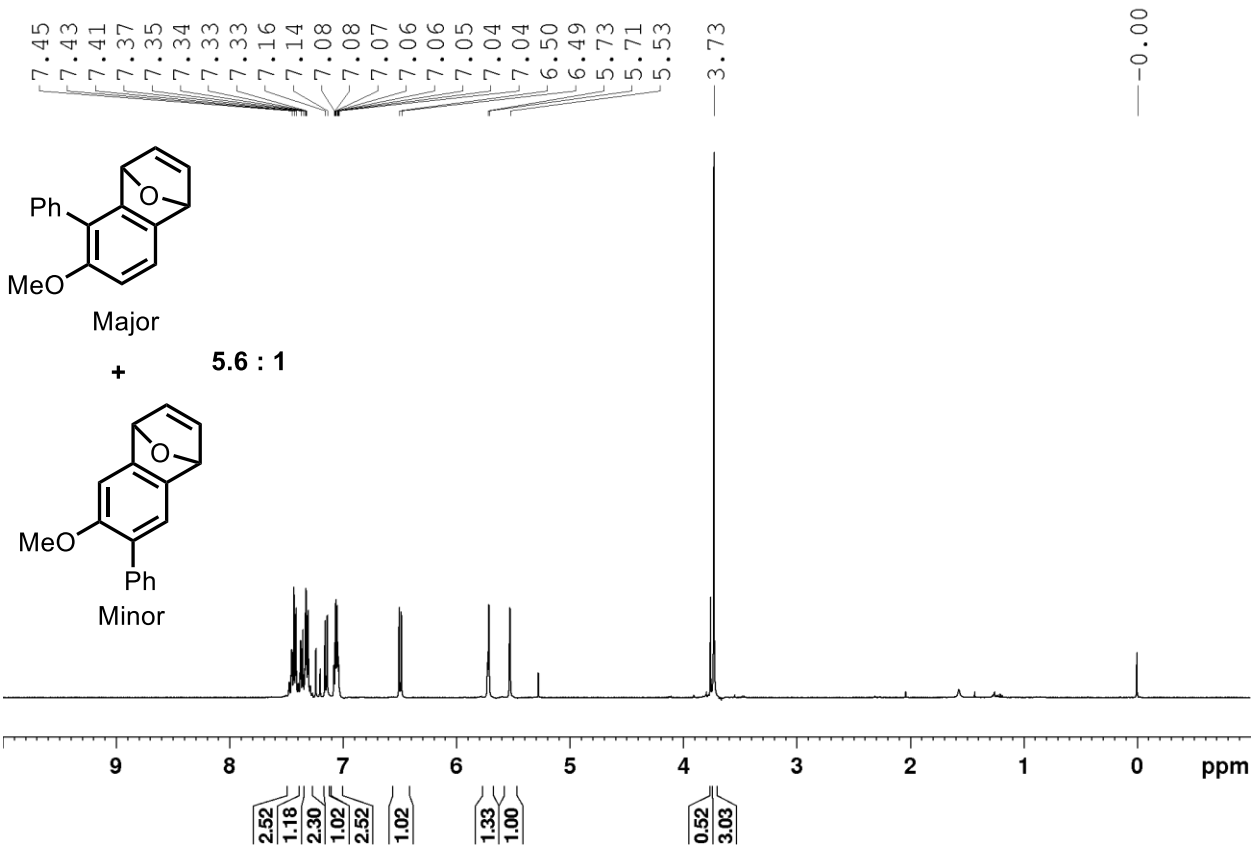
^{1}H NMR spectrum of 3ta in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



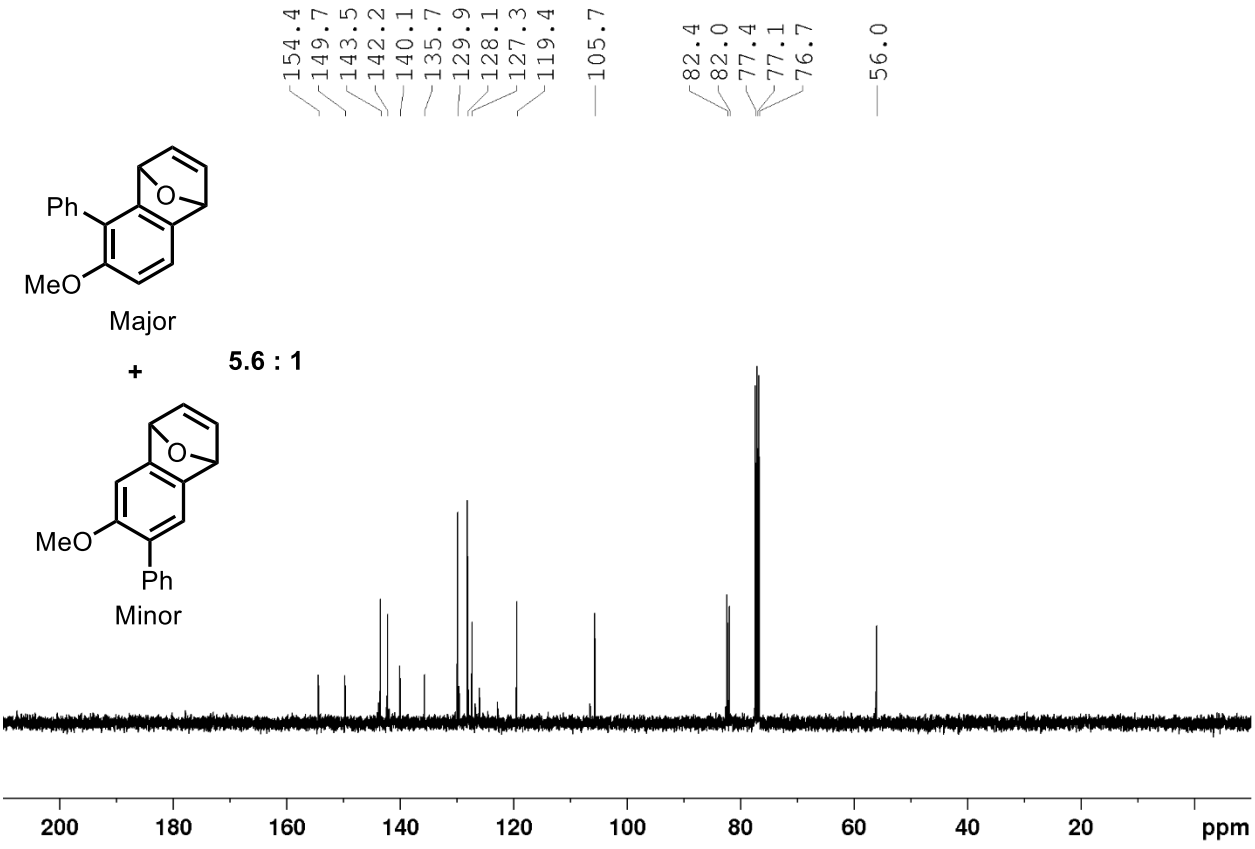
^{13}C{^{1}H} NMR spectrum of 3ta in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



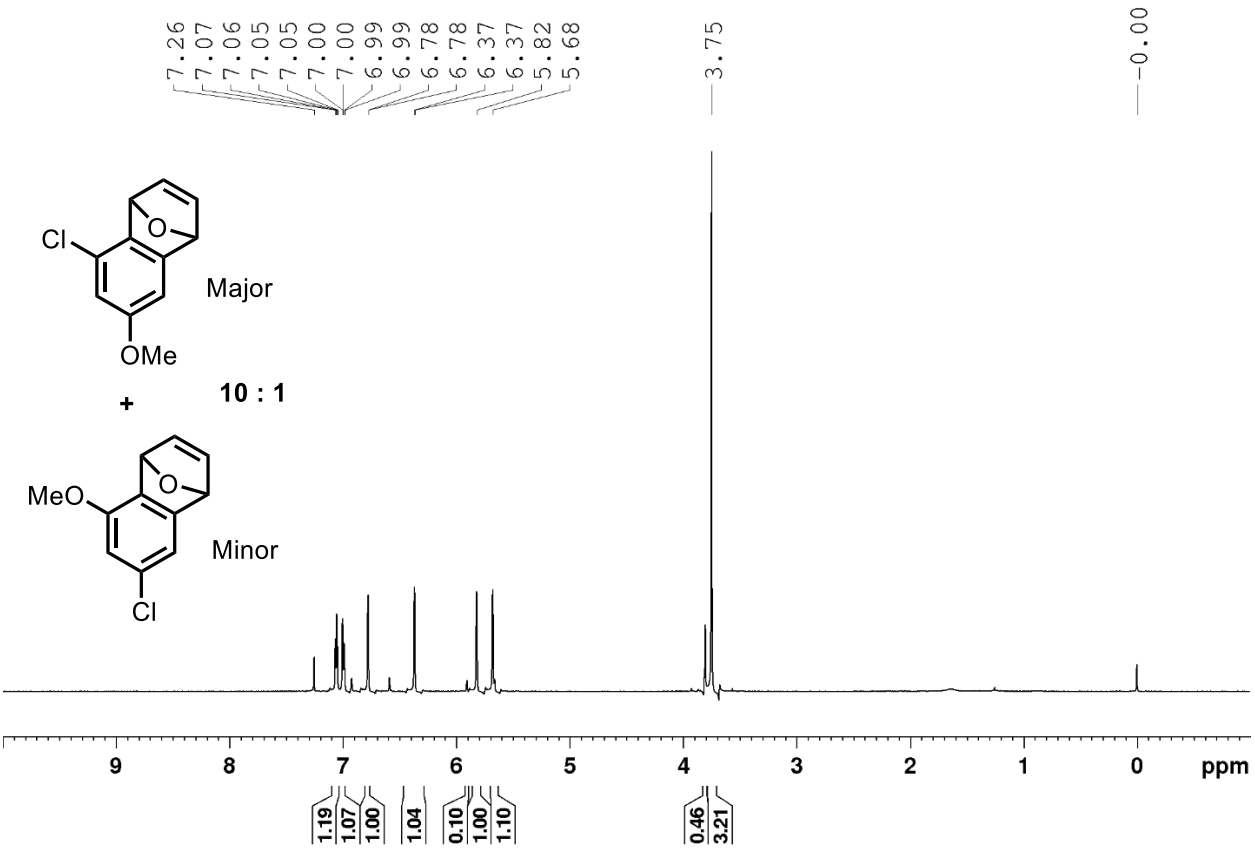
^{1}H NMR spectrum of 3ua in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



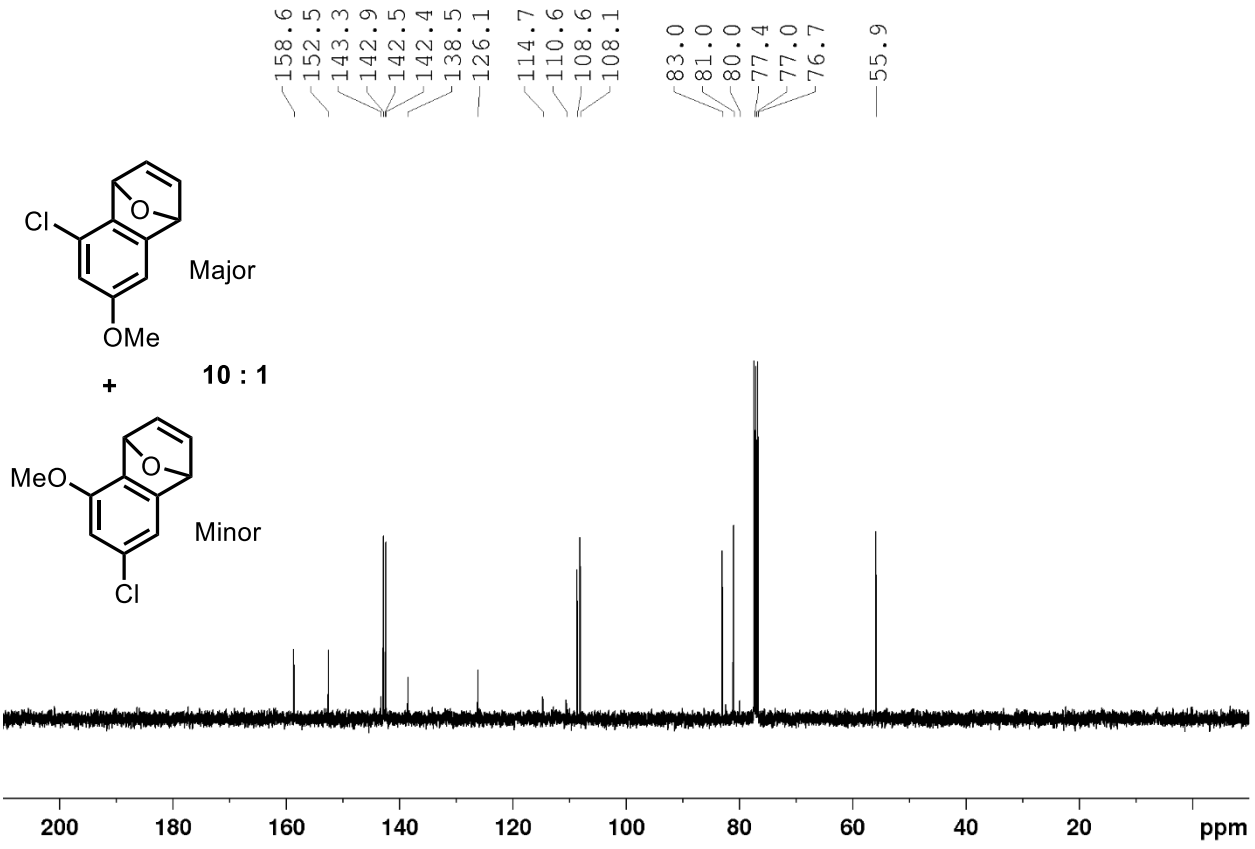
^{13}C{^{1}H} NMR spectrum of 3ua in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



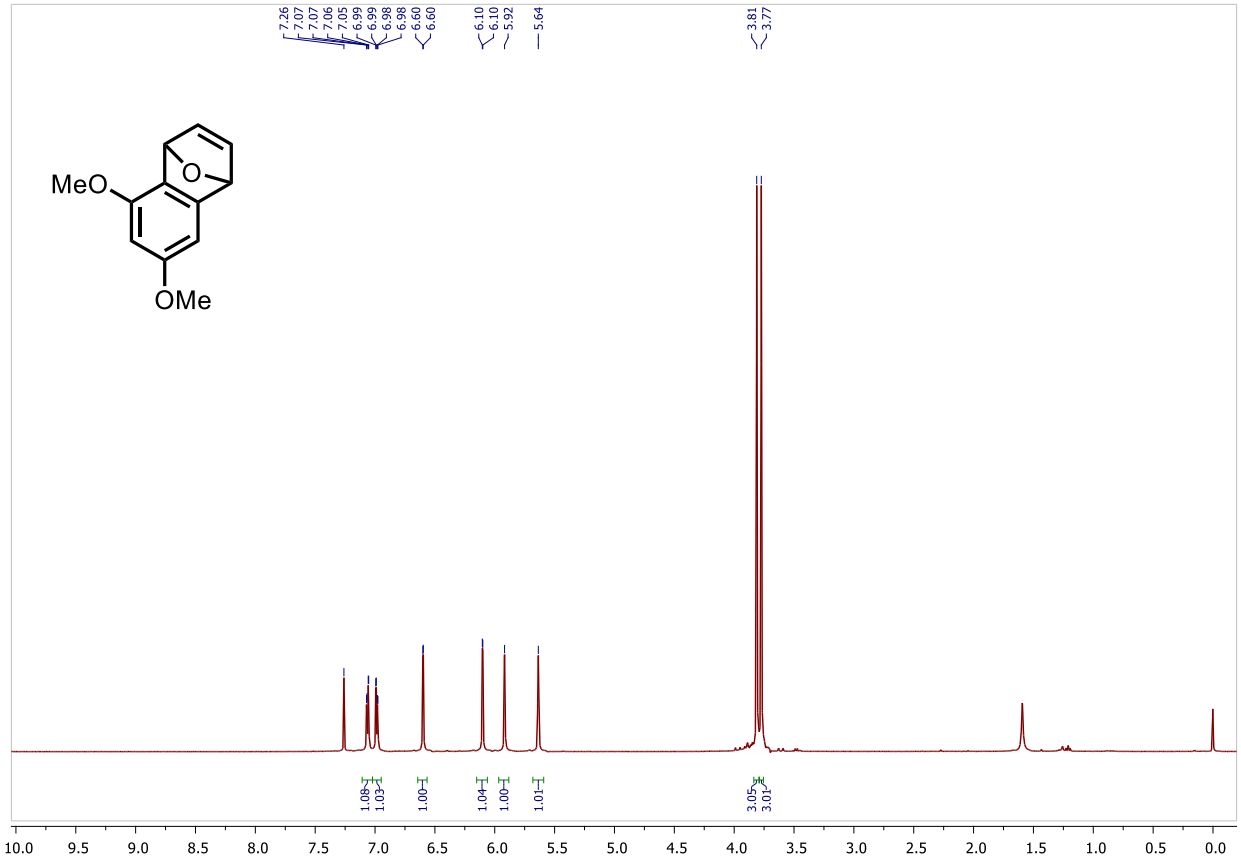
^{1}H NMR spectrum of 3va in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



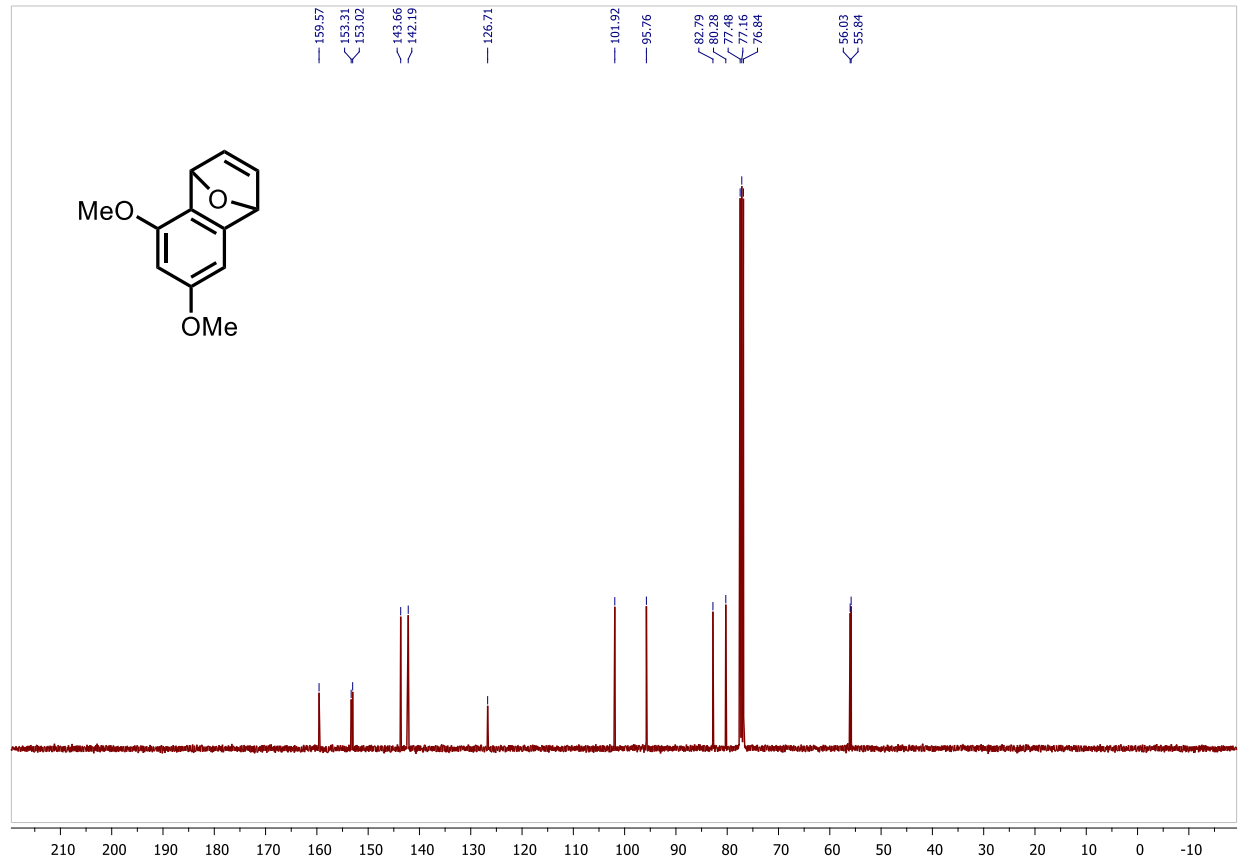
^{13}C{^{1}H} NMR spectrum of 3va in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



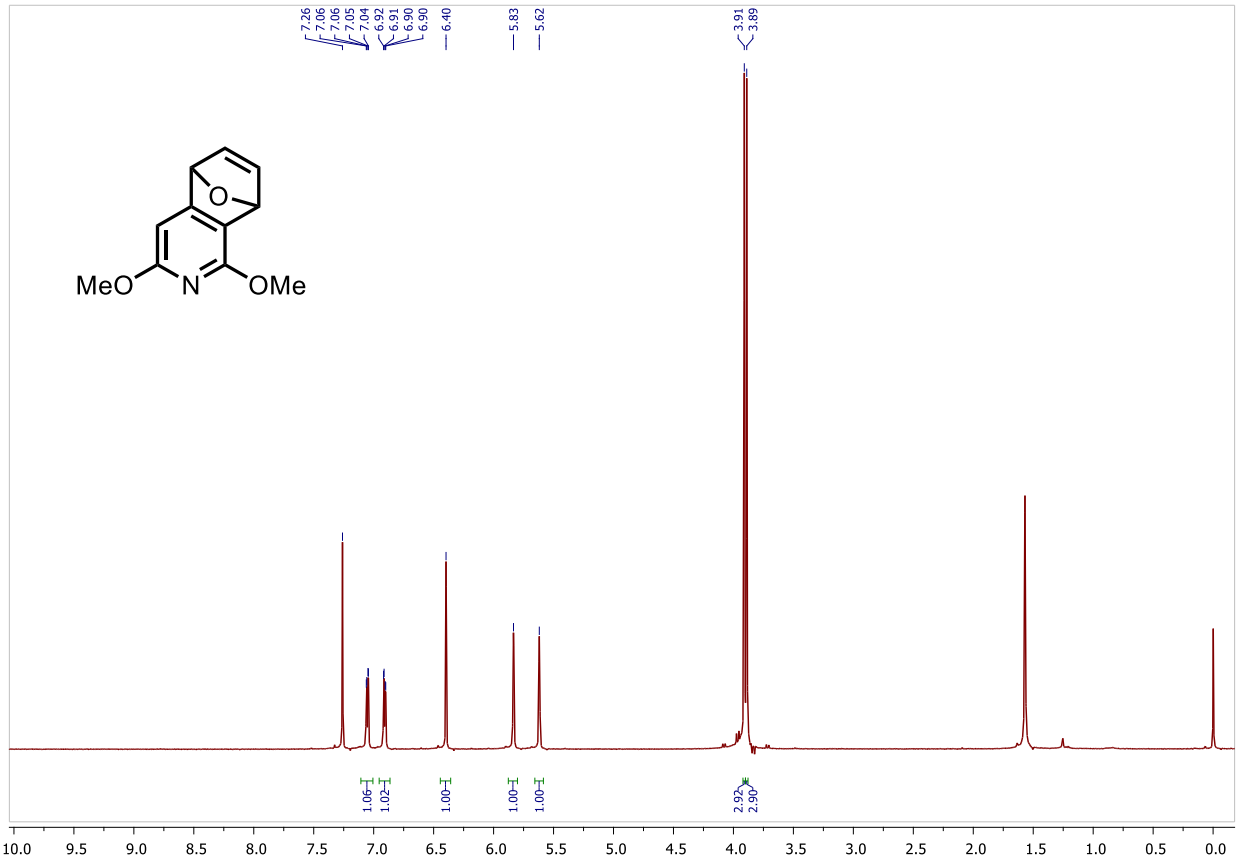
^{1}H NMR spectrum of 3oa in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



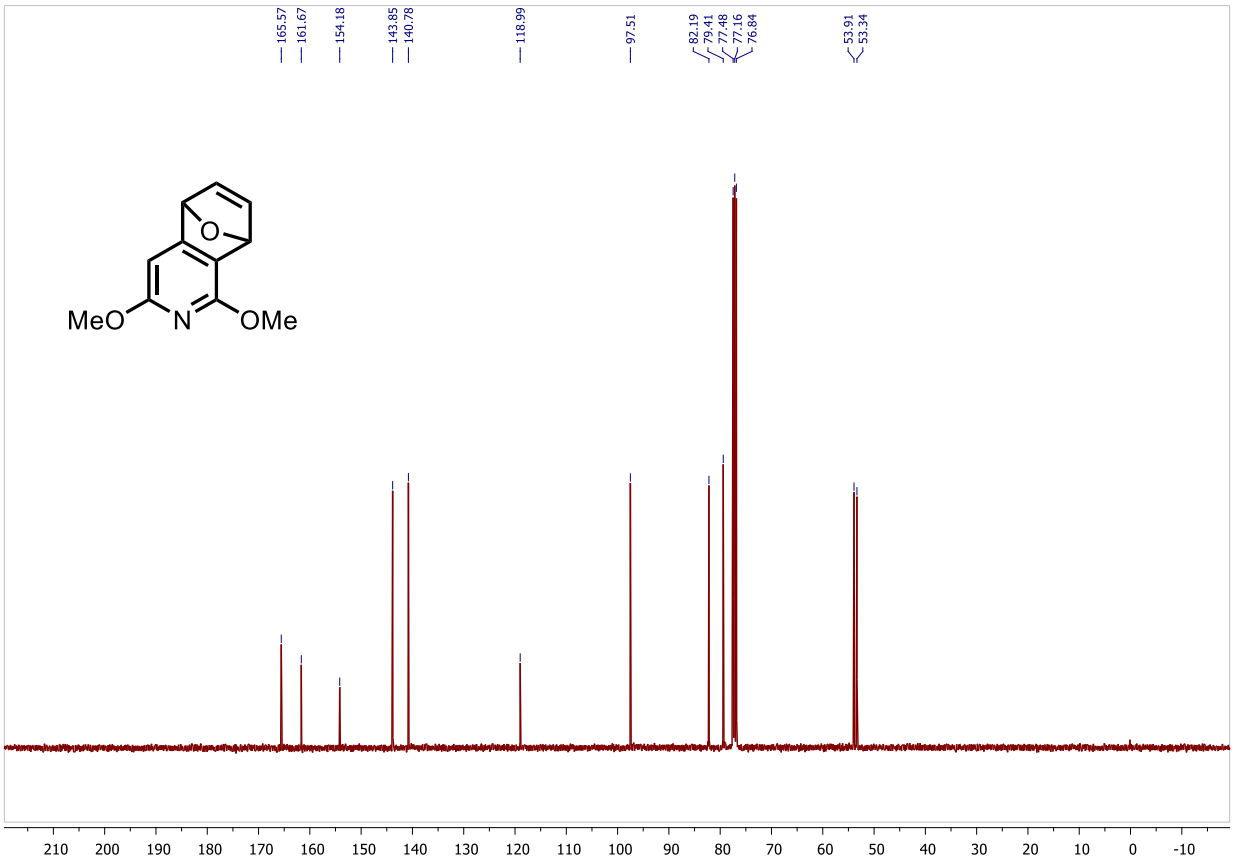
^{13}C{^{1}H} NMR spectrum of 3oa in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



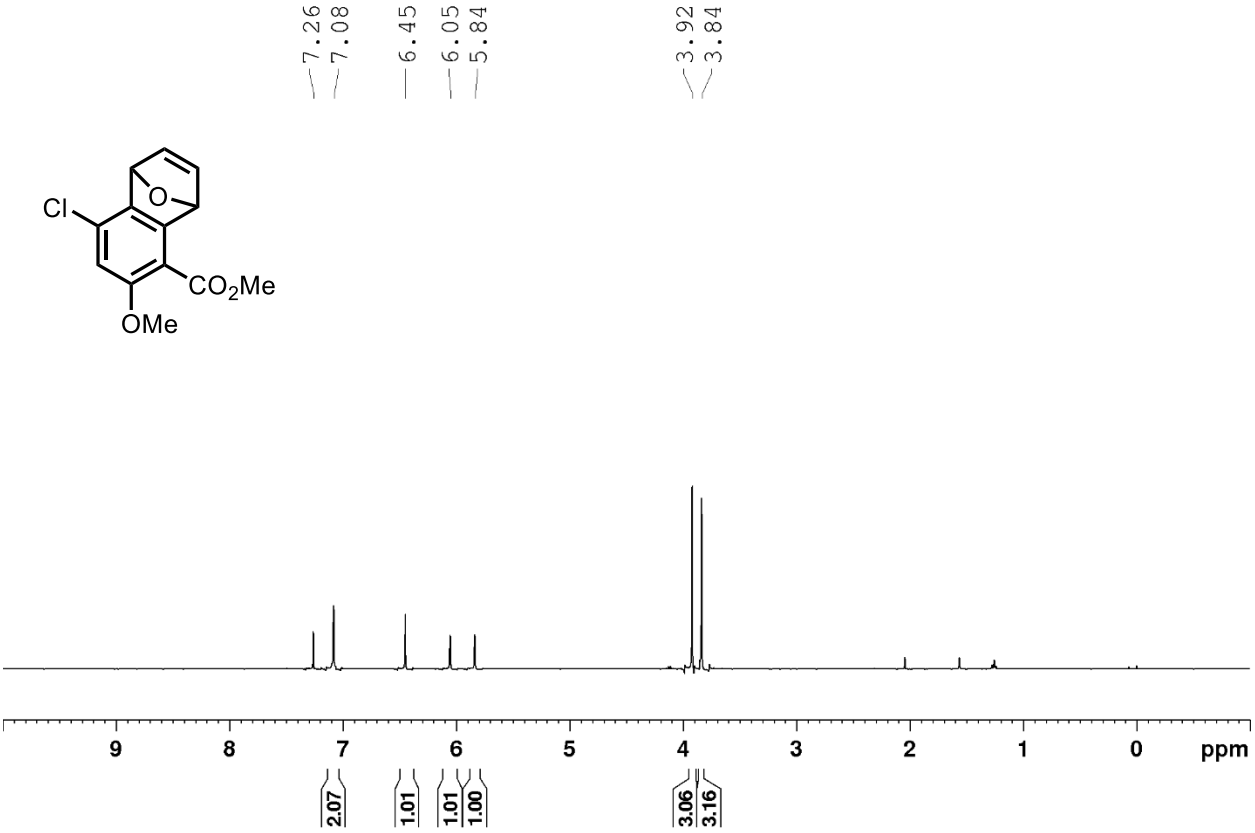
^{1}H NMR spectrum of 3va in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



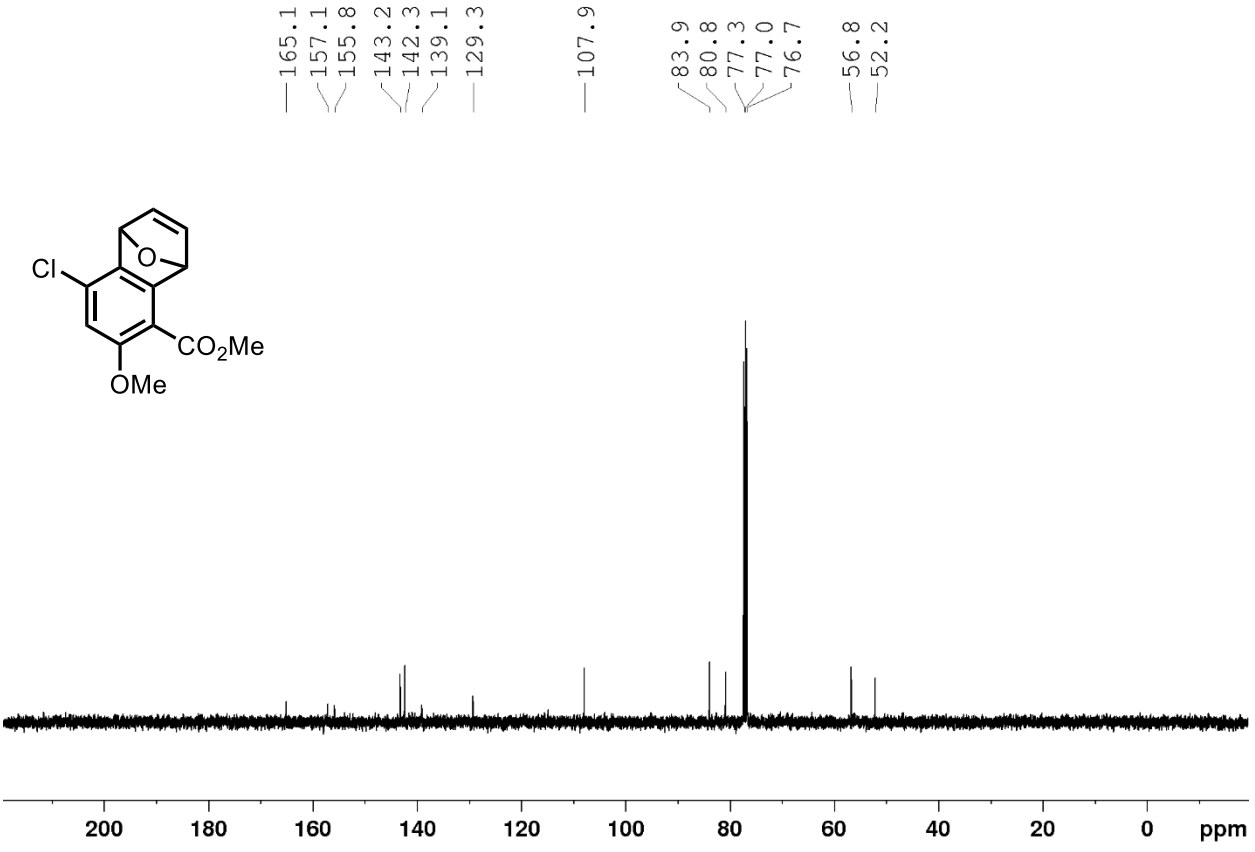
^{13}C{^{1}H} NMR spectrum of 3va in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



