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Supporting Information

Reactivity of 5-(Alkynyl)dibenzothiophenium Salts: Synthesis of Diynes, Vinyl Sulfones, and Phenanthrenes

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1 Experimental Procedures

1.1 General working methods

All reactions were carried out using pre-dried glassware under nitrogen atmosphere unless otherwise stated. Dry and degassed solvents (THF, dichloromethane, toluene, *n*-pentane, diethyl ether) were obtained with the MBraun Solvent Purification System (MB-SPS-800) or by distillation over the drying agents as indicated below and stored under a protective gas atmosphere. Flash chromatography was either performed on Merck 60 (40–63 µm) or Macherey-Nagel 60 (40–63 µm) silica gel. Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates or polygram SIL G/UV254 from Macherey-Nagel and visualized by UV irradiation and/or phosphomolybdic acid, $KMnO_4$ or *p*-anisaldehyde dip.

1.2 Starting materials

All commercially available products (Acros Organics, ABCR, Alfa Aesar, Sigma Aldrich, Fluorochem, TCI) were used as received. Compounds **1a**, **1b** and **1c** were synthesized according to literature procedures.[1,2]

1.3 General analytical methods

NMR: spectra were recorded at ambient temperature on Bruker Avance Neo 600, Avance III HD 500, Avance Neo 400, Avance III HD 400, Avance III 400 or Avance III HD 300. Chemical shifts (δ) are reported in ppm and quoted relative to the residual solvent peaks in $CDCl_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm), CD_3CN (^{1}H: 1.94 ppm, ^{13}C: 118.26 ppm) or $(CD_3)_2CO$ (^{1}H: 2.05 ppm, ^{13}C: 29.45 ppm); coupling constants (J) are given in Hertz (Hz).

HRMS: Finnigan MAT 95 (70 eV, EI), Finnigan LCQ (ESI) and APEX IV 7T FTICR, Bruker Daltonic (HRMS).

IR: Infrared spectra were recorded on JASCO FT/IR-4100, FT/IR-4600 spectrometers and Nicolet FT-7199 and reported in wavenumbers (cm^{-1}).

GC-MS: spectra were recorded with GC system 7820A combined with a mass spectrometer Agilent 5977E.

Preparative HPLC: was conducted by Interchim Puriflash 4250 with column Zorbax SB-C18.

Single crystal X-ray diffraction analysis: Data collection was done on two dual source equipped *Bruker D8 Venture* four-circle-diffractometer from *Bruker AXS GmbH*; used X-ray sources: microfocus *IμS 2.0* Cu/Mo and microfocus *IμS 3.0* Ag/Mo from *Incoatec GmbH* with mirror optics *HELIOS* and single-hole collimator from *Bruker AXS GmbH;* used detector: *Photon III CE14* (Cu/Mo) and Photon III HE (Ag/Mo) from *Bruker AXS GmbH*.

Used programs: *APEX3 Suite* (v2018.7-2) for data collection and therein integrated programs *SAINT* V8.38A (Integration) und *SADABS* 2016/2 (Absorption correction) from *Bruker AXS GmbH*; structure solution was done with *SHELXT,*[3] refinement with *SHELXL*-2018/3[3] was used for data finalization and Figures preparation.[4] The numbering in Figures does not correspond to the IUPAC rules.

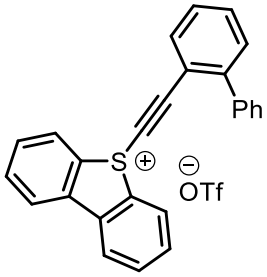
Special Utilities: *SMZ1270* stereomicroscope from *Nikon Metrology GmbH* was used for sample preparation; crystals were mounted on *MicroMounts* or *MicroLoops* from *MiTeGen* in NVH oil.

If not otherwise stated, single crystals were obtained by vapor diffusion method using dichloromethane and diethyl ether as solvents.

Identifier	CCDC	Identifier	CCDC
2g	2068276	**10**	2068282
2k	2068277	**11**	2068283
3e	2068278	**11** with bromide counterion	2068284
5a	2068279	**24**	2068285
6	2068280	**28**	2068286
8	2068281		

1.4 Synthesis and characterization of the compounds prepared:

5-([1,1'-Biphenyl]-2-ylethynyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium Trifluoromethanesulfonate (1d):

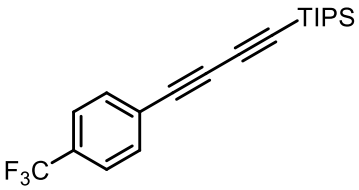


A Schlenk flask was charged with a stirring bar and dibenzo thiophen oxide (DBTO) (1.0 g, 4.99 mmol, 1.0 equiv.). The reaction vessel was purged with nitrogen and anhydrous DCM (40 mL) was added. The reaction mixture was cooled down to –50 °C and stirred for 5 min. Tf_2O (0.91 mL, 4.99 mmol, 1.0 equiv.) was added dropwise and the resulting orange suspension was stirred for 10 minutes. Afterwards ([1,1'-biphenyl]-2-ylethynyl)trimethylsilane (1.25 g, 5.99 mmol, 1.2 equiv.) was added in one portion and the reaction mixture was warmed up to room temperature over 15 min. The solvent was evaporated to a small fraction, the crude compound precipitated with diethyl ether (25 mL) and successively washed with diethyl ether (2 x 25 mL). After drying in *vacuo* the salt **1d** (2.14 g, 4.19 mmol, 84%) was obtained as a yellow solid. **^{1}H NMR** (400 MHz, CD_3CN): δ = 8.27 – 8.22 (m, 4H), 7.95 (td, *J* = 7.6, 1.0 Hz, 2H), 7.81 – 7.74 (m, 3H), 7.68 – 7.63 (m, 1H), 7.49 – 7.45 (m, 2H), 7.30 – 7.25 (m, 3H), 7.18 – 7.13 (m, 2H) ppm. **^{13}C NMR** (101 MHz, CD_3CN): *δ* = 147.3, 140.1, 139.4, 135.9, 135.5, 134.1, 133.1, 131.3, 130.9, 129.6, 129.32, 129.30, 128.92, 128.90, 125.7, 122.1 (q, $^1J_{C–F}$ = 322 Hz), 116.9, 106.1 ppm. **IR** (ATR): $\tilde{\nu}$ = 3088, 2177, 1447, 1274, 1253, 1224, 1159, 1028, 758, 638 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{17}S^+$ $[M–OTf]^+$; 361.1046; found: 361.1045.

General Procedure A (GP A) for the synthesis of compounds 2a-2p

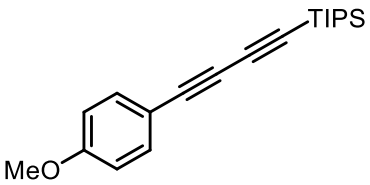
The corresponding 1-alkyne or 1,3 diyne (0.2 mmol, 1.0 equiv.) was dissolved in anhydrous DCM (2 mL, 0.1 M) under inert atmosphere. LiHMDS (0.2 mL of 1 M solution in THF, 0.2 mmol, 1.0 equiv.) was added at –78 °C under stirring. The reaction mixture was allowed to warm up to 0 °C and stirred for 5 min. Successively it was cooled back to –78 °C, and the transfer reagent 5-[(triisopropylsilyl)ethynyl]-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (**1a**) (103 mg, 0.2 mmol, 1.0 equiv.) was added in one portion. The reaction mixture was warmed up to room temperature and stirred for an additional 10 min. The reaction was quenched with water and extracted with EtOAc (3 × 5 mL). After drying over Na_2SO_4 or $MgSO_4$, the solvent was evaporated. The product was isolated by column chromatography (pentane) or HPLC.

Triisopropyl{[4-(trifluoromethyl)phenyl]buta-1,3-diyn-1-yl}silane (2a):



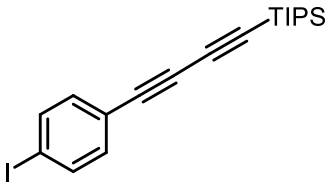
Following GP A, **2a** (26.6 mg, 76 µmol, 38%) was obtained as a colorless oil from 1-ethynyl-4-(trifluoromethyl)benzene (34.0 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 1.12 (m, 21H) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): *δ* = –63.0 ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* = 133.0, 131.1, 125.7, 125.5 (q, $^{3}J_{C-F}$ = 3.9 Hz), 122.1, 89.9, 89.1, 77.0, 74.0, 18.7, 11.4 ppm. **IR** (neat): $\tilde{\nu}$ = 2945, 2865, 2103, 1612, 1462, 1316, 1126, 1064, 841, 594 cm^{-1}. **HRMS** (EI) *m*/*z* calcd for $C_{20}H_{25}F_3Si^+$: 350.1672 [*M*]$^+$; found: 350.1675. The compound was reported in the literature; however, its analytical data are not provided.[5]

Triisopropyl[(4-methoxyphenyl)buta-1,3-diyn-1-yl]silane (2b):



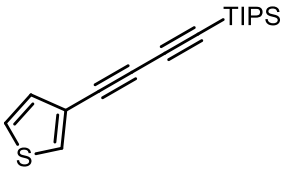
Following GP A, **2b** (17.5 mg, 56 µmol, 28%) was obtained as a yellow oil from 1-ethynyl-4-methoxybenzene (26.4 mg, 0.2 mmol, 1 equiv. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 1.11 (s, 21H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* = 160.5, 134.5, 114.3, 113.6, 89.9, 87.2, 75.9, 73.7, 55.5, 18.7, 11.5 ppm. **IR** (neat): $\tilde{\nu}$ = 2943, 2862, 2199, 2098, 1502, 1298, 1249, 1171, 830, 671 cm^{-1}. **HRMS** (EI) *m/z* calcd for $C_{20}H_{28}OSi^+$ [*M*]$^+$: 312.1903; found: 312.1904. Analytical data corresponds to those reported in the literature.[6] The yield of **2b** was improved to 52% when 1 equiv. of CuCN was added to the reaction mixture under otherwise identical conditions.

[(4-Iodophenyl)buta-1,3-diyn-1-yl]triisopropylsilane (2c):



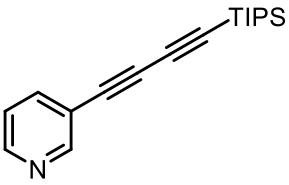
Following GP A, **2c** (58.0 mg, 142 µmol, 71%) was obtained as a slightly yellow oil from 1-ethynyl-4-iodobenzene (45.6 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 1.11 (s, 21H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* = 137.8, 134.1, 121.2, 95.7, 89.4, 89.1, 76.2, 74.7, 18.7, 11.4 ppm. **IR** (neat): $\tilde{\nu}$ = 2943, 2865, 2204, 2101, 1462, 1002, 879, 815, 656, 601 cm^{-1}. **HRMS** (EI) *m/z* calcd for $C_{19}H_{25}ISi^+$ [*M*]$^+$: 408.0765; found: 408.0761.

Triisopropyl(thiophen-3-ylbuta-1,3-diyn-1-yl)silane (2d):



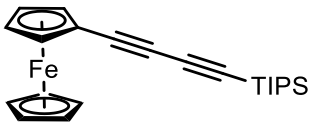
Following GP A, **2d** (28.3 mg, 98 µmol, 49%) was obtained as a slightly brown oil from 3-ethynylthiophene (21.6 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 4.0 Hz, 1H), 7.26 (dd, *J* = 4.9, 3.1 Hz, 1H), 7.15 (d, *J* = 6.1 Hz, 1H), 1.11 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* = 131.7, 130.4, 125.7, 120.8, 89.6, 87.9, 74.5, 70.9, 18.7, 11.5 ppm. **IR** (neat): $\tilde{\nu}$ = 3112, 2940, 2862, 2199, 2101, 1459, 994, 861, 778, 659 cm^{-1}. **HRMS** (EI) *m/z* calcd for $C_{17}H_{24}SSi^+$ [*M*]$^+$:288.1363; found: 288.1374. The spectra correspond to the previously published data.[7]

3-[(Triisopropylsilyl)buta-1,3-diyn-1-yl]pyridine (2e):



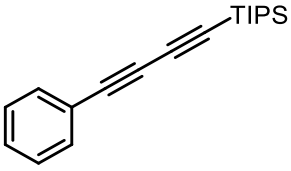
Following GP A, **2e** (35.7 mg, 0.126 mmol, 63%) was obtained as a yellow oil from 3-ethynylpyridine (20.6 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.73 (s, 1H), 8.56 (d, *J* = 4.2 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.22 (m, 1H), 1.11 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* = 153.5, 149.3, 139.6, 123.1, 119.2, 89.9, 89.0, 78.0, 72.2, 18.7, 11.4 ppm. **IR** (neat): $\tilde{\nu}$ = 2940, 2862, 2204, 2106, 1462, 1404, 996, 882, 659, 602 cm^{-1}. **HRMS** (EI) *m/z* calcd for $C_{18}H_{25}NSi^+$ [*M*]$^+$: 283.1751; found: 283.1750.

(Ferrocenylbuta-1,3-diyn-1-yl)triisopropylsilane (2f):



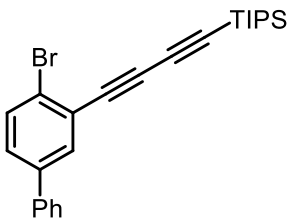
Following GP A, **2f** (28.9 mg, 74 µmol, 37%) was obtained as red crystals from ethynylferrocene (42.0 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 4.50 (q, *J* = 1.6 Hz, 2H), 4.27 – 4.22 (m, 7H), 1.11 (m, 21H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 90.3, 84.8, 76.0, 72.3, 71.1, 70.2, 69.3, 62.9, 18.6, 11.4 ppm. **IR** (ATR): $\tilde{\nu}$ = 2943, 2865, 2360, 2202, 1462, 996, 884, 820, 659 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{23}H_{31}FeSi^+$ [*M*+H]$^+$: 391.1539; found: 391.1530. Analytical data corresponds to those reported in the literature.[8]

Triisopropyl(phenylbuta-1,3-diyn-1-yl)silane (2g):



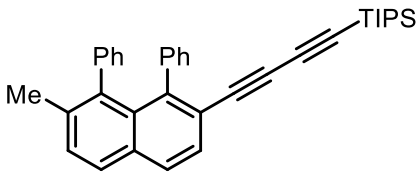
Following GP A, **2g** (29.4 mg, 104 µmol, 52%) was obtained as a colorless oil from ethynylbenzene (20.4 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.54 – 7.49 (m, 2H), 7.39 – 7.28 (m, 3H), 1.12 (s, 21H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* = 132.8, 129.4, 128.5, 121.7, 89.6, 88.0, 75.7, 74.8, 18.7, 11.5 ppm. **IR** (neat): $\tilde{\nu}$ = 2943, 2865, 2202, 2101, 1459, 1017, 879, 755, 677, 602 cm^{-1}. **HRMS** (EI) *m/z* calcd for $C_{19}H_{26}Si^+$ [*M*]$^+$: 282.1798; found: 282.1788. Analytical data corresponds to those reported in the literature.[9]

{(4-Bromo-[1,1'-biphenyl]-3-yl)buta-1,3-diyn-1-yl}triisopropylsilane (2h):



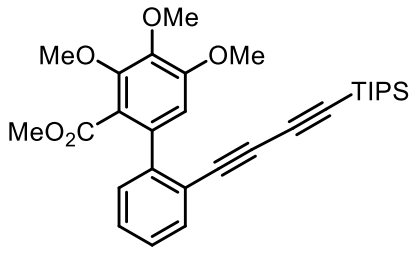
Following GP A, **2h** (50.8 mg, 0.116 mmol, 58%) was obtained as a colorless oil from 4-bromo-3-ethynyl-1,1'-biphenyl (51.4 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.47 – 7.37 (m, 4H), 1.13 (s, 21H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* = 140.5, 139.0, 133.4, 133.0, 129.07, 129.14, 128.2, 127.0, 125.1, 124.5, 90.1, 89.3, 79.0, 73.8, 18.7, 11.5 ppm. **IR** (neat): $\tilde{\nu}$ = 2940, 2862, 2098, 1464, 1238, 1014, 882, 760, 695, 607 cm^{-1}. **HRMS** (EI) *m/z* calcd for $C_{25}H_{29}BrSi^+$ [*M*]$^+$: 436.1216; found: 436.1219.

Triisopropyl[(7-methyl-1,8-diphenylnaphthalen-2-yl)buta-1,3-diyn-1-yl]silane (2i):



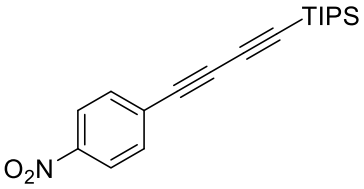
Following GP A, **2i** (39.9 mg, 79,9 µmol, 40%) was obtained as a white solid from 2-ethynyl-7-methyl-1,8-diphenylnaphthalene (63.7 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 9.6 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 4.4 Hz, 6H), 6.78 (d, *J* = 4.9 Hz, 2H), 6.69 (d, *J* = 5.3 Hz, 2H), 1.99 (s, 3H), 1.02 (s, 21H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* = 145.9, 141.2, 141.0, 139.2, 136.7, 133.2, 131.1, 130.6, 130.6, 129.8, 128.0, 127.79, 127.77, 127.3, 126.9, 126.0, 125.7, 121.7, 89.7, 88.2, 78.5, 76.1, 21.6, 18.5, 11.3 ppm. **IR** (ATR): $\tilde{\nu}$ = 2925, 2851, 2360, 2339, 1735, 1646, 1464, 1173, 1036, 697 cm^{-1}. **HRMS** (EI) *m/z* calcd for $C_{36}H_{38}Si^+$ [*M*]$^+$: 498.2737; found: 498.2754.

Methyl 3,4,5-Trimethoxy-2'-[(triisopropylsilyl)buta-1,3-diyn-1-yl]-[1,1'-biphenyl]-2-carboxylate (2j):



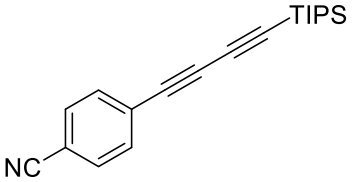
Following GP A, **2j** (65.9 mg, 0.130 mmol, 65%) was obtained as white crystals from methyl 2'-ethynyl-3,4,5-trimethoxy-[1,1'-biphenyl]-2-carboxylate (65.3 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 9.3 Hz, 1H), 7.38 – 7.25 (m, 3H), 6.86 (s, 1H), 3.97 (s, 3H), 3.92 (s, 3H), 3.91 (s, 3H), 3.58 (s, 3H), 1.07 (s, 21H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* = 167.5, 154.1, 151.8, 143.8, 141.9, 134.4, 134.1, 129.3, 129.0, 127.6, 121.6, 120.6, 110.4, 89.7, 88.6, 78.3, 74.7, 62.2, 61.1, 56.3, 52.1, 18.7, 11.4 ppm. **IR** (ATR): $\tilde{\nu}$ = 2943, 2688, 2361, 2340, 1733, 1459, 1113, 1030, 878, 756 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{39}O_5Si^+$ [*M*+H]$^+$: 507.2561; found: 507.2558.

Triisopropyl((4-nitrophenyl)buta-1,3-diyn-1-yl)silane (2k):



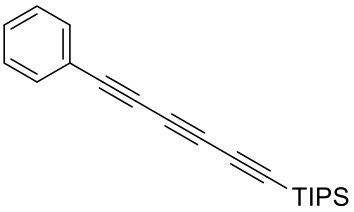
Following GP A, **2k** (49.3 mg, 0.151 mmol, 75%) was obtained as an orange solid from 1-ethynyl-4-nitrobenzene (29.4 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.22–8.17 (m, 2H), 7.67 – 7.62 (m, 2H), 1.12 (s, 21H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 147.7, 133.6, 128.8, 123.8, 92.0, 88.8, 79.6, 73.3, 18.7, 11.4 ppm. **IR** (ATR): $\tilde{\nu}$ = 2943, 2863, 2100, 1592, 1519, 1459, 1341, 851, 654, 604 cm^{-1}. **HRMS** (EI+) *m/z* calcd for $C_{19}H_{25}O_2Si^+$ [*M*]$^+$: 327.1649; found: 327.1646. The analytical data corresponds to those reported in the literature.[10]

4-((triisopropylsilyl)buta-1,3-diyn-1-yl)benzonitrile (2l):



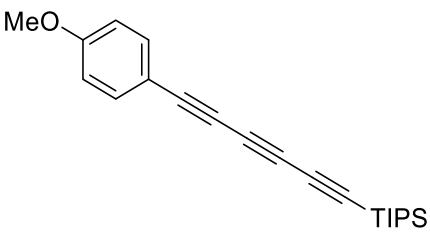
Following GP A, **2l** (43.3 mg, 0.141 mmol, 70%) was obtained as an orange solid from 4-ethynylbenzonitrile (25.4 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.63 – 7.56 (m, 4H), 1.12 (s, 21H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 133.3, 132.2, 126.8, 118.4, 112.6, 91.4, 88.8, 78.9, 73.5, 18.7, 11.4. ppm. **IR** (ATR): $\tilde{\nu}$ = 2944, 2865, 2226, 2099, 1602, 1481, 1004, 995, 882, 664 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{29}N_2Si^+$ [*M*+NH_4]$^+$: 325.2095; found: 325.2094. The analytical data corresponds to those reported in the literature.[10]

Triisopropyl(phenylhexa-1,3,5-triyn-1-yl)silane (2m):



Following GP A, **2m** (44.8 mg, 0.146 mmol, 73%) was obtained as a yellow liquid from (buta-1,3-diyn-1-yl)benzene (25.2 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.55 – 7.48 (m, 2H), 7.42 –7.28 (m, 3H), 1.10 (s, 21H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 133.2, 129.9, 128.6, 121.1, 89.9, 86.9, 76.7, 74.5, 67.4, 60.7, 18.7, 11.5 ppm. **IR** (ATR): $\tilde{\nu}$ = 2942, 2865, 2174, 2073, 1461, 881, 753, 675 cm^{-1} **HRMS** (EI): *m/z* calcd for $C_{21}H_{26}Si^+$ [*M*]$^+$: 306.1798; found: 306.1796. The analytical data corresponds to those reported in the literature.[11]

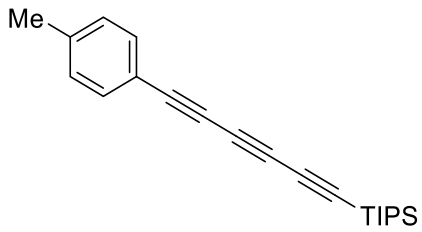
Triisopropyl[(4-methoxyphenyl)hexa-1,3,5-triyn-1-yl]silane (2n):



Following GP A, **2n** (53.2 mg, 0.158 mmol, 79%) was obtained as a yellow liquid from 1-(buta-1,3-diyn-1-yl)-4-methoxybenzene (31.2 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 9.1 Hz, 2H), 6.85 (d, *J* = 9.1 Hz, 2H), 3.82 (s, 3H), 1.09 (s, 21H) ppm. **^{13}C NMR** (101 MHz,

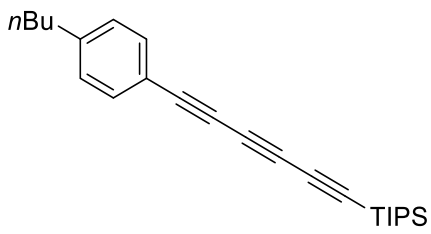
$CDCl_3$): δ = 160.9, 134.9, 134.6, 114.4, 112.8, 90.1, 86.5, 73.5, 67.1, 61.1, 55.5, 18.7, 11.4 ppm. **IR** (ATR): $\tilde{\nu}$ = 2941, 2861, 2177, 2065, 1480, 1266, 1132, 1003, 851, 643 cm^{-1}. **HRMS** (EI): *m/z* calcd for $C_{22}H_{28}OSi^+$ $[M]^+$: 336.1904; found: 336.1904. The analytical data corresponds to those reported in the literature.[11]

Triisopropyl(*p*-tolylhexa-1,3,5-triyn-1-yl)silane (2o):



Following GP A, **2o** (30.8 mg, 96 µmol, 48%) was obtained as a yellow liquid from 1-(buta-1,3-diyn-1-yl)-4-methylbenzene (28.0 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H), 1.10 (s, 21H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 140.4, 133.2, 129.4, 117.9, 90.0, 86.6, 77.0, 74.0, 67.2, 60.9, 21.8, 18.7, 11.4 ppm. **IR** (ATR): $\tilde{\nu}$ = 2941, 2861, 2177, 2065, 1480, 1266, 1132, 1003, 851, 643 cm^{-1} **HRMS** (EI): *m/z* calcd for $C_{22}H_{28}Si^+$ $[M]^+$: 320.1955; found: 320.1954. The analytical data corresponds to those reported in the literature.[13]

[(4-Butylphenyl)hexa-1,3,5-triyn-1-yl]triisopropylsilane (2p):

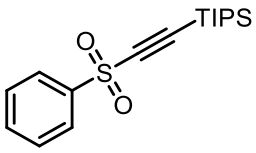


Following GP A, **2p** (37.0 mg, 0.102 mmol, 51%) was obtained as a yellow liquid from 1-(buta-1,3-diyn-1-yl)-4-butylbenzene (36.5 mg, 0.2 mmol, 1 equiv.). **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 2.63 – 2.58 (m, 2H), 1.61 – 1.56 (m, 2H), 1.33 (dt, *J* = 14.7, 7.4 Hz, 2H), 1.09 (d, *J* = 2.7 Hz, 21H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 145.4, 133.2, 128.8, 118.0, 90.0, 86.6, 77.0, 74.0, 67.2, 61.0, 35.9, 33.4, 22.4, 18.7, 14.1, 11.4 ppm. **IR** (ATR): $\tilde{\nu}$ = 2941, 2859, 2183, 2067, 1511, 1463, 1137, 996, 881, 667 cm^{-1}. **HRMS** (EI): *m/z* calcd for $C_{25}H_{34}Si^+$ $[M]^+$: 362.2424; found: 362.2816.

General Procedure B (GP B) for the synthesis of compounds 3a-3h

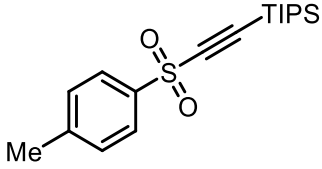
Transfer reagent **1a** (103 mg, 0.2 mmol, 1 equiv.) and the corresponding sulfinate (0.24 mmol, 1.2 equiv.) were dissolved in DCM:MeOH 1:1 (5 mL), and the reaction mixture was stirred for 30 min at ambient temperature on air. The reaction was monitored by TLC. Upon completion of the reaction, pentane (5 mL) was added, and the reaction mixture was transferred directly to a pre-wetted column (hexanes). The pure product was obtained by column chromatography (hexanes).

Triisopropyl[(phenylsulfonyl)ethynyl]silane (3a):



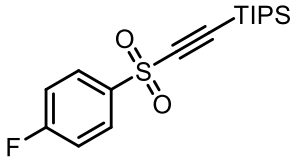
Following GP B, **3a** (57.4 mg 0.178 mmol, 89%) was obtained as a colorless oil from sodium benzenesulfinate (39.4 mg, 0.24 mmol, 1.2 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.05 – 8.00 (m, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 1.16 – 1.00 (m, 21H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* = 142.3, 134.2, 129.4, 127.3, 101.1, 100.8, 18.5, 11.0 ppm. **IR** (neat): $\tilde{\nu}$ = 2946, 2865, 2360, 2119, 1738, 1335, 1159, 784, 681, 570 cm^{-1}. **HRMS** (EI) *m/z* calcd for $C_{17}H_{26}O_2SSi^+$ [*M*]$^+$: 322.1417; found: 322.1422. Analytical data corresponds to those reported in the literature.[14]

Triisopropyl(tosylethynyl)silane (3b):



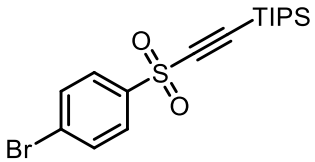
Following GP B, **3b** (57.9 mg, 0.172 mmol, 86%) was obtained as a white solid from sodium 4-methylbenzenesulfinate (42.8 mg, 0.24 mmol, 1.2 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$): 7.88 (d, *J* = 8.9 Hz, 2H), 7.35 (d, *J* = 9.3 Hz, 2H), 2.45 (s, 3H), 1.13 – 1.00 (m, 21H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 145.3, 139.3, 130.0, 127.4, 101.0, 100.2, 21.8, 18.4, 11.0 ppm. **IR** (ATR): $\tilde{\nu}$ = 2942, 2867, 2118, 1461, 1333, 1159, 1084, 771, 670, 545 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{28}NaO_2SSi^+$ [*M*+Na]$^+$: 359.1472; found: 359.1470. Analytical data corresponds to those reported in the literature.[12]

{[(4-Fluorophenyl)sulfonyl]ethynyl}triisopropylsilane (3c):



Following GP B, **3c** (58.6 mg, 0.172 mmol, 86%) was obtained as a colorless oil from sodium 4-fluorobenzenesulfinate (43.7 mg, 0.24 mmol, 1.2 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 9.1, 5.0 Hz, 2H), 7.28 – 7.21 (m, 2H), 1.12 – 1.01 (m, 21H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): *δ* = –102.45 ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 167.1 (d, *J* = 257.5 Hz), 138.3 (d, *J* = 3.3 Hz), 130.3 (d, *J* = 9.9 Hz), 116.8 (d, *J* = 22.8 Hz), 101.3, 100.6, 18.4, 11.0 ppm. **IR** (neat): $\tilde{\nu}$ = 2947, 2864, 2360, 2118, 1592, 1341, 1151, 777, 670, 545 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{17}H_{25}FNaO_2SSi^+$ [*M*+Na]$^+$: 363.1221; found: 363.1221. Analytical data corresponds to those reported in the literature.[14]

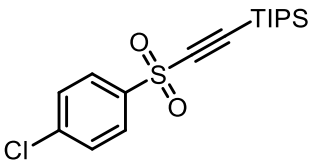
{[(4-Bromophenyl)sulfonyl]ethynyl}triisopropylsilane (3d):



Following GP B, **3d** (66.6 mg, 0.166 mmol, 83%) was obtained as a white solid from sodium 4-bromobenzenesulfinate (58.3 mg, 0.24 mmol, 1.2 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 1.13 – 1.01 (m, 21H) ppm. **^{13}C NMR** (101 MHz,

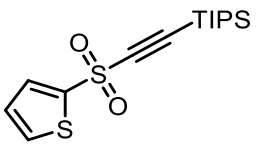
$CDCl_3$): δ = 141.2, 132.7, 129.6, 128.9, 101.8, 100.3, 18.5, 11.0 ppm. **IR** (ATR): $\tilde{\nu}$ = 2945, 2867, 2360, 2337, 2121, 1571, 1464, 1338, 1159, 788 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{17}H_{29}BrNO_2SSi^+$ $[M+NH_4]^+$: 418.0866; found: 418.0864. Analytical data corresponds to those reported in the literature.[14]

{[(4-Chlorophenyl)sulfonyl]ethynyl}triisopropylsilane (3e):



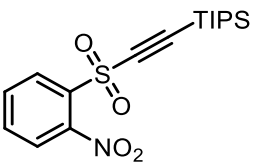
Following GP B, **3e** (32.8 mg, 91.8 µmol, 46%) was obtained as a white solid from sodium 4-chlorobenzenesulfinate (47.7 mg, 0.24 mmol, 1.2 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 2H), 1.13 – 1.01 (m, 21H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 141.0, 140.7, 129.7, 128.8, 101.7, 100.4, 18.4, 11.0 ppm. **IR** (ATR): $\tilde{\nu}$ = 2947, 2867, 1734, 1458, 1341, 1165, 1030, 791, 681, 670 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{17}H_{25}ClNaO_2SSi^+$ $[M+Na]^+$: 379.0925; found: 379.0920. Analytical data corresponds to those reported in the literature.[14]

Triisopropyl[(thiophen-2-ylsulfonyl)ethynyl]silane (3f):



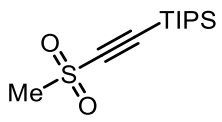
Following GP B, **3f** (60.4 mg, 183.8 µmol, 92%) was obtained as a white solid from sodium thiophene-2-sulfinate (40.8 mg, 0.24 mmol, 1.2 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.75 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.14 (dd, *J* = 5.0, 3.8 Hz, 1H), 1.14 – 1.02 (m, 21H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 143.3, 134.9, 134.2, 127.9, 100.9, 100.8, 18.4, 11.0 ppm. **IR** (ATR): $\tilde{\nu}$ = 2121, 1461, 1402, 1341, 1153, 1012, 884, 785, 670, 574 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{25}O_2S_2Si^+$ $[M+H]^+$: 329.1060; found: 329.1063. Analytical data corresponds to those reported in the literature.[15]

Triisopropyl{[(2-nitrophenyl)sulfonyl]ethynyl}silane (3g):



Following GP B, **3g** (36.0 mg, 97.9 µmol, 49%) was obtained as an orange solid from sodium 2-nitrobenzenesulfinate (50.2 mg, 0.24 mmol, 1.2 equiv.). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.33 – 8.26 (m, 1H), 7.99 – 7.92 (m, 1H), 7.87 – 7.79 (m, 2H), 1.20 – 1.06 (m, 21H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 148.3, 135.4, 135.2, 133.1, 131.0, 125.5, 102.6, 99.3, 18.5, 11.1 ppm. **IR** (ATR): $\tilde{\nu}$ = 2948, 2867, 2360, 2340, 2124, 1542, 1336, 1159, 803, 575 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{17}H_{26}NO_4SSi^+$ $[M+H]^+$: 368.1346; found: 368.1342.

Triisopropyl((methylsulfonyl)ethynyl)silane (3h):



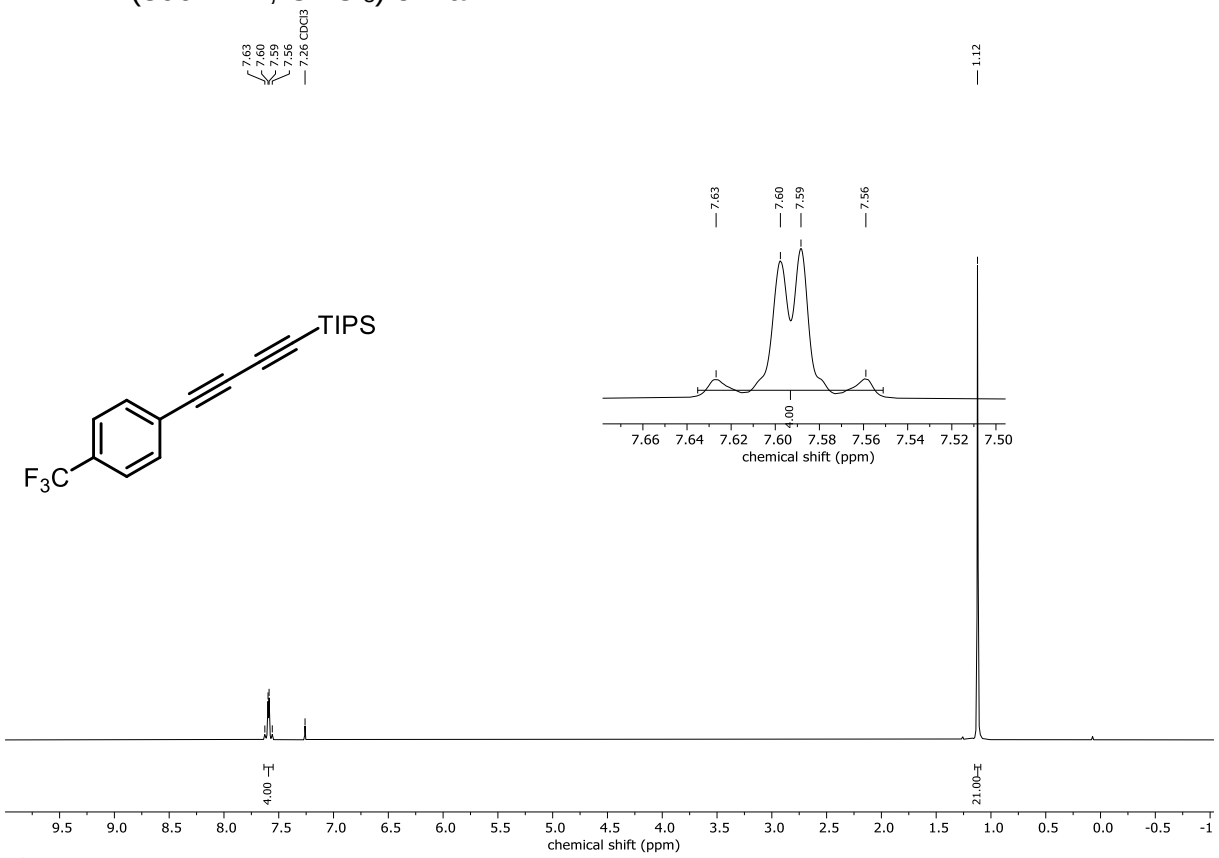
Following GP B, **3h** (30.5 mg, 0.117 mmol, 59%) was obtained as an orange solid from sodium methylsulfinate (24.5 mg, 0.24 mmol, 1.2 equiv.). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 3.21 (s, 3H), 1.20 – 1.10 (m, 21H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 99.8, 98.4, 77.5, 76.8, 47.0, 18.5, 11.0 ppm. **IR** (ATR): $\tilde{\nu}$ = 2945, 2867, 2125, 1463, 1331, 1151, 961, 882, 791, 748 cm^{-1}. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{28}N_2O_4SSi^+$ $[M+NH_4]^+$: 278.1605; found: 278.1605.

Alternative synthesis of 1,2,3-Trimethoxy-6-tosyl-5,6-dihydro-4*H*-dibenzo[*de*,*g*]quinoline (26):

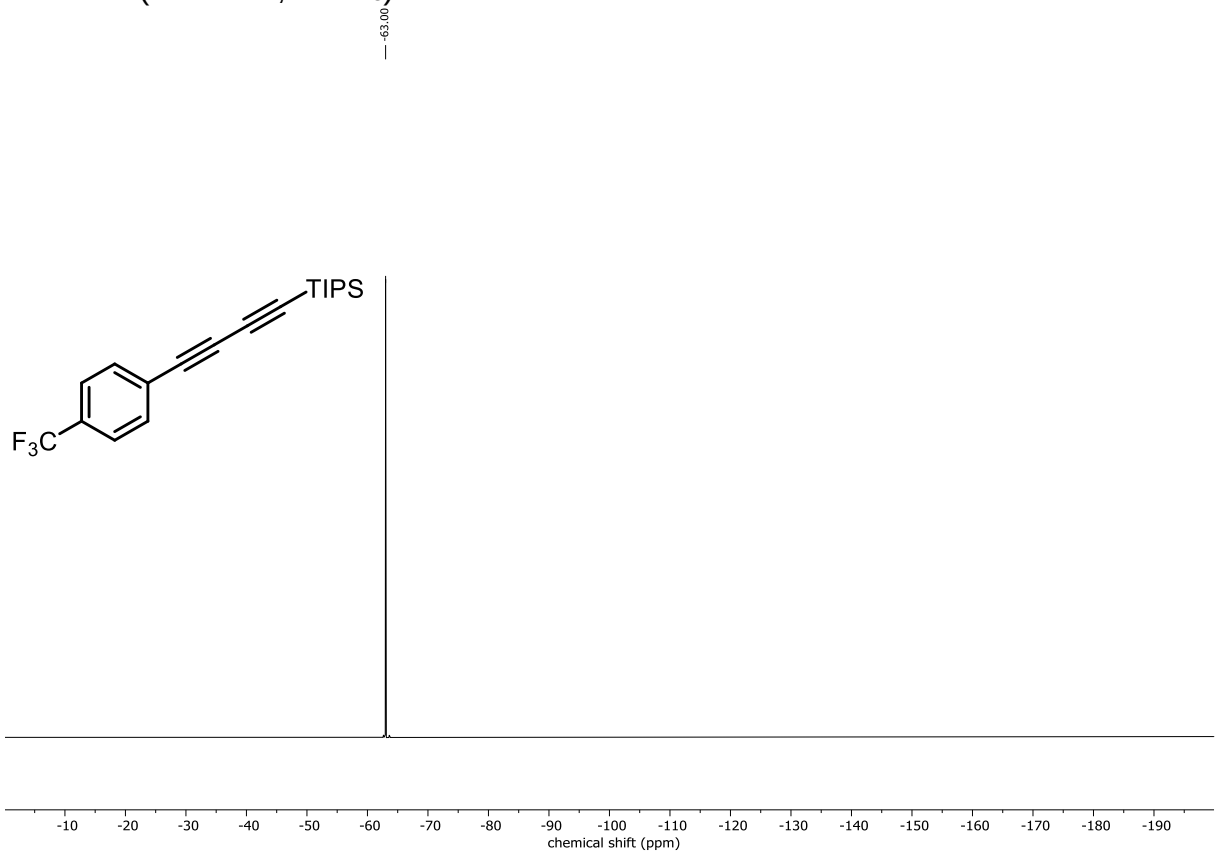
A flame dried Schlenk flask was charged with salt **25** (20 mg, 25 µmol, 1.0 equiv.) then dry THF (1 mL) was added. To the solution KH (3.0 mg, 75 µmol, 3.0 equiv.) and catalytic amounts of KO*t*Bu (few crystals) were added and the reaction mixture was stirred at roomtemperature for 2 h. The reaction was quenched with MeOH (0.5 mL) and water (3 mL) and the aqueous phase was extracted with EtOAc (2 × 5 mL). The combined organic phases were washed with brine (5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification by Isolera flash chromatography (hexane/EtOAc, 5% → 40%) gave product **26** (2.0 mg, 4.3 µmol, 17%) as a brownish oil.

2 NMR Spectra

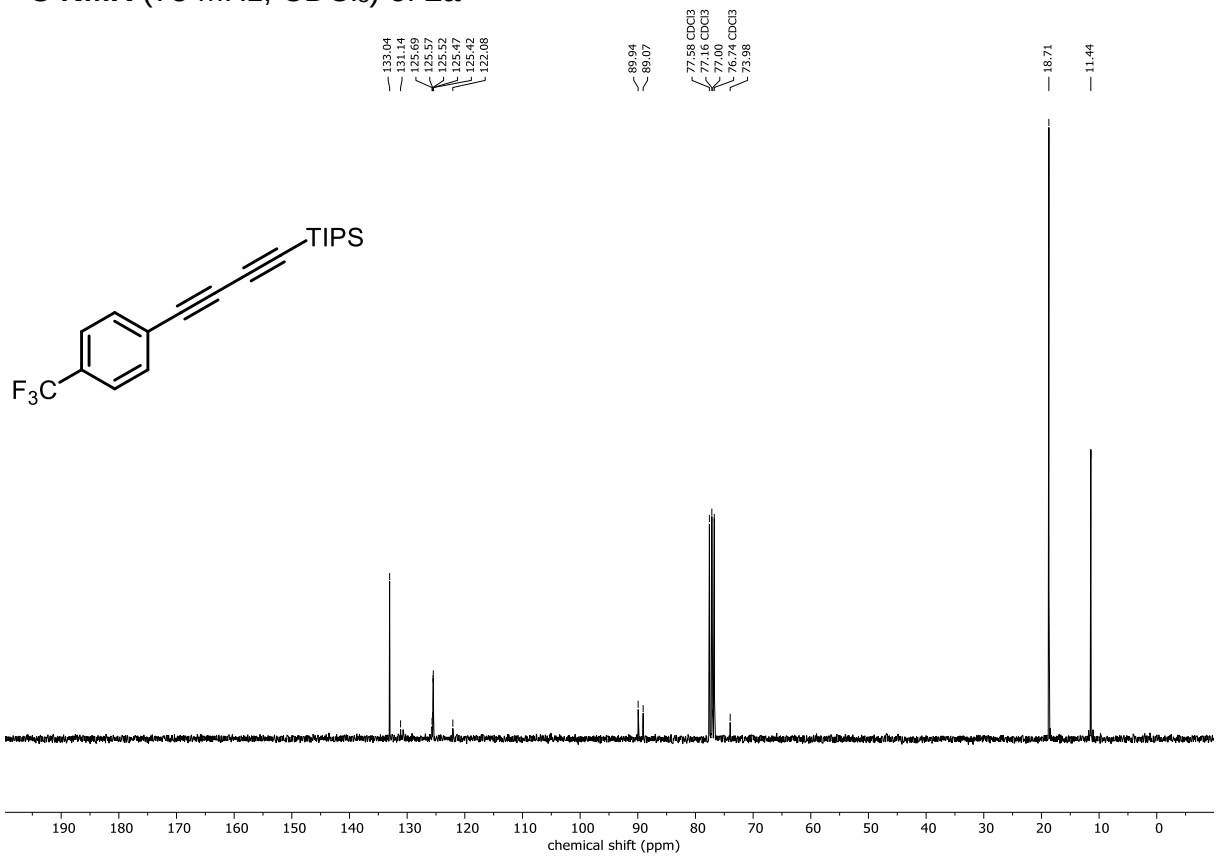
^{1}H NMR (300 MHz, $CDCl_3$) of **2a**



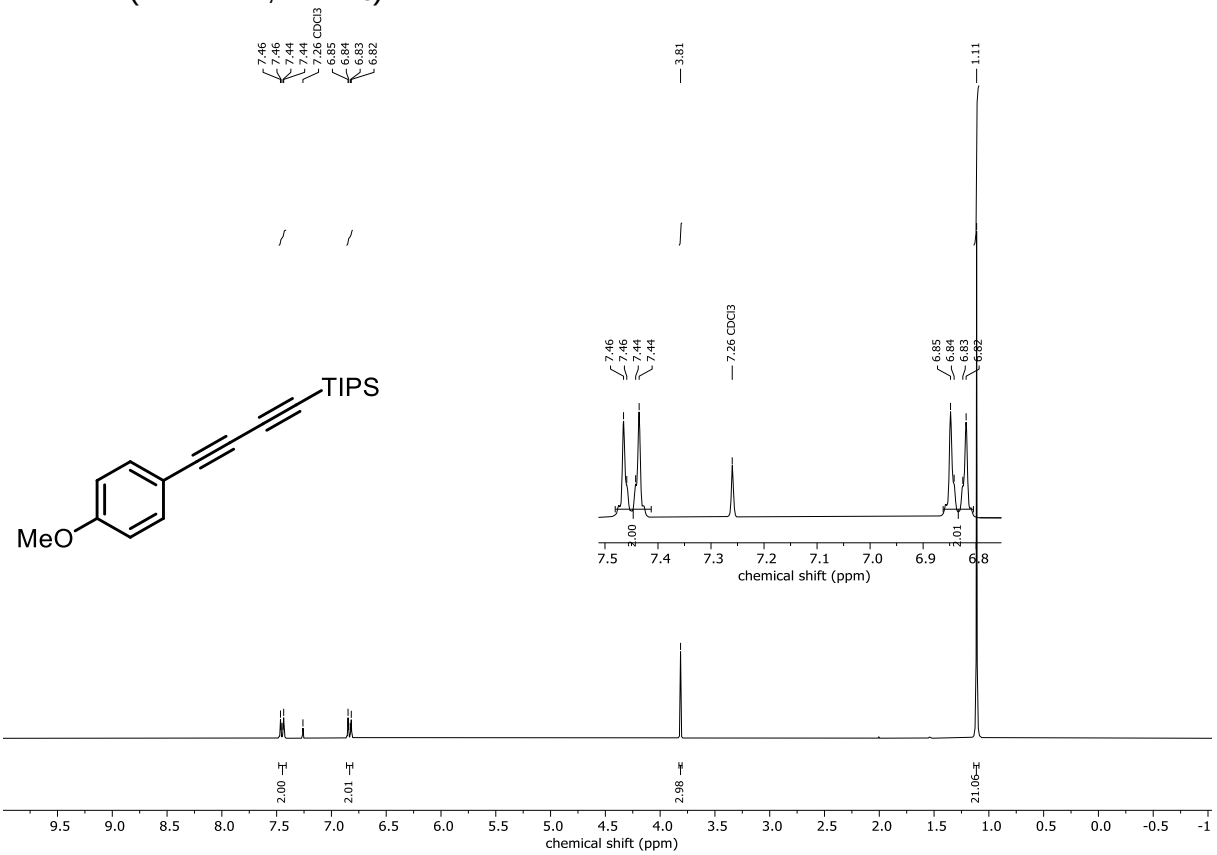
^{19}F NMR (282 MHz, $CDCl_3$) of **2a**



