Second Revised ESI for DT-ART-07-2018-002895

The η^1-H–C···Hg agostic interactions in mercury complexes of N-confused porphyrin

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Contents

Preparation of Hg(2-$NCH_2COOCH_2C_6H_5$-21-NCTPPH)Cl (8)

Compound **8** was prepared in 30 % yield in the same way as described foe **9**, but using $HgCl_2$ and **12**. Compound **8** was dissolved in acetone and layered with isopropanol (IPA) [IPA/acetone = 1:1 (v/v)] to afford dark green crystals for single-crystal X-ray analysis. ^{1}H NMR (599.89 MHz, $CDCl_3$, 298 K): δ 8.18 [d, H_β(2), ^3J (H-H) = 4.8 Hz]; 8.10 [d, *o*-H(40, 44), ^3J(H-H) = 7.2 Hz]; 8.02 [d, H_β(13)), ^3J(H-H) = 4.8 Hz]; 8.00 [d, *o*-H(34, 38), ^3J(H-H) = 7.2 Hz]; 7.86 [d, H_β(8), ^3J(H-H) = 4.8 Hz and ^4J(Hg-H) = 20.4 Hz]; 7.85 [d, H_β(7), ^3J(H-H) = 4.8 Hz and ^4J(Hg-H) = 20.4 Hz]; 7.81 [bs, *o*-H (22, 26; 28, 32)]; 7.70 [d, *m*-H(41, 43), ^3J(H-H) = 7.2 Hz]; 7.68 [t, *p*-H(42), ^3J(H-H) = 7.2 Hz]; 7.61 [d, *m*-H(35, 37), ^3J(H-H) = 7.2 Hz]; 7.60 [d, H_β(3), ^3J(H-H) = 4.8 Hz]; 7.59 [d, H_β(12), ^3J(H-H) = 4.8 Hz]; 7.57 [m, *m*-H(23, 25; 29, 31) and *p*-H(26; 30)]; 7.50 [t, *p*-H(36), ^3J(H-H) = 7.2 Hz]; 7.40 [d, *m*-H(50, 52), ^3J(H-H) = 7.2 Hz]; 7.39 [m, *p*-H(51)]; 7.26 [d, *o*-H(49, 53), ^3J(H-H) = 7.2 Hz]; 6.53 [d, H(19), ^4J(H-H) = 1.2 Hz]; 5.03 [d, H(47A), ^4J(H-H) = 12.0 Hz]; 4.99 [d, H(47B), ^4J(H-H) = 12.0 Hz]; 4.56 [d, H(45A), ^2J(H-H) = 18.6 Hz]; 4.11 [d, H(45B), ^2J(H-H) = 18.6 Hz]; -0.02 [d, H(17), ^4J(H-H) = 1.8 Hz and *J*(Hg-H) = 35.7 Hz]. MS (ESI), *m*/*z* (assignment, rel. intensity): 999.4 (M^+, 29.07 %), 963.4 ($[M\text{-}Cl]^+$, 41.74 %), 763.5 ($[M\text{-}HgCl+H]^+$, 100 %). Anal. Calcd. for $C_{53}H_{37}ClHgN_4O_2$: C, 64.03; H, 3.98; N, 5.53. Found: C, 64.00; H, 3.68; N, 5.98. UV-vis spectrum, λ (nm) [$\varepsilon\times10^{-3}$ (M^{-1} cm^{-1})] in CH_2Cl_2 at 300 K: 354 (22.3), 477 (70.9), 603 (4.1), 664 (5.3), 725 (8.7).

Preparation of Hg(2-$NCH_2COOCH_2C_6H_5$-21-NCTPPH)I (9)

A mixture of the free base 2-$NCH_2COOCH_2C_6H_5$NCTPPH (**12**) (0.0382 g, 0.05 mmol) and HgI_2 0.0908 g (0.2 mmol) in pyridine (10 mL) was refluxed at 130℃ for

2 h (Scheme 1). After concentrating the reaction mixture, the residue was dissolved in CH_2Cl_2, dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated and the residue was purified over an aluminum oxide 90 column (15 g, neutral, activity I) using CH_2Cl_2 as the eluent to yield dark green solution of **9**. Removal of the solvent gave **9** as a dark green solid (0.0180 g, 0.0165 mmol, 33%), which was dissolved in dichloromethane and layered with ethyl acetate [EA/CH_2Cl_2 = 1:1 (v/v)] to afford dark green crystals for single-crystal X-ray analysis. ^{1}H NMR (599.93 MHz, $CDCl_3$, 298 K): δ 8.18 [d, H_β(2), ^3J (H-H) = 4.8 Hz]; 8.11 [d, *o*-H(40, 44), ^3J(H-H) = 7.2 Hz]; 8.03 [d, H_β(13)]; 8.02 [d, *o*-H(34, 38), ^3J(H-H) = 7.2 Hz]; 7.88 [d, H_β(8), ^3J(H-H) = 4.8 Hz and ^4J(Hg-H) = 18.0 Hz]; 7.87 [d, H_β(7), ^3J(H-H) = 4.8 Hz and ^4J(Hg-H) = 18.0 Hz]; 7.82 [bs, *o*-H (22, 26; 28, 32)]; 7.71 [d, *m*-H(41, 43), ^3J(H-H) = 7.2 Hz]; 7.75[d, *m*-H(35, 37), ^3J(H-H) = 7.8 Hz]; 7.69 [d, *p*-H(42), ^3J(H-H) = 7.2 Hz]; 7.63 [d, H_β(3), ^3J(H-H) = 4.8 Hz]; 7.61 [d, H_β(12), ^3J(H-H) = 4.8 Hz]; 7.60 [d, *m*-H(35, 37), ^3J(H-H) = 7.2 Hz]; 7.58 [m, *m*-H(23, 25; 29, 31) and *p*-H(26; 30)]; 7.50 [t, *p*-H(36), ^3J(H-H) = 7.2 Hz]; 7.41 [d, *m*-H(50, 52), ^3J(H-H) = 7.2 Hz]; 7.41 [m, *p*-H(51)]; 7.30 [d, *o*-H(49, 53), ^3J(H-H) = 7.2 Hz]; 6.59 [d, H(19), ^4J(H-H) = 1.2 Hz]; 5.09 [d, H(47A), ^4J(H-H) = 12.0 Hz]; 5.02 [d, H(47B), ^4J(H-H) = 12.0 Hz]; 4.59 [d, H(45A), ^2J(H-H) = 18.6 Hz]; 4.18 [d, H(45B), ^2J(H-H) = 18.6 Hz]; -0.11 [d, H(17), ^4J(H-H) = 1.8 Hz and *J*(Hg-H) = 33.0 Hz]. MS (ESI), *m*/*z* (assignment, rel. intensity): 1090.1 (M^+, 26.12 %), 762.4 ([M-HgI+H]$^+$, 67.95 %), 613.4 [M-HgI+H-$CH_2COOCH_2C_6H_5$]$^+$, 42.74 %). Anal. Calcd. for $C_{53}H_{37}HgIN_4O_2$: C, 58.43; H, 3.42; N, 5.14. Found: C, 58.13; H, 3.42; N, 5.16. UV-vis spectrum, λ (nm) [$\varepsilon\times10^{-3}$ (M^{-1} cm^{-1})] in CH_2Cl_2 at 300 K: 356 (17.9), 479 (60.5), 606 (1.7), 659 (2.4), 730 (5.7).

