Electronic Supplementary Information

Synthesis and electronic properties of carbazole-based core-modified diporphyrins

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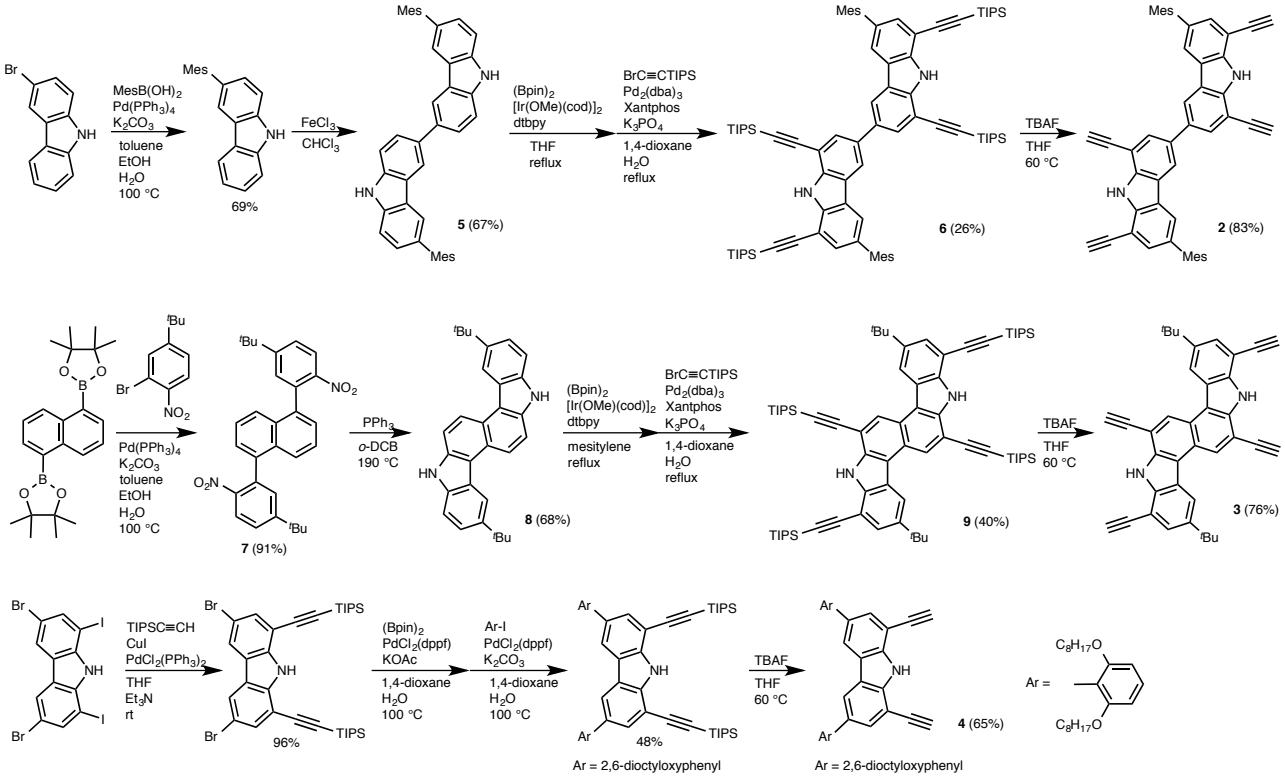
[A] Instrumentation and Materials

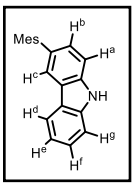
^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECS-400 or JEOL ECZ-600 spectrometer. Spectra recorded in $CDCl_3$ were referenced to residual $CHCl_3$ at 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR. Spectra recorded in DMSO-d_6 were referenced to residual $(CH_3)_2SO$ at 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR. Spectra recorded in pyridine-d_5 were referenced to residual pyridine at 8.71 ppm for ^{1}H NMR and 149.2 ppm for ^{13}C NMR. Mass spectra were recorded on a Bruker micrOTOF. UV/vis/NIR absorption spectra were recorded on a SHIMADZU UV-2600 or UV-3600 spectrometer. Materials obtained from commercial suppliers were used without further purification. 1,5-Bis[(pinacolato)boryl]naphthalene,[S1] 1,3-dioctyloxy-2-iodobenzene[S2] and 3,6-dibromo-1,8-diiodocarbazole[S3] were prepared according to the literature procedure.

[B] Experimental Procedures and Compound Data



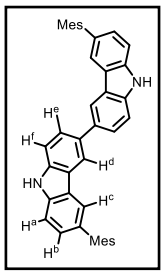
Scheme S1 Synthesis of **2**–**4**.

Synthesis of 3-mesitylcarbazole. A solution of 3-bromocarbazole (148 mg, 602 μmol), 2,4,6-trimethylphenylboronic acid (118 mg, 722 μmol), $Pd(PPh_3)_4$ (74.4 mg, 64.5 μmol), and K_2CO_3 (259 mg, 1.88 mmol) in toluene/EtOH/H_2O (2/1/1 mL) was heated at 100 °C for 15 h under Ar. After cooling to room temperature, organic products were extracted with $CHCl_3$, and the organic layer was passed through a silica gel column with $CHCl_3$ and evaporated. The residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give 3-mesitylcarbazole as a white solid (118 mg, 414 μmol, 69%).



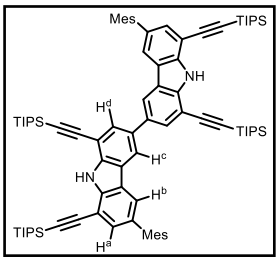
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.08 (s, 1H, NH), 8.03 (d, J = 8.0 Hz, 1H, H^d), 7.83 (d, J = 0.8 Hz, 1H, H^c), 7.49–7.42 (m, 3H, H^a, H^f, H^g), 7.23 (dt, J = 1.4, 8.0 Hz, 1H, H^e), 7.18 (dd, J = 1.8, 8.0 Hz, 1H, H^b), 6.98 (s, 2H, Mes), 2.36 (s, 3H, Me), and 2.04 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 139.9, 139.8, 138.4, 136.8, 136.5, 132.4, 128.2, 127.4, 126.0, 123.6, 123.5, 120.9, 120.4, 119.6, 110.8, 110.6, 21.2, and 21.1 ppm; MS (APCI) calcd for $C_{21}H_{18}N$ 284.1445, found 284.1445 [M−H]$^-$.

Synthesis of 5. To a flask containing 3-mesitylcarbazole (345 mg, 1.21 mmol) and $FeCl_3$ (784 mg, 4.84 mmol) was added dry $CHCl_3$ (15 mL) under Ar, and the mixture was stirred at room temperature for 1 h. MeOH (60 mL), Zn (400 mg, 6.12 mmol), and AcOH (3.0 mL) were added. The mixture was diluted with $CHCl_3$, washed with brine and water, dried with Na_2SO_4, passed through a silica gel column with $CHCl_3$, and evaporated. The residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give **5** as a gray solid (231 mg, 406 μmol, 67%).



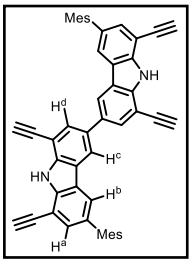
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.39 (s, 2H, H^d), 7.97 (s, 2H, H^c), 7.92 (s, 2H, NH), 7.80 (dd, J = 1.2, 8.0 Hz, 2H, H^e), 7.47 (d, J = 6.8 Hz, 2H, H^a), 7.46 (d, J = 8.0 Hz, 2H, H^f), 7.26 (dd, J = 1.6, 8.4 Hz, 2H, H^b), 7.07 (s, 4H, Mes), 2.45 (s, 6H, Me), and 2.14 ppm (s, 12H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 139.8, 139.0, 138.9, 136.7, 136.4, 134.1, 132.4, 128.2, 127.5, 125.9, 124.0, 123.8, 121.0, 118.9, 111.0, 110.7, 21.2, and 21.1 ppm; MS (APCI) calcd for $C_{42}H_{35}N_2$ 567.2806, found 567.2800 [M−H]$^-$.

Synthesis of 6. A solution of **5** (448 mg, 787 μmol), $(Bpin)_2$ (600 mg, 2.36 mmol), $[Ir(OMe)(cod)]_2$ (52.2 mg, 78.7 μmol), and dtbpy (42.3 mg, 157 μmol) in dry THF (0.50 mL) was heated at reflux for 17 h under Ar. The mixture was passed through a silica gel column with $CHCl_3$ and evaporated. A solution of the residue, bromo(triisopropylsilyl)acetylene (1.05 g, 4.03 mmol), $Pd_2(dba)_3$ (366 mg, 400 μmol), Xantphos (459 mg, 793 μmol), and K_3PO_4 (3.37 g, 15.8 mmol) in 1,4-dioxane/water (9.0 mL/1.0 mL) was heated at reflux for 14 h under Ar. After cooling to room temperature, the mixture was passed through a silica gel column with $CHCl_3$, and evaporated. Purification of the residue by silica gel column chromatography with $CHCl_3$/hexane as an eluent gave **6** as a pale yellow solid (265 mg, 205 μmol, 26%).



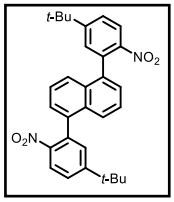
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.52 (s, 2H, NH), 8.27 (d, J = 1.2 Hz, 2H, H^c), 7.91 (d, J = 2.0 Hz, 2H, H^d), 7.89 (d, J = 1.2 Hz, 2H, H^b), 7.41 (d, J = 1.2 Hz, 2H, H^a), 6.98 (s, 4H, Mes), 2.37 (s, 6H, Me), 2.09 (s, 12H, Me), and 1.27–1.24 ppm (m, 84H, TIPS); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 140.0, 139.6, 138.9, 136.8, 136.7, 133.9, 133.3, 131.9, 129.7, 129.6, 128.3, 124.3, 124.2, 122.2, 122.1, 120.1, 107.0, 106.8, 103.2, 103.1, 96.2, 96.1, 21.1, 21.0, 19.01, 18.98, and 11.8 ppm; MS (APCI) calcd for $C_{86}H_{115}N_2Si_4$ 1288.8170, found 1288.8160 [M−H]$^-$.

Synthesis of 2. To a solution of **6** (95.4 mg, 74.0 μmol) in dry THF (1 mL) was added TBAF (1 M in THF, 0.3 mL, 0.3 mmol), and the mixture was heated at 60 °C for 1 h under Ar. After the mixture was evaporated, the residue was purified by silica gel column chromatography with $CHCl_3$/hexane as an eluent to give **2** as a white solid (40.6 mg, 61.1 μmol, 83%).



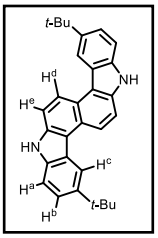
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.68 (s, 2H, NH), 8.28 (d, J = 2.0 Hz, 2H, H^c), 7.92 (s, 2H, H^d), 7.91 (s, 2H, H^b), 7.41 (d, J = 1.2 Hz, 2H, H^a), 6.97 (s, 4H, Mes), 3.54 (s, 2H, C≡CH), 3.53 (s, 2H, C≡CH), 2.36 (s, 6H, Me), and 2.05 ppm (s, 12H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 140.2, 140.1, 138.5, 136.8, 136.6, 133.6, 133.2, 131.3, 129.5, 128.2, 124.1, 123.8, 122.6, 120.4, 105.3, 105.0, 82.4, 79.92, 79.86, 21.2, and 21.1 ppm; MS (APCI) calcd for $C_{50}H_{35}N_2$ 663.2806, found 663.2797 [M−H]$^-$.

Synthesis of 7. A solution of 2-bromo-4-*tert*-butyl-1-nitrobenzene (237 mg, 919 μmol), 1,5-bis[(pinacolato)boryl]naphthalene (112 mg, 295 μmol), $Pd(PPh_3)_4$ (20.3 mg, 17.6 μmol), and K_2CO_3 (121 mg, 877 μmol) in toluene/EtOH/H_2O (2.0/1.0/1.0 mL) was heated at 100 °C for 40 h



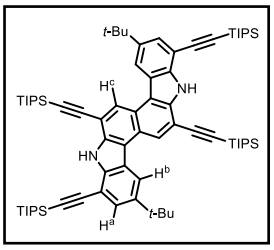
under N_2. After cooling to room temperature, organic products were extracted with EtOAc, and the organic layer was passed through a silica gel column with EtOAc and evaporated. The residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give **7** as a white solid (130 mg, 269 μmol, 91%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.07 (d, J = 9.2 Hz, 2H), 7.62 (dd, J = 2.6, 8.6 Hz, 2H), 7.55 (d, J = 1.8 Hz, 2H), 7.51–7.41 (m, 4H), 7.35 (dd, J = 1.2, 6.8 Hz, 2H), and 1.41 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.2, 147.3, 136.9, 135.3, 131.7, 130.6, 126.3, 125.94, 125.88, 125.5, 124.4, 35.6, and 31.3 ppm; HRMS (APCI) calcd for $C_{30}H_{30}N_2O_4$ 482.2211, found 482.2200 [M]$^-$.



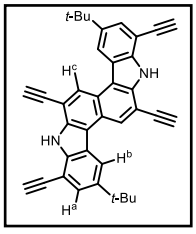
Synthesis of 8. A solution of **7** (83.7 mg, 300 μmol) and PPh_3 (401 mg, 1.53 mmol) in 1,2-dichlorobenzene (2.0 mL) was heated at 190 °C for 10 h under N_2. After cooling to room temperature, excess 1,2-dichlorobenzene was removed by distillation. The residue was passed through a silica gel column with $CHCl_3$ and evaporated. The residue was precipitated with MeOH to give **8** as a beige solid (86.1 mg, 205 μmol, 68%)

^{1}H NMR ($(CD_3)_2SO$, 400 MHz) δ = 11.56 (s, 2H, NH), 8.85 (d, J = 8.4 Hz, 2H, H^d), 8.57 (s, 2H, H^c), 7.98 (d, J = 9.2 Hz, 2H, H^e), 7.58 (d, J = 8.8 Hz, 2H, H^a), 7.54 (dd, J = 1.2, 8.4 Hz, 2H, H^b), and 1.51 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($(CD_3)_2SO$, 100 MHz) δ = 141.4, 137.1, 136.0, 124.1, 122.7, 122.1, 121.5, 117.4, 115.9, 113.5, 111.0, 34.6, and 32.1 ppm; MS (APCI) calcd for $C_{30}H_{29}N_2$ 417.2336, found 417.2335 [M−H]$^-$.



Synthesis of 9. A solution of **8** (83.7 mg, 200 μmol), $(Bpin)_2$ (501 mg, 197 mmol), $[Ir(OMe)(cod)]_2$ (13.6 mg, 20.5 μmol), and dtbpy (10.9 mg, 40.7 μmol) in mesitylene (0.80 mL) was heated at reflux for 3 d 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 (368 mg, 1.41 mmol), $Pd_2(dba)_3$ (17.7 mg, 19.3 μmol), Xantphos (25.0 mg, 43.2 μmol), and K_3PO_4 (356 mg, 1.68 mmol) in 1,4-dioxane/water (2.0 mL/0.20 mL) was heated at reflux for 40 h under N_2. After cooling to room temperature, the mixture was passed through a silica gel column with $CHCl_3$ and evaporated. Purification of the residue by silica gel column chromatography with $CHCl_3$/hexane as an eluent gave **9** as a yellow solid (90.4 mg, 79.3 μmol, 40%).

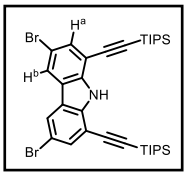
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 9.03 (s, 2H, H^c), 8.75 (s, 2H, NH), 8.61 (s, 2H, H^b), 7.70 (s, 2H, H^a), 1.53 (s, 18H, *t*-Bu), 1.27 (s, 42H, TIPS), and 1.24 ppm (s, 42H, TIPS); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 143.4, 137.8, 135.6, 127.2, 127.0, 125.0, 123.6, 119.4, 116.9, 108.9, 106.2, 103.6, 103.4, 97.1, 95.3, 35.0, 32.1, 19.0, and 11.6 ppm; MS (APCI) calcd for $C_{74}H_{109}N_2Si_4$ 1138.7699, found 1138.7676 [M−H]$^-$.



Synthesis of 3. To a solution of **9** (20.2 mg, 17.7 μmol) in dry THF (1 mL) was added TBAF (1 M in THF, 0.1 mL, 0.1 mmol), and the mixture was heated at 60 °C for 1 h under Ar. After the mixture was evaporated, the residue was purified by silica gel column chromatography with $CHCl_3$/hexane as an eluent to give **3** as a yellow solid (6.90 mg, 13.4 μmol, 76%).

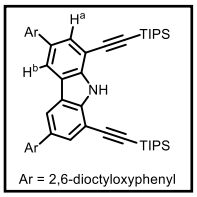
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.95 (s, 2H, H^c), 8.88 (s, 2H, NH), 8.62 (d, J = 1.2 Hz, 2H, H^b), 7.76 (d, J = 1.2 Hz, 2H, H^a), 3.68 (s, 2H, C≡CH), 3.52 (s, 2H, C≡CH), and 1.56 (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 143.8, 138.3, 136.6, 127.1, 126.2, 125.4, 123.8, 119.9, 117.2, 107.9, 104.9, 83.3, 81.8, 80.6, 80.5, 35.1, and 32.2 ppm; HRMS (APCI) calcd for $C_{38}H_{29}N_2$ 513.2336, found 513.2330 [M−H]$^-$.

Synthesis of 1,8-bis(triisopropylsilylethynyl)-3,6-dibromocarbazole. A solution of 3,6-dibromo-1,8-diiodocarbazole (2.17 g, 3.76 mmol), CuI (51.3 mg, 270 μmol), and $PdCl_2(PPh_3)_2$ (46.5 mg, 66.2 μmol) in THF/Et_3N (10/5 mL) was degassed. Triisopropylsilylacetylene (2.5 mL, 11 mmol) was added, and the mixture was stirred at room temperature for 11 h under N_2. After the solvents were evaporated, the residue was separated over a silica gel column with hexane as an eluent to give **12** as a pale yellow solid (2.47 g, 3.60 mmol, 96%).



^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.42 (s, 1H, NH), 8.06 (d, J = 1.2 Hz, 2H, H^b), 7.68 (d, J = 1.6 Hz, 2H, H^a), 1.18 (s, 36H, TIPS), and 1.17 ppm (s, 6H, TIPS); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 139.0, 133.0, 124.0, 123.9, 112.4, 108.4, 100.8, 98.0, 18.9 and 11.4 ppm; MS (APCI) calcd for $C_{34}H_{47}NBr_2Si_2$ 685.1591, found 685.1576 $[M]^+$.

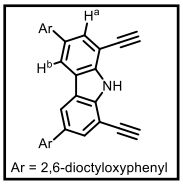
Synthesis of 1,8-bis(triisopropylsilylethynyl)-3,6-bis(2,6-dioctyloxyphenyl) carbazole.



