Eur. J. Org. Chem. **2007** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2007 · ISSN 1434–193X

SUPPORTING INFORMATION

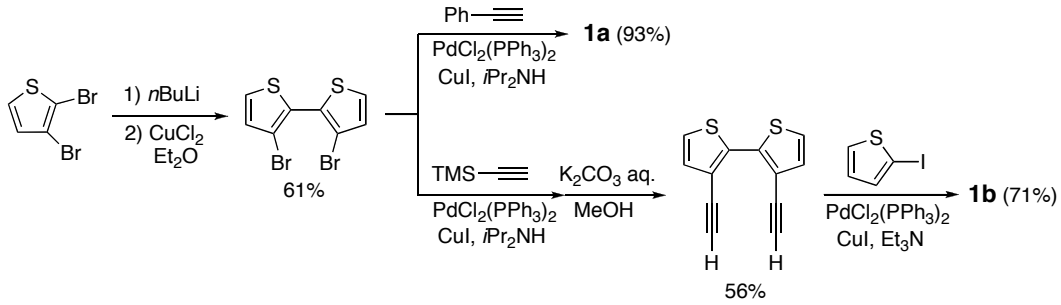
Title: Bithiophene-Fused Benzo[*c*]phospholes: Novel P,S-Containing Hybrid π-Conjugated Systems with Small HOMO–LUMO Energy Gaps
Author(s): Tooru Miyajima, Yoshihiro Matano,* Hiroshi Imahori
Ref. No.: O200701008

General. All melting points are uncorrected. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using $CDCl_3$ as the solvent unless otherwise noted. Chemical shifts are reported as the relative value vs. tetramethylsilane (^{1}H and ^{13}C) and phosphoric acid (^{31}P). MALDI-TOF mass spectra were measured using CHCA as a matrix. All solvents were distilled from sodium benzophenone ketyl (ether), or calcium hydride (CH_2Cl_2, toluene, Et_3N, iPr$_2$NH) before use. All the reactions were performed under an argon or nitrogen atmosphere. 3,3'-Dibromo-2,2'-bithiophene,[1] 3,3'-bis(phenylethynyl)-2,2'-bithiophene **1a**,[1] 3,3'-diethynyl-2,2'-bithiophene, [1] 4,4'-dibromo-3,3'-bithiophene,[2] 3-bromo-2-iodothiophene,[3] and 3-bromo-2-[(trimethylsilyl)ethynyl]thiophene[3] were prepared according to the reported procedure. Other chemicals were of reagent grade quality, purchased commercially, and used without further purification unless otherwise noted.

3,3'-Bis[(2-thienyl)ethynyl]-2,2'-bithiophene 1b: A mixture of 3,3'-bis(ethynyl)-2,2'-bithiophene (214 mg, 1.0 mmol), 2-iodothiopnene (0.33 mL, 3.0 mmol), $PdCl_2(PPh_3)_2$ (28 mg, 0.04 mmol), CuI (4 mg, 0.02 mol), and triethylamine (20 mL) was stirred for 4 h at room temperature. After filtration

[1] U. Dahlmann, R. Neilden, *Helv. Chim, Acta* **1996**, *79*, 755.
[2] A. Rajca, M. Miyasaka, M. Pink, H. Wang, S. Rajca, *J. Am. Chem. Soc.* **2004**, *126*, 15211.
[3] M. J. Mersella, Z.-Q. Wang, R. J. Reid, K. Yoon, *Org. Lett.* **2001**, *3*, 885.

and solvent removal, the residue was subjected to silica-gel column chromatography (hexane/CH_2Cl_2 = 5/1, R_f = 0.4). After recrystallization from MeOH, pure **1b** was obtained as a yellow solid (270 mg, 71%). Mp 154–155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (dd, J = 5.2, 3.9 Hz, 2H), 7.14 (d, J = 5.2 Hz, 2H), 7.26 (d, J = 5.2 Hz, 2H), 7.30–7.37 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 89.1, 89.5, 118.9, 123.3, 124.3, 127.2, 127.7, 130.1, 131.8, 138.4; MS (MALDI-TOF) *m/z* 378 (M^+); Anal. Calcd for $C_{20}H_{10}S_4$: C, 63.46; H, 2.66. Found: C, 63.19; H, 2.63.



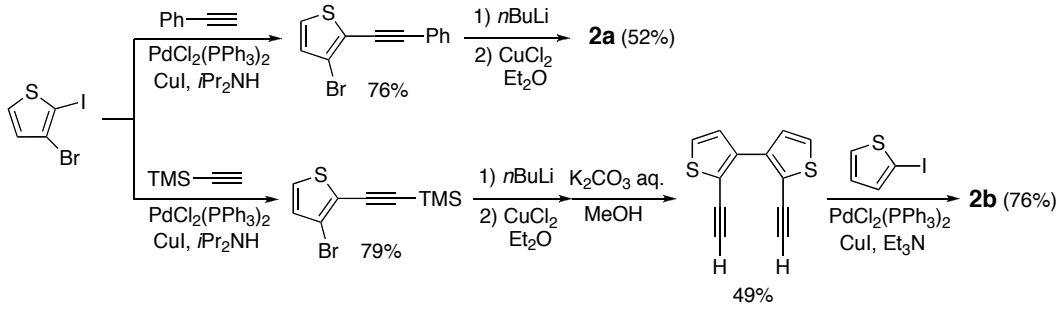
3-Bromo-2-(phenylethynyl)thiophene: A mixture of 3-bromo-2-iodothiophene (1.45 g, 5.0 mmol), phenylacetylene (0.66 mL, 6.0 mmol), $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), CuI (19 mg, 0.10 mmol), diisopropylamine (50 mL), and toluene (100 mL) was stirred for 3 h at room temperature. After filtration and solvent removal, the residue was subjected to silica-gel column chromatography (hexane, R_f = 0.3) to give the title compound as a pale yellow oil (1.0 g, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (d, J = 5.6 Hz, 1H), 7.23 (d, J = 5.6 Hz, 1H), 7.32–7.39 (m, 3H), 7.52–7.58 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$,) δ 81.0, 96.9, 116.0, 120.8, 122.5, 127.0, 128.3, 128.7, 130.1, 131.5; MS (MALDI-TOF) *m/z* 263 (M^+); Anal. Calcd for $C_{12}H_7BrS$: C, 54.77; H, 2.68. Found: C, 54.49; H, 2.78.

2,2'-Bis(phenylethynyl)-3,3'-bithiophene 2a: *n*BuLi (1.58 M × 1.33 mL, 2.1 mmol) was slowly added to a solution of 3-bromo-2-(phenylethynyl)thiophene (530 mg, 2.0 mmol) in Et_2O (5 mL) at –78 °C. The mixture was kept at this temparature for 1 h, and then $CuCl_2$ (350 mg, 2.6 mmol) was added. The resulting mixture was stirred at –50 °C for 15 min, then at room temparature for 9 h. After filtration and solvent removal, the residue was subjected to silica-gel column chromatography (hexane/$CHCl_3$) to give **2a** as a pale yellow solid (190 mg, 52%). Mp 48–49 °C; ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.28–7.37 (m, 8H), 7.43–7.51 (m, 4H), 7.73 (d, J = 5.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 83.2, 96.2, 119.5, 122.9, 125.8, 125.8, 128.2, 128.3, 131.1, 138.9; MS (MALDI-TOF) *m/z* 366 (M^+); Anal. Calcd for $C_{24}H_{14}S_2$: C, 78.65; H, 3.85. Found: C, 78.49; H, 3.85.

