Supporting Information for

An Eight-Membered Ring Formed by the Scholl Reaction of *o*-Quaterarlys

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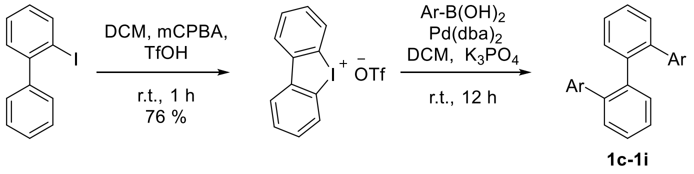
1. Synthesis

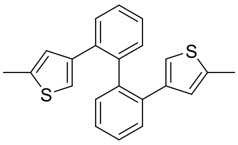
General information: The reagents and starting materials employed were commercially available and used without further purification or otherwise prepared following the reported methods as indicated. Anhydrous and O_2-free toluene were purified with sodium. Anhydrous and O_2-free CH_2Cl_2 and CH_2ClCH_2Cl was purified with calcium hydride. Super dry DMF was purchased from J&K Scientific compony. NMR spectra were recorded on Agilent, Varian and Bruker 400 MHz spectrometers (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz), and Agilent 600 MHz spectrometer (^{1}H NMR: 600 MHz, ^{13}C NMR: 150 MHz). The chemical shift was recorded in ppm and the following abbreviations were used to indicate multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Chemical shift values (δ) are expressed in parts per million using residual solvent protons (^{1}H NMR, $\delta H = 7.26$ for $CDCl_3$, $\delta H = 5.32$ for CD_2Cl_2, and $\delta H = 2.50$ ppm for DMSO-d6, $\delta H = 2.05$ for $(CD_3)_2CO$; ^{13}C NMR, $\delta C = 77.16$ for $CDCl_3$, $\delta C = 53.84$ for CD_2Cl_2, and $\delta C = 39.52$ ppm for DMSO-d6, $\delta C = 29.84$ and 206.26 for $(CD_3)_2CO$) as internal standard. Mass spectra were recorded on a AccuTOF LC-plus 4G spectrometer and Bruker Autoflex speed MALDI-TOFMS. Melting points, without correction, were measured using an Automatic melting point apparatus SGW X-4A from Shanghai INESA Physico-Optical Instrument Co., Ltd.



Scheme S1. Synthesis of **1c-1i**.

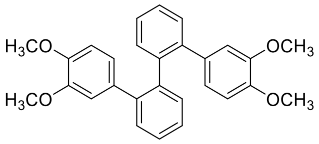
Dibenzo[b,d]iodol-5-ium triflate, **1g** and **1l** were prepared according to the reported procedures.[1]

General Procedure for the Synthesis of compounds **1c–i**:[1] Dibenzo[b,d]iodol-5-ium triflate (0.342 g, 0.80 mmol, 1.0 equiv.), arylboronic acid (2.0 mmol, 2.5 equiv.), $Pd(dba)_2$ (0.008 mmol, 0.01 equiv.), and K_3PO_4 (4 mmol, 5.0 equiv.) were added into a 100 ml Schlenk flask. The flask was charged with nitrogen atmosphere. Then, 20 ml of CH_2Cl_2 that had been pre-bubbled with nitrogen for 30 min was added into the Schlenk flask with continuous stirring. The color of reaction suspension changed from purple to brown within a few minutes. The reaction was kept stirring for 12 hours at room temperature. The solvent was then removed under reduced pressure. The residue was further purified by column chromatography on silica gel using the eluent as indicated below, affording the desired products.

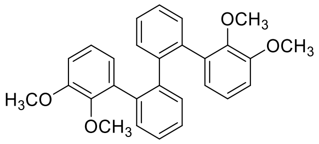


Compound **1c**: The crude product was purified by column chromatography on silica gel using hexane as eluent to obtain **1c** as white solid (0.086 g, 31% yield).

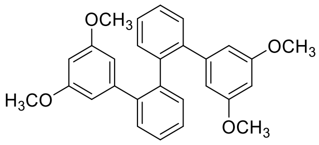
Melting point: 67-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.31$-7.30 (m, 8H), $\delta = 6.27$ (s, 2H), δ = 6.15 (s, 2H), δ = 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 140.2, 137.9, 136.2, 131.2, 129.1, 127.5, 127.0, 126.7, 120.4, 15.2; MS (APCI): calcd. for $C_{22}H_{18}S_2$ ($[M+H]^+$): 347.09227, found: 347.09172.



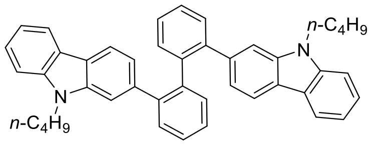
Compound **1d**: The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane 1:2 (V/V) as eluent to obtain **1d** as white solid (0.276 g, 81% yield). Melting point: 110-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.2 Hz, 2H), δ = 7.38 (t, *J* = 7.2 Hz, 2H), δ = 7.33 (t, *J* = 7.2 Hz, 2H), δ = 7.17 (d, *J* = 7.2 Hz, 2H), δ = 6.53 (d, *J* = 8 Hz, 2H), δ = 6.14 (d, *J* = 8 Hz, 2H), δ = 6.09 (s, 2H), δ = 3.82 (s, 6H), δ = 3.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 147.1, 140.5, 140.1, 133.5, 131.3, 129.4, 127.5, 126.9, 121.2, 112.2, 110.1, 55.8, 55.2; MS (APCI): calcd. for $C_{28}H_{26}O_4$ ($[M+H]^+$): 427.19039, found: 427.19009.



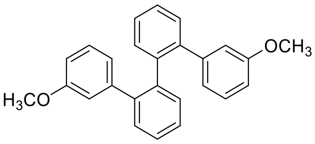
Compound **1e**: The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane 1:5 (V/V) as eluent to obtain **1e** as white solid (0.159 g, 47% yield). Melting point: 175-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 7.6 Hz, 2H), δ = 7.20 (d, *J* = 7.6 Hz, 2H), δ = 7.17-7.09 (m, 4H), δ = 6.85-6.84 (m, 2H), δ = 6.80-6.78 (m, 2H), δ = 6.65-6.64 (m, 2H), δ = 3.85 (s, 6H), δ = 3.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 146.8, 140.1, 137.1, 136.1, 131.5, 131.0, 126.6, 126.3, 124.1, 123.1, 111.2, 60.3, 55.9; MS (APCI): calcd. for $C_{28}H_{26}O_4$ ($[M+H]^+$): 427.19039, found: 427.18994.



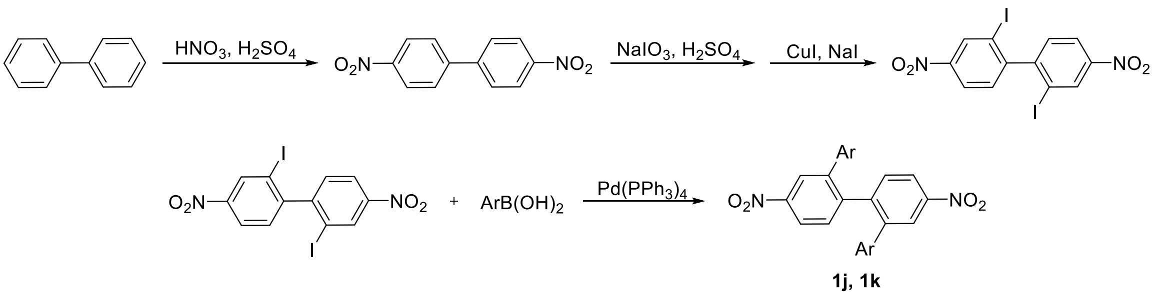
Compound **1f**: The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane 1:3 (V/V) as eluent to obtain **1f** as yellow oil (0.334 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.6 Hz, 2H), δ = 7.42 (t, *J* = 7.2 Hz, 2H), δ = 7.36 (t, *J* = 7.2 Hz, 2H), δ = 7.24 (d, *J* = 7.6 Hz, 2H), δ = 6.24 (s, 2H), δ = 5.79 (s, 4H), δ = 3.50 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 142.7, 141.1, 140.4, 131.4, 129.6, 127.7, 127.4, 107.0, 99.7, 55.0; MS (APCI): calcd. for $C_{28}H_{26}O_4$ ($[M+H]^+$): 427.19039, found: 427.19008.



Compound **1h**: The crude product was purified by column chromatography on silica gel using CH_2Cl_2/hexane 1:1 (V/V) as eluent to obtain **1h** as white solid (0.429 g, 90% yield). Melting point: 108-112 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.6 Hz, 2H), δ = 7.62-7.60 (m, 4H), δ = 7.48-7.42 (m, 4H), δ = 7.41-7.38 (t, *J* = 8 Hz, 2H), δ = 7.24-7.19 (m, 6H), δ = 6.39 (d, *J* = 8 Hz, 2H), δ = 6.28 (s, 2H), δ = 3.35-3.21 (m, 4H), δ = 1.41-1.34 (m, 4H), δ = 1.10-1.04 (m, 4H), δ = 0.77 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 140.7, 140.1, 138.7, 132.0, 130.3, 127.6, 127.2, 125.3, 122.8, 120.51, 120.47, 120.3, 118.9, 118.6, 109.6, 108.5, 41.9, 30.7, 20.3, 13.7; MS (APCI): calcd. for $C_{44}H_{40}N_2$ ($[M+H]^+$): 597.32643, found: 597.32582.



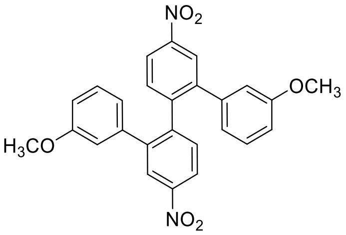
Compound **1i**: The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane 1:50 (V/V) as eluent to obtain **1i** as colorless oil (0.152 g, 52% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.6 Hz, 2H), δ = 7.40-7.35 (m, 4H), δ = 7.21 (d, *J* = 7.2 Hz, 2H), δ = 6.91 (t, *J* = 8 Hz, 2H), δ = 6.66 (d, *J* = 8.4 Hz, 2H), δ = 6.23 (d, *J* = 7.6 Hz, 2H), δ = 6.13 (s, 2H), δ = 3.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 142.3, 141.0, 140.3, 131.6, 129.9, 128.4, 127.7, 127.4, 121.9, 113.9, 112.9, 54.9; MS (APCI): calcd. for $C_{26}H_{22}O_2$ ($[M+H]^+$): 367.16926, found: 367.16855.



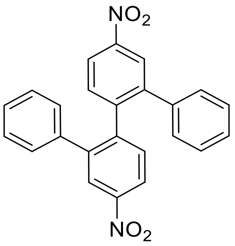
Scheme S2. Synthesis of **1j-1k**.

2,2'-Diiodo-4,4'-dinitrobiphenyl was prepared according to the reported procedures.[2, 3]

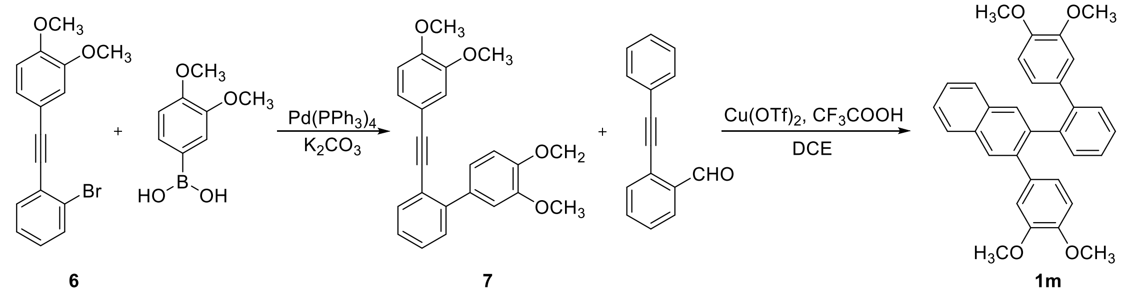
General Procedure for the synthesis of compounds **1j**, **1k**: 2,2'-Diiodo-4,4'-dinitrobiphenyl (1 eq), arylboronic acid (5 eq), Na_2CO_3 (5 eq), $Pd(PPh_3)_4$ (0.1 eq) were dissolved in a degassed mixture of toluene: ethanol: H_2O = 2: 1: 1 (0.1 M) under a N_2 atmosphere. The mixture was stirred at 80 °C overnight. Thereafter, the mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel using the eluent indicated below, affording the desired products.



Compound **1j**: The crude product was purified by column chromatography on silica gel using CH_2Cl_2/hexane 1:3 (V/V) as eluent to give **1j** as yellow solid (187 mg, 41% yield). Melting point: 168-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.4, 2.4 Hz, 2H), 8.08 (d, *J* = 2.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 6.97 (t, *J* = 8.0 Hz, 2H), 6.76 – 6.73 (m, 2H), 6.18 (d, *J* = 7.6 Hz, 2H), 6.09 (t, *J* = 2.4 Hz, 2H), 3.61 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 147.9, 144.8, 142.5, 139.3, 132.3, 129.2, 125.2, 122.3, 121.6, 114.2, 113.8, 55.1. MS (DART): calcd. for $C_{26}H_{21}O_6N_2$ ($[M+H]^+$): 457.1394, found: 457.1393.

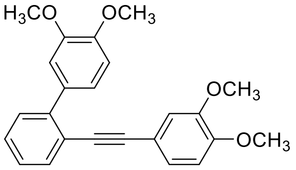


Compound **1k**: The crude product was purified by column chromatography on silica gel using CH_2Cl_2/hexane 1:5 (V/V) as eluent to obtain **1k** as yellow solid (335 mg, 21% yield). Melting point: 209-210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.8, 2.4 Hz, 2H), 8.08 (d, J = 2.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.22 – 7.18 (m, 2H), 7.08 (t, J = 7.6 Hz, 4H), 6.59 (d, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 144.6, 142.7, 138.0, 132.4, 129.0, 128.4, 127.8, 125.3, 122.2. The molecular peak of **1k** was not found in the mass spectrum using different ionization methods. Instead, the structure of 1k was identified with single crystal crystallography (Figure S45).



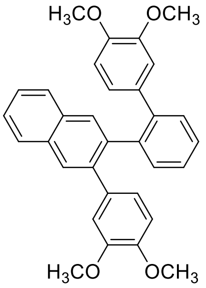
Scheme S3. Synthesis of **1m**.

Compound **6** and 2-(phenylethynyl)benzaldehyde were prepared according to the reported procedures.[4,6]



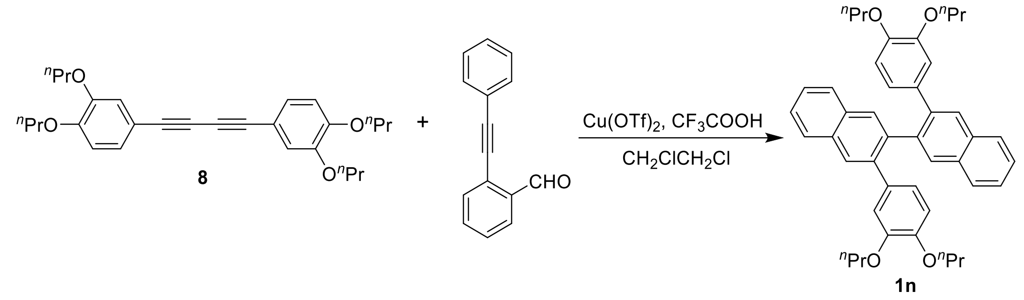
Compound **7**: Under an atmosphere of N_2, compound **6** (1.74 g, 5.49 mmol, 1 eq), 3,4-dimethoxyphenylboronic acid (1.20 g, 6.59 mmol, 1.2 eq), K_2CO_3 (1.90 g, 13.7 mmol, 2.5 eq), and $Pd(PPh_3)_4$ (634 mg, 0.55 mmol, 0.1 eq) were dissolved in a mixed solvent of 25 mL of toluene, 12.5 mL of ethanol and 12.5 mL of H_2O, which was pre-bubbled with a flow of N_2. The mixture was stirred at 80 °C overnight. Thereafter, the mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with hexane/EA 5:1 (V/V) as eluent. 1.94 g (5.19 mmol, 94% yield) of **7** collected as white solid.

Melting point: 98-99 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.28 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.82 (s, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 6H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 148.8, 148.6, 148.3, 143.6, 133.7, 132.8, 129.4, 128.4, 126.9, 124.7, 121.8, 115.8, 114.2, 113.2, 111.2, 110.9, 92.8, 88.4, 56.1, 56.0, 55.9. MS (DART): calcd. for $C_{24}H_{23}O_4$ ($[M+H]^+$): 375.1591, found: 375.1588.



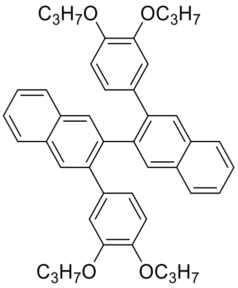
Compound **1m**: Under a nitrogen atmosphere, $Cu(OTf)_2$ (72 mg, 0.2 mmol, 0.2 eq) was added into a 50 ml Schlenk flask. The flask was then charged with a solution of 2-(phenylethynyl)benzaldehyde (412 mg, 2.0 mmol, 2 eq) in CH_2ClCH_2Cl (5.0 mL) via syringe and the mixture was stirred at rt for 30 min. Thereafter, a solution of **7** (374 mg, 1.0 mmol, 1 eq) in CH_2ClCH_2Cl (5.0 mL) and CF_3CO_2H (0.15 mL, 2.0 mmol, 2 eq) was immediately added. The mixture was heated in an oil bath to 80 °C for 3 hours. The reaction mixture was extracted with CH_2Cl_2, the combined organic phases were dried and concentrated. Purification by column chromatography on silica gel using hexane/EA 10:1 (V/V) as eluent to obtain **1m** as light yellow solid (252 mg, 53% yield).[7]

Melting point: 142-144 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.90 – 7.88 (m, 1H), 7.82 – 7.80 (m, 1H), 7.63 – 7.60 (m, 2H), 7.51 – 7.36 (m, 4H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 1H), 6.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.16 – 6.13 (m, 2H), 6.05 (d, *J* = 1.2 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.47 (s, 3H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 147.8, 147.5, 147.4, 140.9, 140.3, 139.6, 139.3, 133.64, 133.61, 133.0, 132.6, 131.8, 130.3, 129.7, 128.2, 127.9, 127.8, 127.6, 127.1, 126.3, 126.1, 121.7, 121.6, 112.5, 112.4, 110.34, 110.28, 55.91, 55.86, 55.4, 55.1. MS (EI): calcd. for $C_{32}H_{28}O_4$ (M^+): 476.1982, found: 476.2001.



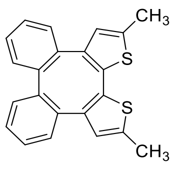
Scheme S4. Synthesis of **1n**.

Compound **8** and 2-(phenylethynyl)benzaldehyde were prepared according to the reported procedures.[5, 6]



Compound **1n**: Under a nitrogen atmosphere, $Cu(OTf)_2$ (72mg, 0.2 mmol, 0.2 eq) were added into a Schlenk flask. The flask was then charged with a solution of 2-(Phenylethynyl)benzaldehyde (618 mg, 3 mmol, 3 eq) in CH_2ClCH_2Cl (10 mL) via syringe and the mixture was stirred at rt for 30 min. Thereafter, the solution of **8** (1.0 mmol, 1 eq) in CH_2ClCH_2Cl (10 mL) and CF_3CO_2H (0.23 mL, 3 mmol, 3 eq) was added immediately. The mixture was heated with an oil bath to 80 °C for 1 hours. The reaction mixture was extracted with CH_2Cl_2, and the combined organic phases were dried and concentrated. The crude product was purified by column chromatography on silica gel using EA/hexane 1:30 (V/V) as eluent to obtain **1n** as yellow solid (364 mg, 57% yield).

Melting point: 98-100 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.93 – 7.91 (m, 2H), 7.83 – 7.81 (m, 2H), 7.63 (s, 2H), 7.53 – 7.48 (m, 4H), 6.51 (d, *J* = 8.0 Hz, 2H), 6.22 – 6.19 (m, 4H), 3.88 (t, *J* = 6.8 Hz, 4H), 3.34 (q, *J* = 7.2 Hz, 2H), 3.06 (q, *J* = 7.2 Hz, 2H), 1.85 – 1.76 (m, 4H), 1.50 – 1.39 (m, 4H), 1.02 (t, *J* = 7.6 Hz, 6H), 0.71 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 147.6, 139.7, 139.6, 133.8, 133.2, 132.7, 130.4, 128.3, 127.8, 127.6, 126.2, 126.1, 121.8, 115.1, 113. 6, 71.0, 70.1, 22.8, 22.4, 10.6, 10.1. MS (DART): calcd. for $C_{44}H_{47}O_4$ ($[M+H]^+$): 639.3469, found: 639.3463.



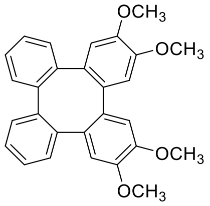
Compound **2c**

Method A: To a solution of **1c** (0.0069 g, 0.02 mmol) in 18 ml of anhydrous CH_2Cl_2, 0.0324 g

(0.2 mmol, 10 equiv.) of $FeCl_3$ in 1.8 ml CH_3NO_2 was added under nitrogen atmosphere. The reaction mixture turned to red brown immediately, which was kept stirred at room temperature for 1.5 hours. The solution was quenched with 8 ml of MeOH, and then washed with water. The resulting solution was extracted with CH_2Cl_2. The organic layers were combined and dried over anhydrous Na_2SO_4. The solution was concentrated under a reduced pressure. The residue was further purified by plate chromatography on silica gel with CH_2Cl_2/hexane 1:10 (V/V) as eluent to afford 4.8 mg of **2c** as white solid in a yield of 70%.

Method B: To a solution of **1c** (13.8 mg, 0.04 mmol) and DDQ (27.2mg, 0.12 mmol) in 36 ml of anhydrous CH_2Cl_2 at room temperature, 3.6 ml of CH_3SO_3H was added slowly. The yellow reaction system became dark immediately. The reaction was stirred for 30 minutes. Triethylamine was added to quench this reaction and the color changed to dark brown. The resulting solution was washed with water and the organic layer was collected, dried with anhydrous Na_2SO_4. After the solution being concentrated by rotary evaporation, CH_2Cl_2/hexane 1:10 (V/V) was used as eluent to further purify the crude product by plate chromatography on silica gel, yielding 8.7 mg (63%) of **2c** as white solid.

Melting point: 245-247 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.32-7.30$ (m, 4H), $\delta = 7.20-7.17$ (m, 2H), $\delta = 7.14-7.11$ (m, 2H), $\delta = 6.71$ (s, 2H), $\delta = 2.44$ (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 141.7, 140.4, 137.2, 131.7, 129.74, 129.70, 127.9, 127.5, 127.1, 15.5; MS (APCI): calcd. for $C_{22}H_{16}S_2$ ($[M+H]^+$): 345.07662, found: 345.07654.

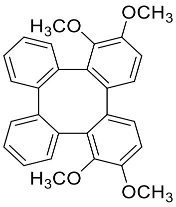


Compound **2d**

Method A: To a solution of **1d** (0.0085 g, 0.02 mmol) in 18 ml of anhydrous CH_2Cl_2, 0.0324 g (0.2 mmol, 10 equiv.) of $FeCl_3$ in 1.8 ml CH_3NO_2 was added under a nitrogen atmosphere. The reaction mixture, which turned red brown immediately, was kept stirred at room temperature for 1 hour. The solution was quenched with 8 ml of MeOH, and then washed with water. The resulting solution was extracted with CH_2Cl_2. The organic layer was combined together and dried over anhydrous Na_2SO_4. The solution was concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane 1:2 (V/V) as eluent to afford 0.0076 g of **2d** as white solid in a yield of 90%.

Method B: To a solution of **1d** (0.0607 g, 0.142 mmol) and DDQ (0.0484 g, 0.213 mmol) in 65 ml of anhydrous CH_2Cl_2 at room temperature, 6.5 ml of CH_3SO_3H was added slowly. The reaction mixture, which turned dark blue immediately, was stirred for at room temperature for 30 minutes. After triethylamine was added to the mixture to quench this reaction, the resulting dark brown solution was washed with water, and then dried with anhydrous Na_2SO_4. The solution was concentrated under a reduced pressure, and the residue was purified by column chromatography on silica gel using ethyl acetate/hexane 1:2 (V/V) as eluent to afford 0.0530 g (88%) of **2d** as white solid.

The ^1H NMR spectrum is consistent with the reported one.[8]

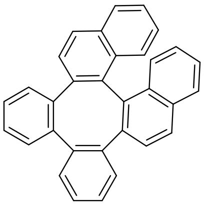


Compound **2e**

Method A: To a solution of **1e** (0.0213 g, 0.05 mmol) in 4 ml of anhydrous CH_2Cl_2, 0.0811 g (0.5 mmol, 10 equiv.) of $FeCl_3$ in 0.4 ml of CH_3NO_2 was added under a nitrogen atmosphere. The reaction mixture was kept stirred at room temperature for 20 min. The solution was quenched with MeOH, and then washed with water, and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined and dried over anhydrous Na_2SO_4. The solution was concentrated under a reduced pressure. The residue was purified by plate chromatography on silica gel with ethyl acetate/hexane 1:5 (V/V) as eluent to afford 0.0123 g of **2e** as white solid in a yield of 58%.

Method B: To a solution of **1e** (0.0212 g, 0.050 mmol) and DDQ (0.0170 g, 0.075 mmol) in 44 ml of anhydrous CH_2Cl_2 at room temperature, 4.4 ml of CH_3SO_3H was added slowly. The yellow reaction mixture, which became dark gradually, was stirred at room temperature for 30 minutes. After triethylamine was added to the mixture to quench this reaction, the resulting yellow solution was washed with water and the organic layer was dried with anhydrous Na_2SO_4. The solution was concentrated under a reduced pressure, and the residue was purified by column chromatography on silica gel using ethyl acetate/hexane 1:4 (V/V) as eluent, yielding 0.0148 g (72%) of **2e** as white solid.

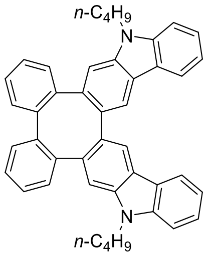
Melting point: 167-169 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.31-7.28 (m, 4H), δ = 7.21 (d, J = 6.8 Hz, 2H), δ = 7.14 (d, J = 6.8 Hz, 2H), δ = 6.89-6.83 (m, 4H), δ = 3.81 (s, 6H), δ = 3.35 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 151.8, 145.7, 142.0, 136.9, 135.6, 135.3, 130.2, 128.5, 127.4, 126.8, 124.4, 111.2, 60.0, 55.8; MS (APCI): calcd. for $C_{28}H_{24}O_4$ ($[M+H]^+$): 425.17474, found: 425.17433.



Compound **2g**

To a solution of **1g** (40.6 mg, 0.1 mmol) in 8 ml of anhydrous CH_2Cl_2, 162.2 mg (1.0 mmol, 10 equiv.) of $FeCl_3$ in 0.8 ml CH_3NO_2 was added under Ar. The reaction was stirred at room temperature for 10 minutes. The reaction mixture was quenched with H_2O, and then extracted with CH_2Cl_2. The organic layers were combined and dried over anhydrous Na_2SO_4. The solution was concentrated under a reduced pressure, and the residue was purified by thin layer chromatography on silica gel using ethyl acetate/hexane 1:30 (V/V) as eluent, yielding 16.2 mg (40%) of **2g** as white solid.

Melting point: 280-281 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 4H), 7.43 – 7.35 (m, 4H), 7.33 – 7.30 (m, 2H), 7.24 – 7.20 (m, 4H), 7.19 – 7.14 (m, 4H), 6.98 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 141.8, 139.9, 135.3, 132.5, 132.4, 129.1, 128.1, 128.0, 127.9, 127.5, 127.4, 127.2, 127.0, 126.3, 125.6. MS (DART): calcd. for $C_{32}H_{24}N$ ($[M+NH_4]^+$):422.1903, found: 422.1901.

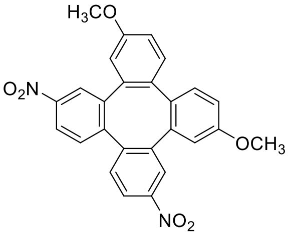


Compound **2h**

Method A: To a solution of **1h** (0.0117 g, 0.02 mmol) in 20 ml of anhydrous CH_2Cl_2, 0.0128 g (0.08 mmol, 4 equiv.) of $FeCl_3$ in 2 ml CH_3NO_2 was added dropwise under a nitrogen atmosphere. The reaction mixture which turned green immediately, was stirred at room temperature for 1 minute. The resulting solution was quenched with 4 ml of MeOH, and washed with water. The aqueous layer was extracted with CH_2Cl_2, and the organic layers were combined and dried over anhydrous Na_2SO_4. The solution was concentrated under a reduced pressure, and the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane 1:4 (V/V) as eluent to afford 0.0090 g of **2h** as white solid in a yield of 77%.

Method B: To a solution of **1h** (0.0045 g, 0.0075 mmol) and DDQ (0.0026 g, 0.0113 mmol) in 7 ml of anhydrous CH_2Cl_2 at room temperature, 0.7 ml of CH_3SO_3H was added slowly. The yellow reaction mixture, which became deep green immediately, was stirred at room temperature for 30 minutes. After triethylamine was added to the mixture to quench this reaction, the resulting yellow solution was washed with water and the organic layer was dried with anhydrous Na_2SO_4. The solution was concentrated under a reduced pressure, and the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane 1:4 (V/V) as eluent, yielding 0.0004 g (9%) of **2h** as white solid.

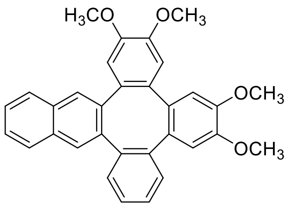
Melting point: 330-332 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.03 (d, J = 8 Hz, 2H), δ = 7.97 (s, 2H), δ = 7.45-7.41 (m, 4H), δ = 7.35-7.30 (m, 6H), δ = 7.25 (s, 2H), δ = 7.23-7.18 (m, 4H), δ = 4.29 (t, J = 8 Hz, 4H), δ = 1.88-1.83 (m, 4H), δ = 1.44-1.39 (m, 4H), δ = 0.95 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 143.3, 142.4, 141.4, 140.3, 140.0, 134.0, 129.7, 129.4, 127.7, 127.5, 126.0, 122.9, 122.3, 121.7, 120.7, 119.2, 109.3, 109.2, 43.4, 31.5, 20.9, 14.1; MS (APCI): calcd. for $C_{44}H_{38}N_2$ ($[M+H]^+$): 595.31078, found: 595.31032.



Compound **2j**

To a solution of **1j** (11.4 mg, 0.025 mmol) and DDQ (17 mg, 0.075 mmol) in 2 ml of anhydrous CH_2Cl_2 under an atmosphere of argon, 0.066 ml of TfOH was added. After being stirred at room temperature for 5 minutes, the reaction mixture was quenched with a saturated aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under a reduced pressure. The residue was purified by thin layer chromatography on silica gel using ethyl acetate/hexane 1:7 (V/V) as eluent, yielding 4.7 mg (41%) of **2j** as yellow solid.

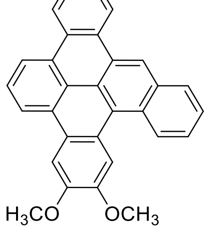
Melting point: 278-279 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.4, 2.4 Hz, 2H), 8.09 (d, J = 2.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.89 (dd, J = 6.0, 2.4 Hz, 2H), 6.70 (d, J = 2.4 Hz, 2H), 3.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 147.8, 146.0, 143.2, 139.8, 132.9, 131.1, 129.9, 124.3, 122.6, 114.4, 114.3, 55.5. MS (DART): calcd. for $C_{26}H_{18}O_6N_2$ (M^+):454.1159, found: 454.1162.



