Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A New Class of N-Doped Ionic PAHs via Intramolecular [4+2]-Cycloaddition between Arylpyridines and Alkynes

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1. General information

Practical considerations

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Screens were performed in 2.5 mL or 5.0 mL glass vials with a PTFE-lined cap, and all other reactions were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining iodine, potassium permanganate solution and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 100-200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in petroleum ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

Materials

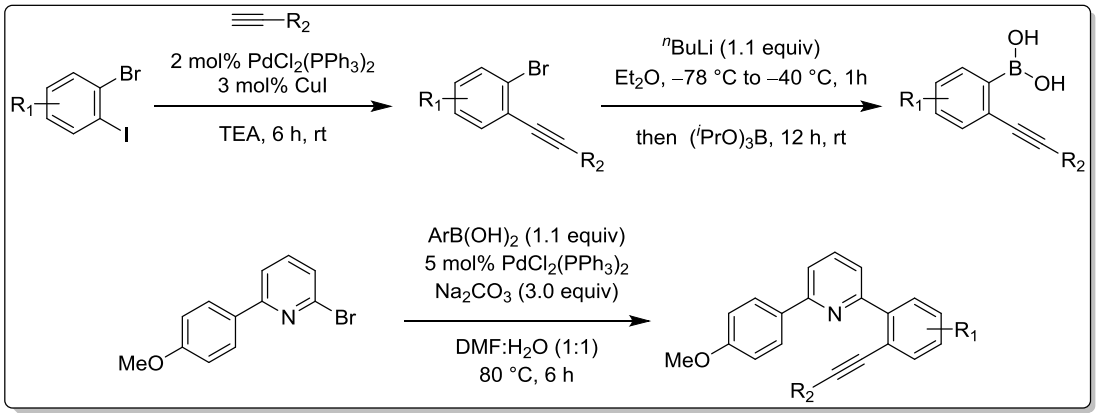
Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran was distilled from Na/benzophenone under an atmosphere of dry nitrogen. Anhydrous dichloromethane, toluene and acetonitrile were dried by using standard protocol under nitrogen. Gold and copper catalysts were purchased from Sigma-Aldrich. Deuterated solvents were used as supplied.

Instrumentation

Melting points are uncorrected and recorded using digital Büchi melting point apparatus B-540. NMR spectra were recorded on Bruker AV, 400/500 spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin(quintet), sextet (sxt), br.s. (broad signal), m (multiplet) etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. UV-visible absorption spectra were measured with a Perkin Elmer LAMBDA 950 UV/Vis Spectrophotometers. Fluorescence spectra were recorded by Photon Technology International, QuantaMaster™ 400

Spectrofluorometer and absolute quantum yields were determined using a calibrated integrating sphere system. Time-resolved fluorescence spectra were measured using a Horiba - Lifetime Fluorescence Spectrofluorometers system equipped with a PLP-10 picosecond light pulser (LED wavelengths: 470 or 570 nm). Single-crystal data was collected on a Super Nova Dual source X-ray diffractometer system (Agilent Technologies) equipped with CCD area detector and graphite-monochromatized (MoK_α= 0.71073Å, CuK_α= 1.54184Å) radiation.

2. Synthesis of starting materials



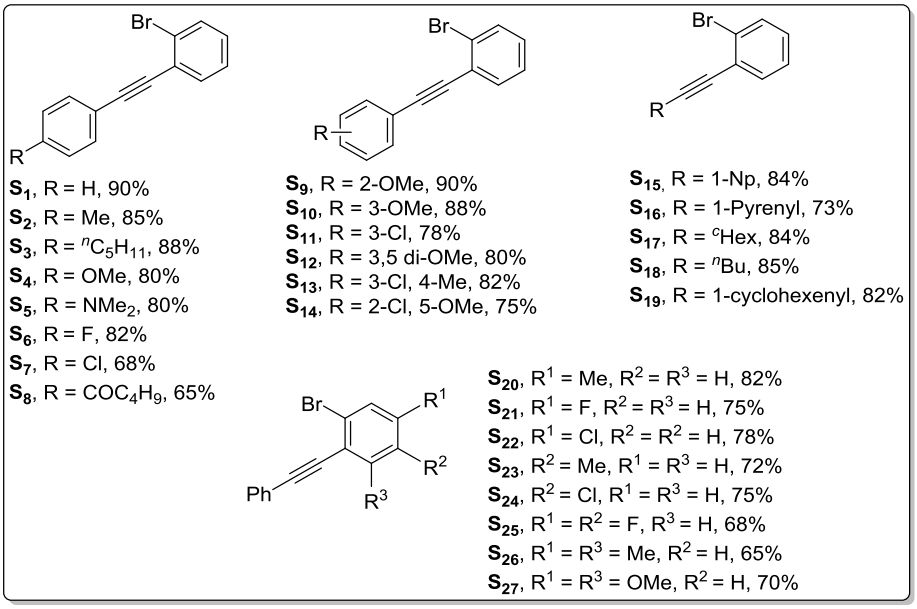
2.1 Experimental procedure for preparation of substituted 2-alkynyl-bromobenzenes

The bromo-alkynes **S_1-S_{12}**, **S_{15}-S_{24}**, and **S_{26}-S_{27}** were reported in the literature and prepared according to the literature known procedures.[1] The other analogues of bromo-alkynes **S_{13}-S_{14}** and **S_{25}** were prepared by slightly modified procedures.

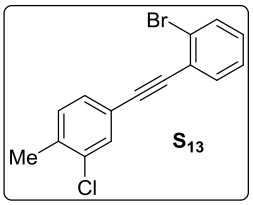
Representative procedure for Sonogashira cross-coupling reaction: A suspension of 2-bromoiodobenzene (1.0 gm, 3.55 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (50 mg, 2 mol%), Cu(I) iodide (20 mg, 3 mol%) in 20 mL of triethylamine was degassed with nitrogen for 5 minutes. After 10 min, a solution of phenyl acetylene (0.49 mL, 1.1 equiv) in triethylamine (3.0 mL) was added drop-wise over 5 min via syringe and the reaction mixture was left to stir for 12 h. After complete consumption of the 2-bromoiodobenzene, as monitored by TLC, the reaction

[1] (a) Shaikh, A. C.; Ranade, D. S.; Rajamohanan, P. R.; Kulkarni, P. P.; Patil, N. T. *Angew. Chem. Int. Ed*. **2017**, *56*, 757. (b) Shinde, P. S.; Shaikh, A. C.; Patil, N. T. *Chem. Commun.* **2016**, *52*, 8152. (c) Guo, R.; Li, K.-N.; Liu, B.; Zhu, H.-J.; Fan, Y.-M.; Gong, L.-Z. *Chem. Commun*. **2014**, *50*, 5451. (d) Yoo, W.-J.; Nguyen, T. V. Q.; Kobayashi, S. *Angew. Chem., Int. Ed*. **2014**, *53*, 10213. (e) Körner, C.; Starkov, P.; Sheppard, T. D. *J. Am. Chem. Soc*. **2010**, *132*, 5968.

mixture was filtered through pad of celite and extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with a saturated solution of NH_4Cl (2 × 10 mL), water (2 × 10 mL), dried over Na_2SO_4 and the organic solvent was removed under vacuo. The reaction mixture was purified by flash chromatography on silica gel, (eluent: petroleum ether) to give the 1-bromo-2-(phenylethynyl) benzene (**S_1**) in 90% yield.

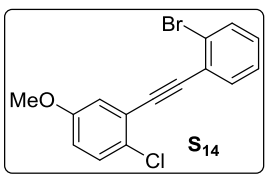


4-((2-bromophenyl)ethynyl)-2-chloro-1-methylbenzene (**S_{13}**):



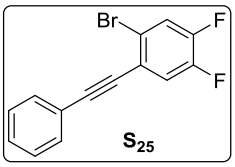
Off white solid, 880 mg, 82% yield; mp = 58-60 °C; $\boldsymbol{R_f}$ = 0.80 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.63 (d, *J* = 7.9 Hz, 1 H), 7.59 (s, 1 H), 7.56 (d, *J* = 7.3 Hz, 1 H), 7.38 (d, *J* = 7.3 Hz, 1 H), 7.30 (t, *J* = 7.6 Hz, 1 H), 7.15 - 7.24 (m, 2 H), 2.41 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 136.9, 133.2, 132.4, 131.8, 130.8, 129.8, 129.5, 127.0, 125.6, 125.1, 121.8, 92.5, 88.4, 20.1; **HRMS (ESI)** calcd for $C_{15}H_{11}BrCl$ $(M + H)^+$ 304.9796, found 304.9794.

2-((2-bromophenyl)ethynyl)-1-chloro-4-methoxybenzene (**S_{14}**):



Off white solid, 850 gm, 75% yield; mp = 60-62 °C; $\boldsymbol{R_f}$ = 0.75 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 7.57 - 7.66 (m, 2 H), 7.27 - 7.35 (m, 2 H), 7.21 (d, *J* = 1.5 Hz, 1 H), 7.13 (d, *J* = 3.1 Hz, 1 H), 6.85 (dd, *J* = 8.8, 3.1 Hz, 1 H), 3.82 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 158.0, 133.8, 132.7, 130.2, 130.0, 127.8, 127.2, 125.8, 125.2, 123.5, 118.0, 116.7, 92.8, 90.8, 55.8; **HRMS (ESI)** calcd for $C_{15}H_{11}BrCl$ $(M + H)^+$ 320.9676, found 320.9674.

1-bromo-4,5-difluoro-2-(phenylethynyl)benzene (**S_{25}**):



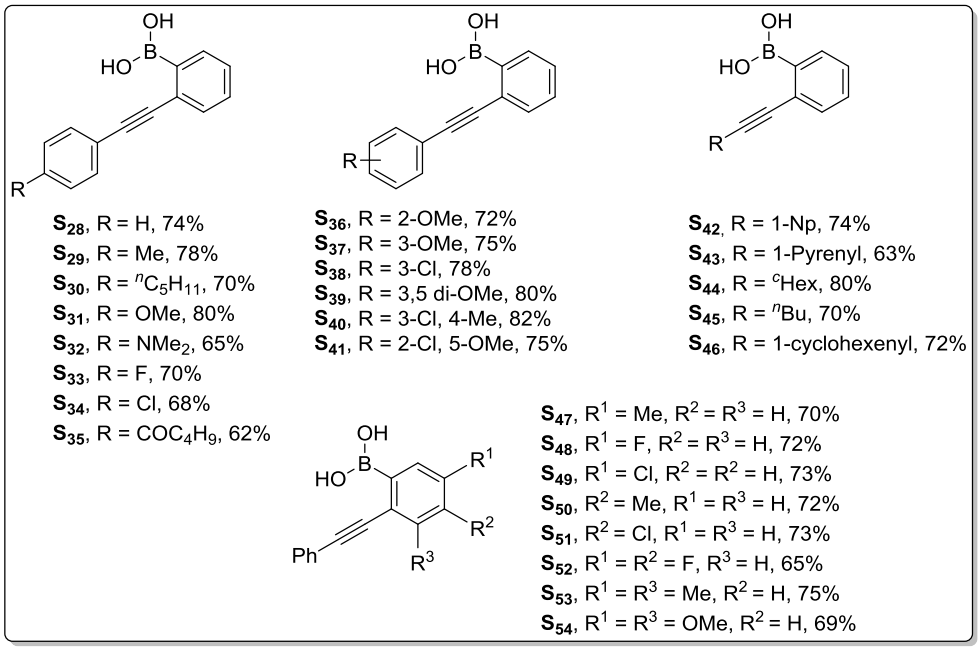
Off white solid, 704 mg, 68% yield; mp = 50-52 °C; $\boldsymbol{R_f}$ = 0.80 (petroleum ether/ethyl acetate = 98/02); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 7.58 (br.s., 2 H), 7.45 (br.s., 1 H), 7.39 (br.s., 4 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 151.0 - 149.0 (dd, *J* = 256.5 Hz, 14.3 Hz), 150.2 - 148.2 (dd, *J* = 249.9, 12.4), 131.7, 129.0, 128.4, 122.3, 122.2 - 122.1 (d, *J* = 3.8 Hz), 121.6 - 121.5(d, *J* = 20.0 Hz), 121.3 - 121.1 (d, *J* = 19.0 Hz), 120.0 - 120.0 (d, *J* = 2.9 Hz), 94.5, 86.2; **HRMS (ESI)** calcd for $C_{14}H_8BrF_2$ $(M + H)^+$ 292.9786, found 292.9782.

2.2 Experimental procedure for preparation of 2-alkynylphenylboronic acids

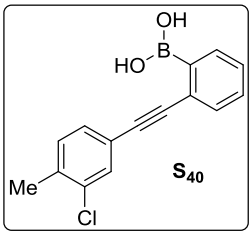
The boronic acid **S_{28}-S_{39}**, **S_{41}-S_{51}** and **S_{54}** were reported in the literature and prepared according to the literature known procedures.[1] The other boronic acids **S_{40}** and **S_{52}-S_{53}** were prepared from slight modifications in literature known procedures.

Representative procedure for the synthesis of boronic acid: In a two-necked round bottom flask, 1.6 M solution of ^{n}BuLi in ^{n}hexanes (3.1 mL, 1.3 equiv) was added drop-wise to a solution of 2-phenylethynyl bromobenzene (**S_1**) (1.0 g, 3.92 mmol, 1.0 equiv) in 30 mL of diethyl ether under nitrogen atmosphere at -78 °C. The mixture was stirred at -78 °C for 1 h and then at -40 °C for 1 h then cool back to -78 °C and $B(O^iPr)_3$ (1.1 g, 1.5 equiv) was added drop-wise. The mixture was allowed to warm up gradually to room temperature, while maintaining vigorous stirring for 16 h. Then, the reaction was quenched with 40 mL of 1N HCl for 30 minutes and extracted with ethyl acetate (3 x 20 mL). The combined organic solution was dried over Na_2SO_4 and the organic solvent was removed under vacuo. The product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate) followed by recrystallization from petroleum ether to give the (2-(phenylethynyl)phenyl)boronic acid (**S_{28}**) in 74% yield.

Note: The boronic acid **S_{52}-S_{53}** were accompanied with slight impurities and hence used directly for next reaction without attempting further purification.



(2-((3-chloro-4-methylphenyl)ethynyl)phenyl)boronic acid (**S_{40}**):

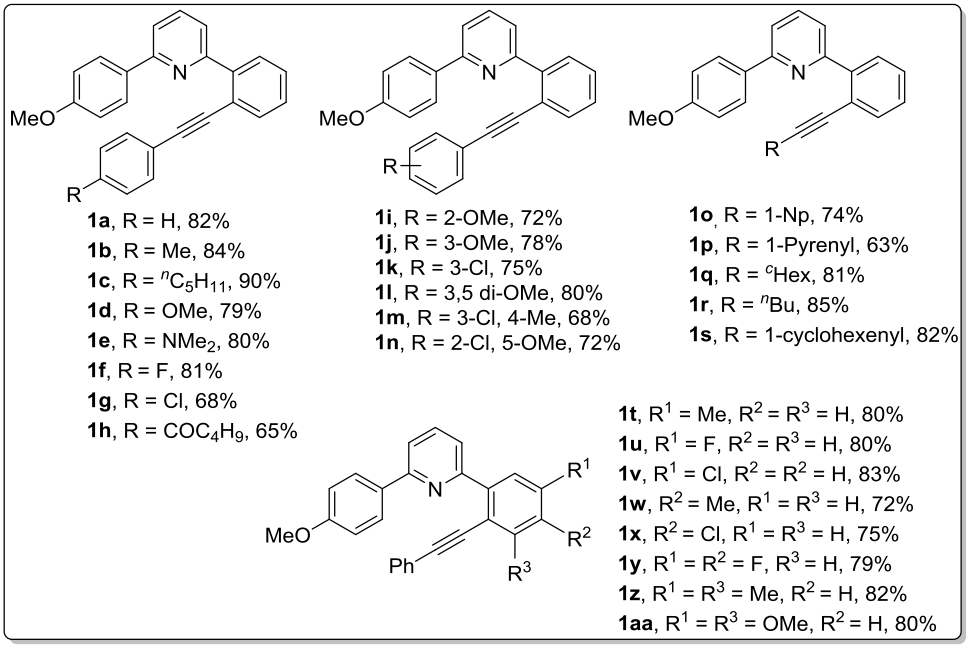


Off white solid, 730 mg, 82% yield; mp = 160-162 °C; R_f = 0.40 (petroleum ether/ethyl acetate = 60/40); **^{1}H NMR (500 MHz, DMSO-d_6) δ** = 8.20 (s, 2 H), 7.52 - 7.59 (m, 2 H), 7.47 - 7.52 (m, 1 H), 7.32 - 7.42 (m, 4 H), 2.36 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d_6) δ** = 136.2, 133.4, 133.0, 131.5, 131.2, 131.0, 129.8, 128.9, 127.8, 124.9, 122.3, 91.8, 88.8, 19.6; **HRMS (ESI)** calcd for $C_{15}H_{13}O_2BCl$ $(M + H)^+$ 271.0692, found 271.0698.

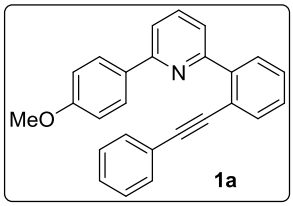
2.3 Synthesis of 2-(4-methoxyphenyl)-6-(2(alkynyl)-phenyl)pyridines

Representative procedure for Suzuki cross-coupling reaction:[1] In a sealed tube, 2-bromo-6-(4-methoxyphenyl)pyridine (200 mg, 0.760 mmol, 1.0 equiv) and (2-(phenylethynyl) phenyl)boronic acid (**S_{28}**) (203 mg, 1.2 equiv) in DMF/H_2O (1:1, 4 mL) was degassed with nitrogen for 5 min. Next, Na_2CO_3 (240 mg, 3 equiv) and $PdCl_2(PPh_3)_2$ (27 mg, 5 mol%) were added under nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 6 h. After complete consumption of starting material, as monitored by TLC, the resulting

mixture was allowed to bring to room temperature. The reaction mixture was diluted with $NaHCO_3$ (5 mL) and then the product was extracted with ethyl acetate (3 × 5 mL). The combined organic layer was dried over Na_2SO_4 and the organic solvent was removed under vacuo. The crude product was purified on a silica gel column using petroleum ether/ethyl acetate as eluent to afford 2-(4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1a**) in 82% yield.

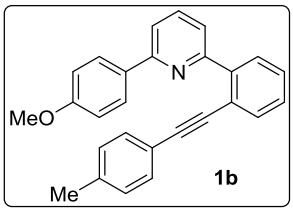


2-(4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1a**):



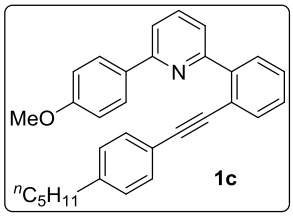
Off white solid, 225 mg, 82% yield; mp = 104-106 °C; $\boldsymbol{R_f}$ = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.12 (d, *J* = 8.4 Hz, 2 H), 7.94 (d, *J* = 7.6 Hz, 1 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.82 (t, *J* = 7.6 Hz, 1 H), 7.67 - 7.73 (m, 2 H), 7.45 - 7.52 (m, 1 H), 7.37 - 7.44 (m, 3 H), 7.28 - 7.34 (m, 3 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 3.87 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.4, 157.1, 156.5, 142.5, 136.3, 133.3, 132.1, 131.4, 129.9, 128.6, 128.3, 128.2, 128.1, 128.1, 123.4, 121.8, 121.4, 118.0, 114.0, 92.5, 89.5, 55.3; **HRMS (ESI)** calcd for $C_{26}H_{20}ON$ $(M + H)^+$ 362.1539, found 362.1545.

2-(4-methoxyphenyl)-6-(2-(*p*-tolylethynyl)phenyl)pyridine (**1b**):



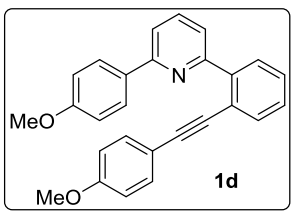
Off white solid, 240 mg, 84% yield; mp = 110-112 °C; R_f = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.12 (d, *J* = 8.5 Hz, 2 H), 7.93 (t, *J* = 8.5 Hz, 2 H), 7.81 (t, *J* = 7.6 Hz, 1 H), 7.64 - 7.73 (m, 2 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.41 (t, *J* = 7.3 Hz, 1 H), 7.27 - 7.34 (d, *J* = 7.9 Hz, 2 H), 7.08 - 7.15 (d, *J* = 7.3 Hz, 2 H), 7.00 (d, *J* = 8.5 Hz, 2 H), 3.87 (s, 3 H), 2.36 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 160.4, 157.2, 156.5, 142.3, 138.3, 136.3, 133.2, 132.2, 131.3, 129.9, 129.0, 128.4, 128.3, 128.1, 121.9, 121.6, 120.4, 118.0, 114.1, 114.0, 92.7, 88.8, 55.3, 21.5; **HRMS (ESI)** calcd for $C_{27}H_{22}ON$ $(M + H)^+$ 376.1696, found 376.1704.

2-(4-methoxyphenyl)-6-(2-((4-pentylphenyl)ethynyl)phenyl)pyridine (**1c**):



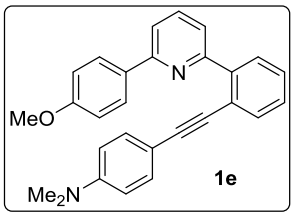
Off white solid, 295 mg, 90% yield; mp = 64-66 °C; R_f = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.13 (d, *J* = 8.5 Hz, 2 H), 7.88 - 7.97 (m, 2 H), 7.82 (t, *J* = 7.6 Hz, 1 H), 7.65 - 7.73 (m, 2 H), 7.45 - 7.52 (m, 1 H), 7.37 - 7.45 (m, 1 H), 7.29 - 7.36 (m, *J* = 7.9 Hz, 2 H), 7.07 - 7.16 (d, *J* = 7.9 Hz, 2 H), 7.00 (d, *J* = 8.5 Hz, 2 H), 3.87 (s, 3 H), 2.61 (t, *J* = 7.6 Hz, 2 H), 1.57 - 1.67 (m, 2 H), 1.30 - 1.40 (m, 4 H), 0.92 (t, *J* = 6.7 Hz, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 160.4, 157.2, 156.4, 143.3, 142.3, 136.3, 133.2, 132.2, 131.3, 129.9, 128.4, 128.3, 128.1, 121.9, 121.6, 120.5, 118.0, 114.0, 92.7, 88.8, 55.3, 35.8, 31.4, 30.9, 22.5, 14.0; **HRMS (ESI)** calcd for $C_{31}H_{30}ON$ $(M + H)^+$ 432.2322, found 432.2332.

2-(4-methoxyphenyl)-6-(2-((4-methoxyphenyl)ethynyl)phenyl)pyridine (**1d**):



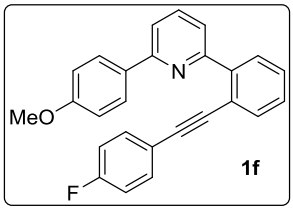
Yellowish solid, 235 mg, 79% yield; mp = 90-92 °C; R_f = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.11 (d, *J* = 8.0 Hz, 2 H), 7.88 - 7.96 (m, 2 H), 7.81 (t, *J* = 7.6 Hz, 1 H), 7.61 - 7.70 (m, 2 H), 7.46 (t, *J* = 7.4 Hz, 1 H), 7.40 (t, *J* = 7.4 Hz, 1 H), 7.29 - 7.36 (m, *J* = 8.0 Hz, 2 H), 6.93 - 7.04 (m, *J* = 8.4 Hz, 2 H), 6.83 (d, *J* = 8.4 Hz, 2 H), 3.87 (s, 3 H), 3.81 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.4, 159.5, 157.3, 156.5, 142.2, 136.3, 133.1, 132.9, 132.2, 129.9, 128.3, 128.2, 128.1, 121.9, 121.7, 118.0, 115.6, 114.0, 113.9, 92.5, 88.2, 55.3, 55.3; **HRMS (ESI)** calcd for $C_{27}H_{22}O_2N$ $(M + H)^+$ 392.1645, found 392.1654.

4-((2-(6-(4-methoxyphenyl)pyridin-2-yl)phenyl)ethynyl)-*N*,*N*-dimethylaniline (**1e**):



Brown solid, 247 mg, 80% yield; mp = 122-124 °C; R_f = 0.50 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.08 - 8.16 (d, *J* = 8.8 Hz, 2 H), 7.98 (d, *J* = 7.6 Hz, 1 H), 7.91 - 7.97 (m, 1 H), 7.80 (t, *J* = 7.6 Hz, 1 H), 7.63 - 7.73 (m, 2 H), 7.41 - 7.47 (m, 1 H), 7.38 (td, *J* = 7.5, 1.0 Hz, 1 H), 7.24 - 7.32 (m, *J* = 8.8 Hz, 2 H), 6.93 - 7.04 (d, *J* = 8.8 Hz, 2 H), 6.59 - 6.65 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 2.98 (s, 6 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.3, 157.3, 156.4, 150.0, 141.8, 136.2, 132.8, 132.5, 132.3, 129.9, 128.3, 128.0, 127.7, 122.2, 122.0, 117.9, 114.0, 111.8, 110.3, 93.9, 87.5, 55.3, 40.2; **HRMS (ESI)** calcd for $C_{28}H_{25}ON_2$ $(M + H)^+$ 405.1961, found 405.1965.

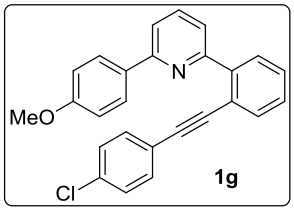
2-(2-((4-fluorophenyl)ethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1f**):



Off white solid, 234 mg, 81% yield; mp = 60-62 °C; R_f = 0.65 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.11 (d, *J* = 9.2 Hz, 2 H), 7.91 (d, *J* = 7.9 Hz, 1 H), 7.87 - 7.75 (m, 2 H), 7.74 - 7.64 (m, 2 H), 7.49 (t, *J* = 7.3 Hz, 1 H), 7.41 (t, *J* = 7.3 Hz, 1 H), 7.35 (dd, *J* = 5.5, 8.5 Hz, 2 H), 7.06 - 6.90 (m, 4 H), 3.87 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 163.6-161.2 (d, *J* = 9.2 Hz), 160.5, 157.2, 156.5, 142.5, 136.4, 133.3, 133.2-133.2 (d, *J* = 3.1 Hz), 132.1, 129.9, 128.6, 128.3, 128.1, 121.7, 121.3, 119.5, 118.0, 115.6-

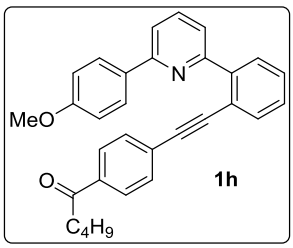
115.4 (d, *J* = 21.8 Hz), 114.0, 91.3, 89.2, 55.3; **HRMS (ESI)** calcd for $C_{26}H_{19}ONF$ $(M + H)^+$ 380.1445, found 380.1450.

2-(2-((4-chlorophenyl)ethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1g**):



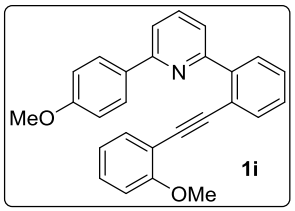
Off white solid, 205 mg, 68% yield; mp = 134-136 °C; $\boldsymbol{R_f}$ = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.13 (d, *J* = 8.5 Hz, 2 H), 7.93 (d, *J* = 7.9 Hz, 1 H), 7.80 - 7.87 (m, 2 H), 7.72 (d, *J* = 7.3 Hz, 2 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.44 (t, *J* = 7.3 Hz, 1 H), 7.22 - 7.34 (m, 4 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 3.89 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 160.4, 157.1, 156.5, 142.6, 136.4, 134.1, 133.3, 132.6, 132.0, 129.9, 128.8, 128.6, 128.3, 128.1, 121.9, 121.7, 121.1, 118.1, 114.0, 91.2, 90.5, 55.3; **HRMS (ESI)** calcd for $C_{26}H_{19}ONCl$ $(M + H)^+$ 396.1150, found 396.1161.

1-(4-((2-(6-(4-methoxyphenyl)pyridin-2-yl)phenyl)ethynyl)phenyl)pentan-1-one (**1h**):



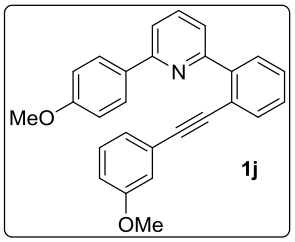
Off white solid, 220 mg, 65% yield; mp = 106-108 °C; $\boldsymbol{R_f}$ = 0.50 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.11 (d, *J* = 8.8 Hz, 2 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.85 - 7.89 (m, *J* = 8.4 Hz, 2 H), 7.78 - 7.84 (m, 2 H), 7.66 - 7.74 (m, 2 H), 7.47 - 7.55 (m, 1 H), 7.37 - 7.46 (m, 3 H), 6.91 - 7.03 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3 H), 2.94 (t, *J* = 7.4 Hz, 2 H), 1.72 (quin, *J* = 7.5 Hz, 2 H), 1.41 (sxt, *J* = 7.5 Hz, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 199.7, 160.4, 157.1, 156.5, 142.8, 136.4, 136.0, 133.4, 132.0, 131.5, 129.9, 129.1, 128.3, 128.2, 128.1, 127.9, 121.7, 120.9, 118.1, 114.0, 92.8, 91.6, 55.3, 38.3, 26.4, 22.4, 13.9; **HRMS (ESI)** calcd for $C_{31}H_{28}O_2N$ $(M + H)^+$ 446.2115, found 446.2125.

2-(4-methoxyphenyl)-6-(2-((2-methoxyphenyl)ethynyl)phenyl)pyridine (**1i**):



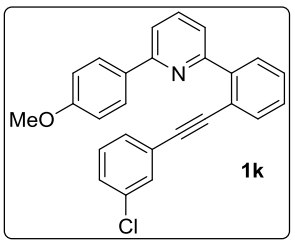
Off white solid, 215 mg, 72% yield; mp = 92-94 °C; R_f = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.10 - 8.17 (m, 3 H), 8.00 - 8.06 (m, 1 H), 7.74 - 7.83 (m, 2 H), 7.69 (d, *J* = 7.8 Hz, 1 H), 7.51 (td, *J* = 7.6, 1.4 Hz, 1 H), 7.36 - 7.46 (m, 2 H), 7.25 - 7.33 (m, 1 H), 6.98 - 7.04 (m, 2 H), 6.82 - 6.95 (m, 2 H), 3.87 (s, 3 H), 3.84 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 160.3, 159.9, 156.8, 156.3, 142.0, 136.2, 133.4, 133.3, 132.1, 129.9, 129.6, 128.4, 128.2, 128.0, 122.0, 121.6, 120.3, 117.8, 113.9, 112.6, 110.6, 93.3, 89.2, 55.5, 55.2; **HRMS (ESI)** calcd for $C_{27}H_{22}O_2N$ $(M + H)^+$ 392.1645, found 392.1652.

2-(4-methoxyphenyl)-6-(2-((3-methoxyphenyl)ethynyl)phenyl)pyridine (**1j**):



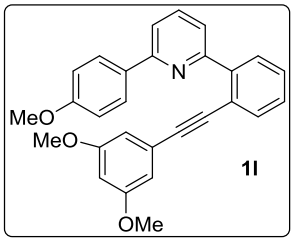
Off white solid, 235 mg, 78% yield; mp = 78-80 °C; R_f = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.07 - 8.18 (m, 2 H), 7.93 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.86 - 7.91 (m, 1 H), 7.76 - 7.85 (m, 1 H), 7.71 (td, *J* = 7.8, 0.9 Hz, 2 H), 7.50 (td, *J* = 7.8, 1.4 Hz, 1 H), 7.42 (td, *J* = 7.6, 1.4 Hz, 1 H), 7.17 - 7.25 (m, 1 H), 6.95 - 7.04 (m, 3 H), 6.89 - 6.95 (m, 1 H), 6.79 - 6.89 (m, 1 H), 3.87 (s, 3 H), 3.74 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 160.7, 159.5, 157.5, 156.7, 142.8, 136.7, 133.6, 132.4, 130.2, 129.6, 128.9, 128.6, 128.4, 124.7, 124.3, 122.1, 121.6, 118.3, 116.5, 115.1, 114.3, 92.7, 89.6, 55.6, 55.4; **HRMS (ESI)** calcd for $C_{27}H_{22}O_2N$ $(M + H)^+$ 392.1645, found 392.1652.

2-(2-((3-chlorophenyl)ethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1k**):



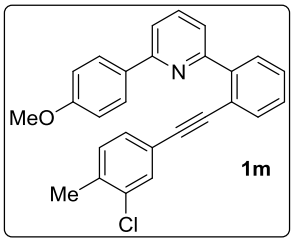
Off white solid, 225 mg, 75% yield; mp = 90-92 °C; R_f = 0.50 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.06 - 8.19 (m, *J* = 8.8 Hz, 2 H), 7.92 (d, *J* = 7.6 Hz, 1 H), 7.79 - 7.86 (m, 2 H), 7.72 (dt, *J* = 6.0, 3.3 Hz, 2 H), 7.48 - 7.56 (m, 1 H), 7.40 - 7.47 (m, 1 H), 7.38 (s, 1 H), 7.21 - 7.31 (m, 3 H), 6.96 - 7.04 (m, *J* = 8.8 Hz, 2 H), 3.88 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.4, 157.1, 156.5, 142.7, 136.4, 134.0, 133.4, 132.0, 131.2, 129.9, 129.5, 129.4, 128.9, 128.3, 128.3, 128.2, 125.2, 121.7, 120.9, 118.1, 114.0, 90.9, 90.7, 55.3; **HRMS (ESI)** calcd for $C_{26}H_{19}ONCl$ $(M + H)^+$ 396.1150, found 396.1155.

2-(2-((3,5-dimethoxyphenyl)ethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1l**):



Yellowish solid, 258 mg, 80% yield; mp = 98-100 °C; R_f = 0.50 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 7.93 (d, *J* = 7.6 Hz, 1 H), 7.84 - 7.89 (m, 1 H), 7.81 (t, *J* = 7.8 Hz, 1 H), 7.73 (d, *J* = 7.2 Hz, 1 H), 7.70 (d, *J* = 7.6 Hz, 1 H), 7.46 - 7.53 (m, 1 H), 7.40 - 7.45 (m, 1 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 6.58 (d, *J* = 2.3 Hz, 2 H), 6.44 - 6.48 (m, 1 H), 3.85 (s, 4 H), 3.73 (s, 6 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.4, 157.1, 156.2, 142.6, 136.3, 133.2, 131.9, 129.8, 128.6, 128.2, 128.1, 124.6, 121.7, 121.2, 117.8, 113.9, 109.1, 101.6, 92.4, 89.0, 55.2; **HRMS (ESI)** calcd for $C_{28}H_{24}O_3N$ $(M + H)^+$ 422.1751, found 422.1760.

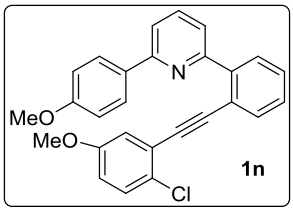
2-(2-((3-chloro-4-methylphenyl)ethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1m**):



Off white solid, 212 mg, 68% yield; mp = 136-138 °C; R_f = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.07 - 8.15 (d, *J* = 8.8 Hz, 2 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.78 - 7.85 (m, 2 H), 7.64 - 7.72 (m, 2 H), 7.45 - 7.52 (m, 1 H), 7.39 - 7.45 (m, 1 H), 7.34 - 7.39 (m, 1 H), 7.10 - 7.19 (m, 2 H), 6.97 - 7.02 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 2.37 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.4, 157.1, 156.5, 142.5, 136.4, 136.4, 134.1, 133.3, 132.1, 131.6, 130.7, 129.9, 129.6, 128.7, 128.3, 128.1, 122.4, 121.7, 121.2,

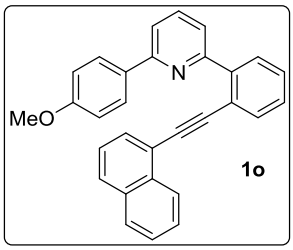
118.1, 114.0, 91.1, 89.9, 55.3, 20.0; **HRMS (ESI)** calcd for $C_{27}H_{21}ONCl$ $(M + H)^+$ 410.1306, found 410.1317.

2-(2-((2-chloro-5-methoxyphenyl)ethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1n**):



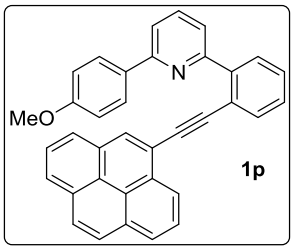
Off white solid, 235 mg, 72% yield; mp = 124-126 °C; $\boldsymbol{R_f}$ = 0.45 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 8.05 - 8.22 (d, *J* = 7.9 Hz, 2 H), 7.95 (d, *J* = 7.3 Hz, 2 H), 7.72 - 7.85 (m, 2 H), 7.68 (d, *J* = 7.9 Hz, 1 H), 7.51 (t, *J* = 7.3 Hz, 1 H), 7.43 (t, *J* = 7.3 Hz, 1 H), 7.25 (s, 1 H), 6.94 - 7.03 (d, *J* = 8.5 Hz, 2 H), 6.89 (br.s., 1 H), 6.78 (d, *J* = 8.5 Hz, 1 H), 3.85 (s, 3 H), 3.67 (s, 3 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 160.3, 157.7, 156.8, 156.3, 142.5, 136.5, 133.7, 132.0, 129.9, 129.8, 128.9, 128.2, 128.1, 127.3, 123.7, 122.0, 120.9, 118.0, 117.5, 116.1, 113.9, 94.1, 89.3, 55.4, 55.2; **HRMS (ESI)** calcd for $C_{27}H_{21}O_2NCl$ $(M + H)^+$ 426.1255, found 426.1267.

2-(4-methoxyphenyl)-6-(2-(naphthalen-1-ylethynyl)phenyl)pyridine (**1o**):



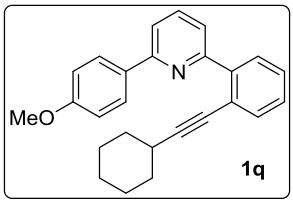
Off white solid, 235 mg, 74% yield; mp = 110-112 °C; $\boldsymbol{R_f}$ = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, CDCl$_3$) δ** = 8.08 - 8.20 (m, 3 H), 7.91 - 8.00 (m, 2 H), 7.77 - 7.88 (m, 4 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.65 (d, *J* = 6.9 Hz, 1 H), 7.52 - 7.58 (m, 1 H), 7.49 (q, *J* = 7.0 Hz, 2 H), 7.42 (td, *J* = 7.6, 2.3 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H); **^{13}C NMR (125 MHz, CDCl$_3$) δ** = 160.4, 157.4, 156.6, 142.6, 136.6, 133.4, 133.1, 133.1, 132.0, 130.3, 129.9, 128.6, 128.6, 128.3, 128.2, 128.1, 126.5, 126.3, 126.3, 125.2, 122.0, 121.6, 121.1, 118.0, 114.0, 94.2, 90.8, 55.3; **HRMS (ESI)** calcd for $C_{30}H_{22}ON$ $(M + H)^+$ 412.1696, found 412.1704.

2-(4-methoxyphenyl)-6-(2-(pyren-4-ylethynyl)phenyl)pyridine (**1p**):



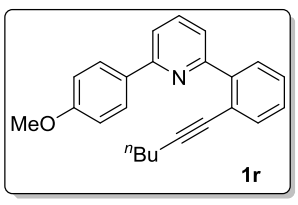
Yellow solid, 235 mg, 63% yield; mp = 154-156 °C; R_f = 0.65 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.35 (d, *J* = 9.2 Hz, 1 H), 8.12 - 8.21 (m, 4 H), 8.04 - 8.09 (m, 3 H), 7.93 - 8.03 (m, 5 H), 7.91 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.85 (t, *J* = 7.8 Hz, 1 H), 7.77 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.46 - 7.59 (m, 2 H), 6.90 - 6.99 (m, 2 H), 3.82 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 160.4, 157.5, 156.7, 142.7, 136.6, 133.4, 132.1, 131.8, 131.2, 131.1, 131.0, 130.0, 129.5, 128.7, 128.4, 128.2, 128.1, 128.0, 127.2, 126.2, 125.6, 125.5, 125.4, 124.4, 124.4, 124.2, 122.1, 121.8, 118.1, 118.0, 114.0, 95.1, 91.9, 55.3; **HRMS (ESI)** calcd for $C_{36}H_{24}ON$ $(M + H)^+$ 486.1852, found 486.1863.

2-(2-(cyclohexylethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1q**):



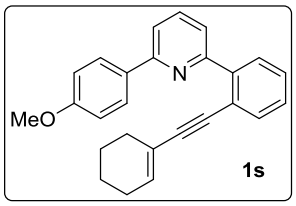
Off white solid, 232 mg, 81% yield; mp = 98-100 °C; R_f = 0.65 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.13 - 8.05 (m, 2 H), 7.92 - 7.83 (m, 2 H), 7.75 (t, *J* = 7.8 Hz, 1 H), 7.65 (d, *J* = 8.0 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.44 - 7.37 (m, 1 H), 7.36 - 7.30 (m, 1 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 3.88 (s, 3 H), 2.56 (t, *J* = 4.0 Hz, 1 H), 1.84 - 1.74 (m, 2 H), 1.71 - 1.62 (m, 2 H), 1.53 - 1.40 (m, 3 H), 1.30 (d, *J* = 7.2 Hz, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.3, 157.3, 156.3, 142.2, 136.0, 133.2, 132.2, 129.8, 128.3, 128.2, 127.9, 127.7, 122.2, 122.0, 117.8, 113.9, 97.7, 80.2, 55.3, 32.3, 29.7, 25.9, 24.7; **HRMS (ESI)** calcd for $C_{26}H_{19}ONF$ $(M + H)^+$ 368.4990, found 368.4996.

2-(2-(hex-1-yn-1-yl)phenyl)-6-(4-methoxyphenyl)pyridine (**1r**):



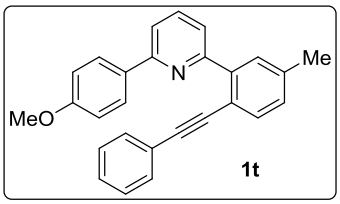
Off white solid, 220 mg, 85% yield; mp = 54-56 °C; R_f = 0.70 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.11 - 8.13 (d, *J* = 8.8 Hz, 2 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.76 (t, *J* = 7.6 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.39 - 7.46 (m, 1 H), 7.30 - 7.38 (m, 1 H), 6.99 - 7.06 (m, 2 H), 3.88 (s, 3 H), 2.38 (t, *J* = 7.1 Hz, 2 H), 1.52 (quin, *J* = 7.2 Hz, 2 H), 1.35 - 1.43 (m, 2 H), 0.90 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.1, 157.1, 156.0, 142.0, 135.8, 133.0, 132.0, 129.5, 127.9, 127.7, 127.5, 121.9, 121.6, 117.5, 113.7, 93.5, 80.0, 55.0, 30.2, 21.6, 19.0, 13.3; **HRMS (ESI)** calcd for $C_{24}H_{24}ON$ $(M + H)^+$ 342.1852, found 342.1860.

2-(2-(cyclohex-1-en-1-ylethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1s**):



Off white solid, 230 mg, 82% yield; mp = 83-85 °C; R_f = 0.70 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.19 - 8.04 (m, *J* = 8.7 Hz, 2 H), 7.87 (d, *J* = 7.8 Hz, 1 H), 7.90 (d, *J* = 7.6 Hz, 1 H), 7.77 (t, *J* = 7.8 Hz, 1 H), 7.65 (d, *J* = 7.8 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.42 (t, *J* = 7.2 Hz, 1 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.10 - 6.88 (m, *J* = 8.7 Hz, 2 H), 6.09 (br. s., 1 H), 3.88 (s, 3 H), 2.21 - 1.98 (m, 4 H), 1.68 - 1.56 (m, 4 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.4, 157.2, 156.4, 142.1, 136.2, 135.0, 133.1, 132.3, 129.8, 128.3, 128.0, 128.0, 121.9, 120.9, 117.9, 114.0, 94.5, 86.8, 55.3, 28.8, 25.7, 22.3, 21.5; **HRMS (ESI)** calcd for $C_{26}H_{23}ON$ $(M + H)^+$ 366.1352, found 366.1355.

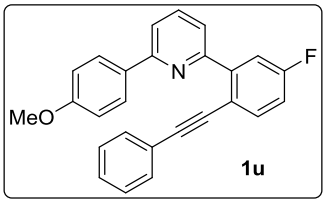
2-(4-methoxyphenyl)-6-(5-methyl-2-(phenylethynyl)phenyl)pyridine (**1t**):



Off white solid, 230 mg, 80% yield; mp = 90-92 °C; R_f = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.12 - 8.23 (d, *J* = 8.5 Hz, 2 H), 7.95 (d, *J* = 7.3 Hz, 1 H), 7.77 - 7.89 (m, 2 H), 7.72 (d, *J* = 7.3 Hz, 1 H), 7.66 (d, *J* = 7.9 Hz, 1 H), 7.45 (d, *J* = 3.7 Hz, 2 H), 7.32 - 7.39 (m, 3 H), 7.29 (s, 1 H), 7.01 - 7.08 (d, *J* = 8.5 Hz, 2 H), 3.90 (s, 3 H), 2.52 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 160.3, 157.2, 156.4, 142.3, 138.7, 136.2, 133.2, 132.1, 131.3, 130.5, 129.0, 128.3, 128.2, 127.9, 123.6, 121.9, 118.4, 118.0, 113.9,

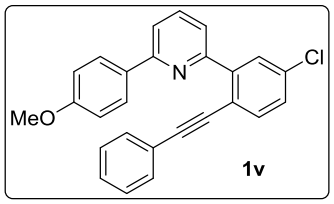
91.7, 89.6, 55.2, 21.5; **HRMS (ESI)** calcd for $C_{27}H_{22}ON$ $(M + H)^+$ 376.1696, found 376.1702.

2-(5-fluoro-2-(phenylethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1u**):



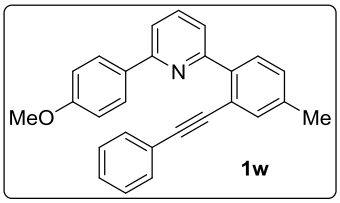
Off white solid, 232 mg, 80% yield; mp = 60-62 °C; $\boldsymbol{R_f}$ = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.12 (d, *J* = 8.5 Hz, 2 H), 7.98 (d, *J* = 7.3 Hz, 1 H), 7.83 (t, *J* = 7.9 Hz, 1 H), 7.63 - 7.76 (m, 3 H), 7.41 (br.s., 2 H), 7.28 - 7.36 (m, 3 H), 7.08 - 7.17 (m, 1 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 3.87 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 163.8-161.3 (d, *J* = 249.6 Hz), 160.5, 156.6, 155.7, 144.6-144.6 (d, *J* = 7.7 Hz), 138.8, 136.5, 135.2-135.1(d, *J* = 7.7 Hz), 131.8, 131.3, 128.3, 128.2, 125.4, 123.2, 121.7, 118.5, 118.1, 117.4, 117.0-116.8 (d, *J* = 23.9 Hz), 115.6-115.4 (d, *J* = 22.3 Hz), 114.1, 92.2, 88.5, 55.3; **HRMS (ESI)** calcd for $C_{26}H_{19}ONF$ $(M + H)^+$ 380.1445, found 380.1452.

2-(5-chloro-2-(phenylethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1v**):



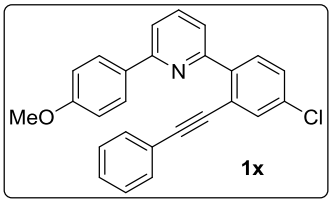
Off white solid, 250 mg, 83% yield; mp = 84-86 °C; $\boldsymbol{R_f}$ = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.11 (d, *J* = 8.5 Hz, 2 H), 7.87 - 8.00 (m, 2 H), 7.82 (t, *J* = 7.9 Hz, 1 H), 7.71 (d, *J* = 7.9 Hz, 1 H), 7.58 - 7.66 (m, 1 H), 7.39 (d, *J* = 4.3 Hz, 3 H), 7.27 - 7.34 (m, 3 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 3.87 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 160.5, 156.7, 155.7, 143.8, 138.8, 136.5, 134.5, 134.4, 131.8, 131.4, 130.0, 128.4, 128.3, 125.4, 123.1, 121.8, 119.9, 118.5, 118.1, 114.1, 114.1, 93.3, 88.5, 55.3; **HRMS (ESI)** calcd for $C_{26}H_{19}ONCl$ $(M + H)^+$ 396.1150, found 396.1159.

2-(4-methoxyphenyl)-6-(4-methyl-2-(phenylethynyl)phenyl)pyridine (**1w**):



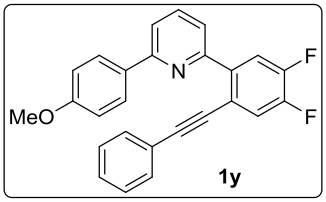
Off white solid, 206 mg, 72% yield; mp = 148-150 °C; R_f = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 8.09 - 8.15 (m, 2 H), 7.90 (d, *J* = 7.8 Hz, 1 H), 7.85 (d, *J* = 7.8 Hz, 1 H), 7.80 (t, *J* = 7.8 Hz, 1 H), 7.67 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.54 (s, 1 H), 7.37 - 7.43 (m, 2 H), 7.28 - 7.33 (m, 4 H), 6.95 - 7.02 (m, 2 H), 3.87 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 160.3, 157.1, 156.4, 139.7, 138.0, 136.3, 133.7, 132.2, 131.4, 129.9, 129.6, 128.3, 128.2, 128.1, 123.5, 121.7, 121.1, 117.8, 113.9, 92.1, 89.7, 55.3, 21.0; **HRMS (ESI)** calcd for $C_{27}H_{22}ON$ $(M + H)^+$ 376.1696, found 376.1703.

2-(4-chloro-2-(phenylethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1x**):



Off white solid, 226 mg, 75% yield; mp = 140-142 °C; R_f = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 8.10 (d, *J* = 9.2 Hz, 2 H), 7.90 (d, *J* = 8.5 Hz, 2 H), 7.81 (t, *J* = 7.6 Hz, 1 H), 7.63 - 7.72 (m, 2 H), 7.46 (dd, *J* = 8.5, 1.8 Hz, 1 H), 7.36 - 7.43 (m, 2 H), 7.27 - 7.36 (m, 3 H), 7.00 (d, *J* = 8.5 Hz, 2 H), 3.87 (s, 3 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 160.5, 156.6, 156.0, 140.8, 136.4, 133.9, 132.7, 131.9, 131.5, 131.3, 128.8, 128.5, 128.3, 128.3, 122.9, 121.6, 118.2, 114.0, 93.5, 88.2, 55.3; **HRMS (ESI)** calcd for $C_{26}H_{19}ONCl$ $(M + H)^+$ 396.1150, found 396.1159.

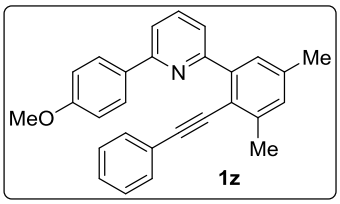
2-(4,5-difluoro-2-(phenylethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1y**):



Off white solid, 240 mg, 79% yield; mp = 100-102 °C; R_f = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 8.09 (d, *J* = 8.5 Hz, 2 H), 7.95 (d, *J* = 7.9 Hz, 1 H), 7.78 - 7.88 (m, 2 H), 7.71 (d, *J* = 7.9 Hz, 1 H), 7.48 (dd, *J* = 10.4, 7.9 Hz, 1 H), 7.37 - 7.43 (m, 2 H), 7.33 (br.s., 3 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 3.88 (s, 3 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 160.6, 156.7, 155.0, 151.8 - 149.1 (dd, *J* = 252.0 Hz, 13.1 Hz), 151.2 - 148.5 (dd, *J* = 250.5 Hz, 13.1 Hz), 139.8, 139.7, 138.9, 136.6, 131.7, 131.4, 128.6, 128.4, 128.3, 128.3, 125.4, 122.8, 121.7 - 121.5 (d, *J* = 18.5 Hz), 121.6, 119.1 - 119.0 (d, *J* = 18.5

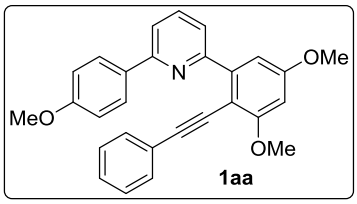
Hz), 118.5, 118.1, 117.9, 114.1, 93.0, 87.5, 55.3; **HRMS (ESI)** calcd for $C_{26}H_{18}ONF_2$ $(M + H)^+$ 398.1351, found 398.1358.

2-(3,5-dimethyl-2-(phenylethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1z**):



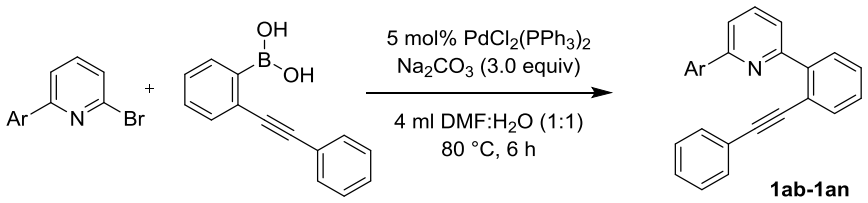
Off white solid, 245 mg, 82% yield; mp = 86-88 °C; $\boldsymbol{R_f}$ = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.07 - 8.17 (d, *J* = 8.8 Hz, 2 H), 7.76 - 7.87 (m, 2 H), 7.68 (d, *J* = 7.2 Hz, 1 H), 7.52 (s, 1 H), 7.34 - 7.41 (m, 2 H), 7.27 - 7.32 (m, 3 H), 7.17 (s, 1 H), 6.95 - 7.03 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 2.62 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 160.3, 158.0, 156.4, 142.8, 141.0, 138.1, 136.1, 132.3, 131.2, 130.3, 128.4, 128.2, 128.0, 127.8, 123.9, 122.1, 118.4, 117.9, 113.9, 96.4, 88.2, 55.3, 21.5, 21.3; **HRMS (ESI)** calcd for $C_{28}H_{24}ON$ $(M + H)^+$ 390.1852, found 390.1861.

2-(3,5-dimethoxy-2-(phenylethynyl)phenyl)-6-(4-methoxyphenyl)pyridine (**1aa**):

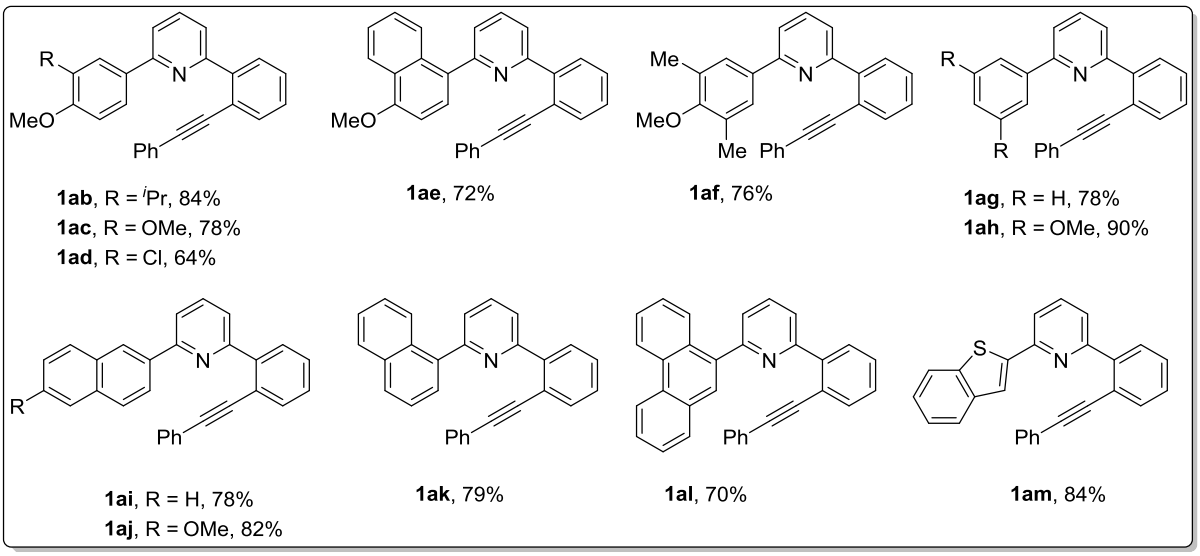


Yellow solid, 258 mg, 80% yield; mp = 102-104 °C; $\boldsymbol{R_f}$ = 0.45 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.08 - 8.16 (m, 2 H), 7.93 (d, *J* = 7.6 Hz, 1 H), 7.81 (t, *J* = 7.6 Hz, 1 H), 7.70 (d, *J* = 6.9 Hz, 1 H), 7.38 - 7.45 (m, 2 H), 7.25 - 7.33 (m, 3 H), 7.10 (d, *J* = 2.3 Hz, 1 H), 6.96 - 7.03 (m, 2 H), 6.59 (d, *J* = 2.3 Hz, 1 H), 3.97 (s, 3 H), 3.92 (s, 3 H), 3.86 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 161.7, 160.5, 160.3, 157.0, 156.3, 145.3, 136.1, 131.9, 131.1, 128.2, 128.0, 127.5, 124.0, 122.2, 118.2, 113.9, 106.3, 103.8, 98.4, 95.6, 85.5, 56.1, 55.4, 55.2; **HRMS (ESI)** calcd for $C_{28}H_{24}O_3N$ $(M + H)^+$ 422.1751, found 422.1756.

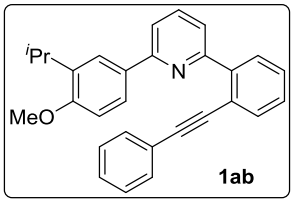
2.4 Synthesis of 2-aryl (phenylethynyl)phenyl)pyridines



Representative procedure for Suzuki cross-coupling reaction:[1] In a sealed tube, 2-bromo-6-(3-isopropyl-4-methoxyphenyl)pyridine (200 mg, 0.65 mmol, 1.0 equiv) and aryl boronic acid (**S_{28}**) (174 mg, 1.2 equiv) in DMF/H_2O 1:1 (4 mL) was degassed with nitrogen for 5 min. Next, Na_2CO_3 (204 mg, 3 equiv) and $PdCl_2(PPh_3)_2$ (22.8 mg, 5 mol%) were added under nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 6 h. After complete consumption of starting material, as monitored by TLC, the resulting mixture was allowed to bring to room temperature. The reaction mixture was diluted with $NaHCO_3$ (5 mL) and then the product was extracted with ethyl acetate (3 × 5 mL). The combined organic layer was dried over Na_2SO_4 and the organic solvent was removed under vacuo. The crude product was purified on a silica gel column using petroleum ether/ethyl acetate as eluent to afford 2-(3-isopropyl-4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl) pyridine (**1ab**) in 84% yield.

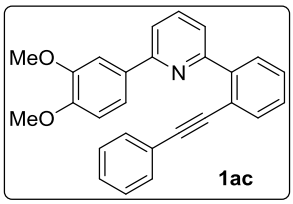


2-(3-isopropyl-4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1ab**):



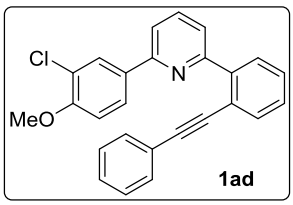
Off white solid, 205 mg, 84% yield; mp = 142-144 °C; R_f = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.92 - 8.03 (m, 3 H), 7.86 - 7.92 (m, 1 H), 7.82 (t, *J* = 7.6 Hz, 1 H), 7.70 (d, *J* = 7.3 Hz, 2 H), 7.45 - 7.53 (m, 1 H), 7.33 - 7.45 (m, 3 H), 7.27 - 7.32 (m, 3 H), 6.93 (d, *J* = 8.5 Hz, 1 H), 3.89 (s, 3 H), 3.36 (dt, *J* = 13.9, 6.8 Hz, 1 H), 1.27 (d, *J* = 6.7 Hz, 6 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 157.8, 157.1, 157.1, 142.6, 137.0, 136.2, 133.2, 132.0, 131.4, 130.0, 128.5, 128.2, 128.1, 128.0, 125.6, 125.0, 123.5, 121.7, 121.4, 118.2, 110.4, 92.4, 89.5, 55.5, 27.2, 22.6; **HRMS (ESI)** calcd for $C_{29}H_{26}ON$ $(M + H)^+$ 404.2009, found 404.2019.

2-(3,4-dimethoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1ac**):



Yellowish solid, 185 mg, 78% yield; mp = 98-100 °C; R_f = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 7.90 (d, *J* = 7.6 Hz, 1 H), 7.83 - 7.88 (m, 2 H), 7.81 (t, *J* = 7.8 Hz, 1 H), 7.67 - 7.75 (m, 2 H), 7.65 (dd, *J* = 8.4, 1.9 Hz, 1 H), 7.49 (t, *J* = 7.1 Hz, 1 H), 7.40 - 7.44 (m, 1 H), 7.34 - 7.40 (m, 2 H), 7.26 - 7.31 (m, 3 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 3.93 (s, 3 H), 3.88 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 157.1, 156.3, 149.8, 149.0, 142.4, 136.3, 133.2, 132.4, 131.3, 129.7, 128.4, 128.2, 128.1, 128.0, 123.3, 121.8, 121.4, 119.4, 118.1, 110.9, 110.1, 92.3, 89.4, 55.8, 55.6; **HRMS (ESI)** calcd for $C_{27}H_{22}ON$ $(M + H)^+$ 392.1645, found 392.1654.

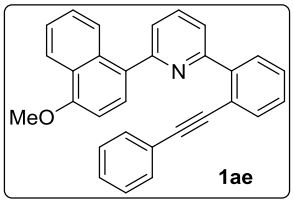
2-(3-chloro-4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1ad**):



Off white solid, 152 mg, 64% yield; mp = 130-132 °C; R_f = 0.55 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.24 (d, *J* = 2.3 Hz, 1 H), 8.03 (dd, *J* = 8.6, 2.1 Hz, 1 H), 7.93 (d, *J* = 8.0 Hz, 2 H), 7.82 (t, *J* = 7.8 Hz, 1 H), 7.73 (d, *J* = 7.6 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 1 H), 7.48 - 7.54 (m, 1 H), 7.37 - 7.47 (m, 3 H), 7.27 - 7.36 (m, 3 H), 6.97 (d, *J* = 8.8 Hz, 1 H), 3.94(s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 157.3, 155.5, 155.1, 142.1, 136.4, 133.3, 132.9, 131.4, 129.8, 128.7, 128.6, 128.2, 128.1, 126.3, 123.3, 122.7,

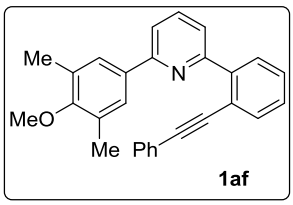
122.3, 121.4, 118.0, 111.8, 92.5, 89.3, 56.1; **HRMS (ESI)** calcd for $C_{26}H_{19}ONCl$ $(M + H)^+$ 396.1150, found 396.1149.

2-(4-methoxynaphthalen-1-yl)-6-(2-(phenylethynyl)phenyl)pyridine (**1ae**):



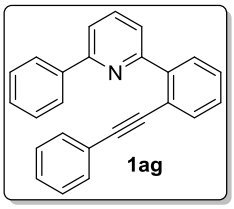
Off white solid, 178 mg, 72% yield; mp = 120-122 °C; $\boldsymbol{R_f}$ = 0.65 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 8.41 (d, *J* = 8.0 Hz, 1 H), 8.32 (d, *J* = 8.4 Hz, 1 H), 8.07 (d, *J* = 7.6 Hz, 1 H), 7.97 (d, *J* = 7.6 Hz, 1 H), 7.91 (t, *J* = 7.8 Hz, 1 H), 7.74 (d, *J* = 7.2 Hz, 1 H), 7.69 (d, *J* = 7.6 Hz, 1 H), 7.59 (d, *J* = 7.6 Hz, 1 H), 7.45 - 7.56 (m, 5 H), 7.38 - 7.45 (m, 1 H), 7.28 - 7.37 (m, 3 H), 6.90 (d, *J* = 7.6 Hz, 1 H), 4.05 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 158.9, 157.3, 155.8, 142.4, 135.9, 133.1, 132.1, 131.4, 131.2, 129.9, 128.6, 128.3, 128.2, 128.1, 128.1, 126.8, 125.7, 125.5, 125.1, 123.5, 123.4, 122.1, 122.0, 121.3, 103.3, 92.6, 89.4, 55.5; **HRMS (ESI)** calcd for $C_{30}H_{22}ON$ $(M + H)^+$ 412.1696, found 412.1698.

2-(4-methoxy-3,5-dimethylphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1af**):



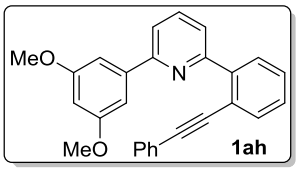
Off white solid, 178 mg, 76% yield; mp = 122-124 °C; $\boldsymbol{R_f}$ = 0.60 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 7.91 (d, *J* = 7.6 Hz, 1 H), 7.86 - 7.89 (m, 1 H), 7.82 (t, *J* = 7.8 Hz, 1 H), 7.79 (s, 2 H), 7.65 - 7.74 (m, 2 H), 7.45 - 7.52 (m, 1 H), 7.36 - 7.45 (m, 3 H), 7.24 - 7.34 (m, 3 H), 3.76 (s, 3 H), 2.33 (s, 7 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** = 157.9, 157.3, 156.8, 142.5, 136.3, 135.0, 133.3, 131.4, 131.0, 129.9, 128.6, 128.2, 128.1, 127.6, 123.5, 122.0, 121.5, 118.6, 92.4, 89.5, 59.7, 16.2; **HRMS (ESI)** calcd for $C_{28}H_{24}ON$ $(M + H)^+$ 390.1852, found 390.1853.

2-phenyl-6-(2-(phenylethynyl)phenyl)pyridine (**1ag**):



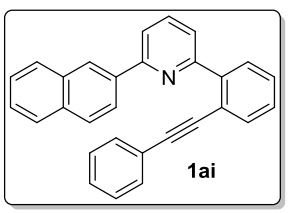
Orange thick liquid, 218 mg, 78% yield; R_f = 0.50 (petroleum ether/EtOAc = 97/03); **^{1}H NMR (500 MHz,$CDCl_3$) δ** = 8.16 (d, *J* = 7.2 Hz, 2 H), 7.96 (t, *J* = 8.6 Hz, 2 H), 7.86 (t, *J* = 7.8 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 7.2 Hz, 1 H), 7.51 - 7.45 (m, 3 H), 7.41 (d, *J* = 3.4 Hz, 2 H), 7.43 (d, *J* = 5.0 Hz, 2 H), 7.34 - 7.28 (m, 3 H); **^{13}C NMR (125 MHz,$CDCl_3$) δ** = 157.3, 156.9, 142.3, 139.5, 136.4, 133.3, 131.4, 129.9, 128.8, 128.6, 128.6, 128.2, 128.2, 128.2, 127.1, 123.4, 122.5, 121.4, 118.8, 92.5, 89.4; **HRMS (ESI)** calcd for $C_{25}H_{18}N$ $(M + H)^+$ 332.1434, found 332.1434.

2-(3, 5-dimethoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1ah**):



Off white solid, 238 mg, 90% yield; mp = 145-147 °C; R_f = 0.30 (petroleum ether/EtOAc = 95/05); **^{1}H NMR (400 MHz,$CDCl_3$) δ** = 8.01 - 7.93 (m, 1 H), 7.91 (d, *J* = 7.9 Hz, 1 H), 7.86 (t, *J* = 7.9 Hz, 1 H), 7.72 (t, *J* = 7.3 Hz, 2 H), 7.48 (d, *J* = 6.7 Hz, 1 H), 7.45 - 7.40 (m, 1 H), 7.40 - 7.35 (m, 2 H), 7.34 - 7.27 (m, 5 H), 6.58 - 6.48 (m, 1 H), 3.83 (s, 6 H); **^{13}C NMR (100 MHz,$CDCl_3$) δ** = 161.0, 157.3, 156.5, 142.3, 141.7, 136.5, 133.2, 131.4, 129.9, 128.6, 128.3, 128.2, 123.3, 122.8, 121.5, 119.0, 105.2, 101.2, 92.4, 89.4, 55.4; **HRMS (ESI)** calcd for $C_{27}H_{22}O_2N^+$ $(M + H)^+$ 392.1648, found 392.1645.

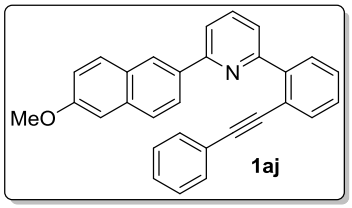
2-(naphthalen-2-yl)-6-(2-(phenylethynyl)phenyl)pyridine (**1ai**):



Orange thick liquid, 165 mg, 78% yield; R_f = 0.50 (petroleum ether/EtOAc = 97/03); **^{1}H NMR (500 MHz,$CDCl_3$) δ** = 8.65 (s, 1 H), 8.40 - 8.29 (m, 1 H), 8.05 - 7.98 (m, 2 H), 7.95 (d, *J* = 8.8 Hz, 1 H), 7.93 - 7.86 (m, 4 H), 7.77 (d, *J* = 7.6 Hz, 1 H), 7.56 - 7.49 (m, 3 H), 7.49

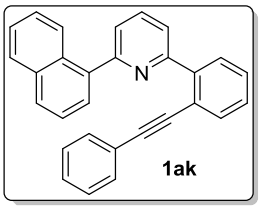
- 7.41 (m, 3 H), 7.36 - 7.27 (m, 3 H); **^{13}C NMR (125 MHz,$CDCl_3$) δ** = 157.5, 156.7, 142.3, 136.8, 136.5, 133.6, 133.5, 133.3, 131.4, 130.0, 128.7, 128.6, 128.3, 128.2, 128.2, 128.1, 127.6, 126.4, 126.3, 126.1, 124.8, 123.4, 122.6, 121.4, 119.1, 92.6, 89.5; **HRMS (ESI)** calcd for $C_{29}H_{19}N$ $(M + H)^+$ 382.1519, found 382.1523.

2-(6-methoxynaphthalen-2-yl)-6-(2-(phenylethynyl)phenyl)pyridine (**1aj**):



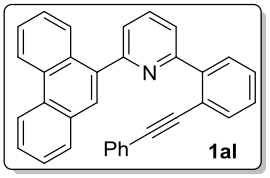
Off white solid, 214 mg, 82% yield; mp = 150-152 °C; R_f = 0.50(petroleum ether/EtOAc = 95/05); **^{1}H NMR (500 MHz,$CDCl_3$) δ** = 8.60 - 8.48 (m, 1 H), 8.25 (dd, *J* = 1.7, 8.6 Hz, 1 H), 7.98 - 7.94 (m, 1 H), 7.94 - 7.89 (m, 1 H), 7.88 - 7.83 (m, 2 H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.73 - 7.67 (m, 1 H), 7.49 (dt, *J* = 1.3, 7.5 Hz, 1 H), 7.42 (dd, *J* = 1.3, 7.4 Hz, 1 H), 7.40 - 7.37 (m, 2 H), 7.28 - 7.24 (m, 3 H), 7.17 - 7.12 (m, 2 H), 3.93 (s, 3 H); **^{13}C NMR (125 MHz,$CDCl_3$) δ** = 158.2, 157.5, 156.9, 142.5, 136.4, 134.9, 134.8, 133.4, 131.5, 130.3, 130.0, 129.0, 128.6, 128.3, 128.2, 127.1, 126.3, 125.3, 123.5, 122.3, 121.5, 119.0, 118.8, 105.7, 92.6, 89.5, 55.3; **HRMS (ESI)** calcd for $C_{30}H_{22}ON^+$ $(M + H)^+$ 412.1693, found 412.1696.

2-(naphthalen-1-yl)-6-(2-(phenylethynyl)phenyl)pyridine (**1ak**):



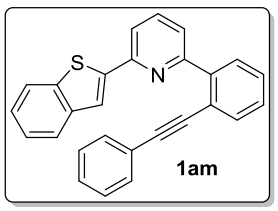
Orange thick liquid, 167 mg, 79% yield; R_f = 0.50 (petroleum ether/EtOAc = 97/03); **^{1}H NMR (500 MHz,$CDCl_3$) δ** = 8.24 (d, *J* = 8.4 Hz, 2 H), 7.97 (t, *J* = 6.9 Hz, 2 H), 7.90 - 7.84 (m, 1 H), 7.83 - 7.78 (m, 1 H), 7.74 - 7.69 (m, 3 H), 7.67 (d, *J* = 7.2 Hz, 2 H), 7.50 - 7.46 (m, 2 H), 7.42 - 7.36 (m, 3 H), 7.34 - 7.28 (m, 3 H); **^{13}C NMR (125 MHz,$CDCl_3$) δ** = 157.4, 156.4, 142.3, 141.6, 140.7, 138.4, 136.5, 133.3, 131.4, 130.0, 128.8, 128.6, 128.3, 128.2, 128.2, 127.5, 127.4, 127.1, 123.4, 122.6, 121.4, 118.7, 92.5, 89.4; **HRMS (ESI)** calcd for $C_{29}H_{19}N$ $(M + H)^+$ 382.1519, found 382.1520.

2-(phenanthren-9-yl)-6-(2-(phenylethynyl)phenyl)pyridine (**1al**):



Off white solid, 180 mg, 70% yield; mp = 112-114 °C; $\boldsymbol{R_f}$ = 0.50 (petroleum ether/EtOAc = 97/03); **^{1}H NMR (500 MHz,$CDCl_3$) δ** =8.78 (d, *J* = 8.0 Hz, 1 H), 8.73 (d, *J* = 8.4 Hz, 1 H), 8.21 (d, *J* = 8.0 Hz, 1 H), 8.09 (d, *J* = 7.6 Hz, 1 H), 7.99 - 7.94 (m, 2 H), 7.94 - 7.90 (m, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.73 - 7.66 (m, 3 H), 7.66 - 7.62 (m, 1 H), 7.62 - 7.57 (m, 1 H), 7.55 - 7.50 (m, 1 H), 7.49 - 7.43 (m, 3 H), 7.43 - 7.38 (m, 1 H), 7.35 - 7.29 (m, 3 H); **^{13}C NMR (125 MHz,$CDCl_3$) δ** = 159.0, 157.6, 142.3, 137.4, 136.1, 133.2, 131.5, 130.8, 130.5, 130.4, 130.0, 129.0, 128.7, 128.7, 128.4, 128.3, 128.2, 126.9, 126.7, 126.6, 126.5, 123.6, 123.4, 122.9, 122.7, 122.5, 121.5, 92.7, 89.4; **HRMS (ESI)** calcd for $C_{33}H_{21}N^+$ $(M + H)^+$ 432.1750, found 432.1756.

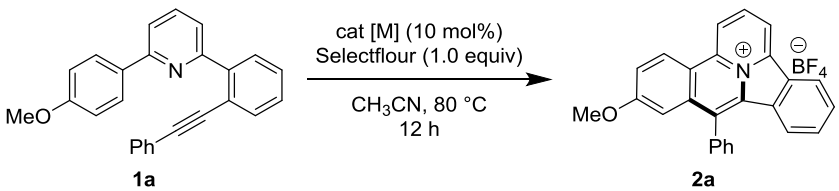
2-(benzo[*b*]thiophen-2-yl)-6-(2-(phenylethynyl)phenyl)pyridine (**1am**):



Off white solid, 223 mg, 84% yield; mp = 115-117 °C; $\boldsymbol{R_f}$ = 0.50(petroleum ether/EtOAc = 95/05); **^{1}H NMR (500 MHz,$CDCl_3$) δ** = 8.00 (d, *J* = 8.0 Hz, 1 H), 8.03 (d, *J* = 7.6 Hz, 1 H), 7.94 (s, 1 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.84 - 7.76 (m, 3 H), 7.71 (d, *J* = 7.6 Hz, 1 H), 7.55 - 7.50 (m, 1 H), 7.46 - 7.40 (m, 3 H), 7.38 - 7.34 (m, 2 H), 7.33 - 7.28 (m, 3 H); **^{13}C NMR (125 MHz,$CDCl_3$) δ** = 157.3, 152.2, 145.2, 141.6, 140.8, 140.5, 136.3, 133.3, 131.4, 130.1, 128.7, 128.4, 128.3, 128.2, 124.9, 124.5, 124.4, 124.2, 124.1, 123.4, 123.2, 122.5, 121.3, 121.1, 118.0, 92.8, 89.3; **HRMS (ESI)** calcd for $C_{27}H_{18}SN^+$ $(M + H)^+$388.1154, found 388.1154.

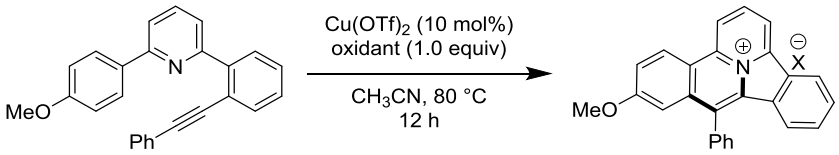
2.5 Optimization of reaction conditions

Screening of metal catalysts:[a]



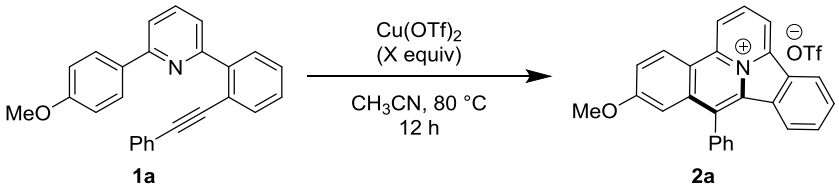
Sr. No.	cat [M]	Yield (%)[b]
1.	$(C_6F_5)_3PAuCl$	--
2.	Ph_3PAuCl	--
3.	JohnPhosAuCl	--
4.	$[Cu(OTf)]_2 \cdot C_6H_6$	48
5.	$CuCl_2$	41
6.	$Cu(OAc)_2$	52
7.	$Cu(OTf)_2$	62
8.	$Cu(ACN)_4BF_4$	57
[a]**Reaction conditions**: 0.13 mmol **1a**, 0.13 mmol Selectfluor, 10 mol% cat [M], CH_3CN (2.0 ml), 80 °C, 12 h. [b]Isolated yields.		

Effect of oxidants:[a]



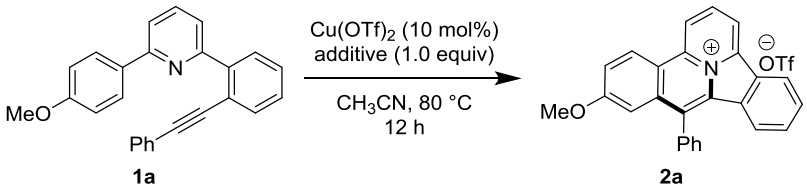
Sr. No.	Oxidant	Yield (%)[b]
1.	Selectfluor	75[c]
2.	$Ph_2I(OTf)$	--
3.	$PhI(OAc)_2$	--
4.	$PhI(CF_3CO_2)_2$	--
5.	AgOAc	16[d]
6.	-	17[d]
[a]**Reaction conditions**: 0.13 mmol **1a**, 0.13 mmol oxidant, 10 mol% $Cu(OTf)_2$, CH_3CN (2.0 ml), 80 °C, 12 h. [b]Isolated yields. [c]Counter anion X = BF_4. [d]Counter anion X = OTf.		

Variation in catalyst loading:[a]



Sr. No.	X mol%	Yield (%)[b]
1.	10	17
2.	50	37
3.	**100**	**78**
4.	120	81
[a]**Reaction conditions**: 0.13 mmol **1a**, X mol% $Cu(OTf)_2$, CH_3CN (2.0 ml), 80 °C, 12 h. [b]Isolated yields		

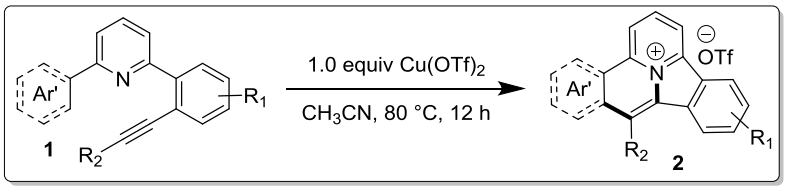
Screening of various additives (1a → 2a):[a]



Sr. No.	Additives	Yield (%)[b]
1.	TfOH	--
2.	NaOTf	15
3.	$Zn(OTf)_2$	36
4.	$Mg(OTf)_2$	25
5.	$Sc(OTf)_3$	28

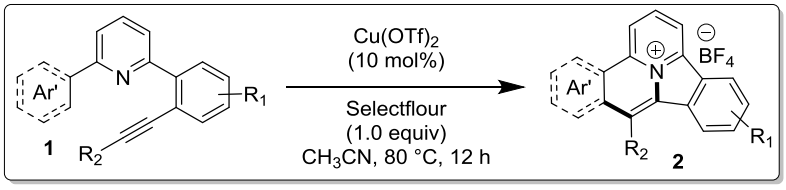
[a]**Reaction conditions**: 0.13 mmol **1a**, 10 mol% $Cu(OTf)_2$, 1.0 equiv additive, CH_3CN (2.0 ml), 80 °C, 12 h. [b]Isolated yields.

2.6 Copper-promoted intramolecular formal [4+2] cycloadditon of alkynes with 2-arylpyridines



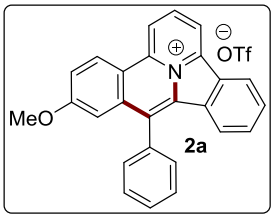
Representative procedure: To a screw-cap vial containing a stir bar were added 2-(4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1a**) (50 mg, 0.13 mmol, 1.0 equiv), $Cu(OTf)_2$ (50 mg, 1.0 equiv) and CH_3CN (4 mL). The reaction vial was fitted with a cap, evacuated and back filled with N_2 and heated at 80 °C for 12 h. When the reaction time was completed, the reaction mixture was allowed to cool at ambient temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and the combined mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica (CH_2Cl_2/MeOH; 95:05) to afford the product **2a** in 78% yield.

2.7 Experimental procedure for catalytic formal [4+2] cycloadditon reaction



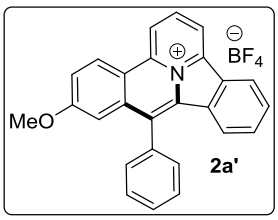
Representative procedure: To a screw-cap vial containing a stir bar were added 2-(4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1a**) (50 mg, 0.13 mmol, 1.0 equiv), $Cu(OTf)_2$ (5.0 mg, 10 mol%), selectfluor (49 mg, 1.0 equiv.) and CH_3CN (4 mL). The reaction vial was fitted with a cap, evacuated and back filled with N_2 and heated at 80 °C for 12 h. When the reaction time was completed, the reaction mixture was allowed to cool at ambient temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and the combined mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica (CH_2Cl_2/MeOH; 95:05) to afford the product **2a'** in 75% yield.

6-methoxy-8-phenylbenzo[1,2]indolizino[5,4,3-*ab*]isoquinolin-13-ium trifluoromethanesulfonate (**2a**):



Off white solid, 52 mg, 78% yield; mp = 312-314 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d_6) δ** = 9.79 (d, *J* = 8.8 Hz, 1 H), 9.55 (d, *J* = 9.2 Hz, 1 H), 9.34 (d, *J* = 7.6 Hz, 1 H), 9.07 (t, *J* = 8.2 Hz, 1 H), 8.86 (d, *J* = 7.6 Hz, 1 H), 8.02 - 7.92 (m, 2 H), 7.88 (br. s., 3 H), 7.75 (t, *J* = 7.6 Hz, 1 H), 7.70 (d, *J* = 3.4 Hz, 2 H), 7.24 - 7.14 (m, 1 H), 6.88 (d, *J* = 8.0 Hz, 1 H), 3.91 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d_6) δ** = 163.0, 141.1, 138.9, 138.2, 134.9, 134.4, 132.5, 132.1, 132.0, 131.0, 130.5, 130.3, 130.0, 129.3, 128.4, 123.4, 123.2, 121.3, 120.7, 118.7, 118.1, 108.2, 56.0; **^{19}F NMR** (**376.5 MHz**, **DMSO-d_6**)**δ =** 77.75; **HRMS (ESI)** calcd for $C_{26}H_{18}ON^+$ $(M - OTf)^+$ 360.1381, found 360.1383.

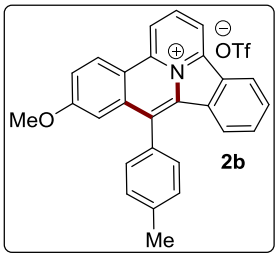
6-methoxy-8-phenylbenzo[1,2]indolizino[5,4,3-*ab*]isoquinolin-13-ium tetrafluoroborate (2a'):



Off white solid, 44 mg, 75% yield; mp = 240-242 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz,DMSO-d_6) δ** = 9.79 (d, *J* = 8.5 Hz, 1 H), 9.55 (d, *J* = 9.2 Hz, 1 H), 9.34 (d, *J* = 7.3 Hz, 1 H), 9.07 (t, *J* = 7.9 Hz, 1 H), 8.86 (d, *J* = 7.9 Hz, 1 H), 8.04 - 7.91 (m, 2 H), 7.91 - 7.82 (m, 3 H), 7.75 (t, *J* = 7.6 Hz, 1 H), 7.70 (d, *J* = 3.1 Hz, 2 H), 7.29 - 7.10 (m, 1 H),

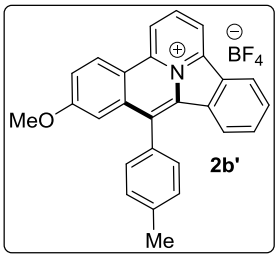
6.88 (d, *J* = 7.9 Hz, 1 H), 3.91 (s, 3 H); **^{13}C NMR (100 MHz,DMSO-d$_6$) δ** = 163.0, 141.1, 138.9, 138.2, 134.9, 134.4, 132.5, 132.1, 132.0, 131.0, 130.4, 130.3, 130.0, 129.3, 128.4, 123.4, 123.2, 121.3, 120.7, 118.7, 118.1, 108.2, 56.0; **^{19}F NMR** (**376.5 MHz**, **DMSO-d$_6$**)**δ** = -148.26; **HRMS (ESI)** calcd for $C_{25}H_{16}ON^+$ $(M - BF_4)^+$ 360.1383, found 360.1380.

6-methoxy-8-(*p*-tolyl)benzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate(**2b**):



Off white solid, 52 mg, 76% yield; mp = 278-280 °C; ***R$_f$*** = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz**, **DMSO-d$_6$) δ** = 9.78 (d, *J* = 8.5 Hz, 1 H), 9.55 (d, *J* = 9.2 Hz, 1 H), 9.33 (d, *J* = 7.3 Hz, 1 H), 9.06 (t, *J* = 7.9 Hz, 1 H), 8.86 (d, *J* = 7.3 Hz, 1 H), 8.02 - 7.89 (m, 2 H), 7.78 (t, *J* = 7.3 Hz, 1 H), 7.72 - 7.63 (m, *J* = 7.3 Hz, 2 H), 7.62 - 7.48 (m, *J* = 7.3 Hz, 2 H), 7.23 (s, 1 H), 6.97 (d, *J* = 7.9 Hz, 1 H), 3.91 (s, 3 H), 2.61 (s, 3 H); **^{13}C NMR (100 MHz**, **DMSO-d$_6$) δ** = 163.0, 141.0, 140.0, 138.8, 138.1, 135.1, 134.6, 132.5, 132.0, 131.0, 130.6, 130.4, 130.3, 129.2, 129.1, 128.4, 123.4, 123.3, 121.2, 120.6, 118.7, 118.0, 108.3, 56.1, 21.2; **HRMS (ESI)** calcd for $C_{27}H_{20}ON^+$ $(M - OTf)^+$ 374.1515, found 374.1537.

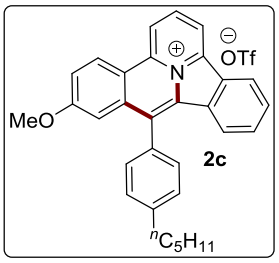
6-methoxy-8-(*p*-tolyl)benzo[1,2]indolizino[5,4,3-*ab*]isoquinolin-13-ium tetrafluoroborate (2b'):



Off white solid, 37 mg, 63% yield; mp = 230-232 °C; ***R$_f$*** = 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz**,**DMSO-d$_6$) δ** = 9.77 (d, *J* = 8.5 Hz, 1 H), 9.54 (d, *J* = 9.2 Hz, 1 H), 9.33 (d, *J* = 7.3 Hz, 1 H), 9.14 - 8.98 (m, 1 H), 8.86 (d, *J* = 7.9 Hz, 1 H), 8.05 - 7.85 (m, 2 H), 7.77 (t, *J* = 7.6 Hz, 1 H), 7.68 (d, *J* = 7.9 Hz, 2 H), 7.63 - 7.51 (m, 2 H), 7.23 (d, *J* = 2.4 Hz, 1 H), 6.97 (d, *J* = 7.9 Hz, 1 H), 3.91 (s, 3 H), 2.61 (s, 3 H); **^{13}C NMR (100 MHz**,**DMSO-d$_6$) δ** = 163.0, 141.0, 140.0, 138.8, 138.1, 135.1, 134.6, 132.5, 132.0, 131.0, 130.6, 130.4, 130.3,

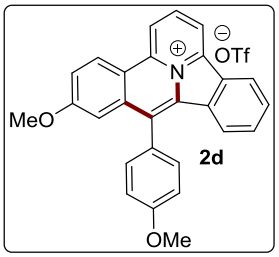
129.2, 129.1, 128.4, 123.4, 123.3, 121.2, 120.6, 118.7, 118.0, 108.3, 56.1, 21.2; **HRMS (ESI)** calcd for $C_{25}H_{16}ON^+$ $(M - BF_4)^+$ 374.1539, found 374.1537.