2,2'-Diethynyl-3,3'-bithiophene: This compound was prepared from 3-bromo-2-[(trimethylsilyl)ethynyl]thiophene according to the similar procedure described for **2a**. Yield 49 %, colorless solid. Mp 84–85 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.48 (s, 2H), 7.27 (d, J = 5.2 Hz, 2H), 7.61 (d, J = 5.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 77.1, 84.6, 118.5, 126.2, 128.2, 139.6; MS (MALDI-TOF) *m/z* 214 (M^+); Anal. Calcd for $C_{12}H_6S_2$: C, 67.25; H, 2.82. Found: C, 67.38; H, 2.88.

2,2'-Bis[(2-thienyl)ethynyl]-3,3'-bithiophene 2b: This compound was prepared from 2,2'-diethynyl-3,3'-bithiophene according to the similar procedure described for **1b**. Yield 76%, colorless solid. Mp 132–133 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (dd, J = 5.2, 3.6 Hz, 2H), 7.24 (dd, J = 3.6, 1.0 Hz, 2H), 7.30 (dd, J = 5.2, 1.0 Hz, 2H), 7.32 (d, J = 5.4 Hz, 2H), 7.65 (d, J = 5,4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 86.8, 89.6, 119.3, 123.0, 126.4, 127.2, 127.8, 128.3, 132.1, 139.1; MS (MALDI-TOF) m/z 378 (M^+); Anal. Calcd for $C_{20}H_{10}S_4$: C, 63.46; H, 2.66. Found: C, 63.34; H, 2.54.

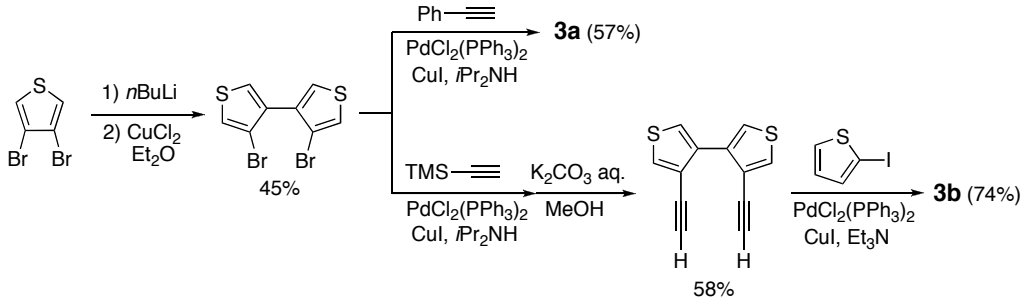


4,4'-Bis(phenylethynyl)-3,3'-bithiopnene 3a: A mixture of 4,4'-dibromo-3,3'-bithiophene (390 mg, 1.2 mmol), phenylacetylene (0.44 mL, 4.0 mmol), $PdCl_2(PPh_3)_2$ (120 mg, 0.17 mmol), CuI (27 mg, 0.17 mol), and diisopropylamine (45 mL) was stirred for 15 h at 70 °C. After filtration and solvent removal, the residue was subjected to silica-gel column chromatography (hexane/CH_2Cl_2 = 5/1, R_f = 0.35). After recrystallization from cold MeOH (–78 °C), pure **3a** was obtained as a colorless solid (250 mg, 57%). Mp 60–61 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24–7.38 (m, 6H),

7.40–7.50 (m, 4H), 7.61 (d, J = 3.3, Hz, 2H), 7.87 (d, J = 3.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 85.0, 91.1, 122.3, 123.2, 123.3, 128.2, 128.4, 129.3, 131.4, 136.1; MS (MALDI-TOF) *m/z* 366 (M^+); Anal. Calcd for $C_{24}H_{14}S_2$: C, 78.65; H, 3.85. Found: C, 78.91; H, 3.84.

4,4'-Diethynyl-3,3'-bithiophene: A mixture of 4,4'-dibromo-3,3'-bithiophene (490 mg, 1.5 mmol), trimethylsilylacetylene (1.1 mL, 7.7 mmol), $PdCl_2(PPh_3)_2$ (170 mg, 0.24 mmol), CuI (46 mg, 0.24 mmol), and diisopropylamine (45 mL) was stirred for 20 h at 90 °C. After filtration and solvent removal, the residue was subjected to silica gel column chromatography (hexane, R_f = 0.15) to give trimethylsilyl-substituted product as a pale brown oil. To the solution of above obtained compound in MeOH (150 mL) was added saturated aq K_2CO_3 (5 mL) and stirred at room temperature. After 5 h, $CHCl_3$ (200 mL) was added. The mixture and washed with water (100 ml × 2), and dried over anhydrous Na_2SO_4. After silica-gel column chromatography (hexane/ CH_2Cl_2 = 10:1, R_f = 0.25) and recrystallization from cold MeOH (–78 °C), the title compound was obtained as a colorless solid (190 mg, 58%). Mp 99–100 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.13 (s, 2H), 7.61 (d, J = 3.3 Hz, 2H), 7.78 (d, J = 3.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 79.1, 79.4, 121.0, 123.4, 131.2, 135.8; MS (MALDI-TOF) *m/z* 214 (M^+); Anal. Calcd for $C_{12}H_6S_2$: C, 67.25; H, 2.82. Found: C, 67.33; H, 2.80.

4,4'-Bis[(2-thienyl)ethynyl]-3,3'-bithiopnene 3b: This compound was prepared from 4,4'-diethynyl-3,3'-bithiophene according to the similar procedure described for **1b**. Yield 74%, colorless solid. Mp 94–95 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (dd, J = 5.1, 3.9 Hz, 2H), 7.22 (dd, J = 3.9, 1.1 Hz, 2H), 7.28 (dd, J = 5.1, 1.1 Hz, 2H), 7.60 (d, J = 3.3 Hz, 2H), 7.81 (d, J = 3.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 84.5, 88.7, 121.9, 123.3, 123.4, 127.1, 127.3, 129.5, 131.7, 135.9; MS (MALDI-TOF) *m/z* 378 (M^+); Anal. Calcd for $C_{20}H_{10}S_4$: C, 63.46; H, 2.66. Found: C, 63.57; H, 2.68.



7b: Yield 57 %, purple solid. Mp 230 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.00 (d, J = 5.2 Hz, 2H), 7.03–7.08 (m, 2H), 7.08–7.13 (m, 4H), 7.35–7.46 (m, 4H), 7.48–7.61 (m, 3H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ +48.1; MS (MALDI-TOF) *m/z* 719 (M^+); HRMS (FAB): Calcd for $C_{26}H_{15}AuClPS_4$ (M^+), 717.9148; Found, 717.9128.

8a: Yield 52%, red solid. Mp 210 °C (dec); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.30 (d, J = 5.1 Hz, 2H), 7.33 (d, J = 5.1 Hz, 2H), 7.32–7.55 (m, 13H), 7.55–7.66 (m, 2H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ +46.3; MS (MALDI-TOF) *m/z* 707 (M^+); HRMS (FAB): Calcd for $C_{30}H_{19}AuClPS_2$ (M^+), 706.0020; Found, 706.0002.

8b: Yield 54%, purple solid. Mp 210 °C (dec); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.06–7.14 (m, 2H), 7.16–7.24 (m, 2H), 7.35 (d, J = 5.1 Hz, 2H), 7.43 (d J = 5.1 Hz, 2H,), 7.35–7.45 (m, 2H), 7.47–7.53 (m, 3H), 7.54–7.65 (m, 2H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ +48.2; MS (MALDI-TOF) *m/z* 719 (M^+); HRMS (FAB): Calcd for $C_{26}H_{15}AuClPS_4$ (M^+), 717.9148; Found, 717.9130.

9a: Yield 54%, pale yellow solid. Mp 220 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.96 (d, J = 3.0 Hz, 2H), 7.03 (br-s, 2H), 7.32 (br, 2H), 7.37–7.45 (m, 4H), 7.45–7.68 (m, 5H), 7.56 (d, J = 3.0 Hz, 2H) 7.78 (br-s, 2H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ +50.2; MS (MALDI-TOF) *m/z* 707 (M^+); HRMS (FAB): Calcd for $C_{30}H_{19}AuClPS_2$ (M^+), 706.0020; Found, 706.0013.

