Supporting Information for

Synthesis of 2-Aryl-5-styrylphospholes: Promising Candidates for the Phosphole-based NLO Chromophores

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General

All melting points are uncorrected. ^{1}H 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 phosphonic acid (^{31}P). The ^{1}H NMR spectra of **3b–d**, **4a–i**, **5a–i**, and **6** are provided in Figures S4–S25. MALDI-TOF mass spectra were measured using CHCA as a matrix. All solvents were distilled from sodium benzophenone ketyl (ether, THF), sodium (hexane), or calcium hydride (CH_2Cl_2, toluene) before use. The solvents used for the measurements of UV-visible absorption and fluorescence spectra were fleshly distilled before use. All the reactions were performed under an argon or nitrogen atmosphere. Column chromatography was performed on silica gel. Commercially available *β*-bromostyrene was used as a mixture of isomers (*E*/*Z* = 5:1). Other bromoalkenes were prepared by the stereoselective reduction[1] of 1,1-dibromoalkenes[2] (*E*/*Z* = 20:1). 2-Iodo-5-methoxythiophene[3] was prepared according to the reported procedure. 1-Arylhepta-1,6-diynes **3a**,**b** and 9-arylnona-8-ene-1,6-diynes **3c**,**d** were prepared by the Sonogashira coupling of 1,6-heptadiyne with the corresponding reagents as illustrated in Scheme 1. Other chemicals were of reagent grade quality, purchased commercially, and used without further purification unless otherwise noted.

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[1] (a) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *J. Org. Chem.* **1981**, *46*, 3745. (b) Kuang, C.; Senboku, H.; Tokuda, M. *Tetrahedron* **2002**, *58*, 1491.

[2] (a) Huh, D. H.; Jeong, J. S.; Lee, H. B.; Ryu, H.; Kim, Y. G. *Tetrahedron* **2002**, *58*, 9925. (b) Donovan, P. M.; Scott, L. T. *J. Am. Chem. Soc.* **2004**, *126*, 3108.

[3] Meier, H.; Mühling, B.; Oehlhof, A.; Theisinger, S.; Kirsten, E. *Eur. J. Org. Chem.* **2006**, 405.

Synthesis of 1-Arylhepta-1,6-diynes 3a,b. Typical Procedure: A mixture of 2-iodothiophene (3.3 mL, 30 mmol), CuI (9 mg, 45 μmol), $PdCl_2(PPh_3)_2$ (840 mg, 1.2 mmol), 1,6-heptadiyne (5.4 mL, 47 mmol), and 120 mL of triethylamine was stirred at 40 °C for 24 h. After filtration and solvent removal, the crude product was purified on a silica gel column using hexane as an eluent to give **3b** (R_f = 0.2) as a yellow oil (2.52 g, 14.5 mmol, 48%).

3a[4]: Pale yellow oil; Yield 44%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.84 (tt, 2H, *J* = 7.3, 7.3 Hz), 1.99 (t, 1H, *J* = 2.4 Hz), 2.39 (td, 2H, *J* = 7.3, 2.4 Hz), 2.55 (t, 2H, *J* = 7.3 Hz), 7.25-7.30 (m, 3H), 7.37-7.40 (m, 2H).

3b: Pale yellow oil; Yield 48%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.83 (tt, 2H, *J* = 7.3, 7.3 Hz), 1.99 (t, 1H, *J* = 2.4 Hz), 2.37 (td, 2H, *J* = 7.3, 2.4 Hz), 2.55 (t, 2H, *J* = 7.3 Hz), 6.93 (dd, 1H, *J* = 5.2, 3.7 Hz), 7.12 (dd, 1H, *J* = 3.7, 1.1 Hz), 7.17 (dd, 1H, *J* = 5.2, 1.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 17.6, 18.7, 27.4, 68.9, 74.3, 83.4, 93.0, 123.8, 126.0, 126.7, 131.1; MS (MALDI-TOF) *m/z* 174 (M^+); Anal. Calcd for $C_{11}H_{10}S$: C, 75.82; H, 5.78. Found: C, 75.81; H, 5.83.