6-methoxy-8-(4-pentylphenyl)benzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2c**):



Off white solid, 50 mg, 74% yield; mp = 220-222 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.78 (d, *J* = 8.8 Hz, 1 H), 9.55 (d, *J* = 9.2 Hz, 1 H), 9.33 (d, *J* = 7.6 Hz, 1 H), 9.06 (t, *J* = 8.0 Hz, 1 H), 8.86 (d, *J* = 7.6 Hz, 1 H), 8.01 - 7.90 (m, 2 H), 7.73 (t, *J* = 7.6 Hz, 1 H), 7.71 - 7.66 (m, *J* = 7.6 Hz, 2 H), 7.63 - 7.52 (m, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 1.9 Hz, 1 H), 6.91 (d, *J* = 8.0 Hz, 1 H), 3.91 (s, 3 H), 2.87 (t, *J* = 7.4 Hz, 2 H), 1.80 (t, *J* = 6.9 Hz, 2 H), 1.47 - 1.37 (m, 4 H), 0.94 (t, *J* = 6.5 Hz, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.0, 144.8, 141.0, 138.8, 138.2, 135.1, 134.6, 132.5, 131.9, 131.0, 130.4, 130.3, 129.9, 129.4, 129.2, 128.5, 123.4, 123.2, 121.2, 120.7, 118.7, 118.1, 108.4, 56.0, 35.0, 30.9, 30.3, 22.0, 14.0; **HRMS (ESI)** calcd for $C_{31}H_{28}ON^+$ $(M - OTf)^+$ 430.2165, found 430.2165.

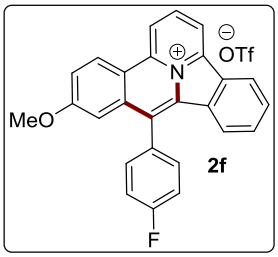
6-methoxy-8-(4-methoxyphenyl)benzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2d**):



Off white solid, 33 mg, 48% yield; mp = 218-220 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.77 (d, *J* = 8.5 Hz, 1 H), 9.53 (d, *J* = 9.3 Hz, 1 H), 9.32 (d, *J* = 7.6 Hz, 1 H), 9.05 (t, *J* = 8.2 Hz, 1 H), 8.86 (d, *J* = 7.8 Hz, 1 H), 8.02 - 7.91 (m, 2 H), 7.82 - 7.75 (m, 1 H), 7.67 - 7.59 (m, 2 H), 7.47 - 7.39 (m, *J* = 8.7 Hz, 2 H), 7.27 (d, *J* = 2.6 Hz, 1 H), 7.04 (d, *J* = 7.9 Hz, 1 H), 3.99 (s, 3 H), 3.93 (s, 3 H); **^{13}C NMR (125 MHz,**

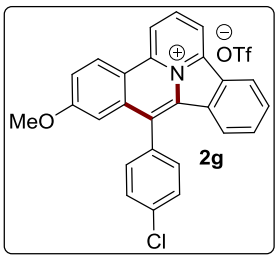
DMSO-d_6) δ = 163.0, 160.6, 141.0, 138.7, 138.1, 135.3, 134.5, 132.6, 132.0, 131.0, 130.9, 130.4, 130.2, 128.4, 123.8, 123.4, 121.2, 120.6, 118.7, 118.0, 115.5, 108.3, 56.1, 55.5; **HRMS (ESI)** calcd for $C_{27}H_{20}O_2N^+$ $(M - OTf)^+$ 390.1489, found 390.1484.

8-(4-fluorophenyl)-6-methoxybenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2f**):



Off white solid, 54 mg, 78% yield; mp = 348-350 °C; $\boldsymbol{R_f}$ = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d_6) δ** = 9.79 (d, *J* = 8.5 Hz, 1 H), 9.56 (d, *J* = 9.2 Hz, 1 H), 9.34 (d, *J* = 7.9 Hz, 1 H), 9.08 (t, *J* = 8.2 Hz, 1 H), 8.87 (d, *J* = 7.9 Hz, 1 H), 8.03 - 7.91 (m, 2 H), 7.86 - 7.69 (m, 5 H), 7.19 (br. s., 1 H), 6.96 (d, *J* = 7.9 Hz, 1 H), 3.93 (s, 3 H); **^{13}C NMR (100 MHz, DMSO-d_6) δ** =163.2 (d, *J* = 247.4 Hz), 163.1, 141.1, 139.0, 138.2, 135.1, 133.5, 132.7, 132.2, 131.9, 131.8, 131.1, 130.3, 130.2 128.4, 128.4 (d, *J* = 3.08 Hz) 123.4 (d, *J* = 13.10 Hz), 121.4, 120.7, 118.7, 118.1, 117.3(d, *J* = 22.35 Hz), 108.1, 56.1; **HRMS (ESI)** calcd for $C_{26}H_{17}FON^+$ $(M - OTf)^+$ 378.1340, found 378.1345.

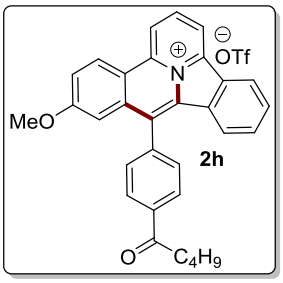
8-(4-chlorophenyl)-6-methoxybenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2g**):



Off white solid, 51 mg, 75% yield; mp = 285-287 °C; $\boldsymbol{R_f}$ = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d_6) δ =** 9.79 (d, *J* = 8.5 Hz, 1 H), 9.56 (d, *J* = 9.3 Hz, 1 H), 9.35 (d, *J* = 7.6 Hz, 1 H), 9.08 (t, *J* = 8.1 Hz, 1 H), 8.88 (d, *J* = 7.8 Hz, 1 H), 8.07 - 7.90 (m, 4 H), 7.82 (t, *J* = 7.6 Hz, 1 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 7.18 (d, *J* = 2.1 Hz, 1 H), 6.99 (d, *J* = 8.1 Hz, 1 H), 3.93 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d_6) δ** = 163.1, 141.1, 139.0, 138.3, 135.3, 134.8, 133.1, 132.6, 132.2, 131.4, 131.2, 131.0, 130.3, 130.3, 130.2, 128.5, 123.5,

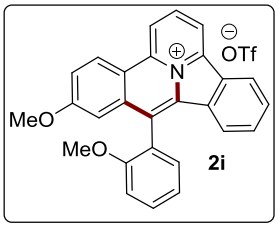
123.3, 121.4, 120.7, 118.7, 118.1, 108.0, 56.2; **HRMS (ESI)** calcd for $C_{26}H_{17}ClON^+$ (M - OTf)$^+$ 394.0993, found 394.0998.

6-methoxy-8-(4-pentanoylphenyl)benzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2h**):



Off white solid, 53 mg, 81% yield; mp = 240-242 °C; $\boldsymbol{R_f}$ = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.81 (d, *J* = 8.5 Hz, 1 H), 9.58 (d, *J* = 9.3 Hz, 1 H), 9.36 (d, *J* = 7.5 Hz, 1 H), 9.10 (t, *J* = 8.2 Hz, 1 H), 8.89 (d, *J* = 7.9 Hz, 1 H), 8.48 - 8.42 (m, *J* = 8.2 Hz, 2 H), 8.02 - 7.95 (m, 2 H), 7.90 - 7.83 (m, *J* = 8.2 Hz, 2 H), 7.80 - 7.71 (m, 1 H), 7.15 (d, *J* = 2.4 Hz, 1 H), 6.93 (d, *J* = 8.1 Hz, 1 H), 3.92 (s, 3 H), 3.27 (t, *J* = 7.2 Hz, 2 H), 1.74 (quin, *J* = 7.4 Hz, 2 H), 1.47 (sxt, *J* = 7.4 Hz, 2 H), 0.99 (t, *J* = 7.3 Hz, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 199.8, 163.1, 141.1, 139.1, 138.3, 138.0, 136.5, 134.6, 133.4, 132.4, 132.2, 131.2, 130.4, 130.1, 129.9, 129.5, 128.5, 123.5, 123.3, 121.3, 120.8, 118.7, 118.1, 108.2, 56.1, 37.9, 25.8, 21.8, 13.9; **HRMS (ESI)** calcd for $C_{31}H_{26}O_2N^+$ (M - OTf)$^+$ 444.1925, found 444.1925.

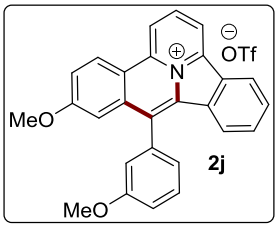
6-methoxy-8-(2-methoxyphenyl)benzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (2i):



Pale yellow solid, 39 mg, 57% yield; mp = 220-222 °C; $\boldsymbol{R_f}$ = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.78 (d, *J* = 8.4 Hz, 1 H), 9.54 (d, *J* = 9.3 Hz, 1 H), 9.32 (d, *J* = 7.6 Hz, 1 H), 9.06 (t, *J* = 8.1 Hz, 1 H), 8.86 (d, *J* = 7.9 Hz, 1 H), 8.02 - 7.93 (m, 2 H), 7.91 - 7.84 (m, 1 H), 7.78 (t, *J* = 7.6 Hz, 1 H), 7.56 (d, *J* = 8.5 Hz, 1 H), 7.53 - 7.46 (m, 1 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.18 (d, *J* = 2.4 Hz, 1 H), 7.01 (d, *J* = 7.9 Hz, 1 H), 3.91 (s, 3 H), 3.69 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.1, 156.8, 141.0, 138.9, 138.2, 134.8,

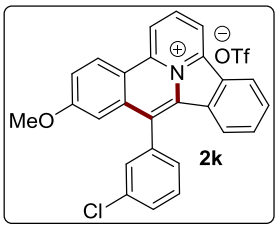
132.6, 132.5, 132.2, 131.9, 131.1, 130.8, 130.3, 130.2, 128.5, 123.5, 122.9, 122.0, 121.3, 120.8, 120.0, 118.6, 118.1, 112.8, 107.9, 56.1, 55.9; **HRMS (ESI)** calcd for $C_{27}H_{20}O_2N^+$ (M - OTf)$^+$ 390.1489, found 390.1474.

6-methoxy-8-(3-methoxyphenyl)benzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2j**):



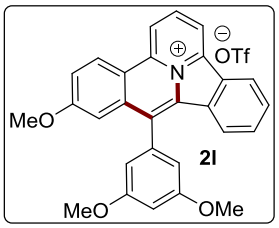
Off white solid, 42 mg, 62% yield; mp = 285-287 °C; R_f = 0.40 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.79 - 9.69 (m, 1 H), 9.52 (dt, *J* = 3.1, 6.1 Hz, 1 H), 9.36 - 9.25 (m, 1 H), 9.08 - 8.97 (m, 1 H), 8.84 (t, *J* = 6.1 Hz, 1 H), 8.00 - 7.89 (m, 2 H), 7.82 - 7.69 (m, 2 H), 7.43 (dd, *J* = 2.3, 8.4 Hz, 1 H), 7.28 - 7.20 (m, 3 H), 6.97 (d, *J* = 8.0 Hz, 1 H), 3.92 (s, 3 H), 3.86 (s, 3 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 163.1, 160.3, 141.1, 138.9, 138.2, 134.9, 134.1, 133.4, 132.4, 132.1, 131.4, 131.1, 130.3, 128.4, 123.4, 121.3, 120.7, 118.7, 118.1, 116.0, 114.6, 108.3, 56.1, 55.5; **HRMS (ESI)** calcd for $C_{27}H_{20}O_2N^+$ (M - OTf)$^+$ 390.1484, found 390.1489.

8-(3-chlorophenyl)-6-methoxybenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (2k):



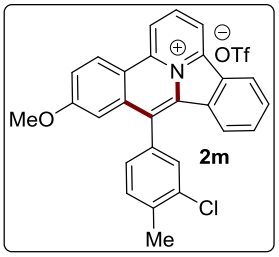
Off white solid, 49 mg, 72% yield; mp = 258-260 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ**9.81 (d, *J* = 8.7 Hz, 1 H), 9.57 (d, *J* = 9.3 Hz, 1 H), 9.36 (d, *J* = 7.6 Hz, 1 H), 9.09 (t, *J* = 8.2 Hz, 1 H), 8.89 (d, *J* = 7.9 Hz, 1 H), 8.02 - 7.97 (m, 2 H), 7.96 (dd, *J* = 1.1, 2.1 Hz, 1 H), 7.95 - 7.88 (m, 1 H), 7.84 - 7.79 (m, 2 H), 7.70 (d, *J* = 7.5 Hz, 1 H), 7.18 (d, *J* = 2.6 Hz, 1 H), 6.93 (d, *J* = 8.1 Hz, 1 H), 3.94 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.2, 141.1, 139.2, 138.3, 134.7, 134.6, 134.2, 132.6, 132.3, 132.1, 131.2, 130.6, 130.4, 130.1, 129.2, 128.5, 128.2, 123.6, 123.2, 121.4, 120.8, 118.7, 118.2, 108.1, 56.2; **HRMS (ESI)** calcd for $C_{26}H_{17}ClON^+$ (M - OTf)$^+$ 394.0993, found 394.0977.

8-(3,5-dimethoxyphenyl)-6-methoxybenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2l**):



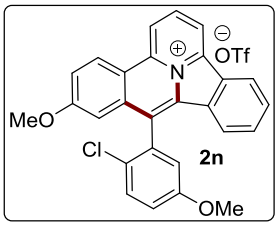
Pale yellow solid, 52 mg, 78% yield; mp = 198-200 °C; R_f = 0.60 (CH_2Cl_2/MeOH = 90/10); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.79 (d, *J* = 8.5 Hz, 1 H), 9.55 (d, *J* = 9.2 Hz, 1 H), 9.34 (d, *J* = 7.8 Hz, 1 H), 9.07 (t, *J* = 8.1 Hz, 1 H), 8.87 (d, *J* = 7.8 Hz, 1 H), 8.00 - 7.95 (m, 2 H), 7.84 (t, *J* = 7.7 Hz, 1 H), 7.31 (d, *J* = 2.4 Hz, 1 H), 7.11 (d, *J* = 7.9 Hz, 1 H), 6.97 (t, *J* = 2.1 Hz, 1 H), 6.83 (d, *J* = 2.1 Hz, 2 H), 3.95 (s, 3 H), 3.85 (s, 6 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.1, 161.6, 141.1, 138.9, 138.1, 134.8, 134.1, 134.0, 132.3, 132.2, 131.1, 130.2, 130.2, 128.4, 123.5, 123.4, 121.3, 120.7, 118.6, 118.1, 108.3, 107.1, 101.8, 56.2, 55.7; **HRMS (ESI)** calcd for $C_{28}H_{22}O_3N^+$ $(M - OTf)^+$ 420.1594, found 420.1566.

8-(3-chloro-4-methylphenyl)-6-methoxybenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2m**):



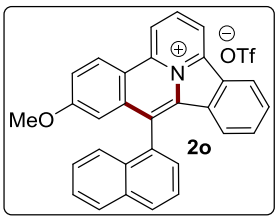
Off white solid, 51 mg, 76% yield; mp = 264-266 °C; R_f = 0.60 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.79 (d, *J* = 8.5 Hz, 1 H), 9.56 (d, *J* = 9.3 Hz, 1 H), 9.34 (d, *J* = 7.6 Hz, 1 H), 9.08 (t, *J* = 8.1 Hz, 1 H), 8.88 (d, *J* = 7.8 Hz, 1 H), 8.04 - 7.93 (m, 2 H), 7.86 (d, *J* = 7.8 Hz, 1 H), 7.82 (t, *J* = 7.5 Hz, 1 H), 7.77 (d, *J* = 1.4 Hz, 1 H), 7.60 (dd, *J* = 1.5, 7.6 Hz, 1 H), 7.21 (d, *J* = 2.4 Hz, 1 H), 6.99 (d, *J* = 8.1 Hz, 1 H), 3.94 (s, 3 H), 2.62 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.1, 141.1, 139.1, 138.2, 138.0, 134.8, 134.8, 132.9, 132.7, 132.7, 132.2, 131.4, 131.2, 130.3, 130.2, 129.6, 128.5, 128.2, 123.5, 123.3, 121.3, 120.7, 118.6, 118.1, 108.2, 56.2, 19.8; **HRMS (ESI)** calcd for $C_{27}H_{19}ClON^+$ $(M - OTf)^+$ 408.1150, found 408.1141.

8-(2-chloro-5-methoxyphenyl)-6-methoxybenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2n**):



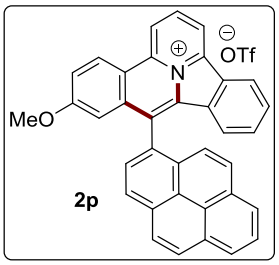
Off white solid, 42 mg, 63% yield; mp = 210-212 °C;R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.82 (d, *J* = 8.5 Hz, 1 H), 9.59 (d, *J* = 9.3 Hz, 1 H), 9.36 (d, *J* = 7.8 Hz, 1 H), 9.10 (t, *J* = 8.2 Hz, 1 H), 8.90 (d, *J* = 7.8 Hz, 1 H), 8.04 - 7.98 (m, 2 H), 7.92 (d, *J* = 9.0 Hz, 1 H), 7.86 (t, *J* = 7.6 Hz, 1 H), 7.49 (dd, *J* = 3.1, 9.0 Hz, 1 H), 7.29 (d, *J* = 2.9 Hz, 1 H), 7.15 (d, *J* = 2.4 Hz, 1 H), 6.99 (d, *J* = 8.1 Hz, 1 H), 3.96 (s, 3 H), 3.83 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.4, 159.2, 141.2, 139.4, 138.4, 134.0, 132.7, 132.6, 131.7, 131.5, 131.0, 130.4, 129.7, 128.7, 123.6, 123.6, 122.9, 121.4, 121.0, 118.6, 118.4, 116.5, 107.8, 56.3, 55.9; **HRMS (ESI)** calcd for $C_{27}H_{19}ClO_2N^+$ (M - OTf)$^+$424.1099, found 424.1099.

6-methoxy-8-(naphthalen-1-yl)benzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2o**):



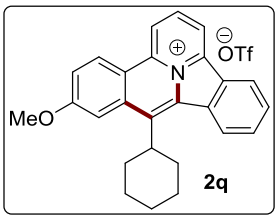
Off white solid, 54 mg, 80% yield; mp = 303-305 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.85 (d, *J* = 8.5 Hz, 1 H), 9.62 (d, *J* = 9.2 Hz, 1 H), 9.36 (d, *J* = 7.3 Hz, 1 H), 9.16 - 9.04 (m, 1 H), 8.85 (d, *J* = 7.9 Hz, 1 H), 8.44 (d, *J* = 7.9 Hz, 1 H), 8.25 (d, *J* = 8.5 Hz, 1 H), 8.03 - 7.92 (m, 2 H), 7.91 - 7.79 (m, 2 H), 7.64 (t, *J* = 7.3 Hz, 1 H), 7.56 (t, *J* = 7.6 Hz, 1 H), 7.42 (d, *J* = 7.9 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 6.94 (br. s., 1 H), 6.45 (d, *J* = 7.9 Hz, 1 H), 3.74 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.0, 141.2, 139.0, 138.7, 135.4, 133.5, 133.4, 132.7, 132.0, 131.1, 131.0, 130.7, 130.5, 130.1, 129.4, 128.8, 128.6, 128.2, 127.5, 127.1, 126.4, 125.0, 123.4, 123.0, 120.9, 120.8, 119.0, 118.0, 108.4, 56.0; **HRMS (ESI)** calcd for $C_{30}H_{20}ON^+$ (M - OTf)$^+$ 410.1539, found 410.1544.

6-methoxy-8-(pyren-1-yl)benzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2p**):



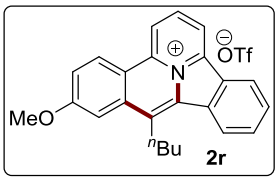
Yellow solid, 55 mg, 85% yield; mp = 337-339 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.90 (d, *J* = 8.8 Hz, 1 H), 9.66 (d, *J* = 9.2 Hz, 1 H), 9.39 (d, *J* = 7.6 Hz, 1 H), 9.15 (t, *J* = 8.2 Hz, 1 H), 8.86 (d, *J* = 7.6 Hz, 1 H), 8.74 (d, *J* = 8.0 Hz, 1 H), 8.58 - 8.40 (m, 3 H), 8.31 (d, *J* = 7.6 Hz, 1 H), 8.34 (d, *J* = 7.2 Hz, 1 H), 8.18 (t, *J* = 7.4 Hz, 1 H), 8.06 (d, *J* = 9.2 Hz, 1 H), 7.98 (d, *J* = 9.2 Hz, 1 H), 7.82 (t, *J* = 7.6 Hz, 1 H), 7.71 (d, *J* = 9.2 Hz, 1 H), 7.39 (t, *J* = 7.6 Hz, 1 H), 7.05 - 6.85 (m, 1 H), 6.19 (d, *J* = 8.0 Hz, 1 H), 3.64 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.1, 141.2, 139.0, 138.7, 135.7, 133.7, 133.1, 132.2, 132.0, 131.0, 130.9, 130.4, 130.4, 130.1, 129.3, 129.1, 128.9, 128.6, 127.5, 127.0, 126.3, 126.2, 126.1, 126.0, 124.2, 124.0, 123.7, 123.4, 122.9, 121.1, 120.8, 119.0, 118.0, 108.5, 55.9; **HRMS (ESI)** calcd for $C_{36}H_{22}ON^+$ $(M - OTf)^+$ 484.1696, found 484.1700.

8-cyclohexyl-6-methoxybenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2q**):



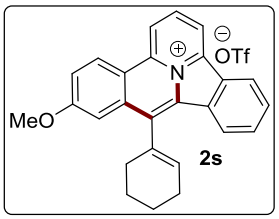
White solid, 50 mg, 72% yield; mp = 280-282 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d$_6$) δ** = 9.65 (d, *J* = 8.5 Hz, 1 H), 9.45 (d, *J* = 9.2 Hz, 1 H), 9.26 (d, *J* = 7.3 Hz, 1 H), 9.03 - 8.86 (m, 2 H), 8.73 (d, *J* = 7.9 Hz, 1 H), 8.25 (br. s., 1 H), 8.18 - 8.10 (m, 1 H), 8.10 - 8.01 (m, 1 H), 7.92 (d, *J* = 9.2 Hz, 1 H), 4.48 (br. s., 1 H), 4.18 (br. s., 3 H), 2.59 (d, *J* = 10.4 Hz, 2 H), 2.06 (d, *J* = 9.8 Hz, 4 H), 1.99 - 1.90 (m, 1 H), 1.79 (d, *J* = 10.4 Hz, 2 H), 1.71 - 1.57 (m, 1 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 162.1, 140.6, 138.2, 137.7, 133.5, 132.8, 130.7, 130.4, 130.2, 128.6, 125.0, 123.5, 121.0, 120.4, 118.9, 117.4, 108.9, 56.3, 30.1, 26.5, 25.4; **HRMS (ESI)** calcd for $C_{26}H_{24}ON^+$ $(M - OTf)^+$ 366.1852, found 366.1852.

8-butyl-6-methoxybenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2r**):



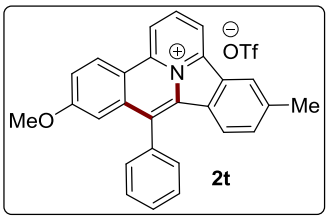
Off white solid, 53 mg, 74% yield; mp = 209-211 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d$_6$) δ** = 9.64 (d, *J* = 8.5 Hz, 1 H), 9.42 (d, *J* = 9.2 Hz, 1 H), 9.24 (d, *J* = 7.9 Hz, 1 H), 9.02 - 8.81 (m, 2 H), 8.69 (d, *J* = 7.9 Hz, 1 H), 8.16 - 8.08 (m, 1 H), 8.08 - 7.99 (m, 2 H), 7.90 (d, *J* = 9.2 Hz, 1 H), 4.17 (s, 3 H), 3.93 (t, *J* = 7.6 Hz, 2 H), 1.87 (d, *J* = 6.7 Hz, 2 H), 1.76 - 1.62 (m, 2 H), 1.02 (t, *J* = 7.3 Hz, 3 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 163.3, 140.5, 138.0, 137.5, 137.0, 134.2, 132.8, 132.2, 130.8, 130.1, 130.0, 128.4, 124.6, 123.4, 121.6, 120.5, 118.4, 117.5, 106.7, 56.5, 40.1, 31.5, 27.1, 22.3, 14.0; **HRMS (ESI)** calcd for $C_{24}H_{22}ON^+$ (M - OTf)$^+$ 340.1696, found 340.1698.

8-(cyclohex-1-en-1-yl)-6-methoxybenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2s**):



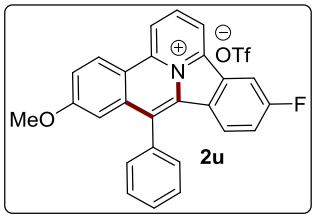
Off white solid, 40 mg, 58% yield; mp = 228-230 °C; R_f = 0.60 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d$_6$) δ** = 9.71 (d, *J* = 8.4 Hz, 1 H), 9.48 (d, *J* = 9.2 Hz, 1 H), 9.29 (d, *J* = 7.3 Hz, 1 H), 9.00 (t, *J* = 8.2 Hz, 1 H), 8.89 (d, *J* = 7.5 Hz, 1 H), 8.52 (d, *J* = 7.8 Hz, 1 H), 8.16 - 7.99 (m, 2 H), 7.95 (dd, *J* = 2.5, 9.1 Hz, 1 H), 7.74 (d, *J* = 2.6 Hz, 1 H), 6.22 (br. s., 1 H), 4.13 (s, 3 H), 2.49 - 2.46 (m, 4 H), 2.14 - 1.94 (m, 4 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.1, 140.9, 138.5, 137.9, 136.6, 134.2, 132.6, 132.2, 131.3, 130.9, 130.3, 130.2, 128.4, 123.9, 123.4, 121.5, 120.5, 118.8, 117.9, 107.4, 56.2, 28.5, 25.1, 22.4, 21.3; **HRMS (ESI)** calcd for $C_{26}H_{22}ON^+$ (M - OTf)$^+$ 364.1696, found 364.1719.

6-methoxy-11-methyl-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2t**):



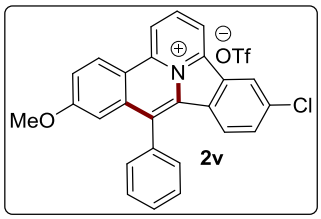
Off white solid, 50 mg, 70% yield; mp = 287-289 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.75 (d, *J* = 8.5 Hz, 1 H), 9.52 (d, *J* = 9.2 Hz, 1 H), 9.24 (d, *J* = 7.3 Hz, 1 H), 9.03 (t, *J* = 7.9 Hz, 1 H), 8.66 (s, 1 H), 7.94 (dd, *J* = 1.8, 9.2 Hz, 1 H), 7.87 (br. s., 3 H), 7.68 (d, *J* = 3.7 Hz, 2 H), 7.56 (d, *J* = 7.9 Hz, 1 H), 7.23 - 7.11 (m, 1 H), 6.74 (d, *J* = 7.9 Hz, 1 H), 3.90 (s, 3 H), 2.56 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.0, 141.6, 141.0, 138.8, 138.2, 134.9, 133.6, 133.1, 132.5, 132.2, 130.5, 130.4, 130.0, 129.3, 128.4, 127.9, 123.2, 123.0, 121.1, 120.6, 118.5, 117.9, 108.1, 56.0, 21.4; **HRMS (ESI)** calcd for $C_{27}H_{20}ON^+$ (M - OTf)$^+$ 374.1538, found 374.1539.

11-fluoro-6-methoxy-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2u**):



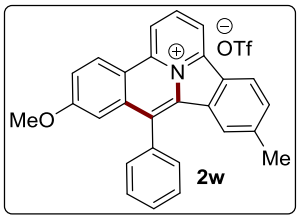
Off white solid, 43 mg, 62% yield; mp = 247-249 °C; R_f = 0.60 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d$_6$) δ** = 9.84 (d, *J* = 8.8 Hz, 1 H), 9.56 (d, *J* = 9.3 Hz, 1 H), 9.34 (d, *J* = 7.8 Hz, 1 H), 9.10 (t, *J* = 8.3 Hz, 1 H), 8.83 (dd, *J* = 2.1, 8.4 Hz, 1 H), 7.98 (dd, *J* = 2.4, 9.1 Hz, 1 H), 7.92 - 7.83 (m, 3 H), 7.75 - 7.64 (m, 3 H), 7.20 (d, *J* = 2.5 Hz, 1 H), 6.87 (dd, *J* = 4.8, 8.8 Hz, 1 H), 3.91 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.2 (d, *J* = 249.7 Hz), 163.2, 140.2 (d, *J* = 4.5 Hz), 138.8, 138.3, 135.0, 134.1, 132.4, 132.3, 131.9, 131.8, 130.6, 130.1, 129.3, 128.5, 126.8 (d, *J* = 1.8 Hz), 125.5 (d, *J* = 10 Hz), 121.4 (d, *J* = 7.27 Hz), 120.2(d, *J* = 24.5 Hz), 118.7 (d, *J* = 21.8 Hz), 110.3, 110.1, 108.2, 56.1; **HRMS (ESI)** calcd for $C_{26}H_{17}FON^+$ (M - OTf)$^+$ 378.1289, found 378.1302.

11-chloro-6-methoxy-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2v**):



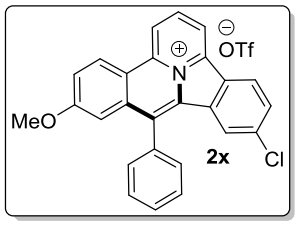
Off white solid, 44 mg, 65% yield; mp = 303-305 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.84 (d, *J* = 8.4 Hz, 1 H), 9.57 (d, *J* = 9.2 Hz, 1 H), 9.37 (d, *J* = 7.6 Hz, 1 H), 9.16 - 9.01 (m, 2 H), 8.00 (dd, *J* = 2.3, 9.2 Hz, 1 H), 7.92 - 7.80 (m, 4 H), 7.69 (d, *J* = 3.4 Hz, 2 H), 7.20 (d, *J* = 2.3 Hz, 1 H), 6.84 (d, *J* = 8.8 Hz, 1 H), 3.91 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.2, 140.0, 139.0, 138.2, 135.8, 134.9, 134.7, 132.1, 131.9, 130.6, 130.1, 129.3, 128.9, 128.5, 124.6, 123.4, 121.6, 121.4, 118.8, 108.3, 56.1; **HRMS (ESI)** calcd for $C_{26}H_{17}ClON^+$ $(M - OTf)^+$ 394.1254, found 394.1054.

6-methoxy-10-methyl-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2w**):



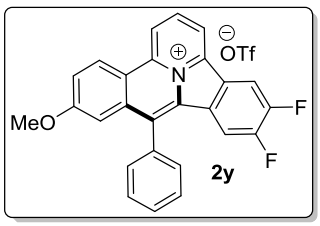
Off white solid, 41 mg, 60% yield; mp = 300-302 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d$_6$) δ** = 9.74 (d, *J* = 8.5 Hz, 1 H), 9.54 (d, *J* = 9.2 Hz, 1 H), 9.25 (d, *J* = 7.3 Hz, 1 H), 9.03 (t, *J* = 7.9 Hz, 1 H), 8.73 (d, *J* = 7.9 Hz, 1 H), 7.96 (dd, *J* = 2.4, 9.2 Hz, 1 H), 7.88 (d, *J* = 3.7 Hz, 3 H), 7.78 (d, *J* = 7.9 Hz, 1 H), 7.69 (d, *J* = 3.7 Hz, 2 H), 7.26 - 7.15 (m, 1 H), 6.59 (s, 1 H), 3.90 (s, 3 H), 2.33 (s, 3 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 163.0, 142.3, 141.2, 138.9, 138.2, 134.9, 134.3, 132.4, 132.2, 132.2, 130.7, 130.4, 130.0, 129.3, 128.4, 128.0, 123.3, 123.2, 121.3, 120.2, 118.7, 117.6, 108.2, 56.1, 21.9; **HRMS (ESI)** calcd for $C_{27}H_{20}ON^+$ $(M - OTf)^+$ 374.1540, found 374.1539.

10-chloro-6-methoxy-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2x**):



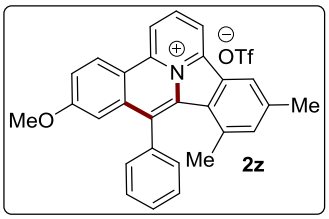
Off white solid, 42 mg, 64% yield; mp = 308-310 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.82 (d, J = 8.5 Hz, 1 H), 9.58 (d, J = 9.4 Hz, 1 H), 9.36 (d, J = 7.7 Hz, 1 H), 9.09 (t, J = 8.1 Hz, 1 H), 8.92 (d, J = 8.5 Hz, 1 H), 8.06 (dd, J = 1.9, 8.3 Hz, 1 H), 8.01 (dd, J = 2.6, 9.2 Hz, 1 H), 7.94 - 7.87 (m, 3 H), 7.74 - 7.67 (m, 2 H), 7.23 (d, J = 2.5 Hz, 1 H), 6.68 (d, J = 1.7 Hz, 1 H), 3.92 (s, 3 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 163.2, 140.3, 139.1, 138.2, 136.4, 135.2, 134.8, 131.8, 131.5, 131.1, 130.7, 130.2, 129.3, 129.0, 128.6, 125.3, 122.7, 121.8, 121.0, 119.0, 118.5, 108.4, 56.2; **HRMS (ESI)** calcd for $C_{26}H_{17}ClON^+$ (M - OTf)$^+$ 394.0988, found 394.0993.

10,11-difluoro-6-methoxy-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2y**):



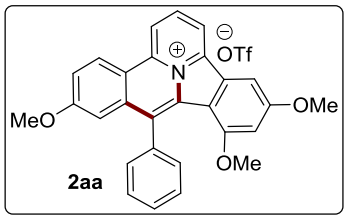
White solid, 47 mg, 68% yield; mp = 238-240 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.85 (d, *J* = 8.4 Hz, 1 H), 9.59 (d, *J* = 9.2 Hz, 1 H), 9.31 (d, *J* = 7.6 Hz, 1 H), 9.12 (q, *J* = 7.5 Hz, 2 H), 8.02 (d, *J* = 8.8 Hz, 1 H), 7.91 (s, 3 H), 7.77 - 7.65 (m, 2 H), 7.24 (s, 1 H), 6.62 - 6.42 (m, 1 H), 3.92 (s, 3 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 163.5, 153.1 (d, *J* = 14 Hz), 153.0 (d, *J* = 14.6 Hz), 150.6 (d, *J* = 14.6 Hz), 150.4 (d, *J* = 13.8 Hz), 140.0, 139.2, 138.5, 135.3, 135.0, 131.7, 131.5, 130.5, 129.8 (d, *J* = 228.8 Hz), 129.5, 127.5 (d, *J* = 10 Hz), 127.4 (d, *J* = 7 Hz), 122.0, 120.0 (d, *J* = 239.6 Hz), 119.1, 112.9 (d, *J* = 21.5 Hz), 111.8 (d, *J* = 21.5 Hz), 108.6, 56.4; **HRMS (ESI)** calcd for $C_{26}H_{16}F_2ON^+$ (M - OTf)$^+$ 396.1194, found 396.1190.

6-methoxy-9,11-dimethyl-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2z**):



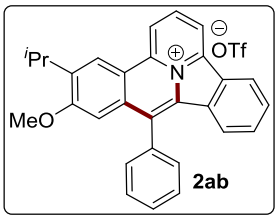
Off white solid, 42 mg, 62% yield; mp = 268-270 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.67 (d, *J* = 8.0 Hz, 1 H), 9.46 (d, *J* = 8.8 Hz, 1 H), 9.20 (d, *J* = 7.2 Hz, 1 H), 8.98 (t, *J* = 7.4 Hz, 1 H), 8.53 (s, 1 H), 7.90 (d, *J* = 8.4 Hz, 1 H), 7.83 - 7.66 (m, 5 H), 7.43 (s, 1 H), 7.23 (s, 1 H), 3.87 (s, 3 H), 2.54 (s, 3 H), 1.56 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 162.9, 141.5, 141.3, 138.7, 138.3, 137.0, 135.4, 135.2, 135.2, 134.6, 134.2, 131.9, 131.9, 130.1, 128.8, 128.1, 127.1, 120.7, 120.4, 118.0, 117.0, 109.0, 55.9, 21.0, 20.9; **HRMS (ESI)** calcd for $C_{28}H_{22}ON^+$ (M - OTf)$^+$ 388.1699, found 388.1696.

6,9,11-trimethoxy-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2aa**):



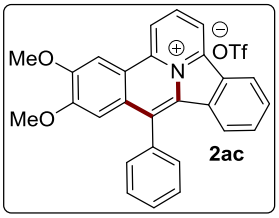
Yellow solid, 50 mg, 74% yield; mp = 263-265 °C; R_f = 0.40 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.67 (d, *J* = 8.4 Hz, 1 H), 9.40 (d, *J* = 9.2 Hz, 1 H), 9.24 (d, *J* = 7.6 Hz, 1 H), 8.97 (t, *J* = 8.0 Hz, 1 H), 7.99 (s, 1 H), 7.83 (d, *J* = 8.4 Hz, 1 H), 7.74 - 7.59 (m, 3 H), 7.50 (d, *J* = 6.9 Hz, 2 H), 7.06 (br. s., 1 H), 6.76 (s, 1 H), 3.98 (s, 3 H), 3.83 (s, 3 H), 3.21 (s, 3 H; **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.7, 162.7, 155.9, 141.2, 138.4, 138.2, 136.0, 135.8, 133.4, 133.1, 132.9, 130.2, 128.7, 128.1, 127.6, 120.8, 120.1, 117.9, 117.5, 111.7, 108.9, 102.4, 98.6, 56.4, 55.8; **HRMS (ESI)** calcd for $C_{28}H_{22}O_3N^+$ (M - OTf)$^+$ 420.1591, found 420.1594.

5-isopropyl-6-methoxy-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2ab**):



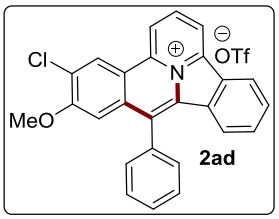
white solid, 51 mg, 74% yield; mp = 270-272 °C; $\boldsymbol{R_f}$ = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.97 (d, *J* = 8.4 Hz, 1 H), 9.41 - 9.30 (m, 2 H), 9.06 (t, *J* = 8.0 Hz, 1 H), 8.88 (d, *J* = 7.6 Hz, 1 H), 7.95 (t, *J* = 7.4 Hz, 1 H), 7.88 (br. s., 3 H), 7.76 (t, *J* = 7.6 Hz, 1 H), 7.71 (br. s., 2 H), 7.21 (s, 1 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 3.85 (s, 3 H), 3.67 - 3.53 (m, 1 H), 1.45 (d, *J* = 6.5 Hz, 6 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 160.8, 143.6, 140.8, 138.2, 137.8, 134.4, 133.3, 132.3, 131.9, 131.8, 130.8, 130.4, 130.4, 130.2, 130.0, 129.3, 123.1, 119.0, 105.7, 56.0, 27.4, 22.3; **HRMS (ESI)** calcd for $C_{29}H_{24}ON^+$ $(M - OTf)^+$ 402.1850, found 402.1852.

5,6-dimethoxy-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2ac**):



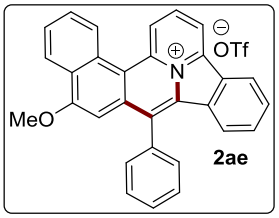
Yellow solid, 54 mg, 78% yield; mp = 295-297 °C; $\boldsymbol{R_f}$ = 0.40 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.94 (d, *J* = 8.4 Hz, 1 H), 9.38 (d, *J* = 7.2 Hz, 1 H), 9.05 (t, *J* = 7.4 Hz, 1 H), 8.89 (br. s., 1 H), 8.87 (d, *J* = 8.0 Hz, 1 H), 7.98 - 7.83 (m, 4 H), 7.79 - 7.65 (m, 3 H), 7.19 (br. s., 1 H), 6.87 (d, *J* = 7.6 Hz, 1 H), 4.23 (br. s., 3 H), 3.82 (br. s., 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 154.2, 152.9, 140.5, 137.2, 136.6, 134.4, 132.4, 131.8, 130.6, 130.4, 130.0, 129.7, 129.4, 128.9, 123.3, 122.7, 121.3, 120.6, 118.3, 106.3, 105.9, 57.1, 56.0; **HRMS (ESI)** calcd for $C_{27}H_{20}O_2N^+$ $(M - OTf)^+$ 390.1486, found 390.1489.

5-chloro-6-methoxy-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2ad**):



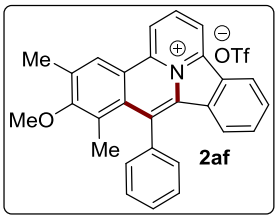
Off white solid, 40 mg, 58% yield; mp = 303-305 °C; $\boldsymbol{R_f}$ = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz**, **DMSO-d$_6$) δ** = 9.87 (d, *J* = 8.7 Hz, 1 H), 9.83 (s, 1 H), 9.40 (d, *J* = 7.6 Hz, 1 H), 9.11 (t, *J* = 8.2 Hz, 1 H), 8.89 (d, *J* = 7.8 Hz, 1 H), 7.97 (t, *J* = 7.5 Hz, 1 H), 7.89 (br. s., 3 H), 7.77 (t, *J* = 7.7 Hz, 1 H), 7.72 (d, *J* = 3.5 Hz, 2 H), 7.31 (s, 1 H), 6.88 (d, *J* = 8.1 Hz, 1 H), 3.92 (s, 3 H); **^{13}C NMR (125 MHz**, **DMSO-d$_6$) δ** = 158.0, 141.2, 139.1, 137.3, 134.1, 133.6, 132.7, 132.1, 131.8, 131.2, 130.6, 130.3, 130.2, 130.1, 129.4, 127.8, 127.6, 123.5, 123.3, 121.2, 119.2, 118.7, 107.5, 56.8; **HRMS (ESI)** calcd for $C_{26}H_{17}ClON^+$ (M - OTf)$^+$388.1696, found 388.1695.

5-methoxy-7-phenylbenzo[h]benzo[1,2]indolizino[5,4,3-ab]isoquinolin-15-ium trifluoromethanesulfonate (**2ae**):



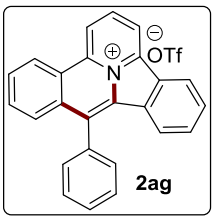
Yellowish solid, 53 mg, 78% yield; mp = 288-290 °C; $\boldsymbol{R_f}$ = 0.40 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz**, **DMSO-d$_6$) δ** = 9.82 (d, *J* = 8.8 Hz, 1 H), 9.43 (d, *J* = 7.6 Hz, 1 H), 9.23 (d, *J* = 8.4 Hz, 1 H), 9.05 (t, *J* = 8.0 Hz, 1 H), 8.93 (d, *J* = 7.6 Hz, 1 H), 8.62 (d, *J* = 8.0 Hz, 1 H), 8.20 - 8.14 (m, 1 H), 8.11 - 8.05 (m, 1 H), 8.00 (t, *J* = 7.6 Hz, 1 H), 7.91 (br. s., 3 H), 7.83 - 7.73 (m, 3 H), 7.07 (s, 1 H), 6.91 (d, *J* = 8.0 Hz, 1 H), 3.99 (s, 3 H); **^{13}C NMR (100 MHz**, **DMSO-d$_6$) δ** = 158.9, 140.6, 137.8, 136.5, 135.9, 133.9, 133.5, 132.6, 131.9, 131.2, 130.5, 130.4, 130.1, 129.9, 129.6, 129.5, 129.4, 129.2, 127.1, 125.4, 123.4, 123.3, 123.0, 119.4, 118.0, 117.7, 99.9, 56.3; **HRMS (ESI)** calcd for $C_{30}H_{20}ON^+$ (M - OTf)$^+$ 410.1535, found 410.1539.

6-methoxy-5,7-dimethyl-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2af**):



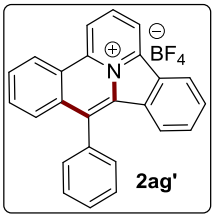
Off white solid, 43 mg, 63% yield; mp = 245-247 °C; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.84 (d, *J* = 8.5 Hz, 1 H), 9.49 (s, 1 H), 9.37 (d, *J* = 7.6 Hz, 1 H), 9.08 (t, *J* = 8.1 Hz, 1 H), 8.84 (d, *J* = 7.6 Hz, 1 H), 7.93 - 7.78 (m, 4 H), 7.71 (d, *J* = 7.0 Hz, 2 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 6.32 (d, *J* = 8.1 Hz, 1 H), 3.80 (s, 3 H), 2.70 (s, 3 H), 2.11 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 161.8, 140.7, 138.6, 138.0, 137.2, 136.5, 136.4, 132.5, 131.8, 131.0, 130.7, 130.6, 130.2, 130.1, 129.9, 129.6, 129.3, 126.5, 123.5, 123.3, 122.3, 121.1, 118.5, 60.5, 17.2, 15.1; **HRMS (ESI)** calcd for $C_{28}H_{22}ON^+$ (M - OTf)$^+$ 388.1696, found 388.1695.

8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2ag**):



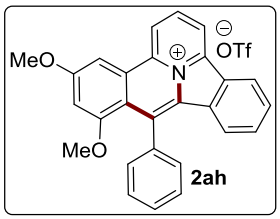
White solid, 43 mg, 60% yield; mp = 288-290 °C; R_f = 0.60 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.94 (d, *J* = 8.5 Hz, 1 H), 9.64 (d, *J* = 8.3 Hz, 1 H), 9.48 (d, *J* = 7.7 Hz, 1 H), 9.17 (t, *J* = 8.3 Hz, 1 H), 8.91 (d, *J* = 8.0 Hz, 1 H), 8.37 - 8.30 (m, 1 H), 8.30 - 8.24 (m, 1 H), 8.02 - 7.94 (m, 2 H), 7.92 - 7.84 (m, 3 H), 7.81 - 7.74 (m, 1 H), 7.73 - 7.63 (m, 2 H), 6.91 (d, *J* = 8.0 Hz, 1 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 141.6, 139.4, 138.5, 135.5, 133.9, 132.3, 132.2, 131.6, 131.0, 130.4, 130.4, 130.2, 130.0, 129.4, 127.5, 126.1, 124.6, 123.6, 123.2, 121.3, 119.5; **HRMS (ESI)** calcd for $C_{25}H_{16}N^+$ (M - OTf)$^+$ 330.1312, found 330.1315.

8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium tetrafluoroborate (**2ag'**):



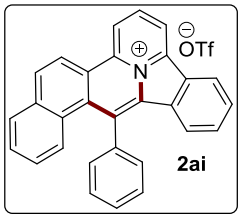
White solid, 35 mg, 65% yield; mp = 288-290 °C; $\boldsymbol{R_f}$ = 0.60 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = = 9.94 (d, *J* = 8.5 Hz, 1 H), 9.64 (d, *J* = 8.2 Hz, 1 H), 9.48 (d, *J* = 7.6 Hz, 1 H), 9.18 (t, *J* = 8.2 Hz, 1 H), 8.91 (d, *J* = 7.9 Hz, 1 H), 8.38 - 8.31 (m, 1 H), 8.31 - 8.22 (m, 1 H), 8.02 - 7.93 (m, 2 H), 7.92 - 7.84 (m, 3 H), 7.78 (t, *J* = 7.6 Hz, 1 H), 7.74 - 7.62 (m, 2 H), 6.91 (d, *J* = 8.1 Hz, 1 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 141.6, 139.4, 138.5, 135.5, 133.9, 132.3, 132.2, 131.6, 131.0, 130.4, 130.4, 130.2, 130.0, 129.4, 127.5, 126.1, 124.6, 123.6, 123.2, 121.3, 119.5; **HRMS (ESI)** calcd for $C_{25}H_{16}N^+$ $(M - BF_4)^+$ 330.1311, found 330.1315.

5,7-dimethoxy-8-phenylbenzo[1,2]indolizino[5,4,3-ab]isoquinolin-13-ium trifluoromethanesulfonate (**2ah**):



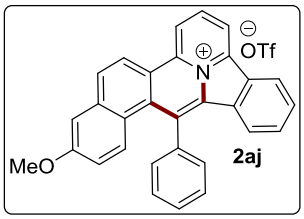
Yellow solid, 58 mg, 84% yield; mp = 302-304 °C; $\boldsymbol{R_f}$ = 0.40 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.90 (d, *J* = 8.4 Hz, 1 H), 9.39 (d, *J* = 7.6 Hz, 1 H), 9.01 (t, *J* = 8.0 Hz, 1 H), 8.80 (d, *J* = 8.0 Hz, 1 H), 8.48 (d, *J* = 1.9 Hz, 1 H), 7.83 (t, *J* = 7.6 Hz, 1 H), 7.75 - 7.66 (m, 3 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.56 - 7.44 (m, 2 H), 7.26 (d, *J* = 1.9 Hz, 1 H), 6.35 (d, *J* = 8.0 Hz, 1 H), 4.16 (s, 3 H), 3.54 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 163.0, 159.5, 140.7, 137.7, 137.0, 136.8, 135.5, 131.7, 130.9, 130.0, 129.9, 129.1, 128.6, 128.4, 127.5, 123.1, 122.9, 121.8, 119.5, 117.5, 105.0, 99.4, 56.8, 56.5; **HRMS (ESI)** calcd for $C_{27}H_{20}O_2N^+$ $(M - OTf)^+$ 390.1488, found 390.1489.

10-phenylbenzo[f]benzo[1,2]indolizino[5,4,3-ab]isoquinolin-15-ium trifluoromethanesulfonate (**2ai**):



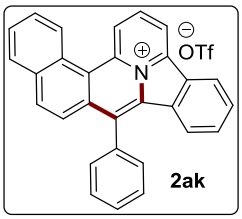
Yellow solid, 45 mg, 65% yield; mp = 306-308 °C; $\boldsymbol{R_f}$ = 0.60 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 10.08 (d, *J* = 8.4 Hz, 1 H), 9.60 - 9.50 (m, 2 H), 9.21 - 9.12 (m, 1 H), 8.94 (d, *J* = 7.6 Hz, 1 H), 8.76 (d, *J* = 8.8 Hz, 1 H), 8.39 (d, *J* = 7.6 Hz, 1 H), 8.01 - 7.93 (m, 5 H), 7.86 (t, *J* = 7.4 Hz, 1 H), 7.78 (d, *J* = 6.9 Hz, 2 H), 7.73 (t, *J* = 7.8 Hz, 1 H), 7.48 (t, *J* = 7.8 Hz, 1 H), 6.50 (d, *J* = 8.4 Hz, 1 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 140.1, 138.1, 137.1, 136.8, 136.0, 135.2, 133.8, 131.9, 131.0, 131.0, 130.6, 130.4, 130.0, 130.0, 129.6, 129.1, 128.7, 127.8, 127.3, 125.7, 123.8, 123.3, 122.5, 121.6, 119.7; **HRMS (ESI)** calcd for $C_{29}H_{18}N^+$ $(M - OTf)^+$ 380.1429, found 380.1434.

7-methoxy-10-phenylbenzo[f]benzo[1,2]indolizino[5,4,3-ab]isoquinolin-15-ium trifluoromethanesulfonate (**2aj**):



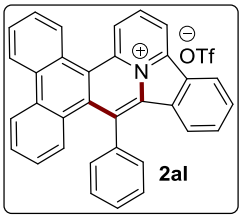
Yellow solid, 52 mg, 76% yield; mp = 294-296 °C; $\boldsymbol{R_f}$ = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.97 (d, *J* = 8.0 Hz, 1 H), 9.59 - 9.36 (m, 2 H), 9.13 (br. s., 1 H), 8.92 (d, *J* = 6.9 Hz, 1 H), 8.62 (d, *J* = 8.0 Hz, 1 H), 7.97 (br. s., 4 H), 7.81 (br. s., 2 H), 7.79 - 7.69 (m, 3 H), 7.09 (d, *J* = 8.4 Hz, 1 H), 6.48 (d, *J* = 7.2 Hz, 1 H), 3.94 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 159.5, 140.0, 137.9, 137.7, 137.1, 136.8, 135.4, 133.7, 133.1, 131.8, 131.1, 130.9, 130.9, 130.7, 130.0, 129.0, 128.7, 124.0, 123.8, 123.4, 123.3, 122.1, 119.1, 118.3, 109.8, 55.7; **HRMS (ESI)** calcd for $C_{30}H_{20}ON^+$ $(M - OTf)^+$ 410.1537, found 410.1539.

7-phenylbenzo[h]benzo[1,2]indolizino[5,4,3-ab]isoquinolin-15-ium trifluoromethanesulfonate (**2ak**):



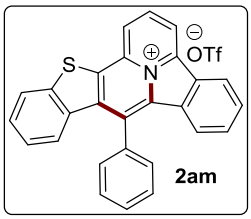
Off white solid, 46 mg, 66% yield; mp = 278-280 °C; $\boldsymbol{R_f}$ = 0.60 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d$_6$) δ =** 9.97 (d, *J* = 8.5 Hz, 1 H), 9.71 (d, *J* = 8.5 Hz, 1 H), 9.47 (d, *J* = 7.3 Hz, 1 H), 9.17 (t, *J* = 8.2 Hz, 1 H), 8.91 (d, *J* = 7.9 Hz, 1 H), 8.65 (d, *J* = 8.5 Hz, 1 H), 8.07 (s, 1 H), 7.98 (t, *J* = 7.3 Hz, 1 H), 7.90 (br. s., 3 H), 7.76 (d, *J* = 6.7 Hz, 3 H), 7.62 - 7.53 (m, 2 H), 7.53 - 7.45 (m, 1 H), 6.92 (d, *J* = 7.9 Hz, 1 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 145.0, 141.6, 139.5, 138.3, 138.0, 135.4, 132.9, 132.6, 132.2, 132.0, 131.1, 130.6, 130.4, 130.3, 130.3, 130.1, 129.5, 129.5, 129.3, 127.5, 127.1, 124.4, 123.7, 123.6, 123.3, 121.4, 119.4; **HRMS (ESI)** calcd for $C_{29}H_{18}N^+$ (M - OTf)$^+$ 380.1440, found 380.1445.

9-phenyldibenzo[f,h]benzo[1,2]indolizino[5,4,3-ab]isoquinolin-17-ium trifluoromethanesulfonate (**2al**):



Yellow solid, 47 mg, 70% yield; mp = 307-309 °C; $\boldsymbol{R_f}$ = 0.60 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.63 (d, *J* = 8.8 Hz, 1 H), 9.56 (d, *J* = 7.6 Hz, 1 H), 9.10 - 9.05 (m, 2 H), 9.03 (d, *J* = 8.0 Hz, 1 H), 8.99 (d, *J* = 8.0 Hz, 1 H), 8.71 (d, *J* = 8.0 Hz, 1 H), 8.09 - 8.05 (m, 1 H), 8.02 (t, *J* = 7.8 Hz, 2 H), 7.94 (d, *J* = 8.8 Hz, 1 H), 7.93 - 7.83 (m, 4 H), 7.83 - 7.75 (m, 3 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 139.3, 137.1, 136.5, 135.1, 134.1, 133.9, 132.4, 131.9, 131.6, 131.1, 130.7, 130.6, 130.5, 130.5, 130.4, 129.8, 128.9, 128.4, 127.3, 127.2, 127.0, 126.2, 124.6, 124.4, 123.8, 123.4, 119.5; **HRMS (ESI)** calcd for $C_{33}H_{20}N^+$ (M - OTf)$^+$ 430.1588, found 430.1590.

8-phenylbenzo[4,5]thieno[2,3-a]isoindolo[1,2,3-de]quinolizin-14-ium trifluoromethanesulfonate (**2am**):

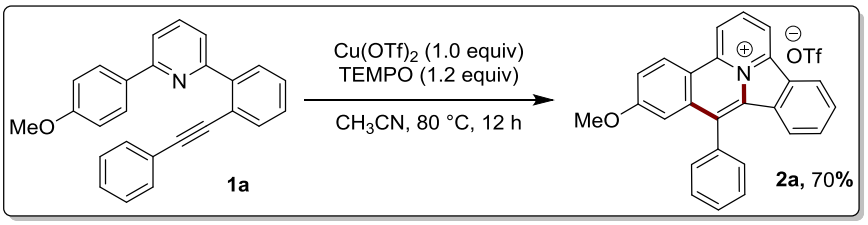


Yellowish solid, 45 mg, 65% yield; mp = 268-270 °C; R_f = 0.40 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.55 (d, *J* = 7.6 Hz, 1 H), 9.51 (d, *J* = 8.4 Hz, 1 H), 9.08 (t, *J* = 8.0 Hz, 1 H), 8.95 (d, *J* = 7.8 Hz, 1 H), 8.56 (d, *J* = 8.1 Hz, 1 H), 8.03 - 7.93 (m, 4 H), 7.85 - 7.75 (m, 4 H), 7.49 (t, *J* = 7.8 Hz, 1 H), 7.08 (d, *J* = 8.4 Hz, 1 H), 6.90 (d, *J* = 8.1 Hz, 1 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 141.3, 140.1, 137.7, 137.6, 135.8, 134.0, 133.7, 133.4, 132.8, 132.7, 132.1, 131.0, 130.7, 130.5, 130.0, 129.8, 128.4, 126.4, 125.4, 124.5, 123.6, 123.1, 122.9, 120.2; **HRMS (ESI)** calcd for $C_{27}H_{16}SN^+$ (M - OTf)$^+$ 386.1010, found 386.1014.

Gram Scale Synthesis of 2a: In a round bottom flask, equipped with magnetic stir bar, were added 2-(4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1a**) (1g, 2.7 mmol, 1.0 equiv), $Cu(OTf)_2$ (997 mg, 2.7 mmol, 1.0 equiv) and CH_3CN (40 mL) under inert atmosphere. The reaction mixture was heated at 80 °C for 12 h. The mixture was diluted with CH_2Cl_2 (10 mL) and the combined mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica (CH_2Cl_2/MeOH; 95:05) to afford the product **2a** (1.05 g) in 76% yield.

3. Control experiments

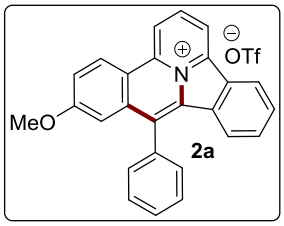
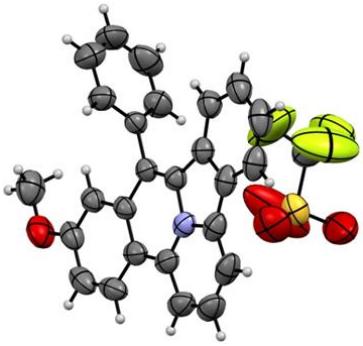
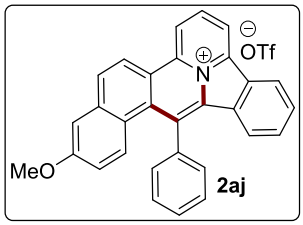
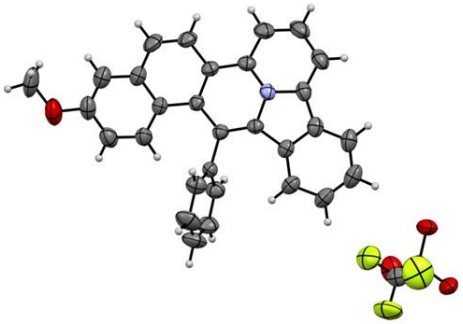
3.1 Reaction of 1a with TEMPO under standard reaction conditions



To a stirred solution of **1a** (20 mg, 0.055 mmol) in CH_3CN (1 ml) was added $Cu(OTf)_2$, (20 mg, 0.055 mmol), TEMPO (11 mg, 0.066 mmol) at rt. The resulting mixture was stirred at 80 °C for 12 h. The mixture was diluted with CH_2Cl_2 and the reaction mixture

was concentrated in vacuo. The resulting residue was purified by column chromatography on silica (CH_2Cl_2/MeOH; 95:05) to afford the product **2a** (18 mg) in 70% yield.

4. ORTEP diagrams

Sr. No	Compound Structure	ORTEP Diagram
1	 **CCDC No 1824190**	
2	 **CCDC No 1824191**	

5. Photophysical data of the representative ionic PAHs

Table S1. Spectral properties of selected ionic PAHs in CH_2Cl_2 at RT (10^{-5}M)

Comp	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	ΔStoke's (nm)[c]	ϕ_f[d]	τ_f (ns)[e]
2a	388	444	56	0.86	6.52
2p	386	619	233	0.06	10.48
2aa	417	482	65	0.38	2.38
2ag	385	434	49	0.74	0.02
2ah	454	507	53	0.88	4.89
2ai	428	470	42	0.54	2.58
2aj	346	495	149	0.73	4.37
2al	415	490	75	0.57	3.65

[a]The maximum absorption bands more than 300 nm; Excited at the longest maximum absorption band in CH_2Cl_2; [b]Excited wavelength; [c]Stokes shift = λ_{em} - λ_{abs}; [d]Quinine sulfate and fluorescein was used as the standard for calculation of quantum yield; [e]Fluorescent lifetime.

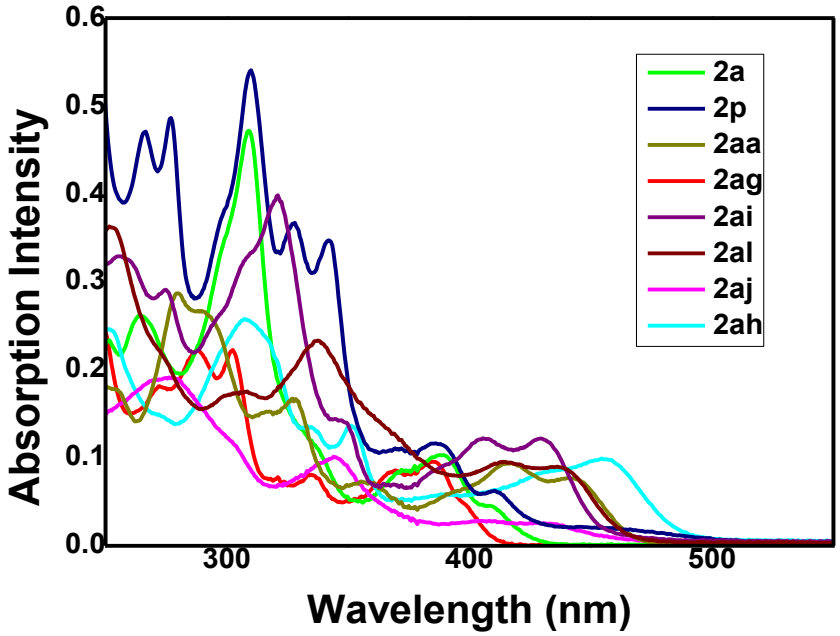


Figure S1. Absorption spectra of selected ionic PAHs in CH_2Cl_2 at RT

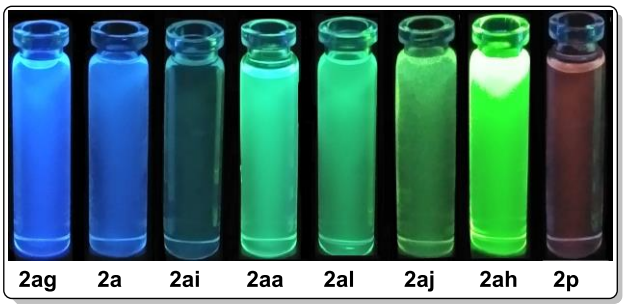


Figure S2. Photographs of selected ionic PAHs in CH_2Cl_2 at RT under UV light (λ_{exc} = 365nm)

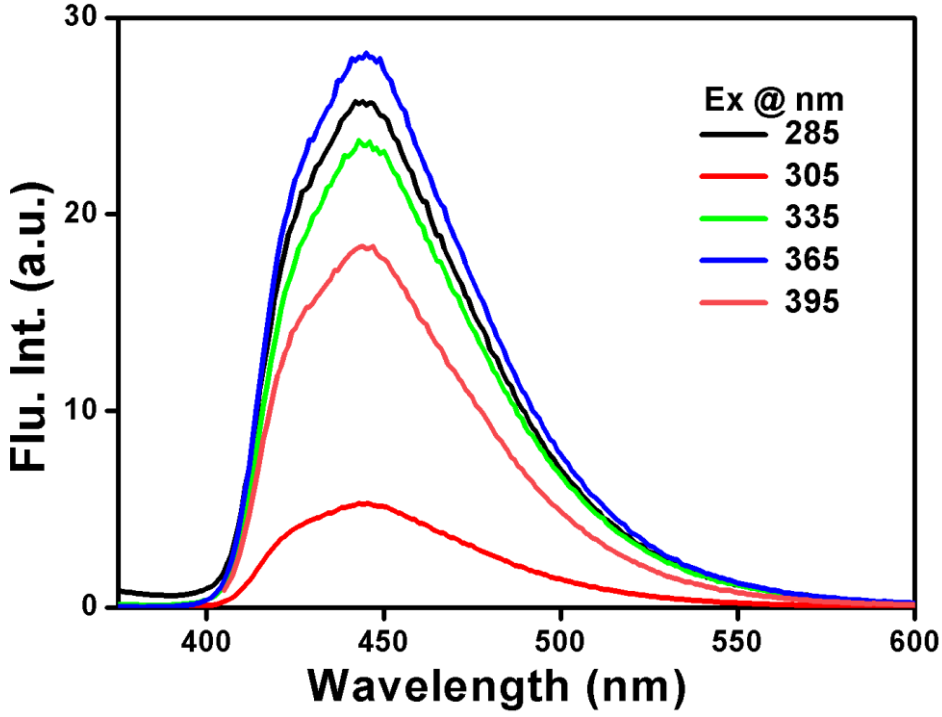


Figure S3: Emission spectra of **2a** in CH_2Cl_2 with different excitation wavelengths

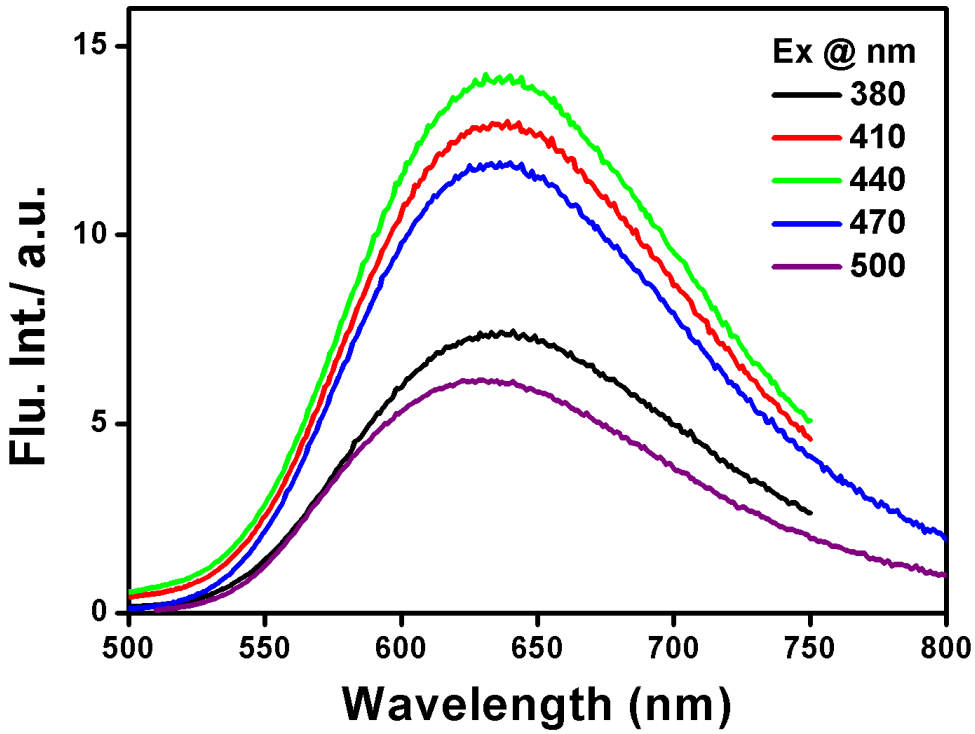


Figure S4: Emission spectra of **2p** in CH_2Cl_2 with different excitation wavelengths

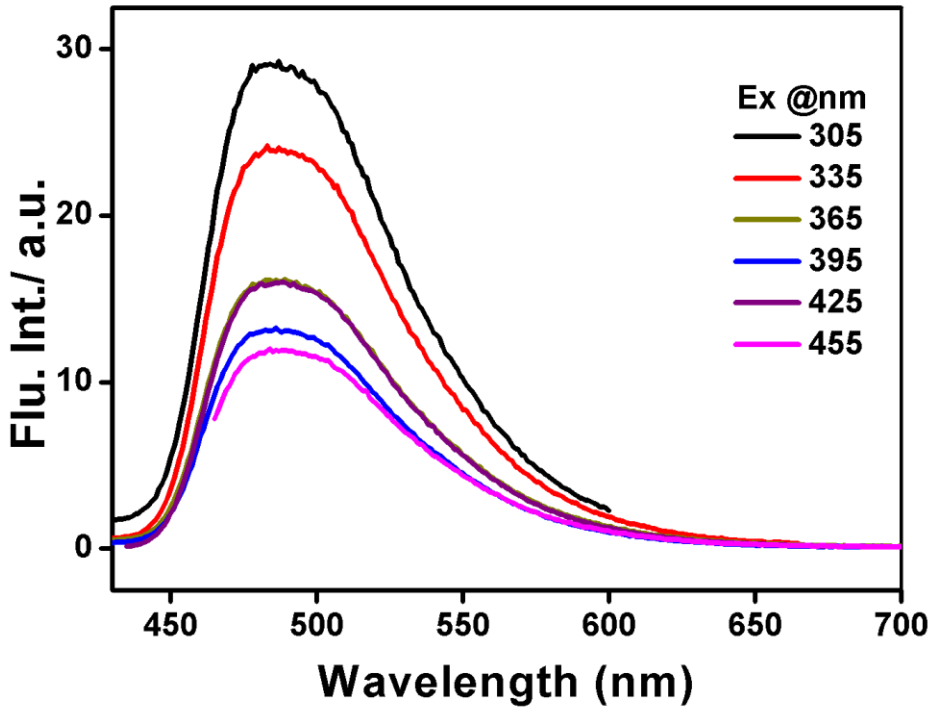


Figure S5: Emission spectra of **2aa** in CH_2Cl_2 with different excitation wavelengths

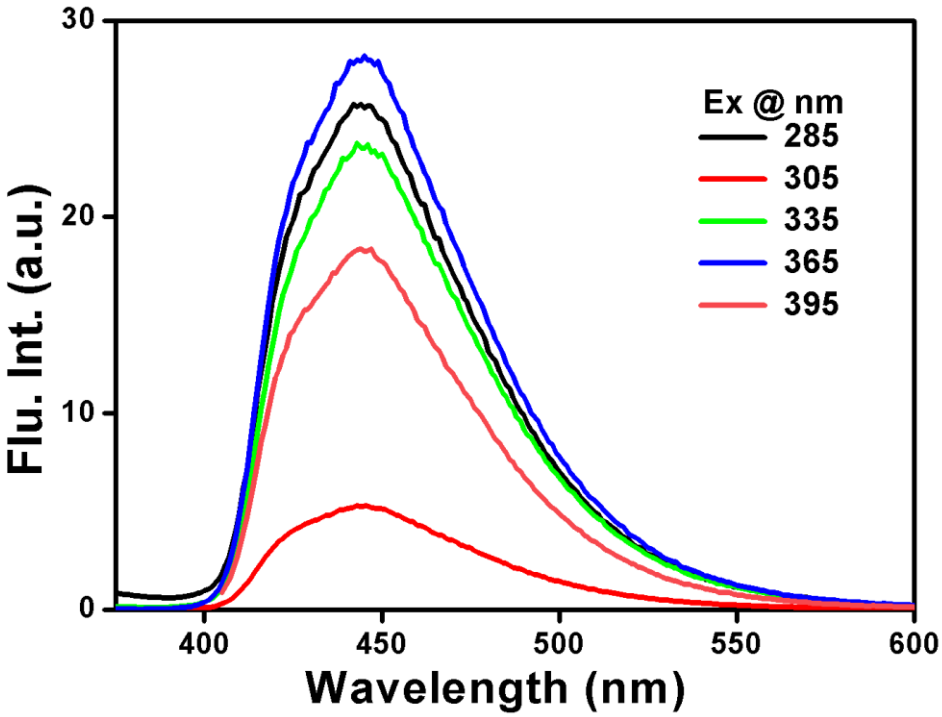


Figure S6: Emission spectra of **2ae** in CH_2Cl_2 with different excitation wavelengths

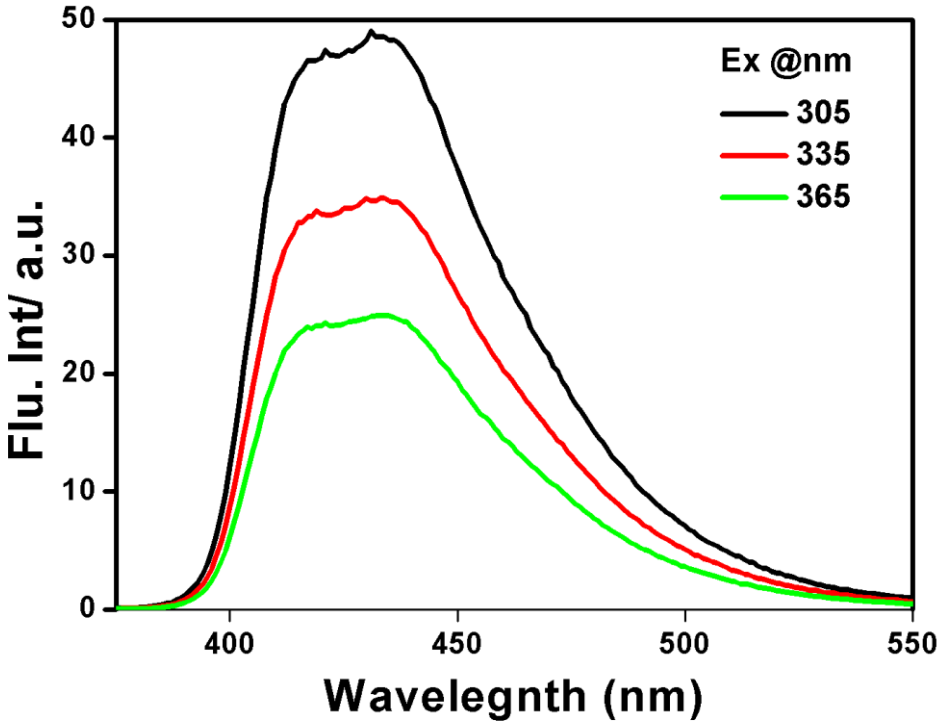


Figure S7: Emission spectra of **2ag** in CH_2Cl_2 with different excitation wavelengths

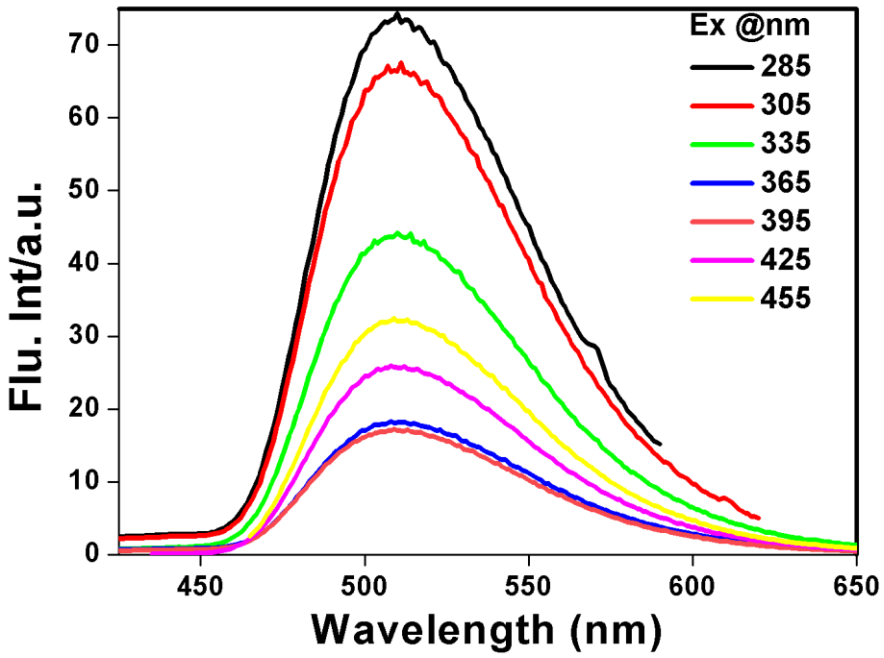


Figure S8: Emission spectra of **2ah** in CH_2Cl_2 with different excitation wavelengths

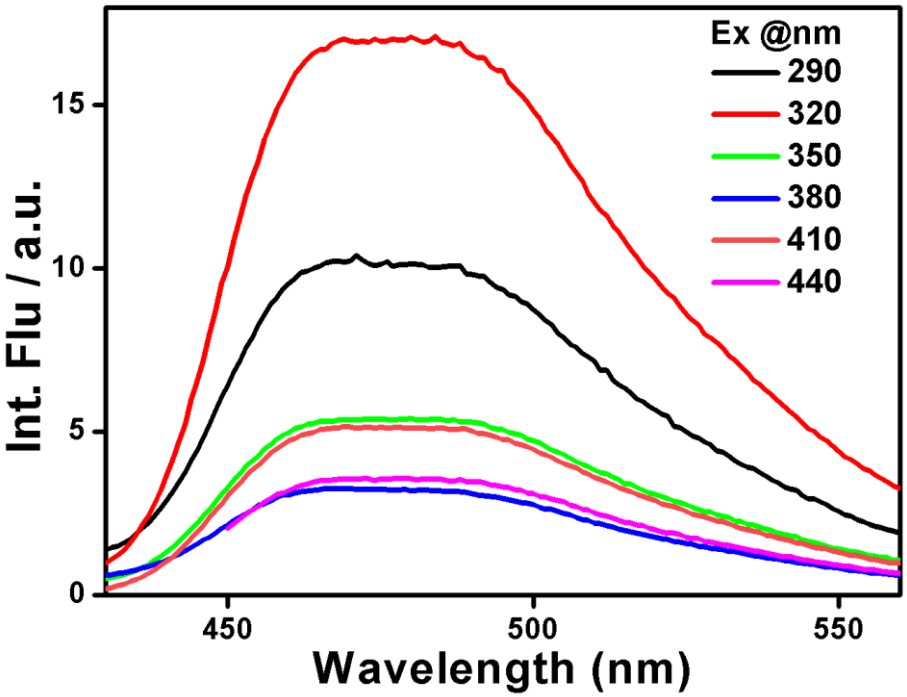


Figure S9: Emission spectra of **2ai** in CH_2Cl_2 with different excitation wavelengths

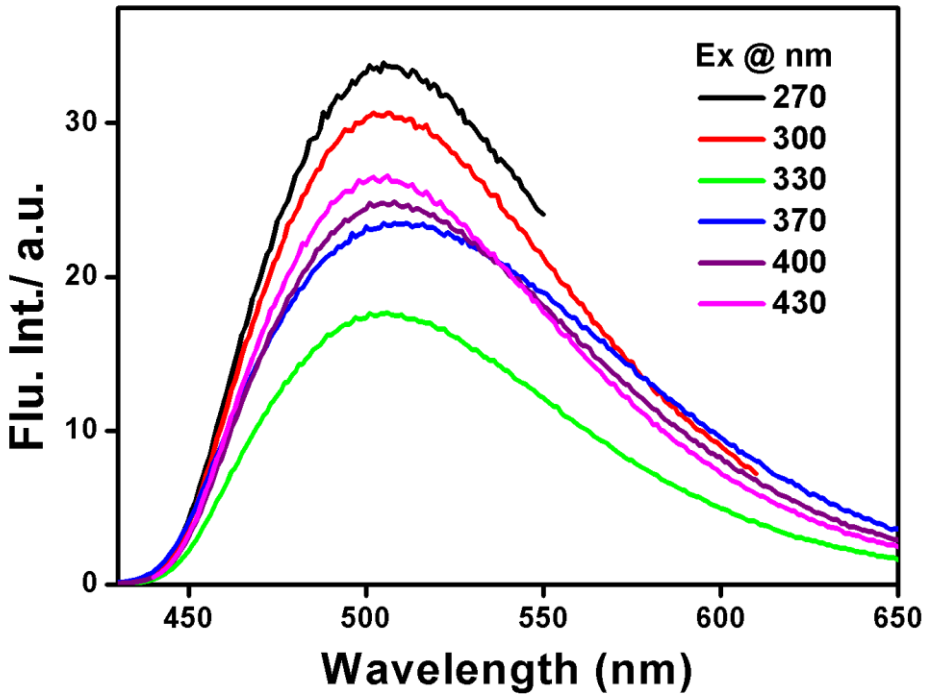


Figure S10: Emission spectra of **2aj** in CH_2Cl_2 with different excitation wavelengths

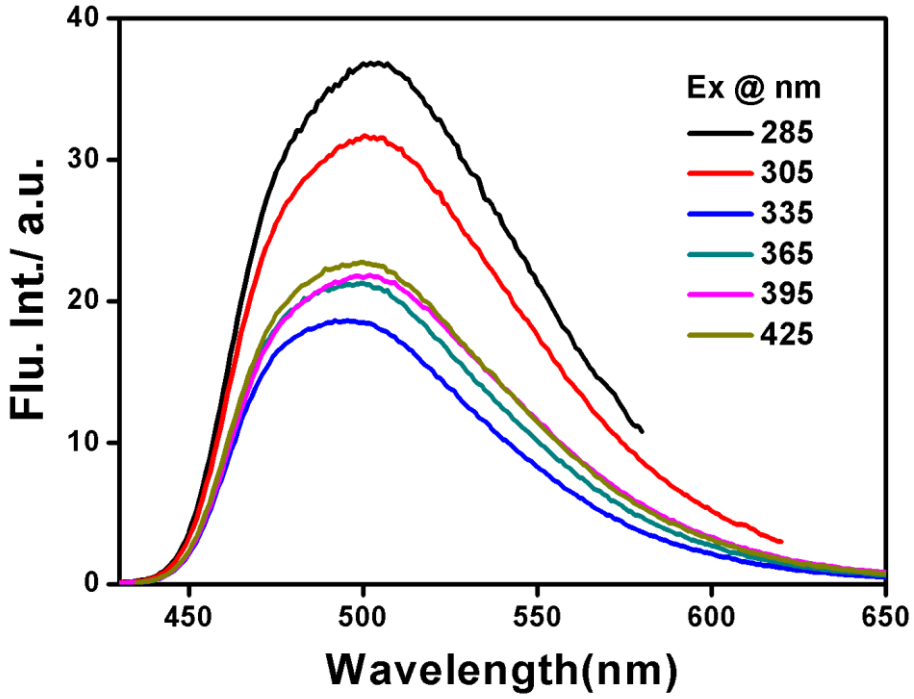


Figure S11: Emission spectra of **2al** in CH_2Cl_2 with different excitation wavelengths