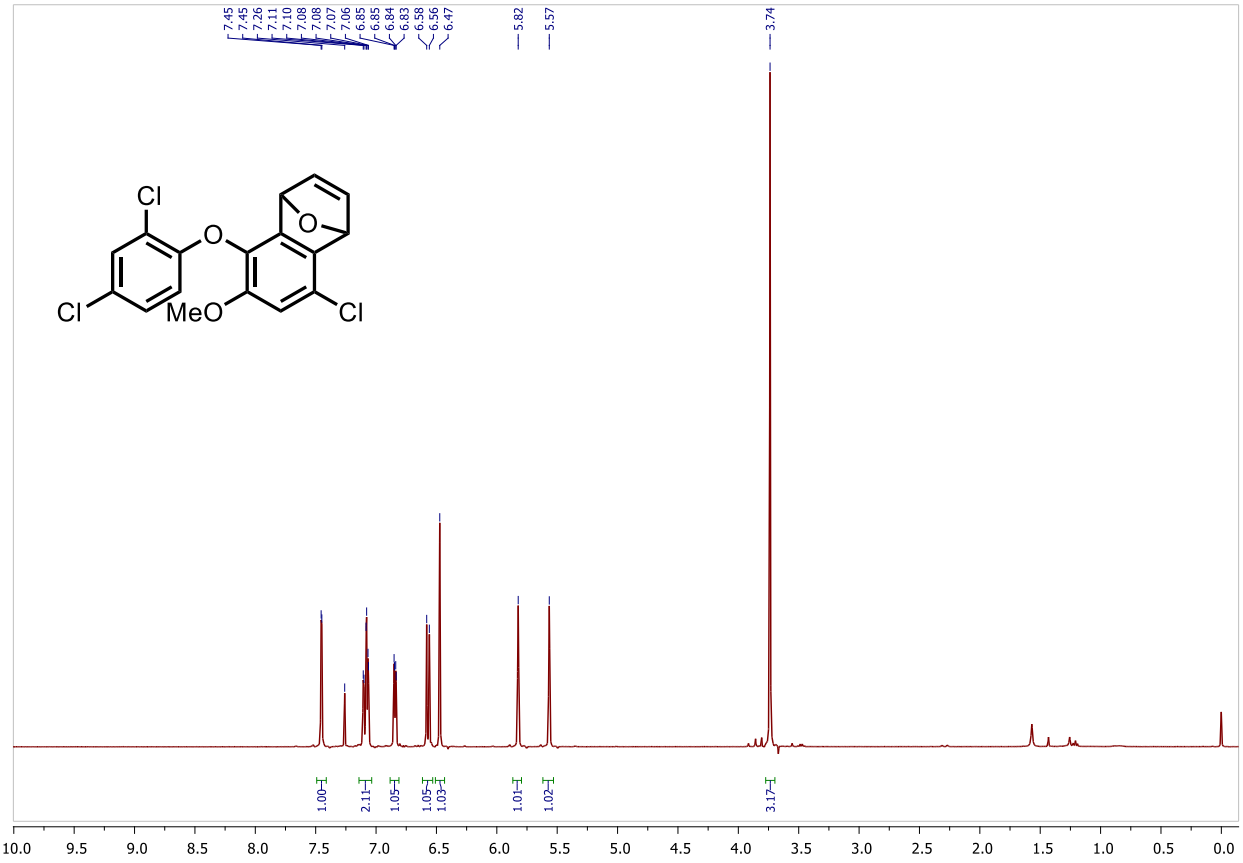
^{1}H NMR spectrum of 3wa in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



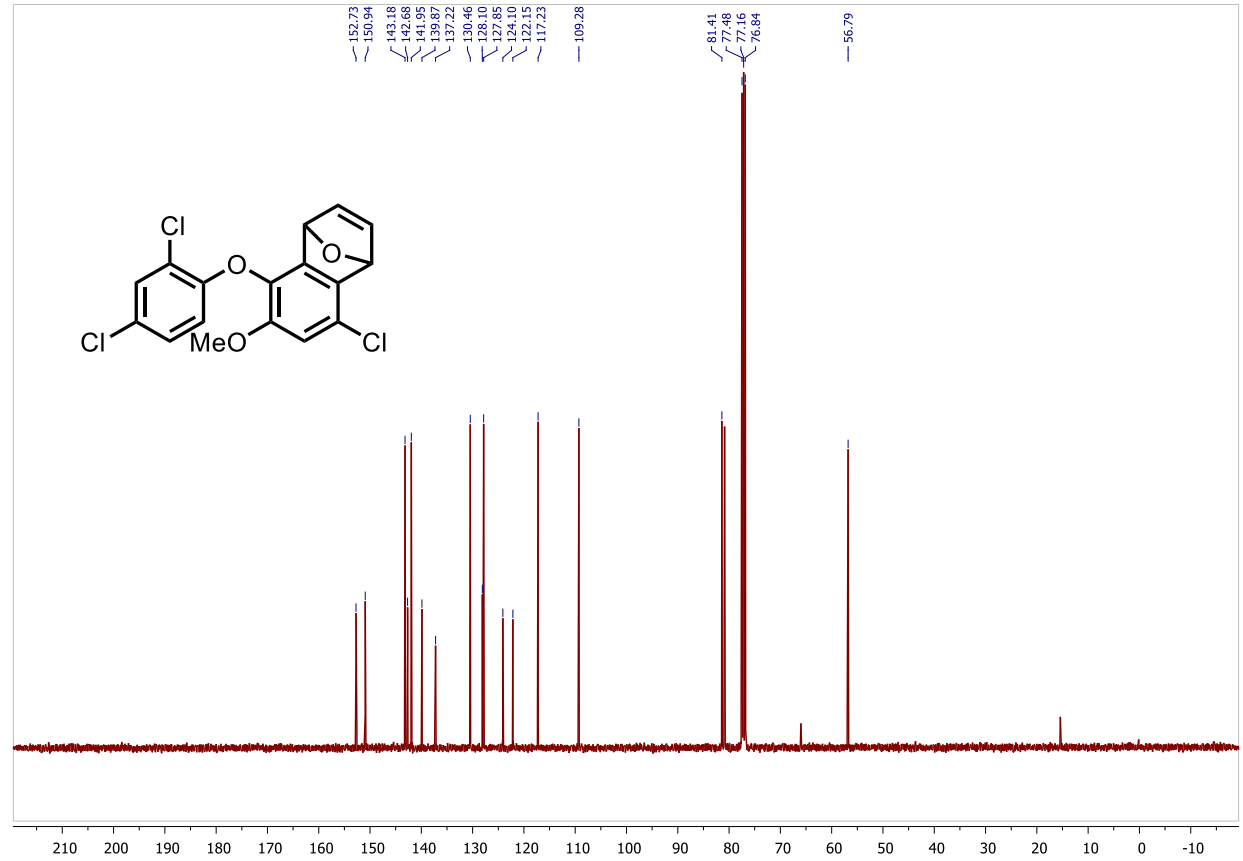
^{13}C{^{1}H} NMR spectrum of 3wa in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



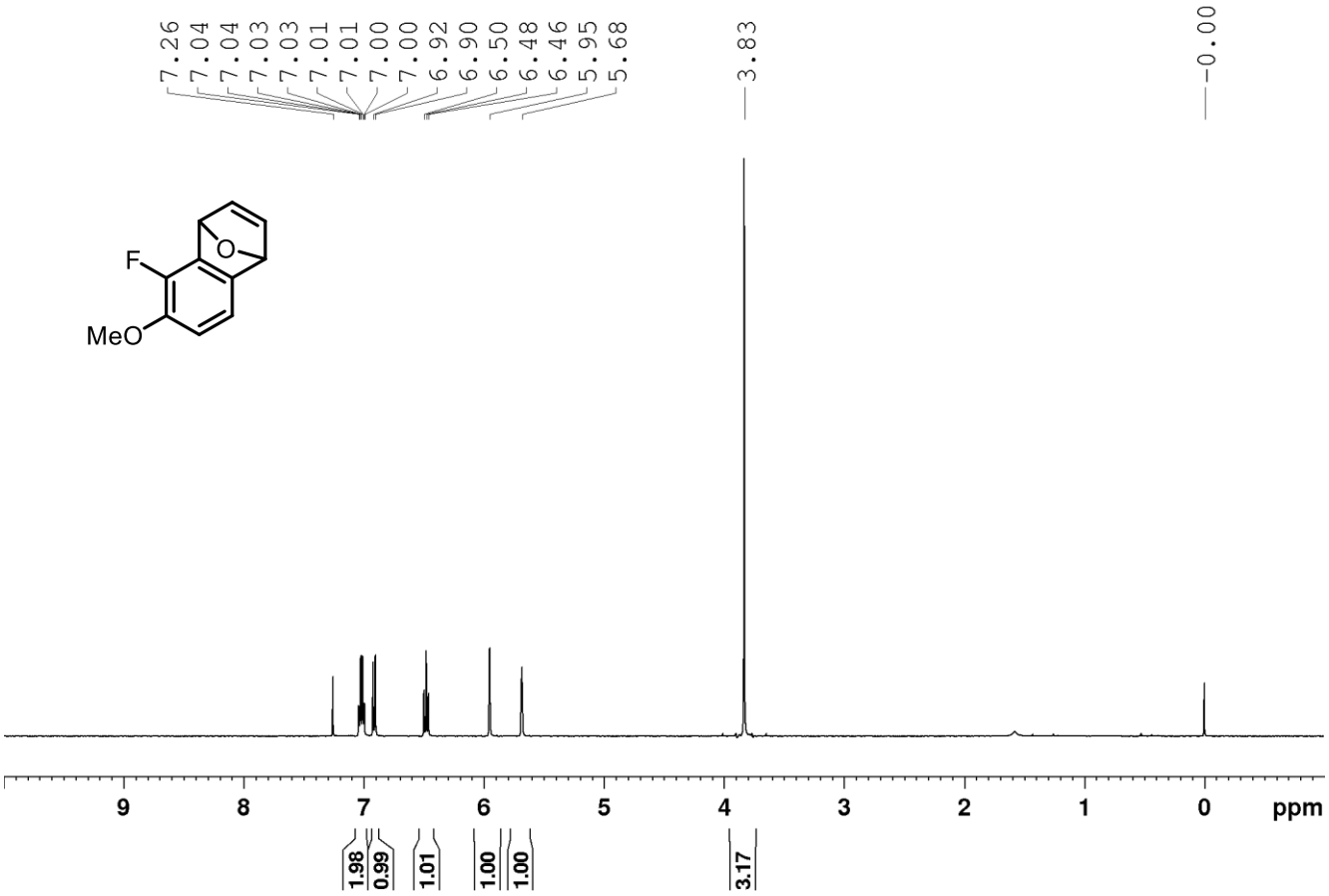
^{1}H NMR spectrum of 3xa in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



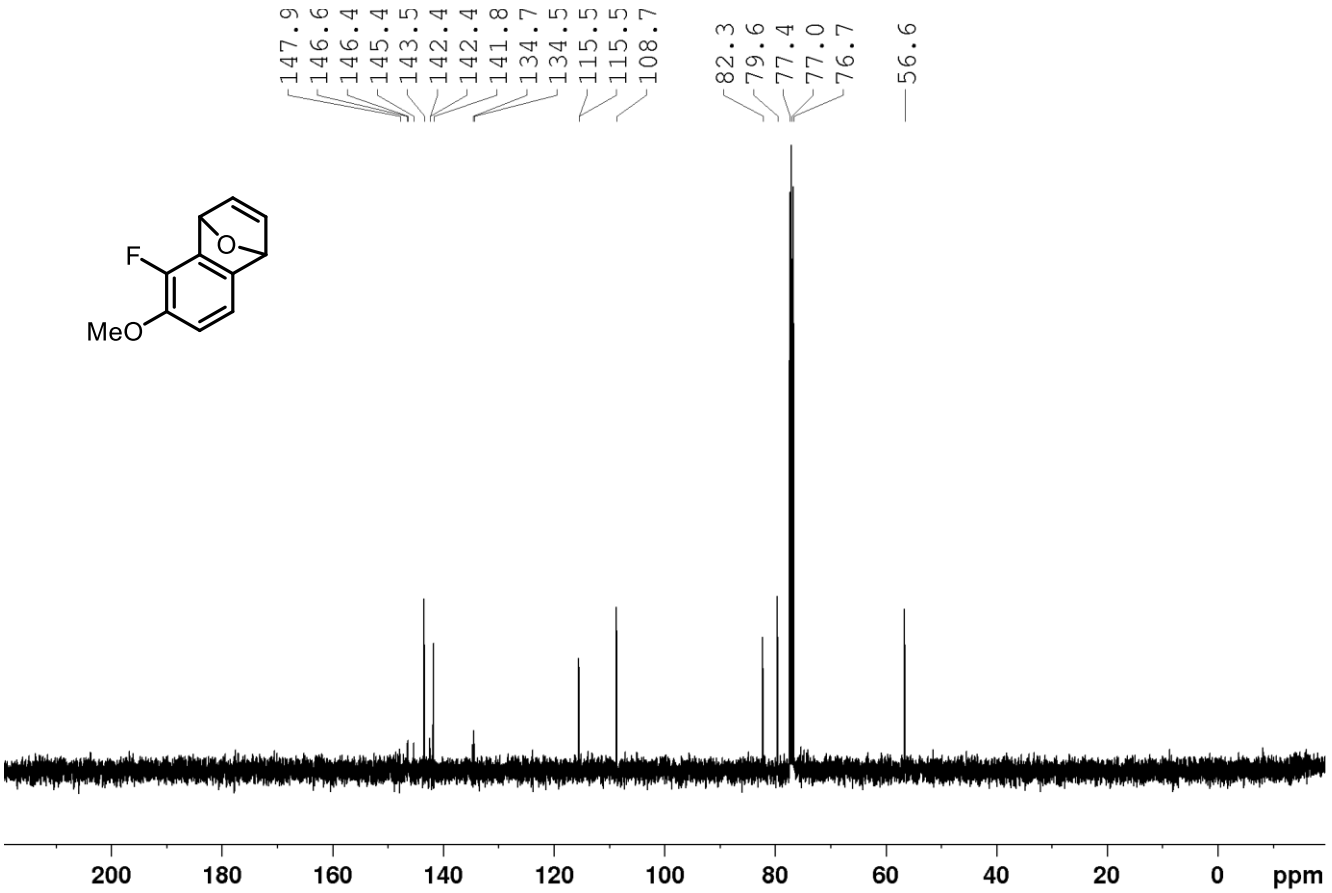
$^{13}C\{^{1}H\}$ NMR spectrum of 3xa in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



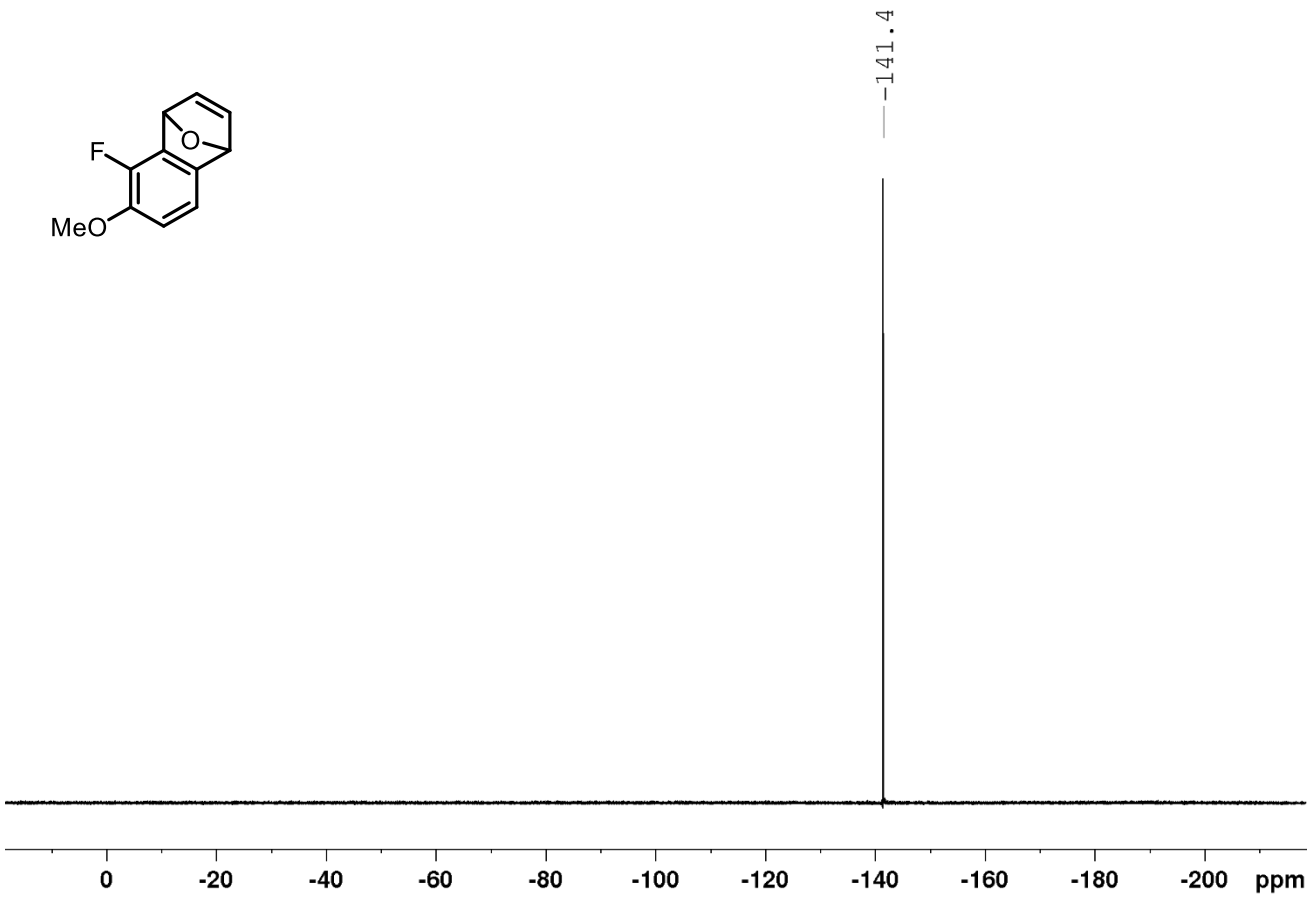
^{1}H NMR spectrum of 3za in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



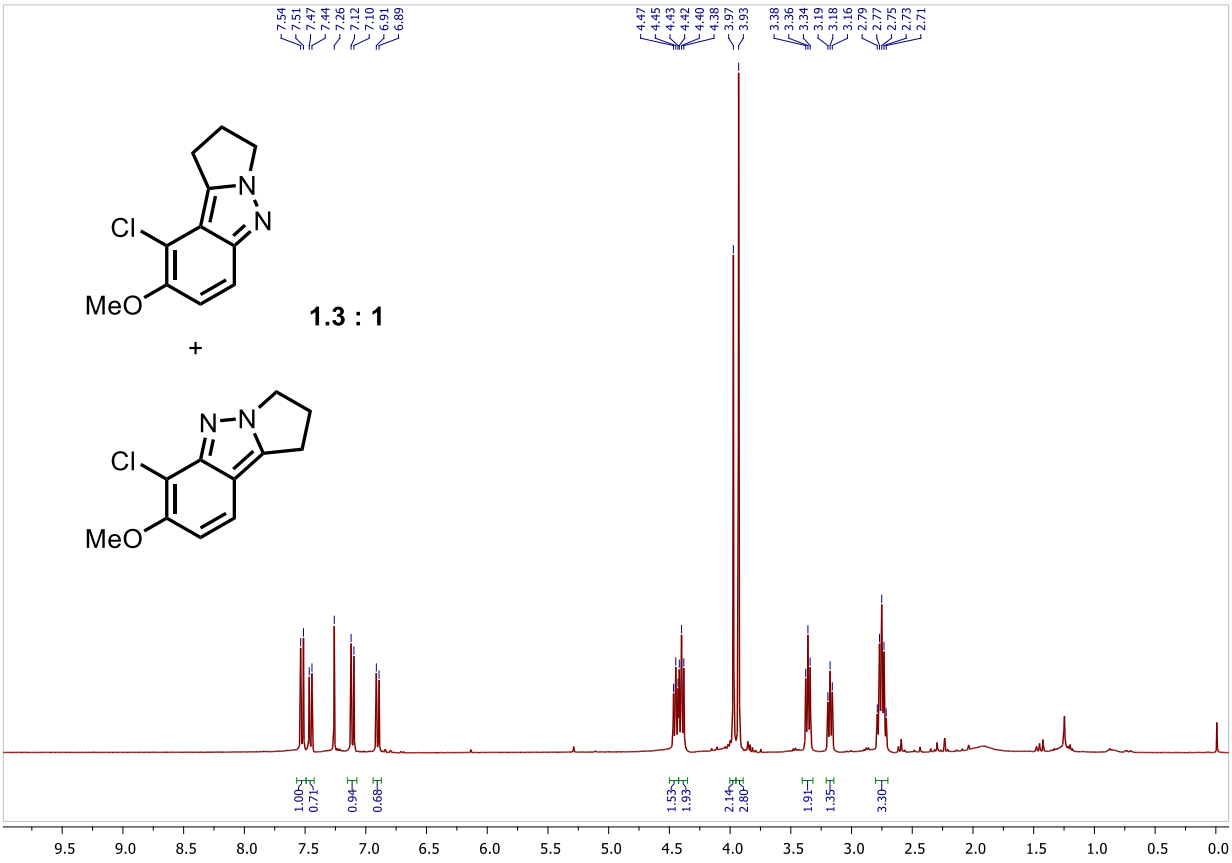
^{13}C{^{1}H} NMR spectrum of 3za in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



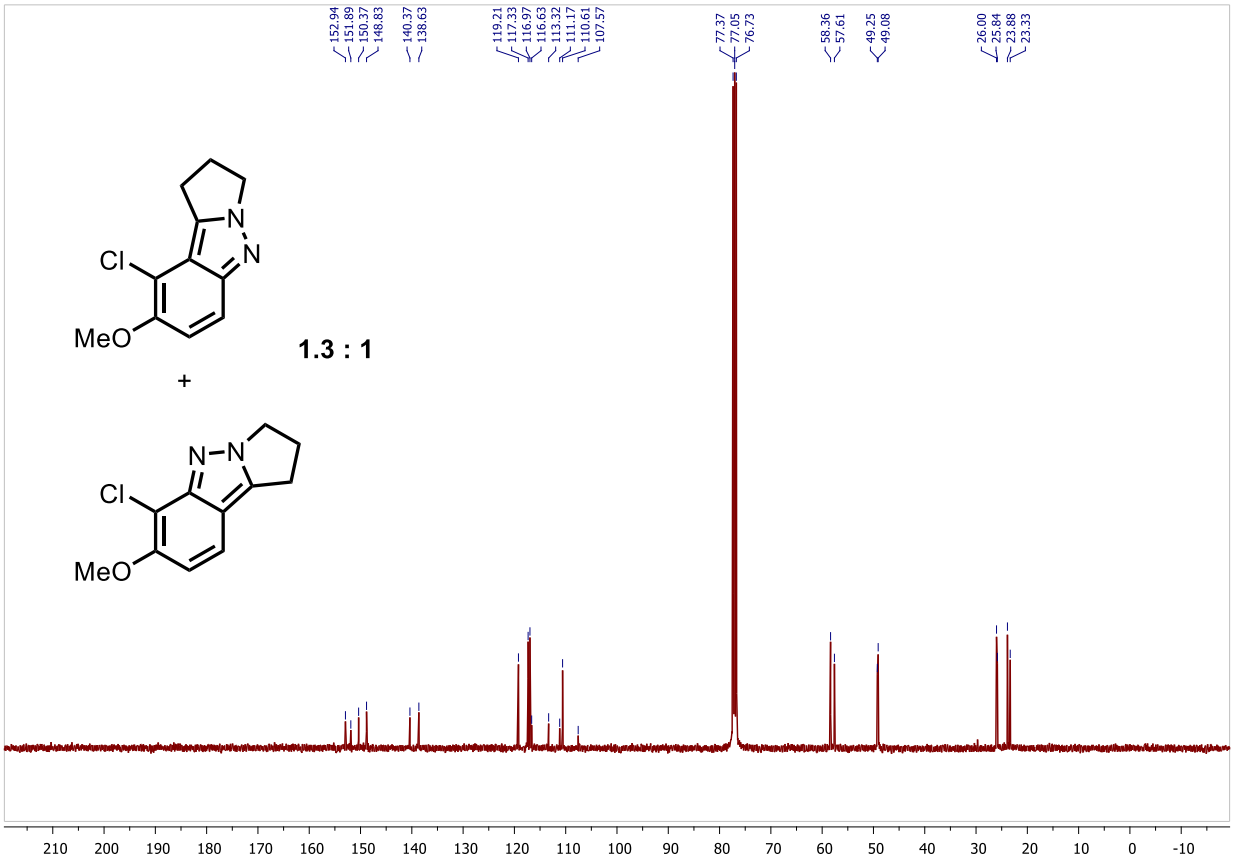
$^{19}F\{^{1}H\}$ NMR spectrum of 3qa in $CDCl_3$ with 1% v/v TMS at 376 MHz at 298 K



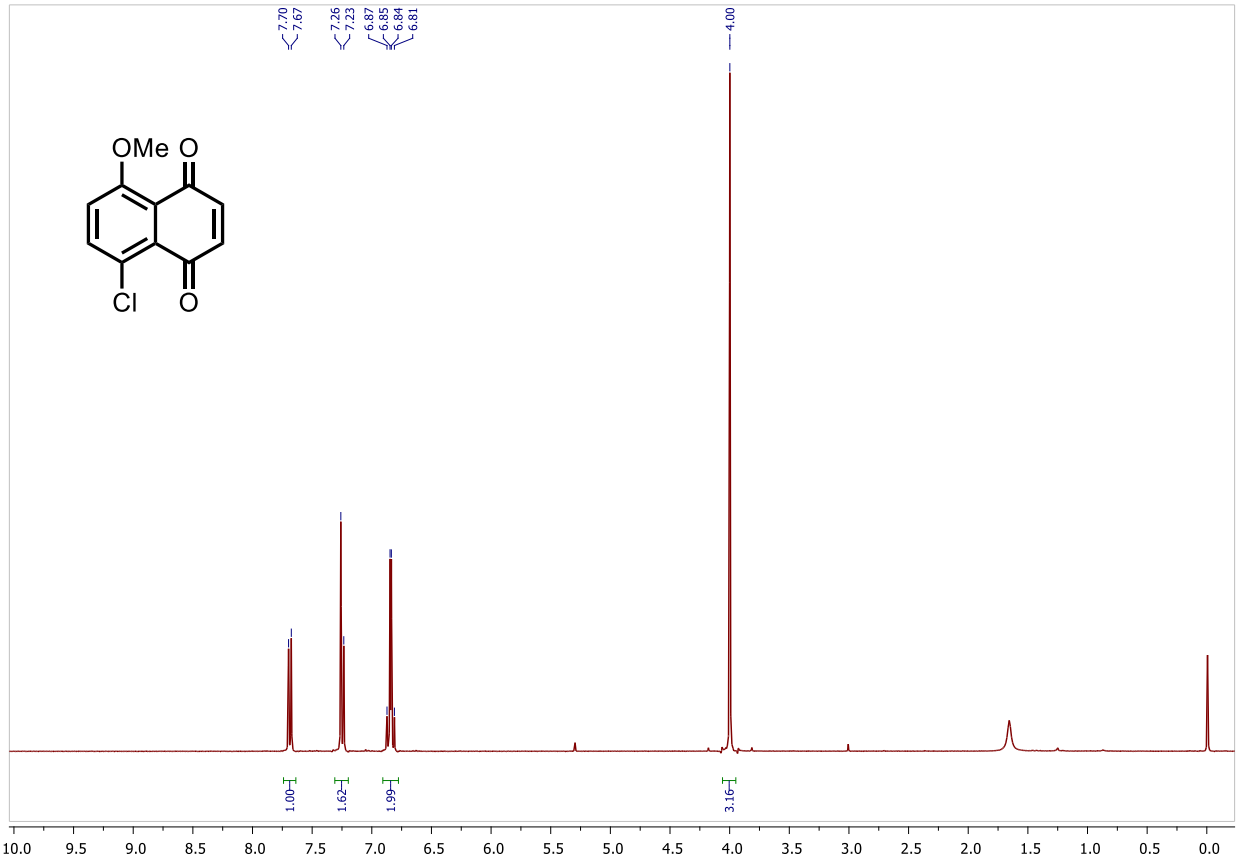
^{1}H NMR spectrum of additional compound in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



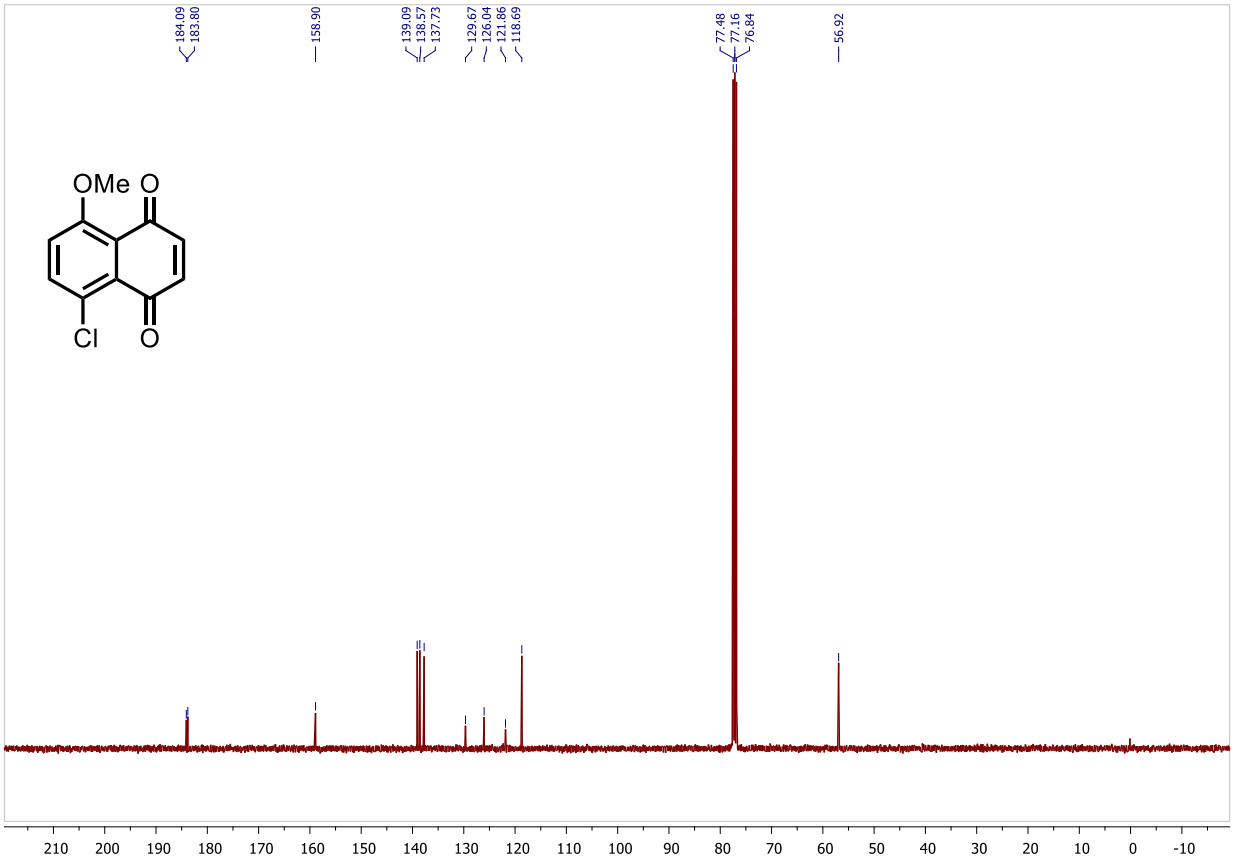
^{13}C{^{1}H} NMR spectrum of additional compound in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



