A One-pot Garratt-Braverman Cyclization and Scholl Oxidation Route to Acene-Helicene Hybrids

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SUPPORTING INFORMATION

Table of Contents

General Remarks:

All the reactions were monitored by TLC using polygram[R] SILG/UV_{254} precoated (0.25 mm) silica gel TLC plates. Column chromatography was done with silica gel (60-120 or 230-400 mesh). NMR data were obtained with 200 MHz and 400 MHz Bruker NMR instruments. Proton and carbon spectra were referenced internally to solvent signals, using values of $\delta = 7.26$ ppm for proton and $\delta = 77.0$ for carbon (middle peak) in $CDCl_3$. The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, app. = apparently and b = broad signal. All coupling constants (*J*) are given in Hz. FT-IR spectra were obtained as KBr discs. Mass spectra were recorded in ESI+ mode (70 eV). Melting points were determined in open capillary tubes and are uncorrected

General procedure for Sonogashira coupling:

The aromatic halide or triflate (1.0 eq.), $PdCl_2(PPh_3)_2$ (0.03 eq.) and propargyl alcohol (1.2 eq.) were added in succession to degassed triethylamine and refluxed at 80 ^{0}C for 8 h. The reaction mixture was then poured into ethyl acetate and the organic layer was washed with saturated NH_4Cl solution and brine, dried over anhydrous sodium sulfate. Evaporation in vacuum gave a residue from which the product was isolated by column chromatography (Si-gel, petroleum ether-ethyl acetate mixture as eluent).

General procedure for synthesis of bromides 4, 7 and 9:

An ice-cold solution of the Sonogahira coupling product (1.0 eq.) and triethylamine (1.5 eq.) in THF was prepared. Mesyl chloride (1.5 eq., 5 times diluted with THF) was added dropwise. The reaction was complete within 5 mins. To the reaction mixture 5 equivalent of LiBr was added and the reactions took 2-3 hours to be complete depending on the substrates. The reaction mixture was then poured into water and extracted with DCM, washed with brine, dried over sodium sulfate, concentrated and subjected to column chromatography (Si-gel, 60-120 mesh, petroleum ether: ethyl acetate as eluent).

General procedure for the synthesis of sulfides:

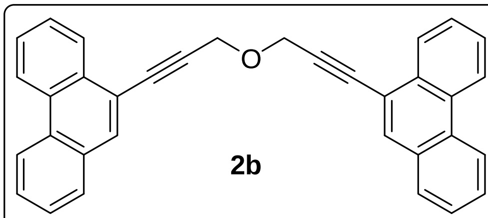
The bromide (1.0 eq.) was taken into THF-water (5:1), TBAB (0.1 eq.) and Na_2S (0.5 eq.) were added to it at 0 °C. The reaction was complete at room-temperature within 1 h. The reaction mixture was extracted with DCM, washed with water and brine, dried over anhydrous sodium sulfate, concentrated in vacuum and subjected to column chromatography (Si-gel, petroleum ether-ethyl acetate mixture as eluent).

Synthesis of sulfones (2a, 2e-h):

To an ice-cold solution of sulfides (1.0 eq.) in dry DCM, m-CPBA (2.0 eq.) was added in succession under inert condition. After 20 minutes the ice was removed and the reaction mixtures were left to attain the room-temperature. The reactions were complete within 10-15 minutes. The reactions were quenched by diluting the reaction mixture with water and DCM and washed with saturated solutions of Na_2SO_3 and Na_2CO_3 successively. DCM layers were dried over anhydrous Na_2SO_4 and the solutions were concentrated under reduced pressure and subjected to column chromatography (Si-gel, pet ether-ethyl acetate mixture as eluent).

Synthesis of ether 2b:

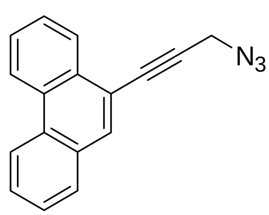
9-bromophenanthrene (1.0 eq.), $PdCl_2(PPh_3)_2$ (0.03 eq.) and bis-propargyl ether alcohol (2.2 eq.) were added in succession to degassed triethylamine and refluxed at 80 ^{0}C for 10 min. The product was isolated by the procedure described earlier for the Sonogashira reactions.



2b

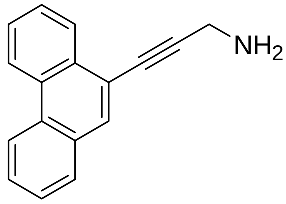
Synthesis of 9-(3-Azido-prop-1-ynyl)-phenanthrene:

The bromide **4** (1 eq.) was treated with 5 eq.. of NaN_3 in dry DMF for 4 h. The reaction was worked up with ethylacetate and water. Organic layer was washed with brine dried over sodium sulfate, evaporated and subjected to column chromatography (Si-gel 60-120 mesh, PE:EA = 20:1 as eluent).



9-(3-Azido-prop-1-ynyl)-phenanthrene

Synthesis of 3-Phenanthren-9-yl-prop-2-ynylamine:

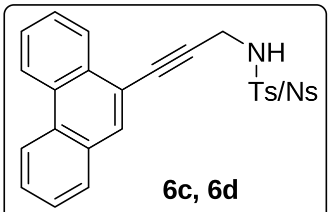


3-Phenanthren-9-yl-prop-2-ynylamine

9-(3-Azido-prop-1-ynyl)-phenanthrene (1.0 eq.) was treated with PPh_3 in THF: H_2O = 15:1 for 8 h. The product was isolated by coulumn chromatography (Si-gel 60-120 mesh, DCM:MeOH = 80:20 as eluent).

Synthesis of mono-propargyl sulfonamides 6c-d:

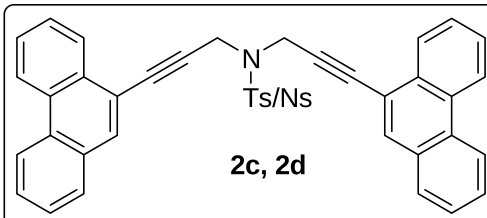
To an ice-cold solution of 9-(3-Azido-prop-1-ynyl)-phenanthrene (1.0 eq.) and triethylamine (1.0 eq.) in anhydrous DCM 1.0 eq. of tosyl chloride (for **6c**) or nosyl chloride (for **6d**) was added dropwise as a solution in DCM and the reaction was left to attain room temperature. The product was separated by column chromatography (Si-gel 60-120 mesh, PE-EA mixture as eluent).



6c, 6d

Synthesis of bis-propargyl sulfonamides 2c-d:

1.0 eq. of bromide **4** was added to a solution of 5.0 eq. of dry K_2CO_3 and 1.0 eq. of 6c (for 2c) or 1.0 eq. of 6d (for 2d) in dry DMF. The reaction was stirred for 4h at room temperature and worked up with ethylacetate and water and brine. The organic layer was dried over sodium sulfate, evaporated and the product was purified by column chromatography (Si-gel 60-120 mesh, PE-EA mixture as eluent).



2c, 2d

Synthesis of acenes 10a-j:

The sulfone starting materials **2a, 2e-h** were treated with catalytic triethylamine in DCM at r.t. to furnish the GB products. The progress of the reactions were monitored by TLC. After the completion of GB, 25 eq. of anh. $FeCl_3$ was added to the reaction mixture in two equal portions. The reaction mixtures were directly subjected to column chromatography (Si-gel 60-120 mesh, PE-EA mixture as eluent). The ether and sulfonamide starting materials **2b-d** were refluxed at 110 ^{0}C in toluene with catalytic

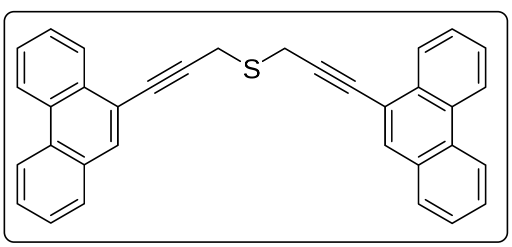
DBU for 10 mins for GB reaction to occur then the reaction mixture was cooled to r.t., dry DCM was added to it and 25 eq. of anh. $FeCl_3$ was added to the reaction mixture in two equal portions. The reactions were found to be complete within 5 mins. The spectral data of the GB products were obtained from the aliquots collected prior to the addition of $FeCl_3$ and purified by column chromatography (Si-gel 60-120 mesh, PE-EA mixture as eluent). The reaction time and the timings of addition of $FeCl_3$ for various sulfone starting materials are tabulated below.

Bis-propargyl sulfone	Time of addition of 1st 12.5 eq. of anh. $FeCl_3$	Time of addition of 2nd 12.5 eq. of anh. $FeCl_3$	Reaction time
2a	15 min.	17 min.	20 min.
2e	5 min.	3 h	6 h
2f	5 min.	2 h	3 h
2g	7 min.	6 h	24 h
2h	7 min.	6 h	24 h

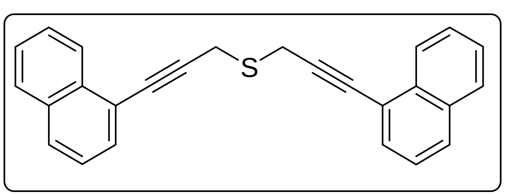
Table 1: One pot reaction condition

Spectral data:

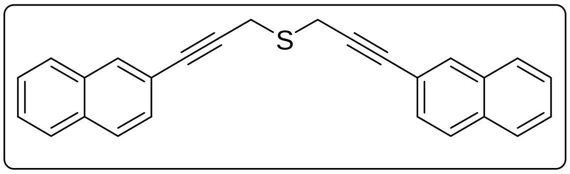
5: Yellow solid; Yield 95%; δ_H ($CDCl_3$, 200 MHz): 4.06 (s, 4H), 7.58-7.86 (m, 10H), 8.52-8.57 (m, 2H), 8.57-8.68 (m, 4H), δ_C ($CDCl_3$, 50 MHz): 20.9, 82.2, 89.4, 119.5, 122.8, 123.0, 127.0, 127.1, 127.2, 127.3, 127.7, 128.7, 130.3, 130.5, 131.3, 131.5, 132.4.



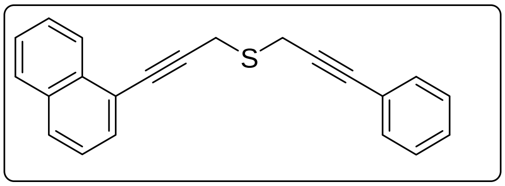
Bis-(1-naphthylpropargyl) sulfide: Yellow liquid; Yield 75%, δ_H ($CDCl_3$, 200 MHz): 4.07 (s, 4H), 7.44-7.55 (bm, 2H), 7.59-7.69 (bm, 4H), 7.82-7.94 (bm, 6H), 8.57 (d, J = 7.8 Hz, 2H); δ_C ($CDCl_3$, 50 MHz): 20.8, 82.1, 89.8, 120.8, 125.4, 126.3, 126.6, 127.1, 128.5, 129.0, 130.9, 133.4, 133.7.



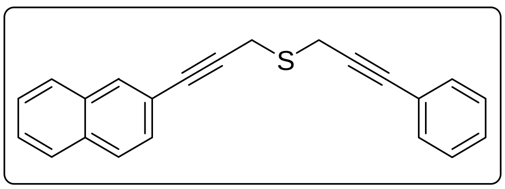
Bis-(2-naphthylpropargyl) sulfide: Yellow liquid; Yield 75%, δ_H ($CDCl_3$, 400 MHz): 3.90 (s, 2H), 3.91 (s, 2H), 7.52-7.61 (m, 6H), 7.81-7.89 (m, 6H), 8.06 (s, 2H). δ_C ($CDCl_3$, 100 MHz) 20.6, 84.0, 85.2, 120.4, 126.6, 126.7, 127.8, 128.0, 128.6, 131.8, 132.9, 133.0 (1C singal was merged).



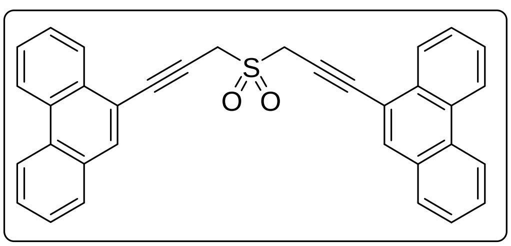
1-[3-(3-Phenyl-prop-2-ynylsulfanyl)-prop-1-ynyl]-naphthalene: Yellow liquid; Yield 95%, δ_H ($CDCl_3$, 200 MHz): 3.84 (s, 2H), 3.94 (s, 2H), 7.35-7.88 (m, 11H), 8.39-8.42 (m, 1H); δ_C ($CDCl_3$, 50 MHz) 20.5, 20.6, 81.9, 83.9, 84.8, 89.7, 120.8, 123.2, 125.4, 126.4, 126.6, 127.0, 128.5, 128.9, 130.8, 132.0, 133.4, 133.7 (2C signals were merged).



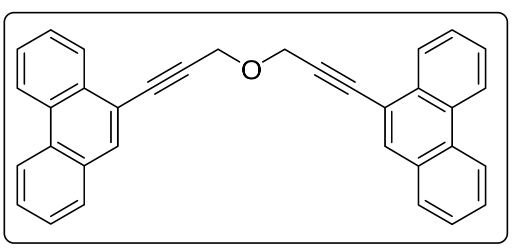
2-[3-(3-Phenyl-prop-2-ynylsulfanyl)-prop-1-ynyl]-naphthalene: Yellow liquid; Yield 95%, δ_H ($CDCl_3$, 200 MHz) 3.81 (s, 2H), 3.83 (s, 2H), 7.35-7.55 (m, 7H), 7.79-7.83 (m, 4H), 8.01 (s, 1H); δ_C ($CDCl_3$, 50 MHz) 20.6, 83.7, 84.0, 84.9, 85.2, 120.5, 122.6, 122.9, 123.2, 126.7, 126.8, 127.9, 128.1, 128.5, 128.8, 131.9, 132.0, 133.0, 133.2 (1C signal was merged).



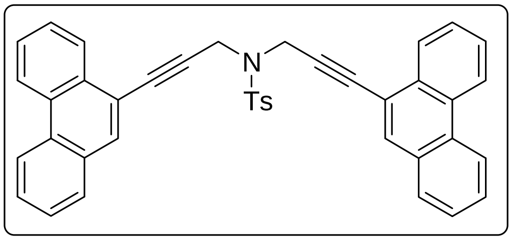
2a: Yellow solid; Yield 90%, δ_H ($CDCl_3$, 200 MHz): 4.61 (s, 4H), 7.54-7.82 9m, 5H), 8.05 (s, 1H), 8.44-8.49 (m, 1H), 8.62-8.68 (m, 2H); δ_C ($CDCl_3$, 50 MHz): 45.4, 80.5, 87.0, 118.0, 122.8, 123.0, 126.8, 127.3, 127.5, 127.6, 128.2, 128.9, 130.2, 130.8, 130.9, 131.1, 133.4.



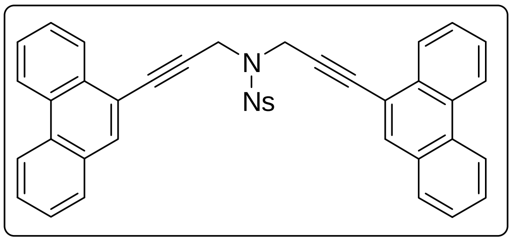
2b: White solid; Yield 70%, δ_H ($CDCl_3$, 200 MHz): 4.89 (s, 4H), 7.56-7.75 (m, 4H), 7.82-7.87 (m, 1H), 8.08 (s, 1H), 8.51-8.63 (m, 1H), 8.67-8.71 (m, 2H); δ_C ($CDCl_3$, 50 MHz): 58.0, 85.5, 89.1, 119.1, 122.8, 122.9, 127.0, 127.1, 127.3, 128.8, 130.2, 130.5, 131.2, 132.7 (3C signals were merged).



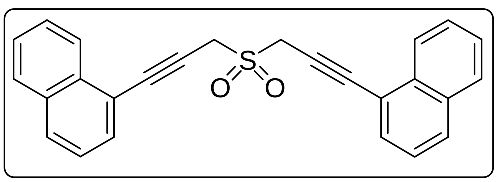
2c: White solid; Yield 95%, δ_H ($CDCl_3$, 200 MHz): 2.14 (s, 3H), 4.80 (s, 4H), 7.22-7.31 (m, 3H), 7.56-7.80 (m, 12H), 7.95 (d, *J* = 7.4 Hz, 2H), 8.24 (d, *J* = 8.4 Hz, 2H), 8.65-8.69 (m, 3H).



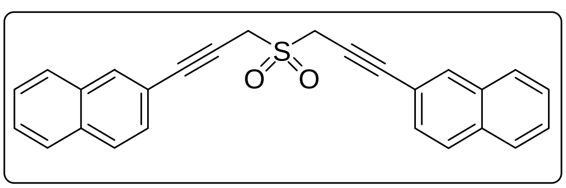
2d: Yellowish solid; Yield 85%, δ_H ($CDCl_3$, 400 MHz): 4.81 (s, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.60-7.70 (m, 8H), 8.11 (d, *J* = 8.0 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 8.61 (t, *J* = 7.6 Hz, 4H); δ_C ($CDCl_3$, 100 MHz): 38.6, 85.1, 85.4, 117.9, 122.5, 122.8, 124.1, 126.2, 127.0, 127.1, 127.2, 127.8, 128.4, 129.3, 129.9, 130.3, 130.5, 130.6, 132.6, 144.6 (1C signal was merged).



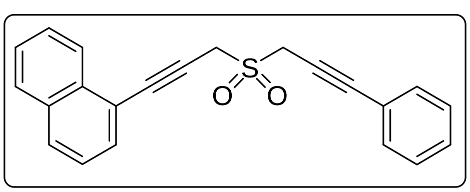
2e: Yellow solid; Yield 82%, δ_H ($CDCl_3$, 200 MHz): 4.57 (s, 4H), 7.40-7.56 (bm, 6H), 7.75-7.90 (bm, 6H), 8.41 (d, *J* = 7.4 Hz, 2H); δ_C ($CDCl_3$, 50 MHz) 45.0, 80.9, 86.6, 119.1, 125.2, 125.9, 126.8, 127.4, 128.5, 130.0, 131.4, 133.2, 133.5.



2f: Yellow solid; Yield 90%, δ_H ($CDCl_3$, 200 MHz): 4.45 (4H, s), 7.52-7.60 (6H, m), 7.78-7.88 (6H, m), 8.07 (2H, s); δ_C ($CDCl_3$, 50 MHz): 45.1, 88.8, 117.8, 124.8, 127.0, 127.4, 127.8, 128.0, 128.4, 128.8, 133.0, 135.6 (1C signal was merged)..

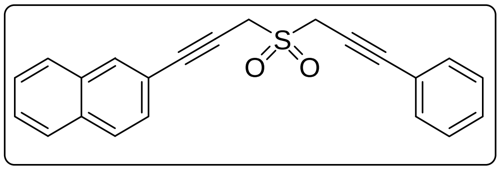


2g: Yellow solid; Yield 95%, δ_H ($CDCl_3$, 200 MHz): 4.40 (s, 2H), 4.50 (s, 2H), 7.30-7.57 (m, 8H), 7.73-7.74 (m, 1H), 7.80-7.90 (m, 2H), 8.30-8.40 (m, 1H); 4.39 (m, 4H), 7.32-7.40 (m, 3H), 7.51-7.53 (m, 5H), 7.79-7.84 (m, 3H), 8.03 (s, 1H); δ_C ($CDCl_3$, 50 MHz): 44.9, 45.0, 76.2,

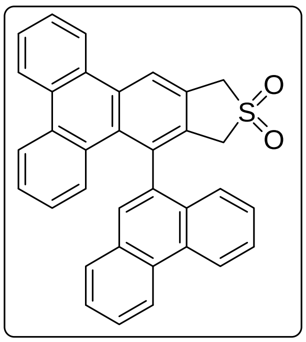


80.9, 86.6, 88.4, 119.2, 121.6, 125.3, 126.0, 126.8, 127.5, 128.6, 129.5, 130.0, 131.5, 132.2, 133.3, 133.7 (1C signal was merged).

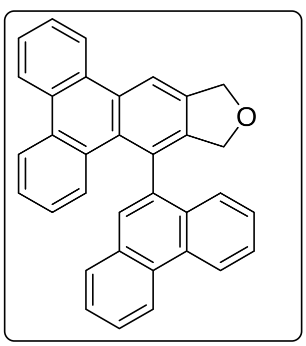
2h: Yellow solid; Yield 93%, δ_H ($CDCl_3$, 200 MHz): 4.37-4.42 (m, 4H), 7.32-7.40 (m, 3H), 7.51-7.53 (m, 3H), 7.79-7.84 (m, 3H), 8.03 (s, 1H); δ_C ($CDCl_3$, 50 MHz): 44.8, 44.8, 76.1, 76.3, 88.2, 88.5, 118.8, 121.6, 126.9, 127.4, 127.9, 128.0, 128.3, 128.3, 128.6, 129.4, 132.2, 132.6, 132.9, 133.3.



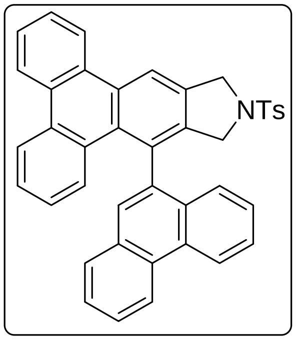
1a: White solid; Yield 95%, δ_H ($CDCl_3$, 400 MHz): 4.01 (d, *J* = 16.0 Hz, 1H), 4.06 (d, *J* = 16.0 Hz, 1H), 4.76 (s, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 7.46-7.60 (m, 4H), 7.62-7.64 (m, 2H), 7.73-7.75 (m, 1H), 7.80-7.94 (m, 6H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H), 8.72-8.81 (m, 3H), 8.91 (d, *J* = 8.8 Hz, 1H), 8.98 (d, *J* = 8.4 Hz, 1H); δ_C ($CDCl_3$, 100 MHz): 57.3, 57.9, 120.6, 120.7, 123.1, 123.3, 123.6, 123.7, 125.7, 126.1, 127.0, 127.1, 127.3, 127.5, 127.6, 127.9, 128.2, 128.4, 128.9, 129.1, 129.6, 129.8, 130.2, 130.4, 131.1, 131.7, 131.9, 132.4, 136.4, 138.4 (4C signals were merged).; MS: m/z = 517.12 [MNa^+], 495.13 [MH^+].



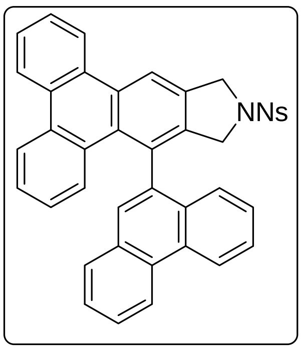
1b: Yellow solid; Yield 95%, δ_H ($CDCl_3$, 400 MHz): 4.64 (d, *J* = 13.2 Hz, 1H), 4.82 (d, *J* = 13.2 Hz, 1H), 5.44 (s, 2H), 6.77 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.61-7.82 (m, 6H). 7.90 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.63-8.65 (m, 1H), 8.70-8.74 (m, 2H), 8.83 (t, *J* = 9.2 Hz, 4H); δ_C ($CDCl_3$, 100 MHz): 74.3, 74.6, 115.6, 123.0, 123.3, 123.5, 123.8, 123.9, 126.2, 126.6, 126.9, 127.2, 127.4, 127.5, 127.6 (2C signals), 127.7, 128.5, 128.6, 129.1, 129.5, 130.2, 130.3, 130.4, 130.5, 130.9, 131.3, 131.8, 132.2, 132.3, 138.4, 139.4, 141.4; MS: m/z = 469.16 [MNa^+], 447.17 [MH^+].



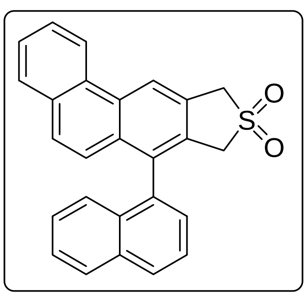
1c: White solid; Yield 95%, δ_H ($CDCl_3$, 200 MHz): 4.22 (d, *J* = 14.4 Hz, 1H), 4.35 (d, *J* = 14.4 Hz, 1H), 4.98 (s, 2H),6.77 (t, *J* = 7.2 Hz, 1H), 7.26-7.87 (m, 15H), 8.54-8.70 (m, 4H), 8.90 (t, *J* = 6.8 Hz, 2H); δ_C ($CDCl_3$, 50 MHz): 21.7, 54.4, 54.7, 117.2, 123.0, 123.2, 123.5, 123.7, 126.2, 126.9, 127.2, 127.4, 127.5, 127.7, 127.9, 128.5, 129.1, 130.0, 130.5, 130.9, 131.4, 132.0, 132.2, 133.8, 134.0, 135.3, 138.1, 138.6, 143.8 (10C signals were merged); MS: m/z = 622.18 [MNa^+], 600.20 [MH^+].



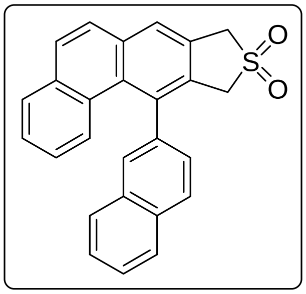
1d: White solid; Yield 90%, δ_H ($CDCl_3$, 400 MHz): 4.17 (d, *J* = 14.4 Hz, 1H), 4.33 (d, *J* = 14.4 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 7.26-7.39 (m, 2H0, 7.45 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 1H), 7.64-7.82 (m, 7H), 7.88 (d, *J* = 8.8 Hz, 2H), 8.27 (d, *J* = 8.8 Hz, 2H), 8.52 (d, J = 8.0 Hz, 1H), 8.59-8.65 (m, 3H), 8.84-8.89 (m, 2H). δ_C ($CDCl_3$, 100 MHz): 54.2, 54.5, 117.0, 118.9, 122.5, 122.8, 123.3, 123.5, 124.4, 126.1, 126.7, 127.0, 127.1, 127.2, 127.3, 127.4, 127.5, 127.8, 128.2, 128.4, 128.5, 128.8, 129.5, 129.7, 130.0, 131.2, 131.8, 131.9, 132.2, 133.6, 134.1, 136.9, 138.1, 142.7, 150.1 (3C signals wre merged); MS: m/z = 653.15 [MNa^+], 631.17 [MH^+].



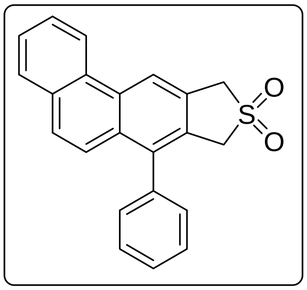
1e: Yellowish white solid; Yield 96%, δ_H ($CDCl_3$, 200 MHz): 4.01, 4.20 (ABq, *J* = 16.2 Hz, 2H), 4.73 (s, 2H), 7.21-7.32 (m, 3H), 7.36-7.42 (m, 1H), 7.49-7.58 (m, 2H), 7.62-7.72 (m, 3H), 7.79-7.83 (d, *J* = 7.2 Hz, 1H), 7.98-8.04 (t, *J* = 6.4 Hz, 2H), 8.68-8.72 (2H, m); δ_C ($CDCl_3$, 50 MHz): 56.5, 57.8, 120.0, 123.0, 124.5, 125.3, 125.8, 126.6, 127.2, 127.3, 127.5, 127.7, 128.1, 129.0, 129.4, 129.8, 130.0, 130.7, 131.4, 131.8, 132.0, 134.0, 135.3, 136.6 (2C signals were merged); MS: m/z = 417.09 [MNa+], 395.11 [MH+].



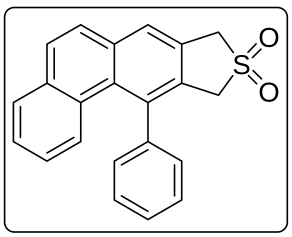
1f: Yellow solid; Yield 95%, δ_H ($CDCl_3$, 200 MHz): 4.02, 4.19 (ABq, *J* = 16.5 Hz, 2H), 4.58 (s, 2H), 6.93 (t, *J* = 7.8 Hz, 1H), 7.19-7.39 (m, 2H), 7.52-7.57 (m, 3H), 7.69-7.80 (m, 6H), 7.91-8.00 (m, 2H). δ_C ($CDCl_3$, 50 MHz): 57.6, 57.7, 125.9, 126.0, 126.6, 126.7, 126.9, 127.0, 127.3, 127.8, 128.2, 128.3, 128.9, 128. 9, 129.1, 130.1, 130.3, 131.2, 132.9, 133.7, 133.8, 134.1, 138.1, 139.6 (2C signals were merged); MS: m/z = 417.08 [MNa+], 395.12 [MH+].



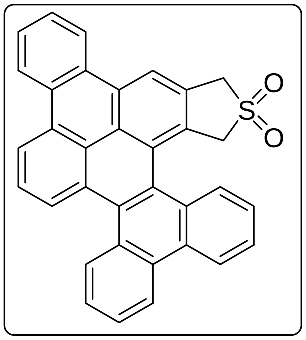
1g: Yellowish white solid; Yield 96%, ^{1}H NMR (Acetone-d_6, 400 MHz): δ 4.27 (s, 2H), 4.77 (s, 2H), 7.41-7.80 (m, 7H), 7.97 (d, J = 8.0 Hz, 1H), 8.88 (d, J = 8.0 Hz, 1H), 9.08 (s, 1H); MS: m/z = 367.08 [MNa+], 345.09 [MH+].



1h: Yellowish white solid; Yield 96%, ^{1}H NMR (Acetone-d_6, 400 MHz): δ 4.16 (s, 2H), 4.71 (s, 2H), 7.09 (t, *J* = 7.2 Hz, 1H)7.35-7.38 (m, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.57-7.65 (m, 4H), 7.88 (s, 2H), 7.92 (d, *J* = 7.6 Hz, 1H), 8.08 (s, 1H). MS: m/z = 367.07 [MNa+], 345.08 [MH+].

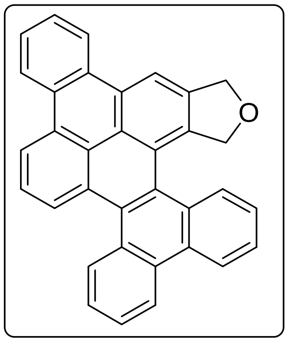


10a: Yellow crystals; m.p. >250 °C; Yield: 75%; δ_H (400 MHz, $CDCl_3$): 3.75 (d, *J* = 16.4 Hz, 1H), 4.64 (d, *J* = 15.2 Hz, 1H), 5.00 (d, *J* = 16.4, 1H), 5.07 (d, *J* = 15.2 Hz, 1H), 7.60-7.84 (m, 7H), 8.10 (t, *J* = 8.0 Hz, 1H), 8.71 (d, *J* = 7.6 Hz, 1H), 8.77-8.89 (m, 5H), 8.96 (d, *J* = 8.0 Hz, 1H), 9.05 (d, *J* = 8.0 Hz, 1H); δ_C (100 MHz, CDCl3): 57.3, 60.5, 118.1, 121.5, 123.9, 124.0, 124.1, 124.2, 124.9, 126.1, 126.6, 126.7, 126.9, 127.0, 127.2, 127.4, 127.6, 127.7, 128.2, 128.6 (2C signals), 129.0, 129.2,

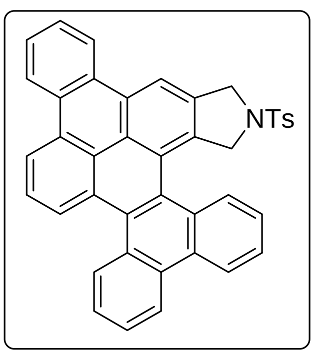


129.3, 129.5, 129.6, 130.0 (2C signals), 130.6, 130.8, 131.6, 131.8 (2C signals were merged); MS: m/z = 515.11 [MNa^+], 493.12 [MH^+]. HRMS: Calcd. for $C_{34}H_{20}O_2S+H^+$ 493.1262 found 493.1263 [MH^+].

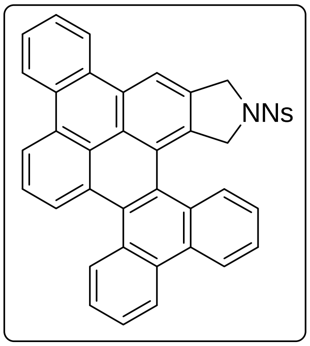
10b: Yellow crystals: m. p. >250 °C; Yield: 74%; δ_H (400 MHz, $CDCl_3$): 4.52 (d, *J* = 13.2 Hz, 1H), 5.34 (d, *J* = 12.0 Hz, 1H), 5.68 (d, *J* = 12.0 Hz, 1H), 5.74 (d, *J* = 13.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.68-7.83 (m, 6H), 8.05 (t, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 8.0 Hz, 1H), 8.88-8.84 (m, 4H), 8.93 (d, *J* = 7.6 Hz, 1H), 9.01 (d, *J* = 8.0 Hz, 1H), δ_C (100 MHz, CDCl3): 73.9, 76.5, 113.0, 120.6, 123.4, 123.6, 123.7, 123.8 (2C signals), 124.6, 125.8, 126.4, 126.7, 126.8 (2C signals), 126.9 (2C signals),127.6 (2C signals), 128.5, 128.7, 129.0, 129.2 (2C signals), 129.9 (2C signals), 130.0, 131.0, 131.3, 134.4, 134.6, 139.4 (2C signals were merged); MS: m/z = 467.14 [MNa^+], 445.16 [MH^+]. HRMS: Calcd. for $C_{34}H_{20}O+H^+$ 445.1592 found 445.1599 [MH^+].



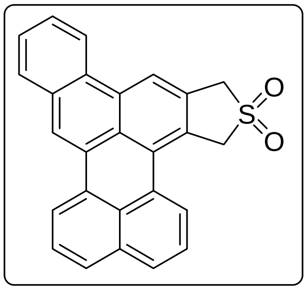
10c: Yellow powder: m. p. >250 °C; Yield: 80%; δ_H (400 MHz, $CDCl_3$): 4.00 (d, *J* = 14.4 Hz, 1H); 4.89 (d, *J* = 13.2 Hz, 1H), 5.08 (d, *J* = 13.2 Hz, 1H), 5.18 (d, *J* = 14.8, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.62-7.47 (m, 3H), 7.81-7.72 (m, 6H), 7.6 Hz, 1H), 8.01 (t, *J* = 8.0 Hz, 8.71-8.65 (m, 3H), 8.84-8.78 (m, 3H), 8.87 (d, *J* = 8.0 Hz, 1H), 8.98 (d, *J* = 8.0 Hz, 1H); δ_C (100 MHz, CDCl3): 21.2, 54.4, 57.1, 114.3, 120.7, 123.5, 123.7, 123.8, 124.1, 124.3, 126.0, 126.3, 126.4, 126.5, 126.9, 127.0 (2C signals), 127.3, 127.7, 127.8, 127.9, 128.4, 128.7, 128.8, 128.9, 129.0, 129.1, 129.2, 129.4, 129.5, 129.9, 130.0, 130.3, 131.4, 131.6, 132.9, 136.1, 143.5 (1C signal was merged); MS: m/z = 620.17 [MNa^+], 598.18 [MH^+]. HRMS: Calcd. for $C_{41}H_{27}NO_2S+H^+$ 598.1841 found 598.1843 [MH^+].



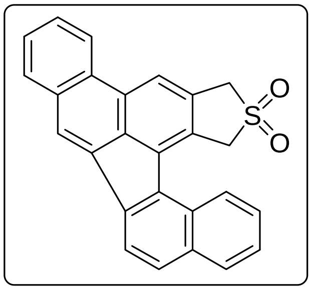
10d: Yellow powder: m. p. >250 °C; Yield: 80%; δ_H (400 MHz, $CDCl_3$): 4.1 (d, *J* = 11.6 Hz, 1H), 4.96 (d, *J* = 13.2 Hz, 1H), 5.21 (d, *J* = 13.6 Hz, 1H), 5.29 (d, *J* = 17.6 Hz, 1H), 743-7.82 (m, 13H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.73-7.83 (m, 4H), 8.88 (d, *J* = 8.0 Hz, 1H), 8.95 (d, *J* = 7.6 Hz, 1H), 9.04 (d, *J* = 8.0 Hz, 1H). MS: m/z = 651.38 [MNa^+], 629.51[MH^+]. HRMS: Calcd. for $C_{40}H_{25}N_2O_4S+H^+$ 629.1535 found 629.1536 [MH^+].



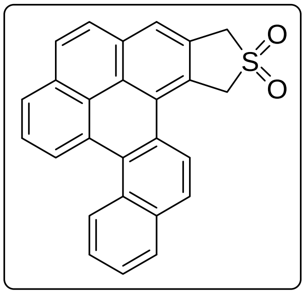
10e: State: yellowish solid; m. p. >250 °C, yield: 30%; δ_H ($CDCl_3$, 400 MHz), 3.96, 4.25 (ABq, *J* = 16 Hz, 2H), 4.86 (s, 2H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.31 (s, 1H), 7.41-7.45 (m, 1H), 7.59-7.62 (m, 2H), 7.76-7.80 (m, 1H), 7.87-7.94 (m, 2H), 8.13 (bd, *J* = 8 Hz, 1H), 8.18 (bd, *J* = 8.4 Hz, 1H), 8.35-8.37 (m, 1H), 9.06 (bd, *J* = 8 Hz, 1H), 9.16 (s, 1H). δ_C ($CDCl_3$, 100 MHz) 55.9, 57.2, 120.6, 123.9, 124.0, 124.6, 125.1, 126.0, 126.7, 127.3, 128.1, 128.6, 128.6, 129.0, 129.3, 129.8, 130.7, 131.3, 131.4, 131.8, 132.0, 132.3, 134.2, 134.7, 135.6 (1C signal was merged). MS: m/z = 415.08 [MNa^+], 393.23, [MH^+]. HRMS: Calcd. for $C_{26}H_{17}O_2S+H^+$ 393.0949 found 393.0943 [MH^+].



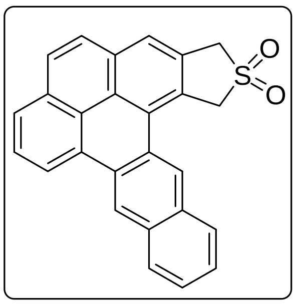
10f: Yellow solid; m. p. >250 °C, Yield 95%, δ_H ($CDCl_3$, 400 MHz): 4.00, 4.30 (ABq, *J* = 16.4 Hz, 2H), 4.85 (s, 2H), 7.10-7.33 (m, 2H), 7.52-7.56 (m, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.76-7.80 (m, 1H), 7.86-7.91 (m, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 8.35-8.38 (m, 1H), 8.46 (bd, *J* = 8.4 Hz, 1H), 9.05-9.07 (m, 1H), 9.17 (s, 1H). δ_C ($CDCl_3$, 100 MHz) 55.9, 57.2, 121.0, 123.9, 123.9, 125.0, 125.2, 126.0, 126.6, 128.1, 128.2, 128.4, 128.6, 128.7, 129.3, 129.8, 130.7, 131.2, 131.3, 131.6, 132.1, 132.5, 133.1, 134.5, 134.6 (1C signal was merged); MS: m/z = 415.05 [MNa^+], 393.15, [MH^+]. HRMS: Calcd. for $C_{26}H_{17}O_2S+H^+$ 393.0949 found 393.0941 [MH^+].



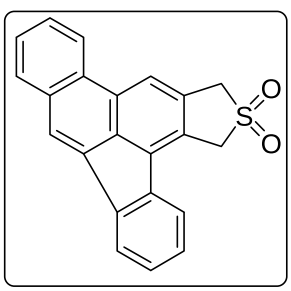
10g: White solid; Yield 90%, mp 240 °C; δ_H ($CDCl_3$, 400 MHz): δ 4.88 (s, 2H), 5.32 (s, 2H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.87 (t, *J* = 7.4 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 1H), 8.20 (d, *J* = 9.6 Hz, 1H), 8.34 (s, 1H), 8.40-8.45 (m, 4H), 8.89-8.92 (m, 2H). δ_C ($CDCl_3$, 100 MHz) 55.6, 60.4, 121.9, 123.5, 123.8, 124.1, 124.7, 124.9, 125.2, 125.7, 125.8, 126.0, 126.8, 127.0, 127.3, 127.5, 127.6, 127.9, 128.1, 128.7, 129.3, 129.9, 130.4, 130.5, 130.6, 130.7; MS: m/z = 415.03 [MNa^+], 393.10, [MH^+]. HRMS: Calcd. for $C_{26}H_{17}O_2S+H^+$ 393.0949 found 393.0953 [MH^+].



10h: Yellow solid; Yield 95%, mp 242 °C. δ_H ($CDCl_3$, 400 MHz): 4.98 (s, 2H), 5.52 (s, 2H), 7.85-7.95 (m, 4H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.30 (s, 1H), 8.47 (d, *J* = 7.6 Hz, 2H), 8.59 (s, 1H), 8.61 (s, 1H), 8.94 (d, *J* = 8.4 Hz, 1H), 9.01 (d, *J* = 8.4 Hz, 1H); δ_C ($CDCl_3$, 100 MHz) 56.0, 59.6, 123.8, 124.8, 124.9, 125.5, 125.6, 125.8, 127.1, 127.3, 127.4, 127.5, 127.5, 127.6, 128.0, 128.1, 128.2, 128.4, 128.9, 129.0, 129.5, 130.7, 130.8, 131.1, 131.4, 131.6; MS: m/z = 415.05 [MNa^+], 393.09, [MH^+]. HRMS: Calcd. for $C_{26}H_{17}O_2S+H^+$ 393.0949 found 393.0951 [MH^+].



10i: Yellow solid; Yield 95%, mp 240 °C. δ_H ($CDCl_3$, 400 MHz): 4.15 (s, 2H), 4.69 9s, 2H), 7.20-7.22 (m, 2H), 7.45-7.46 (m, 3H), 7.75-7.77 (m, 2h, 8.41-8.44 (m, 1H), 8.64-8.67 (m, 1H), 8.71 (s, 1H); δ_C ($CDCl_3$, 100 MHz): 57.9, 58.0, 124.1, 124.7, 126.4, 127.5, 127.9, 128.1, 128.3, 128.5, 128.7, 128.7, 129.1, 129.3, 130.0 130.1, 130.4, 130.5, 130.7, 132.2, 133.3, 138.7, 142.0 ; MS: m/z = 365.10 [MNa^+], 343.08 [MH^+]; HRMS: Calcd. for $C_{16}H_{12}O_4S+H^+$ 343.0793 found 343.0788



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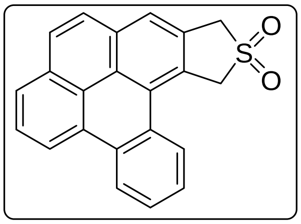
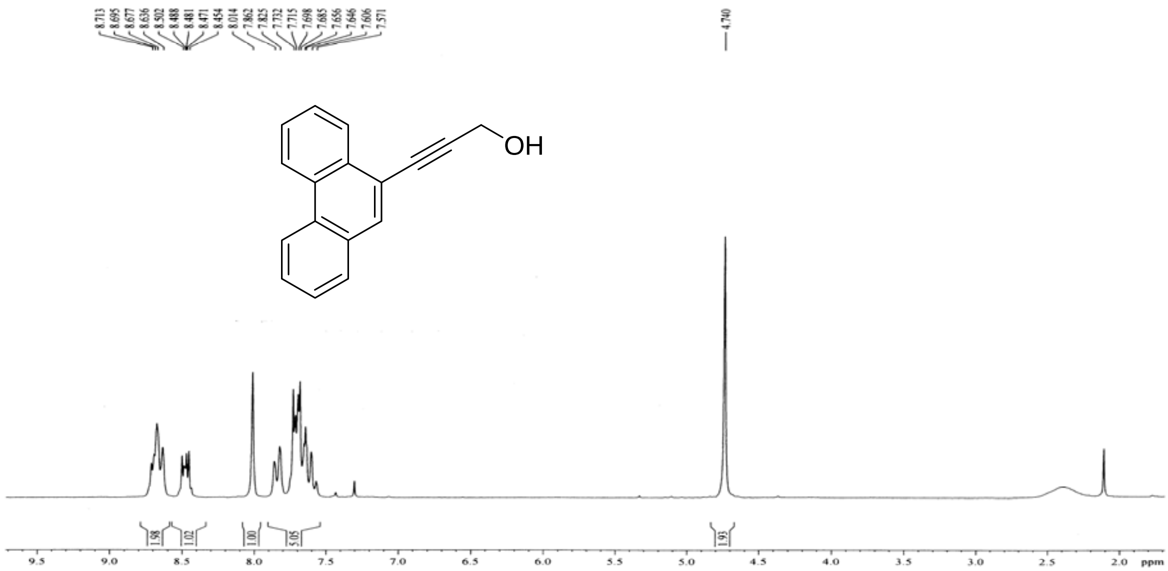
10j: Yellow solid; Yield 95%, mp 240 °C; δ_H ($CDCl_3$, 400 MHz): 4.19 (s, 2H), 4.70 (s,

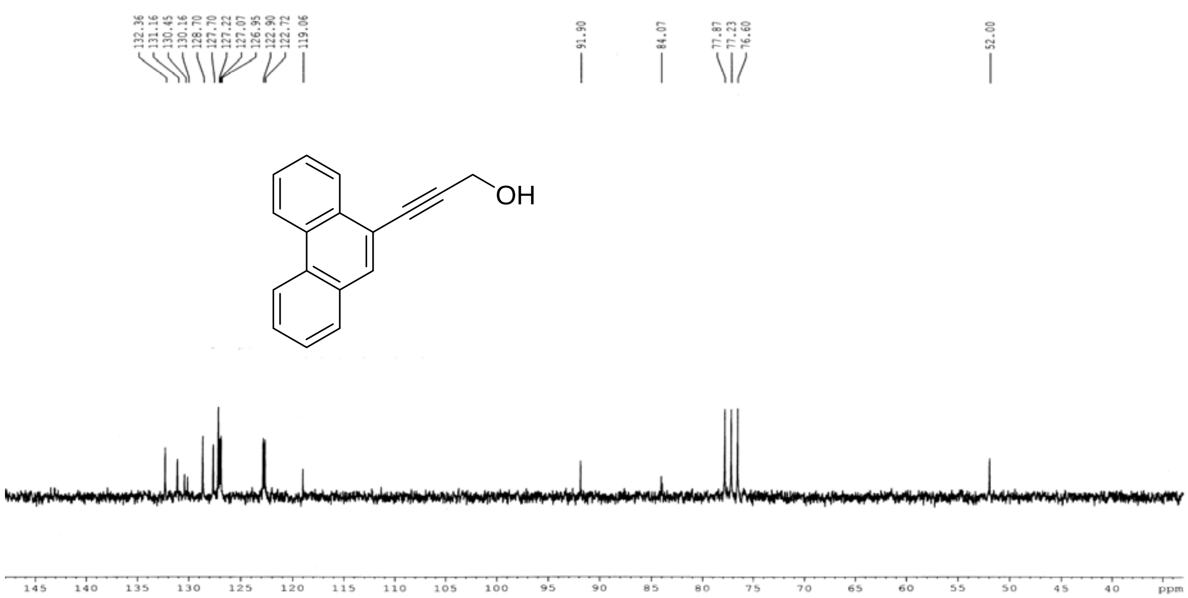


2H), 7.09 (t, *J* = 8.4 Hz, 1H), 7.28 (s, 1H), 7.44-7.74 (m, 5H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.94 (s, 1H), 8.47 (s, 1H); δ_C ($CDCl_3$, 100 MHz): 56.8, 58.8, 119.7, 123.0, 124.0, 125.5, 126.2, 127.9, 128.1, 128.2, 128.6, 128.9, 129.2, 129.4, 129.5, 129.6, 129.8, 130.4, 130.7, 132.1, 137.1, 138.0; MS: m/z = 365.11 [MNa+], 343.07 [MH+]; HRMS: Calcd. for $C_{16}H_{12}O_4S$+H+ 343.0793 found 343.0798.

