Supporting Information

Effective π-Extension of Carbazole-Based Thiaporphyrins by Peripheral Phenylethynyl Substituents

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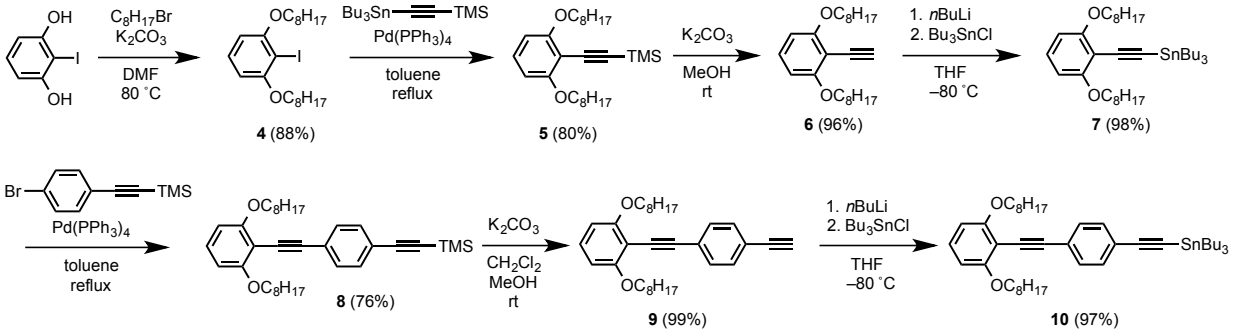
Instrumentation and materials

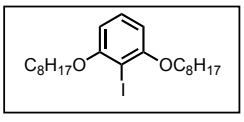
^{1}H and ^{13}C NMR spectra were taken on a JEOL ECA-500 spectrometer, and chemical shifts were reported as the delta scale in ppm as internal reference (δ = 7.260 for ^{1}H NMR, 77.00 for ^{13}C NMR, for $CDCl_3$). UV/vis/NIR absorption spectra were recorded on a JASCO V-650 spectrometer or on a JASCO V-570 spectrometer. Fluorescence spectra were recorded on HORIBA SPEX-Fluorog NIR-KD spectrometer. MALDI-TOF mass spectra were taken on a Bruker microTOF. Redox potentials were measured by cyclic voltammetry method and differential pulse voltammetry method on an ALS electrochemical analyzer model 6102B. Size-exclusion chromatography (SEC) was performed by using Bio-Rad Bio-Beads S-X1. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dry CH_2Cl_2 and toluene were distilled from CaH_2.

Experimental section



Scheme S1. Synthesis of **7** and **10**

1,3-Dioctyloxy-2-iodobenzene (4)

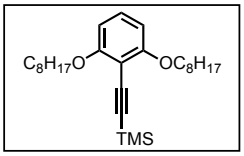


DMF (30 mL) solution of 2-iodoresorcinol (4.59 g, 19.4 mmol), 1-bromooctane (8.0 mL, 49 mmol), and K_2CO_3 (11 g, 80 mmol) was stirred for 16 h at 80˚C. The mixture was diluted with $CHCl_3$, washed with water, passed through a silica gel column with $CHCl_3$, and evaporated. The residue was separated over a silica gel column with

CH_2Cl_2/hexane as an eluent to give **4** (7.88 g, 17.1 mmol, 88%) as a colorless solid.

^{1}H NMR ($CDCl_3$) δ = 7.19 (t, J = 8.15 Hz, 1H, Ph), 6.45 (d, J = 8.30 Hz, 2H, Ph), 4.01 (t, J = 6.45 Hz, 4H, CH_2), 1.84 (m, 4H, CH_2), 1.53 (m, 4H, CH_2), 1.41-1.24 (16H, CH_2), and 0.90 ppm (t, J = 6.88 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 159.09, 129.47, 104.95, 79.10, 69.33, 31.79, 29.25, 29.21, 29.13, 26.07, 22.64, and 14.09 ppm; Mp: 41~42 ˚C.

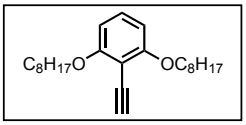
1,3-Dioctyloxy-2-trimethylsilylethynylbenzene (5)



A dry toluene (10 mL) solution of **4** (7.88 g, 17.1 mmol), $Pd(PPh_3)_4$, (154 mg, 133 μmol), and tributyl(trimethylsilylethynyl)tin (8.97 g, 23.2 mmol) was degassed. The mixture was stirred for 18 h at reflux under Ar. After the solvent was evaporated, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **5** (5.92 g, 13.7 mmol, 80%) as colorless oil.

^{1}H NMR ($CDCl_3$) δ = 7.13 (t, J = 8.30 Hz, 1H, Ph), 6.45 (d, J = 8.30 Hz, 2H, Ph), 3.99 (t, J = 6.30 Hz, 4H, CH_2), 1.81 (m, 4H, CH_2), 1.52 (m, 4H, CH_2), 1.34 (m, 4H, CH_2), 1.29 (m, 12H, CH_2), 0.89 (t, J = 7.03 Hz, 6H, CH_3), and 0.26 ppm (s, 9H, TMS); ^{13}C NMR ($CDCl_3$) δ = 161.54, 129.61, 104.58, 102.51, 102.48, 97.41, 68.76, 31.83, 29.38, 29.29, 29.27, 26.01, 22.65, 14.05, and 0.11 ppm.

1,3-Dioctyloxy-2-ethynylbenzene (6)

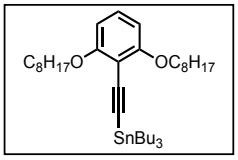


5 (5.92 g, 13.7 mmol) was treated with K_2CO_3 (6.32 g, 45.8 mmol) in MeOH (100 mL) for 14 h. After the solvent was removed under reduced pressure, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **6** (4.70 g, 13.1 mmol, 96%) as a pale orange solid.

^{1}H NMR ($CDCl_3$) δ = 7.17 (t, J = 8.45 Hz, 1H, Ph), 6.48 (d, J = 8.30 Hz, 2H, Ph), 4.02 (t, J = 6.60 Hz, 4H, CH_2), 3.45 (s, 1H, C≡CH), 1.82 (m, 4H, CH_2), 1.49 (m, 4H, CH_2), 1.29 (m, 16H, CH_2), and

0.90 ppm (t, J = 7.03 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.68, 129.75, 104.43, 101.33, 84.94, 76.21, 68.85, 31.73, 29.23, 29.16, 29.02, 25.85, 22.58, and 14.01 ppm; Mp: 37~38 ˚C.

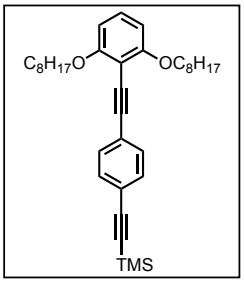
(2,6-Dioctyloxyphenylethynyl)tributyltin (7)



n-BuLi (1.64 M in hexane, 12.0 mL, 19.7 mmol) was added to a dehydrated THF (40 mL) solution of **6** (4.70 g, 13.1 mmol) at –78˚C under Ar, and the mixture was stirred for 20 min at –78˚C. Tributyltin chloride (3.9 mL, 14 mmol) was then added and the mixture was stirred for another 20 min at –78˚C. After warming up to rt, water was added. The mixture was diluted with $CHCl_3$, washed with water and brine, passed through a short silica gel column with $CHCl_3$. Organic solvents were removed under reduced pressure, which provided **7** (8.28 g, 12.8 mmol, 98%) as orange liquid.

^1H NMR ($CDCl_3$) δ = 7.09 (t, J = 8.30 Hz, 1H, Ph), 6.45 (d, J = 8.30 Hz, 2H, Ph), 3.99 (t, J = 6.60 Hz, 4H, CH_2), 1.81 (m, 4H, CH_2), 1.63 (m, 6H, CH_2), 1.49 (m, 4H, CH_2), 1.41-1.25 (22H, CH_2), 1.05 (t, J = 7.03 Hz, 6H, CH_2), 0.92 (t, J = 7.03 Hz, 9H, CH_3), and 0.89 ppm (t, J = 6.30 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.47, 128.71, 104.73, 103.51, 101.58, 101.48, 68.81, 31.90, 29.42, 29.31, 28.86, 27.04, 26.01, 22.67, 14.07, 13.64, and 11.13 ppm.

1,3-Dioctyloxy-2-(4-trimethylsilylethynyphenylethynyl)benzene (8)

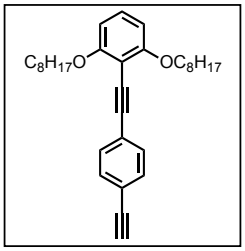


A dry toluene (20 mL) solution of **7** (4.61 g, 7.11 mmol), 1-bromo-4-trimethylsilylethynylbenzene[S1] (1.73 g, 6.84 mmol), $Pd_2(dba)_3$ (64.6 mg, 70.5 μmol), and PPh_3 (161 mg, 615 μmol) was degassed, and the mixture was stirred for 13 h at reflux under Ar. After the solvent was evaporated, the residue was separated over a silica gel column with CH_2Cl_2/hexane to give **8** (2.88 g, 5.42 mmol, 76%) as a yellow solid.

^1H NMR ($CDCl_3$) δ = 7.47 (d, J = 8.30 Hz, 2H, Ph), 7.43 (d, J = 8.55 Hz, 2H, Ph), 7.18 (t, J = 8.45 Hz, 1H, Ph), 6.51 (d, J = 8.30 Hz, 2H, Ph), 4.04 (t, J = 6.43 Hz, 4H, CH_2), 1.85 (m, 4H, CH_2), 1.56 (m,

4H, CH_2), 1.39 (m, 4H, CH_2), 1.35-1.21 (12H, CH_2), 0.90 (t, J = 7.00 Hz, 6H, CH_3), and 0.28 ppm (s, 9H, TMS); ^{13}C NMR ($CDCl_3$) δ = 160.99, 131.68, 131.11, 129.76, 124.66, 122.10, 104.95, 104.59, 102.34, 97.18, 95.61, 84.70, 68.82, 31.80, 29.37, 29.30, 29.26, 26.06, 22.64, 14.05, and –0.10 ppm; Mp: 56~58 ˚C.

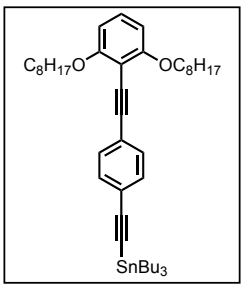
1,3-Dioctyloxy-2-(4-ethynyphenylethynyl)benzene (9)



8 (1.15 g, 2.17 mmol) was treated with K_2CO_3 (1.09 g, 7.90 mmol) in CH_2Cl_2/MeOH (10 mL/10 mL) for 14 h. After the solvents were removed under reduced pressure, the residue was separated over a silica gel column with $CHCl_3$ as an eluent to give **9** (981 mg, 2.14 mmol, 99%) as brown oil.

^{1}H NMR ($CDCl_3$) δ = 7.48 (dd, J = 1.9, 8.75 Hz, 2H, Ph), 7.44 (dd, J = 1.7, 8.60 Hz, 2H, Ph), 7.18 (t, J = 9.30 Hz, 1H, Ph), 6.51 (d, J = 8.30 Hz, 2H, Ph), 4.04 (t, J = 6.40 Hz, 4H, CH_2), 3.16 (s, 1H, C≡CH), 1.85 (m, 4H, CH_2), 1.54 (m, 4H, CH_2), 1.38 (m, 4H, CH_2), 1.34-1.20 (m, 12H, CH_2), and 0.88 ppm (t, J = 6.00 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.05, 131.87, 131.22, 129.84, 125.07, 121.07, 104.64, 102.31, 97.01, 84.76, 83.54, 78.40, 68.89, 31.81, 29.38, 29.31, 29.28, 26.08, 22.66, and 14.07 ppm.

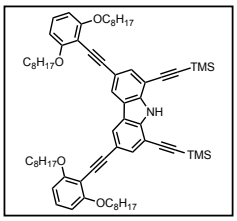
[4-(2,6-Dioctyloxyphenylethynyl)phenylethynyl]tributyltin (10)



n-BuLi (1.64 M in hexane, 2.50 mL, 4.10 mmol) was added to a dehydrated THF (20 mL) solution of **9** (981 mg, 2.14 mmol) at –78˚C under Ar, and the mixture was stirred for 10 min at –78˚C. Tributyltin chloride (0.61 mL, 2.2 mmol) was then added and the mixture was stirred for another 10 min at –78˚C. After warming up to rt, water was added. The mixture was diluted with CH_2Cl_2, washed with water and brine, passed through a short silica gel column with CH_2Cl_2. Organic solvents were removed under reduced pressure, which provided **10** (1.55 g, 2.07 mmol, 97%) as orange oil.

^{1}H NMR ($CDCl_3$) δ = 7.45 (dd, J = 1.2, 8.00 Hz, 2H, Ph), 7.42 (dd, J = 1.5, 8.30 Hz, 2H, Ph), 7.17 (t, J = 8.30 Hz, 1H, Ph), 6.51 (d, J = 8.30 Hz, 2H, Ph), 4.04 (t, J = 6.30 Hz, 4H, CH_2), 1.85 (m, 4H, CH_2), 1.65 (m, 6H, CH_2), 1.56 (m, 4H, CH_2), 1.40 (m, 10H, CH_2), 1.35-1.22 (m, 12H, CH_2), 1.09 (t, J = 7.73 Hz, 6H, CH_2), 0.95 (dt, J = 1.6, 7.25 Hz, 9H, CH_3), and 0.88 ppm (dt, J = 1.7, 6.80 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 160.97, 131.63, 131.08, 129.62, 123.93, 123.08, 109.92, 104.62, 102.50, 97.36, 95.02, 84.26, 68.84, 31.81, 29.39, 29.31, 29.29, 28.87, 26.94, 26.08, 22.65, 14.04, 13.64, and 11.16 ppm.

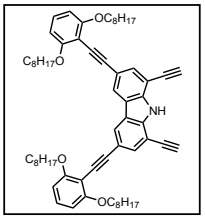
3,6-Bis(2,6-dioctyloxyphenylethynyl)-1,8-bis(trimethylsilylethynyl)carbazole (12a)



A dry toluene (10 mL) solution of 3,6-dibromo-1,8-bis(trimethylsilylethynyl)carbazole (**11**)[S2] (286 mg, 581 μmol), **7** (1.24 g, 1.91 mmol), and $Pd(PPh_3)_4$, (46.0 mg, 23.7 μmol) was degassed. The mixture was stirred for 17 h at reflux under Ar. After the solvent was evaporated, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **12a** (249 mg, 232 μmol, 46%) as orange oil.

^{1}H NMR ($CDCl_3$) δ = 8.62 (s, 1H, NH), 8.19 (d, J = 1.2 Hz, 2H, carbazole-H), 7.76 (d, J = 1.4 Hz, 2H, carbazole-H), 7.18 (t, J = 8.30 Hz, 2H, Ph), 6.55 (d, J = 8.30 Hz, 4H, Ph), 4.09 (t, J = 6.43 Hz, 8H, CH_2), 1.90 (m, 8H, CH_2), 1.59 (m, 8H, CH_2), 1.42 (m, 8H, CH_2), 1.32 (m, 8H, CH_2), 1.27 (m, 16H, CH_2), 0.81 (t, J = 7.03 Hz, 12H, CH_3), and 0.37 ppm (s, 18H, TMS); ^{13}C NMR ($CDCl_3$) δ = 160.94, 139.84, 132.65, 129.17, 124.45, 122.90, 116.41, 106.12, 104.74, 102.93, 99.83, 99.80, 97.47, 81.17, 68.90, 31.74, 29.36, 29.31, 29.28, 26.09, 22.59, 13.98, and 0.03 ppm; MALDI-TOF-MS: m/z = 1070.63. calcd for $C_{70}H_{97}NO_4Si_2$: 1070.69 [$(M–H)^–$]; UV/vis (CH_2Cl_2) λ_{max} (ε) = 292 (49000), 301 (47600), and 340 nm (55600 $mol^{-1}dm^3cm^{-1}$).

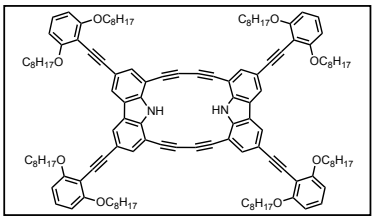
1,8-Diethynyl-3,6-bis(2,6-dioctyloxyphenylethynyl)carbazole (13a)



Tetrabutylammonium fluoride (1.0 M in THF, 0.70 mL, 0.70 mmol) was added to a CH_2Cl_2 (5 mL) solution of **12a** (241 mg, 225 μmol) and stirred for 10 min. After the solvent was evaporated, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **13a** (154 mg, 166 μmol, 74%) as yellow oil.

