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Synthesis and Complexation Study of New ExTTF-Based Hosts for Fullerenes

Supporting Information

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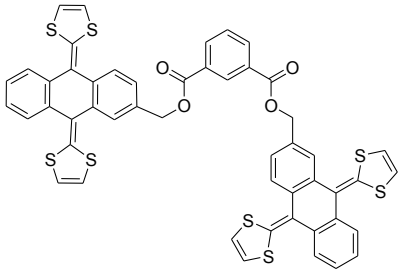
General

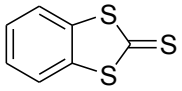
All solvents (ACS grade) were distilled and put through a Vaccum Atmosphere Company (CA, USA) solvent purification system. All the reagents were purchased from Sigma Aldrich Co., TCI America or Oakwood Products and used as received. All reactions were carried out under an atmosphere of argon with freshly distilled solvents, unless otherwise noted. Microwave heating was performed in the single-mode microwave cavity of a Monowave 300 (Anton Paar Co.), and all microwave-irradiated reactions were conducted in a heavy-walled glass vials sealed with Teflon septa. Silica gel (SiliaFlash ® P-60) was used for column chromatography. NMR spectra were recorded at 25 °C on Brucker 400 and 500 MHz instruments and calibrated with tetramethylsilane (TMS) as an internal reference. Mass spectra were performed by the Mass Spectrometry Facilities at Laval University.

Synthesis and characterization of organic compounds



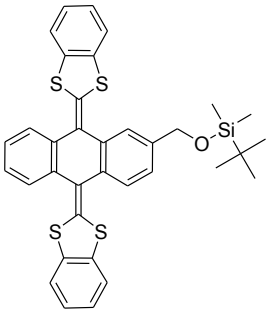
bis((9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methyl) isophthalate 1.

Compounds **1** was prepared according to previously reported synthetic procedures in 84% yield ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 8.86 (m, 1H), 7.79 (m, 2H), 7.68 (s, 1H), 7.68-7.63 (m, 5H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.31 (m, 2H), 7.27-7.24 (m, 6H), 5.41 (d, *J* = 3.8 Hz, 4H), 6.24 (s, 4H), 6.16 (d, *J* = 6.8 Hz, 4H). ^{13}C NMR: 165.5, 135.6, 135.1, 135.0, 135.0, 134.2, 133.8, 132.7, 131.1, 130.6, 128.7, 126.3, 125.9, 125.8, 125.72, 125.60, 125.2, 123.21, 123.1, 120.9, 66.7. *m/z* $[M+H]^+$ calcd for $C_{50}H_{31}O_4S_8$ 950.9983 found 950.9981. (Fernández, G.; Pérez, E. M.; Sánchez, L.; Martín, N. *Angew. Chem. Int. Ed.* **2008**, *47*, 1094.).



Benzo[d][1,3]dithiole-2-thione 7

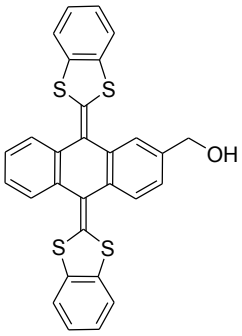
1,2 Benzenedithiol (3.7 g, 26 mmol) was suspended in dry pyridine (100 mL) and carbon disulfide (20 mL) was added over a period of 5 minutes and stirred for 4 hours at room temperature. Solvent was removed under reduced pressure and the crude material purified by precipitation in hexanes, dried under high vacuum to yield the desired product **1** as a yellow solid (3.7g, 77%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.41-7.37 (m, 2H), 7.48 (m, 2H). ^{13}C NMR: 212.2, 141.3, 127.6, 122.0. (Richter, A. M.; Beye, N.; and Fanghänel, E., *Synthesis* 1990, **1990**, 1149-1151).



((9,10-di(benzo[d][1,3]dithiol-2-ylidene)-9,10-dihydroanthracen-7-yl)methoxy)(tert-butyl)dimethylsilane 10

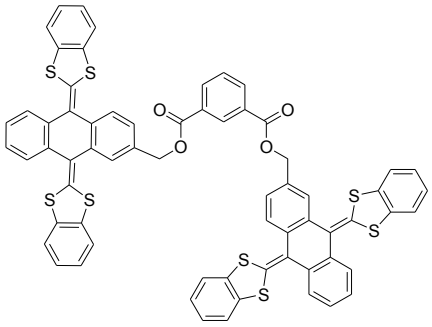
To a solution of dimethyl 1,3-dithiol-2-yl-phosphonate (4.4 mmol) in dry THF (30 ml) at - 78 °C and under argon atmosphere, *n*-BuLi (1.6 M, 12.6 mmol) was added. After 0.5 h, 2-(*tert*-butyldimethylsilanyloxymethyl)-anthraquinone (3.00 g, 11.4 mmol) suspended in dry THF (15 ml) was added with a syringe into the solution of the phosphonate carbanion. The mixture was stirred for 1 h at -78 °C then allowed to warm to room temperature before it was left to stand overnight. The THF was evaporated under reduced pressure, water (75 ml) was added and the residue extracted with CH_2CI_2 (3 X 50 ml). The combined organic layers were dried ($MgSO_4$),

filtered and the solvent removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel with 10% EtOAc/hexanes to yield the desired product **10** as a yellow solid (75%, 2.1 g).^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.78-7.72 (m, 3H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.39-7.34 (m, 2H), 7.32-7.28 (m, 1H), 7.19 (m, 4H), 7.09-7.03 (m, 4H), 4.92-4.78 (m, 2H), 1.03-0.99 (s, 9H), 0.21-0.15 (s, 6H). ^{13}C NMR: 140.0, 135.5, 135.5, 135.4, 134.2, 132.3, 131.7, 126.5, 125.9, 125.9, 125.7, 124.0, 123.5, 121.2, 121.1, 65.1, 26.3, 18.7. *m/z* $[M+H]^+$ calcd for $C_{35}H_{33}OS_4Si$ 625.1178 found 625.1154.



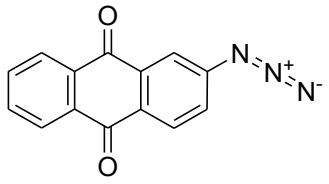
(9,10-di(benzo[d][1,3]dithiol-2-ylidene)-9,10-dihydroanthracen-7-yl)methanol 11

In a 50 ml round bottom flask, 5% HCl (1 mL) was added to a solution of **10** (1.25 g, 2.00 mmol) in THF (8 mL)/MeOH (1 mL) and stirred at room temperature for 3 hours. After reaction completion as monitored by TLC, the crude mixture was poured onto 250 ml of methanol and the precipitate was filtered, washed with methanol and dried under high vacuum to provide the desired product **11** (1.00 g, 98%) as a bright yellow solid. ^{1}H NMR (500 MHz, *CDCl$_3$*)) δ ppm 7.79-7.71 (m, 4H), 7.37 (m, 3H), 7.23-7.16 (m, 4H), 7.09-7.05 (m, 4H), 4.81 (d, *J* = 5.7 Hz, 2H), 1.85 (br t, 1H). ^{13}C NMR: 139.1, 135.6, 135.2, 135.1, 135.1, 135.0, 134.7, 132.3, 132.0, 126.3, 125.9, 125.7, 125.6, 124.8, 124.2, 123.51, 123.49, 120.9, 65.3. *m/z* $[M+H]^+$ calcd for $C_{29}H_{19}OS_4$ 511.0313 found 511.0319.



bis((9,10-di(benzo[d][1,3]dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methyl) isophthalate 2

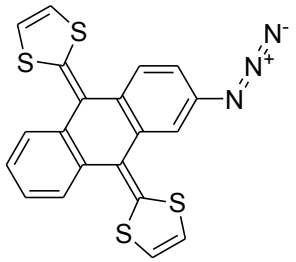
N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) (0.053 g, 0.275 mmol) was added portionwise to a previously cooled solution (0 °C) of (9,10-di(benzo[d][1,3]dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methanol (0.127 g, 0.25 mmol), isophthalic acid (0.021 g, 0.125 mmol) and 4-dimethylaminopyridine (DMAP) (0.034 g, 0.275 mmol) in dry dichloromethane (5 mL) under argon atmosphere. The mixture was allowed to warm up to room temperature and stirred overnight. After evaporation of the solvent under reduced pressure the residue was purified by column chromatography ($CHCl_3$/hexanes, 8/2) affording **2** as a yellow solid (0.1 g, 70%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 8.93 (m, 1H), 8.36 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.83 (m, 2H), 7.75-7.67 (m, 6H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.45-7.39 (m, 2H), 7.38-7.31 (m, 4H), 7.20-7.13 (m, 6H), 7.11-7.08 (m, 2H), 7.07-6.99 (m, 8H), 5.52-5.42 (m, 4H). ^{13}C NMR: 165.5, 135.6, 135.2, 135.2, 135.1, 135.0, 135.0, 134.7, 134.2, 133.8, 132.7, 130.6, 128.7, 126.3, 125.8, 125.7, 125.6, 125.2, 123.2, 123.1, 120.9, 66.7. *m/z* $[M+H]^+$ calcd for $C_{66}H_{39}O_4S_8$ 1151.0609 found 1151.0591.



2-azidoanthracene-9,10-dione 14

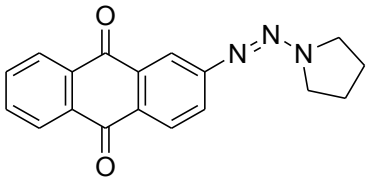
To a mixture of 2-aminoanthracene-9,10-dione (2.23 g, 10.0 mmol) in AcOH (9.2 mL) and concentrated H_2SO_4 (4.3 mL) was added sodium nitrite (0.70 g, 10 mmol) in water (5 mL)

dropwise under vigorous stirring at 0-5 °C. After 10 min, aqueous urea was added to the reaction mixture to remove excess sodium nitrite. Then sodium azide (7.70 g, 118 mmol) in water (50 mL) was added to the reaction mixture at 0-5 °C for 3 h. The reaction mixture was poured into ice water and the resulting mixture was basified with sodium hydroxide and extracted with ethyl acetate. The organic layer was washed with water, dried over anhydrous sodium sulfate and evaporated to give the corresponding crude azide **14**, which was purified by column chromatography (DCM/hexanes, 6/4) to yield pure azide (36%, 0.90 g) as a off-white solid. ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.36-7.33 (m, 1H), 8.29 (m, 3H), 7.90-7.88 (m, 1H), 7.82-7.78 (m, 2H). ^{13}C NMR: 182.7, 182.0, 146.7, 135.3, 134.6, 134.3, 133.7 133.5, 130.3, 129.8, 127.5, 127.51, 124.6, 117.0.



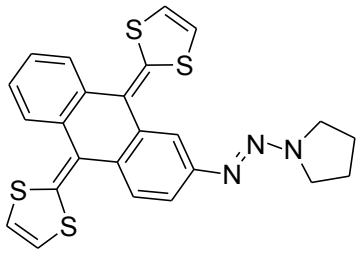
2-(2-azido-10-(1,3-dithiol-2-ylidene)anthracen-9(10H)-ylidene)-1,3-dithiole 16

Method A: Compound **16** was prepared according to the reported synthetic procedures described for compound **10** in 13% yield. Method B: To a solution of triazene **18** (0.48 g, 1.0 mmol) and $KHSO_4$ (1.36 g, 10.0 mmol) in CH_2Cl_2/H_2O (16/8 mL) was added NaN_3 (0.33 g, 5.0 mmol) at room temperature. The reaction mixture was stirred vigorously 3 days at room temperature. The biphasic mixture was poured onto 100 ml of methanol and the precipitate was filtered, washed with methanol and dried under high vacuum to give the pure product **16** (0.30 g, 71%) as a brown-yellow solid. ^{1}H NMR (500 MHz, *CDCl$_3$*) δ ppm 7.72-7.68 (m, 3H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.31-7.29 (m, 2H), 6.95 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.32 (s, 2H), 6.31 (s, 2H). ^{13}C NMR: 137.4, 137.1, 135.5, 135.3, 135.0, 132.5, 126.4, 126.1, 124.9, 121.4, 121.2, 117.3, 117.3, 117.1, 116.2, 115.6 *m/z* $[M+H]^+$ calcd for $C_{20}H_{11}N_3S_4$ 420.983 found 420.9805.



2-(2-(pyrrolidin-1-yl)diazenyl)anthracene-9,10-dione 17

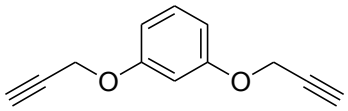
A solution of 2-aminoanthraquinone (1.11g, 5.0 mmol) in 2 mL of conc. HCl was cooled in an ice bath while a solution of $NaNO_2$ (0.35 mg, 5.25 mmol) in cold water (20 mL) was added dropwise. The resulting solution of the diazonium salt was stirred at 0 ^oC for 30 min and then added at once to a solution of pyrrolidine (710 mg g, 10 mmol) and K_2CO_3 (3.45 g, 25 mmol) in 1:2 acetonitrile/water (25 mL). The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was washed twice with brine, dried over $MgSO_4$, filtered, and concentrated by evaporation. The crude product was purified by flash chromatography over silica gel using EtOAc/hexanes (2/8) giving the pure product as a brown-yellow solid in 60% yield. ^1H NMR (500 MHz, *CDCl₃*) δ ppm 8.31-8.26 (m, 2H), 8.25 (m, 2H), 7.78-7.72 (m, 3H), 4.00 (t, *J* = 6.1 Hz, 2H), 3.72 (t, *J* = 6.2 Hz, 2H), 2.07 (m, 4H). ^{13}C NMR: 183.4, 182.473, 156.1, 134.5, 133.8, 133.8, 133.7, 133.5, 129.7, 128.7, 127.0, 125.6, 51.6, 46.8, 23.8, 23.5. *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}N_3O_2$ 307.1268 found 307.1286. (See Liu, C.-Y.; Knochel, P. *Org. Lett.* **2005**, *7*, 2543.)



(5E)-1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-3-yl)-2-(pyrrolidin-1-yl)diazene 18

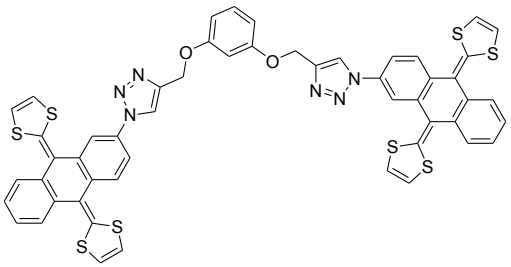
Compound 1**8** was prepared according to the reported synthetic procedures described for compound **10** in 70% yield. ^1H NMR (500 MHz, *DMSOd₆*) δ ppm 7.66-7.60 (m, 3H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.37-7.31 (m, 2H), 7.27 (m, 1H), 6.74-6.69 (m, 4H), 3.98-3.77 (m, 2H), 3.56 (br d, 2H), 1.97 (br s, 4H). ^{13}C NMR: 149.6, 137.0, 136.1, 135.8, 135.4, 135.3, 132.0, 126.8, 126.8,

125.4, 121.5, 121.4, 118.8, 118.7, 116.5, 79.8, 23.8. *m/z* $[M+H]^+$ calcd for $C_{24}H_{20}N_3S_4$ 479.0562 found 479.0554.



1,3-bis(prop-2-ynyloxy)benzene 19

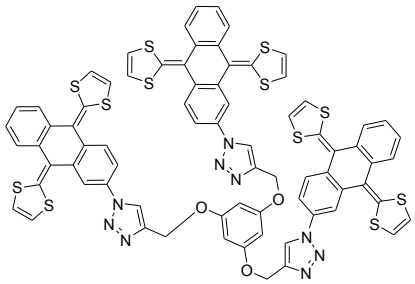
A mixture of resorcinol (3.0 mmole, 0.33g), propargyl bromide (9.0 mmole, 1.070g) and anhydrous potassium carbonate (4.14g, 30 mmole) in dry acetone (40 ml) was refluxed for 12 h. The reaction mixture was cooled and diluted with 500 ml of water and extracted thoroughly with DCM (3x15 mL).The organic layer was washed with 10% sodium hydroxide, water and dried over $MgSO_4$, filtered, and concentrated by evaporation. The residue was purified by silica gel column chromatography to yield the desired product **7** as a clear oil (0.35 g, 56%). ^{1}H NMR (500 MHz, *CDCl₃*) δ ppm 7.25-7.20 (m, 1H), 6.66-6.62 (m, 3H), 4.69 (s, 2H), 4.67(s, 2H), 2.56-2.52 (m, 2H). ^{13}C NMR: 158.7, 129.9, 107.9, 102.4, 78.4, 75.6, 55.8. API *m/z* $[M+H]^+$ calcd for $C_7H_4S_3$ 187.0754 found 187.0745.



1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-7-yl)-4-((3-((1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-7-yl)-1H-1,2,3-triazol-4-yl)methoxy)phenoxy)methyl)-1H-1,2,3-triazole 3

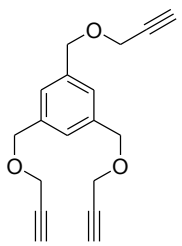
To a 5 mL flask charged with Et_3N (5.5 μL, 0.04 mmol), azide **16** (92 mg, 0.22 mmol), DMSO (1.5 mL) and CuI (2 mg, 0.01 mmol) were added into the mixture under N_2 atmosphere. The

flask was charged with acetylene (0.1 mmol, 19 mg) and then the mixture was stirred under a pressure of nitrogen at room temperature. After 2 days, the mixture was diluted with 25 mL of EtOAc and washed with 20 mL of H_2O four times then with brine. The organic phase dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified on SiO_2 with DCM-hexanes (6:4) to yield the desired product as an orange-yellow solid in 41% yield. ^{1}H NMR (500 MHz, *CDCl$_3$*) δ ppm 8.07 (s, 2H), 7.98 (br s, 2H), 7.75-7.70 (m, 2H), 7.69-7.65 (m, 4H), 7.56 (m, 2H), 7.31-7.26 (m, 5H), 6.80-6.76 (m, 1H), 6.69 (dd, *J* = 8.2, 2.3 Hz, 2H), 6.30-6.23 (m, 8H), 5.31 (s, 4H). ^{13}C NMR: 159.4, 144.7, 138.1, 137.5, 136.9, 135.8, 135.0, 134.8, 134.1, 130.2, 126.2, 125.0, 124.9, 121.0, 120.8, 120.6, 117.6, 117.5, 117.3, 117.2, 117.1, 116.8, 107.9, 102.2, 62.0. *m/z* $[M+H]^+$ calcd for $C_{52}H_{33}N_6O_2S_8$ 1029.0425 found 1029.0389.



