Supporting Information

Synthesis and Oxidation of Cyclic Tetraindole

Shoichi Nakamura, Satoru Hiroto,* and Hiroshi Shinokubo*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Chikusa-ku, Nagoya 464-8603, Japan.

E-mail: hiroto@apchem.nagoya-u.ac.jp; hshino@apchem.nagoya-u.ac.jp

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Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Varian INOVA-500 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.260 ppm) and CD_3CN (δ = 1.940 ppm) for ^{1}H NMR, and $CDCl_3$ (δ = 77.0 ppm) and CD_3CN (δ = 1.320) for ^{13}C NMR. UV/vis absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V670 spectrometer. Mass spectra were recorded on a Bruker microTOF using negative mode ESI-TOF method for acetonitrile solutions. X-ray data were taken on a Bruker SMART APEX X-Ray diffractometer equipped with a large area CCD detector. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Synthesis of 5-*tert*-butyl-7-ethynyl-1*H*-indole (4).

A flask containing 4-*tert*-butyl-2,6-diethynylaniline (**3**, 395 mg, 2.00 mmol) and potassium *tert*-butoxide (471 mg, 4.20 mmol) was flushed with N_2. Dry NMP (20 mL) was added, and then the solution was stirred at room temperature for 16 h. After quenching the reaction with water (4 mL), the mixture was extracted with CH_2Cl_2. The organic layer was washed with water and brine, and dried over Na_2SO_4. After removal of solvents in vacuo, the residue was purified by silica-gel column chromatography (EtOAc/hexane as an eluent) to provide **4** (321 mg, 1.63 mmol) in 82% yield as colorless solid.

^{1}H NMR ($CDCl_3$): δ 8.37 (br, 1H, NH), 7.68 (d, J = 1.5 Hz, 1H, Ar), 7.47 (d, J = 2.0 Hz, 1H, Ar), 7.23 (m, 1H, Ar) 6.55 (dd, J = 2.0, 3.1 Hz, 1H, Ar), 3.37 (s, 1H, ethynyl), and 1.38 (s, 9H, *t*-Bu) ppm; ^{13}C NMR ($CDCl_3$): δ 142.7, 135.2, 127.4, 124.5, 124.3, 118.3, 104.1, 103.3, 80.8, 80.5, 34.5, and 31.8 ppm; HR-MS (ESI-MS): m/z = 196.1132, calcd for $(C_{14}H_{14}N)^-$ = 196.1132 $[(M - H)^-]$.

Synthesis of 2-bromo-4-*tert*-butyl-6-((5-(*tert*-butyl)-1*H*-indol-7-yl)ethynyl)aniline (5).

A flask containing 2-bromo-4-*ter*t-butyl-6-iodoaniline (799 mg, 2.26 mmol), $PdCl_2(PPh_3)_2$ (87.4 mg, 0.125 mmol), and CuI (24.0 mg, 0.126 mmol) was flushed with N_2.. Anhydrous THF (30 mL) and Et_3N (75 mL) were added, and the solution was degassed by freeze-pump-thaw method. To the solution, a solution of **4** (477 mg, 2.42 mmol) in dry and degassed THF (14 mL) was added dropwise under N_2 atmosphere, and then the mixture was stirred at room temperature for 15 h. A saturated aqueous NH_4Cl solution was added, and the mixture was extracted with EtOAc. The organic layer was washed with water and brine, and dried over Na_2SO_4. After solvents were evaporated in vacuo, the residue was purified by silica-gel column chromatography (EtOAc/hexane as an eluent) to afford **5** (835 mg, 1.97 mmol) in 87% yield as colorless solid.

^{1}H NMR ($CDCl_3$): δ 8.48 (br, 1H, NH), 7.69 (d, J = 1.5 Hz, 1H, Ar), 7.48 (d, J = 1.5 Hz, 1H, Ar), 7.45 (d, J = 2.0 Hz, 1H, Ar), 7.40 (d, J = 2.0 Hz, 1H, Ar), 7.25 (m, 1H, Ar), 6.57 (dd, J = 2.0, 3.2 Hz, 1H, Ar) 4.62 (br, 2H, NH_2), 1.40 (s, 9H, *t*-Bu), and 1.30 (s, 9H, *t*-Bu) ppm; ^{13}C NMR ($CDCl_3$): δ 143.0, 142.9, 141.8, 134.7, 130.3, 128.2, 127.5, 124.6, 123.7, 118.2, 108.7, 108.7, 105.0, 103.4, 91.4, 89.0, 34.6, 34.0, 31.9, and 31.3 ppm; HR-MS (ESI-MS): m/z = 421.1295, calcd for $(C_{24}H_{26}N_2Br)^-$ = 421.1285 $[(M-H)^-]$.

Synthesis of 7-bromo-5,5’-di-*tert*-butyl-1*H*,1’*H*-2,7’-diindole (6).

A tube containing **5** (736 mg, 1.74 mmol) and ZnI_2 (27.9 mg 0.0874 mmol) was flushed with N_2. Dry toluene (16 mL) was added, and the solution was degassed by freeze-pump-thaw method. The solution was stirred under reflux for 9 h, and then water was added to the solution. The organic layer was extracted with EtOAc, washed with water and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by silica-gel column chromatography (EtOAc/hexane as an eluent) to provide **6** (587 mg, 1.39 mmol) in 80% yield as white solid.

^{1}H NMR ($CDCl_3$): δ 8.57 (br, 1H, NH), 8.37 (br, 1H, NH), 7.71 (d, J = 1.5 Hz, 1H, Ar), 7.61 (d, J = 1.5 Hz, 1H, Ar), 7.45 (m, 2H, Ar), 7.28 (m, 1H, Ar), 6.86 (d, J = 2.2 Hz, 1H, Ar), 6.62 (dd J = 2.1, 3.0 Hz, 1H, Ar), 1.45 (s, 9H, *t*-Bu), and 1.41 (s, 9H, *t*-Bu) ppm; ^{13}C NMR ($CDCl_3$): δ 145.3, 143.3, 137.1, 133.4, 131.7, 130.1, 128.6, 124.9, 122.9, 118.5, 117.3, 115.7, 115.6, 104.1, 103.3, 101.9, 34.8, 34.7, 32.0, and 31.8 ppm; HR-MS (ESI-MS): m/z = 421.1306, calcd for $(C_{24}H_{26}N_2Br)^-$ = 421.1285 $[(M-H)^-]$.

Synthesis of 5,5’,5’’,5’’’-tetra-*tert*-butyl-1*H*,1’*H*,1’’*H*,1’’’*H*-2,7’:2’7’’:2’’7’’’:2’’’7-tetraindole (1).

A Schlenk tube containing **6** (254 mg, 0.600 mmol), bis(pinacolato)diboron (152 mg, 0.601 mmol), [Ir(OMe)cod]$_2$ (19.8 mg, 0.0299 mmol), and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (16.4 mg, 0.0611 mmol) was flushed with N_2. To the tube, dry and degassed *tert*-butyl methyl ether (6 mL) was added, then the mixture was stirred at 60 °C for 5.5 h. After cooling to room temperature, the mixture was filtered through Celite and evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (3 mL) and the solution was divided into three portions (1 mL each), which were transferred to three tubes separately. After the solvent of each solution was removed, Pd_2dba_3•$CHCl_3$ (10.3 mg, 0.00995 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 16.3 mg, 0.0397 mmol), CsF (30.2 mg, 0.200 mmol), and Cs_2CO_3 (39.0 mg, 0.202 mmol) were added to each tube, and the tube was flushed with N_2. Dry and degassed toluene (2 mL) and DMF (2 mL) were added to each tube. Then the mixtures were stirred at 100 °C for 12 h and cooled to room temperature. The mixtures were combined into one flask, and the resulting mixture was washed with water and brine. The organic layer was separated, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by neutral silica-gel column chromatography (EtOAc/hexane as an eluent) and recrystallization from hexane to furnish **1** (40.4 mg, 0.0590 mmol) in 20% yield as white solid.

^{1}H NMR (CD_3CN): δ 10.06 (s, 4H, NH), 7.60 (d, J = 1.6 Hz, 4H, Ar), 7.50 (d, J = 1.9 Hz, 4H, Ar), 6.78 (d, J = 1.9 Hz, 4H, Ar), and 1.45 (s, 36H, *t*-Bu) ppm; ^{13}C NMR (CD_3CN): δ 144.9, 139.8, 134.1, 131.4, 120.4, 117.5, 117.5, 102.2, 35.3, and 32.2 ppm; UV/vis (toluene): λ_{max} (ε [M^{-1} cm^{-1}]) = 319 (sh) (37000), and 340 (48000), nm; Fluorescence (toluene): λ_{em} = 404 nm (λ_{ex} = 320 nm); HR-MS (ESI-MS): m/z = 683.4139, calcd for $(C_{48}H_{51}N_4)^-$ = 683.4119 [$(M - H)^-$]; Single crystals were obtained by vapor diffusion of pentane into an acetone solution. $C_{54}H_{52}N_4O_2$, M_w = 789.00, tetragonal, space group $I\bar{4}c2$ (No. 120), a = 17.198(4), b = 17.198(4), c = 15.807(7) Å, V = 4675(3) Å^3, Z = 4, D_c = 1.121 g/cm^3, T = 153(2) K, R = 0.0745 ($I > 2.0\ \sigma(I)$), wR = 0.2068 (all data), GOF = 1.029 ($I > 2.0\ \sigma(I)$). Crystallographic data for **1** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-836158. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of 3,3’,3’’,3’’’-tetrabromo-5,5’,5’’,5’’’-tetra-*tert*-butyl-1*H*,1’*H*,1’’*H*,1’’’*H*-2,7’:2’,7’’:2’’,7’’’:2’’’7-tetraindole (7).

A Schlenk tube containing **1** (10.3 mg, 15.0 μmol) was flushed with N_2. To the tube, dry and degassed THF (3 mL) was added. After the solution was cooled to 0 °C in ice bath, a TBAF/THF solution (1 M, 37 μL) was added dropwise, and then the mixture was stirred at 0 °C for 30 min, the reaction mixture turned into green color. To the mixture, a Br_2/THF solution (1.5 M, 0.1 mL, 0.15 mmol, 10 equiv) was added dropwise carefully at 0 °C. The color turned into brown, and then the mixture was stirred at 0 °C for additional 2 h. After warmed to room temperature, the mixture was diluted with CH_2Cl_2. $NaHSO_3$ (aq) was added and the organic layer was separated, washed with water and brine, dried over Na_2SO_4, evaporated in vacuo, then dark purple solids remained. The residue was purified by neutral silica-gel column chromatography (EtOAc/hexane as an eluent) to provide **7** (8.88 mg, 8.92 μmol) in 60% yield as light purple solid.

^{1}H NMR ($CDCl_3$): δ 9.41 (br, 4H, NH), 7.95 (d, J = 1.7 Hz, 4H, Ar), 7.65 (d, J = 1.7 Hz, 4H, Ar), and 1.48 (s, 36H, *t*-Bu) ppm; ^{13}C NMR ($CDCl_3$): δ 145.2, 133.2, 132.0, 129.7, 123.5, 116.0, 114.6, 92.4, 35.0, and 31.8 ppm; HR-MS (ESI-MS): m/z = 995.0493, calcd for $(C_{48}H_{47}N_4Br_4)^-$ = 995.0540 $[(M-H)^-]$.