^{1}H NMR ($CDCl_3$) δ = 8.69 (s, 1H, NH), 8.23 (d, J = 1.2 Hz, 2H, carbazole-H), 7.81 (d, J = 1.5 Hz, 2H, carbazole-H), 7.19 (t, J = 8.30 Hz, 2H, Ph), 6.55 (d, J = 8.55 Hz, 4H, Ph), 4.09 (t, J = 6.43 Hz, 8H, CH_2), 3.50 (s, 2H, C≡CH), 1.91 (m, 8H, CH_2), 1.59 (m, 8H, CH_2), 1.42 (m, 8H, CH_2), 1.33 (m, 8H, CH_2), 1.25 (m, 16H, CH_2), and 0.81 ppm (t, J = 7.00 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 160.97, 140.00, 133.36, 129.28, 124.65, 123.03, 116.54, 105.04, 104.73, 102.80, 97.30, 82.35, 81.35, 78.87, 68.93, 31.80, 29.43, 29.36, 29.30, 26.14, 22.61, and 14.00 ppm; MALDI-TOF-MS: m/z = 926.63. calcd for $C_{64}H_{80}NO_4$: 926.61 [$(M–H)^-$]; UV/vis (CH_2Cl_2) λ_{max} (ε) = 288 (41800), 304 (43200), and 370 (56300 $mol^{-1}dm^3cm^{-1}$).

3,3',6,6'-Tetrakis(2,6-dioctyloxyphenylethynyl)-substituted butadiyne-bridged carbazole dimer (14a)

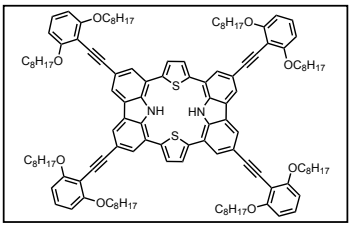


To a pyridine (10 mL) suspension of $Cu(OAc)_2$ (274 mg, 1.50 mmol) was added dropwise a toluene (100 mL) solution of **13a** (169 mg, 182 μmol) for 2 h, and the mixture was stirred for further 2.5 days under air. After the solvents were evaporated, the residue was separated over a silica gel column with $CHCl_3$ and SEC column to give **14a** (92.5 mg, 49.9 μmol, 55%) as an yellow solid.

^{1}H NMR ($CDCl_3$) δ = 9.44 (s, 2H, NH), 8.21 (d, J = 1.2 Hz, 4H, carbazole-H), 7.72 (d, J = 1.2 Hz, 4H, carbazole-H), 7.17 (t, J = 8.30 Hz, 4H, Ph), 6.53 (d, J = 8.30 Hz, 8H, Ph), 4.08 (t, J = 6.60 Hz, 16H, CH_2), 1.91 (m, 16H, CH_2), 1.59 (m, 16H, CH_2), 1.42 (m, 16H, CH_2), 1.34 (m, 16H, CH_2), 1.27 (m, 32H, CH_2), and 0.82 ppm (t, J = 6.88 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 160.98, 142.05, 131.22, 129.34, 125.50, 123.00, 116.78, 104.81, 104.68, 102.66, 97.22, 81.61, 79.79, 79.42, 68.95, 31.87, 29.49, 29.46,

29.33, 26.18, 22.68, and 14.09 ppm; MALDI-TOF-MS: *m*/*z* = 1852.29. calcd for $C_{128}H_{158}N_2O_8$: 1852.21 [M^-]; Mp: 128–130 ˚C; UV/vis (CH_2Cl_2) λ_{max} (ε) = 310 (138000), 332 (166000), and 440 nm (50400 $mol^{-1}dm^3cm^{-1}$).

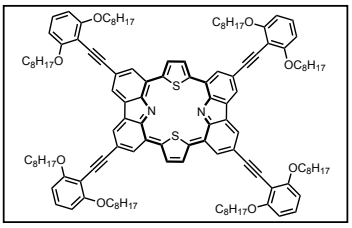
3,3',6,6'-Tetrakis(2,6-dioctyloxyphenylethynyl)-substituted isophlorine (15a)



A *p*-xylene/2-methoxyethanol (5.0 mL/5.0 mL) solution of **14a** (112 mg, 60.4 μmol) and $Na_2S{\cdot}9H_2O$ (147 mg, 613 μmol) was heated refluxed for 9 h under Ar. The mixture was diluted with $CHCl_3$, washed with water, and passed through a silica gel column with $CHCl_3$. Solvents were removed under the reduced pressure, which gave **15a** (109 mg, 56.7 μmol, 94%) as orange oil.

^{1}H NMR ($CDCl_3$) δ = 10.56 (s, 2H, NH), 8.31 (d, *J* = 1.2 Hz, 4H, carbazole-H), 8.00 (d, *J* = 1.5 Hz, 4H, carbazole-H), 7.49 (s, 4H, thiophene-β), 7.13 (t, *J* = 8.30 Hz, 4H, Ph), 6.45 (d, *J* = 8.60 Hz, 8H, Ph), 4.13 (t, *J* = 6.60 Hz, 16H, CH_2), 1.94 (m, 16H, CH_2), 1.63 (m, 16H, CH_2), 1.43 (m, 16H, CH_2), 1.33 (m, 16H, CH_2), 1.24 (m, 32H, CH_2), and 0.80 ppm (t, *J* = 7.00 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.00, 138.93 136.78, 129.22, 127.78, 127.17, 124.21, 124.08, 117.70, 116.94, 104.85, 103.03, 98.10, 81.25, 69.00, 31.82, 29.47, 29.39, 29.32, 26.15, 22.62, and 14.02 ppm; MALDI-TOF-MS: *m*/*z* = 1919.10. calcd for $C_{128}H_{161}N_2O_8S_2$: 1919.17 [$(M-H)^-$]; UV/vis (CH_2Cl_2) λ_{max} (ε) = 312 (120000), 331 (132000), and 417 nm (21100 $mol^{-1}dm^3cm^{-1}$).

3,3',6,6'-Tetrakis(2,6-dioctyloxyphenylethynyl)-substituted carbazole based porphyrin (2a)

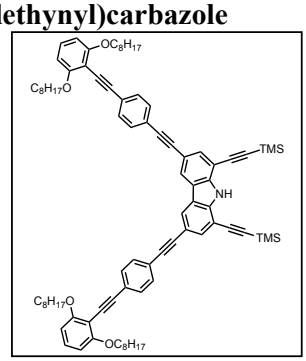


To a dry CH_2Cl_2 (20 mL) solution of **15a** (91.3 mg, 47.5 μmol) was added MnO_2 (971 mg) and resulting suspension was stirred. After 15 h, MnO_2 (898 mg) was added and the mixture was stirred for further 9 h. The mixture was then passed through a pad of silica gel. Evaporation

of the solvent provided **2a** (73.3 mg, 38.2 μmol, 80%) as a black solid.

^{1}H NMR ($CDCl_3$) δ = 9.71 (s, 4H, carbazole-H), 9.50 (s, 4H, carbazole-H), 8.67 (s, 4H, thiophene-β), 7.30 (t, J = 8.15 Hz, 4H, Ph), 6.65 (d, J = 8.45 Hz, 8H, Ph), 4.22 (t, J = 6.45 Hz, 16H, CH_2), 2.07 (m, 16H, CH_2), 1.74 (m, 16H, CH_2), 1.54 (m, 16H, CH_2), 1.41 (m, 16H, CH_2), 1.29 (m, 16H, CH_2), 1.22 (m, 16H, CH_2), and 0.74 ppm (t, J = 7.18 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.28, 151.52, 145.51, 131.87, 129.90, 128.50, 127.10, 125.93, 125.13, 121.85, 104.73, 102.92, 100.23, 86.81, 69.50, 31.85, 29.55, 29.47, 29.42, 26.24, 22.61, and 13.98 ppm; MALDI-TOF-MS: m/z = 1917.15. calcd for $C_{128}H_{159}N_2O_8S_2$: 1917.15 [$(M–H)^–$]; Mp: 93–95 ˚C; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 306 (101000), 339 (90400), 972 (45400), 1030 (54700), and 1122 nm (70200 $mol^{-1}dm^3cm^{-1}$).

3,6-Bis(2,6-dioctyloxyphenylethynylphenylethynyl)-1,8-bis(trimethylsilylethynyl)carbazole (12b)

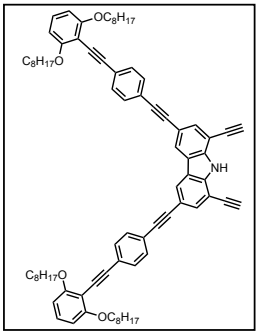


A dry toluene (20 mL) solution of **11** (477 mg, 923 μmol), **10** (2.49 g, 3.33 mmol), and $Pd(PPh_3)_4$, (54.9 mg, 47.5 μmol) was degassed. The mixture was stirred for 18 h at reflux under Ar. After the solvent was evaporated, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **12b** (538 mg, 423 μmol, 46%) as orange oil.

^{1}H NMR ($CDCl_3$) δ = 8.66 (s, 1H, NH), 8.21 (d, J = 1.2 Hz, 2H, carbazole-H), 7.78 (d, J = 1.5 Hz, 2H, carbazole-H), 7.53 (d, J = 5,70 Hz, 4H, Ph), 7.52 (d, J = 8.35 Hz, 4H, Ph), 7.19 (t, J = 8.30 Hz, 2H, Ph), 6.52 (d, J = 8.30 Hz, 4H, Ph), 4.06 (t, J = 6.45 Hz, 8H, CH_2), 1.87 (m, 8H, CH_2), 1.57 (m, 8H, CH_2), 1.40 (m, 8H, CH_2), 1.31 (m, 24H, CH_2), 0.90 (t, J = 6.88 Hz, 12H, CH_3), and 0.37 ppm (s, 18H, TMS); ^{13}C NMR ($CDCl_3$) δ = 160.02. 140.14, 132.85, 131.34, 131.26, 129.73, 124.72, 124.26, 122.92, 122.46, 115.17, 106.53, 104.65, 102.45, 100.52, 99.37, 97.36, 90.86, 88.37, 84.56, 68.90, 31.82, 29.39, 29.33, 29.29, 26.09, 22.67, 14.10, and 0.03 ppm; MALDI-TOF-MS: m/z = 1271.77. calcd for

$C_{86}H_{105}NO_4Si_2$: 1271.762 [M^+]; UV/vis (CH_2Cl_2) λ_{max} (ε) = 343 (95500), and 372 nm (78100 $mol^{-1}dm^3cm^{-1}$).

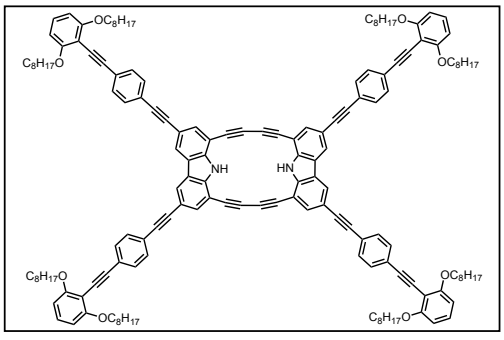
1,8-Diethynyl-3,6-bis(2,6-dioctyloxyphenylethynylphenylethynyl)carbazole (13b)



Tetrabutylammonium fluoride (0.50 mL, 1.0 M in THF, 0.50 mmol) was added to a $CHCl_3$ (20 mL) solution of **12b** (150 mg, 188 μmol) and stirred for 10 min. The mixture was passed through a silica gel column with $CHCl_3$, and solvent was evaporated, which provided **13b** (113 mg, 115 μmol, 97%) as orange oil.

^{1}H NMR ($CDCl_3$) δ = 8.71 (s, 1H, NH), 8.23 (d, J = 1.2 Hz, 2H, carbazole-H), 7.79 (d, J = 1.2 Hz, 2H, carbazole-H), 7.54 (s, 8H, Ph), 7.18 (t, J = 8.30 Hz, 2H, Ph), 6.52 (d, J = 8.30 Hz, 4H, Ph), 4.05 (t, J = 6.30 Hz, 8H, CH_2), 3.53 (s, 2H, C≡CH), 1.88 (m, 8H, CH_2), 1.57 (m, 8H, CH_2), 1.40 (m, 8H, CH_2), 1.31 (m, 8H, CH_2), 1.21 (m, 16H, CH_2), and 0.91 ppm (t, J = 7.03 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 160.99, 140.26, 133.39, 131.34, 131.27, 129.72, 124.94, 124.32, 122.98, 122.35, 115.29, 105.41, 104.61, 102.41, 97.33, 90.65, 88.50, 84.63, 82.86, 78.53, 68.86, 31.81, 29.39, 29.32, 29.28, 26.08, 22.66, and 14.09 ppm; MALDI-TOF-MS: m/z = 1126.67. calcd for $C_{80}H_{88}NO_4$: 1126.67 [$(M–H)^-$]; UV/vis (CH_2Cl_2) λ_{max} (ε) = 344 (92600), and 370 nm (76900 $mol^{-1}dm^3cm^{-1}$).

3,3',6,6'-Tetrakis(2,6-dioctyloxyphenylethynylphenylethynyl)-substituted butadiyne-bridged carbazole dimer (14b)

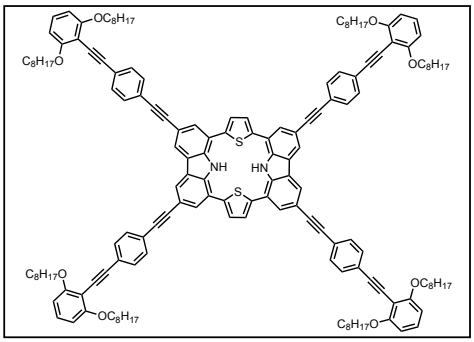


To a pyridine (10 mL) suspension of $Cu(OAc)_2$ (259 mg, 1.42 mmol) was added dropwise a toluene (100 mL) solution of **13b** (113 mg, 115 μmol) for 3 h, and the mixture was stirred for further 4 days under air. After the solvents were evaporated, the residue was separated over a

silica gel column with $CHCl_3$ and SEC column to give **14b** (39.2 mg, 17.4 μmol, 30%) as an orange solid.

^{1}H NMR ($CDCl_3$) δ = 9.92 (s, 2H, NH), 8.12 (s, 4H, carbazole-H), 7.60 (d, J = 1.2 Hz, 4H, carbazole-H), 7.45 (d, J = 8.30 Hz, 8H, Ph), 7.42 (d, J = 8.30 Hz, 8H, Ph), 7.09 (t, J = 8.33 Hz, 4H, Ph), 6.42 (d, J = 8.30 Hz, 8H, Ph), 3.98 (t, J = 6.88 Hz, 16H, CH_2), 1.85 (m, 16H, CH_2), 1.54 (m, 16H, CH_2), 1.38 (m, 16H, CH_2), 1.30 (m, 48H, CH_2), and 0.91 ppm (t, J = 6.88 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 160.92, 142.40, 131.24, 129.63, 125.61, 124.19, 122.83, 122.32, 115.30, 105.05, 104.50, 102.34, 97.53, 90.75, 88.62, 84.74, 80.00, 79.56, 68.90, 31.87, 29.47, 29.37, 29.34, 26.10, 22.71, and 14.15 ppm; MALDI-TOF-MS: m/z = 2252.36. calcd for $C_{160}H_{174}N_2O_8$: 2252.33 [M^-]; Mp: 201–204 ˚C; UV/vis (CH_2Cl_2) λ_{max} (ε) = 346 (261000), 414 (32400), and 436 nm (67900 $mol^{-1}dm^3cm^{-1}$).

3,3',6,6'-Tetrakis(2,6-dioctyloxyphenylethynylphenylethynyl)-substituted isophlorine (15b)

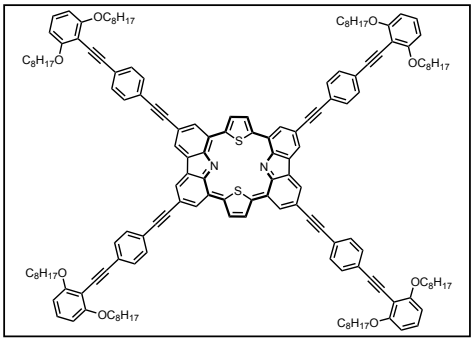


A *p*-xylene/2-methoxyethanol (2.0 mL/2.0 mL) solution of **14b** (39.2mg, 17.4 μmol) and $Na_2S{\cdot}9H_2O$ (77.2 mg, 332 μmol) was heated refluxed for 11 h under Ar. The mixture was diluted with $CHCl_3$, washed with water, and passed through a silica gel column with $CHCl_3$. Solvents were removed under reduced pressure, which gave **15b** (34.2 mg, 14.7 μmol, 84%) as a yellow solid.