9b: Yield 60%, yellow solid. Mp 240 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.05–7.12 (m, 4H), 7.39–7.48 (m, 6H), 7.50–7.56 (m, 1H), 7.58–7.66 (m, 4H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ +51.4; MS (MALDI-TOF) *m/z* 719 (M^+); HRMS (FAB): Calcd for $C_{26}H_{15}AuClPS_4$ (M^+), 717.9148; Found, 717.9164.

4b: Yield 86%, red solid. Mp 175 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.96–7.02 (m, 2H), 7.03–7.08 (m, 2H), 7.11 (d, J = 5.2 Hz, 2H), 7.15 (d, J = 5.2 Hz, 2H), 7.17–7.28 (m, 4H), 7.28–7.37 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ123.2, 126.2, 126.9 (d, $J_{P,C}$ = 1.6 Hz), 127.2 (d, $J_{P,C}$ = 5.8 Hz), 128.1, 128.5 (d, $J_{P,C}$ = 9.9 Hz), 129.1 (d, $J_{P,C}$ = 9.1 Hz), 130.7 (d, $J_{P,C}$ = 1.6 Hz), 132.2 (d, $J_{P,C}$ = 2.5 Hz), 135.1 (d, $J_{P,C}$ = 18.9 Hz), 135.2 (d, $J_{P,C}$ = 1.7 Hz), 138.0 (2.5 Hz), 138.3 (d, $J_{P,C}$ = 14.1 Hz), 138.5 (d, $J_{P,C}$ = 18.3 Hz); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ +28.5; MS (MALDI-TOF) *m/z* 486 (M^+); HRMS (EI): Calcd for $C_{26}H_{15}PS_4$ (M^+), 485.9794; Found, 485.9789.

5a: Yield 91%, orange solid. Mp 200 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.12–7.26 (m, 7H), 7.30–7.42 (m, 8H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ122.7, 126.6 (d, $J_{P,C}$ = 1.6 Hz), 127.9 (d, $J_{P,C}$ = 1.6 Hz), 128.5 (d, $J_{P,C}$ = 9.9 Hz), 128.9, 129.0 (d, $J_{P,C}$ = 9.1 Hz), 130.3 (d, $J_{P,C}$ = 6.6 Hz), 130.4

(d, $J_{P,C}$ = 2.1 Hz), 131.9 (d, $J_{P,C}$ = 2.4 Hz), 134.8 (d, $J_{P,C}$ = 19.0 Hz), 135.4 (d, $J_{P,C}$ = 1.7 Hz), 135.6 (d, $J_{P,C}$ = 15.7 Hz), 136.7 (d, $J_{P,C}$ = 15.7 Hz), 143.8 (d, $J_{P,C}$ = 1.6 Hz); $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ +24.2; MS (MALDI-TOF) *m/z* 474 (M^+); HRMS (EI): Calcd for $C_{30}H_{19}PS_2$ (M^+), 474.0666; Found, 474.0656.

5b: Yield 90 %, red solid. Mp 190 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.08–7.14 (m, 4H), 7.20–7.36 (m, 7H), 7.38–7.45 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) δ 122.7, 127.4 (d, $J_{P,C}$ = 1.7 Hz), 127.8 (d, $J_{P,C}$ = 2.5 Hz), 128.2, 128.3 (d, $J_{P,C}$ = 5.8 Hz), 129.1 (d, $J_{P,C}$ = 9.1 Hz), 130.8 (d, $J_{P,C}$ = 1.7 Hz), 131.4 (d, $J_{P,C}$ = 1.7 Hz), 134.9 (d, $J_{P,C}$ = 19.0 Hz), 135.9 (d, $J_{P,C}$ = 1.7 Hz), 136.0 (d, $J_{P,C}$ = 3.3 Hz), 136.9 (d, $J_{P,C}$ = 18.1 Hz), 137.8 (d, $J_{P,C}$ = 14.8 Hz); $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ +29.2; MS (MALDI-TOF) *m/z* 486 (M^+); HRMS (EI): Calcd for $C_{26}H_{15}PS_4$ (M^+), 485.9794; Found, 485.9790. One of the carbons could not be detected clearly in the ^{13}C NMR.

6a: Yield 88%, pale yellow solid. Mp 210 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.97 (d, J = 3.0 Hz, 2H), 7.12–7.22 (m, 2H), 7.22–7.46 (m, 13H), 7.54 (d, 2H, J = 3.0 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2) δ 116.8, 122.9 (d, $J_{P,C}$ = 1.9 Hz), 127.7, 128.9 (d, $J_{P,C}$ = 8.7 Hz), 129.2, 129.3 (d, $J_{P,C}$ = 6.2 Hz), 129.6 (d, $J_{P,C}$ = 13.0 Hz), 130.3 (d, $J_{P,C}$ = 1.9 Hz), 132.9 (d, $J_{P,C}$ = 2.5 Hz), 133.9, 134.9 (d, $J_{P,C}$ = 19.8 Hz), 135.2 (d, $J_{P,C}$ = 14.3 Hz), 138.3 (d, $J_{P,C}$ = 16.1 Hz), 145.9; $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ +26.3; MS (MALDI-TOF) *m/z* 474 (M^+); HRMS (EI): Calcd for $C_{30}H_{19}PS_2$ (M^+), 474.0666; Found, 474.0653.

6b: Yield 86%, pale yellow solid. Mp 215 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.96–7.00 (m, 2H), 7.03–7.08 (m, 2H), 7.24–7.28 (m, 2H), 7.28–7.38 (m, 7H), 7.57 (d, J= 3.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2) δ 117.0, 123.7 (d, $J_{P,C}$ = 2.5 Hz), 126.7 (d, $J_{P,C}$ = 5.6 Hz), 127.0 (d, $J_{P,C}$ = 2.5 Hz), 128.2, 129.1 (d, $J_{P,C}$ = 8.7 Hz), 129.5 (d, $J_{P,C}$ = 15.0 Hz), 130.7 (d, $J_{P,C}$ = 1.3 Hz), 132.3 (d, $J_{P,C}$ = 1.3 Hz), 133.9, 134.9 (d, $J_{P,C}$ = 19.8 Hz), 137.7 (d, $J_{P,C}$ = 14.3 Hz), 138.4, 138.7 (d, $J_{P,C}$ = 18.6 Hz); $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ +29.6; MS (MALDI-TOF) *m/z* 486 (M^+); HRMS (EI): Calcd for $C_{26}H_{15}PS_4$ (M^+), 485.9794; Found, 485.9796.

X-ray Crystal Structure Analysis: Single crystals of **4a** and **7a** were grown from CH_2Cl_2–MeOH. All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated

Mo–Kα radiation. The structures were solved by direct methods,[4] and expanded using Fourier techniques.[5] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the rigid model. All calculations were performed using Crystal Structure[6] crystallographic software package except for refinement, which was performed using SHELXL-97.[7] CCDC-660029 (**4a**) and CCDC-660028 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical measurements: These were performed using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag^+ [0.01 M $AgNO_3$, 0.1 M $n Bu_4NPF_6$ (MeCN)] reference electrode. The potentials were calibrated with ferrocene/ferrocenium as an internal standard.

Density Functional Theory (DFT) Calculations: All calculations were performed using the Gaussian 03[8] suite of programs with the 6-31G* basis set and the B3LYP functional. The geometries were fully optimized without any symmetry constraints. The molecular orbital diagrams were drawn using MolStudio R3.0 (NEC Corp., Japan).

---

[4] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* **1994**, *27*, 435.

[5] DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen*, (1999) The Netherlands.

[6] CrystalStructure 3.8.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000–2006). 9009 New Trails Dr. The Woodlands, TX 77381, USA.

[7] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**.

[8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian* 03; Gaussian, Inc., Pittsburgh, PA, 2003.

