BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Synthesis, structural characterization, and optical properties of benzo[*f*]naphtho[2,3-*b*]phosphoindoles

Mio Matsumura, Takahiro Teramoto, Masato Kawakubo, Masatoshi Kawahata,
Yuki Murata, Kentaro Yamaguchi, Masanobu Uchiyama and Shuji Yasuike

Beilstein J. Org. Chem. **2021,** *17,* 671–677. doi:10.3762/bjoc.17.56

Further analytical and experimental data

1. General information

Melting point measurements were conducted on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and reported as uncorrected values. ^{1}H NMR (TMS: δ = 0.00 ppm as an internal standard), ^{13}C NMR ($CDCl_3$: δ = 77.0 or CD_3OD: δ = 49.0 ppm as an internal standard) and ^{31}P NMR (85% H_3PO_4: δ = 0.0 as an external standard) spectra were recorded on JEOL ECZ-400S (for ^{1}H, ^{13}C and ^{31}P NMR, 400, 100 and 161 MHz, respectively) spectrometers. Mass spectra were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 μA). IR spectra were recorded on a FTIR-8400S system from Shimadzu spectrometer and were reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. UV–vis spectra were recorded at room temperature on a HITACHI U-2800A spectrophotometer (**2**: $C = 3.0 \times 10^{-5}$, **3**: $C = 1.7 \times 10^{-5}$, **4**: $C = 2.6 \times 10^{-5}$, **5**: $C = 2.7 \times 10^{-5}$, **6**: $C = 2.7 \times 10^{-5}$ and **7**: $C = 1.8 \times 10^{-5}$ M in $CHCl_3$) and fluorescence spectra on a JASCO FP-8300 luminescence spectrometer (**2**: $C = 3.4 \times 10^{-6}$, **3**: $C = 2.2 \times 10^{-6}$, **4**: $C = 1.4 \times 10^{-6}$, **5**: $C = 2.1 \times 10^{-6}$, **6**: $C = 1.5 \times 10^{-6}$ and **7**: $C = 2.6 \times 10^{-6}$ M in $CHCl_3$). Cyclic voltammograms were recorded at room temperature on HZ-7000 systems from Hokuto Denko (Pt lod as working electrode; in dichlorobenzene solution (≈1.0 mM) with 0.1 M NBu_4ClO_4 as supporting electrolyte; scan rate 100 $m \cdot Vs^{-1}$; potentials are referred to an Ag/AgCl/KCl 1 M electrode). All chromatographic separations were accomplished with Silica Gel 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed using Macherey-Nagel precoated TLC plates Sil G25 UV_{254}.

2. Preparation and characterization of phospholes

6-Phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindoles **2**

A solution of *n*-BuLi (1.63 M in hexane, 1.5 mL, 2.4 mmol, 2.4 equiv) was added dropwise to a solution of 3,3′-dibromo-2,2′-binaphthyl (**1**, 412 mg, 1 mmol) in dry THF (16 mL) at −78 °C under Ar atmosphere. After 10 min, to the reaction mixture, dichlorophenylphosphine (0.32 mL, 2.4 mmol, 2.4 equiv) was added, and the resulting mixture was stirred for 1 h. The reaction mixture was diluted with

CH_2Cl_2 (30 mL) and water (30 mL) at 0 °C. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was washed with water (30 mL × 3), dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using *n*-hexane/CH_2Cl_2 4:1 as eluent to give **2** as colorless prisms (189 mg, 52%). mp 214-216 °C (CH_2Cl_2/*n*-hexane). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.54 (s, 2H, Ar-H), 8.20 (d, $J = 5.9$ Hz, 2H, Ar-H), 7.98 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.83 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.54-7.46 (m, 4H, Ar-H), 7.36 (t, $J = 7.8$ Hz, 2H, Ar-H), 7.21 (d, $J = 7.3$ Hz, 3H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1 (C, s), 140.6 (C, d, $J_{C,P} = 4.1$ Hz), 138.3 (C, d, $J_{C,P} = 21.5$ Hz), 133.8 (C), 133.6 (C, d, $J_{C,P} = 8.2$ Hz), 132.6 (CH, d, $J_{C,P} = 19.9$ Hz), 130.8 (CH, d, $J_{C,P} = 24.0$ Hz), 129.2 (CH), 128.6 (CH, d, $J_{C,P} = 7.4$ Hz), 128.4 (CH), 128.0 (CH), 126.6 (CH), 126.1 (CH), 120.2 (CH). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ: −13.27 (s). FTIR (KBr): 3053, 1431, 874, 741 cm^{-1}. LRMS (EI) *m/z*: 360 ($[M]^+$). HRMS: *m/z* $[M]^+$ calcd for $C_{26}H_{17}P$: 360.1068. Found: 360.1052.

6-Phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindole oxide (**3**) [1]

To a solution of 6-phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindole (**2**, 180 mg, 0.5 mmol) in dry CH_2Cl_2 (5 mL), hydrogen peroxide (30% solution in water, 0.6 mL, 5.9 mmol, 12 equiv) was added, and this was stirred at 0 °C under air. After 30 min, the mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and water (15 mL). The aqueous phase was extracted with CH_2Cl_2 (10 mL × 2). The combined extracts were washed with water (10 mL × 2) and brine (10 mL × 2), dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by recrystallization to give **3** as colorless plates (173 mg, 92%). mp > 300 °C (CH_2Cl_2/*n*-hexane), (Lit. 325 °C [1]). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.40 (d, $J =$ 2.4 Hz, 2H, Ar-H), 8.27 (d, $J = 11.2$ Hz, 2H, Ar-H), 7.93 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.81 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.71 (dd, $J = 7.8, 13.1$ Hz, 2H, Ar-H), 7.54 (t, $J = 7.8$ Hz, 2H, Ar-H), 7.47 (t, $J = 7.8$ Hz, 3H, Ar-H), 7.38 (td, $J = 2.4, 7.3$ Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.5 (C, d, $J_{C,P} =$

20.7 Hz), 136.0 (C, d, $J_{C,P}$ = 1.7 Hz), 133.6 (C, d, $J_{C,P}$ = 12.4 Hz), 132.1 (C, d, $J_{C,P}$ = 105.9 Hz), 132.0 (CH, d, $J_{C,P}$ = 2.5 Hz), 131.7 (CH, d, $J_{C,P}$ = 9.9 Hz), 131.1 (CH, d, $J_{C,P}$ = 10.7 Hz), 131.0 (C), 129.2 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH, d, $J_{C,P}$ = 2.5 Hz), 127.0 (CH), 120.3 (CH, d, $J_{C,P}$ = 9.1 Hz). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ: 32.29 (s). FTIR (KBr): 3032, 1194, 748, 731, 542 cm^{-1}. LRMS (EI) *m/z*: 376 ([M]$^+$). HRMS: *m/z* [M]$^+$ calcd for $C_{26}H_{17}P$: 376.1017. Found: 376.1019.

6-Phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindole sulfide (**4**)

To a solution of 6-phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindole (**2**, 125 mg, 0.35 mmol) in dry toluene (2 mL), element sulfur (55 mg, 1.7 mmol, 5 equiv) was added and stirred at 60 °C under air. After 1.5 h, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and water (10 mL). The aqueous phase was extracted with CH_2Cl_2 (10 mL × 2). The combined extracts were washed with water (10 mL × 2), dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using *n*-hexane/CH_2Cl_2 1:1 as eluent to give **4** as pale yellow plates (119 mg, 88%). mp 298-300 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (d, *J* = 3.2 Hz, 2H, Ar-H), 8.27 (d, *J* = 12.8 Hz, 2H, Ar-H), 7.95 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.81 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.76 (ddd, *J* = 1.4, 8.0, 14.6 Hz, 2H, Ar-H), 7.56 (td, *J* = 0.9, 8.2 Hz, 2H, Ar-H), 7.47 (td, *J* = 0.9, 8.2 Hz, 2H, Ar-H), 7.41 (td, *J* = 2.3, 7.3 Hz, 1H, Ar-H), 7.33 (td, *J* = 3.2, 7.8 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3 (C, d, $J_{C,P}$ = 18.3 Hz), 135.6 (C), 134.1 (C, d, $J_{C,P}$ = 90.5 Hz), 133.8 (C, d, $J_{C,P}$ = 12.5 Hz), 132.7 (C, d, $J_{C,P}$ = 81.7 Hz), 131.7 (CH, d, $J_{C,P}$ = 3.0 Hz), 131.2 (CH, d, $J_{C,P}$ = 10.6 Hz), 131.0 (CH, d, $J_{C,P}$ = 11.6 Hz), 129.0 (CH), 128.52 (CH), 128.51 (CH, d, $J_{C,P}$ = 13.5 Hz), 128.4 (CH), 127.0 (CH), 120.5 (CH, d, $J_{C,P}$ = 9.6 Hz). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ: 39.27 (s). FTIR (KBr): 3055, 1508, 1497, 1437, 883, 744 cm^{-1}. LRMS (EI) *m/z*: 393.05 ([M+H]$^+$). HRMS: *m/z* [M]$^+$ calcd for $C_{26}H_{17}PS$: 392.0789. Found: 392.0792.