Compound **2m**

Method B: To a solution of **1m** (11.9 mg, 0.025 mmol) and DDQ (17 mg, 0.075 mmol) in 5 ml of anhydrous CH_2Cl_2 under an atmosphere of argon, 0.049 ml of CH_3SO_3H was added. The reaction mixture, which was cooled with an ice-salt bath, was stirred for 2 minutes. It was quenched with a saturated aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by thin layer chromatography on silica gel using ethyl acetate/hexane 1:3 (V/V) as eluent, yielding 4.8 mg (41%) of **2m** as white solid and 2.4 mg (21%) of **3m** as yellow solid.

Melting point: 153-154 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.27 (m, 1H), 7.23 – 7.21 (m, 1H), 6.78 (s, 1H), 6.71 (s, 1H), 6.69 (s, 1H), 6.68 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.21, 148.19, 148.1, 148.0, 142.02, 141.96, 141.0, 140.6, 134.1, 134.0, 133.6, 132.7, 132.6, 129.7, 129.3, 128.1, 127.9, 127.8, 127.7, 127.5, 127.3, 126.2, 126.1, 112.8, 112.4, 56.2, 56.12, 56.10, 56.06. MS (DART): calcd. for $C_{32}H_{27}O_4$ ($[M+H]^+$): 475.1904, found: 475.1905.

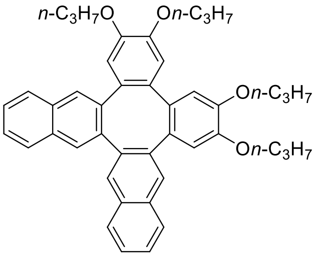


Compound **3m**

Method A: To a solution of **1m** (11.9 mg, 0.025 mmol) in 10 ml of anhydrous CH_2Cl_2, 41 mg (0.25 mmol, 10 equiv.) of $FeCl_3$ in 0.2 ml CH_3NO_2 was added under an atmosphere of argon. After being stirred at 0 ºC for 5 minutes, the reaction mixture was quenched with H_2O and extracted with CH_2Cl_2. The organic layers were combined together and dried over anhydrous

Na_2SO_4. The solution was concentrated under a reduced pressure. The residue was purified by thin layer chromatography on silica gel using CH_2Cl_2/hexane 2:1 (V/V), yielding 9.2 mg (78%) of **3m** as off-white solid.

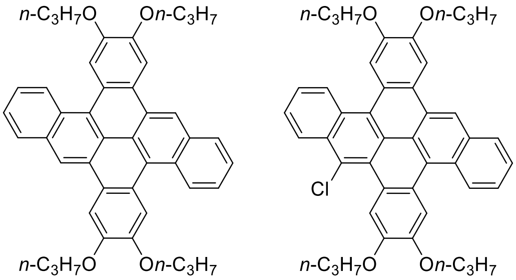
Melting point: 185-186 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, J = 8.0 Hz, 1H), 8.95 (s, 1H), 8.70 (d, J = 8.0 Hz, 1H), 8.59 (d, J = 8.0 Hz, 1H), 8.51 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 8.20 – 8.19 (m, 2H), 8.04 (s, 1H), 7.99 (t, J = 8.0 Hz, 1H), 7.72 – 7.64 (m, 2H), 4.23 (s, 3H), 4.22 (s, 3H), 4.18 (s, 3H), 4.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 149.6, 149.0, 148.4, 132.4, 129.4, 129.1, 128.7, 127.5, 127.3, 127.0, 126.2, 126.1, 125.8, 125.6, 124.8, 124.33, 124.30, 124.1, 123.0, 122.2, 119.9, 119.8, 119.5, 111.4, 105.1, 105.0, 104.8, 56.2, 56.14, 56.12, 56.0. MS (DART): calcd. for $C_{32}H_{25}O_4$ ([M+H]+):473.1747, found: 473.1749.



Compound **2n**

Method B: To a solution of **1n** (16mg, 0.025 mmol) and DDQ (17 mg, 0.075 mmol) in 5 ml of anhydrous CH_2Cl_2 under an atmosphere of argon, 0.049 ml of CH_3SO_3H was added. The reaction mixture, which was cooled with an ice-salt bath, was stirred for 2 minutes. It was quenched with a saturated aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2. The combined organic phases were combined, dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by thin layer chromatography on silica gel using CH_2Cl_2/hexane 1:1 (V/V) as eluent, yielding 12.8 mg (81%) of **2n** as white solid.

Melting point: 117-118 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 - 7.81 (m, 4H), 7.72 (s, 2H), 7.66 (s, 2H), 7.49 – 7.44 (m, 4H), 6.78 (s, 2H), 6.72 (s, 2H), 3.99 – 3.94 (m, 4H), 3.91 – 3.83 (m, 4H), 1.84 –1.74 (m, 8H), 0.99 (q, J = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 148.2, 141.0, 140.9, 134.15, 134.07, 132.8, 132.6, 128.2, 127.9, 127.8, 127.7, 126.1, 126.0, 115.2, 115.0, 71.0, 70.9, 22.82, 22.78, 10.63, 10.62. MS (DART): calcd. for $C_{44}H_{44}O_4$ (M^+): 636.3234, found: 636.3237.

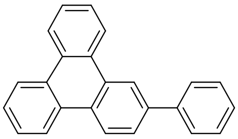


Compounds **3n** and **3n-Cl**

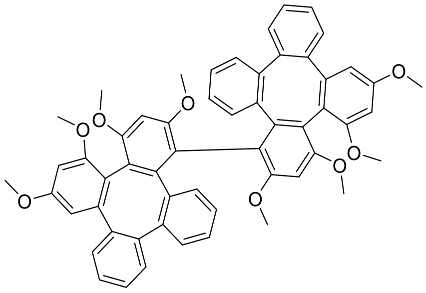
Method A: To a solution of **1n** (16 mg, 0.025 mmol) in 10 ml of anhydrous CH_2Cl_2 under an atmosphere of argon, 41 mg (0.25 mmol, 10 equiv.) of $FeCl_3$ in 0.2 ml CH_3NO_2 was added. After being stirred at 0 °C for 5 minutes, the reaction mixture was quenched with H_2O. The resulting solution was extracted with CH_2Cl_2. The organic layers were combined and dried over anhydrous Na_2SO_4. The solution was then concentrated under a reduced pressure. The residue was purified by thin layer chromatography on silica gel using CH_2Cl_2/hexane 1:1 (V/V) as eluent, yielding 6.6 mg (41%) of **3n** as yellow solid and 4.2 mg (25%) of **3n-Cl** as yellow solid.

Compound **3n**
Melting point: 257-258 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.03 (d, J = 8.4 Hz, 2H), 8.91 (s, 2H), 8.29 – 8.26 (m, 6H), 7.65 – 7.59 (m, 4H), 4.36 (t, J = 6.6 Hz, 4H), 4.18 (t, J = 6.6 Hz, 4H), 2.10 – 2.04 (m, 4H), 2.02 – 1.96 (m, 4H), 1.22 (t, J = 7.2 Hz, 6H), 1.15(t, J = 7.2 Hz, 6H).1 ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.4, 148.8, 133.0, 128.9, 127.6, 127.3, 127.2, 126.0, 125.7, 125.6, 125.2, 124.7, 123.5, 119.5, 114.3, 108.3, 71.2, 71.1, 23.0, 22.9, 10.9, 10.7. MS (MALDI): calcd. for $C_{44}H_{42}O_4$ (M+): 634.3078, found: 634.3075.

Compound **3n-Cl**
Melting point: 227-229 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, J = 8.4 Hz, 1H), 9.00 – 8.96 (m, 2H), 8.86 – 8.83 (m, 2H), 8.23 (dd, J = 6.4, 3.2 Hz, 1H), 8.16 (s, 1H), 8.15 (s, 2H), 7.75 (t, J = 7.6 Hz, 1H), 7.67 – 7.62 (m, 3H), 4.34 (t, J = 6.4 Hz, 2H), 4.27 (t, J = 6.4 Hz, 2H), 4.16 (t, J = 6.4 Hz, 4H), 2.10 – 1.92 (m, 8H), 1.23 – 1.10 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 148.64, 148.62, 146.9, 133.2, 130.8, 128.8, 128.6, 127.2, 127.1, 126.85, 126.80, 126.6, 126.4, 126.1, 125.9, 125.8, 125.7, 125.5, 125.4, 125.3, 125.25, 125.23, 124.3, 123.7, 123.6, 123.5, 119.6, 114.4, 114.3, 113.4, 108.1, 71.02, 70.97, 70.9, 70.8, 22.9, 22.8, 22.72, 22.71, 10.9, 10.8, 10.72, 10.71. MS (MALDI): calcd. for $C_{44}H_{41}O_4Cl$ (M^+): 668.2688, found: 668.2685.



Compound **4l**
To a solution of **1l** (7.7 mg, 0.025 mmol) and DDQ (17 mg, 0.075 mmol) in 2 ml of anhydrous CH_2Cl_2 under an atmosphere of argon, 0.066 ml of TfOH was added. After being stirred at room temperature for 10 minutes, the reaction mixture was quenched with a saturated aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under a reduced pressure. The residue was purified by thin layer chromatography on silica gel using hexane as eluent, yielding 0.8 mg (11%) of **4l** as white solid.
The ^{1}H NMR spectrum is consistent with the reported one.[9]



Compound **5**

To a solution of **1f** (0.0355 g, 0.08 mmol) in 5 ml of anhydrous CH_2Cl_2, 0.063 g (0.2 3mmol, 2.7 equiv.) of $MoCl_5$ was added under a nitrogen atmosphere. The reaction mixture, which turned dark gradually, was stirred at room temperature for 40 min. After being quenched with a saturated $NaHCO_3$ aqueous solution, the reaction mixture was washed with water. The aqueous layer was extracted with CH_2Cl_2, and the organic layers were combined and dried over anhydrous Na_2SO_4. The solution was concentrated under a reduced pressure. The residue was further purified by column chromatography on silica gel with ethyl acetate /hexane 1:1 (V/V) as eluent to afford 0.0092 g of **5** as white solid in a yield of 26%.

Melting point: 334-336 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.36-7.31 (m, 4H), δ = 7.28-7.23 (m, 4H), δ = 7.06 (t, *J* = 7.2 Hz, 2H), δ = 7.02-6.97 (m, 4H), δ = 6.87 (t, *J* = 7.6 Hz, 2H), δ = 6.42 (d, *J* = 2.4 Hz, 2H), δ = 6.29 (d, *J* = 2.4 Hz, 2H), δ = 6.04 (s, 2H), δ = 3.76 (s, 12H), δ = 3.55 (s, 6H), δ = 3.31 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ =159.7, 158.5, 157.9, 156.9, 143.9, 143.0, 142.8, 142.7, 142.6, 139.7, 129.9, 129.8, 128.1, 127.7, 127.4, 127.2, 126.1, 125.6, 120.1, 119.3, 117.5, 105.1, 97.9, 95.9, 56.8, 56.5, 55.9, 55.6; MS (APCI): calcd. for $C_{56}H_{46}O_8$ ($[M+H]^+$): 847.32654, found: 847.32618.

2. NMR spectra

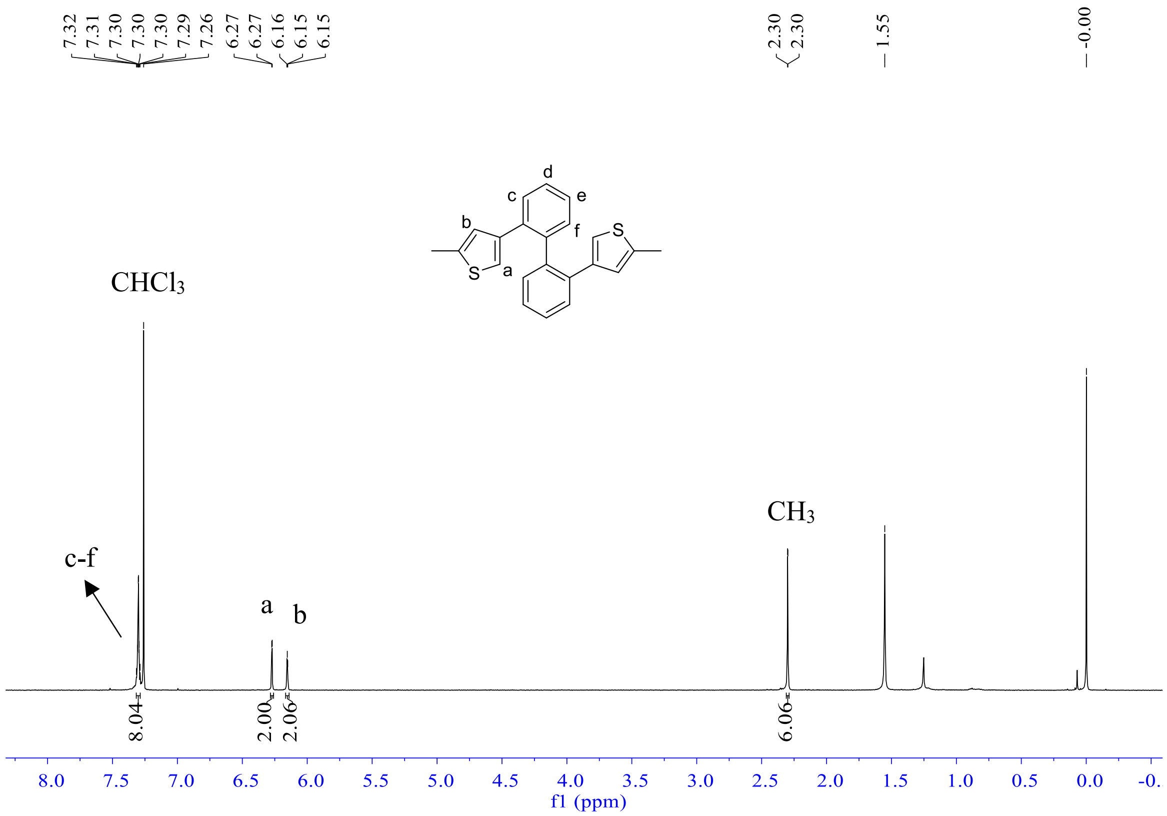


Figure S1 ^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$)

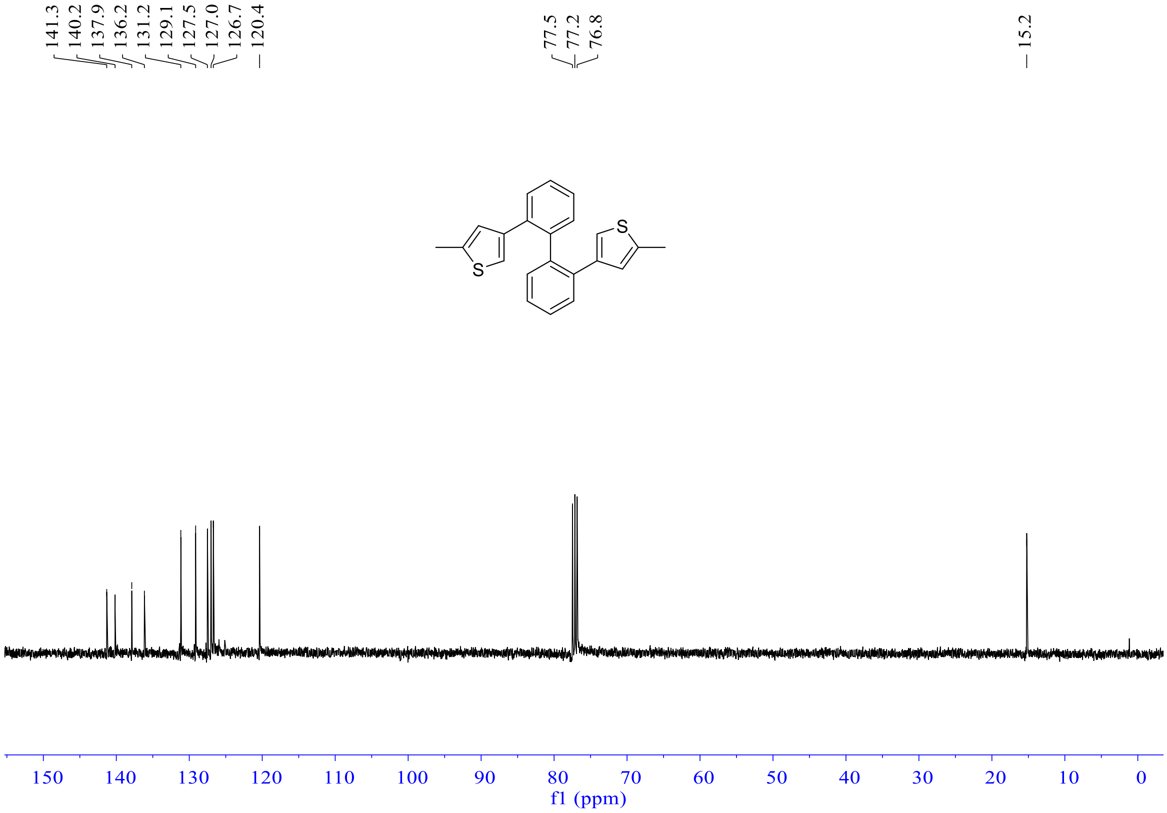


Figure S2 ^{13}C NMR spectrum of **1c** (100 MHz, $CDCl_3$)

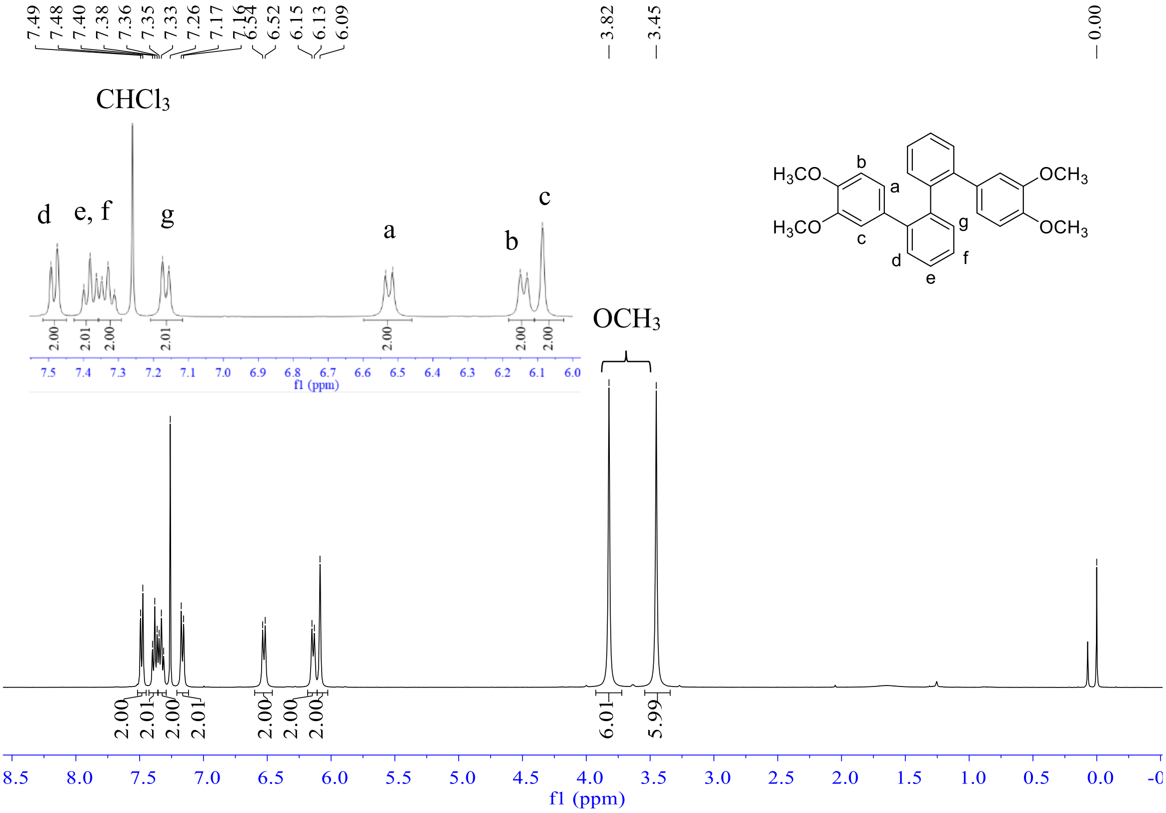


Figure S3 ^{1}H NMR spectrum of **1d** (400 MHz, $CDCl_3$)

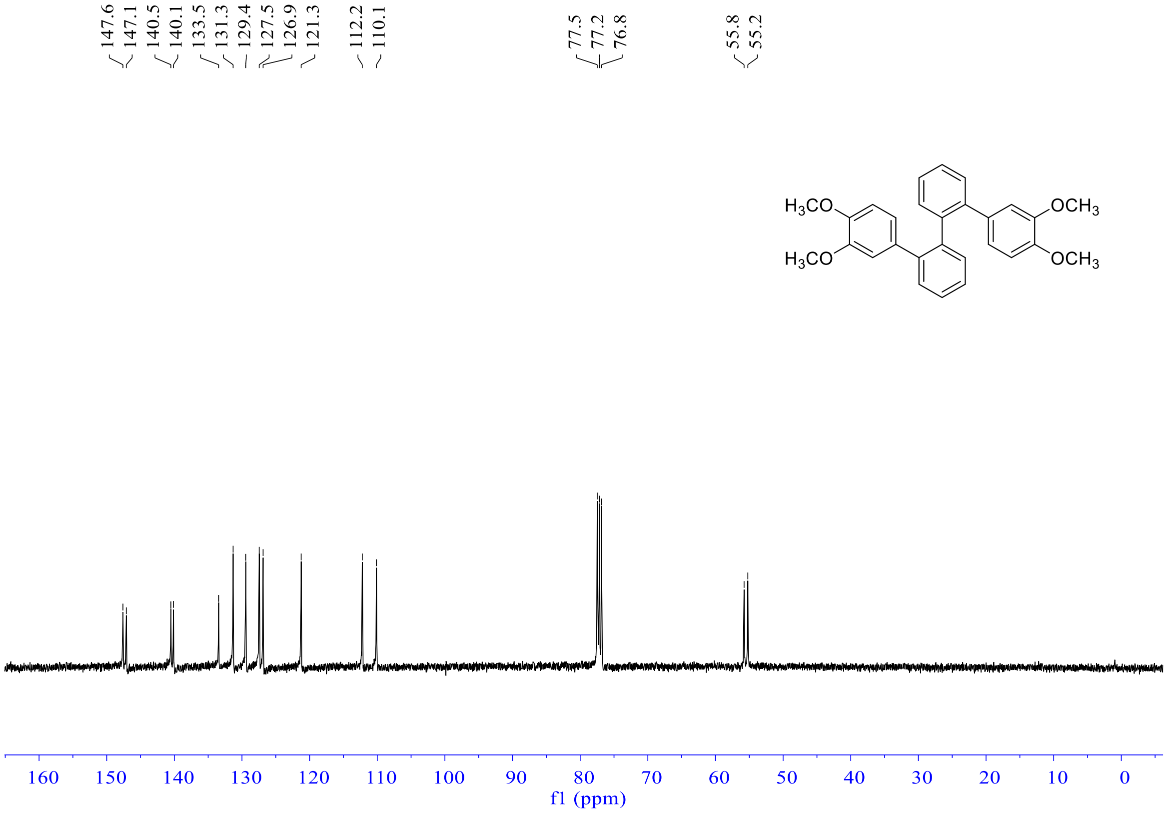


Figure S4 ^{13}C NMR spectrum of **1d** (100 MHz, $CDCl_3$)

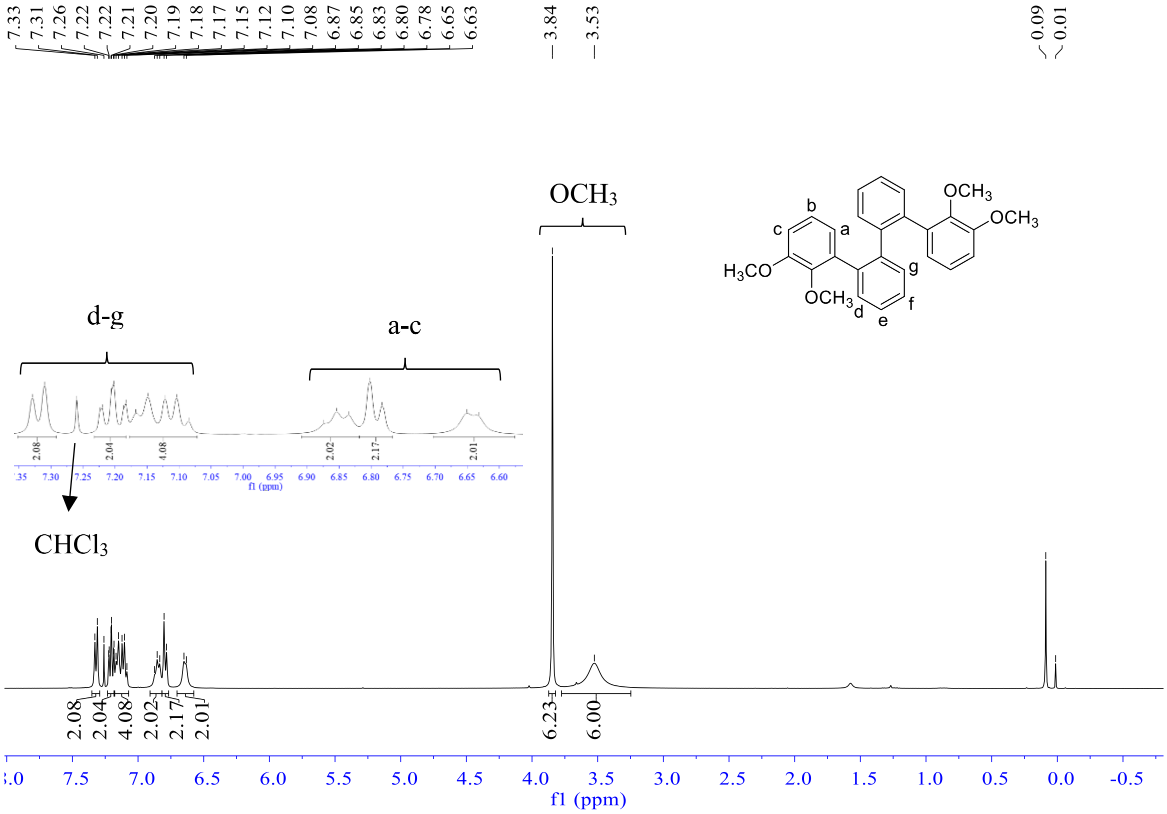


Figure S5 ^{1}H NMR spectrum of **1e** (400 MHz, CDCl$_3$)

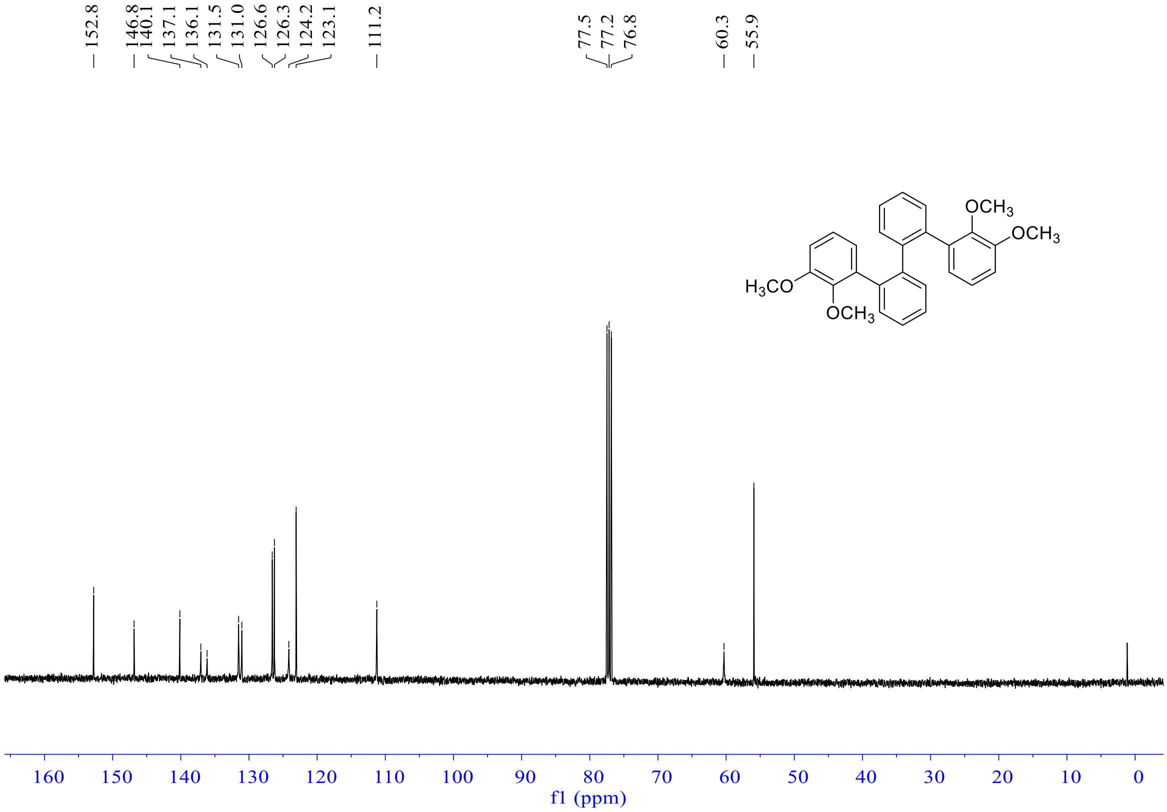


Figure S6 ^{13}C NMR spectrum of **1e** (100 MHz, CDCl$_3$)

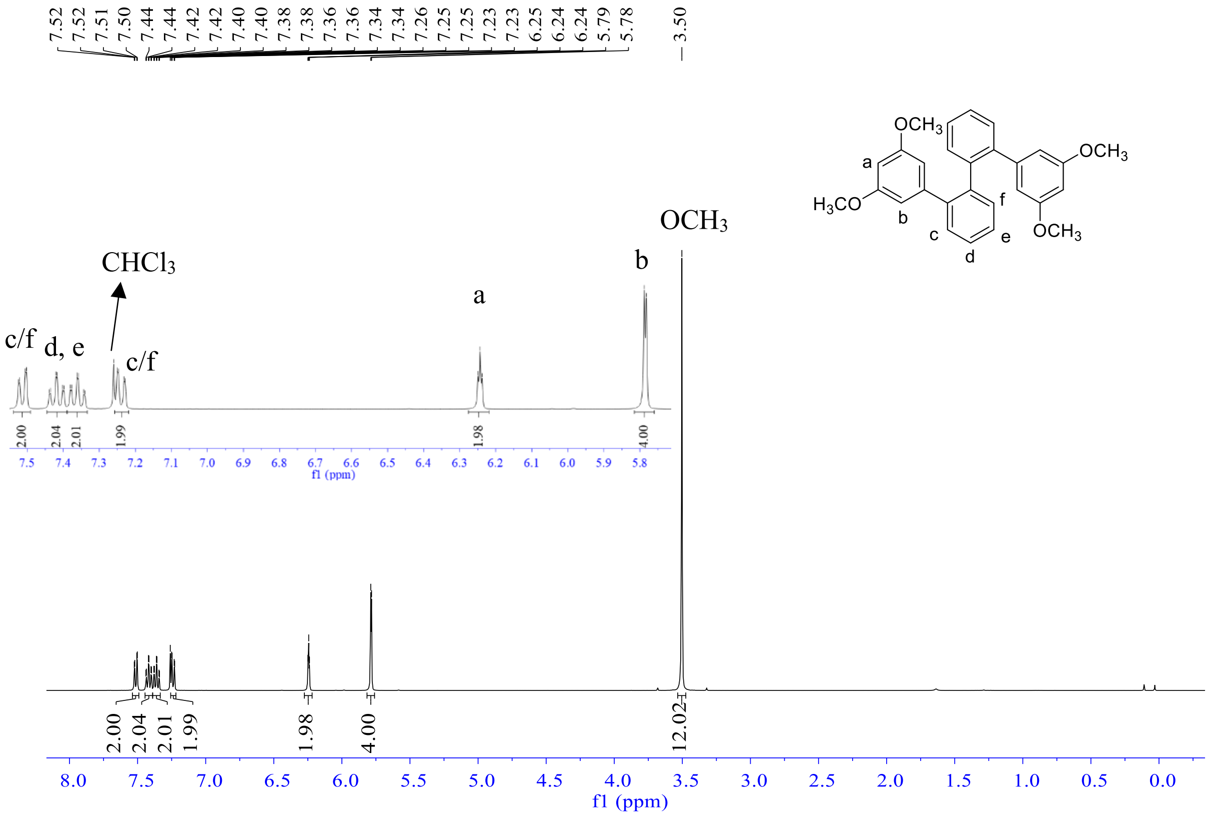


Figure S7 ^{1}H NMR spectrum of **1f** (400 MHz, $CDCl_3$)