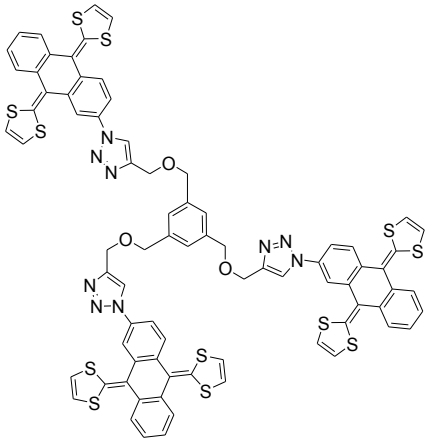
1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)-4-((3,5-bis((1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)-1H-1,2,3-triazol-4-yl)methoxy)phenoxy) methyl)-1H-1,2,3-triazole 5

1,3,5-tris(prop-2-ynyloxy)benzene (19 mg, 1 equiv), compound **16** (134 mg, 4.0 equiv), CuI (4 mg, 0.33 equiv), and *N*-ethyldiiso- propylamine (0.068 mL, 6 equiv) were dissolved in 3 mL of DMF in an 10 mL glass vial equipped with magnetic stirring bar. The mixture was then irradiated for 1 h at 80 °C using microwave irradiation. After cooling, the mixture was dissolved in CH_2Cl_2, washed with water and brine. The organic extract was dried ($MgSO_4$), concentrated, and then purified by column chromatography (SiO_2, MeOH/CH_2Cl_2, 5/95) to yield a yellow solid (60% yield). ^{1}H NMR (400 MHz, *DMSOd$_6$*) δ ppm 8.98 (s, 3H), 8.18 (s, 3H), 7.86-7.78 (m, 6H), 7.71-7.63 (m, 6H), 7.39-7.33 (m, 6H), 6.76 (m, 12H), 6.48 (s, 3H), 5.25 (s, 6H). ^{13}C NMR: 159.9, 143.9, 138.7, 138.1, 136.1, 134.8, 134.5, 133.9, 126.5, 126.1, 124.8, 122.9, 119.6, 118.4, 117.7, 116.2, 109.4, 79.2. *m/z* $[M+H]^+$ calcd for $C_{75}H_{46}N_9O_3S_{12}$ 1504.0367 found 1504.0386.



1,3,5-tribromo-2,4,6-tris((prop-2-ynyloxy)methyl)benzene 21

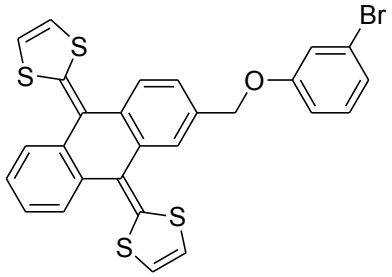
1,3,5-tribromo-2,4,6 tris (hydroxymethyl)benzene (200 mg, 0.5 mmol) was added in portions to a suspension of NaH (70 mg, 1.75 mmol, 60% in mineral oil) in DMF (3 mL) at 0°C. After 30 minutes, propargyl bromide (297 mg, 2.5 mmol) was added and the resulting mixture was stirred at room temperature overnight. The mixture was poured onto ice and then diluted by DCM (30 mL) and washed by HCl 1N (30 mL) and dried on $MgSO_4$. The reaction mixture was then concentrated to obtain the desired compound (160 m g, 56%) as a colorless solid. ^{1}H NMR (400 MHz, *CDCl₃)* δ ppm7.30 (s, 3H), 4.61 (s, 6H), 4.19 (t, *J* = 2.4 Hz, 6H), 2.50-2.41 (m, 3H). ^{13}C NMR: 137.9, 127.1, 79.5, 74.8, 71.2, 57.3. API *m/z* M^{*+} calcd for $C_{18}H_{18}O_3$ 282.125 found 282.1242.



1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)-4-((3,5-bis(((1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)-1H-1,2,3-triazol-4-yl)methoxy) methyl) benzyloxy)methyl)-1H-1,2,3-triazole 6

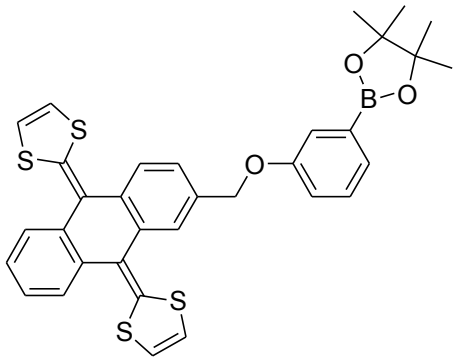
The product was prepared according to the procedure described for compound **5** with the following exception, 1,3,5-tris(prop-2-ynyloxy)benzene was replaced for 1,3,5-tris((prop-2-

ynyloxy)methyl)benzene. Product was purified by column chromatography (39% yield). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 8.03 (s, 3H), 7.92 (s, 3H), 7.72-7.57 (m, 9H), 7.57-7.50 (m, 3H), 7.40 (s, 3H), 7.26-7.20 (m, 6H), 6.29-6.16 (m, 12H), 4.78 (s, 6H), 4.69 (s, 6H). ^{13}C NMR: 145.7, 138.4, 137.4, 136. 7, 135.6, 134.9, 134.1, 126.9, 126.2, 124.9, 124.8, 120.8, 120.5, 117.5, 117.3, 117.2, 116.6, 72.3, 63.6. *m/z* $[M+H]^+$ calcd for $C_{78}H_{51}N_9O_3S_{12}$ 1546.0786 found 1546.0898.



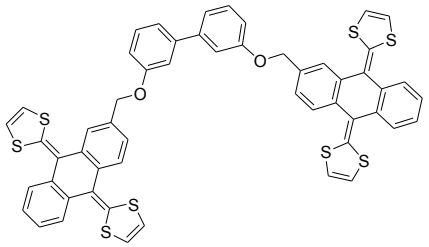
2-(2-((3-bromophenoxy)methyl)-10-(1,3-dithiol-2-ylidene)anthracen-9(10H)-ylidene)-1,3-dithiole 23

A 50 mL round-bottomed flask was charged with triphenylphosphine (PPh_3) (1.57 g, 6.0 mmol), and THF (12 mL). The flask is immersed in an ice bath and diethyl azodicarboxylate (1.04 g, 6 mmol) was added dropwise. Upon completion of the addition, the solution was allowed to stir at 0 ^{o}C for 15 min. Alcohol **22** (1.64 g, 4.0 mmol) and 3-bromophenol (0.69 g, 4.0 mmol) were then added and the mixture was allowed to stir for further 18 hours at room temperature. Excess solvent was removed under reduced pressure. The resulting solid was suspended in 100 mL of isopropanol, the resulting yellow solid was filtered under vacuum and the filter cake was washed with isopropanol. The solid was purified by flash chromatography and eluted with 40% DCM-hexanes to yield 1.0 g (44%) of pure ether **23** as a yellow solid. ^{1}H NMR (500 MHz, *CDCl3*) δ ppm 7.74 (br d, 1H), 7.73-7.68 (m, 3H), 7.33-7.29 (m, 3H), 7.21-7.19 (m, 1H), 7.17-7.13 (m, 1H), 7.12-7.09 (m, 1H), 6.93 (m, 1H), 6.29 (d, *J* = 2.0 Hz, 2H), 6.29 (s, 2H), 6.28 (br m, 2H), 5.11 (s, 2H). ^{13}C NMR: 159.4, 135.9, 135.7, 135.2, 135.1, 134.0, 130.6, 126.0, 125.2, 124.9, 124.88, 124.8, 124.0, 123.9, 122.8, 121.8, 121.7, 118.3, 117.2, 117.1, 113.9, 70.0. *m/z* $[M+H]^+$ calcd for $C_{27}H_{18}BrOS_4$ 564.9418 found 564.9414.



2-(3-((9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 24

A flask charged with palladium acetate (7 mg, 0.03 mmol), X-phos (29 mg, 0.06 mmol), KOAc (550 mg, 5.6 mmol), and bis-pinacolatodiboron (400 mg, 1.575 mmol) was flushed with nitrogen. Dioxane (5 mL) and compound **23** (0.85 g, 1.5 mmol) were then added. After being stirred at 80 ^{o}C for 12 h, the product was extracted with DCM, washed with water, and dried over anhydrous magnesium sulfate. Purification on silica gel (DCM/hexanes, 4/6) yields the desired product (0.35 g, 38% yield) as a yellow solid. ^{1}H NMR (500 MHz, *CDCl$_3$*) δ ppm 7.78 (br d, , 1H), 7.73-7.67 (m, 3H), 7.50-7.42 (m, 2H), 7.36 (m 1H), 7.32 (m, 1H), 7.30 (m, 2H), 7.14-7.08 (m, 1H), 6.31- (s, 2H), 6.26 (m, 2H) 5.18-5.14 (s, 2H), 1.37 (s, 12H). ^{13}C NMR: 158.2, 136.0, 135.6, 135.3, 134.9, 134.8, 129.0, 127.4, 125.9, 125.9, 125.1, 124.9, 124.9, 123.9, 121.9, 121.9, 119.9, 118.6, 117.2, 117.1, 117.1, 117.0, 83.8, 69.7, 24.9. *m/z* $[M+H]^+$ calcd for $C_{33}H_{30}BO_3S_4$ 613.1171 found 613.1188.



3,3'-Di[(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methoxy]biphenyl 4

Product **4** was isolated as side product of Suzuki-cross coupling reaction in 26% yield, purified on silica gel (DCM/hexanes, 4/6). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.77-7.72 (m, 2H), 7.67 (m, 6H), 7.33 (s, 2H), 7.31 (s, 2H), 7.29-7.24 (m, 4H), 7.24-7.15 (m, 4H), 6.98 (br d, 2H), 6.22 (d, *J* = 4.2 Hz, 4H), 6.15 (m 4H), 5.18-5.12 (br s, 4H). ^{13}C NMR: 159.0, 136.3, 135.7, 135.2, 134.9, 134.6, 129.7, 125.9, 125.2, 124.9, 123.9, 121.7, 119.9, 117.2, 117.1, 114.3, 113.9, 69.8. *m/z* $[M+H]^+$ calcd for $C_{54}H_{34}O_2S_8$ 971.0319 found 971.0398.

Figure S1: Complexation of C_{60} by receptor **1** [22 μM] in chlorobenzene

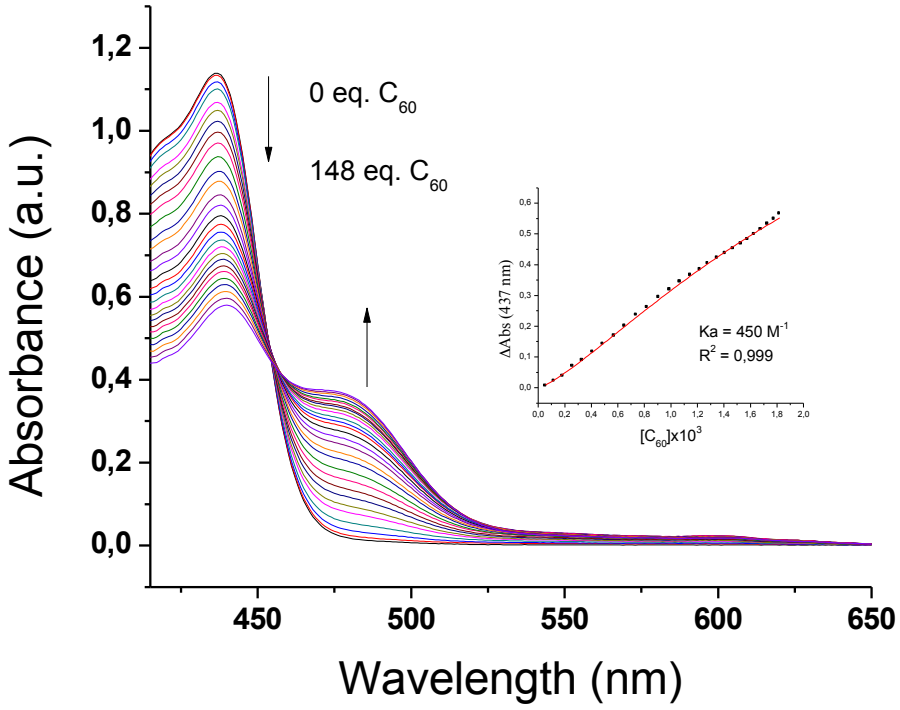


Figure S2: Job's plot of **1** with C_{60} in chlorobenzene at a fixed [**1**]+[C_{60}]=1.1x10^{-5} M

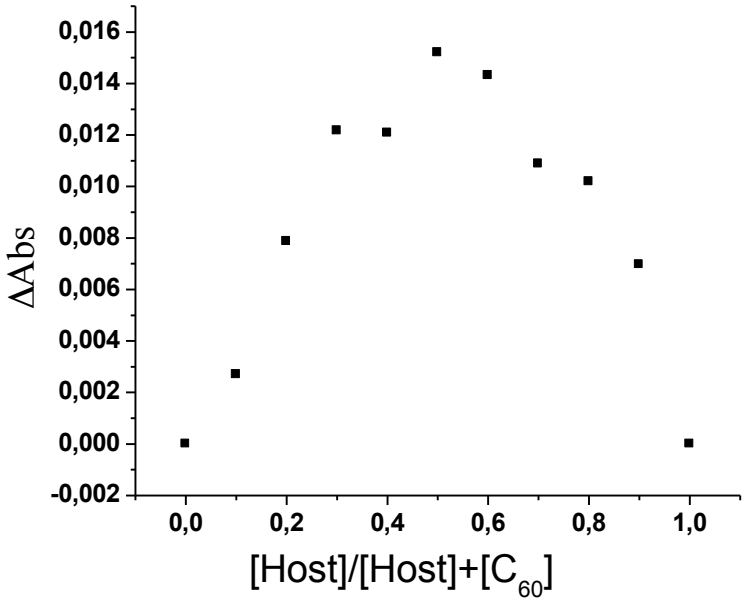


Figure S3: Complexation of C_{60} by receptor **1** [12 µM] in toluene

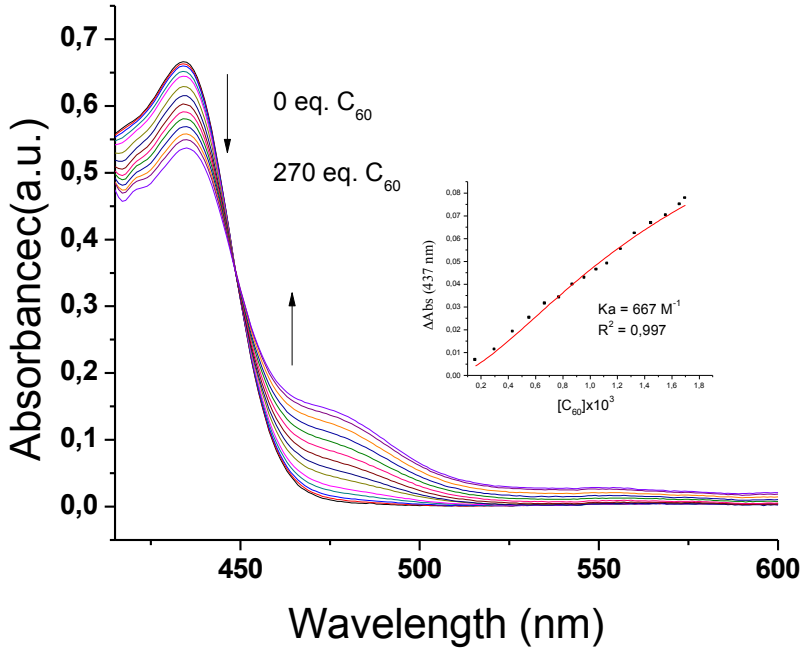


Figure S4: Job's plot of **1** with C_{60} in toluene at a fixed [**1**]+[C_{60}]=1.1x10^{-5} M

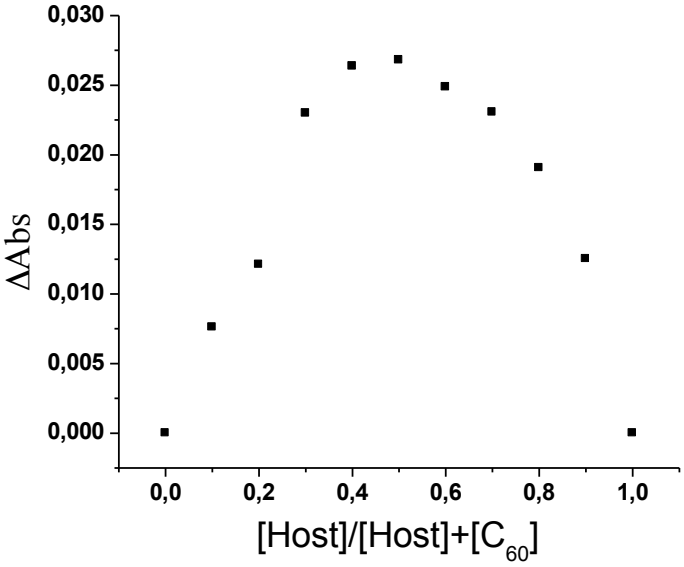


Figure S5: Complexation of C_{60} by receptor **1** [11 μM] in DCM/toluene 1:2

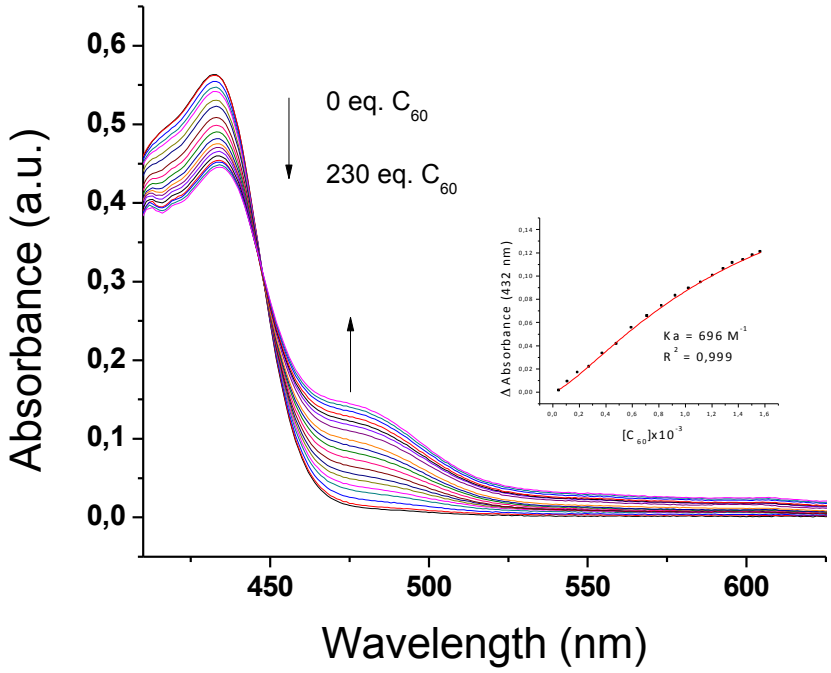


Figure S6: Job's plot of **1** with C_{60} in DCM/toluene 1:2 at a fixed [**1**]+[C_{60}]=1.1x10^{-5} M

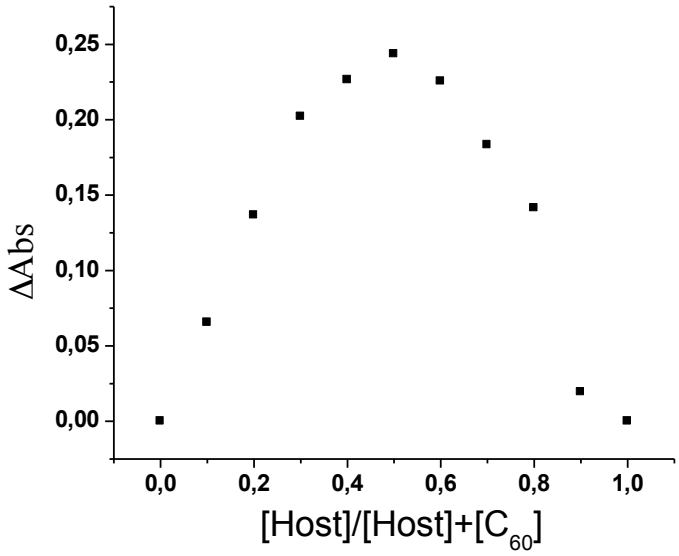


Figure S7: Complexation of C_{60} by receptor **1** [11 μM] in CS_2

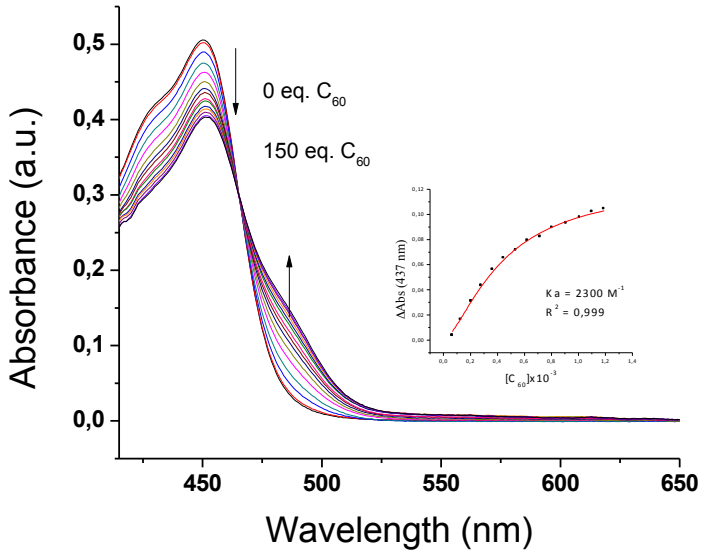


Figure S8: Job's plot of **1** with C_{60} in CS_2 at a fixed [**1**]+[C_{60}]=1.1x10^{-5} M