Direct synthesis of 3,3’’-dibromo-5,5’,5’’,5’’’-tetra-*tert*-butyl-1*H*,1’’*H*,3’*H*,3’’’*H*-[2,7’:2’,7’’:2’’,7’’’:2’’’,7-tetraindole]-3’,3’’’-dione (8) from 1.

A Schlenk tube containing **1** (9.62 mg, 14.0 μmol) was flushed with N_2. To the tube, dry and degassed THF (3 mL) was added. After the solution was cooled to 0 °C in ice bath, a TBAF/THF solution (1 M, 37 μL) was added dropwise, and then the mixture was stirred at 0 °C for 30 min. To the mixture, Br_2 (0.1 mL, 1.95 mmol, 134 equiv) was added slowly. The color turned into dark brown, and then the mixture was stirred at 0 °C for 2 h. After an addition of water, the mixture was stirred at room temperature for additional 30 min. To the mixture, $NaHSO_3$ (aq) was added and extracted with CH_2Cl_2, washed with water and brine, dried over Na_2SO_4, evaporated in vacuo. The residue was purified by recrystallization from CH_2Cl_2/MeOH to furnish **8** (7.68 mg, 8.82 μmol) in 63% yield as purple crystals.

^{1}H NMR ($CDCl_3$): δ 11.35 (s, 2H, NH), 9.06 (d, J = 1.9 Hz, 2H, Ar), 8.90 (d, J = 1.7 Hz 2H, Ar), 7.48 (d, J = 1.7 Hz, 2H, Ar), 7.28 (d, J = 1.9 Hz, 2H, Ar), 1.53 (s, 18H, *t*-Bu), and 1.49 (s, 18H, *t*-Bu) ppm; ^{13}C NMR ($CDCl_3$): δ 193.3, 157.9, 152.5, 150.5, 143.6, 132.4, 131.6, 130.7, 129.4, 128.2, 122.5, 122.4, 121.5, 121.3, 113.0, 93.1, 35.4, 34.9, 31.6, and 31.3 ppm; UV/vis (toluene): λ_{max} (ε [M^{-1} cm^{-1}]) = 312 (35000), 364 (22000), 518 (br) (12000), and 541 (br) (12000), and 662 (sh) (2200) nm; HR-MS (ESI-MS): m/z = 867.1935, calcd for $(C_{48}H_{45}N_4O_2Br_2)^-$ = 867.1915 $[(M - H)^-]$. Single crystals were obtained by vapor diffusion of EtOH into a dichloromethane solution; $C_{48}H_{46}Br_2N_4O_2$, M_w = 870.71, tetragonal, space group $I4_1/acd$ (No. 142), a = 23.2637(17), b = 23.2637(17), c = 62.003(9) Å, V = 33556(6) Å^3, Z = 32, D_{calc} = 1.379 g/cm^3, T = 153(2) K, R = 0.0762 ($I > 2.0\ \sigma(I)$), wR = 0.2003 (all data), GOF = 1.124 ($I > 2.0\ \sigma(I)$). Crystallographic data for **8** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-836157. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of 8 from 7.

A Schlenk tube containing **7** (3.95 mg, 3.97 μmol) was flushed with N_2. To the tube, dry and degassed THF (1 mL) was added, and Br_2 (0.1 mL, 1.95 mmol, 492 equiv) was added dropwise. The mixture was stirred at room temperature for 1 h. The mixture was diluted with CH_2Cl_2 and water. $NaHSO_3$ (aq) was added to the mixture, and organic layer was separated. The organic layer was washed with water and brine, dried over Na_2SO_4, evaporated in vacuo. The residue was purified by neutral silica-gel column chromatography (EtOAc/hexane as an eluent) to afford **8** (2.35 mg, 2.70 μmol) in 68% yield.

Synthesis of Cu complex 9a.

To a flask containing **8** (5.03 mg, 5.78 μmol) in $CHCl_3$ (4 mL), a saturated $Cu(OAc)_2$/MeOH solution was added. Then, the mixture was stirred under reflux for 8 h. After cooling to room temperature, the mixture was washed with water and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by neutral silica-gel column chromatography (EtOAc/hexane as an eluent) and recrystallization from CH_2Cl_2/MeOH to provide **9a** (2.52 mg, 2.70 μmol) in 47% yield as blue crystals.

UV/vis (toluene): λ_{max} (ε [M^{-1} cm^{-1}]) = 399 (11000), 414 (11000), 556 (sh) (10000), 658 (12000), 752 (sh) (8500), and 845 (sh) (3900) nm; HR-MS (ESI-MS): *m/z* = 964.0790, calcd for $(C_{48}H_{44}N_4O_2Br_2ClCu)^-$ = 964.0821 [$(M + Cl)^-$].

Synthesis of Zn complex 9b.

A Schlenk tube containing **8** (9.08 mg, 10.4 μmol) was flushed with N_2. To the tube, dry DMF (4.5 mL) was added. After the solution was cooled to 0 °C in ice bath, NaH (60% dispersion in oil, 3.62 mg, 0.151 mmol) in DMF (4 mL) was added dropwise. The mixture was stirred at 0 °C for 1 h, the color turned into blue-green. A $Zn(OAc)_2$ (19.4 mg, 0.106 mmol)/DMF (4 mL) solution was added in N_2 atmosphere, and then the mixture was stirred at room temperature for 5 h, the color turned into blue. The mixture was poured into water, and the resulting mixture was extracted with CH_2Cl_2. The organic layer was separated, washed with water and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by silica-gel column chromatography (EtOAc/hexane as an eluent) to afford **9b** (6.52 mg, 6.98 μmol) in 67% yield as blue solid.

^{1}H NMR ($CDCl_3$): δ 9.11 (s, 2H, Ar), 8.95 (s, 2H, Ar), 7.63 (s, 2H, Ar), 7.34 (s, 2H, Ar), 1.53 (s, 18H, *t*-Bu), and 1.46 (s, 18H, *t*-Bu) ppm; UV/vis (toluene): λ_{max} (ε [M^{-1} cm^{-1}]) = 402 (7700), 637 (9600), 723 (5900), and 819 (2200) nm; HR-MS (ESI-MS): *m/z* = 965.0794, calcd for $(C_{48}H_{44}N_4O_2Br_2ClZn)^-$ = 965.0816 [$(M + Cl)^-$].

Synthesis of Ni complex 9c.

A Schlenk tube containing NaH (60% dispersion in oil, 11.8 mg, 0.295 mmol) was flushed with N_2. To the tube, dry DMF (2 mL) was added. After the solution was cooled to 0 °C in ice bath, **8** (5.13 mg, 5.89 μmol) in dry DMF was added dropwise in N_2 atmosphere. The mixture was stirred at 0 °C for 1 h. $Ni(OAc)_2$•$4H_2O$ (7.27 mg, 29.2 μmol) was heated in vacuo, its color turned into green from blue. The Ni reagent was dissolved in dry DMF (1mL), and the solution was added to the **8** and NaH/DMF mixture at 0 °C in N_2 atmosphere. Then, the resulting mixture was stirred at room temperature for 3 h. The mixture was poured into water, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by recrystallization from CH_2Cl_2/MeOH to provide **9c** (2.12 mg, 2.29 μmol) in 39% yield as black solid.

^{1}H NMR ($CDCl_3$): δ 8.79 (s, 2H, Ar), 8.75 (s, 2H, Ar), 7.84 (s, 2H, Ar), 7.56 (s, 2H, Ar), 1.48 (s, 18H, *t*-Bu), and 1.43 (s, 18H, *t*-Bu) ppm; ^{13}C NMR ($CDCl_3$): δ 189.4, 151.0, 150.5, 145.8, 144.2, 138.8, 132.9, 132.8, 131.8, 125.6, 125.2, 124.3, 123.3, 121.3, 113.7, 93.8, 35.2, 34.9, 31.7, and 31.1 ppm; λ_{max} (ε [M^{-1} cm^{-1}]) = 312 (41000), 343 (sh) (23000), 432 (15000), 520 (8800), 606 (sh) (7000), 808 (8300), and 900 (sh) (6000) nm; HR-MS (ESI-MS): *m/z* = 924.1193, calcd for $(C_{48}H_{44}N_4O_2Br_2Ni)^-$ = 924.1190 [M^-].

* = solvents and impurities

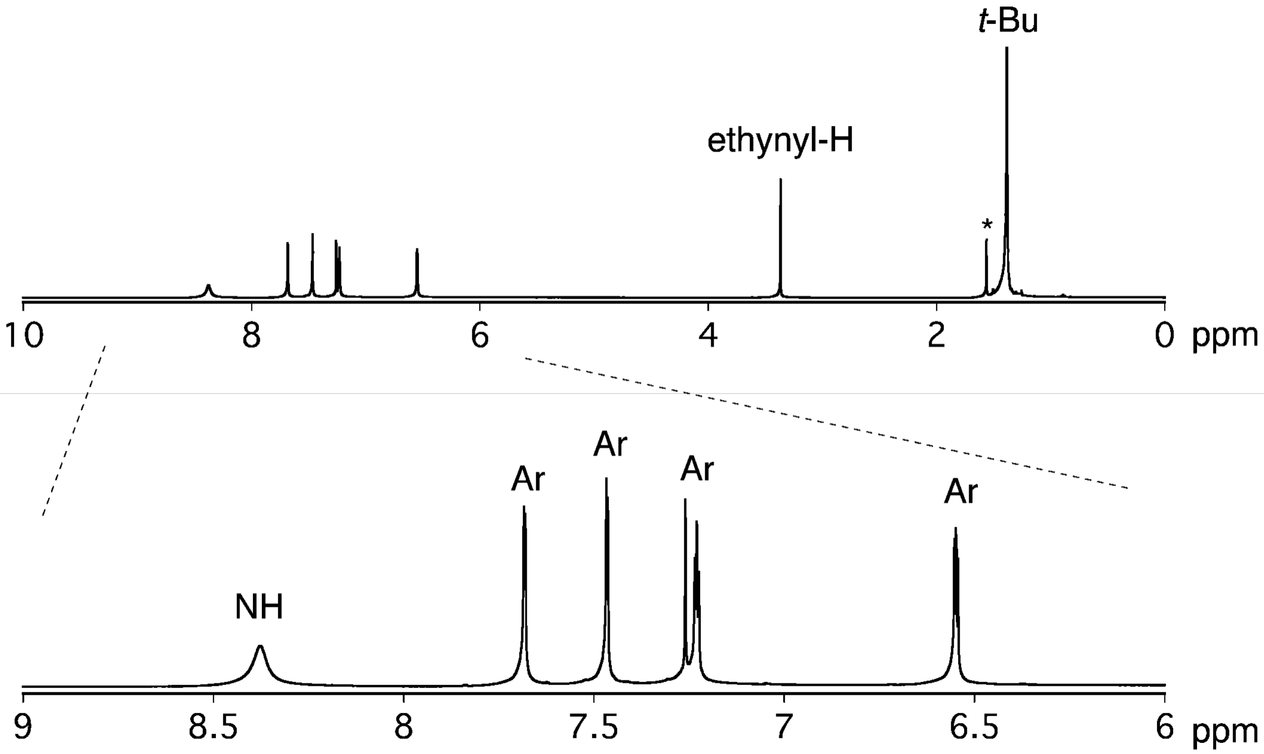


Fig S1. ^{1}H NMR spectrum of **4** in $CDCl_3$.