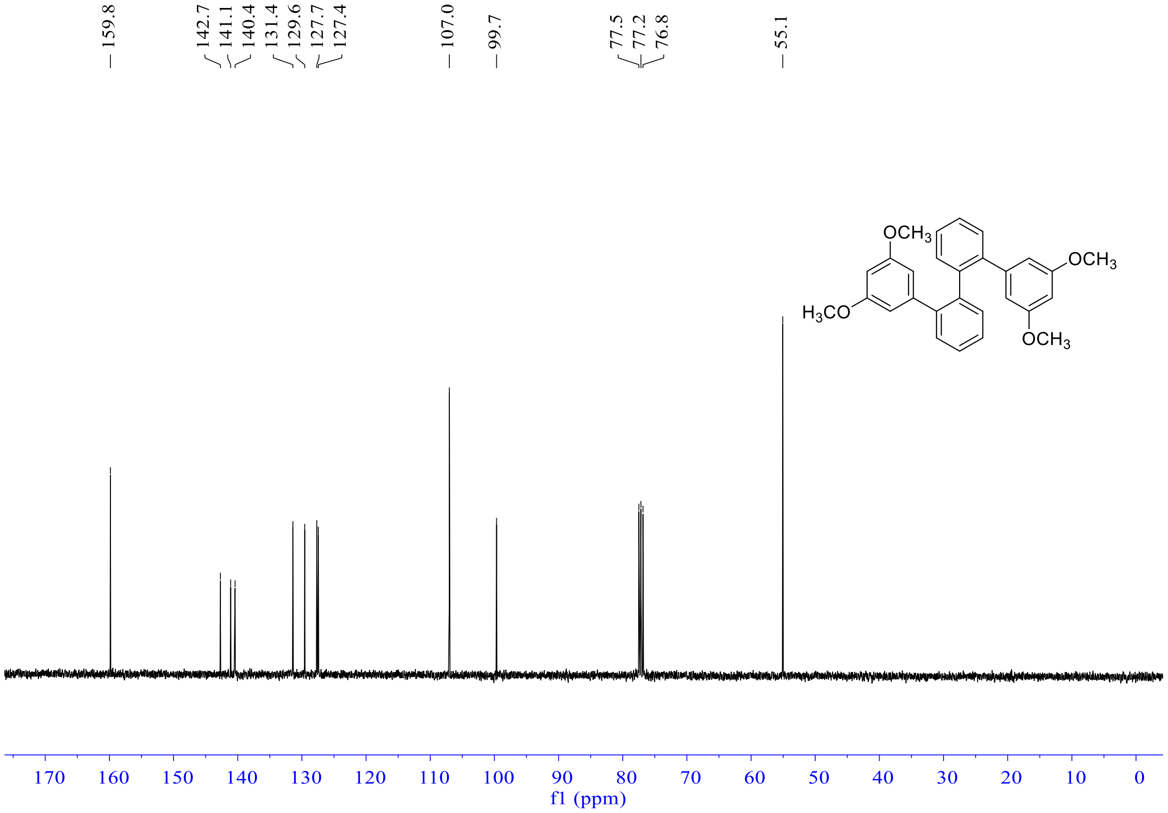


Figure S8 ^{13}C NMR spectrum of **1f** (100 MHz, $CDCl_3$)

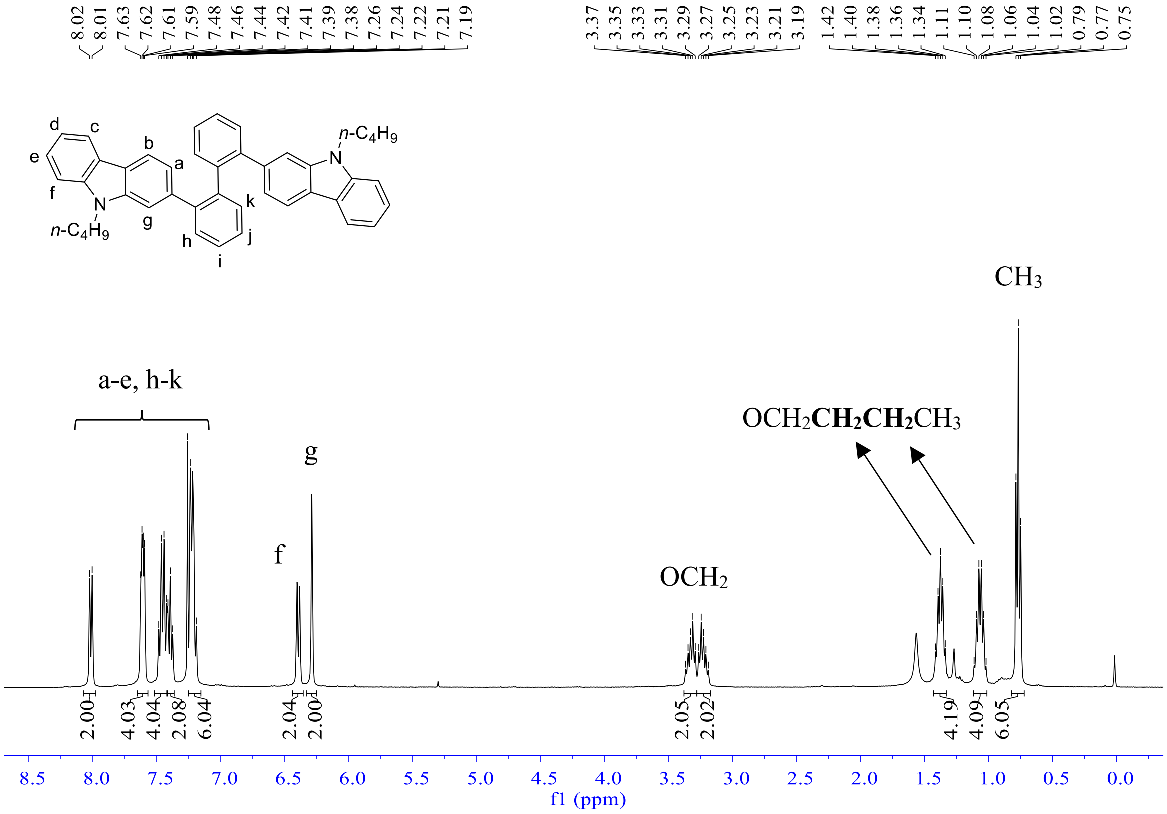


Figure S9 ^{1}H NMR spectrum of **1h** (400 MHz, $CDCl_3$)

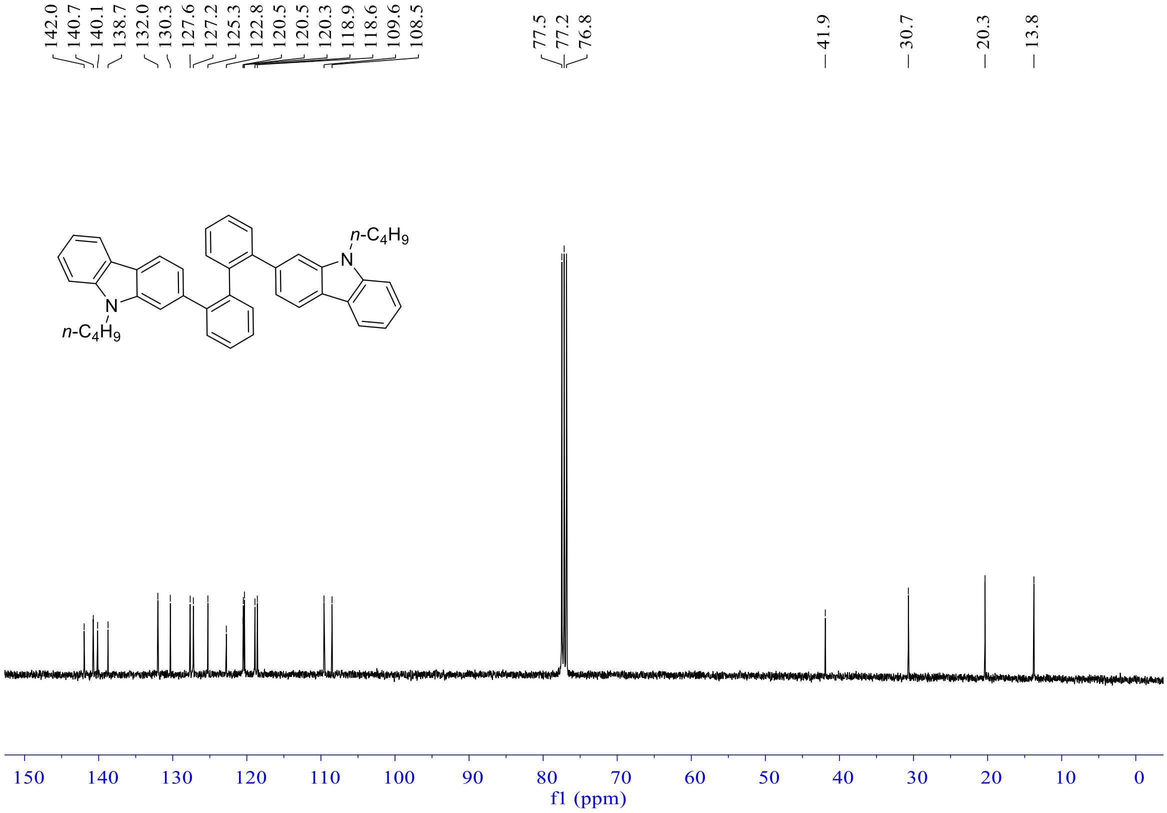


Figure S10 ^{13}C NMR spectrum of **1h** (100 MHz, $CDCl_3$)

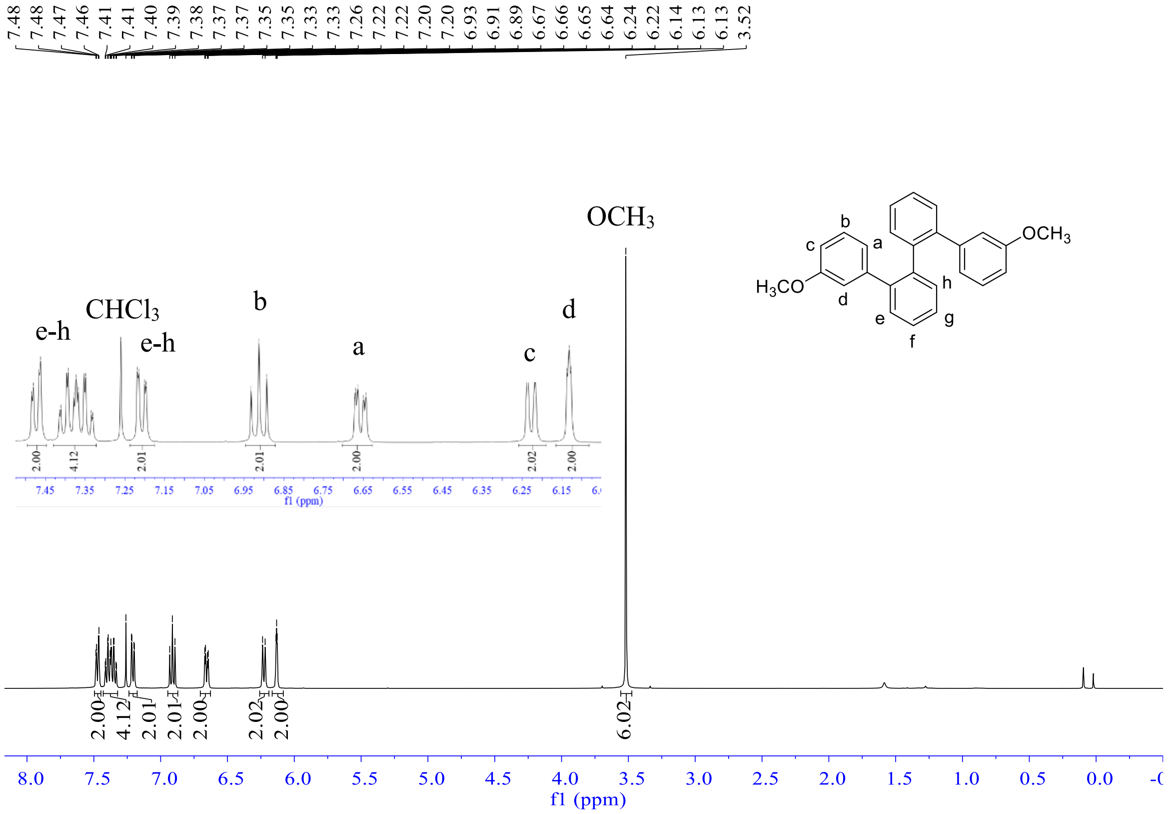


Figure S11 ^{1}H NMR spectrum of **1i** (400 MHz, $CDCl_3$)

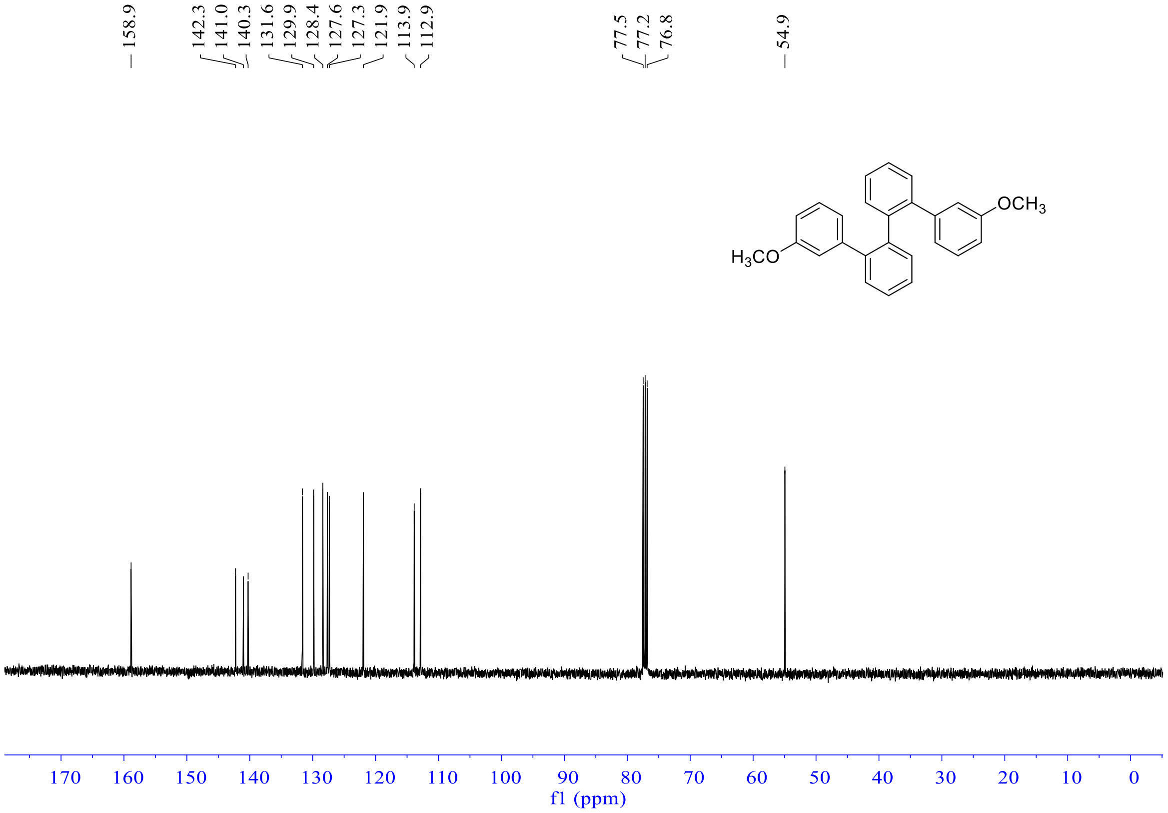


Figure S12 ^{13}C NMR spectrum of **1i** (100 MHz, $CDCl_3$)

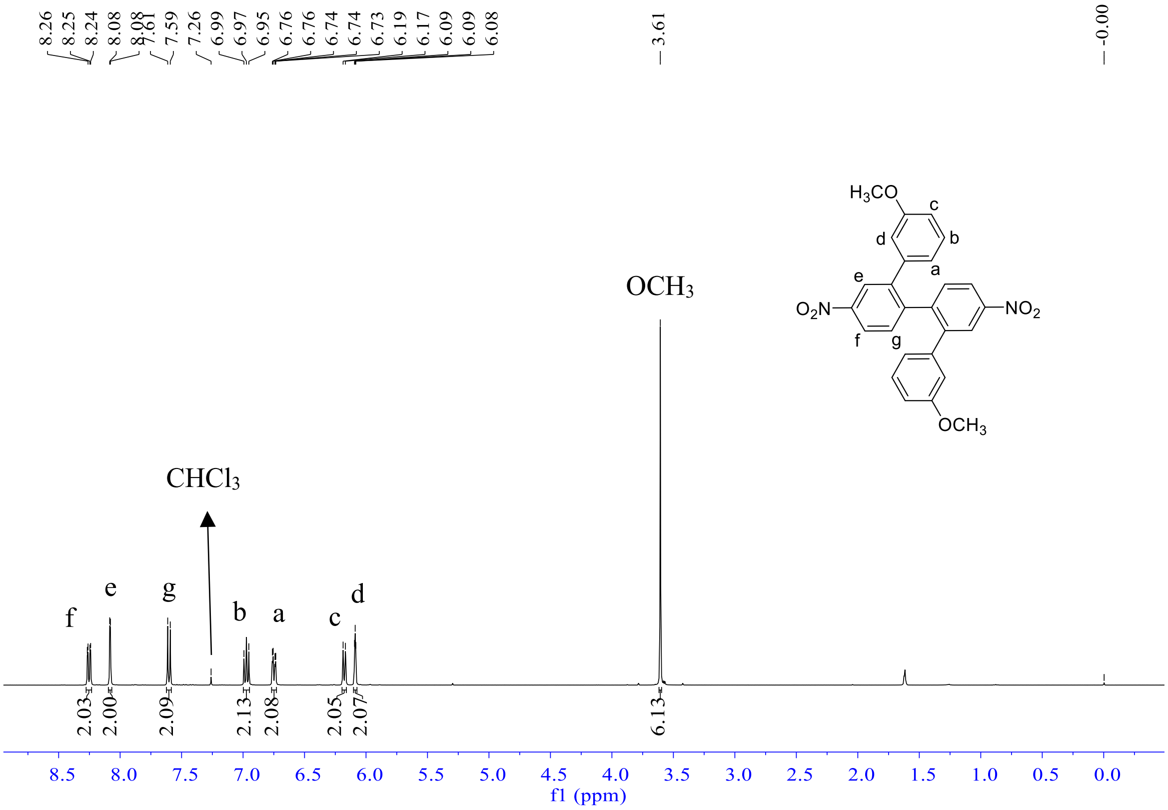


Figure S13 ^{1}H NMR spectrum of **1j** (400 MHz, CDCl$_3$)

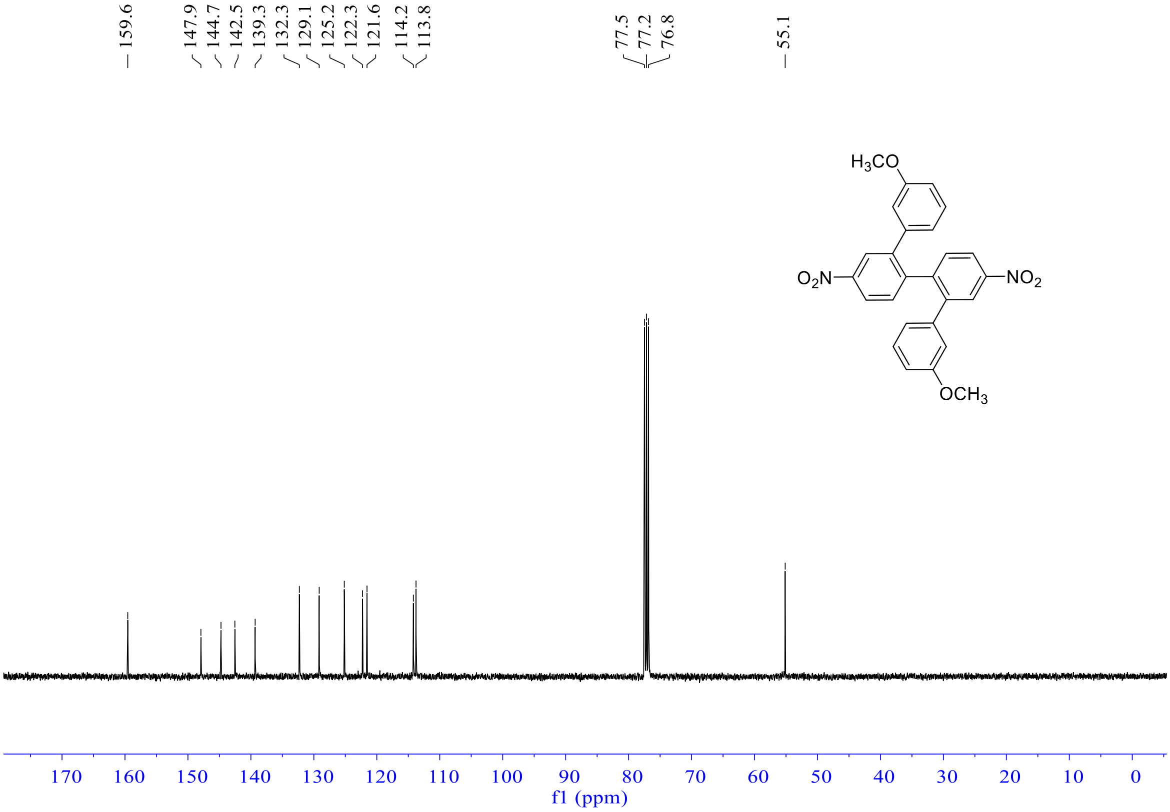


Figure S14 ^{13}C NMR spectrum of **1j** (100 MHz, CDCl$_3$)

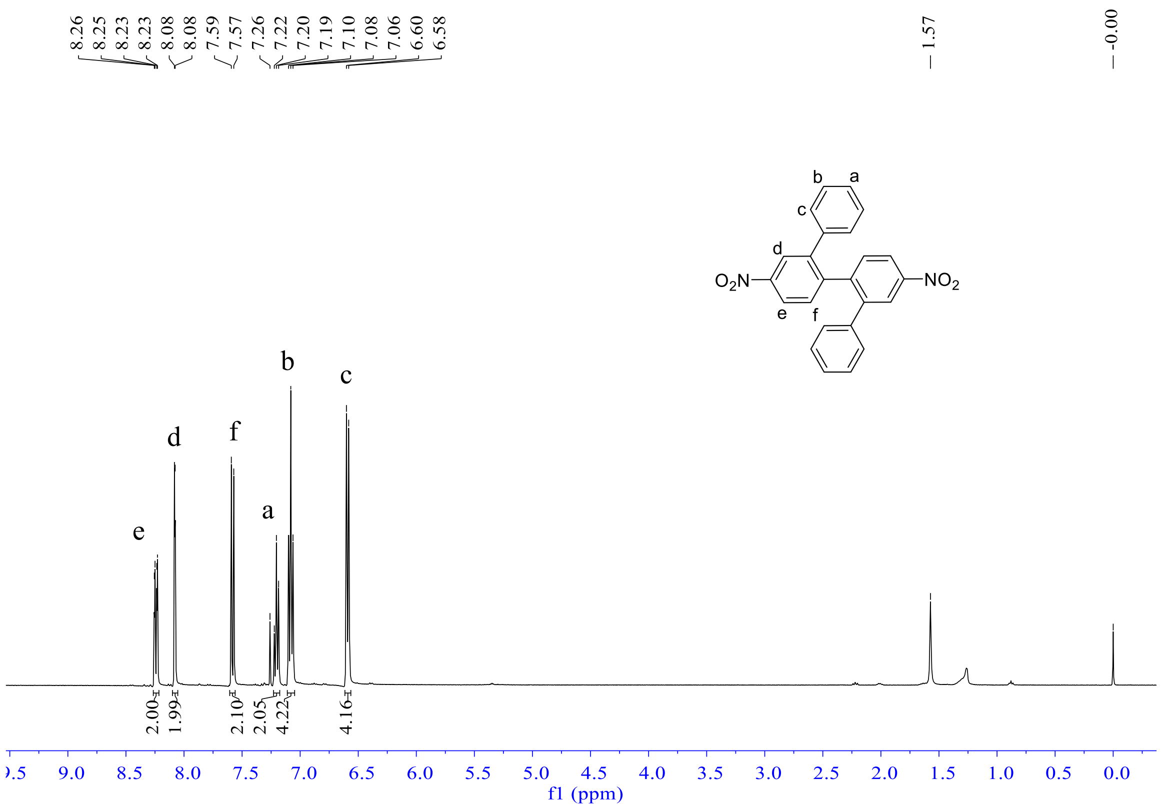


Figure S15 ^{1}H NMR spectrum of **1k** (400 MHz, $CDCl_3$)

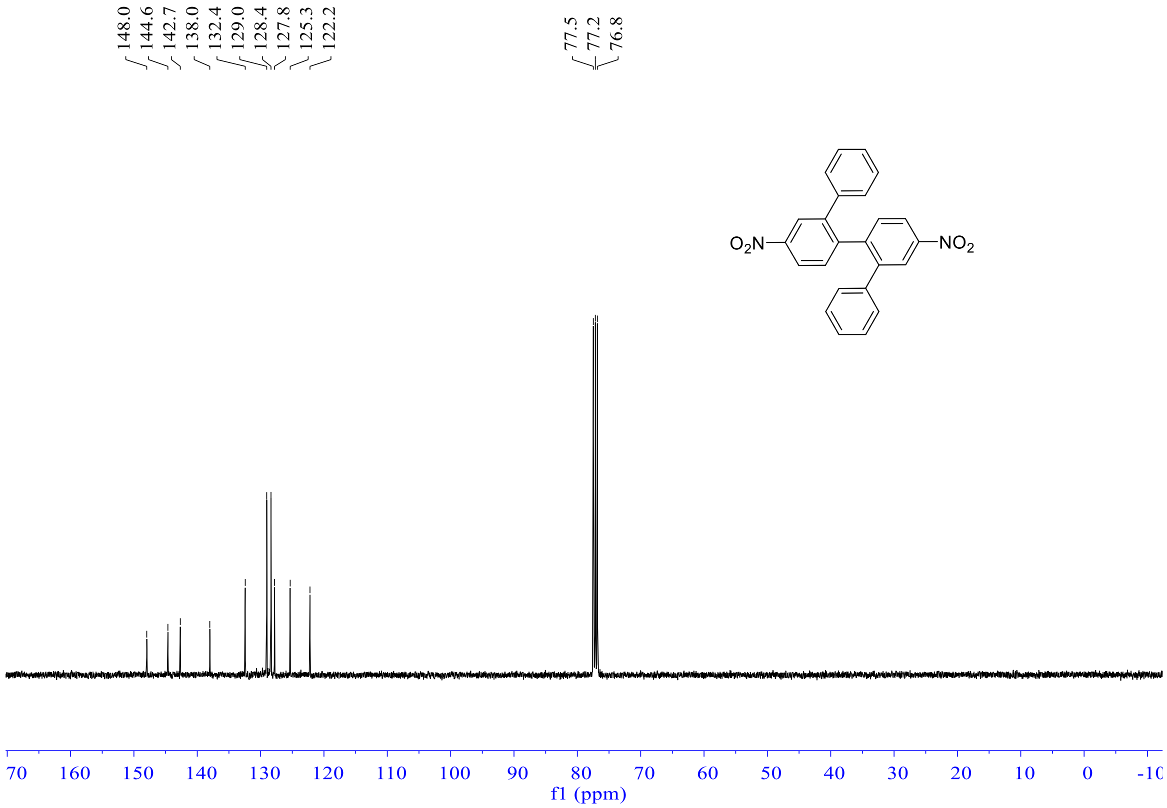


Figure S16 ^{13}C NMR spectrum of **1k** (100 MHz, $CDCl_3$)

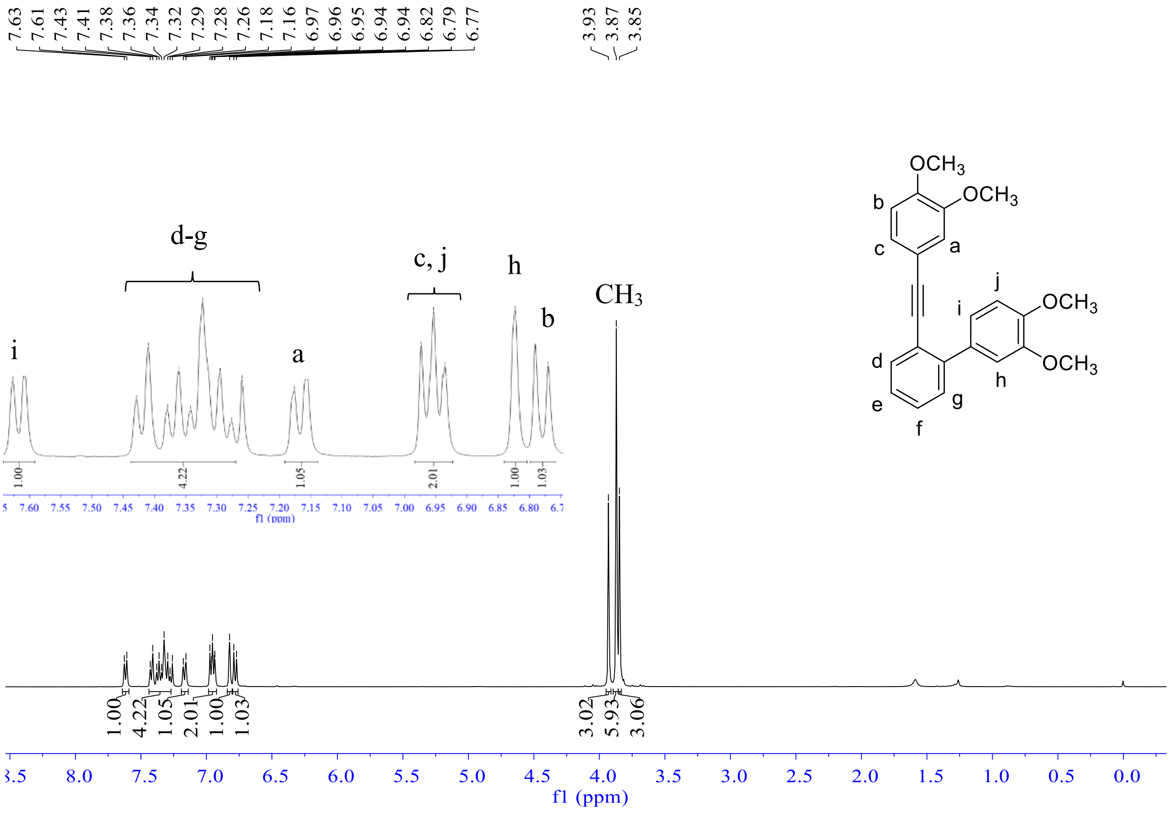


Figure S17 ^{1}H NMR spectrum of **7** (400 MHz, CDCl$_3$)