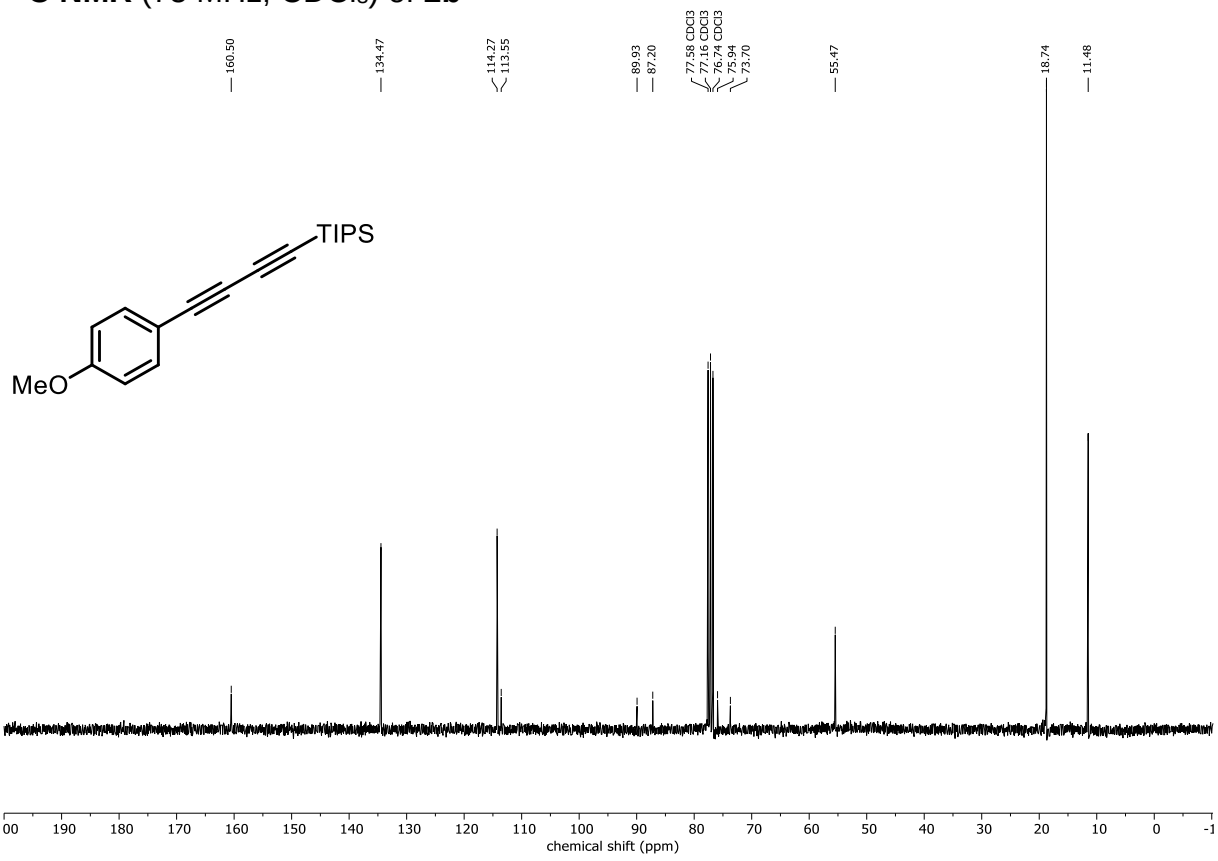
^{13}C NMR (75 MHz, $CDCl_3$) of **2a**



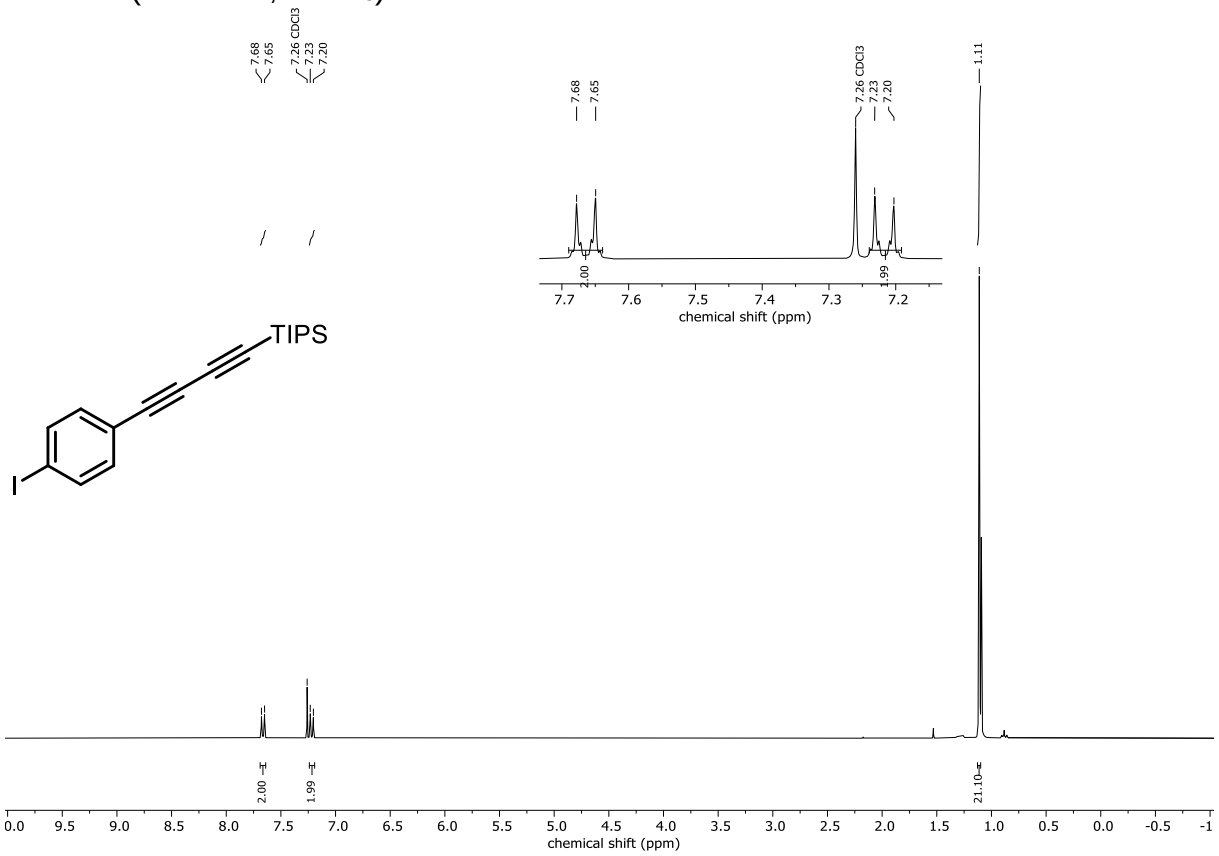
^{1}H NMR (300 MHz, $CDCl_3$) of **2b**



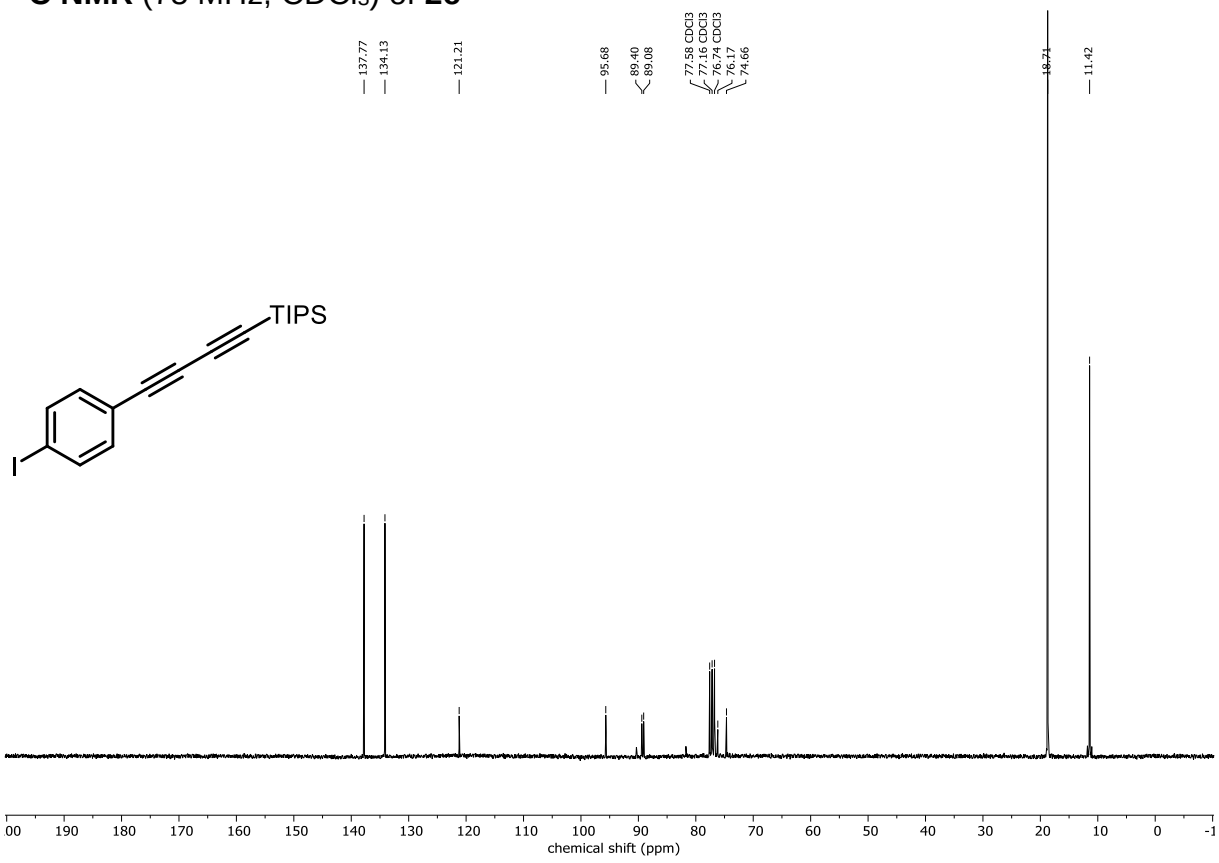
^{13}C NMR (75 MHz, $CDCl_3$) of **2b**



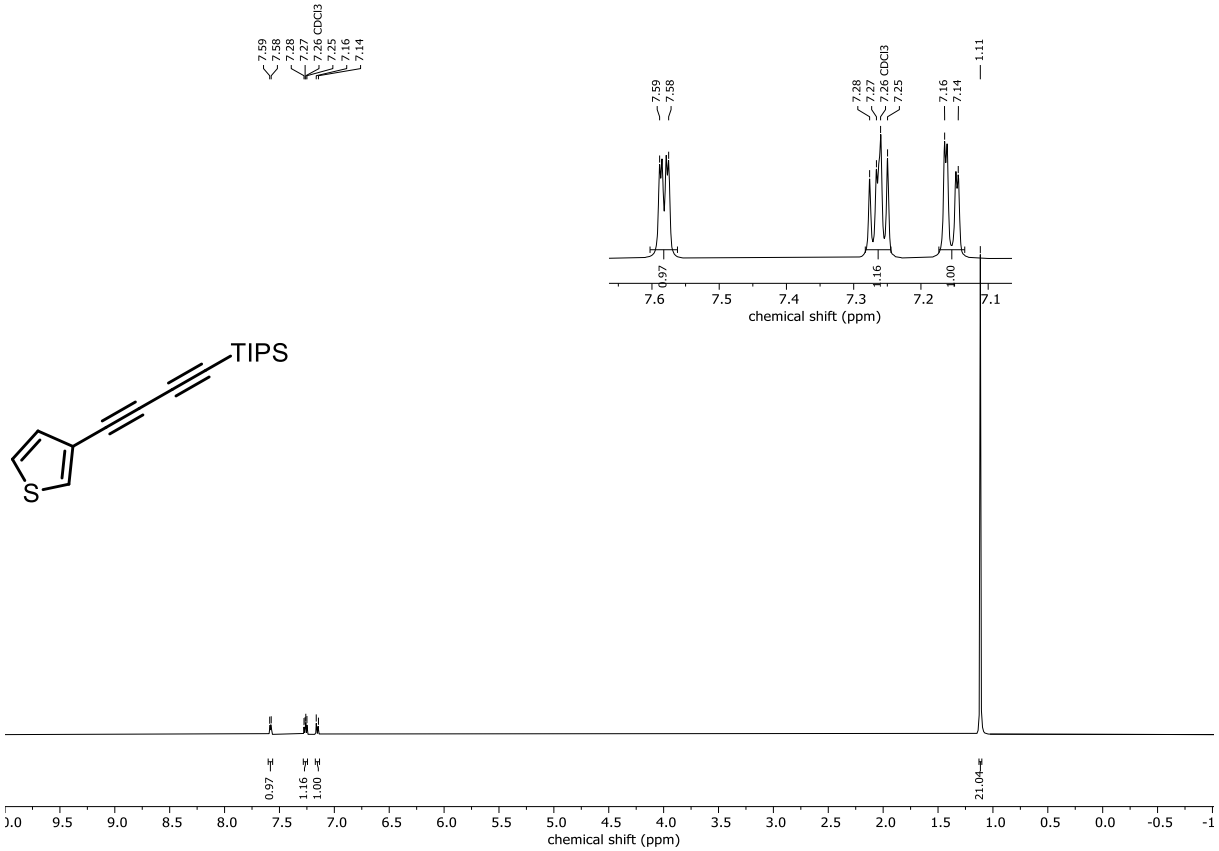
^{1}H NMR (300 MHz, $CDCl_3$) of **2c**



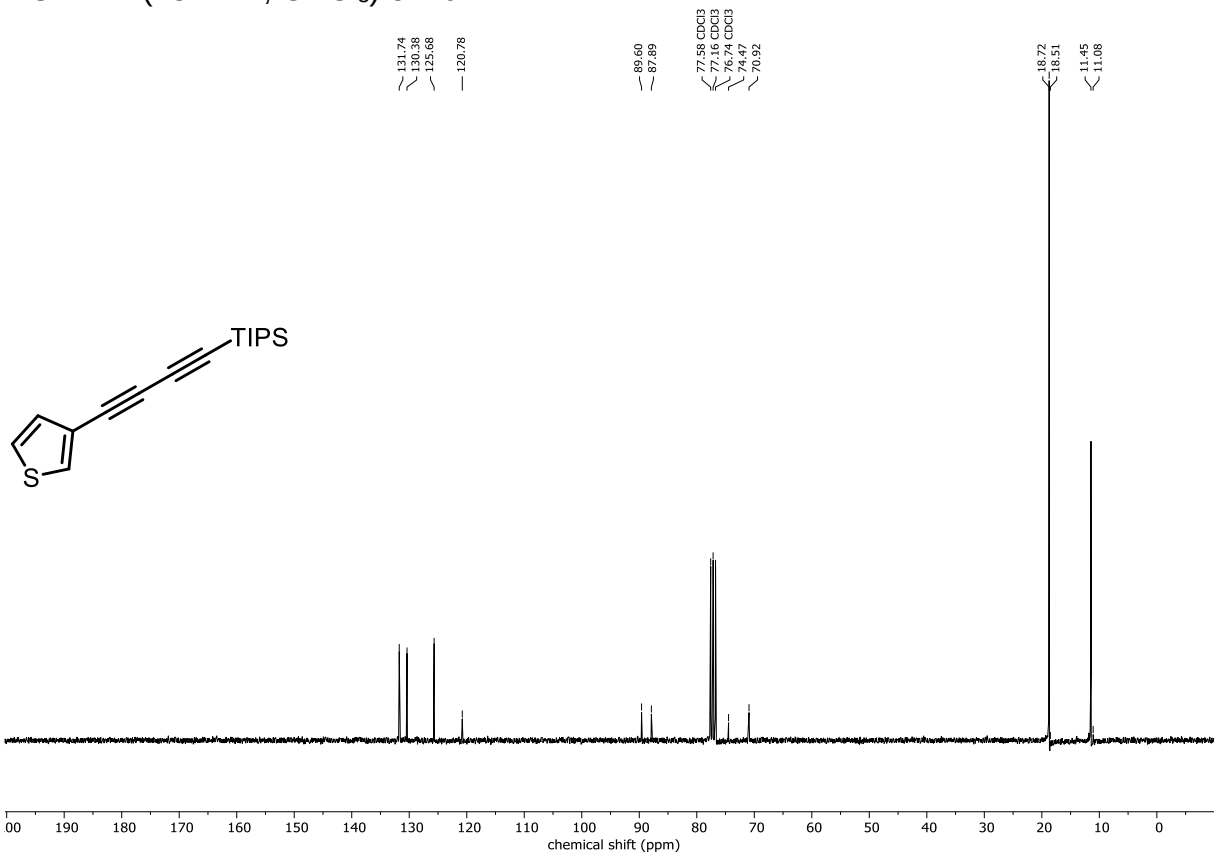
^{13}C NMR (75 MHz, $CDCl_3$) of **2c**



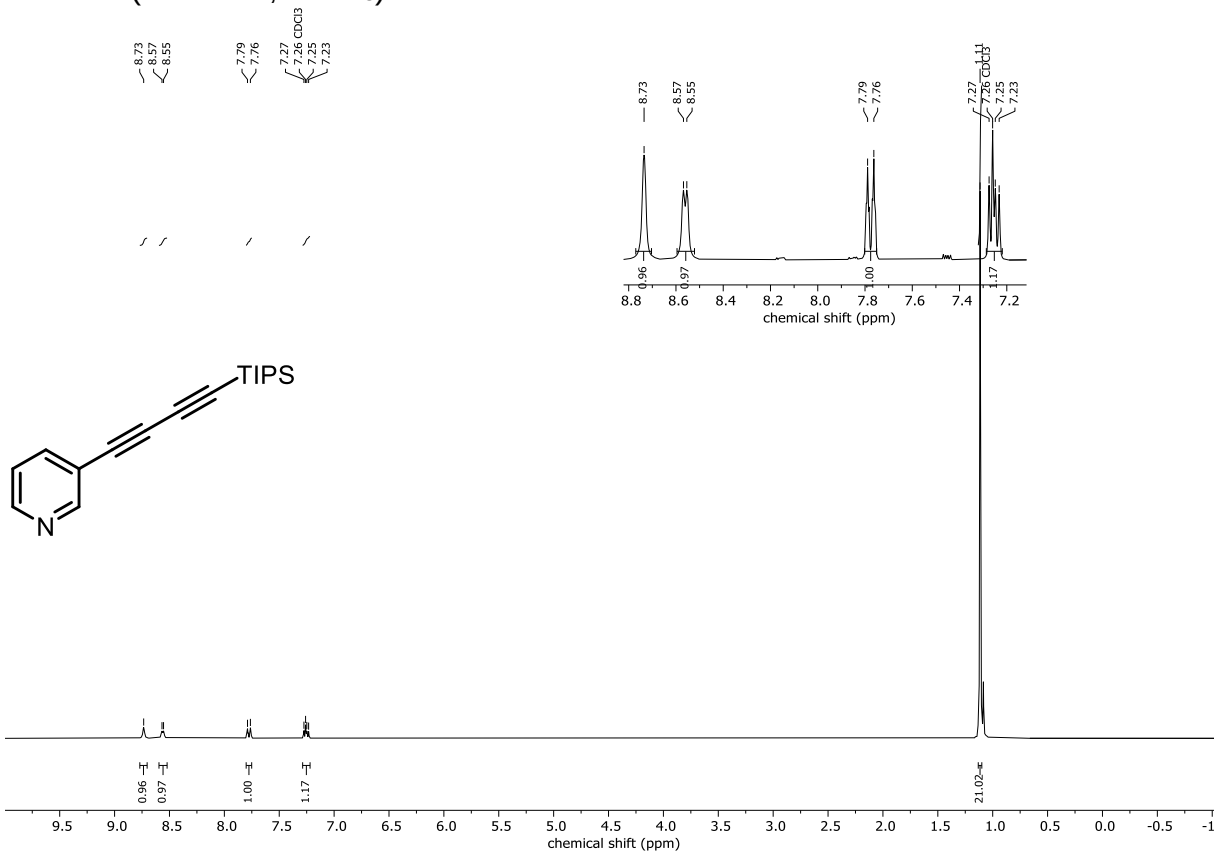
^{1}H NMR (300 MHz, $CDCl_3$) of **2d**



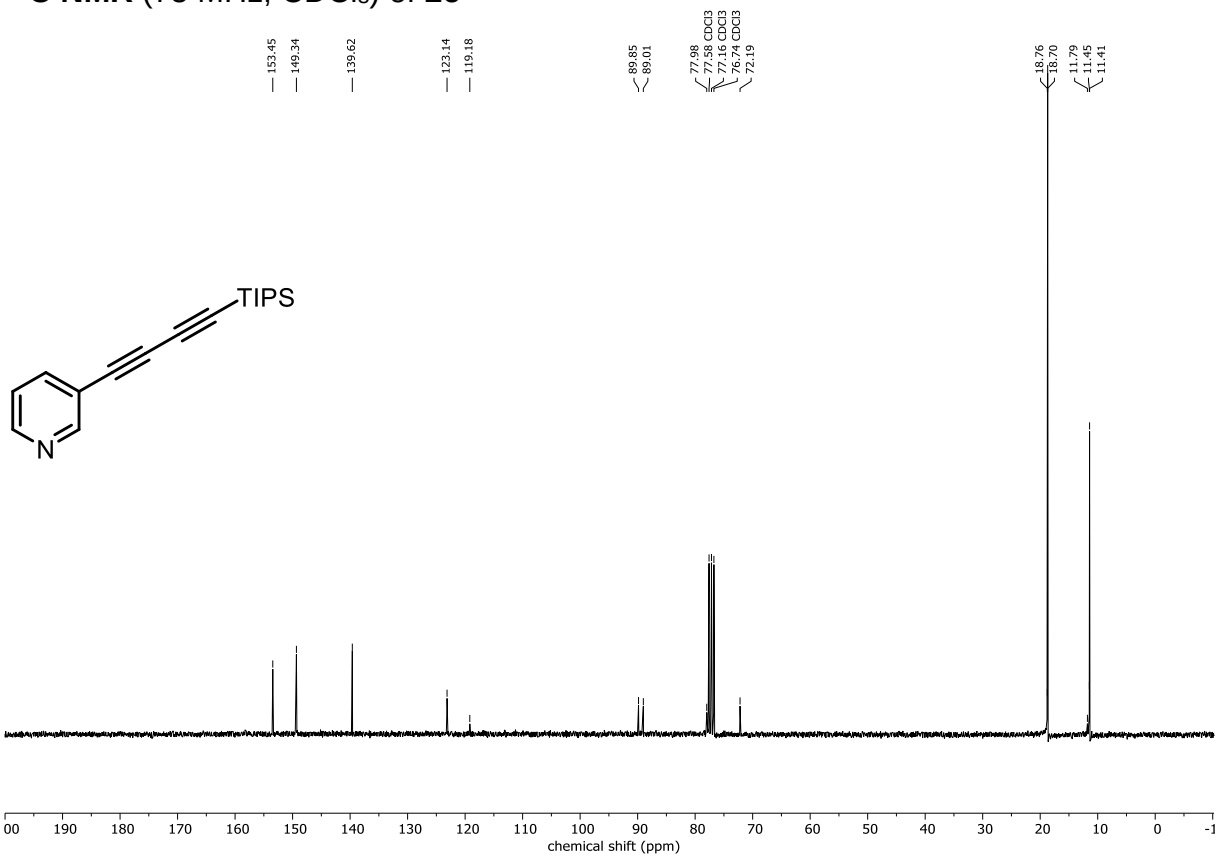
^{13}C NMR (75 MHz, $CDCl_3$) of **2d**



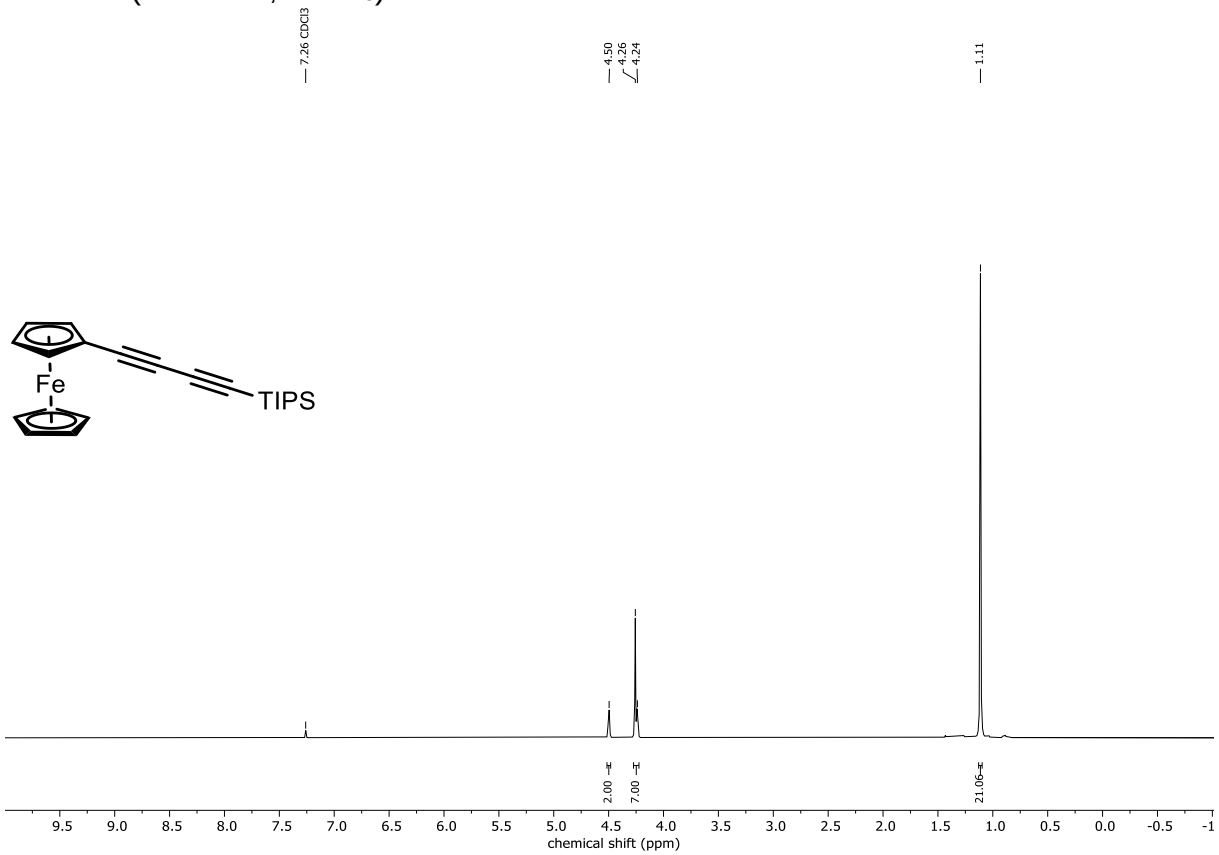
^{1}H NMR (300 MHz, $CDCl_3$) of **2e**



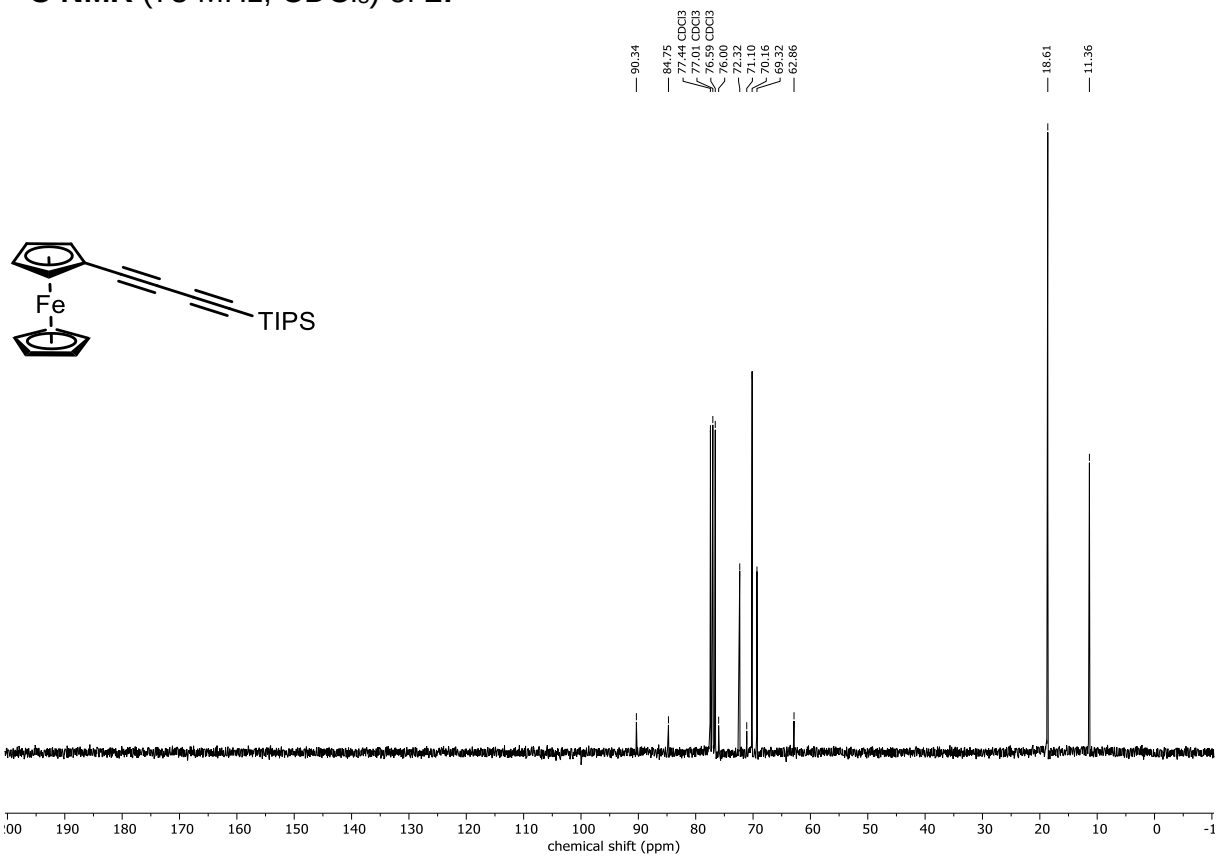
^{13}C NMR (75 MHz, $CDCl_3$) of **2e**



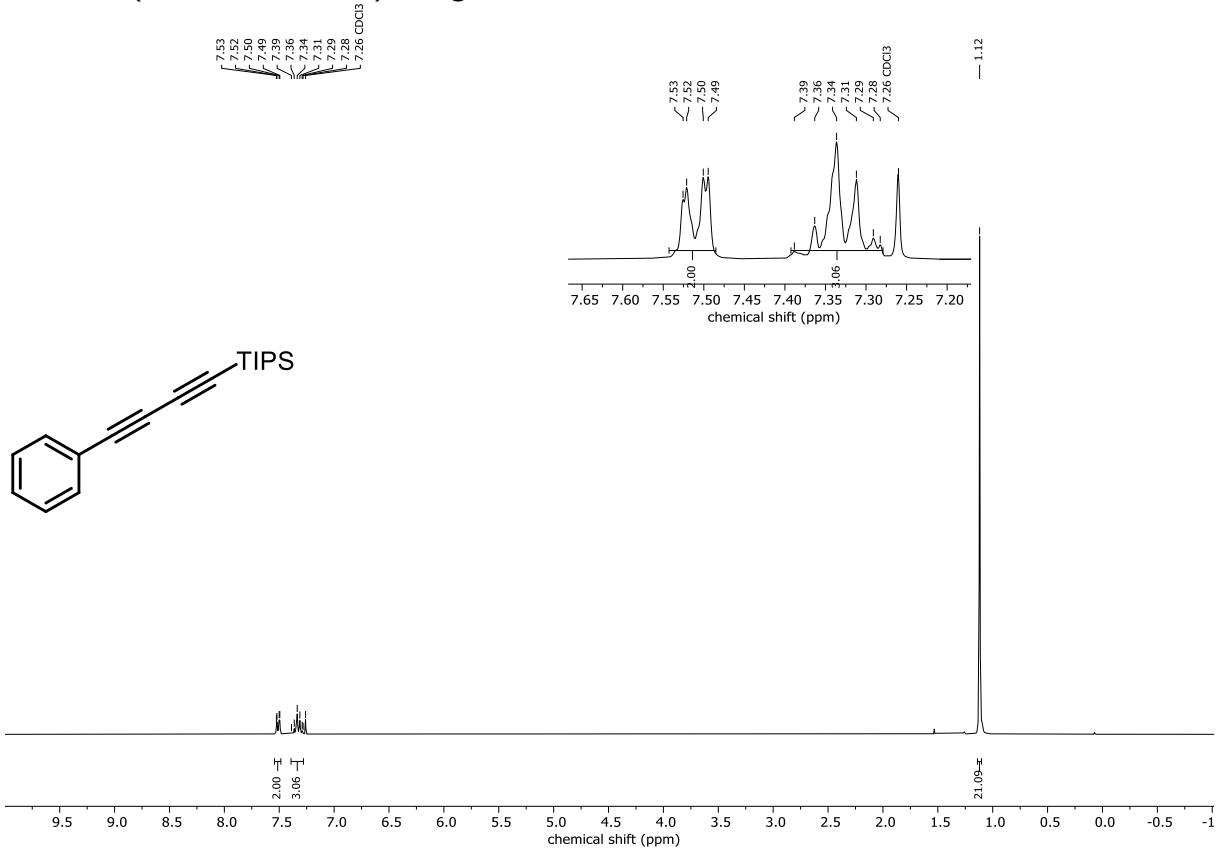
^{1}H NMR (300 MHz, $CDCl_3$) of **2f**



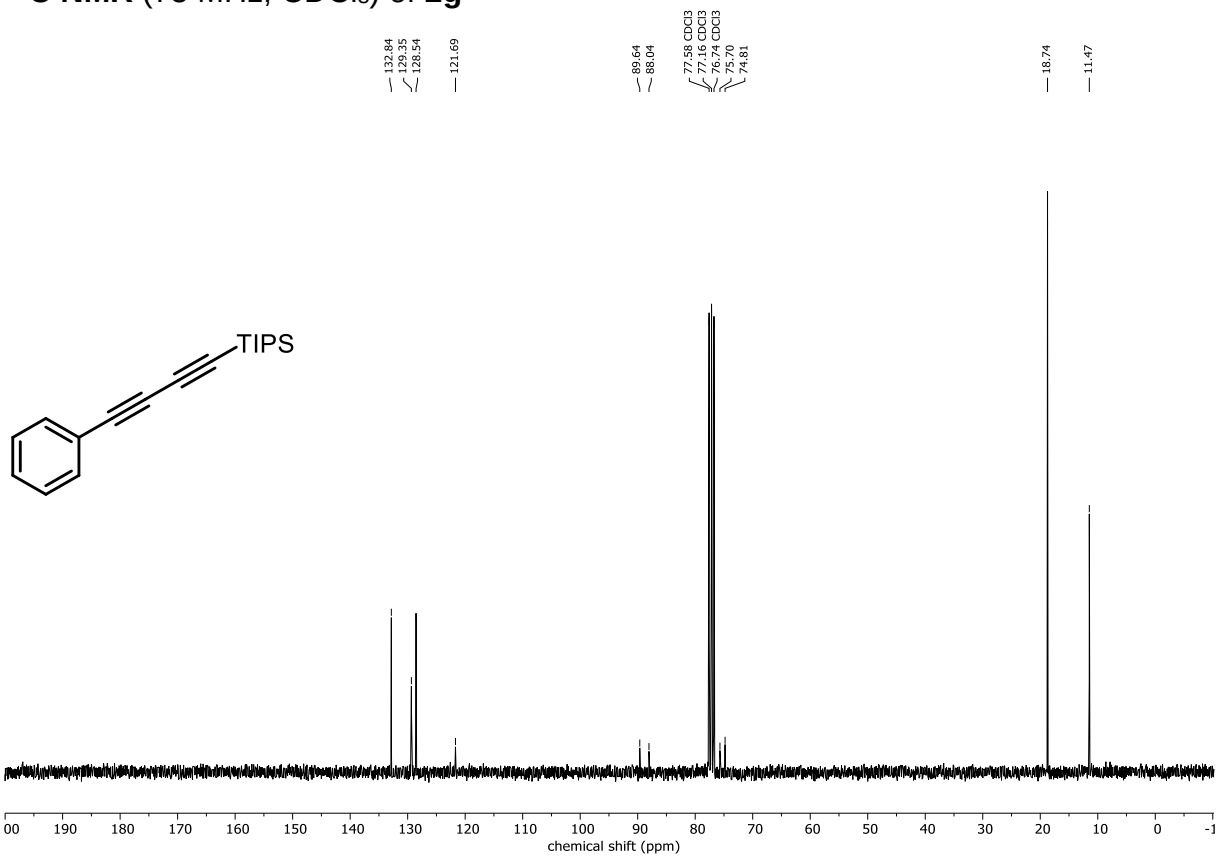
^{13}C NMR (75 MHz, $CDCl_3$) of **2f**



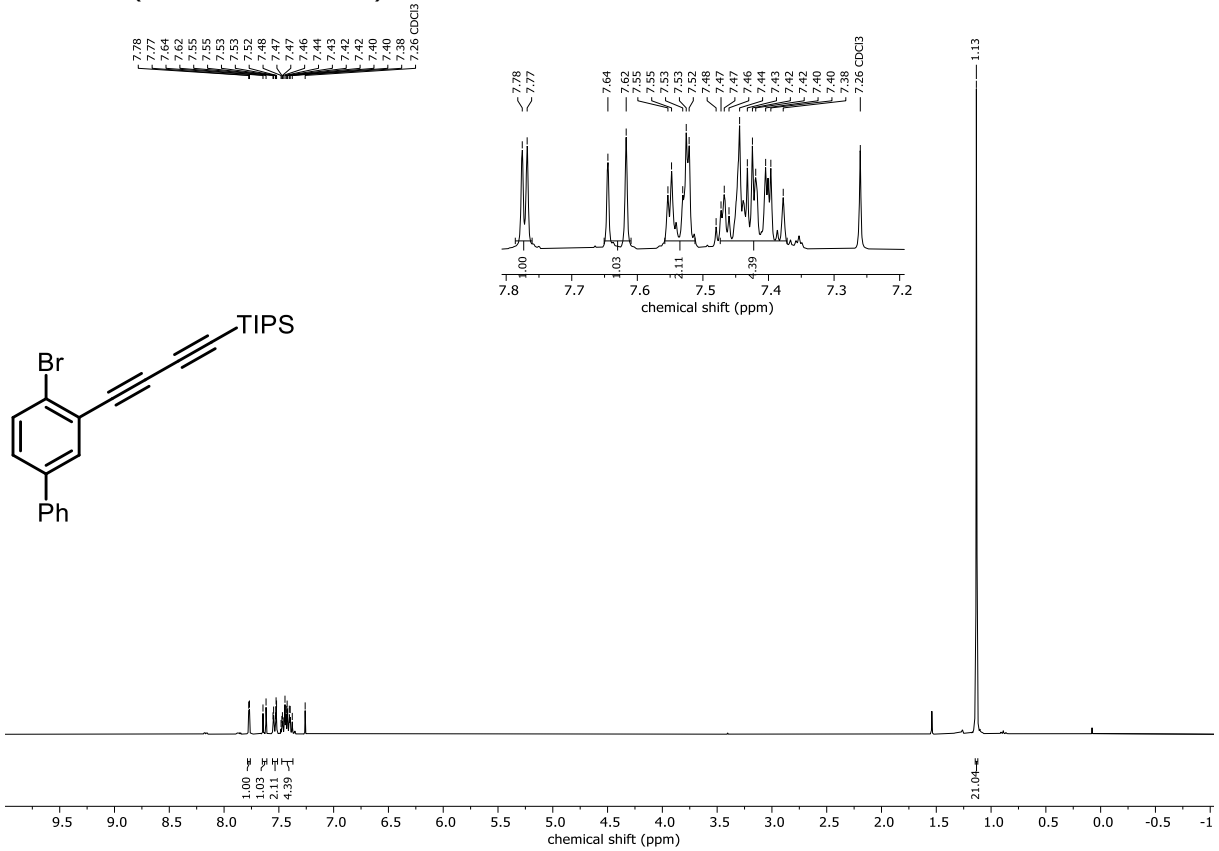
^{1}H NMR (300 MHz, $CDCl_3$) of **2g**



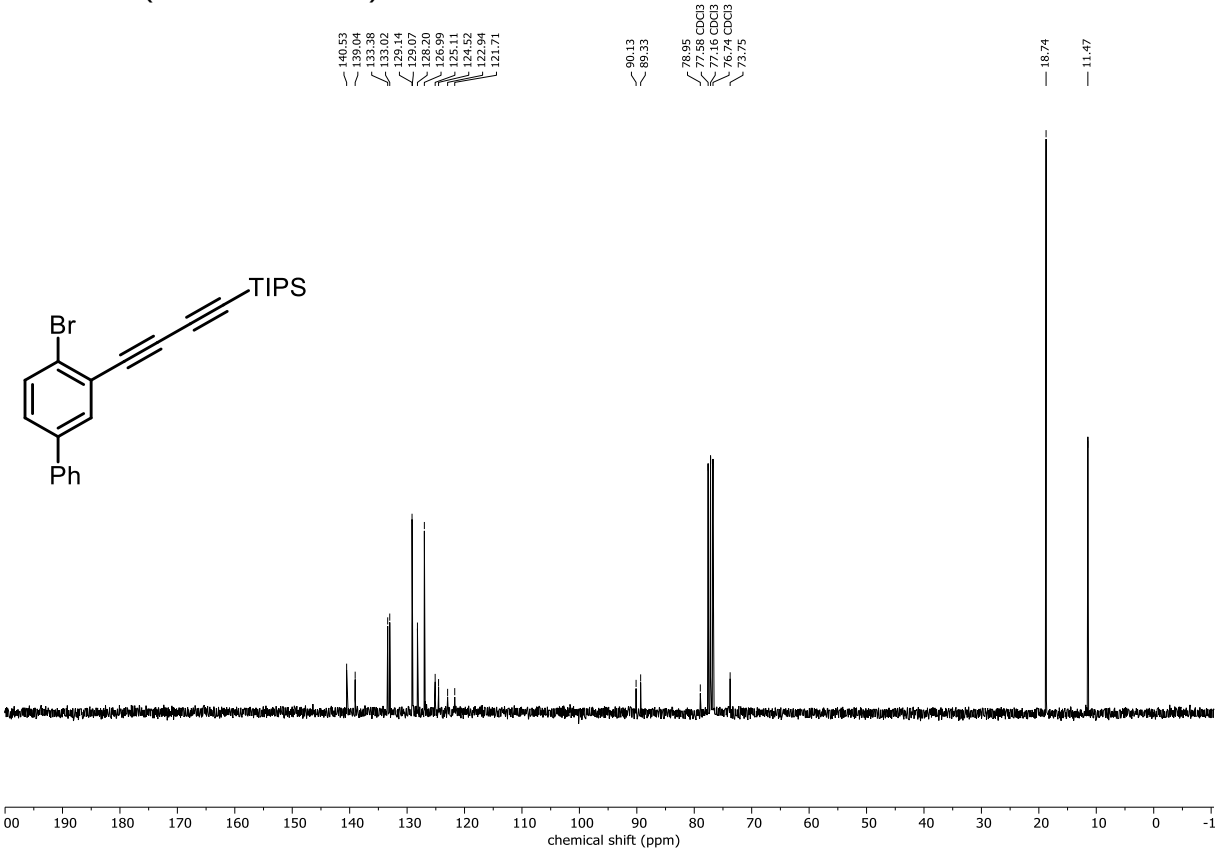
^{13}C NMR (75 MHz, $CDCl_3$) of **2g**



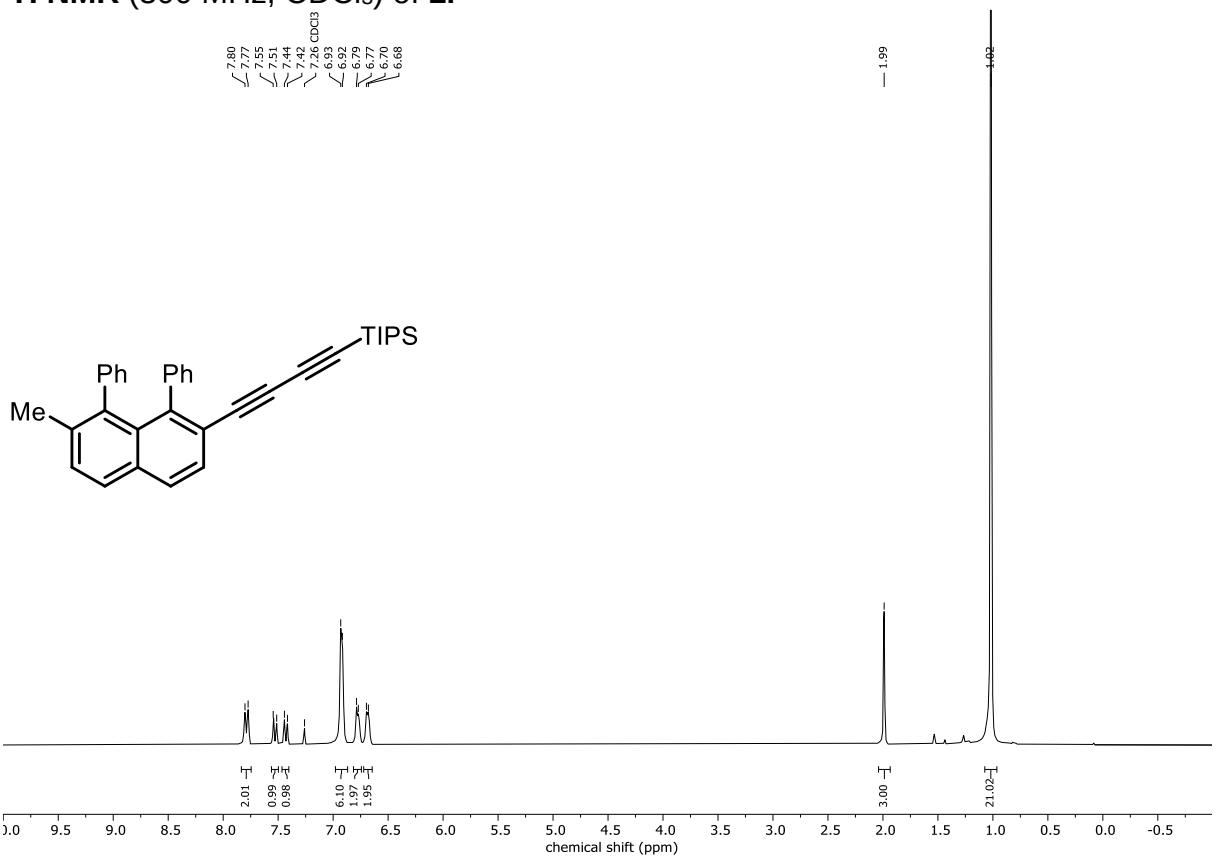
^{1}H NMR (300 MHz, $CDCl_3$) of **2h**



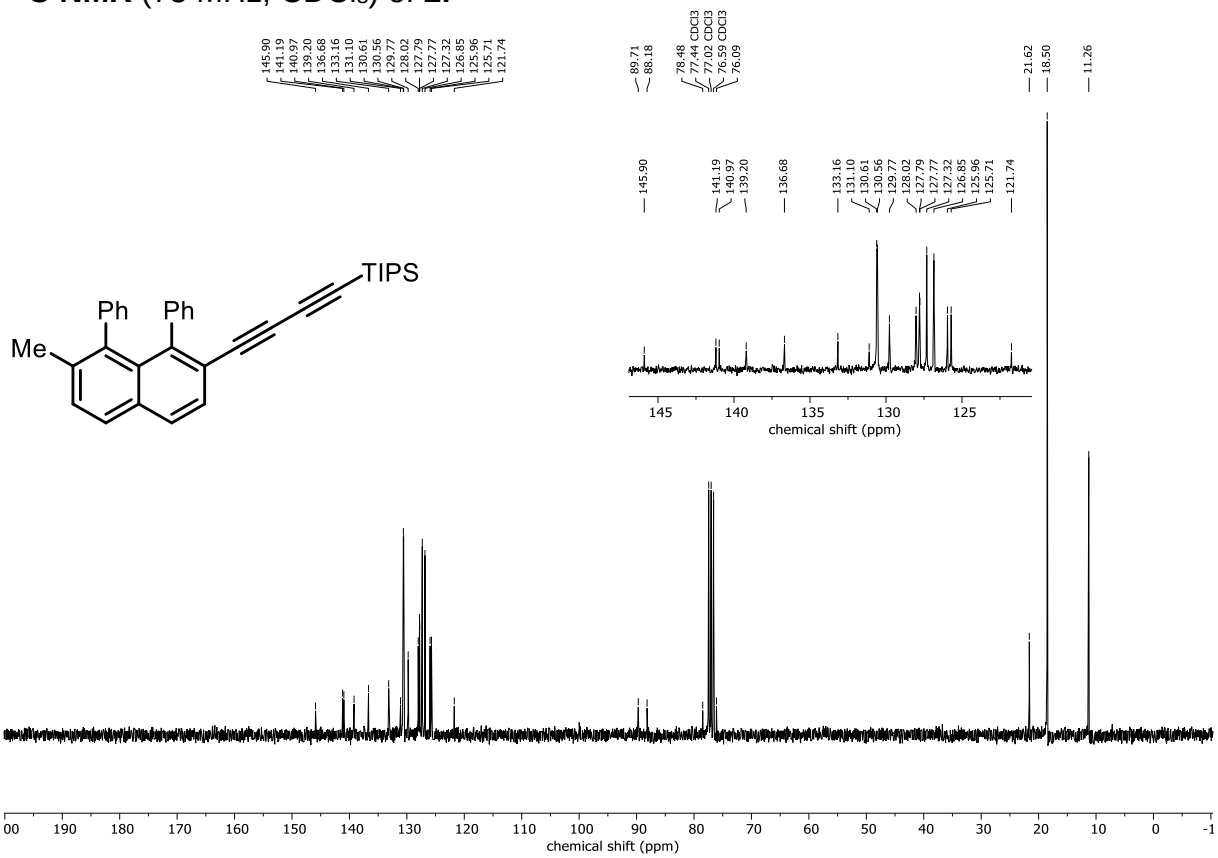
^{13}C NMR (75 MHz, $CDCl_3$) of **2h**



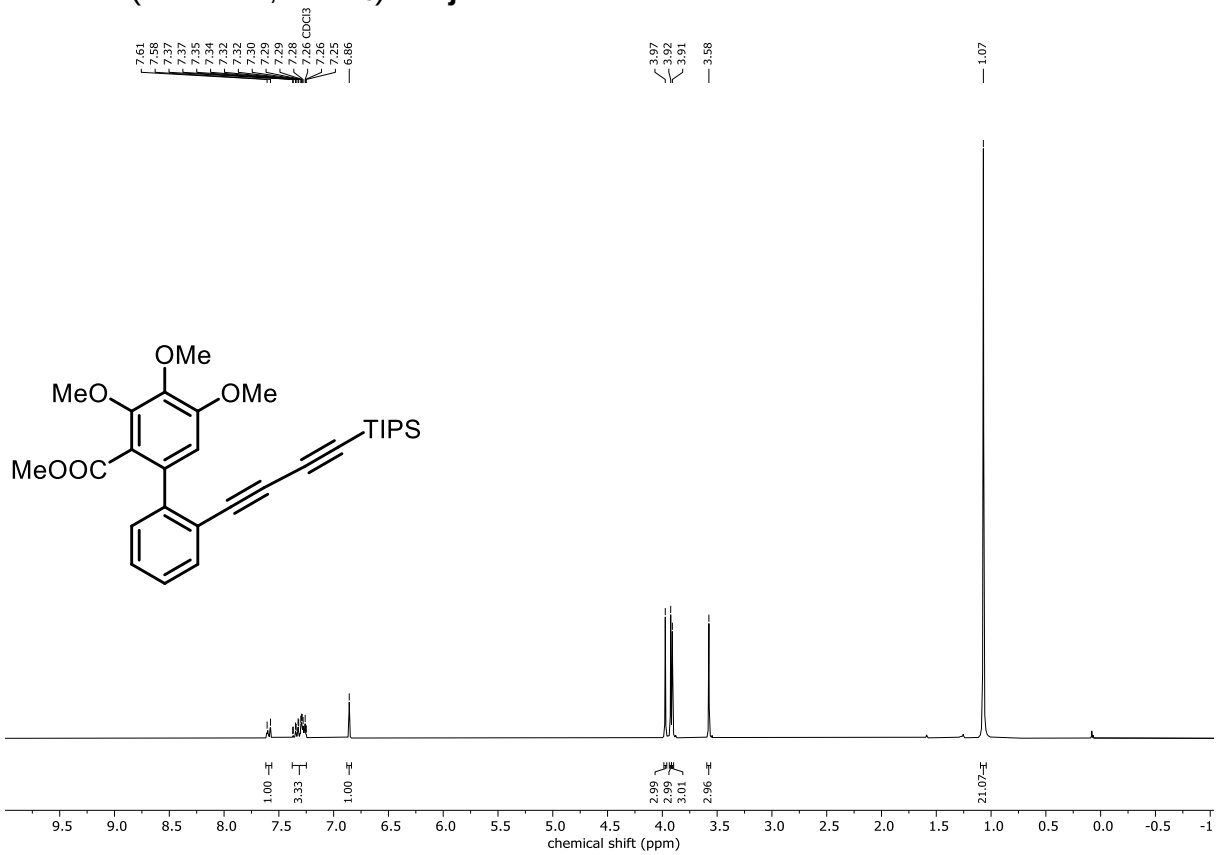
^{1}H NMR (300 MHz, $CDCl_3$) of **2i**



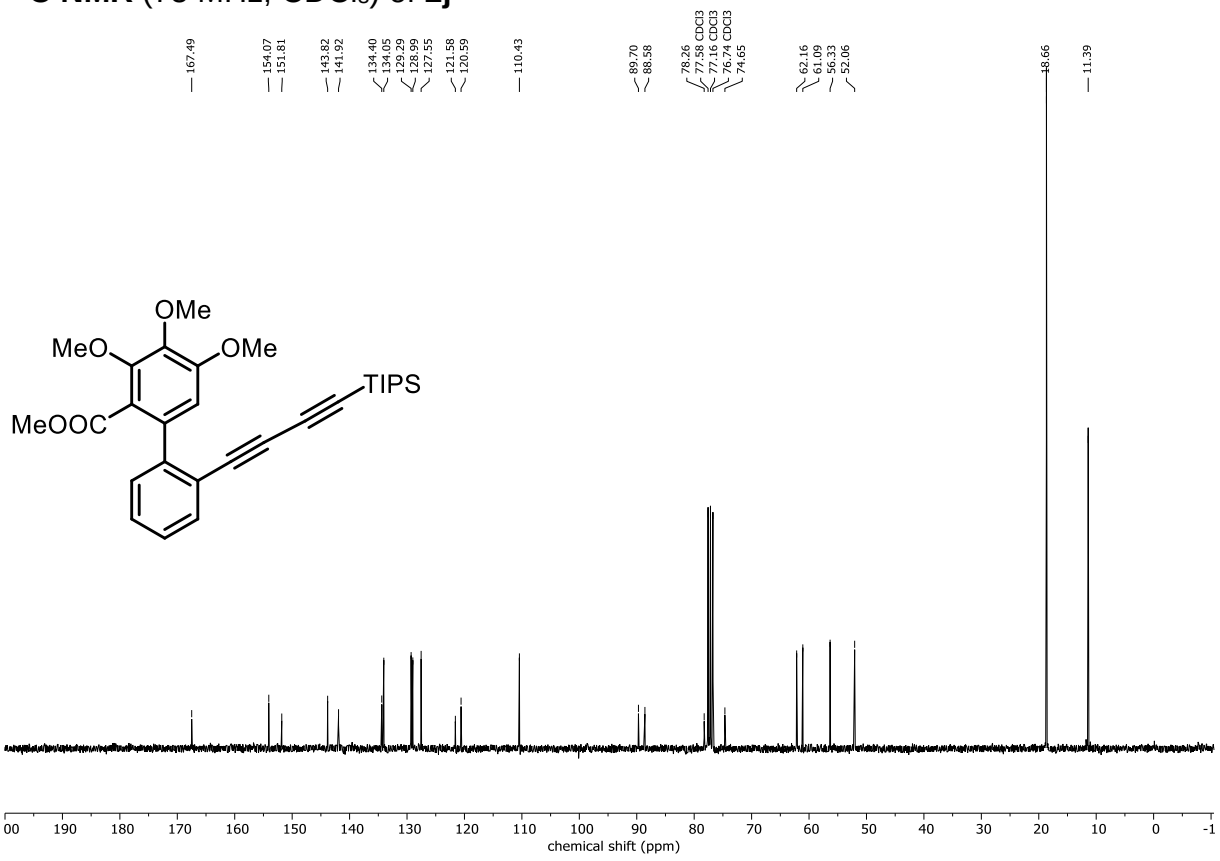
^{13}C NMR (75 MHz, $CDCl_3$) of **2i**



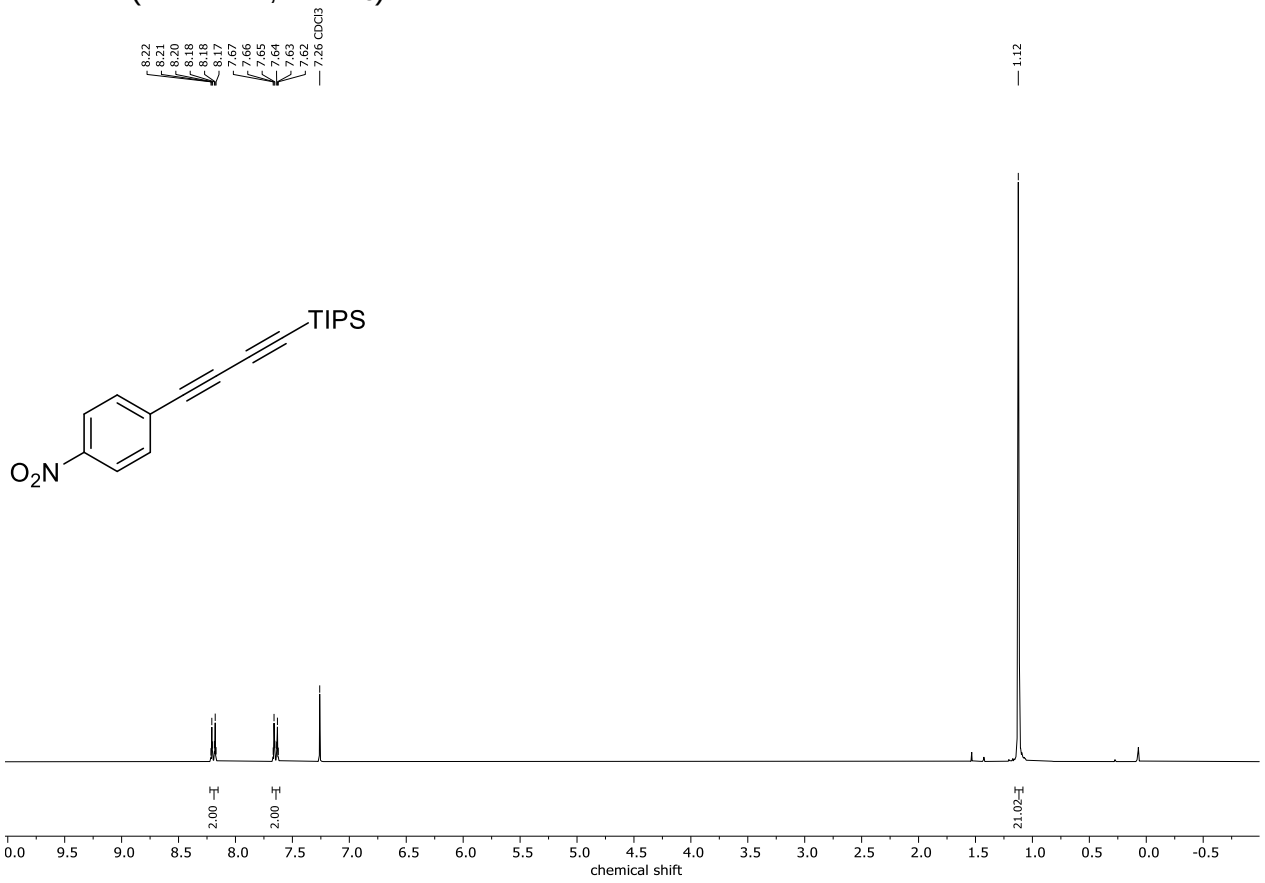
^{1}H NMR (300 MHz, $CDCl_3$) of **2j**



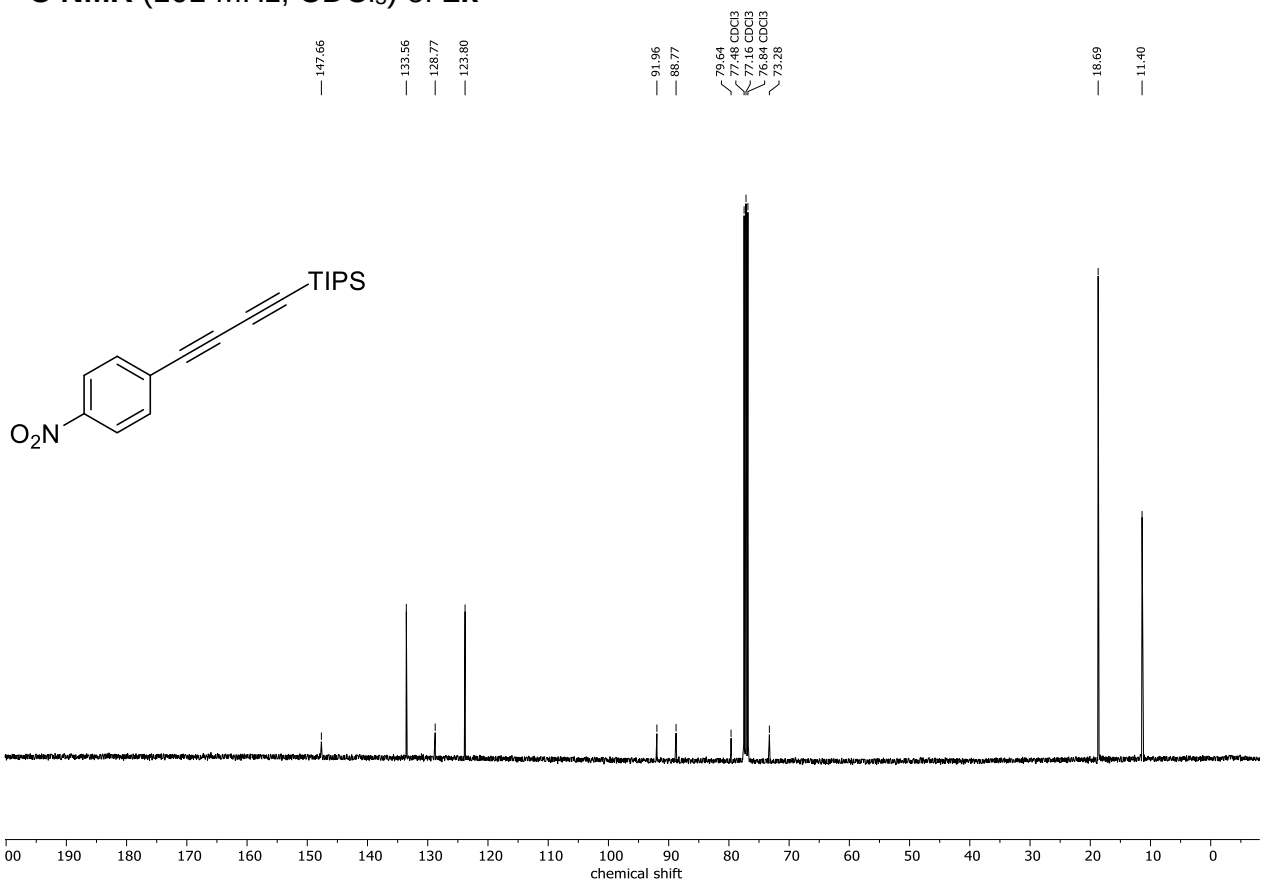
^{13}C NMR (75 MHz, $CDCl_3$) of **2j**



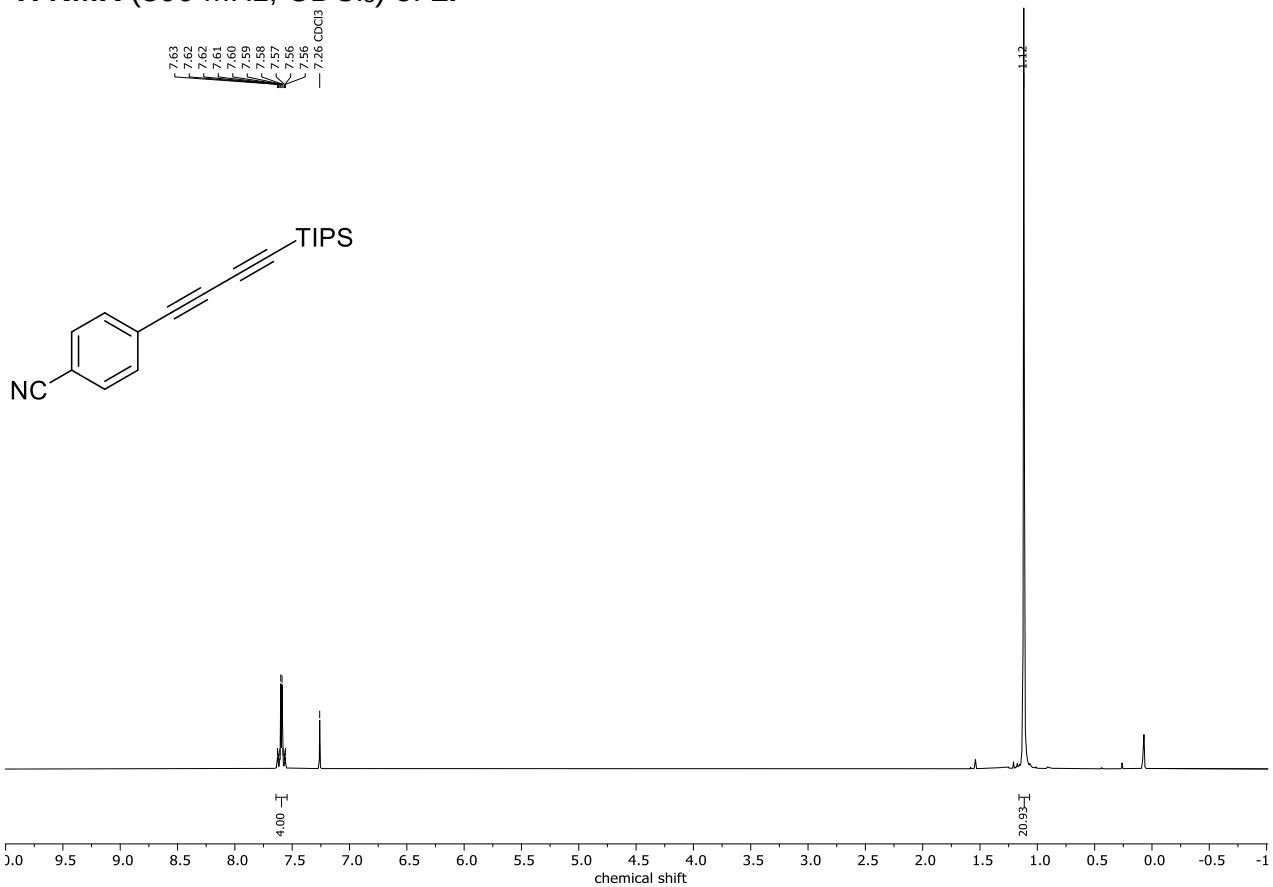
^{1}H NMR (300 MHz, $CDCl_3$) of **2k**



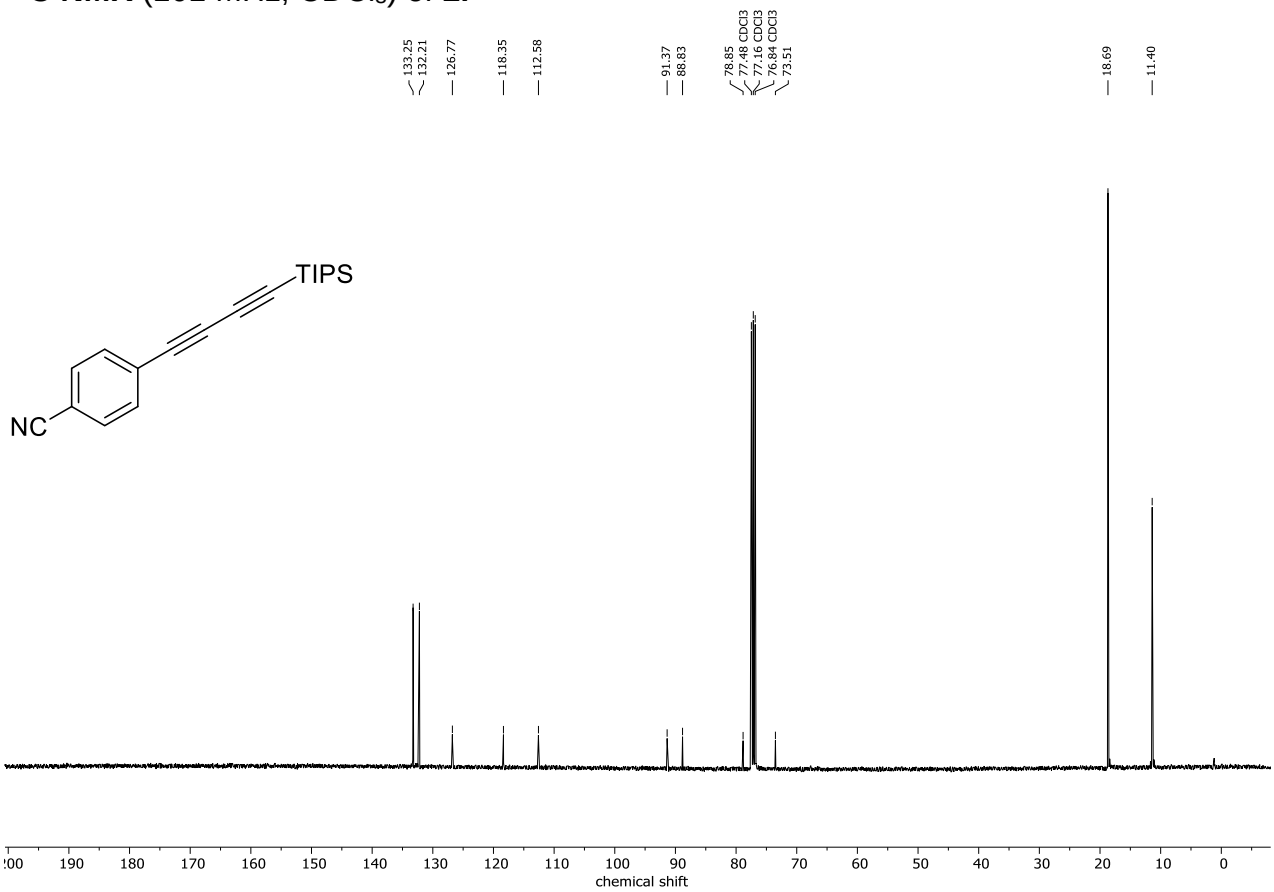
^{13}C NMR (101 MHz, $CDCl_3$) of **2k**



