Electronic Supplementary Information

Synthesis and electronic properties of π-expanded carbazole-based porphyrins

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Table of Contents

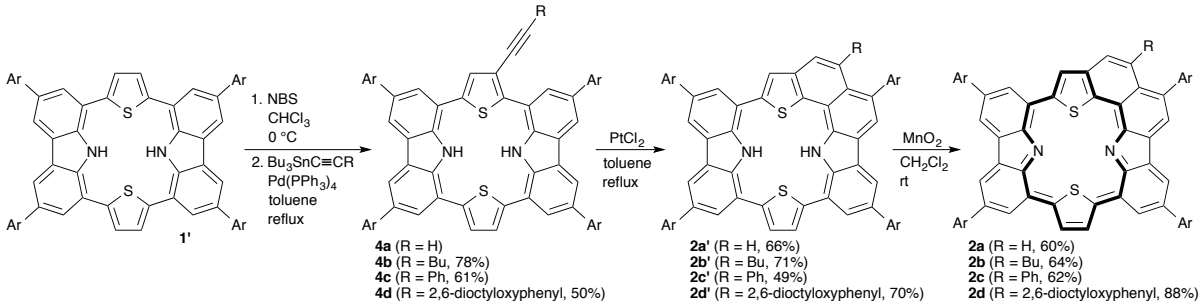
[A] Instrumentation and Materials…… S2
[B] Experimental Procedures and Compound Data…… S2
[C] References…… S15
[D] UV/vis/NIR Absorption Spectra …… S15
[E] DFT Calculations…… S16
[F] NMR Spectra…… S18

[A] Instrumentation and Materials

^{1}H and ^{13}C NMR spectra were taken on a JEOL ECS-400 spectrometer, and chemical shifts are reported as the delta scale in ppm using an internal reference (δ = 7.26 for ^{1}H NMR, 77.00 for ^{13}C NMR, for $CDCl_3$, and δ = 8.71 for ^{1}H NMR for pyridine-d_5). UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Mass spectra were taken on a Bruker micrOTOF. Redox potentials were measured by the cyclic voltammetry method on an ALS electrochemical analyzer model CHI-600B. Gel permeation chromatography (GPC) was performed with BIO-Rad Bio-Beads (ϕ 4 cm × 70 cm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. **1'**,[S1] **4a**,[S1] **11a**,[S1] tributyl(1-hexynyl)tin,[S2] 1,3,5-tribromo-2-nitrobenzene,[S3] bromo(triisopropylsilyl)acetylene,[S4] and tributyl(triisopropylsilylethynyl)tin[S5] were prepared according to the literature method.

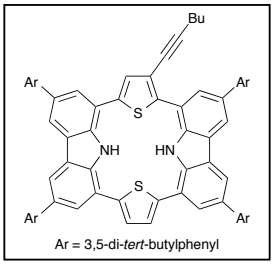
Single crystals of **3b'** were obtained by slow diffusion of acetonitrile vapor into a chloroform solution of **3b'**. X-ray data at 93 K were taken on a Rigaku XtaLAB P200 with Cu-K_α radiation (λ = 1.54187 Å). The structures were solved by direct methods and refined with the full-matrix least square technique. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were calculated in ideal positions.

[B] Experimental Procedures and Compound Data



Scheme S1 Synthesis of **2a**–**d**

Synthesis of 4b

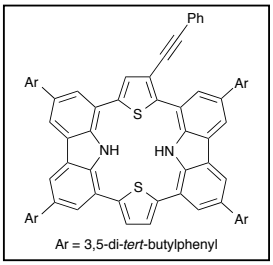


To a suspension of **1'** (188 mg, 151 μmol) and SiO_2 (6.00 g) in $CHCl_3$ (70 mL) was added dropwise a solution of *N*-bromosuccinimide (NBS) (36.8 mg, 207 μmol) in $CHCl_3$ (30 mL) over 5 min at 0 °C. The mixture was stirred at rt for 15 h. The reaction mixture was passed through a silica gel column with $CHCl_3$ and evaporated. The residue was dissolved in toluene (10 mL), and tributyl(1-hexynyl)tin (137 mg, 369 μmol) and $Pd(PPh_3)_4$ (10.9 mg, 9.43 μmol) were added. The mixture

was degassed and heated at reflux for 15 h under N_2. After cooling to rt and concentrating, the residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give **4b** as a reddish-brown solid (156 mg, 117 μmol, 78%).

^{1}H NMR ($CDCl_3$) δ = 10.45 (s, 1H, NH), 10.40 (s, 1H, NH), 8.47 (d, J = 1.2 Hz, 1H, carbazole-H), 8.39 (s, 1H, carbazole-H), 8.38 (s, 1H, carbazole-H), 8.36 (s, 2H, carbazole-H), 8.01 (d, J = 1.2 Hz, 1H, carbazole-H), 7.99 (d, J = 0.8 Hz, 1H, carbazole-H), 7.98 (d, J = 1.2 Hz, 1H, carbazole-H), 7.63–7.61 (m, 8H for Ar, 1H for thiophene-H), 7.56 (s, 2H, thiophene-H), 7.51 (d, J = 2.4 Hz, 3H, Ar), 7.48 (s, 1H, Ar), 2.41 (t, J = 7.2 Hz, 2H, CH_2), 1.47 (s, 54H, *t*-Bu), 1.46 (s, 18H, *t*-Bu), 1.27 (m, 4H, CH_2), and 0.69 ppm (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 151.44, 151.18, 141.50, 141.37, 139.90, 139.76, 139.22, 137.89, 137.32, 137.16, 137.00, 136.00, 135.89, 135.42, 130.74, 127.10, 126.98, 126.11, 125.09, 125.02, 124.96, 124.57, 124.42, 122.36, 122.31, 122.27, 121.31, 121.05, 120.35, 120.12, 120.03, 118.06, 117.93, 117.44, 116.91, 94.01, 75.62, 35.23, 35.19, 31.79, 30.71, 22.05, 19.46, and 13.50 ppm; MS (ESI): m/z = 1326.7735. calcd for $C_{94}H_{105}N_2S_2$: 1326.7757 [M–H]$^-$.

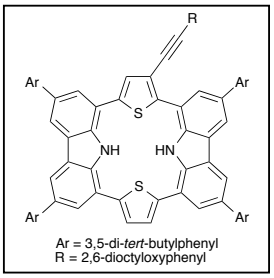
Synthesis of 4c



Compound **4c** was synthesized according to the method similar to the synthesis of **4b**.

Reddish-brown solid, 108 mg, 61% yield: ^{1}H NMR ($CDCl_3$) δ = 10.48 (s, 1H, NH), 10.47 (s, 1H, NH), 8.62 (s, 1H, carbazole-H), 8.45 (s, 1H, carbazole-H), 8.41 (s, 1H, carbazole-H), 8.39 (s, 1H, carbazole-H), 8.38 (s, 1H, carbazole-H), 8.03 (s, 3H, carbazole-H), 7.65 (s, 1H, thiophene-H), 7.63 (s, 8H, Ar), 7.58 (s, 2H, thiophene-H), 7.53 (s, 3H, Ar), 7.49 (s, 1H, Ar), 7.31 (d, J = 7.2 Hz, 2H, Ph), 7.26 (t, J = 7.0 Hz, 1H, Ph), 7.16 (t, J = 7.6 Hz, 2H, Ph), 1.48 (s, 54H, *t*-Bu), and 1.37 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 151.44, 151.37, 141.52, 141.48, 141.38, 141.33, 140.39, 139.89, 139.74, 138.29, 137.31, 137.16, 137.01, 136.06, 136.00, 135.97, 135.45, 131.76, 129.92, 128.47, 127.16, 127.09, 126.44, 125.17, 125.13, 125.11, 124.99, 124.58, 124.50, 124.42, 122.87, 122.37, 122.31, 122.26, 121.72, 121.33, 121.05, 120.49, 120.32, 120.14, 120.10, 118.09, 117.97, 117.30, 116.78, 92.82, 84.71, 35.24, 35.12, 31.80, and 31.70 ppm; MS (APCI): m/z = 1346.7447. calcd for $C_{96}H_{101}N_2S_2$: 1346.7444 [M−H]$^-$.

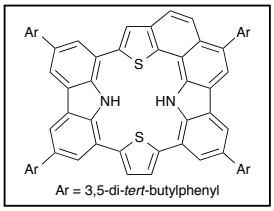
Synthesis of 4d



Compound **4d** was synthesized according to the method similar to the synthesis of **4b**.

Reddish-brown solid, 99.1 mg, 50% yield: ^{1}H NMR ($CDCl_3$) δ = 10.51 (s, 1H, NH), 10.42 (s, 1H, NH), 8.66 (s, 1H, carbazole-H), 8.39 (s, 2H, carbazole-H), 8.38 (s, 2H, carbazole-H), 8.033 (s, 1H, carbazole-H), 8.027 (d, J = 1.6 Hz, 1H, carbazole-H), 8.00 (s, 1H, carbazole-H), 7.66 (s, 1H, thiophene-H), 7.63 (s, 6H, Ar), 7.60 (d, J = 1.2 Hz, 2H, Ar), 7.58 (d, J = 4.0 Hz, 1H, thiophene-H), 7.57 (d, J = 3.6 Hz, 1H, thiophene-H), 7.52 (s, 3H, Ar), 7.39 (s, 1H, Ar), 7.16 (t, J = 8.4 Hz, 1H, Ph), 6.46 (d, J = 8.4 Hz, 2H, Ph), 3.85 (t, J = 6.6 Hz, 4H, CH_2), 1.48 (s, 54H, *t*-Bu), 1.30 (s, 18H, *t*-Bu), 1.23 (m, 4H, CH_2), 1.09–0.98 (m, 20H, CH_2), 0.70 ppm (t, J = 7.0 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.30, 151.42, 151.40, 151.36, 151.06, 141.68, 141.56, 141.45, 139.99, 139.79, 139.25, 137.62, 137.29, 137.14, 137.05, 135.95, 135.92, 135.88, 135.41, 130.80, 129.82, 127.04, 127.01, 126.85, 125.19, 125.01, 124.99, 124.97, 124.53, 124.42, 124.35, 122.71, 122.37, 122.27, 121.28, 121.22, 120.77, 120.26, 120.09, 119.99, 119.91, 118.10, 117.93, 117.57, 117.06, 104.97, 102.69, 92.33, 85.62, 69.04, 35.23, 34.98, 31.80, 31.60, 29.33, 29.28, 29.06, 25.99, 22.68, and 14.17 ppm; MS (APCI): m/z = 1602.9838. calcd for $C_{112}H_{133}N_2O_2S_2$: 1602.9847 $[M-H]^-$.

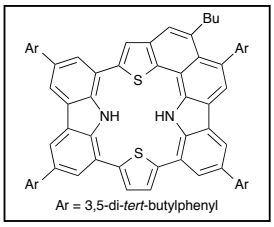
Synthesis of 2a'



A suspension of **4a** (67.4 mg, 53.0 μmol) and $PtCl_2$ (5.65 mg, 21.2 μmol) in toluene (10 mL) was degassed and heated at reflux for 48 h under N_2. After cooling to rt and concentrating, the residue was purified by silica gel column chromatography with $CHCl_3$/hexane as an eluent to give **2a'** as a yellow solid (44.7 mg, 35.1 μmol, 66%).

^{1}H NMR ($CDCl_3$) δ = 11.44 (s, 1H, NH), 11.13 (s, 1H, NH), 8.39 (s, 1H, carbazole-H), 8.37 (s, 2H, carbazole-H), 8.33 (s, 1H, carbazole-H), 8.29 (s, 1H, carbazole-H), 8.09 (d, J = 9.2 Hz, 1H, -CH=CH-), 8.05 (s, 2H for carbazole-H, 1H for thiophene-H), 7.95 (d, J = 8.4 Hz, 1H, -CH=CH-), 7.66–7.62 (m, 6H, Ar), 7.60 (s, 2H, thiophene-H), 7.57 (t, J = 2.0 Hz, 1H, Ar), 7.56–7.51 (m, 5H, Ar), 1.49 (s, 18H, *t*-Bu), 1.48 (s, 18H, *t*-Bu), 1.473 (s, 18H, *t*-Bu), and 1.468 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 151.44, 150.80, 141.71, 141.56, 141.49, 140.70, 140.02, 139.69, 139.26, 137.44, 136.95, 136.70, 136.35, 136.23, 136.00, 134.80, 134.33, 130.95, 128.53, 127.89, 127.61, 126.34, 125.57, 125.38, 125.05, 123.19, 123.05, 122.37, 121.56, 121.40, 121.34, 121.23, 121.13, 121.05, 120.59, 120.22, 120.14, 119.75, 119.28, 118.61, 118.45, 117.65, 116.05, 35.23, 35.18, and 31.81 ppm; MS (APCI): m/z = 1270.7146. calcd for $C_{90}H_{97}N_2S_2$: 1270.7132 $[M-H]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 299 (85800), 405 (19800), 423 nm (27600 $M^{-1}cm^{-1}$).

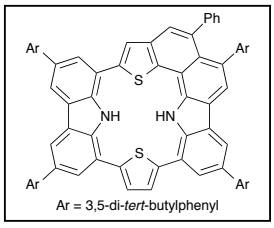
Synthesis of 2b'



Compound **2b'** was synthesized according to the method similar to the synthesis of **2a'**.

Yellow solid, 27.2 mg, 71% yield: ^{1}H NMR ($CDCl_3$) δ = 11.42 (s, 1H, NH), 11.16 (s, 1H, NH), 8.38 (s, 2H, carbazole-H), 8.36 (d, J = 0.8 Hz, 1H, carbazole-H), 8.29 (d, J = 1.2 Hz, 1H, carbazole-H), 8.20 (s, 1H, carbazole-H), 8.055 (d, J = 1.2 Hz, 1H, carbazole-H), 8.047 (d, J = 1.6 Hz, 1H, carbazole-H), 8.03 (s, 1H, thiophene-H), 7.86 (s, 1H, -C*H*=CBu-), 7.640 (d, J = 1.2 Hz, 2H, Ar), 7.636 (d, J = 2.0 Hz, 2H, Ar), 7.63 (d, J = 2.0 Hz, 2H, Ar), 7.61–7.59 (m, 2H, thiophene-H), 7.53 (t, J = 1.2 Hz, 1H, Ar), 7.52 (t, J = 1.8 Hz, 2H, Ar), 7.50 (t, J = 1.6 Hz, 1H, Ar), 7.43 (d, J = 2.0 Hz, 2H, Ar), 2.58 (t, J = 8.0 Hz, 2H, CH_2), 1.48 (s, 18H, *t*-Bu), 1.47 (s, 18H, *t*-Bu), 1.45 (s, 18H, *t*-Bu), 1.42 (s, 18H, *t*-Bu), 1.34 (m, 2H, CH_2), 0.91 (m, 2H, CH_2), and 0.71 ppm (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 151.45, 151.41, 150.20, 144.54, 141.61, 141.58, 141.54, 140.38, 140.07, 139.76, 139.17, 137.71, 137.50, 137.09, 136.75, 136.24, 136.19, 135.97, 135.29, 134.79, 129.51, 127.81, 127.74, 127.57, 126.22, 125.36, 125.00, 124.92, 124.63, 123.82, 123.54, 123.26, 123.08, 122.39, 122.32, 121.38, 121.33, 121.21, 120.74, 120.53, 120.24, 120.04, 119.26, 118.97, 118.61, 118.47, 117.70, 117.28, 36.34, 35.12, 34.57, 31.80, 22.82, and 14.02 ppm; MS (ESI): m/z = 1326.7773. calcd for $C_{94}H_{105}N_2S_2$: 1326.7757 $[M-H]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 300 (88300), 408 (20600), 427 nm (30400 $M^{-1}cm^{-1}$).

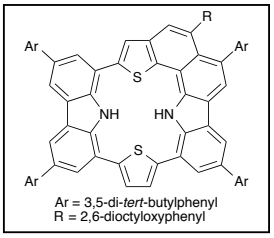
Synthesis of 2c'



Compound **2c'** was synthesized according to the method similar to the synthesis of **2a'**.

Yellow solid, 44.3 mg, 49% yield: ^{1}H NMR ($CDCl_3$) δ = 11.47 (s, 1H, NH), 11.16 (s, 1H, NH), 8.38 (s, 3H, carbazole-H), 8.30 (s, 1H, carbazole-H), 8.26 (s, 1H, carbazole-H), 8.09 (s, 1H, thiophene-H), 8.07 (s, 1H, carbazole-H), 8.06 (s, 1H, carbazole-H), 7.90 (s, 1H, -C*H*=CPh-), 7.64–7.63 (m, 6H for Ar, 2H for thiophene-H), 7.53–7.52 (m, 2H, Ar), 7.51 (t, J = 1.2 Hz, 1H, Ar), 7.17 (d, J = 6.4 Hz, 2H, Ph), 7.06 (t, J = 1.6 Hz, 1H, Ar), 7.03 (d, J = 1.6 Hz, 2H, Ar), 7.01–6.92 (m, 3H, Ph), 1.47 (s, 36H, *t*-Bu), 1.46 (s, 18H, *t*-Bu), and 1.28 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 151.47, 151.43, 149.15, 143.52, 143.27, 141.62, 141.56, 141.50, 140.40, 140.03, 139.77, 139.64, 137.53, 137.25, 137.17, 136.75, 136.42, 136.26, 136.06, 135.52, 134.86, 130.53, 130.11, 127.89, 127.62, 127.47, 126.78, 126.39, 126.33, 125.88, 125.45, 125.04, 125.00, 124.82, 124.64, 123.33, 123.24, 122.38, 121.42, 121.36, 121.27, 120.68, 120.38, 120.28, 120.20, 119.80, 119.43, 118.69, 118.49, 117.59, 117.50, 35.25, 34.82, 31.81, and 31.58 ppm; MS (APCI): m/z = 1346.7432. calcd for $C_{96}H_{101}N_2S_2$: 1346.7444 $[M-H]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 293 (86700), 409 (21800), 426 nm (23900 $M^{-1}cm^{-1}$).

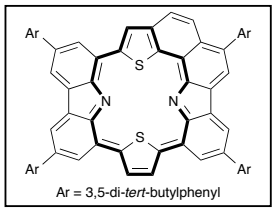
Synthesis of 2d'



Compound **2d'** was synthesized according to the method similar to the synthesis of **2a'**.

Yellow solid, 39.8 mg, 70% yield: ^{1}H NMR ($CDCl_3$) δ = 11.45 (s, 1H, NH), 11.26 (s, 1H, NH), 8.39 (s, 1H, carbazole-H), 8.38 (s, 1H, carbazole-H), 8.35 (s, 1H, carbazole-H), 8.29 (d, J = 0.8 Hz, 1H, carbazole-H), 8.07 (d, J = 1.2 Hz, 1H, carbazole-H), 8.06 (s, 1H, carbazole-H), 8.05 (s, 1H, carbazole-H), 8.03 (s, 1H, thiophene-H), 7.81 (s, 1H, -C*H*=CR-), 7.64–7.63 (m, 6H for Ar, 2H for thiophene-H), 7.53 (t, J = 1.6 Hz, 2H, Ar), 7.50 (t, J = 1.6 Hz, 1H, Ar), 7.13 (d, J = 2.0 Hz, 2H, Ar), 7.11 (t, J = 1.6 Hz, 1H, Ar), 6.84 (t, J = 8.2 Hz, 1H, Ph), 6.20 (d, J = 8.4 Hz, 2H, Ph), 3.97–3.92 (m, 2H, CH_2), 3.73–3.67 (m, 2H, CH_2), 1.48 (s, 36H, *t*-Bu), 1.46 (s, 18H, *t*-Bu), 1.30 (s, 18H, *t*-Bu), 1.12–0.90 (m, 24H, CH_2), and 0.65 ppm (t, J = 7.0 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 156.36, 151.45, 151.38, 151.35, 148.44, 143.41, 141.80, 141.67, 141.62, 140.38, 139.73, 138.77, 137.54, 137.29, 137.05, 136.76, 136.21, 136.13, 136.08, 136.03, 134.96, 132.45, 130.29, 128.89, 128.07, 127.79, 127.62, 126.67, 126.21, 125.71, 125.02, 124.96, 123.97, 123.39, 123.24, 122.67, 122.43, 122.39, 122.35, 121.62, 121.35, 121.31, 121.08, 120.22, 119.48, 119.02, 118.53, 117.86, 116.66, 104.53, 68.01, 35.24, 35.21, 34.73, 31.80, 31.65, 29.37, 29.32, 29.29, 26.22, 22.64, and 14.16 ppm; MS (APCI): m/z = 1602.9839. calcd for $C_{112}H_{133}N_2O_2S_2$: 1602.9847 $[M-H]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 301 (89400), 407 (20000), 427 nm (28900 $M^{-1}cm^{-1}$).

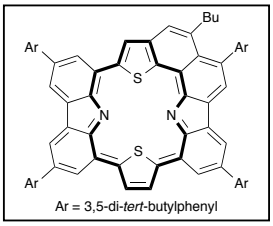
Synthesis of 2a



To a solution of **2a'** (30.8 mg, 24.2 μmol) in CH_2Cl_2 (15 mL) was added MnO_2 (940 mg, 10.8 mmol), and the resulting suspension was stirred. After 14 h, MnO_2 (745 mg, 8.57 mmol) was added, and the mixture was stirred for further 5 h. The reaction mixture was then passed through a silica gel column with CH_2Cl_2. The solvent was evaporated to give **2a** as a green solid (18.6 mg, 14.6 μmol, 60% yield).

Green solid, 18.6 mg, 60% yield: ^{1}H NMR (pyridine-d_5) δ = 10.21 (s, 1H), 10.07 (s, 2H), 9.97 (s, 1H), 9.77 (s, 1H), 9.57 (s, 1H), 9.48 (s, 2H), 9.25 (s, 1H), 9.09 (s, 1H), 8.74–8.62 (m, 2H, CH=CH), 8.25 (s, 2H, Ar), 8.23 (s, 2H, Ar), 8.21 (s, 2H, Ar), 8.00 (s, 2H, Ar), 7.91 (s, 2H, Ar), 7.84 (s, 2H, Ar), 1.54 (s, 36H, *t*-Bu), 1.52 (s, 18H, *t*-Bu), and 1.51 ppm (s, 18H, *t*-Bu); ^{13}C NMR couldn't detect peaks due to very low solubility; MS (ESI): m/z = 1270.7127. calcd for $C_{90}H_{97}N_2S_2$: 1270.7121 $[M+H]^+$; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 277 (60100), 421 (15700), 963 (14700), 1180 nm (4490 $M^{-1}cm^{-1}$).

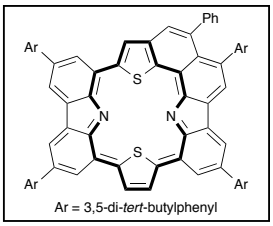
Synthesis of 2b



Compound **2b** was synthesized according to the method similar to the synthesis of **2a**.

Green solid, 14.0 mg, 64% yield: ^{1}H NMR (pyridine-d_5) δ = 10.24 (s, 1H), 10.08 (s, 2H), 10.01 (s, 1H), 9.79 (s, 1H), 9.60 (s, 1H), 9.50 (s, 2H), 9.19 (s, 1H), 8.97 (s, 1H), 8.64 (s, 1H, -C*H*=CBu-), 8.25 (s, 4H, Ar), 8.22 (s, 2H, Ar), 7.84 (s, 6H, Ar), 3.06 (s, 2H, CH_2), 1.67 (m, 2H, CH_2), 1.52 (s, 72H, *t*-Bu), 1.15 (m, 2H, CH_2), and 0.85 ppm (s, 3H, CH_3); ^{13}C NMR couldn't detect peaks due to very low solubility; MS (ESI): *m*/*z* = 1326.7714. calcd for $C_{94}H_{105}N_2S_2$: 1326.7747 $[M+H]^+$; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 277 (52700), 328 (44700), 960 (22000), 1176 nm (6460 $M^{-1}cm^{-1}$).

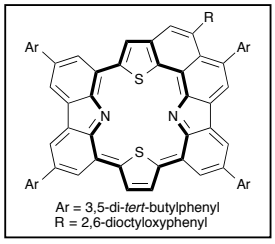
Synthesis of 2c



Compound **2c** was synthesized according to the method similar to the synthesis of **2a**.