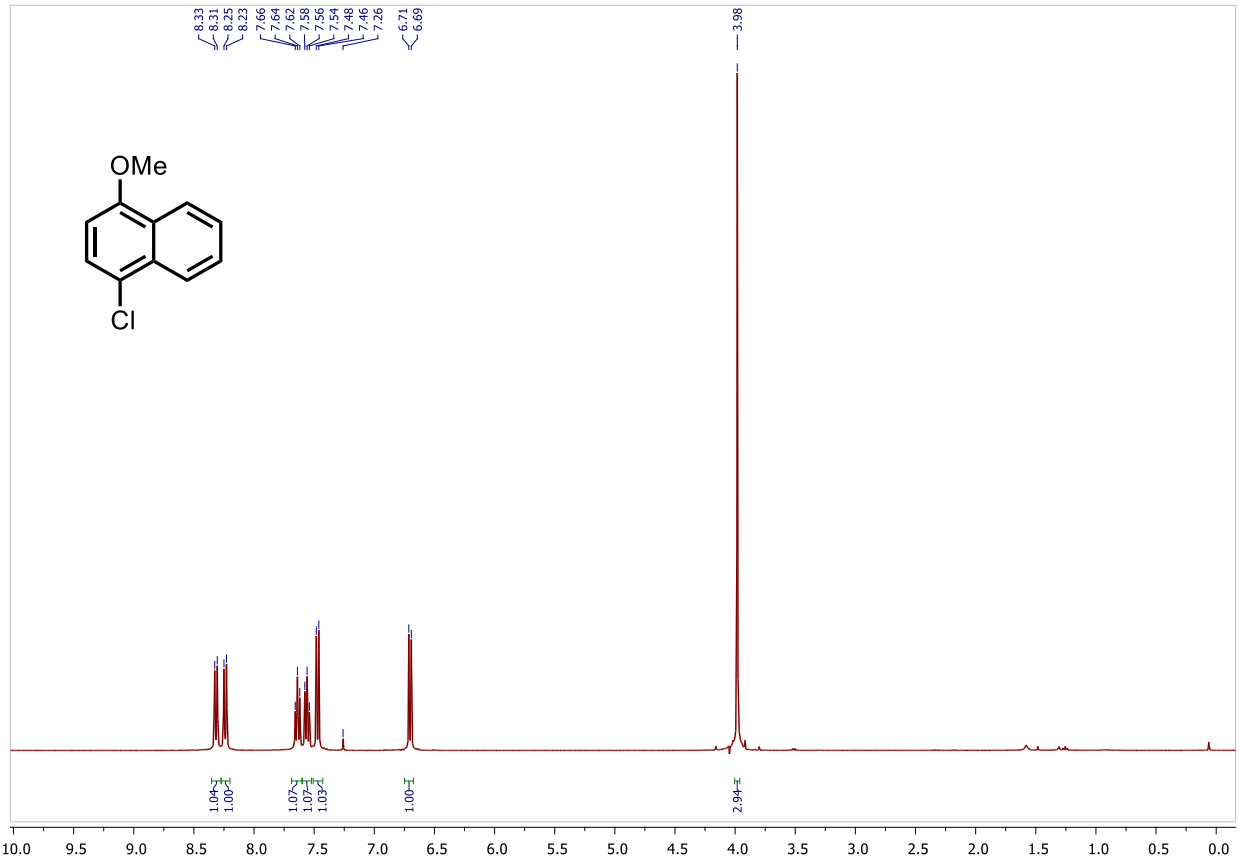
^{1}H NMR spectrum of 4 in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



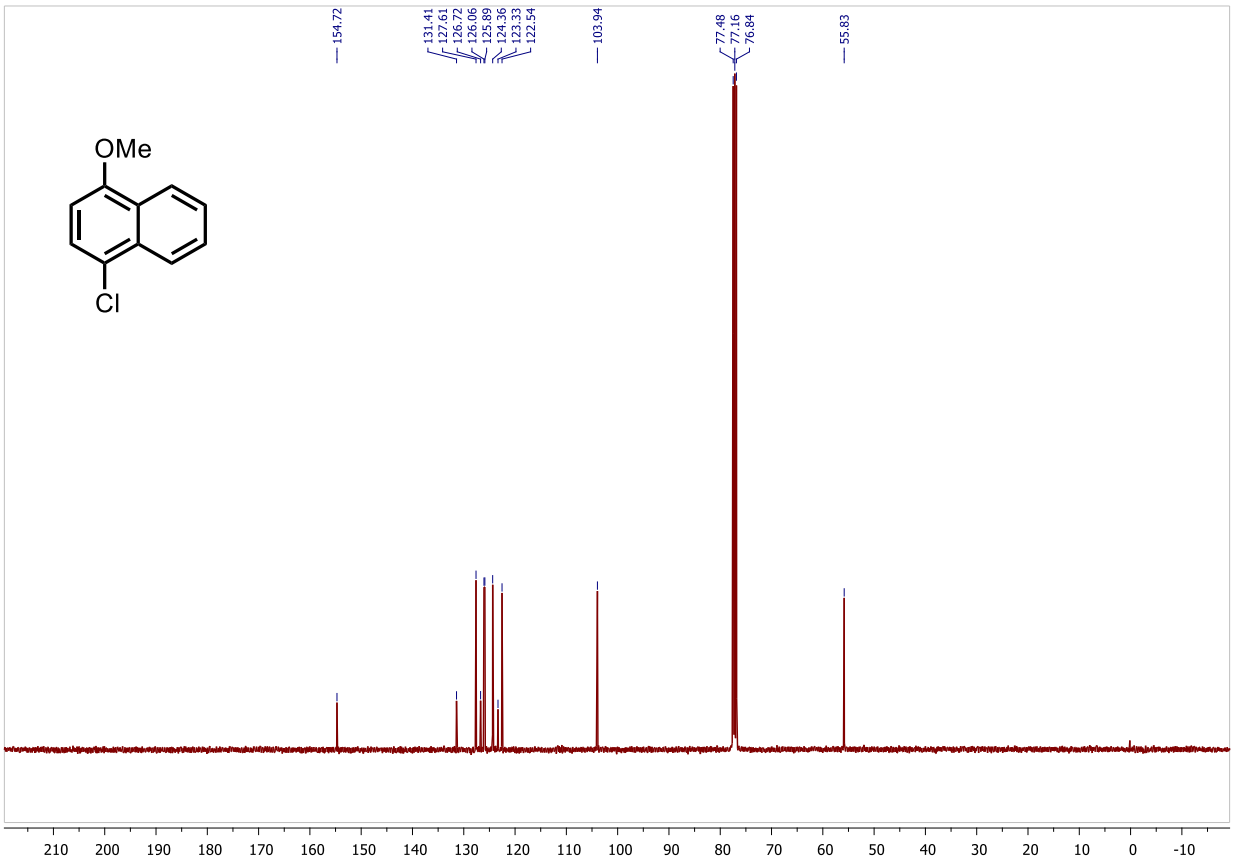
^{13}C{^{1}H} NMR spectrum of 4 in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



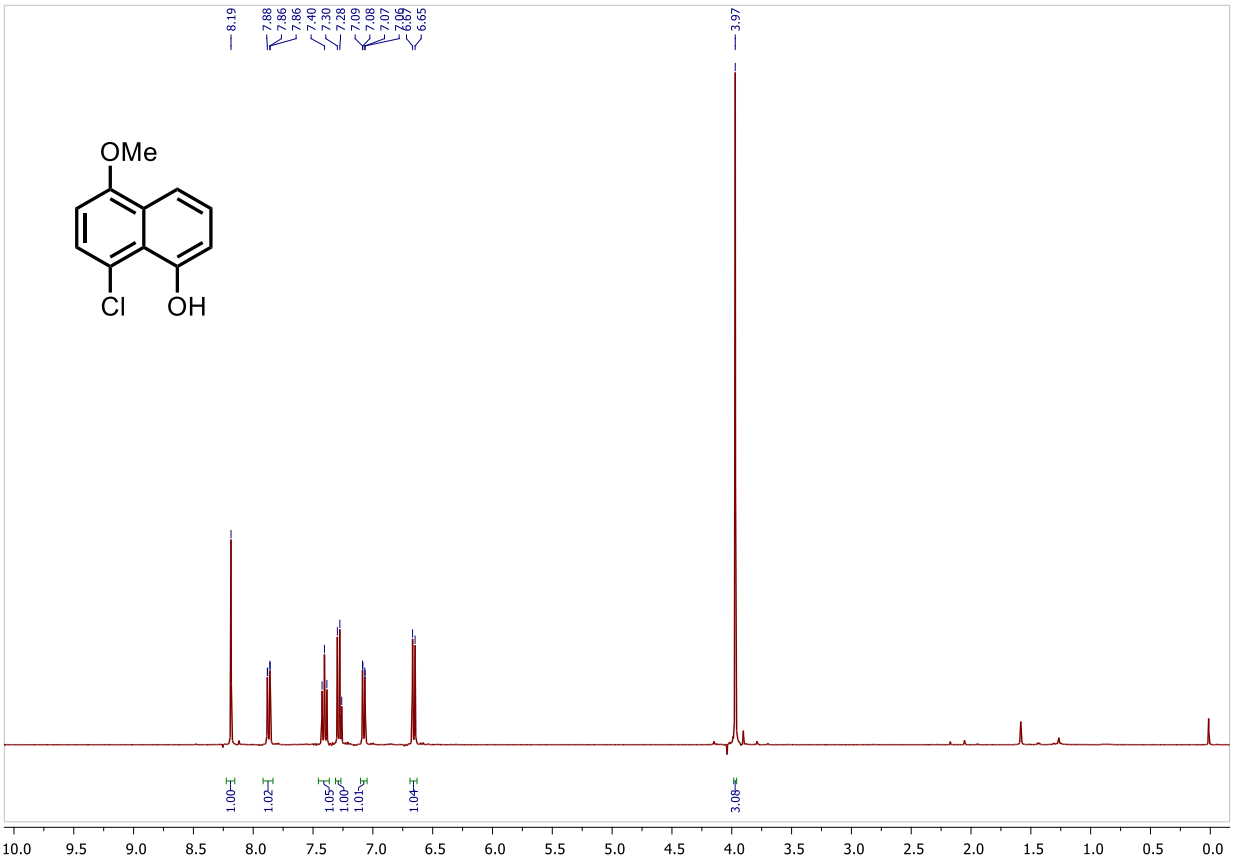
^{1}H NMR spectrum of 5 in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



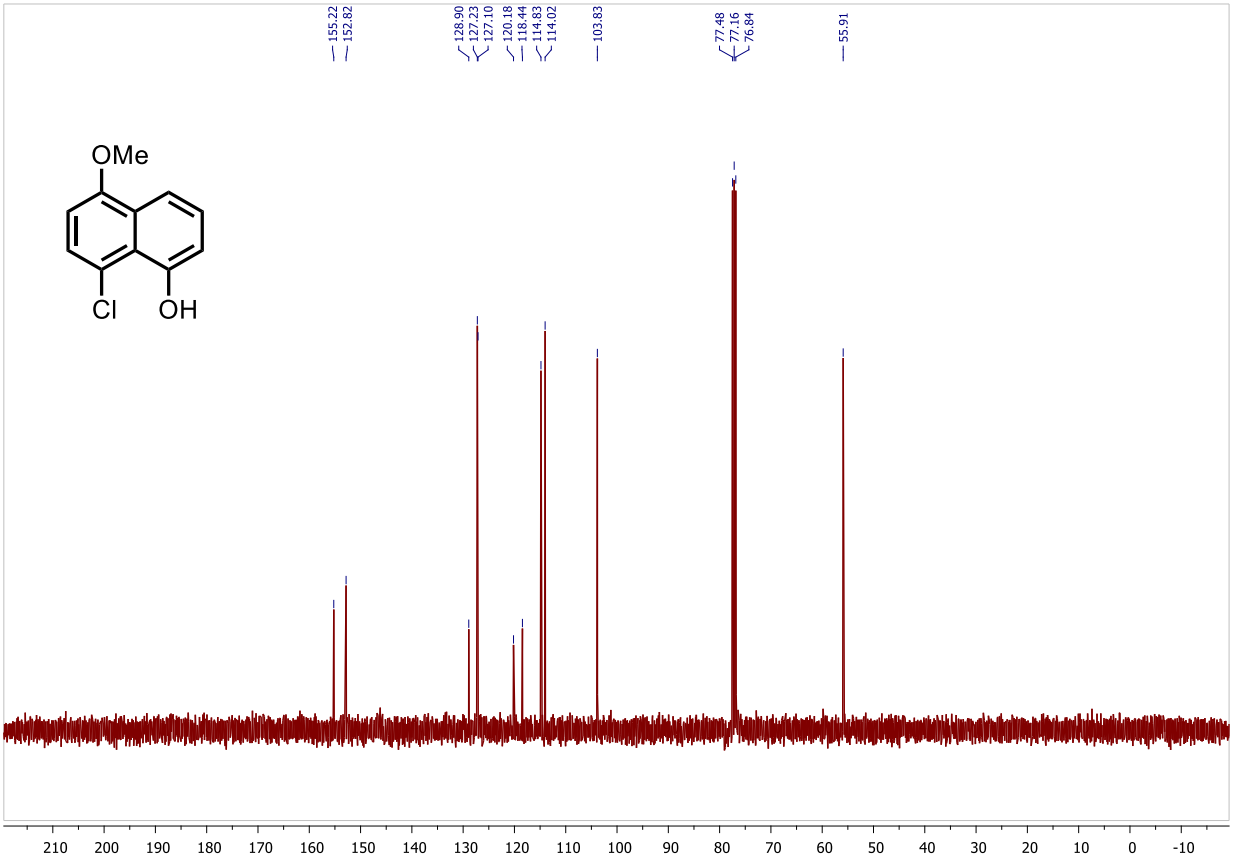
$^{13}C\{^{1}H\}$ NMR spectrum of 5 in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



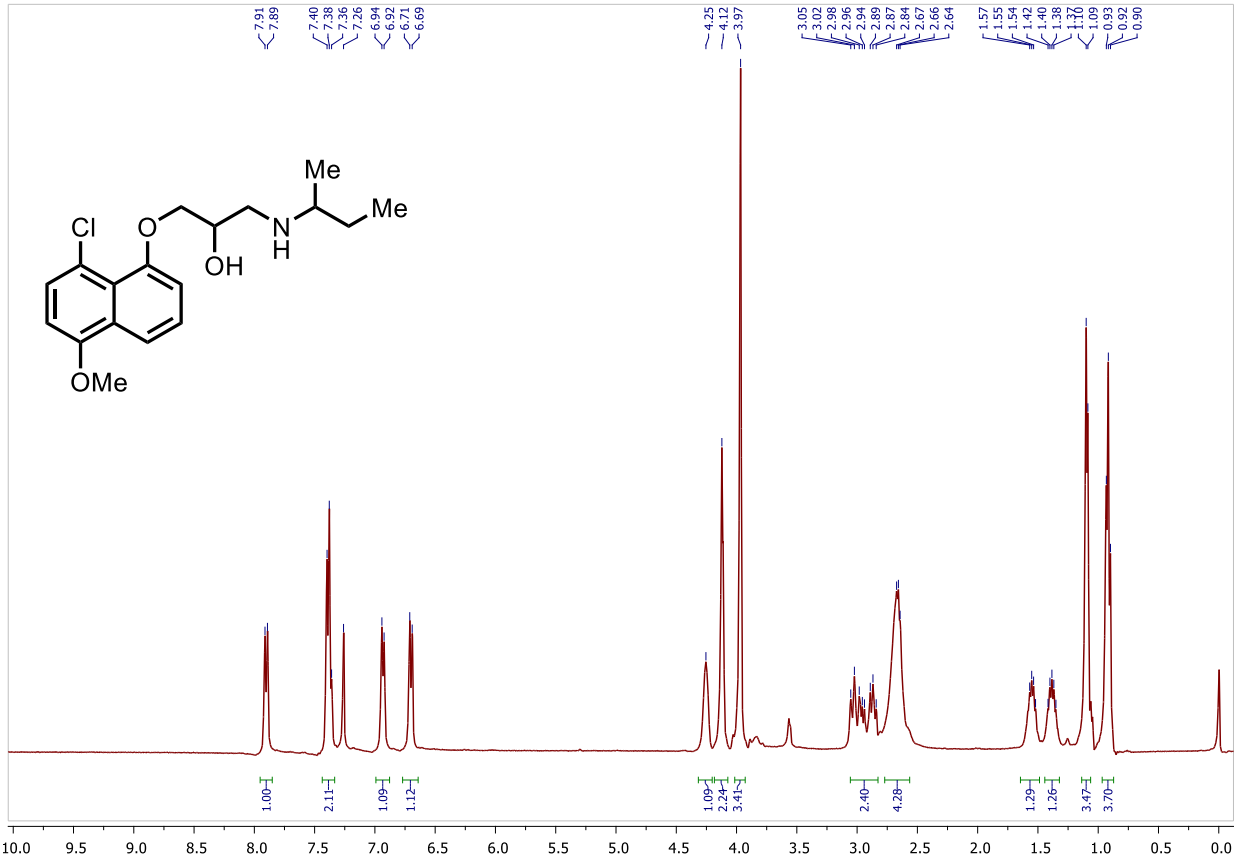
^{1}H NMR spectrum of 6 in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



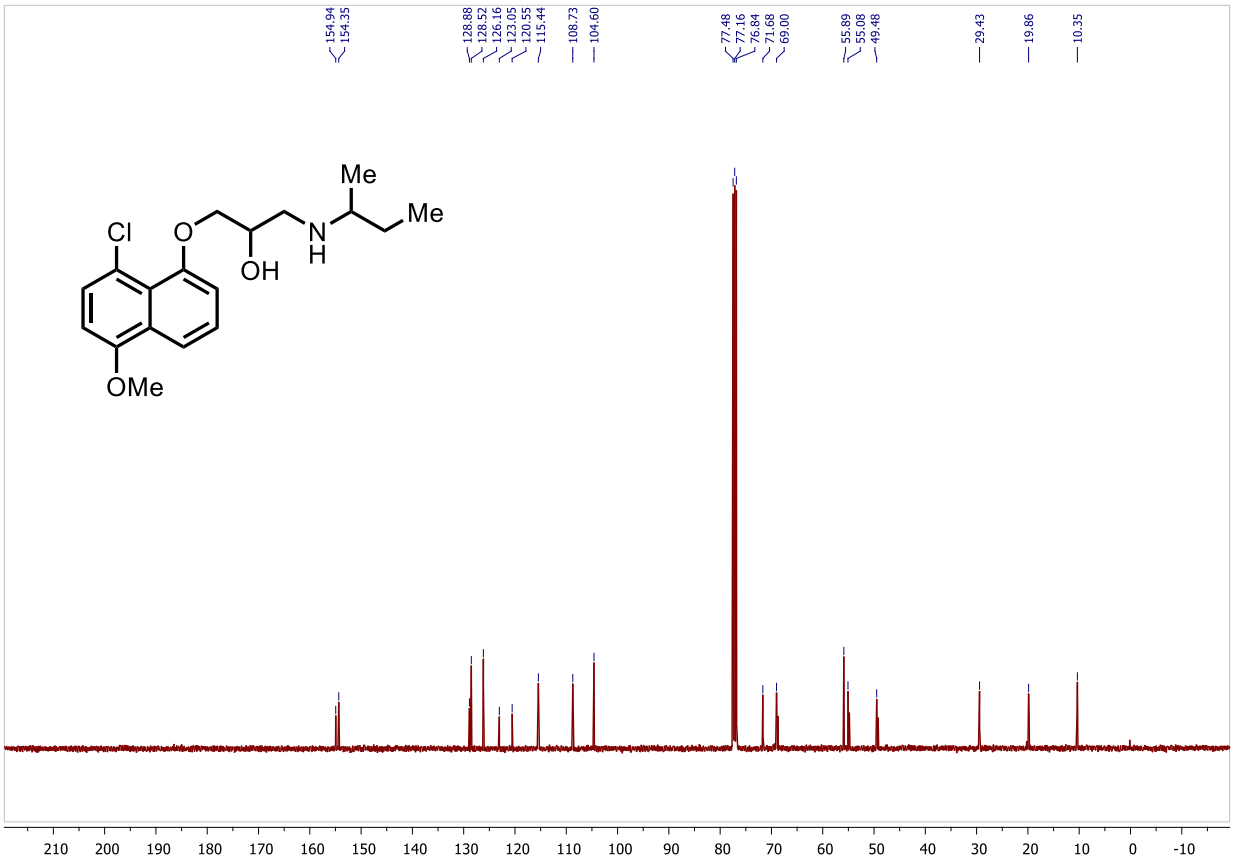
^{13}C{^{1}H} NMR spectrum of 6 in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



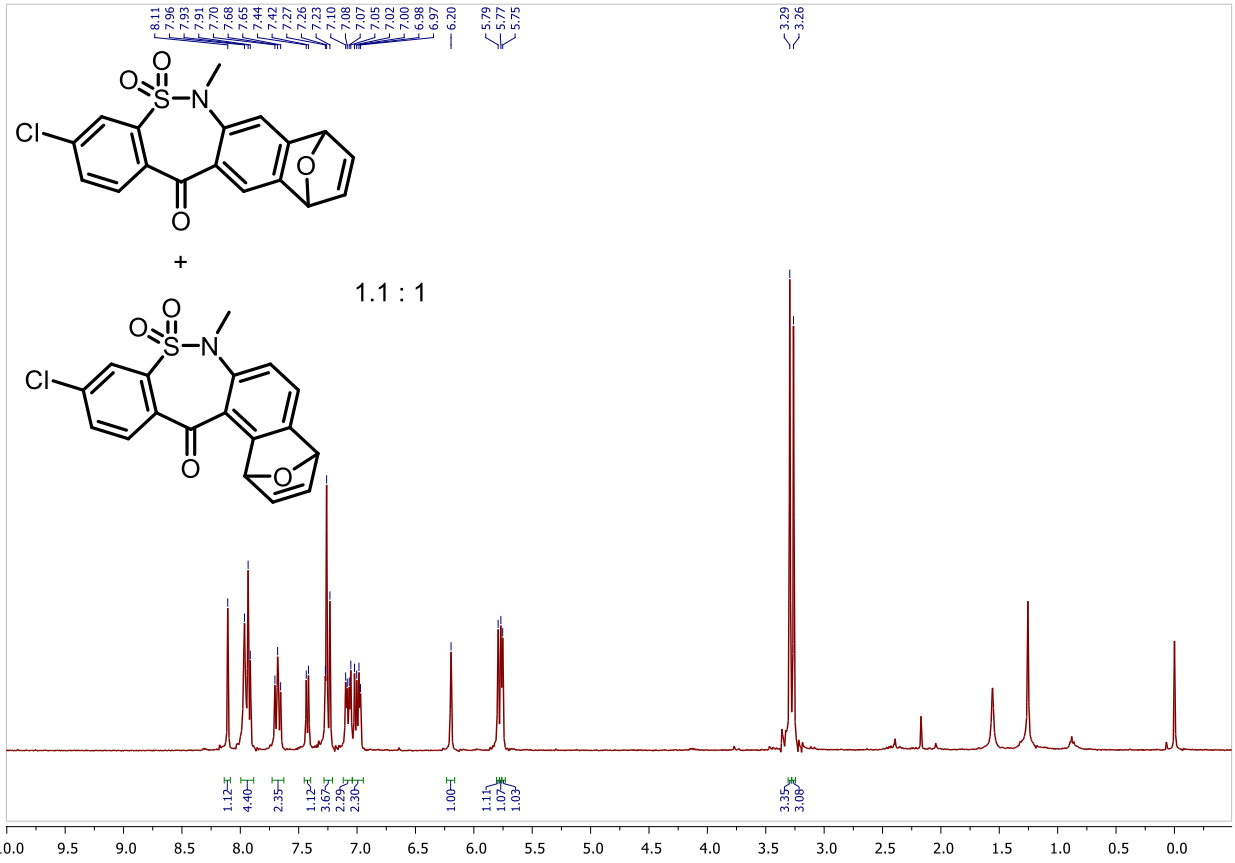
^{1}H NMR spectrum of 7 in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



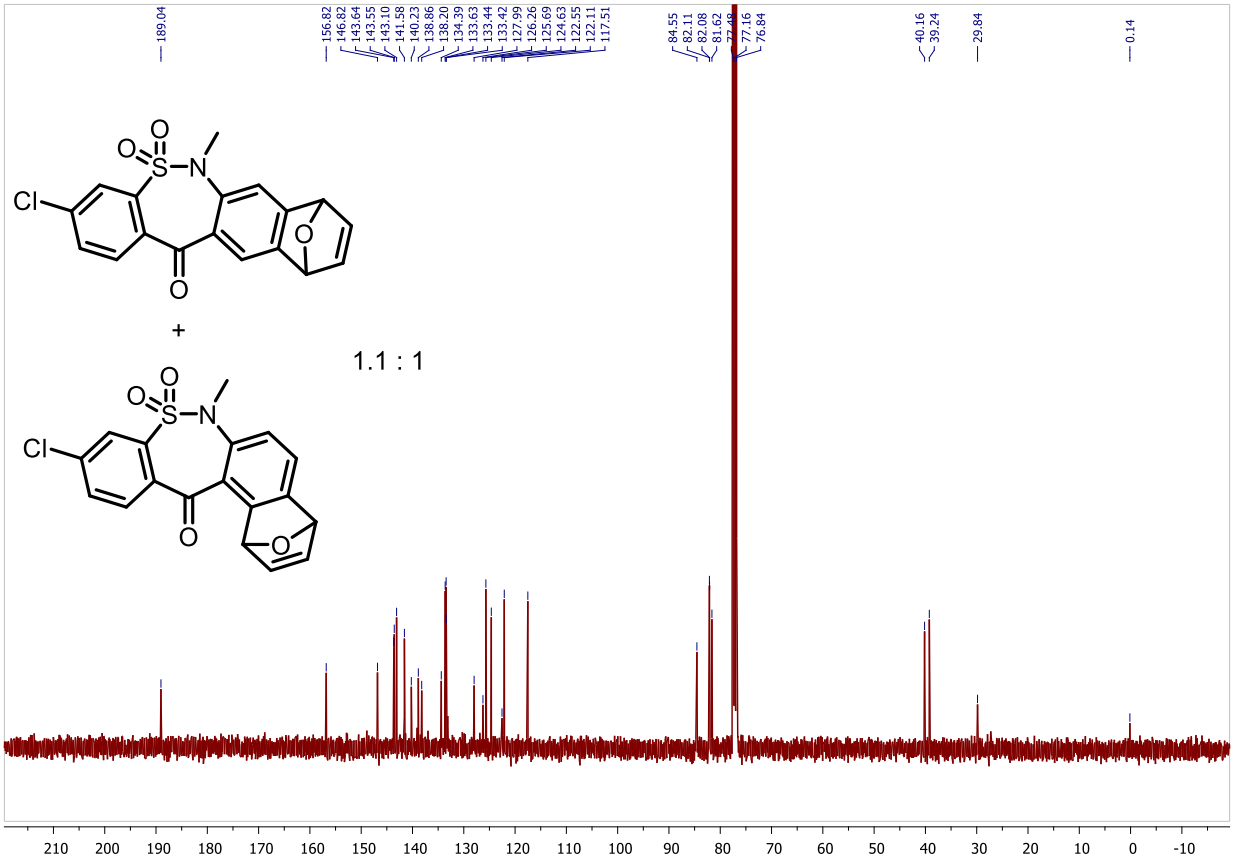
^{13}C{^{1}H} NMR spectrum of 7 in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



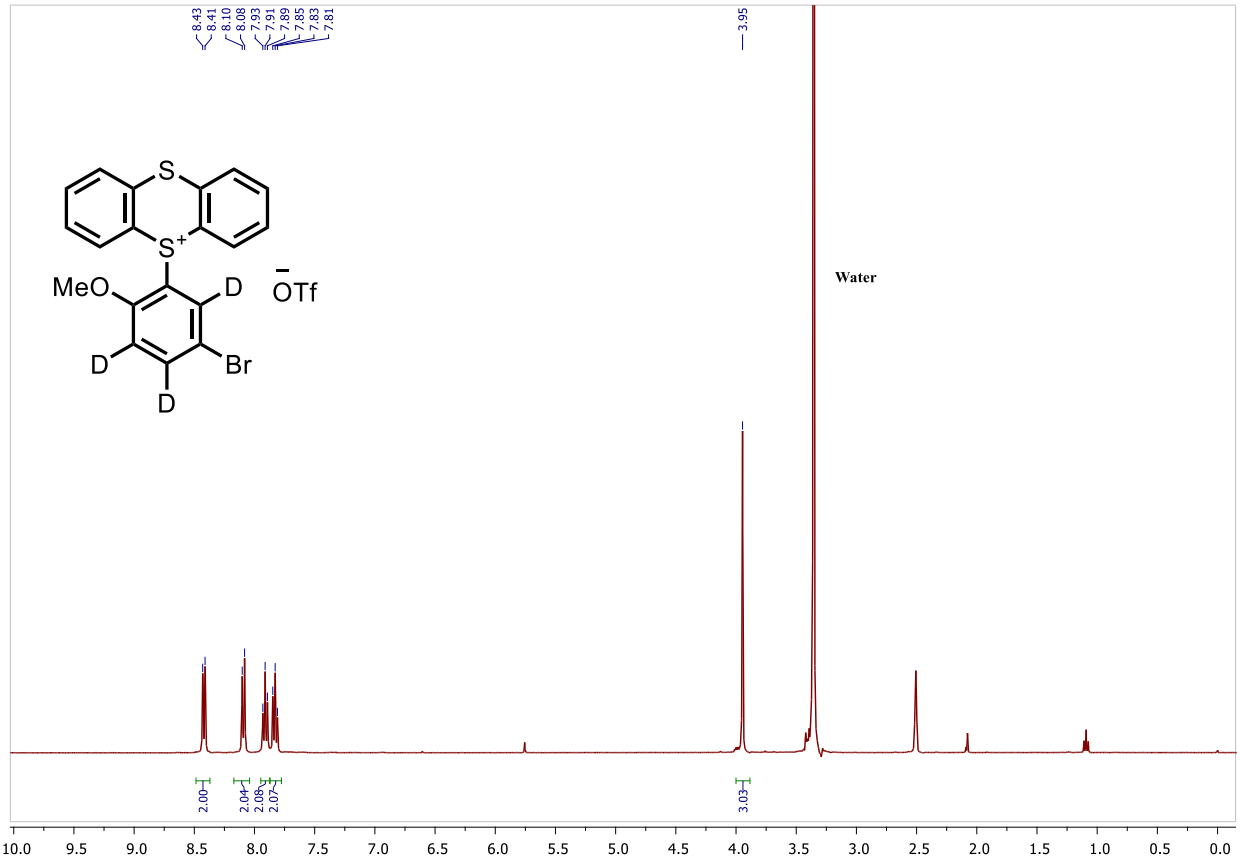
^{1}H NMR spectrum of 8 in $CDCl_3$ with 1% v/v TMS at 400 MHz at 298 K



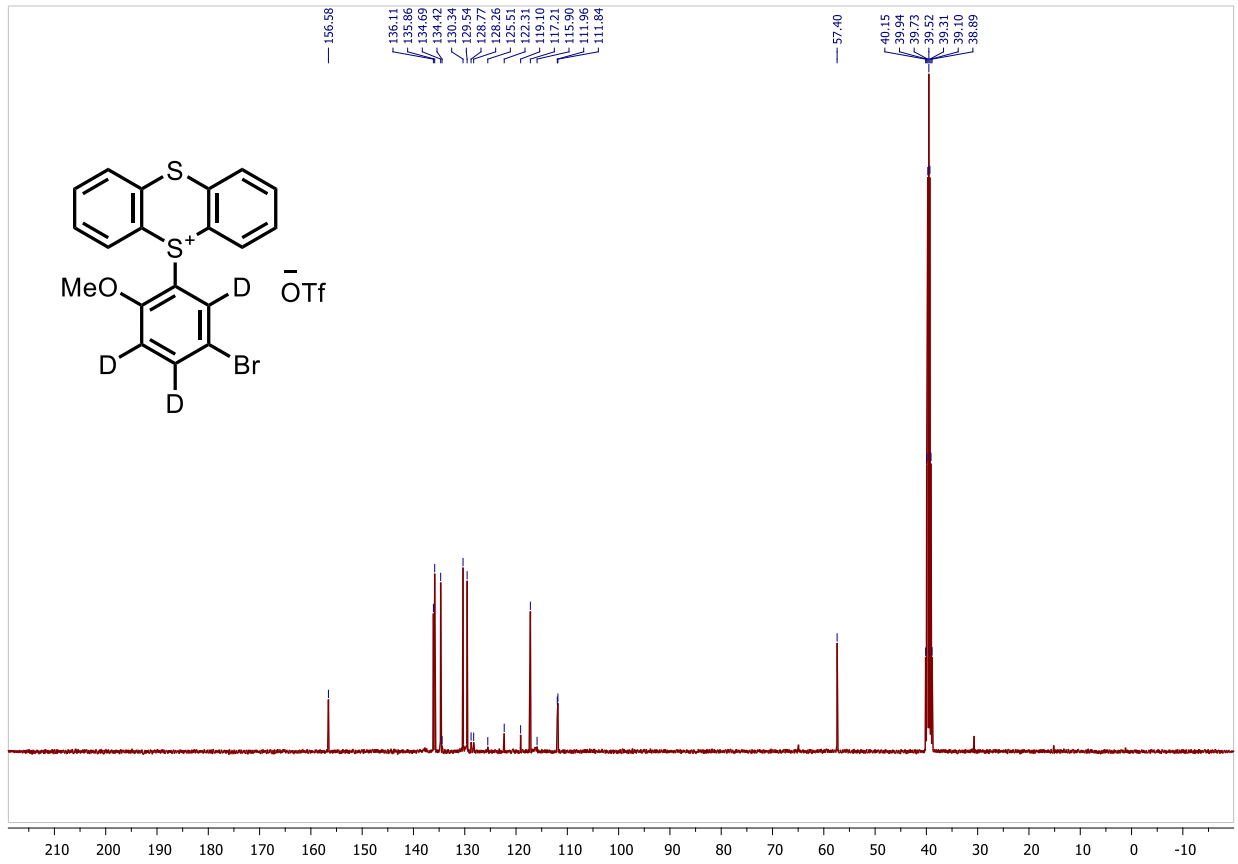
^{13}C{^{1}H} NMR spectrum of 8 in $CDCl_3$ with 1% v/v TMS at 101 MHz at 298 K