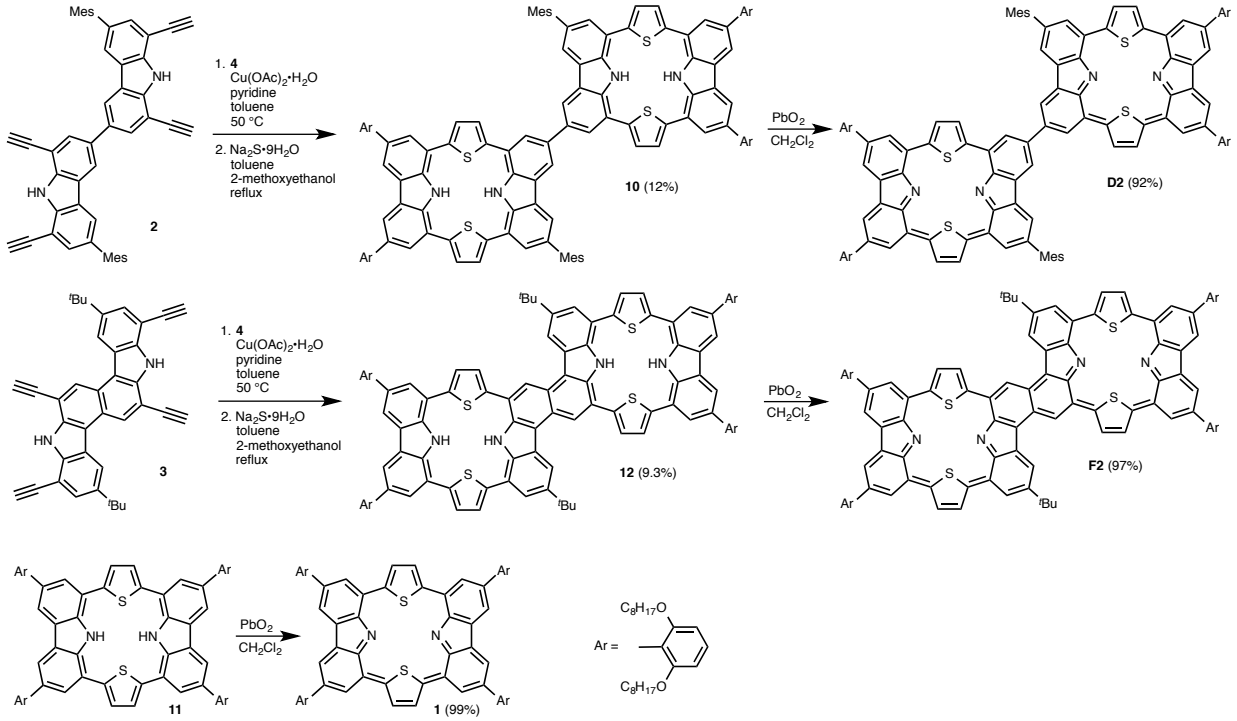
A flask containing 1,8-bis(triisopropylsilylethynyl)-3,6-dibromocarbazole (235 mg, 343 μmol), $(Bpin)_2$ (444 mg, 1.75 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (37.3 mg, 45.7 μmol), and KOAc (396 mg, 4.04 mmol) in 1,4-dioxane/H_2O (3.6/0.4 mL) was heated at reflux for 16 h under N_2. After cooling to room temperature, the solvents were evaporated, and the residue was passed through a silica gel column with $CHCl_3$ to give a crude borylated product. A flask containing the residue, 1,3-dioctyloxy-2-iodobenzene (786 mg, 1.71 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (31.8 mg, 38.9 μmol), and K_2CO_3 (518 mg, 3.75 mmol) in 1,4-dioxane/H_2O (3.6/0.4 mL) was heated at reflux for 39 h under N_2. After cooling to room temperature, the solvents were evaporated, and the residue was passed through a silica gel column with $CHCl_3$. The residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give 1,8-bis(triisopropylsilylethynyl)-3,6-bis(2,6-dioctyloxyphenyl) carbazole as a pale yellow oil (197 mg, 165 μmol, 48%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.49 (s, 1H, NH), 8.05 (d, J = 1.2 Hz, 2H, H^b), 7.66 (d, J = 1.2 Hz, 2H, H^a), 7.27 (t, J = 8.6 Hz, 2H, Ar), 6.70 (d, J = 8.4 Hz, 4H, Ar), 3.93 (t, J = 6.4 Hz, 8H, OCH_2), 1.63 (m, 8H, CH_2), 1.32–1.09 (m, 40H, CH_2), 1.24 (s, 42H, TIPS), and 0.84 ppm (t, J = 6.4 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.9, 139.4, 133.5, 128.4, 125.9, 124.1, 123.6, 121.5, 106.7, 105.3, 104.1, 94.4, 69.4, 31.9, 29.4, 29.3, 29.2, 26.1, 22.7, 19.0, 14.1, and 11.8 ppm; MS (APCI) calcd for $C_{78}H_{122}NO_4Si_2$ 1192.8907, found 1192.8946 $[M+H]^+$.

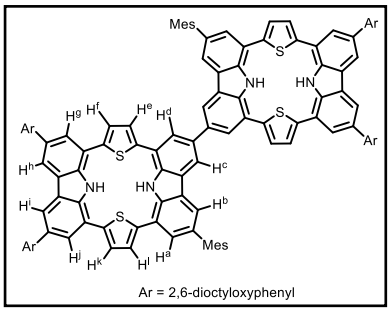
Synthesis of 4. To a solution of **13** (1.19 g, 995 μmol) in dry THF (5 mL) was added TBAF (1 M in THF, 2.0 mL, 2.0 mmol), and the mixture was stirred at 60 °C for 1 h. The solvent was evaporated, and the residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give **4** (569 mg, 647 μmol, 65%).



^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.59 (s, 1H, NH), 8.04 (s, 2H, H^b), 7.62 (s, 2H, H^a), 7.23 (t, J = 8.2 Hz, 2H, Ar), 6.65 (d, J = 8.8 Hz, 4H, Ar), 3.90 (t, J = 6.0 Hz, 8H, OCH_2), 3.43 (s, 2H, C≡CH), 1.59 (m, 8H, CH_2), 1.27 (m, 8H, CH_2), 1.21–1.06 (m, 32H, CH_2), and 0.81 ppm (t, J = 7.0 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.9, 140.0, 133.2, 128.5, 126.1, 124.6, 123.5, 121.2, 106.5, 103.8, 81.0, 80.7, 69.3, 31.9, 29.4, 29.34, 29.29, 26.2, 22.7, and 14.1 ppm; MS (APCI) calcd for $C_{60}H_{81}NO_4$ 879.6160, found 879.6168 $[M]^+$.



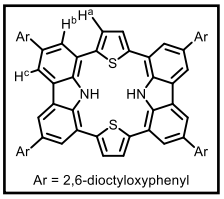
Scheme S2 Synthesis of **D2**, **F2**, and **1**.



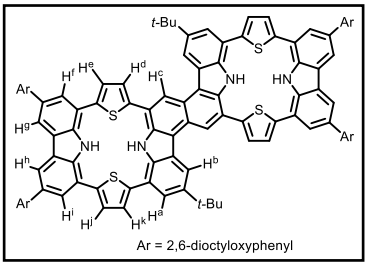
Synthesis of 10. To a suspension of $Cu(OAc)_2 \cdot H_2O$ (506 mg, 2.53 mmol) in pyridine (20 mL) was added dropwise a solution of **2** (40.6 mg, 61.1 μmol) and **4** (164 mg, 186 μmol) in toluene (67 mL) over 1 h, and the resulting mixture was heated at 50 °C for 3 d under air. After the solvents were evaporated, the residue was passed through a silica gel column with $CHCl_3$ and evaporated. A solution of the residue and $Na_2S \cdot 9H_2O$ (1.20 g, 5.00 mmol) in toluene/2-methoxyethanol (5.0/5.0 mL) was heated at reflux for 12 h under Ar. After cooling to room temperature, the mixture was diluted with $CHCl_3$, washed with water, passed through a silica gel column with $CHCl_3$, and evaporated. The residue was separated over GPC with $CHCl_3$ as an eluent to give **10** as a yellow solid (18.1 mg, 7.09 μmol, 12%) along with **11** as a yellow solid (80.2 mg, 44.0 μmol, 48%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 10.76 (s, 2H, NH), 10.57 (s, 2H, NH), 8.46 (s, 2H, H^d), 8.21 (d, J = 1.2 Hz, 2H, H^c), 8.13 (s, 4H, H^h and H^j), 8.00 (s, 2H, H^b), 7.86 (d, J = 1.2 Hz, 2H, H^g), 7.84 (d, J = 1.2 Hz, 2H, H^i), 7.62 (d, J = 0.8 Hz, 2H, H^a), 7.59 (d, J = 3.6 Hz, 2H, H^e), 7.47 (d, J = 3.6 Hz, 2H, H^f), 7.43 (d, J = 3.6 Hz, 2H, H^k), 7.42 (d, J = 3.6 Hz, 2H, H^l), 7.28 (t, J = 8.4 Hz, 4H, Ar), 7.04 (s, 4H, Mes), 6.72 (d, J = 8.8 Hz, 8H, Ar), 3.96 (t, J = 6.0 Hz, 16H, OCH_2), 2.40 (s, 6H, Me), 2.18 (s, 12H, Me), 1.67–1.60 (m, 16H, CH_2), 1.32–1.27 (m, 16H, CH_2), 1.16–1.08 (m, 64H, CH_2), 0.74 (t, J = 6.8 Hz, 12H, CH_2), and 0.73 ppm (t, J = 7.0 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.7, 140.8, 140.6, 139.4, 139.0, 136.84, 136.79, 136.7, 136.6, 136.4, 136.3, 135.0, 133.5, 128.4, 128.3, 127.4, 127.3, 126.9, 126.6, 126.3, 126.2, 125.3, 125.2, 124.9, 124.53, 124.49, 123.9, 121.5, 121.0, 119.7, 118.5, 118.2, 116.60, 116.57, 105.9, 69.0, 31.9, 31.8, 29.37, 29.35, 29.32, 29.29, 26.3, 22.73, 22.69, 21.3, 14.21, and 14.18 ppm; MS (ESI) calcd for $C_{170}H_{197}N_4O_8S_4$ 2592.3788, found 2592.3727 $[M+K]^+$.

Compound data for 11. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 10.65 (s, 2H, NH), 8.13 (d, J = 1.2 Hz, 4H, H^c), 7.85 (d, J = 1.6 Hz, 4H, H^b), 7.42 (s, 4H, H^a), 7.30 (t, J = 8.2 Hz, 4H, Ar), 6.74 (t, J = 8.8 Hz, 8H, Ar), 3.98 (t, J = 6.6 Hz, 16H, OCH_2), 1.66 (m, 16H, CH_2), 1.33 (m, 16H, CH_2), 1.24–1.06 (m, 64H, CH_2), and 0.76 ppm (t, J = 7.0 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.1, 140.1, 136.6, 128.3, 127.2, 126.4, 126.1, 124.7, 123.7, 122.1, 117.0, 106.7, 69.5, 31.9, 29.5, 29.4, 29.3, 26.2, 22.7, and 14.0 ppm; MS (APCI) calcd for $C_{120}H_{161}N_2O_8S_2$ 1823.1733, found 1823.1729 $[M-H]^-$.

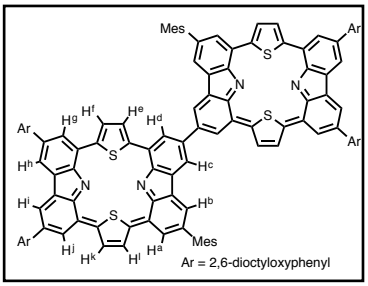


Synthesis of 12. To a suspension of $Cu(OAc)_2 \cdot H_2O$ (296 mg, 1.48 mmol) in pyridine (12 mL) was added dropwise a solution of **3** (18.9 mg, 36.7 μmol) and **4** (115 mg, 131 μmol) in toluene (40 mL) over 1 h, and the resulting mixture was heated at 50 °C for 3 d under air. After the solvents were evaporated, the residue was passed through a silica gel column with $CHCl_3$ and evaporated. A solution of the residue and $Na_2S \cdot 9H_2O$ (827 mg, 3.45 mmol) in toluene/2-methoxyethanol (5.0/5.0 mL) was heated at reflux for 12 h under Ar. After cooling to room temperature, the mixture was diluted with $CHCl_3$, washed with water, passed through a silica gel column with $CHCl_3$, and evaporated. The residue was separated over GPC with $CHCl_3$ as an eluent to give **12** as a red solid (8.20 mg, 3.41 μmol, 9.3%) along with **11** as a yellow solid (42.6 mg, 23.3 μmol, 42%).



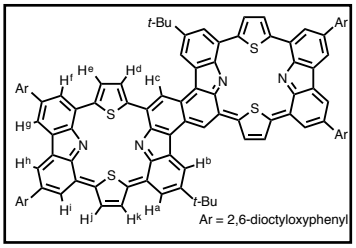
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 10.82 (s, 2H, NH), 10.56 (s, 2H, NH), 9.28 (s, 2H, H^c), 8.83 (s, 2H, H^b), 8.15 (s, 2H, H^g), 8.13 (s, 2H, H^h), 7.94 (s, 2H, H^a), 7.91 (d, J = 1.2 Hz, 2H, H^f), 7.85 (s, 2H, H^i), 7.80 (d, J = 3.6 Hz, 2H, H^d), 7.60 (d, J = 2.8 Hz, 2H, H^e), 7.51 (s, 2H, H^k), 7.45 (s, 2H, H^j), 7.29 (t, J = 8.4 Hz, 2H, Ar), 7.28 (t, J = 8.2 Hz, 2H, Ar), 6.75 (d, J = 8.0 Hz, 4H, Ar), 6.73 (d, J = 8.4 Hz, 4H, Ar), 3.98 (t, J = 5.6 Hz, 8H, OCH_2), 3.97 (t, J = 5.4 Hz, 8H, OCH_2), 1.68 (s, 18H, *t*-Bu), 1.66–1.61 (m, 16H, CH_2), 1.35–1.28 (m, 16H, CH_2), 1.27–1.09 (m, 64H, CH_2), 0.76 (t, J = 7.8 Hz, 12H, CH_3), and 0.73 ppm (t, J = 7.8 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.0, 144.2, 141.6, 140.7, 139.7, 139.6, 136.6, 135.1, 134.5, 128.4, 127.5, 127.1, 126.7, 126.6, 126.52, 126.49, 126.3, 126.0, 125.2, 124.7, 124.6, 124.2, 123.9, 121.7, 121.3, 120.2, 120.0, 118.80, 118.77, 118.2, 116.8, 116.7, 106.5, 69.3, 35.3, 32.4, 31.90, 31.88, 29.5, 29.42, 29.39, 29.3, 26.3, 22.7, and 14.1 ppm; MS (APCI) calcd for $C_{158}H_{191}N_4O_8S_4$ 2401.3583, found 2401.3513 $[M-H]^-$.

Synthesis of D2. To a solution of **10** (17.0 mg, 6.66 μmol) in CH_2Cl_2 (10 mL) was added PbO_2 (636 mg, 2.13 mmol), and the resulting suspension was stirred for 13 h. The reaction mixture was passed through a Cerite with CH_2Cl_2 and evaporated to give **D2** as a deep green solid (15.6 mg, 6.12 μmol, 92%).



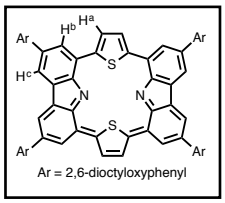
^{1}H NMR (pyridine-d_5, 600 MHz) δ = 10.90 (s, 2H, H^d), 10.76 (d, J = 3.6 Hz, 2H, H^e), 10.32 (d, J = 3.6 Hz, 2H, H^f), 10.28 (d, J = 4.8 Hz, 2H, H^l), 10.24 (d, J = 3.6 Hz, 2H, H^k), 10.18 (s, 2H, H^c), 9.95 (s, 2H, H^g), 9.94 (s, 2H, H^j), 9.67 (s, 2H, H^a), 9.19 (s, 4H, H^h, H^i), 8.73 (s, 2H, H^b), 7.650 (t, J = 8.1 Hz, 2H, Ar), 7.647 (t, J = 8.7 Hz, 2H, Ar), 7.25 (s, 4H, Mes), 7.09 (d, J = 8.4 Hz, 8H, Ar), 4.16 (t, J = 6.0 Hz, 16H, OCH_2), 2.50 (s, 6H, Me), 2.46 (s, 12H, Me), 1.65 (m, 16H, CH_2), 1.38 (m, 16H, CH_2), 1.00 (m, 16H, CH_2), 0.87 (m, 16H, CH_2), 0.79 (m, 32H, CH_2), and 0.46–0.44 ppm (m, 24H, CH_3); ^{13}C NMR (pyridine-d_5, 150 MHz) δ = 157.7, 157.4, 151.9, 151.3, 151.2, 150.8, 146.8, 146.6, 146.3, 146.0, 139.2, 138.3, 138.1, 136.7, 136.1, 133.1, 132.93, 132.88, 132.1, 131.4, 131.3, 129.5, 128.64, 128.56, 128.5, 128.2, 128.0, 127.6, 126.3, 125.4, 125.21, 125.17, 125.1, 124.8, 124.2, 123.7, 120.1, 105.7,

68.5, 31.11, 31.07, 29.0, 28.92, 28.86, 28.8, 28.7, 25.94, 25.87, 21.9, 20.7, 20.6, and 13.3 ppm; MS (ESI) calcd for $C_{170}H_{194}N_4O_8S_4$ 2549.3838, found 2549.3813 $[M]^+$; UV/Vis/NIR (CH_2Cl_2) λ_{max} (ε) = 389 (59400), 990 (39800), 1086 (54200), and 1130 nm (60900 $M^{-1}cm^{-1}$).



Synthesis of F2. To a solution of **12** (8.20 mg, 3.41 μmol) in CH_2Cl_2 (5 mL) was added PbO_2 (650 mg, 2.72 mmol), and the resulting suspension was stirred for 24 h. The reaction mixture was passed through a Cerite with CH_2Cl_2 and evaporated to give **F2** as a deep green solid (7.95 mg, 3.31 μmol, 69%).

The ^{1}H NMR (pyridine-d_5, 600 MHz) δ = 11.11 (d, J = 4.8 Hz, 2H, H^d), 10.40 (s, 2H, H^c), 10.19 (d, J = 4.8 Hz, 2H, H^e), 9.96 (s, 2H, H^j or H^k), 9.92 (s, 2H, H^j or H^k), 9.77 (s, 2H, H^a or H^f or H^i), 9.71 (s, 2H, H^a or H^f or H^i), 9.65 (s, 2H, H^a or H^f or H^i), 9.18 (s, 2H, H^b), 9.06 (s, 2H, H^g or H^h), 9.05 (s, 2H, H^g or H^h), 7.62 (t, J = 9.0 Hz, 4H, Ar), 7.08 (d, J = 7.8 Hz, 4H, Ar), 7.07 (d, J = 7.8 Hz, 4H, Ar), 4.17 (t, J = 6.3 Hz, 8H, OCH_2), 4.13 (t, J = 5.7 Hz, 8H, OCH_2), 2.01 (s, 18H, *t*-Bu), 1.71 (m, 16H, CH_2), 1.30 (m, 16H, CH_2), 1.01–0.83 (m, 64H, CH_2), and 0.51 ppn (m, 24H, CH_3); MS (ESI) calcd for $C_{158}H_{188}N_4O_8S_4$ 2398.3337, found 2398.3349 $[M]^+$; UV/Vis/NIR (CH_2Cl_2) λ_{max} (ε) = 948 (28800), 1085 (29400), and 1269 nm (32600 $M^{-1}cm^{-1}$).



Synthesis of 1. To a solution of **11** (122 mg, 66.8μmol) in CH_2Cl_2 (20 mL) was added PbO_2 (391 mg, 1.64 mmol), and the resulting suspension was stirred for 4 d. Further PbO_2 was added after 1 d (423 mg, 1.77 mmol), 2 d (351 mg, 1.74 mmol), and 3 d (407 mg, 1.70 mmol). The reaction mixture was passed through a Cerite with CH_2Cl_2 and evaporated to give **1** as a deep green solid (120 mg, 65.8 μmol, 99%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 9.91 (s, 4H, H^a), 9.62 (s, 4H, H^b), 8.85 (d, J = 1.2 Hz, 4H, H^c), 7.47 (t, J = 8.2 Hz, 4H), 6.91 (d, J = 8.4 Hz, 8H, Ar), 4.12 (t, J = 6.4 Hz, 16H, OCH_2), 1.76–1.62 (m, 16H, CH_2), 1.45–1.30 (m, 16H, CH_2), 1.19–1.06 (m, 16H, CH_2), 1.06–0.88 (m, 48H, CH_2), and 0.58 ppm (t, J = 6.6 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.0, 151.5, 146.2, 131.7, 131.5, 129.1, 128.0, 126.8, 126.7, 124.7, 121.2, 106.1, 69.2, 31.7, 29.4, 29.3, 29.2, 26.2, 22.7, 22.5, and 14.0 ppm; MS (ESI) calcd for $C_{120}H_{161}N_2O_8S_2$ 1823.1722, found 1823.1714 $[M+H]^+$; UV/Vis/NIR (CH_2Cl_2) λ_{max} (ε) = 313 (34200), 356 (35200), 389 (33500), 887 (29500), 932 (21200), 969 (19300), and 1077 nm (50200 $M^{-1}cm^{-1}$).

[C] References

[S1] K. Xu, Y. Fu, Y. Zhou, F. Hennersdorf, P. Machata, I. Vincon, J. J. Weigand, A. A. Popov, R. Berger and X. Feng, *Angew. Chem., Int. Ed.*, 2017, **56**, 15876.

[S2] C. Maeda, M. Masuda and N. Yoshioka, *Org. Lett.*, 2013, **15**, 3566.

[S3] C. Maeda and N. Yoshioka, *Org. Biomol. Chem.*, 2012, **10**, 5182.

[D] DFT Calculations

The optimized structures and molecular orbitals were obtained via the DFT calculations at the B3LYP/6-31G* level. TD-DFT calculations were performed at the CAM/B3LYP/6-31G* level using the geometry of the optimized structures.

