Supplementary Information
for
Synthesis of Carbazole-Based Hetero-Core-Modified Porphyrins

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Fig. S1 ^{1}H and ^{13}C NMR spectra of **7** in $CDCl_3$

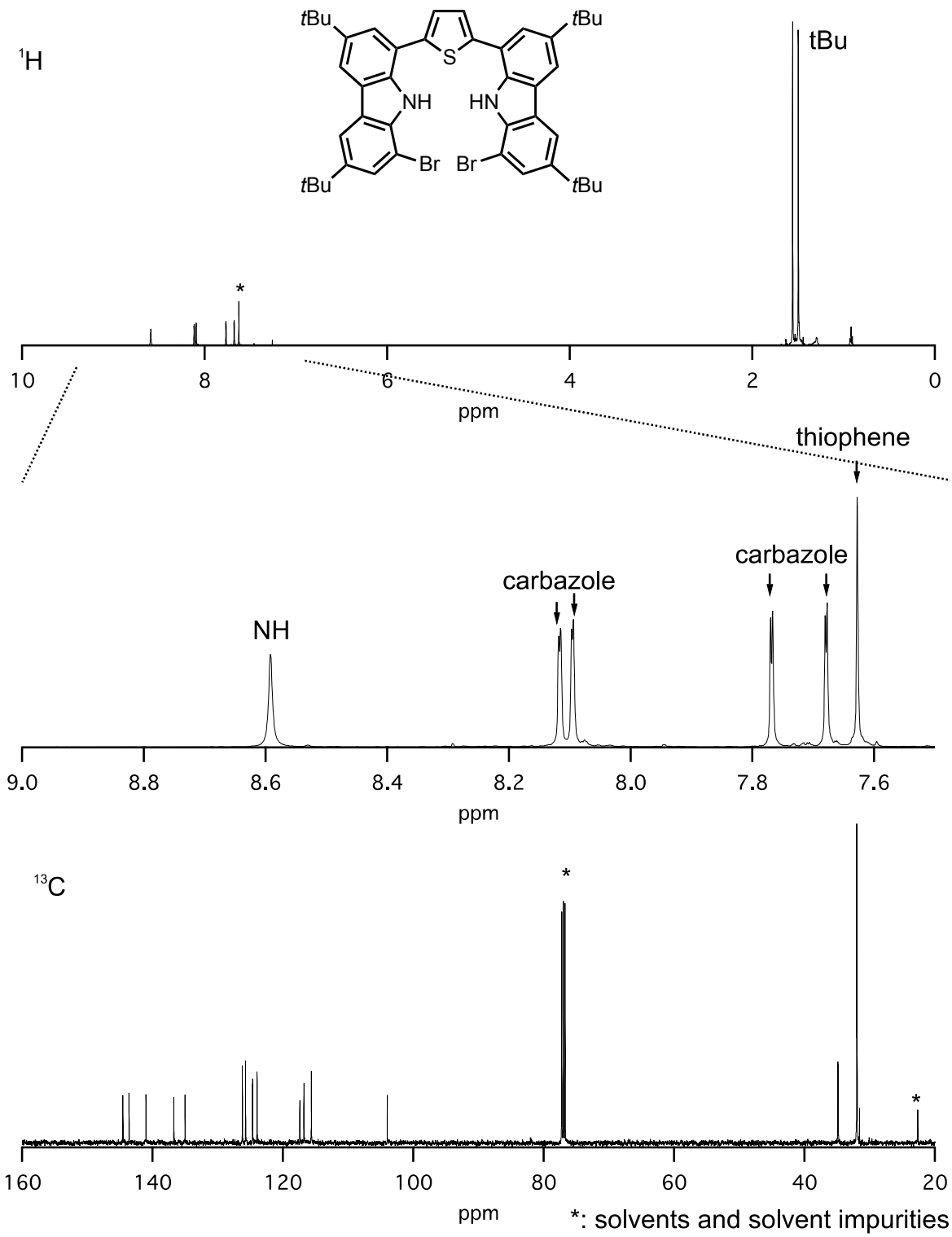


Fig. S2 ^{1}H and ^{13}C NMR spectra of **8** in $CDCl_3$

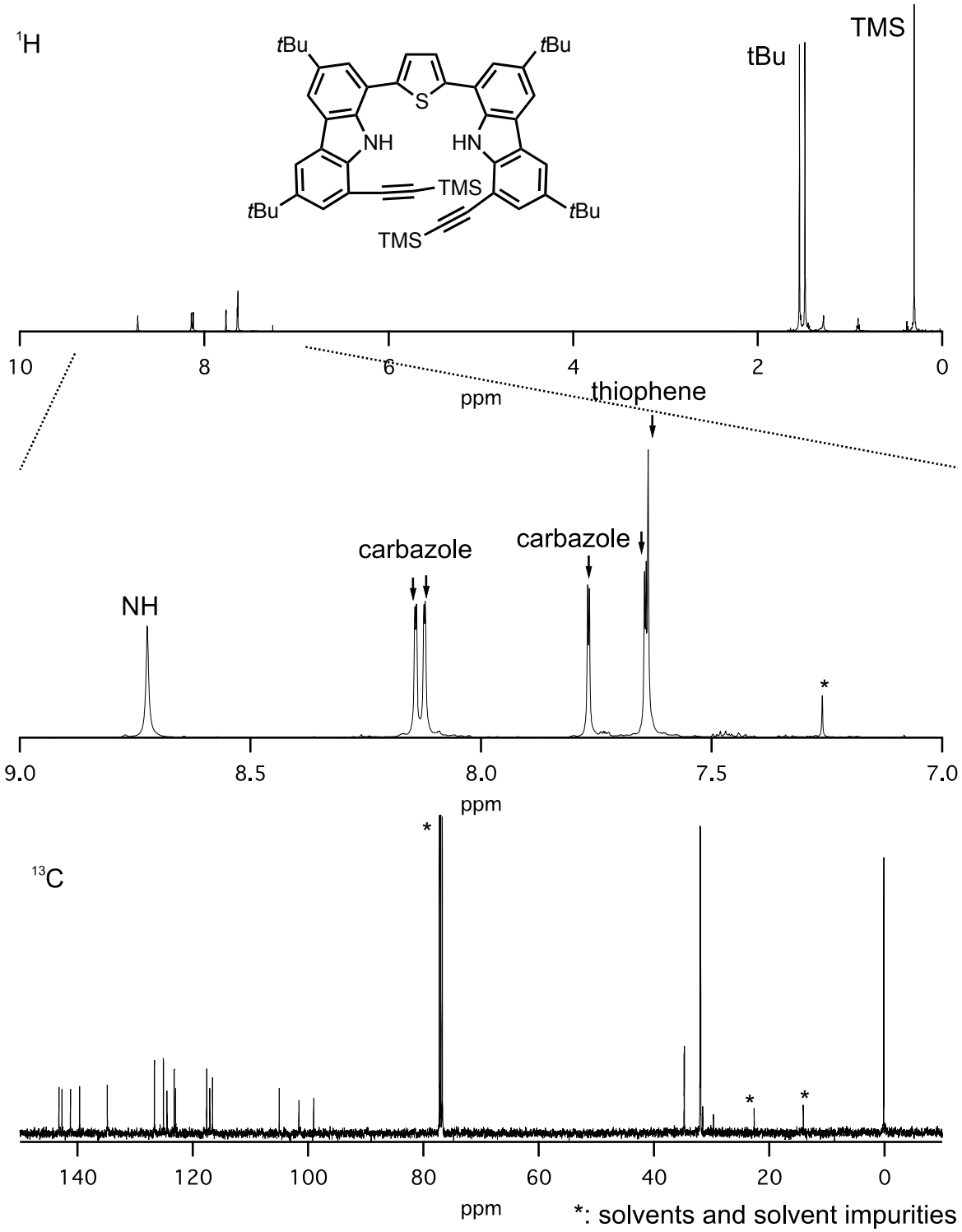


Fig. S3 ^{1}H and ^{13}C NMR spectra of **9** in $CDCl_3$

