

Supplementary Information
for
Peripherally ethynylated carbazole-based core-modified porphyrins

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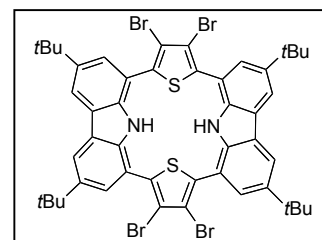
Instrumentation and materials

^1H 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 ($\delta = 7.260$ for ^1H 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 a JASCO FP-777W spectrometer and relative fluorescence quantum yields were determined with the reference value of **1a** (0.274 in CH_2Cl_2). High resolution ESI-TOF mass spectra and 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. X-ray data were taken on a Rigaku-Raxis imaging plate system. Recycling preparative GPC-HPLC was carried out on JAI LC-9225NEXT using preparative JAIGEL-1H, and 2H. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dry CH_2Cl_2 and toluene was distilled from CaH_2 .

Experimental section

β -Tetrabrominated thiophene-bridged carbazole dimer (**2**)

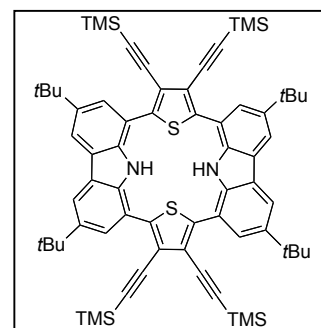
To a CH_2Cl_2 (50 mL) solution of **1a** (78.4 mg, 109 μmol) was added *N*-bromosuccinimide (97.0 mg, 545 μmol) and the resulting solution was stirred for 2 h. The mixture was passed through a silica gel column with CH_2Cl_2 , and the solvent was evaporated, to give **2** (99.0 mg, 95.7 μmol , 88%).



^1H NMR (CDCl_3) δ = 9.47 (s, 2H, NH), 8.20 (d, J = 1.5 Hz, 4H, carbazole-H), 7.99 (d, J = 1.7 Hz, 4H, carbazole-H), and 1.56 ppm (s, 36H, *t*Bu); ^{13}C NMR (CDCl_3) δ = 143.13, 136.32, 133.82, 125.00, 124.20, 117.91, 114.84, 114.65, 35.04, and 31.98 ppm; HR-ESI-MS: m/z = 1032.9702. calcd for $\text{C}_{48}\text{H}_{45}\text{N}_2\text{S}_2\text{Br}_4$: 1032.9728 [(M-H) $^-$]; Mp: > 300 °C; UV/Vis (CH_2Cl_2) λ_{max} (ϵ) = 318 (31900) and 394 nm ($18300 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$).

β -Tetraethynylated thiophene-bridged carbazole dimer (**3a**)

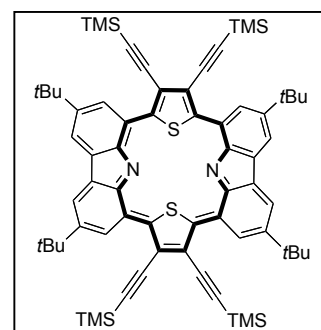
A dry toluene (5.0 mL) solution of **2** (151 mg, 146 μmol), $\text{Pd}(\text{PPh}_3)_4$ (50.5 mg, 43.7 μmol), and tributyl(trimethylsilylethynyl)tin (336 mg, 868 μmol) was degassed. The mixture was stirred for 16 h at reflux under Ar. After the solvent was evaporated, the residue was separated over a silica gel column with dichloromethane/hexane as an eluent to give **3a** (130 mg, 118 μmol , 81%).



^1H NMR (CDCl_3) δ = 9.63 (s, 2H, NH), 8.21 (d, J = 1.5 Hz, 4H, carbazole-H), 8.15 (d, J = 1.5 Hz, 4H, carbazole-H), 1.54 (s, 36H, *t*-Bu), and 0.25 ppm (s, 36H, TMS); ^{13}C NMR (CDCl_3) δ = 143.06, 140.04, 135.86, 124.23, 124.09, 123.49, 117.69, 115.30, 99.61, 98.55, 35.14, 32.13, and 0.23 ppm; HR-ESI-MS: m/z = 1101.4871. calcd for $\text{C}_{68}\text{H}_{81}\text{N}_2\text{S}_2\text{Si}_4$: 1101.4924 [(M-H) $^-$]; Mp: > 300 °C; UV/Vis (CH_2Cl_2) λ_{max} (ϵ) = 296 (52600), 331 (35700), and 414 nm ($18700 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$); Fluorescence (CH_2Cl_2 , λ_{ex} = 360 nm); λ_{max} = 452 nm, Φ_{F} = 0.0713.

β -Tetraethynylated thiophene-bridged carbazole dimer (**3b**)

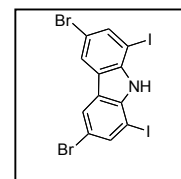
To a dry CH_2Cl_2 (10 mL) solution of **3a** (18.9 mg, 17.1 μmol) was added MnO_2 (590 mg) and resulting suspension was stirred. After 14 h, MnO_2 (914 mg) was added and the mixture was stirred for further 5 h. The



mixture was then passed through a pad of celite. Evaporation of the solvent provided **8** (18.6 mg, 16.9 μmol , 99%).

^1H NMR (CDCl_3) δ = 10.48 (s, 4H, carbazole-H), 8.65 (s, 4H, carbazole-H), 1.79 (s, 36H, *t*Bu), and 0.55 ppm (s, 36H, TMS); The ^{13}C NMR spectrum couldn't detect peaks due to poor solubility; MALDI-TOF-MS: m/z = 1099.12. calcd for $\text{C}_{68}\text{H}_{79}\text{N}_2\text{S}_2\text{Si}_4$: 1099.48 [(M-H) $^-$]; Mp: > 300 $^\circ\text{C}$; UV/Vis/NIR (CH_2Cl_2) λ_{max} (ϵ) = 319 (40600), 359 (34000), 393 (35500), 484 (28500), 877 (36200), 939 (26400), 976 (23100), and 1083 nm (72600 $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$).

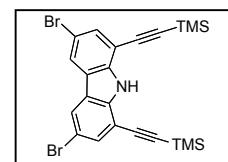
3,6-Dibromo-1,8-diiodocarbazole (**4**)



To an AcOH (50mL) and conc. H_2SO_4 (1.0 mL) suspension of 3,6-dibromocarbazole (2.05 mg, 6.31 mmol) was added ICl (1.4 mL, 27 mmol), and the mixture was heated for 17 h at 90 $^\circ\text{C}$ under Ar. After cooling to rt, water was added and resulting suspension was filtered, washed well with water and hexane to provided crude **4** (2.76 mg, 4.78 mmol, 76%). This product was used for next step without purification due to low solubility.

^1H NMR (CDCl_3) δ = 8.09 (s, 1H, NH), 8.03 (s, 2H, carbazole-H), and 7.91 ppm (s, 2H, carbazole-H); The ^{13}C NMR spectrum couldn't detect peaks due to poor solubility; MALDI-TOF-MS: m/z = 576.58. calcd for $\text{C}_{12}\text{H}_5\text{NBr}_2\text{I}_2$: 576.69 [M^+]; Mp: 225–227 $^\circ\text{C}$; UV/Vis (CH_2Cl_2) λ_{max} (ϵ) = 295 (12900), 303 (18700), 344 (4990) and 359 nm (5580 $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$).

3,6-Dibromo-1,8-bis(trimethylsilylethynyl)carbazole (**5**)



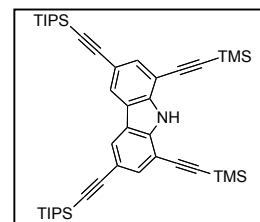
A flask containing **4** (2.76 mg, 4.78 mmol), CuI (33.8 mg, 178 μmol), and $\text{PdCl}_2(\text{PPh}_3)_2$ (68.5 mg, 97.6 μmol) was purged with Ar, and then charged with anhydrous THF (24 mL) and Et_3N (6 mL). After this solution was degassed, trimethylsilylacetylene (4.0 mL, 28 mmol)

was added and the mixture was stirred for 19 h at room temperature. After the solvents were evaporated, the residue was separated over a silica gel column with CH₂Cl₂/hexane to give **5** (1.88 mg, 3.64 mmol, 76%)

¹H NMR (CDCl₃) δ = 8.50 (s, 1H, NH), 8.06 (d, *J* = 1.5 Hz, 2H, carbazole-H), 7.66 (d, *J* = 1.7 Hz, 2H, carbazole-H), 0.34 ppm (s, 18H, TMS); ¹³C NMR (CDCl₃) δ = 139.03, 131.88, 123.90, 123.33, 112.16, 107.64, 101.32, 98.73, and 0.02 ppm; MALDI-TOF-MS: *m/z* = 516.96. calcd for C₂₂H₂₃NBr₂Si₂: 516.97 [M⁺]; Mp: 183–185 °C; UV/Vis (CH₂Cl₂) λ_{max} (ε) = 309 (22800), 319 (22100), 366 (7450), and 379 nm (9000 mol⁻¹dm³cm⁻¹).