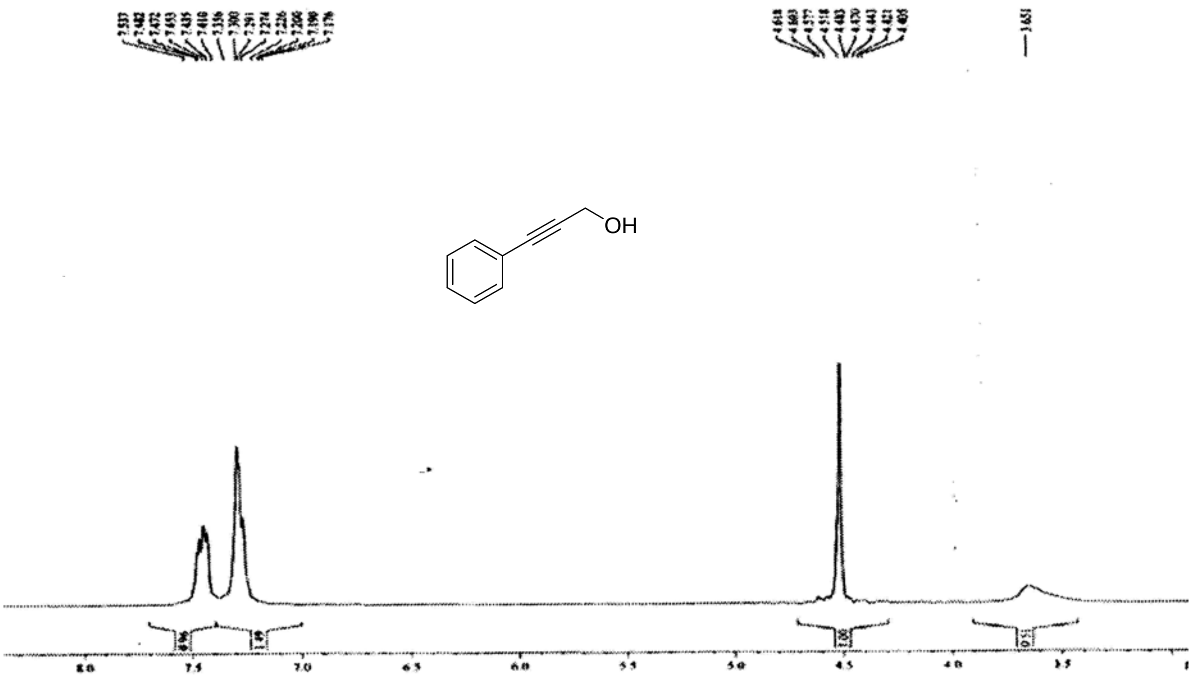
[1]H and [13]C NMR spectra of all compounds (all were recorded in $CDCl_3$ unless otherwise specified)



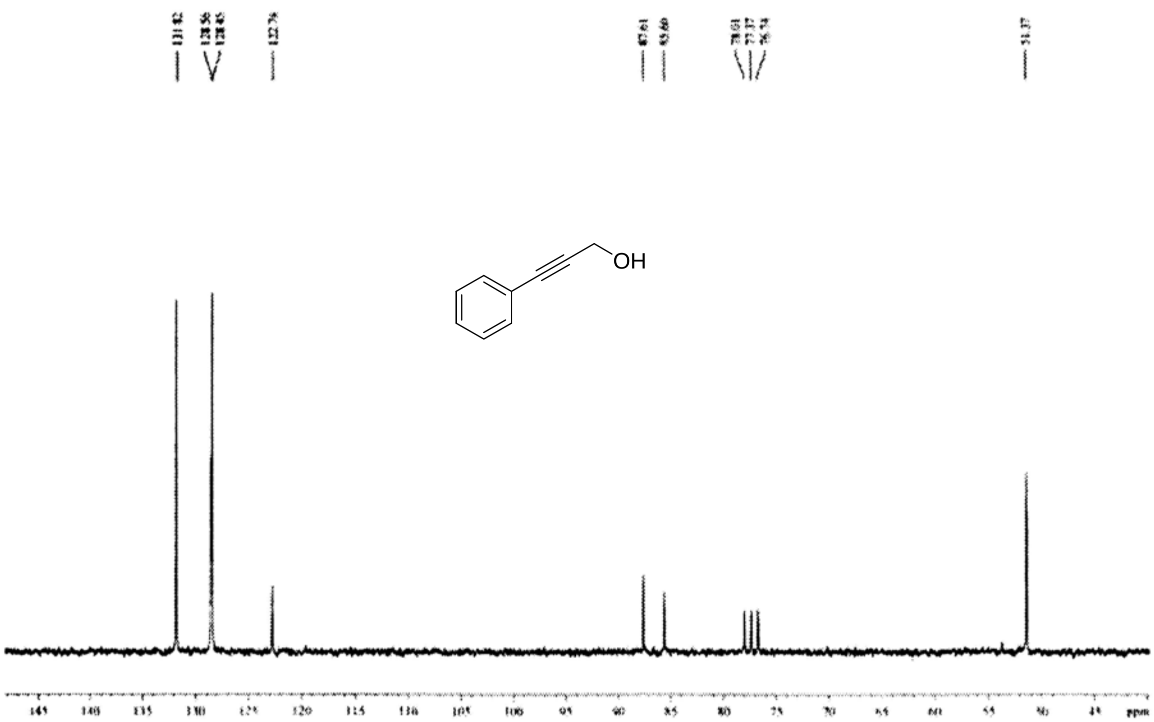
[1]H NMR (200 MHz)



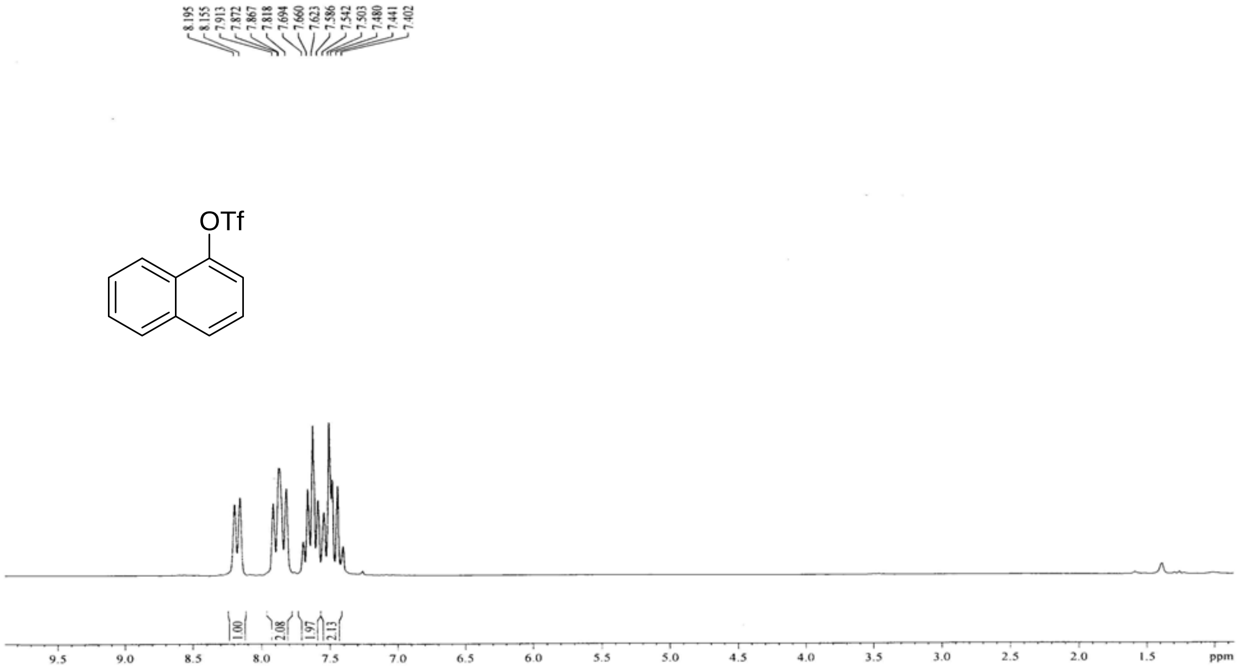
[13]C NMR (50 MHz)



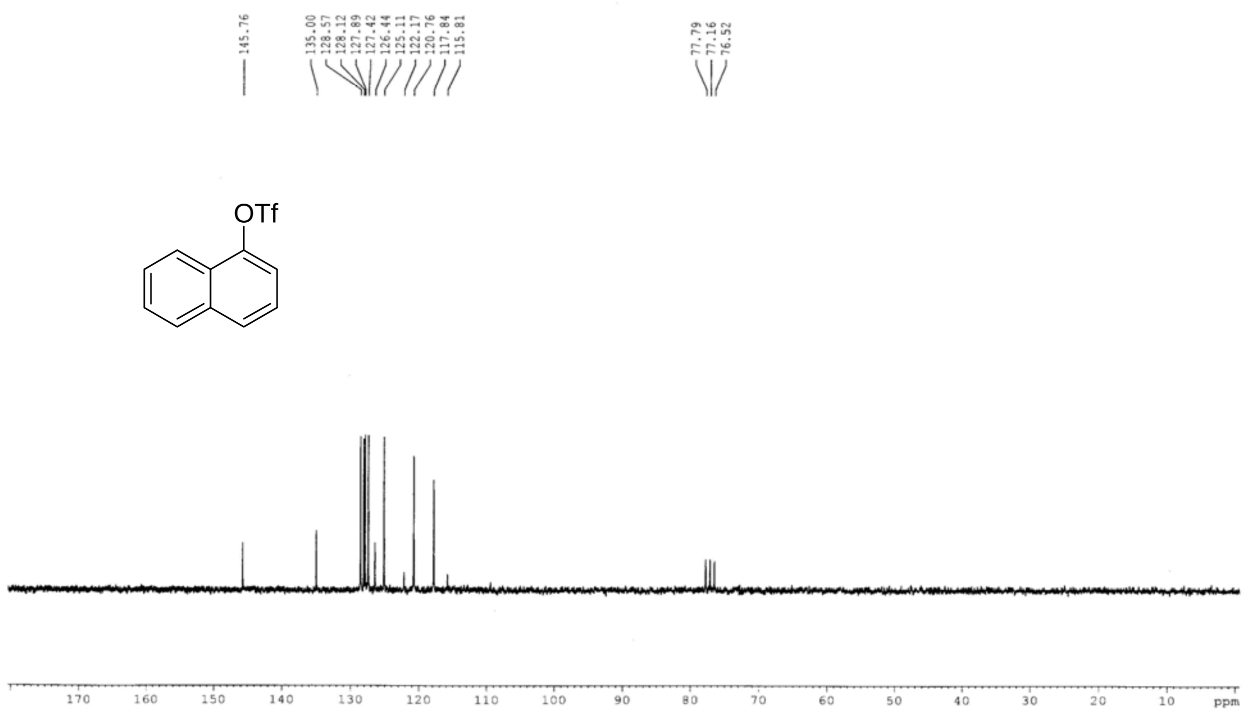
^{1}H NMR (200 MHz)



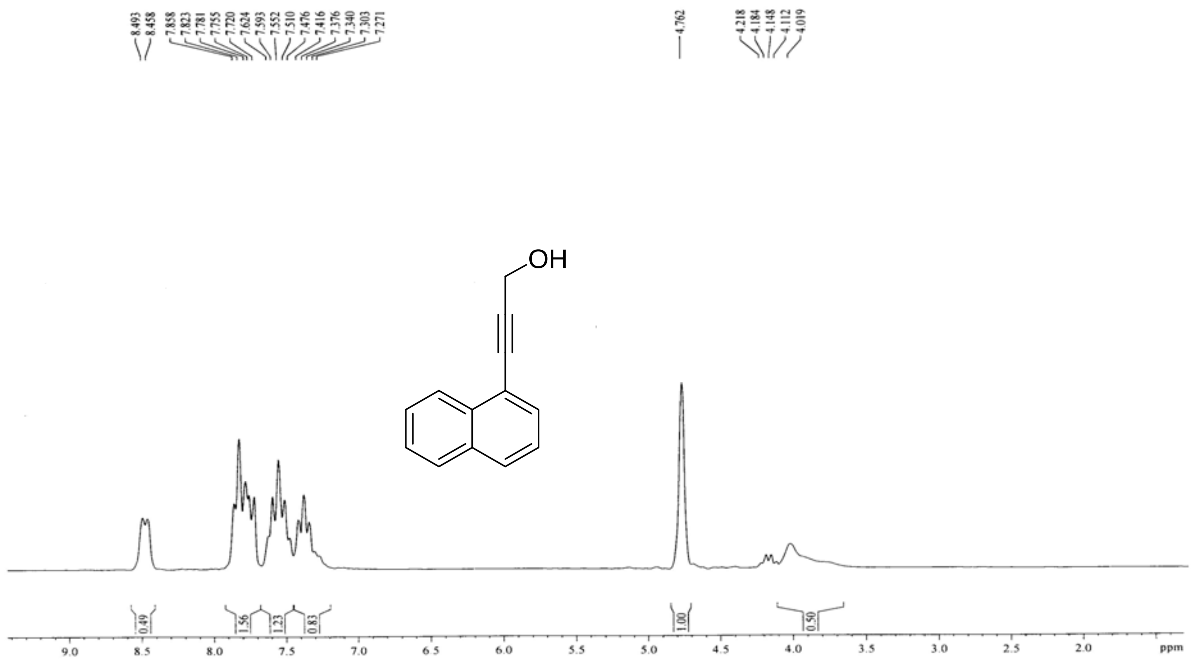
^{13}C NMR (50 MHz)



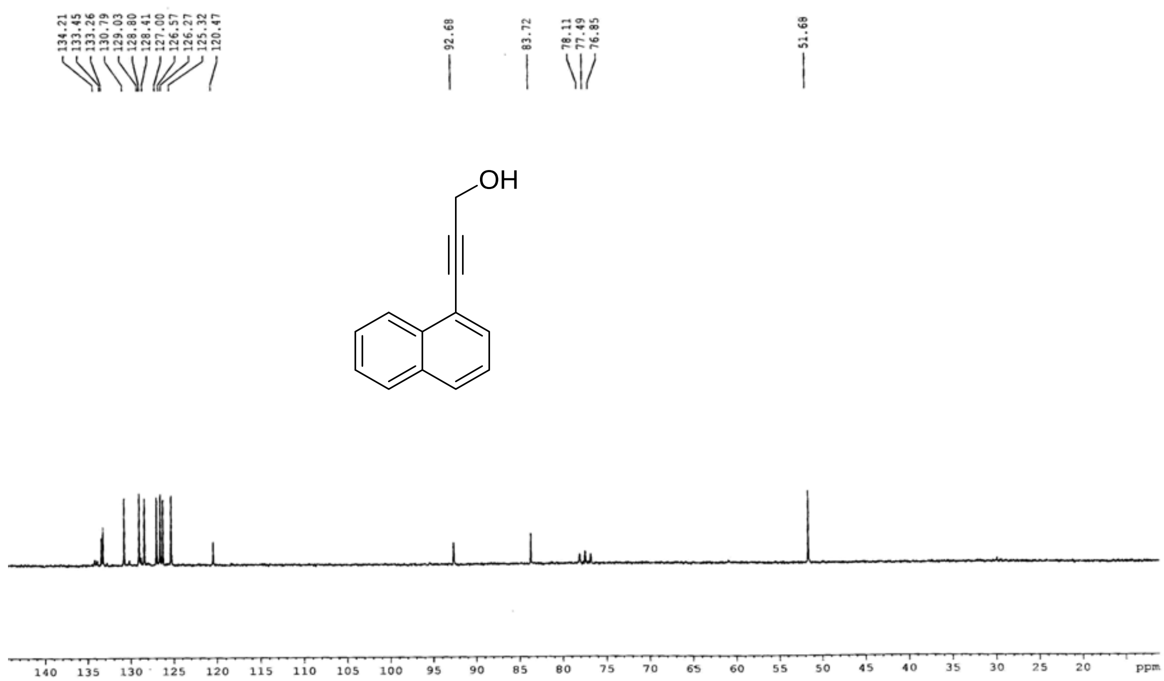
^{1}H NMR (200 MHz)



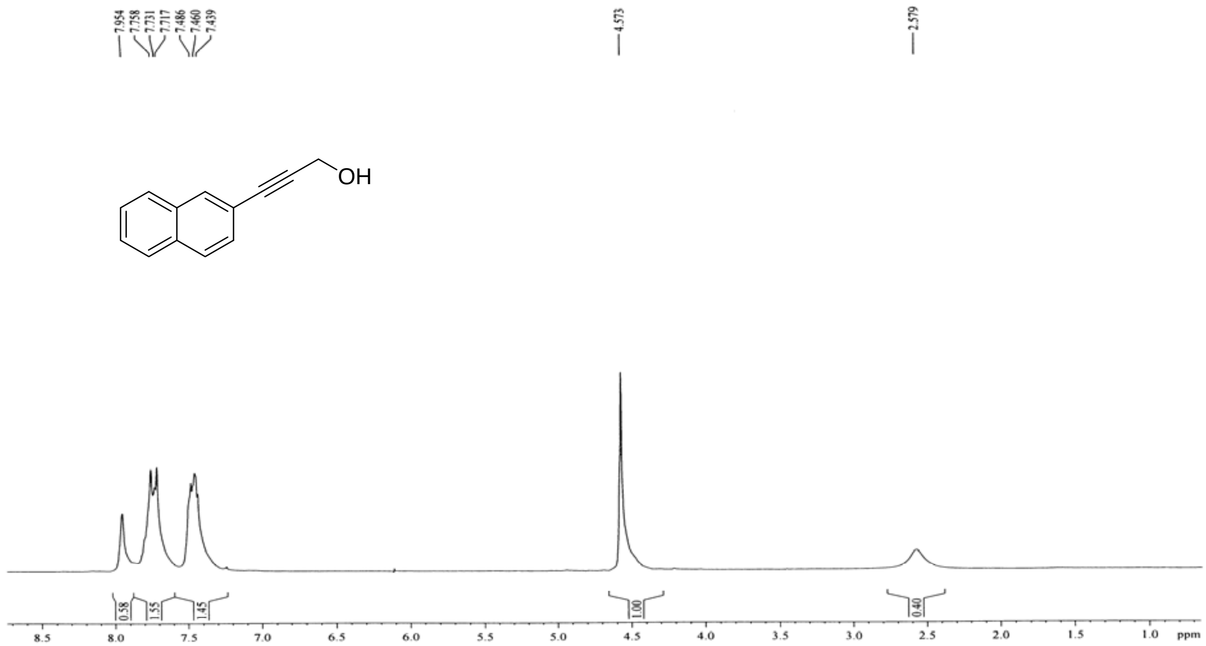
^{13}C NMR (50 MHz)



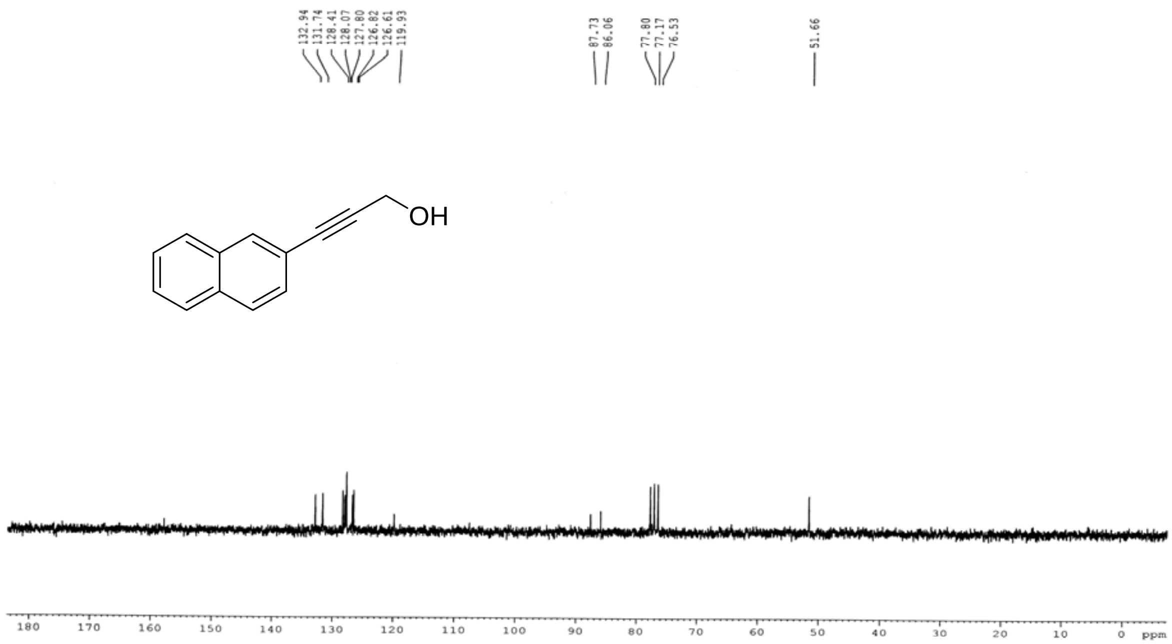
[1]H NMR (200 MHz)



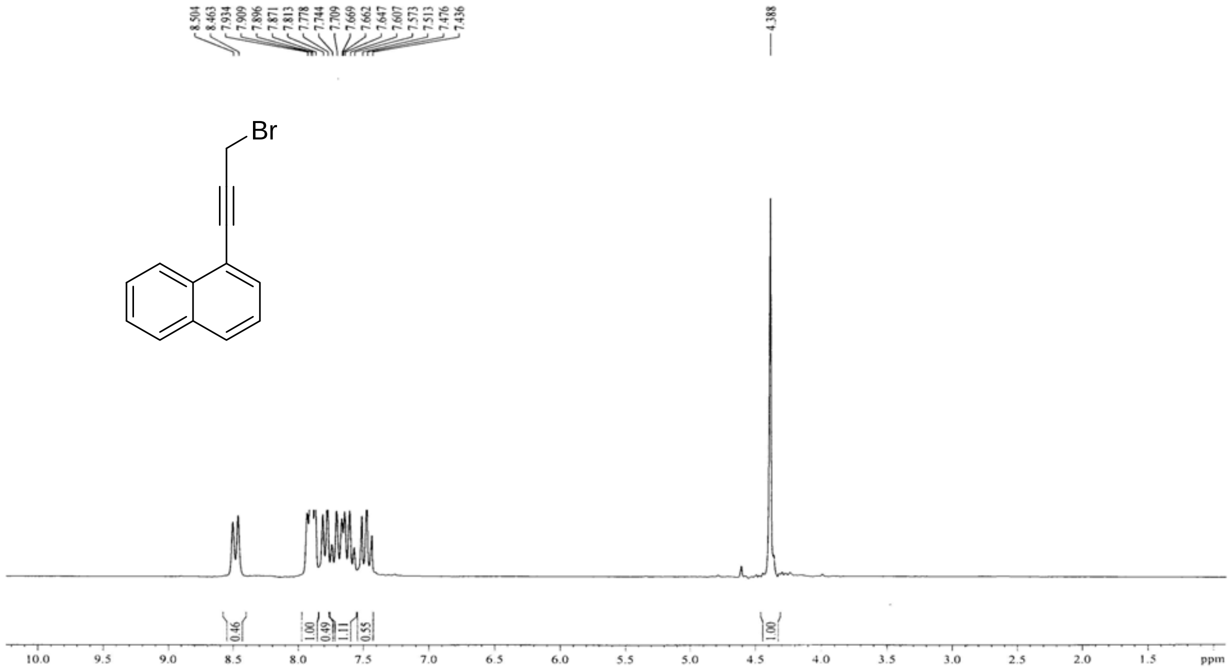
[13]C NMR (50 MHz)



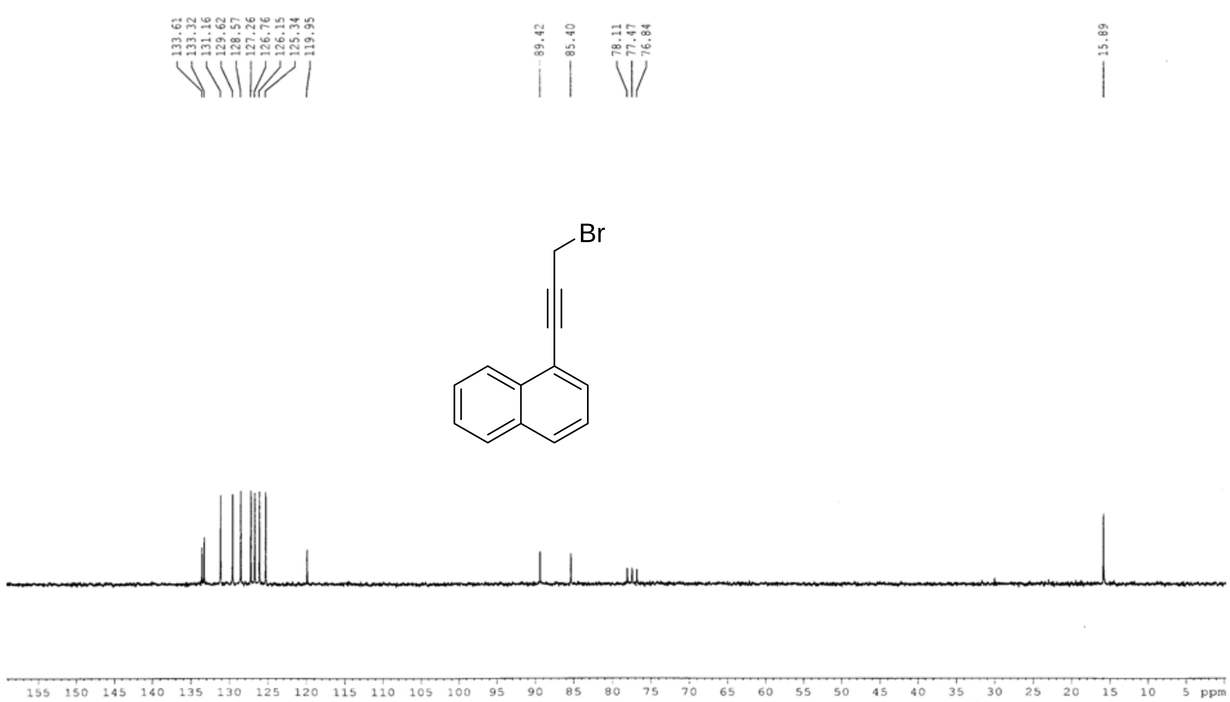
[1]H NMR (200 MHz)



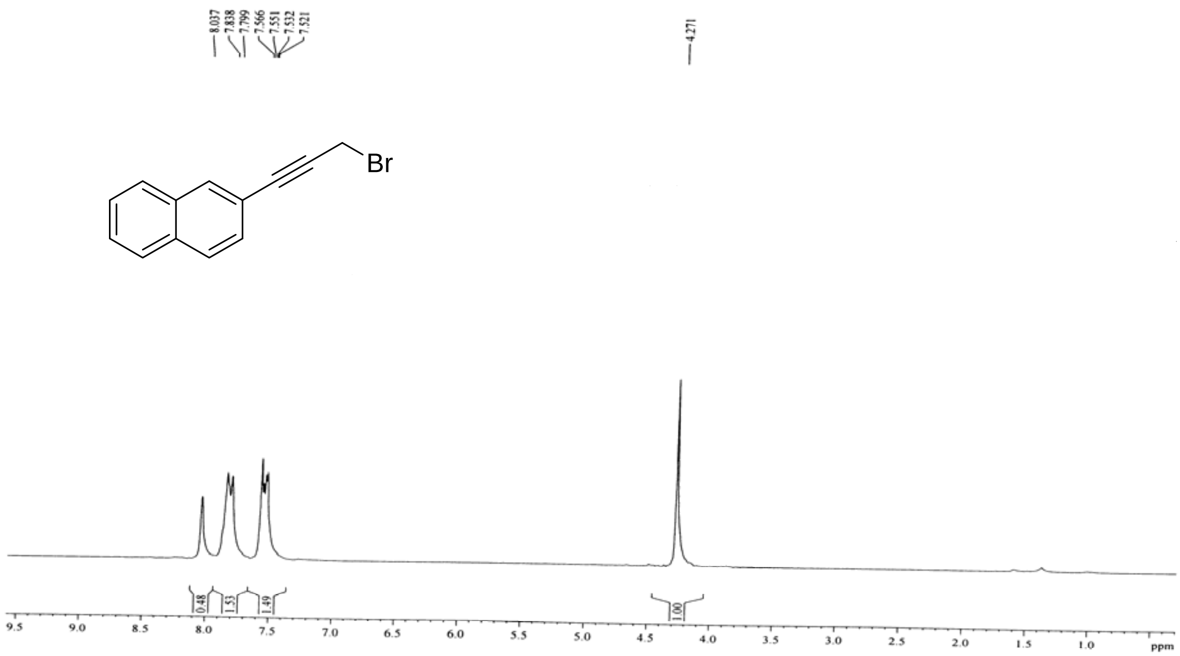
[13]C NMR (50 MHz)



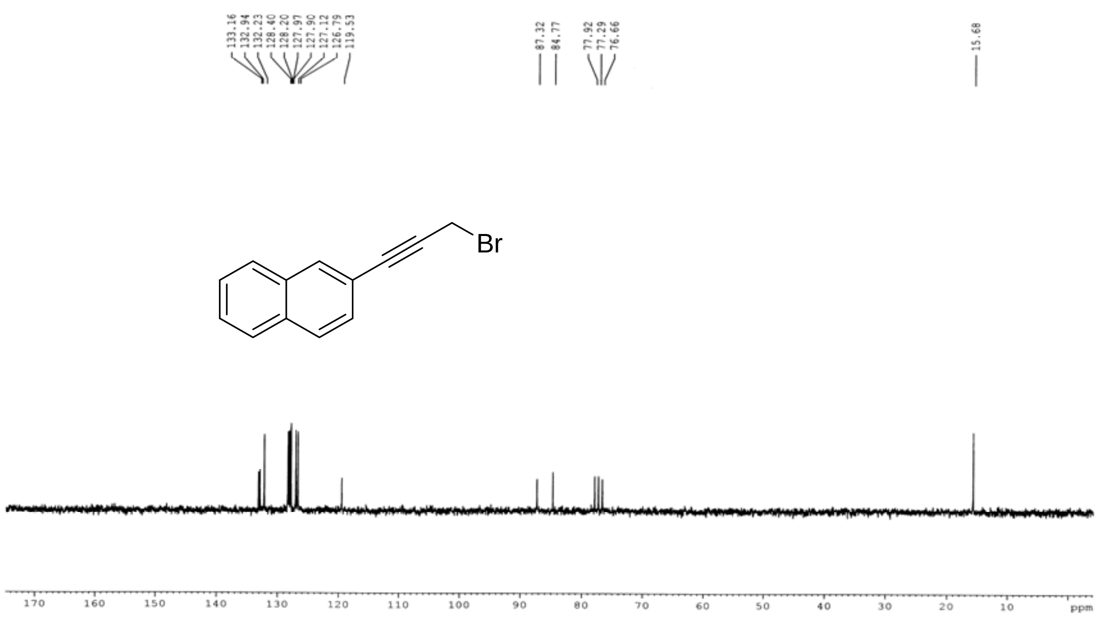
[1]H NMR (200 MHz)



[13]C NMR (50 MHz)

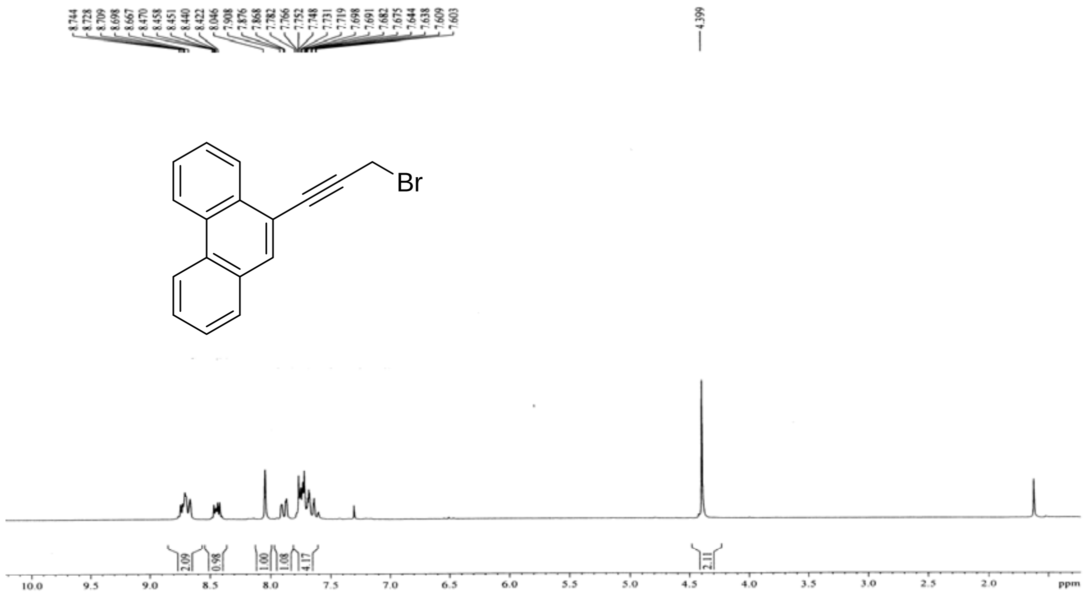


[1]H NMR (200 MHz)

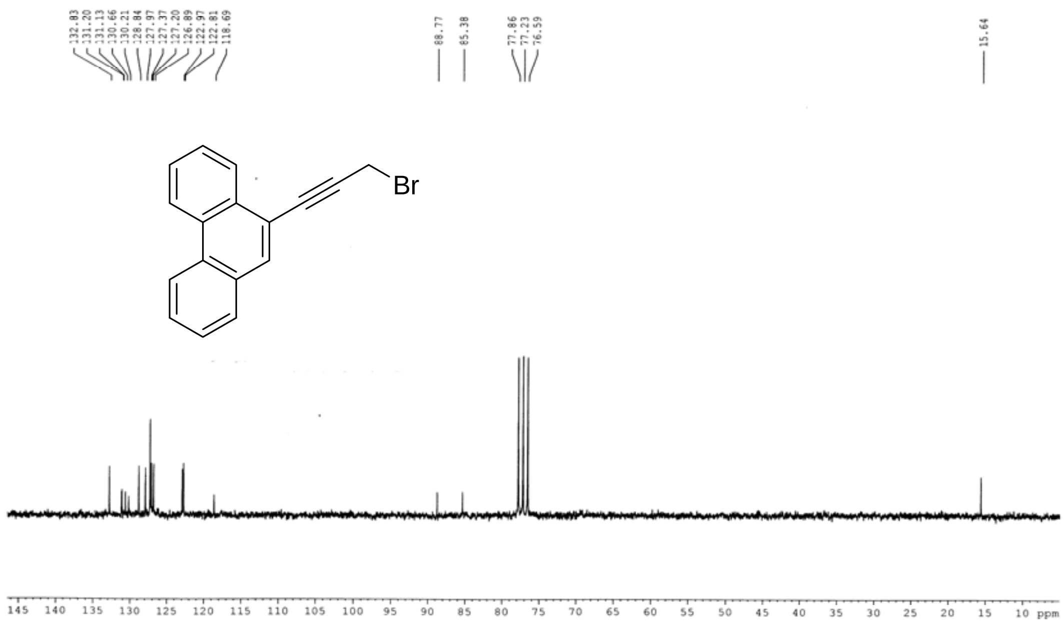


[13]C NMR (50 MHz)

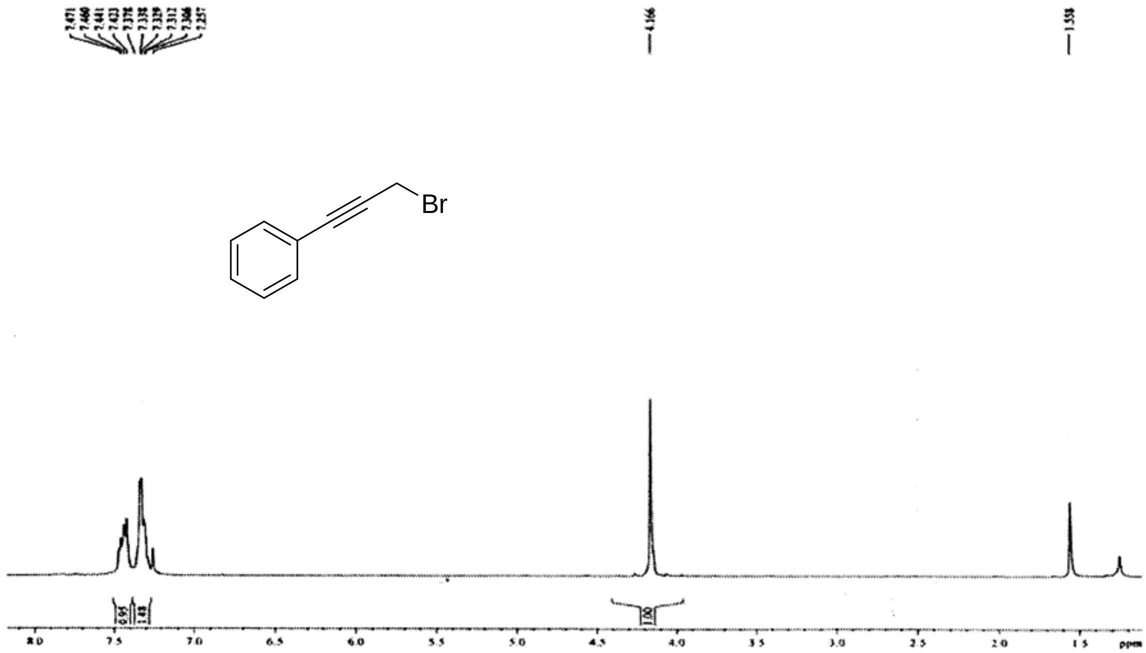
Electronic Supplementary Material (ESI) for RSC Advances



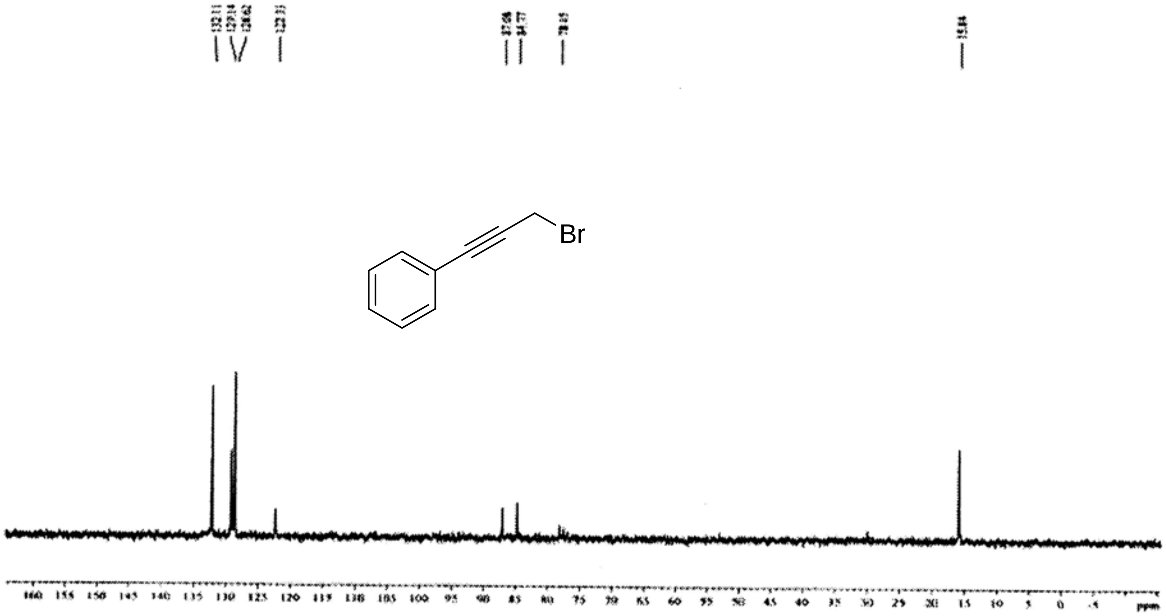
[1]H NMR (200 MHz)



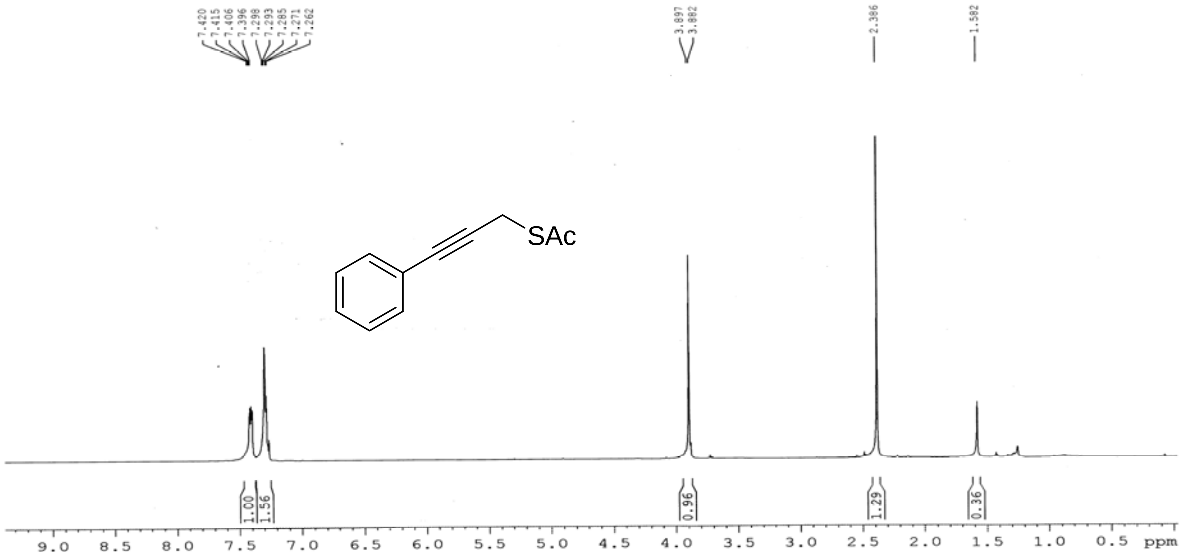
[13]C NMR (50 MHz)



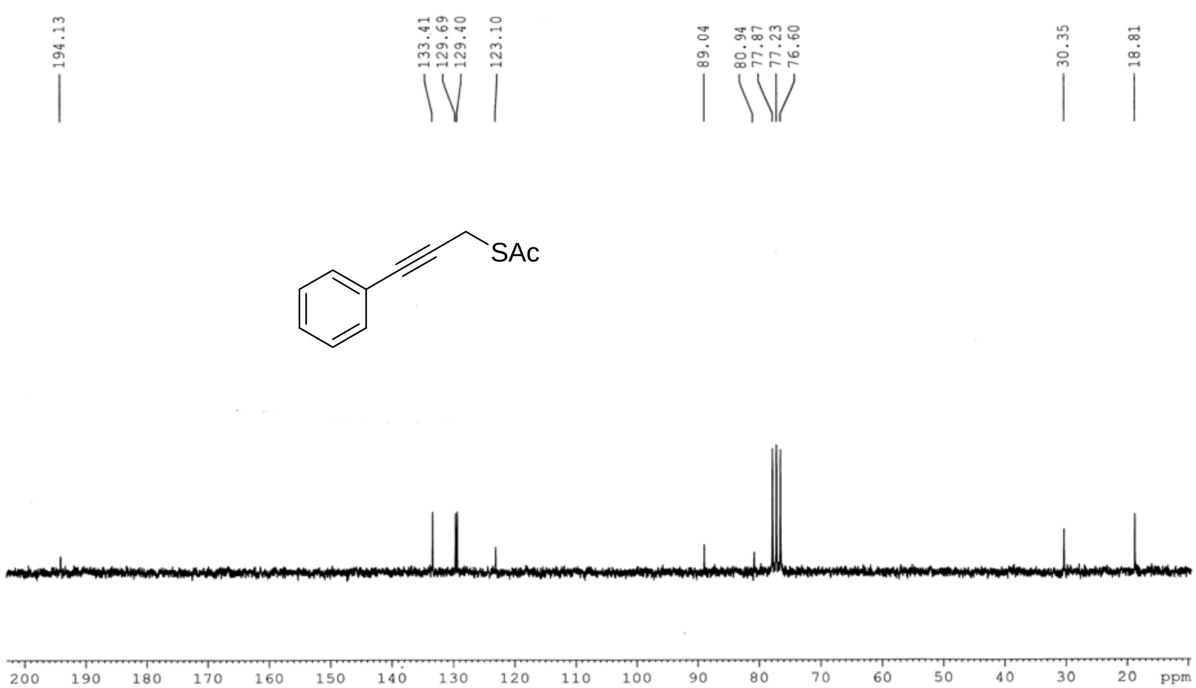
[1]H NMR (200 MHz)