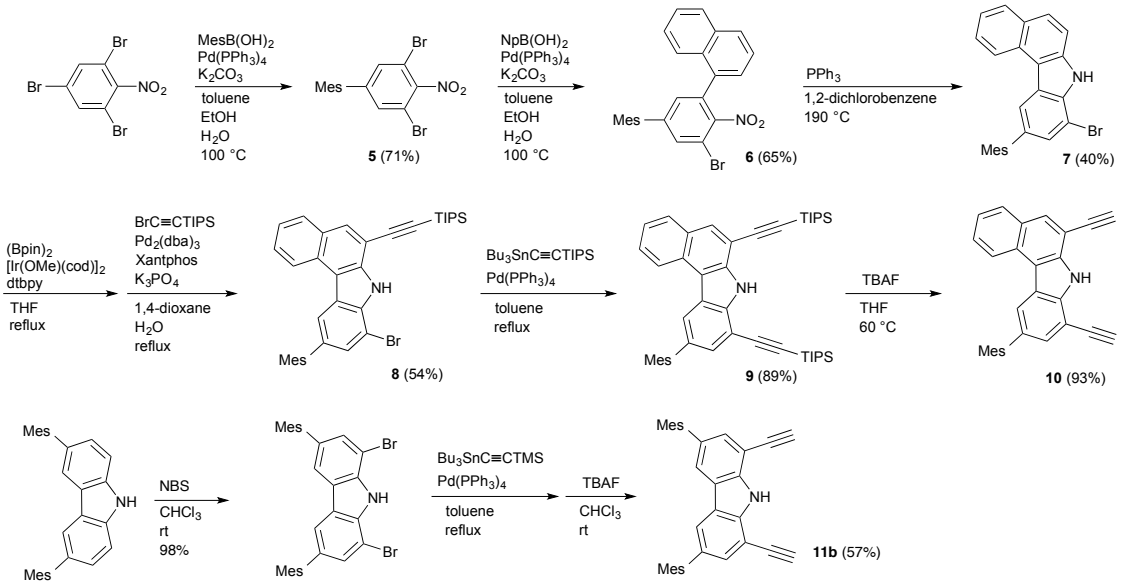
Green solid, 10.9 mg, 62% yield: ^{1}H NMR (pyridine-d_5) δ = 10.16 (s, 1H), 9.99 (s, 2H), 9.92 (s, 1H), 9.72 (s, 1H), 9.56 (s, 1H), 9.43 (s, 2H), 9.19 (s, 1H), 9.03 (s, 1H), 8.65 (s, 1H, -C*H*=CPh-), 8.24 (s, 4H, Ar), 8.22 (s, 2H, Ar), 7.85 (s, 3H, Ar), 7.63 (d, *J* = 6.4 Hz, 2H, Ph), 7.49 (s, 2H, Ar), 7.38 (s, 1H, Ar), 7.25 (t, *J* = 7.2 Hz, 2H, Ph), 7.14 (t, *J* = 8.0 Hz, 1H, Ph), 1.56 (s, 18H, *t*-Bu), 1.55 (s, 18H, *t*-Bu), 1.54 (s, 18H, *t*-Bu), and 1.42 ppm (s, 18H, *t*-Bu); ^{13}C NMR couldn't detect peaks due to very low solubility; MS (ESI): *m*/*z* = 1346.7406. calcd for $C_{96}H_{101}N_2S_2$: 1346.7434 $[M+H]^+$; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 276 (68400), 962 (15900), 1177 nm (4970 $M^{-1}cm^{-1}$).

Synthesis of 2d



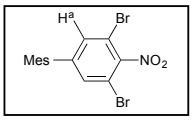
Compound **2d** was synthesized according to the method similar to the synthesis of **2a**.

Green solid, 17.2 mg, 88% yield: ^{1}H NMR ($CDCl_3$) δ = 9.71 (s, 3H, thiophene-H), 9.49 (s, 1H, carbazole-H), 9.43 (s, 1H, carbazole-H), 9.18 (s, 1H, carbazole-H), 8.89 (s, 2H, carbazole-H), 8.61 (s, 1H, carbazole-H), 8.54 (s, 1H, carbazole-H), 8.39 (s, 1H, -C*H*=CR-), 7.96 (s, 2H, Ar), 7.92 (s, 2H, Ar), 7.87 (s, 2H, Ar), 7.66–7.61 (m, 3H, Ar), 7.35 (s, 2H, Ar), 7.22 (s, 1H, Ar), 6.92 (t, *J* = 8.0 Hz, 1H, 2,6-dioctyloxyphenyl-*p*-H), 6.30 (d, *J* = 7.6 Hz, 2H, 2,6-dioctyloxyphenyl-*m*-H), 4.01 (m, 2H, CH_2), 3.80 (m, 2H, CH_2), 1.57–1.54 (s, 54H, *t*-Bu), 1.37 (s, 18H, *t*-Bu), 0.94–0.82 (m, 24H, CH_2), 0.49 ppm (s, 6H, CH_3); ^{13}C NMR couldn't detect peaks due to very low solubility; MS (ESI): *m*/*z* = 1602.9800 calcd for $C_{112}H_{133}N_2O_2S_2$: 1602.9836 $[M+H]^+$; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 279 (61900), 424 (17500), 951 (19800), 1180 nm (5980 $M^{-1}cm^{-1}$).



Scheme S2 Synthesis of **10** and **11b**

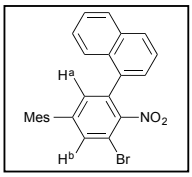
Synthesis of 5



A solution of 1,3,5-tribromo-2-nitrobenzene (644 mg, 1.79 mmol), 2,4,6-trimethylphenylboronic acid (362 mg, 1.97 mmol), $Pd(PPh_3)_4$ (113 mg, 97.8 μmol), and K_2CO_3 (735 mg, 5.33 mmol) in toluene/EtOH/H_2O (4/2/2 mL) was heated at 100 °C for 41 h under N_2. After cooling to rt, organic products were extracted with EtOAc, and the organic layer was passed through a silica gel column with EtOAc and evaporated. The residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give **5** as a white solid (506 mg, 1.27 mmol, 71%).

^{1}H NMR ($CDCl_3$) δ = 7.50 (s, 2H, H^a), 7.02 (s, 2H, Mes), 2.40 (s, 3H, Me), and 2.10 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 150.13, 145.92, 138.31, 135.25, 134.50, 133.58, 128.58, 113.73, 21.08, and 20.72 ppm; MS (APCI): m/z = 398.9294. calcd for $C_{15}H_{13}NO_2Br_2$: 398.9288 $[M]^+$.

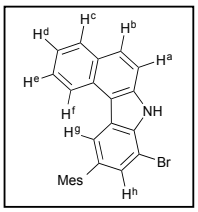
Synthesis of 6



A solution of **5** (506 mg, 1.27 mmol), naphthalene-1-boronic acid (175 mg, 1.02 mmol), $Pd(PPh_3)_4$ (50.2 mg, 43.4 μmol), and K_2CO_3 (409 mg, 2.96 mmol) in toluene/EtOH/H_2O (2/1/1 mL) was heated at 100 °C for 15 h under N_2. After cooling to rt, organic products were extracted with EtOAc, and the organic layer was passed through a silica gel column with EtOAc and evaporated. The residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give **6** as a white solid (367 mg, 823 μmol, 65%).

^{1}H NMR ($CDCl_3$) δ = 7.949 (d, J = 7.2 Hz, 1H, Np), 7.945 (t, J = 7.2 Hz, 1H, Np), 7.68 (d, J = 8.4 Hz, 1H, Np), 7.65 (d, J = 1.2 Hz, 1H, H^b), 7.58–7.50 (m, 4H, Np), 7.27 (d, J = 1.2 Hz, 1H, H^a), 7.00 (s, 1H, Mes), 6.99 (s, 1H, Mes), 2.38 (s, 3H, Me), 2.22 (s, 3H, Me), and 2.14 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$) δ = 150.24, 144.42, 137.91, 135.49, 135.35, 134.92, 133.76, 133.61, 132.58, 132.52, 131.58, 129.59, 128.55, 128.52, 127.10, 126.85, 126.33, 125.09, 125.06, 113.16, 21.09, 20.95, and 20.82 ppm; MS (APCI): m/z = 447.0634. calcd for $C_{25}H_{20}NO_2Br$: 447.0655 $[M]^+$.

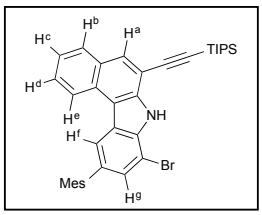
Synthesis of 7



A solution of **6** (872 mg, 1.96 mmol) and PPh_3 (5.23 g, 19.9 mmol) in 1,2-dichlorobenzene (8.0 mL) was heated at 190 °C for 42 h under Ar. After cooling to rt, excess 1,2-dichlorobenzene was removed by distillation. The residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give **7** as a white solid (324 mg, 783 μmol, 40%).

^{1}H NMR ($CDCl_3$) δ = 8.77 (d, J = 8.0 Hz, 1H, H^f), 8.68 (s, 1H, NH), 8.42 (s, 1H, H^g), 8.07 (d, J = 8.0 Hz, 1H, H^c), 7.95 (d, J = 8.4 Hz, 1H, H^b), 7.74 (dt, J = 1.5, 7.5 Hz, 1H, H^e), 7.69 (d, J = 8.8 Hz, 1H, H^a), 7.57 (t, J = 6.8 Hz, 1H, H^d), 7.57 (d, J = 0.8 Hz, 1H, H^h), 7.16 (s, 2H, Mes), 2.52 (s, 3H, Me), and 2.25 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 138.80, 137.29, 137.02, 136.78, 135.93, 134.49, 129.92, 129.44, 129.37, 128.30, 128.25, 127.64, 127.17, 125.42, 123.48, 123.19, 121.76, 116.12, 112.75, 104.64, 21.22, and 21.18 ppm; MS (APCI): m/z = 414.0679. calcd for $C_{25}H_{19}NBr$: 414.0689 $[M–H]^–$.

Synthesis of 8

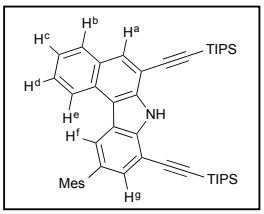


A solution of **7** (197 mg, 476 μmol), $(Bpin)_2$ (92.8 mg, 365 μmol), $[Ir(OMe)(cod)]_2$ (8.3 mg, 13 μmol), and dtbpy (6.5 mg, 24 μmol) in dry THF (0.50 mL) was heated at reflux for 18 h under N_2. The mixture was passed through a silica gel column with $CHCl_3$ and evaporated. A solution of the residue, bromo(triisopropylsilyl)acetylene (595 mg, 2.24 mmol), $Pd_2(dba)_3$ (11.3 mg, 12.3 μmol), Xantphos (26.3 mg, 45.4 μmol), and K_3PO_4 (235 mg, 1.11 mmol) in 1,4-dioxane/water (0.9 mL/0.1 mL) was heated at reflux for 16 h under N_2. After cooling to rt, the solvents were evaporated, and the residue was passed through a silica gel column with $CHCl_3$. Purification of the residue by silica gel column chromatography with $CHCl_3$/hexane as an eluent gave **8** as a white solid (152 mg, 255 μmol, 54%).

^{1}H NMR ($CDCl_3$) δ = 8.91 (s, 1H, NH), 8.60 (d, J = 8.0 Hz, 1H, H^e), 8.25 (s, 1H, H^f), 8.07 (s, 1H, H^a), 7.96 (d, J = 8.0 Hz, 1H, H^b), 7.65 (dt, J = 1.3, 7.7 Hz, 1H, H^d), 7.48 (t, J = 8.0 Hz, 1H, H^c), 7.46 (s, 1H, H^g), 7.04 (s, 2H, Mes), 2.41 (s, 3H, Me), 2.11 (s, 6H, Me), and 1.29 ppm (m, 21H, TIPS); ^{13}C NMR

($CDCl_3$) δ = 138.74, 137.83, 137.12, 136.81, 135.66, 134.78, 130.90, 129.93, 129.48, 129.18, 128.28, 127.98, 125.68, 123.94, 123.23, 121.90, 115.68, 108.32, 104.91, 102.36, 97.17, 21.25, 21.15, 19.02, and 11.46 ppm; MS (APCI): *m*/*z* = 594.2009. calcd for $C_{36}H_{39}NBrSi$: 594.2027 [*M*–H]$^-$.

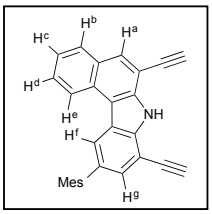
Synthesis of 9



A solution of **8** (202 mg, 339 μmol), tributyl(triisopropylsilylethynyl)tin (330 mg, 701 μmol), and $Pd(PPh_3)_4$ (23.2 mg, 20.1 μmol) in toluene (5 mL) was heated at reflux for 12 h under N_2. After cooling to rt, the mixture was evaporated. The residue was purified by silica gel column chromatography with $CHCl_3$/hexane as an eluent to give **9** as a white solid (211 mg, 303 μmol, 89%).

^{1}H NMR ($CDCl_3$) δ = 8.88 (s, 1H, NH), 8.63 (d, *J* = 8.0 Hz, 1H, H^e), 8.30 (s, 1H, H^f), 8.09 (s, 1H, H^a), 7.97 (d, *J* = 8.0 Hz, 1H, H^b), 7.64 (dt, *J* = 1.2, 7.6 Hz, 1H, H^d), 7.47 (t, *J* = 7.2 Hz, 1H, H^c), 7.44 (d, *J* = 1.2 Hz, 1H, H^g), 7.04 (s, 2H, Mes), 2.41 (s, 3H, Me), 2.11 (s, 6H, Me), 1.25 (m, 21H, TIPS), and 1.22 ppm (m, 21H, TIPS); ^{13}C NMR ($CDCl_3$) δ = 139.15, 137.77, 137.11, 137.02, 136.92, 133.39, 132.00, 130.10, 129.83, 129.26, 129.07, 128.25, 127.84, 124.50, 123.80, 123.38, 123.29, 115.67, 108.23, 106.93, 102.96, 102.59, 96.34, 96.05, 21.24, 21.20, 18.96, and 11.54 ppm; MS (APCI): *m*/*z* = 694.4285. calcd for $C_{47}H_{60}NSi_2$: 694.4270 [*M*–H]$^-$.

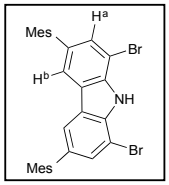
Synthesis of 10



To a solution of **9** (203 mg, 292 μmol) in dry THF (10 mL) was added TBAF (1 M in THF, 1.2 mL, 1.2 mmol), and the resulting mixture was heated at 60 °C for 1 h under N_2. After the mixture was evaporated, the residue was purified by silica gel column chromatography with $CHCl_3$/hexane as an eluent to give **10** as a pale yellow solid (104 mg, 272 μmol, 93%).

^{1}H NMR ($CDCl_3$) δ = 9.02 (s, 1H, NH), 8.64 (d, *J* = 8.4 Hz, 1H, H^e), 8.36 (s, 1H, H^f), 8.08 (s, 1H, H^a), 7.96 (d, *J* = 8.0 Hz, 1H, H^b), 7.67 (t, *J* = 7.0 Hz, 1H, H^d), 7.491 (t, *J* = 7.4 Hz, 1H, H^c), 7.488 (s, 1H, H^g), 7.07 (s, 2H, Mes), 3.59 (s, 2H, C≡CH), 2.43 (s, 3H, Me), and 2.14 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 138.95, 138.48, 137.40, 137.02, 136.83, 133.46, 131.85, 129.97, 129.46, 129.40, 128.88, 128.28, 128.13, 124.36, 123.95, 123.89, 123.24, 115.66, 106.67, 105.30, 82.50, 80.03, 79.68, 21.24, and 21.18 ppm; MS (APCI): *m*/*z* = 382.1596. calcd for $C_{29}H_{20}N$: 382.1601 [*M*–H]$^-$.

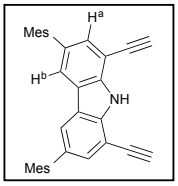
Synthesis of 3,6-bis(2,4,6-trimethylphenyl)-1,8-dibromocarbazole



To a suspension of 3,6-bis(2,4,6-trimethylphenyl)carbazole (500 mg, 1.24 mmol) and SiO_2 (2.09 g) in $CHCl_3$ (70 mL) was added dropwise a solution of NBS (883 mg, 4.96 mmol) in $CHCl_3$ (30 mL) over 10 min, and the mixture was stirred at rt for 19 h. After concentrating, the residue was passed through a silica gel column with $CHCl_3$ and evaporated to give a desired product as a pale brown solid (685 mg, 1.22 mmol, 98%).

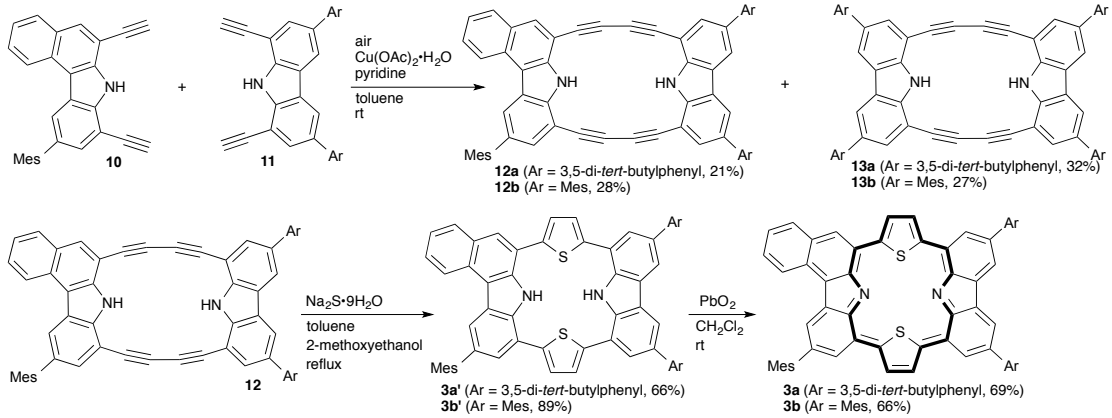
^{1}H NMR ($CDCl_3$) δ = 8.46 (s, 1H, NH), 7.76 (d, J = 0.8 Hz, 2H, H^b), 7.48 (d, J = 1.2 Hz, 2H, H^a), 7.02 (s, 4H, Mes), 2.40 (s, 6H, Me), and 2.10 ppm (s, 12H, Me); ^{13}C NMR ($CDCl_3$) δ= 138.18, 137.06, 137.03, 136.57, 134.63, 130.11, 128.27, 125.15, 120.60, 104.51, 21.19, and 21.10 ppm; MS (APCI): m/z = 560.0437. calcd for $C_{30}H_{26}NBr_2$: 560.0419 [M–H]$^-$.

Synthesis of 11b



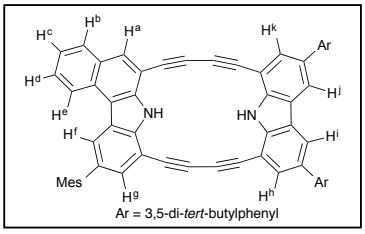
A solution of 3,6-bis(2,4,6-trimethylphenyl)-1,8-dibromocarbazole (685 mg, 1.22 mmol), tributyl(trimethylsilylethynyl)tin (1.91 g, 4.94 mmol), and $Pd(PPh_3)_4$ (141 mg, 122 μmol) in toluene (10 mL) was degassed and heated at reflux for 17 h under N_2. After cooling to rt, the reaction mixture was passed through a silica gel column with $CHCl_3$ and evaporated. To a solution of the residue in $CHCl_3$ (10 mL) was added TBAF (1.0 M in THF, 5.0 mL, 5.0 mmol), and the mixture was stirred at rt for 10 min. After concentrating, the residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give **11b** as a yellow solid (315 mg, 697 μmol, 57%).

^{1}H NMR ($CDCl_3$) δ = 8.73 (s, 1H, NH), 7.81 (d, J = 1.6 Hz, 2H, H^b), 7.42 (d, J = 1.6 Hz, 2H, H^a), 7.00 (s, 4H, Mes), 3.55 (s, 2H, C≡CH), 2.38 (s, 6H, Me), and 2.07 ppm (s, 12H, Me); ^{13}C NMR ($CDCl_3$) δ = 139.90, 138.57, 136.87, 136.66, 132.96, 131.16, 128.25, 123.67, 122.43, 104.93, 82.35, 79.98, 21.20, and 21.11 ppm; MS (APCI): m/z = 450.2249. calcd for $C_{34}H_{28}N$: 450.2227 [M–H]$^-$.



Scheme S3 Synthesis of **3**

Synthesis of 12a

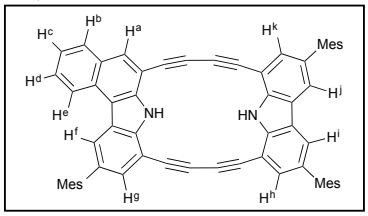


To a suspension of $Cu(OAc)_2 \cdot H_2O$ (2.00 g, 10.0 mmol) in pyridine (75 mL) was added dropwise a solution of **10** (174 mg, 454 μmol) and **11a** (323 mg, 546 μmol) in toluene (250 mL) over 2 h. The mixture was stirred for further 4.5 d under air. After the solvents were evaporated, the residue was separated over a silica gel column with $CHCl_3$ and GPC to give **12a** as a yellow solid (101 mg, 104 μmol, 21%) and **13a** as a yellow solid (190 mg, 161 μmol, 32%). Separation of **12a** and **13a** was achieved by GPC with TLC analysis ($CHCl_3$/hexane = 1/2). **13a** (R_f = 0.80) is faster fraction in GPC than **12a** (R_f = 0.75).

^{1}H NMR ($CDCl_3$) δ = 9.33 (s, 1H, NH), 9.04 (s, 1H, NH), 8.58 (d, J = 8.4 Hz, 1H, H^e), 8.33 (s, 1H, H^f), 8.32 (s, 1H, H^i or H^j), 8.30 (d, J = 1.6 Hz, 1H, H^i or H^j), 8.03 (s, 1H, H^a), 7.95 (d, J = 8.0 Hz, 1H, H^b), 7.83 (d, J = 1.2 Hz, 1H, H^h or H^k), 7.79 (d, J = 1.2 Hz, 1H, H^h or H^k), 7.63 (t, J = 7.6 Hz, 1H, H^d), 7.52–7.48 (m, 6H, Ar), 7.47 (t, J = 7.2 Hz, 1H, H^d), 7.42 (d, J = 0.8 Hz, 1H, H^g), 7.06 (s, 2H, Mes), 2.41 (s, 3H, Me), 2.13 (s, 6H, Me), 1.45 (s, 18H, *t*Bu), and 1.44 ppm (s, 18H, *t*Bu); ^{13}C NMR ($CDCl_3$) δ = 151.50, 142.38, 142.33, 140.61, 140.25, 138.78, 138.42, 137.23, 136.88, 135.69, 133.86, 130.39, 129.81, 129.07, 128.59, 128.37, 127.75, 127.58, 124.83, 124.40, 124.24, 123.98, 123.87, 123.40, 122.15, 121.93, 121.71, 121.51, 115.97, 106.44, 105.04, 104.84, 104.61, 80.61, 80.38, 80.21, 79.78, 79.66, 79.54, 79.46, 35.21, 31.77, and 21.25 ppm; MS (APCI): m/z = 969.5134. calcd for $C_{73}H_{65}N_2$: 969.5153 [M–H]$^-$.

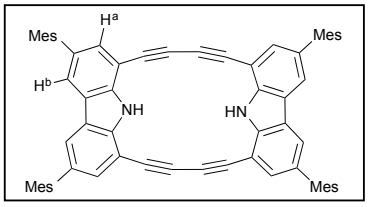
Synthesis of 12b

To a suspension of $Cu(OAc)_2 \cdot H_2O$ (1.06 g, 5.30 mmol) in pyridine (30 mL) was added dropwise a solution of **10** (98.4 mg, 257 μmol) and **11b** (115 mg, 254 μmol) in toluene (100 mL) over 2.5 h. The mixture was stirred for further 4.5 d under air. After the solvents were evaporated, the residue was separated over a silica gel column with $CHCl_3$ and GPC to give **12b** as a yellow solid (60.1 mg, 72.3 μmol, 28%) and **13b** as a yellow solid (62.0 mg, 69.0 μmol, 27%). Separation of **12b** and **13b** was achieved by GPC with TLC analysis ($CHCl_3$/hexane = 1/2). **13b** (R_f = 0.73) is faster fraction in GPC than **12b** (R_f = 0.66).