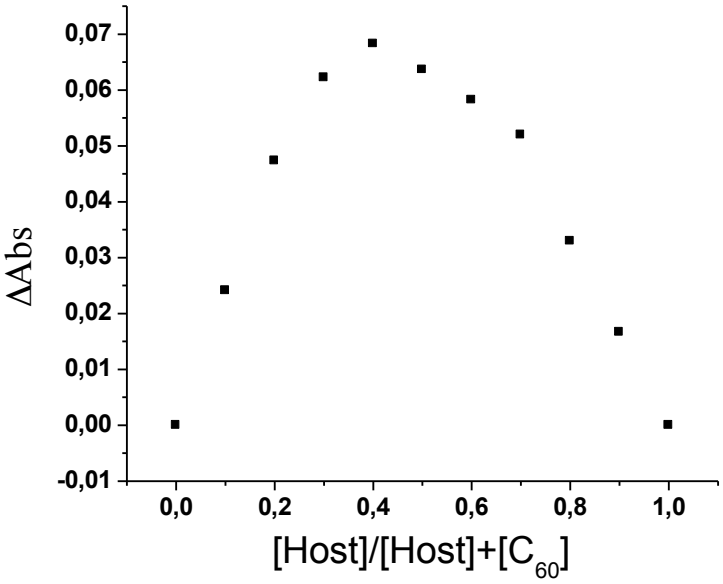


Figure S9: Complexation of C_{70} by receptor **1** [11 μM] in chlorobenzene

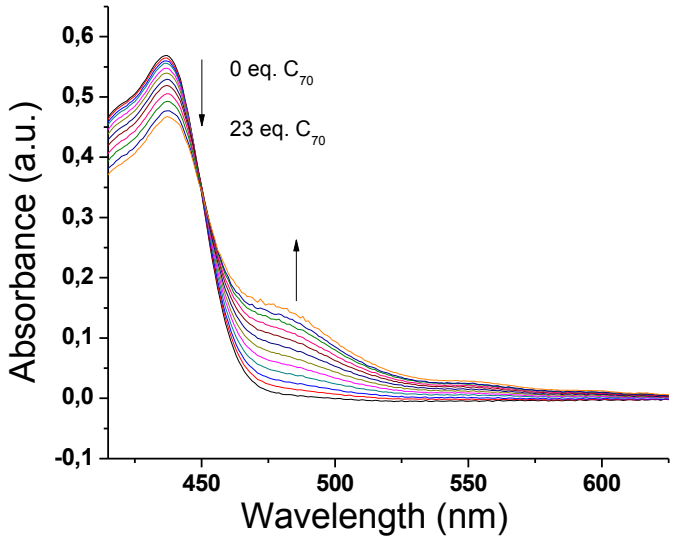


Figure S10: Job's plot of **1** with C_{70} in chlorobenzene at a fixed [**1**]+[C_{70}]=1.75x10^{-5} M

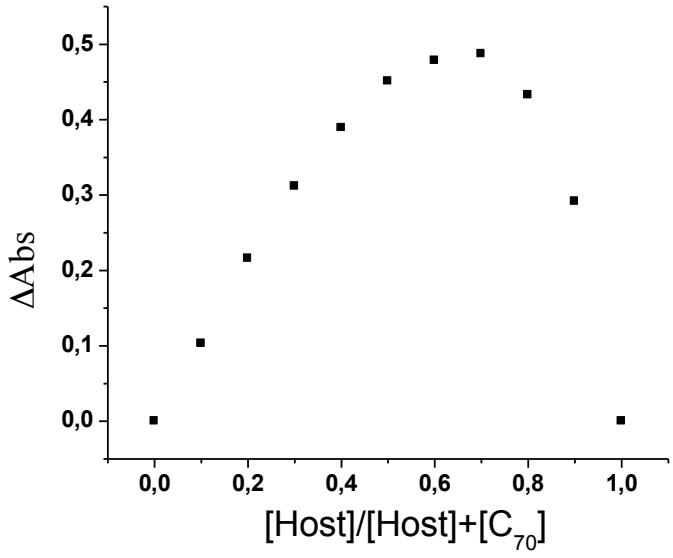


Figure S11: Job's plot of **3** with C_{60} in chlorobenzene at a fixed [**3**]+[C_{60}]=1.1x10^{-5} M

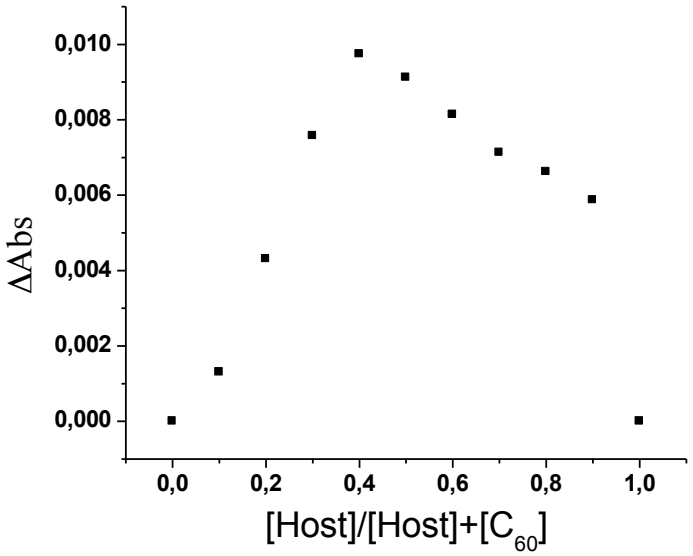


Figure S12: Complexation of C_{60} by receptor **3** [22 µM] in chlorobenzene (305.5 K)

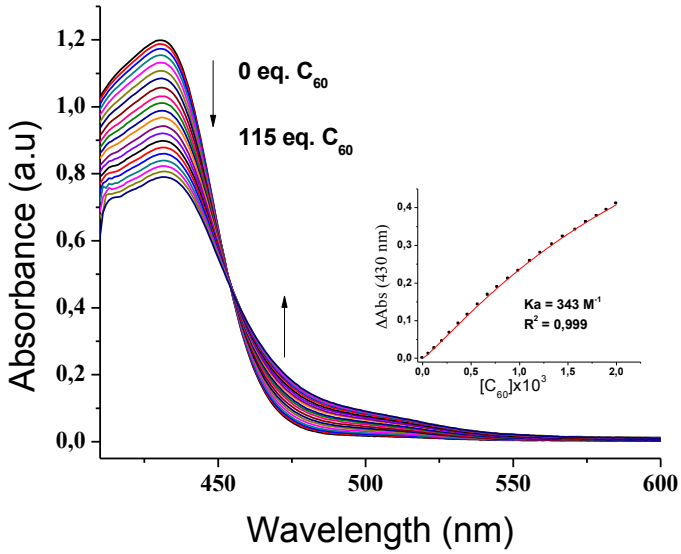


Figure S13: Complexation of C_{60} by receptor **3** [22 µM] in chlorobenzene (315.5 K)

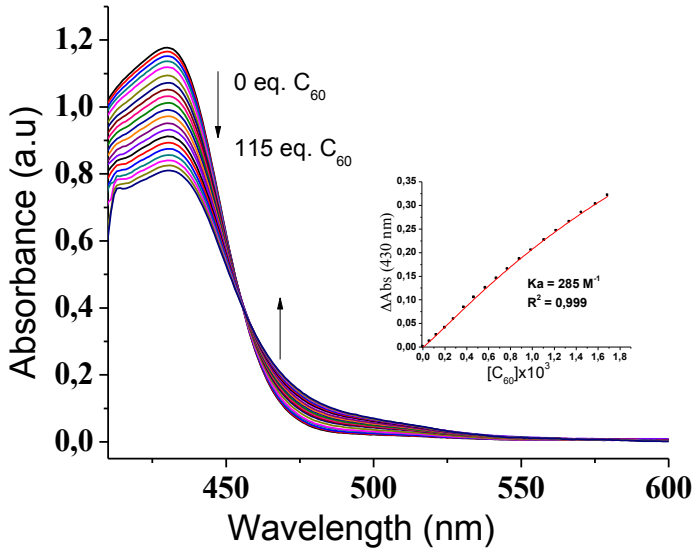
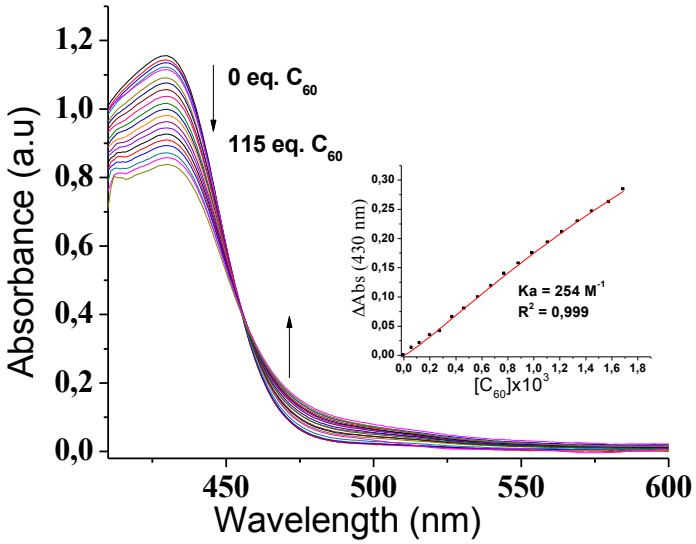


Figure S14: Complexation of C_{60} by receptor **3** [22 µM] in chlorobenzene (325.5 K)



Thermodynamic parameters

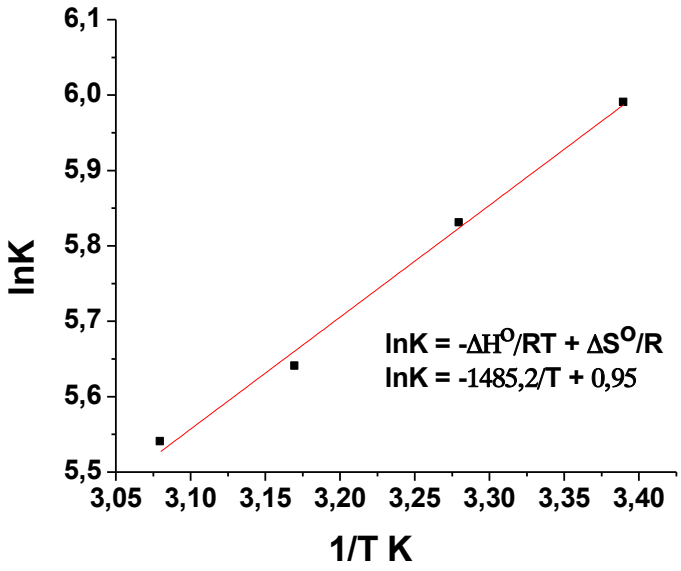


Figure S15: Van't Hoff plots of the **Host 3**-C_{60} complexes in chlorobenzene

Table S1: Thermodynamic parameters of the **Host 3**-C_{60} complexes in chlorobenzene

Complexes	**ΔH (Kcal/mol)**	**ΔS (cal/mol)**
Host **3**-C_{60}	-2.95	1.89

Figure S16: Complexation of C_{60} by receptor **3** [22 μM] in toluene

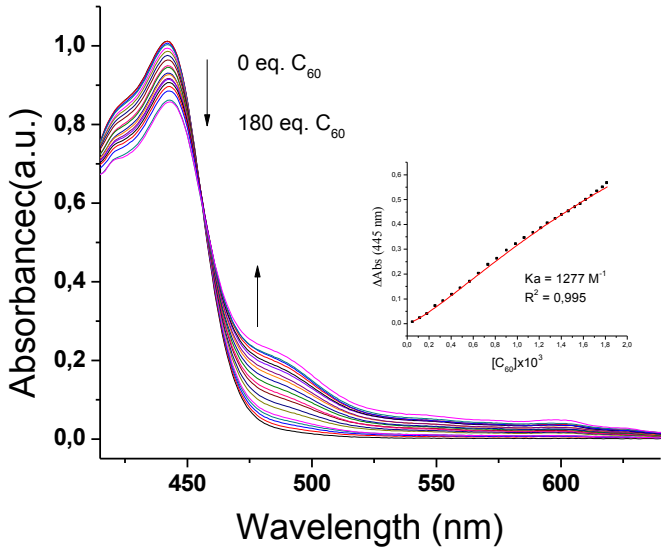


Figure S17: Job's plot of **3** with C_{60} in toluene at a fixed [**3**]+[C_{60}]=1.1x10^{-5} M

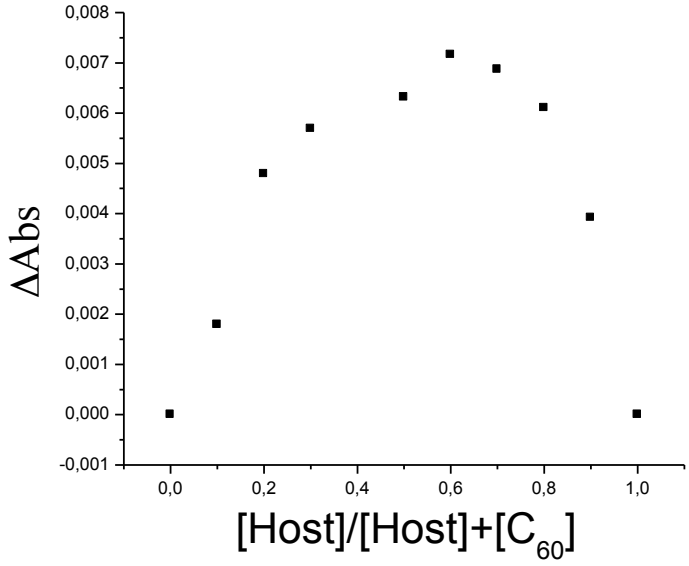


Figure S18: Complexation of C_{60} by receptor **3** [22 μM] in DCM/toluene 1:2

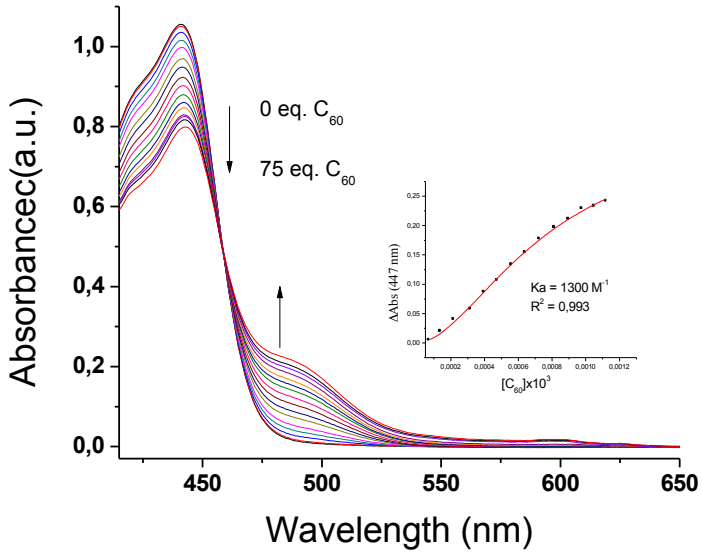


Figure S19: Job's plot of **3** with C_{60} in DCM/toluene 1:2 at a fixed [**3**]+[C_{60}]=1.1x10^{-5} M

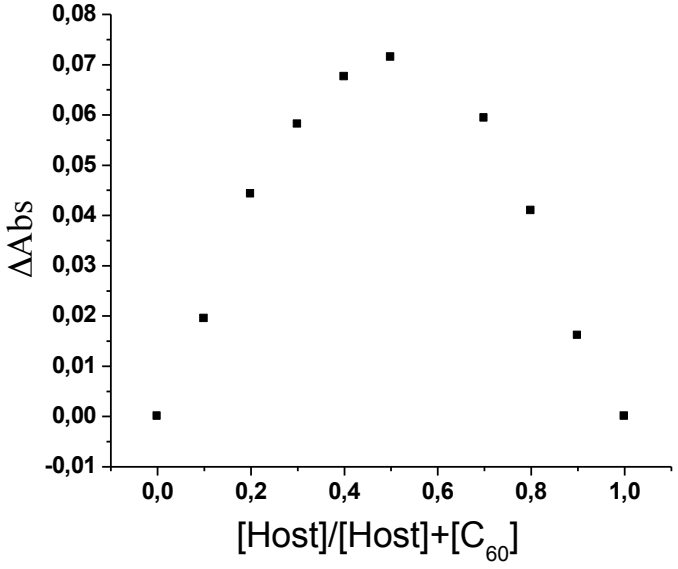


Figure S20: Complexation of C_{60} by receptor **3** [11 μM] in CS_2

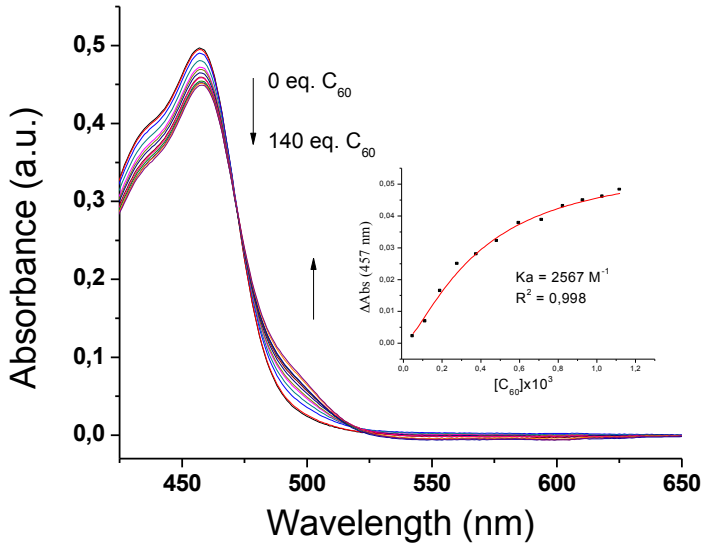


Figure S21: Job's plot of **3** with C_{60} in CS_2 at a fixed [**3**]+[C_{60}]=1.1x10^{-5} M