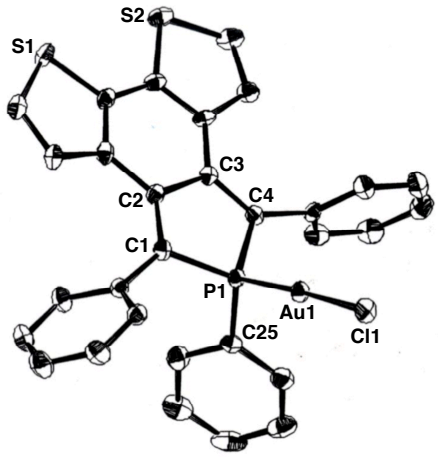


Figure S1. ORTEP diagram of **7a** (50% probability ellipsoids). Solvent molecule and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.787(4), P1–C4 1.792(4), P1–C25 1.811(4), C1–C2 1.374(5), C2–C3 1.502(7), C3–C4 1.353(6), P1–Au1 2.2283(10), Au1–Cl1 2.2833(10), C1–P1–C4 94.1(2), C1–P1–C25 109.9(2), C4–P1–C25 106.9(2), P1–Au1–Cl1 177.27(4).

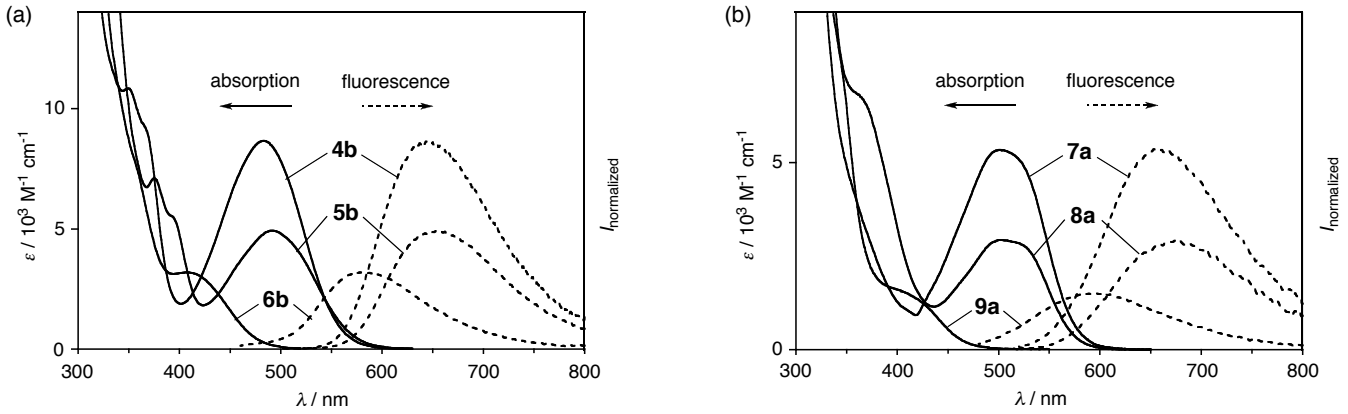


Figure S2. UV-vis absorption and fluorescence spectra of (a) **4b**, **5b** and **6b** and (b) **7a**, **8a**, and **9a** in CH_2Cl_2.

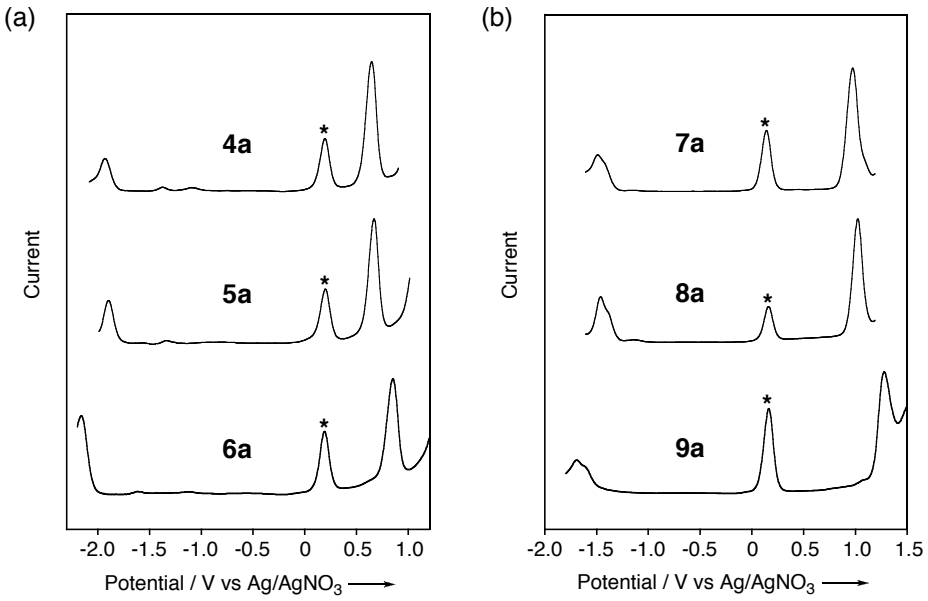


Figure S3. Differential pulse voltammograms of (a) **4a**, **5a** and **6a** and (b) **7a**, **8a**, and **9a**. Asterisk indicates the Fc/Fc^{+} couple.

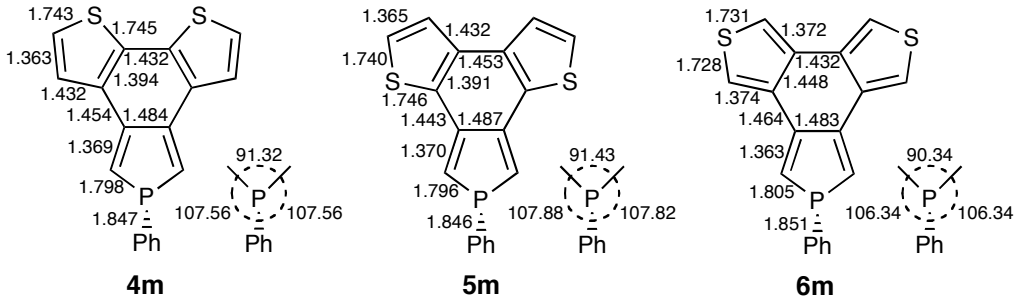


Figure S4. Bond lengths [Å] and angles [°] of the model compounds **4m**, **5m**, and **6m.**