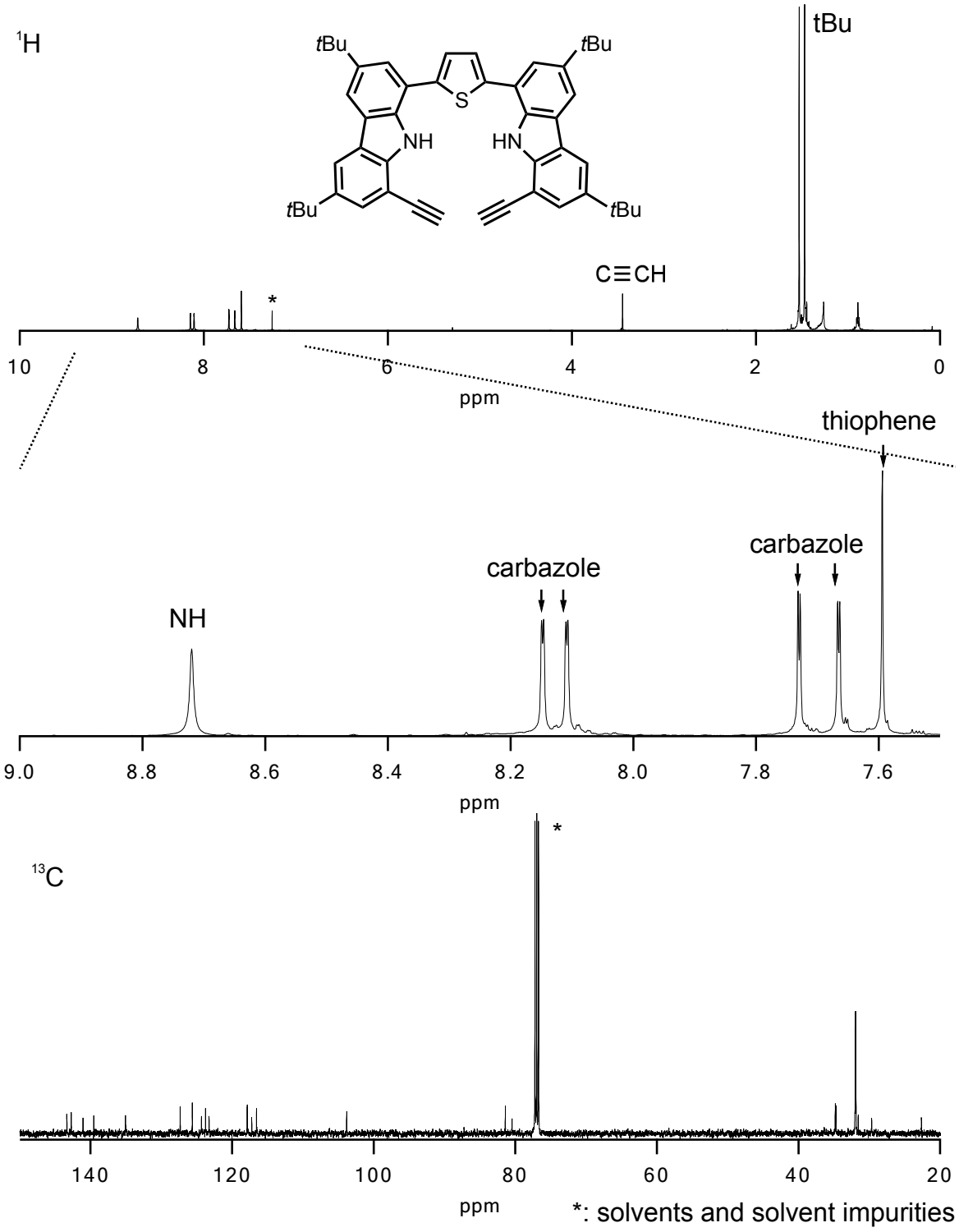


Fig. S4 ^{1}H and ^{13}C NMR spectra of **10** in $CDCl_3$

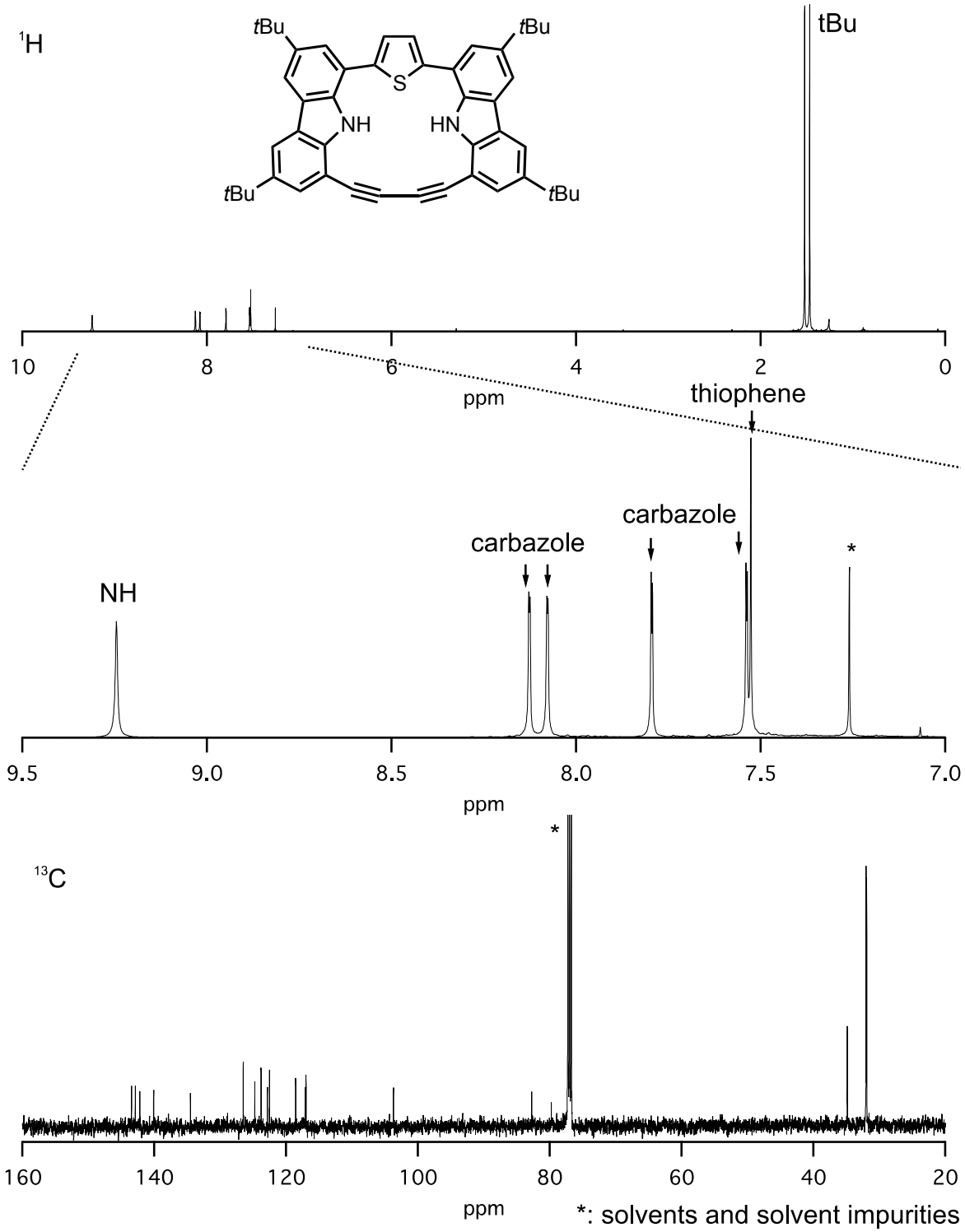


Fig. S5 ^{1}H and ^{13}C NMR spectra of **11a** in $CDCl_3$

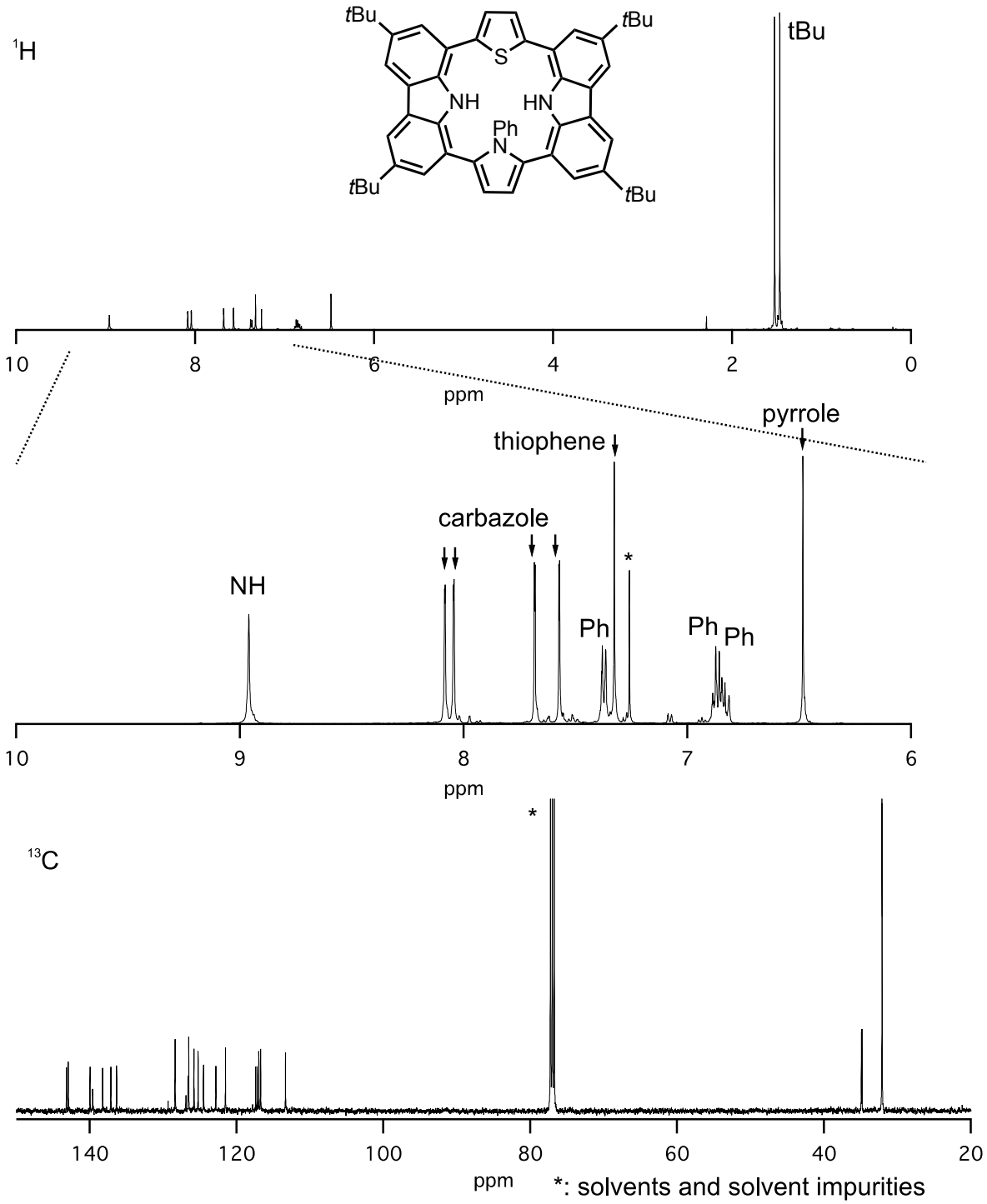