^{1}H NMR ($CDCl_3$) δ = 10.45 (s, 2H, NH), 8.25 (s, 4H, carbazole-H), 7.94 (d, J = 1.2 Hz, 4H, carbazole-H), 7.54 (d, J = 8.60 Hz, 8H, Ph), 7.52 (d, J = 8.60 Hz, 8H, Ph), 7.51 (s, 4H, thiophene-β), 7.18 (t, J = 8.30 Hz, 4H, Ph), 6.51 (d, J = 8.60 Hz, 8H, Ph), 4.04 (t, J = 6.48 Hz, 16H, CH_2), 1.87 (m, 16H, CH_2), 1.56 (m, 16H, CH_2), 1.40 (m, 16H, CH_2), 1.31 (m, 48H, CH_2), and 0.91 ppm (t, J = 6.88 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.03, 138.62, 136.94, 131.35, 131.29, 129.70, 127.71, 127.31, 124.45, 124.24, 124.07, 122.51, 117.89, 115.74, 104.64, 102.49, 97.44, 91.46, 88.60, 84.61, 68.91,

31.85, 29.42, 29.36, 29.31, 26.10, 22.70, and 14.13 ppm; MALDI-TOF-MS: *m*/*z* = 2320.31. calcd for $C_{160}H_{178}N_2O_8S_2$: 2320.31 [M^-]; Mp: 197–199 ˚C; UV/vis (CH_2Cl_2) λ_{max} (ε) = 346 (205000), 373 (145000), and 410 nm (27200 $mol^{-1}dm^3cm^{-1}$).

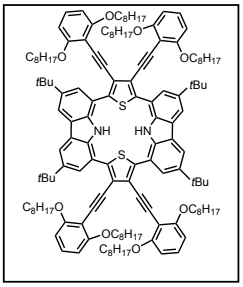
3,3',6,6'-Tetrakis(2,6-dioctyloxyphenylethynylphenylethynyl)-substituted carbazole-based porphyrin (2b)



To a dry CH_2Cl_2 (20 mL) solution of **15b** (69.2 mg, 29.8 μmol) was added MnO_2 (746 mg) and resulting suspension was stirred. After 17 h, the mixture was then passed through a silica gel column with CH_2Cl_2. Evaporation of the solvent provided **2b** (49.8 mg, 21.5 μmol, 72%) as a black solid.

^{1}H NMR ($CDCl_3$) δ = 8.83 (s, 4H, carbazole-H), 8.72 (s, 4H, carbazole-H), 8.08 (s, 4H, thiophene-β), 7.81 (s, *J* = 7.20 Hz, 8H, Ph), 7.71 (d, *J* = 7.20 Hz, 8H, Ph), 7.21 (t, *J* = 8.15 Hz, 4H, Ph), 6.55 (d, *J* = 8.00 Hz, 8H, Ph), 4.04 (t, *J* = 6.03 Hz, 16H, CH_2), 1.92 (m, 16H, CH_2), 1.61 (m, 16H, CH_2), 1.47–1.21 (64H, CH_2), and 0.99 ppm (t, *J* = 6.75 Hz, 24H, CH_3); ^{13}C NMR δ = 161.17, 149.80, 145.07, 131.80, 131.64, 131.40, 130.64, 129.50, 128.06, 126.19, 124.84, 123.22, 122.68, 119.23, 104.59, 102.77, 97.75, 93.69, 92.81, 85.19, 68.95, 31.96, 29.52, 29.47, 29.37, 26.16, 22.81, and 14.25 ppm; MALDI-TOF-MS: *m*/*z* = 2317.31. calcd for $C_{160}H_{175}N_2O_8S_2$: 2317.28 [(M–H)]$^-$]; 207–209 ˚C; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 352 (206000), 972 (54800), 1029 (60100), and 1126 nm (70600 $mol^{-1}dm^3cm^{-1}$).

***β*-Tetrakis(2,6-dioctyloxyphenylethynyl)-substituted isophlorine (17a)**

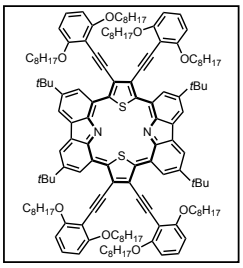


A dry toluene (2.5 mL) solution of **9**[S2] (33.5 mg, 32.4 μmol), $Pd_2(dba)_3$ (5.9 mg, 6.4 μmol), PPh_3 (14.0 mg, 53.4 μmol), and **7** (939 mg, 1.46 mmol) was degassed. The mixture was stirred for 15 h at reflux under Ar. After the

solvent was evaporated, the residue was separated by SEC column with $CHCl_3$ and by a silica gel column with CH_2Cl_2/hexane as an eluent to give **17a** (51.2 mg, 23.9 μmol, 74%).

^{1}H NMR ($CDCl_3$) δ = 10.10 (s, 2H, NH), 8.53 (d, J = 1.7 Hz, 4H, carbazole-H), 8.07 (d, J = 1.5 Hz, 4H, carbazole-H), 7.20 (t, J = 8.30 Hz, 4H, Ph), 6.43 (d, J = 8.55 Hz, 8H, Ph), 3.80 (t, J = 7.03 Hz, 16H, CH_2), 1.43 (s, 36H, *t*-Bu; m, 16H, CH_2), 1.21~1.02 (80H, CH_2), and 0.78 ppm (t, J = 7.15 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.40, 142.66, 137.69, 135.61, 129.05, 124.66, 124.64, 124.10, 116.68, 116.09, 105.17, 103.90, 92.06, 87.10, 69.33, 34.95, 31.92, 31.73, 29.16, 28.74, 25.76, 22.61, and 14.03 ppm; MALDI-TOF-MS: m/z = 2145.44. calcd for $C_{144}H_{195}N_2O_8S_2$: 2145.44 [$(M–H)^–$]; Mp: 46–50 ˚C; UV/vis (CH_2Cl_2) λ_{max} (ε) = 306 (73100), 334 (72400), and 420 nm (19900 $mol^{-1}dm^3cm^{-1}$).

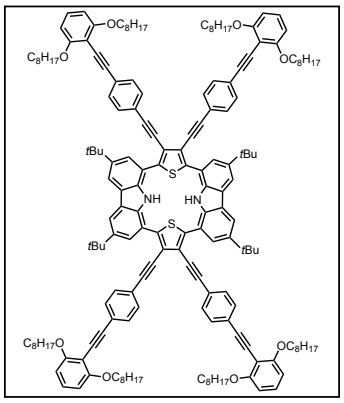
***β*-Tetrakis(2,6-dioctyloxyphenylethynyl)-substituted thiaporphyrin (3a)**



To a dry CH_2Cl_2 (5 mL) solution of **17a** (51.2 mg, 23.9 μmol) was added PbO_2 (143 mg) and resulting suspension was stirred for 4 days, during which further PbO_2 (1.94 g) was added in several portions. The mixture was then passed through a pad of celite. Evaporation of the solvent provided **3a** (38.1 mg, 17.8 μmol, 76%).

^{1}H NMR ($CDCl_3$) δ = 10.98 (s, 4H, carbazole-H), 8.72 (s, 4H, carbazole-H), 7.25 (t, J = 8.30 Hz, 4H, Ph), 6.57 (d, J = 8.60 Hz, 8H, Ph), 3.90 (t, J = 6.88 Hz, 16H, CH_2), 1.67 (s, 36H, *t*-Bu), 1.57 (m, 16H, CH_2), 1.22 (m, 16H, CH_2), 1.03 (m, 16H, CH_2), 0.91 (m, 48H, CH_2), and 0.55 ppm (t, J = 6.38 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.39, 151.74, 148.40, 143.06, 131.64, 129.33, 128.15, 124.98, 123.84, 121.02, 104.78, 104.32, 96.48, 94.83, 69.29, 36.21, 31.64, 31.57, 29.31, 29.12, 29.01, 26.03, 22.40, and 13.85 ppm; MALDI-TOF-MS: m/z = 2142.39. calcd for $C_{144}H_{192}N_2O_8S_2$: 2142.42 [$M^–$]; Mp: 98–100 ˚C; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 306 (51600), 339 (54600), 397 (38000), 490 (37100), 879 (34100), 959 (20800), and 1111 nm (88100 $mol^{-1}dm^3cm^{-1}$).

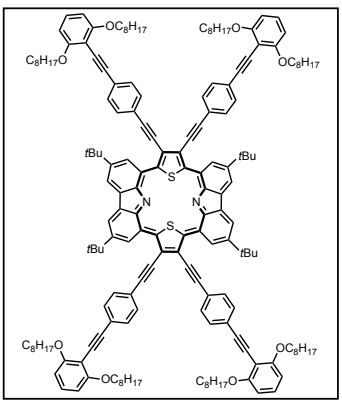
β-Tetrakis(2,6-dioctyloxyphenylethynylphenylethynyl)-substituted isophlorine (17b)



A dry toluene (3 mL) solution of **16** (31.9 mg, 31.0 μmol), $Pd(PPh_3)_4$, (9.9 mg, 8.6 μmol), and **10** (240 mg, 322 μmol) was degassed. The mixture was stirred for 23 h at reflux under Ar. After the solvent was evaporated, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **17b** (78.7 mg, 30.9 μmol, 99.7%).

^{1}H NMR ($CDCl_3$) δ = 9.95 (s, 2H, NH), 8.39 (d, J = 1.7 Hz, 4H, carbazole-H), 8.23 (d, J = 1.2 Hz, 4H, carbazole-H), 7.53 (d, J = 8.55 Hz, 8H, Ph), 6.51 (d, J = 8.55 Hz, 8H, Ph), 7.19 (t, J = 8.30 Hz, 4H, Ph), 6.53 (d, J = 8.60 Hz, 8H, Ph), 4.06 (t, J = 6.30 Hz, 16H, CH_2), 1.87 (m, 16H, CH_2), 1.56 (s, 36H, *t*Bu, and m, 16H, CH_2), 1.39 (m, 16H, CH_2), 1.36-1.20 (m, 48H, CH_2), and 0.86 ppm (t, J = 6.88 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 161.04, 143.26, 139.33, 135.99, 131.51, 131.30, 129.72, 124.66, 124.44, 123.93, 123.30, 122.10, 117.79, 115.57, 104.61, 102.47, 97.32, 94.51, 85.50, 84.82, 68.88, 35.02, 32.10, 31.76, 29.31, 29.28, 29.23, 26.03, 22.63, and 14.06 ppm; MALDI-TOF-MS: m/z = 2543.80. $C_{176}H_{209}N_2O_8S_2$: 2543.55 [$(M–H)^-$]; Mp: > 300 ˚C; UV/vis (CH_2Cl_2) λ_{max} (ε) = 346 nm (140000 $mol^{-1}dm^3cm^{-1}$).

β-Tetrakis(2,6-dioctyloxyphenylethynylphenylethynyl)-substituted thiaporphyrin (3b)



To a dry CH_2Cl_2 (1.0 mL) solution of **17b** (25.3 mg, 9.94 μmol) was added PbO_2 (379 mg) and resulting suspension was stirred. After 42 h, the mixture was passed through a pad of celite. Evaporation of the solvent provided **3b** (23.5 mg, 9.24 μmol, 93%).

3b is not stable enough to measure ^{13}C NMR and absorption coefficient.

^{1}H NMR ($CDCl_3$) δ = 10.71 (s, 4H, carbazole-H), 8.75 (s, 4H,

carbazole-H), 7.83 (d, J = 8.05 Hz, 8H, Ph), 7.61 (d, J = 8.05 Hz, 8H, Ph), 7.21 (t, J = 8.45 Hz, 4H, Ph), 6.54 (d, J = 8.05 Hz, 8H, Ph), 4.07 (t, J = 6.45 Hz, 16H, CH_2), 1.89 (m, 16H, CH_2), 1.76 (s, 36H, *t*Bu), 1.56 (m, 16H, CH_2), 1.41-1.20 (m, 64H, CH_2), and 0.86 ppm (t, J = 6.73 Hz, 24H, CH_3); MALDI-TOF-MS: m/z = 2541.32. calcd for $C_{176}H_{207}N_2O_8S_2$: 2541.53 [$(M–H)^-$]; Mp: > 300 ˚C; UV/vis/NIR (CH_2Cl_2) λ_{max} (relative intensity) = 345 (18.9), 495 (2.69), 888 (1.49), 967 (1), and 1109 nm (3.82).

References

[S1] Schmittel, M.; Ammon, H. *Synlett*, **1999**, 750.

[S2] Maeda, C.; Yoshioka, N. *Org. Biomol. Chem.* **2012**, *10*, 5153.