6-Methyl-6-phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindorium trifluoromethansulfonate (**5**)

To a solution of 6-phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindole (**2**, 126 mg, 0.35 mmol) in dry CH_2Cl_2 (10 mL), methyl trifluoromethanesulfonate (47 µL, 0.43 mmol, 1.2 equiv) was added and stirred at room temperature. After 2 h, the reaction mixture was concentrated under reduced pressure. The residue was washed with *n*-hexane and purified by recrystallization from a toluene/methanol mixture to give **5** as colorless plates (149 mg, 81%). mp 295-297 °C (toluene/methanol). ^{1}H NMR (400 MHz, CD_3OD) δ: 8.90 (d, J = 2.7 Hz, 2H, Ar-H), 8.81 (d, J = 12.4 Hz, 2H, Ar-H), 8.18 (d, J = 8.3 Hz, 2H, Ar-H), 8.07 (d, J = 7.8 Hz, 2H, Ar-H), 7.94 (dd, J = 7.3, 14.2 Hz, 2H, Ar-H), 7.83-7.78 (m, 3H, Ar-H), 7.73-7.68 (m, 4H, Ar-H), 2.99 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.7 (C, d, $J_{C,P}$ = 18.3 Hz), 138.4 (C), 136.4 (CH, d, $J_{C,P}$ = 2.9 Hz), 136.0 (CH, d, $J_{C,P}$ = 10.6 Hz), 135.1 (C, d, $J_{C,P}$ = 13.4 Hz), 133.3 (CH, d, $J_{C,P}$ = 11.5 Hz), 131.7 (CH), 131.6 (CH, d, $J_{C,P}$ = 13.5 Hz), 130.5 (CH), 130.2 (CH), 129.5 (CH), 123.9 (CH, d, $J_{C,P}$ = 8.7 Hz), 121.5 (C, d, $J_{C,P}$ = 87.1 Hz), 121.4 (C, d, $J_{C,P}$ = 94.4 Hz), 8.2 (CH_3, d, $J_{C,P}$ = 53.0 Hz). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ: 22.79 (s). FTIR (KBr): 3061, 2914, 1282, 1253, 1030, 637 cm^{-1}. LRMS (EI) *m/z*: 375.15 ([M-OTf]$^+$). HRMS: *m/z* [M]$^+$ calcd for $C_{27}H_{20}P$: 375.1303. Found: 375.1300.

6-Phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindole borane complex **6**

To a solution of 6-phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindole (**2**, 126 mg, 0.35 mmol) in dry THF (5 mL), borane THF complex (1.0 M in THF solution, 0.7 mL, 0.7 mmol, 2 equiv) was added at 0 °C and stirred. After 15 min, the reaction mixture was stirred at room temperature for 3 h. Then, the reaction mixture was concentrated under reduced pressure. The residue was concentrated under reduced pressure and purified by column chromatography using *n*-hexane/CH_2Cl_2 1:1 as eluent to give **6** as a colorless plates (120 mg, 91%). mp 294-296 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (s, 2H, Ar-H), 8.25 (d, J = 9.7 Hz, 2H, Ar-H), 7.96 (d, J = 7.8 Hz, 2H, Ar-H), 7.83 (d, J = 7.8 Hz, 2H, Ar-H), 7.65-7.55 (m, 4H, Ar-H), 7.50 (td, J = 1.3, 7.3 Hz, 2H, Ar-H), 7.41 (td, J = 2.3, 7.3 Hz, 1H, Ar-H), 7.32 (td, J = 2.3, 7.3 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.3 (C, d, $J_{C,P}$ = 9.6 Hz), 135.2 (C), 133.6 (C, d, $J_{C,P}$ = 11.5 Hz), 130.9(C), 132.2 (CH, d, $J_{C,P}$ = 10.6 Hz), 132.0 (CH, d, $J_{C,P}$ = 12.5 Hz), 131.6 (CH, d, $J_{C,P}$ = 3.9 Hz), 129.8 (C, d, $J_{C,P}$ = 51.0 Hz), 128.9 (CH, d, $J_{C,P}$ = 10.5 Hz), 128.6 (CH), 128.5 (CH), 128.2 (CH), 126.9 (CH), 120.8 (CH, d, $J_{C,P}$ = 5.8 Hz). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ: 22.53 (s). FTIR (KBr): 3055, 2376, 1055, 881, 741 cm^{-1}. Anal. Calc. for $C_{26}H_{20}BP$: C, 83.45; H, 5.39. Found: C, 83.47; H, 1.47.

6-Phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindole–gold(I) chloride complex **7**

To a solution of chloro(dimethyl sulfide)gold(I) (87 mg, 0.3 mmol) in dry CH_2Cl_2 (6 mL), 6-phenyl-6*H*-benzo[*f*]naphtho[2,3-*b*]phosphoindole (**2**, 127 mg, 0.35 mmol, 1.1 equiv) was added and stirred at room temperature. After 3 h, the reaction mixture was concentrated under reduced pressure. The residue was washed with *n*-hexane and acetone and purified by recrystallization to give **7** as colorless powder (81 mg, 39%). mp 283-286 °C ($CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (s, 2H, Ar-H), 8.22 (d, J = 11.9 Hz, 2H, Ar-H), 7.98 (d, J = 8.3 Hz, 2H, Ar-H), 7.82 (d, J = 8.3 Hz, 2H, Ar-H), 7.62-7.50 (m, 6H, Ar-H), 7.44 (t, J = 7.3 Hz, 1H, Ar-H), 7.34 (t, J = 7.3 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8 (C, d, $J_{C,P}$ = 9.5 Hz), 135.2 (C), 133.7 (CH, d, $J_{C,P}$ = 15.4 Hz), 133.4 (C, d, $J_{C,P}$ = 13.5 Hz), 133.1 (CH, d, $J_{C,P}$ = 14.4 Hz), 132.4 (CH), 130.4 (C, d, $J_{C,P}$ = 67.4 Hz), 129.4 (CH, d, $J_{C,P}$ = 12.5 Hz), 128.72 (CH), 128.68 (CH), 128.5 (CH), 127.3 (CH), 121.0 (CH, d, $J_{C,P}$ = 6.7 Hz). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ: 23.46 (s). FTIR (KBr): 3050, 1497, 1435, 883, 742 cm^{-1}. LRMS (EI) *m/z*: 598.15 ([M+Li]$^{+}$). HRMS: *m/z* [M]$^{+}$ calcd for $C_{26}H_{17}AuClP$: 592.0422. Found: 592.0422.

3. Single crystal X-ray diffraction experiment

Crystals were immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. The diffraction experiment was performed on a Bruker D8 VENTURE system (Cu Kα: $\lambda = 1.54178$ Å). Absorption correction was performed by an empirical method implemented in SADABS [2]. Structure solution and refinement were performed by using SHELXT-2014/5 [3] and SHELXL-2014/7 [4].

Crystal data and structure refinement for 2

The colorless plate crystal ($0.200 \times 0.050 \times 0.020$ mm^3) was obtained from dichloromethane/hexane. $C_{26}H_{17}P$, $M\mathrm{r} = 451.14$; monoclinic, space group $P2_1/\mathrm{n}$, $Z = 4$, $D_{\mathrm{calc}} = 1.341$ g·cm^{-3}, $a = 12.2188(7)$, $b = 8.1128(5)$, $c = 18.0118(10)$ Å, $\beta = 91.876(2)°$, $V = 1784.53(18)$ Å^3, 23358 measured and 3789 independent [$I > 2\sigma(I)$] reflections, 244 parameters, final $R_1 = 0.0347$, $wR_2 = 0.0919$, $S = 1.049$ [$I > 2\sigma(I)$]. CCDC 2051842.

All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 43) with U_{iso} values constrained to 1.2 U_{eq} of the parent atoms.

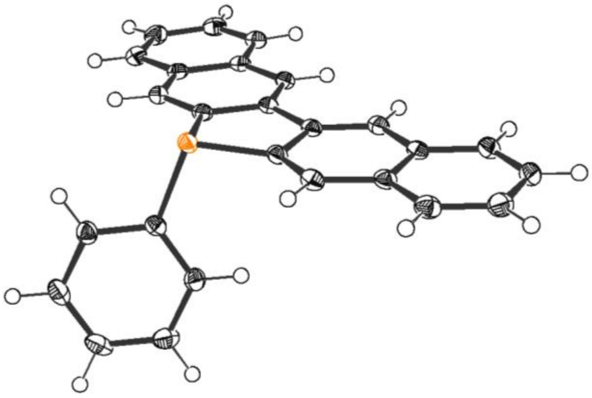

Figure S1: Ortep drawing of **2** (50% probability).