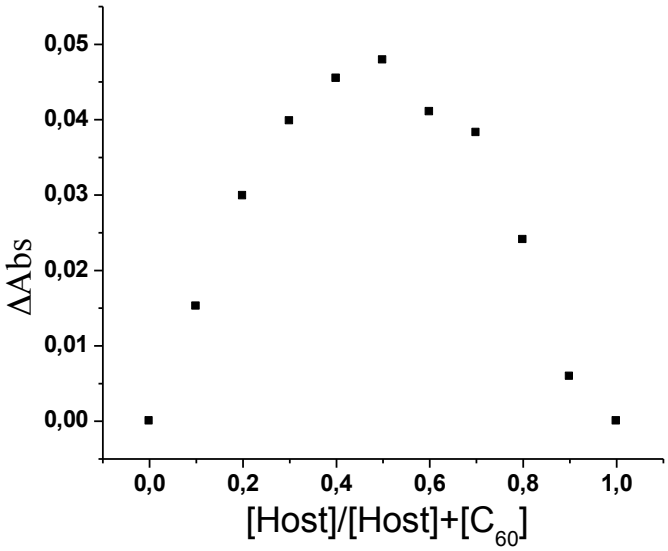


Figure S22: Job's plot of **3** with C_{70} in chlorobenzene at a fixed [**3**]+[C_{70}]=1.75x10^{-5} M

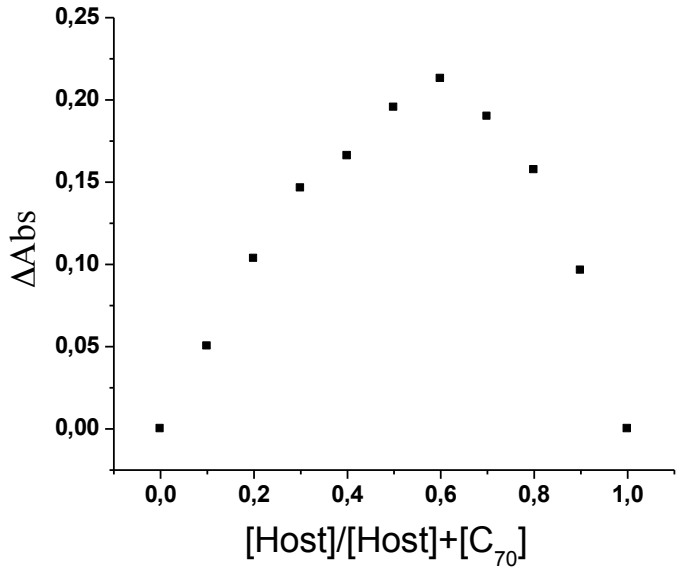


Figure S23: Complexation of C_{60} by receptor **4** [16 μM] in chlorobenzene

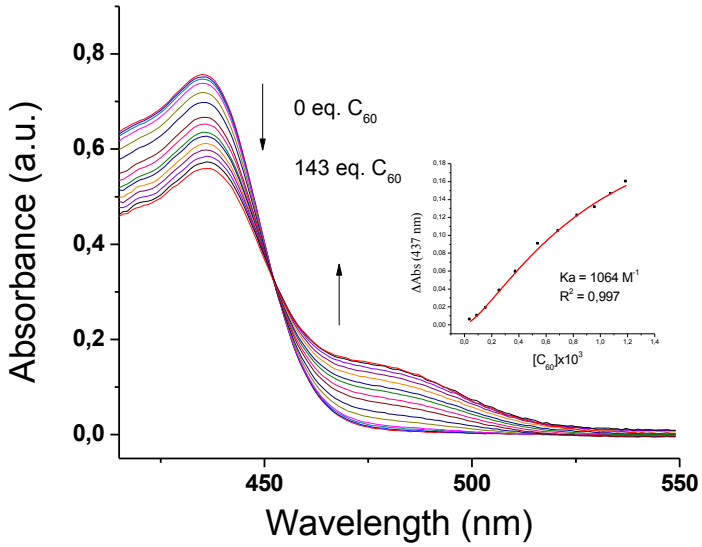


Figure S24: Job's plot of **4** with C_{60} in chlorobenzene at a fixed [**4**]+[C_{60}]=1.75x10^{-5} M

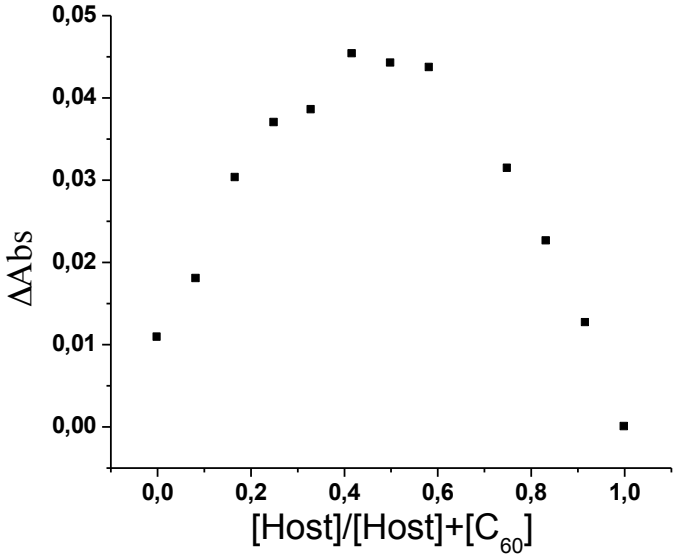


Figure S25: Complexation of C_{60} by receptor **4** [16 µM] in toluene/DCM 2/1

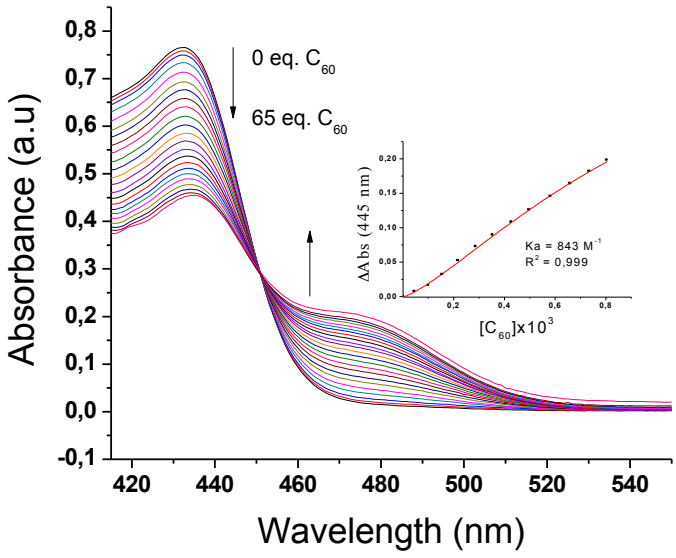


Figure S26: Job's plot of **4** with C_{60} in toluene/DCM 2/1 at a fixed [**4**]+[C_{60}]=1.75x10^{-5} M

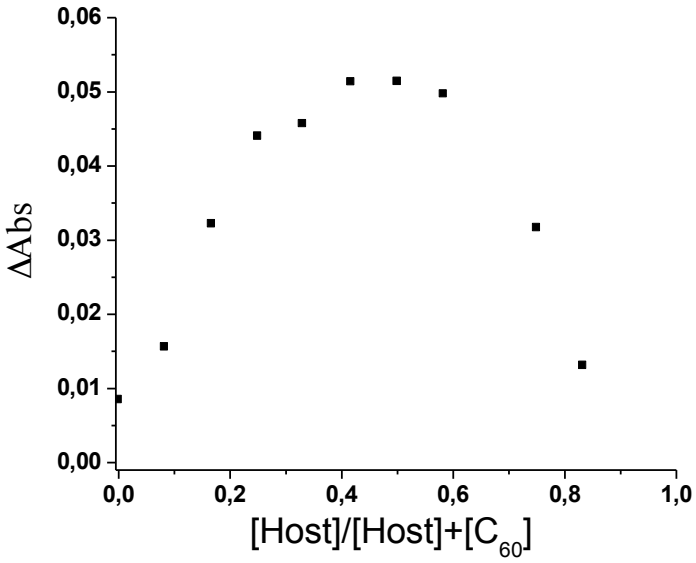


Figure S27: Complexation of C_{60} by receptor **4** [16 µM] in CS_2

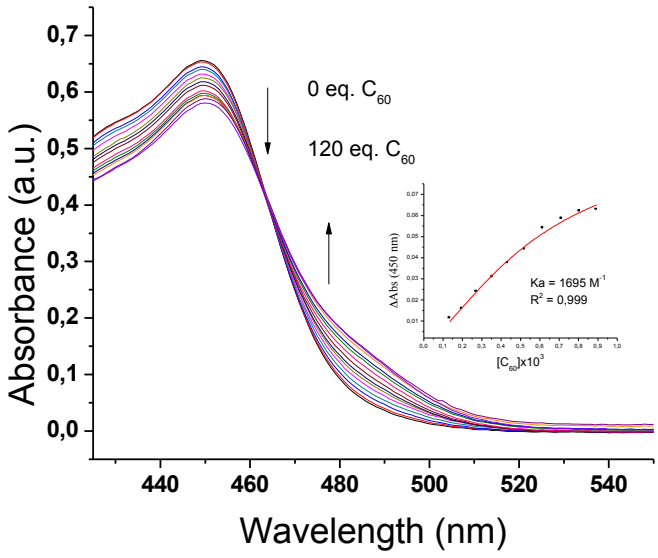


Figure S28: Job's plot of **4** with C_{60} in CS_2 at a fixed [**4**]+[C_{60}]=1.75x10^{-5} M

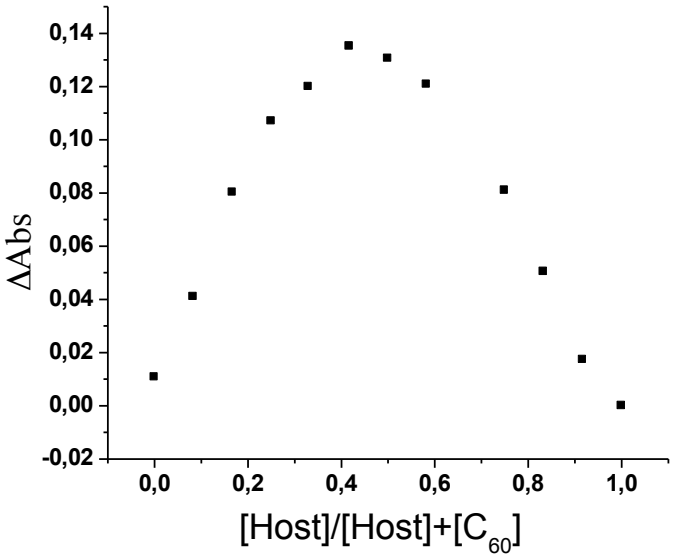


Figure S29: Complexation of C_{70} by receptor **4** [16 μM] in chlorobenzene

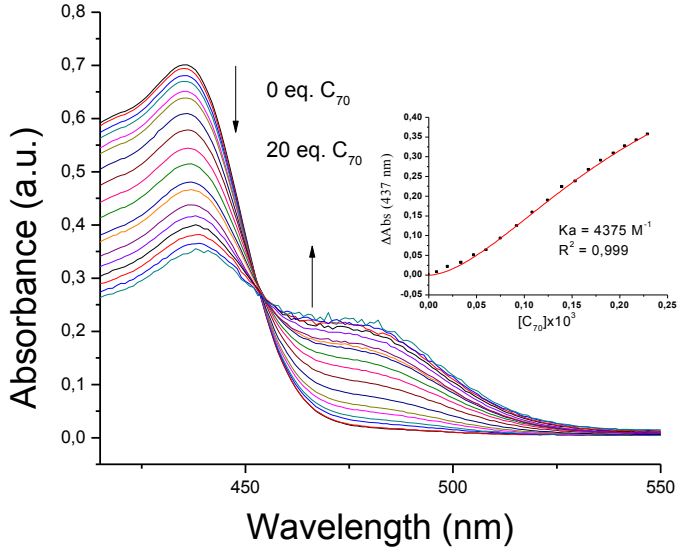


Figure S30: Job's plot of **4** with C_{70} in chlorobenzene at a fixed [**4**]+[C_{70}]=1.75x10^{-5} M

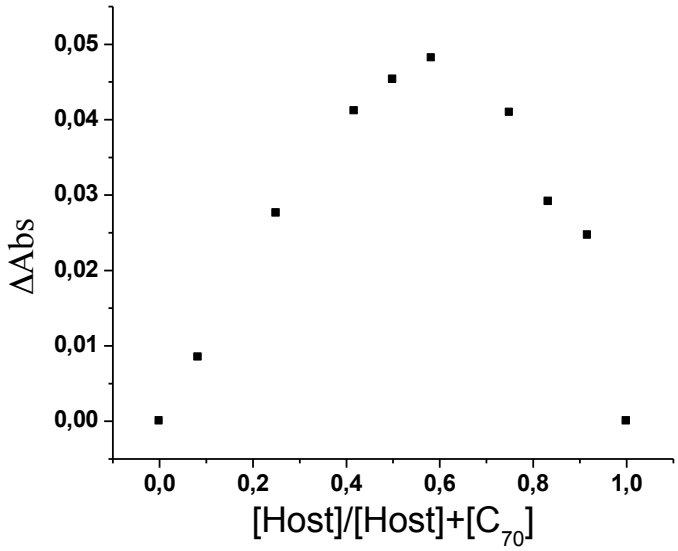


Figure S31: ^{1}H NMR spectrum of compound 1 (400 MHz, *$CDCl_3$*)

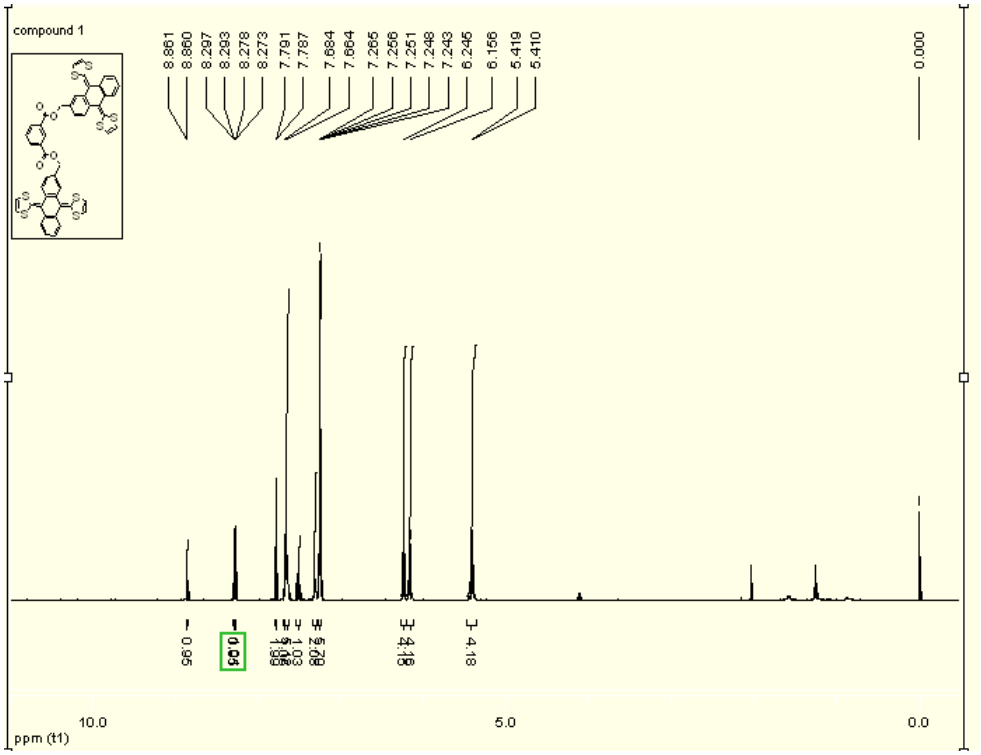


Figure S32: ^{13}C{^{1}H} NMR spectrum of compound 1 (400 MHz, *$CDCl_3$*)

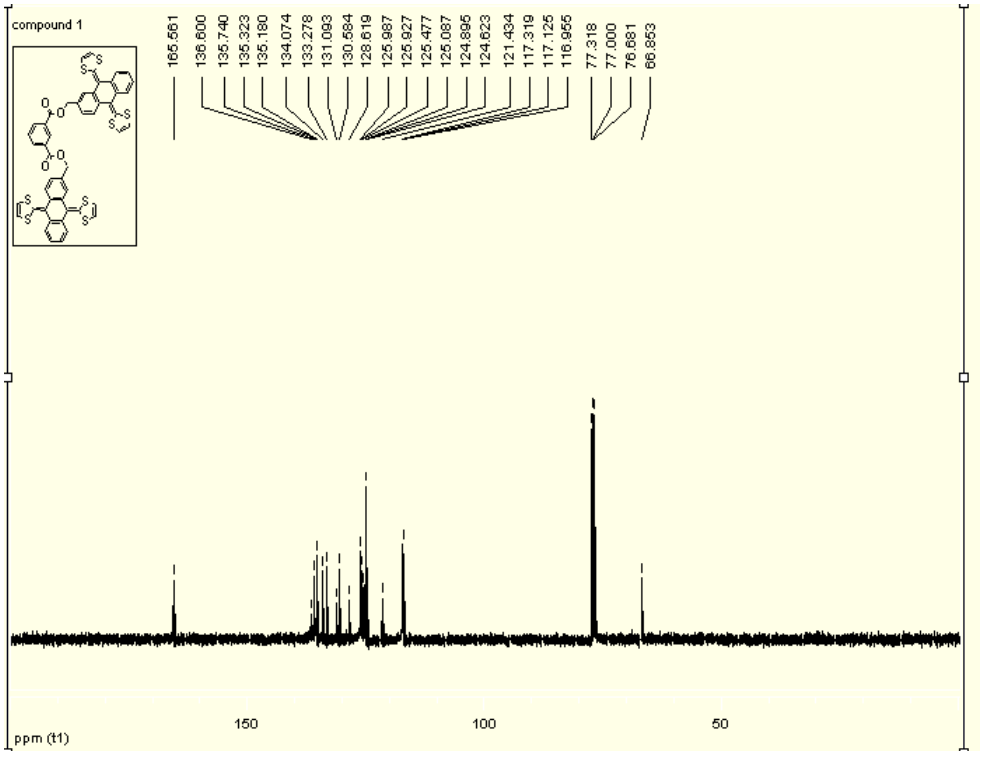


Figure S33: ^{1}H NMR spectrum of compound 2 (400 MHz, *$CDCl_3$*)

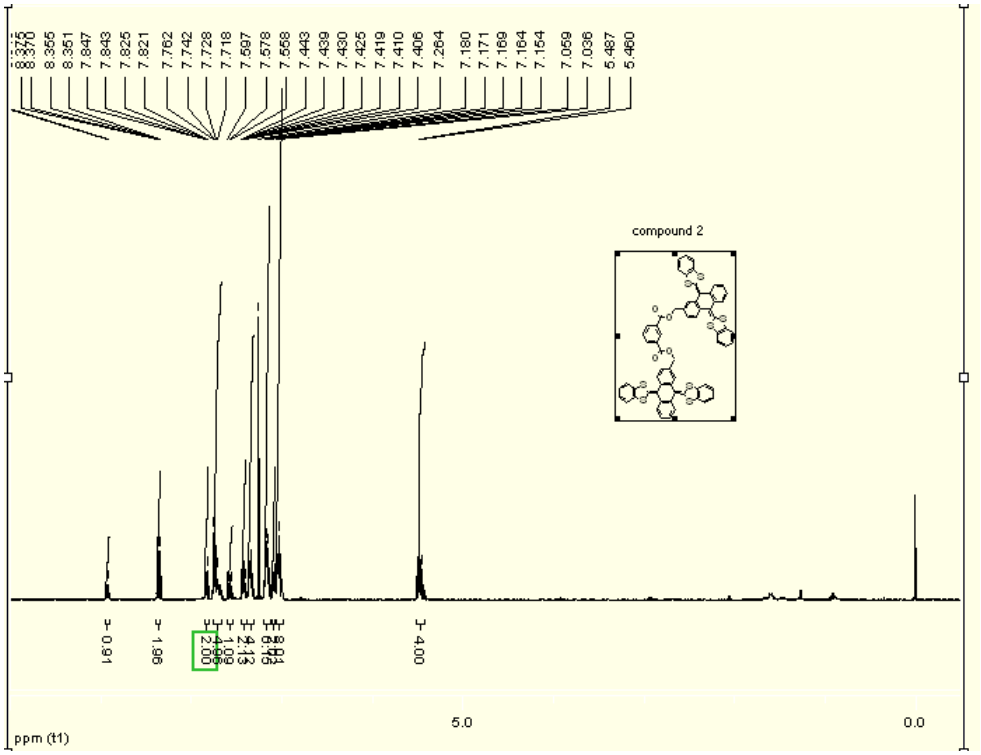


Figure S34: ^{13}C{^{1}H} NMR spectrum of compound 2 (400 MHz, *$CDCl_3$*)