Figure S1. ^{1}H and ^{13}C NMR spectra of **4** in $CDCl_3$

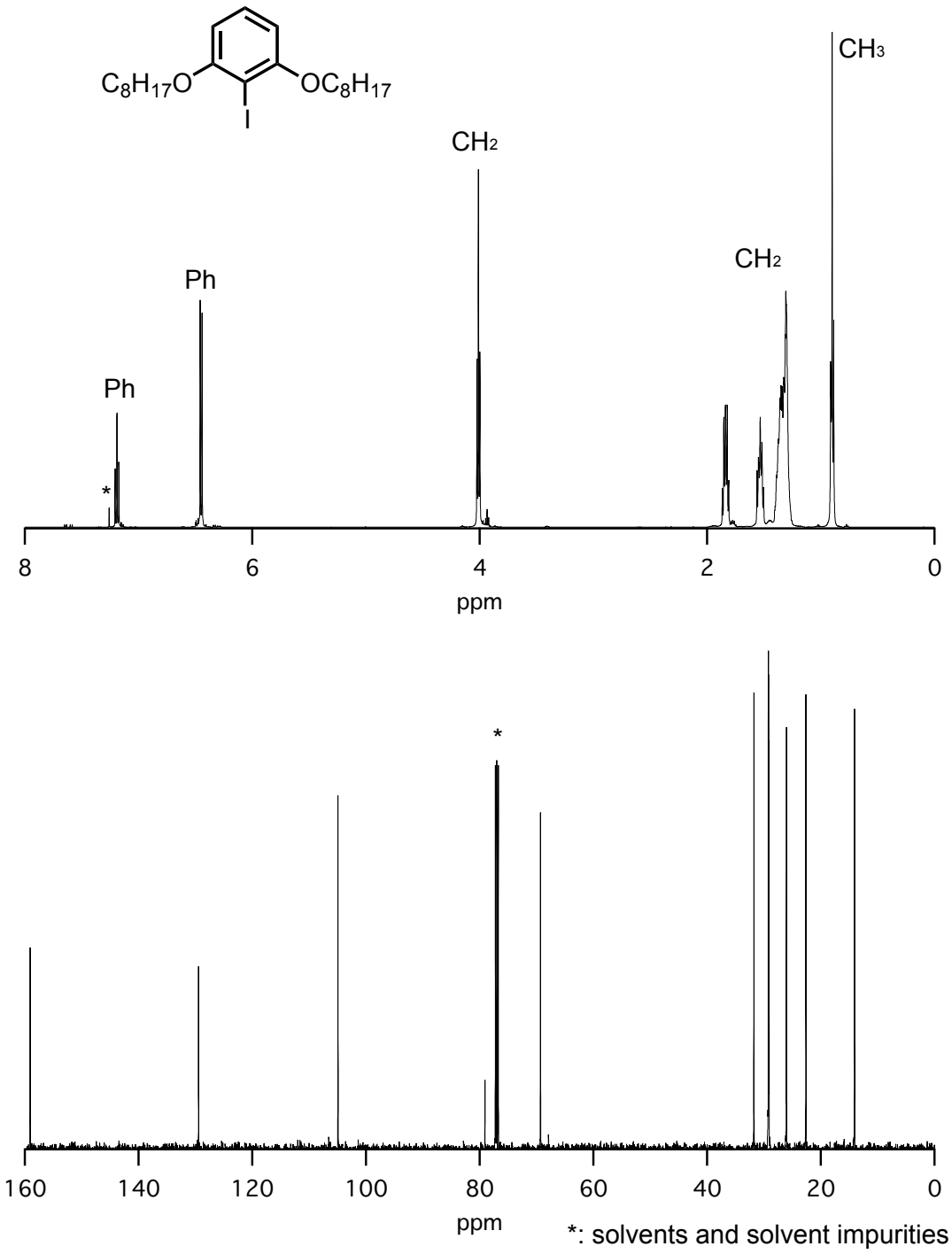


Figure S2. ^{1}H and ^{13}C NMR spectra of **5** in $CDCl_3$

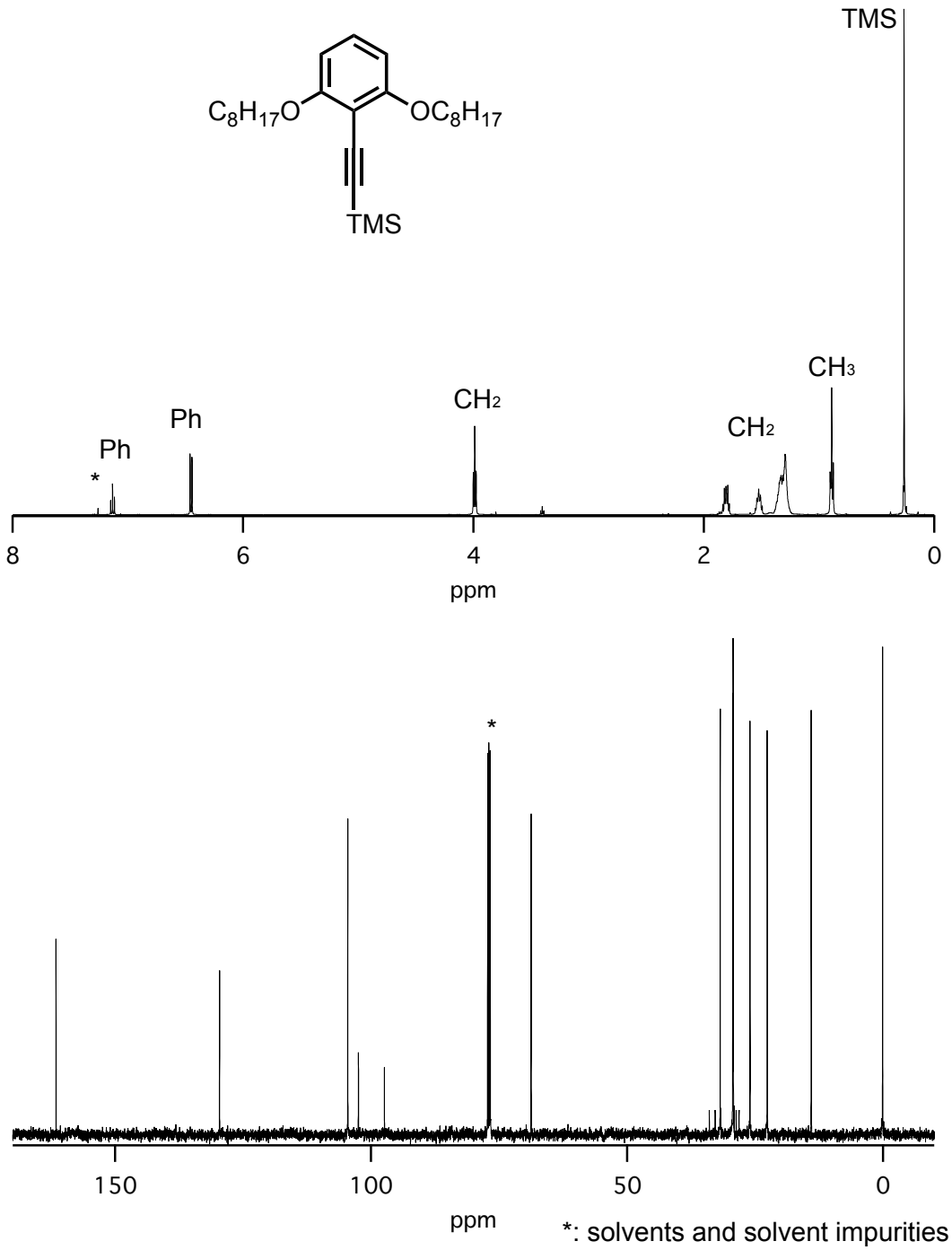


Figure S3. ^{1}H and ^{13}C NMR spectra of **6** in $CDCl_3$

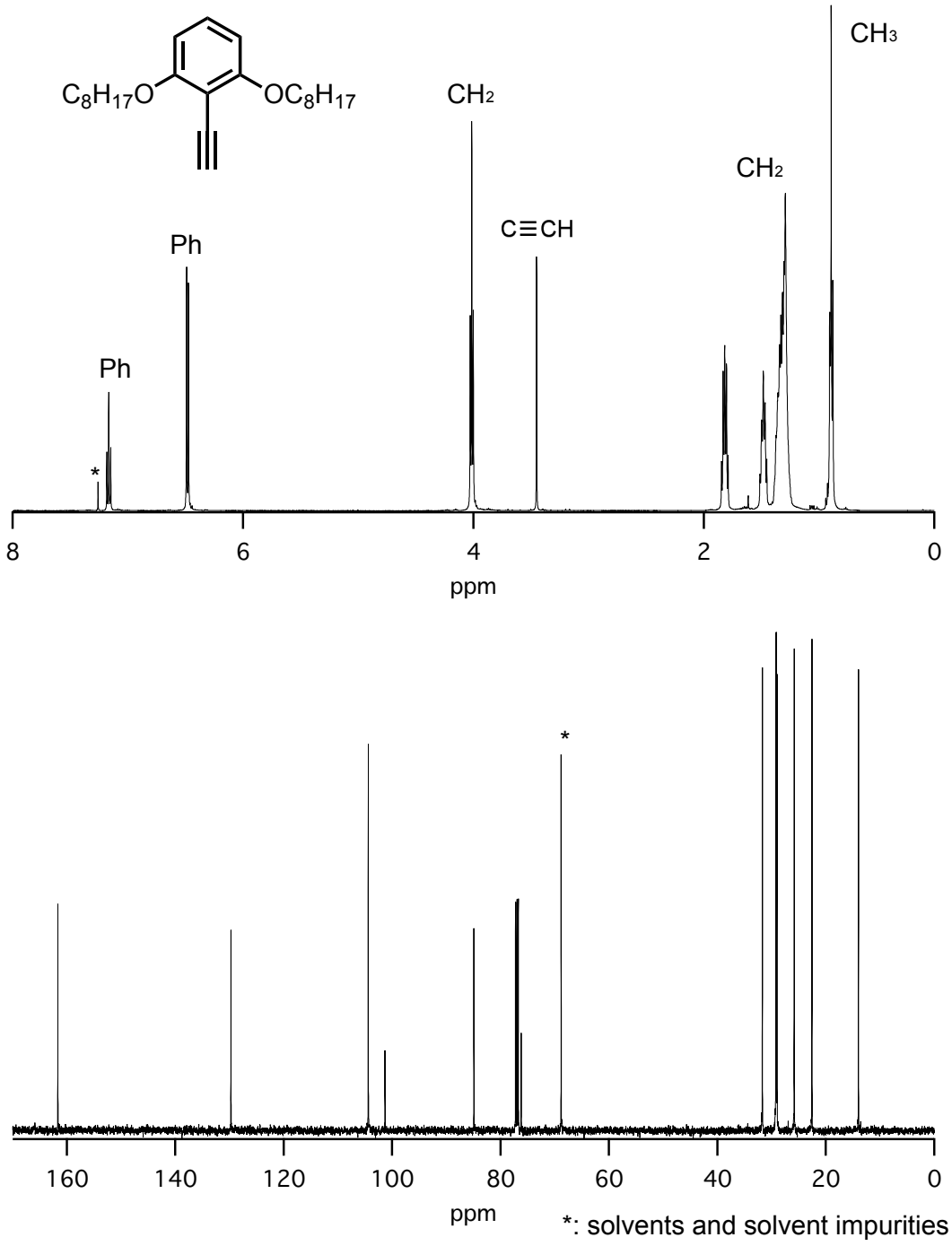


Figure S4. ^{1}H and ^{13}C NMR spectra of **7** in $CDCl_3$

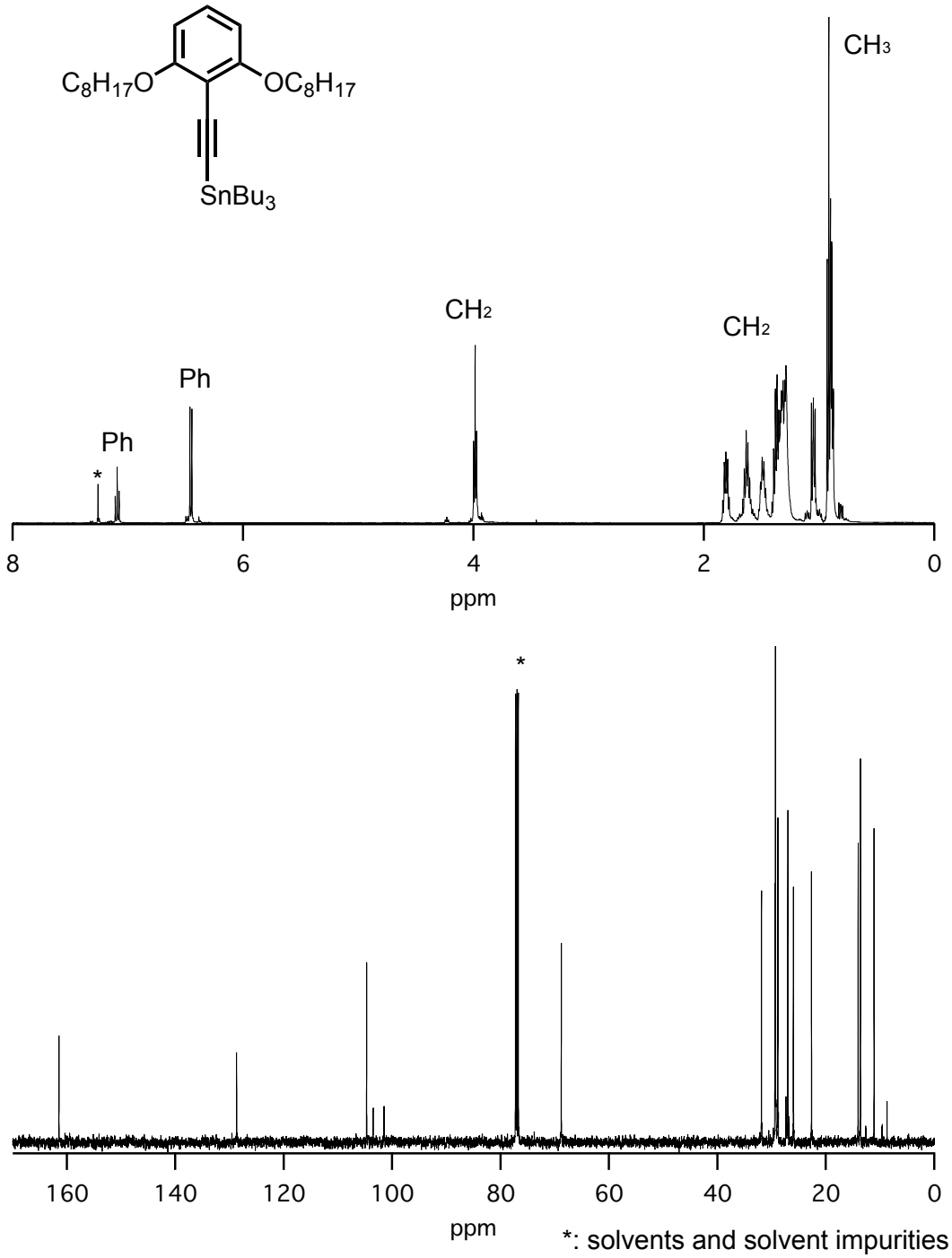


Figure S5. ^{1}H and ^{13}C NMR spectra of **8** in $CDCl_3$

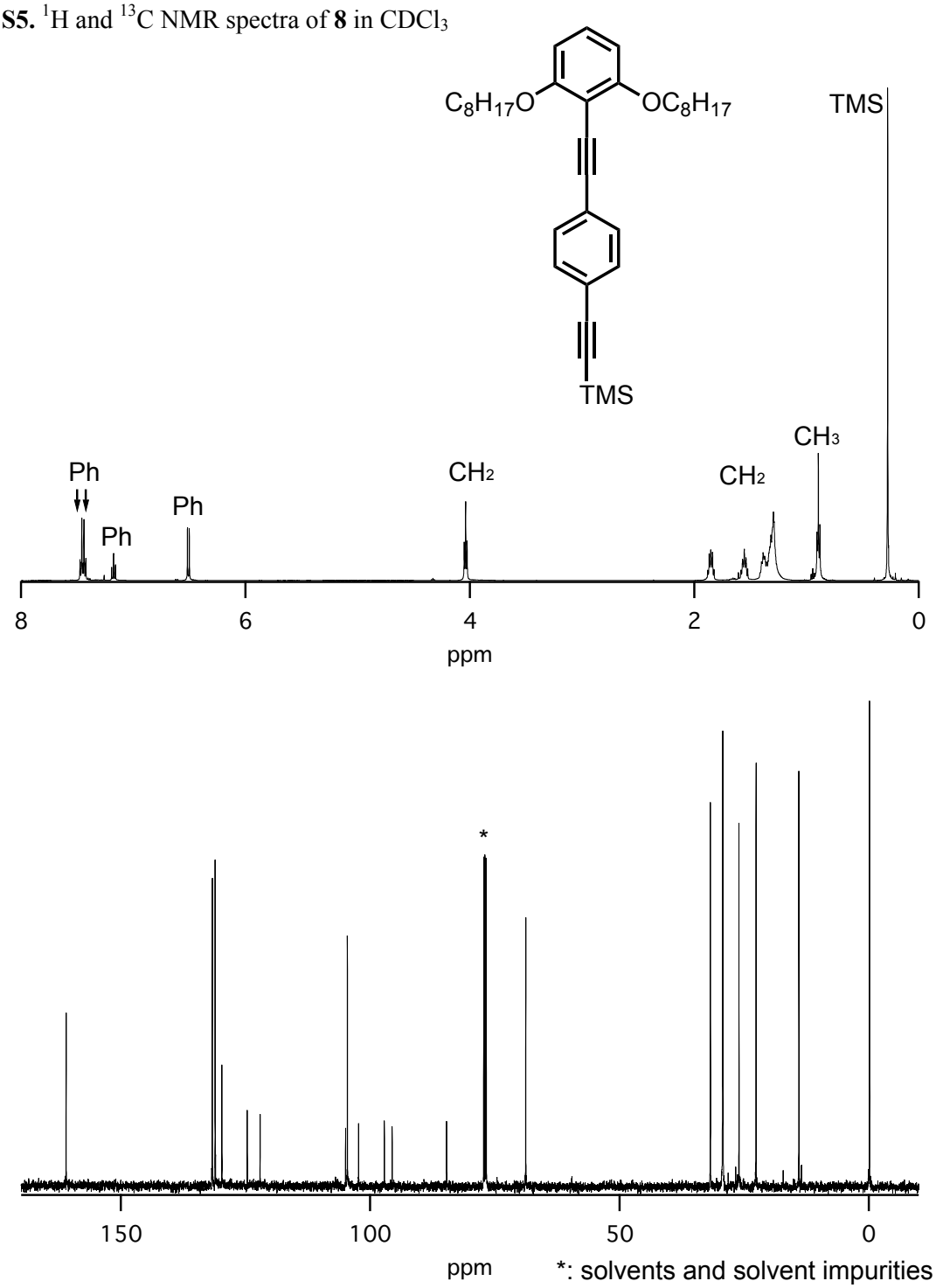


Figure S6. ^{1}H and ^{13}C NMR spectra of **9** in $CDCl_3$