Synthesis of 1-Styrylhepta-1,6-diynes 3c,d. Typical Procedure: A mixture of 1,6-heptadiyne (1.74 mL, 15 mmol), 4-trifluoromethyl-*β*-bromostyrene (mixture of isomers, *E*/*Z* = 20:1, 2.4 g, 9.5 mmol), $Pd(PPh_3)_4$ (250 mg, 0.22 mmol), and pyrrolidine (8 mL) was

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[4] Pearson, A.; Shively, R., Jr.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096.

stirred at room temperature. After 4 h, a fluffy precipitate was formed. The suspension was treated with saturated aq. NH_4Cl (10 mL) and extracted with Et_2O (15 mL × 2). The combined organic extracts were washed with water (20 mL), saturated aq. $NaHCO_3$ (20 mL), brine (20 mL), and dried over anhydrous Na_2SO_4. After removal of the volatile components under reduced pressure, the residue was subjected to silica gel column chromatography (hexane) to afford **3c** (R_f = 0.3) as a yellow oil (1.4 g, 55%).

3c: Yellow oil; Yield 55%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.80 (tt, 2H, *J* = 7.0, 7.0 Hz), 1.99 (t, 1H, *J* = 2.7 Hz), 2.36 (td, 2H, *J* = 7.0, 2.7 Hz), 2.53 (td, 2H, *J* = 7.1, 2.4 Hz), 6.23 (dt, 1H, *J* = 16.5, 2.4 Hz), 6.88 (d, 2H, *J* = 16.5 Hz), 7.45 (d, 2H, *J* = 8.4 Hz), 7.56 (d, 2H, *J* = 8.4 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 17.6, 18.7, 27.5, 69.0, 77.5, 83.4, 93.2, 111.4, 124.1 (q, $^1J_{F–C}$ = 272 Hz), 125.6 (q, $^3J_{F–C}$ = 3.7 Hz), 126.2, 130.0 (q, $^2J_{F–C}$ = 32.4 Hz), 138.7, 139.9; MS (MALDI-TOF) *m*/*z* 262 (M^+); Anal. Calcd for $C_{16}H_{13}F_3$: C, 73.27; H, 5.00. Found: C, 72.79; H, 5.14.

3d: Pale yellow solid; Yield 47%; Mp 37–38 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.80 (tt, 2H, *J* = 7.1, 7.1 Hz), 1.99 (t, 1H, *J* = 2.7 Hz), 2.36 (td, 2H, *J* = 7.1, 2.7 Hz), 2.53 (td, 2H, *J* = 7.1, 2.4 Hz), 3.91 (s, 3H), 6.25 (dt, 1H, *J* = 16.2, 2.4 Hz), 6.89 (d, 2H, *J* = 16.2 Hz), 7.41 (d, 2H, *J* = 8.8 Hz), 7.98 (d, 2H, *J* = 8.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 17.6, 18.7, 27.5, 52.1, 68.9, 80.1, 83.4, 93.2, 111.3, 125.9, 129.6, 130.0, 139.1, 140.8, 166.7; MS (MALDI-TOF) *m*/*z* 252 (M^+); Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C,

80.91; H, 6.58.

Synthesis of Enediynes 4a–f. Typical Procedure: A mixture of **3b** (1.74 g, 10 mmol), *β*-bromostyrene (mixture of isomers, *E*/*Z* = 5:1, 1.55 mL, 12 mmol), and $Pd(PPh_3)_4$ (290 mg, 0.25 mmol) in 10 mL of pyrrolidine was stirred for 15 h at room temperature. At this time, a fluffy precipitate formed. The suspension was treated with saturated aq. NH_4Cl (20 mL) and extracted with Et_2O (20 mL × 2). The combined organic extracts were washed with water (30 mL), saturated aq. $NaHCO_3$ (30 mL), brine (30 mL), and dried over anhydrous Na_2SO_4. After removal of the volatile components under reduced pressure, the residue was subjected to silica gel column chromatography (hexane/AcOEt = 10/1: R_f = 0.6) to afford enediyne **4c** as a pale yellow oil (2.6 g, 94%; *E*-isomer).