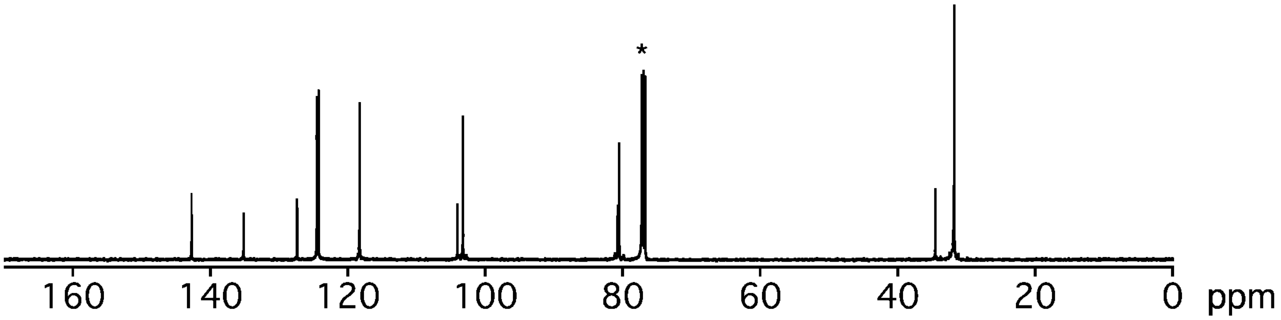


Fig S2. ^{13}C NMR spectrum of **4** in $CDCl_3$.

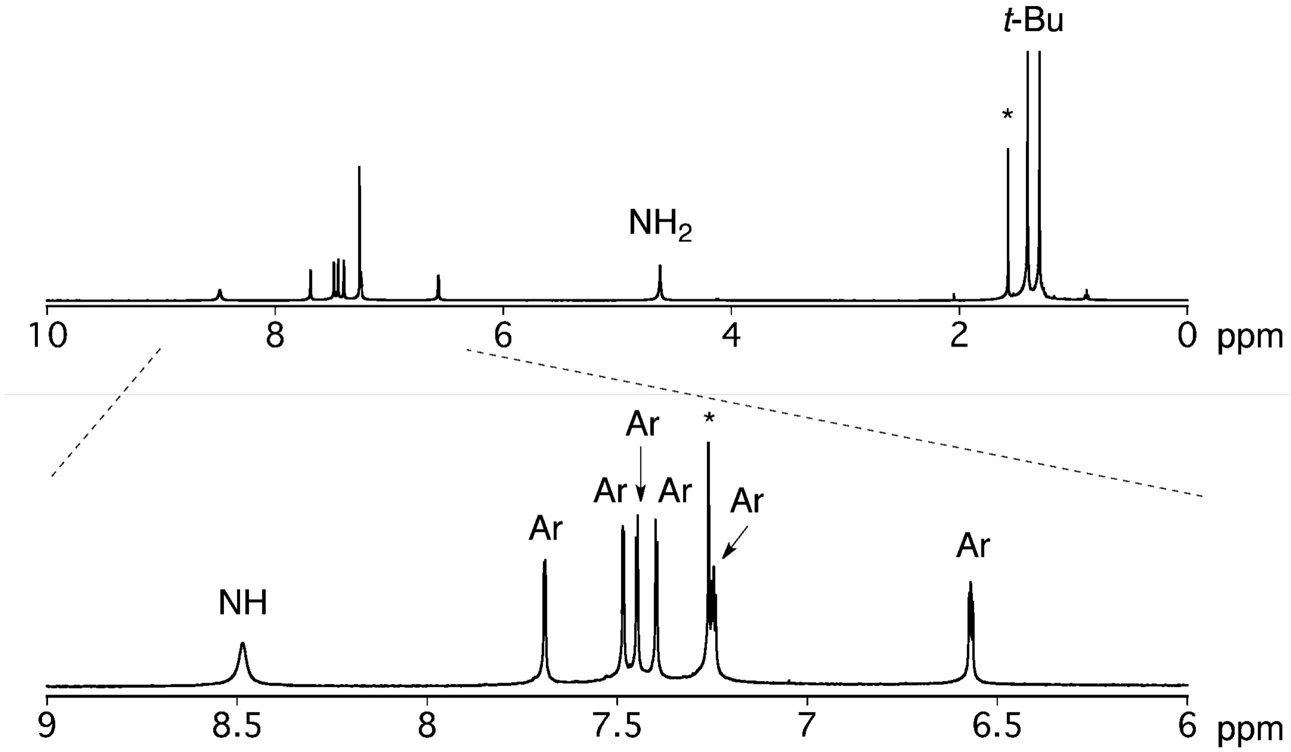


Fig S3. ^{1}H NMR spectrum of **5** in $CDCl_3$.

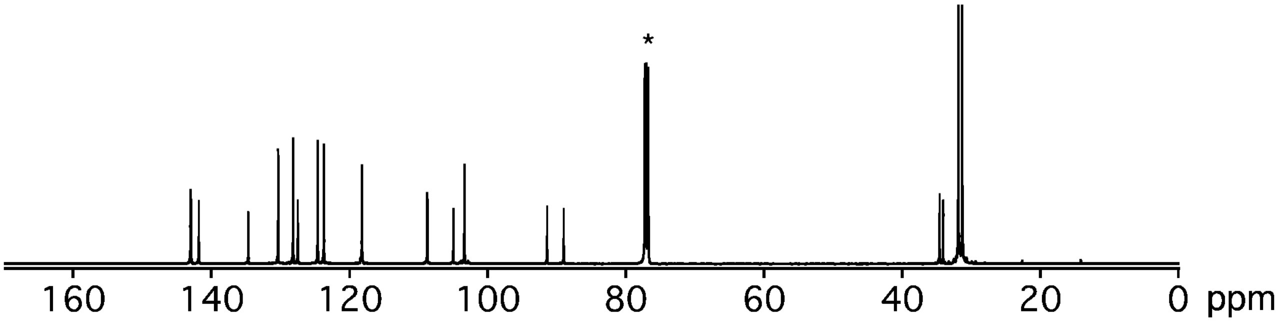


Fig S4. ^{13}C NMR spectrum of **5** in $CDCl_3$.

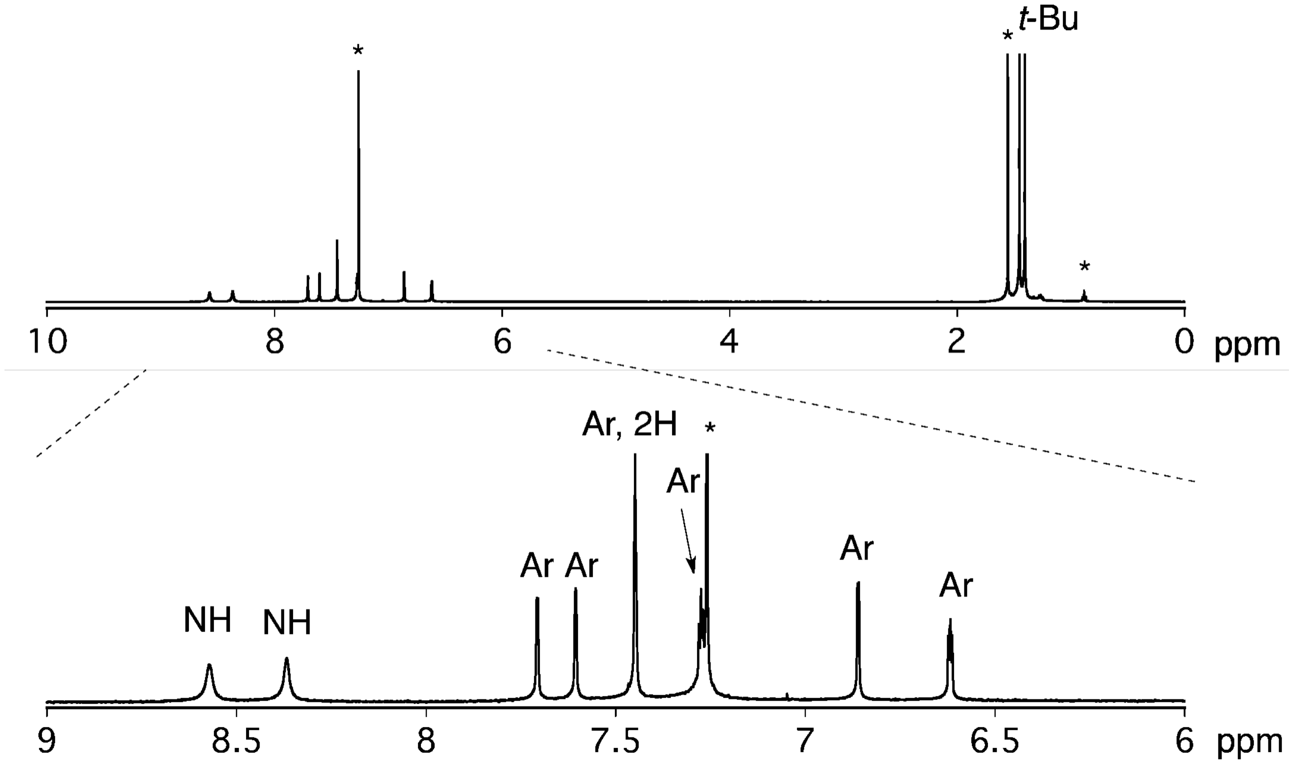


Fig S5. ^{1}H NMR spectrum of **6** in $CDCl_3$.

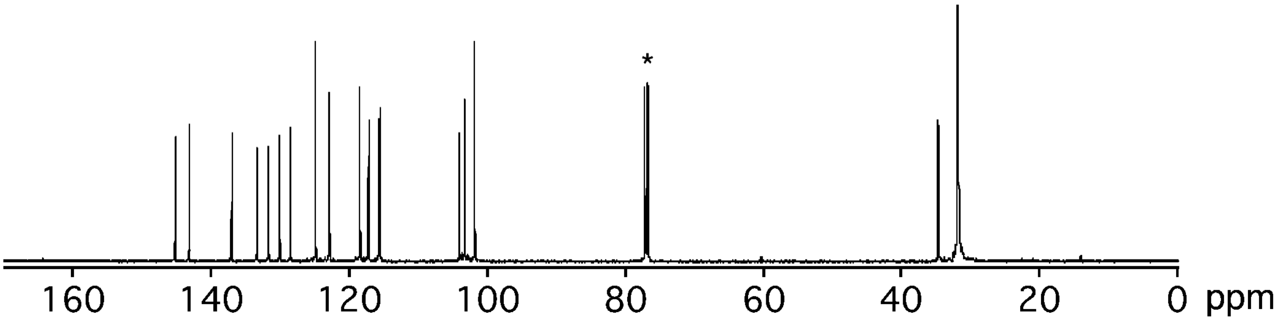


Fig S6. ^{13}C NMR spectrum of **6** in $CDCl_3$.