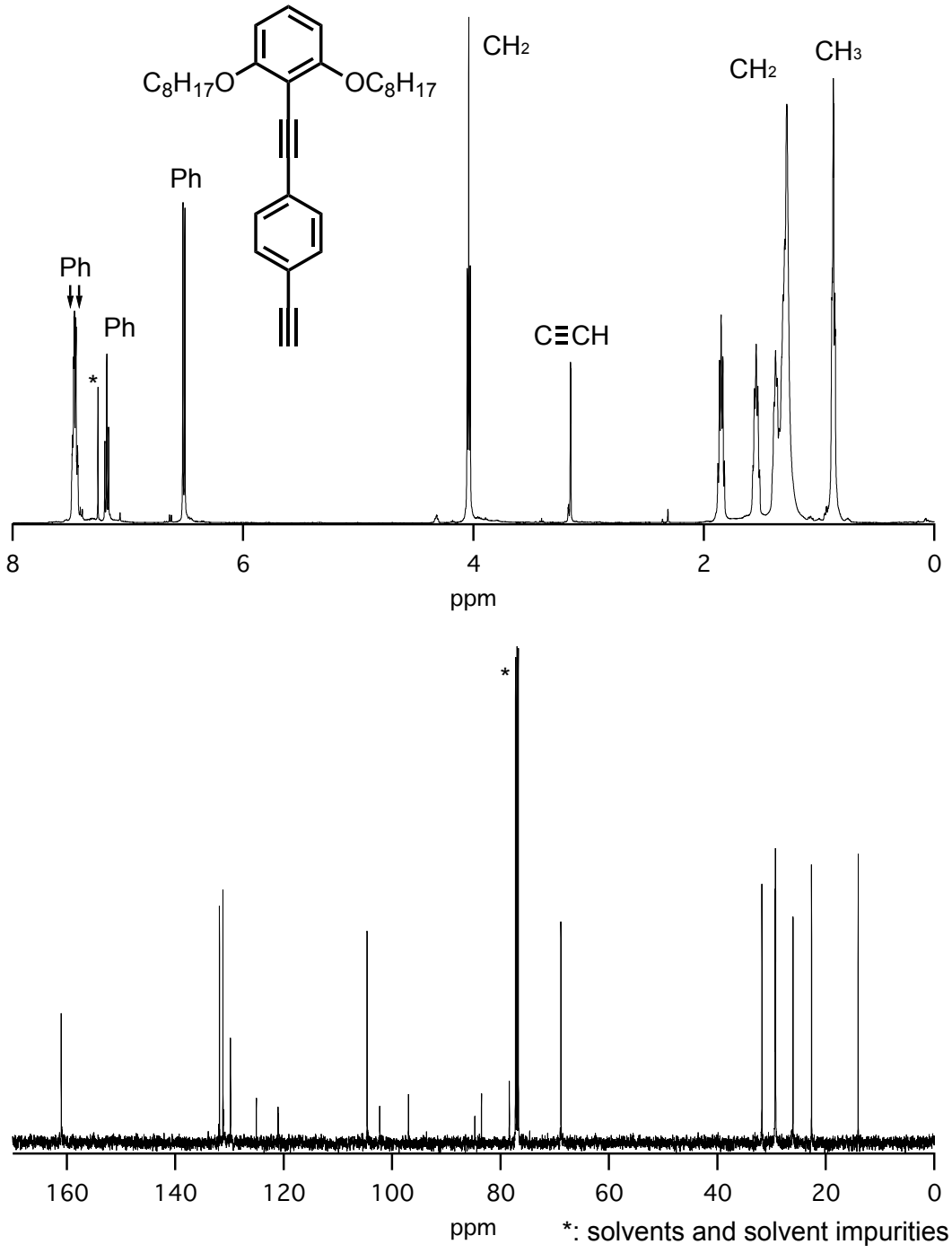


Figure S7. ^{1}H and ^{13}C NMR spectra of **10** in $CDCl_3$

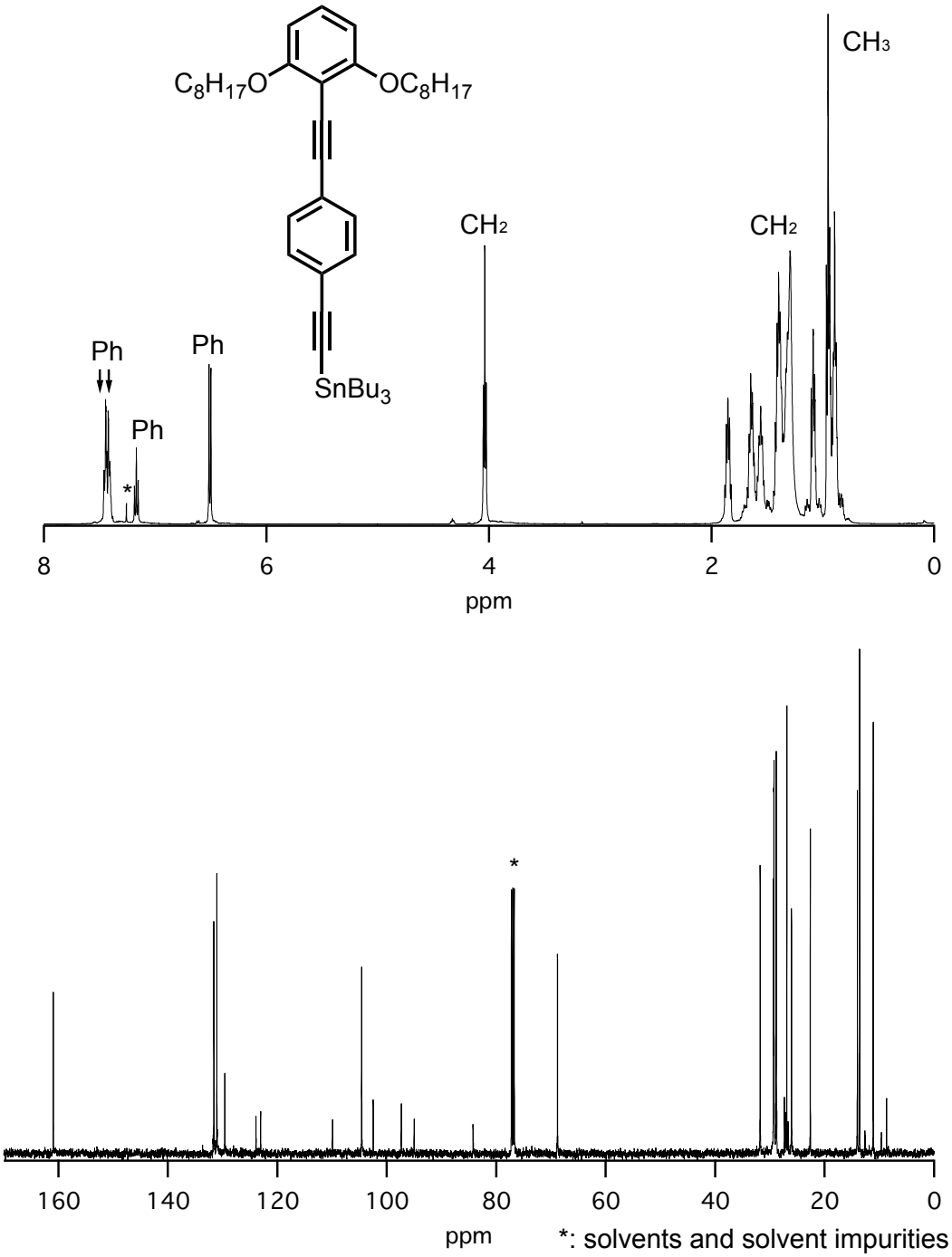


Figure S8. ^{1}H and ^{13}C NMR spectra of **12a** in $CDCl_3$

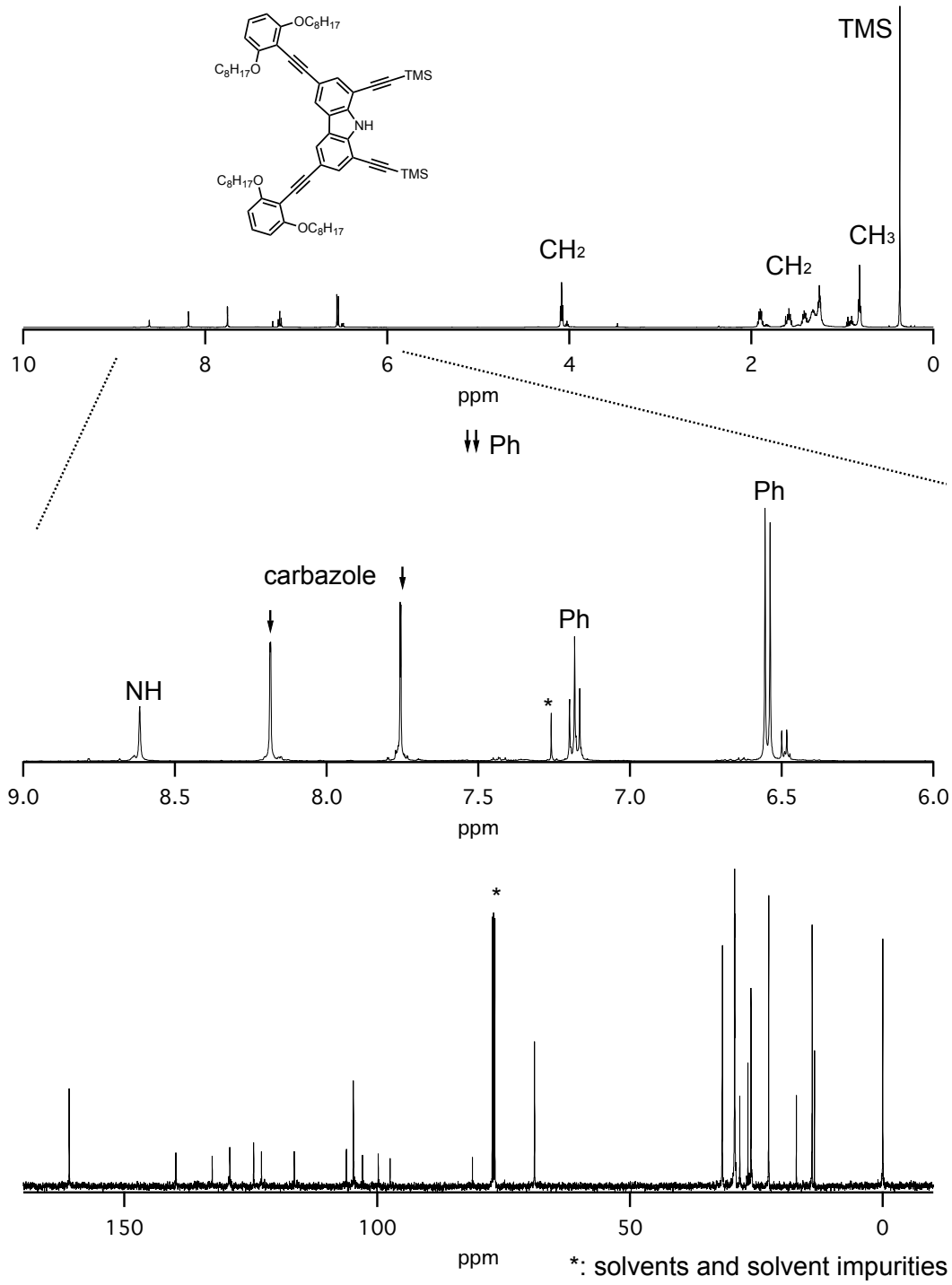


Figure S9. ^{1}H and ^{13}C NMR spectra of **13a** in $CDCl_3$

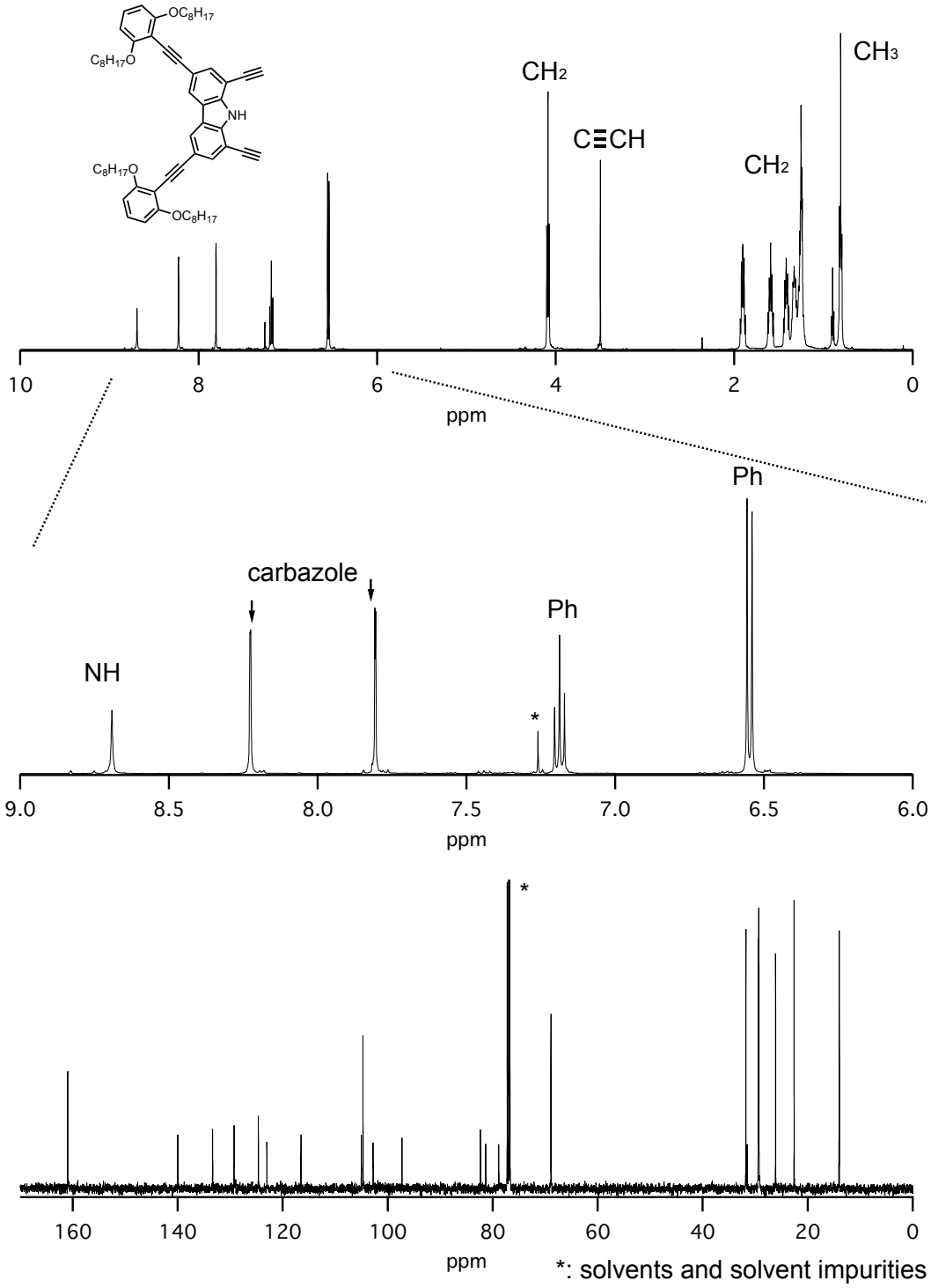


Figure S10. ^{1}H and ^{13}C NMR spectra of **14a** in $CDCl_3$

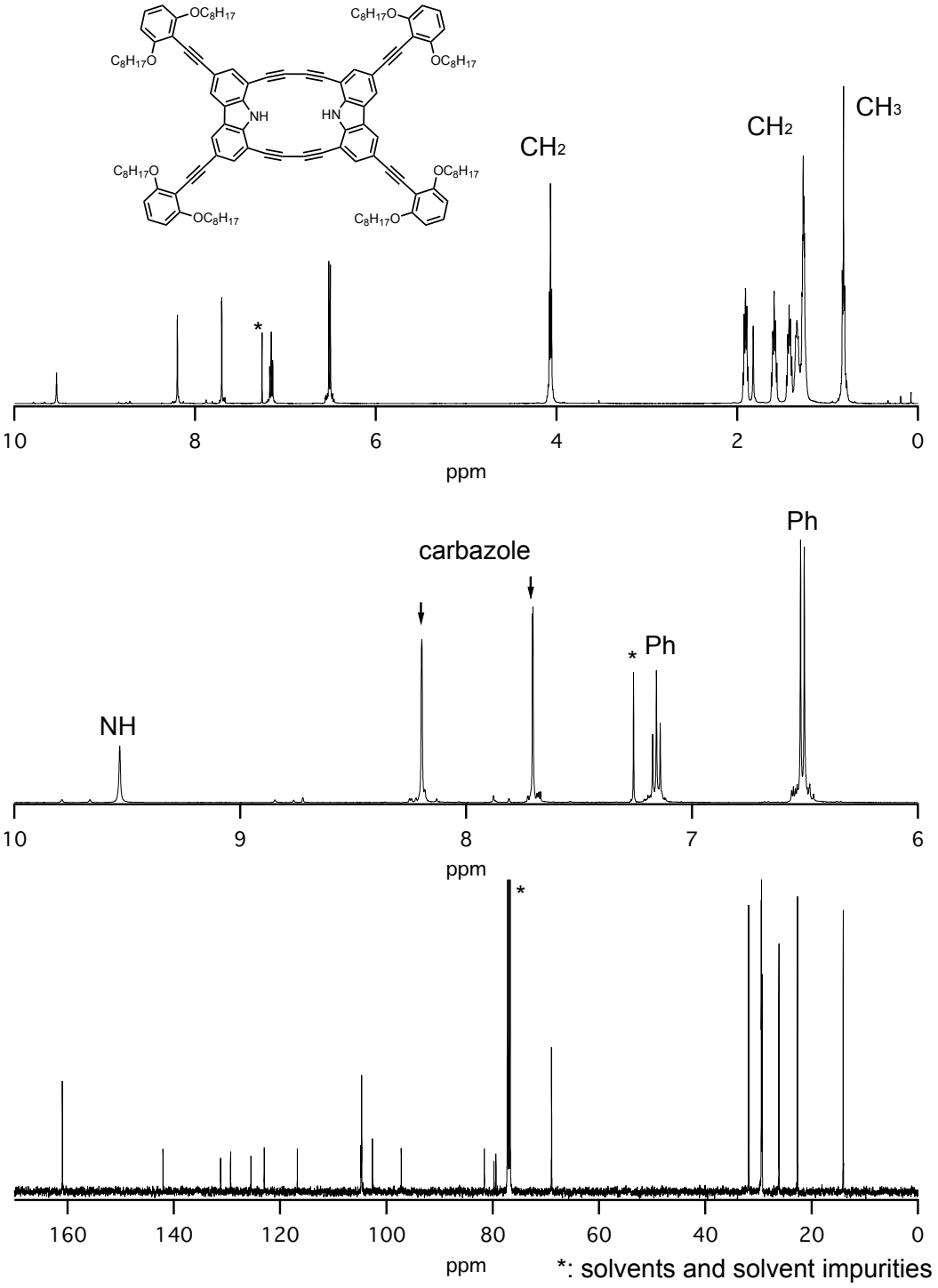


Figure S11. ^{1}H and ^{13}C NMR spectra of **15a** in $CDCl_3$

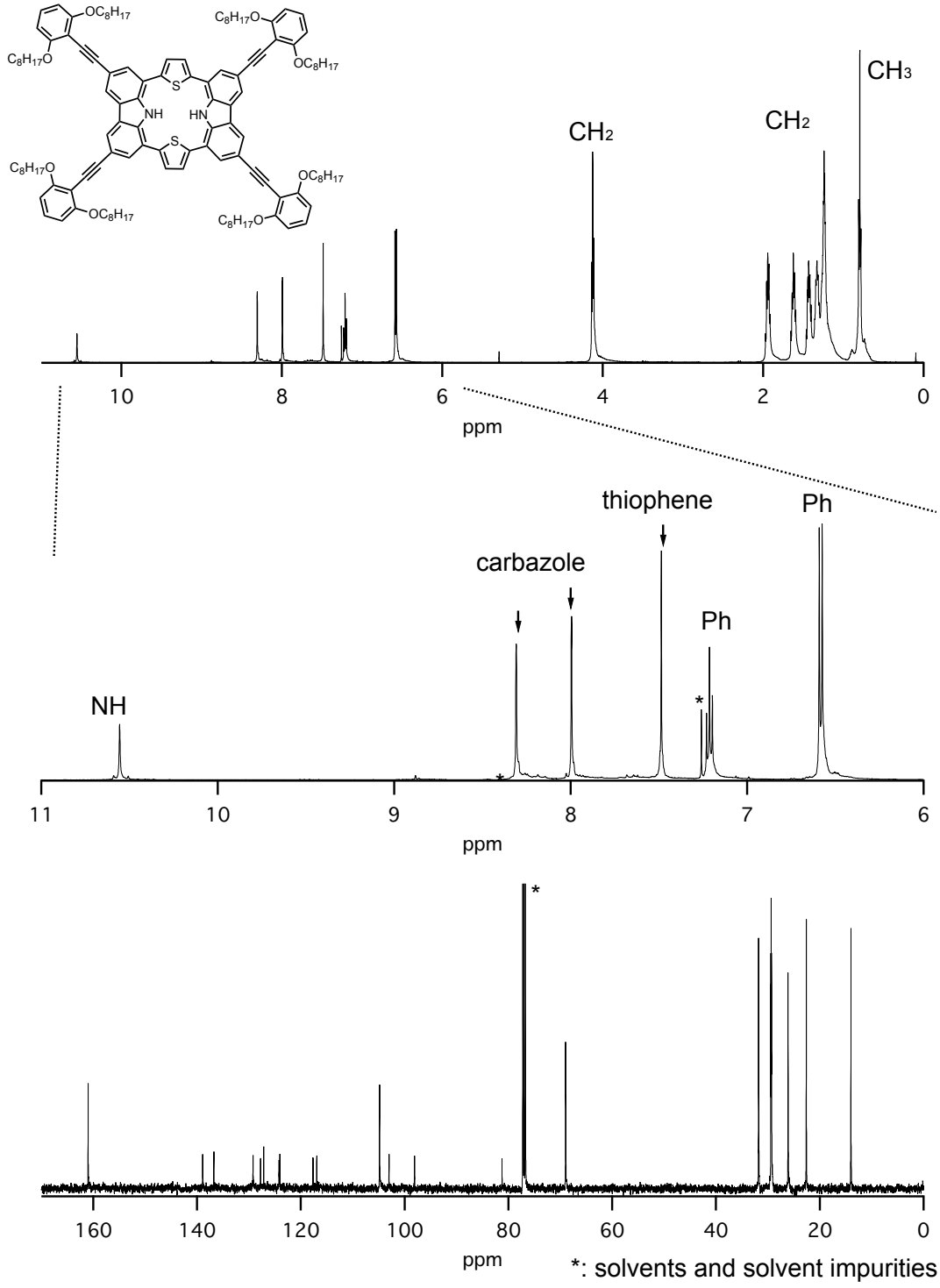