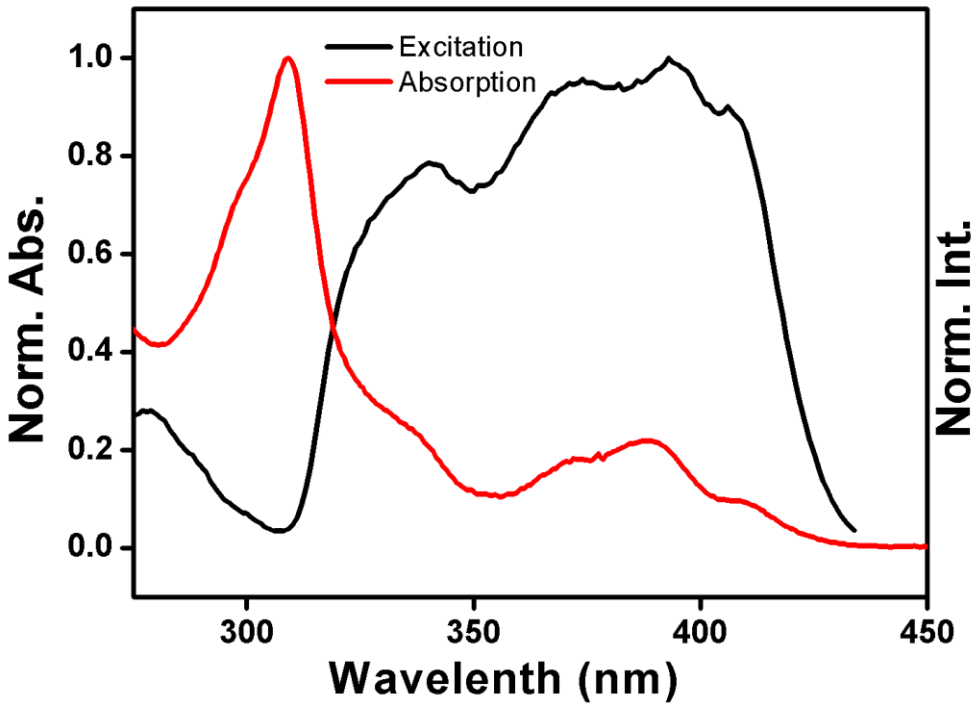


Figure S12: Overlapping of absorption and excitation spectra of **2a**

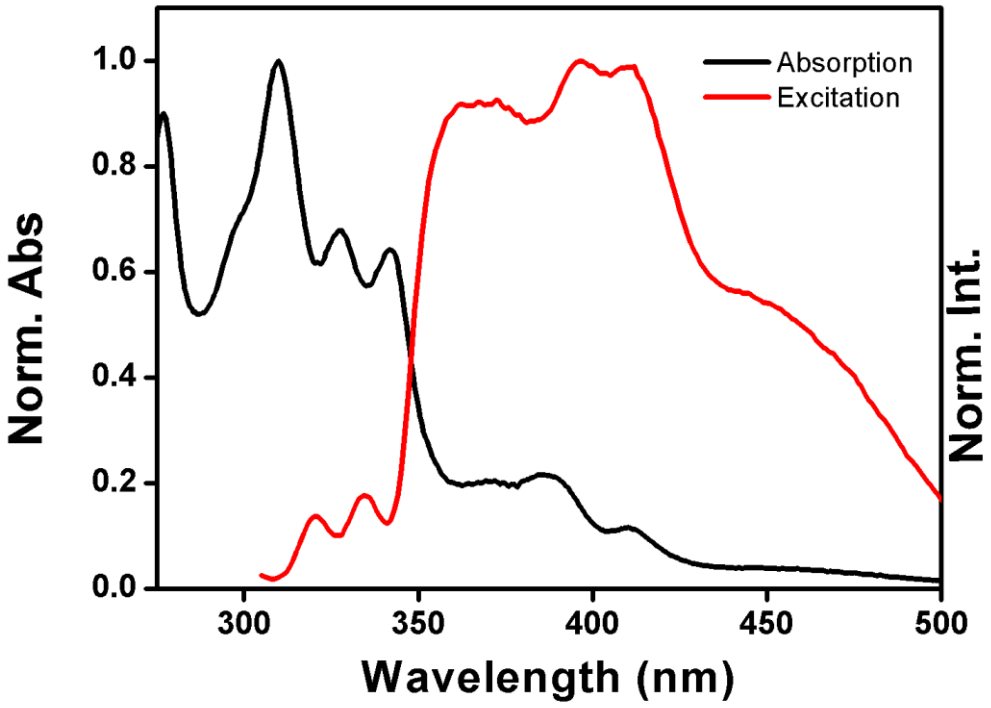


Figure S13: Overlapping of absorption and excitation spectra of **2p**

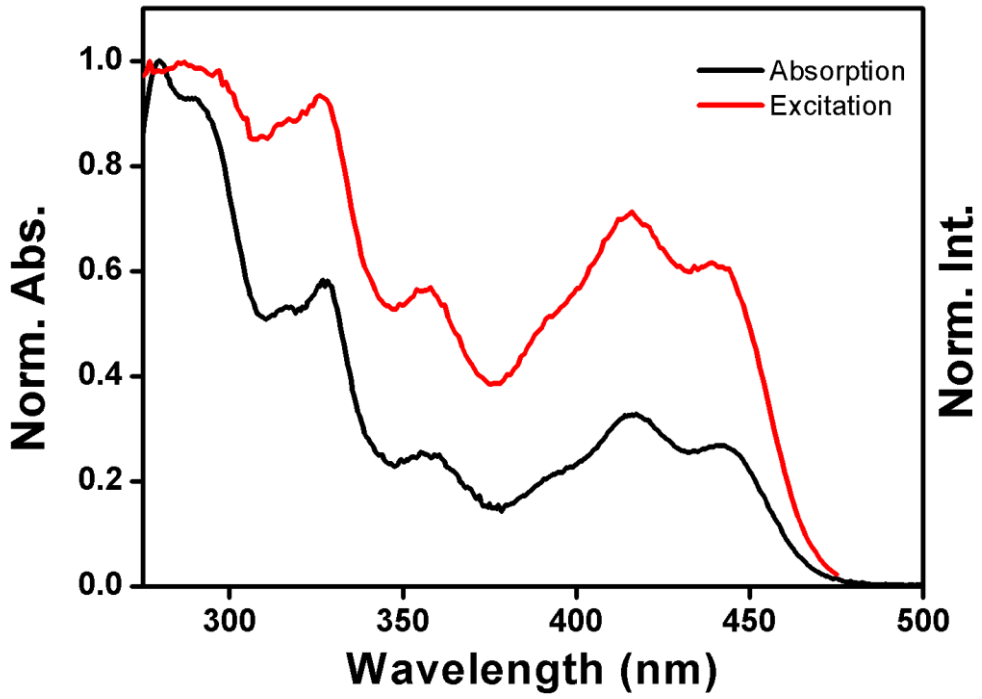


Figure S14: Overlapping of absorption and excitation spectra of **2aa**

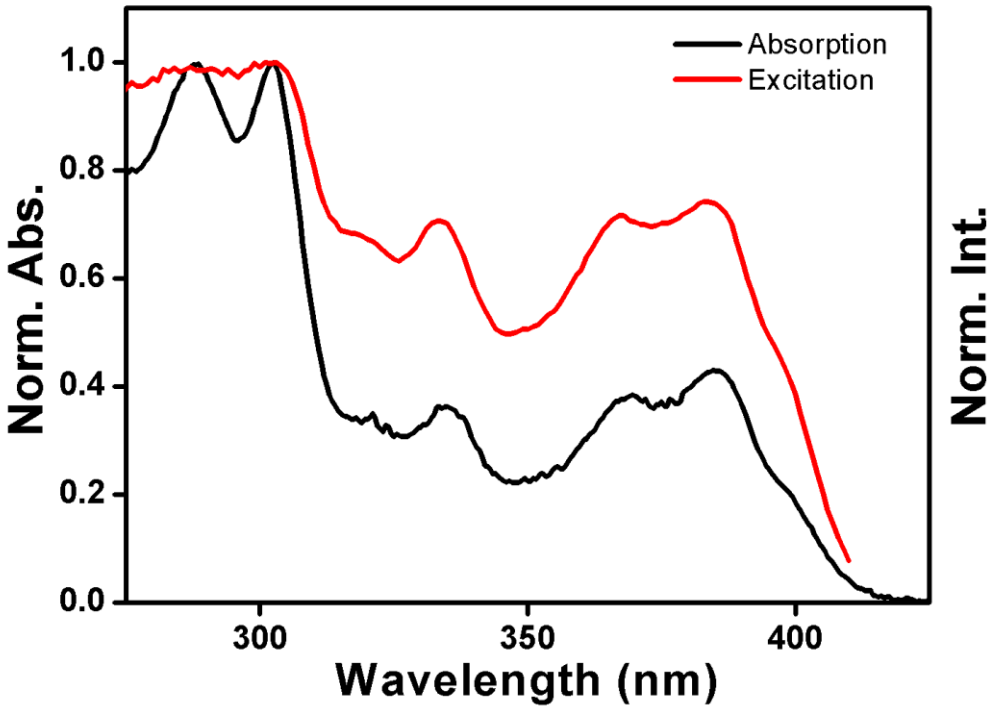


Figure S15: Overlapping of absorption and excitation spectra of **2ag**

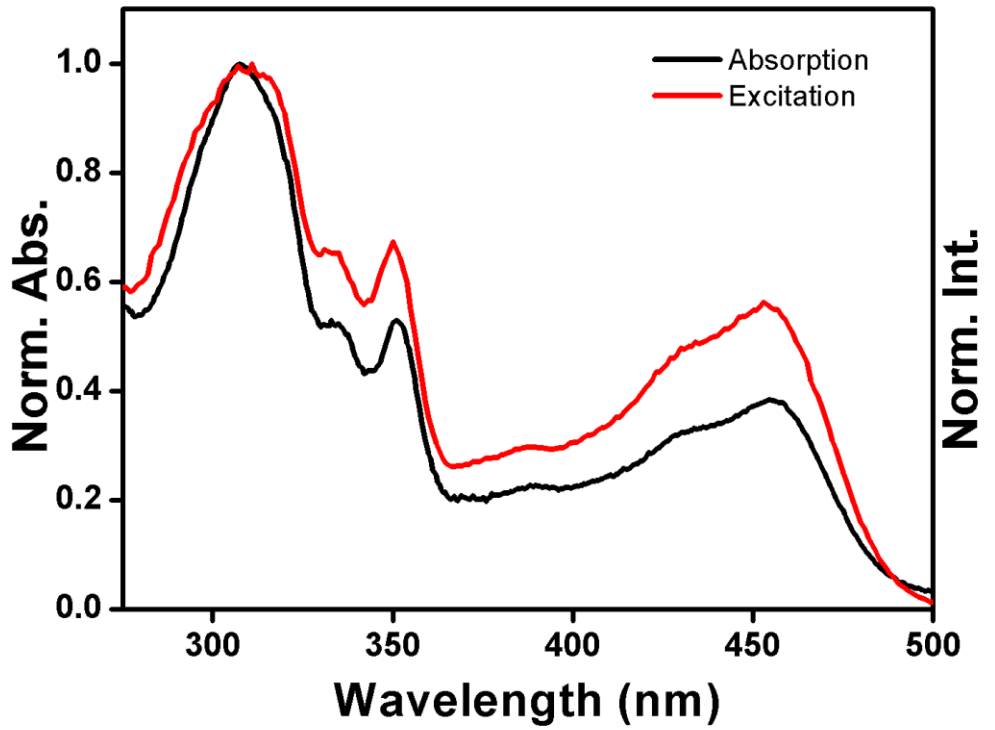


Figure S16: Overlapping of absorption and excitation spectra of **2ah**

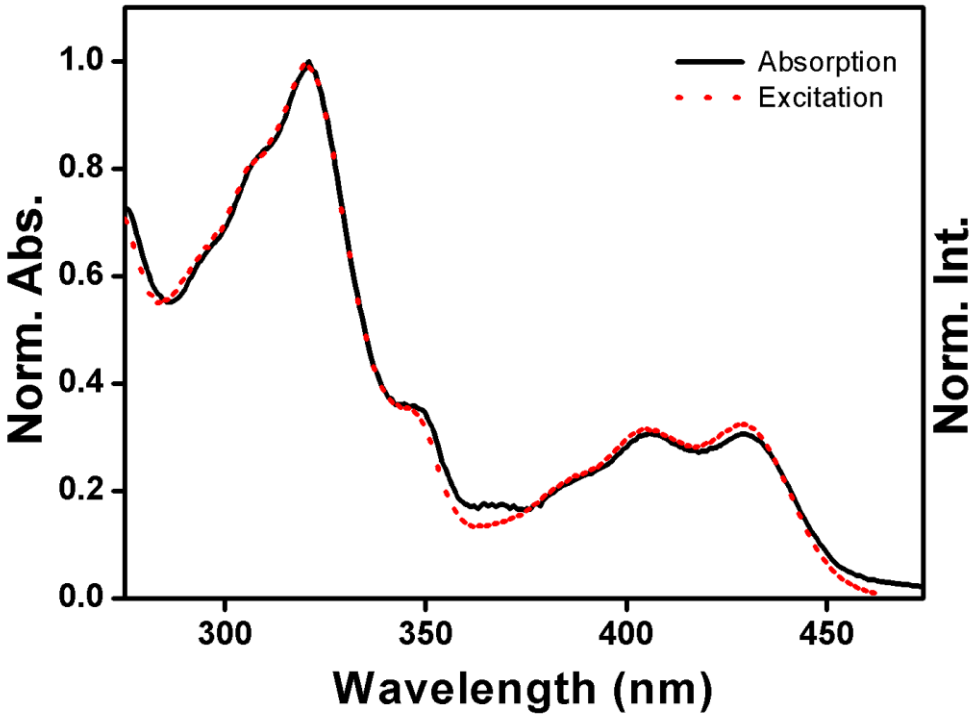


Figure S17: Overlapping of absorption and excitation spectra of **2ai**

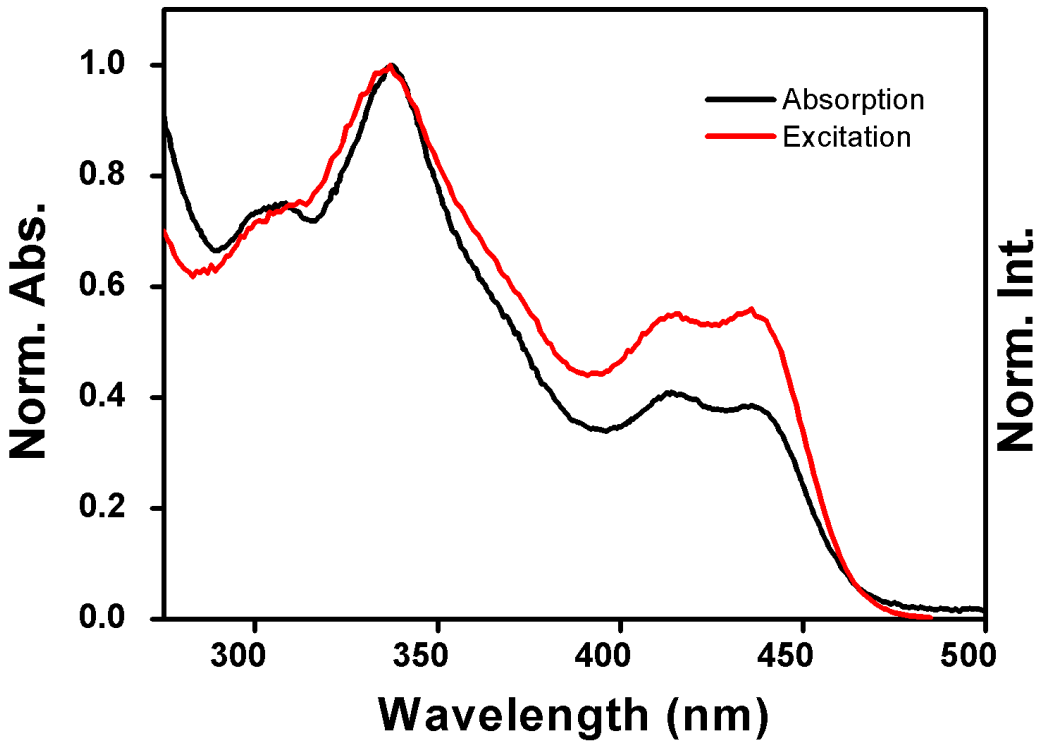


Figure S18: Overlapping of absorption and excitation spectra of **2aj**

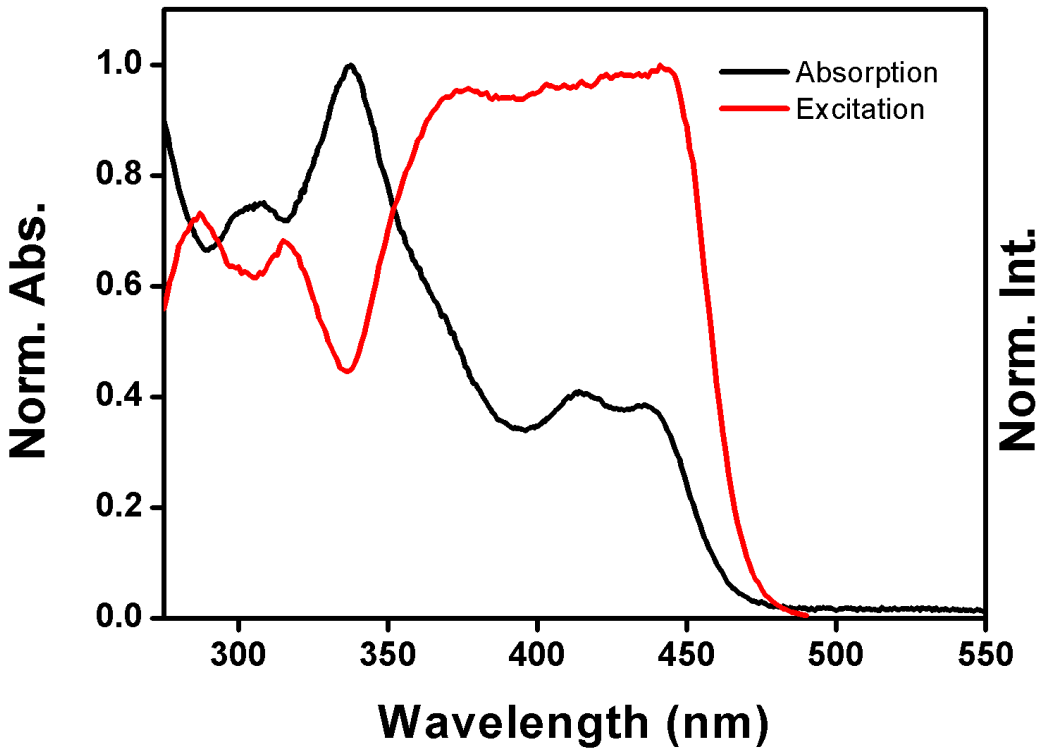


Figure S19: Overlapping of absorption and excitation spectra of **2al**

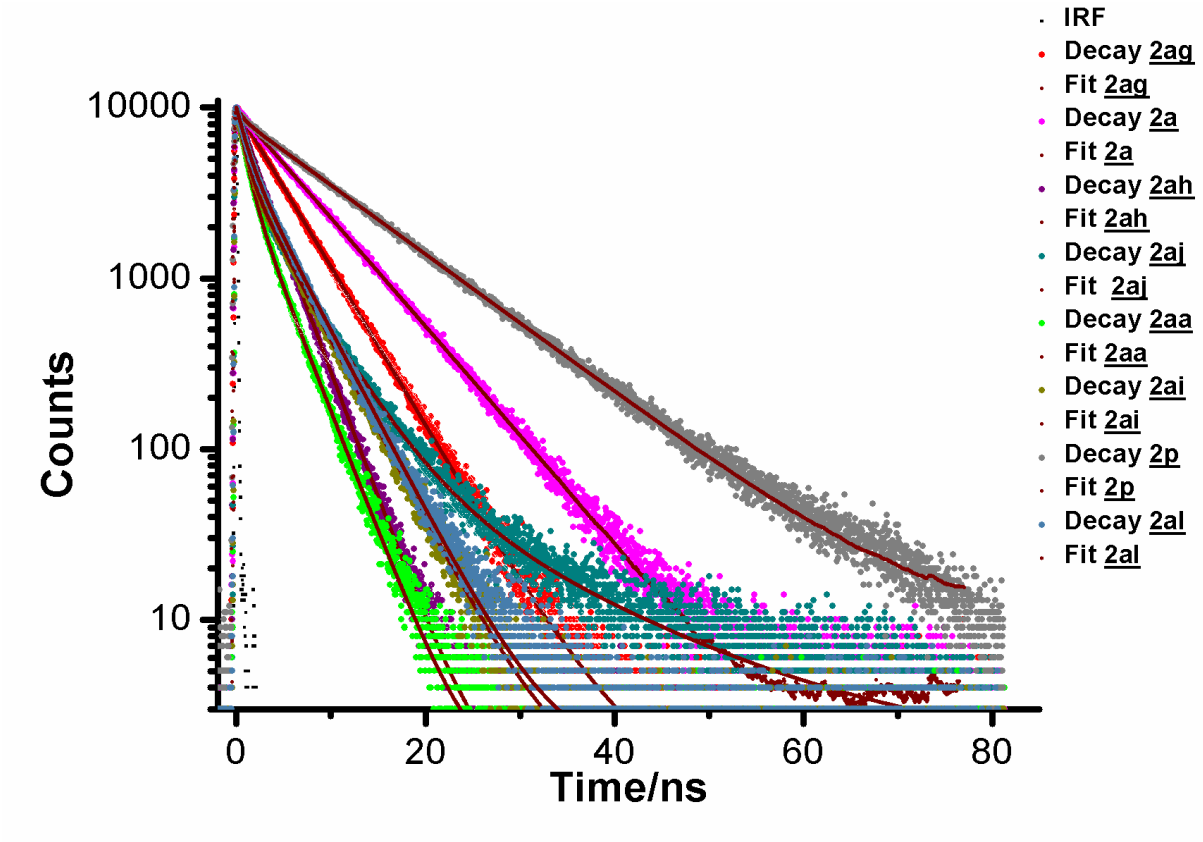


Figure S20: Emission decay profile of selected PAHs

Discussion on the photophysical data of the selected ionic PAHs:

Most of these compounds display bright fluorescence. These PAHs appear to be a new class of fluorescent materials and their photo- physical properties of selected ionic PAHs were studied in CH_2Cl_2 at RT. The absorption and excitation maxima, the photoluminescence (PL) maxima and quantum yields (ϕ_f), as well as the excited state lifetimes (τ_f) of these compounds in CH_2Cl_2 solution are listed in Tables 1, whereas the corresponding absorption spectra are depicted in Figures S1. The photoluminescence spectra of fluorophore show intense peaks between λ_{em}: 434–619 nm (Table S1) with Stokes shifts varies between (50-233 nm)which reveals violet-to-red fluorescence emissions depending on the functional group present. Substituent's like methoxy and plain phenyl core had only a modest effect on the fluorescent properties (**2ag** and **2a,** Table S1). Extension of the π-conjugated systems leads to significant bathochromic shifts in emission (**2p**, Table S1). These fluorophores have good photoluminescence capabilities with Φ_f values ranging between 0.40 to 10.48. The life time τ_f values are consistent with a doublet multiplicity.

6. Cyclic voltammetry

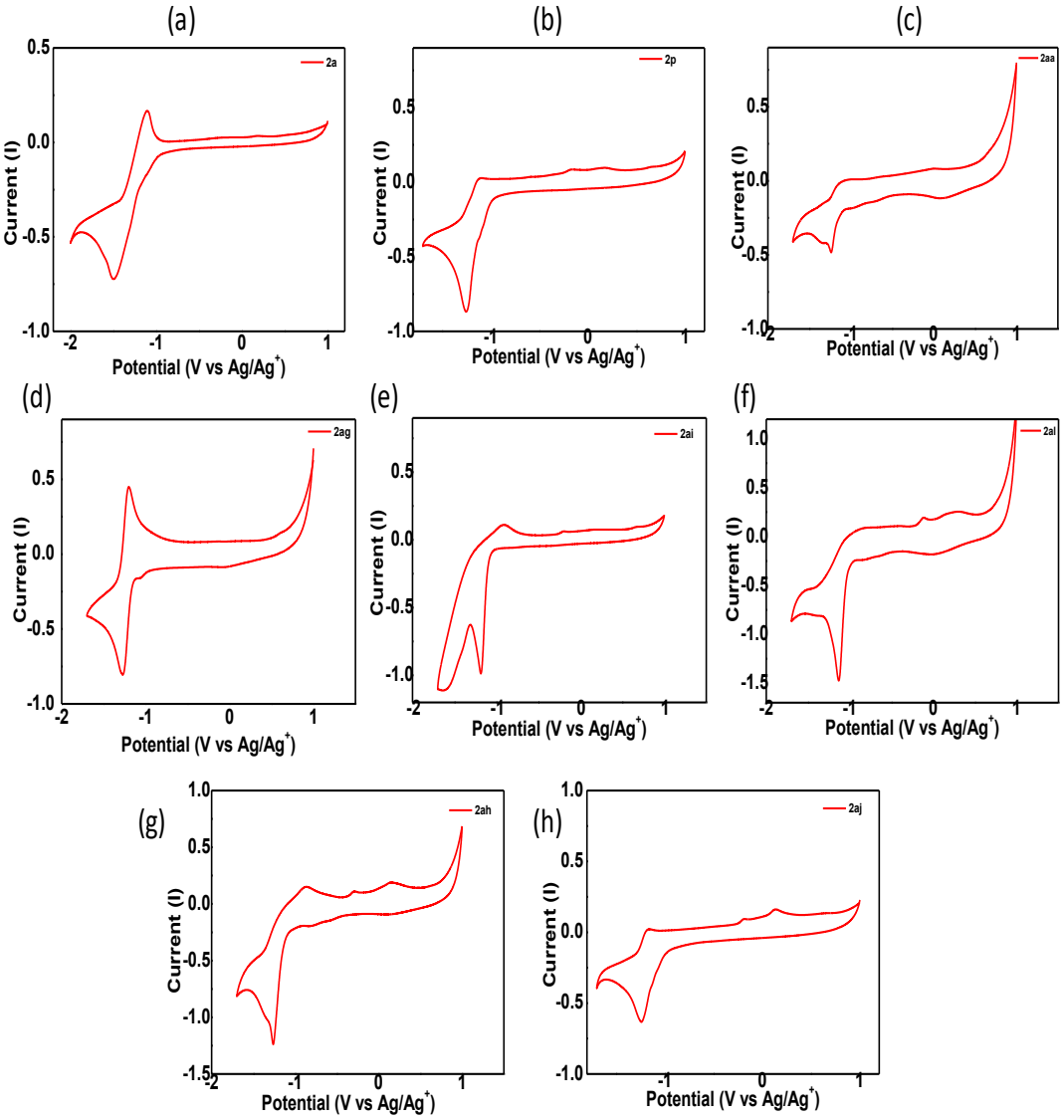


Figure S21. Cyclic voltammograms recorded for **2a**(a), **2p**(b), **2aa**(c), **2ag**(d), **2ai**(e), **2al**(f), **2ah**(g), **2aj**(h) in acetonitrile and 0.1 M TBAP using Pt disc as working electrode. Scan rate – 100 mV/s.

Table S2. Electrochemical data of representative ionic PAHs:

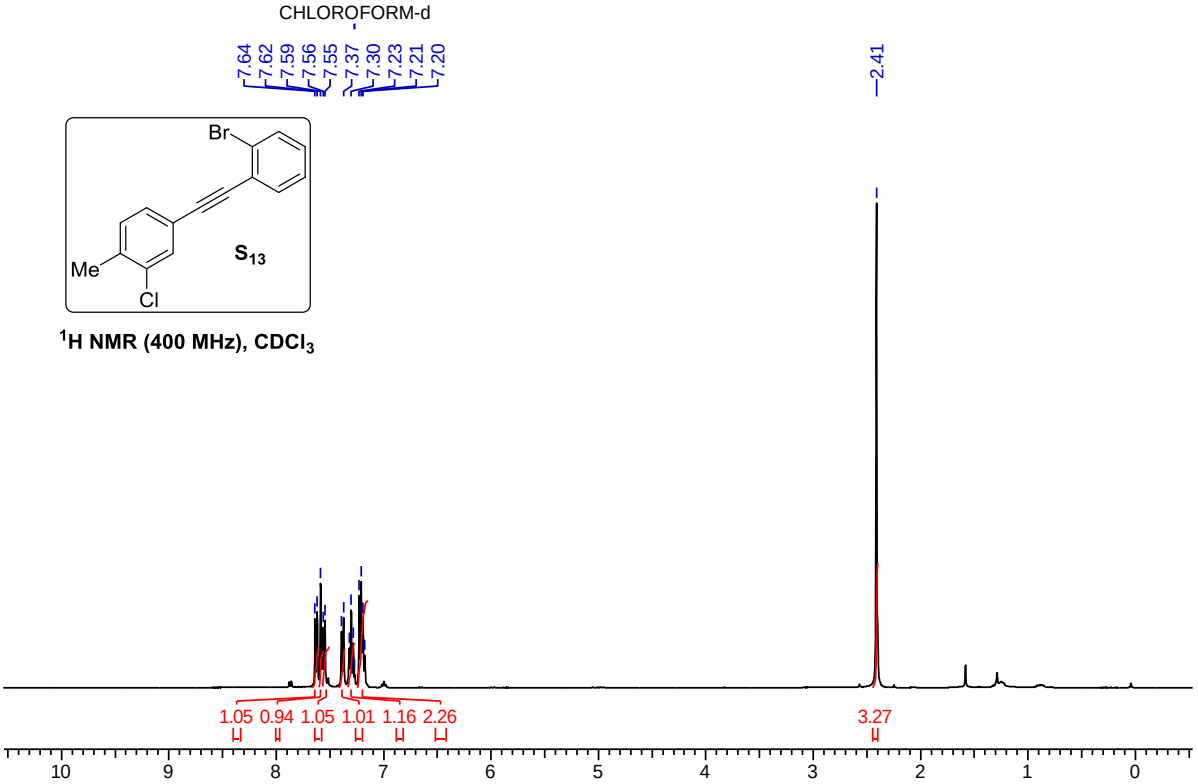
Comp	λ(nm) onset	E_g opt (eV)	E_{red} (V)	LUMO (eV)	HOMO[2] (eV)
2a	410	3.03	-1.57	-2.83	-5.86
2p	526	2.36	-1.32	-3.08	-5.44
2aa	457	2.71	-1.29	-3.11	-5.82
2ag	400	3.10	-1.34	-3.06	-6.16
2ai	428	2.90	-1.25	-3.15	-6.05
2al	453	2.74	-1.21	-3.19	-5.93
2ah	474	2.62	-1.33	-3.07	-5.69
2aj	448	2.77	-1.32	-3.08	-5.85

Discussion on the electrochemical data of the representative ionic PAHs:

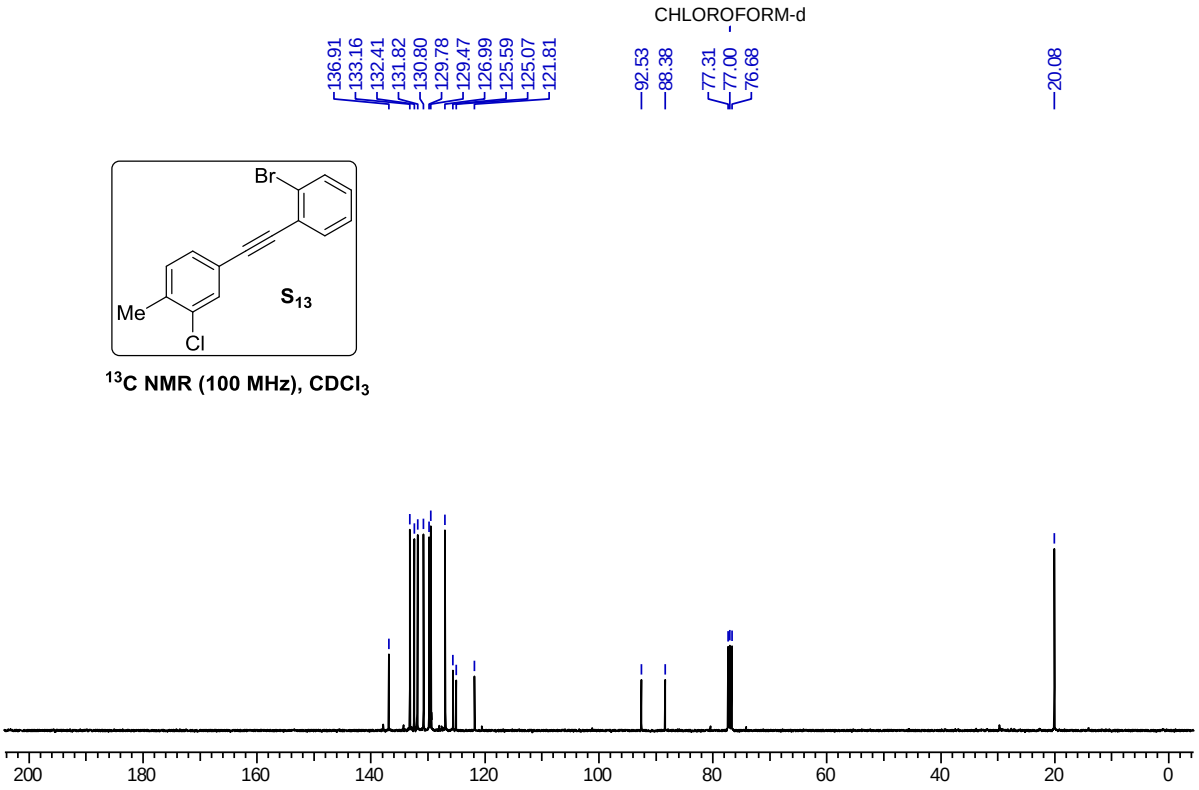
The electrochemical properties of representative PAHs was investigated by cyclic voltammetry in MeCN containing 0.1 M tetrabutylammonium perchlorate ((Bu_4NClO_4)) using platinum (Pt) as working electrode, Ag/Ag^+ and Pt wire as reference and counter electrode respectively (Figure **S21**). Potential was calibrated using ferrocene as internal standard. The cyclic voltammogram of **2p** and **2am** showed irreversible reduction wave with peak potential (E_p^c) at **-1.22** V and **-1.13** V vs Fc/Fc^+ respectively. From these data, lowest unoccupied molecular orbital (LUMO) levels of **2p** and **2am** were estimated to be -3.08 and -3.19 eV respectively using equation $–[E_p^c(vs\ NHE) + 4.4]$ ev. Highest occupied molecular orbital (HOMO) level was estimated using the HOMO-LUMO gap as obtained from emission spectra by considering electrochemically determined LUMO as reference.

[2]. HOMO level is calculated using electrochemically determined LUMO level and energy gap as obtained spectro-photometrically.

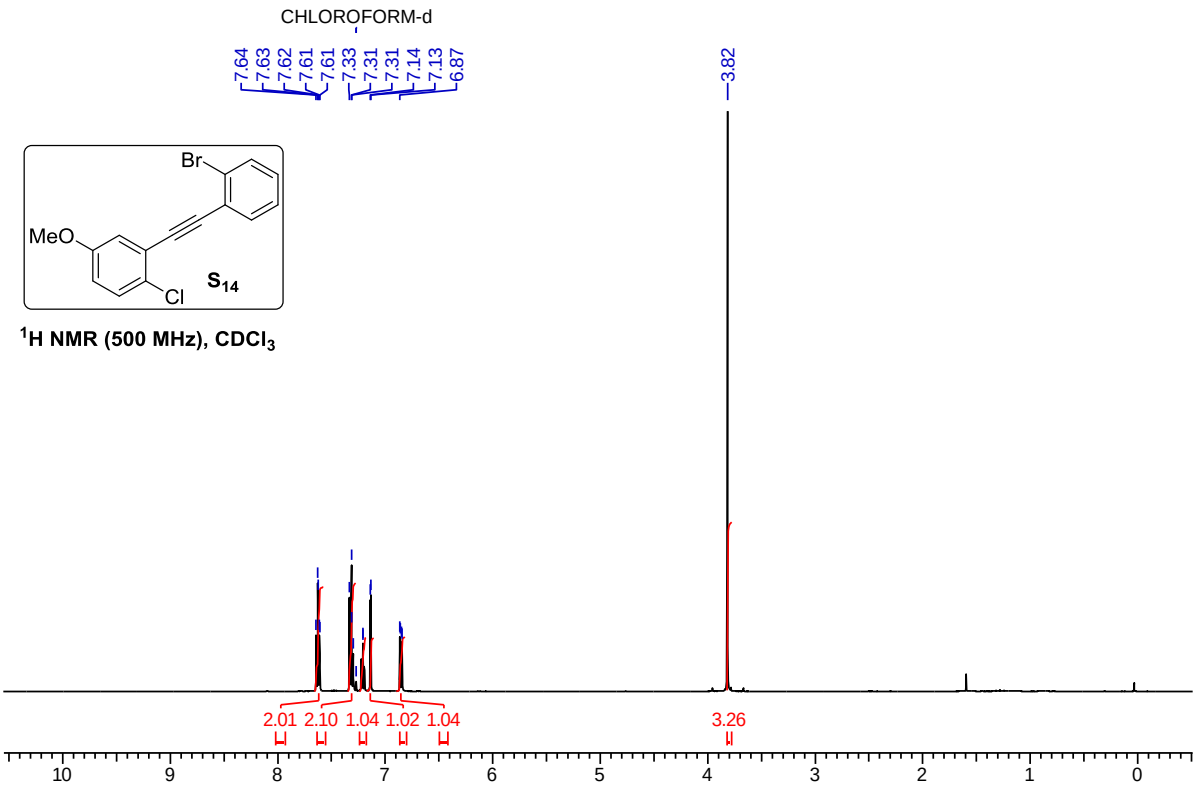
7. NMR spectra



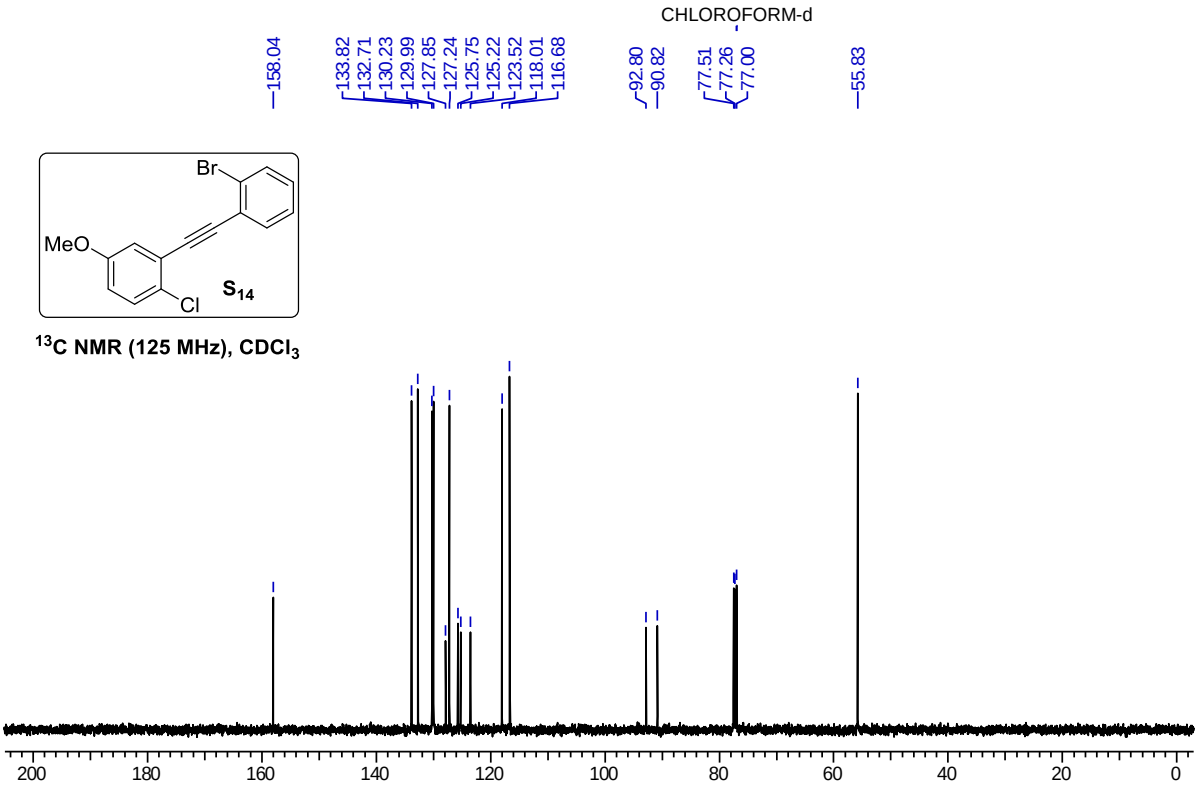
^{1}H NMR (400 MHz), $CDCl_3$



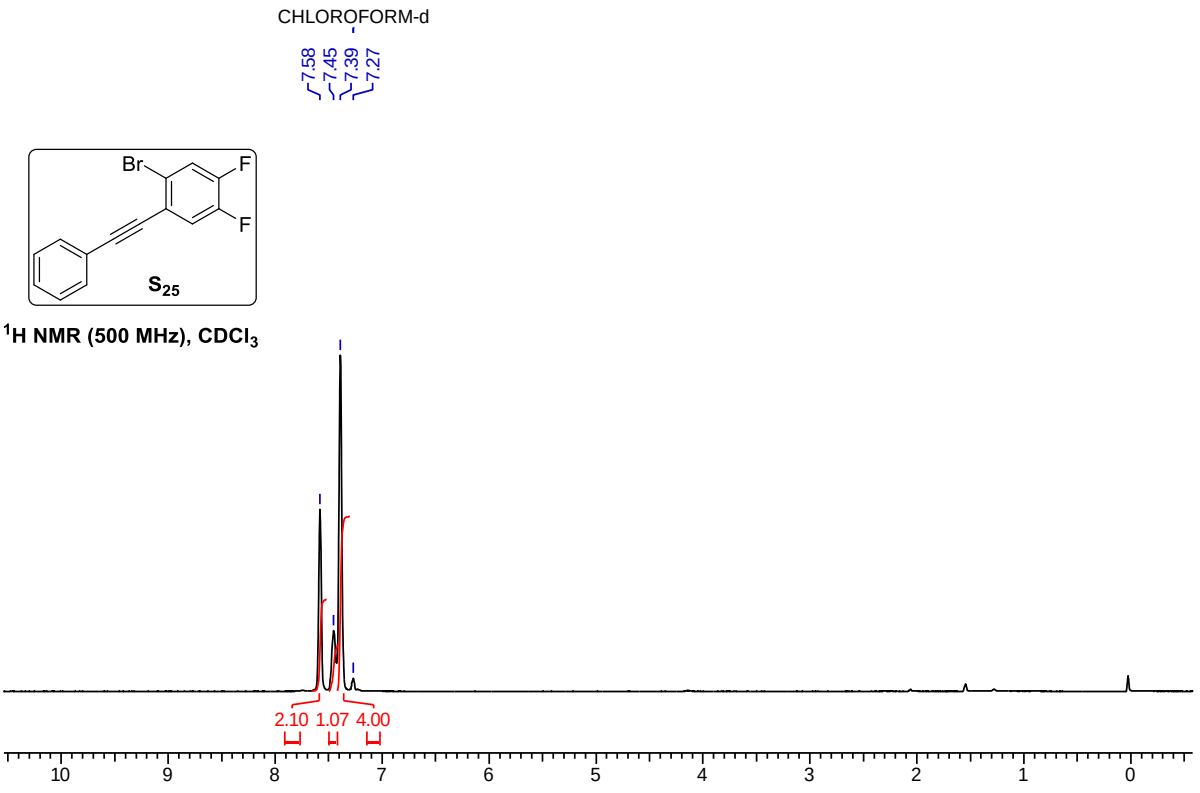
^{13}C NMR (100 MHz), $CDCl_3$



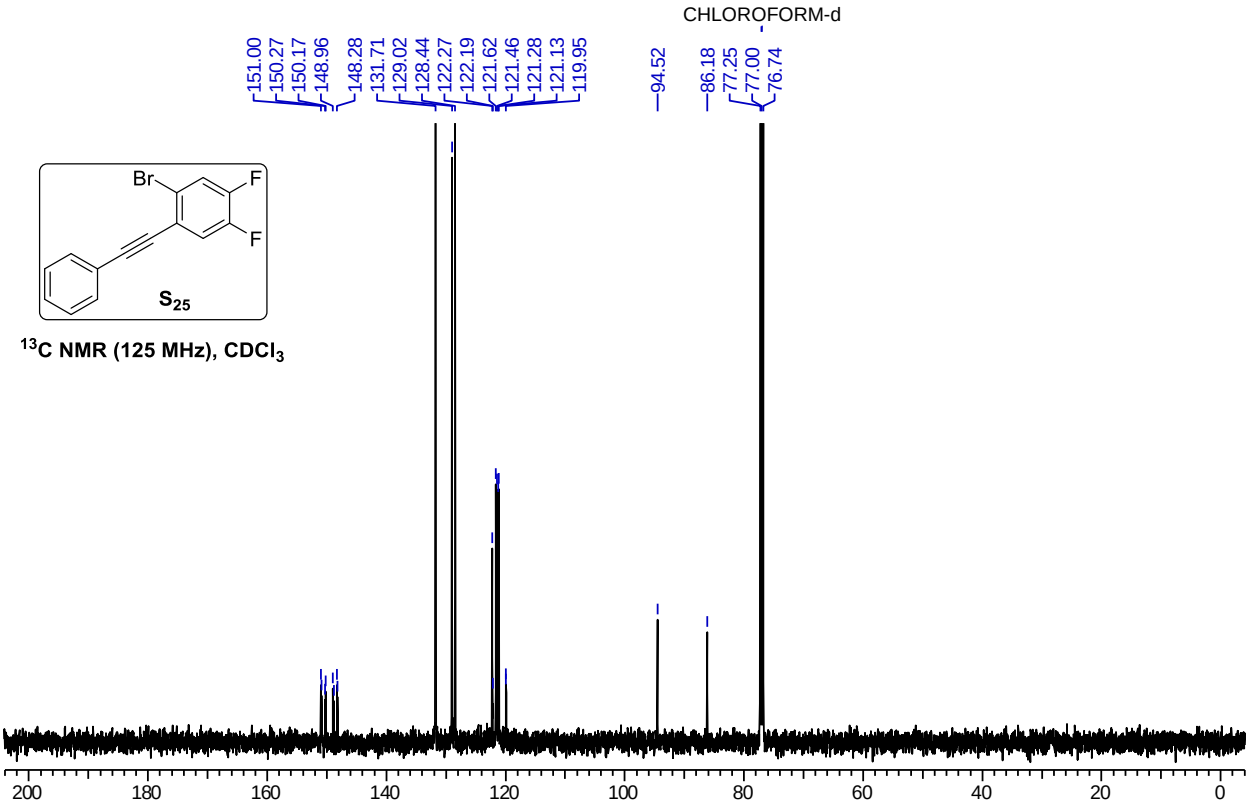
^{1}H NMR (500 MHz), $CDCl_3$



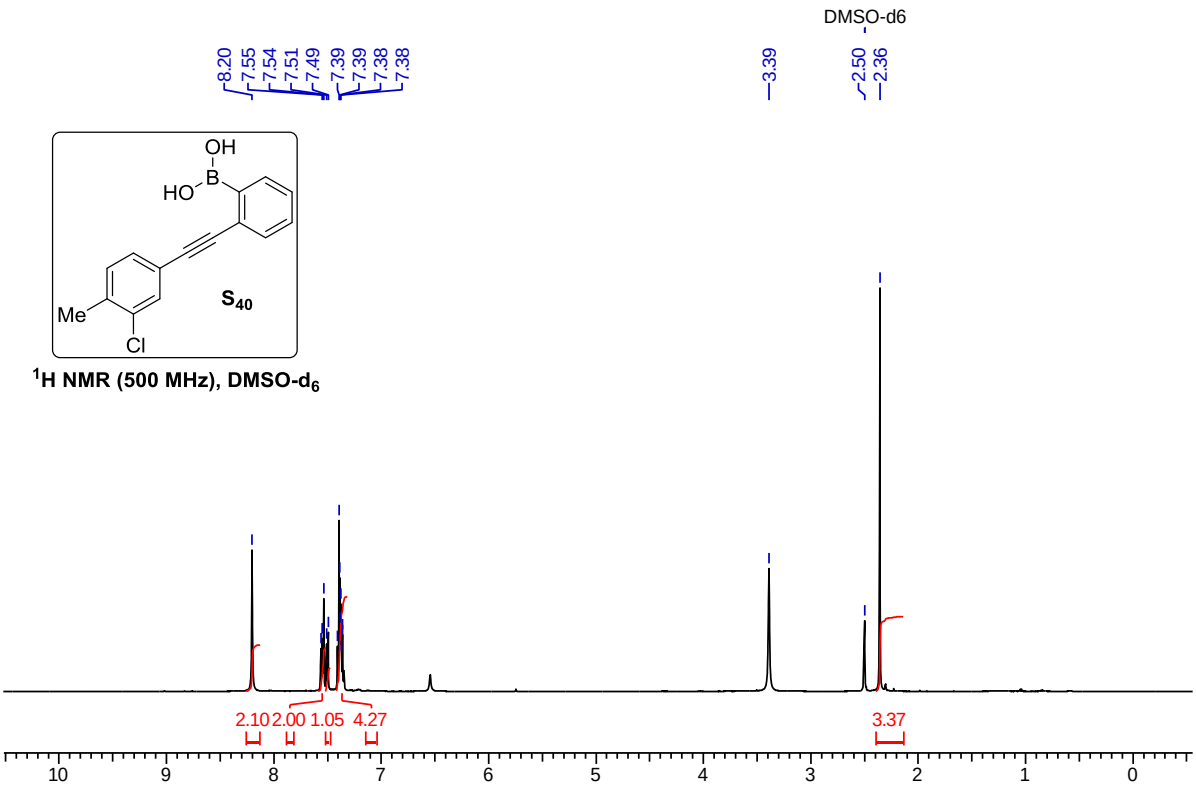
^{13}C NMR (125 MHz), $CDCl_3$



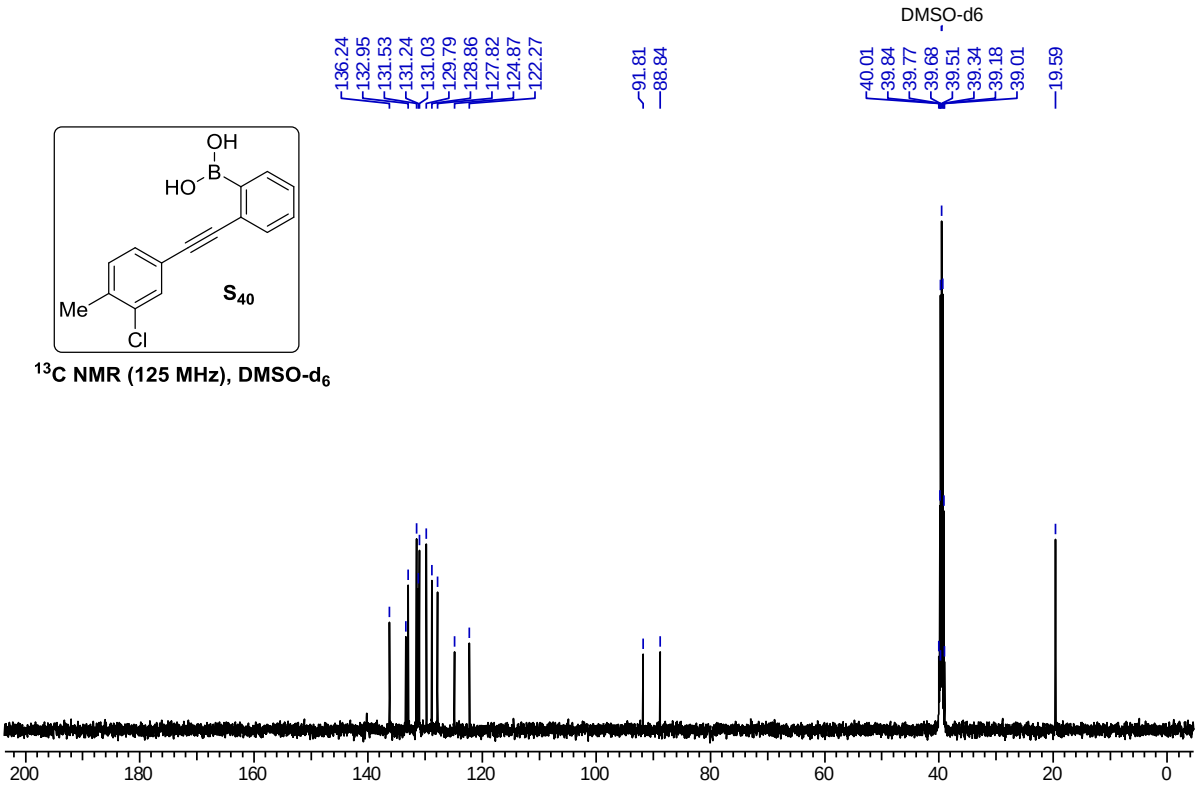
^{1}H NMR (500 MHz), $CDCl_3$



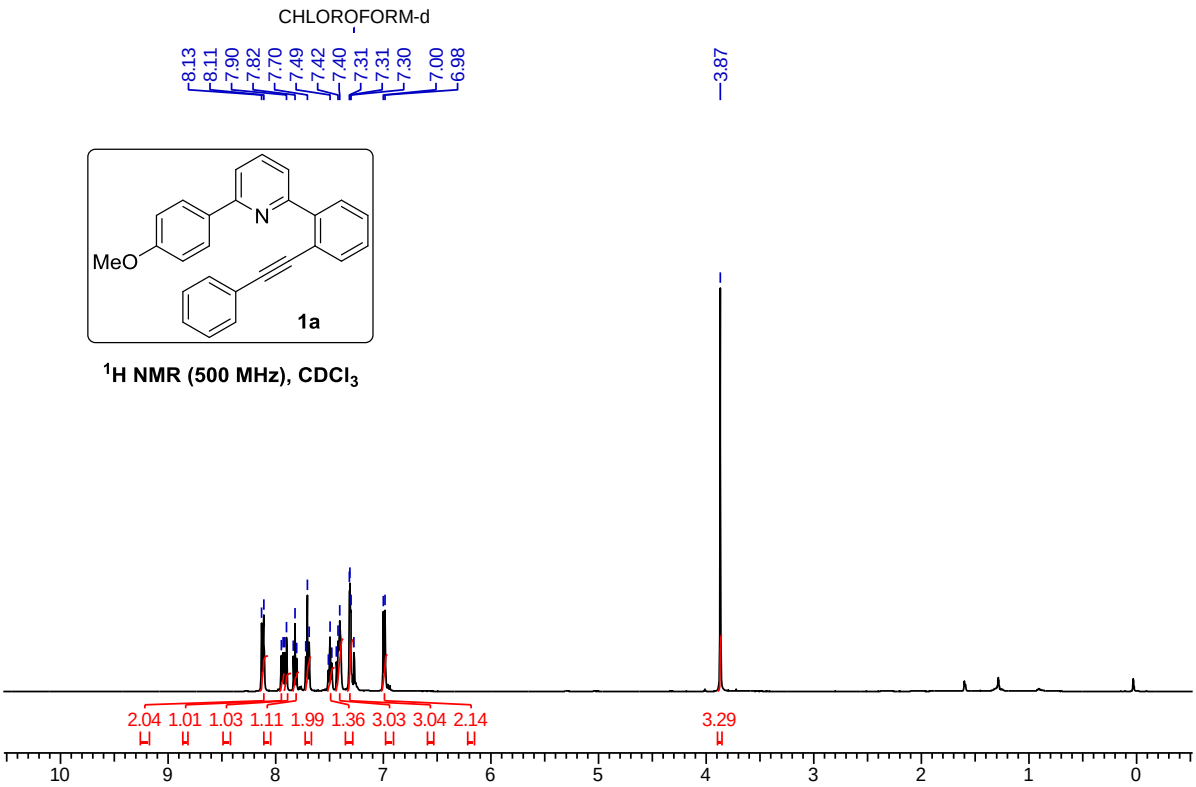
^{13}C NMR (125 MHz), $CDCl_3$



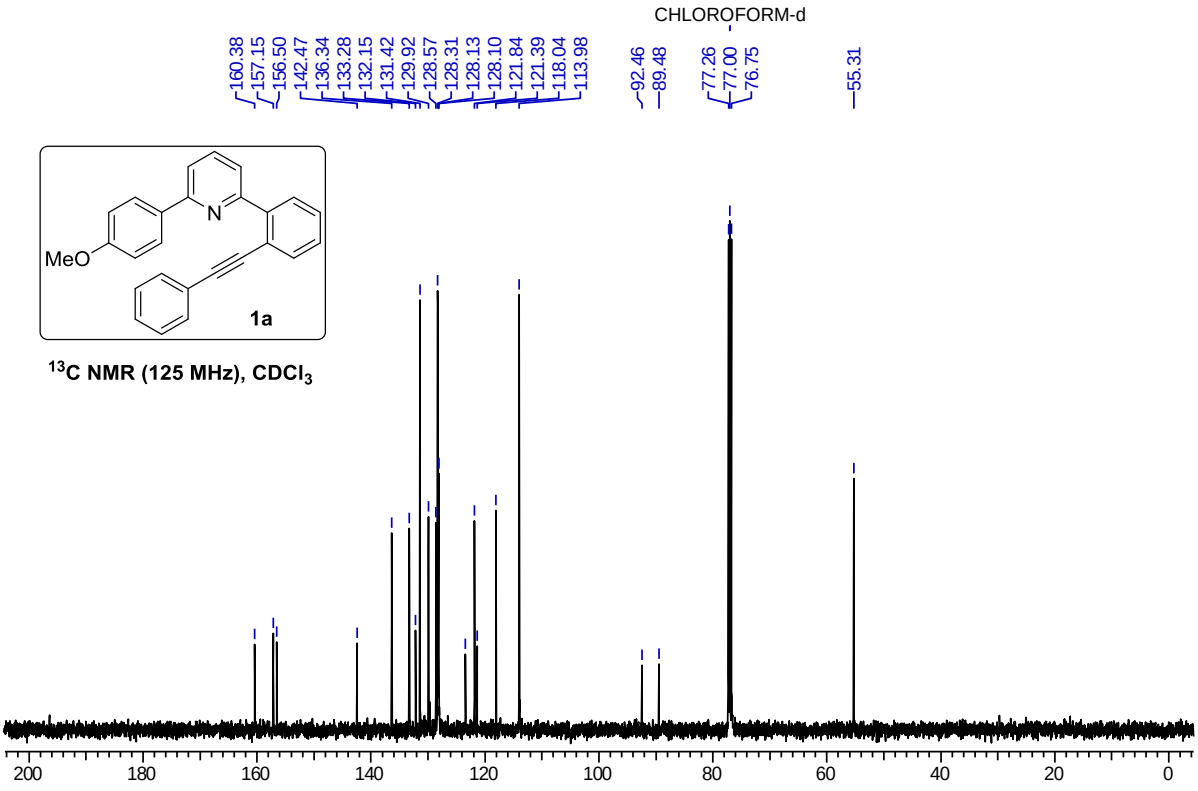
^{1}H NMR (500 MHz), DMSO-d_6



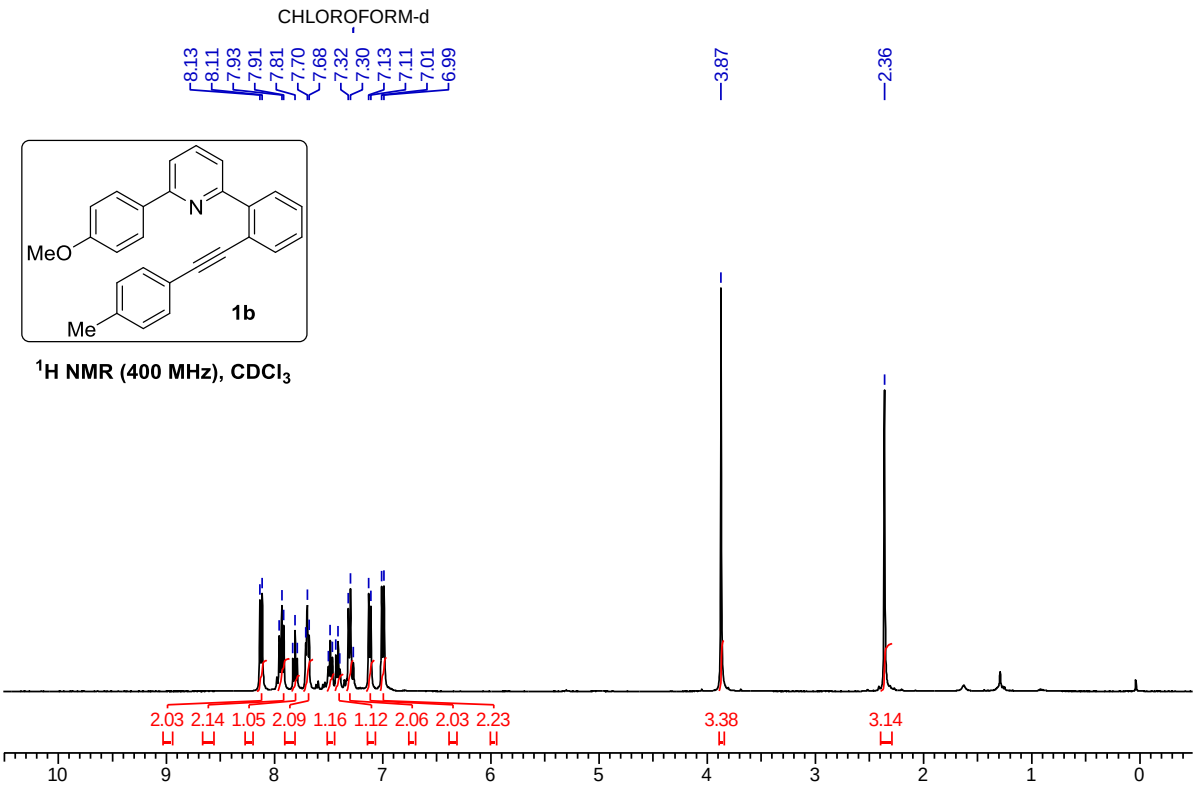
^{13}C NMR (125 MHz), DMSO-d_6



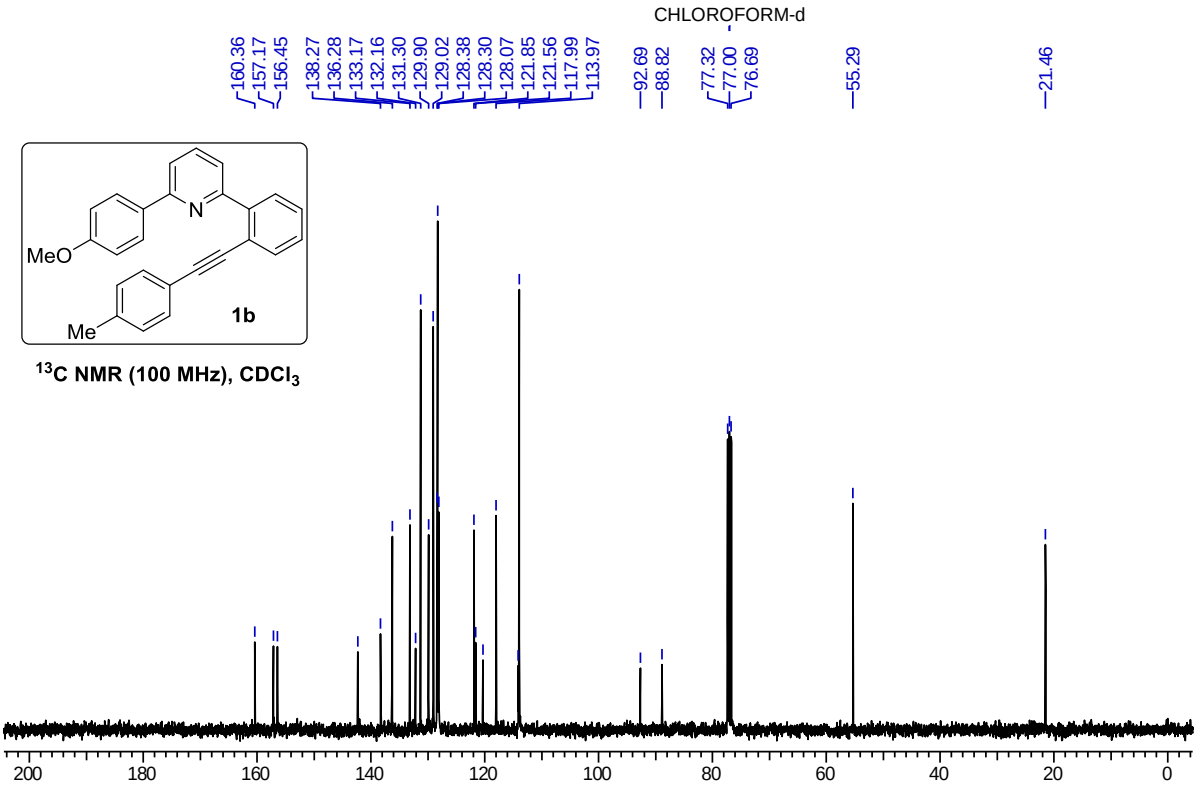
^{1}H NMR (500 MHz), $CDCl_3$



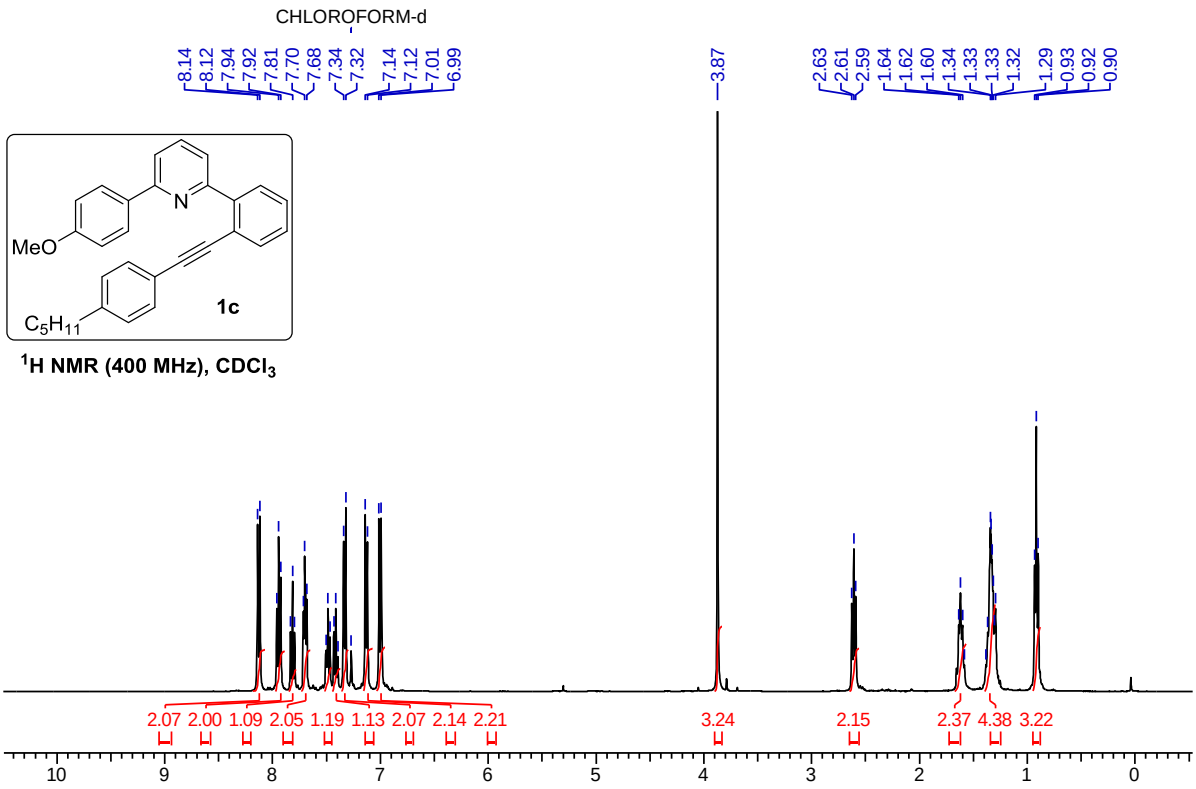
^{13}C NMR (125 MHz), $CDCl_3$



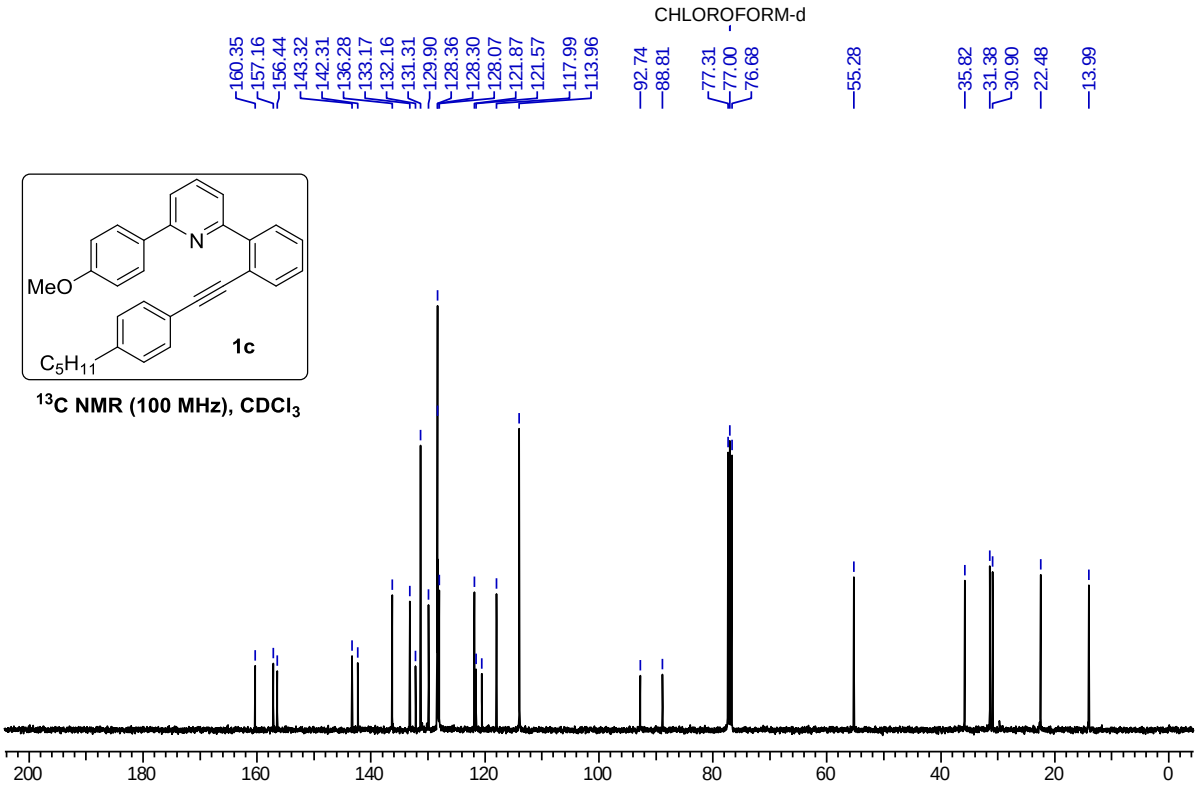
^{1}H NMR (400 MHz), $CDCl_3$



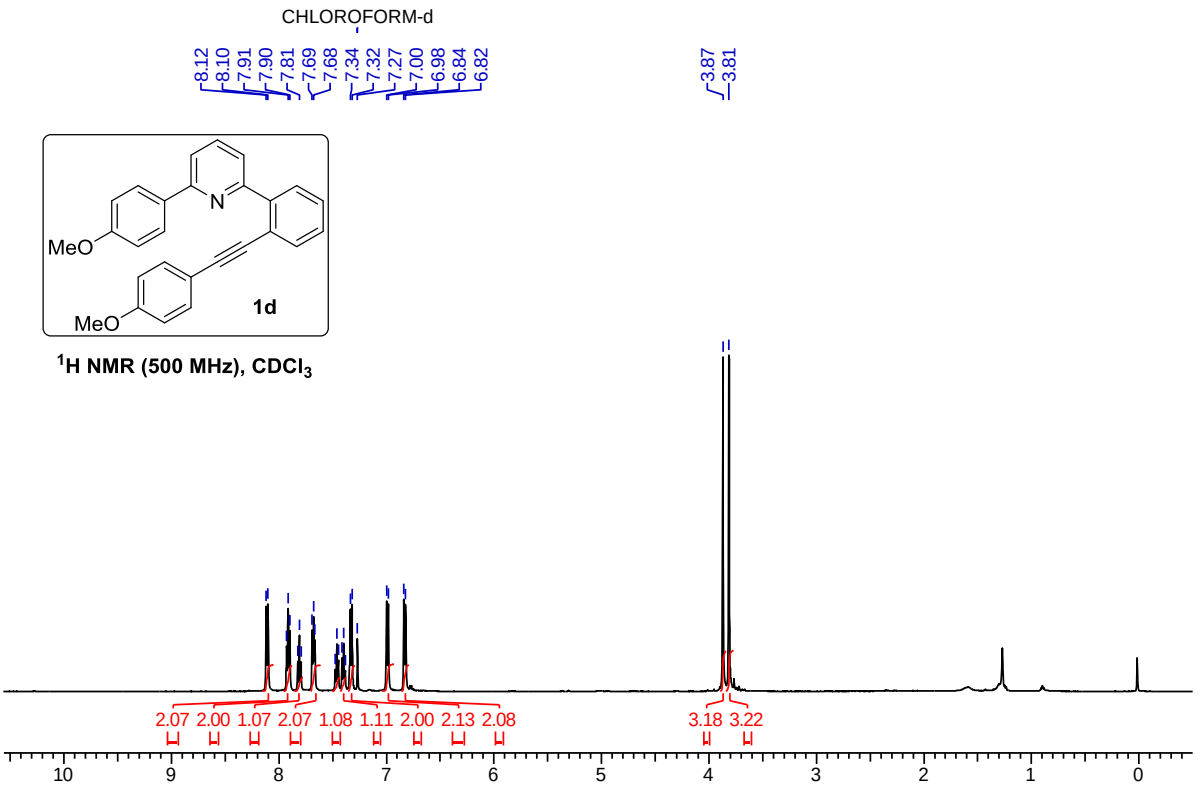
^{13}C NMR (100 MHz), $CDCl_3$



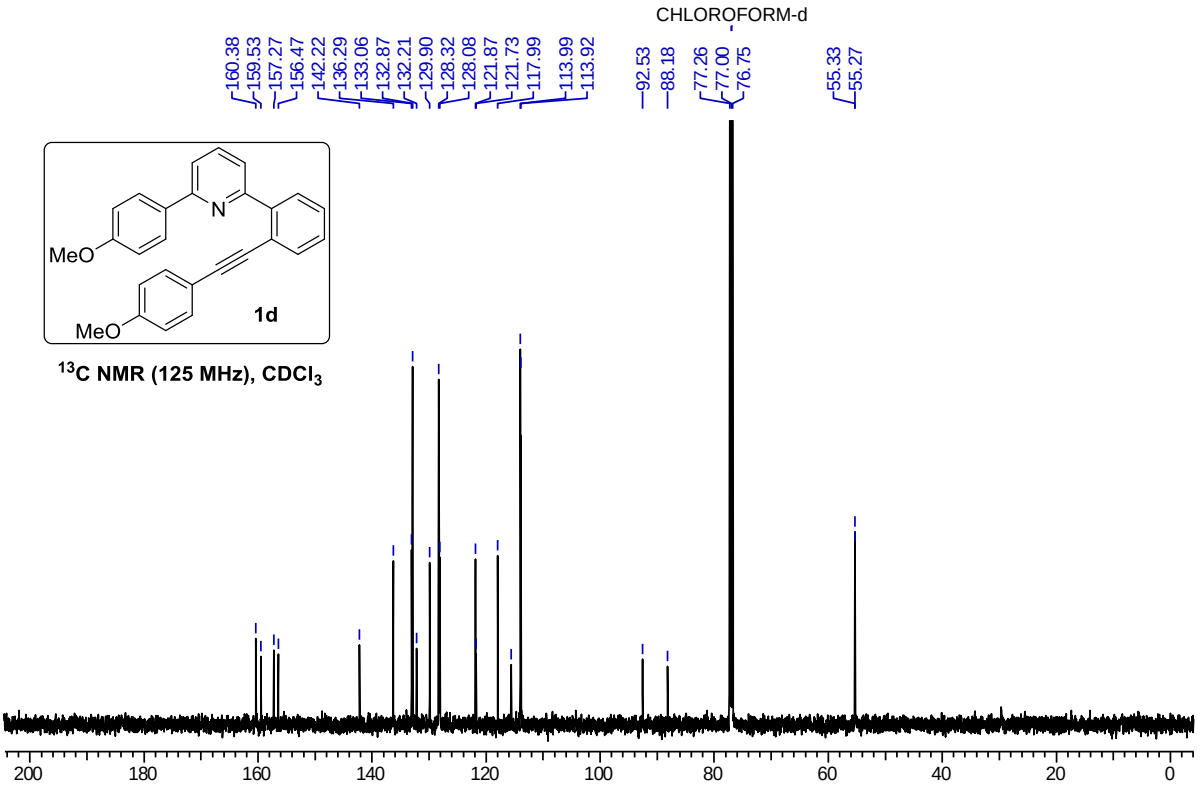
^{1}H NMR (400 MHz), $CDCl_3$



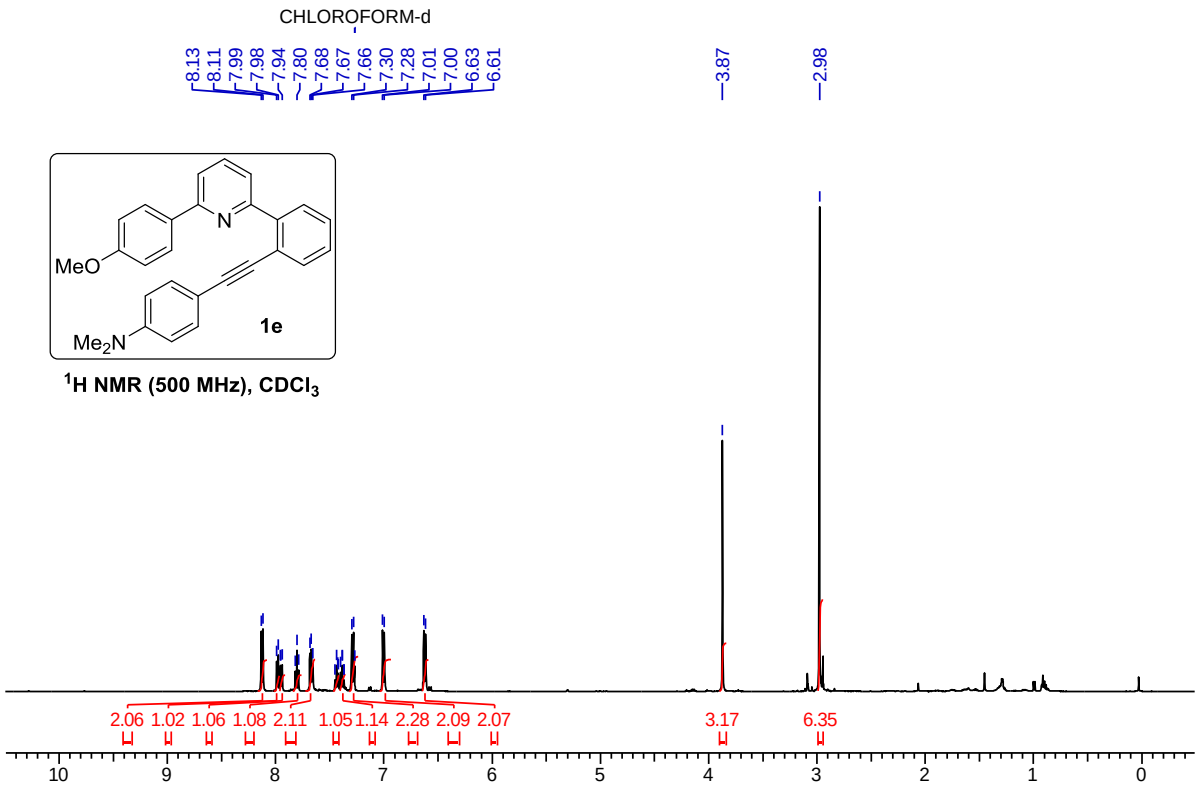
^{13}C NMR (100 MHz), $CDCl_3$



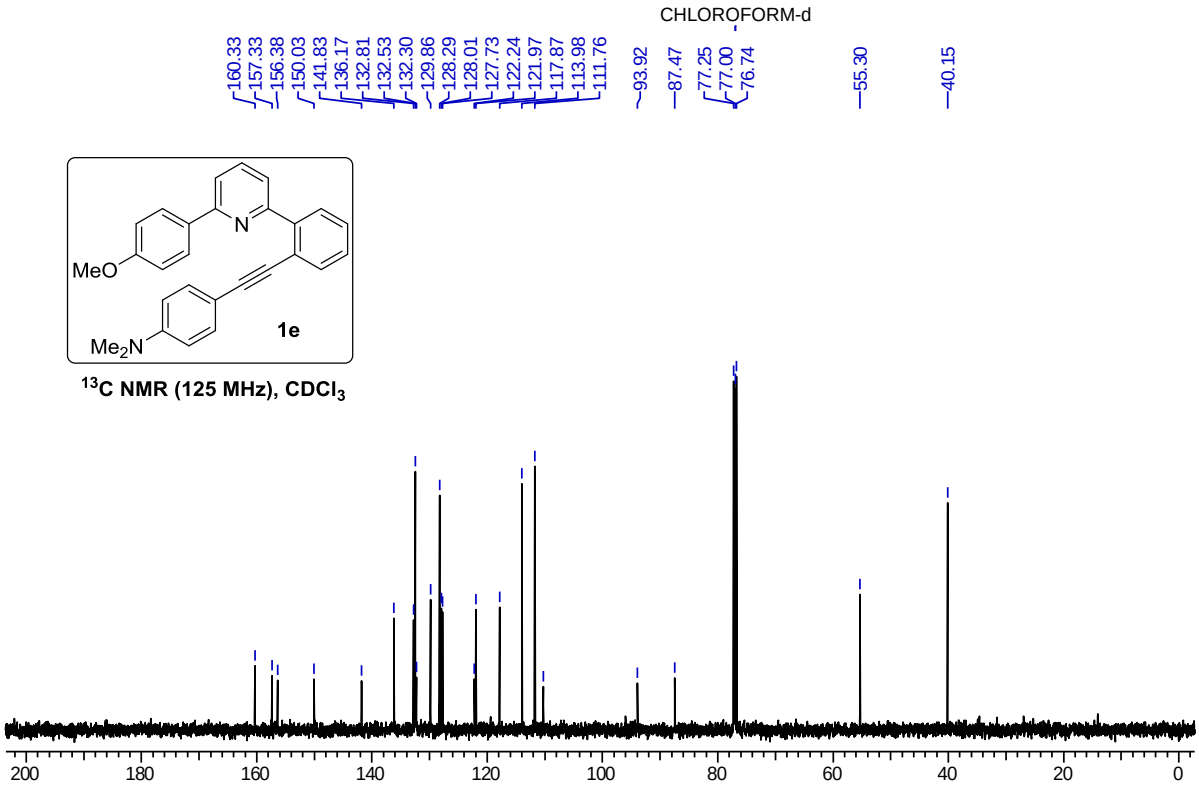
^{1}H NMR (500 MHz), $CDCl_3$



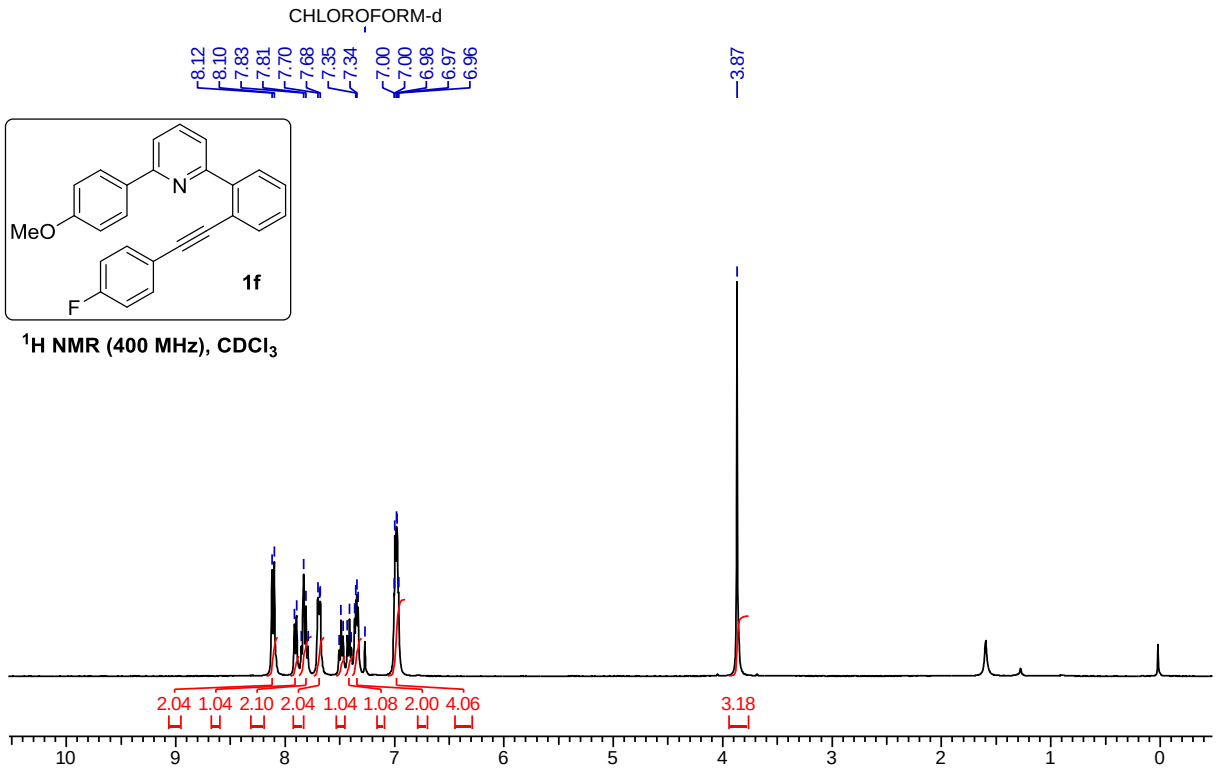
^{13}C NMR (125 MHz), $CDCl_3$



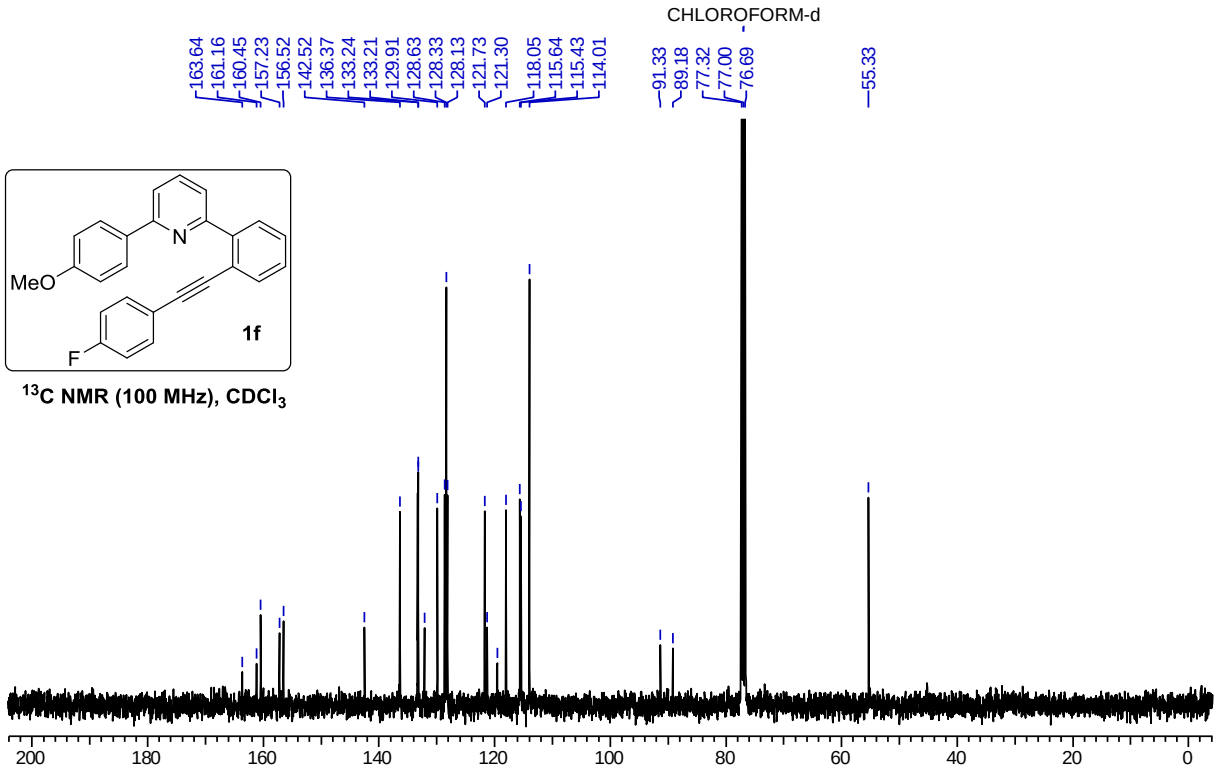
^{1}H NMR (500 MHz), $CDCl_3$



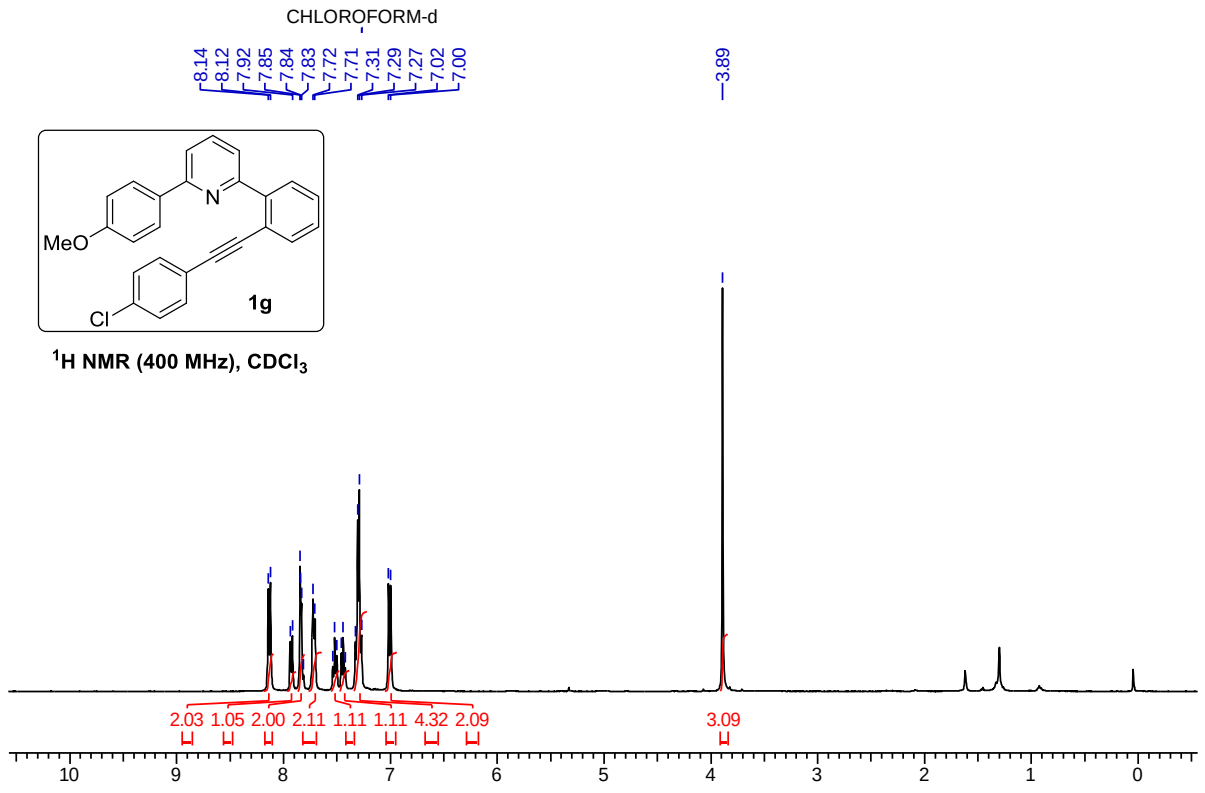
^{13}C NMR (125 MHz), $CDCl_3$



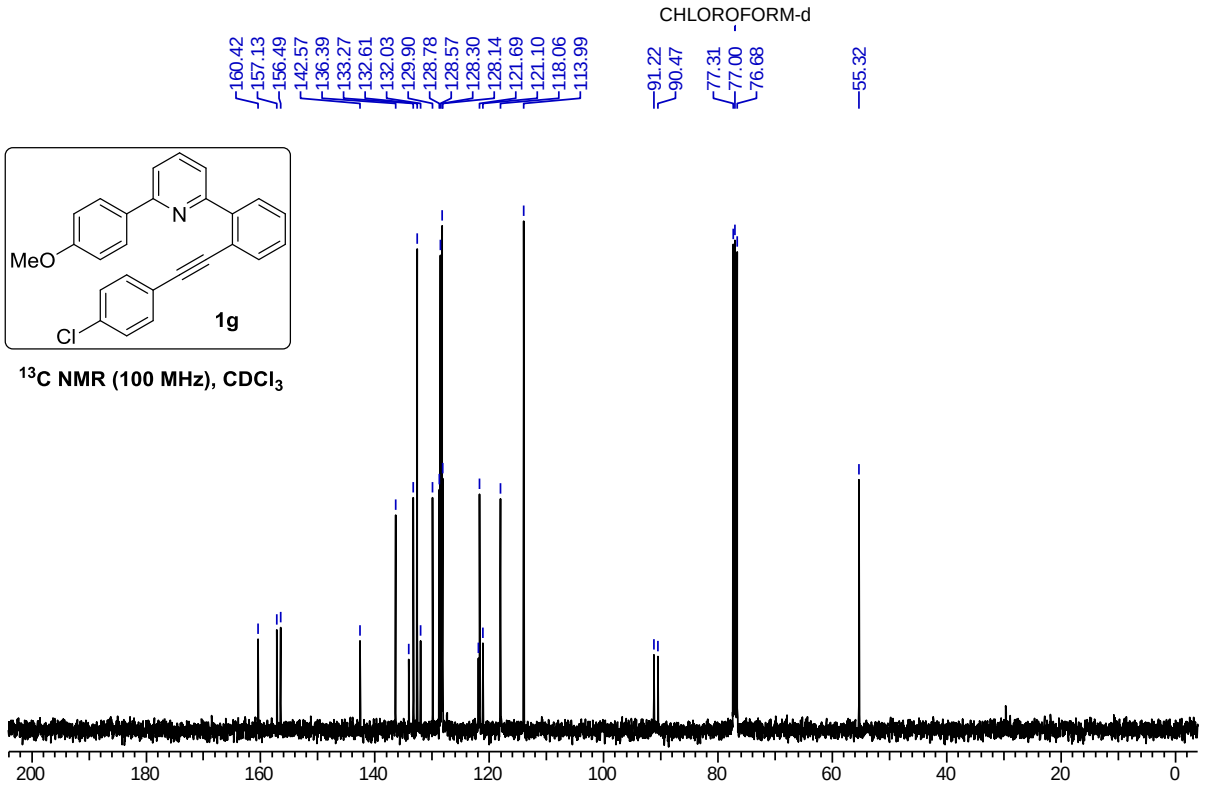
^{1}H NMR (400 MHz), $CDCl_3$



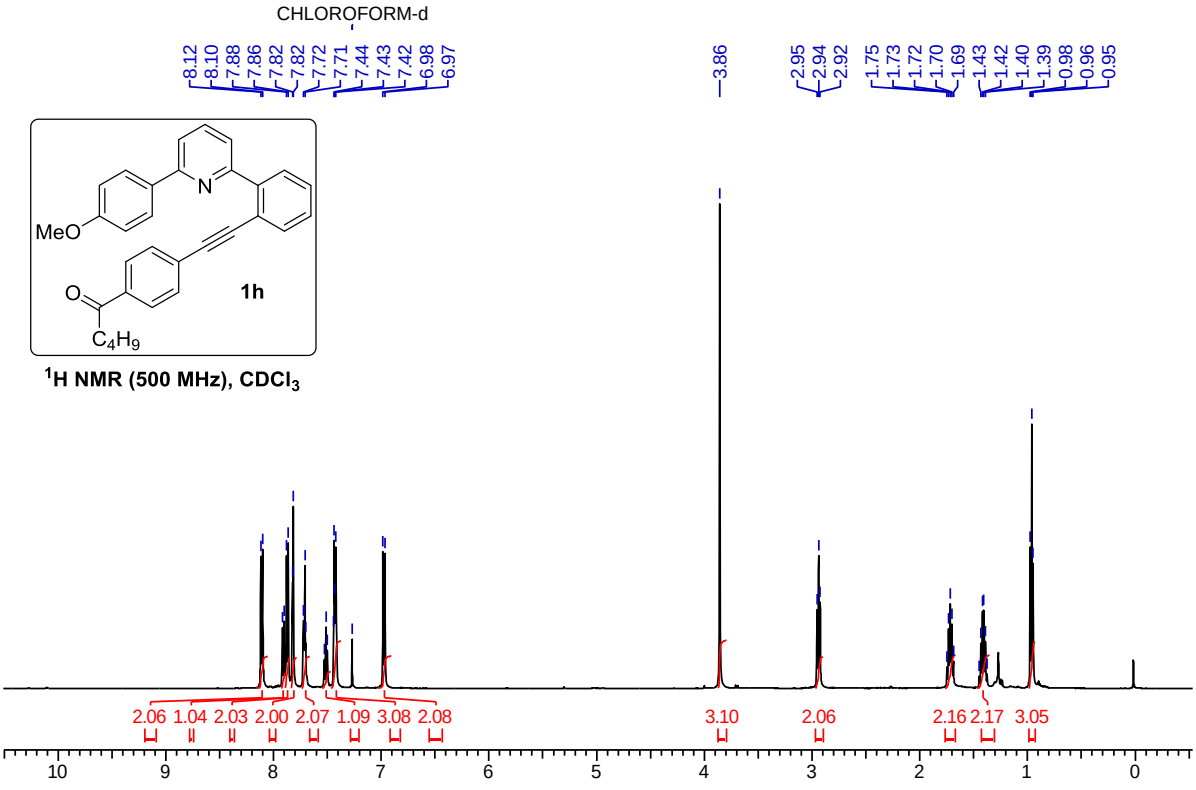
^{13}C NMR (100 MHz), $CDCl_3$



^{1}H NMR (400 MHz), $CDCl_3$



^{13}C NMR (100 MHz), $CDCl_3$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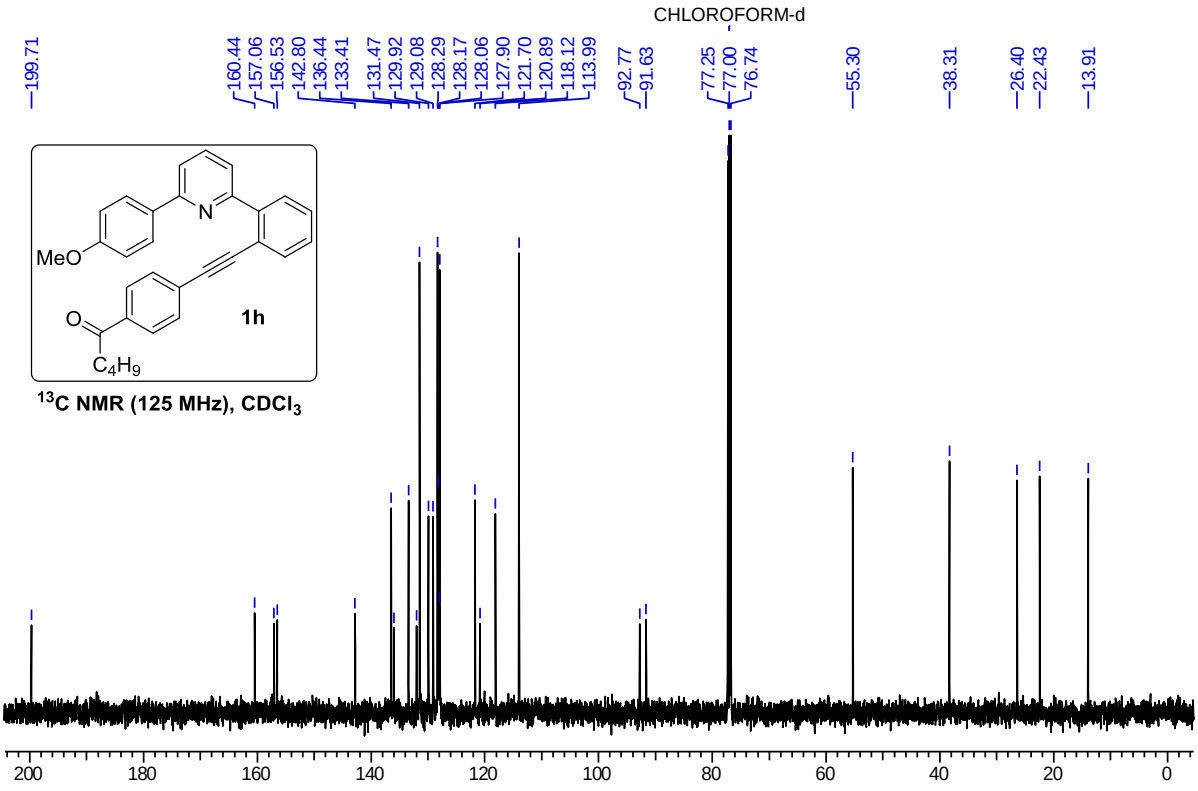
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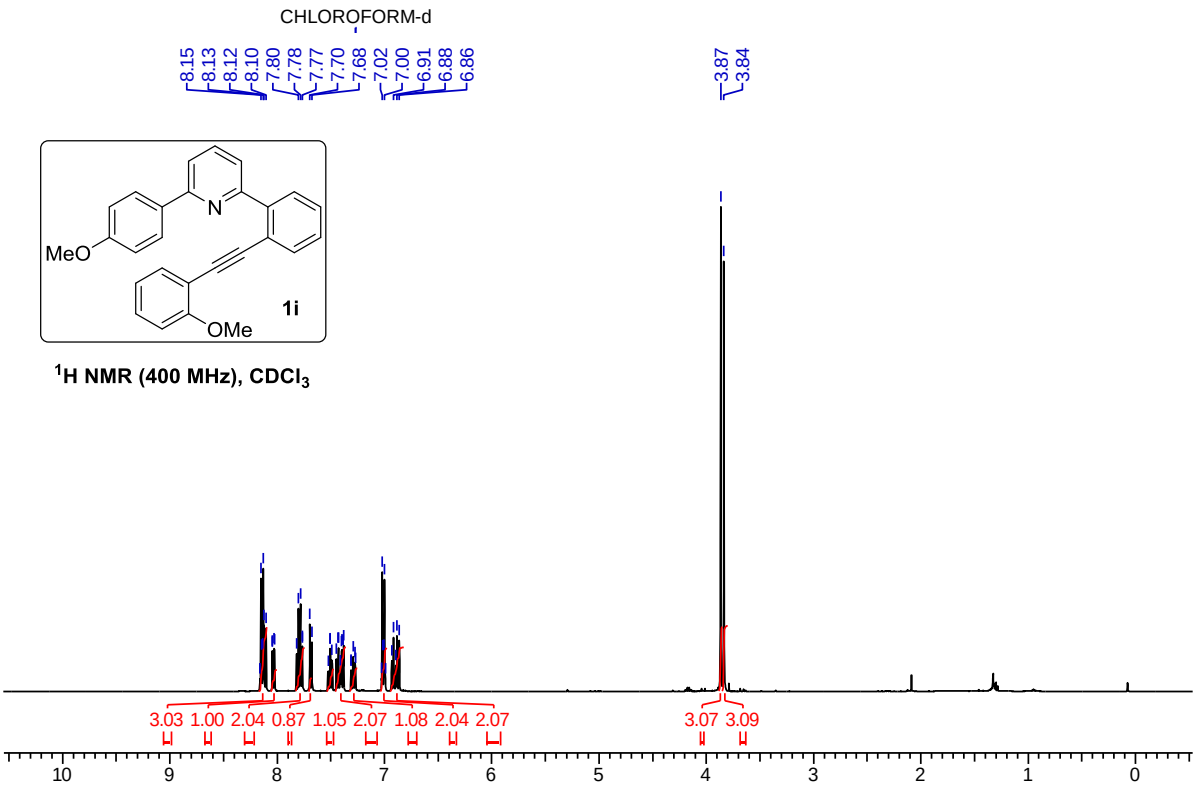
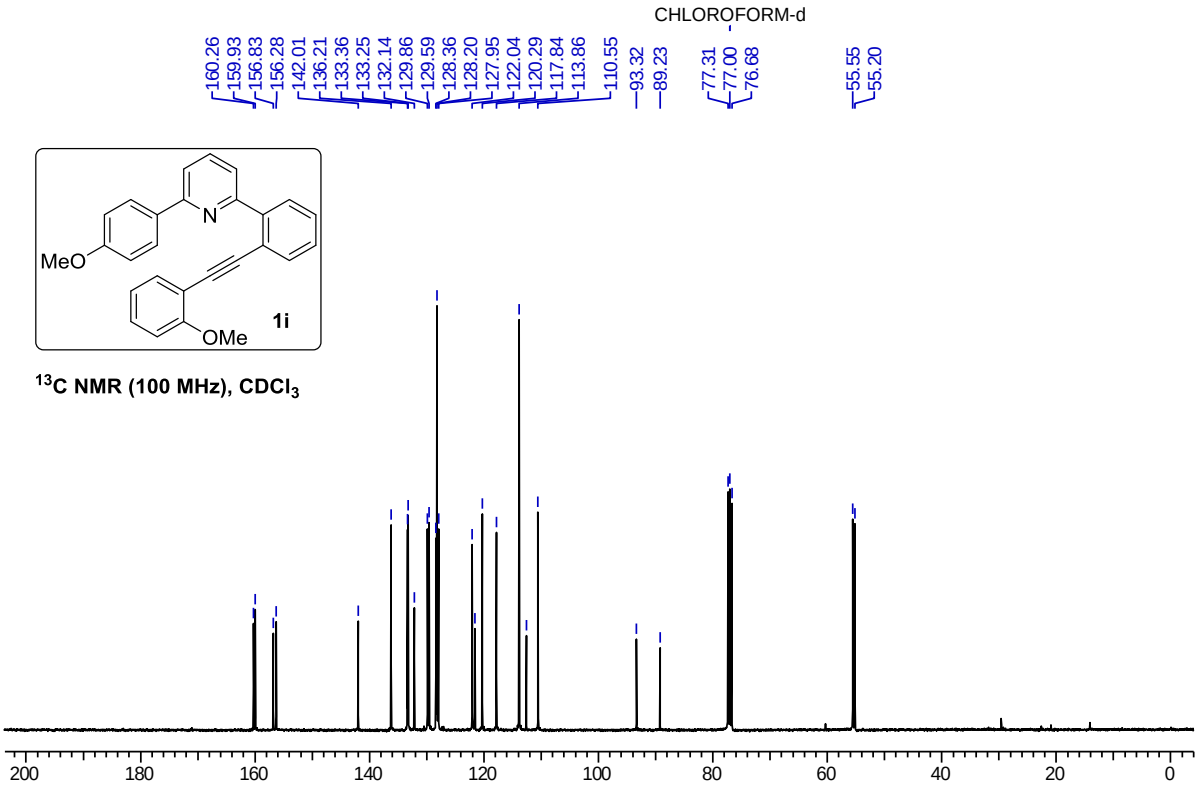
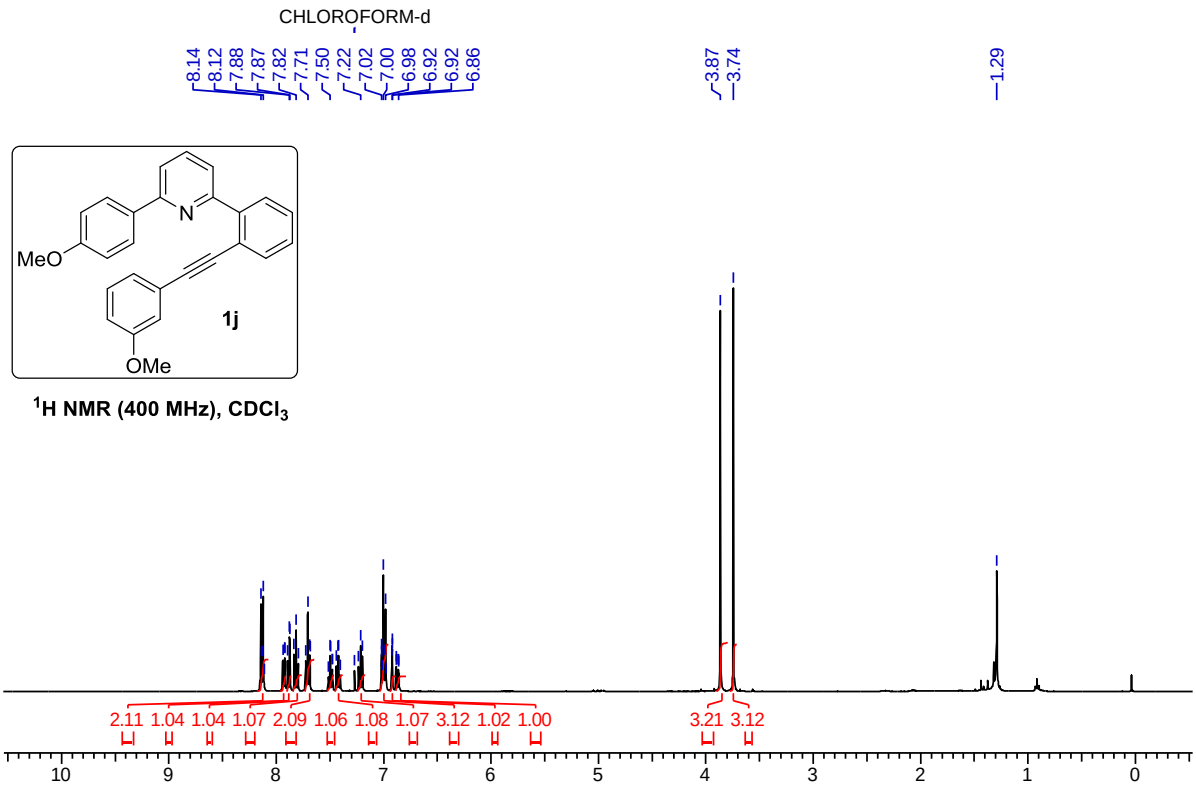
129.92
129.08
128.29
128.17
128.06
127.90
121.70
120.89
118.12
113.99
92.77
91.63
77.25
77.00
76.74
55.30
38.31
26.40
22.43
13.91
MeO
N
O
C4H9
1h
13C NMR (125 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0