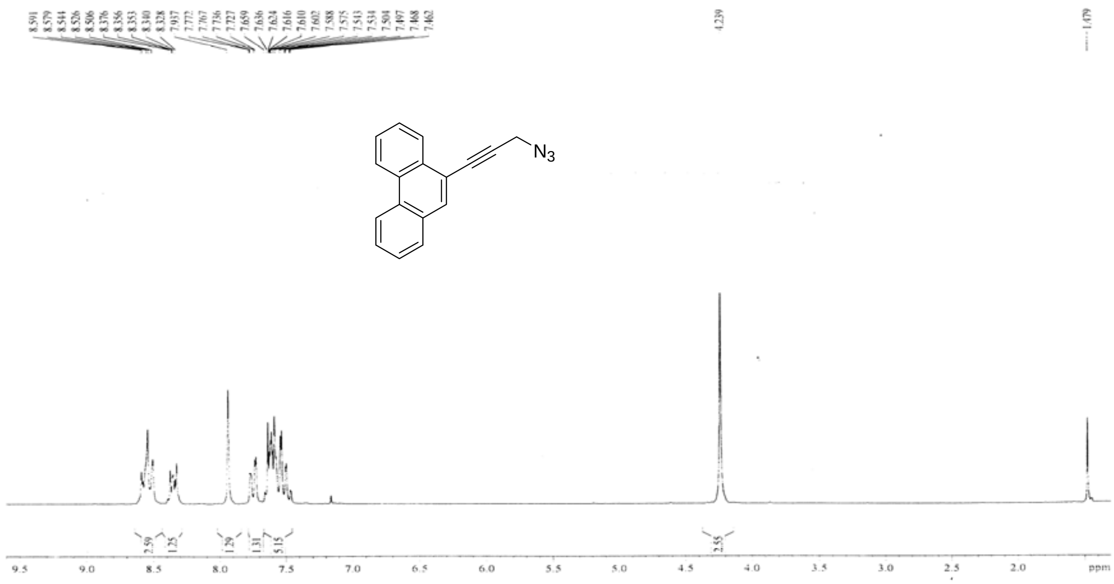
[13]C NMR (50 MHz)



^{1}H NMR (200 MHz)



^{13}C NMR (50 MHz)



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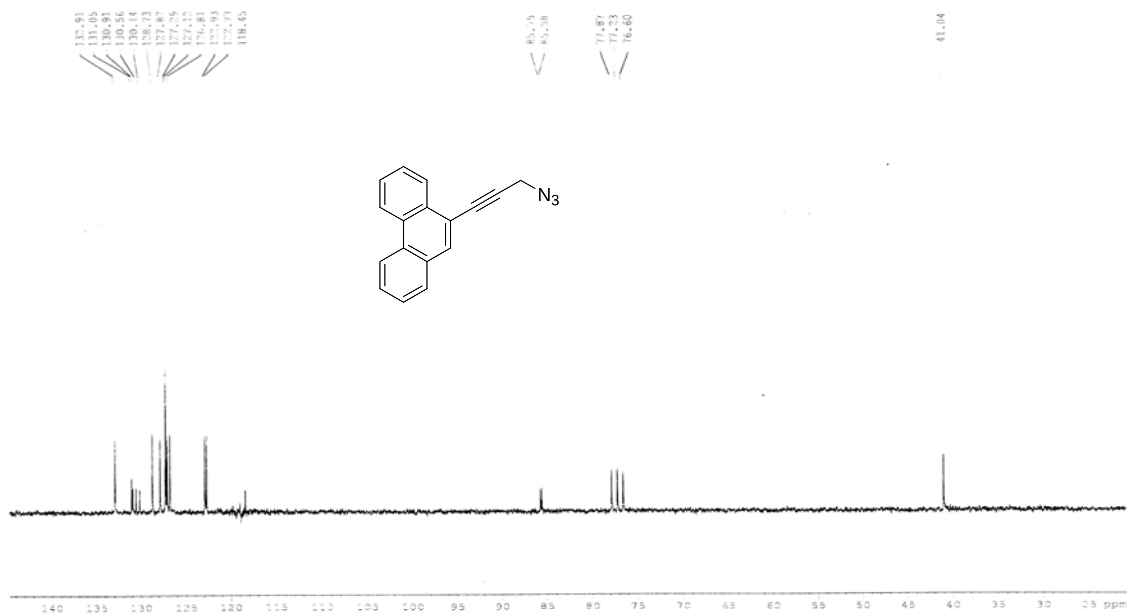
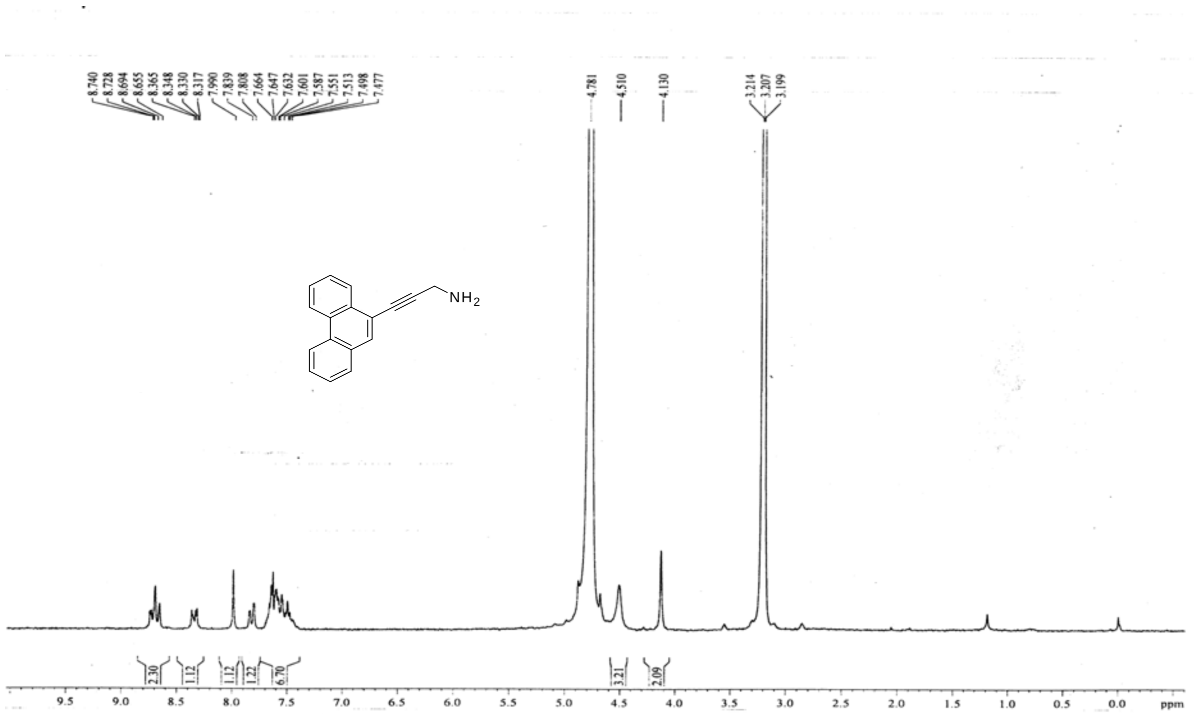
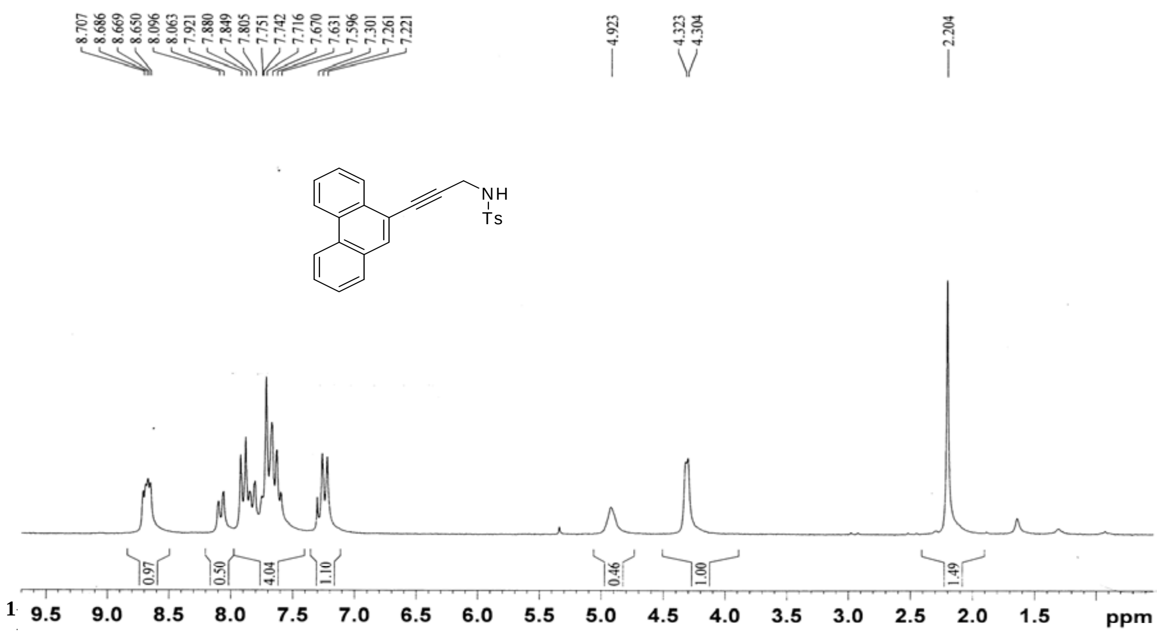


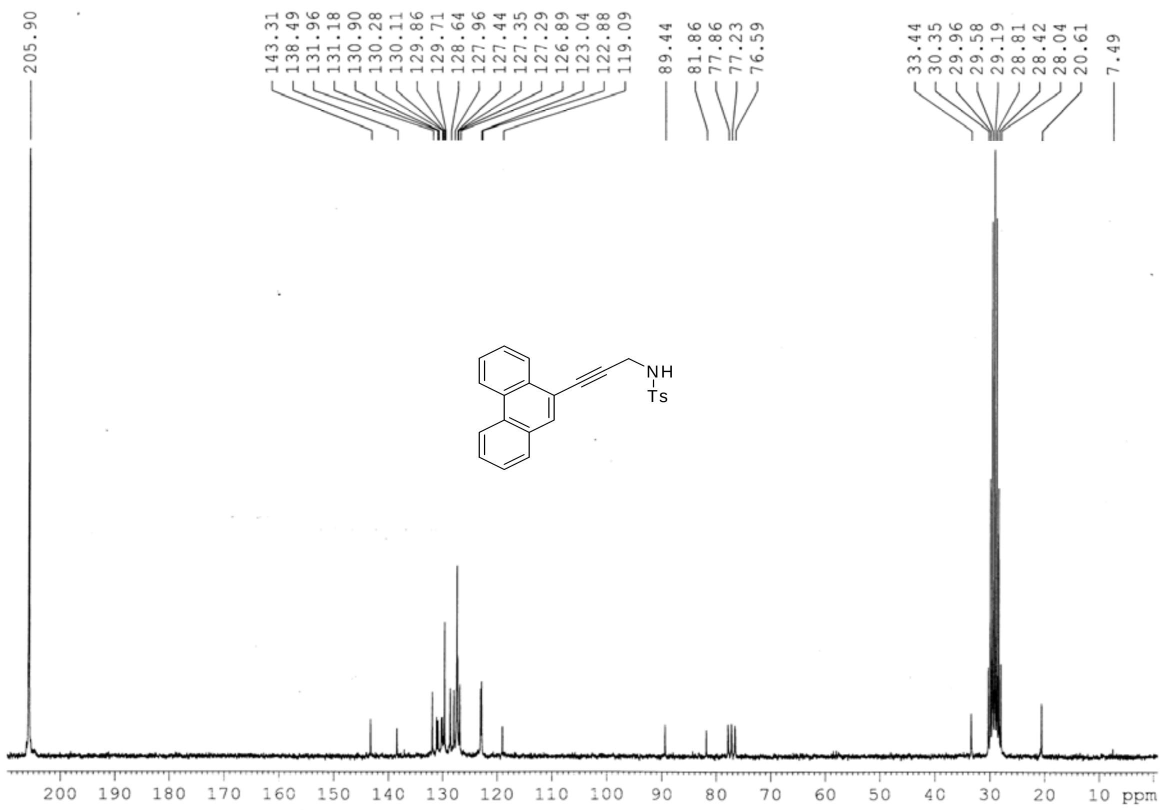
^{13}C NMR (50 MHz)



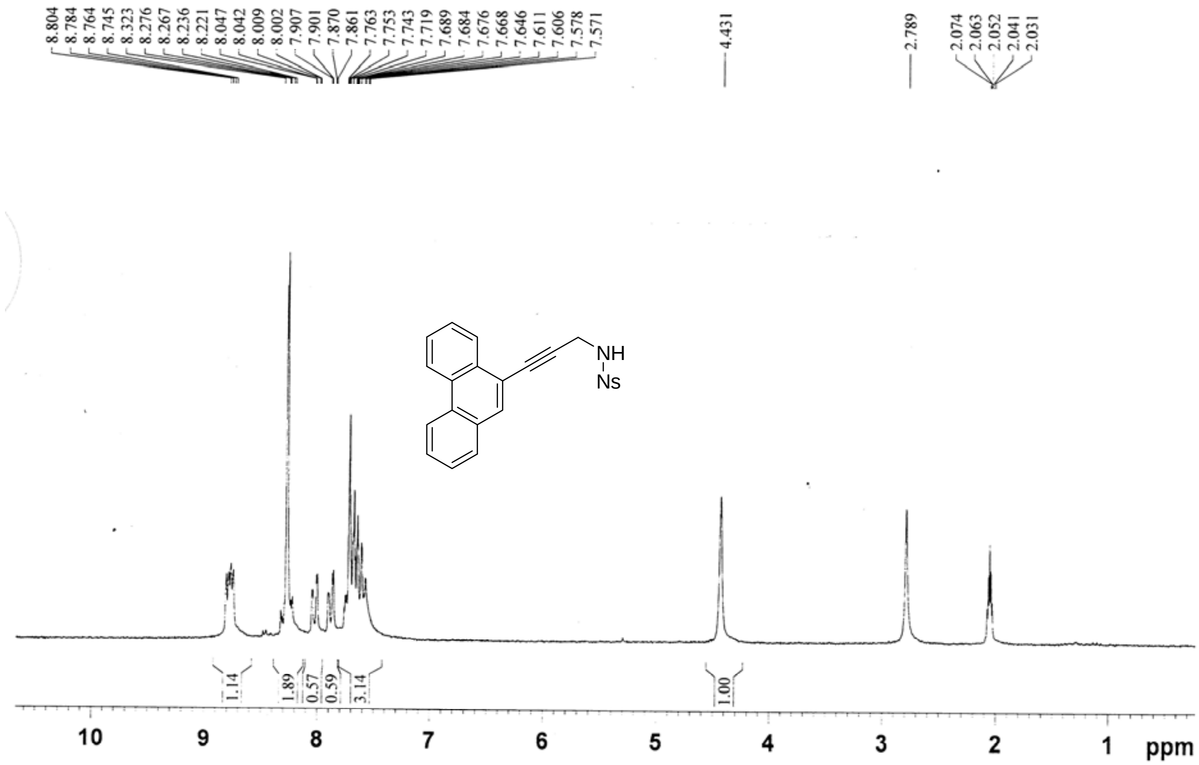
^{1}H NMR in d_4-Methanol (200 MHz)



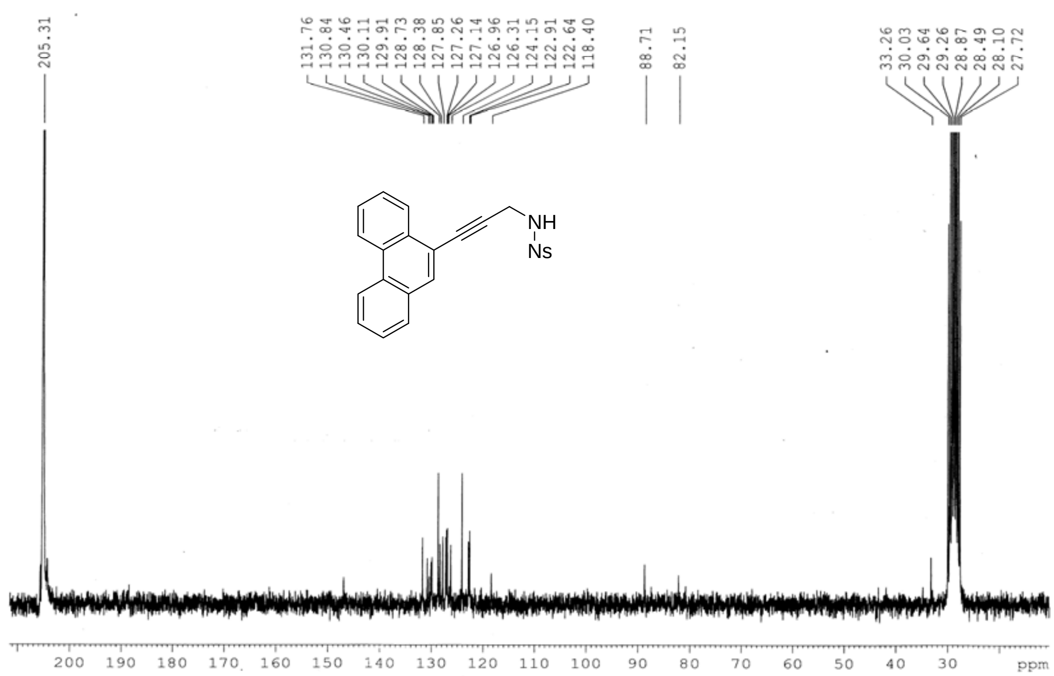
^{1}H NMR (200 MHz)



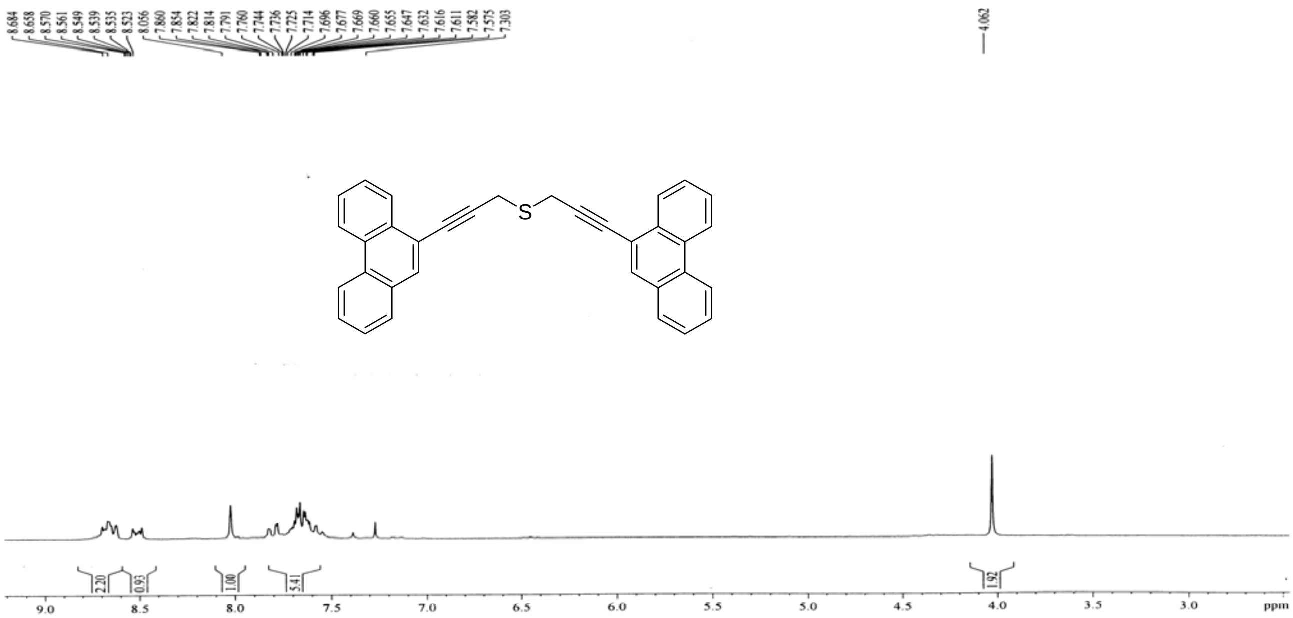
^{13}C NMR in d_6-Acetome + $CDCl_3$(50 MHz)



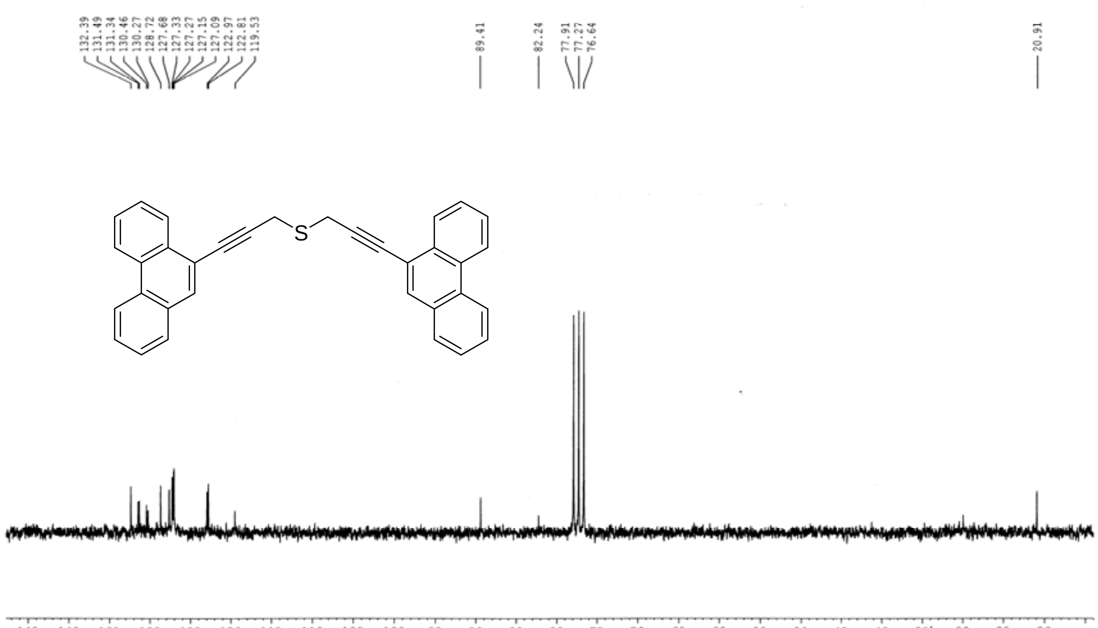
^{1}H NMR in d$_6$-Acetome(200 MHz)



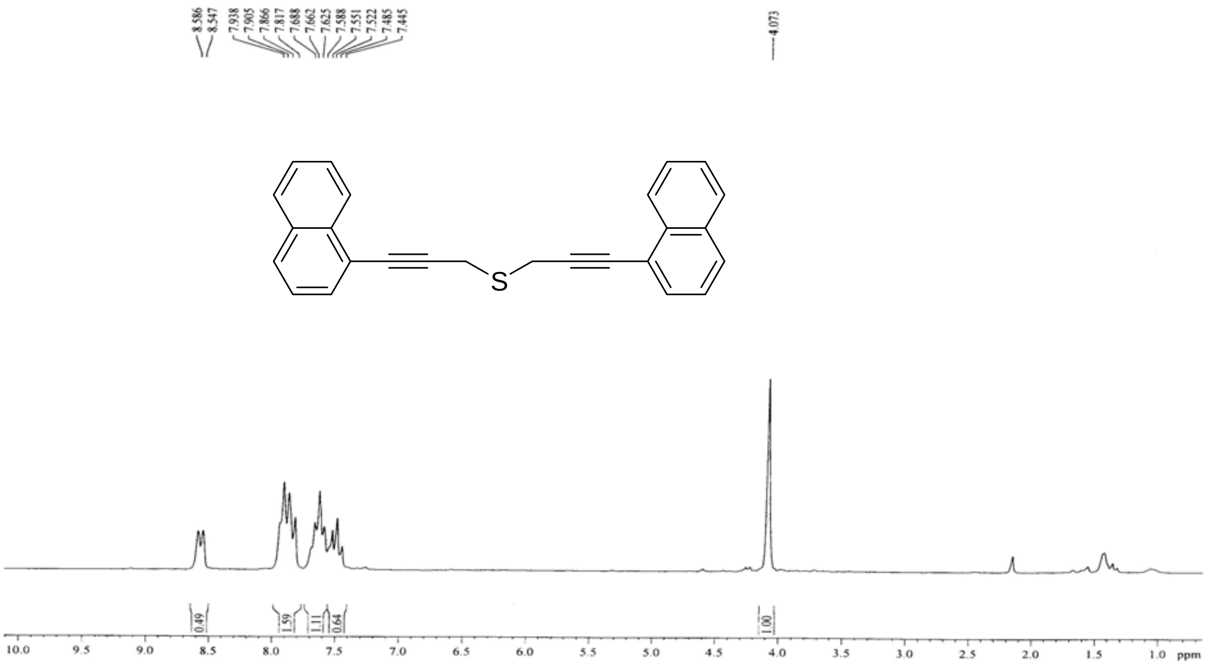
^{13}C NMR in d$_6$-Acetome (50 MHz)



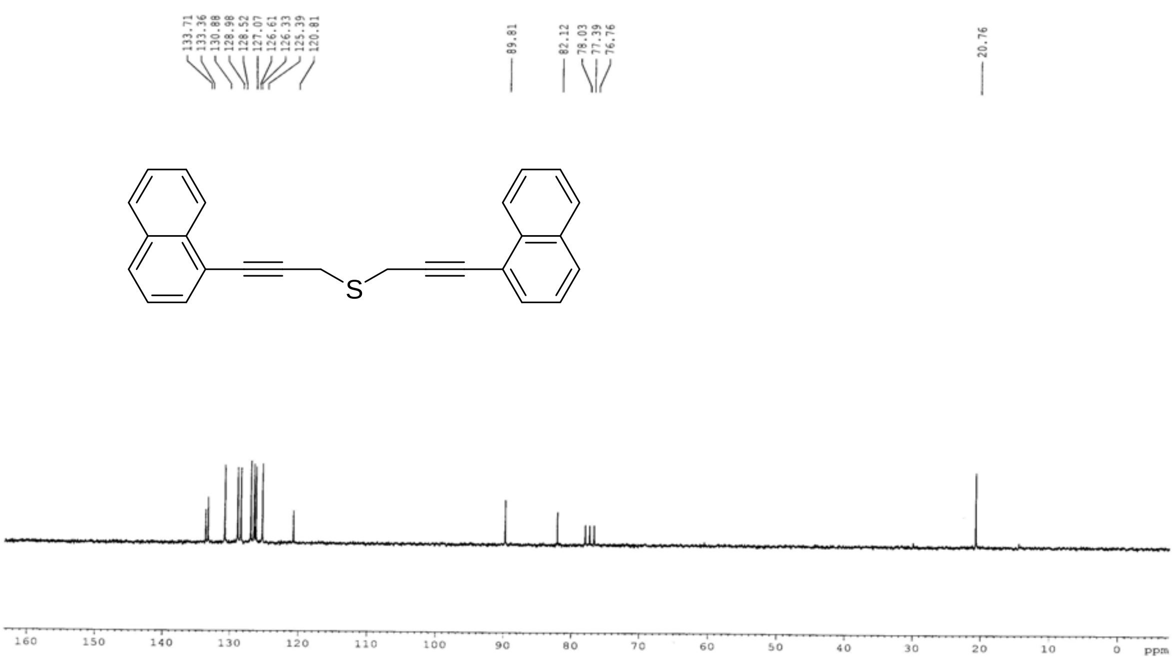
^{1}H NMR (200 MHz)



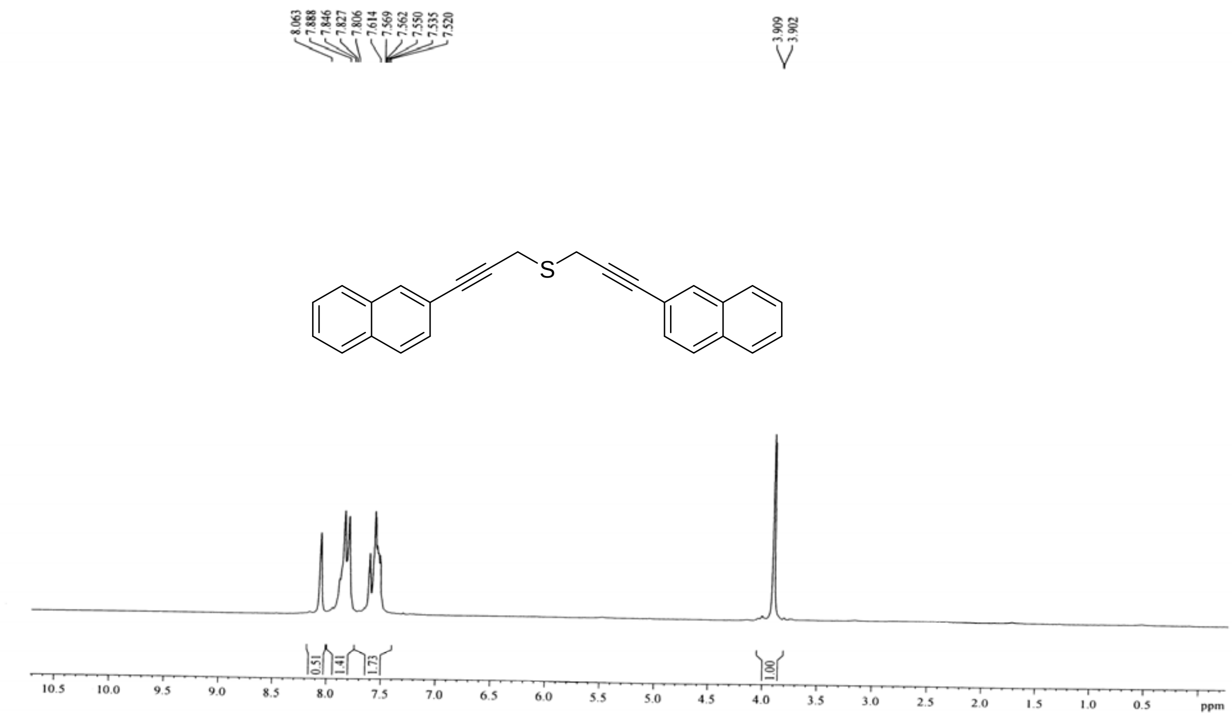
^{13}C NMR (50 MHz)



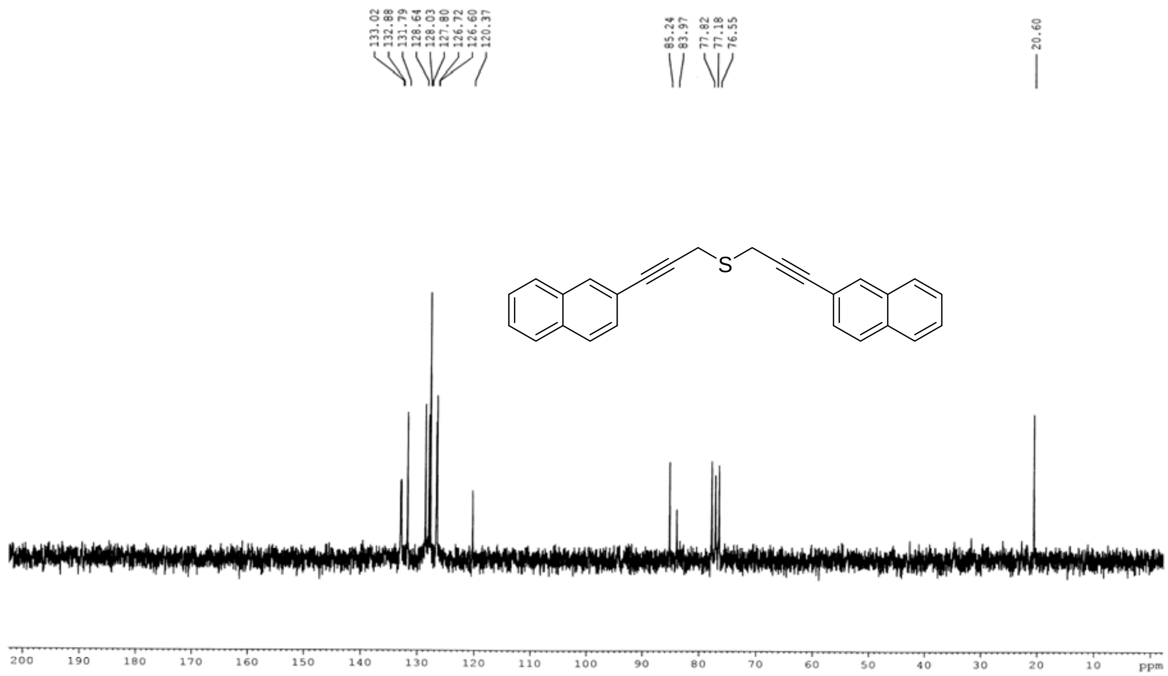
^{1}H NMR (200 MHz)



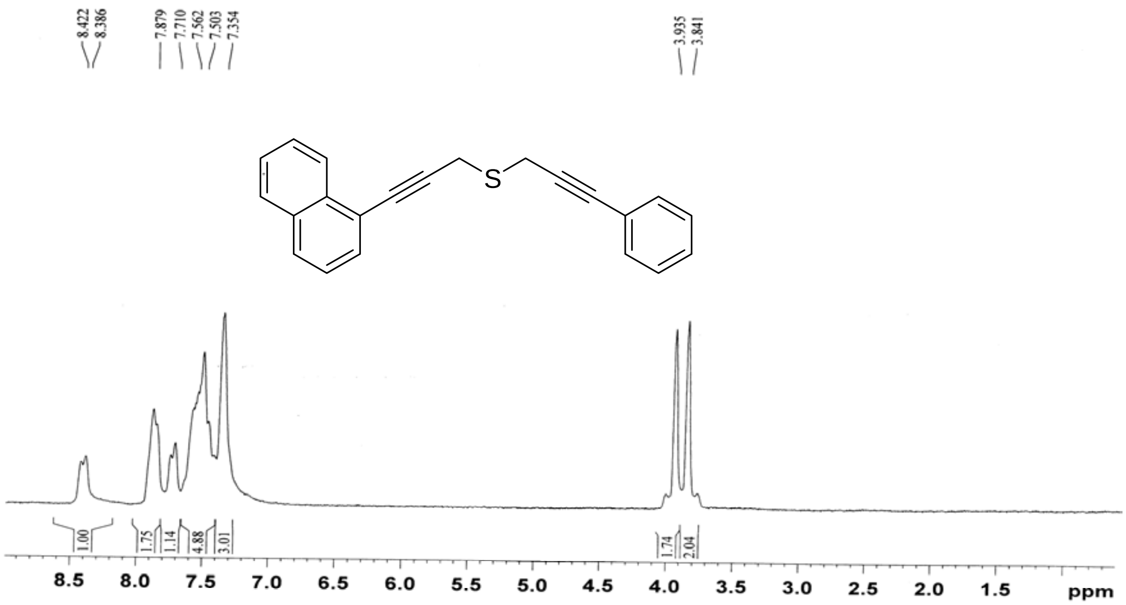
^{13}C NMR (50 MHz)



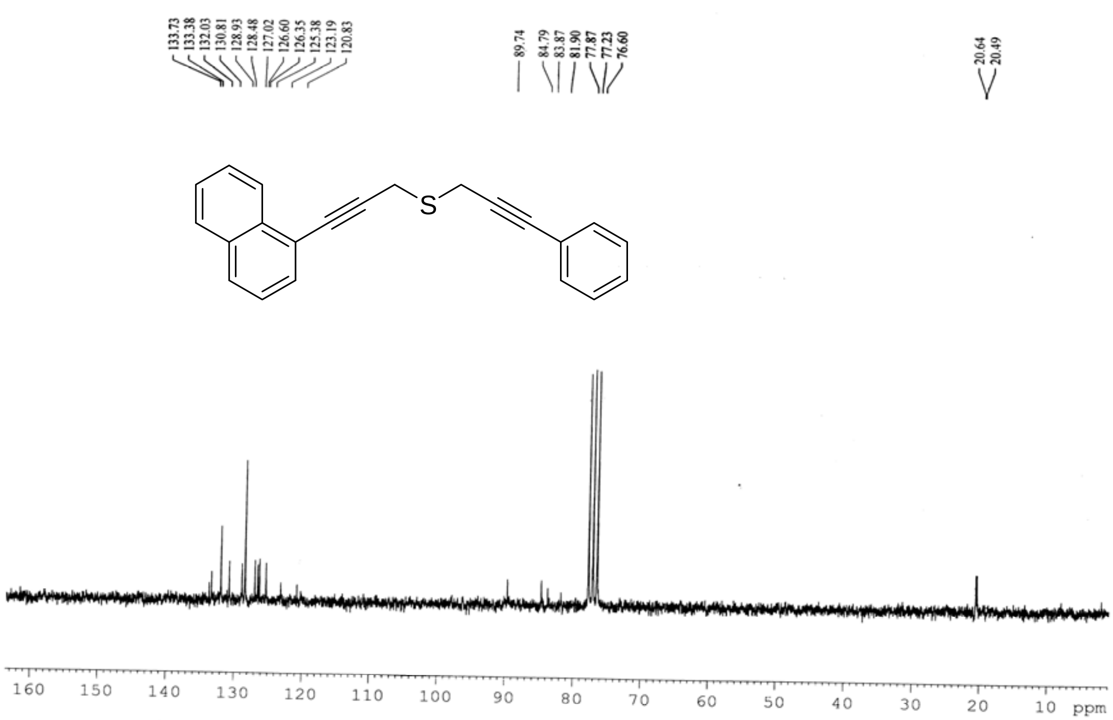
[1]H NMR (200 MHz)



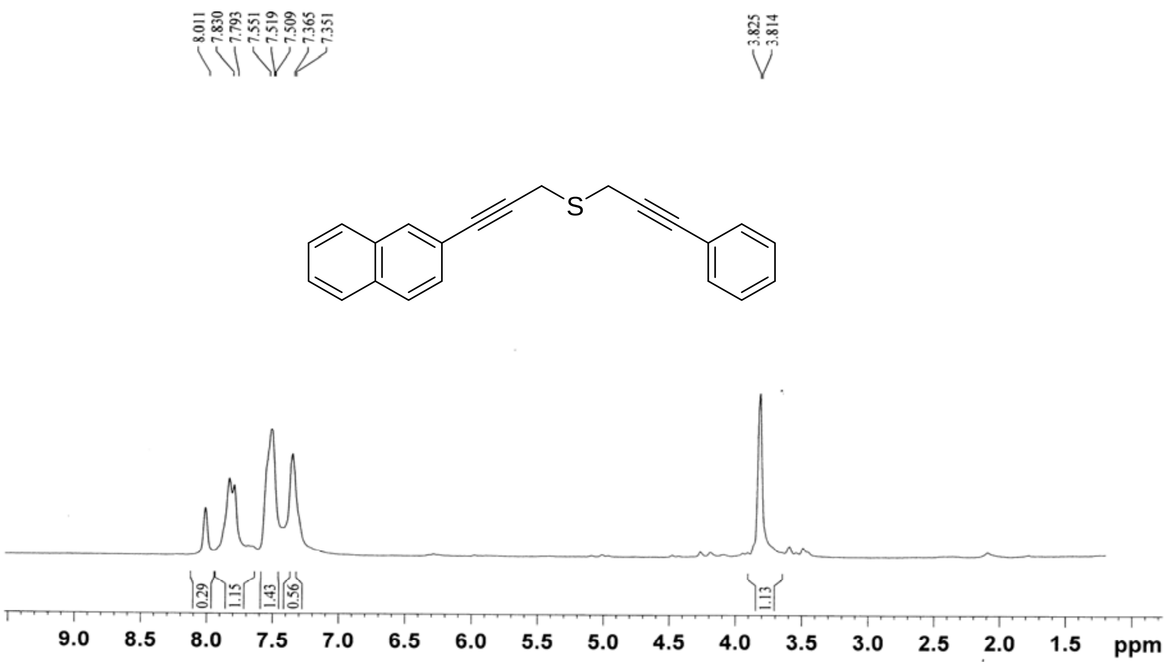
[13]C NMR (50 MHz)



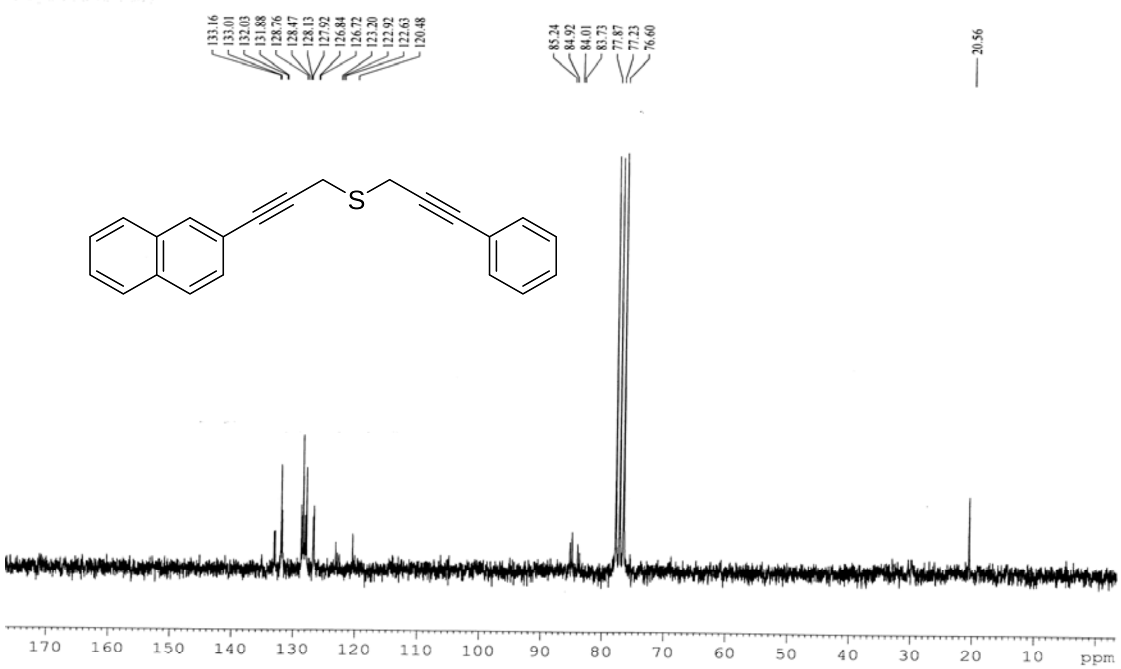
^{1}H NMR (200 MHz)



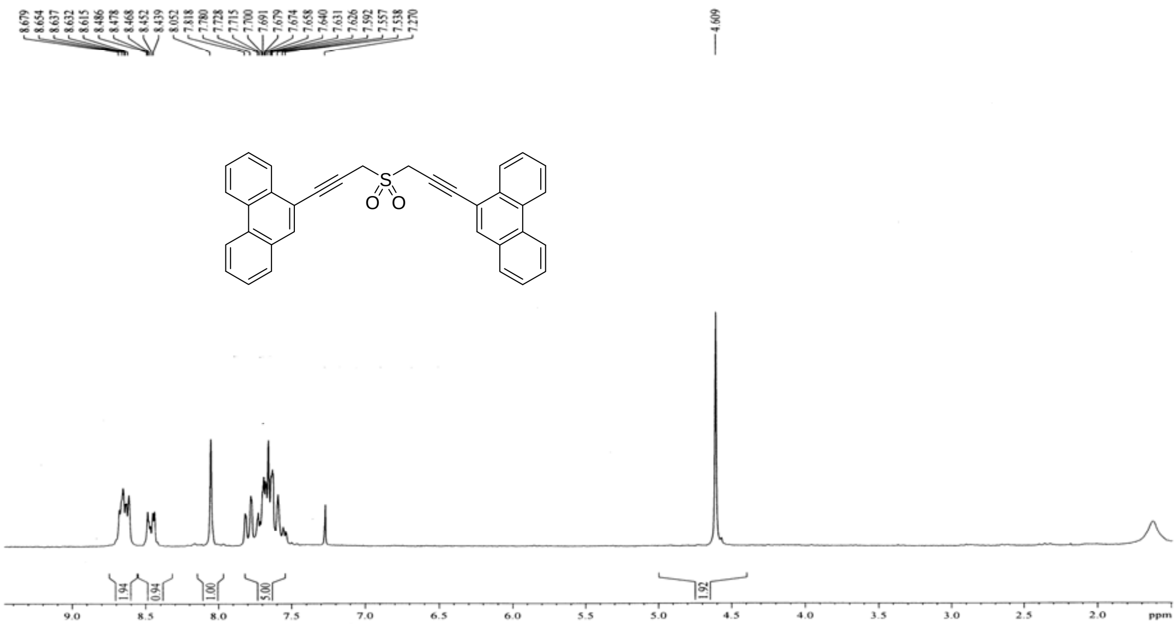
^{13}C NMR (50 MHz)



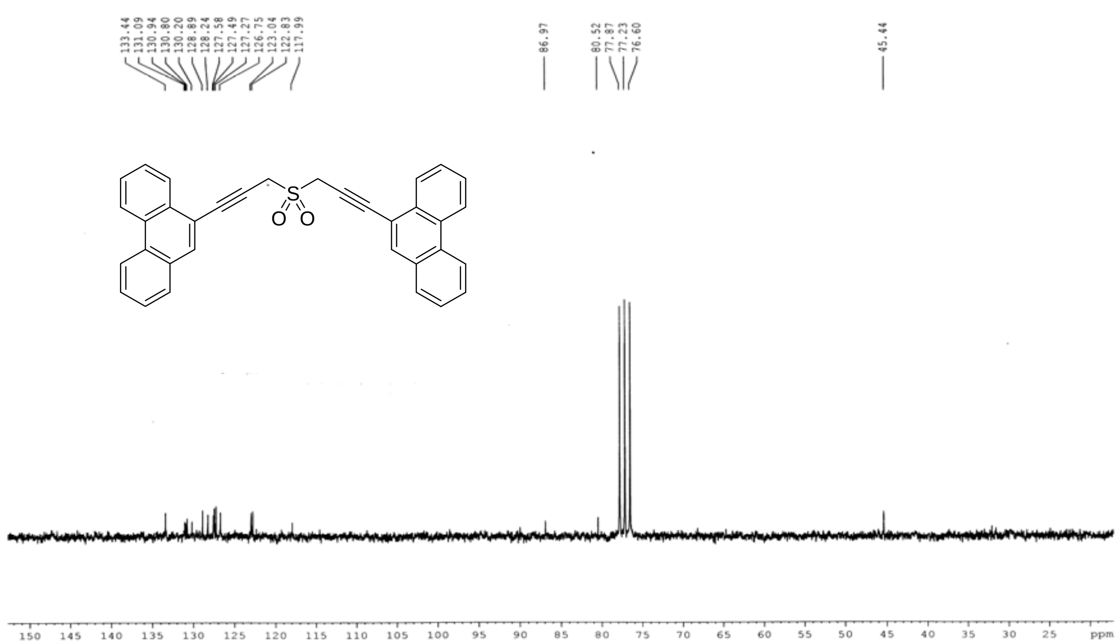
^{1}H NMR (200 MHz)