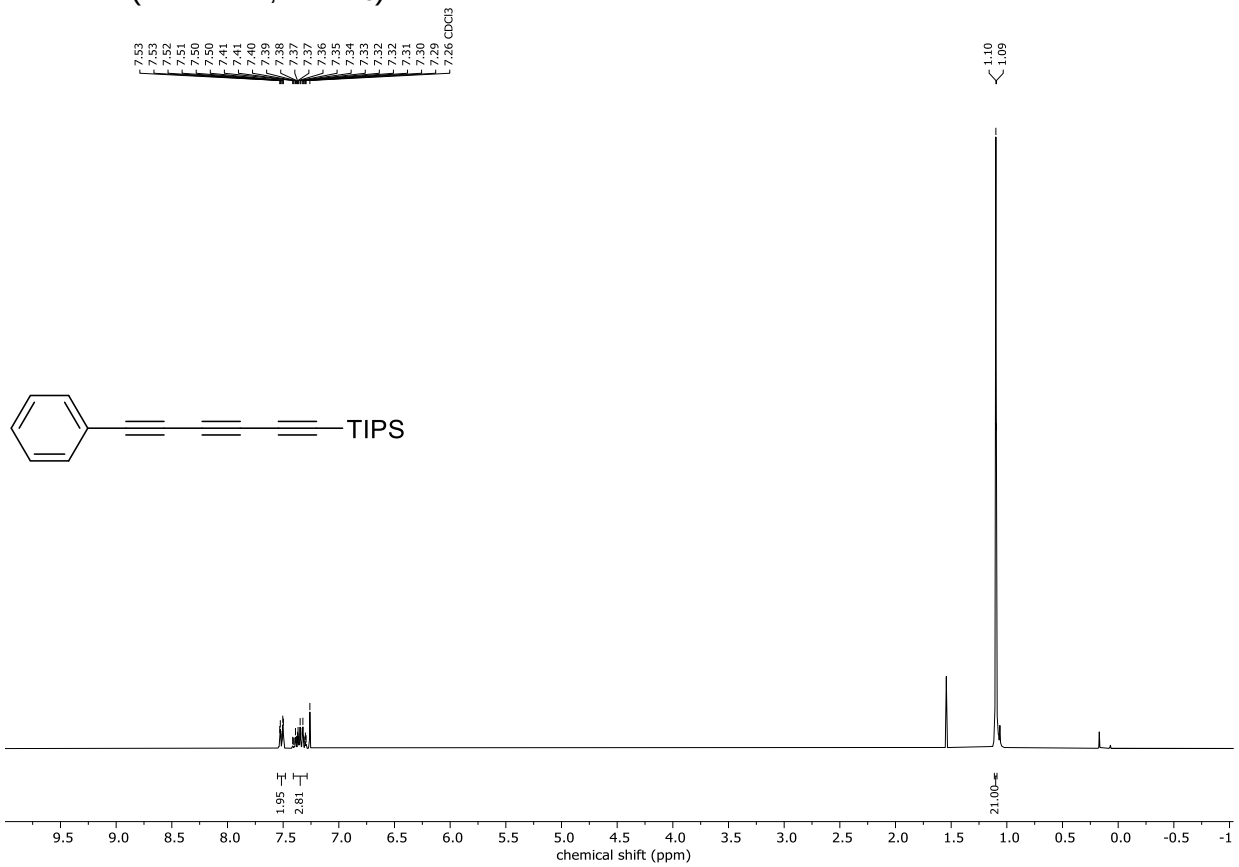
^{1}H NMR (300 MHz, $CDCl_3$) of **2l**



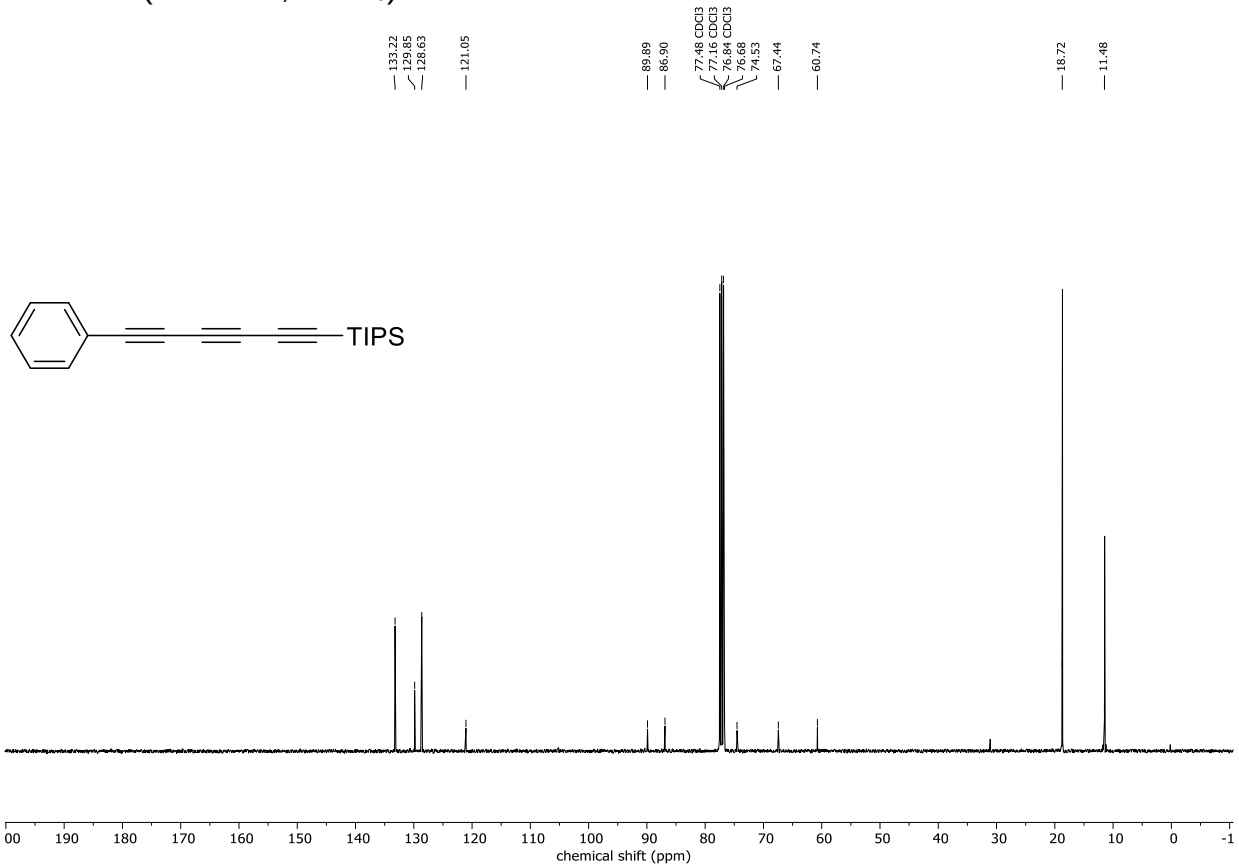
^{13}C NMR (101 MHz, $CDCl_3$) of **2l**



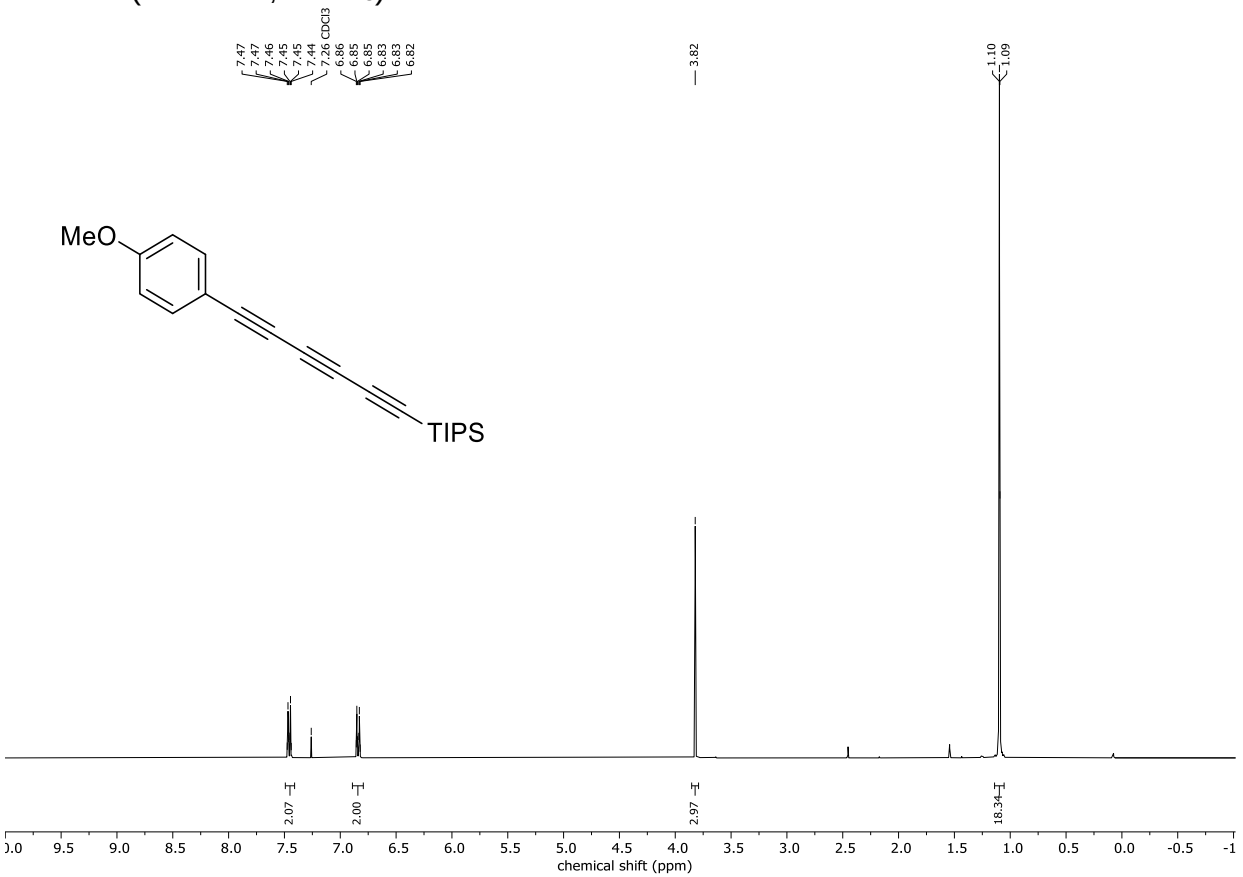
^{1}H NMR (300 MHz, $CDCl_3$) of **2m**



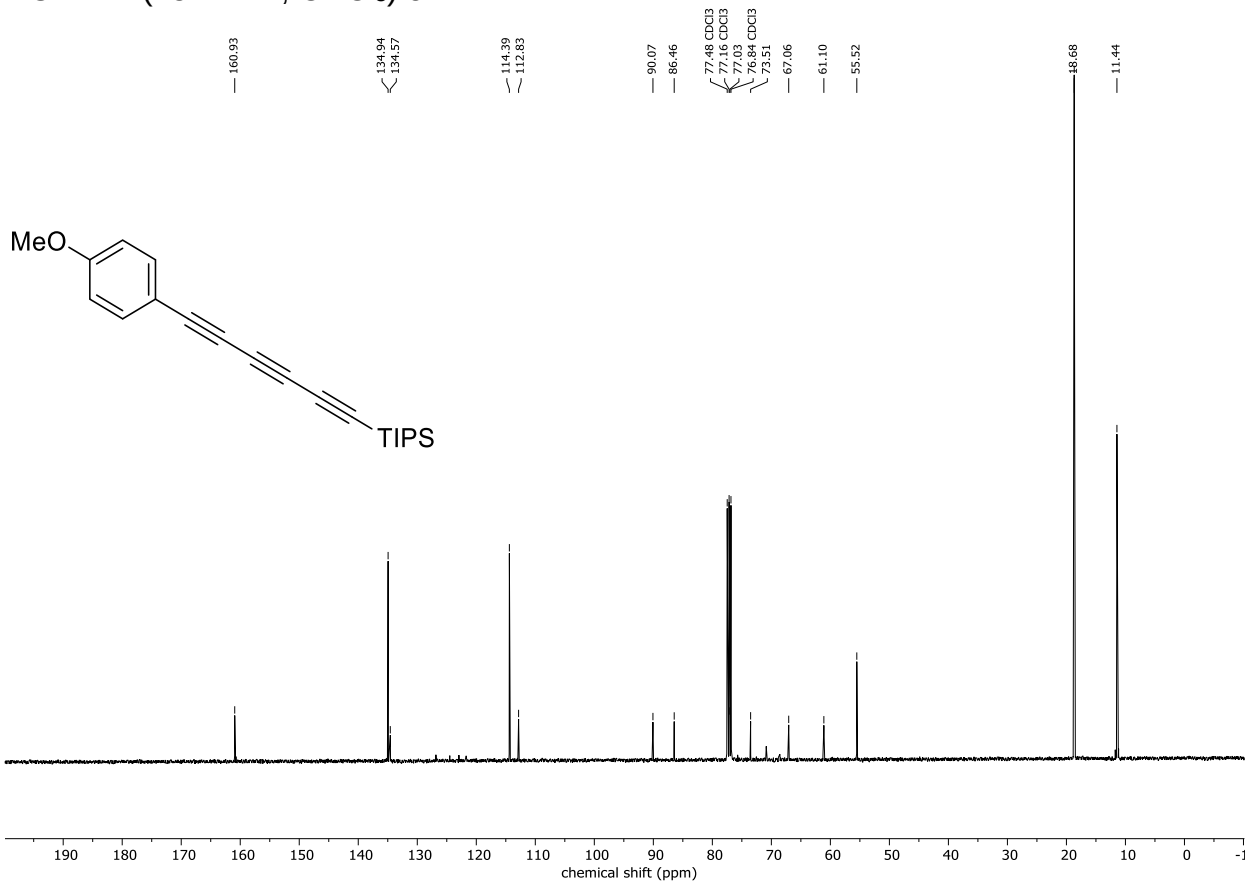
^{13}C NMR (101 MHz, $CDCl_3$) of **2m**



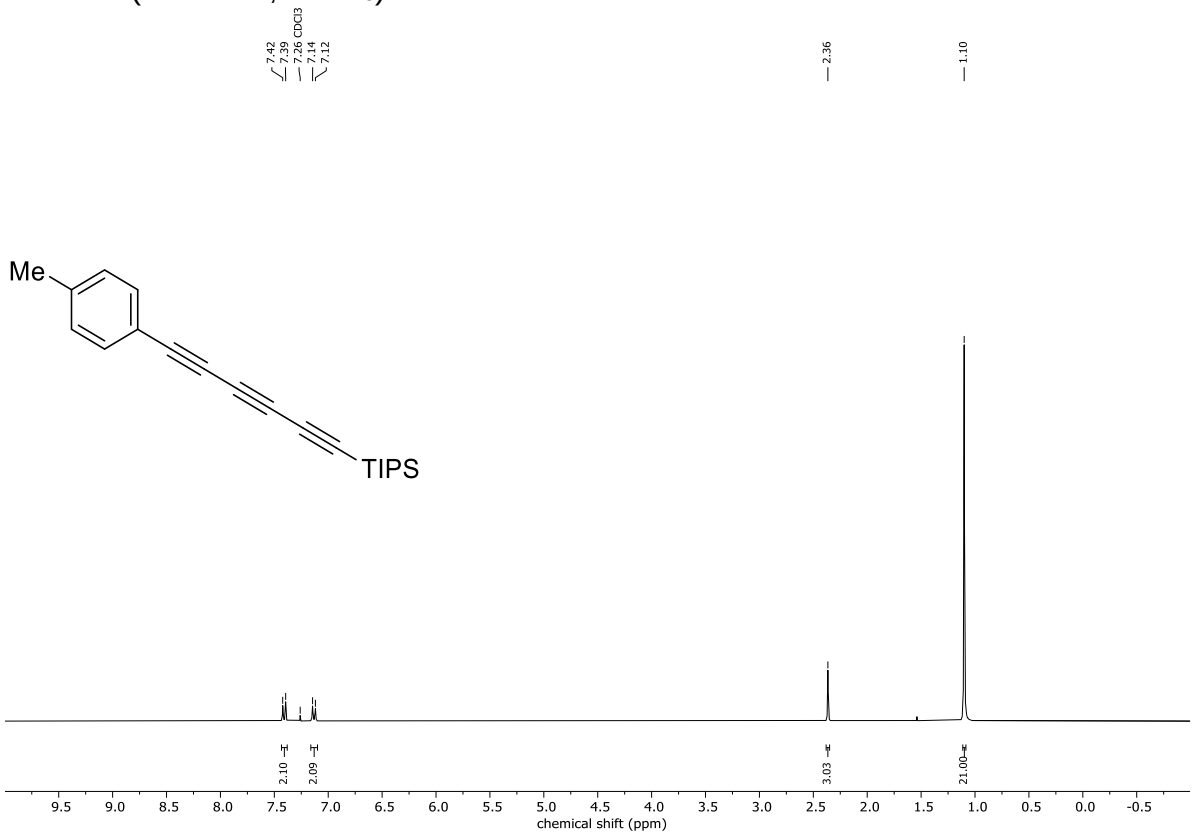
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



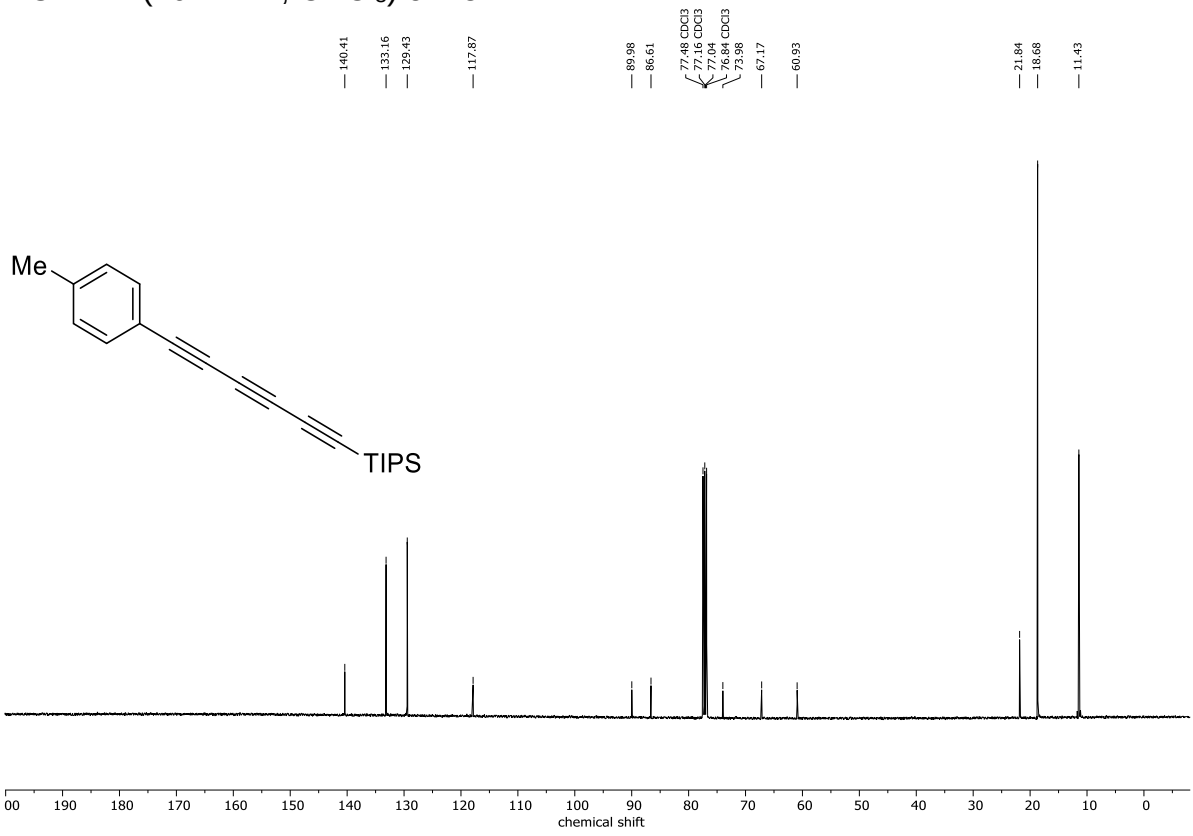
^{13}C NMR (151 MHz, $CDCl_3$) of **2n**



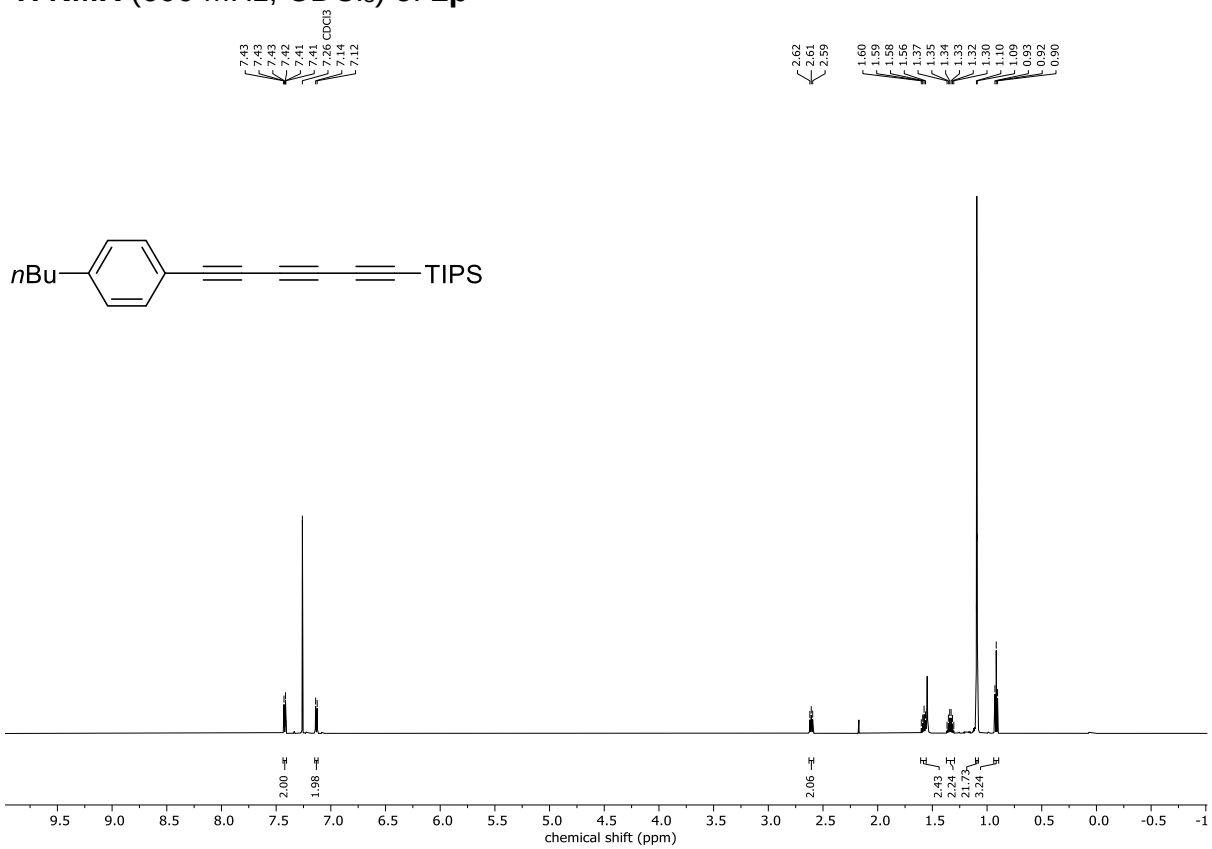
^{1}H NMR (300 MHz, $CDCl_3$) of **2o**



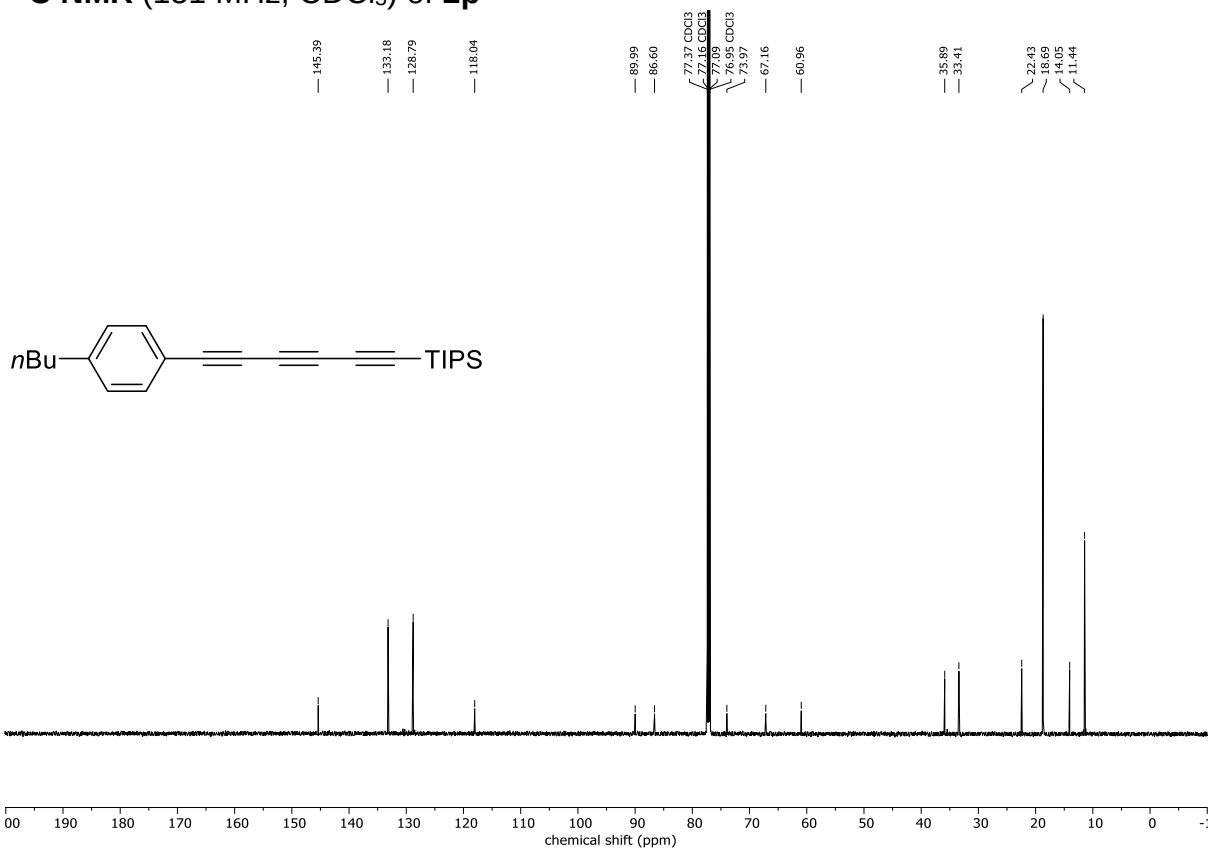
^{13}C NMR (101 MHz, $CDCl_3$) of **2o**



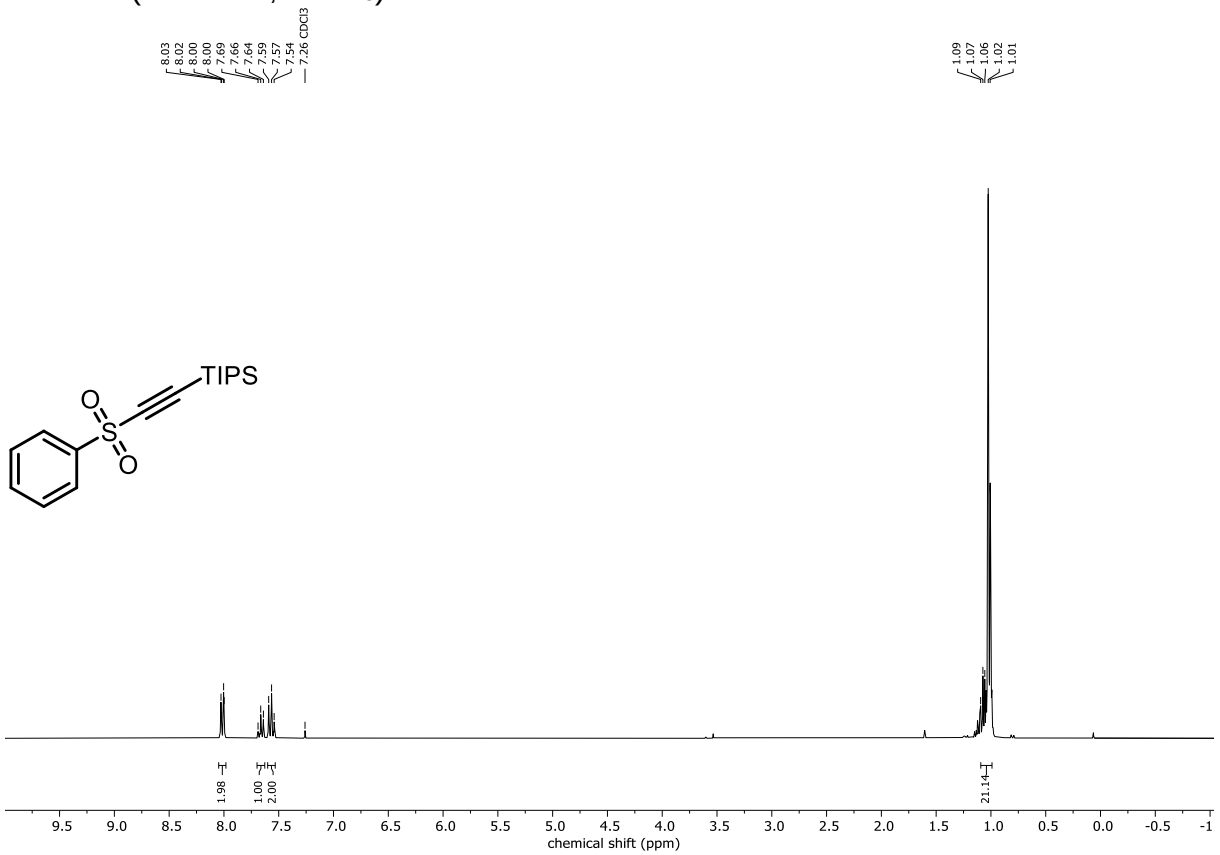
^{1}H NMR (600 MHz, $CDCl_3$) of **2p**



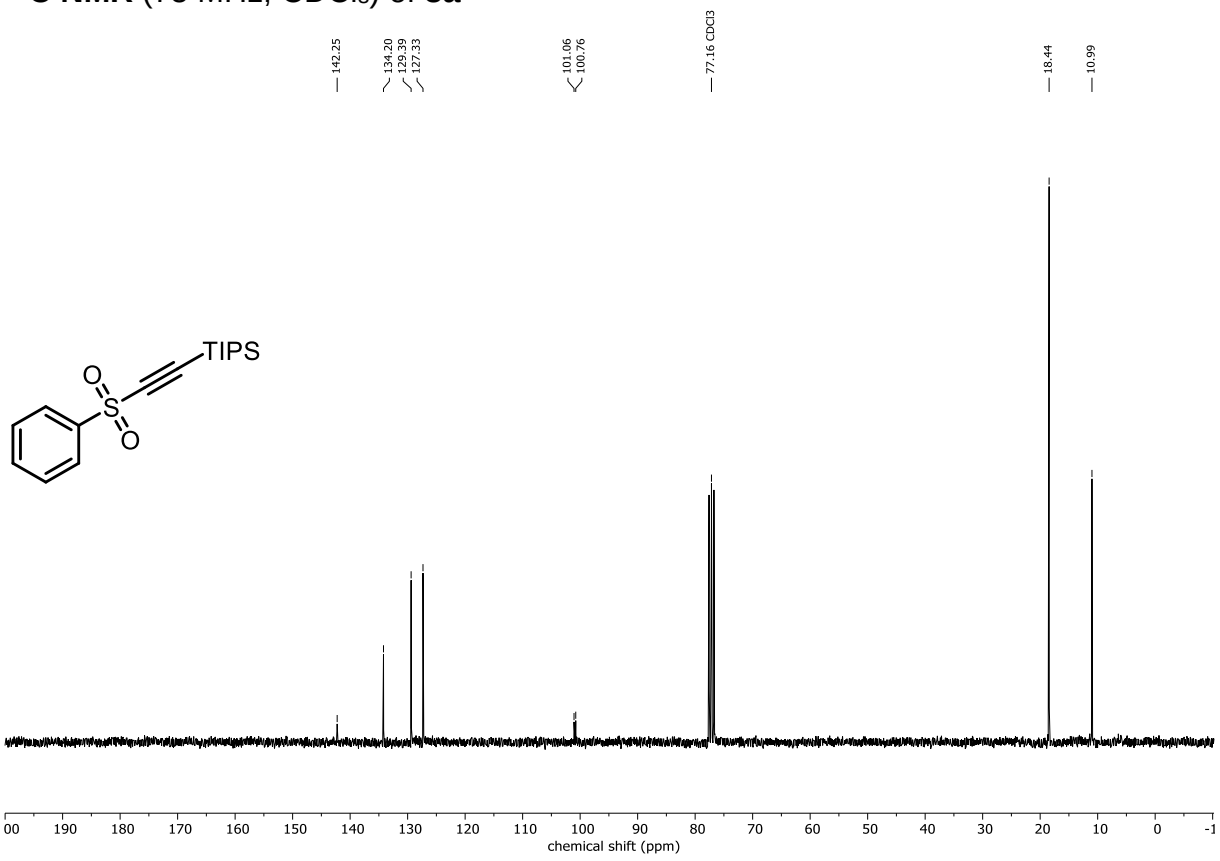
^{13}C NMR (151 MHz, $CDCl_3$) of **2p**



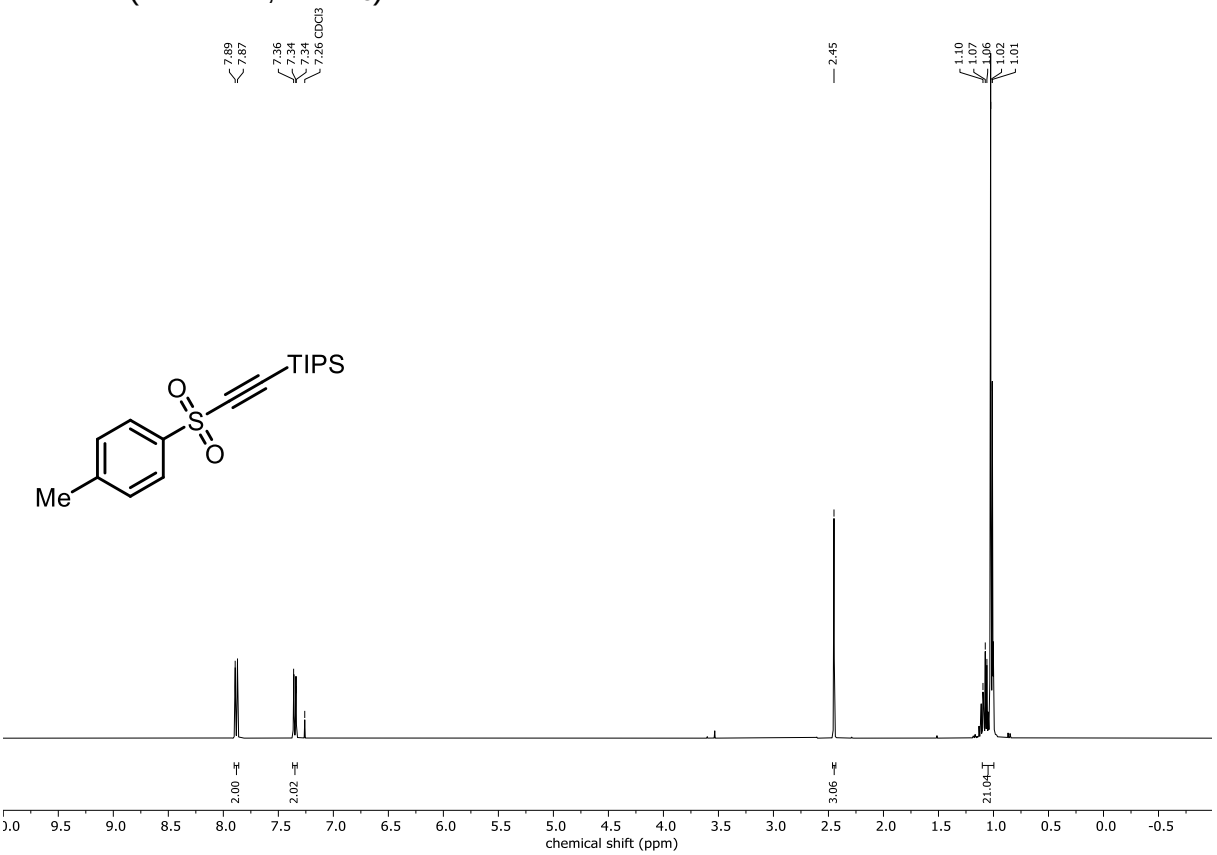
^{1}H NMR (300 MHz, $CDCl_3$) of **3a**



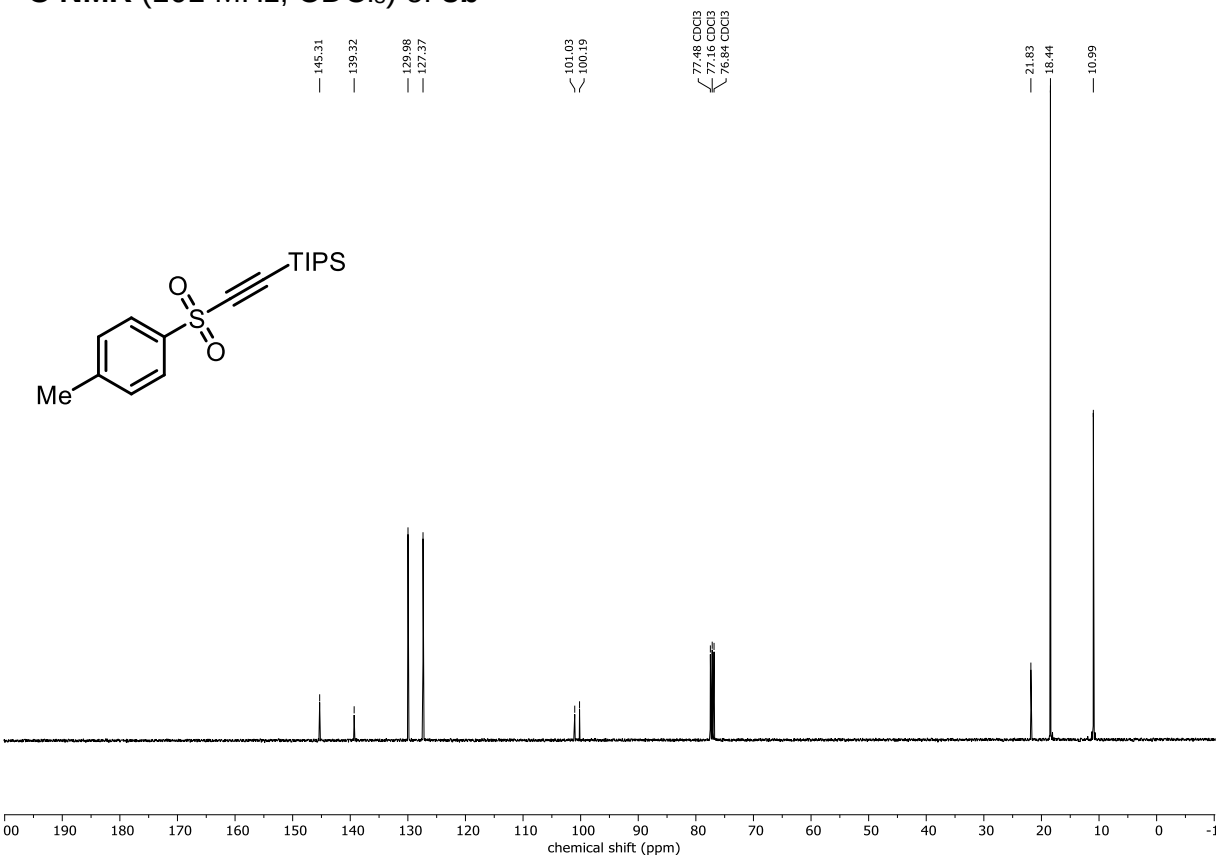
^{13}C NMR (75 MHz, $CDCl_3$) of **3a**



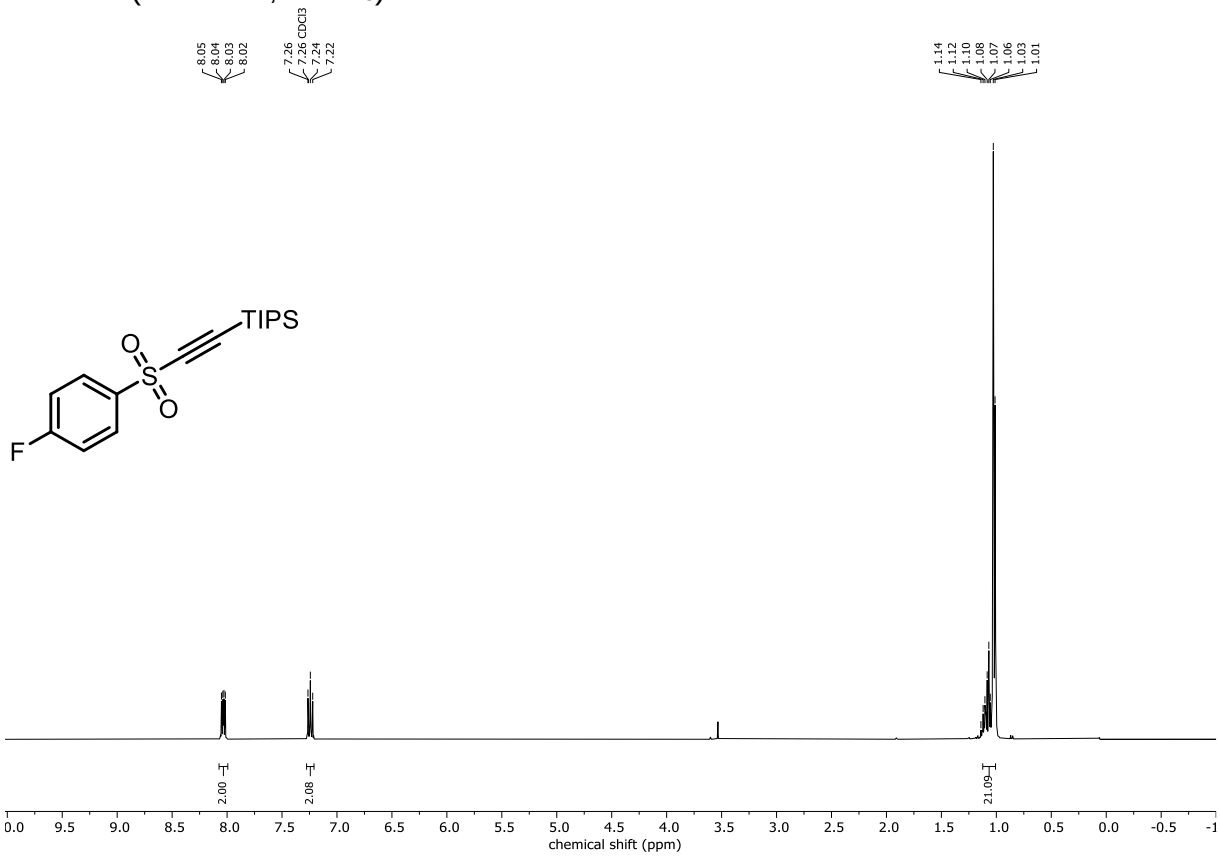
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



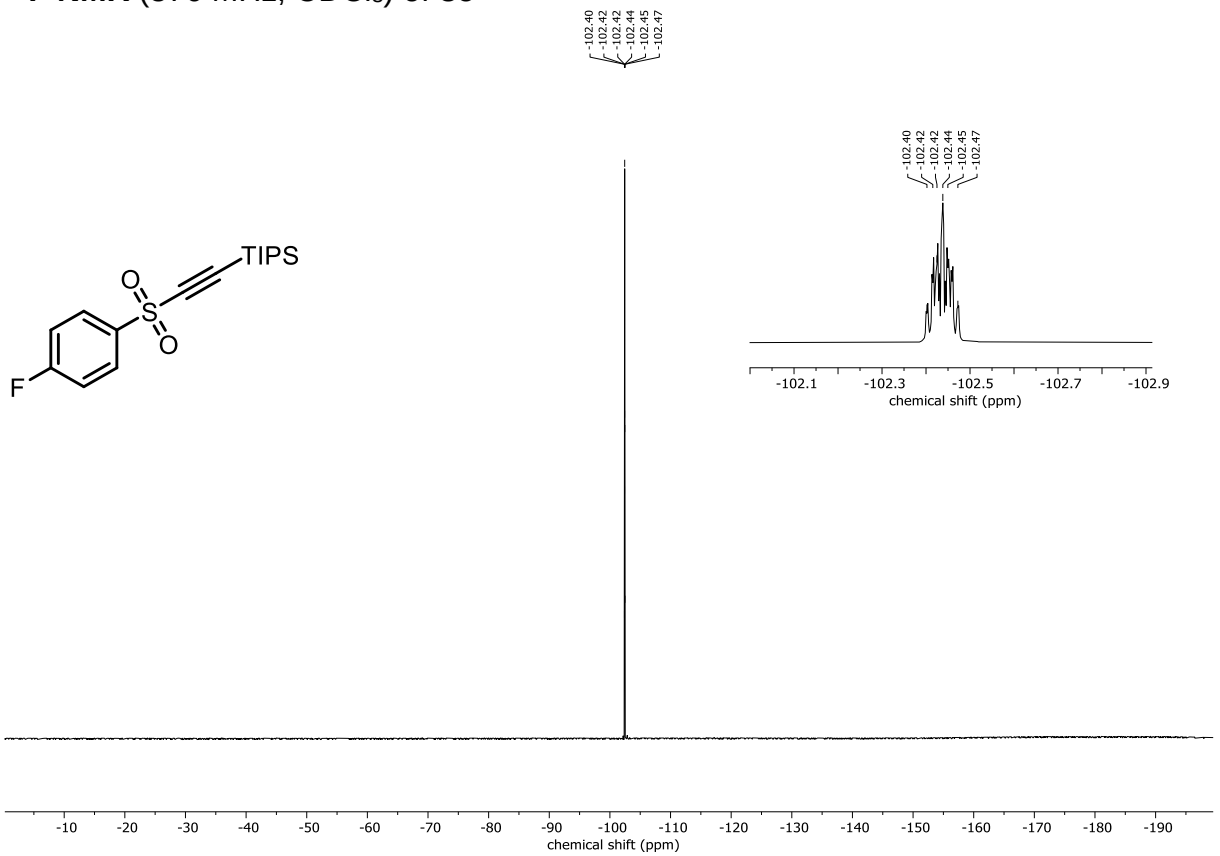
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



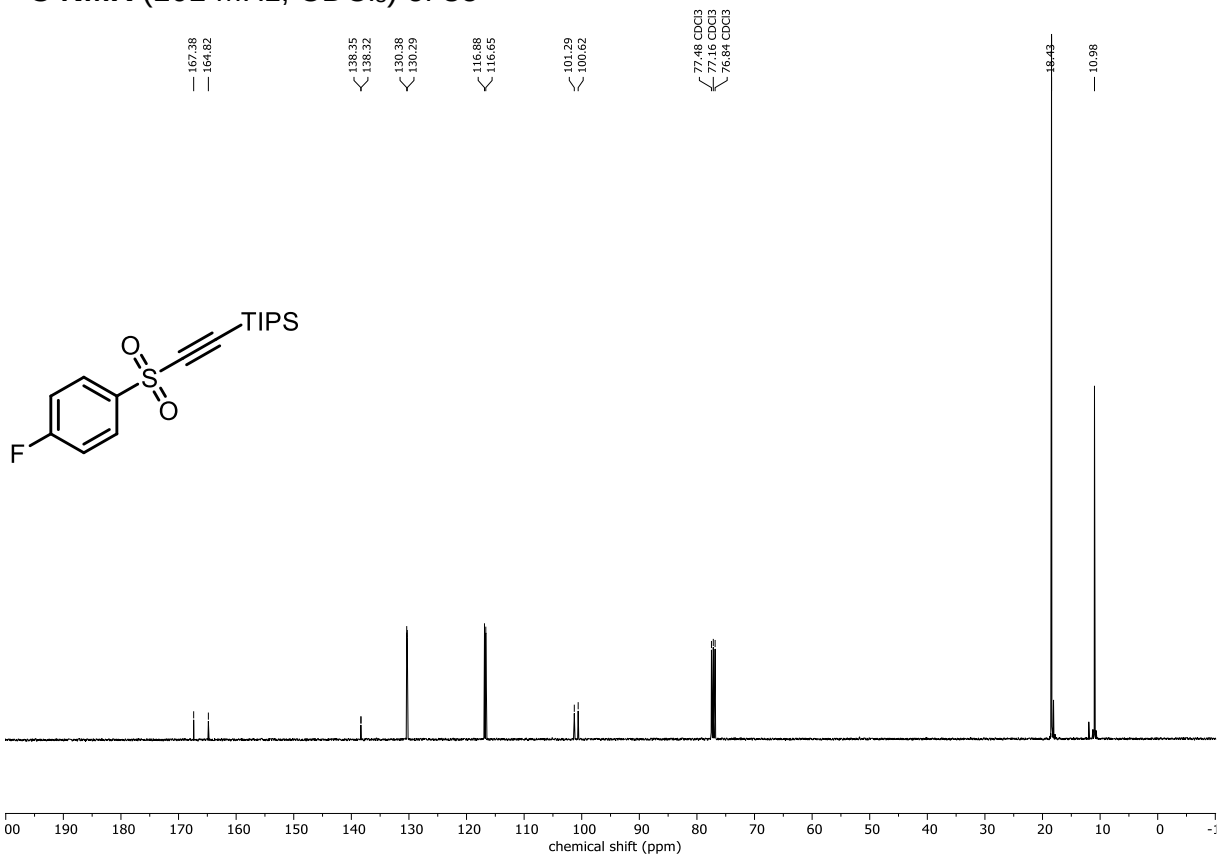
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



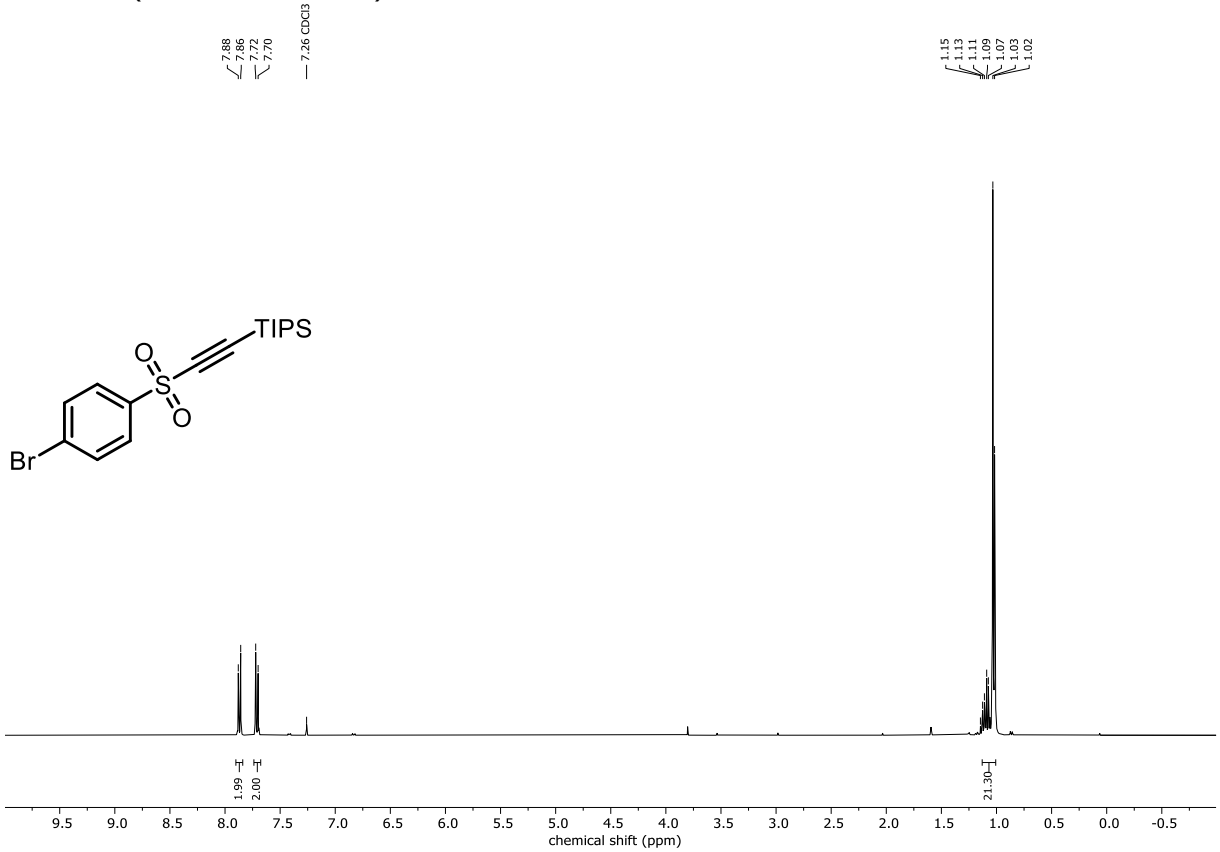
^{19}F NMR (376 MHz, $CDCl_3$) of **3c**