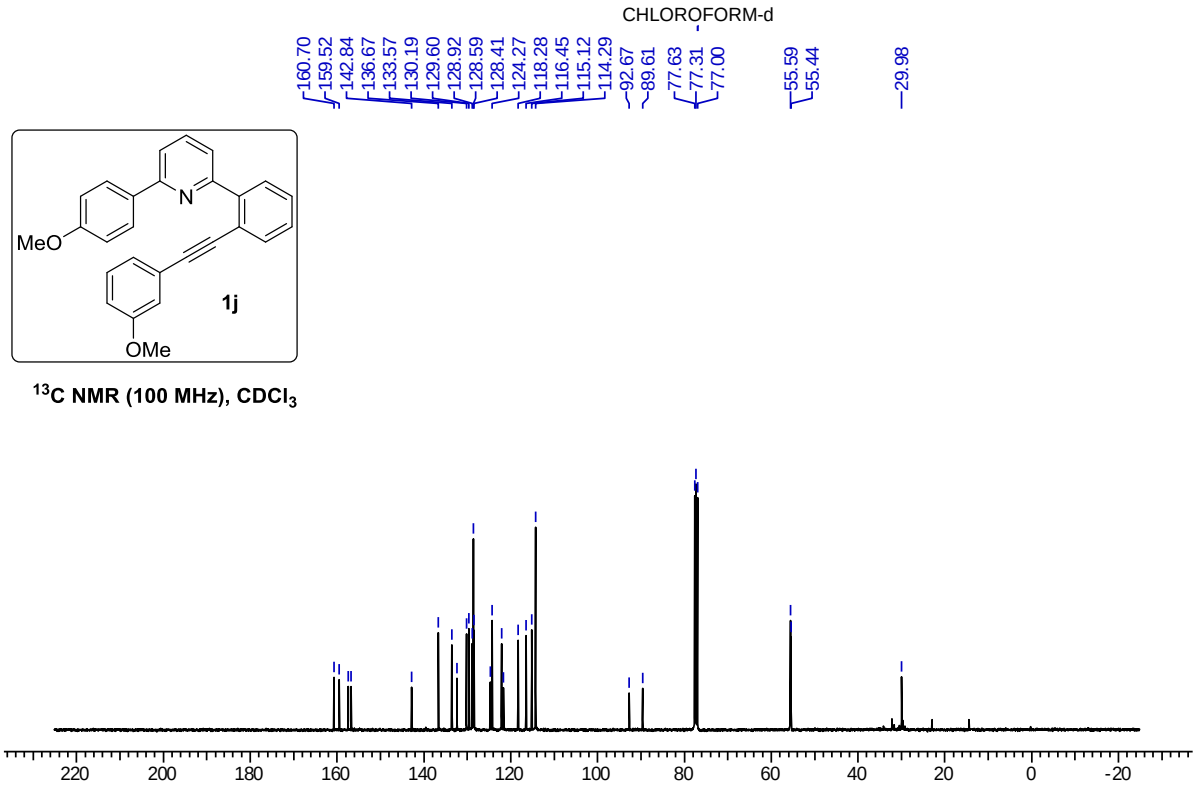
^{1}H NMR (400 MHz), $CDCl_3$



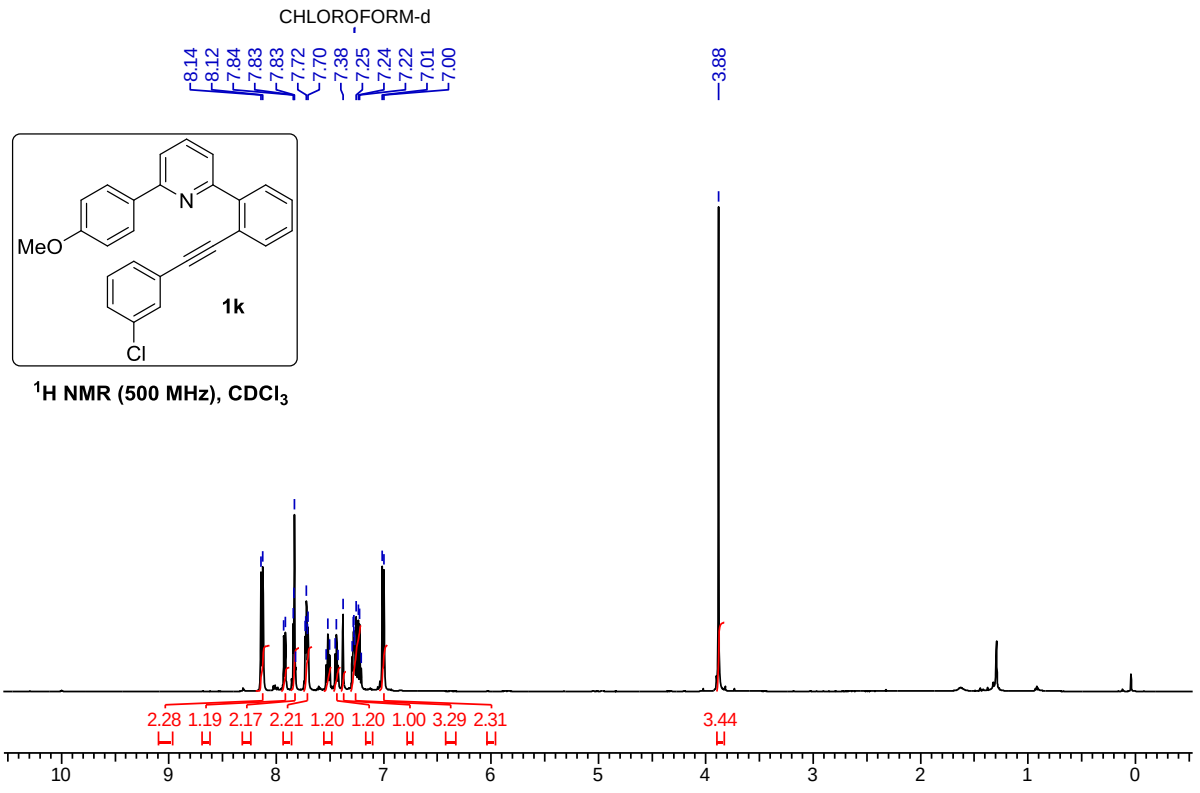
^{13}C NMR (100 MHz), $CDCl_3$



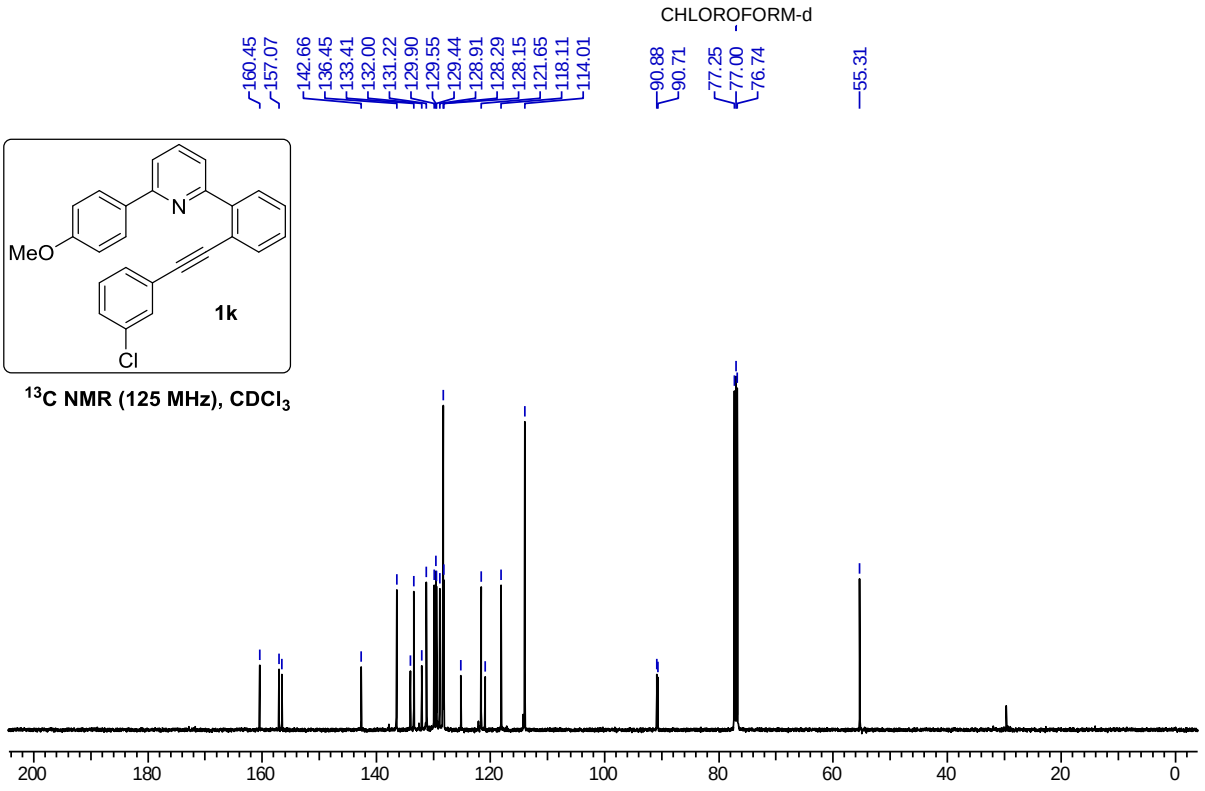
^{1}H NMR (400 MHz), $CDCl_3$



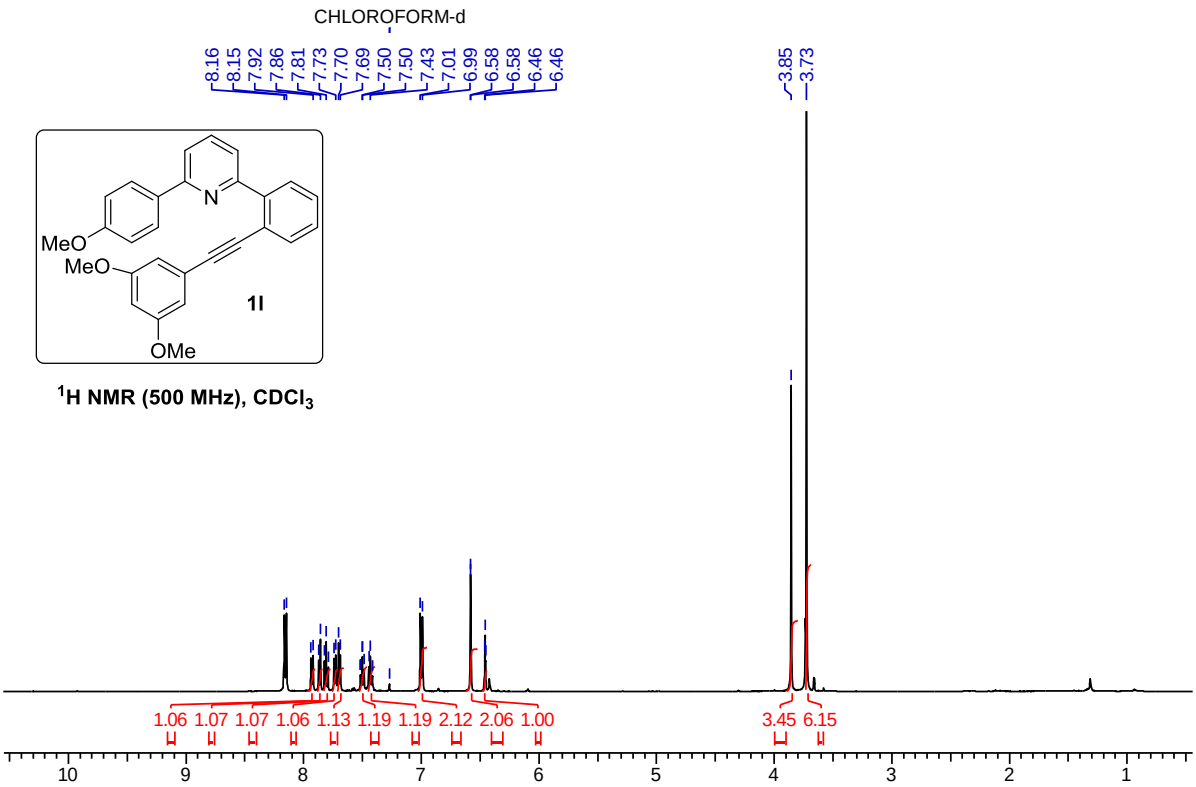
^{13}C NMR (100 MHz), $CDCl_3$



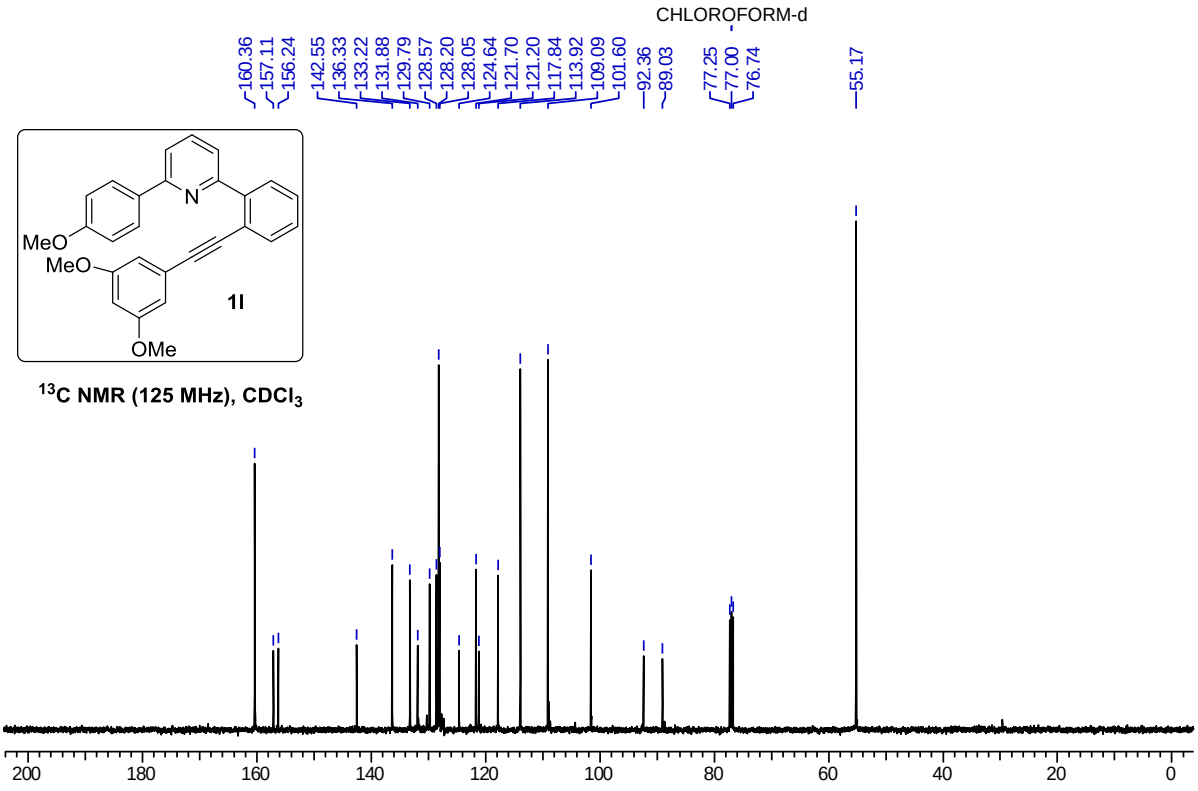
^{1}H NMR (500 MHz), $CDCl_3$



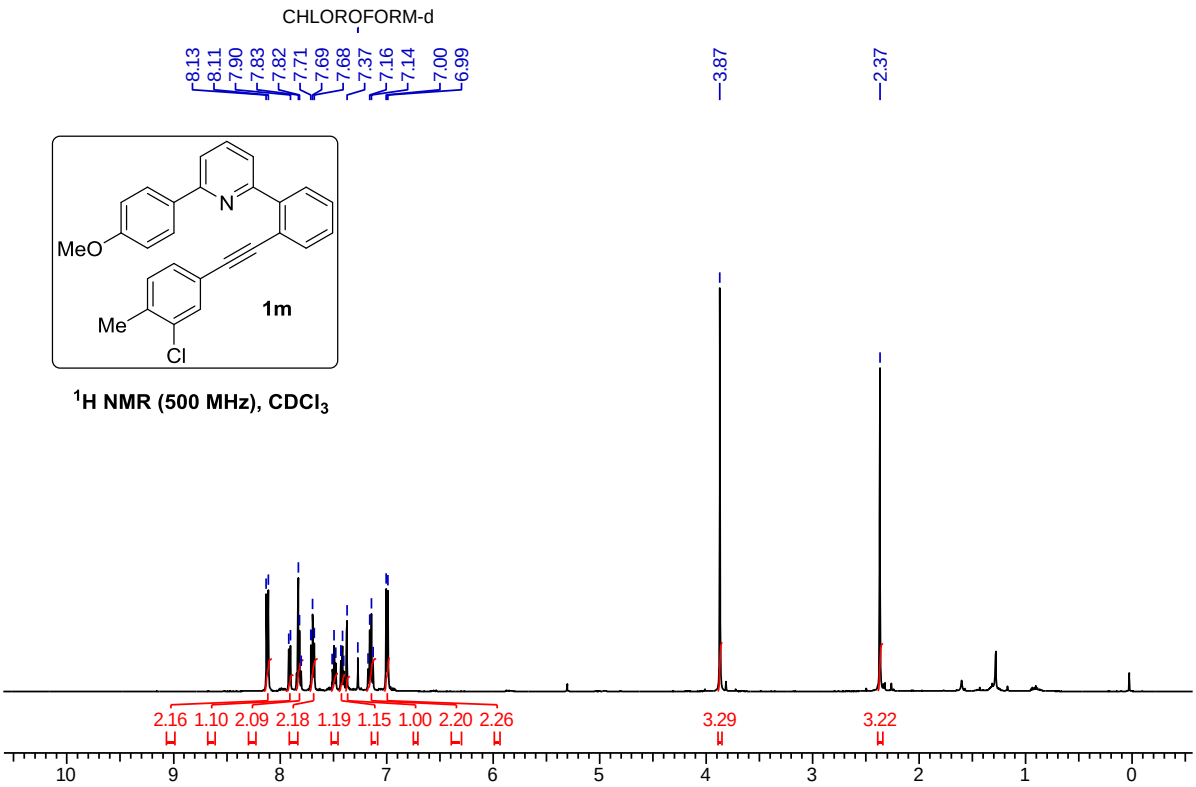
^{13}C NMR (125 MHz), $CDCl_3$



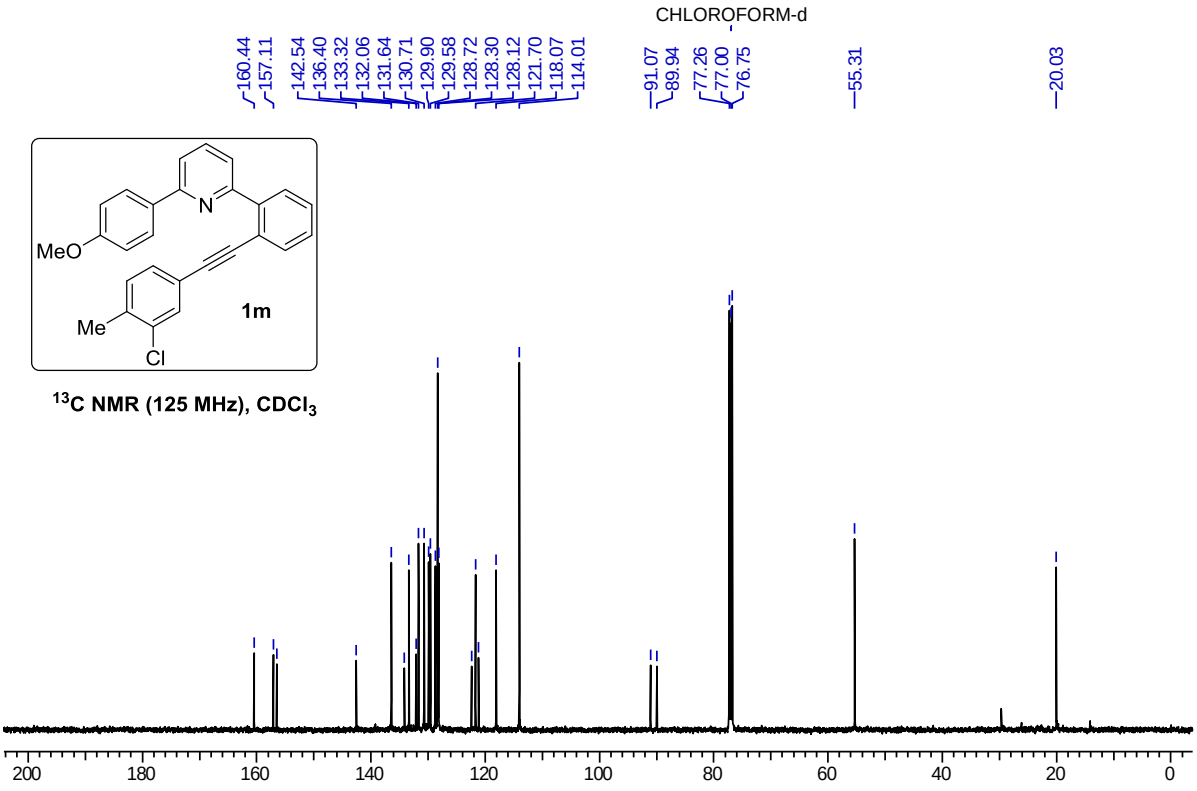
^{1}H NMR (500 MHz), $CDCl_3$



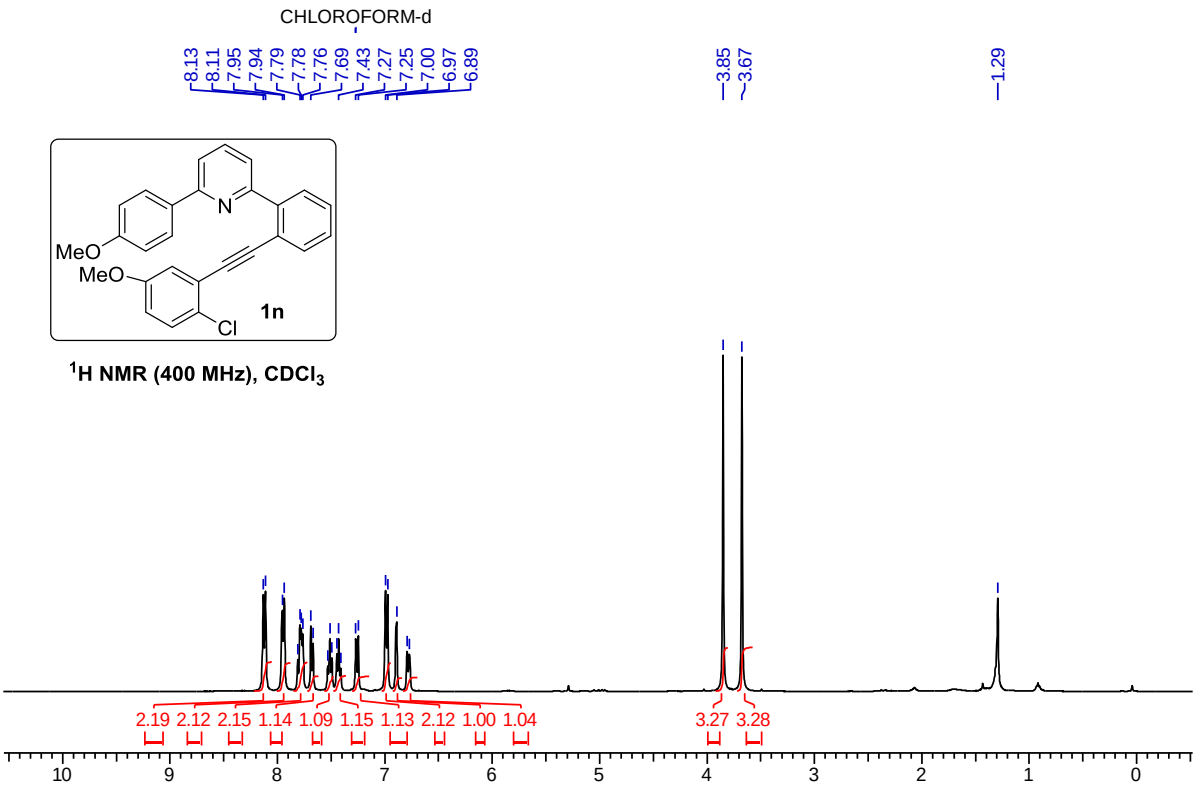
^{13}C NMR (125 MHz), $CDCl_3$



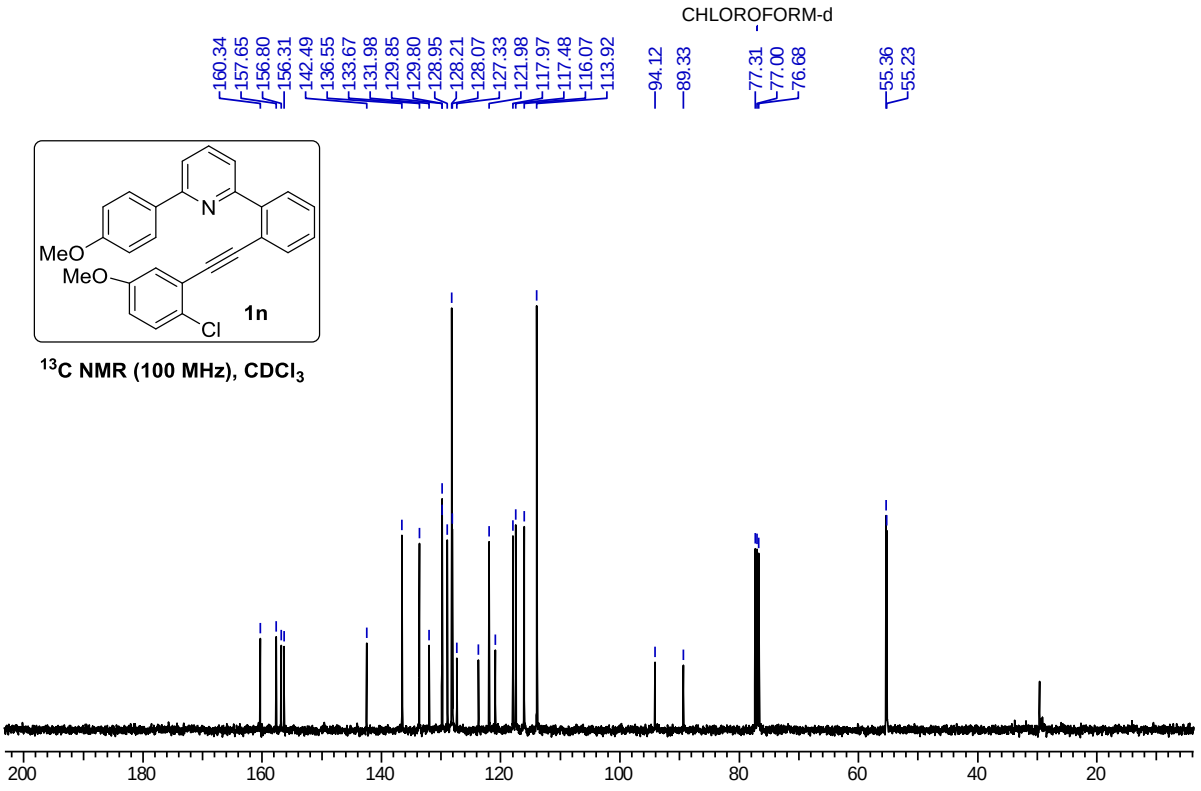
^{1}H NMR (500 MHz), $CDCl_3$



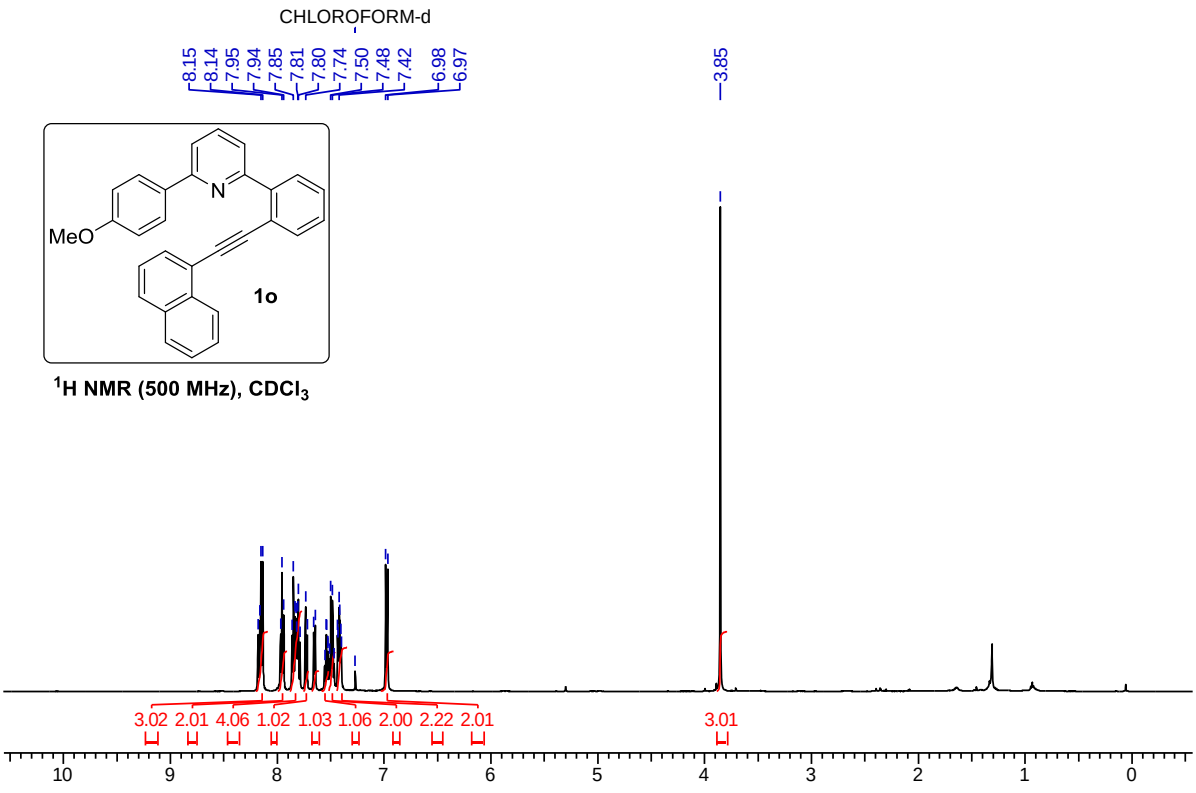
^{13}C NMR (125 MHz), $CDCl_3$



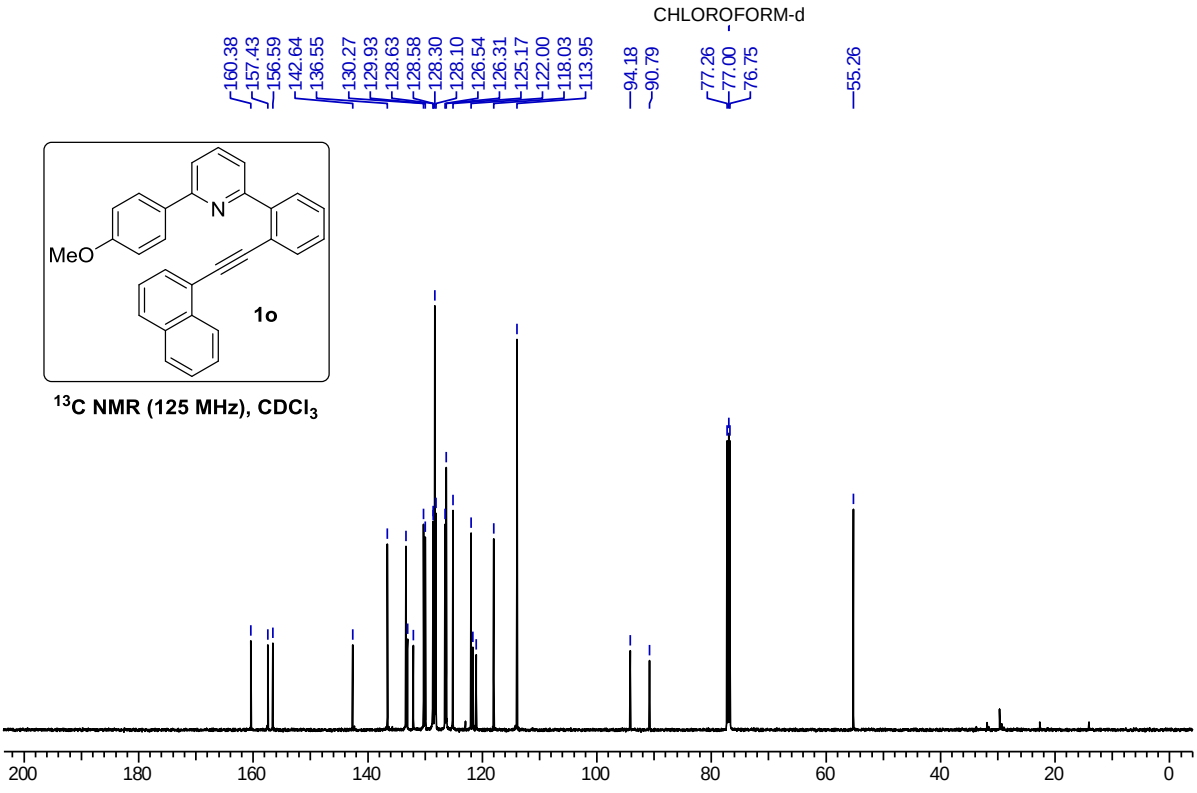
^{1}H NMR (400 MHz), $CDCl_3$



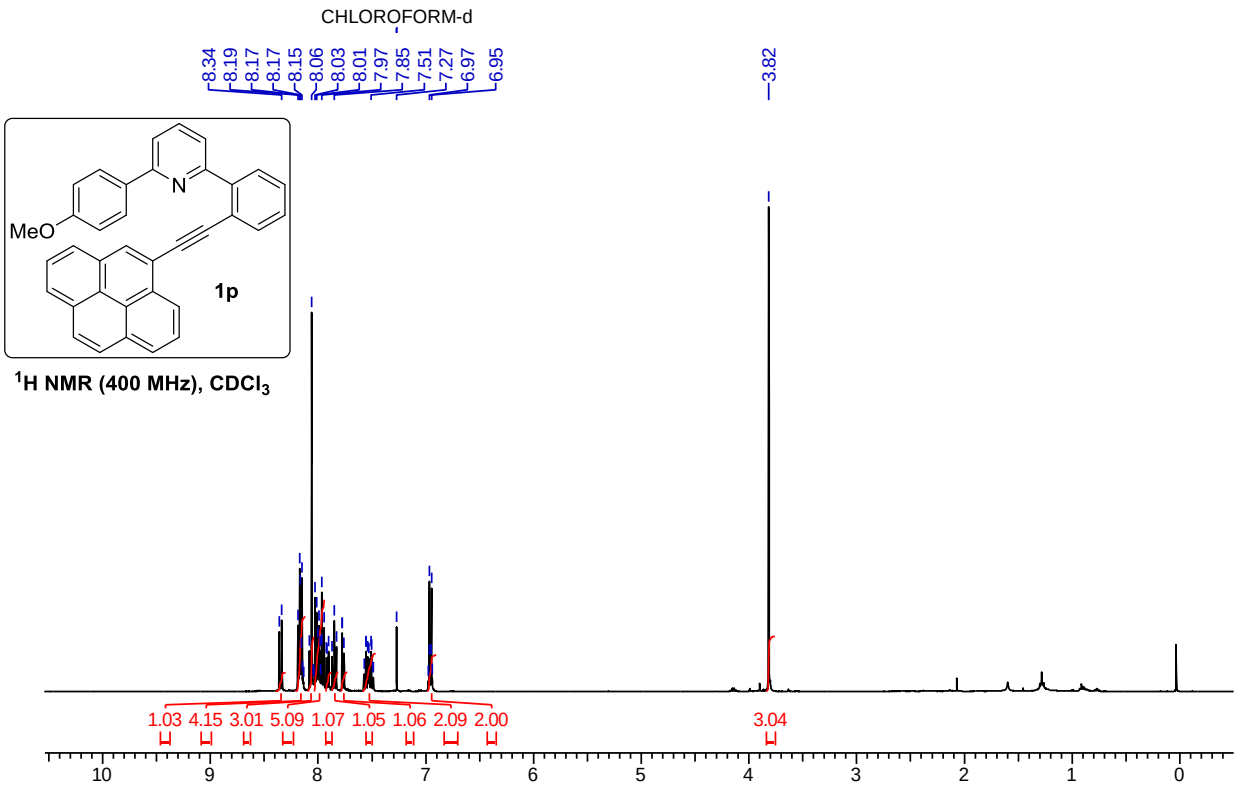
^{13}C NMR (100 MHz), $CDCl_3$



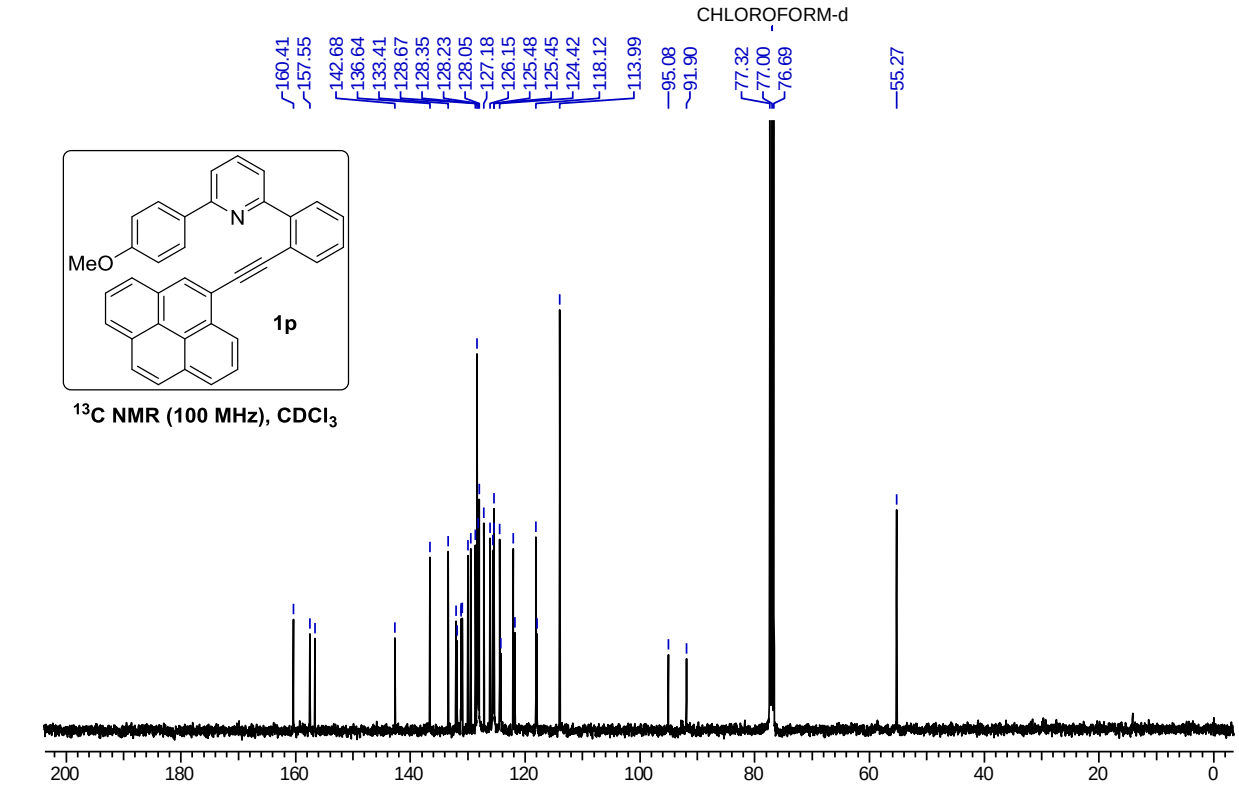
^{1}H NMR (500 MHz), $CDCl_3$



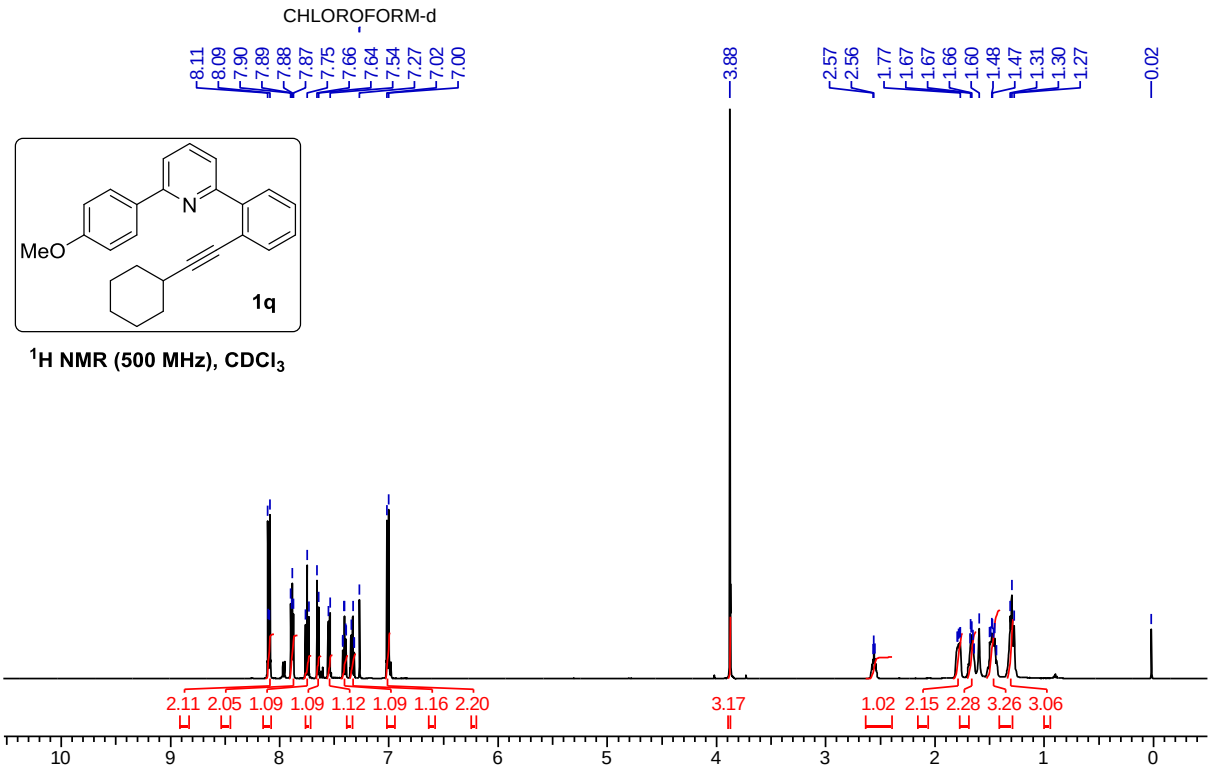
^{13}C NMR (125 MHz), $CDCl_3$



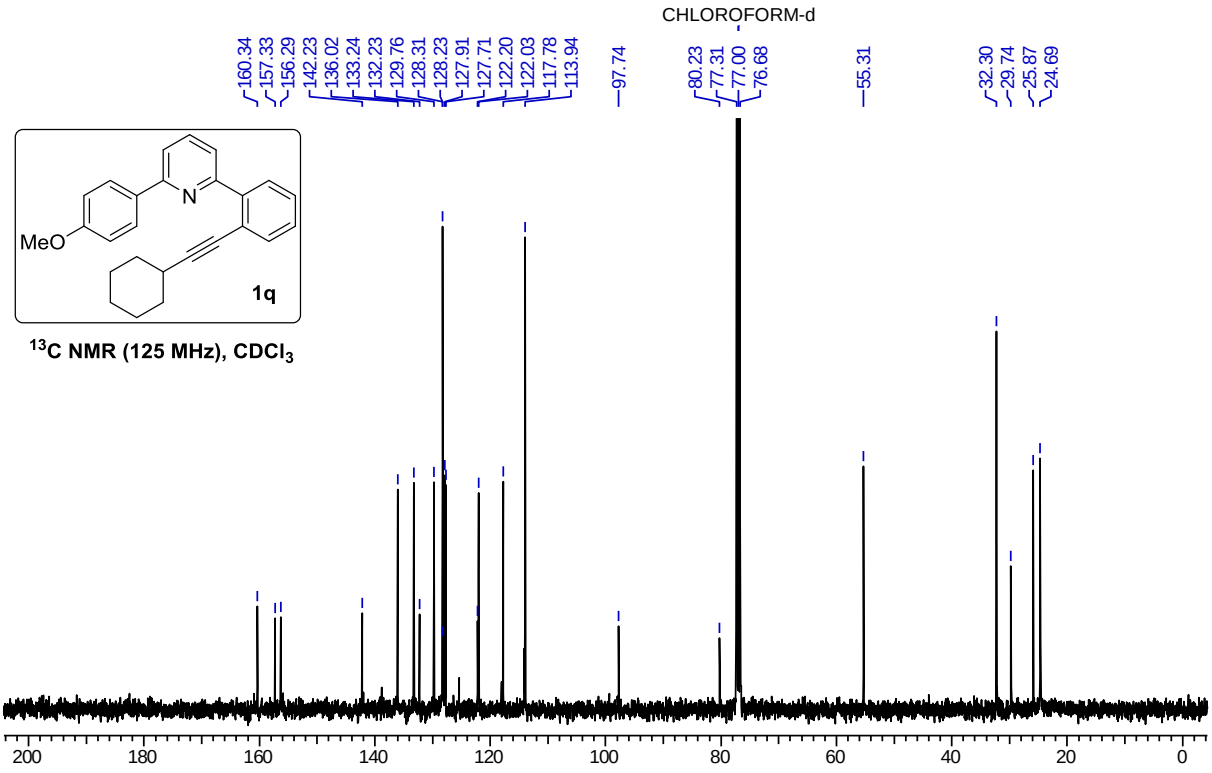
^{1}H NMR (400 MHz), $CDCl_3$



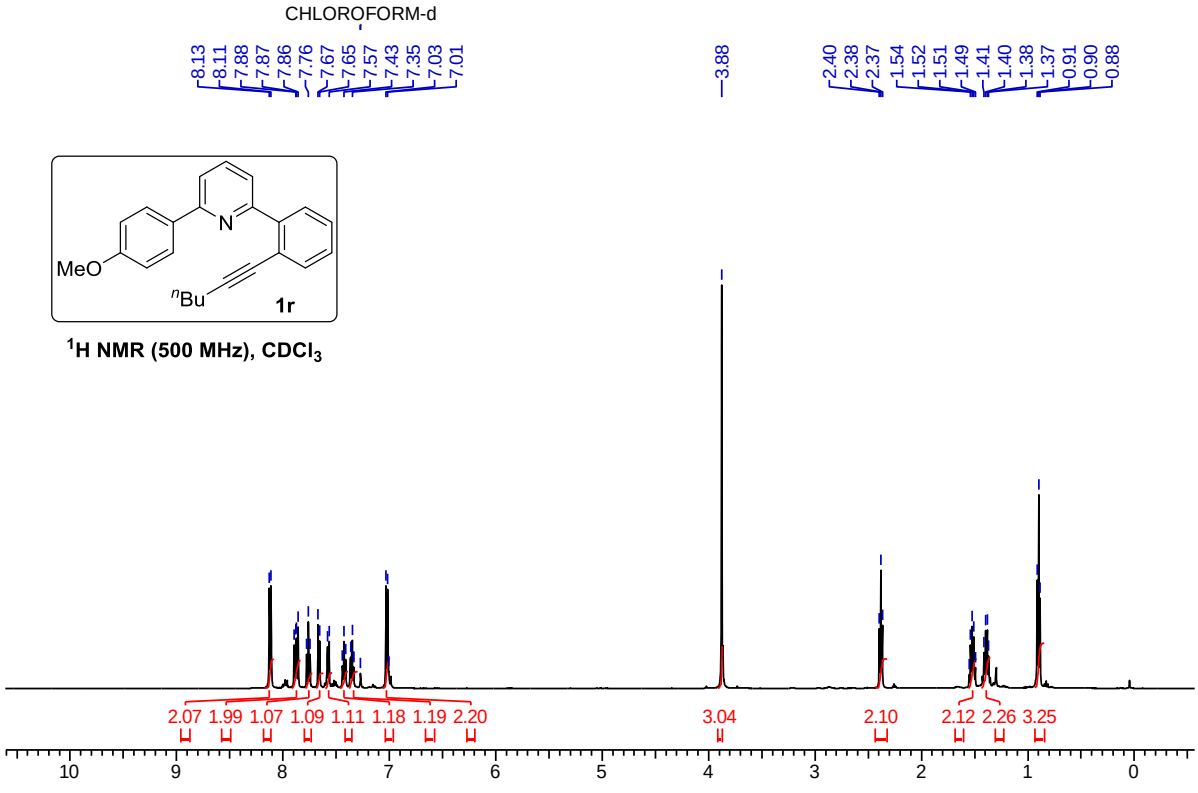
^{13}C NMR (100 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (125 MHz), $CDCl_3$



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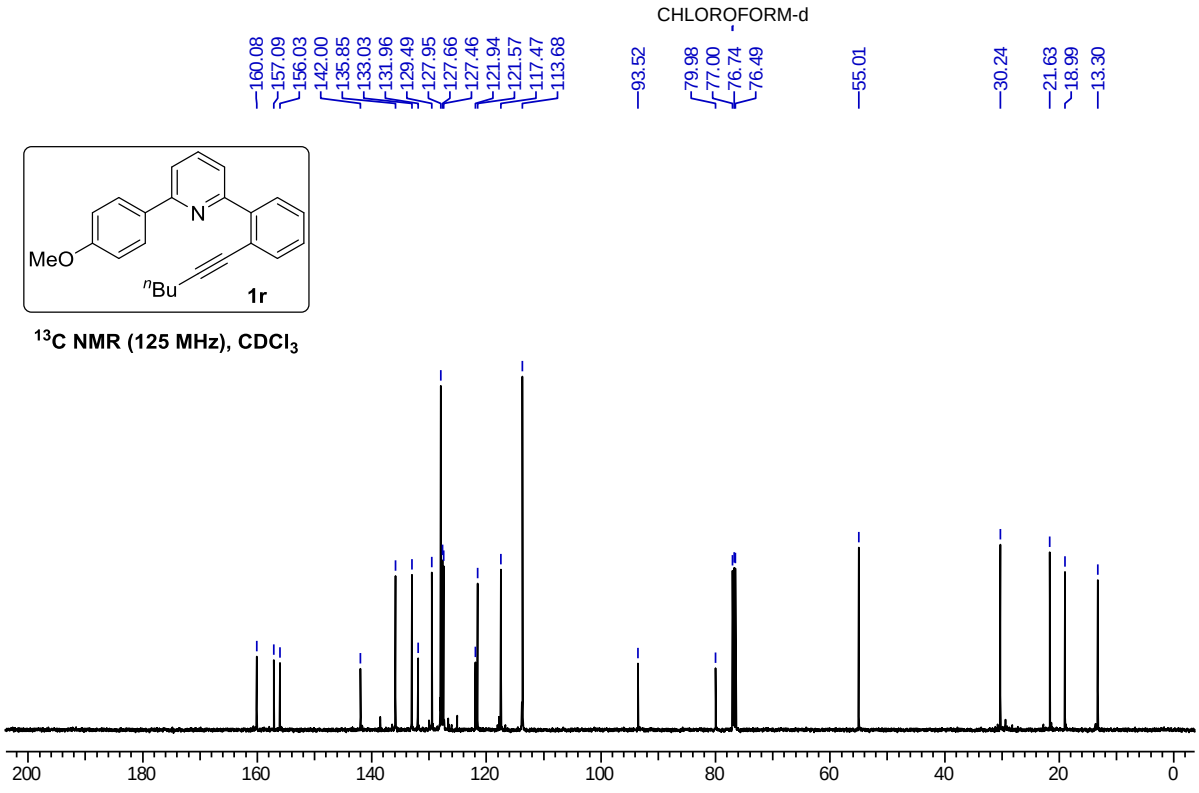

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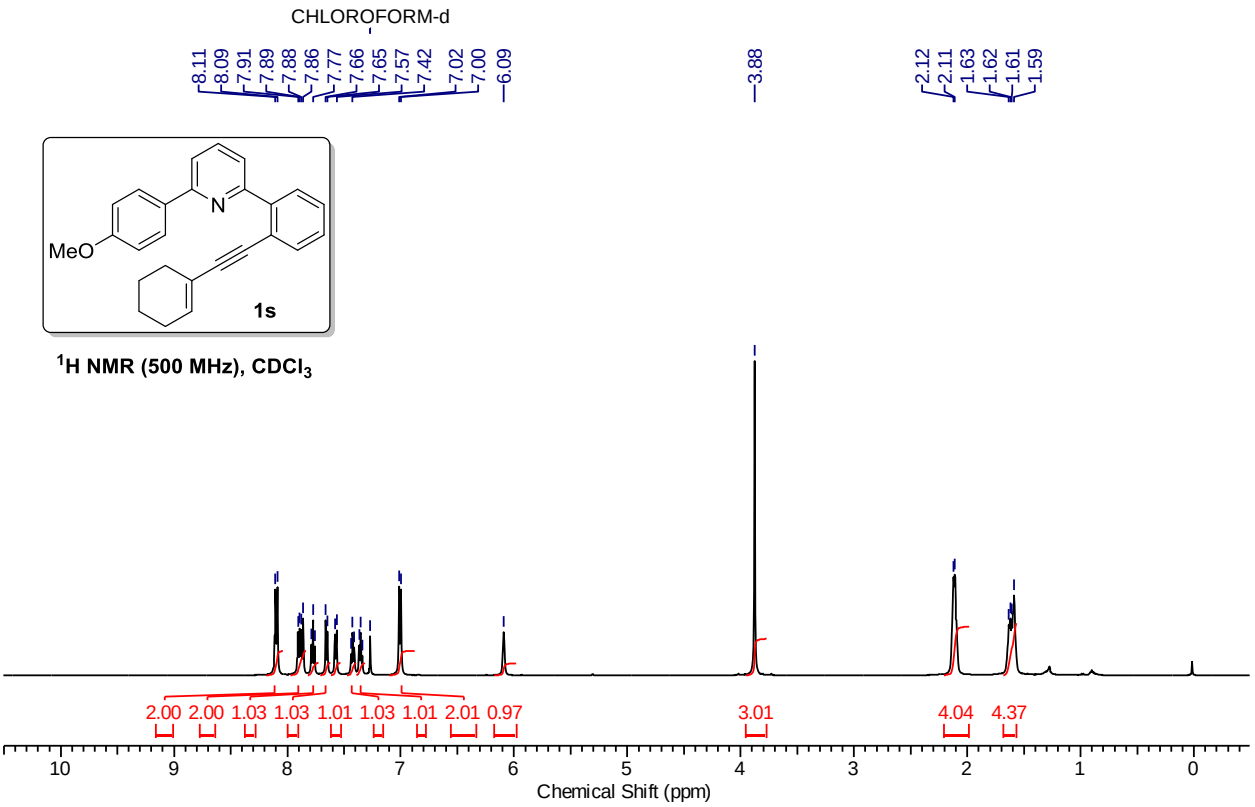

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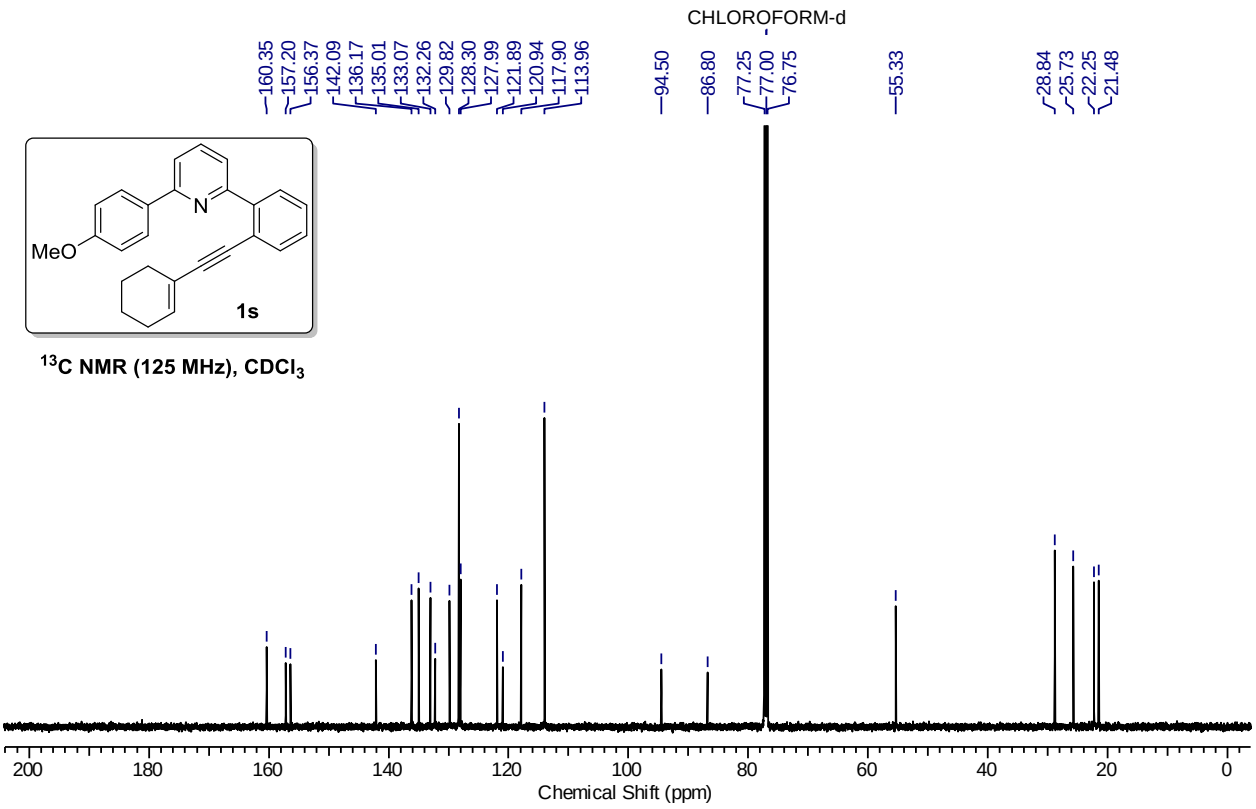
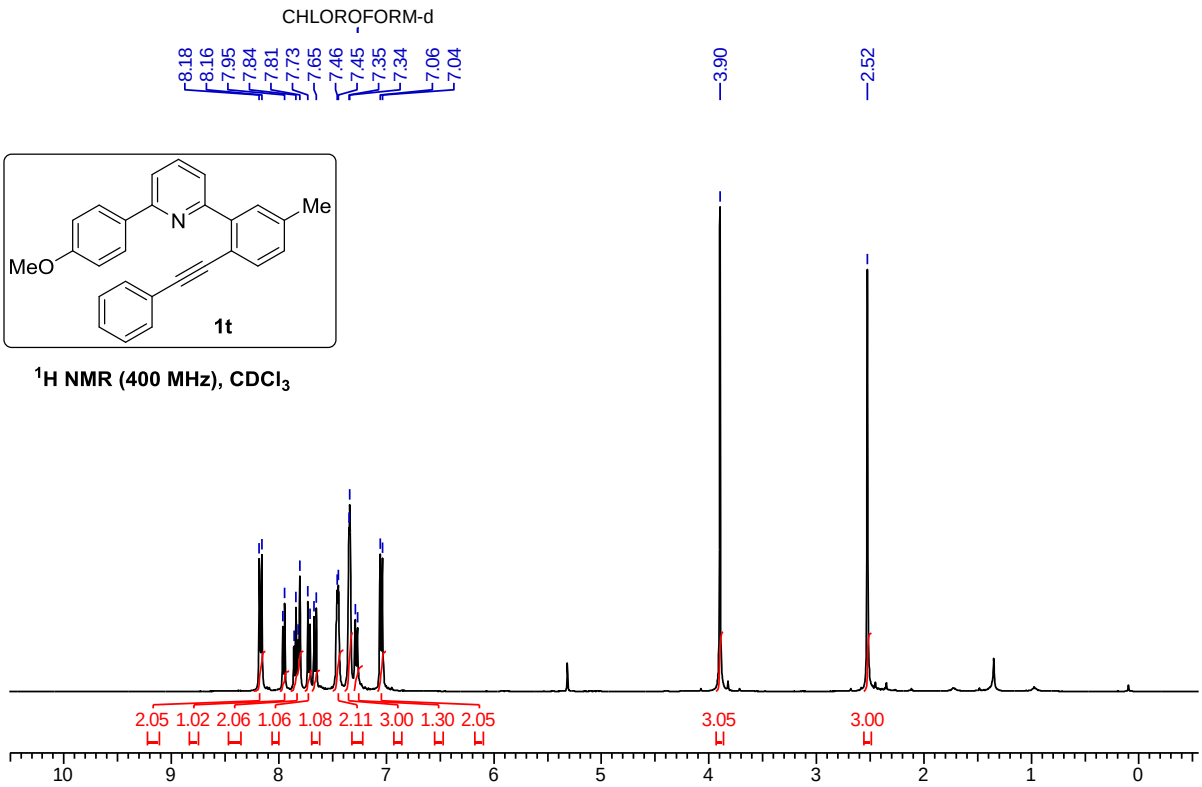


^{13}C NMR (125 MHz), $CDCl_3$



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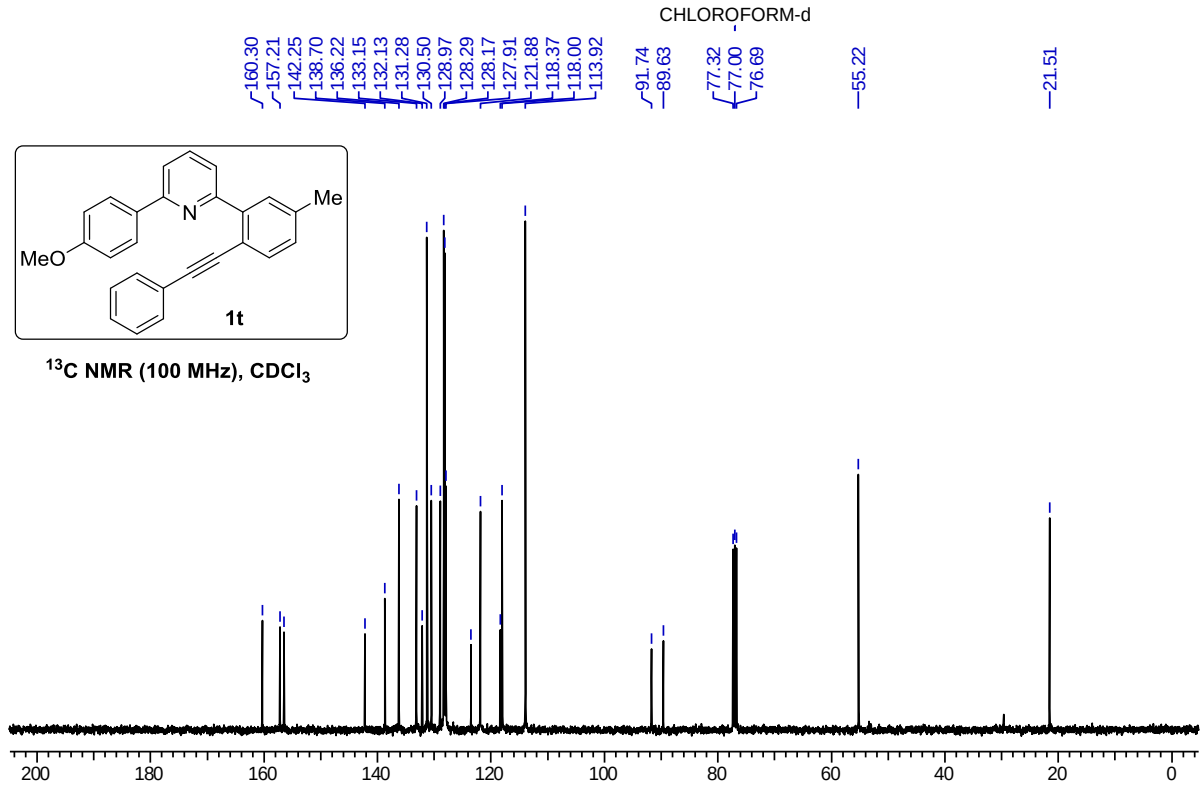

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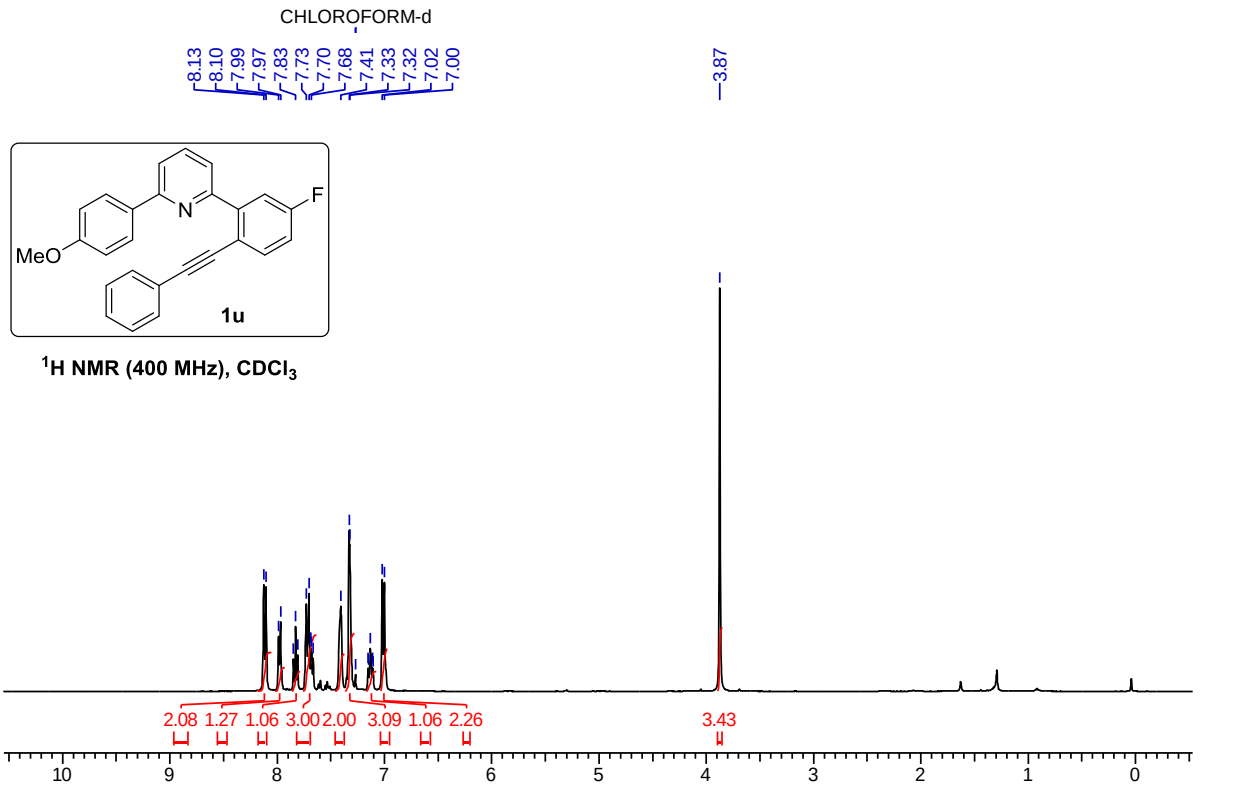

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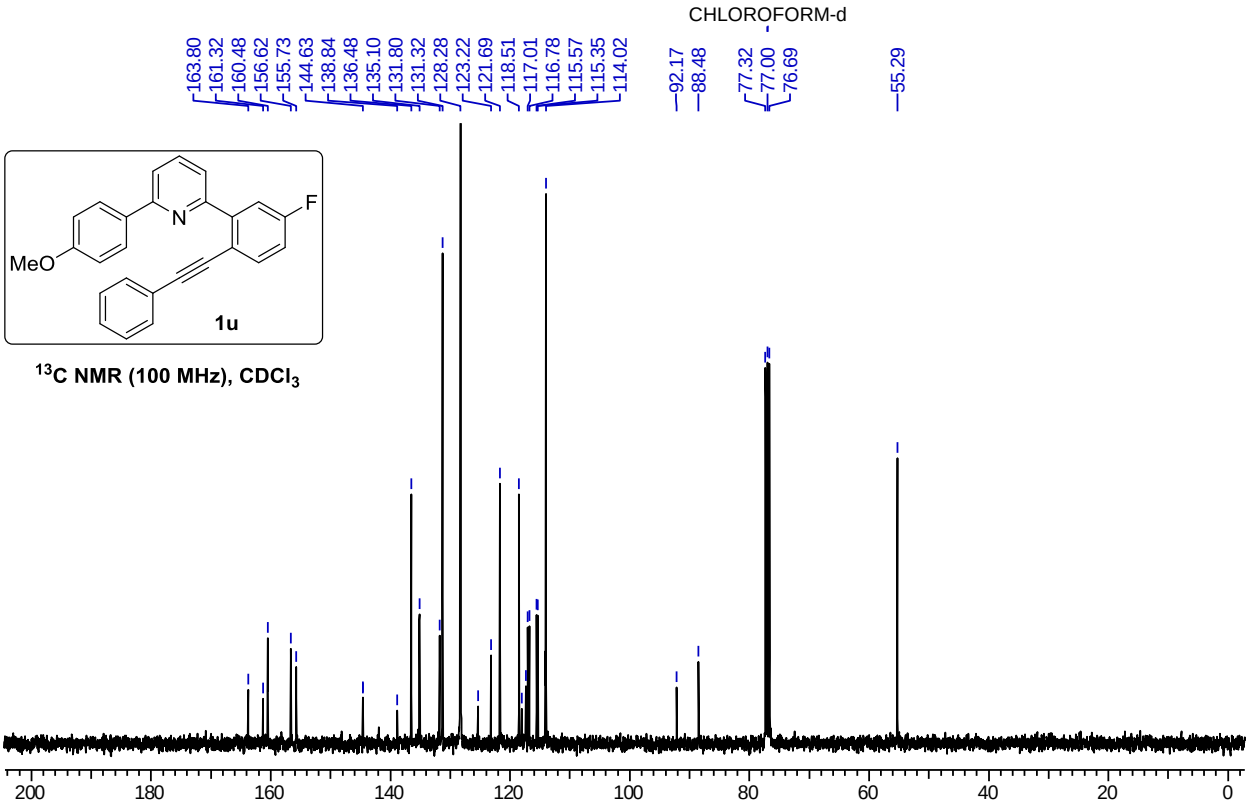
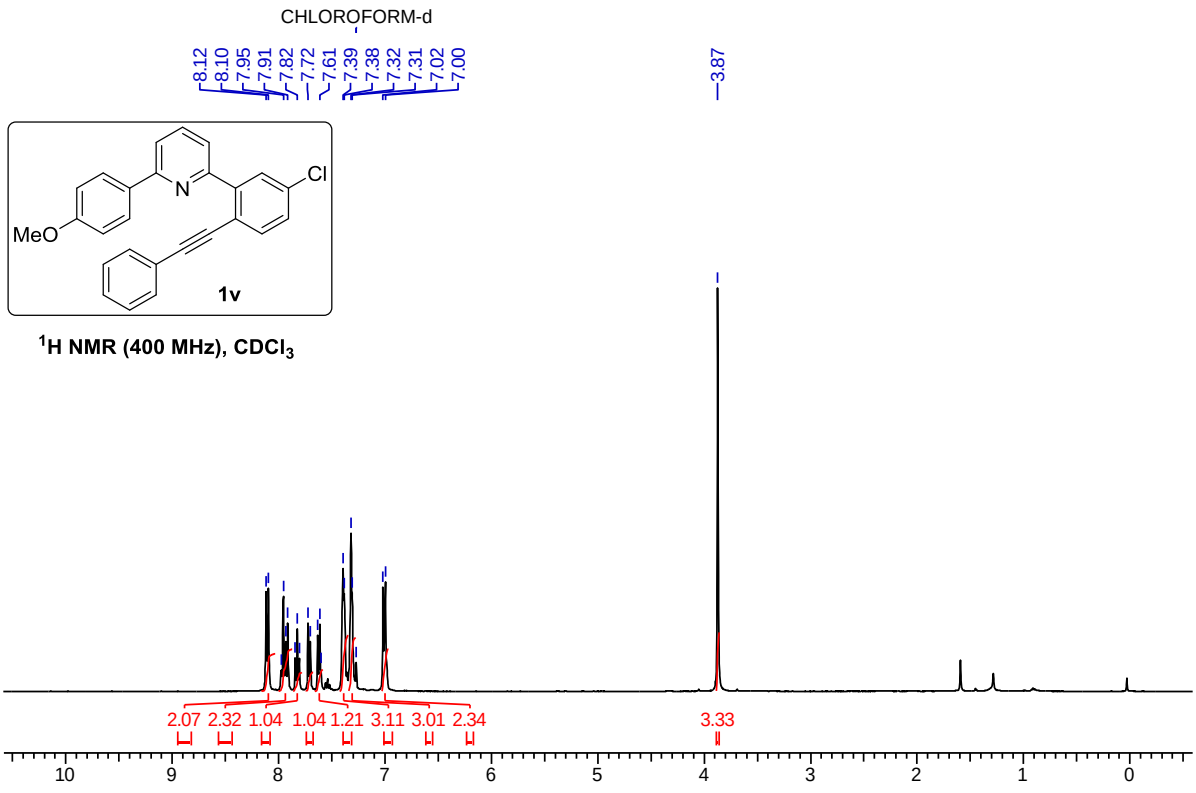
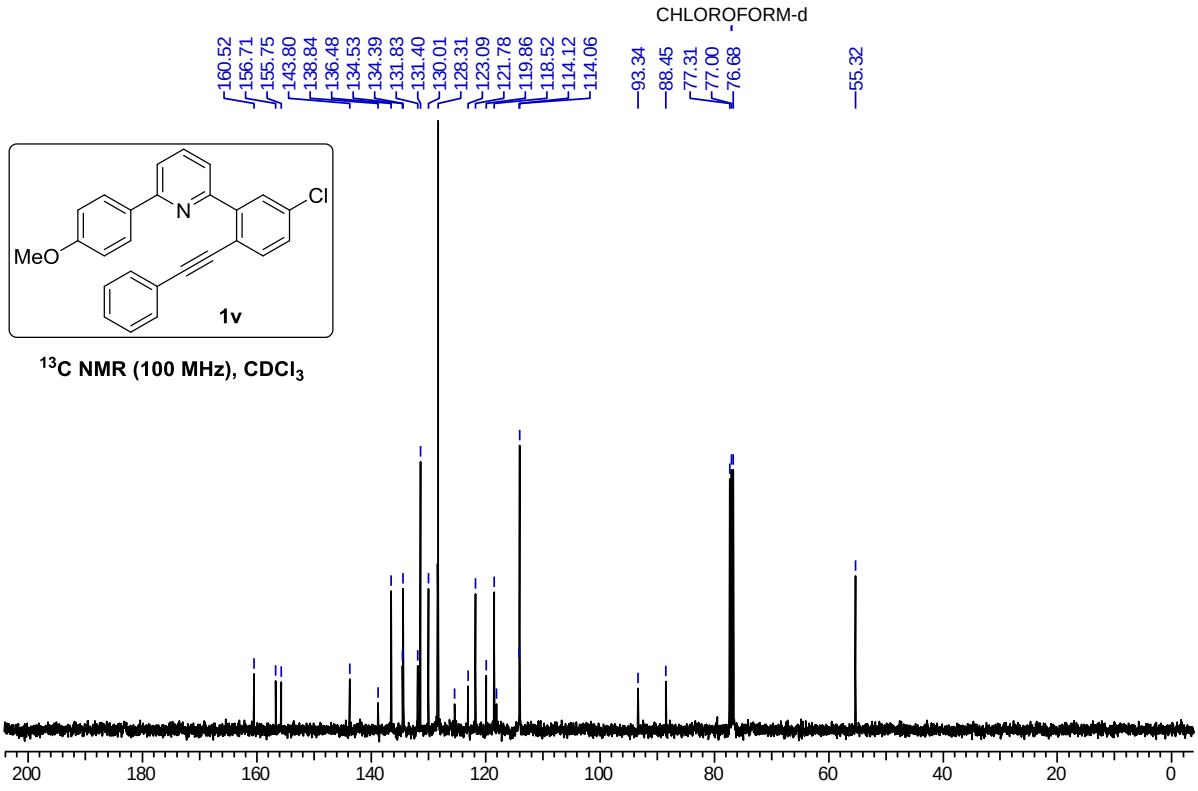