Figure S12. ^{1}H and ^{13}C NMR spectra of **2a** in $CDCl_3$

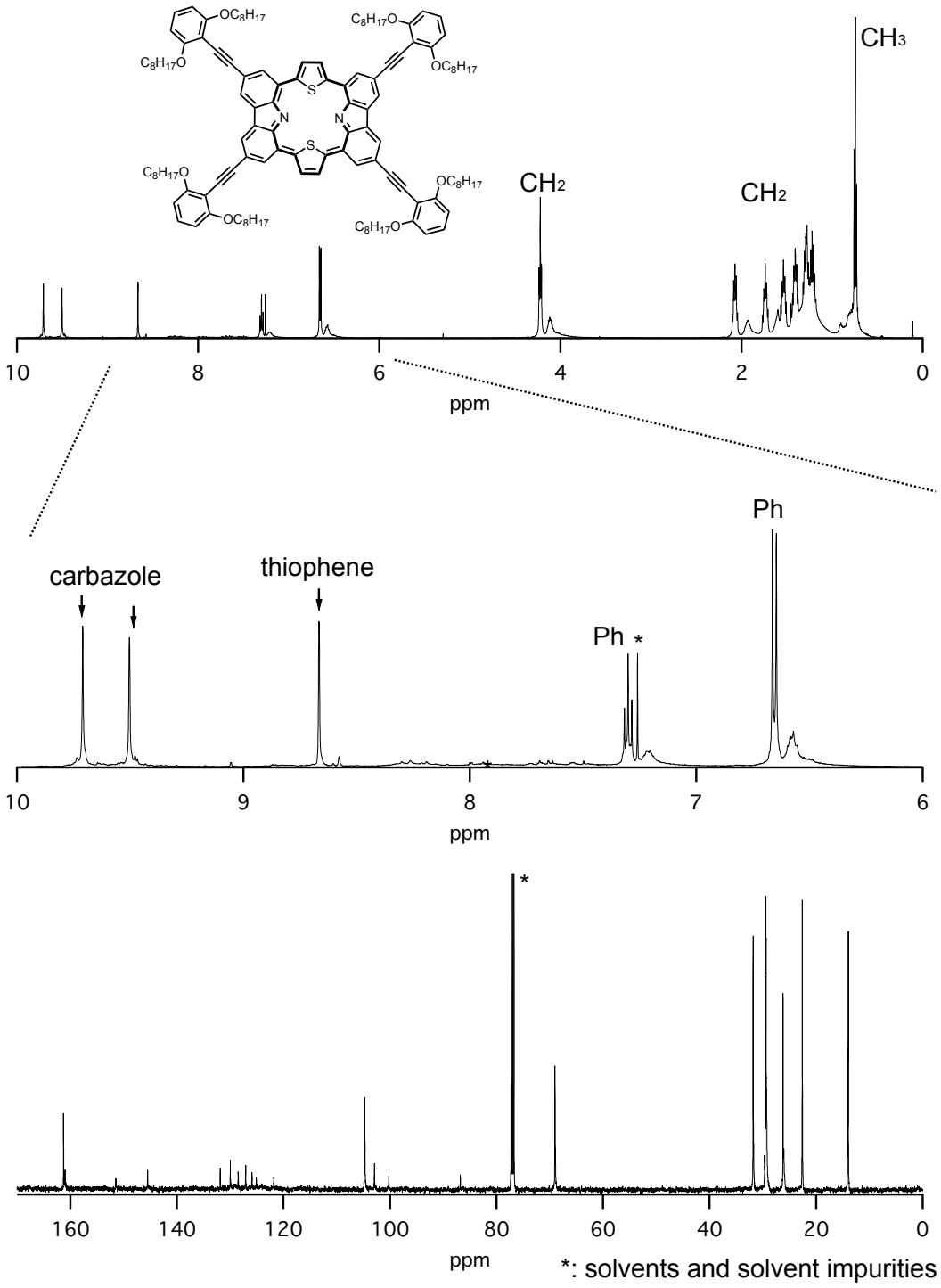


Figure S13. ^{1}H and ^{13}C NMR spectra of **12b** in $CDCl_3$

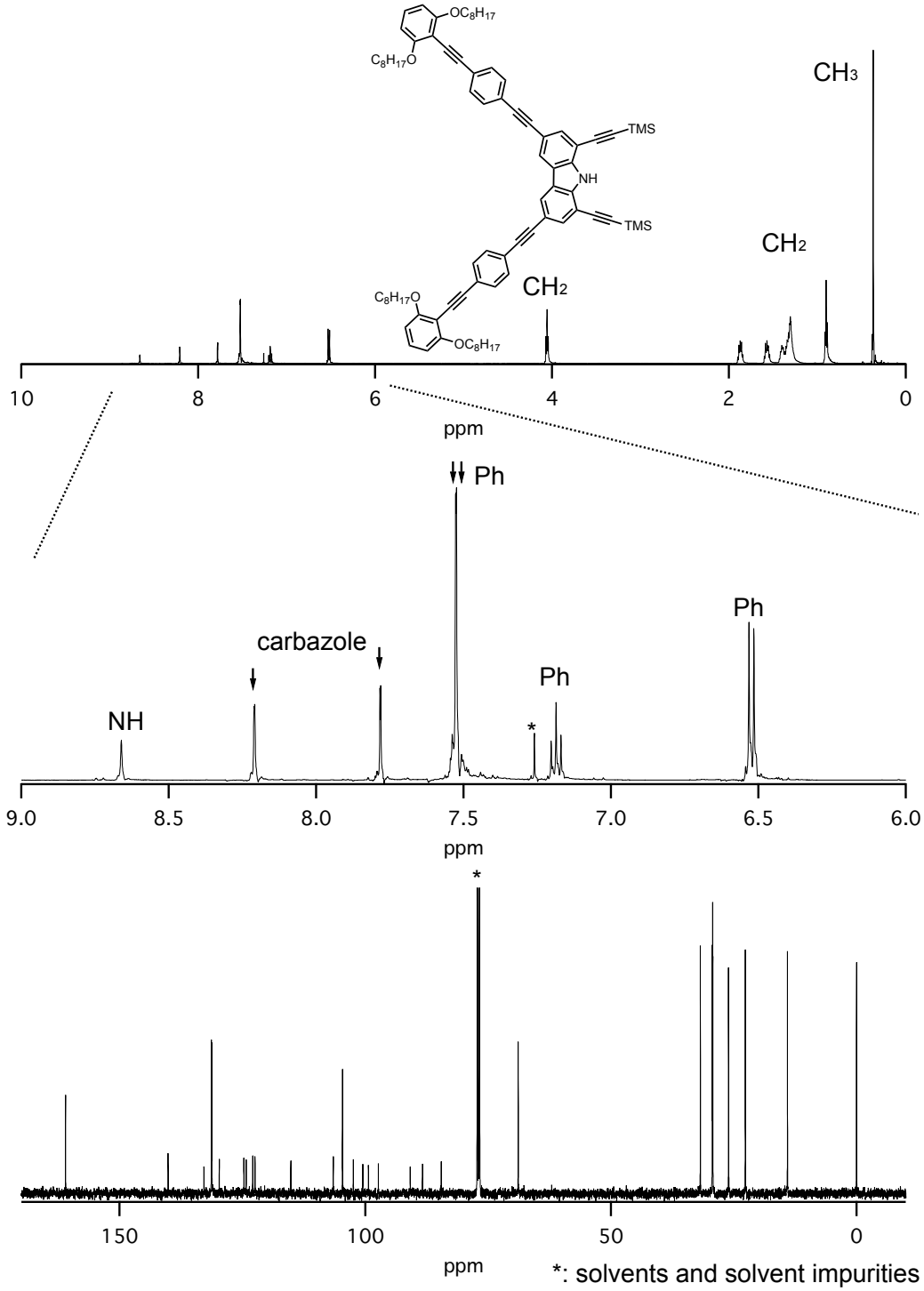


Figure S14. ^{1}H and ^{13}C NMR spectra of **13b** in $CDCl_3$

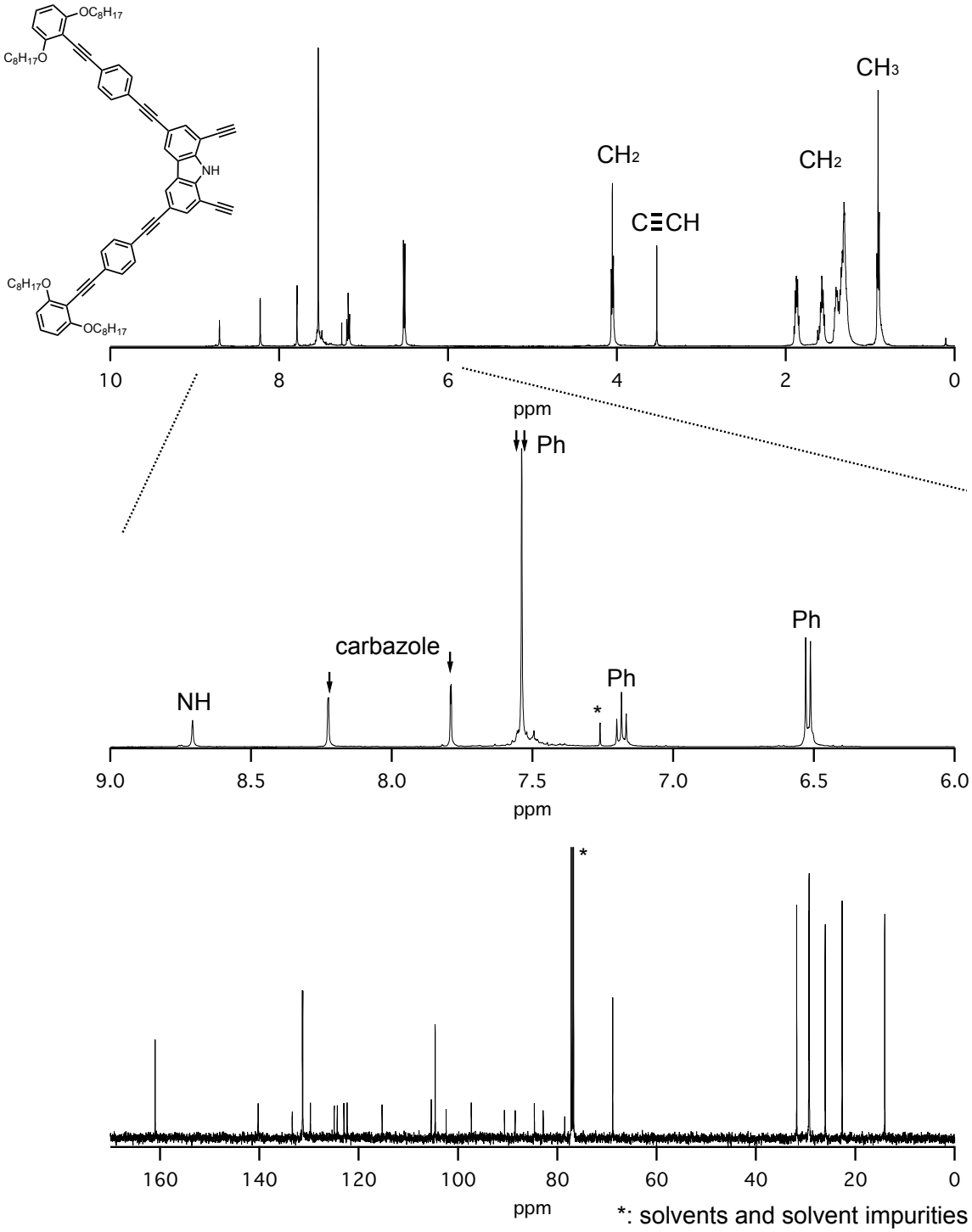


Figure S15. ^{1}H and ^{13}C NMR spectra of **14b** in $CDCl_3$

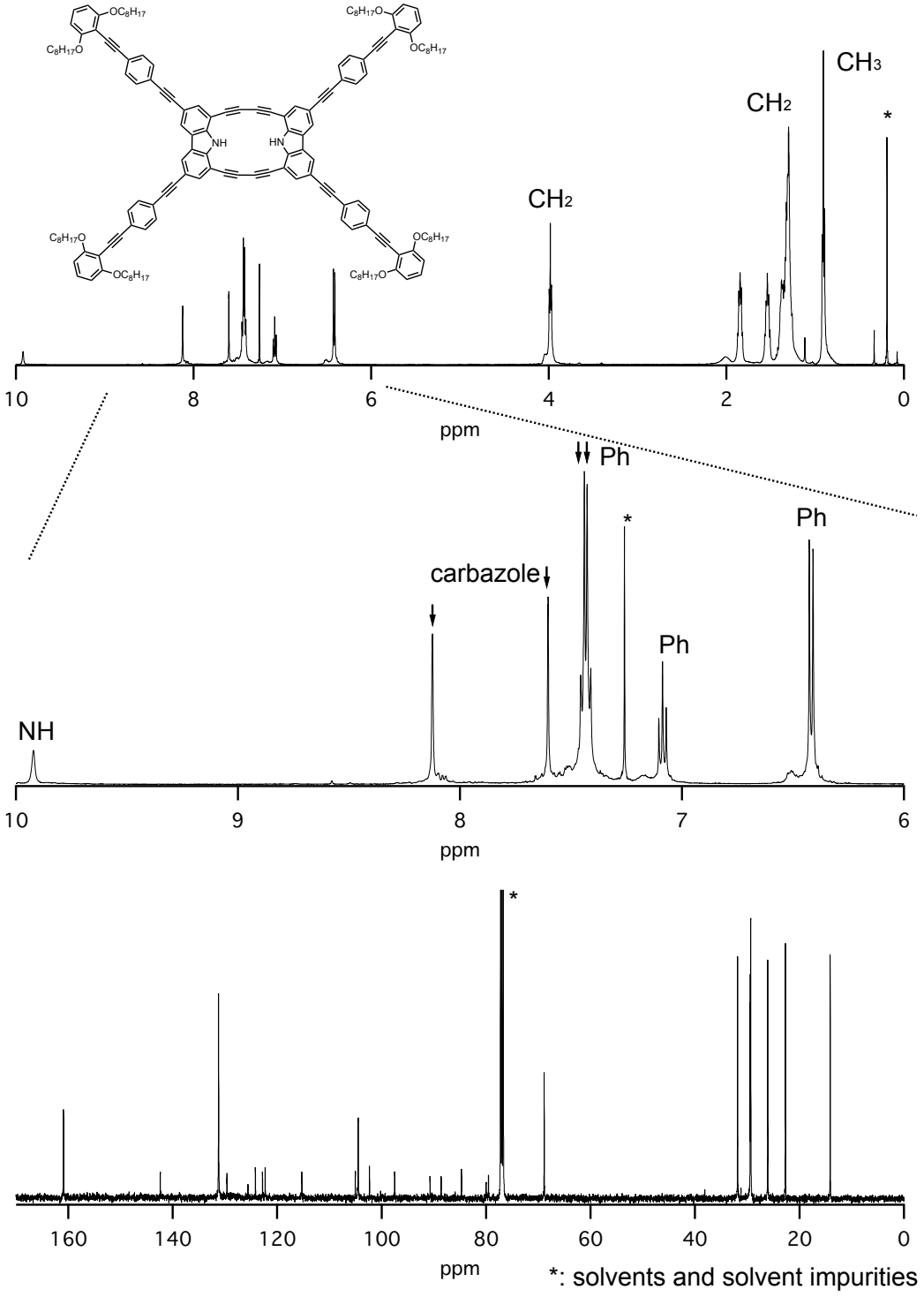


Figure S16. ^{1}H and ^{13}C NMR spectra of **15b** in $CDCl_3$

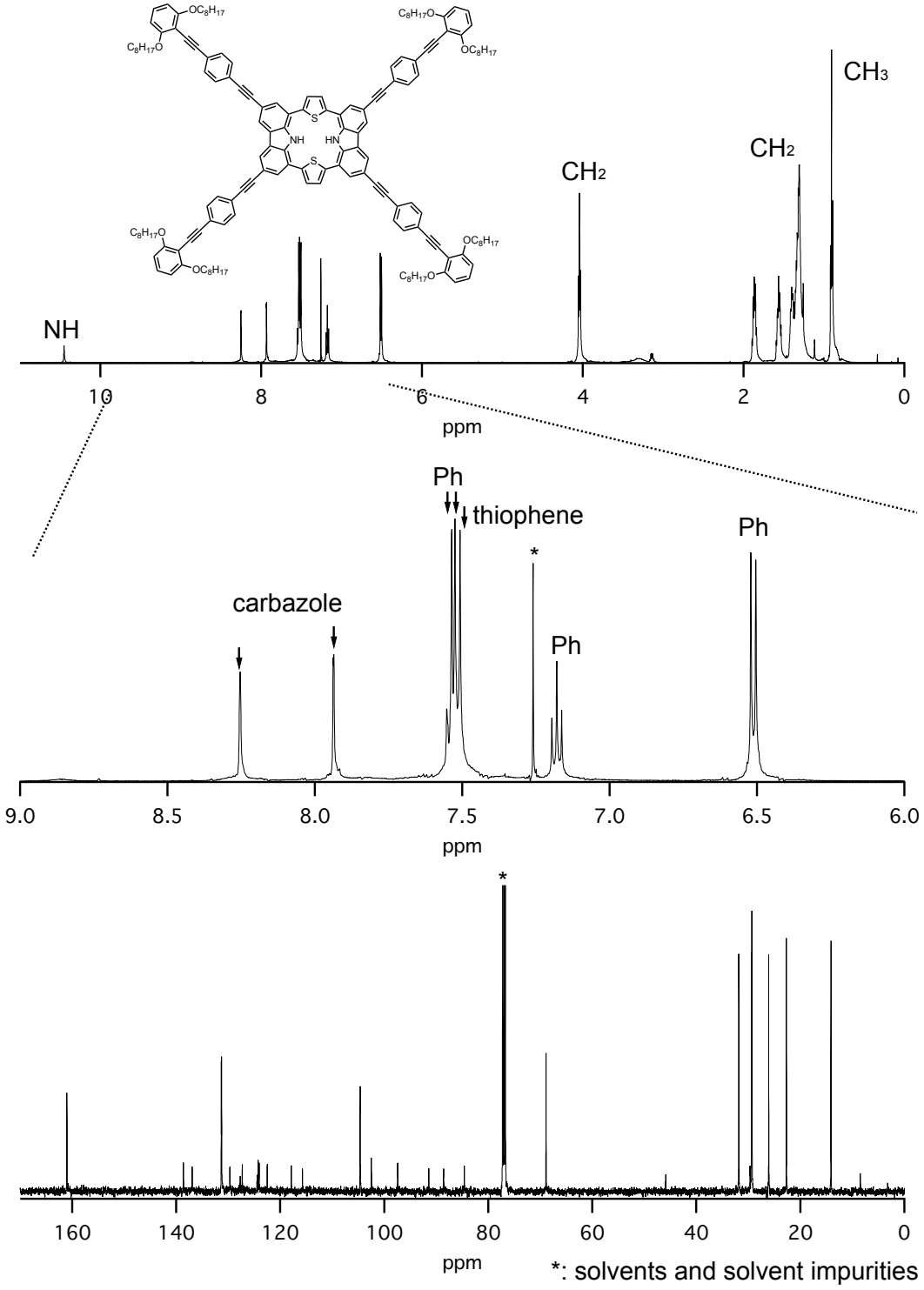