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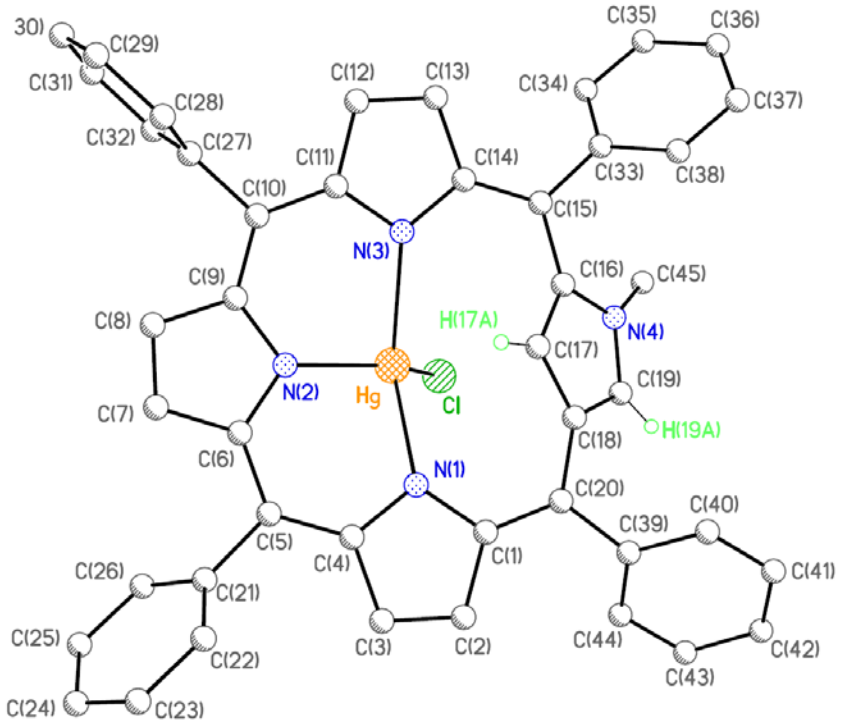
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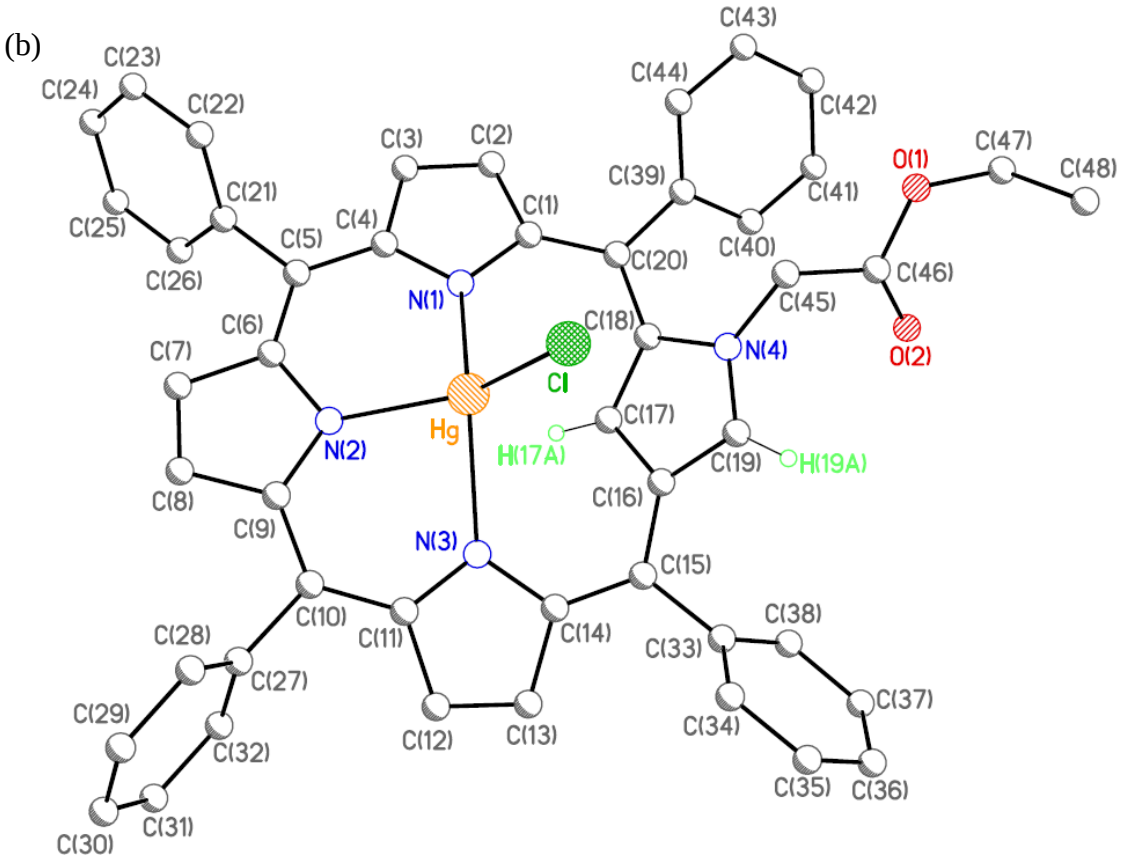
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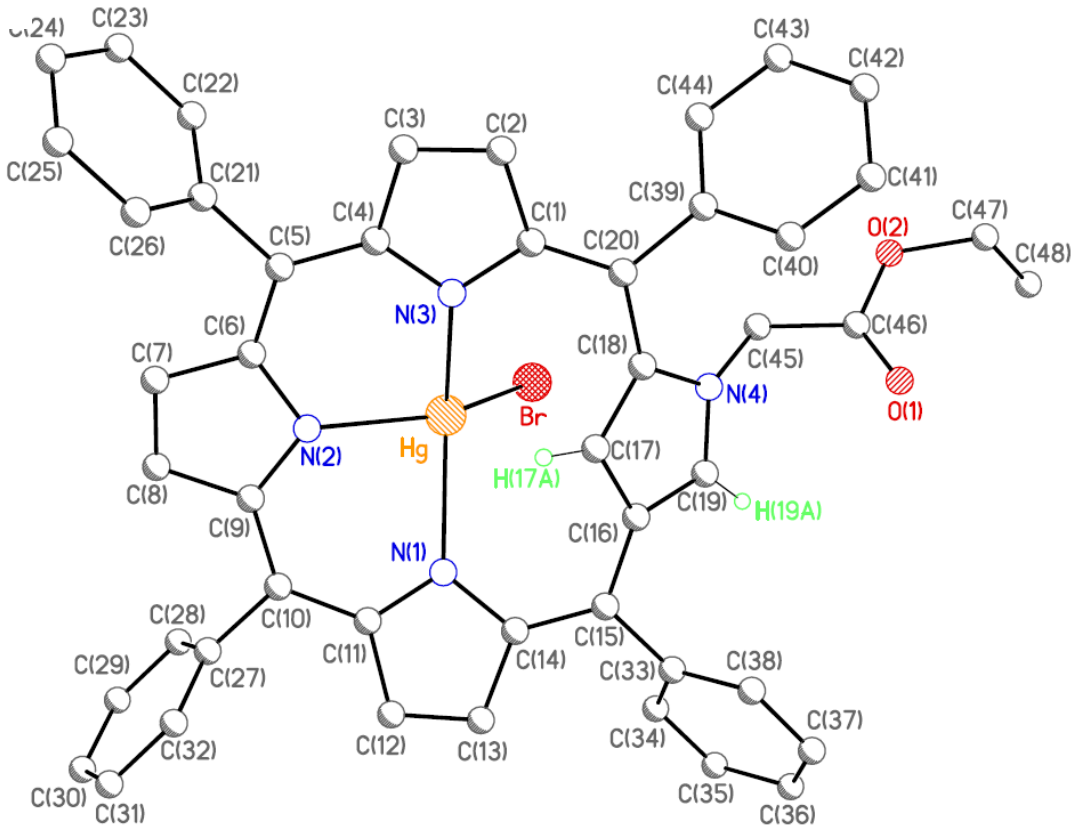
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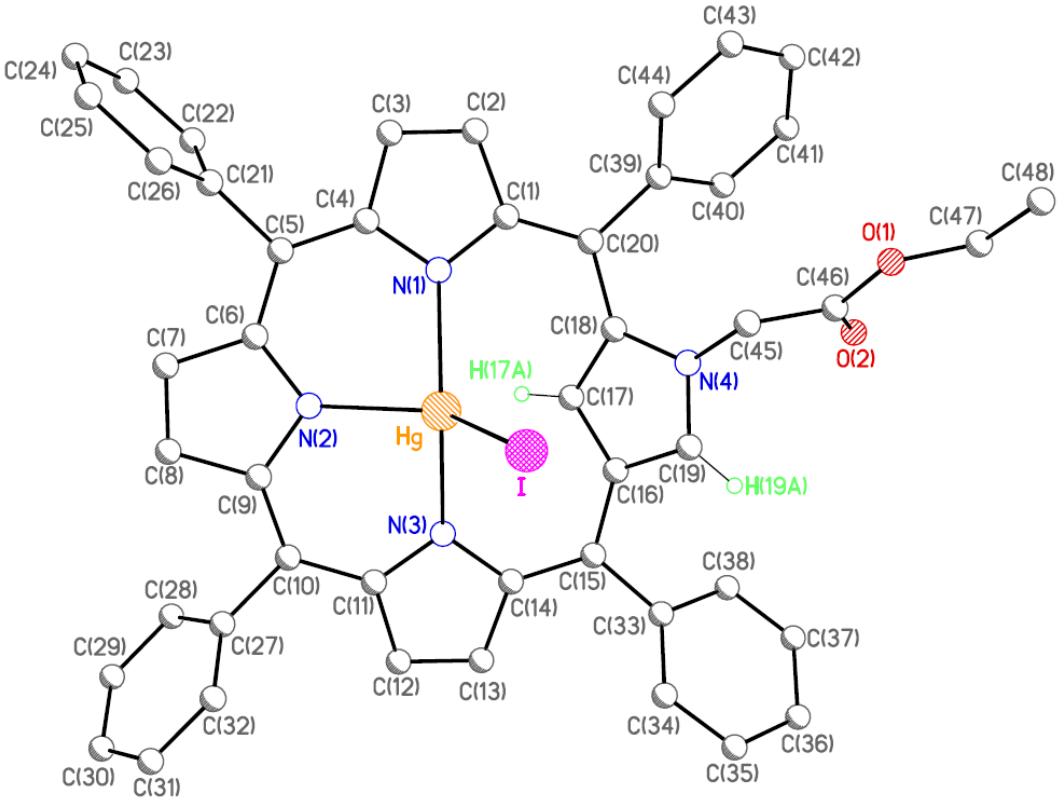
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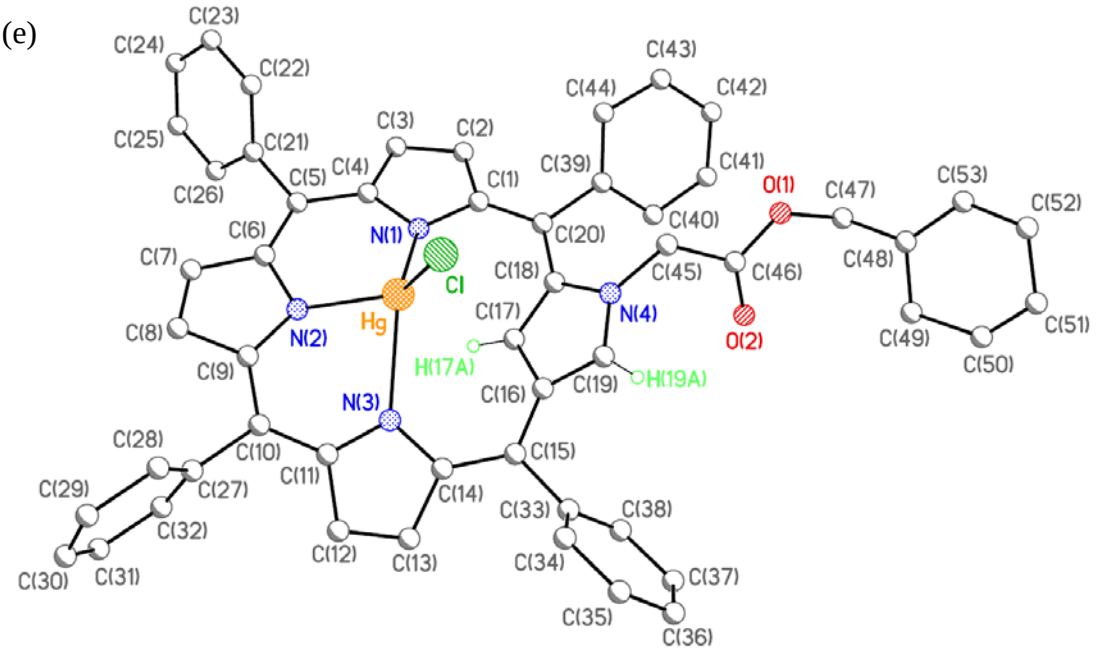