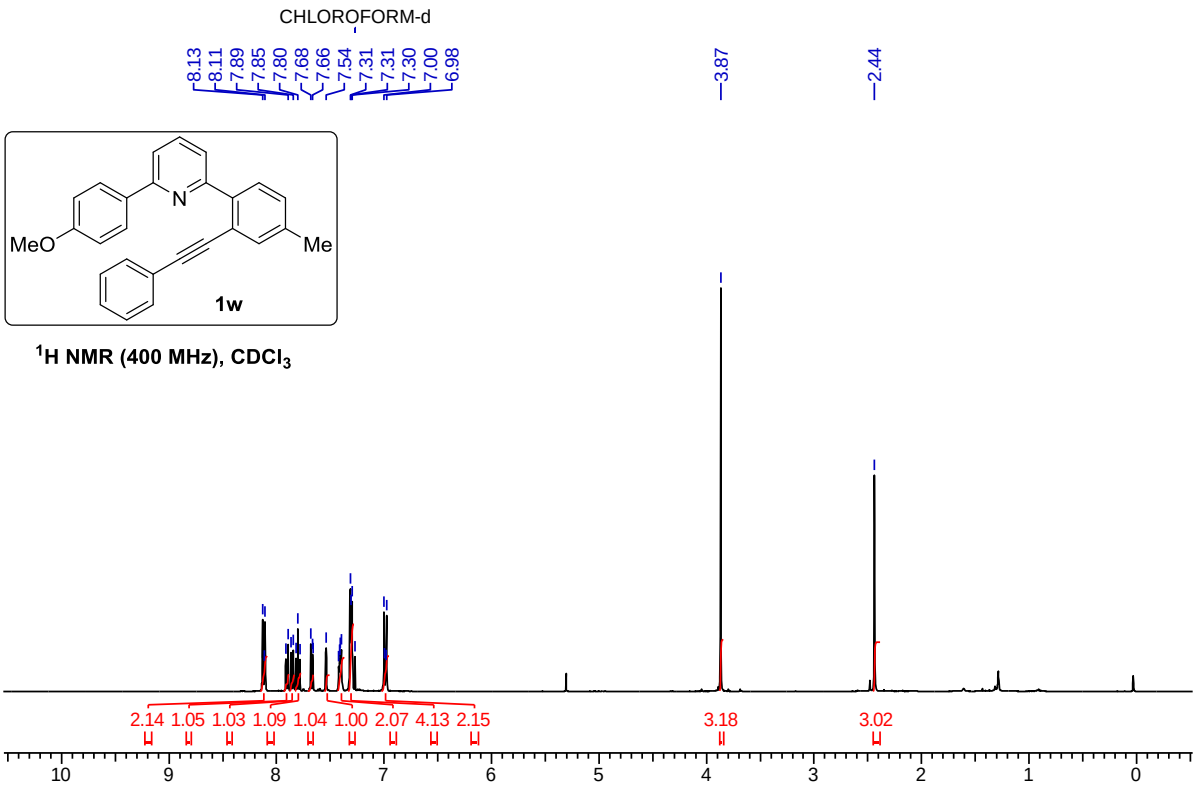
^{13}C NMR (100 MHz), $CDCl_3$



^{1}H NMR (400 MHz), $CDCl_3$



^{13}C NMR (100 MHz), $CDCl_3$



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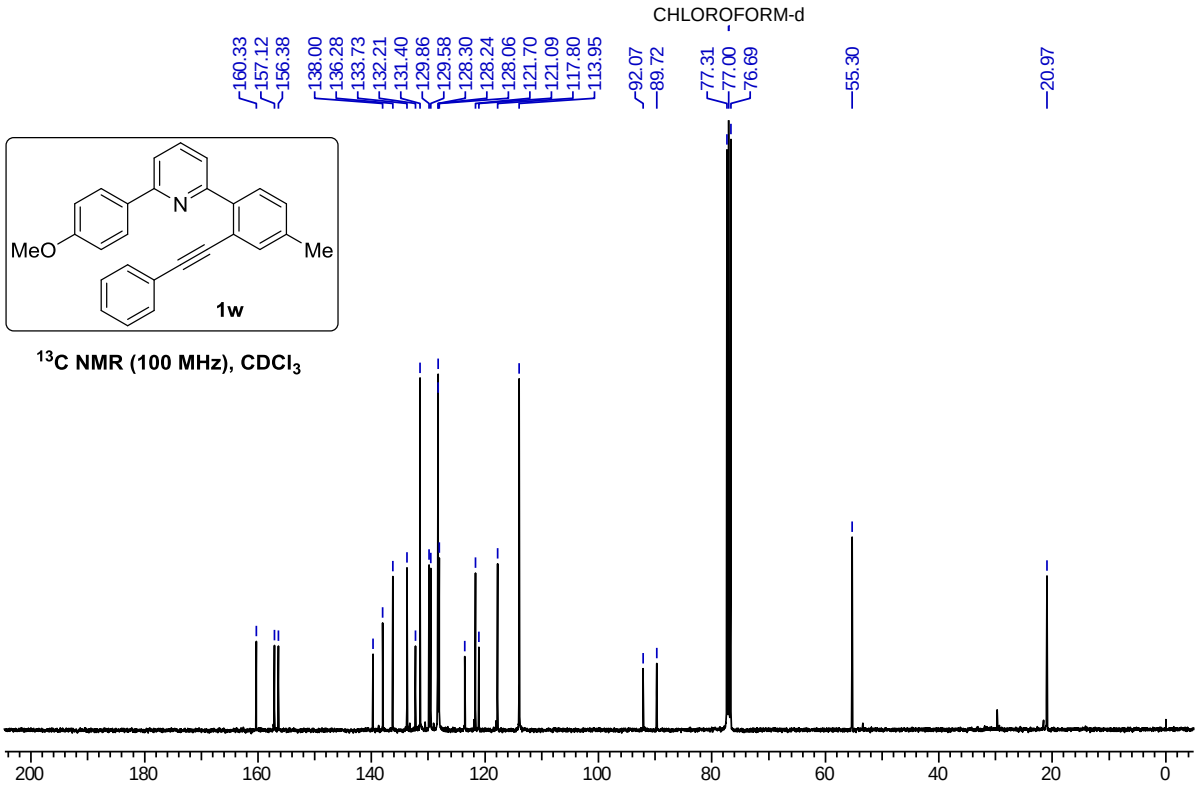
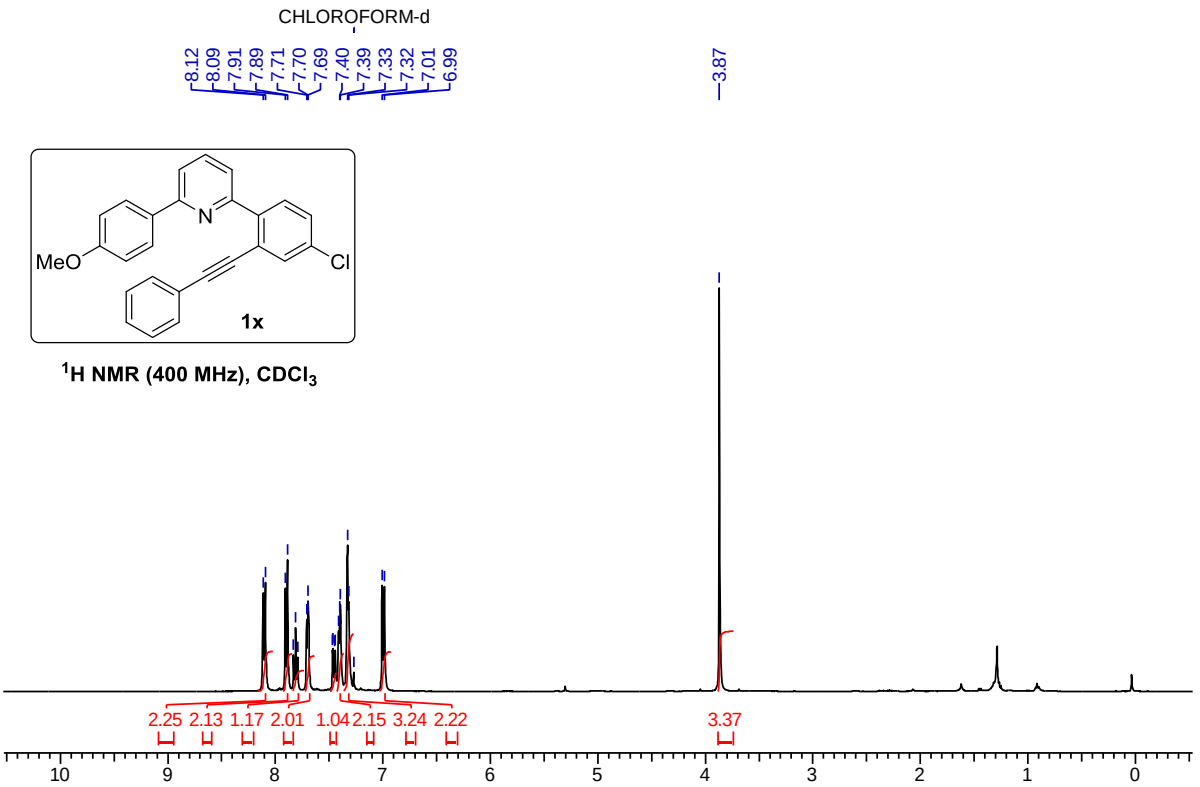


^{13}C NMR (100 MHz), $CDCl_3$



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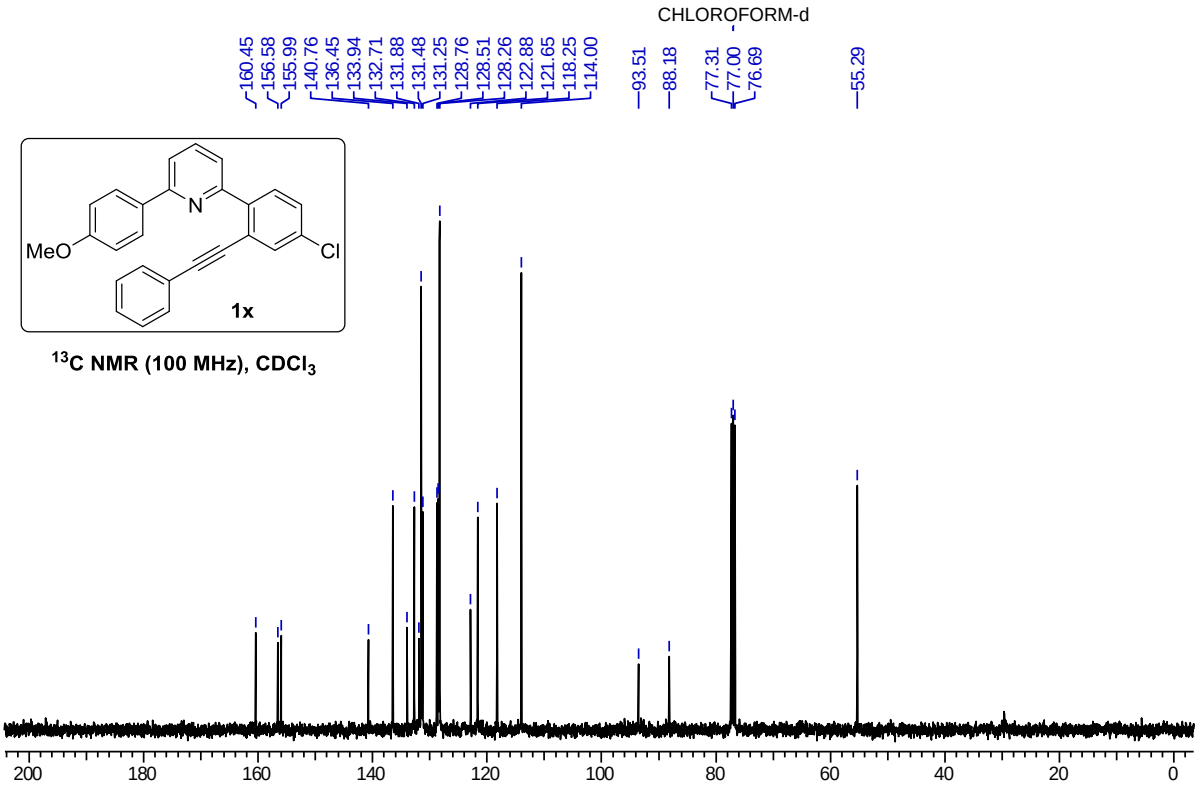

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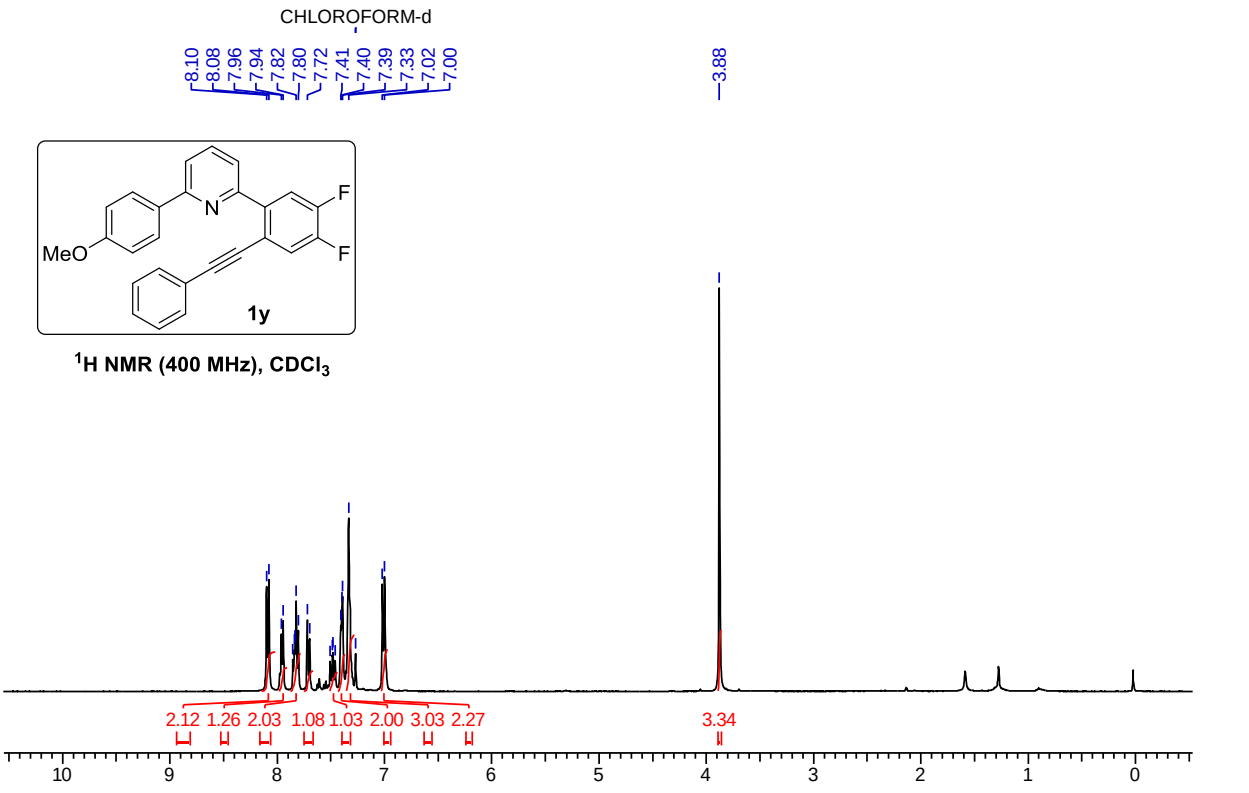

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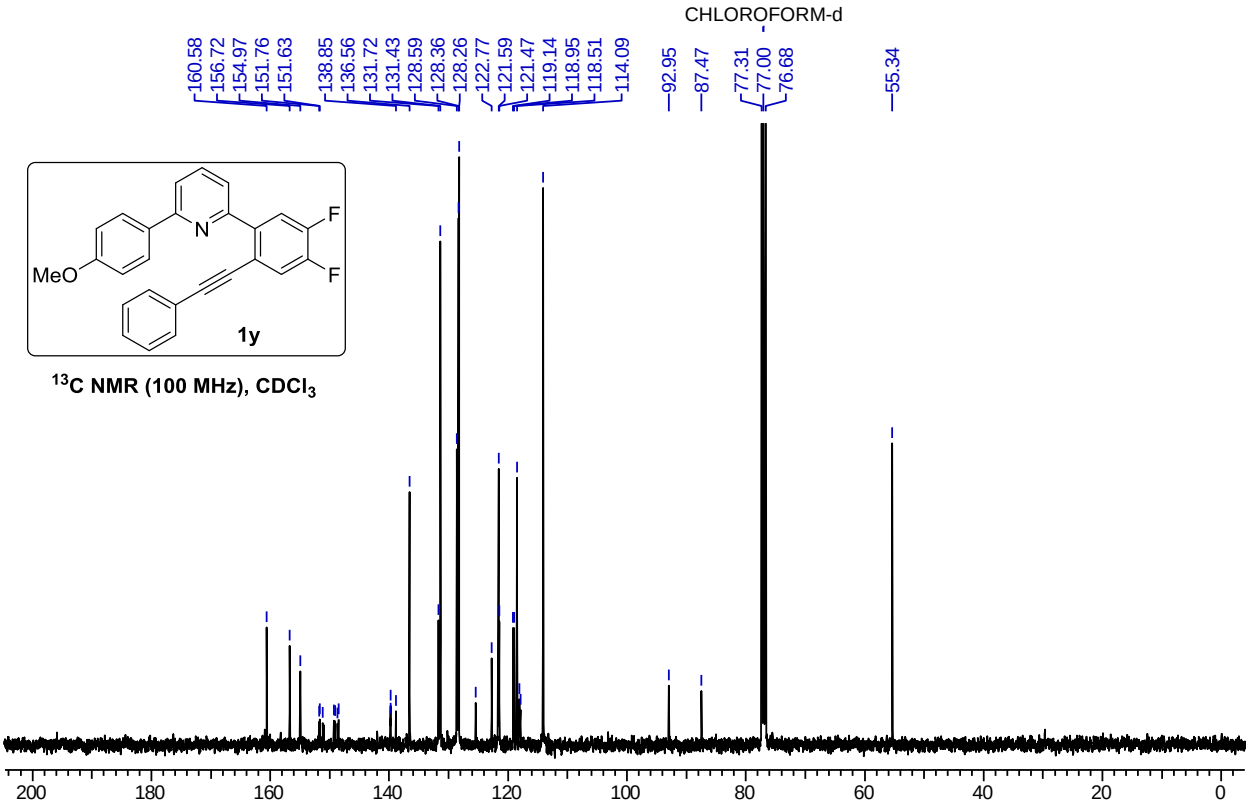
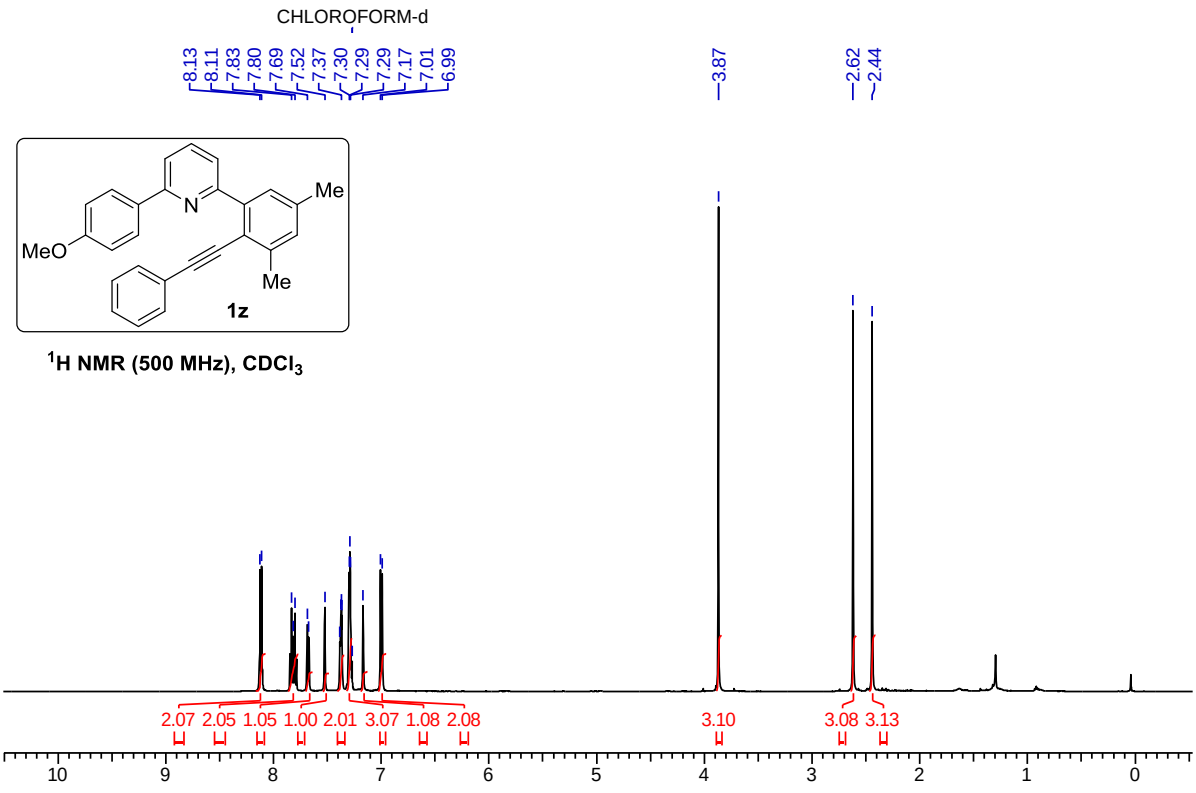
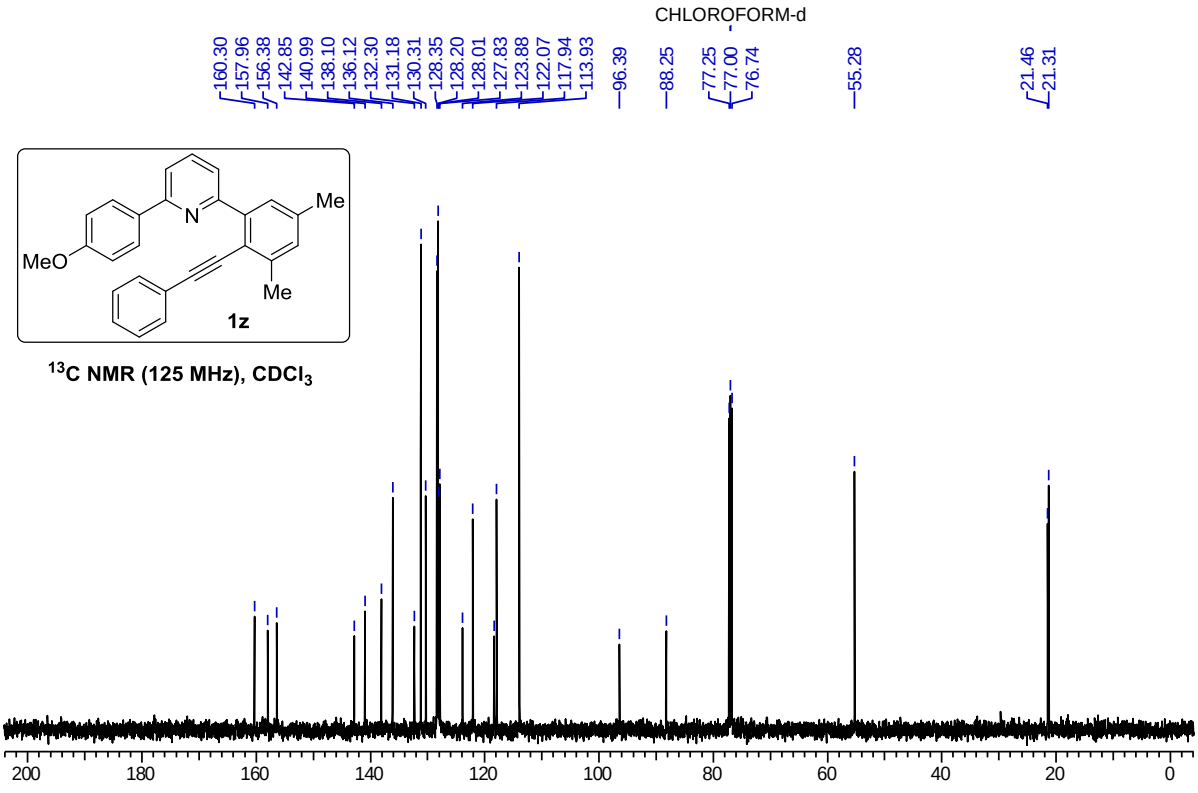


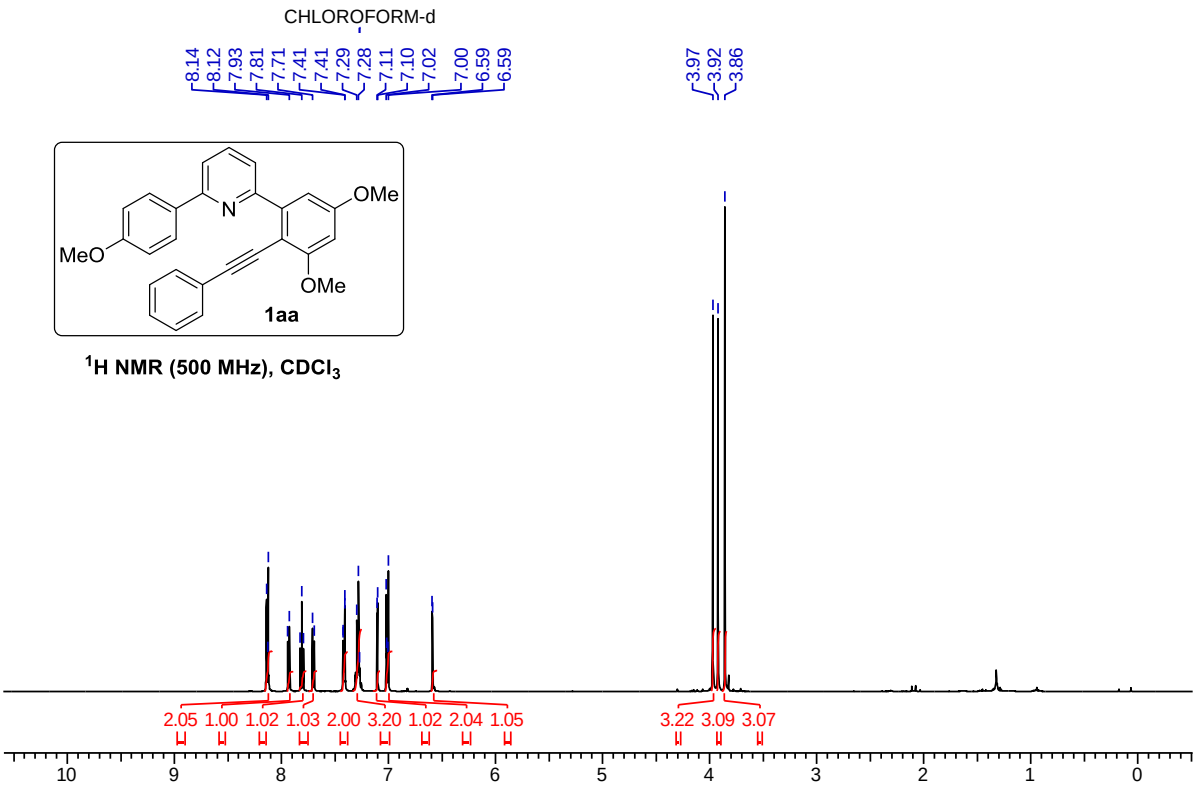
^{13}C NMR (100 MHz), $CDCl_3$



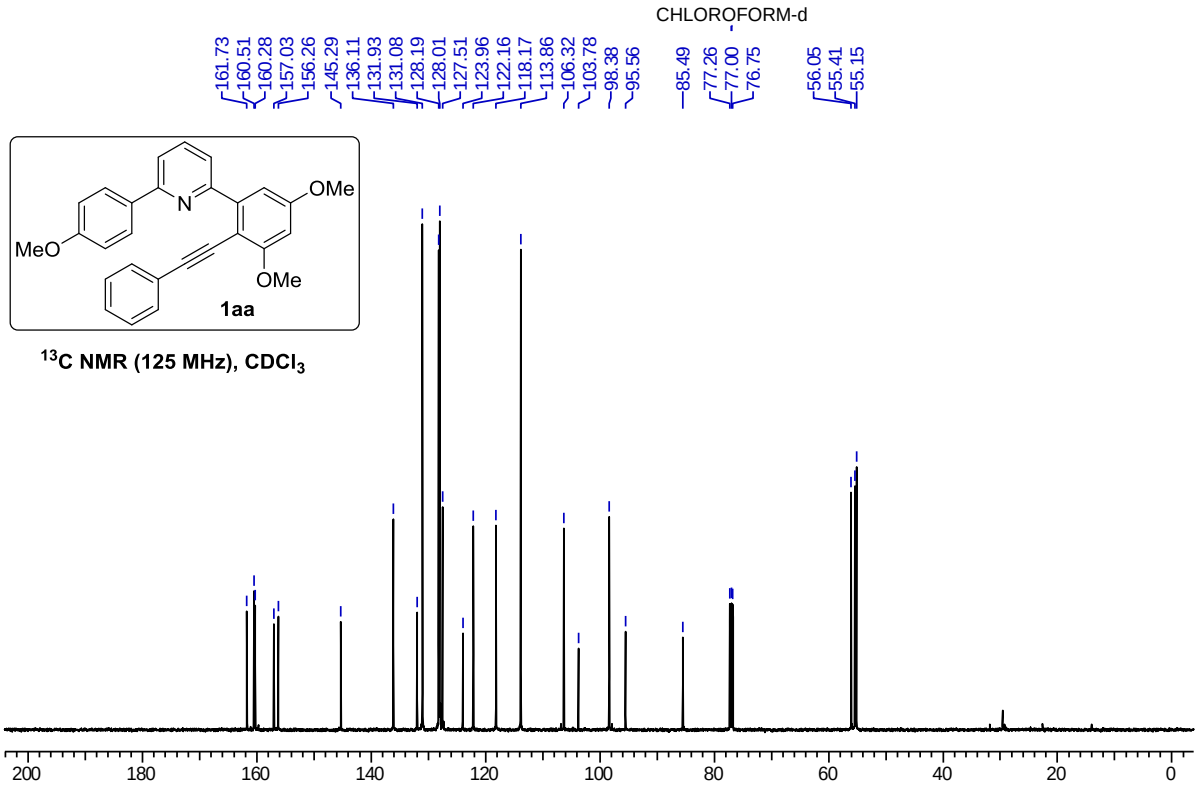
^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (125 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$



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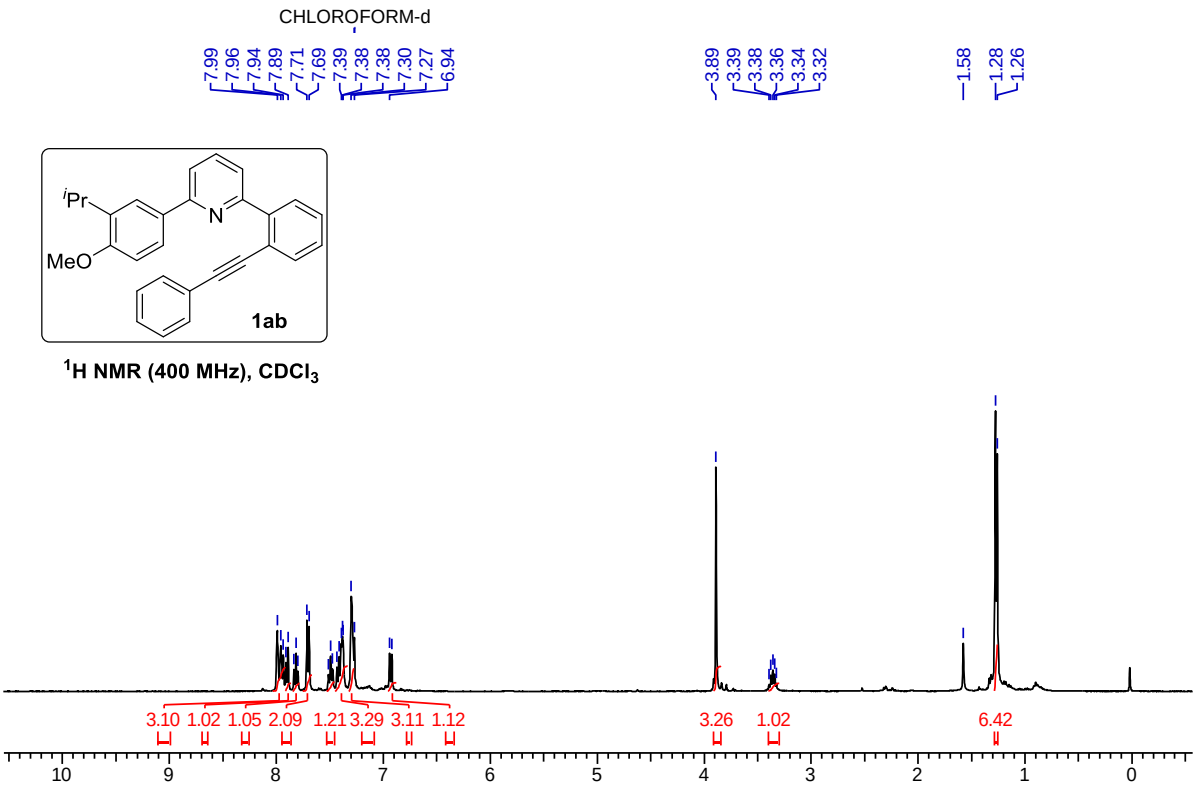
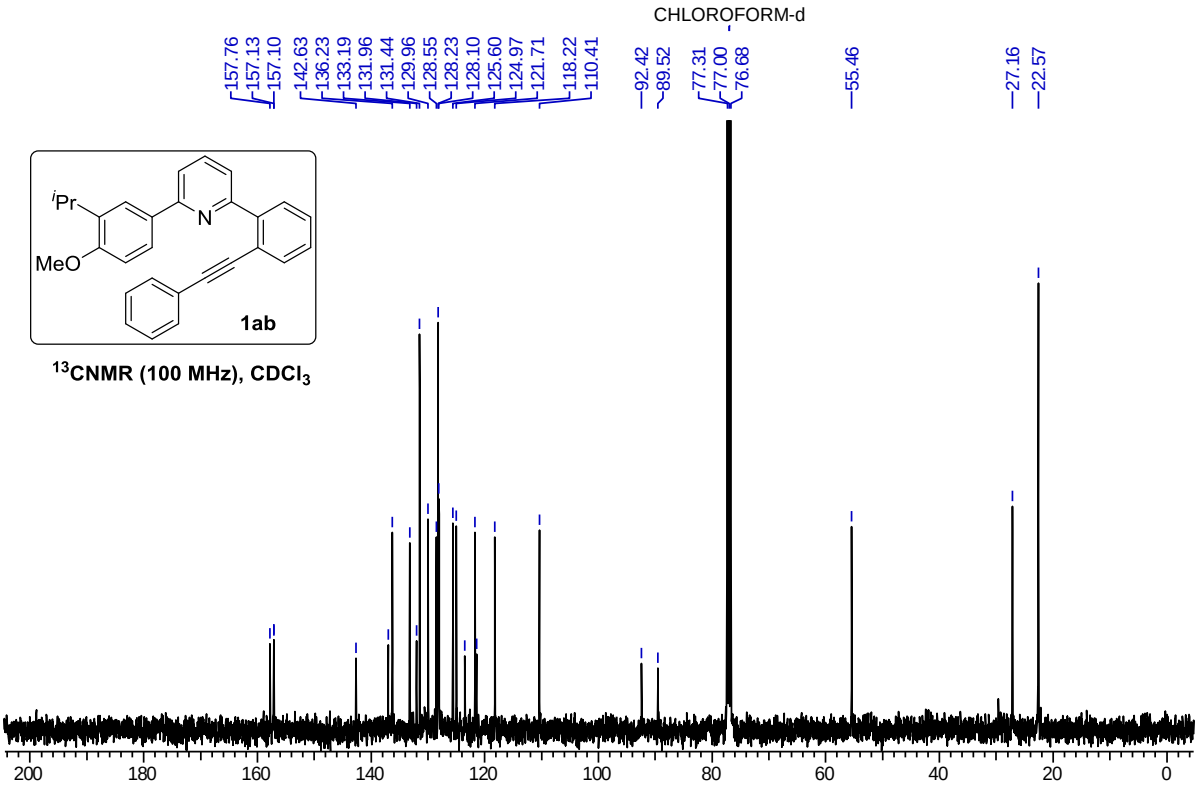


^{1}H NMR (400 MHz), $CDCl_3$



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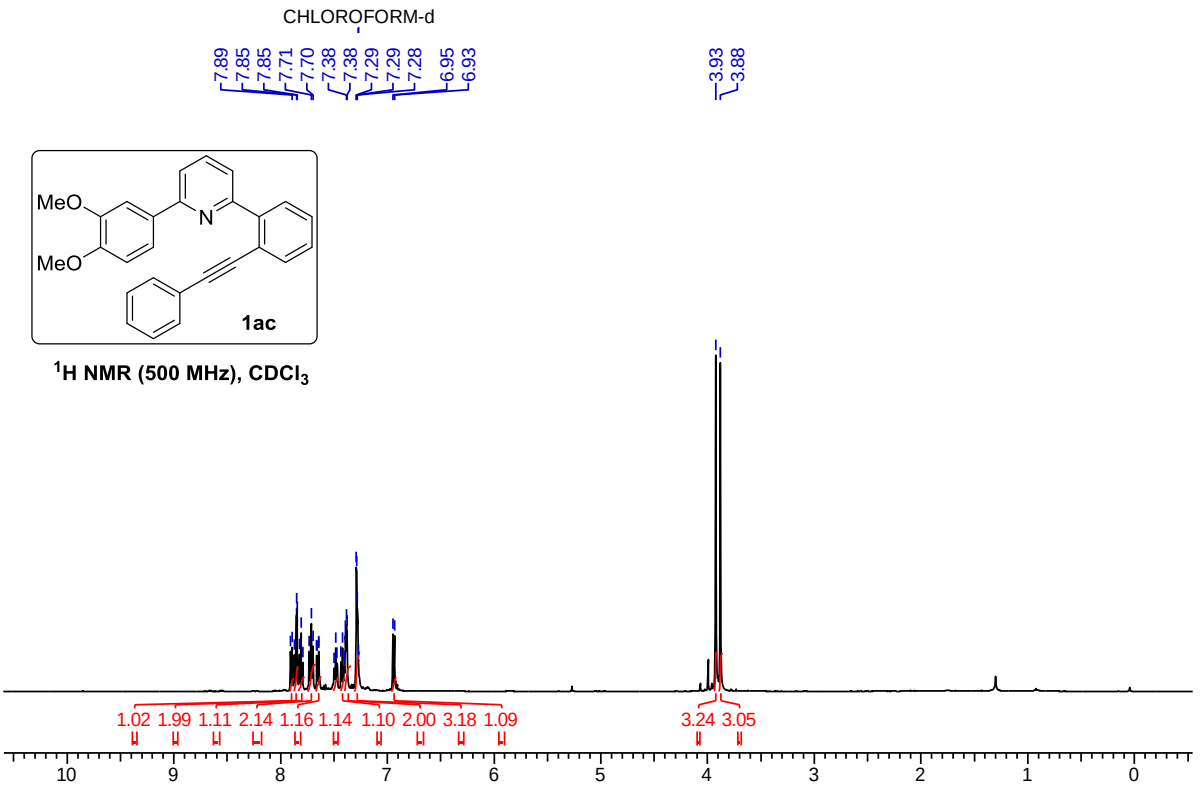
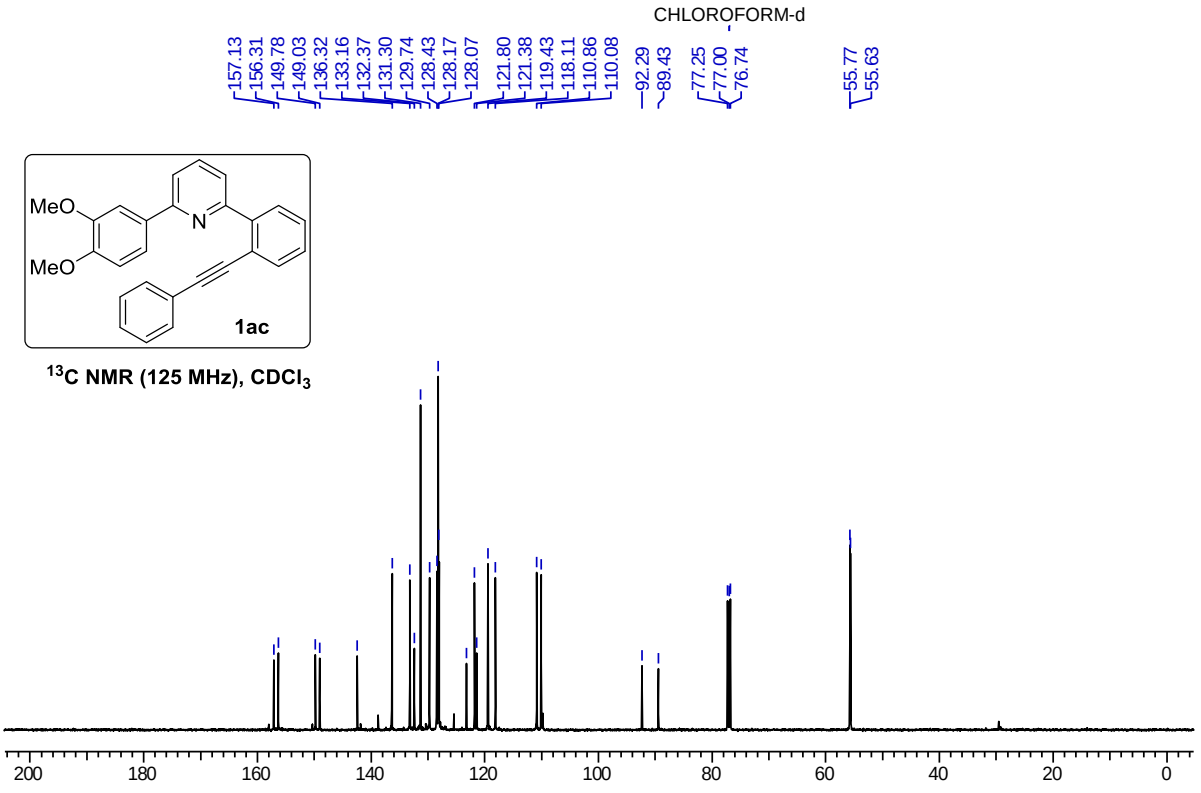
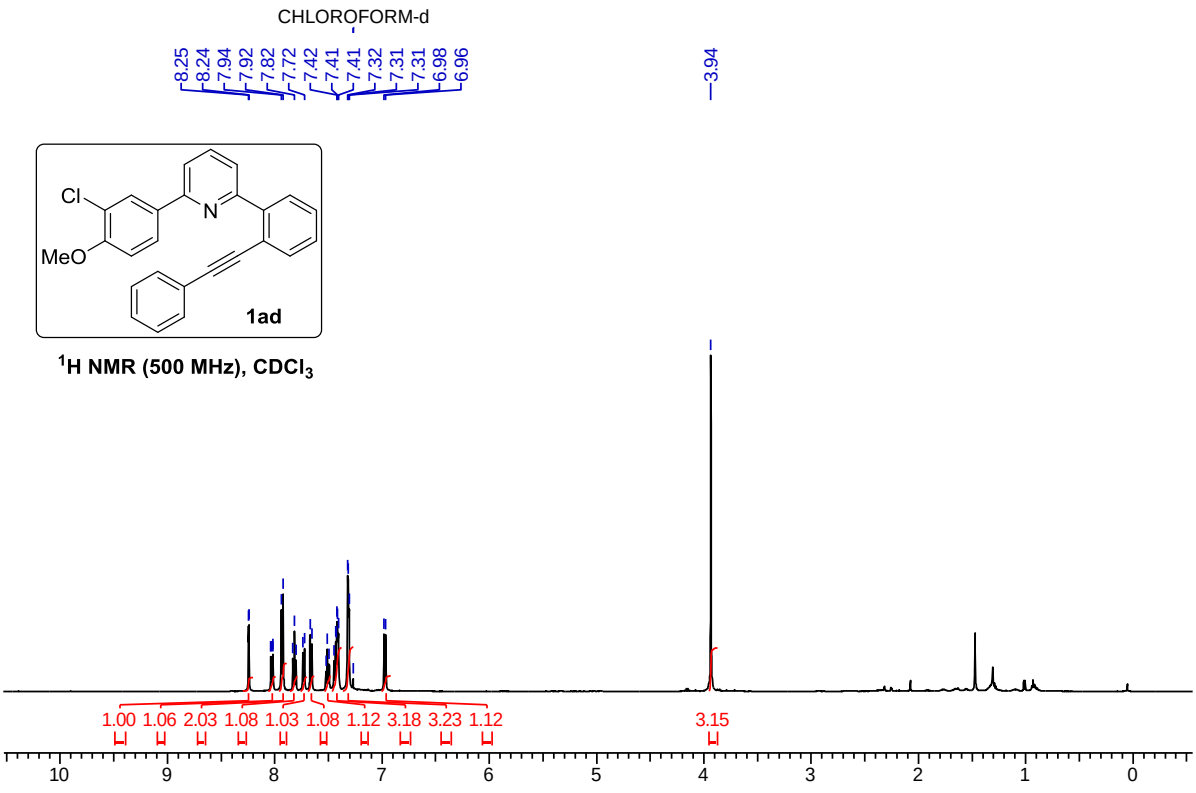


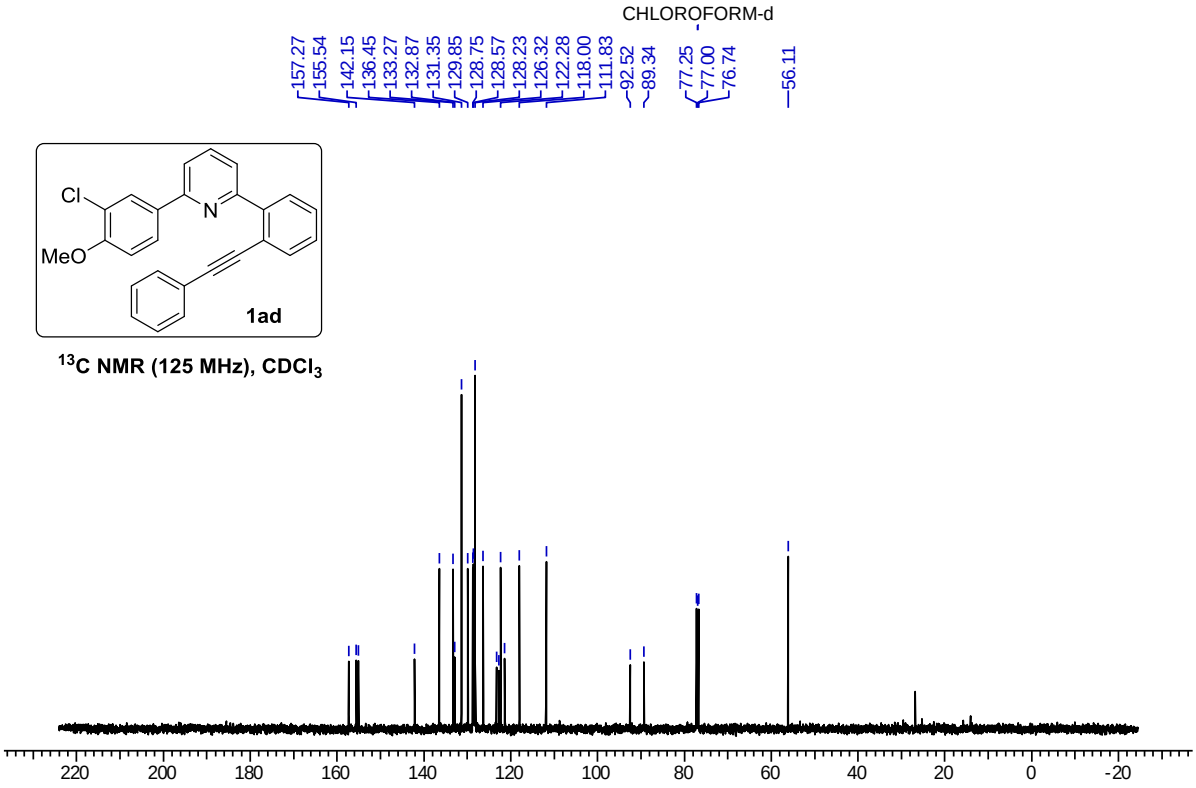
^{1}H NMR (500 MHz), $CDCl_3$



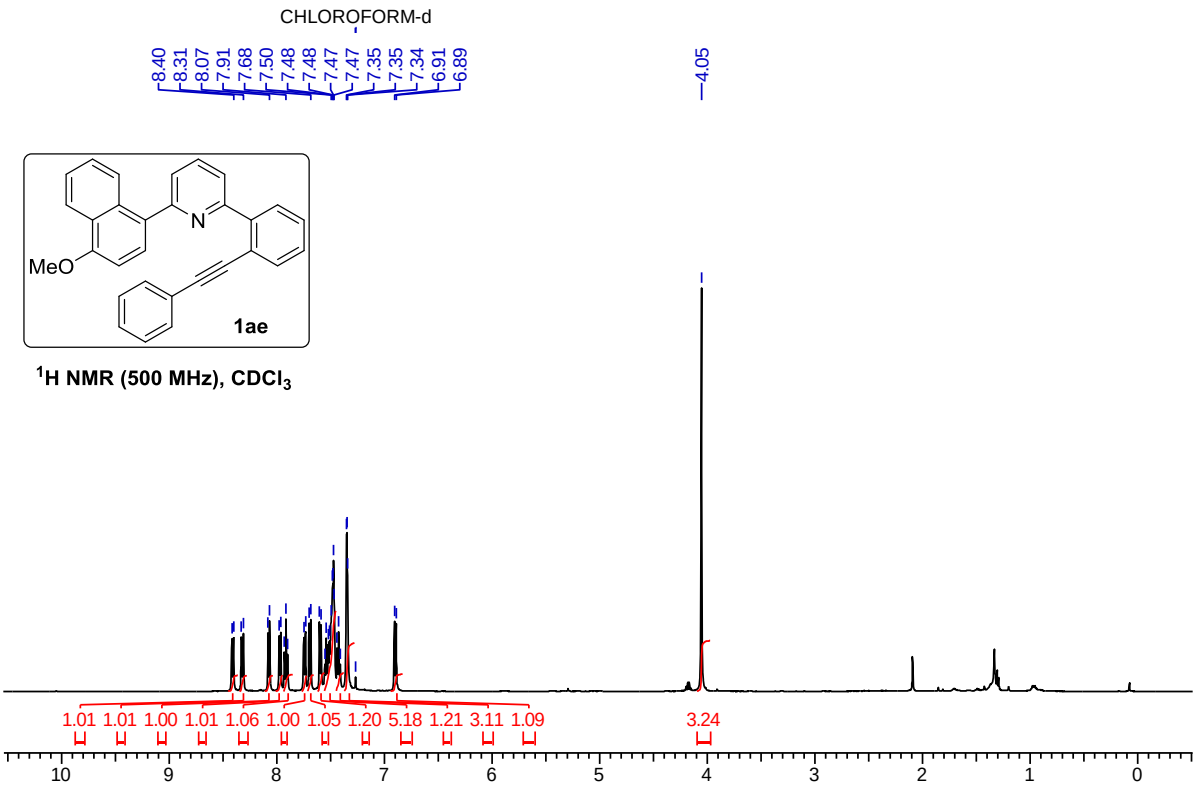
^{13}C NMR (125 MHz), $CDCl_3$



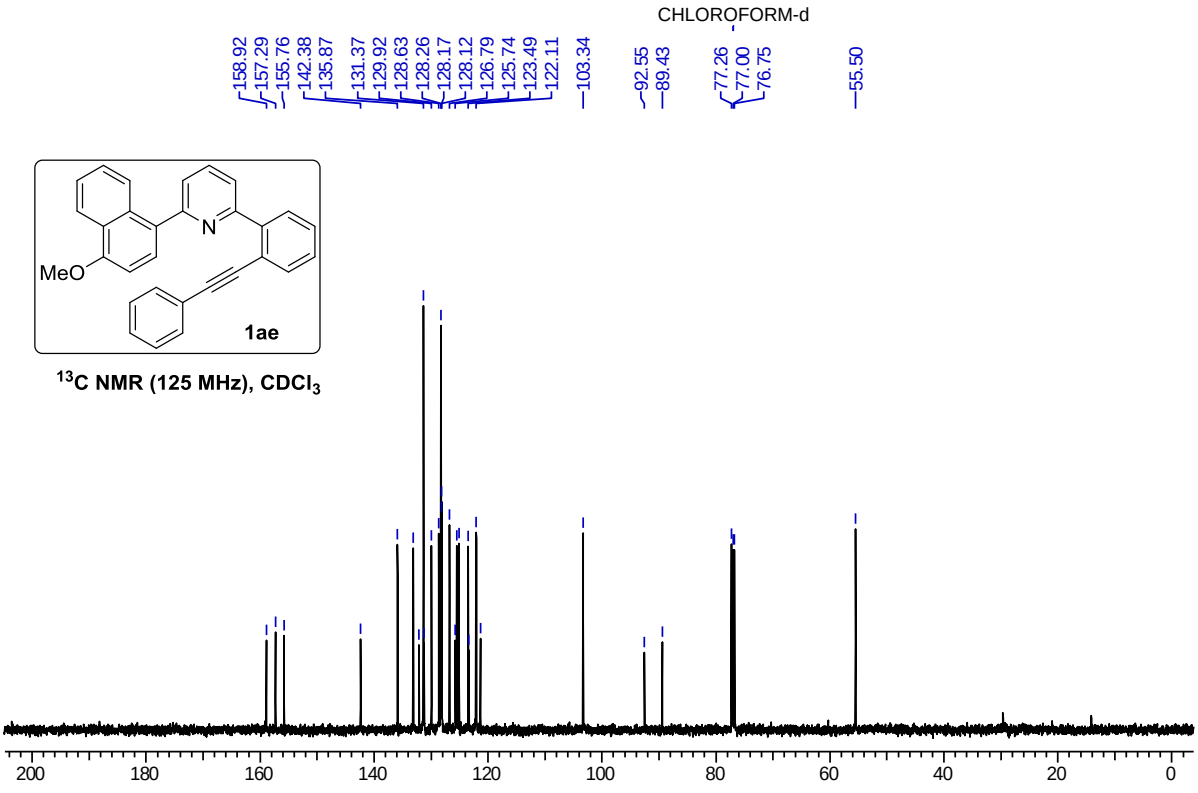
^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (125 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$



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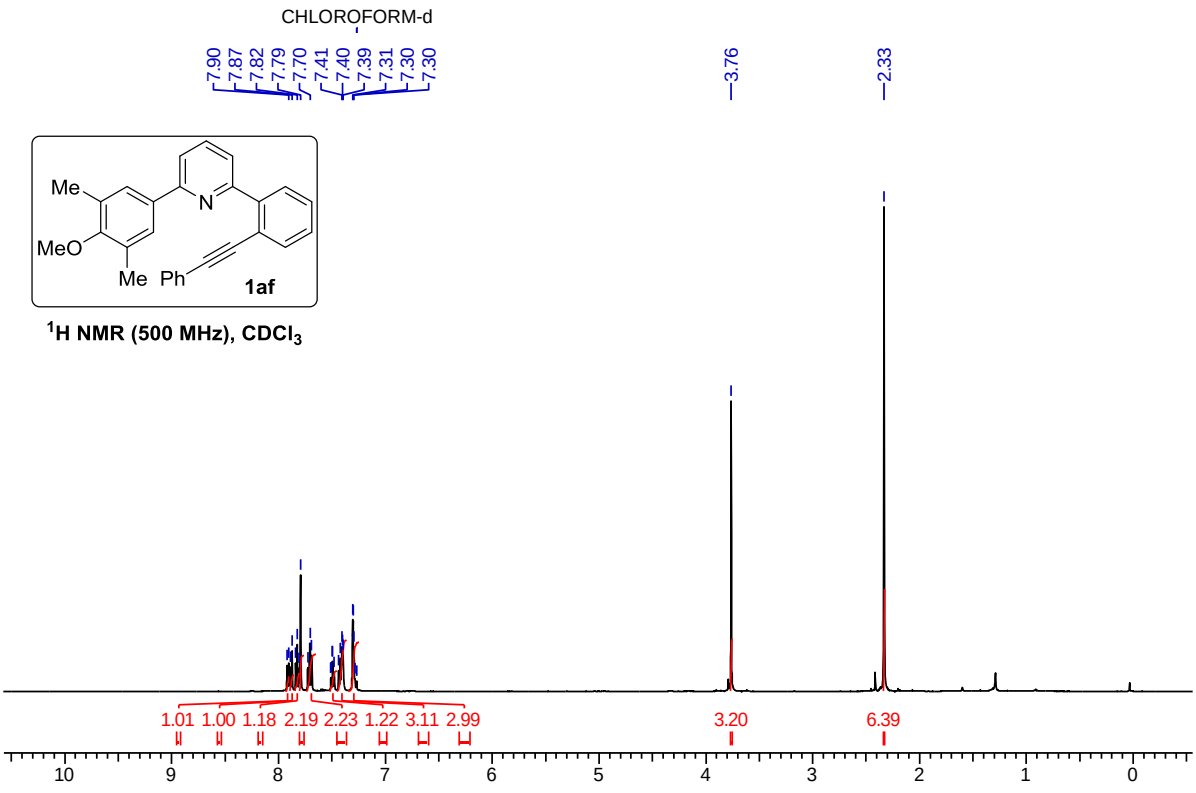

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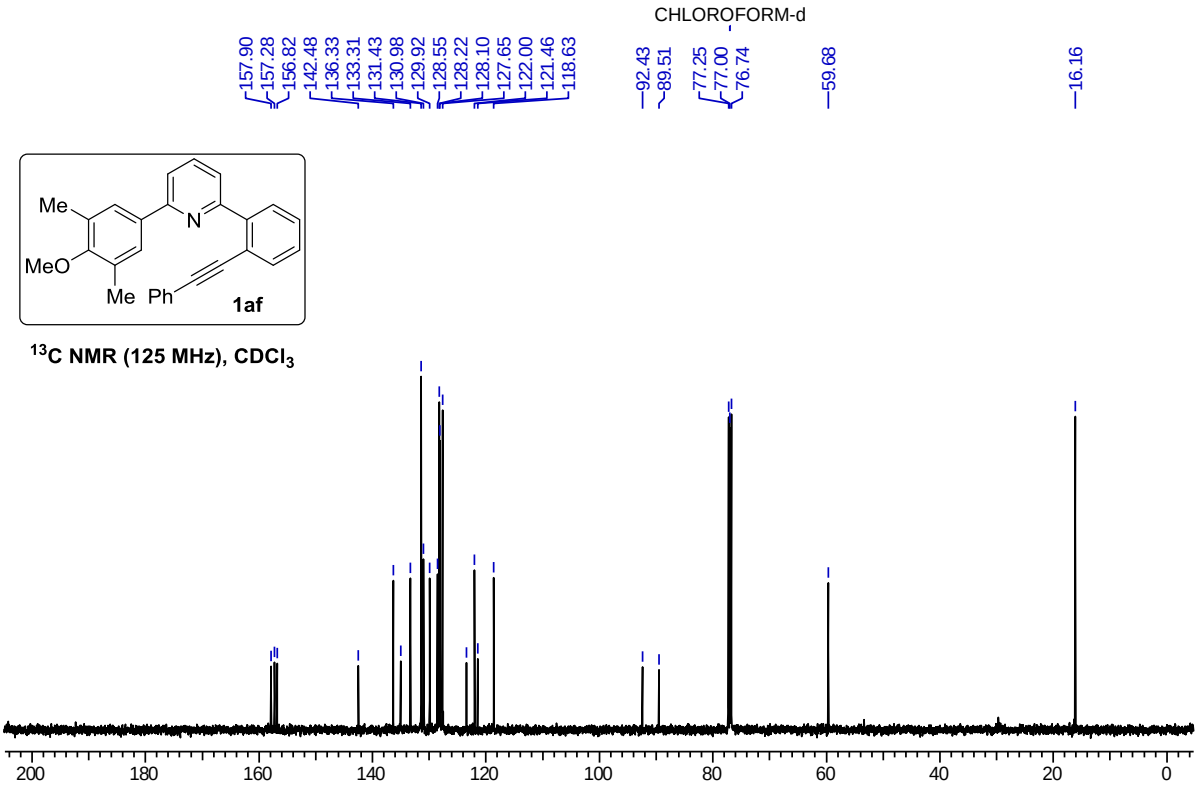
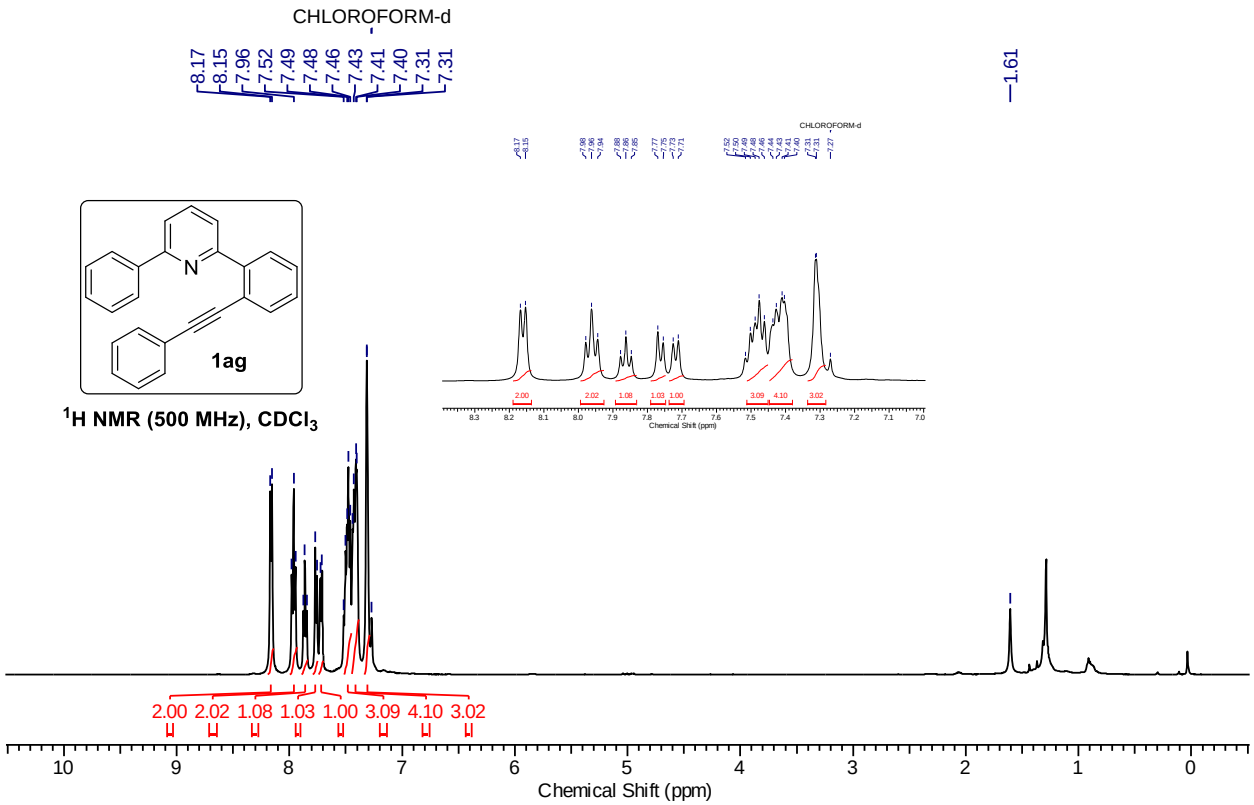


^{13}C NMR (125 MHz), $CDCl_3$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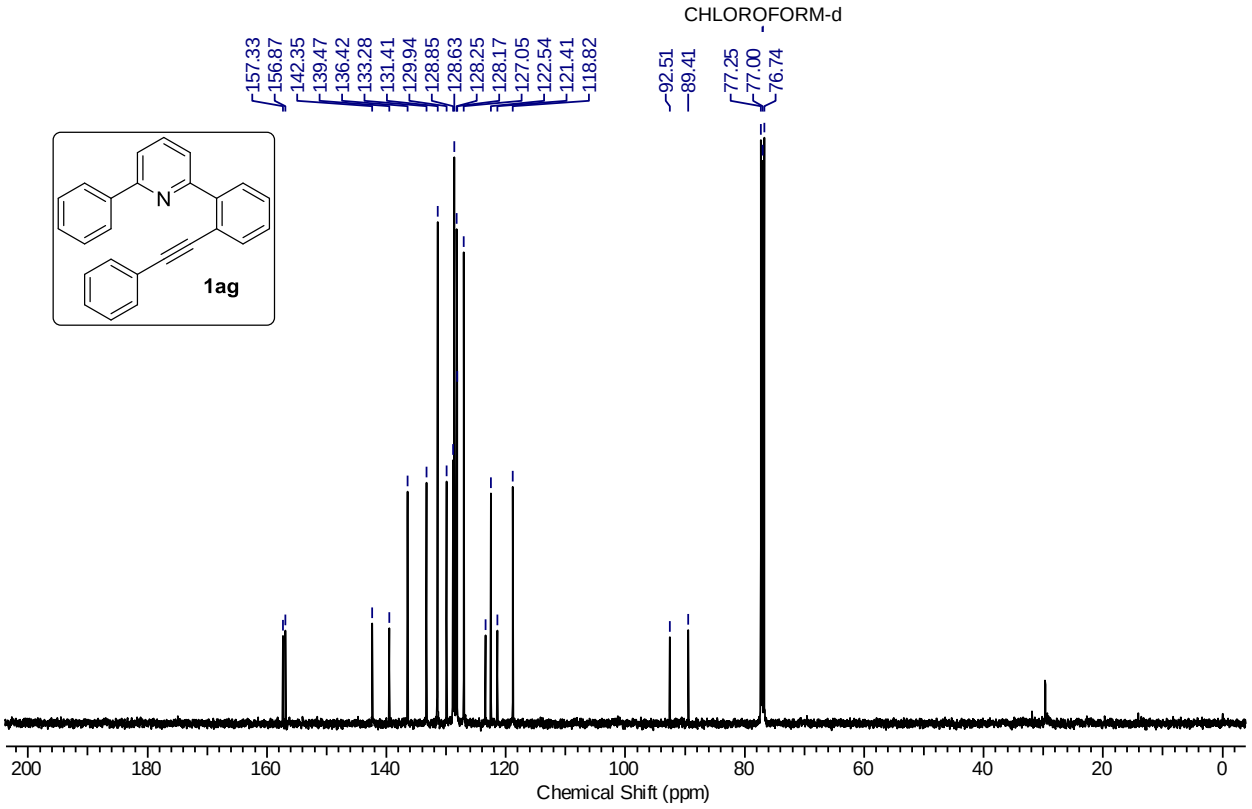
8.15
7.96
7.52
7.49
7.48
7.46
7.43
7.41
7.40
7.31
7.31
1.61
N
1ag
^{1}H NMR (500 MHz), CDCl$_3$
2.00 2.02 1.08 1.03 1.00 3.09 4.10 3.02
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)


CHLOROFORM-d
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77.00
76.74
N
1ag
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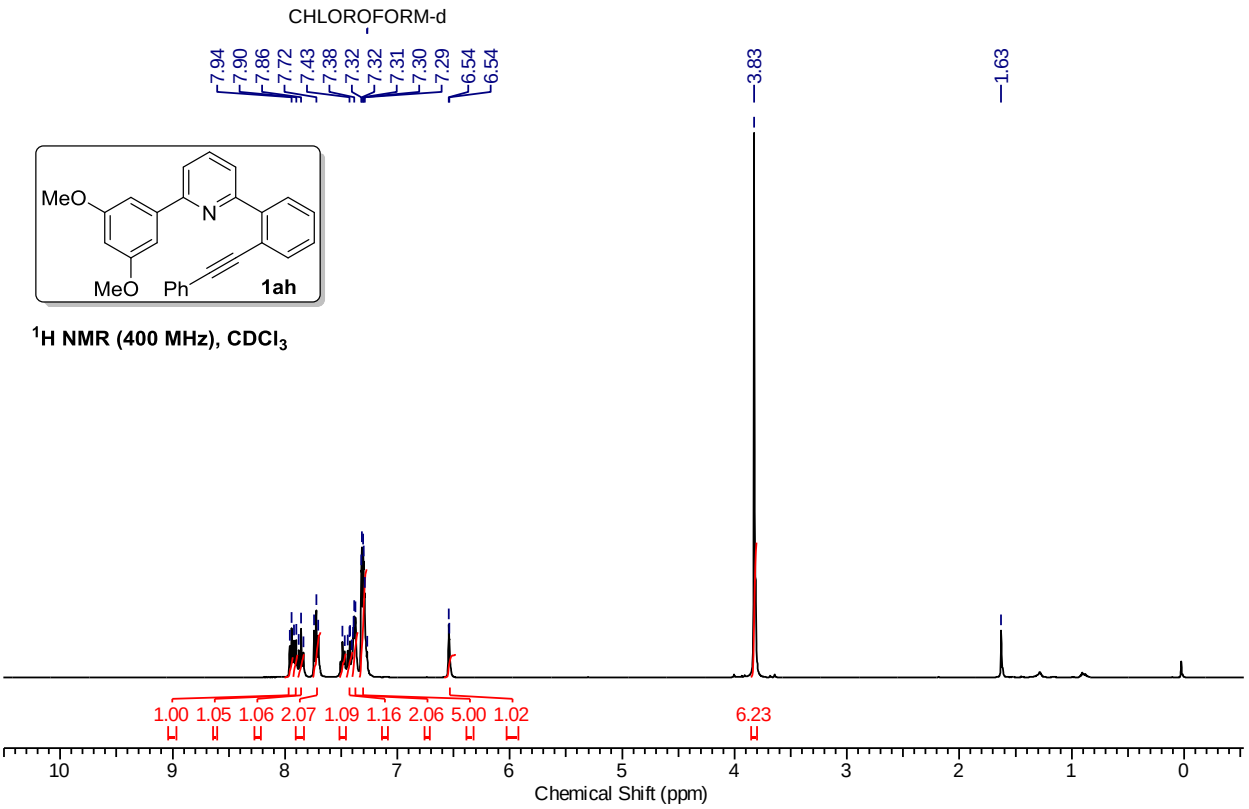
Chemical Shift (ppm)



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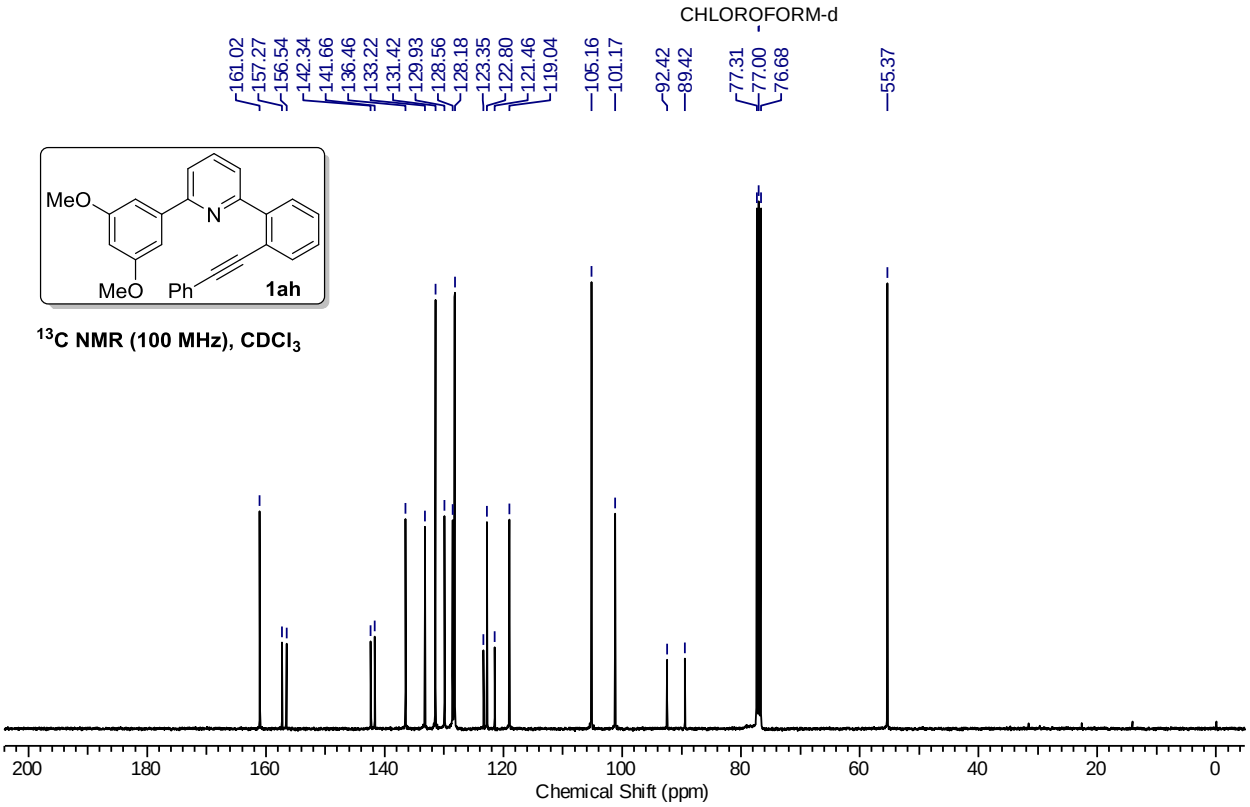

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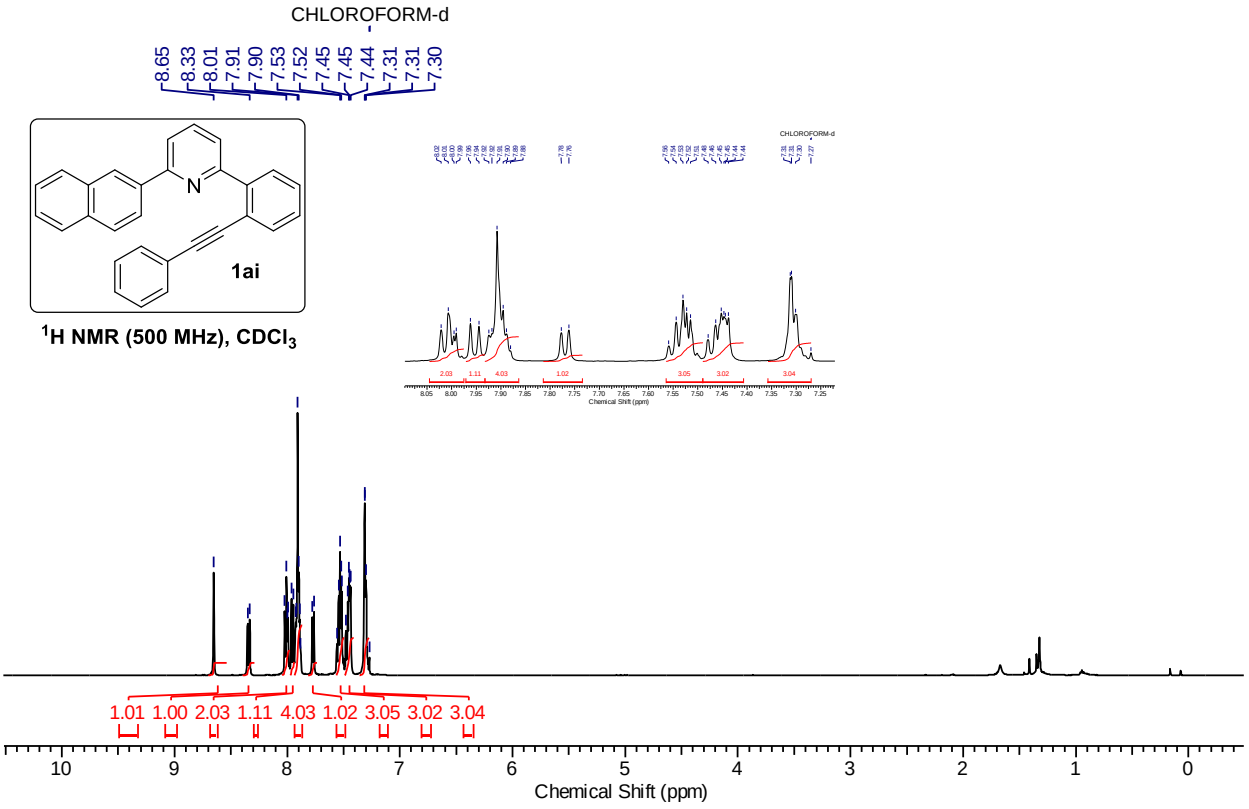
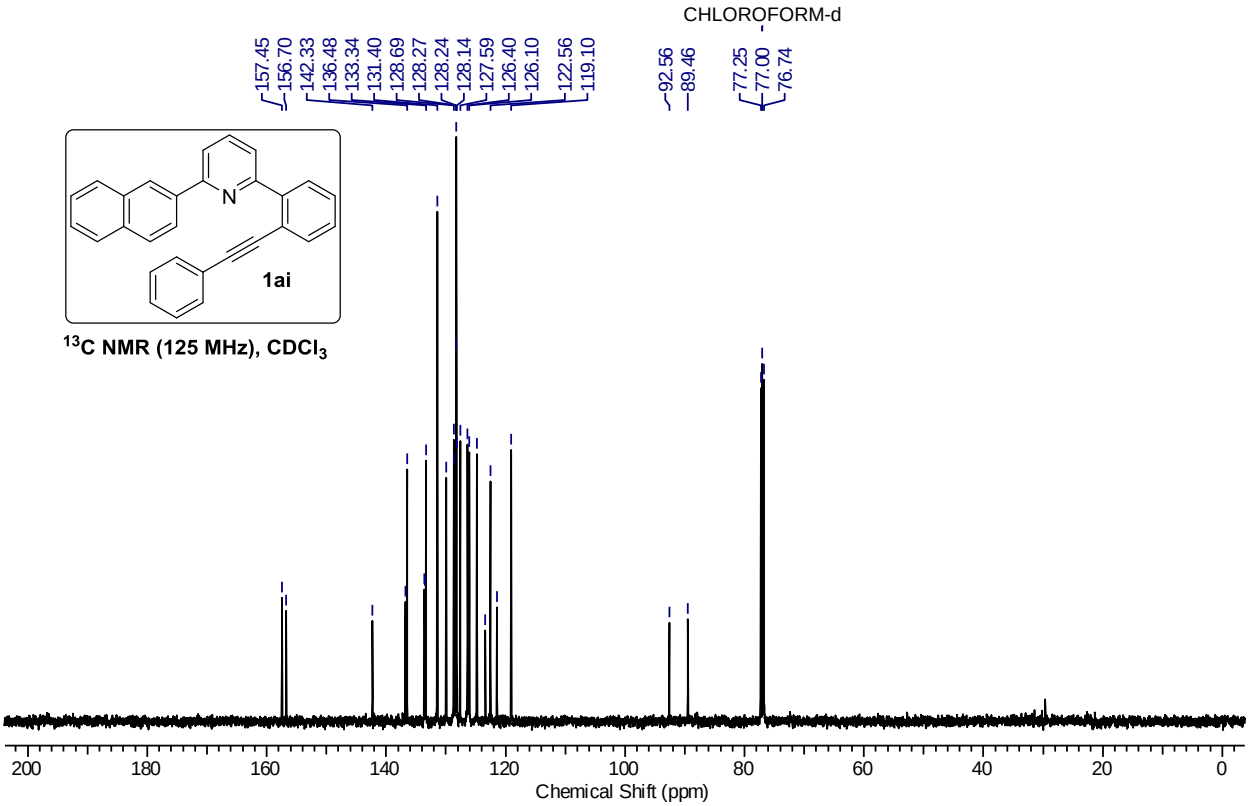
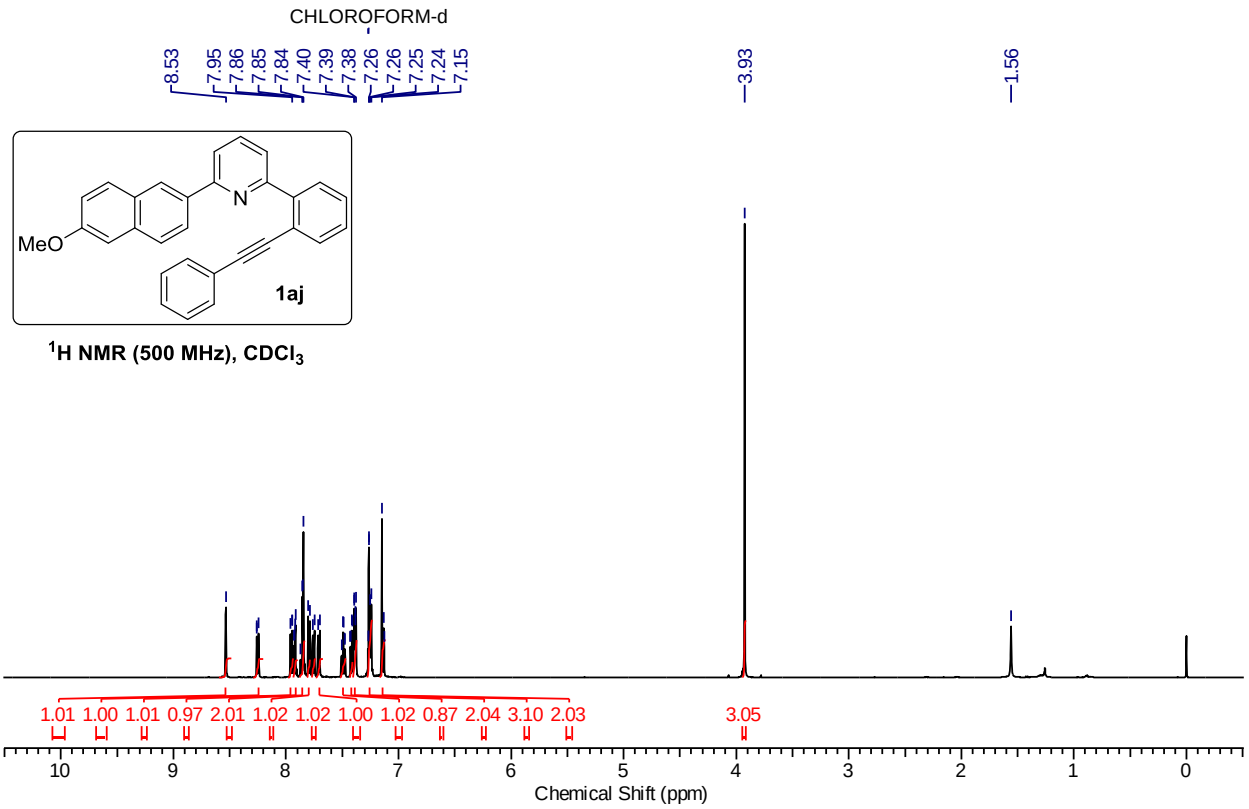