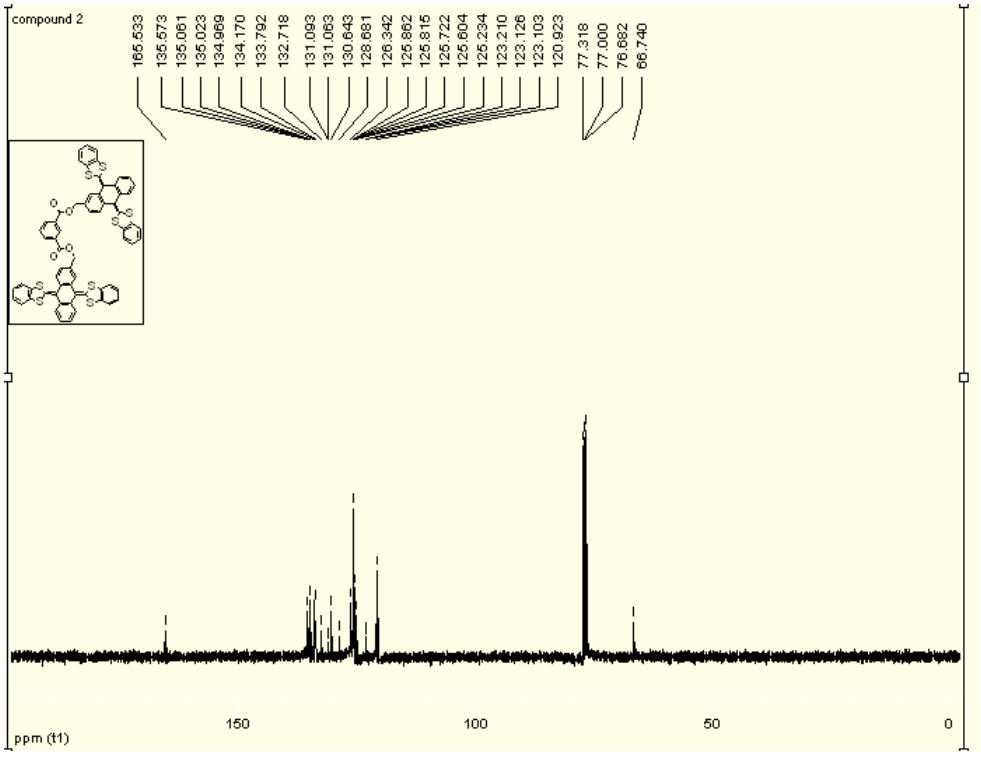


Figure S35: ^{1}H NMR spectrum of compound 3 (500 MHz, *$CDCl_3$*)

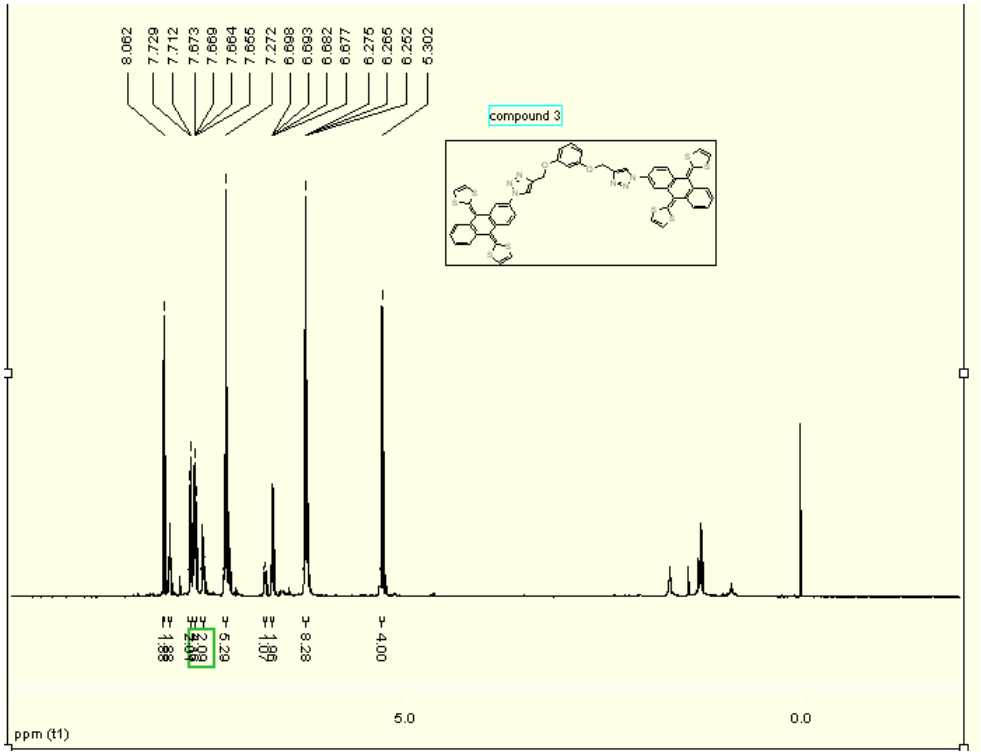


Figure S36: $^{13}C\{^{1}H\}$ NMR spectrum of compound 3 (500 MHz, *$CDCl_3$*)

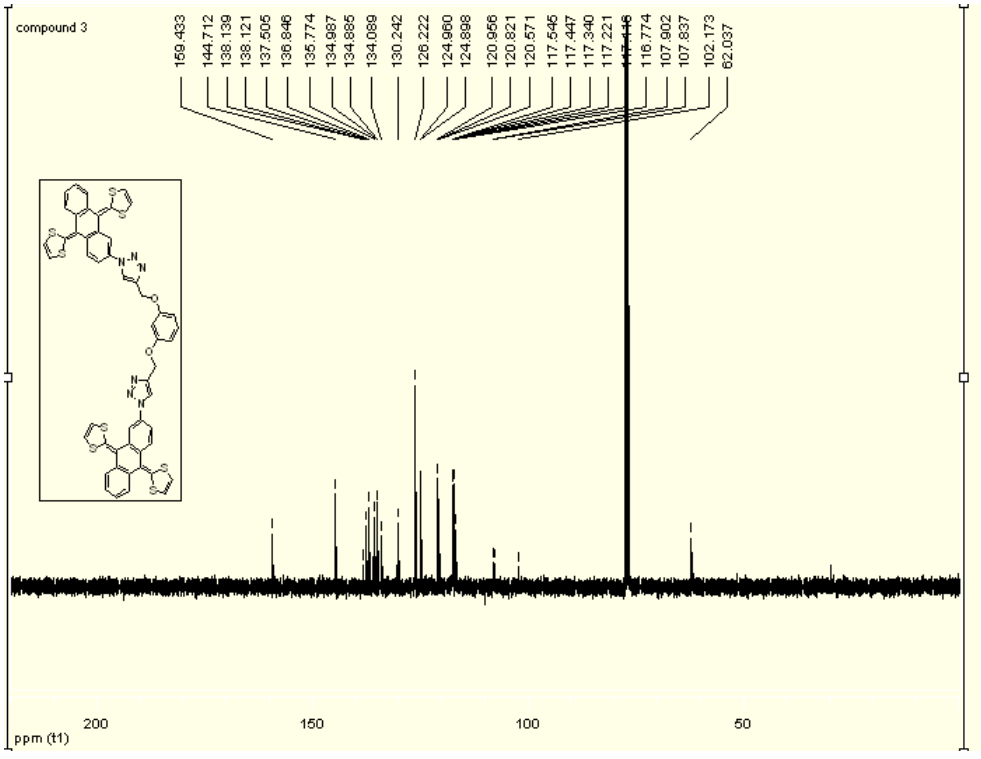


Figure S37: ^{1}H NMR spectrum of compound 4 (500 MHz, *$CDCl_3$*)

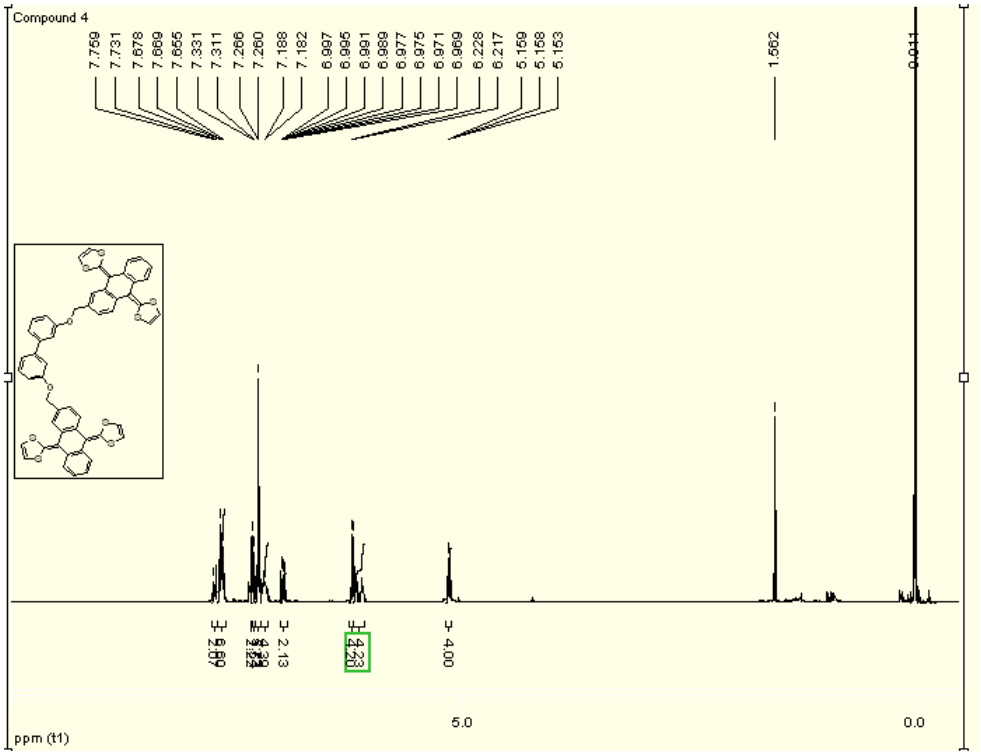


Figure S38: ^{13}C{^{1}H} NMR spectrum of compound 4 (500 MHz, *$CDCl_3$*)

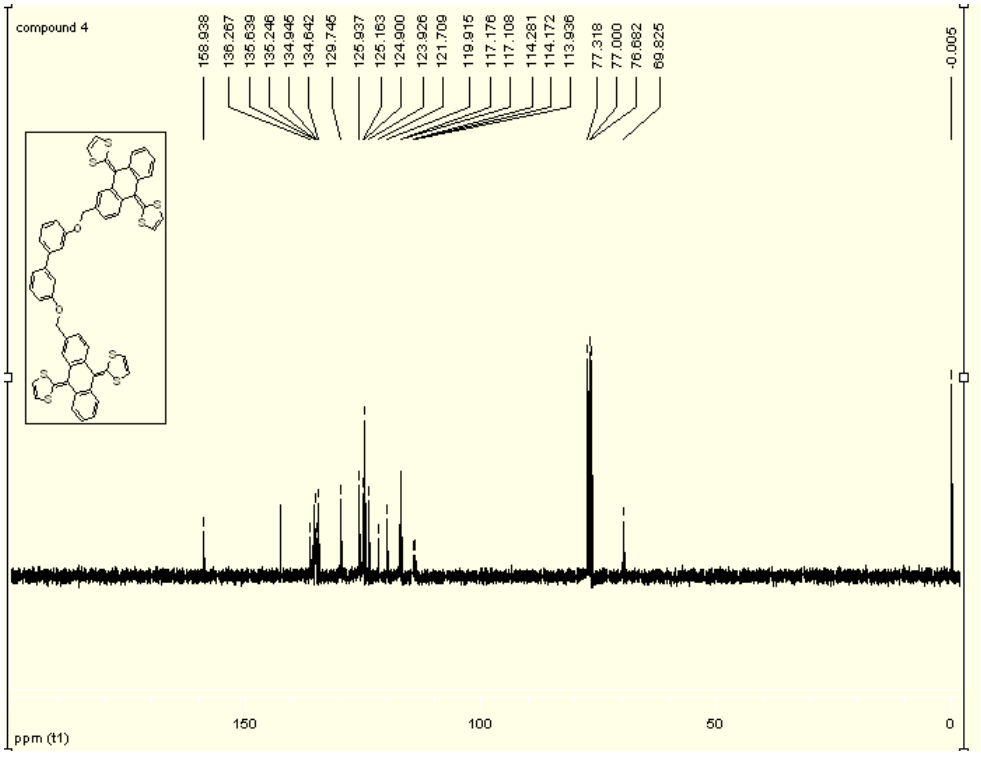


Figure S39: ^{1}H NMR spectrum of compound 5 (400 MHz, *DMSOd$_6$*)

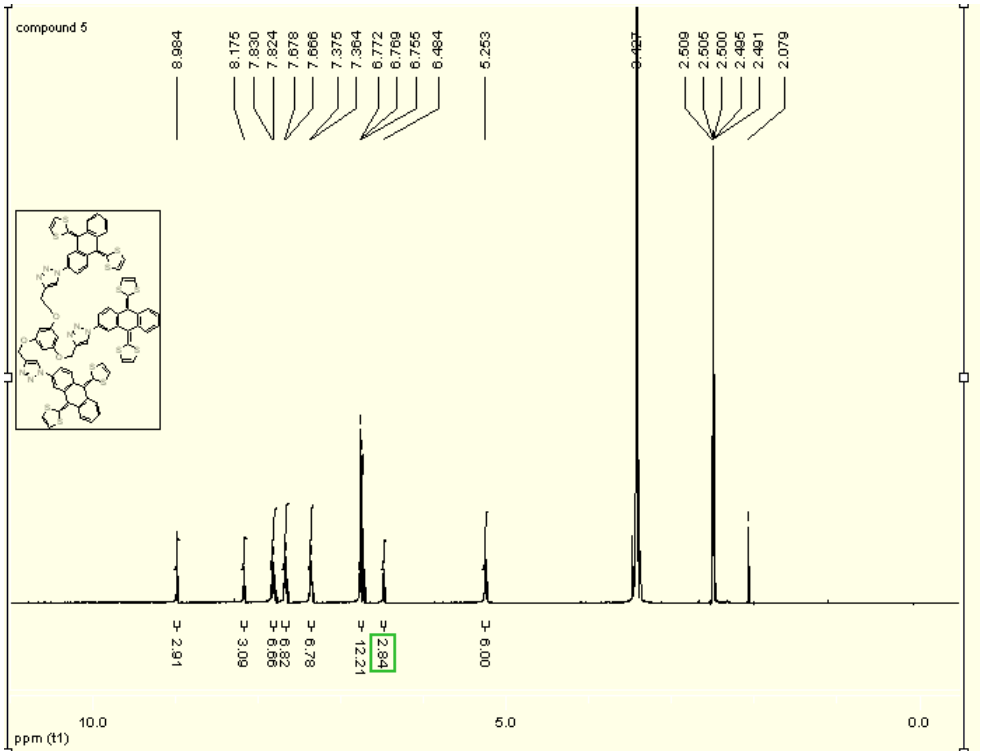


Figure S40: ^{13}C{^{1}H} NMR spectrum of compound 5 (500 MHz, *DMSOd$_6$*)

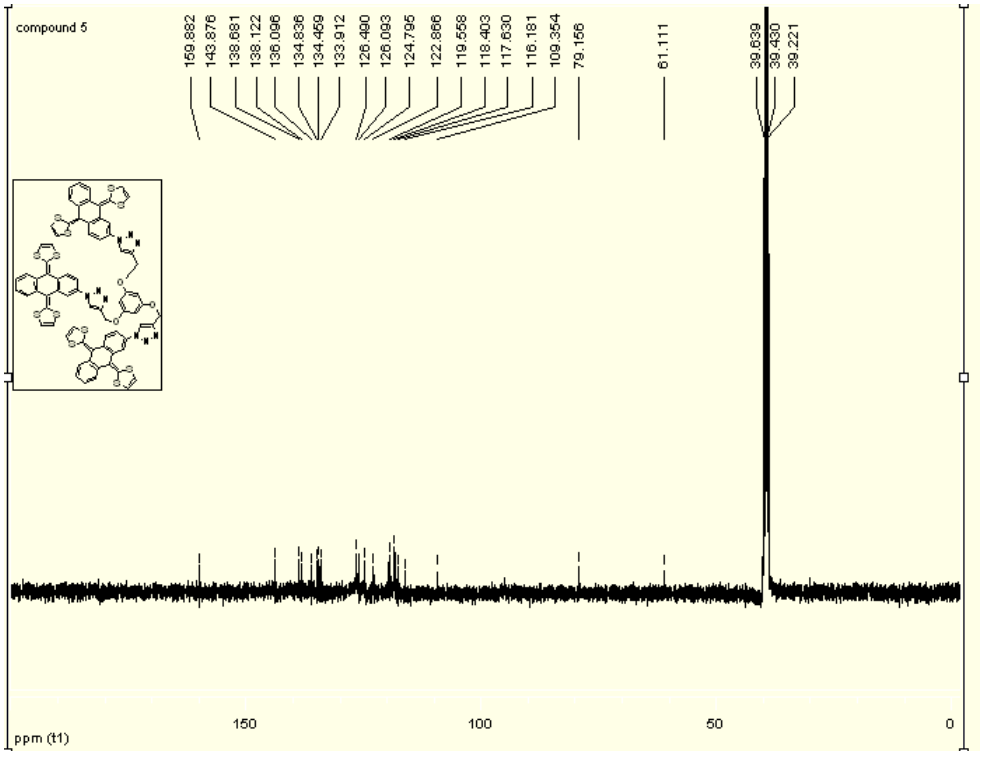


Figure S41: ^{1}H NMR spectrum of compound 6 (400 MHz, *$CDCl_3$*)