3,6-Bis(triisopropylsilylethynyl)-1,8-bis(trimethylsilylethynyl)carbazole (**6**)

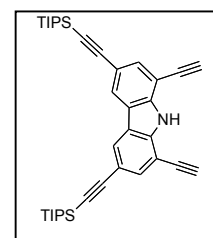
A dry toluene (30 mL) solution of **5** (1.32 g, 2.55 mmol), Pd(PPh₃)₄, (27.4 mg, 23.7 μmol), and tributyl(triisopropylsilylethynyl)tin^[S1] (2.59 g, 5.50 mmol) was degassed. The mixture was stirred for overnight at reflux under



Ar. After the solvent was evaporated, the residue was separated over a silica gel column with dichloromethane/hexane as an eluent and recycling GPC to give **6** (954 mg, 1.33 mmol, 52%) as yellow oil.

¹H NMR (CDCl₃) δ = 8.61 (s, 1H, NH), 8.14 (d, *J* = 1.5 Hz, 2H, carbazole-H), 7.70 (d, *J* = 1.5 Hz, 2H, carbazole-H), 1.17 (s, 42H, TIPS), and 0.35 ppm (s, 18H, TMS); ¹³C NMR (CDCl₃) δ = 140.09, 133.25, 125.22, 122.71, 115.48, 106.94, 106.23, 100.32, 99.42, 88.94, 18.73, 11.37, and 0.04 ppm; MALDI-TOF-MS: *m/z* = 719.53. calcd for C₄₄H₆₅NSi₄: 719.42 [M⁺]; Mp: 210–212 °C; UV/Vis (CH₂Cl₂) λ_{max} (ε) = 315 (40000), 321 (39700), 364 (8600), and 381 nm (9220 mol⁻¹dm³cm⁻¹).

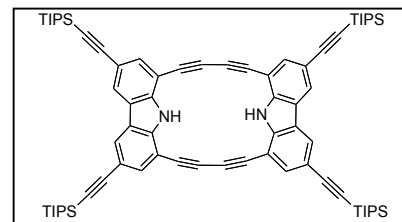
1,8-Diethynyl-3,6-bis(triisopropylsilylethynyl)carbazole (**7**)



Tetrabutylammonium fluoride (3.4 mL, 1.0 M in THF, 3.4 mmol) was added to the CH₂Cl₂ (20 mL) solution of **6** (954 mg, 1.33 mmol) and stirred for 5 min. The mixture was passed through a silica gel column with CH₂Cl₂, and solvent was evaporated, which provided **7** (645 mg, 1.12 mmol, 84%).

¹H NMR (CDCl₃) δ = 8.63 (s, 1H, NH), 8.17 (s, 2H, carbazole-H), 7.73 (s, 2H, carbazole-H), 3.49 (s, 2H, C \equiv CH), 1.18 ppm (s, 42H, TIPS); ¹³C NMR (CDCl₃) δ = 140.22, 133.86, 125.43, 122.78, 115.63, 106.74, 105.11, 89.24, 82.68, 78.60, 18.73, 11.38 78.95 ppm; MALDI-TOF-MS: m/z = 576.27. calcd for C₃₈H₅₀NSi₂: 576.35 [(M+H)⁺]; Mp: 158–160 °C; UV/Vis (CH₂Cl₂) λ_{\max} (ϵ) = 308 (41600), 316 (44900), 360 (5540), and 377 nm (5600 mol⁻¹dm³cm⁻¹).

Tetrakis(triisopropylsilylethynyl)-substituted butadiyne-bridged carbazole dimer (**8**)



To a pyridine (60 mL) suspension of Cu(OAc)₂·H₂O (1.52 g, 7.60 mmol) was added dropwise a toluene (200 mL) solution of **7** (585 mg, 1.02 mmol) for 3 h, and the mixture was stirred for further 3.5 days under air. After the solvents were evaporated, the residue was separated over a silica gel column with CHCl₃ and GPC to give **8** (157 mg, 137 μ mol, 27%).

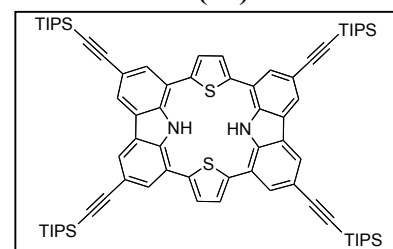
¹H NMR (CDCl₃) δ = 9.48 (s, 2H, NH), 8.11 (d, J = 1.2 Hz, 4H, carbazole-H), 7.59 (d, J = 1.2 Hz, 4H, carbazole-H), 1.19 ppm (s, 84H, TIPS); ¹³C NMR (CDCl₃) δ = 142.18, 131.81, 126.19, 122.73, 115.91, 106.50, 104.71, 89.59, 79.62, 79.49, 18.75, and 11.38 ppm; HR-ESI-MS: m/z = 1146.6409. calcd for C₇₆H₉₃N₂Si₄: 1146.6453 [(M-H)⁻]; Mp: 260–270 °C (decomp.); UV/Vis (CH₂Cl₂) λ_{\max} (ϵ) =

300 (104000), 325 (98200) and 429 nm (60200 mol⁻¹dm³cm⁻¹); Fluorescence (CH₂Cl₂, λ_{ex} = 360 nm);

λ_{max} = 436 nm, Φ_F = 0.975.

Tetrakis(triisopropylsilylethynyl)-substituted thiophene-bridged carbazole dimer (9a)

A *p*-xylene/2-methoxyethanol (10.0 mL/10.0 mL) solution of **8** (157 mg, 137 μmol) and Na₂S·9H₂O (604 mg, 2.52 mmol) was heated refluxed for 14 h under Ar. The mixture was diluted with CH₂Cl₂, washed with water, and passed through a silica gel column with CH₂Cl₂.

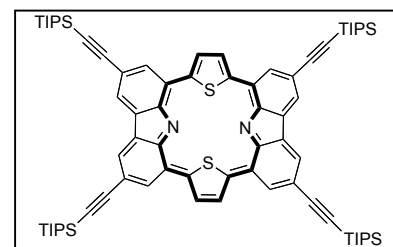


After the solvent was evaporated, the residue was purified by recycling GPC to give **9a** (68.2 mg, 56.1 μmol, 41%).

¹H NMR (CDCl₃) δ = 10.47 (s, 2H, NH), 8.25 (d, *J* = 1.5 Hz, 4H, carbazole-H), 7.87 (d, *J* = 1.5 Hz, 4H, carbazole-H), 7.46 (s, 4H, thiophene-β), and 1.21 ppm (s, 84H, TIPS); ¹³C NMR (CDCl₃) δ = 138.45, 136.80, 128.10, 127.19, 124.95, 123.72, 117.53, 116.04, 107.49, 89.13, 18.81, and 11.46 ppm; HR-ESI-MS: *m/z* = 1214.6260. calcd for C₇₆H₉₇N₂S₂Si₄: 1214.6207 [(M-H)⁻]; Mp: > 300 °C; UV/Vis (CH₂Cl₂) λ_{max} (ε) = 315 (83600) and 410 nm (23600 mol⁻¹dm³cm⁻¹); Fluorescence (CH₂Cl₂, λ_{ex} = 360 nm); λ_{max} = 442 nm, Φ_F = 0.522.

Tetrakis(triisopropylsilylethynyl)-substituted thiophene bridged carbazole dimer (9b)

To a dry CH₂Cl₂ (20 mL) solution of **9a** (23.9 mg, 19.7 μmol) was added MnO₂ (418 mg) and resulting suspension was stirred. After 14 h, MnO₂ (918 mg) was added and the mixture was stirred for further 9 h. the mixture was then passed through a pad of celite. Evaporation of the solvent provided **9b** (19.4 mg, 16.0 μmol, 81%).