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

State	Transition energy (nm)	Oscillator strength	Composition of band and CI coefficiencies
1	968.37	0.2291	H−1 → L (94%)
2	853.05	0.7529	H → L (98%)
3	615.48	0.0000	H−2 → L (92%)
4	601.79	0.0000	H−3 → L (92%)
5	482.73	0.0000	H−13 → L (96%)
6	463.23	0.0000	H−4 → L (93%)
7	455.90	0.0000	H−12 → L (44%), H−5 → L (45%)
8	409.06	0.0038	H−10 → L (92%)
9	392.61	0.0003	H−12 → L (43%), H−5 → L (32%)
10	373.26	0.0007	H−17 → L (81%)
11	364.80	0.5695	H → L+1 (55%)
12	358.55	0.3296	H−10 → L (66%)

Table S2 Selected data of calculated electronic transitions in **D2**

State	Transition energy (nm)	Oscillator strength	Composition of band and CI coefficiencies
1	1032.70	1.1866	H → L (50%), H−2 → L (23%), H−3 → L+1 (16%)
2	970.37	0.0272	H−1 → L (49%), H−2 → L+1 (37%)
3	922.32	0.9542	H−2 → L (34%), H → L (33%), H−1 → L+1 (29%)
4	827.09	0.0615	H → L+1 (67%), H−2 → L (23%)
5	671.47	0.0007	H−3 → L (53%), H → L+1 (21%), H−6 → L+1 (11%)
6	638.16	0.0137	H−4 → L (44%), H−5 → L+1 (25%), H−3 → L+1 (15%)
7	632.20	0.0001	H−5 → L (52%), H−4 → L+1 (32%)
8	623.35	0.0261	H−3 → L+1 (37%), H−6 → L (24%), H−5 → L+1 (12%)
9	570.13	0.0035	H−2 → L+1 (40%), H−2 → L (29%), H−2 → L+1 (13%)
10	569.78	0.0012	H−2 → L+1 (45%), H−1 → L (27%), H−2 → L (11%)

Table S3 Selected data of calculated electronic transitions in **F2**

State	Transition energy (nm)	Oscillator strength	Composition of band and CI coefficiencies
1	1382.85	0.4032	H → L (88%), H−1 → L (7%)
2	1143.11	1.1401	H−2 → L (82%), H−4 → L+1 (7%), H → L (6%)
3	1028.08	0.0001	H−2 → L (50%), H → L+1 (25%), H−1 → L+1 (20%)
4	945.72	0.0000	H → L+1 (51%), H−3 → L+2 (23%), H−2 → L (21%)
5	835.09	0.6148	H−3 → L (66%), H−2 → L+1 (24%)
6	792.75	0.0001	H−1 → L+1 (60%), H−2 → L (13%), H−4 → L (12%)
7	653.15	0.0000	H−6 → L (50%), H−5 → L+1 (24%), H−4 → L (10%)
8	651.10	0.0110	H−5 → L (61%), H−6 → L+1 (27%)
9	624.22	0.0000	H−4 → L (68%), H−6 → L (11%), H−1 → L+1 (10%)
10	589.88	0.1629	H−2 → L+1 (68%), H−3 → L (21%)

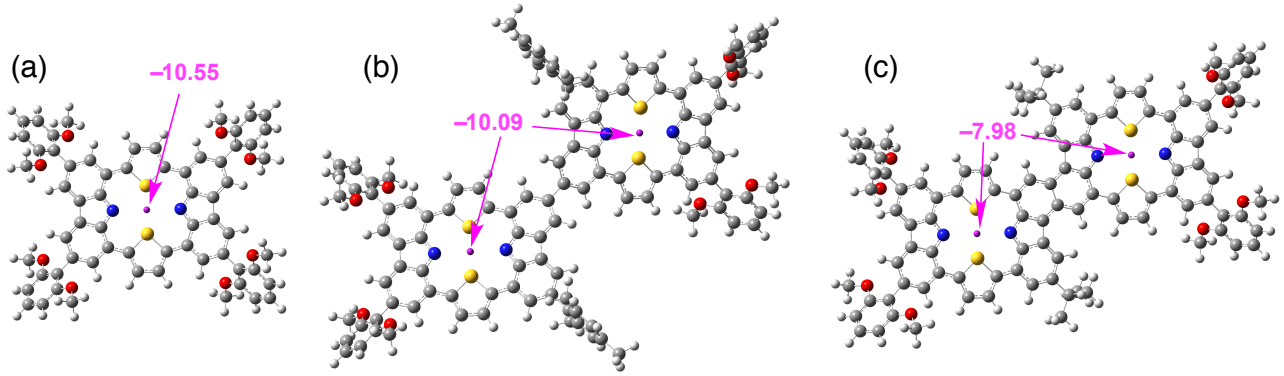
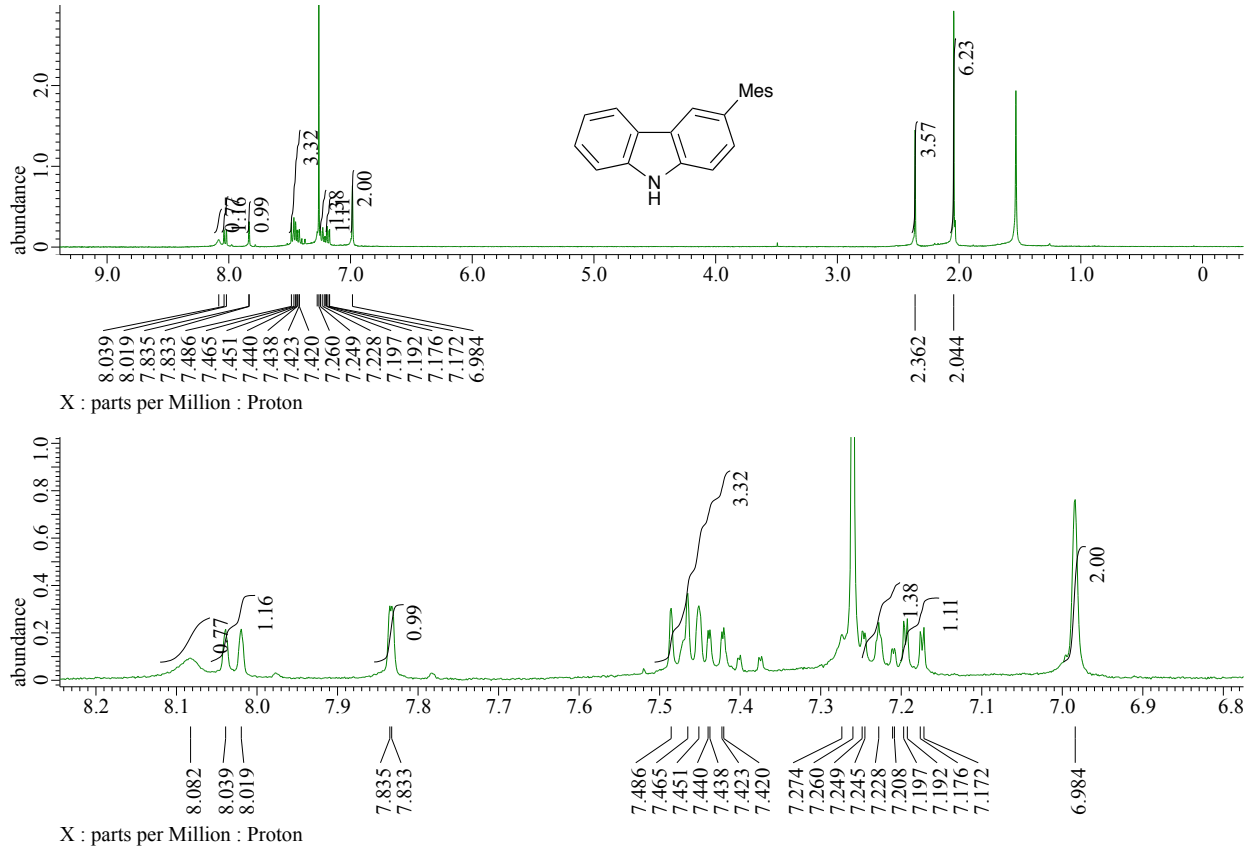


Fig. S1 NICS(0) values at the selected points of (a) **1**, (b) **D2**, and (c) **F2** calculated at the B3LYP/6-31G(d) level.

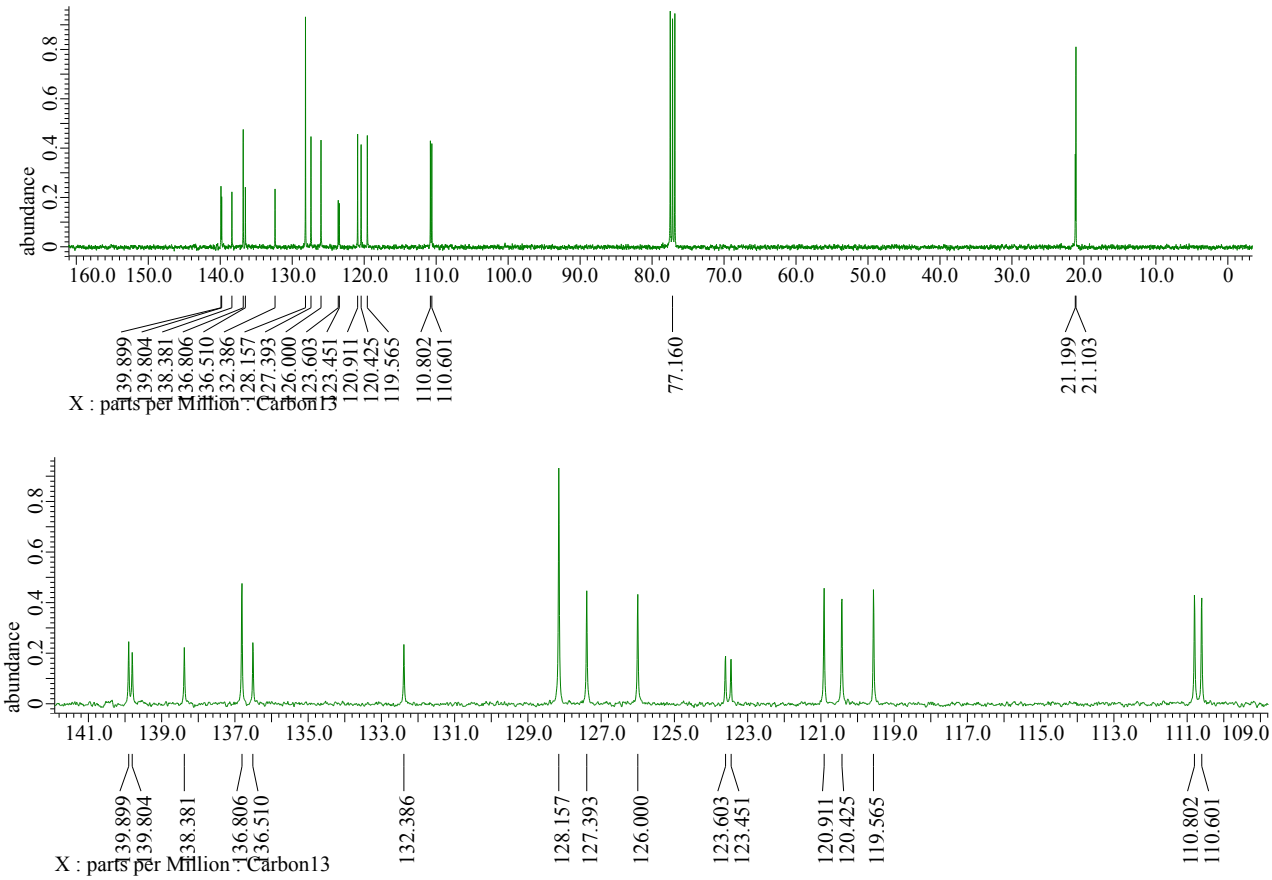
The full citation of reference 14:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *GAUSSIAN 16 (Revision C.01)*, Gaussian, Inc., Wallingford CT, 2019.

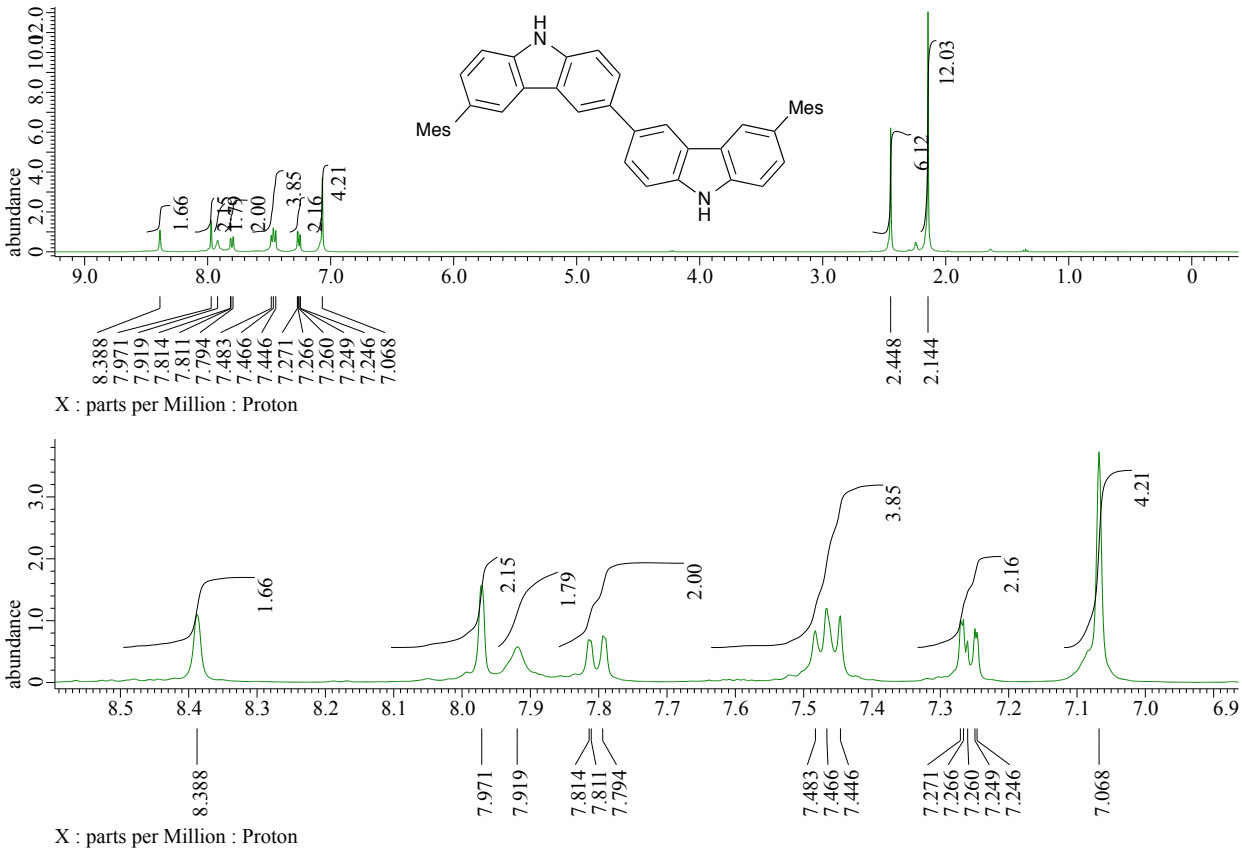
[E] NMR Spectra



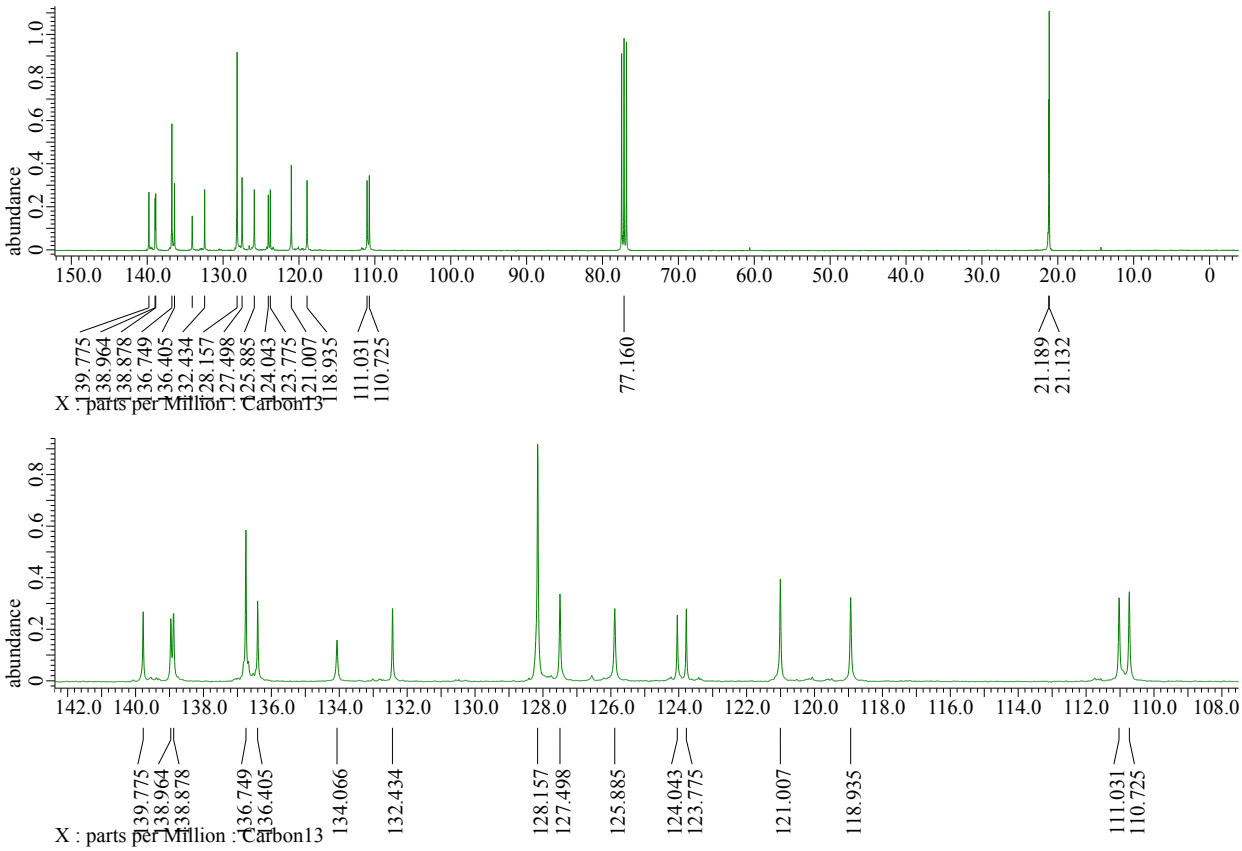
400 MHz ^{1}H NMR spectrum of 3-mesitylcarbazole in $CDCl_3$.



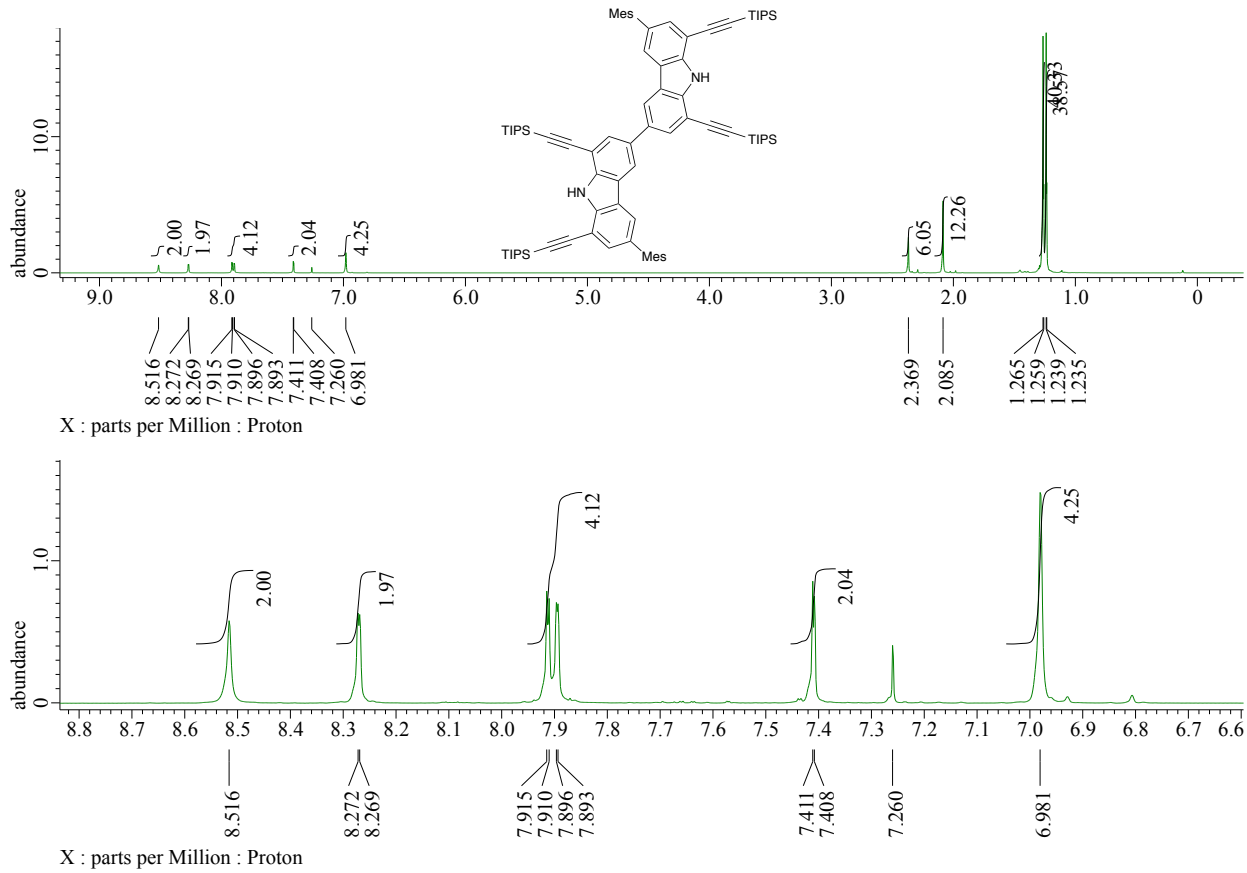
100 MHz ^{13}C NMR spectrum of 3-mesitylcarbazole in $CDCl_3$.