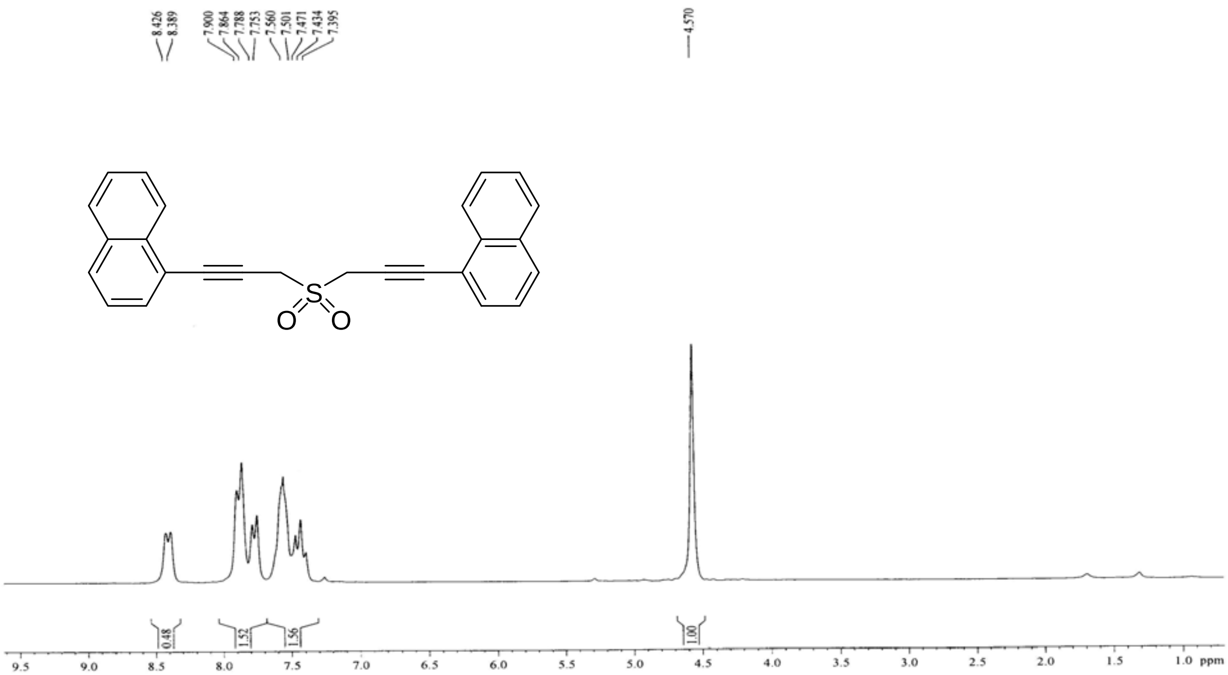
^{13}C NMR (50 MHz)



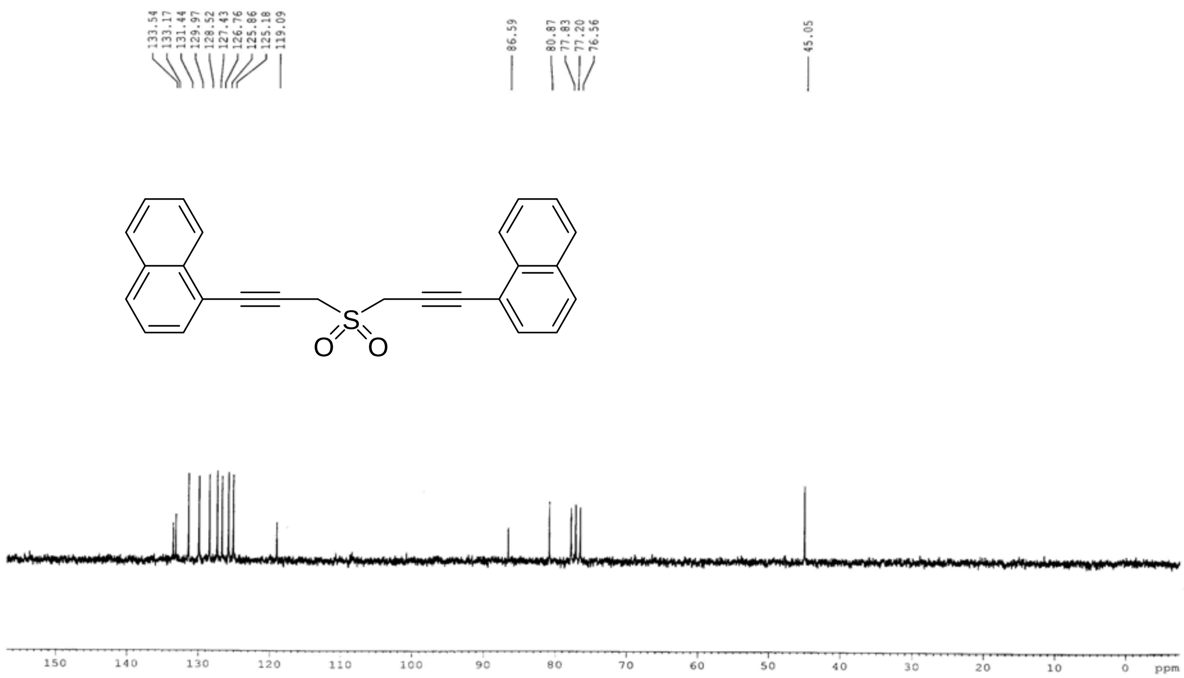
^{1}H NMR (200 MHz)



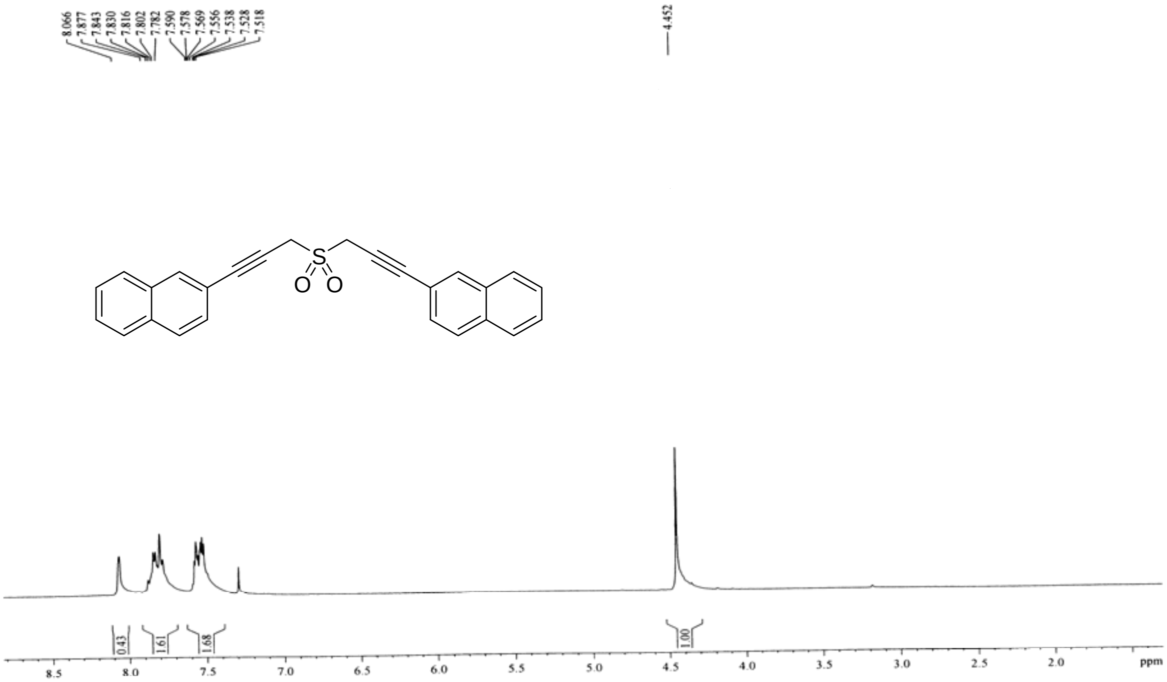
^{13}C NMR (50 MHz)



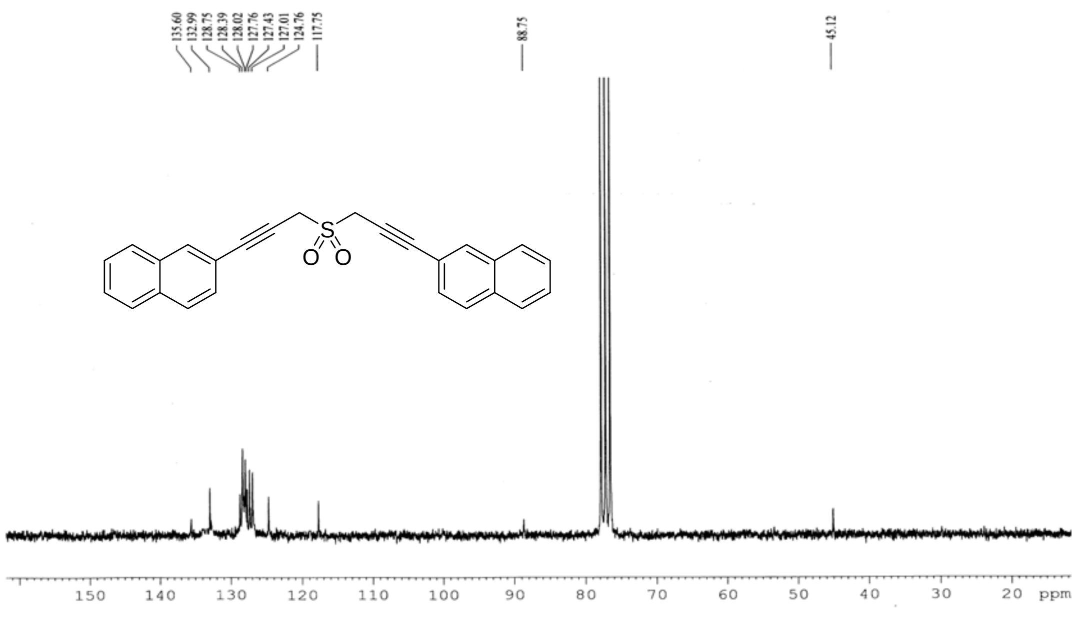
[1]H NMR (200 MHz)



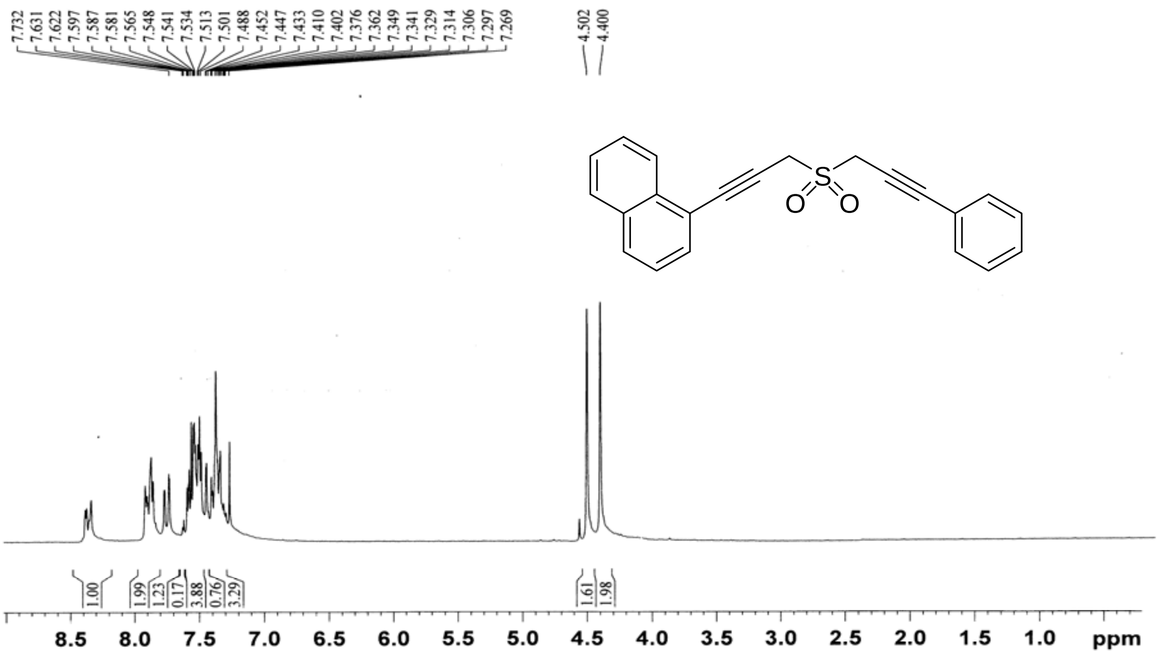
[13]C NMR (100 MHz)



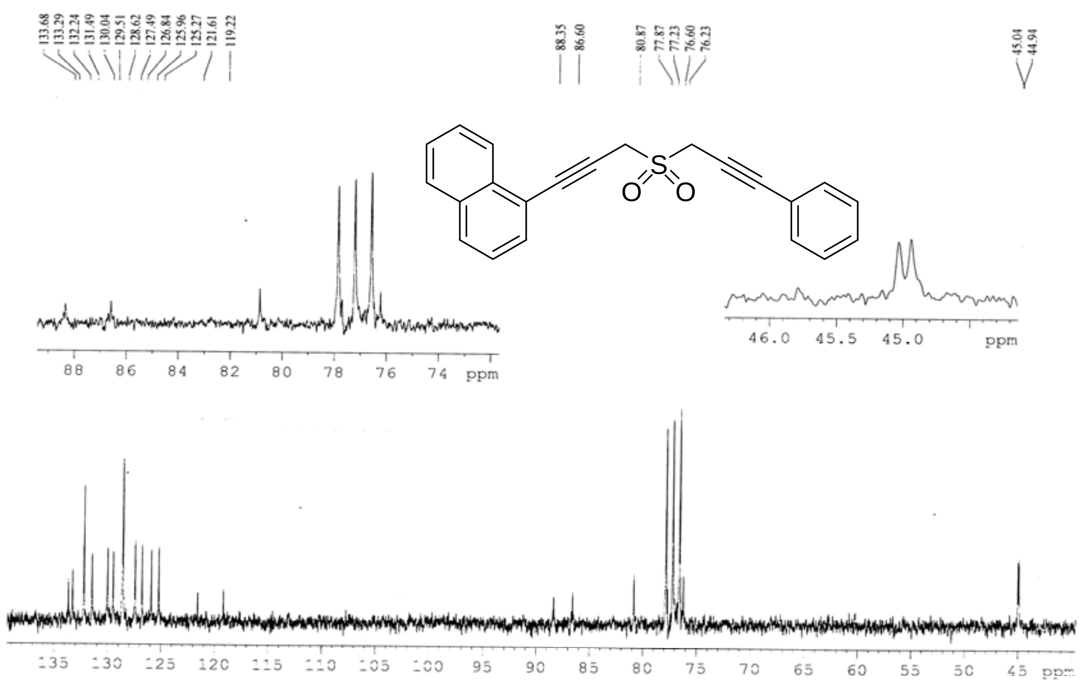
^{1}H NMR (200 MHz)



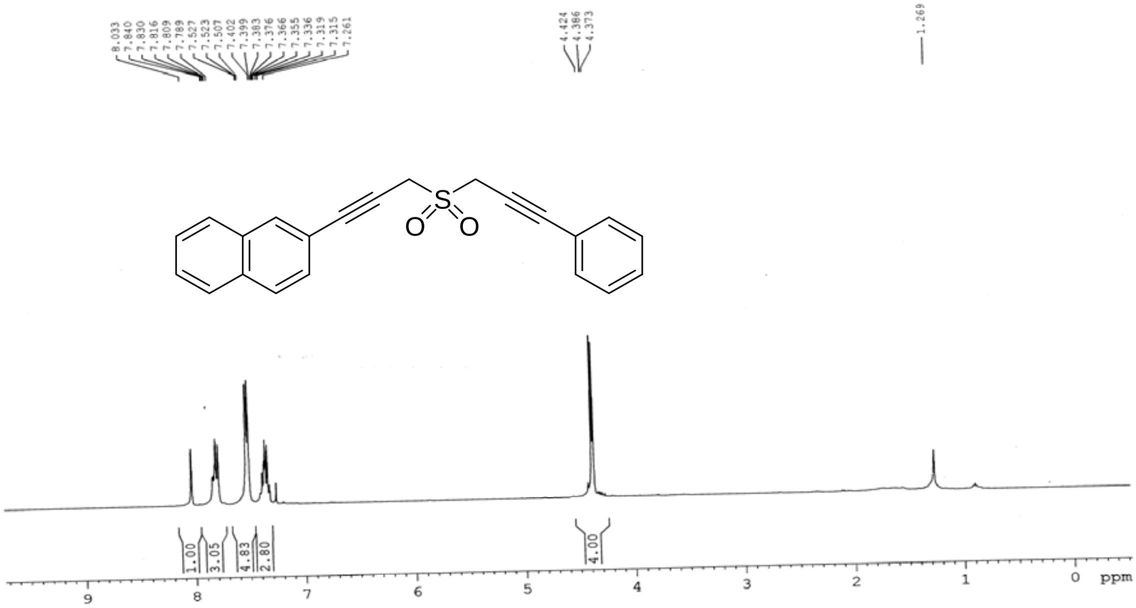
^{13}C NMR (50 MHz)



^{1}H NMR (200 MHz)



^{13}C NMR (50 MHz)



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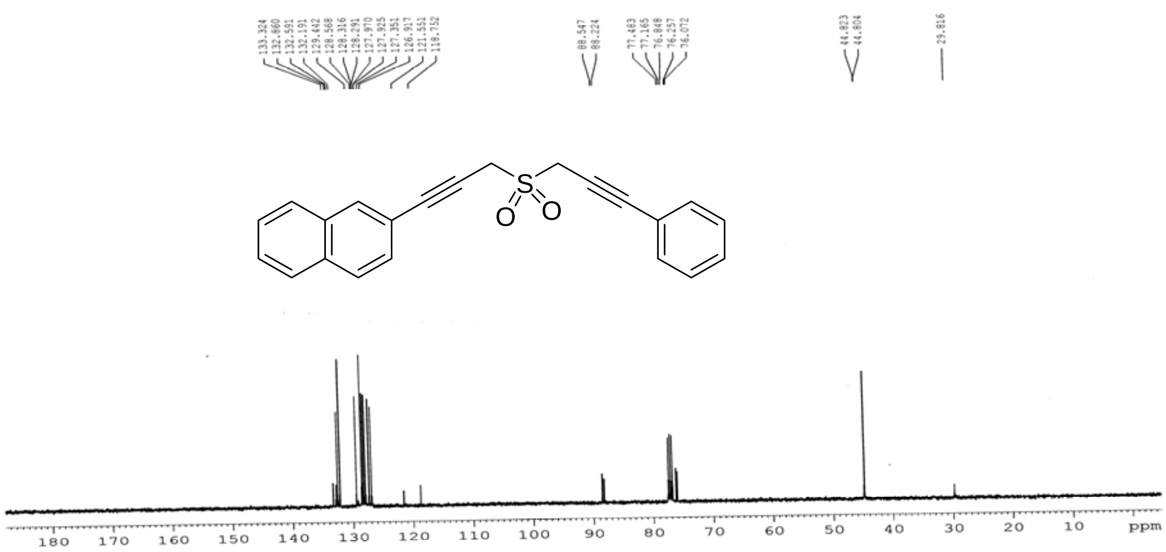
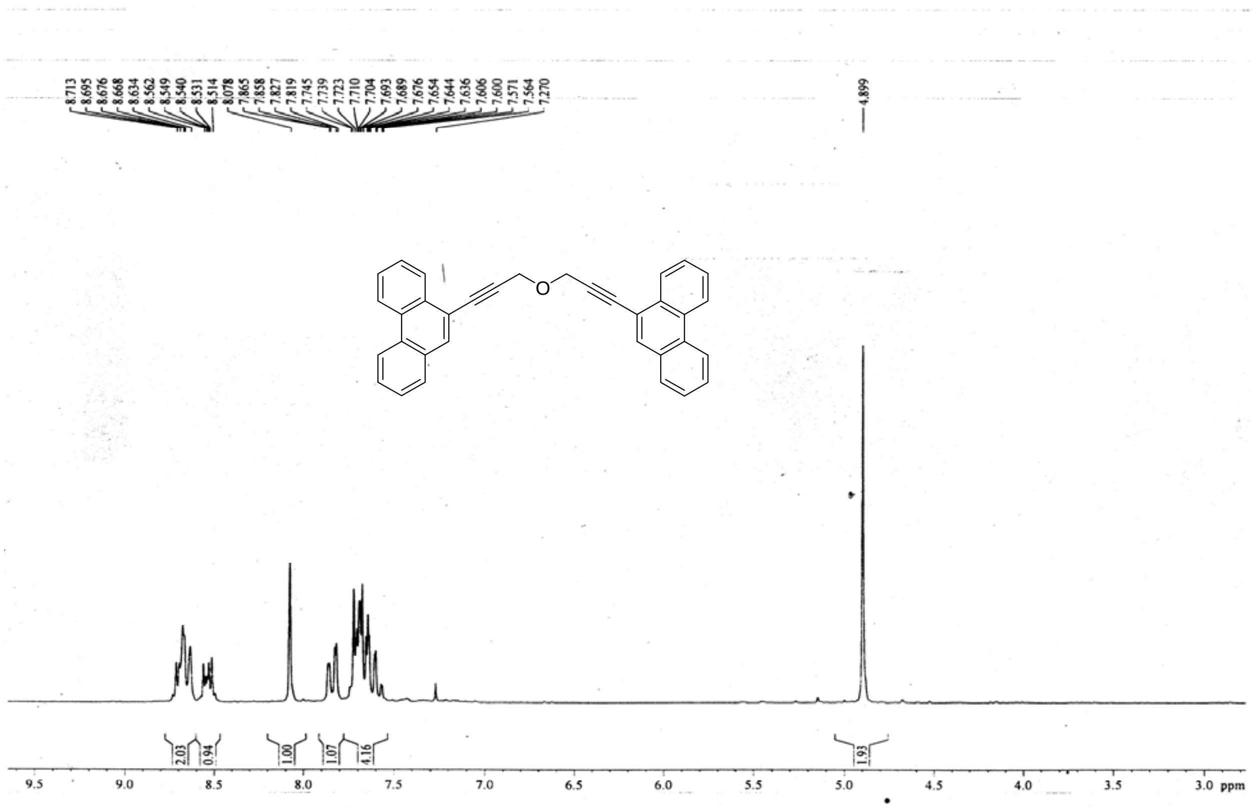
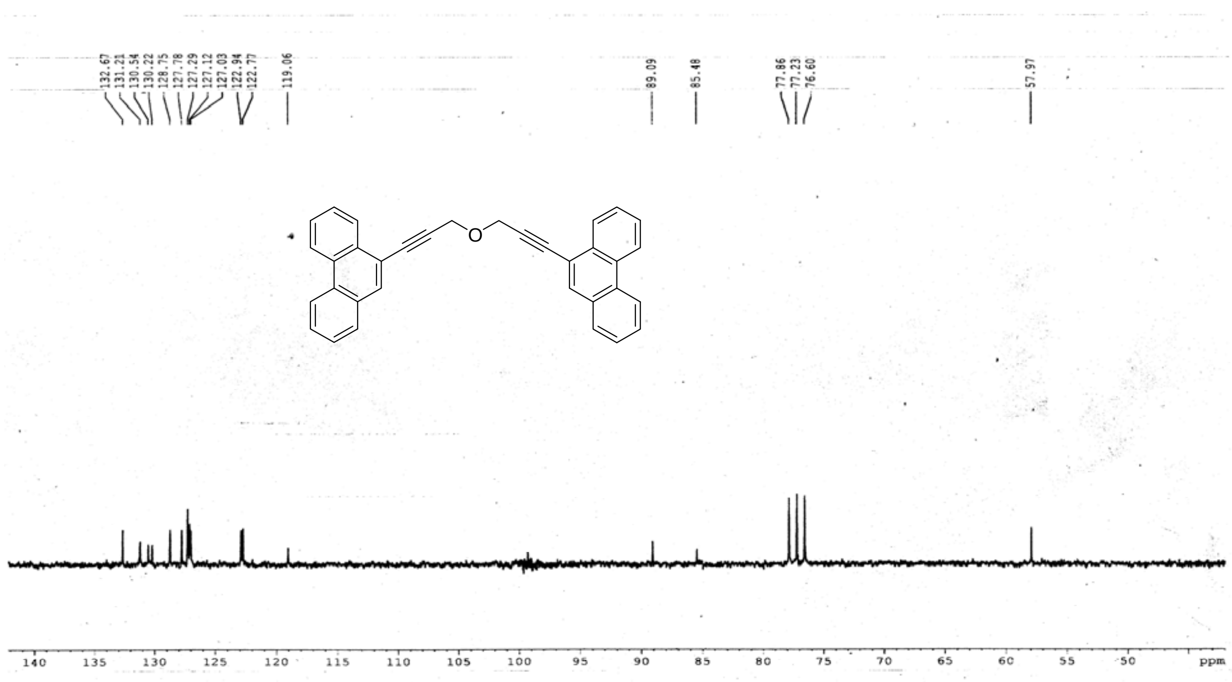


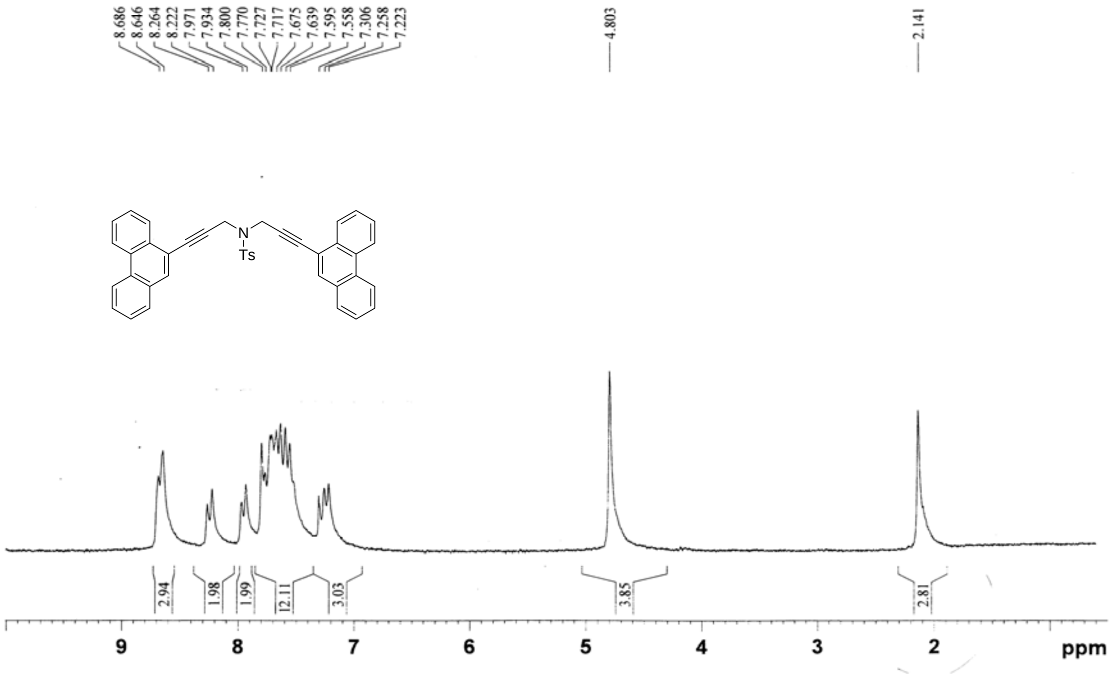
[13]C NMR (50 MHz)



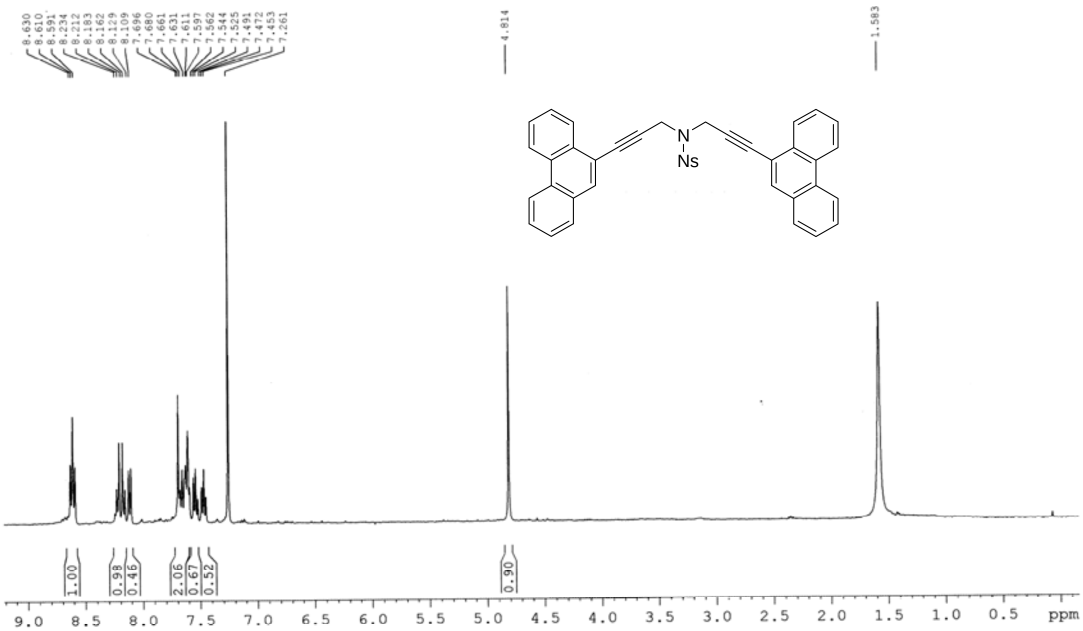
^{1}H NMR (400 MHz)



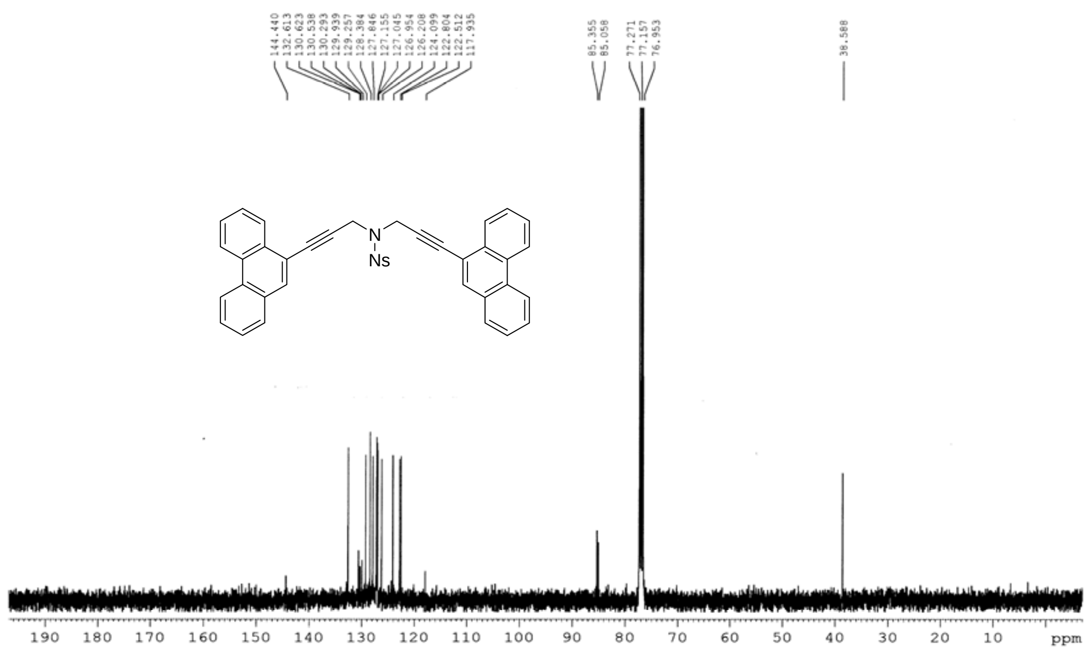
^{13}C NMR (100 MHz)



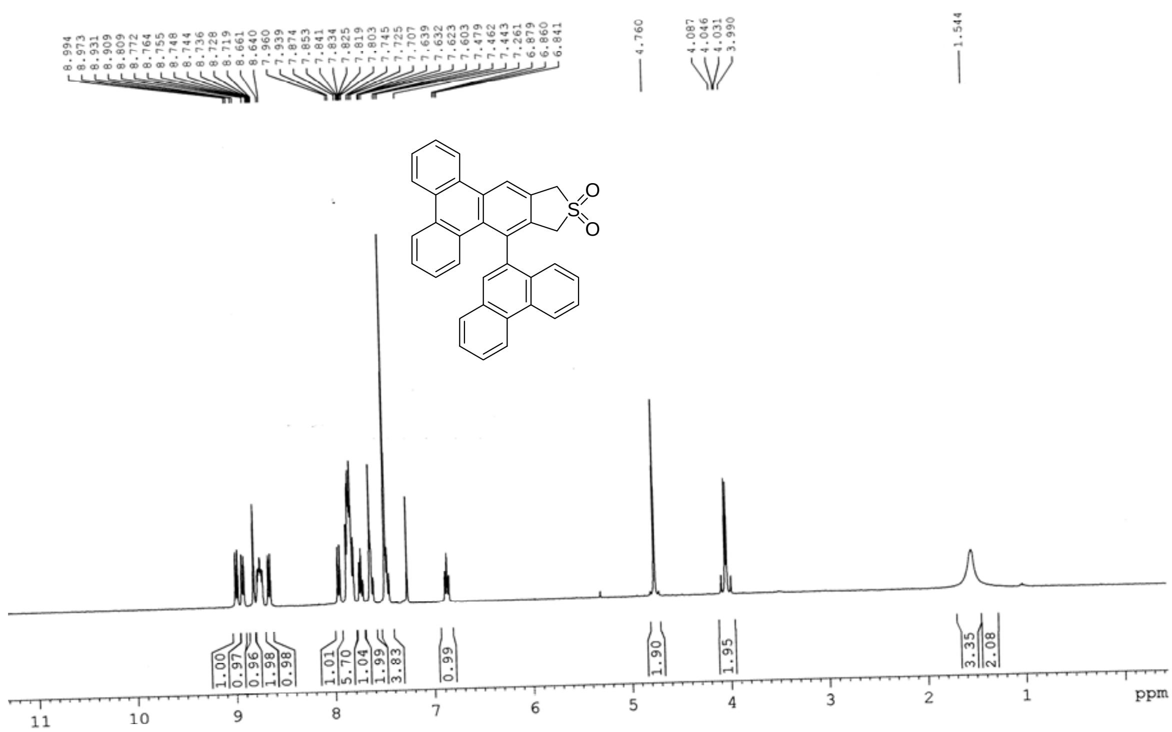
^{1}H NMR (200 MHz)



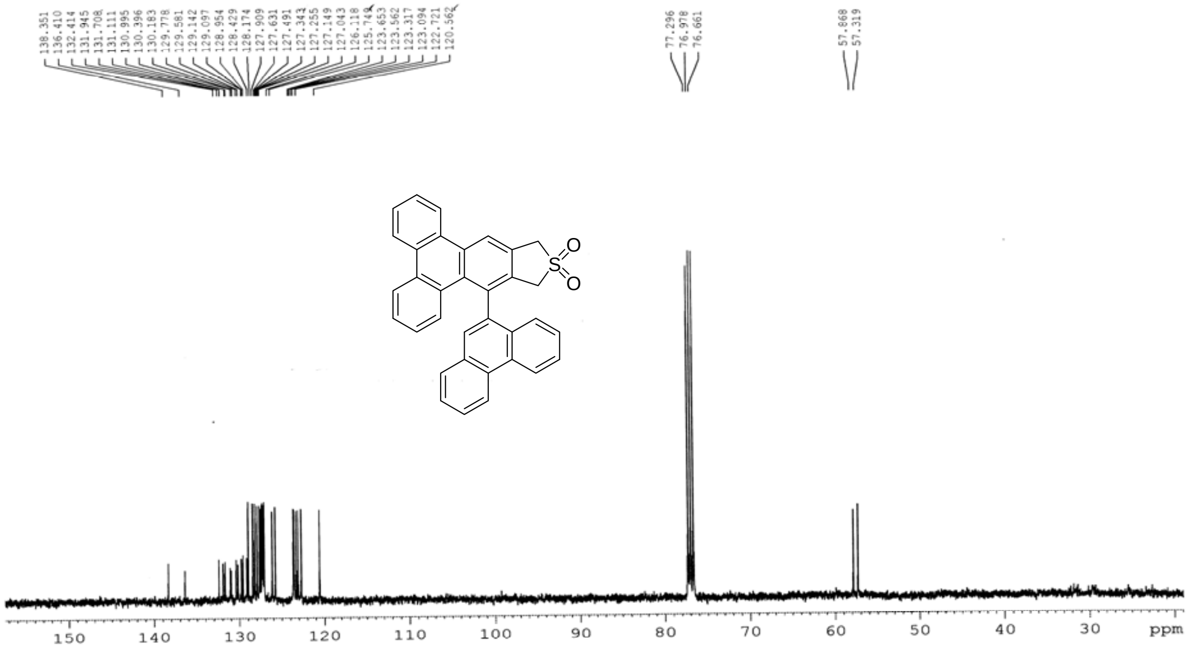
^{1}H NMR (400 MHz)



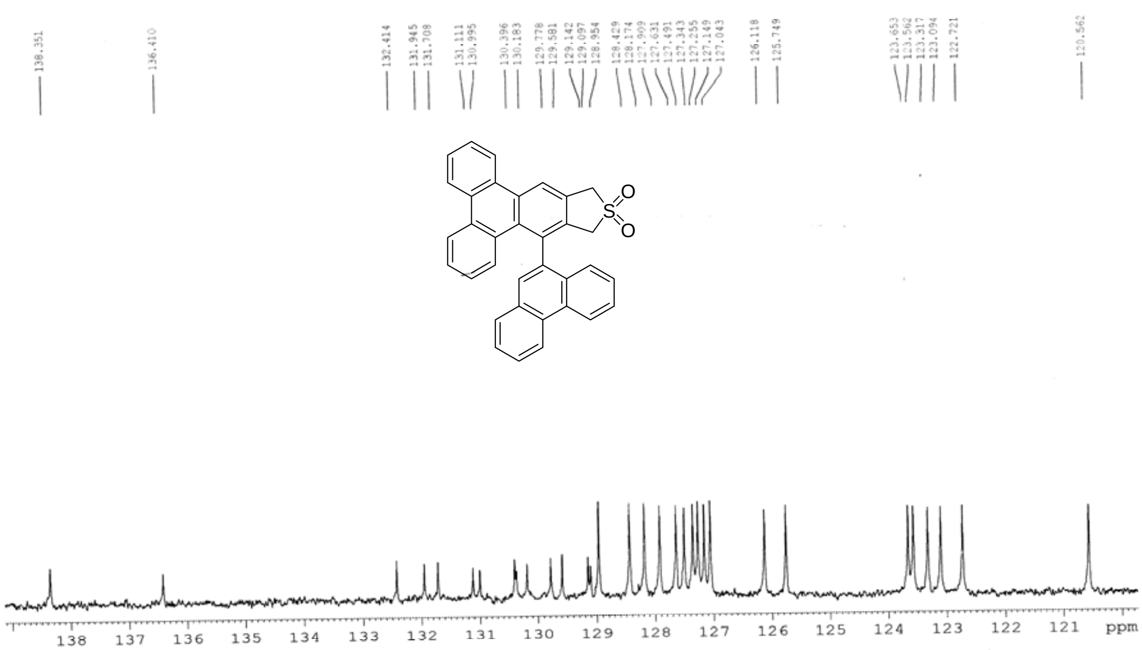
^{13}C NMR (100 MHz)



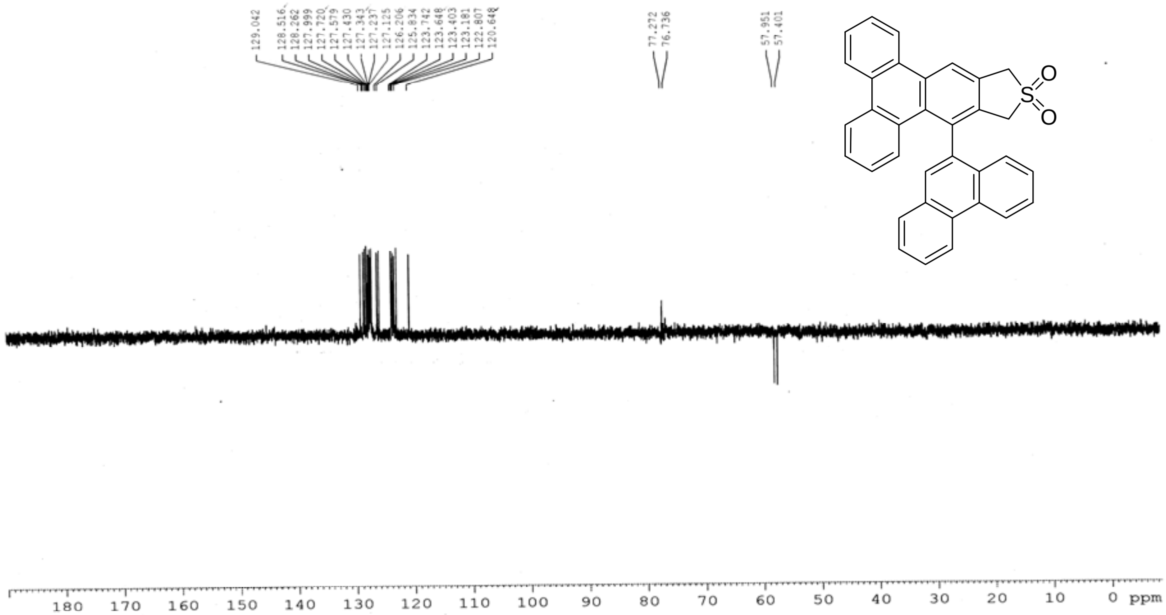
^{1}H NMR (400 MHz)



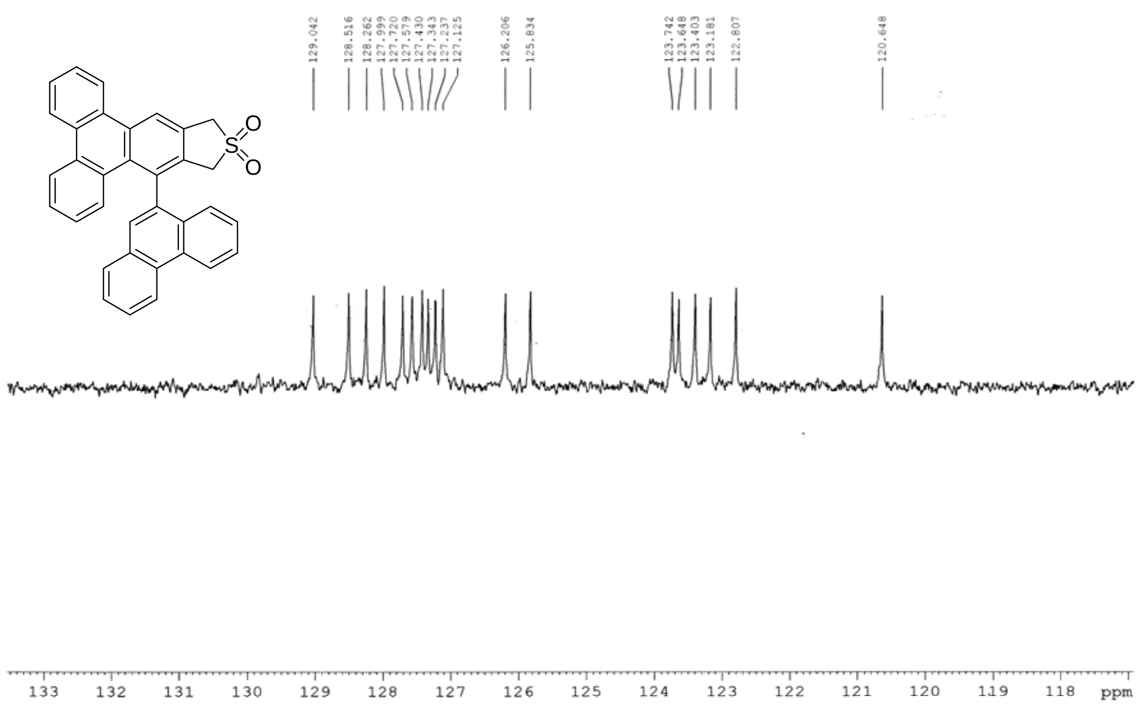
[13]C NMR (100 MHz)