Crystal data and structure refinement for *N*-phenyldibenzo[*b,h*]carbazole

The colorless plate crystal (0.120 × 0.100 × 0.070 mm^3) wasobtained from dichloromethane/hexane. $C_{26}H_{17}N$, *M*r = 343.40; monoclinic, space group $P2_1/n$, $Z = 8$, $D_{calc} = 1.335$ g·cm^{-3}, $a = 9.7796(4)$, $b = 19.3772(9)$, $c = 18.4168(8)$ Å, $\beta = 101.827(2)°$, $V = 3415.9(3)$ Å^3, 45118 measured and 6725 independent [$I > 2\sigma(I)$] reflections, 487parameters, final $R_1 = 0.0356$, $wR_2 = 0.0920$, $S = 1.022$ [$I > 2\sigma(I)$]. CCDC 2051843

All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 43) with U_{iso} values constrained to 1.2 U_{eq} of the parent atoms.

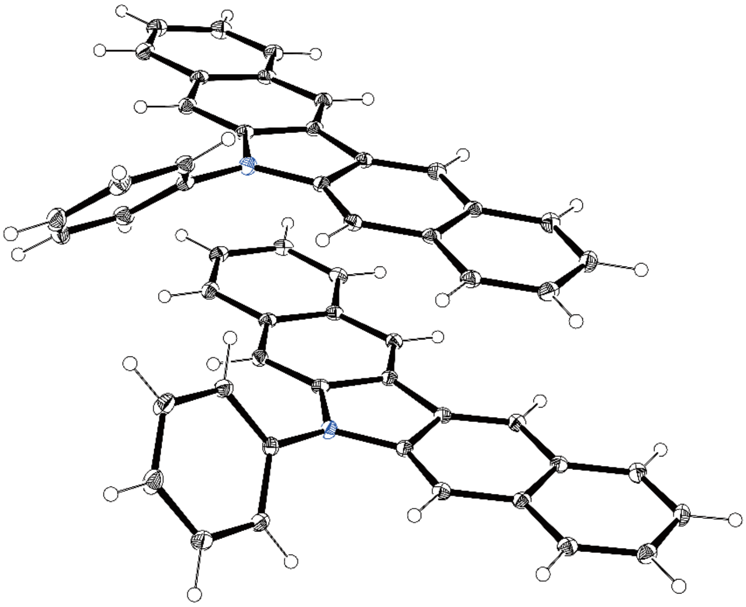

Figure S2: Ortep drawing of *N*-phenyldibenzo[*b*,*h*]carbazole (50% probability).

4. Fluorescence spectra of all product

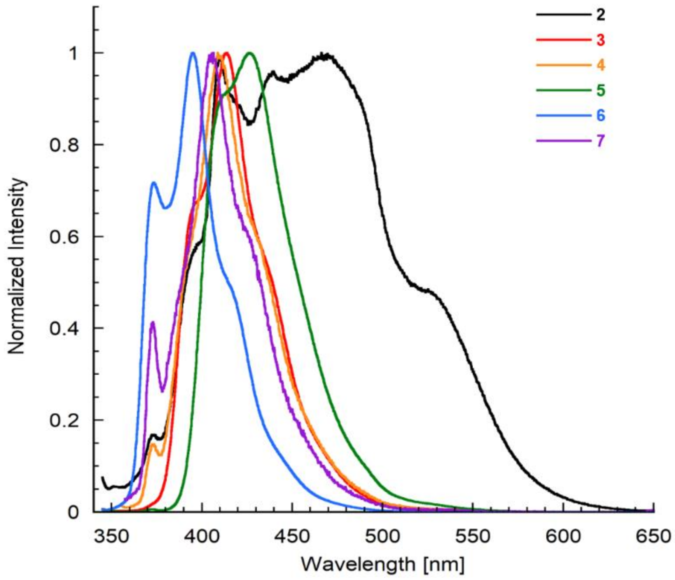

Figure S3: Normalized fluorescence spectra in $CHCl_3$ (excited at 335 nm).

5. Cyclic voltammograms of all products

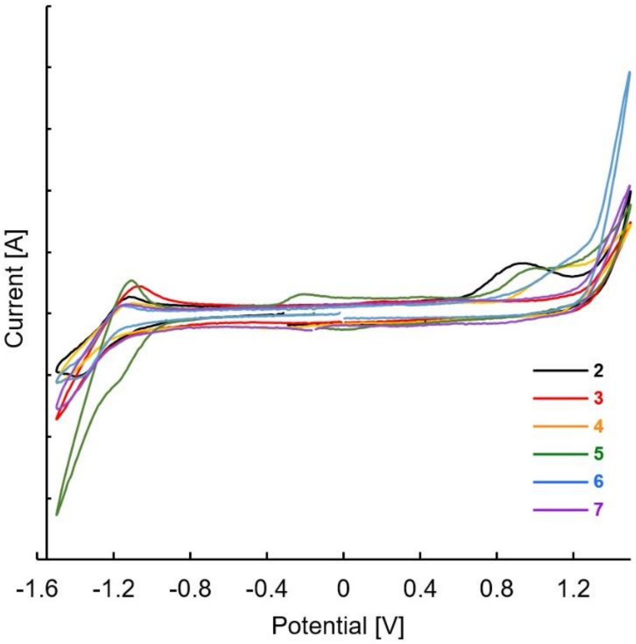

Figure S4: Cyclic voltammograms in DCB.

6. Computational details

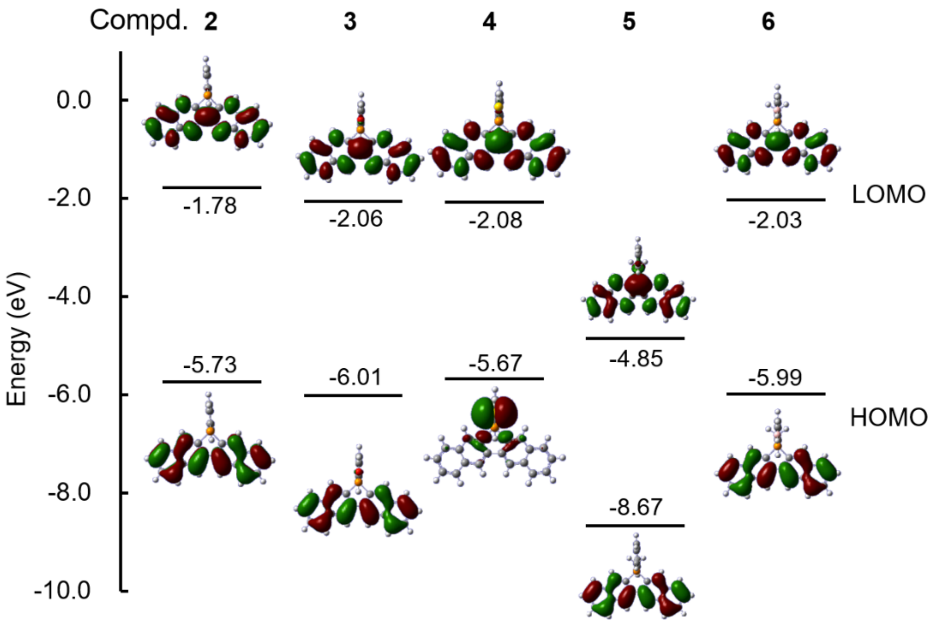

Figure S5: The spatial plots and energy levels of the HOMO and LUMO of selected compounds. The calculations were performed at the level of B3LYP/LanL2DZ.

Table S1: Excitation energies and oscillator strengths calculated by the TDDFT method.

compound	state	wavelength (nm)	oscillator strength	excitation	weight
2	1	346.19	0.0095	HUMO−1 >> LUMO	88%
	2	339.15	0.1999	HOMO >> LUMO	93%
	3	320.47	0.0061	HOMO−2 >> LUMO	50%
3	1	344.05	0.0573	HOMO >> LUMO	78%
	2	331.45	0.0496	HOMO−2 >> LUMO	43%
				HOMO >> LUMO+1	35%
	3	318.67	0.0027	HUMO−1 >> LUMO	73%
4	1	410.40	0.0031	HOMO >> LUMO	96%
	2	406.67	0.0009	HUMO−1 >> LUMO	97%
	3	370.11	0.0026	HOMO >> LUMO+1	93%
5	1	372.27	0.0073	HOMO >> LUMO	94%
	2	337.46	0.2071	HOMO >> LUMO+1	66%
	3	328.91	0.0006	HOMO >> LUMO+2	99%
6	1	340.50	0.1423	HOMO >> LUMO	90%
	2	323.80	0.0058	HUMO−1 >> LUMO	72%
	3	323.01	0.0530	HOMO >> LUMO+1	52%

All calculations were performed at the DFT level, by means of the B3LYP functional as implemented in Gaussian 16. [5] The LanL2DZ basis sets were used. The X-ray structure of **2** was used as initial structures for geometry optimization calculations.