(f)

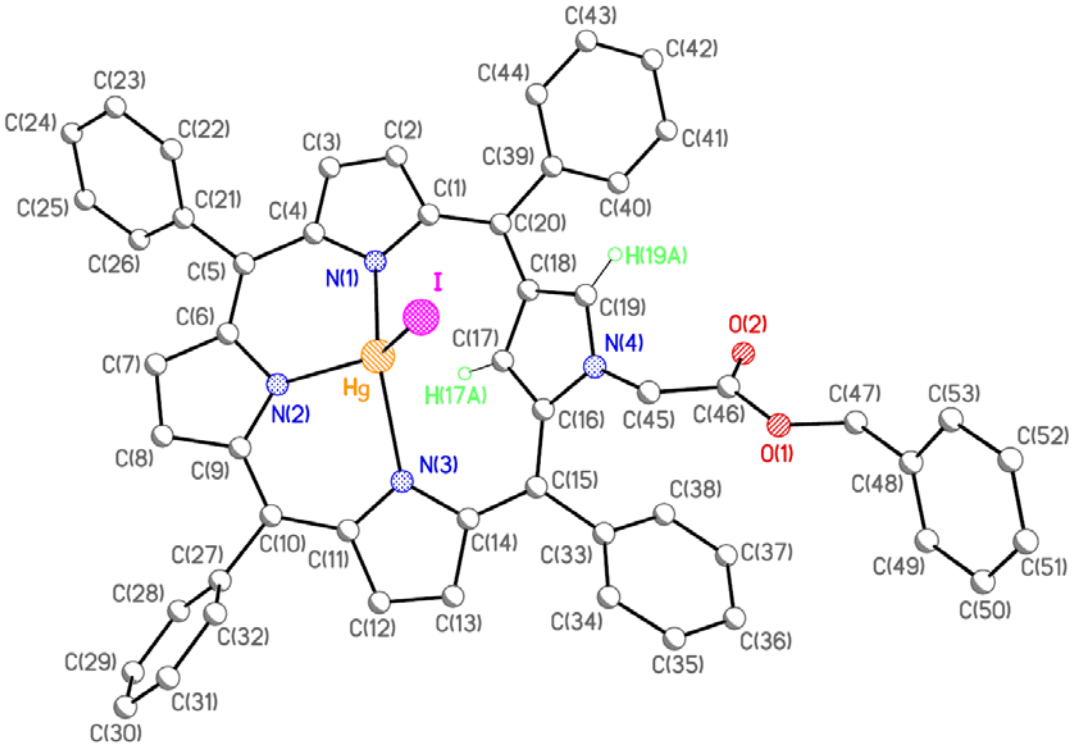

Fig. S1. X-ray structures of (a) **4** · C_8H_{10}, (b) **5**, (c) **6**, (d) **7,** (e) **8**, and (f) **9** with ellipsoids drawn at 30 % probability. All hydrogen atoms except H(17A) and H(19A), and solvent are omitted for clarity.

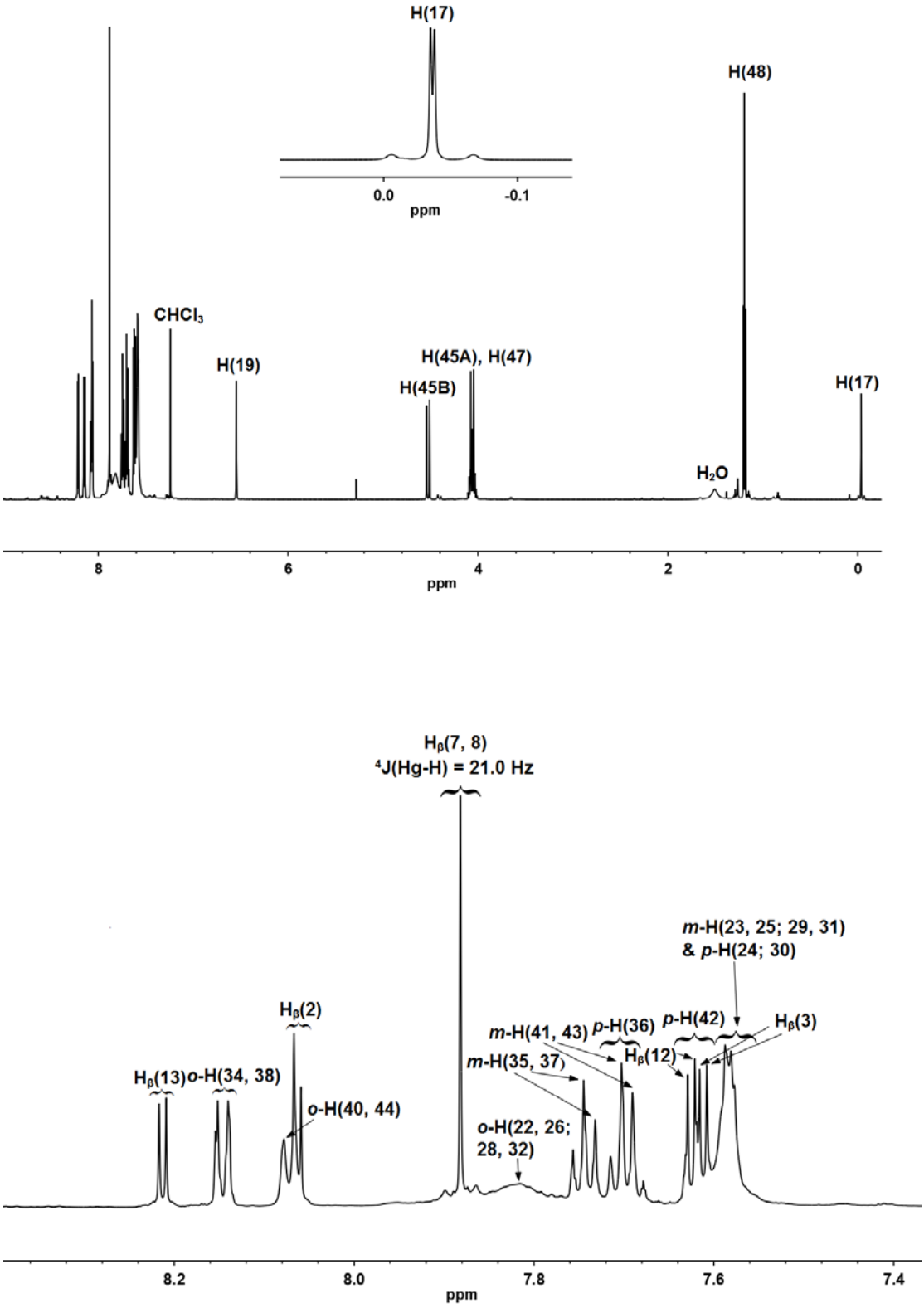

Fig S2. ^{1}H NMR spectra for **5** at 599.93 MHz in $CDCl_3$ at 298 K：(a) entire spectrum; (b) expansion of the region 7.4-8.4 ppm of (a) showing six different β-pyrrole protons H_β and phenyl protons (*o*-H, *m*, *p*-H).