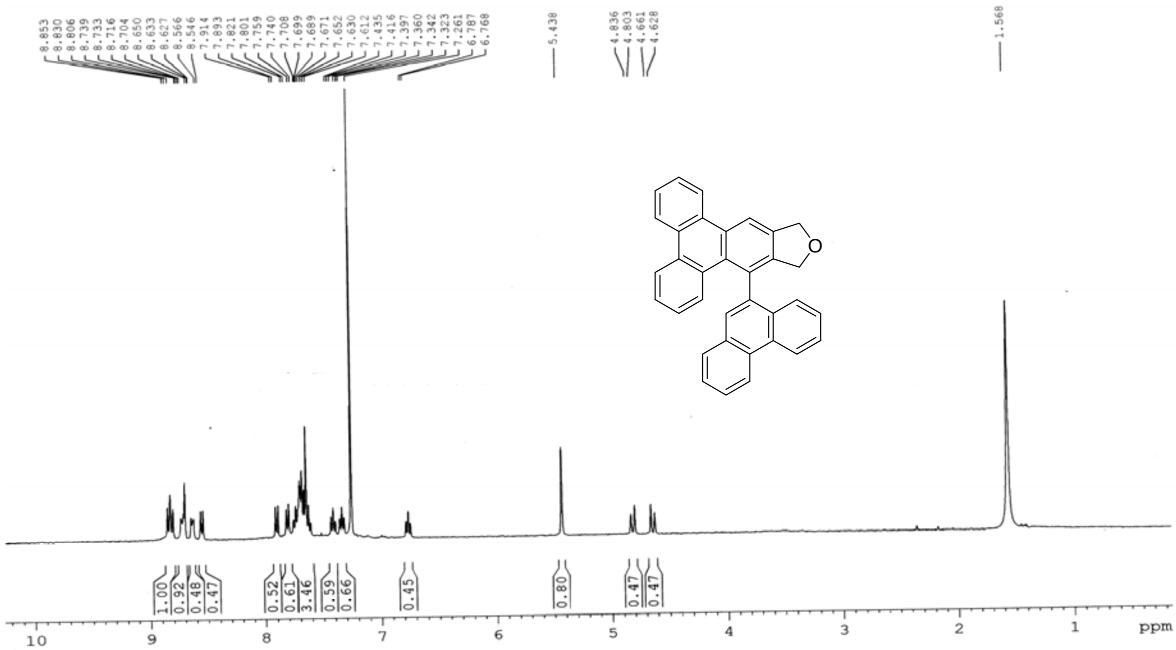
[13]C NMR (100 MHz) expanded



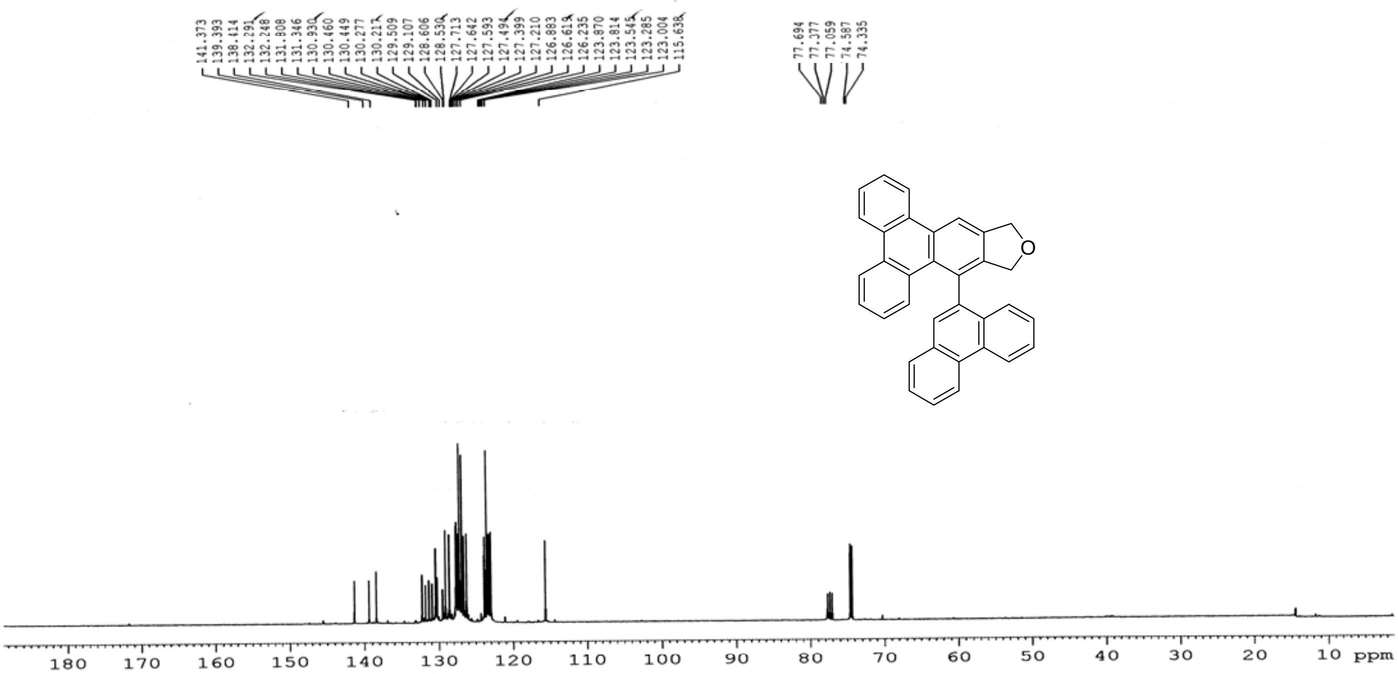
DEPT-135 (100 MHz)



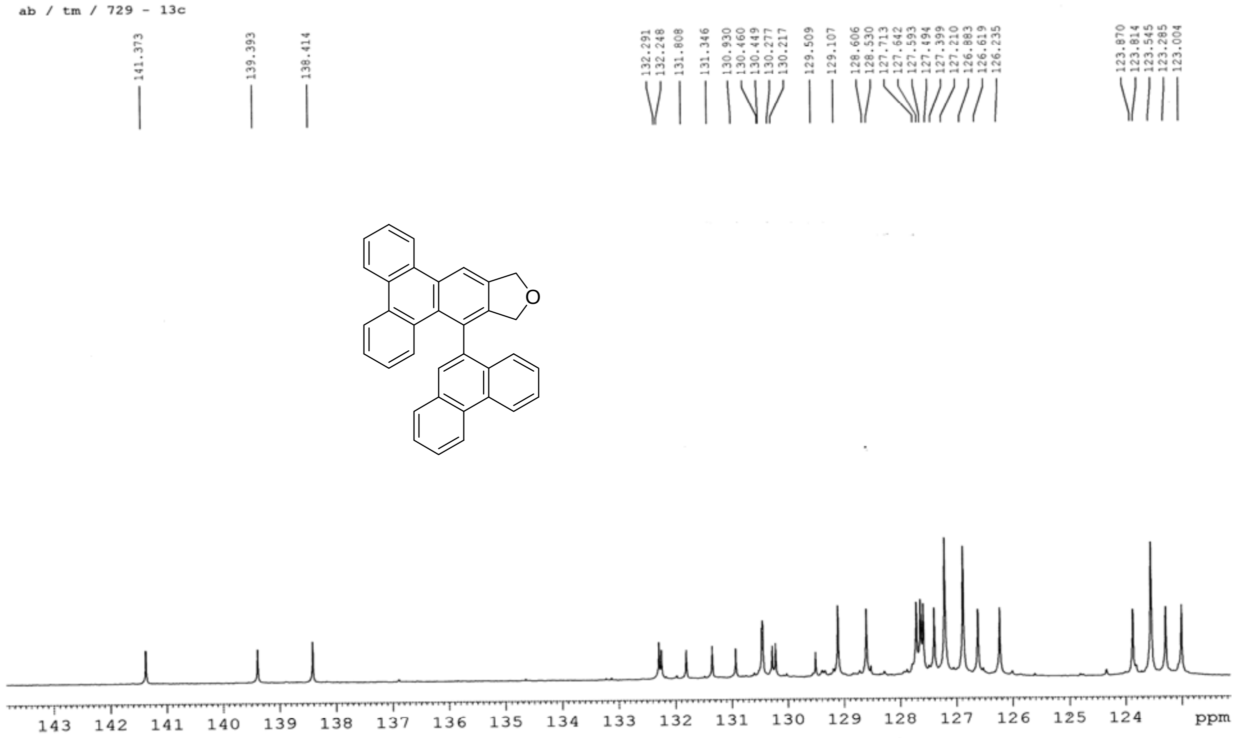
DEPT-135 (100 MHz) expanded



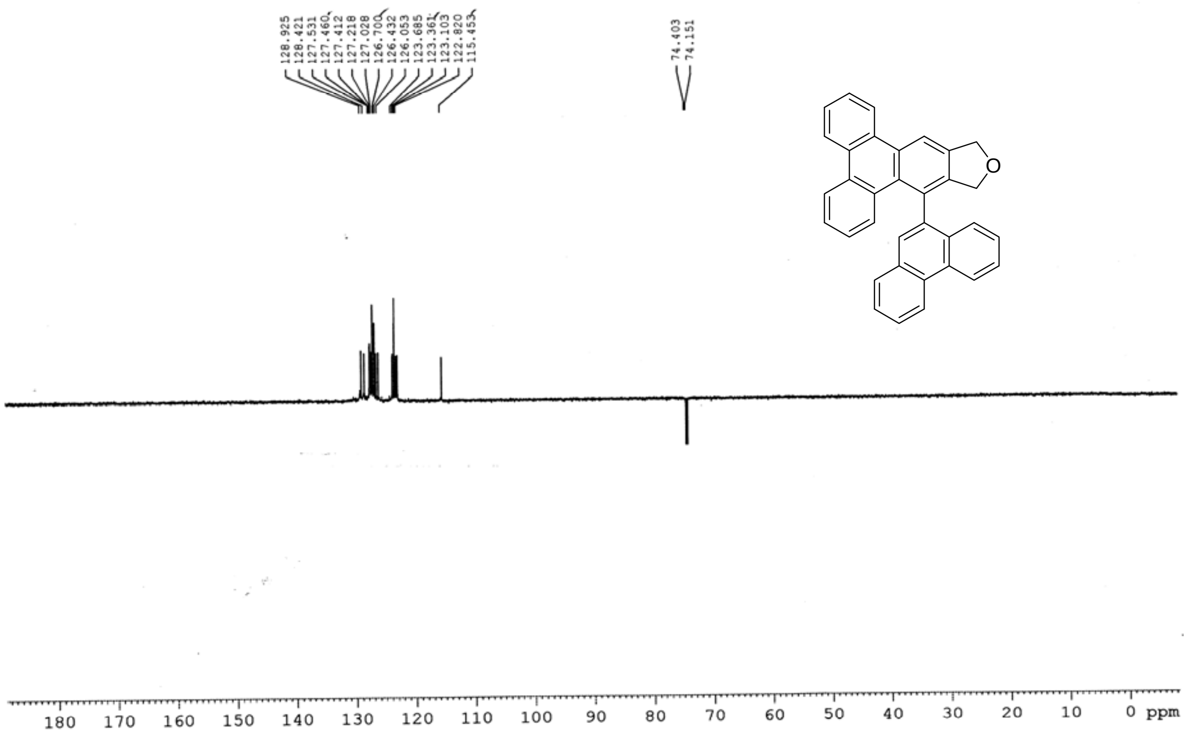
[1]H NMR (400 MHz)



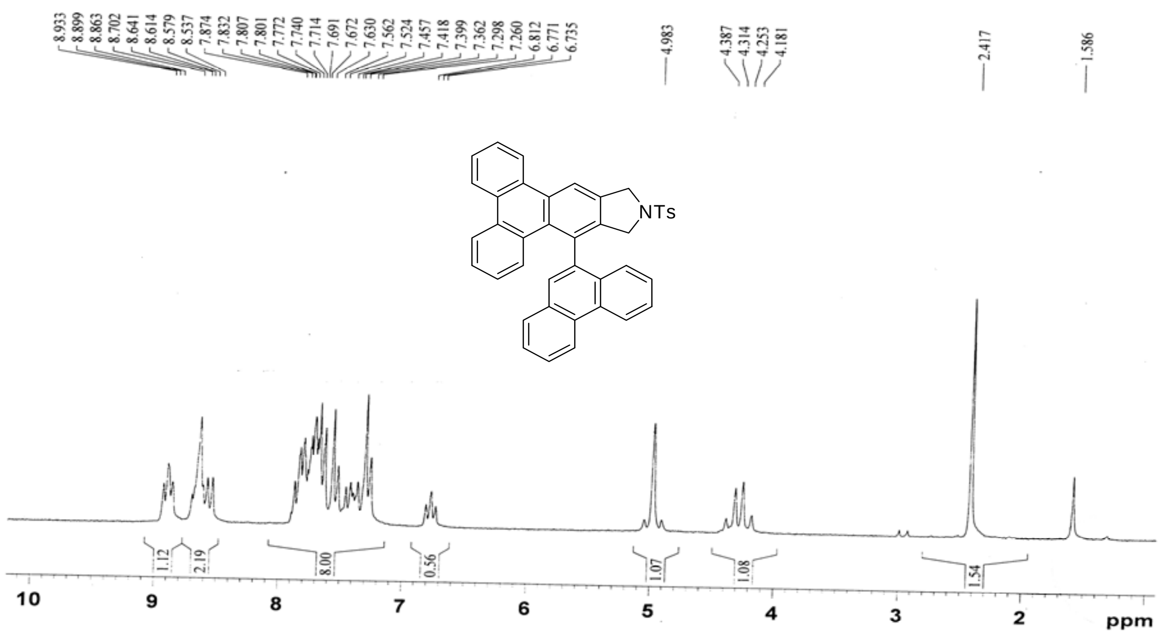
[13]C NMR (100 MHz)



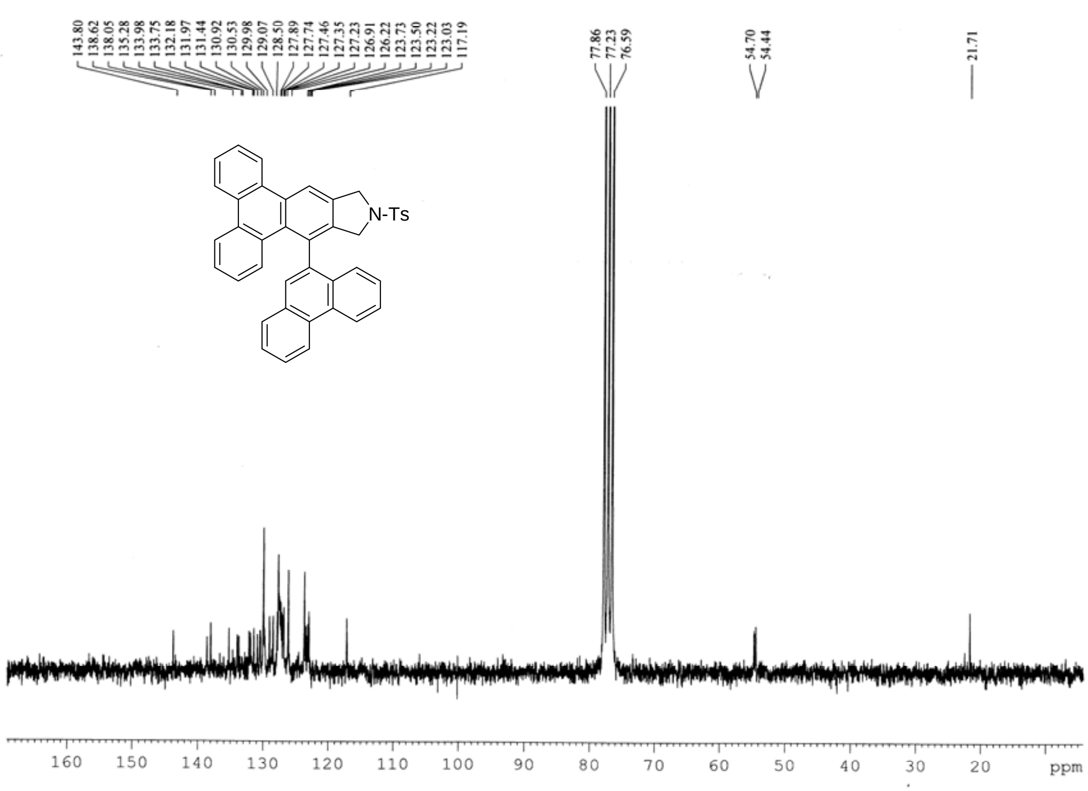
^{13}C NMR (100 MHz) expanded



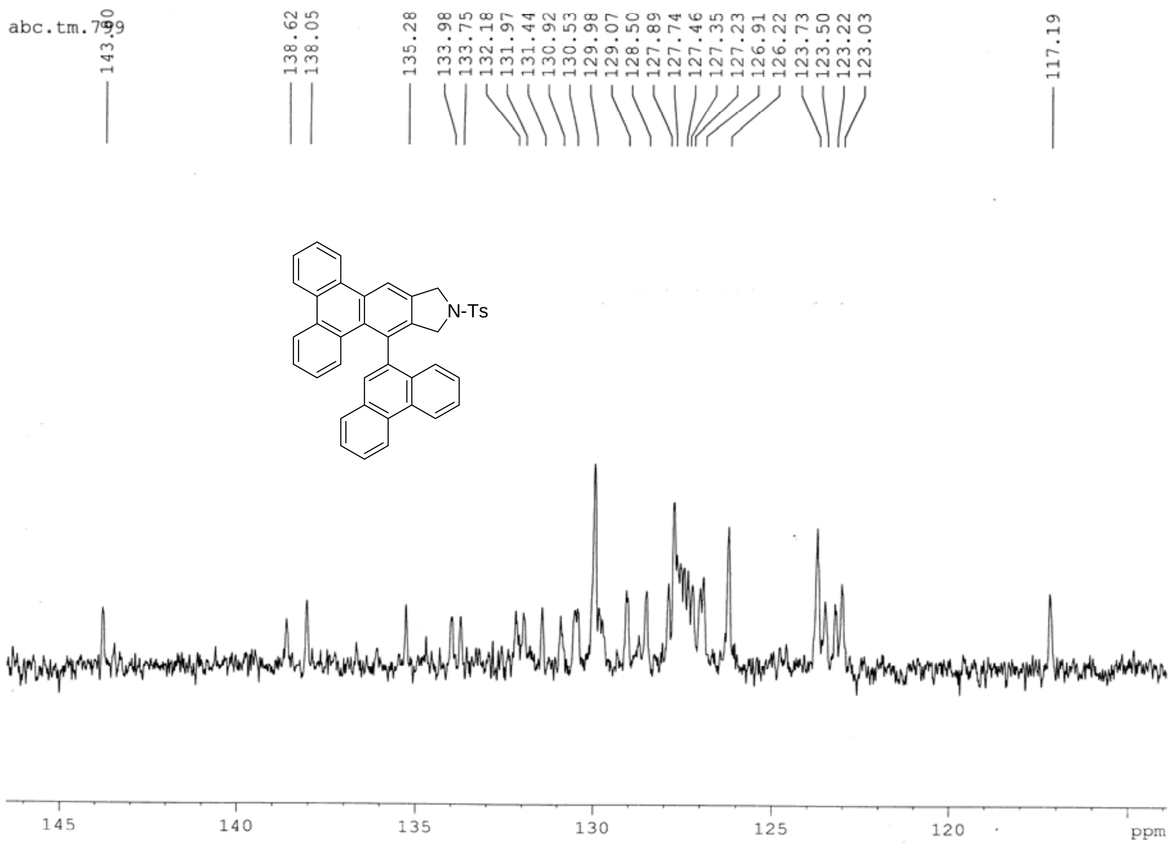
DEPT-135 (100 MHz)



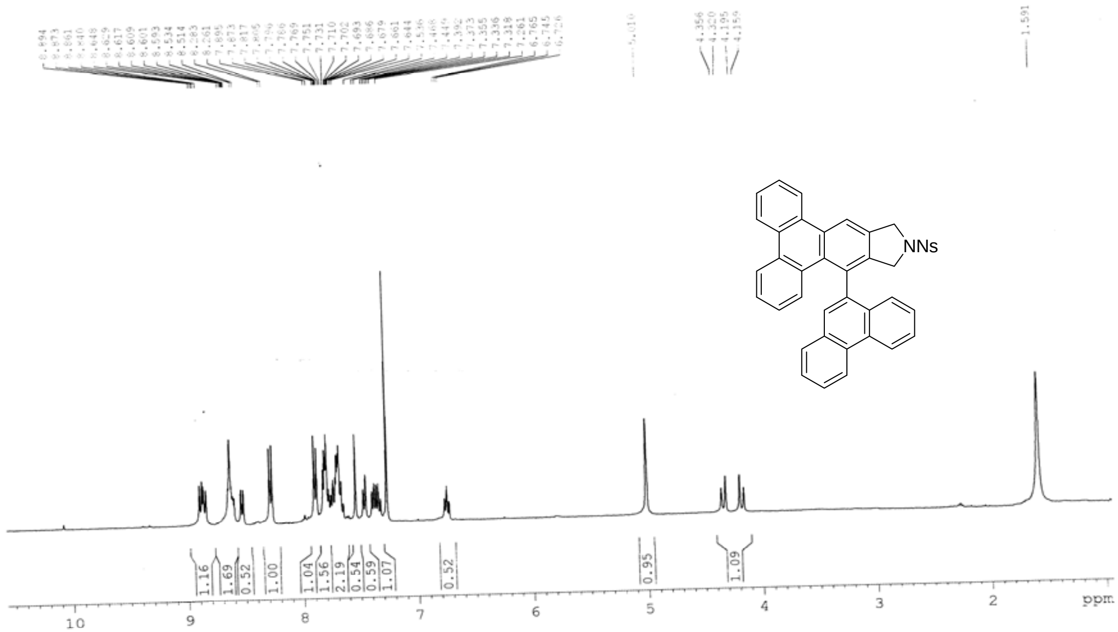
[1]H NMR (400 MHz)



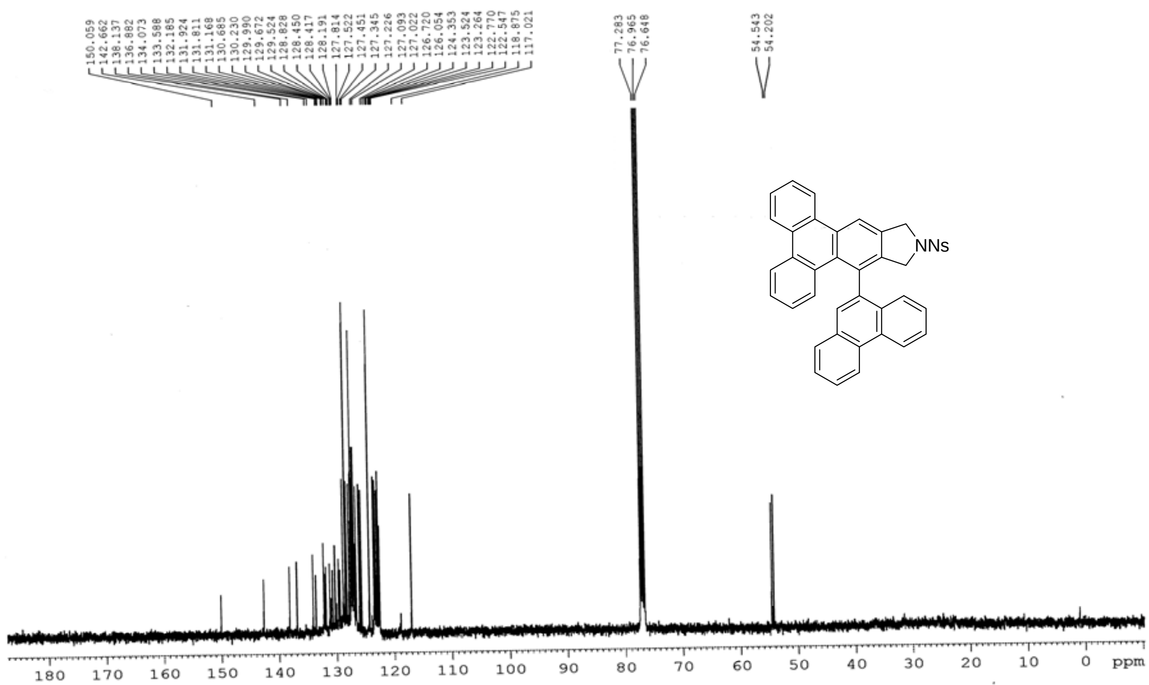
[13]C NMR (50 MHz)



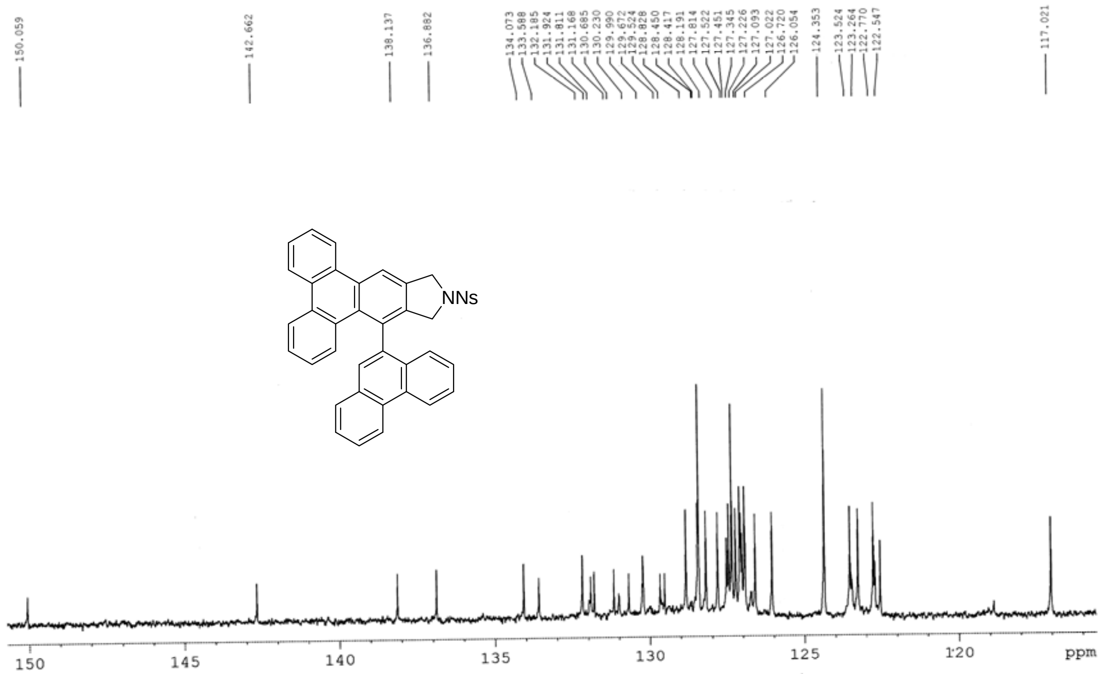
^{13}C NMR (50 MHz) expanded



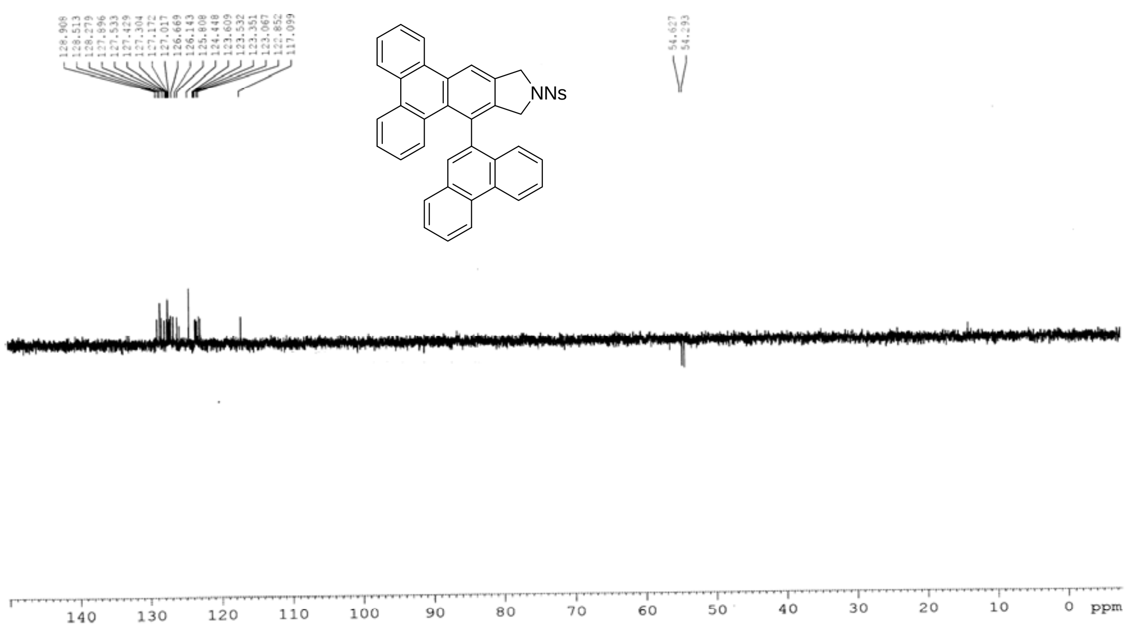
[1]H NMR (400 MHz)



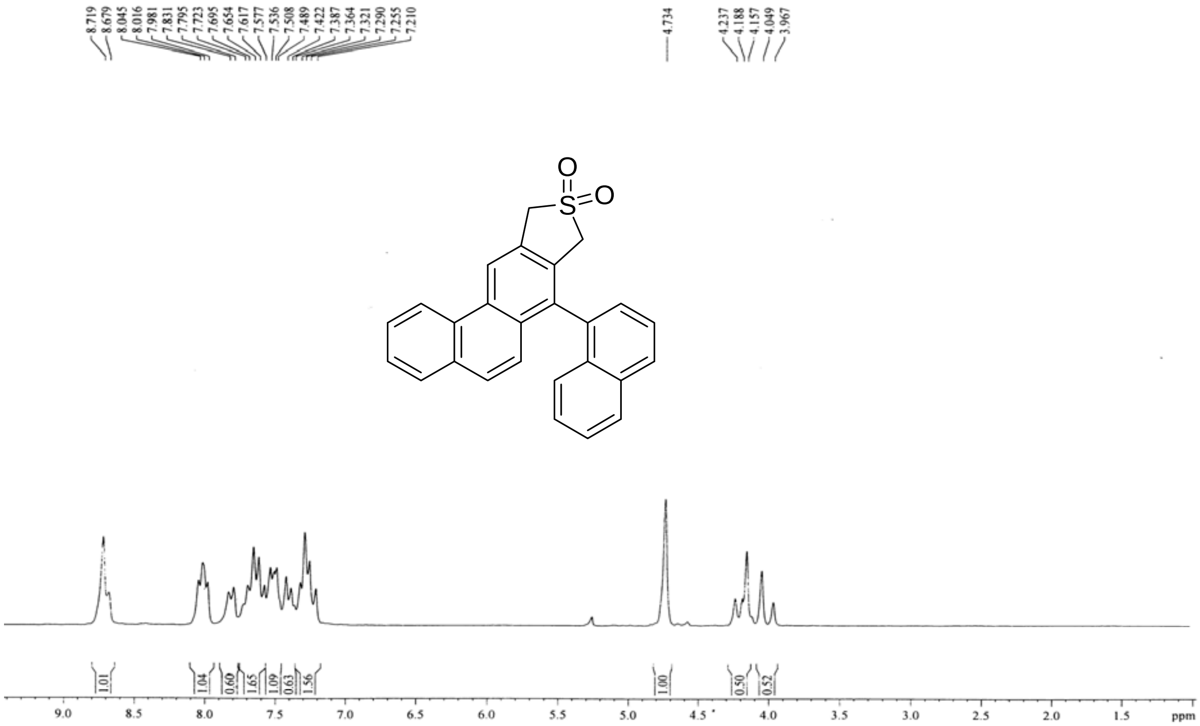
[13]C NMR (100 MHz)



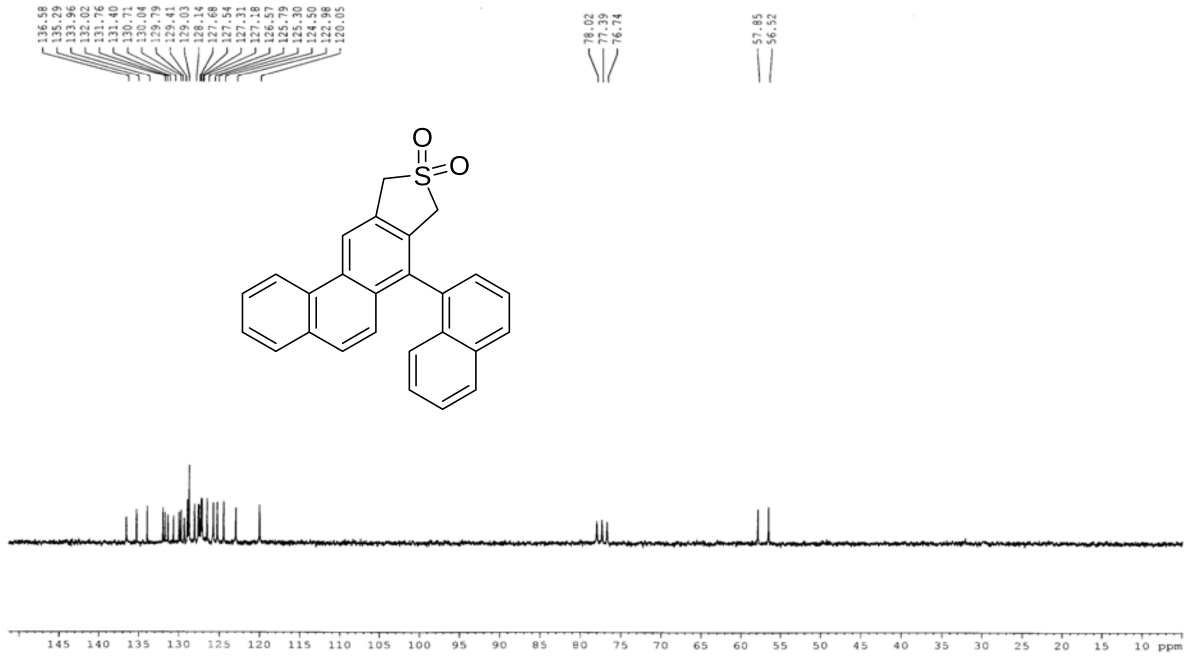
^{13}C NMR (100 MHz) expanded



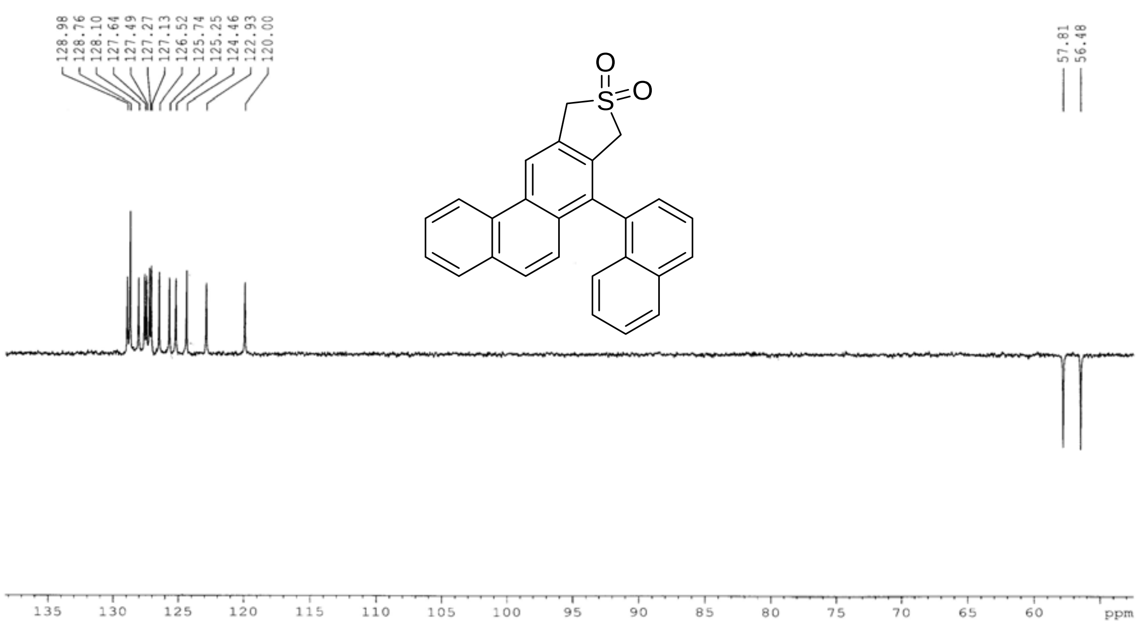
DEPT-135 (100 MHz)



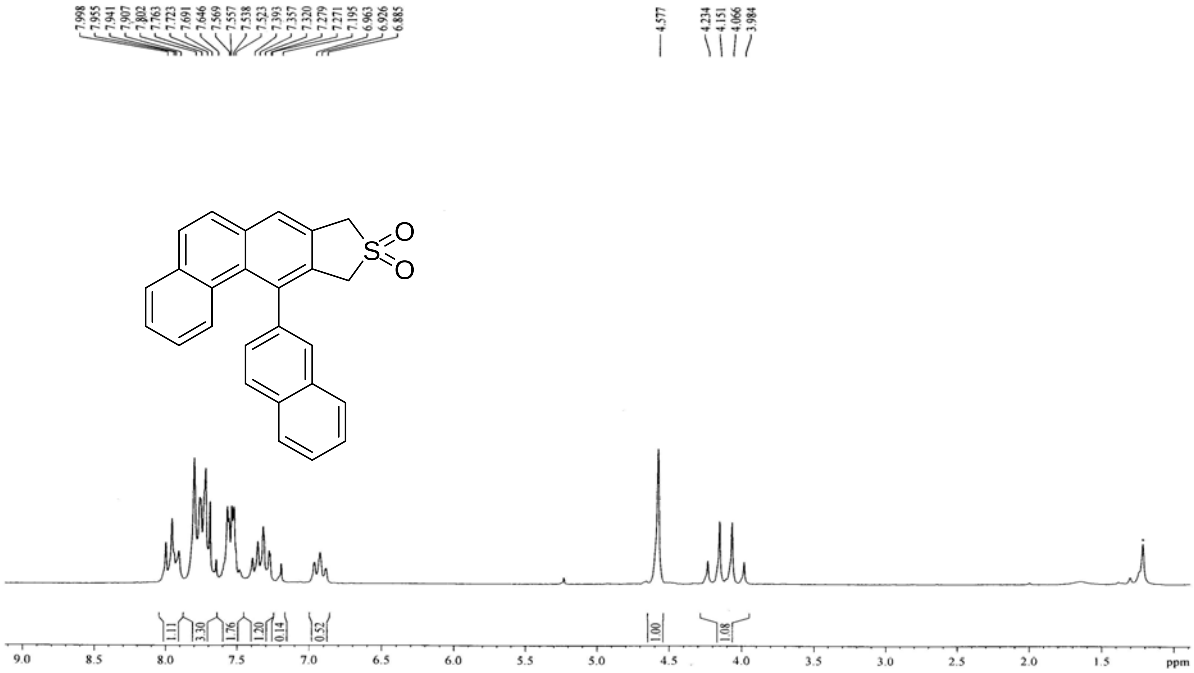
^{1}**H NMR (400 MHz)**



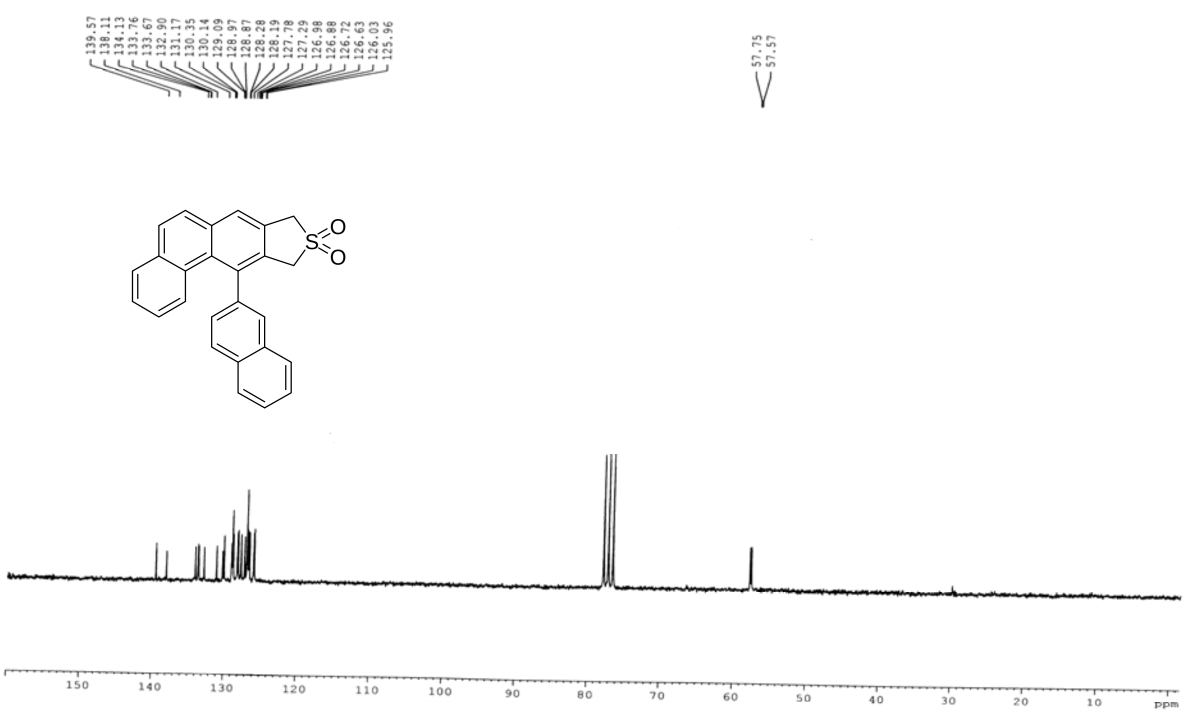
^{13}C NMR (100 MHz)



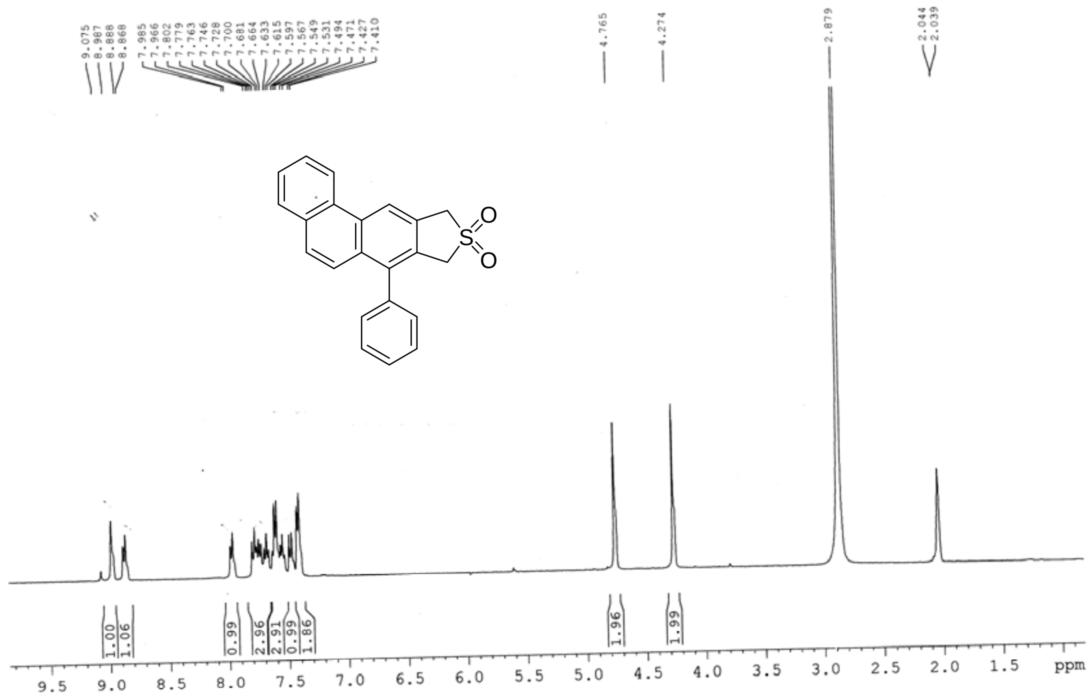
DEPT-135 (100 MHz)



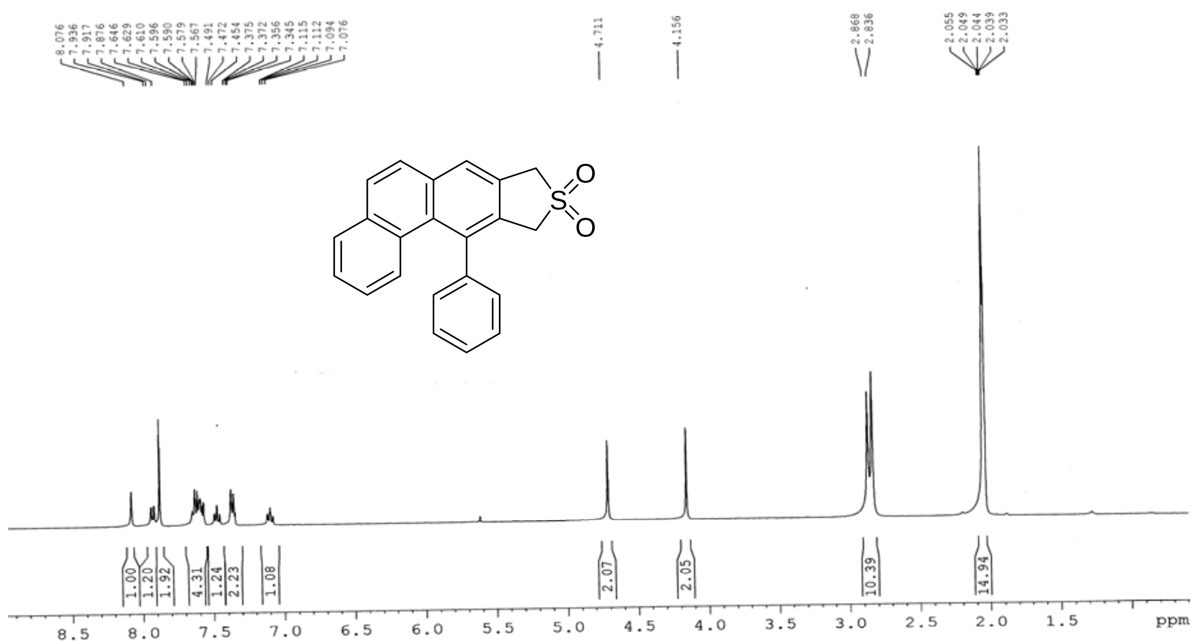
^{1}H NMR (200 MHz)