Cartesian coordinates and energies of **2**
E(B3LYP) = -1007.24434090 A.U.

C	-1.31196	0.14151	-0.82171
C	-0.75174	-1.04601	-0.22337
C	-1.59821	-2.02864	0.27908
H	-1.19207	-2.93271	0.72865
C	-3.01639	-1.87241	0.21968
C	-3.90923	-2.86582	0.73456
H	-3.49252	-3.76549	1.18317
C	-5.28518	-2.69068	0.66595
H	-5.95419	-3.45162	1.06032
C	-5.83266	-1.50993	0.07679
H	-6.91167	-1.38545	0.02934
C	-4.99151	-0.52844	-0.43226
H	-5.40692	0.37116	-0.88195
C	-3.57077	-0.68015	-0.37625
C	-2.68187	0.3127	-0.90043
H	-3.10673	1.20366	-1.35873
C	1.30845	0.11846	-0.81928
C	0.7265	-1.05844	-0.22114
C	1.55471	-2.05451	0.28511
H	1.13216	-2.95109	0.73458
C	2.97548	-1.92219	0.22985
C	3.8499	-2.92963	0.74901
H	3.41672	-3.82144	1.19775
C	5.22881	-2.77776	0.68449
H	5.88375	-3.54915	1.08216
C	5.79777	-1.60726	0.09529
H	6.87886	-1.50086	0.05115
C	4.97477	-0.61258	-0.41785
H	5.40665	0.27931	-0.86739
C	3.55154	-0.74032	-0.36612
C	2.68104	0.26659	-0.89446
H	3.12229	1.14982	-1.35232
P	0.00777	1.30098	-1.50598
C	0.02263	2.69942	-0.21806
C	0.15042	4.02101	-0.69675
C	-0.08398	2.47719	1.17241
C	0.17577	5.108	0.20111
H	0.22822	4.20146	-1.76698
C	-0.06043	3.56054	2.06878
H	-0.18744	1.46458	1.55455
C	0.07047	4.87884	1.58504
H	0.27497	6.12207	-0.17934
H	-0.14328	3.37878	3.13791
H	0.08861	5.71539	2.27997

Cartesian coordinates and energies of **3**

E(B3LYP) = -1082.44015671 A.U.

C	1.32260	0.06677	0.62261
C	0.74251	-1.13659	0.08597
C	1.57903	-2.15499	-0.35249
H	1.16719	-3.07468	-0.76258
C	3.00000	-2.02028	-0.26681
C	3.88220	-3.05566	-0.71020
H	3.45775	-3.96707	-1.12619
C	5.25975	-2.90632	-0.61186
H	5.92109	-3.69968	-0.95115
C	5.81928	-1.71230	-0.06378
H	6.89905	-1.61032	0.00829
C	4.98808	-0.68924	0.37542
H	5.41139	0.22073	0.79529
C	3.56743	-0.81361	0.28607
C	2.68807	0.22625	0.72941
H	3.11182	1.13527	1.15106
C	-1.32274	0.06704	0.62248
C	-0.74286	-1.13646	0.08594
C	-1.57955	-2.15473	-0.35247
H	-1.16788	-3.07454	-0.76247
C	-3.00050	-2.01974	-0.26684
C	-3.88287	-3.05500	-0.71018
H	-3.45858	-3.96652	-1.12609
C	-5.26040	-2.90540	-0.61189
H	-5.92187	-3.69866	-0.95114
C	-5.81973	-1.71124	-0.06391
H	-6.89948	-1.60906	0.00812
C	-4.98835	-0.68830	0.37525
H	-5.41151	0.22178	0.79504
C	-3.56773	-0.81293	0.28594
C	-2.68819	0.22679	0.72924
H	-3.11176	1.13591	1.15083
C	0.00035	2.70479	-0.04251
C	0.00066	4.00131	0.50730
C	0.00030	2.52160	-1.43942
C	0.00098	5.12056	-0.34688
H	0.00064	4.11149	1.58922
C	0.00063	3.64264	-2.28939
H	0.00003	1.52065	-1.86610
C	0.00097	4.94233	-1.74353
H	0.00123	6.12303	0.07417
H	0.00060	3.50482	-3.36791
H	0.00122	5.80753	-2.40266
P	0.00001	1.27109	1.15758
O	-0.00009	1.82117	2.67247

Cartesian coordinates and energies of **4**

E(B3LYP) = -1017.36608899 A.U.

C	1.32263	0.02299	0.51108
C	0.74109	-1.20626	0.03709
C	1.57899	-2.24436	-0.35090
H	1.16666	-3.18450	-0.71111
C	2.99953	-2.10258	-0.27983
C	3.88223	-3.15718	-0.67457
H	3.45810	-4.08981	-1.04083
C	5.25975	-2.99937	-0.59192
H	5.92149	-3.80729	-0.89395
C	5.81884	-1.77735	-0.10852
H	6.89868	-1.66915	-0.04761
C	4.98745	-0.73533	0.28282

H	5.41038	0.19572	0.65381
C	3.56652	-0.86767	0.20765
C	2.68772	0.19097	0.60433
H	3.10979	1.11855	0.98462
C	-1.32291	0.02351	0.51077
C	-0.74176	-1.20599	0.03697
C	-1.57999	-2.24384	-0.35097
H	-1.16796	-3.18419	-0.71097
C	-3.00049	-2.10154	-0.28008
C	-3.88352	-3.15587	-0.67479
H	-3.45968	-4.08870	-1.04089
C	-5.26099	-2.99756	-0.59231
H	-5.92299	-3.80528	-0.89430
C	-5.81970	-1.77528	-0.10912
H	-6.89950	-1.66669	-0.04833
C	-4.98798	-0.73351	0.28219
H	-5.41062	0.19774	0.65303

C	-3.56709	-0.86637	0.20719
C	-2.68795	0.19200	0.60386
H	-3.10971	1.11976	0.98404
C	0.00078	2.59830	-0.33519
C	0.00144	3.94684	0.06298
C	0.00075	2.25861	-1.70420
C	0.00210	4.96272	-0.91273
H	0.00138	4.18624	1.12388
C	0.00140	3.27631	-2.67483
H	0.00022	1.21681	-2.01665
C	0.00209	4.62969	-2.28032
H	0.00262	6.00539	-0.60472
H	0.00136	3.01607	-3.73048
H	0.00260	5.41495	-3.03275
P	0.00002	1.25528	0.97828
S	-0.00055	2.03774	2.94620

Cartesian coordinates and energies of **5**

E(B3LYP) = -1046.94604757 A.U.

C	1.33079	0.04276	0.50773
C	0.74013	-1.20800	0.09558
C	1.58399	-2.25100	-0.26059
H	1.17562	-3.20789	-0.57636
C	3.00509	-2.09313	-0.22507
C	3.88491	-3.15883	-0.58941
H	3.46317	-4.11272	-0.89653
C	5.26249	-2.98231	-0.55297
H	5.92390	-3.79800	-0.83117
C	5.82340	-1.73201	-0.15149
H	6.90285	-1.61293	-0.12969
C	4.99533	-0.67652	0.20859
H	5.42250	0.27569	0.51437
C	3.57520	-0.82909	0.18210
C	2.69785	0.23941	0.54977

H	3.12942	1.19213	0.84960
C	-1.33455	0.04195	0.50492
C	-0.74229	-1.20835	0.09378
C	-1.58472	-2.25177	-0.26450
H	-1.17511	-3.20844	-0.57933
C	-3.00597	-2.09465	-0.23235
C	-3.88435	-3.16074	-0.59903
H	-3.46137	-4.11436	-0.90529
C	-5.26210	-2.98491	-0.56601
H	-5.92242	-3.80085	-0.84601
C	-5.82458	-1.73492	-0.16576
H	-6.90413	-1.61633	-0.14671
C	-4.99791	-0.67910	0.19655
H	-5.42631	0.27289	0.50130
C	-3.57767	-0.83099	0.17364

C	-2.70172	0.23793	0.54356
H	-3.13464	1.19045	0.84214
C	0.00331	2.80080	-0.03990
C	-0.04558	4.05936	0.59560
C	0.05399	2.70763	-1.44861
C	-0.04379	5.22991	-0.18568
H	-0.08411	4.14704	1.67785
C	0.05519	3.88201	-2.21909
H	0.09316	1.73951	-1.94225
C	0.00621	5.14254	-1.58939
H	-0.08102	6.20084	0.29967
H	0.09429	3.81569	-3.30245
H	0.00748	6.04830	-2.18930
P	-0.00232	1.23814	0.95179
C	-0.00689	1.64092	2.77069
H	0.88238	2.22260	3.03092
H	-0.90900	2.20209	3.03175
H	0.00341	0.69870	3.32467

Cartesian coordinates and energies of **6**

E(B3LYP) = -1033.88327825 A.U.