¹H NMR (CDCl₃) δ = 9.08 (s, 4H, carbazole-H), 8.97 (s, 4H, carbazole-H), 8.42 (s, 4H, thiophene-β), and 1.21 ppm (s, 84H, TIPS); The ¹³C NMR spectrum couldn't detect peaks due to poor solubility;

MALDI-TOF-MS: $m/z = 1213.85$. calcd for $C_{76}H_{96}N_2S_2Si_4$: 1213.61 [M^+]; Mp: $> 300\text{ }^\circ\text{C}$; UV/Vis/NIR (CH_2Cl_2) λ_{max} (ϵ) = 329 (53500), 361 (59300), 395 (40000), 925 (52100), 998 (38200), and 1110 nm ($59300\text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$).

Fig. S1 ^1H and ^{13}C NMR spectra of **2** in CDCl_3

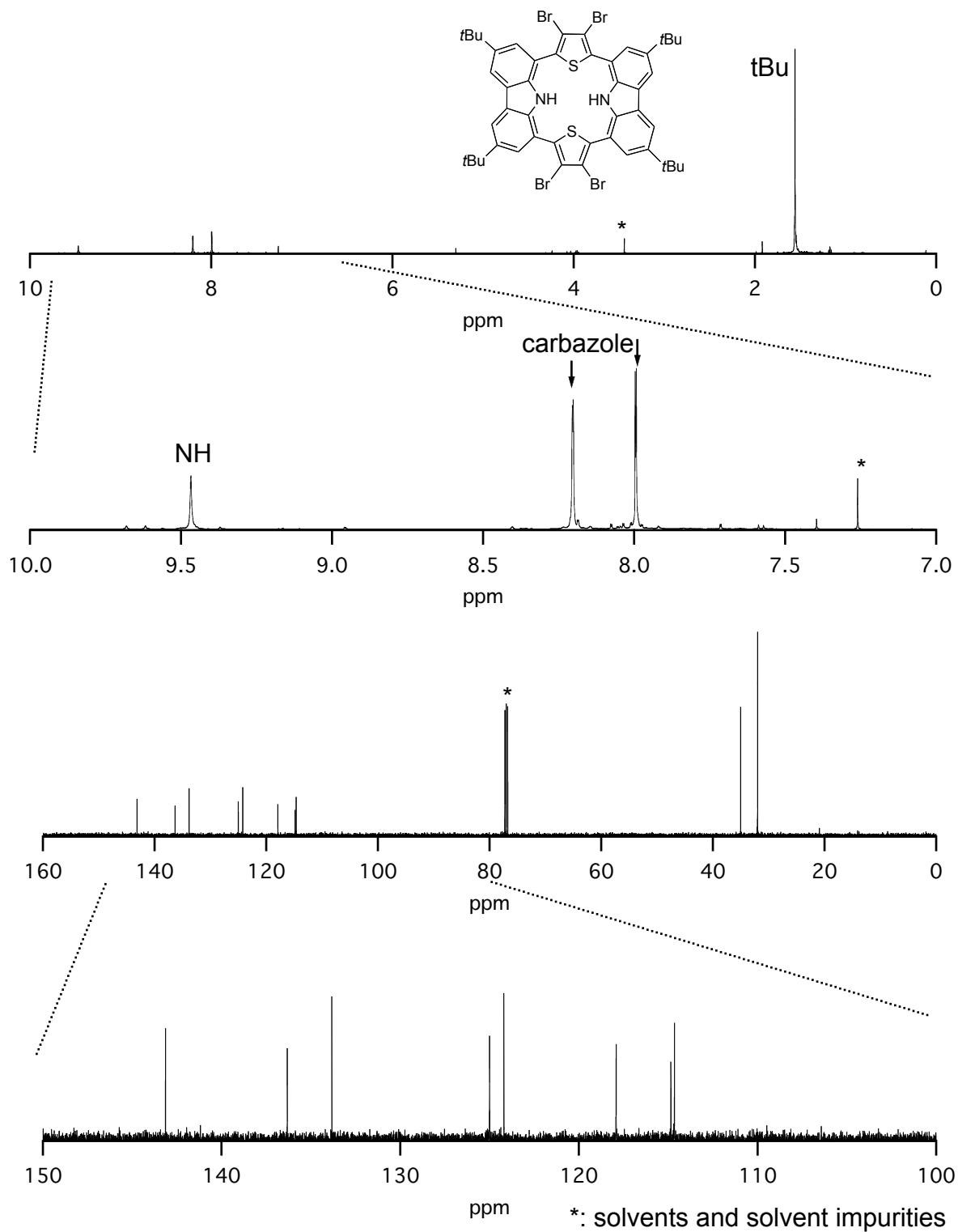


Fig. S2 ^1H and ^{13}C NMR spectra of **3a** in CDCl_3

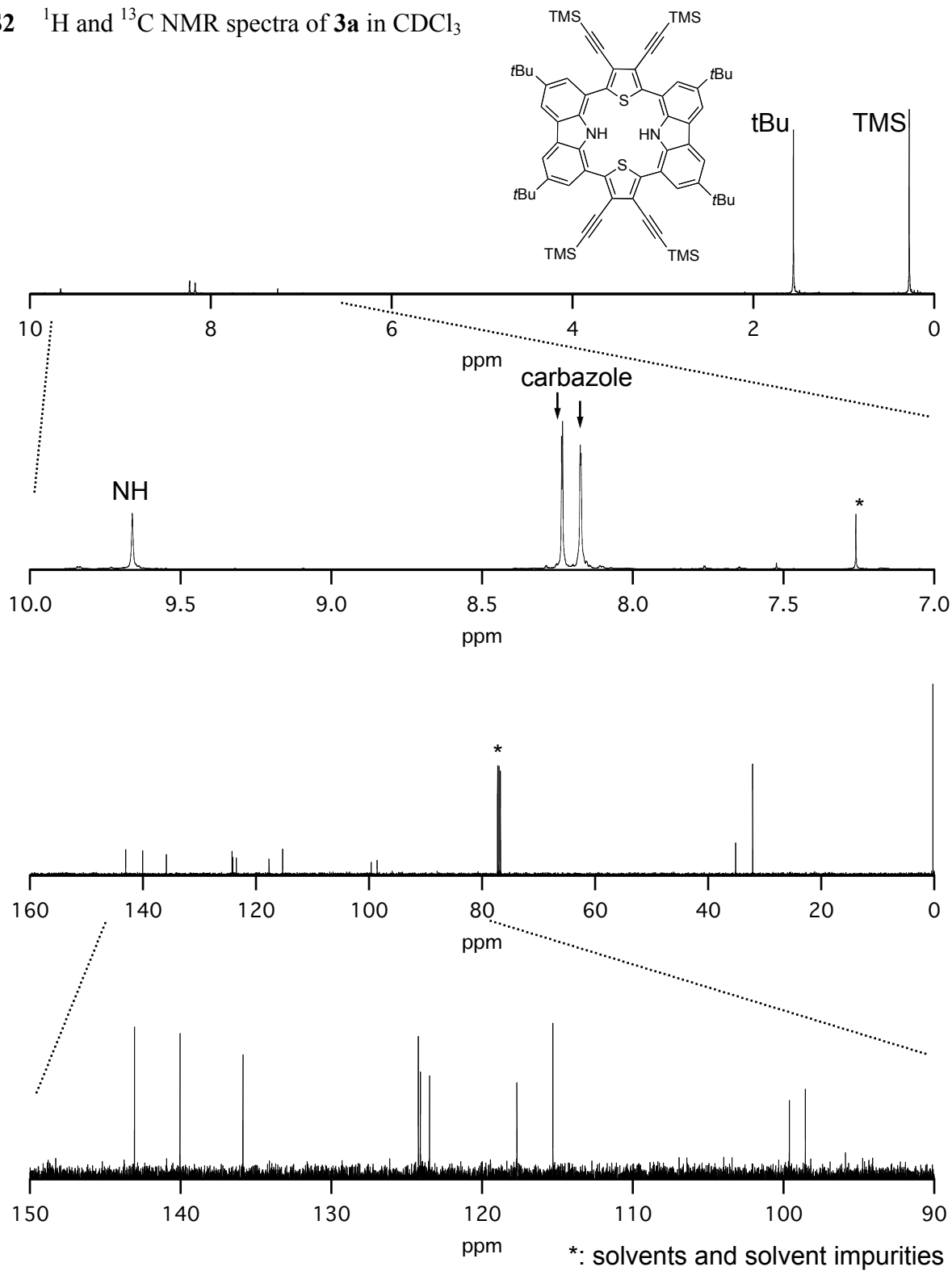