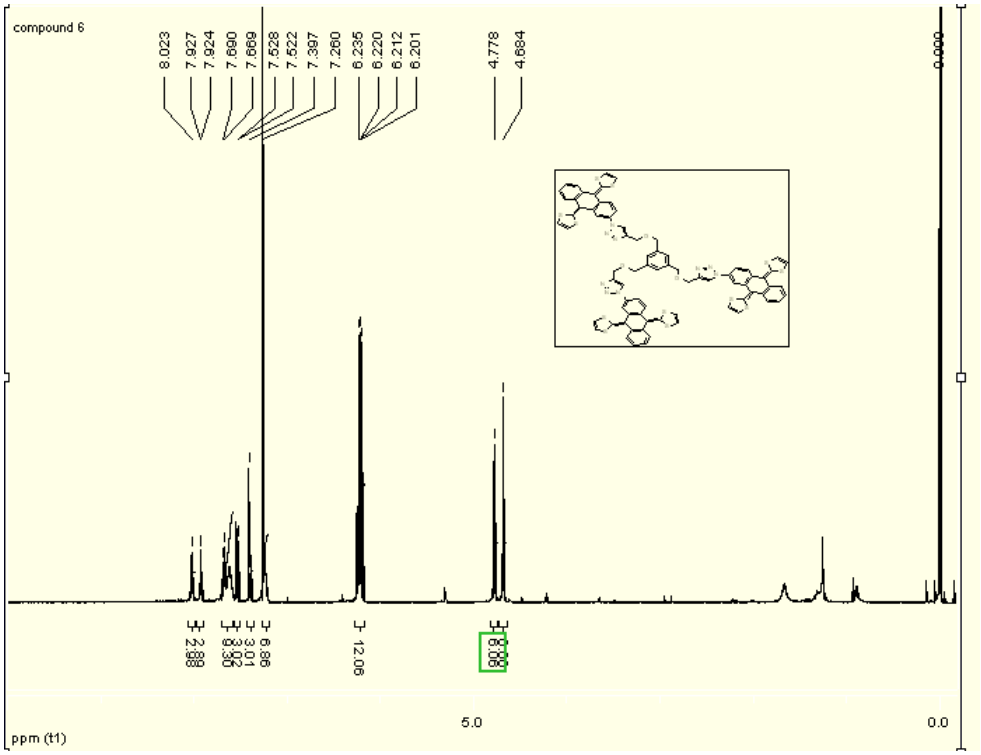


Figure S42: ^{13}C{^{1}H} NMR spectrum of compound 6 (400 MHz, *$CDCl_3$*)

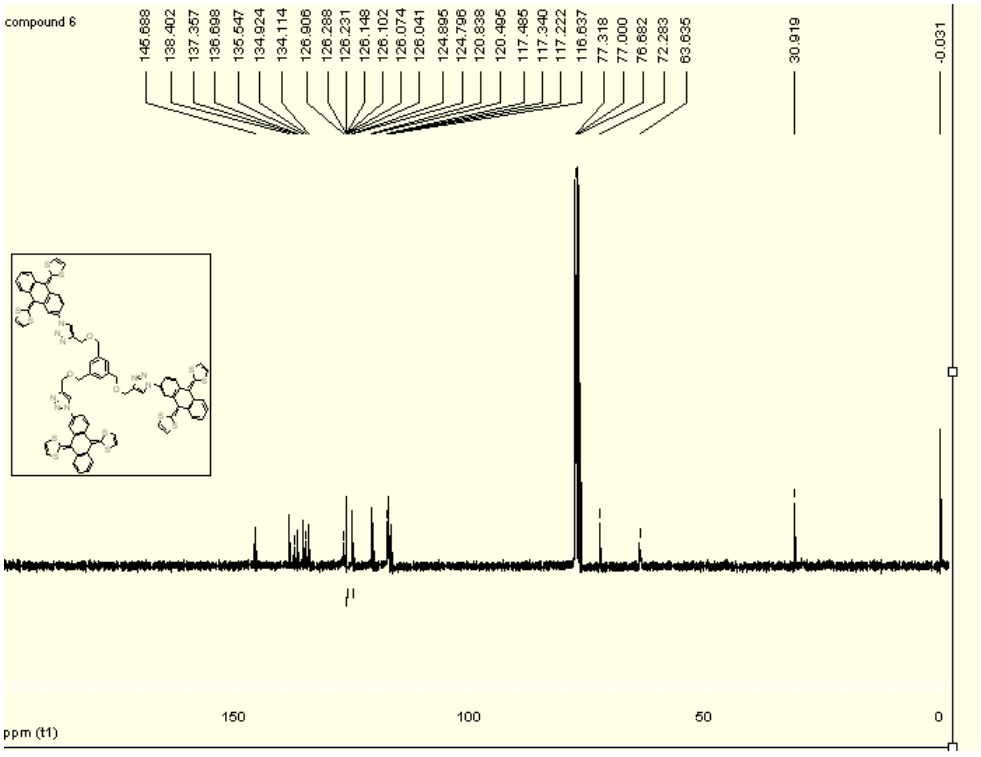


Figure S43: ^{1}H NMR spectrum of compound 7 (400 MHz, *$CDCl_3$*)

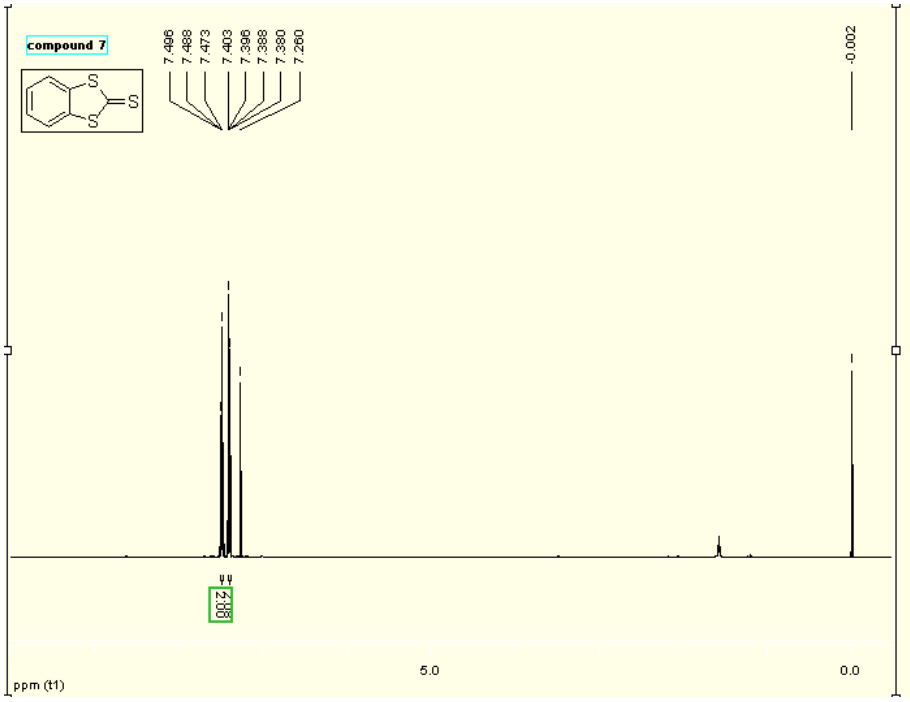


Figure S44: $^{13}C\{^{1}H\}$ NMR spectrum of compound 7 (400 MHz, *$CDCl_3$*)

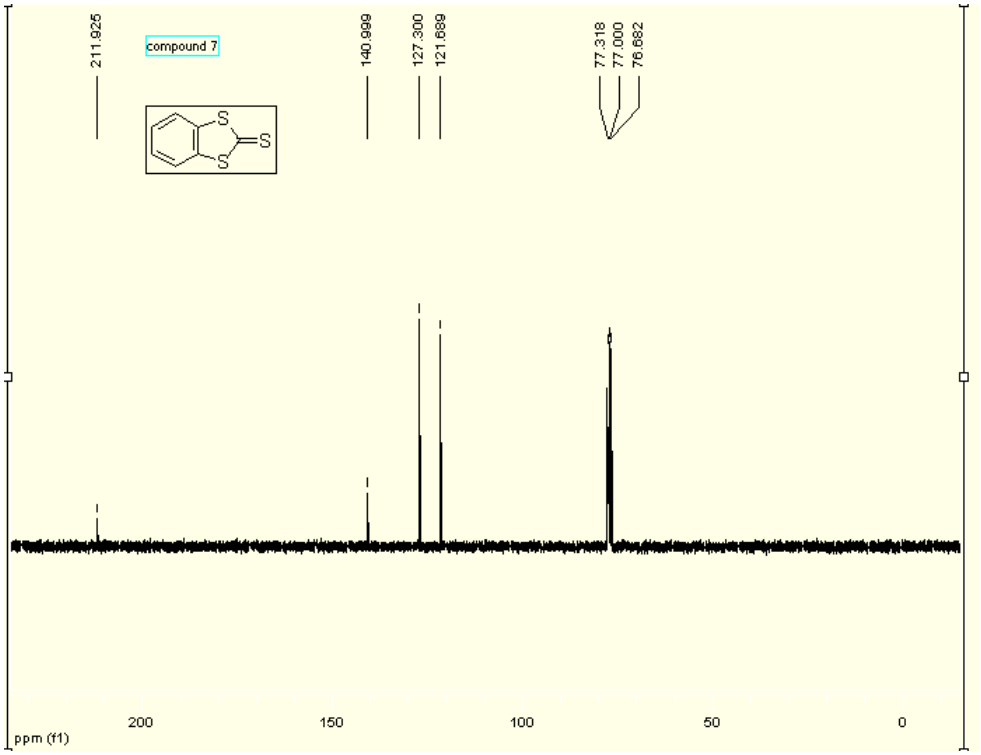


Figure S45: ^{1}H NMR spectrum of compound 10 (400 MHz, *$CDCl_3$*)

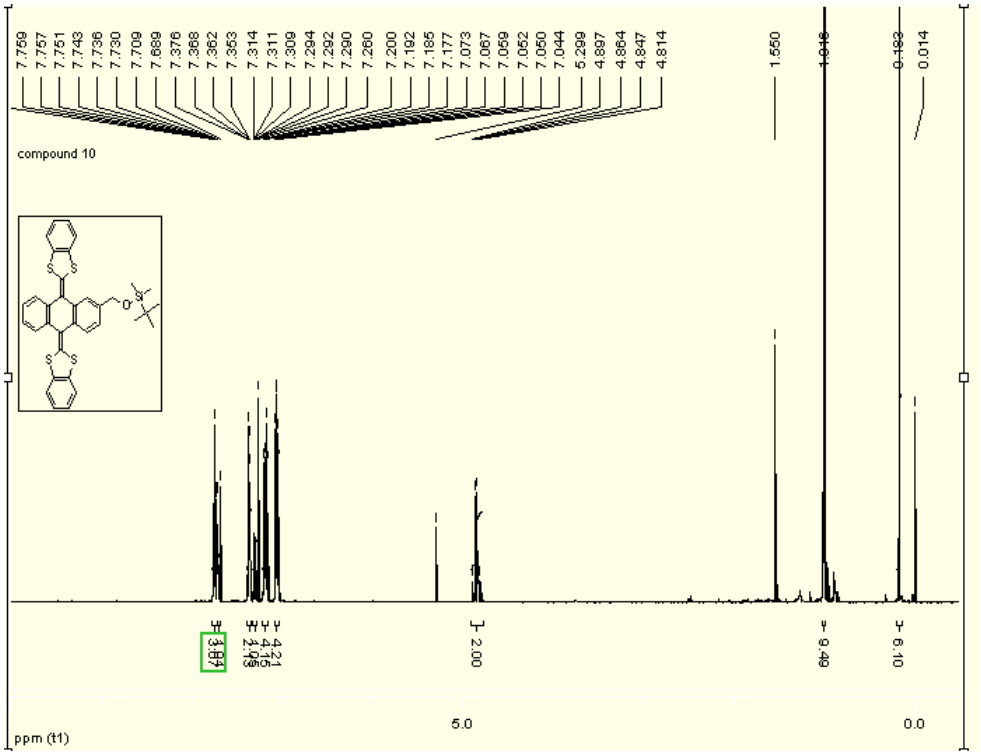


Figure S46: $^{13}C\{^{1}H\}$ NMR spectrum of compound 10 (400 MHz, *$CDCl_3$*)

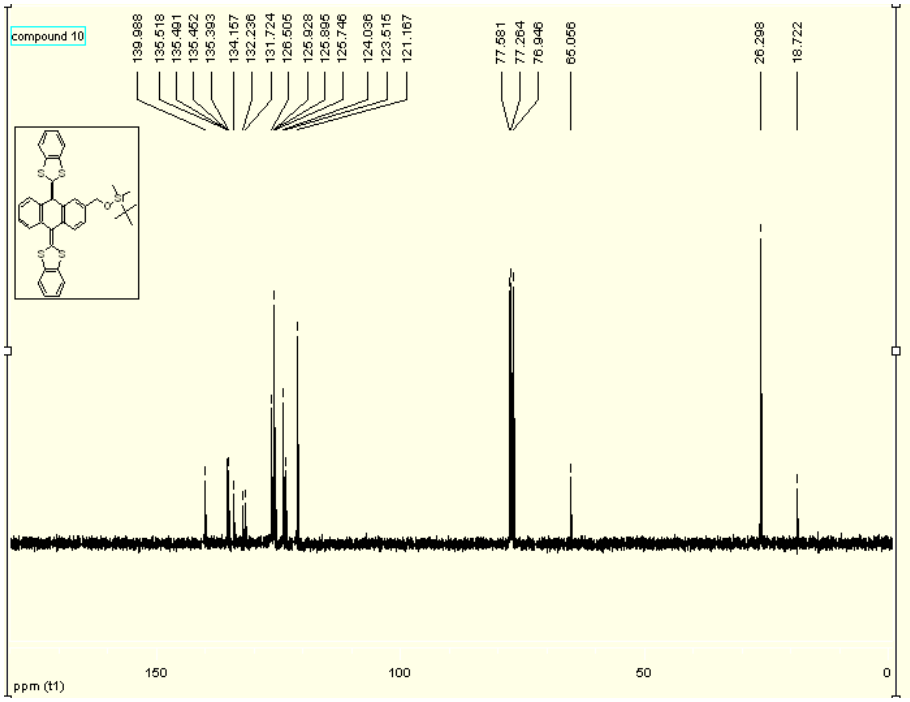


Figure S47: ^{1}H NMR spectrum of compound 11(500 MHz, *$CDCl_3$*)

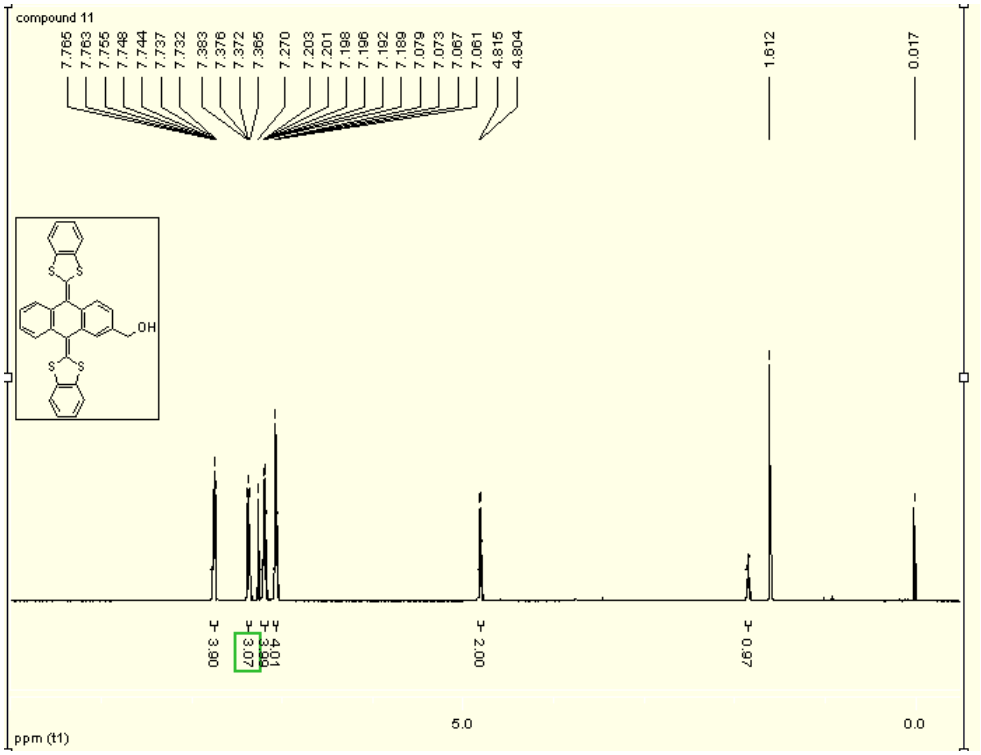


Figure S48: ^{13}C{^{1}H} NMR spectrum of compound 11 (500 MHz, *$CDCl_3$*)

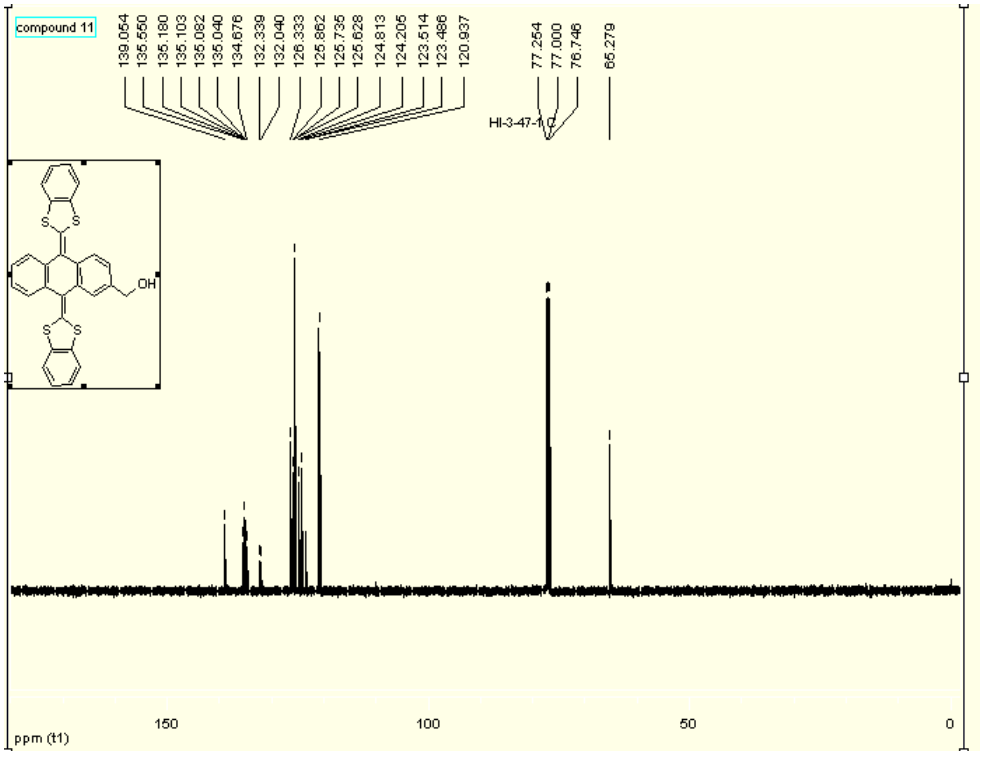


Figure S49: ^{1}H NMR spectrum of compound 14 (400 MHz, *$CDCl_3$*)