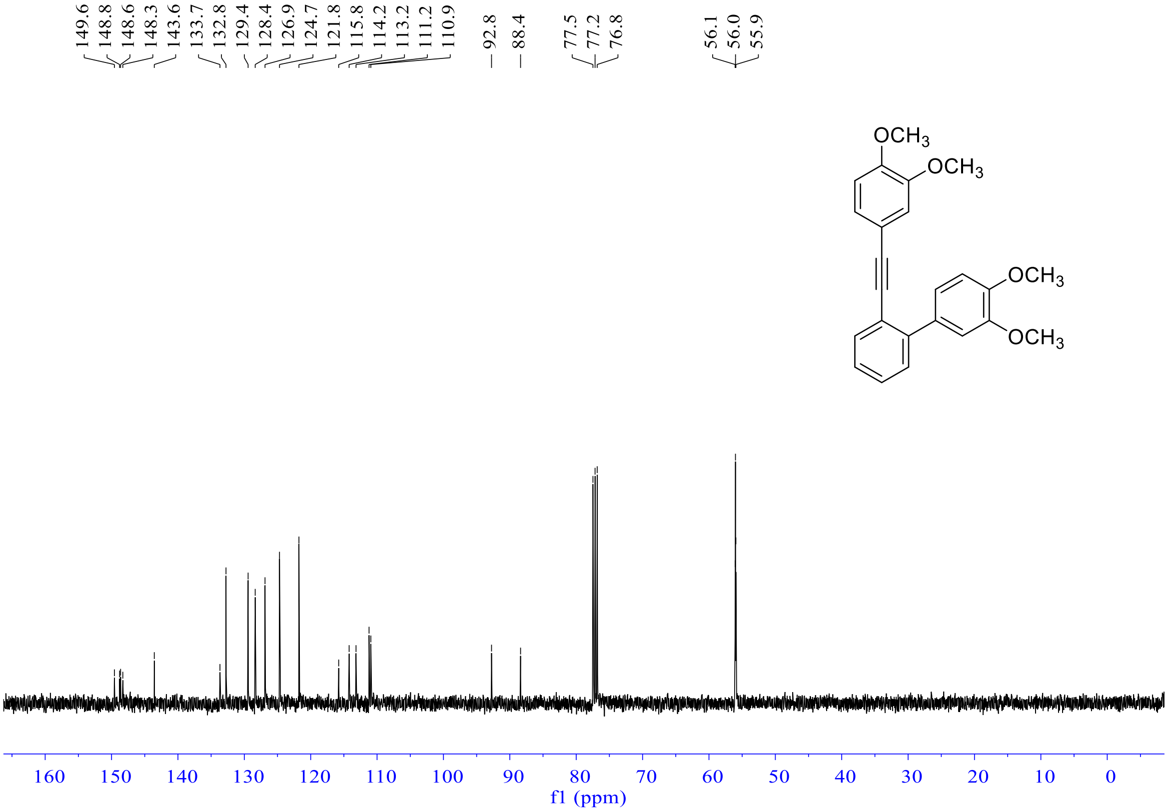


Figure S18 ^{1}H NMR spectrum of **7** (100 MHz, CDCl$_3$)

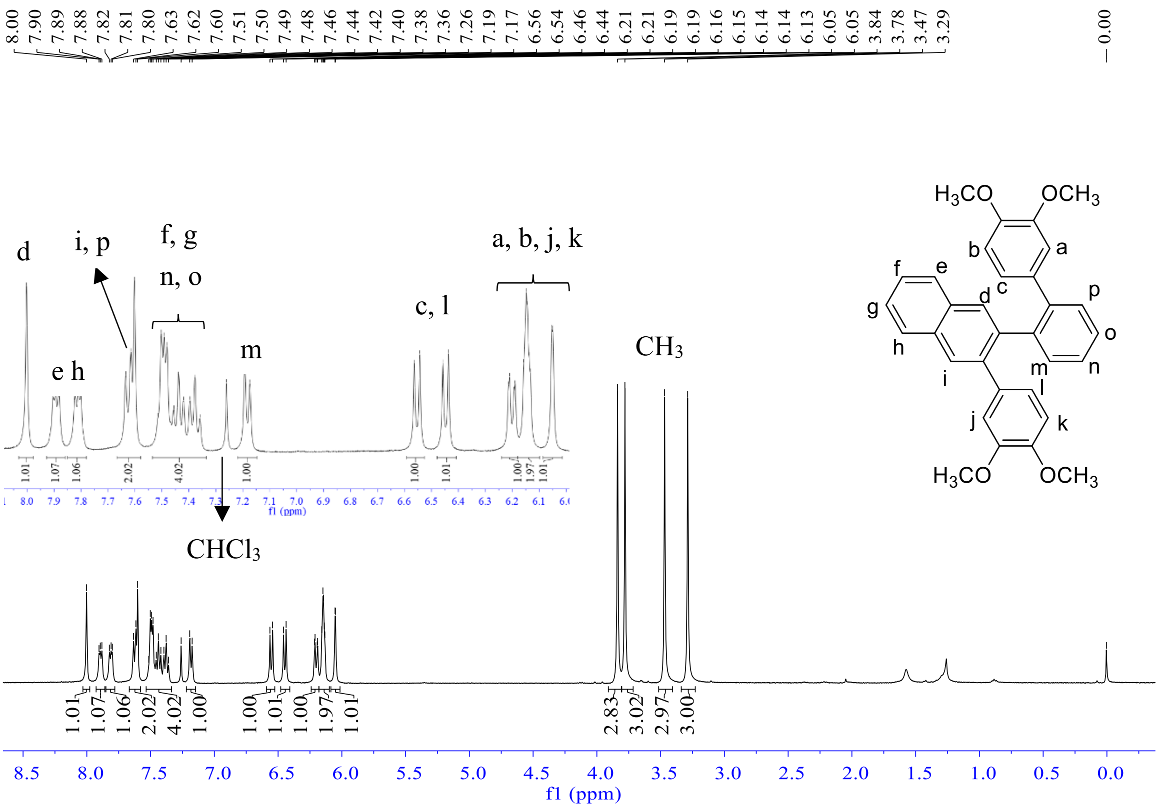


Figure S19 ^{1}H NMR spectrum of **1m** (400 MHz, CDCl$_3$)

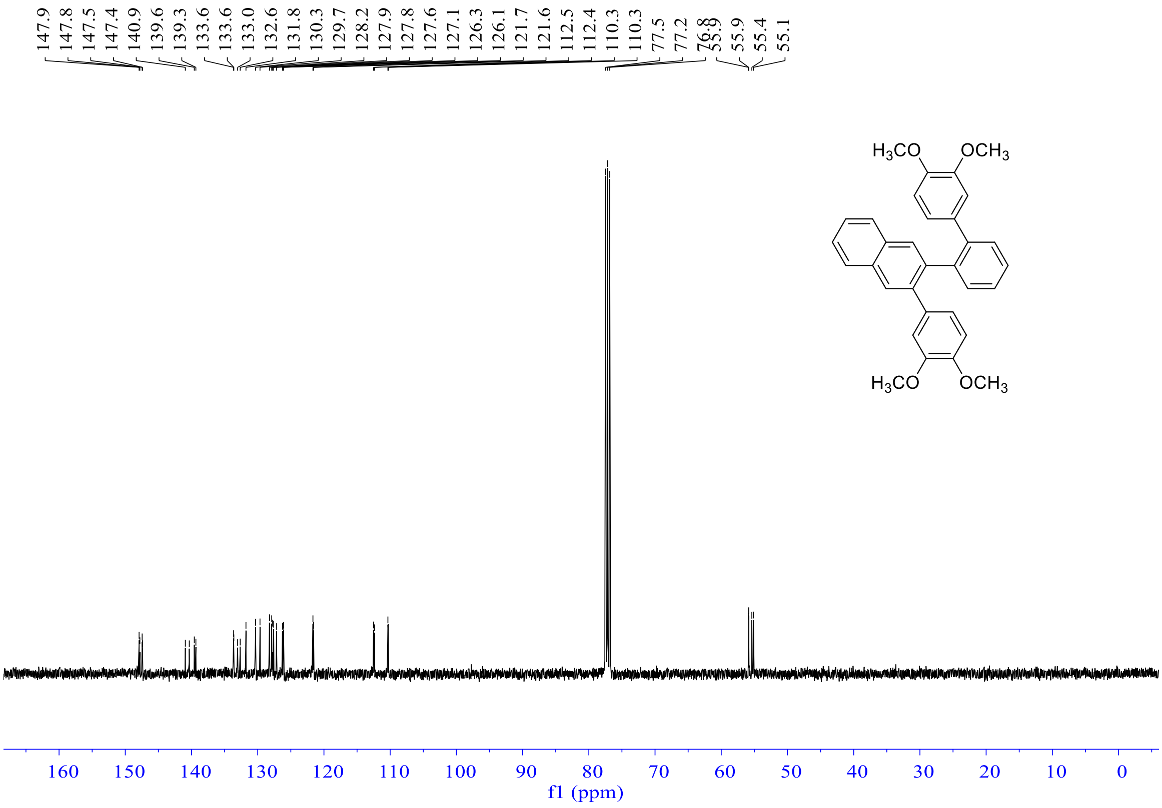


Figure S20 ^{13}C NMR spectrum of **1m** (100 MHz, CDCl$_3$)

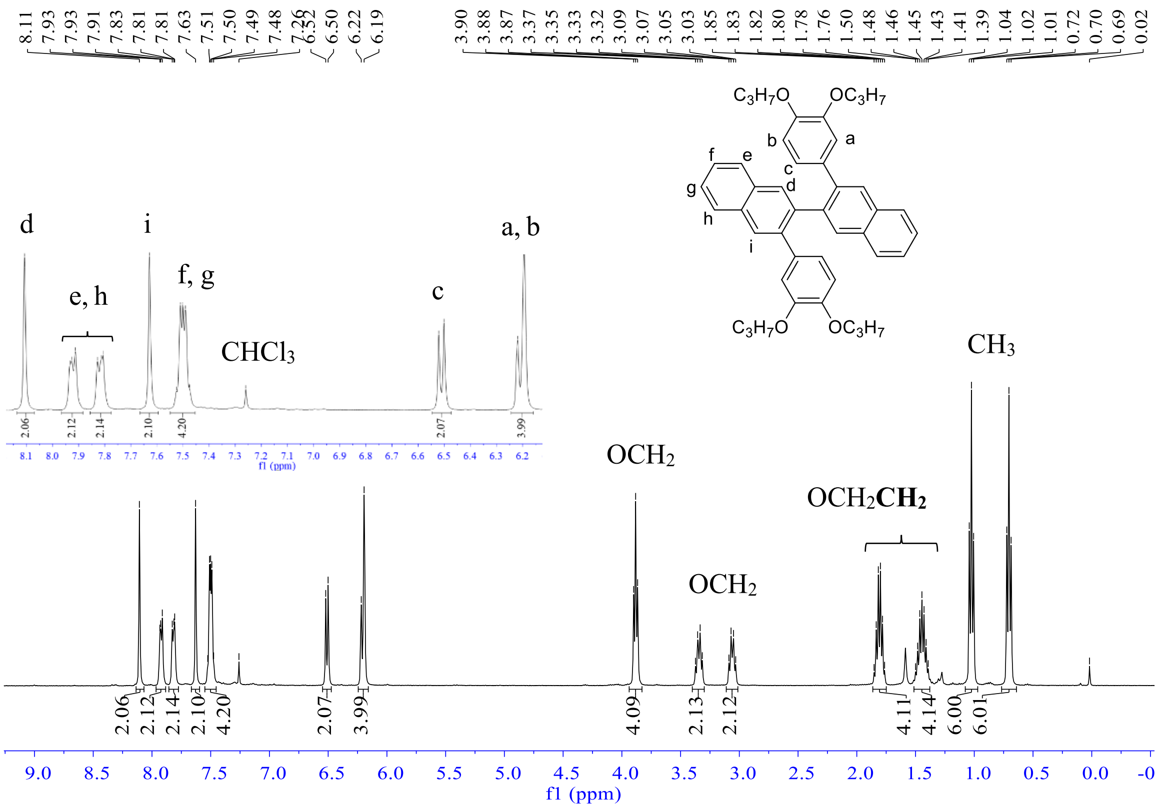


Figure S21 ^{1}H NMR spectrum of **1n** (400 MHz, $CDCl_3$)

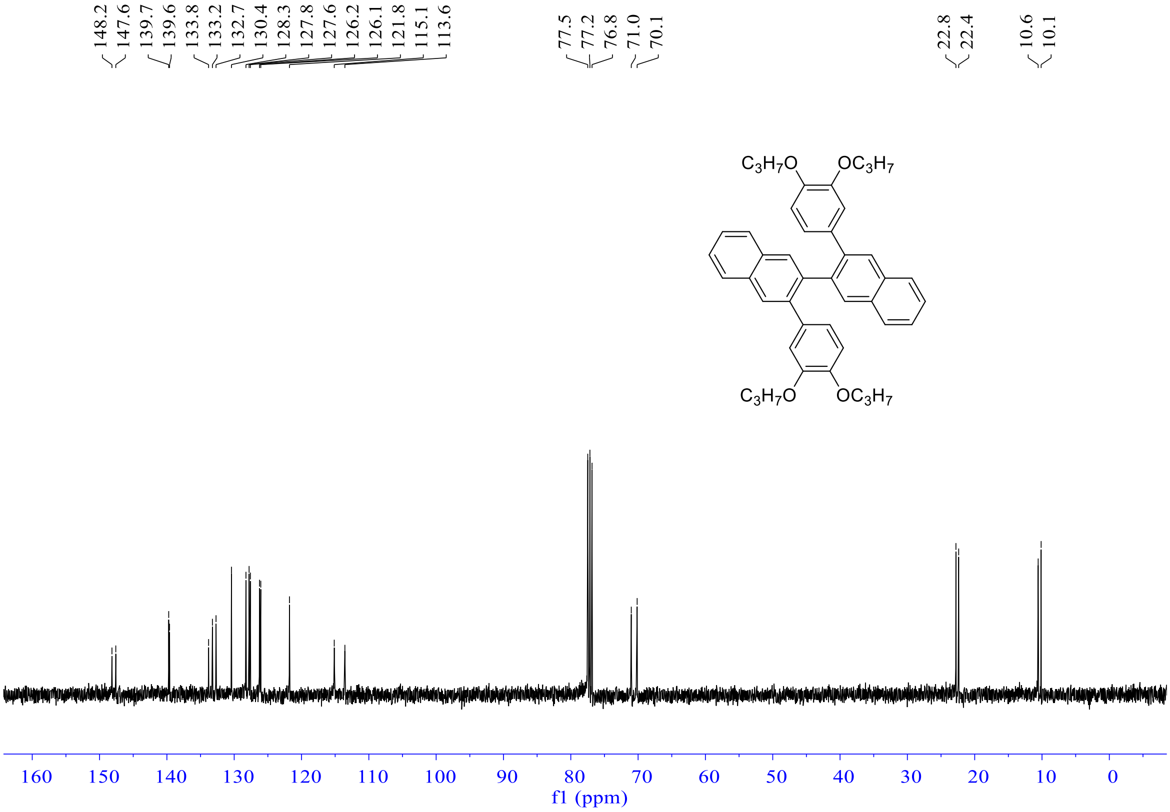


Figure S22 ^{13}C NMR spectrum of **1n** (100 MHz, $CDCl_3$)

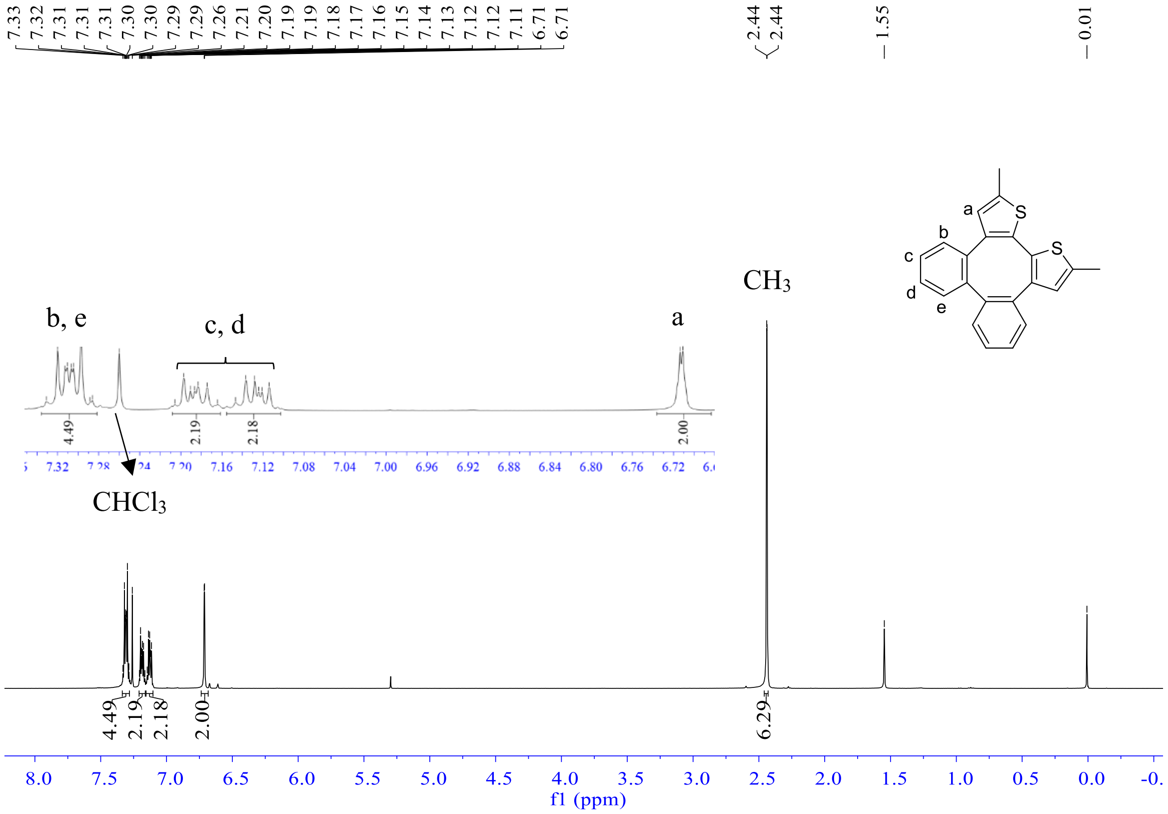


Figure S23 ^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$)

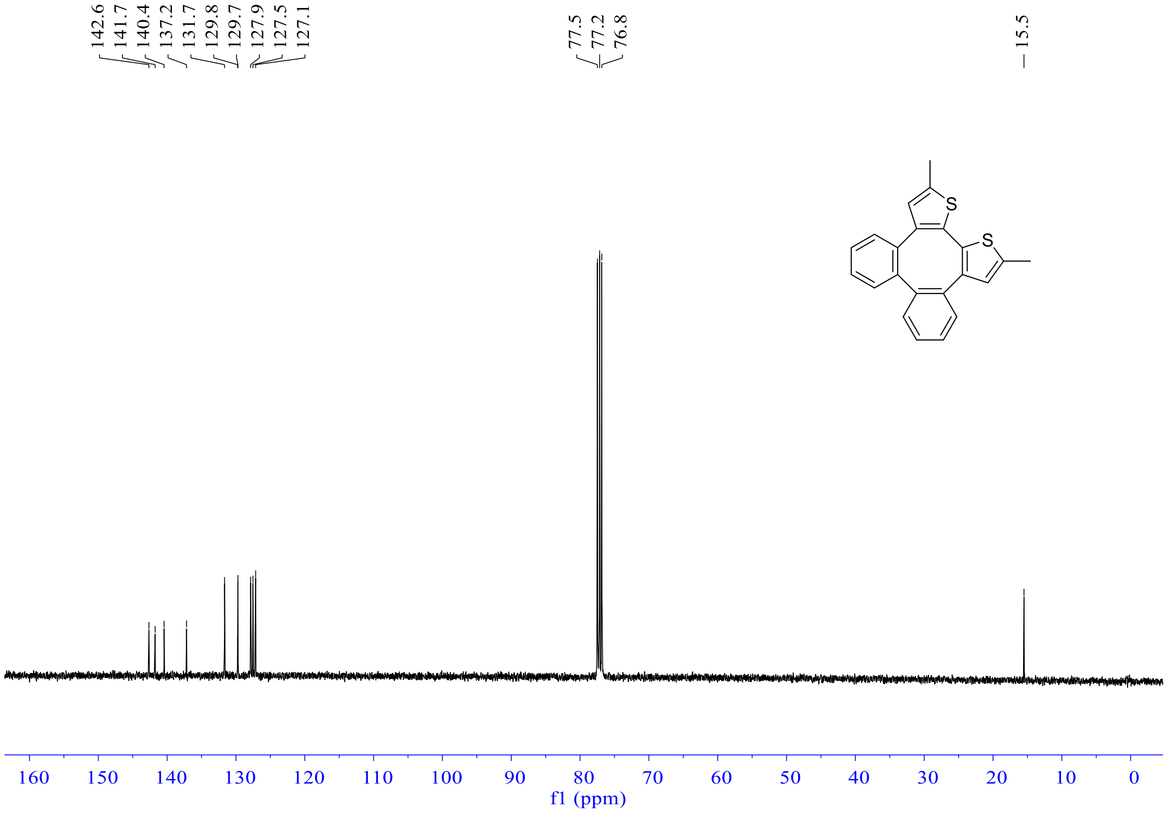


Figure S24 ^{13}C NMR spectrum of **2c** (100 MHz, $CDCl_3$)

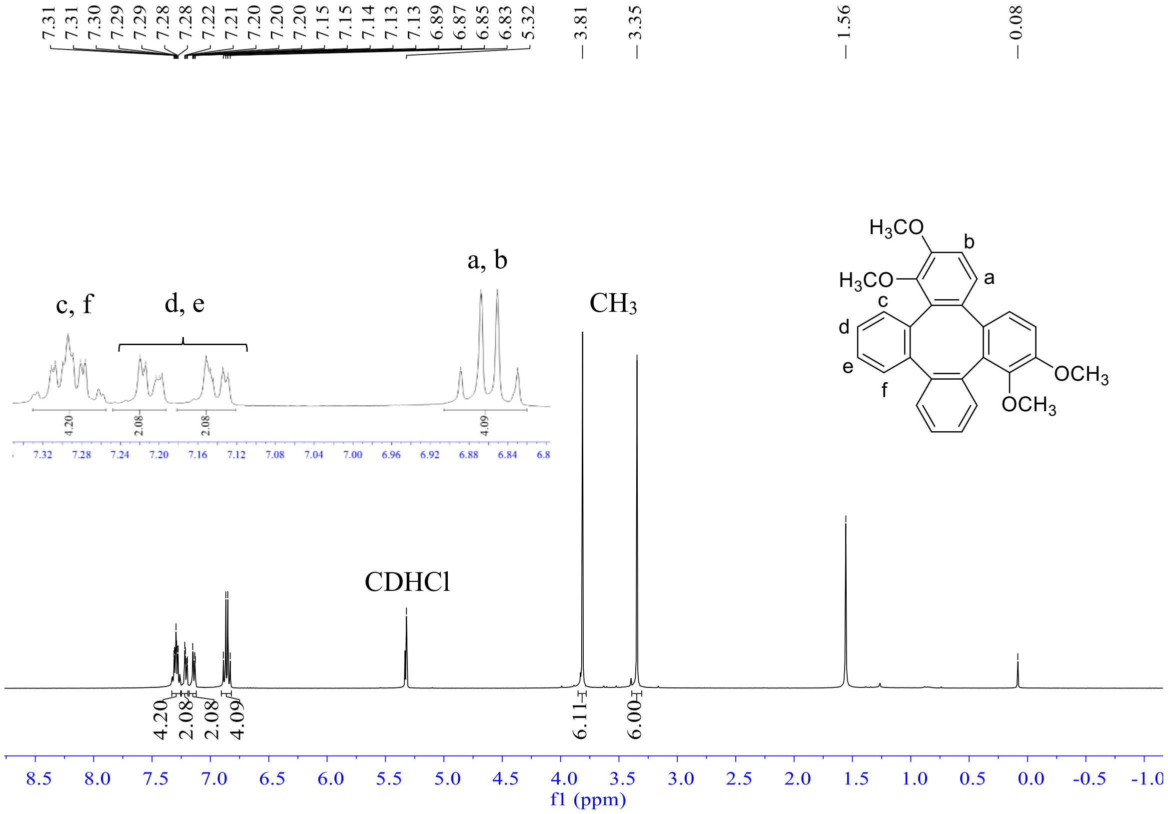


Figure S25 ^{1}H NMR spectrum of **2e** (400 MHz, CD_2Cl_2)

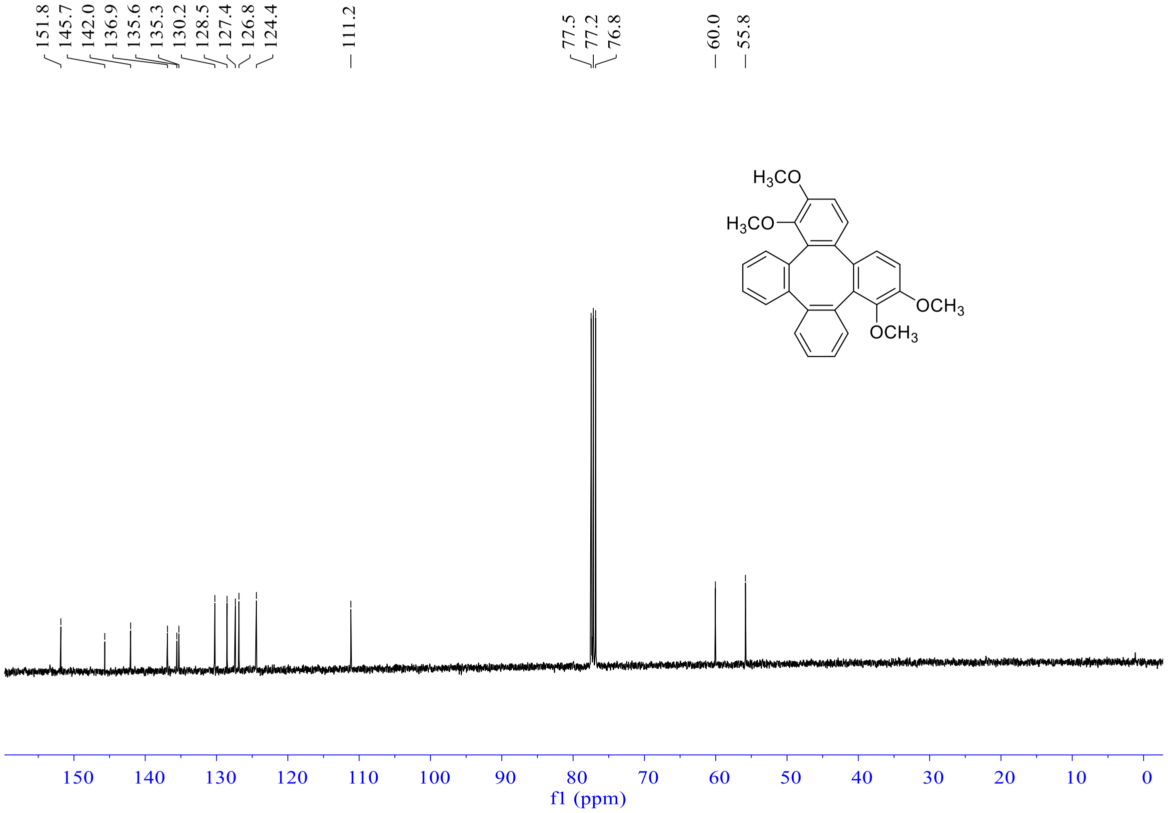


Figure S26 ^{13}C NMR spectrum of **2e** (100 MHz, $CDCl_3$)

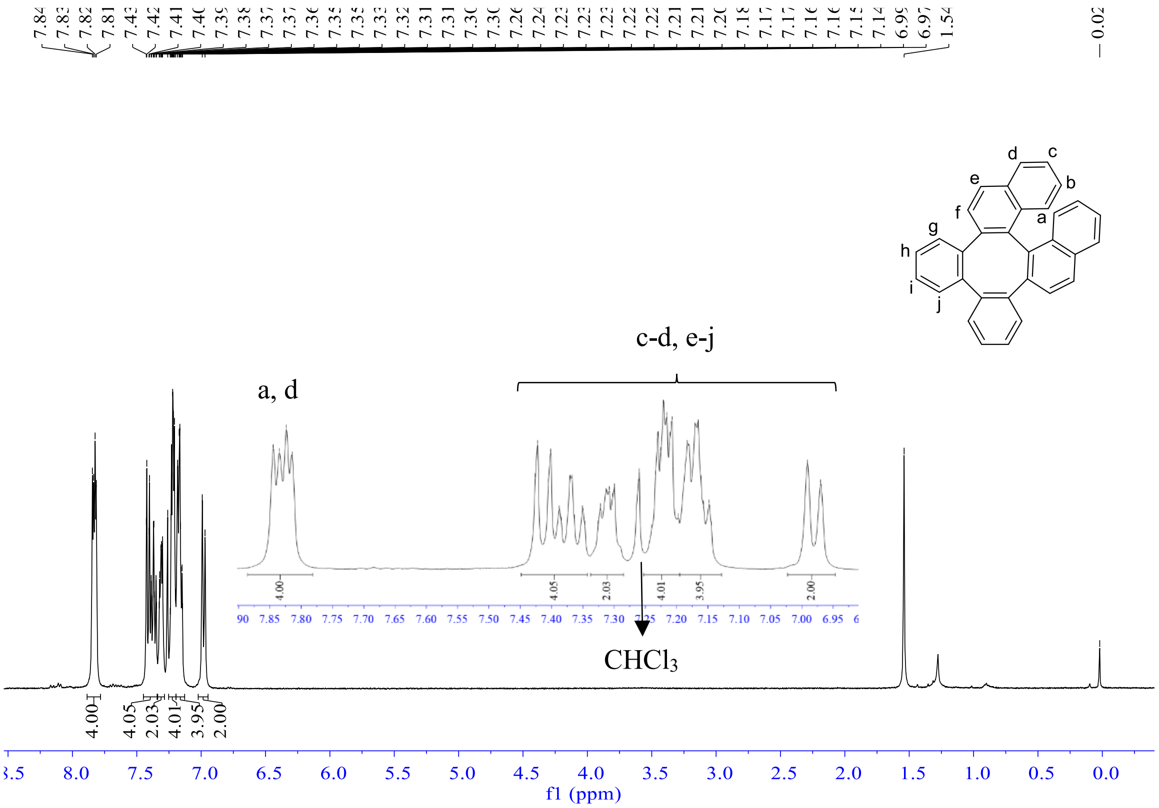


Figure S27 ^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$)