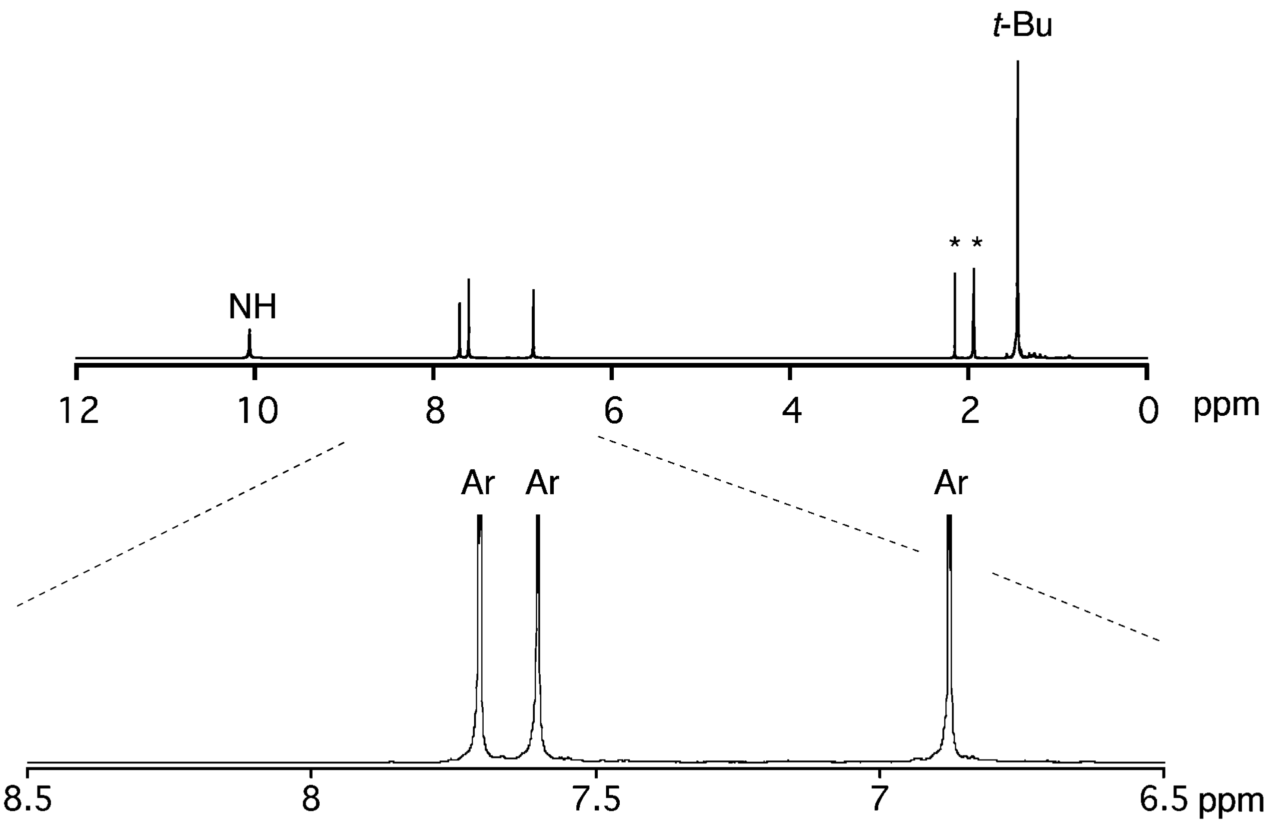


Fig S7. ^{1}H NMR spectrum of **1** in CD_3CN.

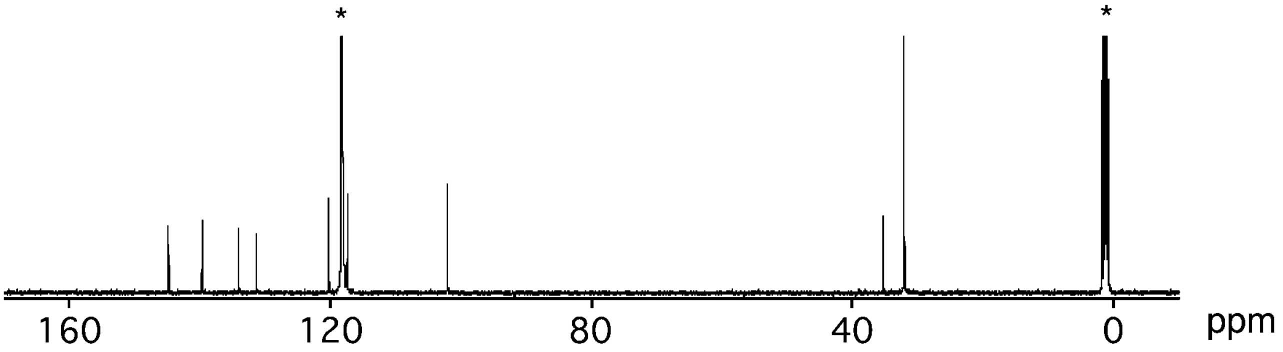


Fig S8. ^{13}C NMR spectrum of **1** in CD_3CN.

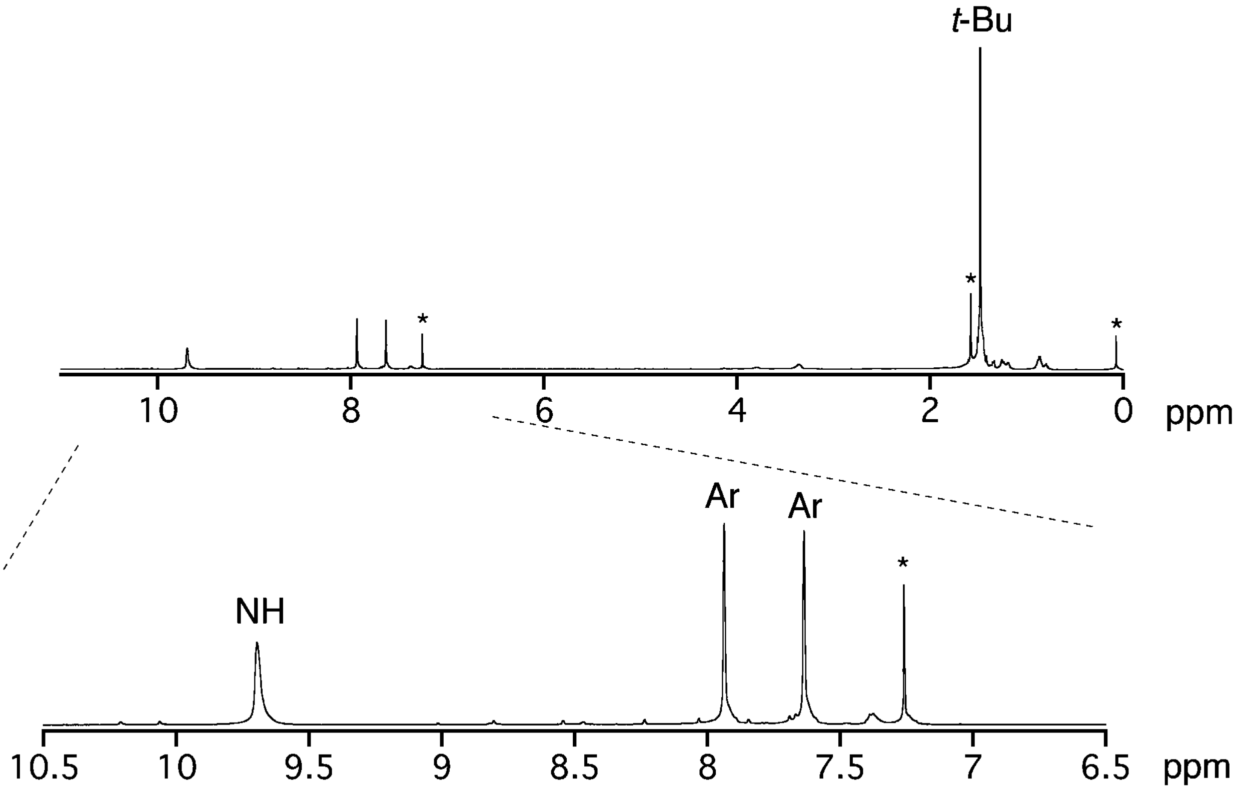


Fig S9. ^{1}H NMR spectrum of **7** in $CDCl_3$.

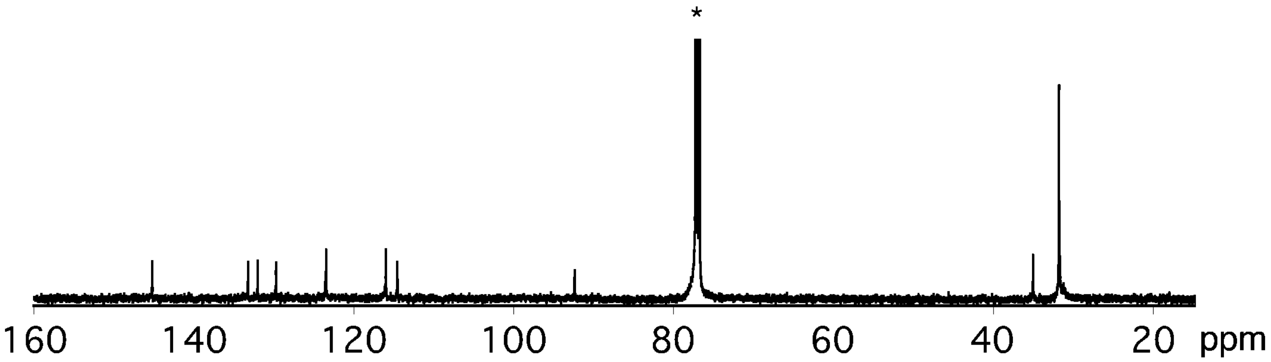


Fig S10. ^{13}C NMR spectrum of **7** in $CDCl_3$.