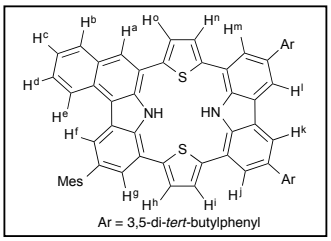
12b: ^{1}H NMR ($CDCl_3$) δ = 9.45 (s, 1H, NH), 9.16 (s, 1H, NH), 8.60 (d, J = 8.4 Hz, 1H, H^e), 8.32 (s, 1H, H^f), 8.09 (s, 1H, H^a), 7.99 (d, J = 7.6 Hz, 1H, H^b), 7.82 (d, J = 1.6 Hz, 1H, H^i or H^j), 7.81 (d, J = 0.8 Hz, 1H, H^i or H^j), 7.68 (t, J = 7.0 Hz, 1H, H^d), 7.50 (t, J = 6.8 Hz, 1H, H^c), 7.41 (s, 1H, H^a), 7.38 (d, J = 1.6 Hz, 1H, H^h or H^k), 7.36 (d, J = 1.2 Hz, 1H, H^h or H^k), 7.04 (s, 2H, Mes), 7.00 (s, 2H, Mes), 6.99 (s, 2H, Mes), 2.40 (s, 3H, Me), 2.37 (s, 3H, Me), 2.36 (s, 3H, Me), 2.11 (s, 6H, Me), 2.074 (s, 6H, Me), and 2.068 ppm

(s, 6H, Me); ^{13}C NMR couldn't detect peaks due to very low solubility; MS (APCI): *m*/*z* = 829.3617. calcd for $C_{63}H_{45}N_2$: 829.3588 [*M*–H]$^-$.



13b: ^{1}H NMR ($CDCl_3$) δ = 9.24 (s, 2H, NH), 7.81 (d, *J* = 1.2 Hz, 4H, H^b), 7.35 (d, *J* = 1.2 Hz, 4H, H^a), 6.99 (s, 8H, Mes), 2.34 (s, 12H, Me), and 2.07 ppm (s, 24H, Me); ^{13}C NMR ($CDCl_3$) δ = 141.89, 138.39, 137.06, 136.67, 133.35, 129.00, 128.33, 123.64, 123.44, 80.57, 79.64, 21.23, and 21.17 ppm; MS (APCI): *m*/*z* = 897.4232. calcd for $C_{68}H_{53}N_2$: 897.4214 [*M*–H]$^-$.

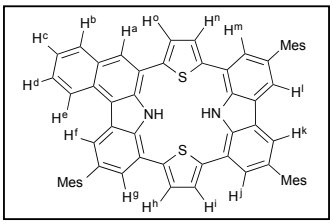
Synthesis of 3a'



A solution of **12a** (75.5 mg, 77.8 μmol) and $Na_2S{\cdot}9H_2O$ (189 mg, 788 μmol) in toluene/2-methoxyethanol (2.3/2.3 mL) was heated at reflux at 17 h under Ar. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, passed through a silica gel column with $CHCl_3$, and evaporated to dryness to give **3a'** as a yellow solid (53.5 mg, 51.5 μmol, 66%).

^{1}H NMR ($CDCl_3$) δ = 10.83 (s, 1H, NH), 10.57 (s, 1H, NH), 8.74 (d, *J* = 8.4 Hz, 1H, H^e), 8.39 (s, 1H, H^f), 8.37 (d, *J* = 1.6 Hz, 1H, H^k or H^l), 8.36 (d, *J* = 0.8 Hz, 1H, H^k or H^l), 8.22 (s, 1H, H^a), 8.12 (d, *J* = 8.0 Hz, 1H, H^b), 8.02 (d, *J* = 1.6 Hz, 1H, H^j or H^m), 8.01 (d, *J* = 1.6 Hz, 1H, H^j or H^m), 7.70 (t, *J* = 8.0 Hz, 1H, H^d), 7.64 (d, *J* = 1.2 Hz, 1H, H^g), 7.63 (d, *J* = 3.6 Hz, 1H, H^o), 7.62 (d, *J* = 1.6 Hz, 2H, Ar), 7.61 (d, *J* = 1.6 Hz, 2H, Ar), 7.58 (d, *J* = 3.6 Hz, 1H, H^n), 7.56 (d, *J* = 3.2 Hz, 1H, H^h or H^i), 7.54 (t, *J* = 7.6 Hz, 1H, H^c), 7.51 (t, *J* = 2.0 Hz, 1H, Ar), 7.50 (t, *J* = 2.0 Hz, 1H, Ar), 7.48 (d, *J* = 4.0 Hz, 1H, H^h or H^i), 7.09 (s, 2H, Mes), 2.43 (s, 3H, Me), 2.19 (s, 6H, Me), 1.47 (s, 18H, *t*-Bu), and 1.46 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 151.44, 141.50, 140.41, 139.85, 139.74, 139.61, 139.35, 137.15, 137.07, 137.00, 135.97, 135.69, 134.99, 134.11, 129.98, 129.79, 128.38, 127.72, 127.56, 127.39, 127.10, 126.88, 125.59, 125.52, 125.02, 124.99, 124.45, 124.25, 124.13, 123.93, 123.37, 123.05, 122.34, 121.32, 120.31, 120.14, 119.65, 118.34, 118.01, 117.97, 116.89, 35.23, 31.80, 21.34, and 21.29 ppm; MS (APCI): *m*/*z* = 1037.4886. calcd for $C_{73}H_{69}N_2S_2$: 1037.4908 [*M*–H]$^-$. UV/vis (CH_2Cl_2) λ_{max} (ε) = 277 (66400), 410 nm (22200 $M^{-1}cm^{-1}$).

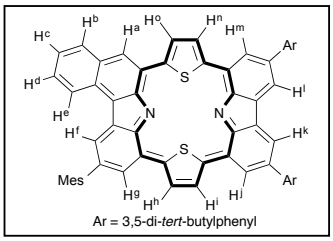
Synthesis of 3b'



A solution of **21b** (76.8 mg, 92.4 μmol) and $Na_2S{\cdot}9H_2O$ (222 mg, 924 μmol) in toluene/2-methoxyethanol (2.3/2.3 mL) was heated at reflux for 13 h under Ar. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, passed through a silica gel column with $CHCl_3$ to give **3b'** as a brown solid (68.2 mg, 82.1 μmol, 89%).

^{1}H NMR ($CDCl_3$) δ = 10.86 (s, 1H, NH), 10.59 (s, 1H, NH), 8.72 (d, J = 8.0 Hz, 1H, H^e), 8.39 (s, 1H, H^f), 8.20 (s, 1H, H^a), 8.08 (d, J = 8.4 Hz, 1H, H^b), 7.872 (s, 1H, H^l or H^k), 7.865 (s, 1H, H^l or H^k), 7.68 (t, J = 7.0 Hz, 1H, H^d), 7.64 (d, J = 0.8 Hz, 1H, H^g), 7.61–7.60 (m, 3H, H^j, H^m, H^o), 7.51 (t, J = 7.6 Hz, 1H, H^c), 7.47–7.44 (m, 3H, H^h, H^i, H^n), 7.09 (s, 2H, Mes), 7.05 (s, 2H, Mes), 7.04 (s, 2H, Mes), 2.43 (s, 3H, Me), 2.41 (s, 3H, Me), 2.40 (s, 3H, Me), 2.19 (s, 6H, Me), 2.16 (s, 6H, Me), and 2.15 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 140.37, 139.75, 139.65, 139.58, 139.30, 139.11, 137.04, 136.94, 136.89, 136.82, 136.47, 136.34, 135.59, 134.90, 134.12, 133.55, 129.91, 129.77, 129.74, 128.36, 128.33, 127.52, 127.00, 126.71, 125.61, 125.53, 125.37, 124.72, 124.70, 124.04, 123.89, 123.35, 123.00, 121.70, 121.58, 119.61, 118.34, 117.93, 116.90, 21.31, and 21.28 ppm; MS (APCI): m/z = 897.3347. calcd for $C_{63}H_{49}N_2S_2$: 897.3343 [M–H]$^-$. UV/vis (CH_2Cl_2) λ_{max} (ε) = 317 (40500), 406 nm (26900 $M^{-1}cm^{-1}$).

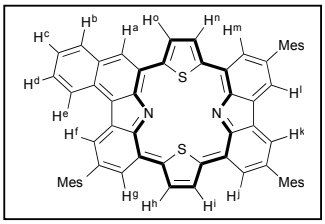
Synthesis of 3a



To a solution of **3a'** (4.90 mg, 4.72 μmol) in CH_2Cl_2 (20 mL) was added PbO_2 (1.75 g, 7.32 mmol), and the resulting suspension was stirred for 15 h. The reaction mixture was passed through a Cerite with CH_2Cl_2 and evaporated to give **3a** as a deep green solid (3.40 mg, 3.28 μmol, 69%).

^{1}H NMR ($CDCl_3$) δ = 9.68 (s, 1H, H^a), 9.56 (s, 1H, H^o), 9.51 (s, 2H, H^h, H^i), 9.43 (s, 1H, H^n), 9.32 (s, 1H, H^m), 9.15 (s, 1H, H^j), 8.95 (s, 1H, H^e), 8.87 (s, 1H, H^g), 8.78 (s, 1H, H^f), 8.75 (s, 2H, H^l, H^k), 8.40 (d, J = 9.2 Hz, 1H, H^b), 7.93 (s, 2H, Ar), 7.88 (s, 2H, Ar), 7.78 (t, J = 7.4 Hz, 1H, H^d), 7.66 (s, 3H, Ar, H^c), 7.21 (s, 2H, Mes), 2.52 (s, 3H, Me), 2.45 (s, 6H, Me), 1.59 (s, 18H, *t*-Bu), and 1.56 ppm (s, 18H, *t*-Bu); ^{13}C NMR couldn't detect peaks due to very low solubility; MS (ESI): m/z = 1037.4843. calcd for $C_{73}H_{69}N_2S_2$: 1037.4897 [M+H]$^+$. UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 271 (50000), 356 (39700), 910 (25900), 1100 nm (16300 $M^{-1}cm^{-1}$).

Synthesis of 3b



To a solution of **3b'** (63.9 mg, 71.1 μmol) in CH_2Cl_2 (20 mL) was added PbO_2 (6.04 g, 25.3 mmol), and the resulting suspension was stirred for 15 h. The reaction mixture was passed through a Celite with CH_2Cl_2 and evaporated to give **3b** as a deep green solid (42.2 mg, 47.0 μmol, 66%).

^{1}H NMR ($CDCl_3$) δ = 9.92 (s, 1H, H^a), 9.76 (d, J = 4.8 Hz, 1H, H^o), 9.61 (d, J = 4.8 Hz, 1H, H^h or H^i), 9.57 (d, J = 4.8 Hz, 1H, H^h or H^i), 9.53 (d, J = 4.0 Hz, 1H, H^n), 9.08 (s, 1H, H^m), 9.01 (d, J = 8.4 Hz, 1H, H^e), 8.92 (s, 1H, H^g), 8.89 (s, 1H, H^j), 8.85 (s, 1H, H^f), 8.52 (d, J = 8.8 Hz, 1H, H^b), 8.29 (s, 2H, H^l, H^k), 7.84 (t, J = 7.0 Hz, 1H, H^d), 7.71 (t, J = 7.6 Hz, 1H, H^c), 7.20 (s, 2H, Mes), 7.164 (s, 2H, Mes), 7.157 (s, 2H, Mes), 2.51 (s, 3H, Me), 2.48 (s, 3H, Me), 2.47 (s, 3H, Me), 2.39 (s, 6H, Me), 2.34 (s, 6H, Me), and

2.31 ppm (s, 6H, Me); ^{13}C NMR couldn't detect peaks due to very low solubility; MS (ESI): *m*/*z* = 897.3340. calcd for $C_{63}H_{49}N_2S_2$: 897.3332 $[M+H]^+$; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 271 (49700), 359 (39300), 392 (35600), 870 (25700), 1103 nm (15200 $M^{-1}cm^{-1}$).

[C] References

[S1] C. Maeda, M. Takata, A. Honsho and T. Ema, *Org. Lett.*, 2016, **22**, 6070.

[S2] I. Meana, A. C. AlbØniz and P. Espinet, *Adv. Synth. Catal.*, 2010, **352**, 2887.

[S3] J. T. Manka, F. Guo, J. Huang, H. Yin, J. M. Farrar, M. Sienkowska, V. Benin and P. Kaszynski, *J. Org. Chem.*, 2003, **68**, 9574.

[S4] T. Ohmura, A. Kijima, Y. Komori and M. Suginome, *Org. Lett.* 2013, **15**, 3510.

[S5] M. Toganoh, T. Kimura and H. Furuta, *Chem. Eur. J.*, 2008, **14**, 10585.

[D] UV/vis/NIR Absorption Spectra

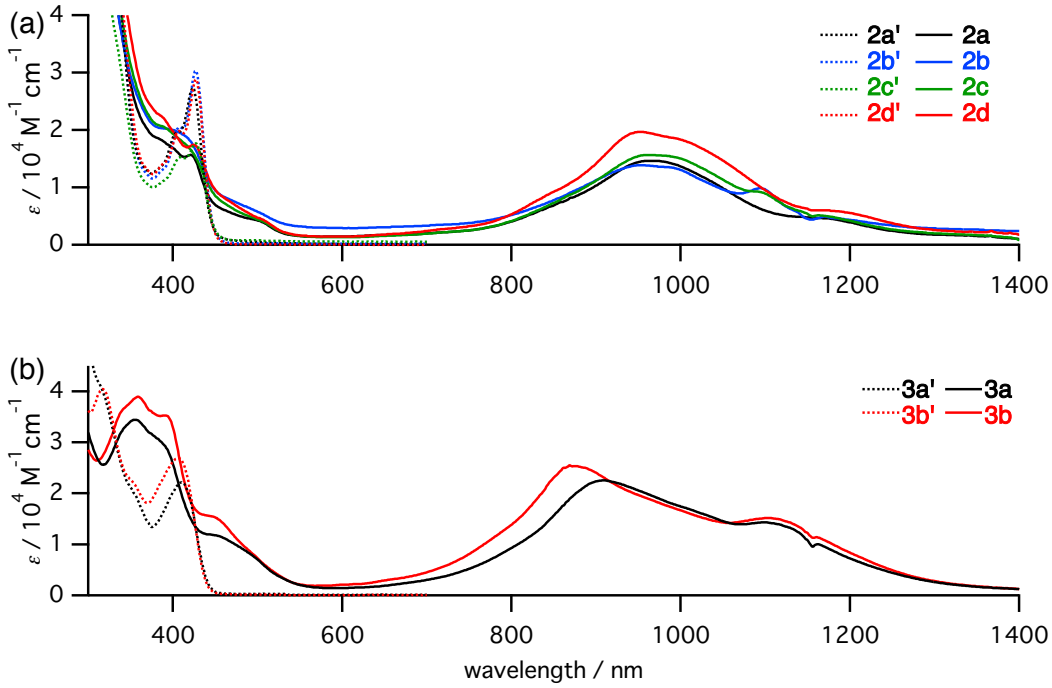


Fig. S1 UV/vis/NIR absorption spectra of (a) **2'** and **2**, (b) **3'** and **3**.

[E] DFT Calculations

Table S1 Selected data of calculated electronic transitions in **1**

State	Transition energy (nm)	Oscillator strength	Composition of band and CI coefficiencies
1	918.53	0.2160	H–1 → L (95%), H → L+2 (3%)
2	885.61	0.7529	H → L (97%), H–1 → L+2 (3%)
3	760.95	0.0000	H–2 → L (98%)
4	740.57	0.0069	H–3 → L (98%)
5	586.52	0.0000	H–4 → L (98%)
6	561.97	0.0000	H–10 → L (93%)
7	529.37	0.0000	H–9 → L (63%), H–11 → L (30%), H–6 → L (5%)
8	499.32	0.0006	H–6 → L (92%), H–9 → L (7%),
9	499.12	0.0000	H–7 → L (100%)
10	499.11	0.0006	H–8 → L (100%)

Table S2 Selected data of calculated electronic transitions in **2a**

State	Transition energy (nm)	Oscillator strength	Composition of band and CI coefficiencies
1	1130.59	0.1106	H–1 → L (58%), H–2 → L (24%), H → L (18%)
2	942.65	0.6195	H → L (72%), H–1 → L (25%)
3	847.19	0.1853	H–2 → L (75%), H–1 → L (16%), H → L (8%)
4	782.23	0.0122	H–3 → L (98%)
5	639.04	0.0078	H–4 → L (74%), H–5 → L (22%)
6	586.54	0.0001	H–10 → L (86%), H–6 → L (5%), H–9 → L (2%)

Table S3 Selected data of calculated electronic transitions in **3a**

State	Transition energy (nm)	Oscillator strength	Composition of band and CI coefficiencies
1	1130.78	0.1074	H → L (70.5%), H–2 → L (20%), H–1 → L (9.5%)
2	920.20	0.1202	H–2 → L (65%), H–1 → L (26%), H → L (6%)
3	867.79	0.6016	H–1 → L (61%), H → L (23%), H–2 → L (13%)
4	771.26	0.0103	H–3 → L (97%)
5	608.62	0.0209	H–4 → L (95%)
6	583.35	0.0001	H–10 → L (88%), H–9 → L (9%)
7	572.73	0.0021	H–5 → L (98%)
8	550.07	0.0008	H–8 → L (73%), H–11 → L (13%), H–6 → L (6%)
9	543.58	0.0003	H–6 → L (93%), H–8 → L (5%)
10	516.34	0.0003	H–7 → L (98%)

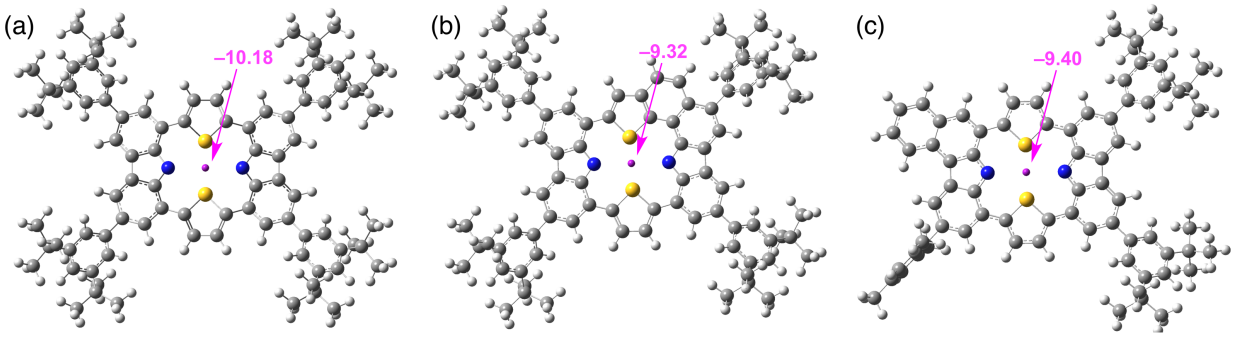
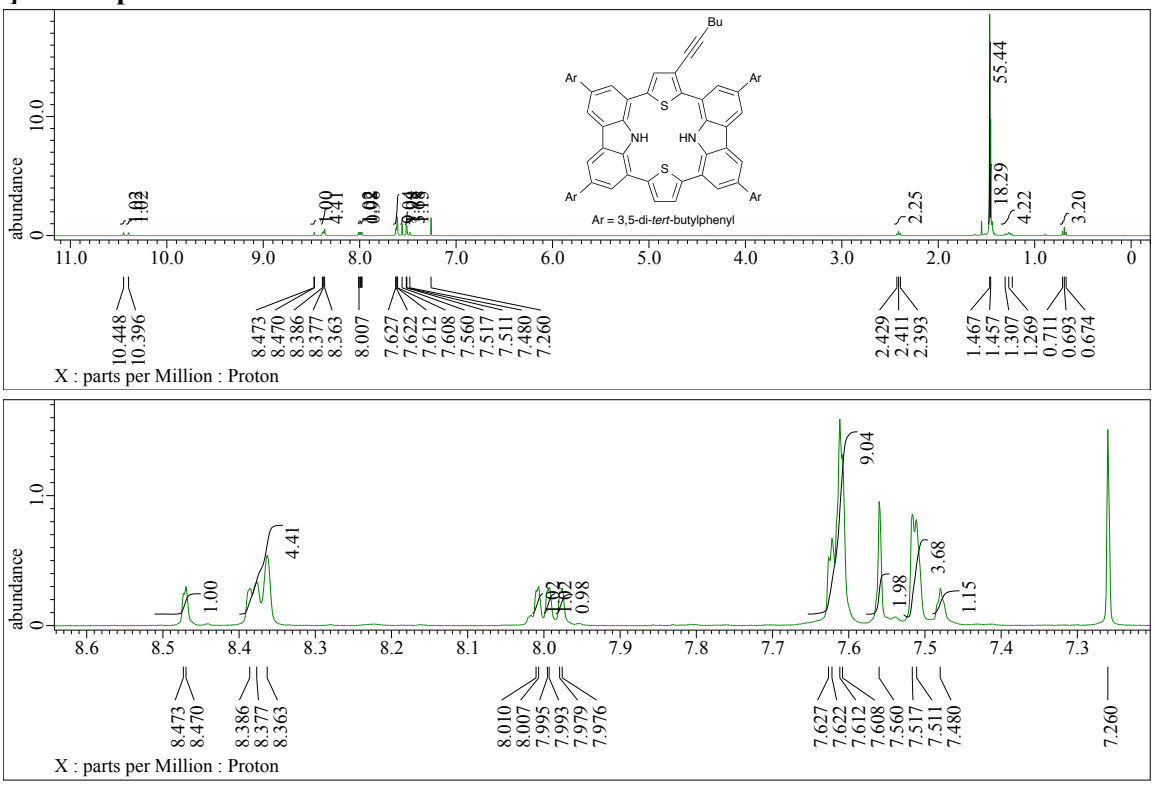
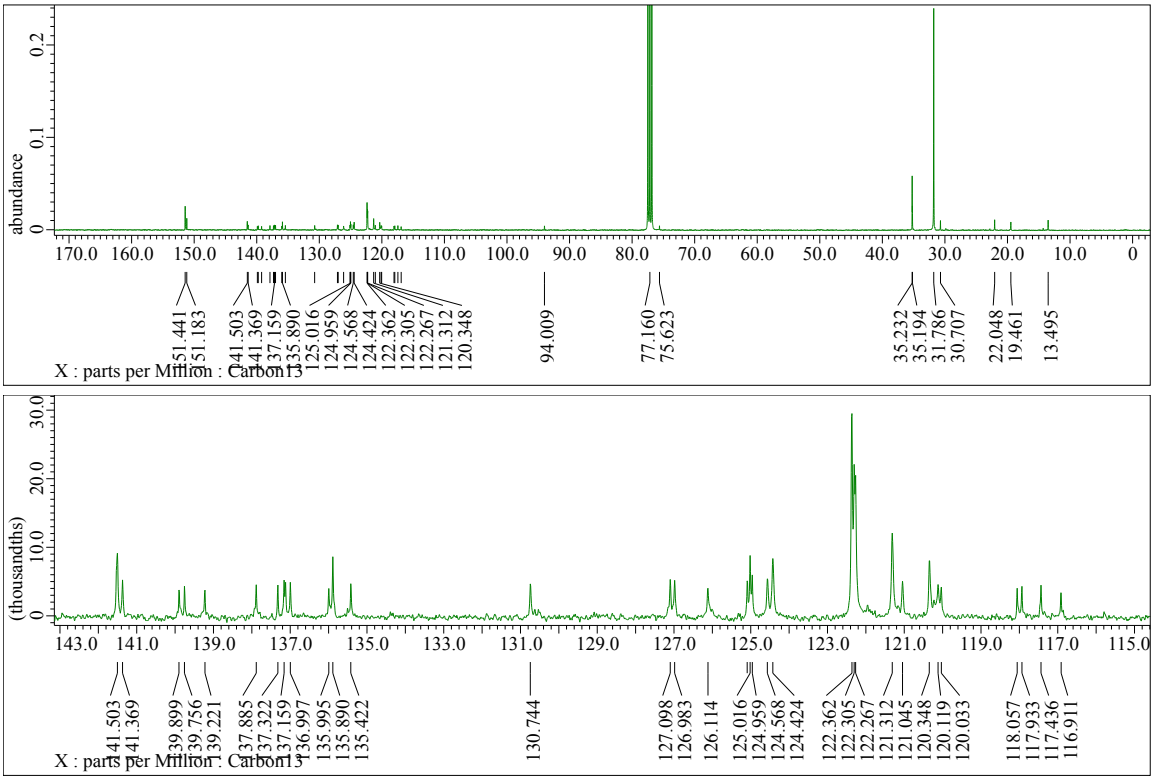


Fig. S2 NICS(0) values at the selected points of (a) **1**, (b) **2a**, and (c) **3a** calculated at B3LYP/6-31G(d) levels.