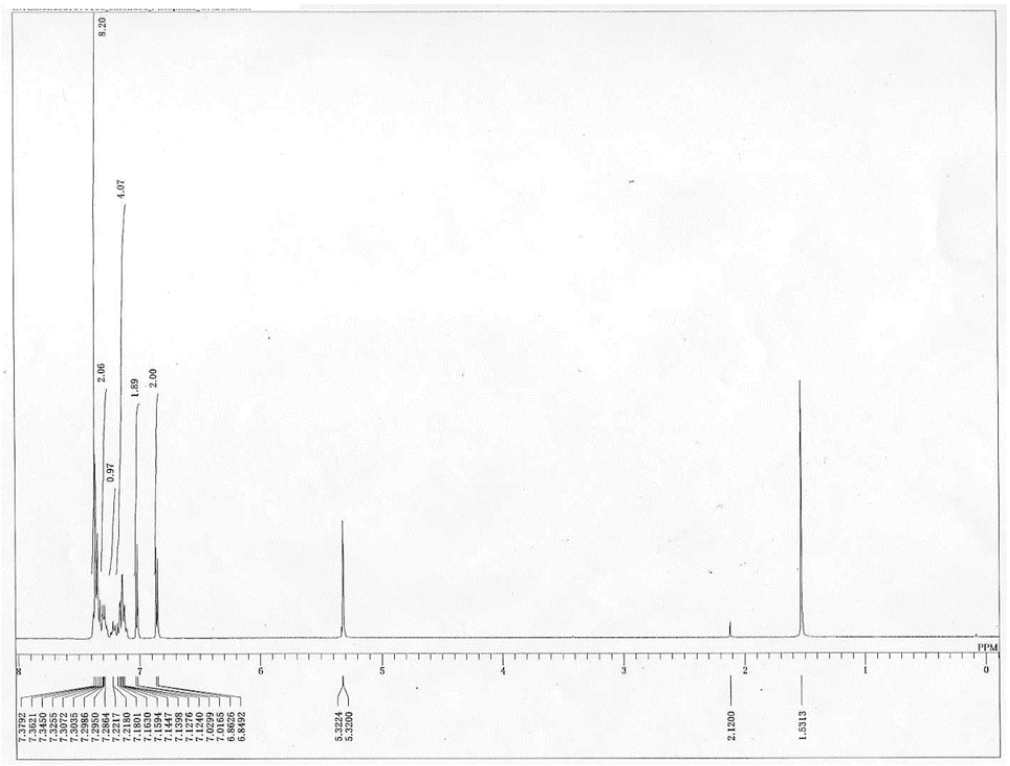


Figure S5. ^{1}H NMR spectrum of **4a** in CD_2Cl_2.

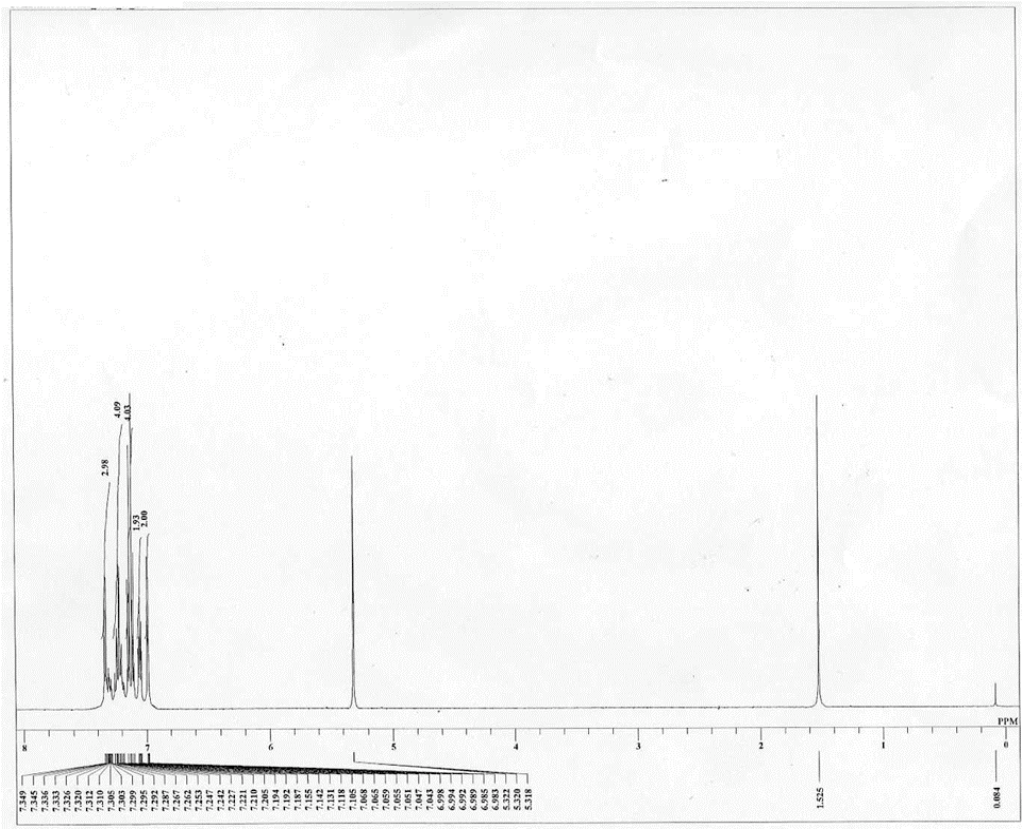


Figure S6. ^{1}H NMR spectrum of **4b** in CD_2Cl_2.

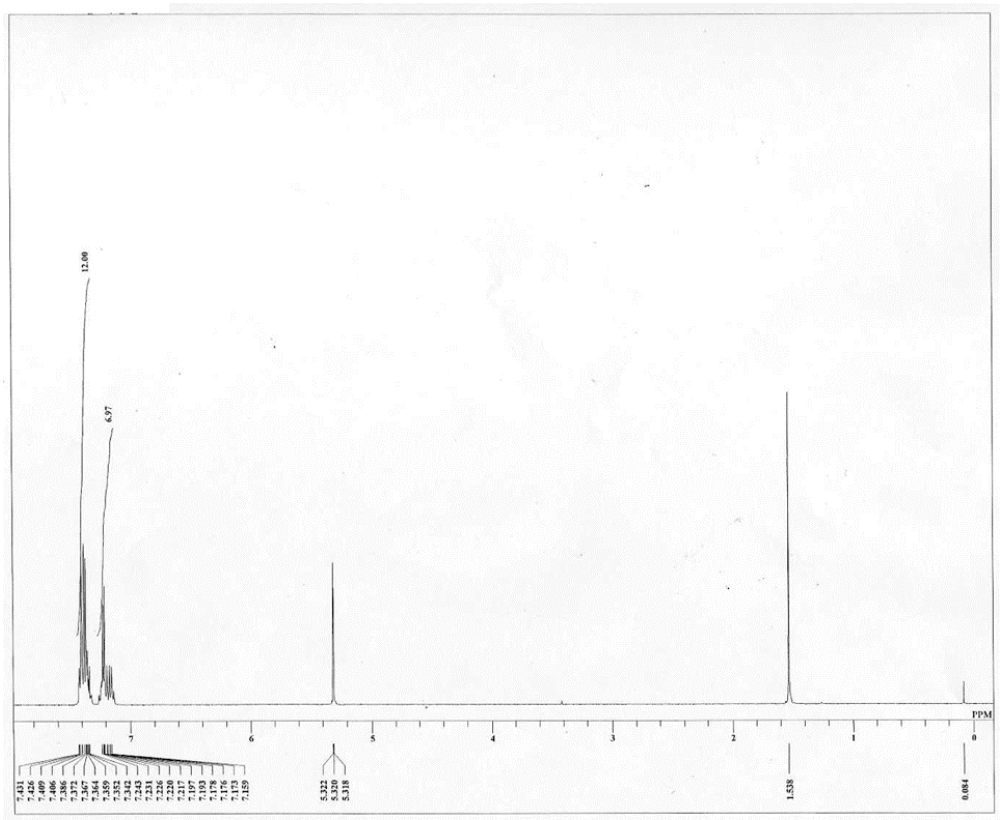


Figure S7. ^{1}H NMR spectrum of **5a** in CD_2Cl_2.