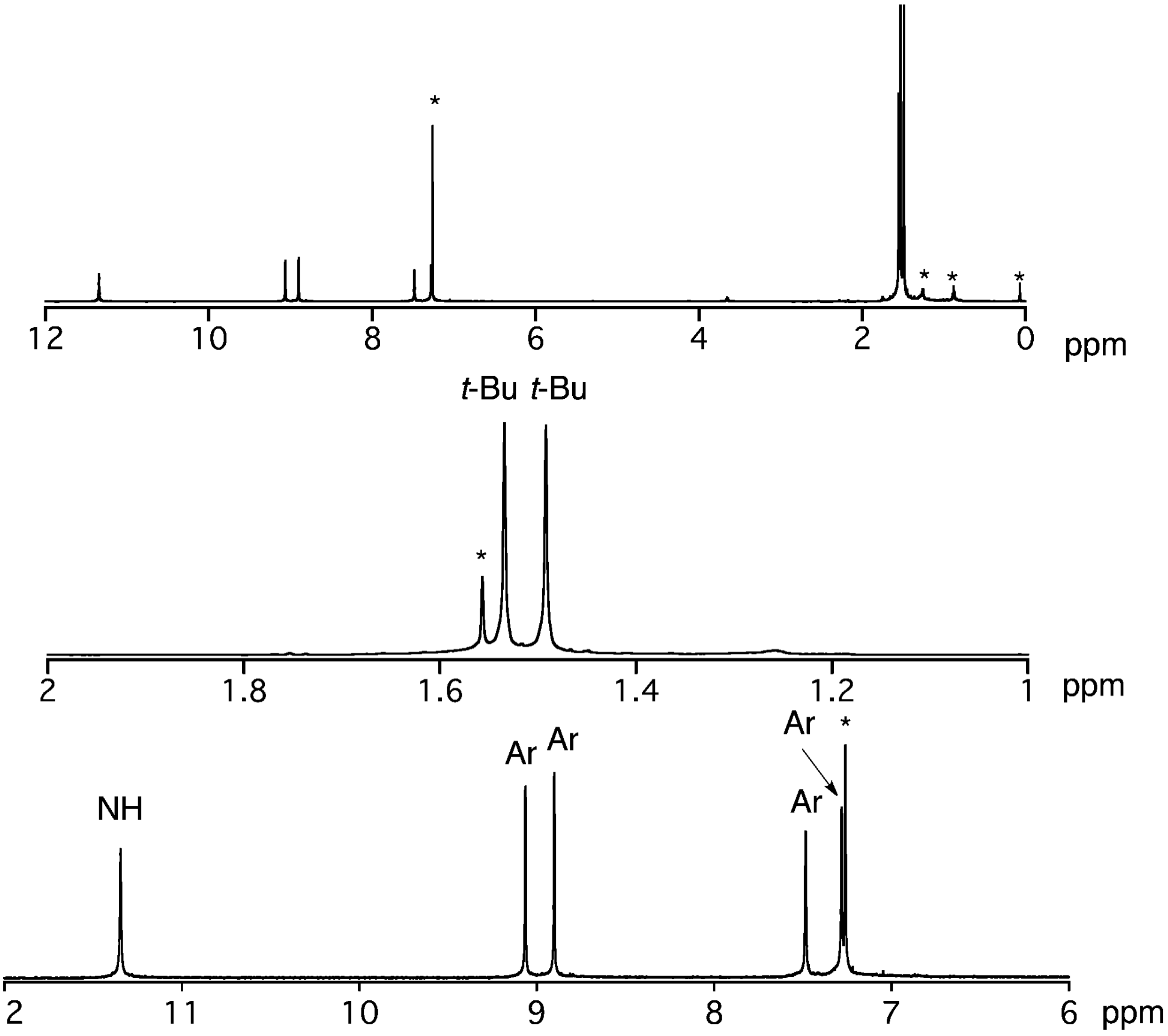


Fig S11. ^{1}H NMR spectrum of **8** in $CDCl_3$.

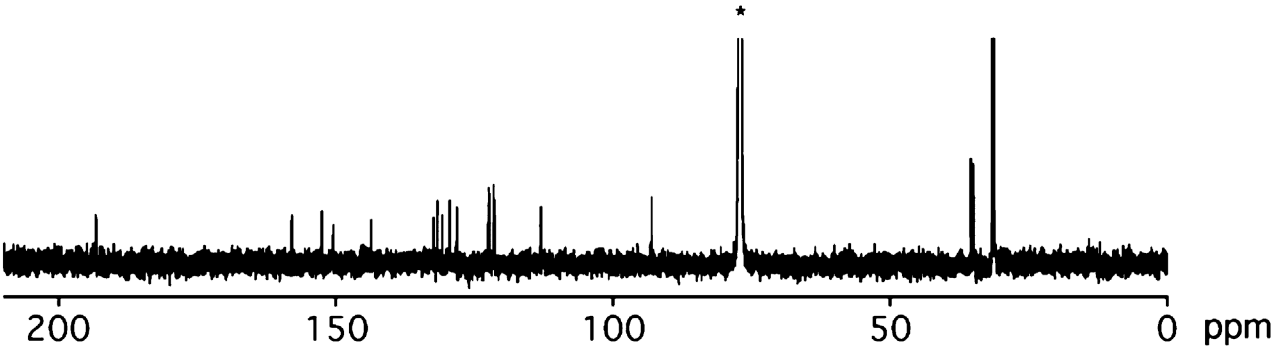


Fig S12. ^{13}C NMR spectrum of **8** in $CDCl_3$.

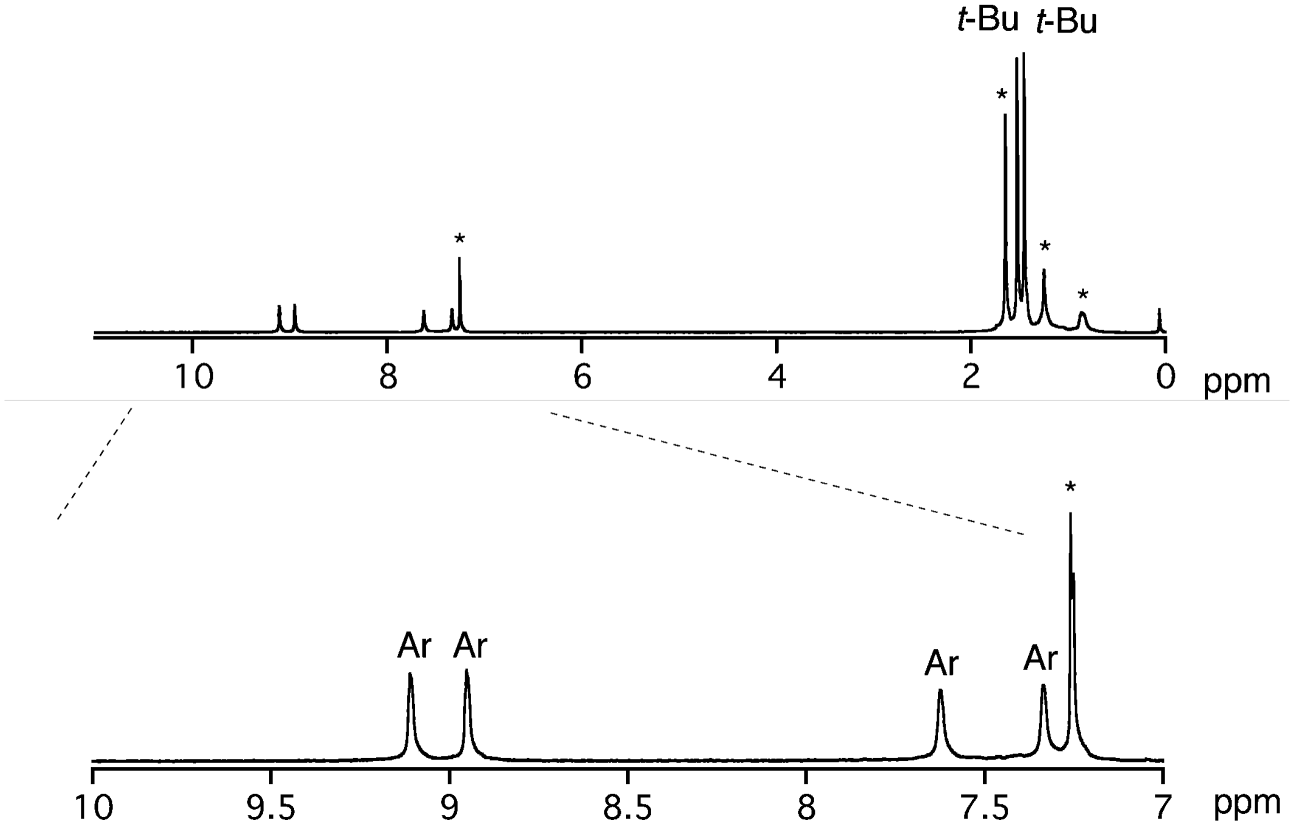


Fig S13. ^{1}H NMR spectrum of **9b** in $CDCl_3$.

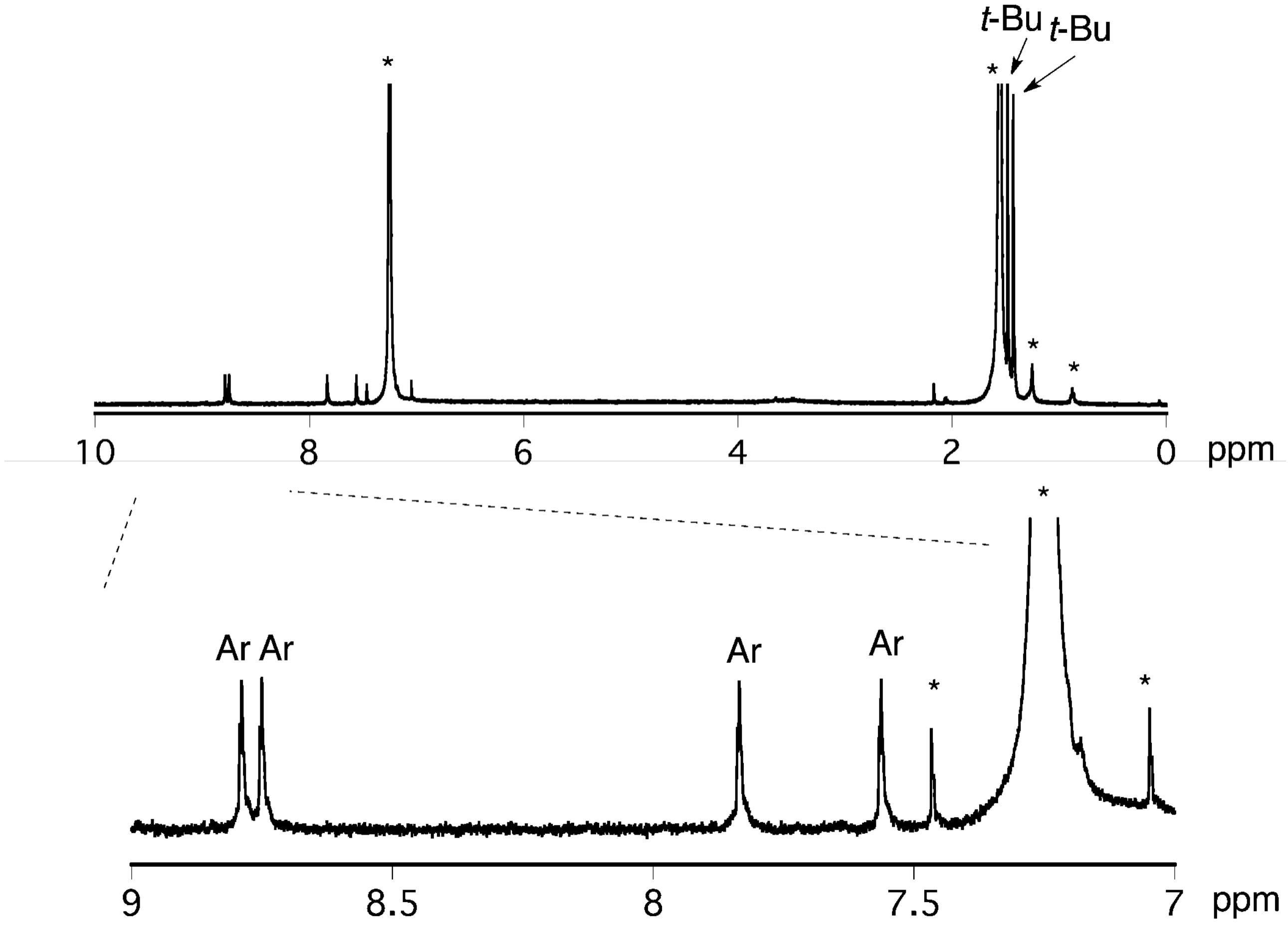


Fig S14. ^{1}H NMR spectrum of **9c** in $CDCl_3$.