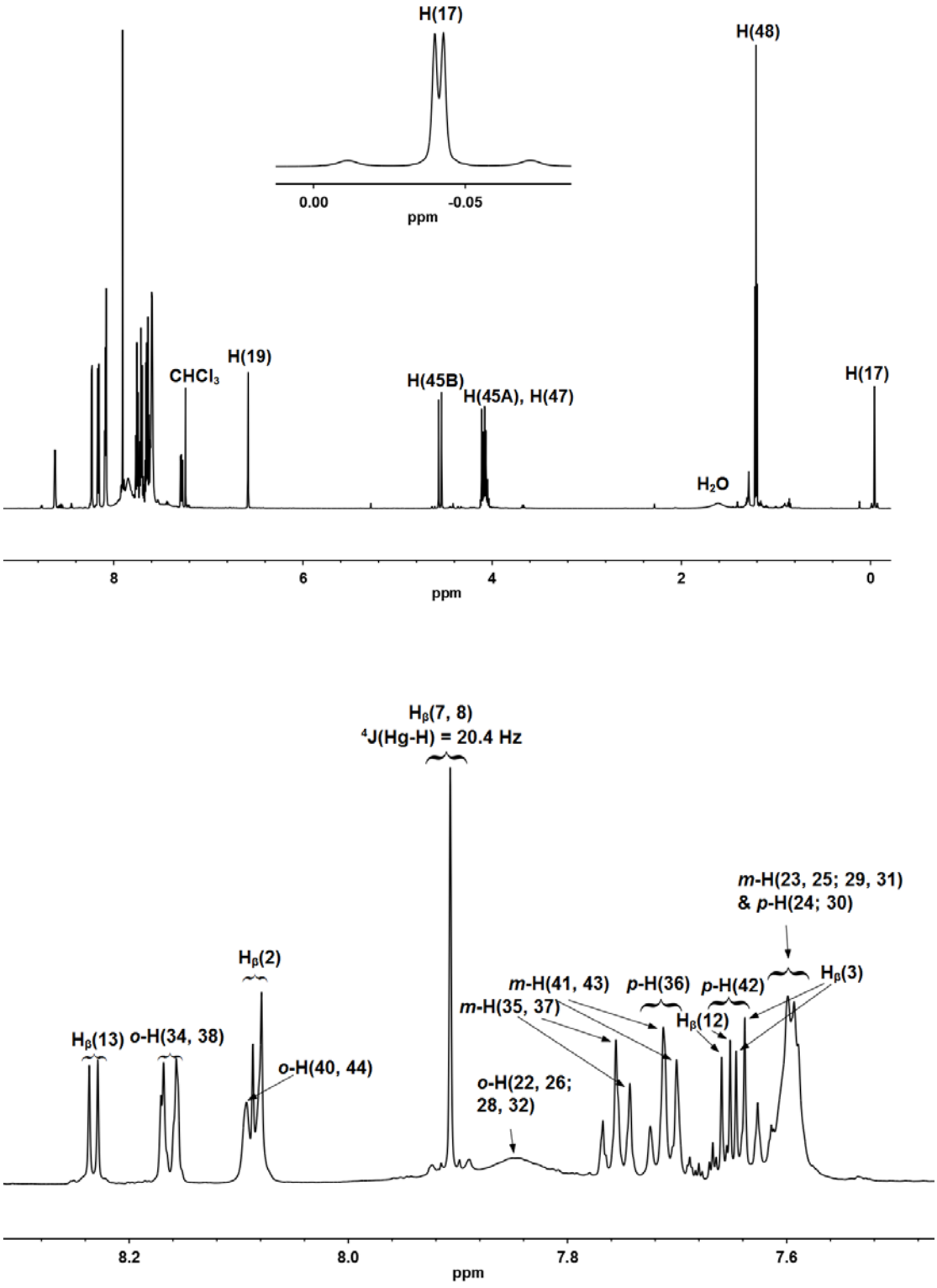

Fig S3. ^{1}H NMR spectra for **6** at 599.87 MHz in $CDCl_3$ at 298 K : (a) entire spectrum; (b) expansion of the region 7.4-8.4 ppm of (a) showing six different β-pyrrole protons H_β and phenyl protons (*o*-H, *m*, *p*-H).

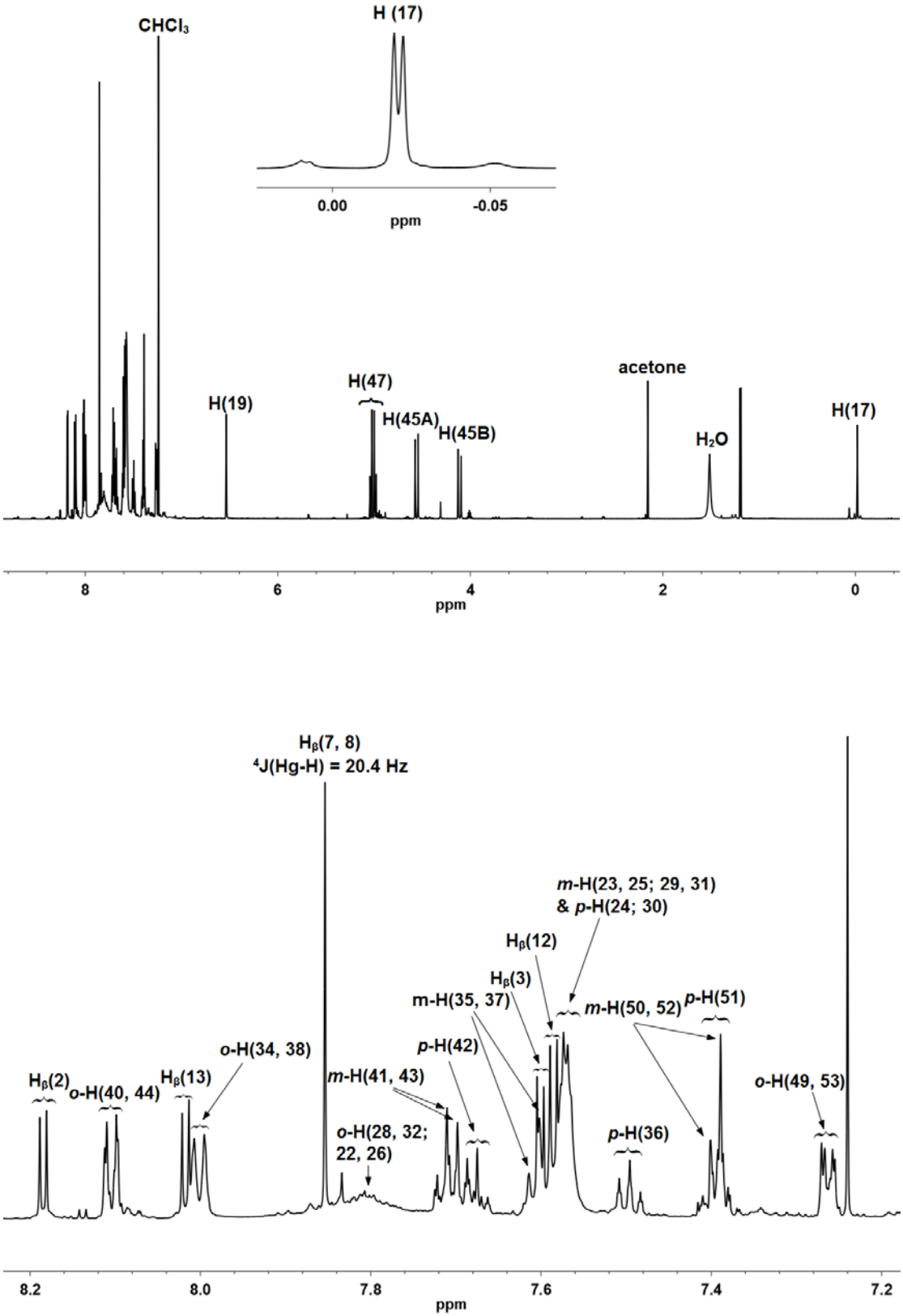

Fig S4. ^{1}H NMR spectra for **8** at 599.93 MHz in $CDCl_3$ at 298 K : (a) entire spectrum; (b) expansion of the region 7.2-8.4 ppm of (a) showing six different β-pyrrole protons H_β and phenyl protons (*o*-H, *m*, *p*-H).