Fig. S6 ^{1}H and ^{13}C NMR spectra of **11b** in $CDCl_3$

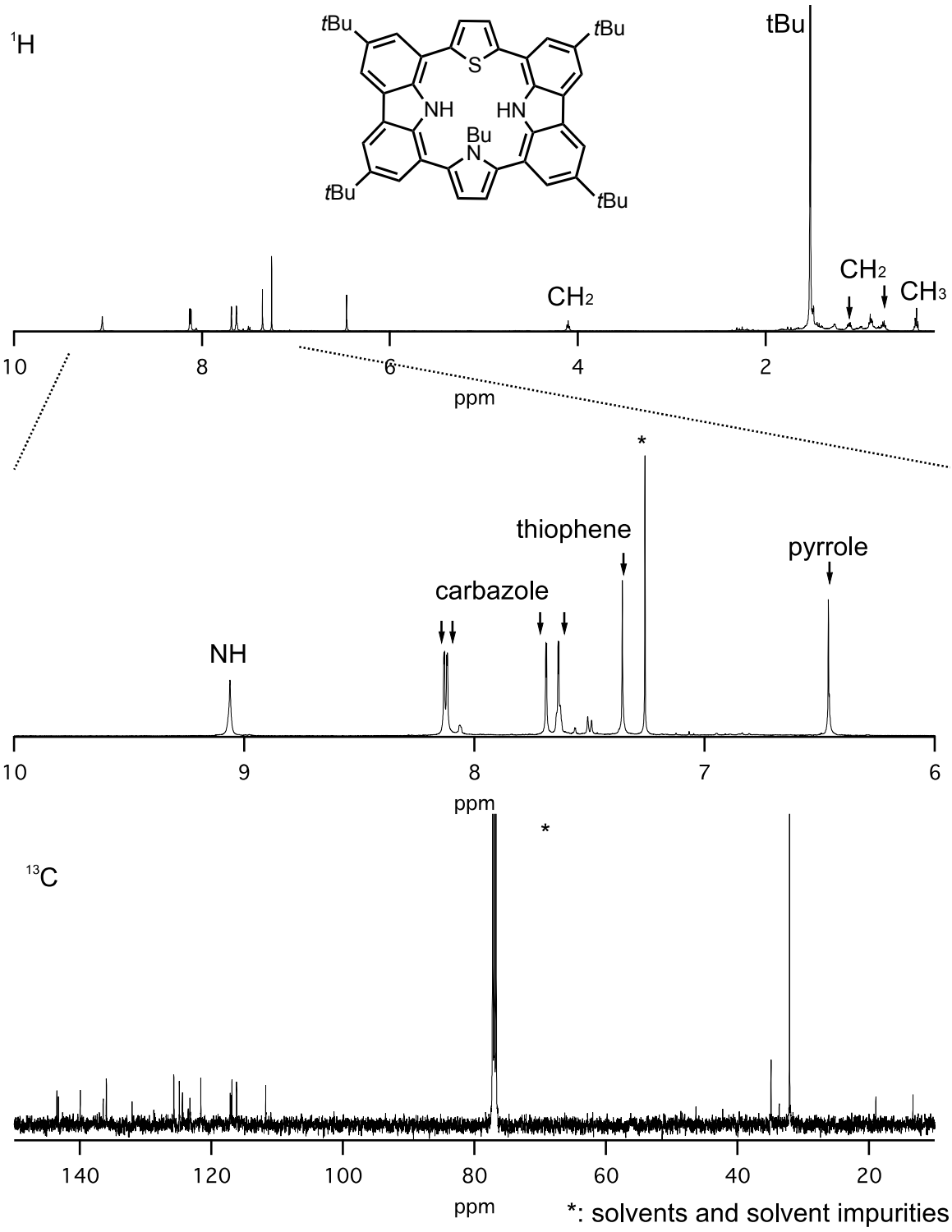


Fig. S7 ^{1}H and ^{13}C NMR spectra of **11c** in $CDCl_3$

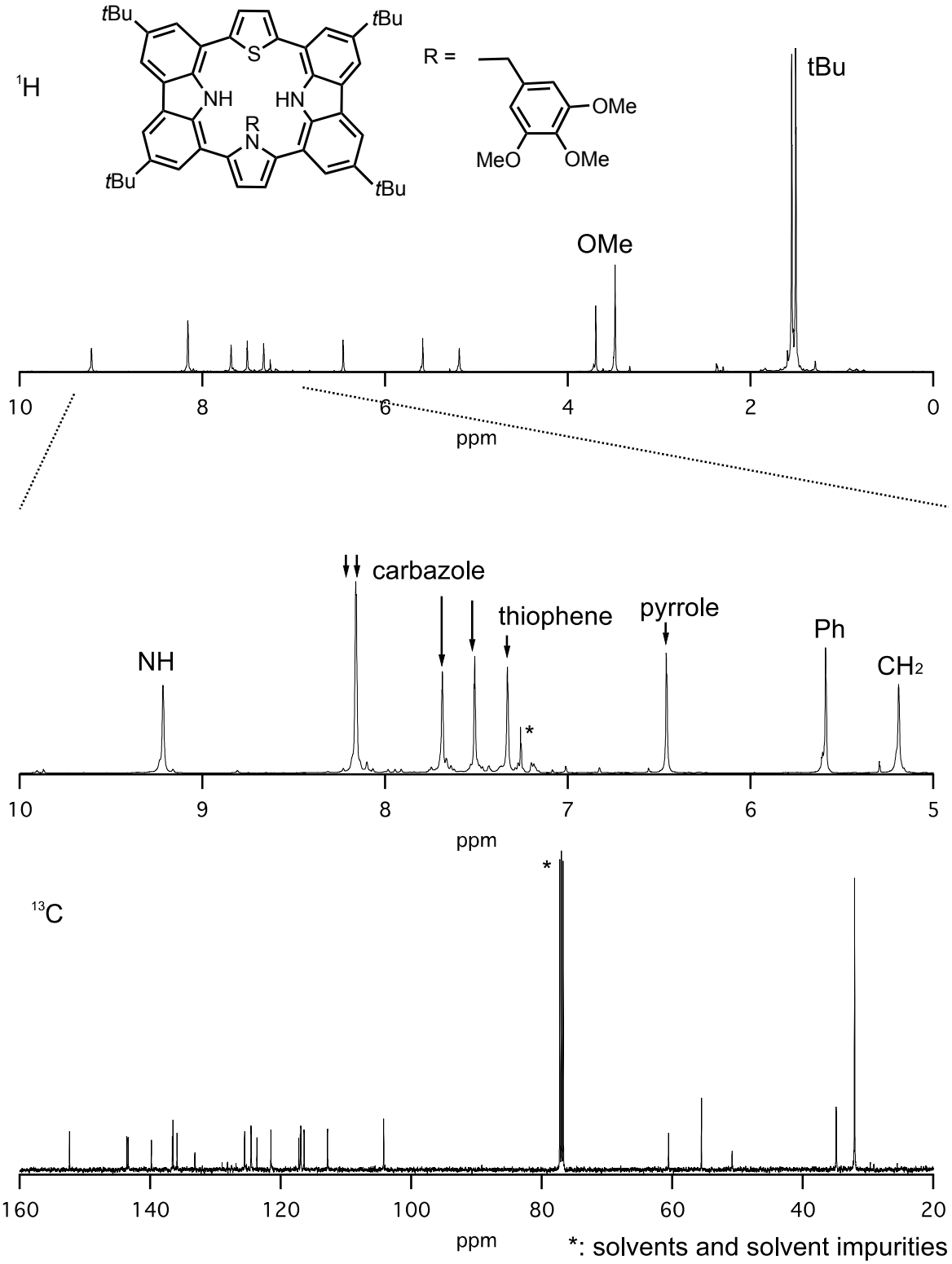