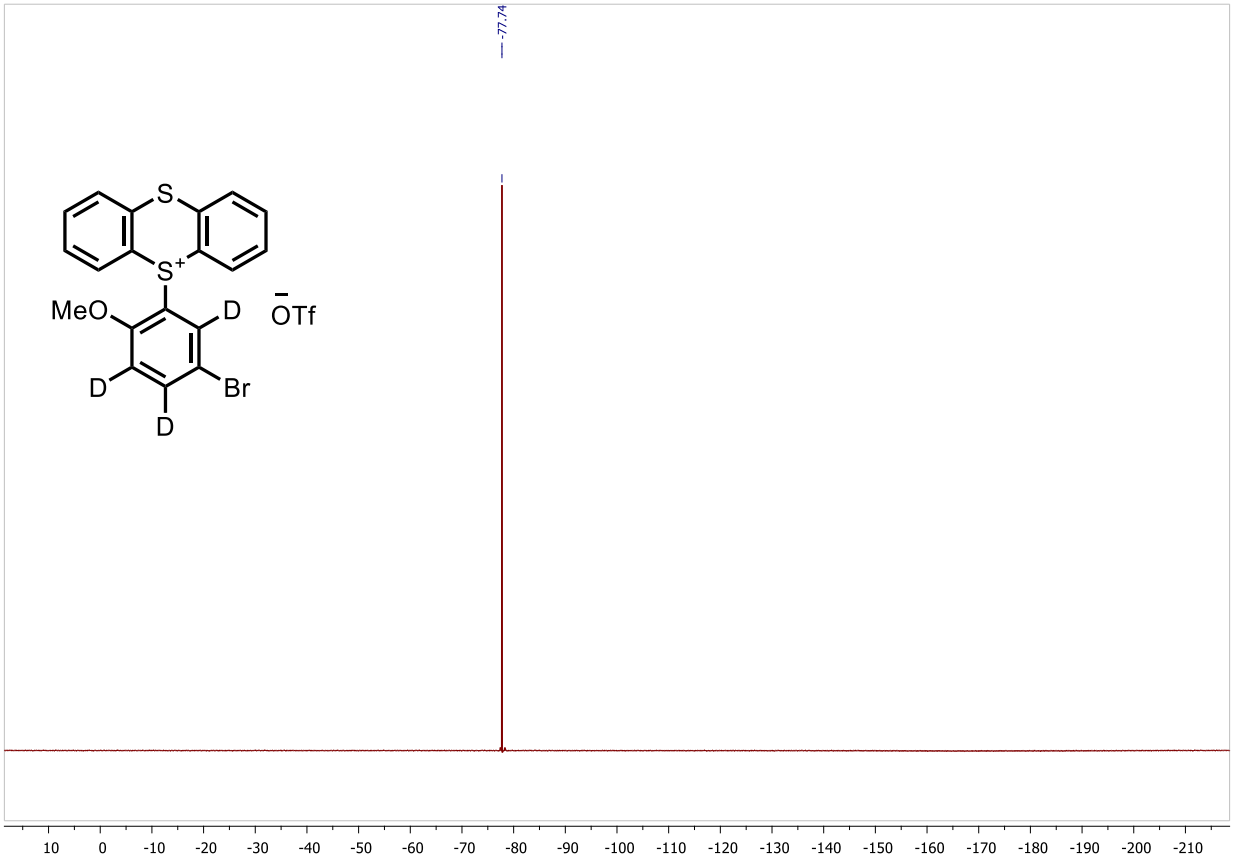
^{1}H NMR spectrum of 1b-TT-d_3 in DMSO-d6 at 400 MHz at 298 K



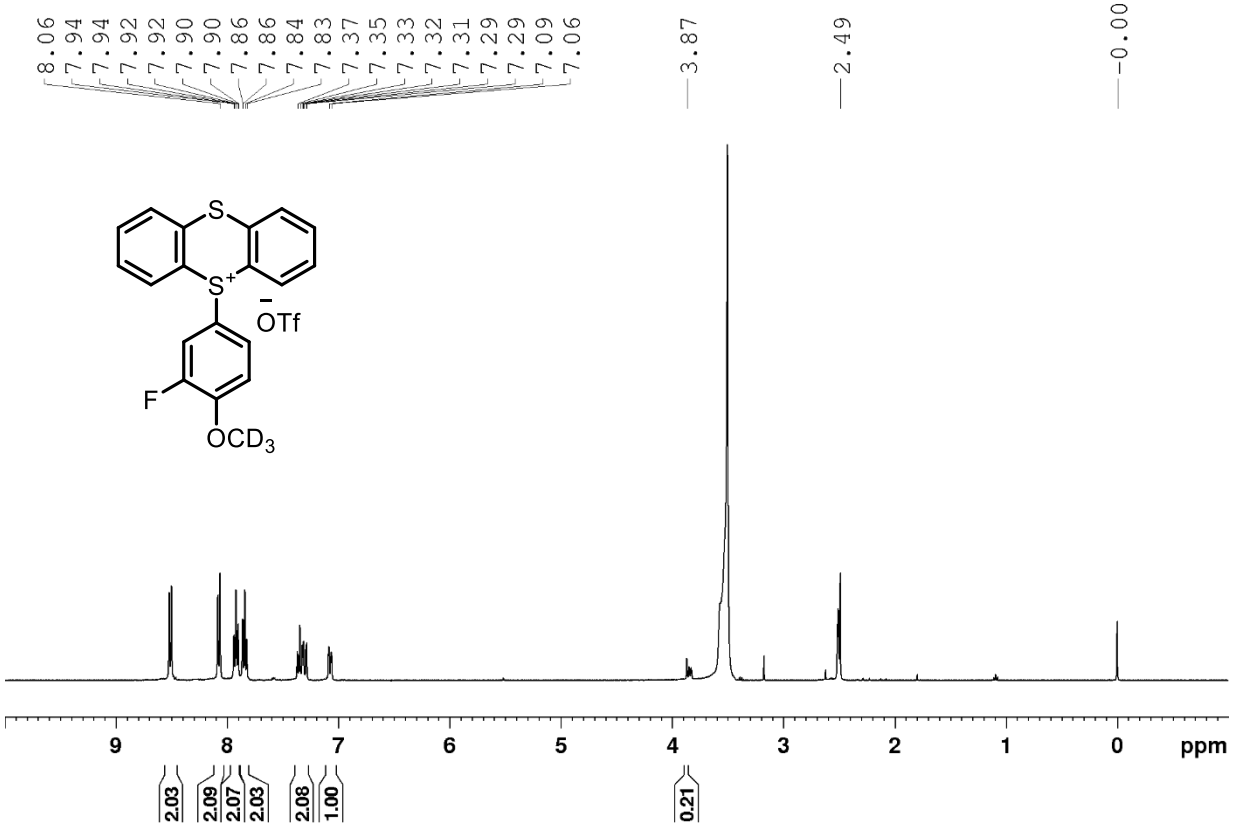
^{13}C{^{1}H} NMR spectrum of 1b-TT-d_3 in DMSO-d6 at 101 MHz at 298 K



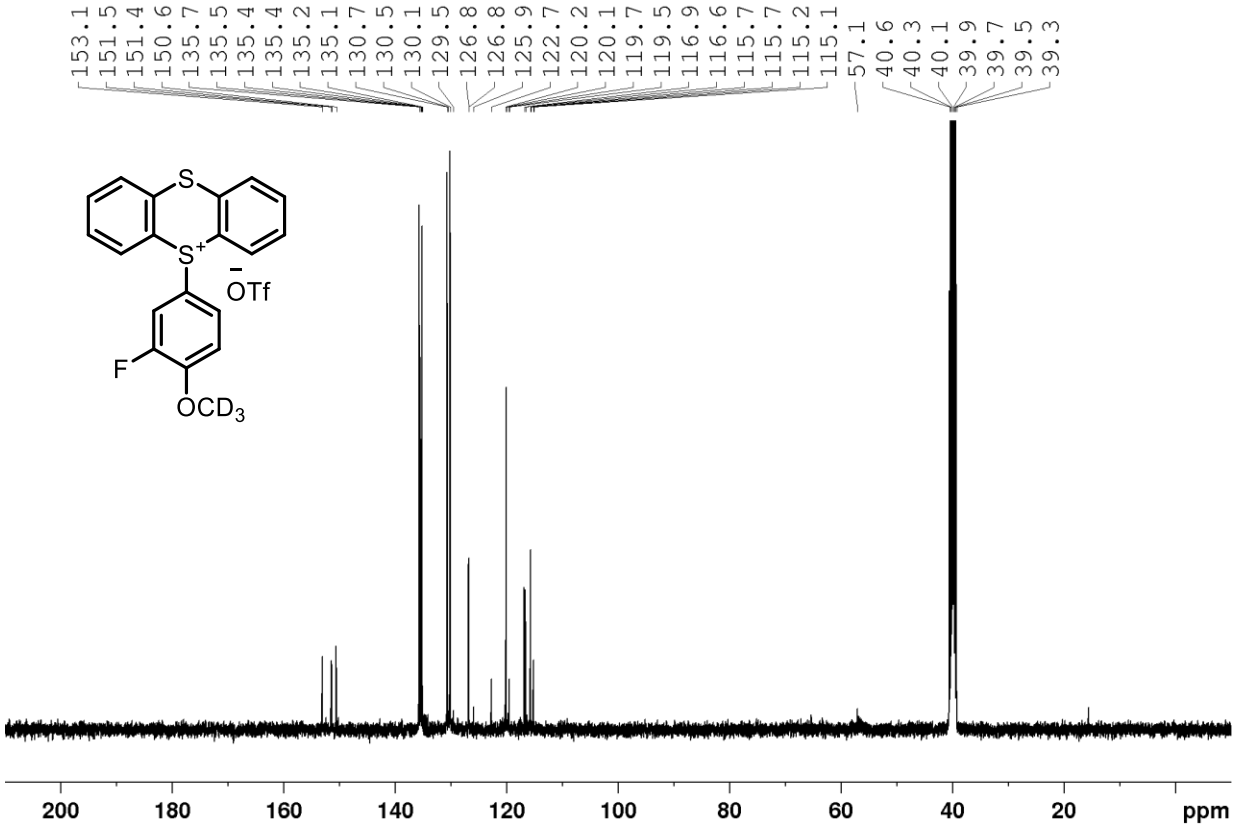
$^{19}F\{^{1}H\}$ NMR spectrum of 1b-TT-d_3 in DMSO-*d*6 at 376 MHz at 298 K



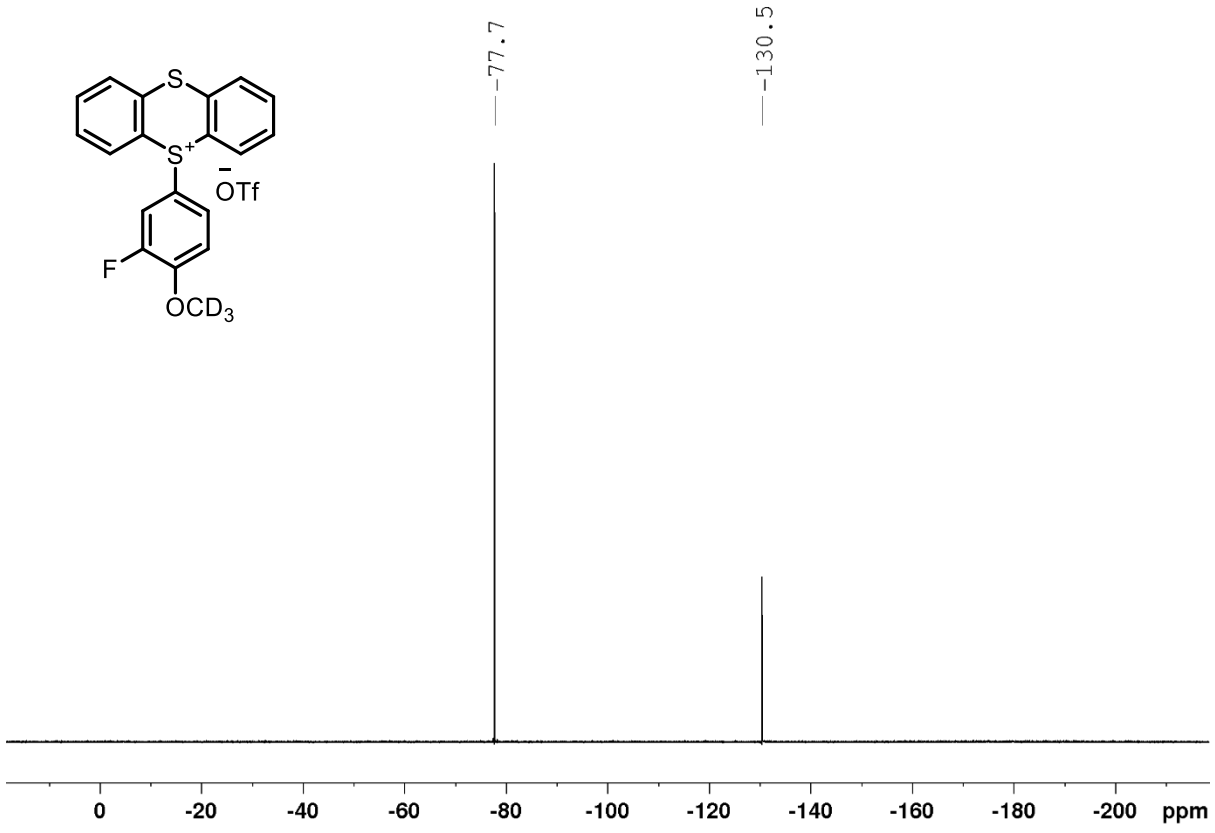
^{1}H NMR spectrum of 1z-TT-d_3 in DMSO-*d*6 at 400 MHz at 298 K



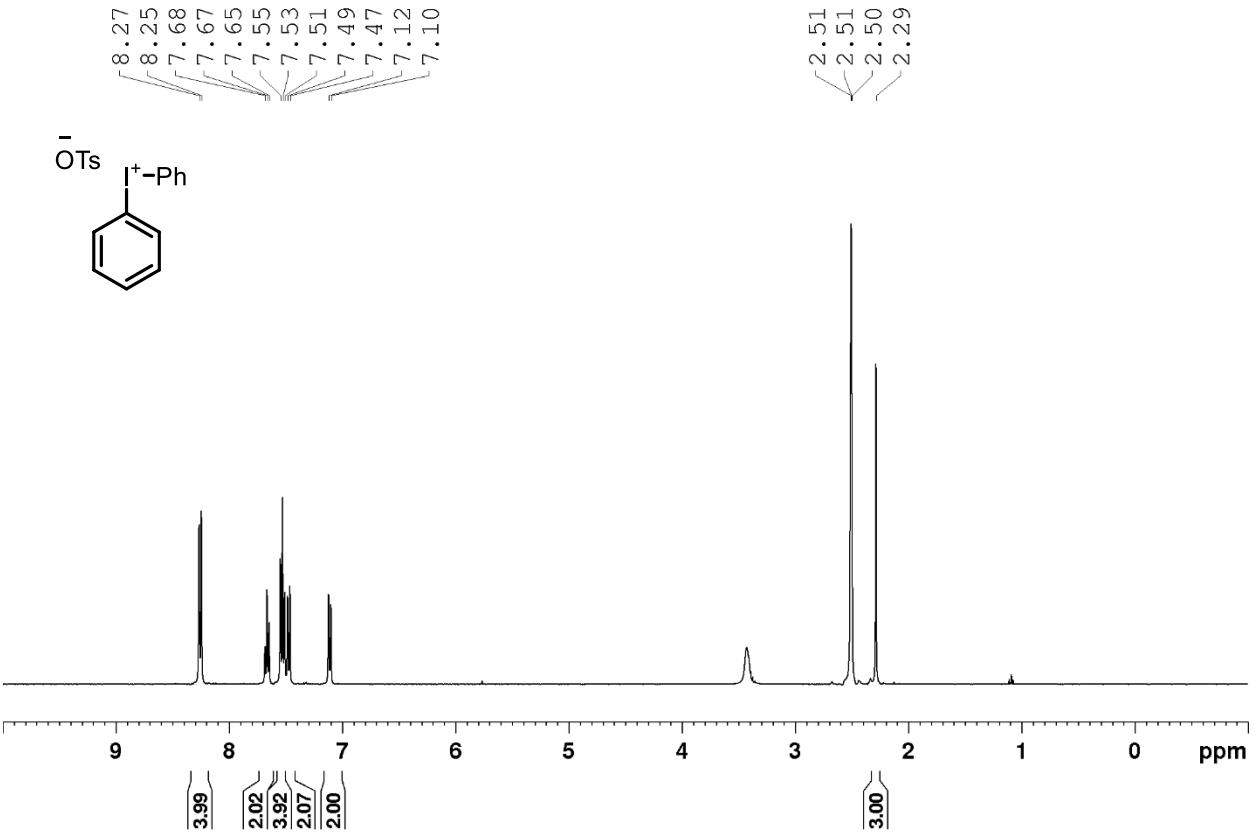
$^{13}C\{^{1}H\}$ NMR spectrum of 1z-TT-d_3 in DMSO-*d*6 at 101 MHz at 298 K



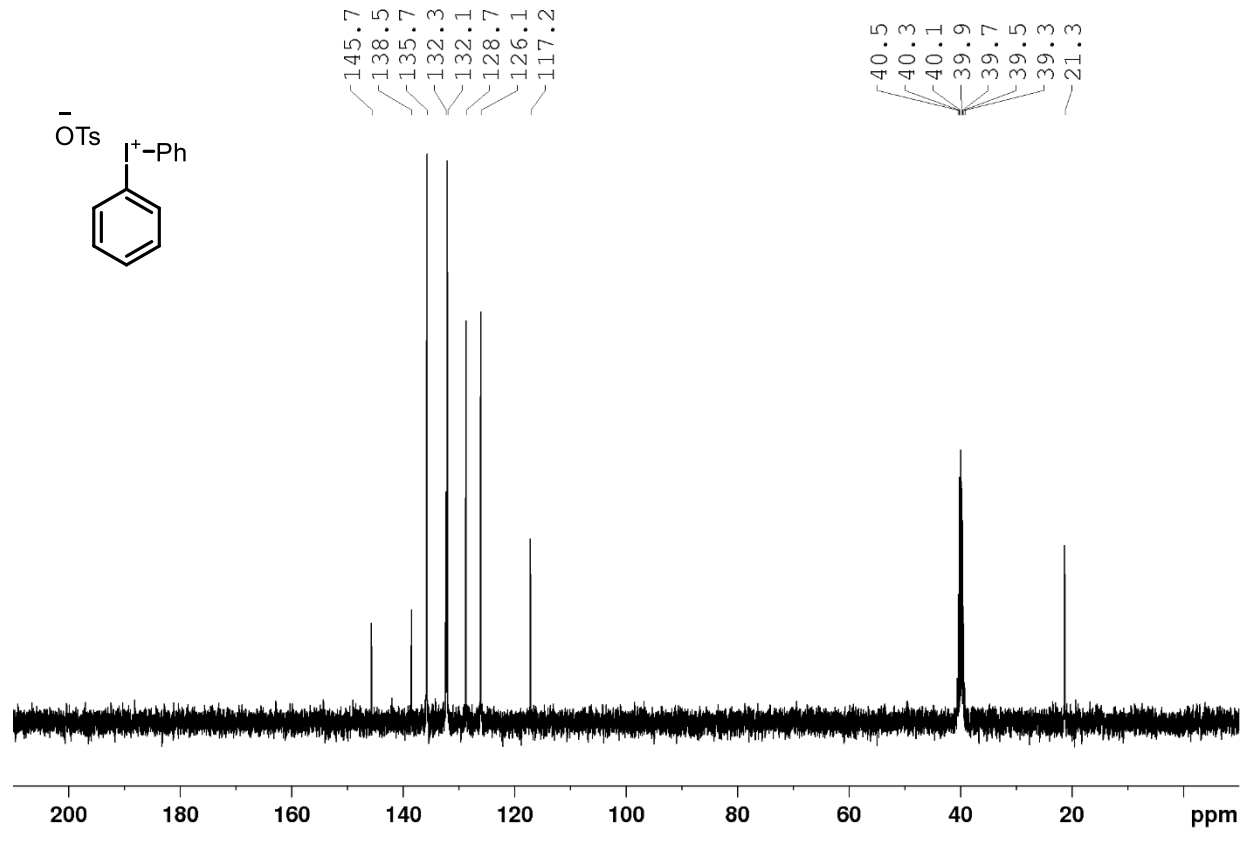
$^{19}F\{^{1}H\}$ NMR spectrum of 1z-TT-d_3 in DMSO-*d*6 at 376 MHz at 298 K



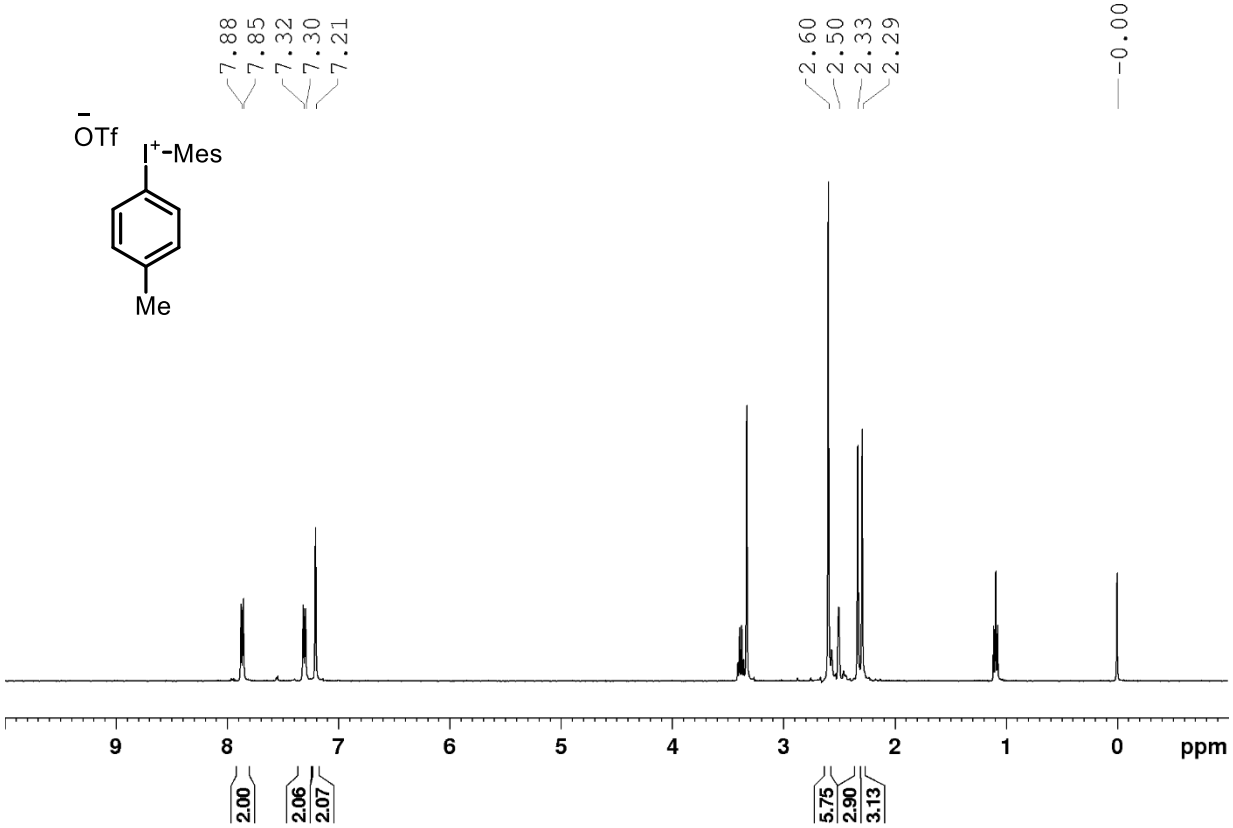
^{1}H NMR spectrum of 1l-IMes in DMSO-*d*6 at 400 MHz at 298 K



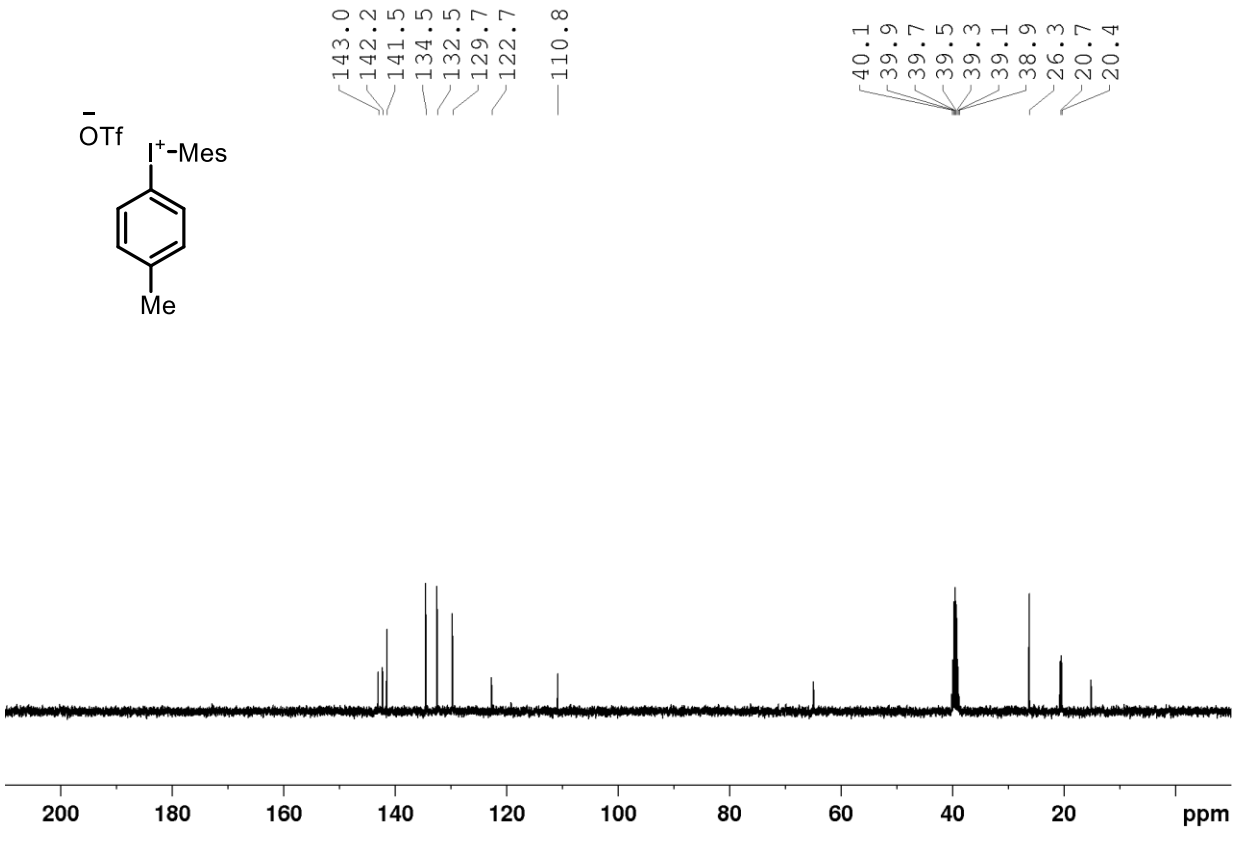
^{13}C{^{1}H} NMR spectrum of 1l-IMes in DMSO-*d*6 at 101 MHz at 298 K



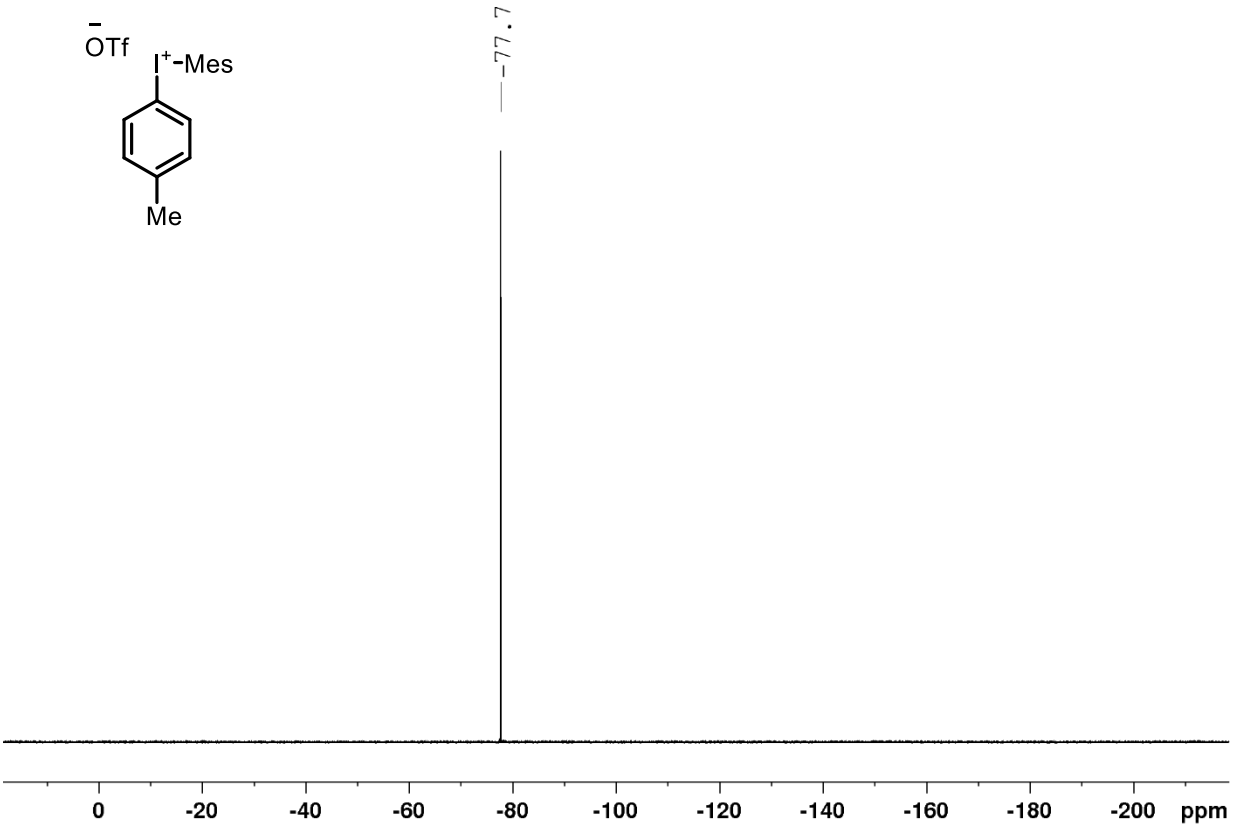
^{1}H NMR spectrum of 1m-IMes in DMSO-*d*6 at 400 MHz at 298 K



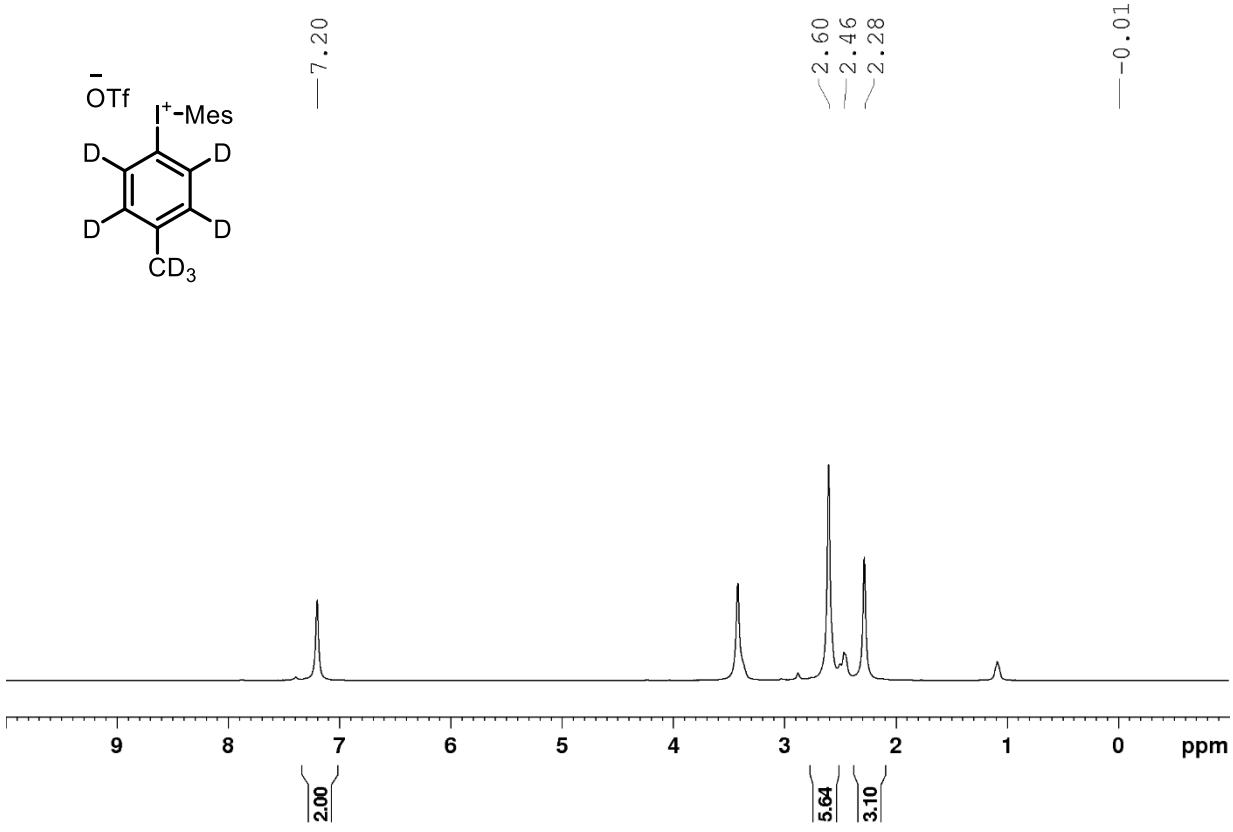
^{13}C{^{1}H} NMR spectrum of 1m-IMes in DMSO-*d*6 at 101 MHz at 298 K