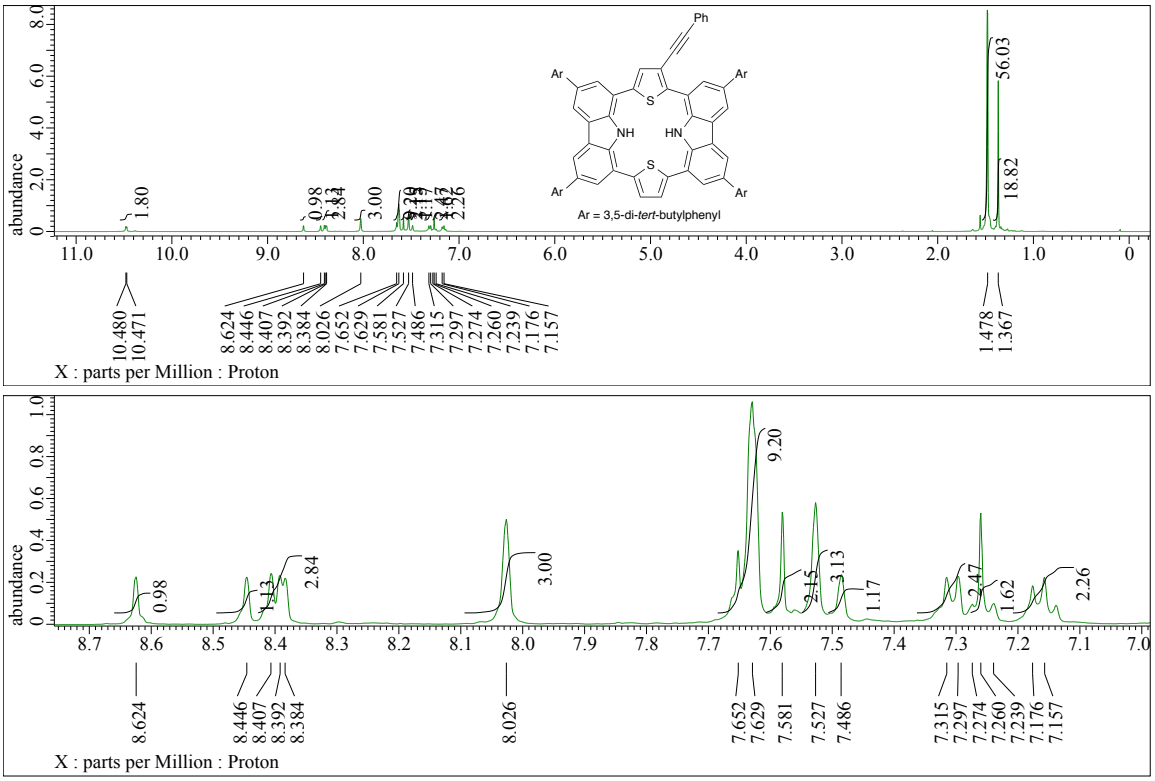
[F] NMR spectra



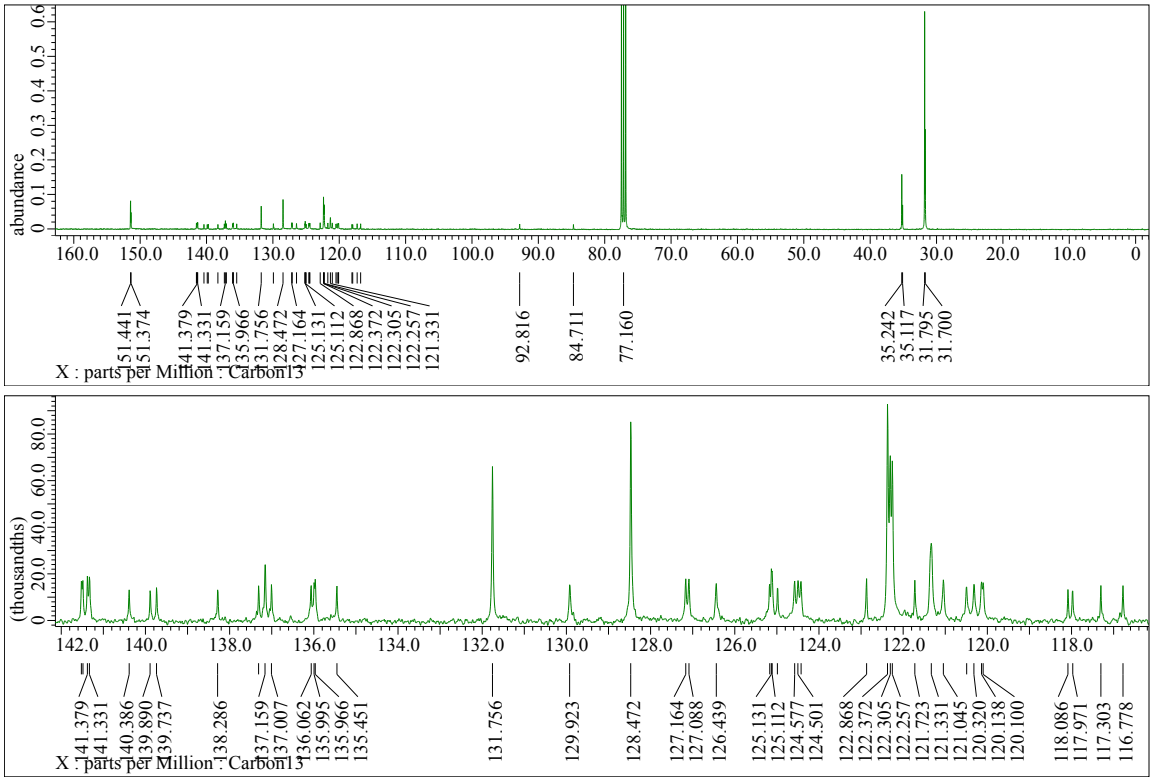
^{1}H NMR spectrum of **4b** in $CDCl_3$



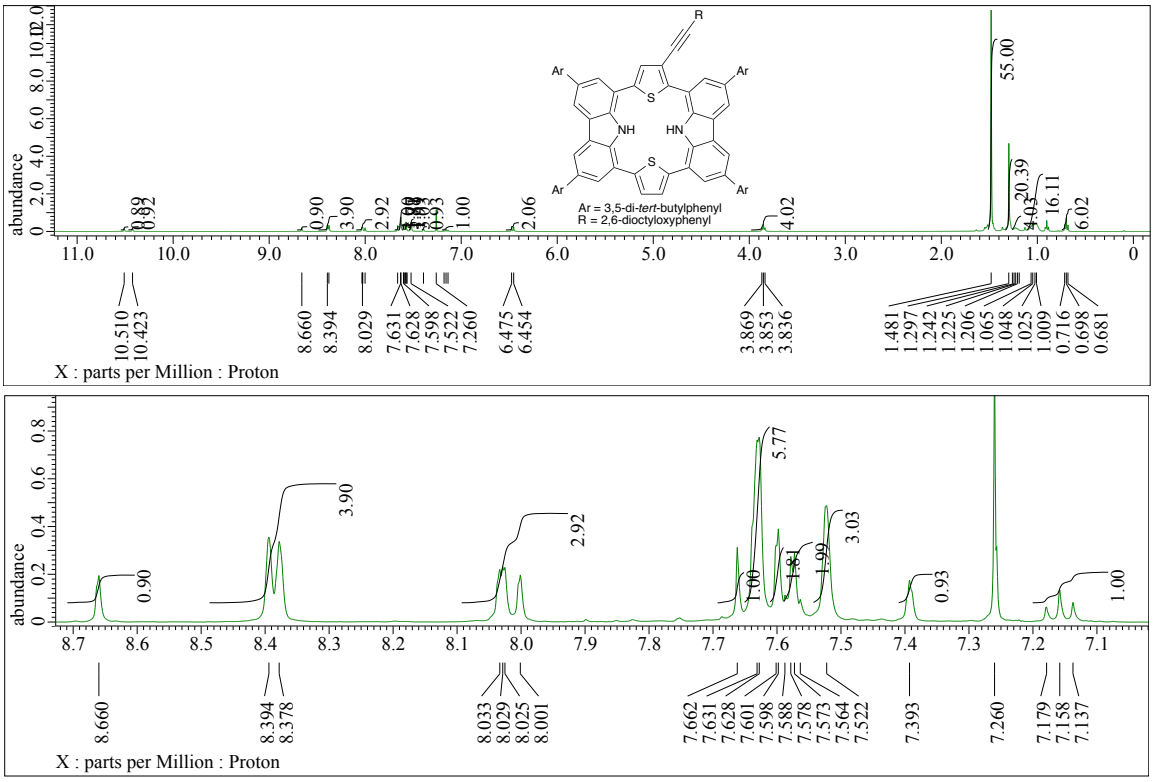
^{13}C NMR spectrum of **4b** in $CDCl_3$



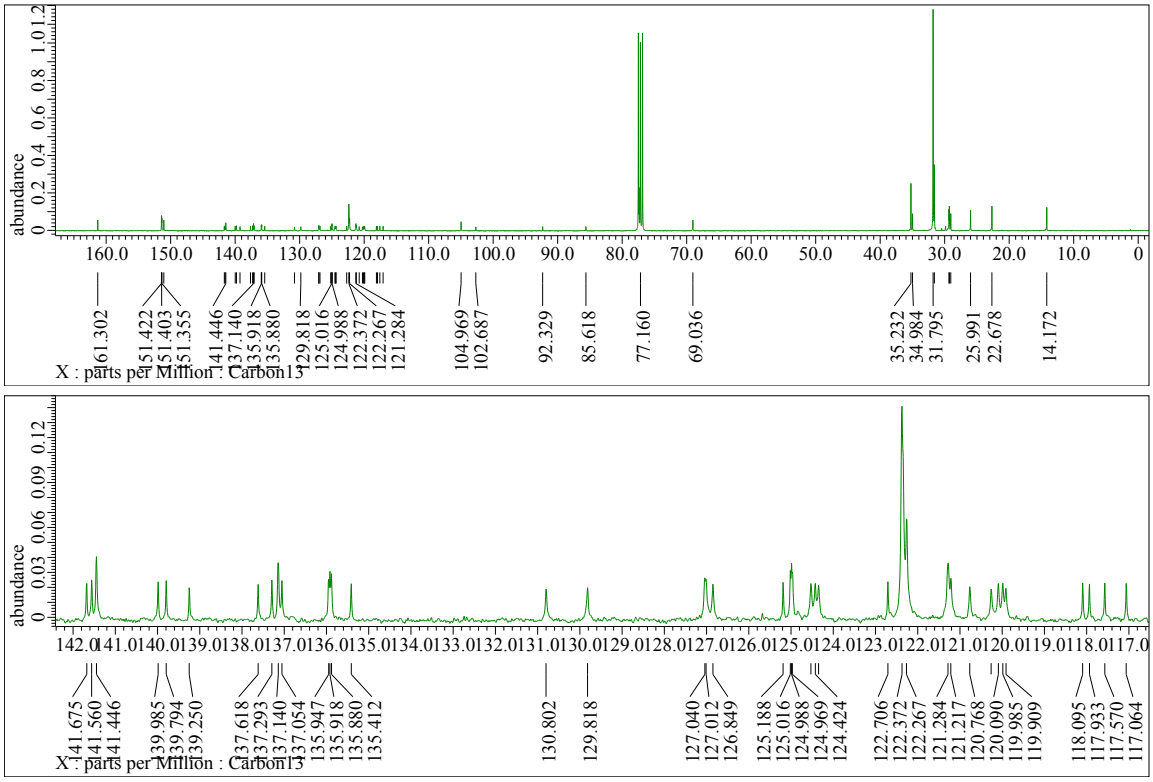
^{1}H NMR spectrum of **4c** in $CDCl_3$



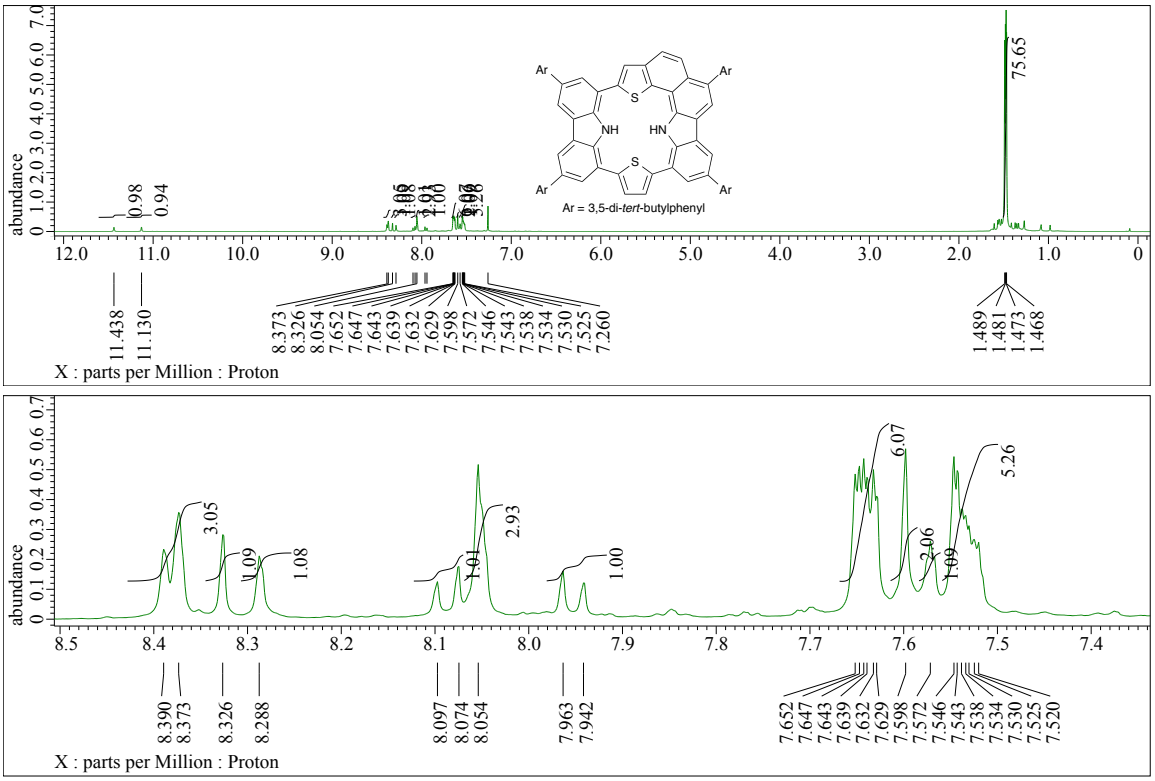
^{13}C NMR spectrum of **4c** in $CDCl_3$



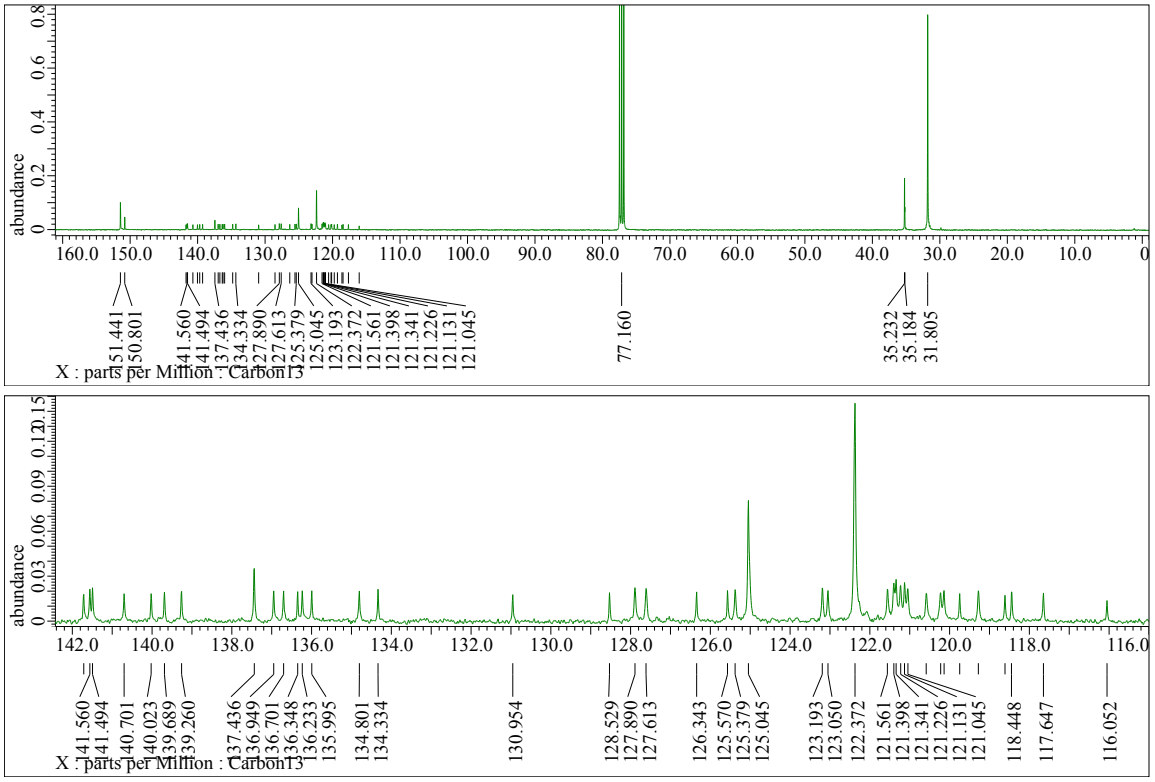
^{1}H NMR spectrum of **4d** in $CDCl_3$



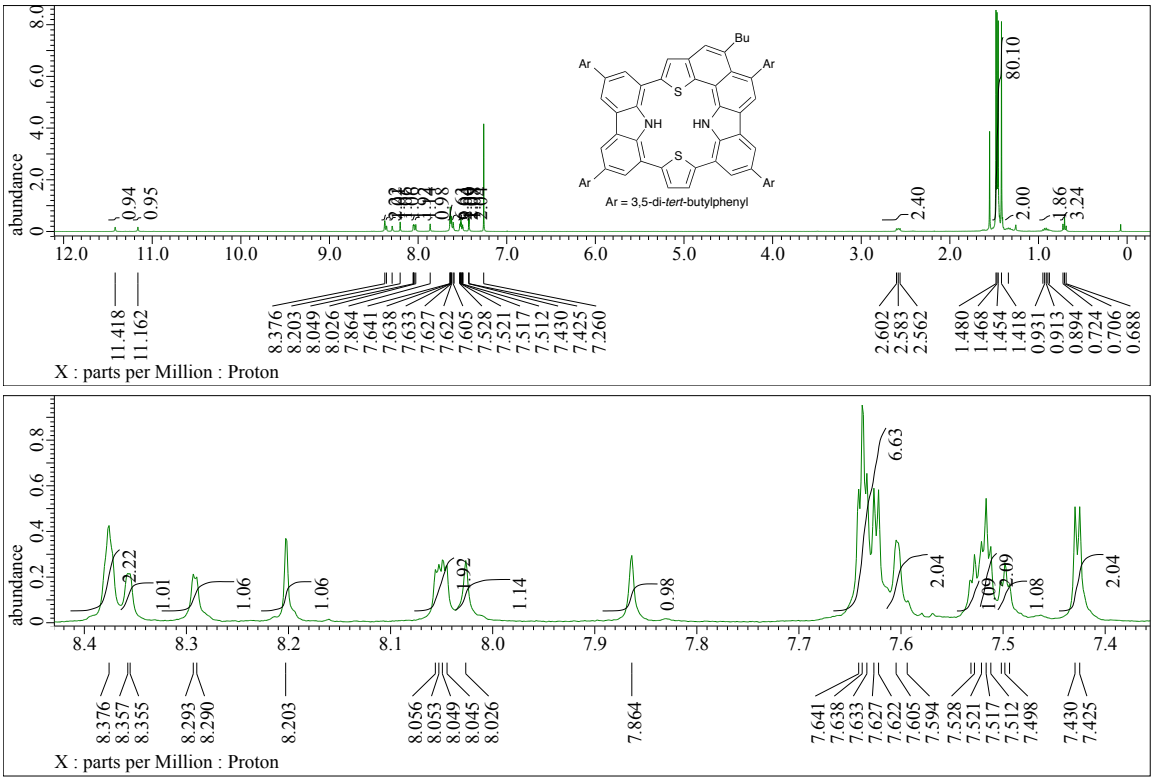
^{13}C NMR spectrum of **4d** in $CDCl_3$



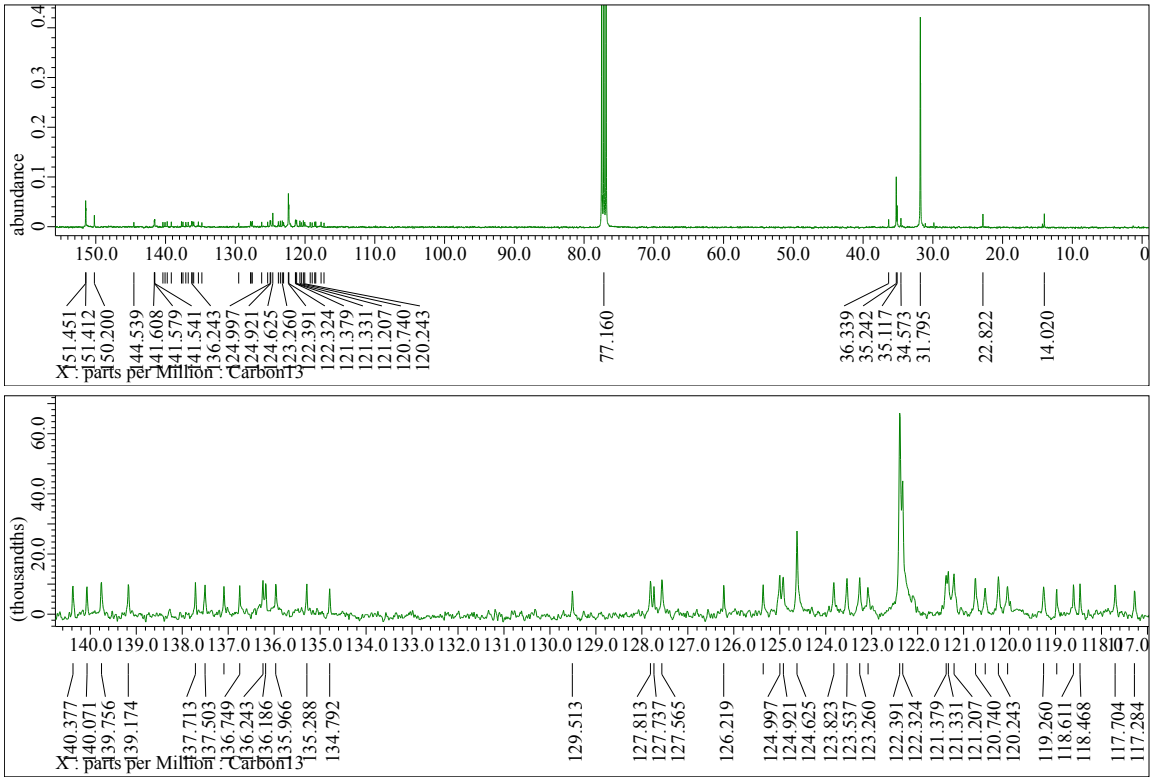
^{1}H NMR spectrum of **2a'** in $CDCl_3$



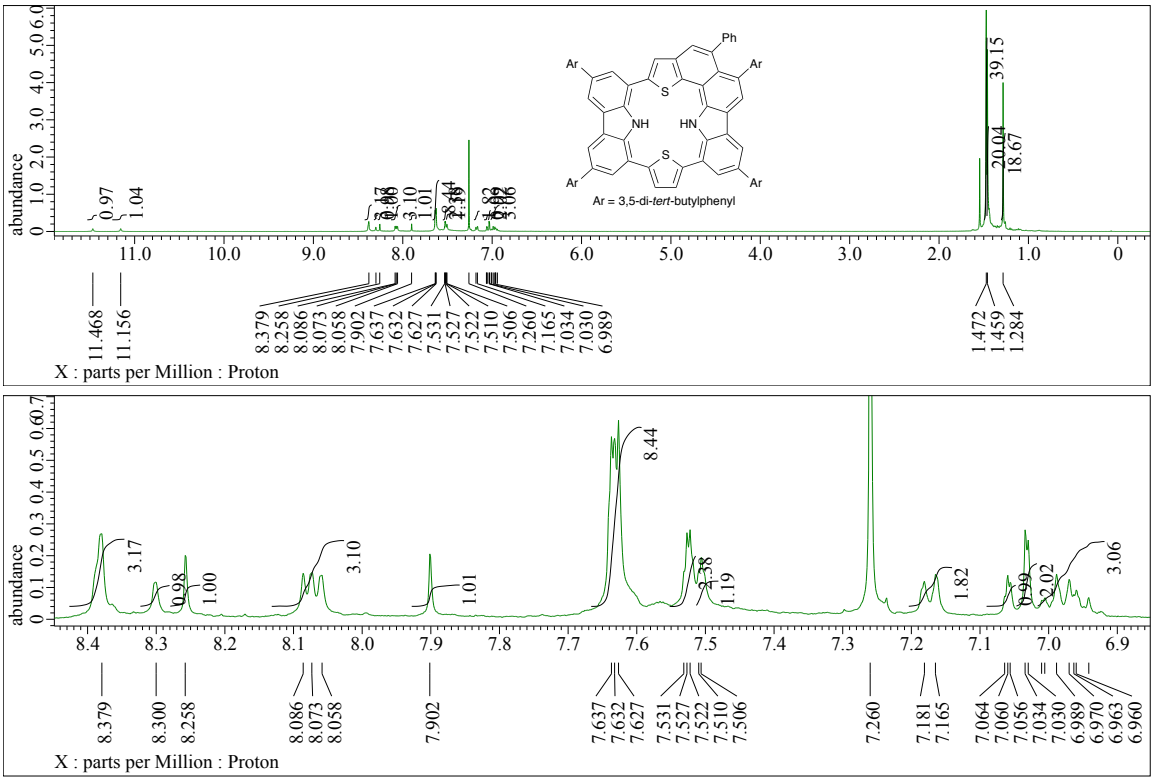
^{13}C NMR spectrum of **2a'** in $CDCl_3$