Fig. S3 ^1H NMR spectrum of **3b** in CDCl_3

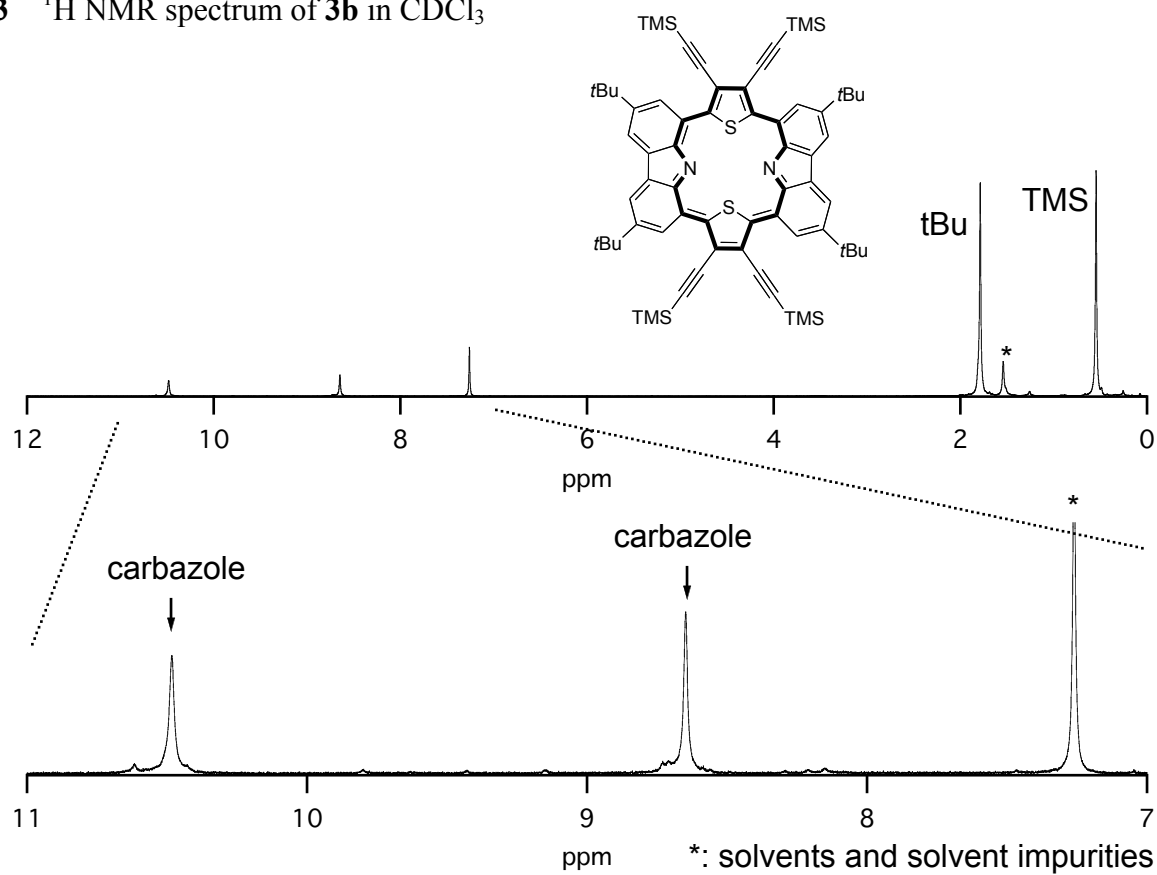


Fig. S4 ^1H NMR spectrum of **4** in CDCl_3

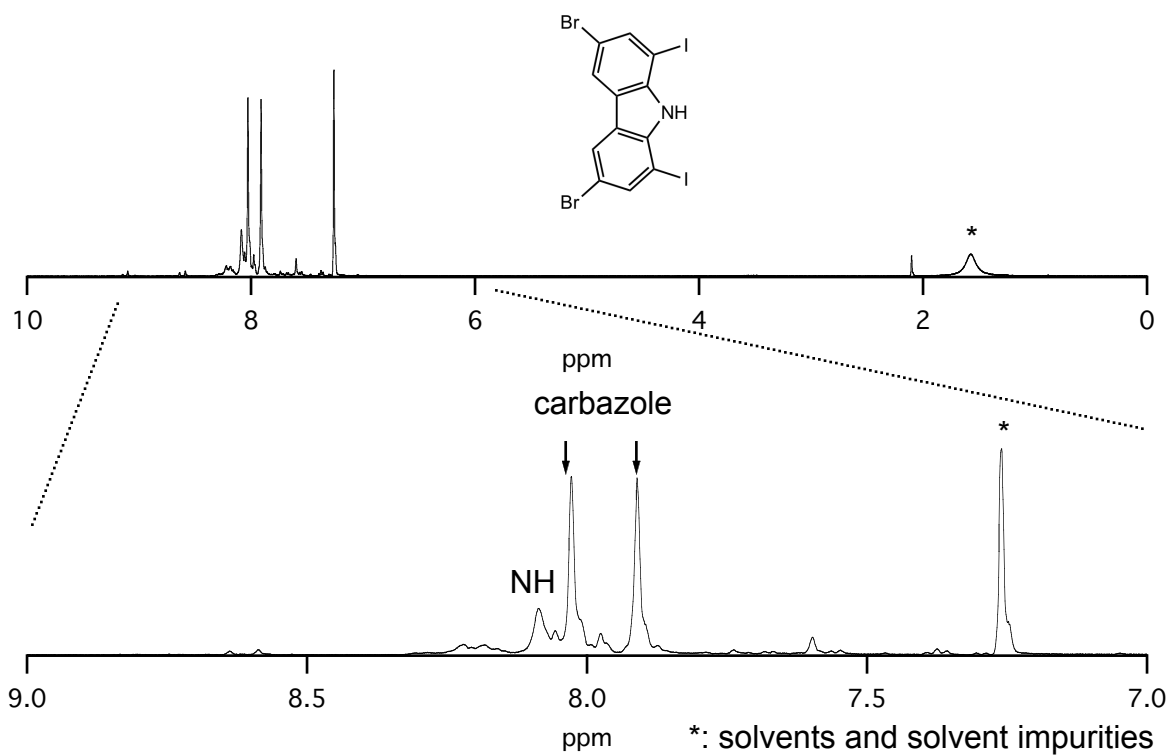


Fig. S5 ^1H and ^{13}C NMR spectra of **5** in CDCl_3

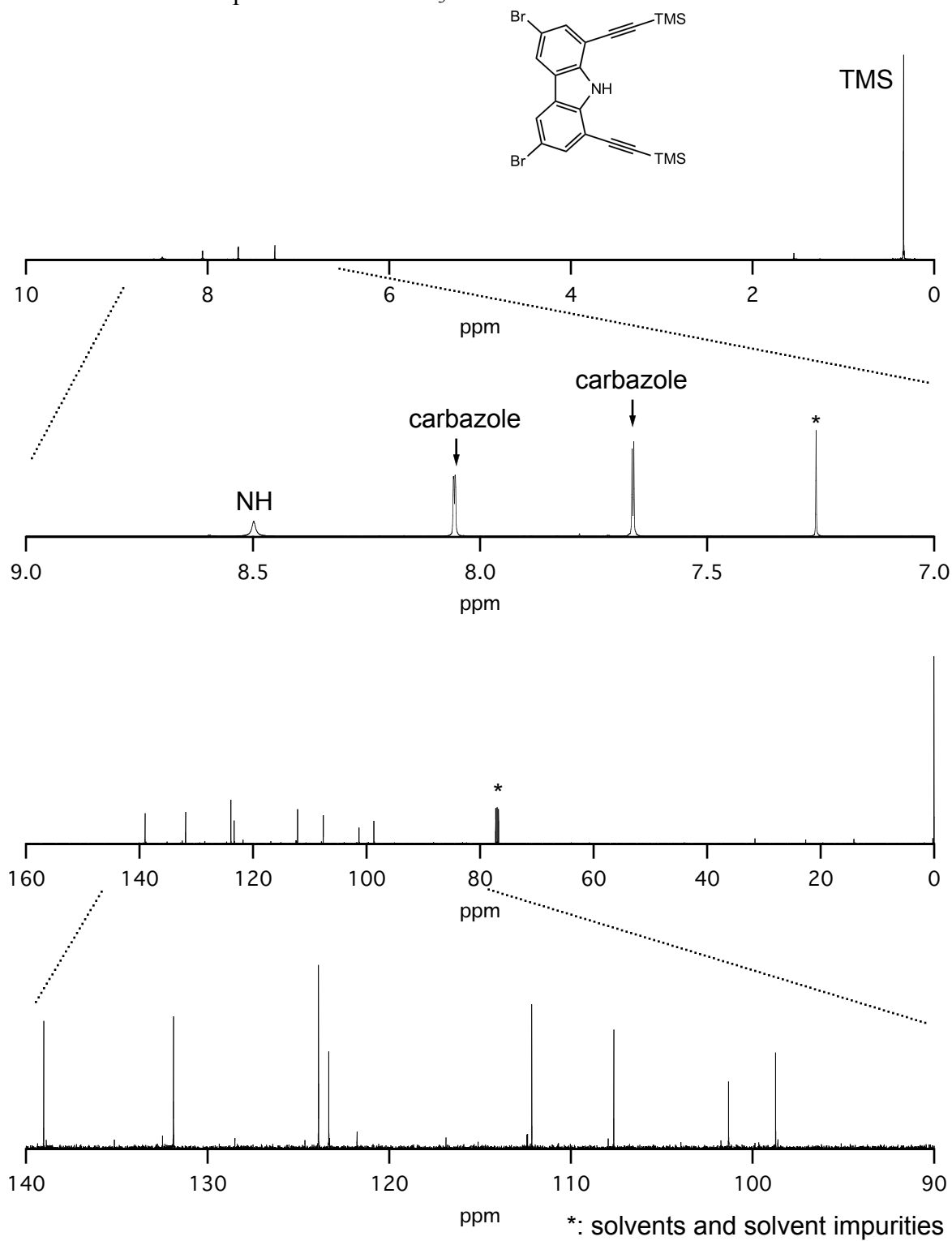


Fig. S6 ^1H and ^{13}C NMR spectra of **6** in CDCl_3