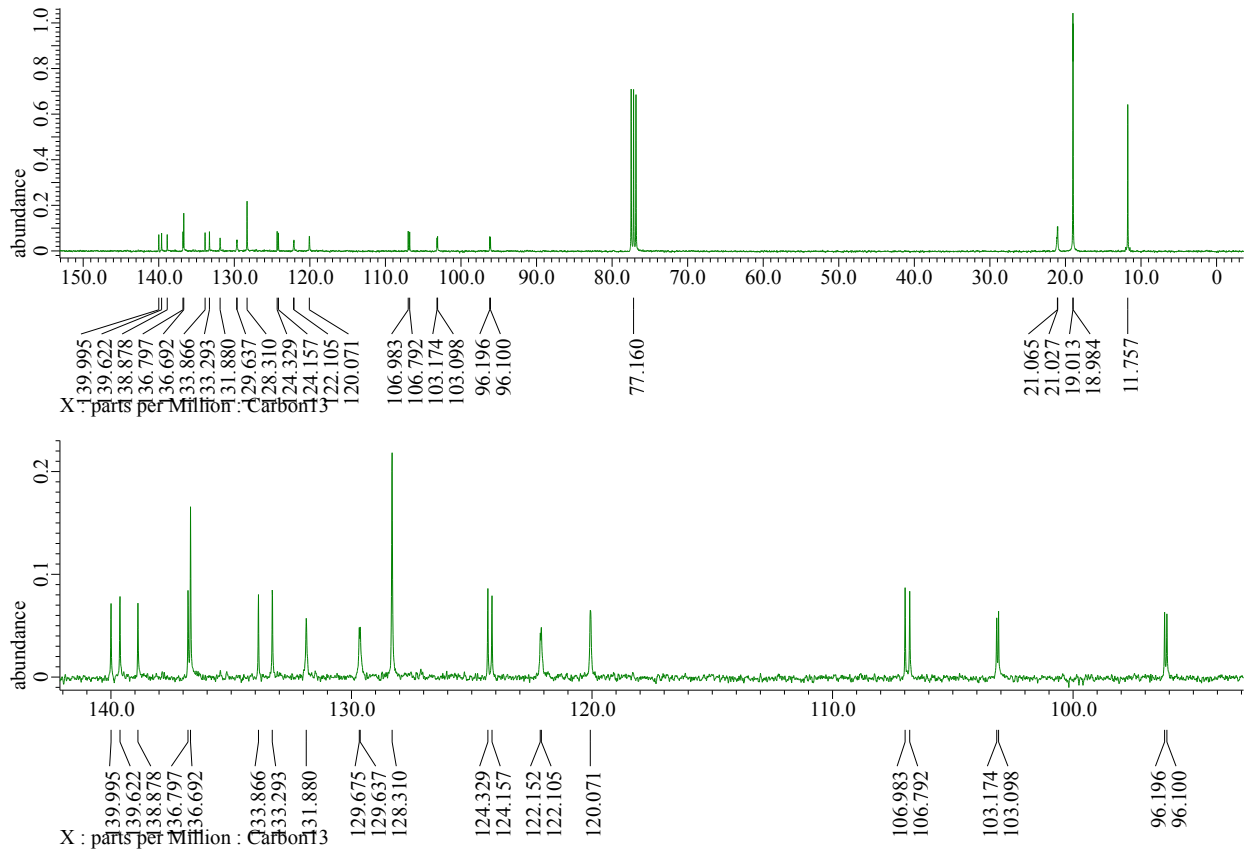
400 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$.



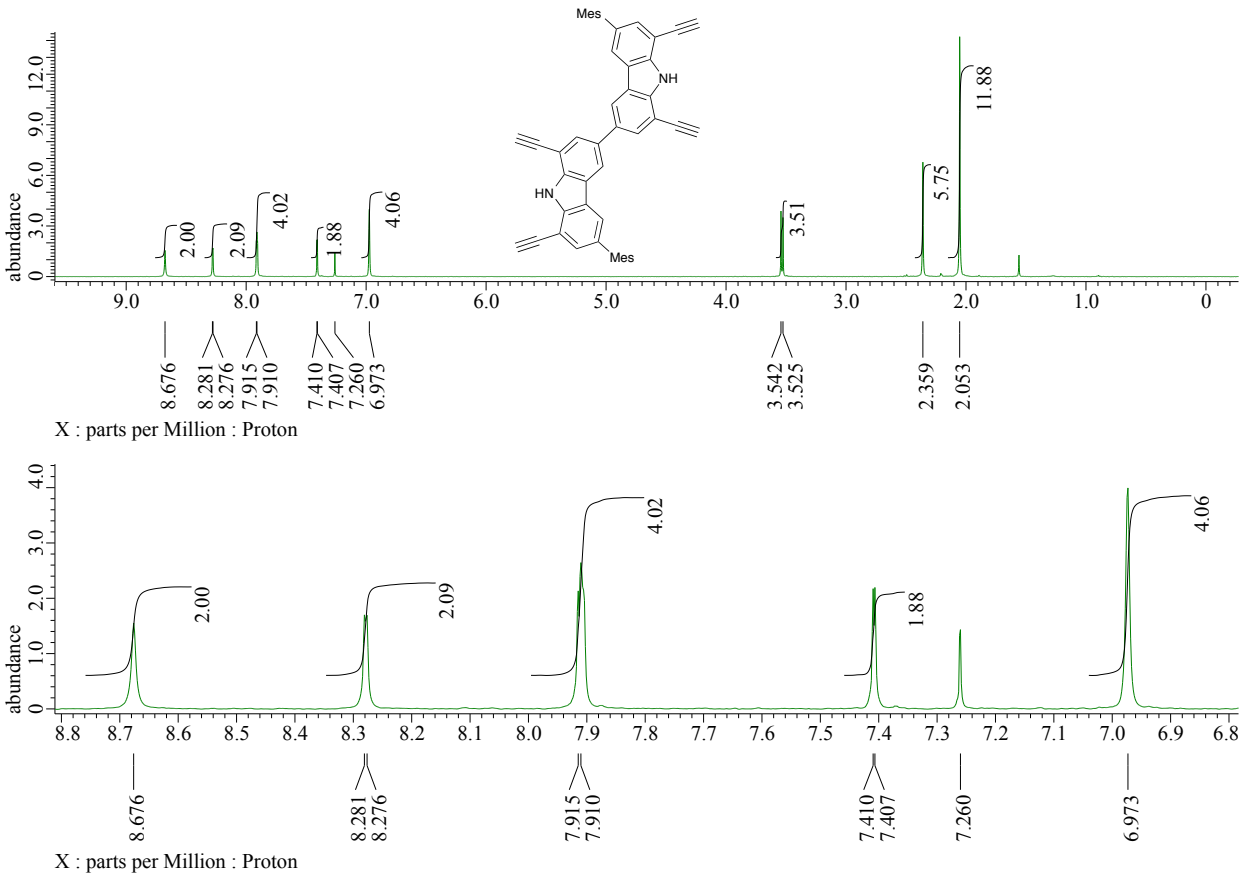
100 MHz ^{13}C NMR spectrum of **5** in $CDCl_3$.



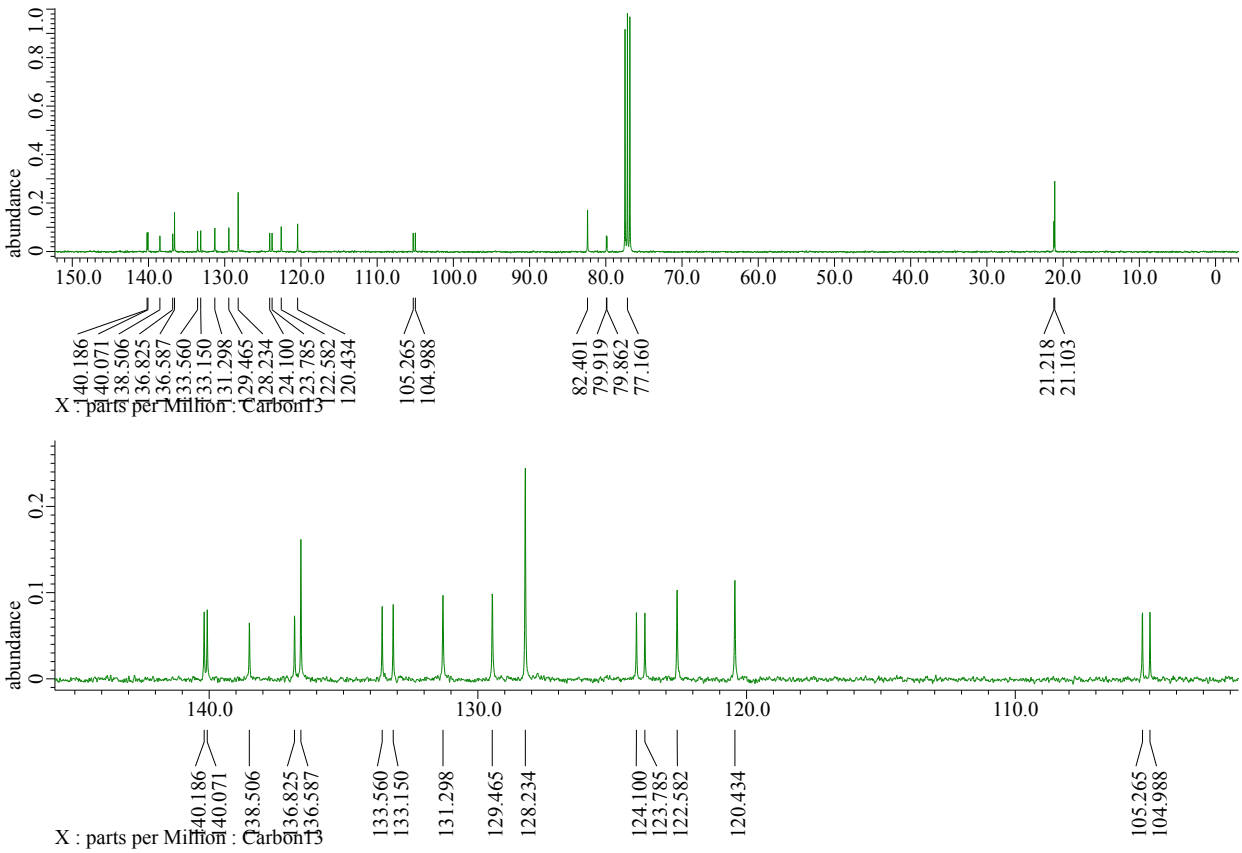
400 MHz ^{1}H NMR spectrum of **6** in $CDCl_3$.



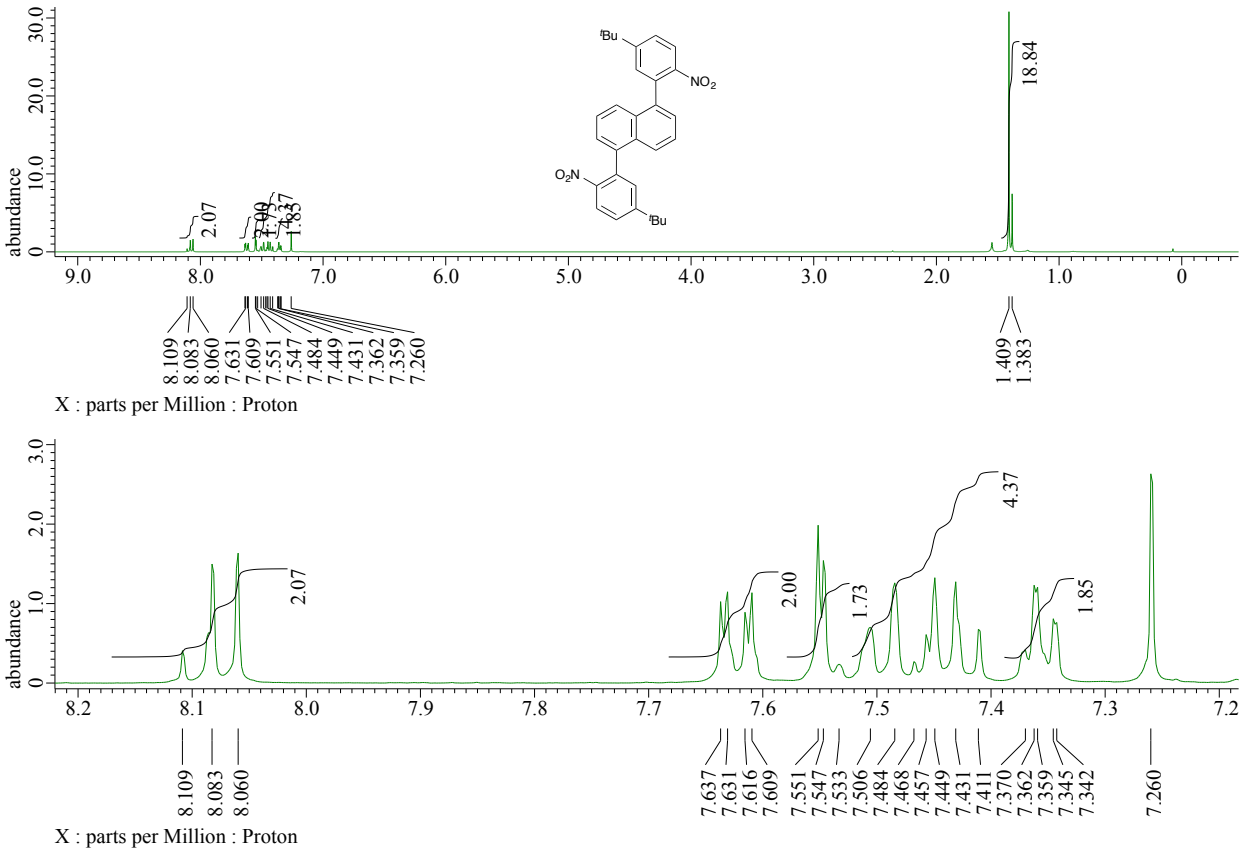
100 MHz ^{13}C NMR spectrum of **6** in $CDCl_3$.



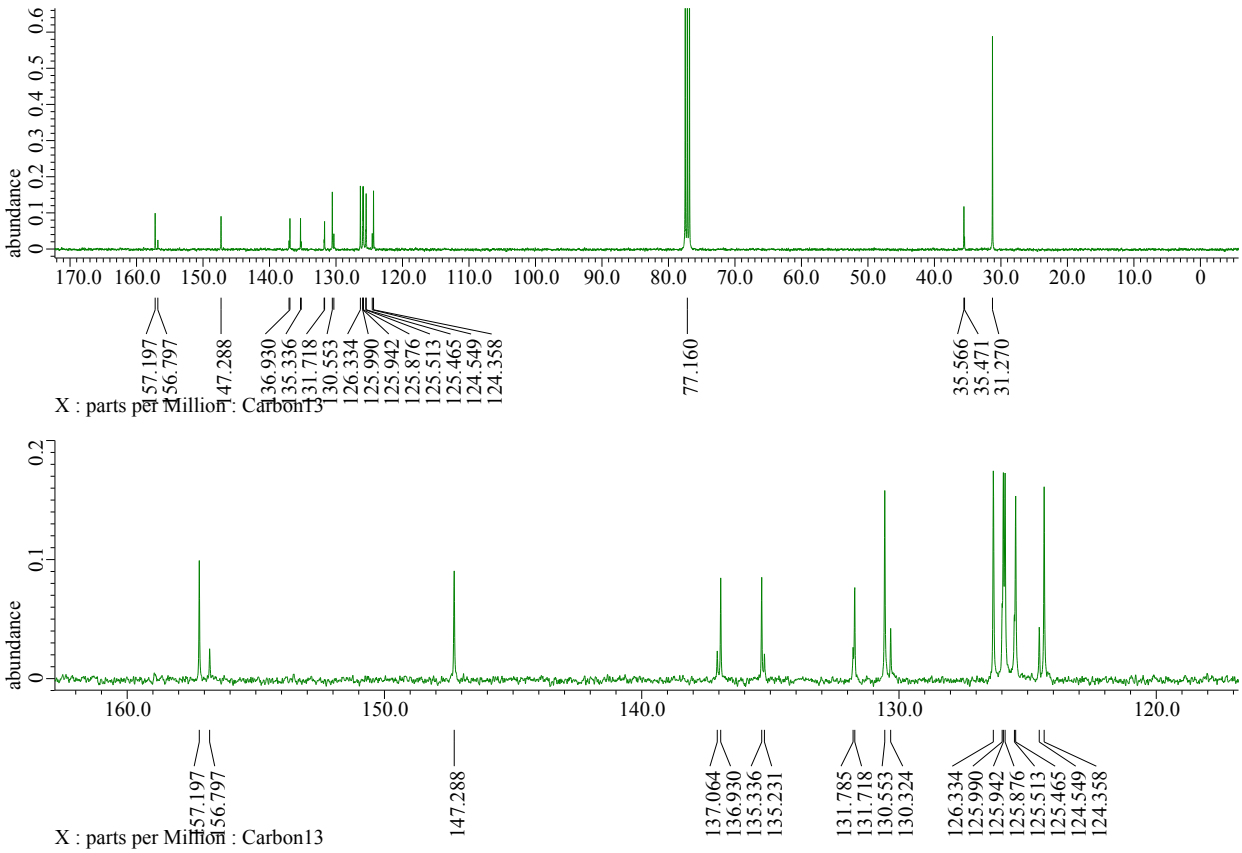
400 MHz ^{1}H NMR spectrum of **2** in $CDCl_3$.



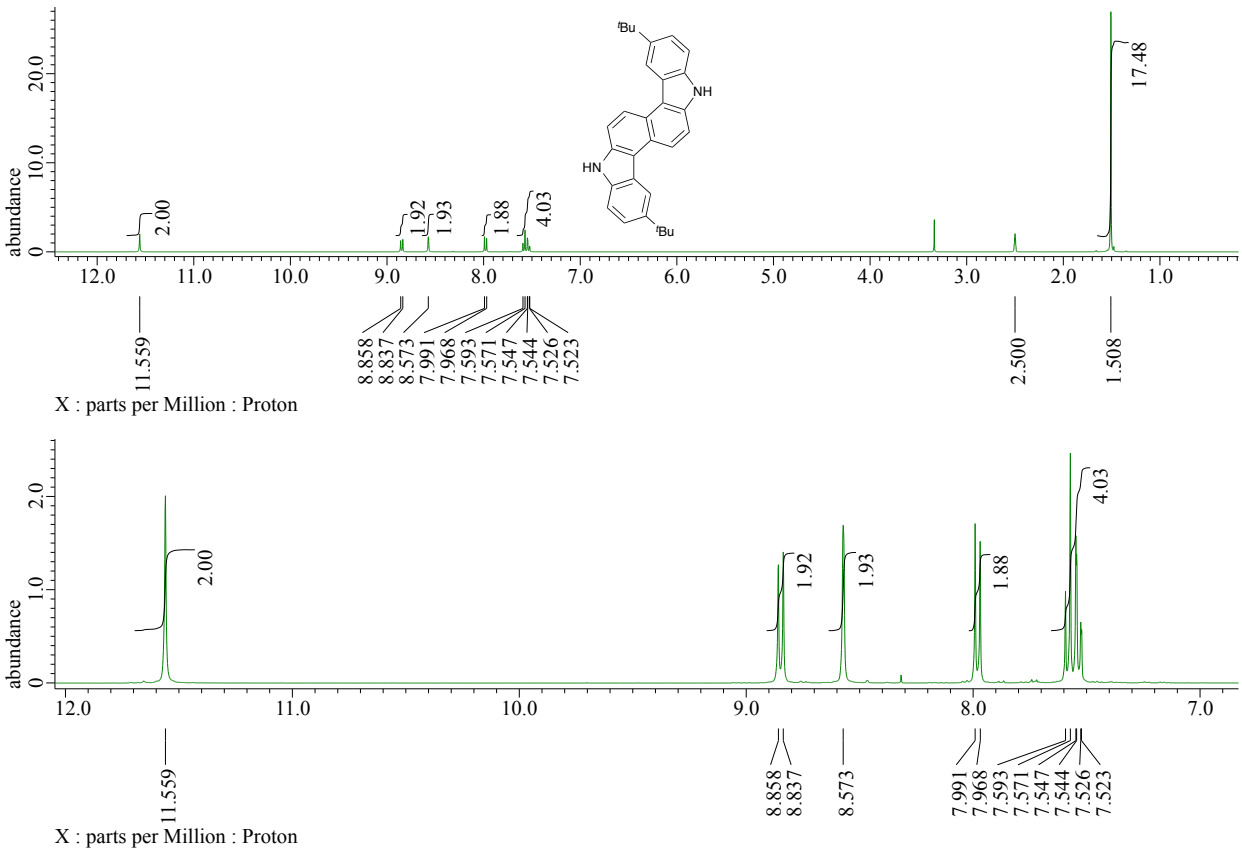
100 MHz ^{13}C NMR spectrum of **2** in $CDCl_3$.