C	1.31875	0.07644	0.63498
C	0.74064	-1.13180	0.10231
C	1.57887	-2.14960	-0.33677
H	1.16637	-3.07256	-0.73890
C	2.99907	-2.00869	-0.26558
C	3.88248	-3.04179	-0.71302
H	3.45847	-3.95764	-1.11965
C	5.25991	-2.88444	-0.63041
H	5.92210	-3.67584	-0.97258
C	5.81831	-1.68411	-0.09431
H	6.89820	-1.57565	-0.03409
C	4.98632	-0.66347	0.34860
H	5.40915	0.25079	0.75945
C	3.56519	-0.79594	0.27511
C	2.68587	0.24050	0.72670
H	3.11331	1.14959	1.14364
C	-1.31874	0.07646	0.63493
C	-0.74065	-1.13179	0.10229
C	-1.57888	-2.14958	-0.33680
H	-1.16640	-3.07255	-0.73891
C	-2.99908	-2.00864	-0.26564
C	-3.88251	-3.04172	-0.71310
H	-3.45851	-3.95758	-1.11972
C	-5.25994	-2.88434	-0.63051
H	-5.92213	-3.67573	-0.97269
C	-5.81832	-1.68400	-0.09443
H	-6.89821	-1.57552	-0.03422
C	-4.98632	-0.66338	0.34850
H	-5.40913	0.25090	0.75934
C	-3.56519	-0.79587	0.27503
C	-2.68586	0.24055	0.72663
H	-3.11328	1.14965	1.14358
C	0.00005	2.67554	-0.07126
C	0.00019	4.00360	0.40174
C	0.00000	2.42170	-1.45955
C	0.00026	5.07472	-0.51348
H	0.00019	4.19494	1.47110
C	0.00009	3.49329	-2.36958
H	-0.00012	1.39973	-1.83143
C	0.00021	4.82190	-1.89762
H	0.00035	6.09773	-0.14540
H	0.00004	3.29452	-3.43854
H	0.00027	5.64955	-2.60312
P	0.00000	1.27837	1.18319
H	1.01196	2.55823	3.19734
H	-1.01362	2.55763	3.19652

H	-0.00047	0.89273	3.75319	B	-0.00059	1.90165	3.09371

7. Refereneces

1. Baba, K.; Tobisu, M.; Chatani, N. Chatani, *Org. Lett.*, **2014**, *17*, 70–73.

2. Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

3. Sheldrick, G. M. *Acta. Cryst.* **2015**, *A71*, 3-8.

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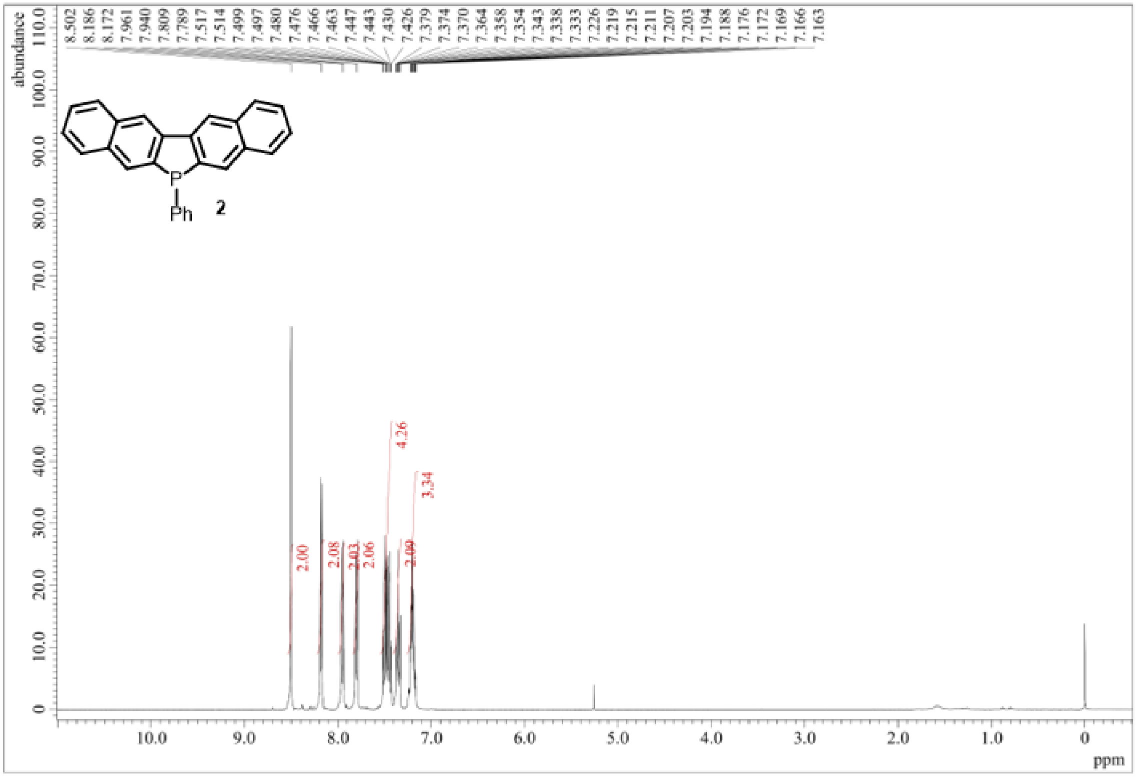
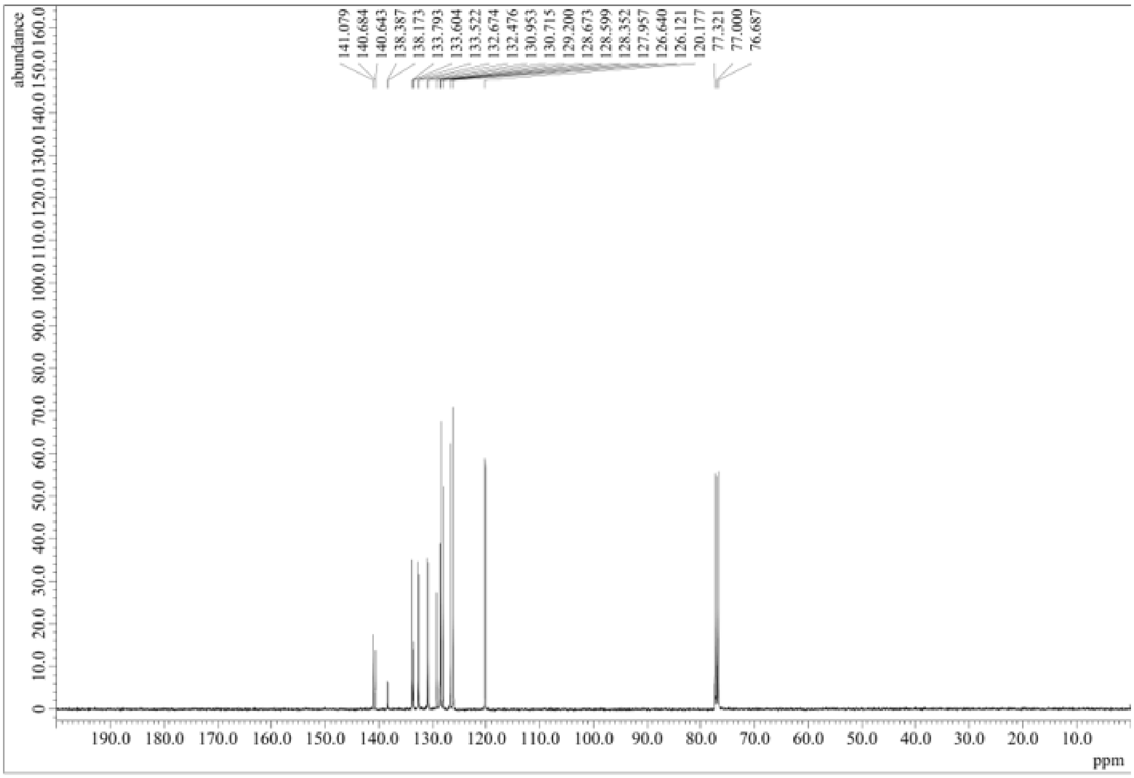
5. Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