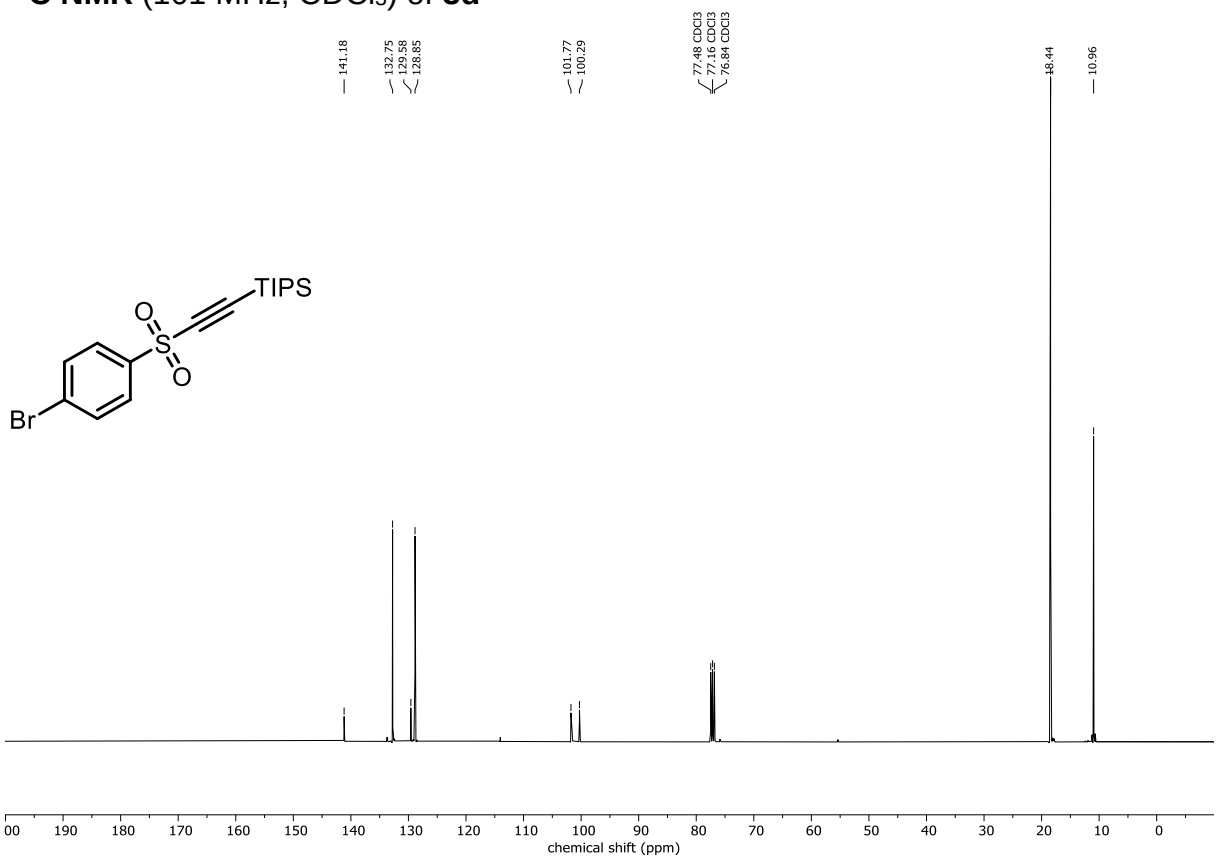
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



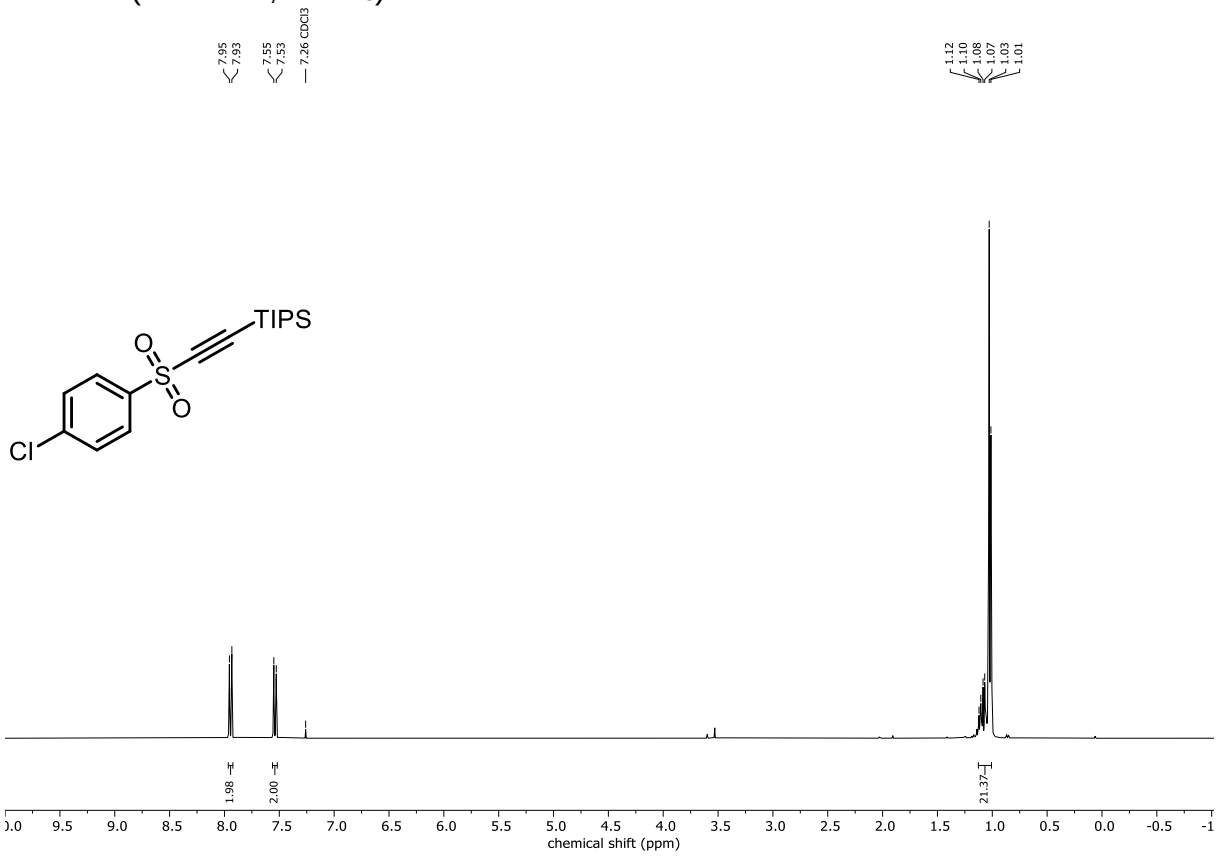
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



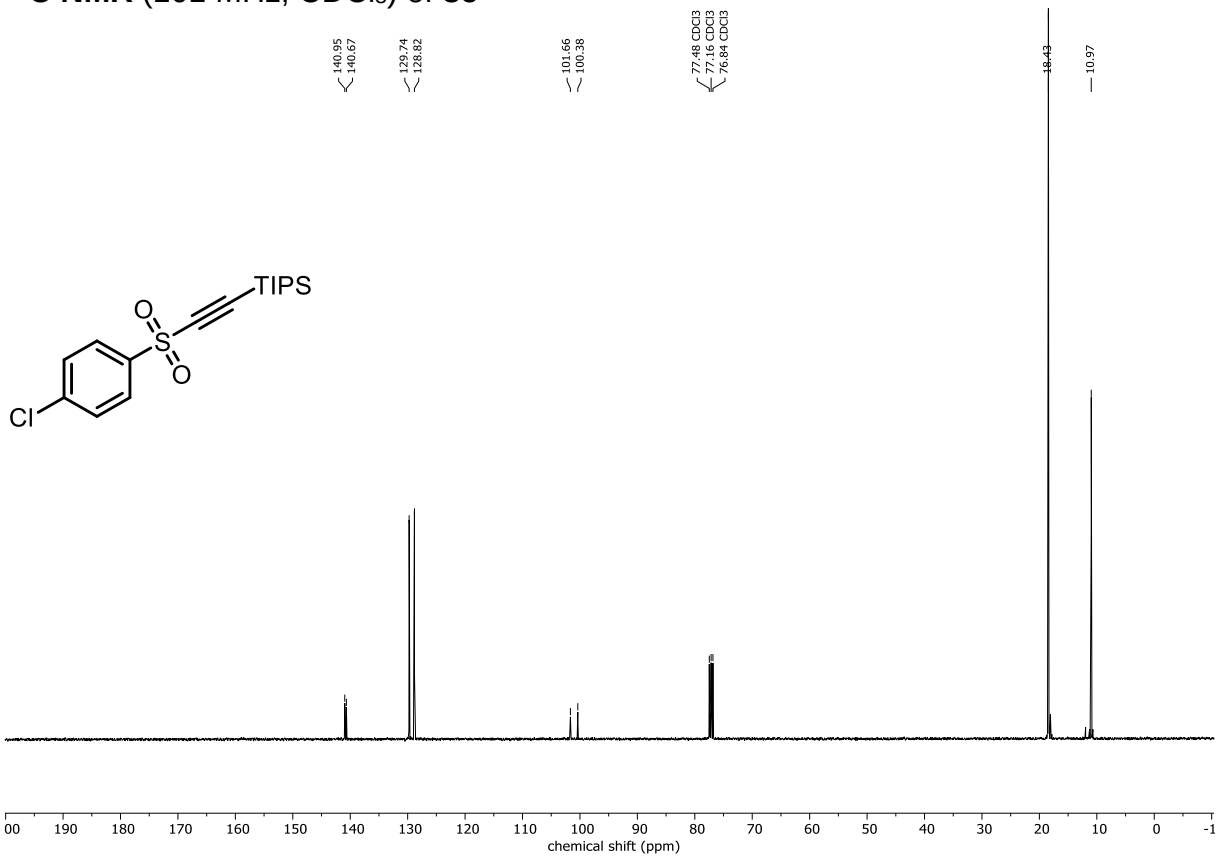
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



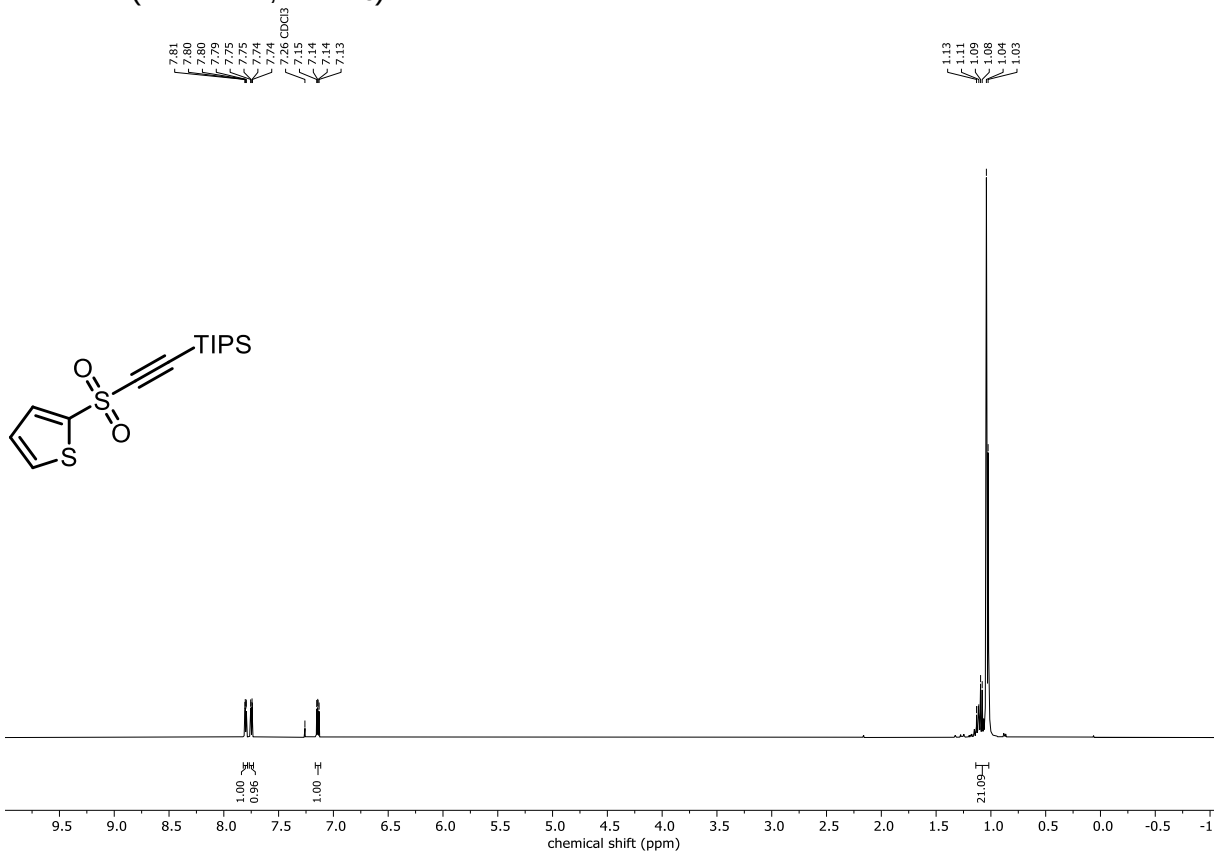
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



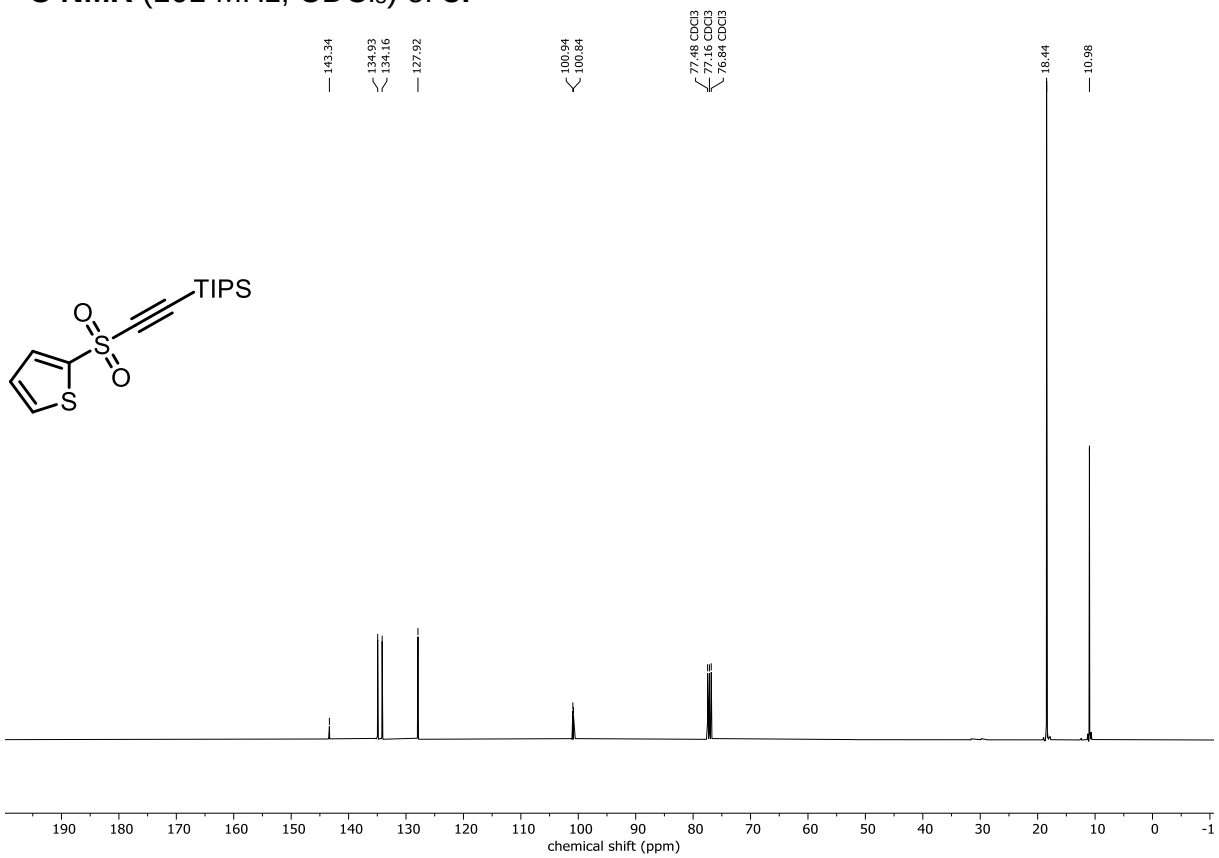
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



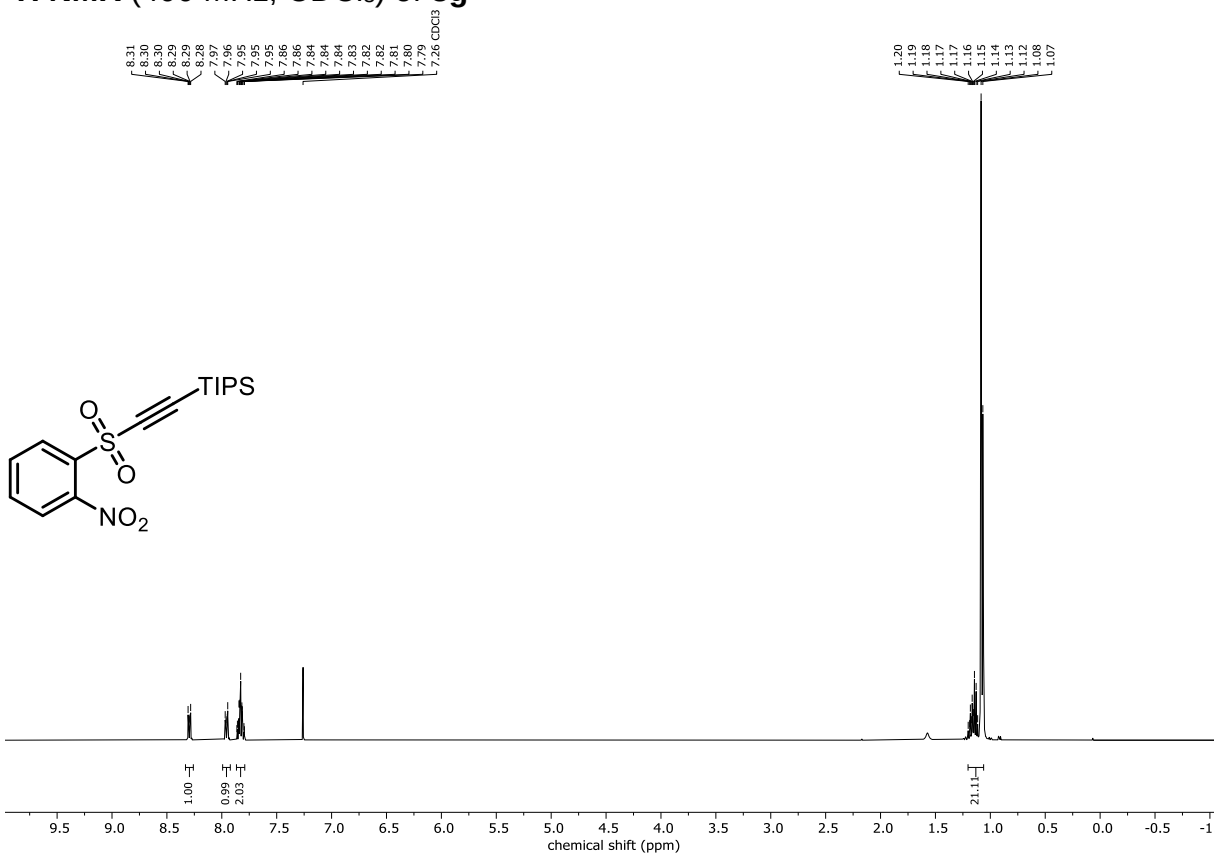
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



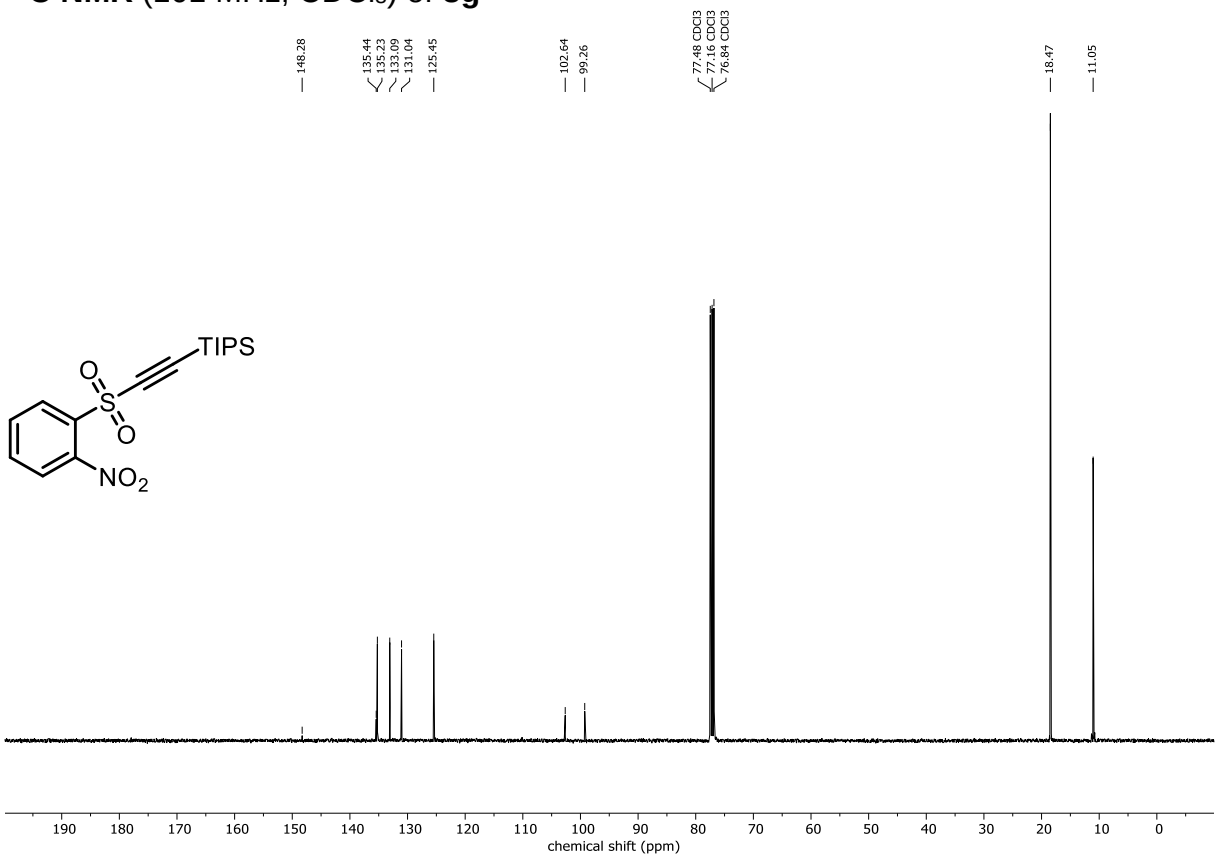
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



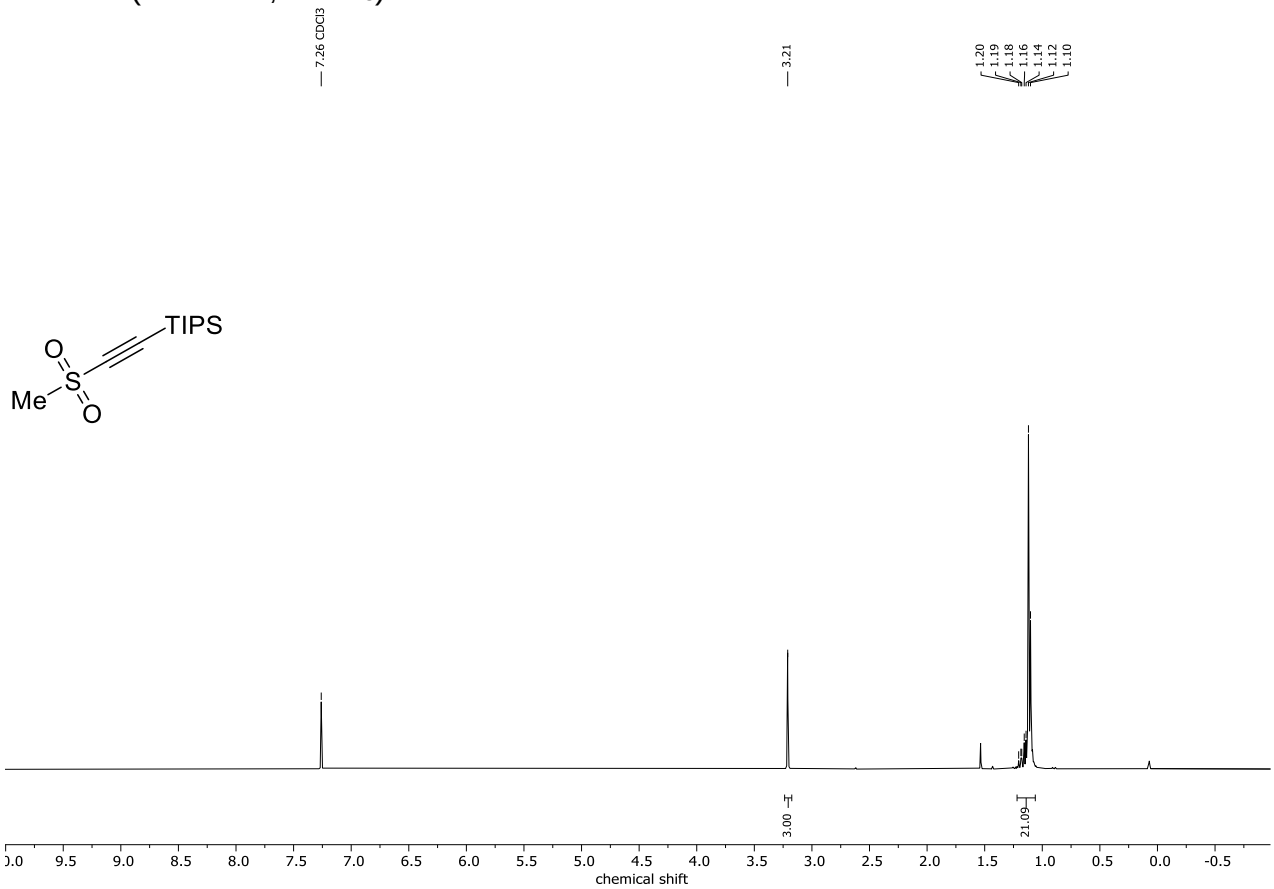
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



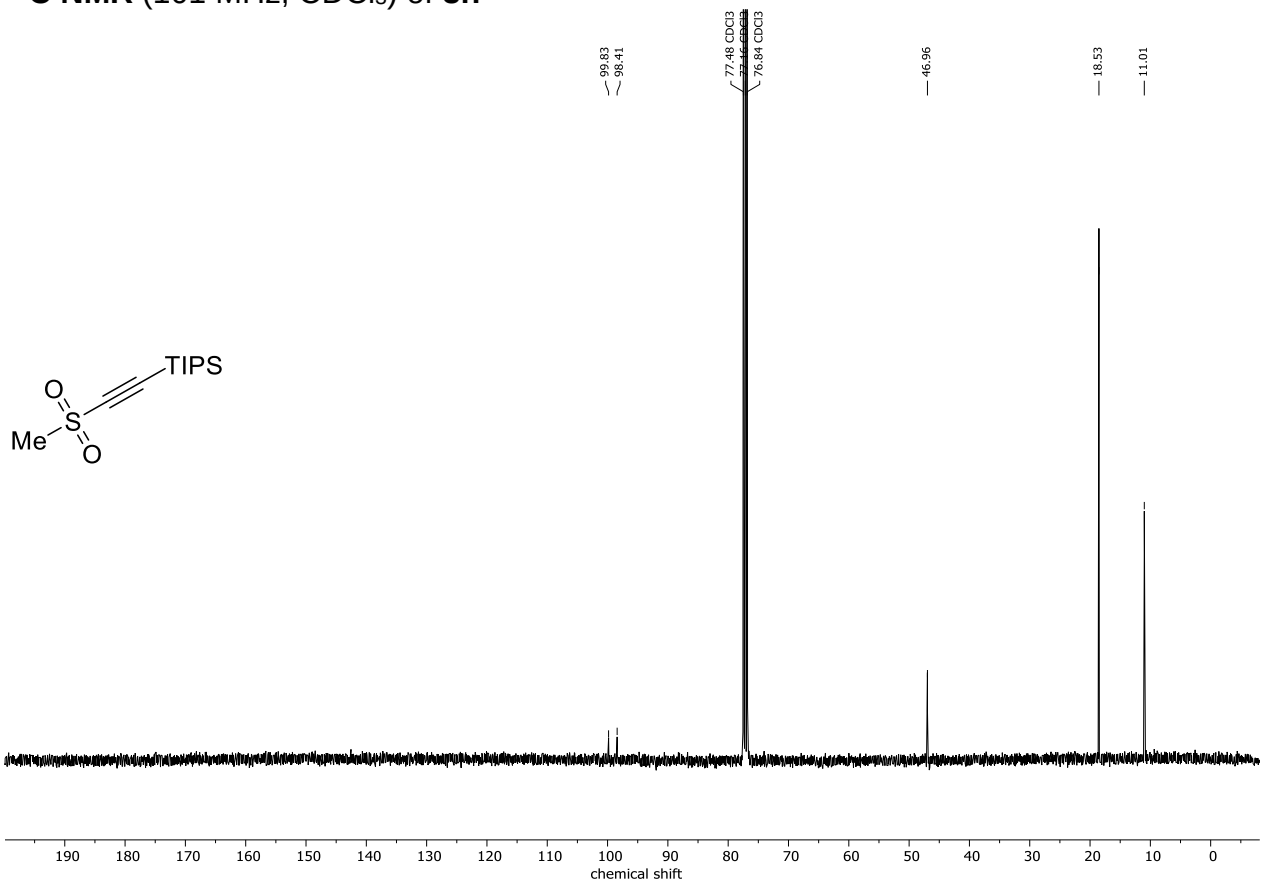
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



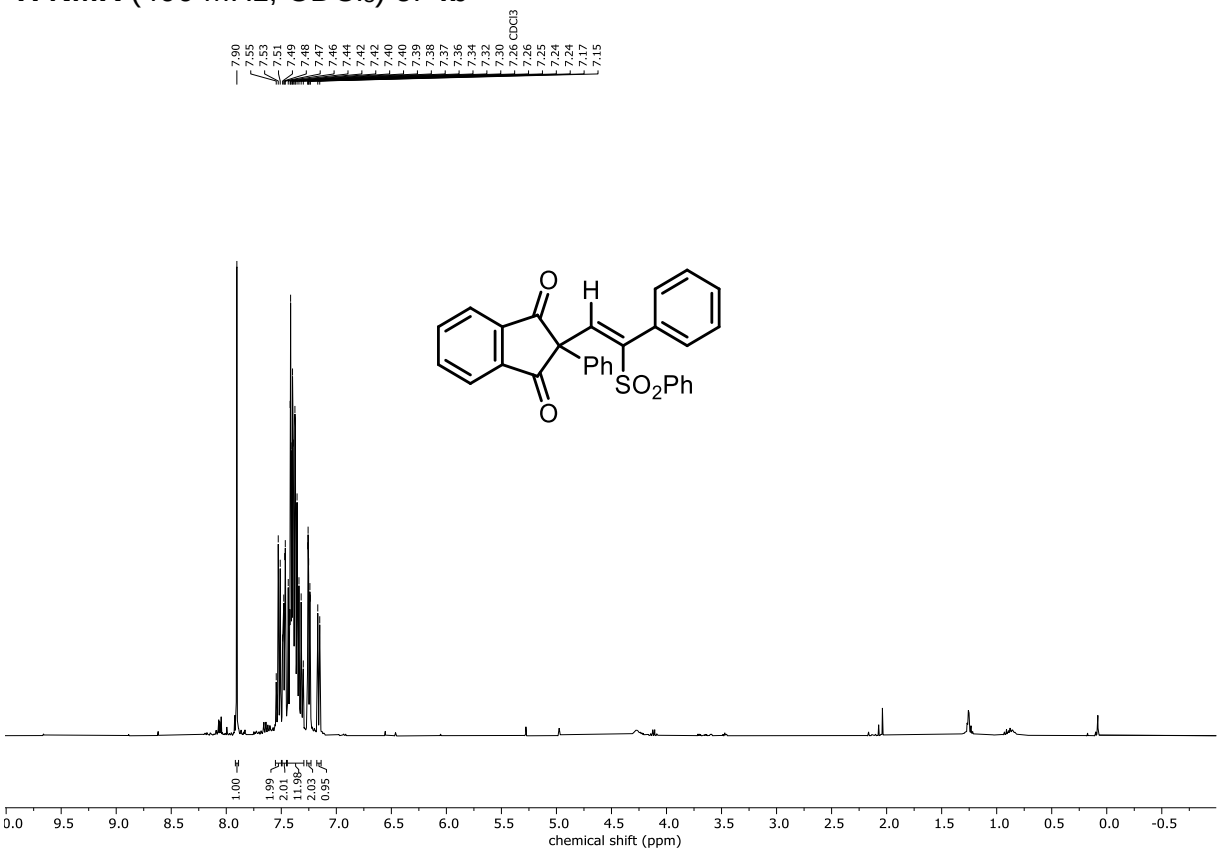
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



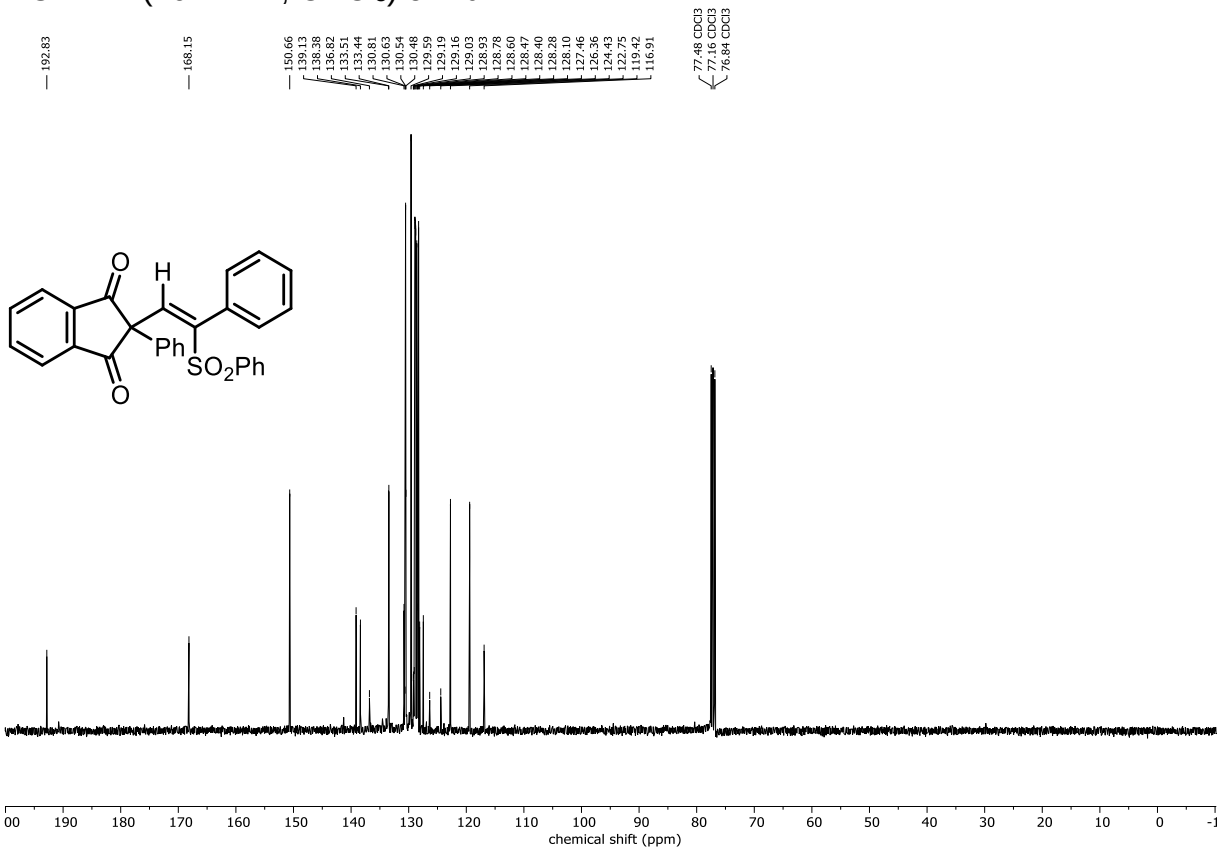
^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



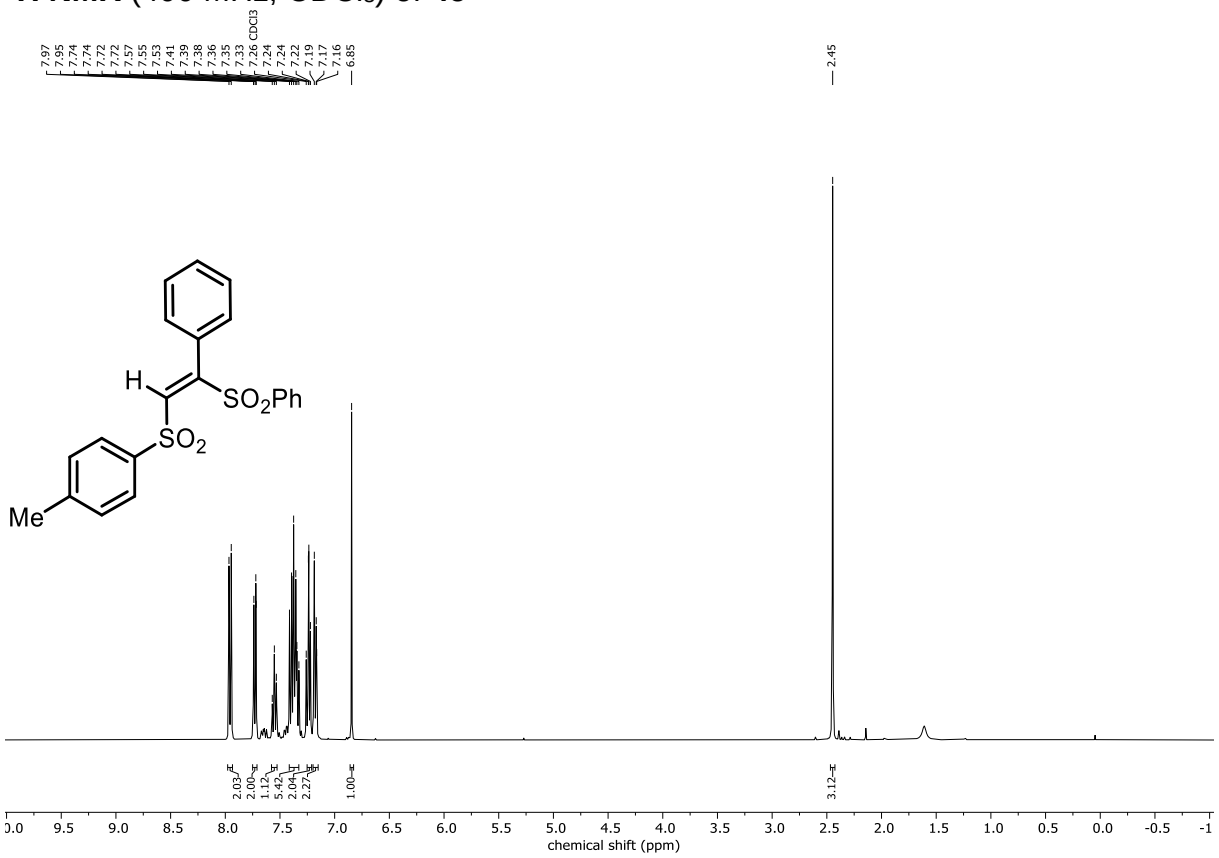
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



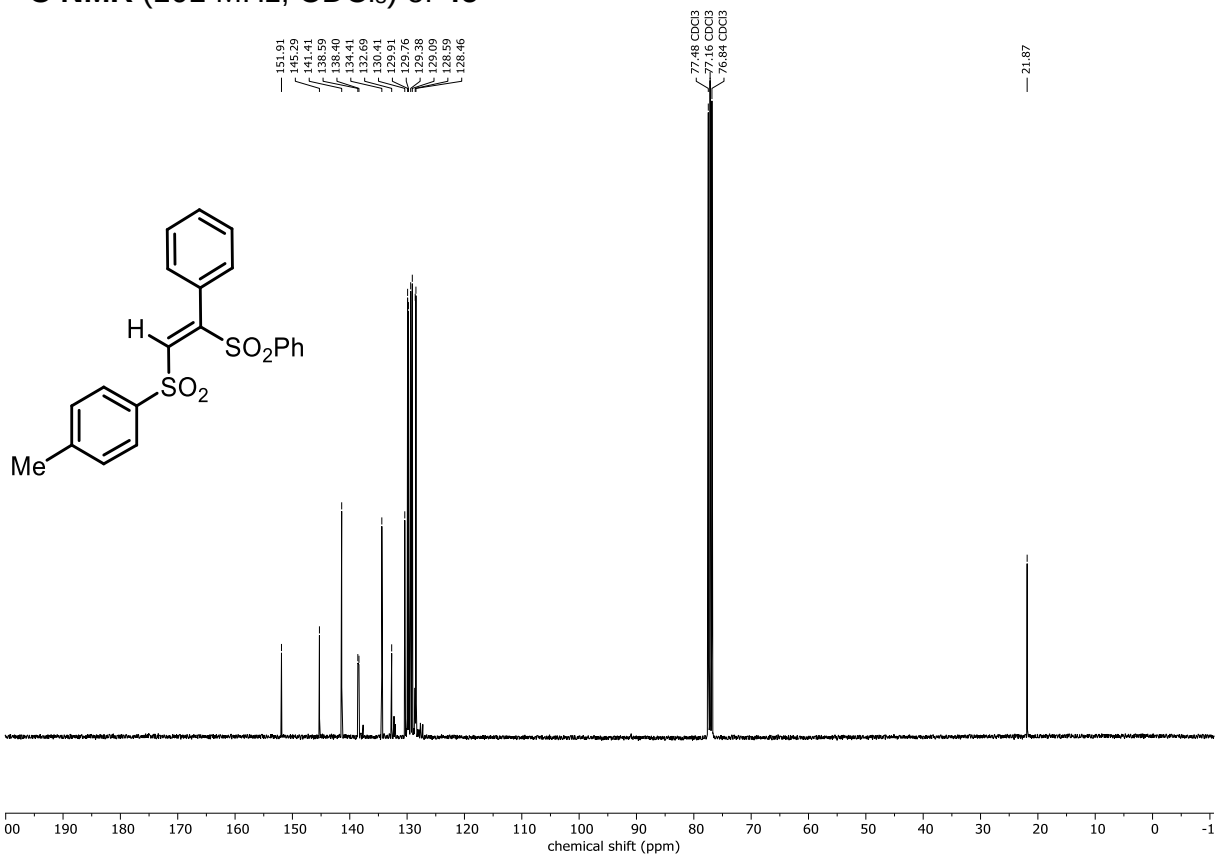
^{13}C NMR (101 MHz, $CDCl_3$) of **4b**



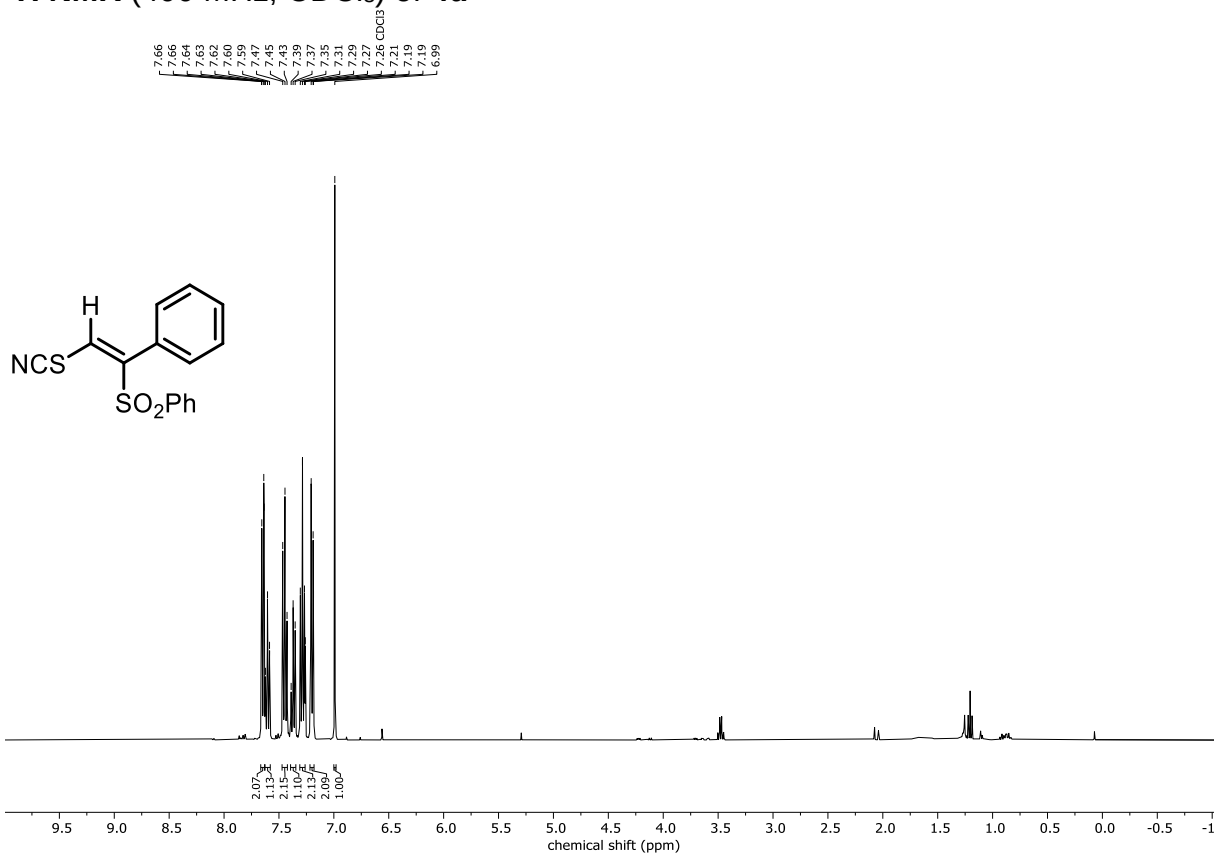
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



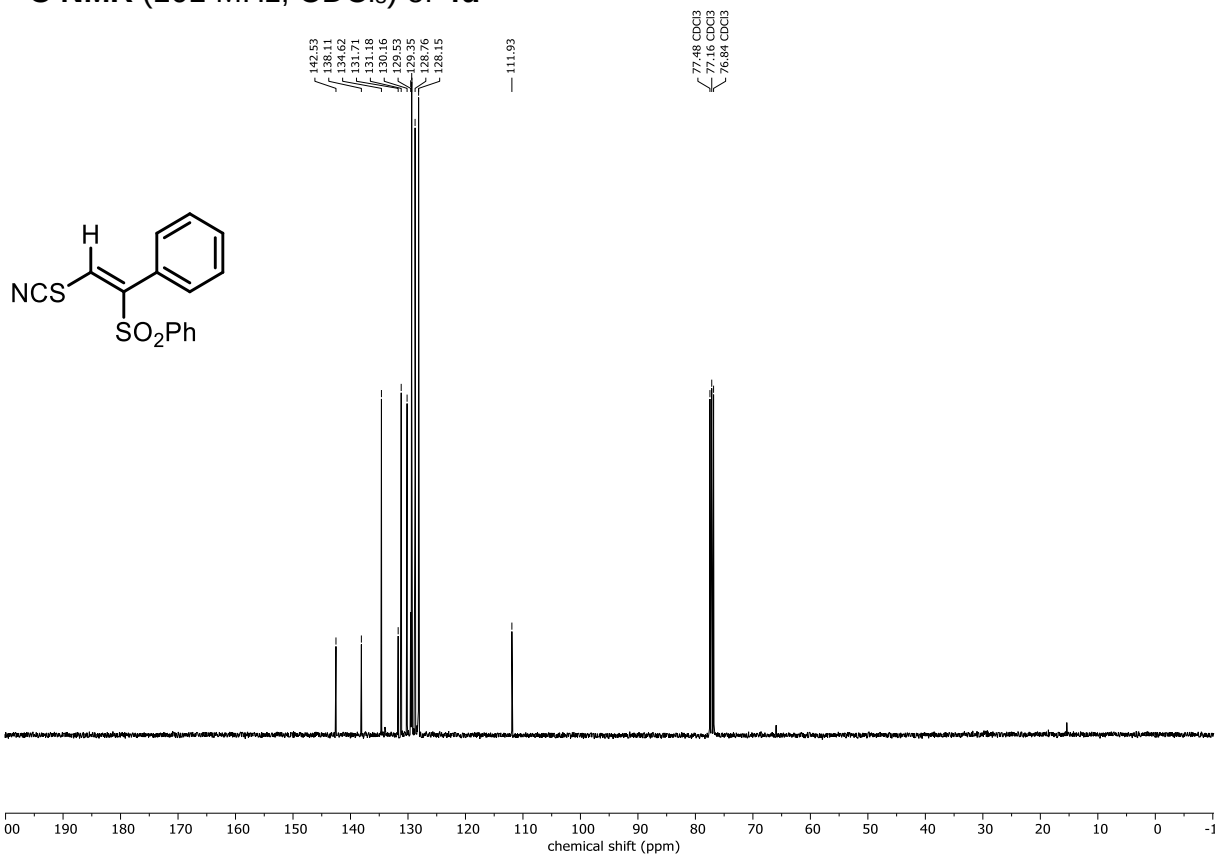
^{13}C NMR (101 MHz, $CDCl_3$) of **4c**



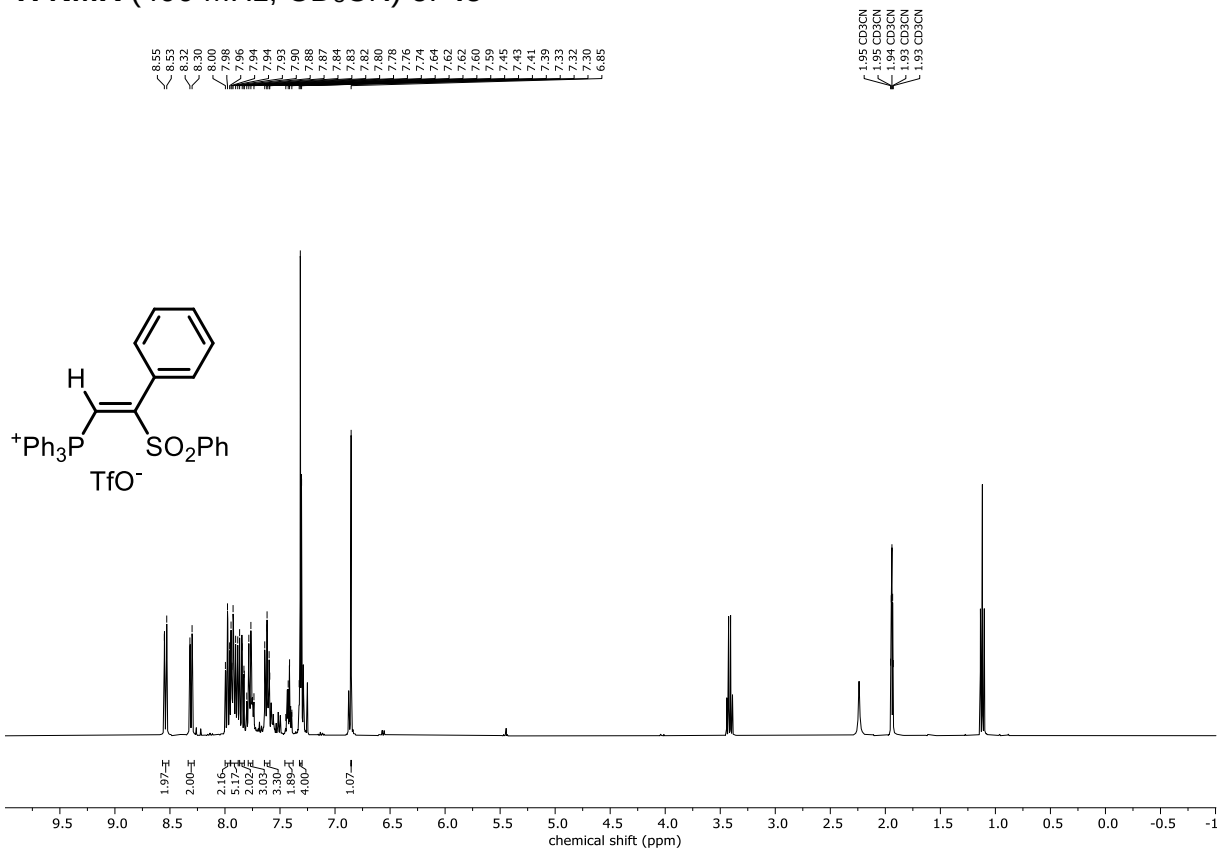
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



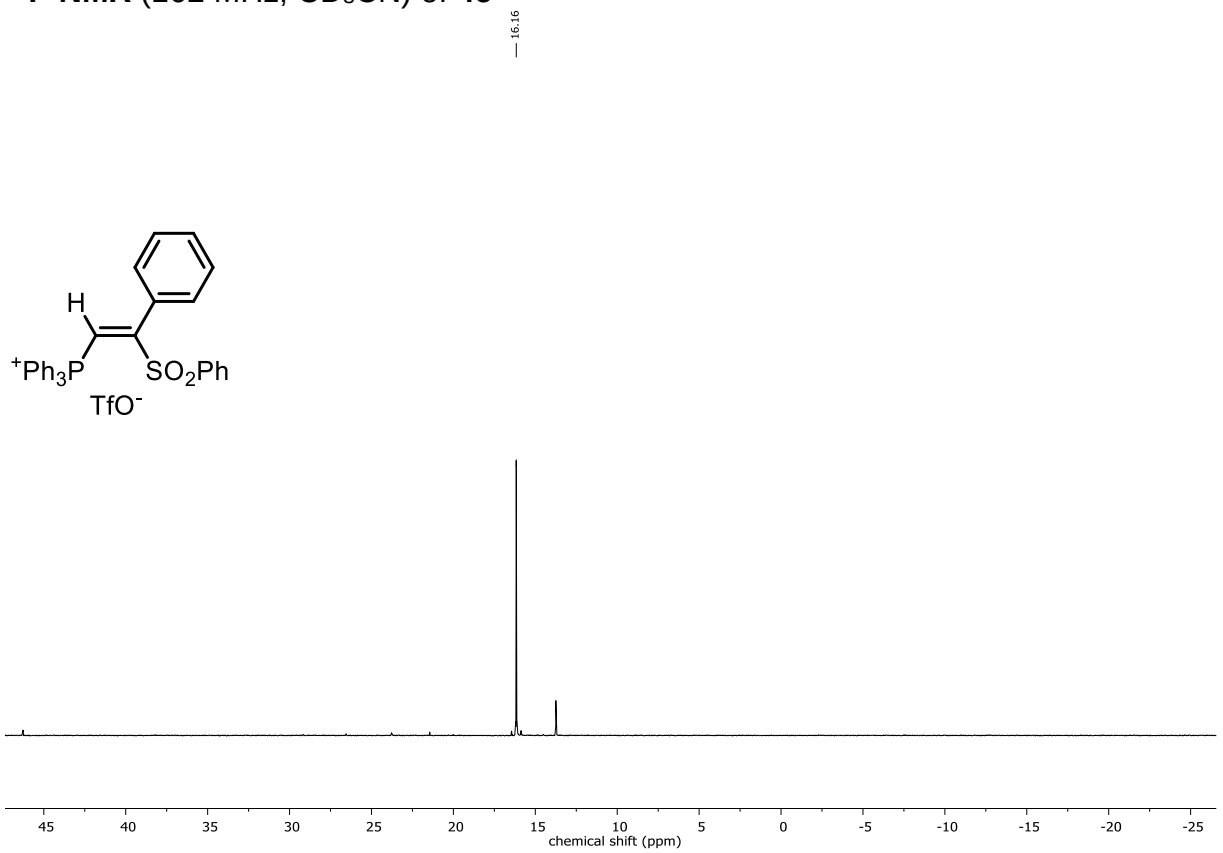
^{13}C NMR (101 MHz, $CDCl_3$) of **4d**