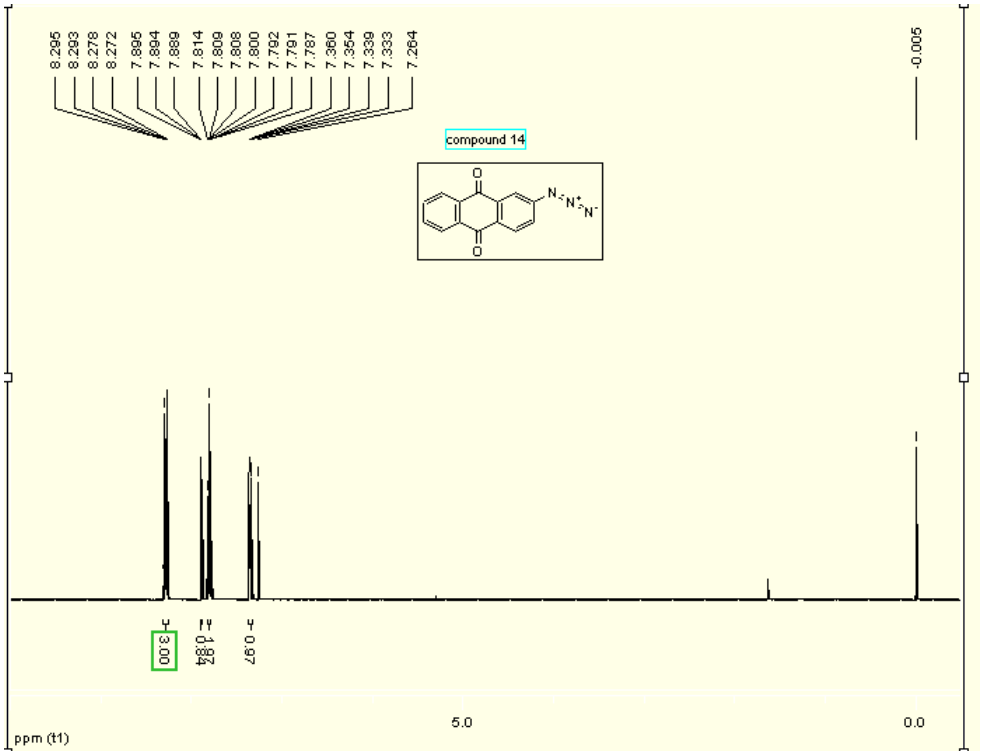


Figure S50: $^{13}C\{^{1}H\}$ NMR spectrum of compound 14 (400 MHz, *$CDCl_3$*)

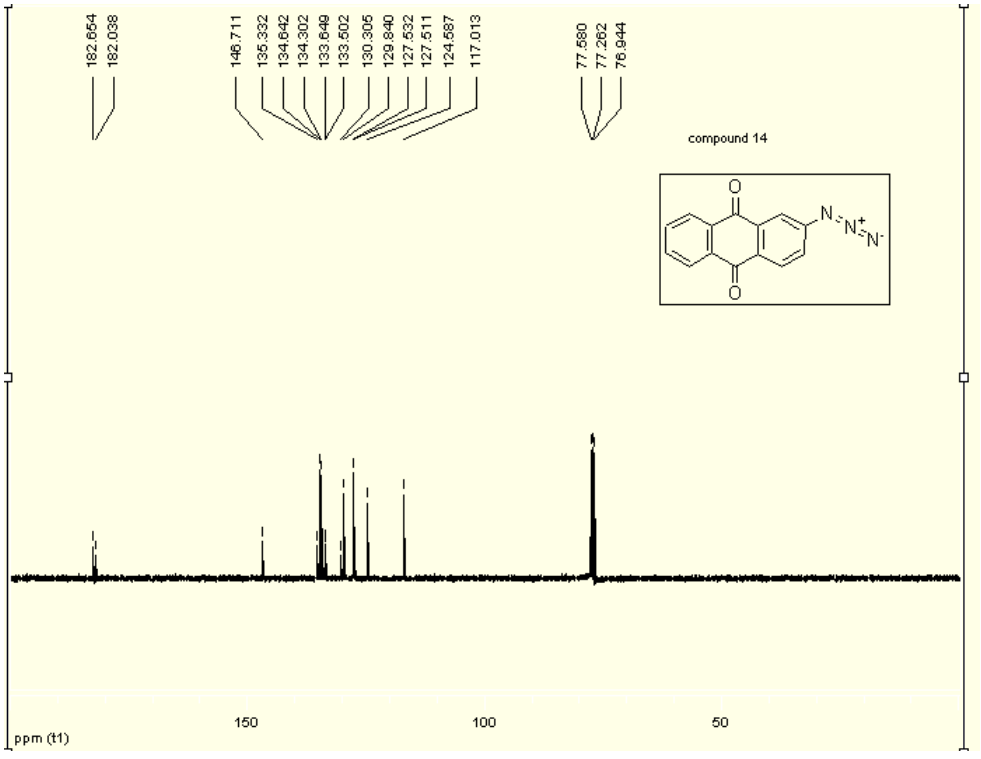


Figure S51: ^{1}H NMR spectrum of compound 16 (500 MHz, *$CDCl_3$*)

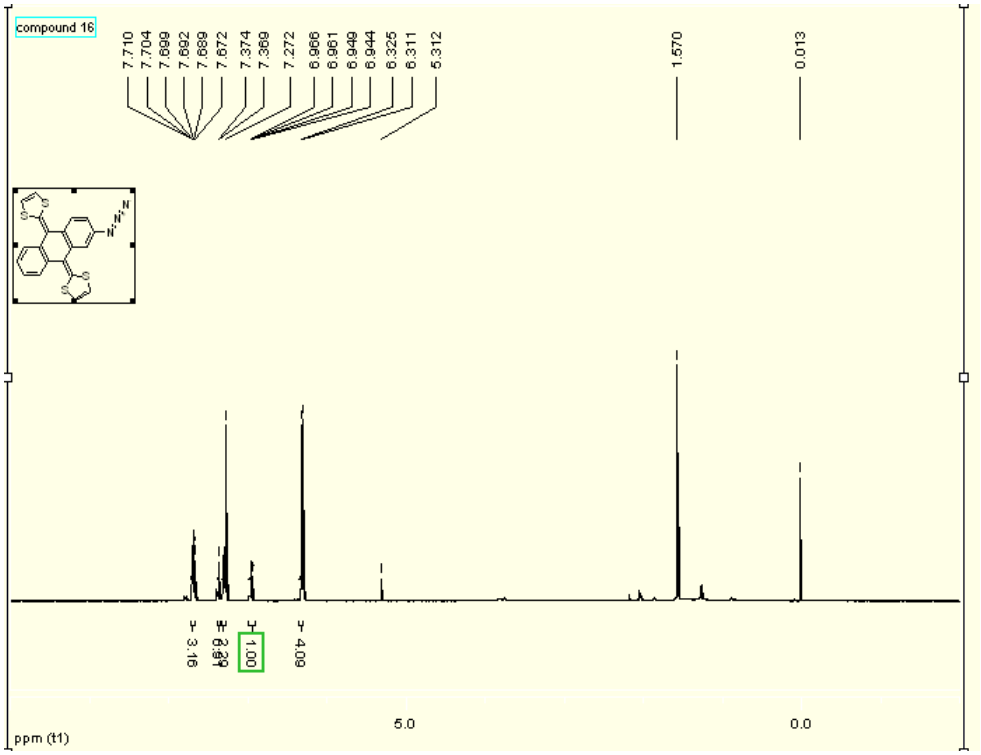


Figure S52: $^{13}C\{^{1}H\}$ NMR spectrum of compound 16 (500 MHz, *$CDCl_3$*)

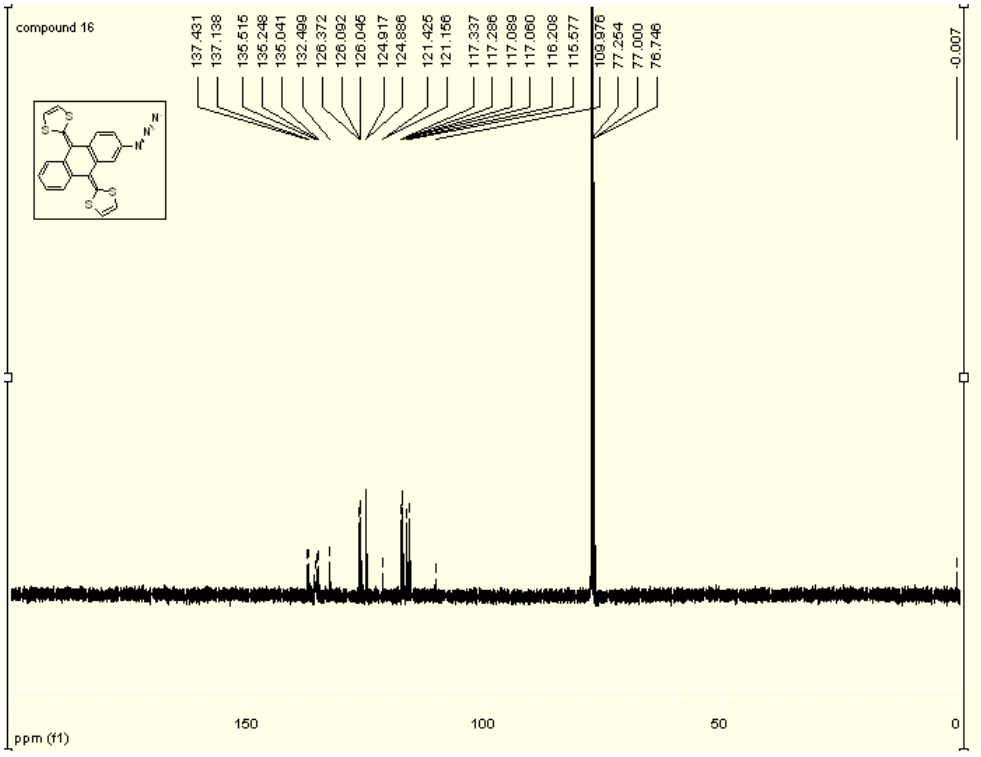


Figure S53: ^{1}H NMR spectrum of compound 17 (500 MHz, *$CDCl_3$*)

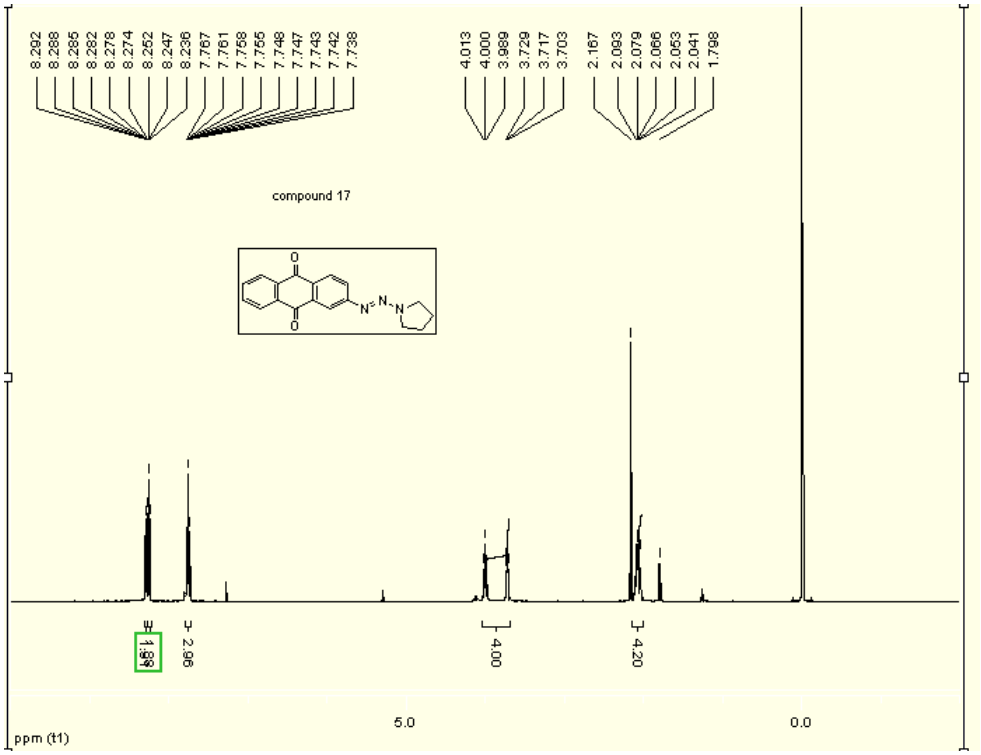


Figure S54: $^{13}C\{^{1}H\}$ NMR spectrum of compound 17 (500 MHz, *$CDCl_3$*)

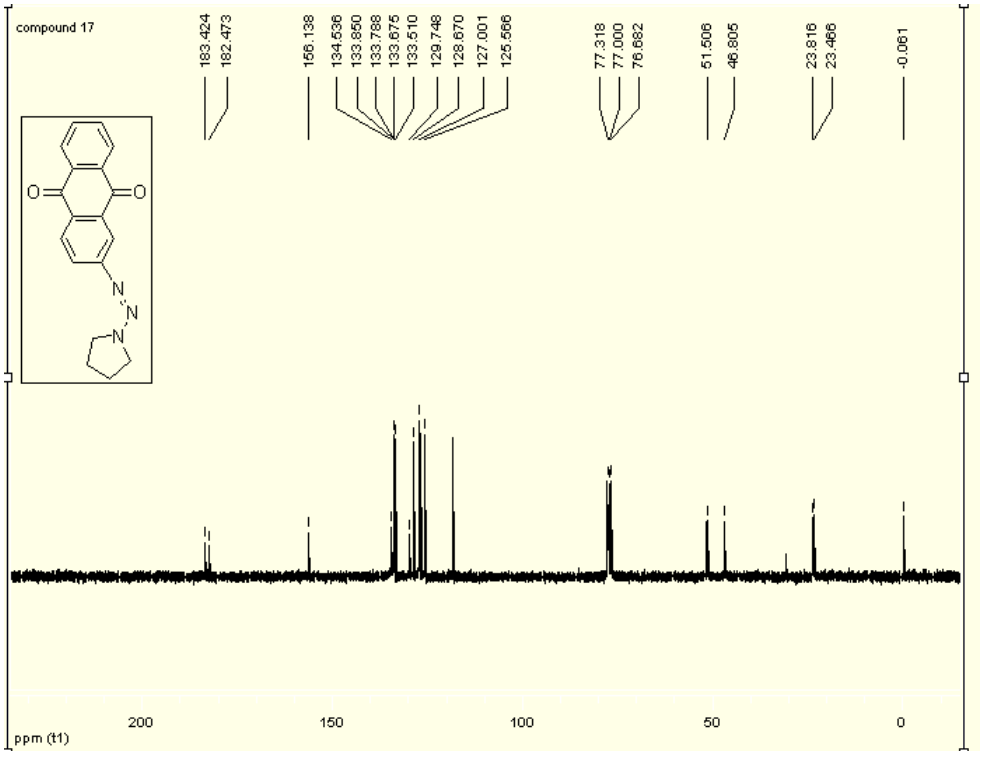


Figure S55: ^{1}H NMR spectrum of compound 18 (500 MHz, *DMSOd$_6$*)

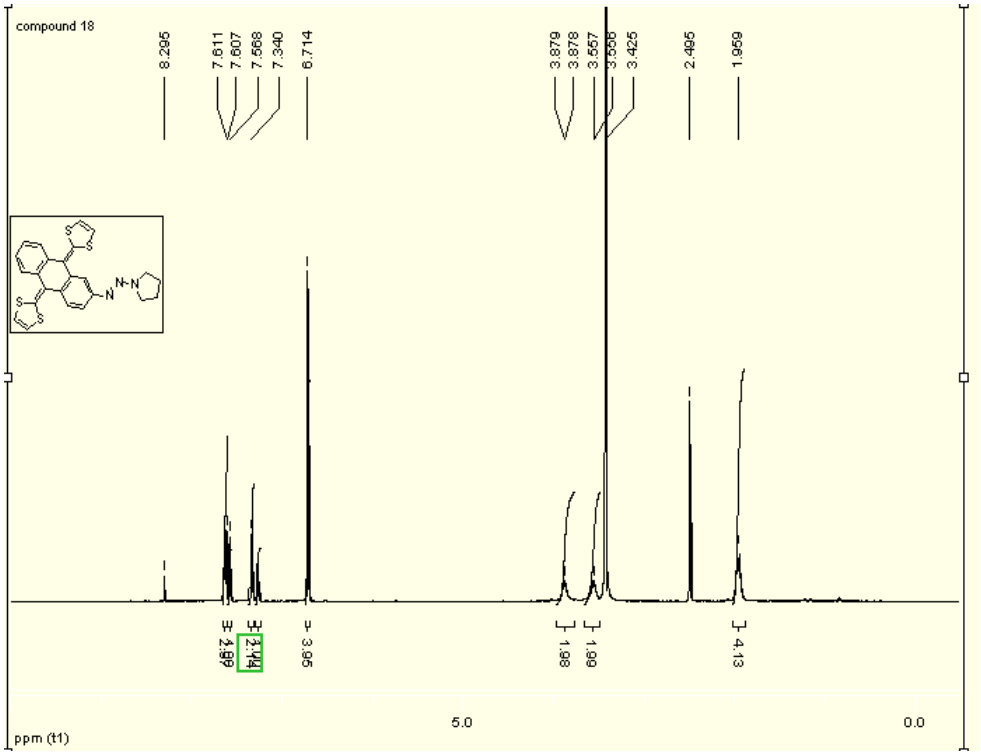


Figure S56: ^{13}C{^{1}H} NMR spectrum of compound 18 (500 MHz, *DMSOd$_6$*)

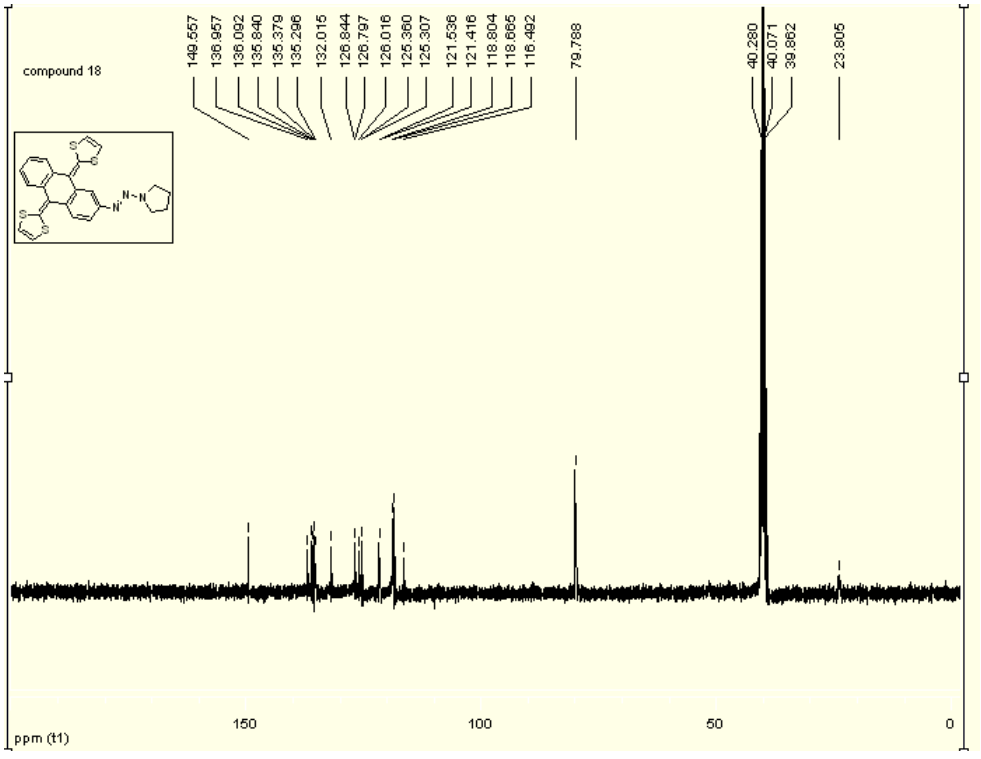


Figure S57: ^{1}H NMR spectrum of compound 19 (500 MHz, *$CDCl_3$*)