8. NMR spectra of products

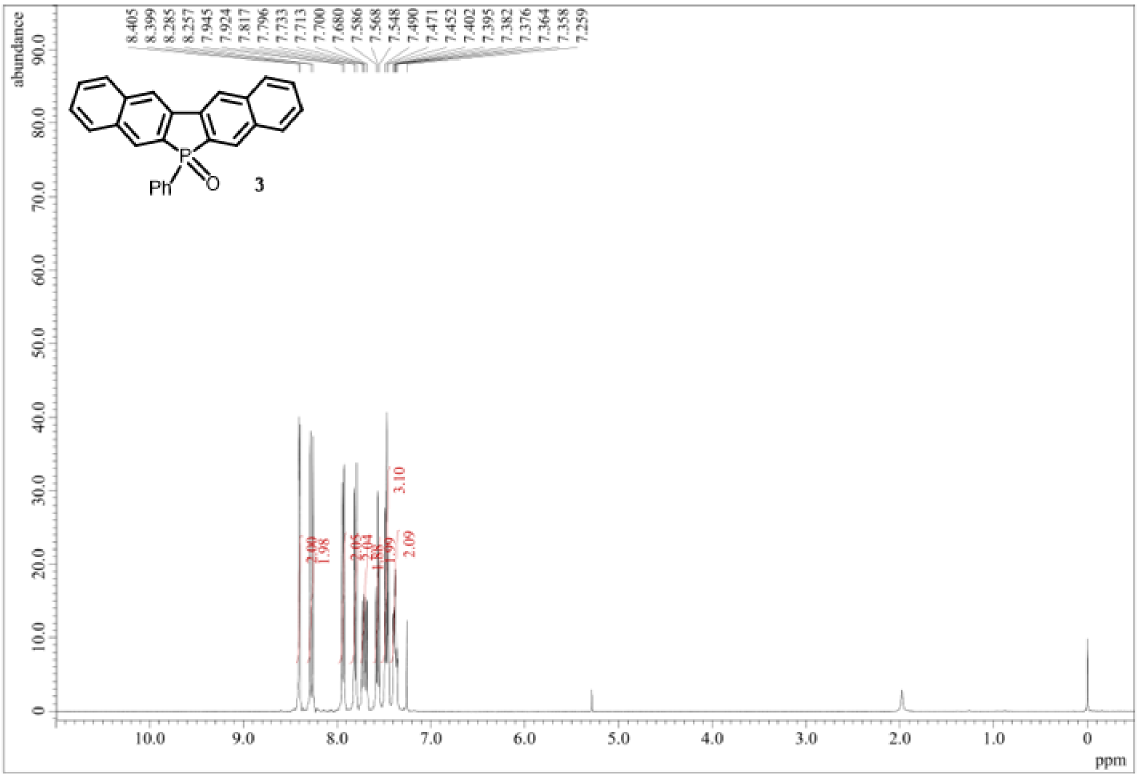
^{1}H NMR spectrum of **2**



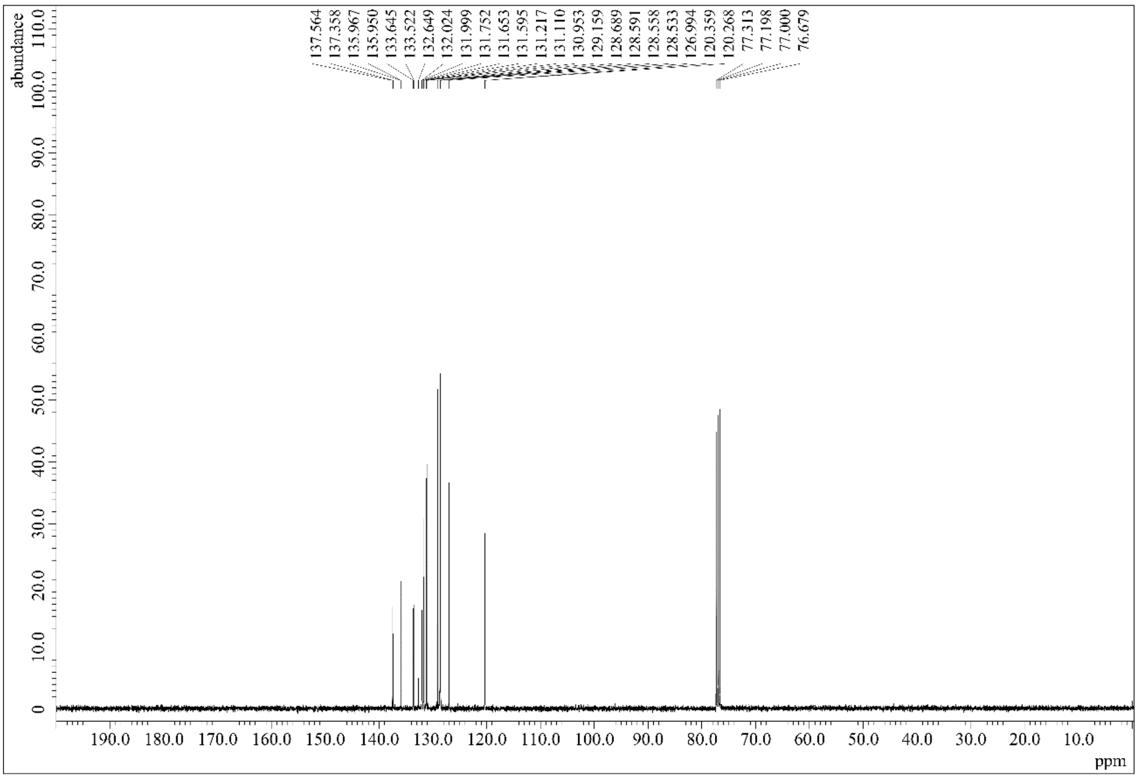
^{13}C NMR spectrum of **2**



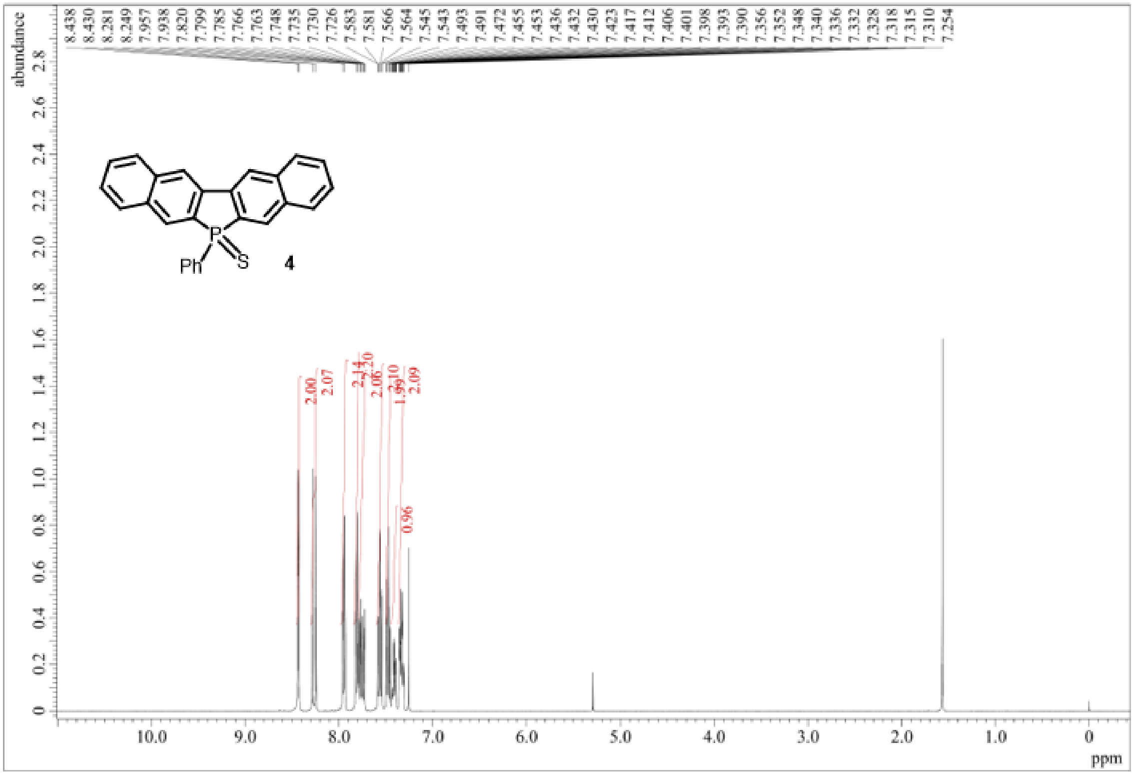
^{1}H NMR spectrum of **3**