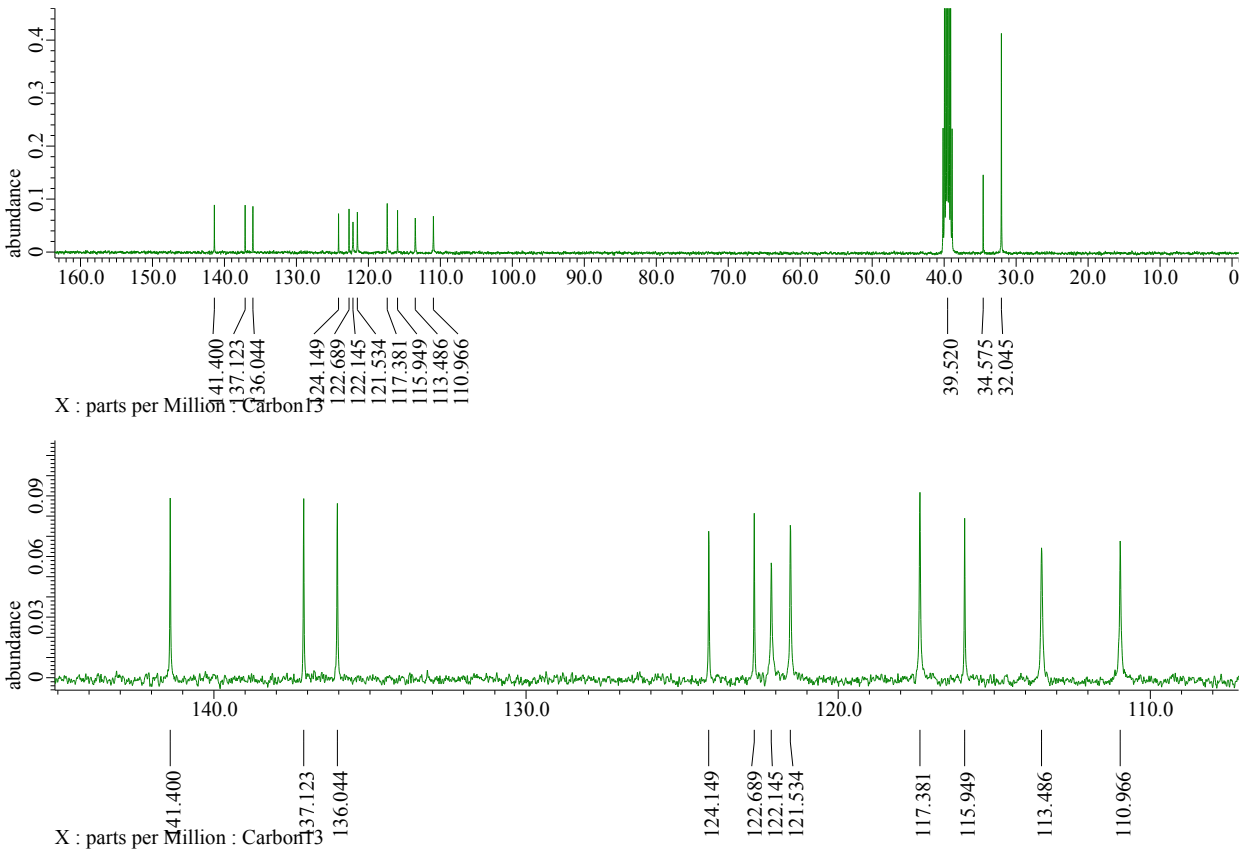
400 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$.



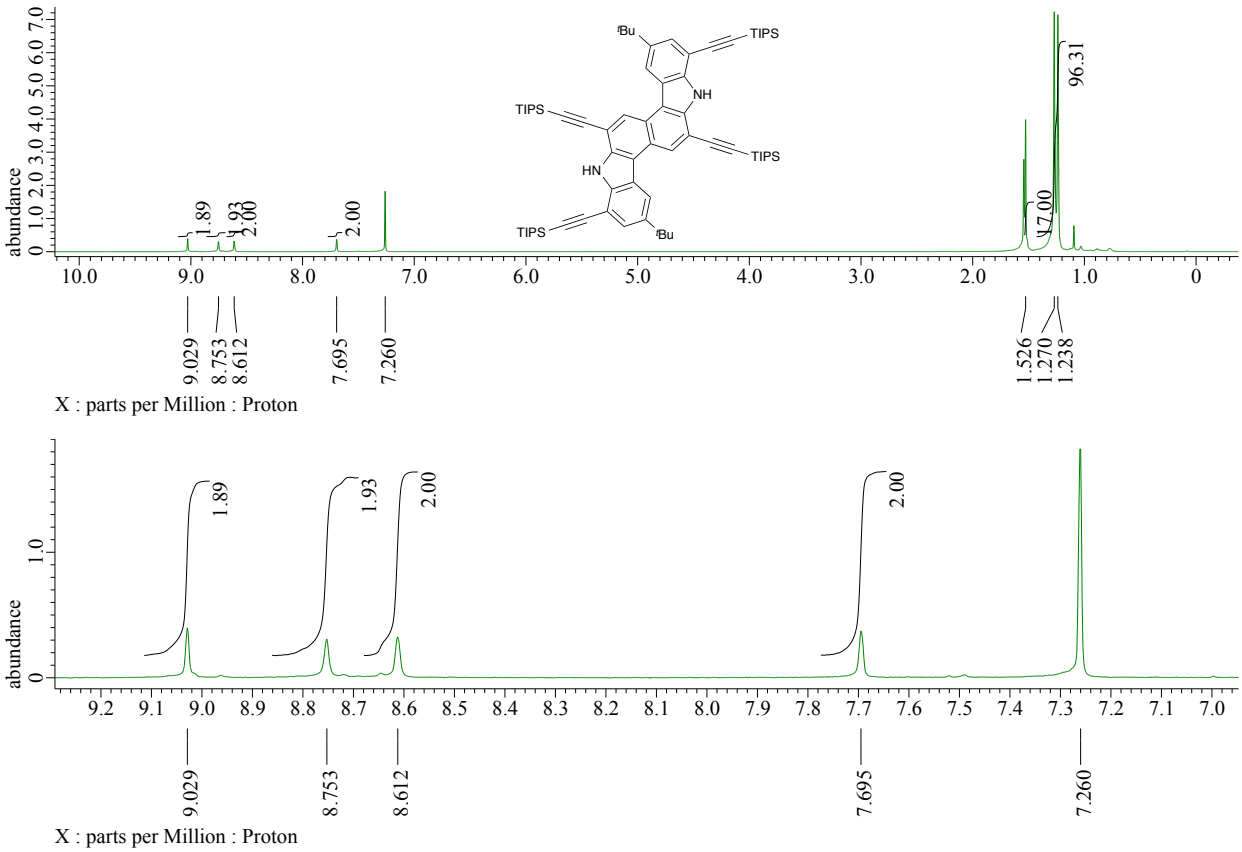
100 MHz ^{13}C NMR spectrum of **7** in $CDCl_3$.



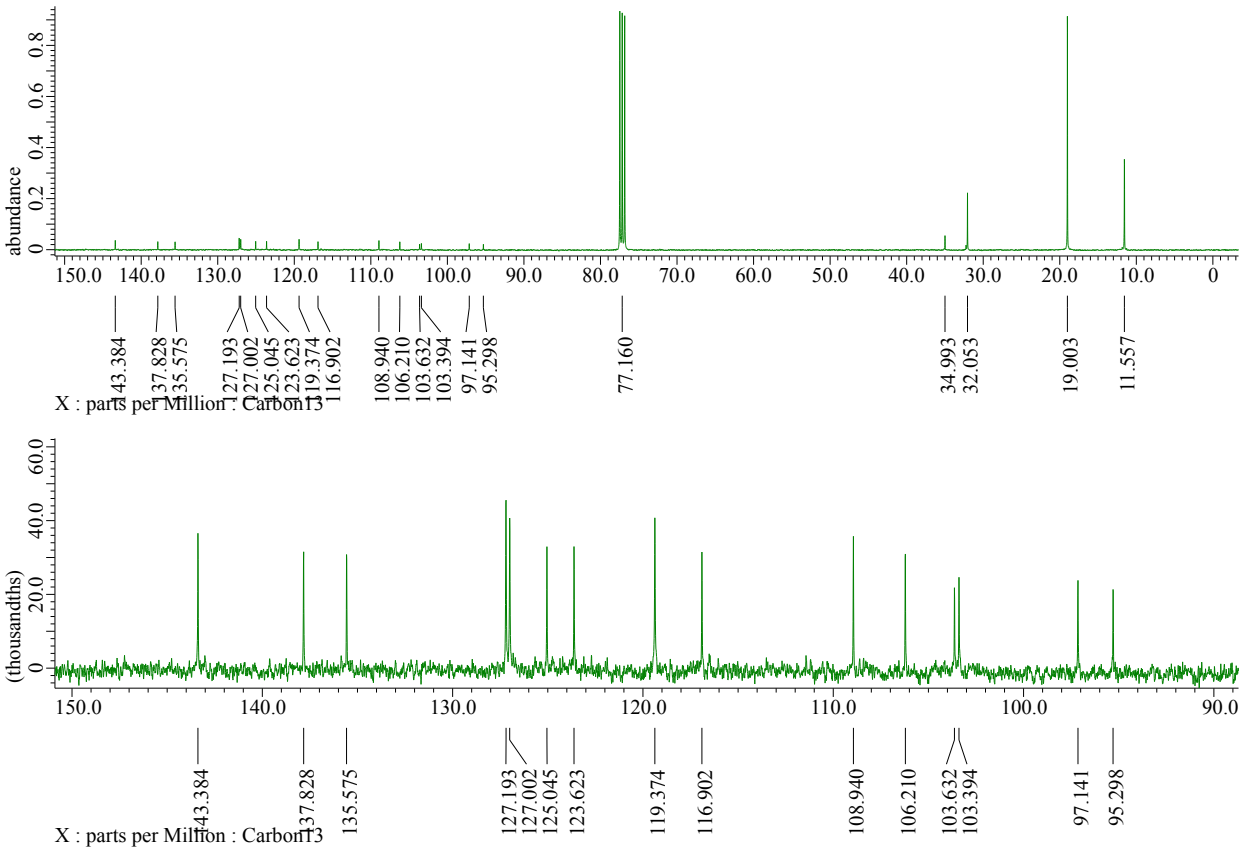
400 MHz ^{1}H NMR spectrum of **8** in $(CD_3)_2SO$.



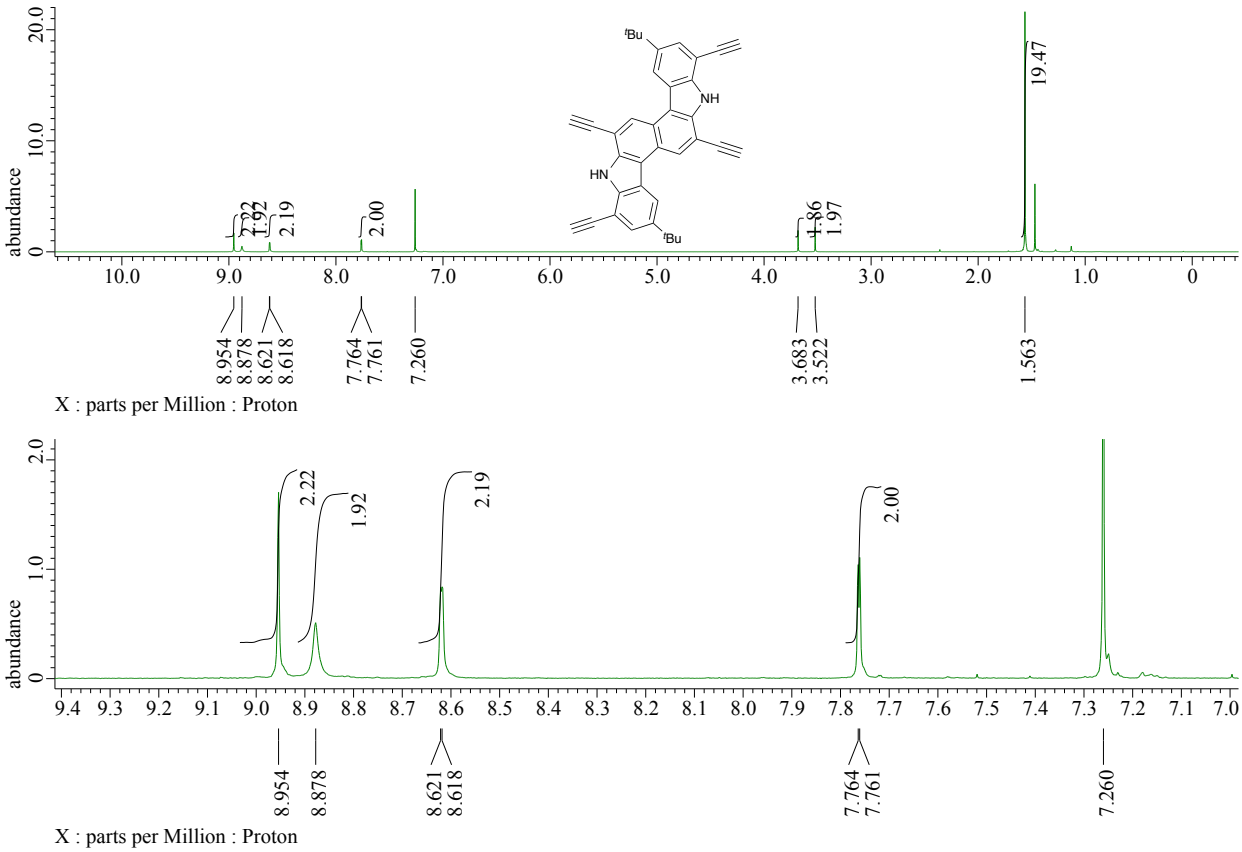
100 MHz ^{13}C NMR spectrum of **8** in $(CD_3)_2SO$.



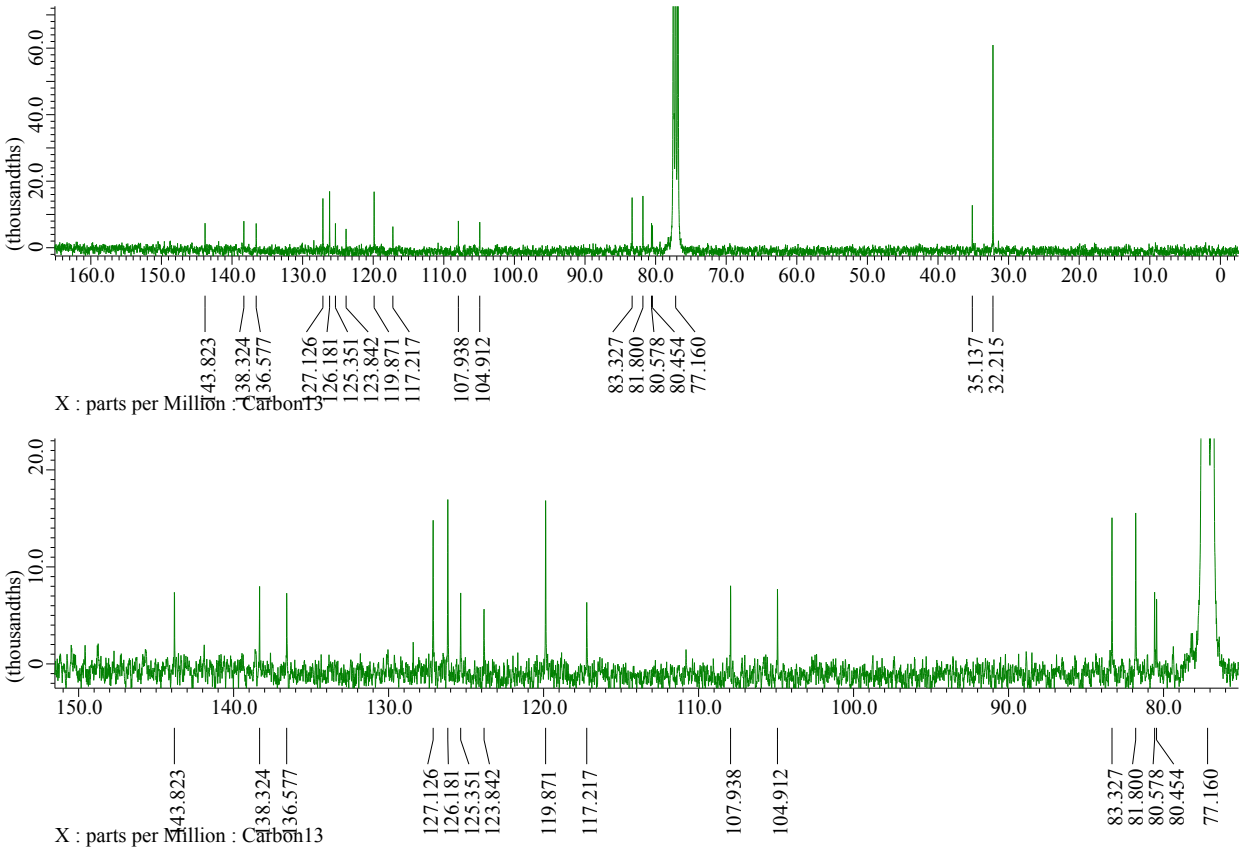
400 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$.



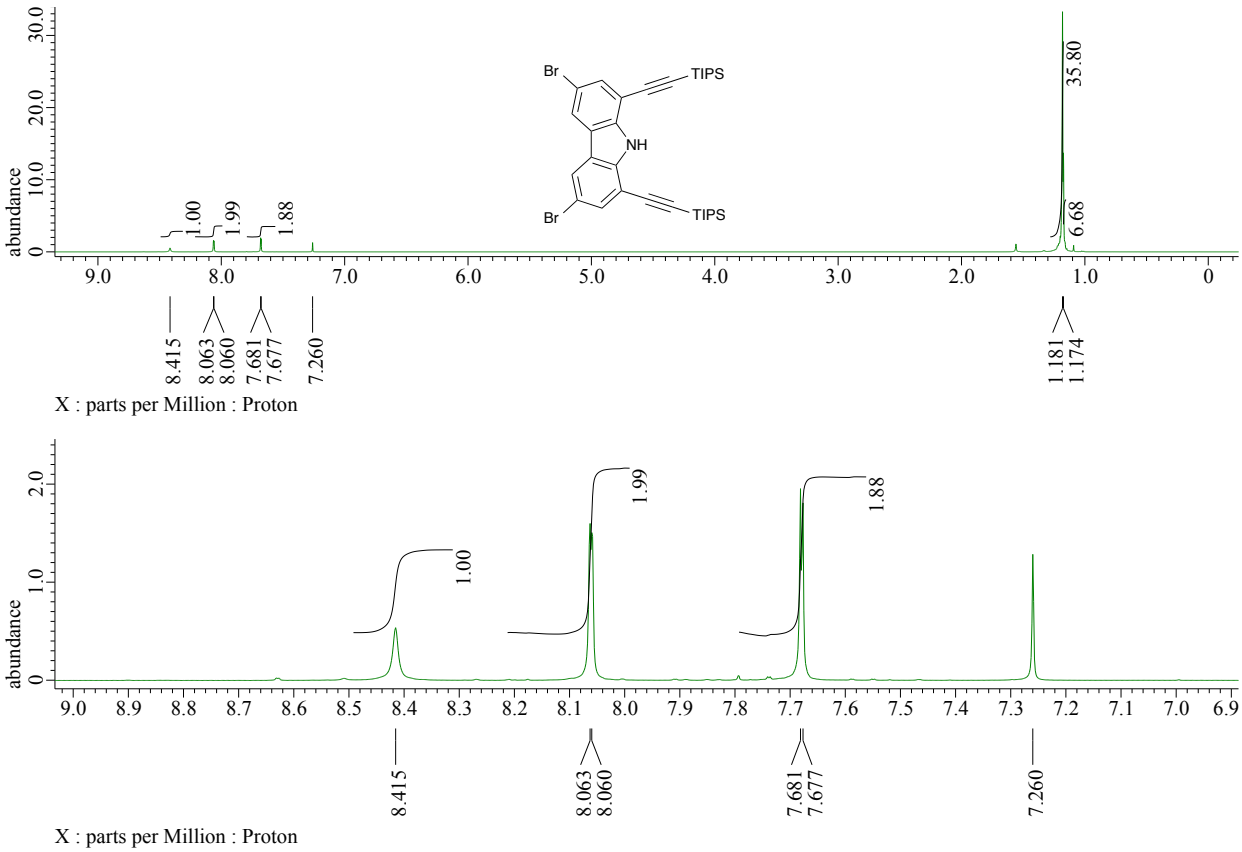
100 MHz ^{13}C NMR spectrum of **9** in $CDCl_3$.