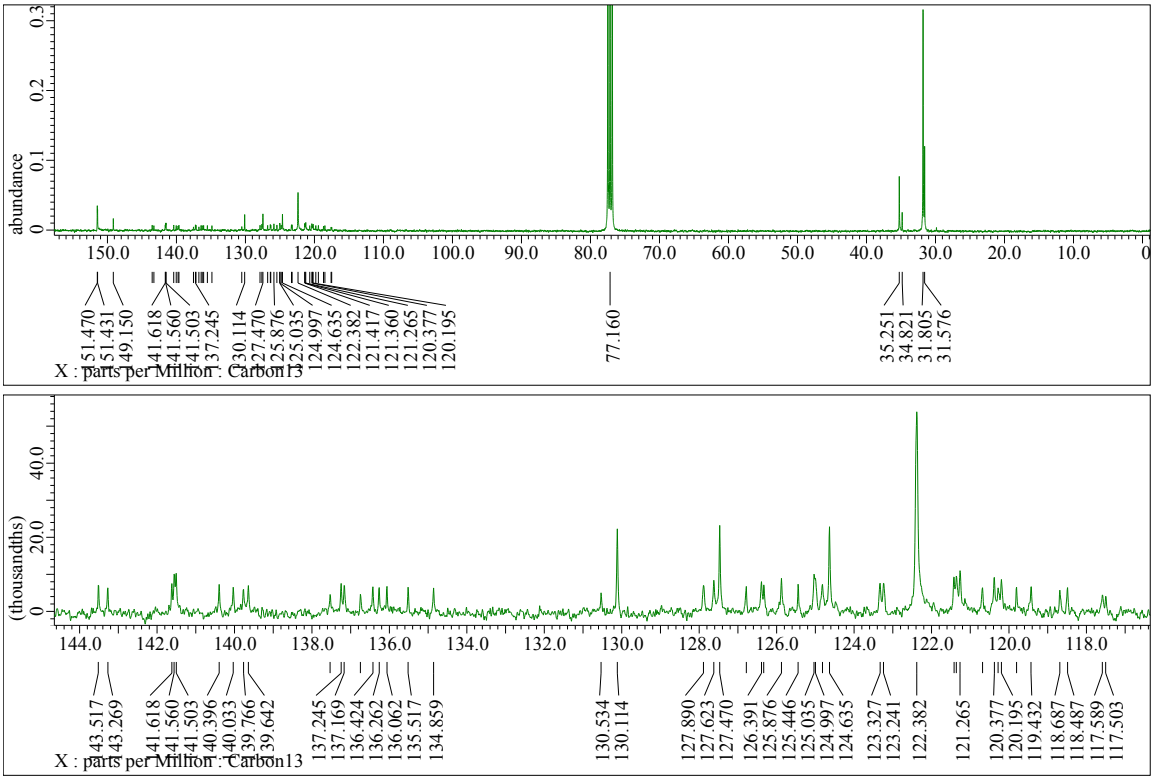
^{1}H NMR spectrum of **2b'** in $CDCl_3$



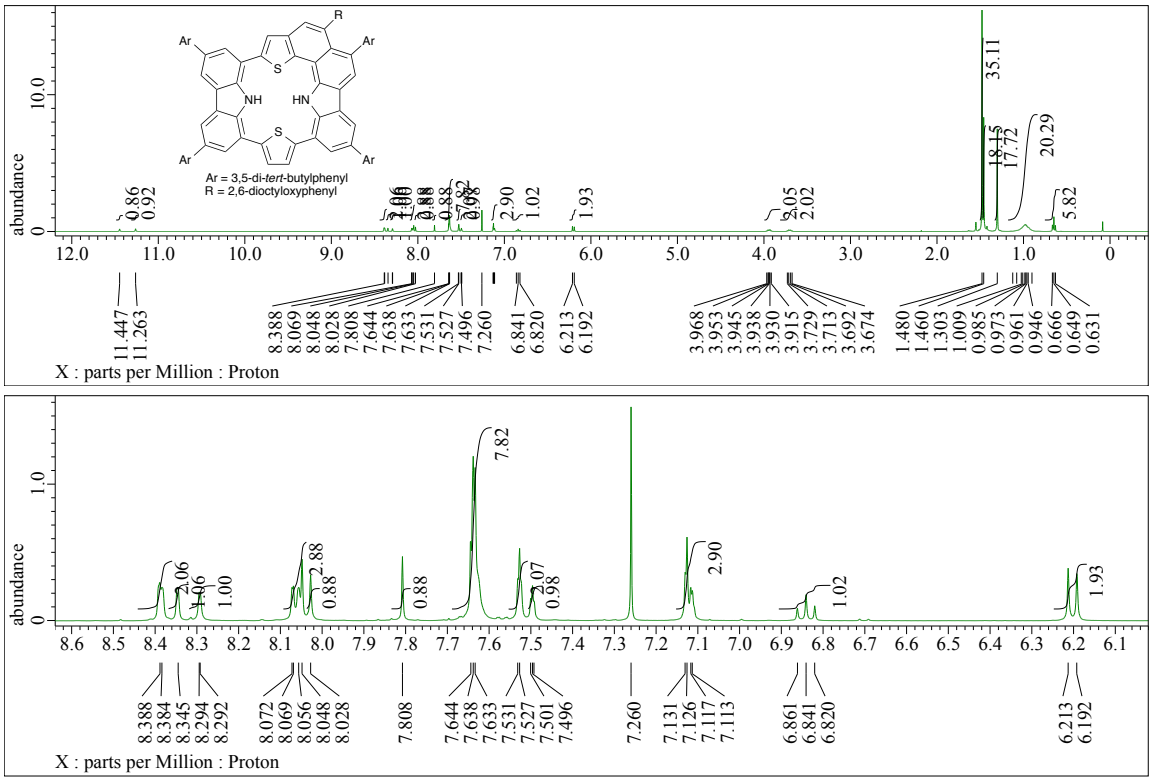
^{13}C NMR spectrum of **2b'** in $CDCl_3$



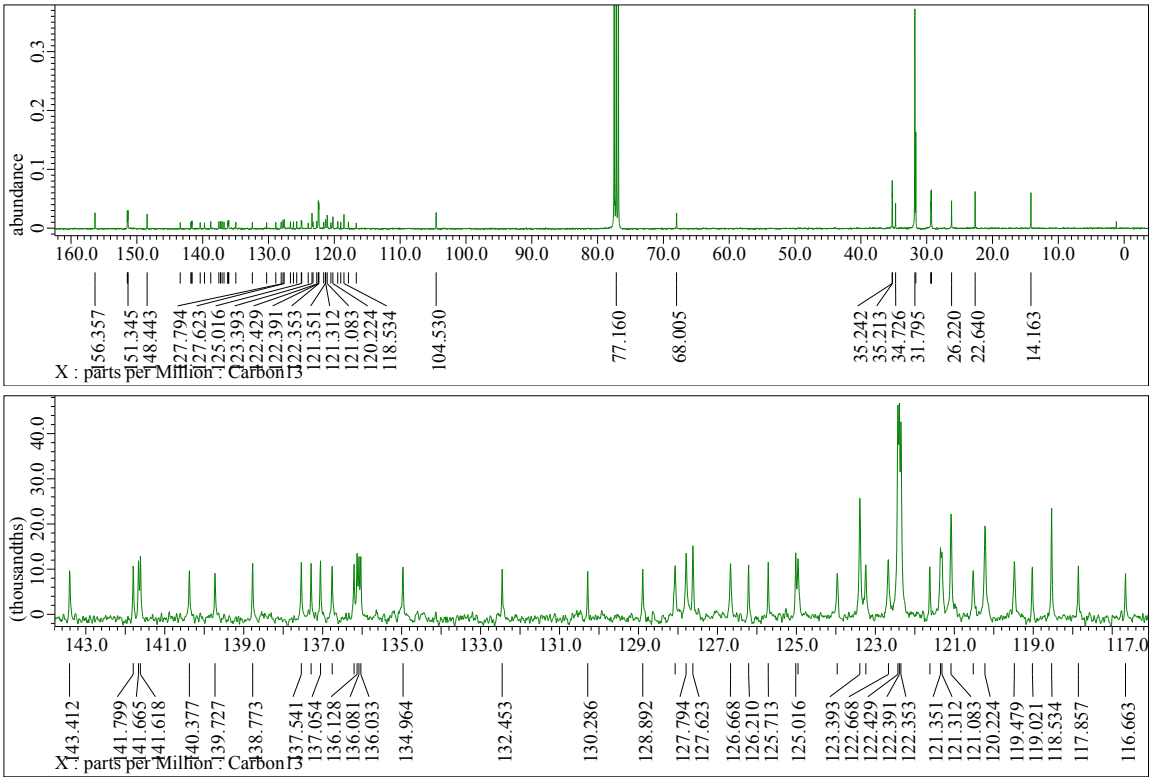
^{1}H NMR spectrum of **2c'** in $CDCl_3$



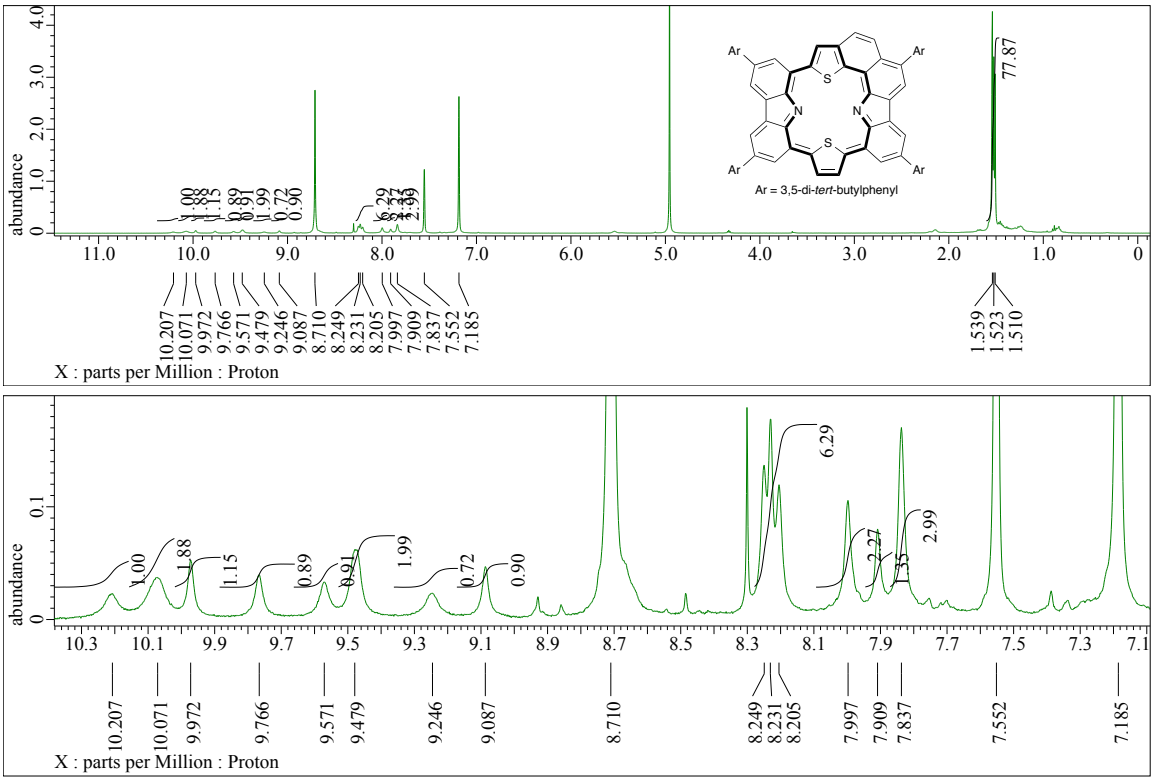
^{13}C NMR spectrum of **2c'** in $CDCl_3$



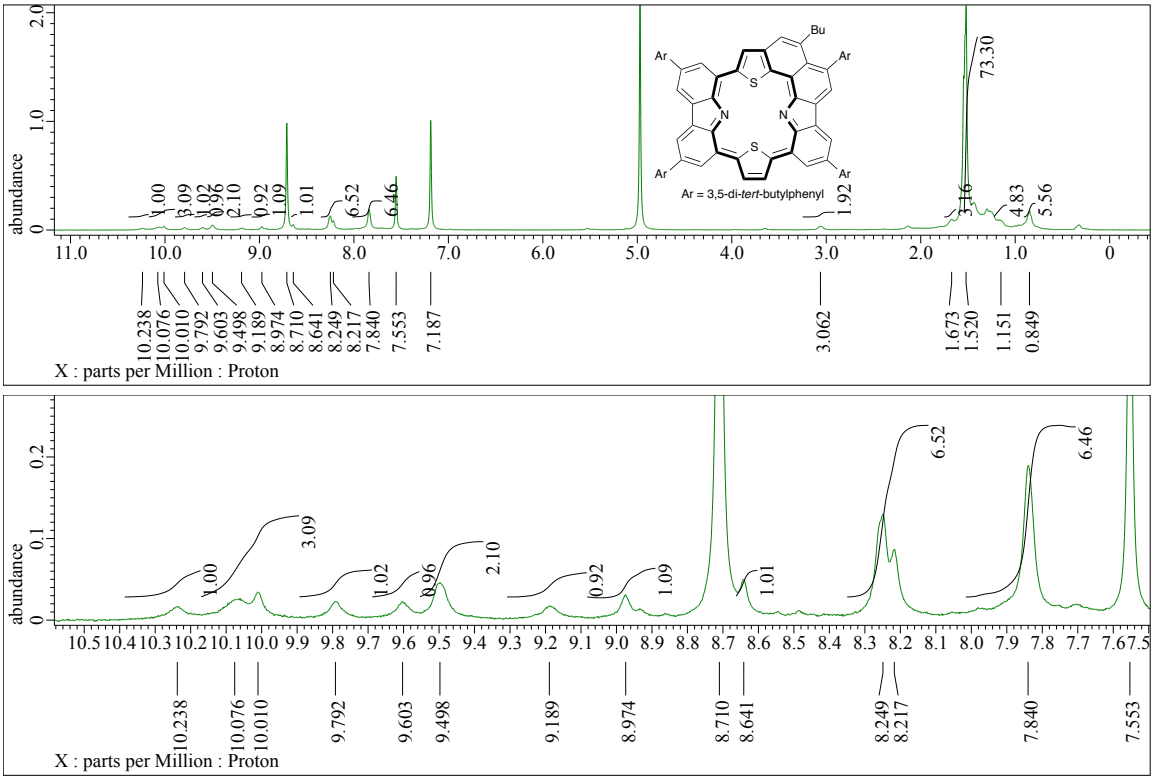
^{1}H NMR spectrum of **2d'** in $CDCl_3$



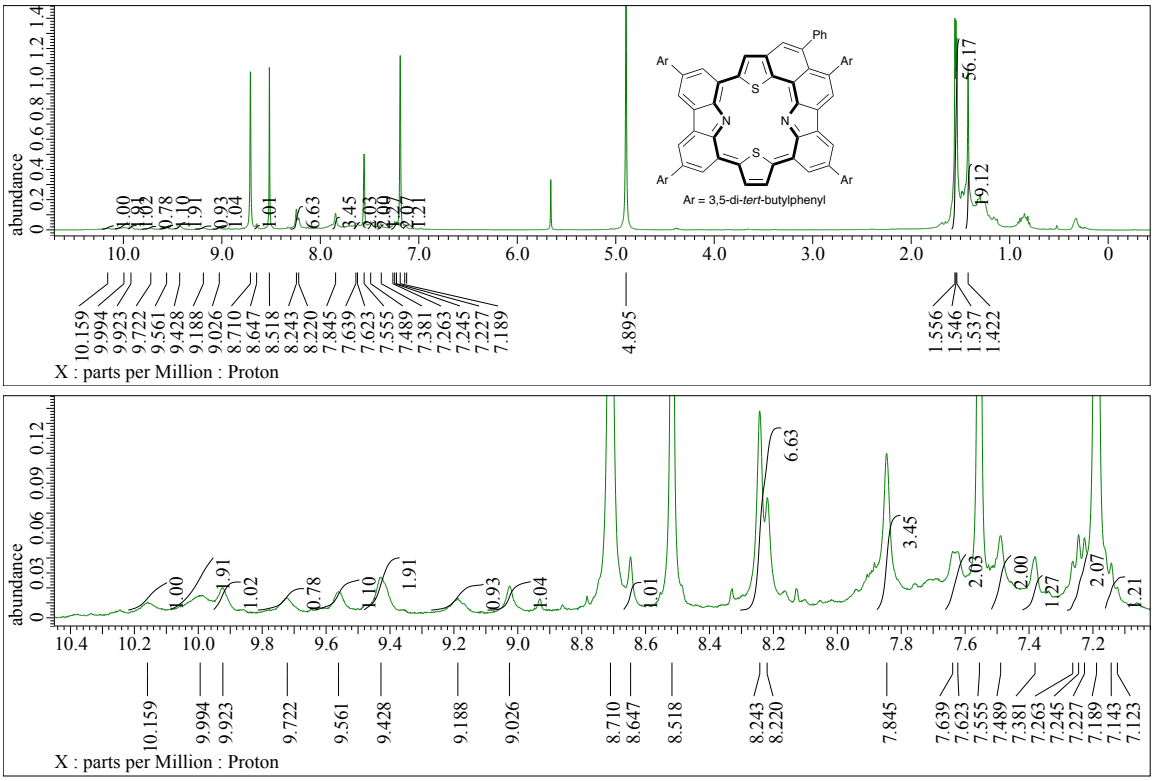
^{13}C NMR spectrum of **2d'** in $CDCl_3$



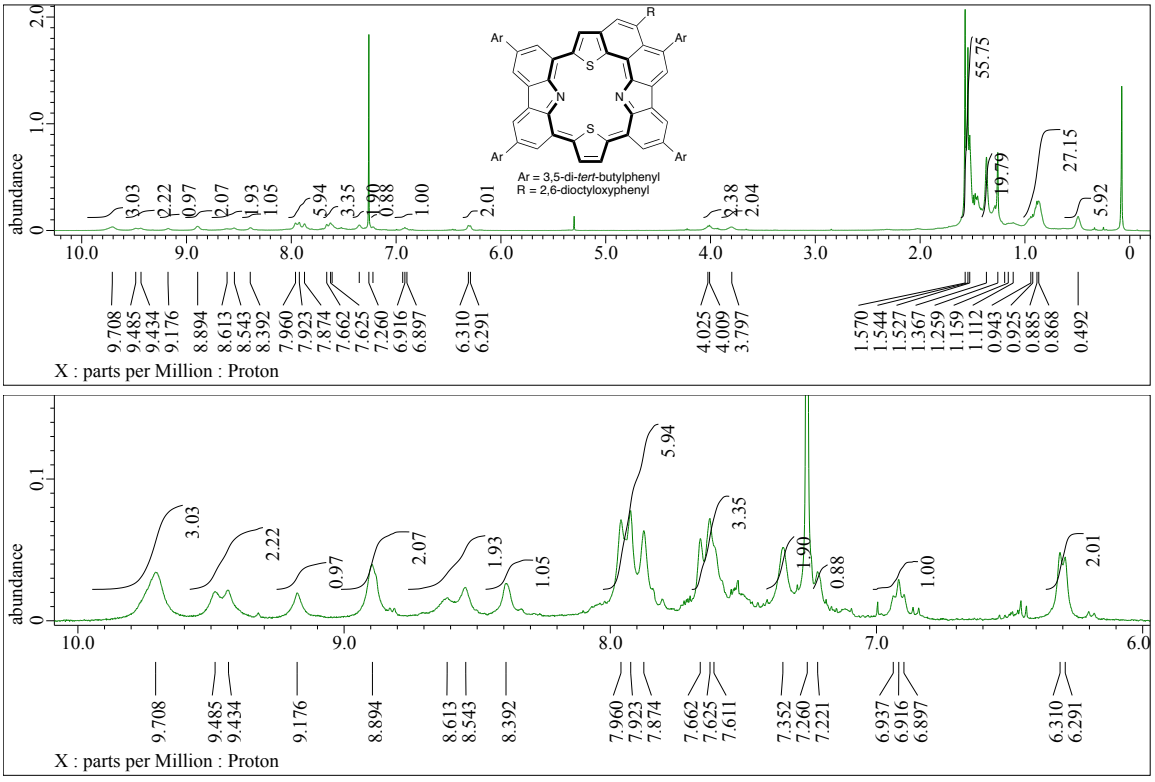
^{1}H NMR spectrum of **2a** in pyridine-d_5



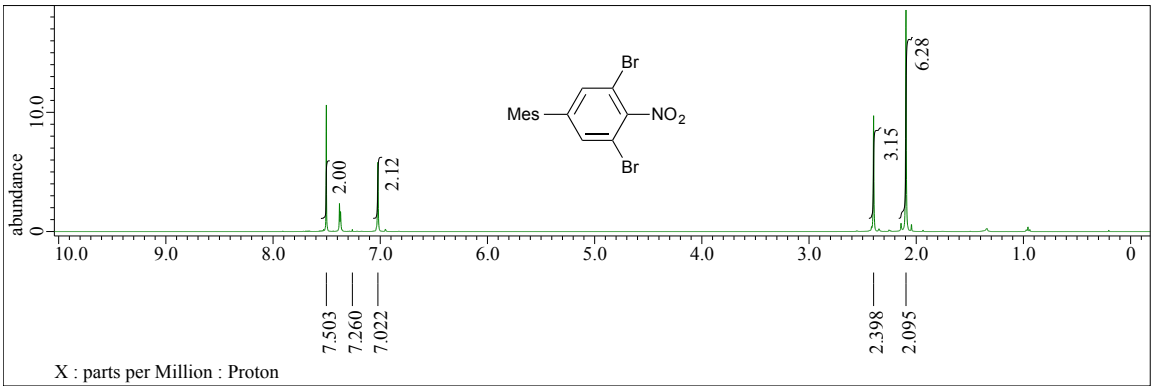
^{1}H NMR spectrum of **2b** in pyridine-d_5



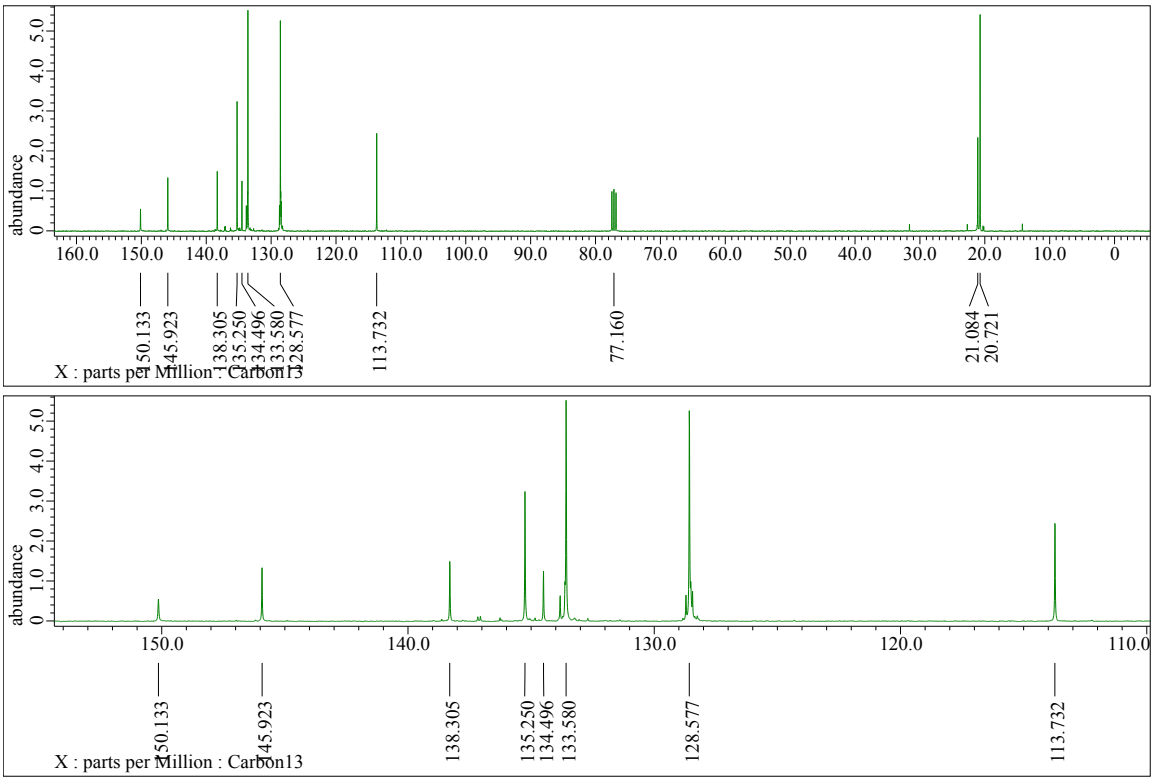
^{1}H NMR spectrum of **2c** in pyridine-d_5