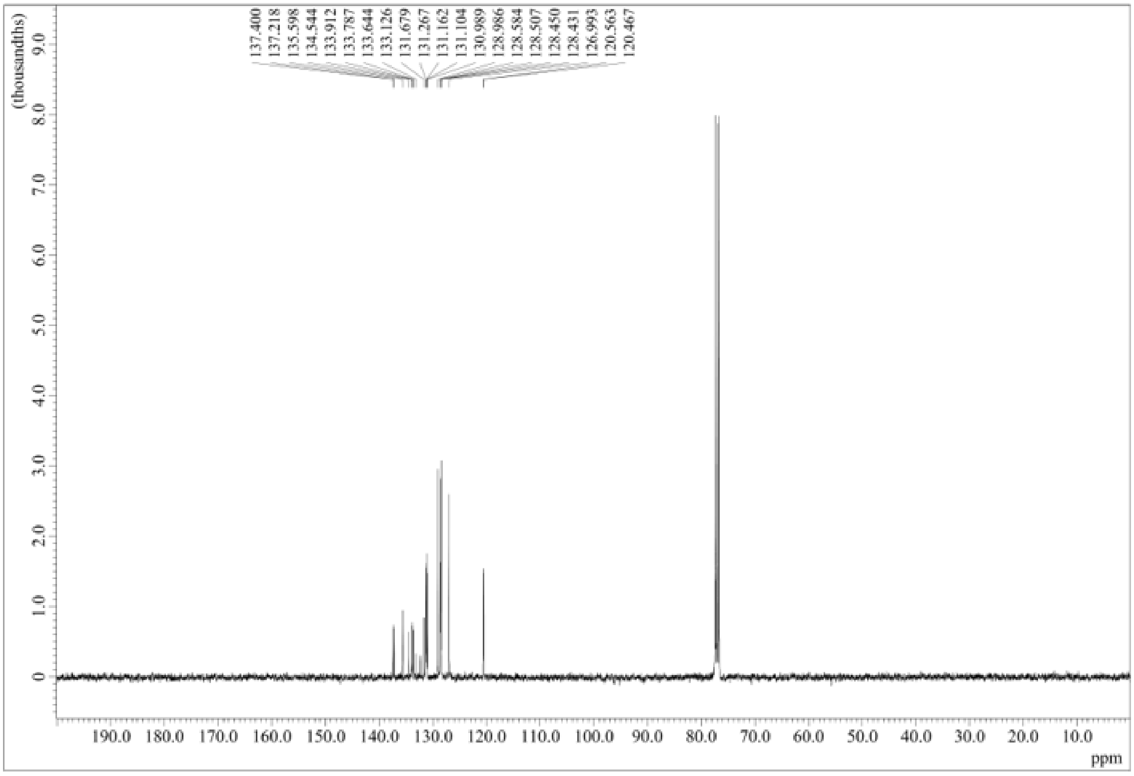
^{13}C NMR spectrum of **3**



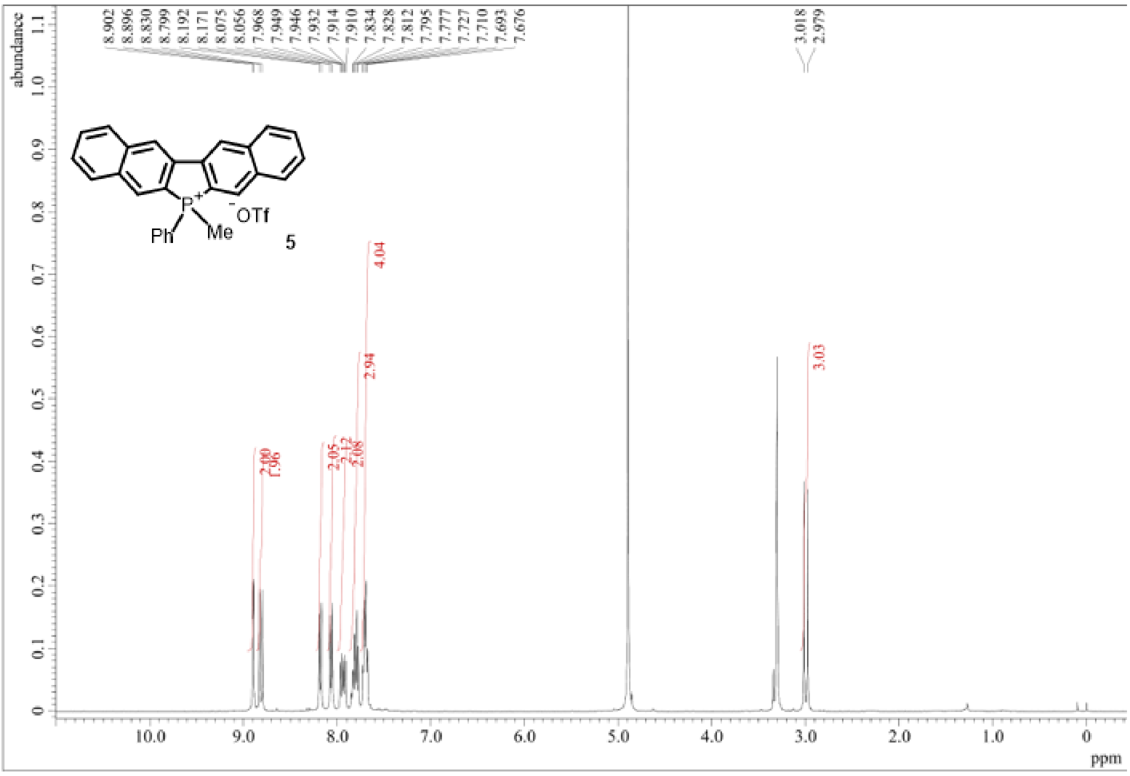
^{1}H NMR spectrum of **4**



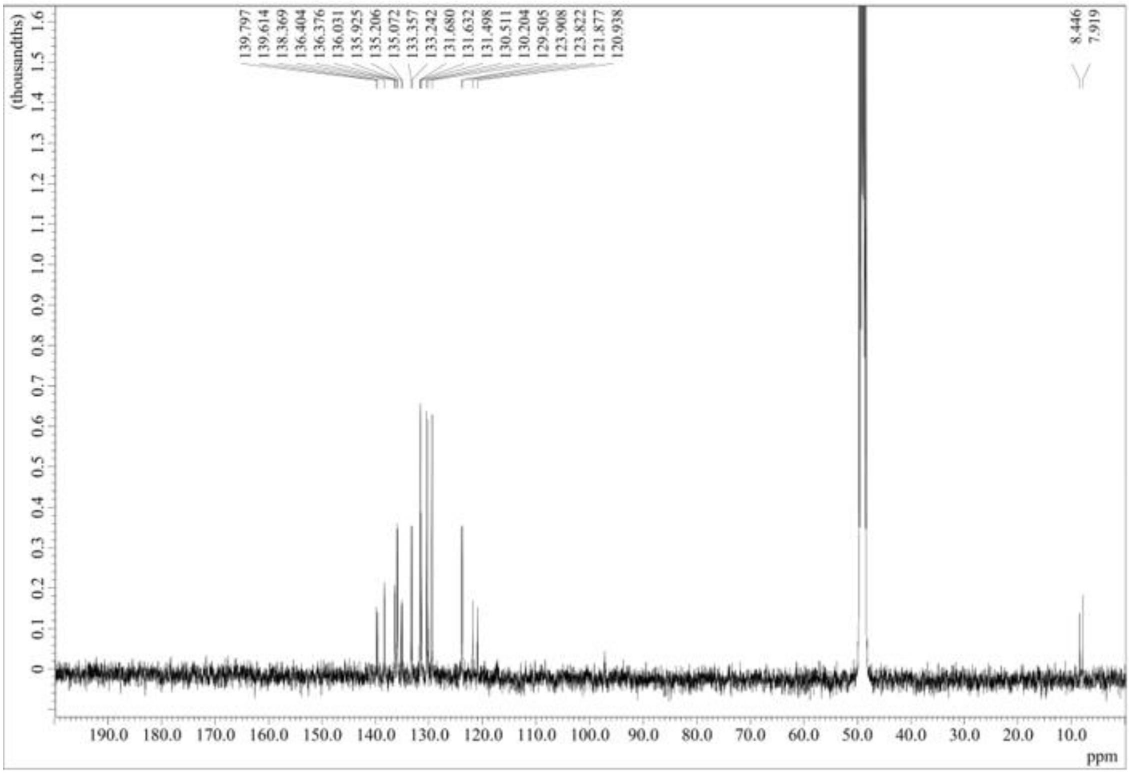
^{13}C NMR spectrum of **4**



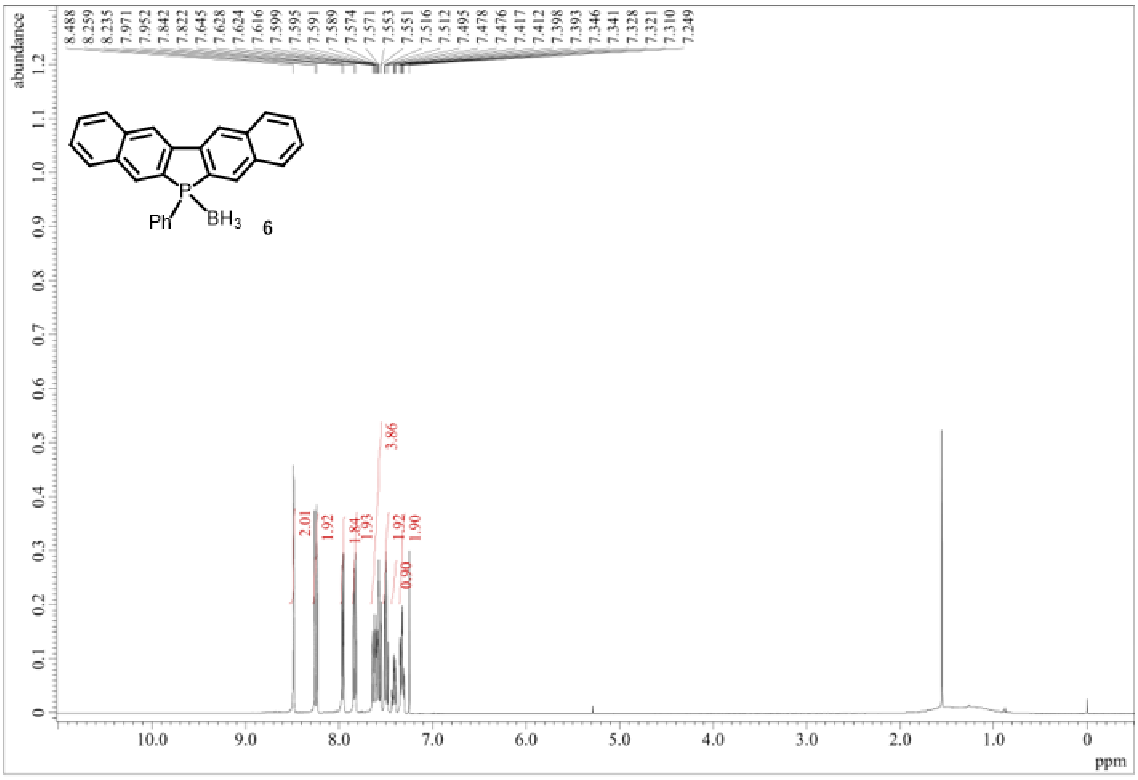