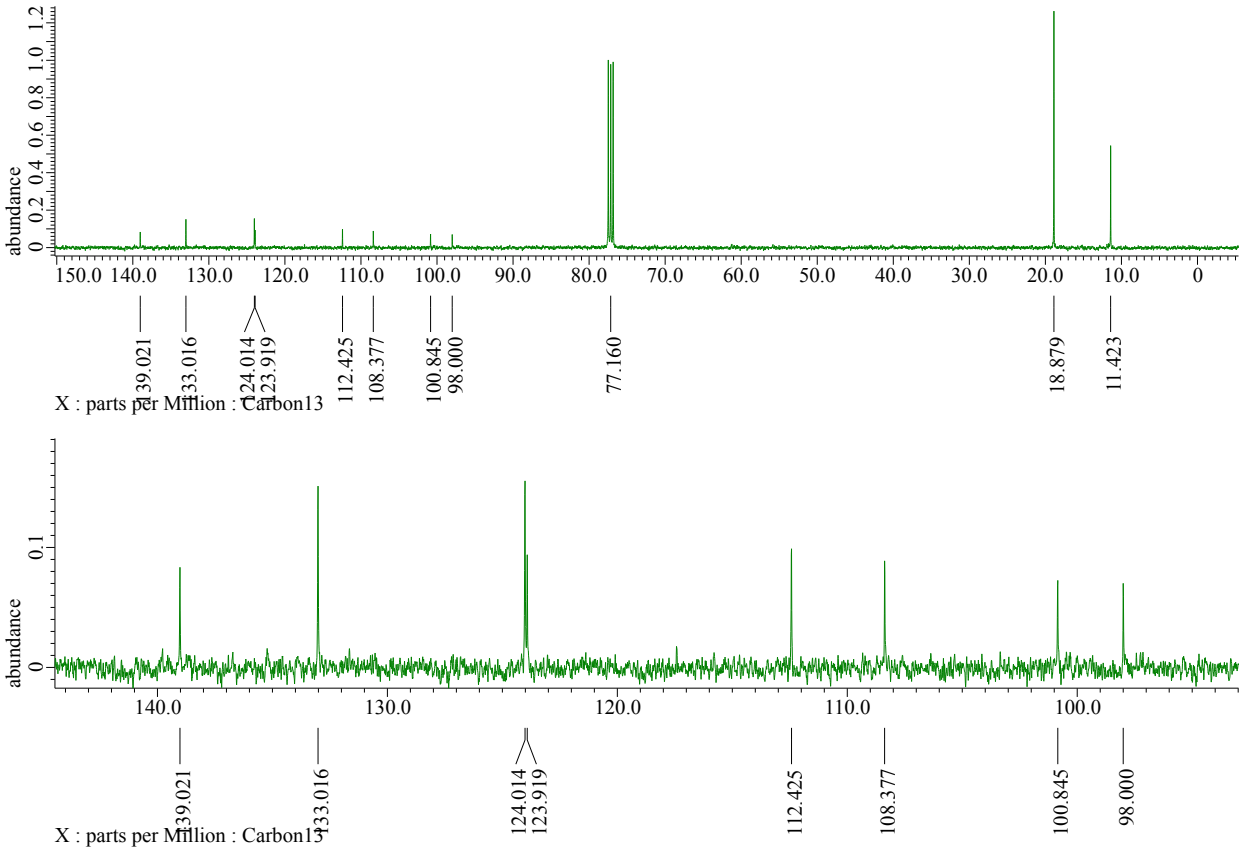
400 MHz ^{1}H NMR spectrum of **3** in $CDCl_3$.



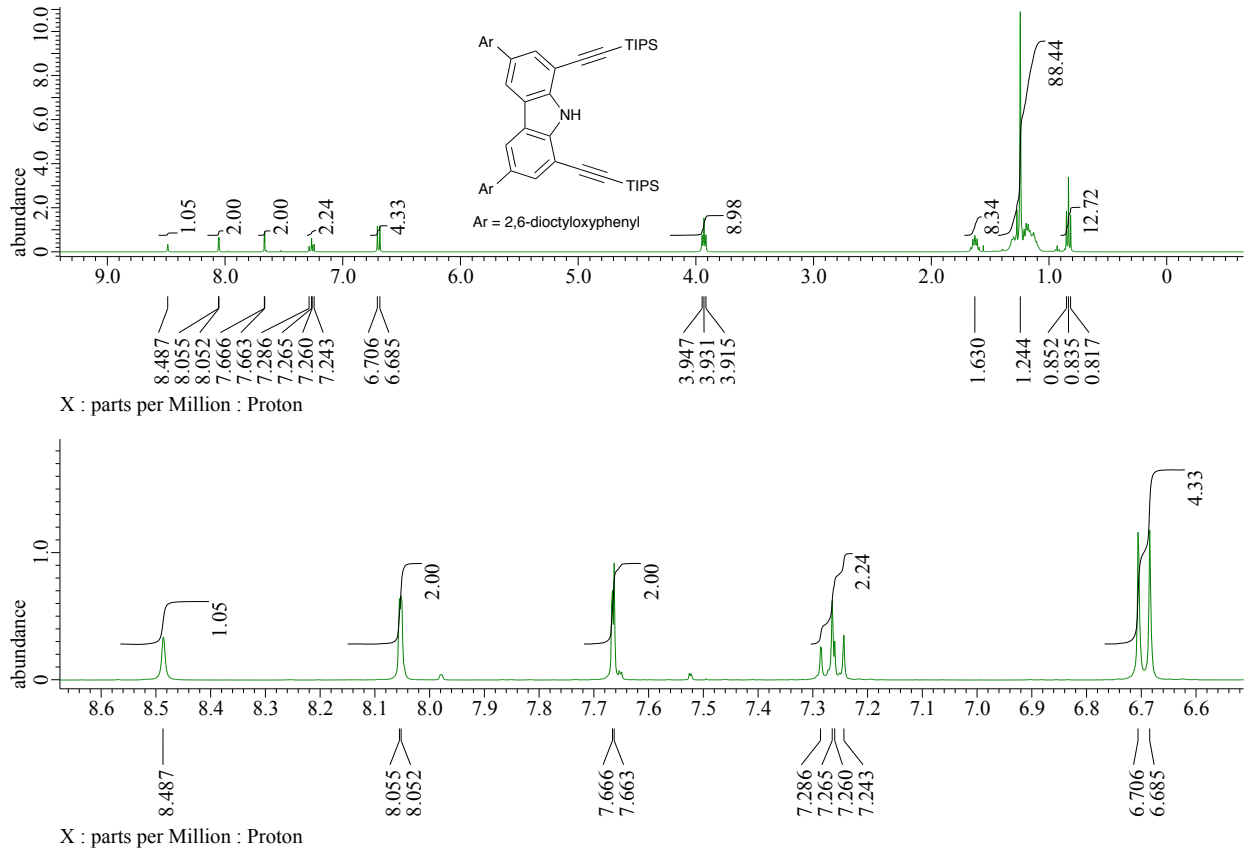
100 MHz ^{13}C NMR spectrum of **3** in $CDCl_3$.



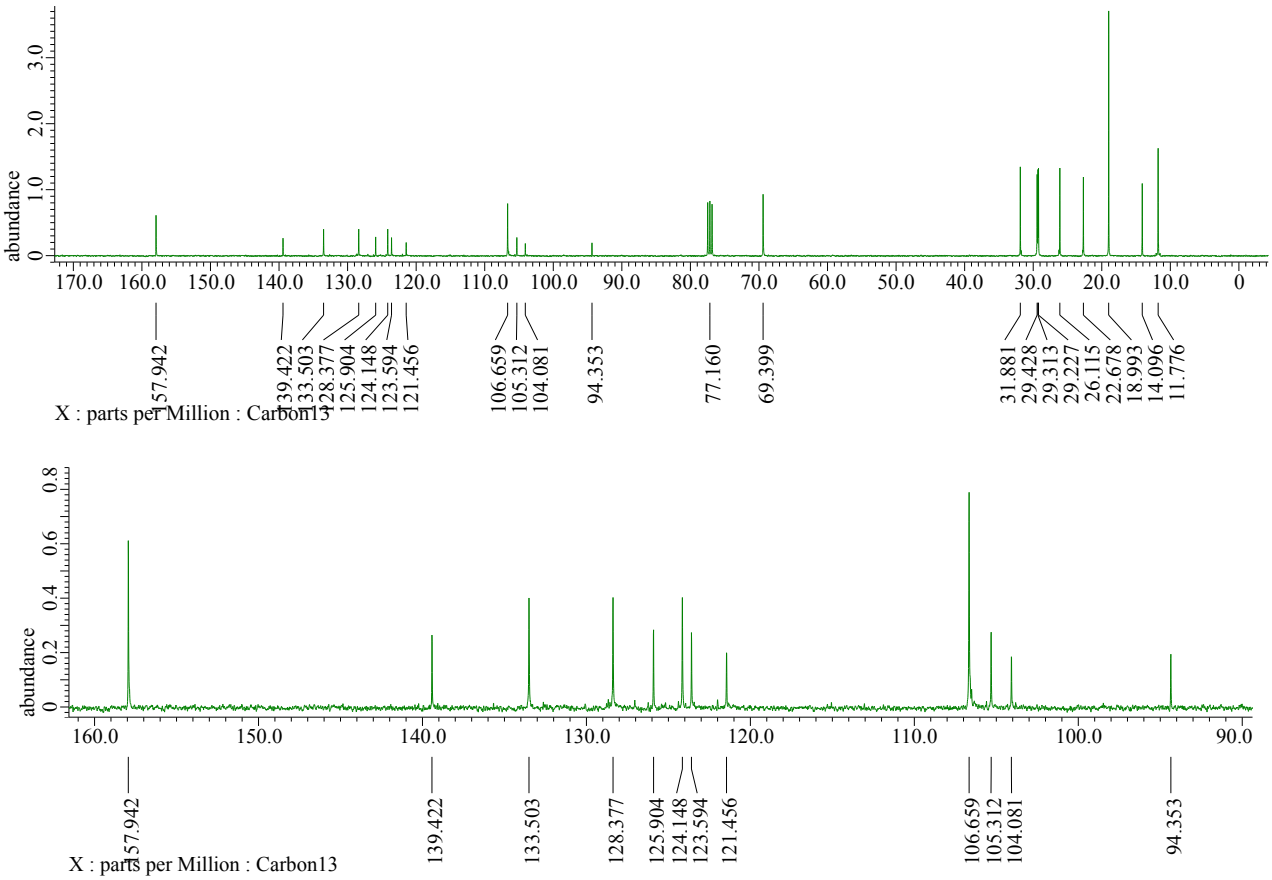
400 MHz ^{1}H NMR spectrum of 1,8-bis(triisopropylsilylethynyl)-3,6-dibromocarbazole in $CDCl_3$.



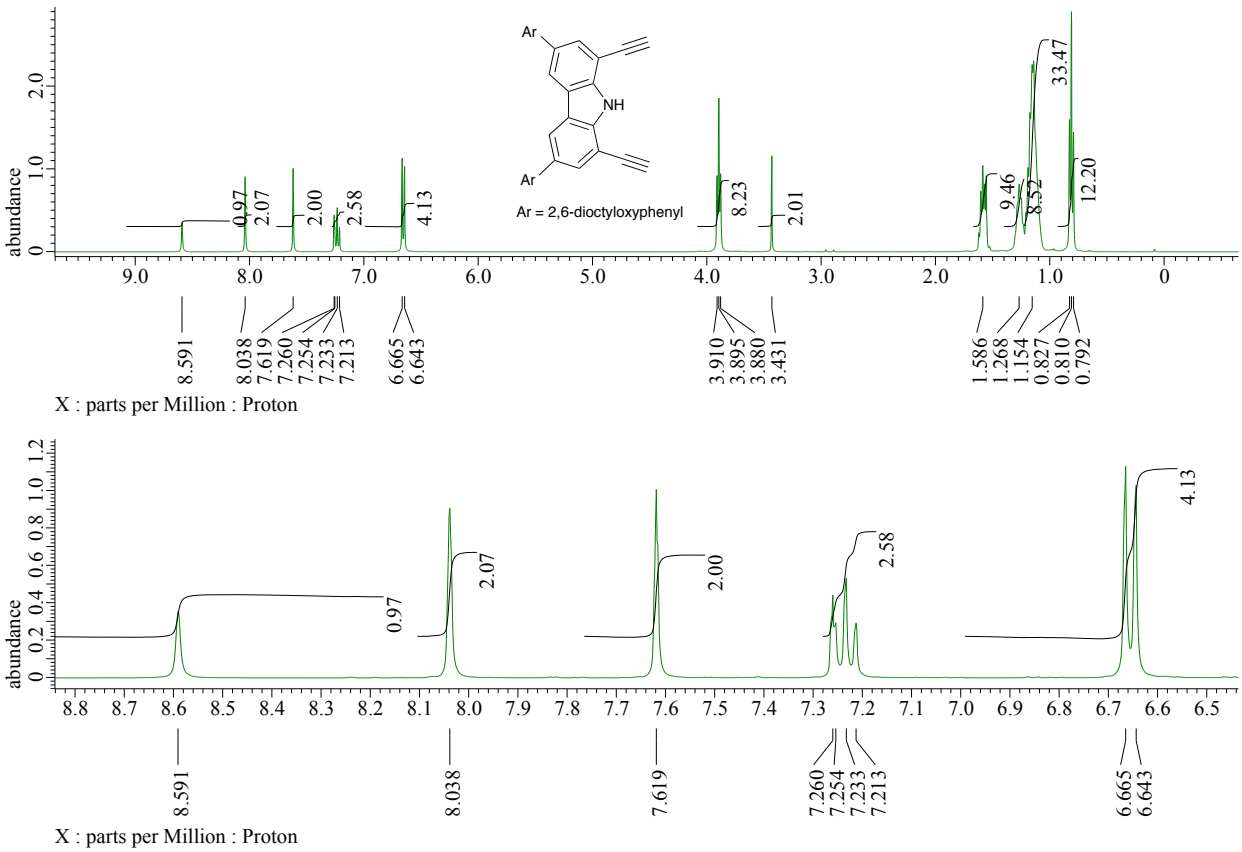
100 MHz ^{13}C NMR spectrum of 1,8-bis(triisopropylsilylethynyl)-3,6-dibromocarbazole in $CDCl_3$.



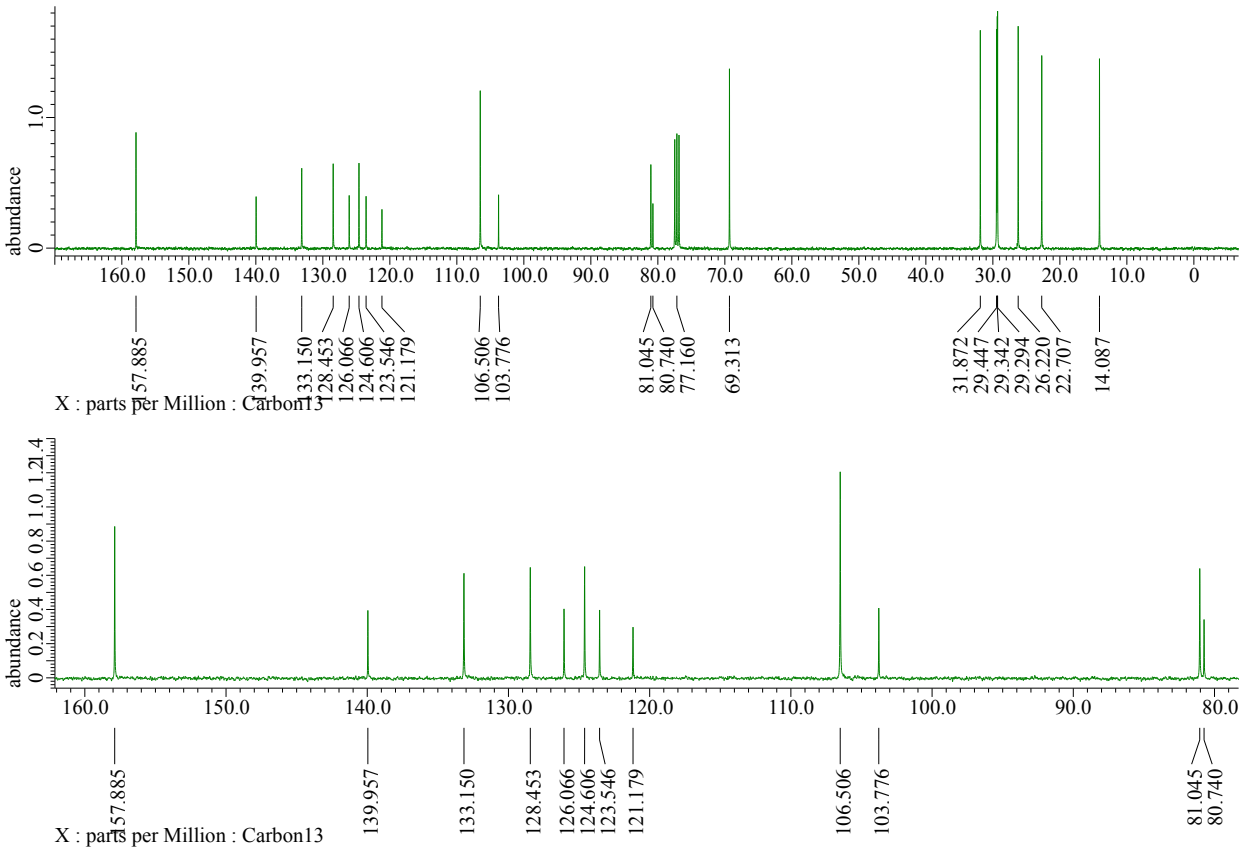
400 MHz ^{1}H NMR spectrum of 1,8-bis(triisopropylsilylethynyl)-3,6-bis(2,6-dioctyloxyphenyl)dibromocarbazole in $CDCl_3$.