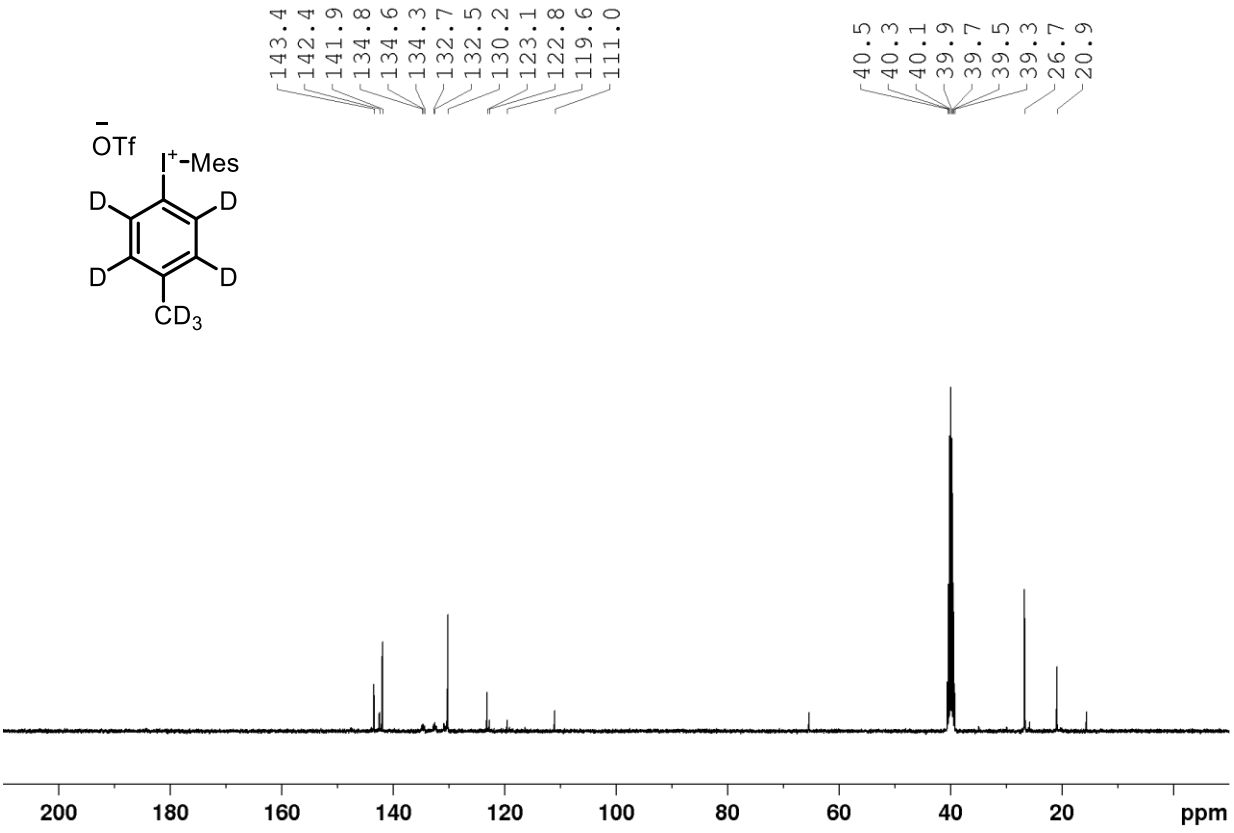
$^{19}F\{^{1}H\}$ NMR spectrum of 1m-IMes in DMSO-*d*6 at 376 MHz at 298 K



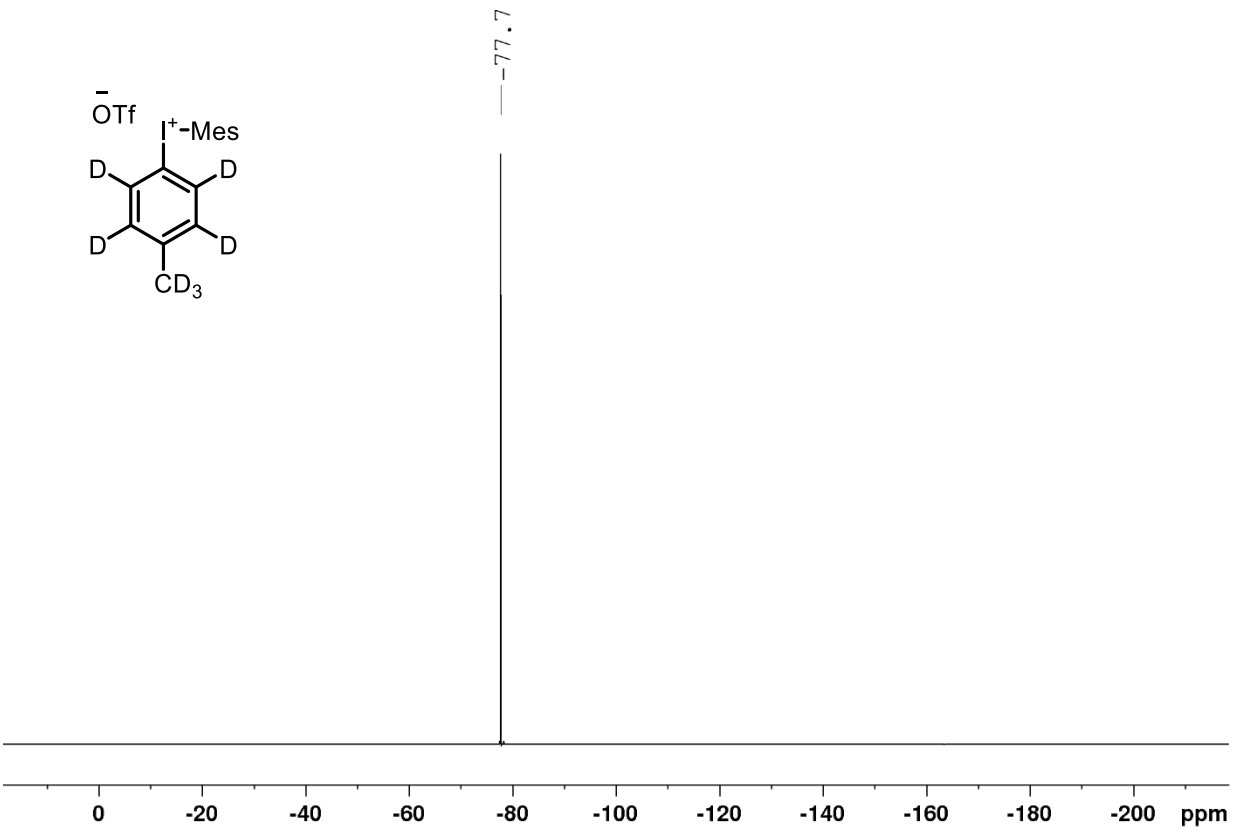
^{1}H NMR spectrum of 1m-IMes-d7 in DMSO-*d*6 at 400 MHz at 298 K



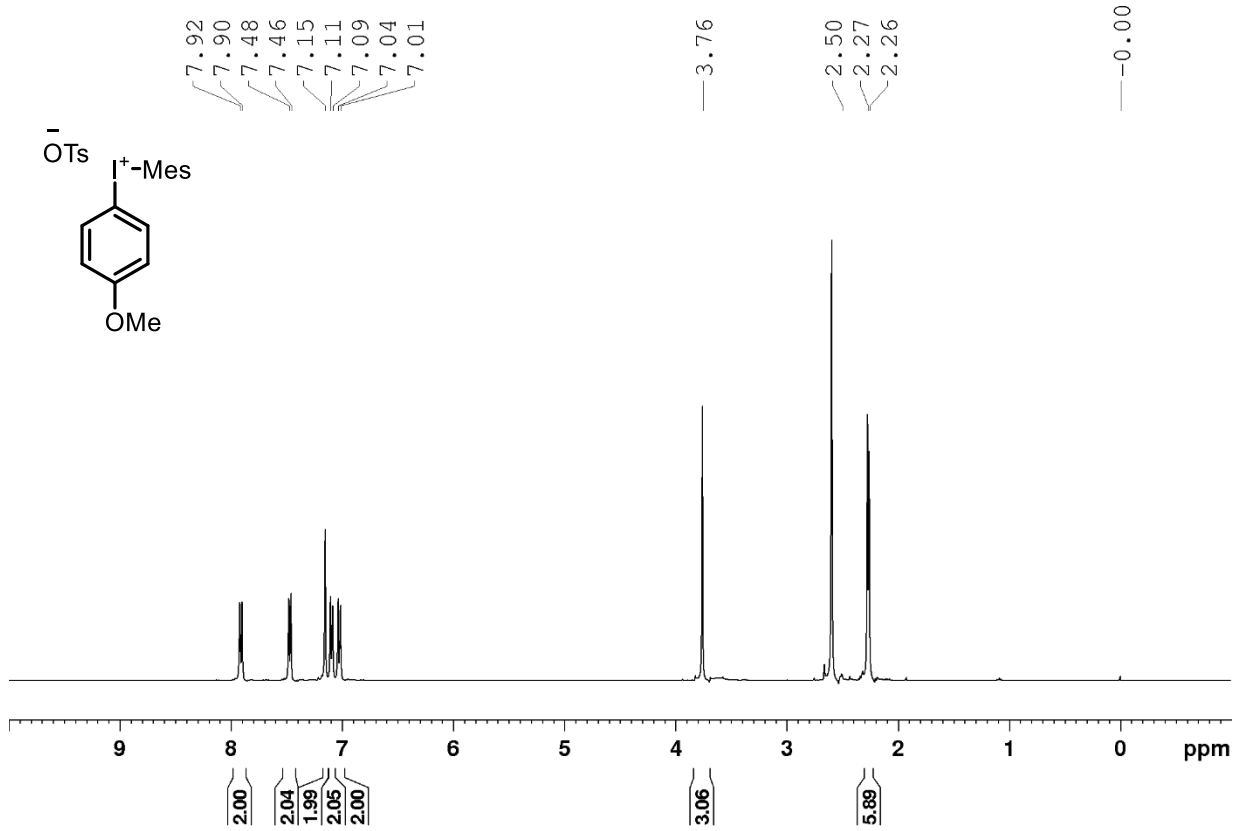
$^{13}C\{^{1}H\}$ NMR spectrum of 1m-IMes-d7 in DMSO-*d*6 at 101 MHz at 298 K



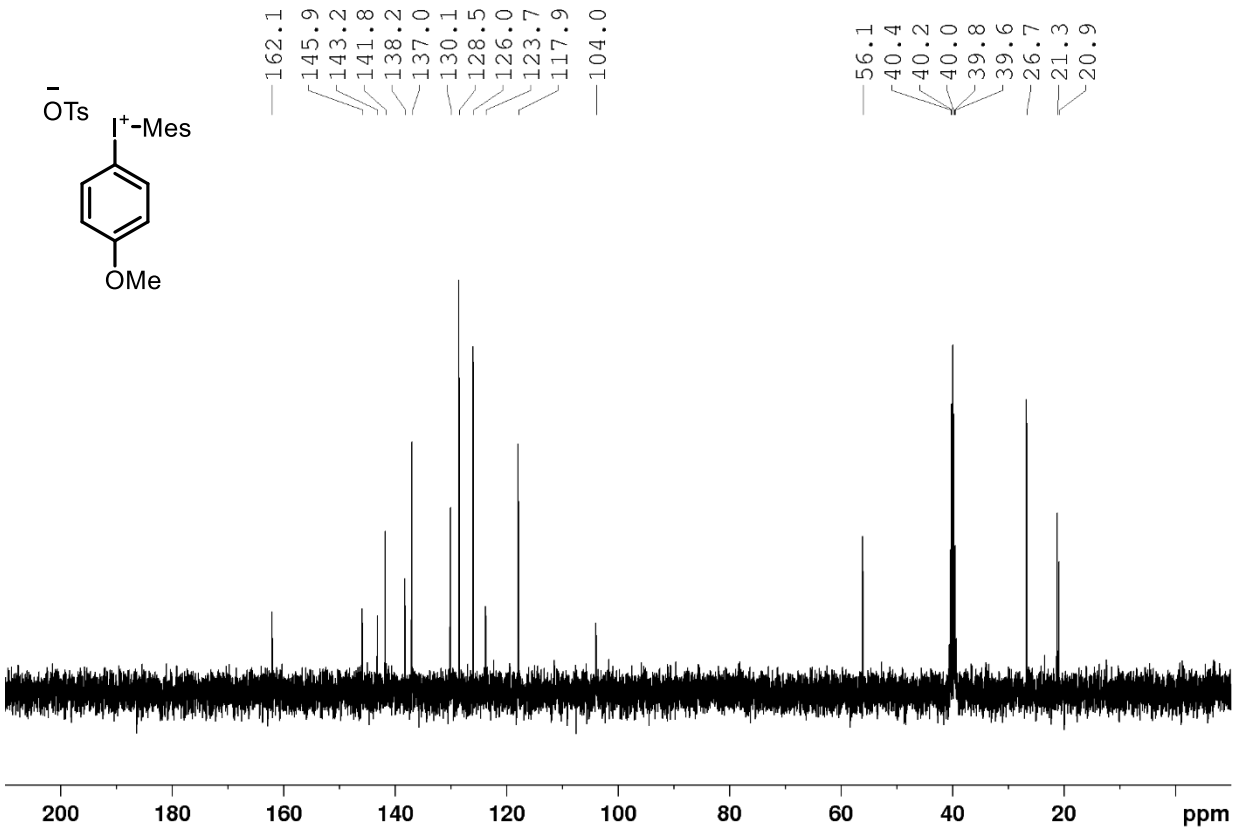
$^{19}F\{^{1}H\}$ NMR spectrum of 1m-IMes-d7 in DMSO-*d*6 at 376 MHz at 298 K



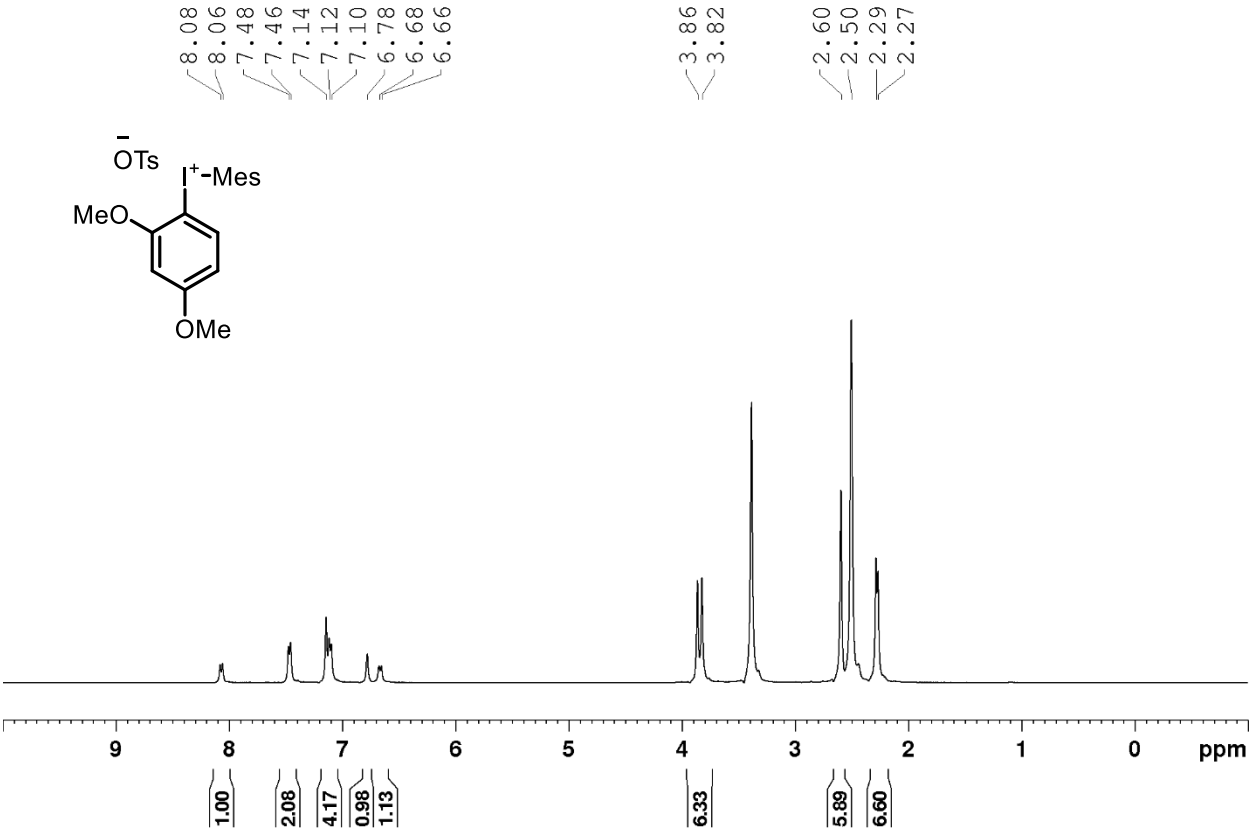
^{1}H NMR spectrum of 1n-IMes in DMSO-*d*6 at 400 MHz at 298 K



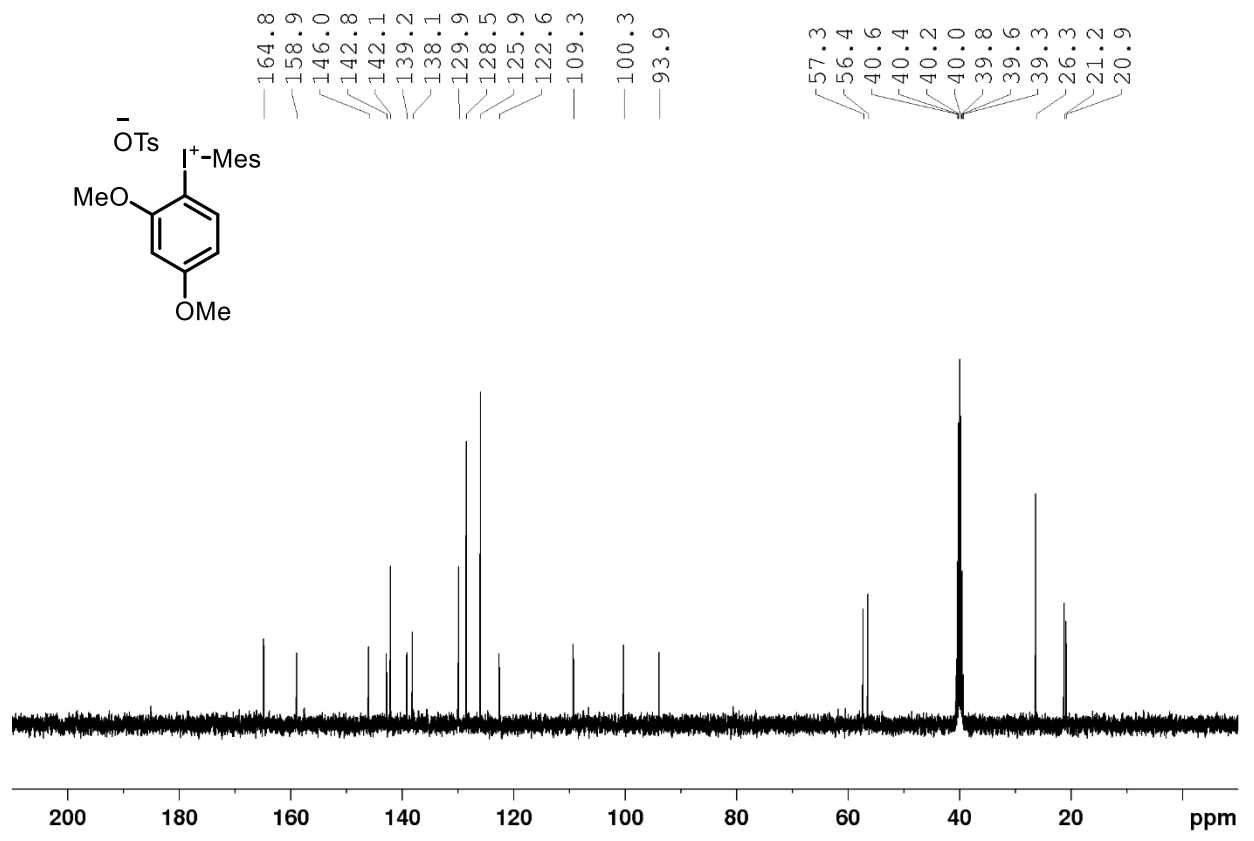
^{13}C{^{1}H} NMR spectrum of 1n-IMes in DMSO-*d*6 at 101 MHz at 298 K



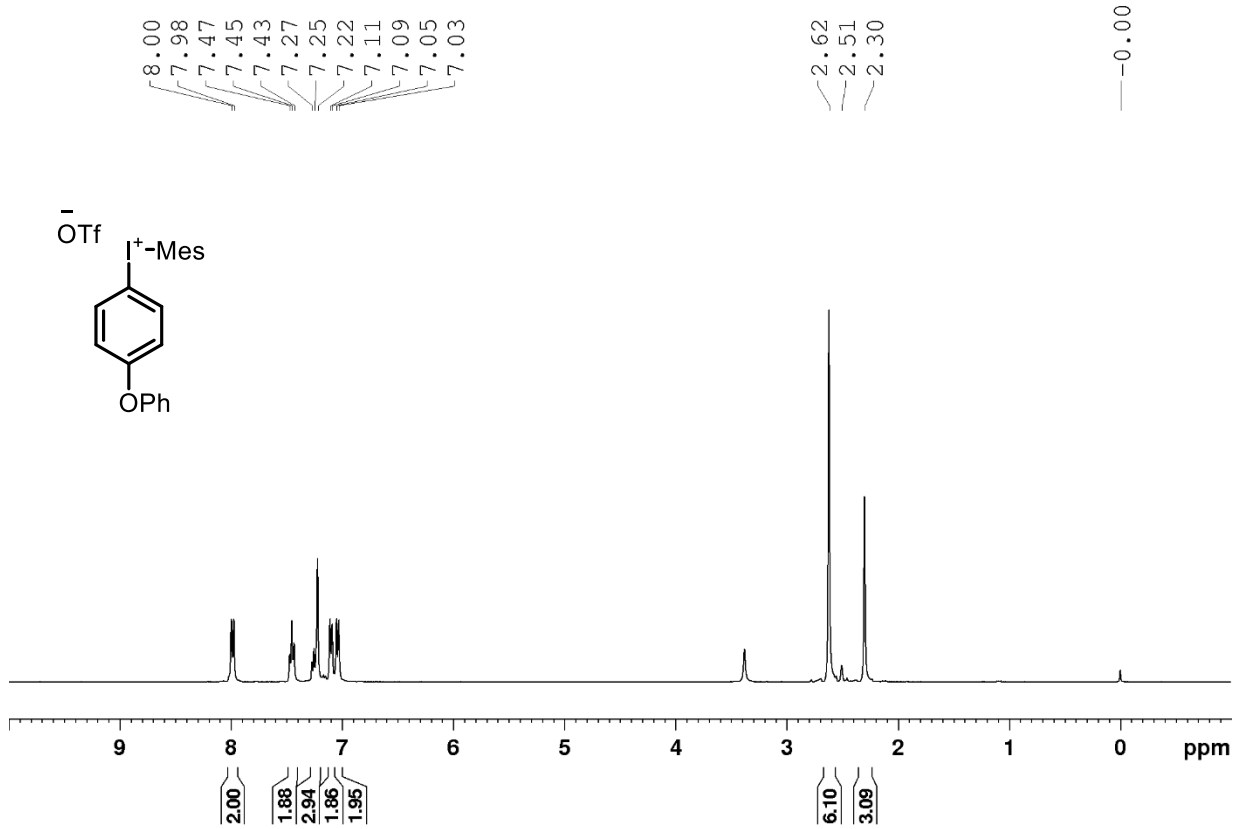
^{1}H NMR spectrum of 1o-IMes in DMSO-*d*6 at 400 MHz at 298 K



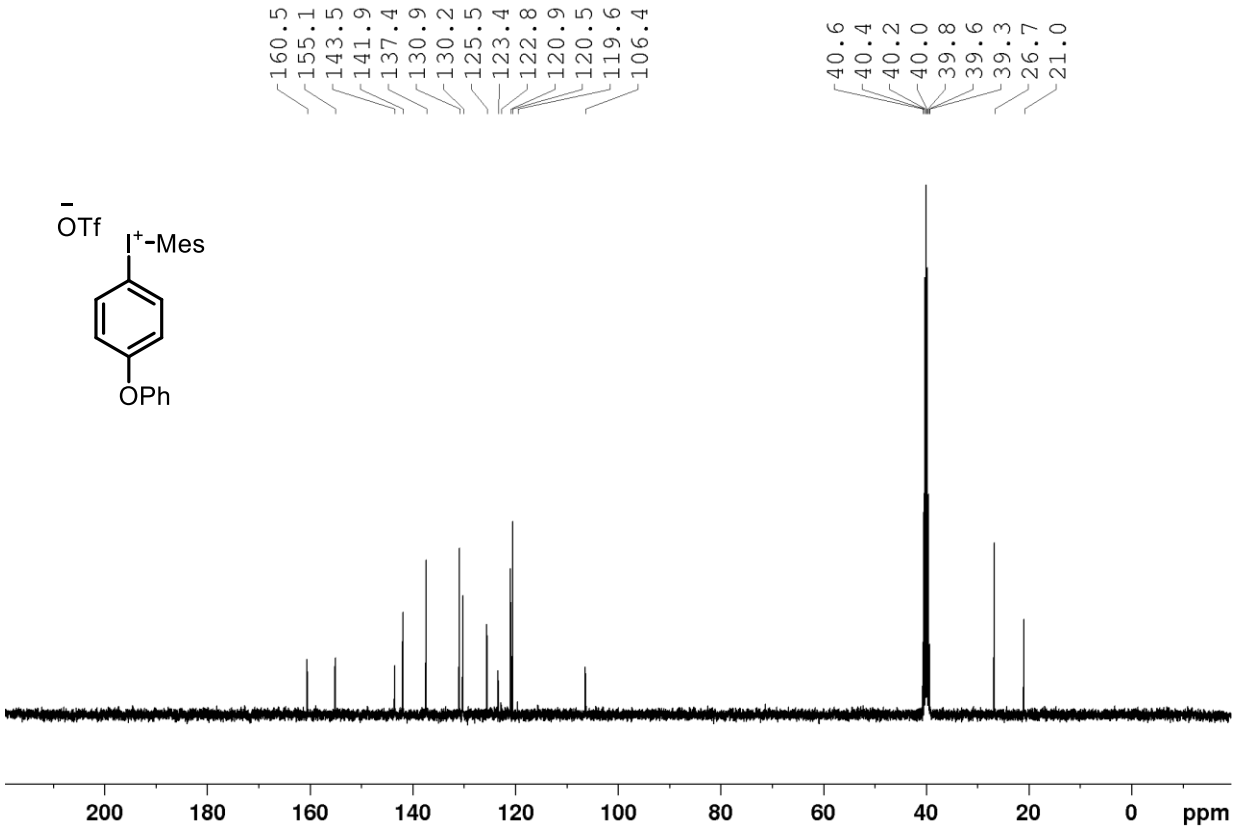
^{13}C{^{1}H} NMR spectrum of 1o-IMes in DMSO-*d*6 at 101 MHz at 298 K



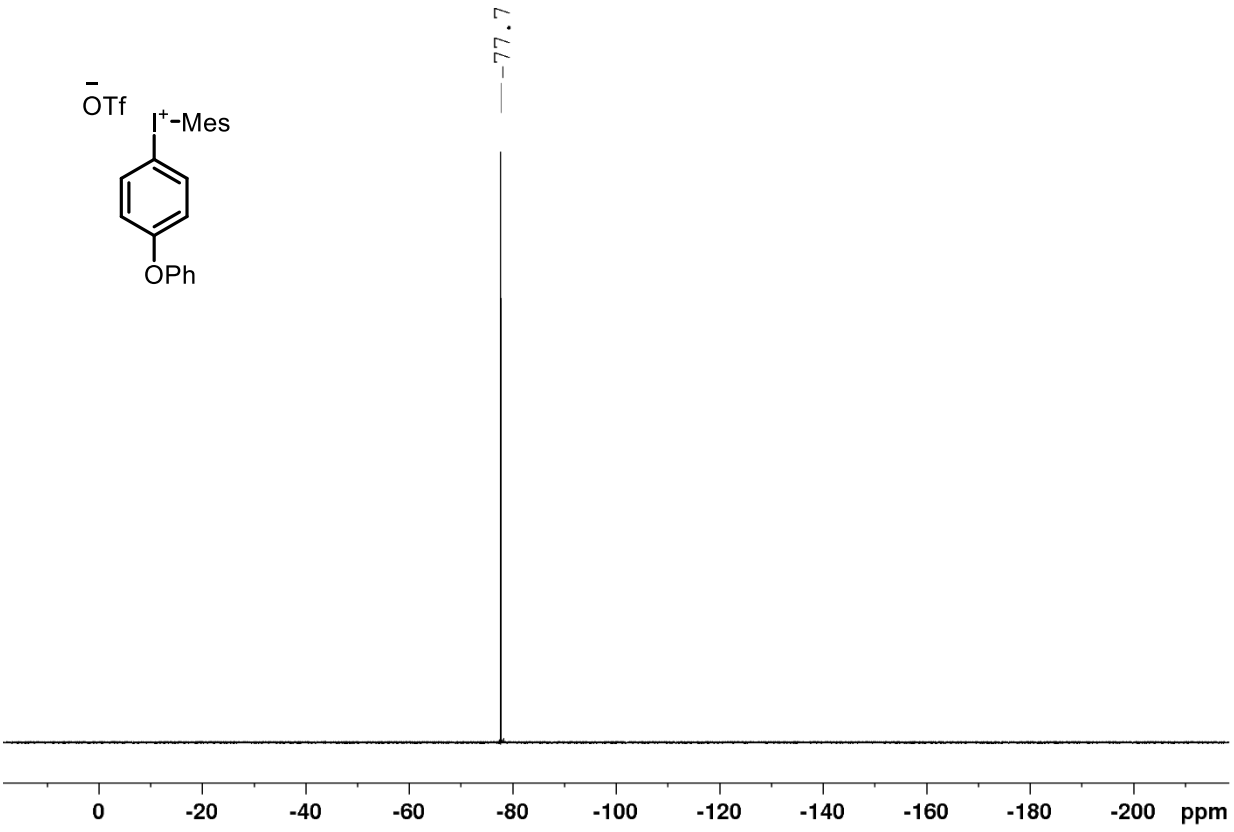
^{1}H NMR spectrum of 1p-IMes in DMSO-*d*6 at 400 MHz at 298 K



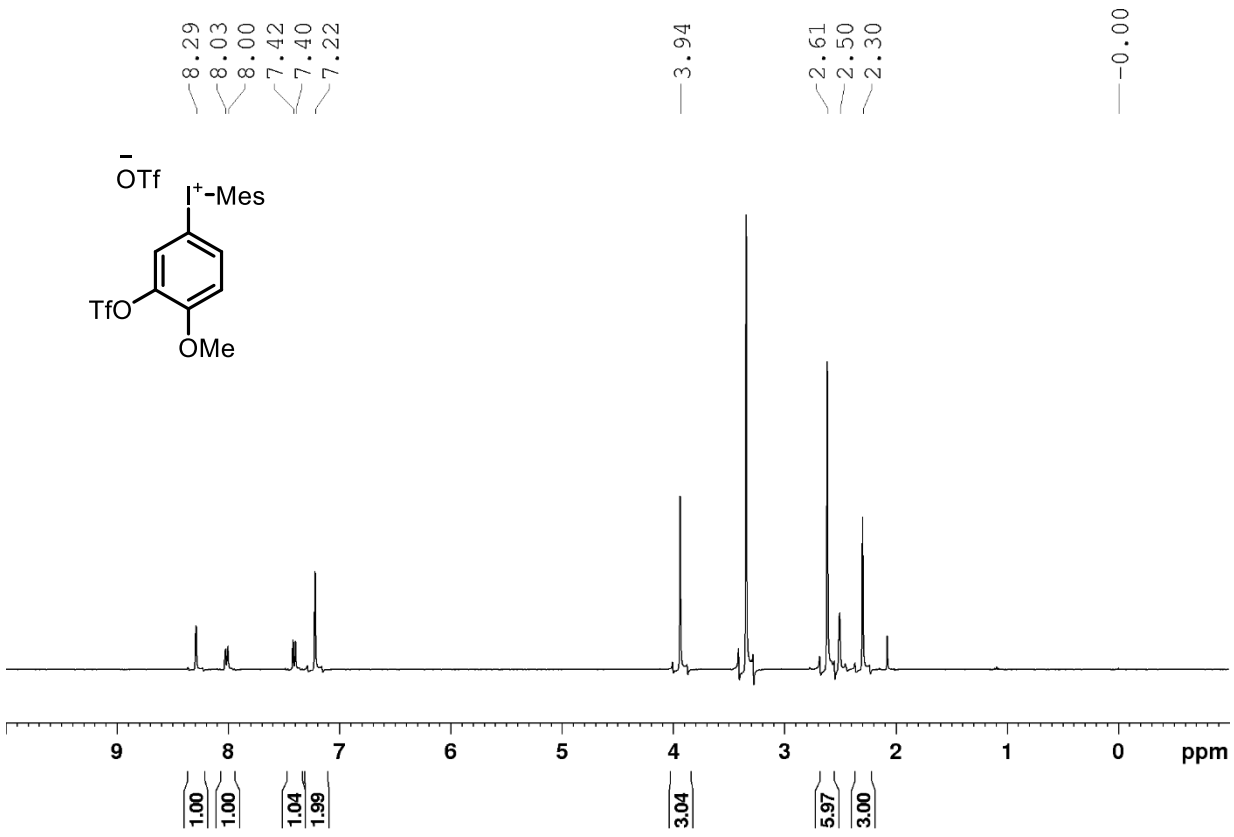
^{13}C{^{1}H} NMR spectrum of 1p-IMes in DMSO-*d*6 at 101 MHz at 298 K