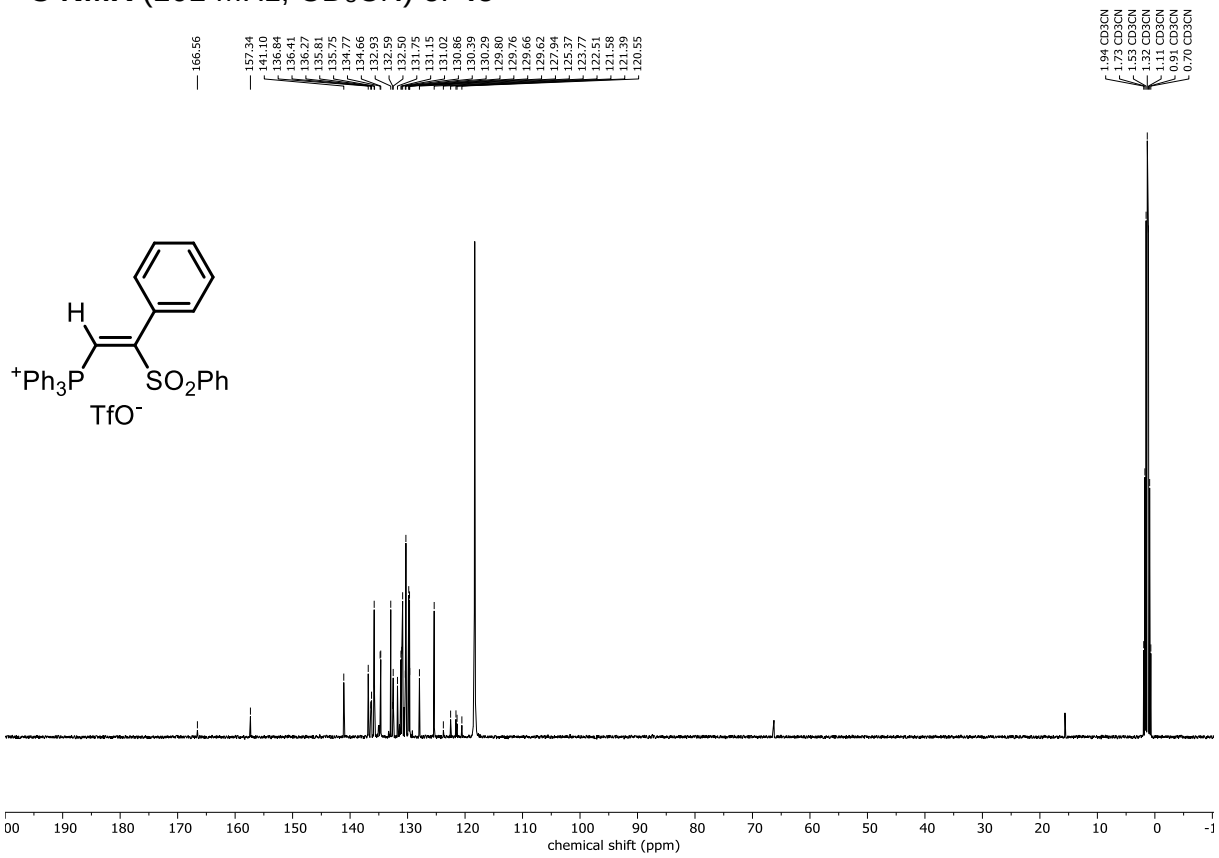
^{1}H NMR (400 MHz, CD_3CN) of **4e**



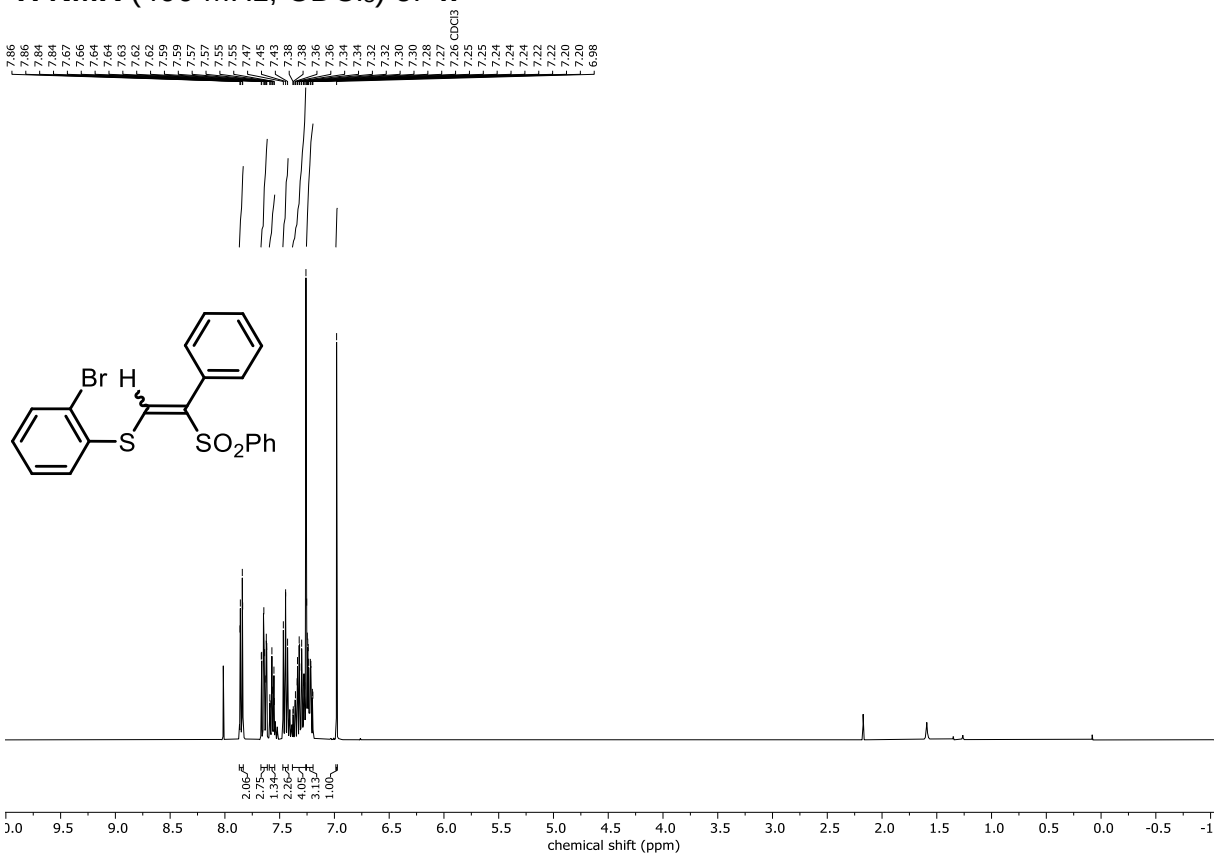
^{31}P NMR (162 MHz, CD_3CN) of **4e**



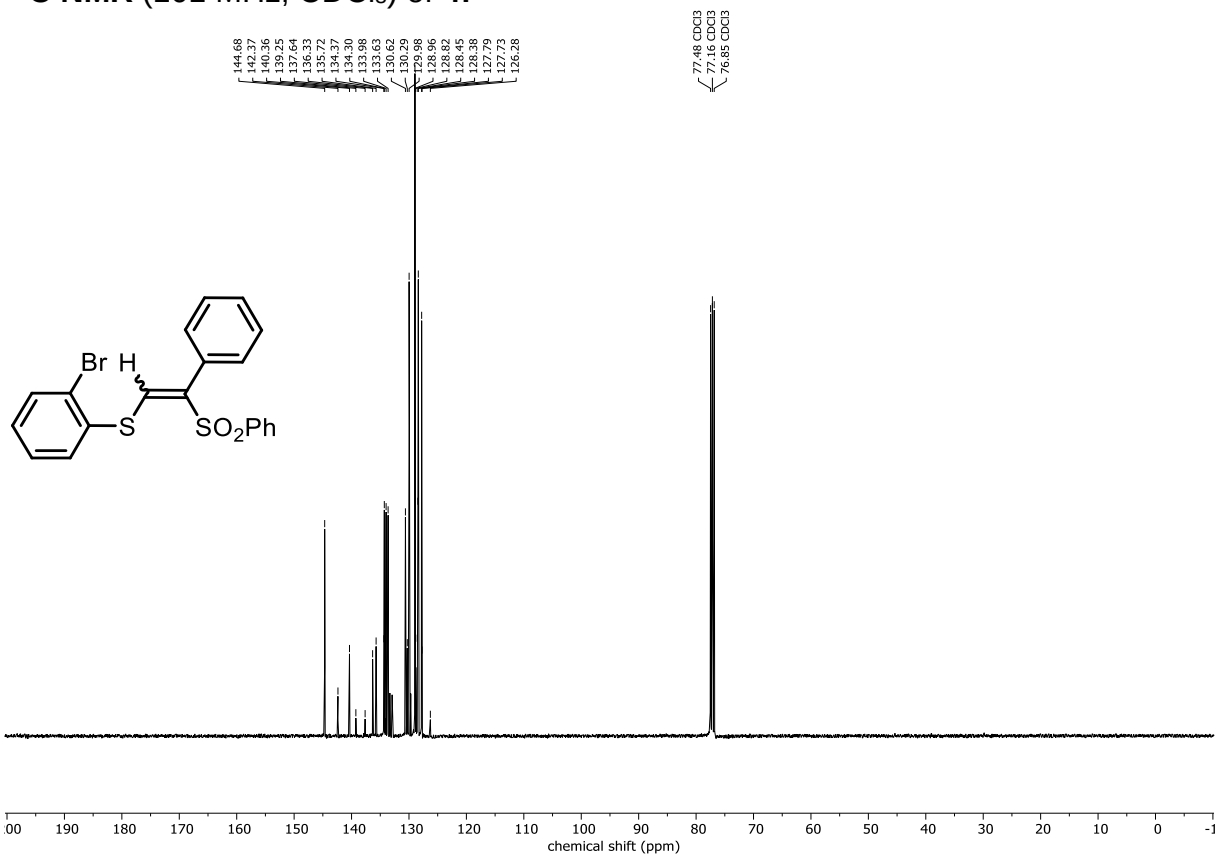
^{13}C NMR (101 MHz, CD_3CN) of **4e**



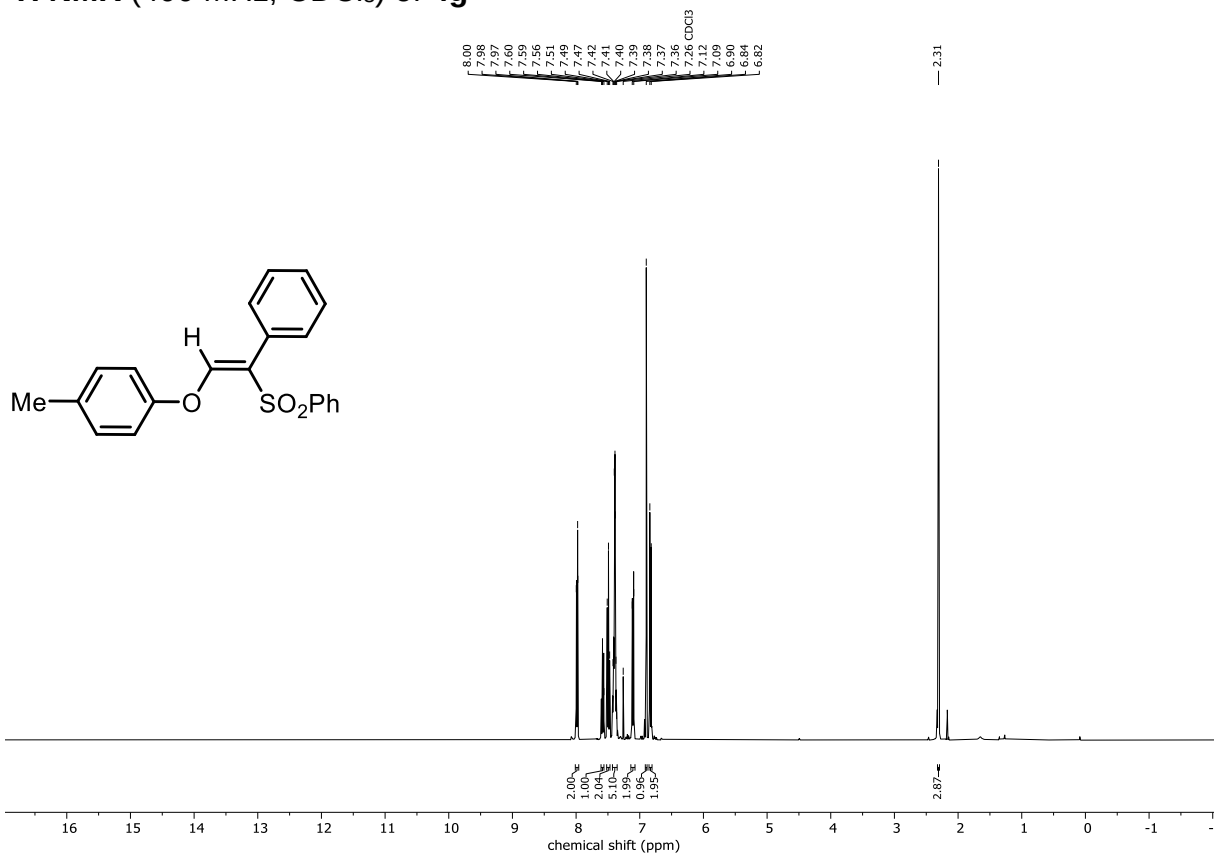
^{1}H NMR (400 MHz, $CDCl_3$) of **4f**



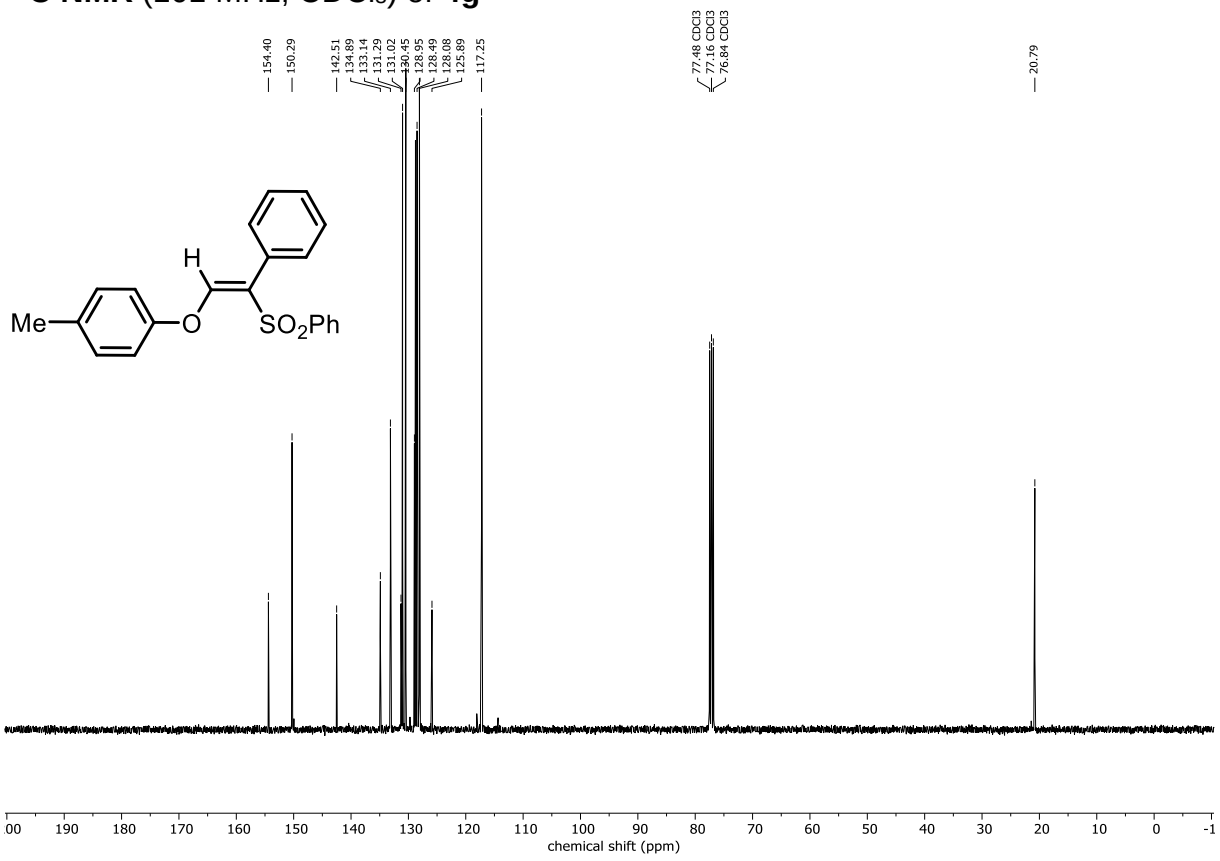
^{13}C NMR (101 MHz, $CDCl_3$) of **4f**



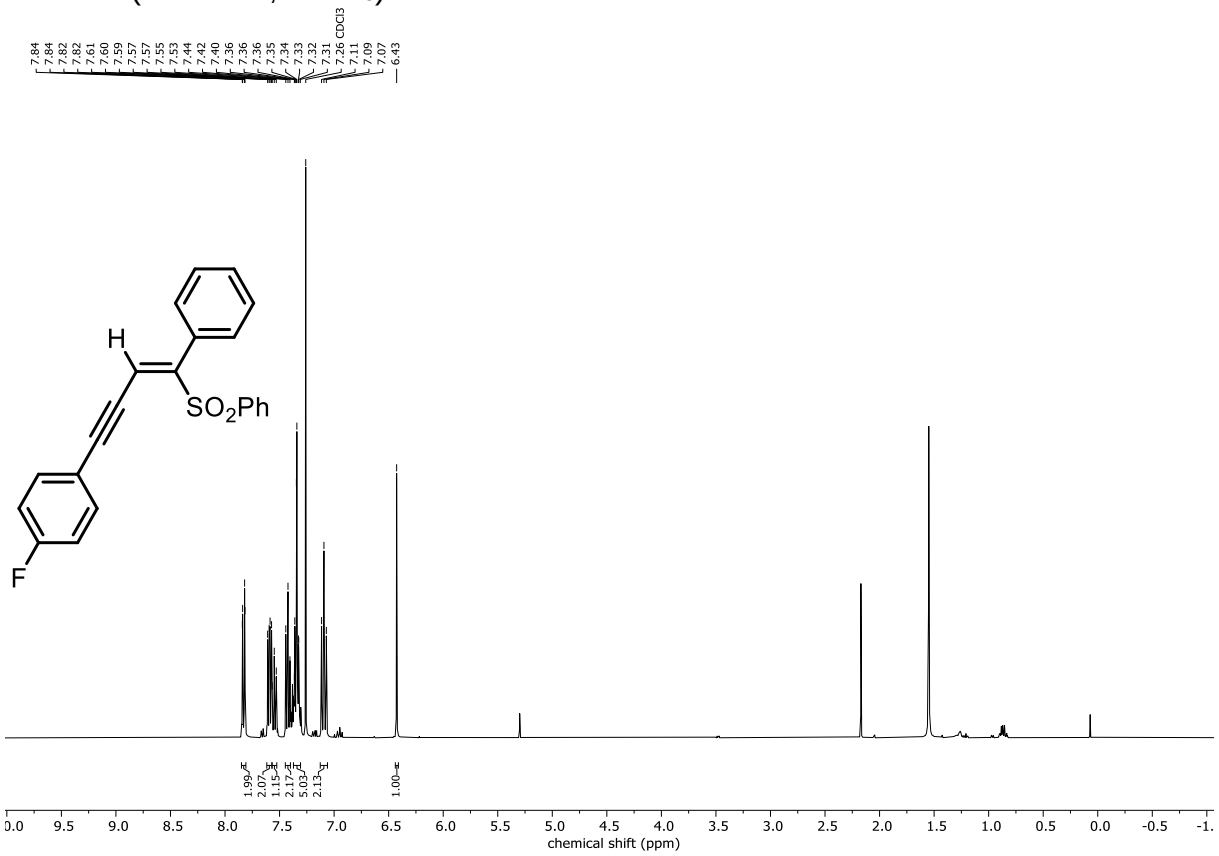
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



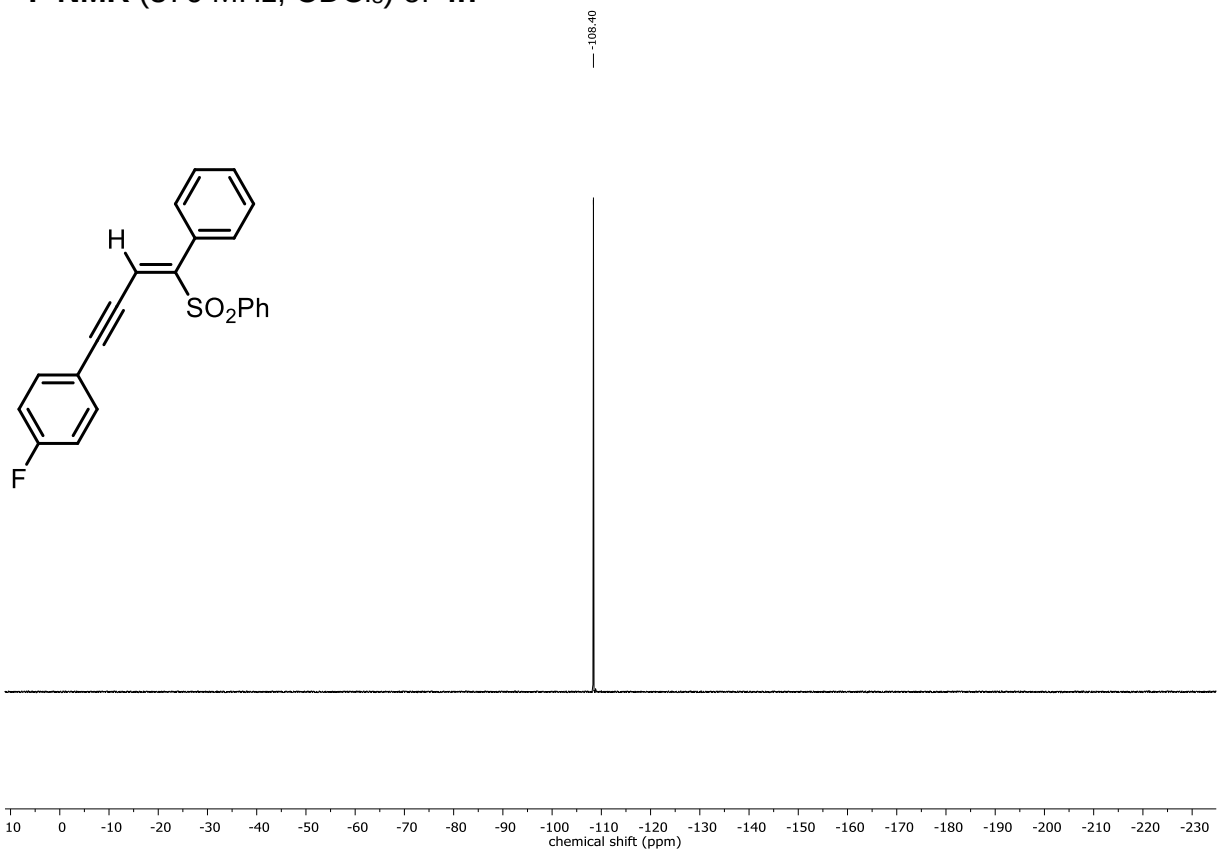
^{13}C NMR (101 MHz, $CDCl_3$) of **4g**



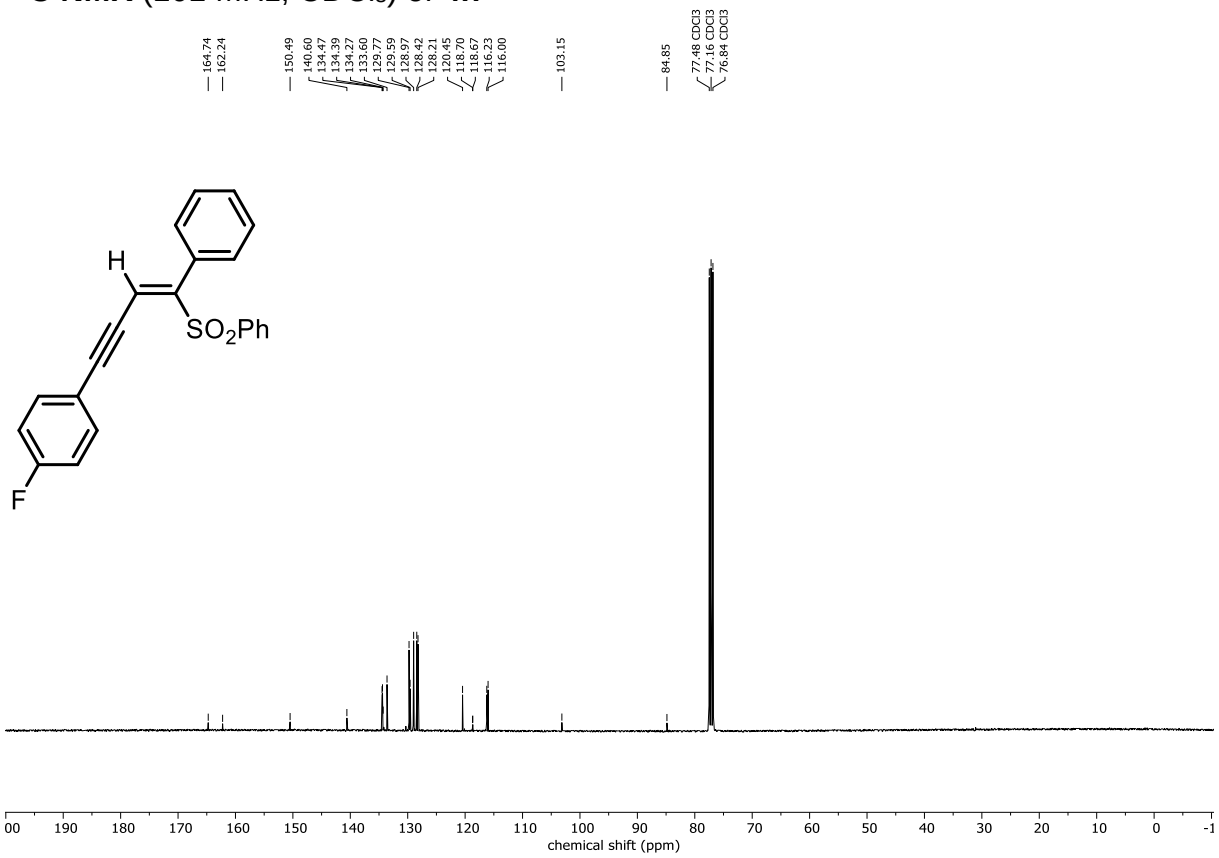
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



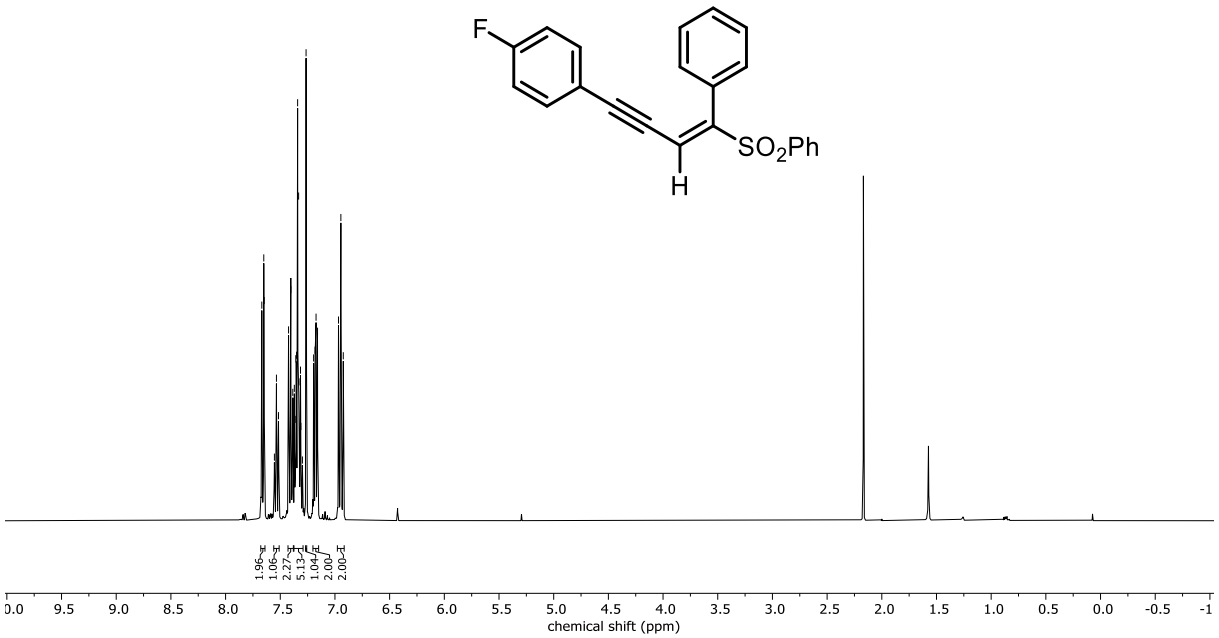
^{19}F NMR (376 MHz, $CDCl_3$) of **4h**



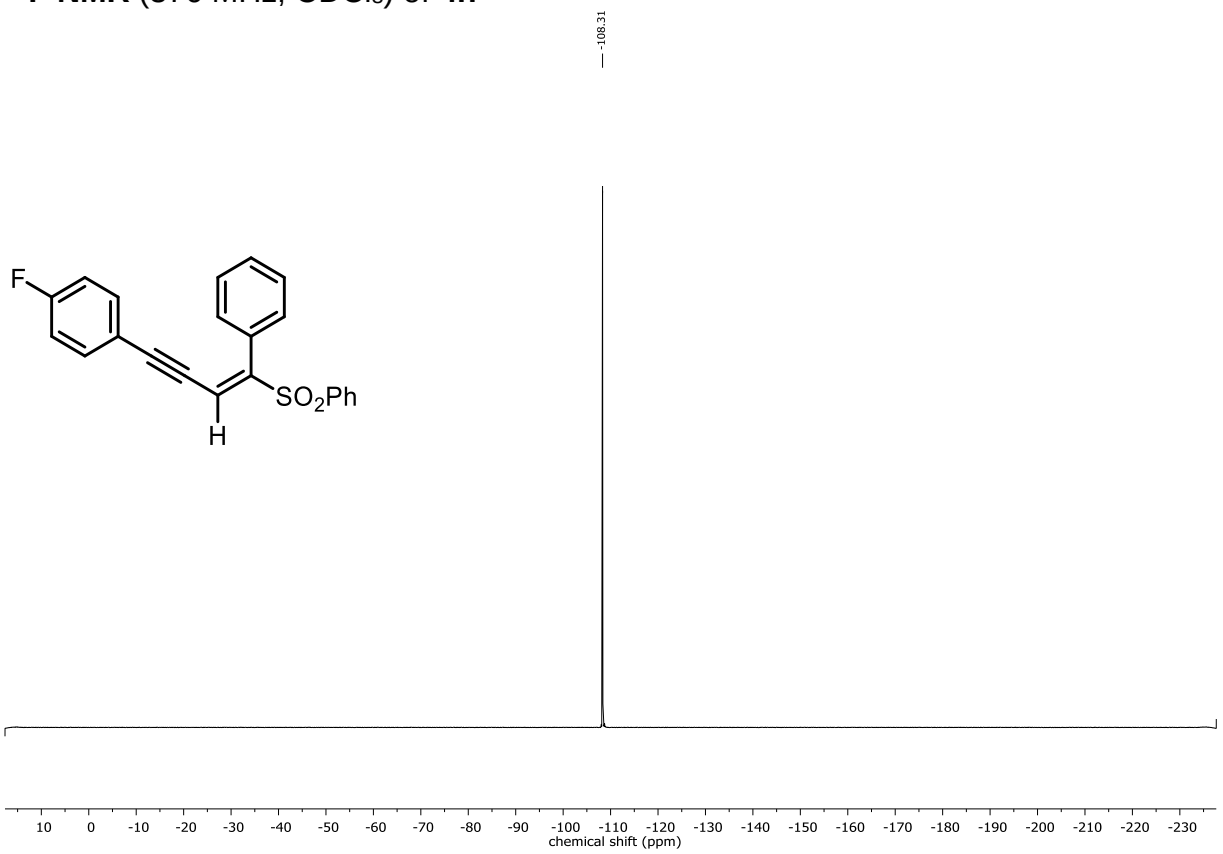
^{13}C NMR (101 MHz, $CDCl_3$) of **4h**



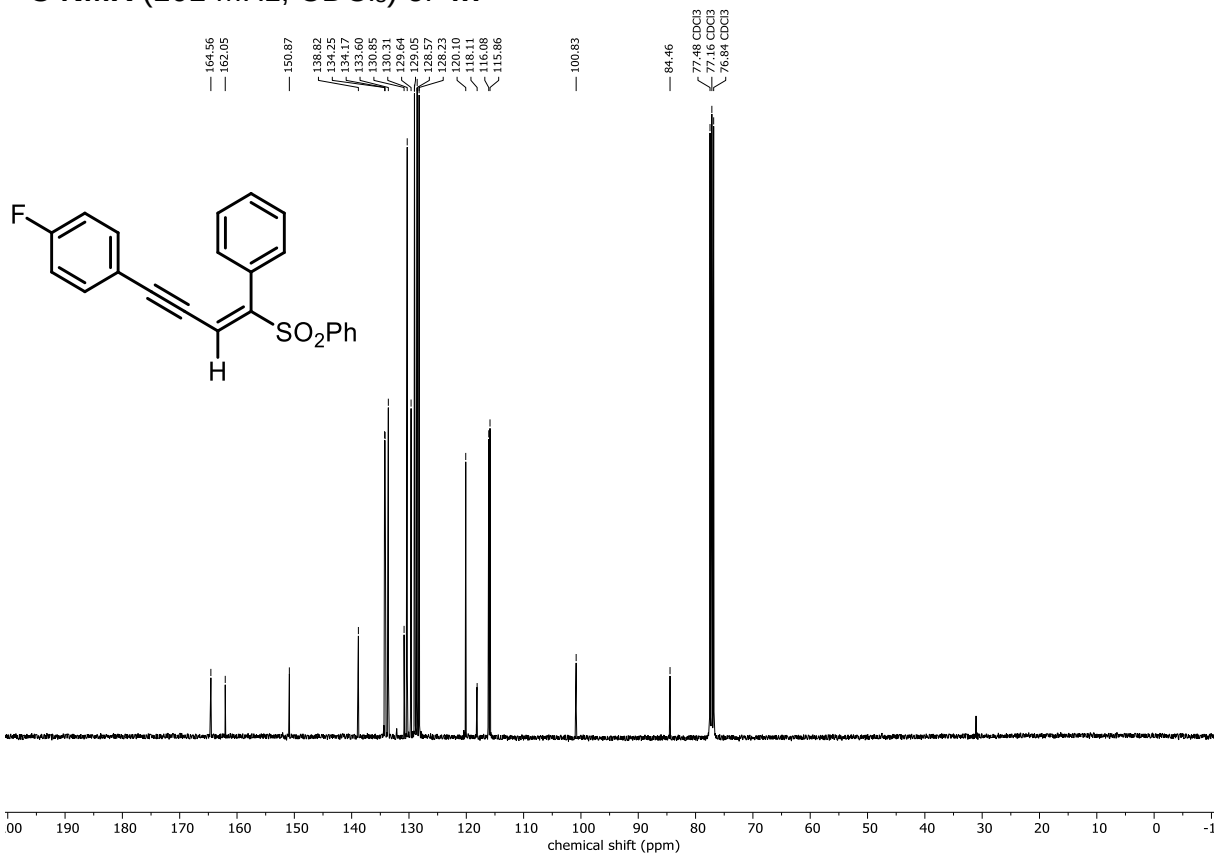
^{1}H NMR (400 MHz, $CDCl_3$) of **4h'**



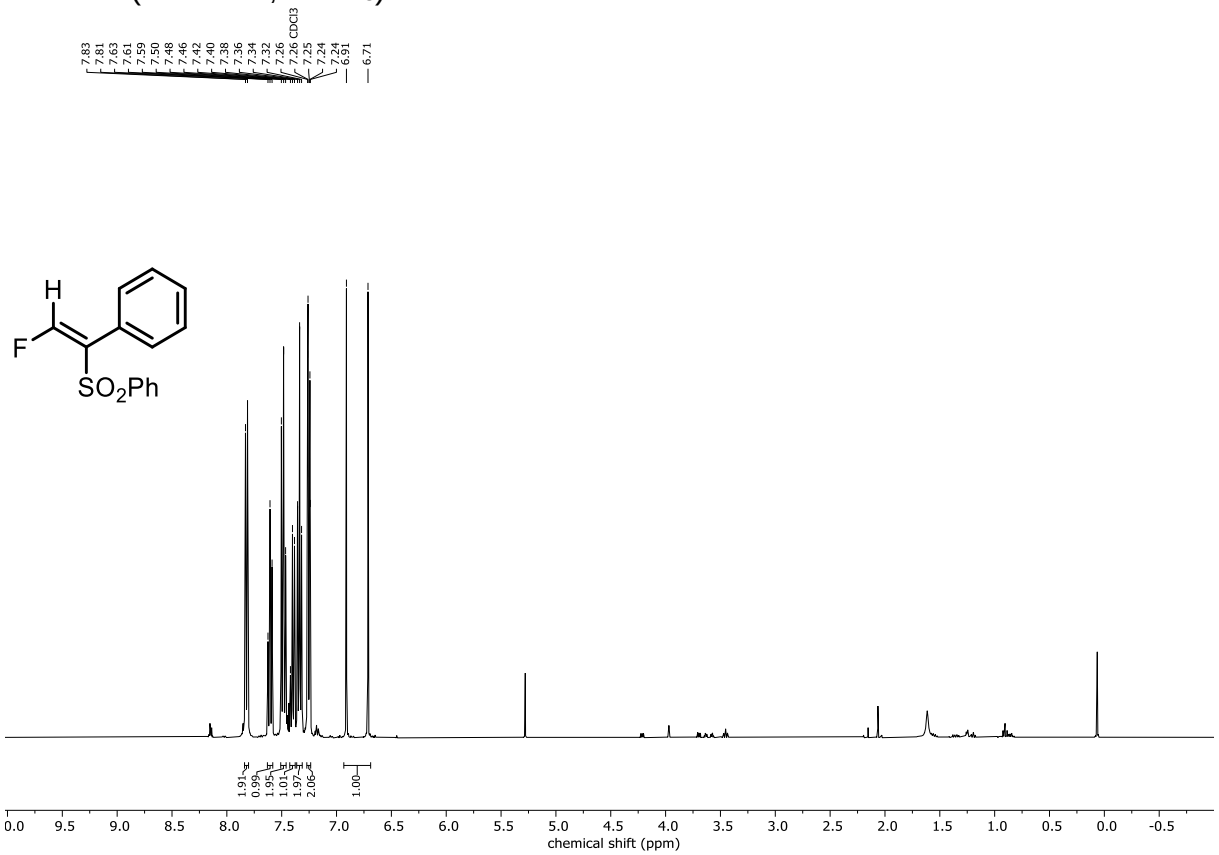
^{19}F NMR (376 MHz, $CDCl_3$) of **4h'**



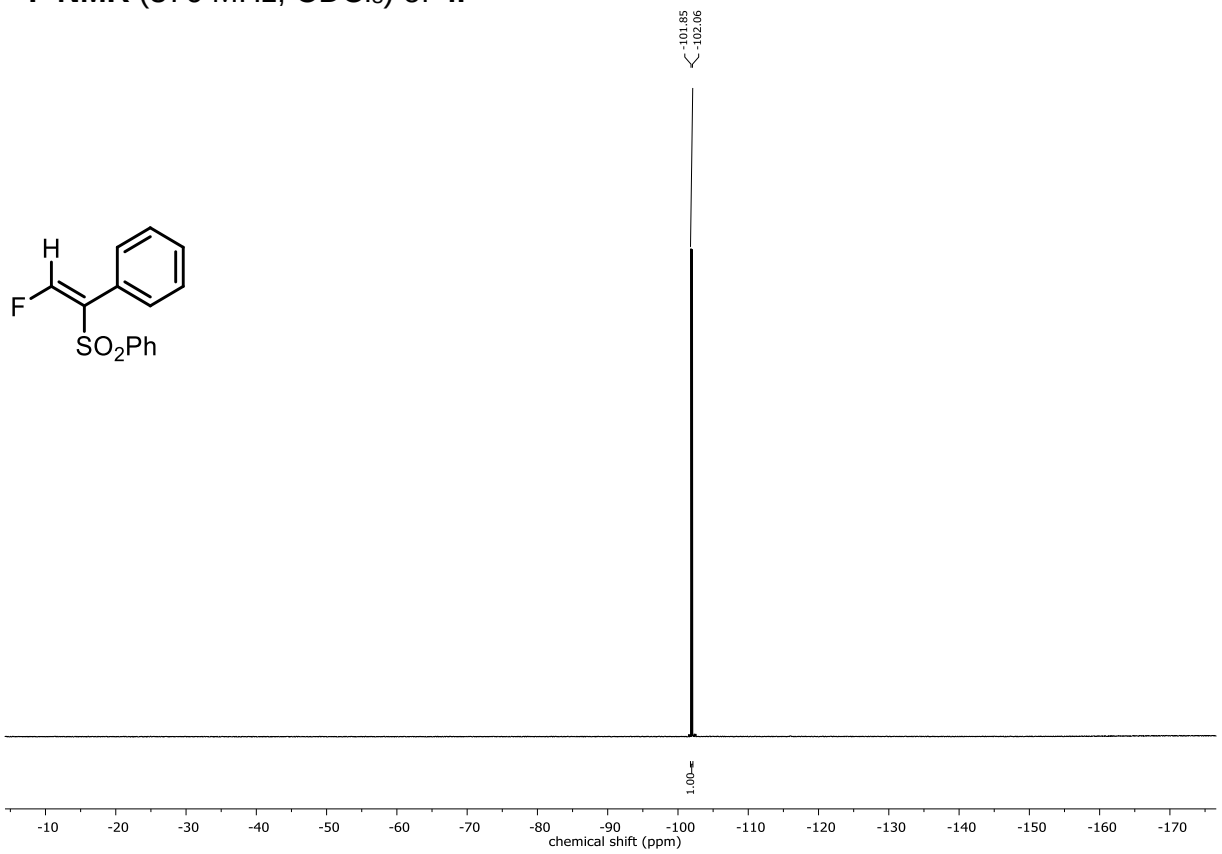
^{13}C NMR (101 MHz, $CDCl_3$) of **4h'**



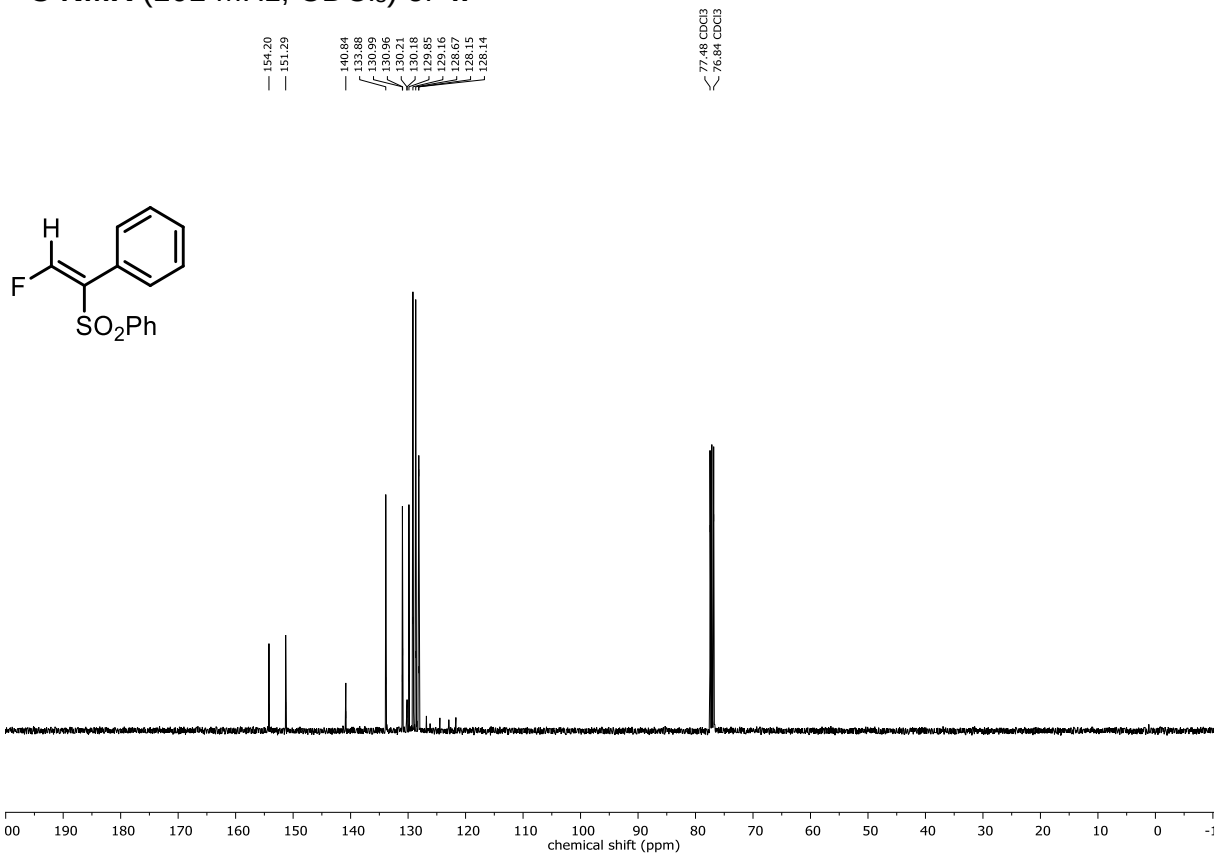
^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



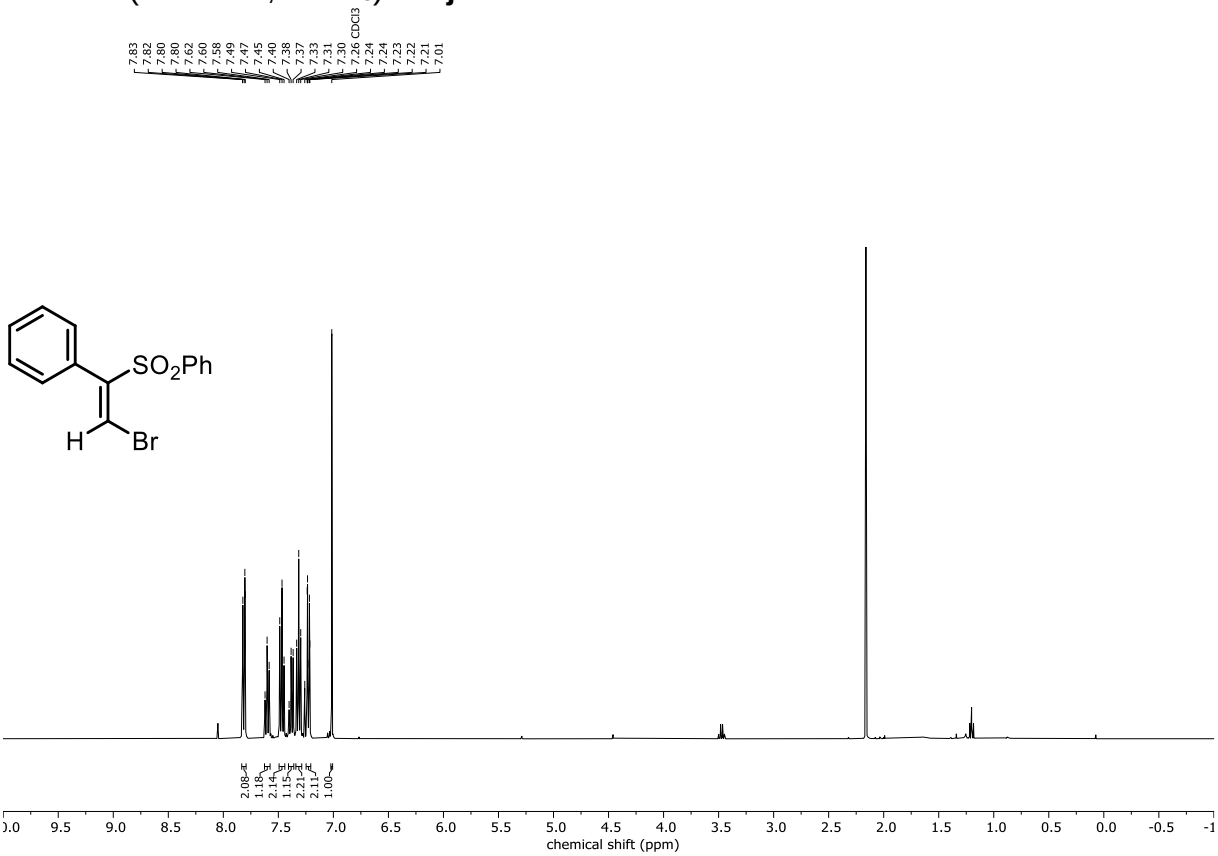
^{19}F NMR (376 MHz, $CDCl_3$) of **4i**



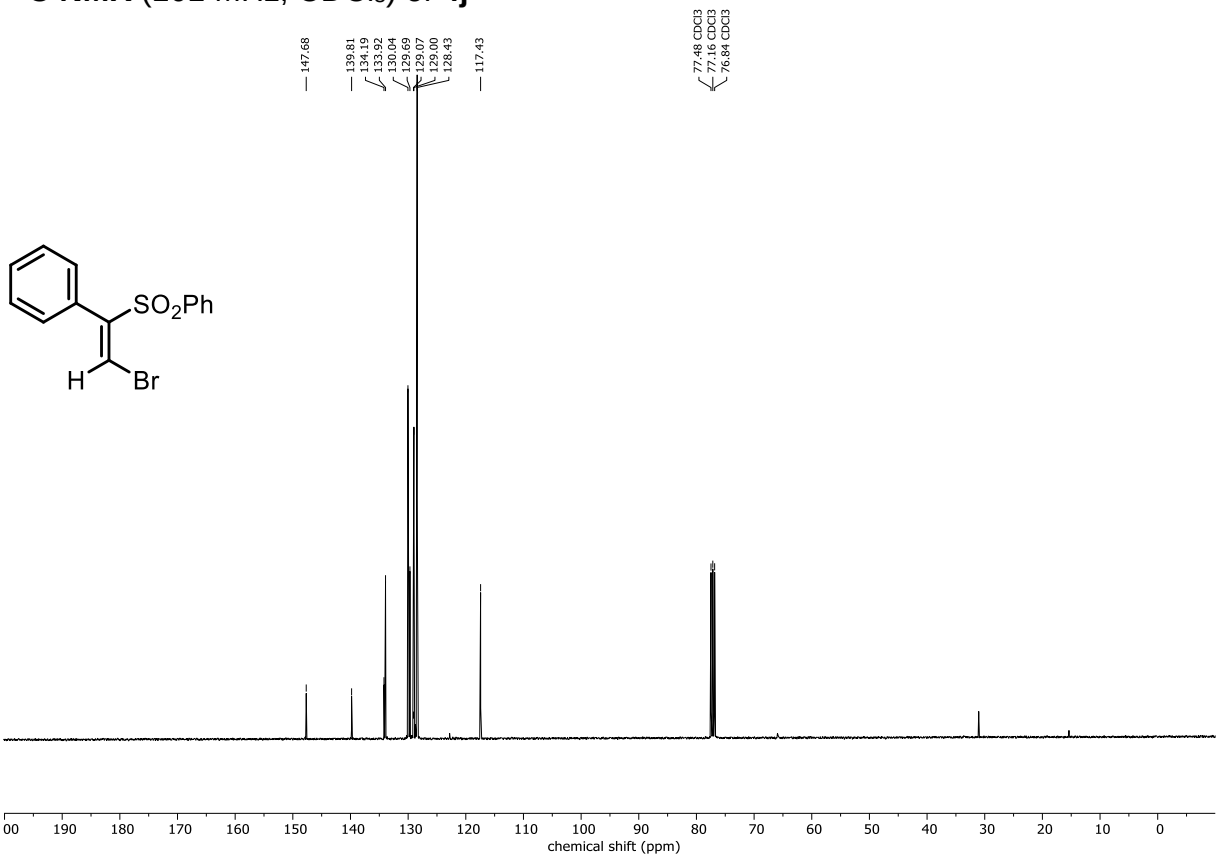
^{13}C NMR (101 MHz, $CDCl_3$) of **4i**



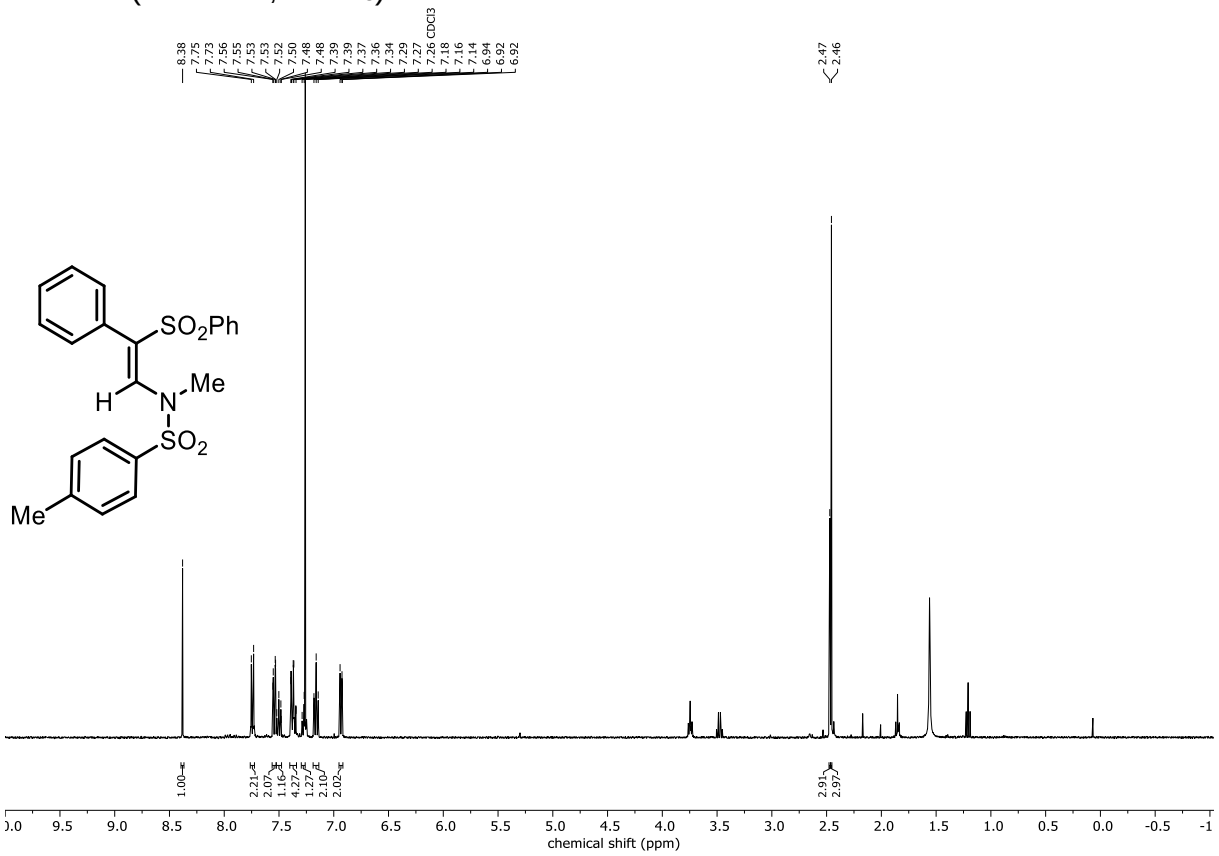
^{1}H NMR (400 MHz, $CDCl_3$) of **4j**



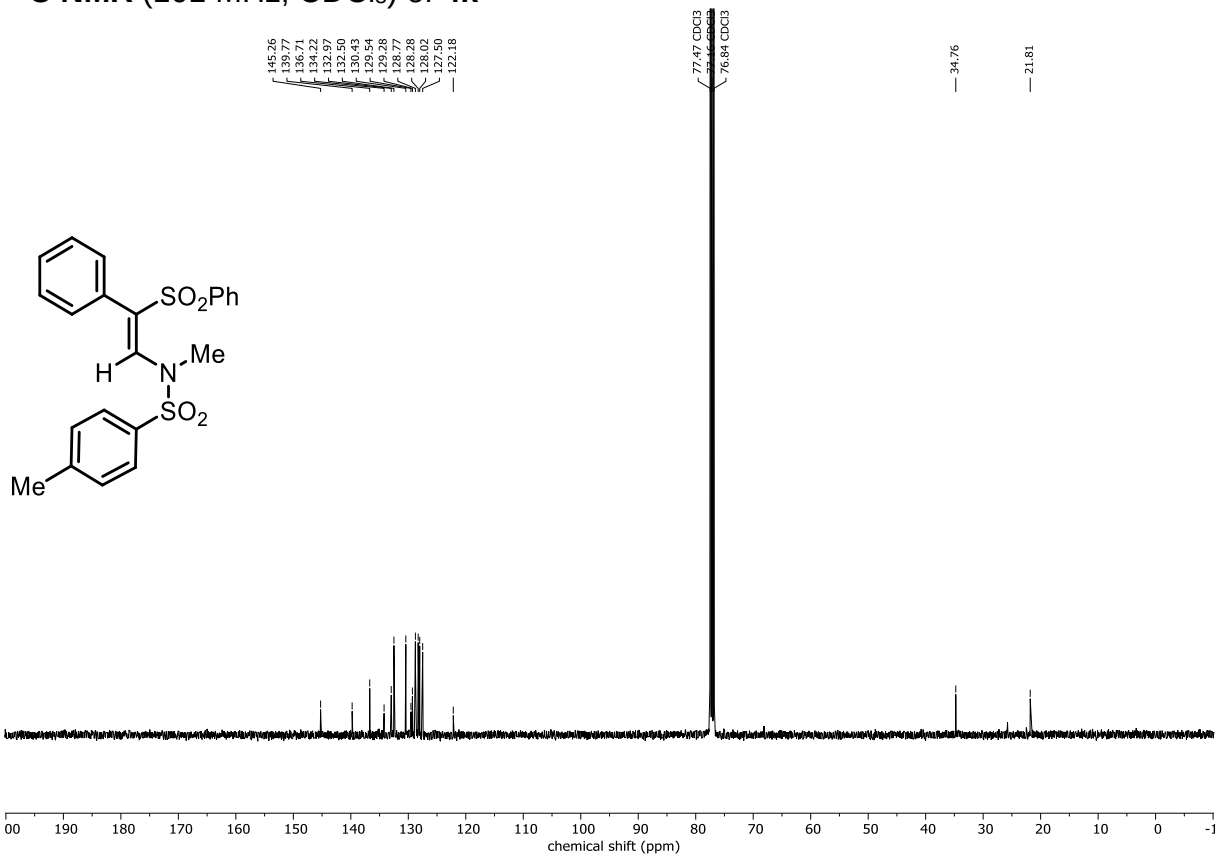
^{13}C NMR (101 MHz, $CDCl_3$) of **4j**