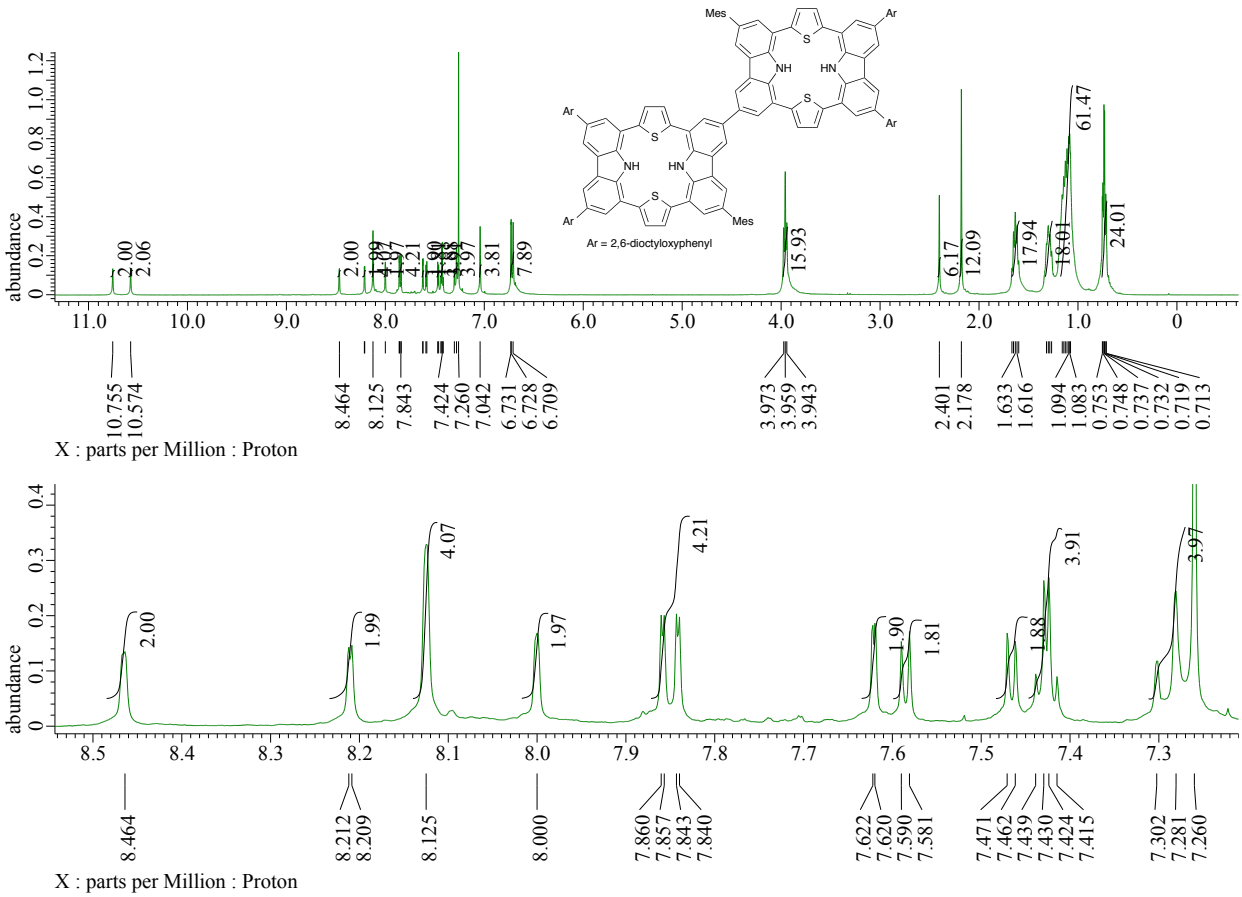
100 MHz ^{13}C NMR spectrum of 1,8-bis(triisopropylsilylethynyl)-3,6-bis(2,6-dioctyloxyphenyl)carbazole in $CDCl_3$.



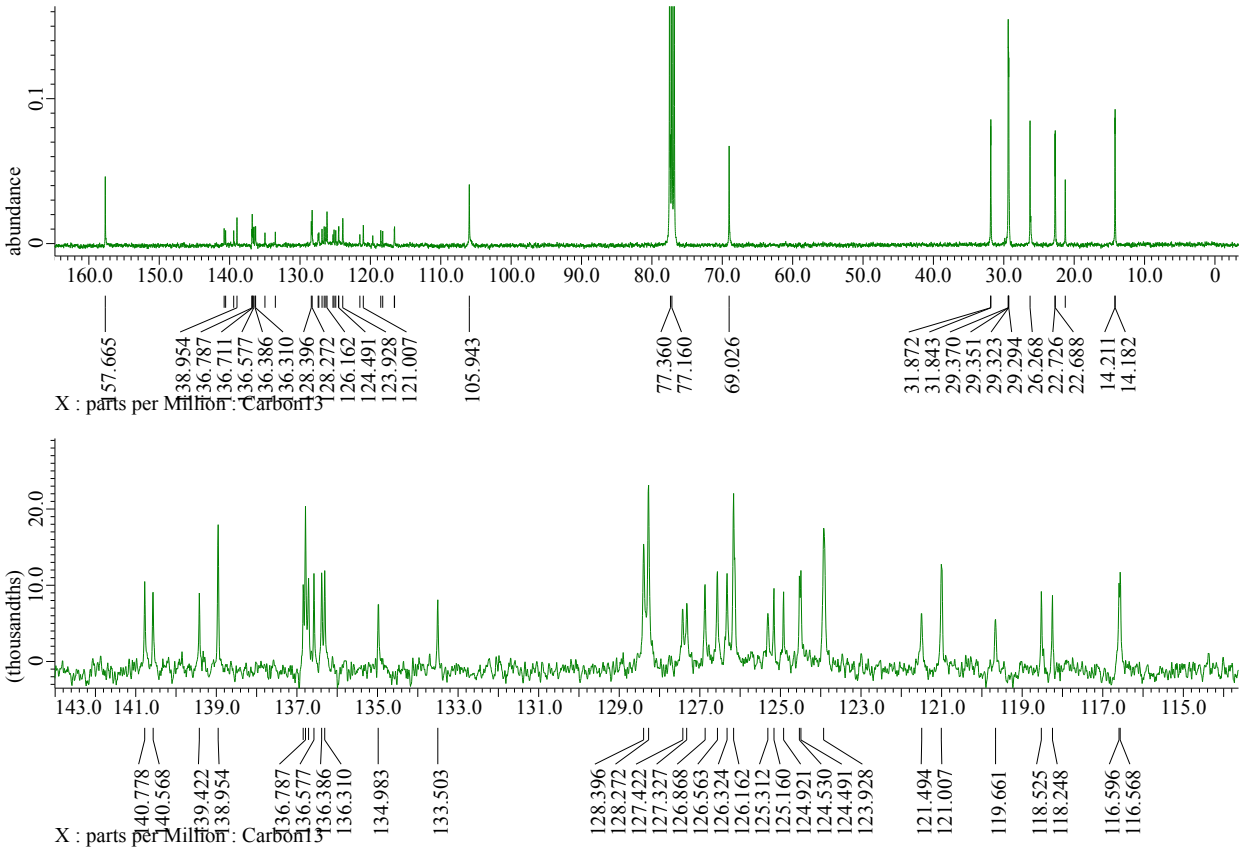
400 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$.



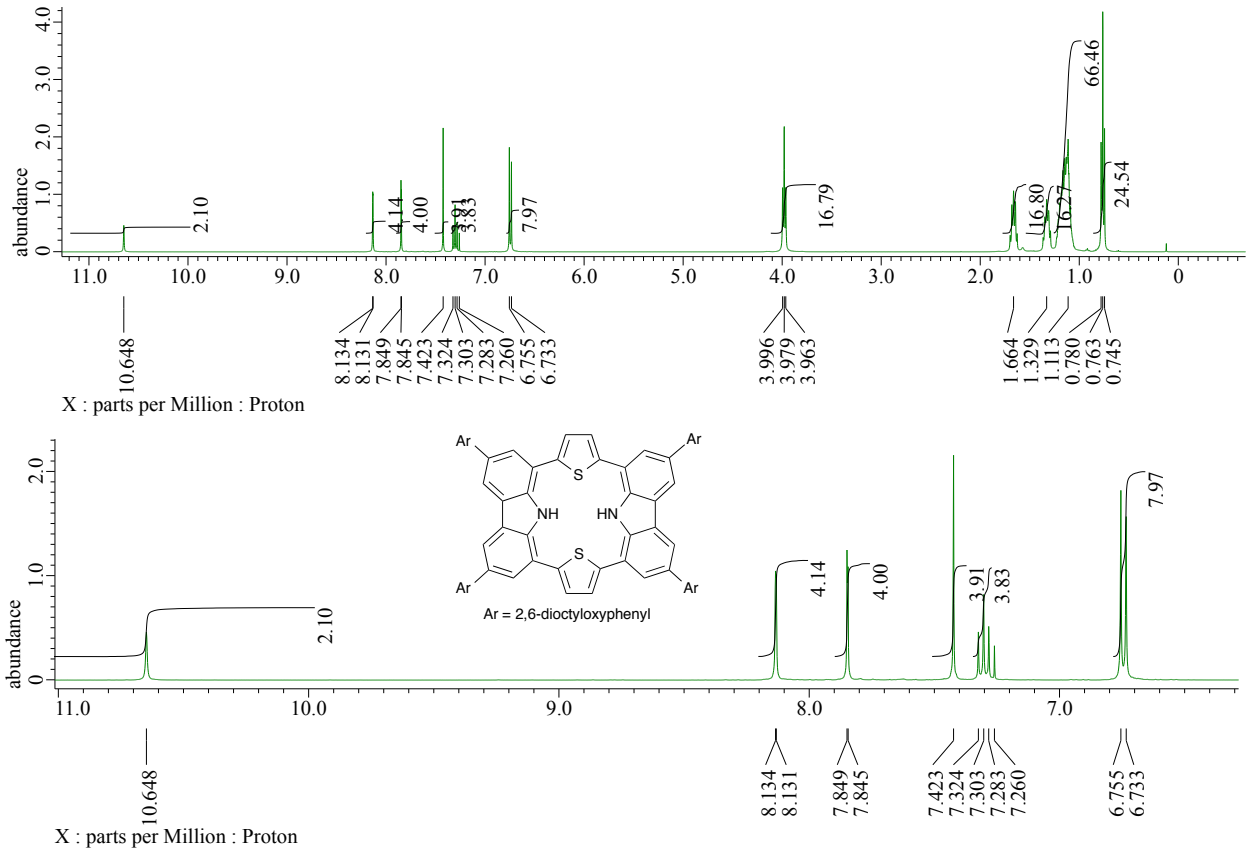
100 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$.



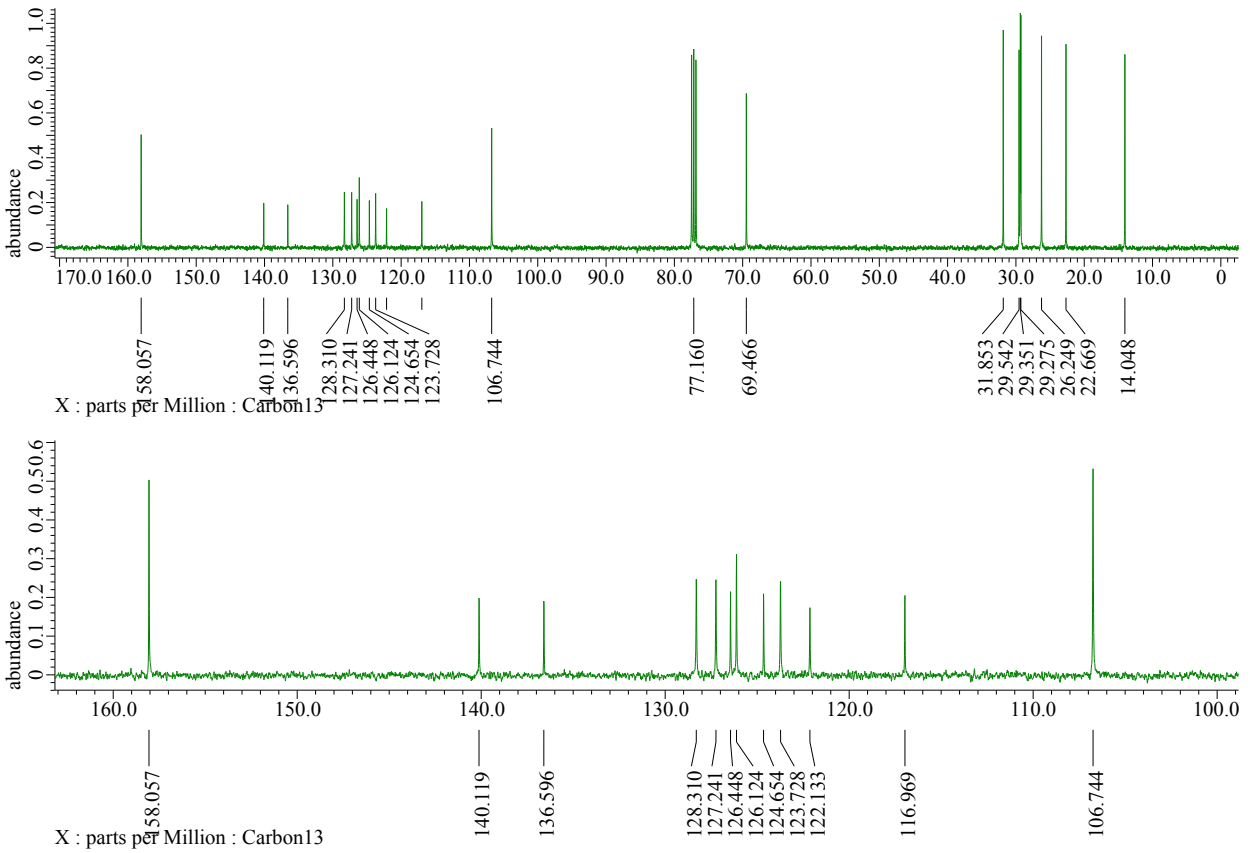
400 MHz ^{1}H NMR spectrum of **10** in $CDCl_3$.



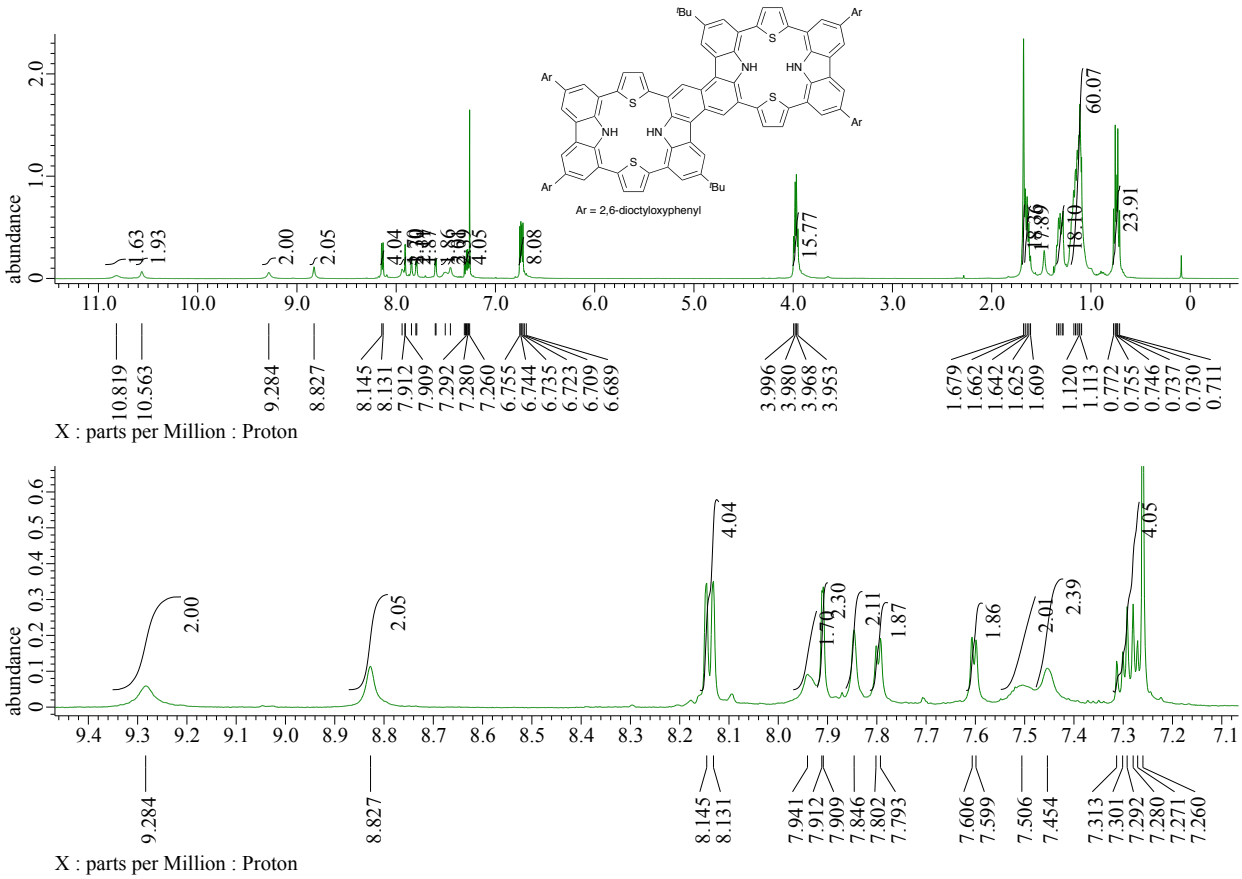
100 MHz ^{13}C NMR spectrum of **10** in $CDCl_3$.



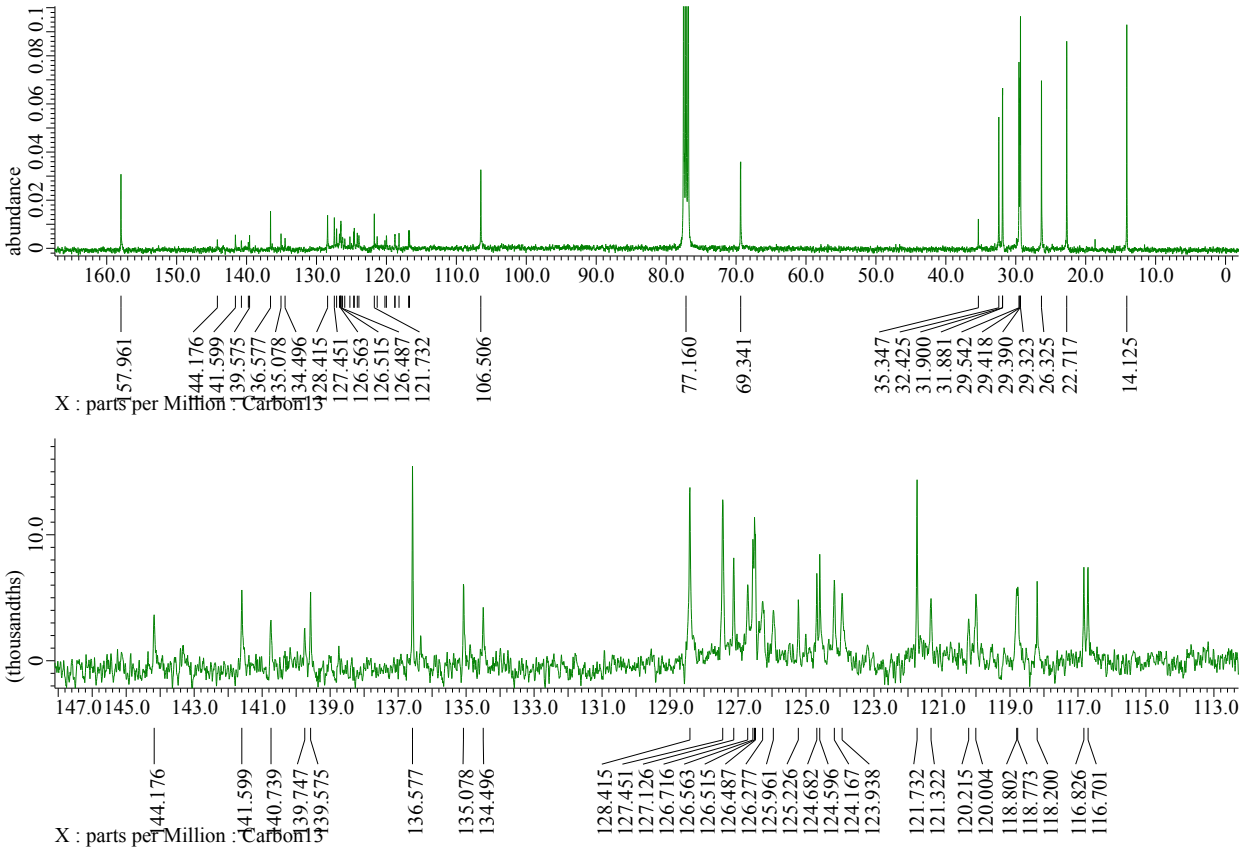
400 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$.