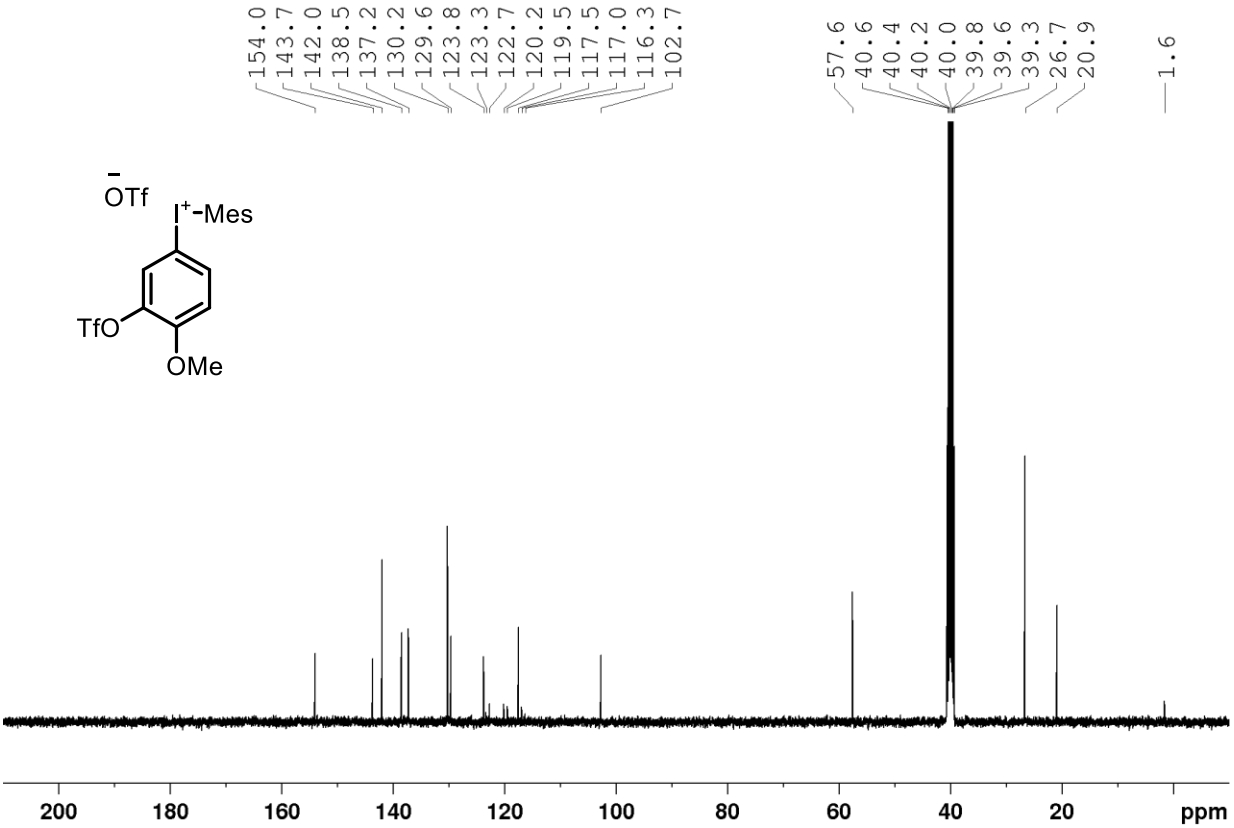
$^{19}F\{^{1}H\}$ NMR spectrum of 1p-IMes in DMSO-*d*6 at 376 MHz at 298 K



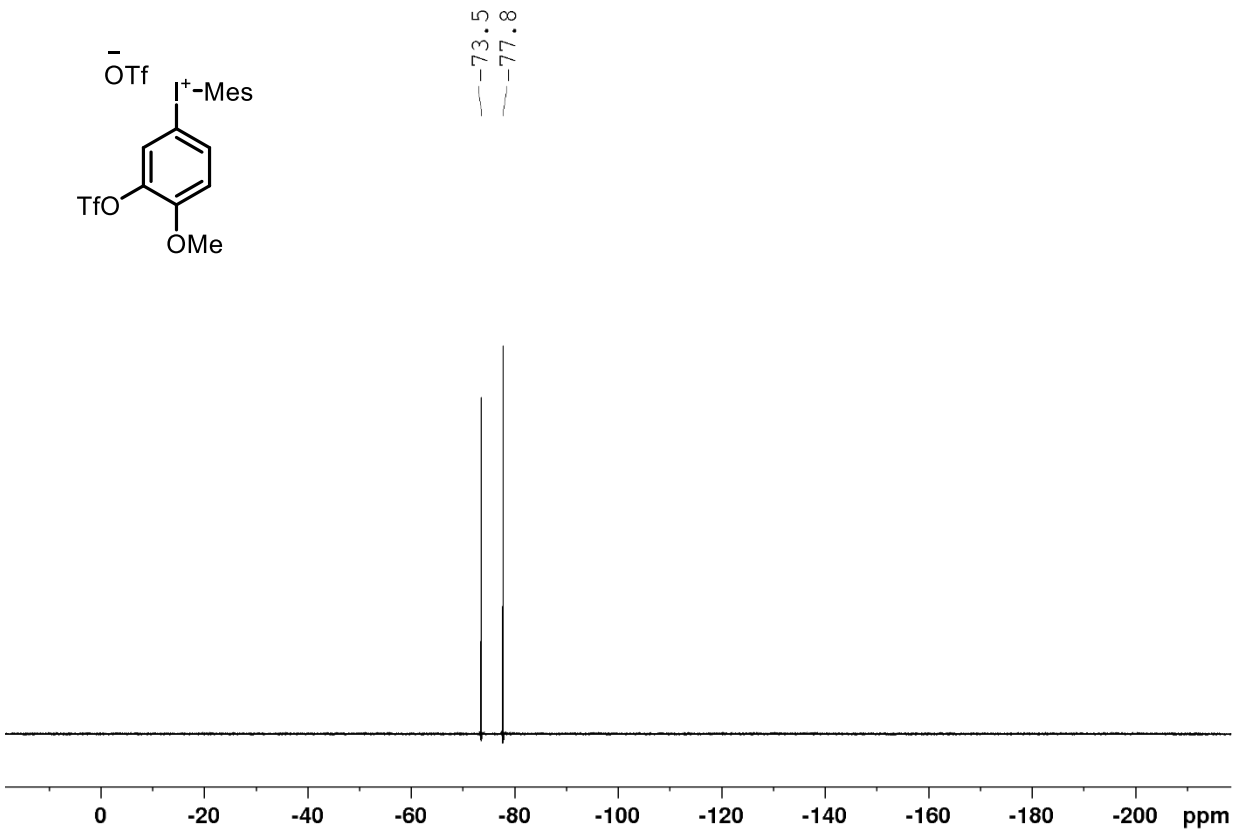
^{1}H NMR spectrum of 1q-IMes in DMSO-*d*6 at 400 MHz at 298 K



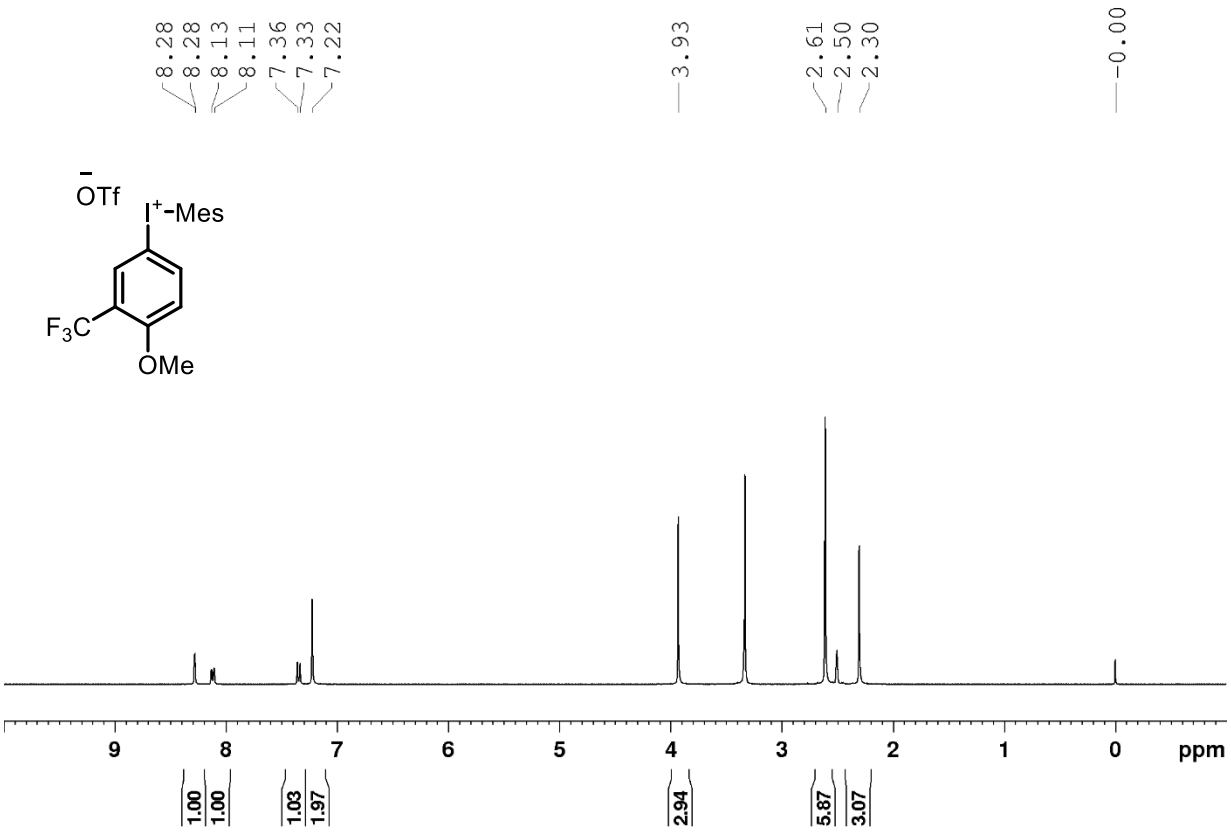
$^{13}C\{^{1}H\}$ NMR spectrum of 1q-IMes in DMSO-*d*6 at 101 MHz at 298 K



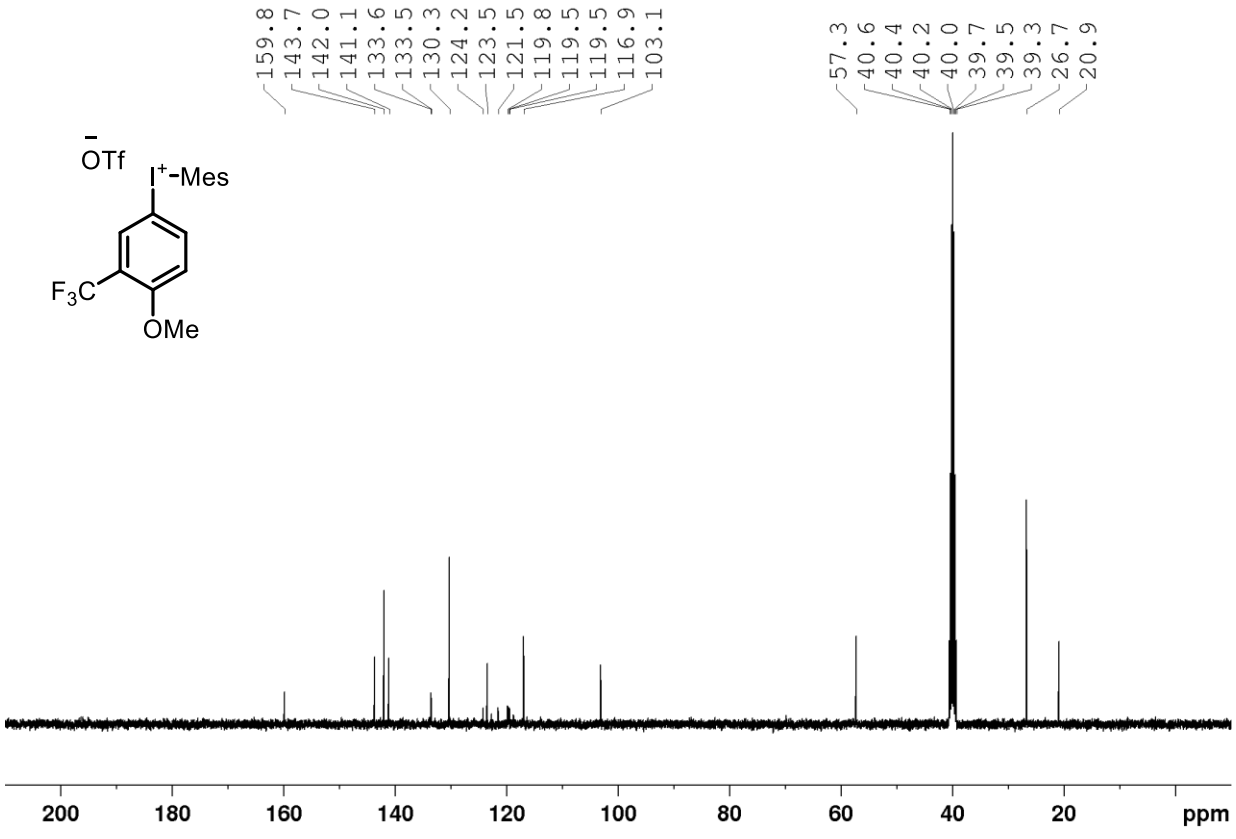
$^{19}F\{^{1}H\}$ NMR spectrum of 1q-IMes in DMSO-*d*6 at 376 MHz at 298 K



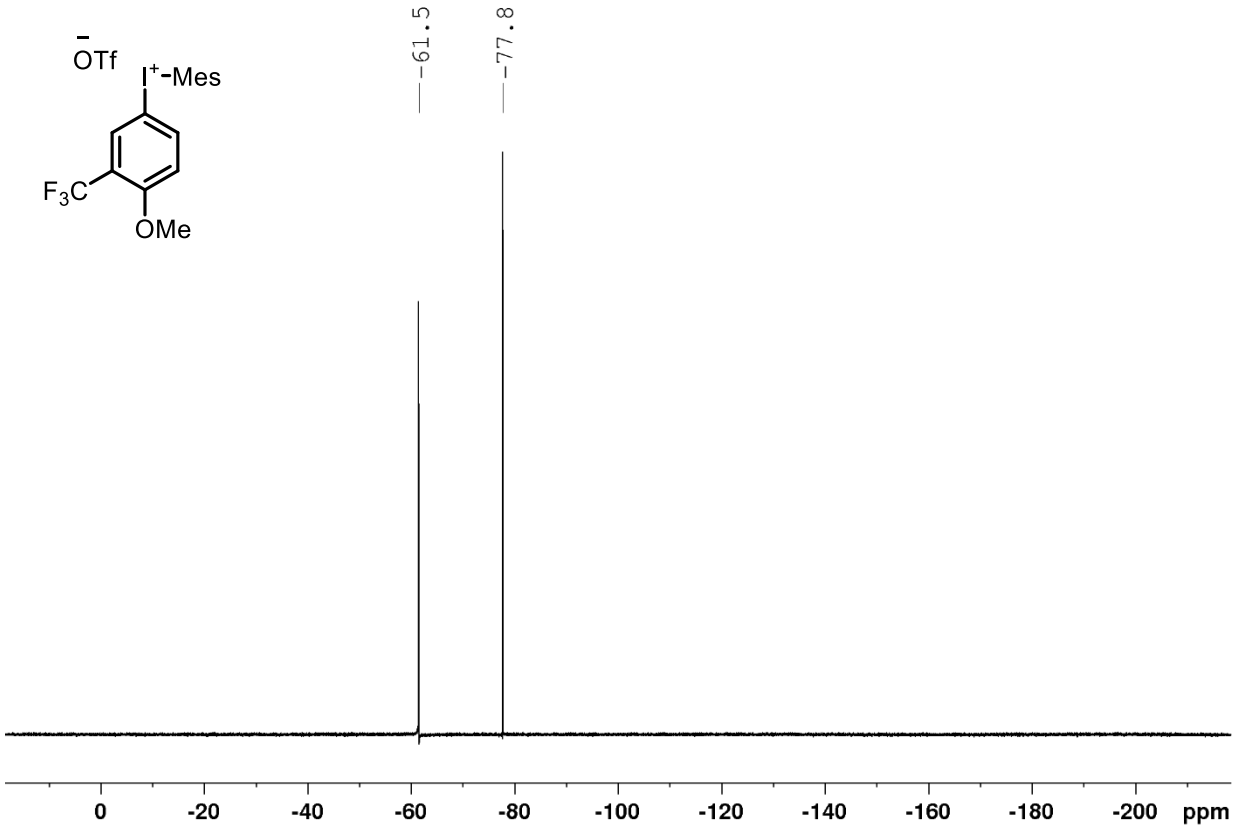
^{1}H NMR spectrum of 1r-IMes in DMSO-*d*6 at 400 MHz at 298 K



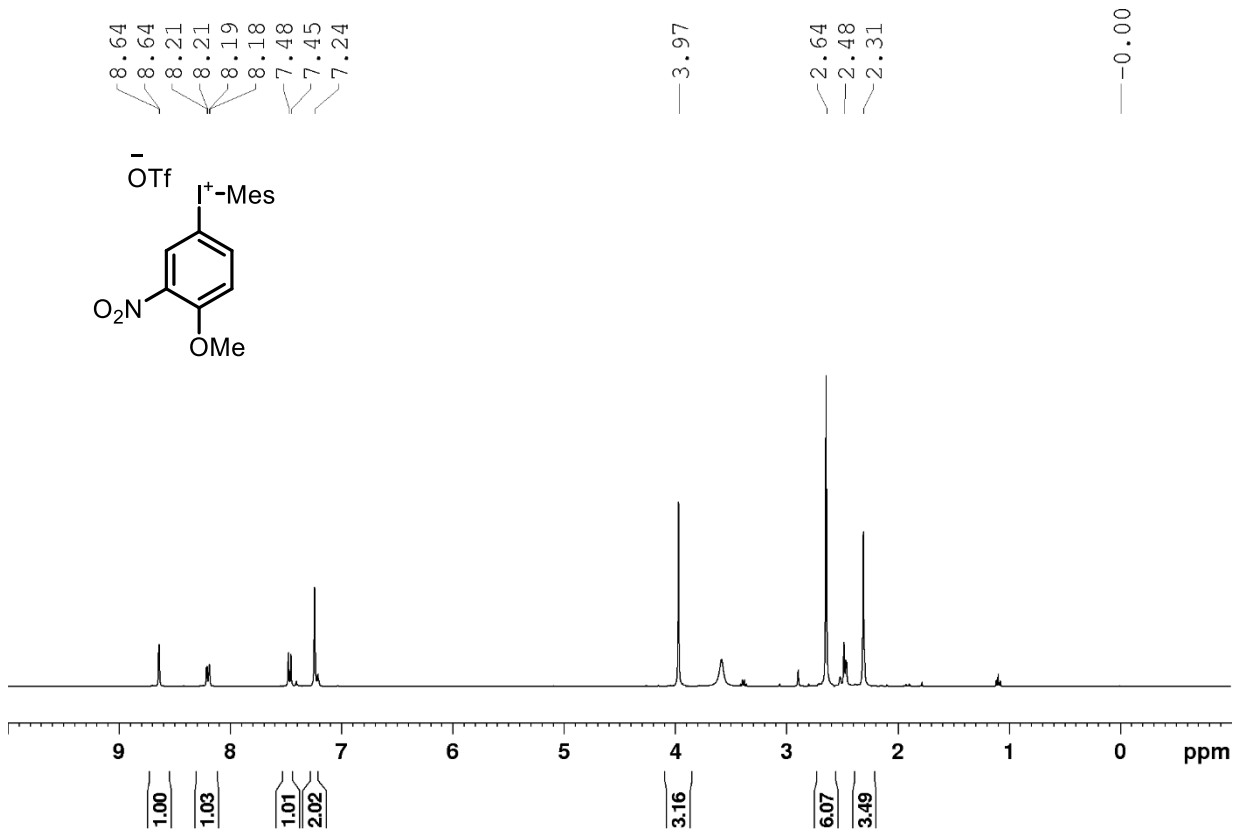
^{13}C{^{1}H} NMR spectrum of 1r-IMes in DMSO-*d*6 at 101 MHz at 298 K



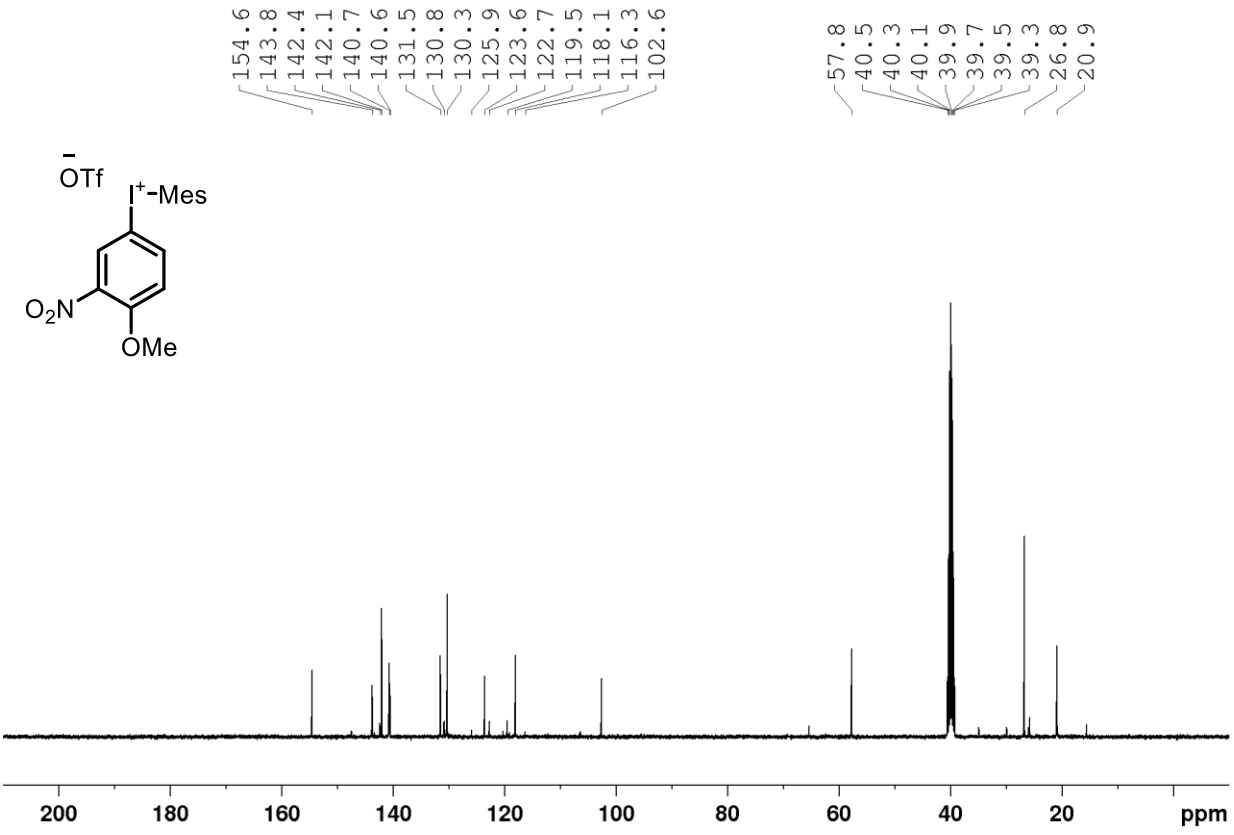
$^{19}F\{^{1}H\}$ NMR spectrum of 1r-IMes in DMSO-*d*6 at 376 MHz at 298 K



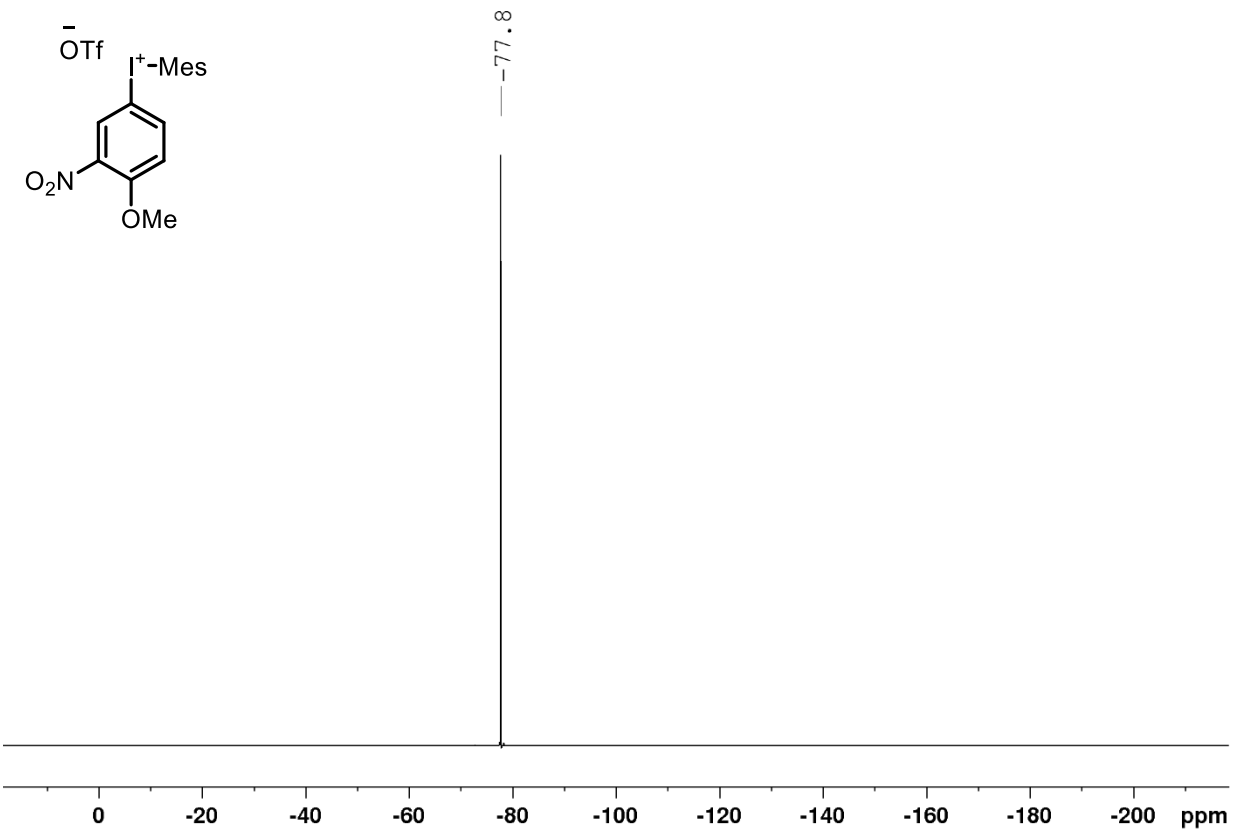
^{1}H NMR spectrum of 1s-IMes in DMSO-*d*6 at 400 MHz at 298 K



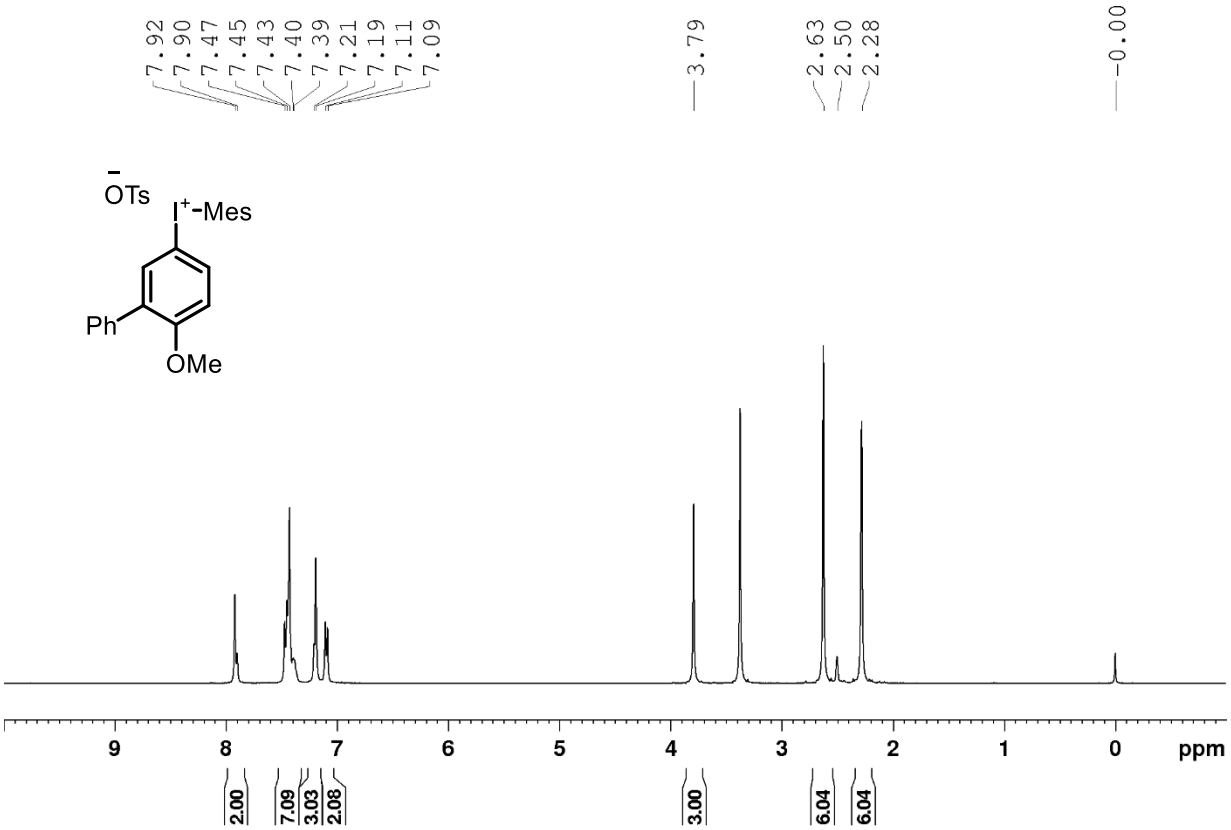
$^{13}C\{^{1}H\}$ NMR spectrum of 1s-IMes in DMSO-*d*6 at 101 MHz at 298 K



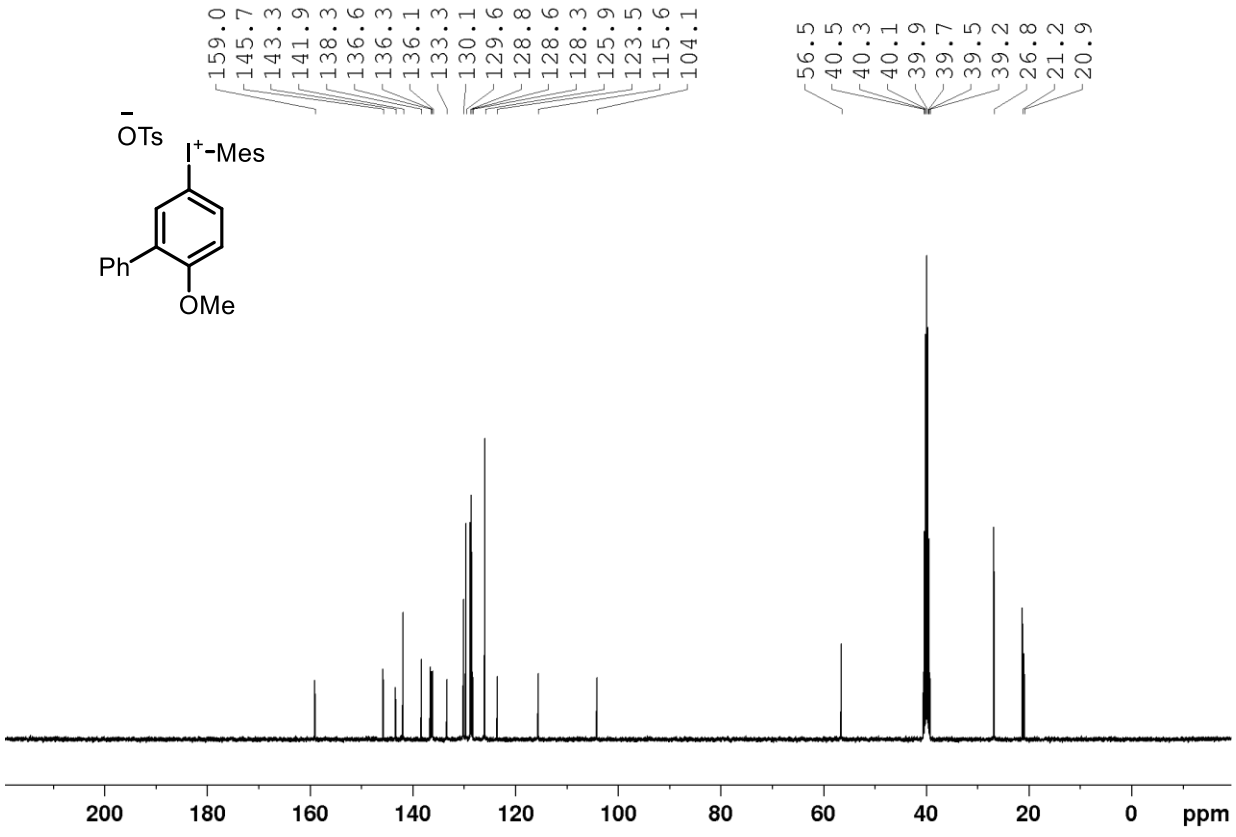
$^{19}F\{^{1}H\}$ NMR spectrum of 1s-IMes in DMSO-*d*6 at 376 MHz at 298 K