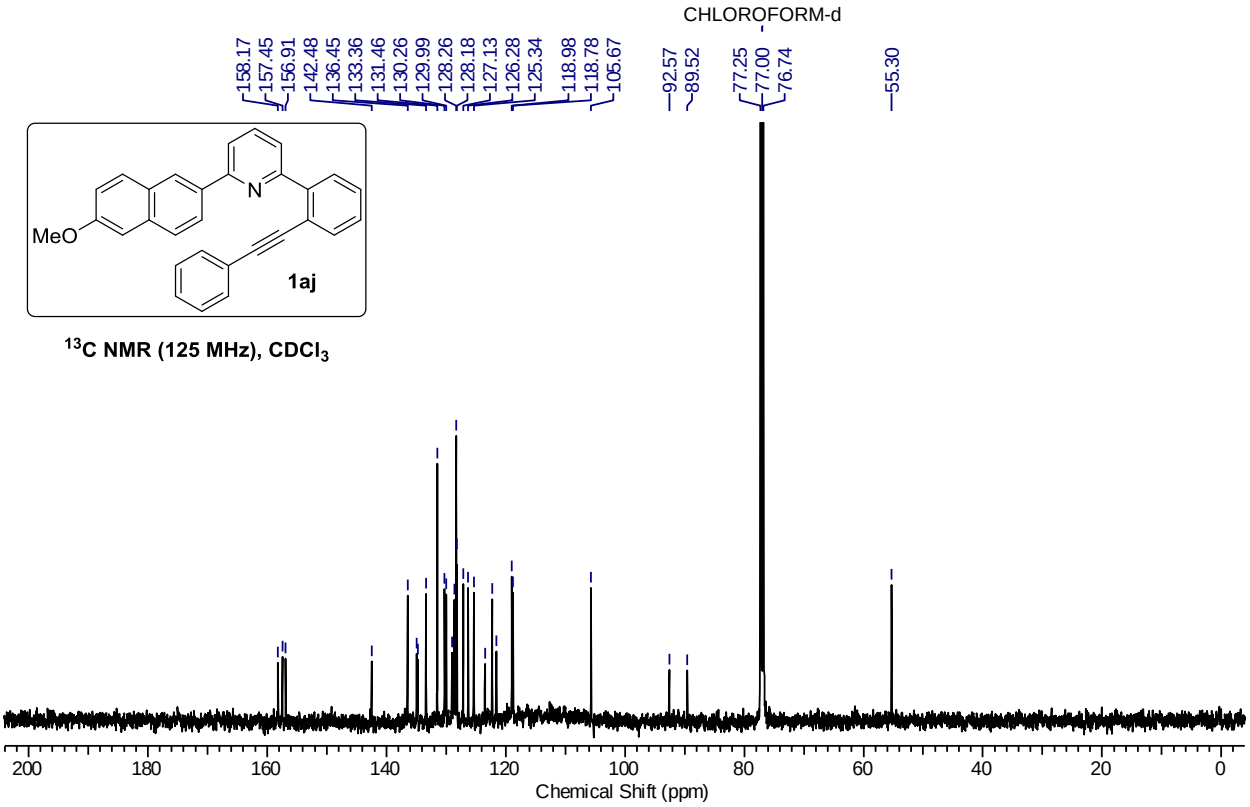
^{1}H NMR (500 MHz), $CDCl_3$



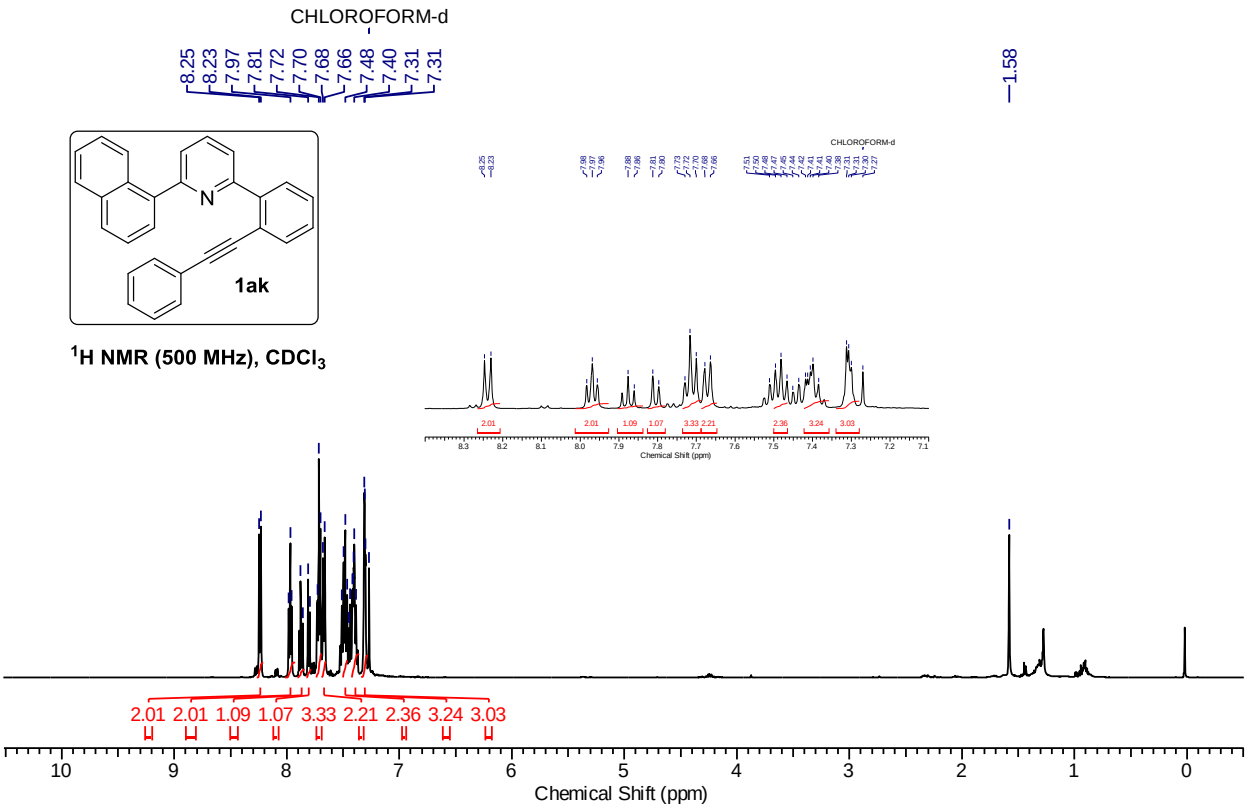
^{13}C NMR (125 MHz), $CDCl_3$



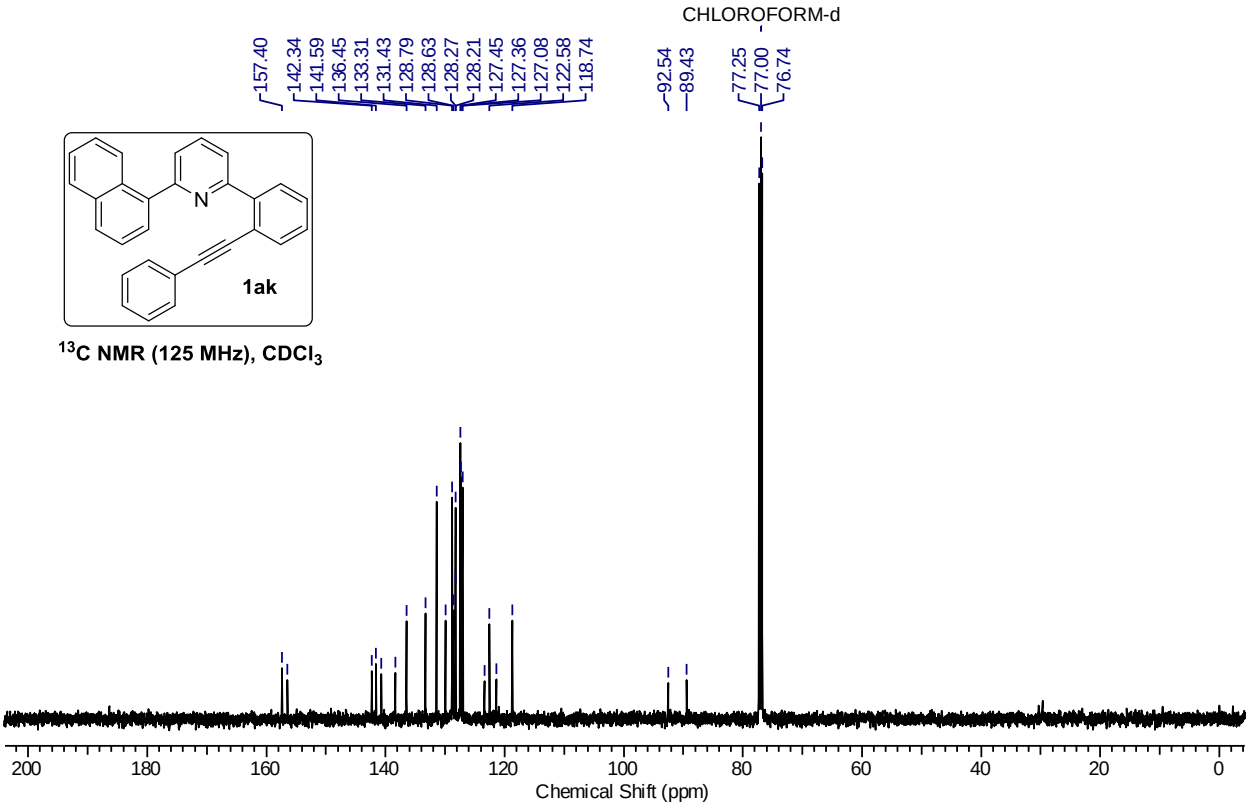
^{1}H NMR (500 MHz), $CDCl_3$



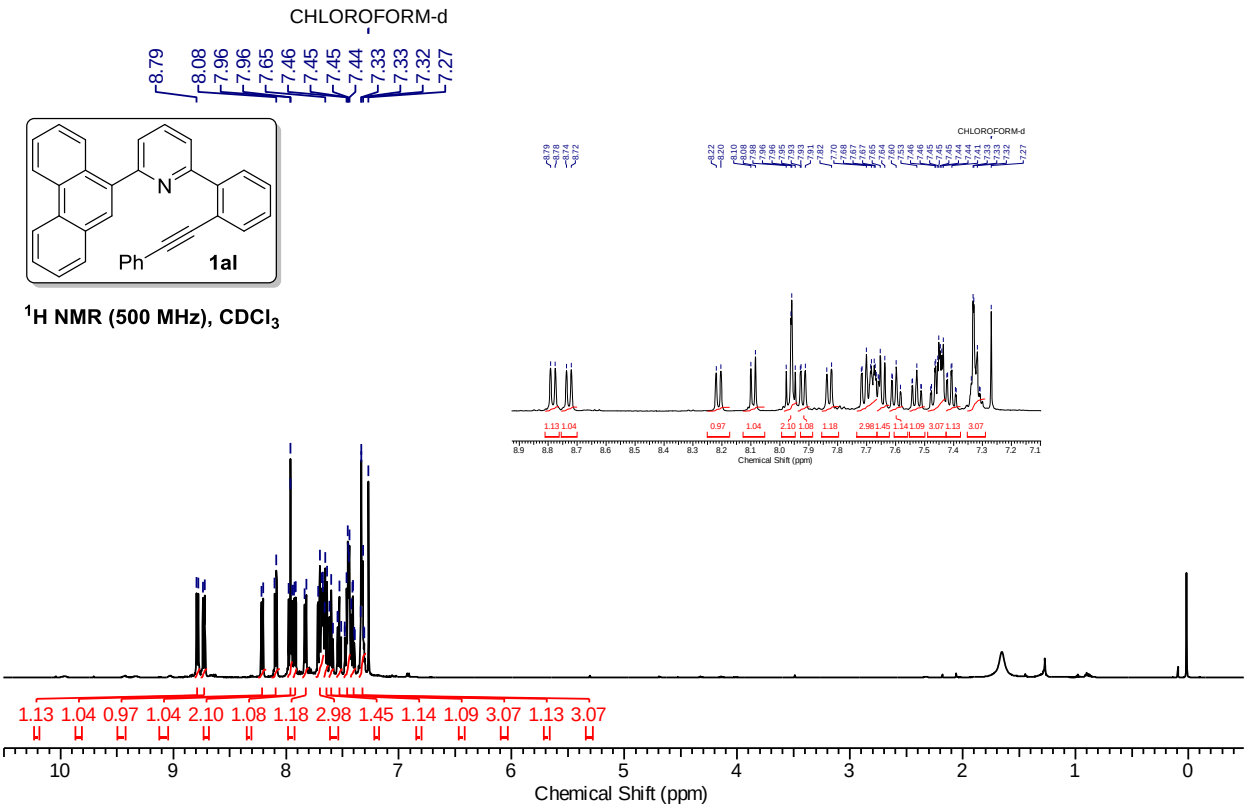
^{13}C NMR (125 MHz), $CDCl_3$



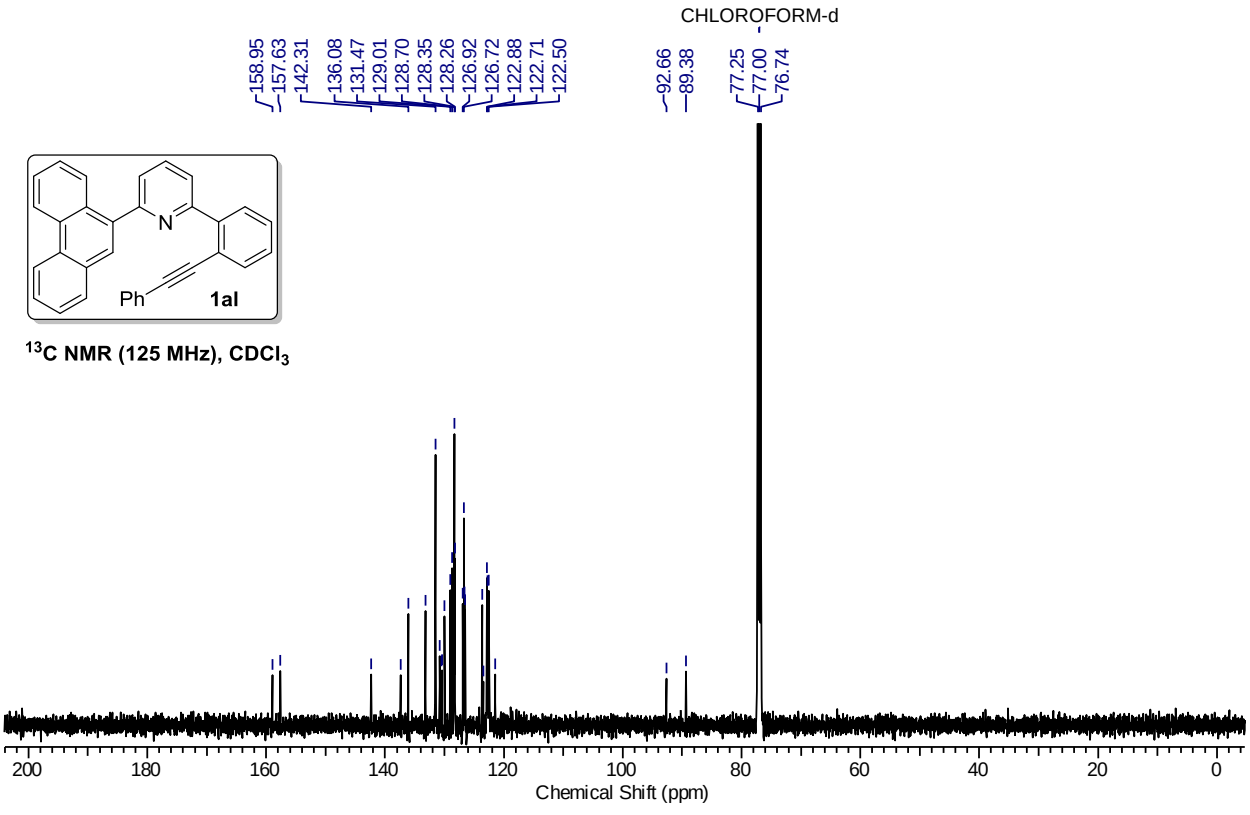
^{1}H NMR (500 MHz), $CDCl_3$



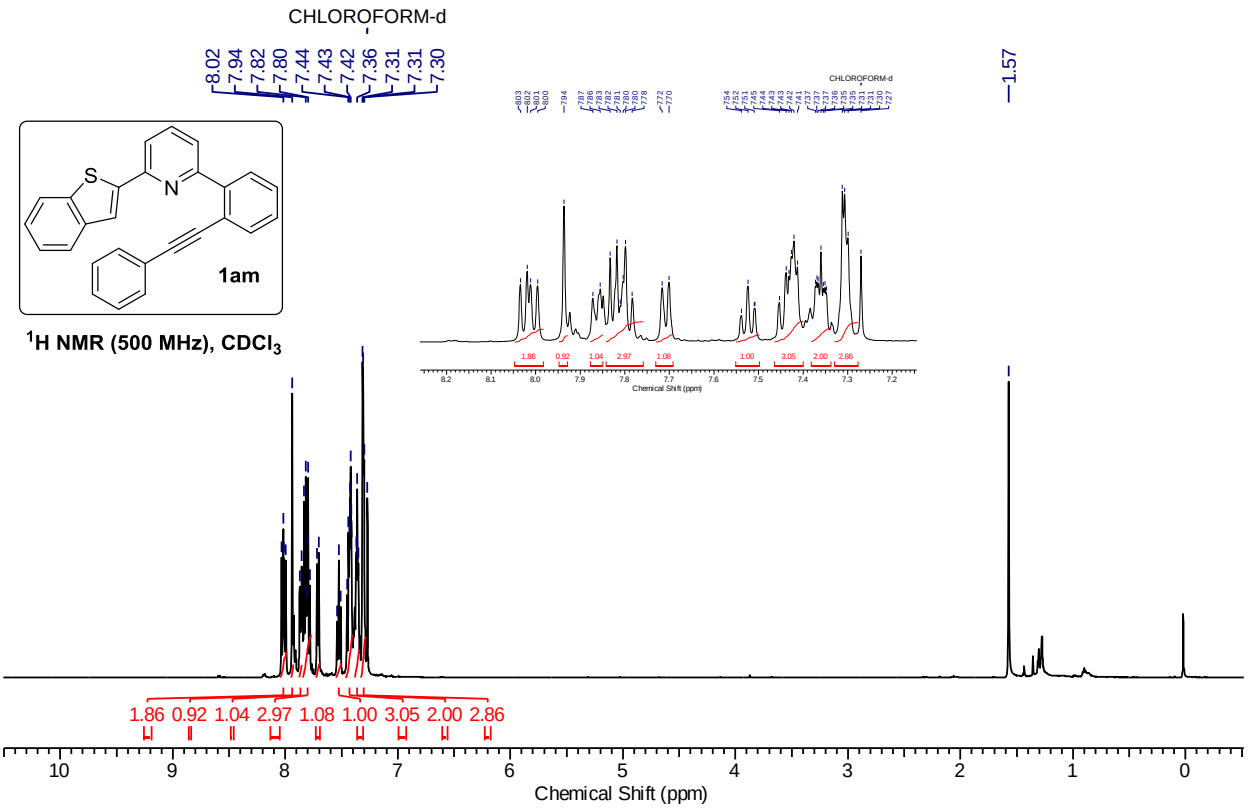
^{13}C NMR (125 MHz), $CDCl_3$

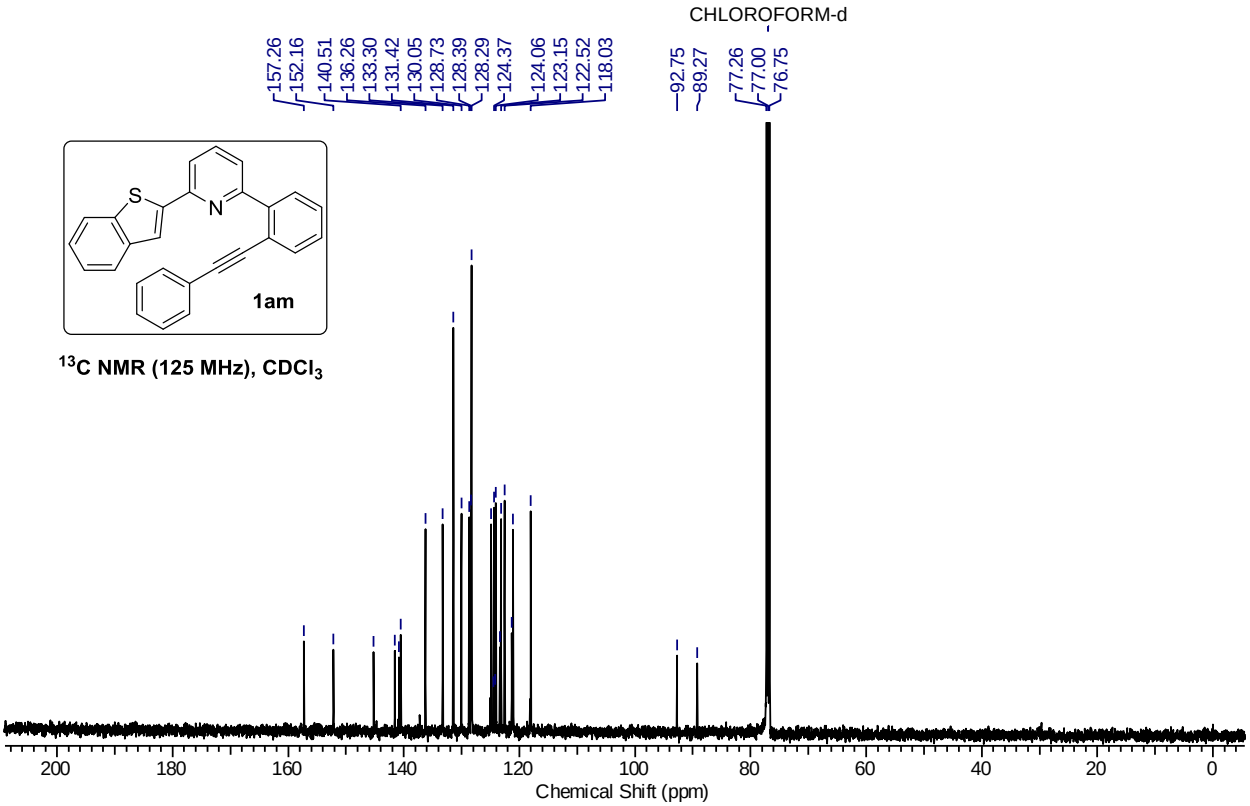


^{1}H NMR (500 MHz), $CDCl_3$



^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
8.02
7.94
7.82
7.80
7.44
7.43
7.42
7.36
7.31
7.31
7.30
1.57
S
N
1am
1H NMR (500 MHz), CDCl3
1.86 0.92 1.04 2.97 1.08 1.00 3.05 2.00 2.86
Chemical Shift (ppm)


CHLOROFORM-d
157.26
152.16
140.51
136.26
133.30
131.42
130.05
128.73
128.39
128.29
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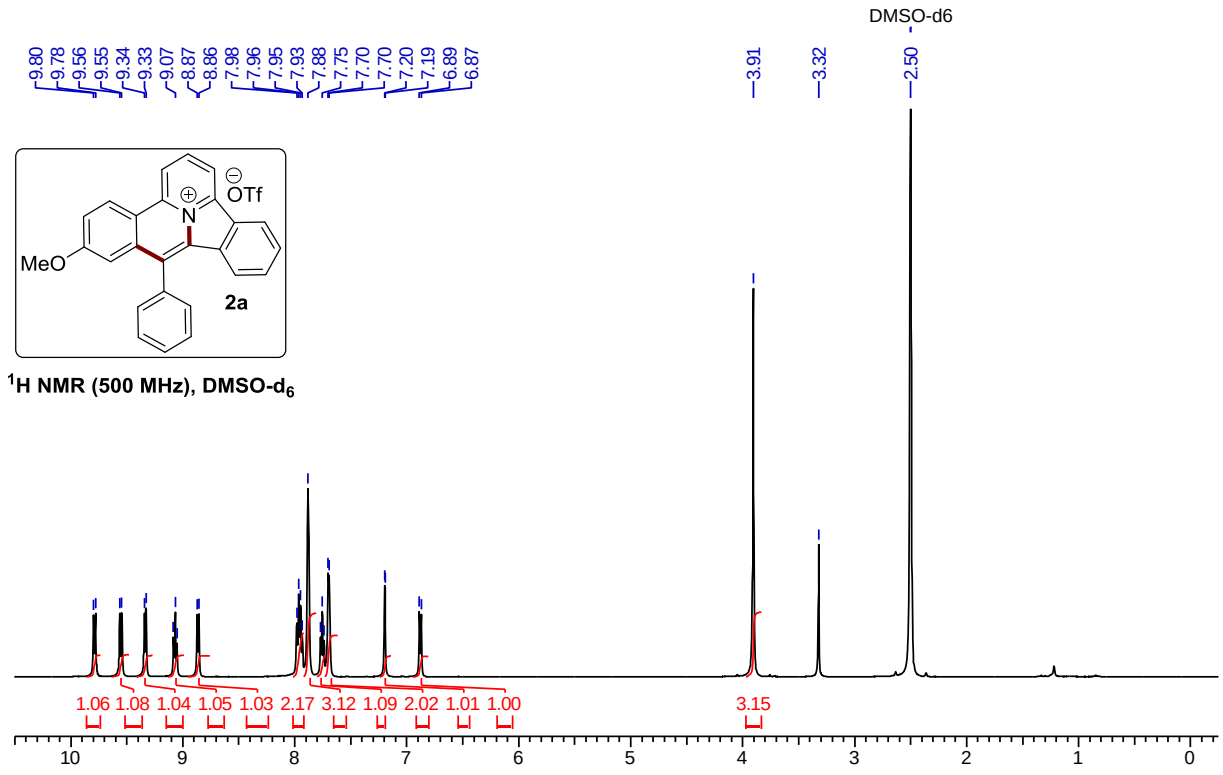
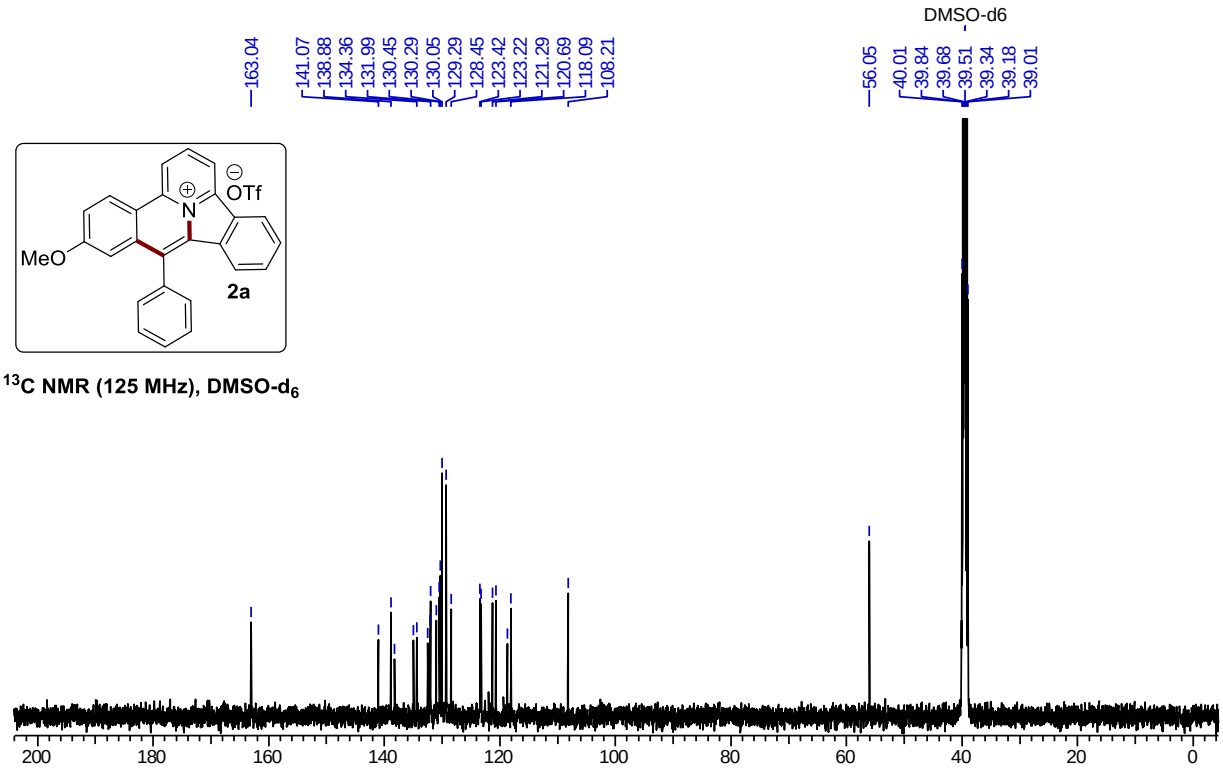
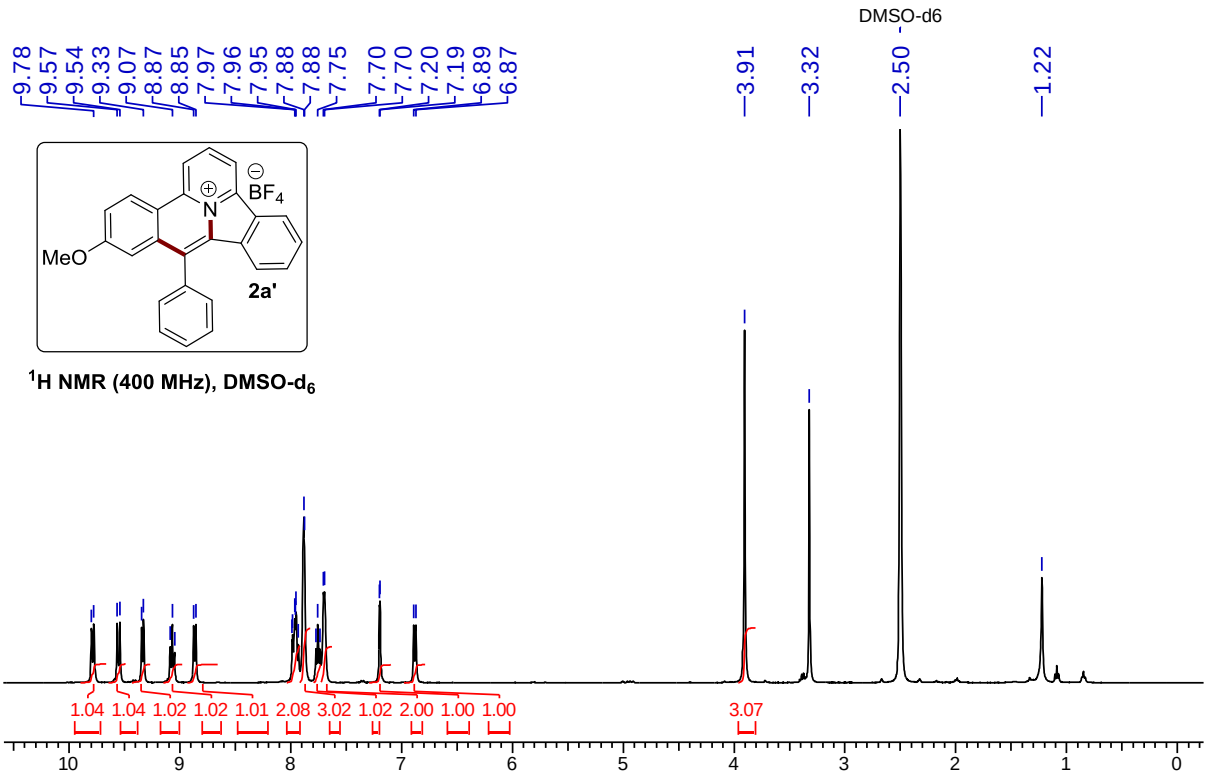
124.06
123.15
122.52
118.03
92.75
89.27
77.26
77.00
76.75
S
N
1am
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)



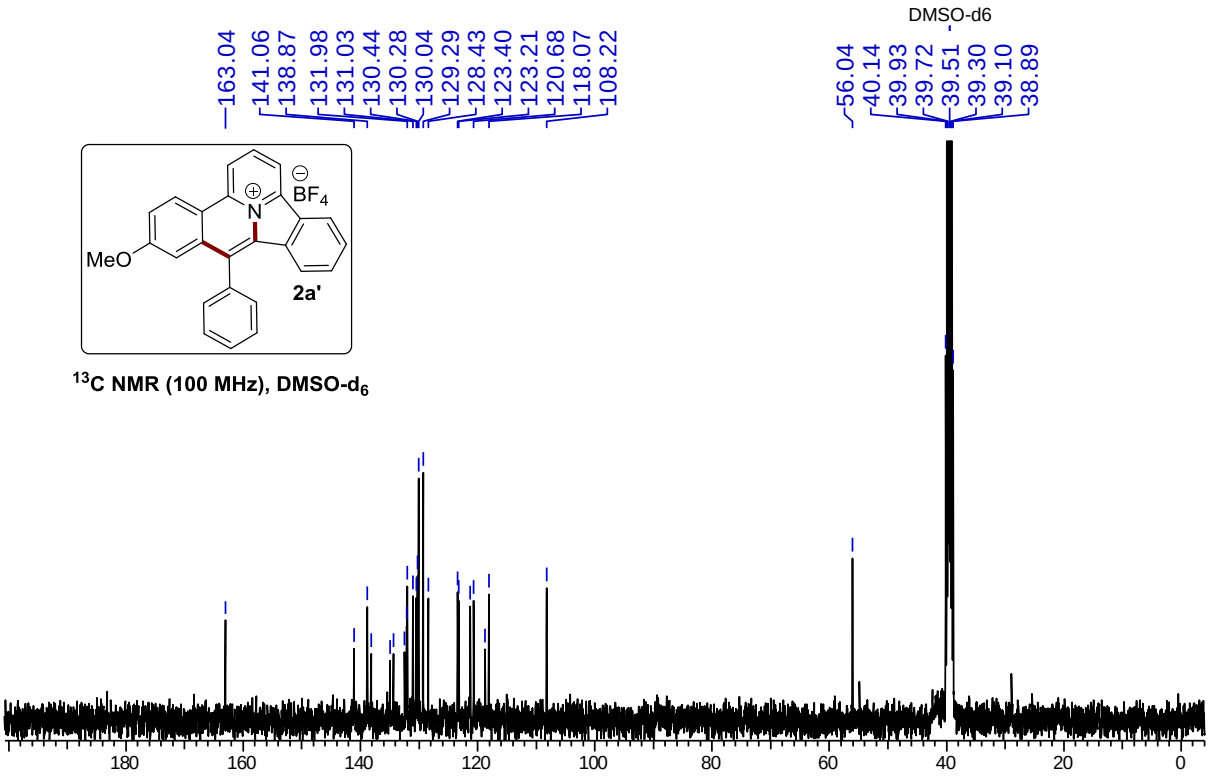
^{1}H NMR (500 MHz), DMSO-d$_6$



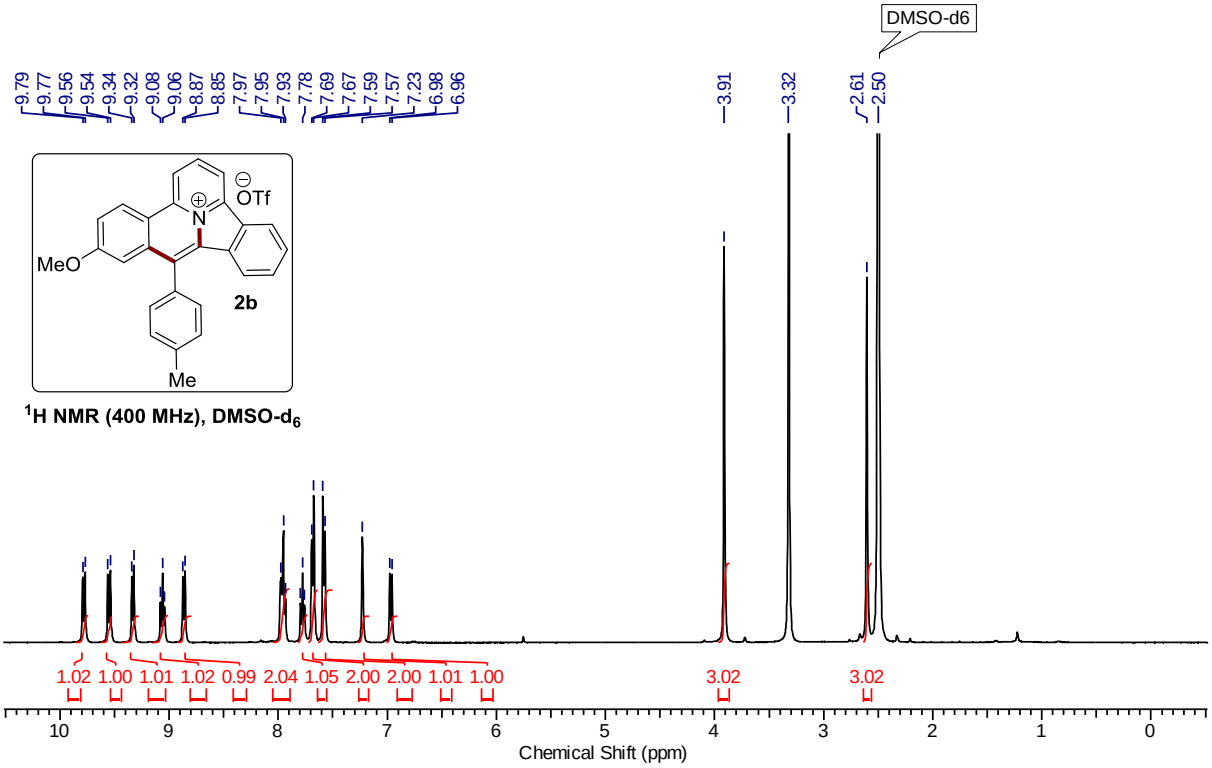
^{13}C NMR (125 MHz), DMSO-d$_6$



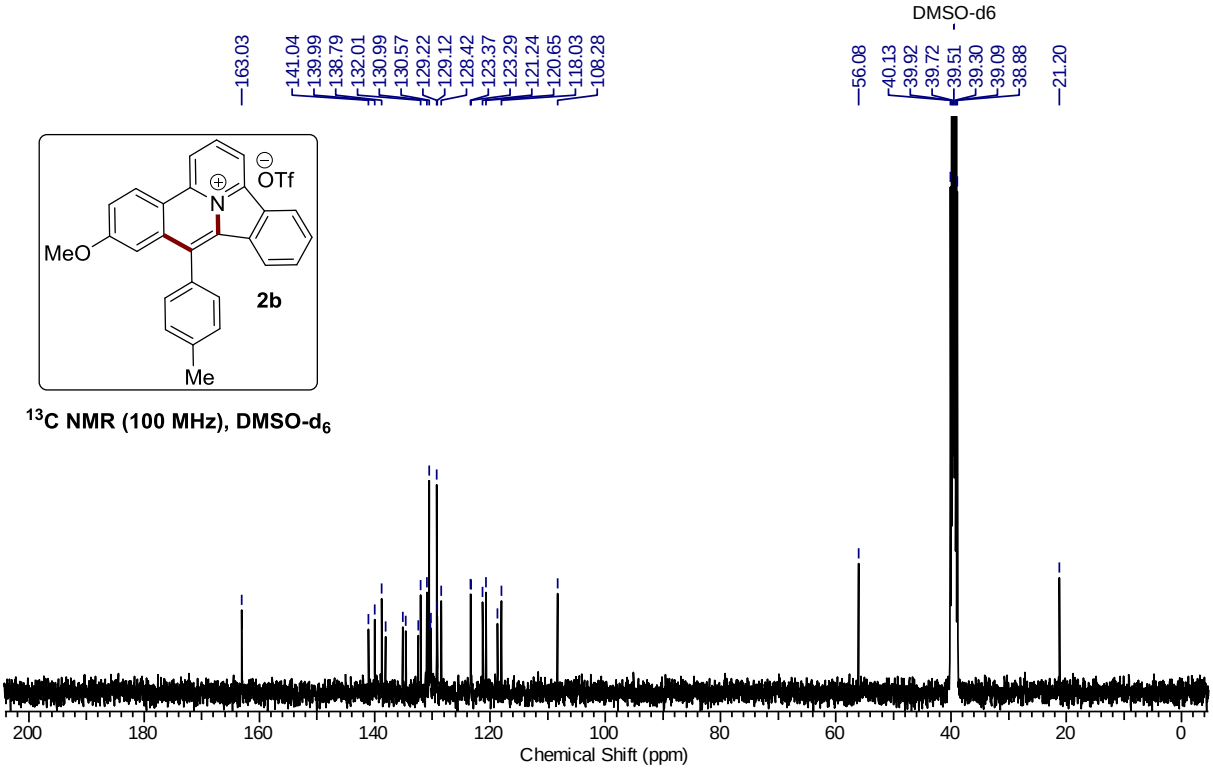
^{1}H NMR (400 MHz), DMSO-d$_6$



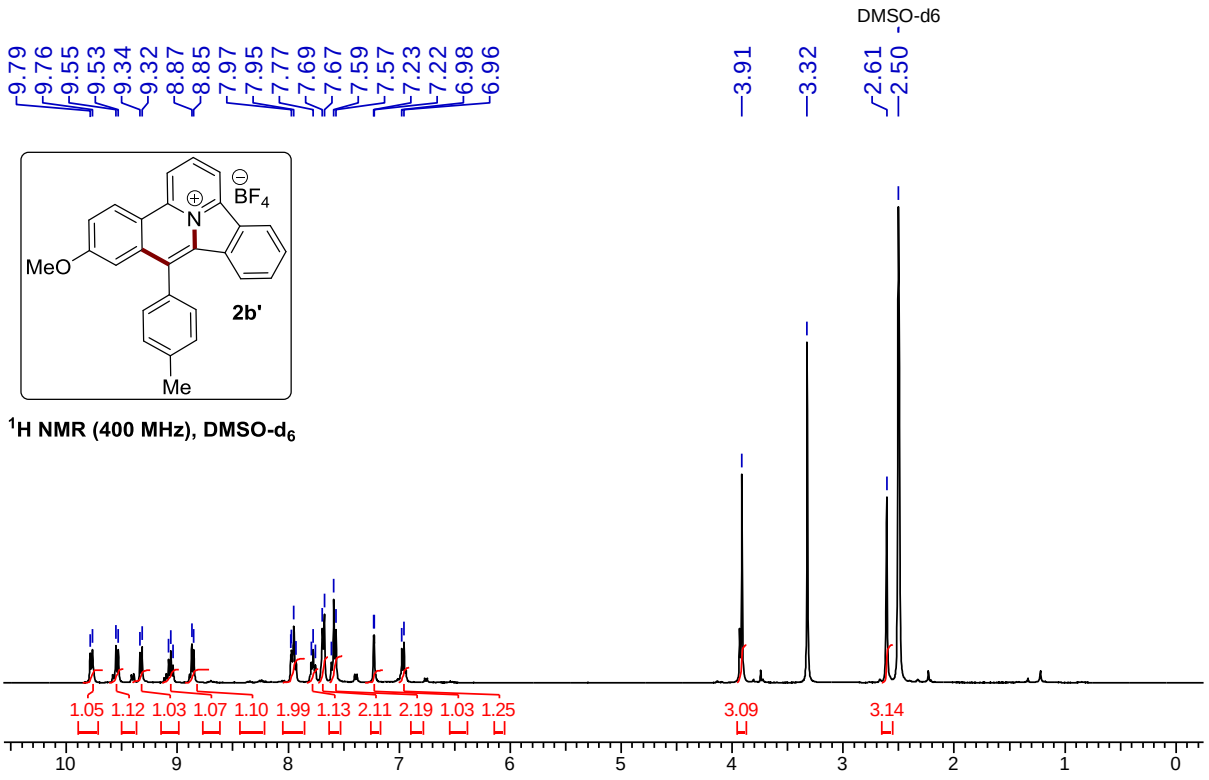
^{13}C NMR (100 MHz), DMSO-d$_6$



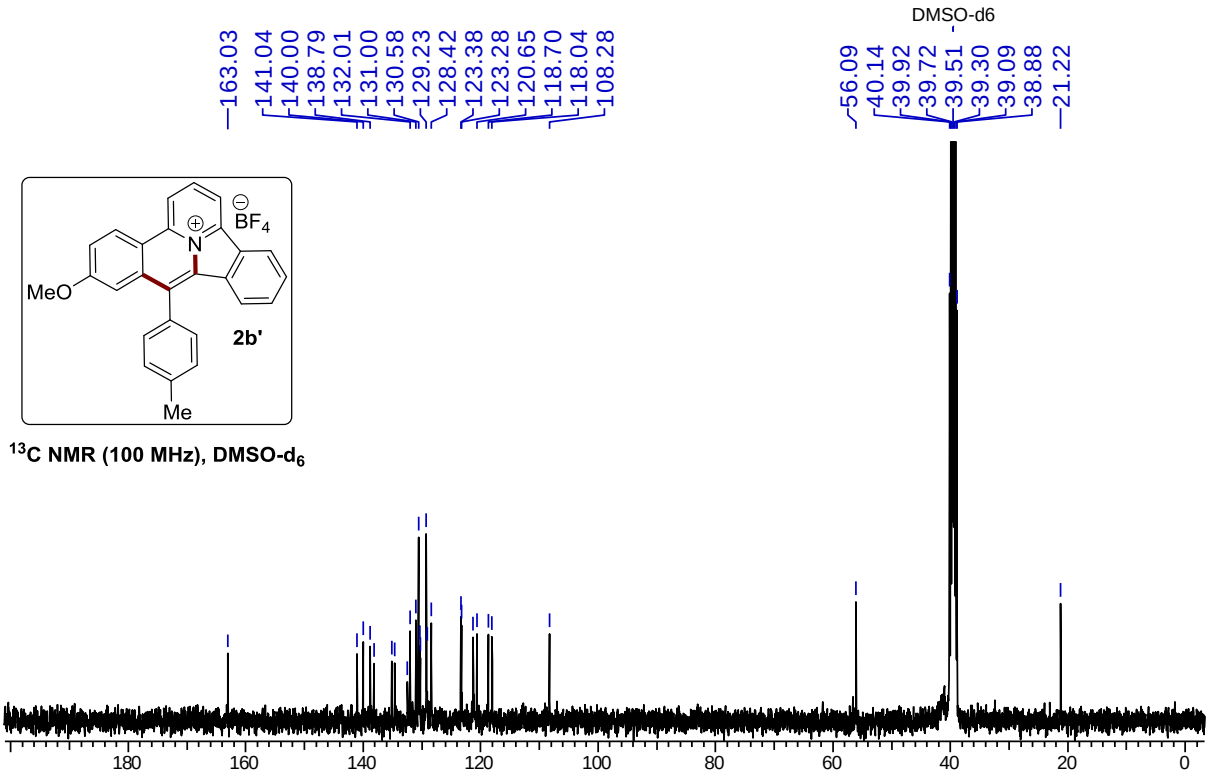
^{1}H NMR (400 MHz), DMSO-d_6



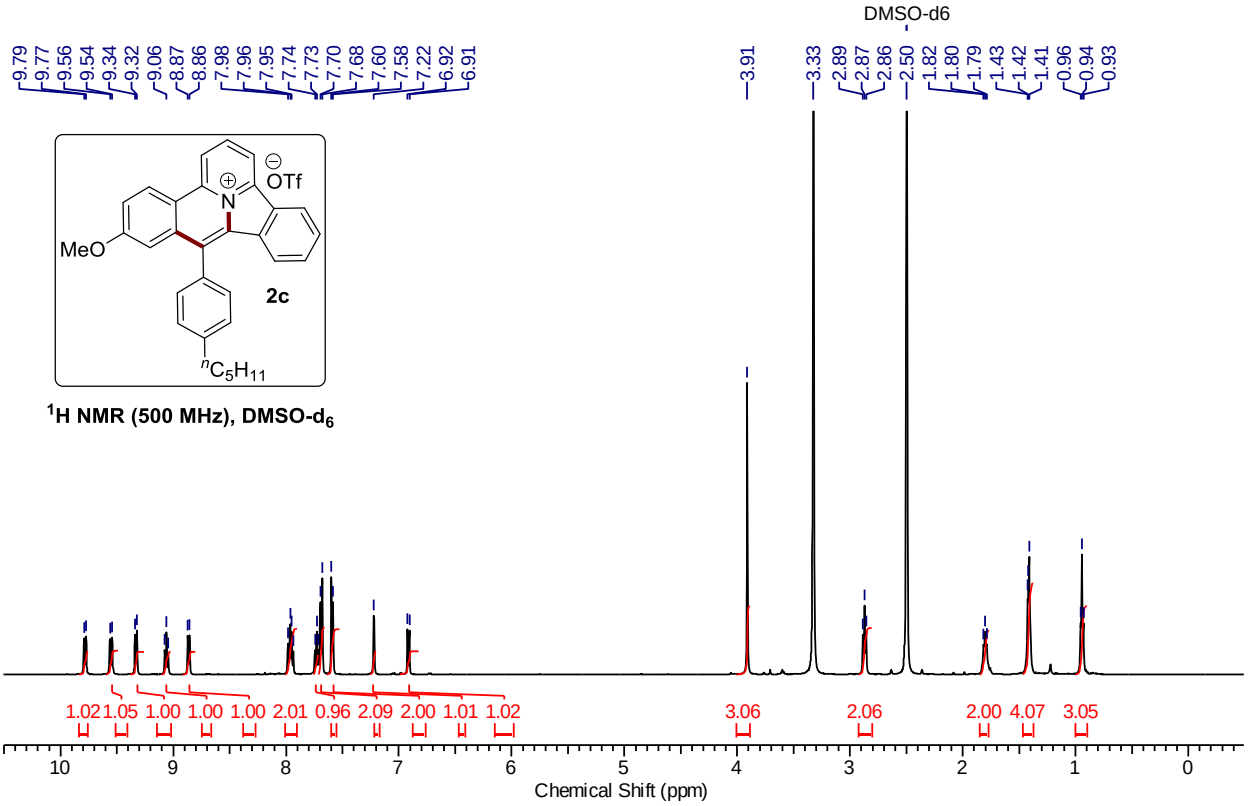
^{13}C NMR (100 MHz), DMSO-d_6



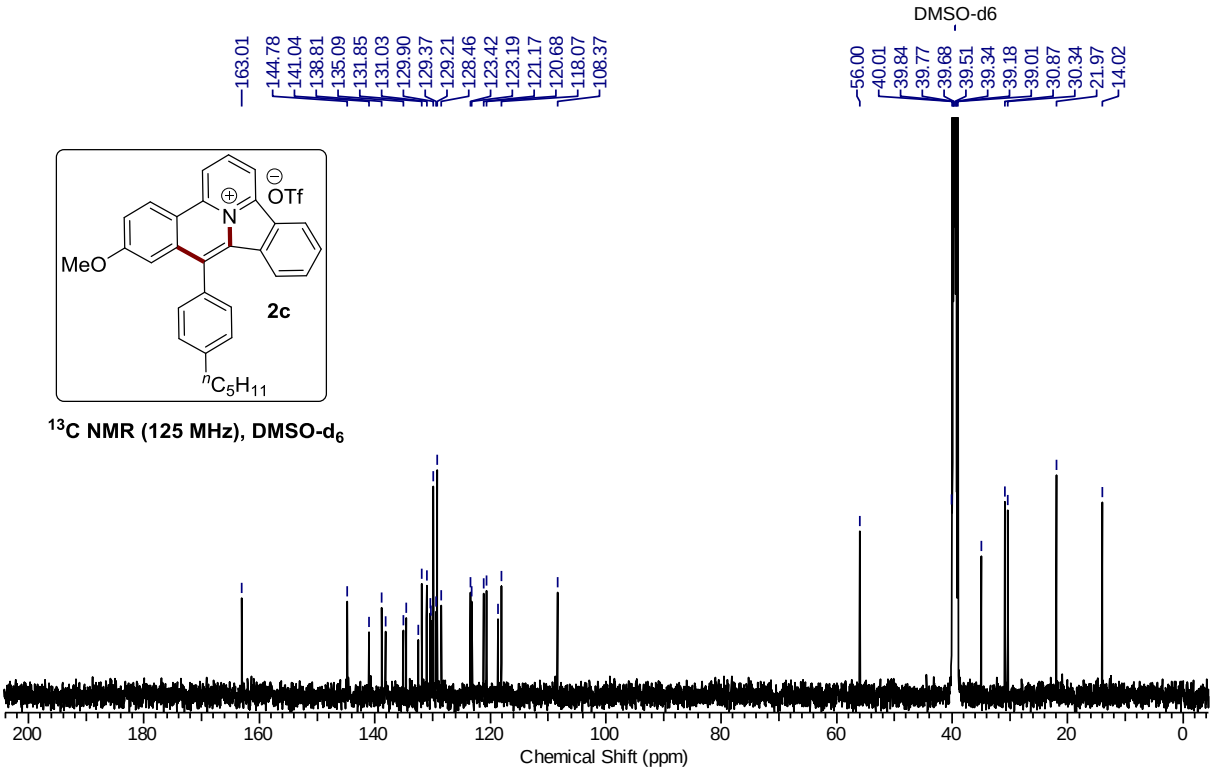
^{1}H NMR (400 MHz), DMSO-d_6



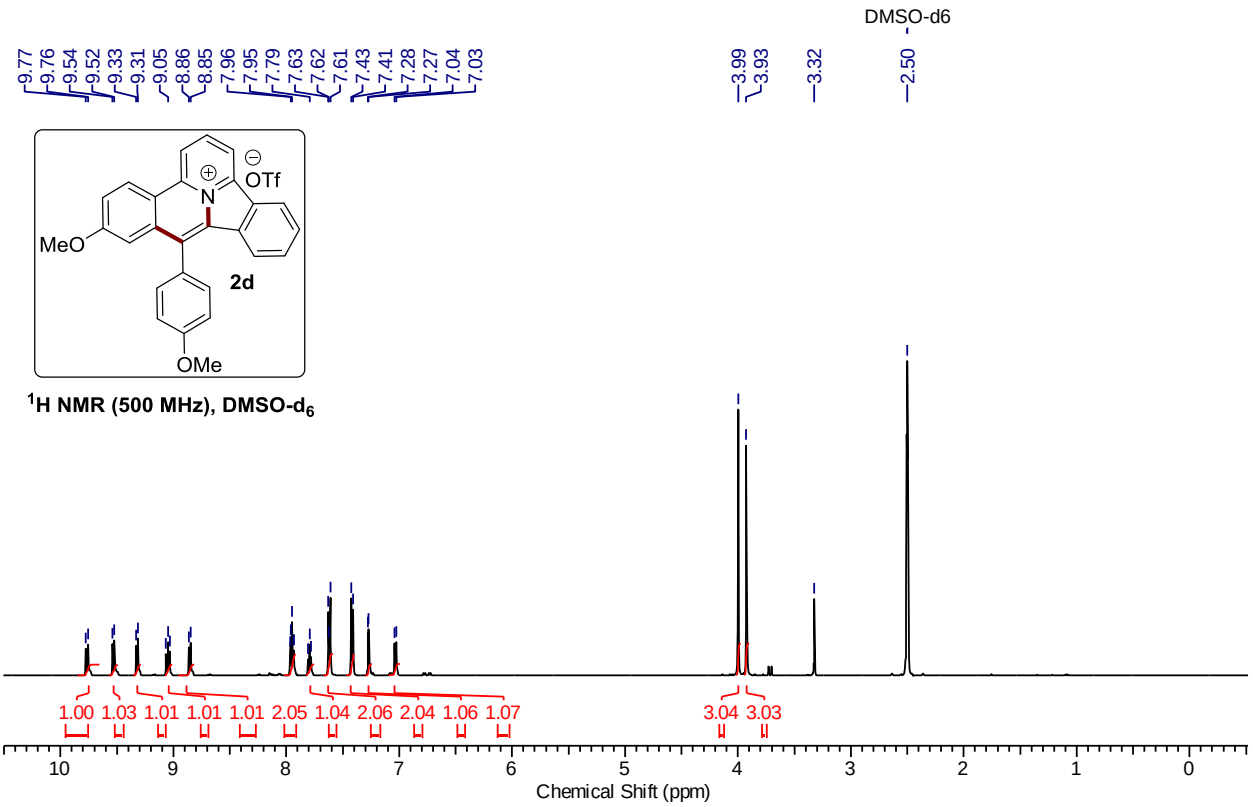
^{13}C NMR (100 MHz), DMSO-d_6



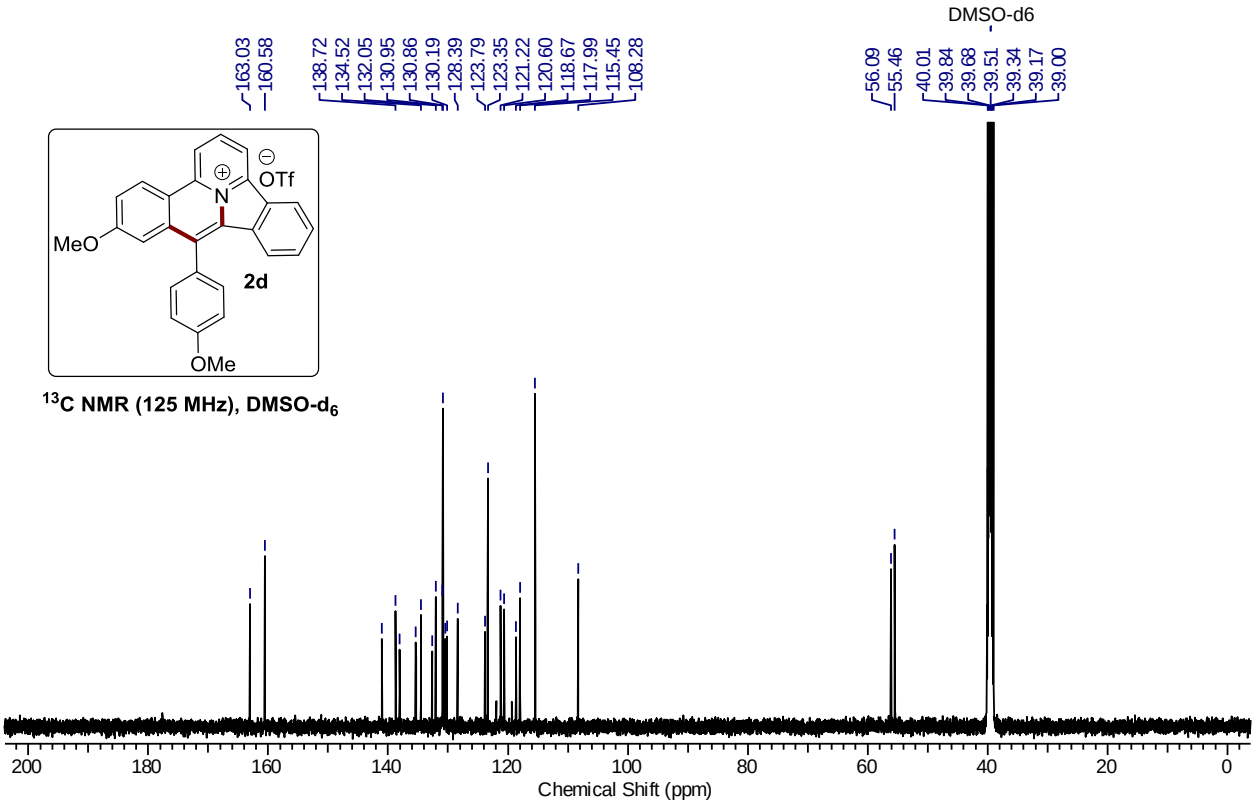
^{1}H NMR (500 MHz), DMSO-d_6



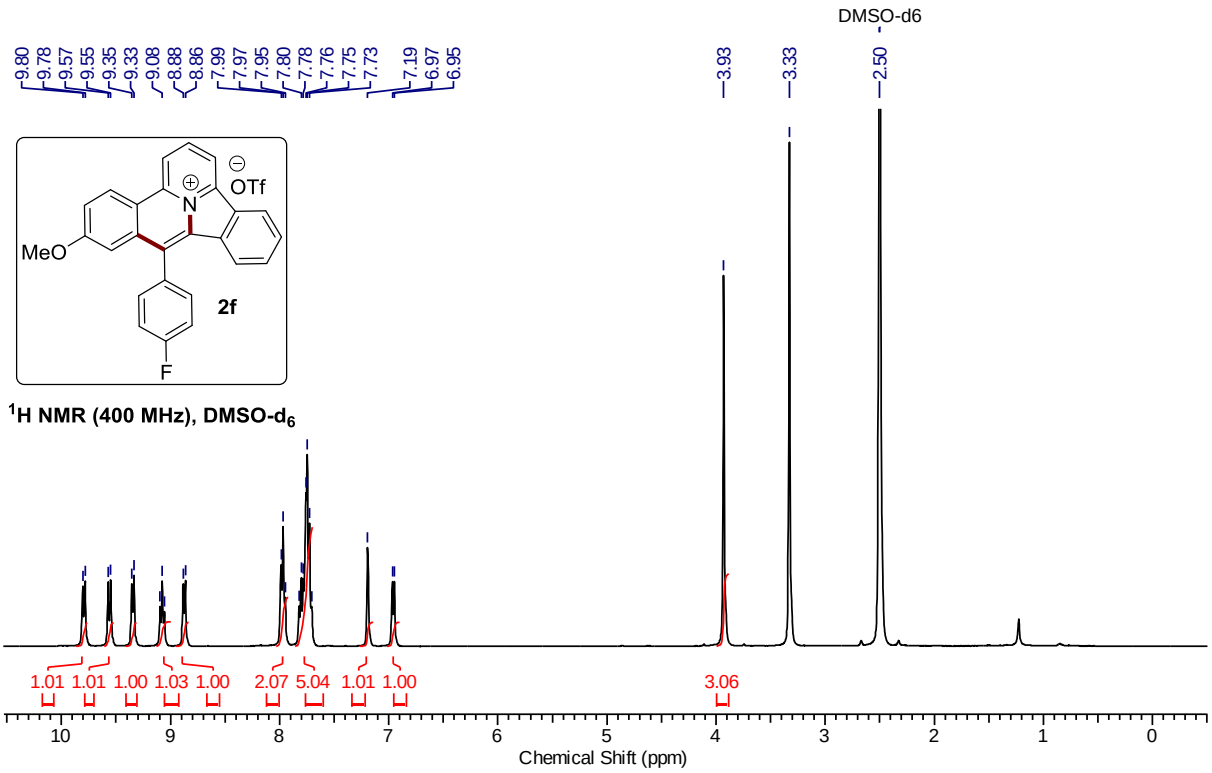
^{13}C NMR (125 MHz), DMSO-d_6



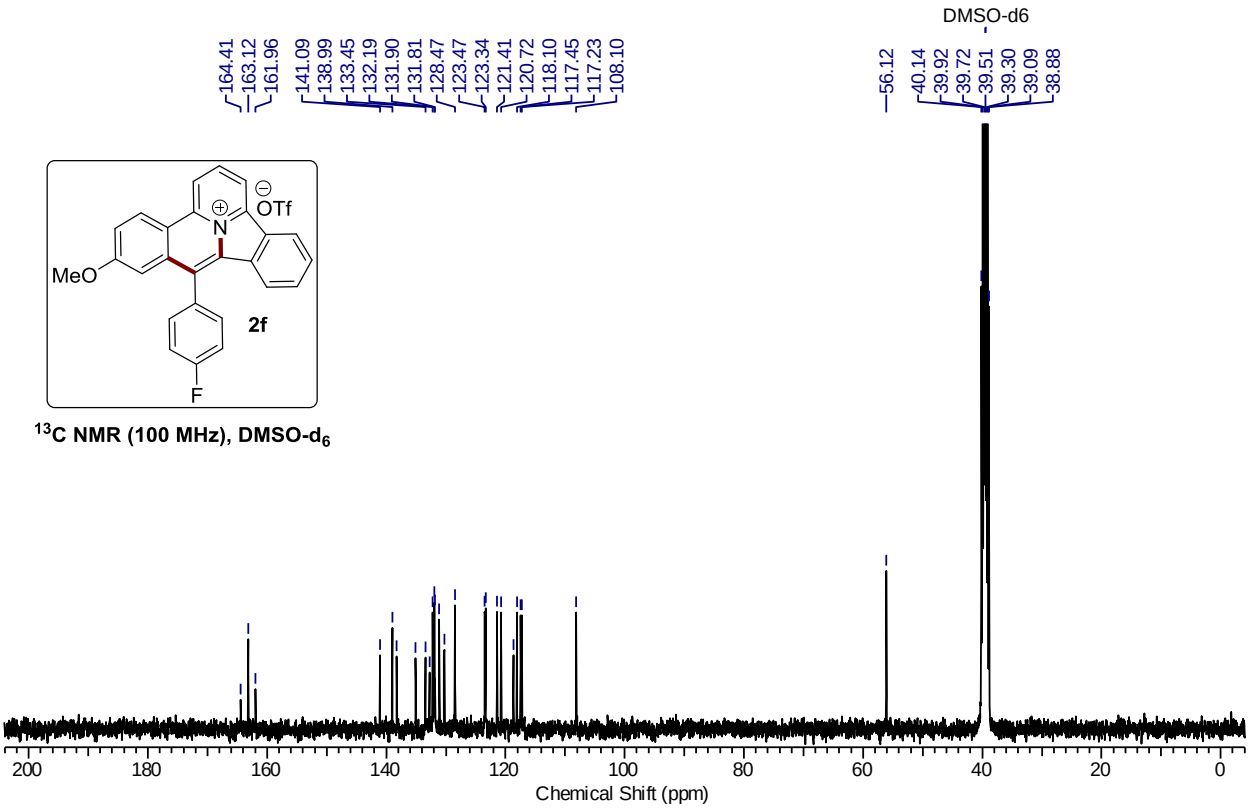
^{1}H NMR (500 MHz), DMSO-d_6



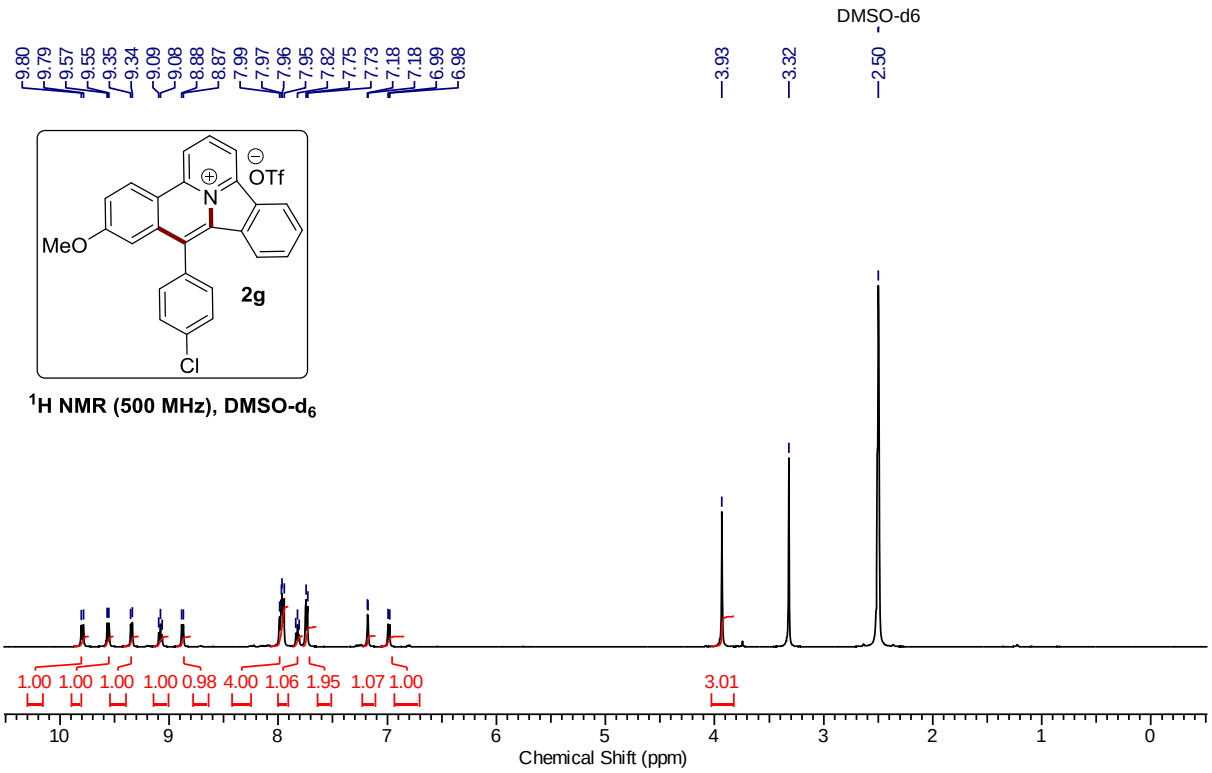
^{13}C NMR (125 MHz), DMSO-d_6



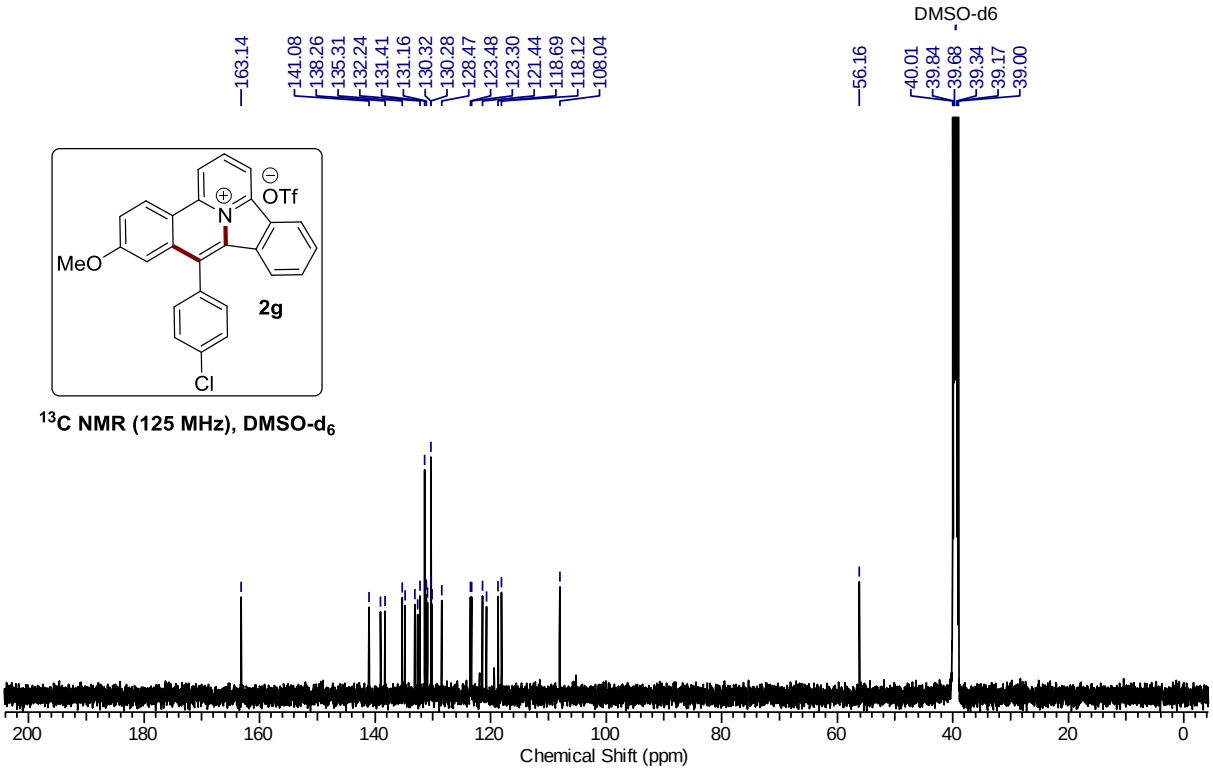
^{1}H NMR (400 MHz), DMSO-d$_6$



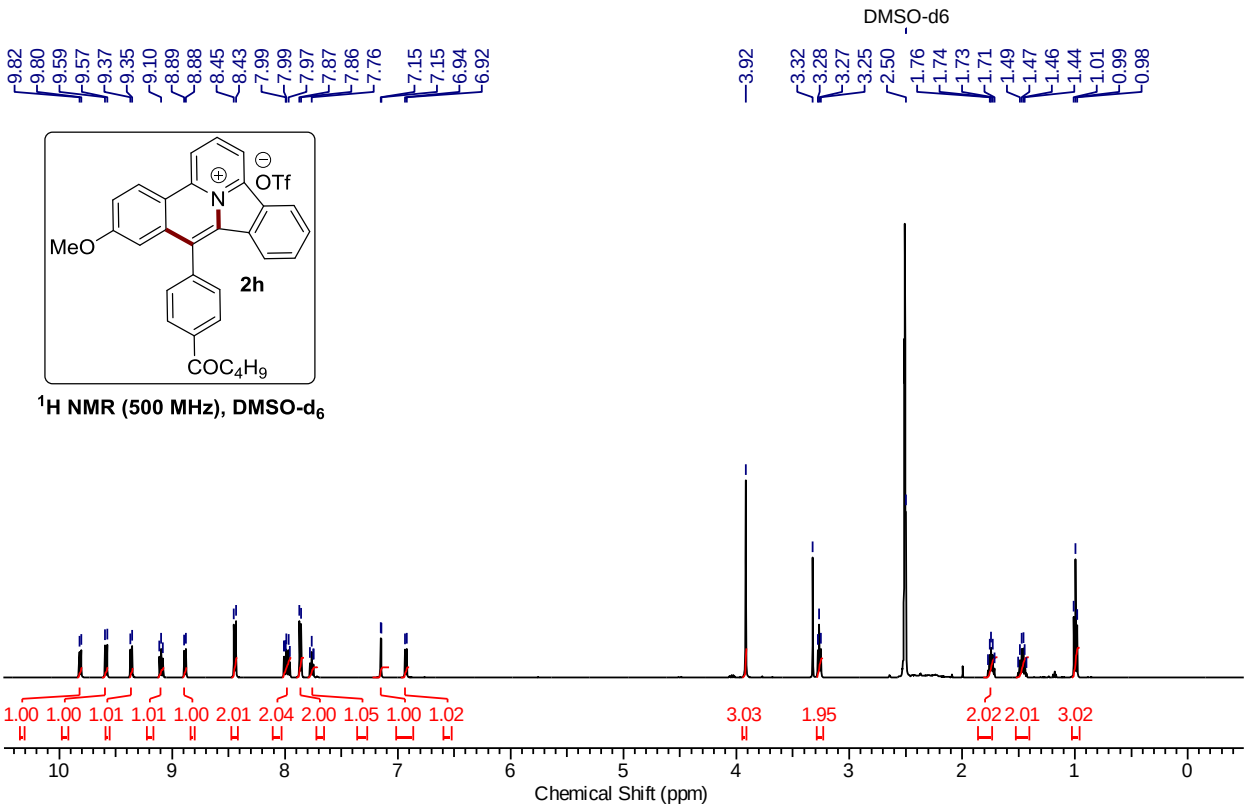
^{13}C NMR (100 MHz), DMSO-d$_6$

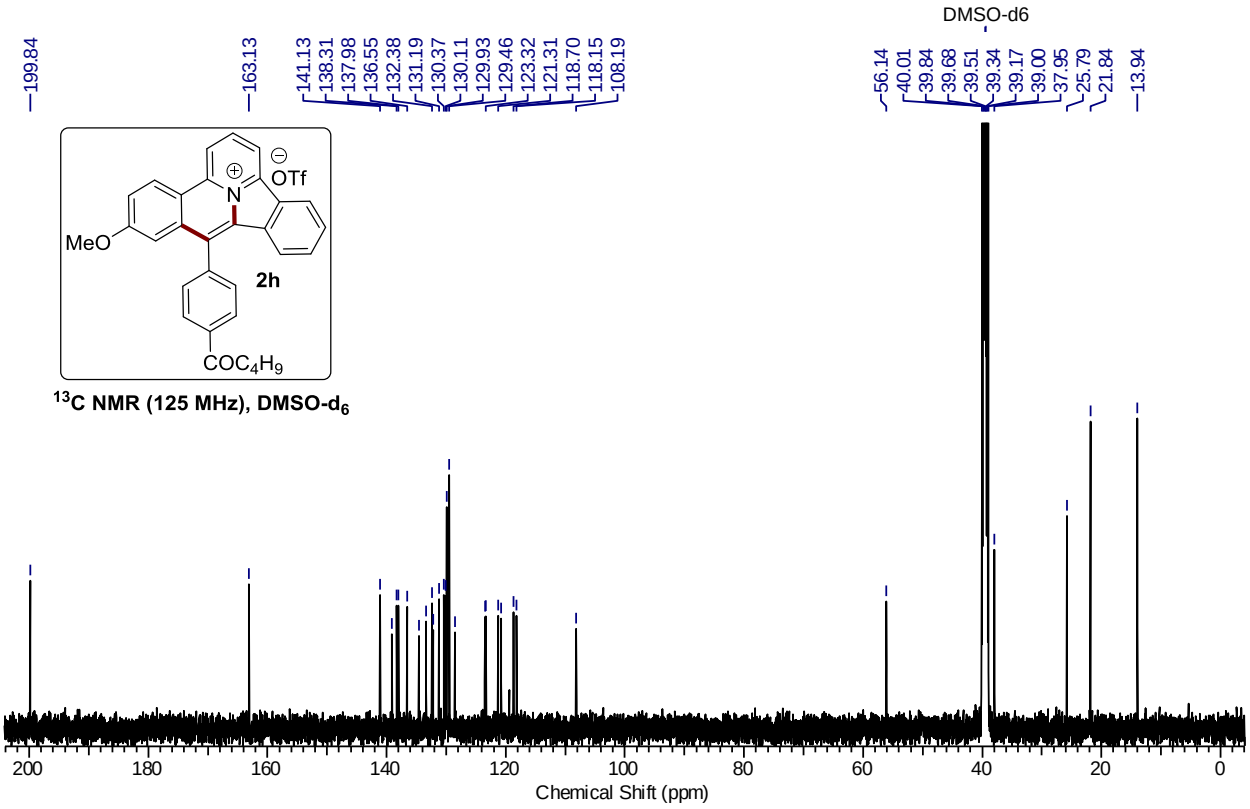


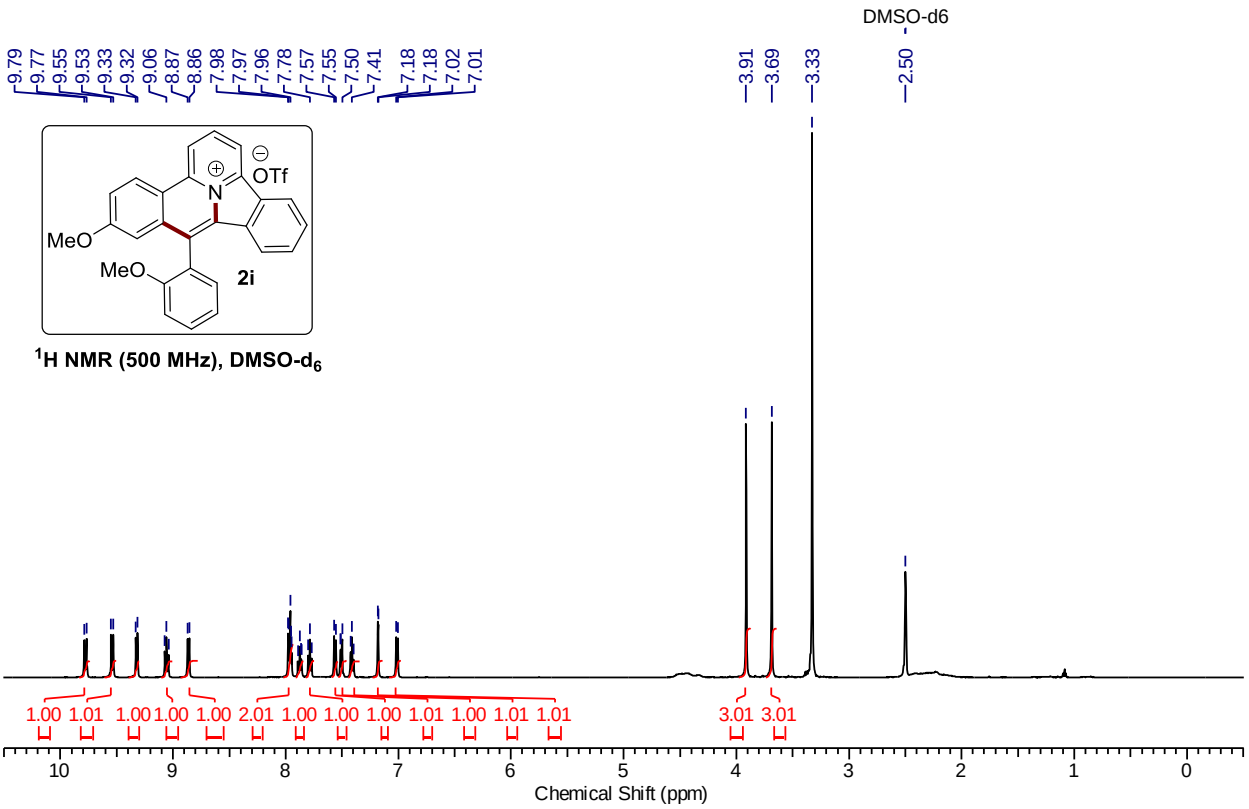
^{1}H NMR (500 MHz), DMSO-d$_6$



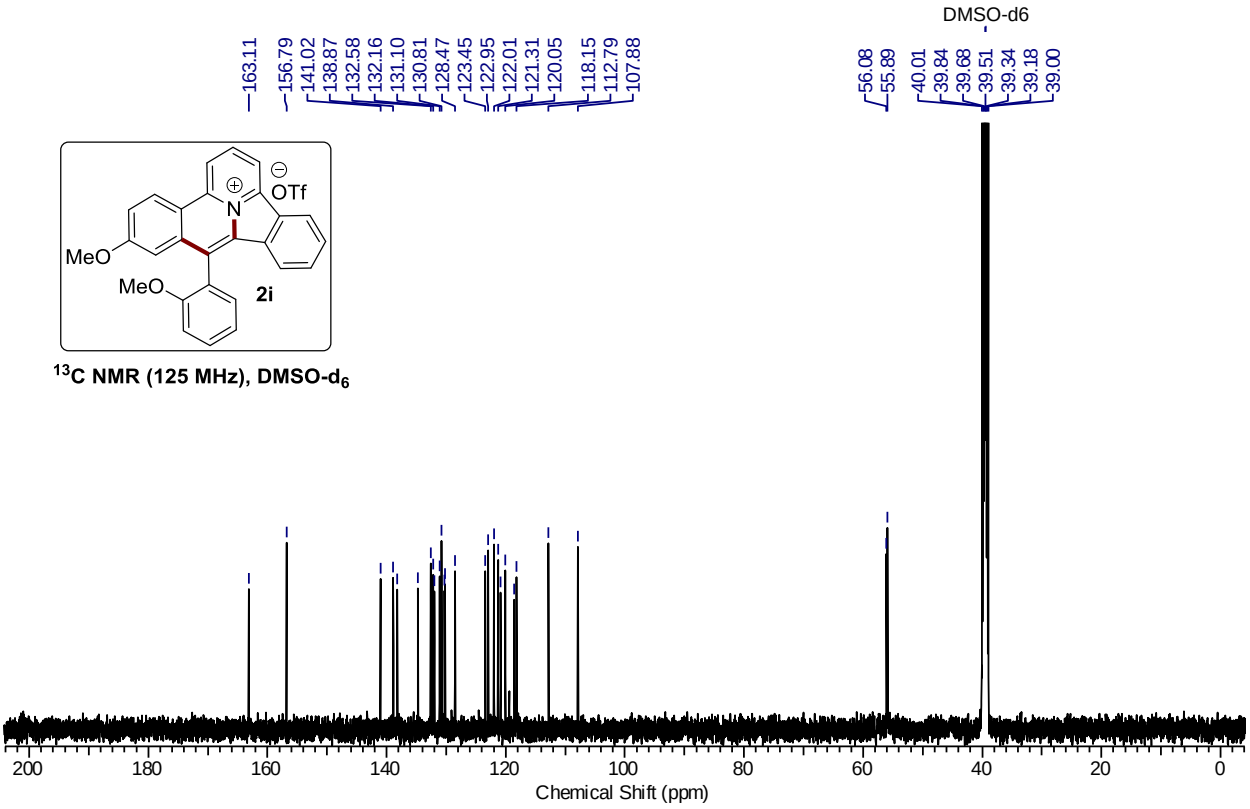
^{13}C NMR (125 MHz), DMSO-d$_6$


DMSO-d6
9.82 9.80 9.59 9.57 9.37 9.35 9.10 8.89 8.88 8.45 8.43 7.99 7.99 7.97 7.87 7.86 7.76 7.15 7.15 6.94 6.92
3.92
3.32 3.28 3.27 3.25 2.50 1.76 1.74 1.73 1.71 1.49 1.47 1.46 1.44 1.01 0.99 0.98
OTf
MeO
2h
COC4H9
1H NMR (500 MHz), DMSO-d6
1.00 1.00 1.01 1.01 1.00 2.01 2.04 2.00 1.05 1.00 1.02
3.03 1.95 2.02 2.01 3.02
Chemical Shift (ppm)

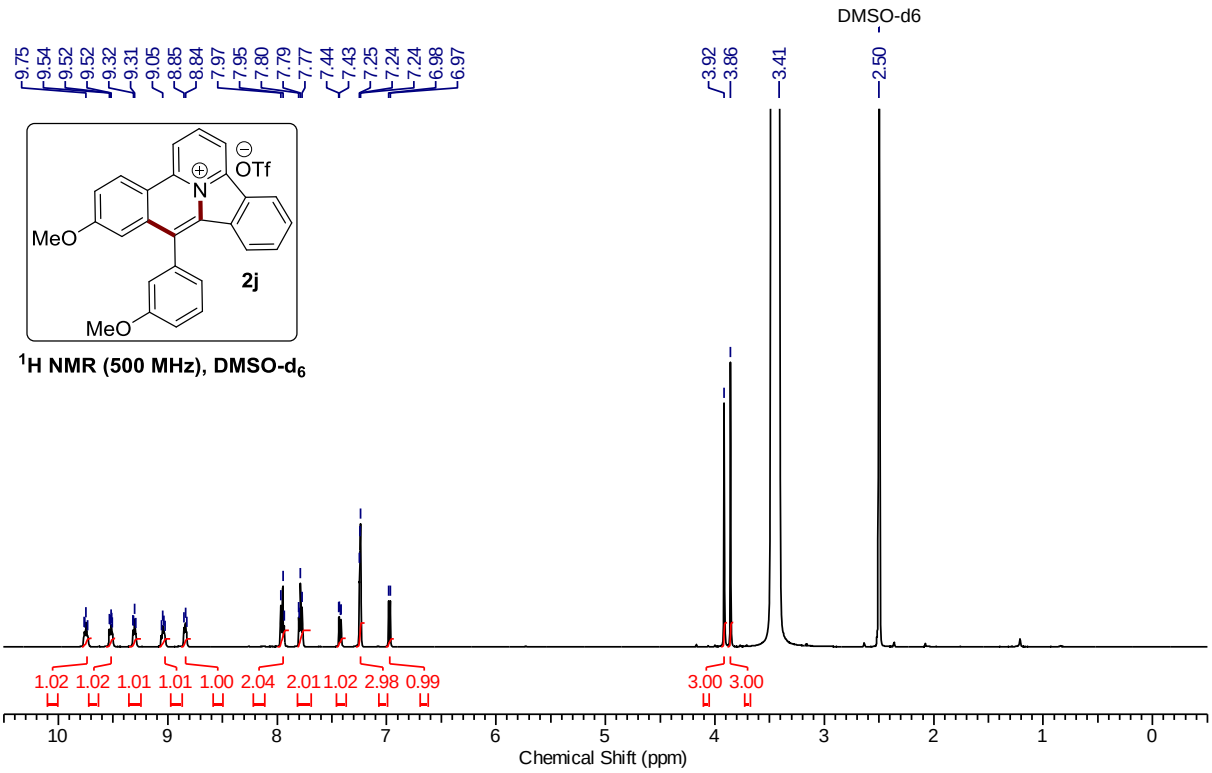

DMSO-d6
199.84 163.13 141.13 138.31 137.98 136.55 132.38 131.19 130.37 130.11 129.93 129.46 123.32 121.31 118.70 118.15 108.19
56.14 40.01 39.84 39.68 39.51 39.34 39.17 39.00 37.95 25.79 21.84 13.94
OTf
MeO
2h
COC4H9
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)