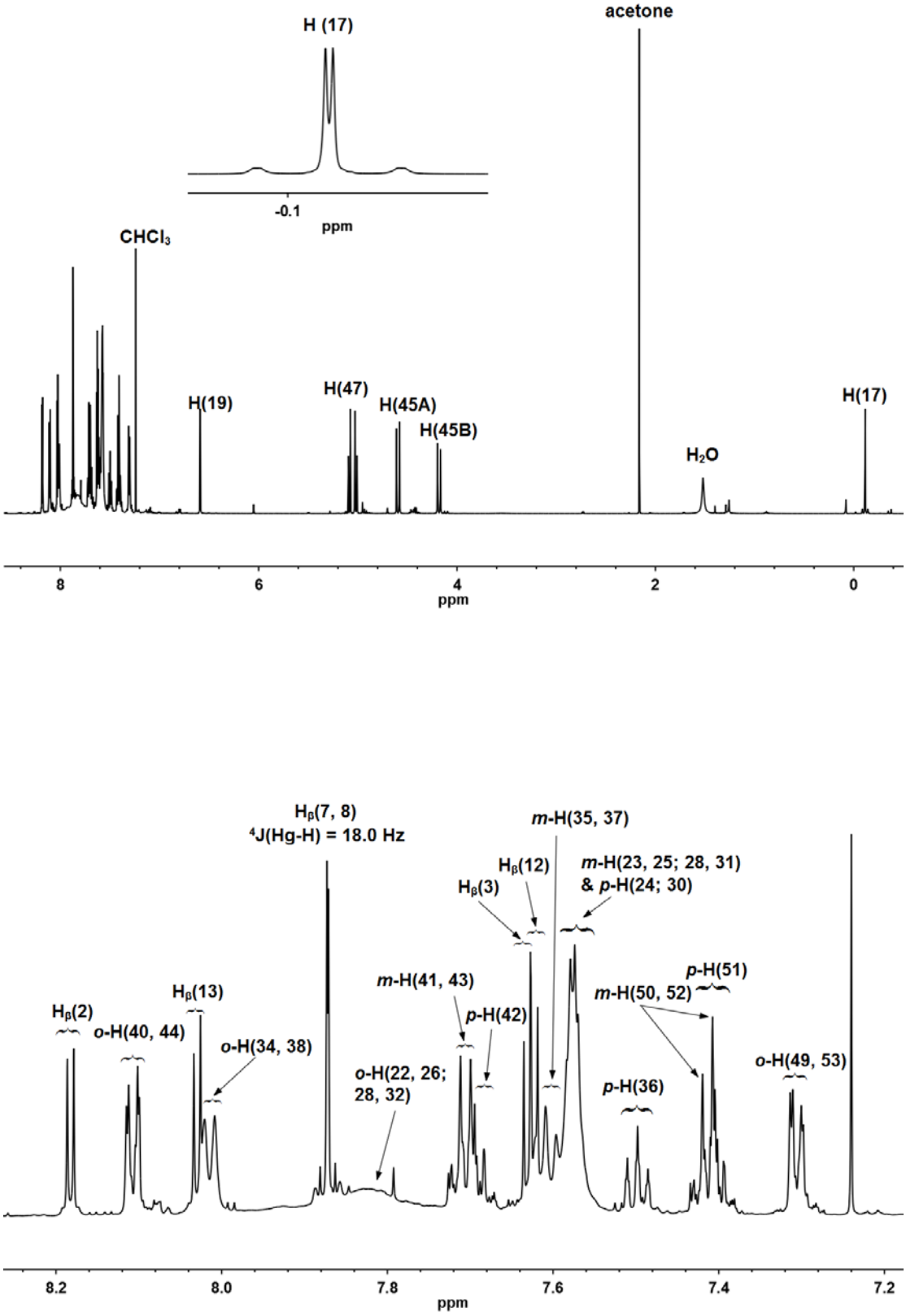

Fig S5. ^{1}H NMR spectra for **9** at 599.93 MHz in $CDCl_3$ at 298 K : (a) entire spectrum; (b) expansion of the region 7.2-8.4 ppm of (a) showing six different β-pyrrole protons H_β and phenyl protons (*o*-H, *m*, *p*-H).

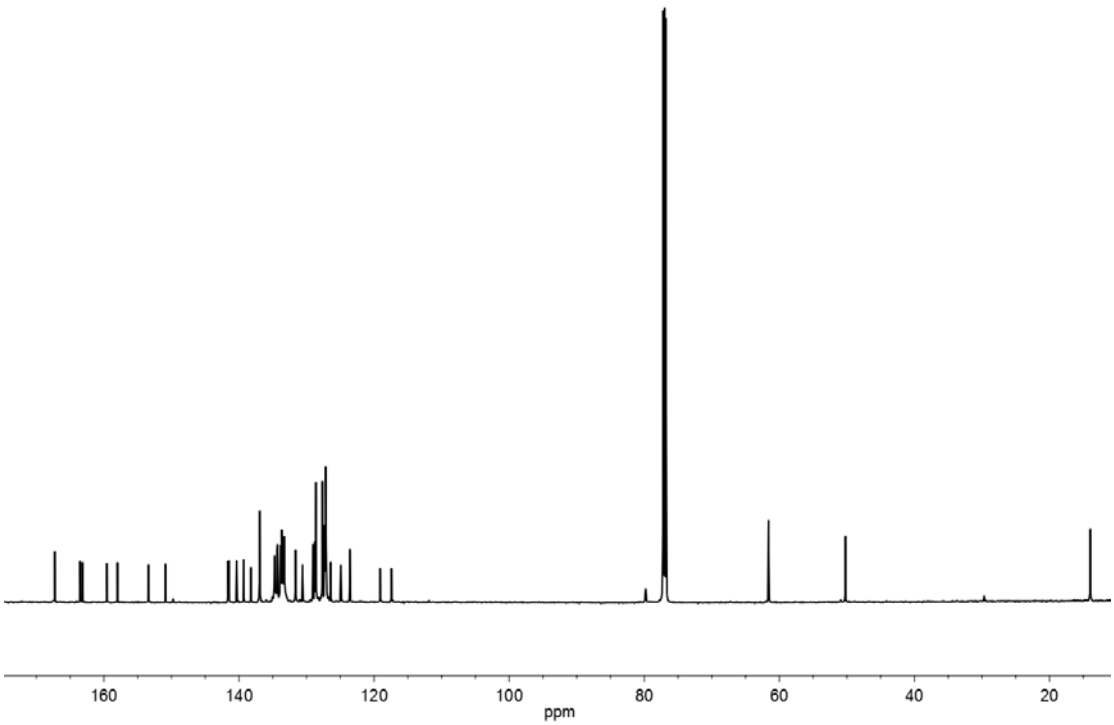

Fig. S6. ^{13}C NMR spectra for **5** at 150.87 MHz in $CDCl_3$ at 25℃

^{13}C NMR (150.87 MHz, $CDCl_3$, 25℃, partial data) of **5** :

δ 167.3 [s, C(46)]; 163.6 (s) and 153.4 (s) for C_α(1) and C_α(4); 163.2 (s) and 150.9 (s) for C_α(11) and C_α(14); 159.6 (s) and 158.0 (s) for C_α(6) and C_α(9); 140.4 [s, C(33)]; 139.3 [s, C(39)]; 138.2 [s, C(15)]; 137.0 [s, C(34, 38)]; 134.7 [s, C(40, 44)]; 134.4 [s, C_β(13)]; 134.3 [s, C_β(7)]; 133.9 [s, C_β(8)]; 133.7 [s, C_β(2)]; 133.3 [s, C_β(3)]; 131.6 [s, C_β(12)]; 130.6 [s, C(18)]; 129.1 [s, C(36)]; 128.8 [s, C(42)]; 128.6[s, C(41, 43)]; 127.7 [s, C(35, 37)]; 126.5 [s, C(16)]; 125.0 [s, C(20)]; 123.6 [s, C_α(19)]; 79.8 [s, C(17)]; 61.6 [s, C(47)]; 50.2 [s, C(45)]; 14.0 [s, C(48)].

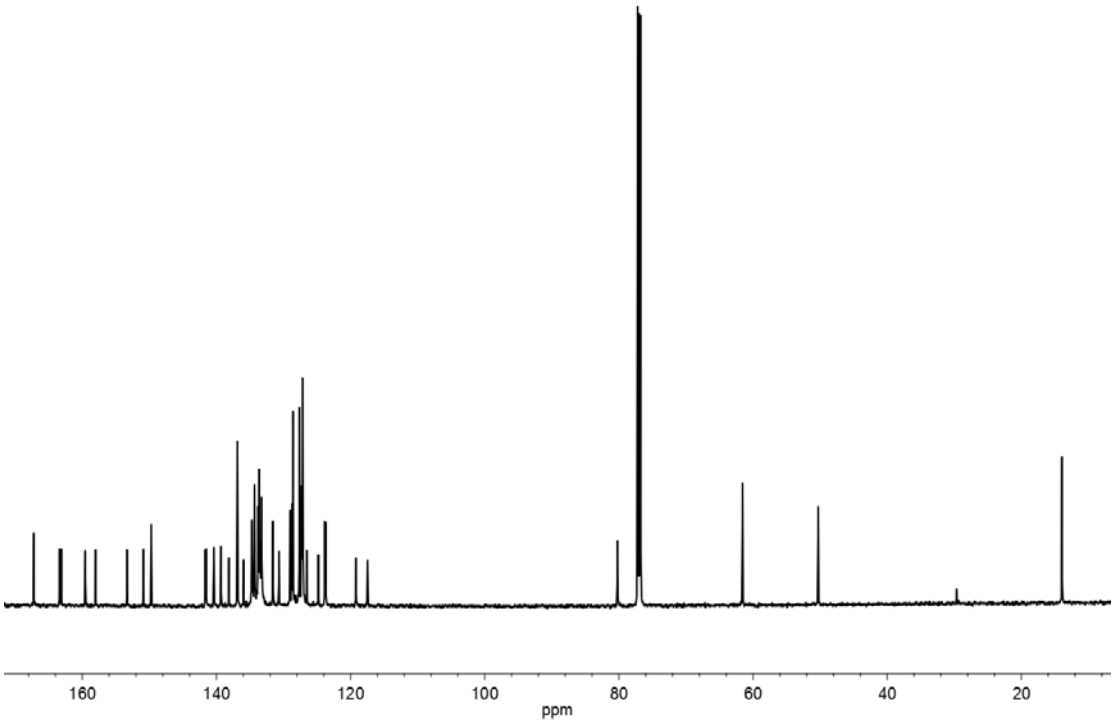

Fig. S7. ^{13}C NMR spectra for **6** at 150.87 MHz in $CDCl_3$ at 25℃

^{13}C NMR (150.87 MHz, $CDCl_3$, 25℃, partial data) of **6** :

δ 167.2 [s, C(46)]; 163.4 (s) and 153.3 (s) for C_α(1) and C_α(4); 163.1 (s) and 150.9 (s) for C_α(11) and C_α(14); 159.6 (s) and 158.0 (s) for C_α(6) and C_α(9); 140.4 [s, C(33)]; 139.3 [s, C(39)]; 138.2 [s, C(15)]; 136.9 [s, C(34, 38)]; 134.7 [s, C(40, 44)]; 134.3 [s, C_β(13)]; 134.3 [s, C_β(7)]; 133.8 [s, C_β(8)]; 133.6 [s, C_β(2)]; 133.3 [s, C_β(3)]; 131.6 [s, C_β(12)]; 130.7 [s, C(18)]; 129.0 [s, C(36)]; 128.8 [s, C(42)]; 128.6[s, C(41, 43)]; 127.6 [s, C(35, 37)]; 126.5 [s, C(16)]; 124.8 [s, C(20)]; 123.9 [s, C_α(19)]; 80.2 [s, C(17)]; 61.6 [s, C(47)]; 50.3 [s, C(45)]; 14.0 [s, C(48)].