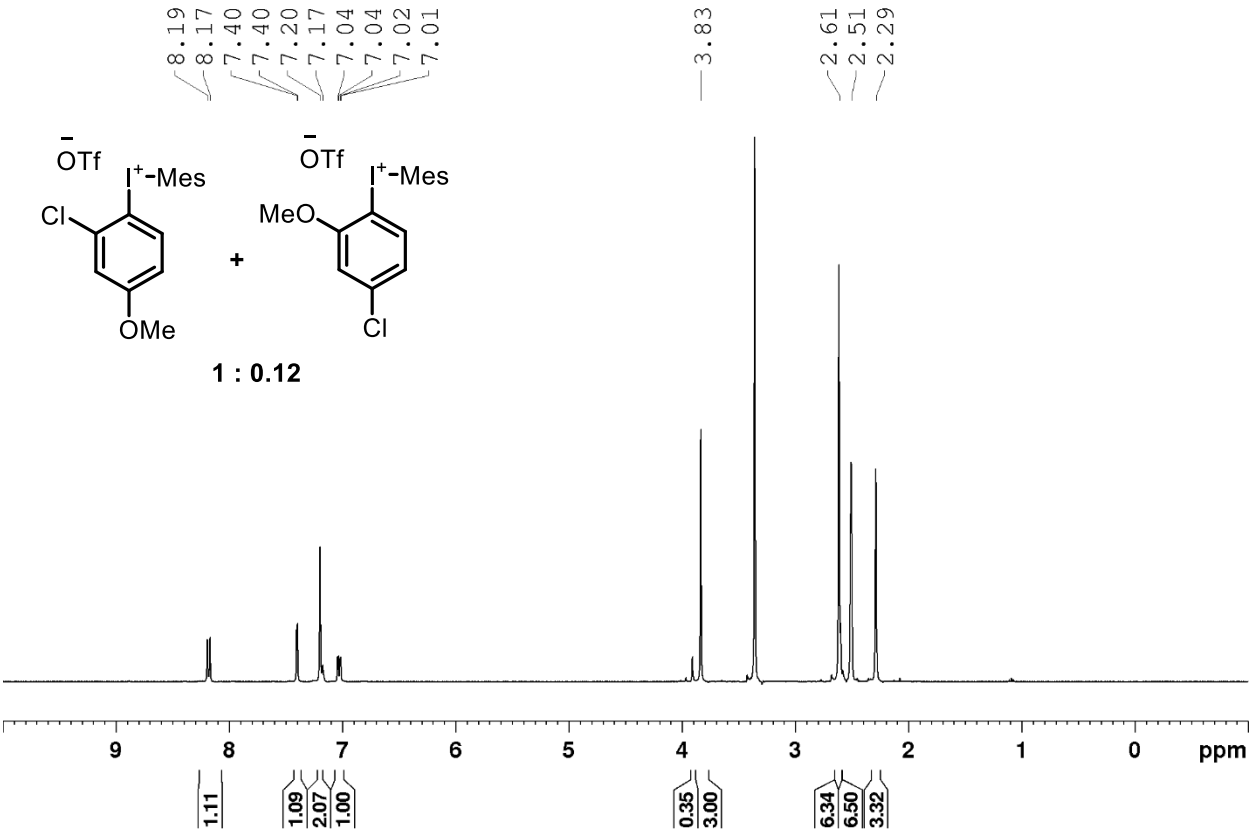
^{1}H NMR spectrum of 1t-IMes in DMSO-*d*6 at 400 MHz at 298 K



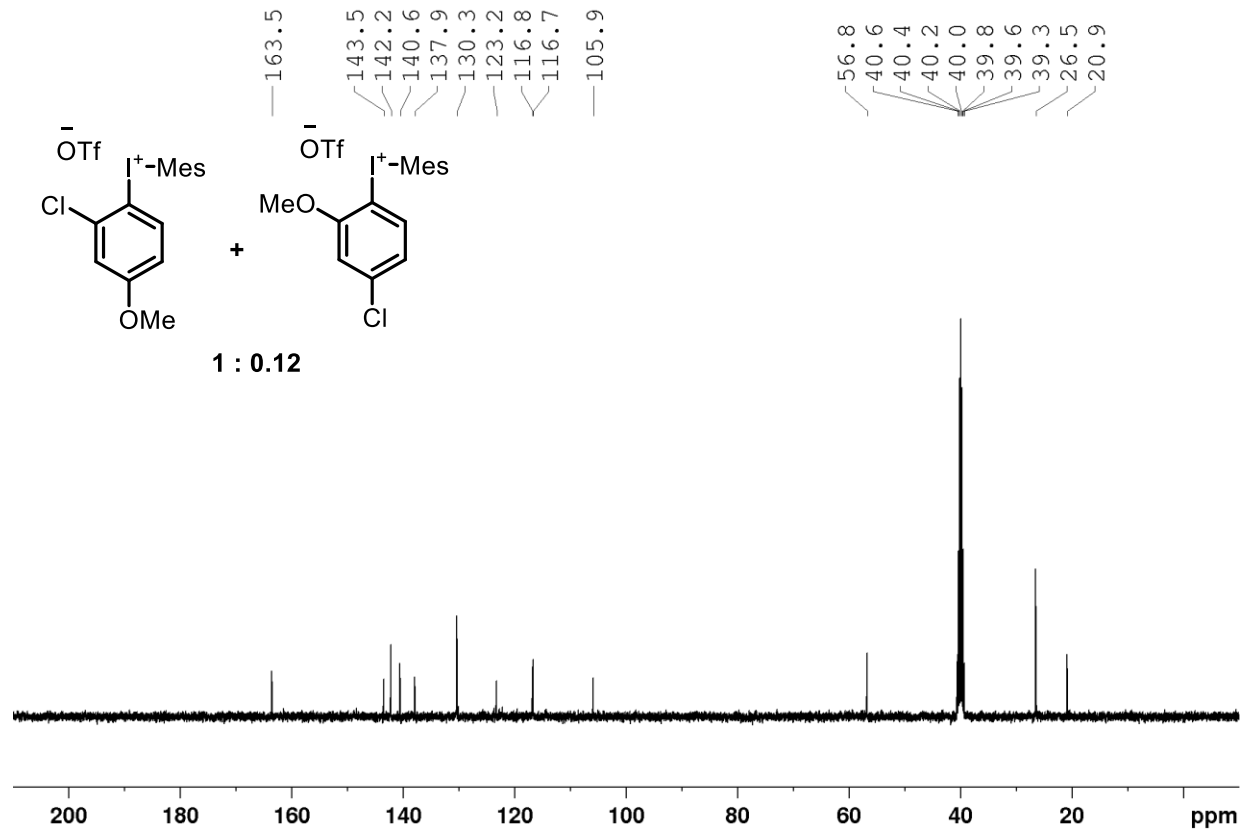
^{13}C{^{1}H} NMR spectrum of 1t-IMes in DMSO-*d*6 at 101 MHz at 298 K



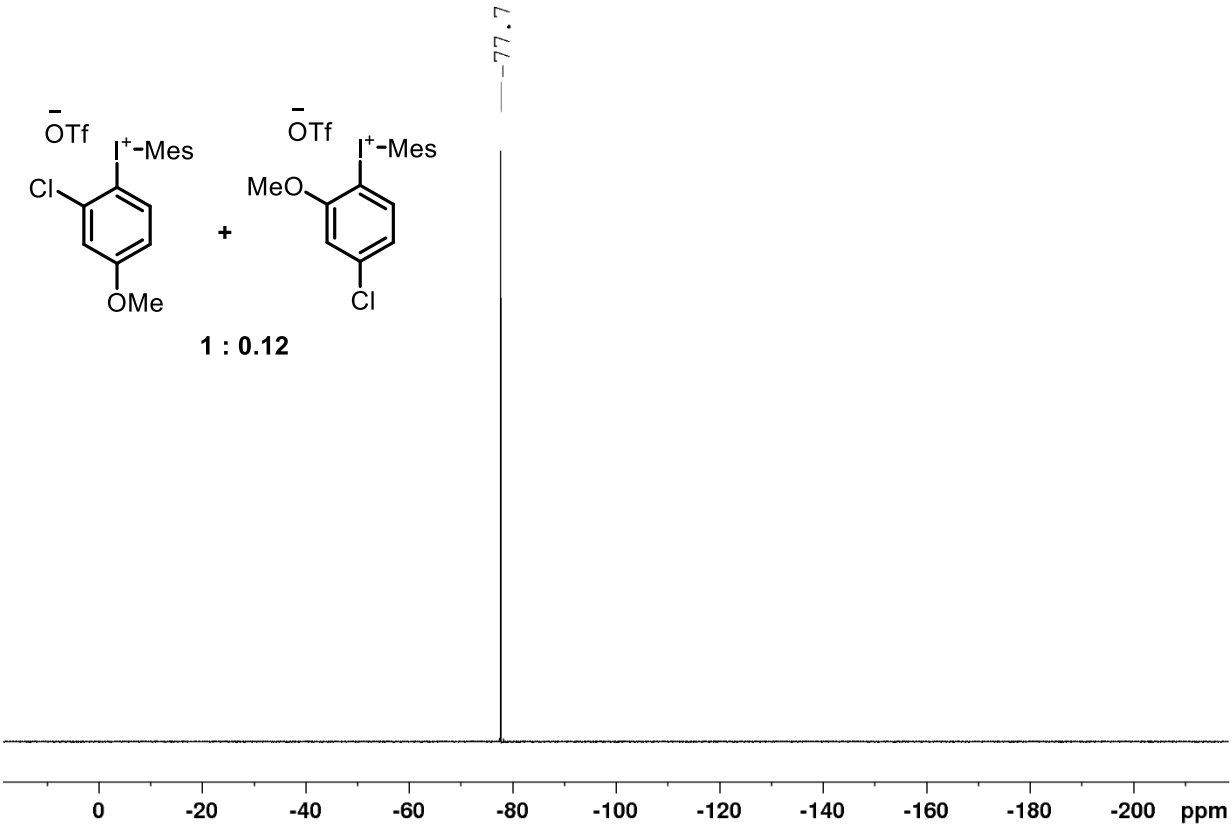
^{1}H NMR spectrum of 1u-IMes in DMSO-*d*6 at 400 MHz at 298 K



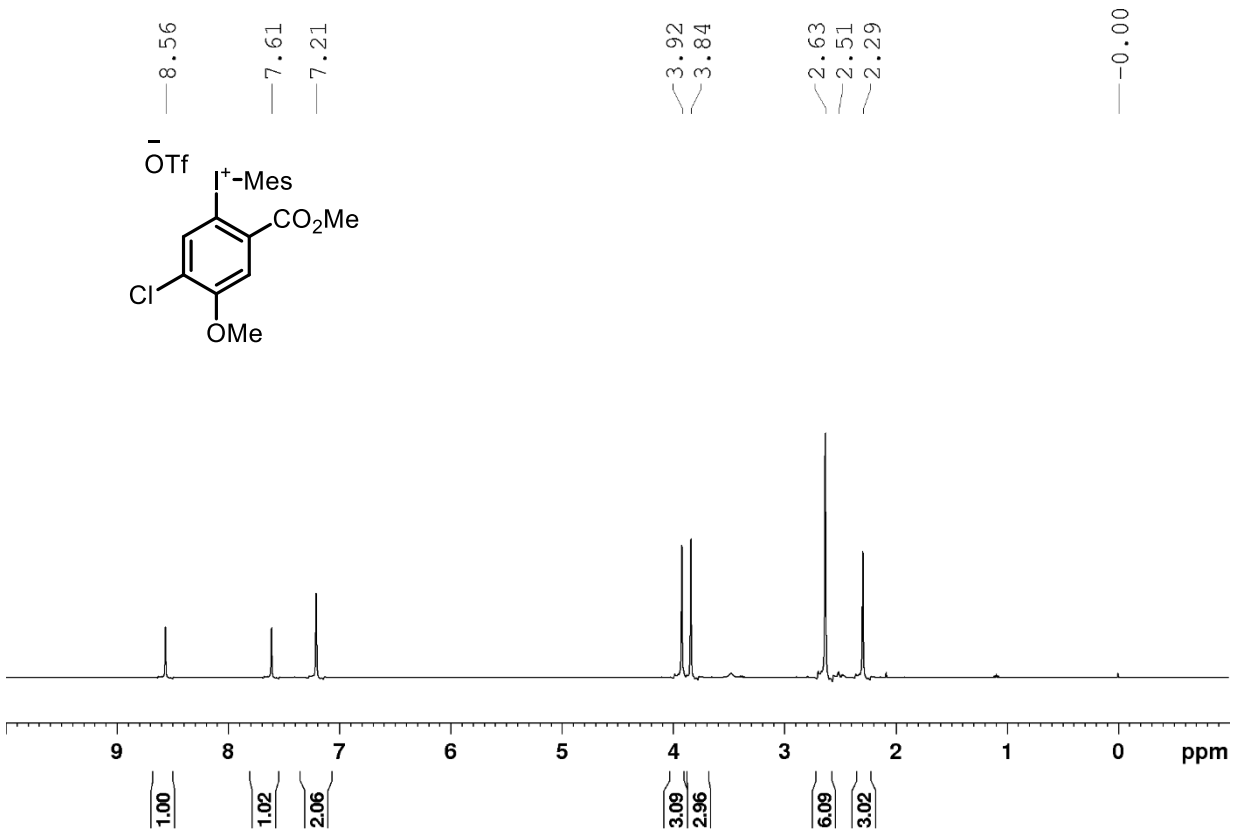
^{13}C{^{1}H} NMR spectrum of 1u-IMes in DMSO-*d*6 at 101 MHz at 298 K



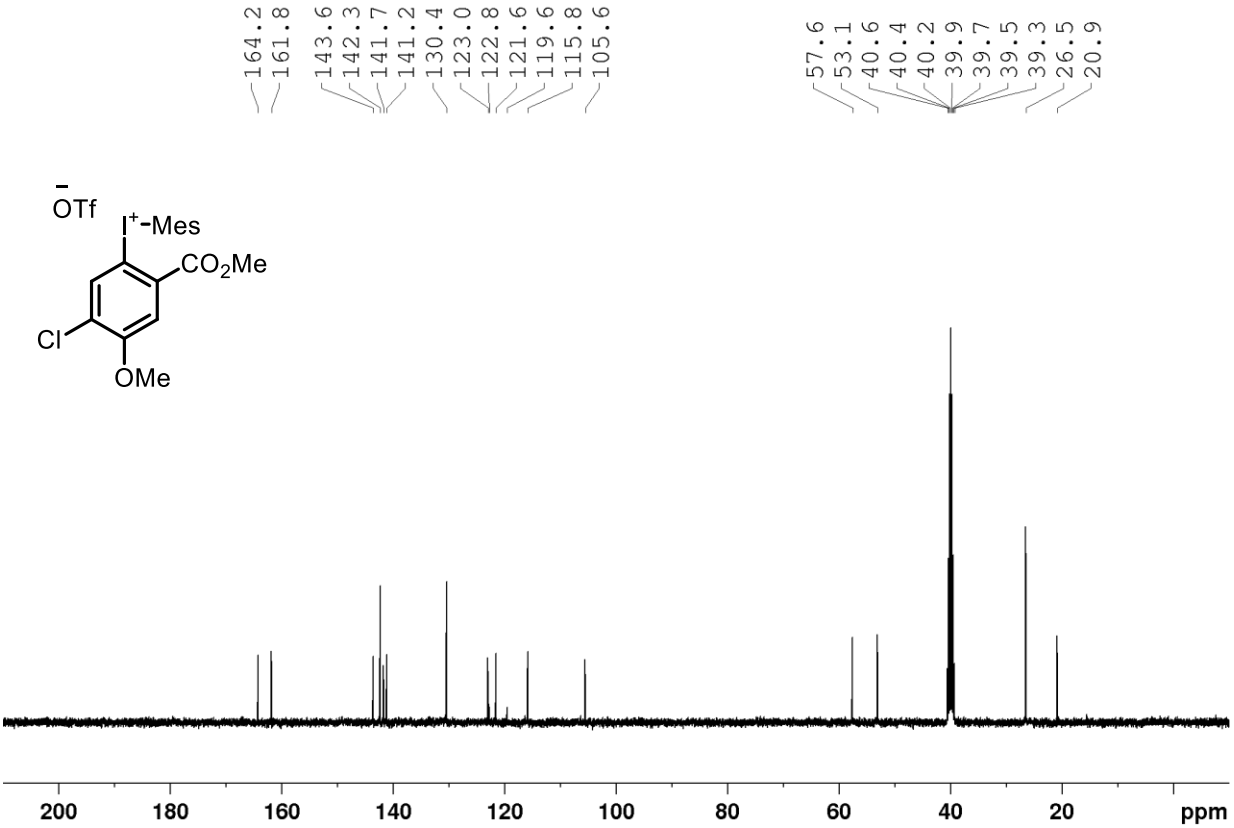
$^{19}F\{^{1}H\}$ NMR spectrum of 1u-IMes in DMSO-*d*6 at 376 MHz at 298 K



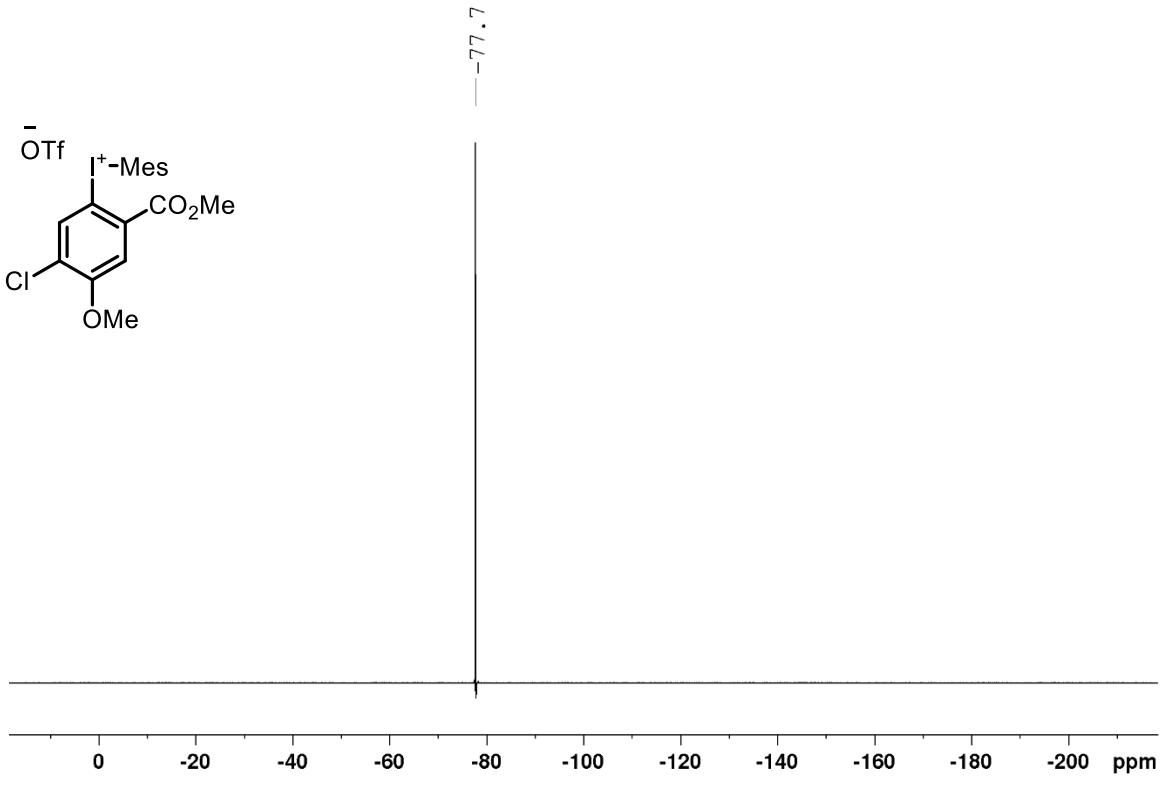
^{1}H NMR spectrum of 1w-IMes in DMSO-*d*6 at 400 MHz at 298 K



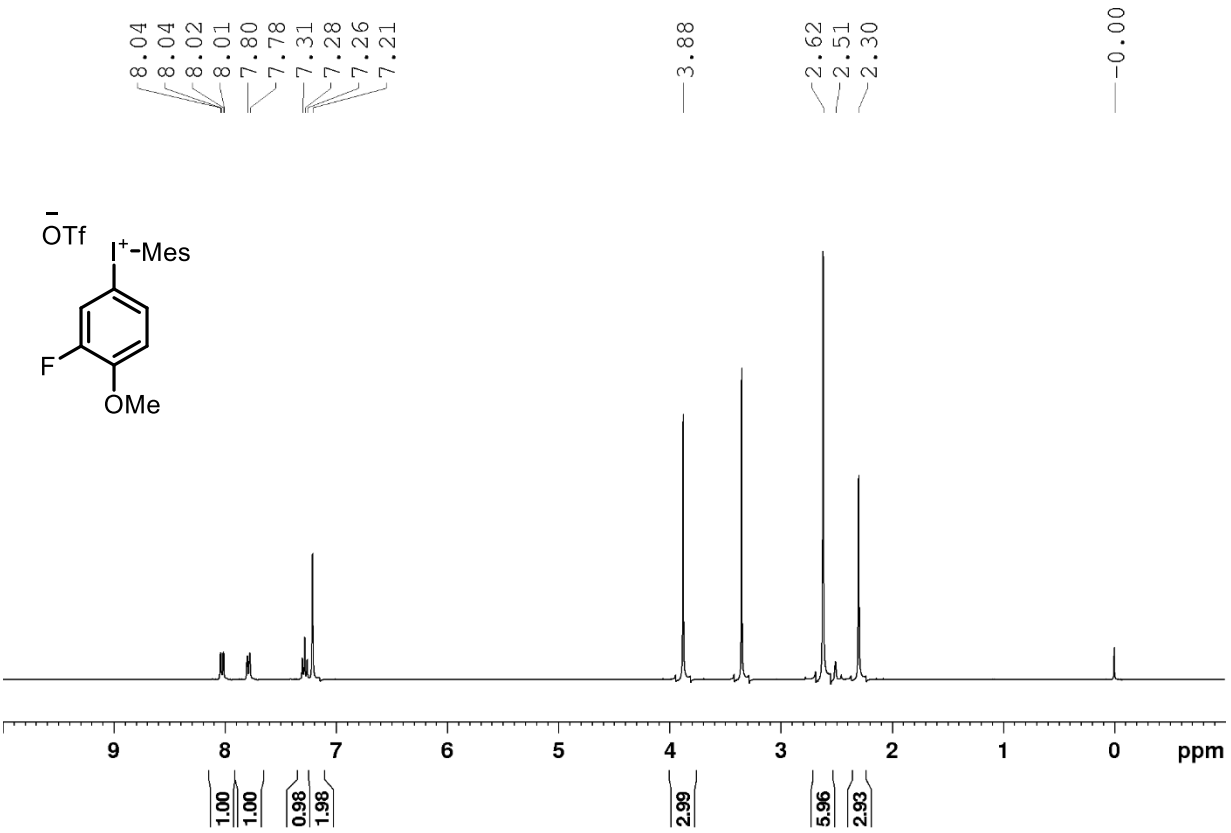
$^{13}C\{^{1}H\}$ NMR spectrum of 1w-IMes in DMSO-*d*6 at 101 MHz at 298 K



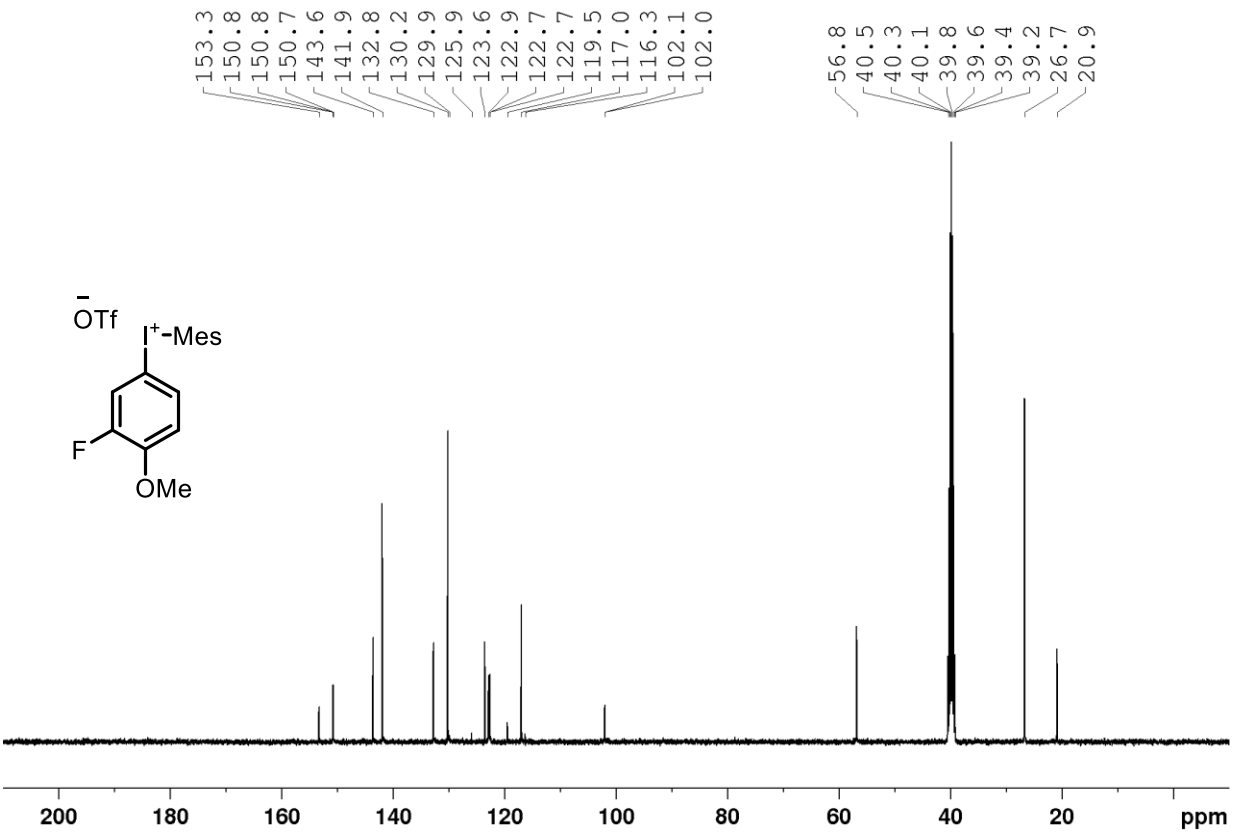
$^{19}F\{^{1}H\}$ NMR spectrum of 1w-IMes in DMSO-*d*6 at 376 MHz at 298 K



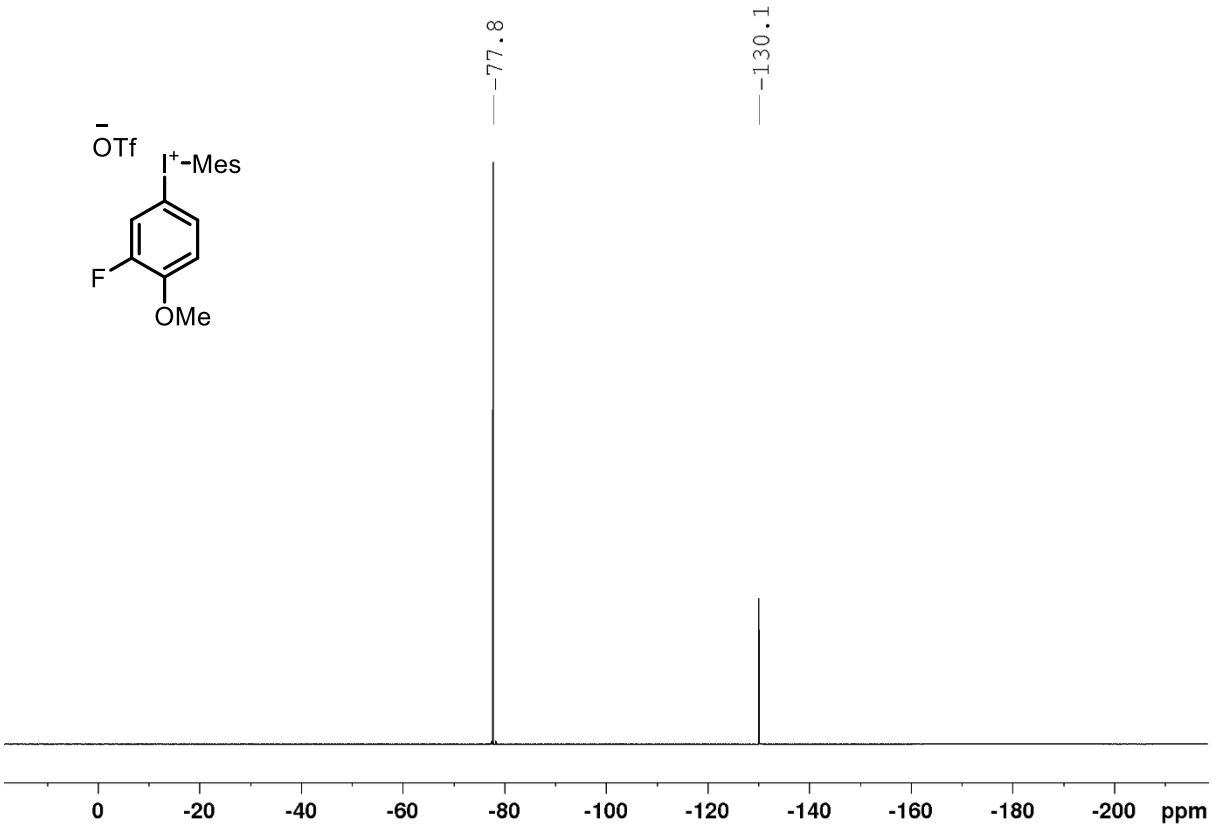
^{1}H NMR spectrum of 1z-IMes in DMSO-*d*6 at 400 MHz at 298 K



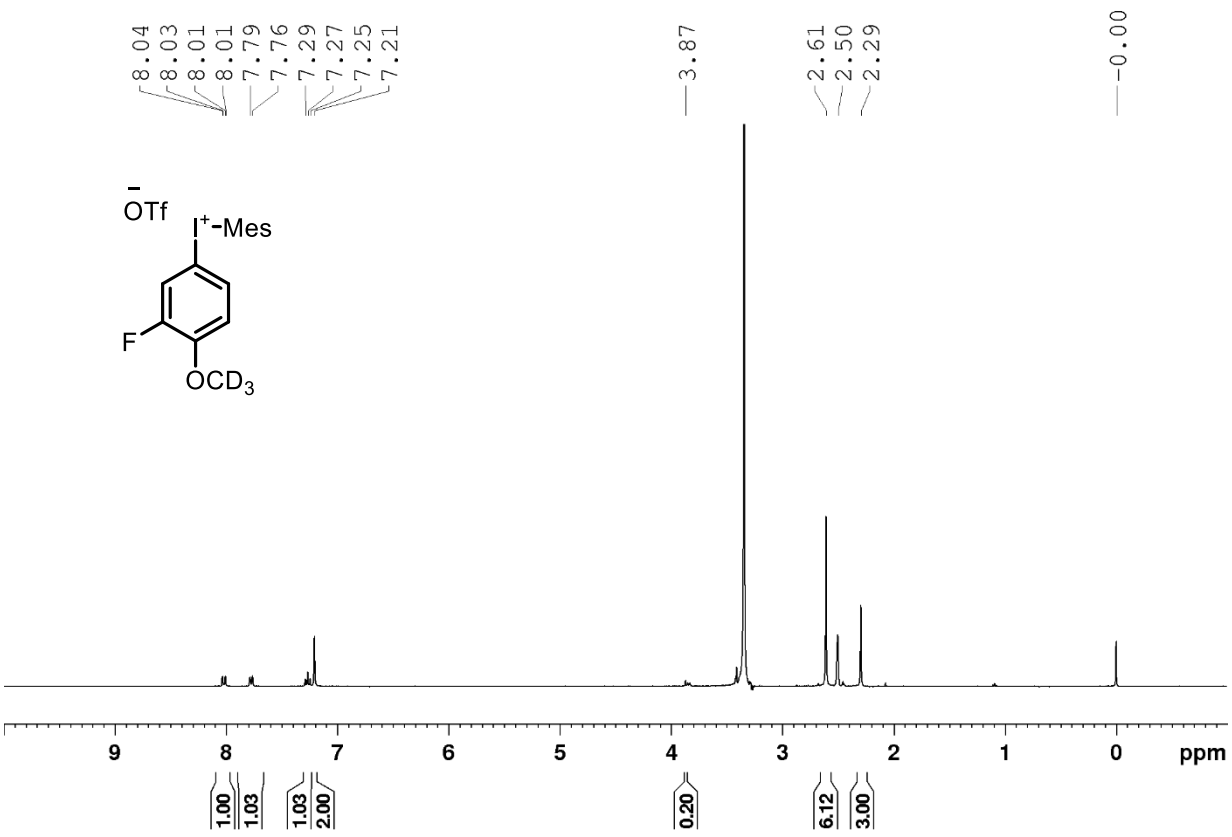
^{13}C{^{1}H} NMR spectrum of 1z-IMes in DMSO-*d*6 at 101 MHz at 298 K