Figure S17. ^{1}H and ^{13}C NMR spectra of **2b** in $CDCl_3$

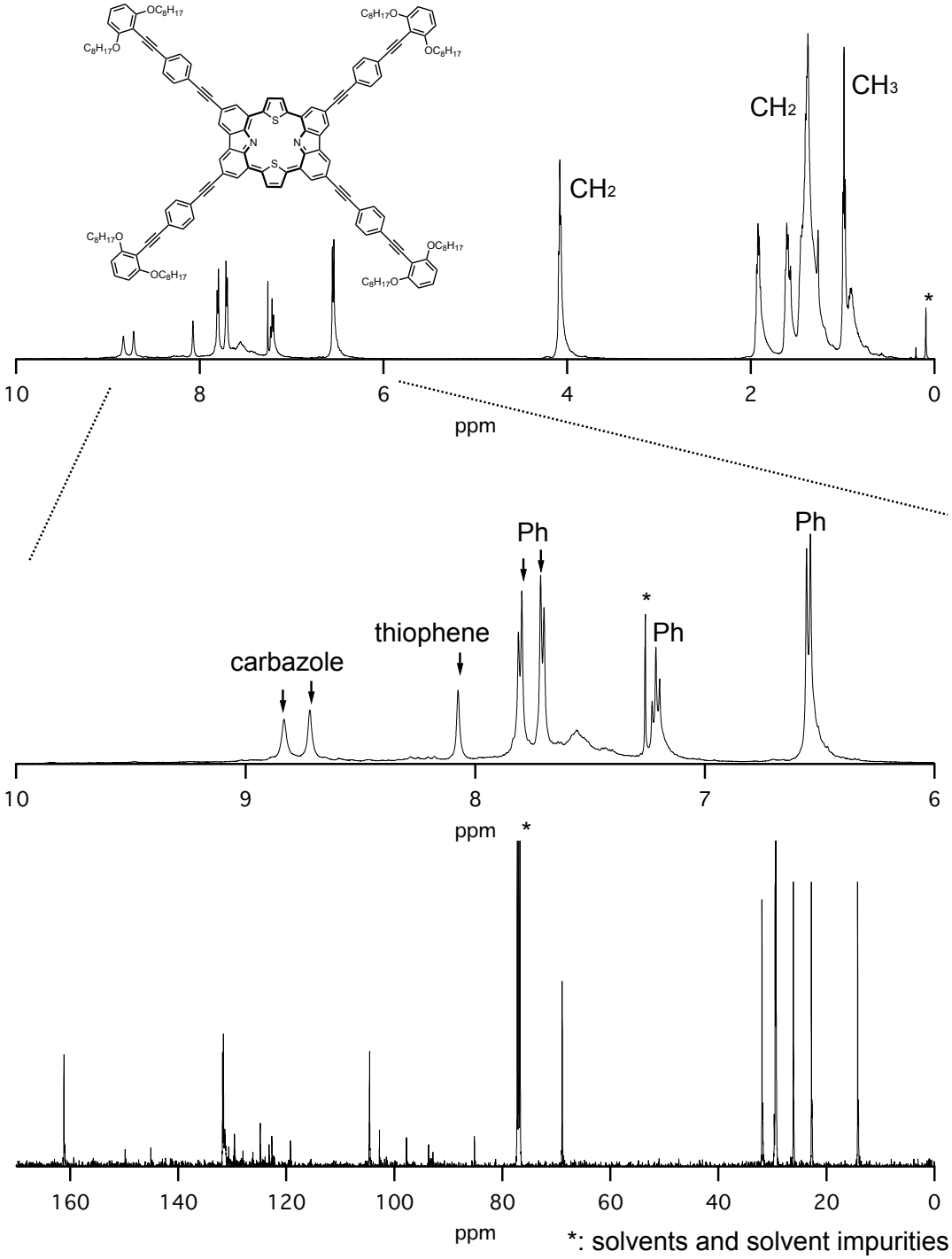


Figure S18. ^{1}H and ^{13}C NMR spectra of **17a** in $CDCl_3$

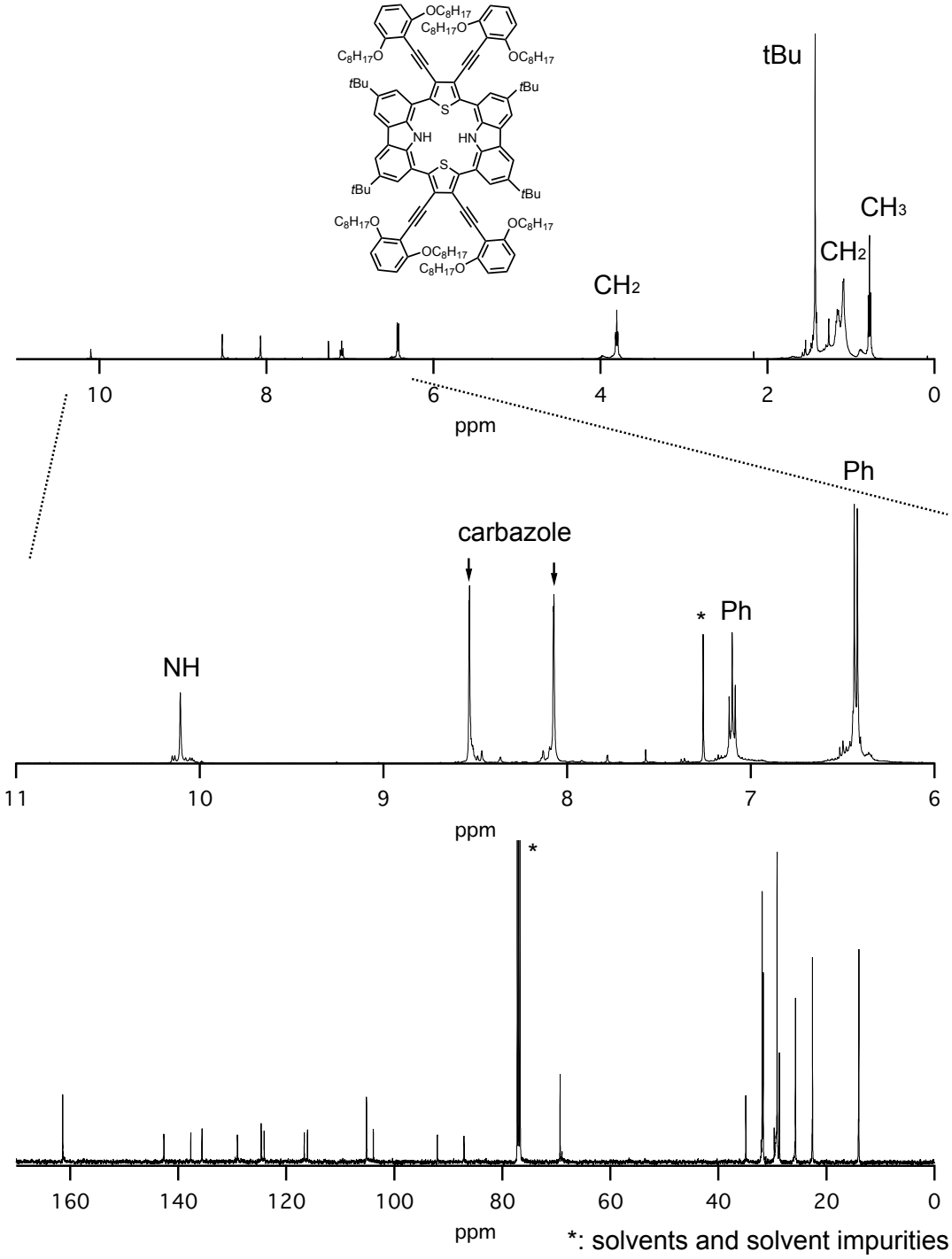


Figure S19. ^{1}H and ^{13}C NMR spectra of **3a** in $CDCl_3$

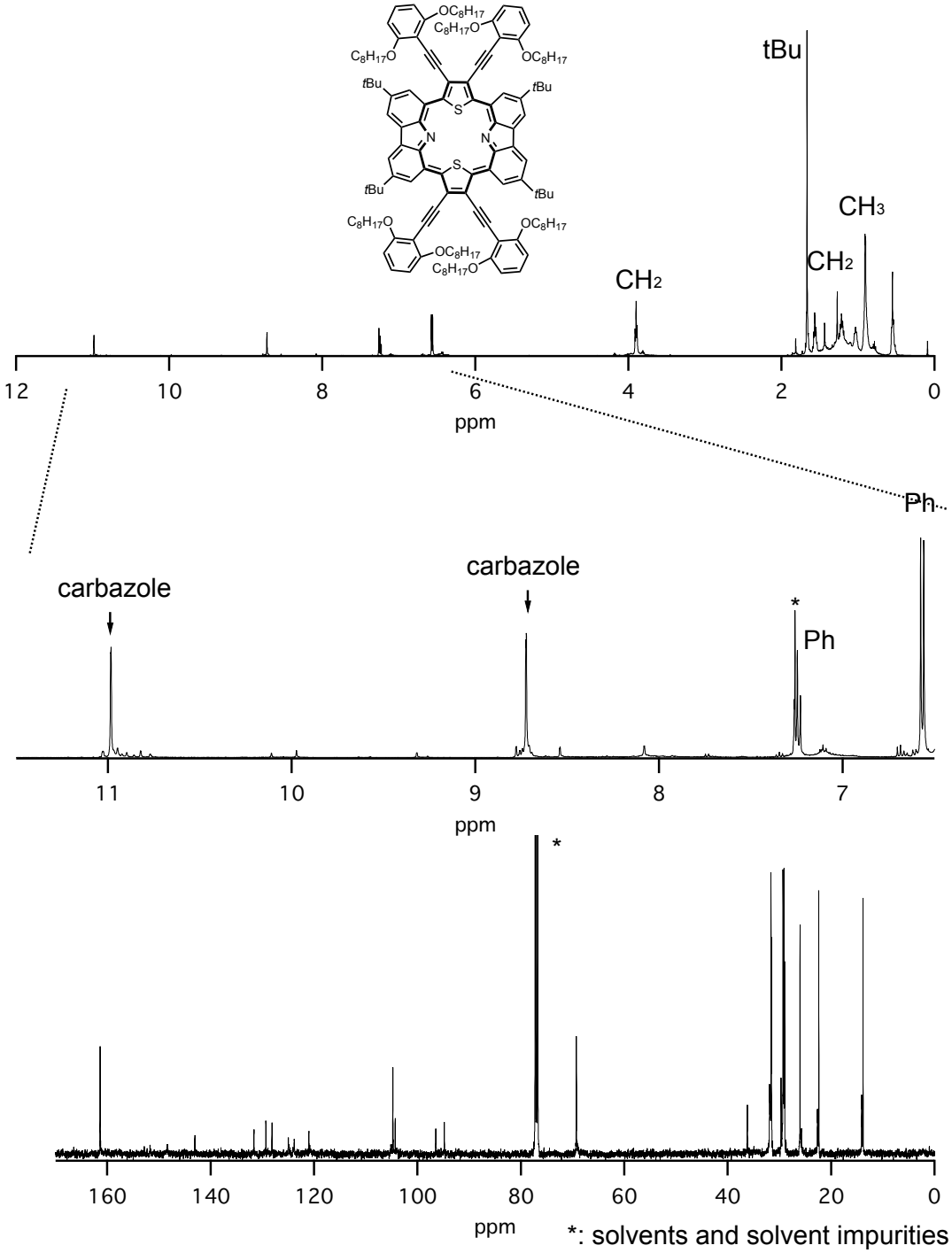


Figure S20. ^{1}H and ^{13}C NMR spectra of **17b** in $CDCl_3$

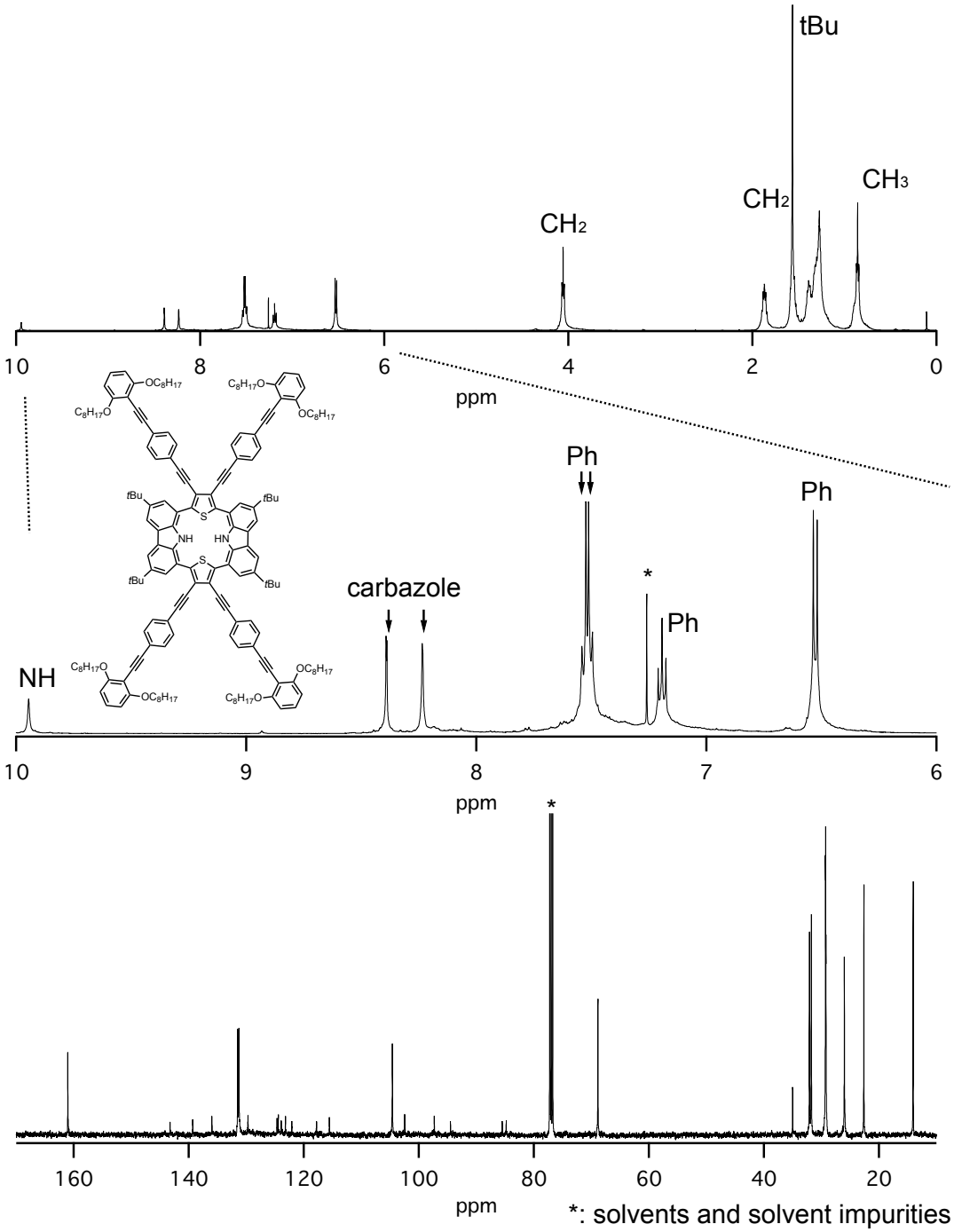


Figure S21. ^{1}H NMR spectrum of **3b** in $CDCl_3$

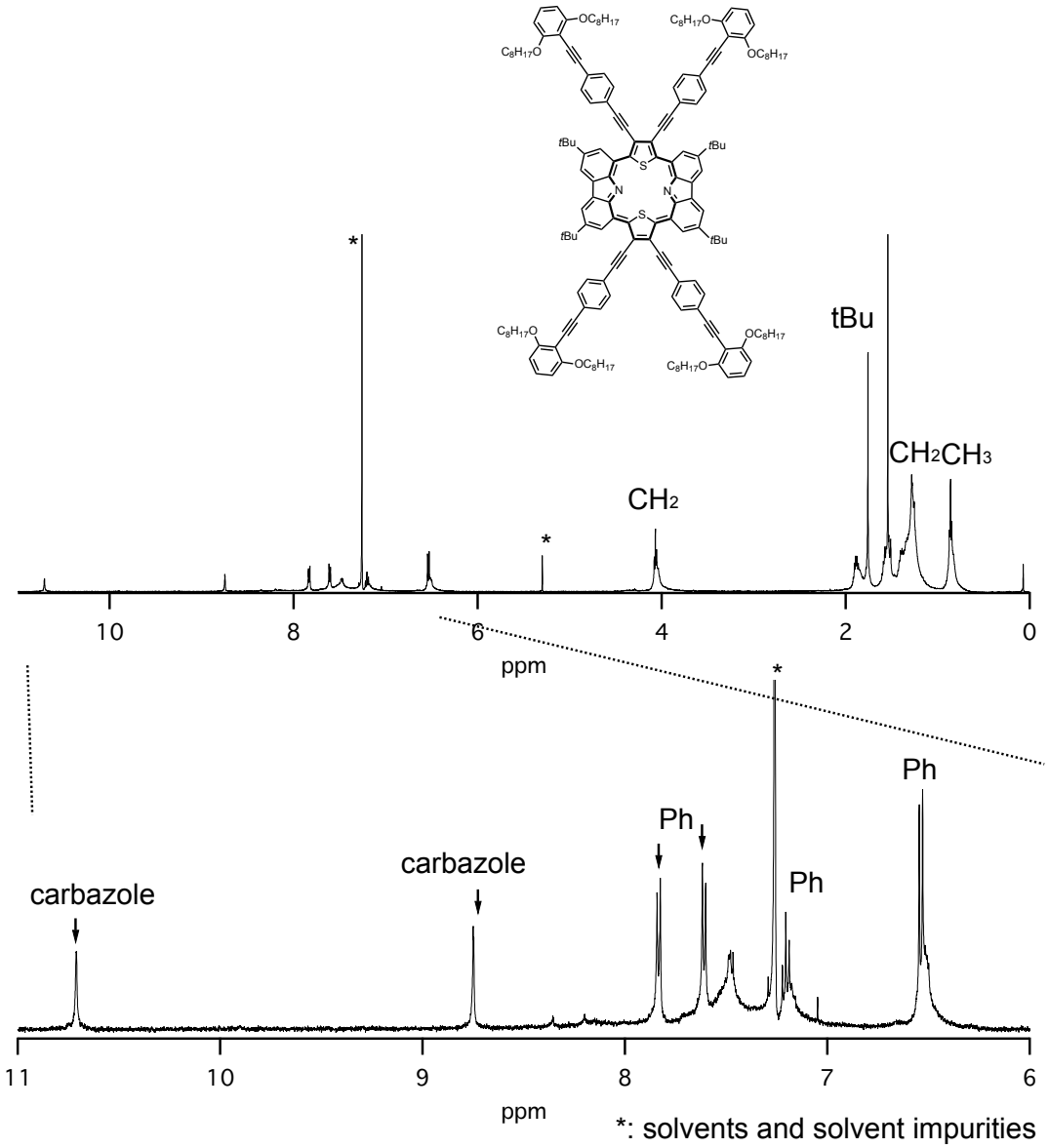