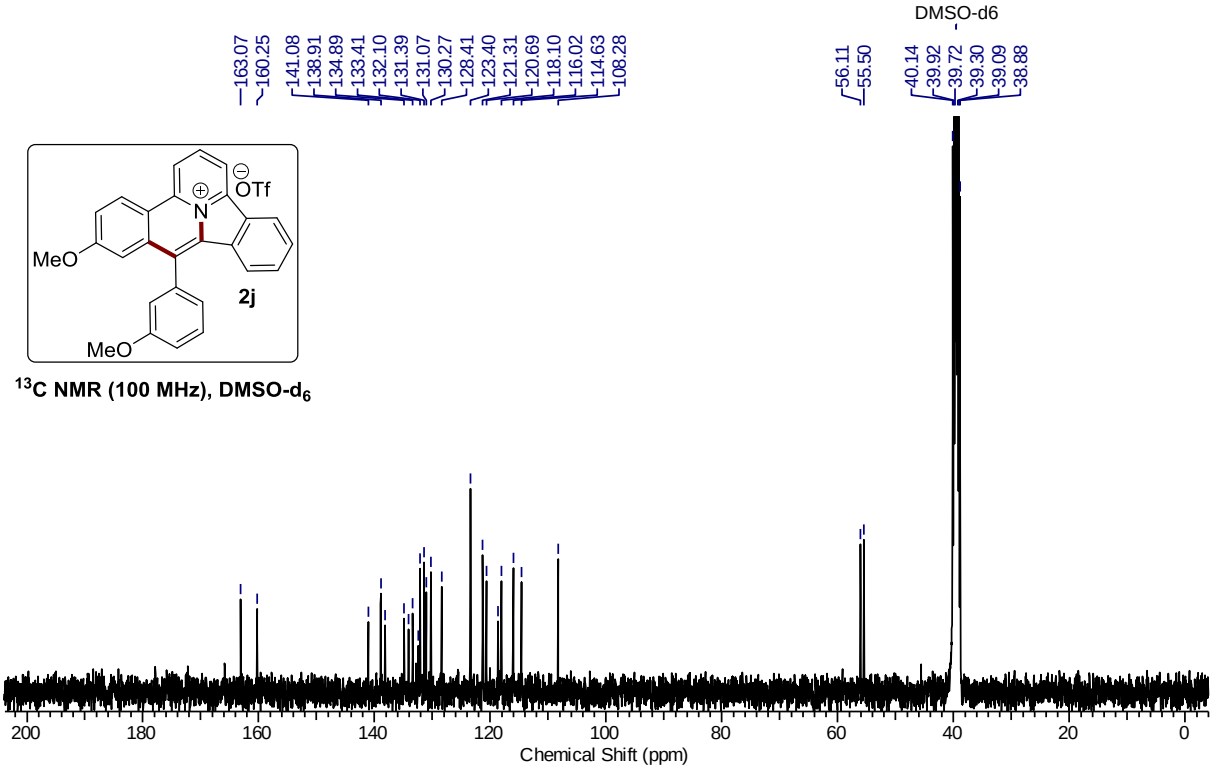
^{1}H NMR (500 MHz), DMSO-d$_6$



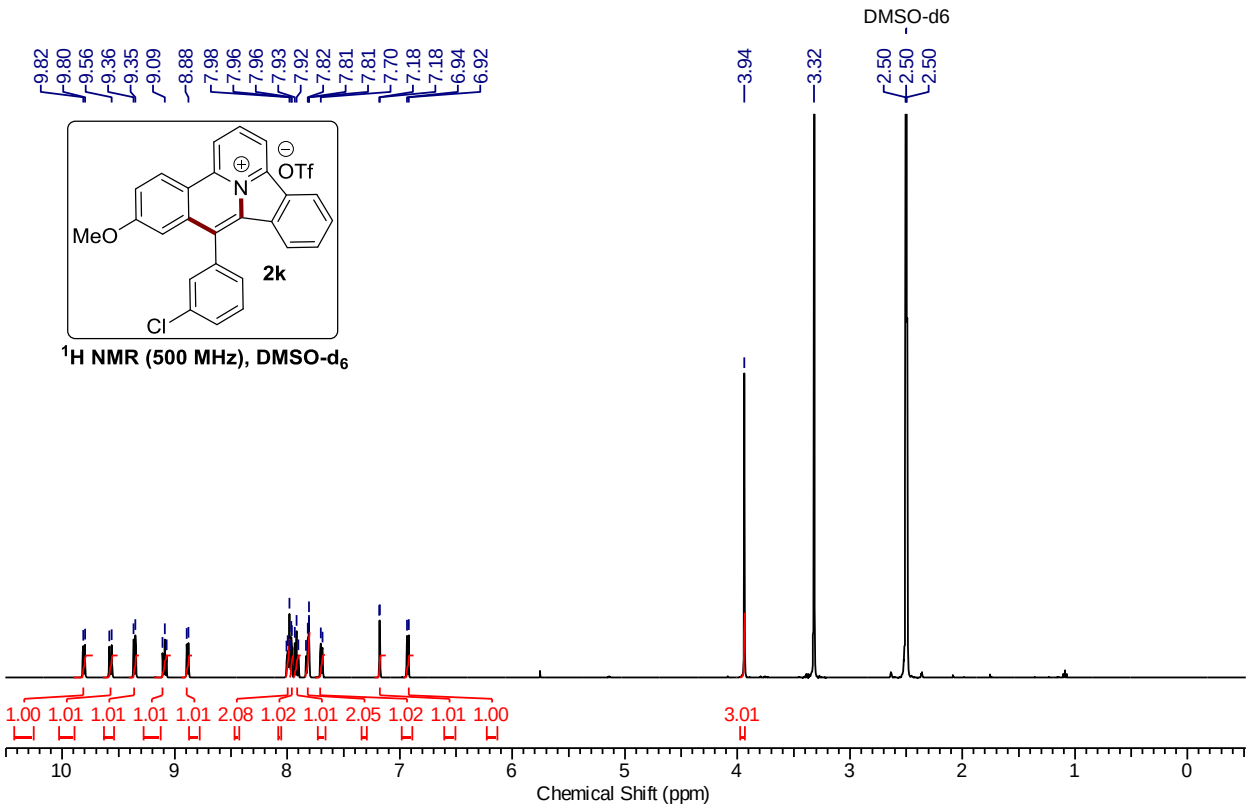
^{13}C NMR (125 MHz), DMSO-d$_6$



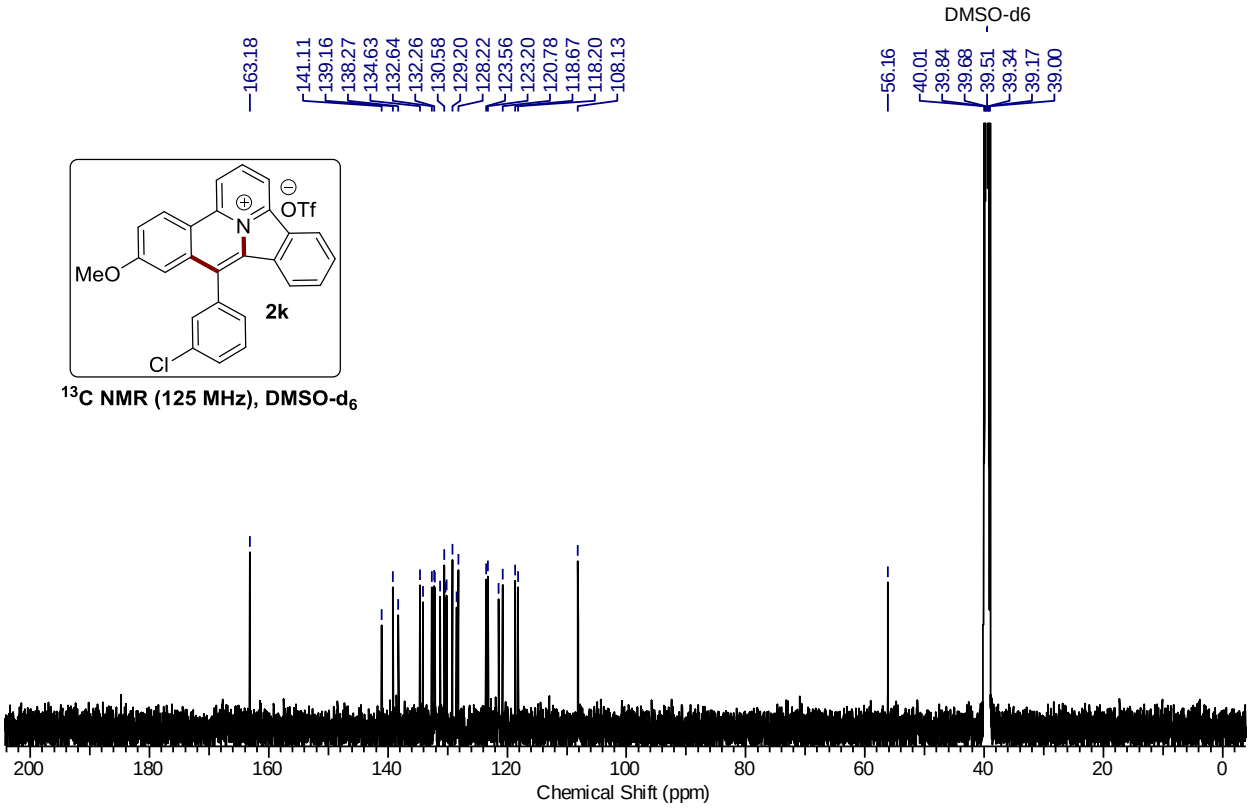
^{1}H NMR (500 MHz), DMSO-d_6



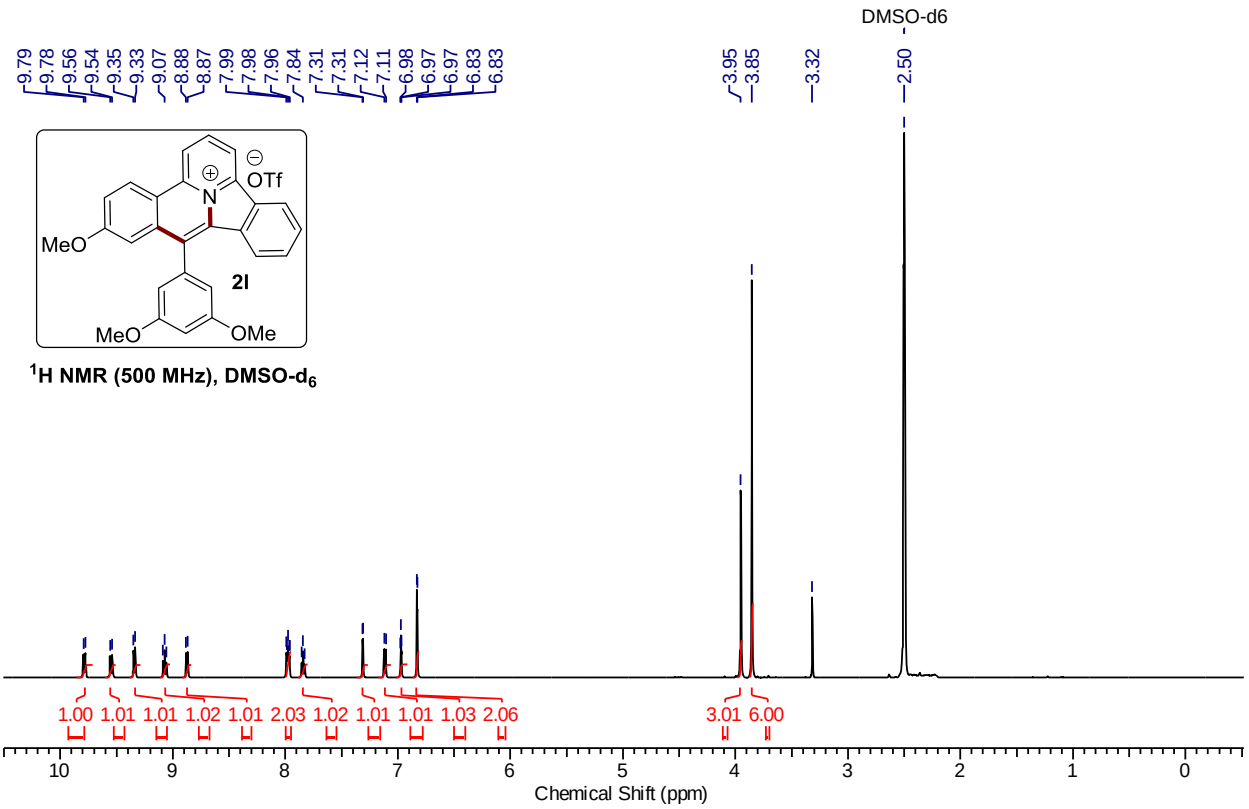
^{13}C NMR (100 MHz), DMSO-d_6



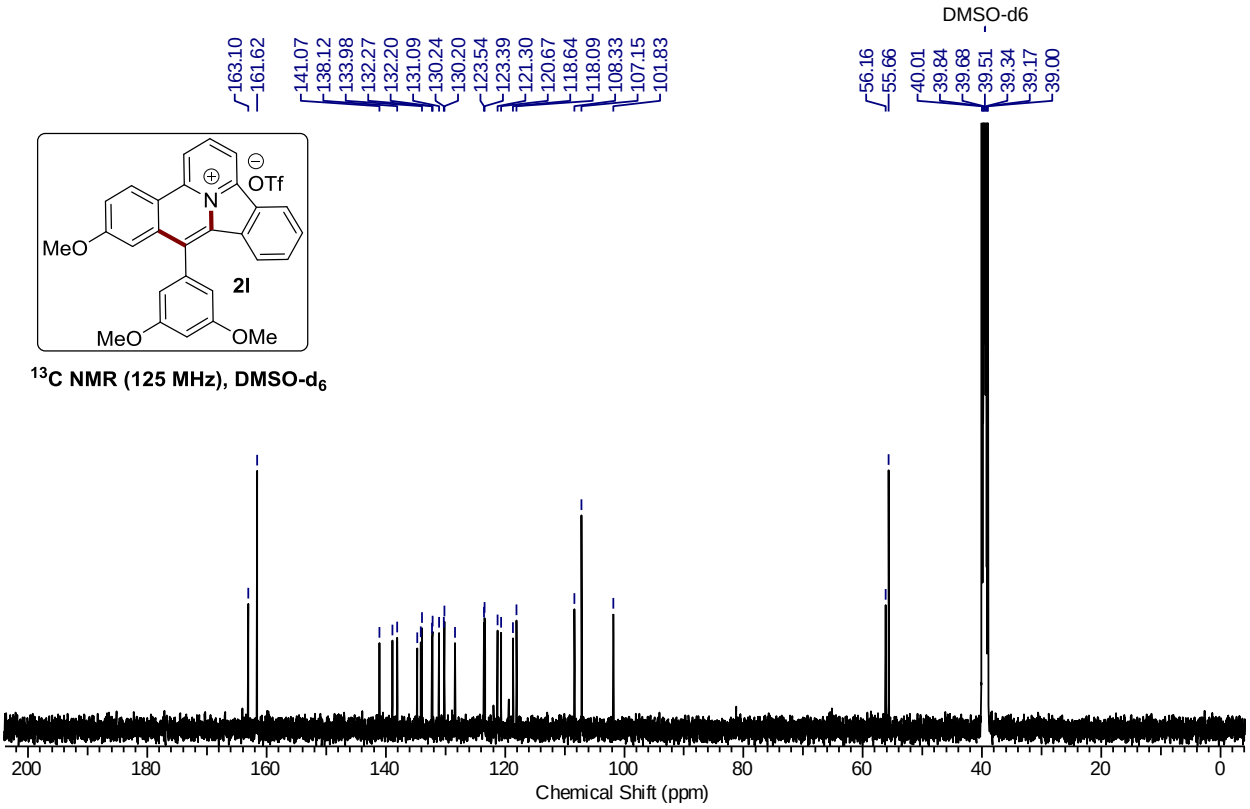
^{1}H NMR (500 MHz), DMSO-d$_6$



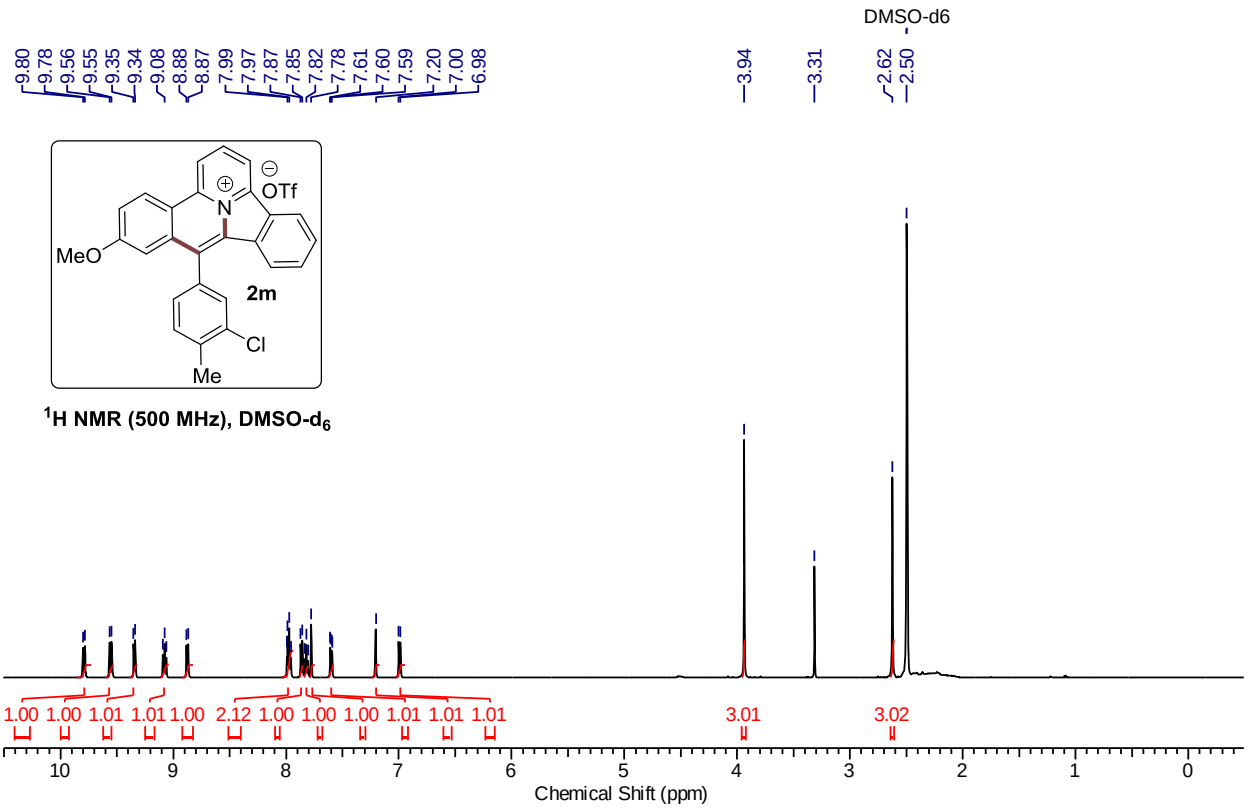
^{13}C NMR (125 MHz), DMSO-d$_6$



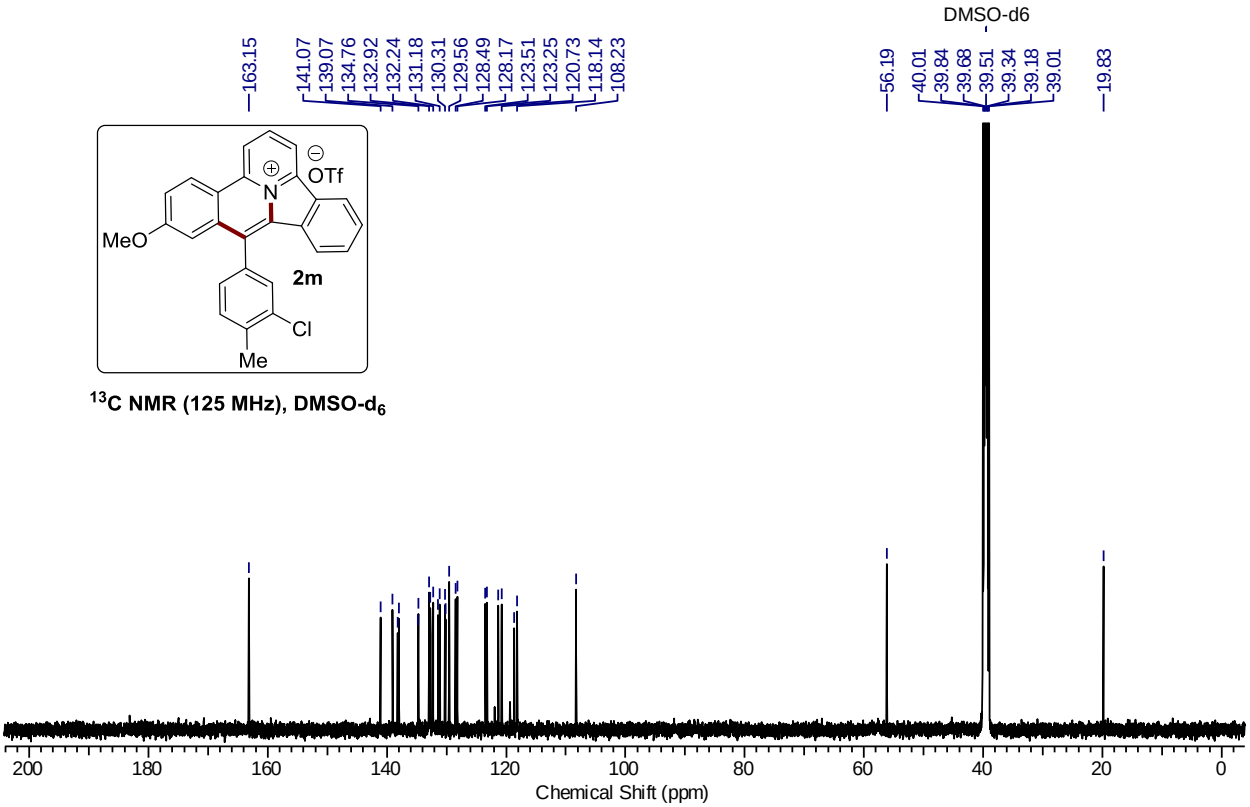
^{1}H NMR (500 MHz), DMSO-d_6



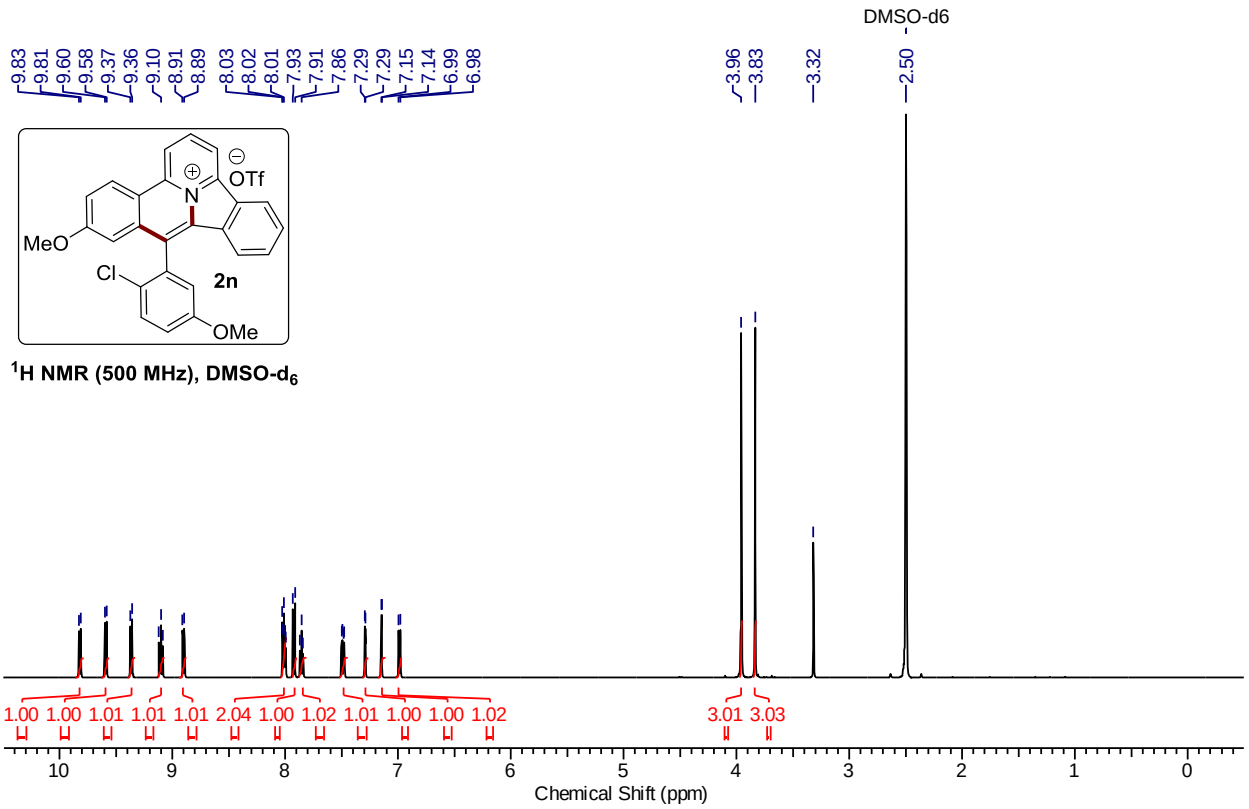
^{13}C NMR (125 MHz), DMSO-d_6



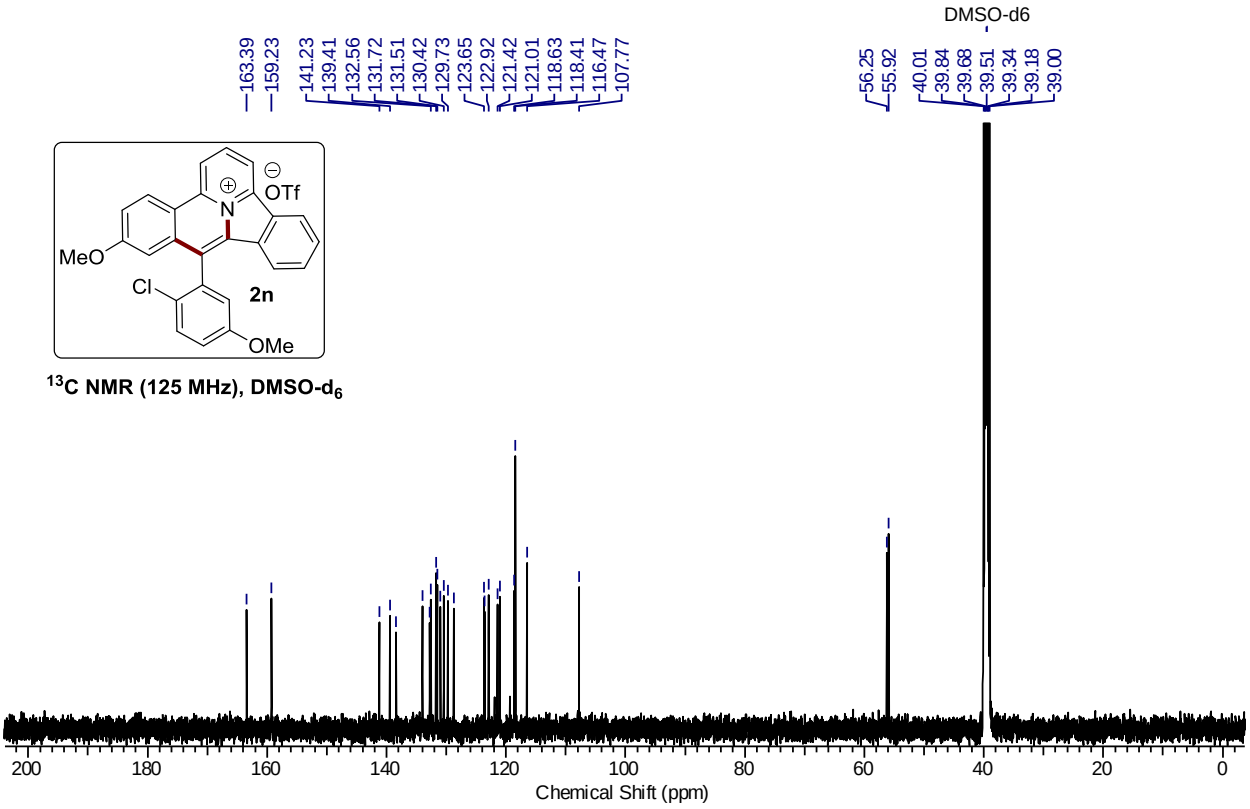
^{1}H NMR (500 MHz), DMSO-d_6



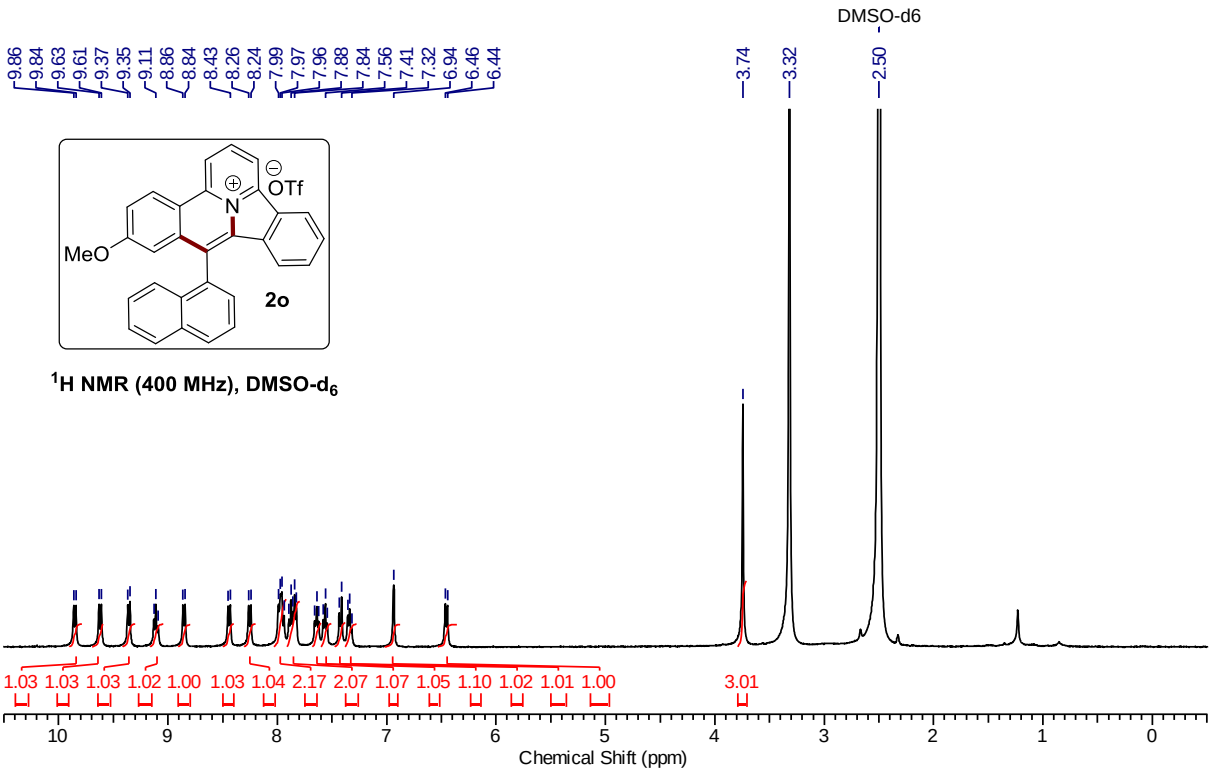
^{13}C NMR (125 MHz), DMSO-d_6



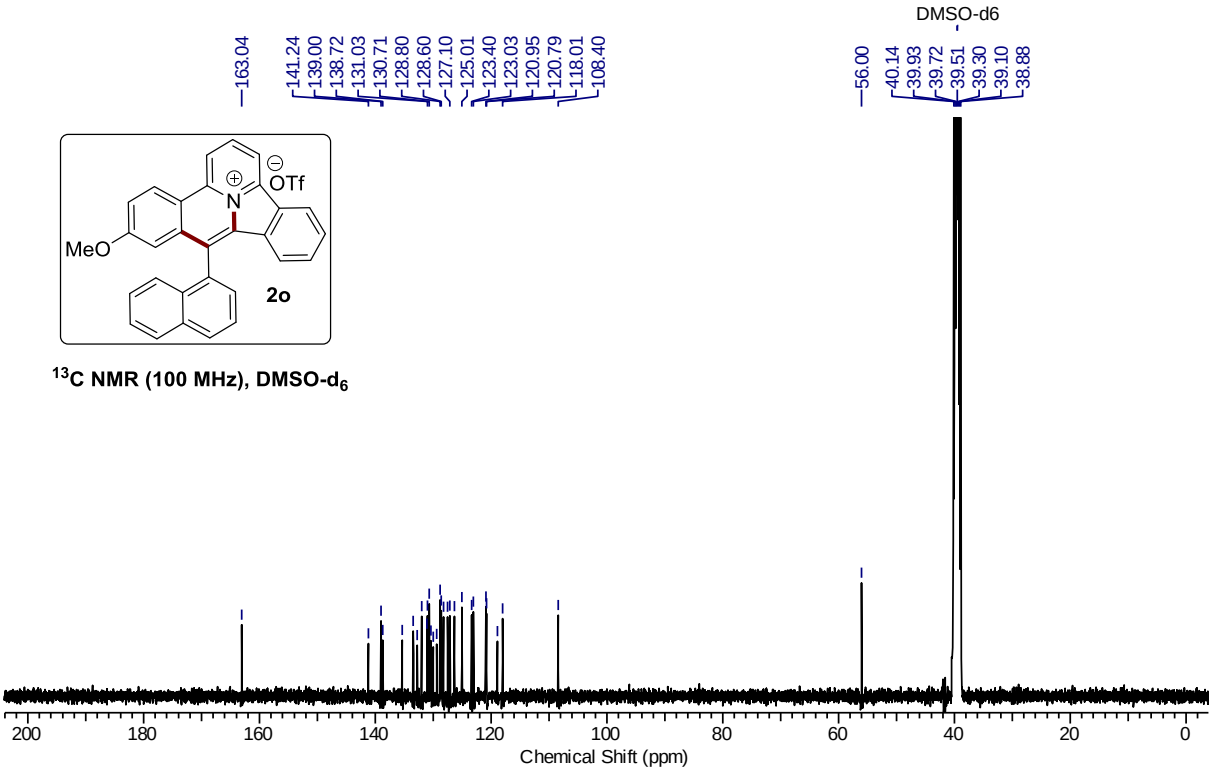
^{1}H NMR (500 MHz), DMSO-d_6



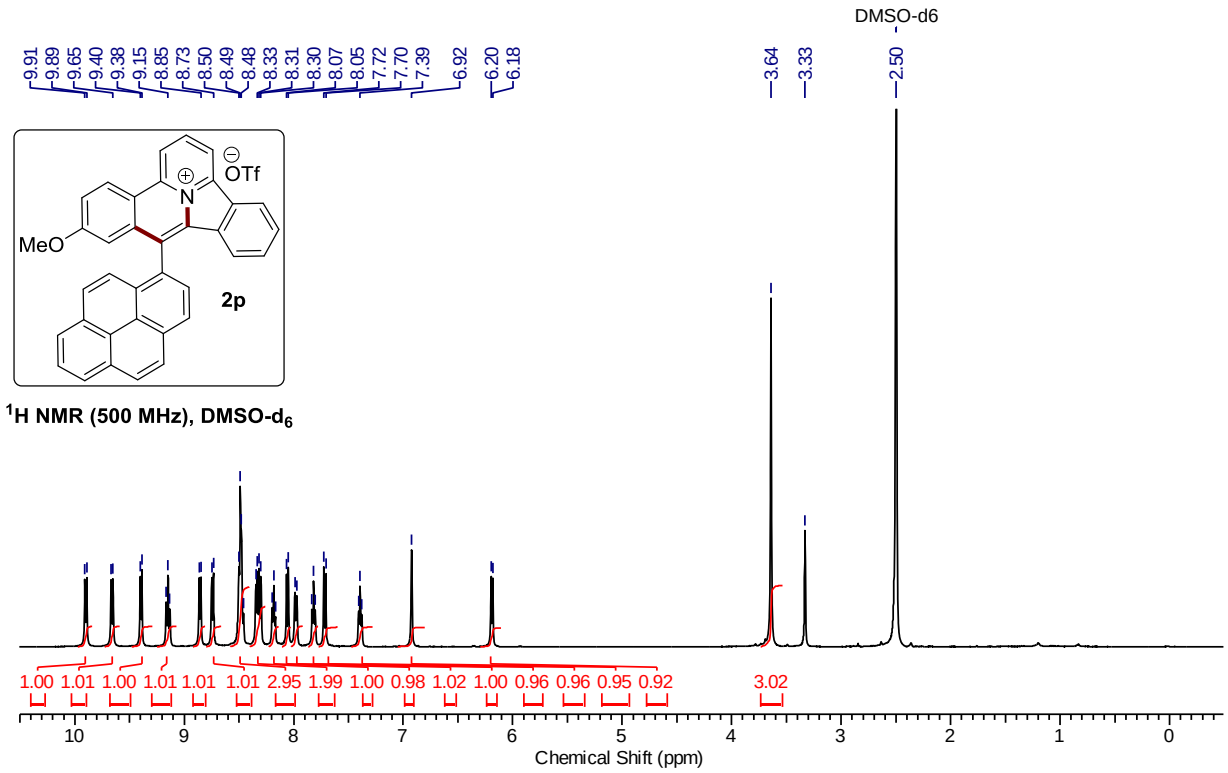
^{13}C NMR (125 MHz), DMSO-d_6



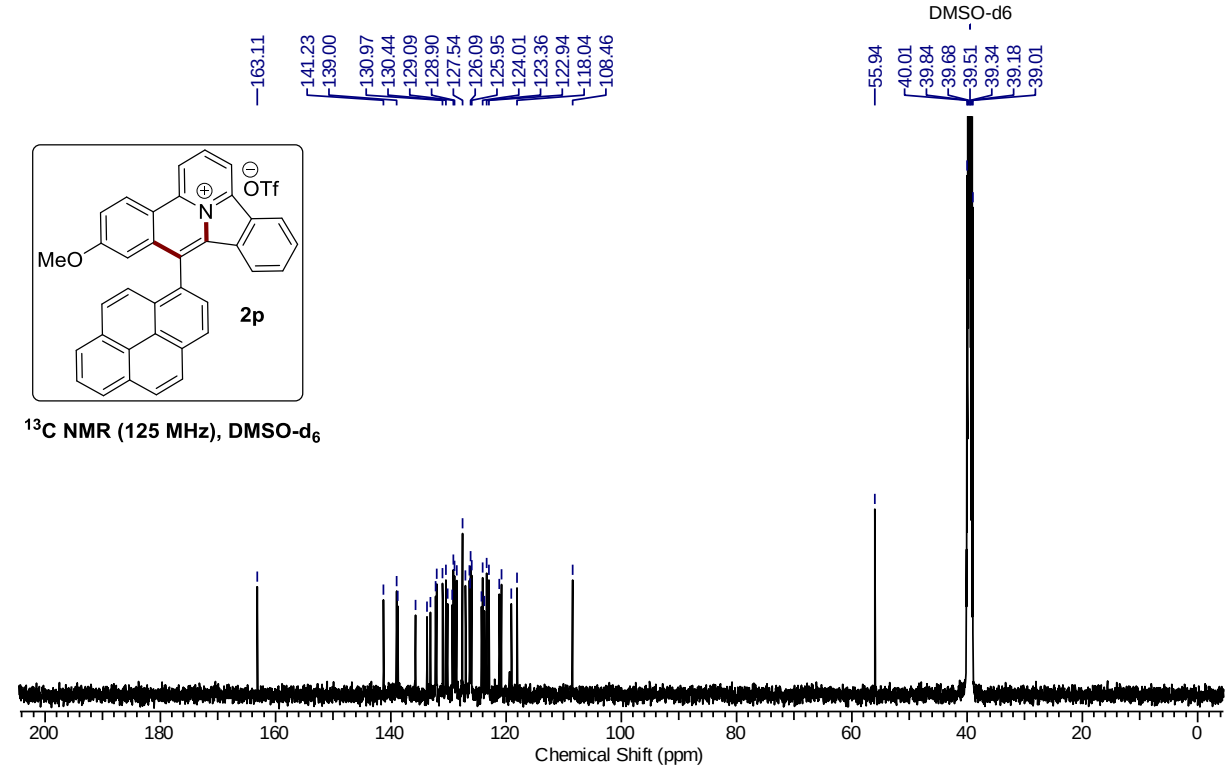
^{1}H NMR (400 MHz), DMSO-d_6



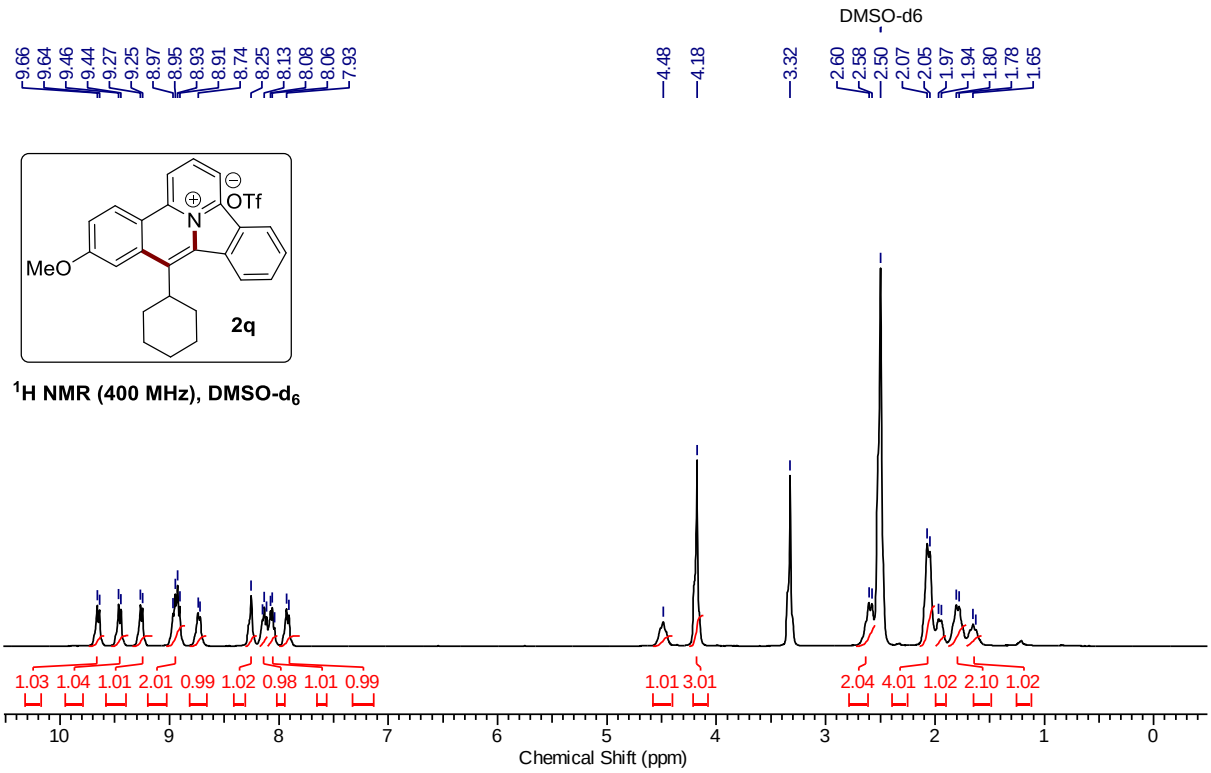
^{13}C NMR (100 MHz), DMSO-d_6



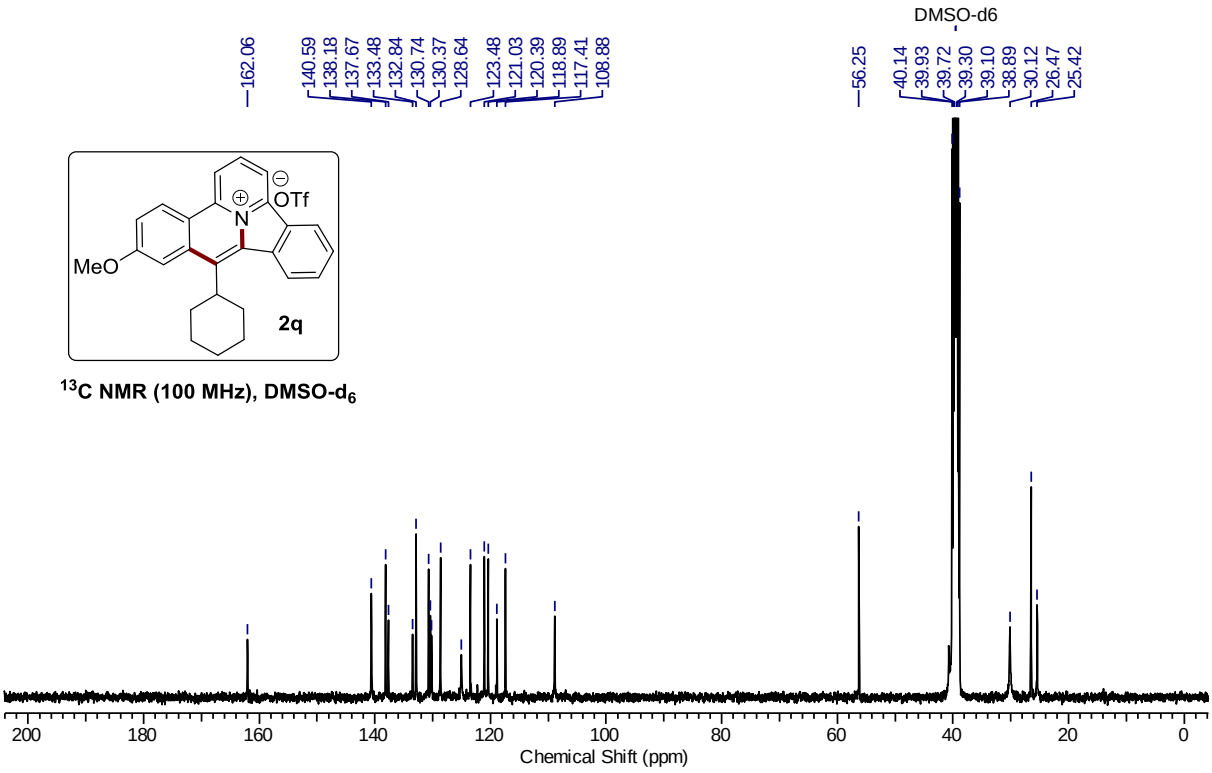
^{1}H NMR (500 MHz), DMSO-d_6



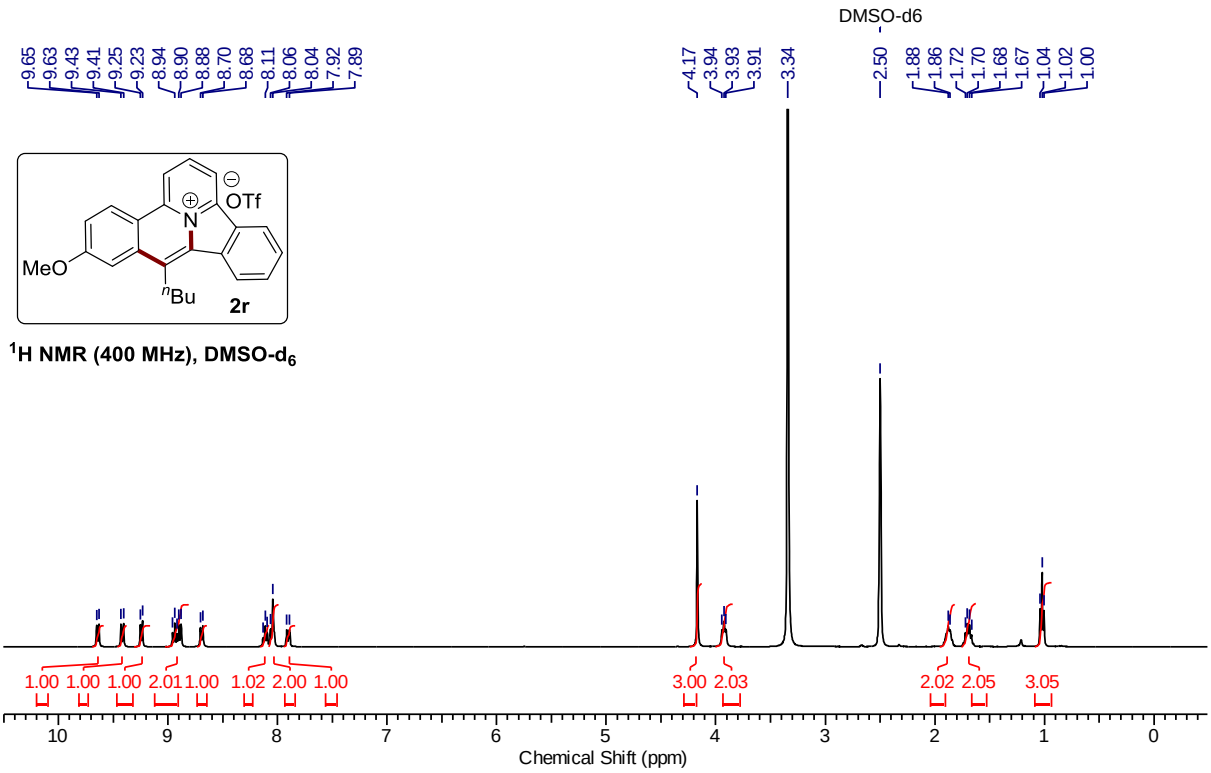
^{13}C NMR (125 MHz), DMSO-d_6



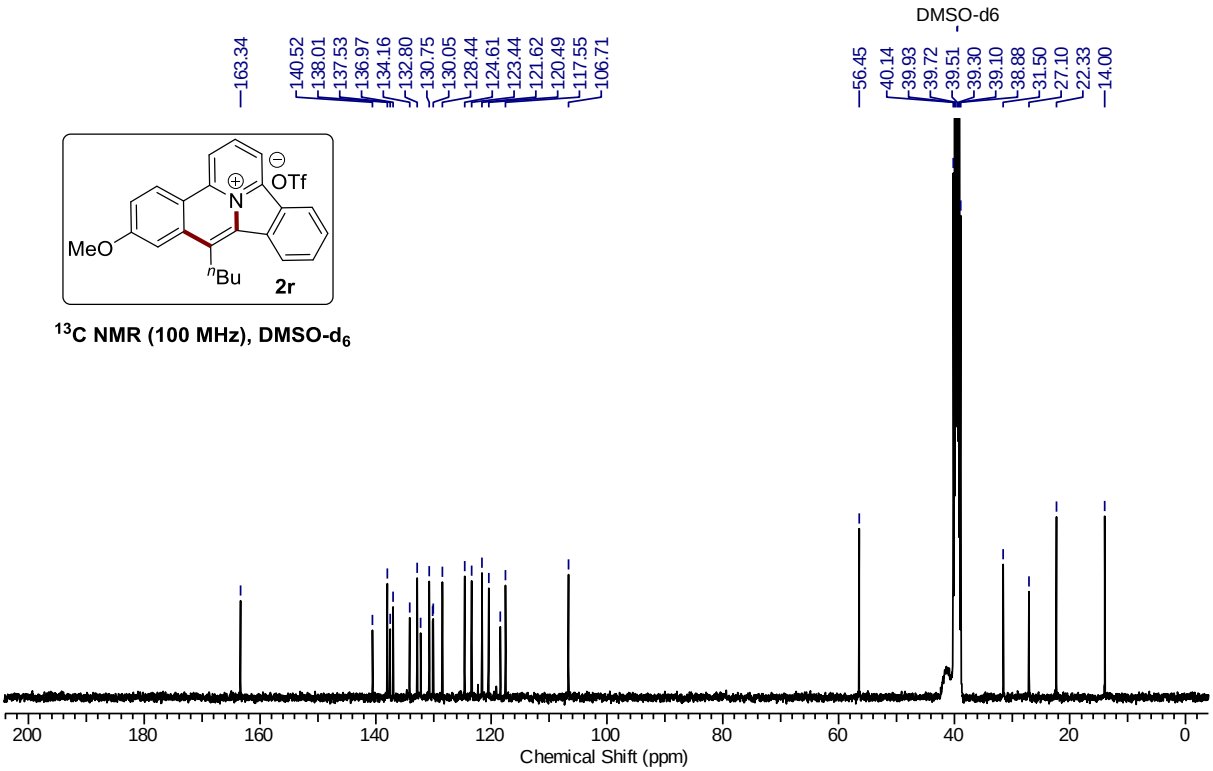
^{1}H NMR (400 MHz), DMSO-d_6



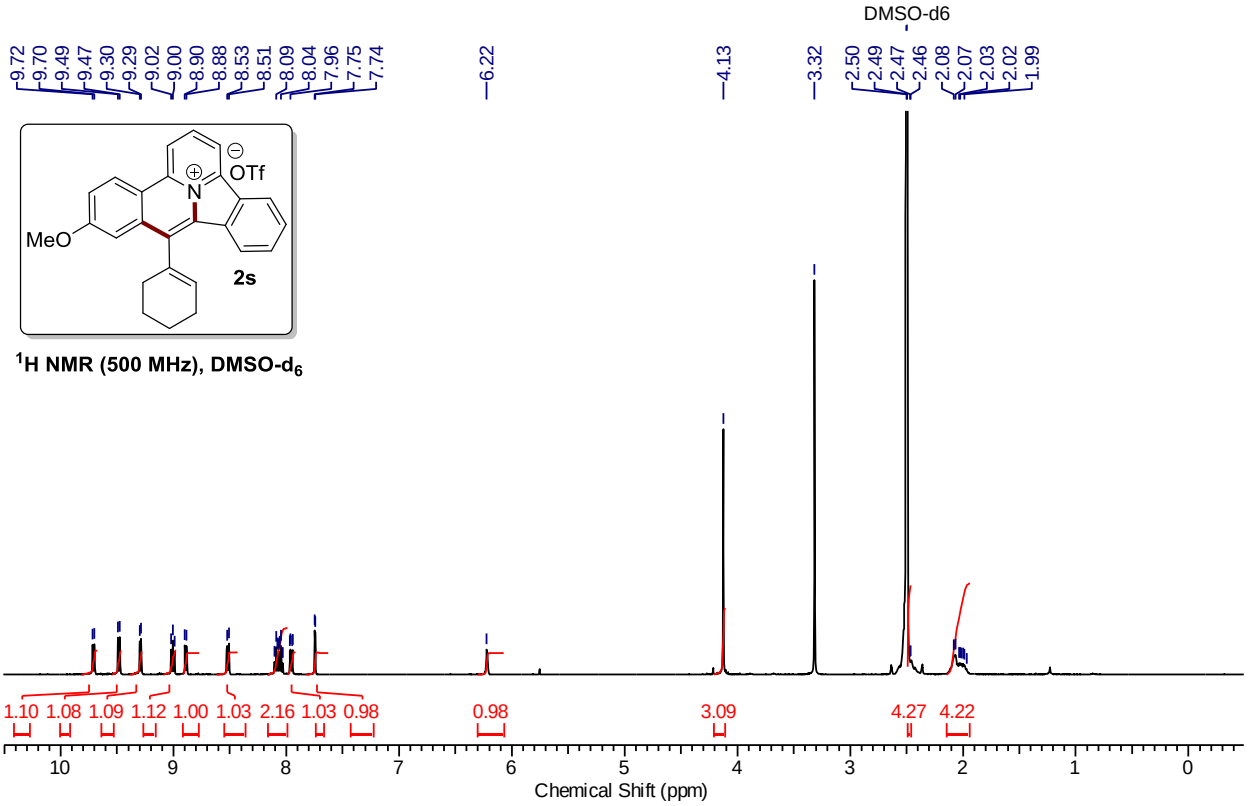
^{13}C NMR (100 MHz), DMSO-d_6



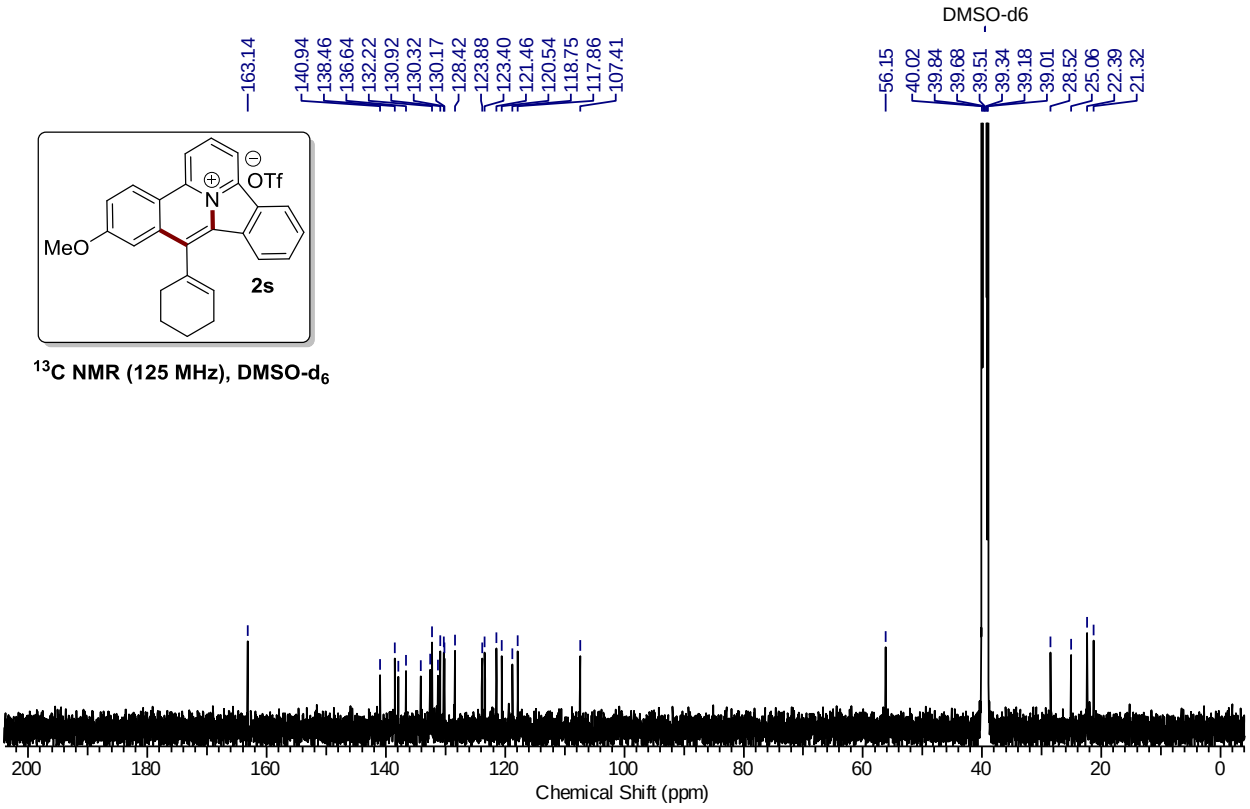
^{1}H NMR (400 MHz), DMSO-d$_6$



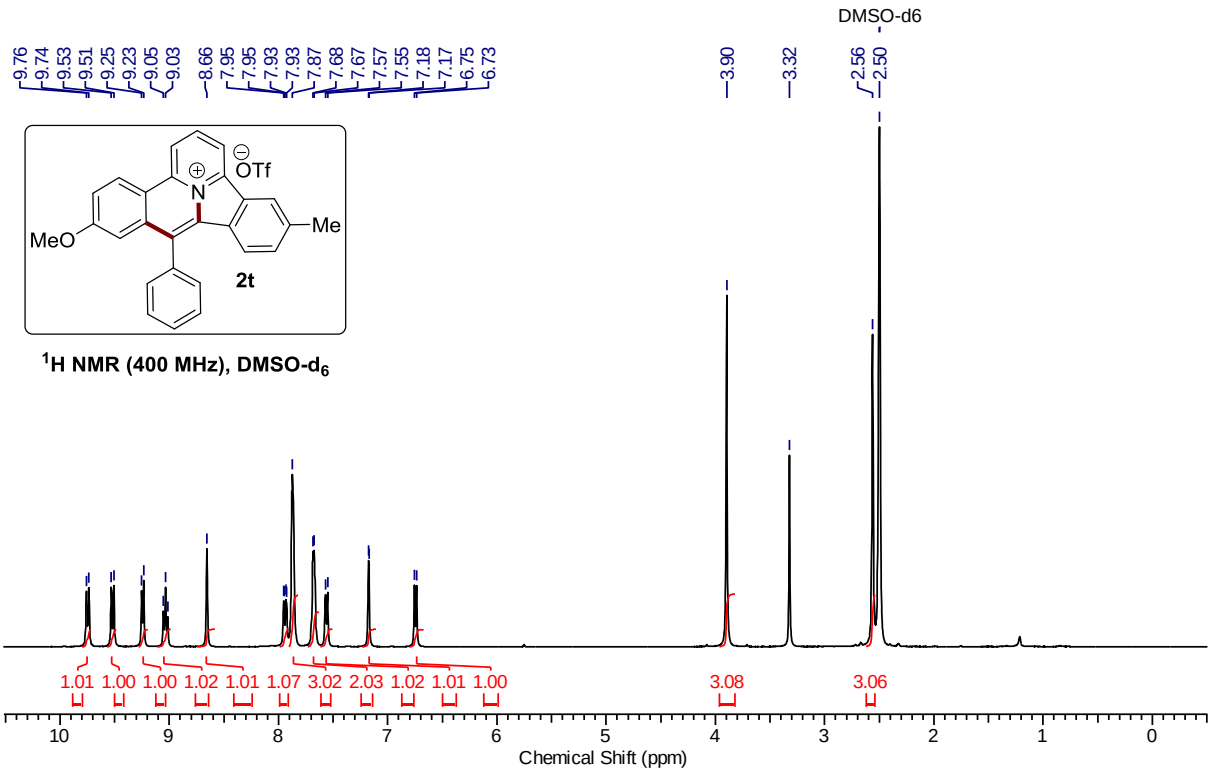
^{13}C NMR (100 MHz), DMSO-d$_6$



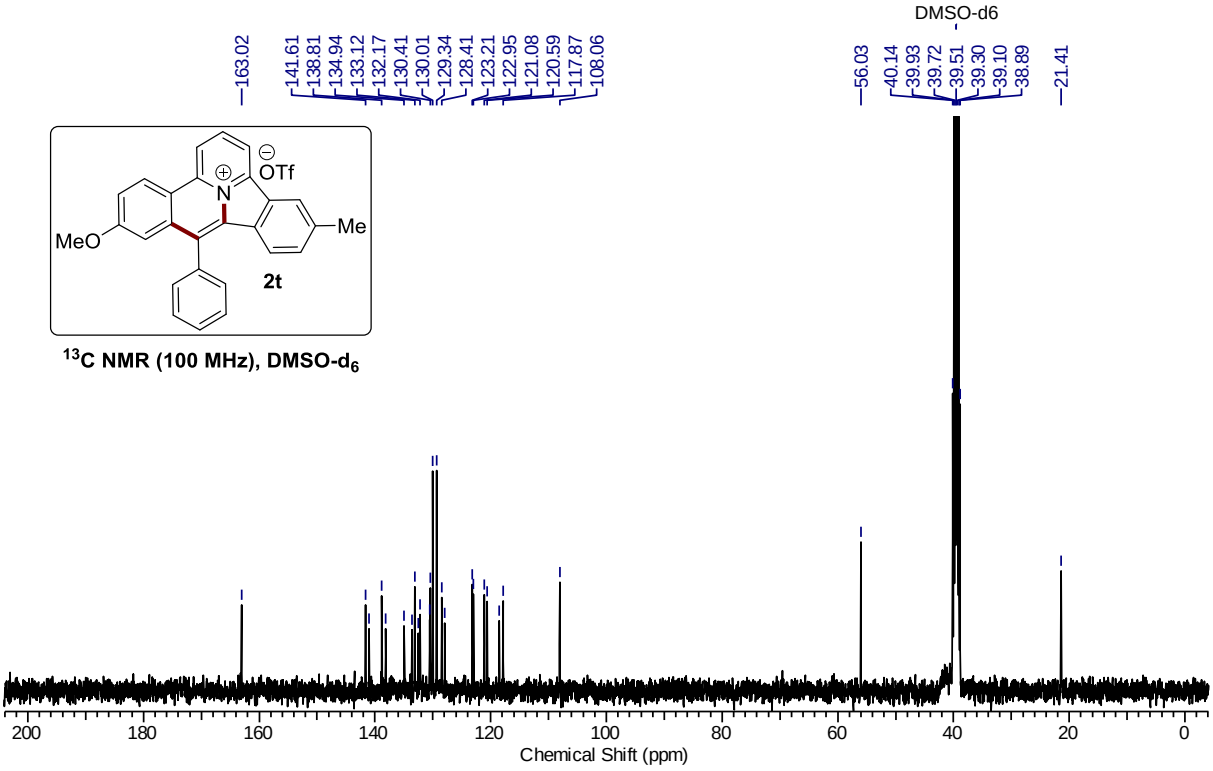
^{1}H NMR (500 MHz), DMSO-d_6



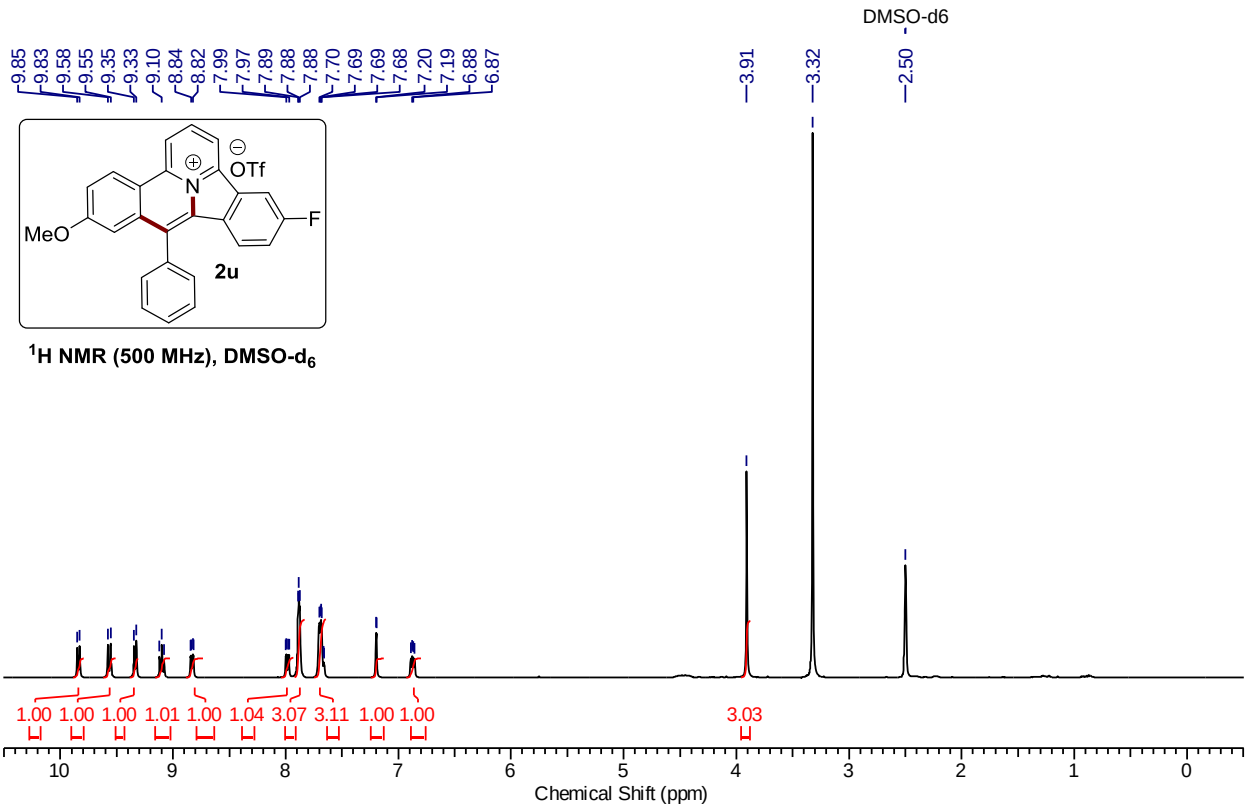
^{13}C NMR (125 MHz), DMSO-d_6



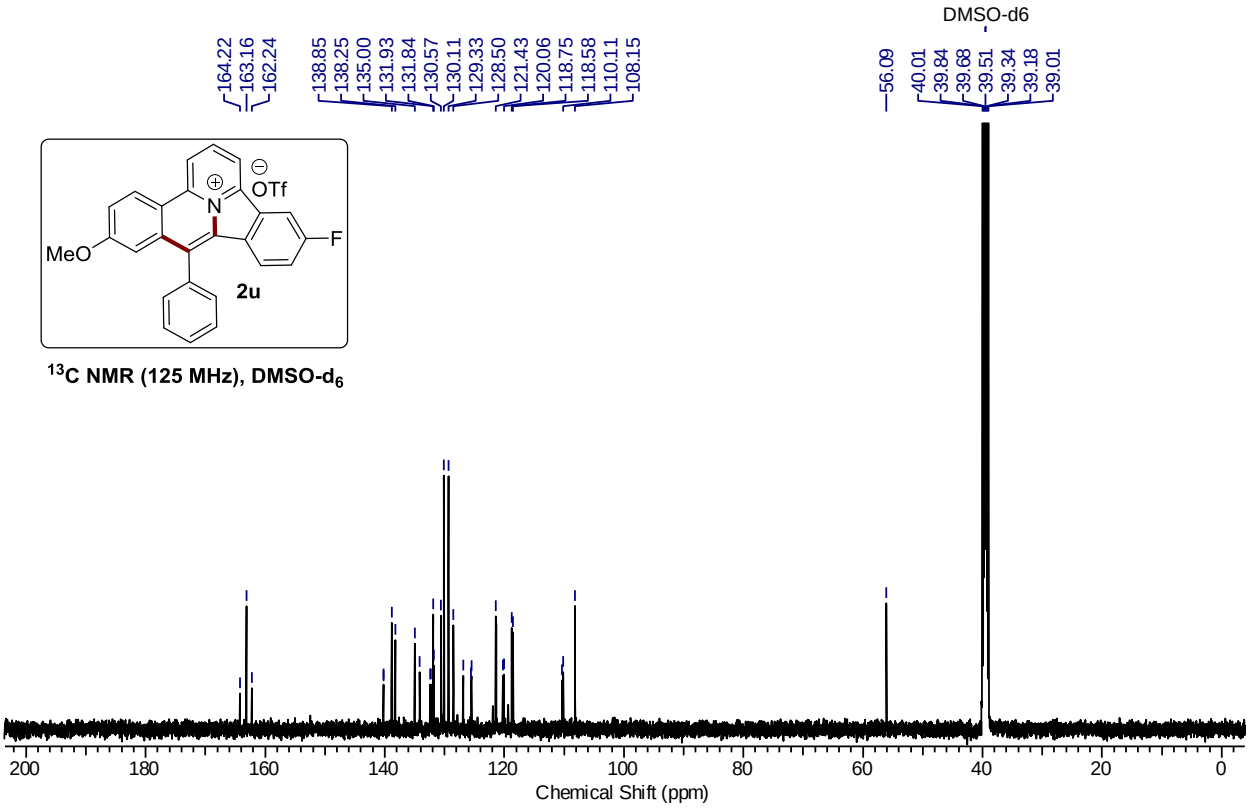
^{1}H NMR (400 MHz), DMSO-d_6



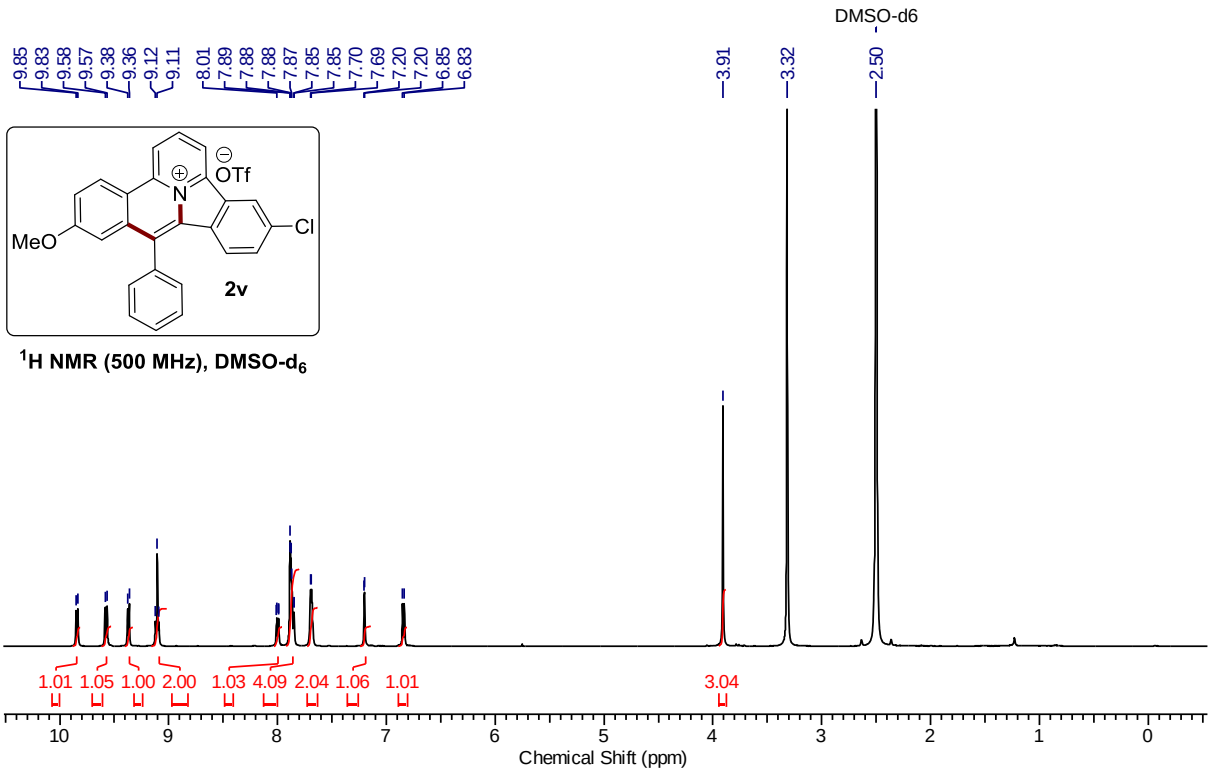
^{13}C NMR (100 MHz), DMSO-d_6



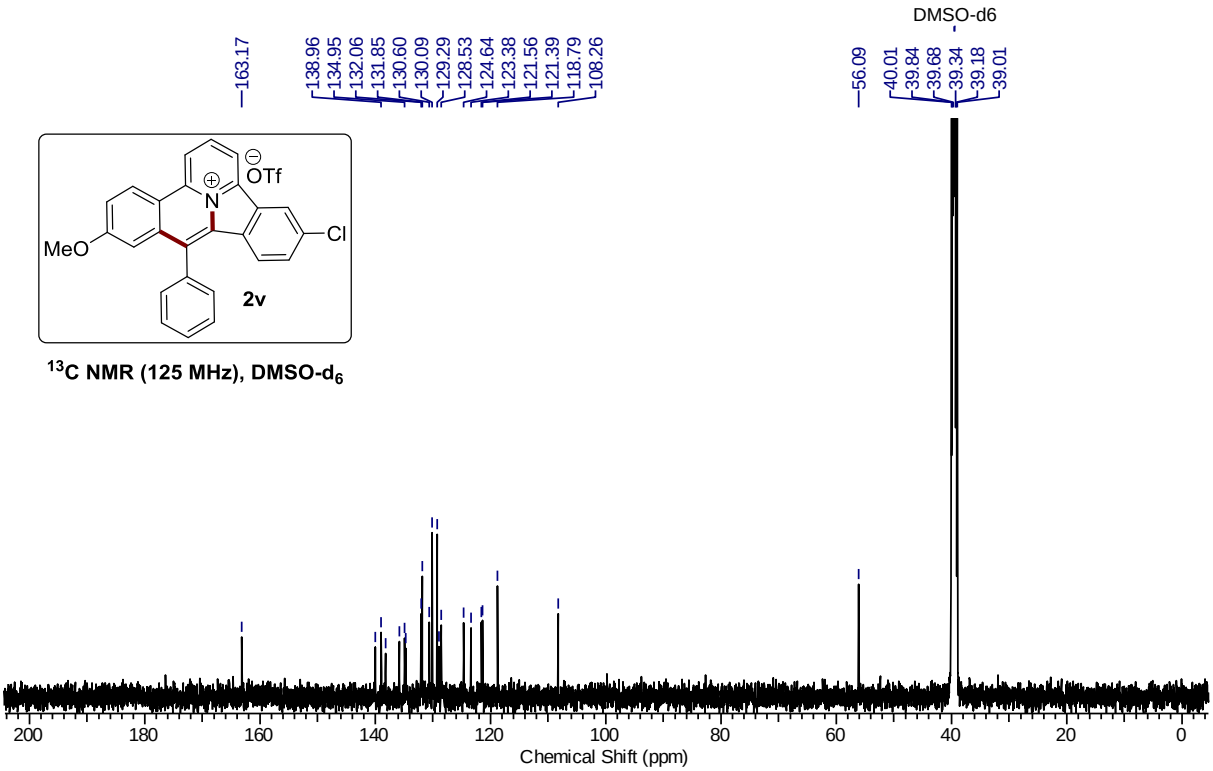
^{1}H NMR (500 MHz), DMSO-d_6



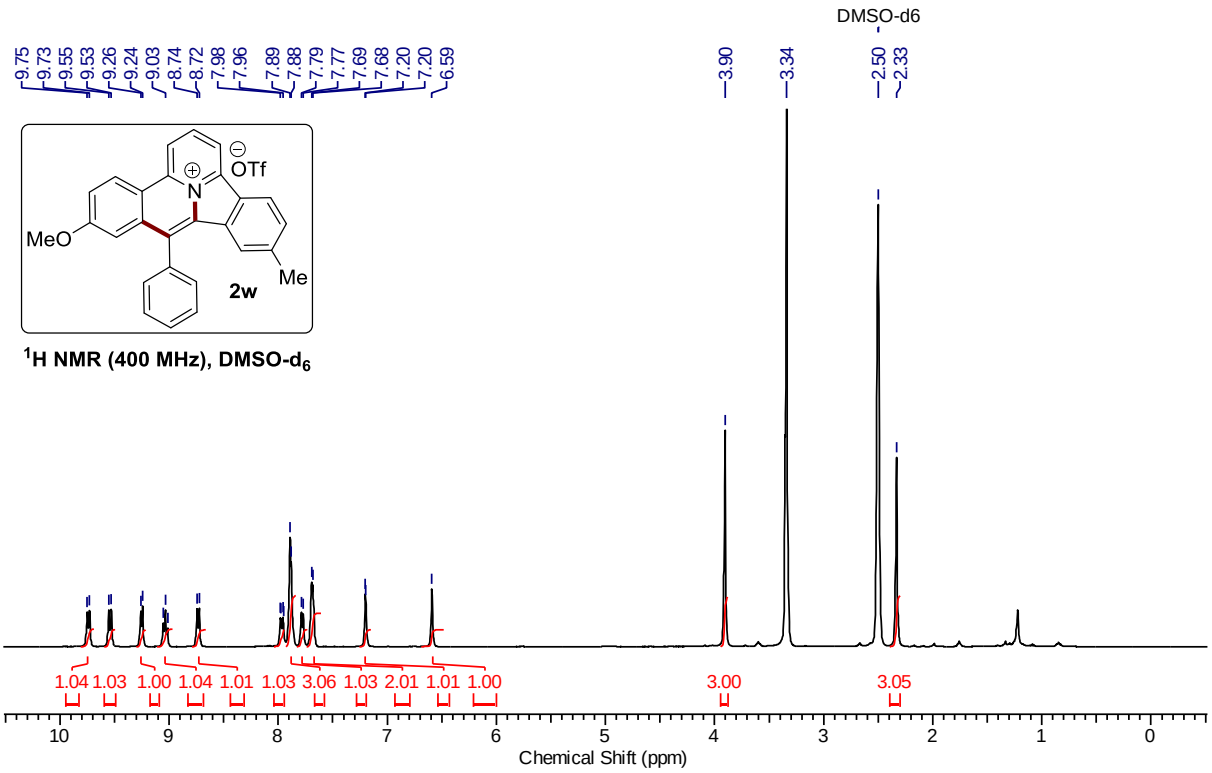
^{13}C NMR (125 MHz), DMSO-d_6



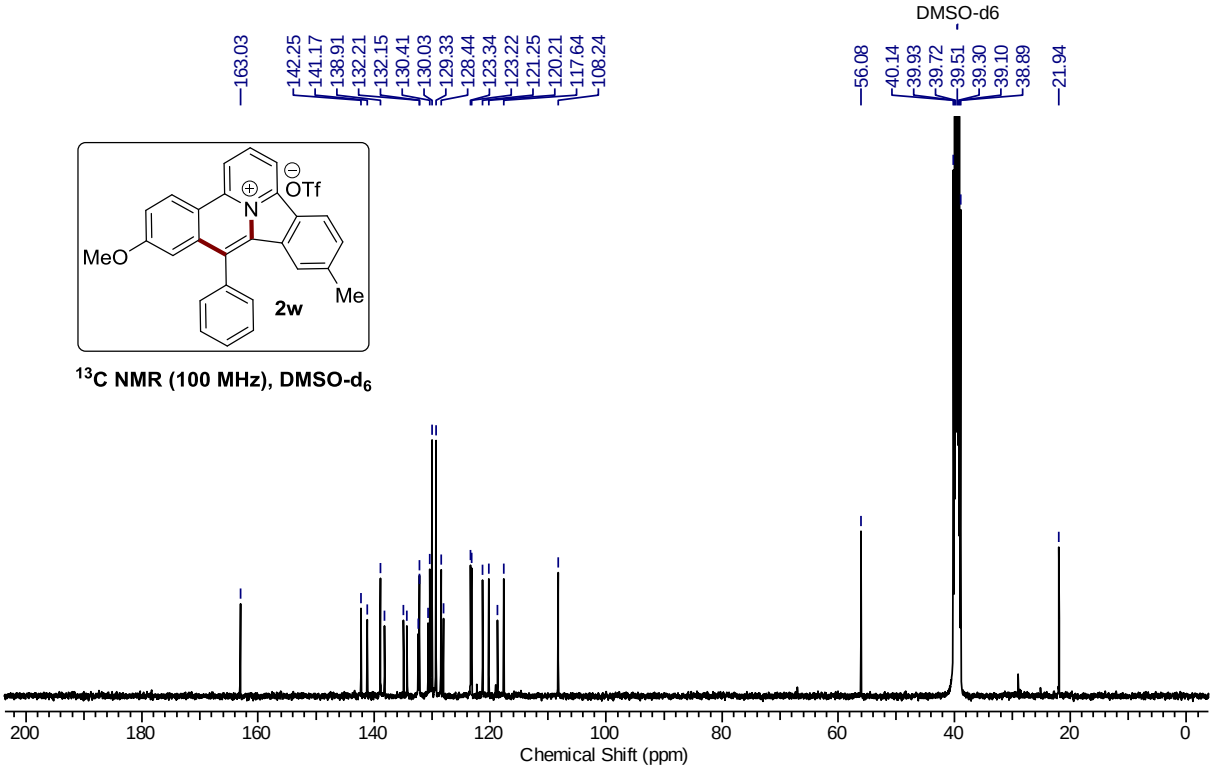
^{1}H NMR (500 MHz), DMSO-d_6



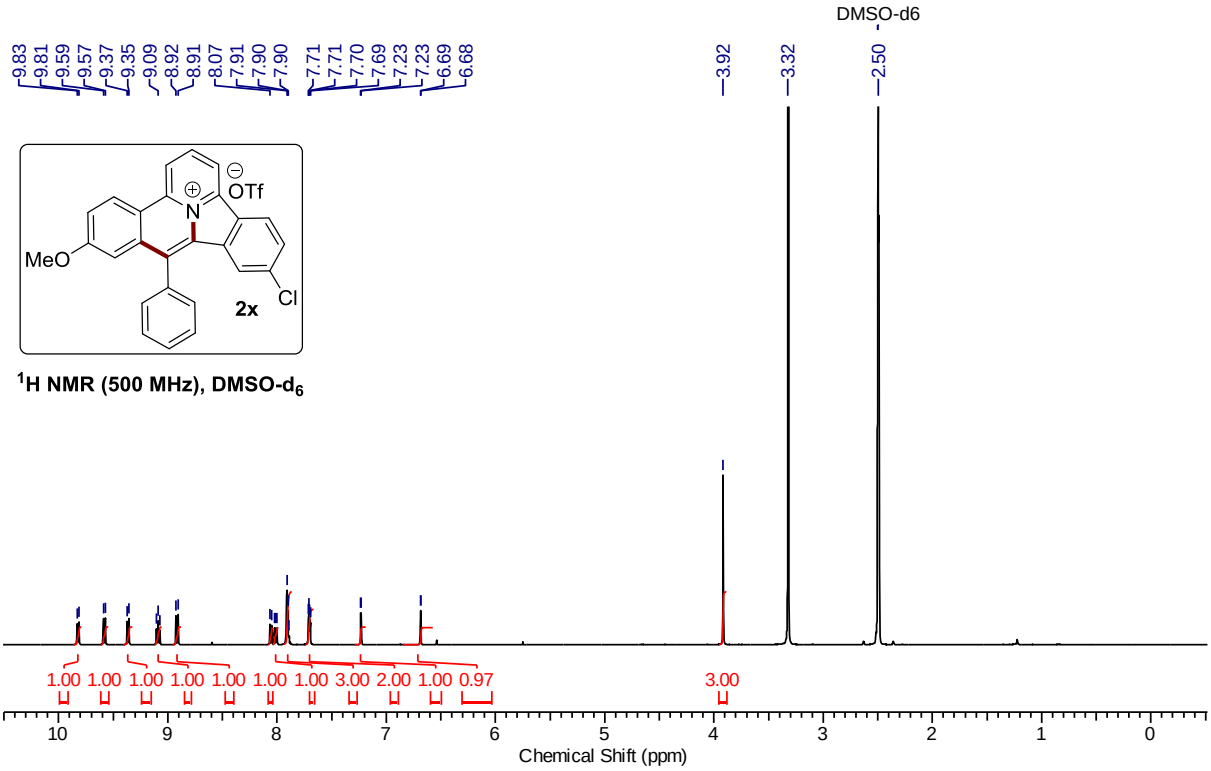
^{13}C NMR (125 MHz), DMSO-d_6



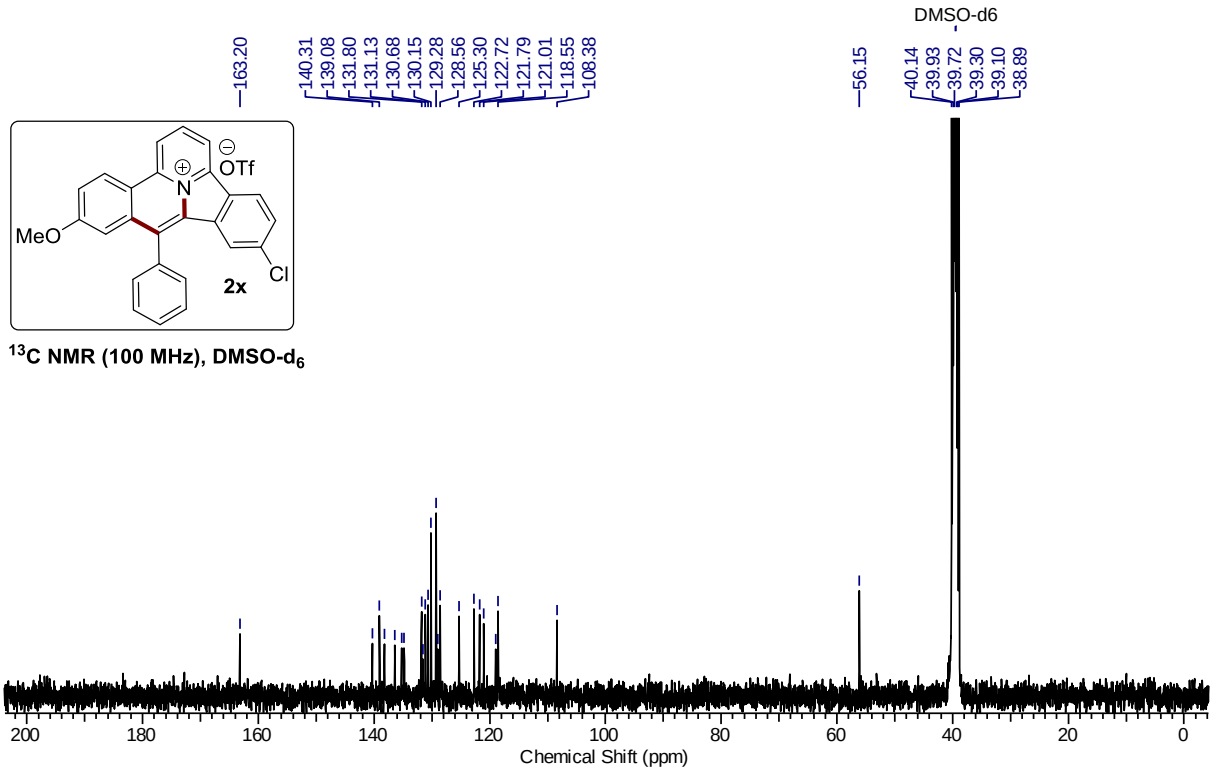
^{1}H NMR (400 MHz), DMSO-d_6



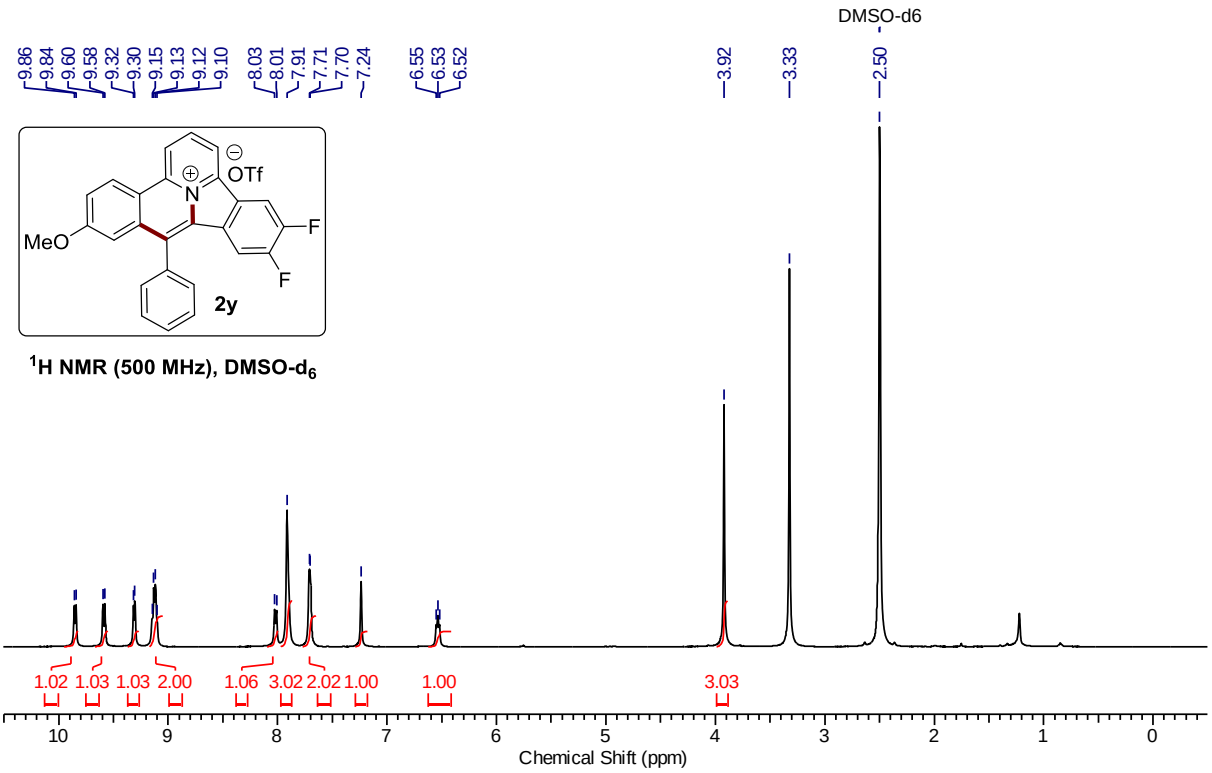
^{13}C NMR (100 MHz), DMSO-d_6



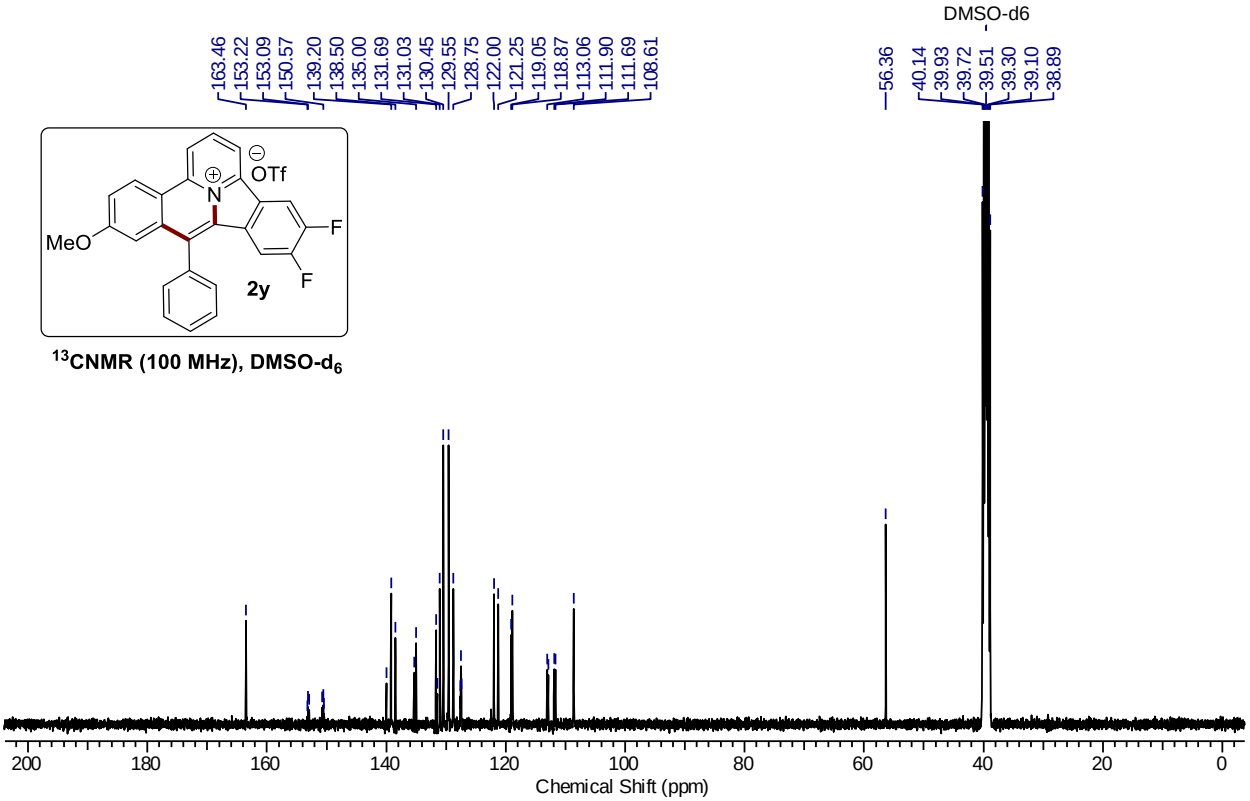
^{1}H NMR (500 MHz), DMSO-d_6



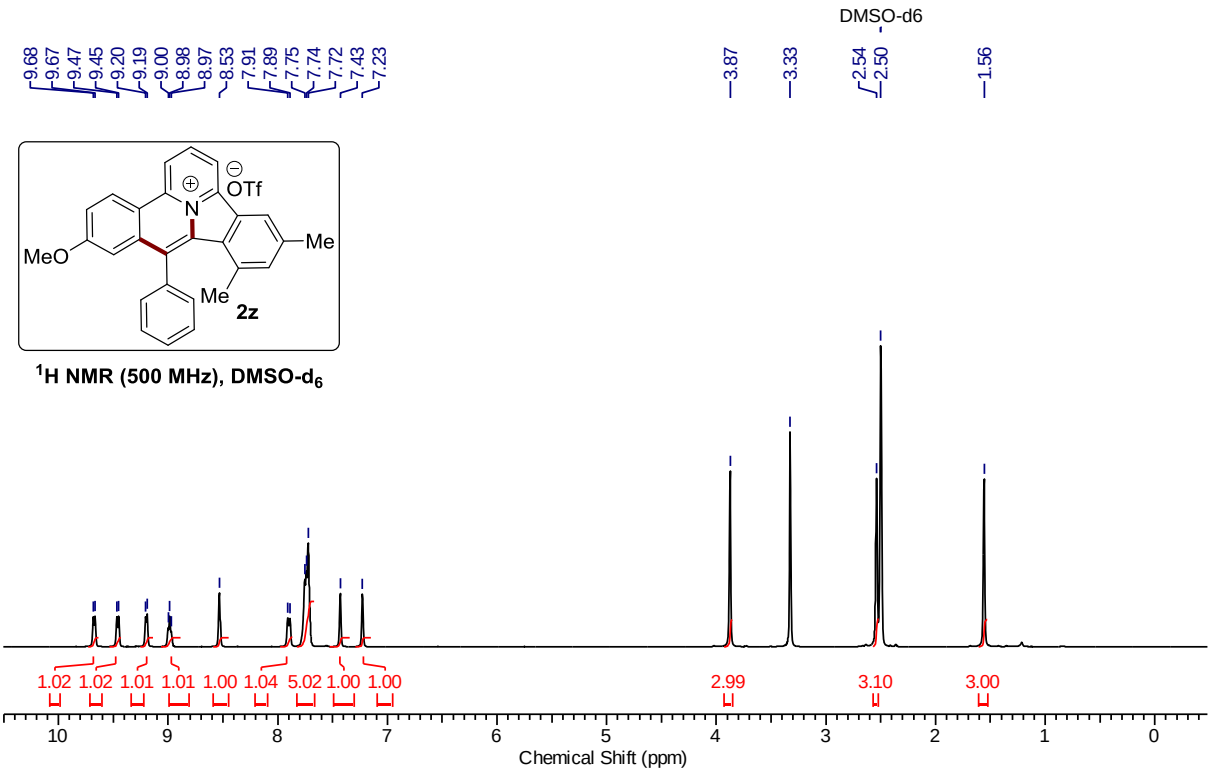
^{13}C NMR (100 MHz), DMSO-d_6