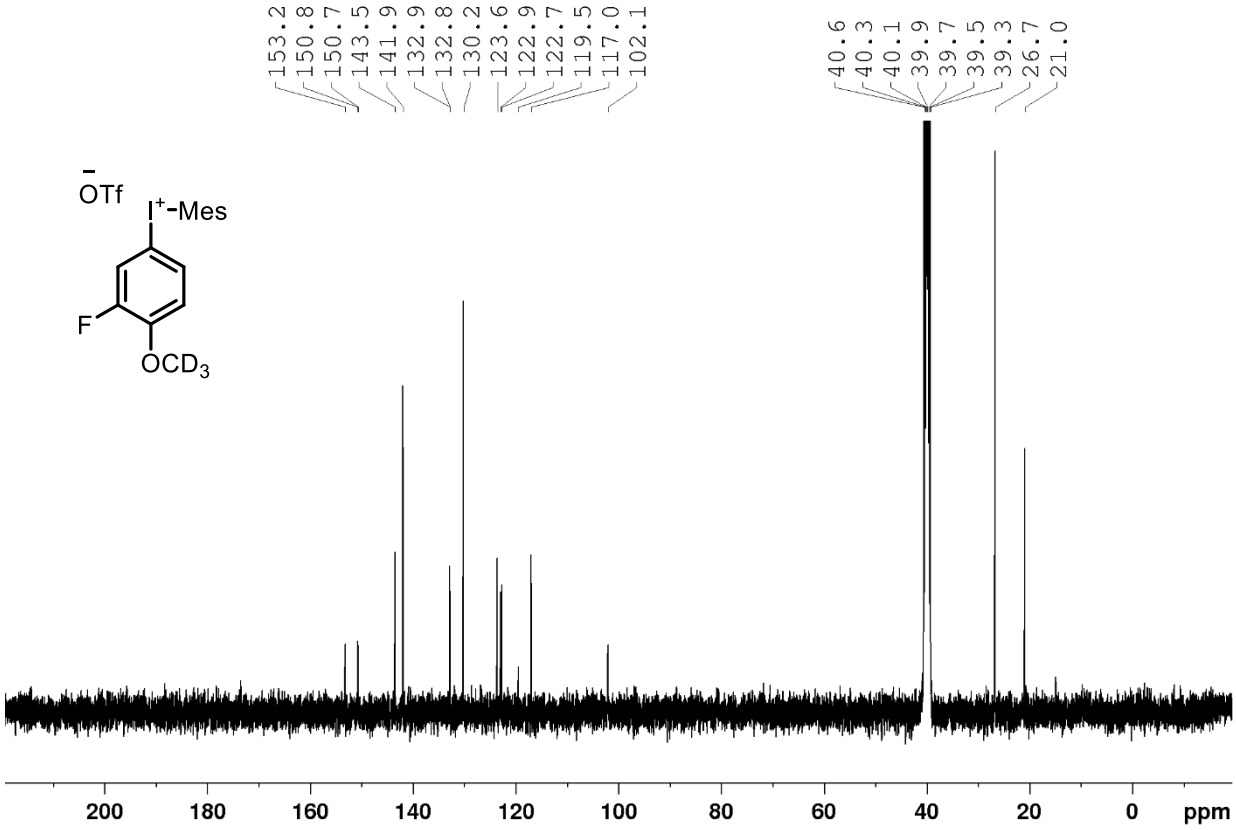
$^{19}F\{^{1}H\}$ NMR spectrum of 1z-IMes in DMSO-*d*6 at 376 MHz at 298 K



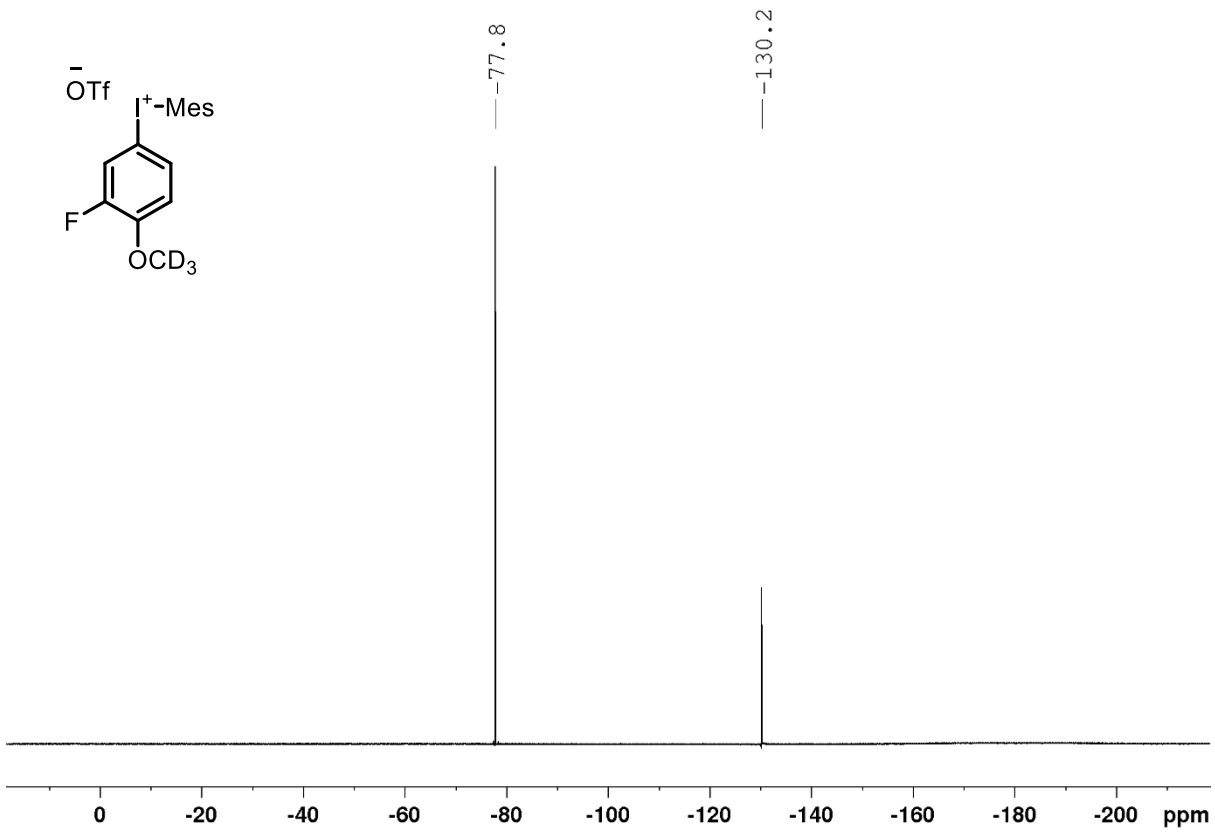
^{1}H NMR spectrum of 1z-IMes-d3 in DMSO-*d*6 at 400 MHz at 298 K



$^{13}C\{^{1}H\}$ NMR spectrum of 1z-IMes-d3 in DMSO-*d*6 at 101 MHz at 298



$^{19}F\{^{1}H\}$ NMR spectrum of 1z-IMes-d3 in DMSO-*d*6 at 376 MHz at 298 K



DFT Calculated Reaction Schemes:

Figure 1: Reaction coordinate diagram for phenyl thianthrenium salt extrusion of benzyne, as calculated at M062x/Def2-TZVPP with SMD solvation in toluene

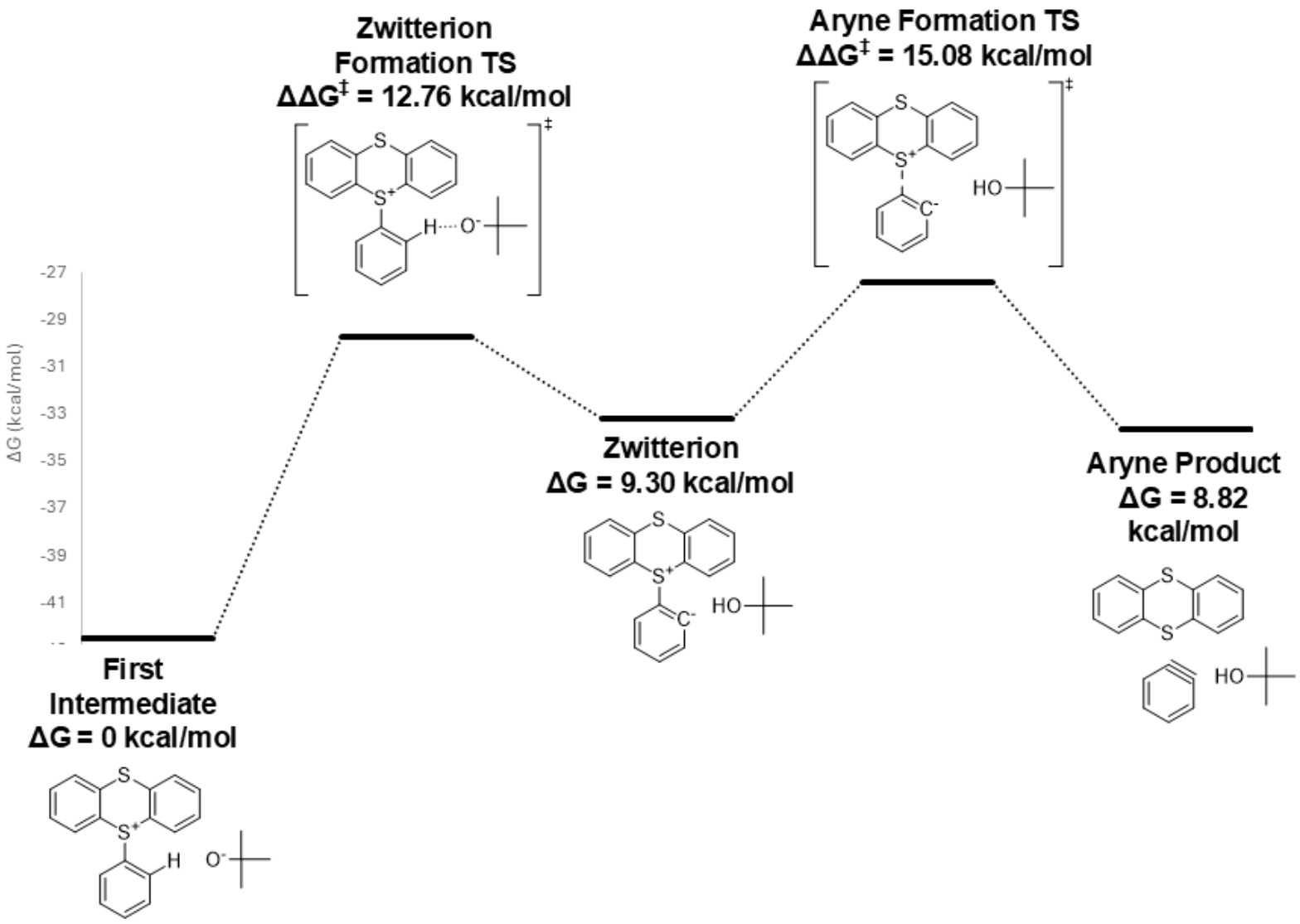


Figure 2: Diagram of benzyne extrusion from Phenyl(Mes)Iodonium with t-butoxide at M06-2x/Def2-tzvpp with SMD solvation in toluene

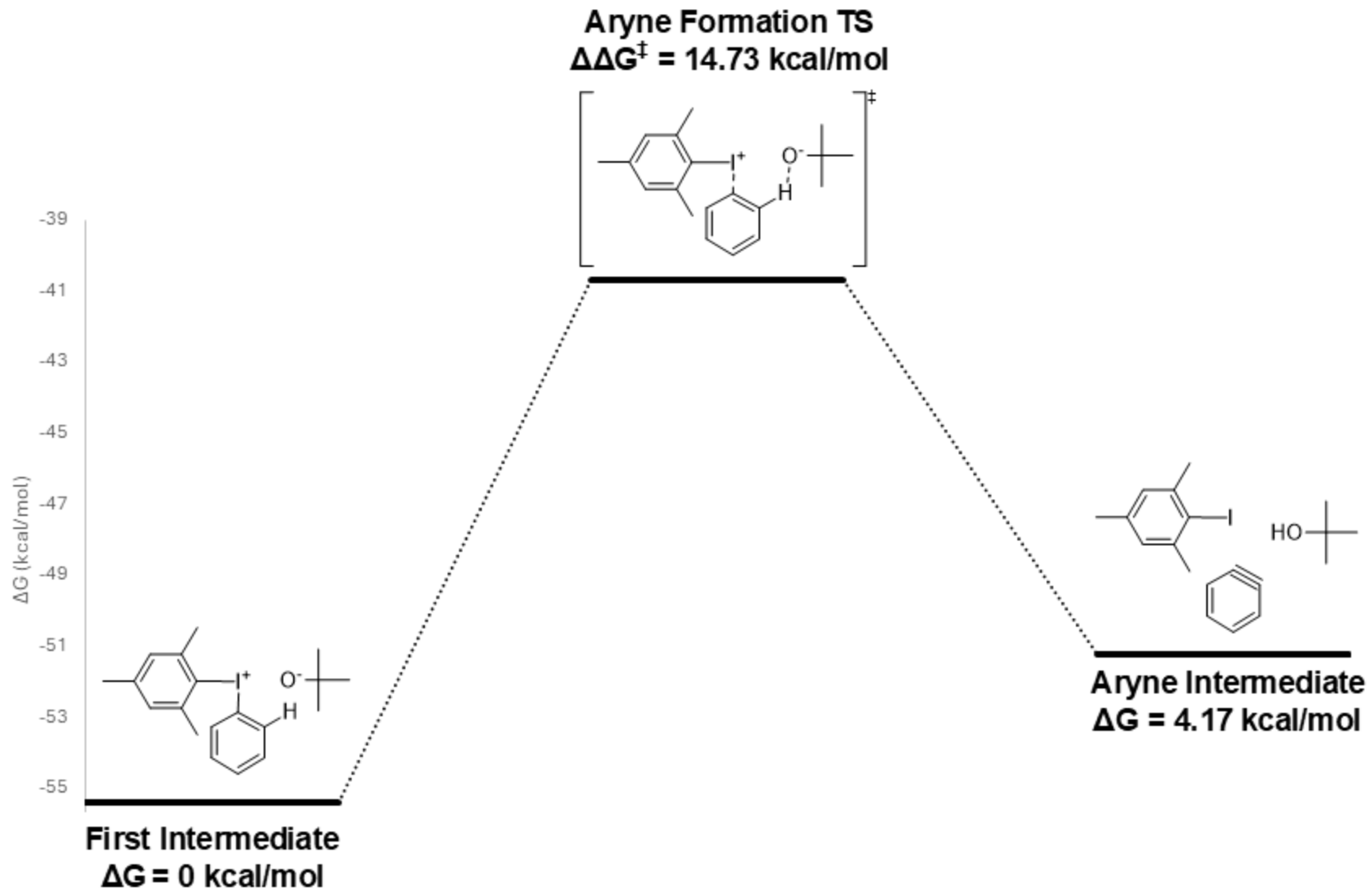


Figure 3: Aryne extrusion from 4-chlorophenylthianthrenium salt, calculated at M06-2x/Def2-tzvpp with SMD solvation in toluene

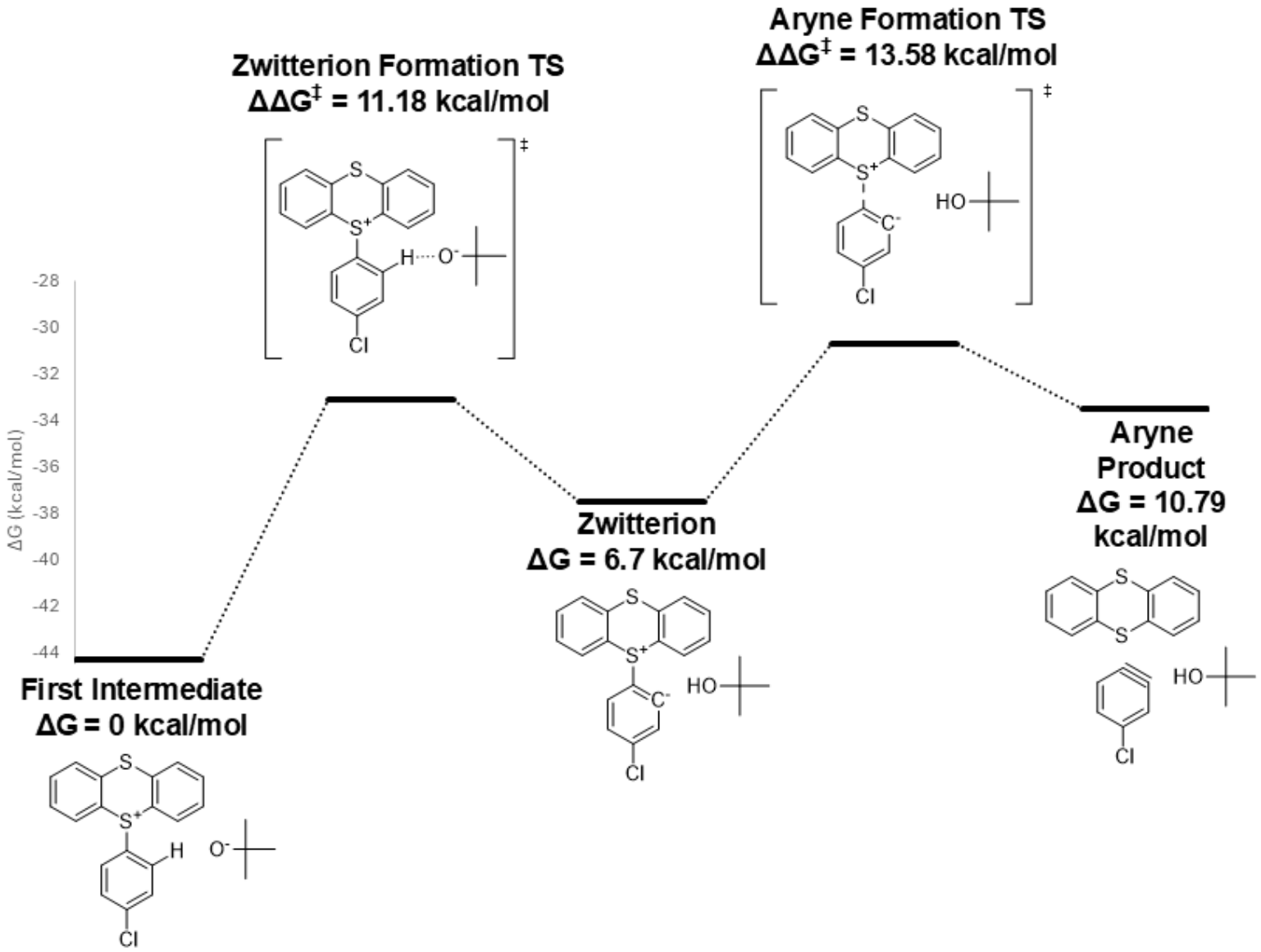


Figure 4: Aryne extrusion from 4-chlorophenyl(Mes)Iodonium as calculated at M06-2x/Def2-tzvpp with SMD solvation in toluene

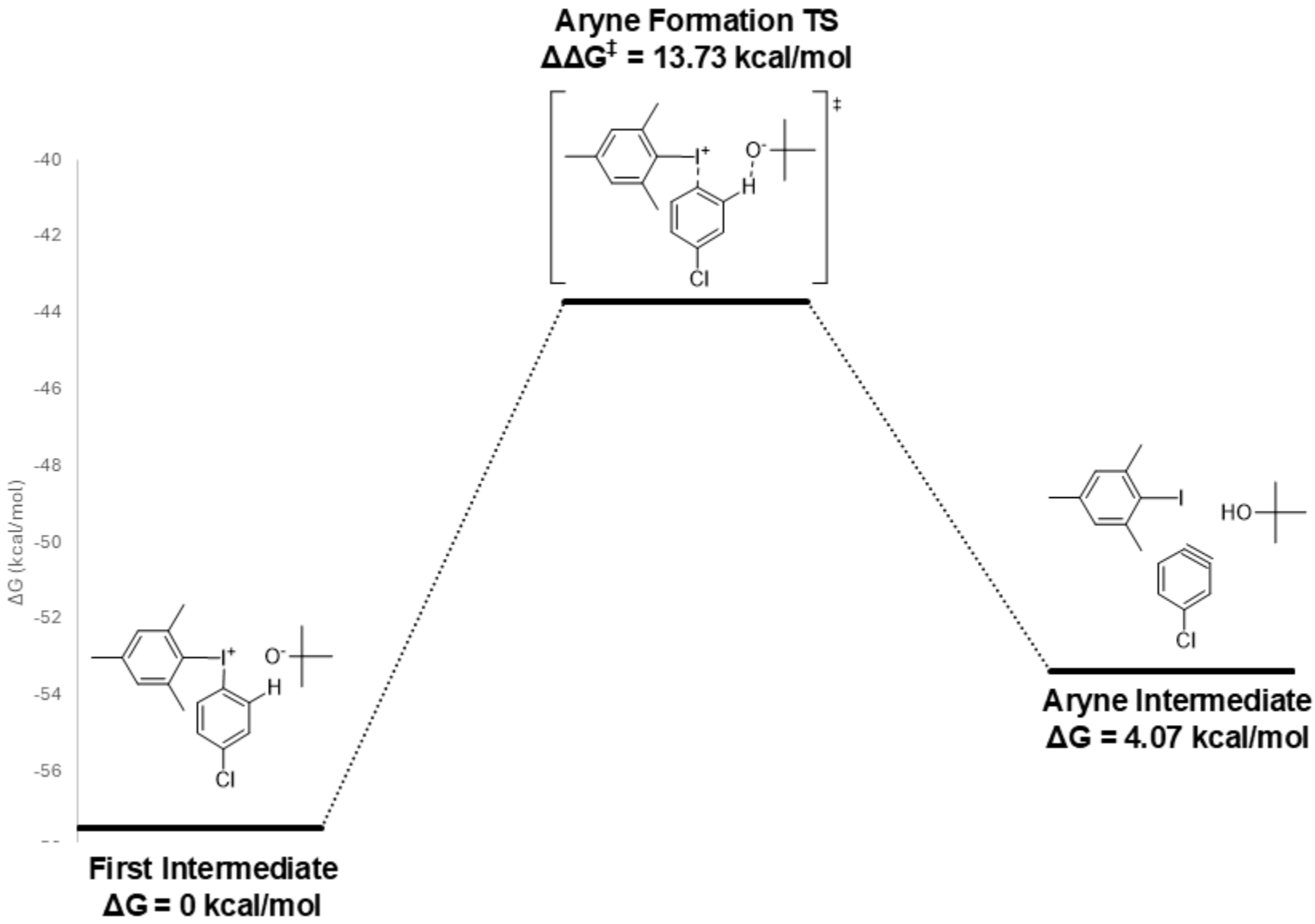


Figure 5: Aryne extrusion from 3-bromo-6-methoxyphenylthianthrenium salt calculated at M06-2x/Def2-tzvpp with SMD solvation in toluene

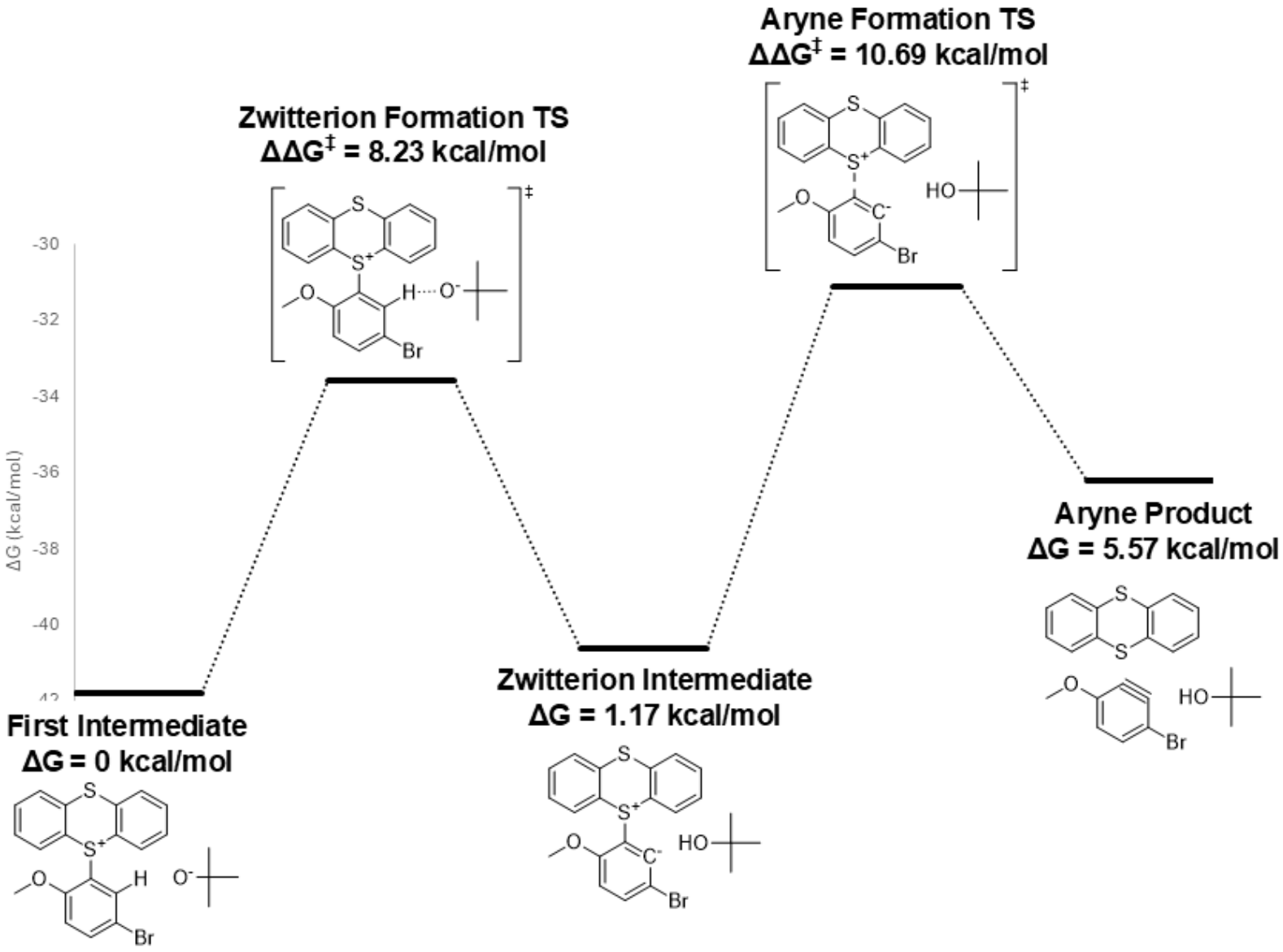
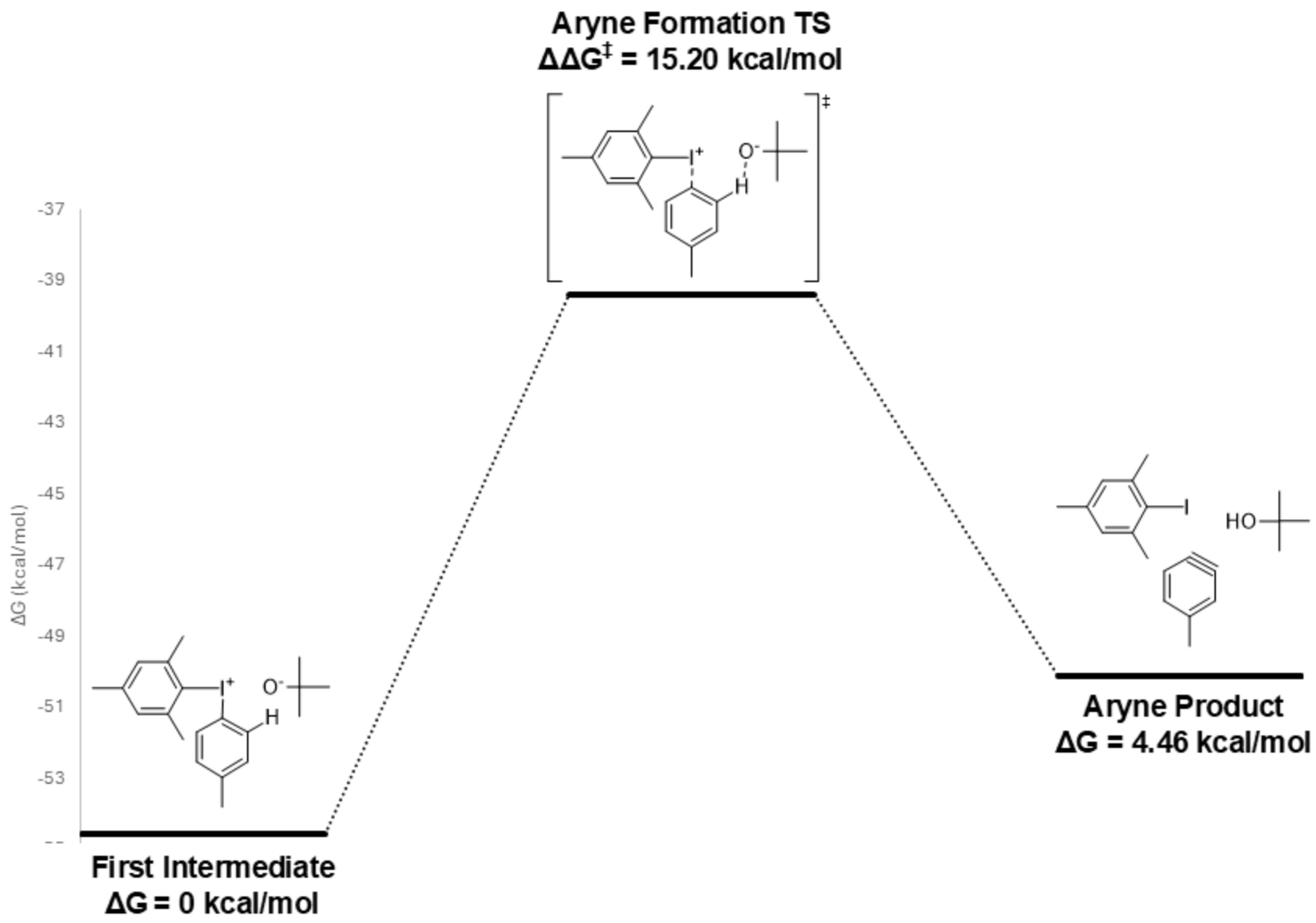


Figure 6: Aryne extrusion from p-tolyl(Mesityl)Iodonium salt as calculated at M06-2x/Def2-tzvpp with SMD solvation in toluene



Solvent Assessment

Given the variation in solvents used for the aryne extrusion reactions described here, the impact of varying solvents on the ΔG values between stable points in the reaction coordinates was modeled and assessed. All compounds were optimized and confirmed to have no negative vibrational frequencies at the M06-2x/Def2-tzvpp level of theory. SMD implicit solvation[10] was used for all tested solvents; gas phase calculations were included for comparison. In addition to the toluene used for all main calculations, dichloromethane, acetonitrile, and water were included. Based on literature suggesting methyl-tert-butyl ether as a solvent has similar electronic properties to diisopropylether (DIPE), diisopropylether was also included.[28]

ΔG values are given as the difference between the intermediate point (zwitterion or aryne) and the initial coordinated reactants; only the product point (zwitterion or aryne) is shown. All values are given in kcal/mol

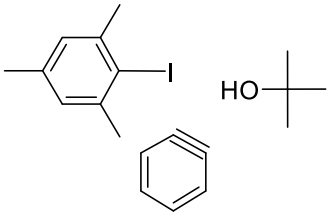
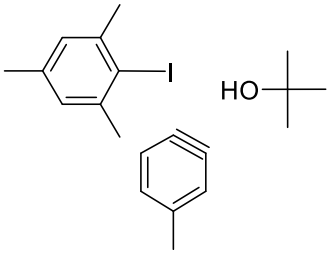
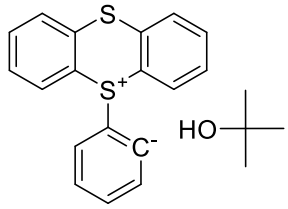
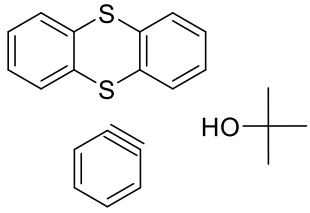
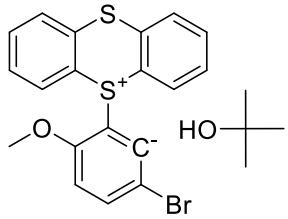
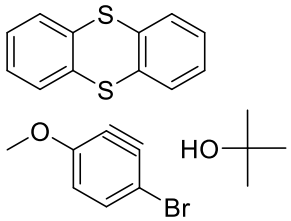
	Gas (no solvation)	Toluene	DIPE	DCM	MeCN	Water
ε	**0**	**2.3741**	**3.38**	**8.93**	**35.688**	**78.3553**
 **ΔG**	2.74	4.17	3.07	4.21	4.27	7.94
 **ΔG**	3.64	4.46	4.2	4.68	5.02	7.93
 **ΔG**	11.91	9.29	8.57	7.46	6.46	9.31
 **ΔG**	8.88	8.82	8.58	9.58	9.14	14.7
 **ΔG**	4.46	1.17	0.05	-0.14	-0.14	2.31
 **ΔG**	5.6	5.56	5.33	6.83	6.83	11.53

Table 1: ΔG values of stable points in aryne extrusion reactions as calculated at M06-2x/Def2-tzvpp with SMD solvation in the listed solvent (or without solvation, as noted). Solvents assessed include Toluene, diisopropylether (DIPE), dichloromethane (DCM), acetonitrile (MeCN), and water; as well as without any solvation (Gas phase). All ΔG values are given in kcal/mol.