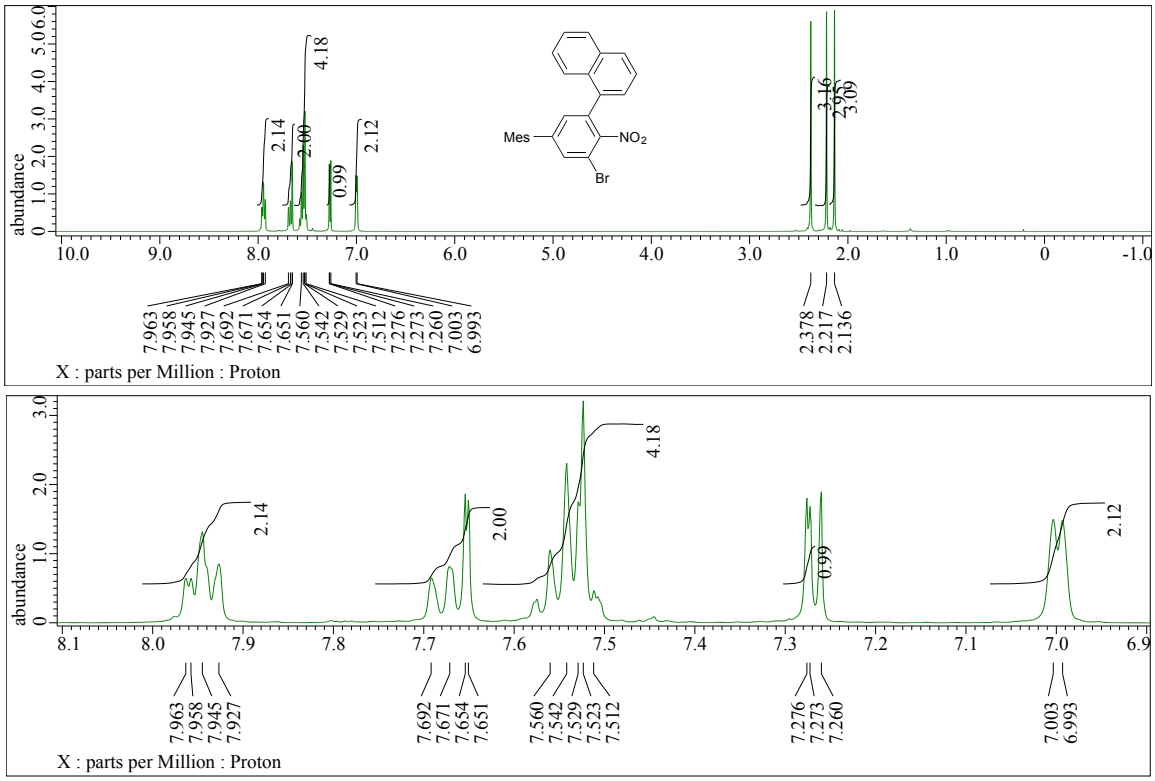
^{1}H NMR spectrum of **2d** in $CDCl_3$



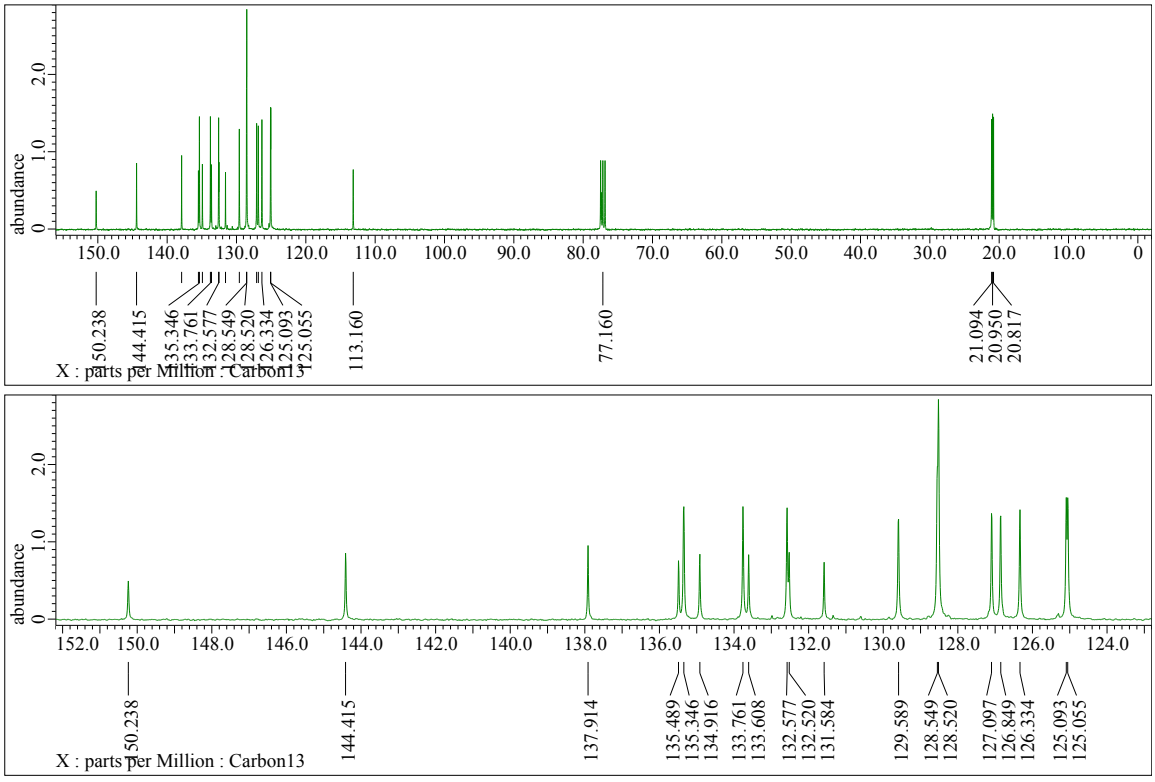
^{1}H NMR spectrum of **5** in $CDCl_3$



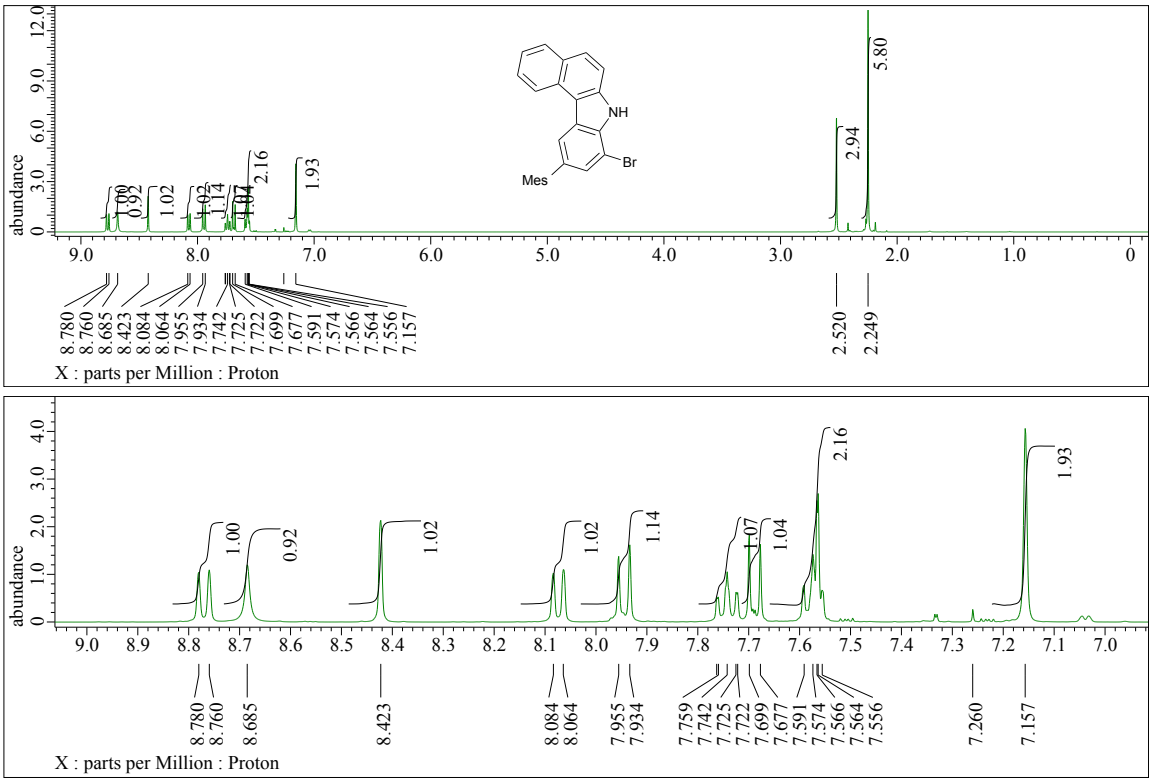
^{13}C NMR spectrum of **5** in $CDCl_3$



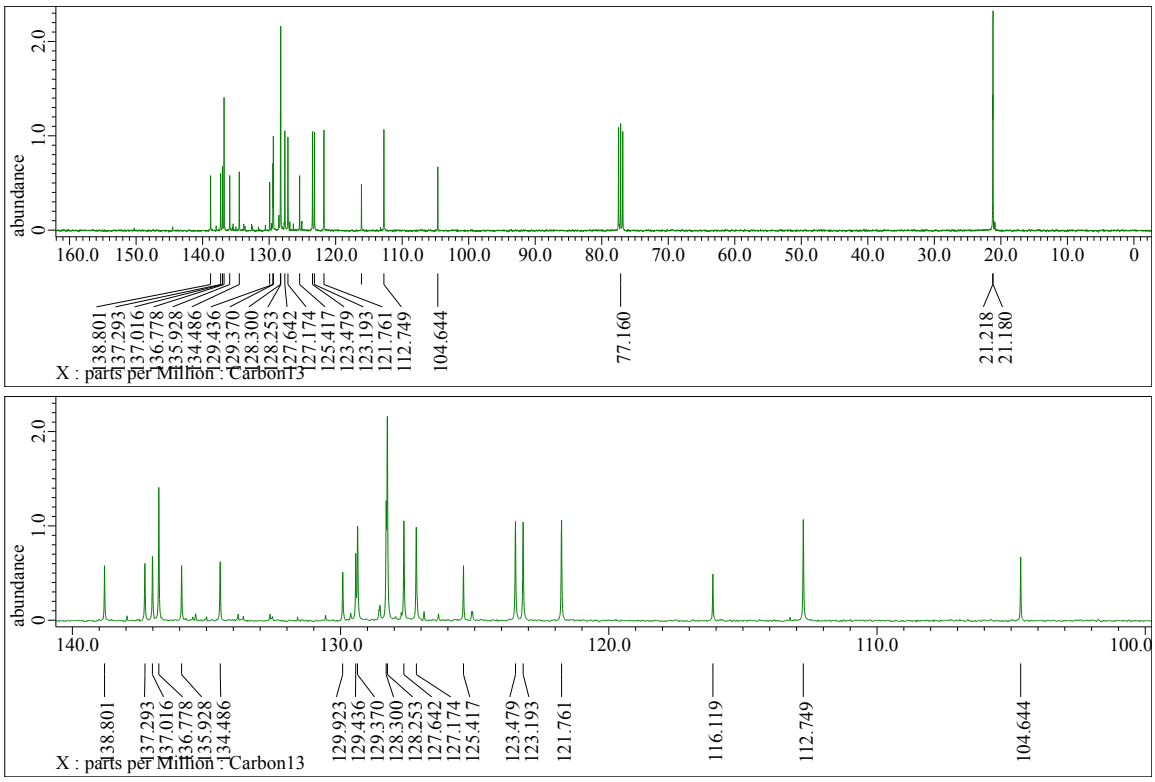
^{1}H NMR spectrum of **6** in $CDCl_3$



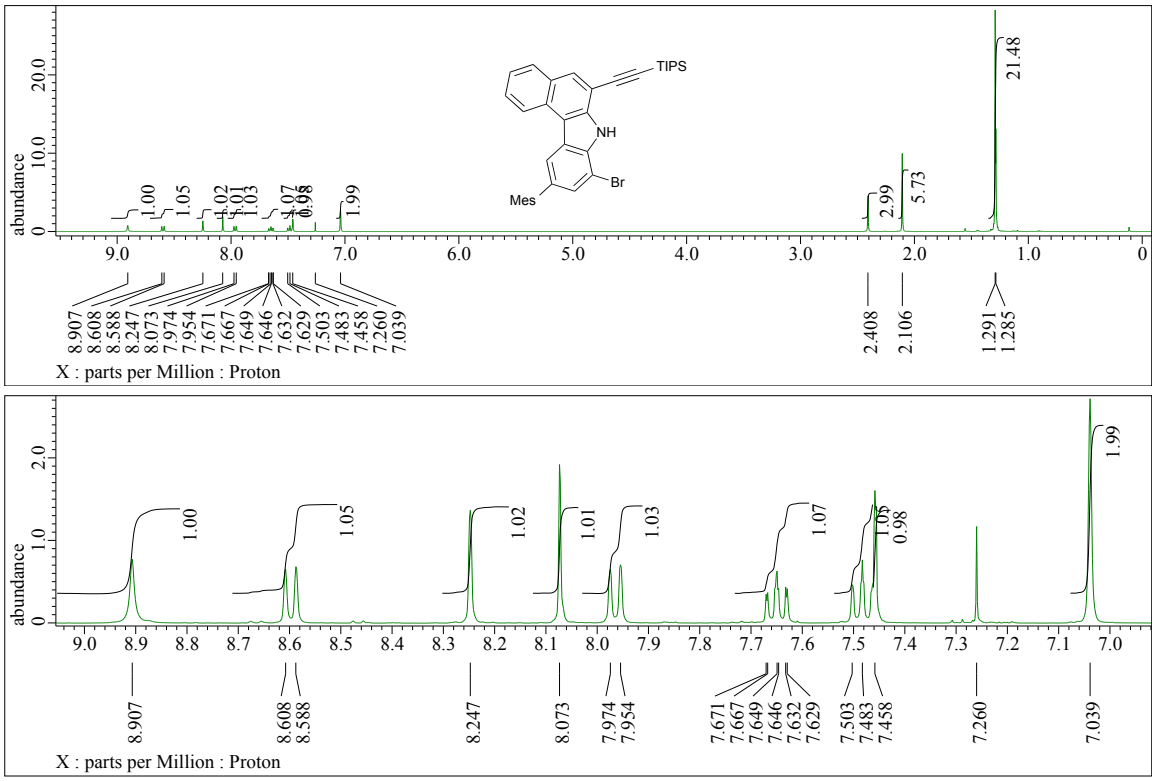
^{13}C NMR spectrum of **6** in $CDCl_3$



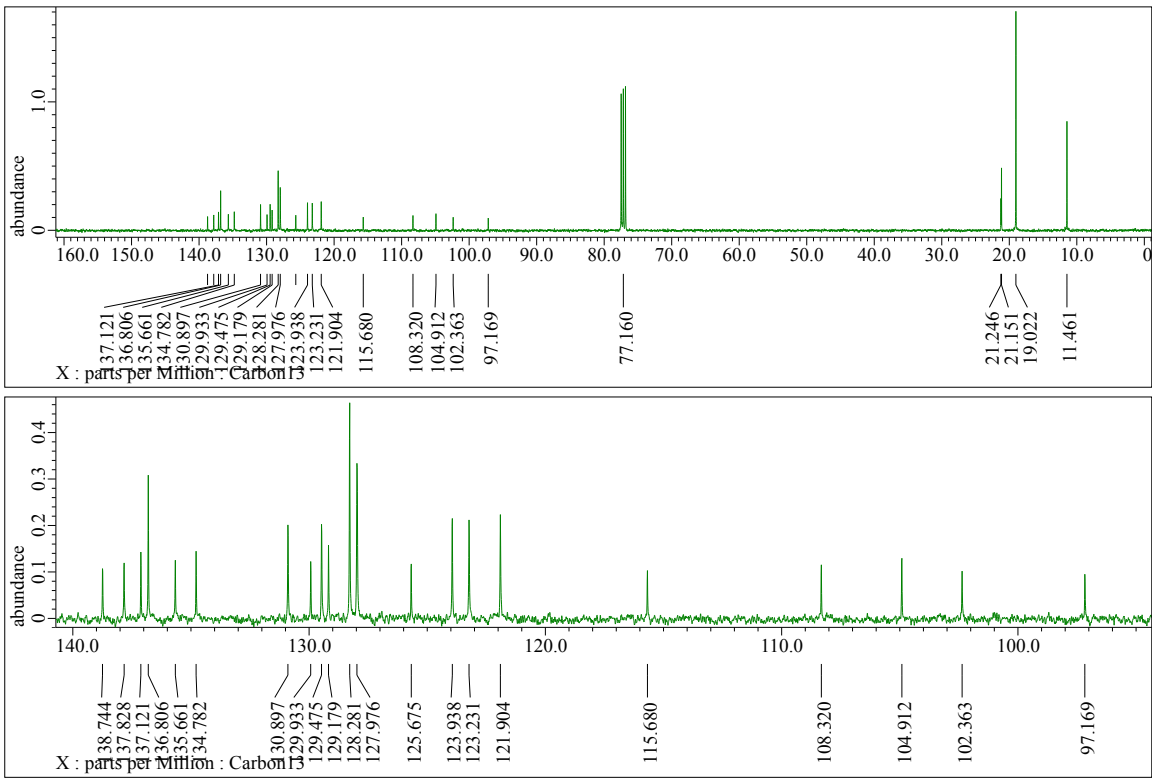
^{1}H NMR spectrum of **7** in $CDCl_3$



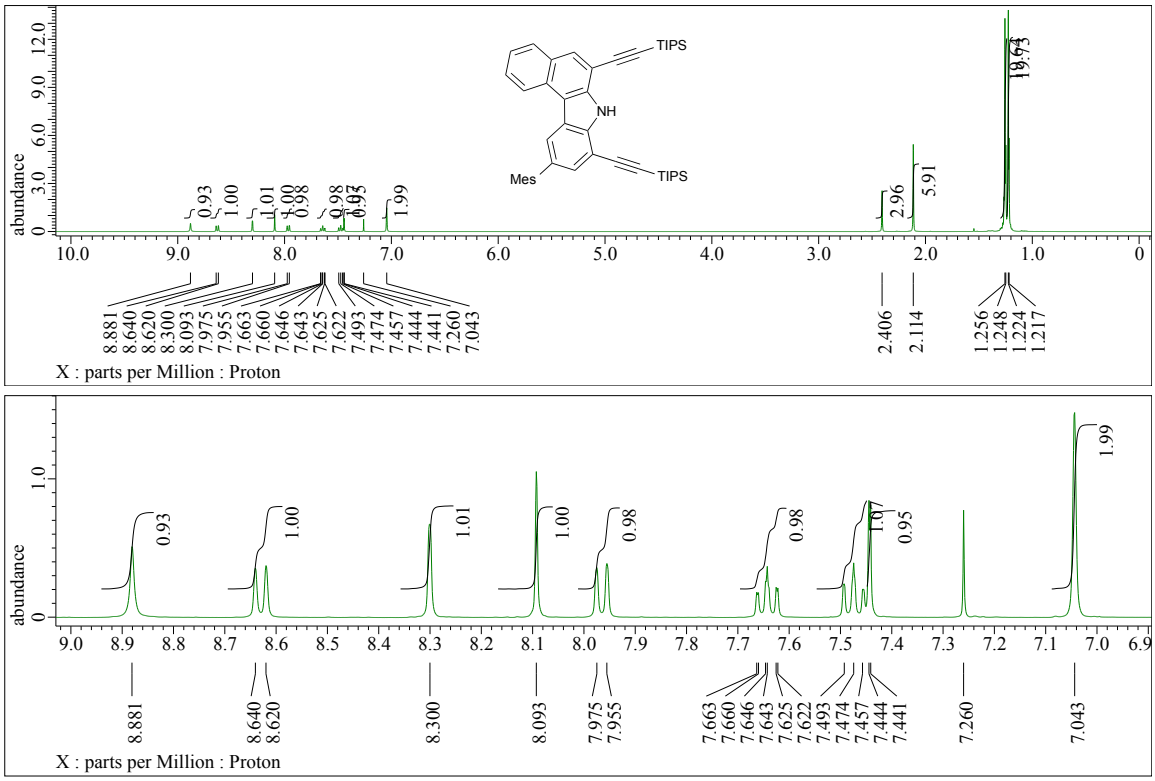
^{13}C NMR spectrum of **7** in $CDCl_3$



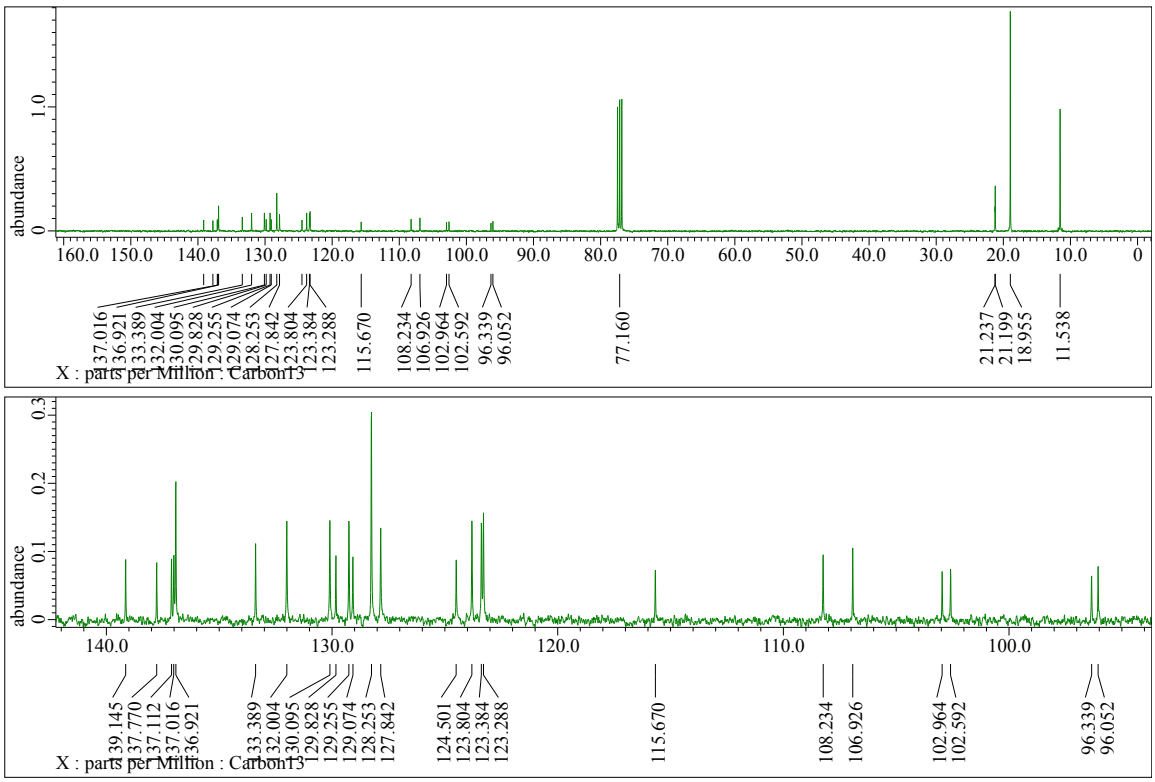
^{1}H NMR spectrum of **8** in $CDCl_3$



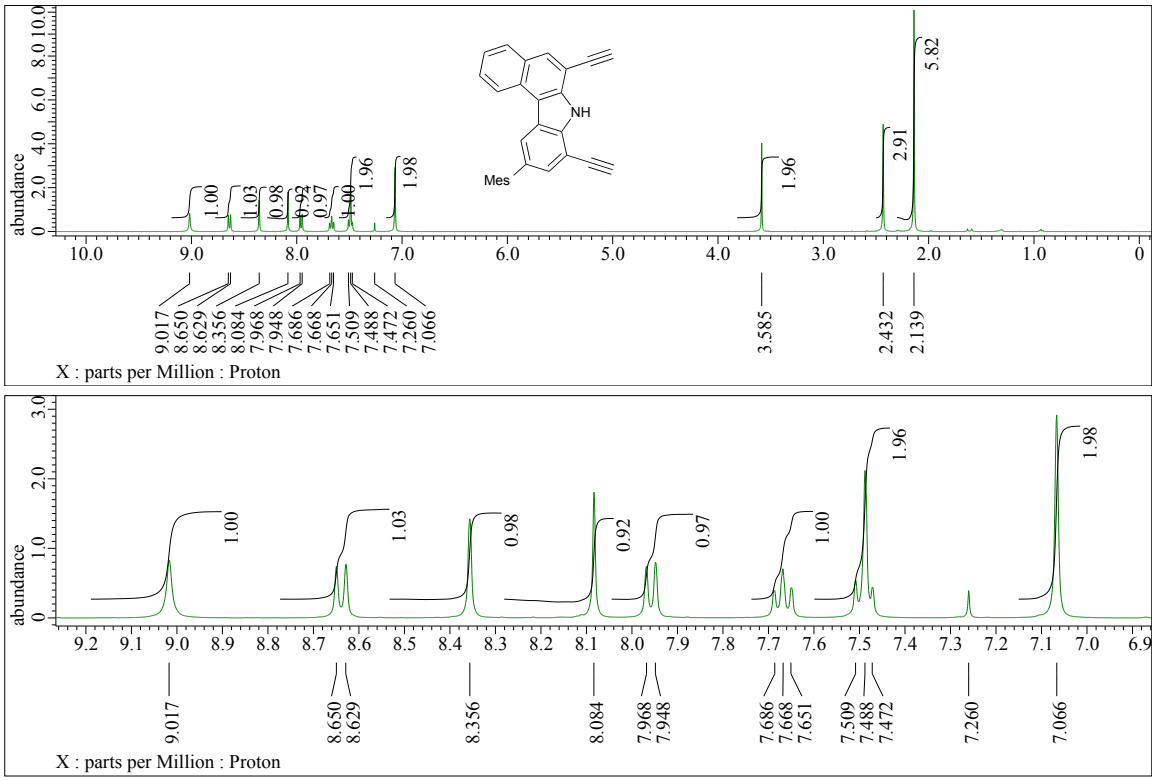
^{13}C NMR spectrum of **8** in $CDCl_3$