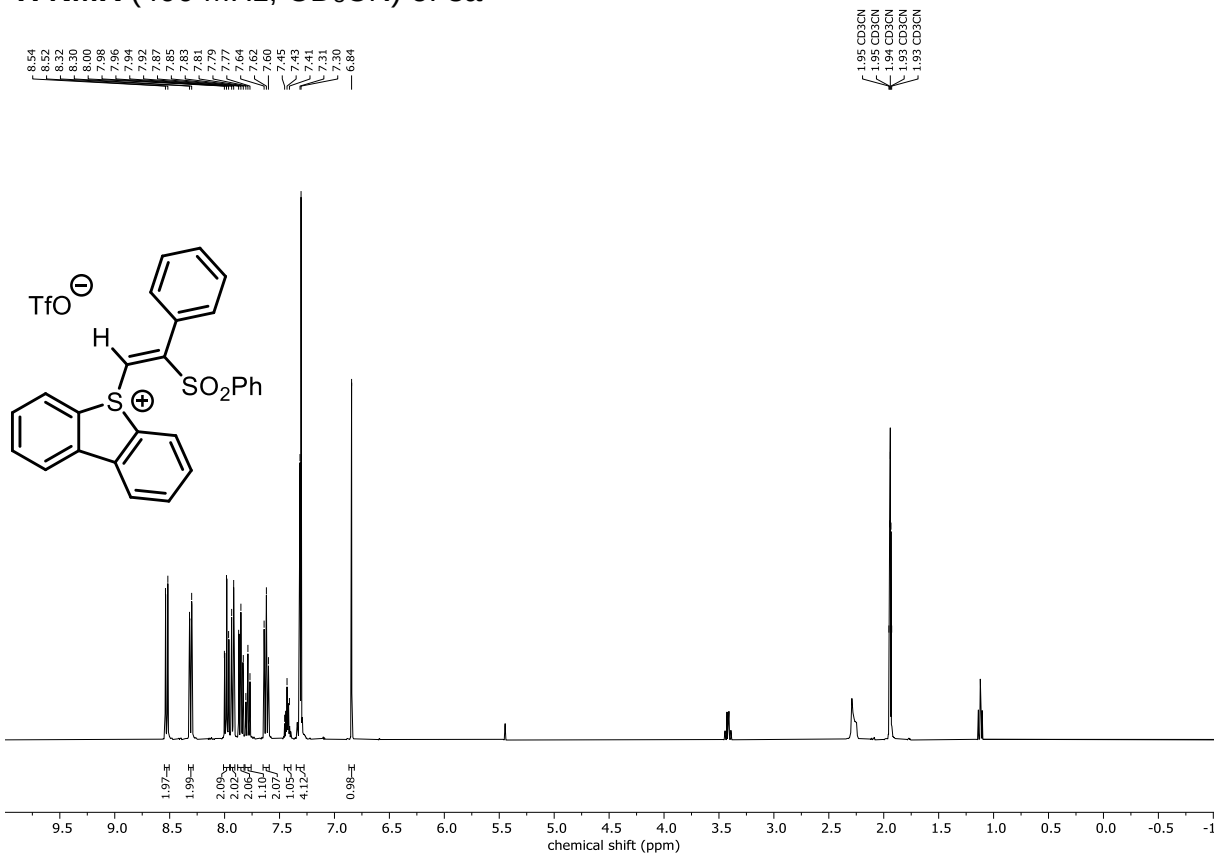
^{1}H NMR (400 MHz, $CDCl_3$) of **4k**



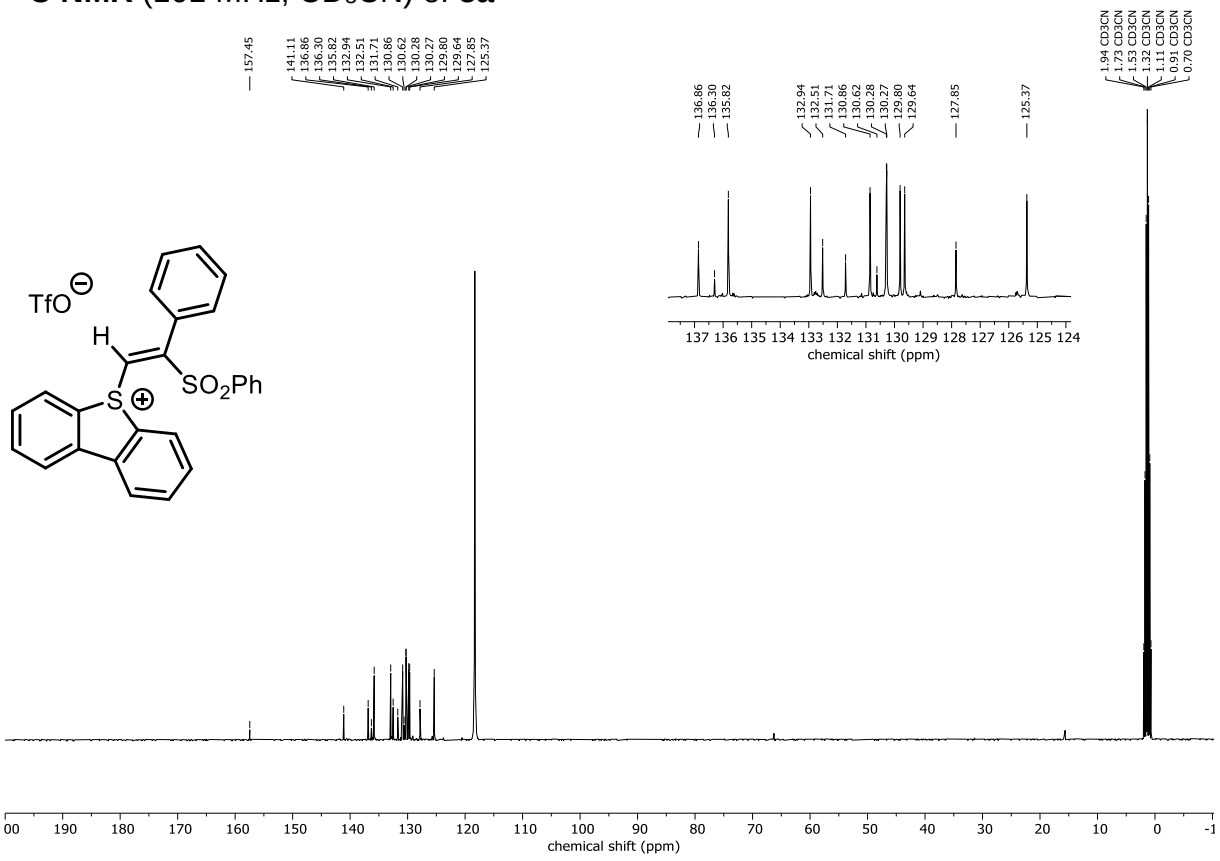
^{13}C NMR (101 MHz, $CDCl_3$) of **4k**



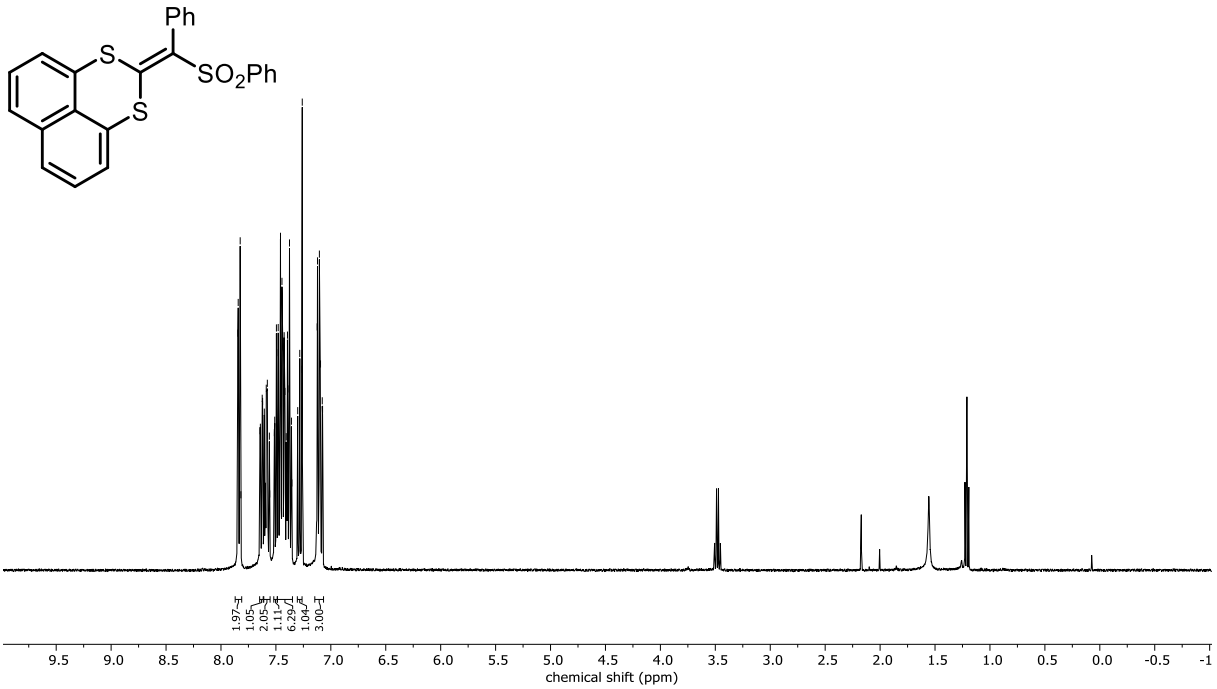
^{1}H NMR (400 MHz, CD_3CN) of **5a**



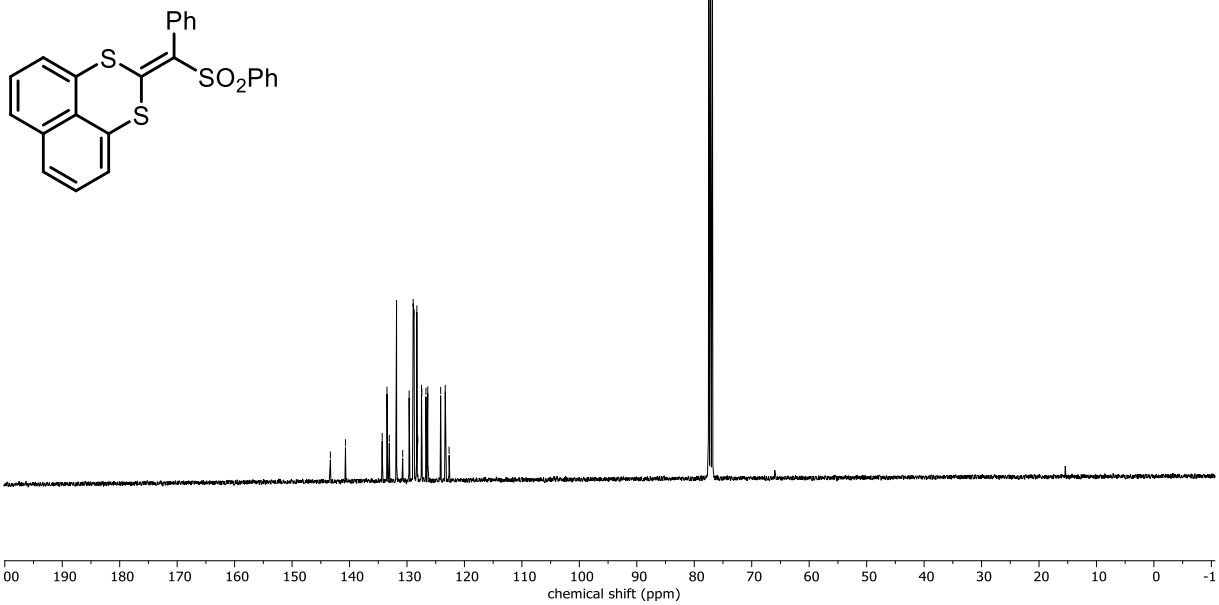
^{13}C NMR (101 MHz, CD_3CN) of **5a**



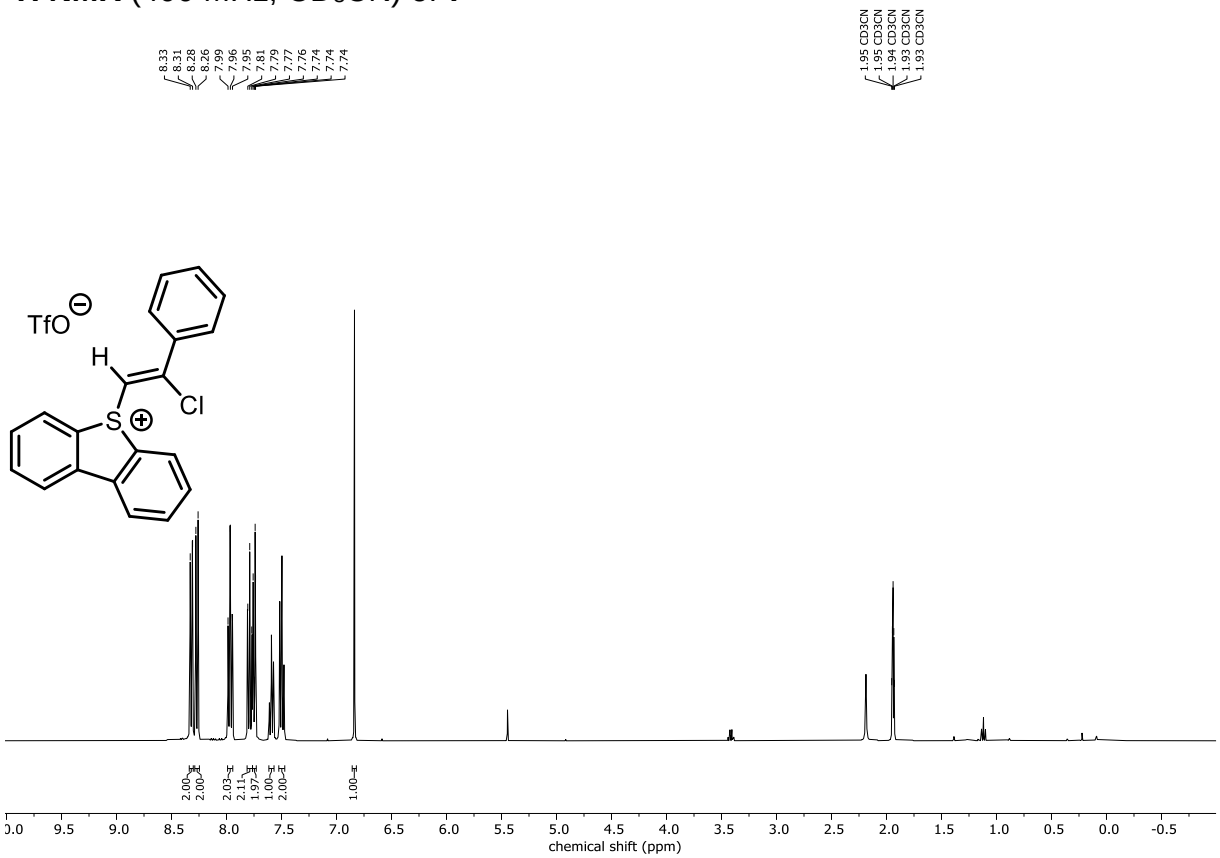
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



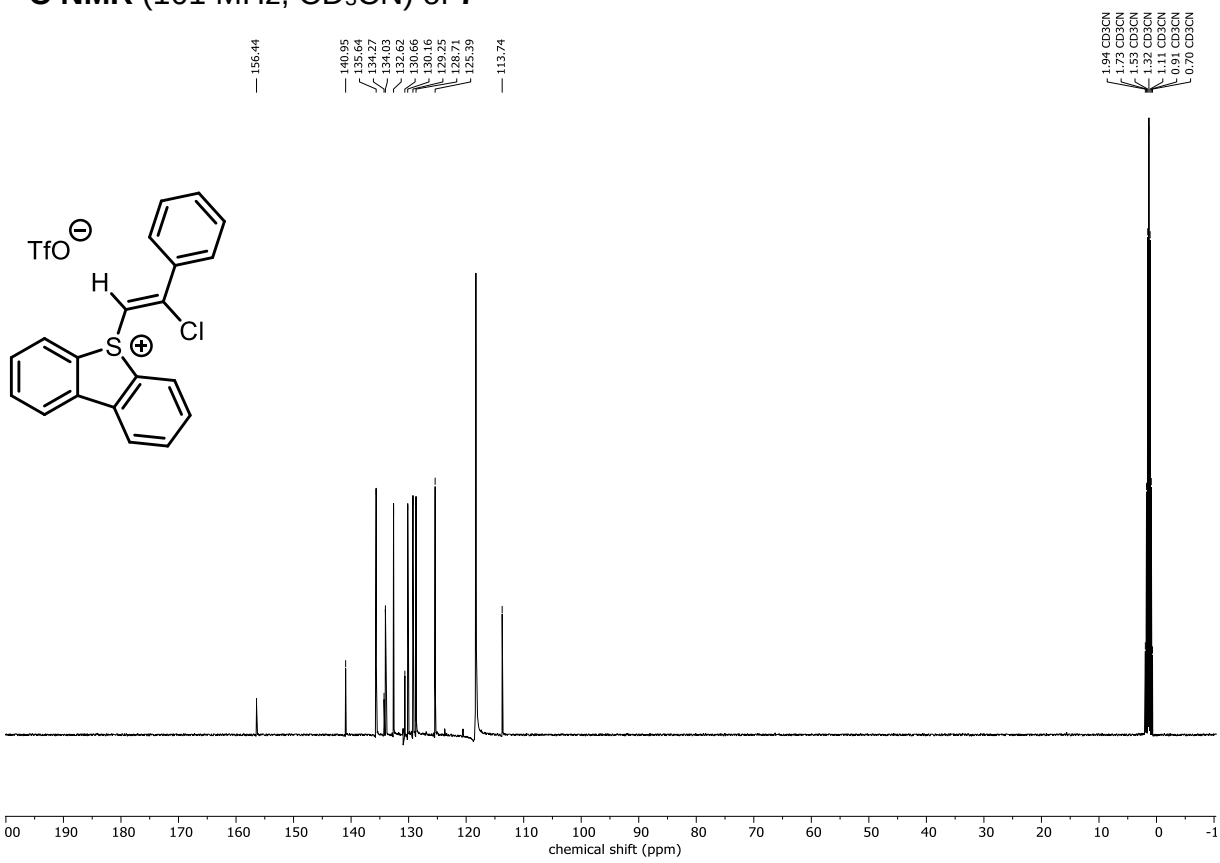
^{13}C NMR (101 MHz, $CDCl_3$) of **6**



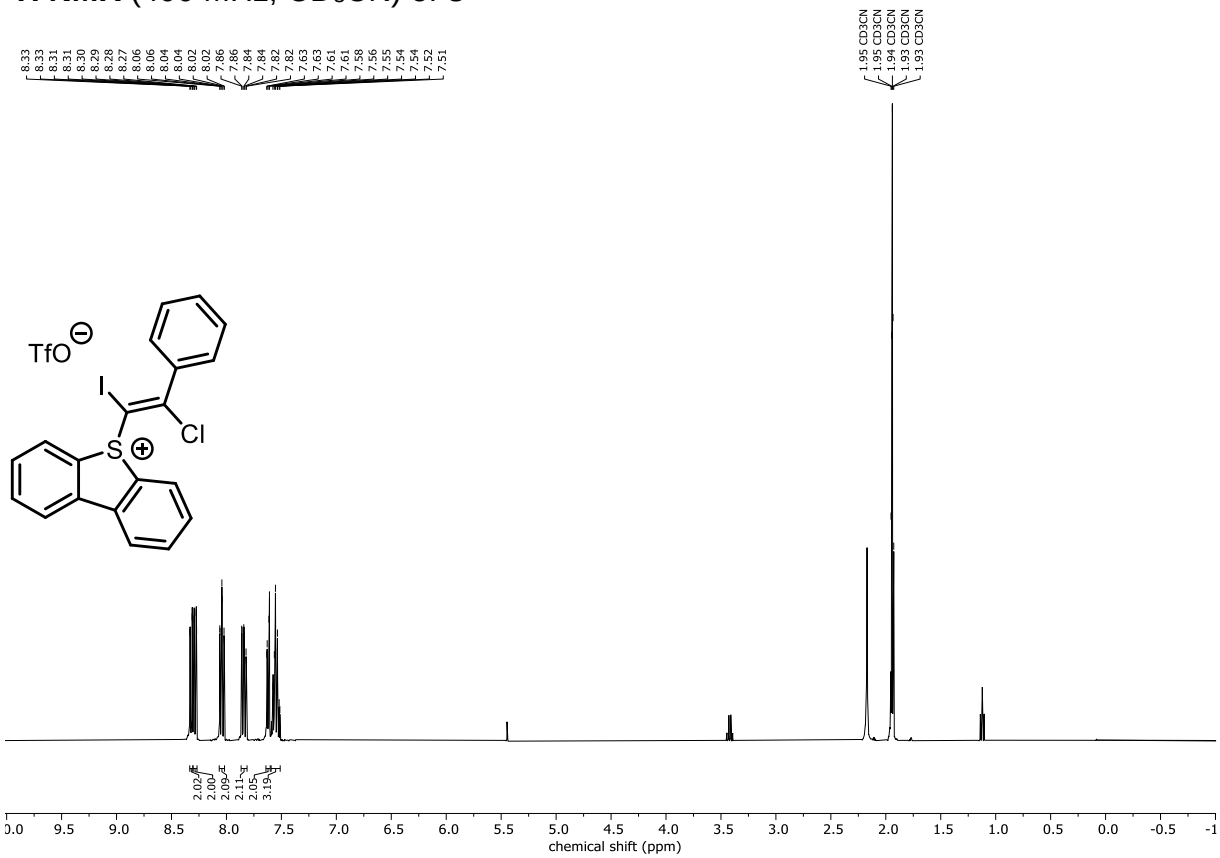
^{1}H NMR (400 MHz, CD_3CN) of **7**



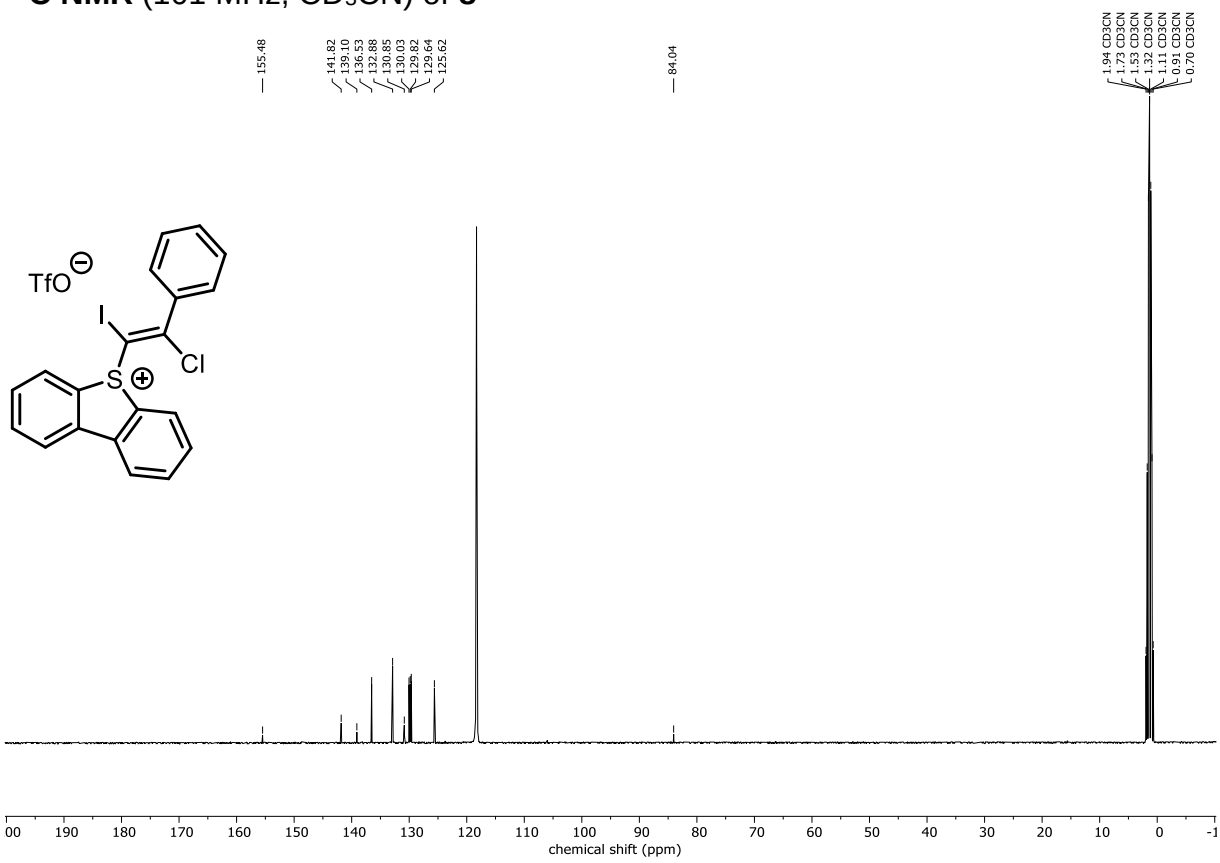
^{13}C NMR (101 MHz, CD_3CN) of **7**



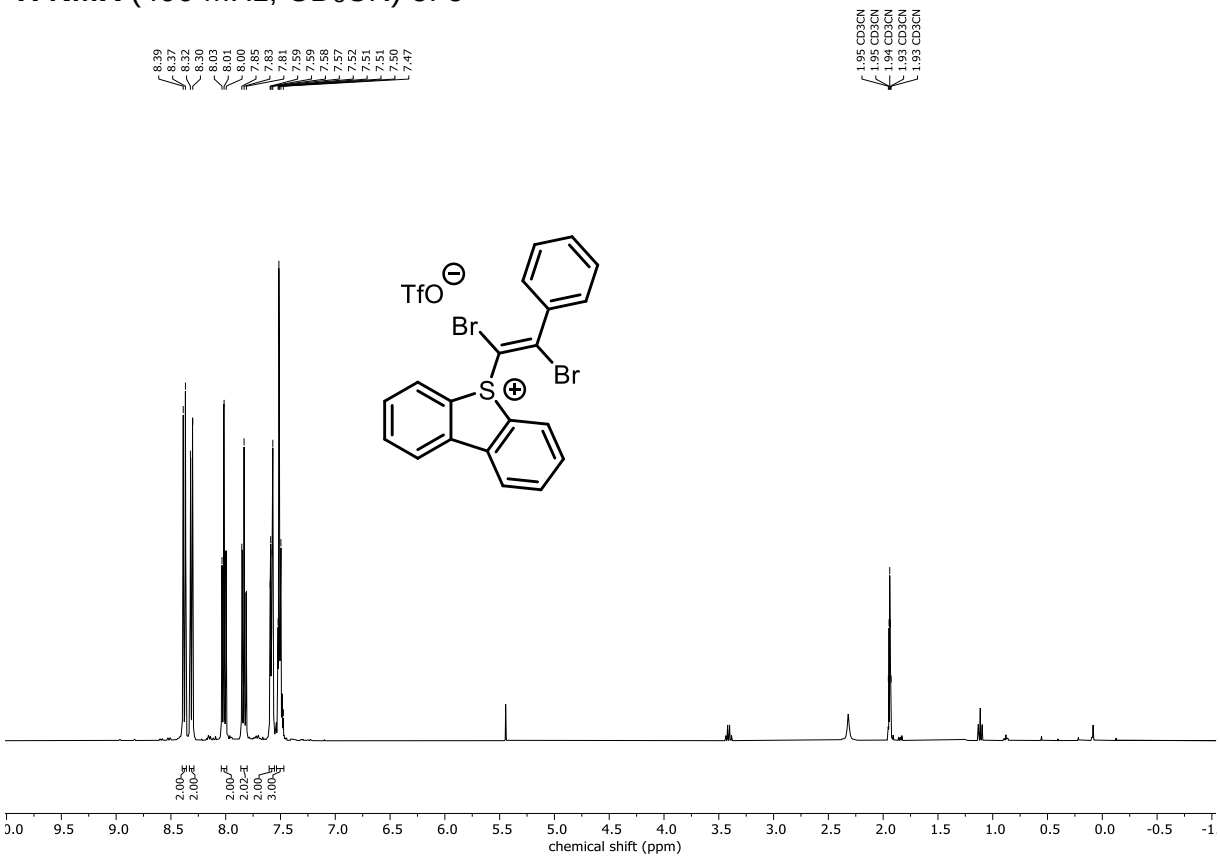
^{1}H NMR (400 MHz, CD_3CN) of **8**



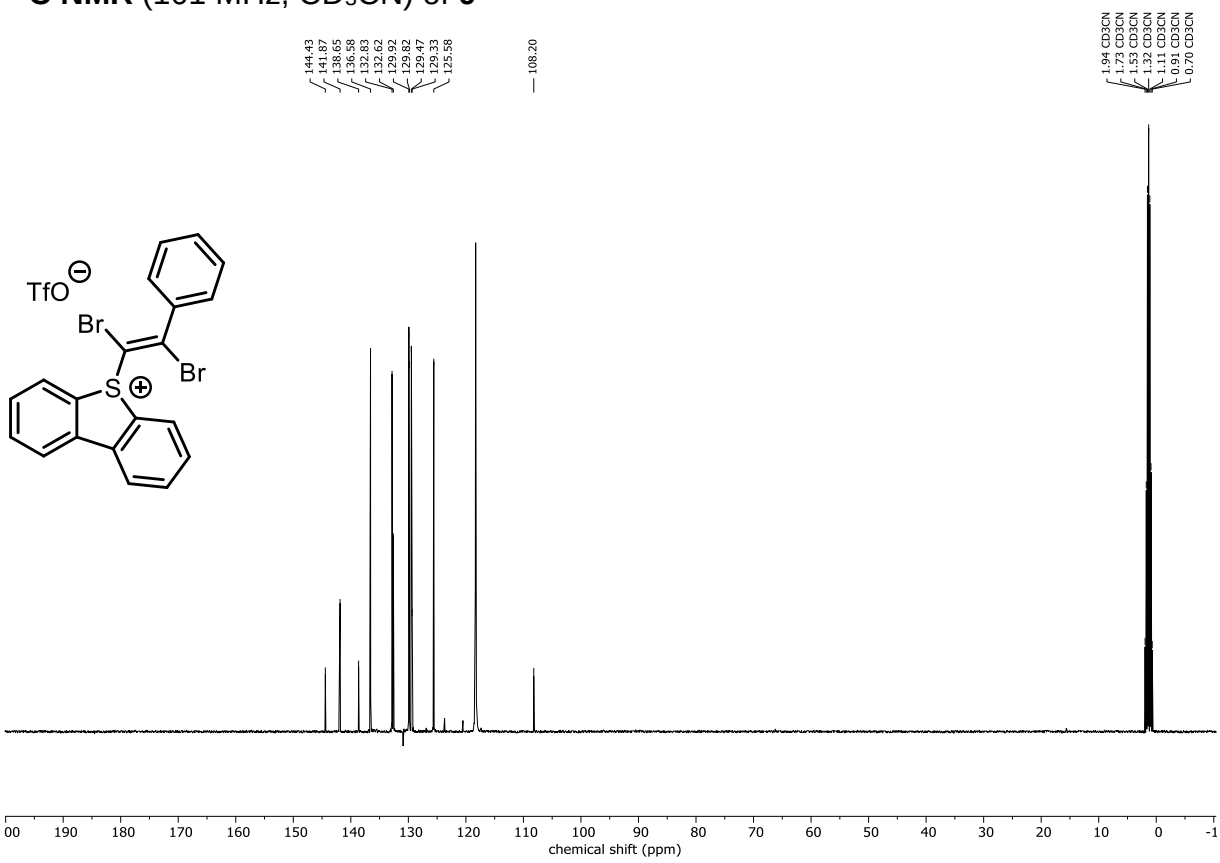
^{13}C NMR (101 MHz, CD_3CN) of **8**



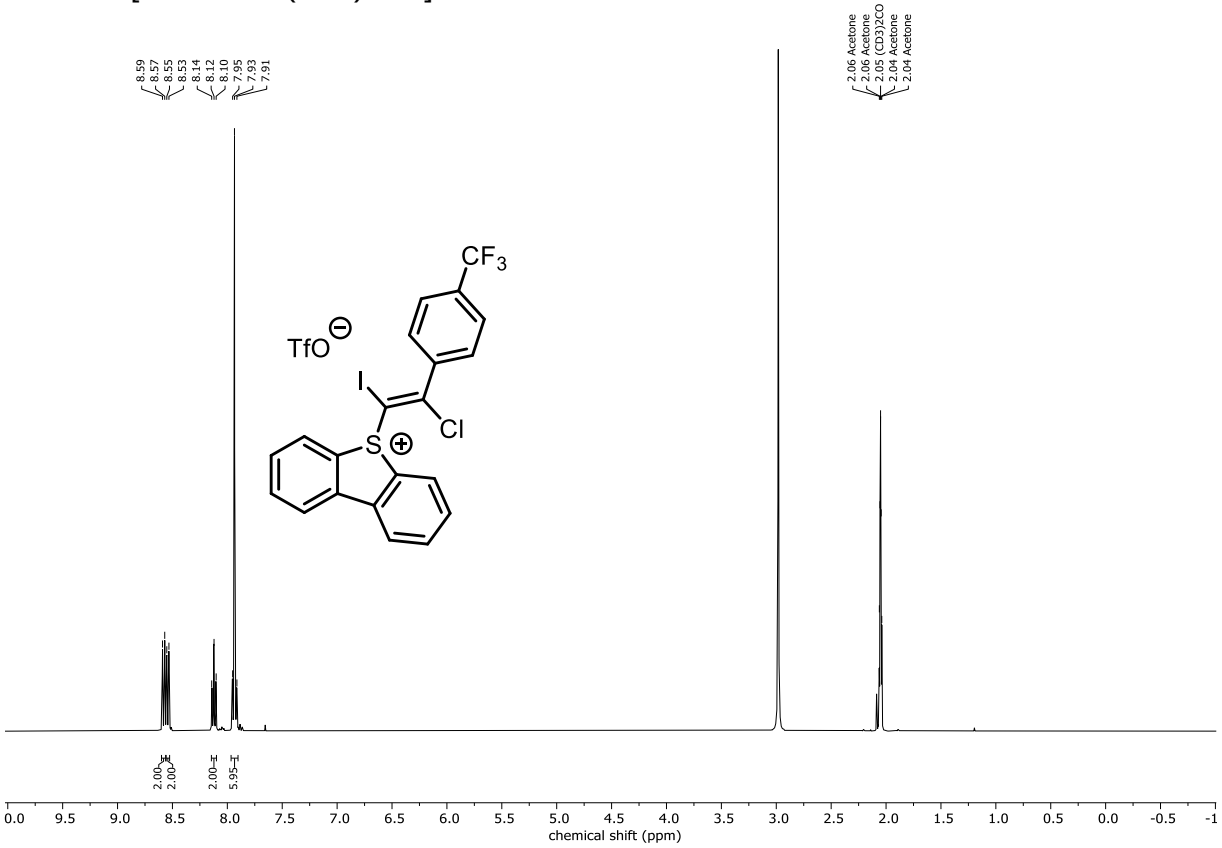
^{1}H NMR (400 MHz, CD_3CN) of **9**



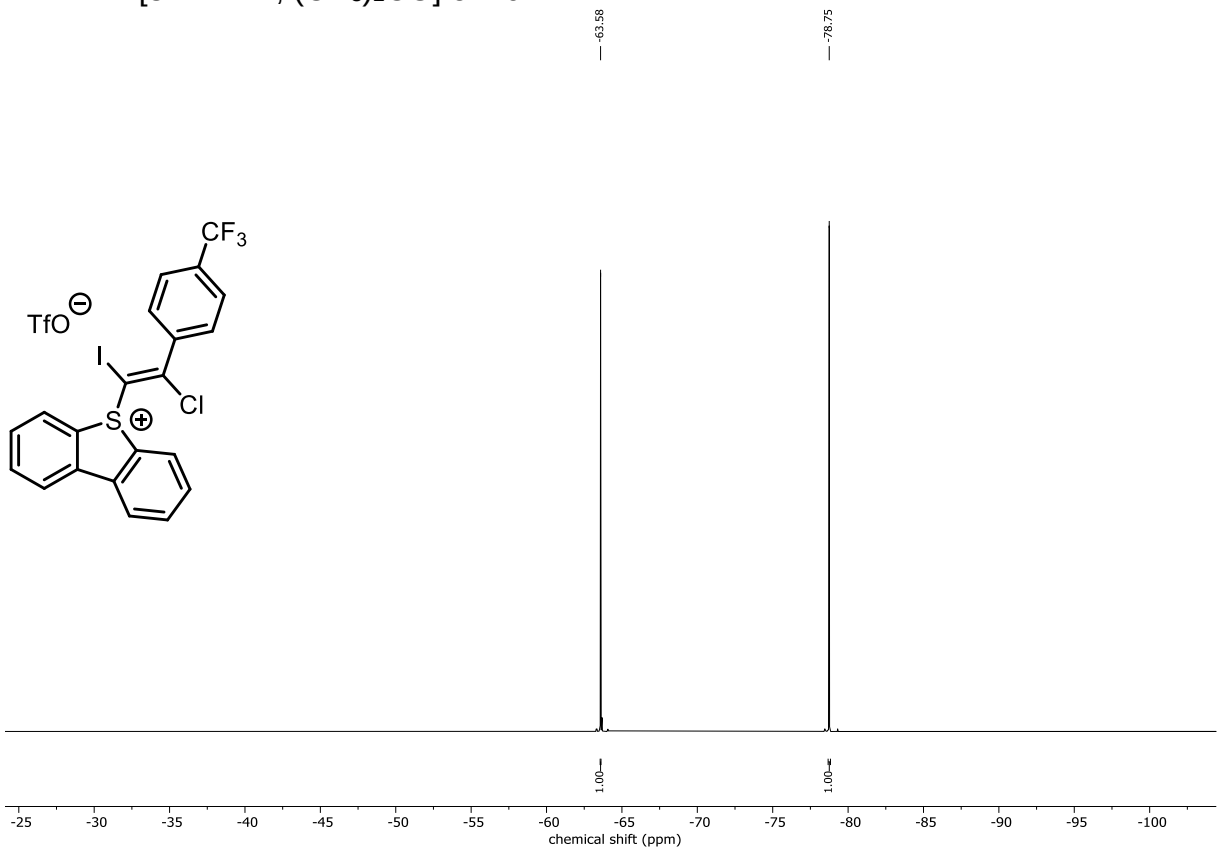
^{13}C NMR (101 MHz, CD_3CN) of **9**



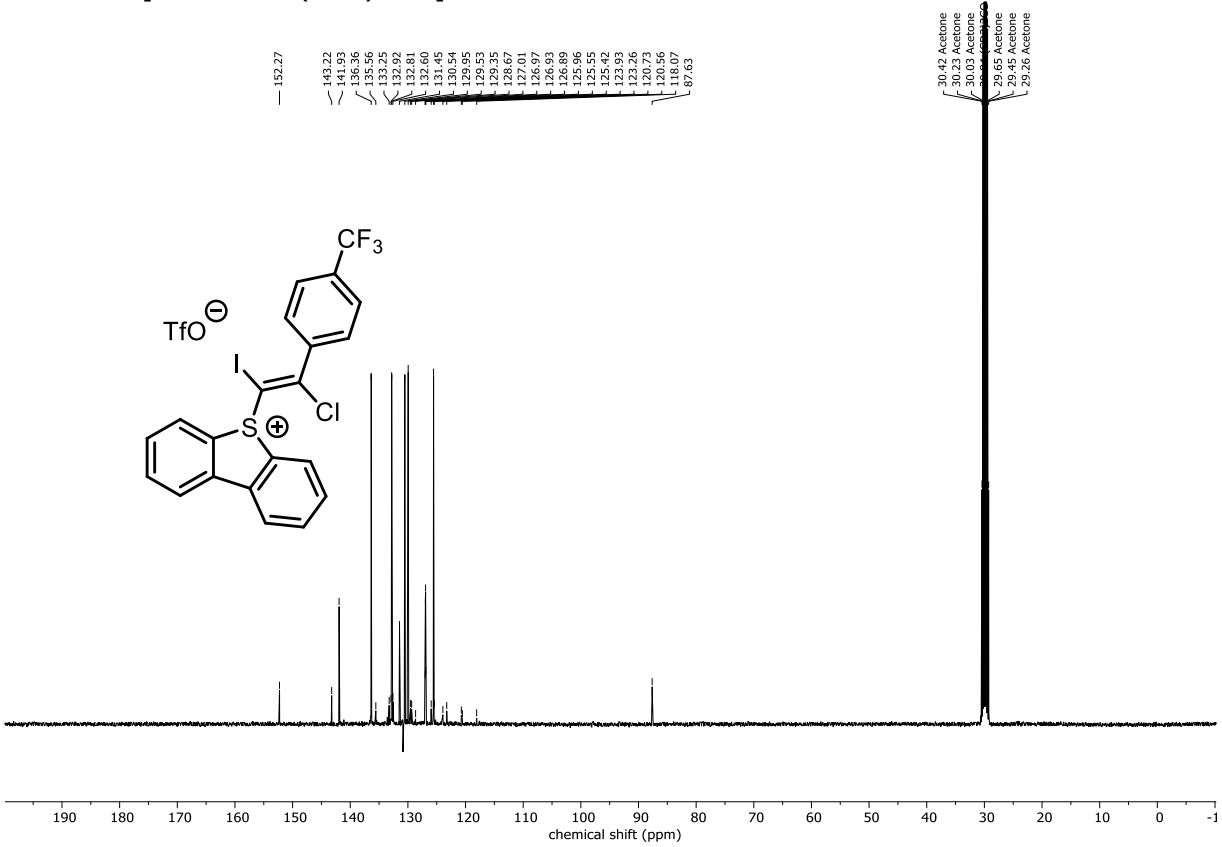
^{1}H NMR [400 MHz, $(CD_3)_2CO$] of **10**



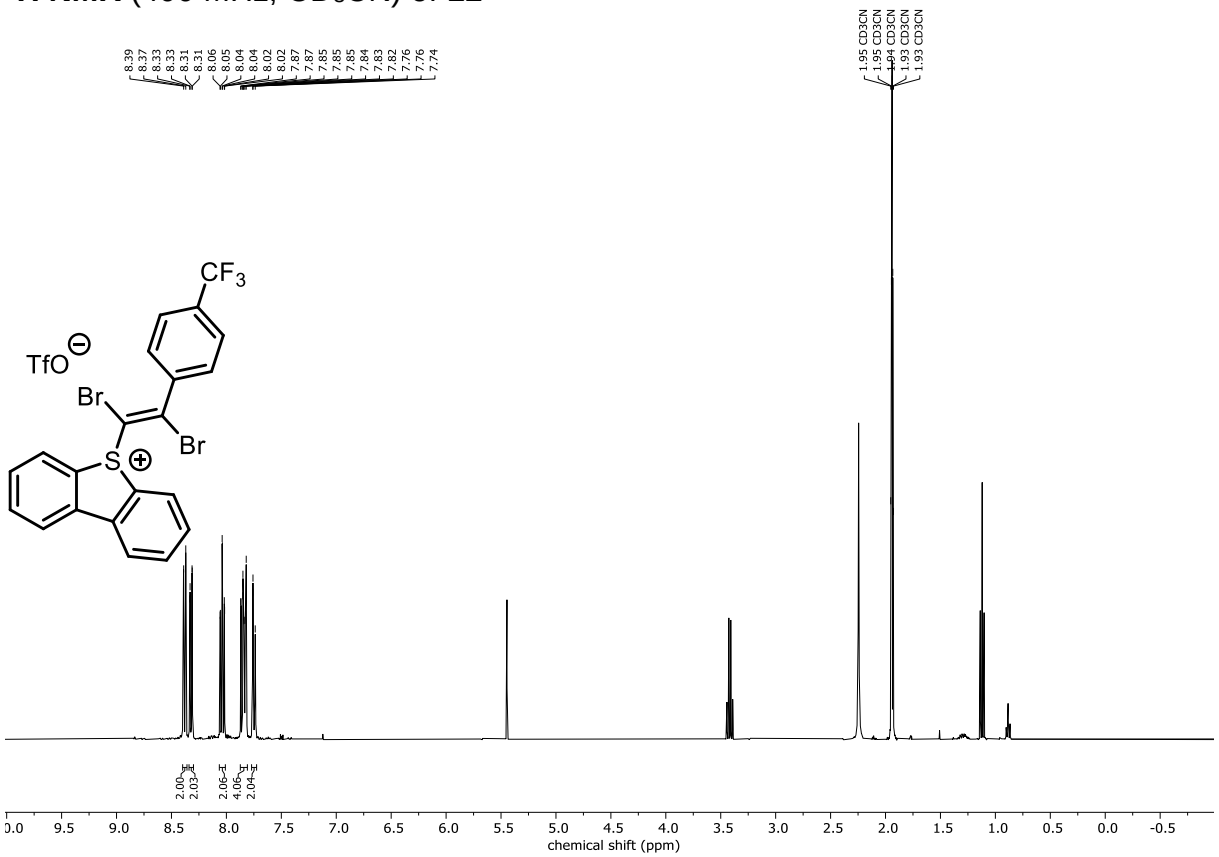
^{19}F NMR [377 MHz, $(CD_3)_2CO$] of **10**



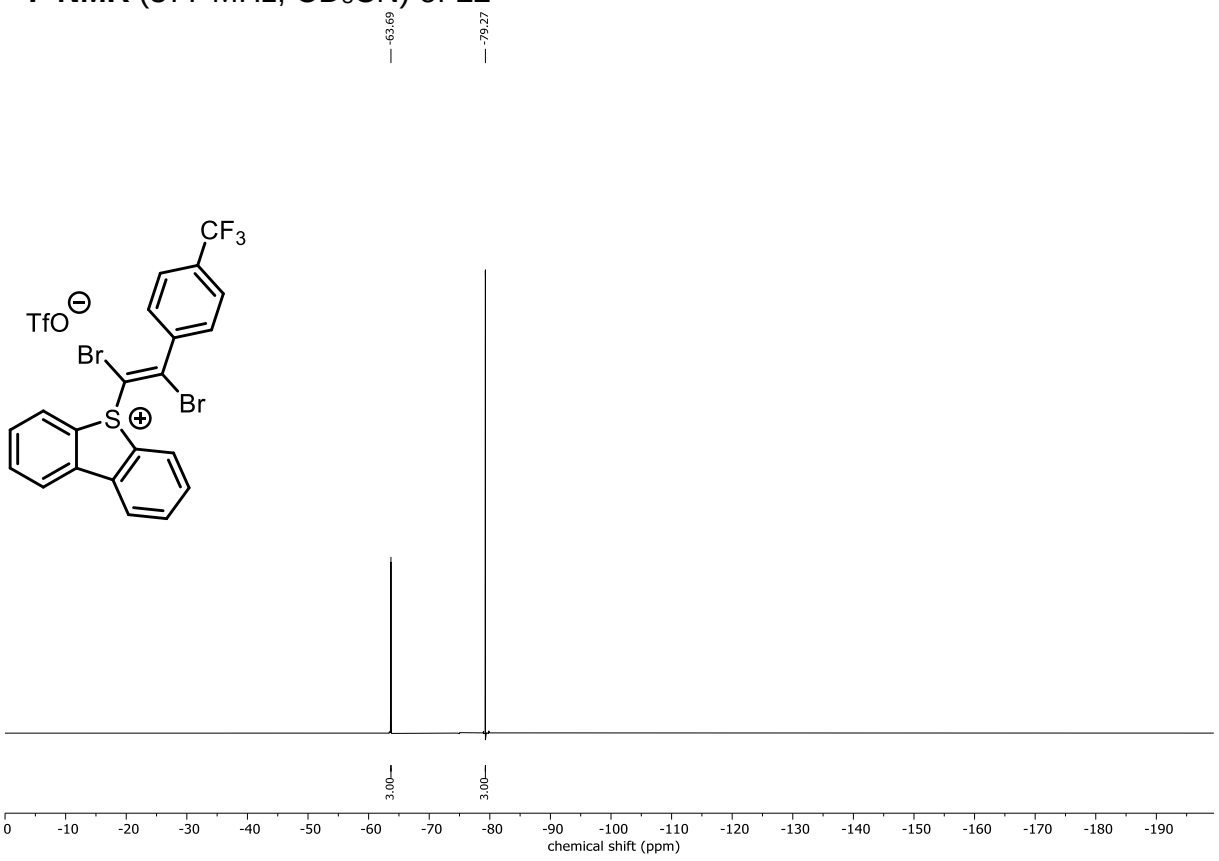
^{13}C NMR [101 MHz, $(CD_3)_2CO$] of **10**