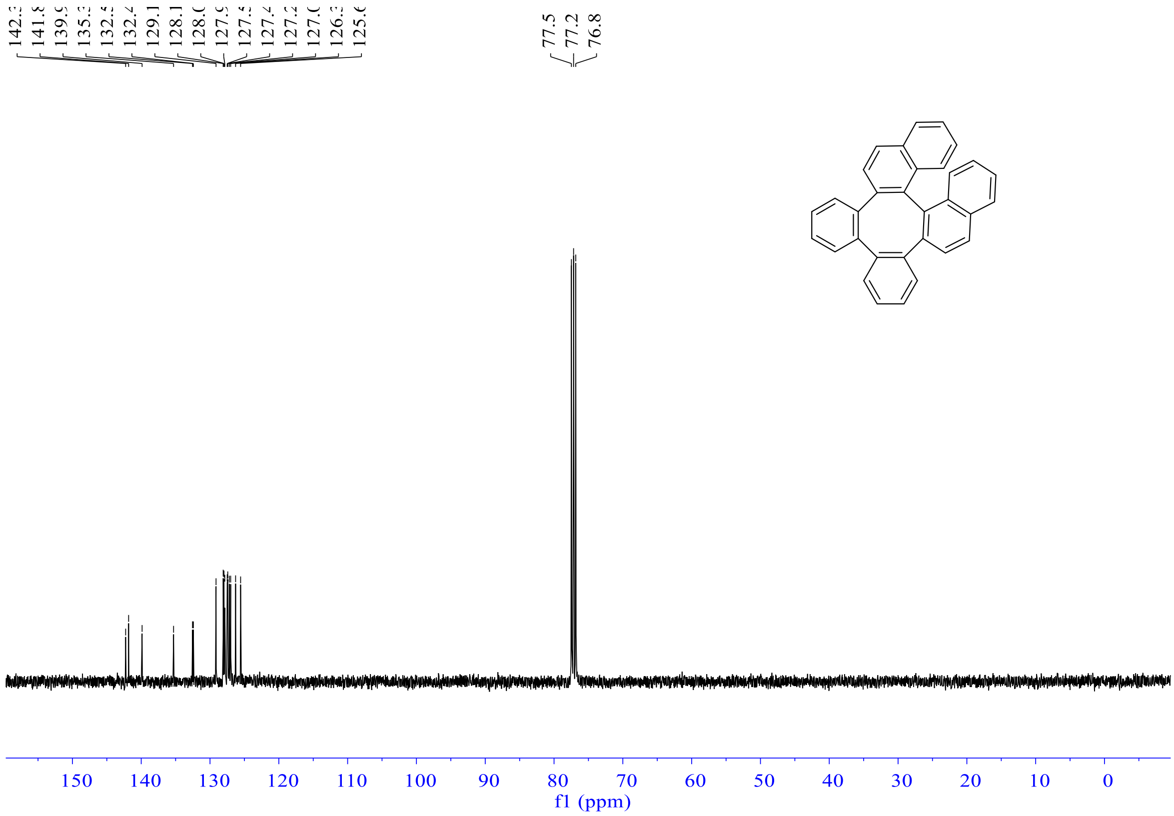


Figure S28 ^{13}C NMR spectrum of **2g** (100 MHz, $CDCl_3$)

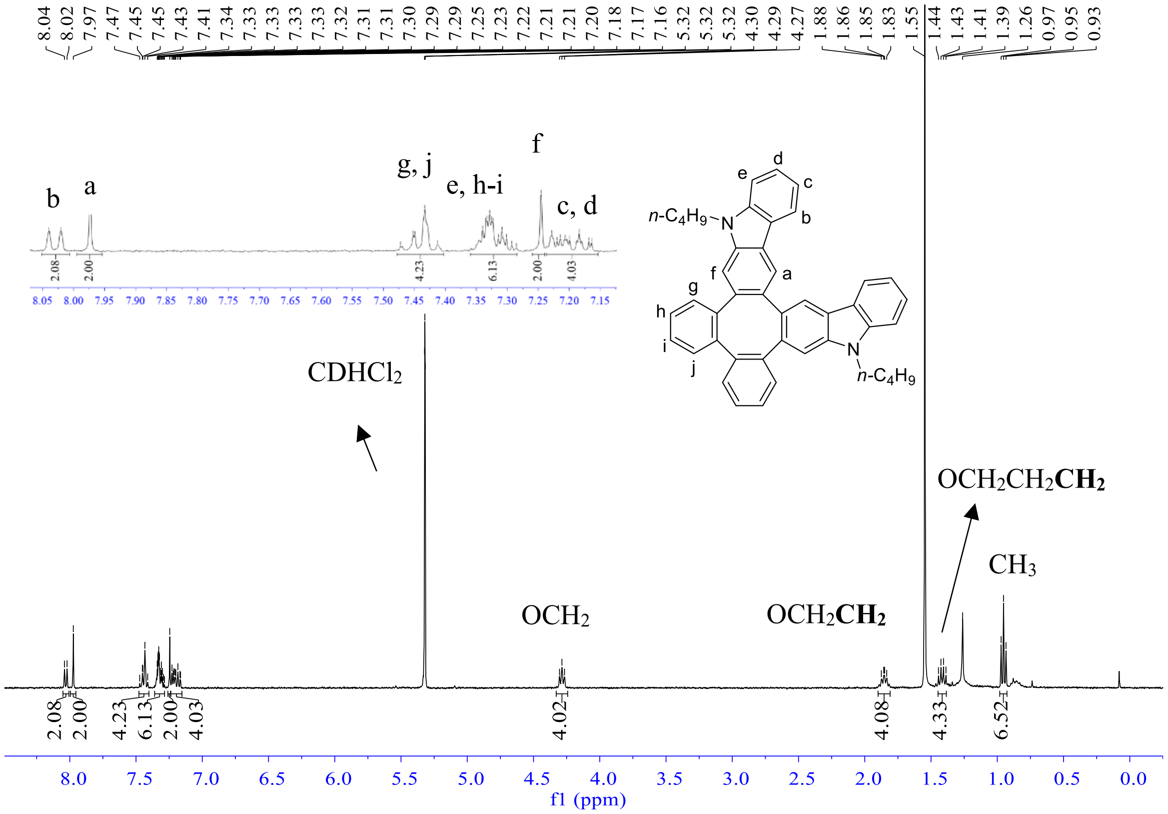


Figure S29 ^{1}H NMR spectrum of **2h** (400 MHz, CD$_2$Cl$_2$)

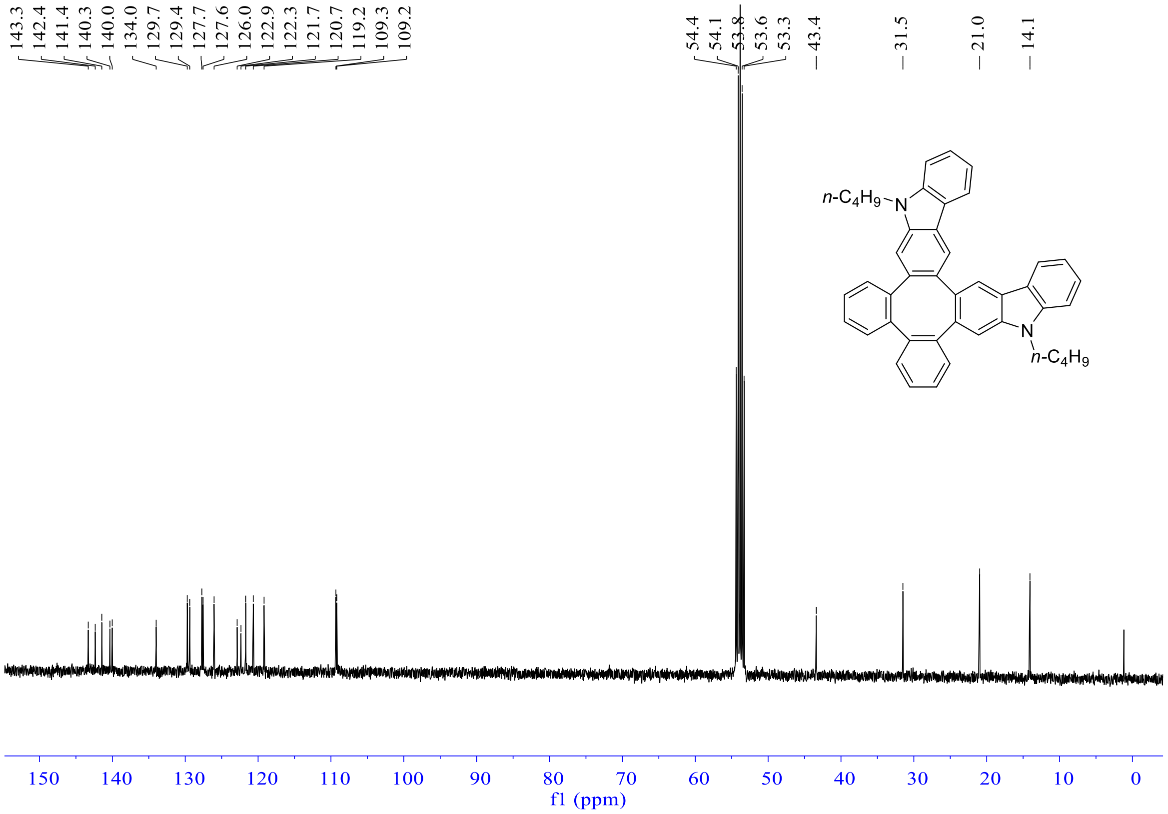


Figure S30 ^{13}C NMR spectrum of **2h** (100 MHz, CD$_2$Cl$_2$)

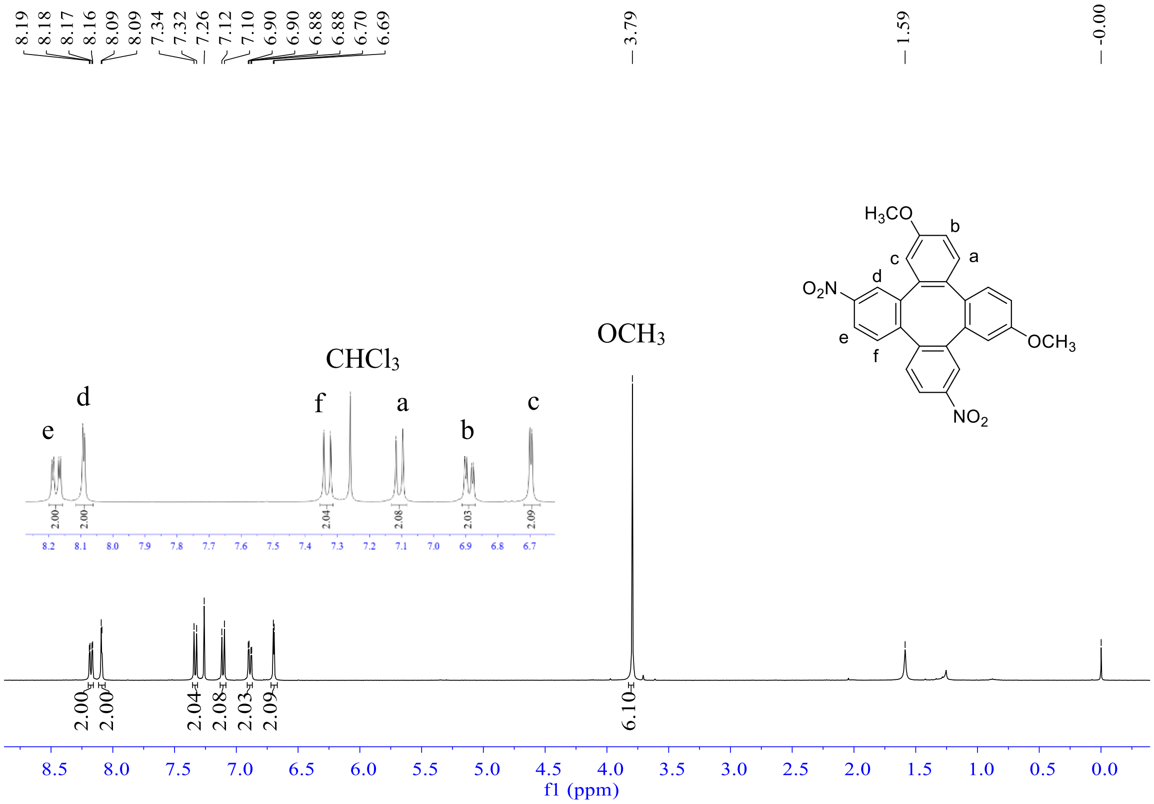


Figure S31 ^{1}H NMR spectrum of **2j** (400 MHz, CDCl$_3$)

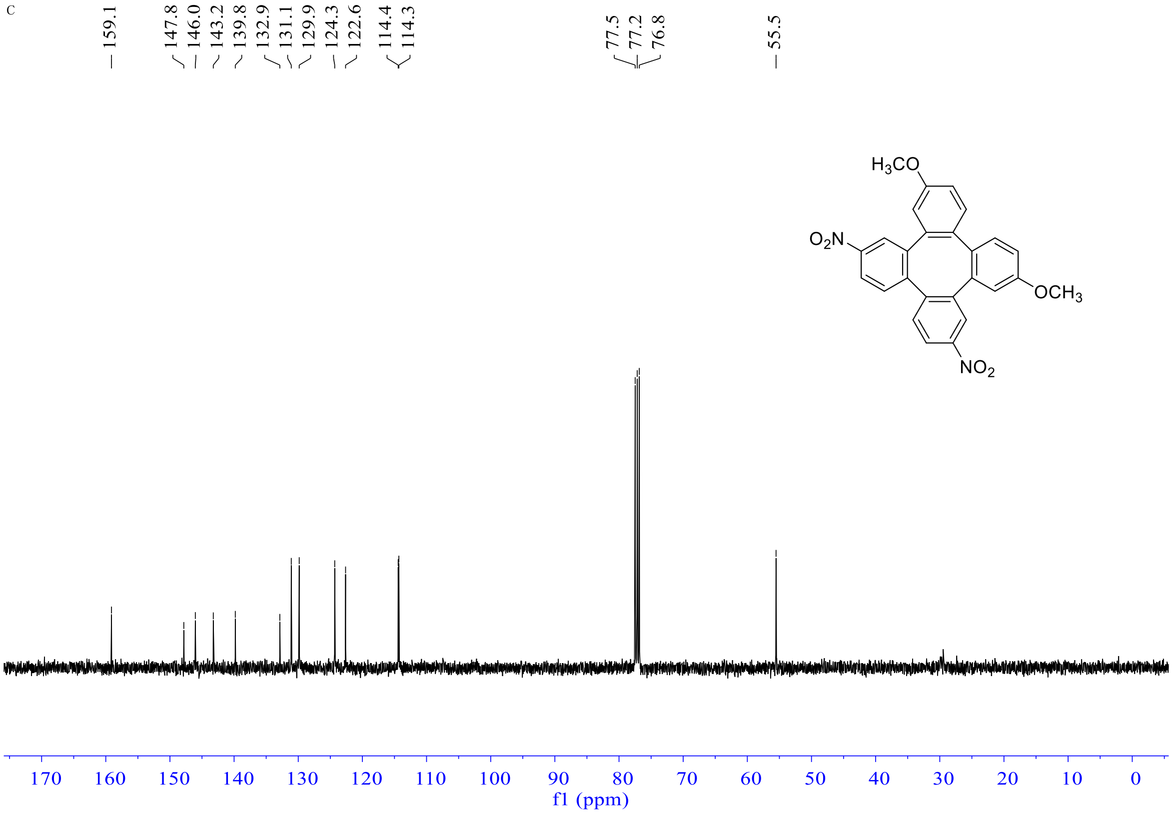


Figure S32 ^{13}C NMR spectrum of **2j** (100 MHz, CDCl$_3$)

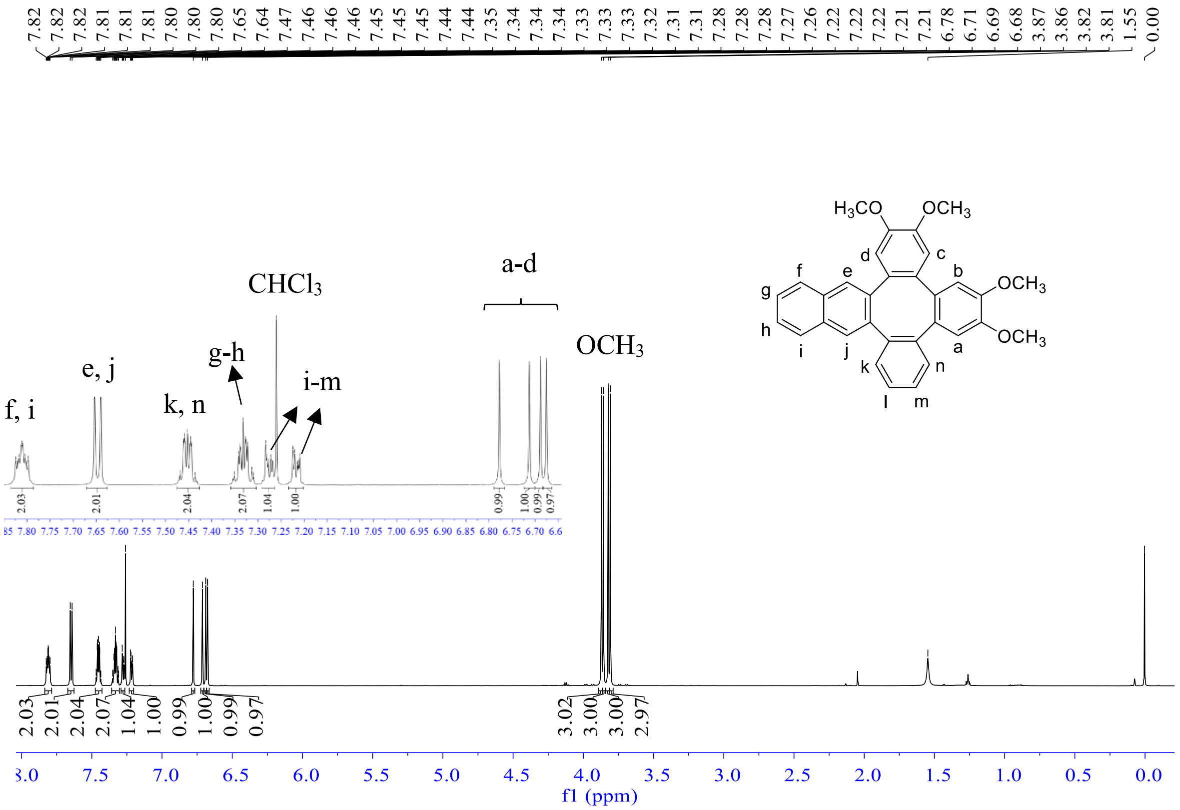


Figure S33 ^{1}H NMR spectrum of **2m** (600 MHz, $CDCl_3$)

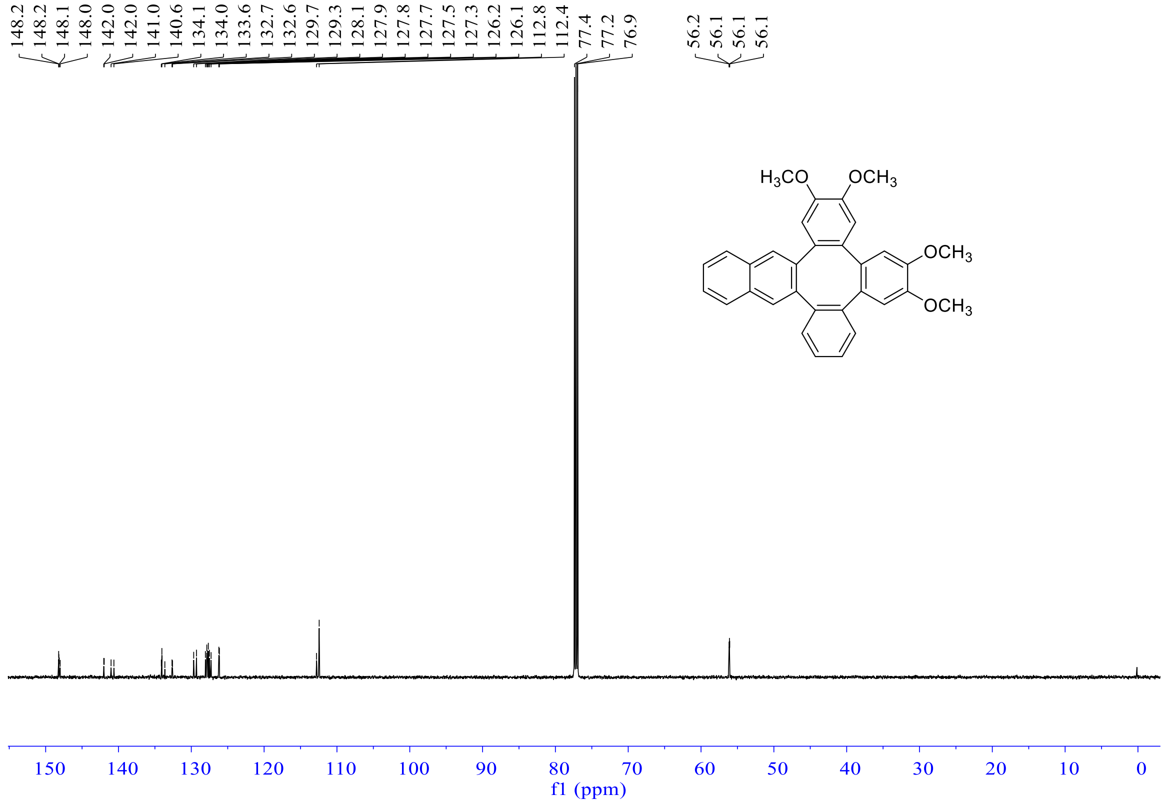


Figure S34 ^{13}C NMR spectrum of **2m** (150 MHz, $CDCl_3$)

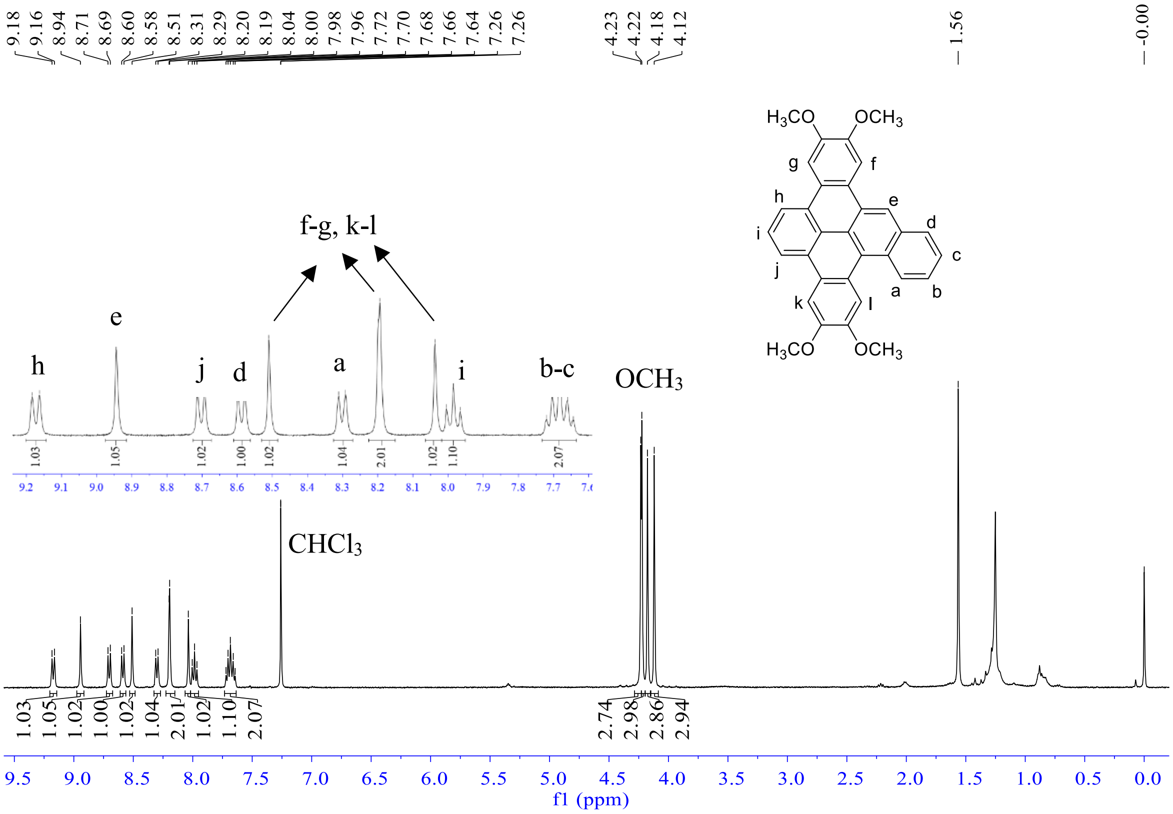


Figure S35 ^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)

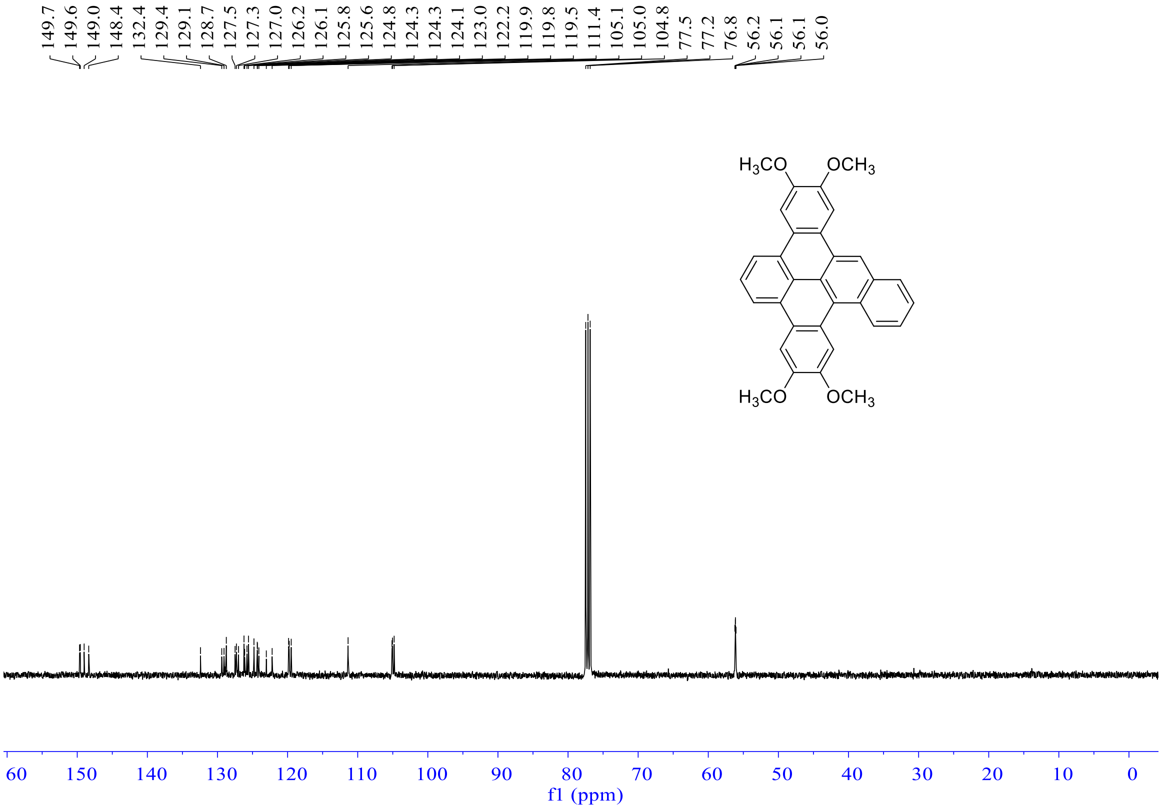


Figure S36 ^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)

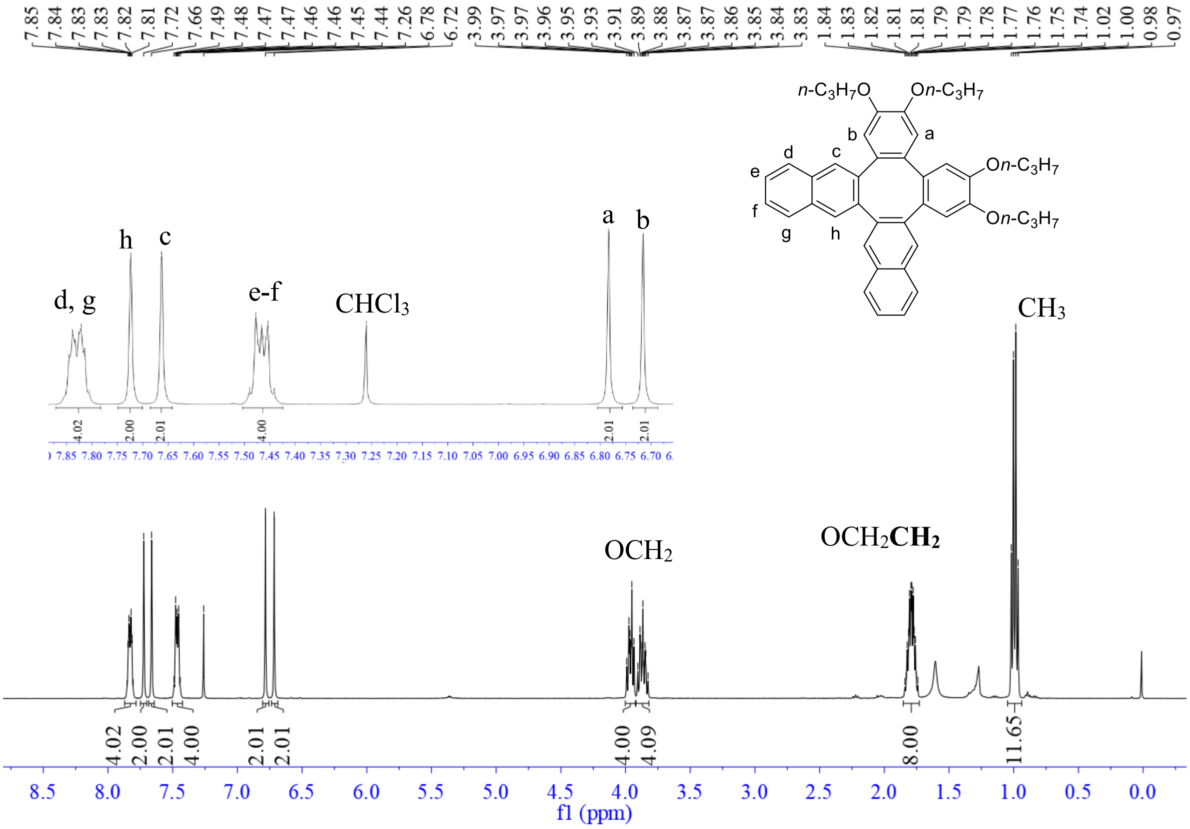


Figure S37 ^{1}H NMR spectrum of **2n** (400 MHz, $CDCl_3$)