Fig. S8 ^{1}H and ^{13}C NMR spectra of **12** in $CDCl_3$

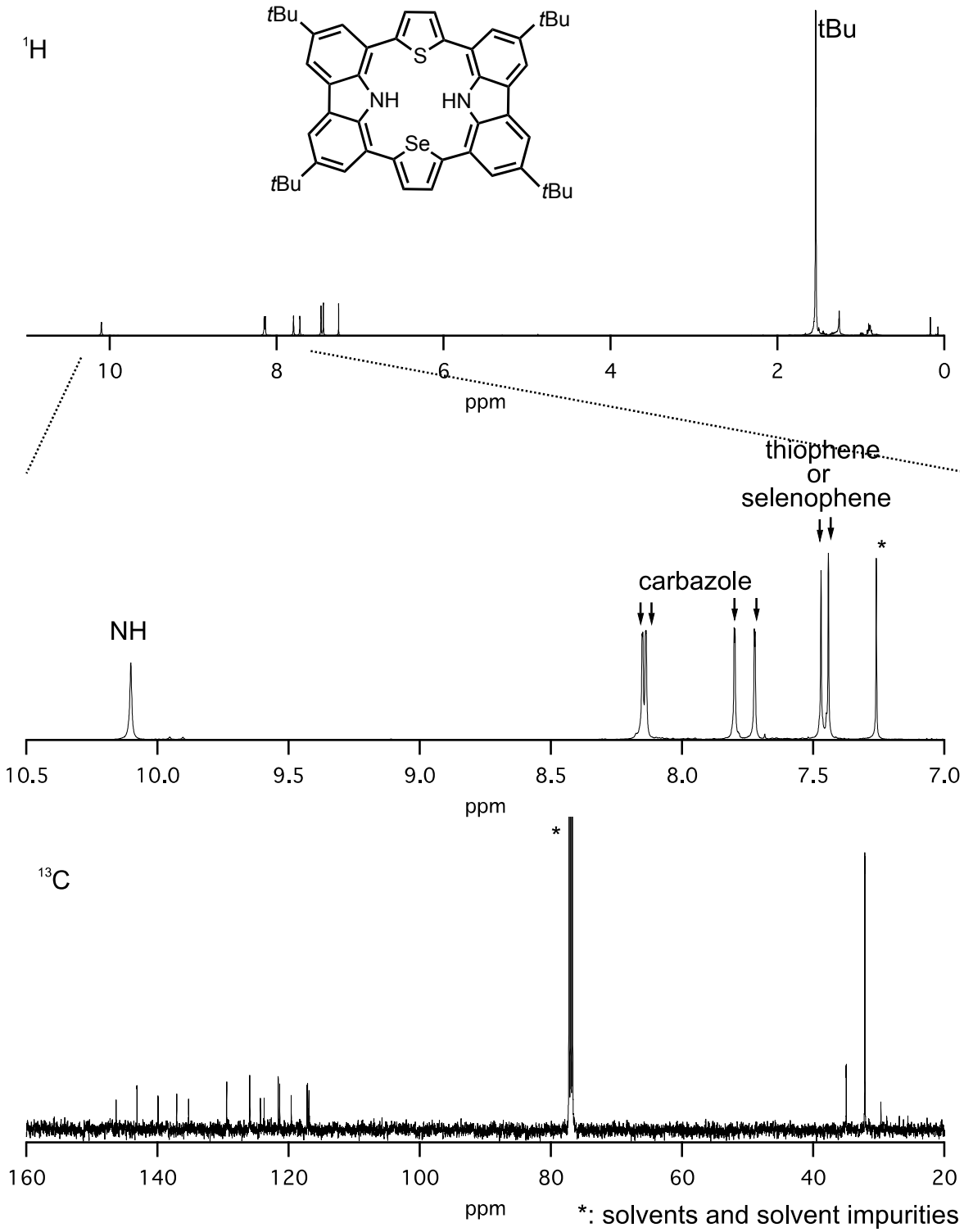


Fig. S9 ^{1}H and ^{13}C NMR spectra of **13** in $CDCl_3$

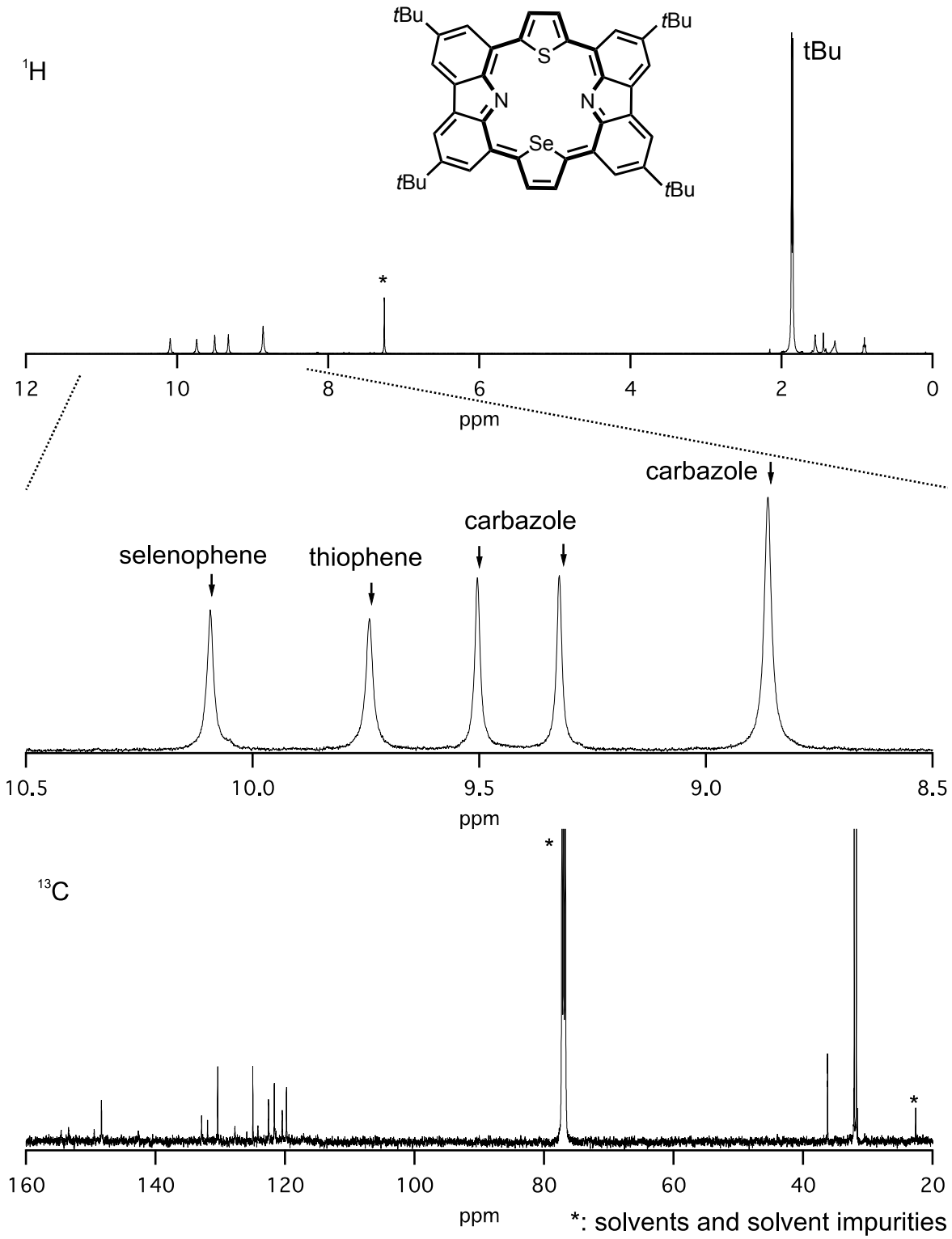


Fig. S10 Cyclic voltammogram and differential pulse voltammogram of **13**. (solvent: CH_2Cl_2, supporting electrolyte: Bu_4NPF_6 (0.10 M), counter electrode: Pt, reference electrode: Ag/Ag^+, scan rate: 0.05 V/s).