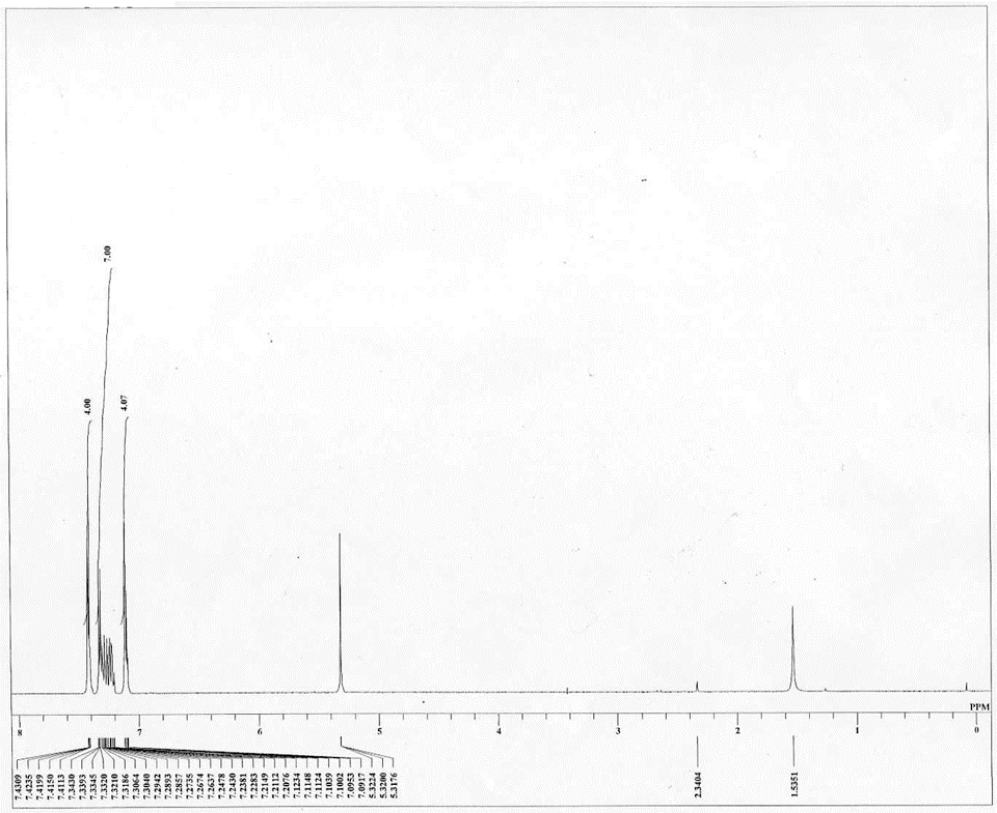


Figure S8. ^{1}H NMR spectrum of **5b** in CD_2Cl_2.

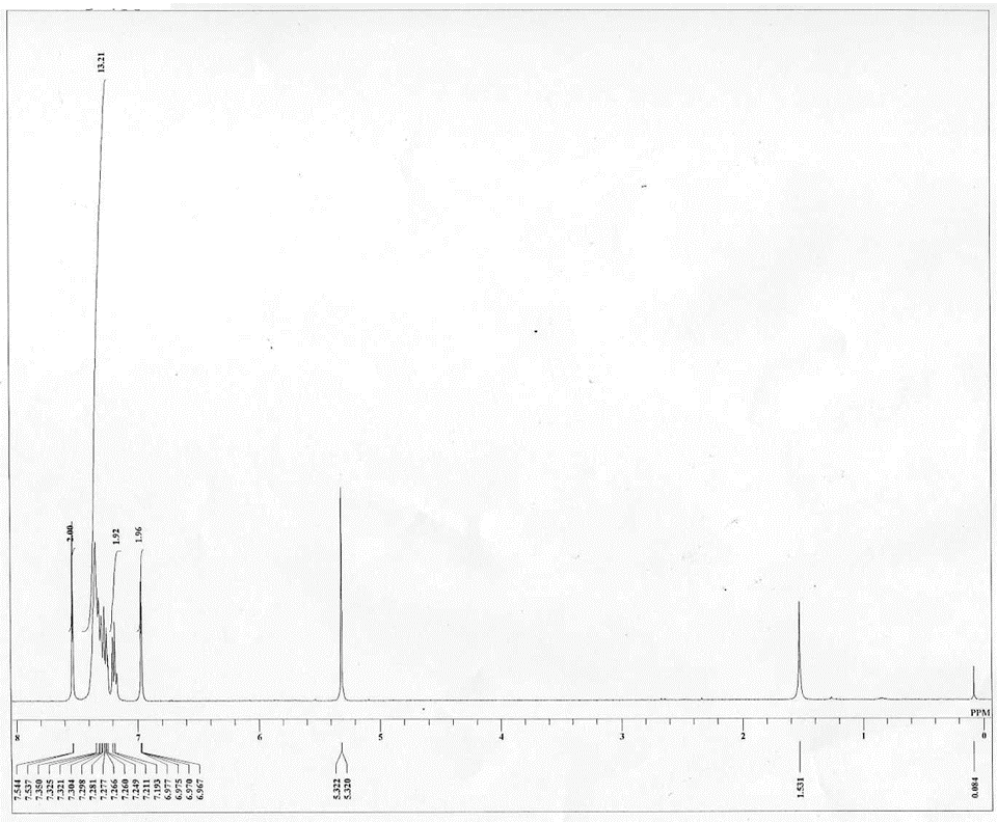


Figure S9. ^{1}H NMR spectrum of **6a** in CD_2Cl_2.

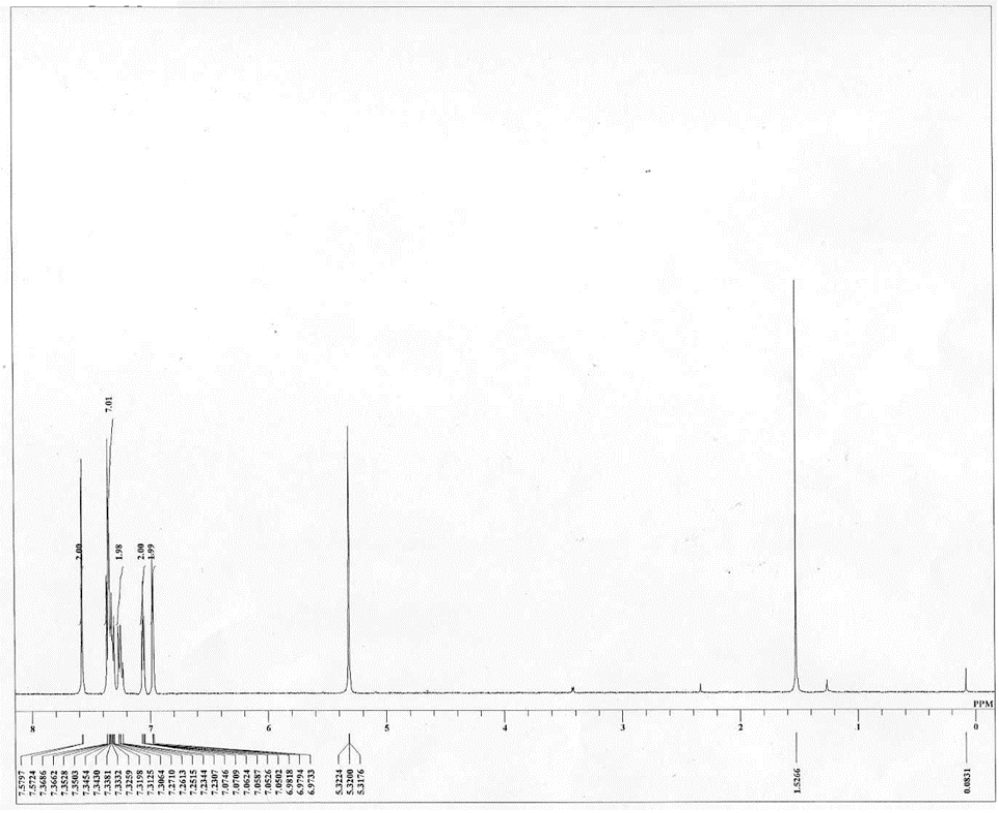


Figure S10. ^{1}H NMR spectrum of **6b** in CD_2Cl_2.