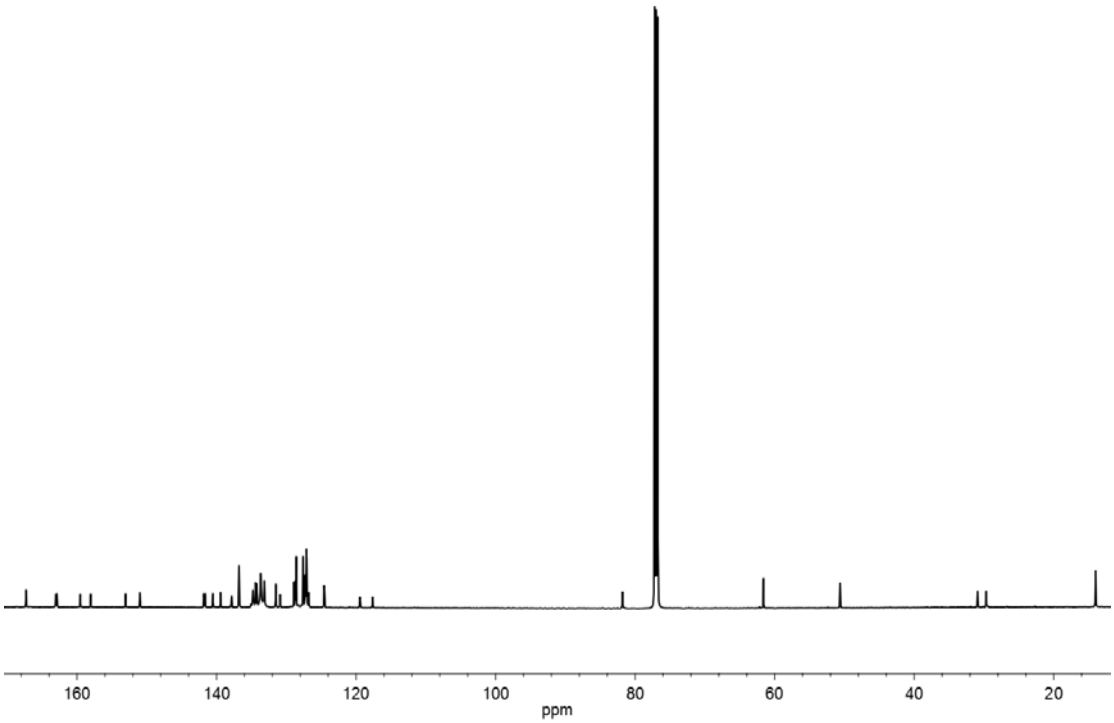

Fig. S8. ^{13}C NMR spectra for **7** at 150.87 MHz in $CDCl_3$ at 25℃

^{13}C NMR (150.87 MHz, $CDCl_3$, 25℃, partial data) of **7** :

δ 167.3 [s, C(46)]; 163.1 (s) and 153.1 (s) for C_α(1) and C_α(4); 162.9 (s) and 151.0 (s) for C_α(11) and C_α(14); 159.5 (s) and 158.0 (s) for C_α(6) and C_α(9); 140.5 [s, C(33)]; 139.4 [s, C(39)]; 137.8 [s, C(15)]; 136.8 [s, C(34, 38)]; 134.8 [s, C(40, 44)]; 134.4 [s, C_β(13)]; 134.2 [s, C_β(7)]; 133.7 [s, C_β(8)]; 133.6 [s, C_β(2)]; 133.2 [s, C_β(3)]; 131.5 [s, C_β(12)]; 130.9 [s, C(18)]; 128.9 [s, C(36)]; 128.7 [s, C(42)]; 128.6[s, C(41, 43)]; 127.6 [s, C(35, 37)]; 126.8 [s, C(16)]; 124.6 [s, C(20)]; 124.5 [s, C_α(19)]; 81.8 [s, C(17)]; 61.6 [s, C(47)]; 50.6 [s, C(45)]; 14.0 [s, C(48)].

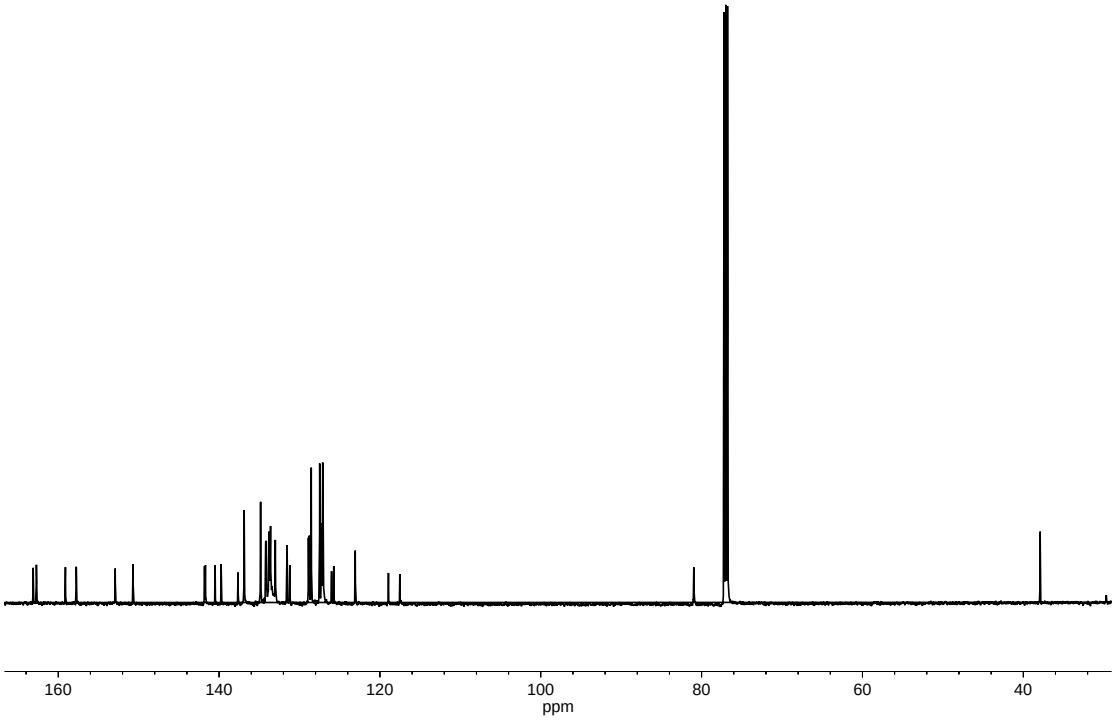

Fig. S9. ^{13}C NMR spectra for **4** at 150.87 MHz in $CDCl_3$ at 25℃

^{13}C NMR (150.85 MHz, $CDCl_3$, 25℃, partial data) of **4** :

δ163.1 (s) and 152.9 (s) for C_α(11) and C_α(14); 162.7 (s) and 150.7 (s) for C_α(1) and C_α(4); 159.1 (s) and 157.8 (s) for C_α(6) and C_α(9); 140.5 [s, C(20)]; 136.9 [s, C(40, 44)]; 134.9 [s, C(34, 38)]; 134.2 [s, C_β(2)]; 134.1 [s, C_β(7)]; 133.8 [s, C_β(8)]; 133.6 [s, C_β(13)]; 133.0 [s, C_β(12)]; 131.6 [s, C_β(3)]; 131.2 [s, C(16)]; 128.9 [s, C(42)]; 128.8 [s, C (36)]; 128.6 [s, C(35, 37)]; 127.5 [s, C(41, 43)]; 126.0 [s, C(15)]; 125.8 [s, C(18)]; 123.1 [s, C_α(19)]; 81.0 [s, C(17)]; 37.9 [s, C(45)].

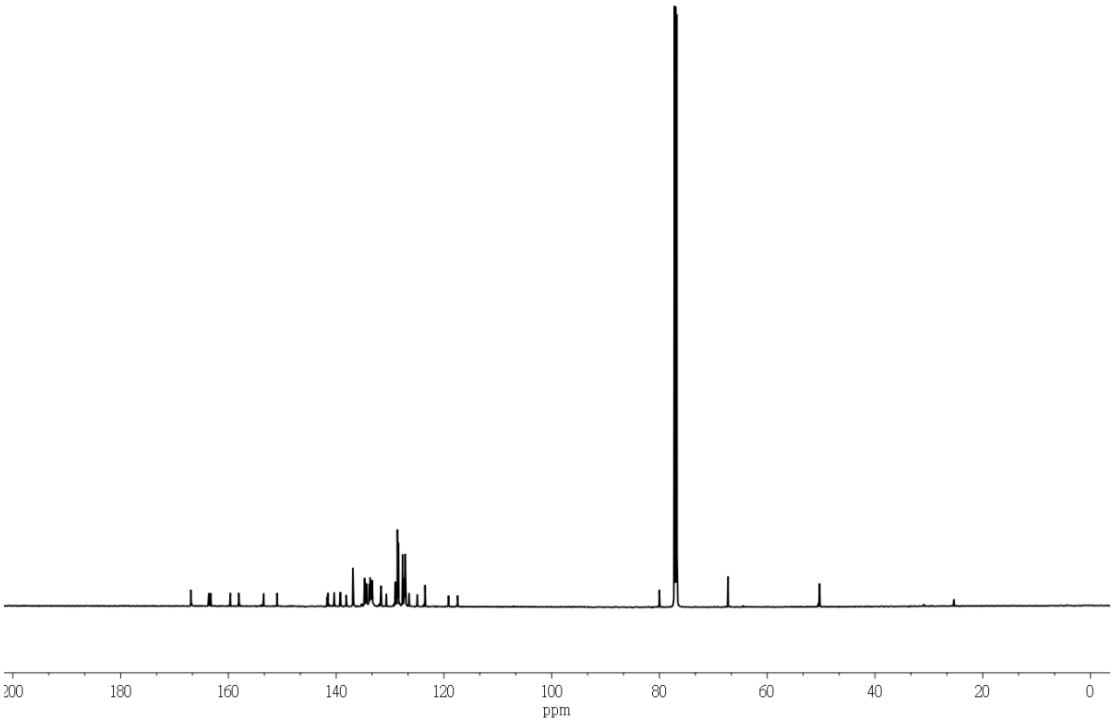

Fig. S10. ^{13}C NMR spectra for **8** at 150.87 MHz in $CDCl_3$ at 25℃

^{13}C NMR (150.85 MHz, $CDCl_3$, 25℃, partial data) of **8** :