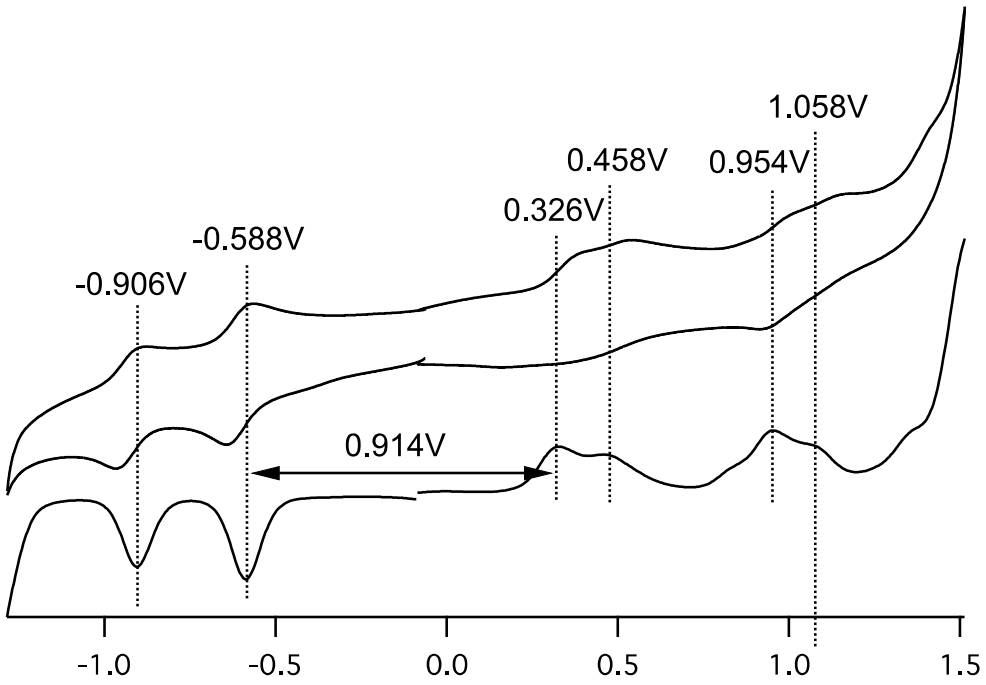
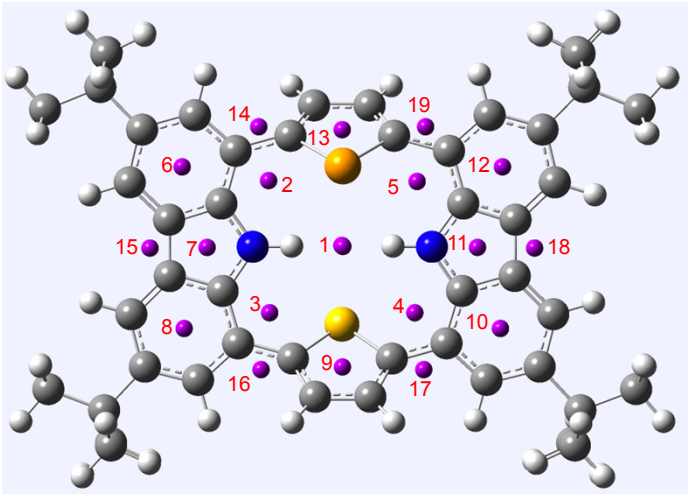


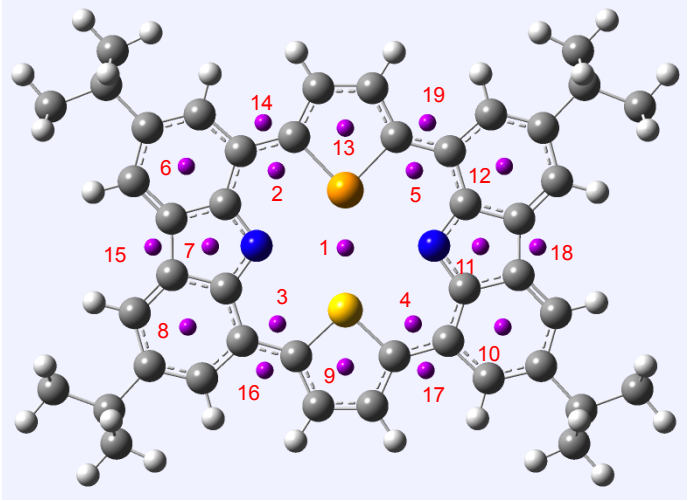
Fig. S11 NICS(0) values at selected points of (a) **12** and (b) **13** calculated at B3LYP/6-31G(d)/LANL2DZ level using Gaussian 09 package.[S1–3]

(a)



1	+0.85
2	+0.04
3	–0.05
4	–0.05
5	+0.04
6	–10.08
7	–9.89
8	–10.08
9	–9.91
10	–10.08
11	–9.89
12	–10.08
13	–0.87
14	–10.64
15	–14.40
16	–8.98
17	–8.98
18	–14.40
19	–10.64

(b)



1	–12.24
2	–17.72
3	–19.61
4	–19.61
5	–17.72
6	–6.69
7	+10.49
8	–7.79
9	–16.02
10	–7.79
11	+10.49
12	–6.69
13	–14.72
14	–6.34
15	–12.88
16	–5.09
17	–5.09
18	–12.88
19	–6.34