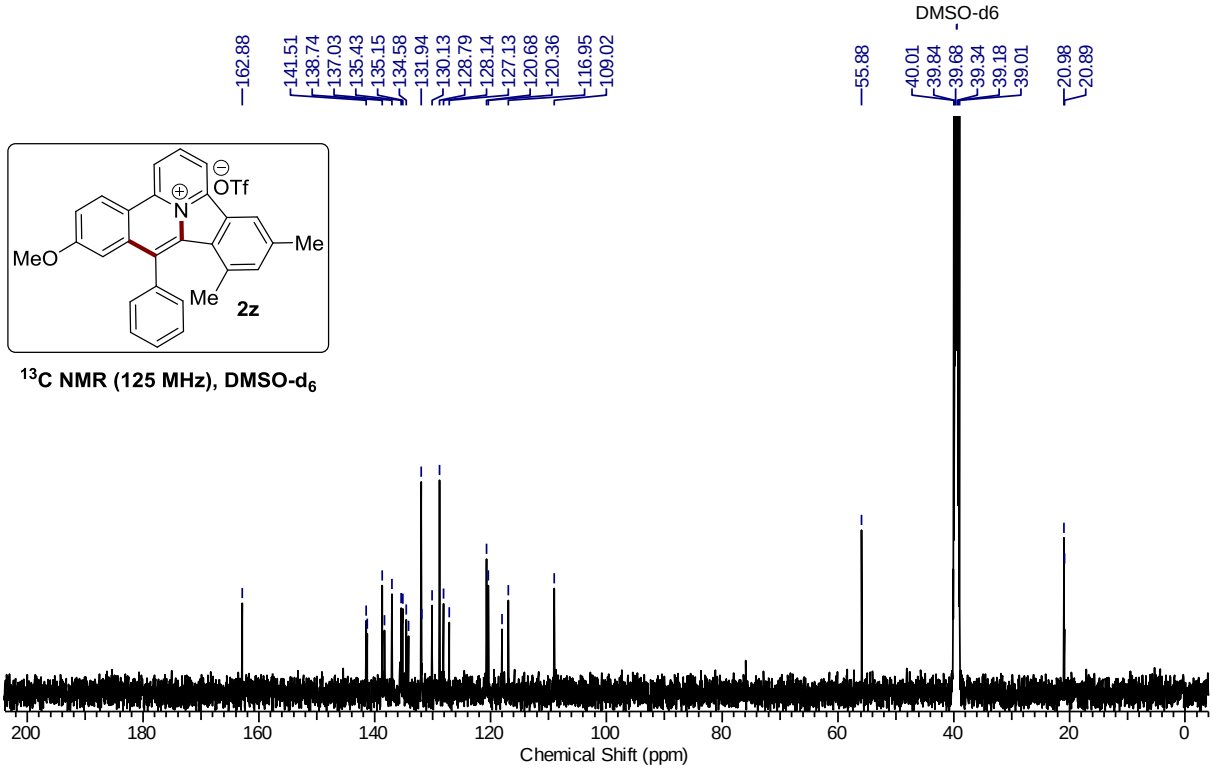
^{1}H NMR (500 MHz), DMSO-d_6



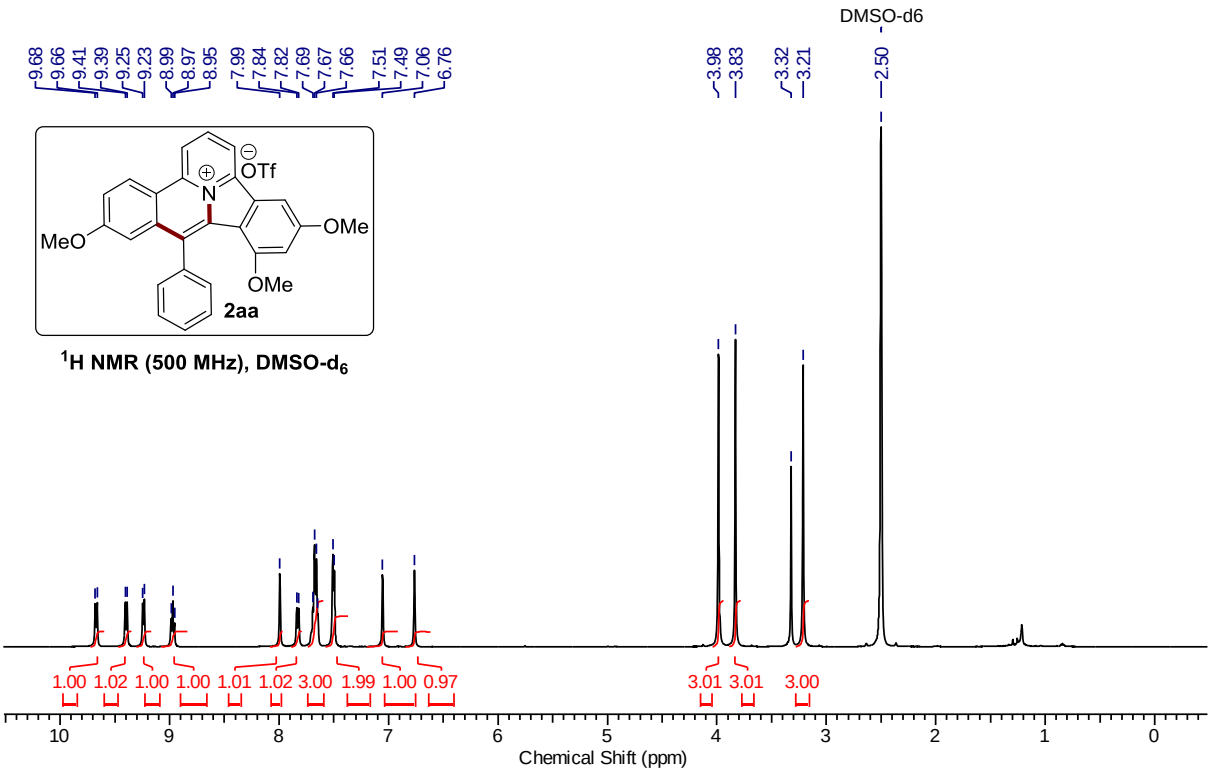
^{13}CNMR (100 MHz), DMSO-d_6



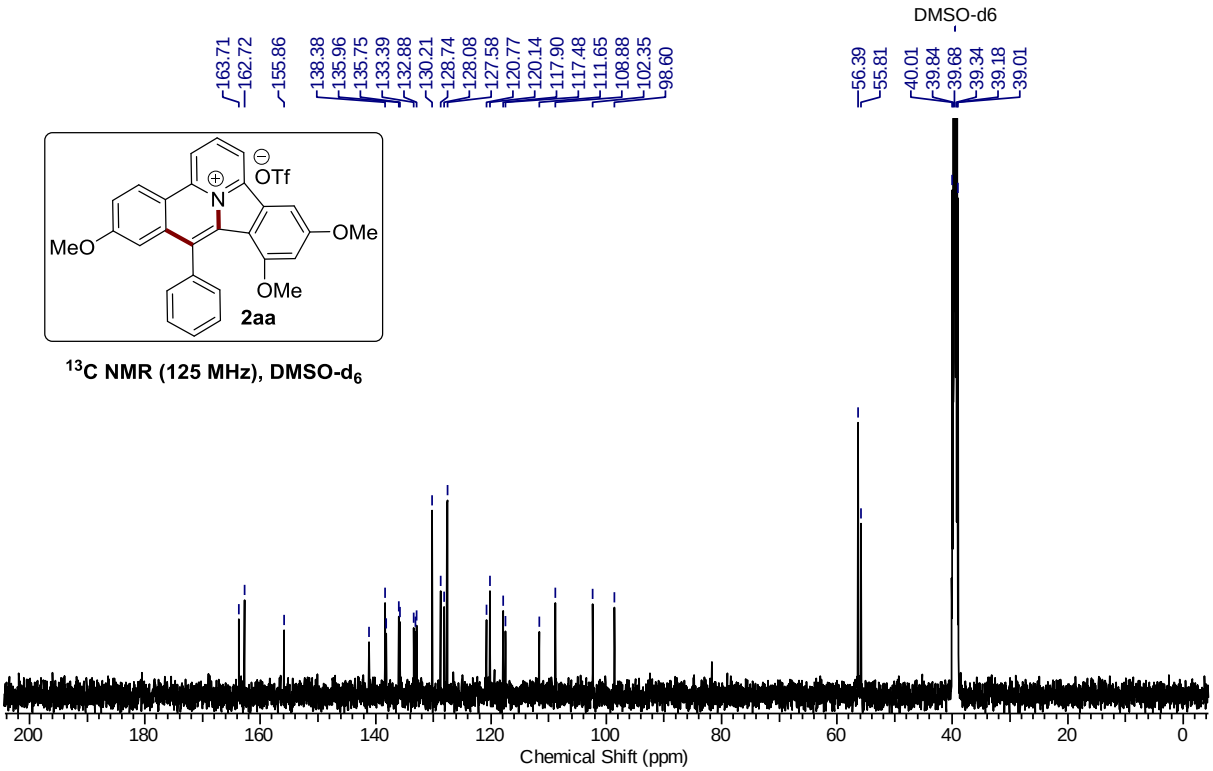
^{1}H NMR (500 MHz), DMSO-d$_6$



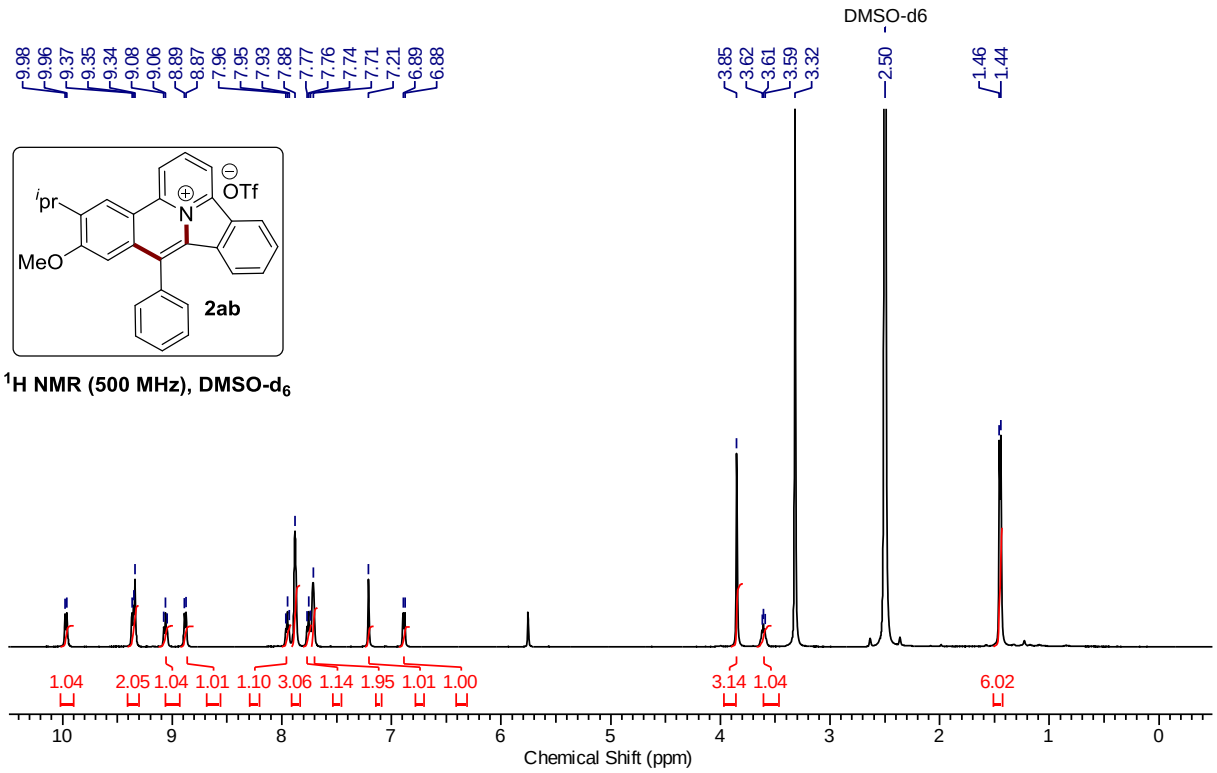
^{13}C NMR (125 MHz), DMSO-d$_6$



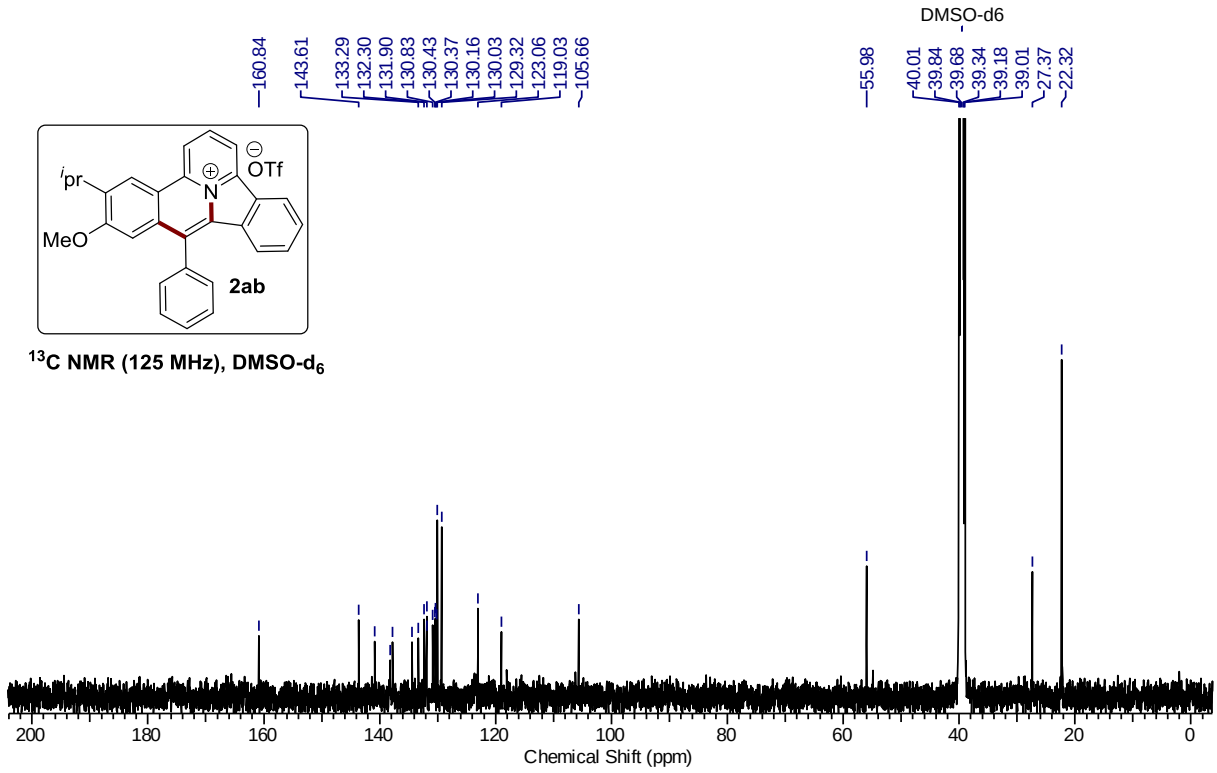
^{1}H NMR (500 MHz), DMSO-d$_6$



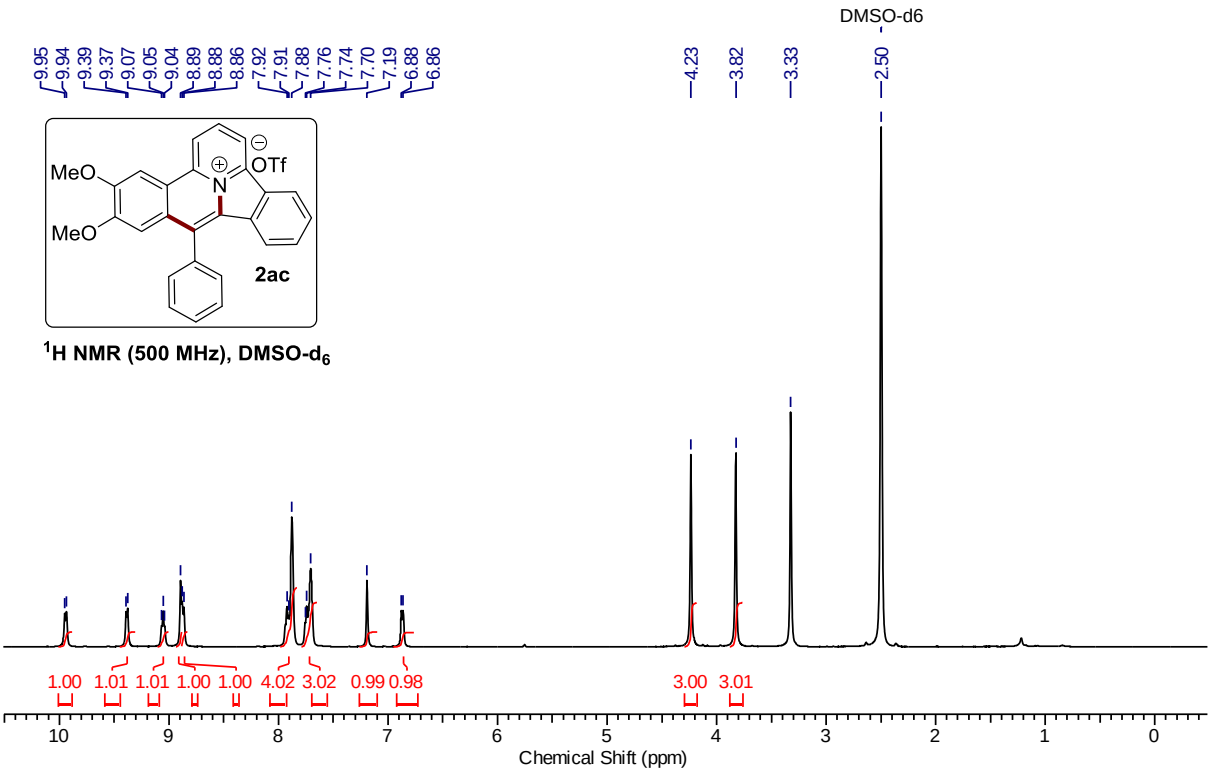
^{13}C NMR (125 MHz), DMSO-d$_6$



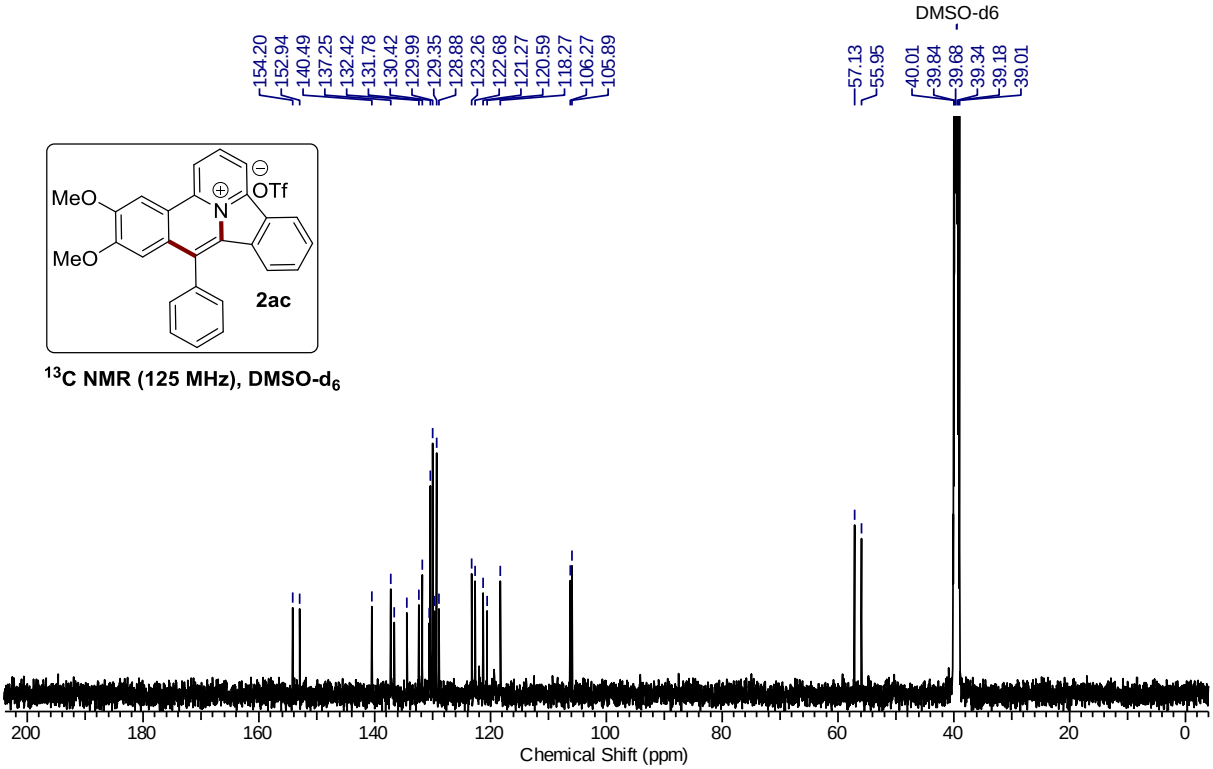
^{1}H NMR (500 MHz), DMSO-d$_6$



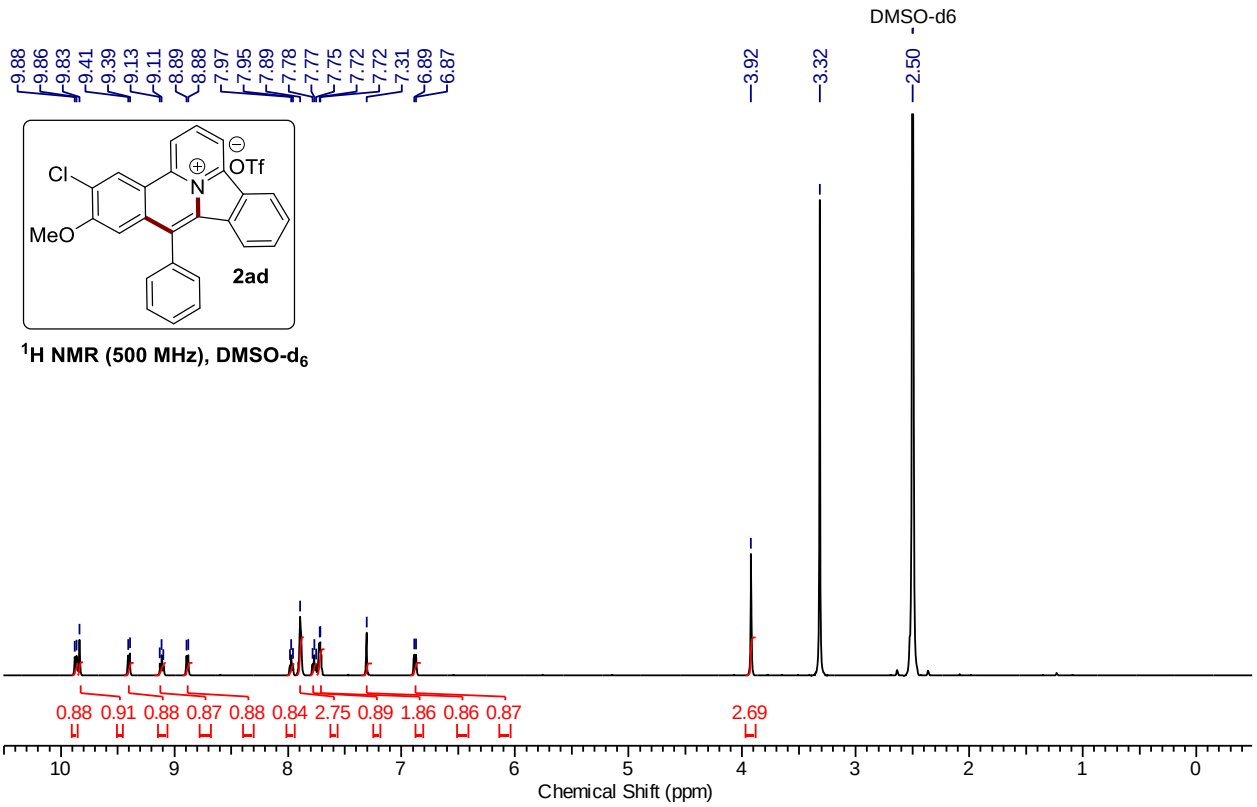
^{13}C NMR (125 MHz), DMSO-d$_6$



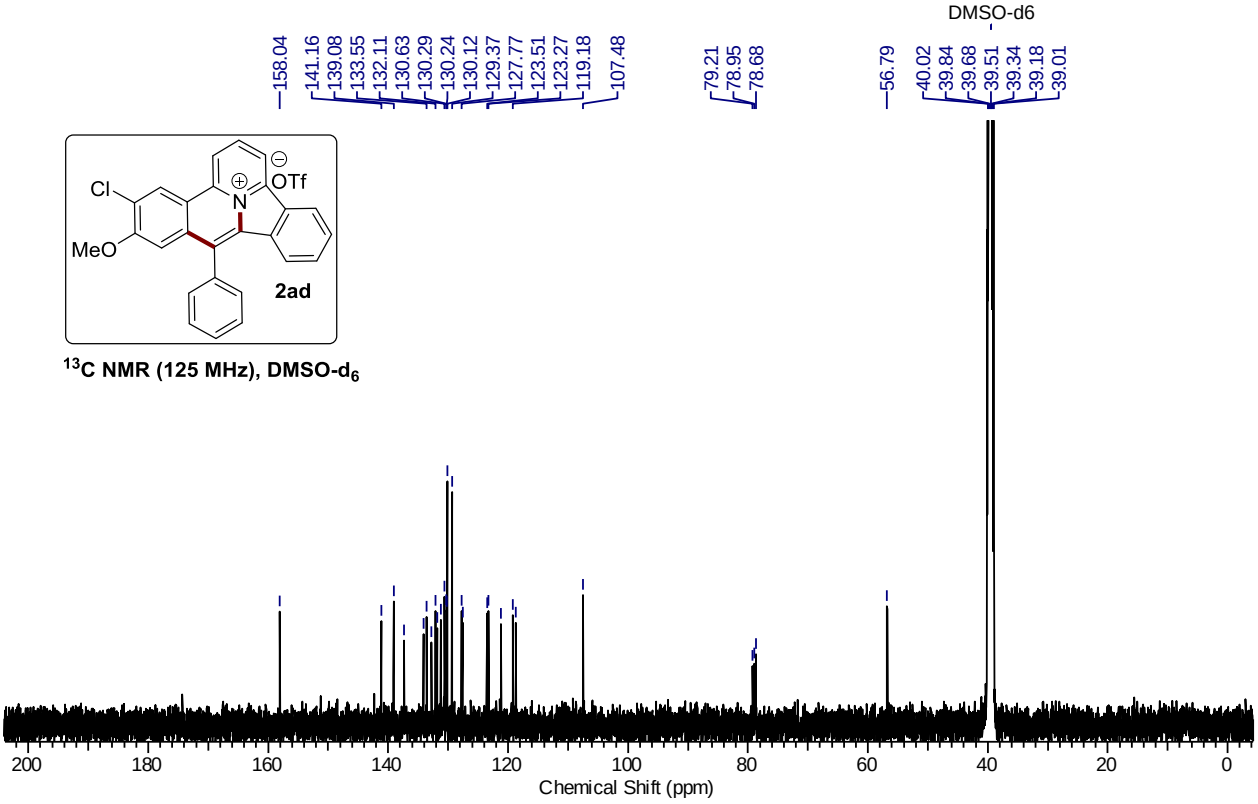
^{1}H NMR (500 MHz), DMSO-d$_6$



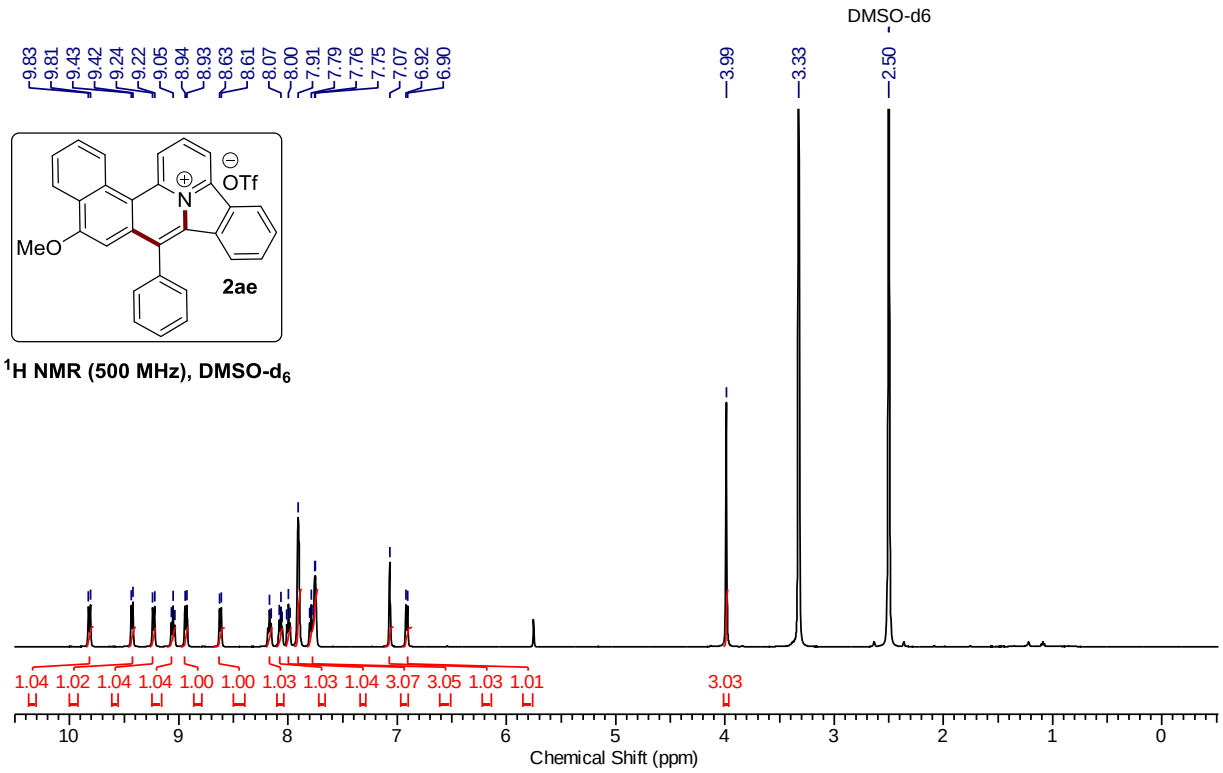
^{13}C NMR (125 MHz), DMSO-d$_6$



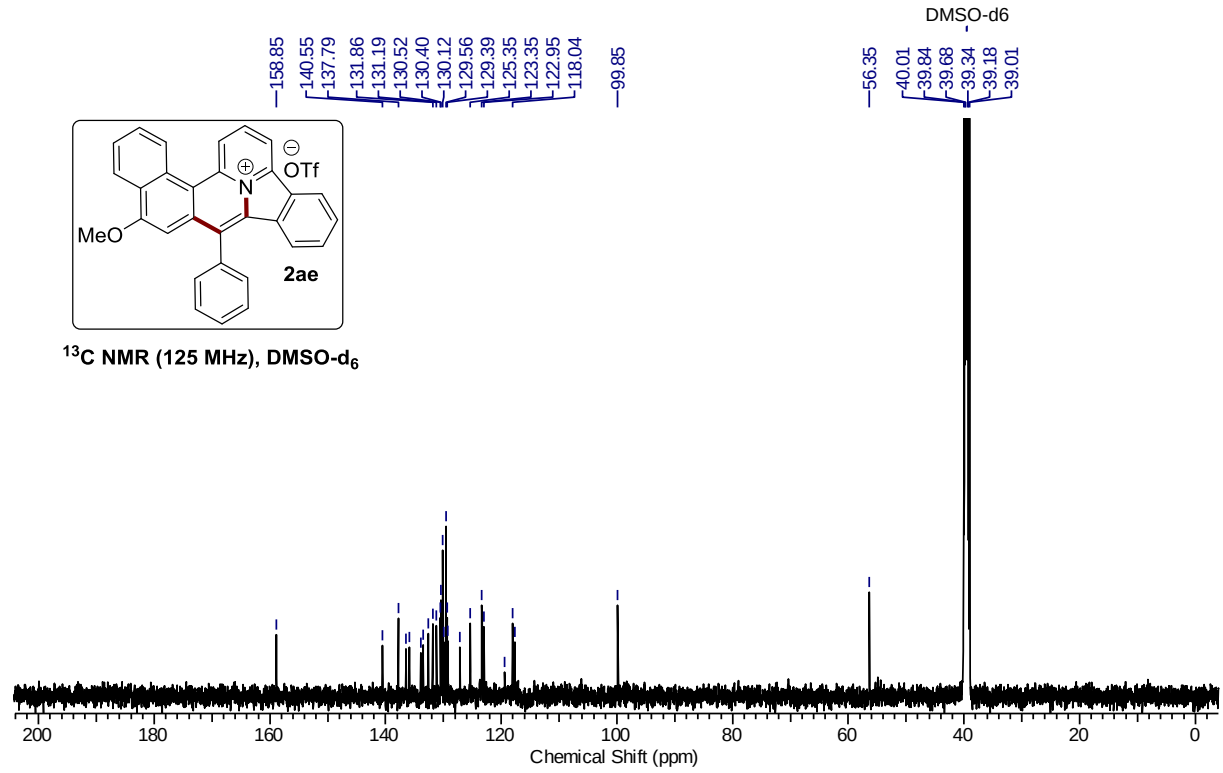
^{1}H NMR (500 MHz), DMSO-d_6



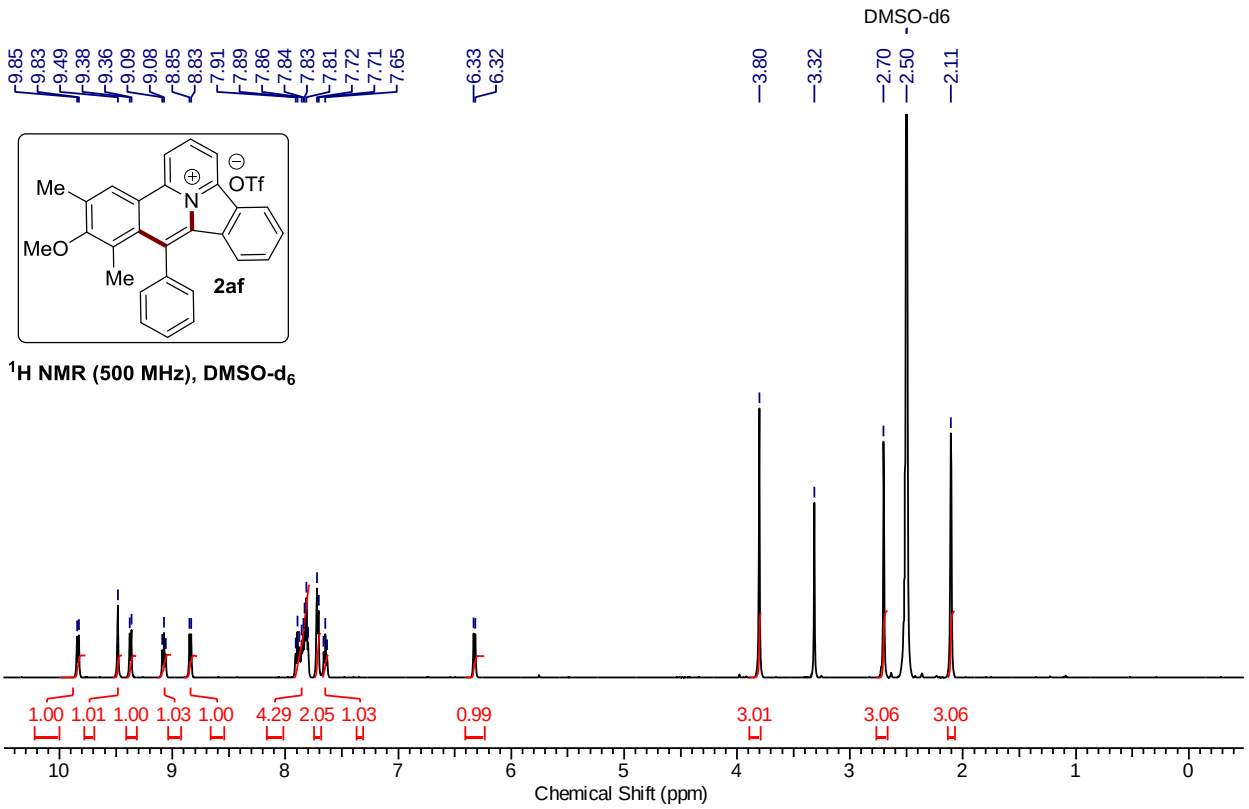
^{13}C NMR (125 MHz), DMSO-d_6



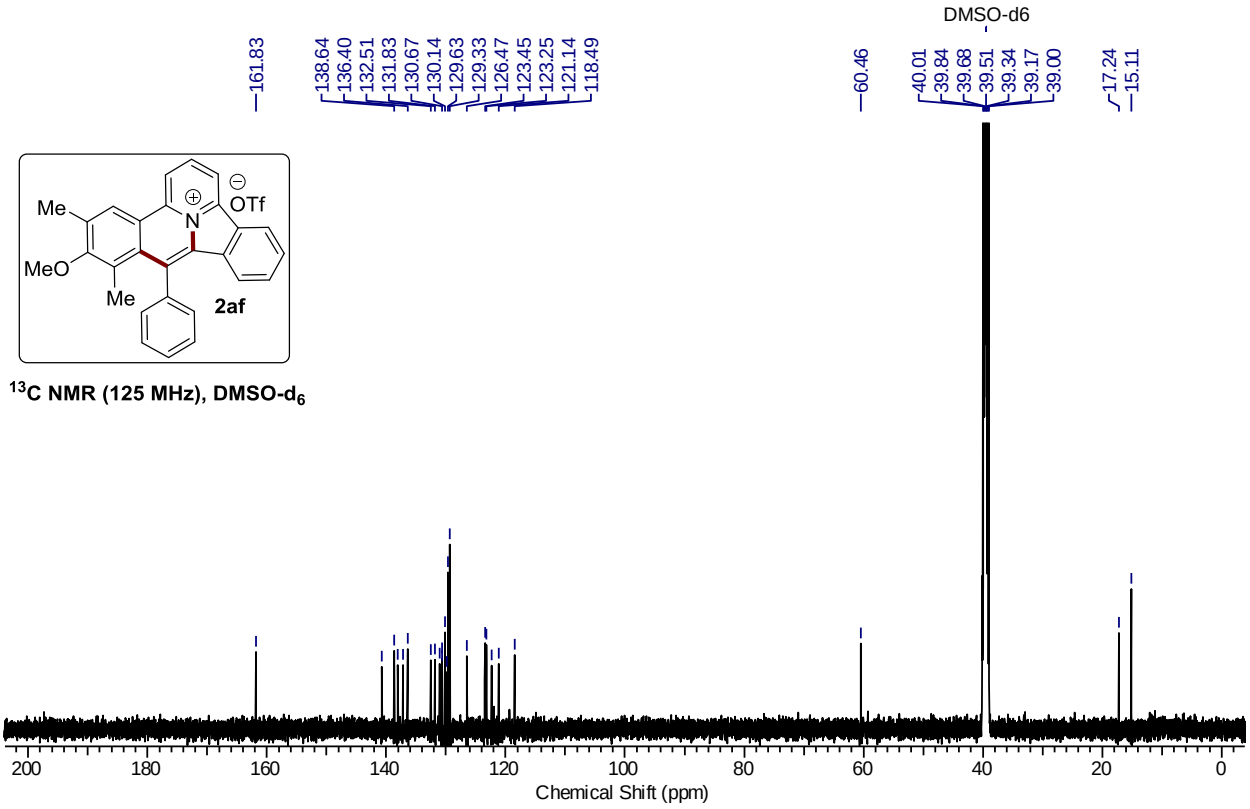
^{1}H NMR (500 MHz), DMSO-d_6



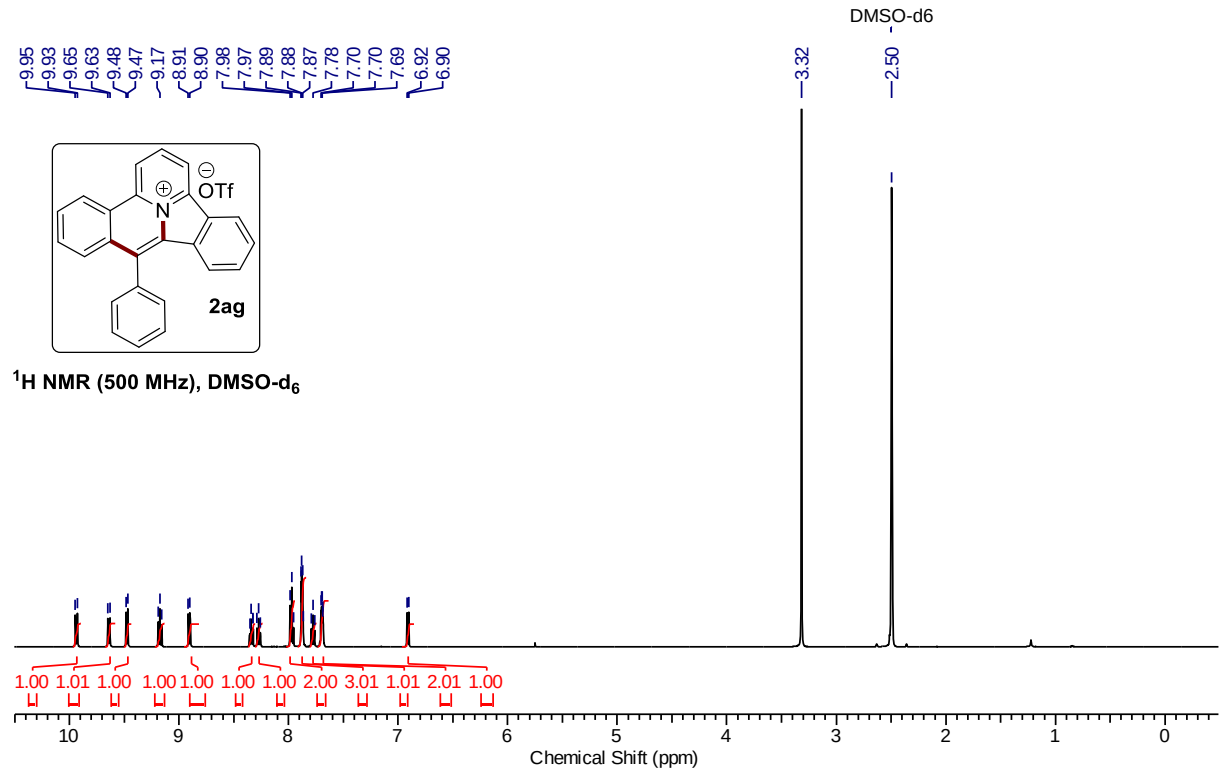
^{13}C NMR (125 MHz), DMSO-d_6



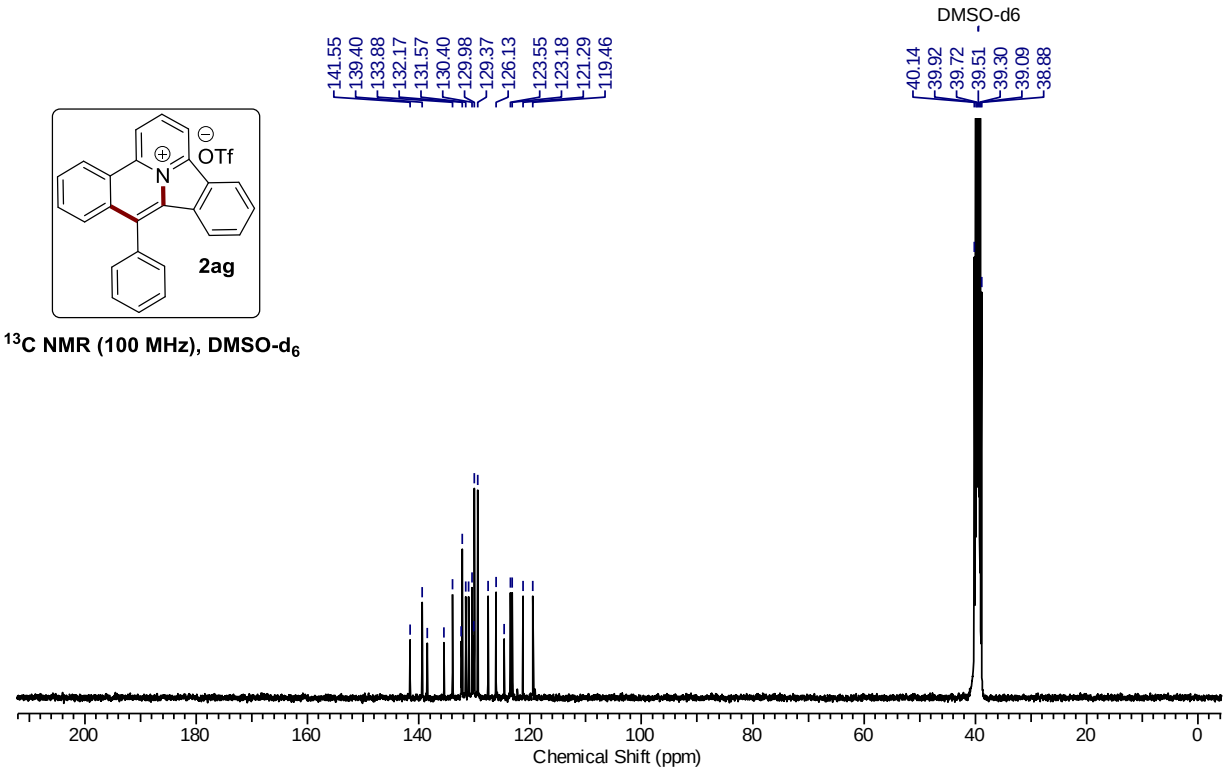
^{1}H NMR (500 MHz), DMSO-d$_6$



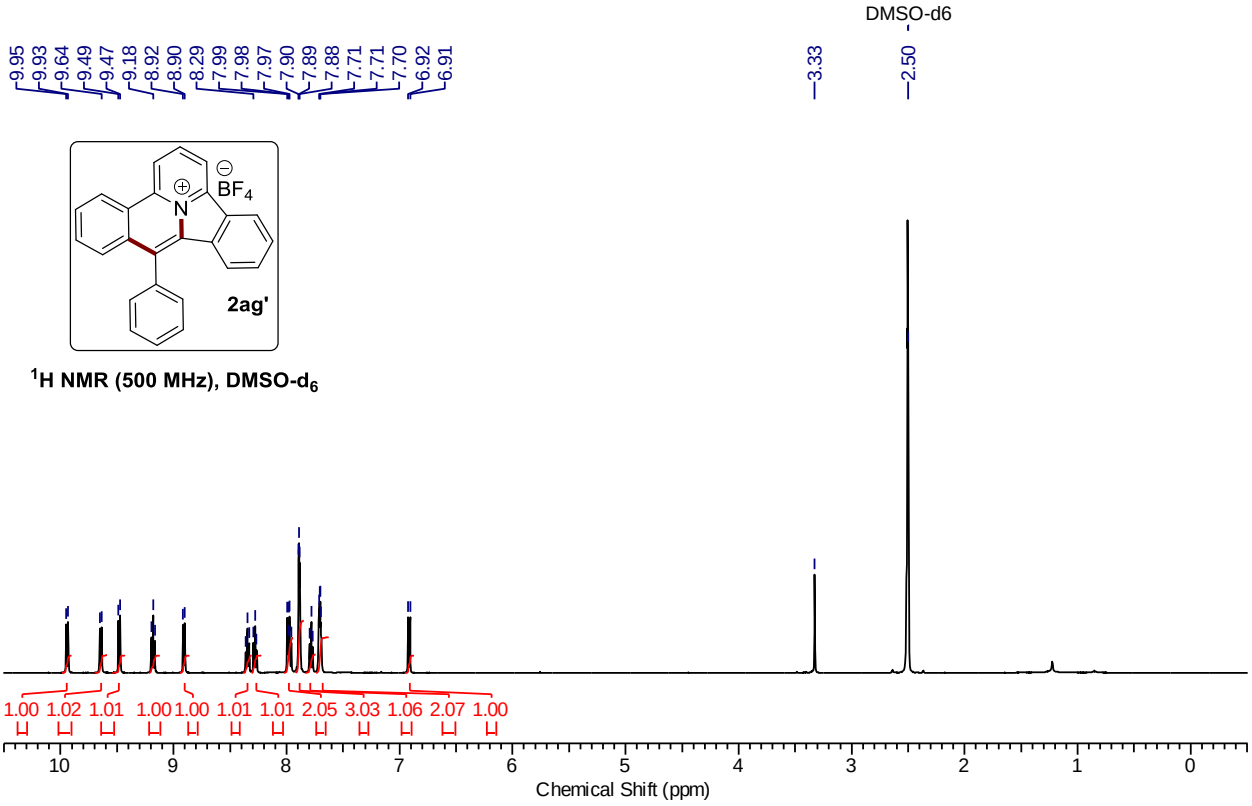
^{13}C NMR (125 MHz), DMSO-d$_6$



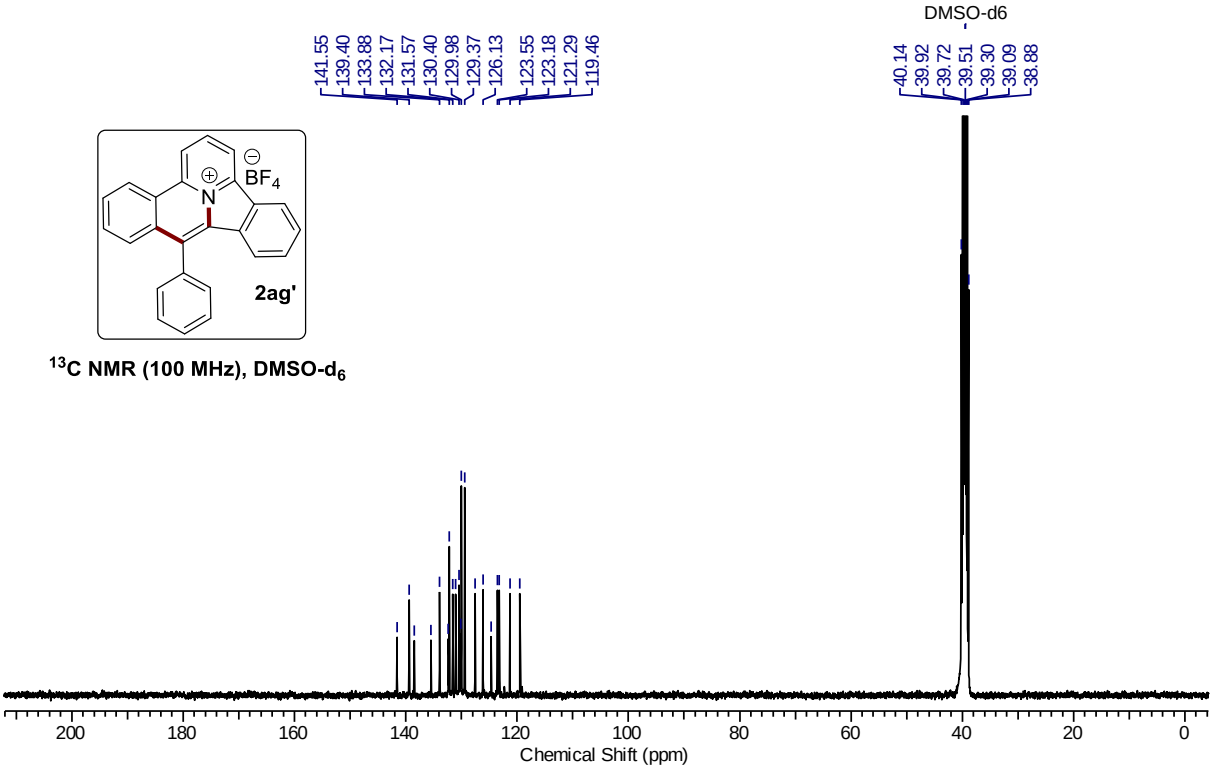
^{1}H NMR (500 MHz), DMSO-d_6



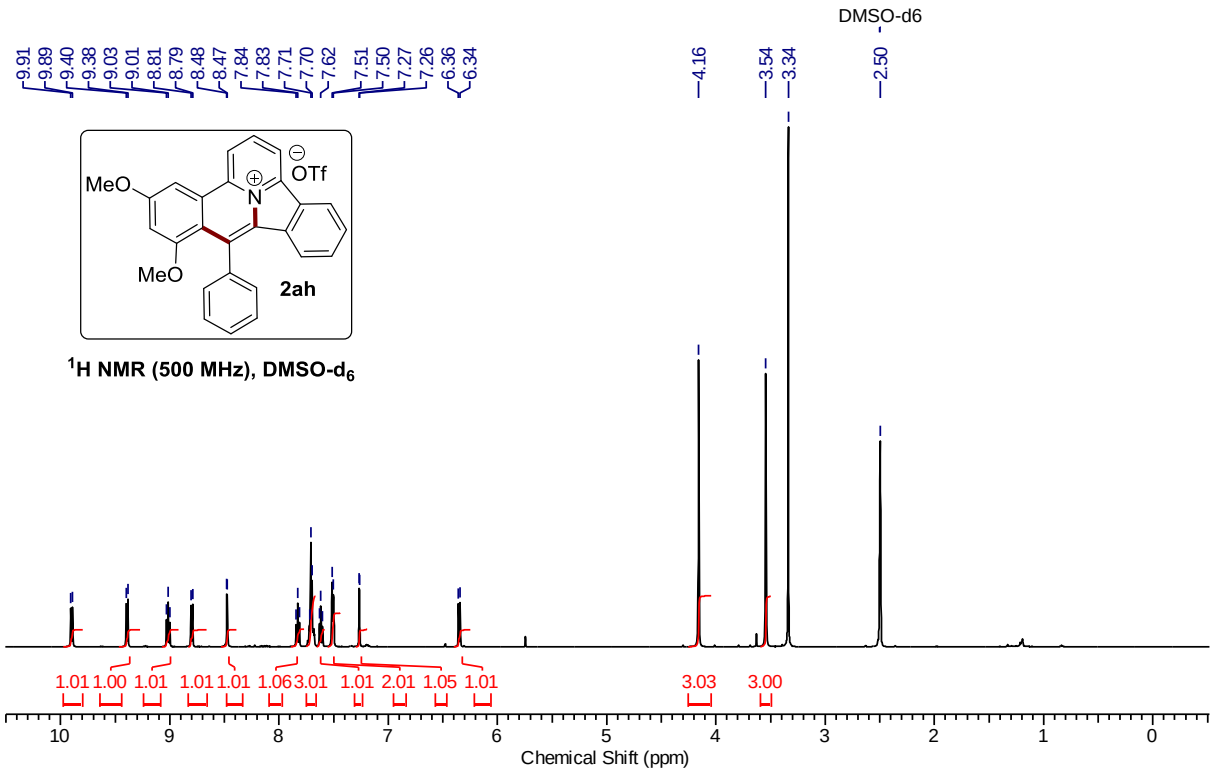
^{13}C NMR (100 MHz), DMSO-d_6



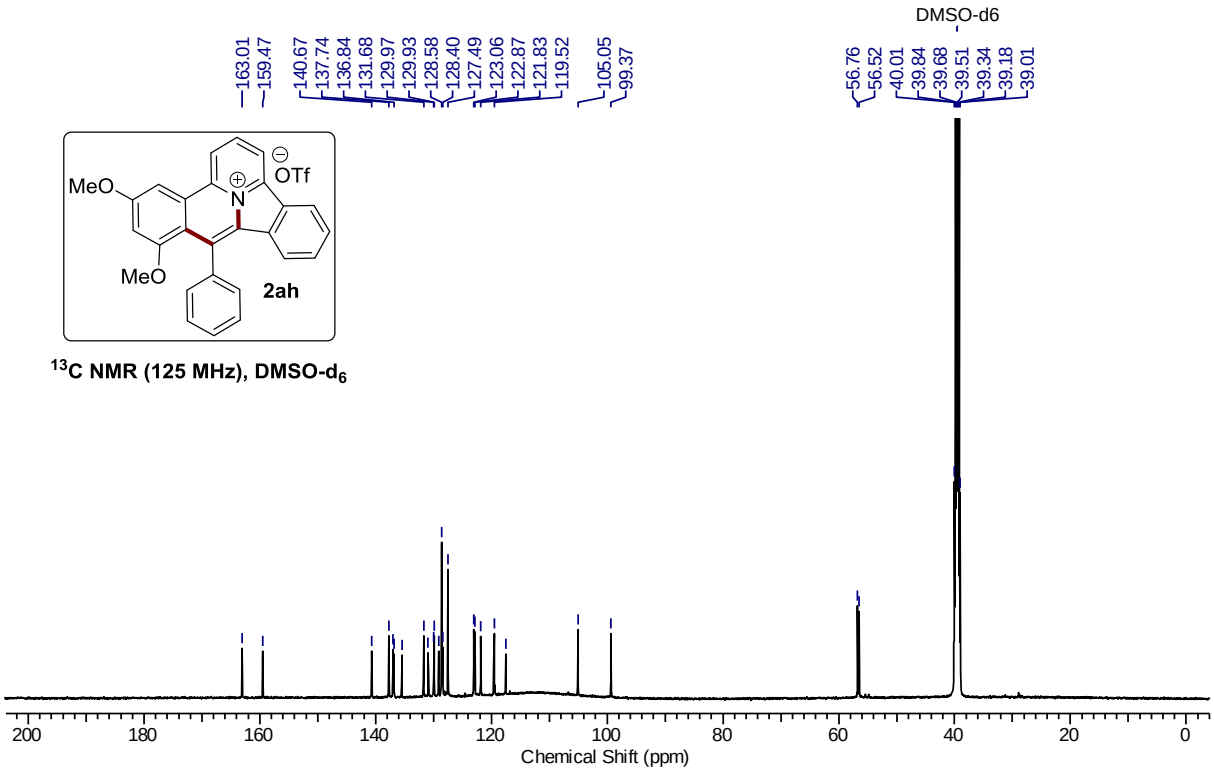
^{1}H NMR (500 MHz), DMSO-d_6



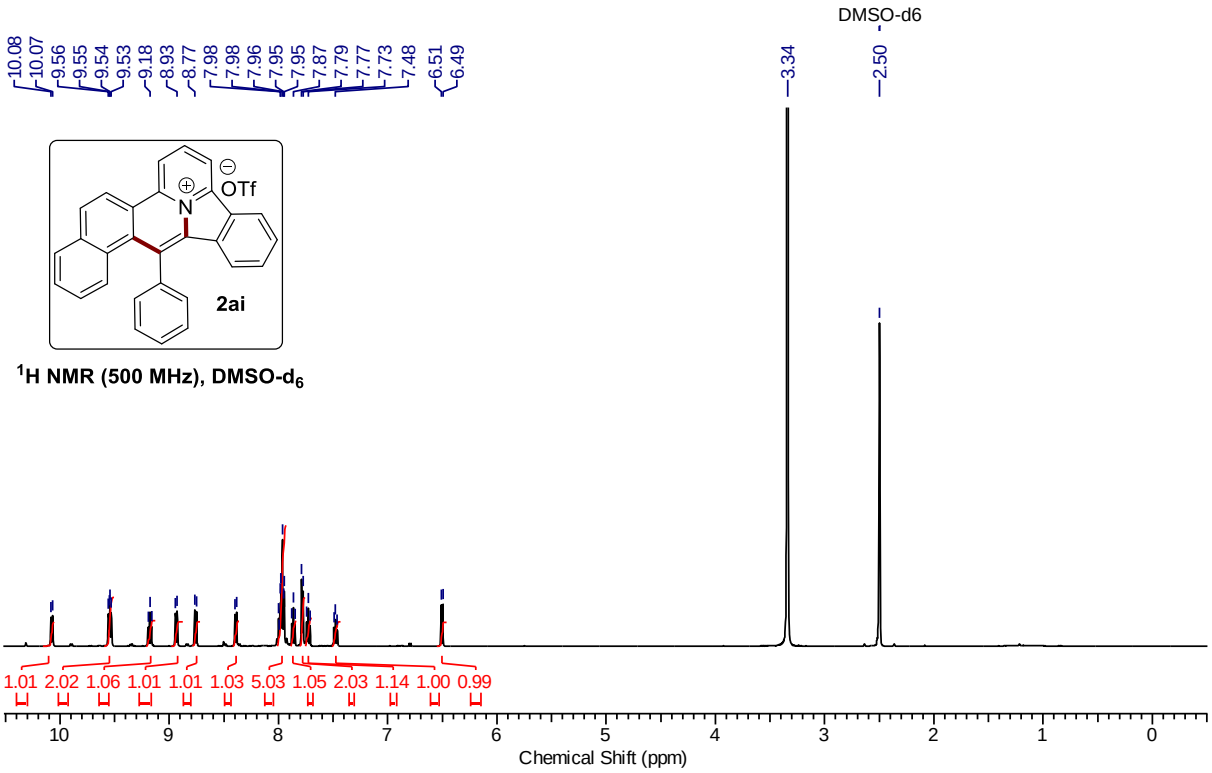
^{13}C NMR (100 MHz), DMSO-d_6



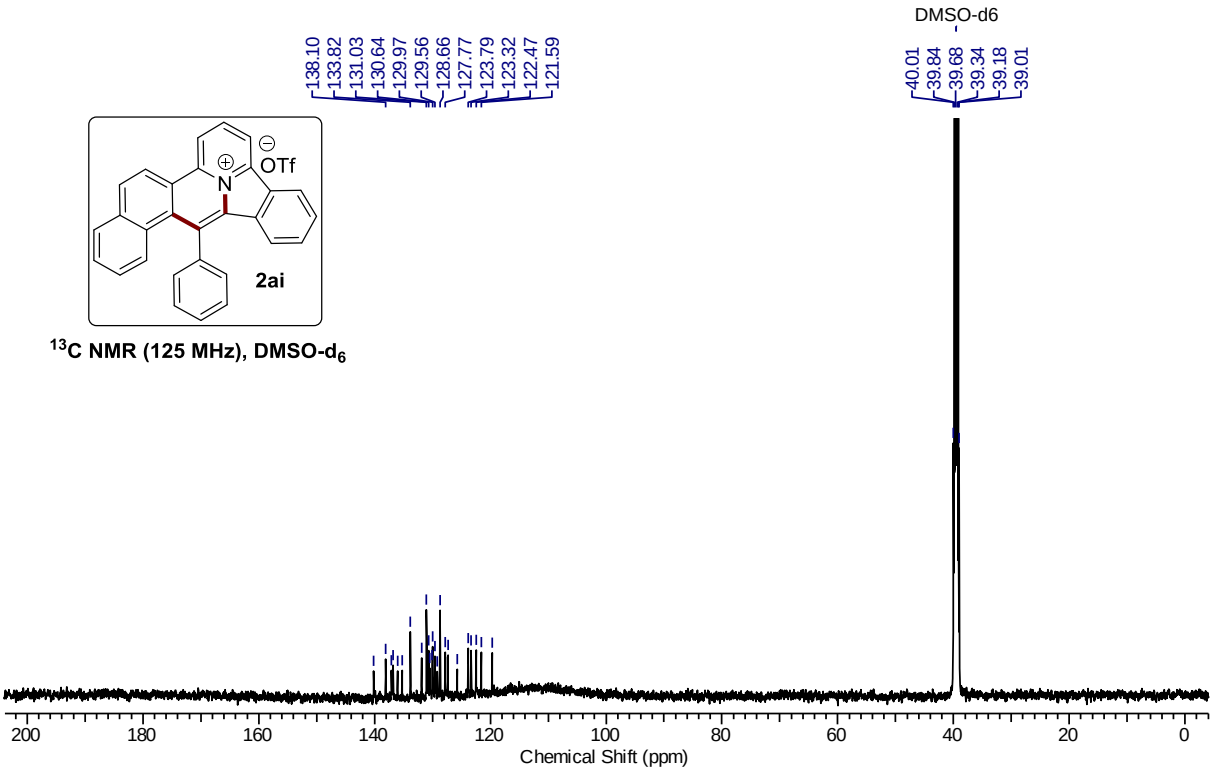
^{1}H NMR (500 MHz), DMSO-d_6



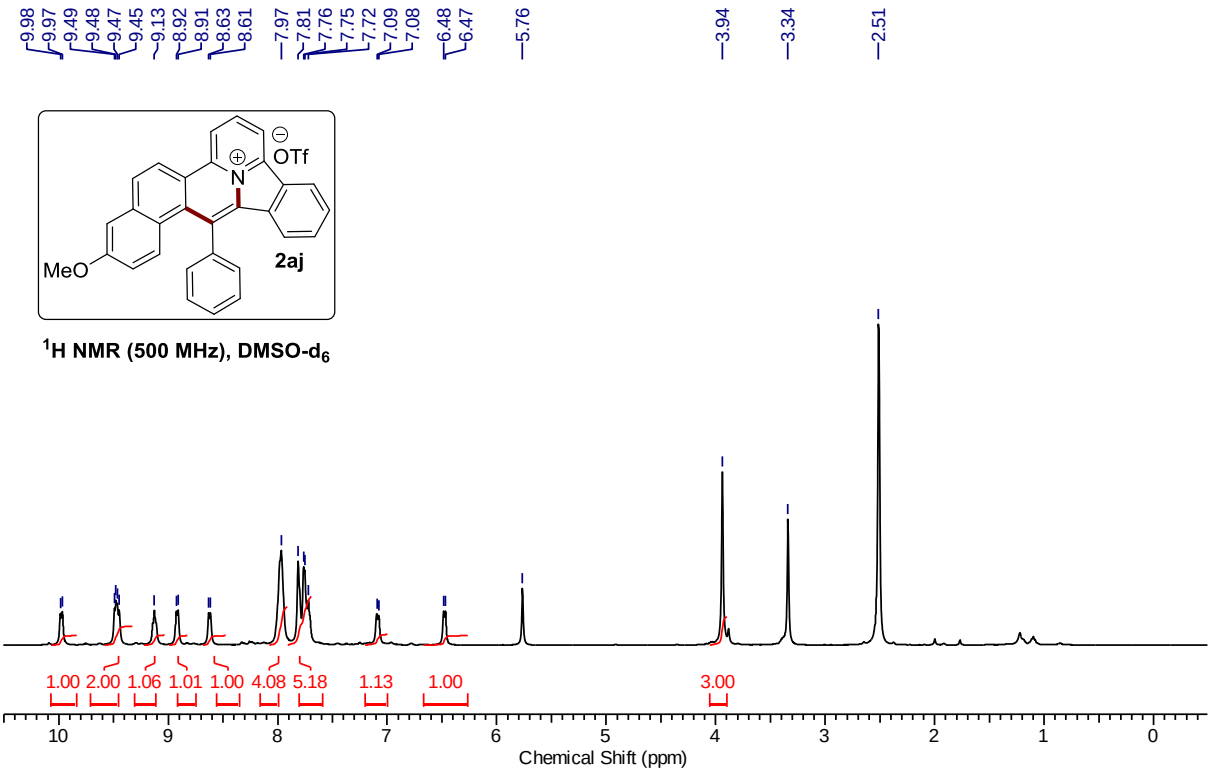
^{13}C NMR (125 MHz), DMSO-d_6



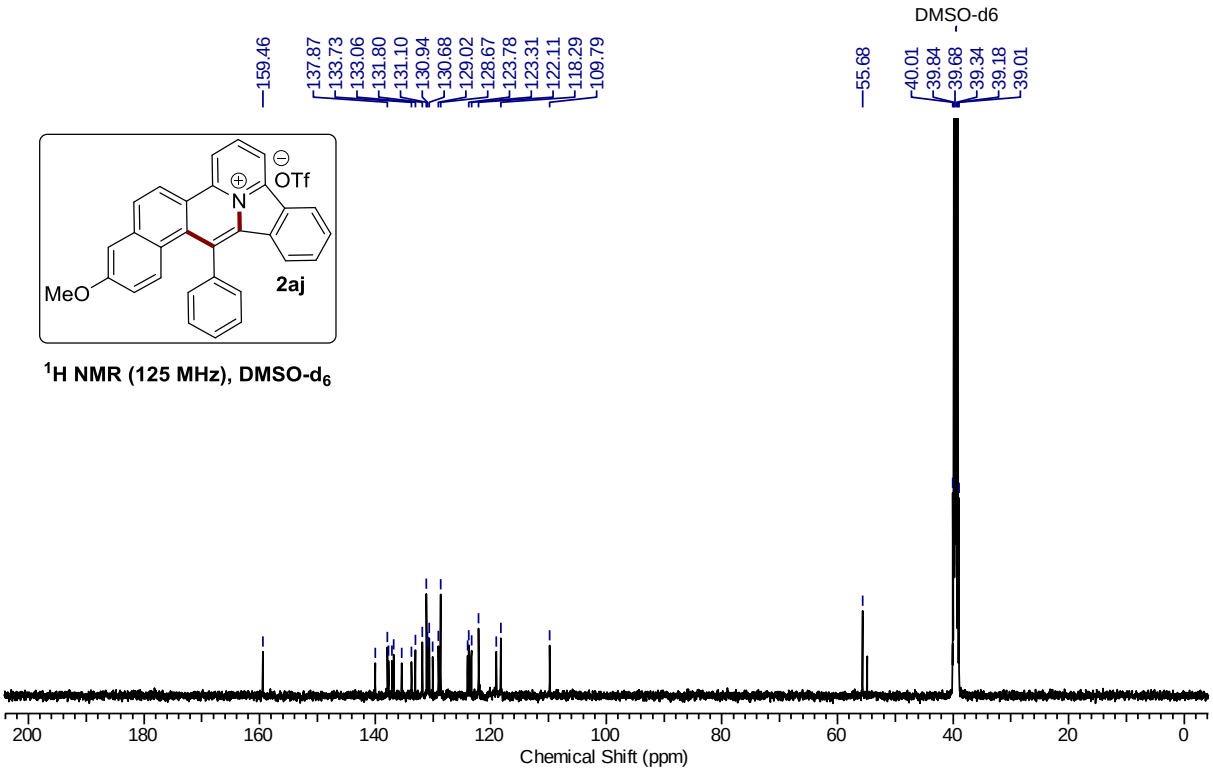
^{1}H NMR (500 MHz), DMSO-d_6



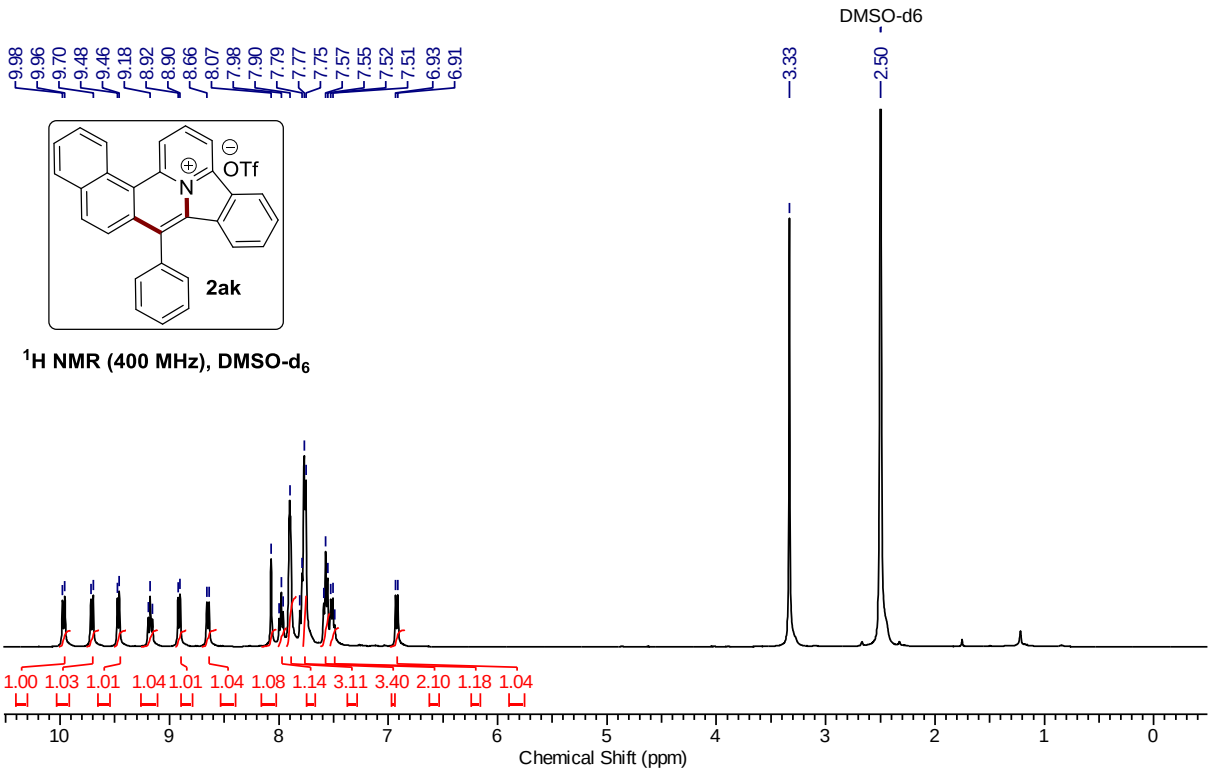
^{13}C NMR (125 MHz), DMSO-d_6



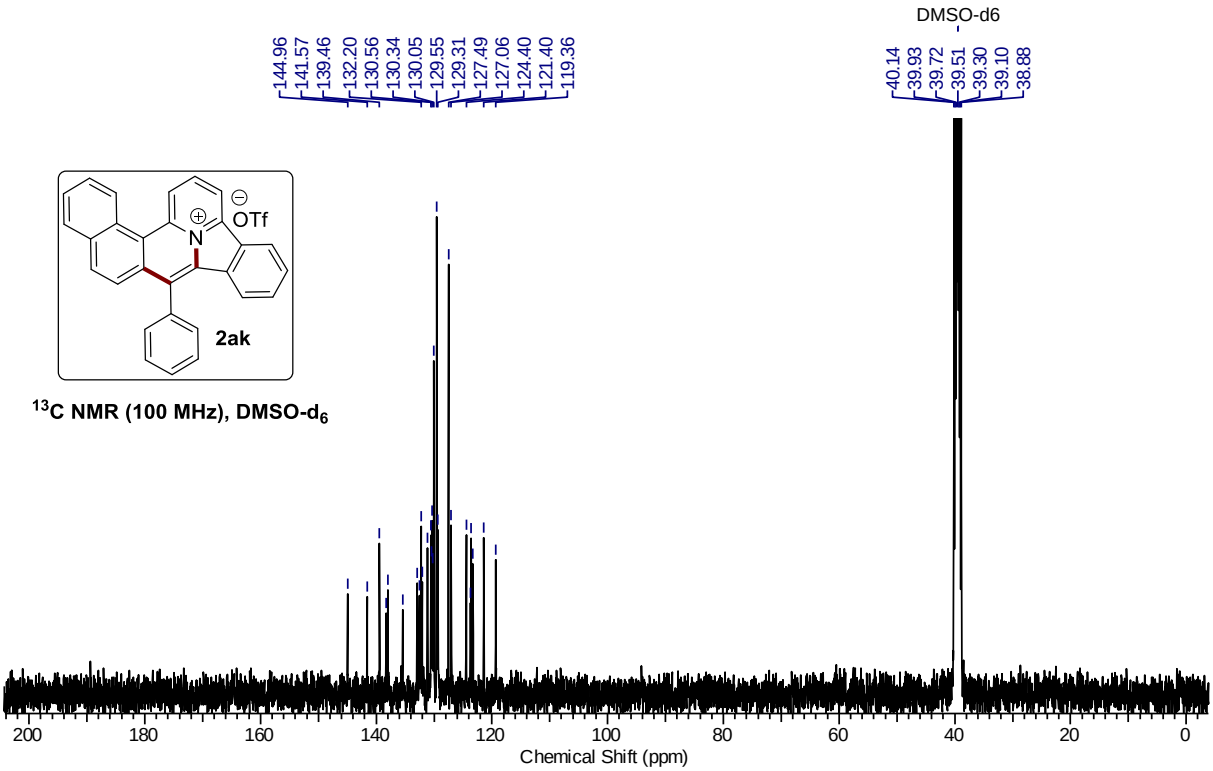
^{1}H NMR (500 MHz), DMSO-d$_6$



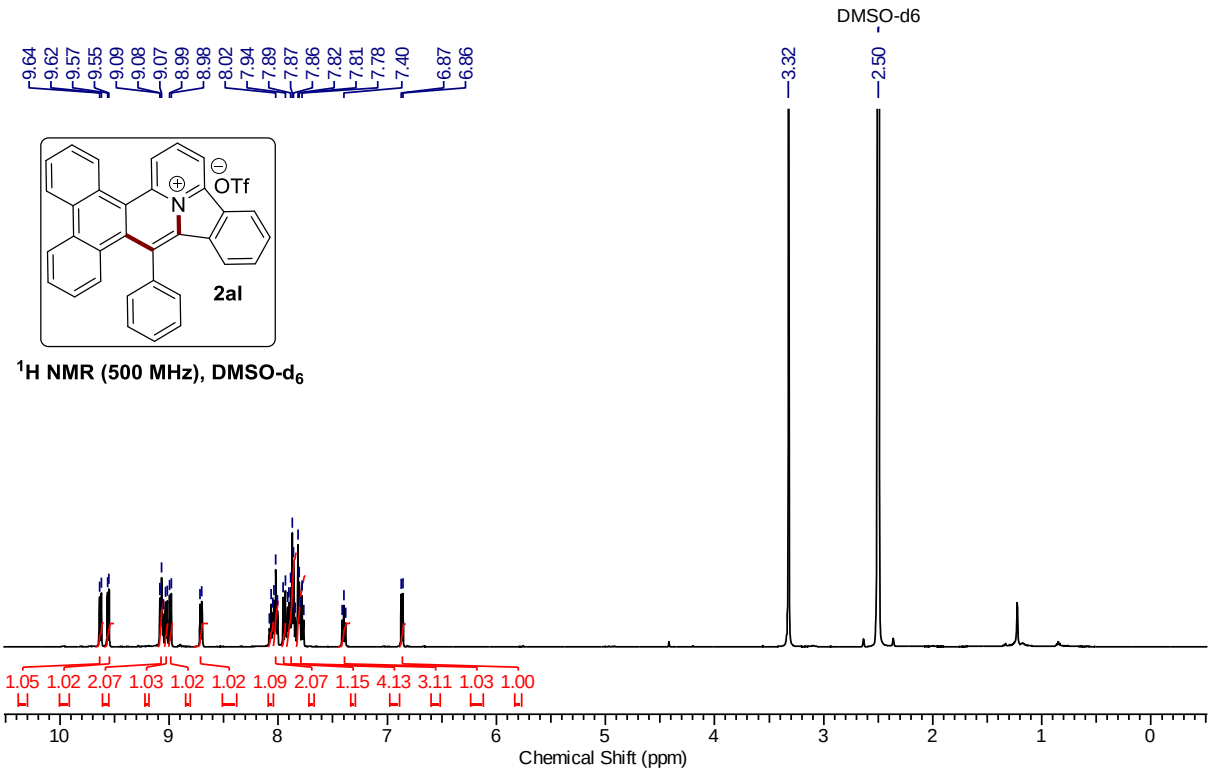
^{1}H NMR (125 MHz), DMSO-d$_6$



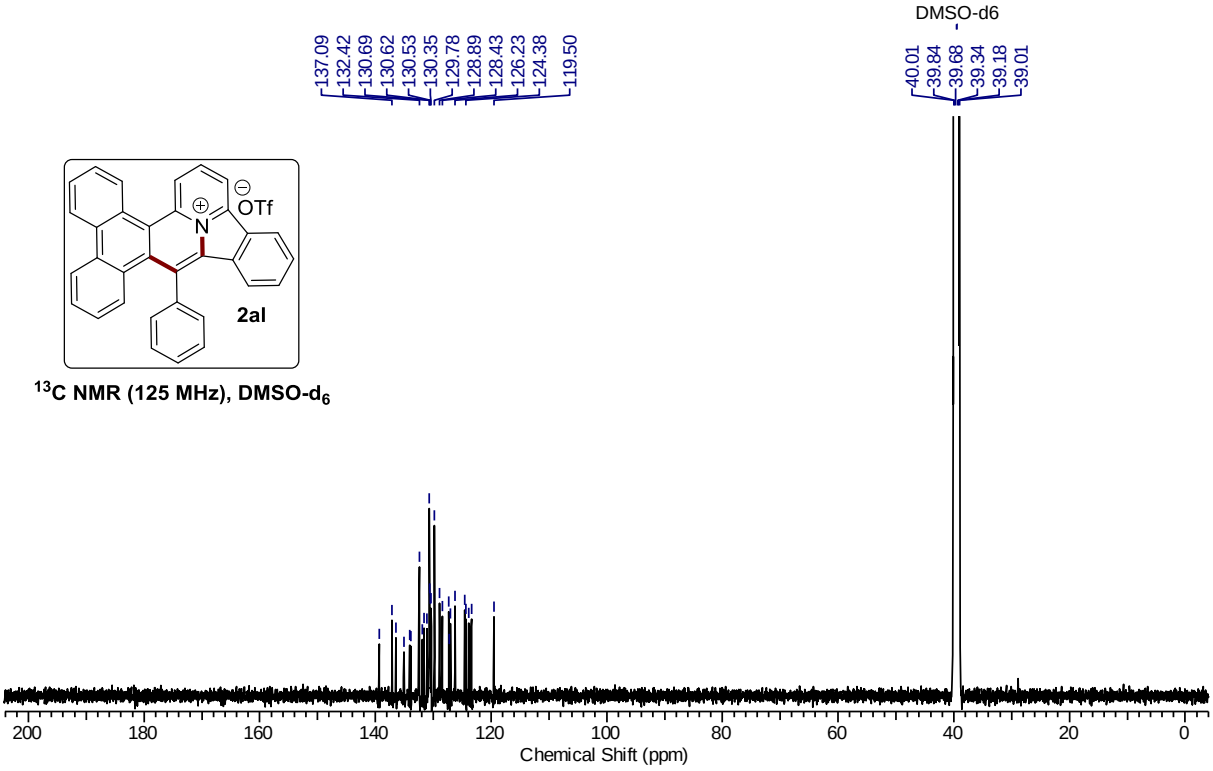
^{1}H NMR (400 MHz), DMSO-d_6



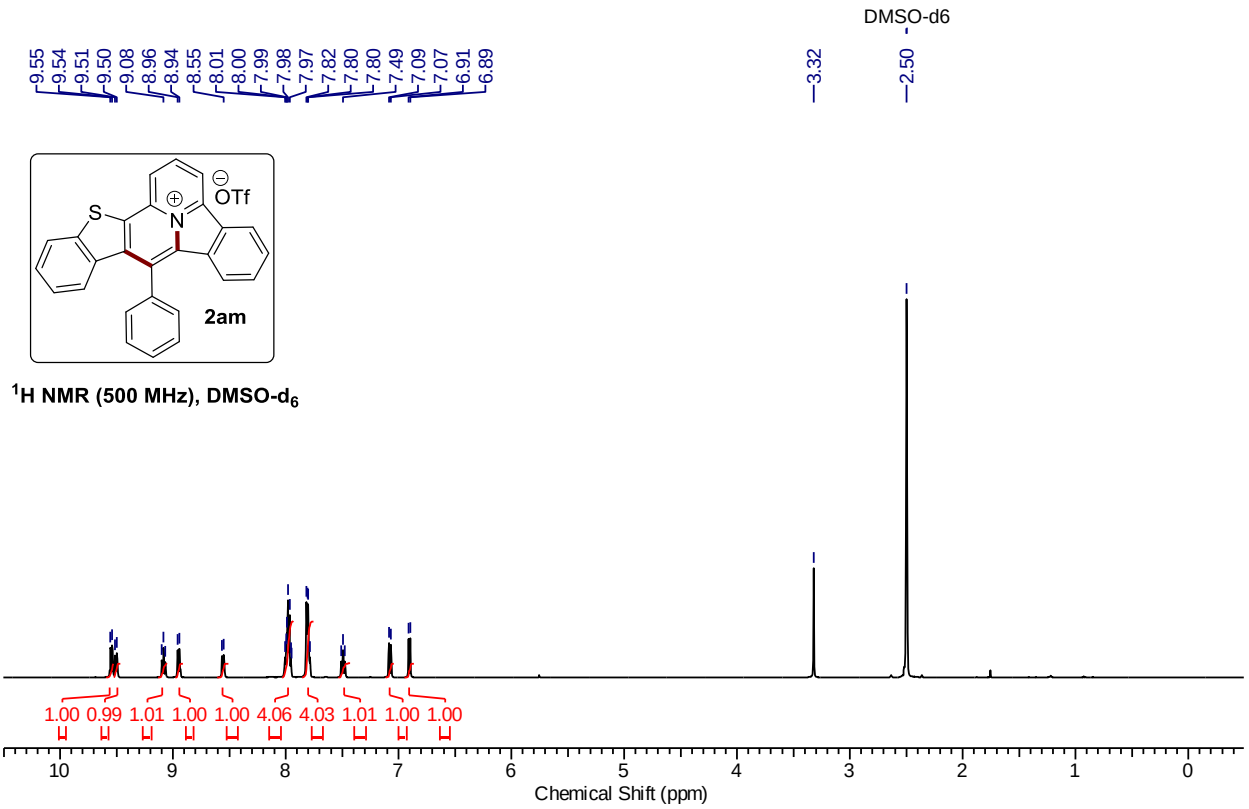
^{13}C NMR (100 MHz), DMSO-d_6



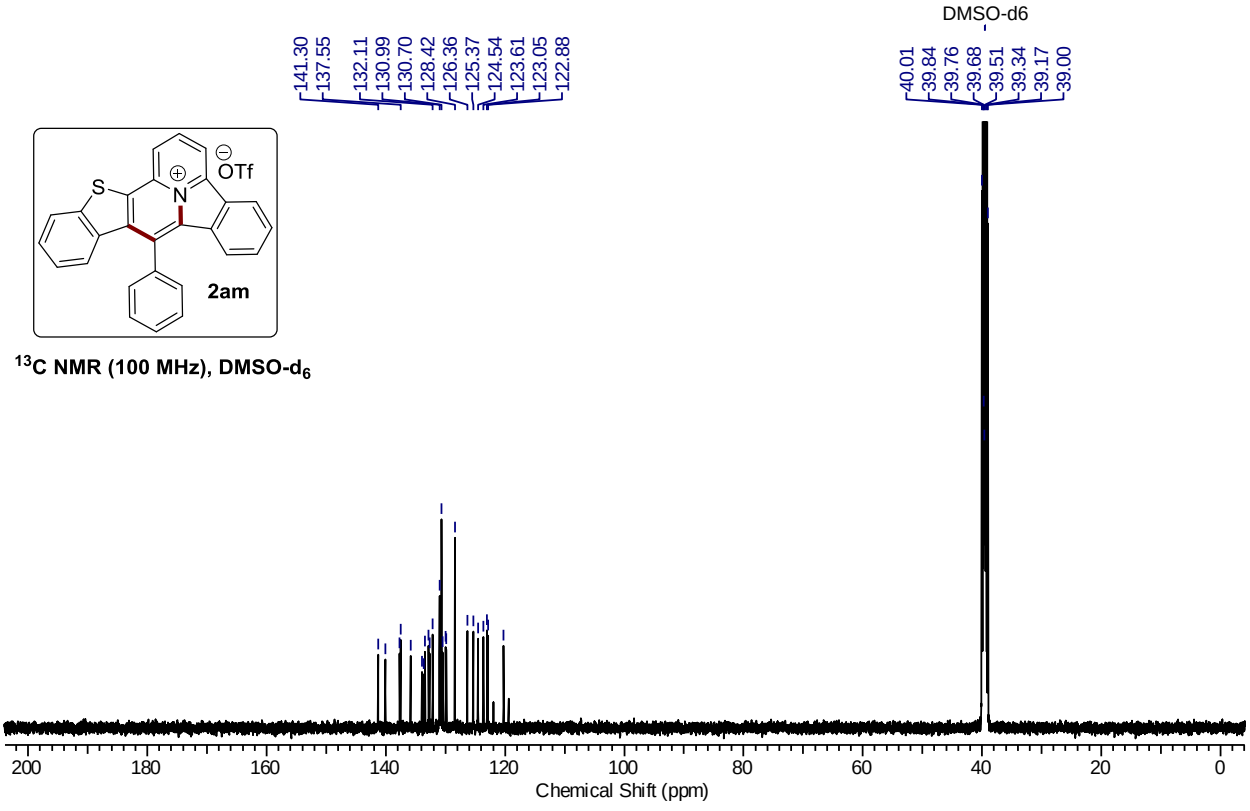
^{1}H NMR (500 MHz), DMSO-d$_6$



^{13}C NMR (125 MHz), DMSO-d$_6$

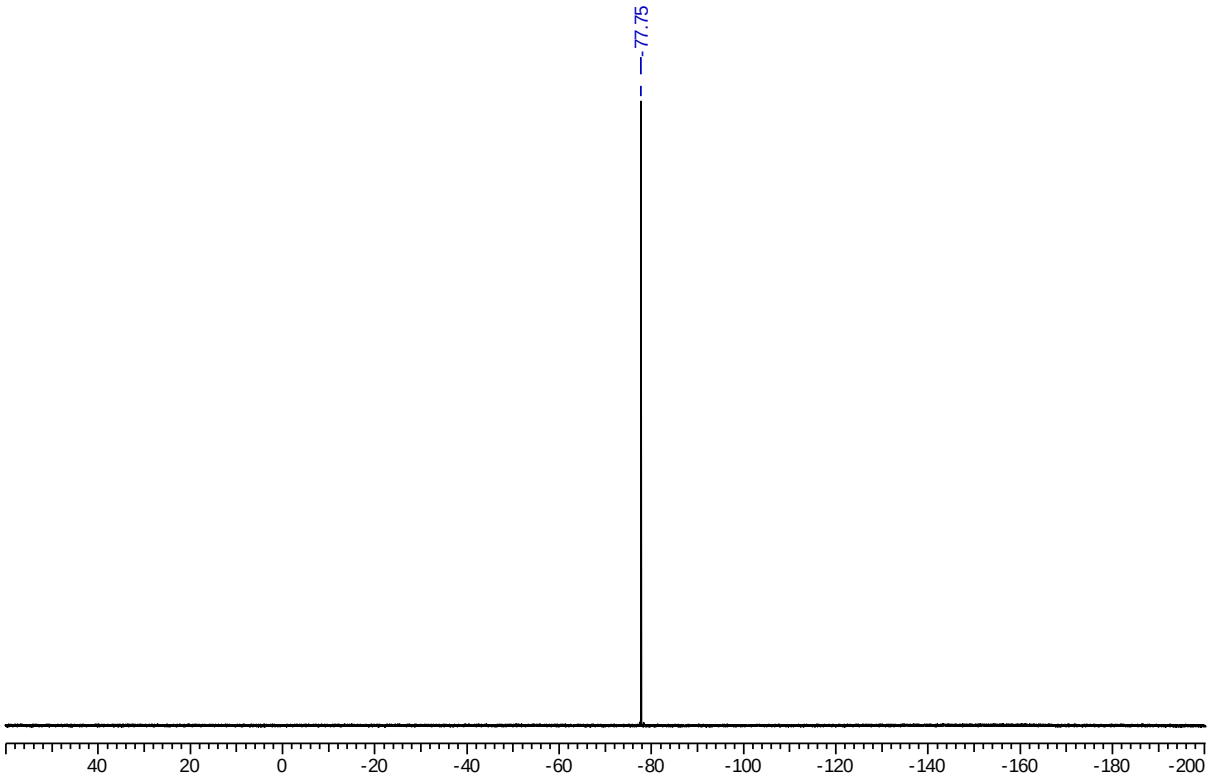


^{1}H NMR (500 MHz), DMSO-d_6



^{13}C NMR (100 MHz), DMSO-d_6

^{19}F NMR (376.5 MHz, DMSO-d_6) of 2a for OTf anion



^{19}F NMR (376.5 MHz, DMSO-d_6)of 2a' for BF_4 anion