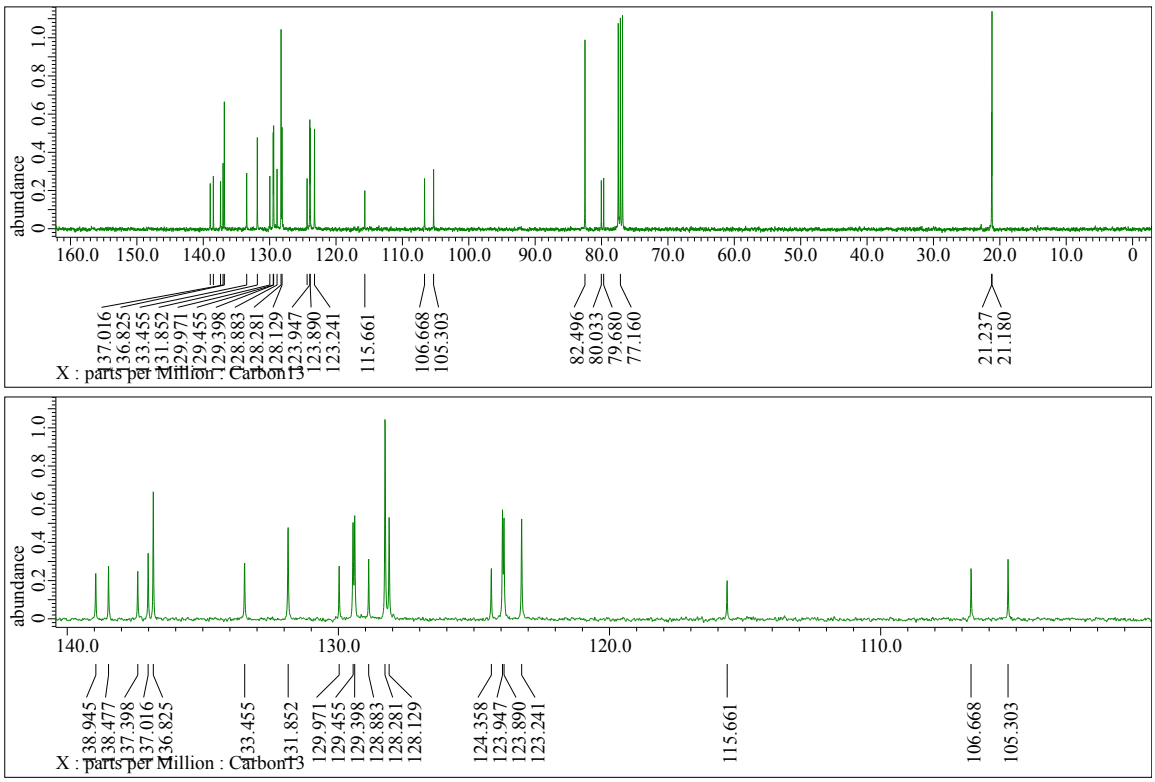
^{1}H NMR spectrum of **9** in $CDCl_3$



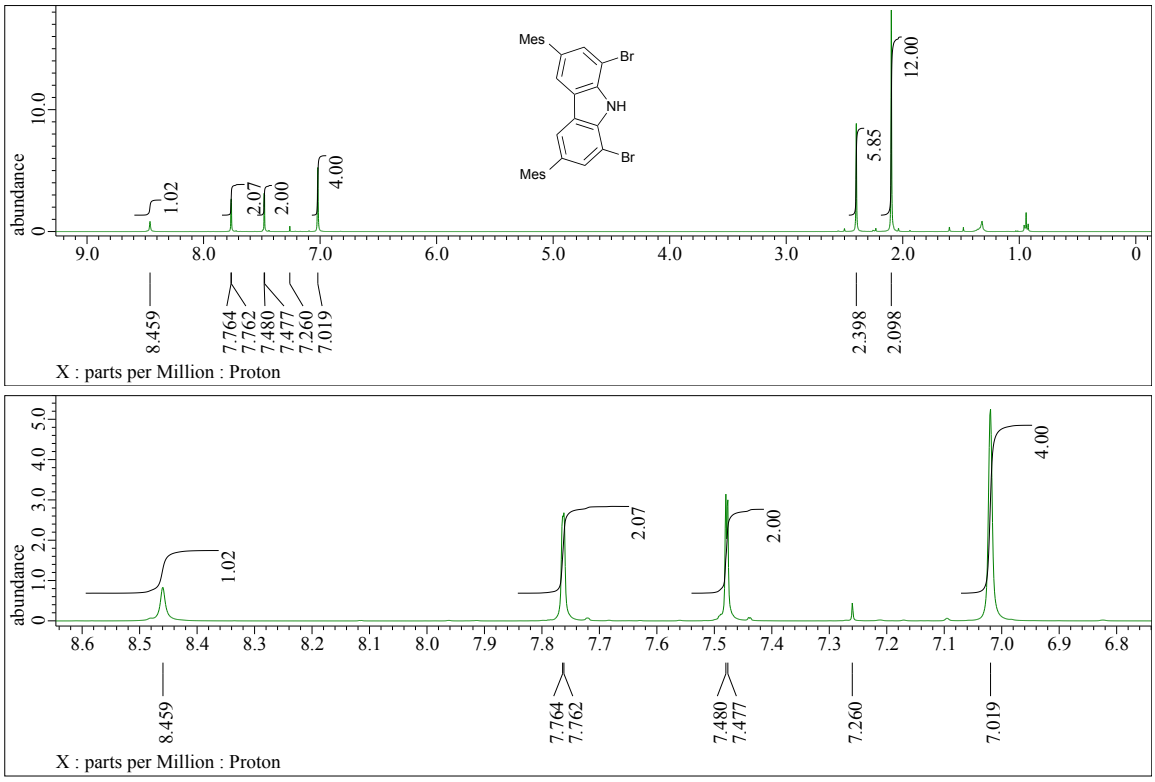
^{13}C NMR spectrum of **9** in $CDCl_3$



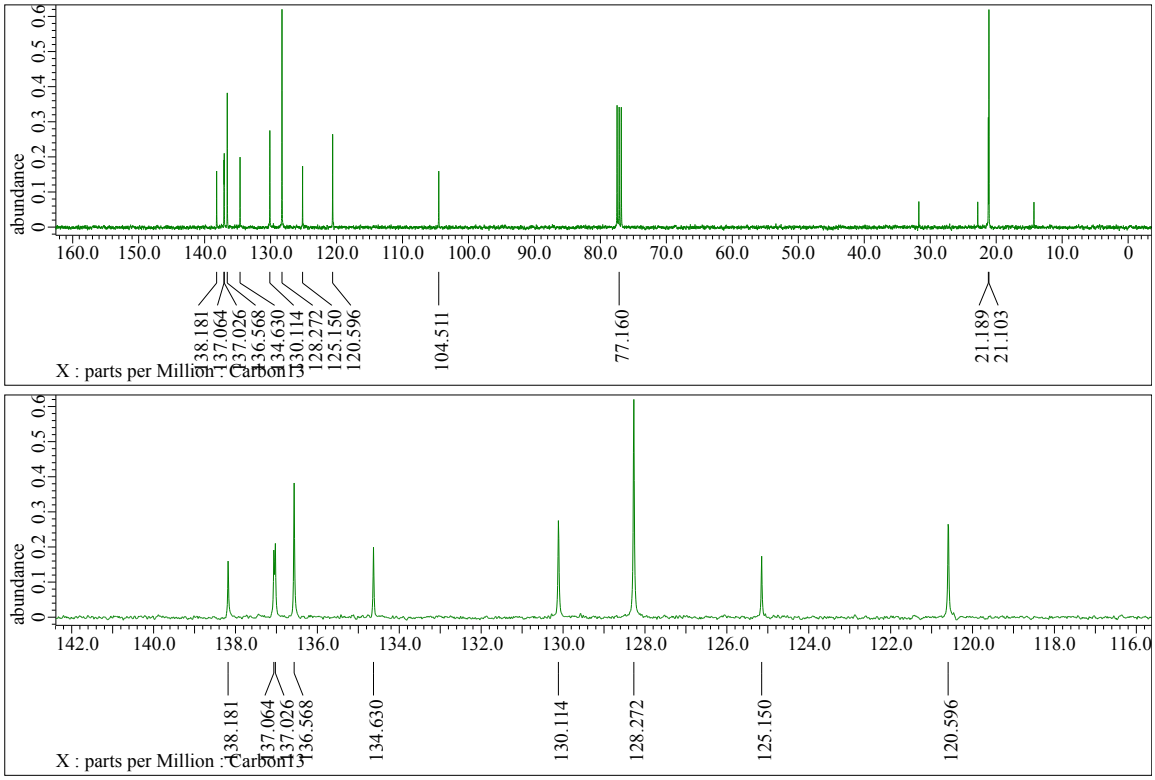
^{1}H NMR spectrum of **10** in $CDCl_3$



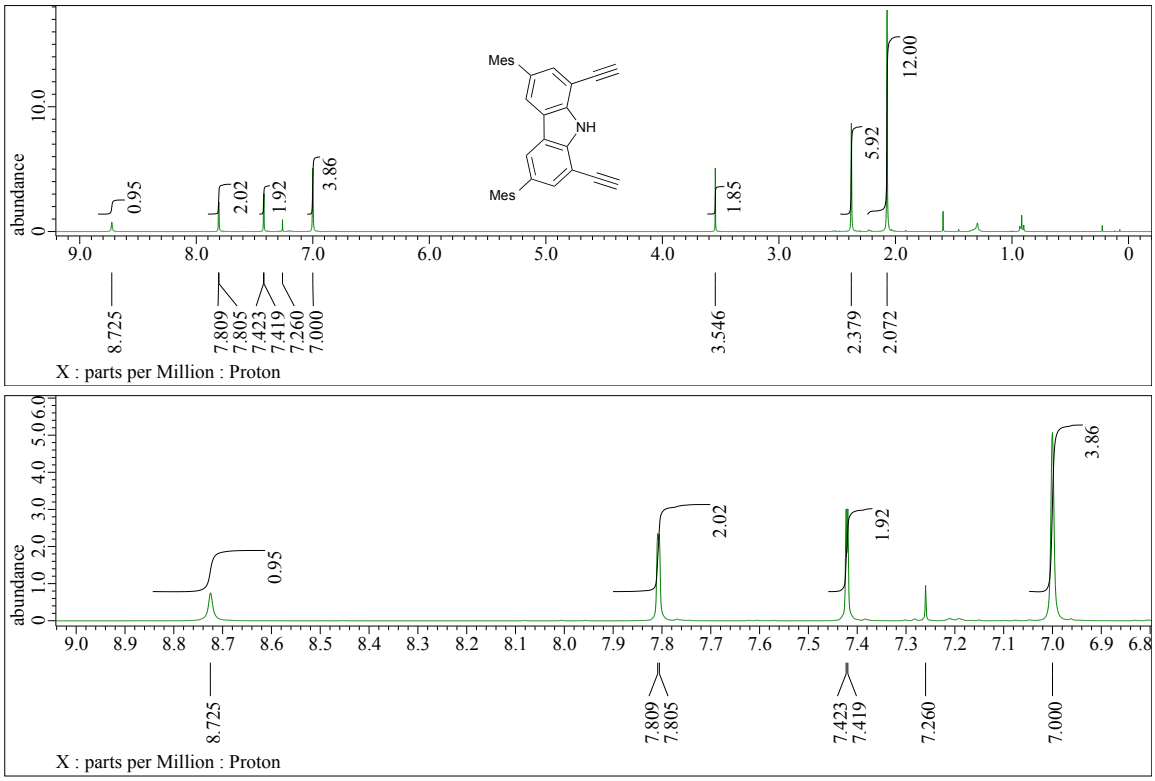
^{13}C NMR spectrum of **10** in $CDCl_3$



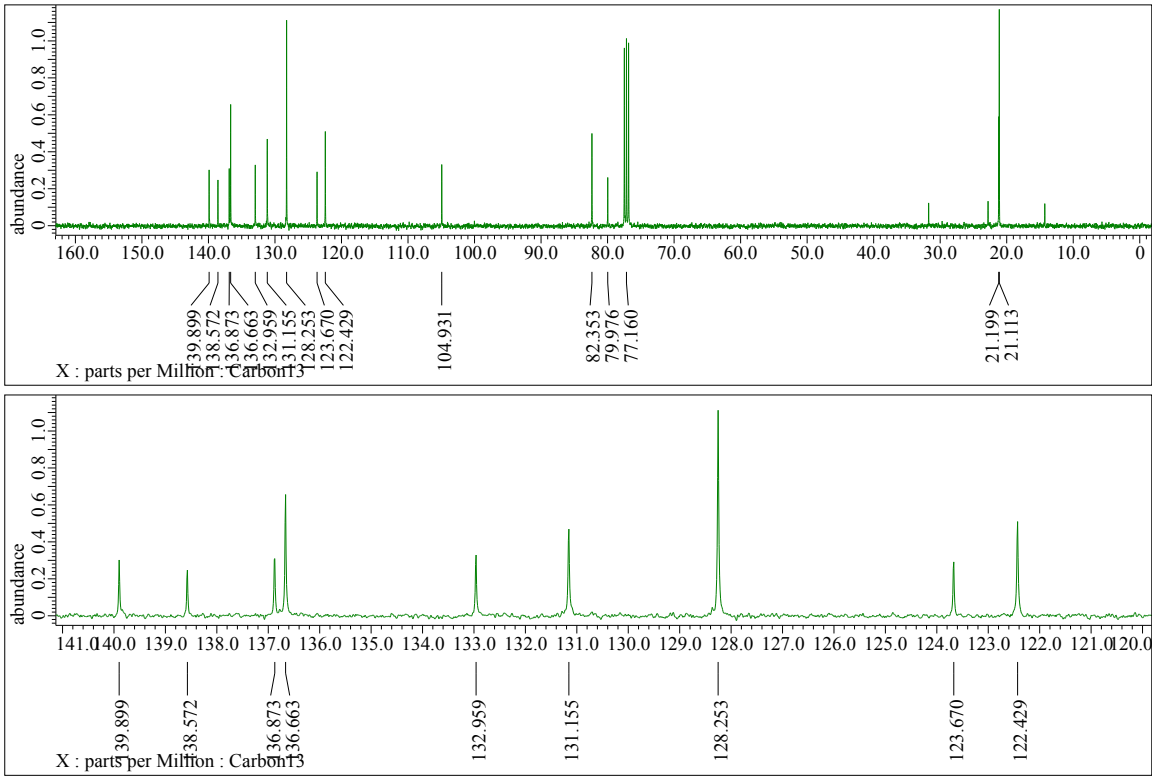
^{1}H NMR spectrum of 3,6-bis(2,4,6-trimethylphenyl)-1,8-dibromocarbazole in $CDCl_3$



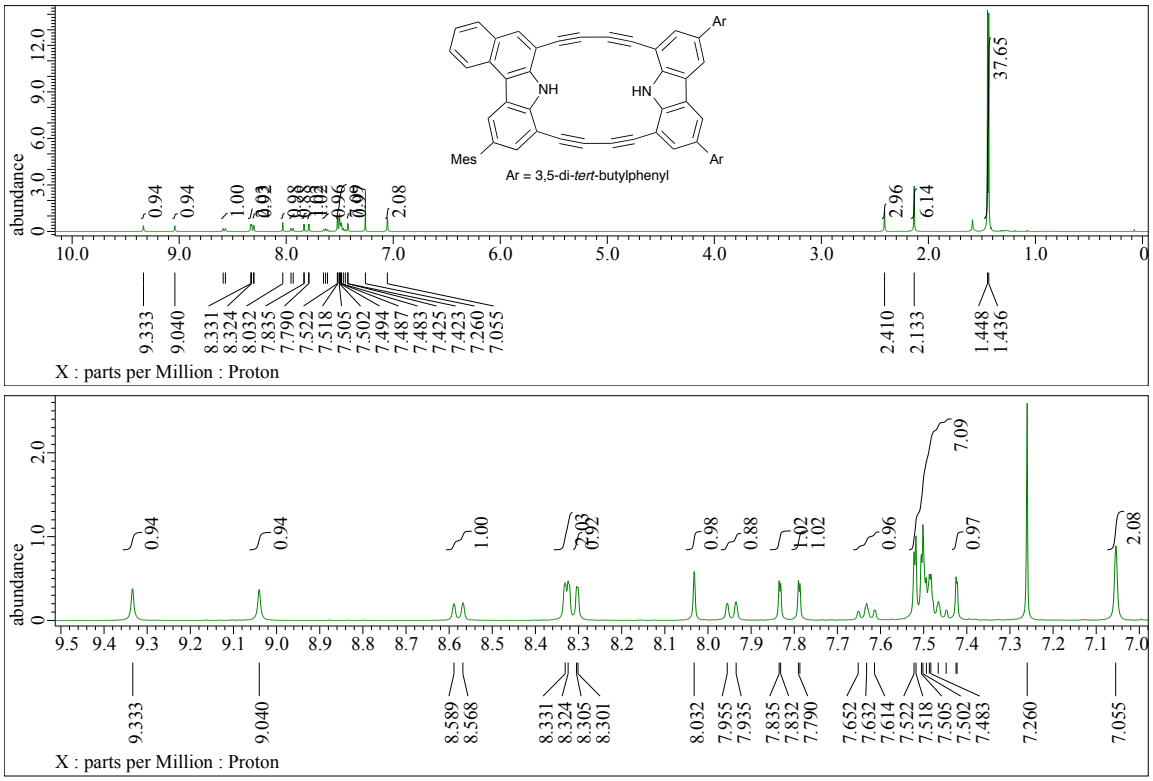
^{13}C NMR spectrum of 3,6-bis(2,4,6-trimethylphenyl)-1,8-dibromocarbazole in $CDCl_3$



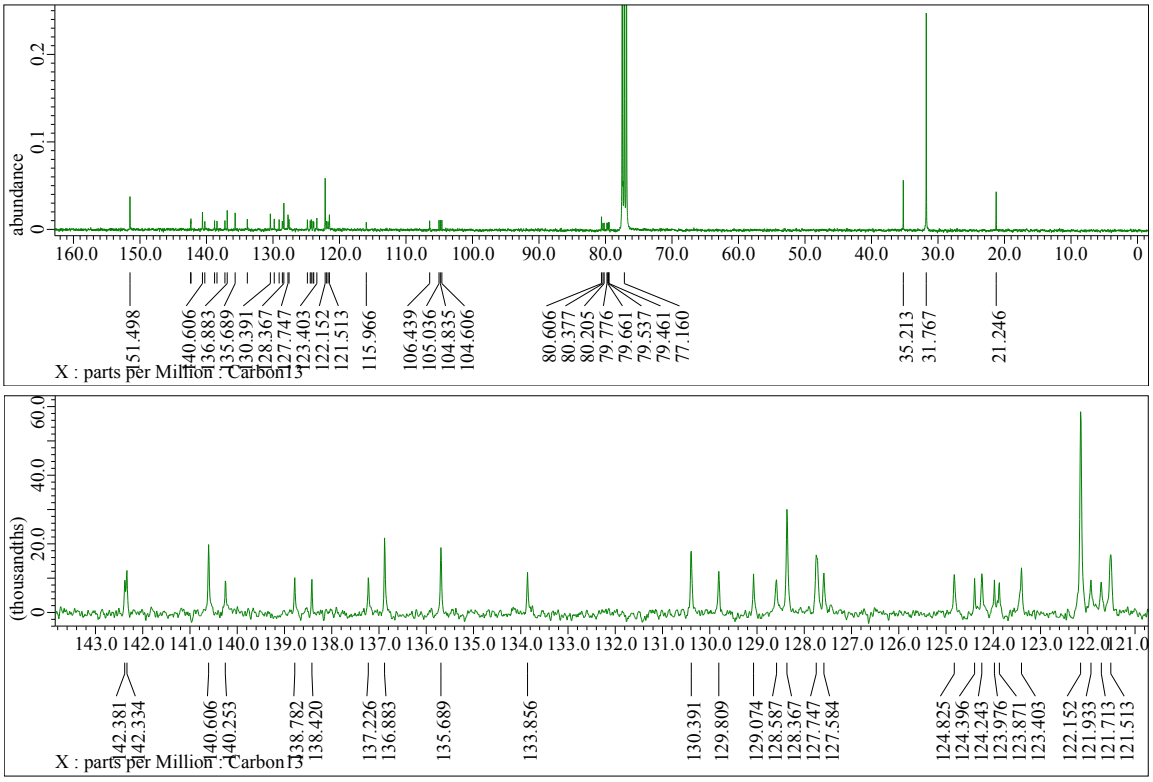
^{1}H NMR spectrum of **11b** in $CDCl_3$



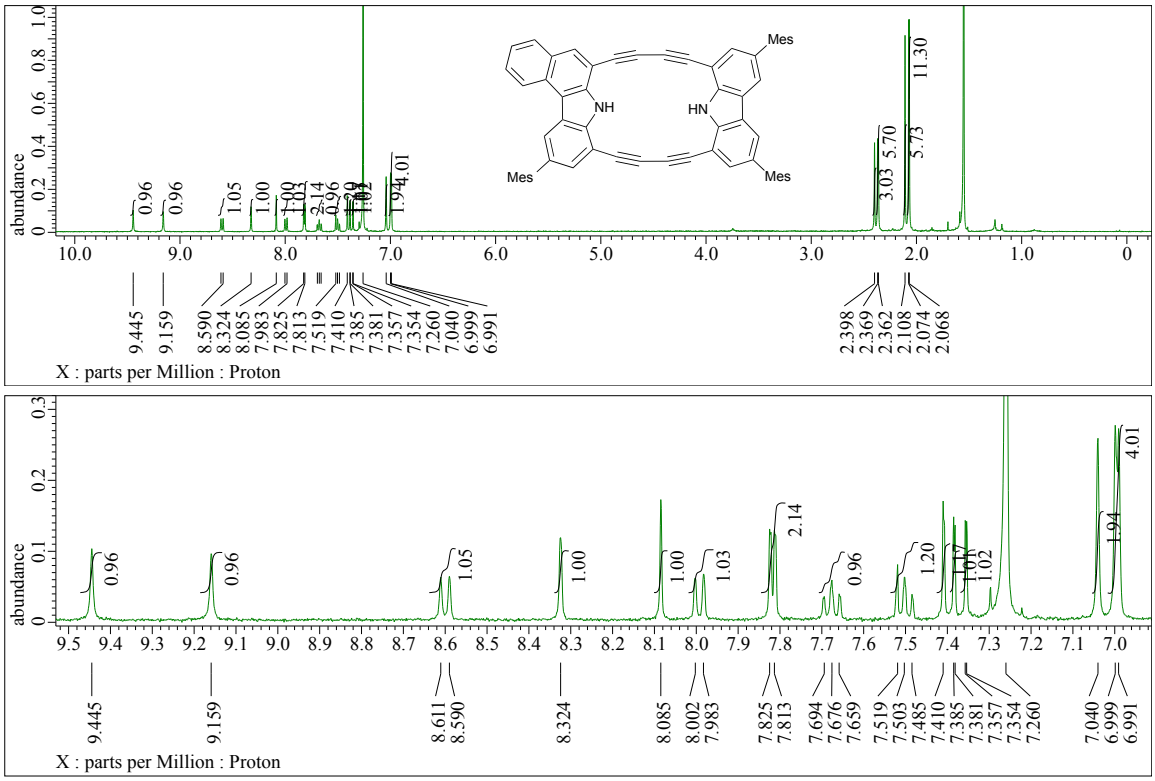
^{13}C NMR spectrum of **11b** in $CDCl_3$