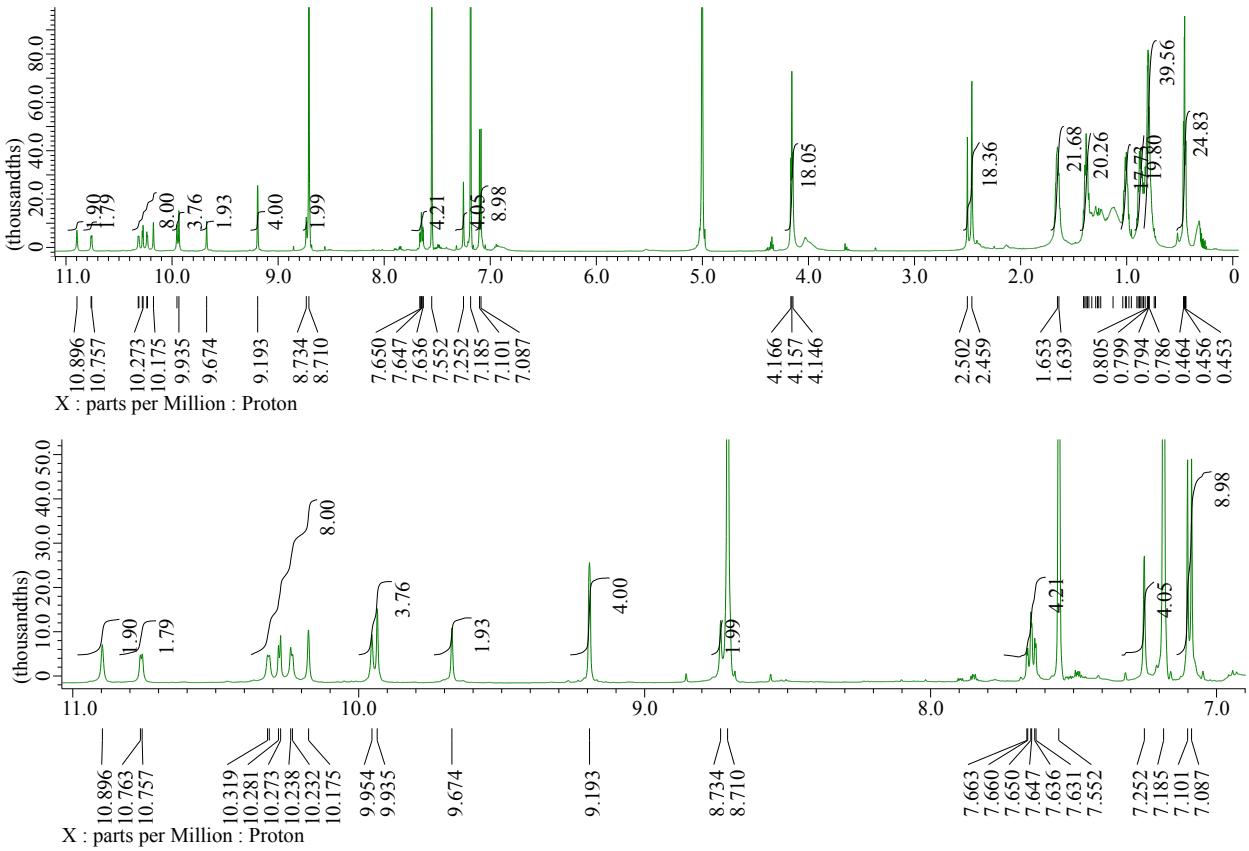
100 MHz ^{13}C NMR spectrum of **11** in $CDCl_3$.



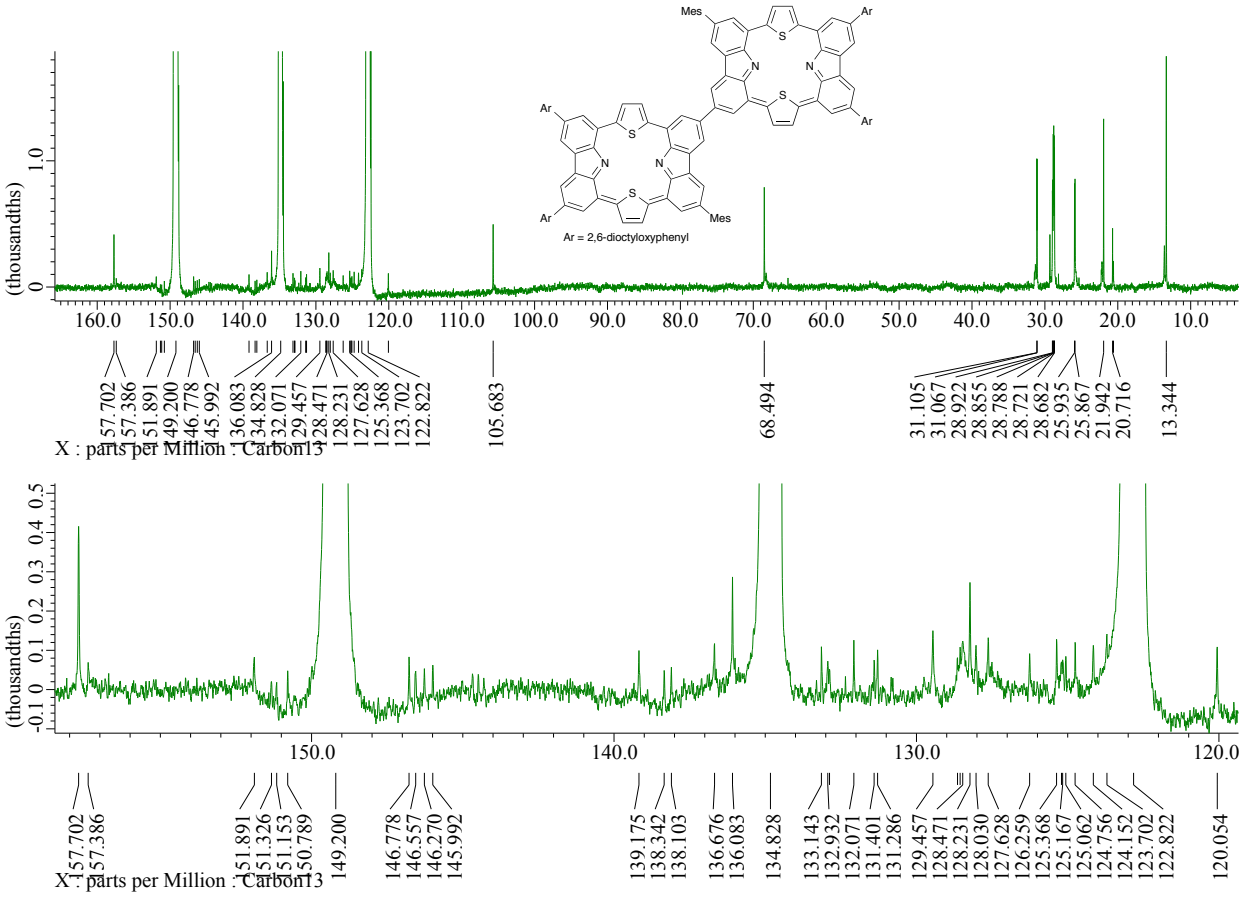
400 MHz ^{1}H NMR spectrum of **12** in $CDCl_3$.



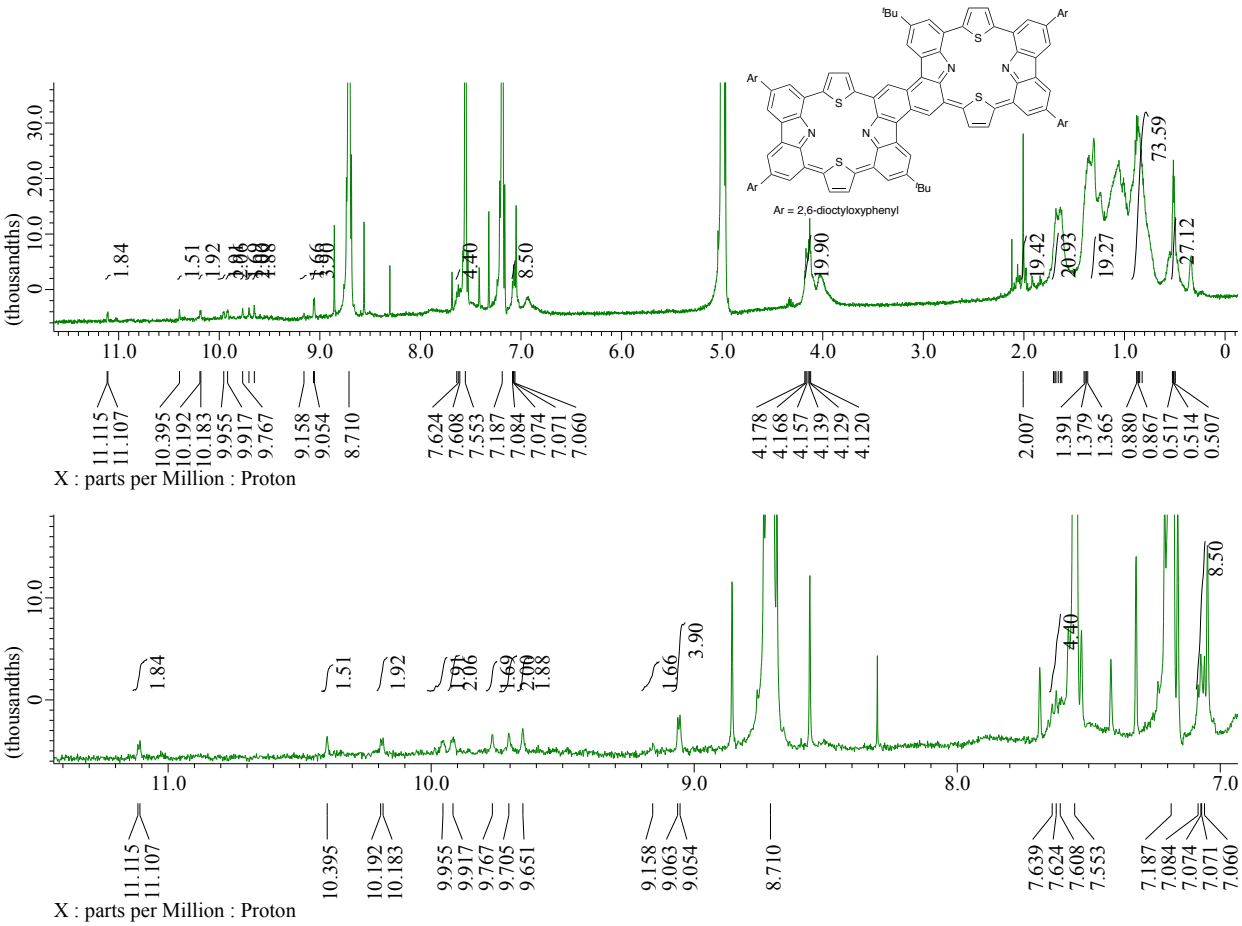
100 MHz ^{13}C NMR spectrum of **12** in $CDCl_3$.



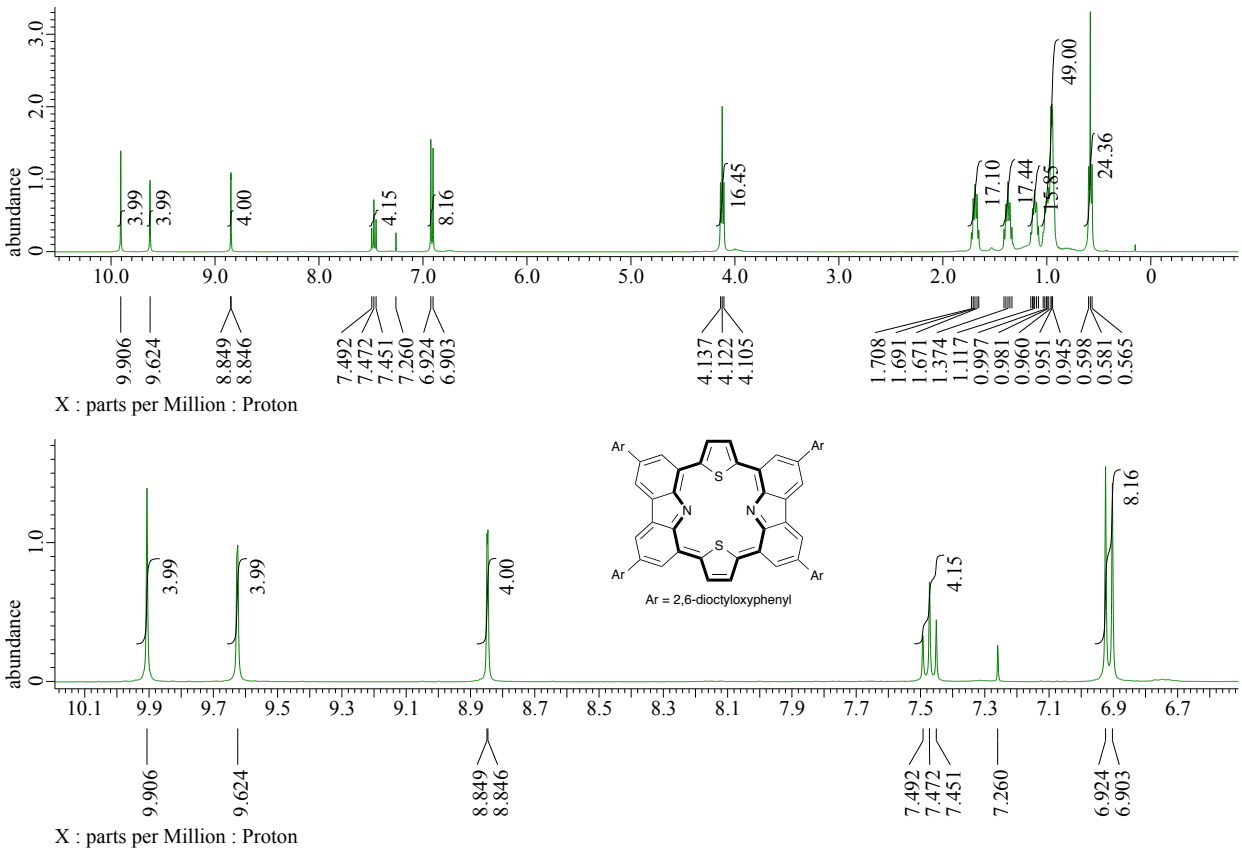
600 MHz ^{1}H NMR spectrum of **D2** in pyridine-d_5.



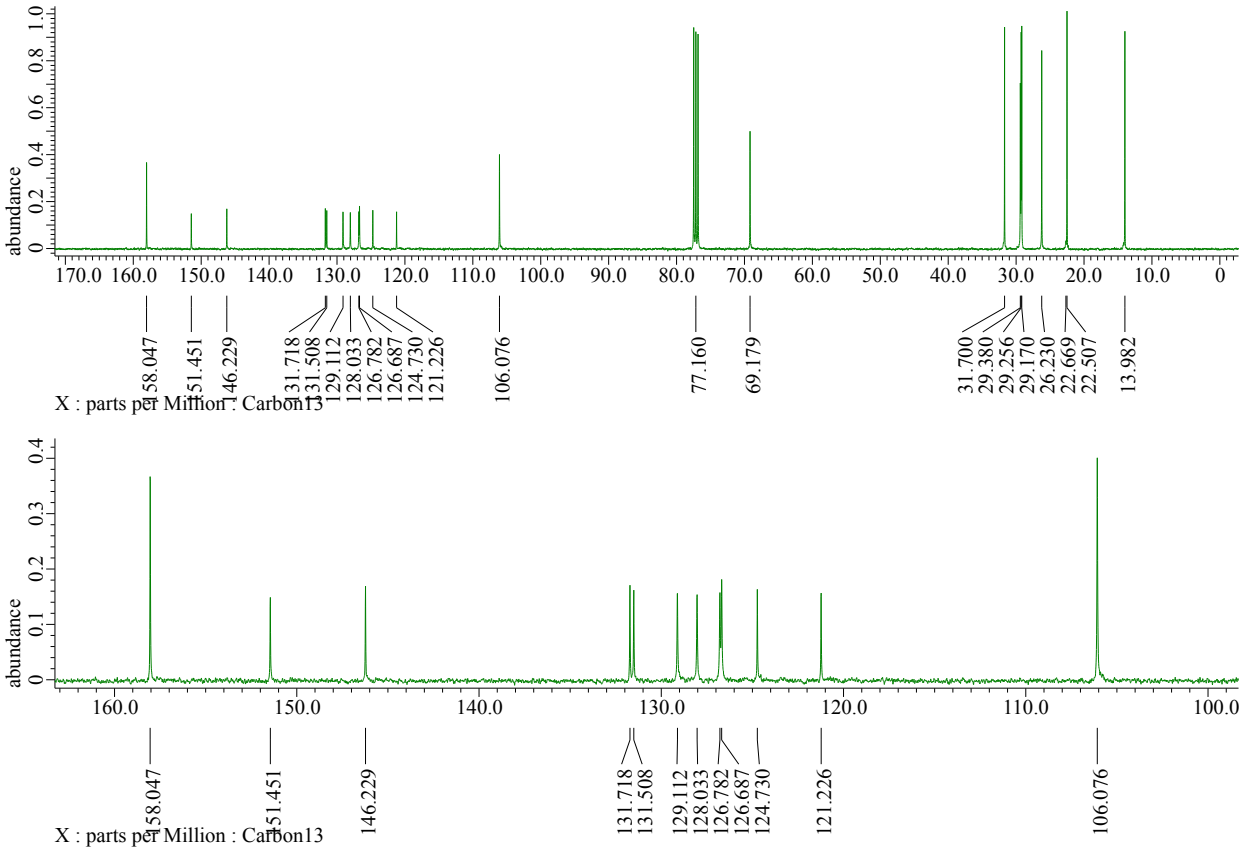
150 MHz ^{13}C NMR spectrum of **D2** in pyridine-d_5.



600 MHz ^{1}H NMR spectrum of **F2** in pyridine-d_5.

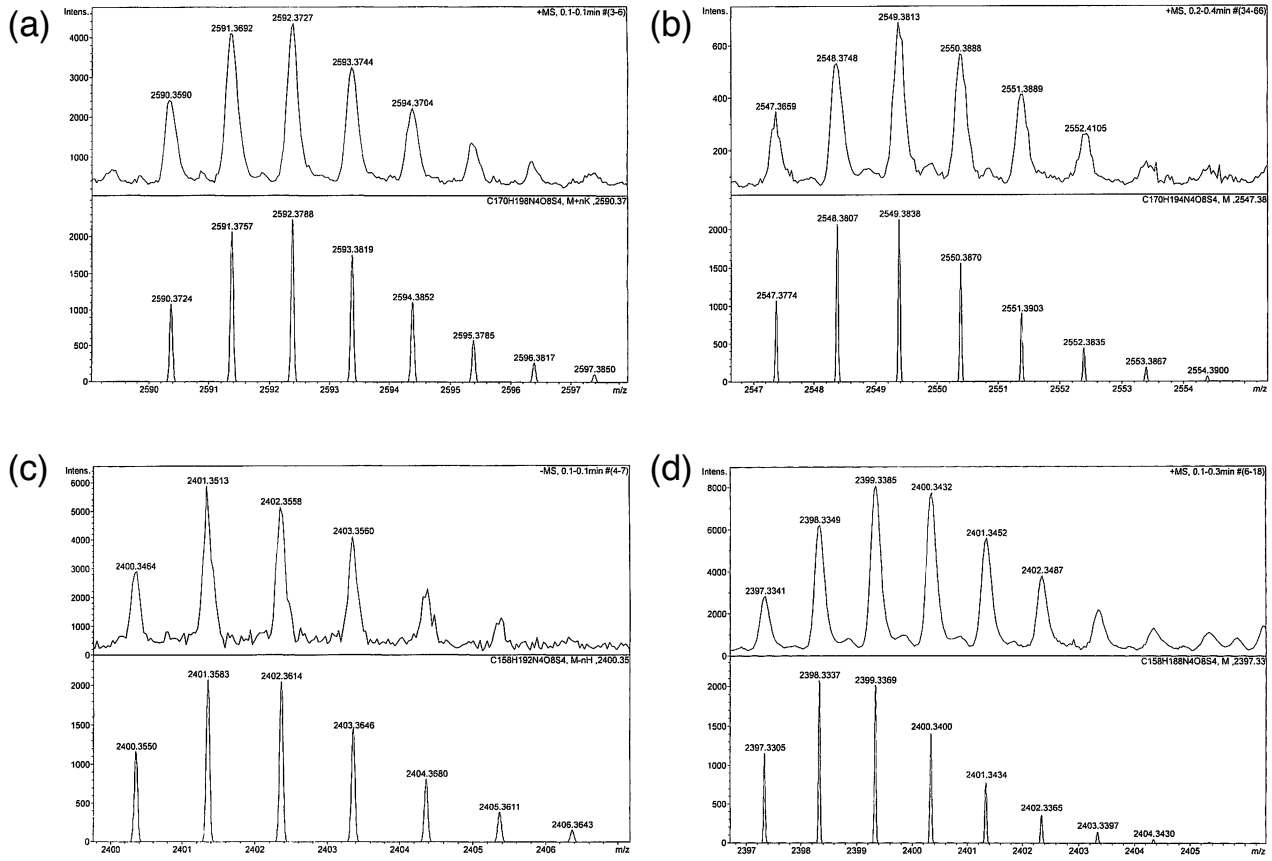


400 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$.



100 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$.

[F] Mass Spectra



Mass spectra of (a) **10**, (b) **D2**, (c) **12**, and (d) **F2**.