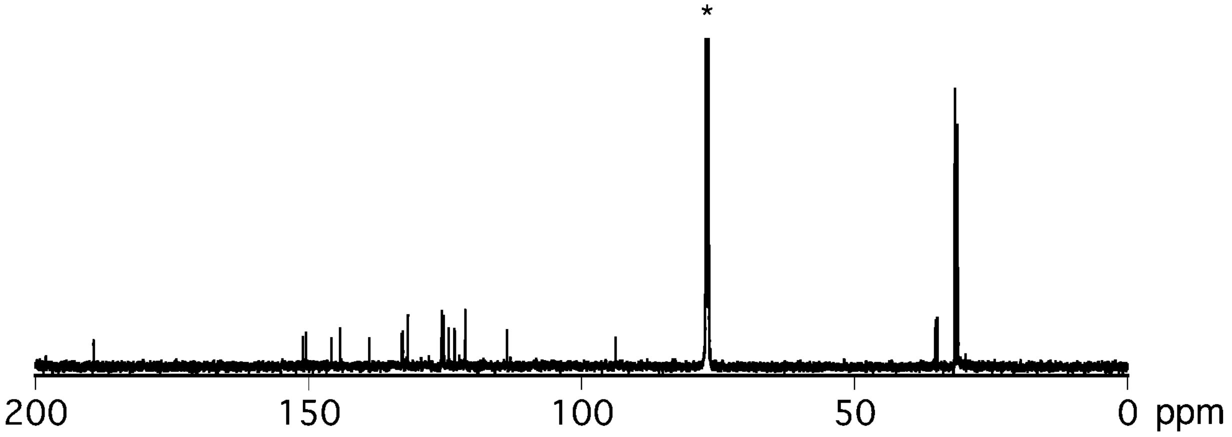
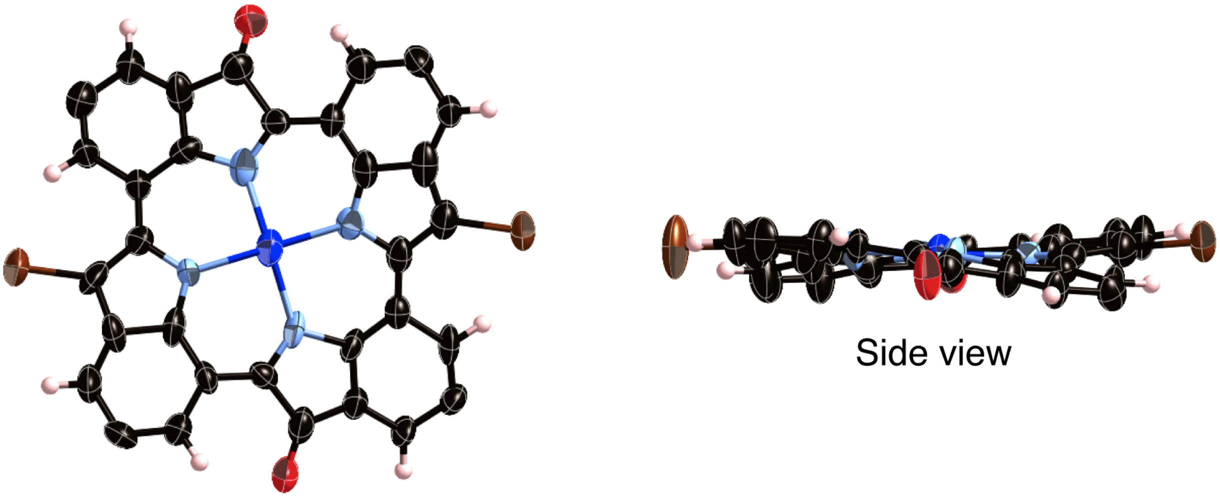


Fig S15. ^{13}C NMR spectrum of **9c** in $CDCl_3$.



Top view

Side view

Fig S16. Preliminary X-ray crystal structure of **9a**. *tert*-Butyl groups are omitted for clarity. The thermal ellipsoids are scaled to the 50% probability level.

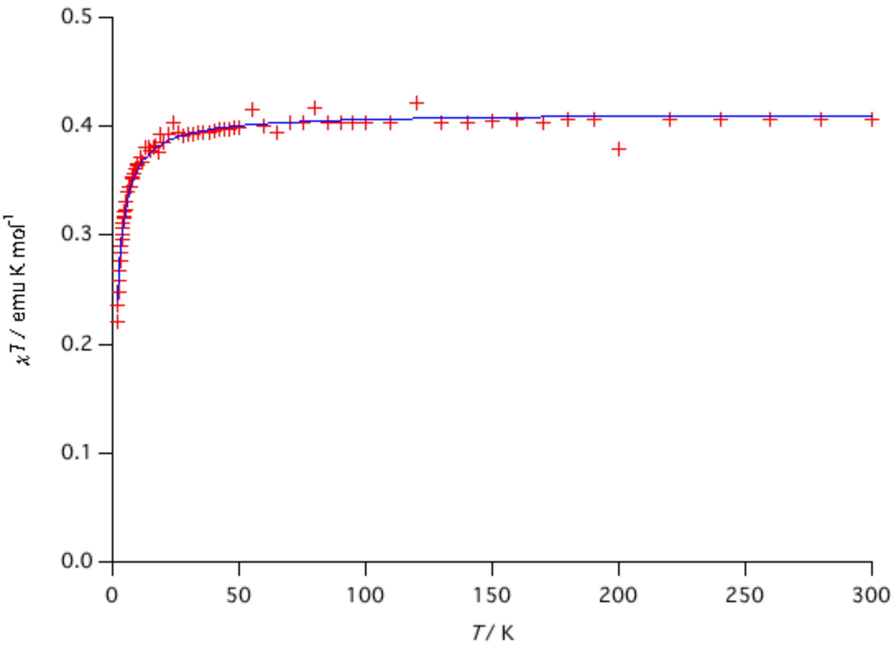


Fig S17. Temperature-dependent magnetic susceptibility of **9a**. The measurement was performed with SQUID magnetometer for powder of **9a**. The solid line is calculated values estimated by Curie's law with Weiss parameter $\theta = -1.4$ K

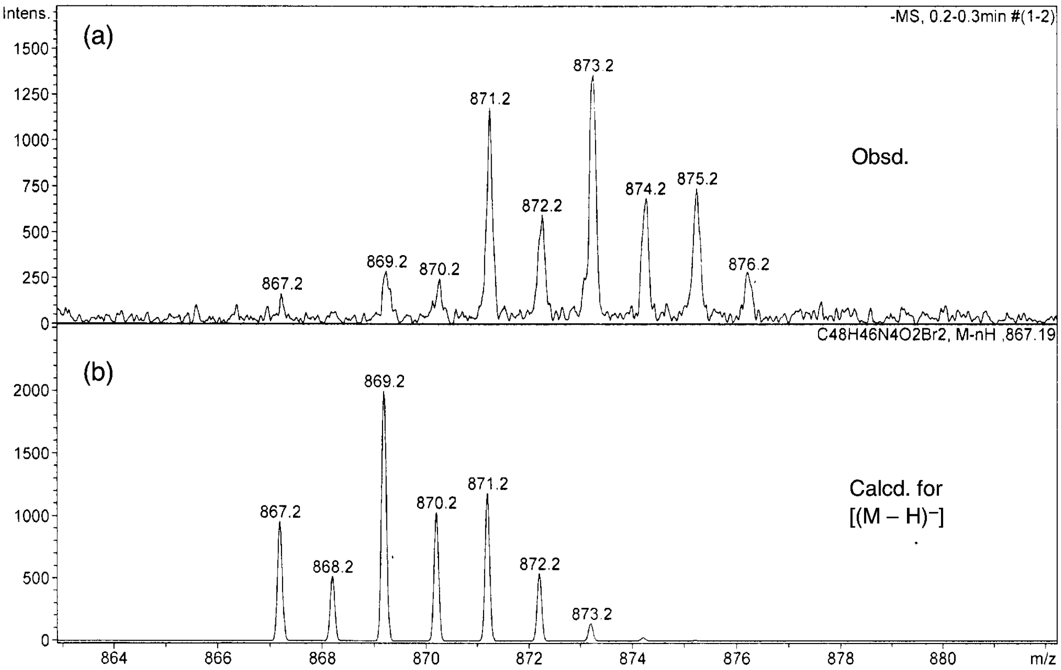


Fig S18. ESI-TOF mass spectrum of **7** prepared in the presence of H_2O^{18}. (a) observed spectrum, (b) calculated spectrum for $[(M\text{–}H)^-]$ were described.

Cyclic Voltammetry

Cyclic voltammetry of **8**, **9a**, **9b** and **9c** were recorded on ALS electrochemical analyser 612C. Measurements were performed in freshly distilled dichloromethane with tetrabutylammonium hexafluorophosphate as electrolyte. A three electrode system was used and consisted of a glasy carbon working electrode, a platinum wire and Ag/$AgClO_4$ as the reference electrode. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple. For compounds **8**, **9a** and **9c**, the oxidation potentials were determined by differential pulse voltammetry due to their irriversible feature.