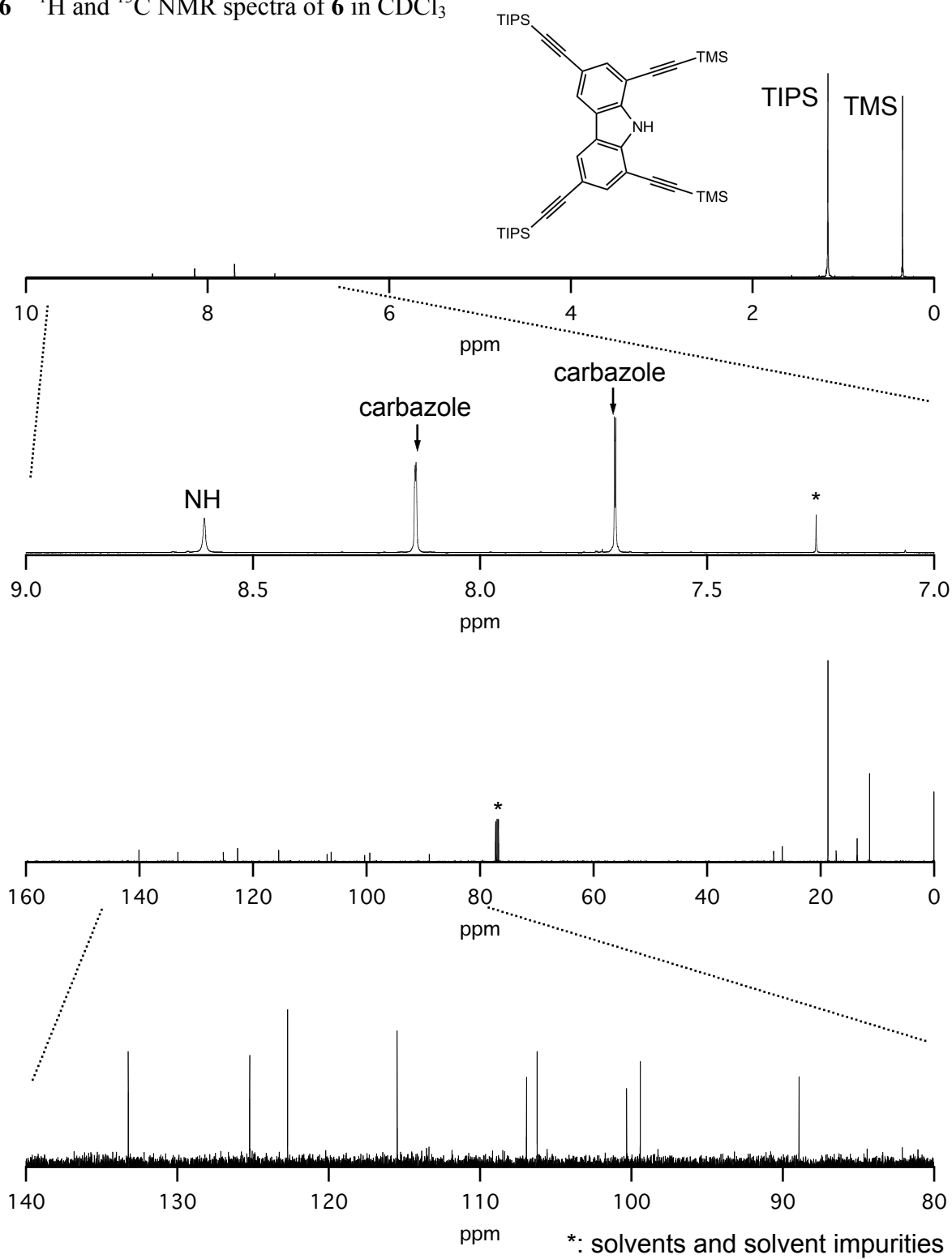


Fig. S7 ^1H and ^{13}C NMR spectra of **7** in CDCl_3

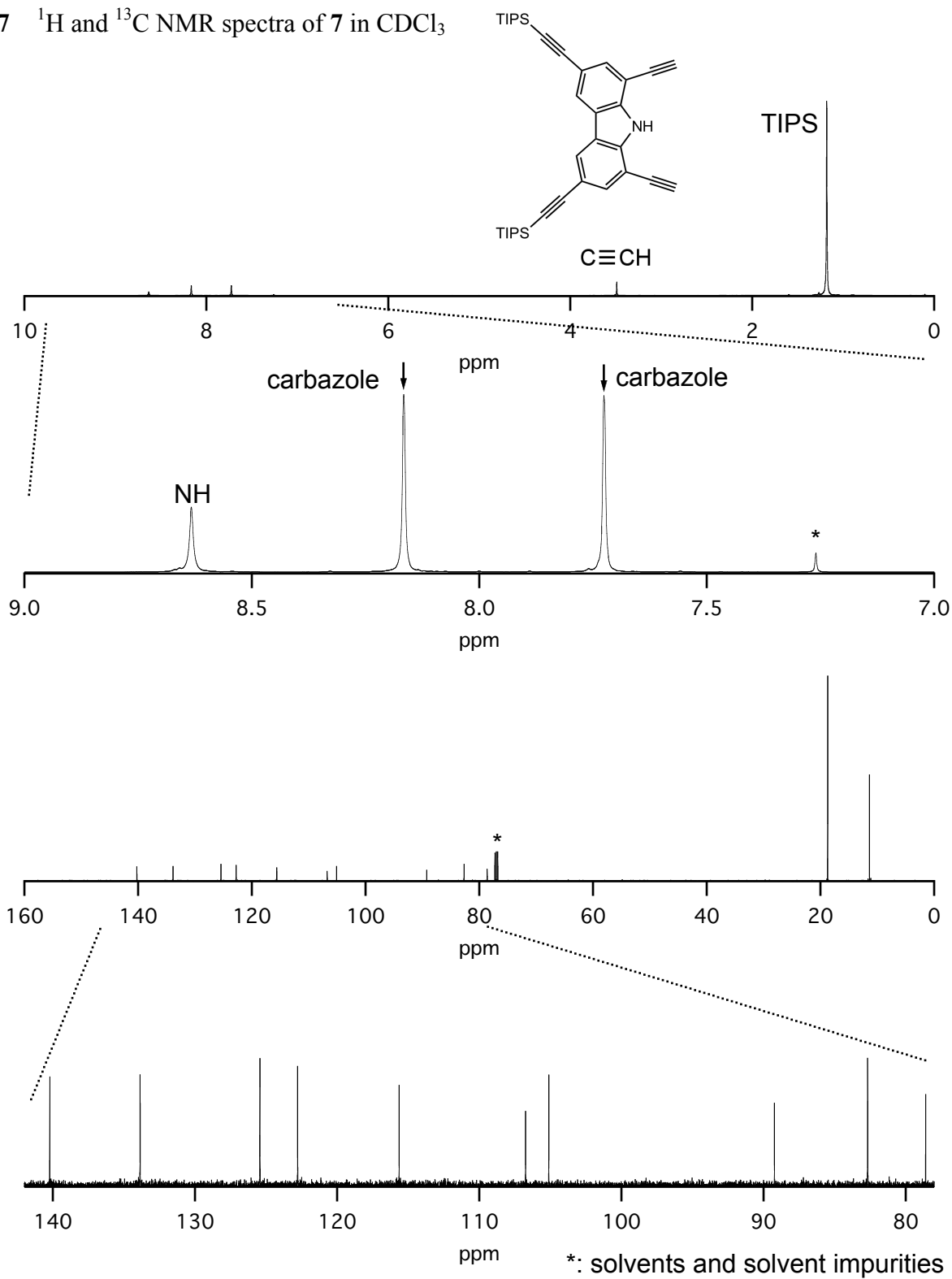


Fig. S8 ^1H and ^{13}C NMR spectra of **8** in CDCl_3

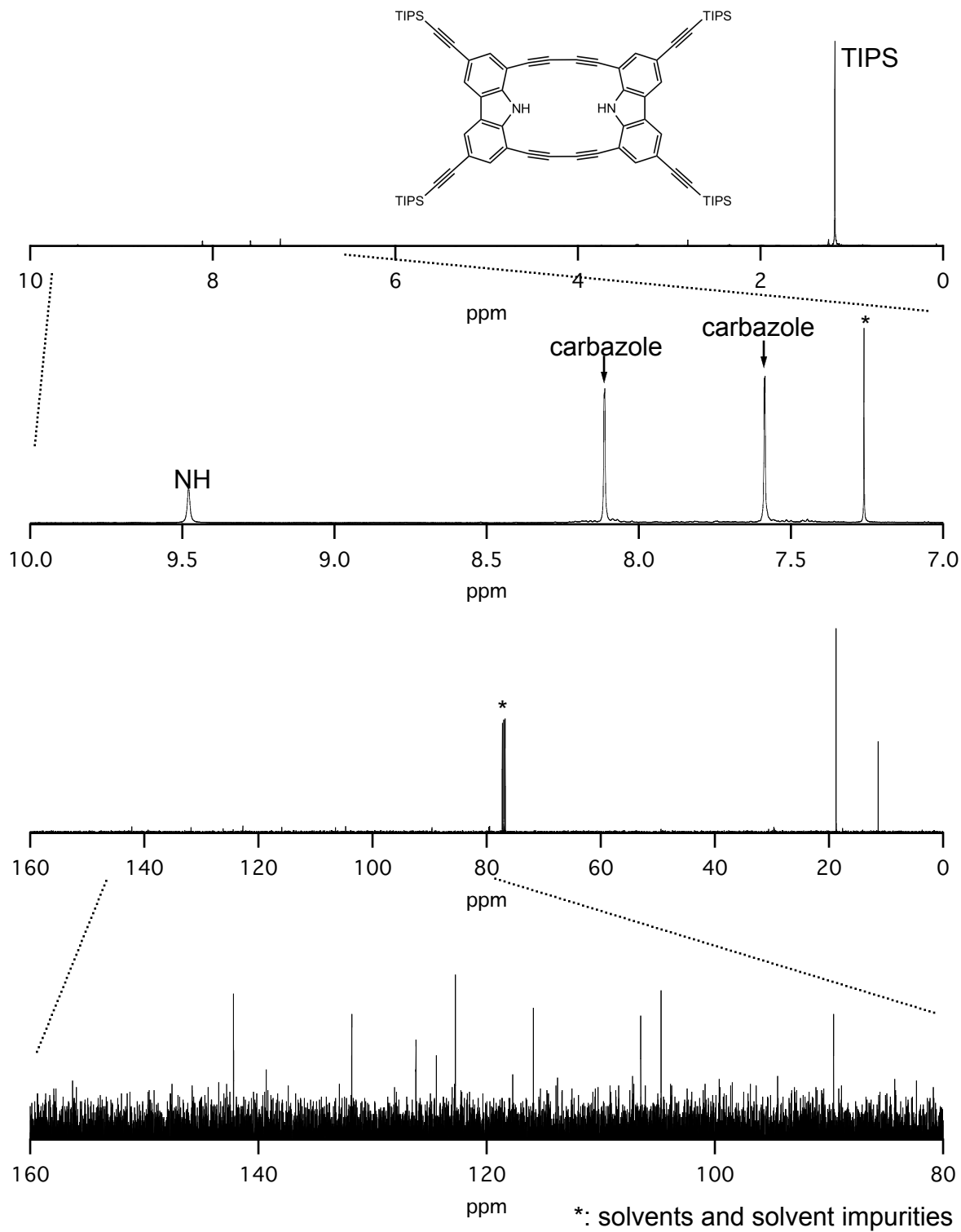


Fig. S9 ^1H and ^{13}C NMR spectra of **9a** in CDCl_3

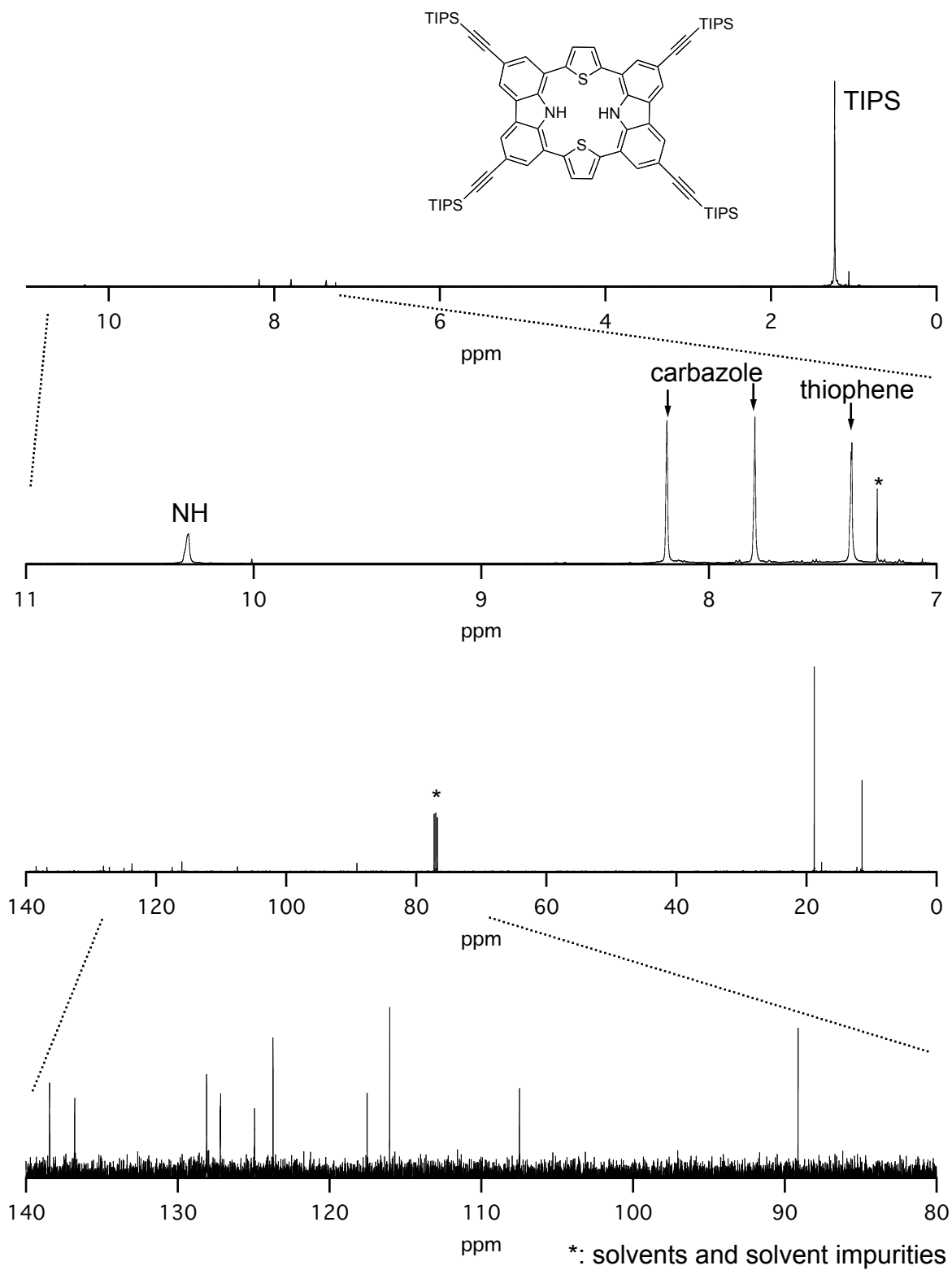