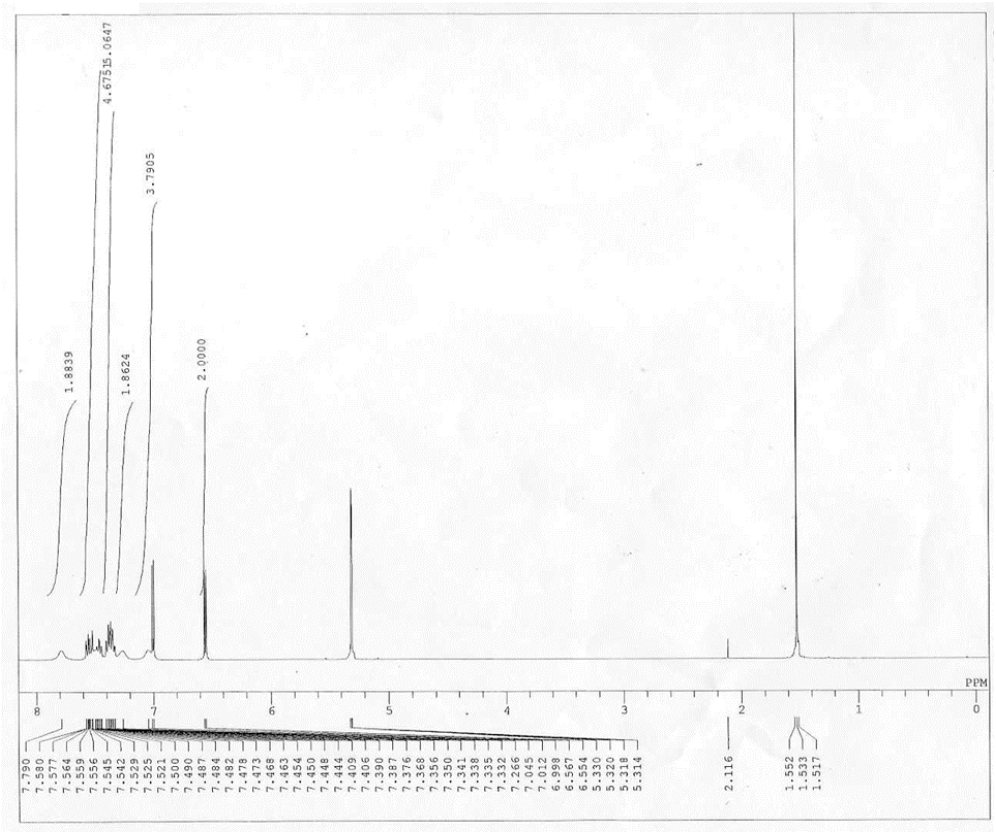


Figure S11. ^{1}H NMR spectrum of **7a** in CD_2Cl_2.

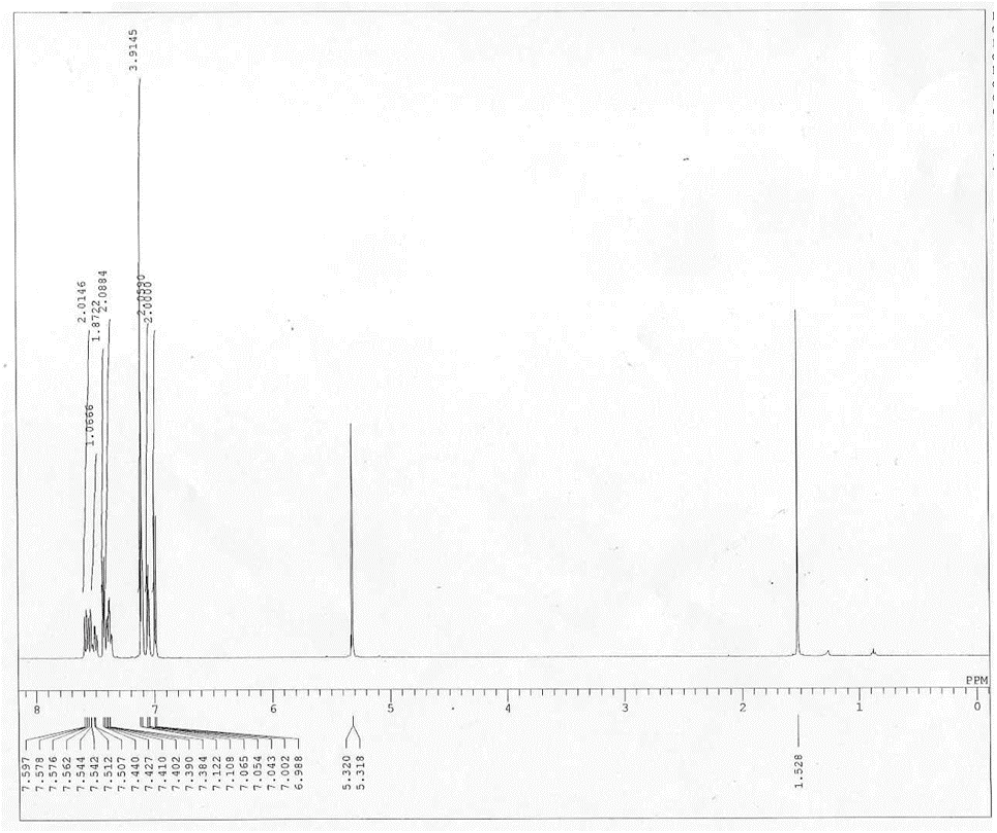


Figure S12. ^{1}H NMR spectrum of **7b** in CD_2Cl_2.

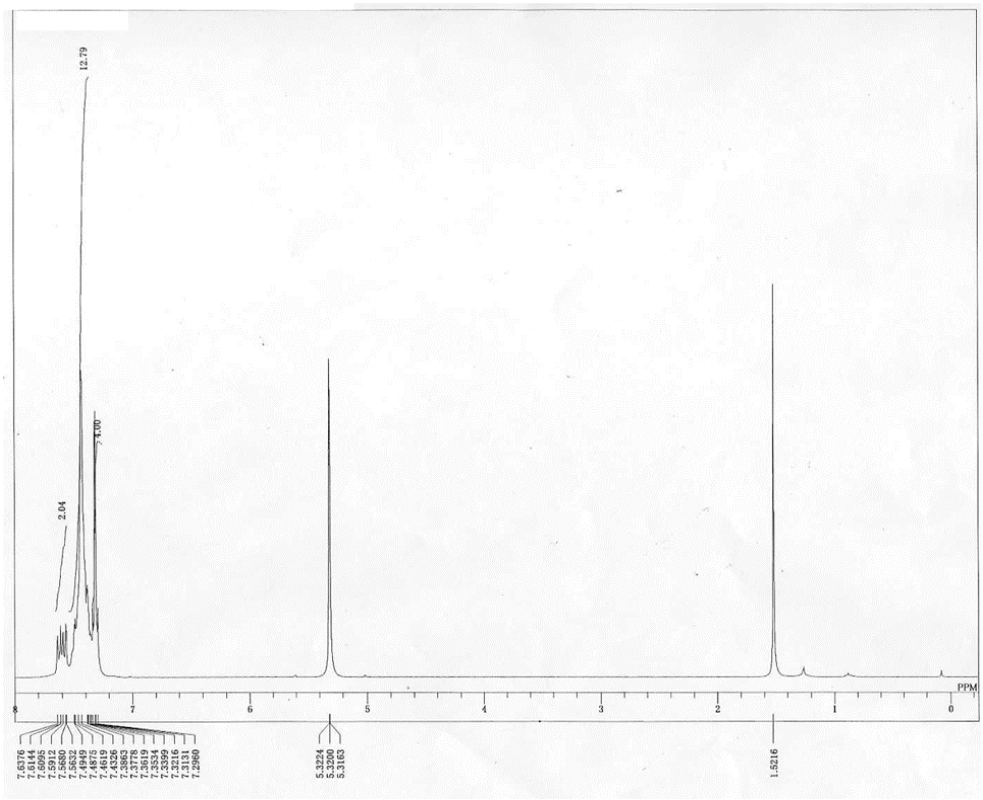


Figure S13. ^{1}H NMR spectrum of **8a** in CD_2Cl_2.