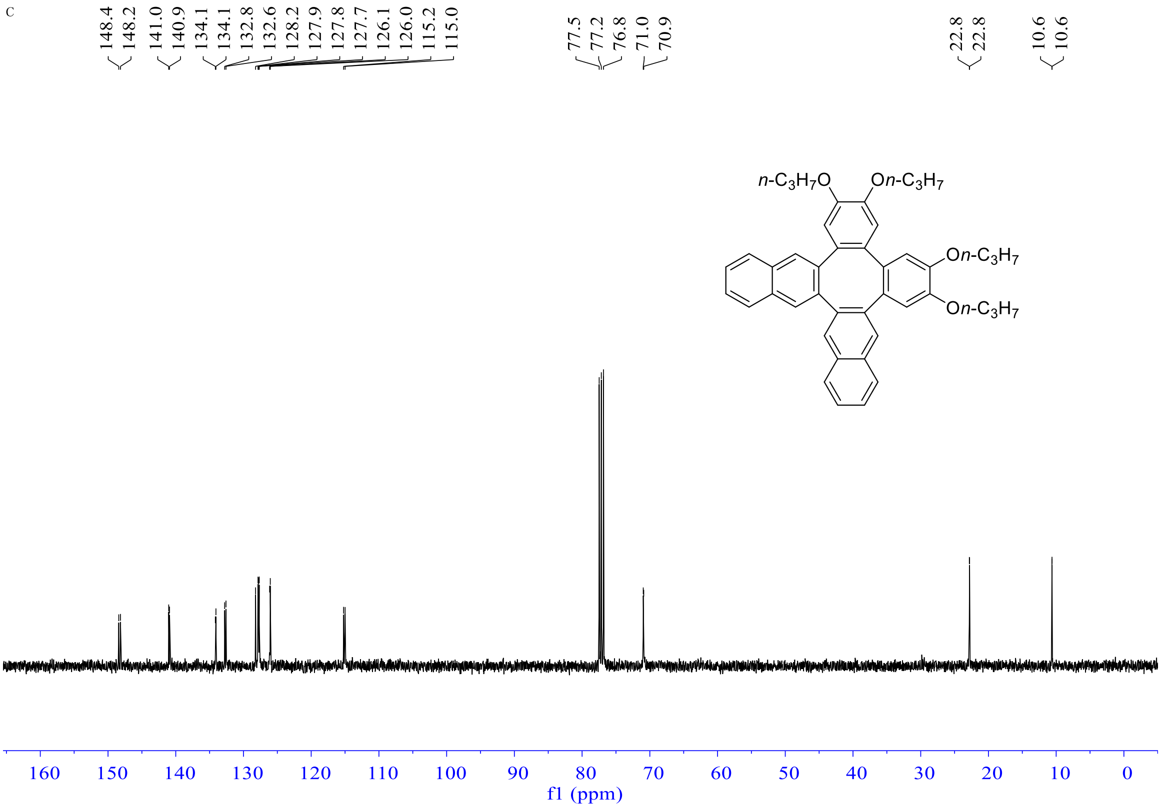


Figure S38 ^{13}C NMR spectrum of **2n** (100 MHz, $CDCl_3$)

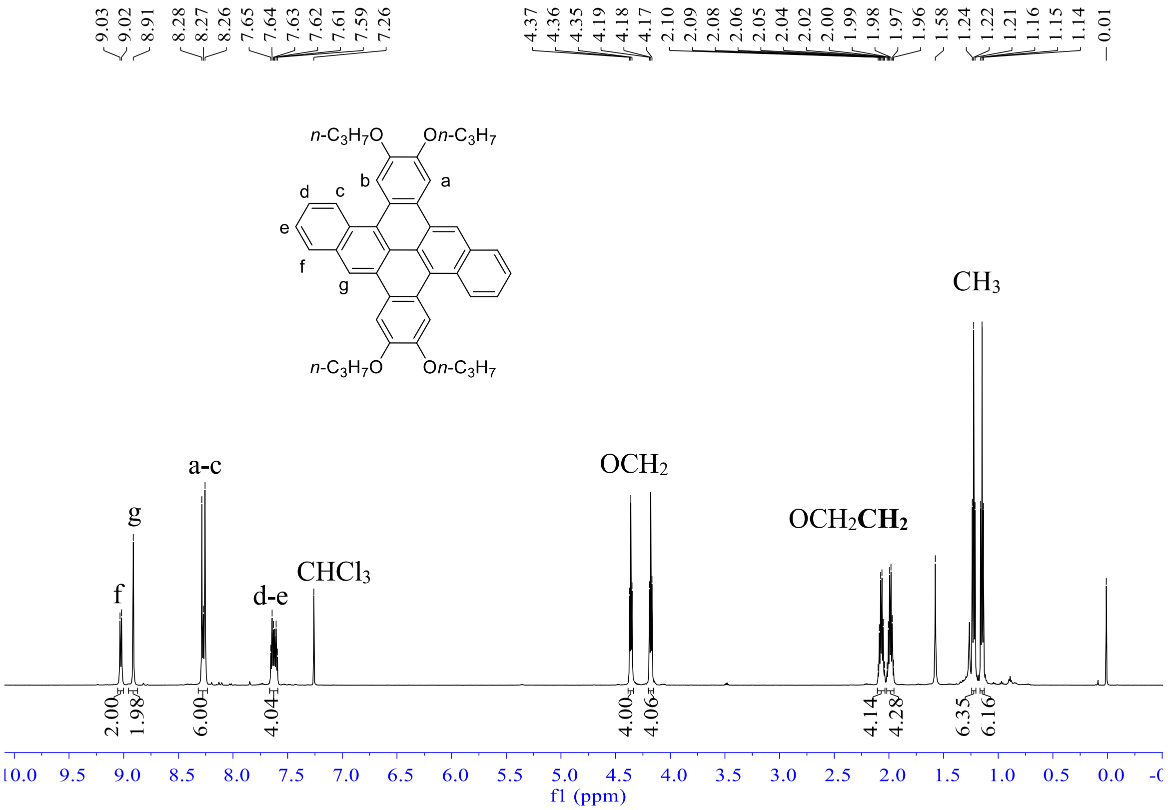


Figure S39 ^{1}H NMR spectrum of **3n** (600 MHz, CDCl$_3$)

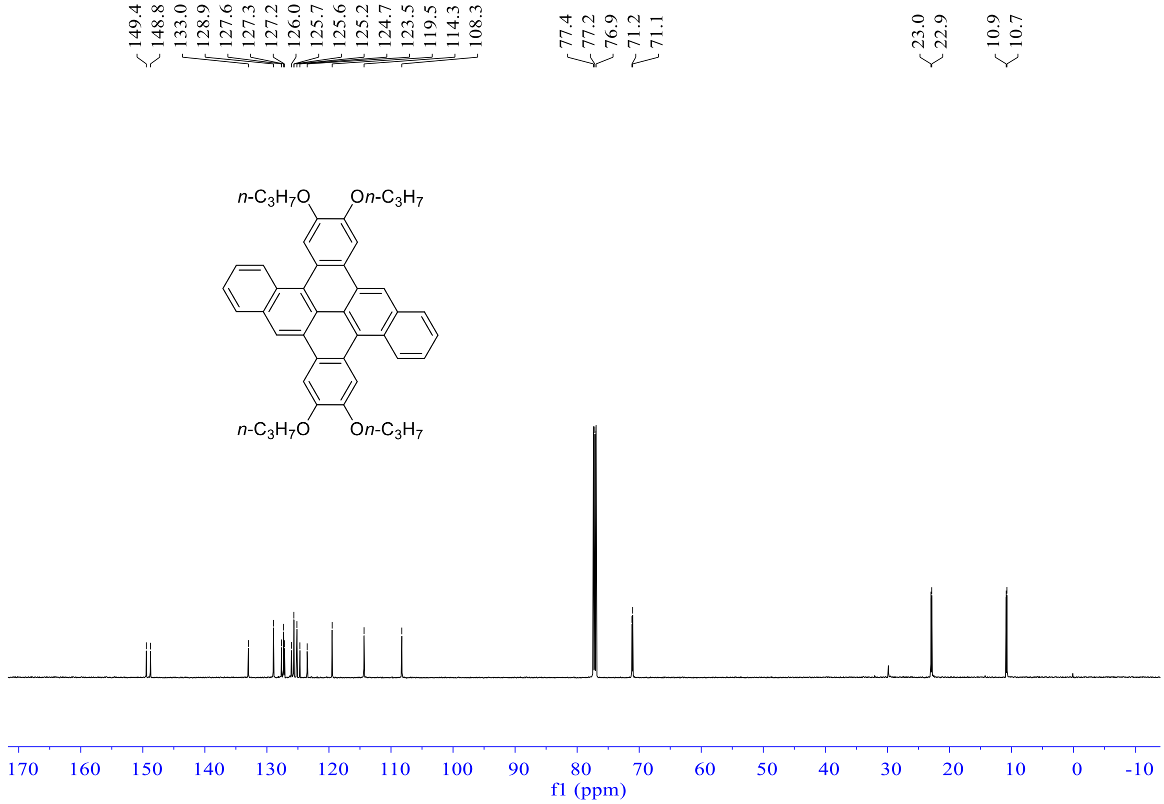


Figure S40 ^{13}C NMR spectrum of **3n** (150 MHz, CDCl$_3$)

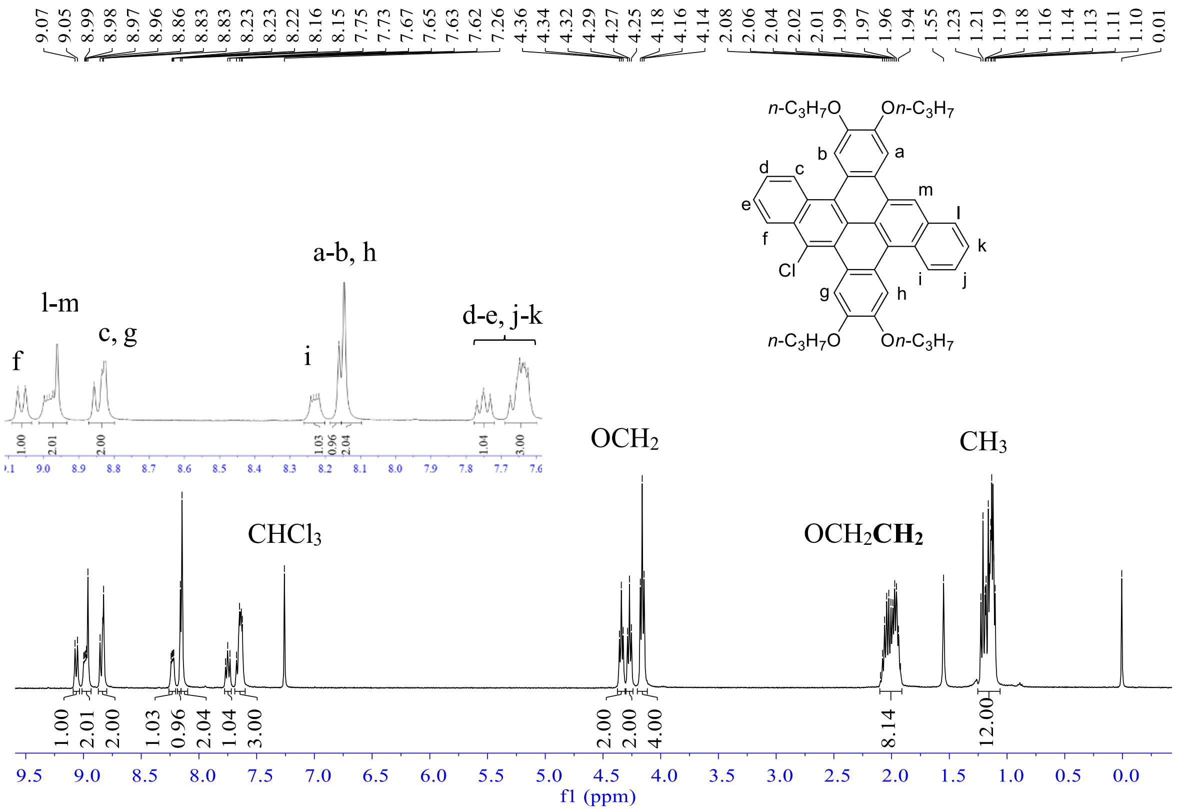


Figure S41 ^{1}H NMR spectrum of **3n-Cl** (400 MHz, $CDCl_3$)

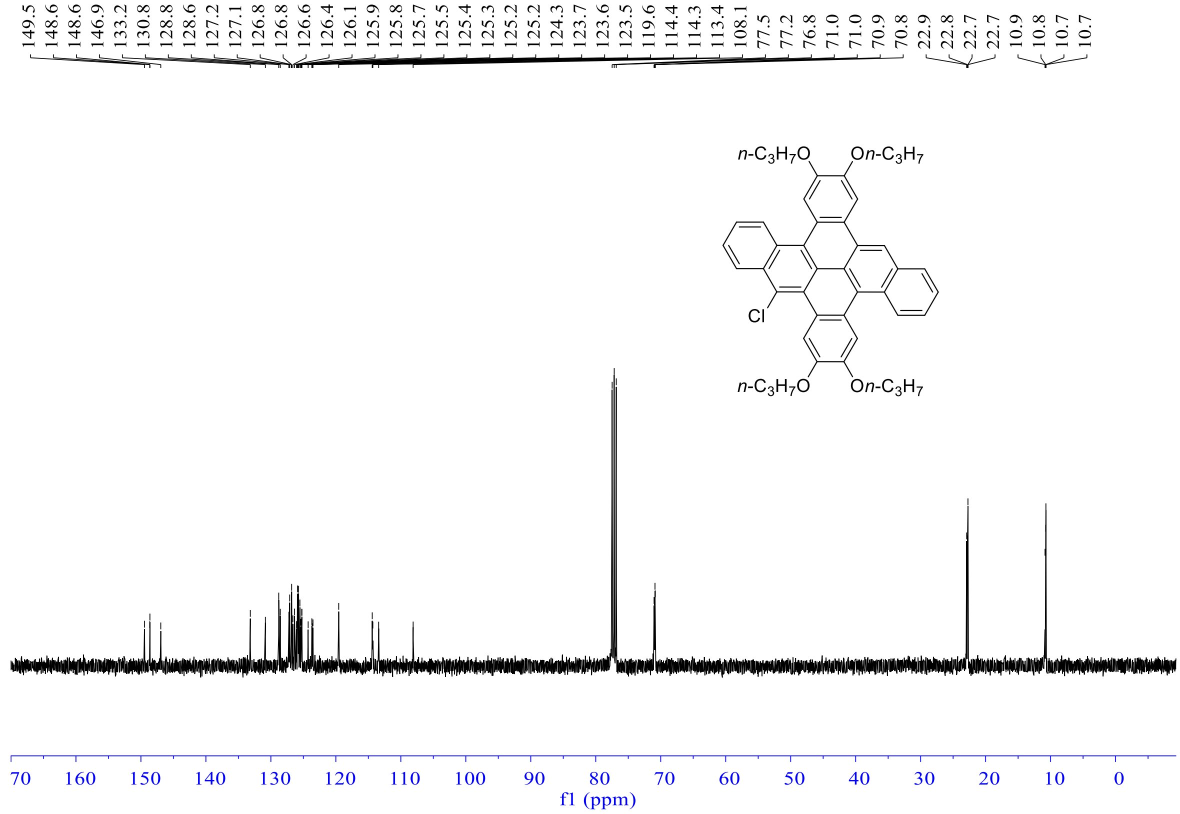


Figure S42 ^{13}C NMR spectrum of **3n-Cl** (100 MHz, $CDCl_3$)

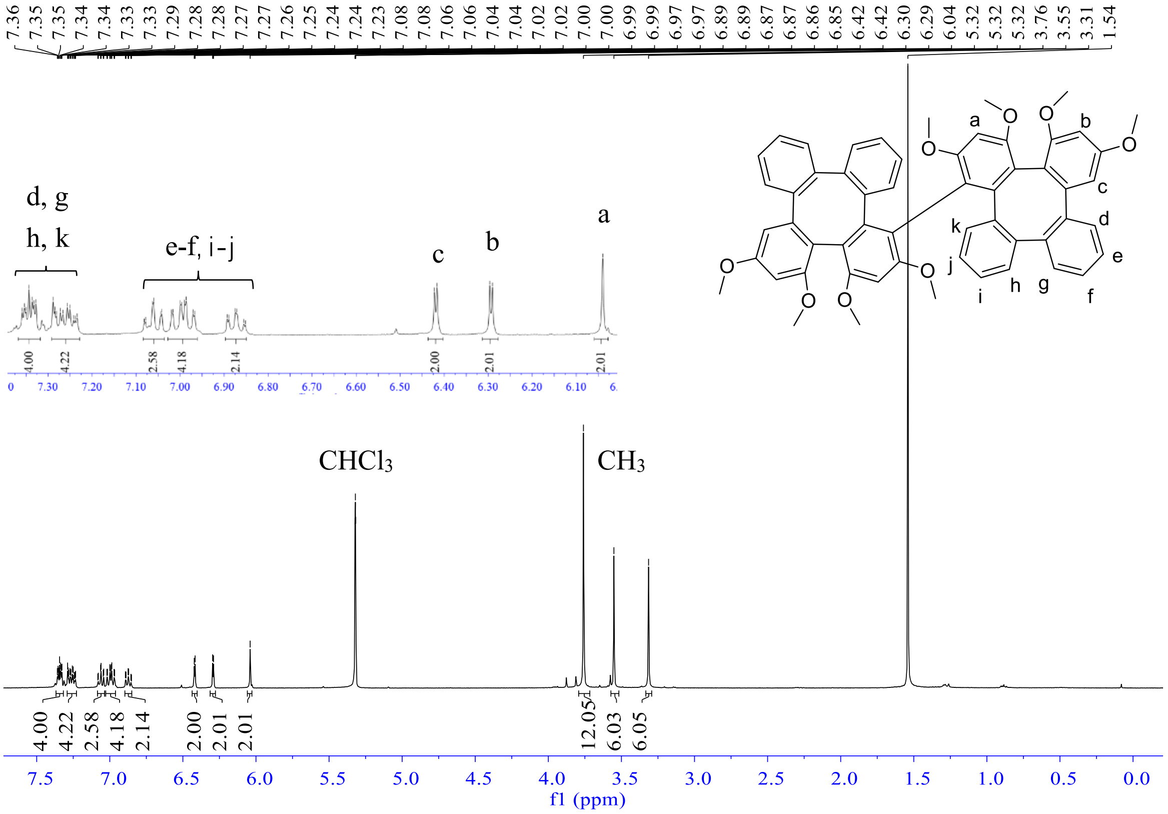


Figure S43 ^{1}H NMR spectrum of **5** (400 MHz, CD_2Cl_2)

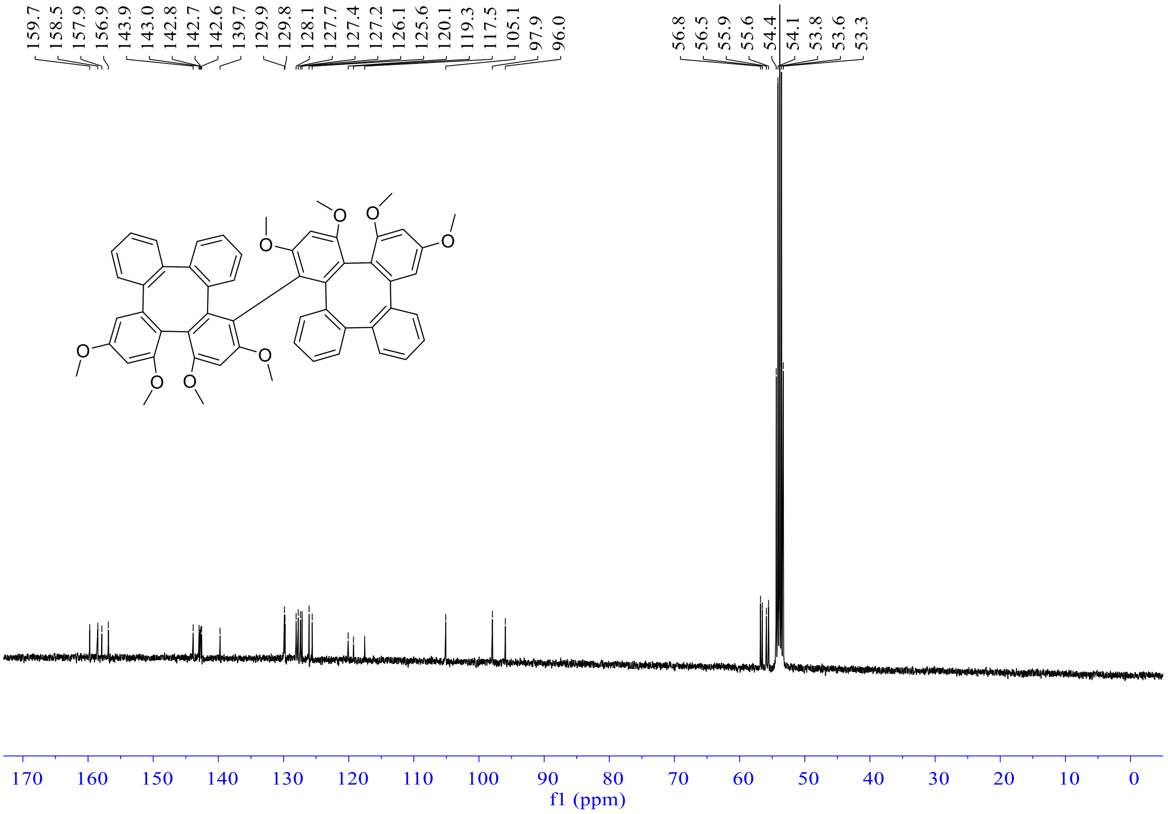


Figure S44 ^{13}C NMR spectrum of **5** (100 MHz, CD_2Cl_2)

3. Mass spectra

Accurate Mass Measurement

Molecular formula :	$C_{22}H_{16}S_2$
Experimental Mass $[M+H]^+$:	345.07654
Theoretical Mass $[M+H]^+$:	345.07662
Error (ppm) :	-0.2

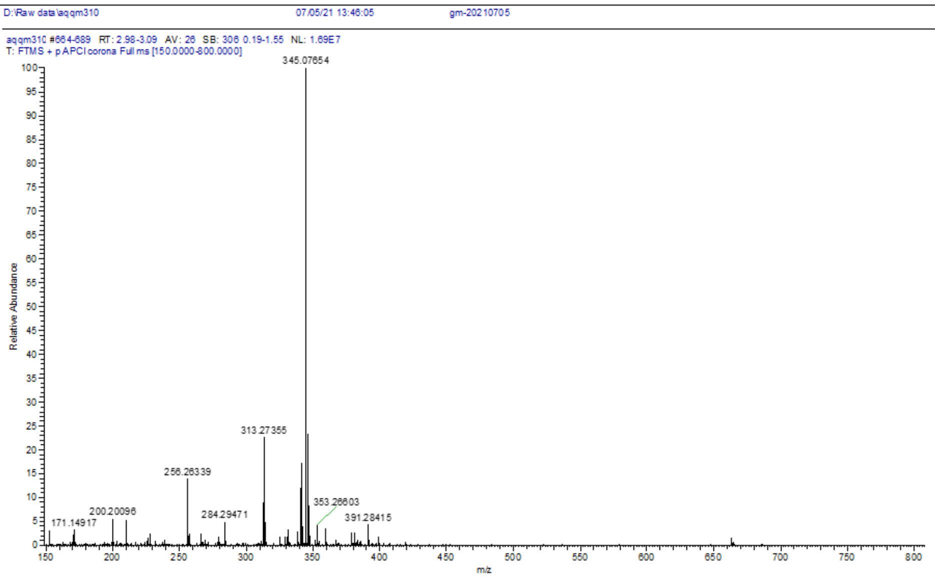


Figure S45 Mass spectrum (APCI) of **2c**

Accurate Mass Measurement

Molecular formula :	$C_{28}H_{24}O_4$
Experimental Mass $[M+H]^+$:	425.17433
Theoretical Mass $[M+H]^+$:	425.17474
Error (ppm) :	-1.0

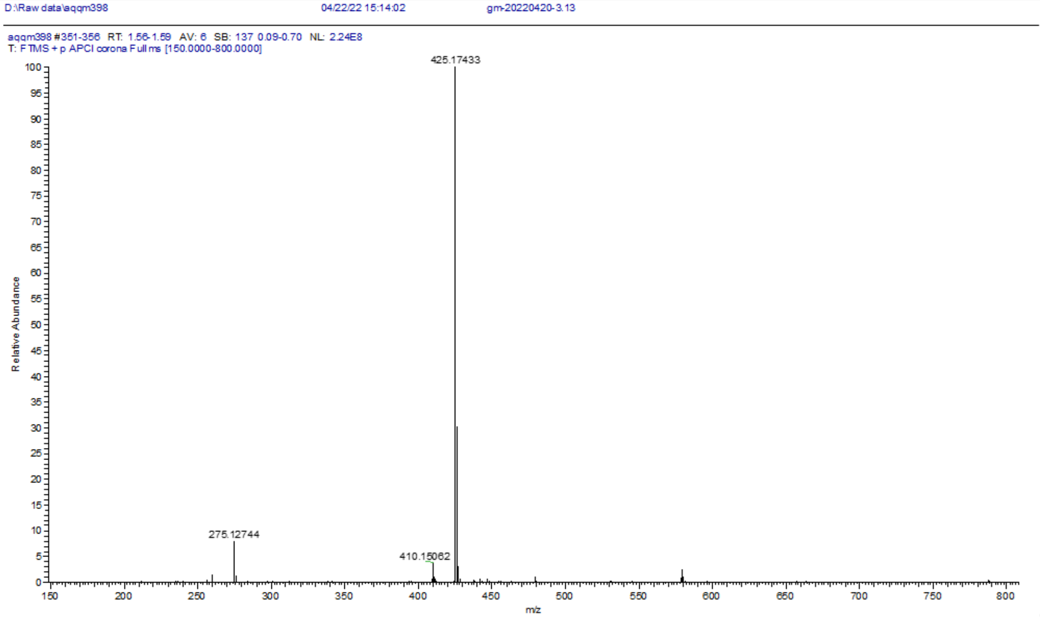


Figure S46 Mass spectrum (APCI) of **2e**

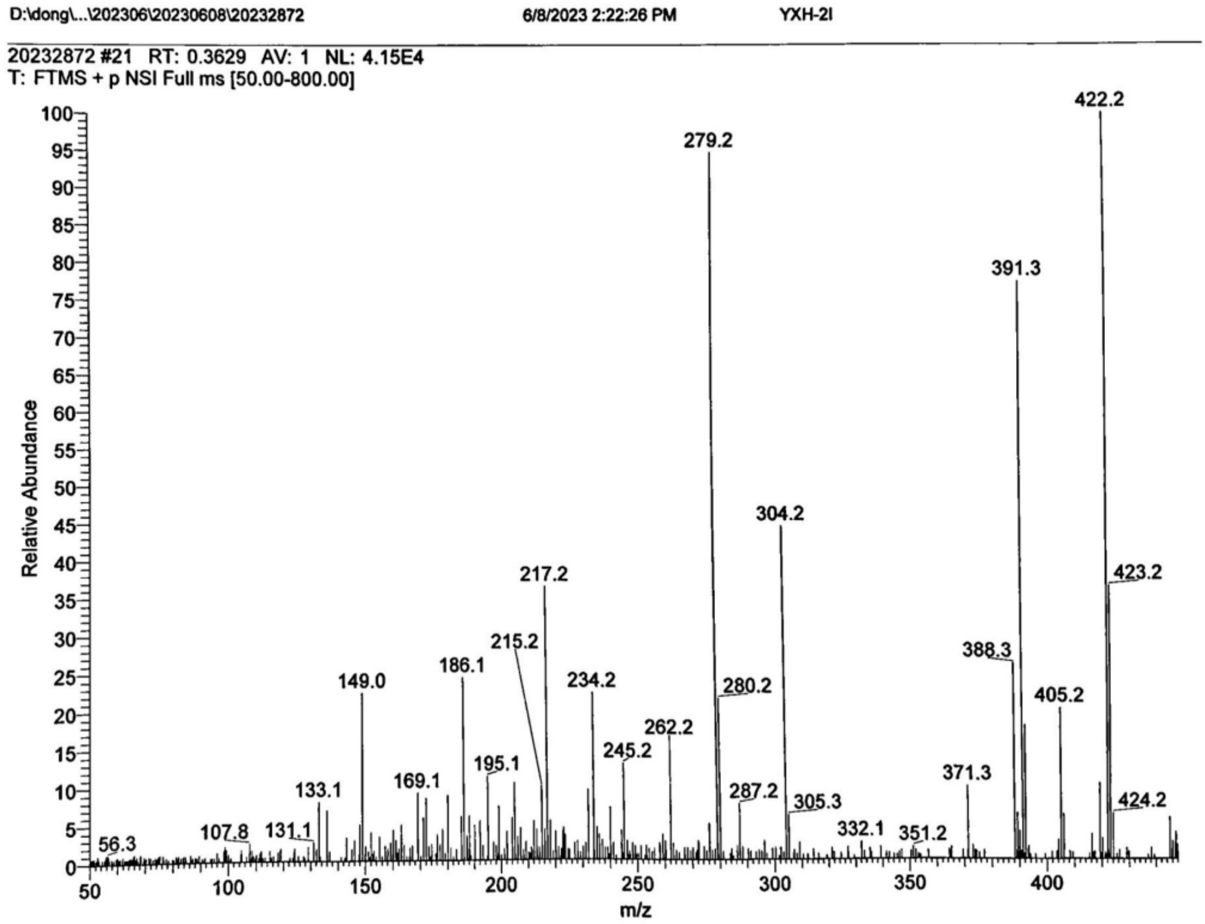


Figure S47 Mass spectrum (DART) of **2g**

Accurate Mass Measurement

Molecular formula :	$C_{44}H_{38}N_2$
Experimental Mass [M+H]$^+$:	595.31032
Theoretical Mass [M+H]$^+$:	595.31078
Error (ppm) :	-0.8