X-ray Crystal Structures

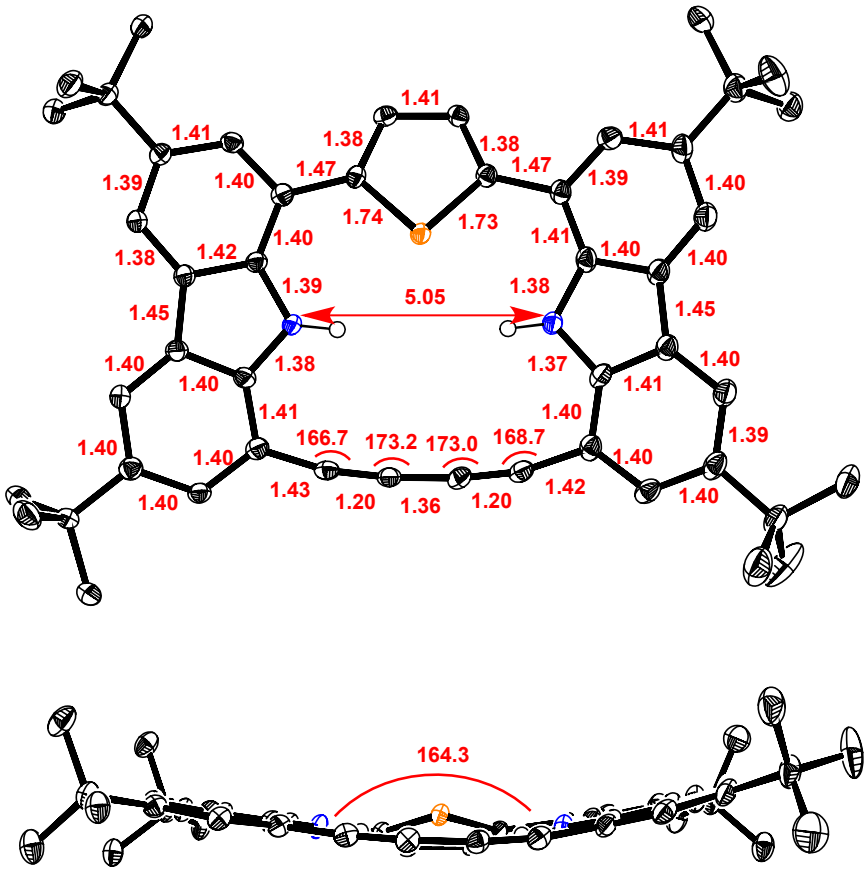
Single crystals of **10** and **11a** were obtained by slow diffusion of MeOH vapor into a toluene solution of **10**, and MeOH vapor into a CH_2Cl_2 solution of **11a**, respectively. X-ray data of **10** at 90 K were taken on a Bruker D8 Venture system with Mo-*K*α radiation (λ = 0.71073 Å), and structures were processed and refined by APEX2 and Yadokari. X-ray data of **11a** at 93 K were taken on Rigaku-Raxis-RAPID imaging plate system with Cu-*K*α radiation (λ = 1.54187 Å), and structures were processed and refined by CrystalStructure and Yadokari. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated in ideal positions.

The contribution to the scattering arising from the presence of disordered solvents in the crystals was removed by use of the utility SQUEEZE in the PLATON software package for **10**.

(a) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*; Utrecht, The Netherlands, 2005;

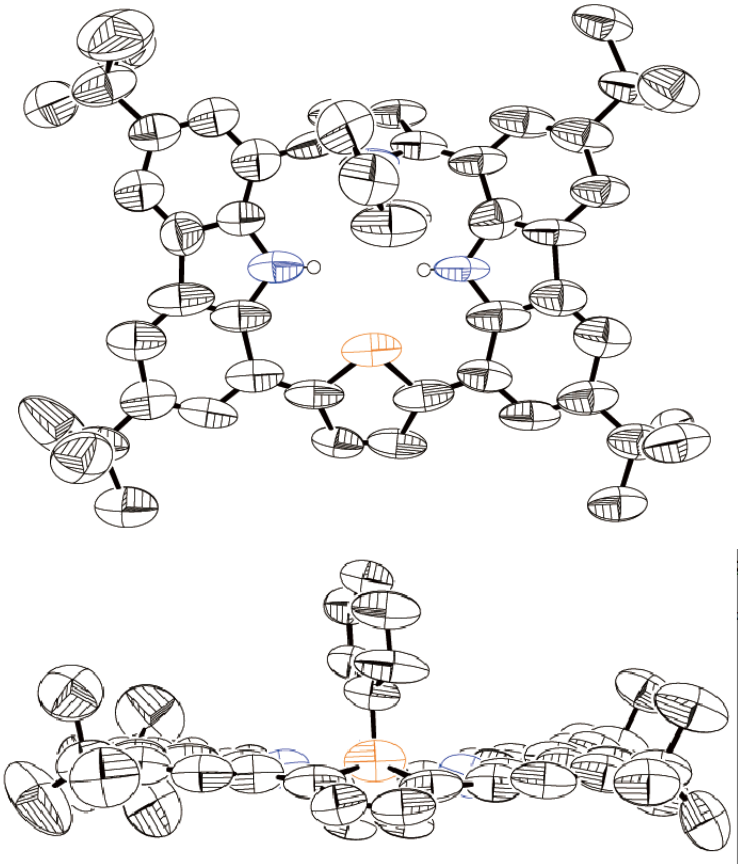
(b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **46**, 194.

Fig. S12 X-ray crystal structure of **10**. Top view and side view. Hydrogen atoms except for NH and protons are omitted for clarity. The selected bond distances(Å) and angles(˚) are shown. The thermal ellipsoids were at 50% probability level.



Crystallographic data for **10**: formula: $2(C_{46}H_{46}N_4S_2)CHCl_3$, M_w = 1489.26, triclinic, space group *P*-1, a = 15.7704(9), b = 17.0399(9), c = 17.7847(9) Å, α = 82.2120(10), β = 72.642(2), γ = 85.179(2)˚, V = 4514.7(4) Å^3, Z = 2, ρ_{calcd} = 1.096 gcm^{-3}, T = –183 °C, 15761 measured reflections, 35820 unique reflections (R_{int} = 0.0315), R_1 = 0.0642 ($I > 2\sigma(I)$), wR_2 = 0.1751 (all data), GOF = 1.106.

Fig. S13 Preliminaly X-ray crystal structure of **11a**. Top view, and side view. Hydrogen atoms except for NH protons are omitted for clarity.



Crystallographic data for **11a**: formula: $C_{54}H_{55}N_3S_2 \cdot C_{3.26}H_{5.54}Cl_{6.51}$, M_w = 1053.65, triclinic, space group *P*-1, a = 11.6816(4), b = 14.7251(5), c = 17.4612(9) Å, α = 66.3359(19), β = 87.8654(18), γ = 80.034(2)˚, V = 2707.75(19) Å^3, Z = 2, ρ_{calcd} = 1.292 gcm^{-3}, T = –180 °C, 2481 measured reflections, 8383 unique reflections (R_{int} = 0.1080), R_1 = 0.1504 ($I > 2\sigma(I)$), wR_2 = 0.3750 (all data), GOF = 1.024.

References

[S1] *Gaussian 09, Revision C.01*. 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, 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[S2] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372.

[S3] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.