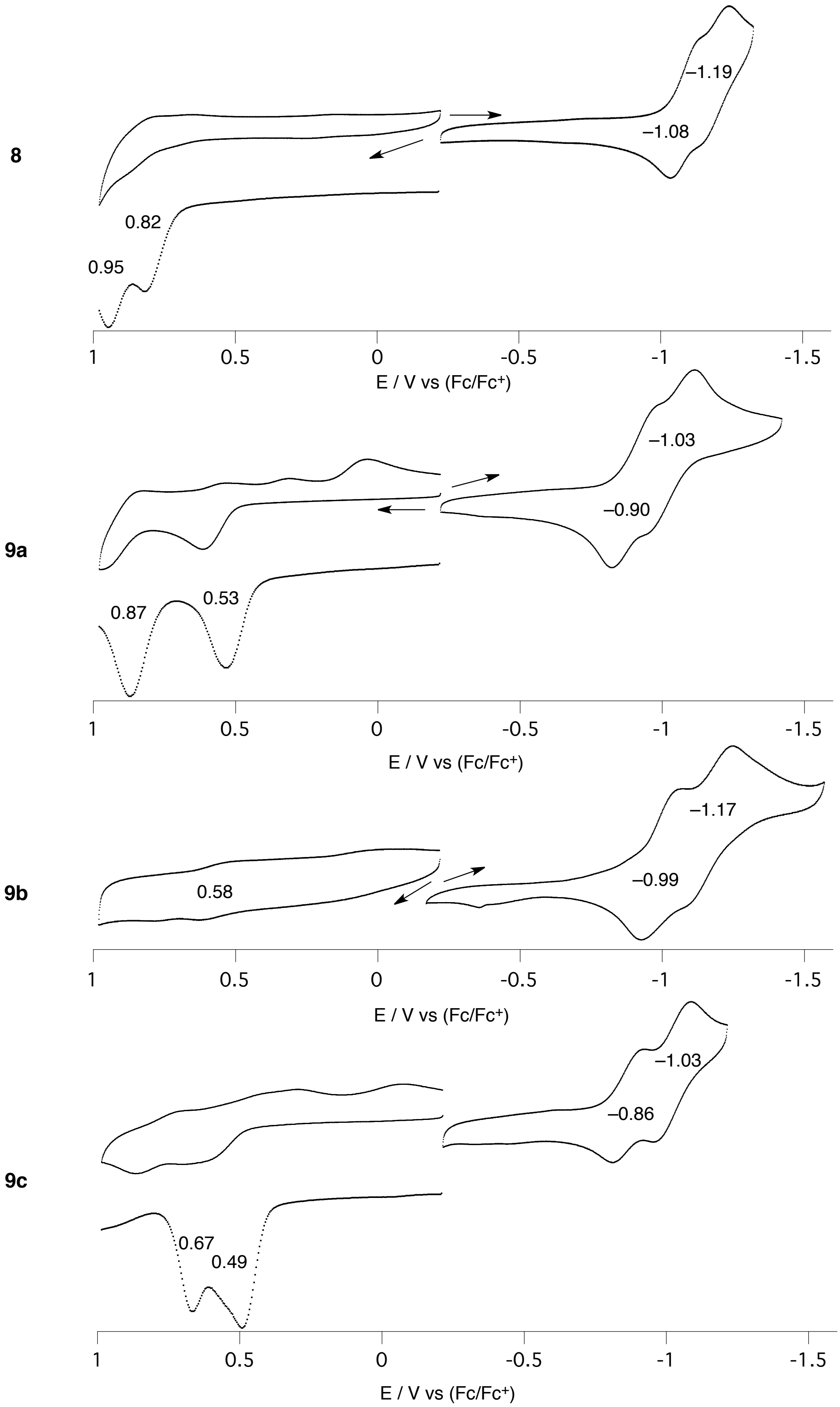


Fig S19. Cyclic voltammograms (0.1 $V\cdot s^{-1}$) of **8, 9a**, **9b** and **9c** in CH_2Cl_2 (0.1 M $TBAPF_6$).

Theoretical calculations

All calculations were carried out using the *Gaussian 03* program. Crystal structure was used for the initial geometry of **8**. Full optimization for **8, 9a** and **9c** were performed by the B3LYP method with LANL2DZ basis for heavy atoms (Br, Ni and Zn) and 6-31G(d) basis set for the rest. Molecular orbitals were further obtained by B3LYP/6-31G(d) + SDD (for Zn, Ni and Br). The oscillator strength of **8** was calculated by time-dependent DFT (TD-DFT) method.

References

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2) (a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

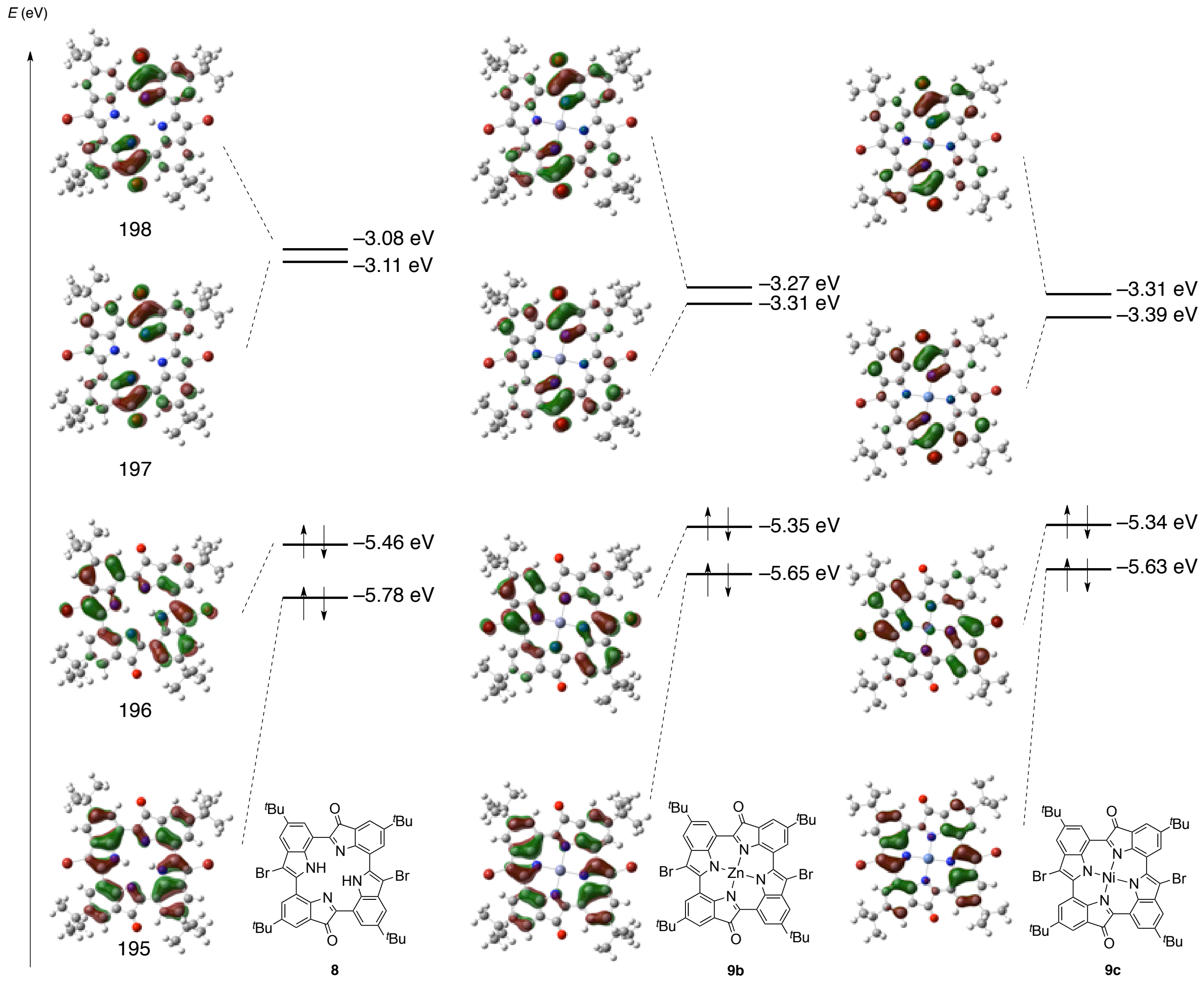
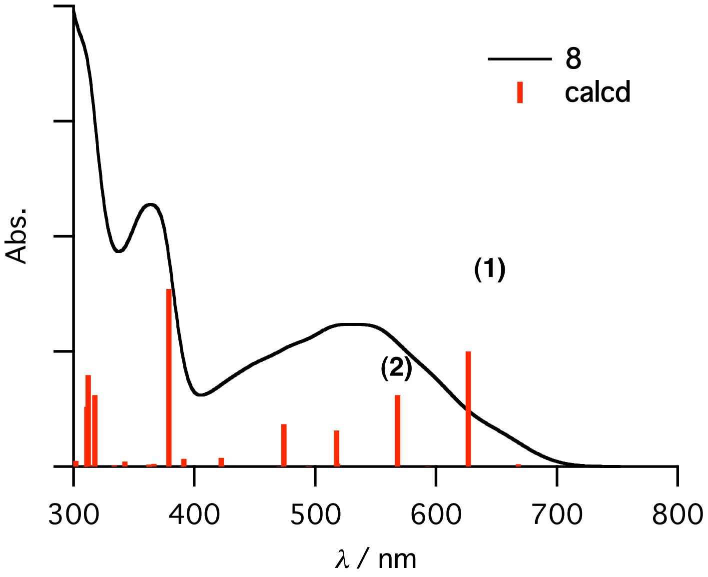


Fig S20. MO diagrams of **8**, **9b and 9c**.



configuration

transition (1) (*f* =0.1930)
196 -> 197 0.65852

transition (2) (*f* = 0.1196)
195 -> 198 0.66776

Fig S21. Observed (black line) and calculated (red bar) absorption spectra of **8**.

Table S1. Molecular geometry for **8**.

Symbol	X	Y	Z
O	−0.523889	5.438372	0.423924
Br	−6.095682	−0.462759	−0.596336
C	−0.002683	3.029948	−0.001142
C	−0.862465	4.271886	0.351362
C	−2.19236	3.690859	0.600194
C	−3.375251	4.304593	0.954867
H	−3.390392	5.37784	1.120772
C	−4.532307	3.50937	1.105449
C	−4.414785	2.145467	0.834554
H	−5.287895	1.52239	0.948412
C	−3.212036	1.501969	0.425166
C	−2.07109	2.312936	0.367546
C	−3.212036	0.077871	0.09225
C	−4.220206	−0.803459	−0.270774
C	−3.660293	−2.097836	−0.471534
C	−4.204845	−3.338352	−0.819448
H	−5.271284	−3.406724	−1.009773
C	−3.385153	−4.467867	−0.910683
C	−2.015633	−4.319137	−0.631694
H	−1.371608	−5.183918	−0.668689
C	−1.414913	−3.08971	−0.285553
C	−2.267639	−1.962341	−0.224335
C	−5.852904	4.161488	1.550554
C	−5.649357	4.836442	2.928392
H	−5.365924	4.099704	3.688762
H	−6.577685	5.320801	3.254175
H	−4.868079	5.603359	2.897013
C	−6.265147	5.232103	0.5113
H	−5.504946	6.013303	0.40316
H	−7.198965	5.718031	0.818646
H	−6.425215	4.780847	−0.474514
C	−7.002358	3.144192	1.676291
H	−7.219734	2.652091	0.721703
H	−7.914064	3.66024	1.997228
H	−6.784119	2.368829	2.419577
C	−4.00154	−5.827919	−1.29433

C	−5.062091	−6.224936	−0.239515
H	−5.516707	−7.188673	−0.499846
H	−5.867422	−5.485445	−0.170945
H	−4.60946	−6.320111	0.754078
C	−2.949717	−6.951903	−1.36293
H	−2.180637	−6.746978	−2.116461
H	−3.438204	−7.893417	−1.638558
H	−2.449933	−7.107216	−0.400447
C	−4.677245	−5.714201	−2.681665
H	−3.947628	−5.440041	−3.452286
H	−5.470801	−4.959124	−2.689364
H	−5.127688	−6.67304	−2.965909
N	−0.725293	1.939961	0.054016
N	−2.028348	−0.65823	0.105206
H	−1.117089	−0.227073	0.20313
O	0.523889	−5.438372	0.423924
Br	6.095682	0.462759	−0.596336
C	0.002683	−3.029948	−0.001142
C	0.862465	−4.271886	0.351362
C	2.19236	−3.690859	0.600194
C	3.375251	−4.304593	0.954867
H	3.390392	−5.37784	1.120772
C	4.532307	−3.50937	1.105449
C	4.414785	−2.145467	0.834554
H	5.287895	−1.52239	0.948412
C	3.212036	−1.501969	0.425166
C	2.07109	−2.312936	0.367546
C	3.212036	−0.077871	0.09225
C	4.220206	0.803459	−0.270774
C	3.660293	2.097836	−0.471534
C	4.204845	3.338352	−0.819448
H	5.271284	3.406724	−1.009773
C	3.385153	4.467867	−0.910683
C	2.015633	4.319137	−0.631694
H	1.371608	5.183918	−0.668689
C	1.414913	3.08971	−0.285553
C	2.267639	1.962341	−0.224335
C	5.852904	−4.161488	1.550554
C	5.649357	−4.836442	2.928392
H	5.365924	−4.099704	3.688762