δ167.0 [s, C(46)]; 163.6 (s) and 153.5 (s) for C_α(1) and C_α(4); δ163.3 (s) and 153.5 (s) for C_α(11) and C_α(14); 160.0 (s) and 158.1 (s) for C_α(6) and C_α(9); δ140.4 [s, C(39)] ; 139.2 [s, C(33)] ; 138.2 [s, C(20)]; 136.9 [s, C(40, 44)] ; 134.7 [s, C(34, 38)]; 134.7 [s, C(48)]; 134.4 [s, C_β(2)]; 134.3 [s, C_β(8)]; 133.9 [s, C_β(7)]; 133.7 [s, C_β(13)]; 133.3 [s, C_β(12)]; 131.7 [s, C_β(3)] ; 130.7 [s, C(18)]; 129.1 [s, C(42)]; 128.9 [s, C(36)]; 128.4 (s) and 127.1 (s) for C(49, 53); 127.7 [s, C(41, 43)]; 127.3 [s, C(35, 37)]; 126.5 [s, C(16)]; 124.9 [s, C_α(19)]; 80.0 [s, C(17)]; 67.3 [s, C(47)]; 50.3 [s, C(45)]

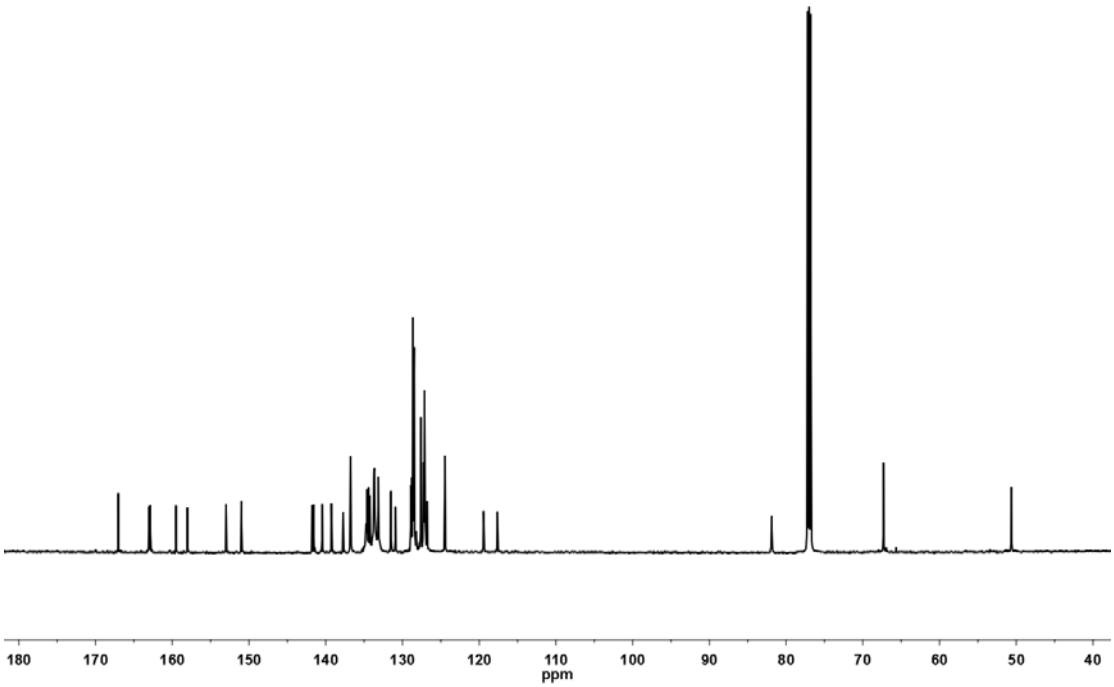

Fig. S11. ^{13}C NMR spectra for **9** at 150.87 MHz in $CDCl_3$ at 25℃

^{13}C NMR (150.85 MHz, $CDCl_3$, 25℃, partial data) of **9** :

δ167.0 [s, C(46)]; 163.6 (s) and 151.0 (s) for C_α(1) and C_α(4); 162.9 (s) and 153.0 (s) for C_α(11) and C_α(14); 159.5 (s) and 158.0 (s) for C_α(6) and C_α(9); 140.5 [s, C(39)] ; 139.3 [s, C(33)] ; 137.7 [s, C(20)]; 136.8 [s, C(40, 44)] ; δ134.7 [s, C(34, 38)]; 134.6 [s, C(48)]; 134.4 [s, C_β(2)]; 134.2 [s, C_β(8)]; 133.7 [s, C_β(7)]; 133.6 [s, C_β(13)]; 133.2 [s, C_β(12)]; 133.2 [s, C_β(3)] ; 130.9 [s, C(18)]; 128.9 [s, C(42)]; 128.8 [s, C(36)]; 128.5 (s) and 127.1 (s) for C(49, 53); 127.6 [s, C(41, 43)]; 127.3 [s, C(35, 37)]; 126.8 [s, C(16)]; 124.5 [s, C_α(19)]; 81.9 [s, C(17)]; 67.3 [s, C(47)]; 50.6 [s, C(45)]