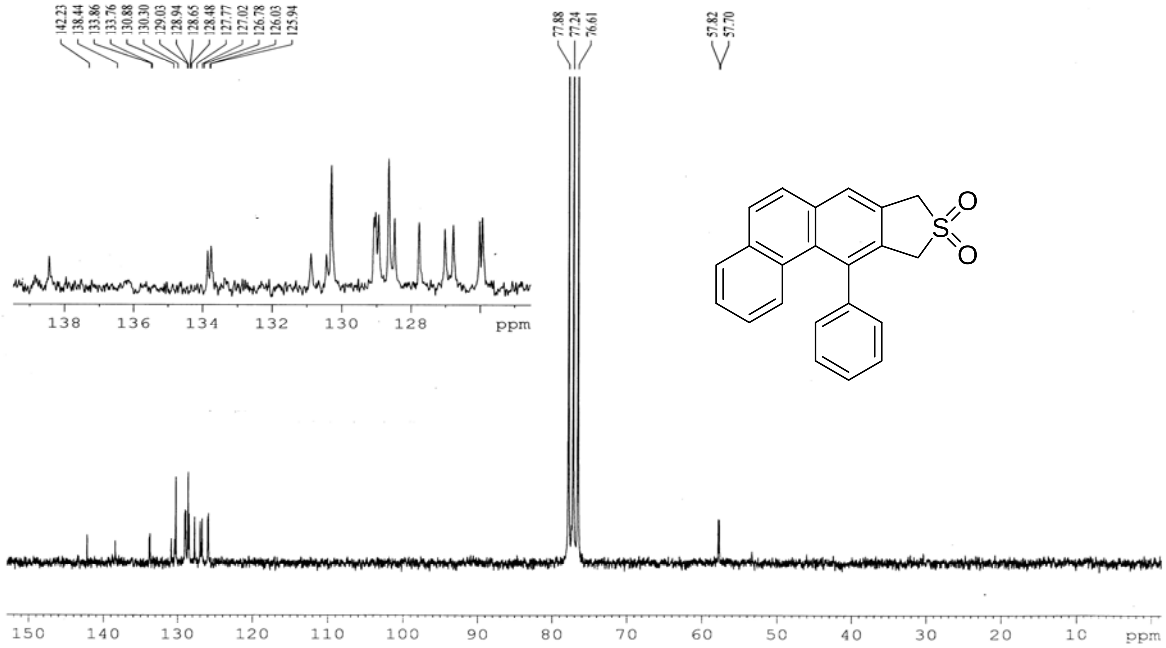
^{13}C NMR (100 MHz)



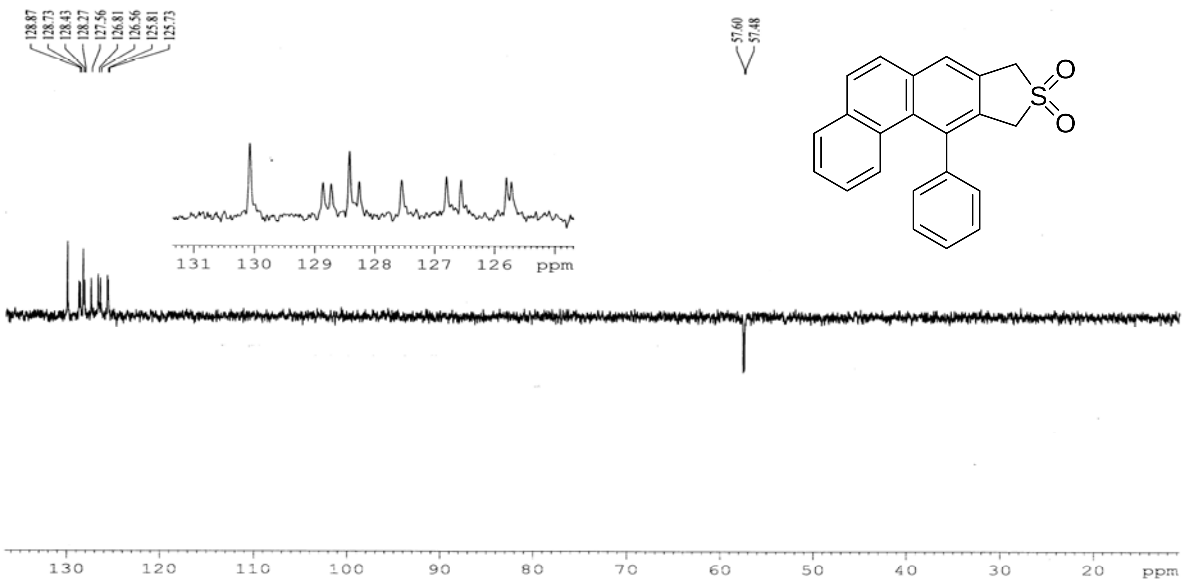
^{1}H NMR (400 MHz)



^{1}H NMR (400 MHz)

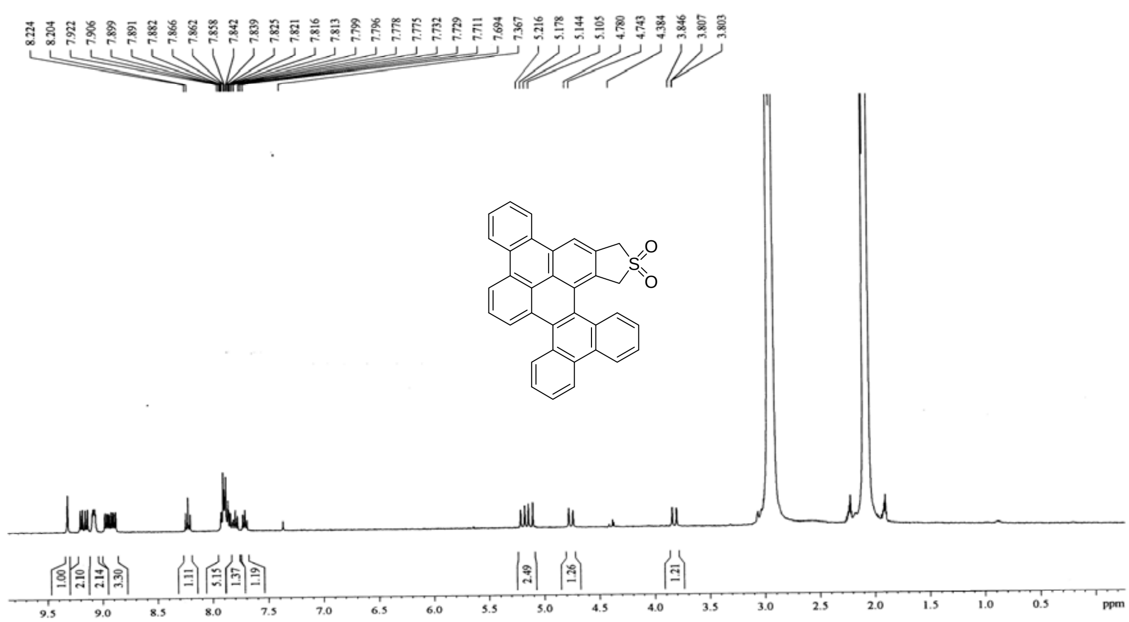


^{13}C NMR (100 MHz)

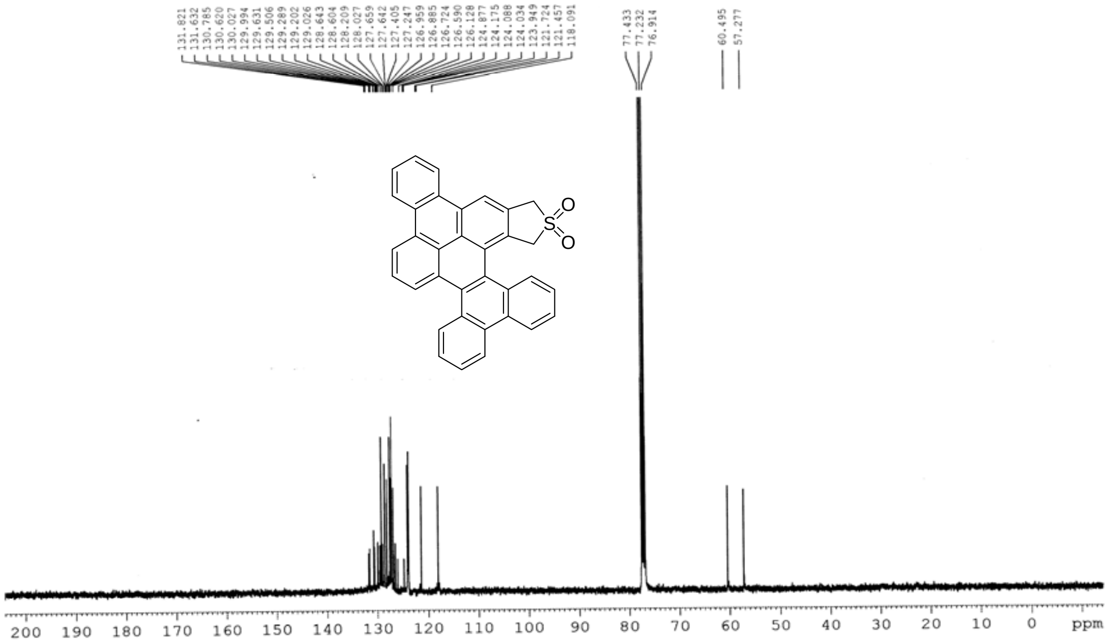


DEPT-135 (100 MHz)

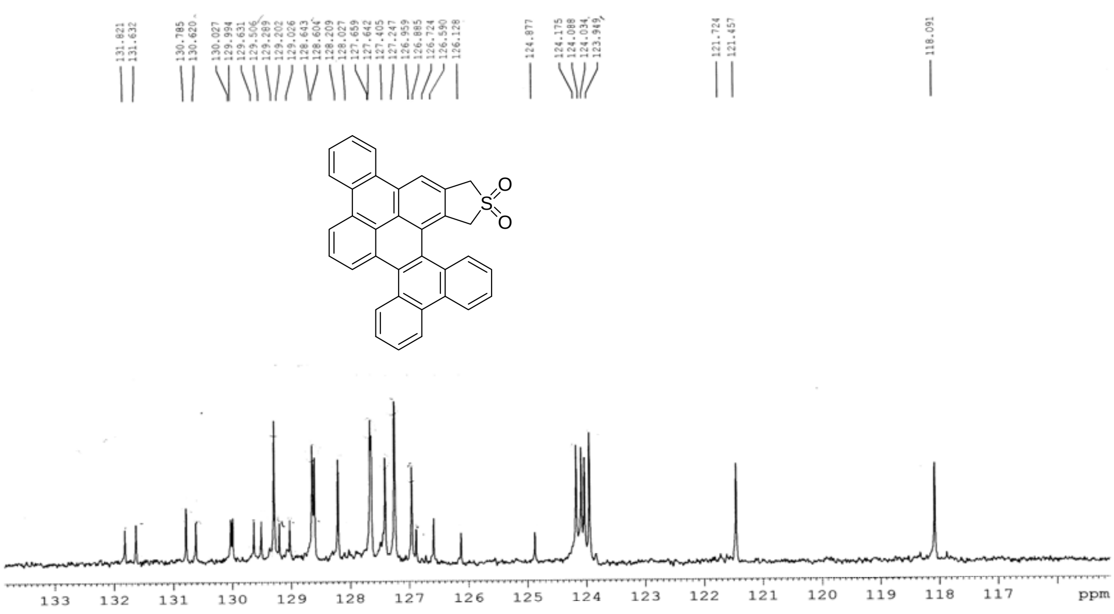
[1]H NMR (400 MHz)



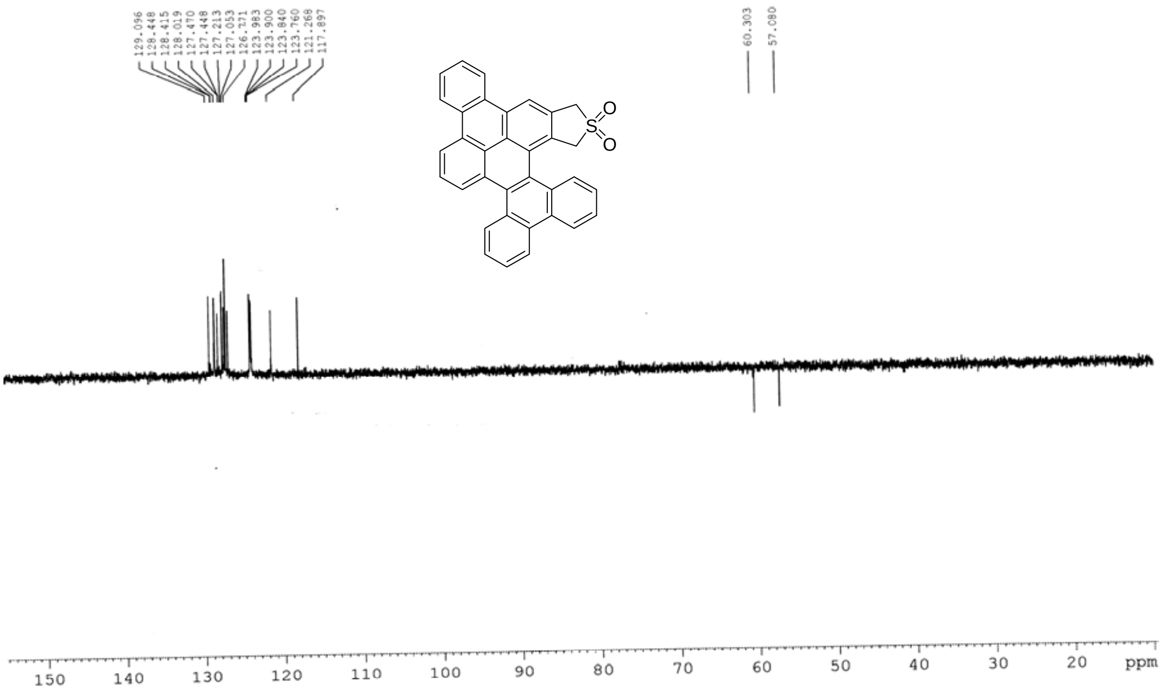
^{1}H NMR in d_6-Acetone (400 MHz)



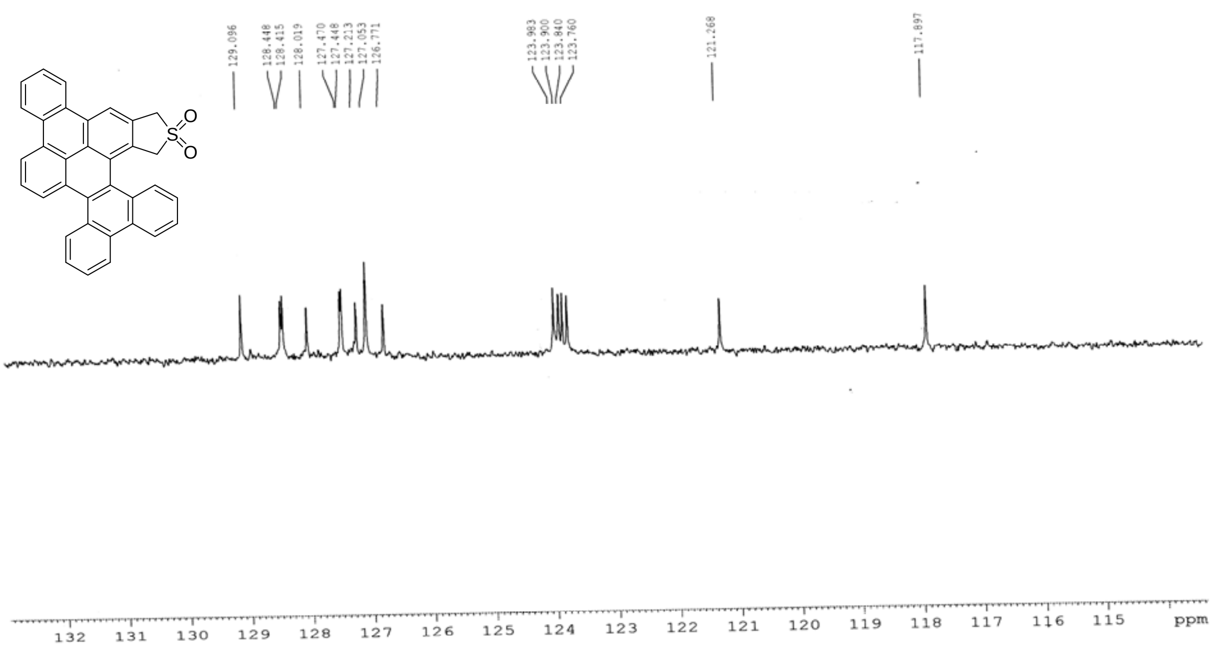
^{13}C NMR (100 MHz)



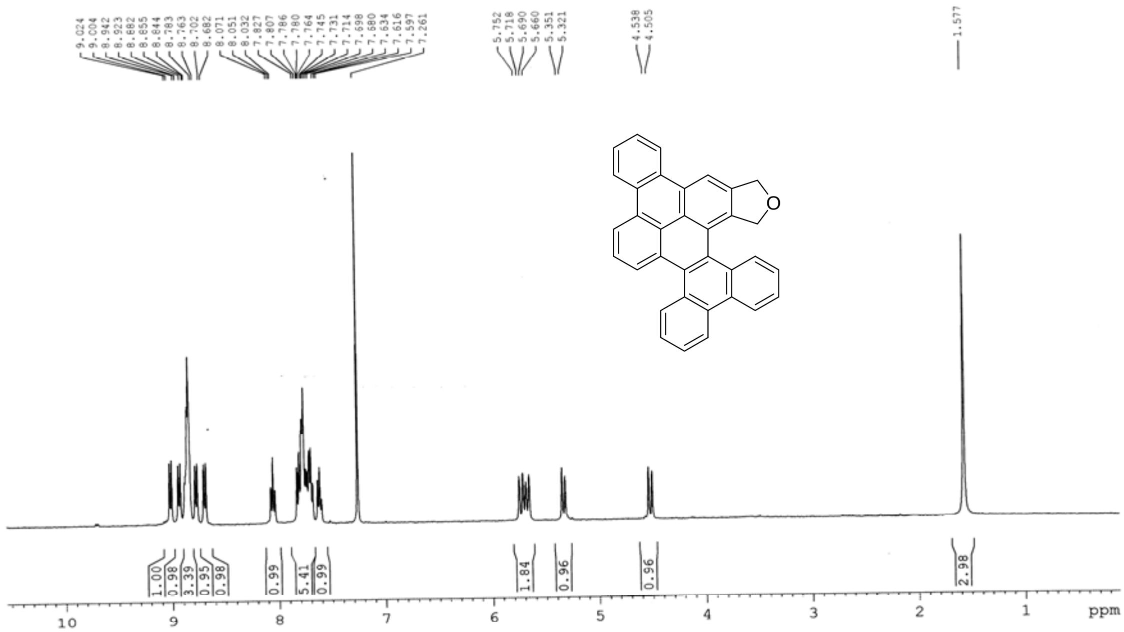
^{13}C NMR (100 MHz) expanded



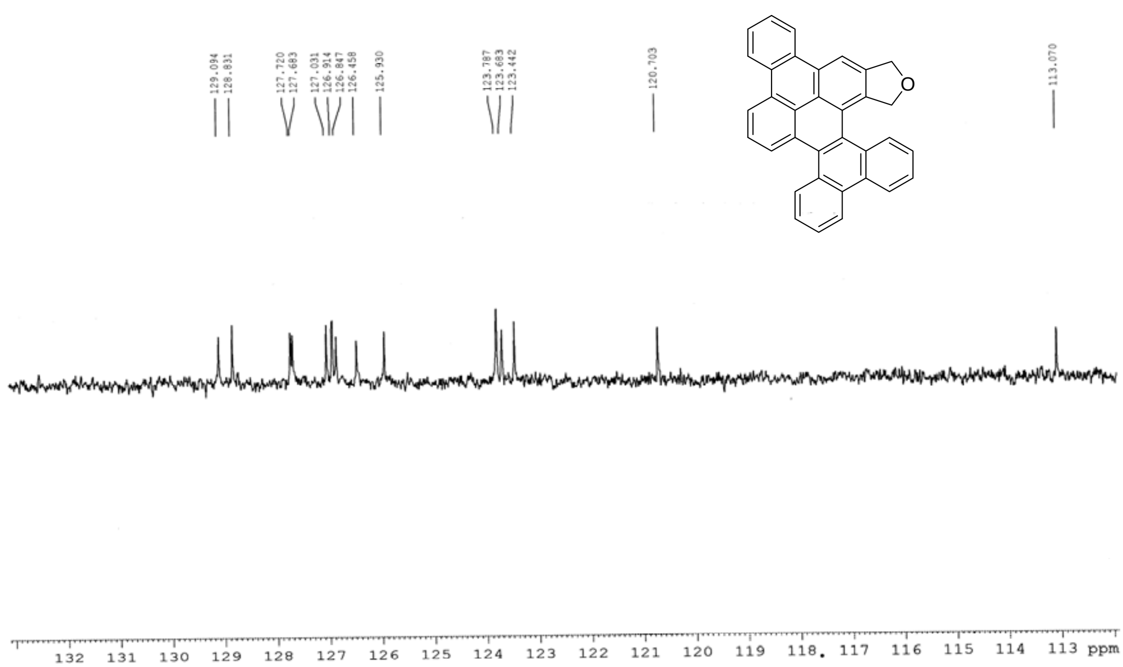
DEPT-135 (100 MHz)



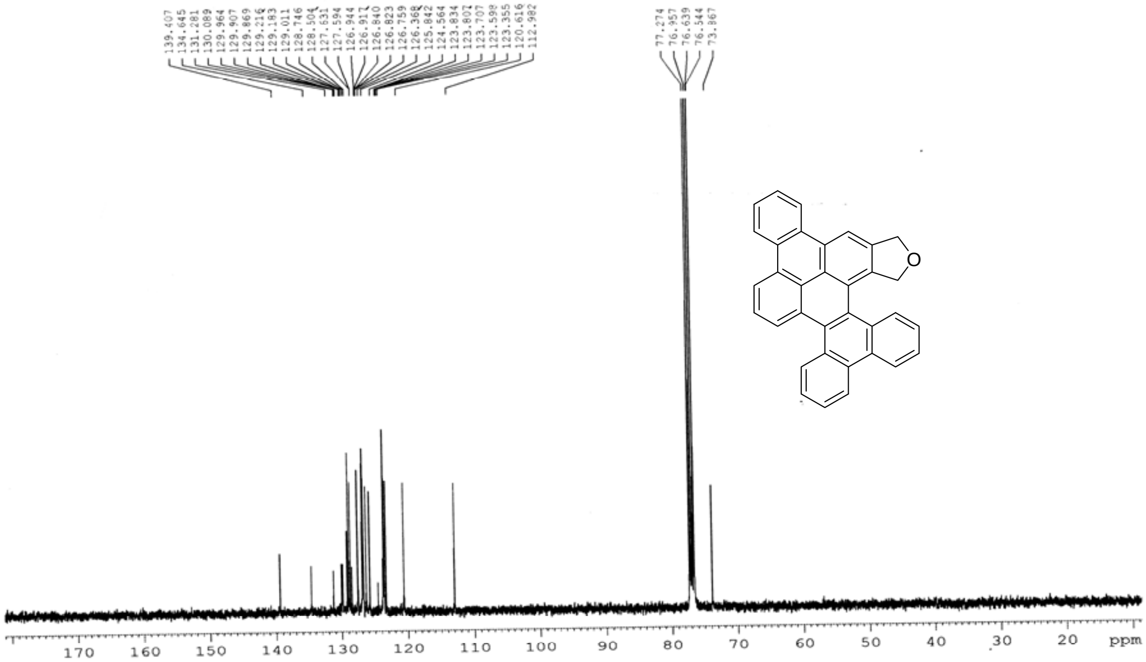
DEPT-135 (100 MHz) expanded



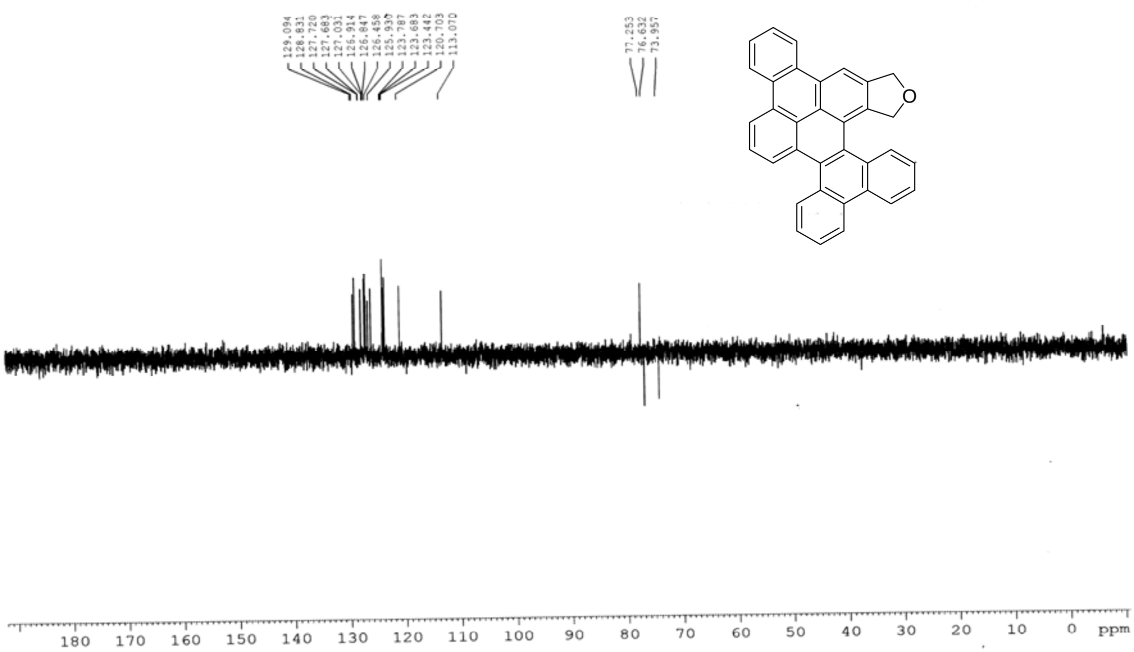
[1]H NMR (400 MHz)



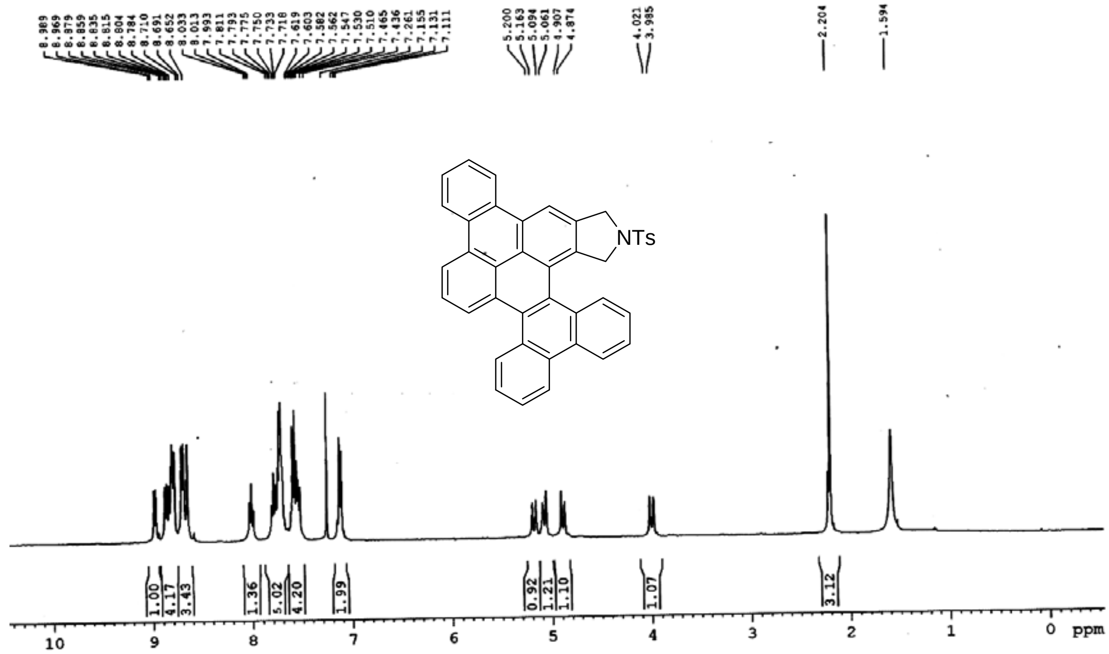
DEPT-135 (100 MHz) expanded



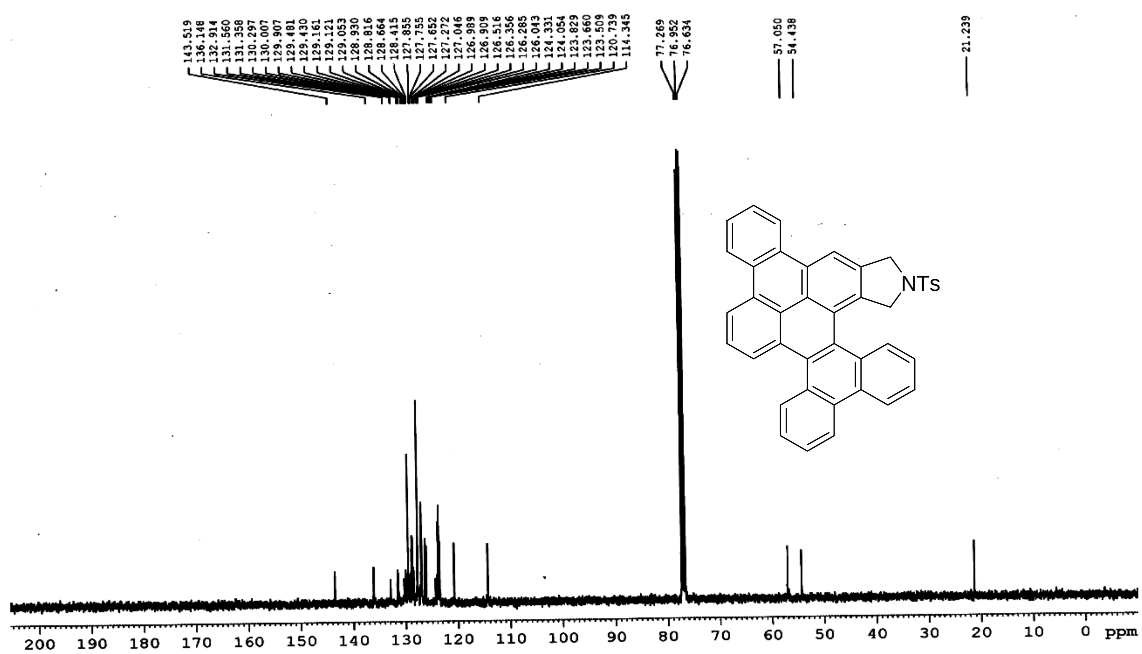
[13]C NMR (100 MHz)



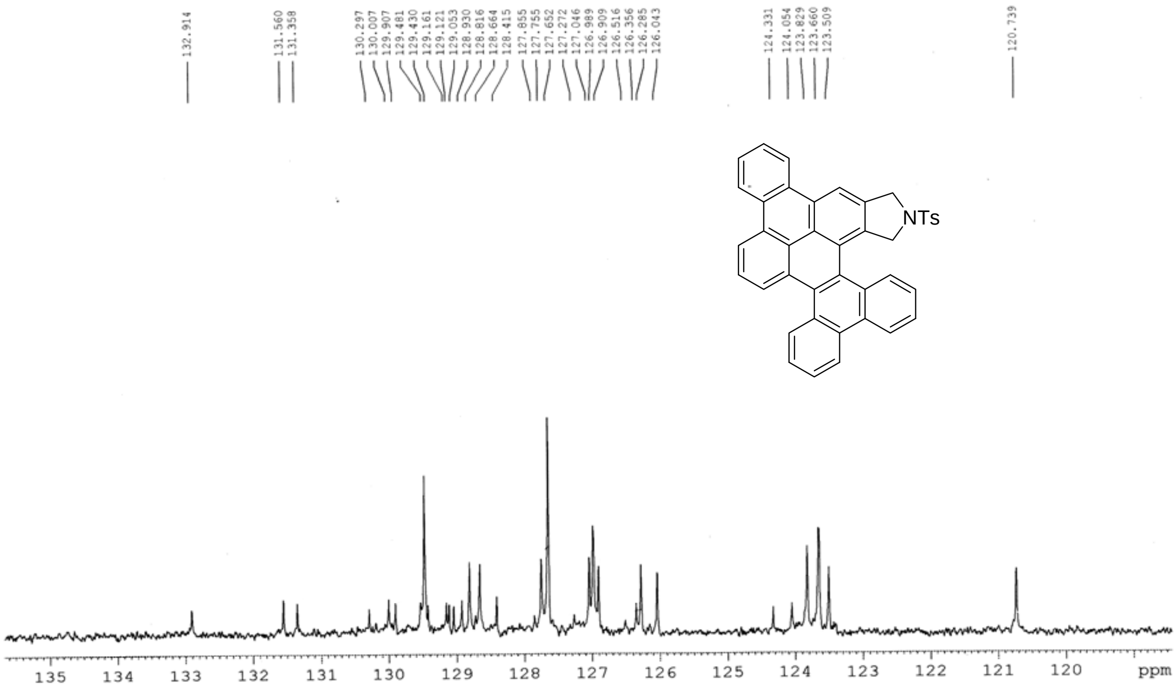
DEPT-135 (100 MHz)



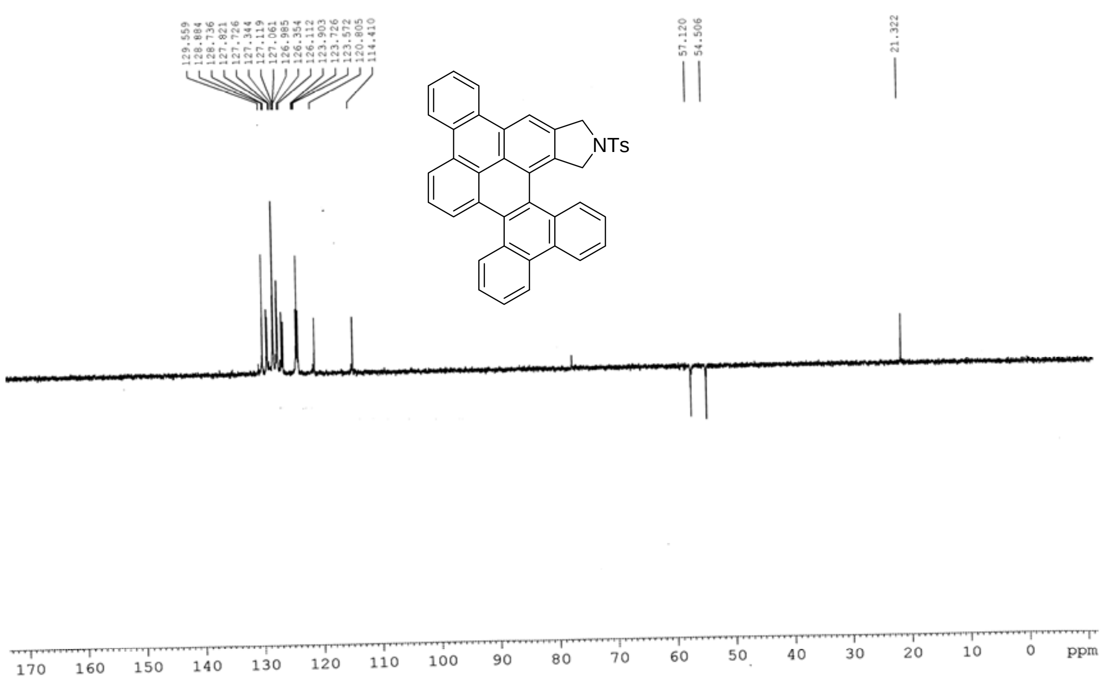
^{1}H NMR (400 MHz)



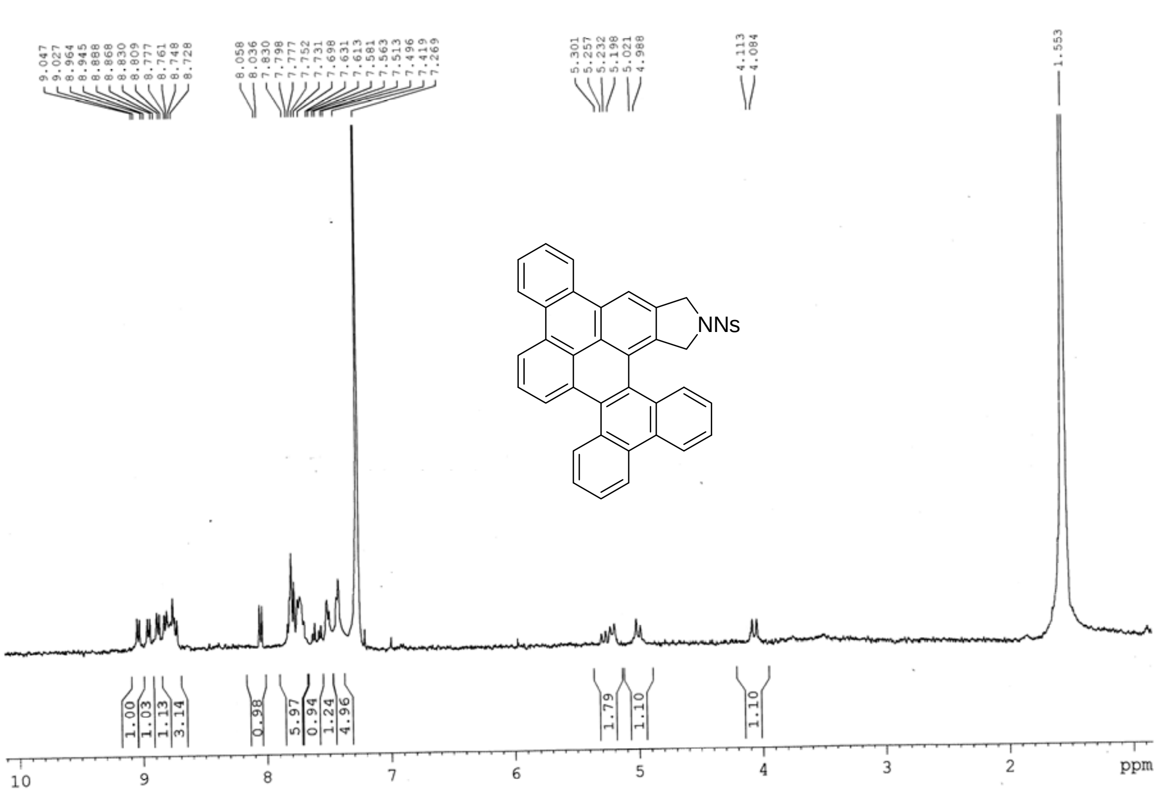
^{13}C NMR (100 MHz)



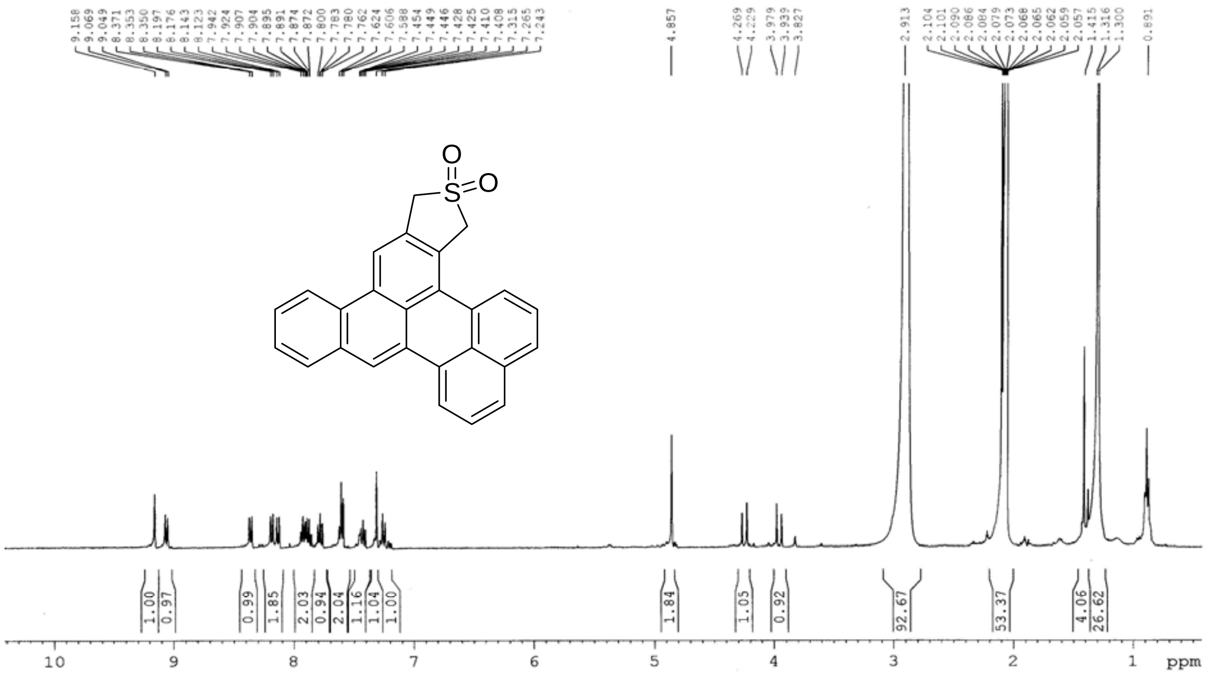
^{13}**C NMR (100 MHz) expanded**



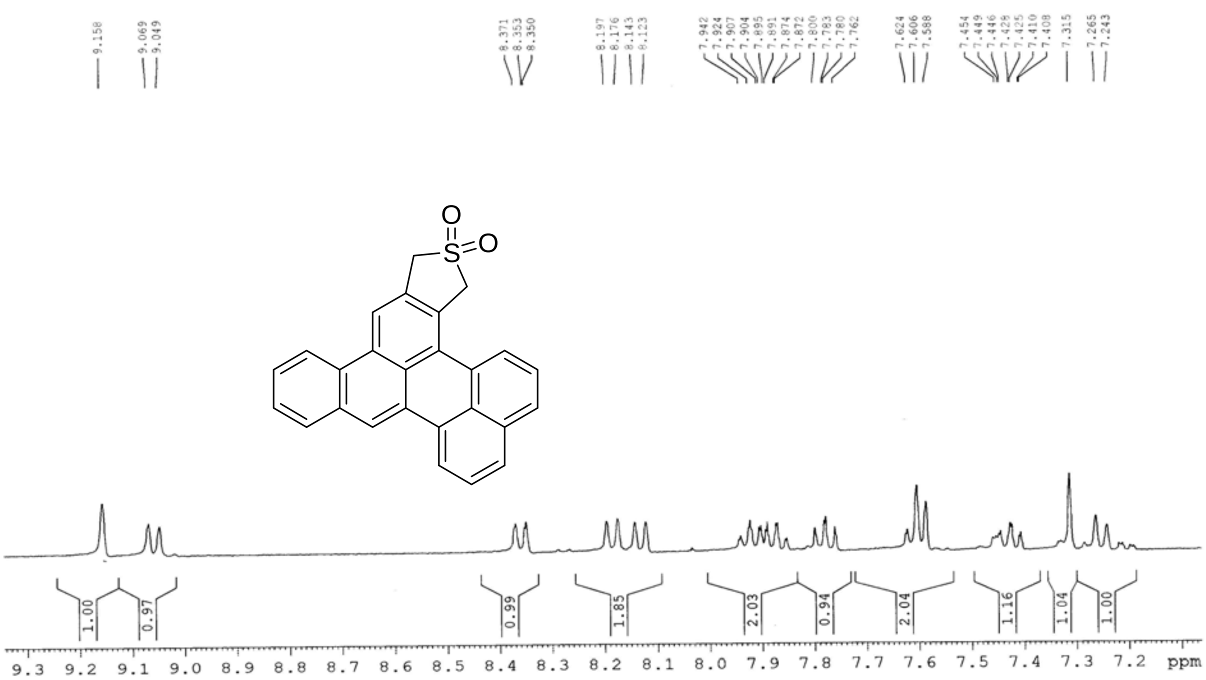
DEPT-135 (100 MHz)



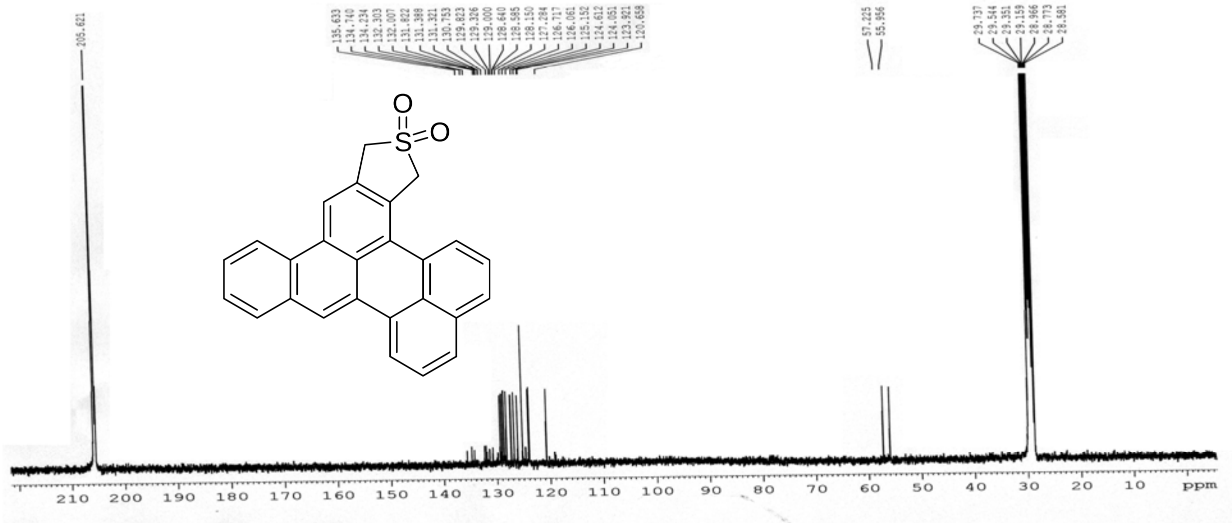
^{1}H NMR (400 MHz)