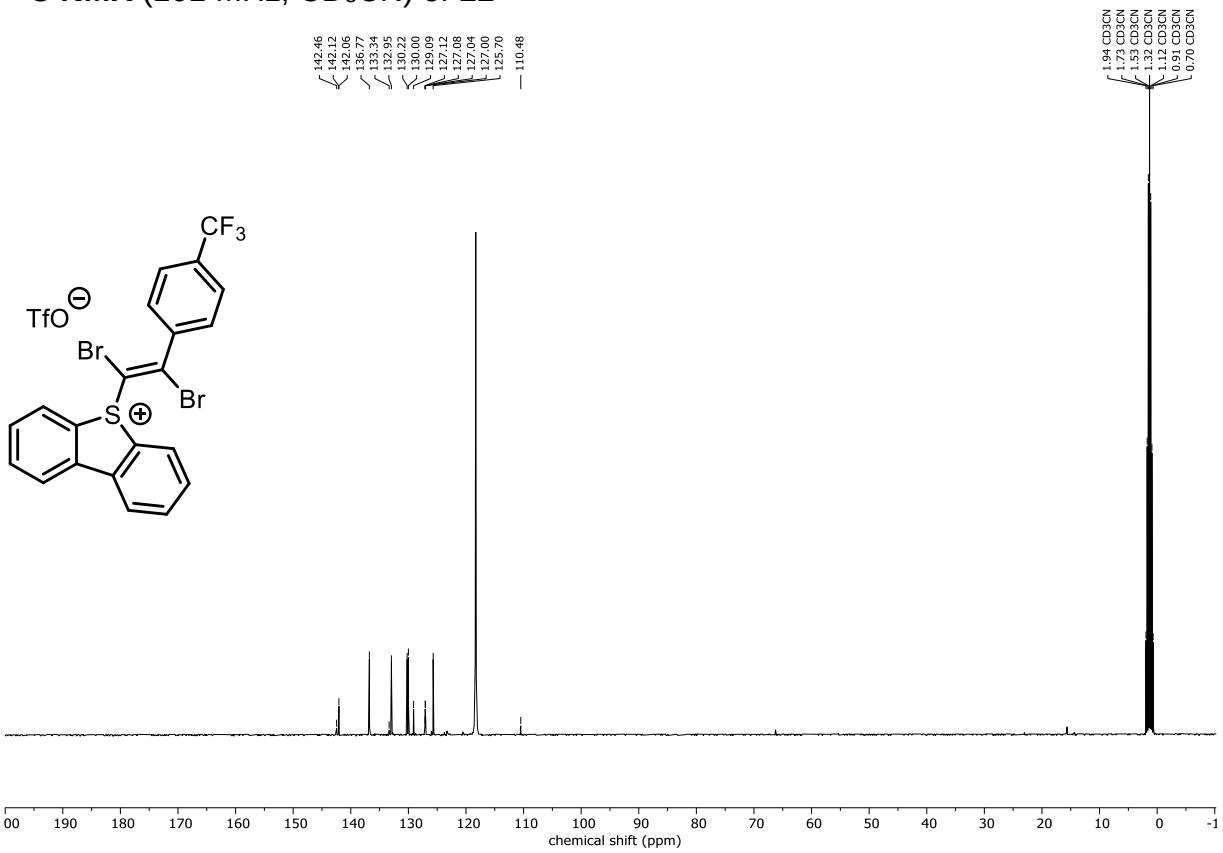
^{1}H NMR (400 MHz, CD_3CN) of **11**



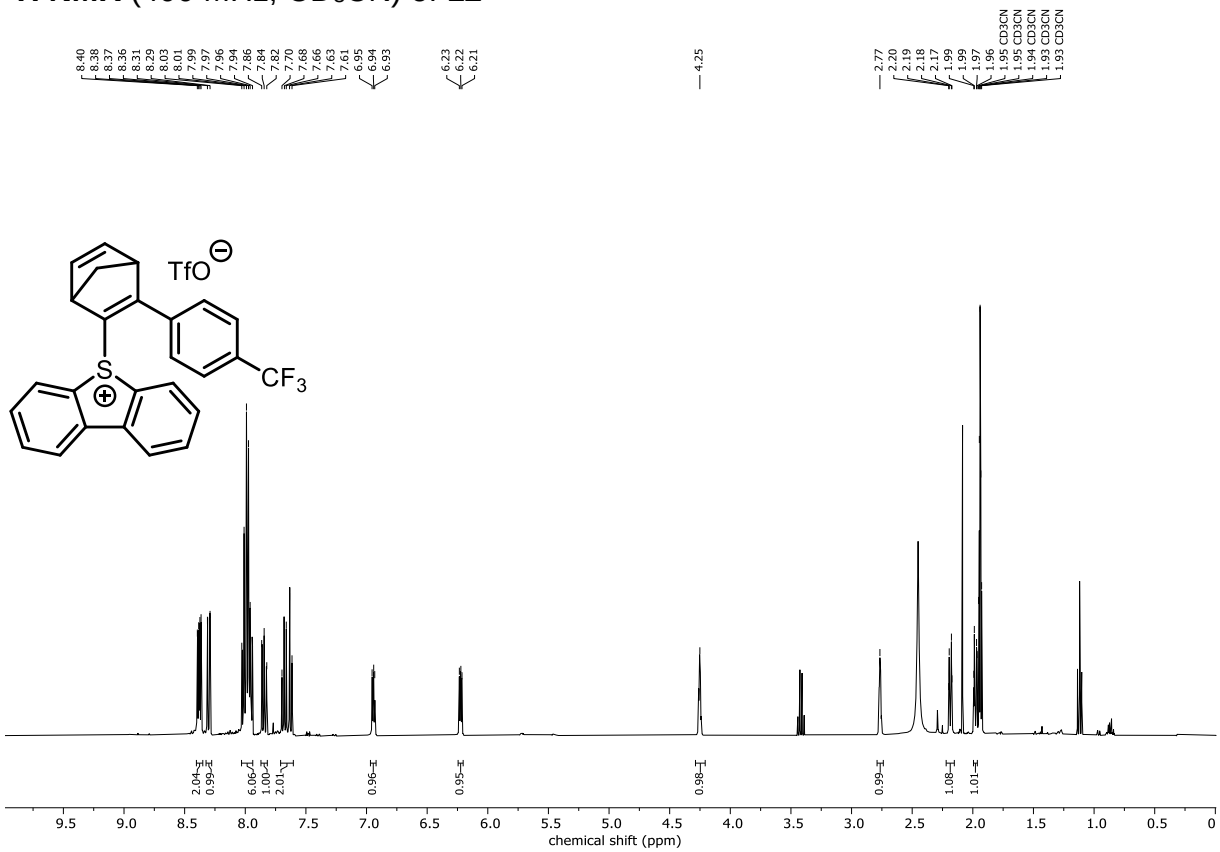
^{19}F NMR (377 MHz, CD_3CN) of **11**



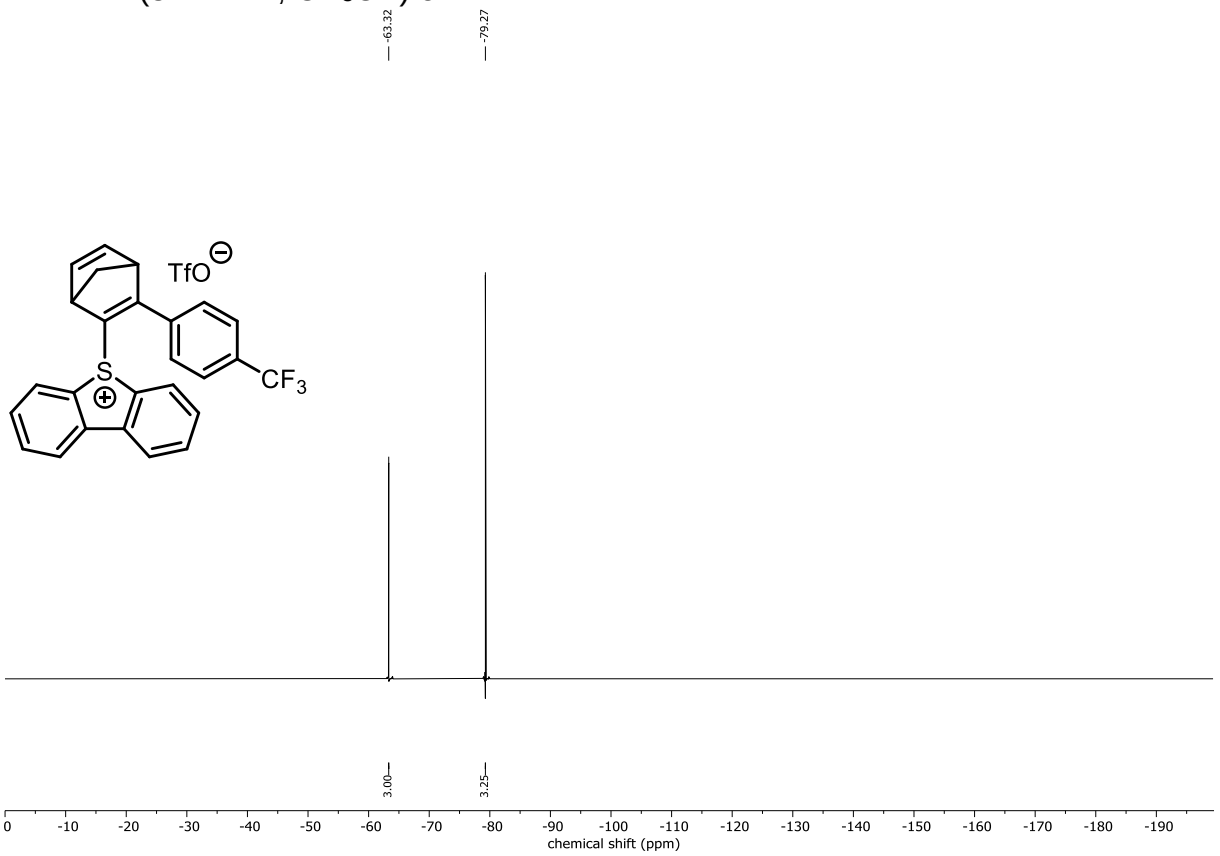
^{13}C NMR (101 MHz, CD_3CN) of **11**



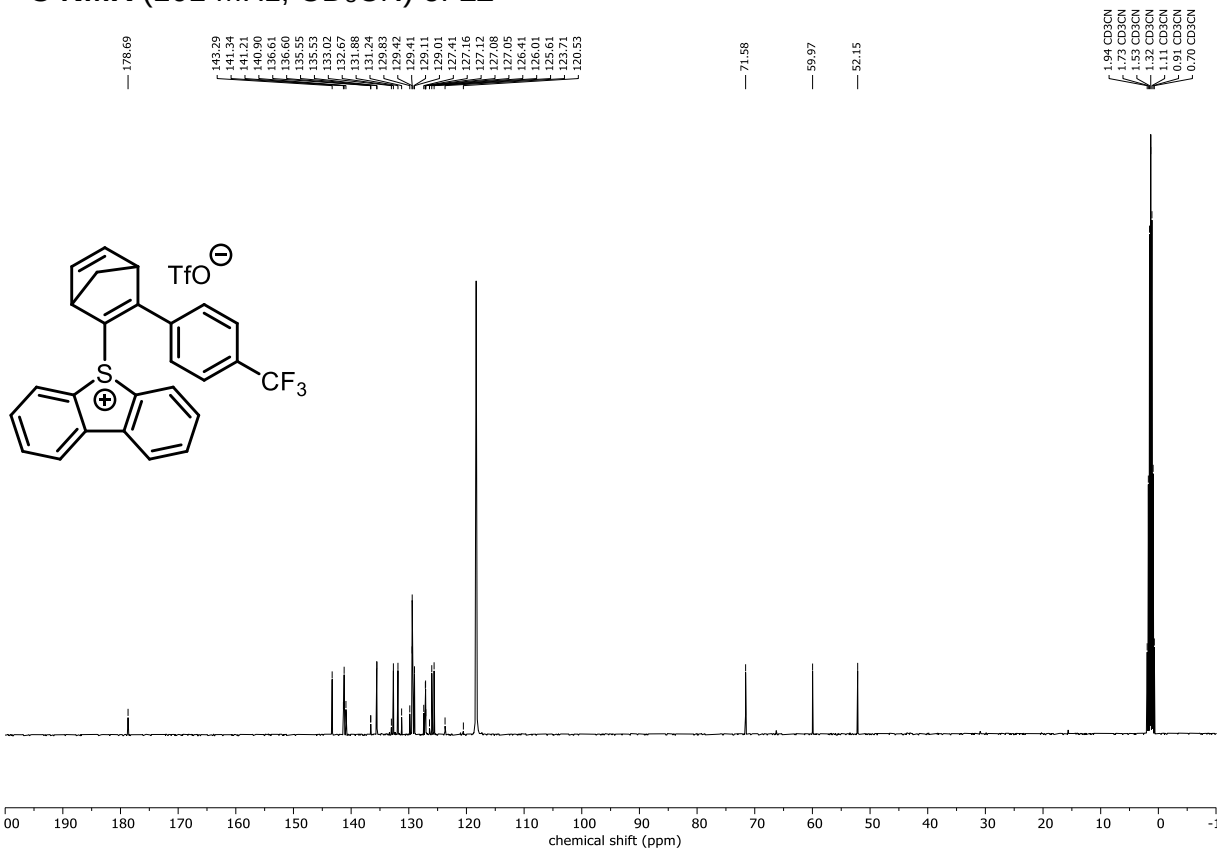
^{1}H NMR (400 MHz, CD_3CN) of **12**



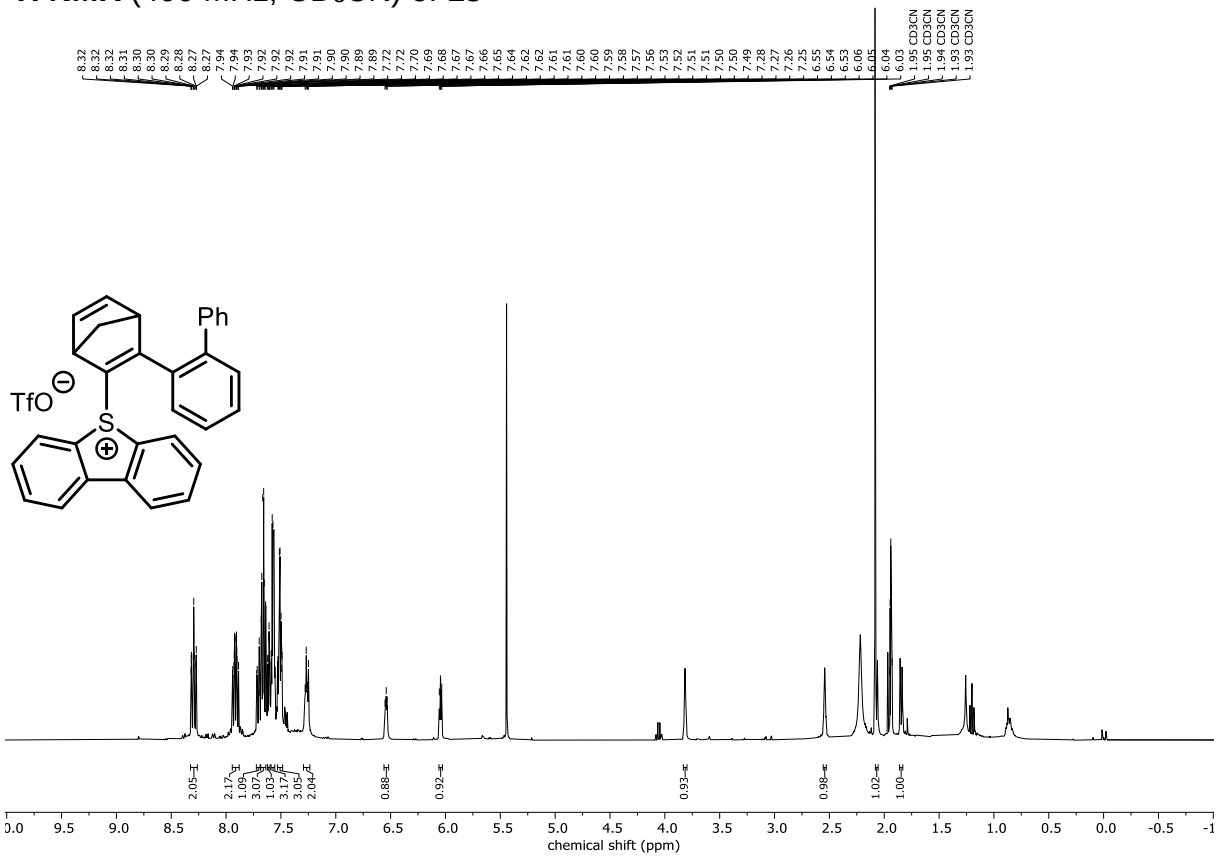
^{19}F NMR (377 MHz, CD_3CN) of **12**



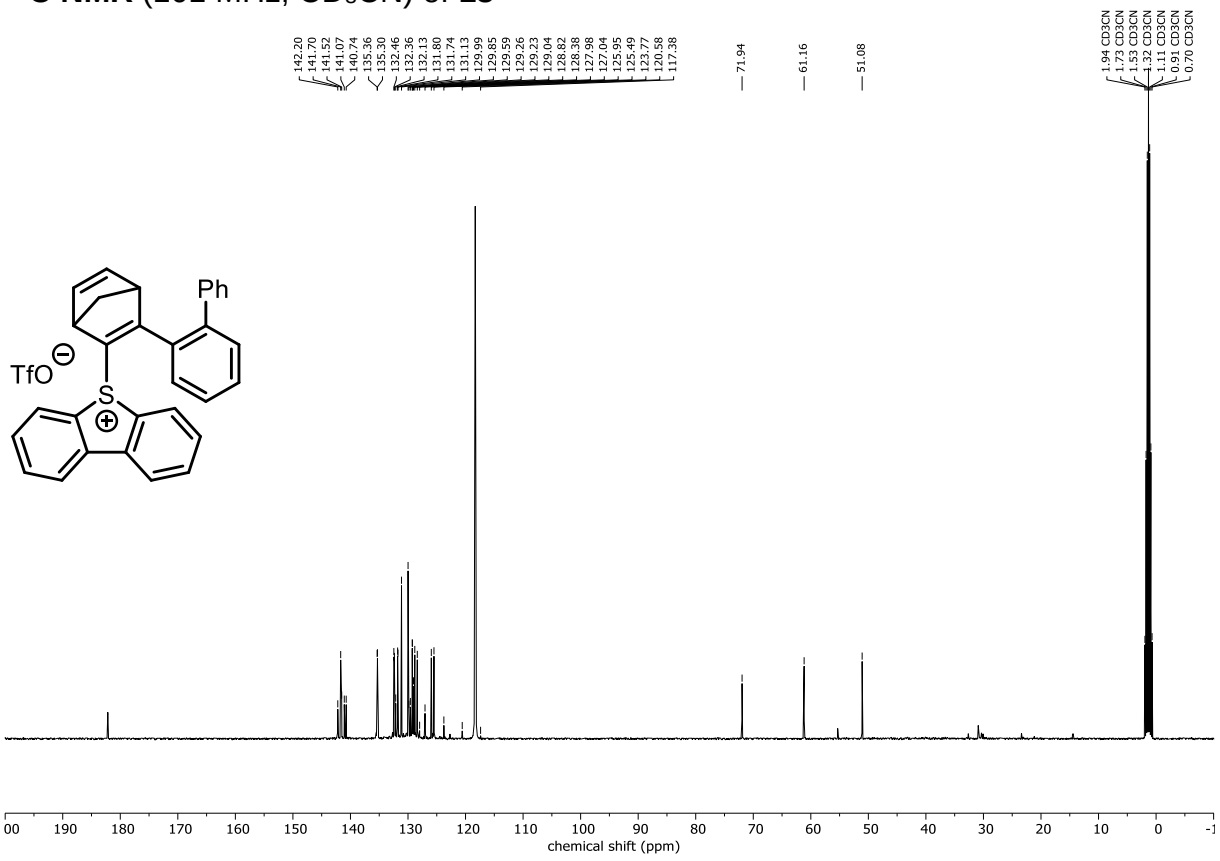
^{13}C NMR (101 MHz, CD_3CN) of **12**



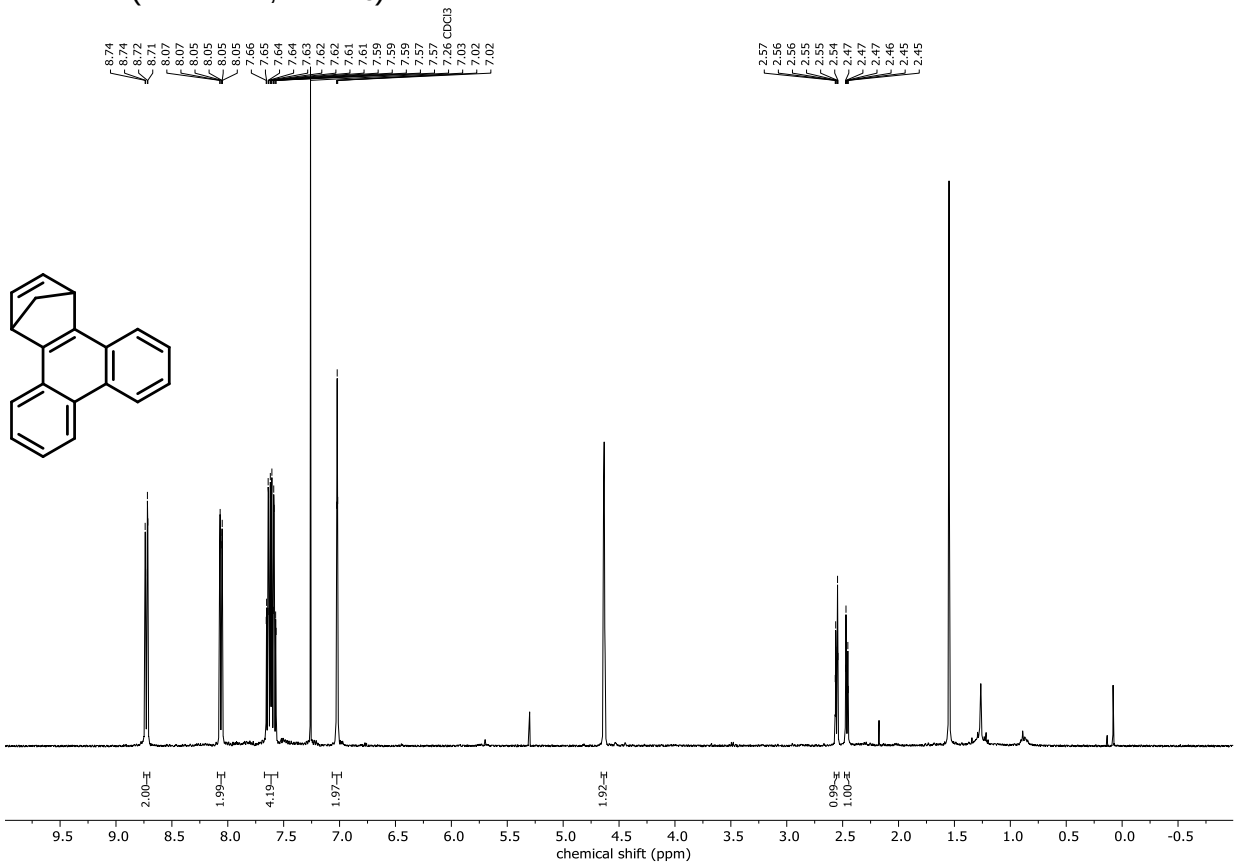
^{1}H NMR (400 MHz, CD_3CN) of **13**



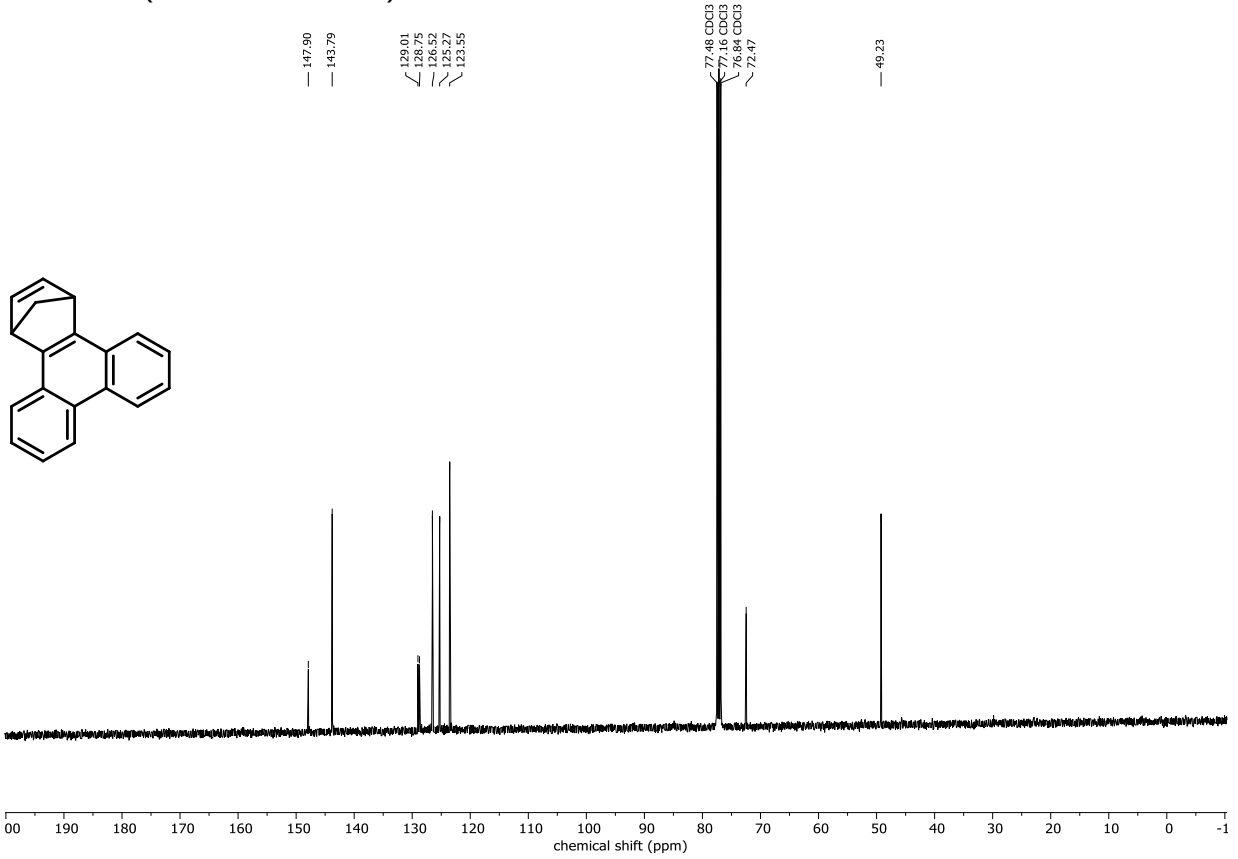
^{13}C NMR (101 MHz, CD_3CN) of **13**



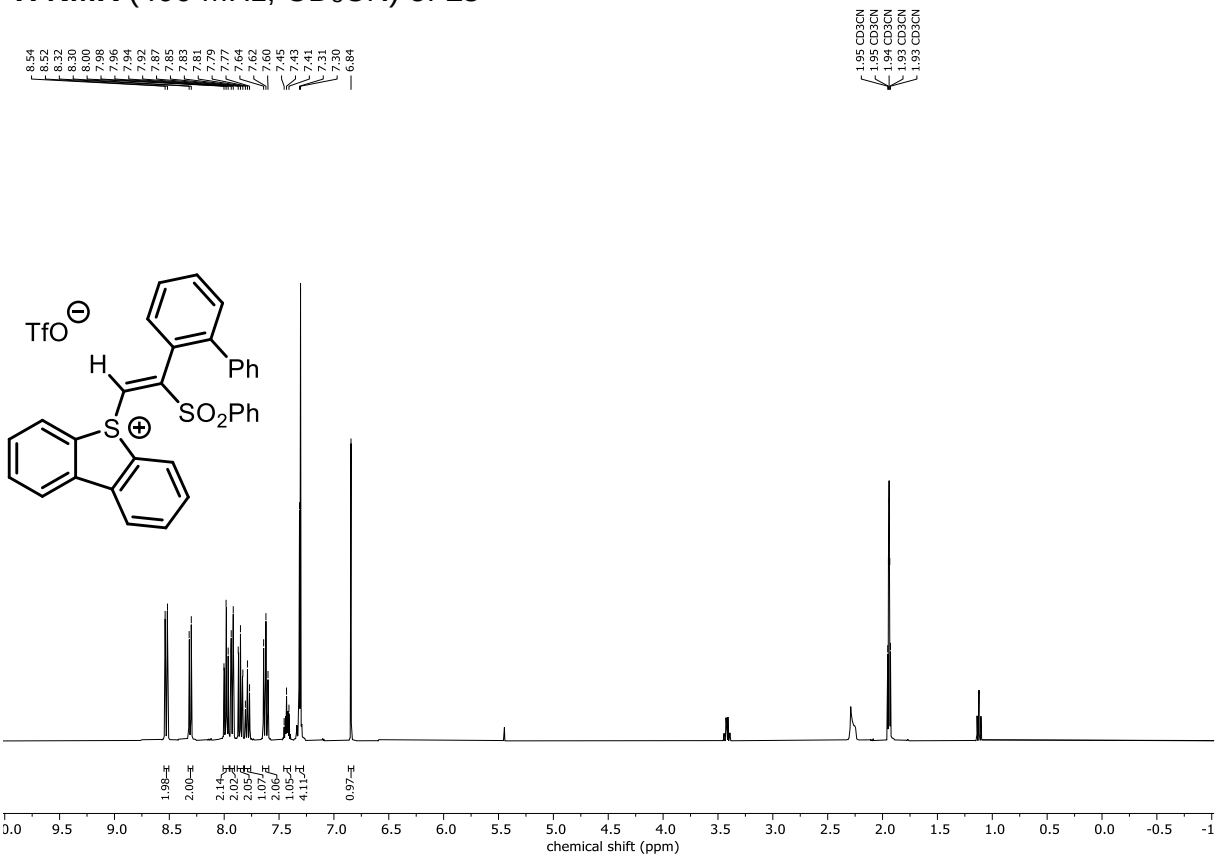
^{1}H NMR (400 MHz, $CDCl_3$) of **14**



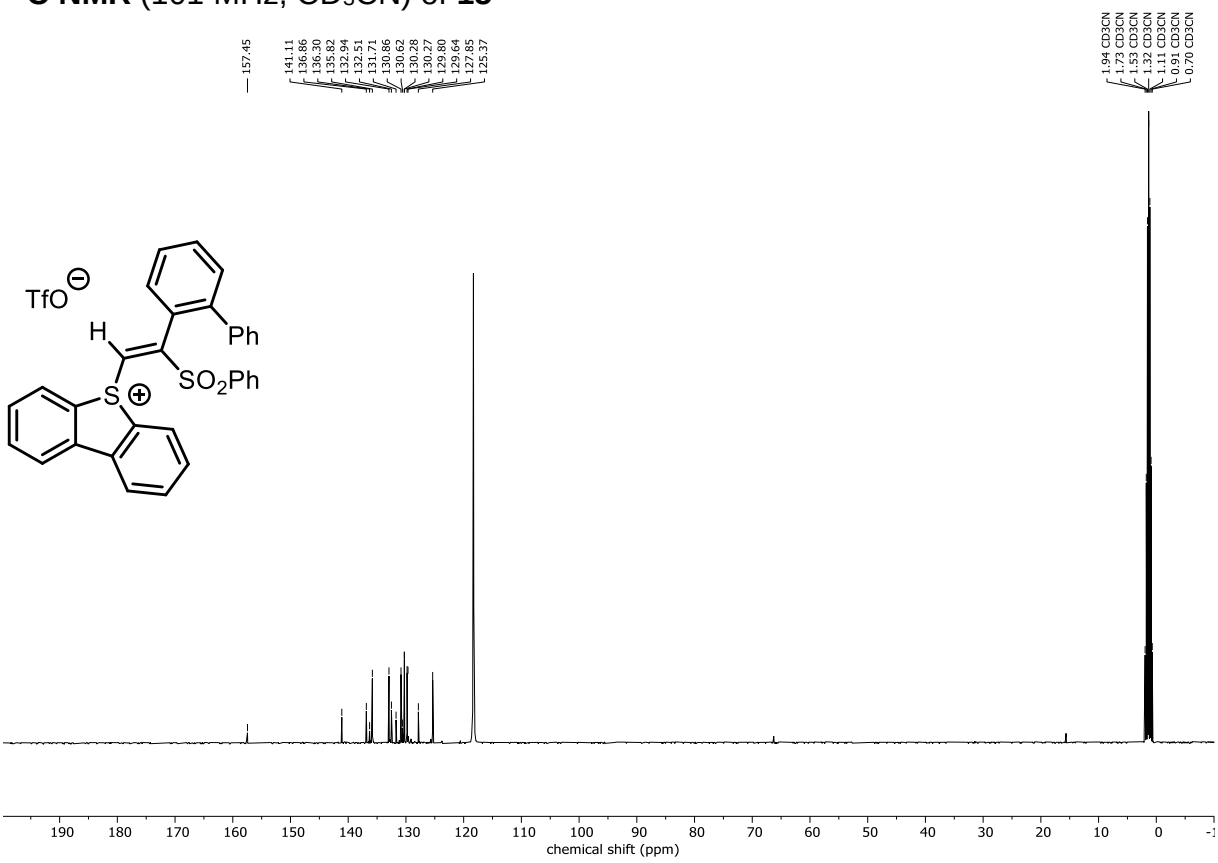
^{13}C NMR (101 MHz, $CDCl_3$) of **14**



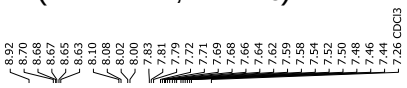
^{1}H NMR (400 MHz, CD_3CN) of **15**

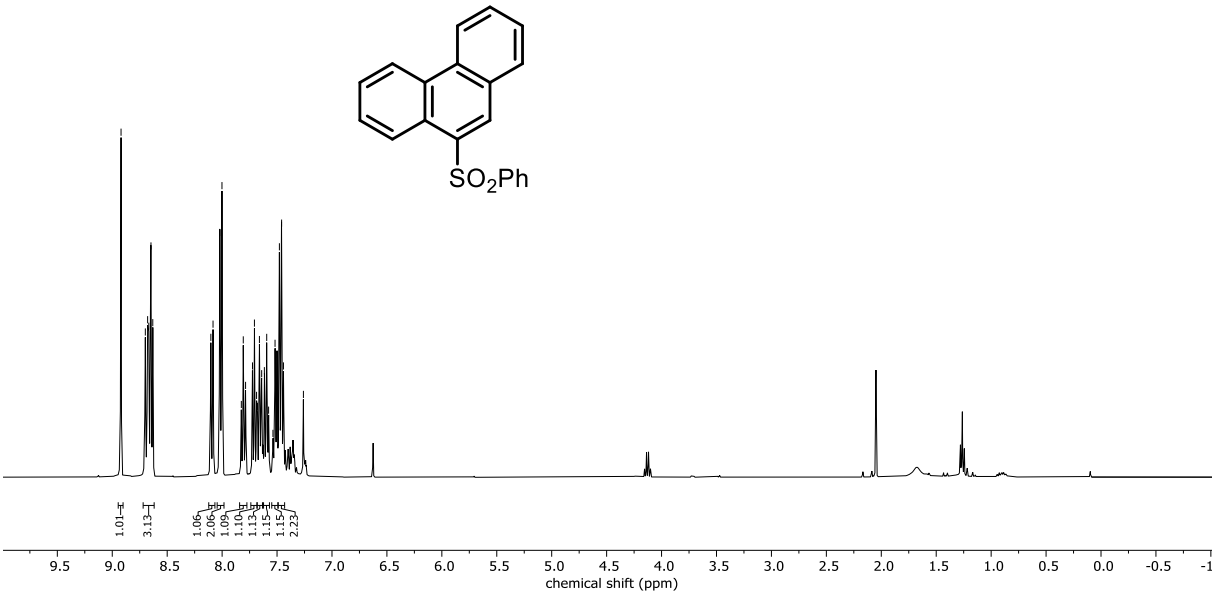


^{13}C NMR (101 MHz, CD_3CN) of **15**

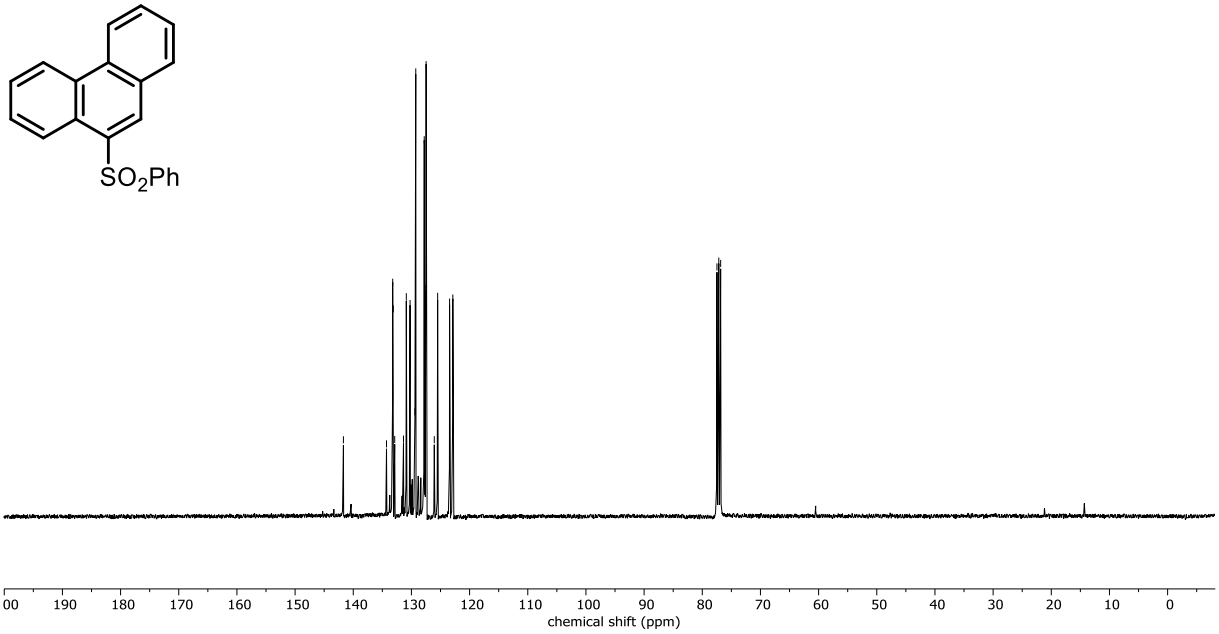


^{1}H NMR (400 MHz, $CDCl_3$) of **16**

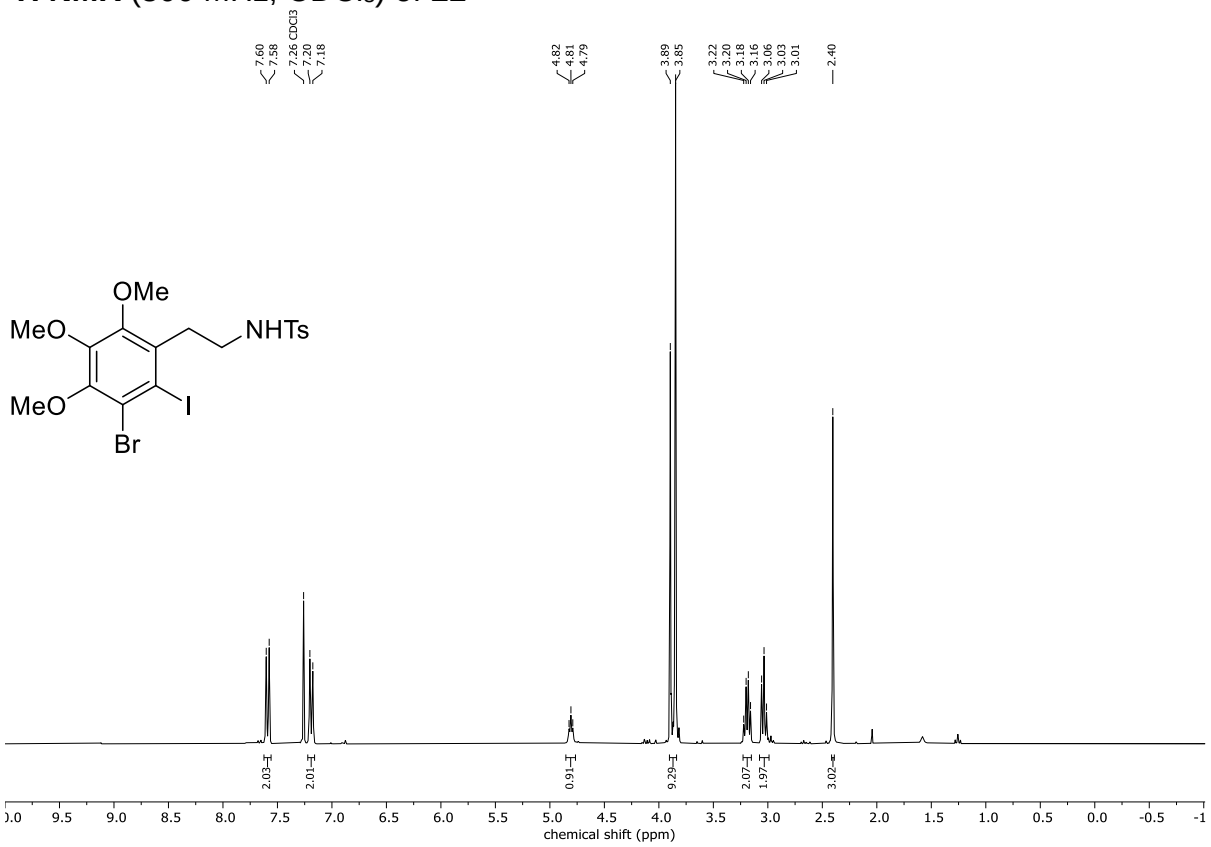




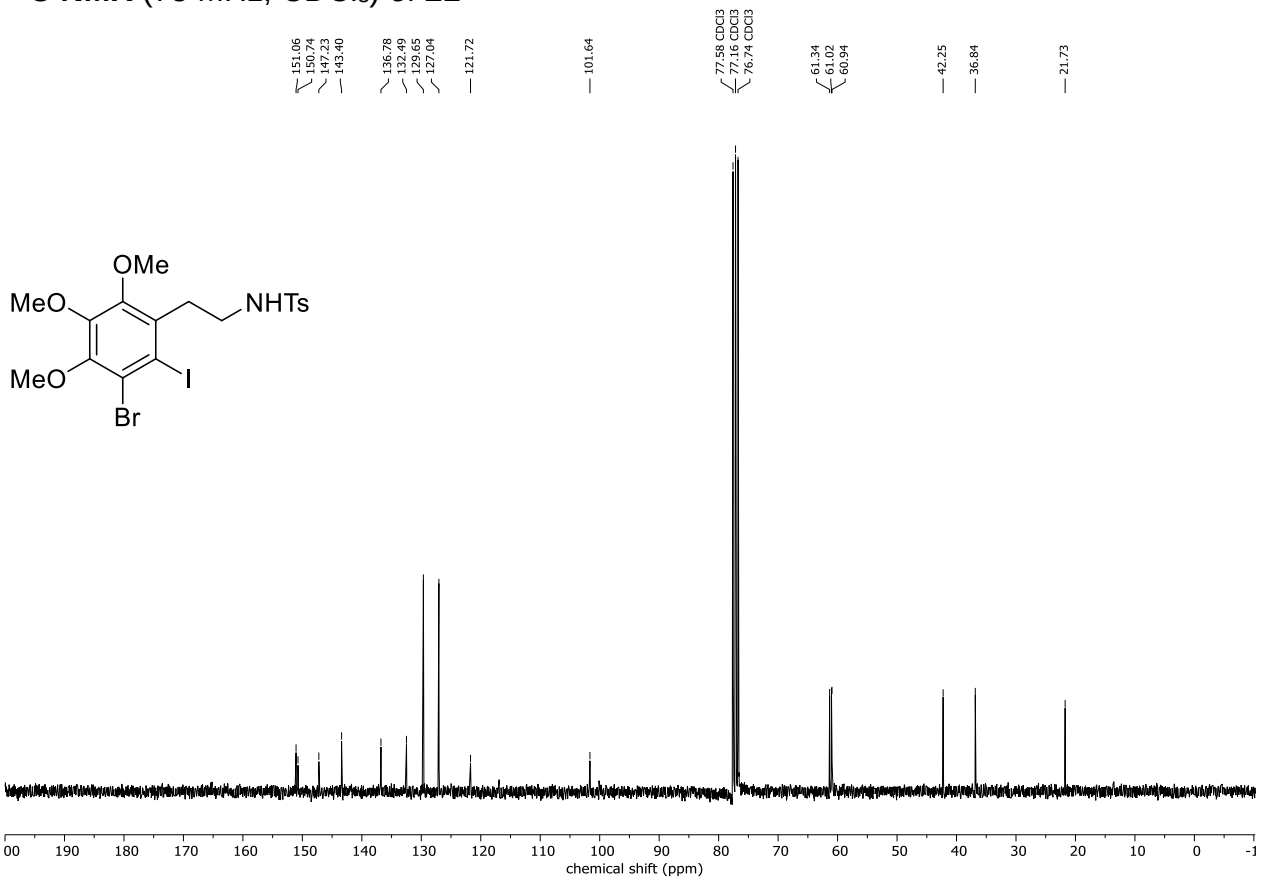
^{13}C NMR (101 MHz, $CDCl_3$) of **16**



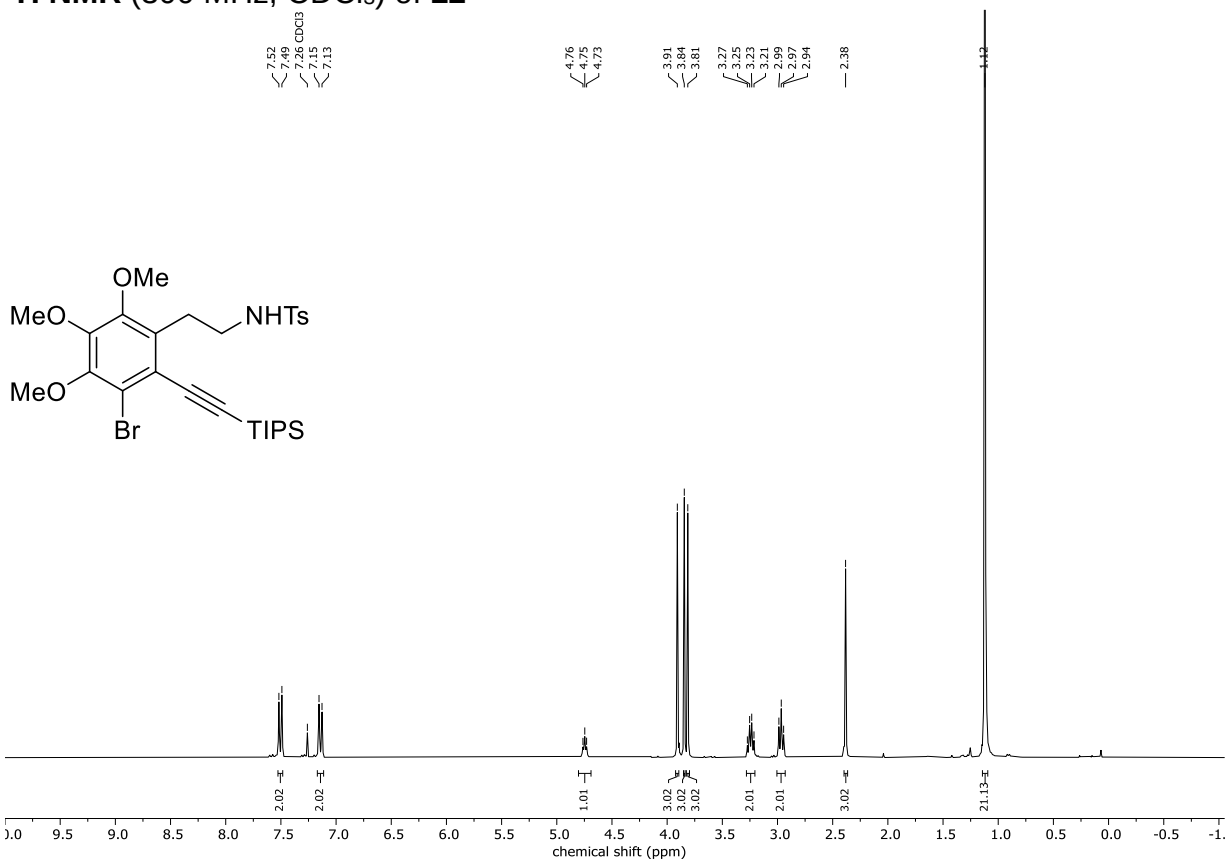
^{1}H NMR (300 MHz, $CDCl_3$) of **21**



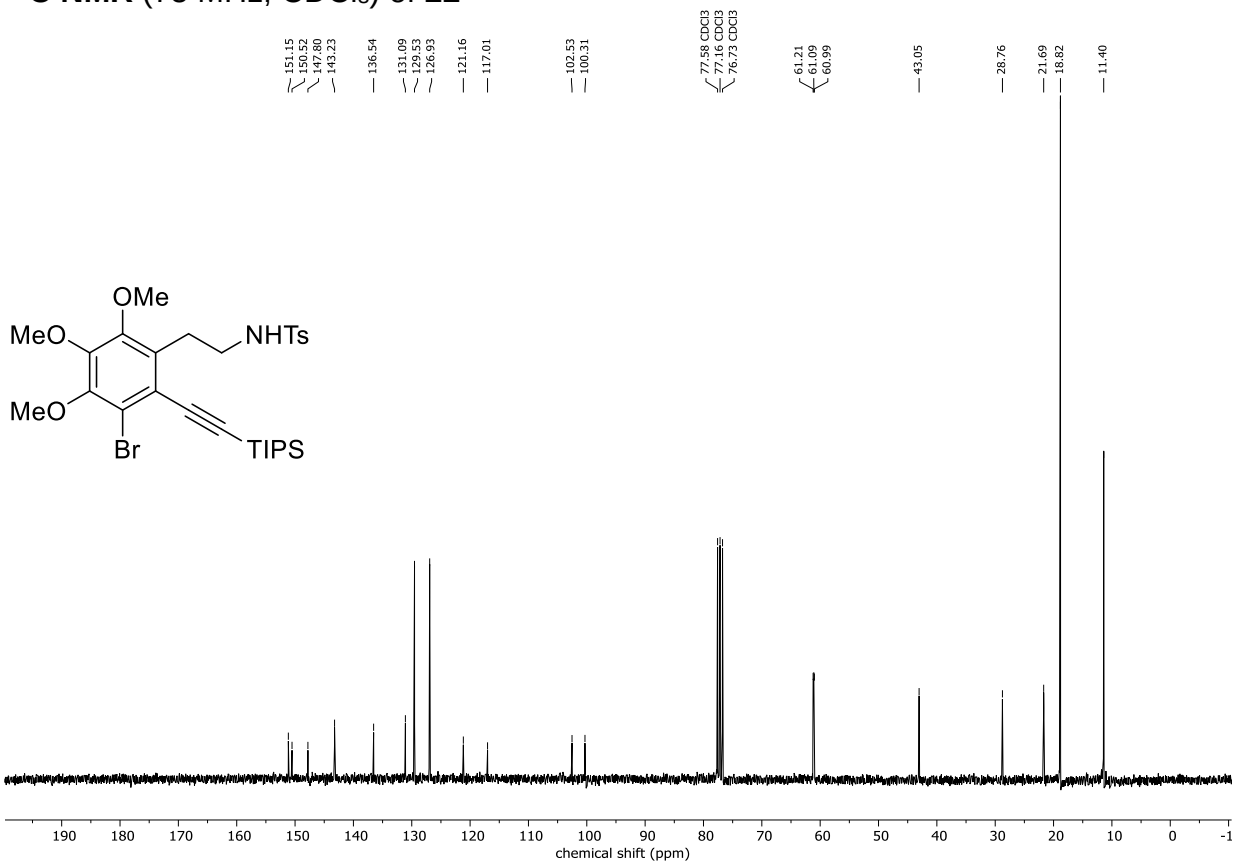
^{13}C NMR (75 MHz, $CDCl_3$) of **21**



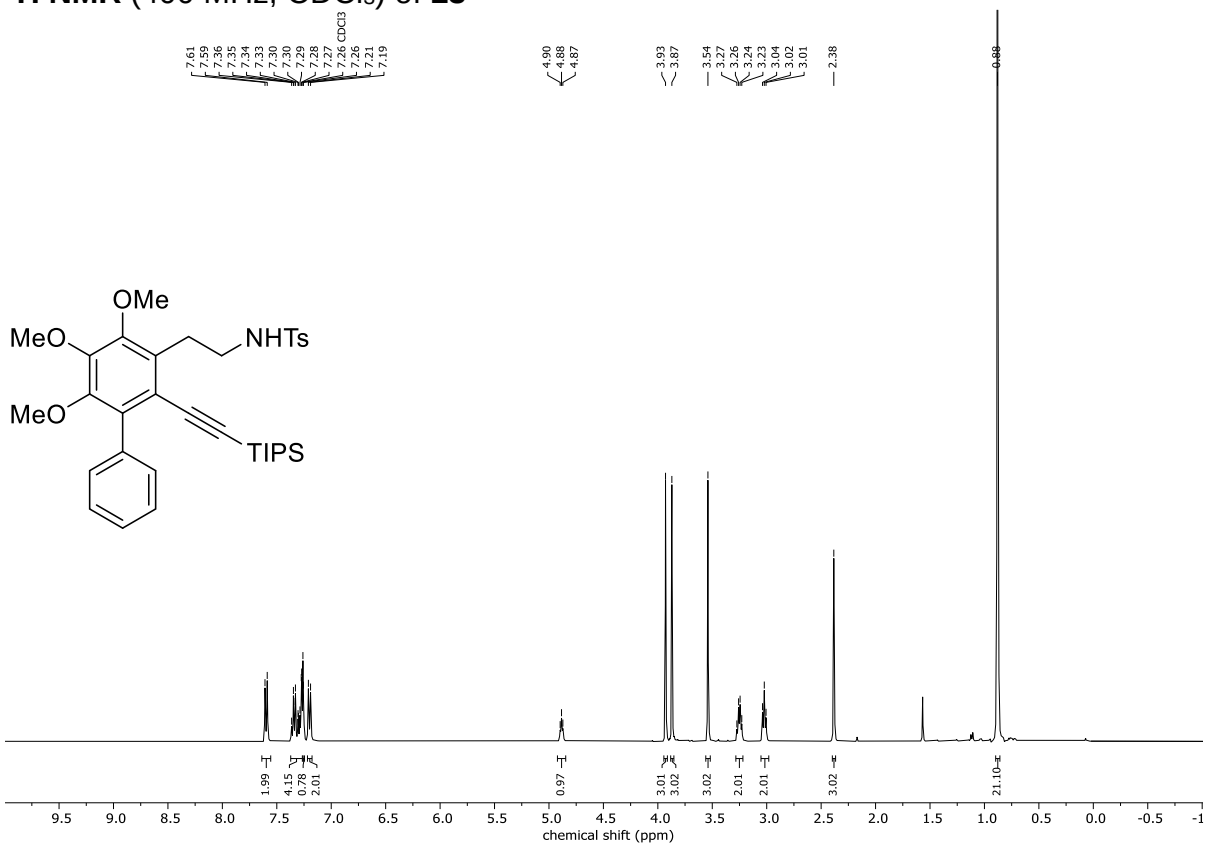
^{1}H NMR (300 MHz, $CDCl_3$) of **22**



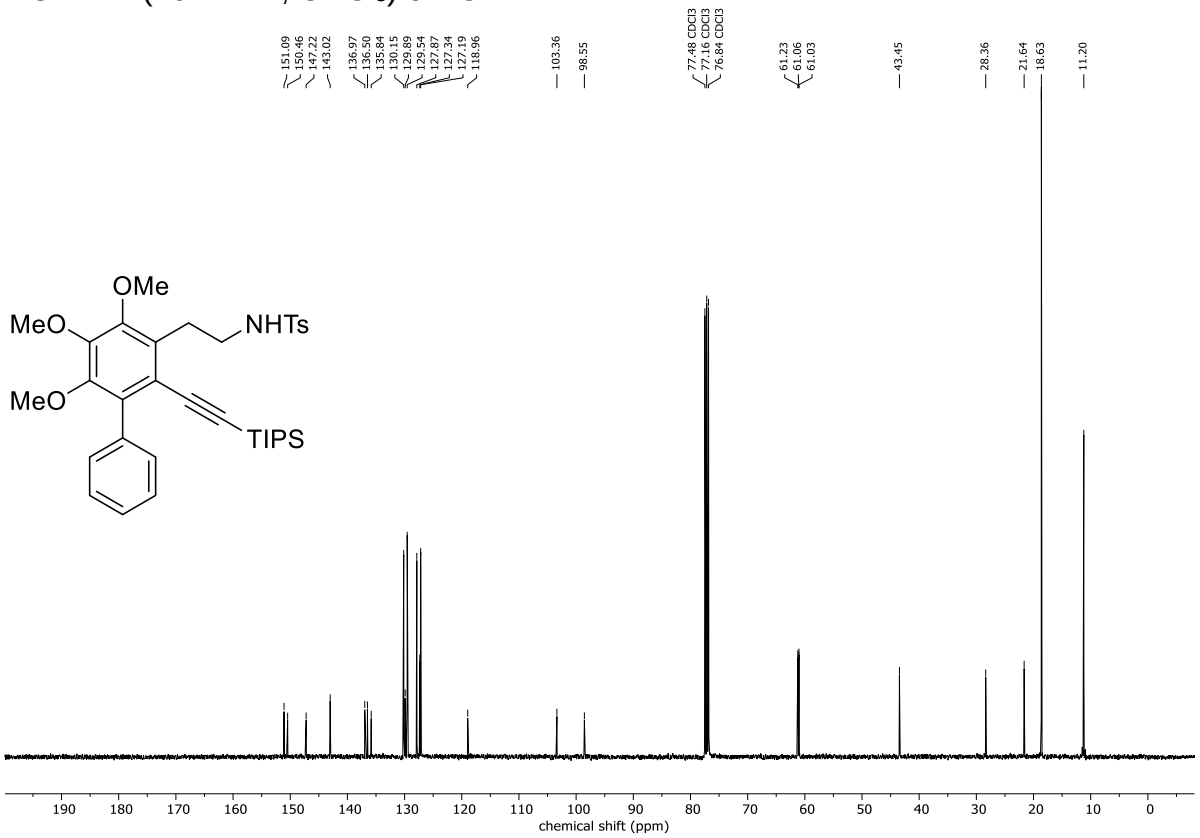
^{13}C NMR (75 MHz, $CDCl_3$) of **22**



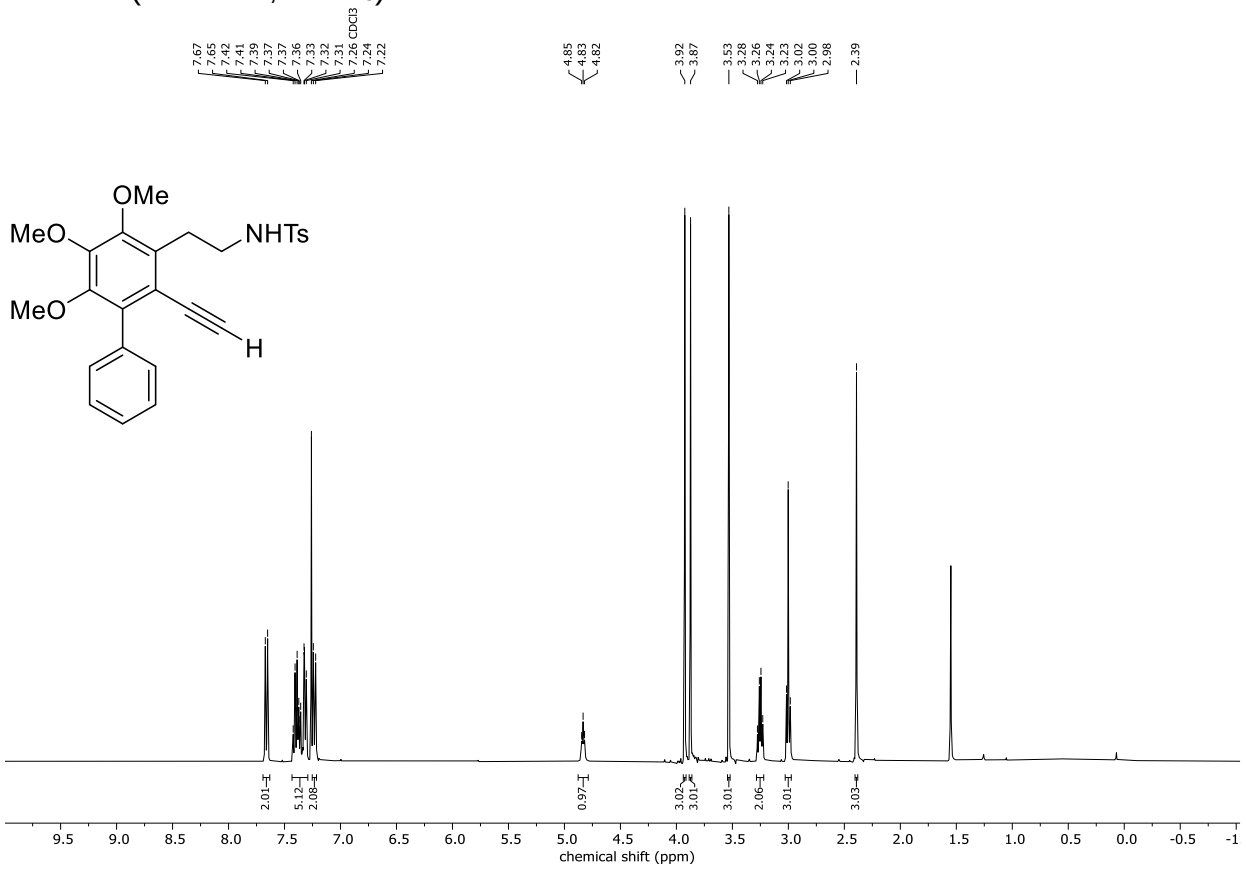
^{1}H NMR (400 MHz, $CDCl_3$) of **23**



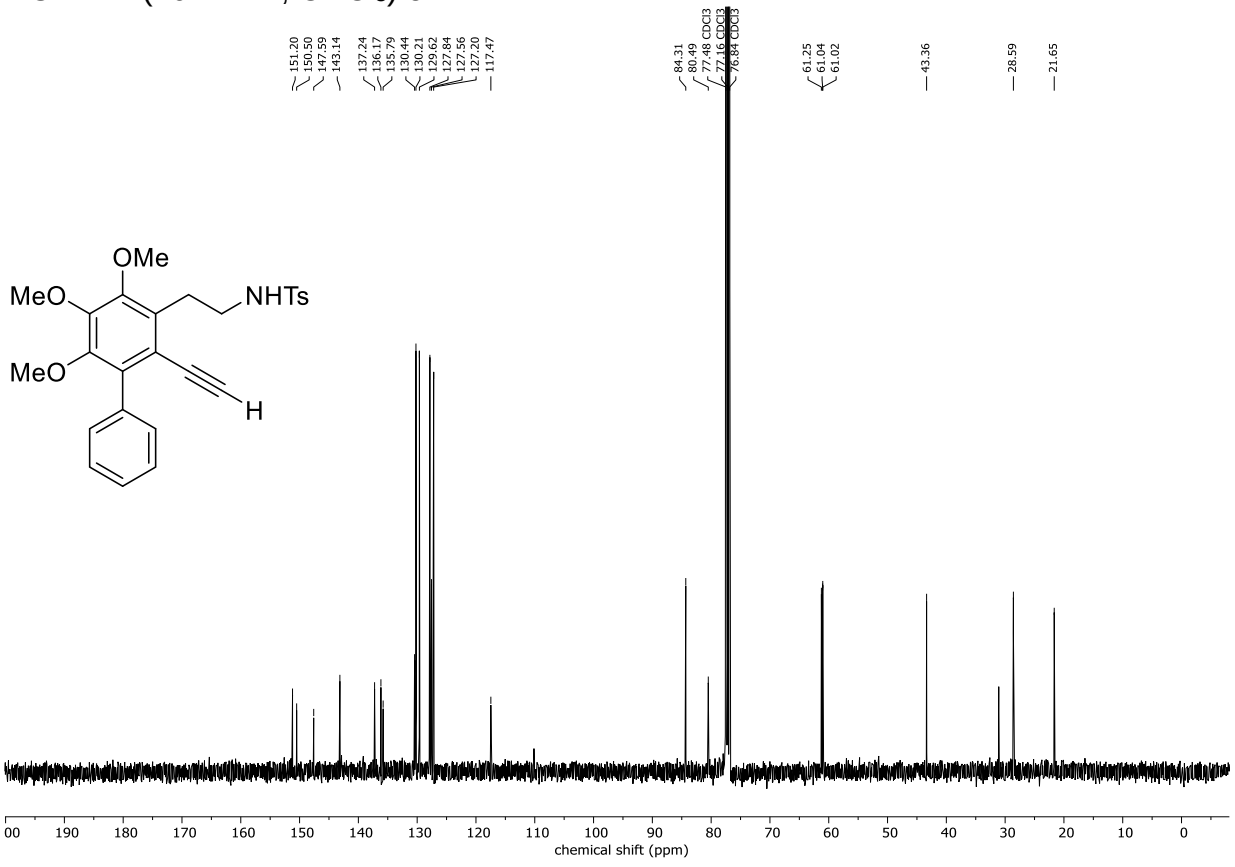
^{13}C NMR (101 MHz, $CDCl_3$) of **23**



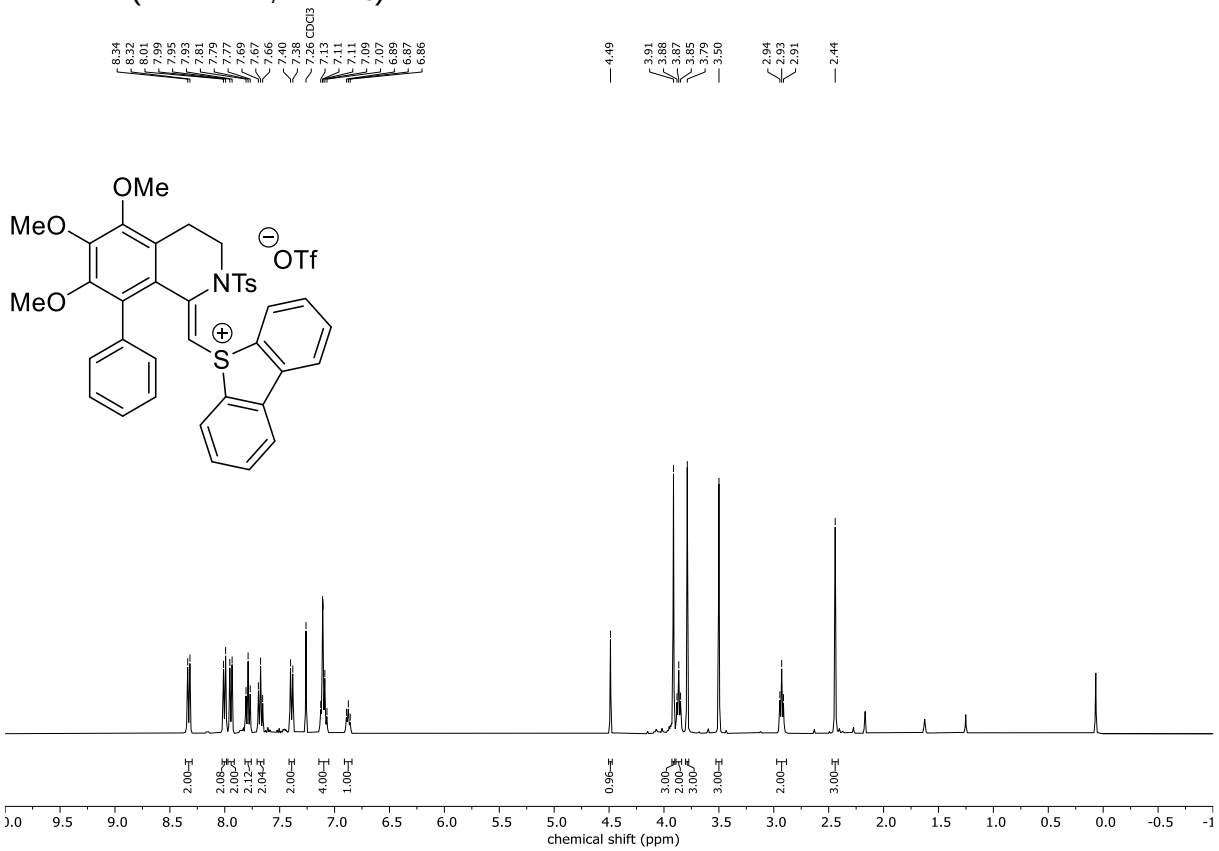
^{1}H NMR (400 MHz, $CDCl_3$) of **24**



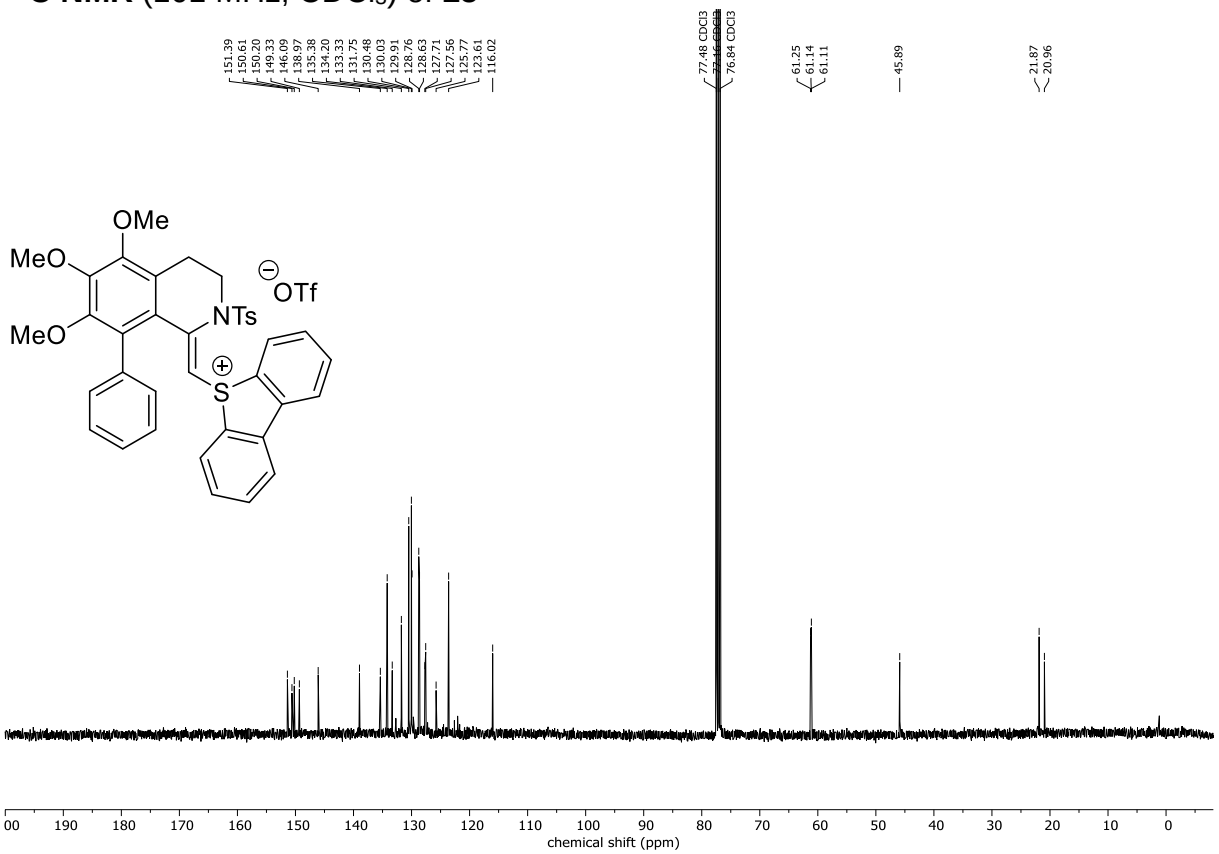
^{13}C NMR (101 MHz, $CDCl_3$) of **24**