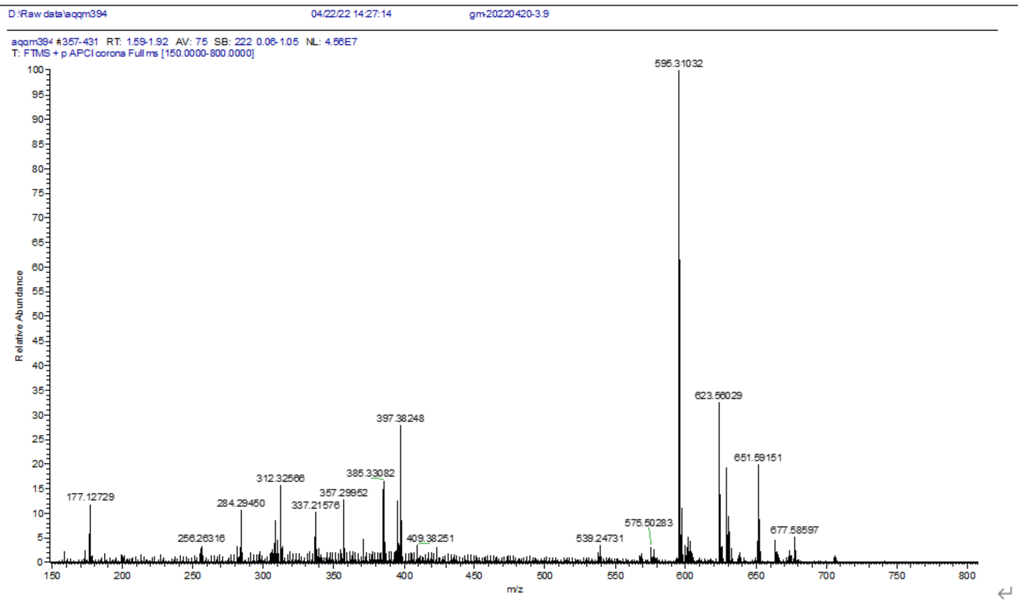


Figure S48 Mass spectrum (APCI) of **2h**

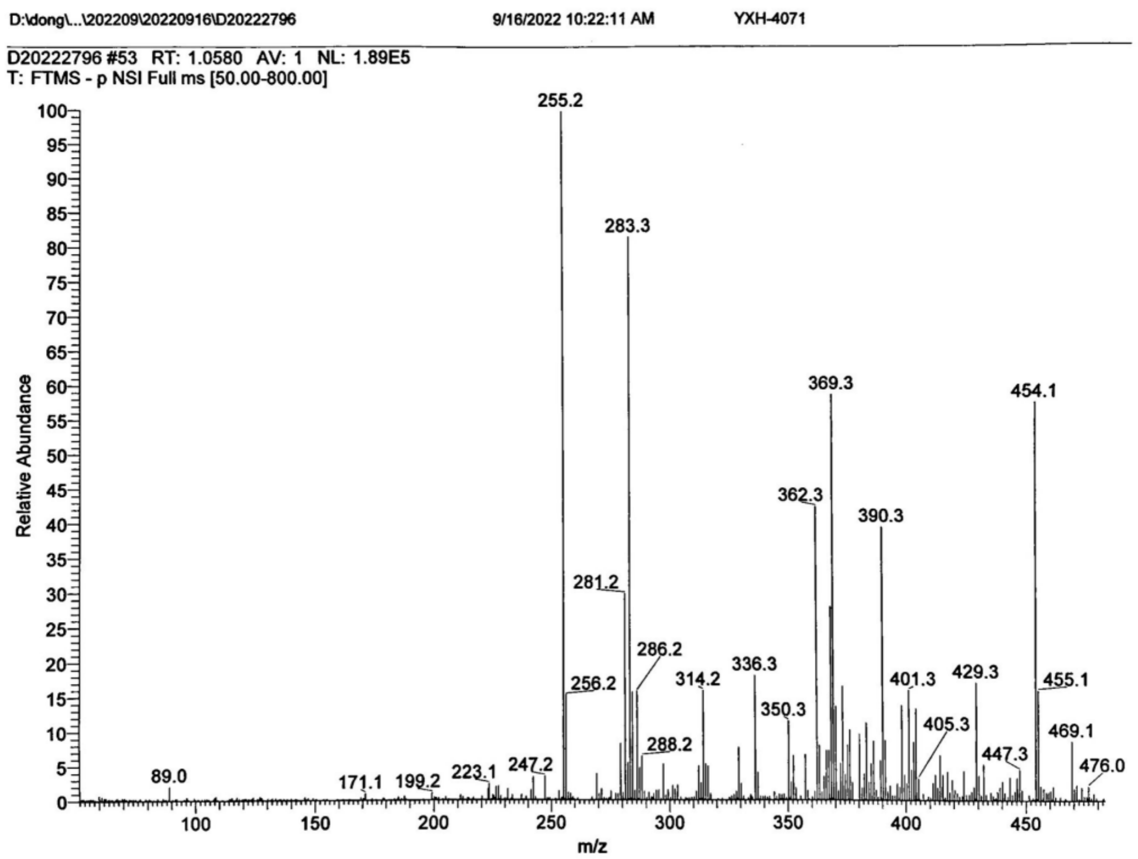


Figure S49 Mass spectrum (DART) of **2j**

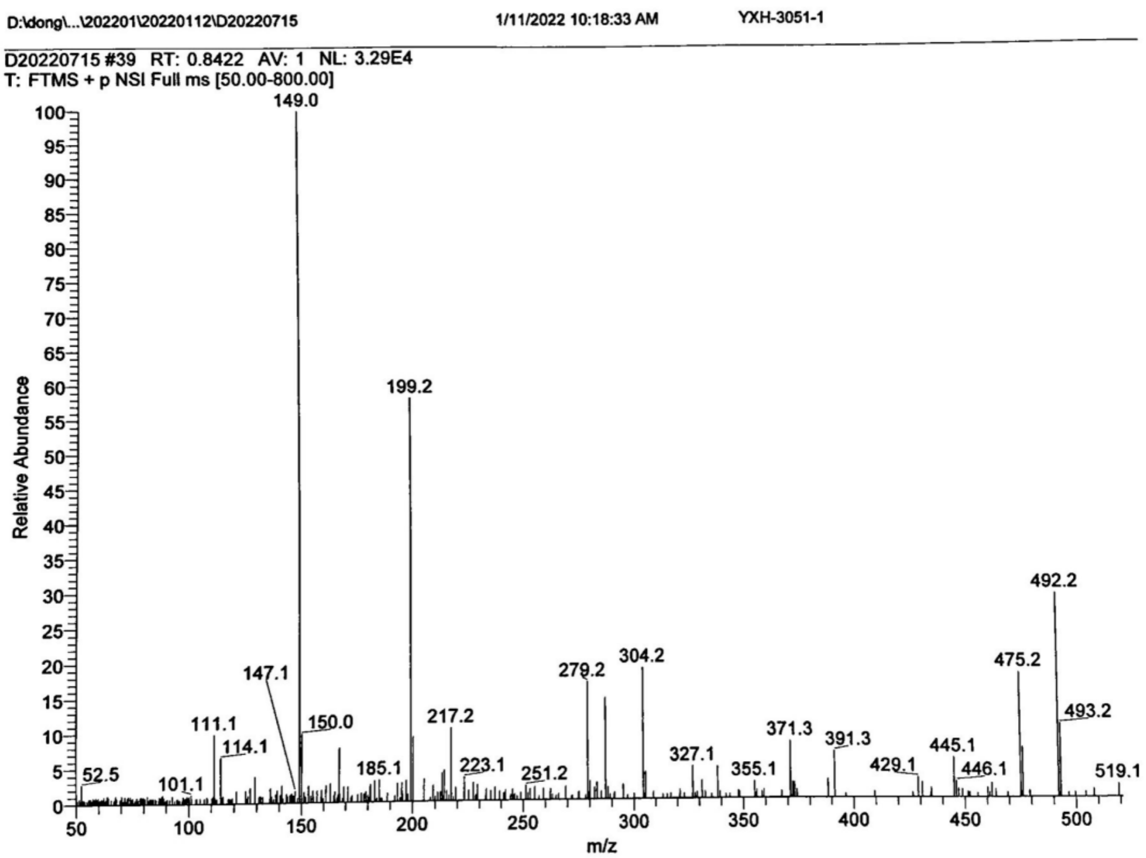


Figure S50 Mass spectrum (DART) of **2m**

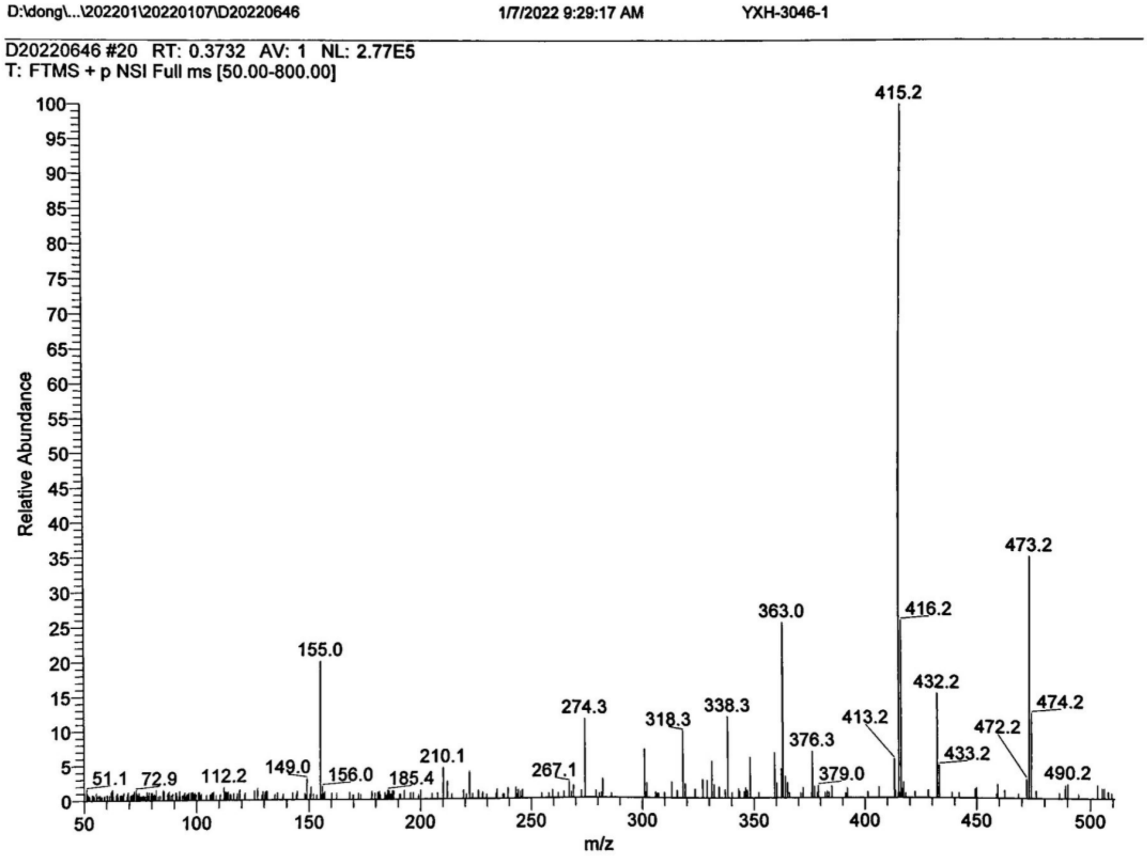


Figure S51 Mass spectrum (DART) of **3m**

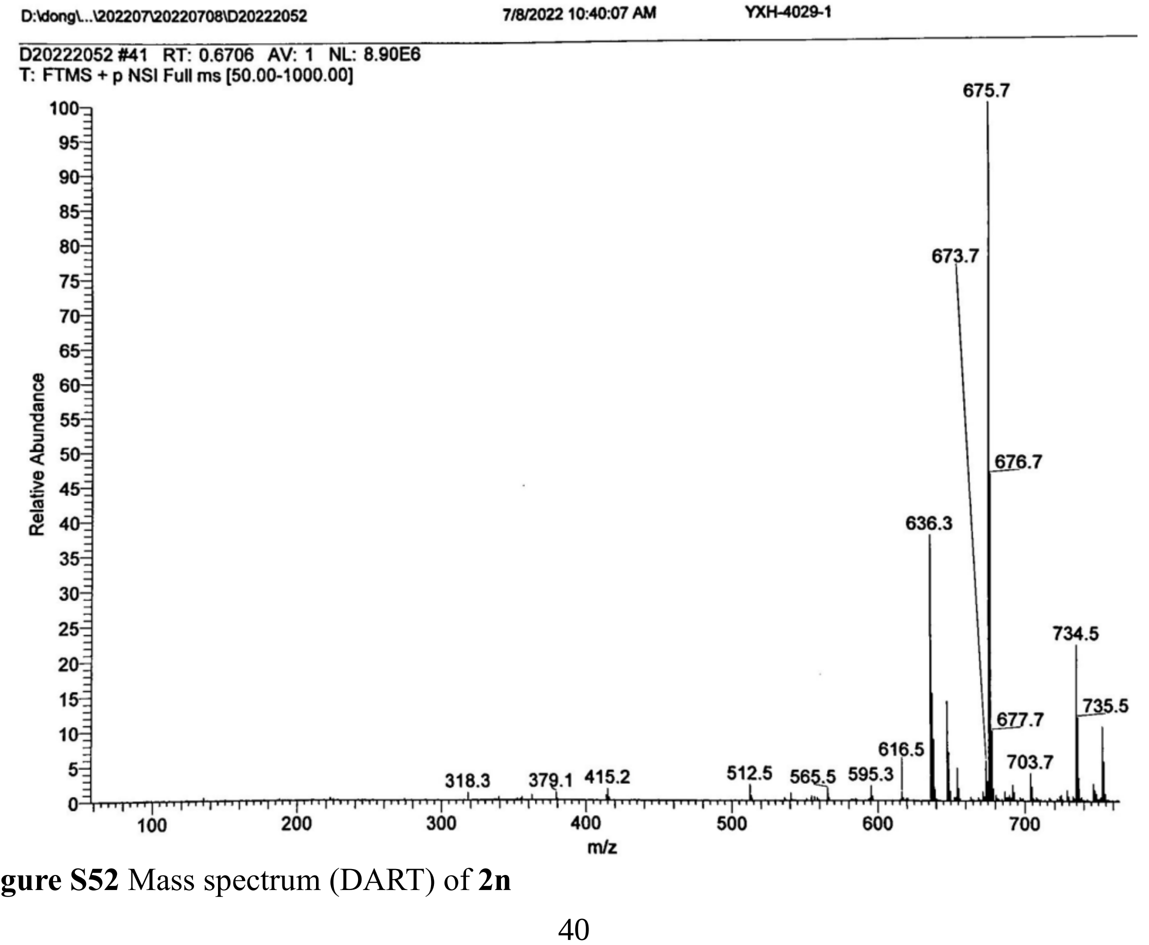
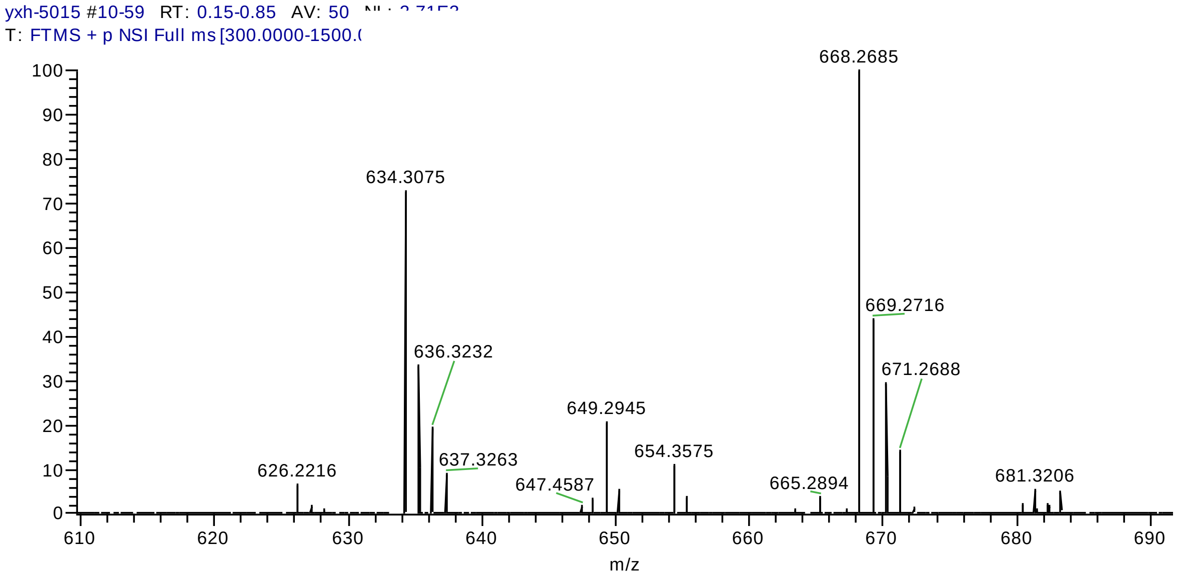
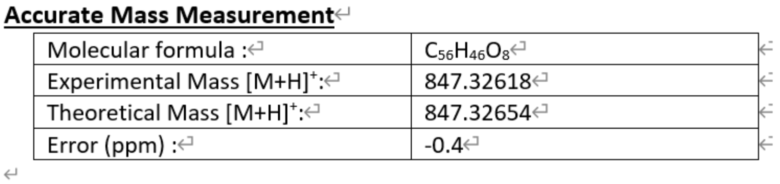


Figure S52 Mass spectrum (DART) of **2n**



Theoretical mass of $C_{44}H_{42}O_4$ is 634.3078, and theoretical mass of $C_{44}H_{41}O_4Cl$ is 668.2688.

Figure S53 Mass spectra (MALDI) of **3n** and **3n-Cl**.



Accurate Mass Measurement

Molecular formula :	$C_{56}H_{46}O_8$
Experimental Mass $[M+H]^+$:	847.32618
Theoretical Mass $[M+H]^+$:	847.32654
Error (ppm) :	-0.4

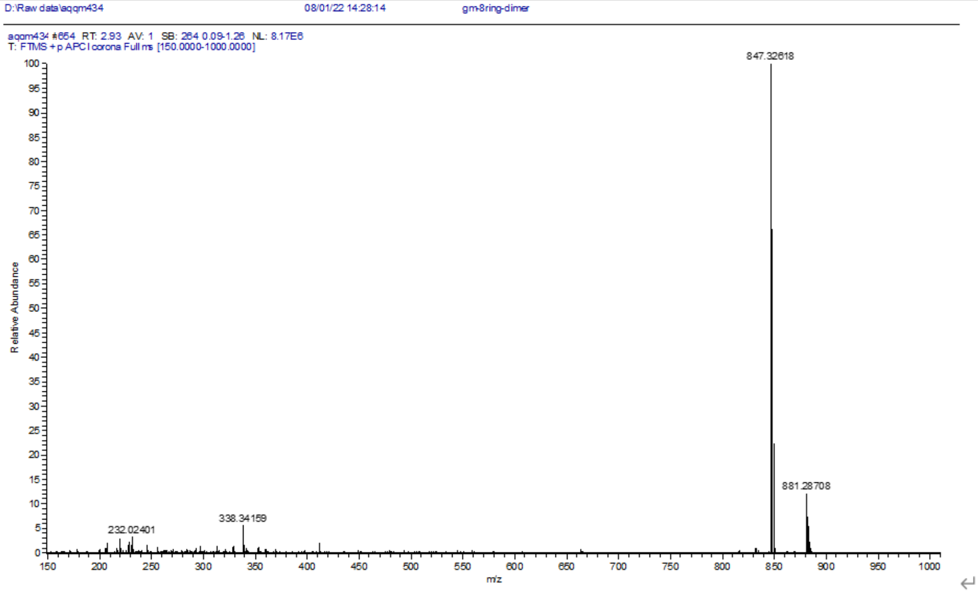


Figure S54 Mass spectrum (APCI) of **5**

4. Single crystal structures

X-ray crystallography data were collected on a Bruker D8 Venture Diffractometer.

Crystal data and structure refinement for **1k**.

Empirical formula	C24 H16 N2 O4	
Formula weight	396.39	
Temperature	213.00 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 19.9133(3) Å	α = 90°.
	b = 8.79260(10) Å	β = 129.2540(10)°.
	c = 13.9176(2) Å	γ = 90°.
Volume	1886.95(5) Å^3	
Z	4	
Density (calculated)	1.395 Mg/m^3	
Absorption coefficient	0.503 mm^{-1}	
F(000)	824	
Crystal size	0.07 x 0.07 x 0.05 mm^3	
Theta range for data collection	4.991 to 54.898°.	
Index ranges	-24<=h<=24, -10<=k<=10, -16<=l<=16	
Reflections collected	8005	
Independent reflections	1761 [R(int) = 0.0289]	
Completeness to theta = 53.594°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.6358	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1761 / 0 / 136	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.1112	
R indices (all data)	R1 = 0.0414, wR2 = 0.1136	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.214 and -0.193 e.Å^{-3}	

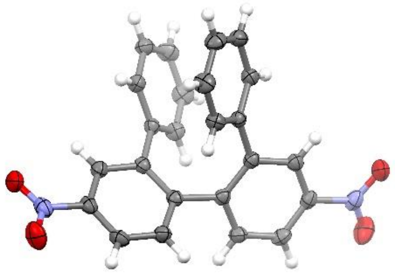


Figure S55 Structure of **1k** in the crystal (Carbon, oxygen and chlorine atoms are shown as ellipsoids at 50% probability level.)

Crystal data and structure refinement for **2g**.

Empirical formula	C32 H20	
Formula weight	404.48	
Temperature	213.00 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.9132(3) Å	α = 90°.
	b = 9.3178(2) Å	β = 102.4290(10)°.
	c = 21.1891(5) Å	γ = 90°.
Volume	2104.16(9) Å^3	
Z	4	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.350 mm^{-1}	
F(000)	848	
Crystal size	0.07 x 0.07 x 0.05 mm^3	
Theta range for data collection	3.686 to 54.983°.	
Index ranges	-13<=h<=12, -11<=k<=11, -25<=l<=25	
Reflections collected	20561	
Independent reflections	3988 [R(int) = 0.0625]	
Completeness to theta = 53.594°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5953	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3988 / 0 / 289	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0512, wR2 = 0.1165	
R indices (all data)	R1 = 0.0874, wR2 = 0.1373	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.208 and -0.241 e.Å^{-3}	

Crystal data and structure refinement for **2j**.

Empirical formula	C26 H18 N2 O6	
Formula weight	454.42	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.7120(6) Å	α = 90°.
	b = 14.6556(7) Å	β = 107.758(2)°.
	c = 14.1174(8) Å	γ = 90°.
Volume	2110.7(2) Å^3	
Z	4	
Density (calculated)	1.430 Mg/m^3	
Absorption coefficient	0.103 mm^{-1}	
F(000)	944	
Crystal size	0.180 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.523 to 25.999°.	
Index ranges	-11<=h<=13, -18<=k<=18, -17<=l<=16	
Reflections collected	24873	
Independent reflections	4123 [R(int) = 0.0651]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5074	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4123 / 0 / 310	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1038	
R indices (all data)	R1 = 0.0516, wR2 = 0.1131	
Extinction coefficient	0.018(3)	
Largest diff. peak and hole	0.229 and -0.196 e.Å^{-3}	

Crystal data and structure refinement for **2m**.

Empirical formula	C32 H26 O4	
Formula weight	474.53	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.048(4) Å	α = 81.328(8)°.
	b = 13.076(3) Å	β = 73.961(8)°.
	c = 15.272(4) Å	γ = 88.817(7)°.
Volume	2474.9(12) Å^3	
Z	4	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	1000	
Crystal size	0.180 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.752 to 24.995°.	
Index ranges	-15<=h<=15, -15<=k<=15, -18<=l<=18	
Reflections collected	46602	
Independent reflections	8697 [R(int) = 0.1122]	
Completeness to theta = 25.242°	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.3980	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8697 / 0 / 657	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0794, wR2 = 0.2082	
R indices (all data)	R1 = 0.1358, wR2 = 0.2583	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.252 and -0.293 e.Å^{-3}	

Crystal data and structure refinement for **2n**.

Empirical formula	C44 H44 O4	
Formula weight	636.79	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 25.2475(12) Å	α = 90°.
	b = 16.4517(9) Å	β = 91.9950(10)°.
	c = 17.0389(8) Å	γ = 90°.
Volume	7073.1(6) Å^3	
Z	8	
Density (calculated)	1.196 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	2720	
Crystal size	0.120 x 0.090 x 0.060 mm^3	
Theta range for data collection	2.392 to 24.998°.	
Index ranges	-30<=h<=30, -19<=k<=17, -20<=l<=20	
Reflections collected	31370	
Independent reflections	6206 [R(int) = 0.0952]	
Completeness to theta = 25.242°	96.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5542	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6206 / 0 / 437	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0768, wR2 = 0.1718	
R indices (all data)	R1 = 0.1298, wR2 = 0.2072	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.440 and -0.301 e.Å^{-3}	

Crystal data and structure refinement for **3n-Cl**.

Empirical formula	C44 H41 Cl O4	
Formula weight	669.22	
Temperature	213.00 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 24.4083(11) Å	α = 90°.
	b = 7.5812(3) Å	β = 90°.
	c = 36.9842(15) Å	γ = 90°.
Volume	6843.7(5) $\mathrm{Å}^3$	
Z	8	
Density (calculated)	1.299 $\mathrm{Mg/m}^3$	
Absorption coefficient	0.874 mm^{-1}	
F(000)	2832	
Crystal size	0.07 x 0.07 x 0.05 mm^3	
Theta range for data collection	3.775 to 54.976°.	
Index ranges	-29<=h<=29, -8<=k<=9, -45<=l<=45	
Reflections collected	69449	
Independent reflections	6429 [R(int) = 0.0874]	
Completeness to theta = 53.594°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.6063	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6429 / 0 / 446	
Goodness-of-fit on F^2	1.169	
Final R indices [I>2sigma(I)]	R1 = 0.0974, wR2 = 0.2570	
R indices (all data)	R1 = 0.1383, wR2 = 0.3152	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.578 and -0.917 $\mathrm{e.Å}^{-3}$	

Crystal data and structure refinement for **5**.

Empirical formula	C114 H96 Cl4 O16	
Formula weight	1863.70	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 16.5308(18) Å	α = 90°.
	b = 34.980(4) Å	β = 111.110(6)°.
	c = 19.638(3) Å	γ = 90°.
Volume	10594(2) Å^3	
Z	4	
Density (calculated)	1.169 Mg/m^3	
Absorption coefficient	1.515 mm^{-1}	
F(000)	3904	
Crystal size	0.400 x 0.300 x 0.200 mm^3	
Theta range for data collection	2.526 to 72.249°.	
Index ranges	-19<=h<=18, -42<=k<=42, -23<=l<=23	
Reflections collected	165706	
Independent reflections	19503 [R(int) = 0.1523]	
Completeness to theta = 67.679°	99.3 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7531 and 0.3706	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19503 / 3 / 1234	
Goodness-of-fit on F^2	1.567	
Final R indices [I>2sigma(I)]	R1 = 0.1377, wR2 = 0.3774	
R indices (all data)	R1 = 0.1881, wR2 = 0.4310	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.960 and -0.519 e.Å^{-3}	

5. UV/Vis absorption and fluorescent spectra

UV-vis absorption spectra were recorded on a Hitachi U-3310 UV-vis spectrophotometer. Fluorescence spectra were taken on a Hitachi F-2700 spectrofluorometer.

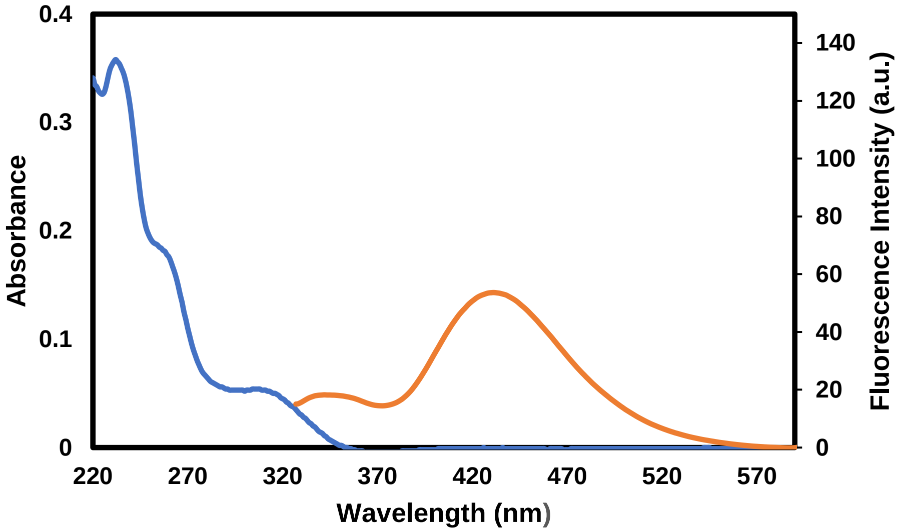


Figure S56 Absorption (full line) and Fluorescence (dashed line, excited at 306 nm) spectra of **2c** in CH_2Cl_2 (1× 10^{-5} mol/L).

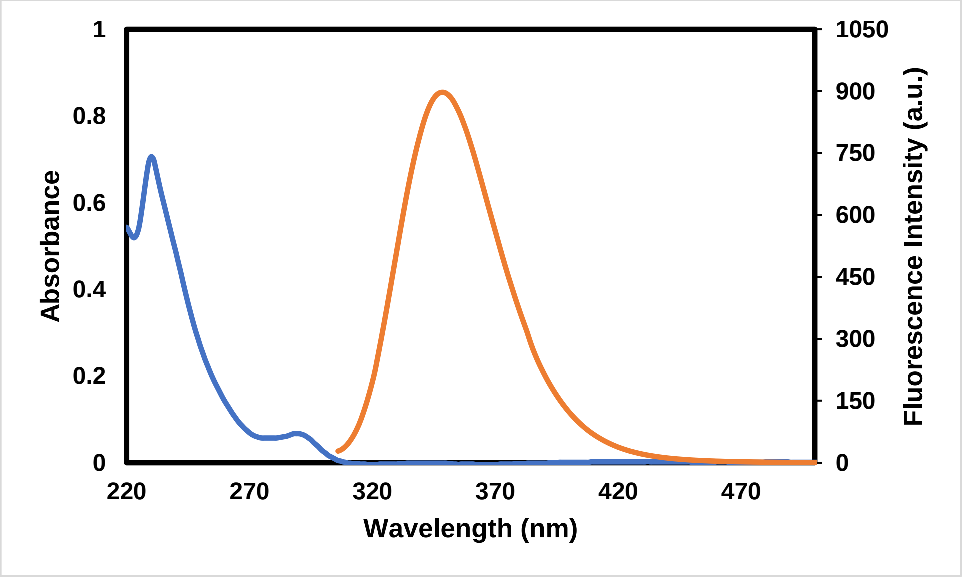


Figure S57 Absorption (full line) and Fluorescence (dashed line, excited at 289 nm) spectra of **2e** in CH_2Cl_2 (1× 10^{-5} mol/L).

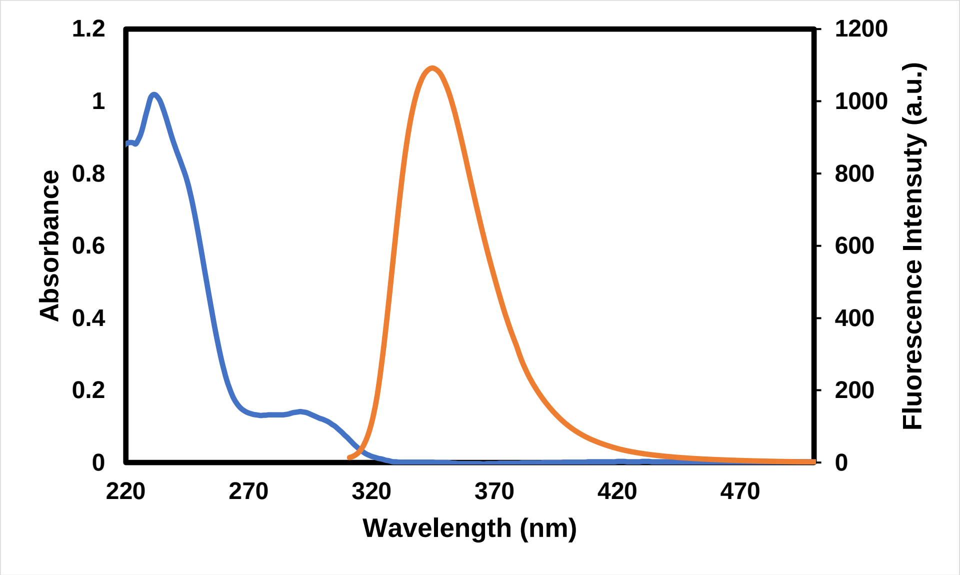


Figure S58 Absorption (full line) and Fluorescence (dashed line, excited at 290 nm) spectra of **2g** in CH_2Cl_2 (1× 10^{-5} mol/L).

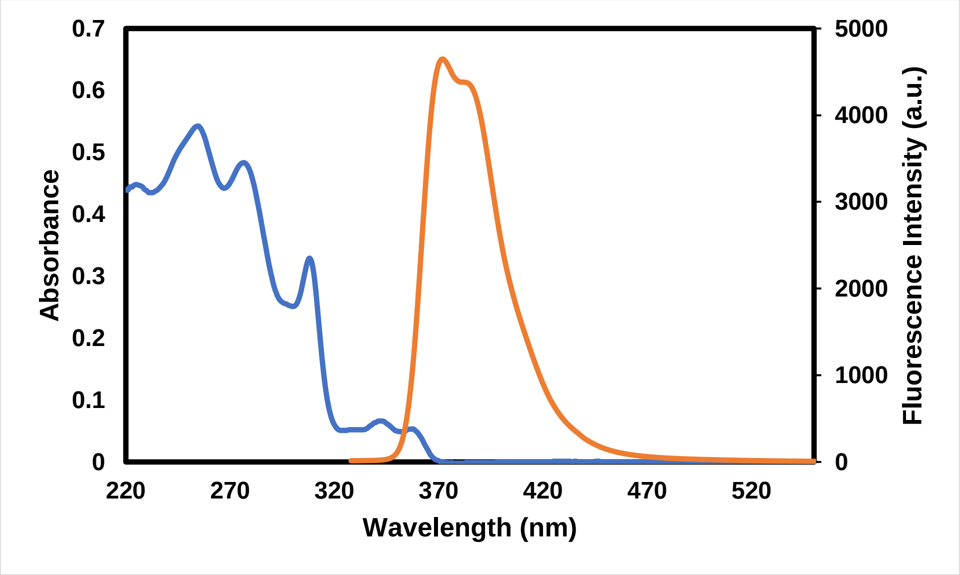


Figure S59 Absorption (full line) and Fluorescence (dashed line, excited at 308 nm) spectra of **2h** in CH_2Cl_2 (1× 10^{-5} mol/L).