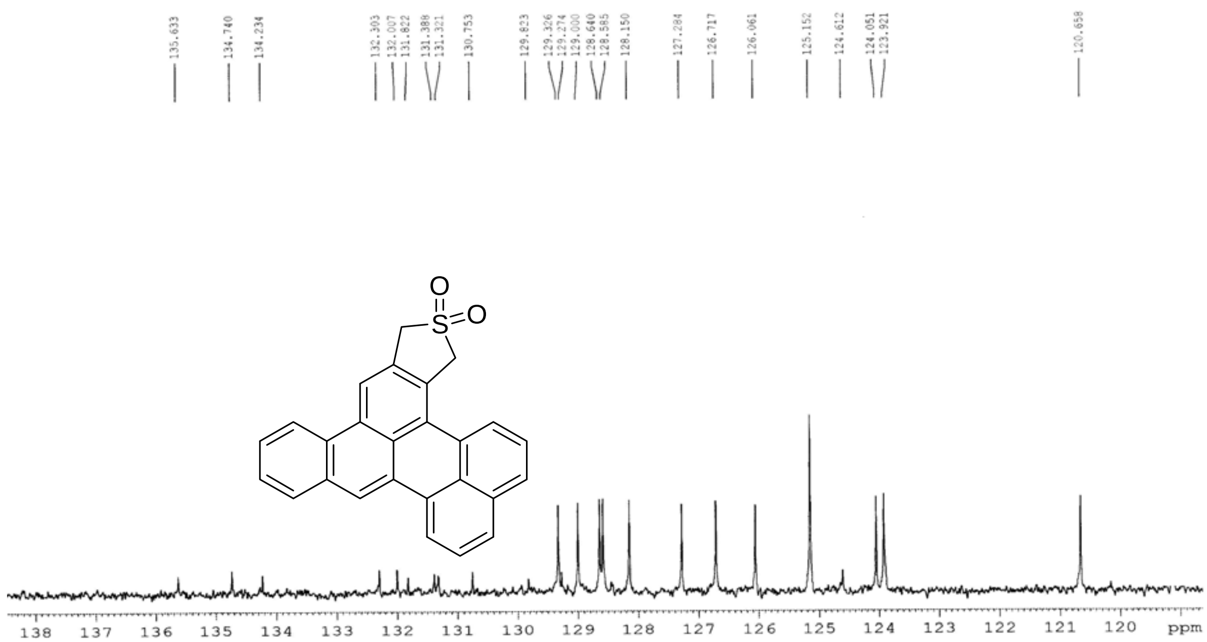
^{1}H NMR (400 MHz) in d_6-Acetone



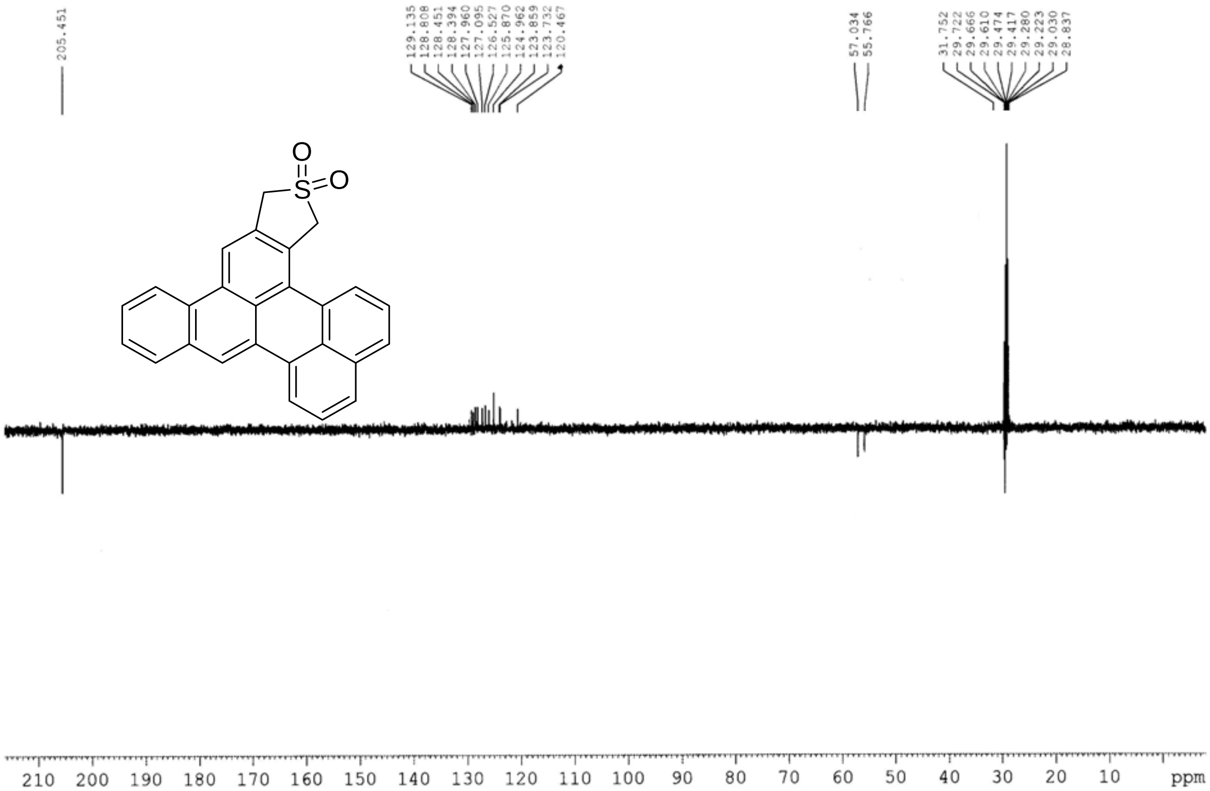
^{1}H NMR (400 MHz) in d_6-Acetone expanded



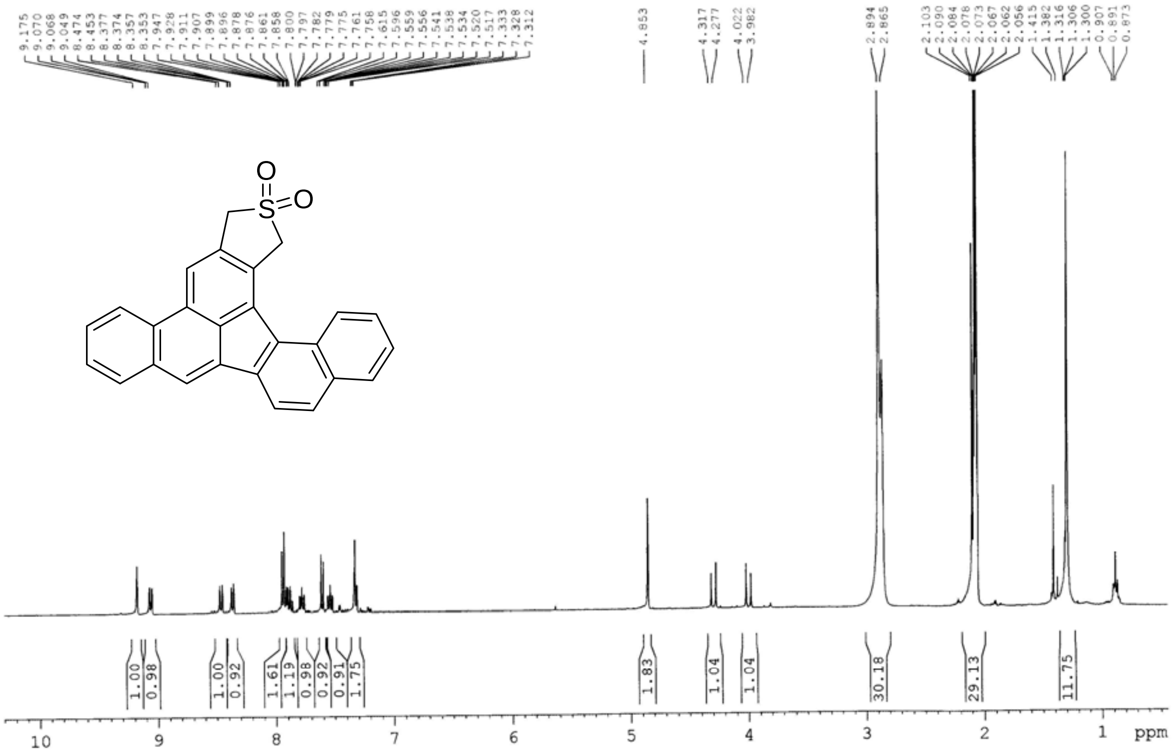
^{13}C NMR (100 MHz) in d_6-Acetone



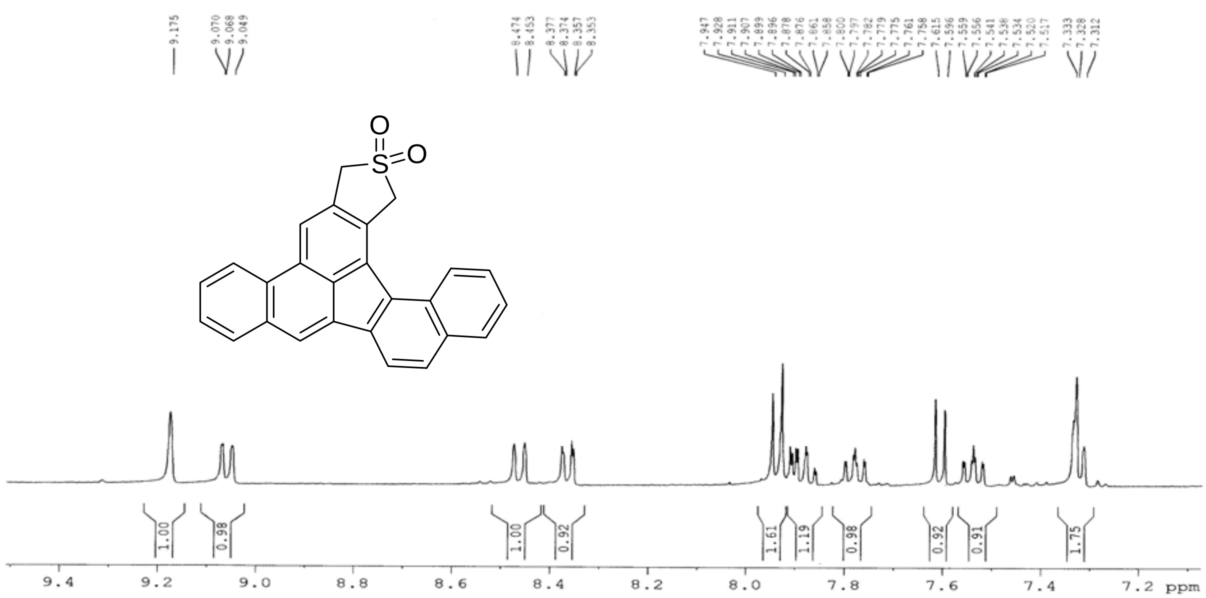
^{13}C NMR (100 MHz) in d_6-Acetone expanded



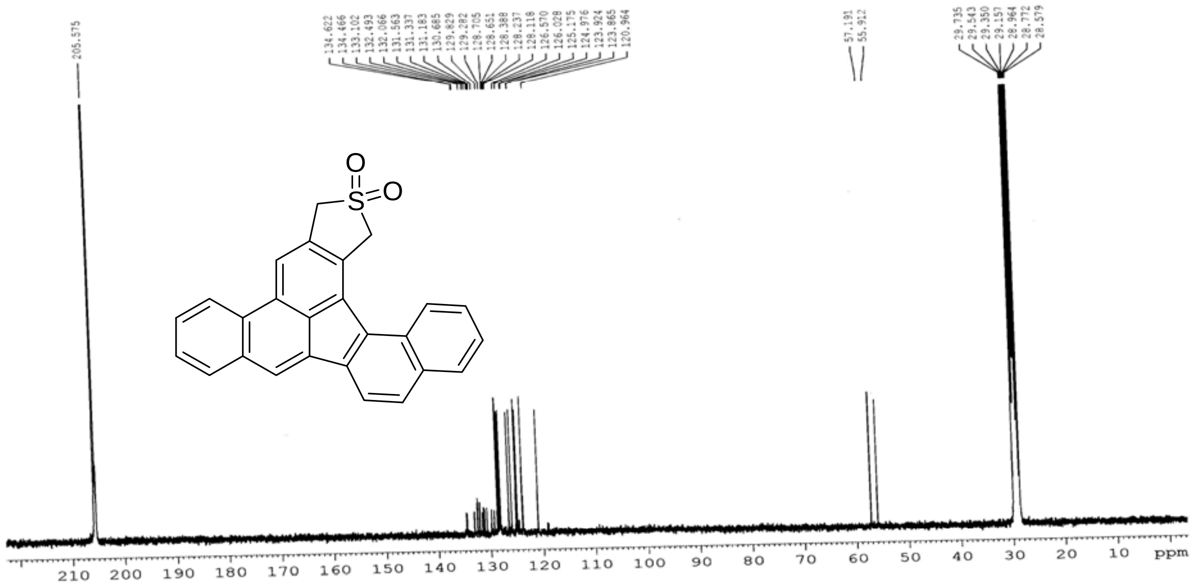
DEPT-135 (100 MHz) in d_6-Acetone



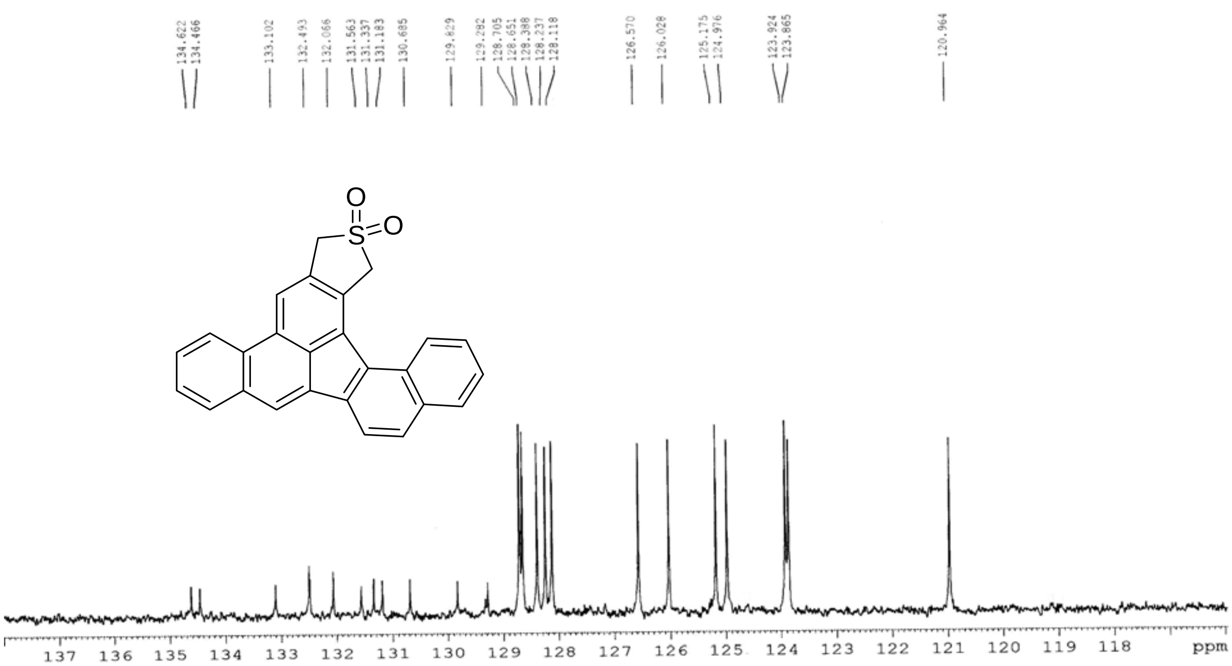
^{1}H NMR (400 MHz) in d$_6$-Acetone



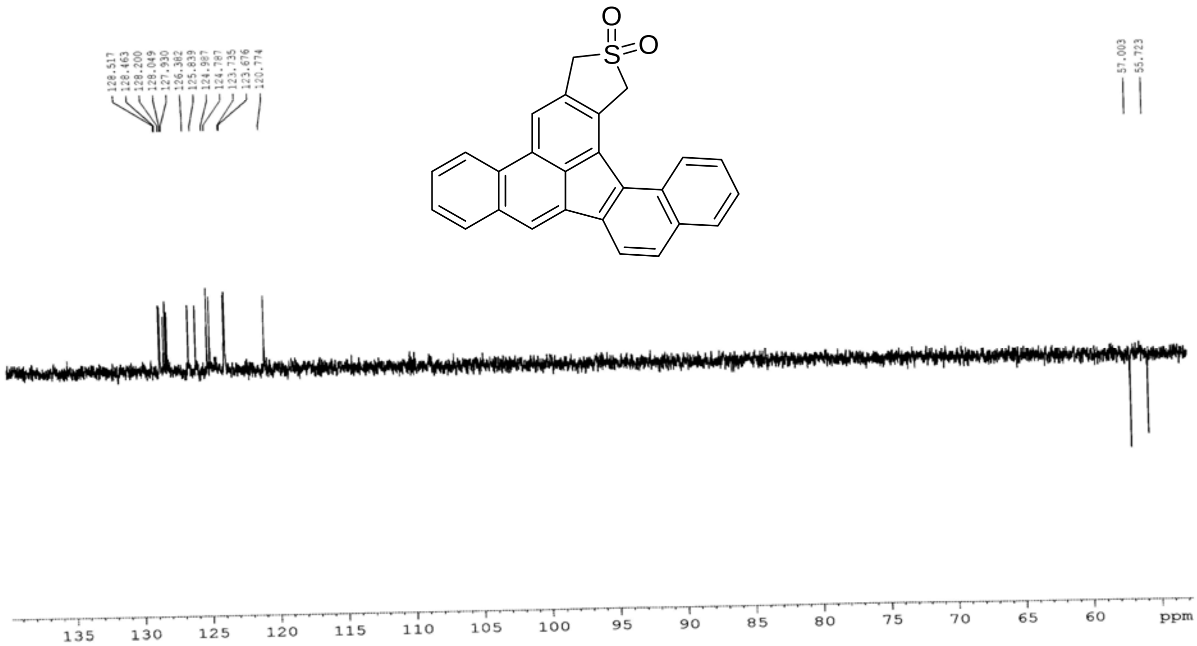
^{1}H NMR (400 MHz) in d$_6$-Acetone expanded



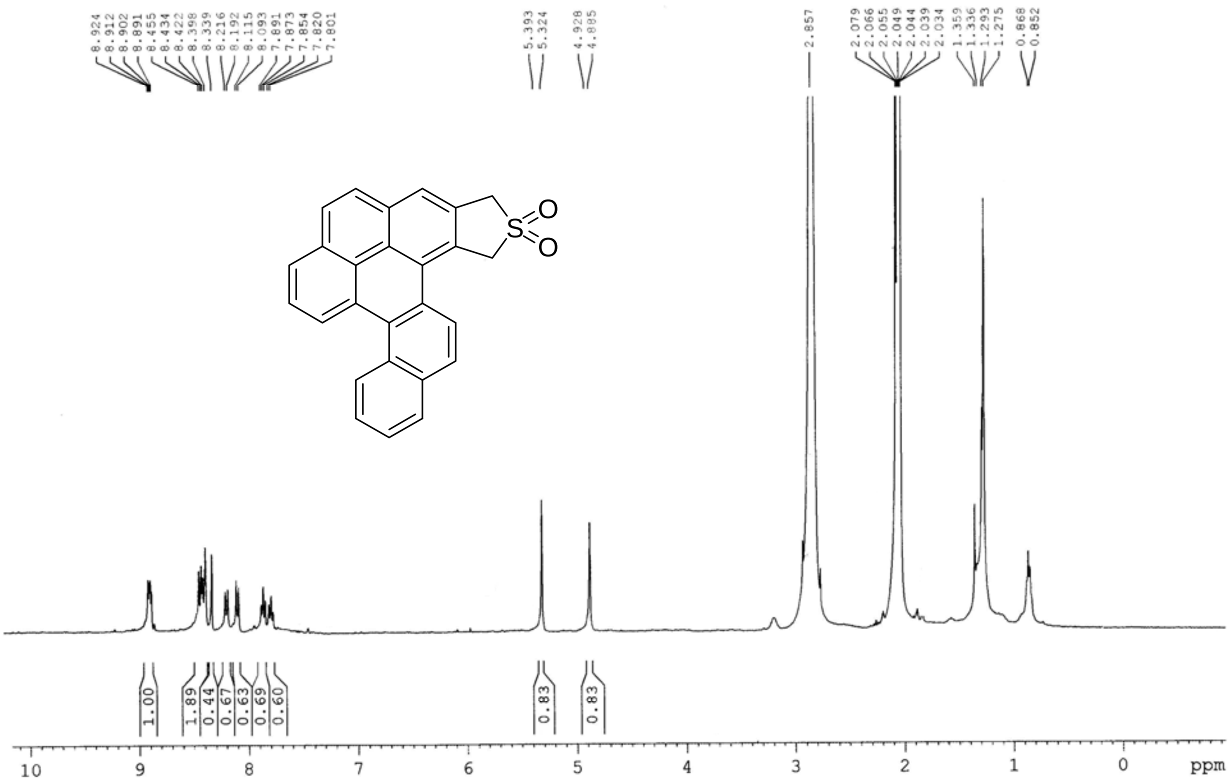
^{13}C NMR (100 MHz)) in d_6-Acetone



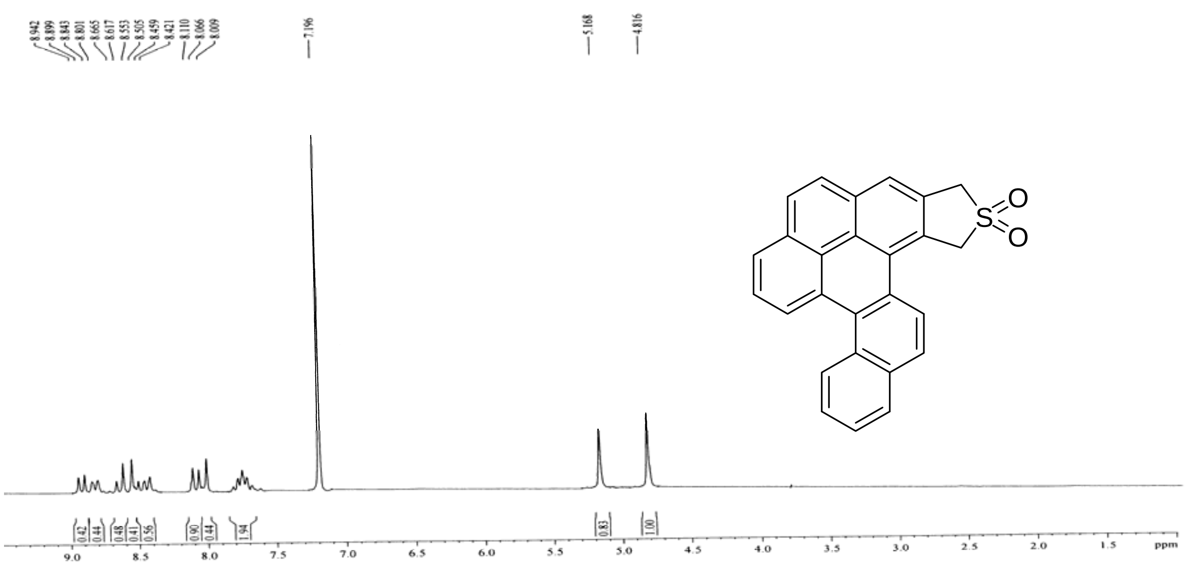
^{13}C NMR (100 MHz) in d_6-Acetone expanded



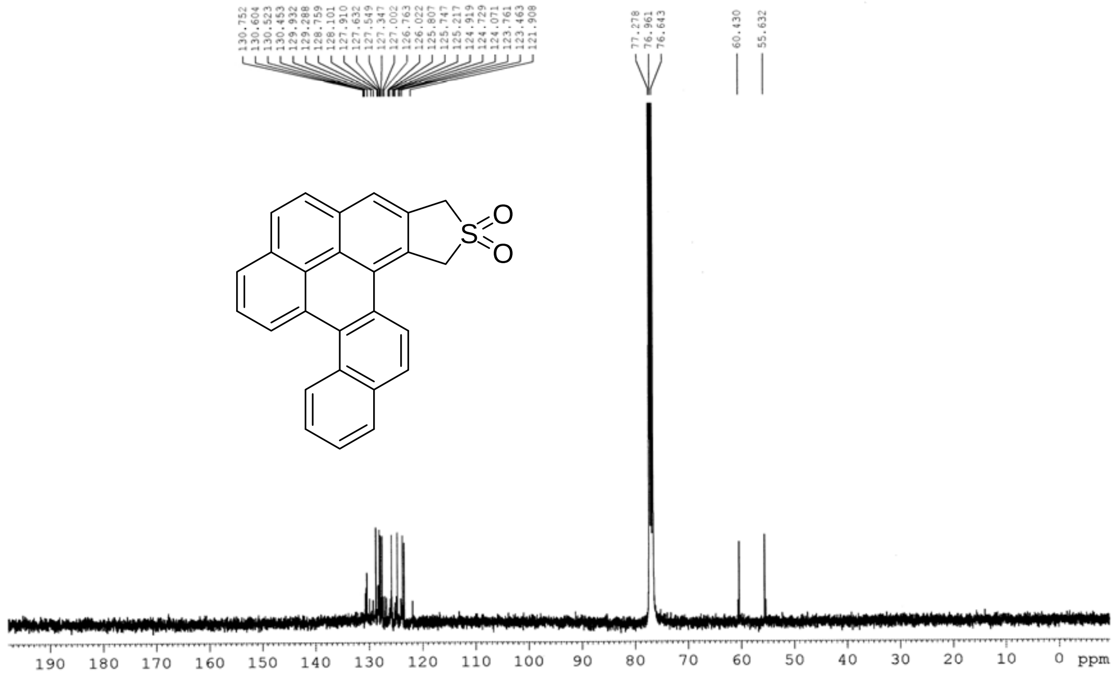
DEPT-135 (100 MHz) in d_6-Acetone expanded



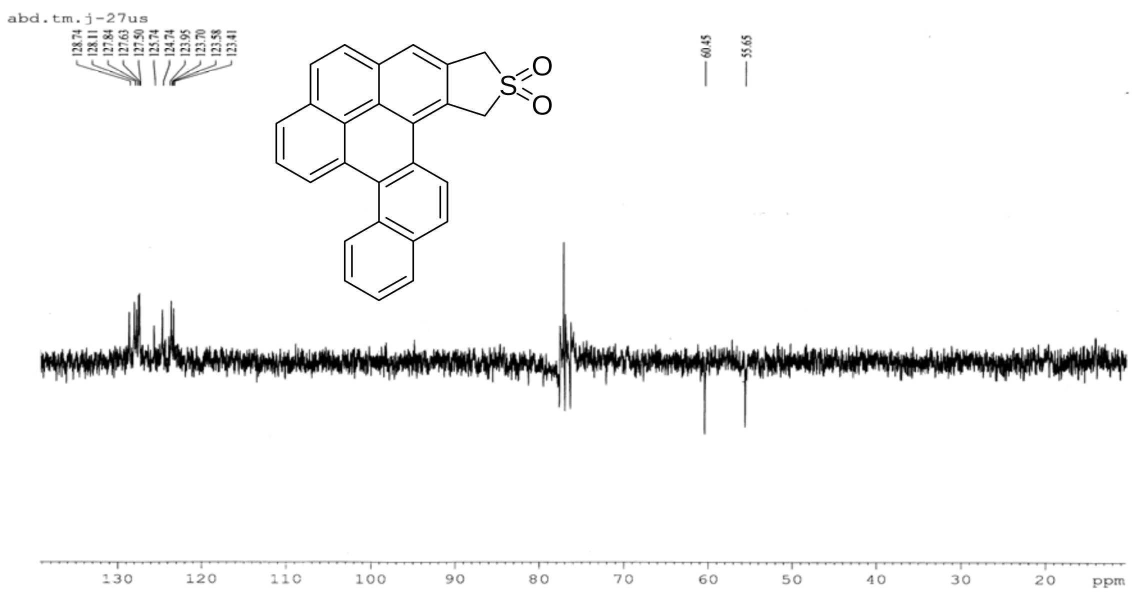
^{1}H NMR (400 MHz) in d_6-Acetone



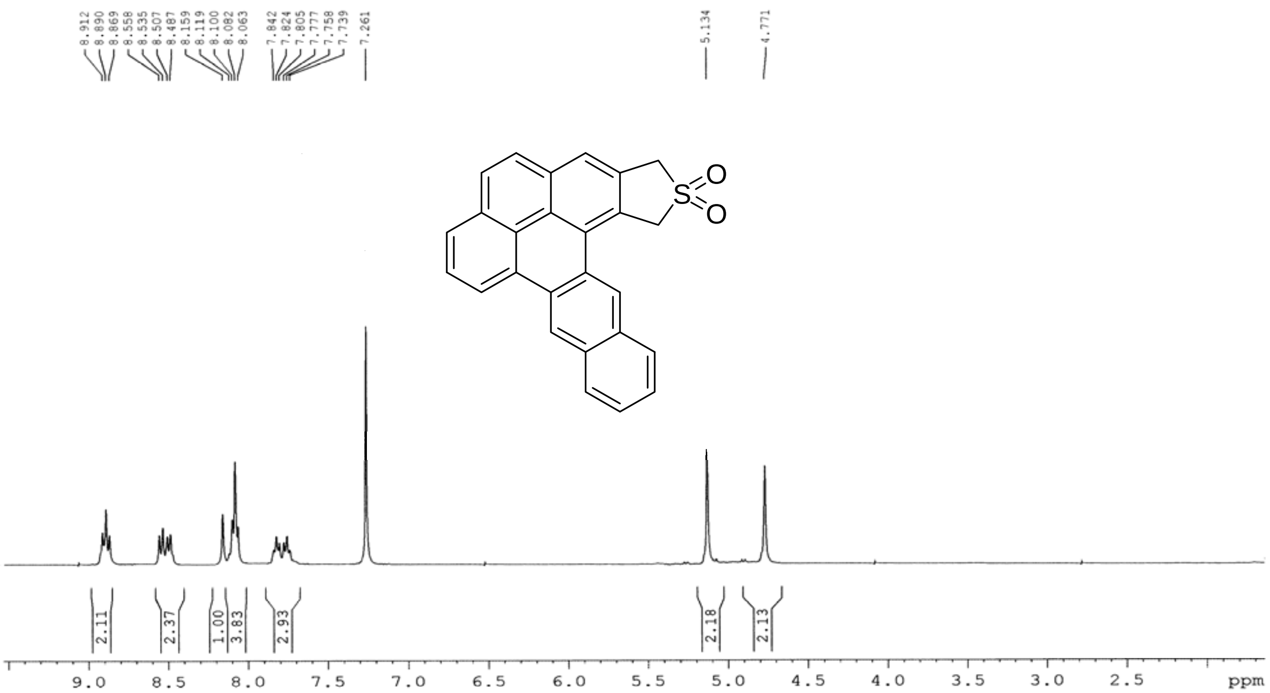
^{1}H NMR (400 MHz)



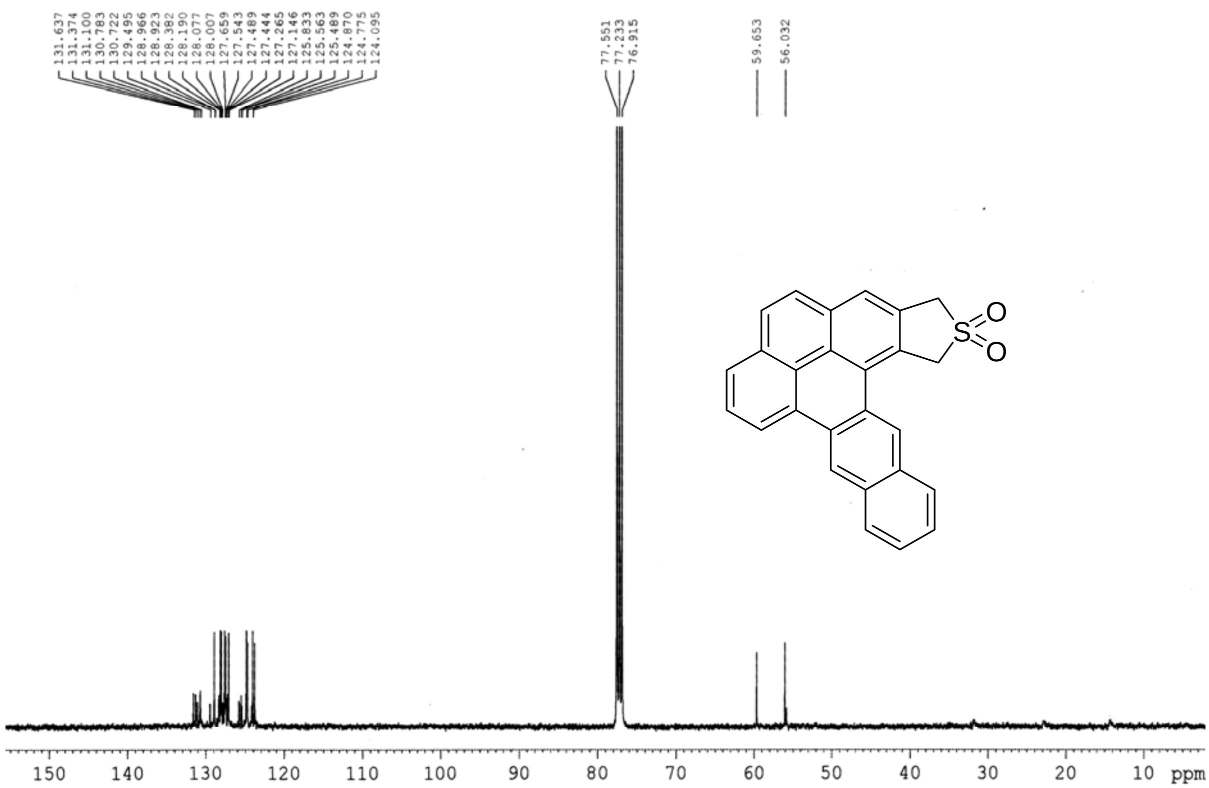
[13]C NMR (100 MHz)



DEPT-135 (50 MHz)



^{1}H NMR (400 MHz)



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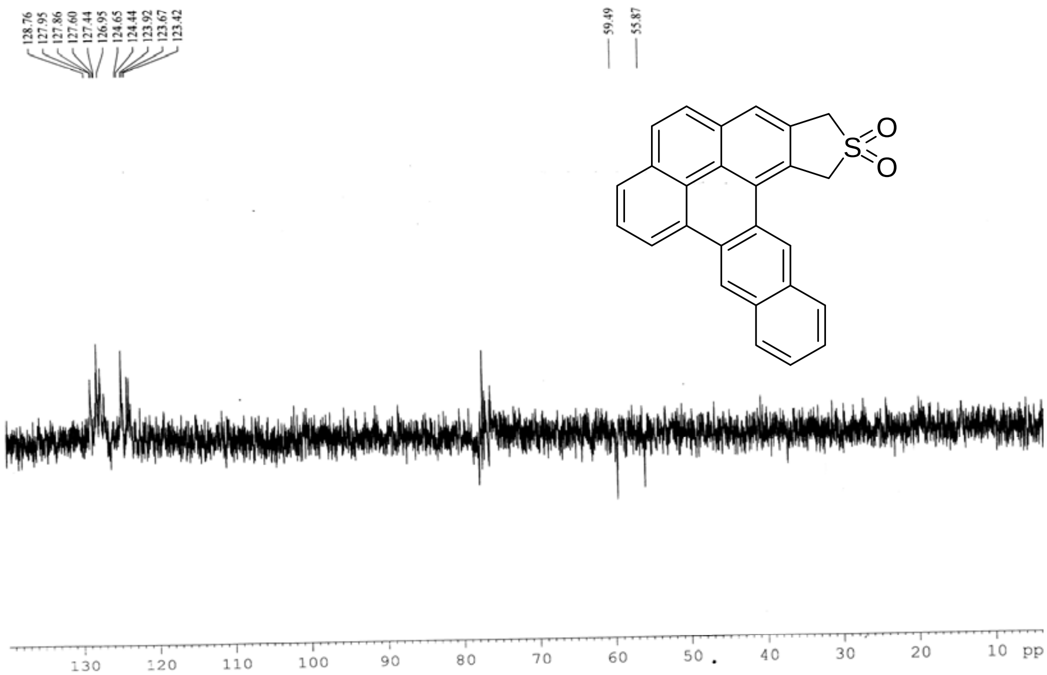
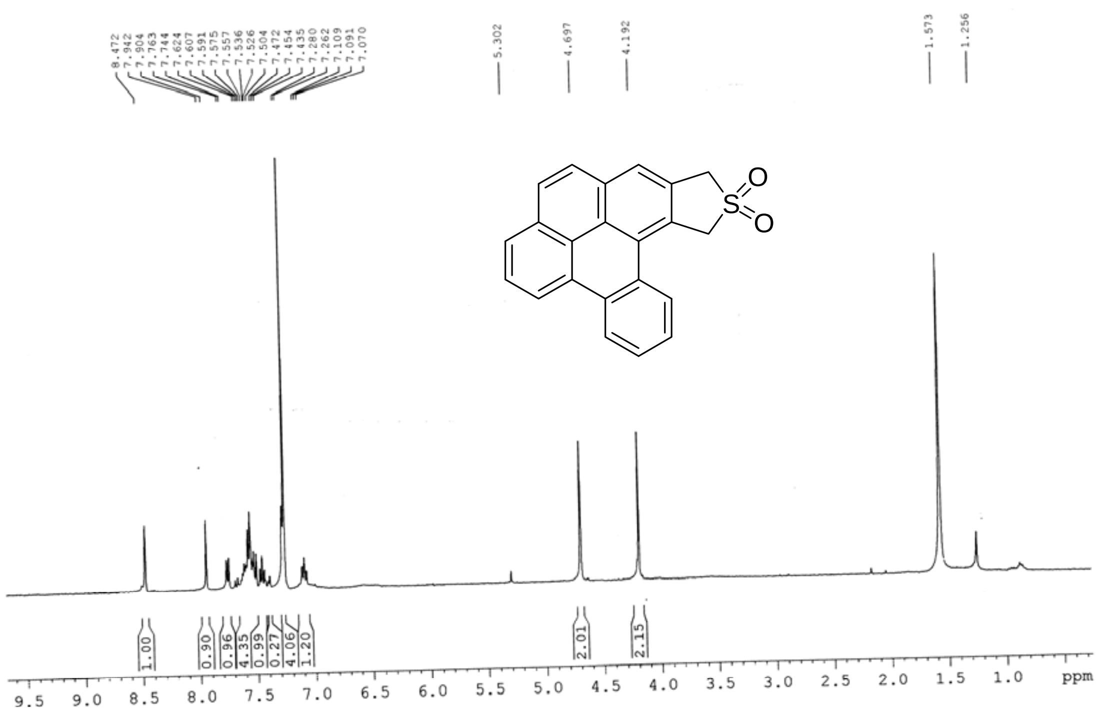
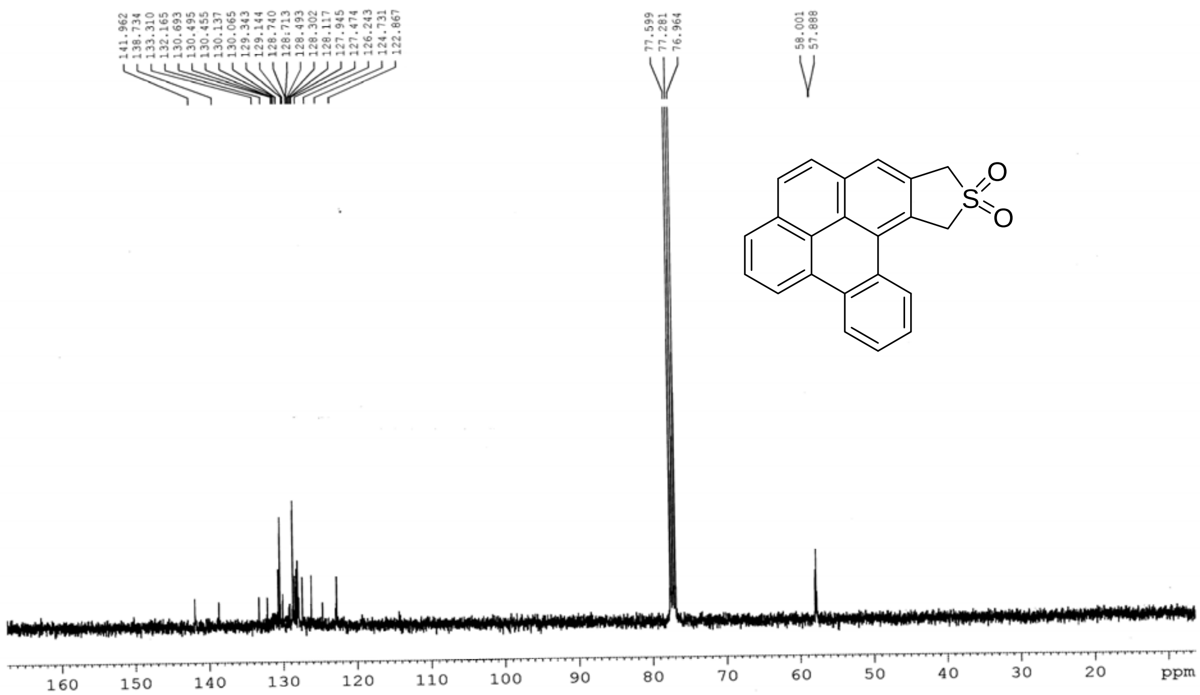


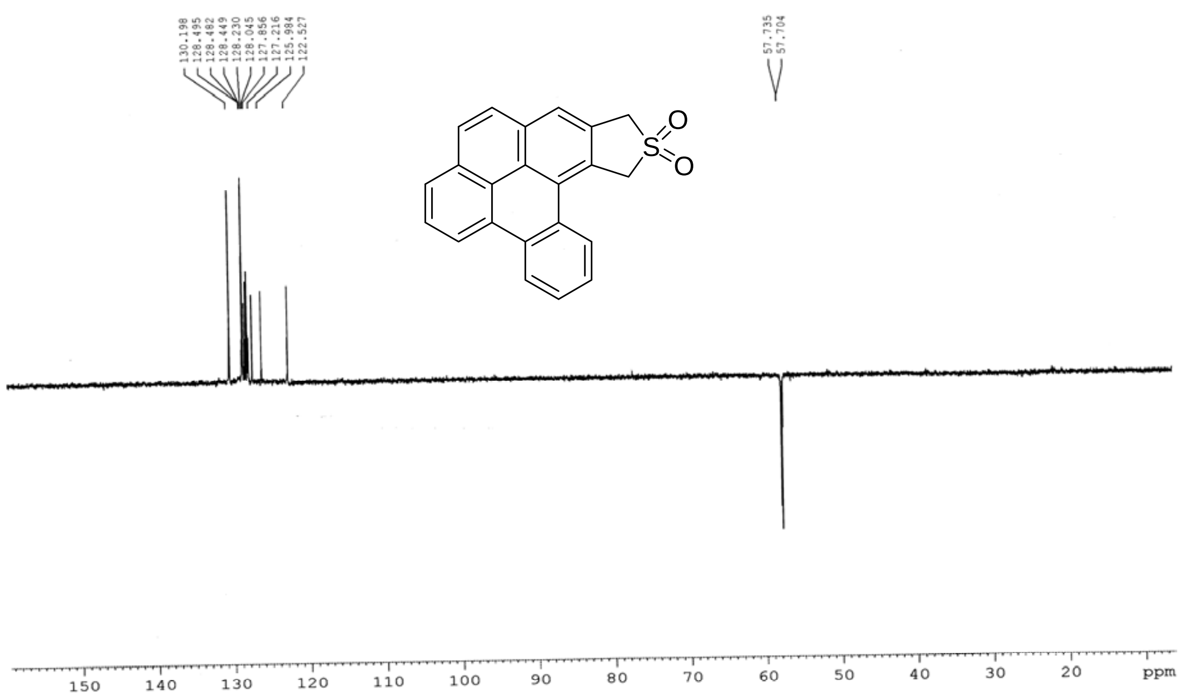
DEPT-135 (50 MHz)



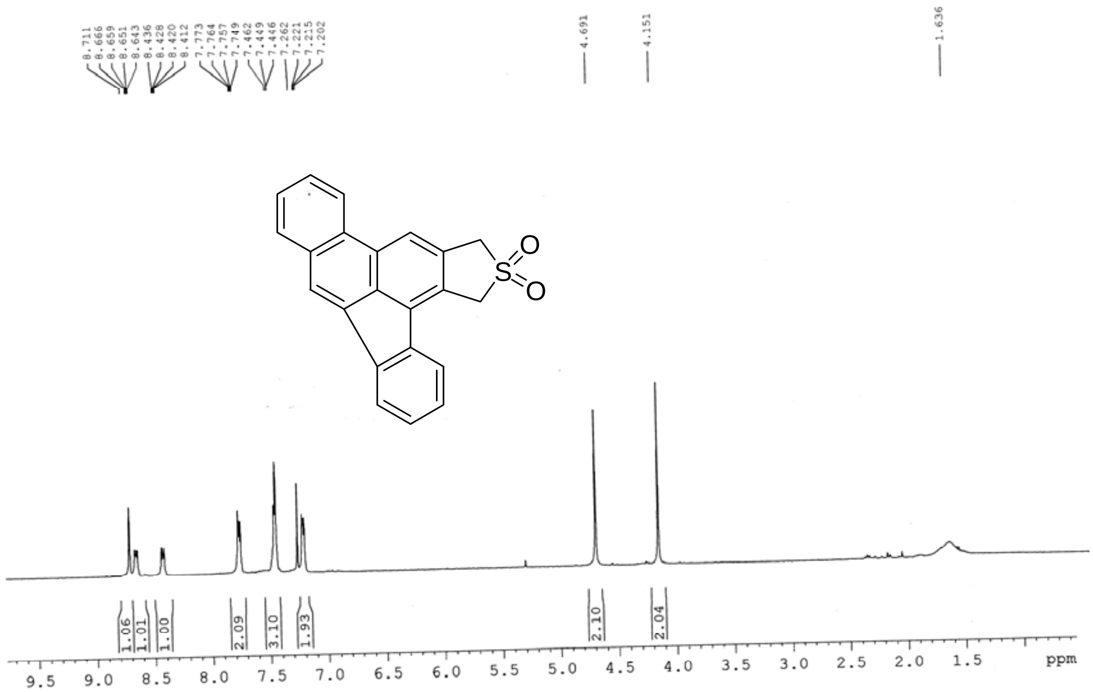
^{1}H NMR (400 MHz)



^{13}C NMR (100 MHz)



DEPT-135 (100 MHz)