^{1}H NMR spectrum of **5**



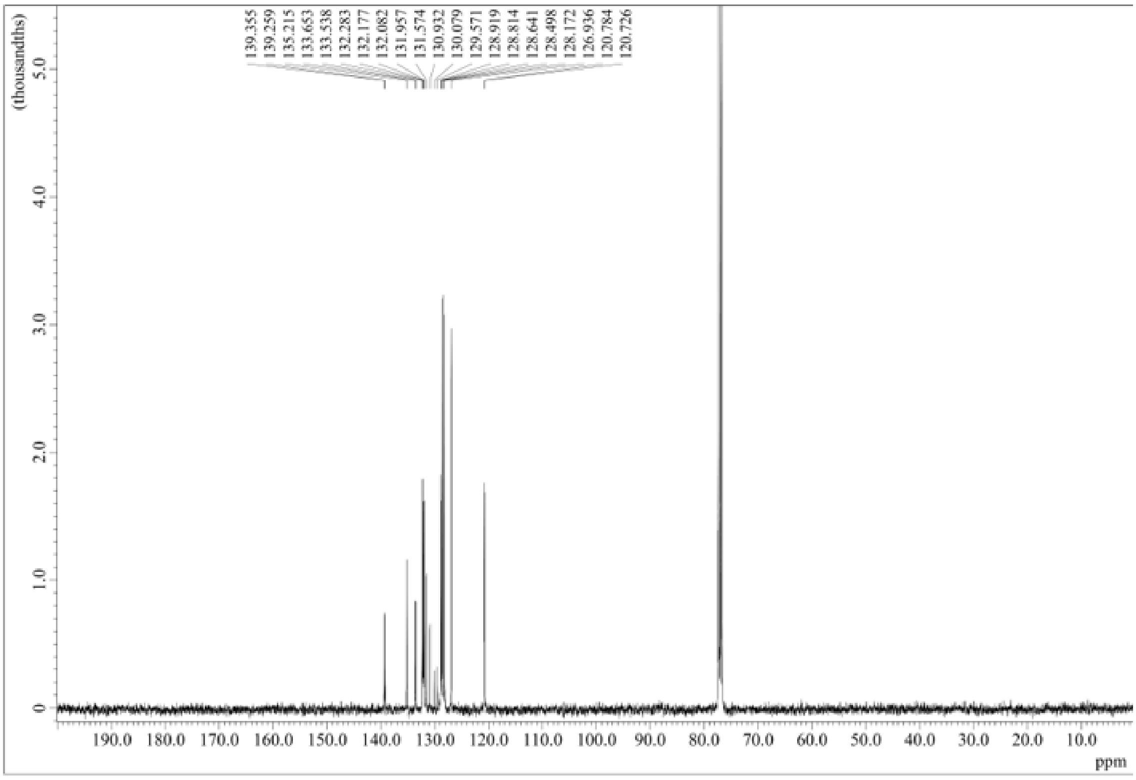
^{13}C NMR spectrum of **5**



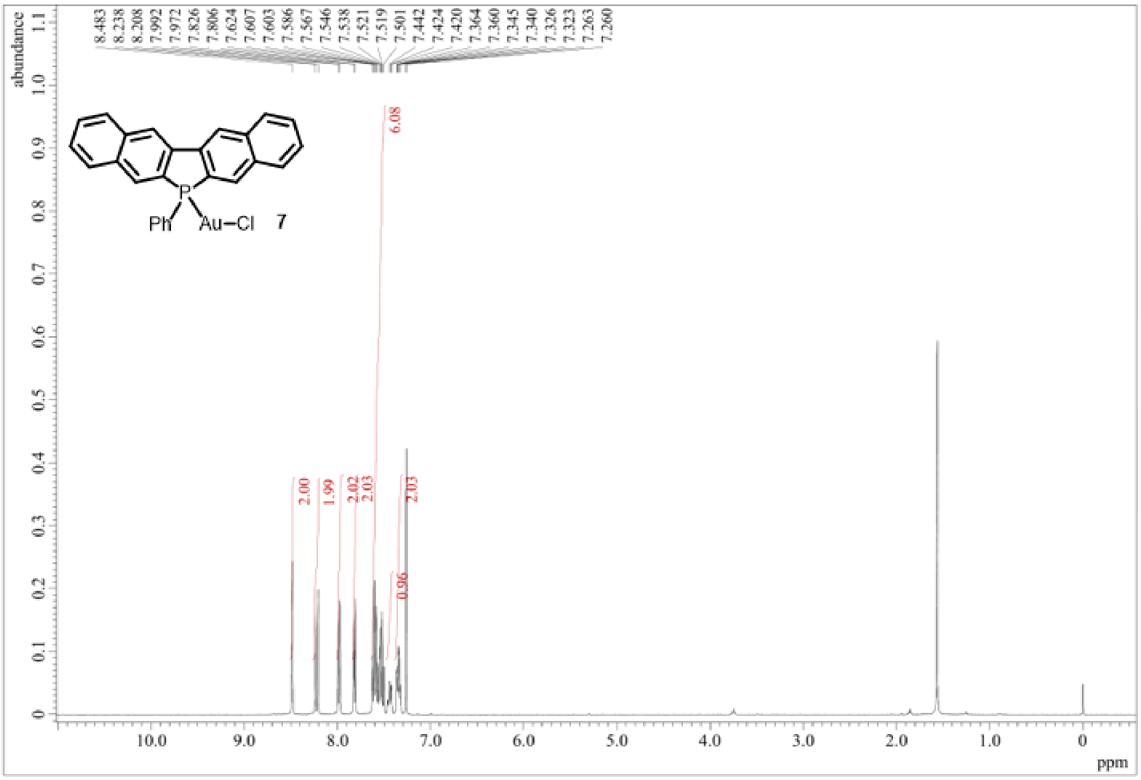
^{1}H NMR spectrum of **6**



^{13}C NMR spectrum of **6**



^{1}H NMR spectrum of **7**



^{13}C NMR spectrum of **7**