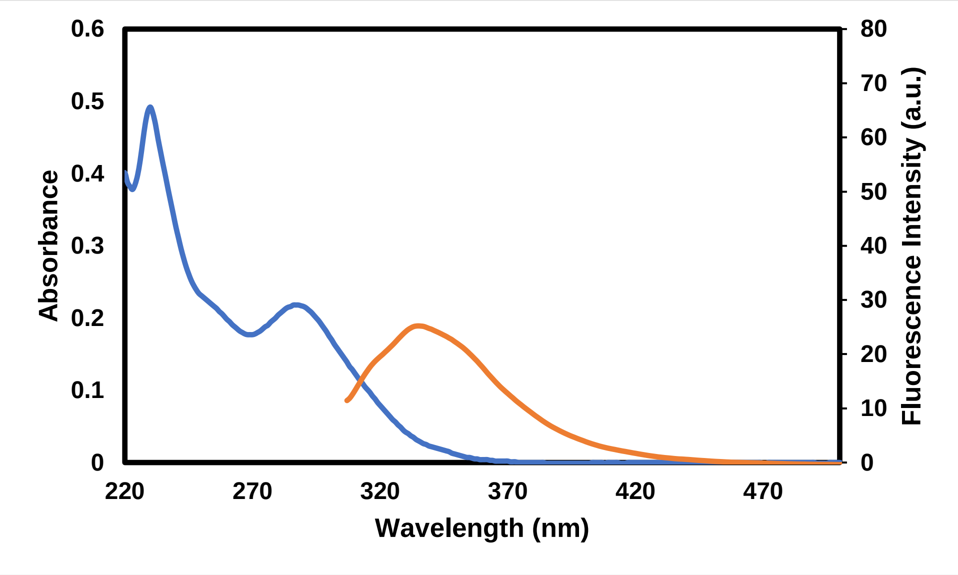


Figure S60 Absorption (full line) and Fluorescence (dashed line, excited at 288 nm) spectra of **2j** in CH_2Cl_2 (1× 10^{-5} mol/L).

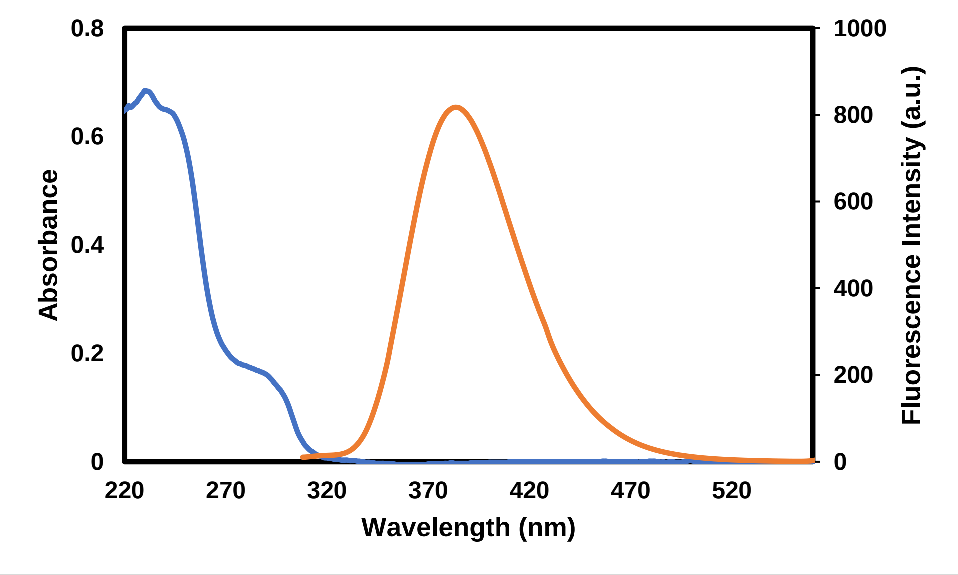


Figure S61 Absorption (full line) and Fluorescence (dashed line, excited at 288 nm) spectra of **2m** in CH_2Cl_2 (1× 10^{-5} mol/L).

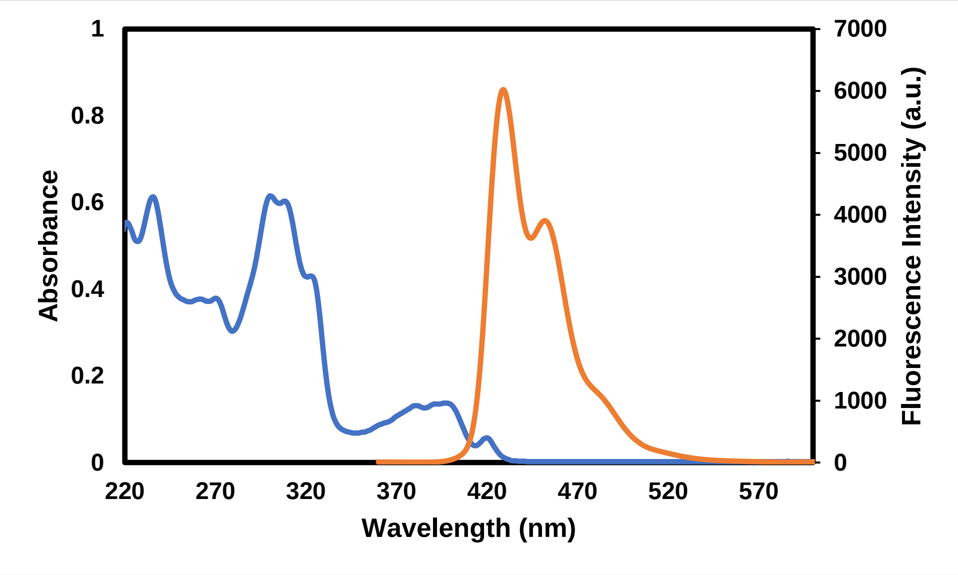


Figure S62 Absorption (full line) and Fluorescence (dashed line, excited at 301 nm) spectra of **3m** in CH_2Cl_2 (1× 10^{-5} mol/L).

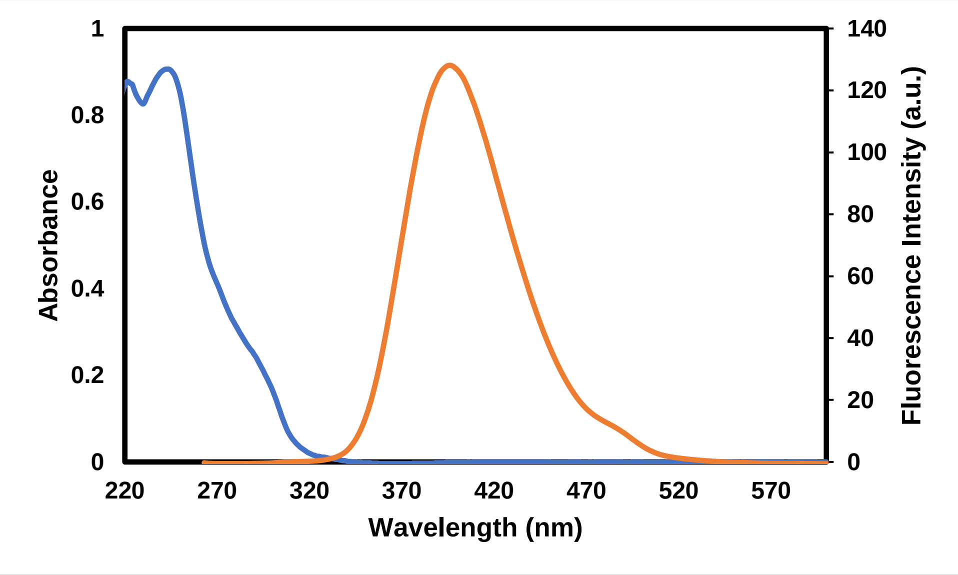


Figure S63 Absorption (full line) and Fluorescence (dashed line, excited at 242 nm) spectra of **2n** in CH_2Cl_2 (1× 10^{-5} mol/L).

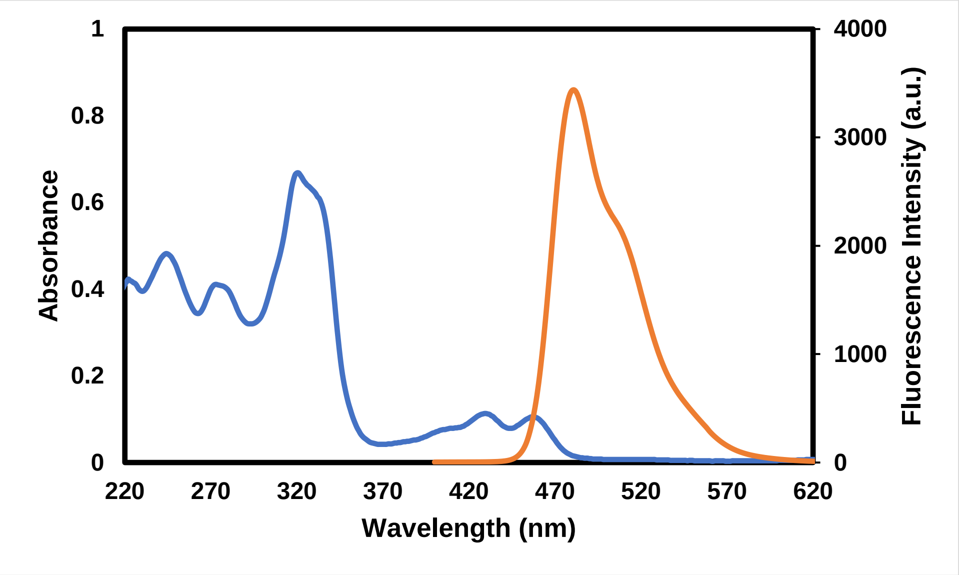


Figure S64 Absorption (full line) and Fluorescence (dashed line, excited at 320 nm) spectra of **3n** in CH_2Cl_2 (1× 10^{-5} mol/L).

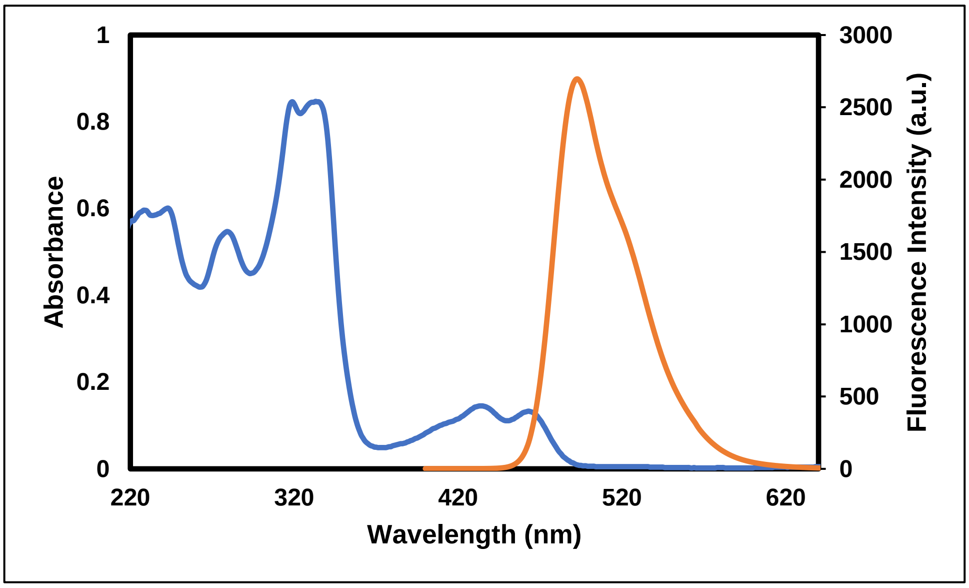
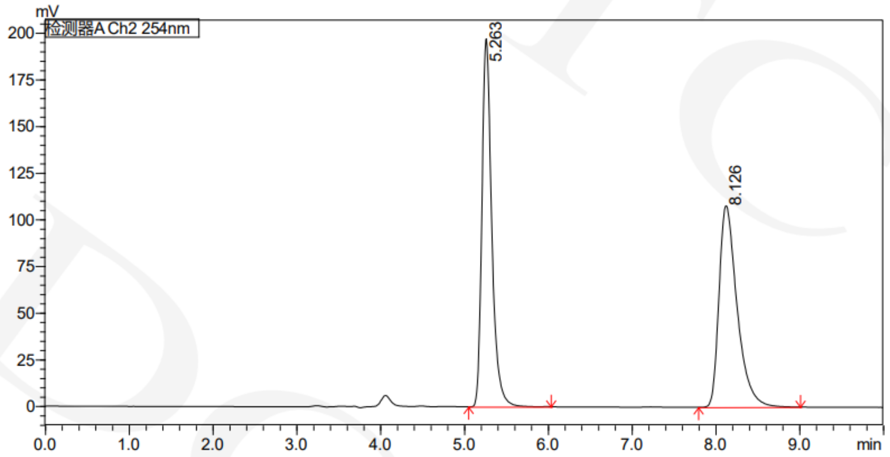


Figure S65 Absorption (full line) and Fluorescence (dashed line, excited at 334 nm) spectra of **3n-Cl** in CH_2Cl_2 (1× 10^{-5} mol/L).

6. Chiral resolution and circular dichroism spectrum of 2g

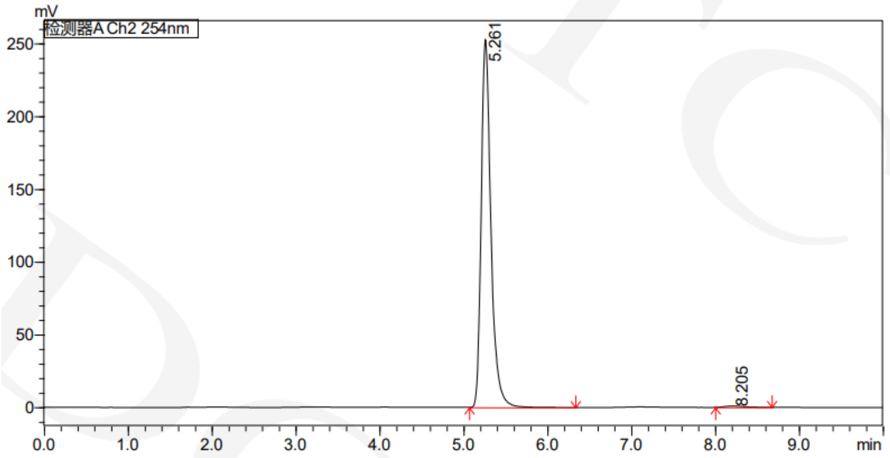
Compound **2g** was resolved to two enantiomers by Daicel Chiral Technologies (China) Co., Ltd. with a Shimadzu LC-20AT CP-HPLC-06 on a CHIRALCEL OD-H(ODH0CE-KJ063) column using MeOH/ACN=90/10(V/V) as the eluent. From 143 mg of racemic Compound **2g**, 34 mg of one enantiomer (the first fraction) and 38 mg of the other enantiomer (the second fraction) were obtained. Circular dichroism (CD) spectra were recorded on an Applied Photophysics Chirascan TM Spectrometer.



<Peak Table>

Peak#	Ret. Time	Area	Area%	T.Plate#	Tailing F.	Resolution
1	5.263	1611250	49.896	1.348	9411	15.938
2	8.126	1617973	50.104	1.527	7049	21.280

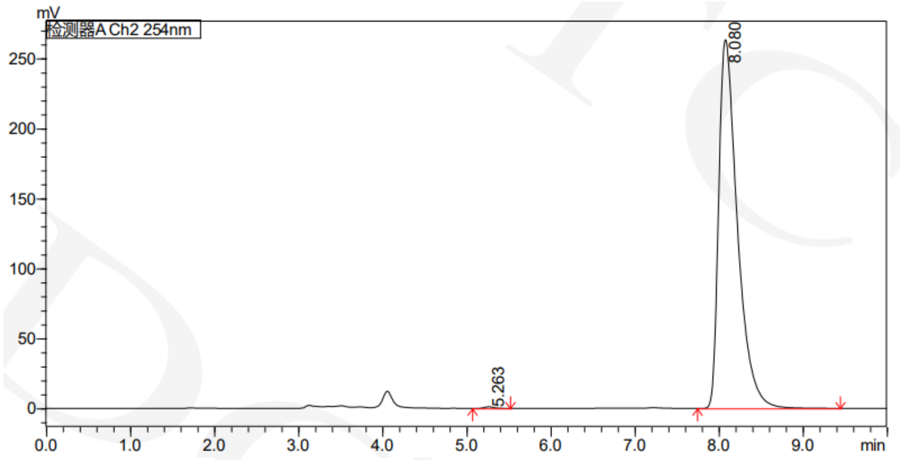
Figure S66 Chiral HPLC trace for resolution of Compound **2g**.



<Peak Table>

Peak#	Ret. Time	Area	Area%	T.Plate#	Tailing F.	Resolution
1	5.261	2040753	99.337	1.359	9701	15.463
2	8.205	13626	0.663	1.411	6214	24.141

Figure S67 Chiral HPLC analysis for the first fraction of Compound **2g**. $[\alpha]^{25}_{D} = -117$ ($c = 1.5\times10^{-3}$ g/ml in CH_3CN).



<Peak Table>

Peak#	Ret. Time	Area	Area%	T.Plate#	Tailing F.	Resolution
1	5.263	9316	0.229	1.350	9605	15.618
2	8.080	4067395	99.771	1.704	6586	22.777

Figure S68 Chiral HPLC analysis for the second fraction of Compound **2g**. $[\alpha]^{25}_{D} = +100$ ($c = 1.5\times10^{-3}$ g/ml in CH$_3$CN).

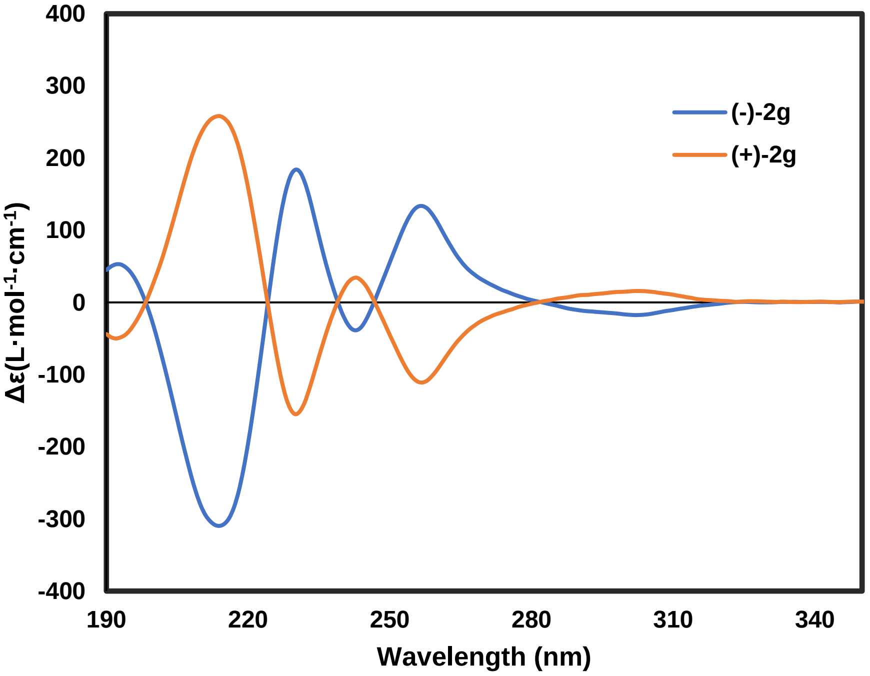
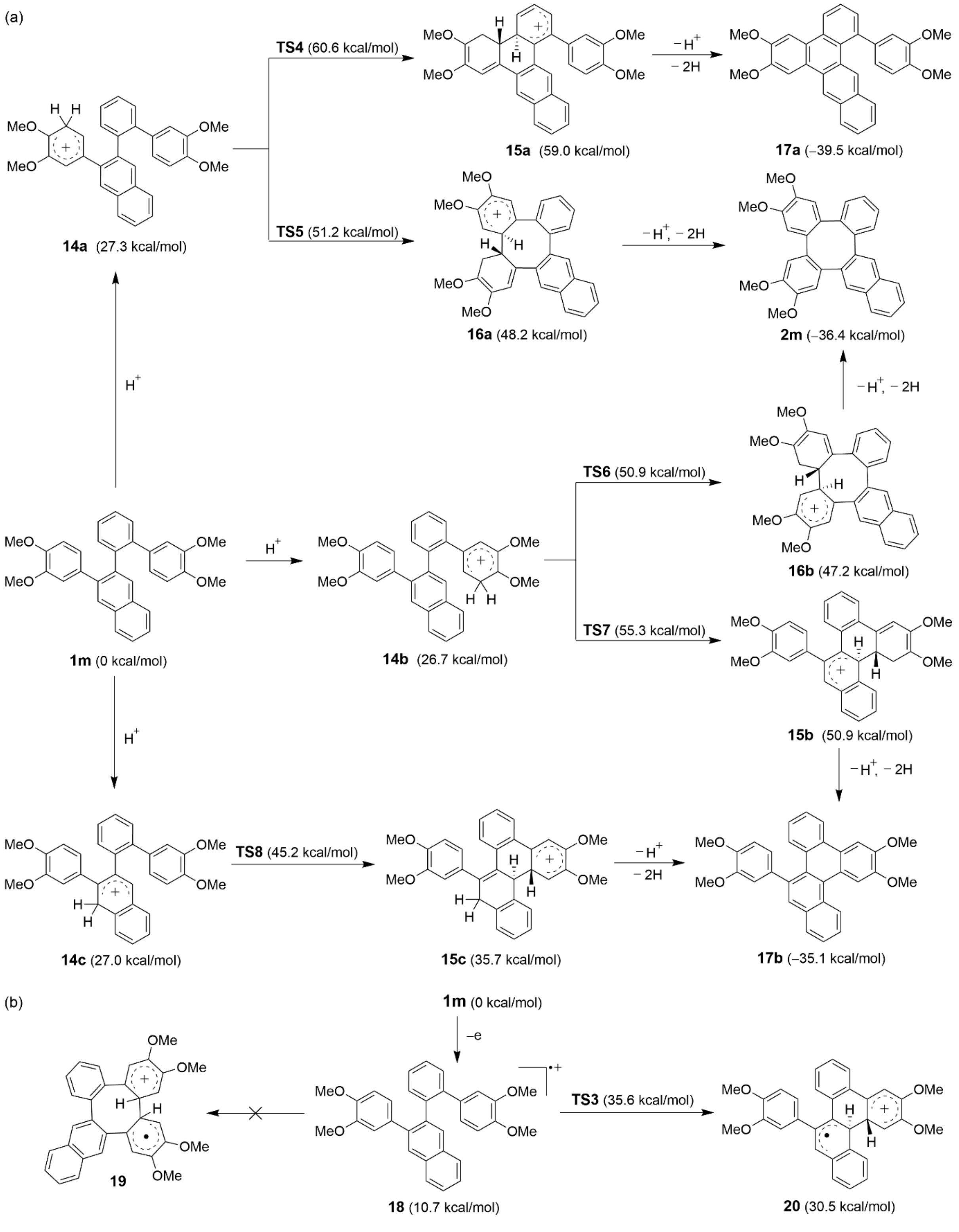


Figure S69 Circular dichroism spectrum of **2g** in CH$_3$CN (1.2×10^{-4} mol/L).

7. Density Functional Theory (DFT) Calculations

The Density Function Theory (DFT) calculations were conducted at the level of wB97XD/def2svp with CH_2Cl_2 solvation using Gaussian 16 program.[10]



Scheme S5. Proposed arenium cation (a) and radical cation (b) mechanisms for the Scholl reaction of **1m** with the relative Gibbs free energies (shown in the parenthesis).

8. Cyclic voltammetry

Cyclic voltammetry was performed in a solution of anhydrous CH_2Cl_2 with 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte, at a scan rate of 30 mV s^{-1}. A platinum bead was used as a working electrode, a platinum wire was used as an auxiliary electrode, and a silver wire was used as a pseudo-reference. Ferrocenium/ferrocene (Fc^+/Fc) was used as an internal standard.

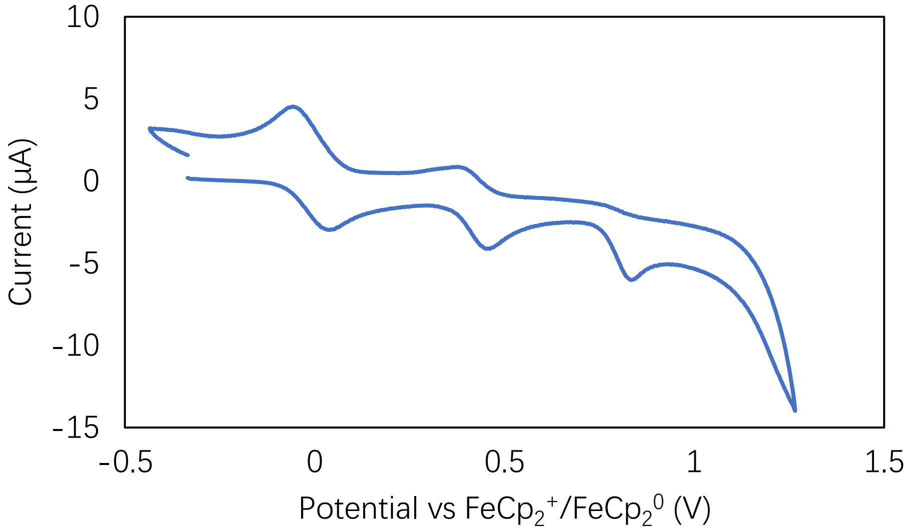


Figure S70 Cyclic voltammogram of **3n-Cl**

From the first half-wave potential of the first oxidation wave E_{ox}^1= 0.43 V, the HOMO energy level of **3n-Cl** is estimated as −5.52 eV according to the equation

$E_{HOMO} = E_{Fc^+/Fc} - E_{ox}$. Here, $E_{Fc^+/Fc}$, the formal potential of the redox couple of ferrocenium/ferrocene (Fc^+/Fc) in the Fermi scale is −5.1 eV, which is calculated on the basis of an approximation neglecting solvent effects using a work function of 4.46 eV for the normal hydrogen electrode (NHE) and an electrochemical potential of 0.64 V for (Fc^+/Fc) versus NHE.[11]

9. Fabrication and characterization of organic field effect transistors

The organic field effect transistors (OFETs) of **3n-Cl** were fabricated on a silicon substrate, which was layered with silica, alumina, and 12-cyclohexyldodecylphosphonic acid (CDPA) to form a composite dielectric material. The CDPA-modified AlO_x/SiO_2 dielectric was prepared following the reported procedure.[11] Thin film of **3n-Cl** was formed by immersing the substrate into its solution (1.5 mg/mL) in a mixed solvent of CH_2Cl_2/Acetone (V/V=2/1) and then pulling it up with a constant speed of 50 um/min using a LongerPump TJ-3A syringe pump. The dip-coated films were placed in vacuum at room temperature for 3 h to remove the solvent residue. To complete the fabrication of OFETs, top contact drain and source gold electrodes (30 nm) were vacuum-deposited through a shadow mask onto the organic films using an Edward Auto 306 vacuum coating system with a Turbomolecular pump at a pressure of 4.0×10^{-6} torr or lower, with a deposition rate of ca. 2 nm/min to a thickness about 30 nm as measured by a quartz crystal sensor. The resulting semiconducting channels were 0.5 mm (W)×50 μm (L). The field effect mobility in the saturation regime was extracted from these curves using the equation: $I_{DS} = (\mu W C_i/2L)(V_{GS}-V_{th})^2$, where I_{DS} is the drain current, μ is field effect mobility, C_i (= 29.5±0.5 nF/cm^2) is the capacitance per unit area for the CDPA-modified AlO_x/SiO_2,[12] W is the channel width, L is the channel length, and V_{GS} and V_{th} are the gate and threshold voltage, respectively. 3 films and 15 channels were tested.

Polarized light micrographs were obtained using a Nikon 50IPOL microscope. X-ray diffractions from thin films were recorded with a SmartLab X-Ray Refractometer. Current-voltage measurement of OFETs was conducted using a probe station and a Keithley 4200 Semiconductor Characterization System in air under ambient conditions.

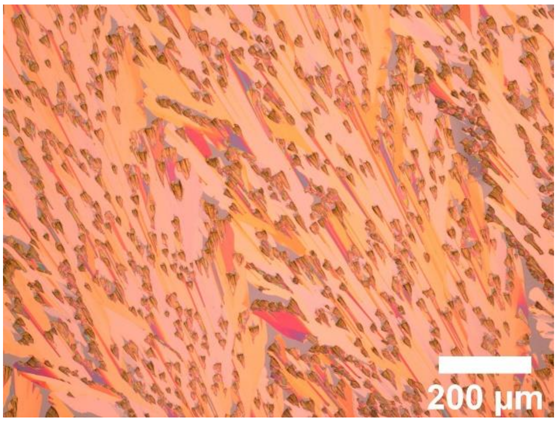


Figure S71 Reflection polarized light micrograph from dip coated film of **3n-Cl** on CDPA-modified AlO_x/SiO_2 using CH_2Cl_2/Acetone as solvent.

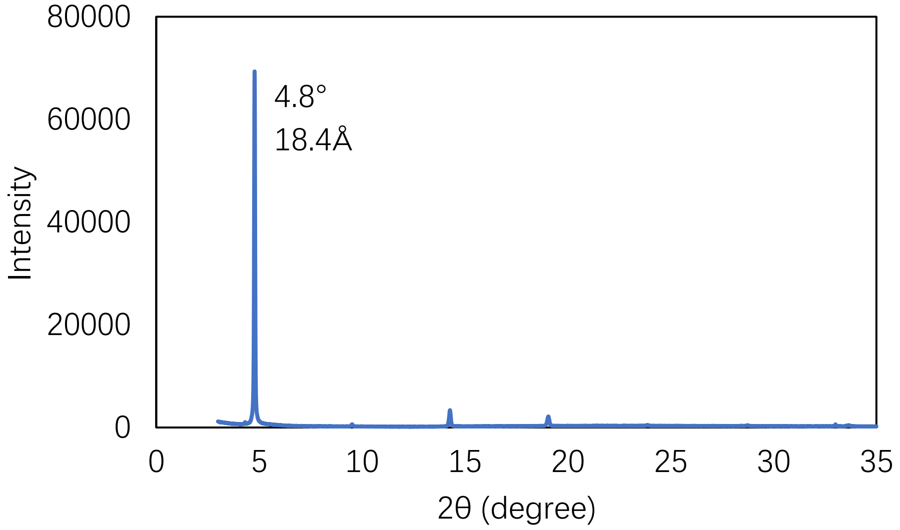


Figure S72 XRD patterns of thin film of **3n-Cl** on CDPA-modified AlO_x/SiO_2.

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