H	6.577685	−5.320801	3.254175
H	4.868079	−5.603359	2.897013
C	6.265147	−5.232103	0.5113
H	5.504946	−6.013303	0.40316
H	7.198965	−5.718031	0.818646
H	6.425215	−4.780847	−0.474514
C	7.002358	−3.144192	1.676291
H	7.219734	−2.652091	0.721703
H	7.914064	−3.66024	1.997228
H	6.784119	−2.368829	2.419577
C	4.00154	5.827919	−1.29433
C	5.062091	6.224936	−0.239515
H	5.516707	7.188673	−0.499846
H	5.867422	5.485445	−0.170945
H	4.60946	6.320111	0.754078
C	2.949717	6.951903	−1.36293
H	2.180637	6.746978	−2.116461
H	3.438204	7.893417	−1.638558
H	2.449933	7.107216	−0.400447
C	4.677245	5.714201	−2.681665
H	3.947628	5.440041	−3.452286
H	5.470801	4.959124	−2.689364
H	5.127688	6.67304	−2.965909
N	0.725293	−1.939961	0.054016
N	2.028348	0.65823	0.105206
H	1.117089	0.227073	0.20313

Table S2. Molecular geometry of **9a**

Symbol	X	Y	Z
Br	−6.0876044	−0.143811	−0.619766
Br	6.0875675	0.1437589	−0.619894
O	0.300864	−5.5183585	0.2713621
O	−0.3008969	5.5183744	0.2711511
N	1.9767032	0.582909	0.0815001
N	0.596188	−2.0233942	0.0288511
N	−1.9767031	−0.5829091	0.0815141
N	−0.596199	2.0233881	0.0288621
C	−4.3790254	−5.6541524	−1.115253
C	2.3580252	1.8627551	−0.1965509

C	3.7646783	1.9310041	−0.425693
C	4.2238683	0.597629	−0.2609699
C	3.1367743	−0.2069051	0.0694351
C	3.6575704	4.3334663	−0.786003
C	2.2843753	4.2727343	−0.533802
H	1.6956962	5.1773303	−0.553124
C	1.5936002	3.0651552	−0.2481109
C	0.1838691	3.0919882	−0.0302279
C	−2.0101131	3.8156633	0.4842351
C	−1.9350671	2.4271862	0.2994831
C	−3.1786402	4.4714274	0.8192841
H	−3.1649862	5.5493944	0.9495471
C	−4.3498563	3.7093253	1.0067592
C	−4.2676073	2.3332222	0.7801681
H	−5.1551574	1.7385452	0.9267591
C	−3.0904952	1.6397101	0.3764661
C	−3.1367792	0.206896	0.0694641
C	−2.3580232	−1.8627531	−0.1965439
C	−4.2238743	−0.597636	−0.2609459
C	−3.7646783	−1.9310091	−0.425685
C	−4.3941094	−3.1363872	−0.727702
H	−5.4646154	−3.1367432	−0.91082
C	−1.5936021	−3.0651572	−0.2481209
C	−2.2843692	−4.2727343	−0.533825
H	−1.6956972	−5.1773374	−0.553119
C	−3.6575553	−4.3334643	−0.78605
C	−0.183881	−3.0919923	−0.0301769
C	0.664781	−4.3561264	0.2442791
C	2.0100931	−3.8156484	0.4843361
C	1.9350571	−2.4271822	0.2995121
C	3.0904882	−1.6397062	0.3764611
C	4.2676113	−2.3332143	0.7801381
H	5.1551684	−1.7385352	0.9266931
C	4.3498633	−3.7093134	1.0067471
C	3.1786322	−4.4714124	0.8193511
H	3.1649812	−5.5493755	0.9496471
C	−3.4135793	−6.8540175	−1.158667
H	−2.9145343	−7.0149525	−0.1966669
H	−2.6406293	−6.7296095	−1.9256451
H	−3.9726534	−7.7656206	−1.398205

C	−5.0643174	−5.5360304	−2.4976361
H	−5.5882285	−6.4676665	−2.7438441
H	−4.3276534	−5.3419954	−3.2856832
H	−5.8007105	−4.7255493	−2.5215121
C	−5.4512825	−5.9356284	−0.0353629
H	−5.9852655	−6.8667915	−0.2613379
H	−6.1939585	−5.1324523	0.0217641
H	−4.9921664	−6.0386264	0.9544751
C	−5.6502174	4.4055374	1.4464082
C	−5.4158703	5.1174814	2.8004853
H	−4.6189723	5.8662385	2.7381733
H	−5.1396873	4.3976764	3.5795513
H	−6.3297914	5.6313275	3.1219873
C	−6.0510754	5.4526275	0.3792191
H	−5.2752093	6.2130015	0.2379431
H	−6.9701134	5.9689525	0.6816681
H	−6.2329524	4.9749784	−0.590187
C	−6.8201834	3.4189983	1.6171972
H	−7.7163935	3.9651254	1.9319932
H	−6.6093865	2.6631873	2.3823543
H	−7.0594015	2.9009783	0.6821421
C	4.3790574	5.6541694	−1.115147
C	3.4136194	6.8540305	−1.158728
H	2.9143933	7.0149785	−0.1968209
H	2.6408143	6.7296175	−1.9258541
H	3.9727434	7.7656355	−1.398145
C	5.4511745	5.9356483	−0.0351229
H	6.1939096	5.1325233	0.0219911
H	4.9919615	6.0385154	0.9546851
H	5.9851036	6.8668764	−0.2609559
C	5.0645455	5.5360653	−2.4974421
H	5.8008175	4.7254813	−2.5212931
H	5.5886345	6.4676484	−2.7434641
H	4.3279664	5.3422263	−3.2856142
C	5.6502154	−4.4055184	1.4464362
C	5.4158954	−5.1171285	2.8006933
H	4.6191163	−5.8660265	2.7384973
H	5.1395454	−4.3971614	3.5795493
H	6.3298744	−5.6307545	3.1223853
C	6.8202655	−3.4190194	1.6168902

H	6.6096925	−2.6631603	2.3820633
H	7.0592625	−2.9010554	0.6817491
H	7.7165315	−3.9651724	1.9314832
C	6.0509324	−5.4528975	0.3794881
H	6.2327994	−4.9755155	−0.590054
H	5.2750113	−6.2132586	0.2384491
H	6.9699535	−5.9692016	0.6820271
C	4.3941144	3.1363842	−0.727696
H	5.4646155	3.1367401	−0.910846
C	−0.664804	4.3561353	0.2441441
Zn	0.00002	0.000003	0.0721601

Table S3. Molecular geometry of **9c**.

Symbol	X	Y	Z
C	−1.260989	2.714844	0
C	−1.045663	4.121325	0
C	−2.09133	5.045078	0
C	−3.420899	4.608038	0
C	−3.641984	3.229151	0
C	−2.599382	2.266233	0
C	0.928324	3.000263	0
H	−1.847034	6.100789	0
H	−4.654469	2.857287	0
C	2.33209	2.653243	0
C	2.771402	1.332908	0
C	3.348414	3.646989	0
C	4.150348	1.090291	0
C	4.724767	3.408099	0
H	3.031709	4.674446	0
C	5.129692	2.068188	0
C	2.891743	−0.888356	0
H	6.169902	1.763306	0
C	2.599382	−2.266233	0
C	1.260989	−2.714844	0
C	3.641984	−3.229151	0
C	1.045663	−4.121325	0
C	3.420899	−4.608038	0
H	4.654469	−2.857287	0
C	2.09133	−5.045078	0

C	−0.928324	−3.000263	0
H	1.847034	−6.100789	0
C	−2.33209	−2.653243	0
C	−2.771402	−1.332908	0
C	−3.348414	−3.646989	0
C	−4.150348	−1.090291	0
C	−4.724767	−3.408099	0
H	−3.031709	−4.674446	0
C	−5.129692	−2.068188	0
C	−2.891743	0.888356	0
H	−6.169902	−1.763306	0
N	0.089525	−2.016526	0
N	2.011731	0.112718	0
N	−0.089525	2.016526	0
N	−2.011731	−0.112718	0
C	−4.33476	0.34366	0
C	−0.352488	−4.269077	0
C	4.33476	−0.34366	0
C	0.352488	4.269077	0
O	−5.387063	0.961459	0
O	5.387063	−0.961459	0
Br	1.085248	6.084184	0
Br	−1.085248	−6.084184	0
Ni	0	0	0
C	−4.622155	5.57147	0
C	5.710921	4.589093	0
C	7.174961	4.109287	0
H	7.408595	3.510699	0.888108
H	7.408595	3.510699	−0.888108
H	7.846773	4.974674	0
C	5.481742	5.453055	1.263136
H	4.466216	5.860985	1.300595
H	5.641262	4.865879	2.174839
H	6.181156	6.297795	1.276896
C	5.481742	5.453055	−1.263136
H	5.641262	4.865879	−2.174839
H	4.466216	5.860985	−1.300595
H	6.181156	6.297795	−1.276896
C	−4.180857	7.047473	0
H	−3.588822	7.297418	0.888153

H	−3.588822	7.297418	−0.888153
H	−5.063893	7.69625	0
C	−5.481742	5.321762	1.262188
H	−6.343715	6.00012	1.276919
H	−5.864685	4.296425	1.297451
H	−4.898632	5.494006	2.174311
C	−5.481742	5.321762	−1.262188
H	−5.864685	4.296425	−1.297451
H	−6.343715	6.00012	−1.276919
H	−4.898632	5.494006	−2.174311
C	−5.710921	−4.589093	0
C	−5.481742	−5.453055	1.263136
H	−6.181156	−6.297795	1.276896
H	−4.466216	−5.860985	1.300595
H	−5.641262	−4.865879	2.174839
C	−5.481742	−5.453055	−1.263136
H	−4.466216	−5.860985	−1.300595
H	−6.181156	−6.297795	−1.276896
H	−5.641262	−4.865879	−2.174839
C	−7.174961	−4.109287	0
H	−7.408595	−3.510699	0.888108
H	−7.408595	−3.510699	−0.888108
H	−7.846773	−4.974674	0
C	4.622155	−5.57147	0
C	5.481742	−5.321762	1.262188
H	6.343715	−6.00012	1.276919
H	5.864685	−4.296425	1.297451
H	4.898632	−5.494006	2.174311
C	5.481742	−5.321762	−1.262188
H	5.864685	−4.296425	−1.297451
H	6.343715	−6.00012	−1.276919
H	4.898632	−5.494006	−2.174311
C	4.180857	−7.047473	0
H	3.588822	−7.297418	0.888153
H	3.588822	−7.297418	−0.888153
H	5.063893	−7.69625	0