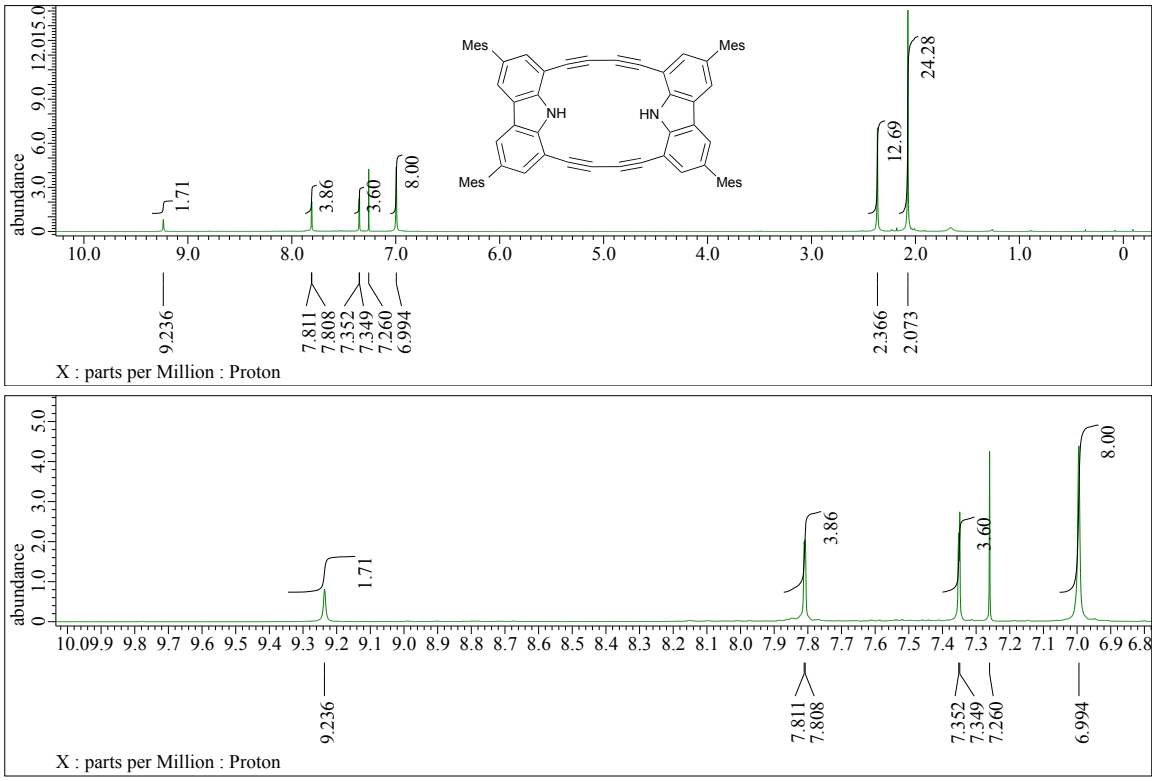
^{1}H NMR spectrum of **12a** in $CDCl_3$



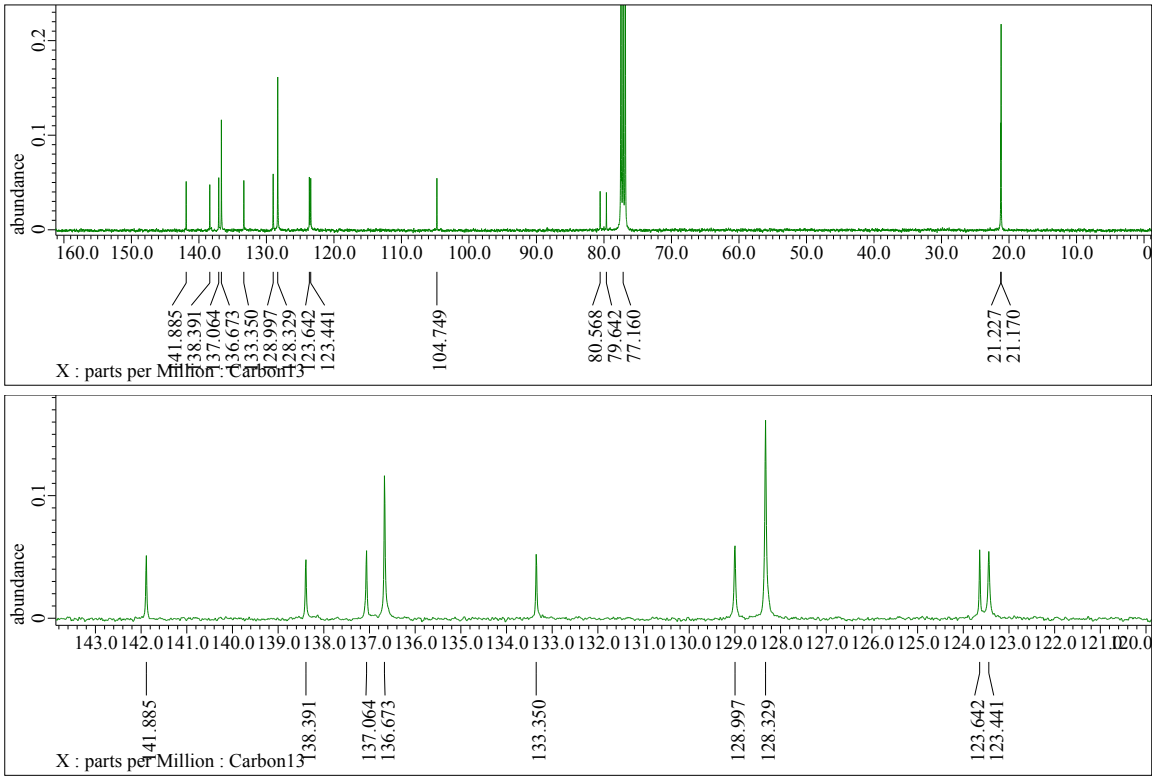
^{13}C NMR spectrum of **12a** in $CDCl_3$



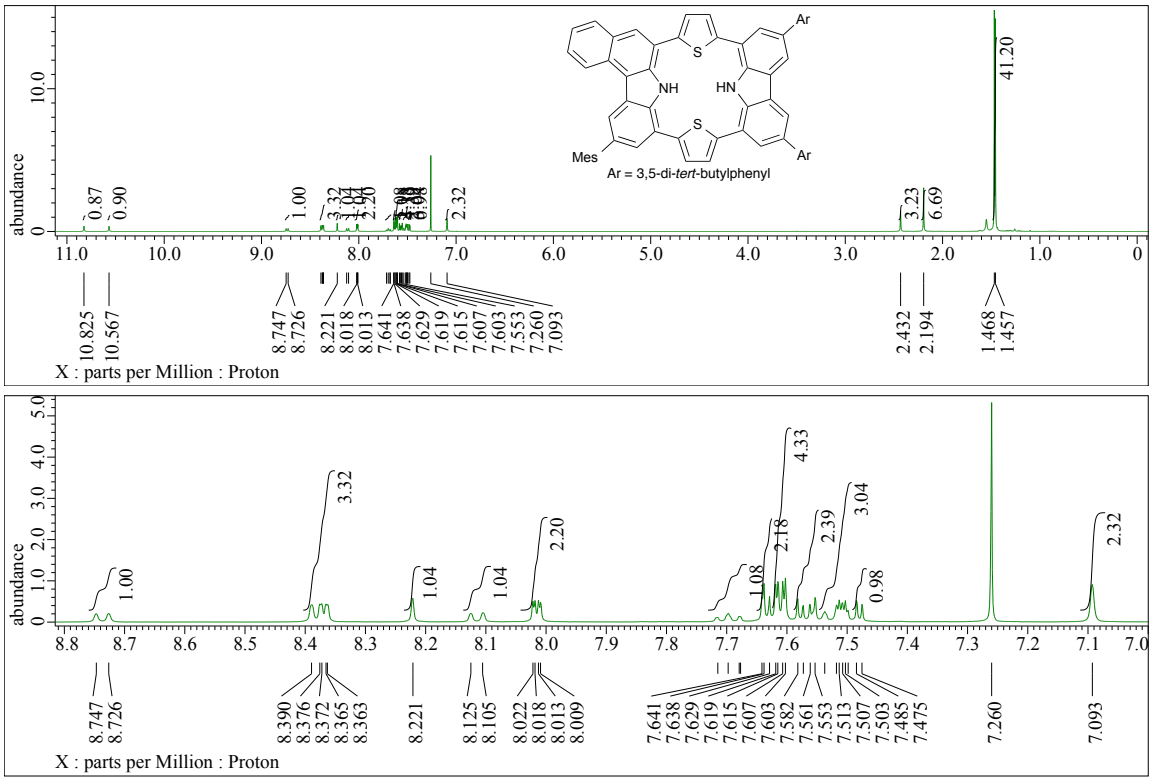
^{1}H NMR spectrum of **12b** in $CDCl_3$



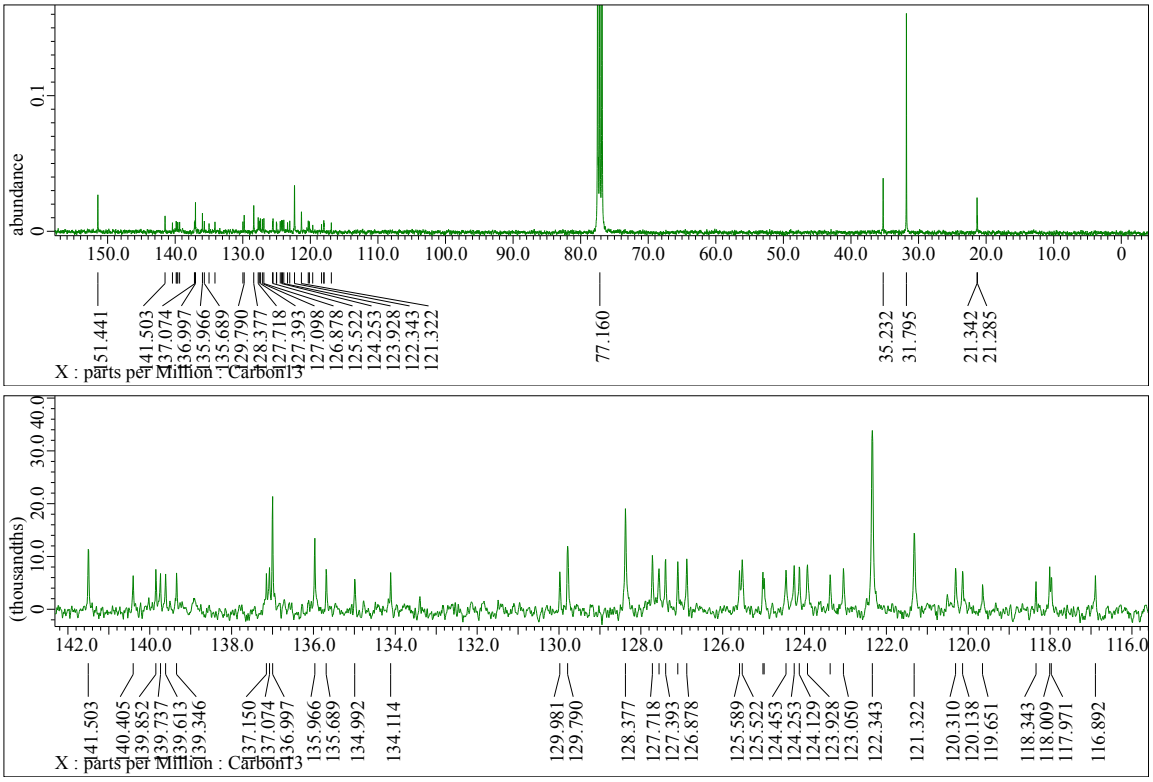
^{1}H NMR spectrum of **13b** in $CDCl_3$



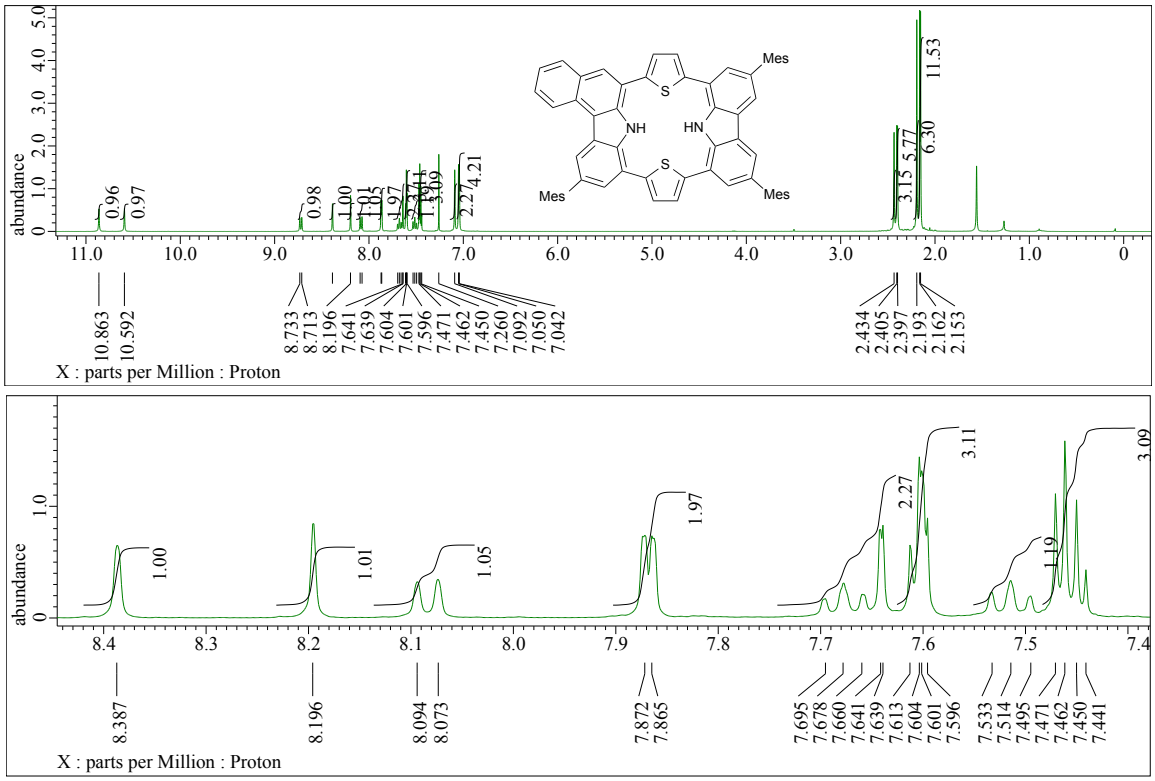
^{13}C NMR spectrum of **13b** in $CDCl_3$



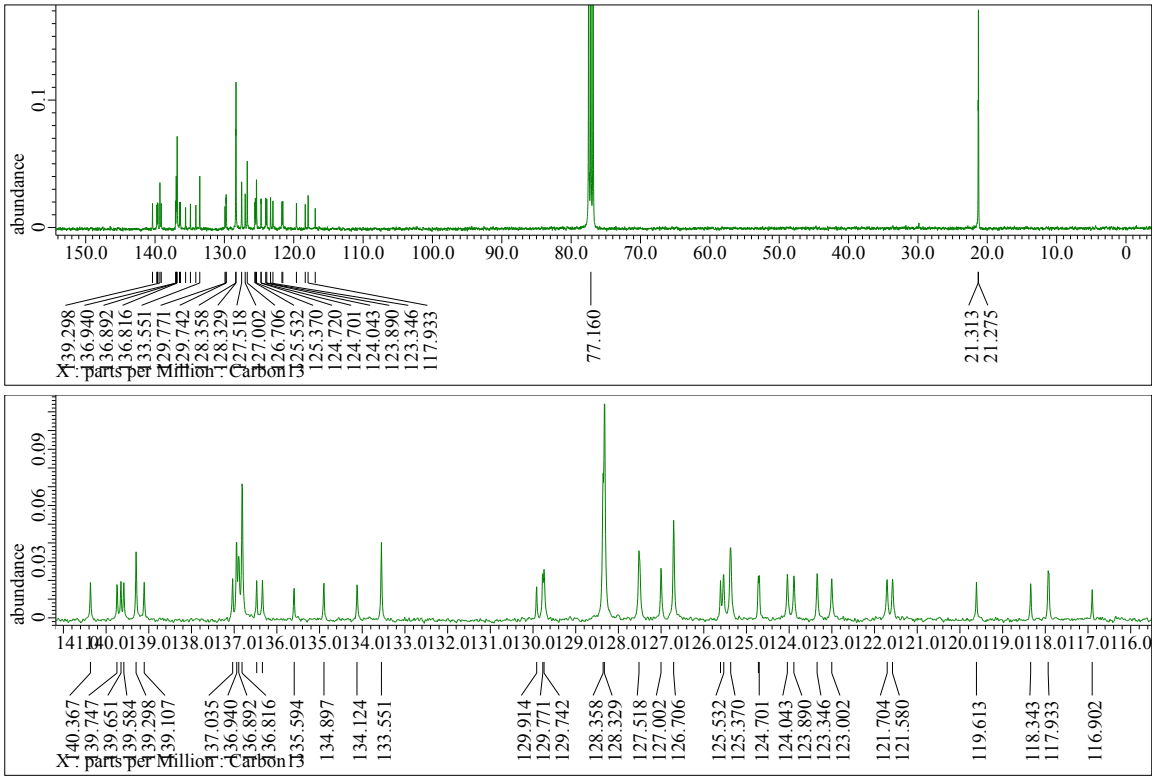
^{1}H NMR spectrum of **3a'** in $CDCl_3$



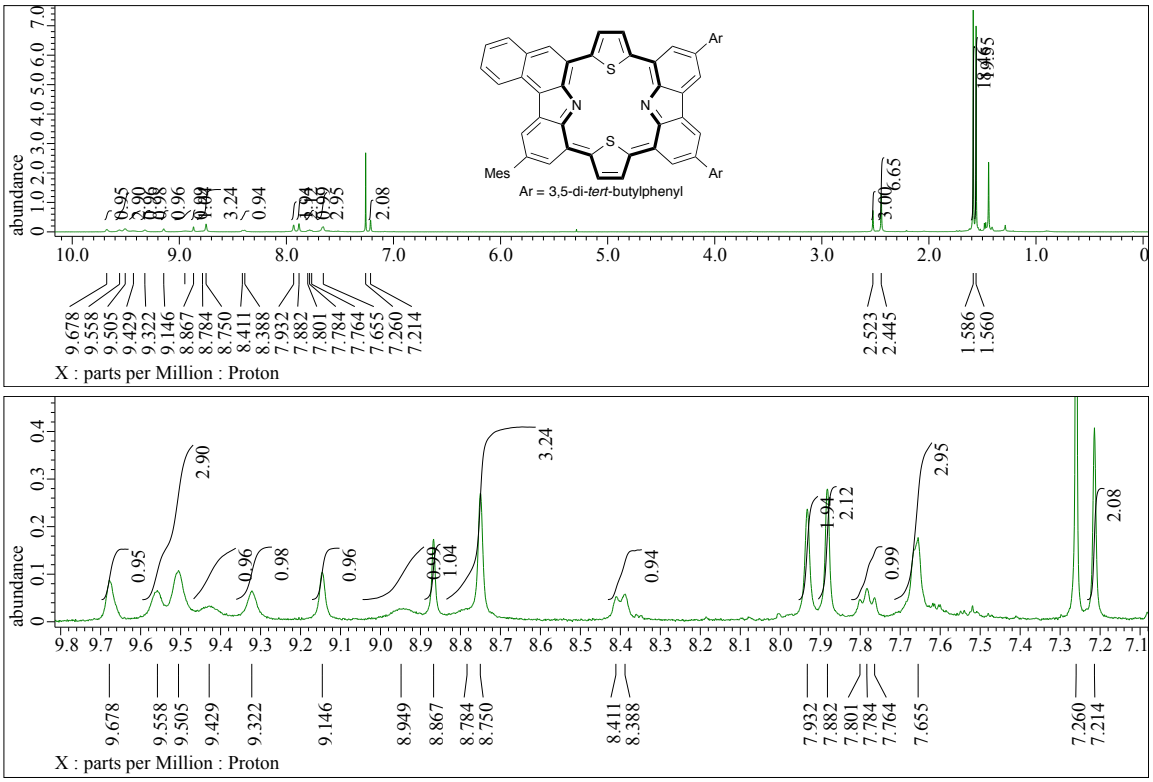
^{13}C NMR spectrum of **3a'** in $CDCl_3$



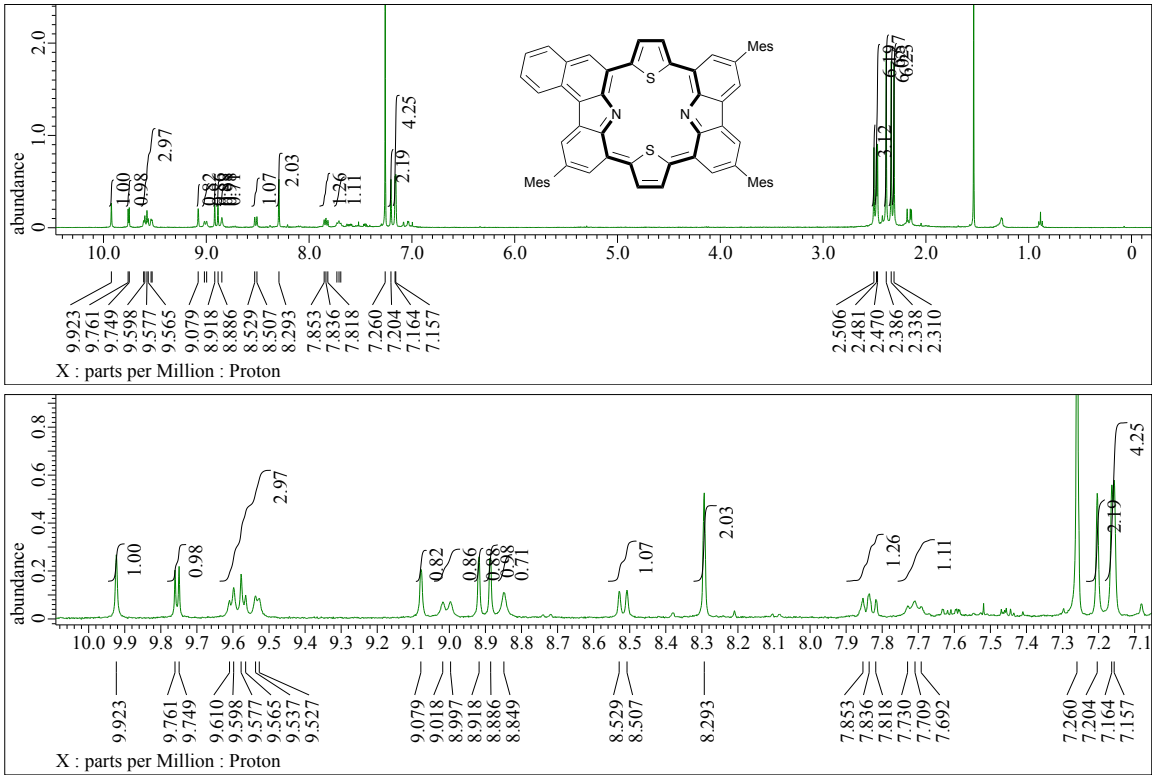
^{1}H NMR spectrum of **3b'** in $CDCl_3$



^{13}C NMR spectrum of **3b'** in $CDCl_3$



^{1}H NMR spectrum of **3a** in $CDCl_3$



^{1}H NMR spectrum of **3b** in $CDCl_3$