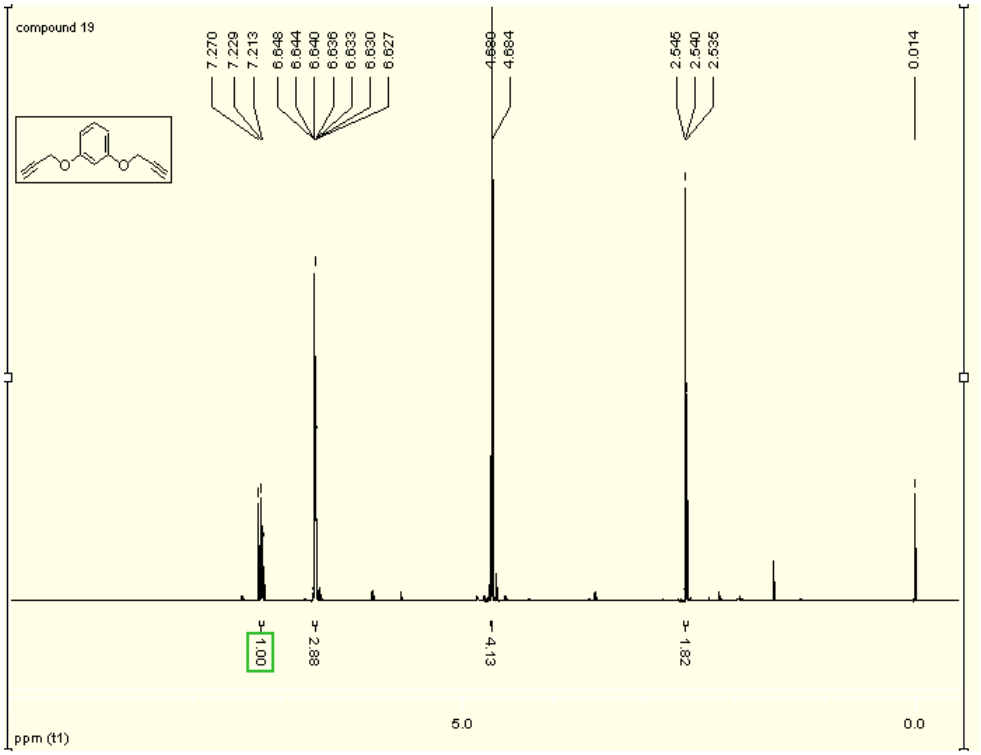


Figure S58: $^{13}C\{^{1}H\}$ NMR spectrum of compound 19 (500 MHz, *$CDCl_3$*)

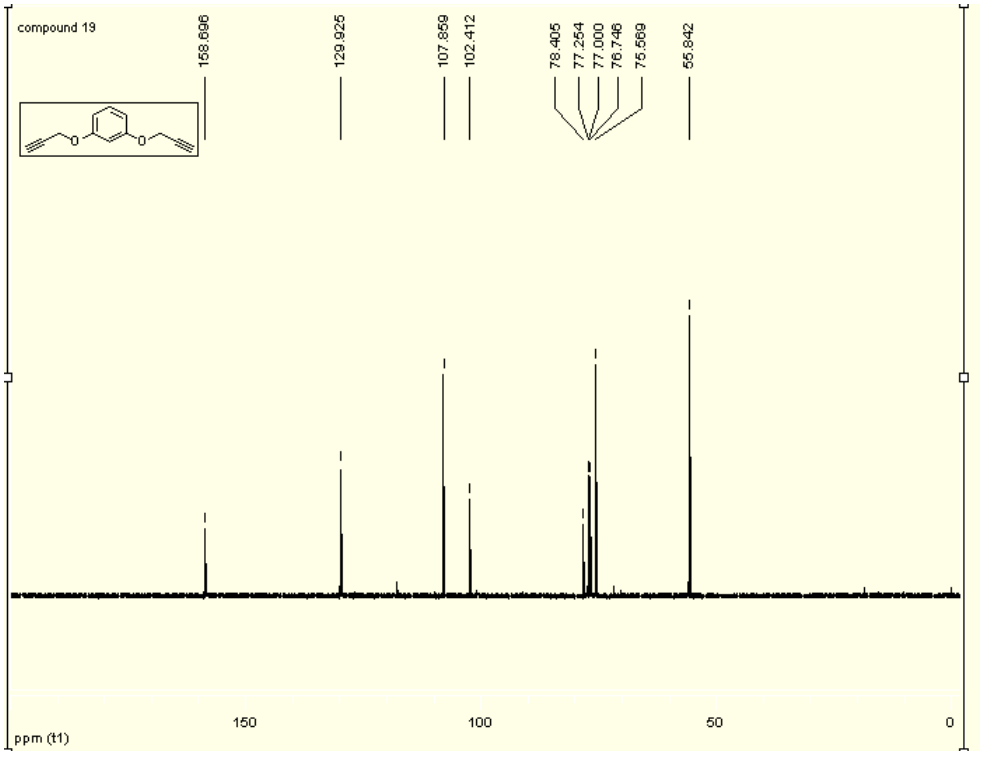


Figure S59: ^{1}H NMR spectrum of compound 21 (400 MHz, *$CDCl_3$*)

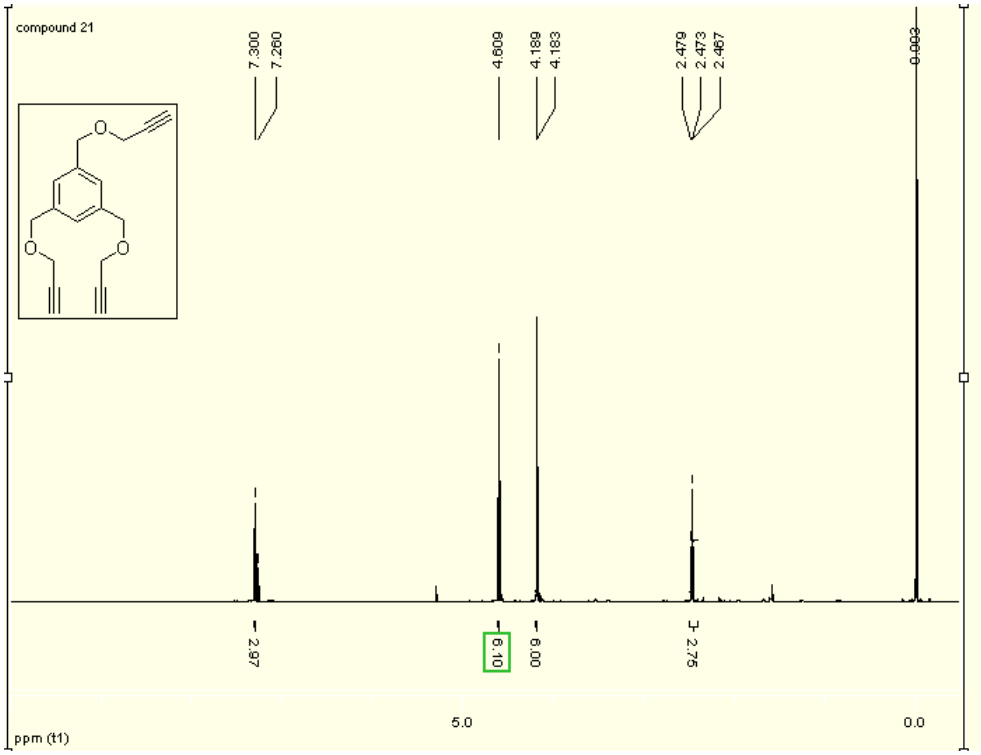


Figure S60: $^{13}C\{^{1}H\}$ NMR spectrum of compound 21 (400 MHz, *$CDCl_3$*)

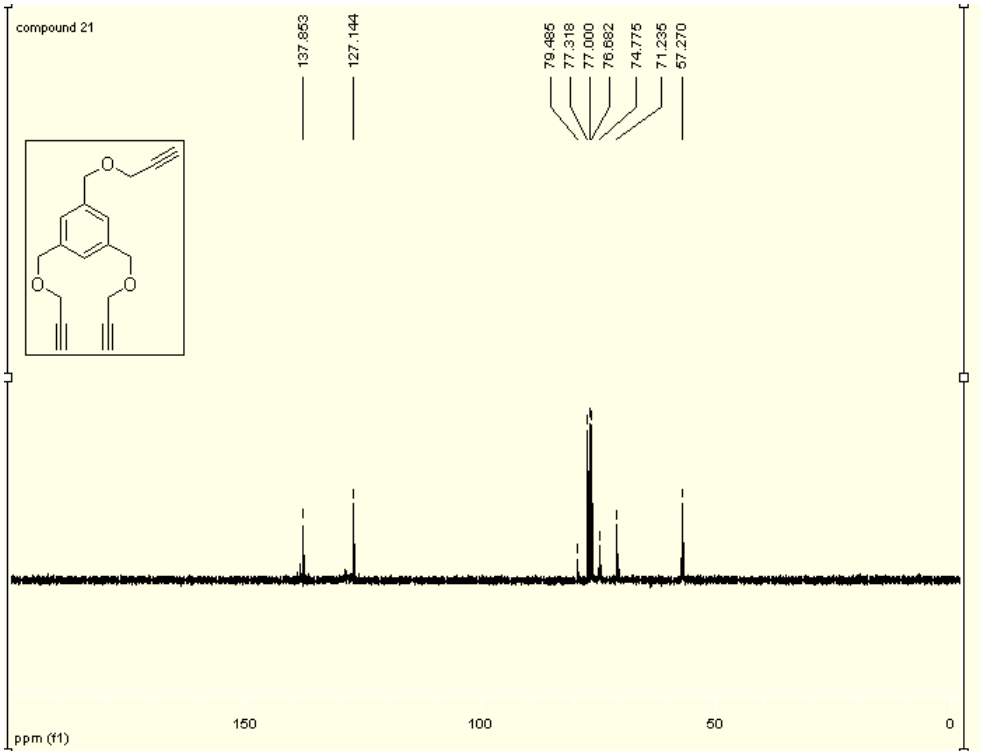


Figure S61: ^{1}H NMR spectrum of compound 23 (500 MHz, *$CDCl_3$*)

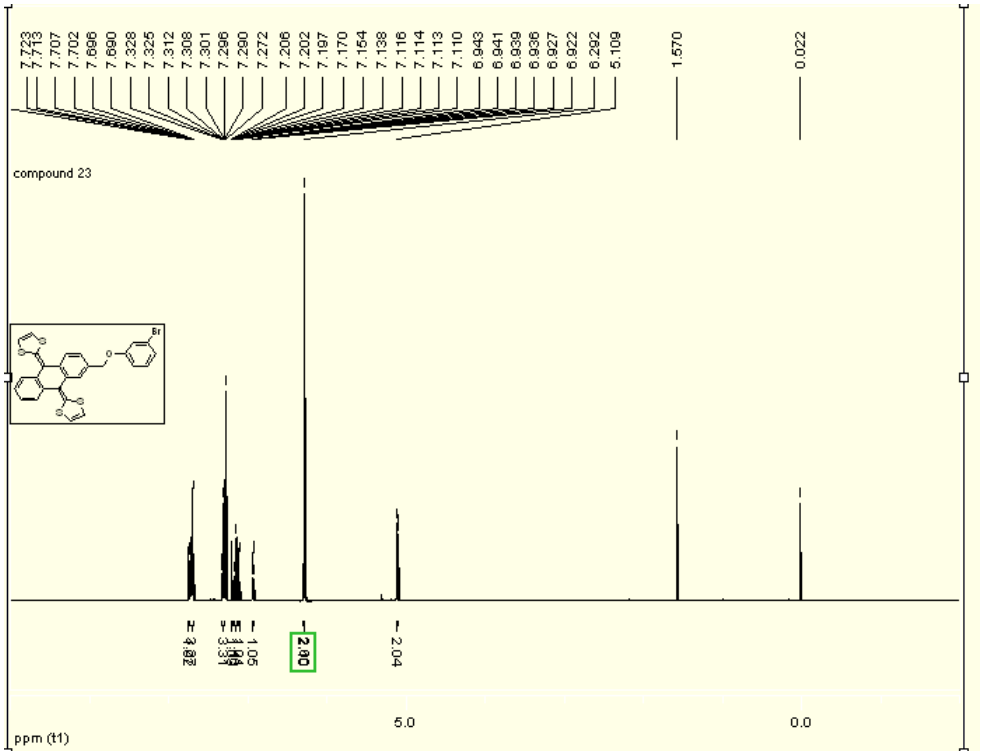


Figure S62: $^{13}C\{^{1}H\}$ NMR spectrum of compound 23 (500 MHz, *$CDCl_3$*)

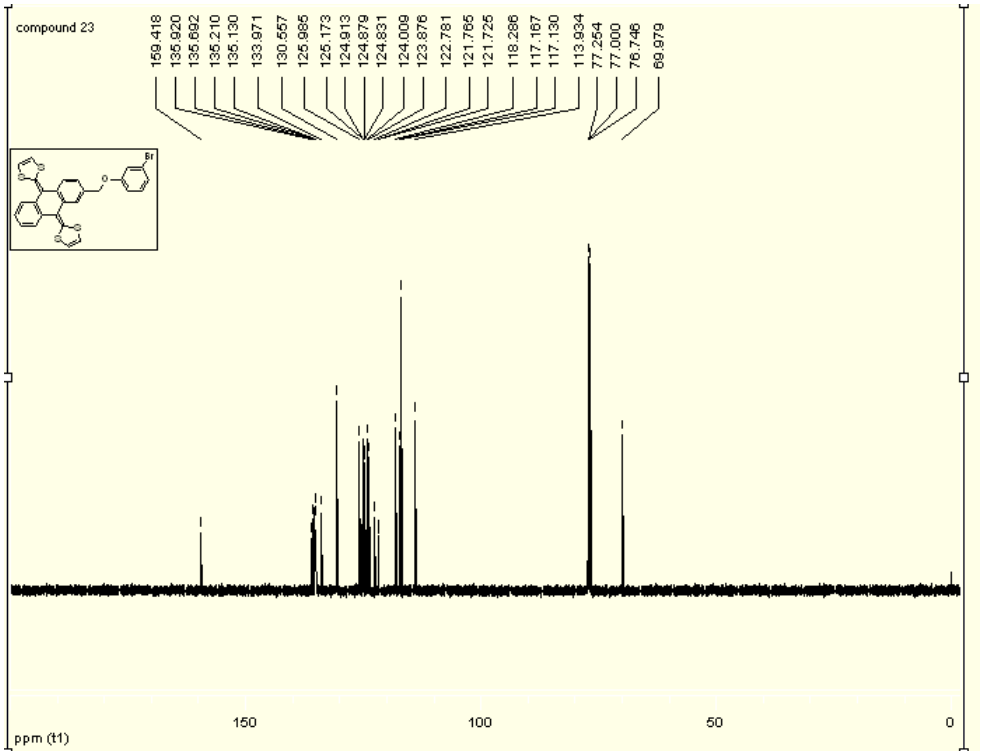


Figure S63: ^{1}H NMR spectrum of compound 24 (500 MHz, *$CDCl_3$*)

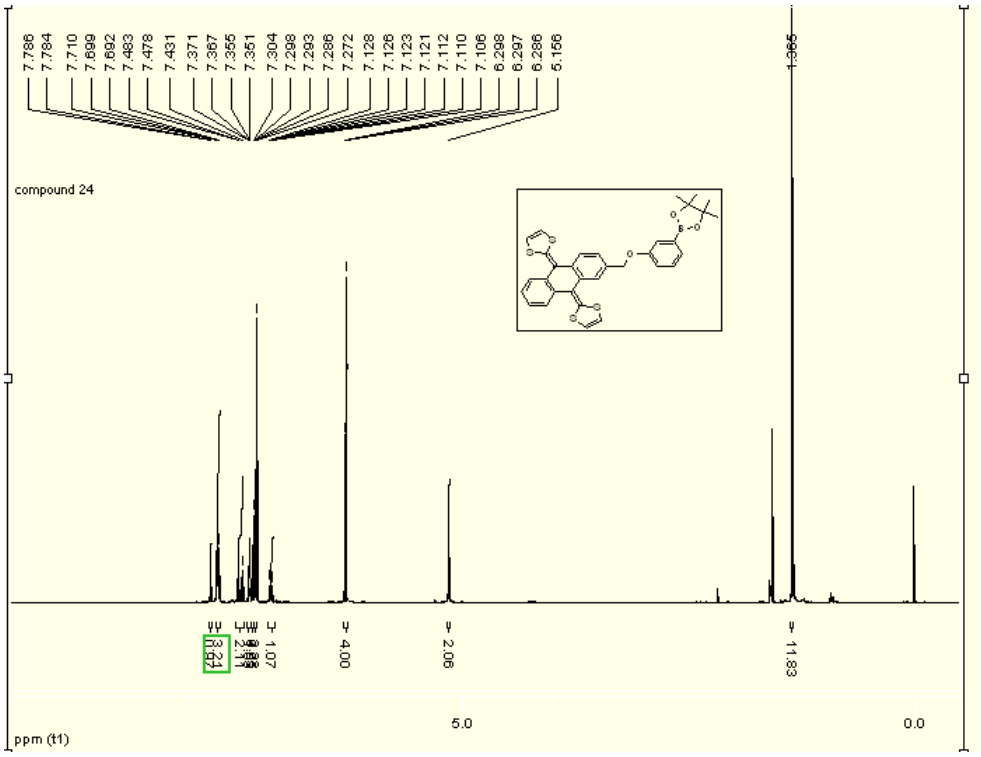
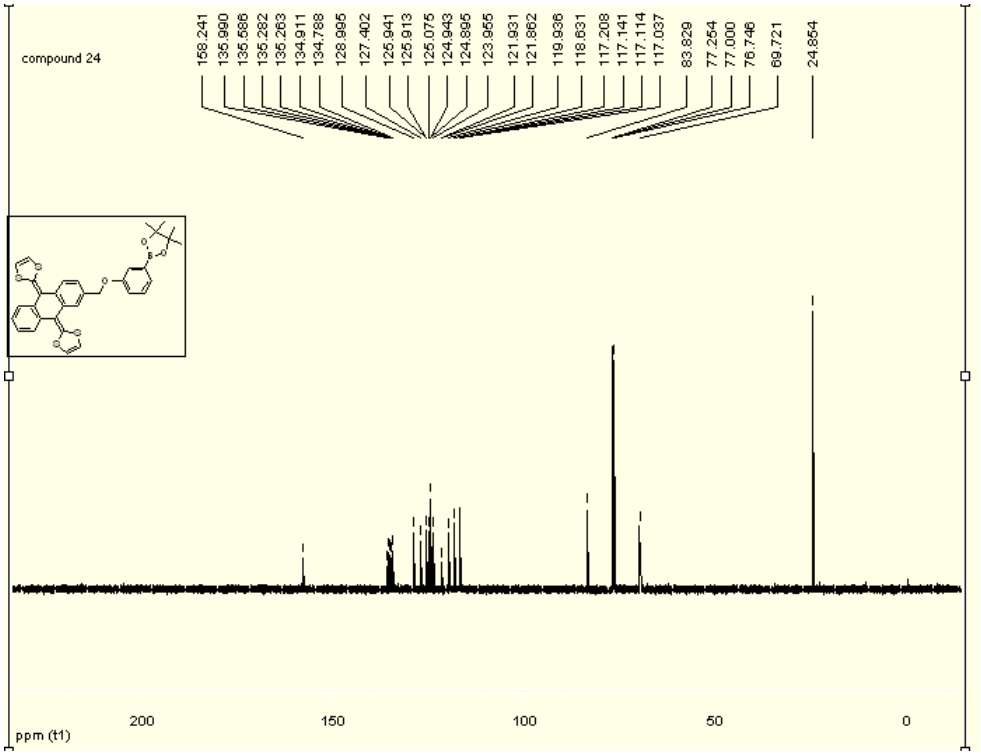



Figure S64: $^{13}C\{^{1}H\}$ NMR spectrum of compound 24 (500 MHz, *$CDCl_3$*)