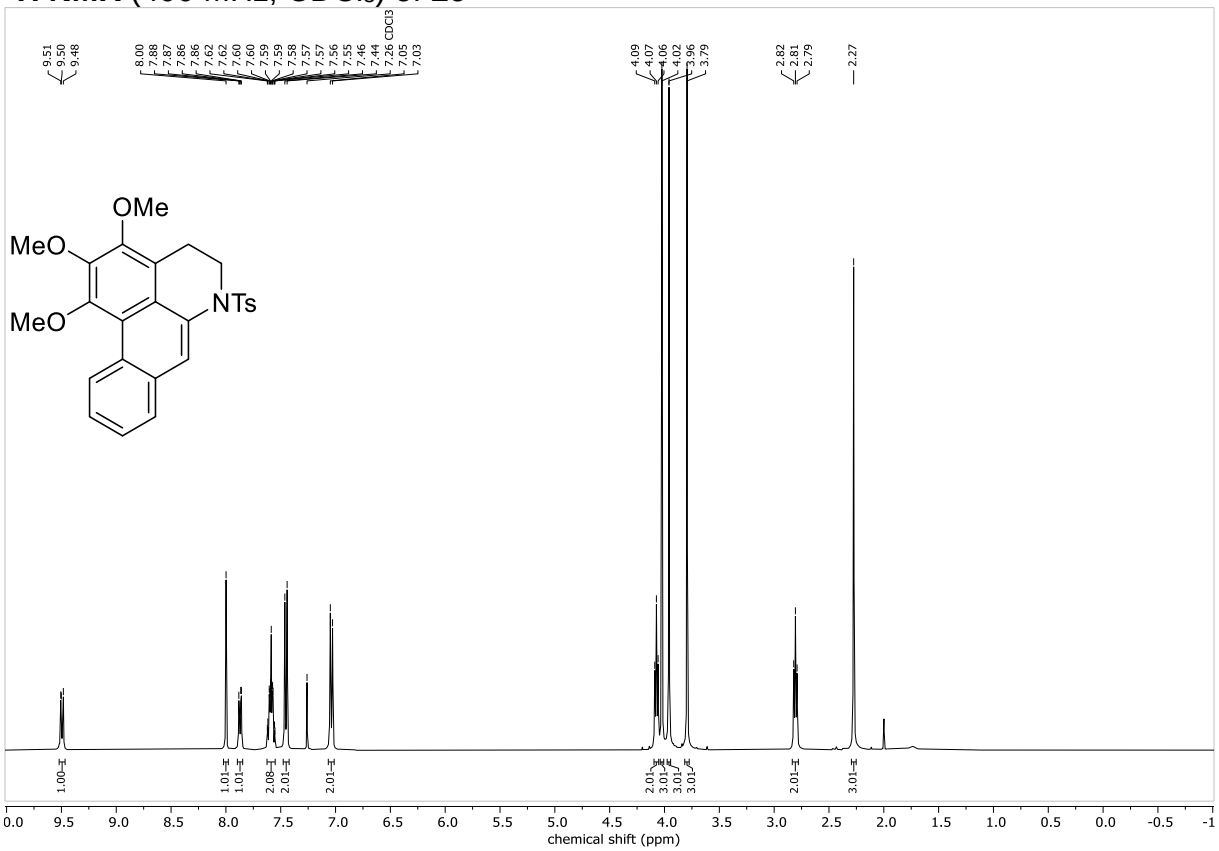
^{1}H NMR (400 MHz, $CDCl_3$) of **25**



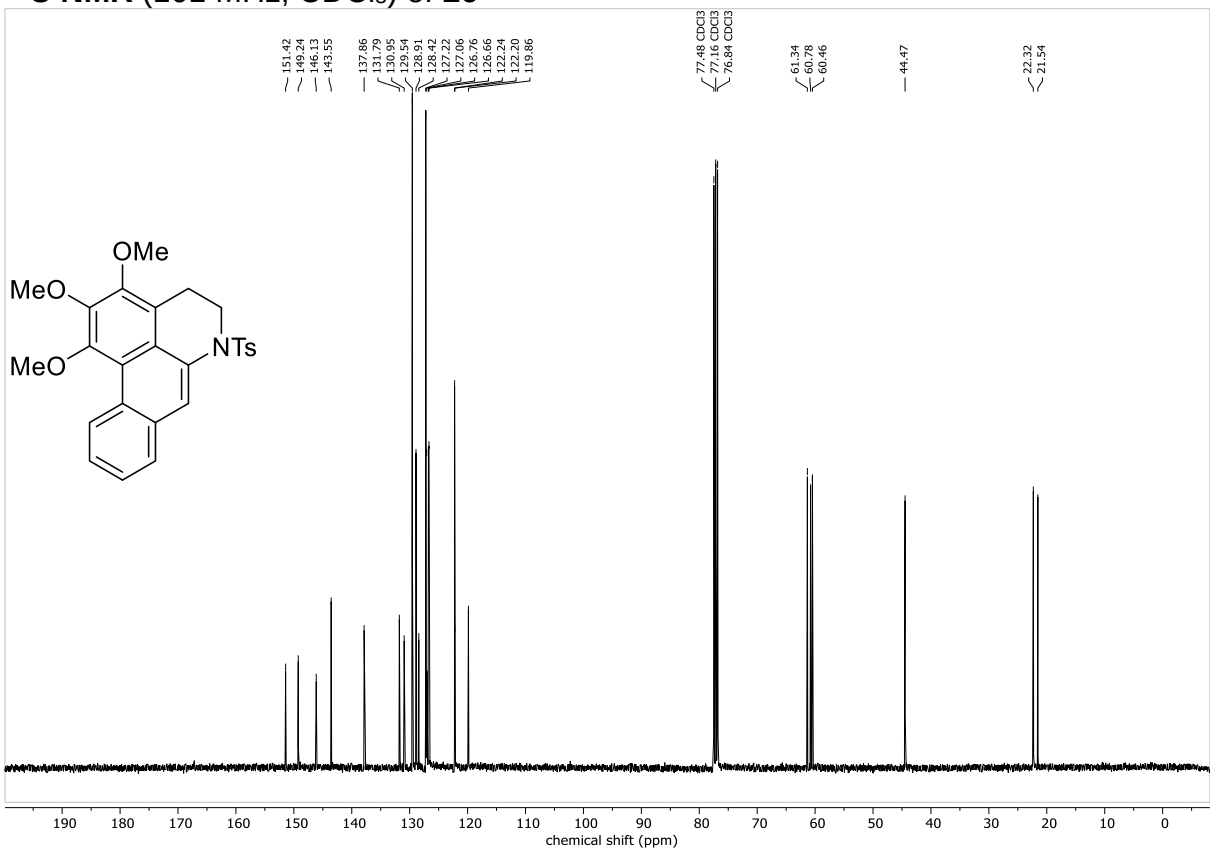
^{13}C NMR (101 MHz, $CDCl_3$) of **25**



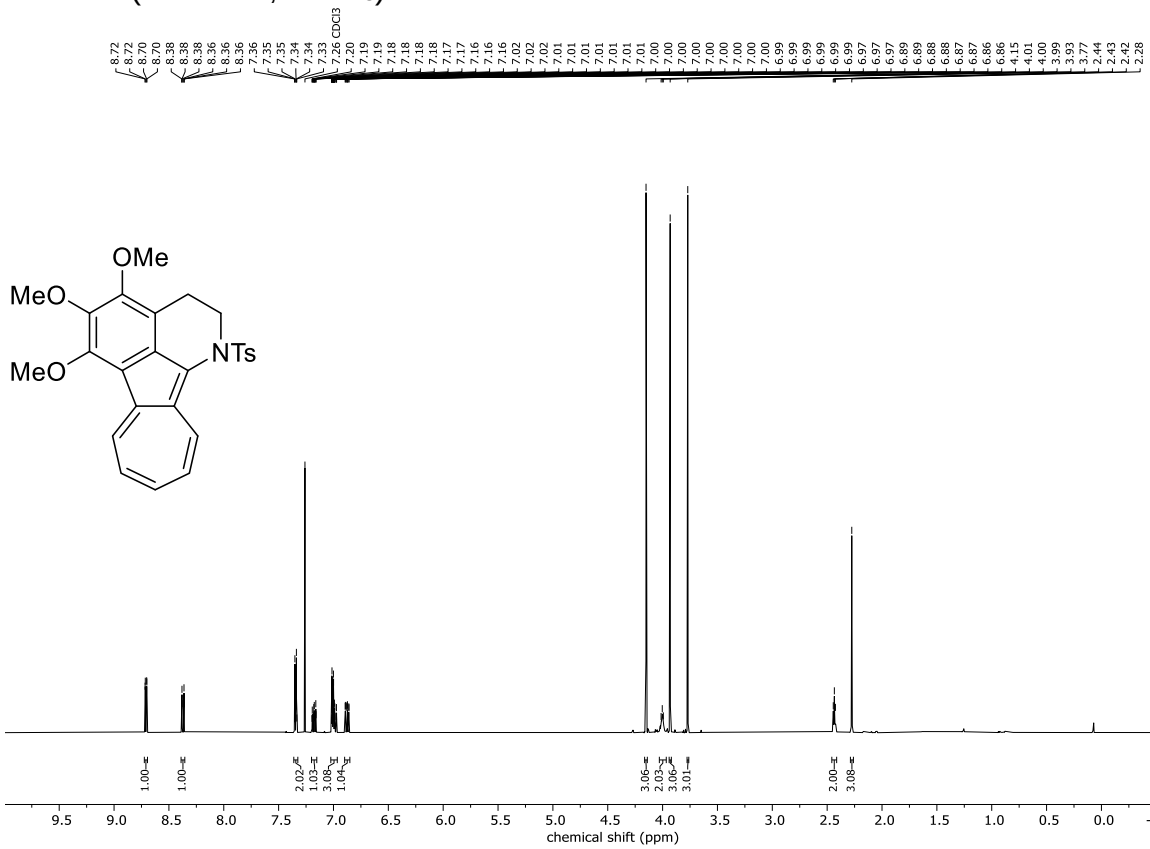
^{1}H NMR (400 MHz, $CDCl_3$) of **26**



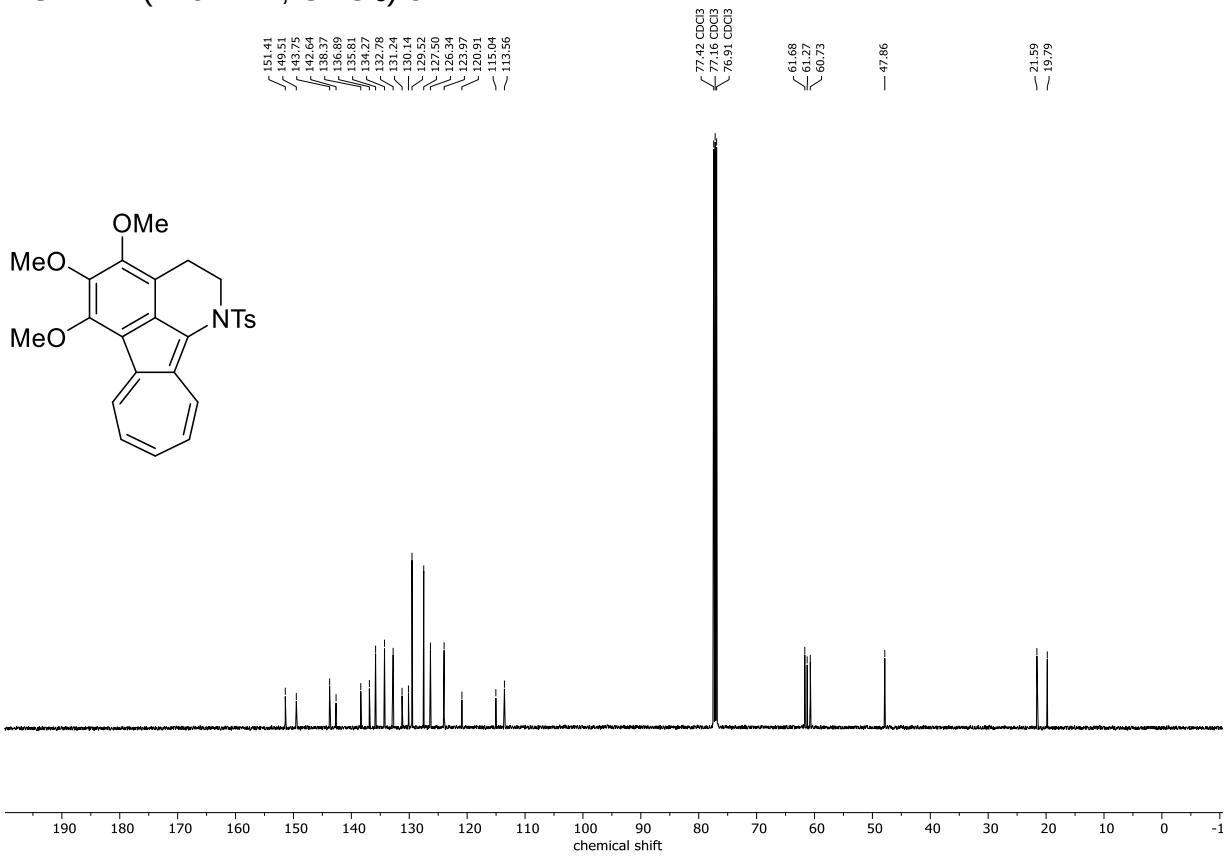
^{13}C NMR (101 MHz, $CDCl_3$) of **26**



^{1}H NMR (600 MHz, $CDCl_3$) of **27**



^{13}C NMR (126 MHz, $CDCl_3$) of **27**



3 X-Ray crystal structures

Compound 2f:

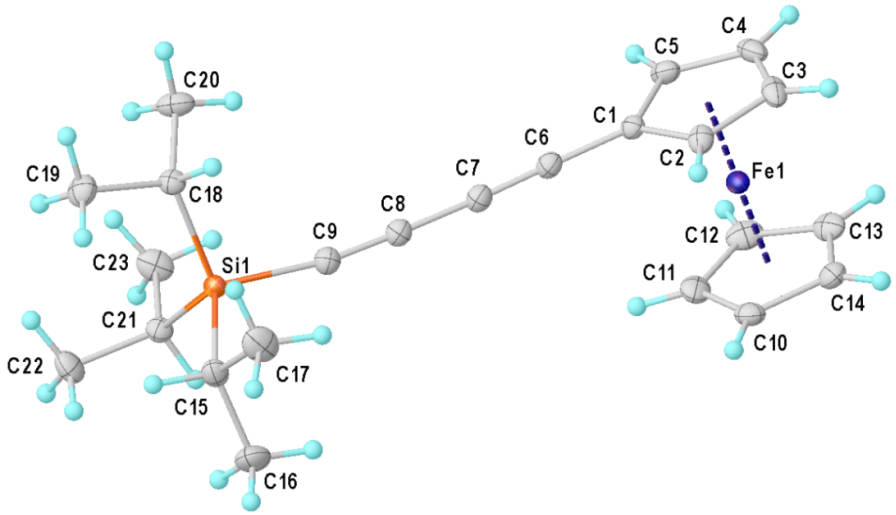


Figure 1: **Molecular structure of full asymmetric unit and numbering scheme of compound 2f. Ellipsoids drawn at 50% probability level.**

Table 1: Crystal data and structure refinement for 2f.

CCDC	2068276
Empirical formula	$C_{23}H_{30}FeSi$
Formula weight	390.41
Temperature/K	100
Crystal system	Triclinic
Space group	*P*-1
a/Å	9.2172(6)
b/Å	11.4974(7)
c/Å	11.6210(8)
α/°	104.064(2)
β/°	108.843(2)
γ/°	106.313(2)
Volume/Å^3	1040.36(12)
Z	2
ρ_{calc} g/cm^3	1.246
μ/mm^{-1}	0.785
F(000)	416.0
Crystal size/mm^3	0.334 × 0.322 × 0.196
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.472 to 61.126
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected	49311
Independent reflections	6348 [R_{int} = 0.0307, R_{sigma} = 0.0151]
Data/restraints/parameters	6348/0/232
Goodness-of-fit on F^2	1.055
Final *R* indexes [*I*≥2σ (*I*)]	R_1 = 0.0227, wR_2 = 0.0599
Final *R* indexes [all data]	R_1 = 0.0256, wR_2 = 0.0619
Largest diff. peak/hole / e Å^{-3}	0.40/–0.29

Compound 2j:

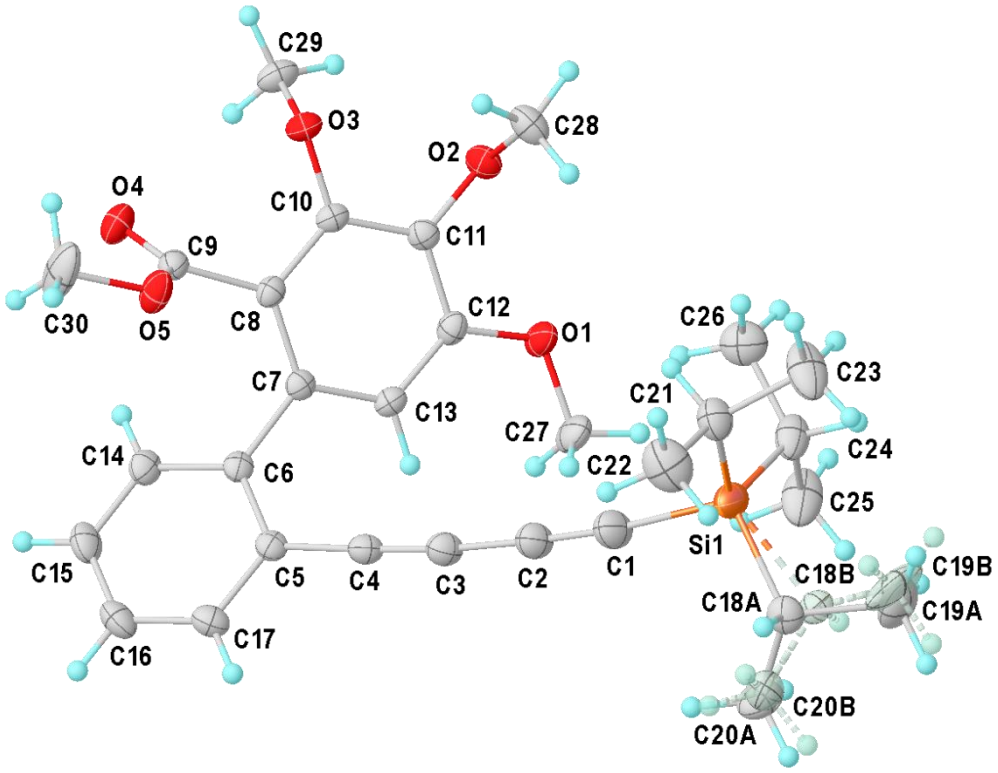


Figure 2: **Molecular structure of full asymmetric unit and numbering scheme of compound 2j. Ellipsoids drawn at 50% probability level; minor part of disorder drawn translucent with stippled cones.**

Table 2: Crystal data and structure refinement for 2j.

CCDC	2068277
Empirical formula	$C_{30}H_{38}O_5Si$
Formula weight	506.69
Temperature/K	100.
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	16.2204(17)
b/Å	17.1259(18)
c/Å	10.4293(9)
α/°	90
β/°	101.021(4)
γ/°	90
Volume/Å^3	2843.7(5)
Z	4
ρ_{calc}g/cm^3	1.183
μ/mm^{-1}	0.118
F(000)	1088.0
Crystal size/mm^3	0.682 × 0.595 × 0.482
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.756 to 57.462
Index ranges	-21 ≤ h ≤ 21, -23 ≤ k ≤ 23, -14 ≤ l ≤ 12

Reflections collected	52337
Independent reflections	7342 [R_{int} = 0.0263, R_{sigma} = 0.0163]
Data/restraints/parameters	7342/0/365
Goodness-of-fit on F^2	1.021
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0451, wR_2 = 0.1094
Final *R* indexes [all data]	R_1 = 0.0497, wR_2 = 0.1131
Largest diff. peak/hole / e Å^{-3}	0.91/–1.10

Compound 3e:

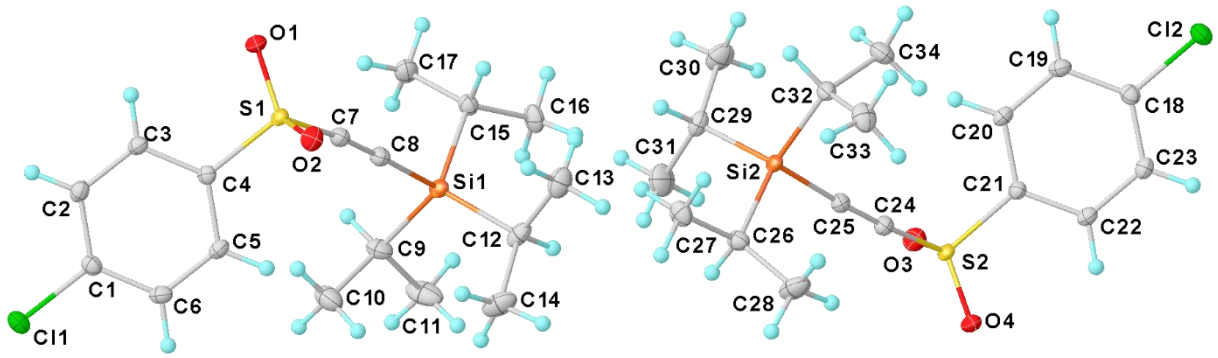


Figure 3: **Molecular structure of full asymmetric unit and numbering scheme of compound 3e. Ellipsoids drawn at 50% probability level.**

Table 3: Crystal data and structure refinement for 3e.

CCDC	2068278
Empirical formula	$C_{17}H_{25}ClO_2SSi$
Formula weight	356.97
Temperature/K	100
Crystal system	Triclinic
Space group	*P*-1
a/Å	11.080(3)
b/Å	11.614(3)
c/Å	15.962(4)
α/°	85.015(7)
β/°	80.704(7)
γ/°	67.483(6)
Volume/Å^3	1871.8(8)
Z	4
ρ_{calc}g/cm^3	1.267
μ/mm^{-1}	0.384
F(000)	760.0
Crystal size/mm^3	0.465 × 0.264 × 0.158
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.798 to 57.558
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	40097
Independent reflections	9499 [R_{int} = 0.0278, R_{sigma} = 0.0257]
Data/restraints/parameters	9499/0/409
Goodness-of-fit on F^2	1.106
Final *R* indexes [*I*≥2σ (*I*)]	R_1 = 0.0365, wR_2 = 0.0841
Final *R* indexes [all data]	R_1 = 0.0422, wR_2 = 0.0869
Largest diff. peak/hole / e Å^{-3}	0.45/–0.55

Compound 5a:

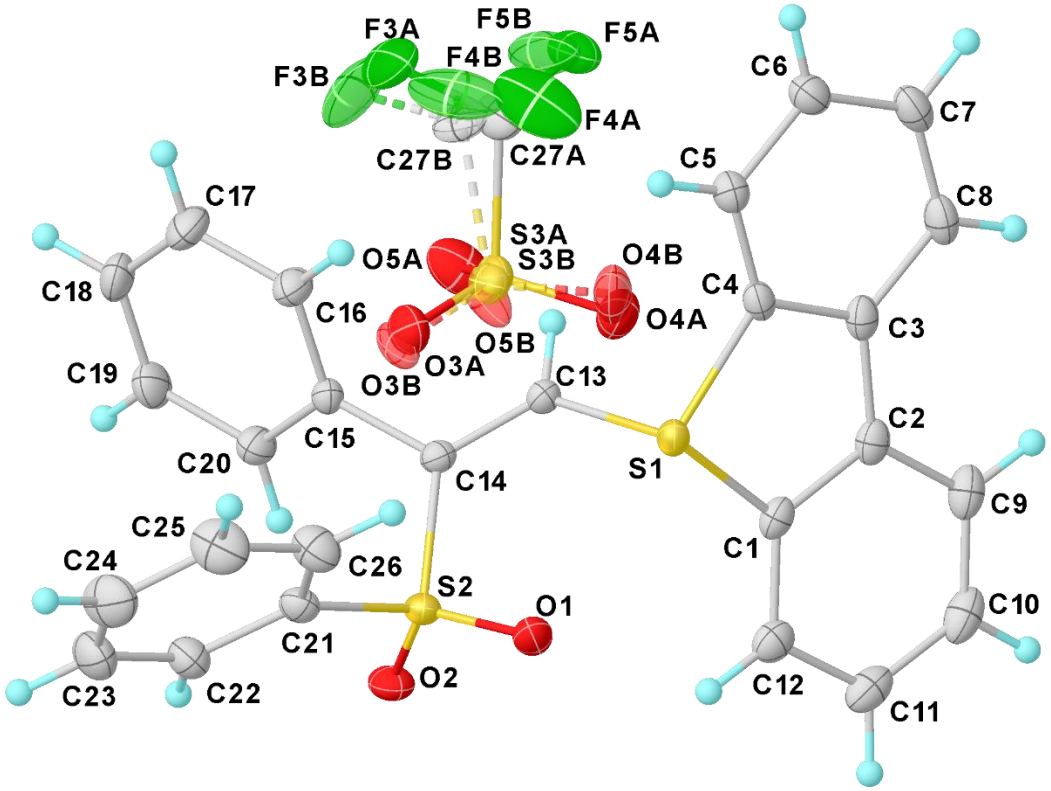


Figure 4: **Molecular structure of full asymmetric unit and numbering scheme of compound 5a. Ellipsoids drawn at 50% probability level; minor part of disorder drawn translucent with stippled cones.**

Table 4: Crystal data and structure refinement for 5a.

CCDC	2068279
Empirical formula	$C_{27}H_{19}F_3O_5S_3$
Formula weight	576.60
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.815(2)
b/Å	14.4185(16)
c/Å	11.1988(14)
α/°	90
β/°	92.768(4)
γ/°	90
Volume/Å^3	2550.7(5)
Z	4
ρ_{calc}g/cm^3	1.501
μ/mm^{-1}	0.351
F(000)	1184.0
Crystal size/mm^3	0.164 × 0.152 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.608 to 57.466
Index ranges	-21 ≤ h ≤ 21, -19 ≤ k ≤ 19, -15 ≤ l ≤ 15

Reflections collected	121187
Independent reflections	6605 [R_{int} = 0.0252, R_{sigma} = 0.0094]
Data/restraints/parameters	6605/131/419
Goodness-of-fit on F^2	1.050
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0304, wR_2 = 0.0787
Final *R* indexes [all data]	R_1 = 0.0335, wR_2 = 0.0814
Largest diff. peak/hole / e Å^{-3}	0.42/–0.33

Compound 6:

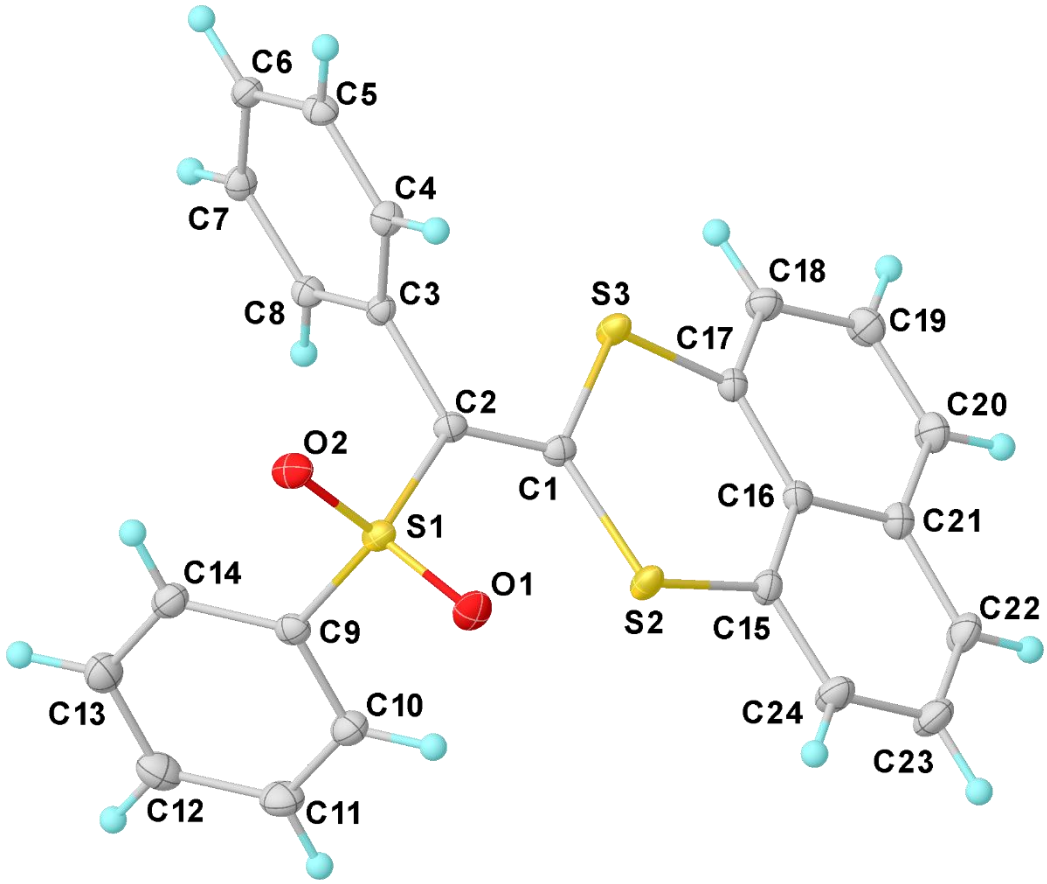


Figure 5: **Molecular structure of full asymmetric unit and numbering scheme of compound 6. Ellipsoids drawn at 50% probability level.**

Table 5: Crystal data and structure refinement for 6.

CCDC	2068280
Empirical formula	$C_{24}H_{16}O_2S_3$
Formula weight	432.55
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	14.492(2)
b/Å	5.4785(10)
c/Å	23.842(4)
α/°	90
β/°	94.389(5)
γ/°	90
Volume/Å^3	1887.3(5)
Z	4
ρ_{calc}g/cm^3	1.522
μ/mm^{-1}	0.413
F(000)	896.0
Crystal size/mm^3	0.256 × 0.097 × 0.074
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.268 to 57.468
Index ranges	-19 ≤ h ≤ 19, -7 ≤ k ≤ 7, -32 ≤ l ≤ 32
Reflections collected	46896
Independent reflections	4899 [R_{int} = 0.0395, R_{sigma} = 0.0194]
Data/restraints/parameters	4899/0/262
Goodness-of-fit on F^2	1.036
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0292, wR_2 = 0.0746
Final R indexes [all data]	R_1 = 0.0351, wR_2 = 0.0793
Largest diff. peak/hole / e Å^{-3}	0.38/–0.40

Compound 8:

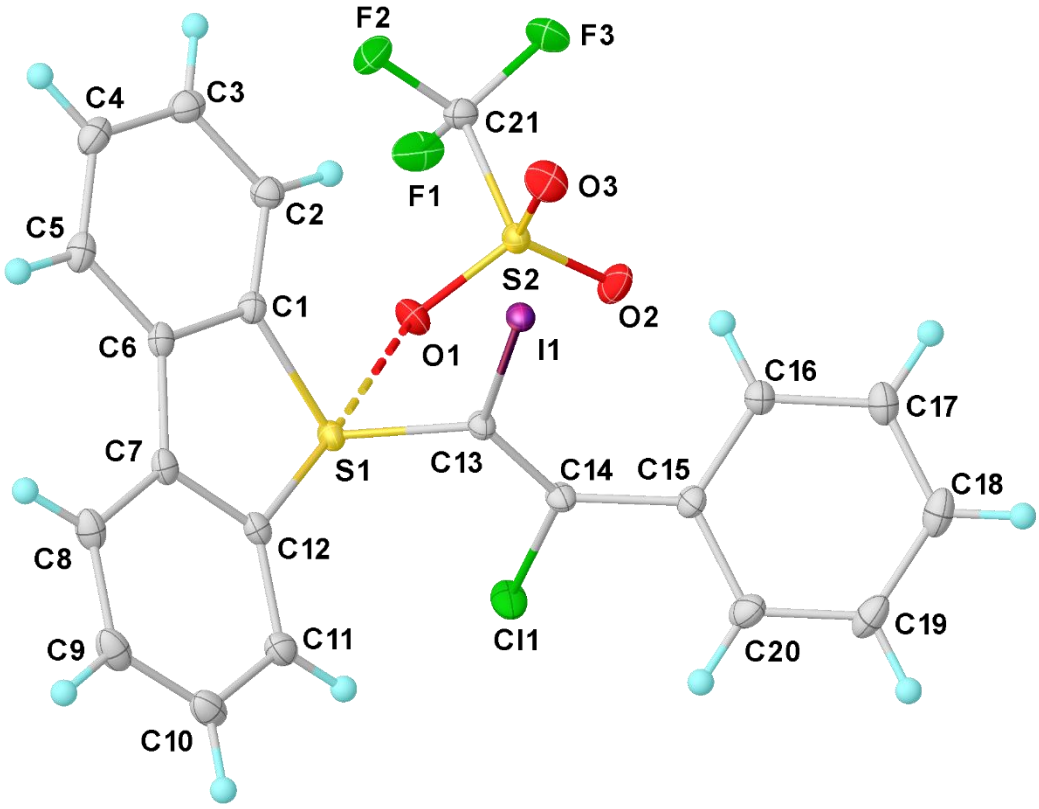


Figure 6: **Molecular structure of full asymmetric unit and numbering scheme of compound 8. Ellipsoids drawn at 50% probability level. Stippled cone bond indicates chalcogenic interaction between O1 and S1 [2.995(1) Å].**

Table 6: Crystal data and structure refinement for 8.

CCDC	2068281
Empirical formula	$C_{21}H_{13}ClF_3IO_3S_2$
Formula weight	596.78
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	7.6018(4)
b/Å	17.2223(6)
c/Å	16.2066(8)
α/°	90
β/°	101.823(2)
γ/°	90
Volume/Å^3	2076.76(17)
Z	4
ρ_{calc}g/cm^3	1.909
μ/mm^{-1}	1.014
F(000)	1168.0
Crystal size/mm^3	0.326 × 0.258 × 0.243
Radiation	AgKα (λ = 0.56086)
2*Θ* range for data collection/°	4.248 to 55.754

Index ranges	-12 ≤ h ≤ 12, -28 ≤ k ≤ 28, -26 ≤ l ≤ 26
Reflections collected	225496
Independent reflections	10073 [R_{int} = 0.0347, R_{sigma} = 0.0115]
Data/restraints/parameters	10073/0/280
Goodness-of-fit on F^2	1.068
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0175, wR_2 = 0.0406
Final *R* indexes [all data]	R_1 = 0.0217, wR_2 = 0.0424
Largest diff. peak/hole / e Å^{-3}	0.84/–0.64

Compound 10:

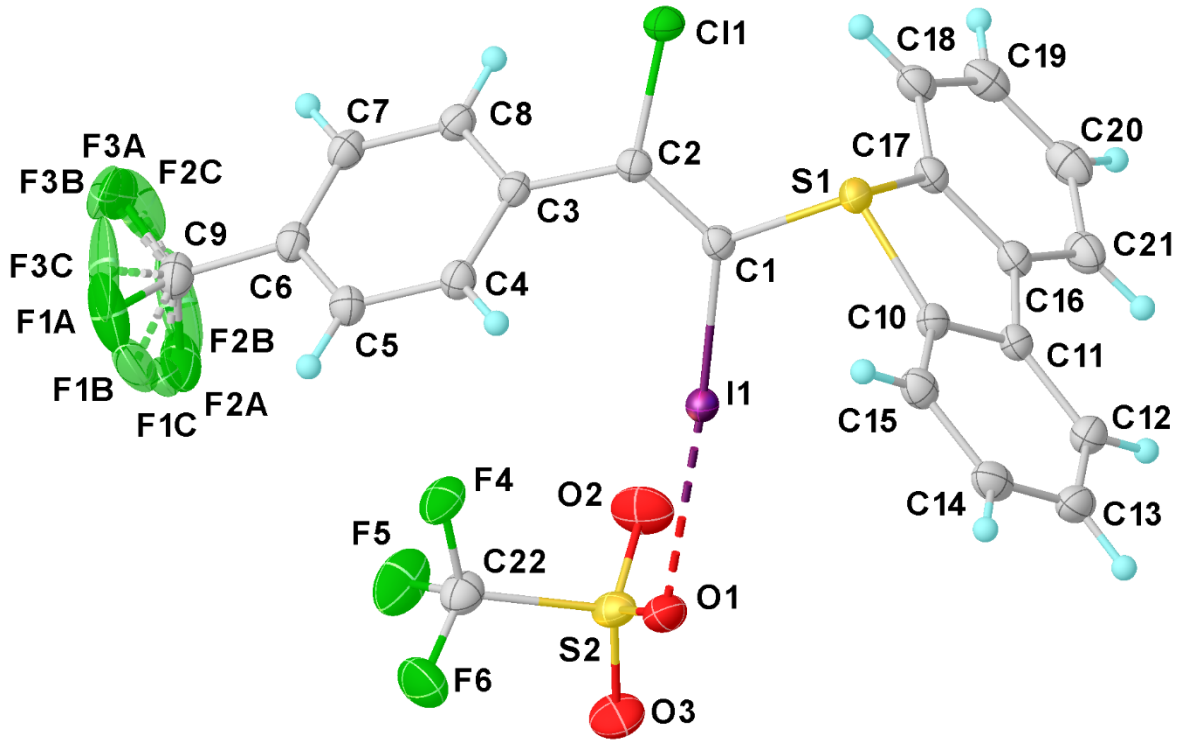


Figure 7: **Molecular structure of full asymmetric unit and numbering scheme of compound 10. Ellipsoids drawn at 50% probability level; minor part of disorder drawn translucent with stippled cones. Stippled cone bond indicates halogen bond between O1 and I1 [2.831(1) Å].**

Compound **10** was crystalized from a mixture of acetone and diethylether.

Table 7: Crystal data and structure refinement for 10.

CCDC	2068282
Empirical formula	$C_{22}H_{12}ClF_6IO_3S_2$
Formula weight	664.79
Temperature/K	100
Crystal system	Triclinic
Space group	*P*-1
a/Å	8.7606(4)
b/Å	9.1079(5)
c/Å	14.7027(8)
α/°	85.481(2)
β/°	87.424(2)
γ/°	79.608(2)
Volume/Å^3	1149.74(10)
Z	2
ρ_{calc}g/cm^3	1.920
μ/mm^{-1}	1.764
F(000)	648.0
Crystal size/mm^3	0.333 × 0.197 × 0.052
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.558 to 63.196
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21
Reflections collected	102665
Independent reflections	7675 [R_{int} = 0.0274, R_{sigma} = 0.0117]
Data/restraints/parameters	7675/10/373
Goodness-of-fit on F^2	1.084
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0151, wR_2 = 0.0395
Final R indexes [all data]	R_1 = 0.0159, wR_2 = 0.0400
Largest diff. peak/hole / e Å^{-3}	0.45/–0.55

Compound 11:

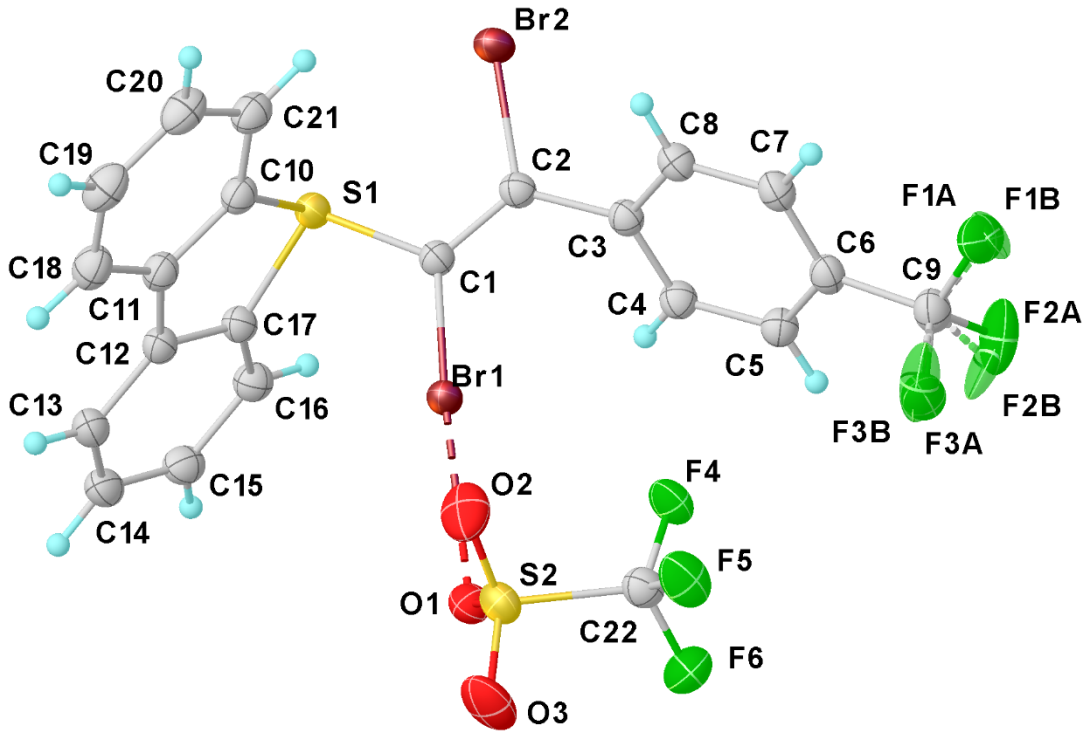


Figure 8: **Molecular structure of full asymmetric unit and numbering scheme of compound 11. Ellipsoids drawn at 50% probability level; minor part of disorder drawn translucent with stippled cones. Stippled cone bond indicates halogen bond between O1 and Br1 [2.885(1) Å].**

Table 8: Crystal data and structure refinement for 11.

CCDC	2068283
Empirical formula	$C_{22}H_{12}Br_2F_6O_3S_2$
Formula weight	662.26
Temperature/K	100
Crystal system	Triclinic
Space group	*P*-1
a/Å	8.7933(5)
b/Å	8.9573(4)
c/Å	14.6326(8)
α/°	85.968(2)
β/°	87.299(2)
γ/°	80.687(2)
Volume/Å^3	1133.77(10)
Z	2
ρ_{calc}g/cm^3	1.940
μ/mm^{-1}	3.833
F(000)	648.0
Crystal size/mm^3	0.423 × 0.377 × 0.375
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.618 to 65.464
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	148044

Independent reflections	8316 [R_{int} = 0.0313, R_{sigma} = 0.0160]
Data/restraints/parameters	8316/21/344
Goodness-of-fit on F^2	1.121
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0250, wR_2 = 0.0680
Final *R* indexes [all data]	R_1 = 0.0254, wR_2 = 0.0683
Largest diff. peak/hole / e Å^{-3}	0.71/–0.36

Compound 11 with bromide anion:

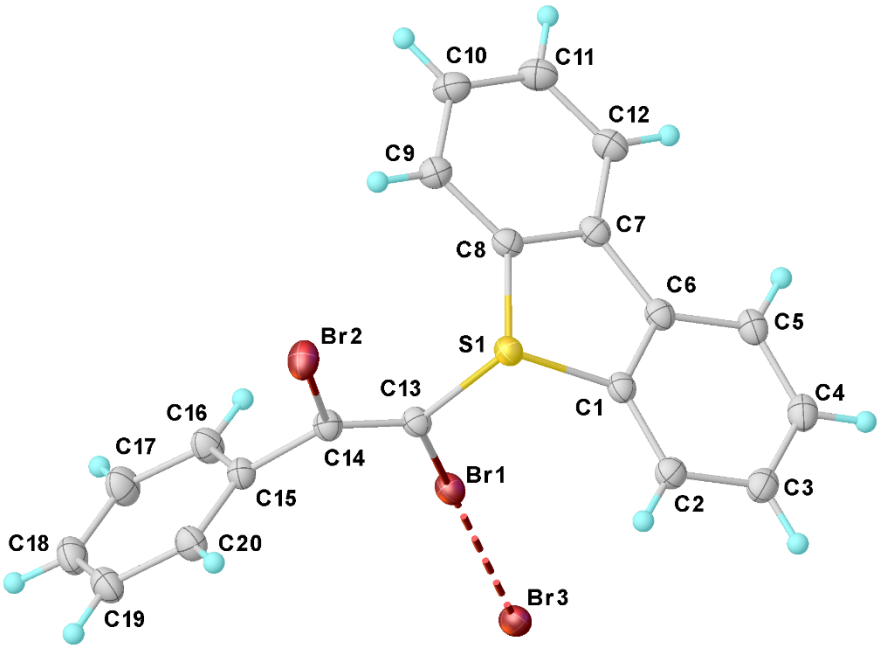


Figure 9: **Molecular structure of full asymmetric unit and numbering scheme of compound 11 with bromide anion. Ellipsoids drawn at 50% probability level. Stippled cone bond indicates halogen bond between Br1 and Br3 [3.1900(3) Å].**

Small amounts of **11** crystalize with bromide anion, instead of triflate, when bromine was added in slight excess to **1c** (compare scheme 4).

Table 9: Crystal data and structure refinement for 11 with bromide anion.

CCDC	2068284
Empirical formula	$C_{20}H_{13}Br_3S$
Formula weight	525.09
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.4052(16)
b/Å	7.3752(8)
c/Å	18.247(2)
α/°	90
β/°	91.642(4)
γ/°	90
Volume/Å^3	1803.3(4)
Z	4
ρ_{calc}g/cm^3	1.934
μ/mm^{-1}	3.654
F(000)	1016.0
Crystal size/mm^3	0.845 × 0.13 × 0.082
Radiation	AgKα (λ = 0.56086)
2Θ range for data collection/°	4.976 to 53.824
Index ranges	-21 ≤ h ≤ 21, -11 ≤ k ≤ 11, -29 ≤ l ≤ 29
Reflections collected	205121
Independent reflections	7919 [R_{int} = 0.0314, R_{sigma} = 0.0092]

Data/restraints/parameters	7919/0/217
Goodness-of-fit on F^2	1.069
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0182, wR_2 = 0.0495
Final *R* indexes [all data]	R_1 = 0.0199, wR_2 = 0.0507
Largest diff. peak/hole / e Å^{-3}	0.99/–0.26

Compound 24:

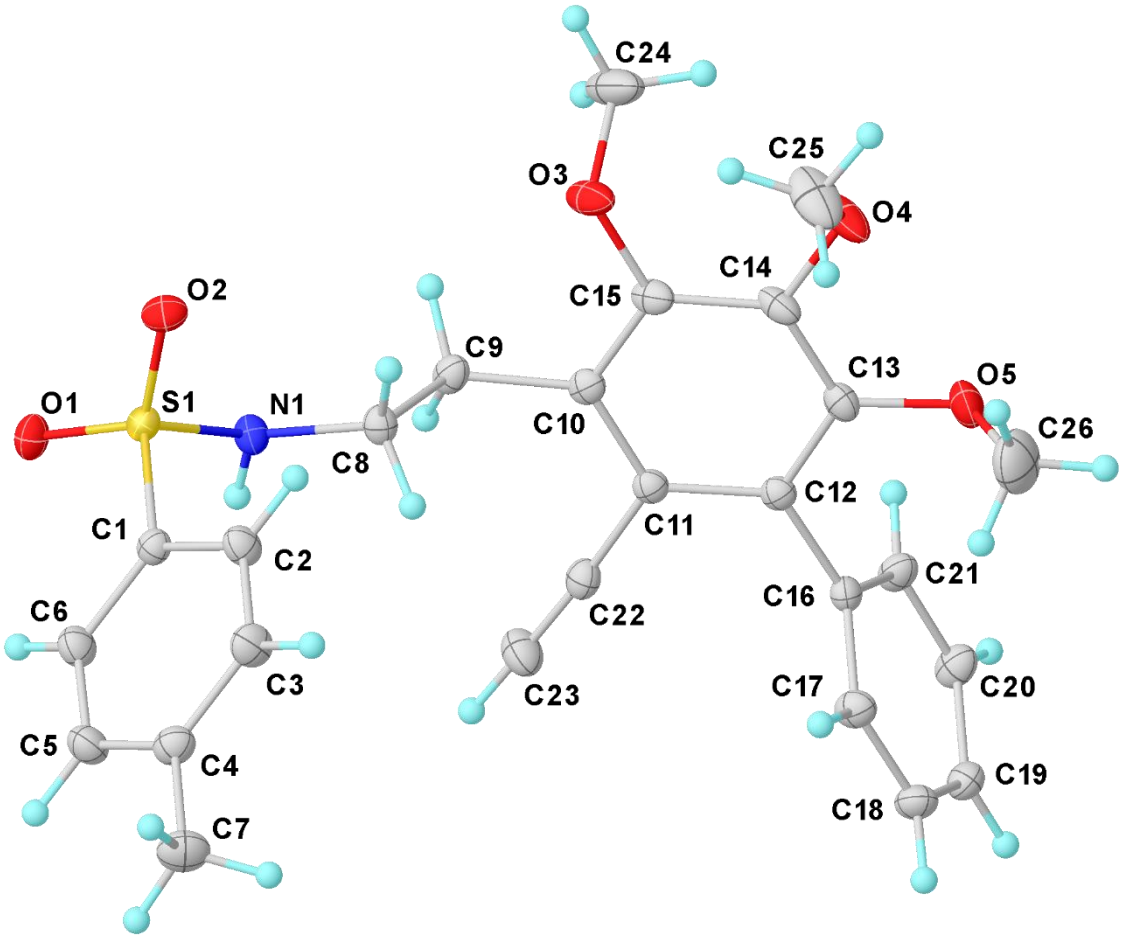


Figure 10: **Molecular structure of full asymmetric unit and numbering scheme of compound 24. Ellipsoids drawn at 50% probability level.**

Compound **24** was crystalized by simple evaporation from dichloromethane.

Table 10: **Crystal data and structure refinement for 24.**

CCDC	2068285
Empirical formula	$C_{26}H_{27}NO_5S$
Formula weight	465.54
Temperature/K	100
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	19.1173(15)
b/Å	9.5367(6)
c/Å	26.398(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4812.9(6)
Z	8
ρ_{calc}g/cm^3	1.285
μ/mm^{-1}	0.171
F(000)	1968.0

Crystal size/mm^3	0.288 × 0.238 × 0.178
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.016 to 57.408
Index ranges	-25 ≤ h ≤ 25, -12 ≤ k ≤ 11, -35 ≤ l ≤ 35
Reflections collected	43314
Independent reflections	6201 [R_{int} = 0.0276, R_{sigma} = 0.0176]
Data/restraints/parameters	6201/0/310
Goodness-of-fit on F^2	1.051
Final R indexes [I≥2σ (I)]	R_1 = 0.0356, wR_2 = 0.0907
Final R indexes [all data]	R_1 = 0.0415, wR_2 = 0.0950
Largest diff. peak/hole / e Å^{-3}	0.36/–0.42

Compound 28:

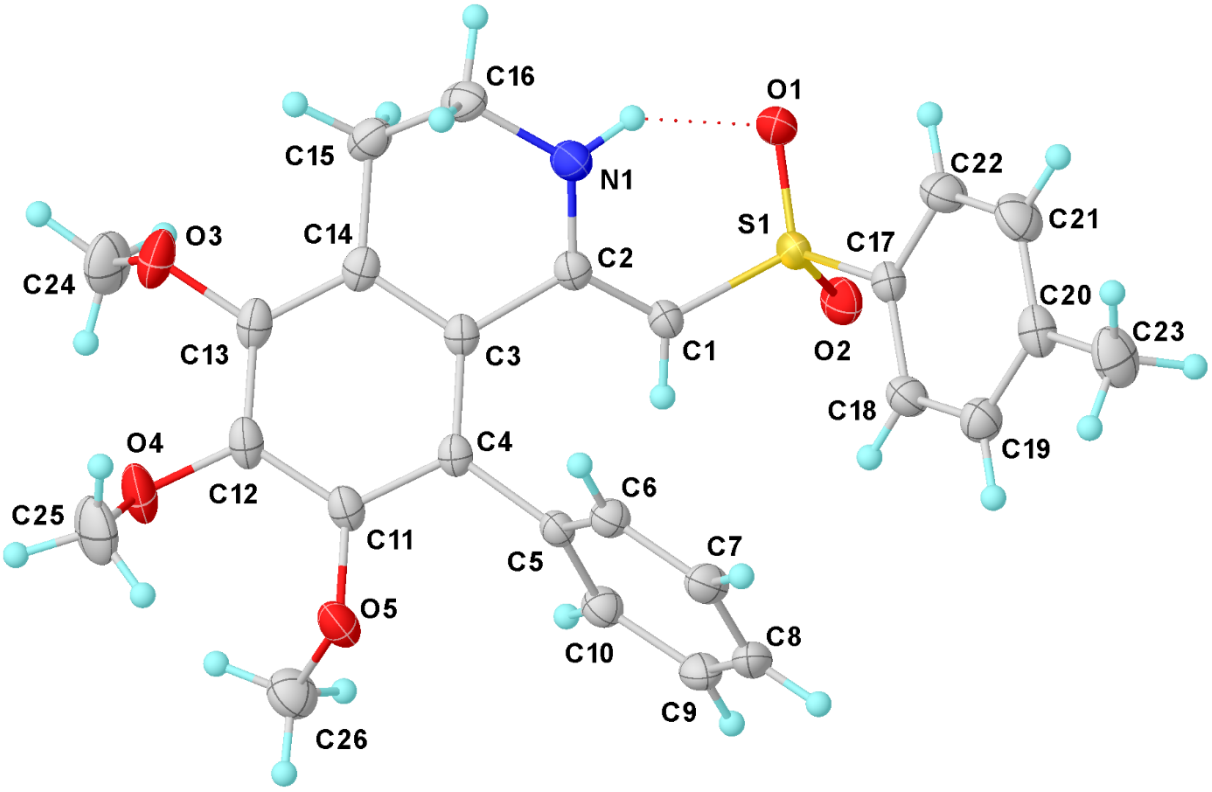


Figure 11: **Molecular structure of full asymmetric unit and numbering scheme of compound 28. Ellipsoids drawn at 50% probability level.**

Compound **28** crystalizes directly from the crude reaction while trying to charge it to a flash column (mixture of hexane and ethyl acetate as solvent). Twinned yellow block. Non-merohedral twinning was found with the two twin domain transformation matrix (0.999 0.042 0.070 / -0.020 0.981 -0.039 / -0.293 0.072 0.996). Final refinement against hklf5 data with refined batch scale factor of 0.289(2).

Table 11: **Crystal data and structure refinement for 28.**

CCDC	2068286
Empirical formula	$C_{26}H_{27}NO_5S$
Formula weight	465.54
Temperature/K	150
Crystal system	Triclinic
Space group	*P*1
a/Å	5.9594(19)
b/Å	7.747(2)
c/Å	12.894(4)
α/°	103.174(8)
β/°	91.499(8)
γ/°	95.991(9)
Volume/Å^3	575.6(3)
Z	1
ρ_{calc}g/cm^3	1.343
μ/mm^{-1}	0.179

F(000)	246.0
Crystal size/mm^3	0.33 × 0.246 × 0.094
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.5 to 57.592
Index ranges	-8 ≤ h ≤ 8, -10 ≤ k ≤ 10, -17 ≤ l ≤ 17
Reflections collected	5911
Independent reflections	5911 [R_{int} = ?, R_{sigma} = 0.0137]
Data/restraints/parameters	5911/3/311
Goodness-of-fit on F^2	1.074
Final *R* indexes [*I*≥2σ (*I*)]	R_1 = 0.0269, wR_2 = 0.0733
Final *R* indexes [all data]	R_1 = 0.0272, wR_2 = 0.0739
Largest diff. peak/hole / e Å^{-3}	0.21/–0.17
Flack parameter	–0.005(14)

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