Figure S22. Fluorescence spectra in CH_2Cl_2 (black line: **1**, red line: **2a**, blue line: **2b**, pink line: **3a**, green line: **3b**). The excitation wavelengths are 980 nm.

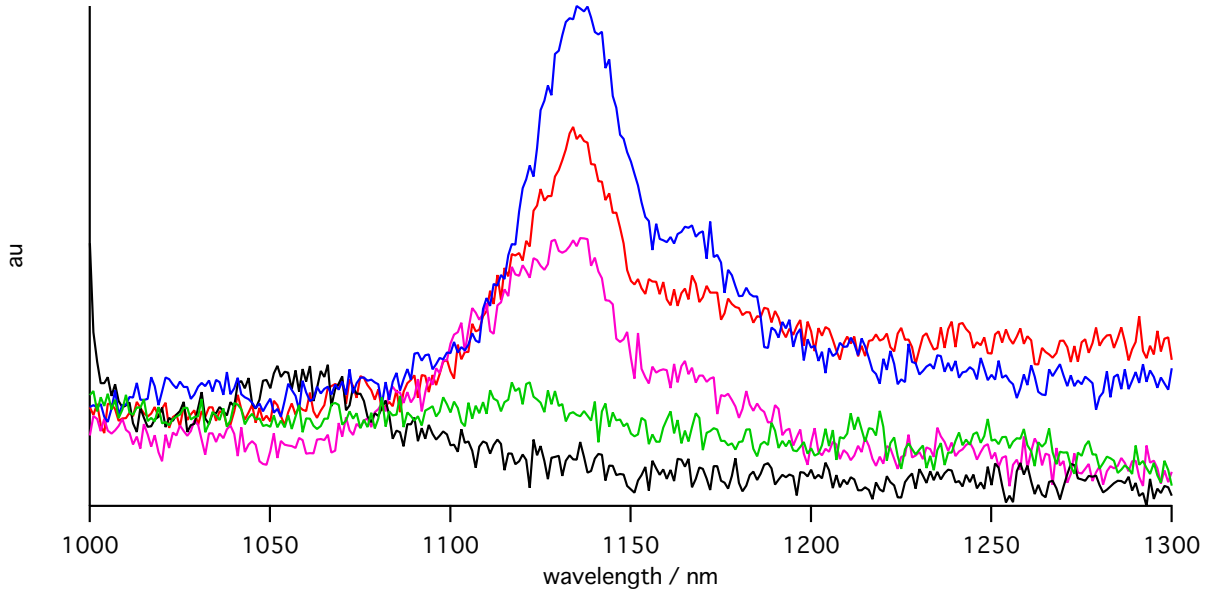


Figure S23. Molecular orbitals of (a) **1**, (b) **2a**, (c) **2b**, (d) **3a**, and (e) **3b** calculated at the B3LYP/6-31G(d) level.

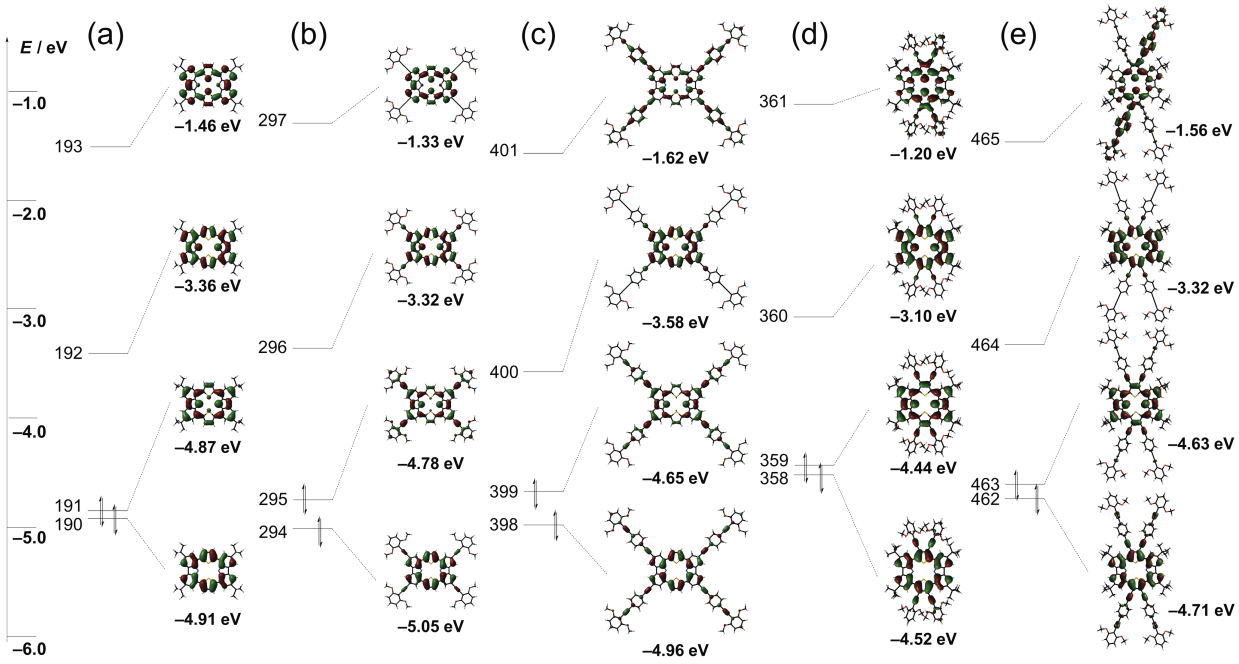


Figure S24. Cyclic and differential pulse voltammograms of (a) **2a**, (b) **2b**, (c) **3a**, and (d) **3b** (solvent: CH_2Cl_2 supporting electrolyte: Bu_4NPF_6 (0.10 M), counter electrode: Pt, reference electrode: Ag/Ag^+, scan rate: 0.05 V/s).