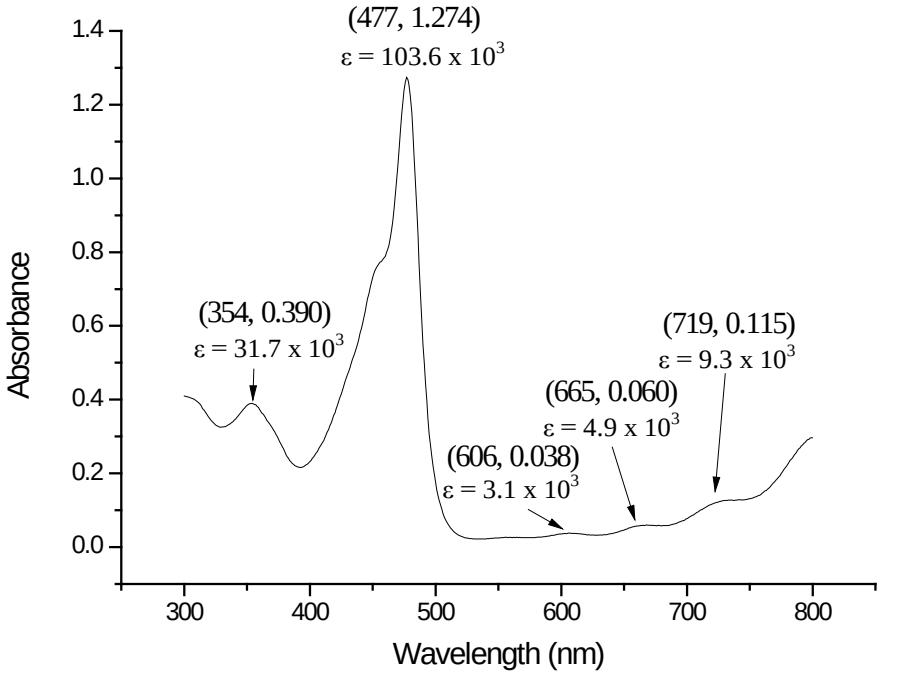

Fig. S12. UV-Vis spectra of **5** in CH_2Cl_2 at 300 K : 300 – 800 nm

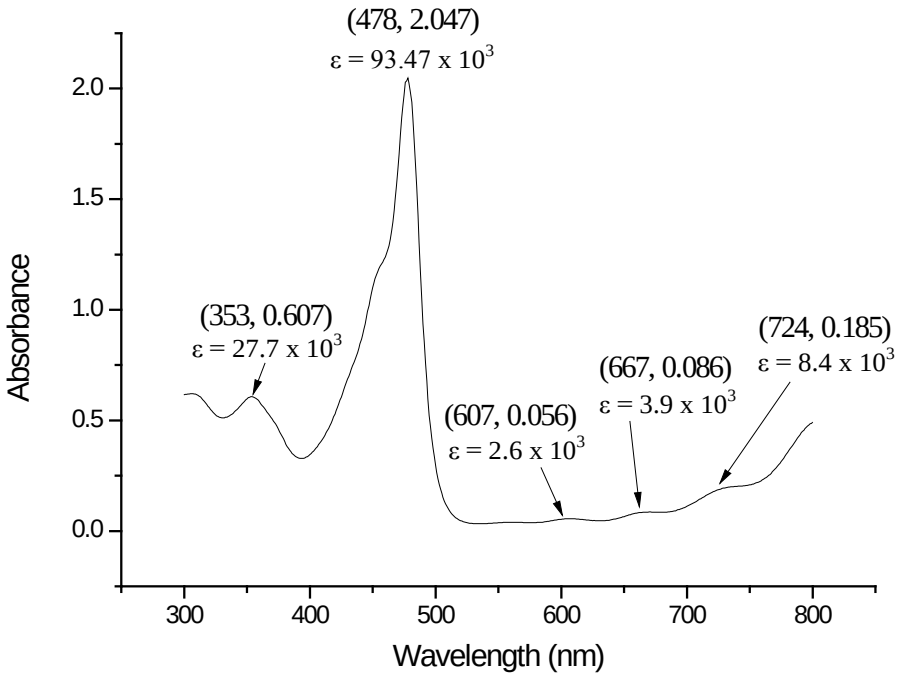

Fig. S13. UV-Vis spectra of **6** in CH_2Cl_2 at 300 K : 300 – 800 nm

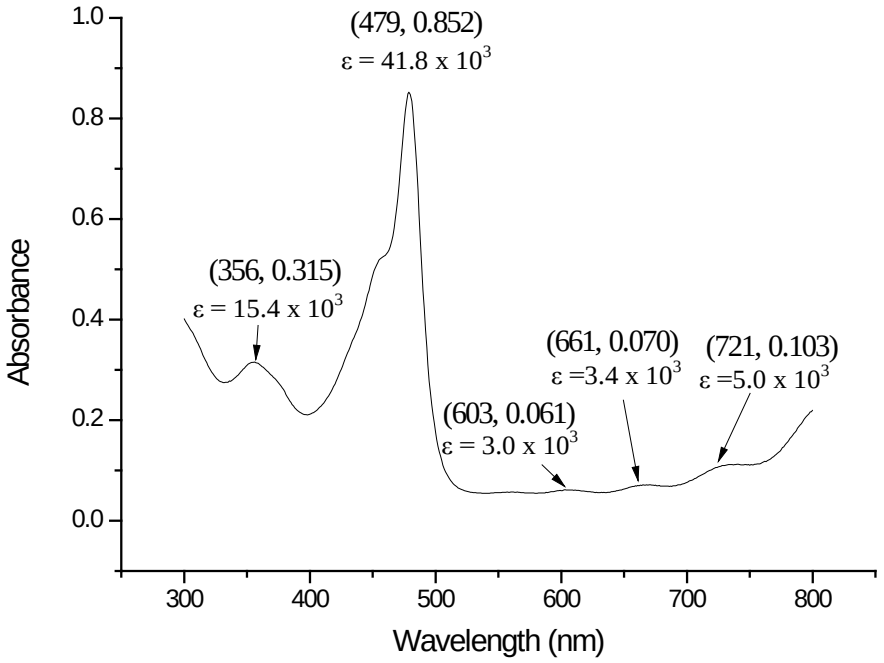

Fig. S14. UV-Vis spectra of **7** in CH_2Cl_2 at 300 K : 300 – 800 nm

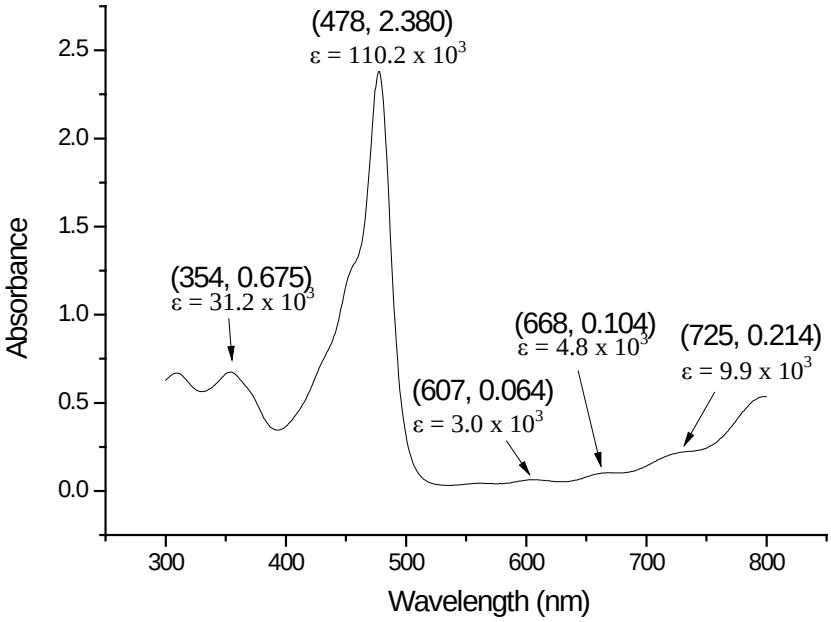

Fig. S15. UV-Vis spectra of **4** in CH_2Cl_2 at 300 K : 300 – 800 nm

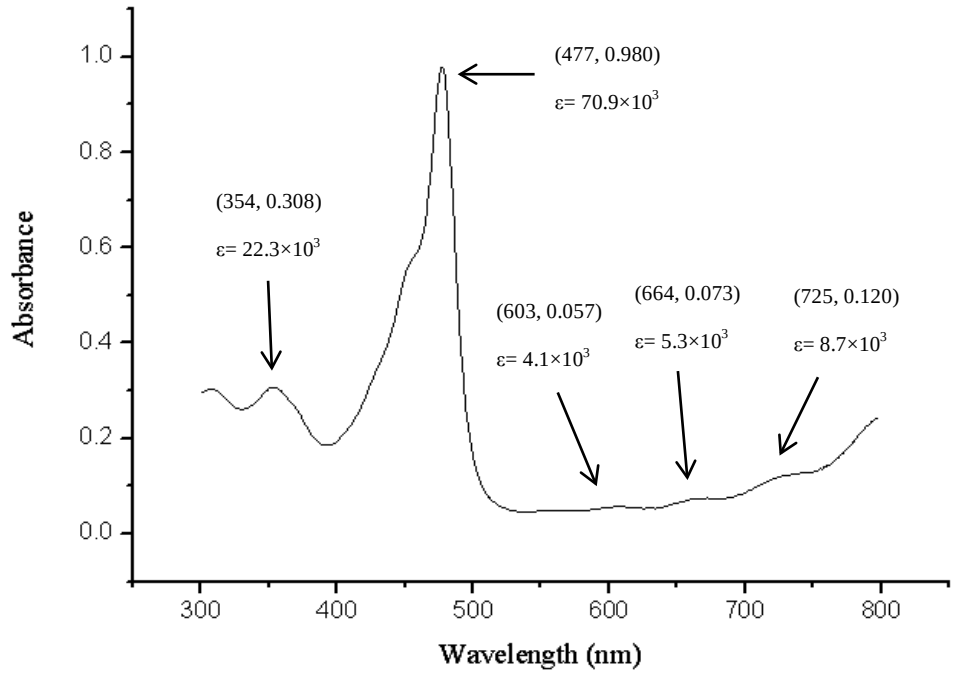

Fig. S16. UV-Vis spectra of **8** in CH_2Cl_2 at 300 K : 300 – 800 nm

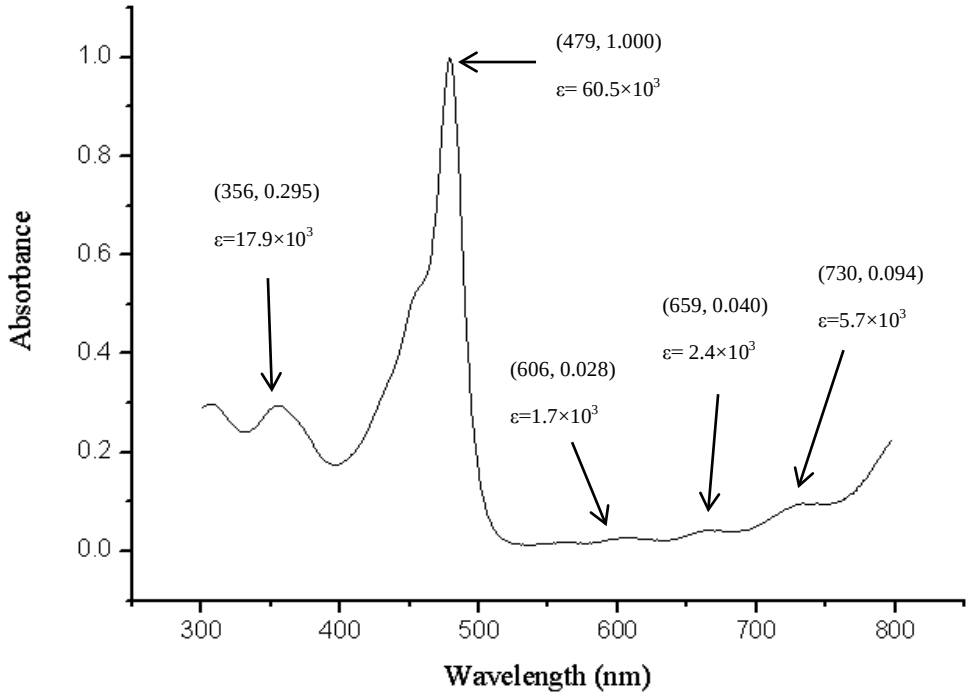

Fig. S17. UV-Vis spectra of **9** in CH_2Cl_2 at 300 K : 300 – 800 nm

Comparison of empirical formula between data of X-ray diffraction and EA measurement

The X-ray structure data were obtained from single crystal. Moreover, all of elemental analyses data were measured from the powder sample through recrystallization, not from single crystal. Hence, solvent molecule might be different between the data of X-ray diffraction and elemental analyses. Hence, X-ray diffraction data indicates the empirical formula of **4** · C_8H_{10} (or **5**-**9**), but elemental analyses shows **4** · 0.1C_6H_{14} (or **5** · 0.4 C_8H_{18}, **6** · 0.3 C_8H_{18}, **7** · 0.2 C_3H_7NO, **8**, **9**) for the same complexes. Compound **4** was dissolved in CH_2Cl_2 and layered with hexane to afford green powder sample for elemental analyses.