Fig. S10 ^1H and ^{13}C NMR spectra of **9b** in CDCl_3

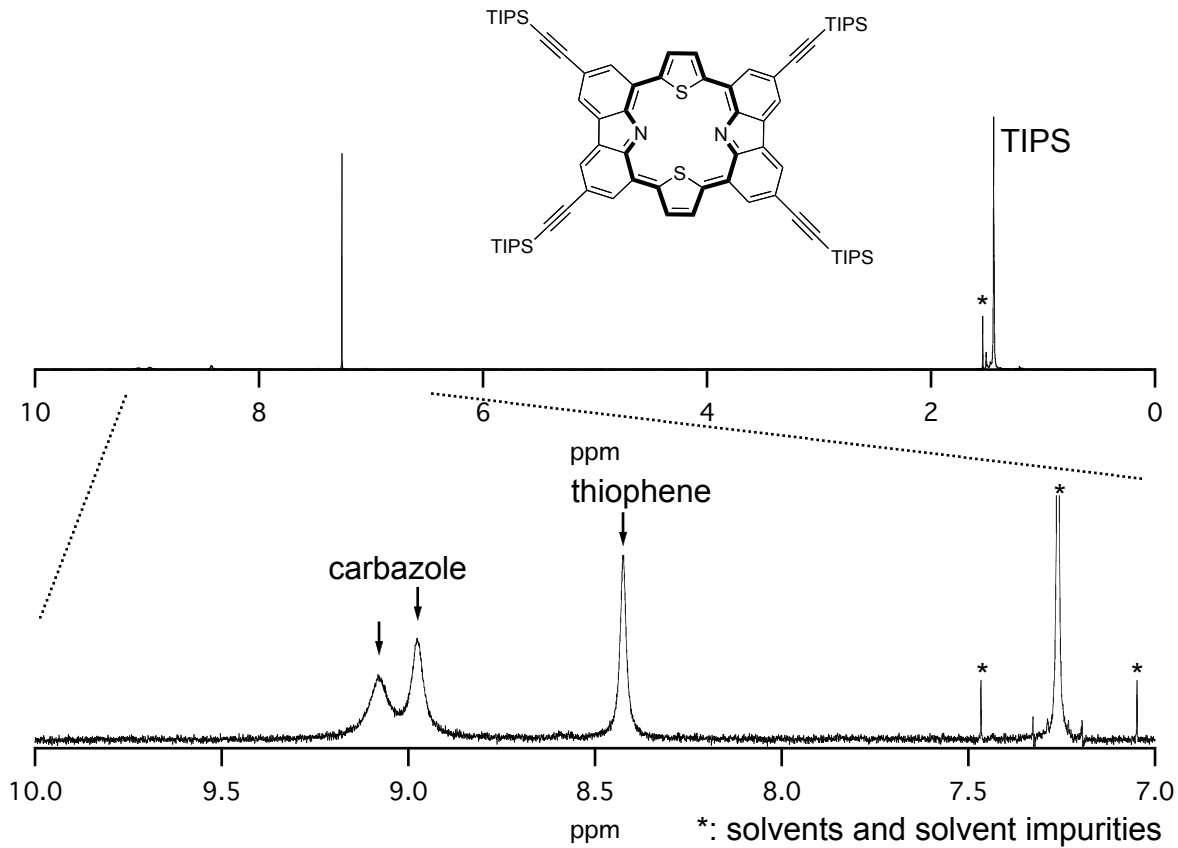


Fig. S11 Cyclic and differential pulse voltammograms of (a) **1b**, (b) **3b**, and (c) **9b**
(solvent: CH₂Cl₂ supporting electrolyte: Bu₄NPF₆ (0.10 M), counter electrode: Pt, reference electrode: Ag/Ag⁺, scan rate: 0.05 V/s).