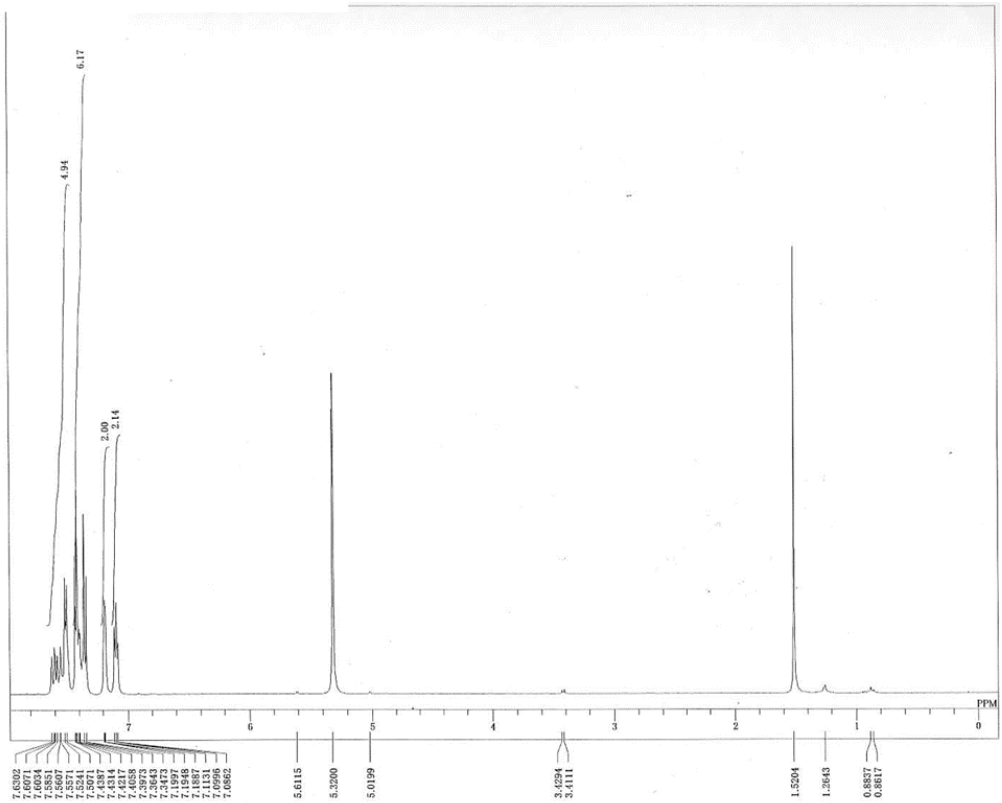


Figure S14. ^{1}H NMR spectrum of **8b** in CD_2Cl_2.

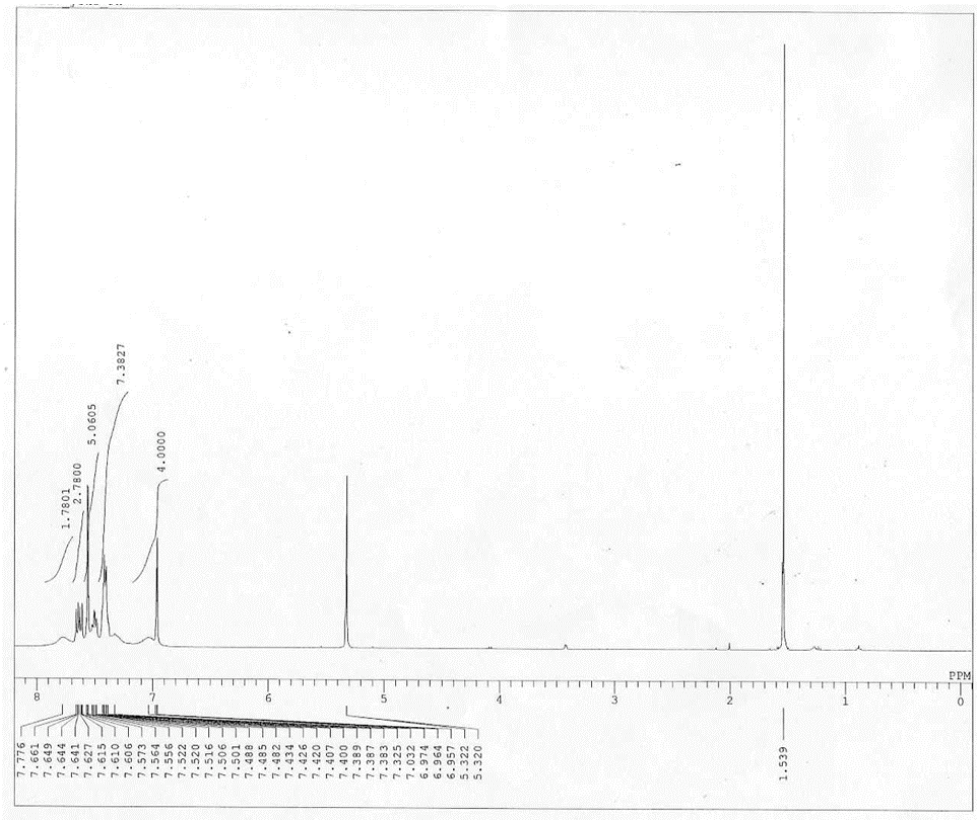


Figure S15. ^{1}H NMR spectrum of **9a** in CD_2Cl_2.

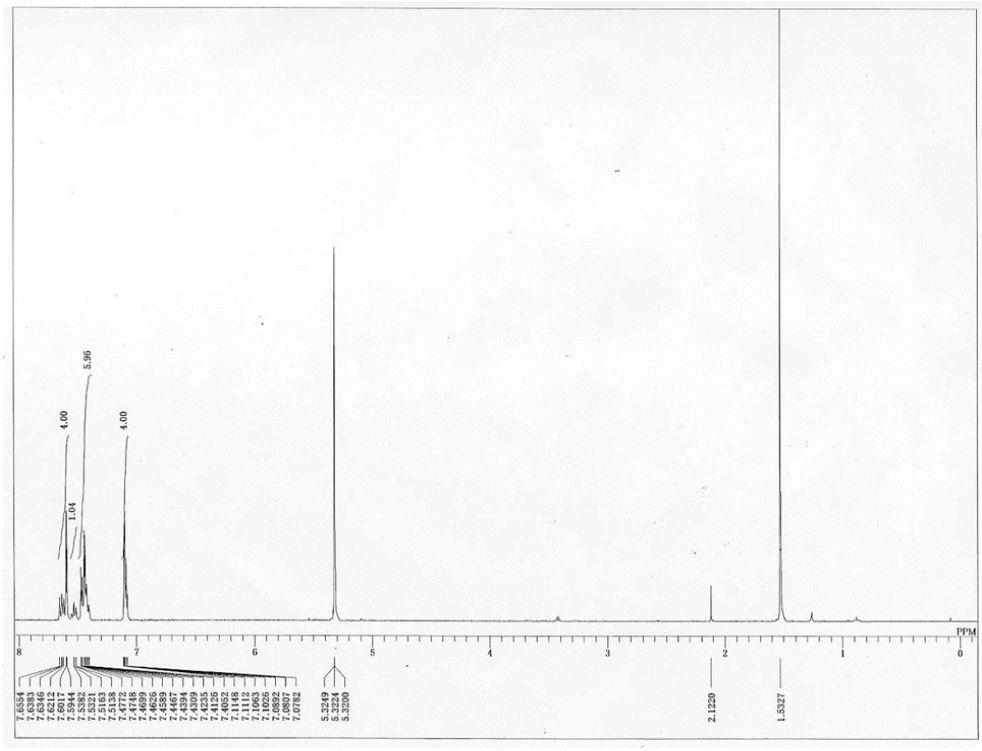


Figure S16. ^{1}H NMR spectrum of **9b** in CD_2Cl_2.