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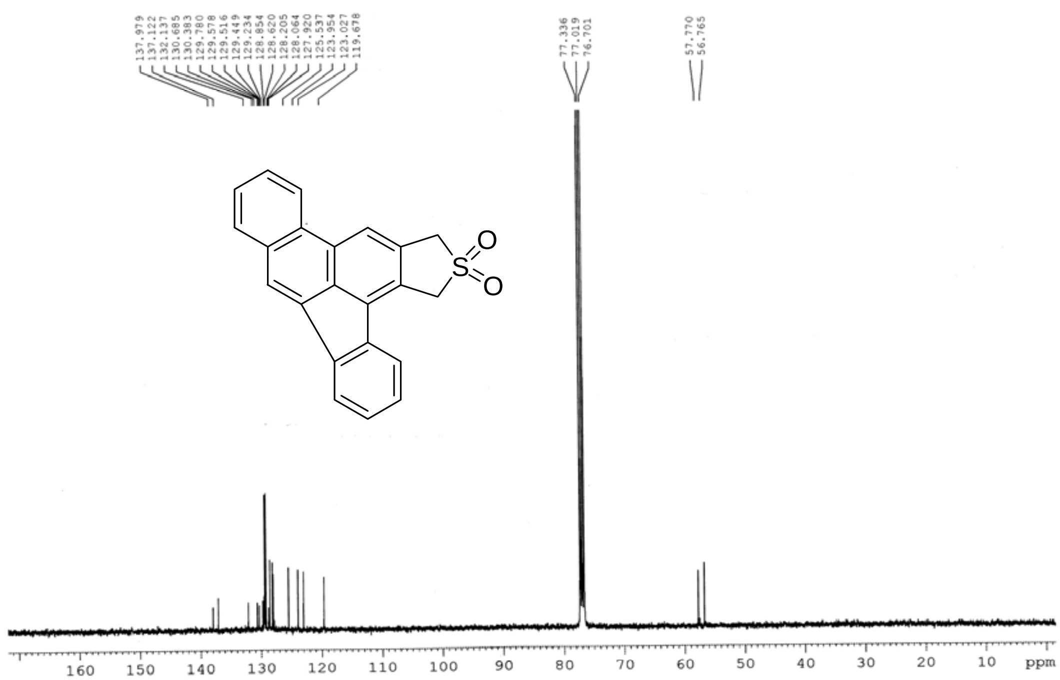
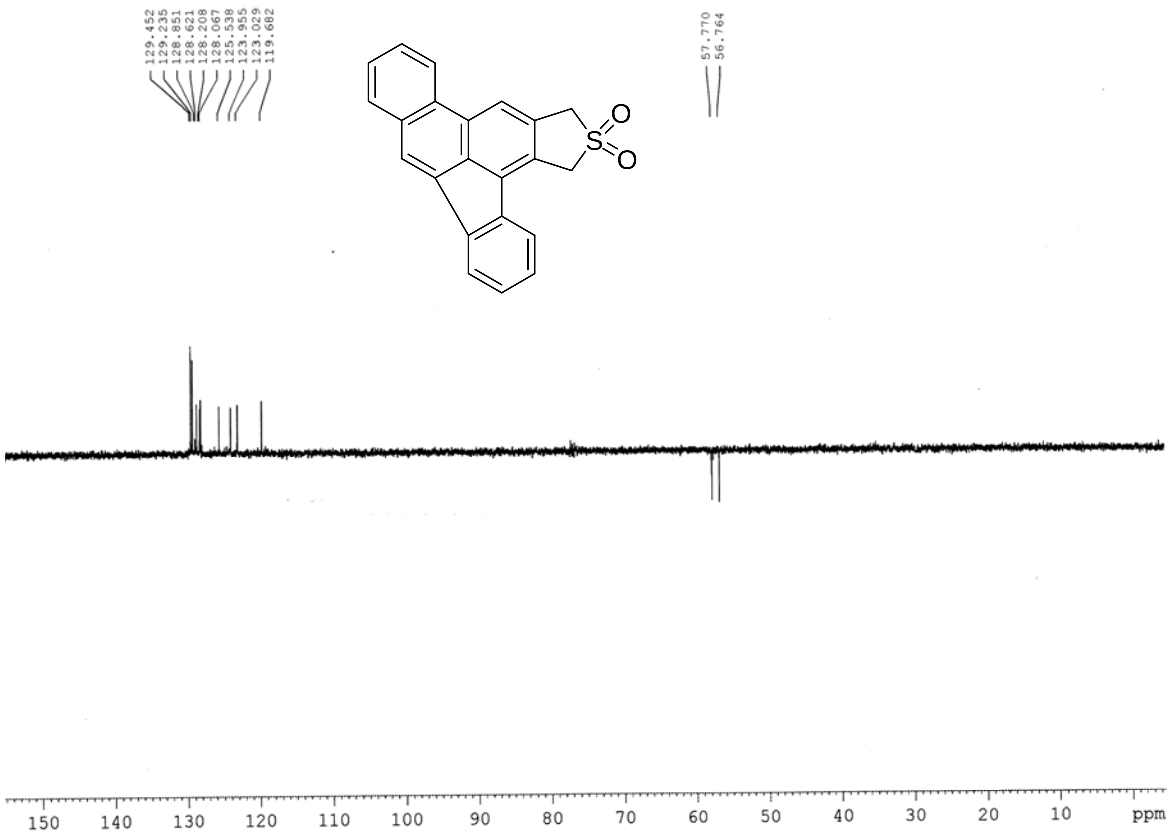
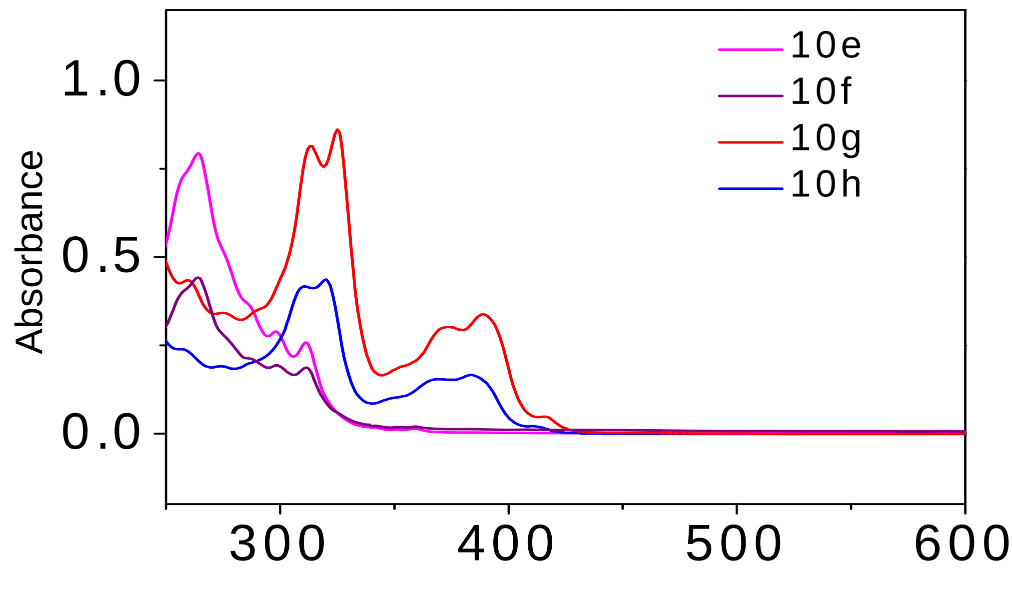
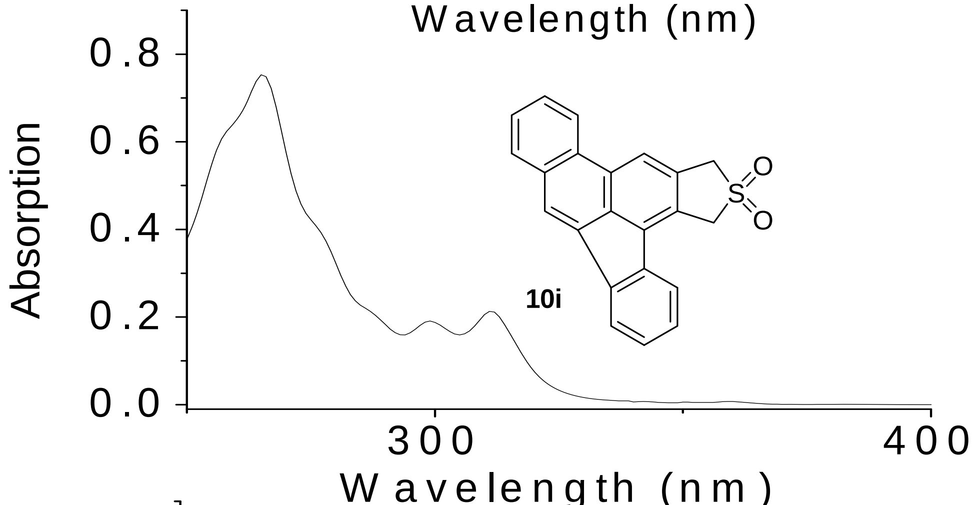


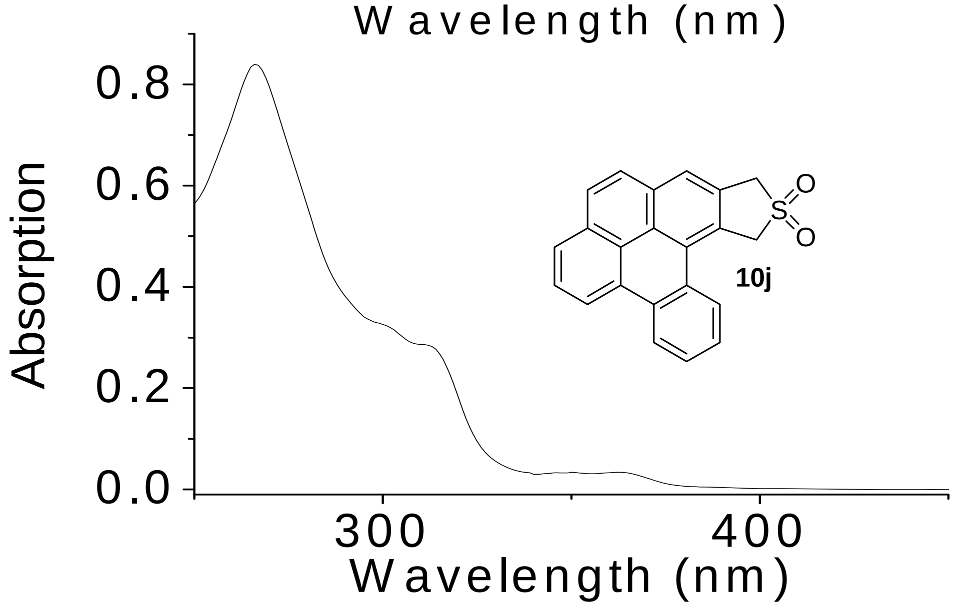
[13]C NMR (100 MHz)



DEPT-135 (100 MHz)


10e
10f
10g
10h
Absorbance
1.0
0.5
0.0
300
400
500
600
Wavelength (nm)


Absorption
0.8
0.6
0.4
0.2
0.0
300
400
W avelength (nm)
10i


Absorption
0.8
0.6
0.4
0.2
0.0
300
400
Wavelength (nm)
10j

Electrochemical data:

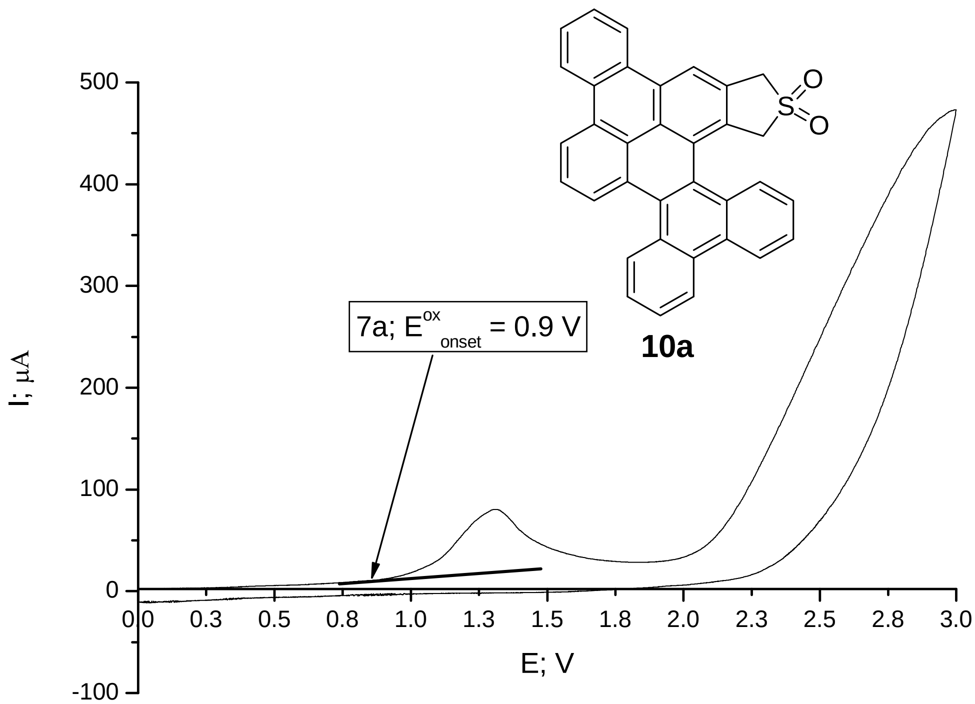


Fig. 1: Cyclic voltammogram of **10a**

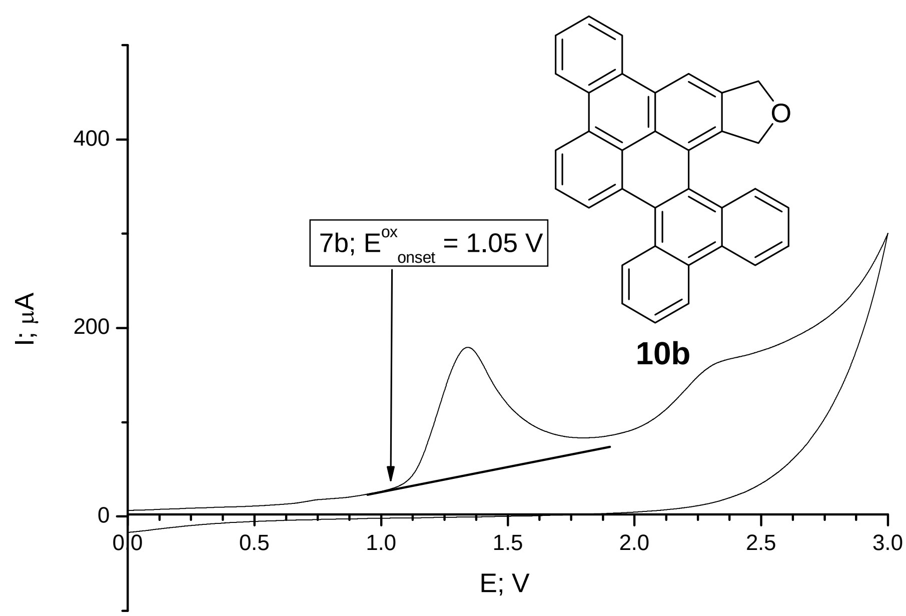


Fig. 2: Cyclic voltammogram of **10b**

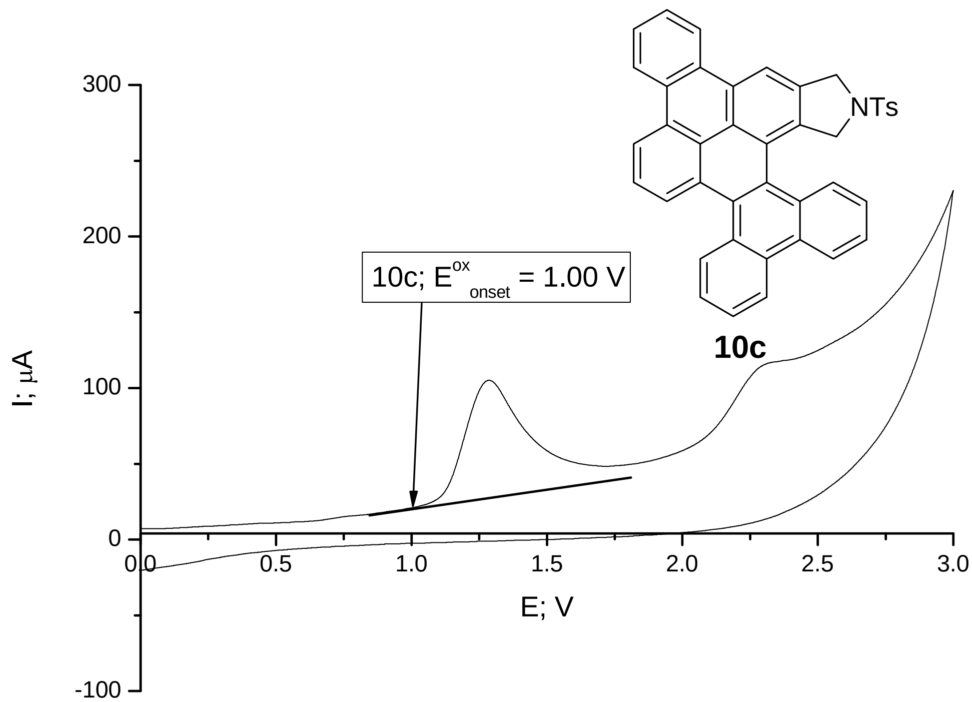


Fig. 3: Cyclic voltammogram of **10c**

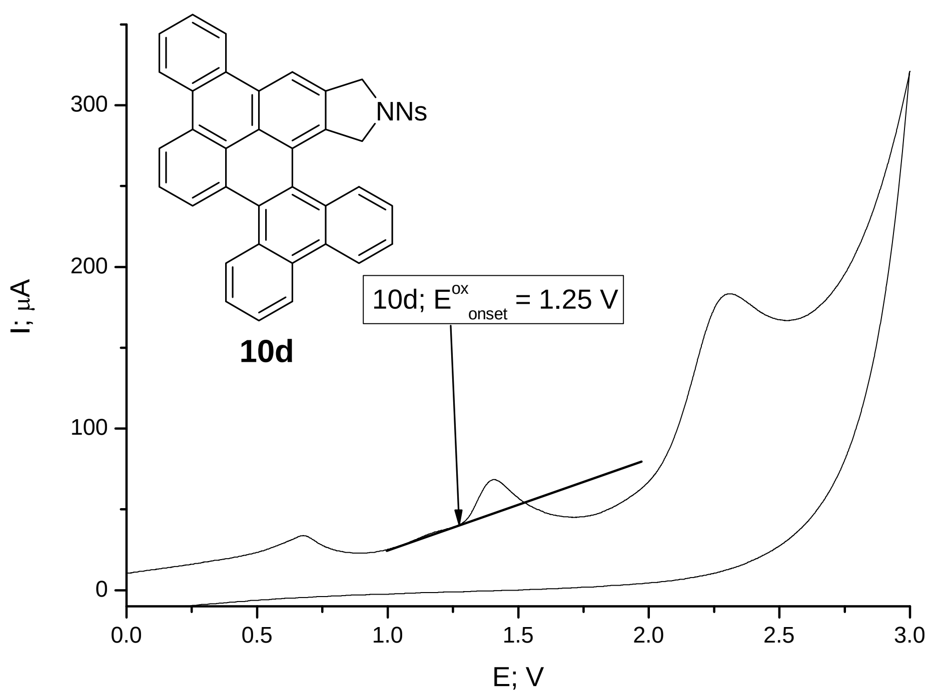


Fig. 4: Cyclic voltammogram of **10d**

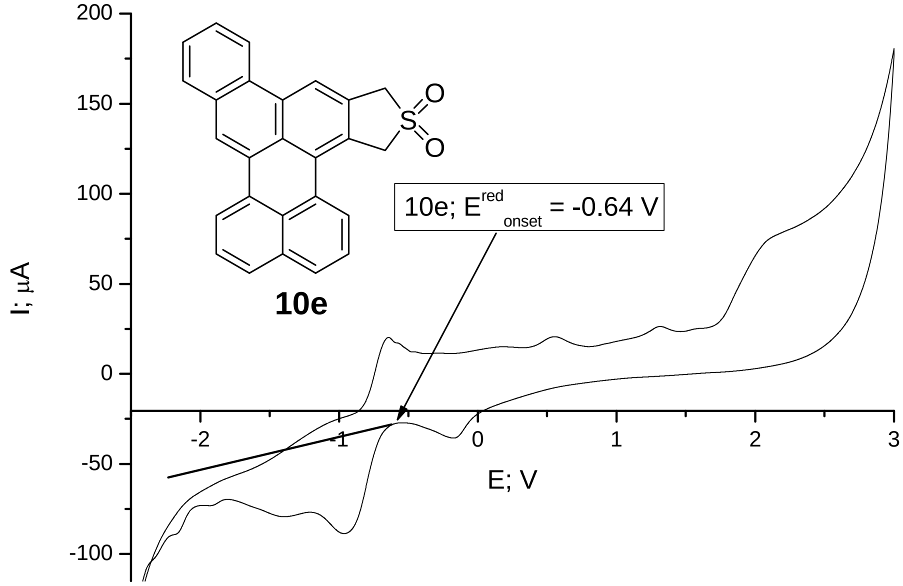


Fig. 5: Cyclic voltammogram of **10e**

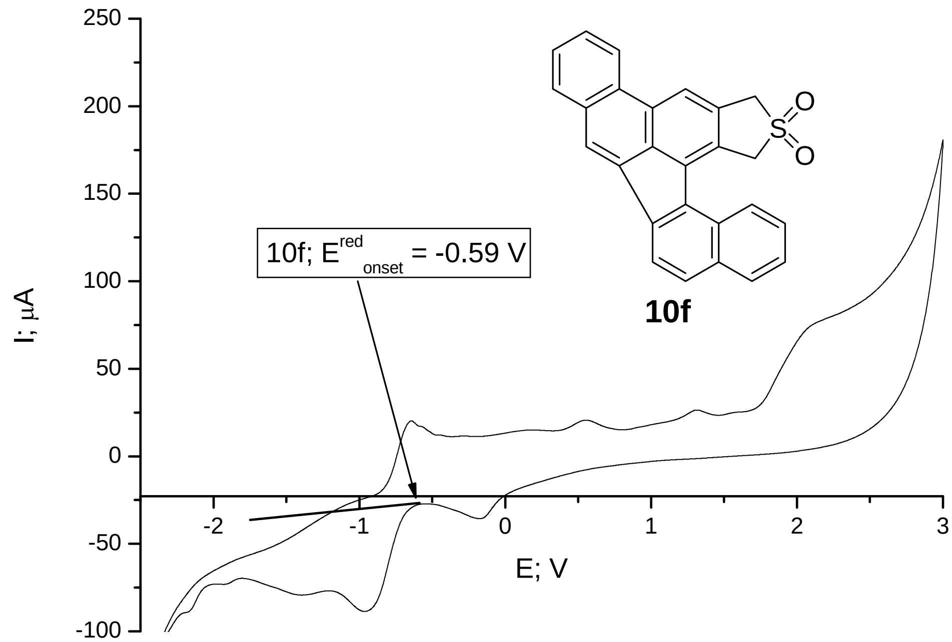


Fig. 6: Cyclic voltammogram of **10f**

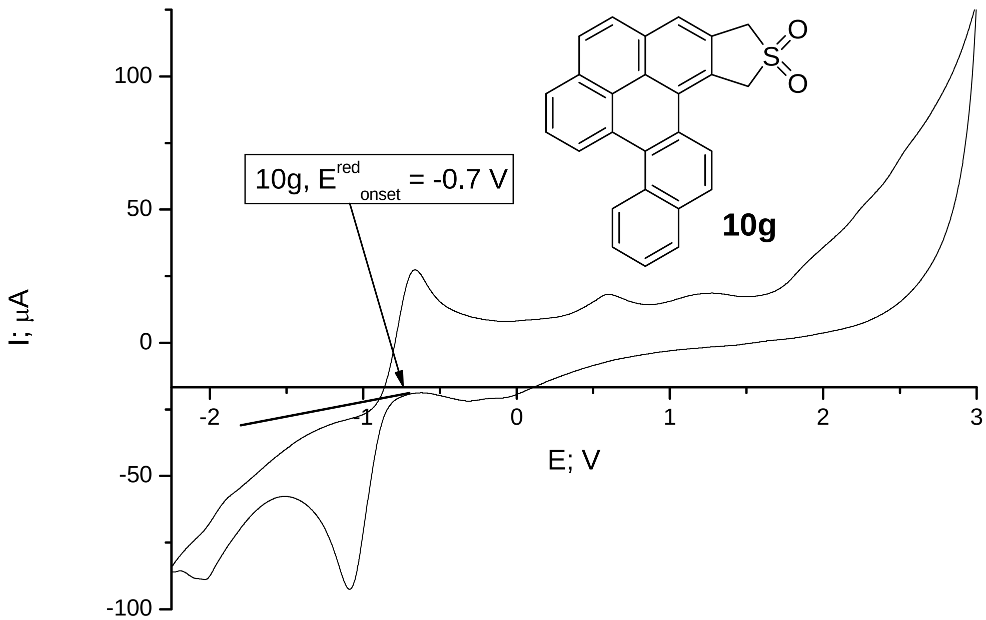


Fig. 7: Cyclic voltammogram of **10g**

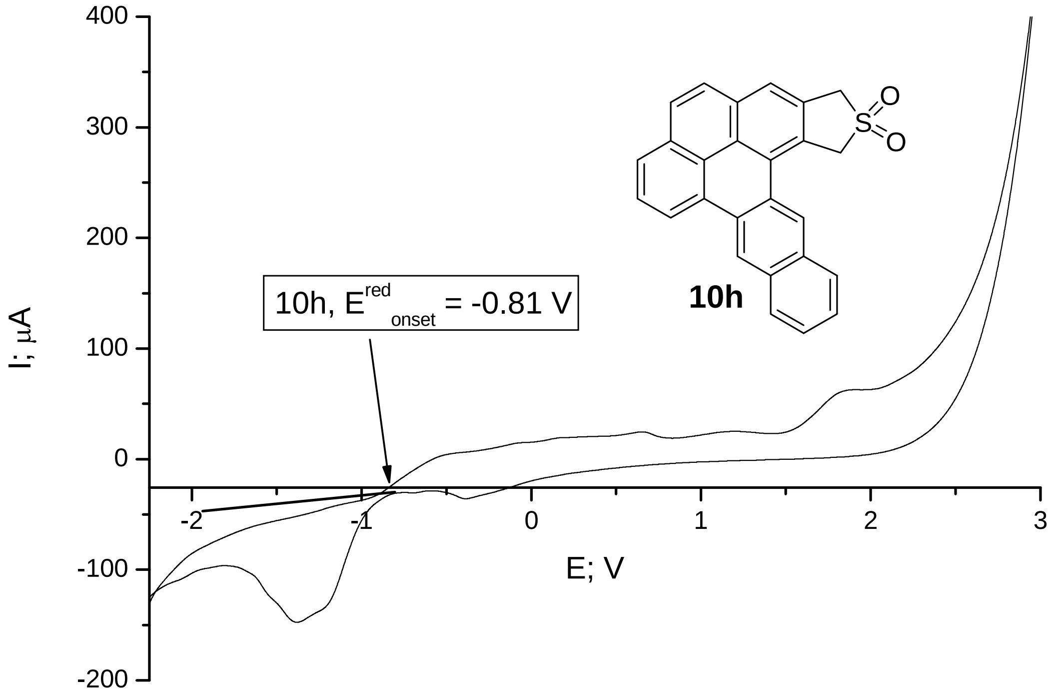


Fig. 8: Cyclic voltammogram of **10h**

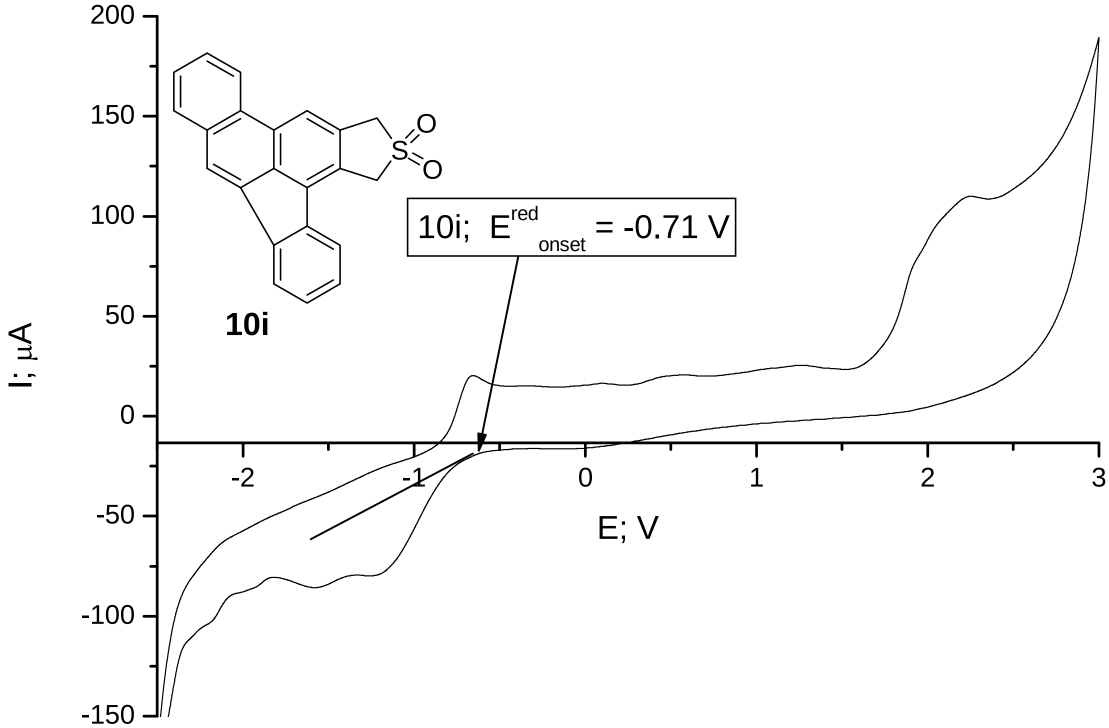


Fig. 9: Cyclic voltammogram of **10i**

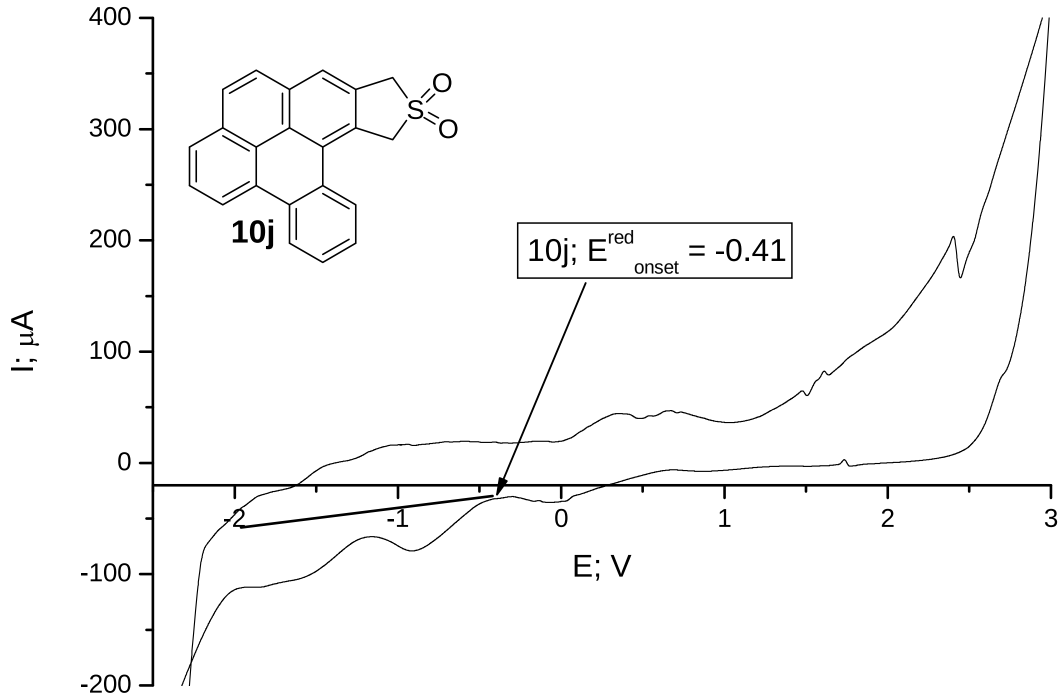


Fig. 10: Cyclic voltammogram of **10j**

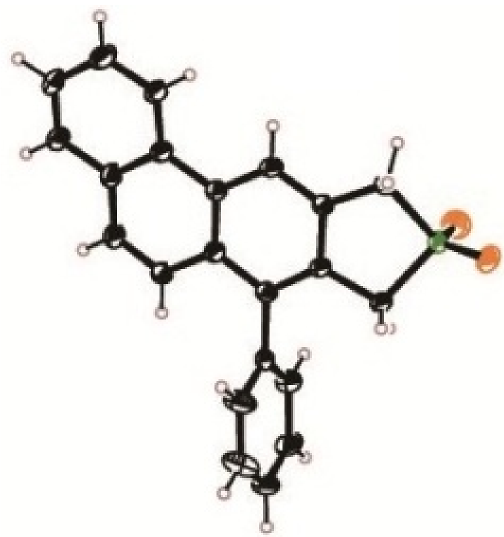


Fig. 11: Crystal structure of **1g**

Computational details:

The HOMA is obtained from the following equation

$$HOMA = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}\left(R_{opt} - R_i\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where n is the number of bonds considered, and α is an empirical constant (for C-C bonds, α = 257.7)((Ref: Jordi Poater, Miquel Solà , Rosario G. Viglione, Riccardo Zanas J. Org. Chem. 2004, 69, 7537-7542) chosen in such a way that HOMA = 0 for model nonaromatic systems and HOMA = 1 for systems having all bonds equal to an optimal value R_{opt}, presumed to be achieved for completely aromatic systems (for C-C bonds, R_{opt} is equal to 1.388 Å) and R_i is the running bond length. The calculated HOMA indices for individual **rings** of each compound are listed in **Table 2**. The HOMA, structural indicator of aromaticity, provides a parallel trend to NICS (in most cases). The trend of aromaticity of individual rings of 10(a-c) are almost similar (both HOMA and NICS indices). In the same way the trend is similar for 10(e-h) compounds with a very few **exceptions**. The HOMA and NICS indices are appeared to be in good agreement with the Clar's sextet structures.

	Ring	Compound									
		10a	**10b**	**10c**	**10d**	**10e**	**10f**	**10g**	**10h**	**10i**	**10j**
HOMA	**A**	**0.909**	**0.906**	**0.908**	**0.908**	**0.872**	**0.856**	**0.843**	**0.866**	**0.952**	**0.850**
	B	**0.245**	**0.245**	**0.237**	**0.237**	**0.498**	**0.518**	**0.557**	**0.528**	**0.666**	**0.486**
	C	**0.853**	**0.838**	**0.852**	**0.851**	**0.793**	**0.840**	**0.804**	**0.802**	**0.942**	**0.050**
	D	**0.842**	**0.850**	**0.844**	**0.841**	**0.809**	**-0.026**	**0.284**	**0.037**	**0.250**	**0.931**
	E	**0.337**	**0.320**	**0.333**	**0.327**	**0.786**	**0.716**	**0.593**	**0.778**	**0.575**	**0.880**
	F	**0.263**	**0.264**	**0.265**	**0.266**		**0.757**	**0.823**	**0.764**		
	G	**0.891**	**0.899**	**0.891**	**0.891**						
	H	**0.898**	**0.889**	**0.900**	**0.900**						
NICS NICS$_{zz}$ **(ppm)**	**A**	**-7.14**	**-6.91**	**-6.99**	**-6.935**	**-7.84**	**-7.85**	**-10.27**	**-9.35**	**-9.653**	**-8.068**
		-7.78	-7.42	-7.40	-7.340	-10.29	-10.38	-16.38	-13.3	-14.665	-11.143
	B	**-0.21**	**-0.18**	**-0.17**	**-0.284**	**-4.43**	**-4.08**	**-4.11**	**-4.48**	**-4.309**	**-4.024**
		16.13	16.11	15.92	16.129	3.10	4.43	2.93	1.87	2.500	5.410
	C	**-8.96**	**-9.25**	**-8.88**	**-8.867**	**-6.62**	**-6.92**	**-10.44**	**-9.81**	**-10.280**	**4.660**
		-12.05	-11.39	-11.34	-11.573	-3.59	-3.69	-14.38	-12.7	-13.998	37.087
	D	**-8.91**	**-8.84**	**-9.28**	**-9.230**	**-6.74**	**5.00**	**-0.68**	**1.89**	**0.262**	**-5.589**
		-11.25	-11.66	-11.03	-11.176	-5.17	37.33	13.42	21.5	15.664	-4.008
	E	**-0.82**	**-0.77**	**-0.89**	**-0.870**	**-6.29**	**-6.21**	**-5.92**	**-8.88**	**-6.700**	**-7.454**
		11.87	13.82	13.54	13.509	-4.01	-3.04	-2.80	-10.0	-6.098	-5.088
	F	**-1.96**	**-2.11**	**-1.946**	**-1.874**		**-7.77**	**-8.22**	**-7.77**		
		7.19	8.51	9.50	9.426		-9.88	-11.12	-9.99		
	G	**-7.75**	**-8.32**	**-7.54**	**-7.393**						
		-8.47	-10.30	-8.32	-8.043						
	H	**-7.87**	**-7.51**	**-8.01**	**-7.983**						
		-8.43	-8.21	-9.08	-8.822						

Table 2: HOMA and NICS values for the PAHs studied at B3LYP/6-311+G (d, p) level

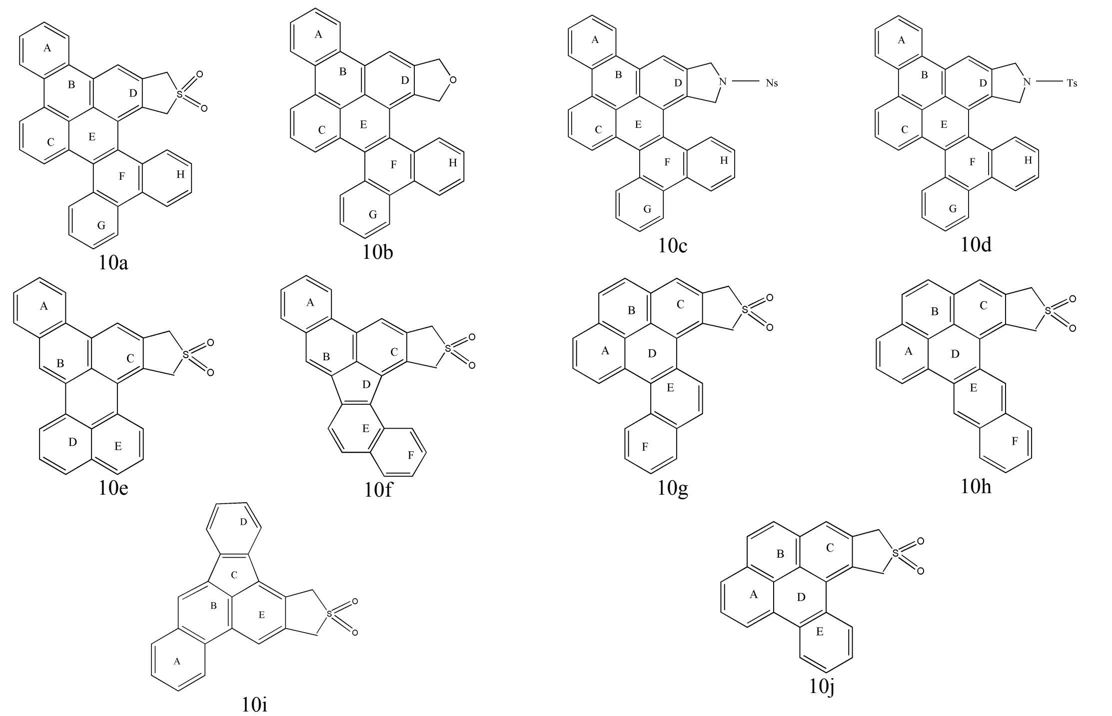
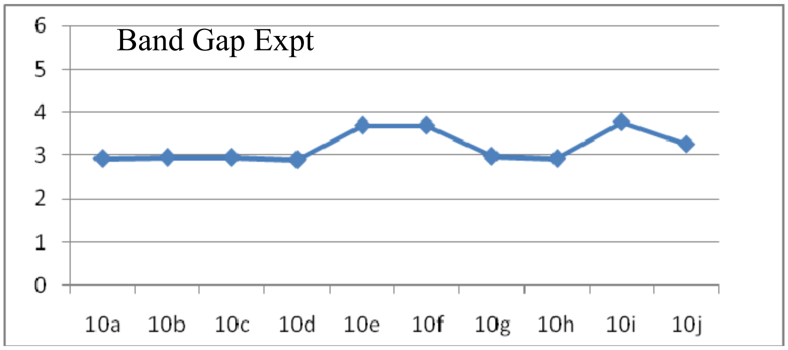


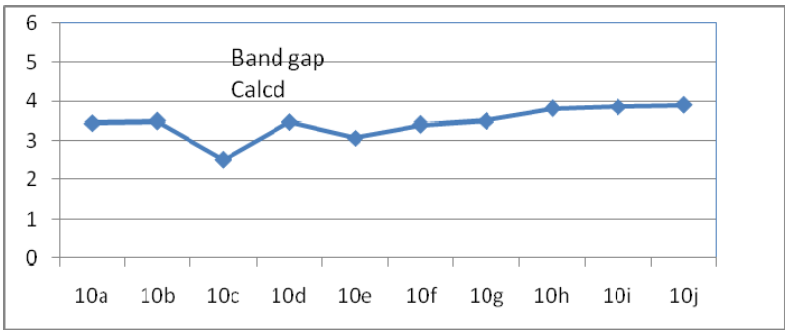
Fig. 12: Structures with individual rings labeled

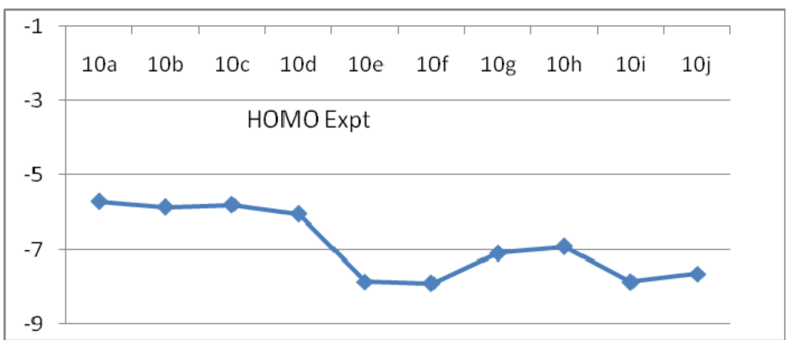
Compd	Optical band gap (1240/λ_{edge}) eV	Theoretical band gap (eV)	HOMO **energy** (Expt) (eV)	HOMO **energy** (Calcd) (eV)	LUMO **energy** (Expt) (eV)	LUMO **energy** Calcd (eV)
10a	2.92	3.455	-5.700	-5.827	-2.780	-2.373
10b	2.95	3.492	-5.850	-5.579	-2.900	-2.087
10c	2.95	2.510	-5.800	-5.820	-2.850	-3.310
10d	2.90	3.483	-6.050	-5.664	-3.150	-2.181
10e	3.70	3.076	-7.86	-5.676	-4.160	-2.601
10f	3.70	3.411	-7.91	-6.075	-4.210	-2.664
10g	2.98	3.505	-7.08	-5.872	-4.100	-2.368
10h	2.92	3.814	-6.91	-6.035	-3.990	-2.221
10i	3.78	3.860	-7.87	-6.385	-4.090	-2.525
10j	3.26	3.896	-7.65	-6.111	-4.390	-2.215
Pentacene			-4.96		-3.0	
Tetracene			-5.4		-3.0	

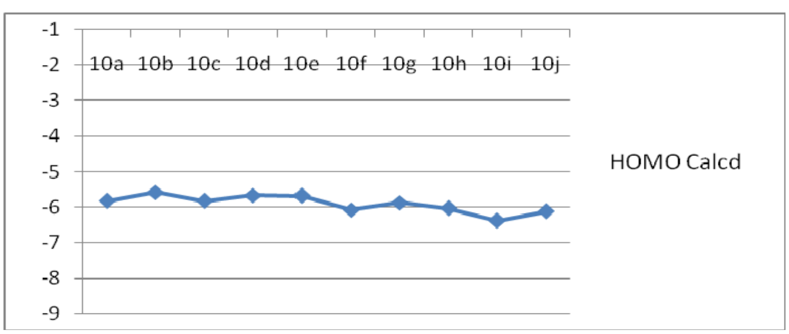
Table 3: Experimental and Calculated Band gap and HOMO-LUMO Energy Values

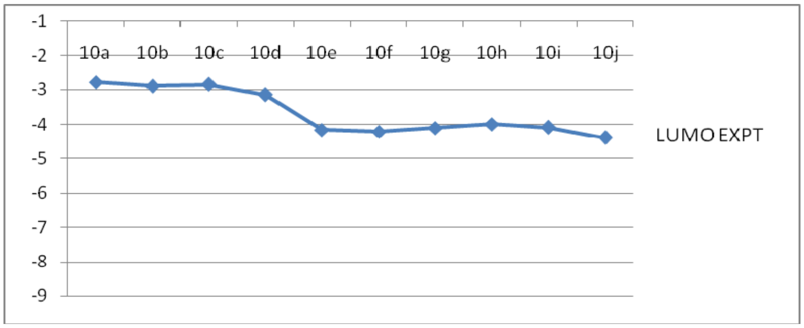
Trend in Band gap and HOMO-LUMO Energies (Experimental and Calculated)







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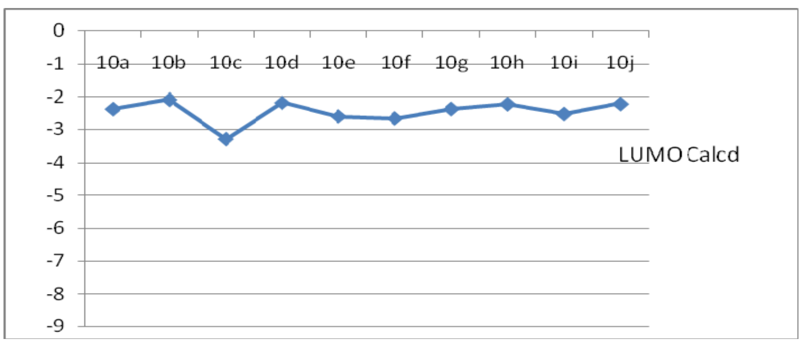
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