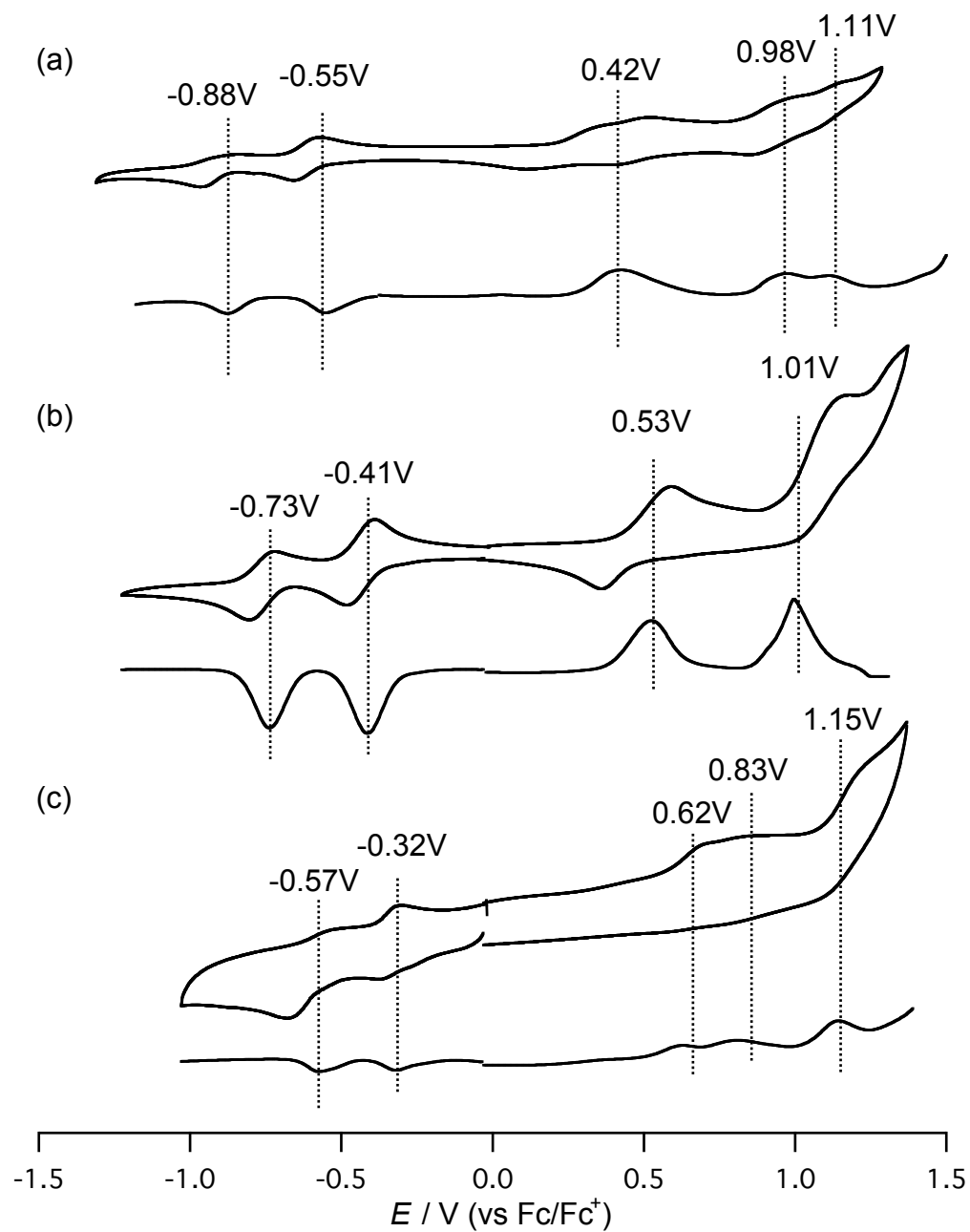
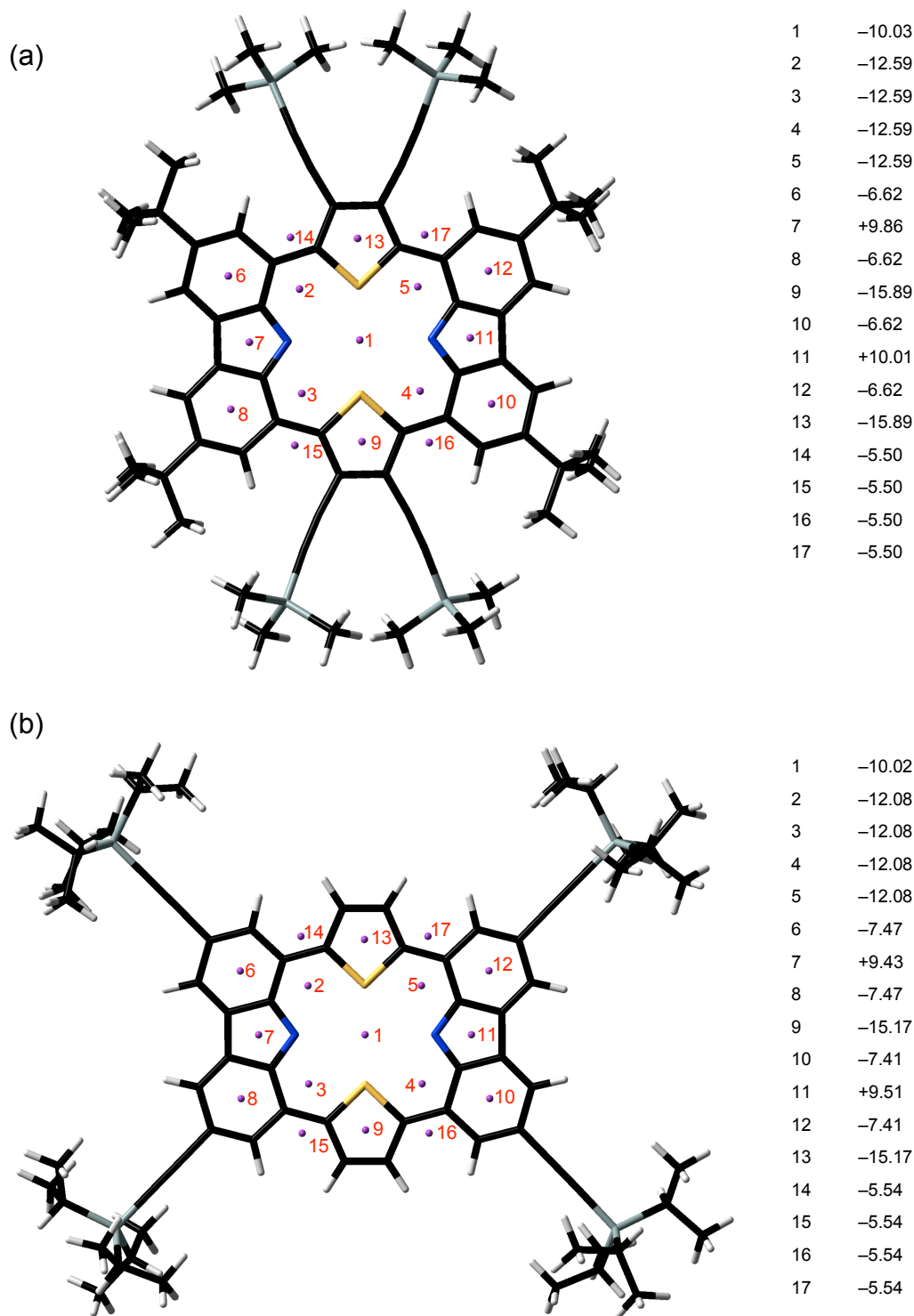


Fig. S12 NICS(0) values at the selected points of (a) **3b** and (b) **9b** calculated at B3LYP/6-31G* level using Gaussian 09 package^[S2-4]



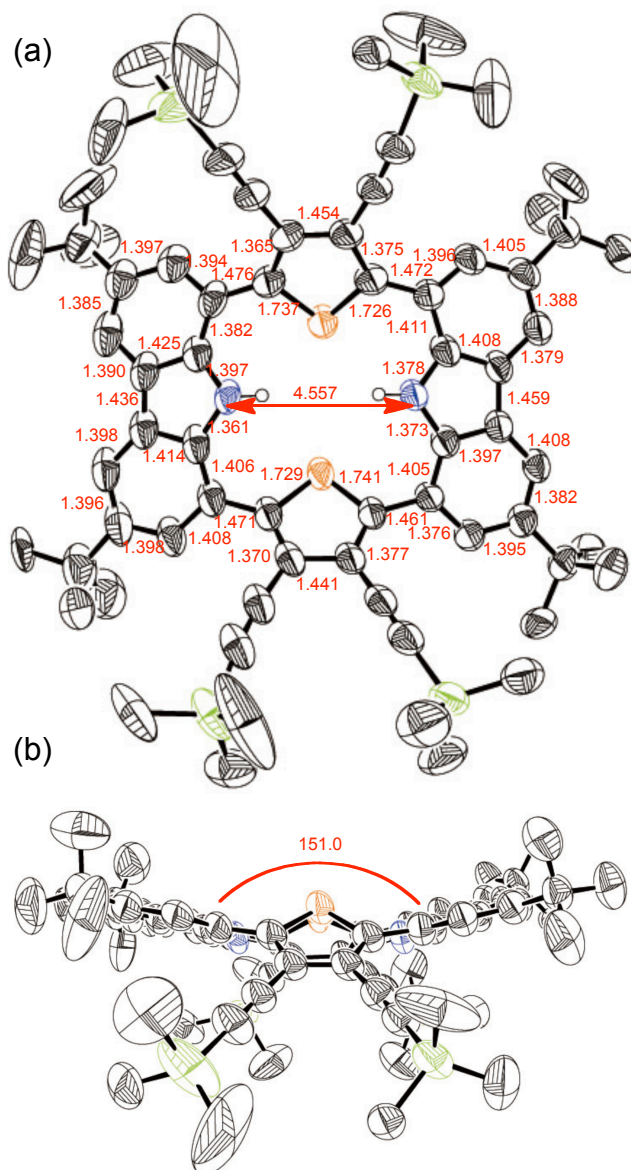
X-ray crystal structure

Single crystals of **3a** suitable for X-ray crystal analysis were obtained by slow diffusion of methanol into a CH₂Cl₂ solution of **3a**. X-ray data of **3a** at 93 K were taken on Rigaku-Raxis-RAPID imaging plate system with Cu-K α radiation (λ = 1.54187 Å) and graphite monochromator. Structure was processed by CrystalStructure and then refined by YADOKARI. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated in ideal positions. The solvent molecules contained in the lattice were severely disordered for **3a**. The contribution to the scattering arising from the presence of the disordered solvents in the crystals was removed by use of the utility SQUEEZE in the PLATON software package: (a) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*; Utrecht, The Netherlands, 2005; (b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **46**, 194.

The following serious alerts were generated due to the rotation of *t*-butyl and trimethylsilyl groups.

Large Non-Solvent	H	Ueq(max)/Ueq(min) ...	10.0 Ratio
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Fig. S13 X-ray crystal structure of **3a**: (a) top view and (b) side view. Hydrogen atoms except for NH protons are omitted for clarity. The selected bond distances(Å) and angle(°) are shown. The thermal ellipsoids were at 50% probability level.



References

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