4a: Yield 93%; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.88 (tt, 2H, *J* = 6.8, 6.8 Hz), 2.50–2.65 (m, 4H), 6.15 (dt, 1H, *J* = 16.2, 2.2 Hz), 6.88 (d, 2H, *J* = 16.2 Hz), 7.23–7.45 (m, 10H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 18.7, 18.9, 28.0, 80.4, 81.3, 89.1, 91.7, 108.7, 123.8, 126.1, 127.6, 128.2, 128.3, 128.6, 131.6, 136.5, 140.3; MS (MALDI-TOF) *m*/*z* 270 (M^+). Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.37; H, 6.83.

4b: Yield 87%; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.88 (tt, 2H, *J* = 7.0, 7.0 Hz), 2.50–2.65 (m, 4H), 6.24 (dt, 1H, *J* = 16.0, 2.2 Hz), 6.89 (d, 2H, *J* = 16.0 Hz), 7.25–7.32 (m, 3H), 7.35–7.43 (m, 2H), 7.44 (d, 2H, *J* = 8.4 Hz), 7.56 (d, 2H, *J* = 8.4 Hz); ^{13}C{^{1}H} NMR

($CDCl_3$, 75 MHz) δ 18.7, 18.9, 27.8, 79.9, 81.4, 88.9, 93.3, 111.3, 123.6, 123.9 (q, $^1J_{F–C}$ = 274 Hz), 125.5 (q, $^3J_{F–C}$ = 3.8 Hz), 126.0, 127.5, 128.1, 129.6 (q, $^2J_{F–C}$ = 32.4 Hz), 131.4, 138.5, 139.7; MS (MALDI-TOF) *m/z* 338 (M^+). Anal. Calcd for $C_{22}H_{17}F_3$: C, 78.09; H, 5.06. Found: C, 78.19; H, 5.17.

4c: Yield 94%; Pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.87 (tt, 2H, *J* = 7.1, 7.1 Hz), 2.55 (td, 2H, *J* = 7.1, 2.2 Hz), 2.59 (t, 2H, *J* = 7.1 Hz), 6.15 (dt, 1H, *J* = 16.2, 2.2 Hz), 6.88 (d, 2H, *J* = 16.2 Hz), 6.94 (dd, 1H, *J* = 5.1, 3.6 Hz), 7.13 (dd, 1H, *J* = 3.6, 1.2 Hz), 7.17 (dd, 1H, *J* = 5.1, 1.2 Hz), 7.25–7.40 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 19.0, 19.0, 27.8, 74.4, 80.5, 91.5, 93.2, 108.6, 123.9, 126.0, 126.0, 126.7, 128.2, 128.6, 131.0, 136.4, 140.2; MS (MALDI-TOF) *m/z* 277 (M^+). Anal. Calcd for $C_{19}H_{16}S$: C, 82.56; H, 5.83. Found: C, 82.29; H, 5.76.

4d: Yield 74%; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.86 (tt, 2H, *J* = 6.8, 6.8 Hz), 2.54 (td, 2H, *J* = 6.8, 2.0 Hz), 2.59 (t, 2H, *J* = 6.8 Hz), 6.12 (dt, 1H, *J* = 16.2, 2.0 Hz), 6.82 (d, 2H, *J* = 16.2 Hz), 6.94 (dd, 1H, *J* = 5.1, 3.6 Hz), 7.13 (dd, 1H, *J* = 3.6, 1.2 Hz), 7.18 (dd, 1H, *J* = 5.1, 1.2 Hz), 7.27 (d, 2H, *J* = 6.4 Hz), 7.27 (d, 2H, *J* = 6.4 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 19.0, 19.0, 27.7, 74.4, 80.2, 92.2, 93.1, 109.3, 123.8, 126.0, 126.7, 127.1, 128.7, 131.0, 133.8, 134.9, 138.9; MS (MALDI-TOF) *m/z* 311 (M^+). Anal. Calcd for $C_{19}H_{15}ClS$: C, 73.41; H, 4.86. Found: C, 73.67; H, 4.92.

4e: Yield 87%; White solid; Mp 62–63 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.88 (tt, 2H, *J* =

7.1, 7.1 Hz), 2.56 (td, 2H, *J* = 7.1, 2.2 Hz), 2.59 (t, 2H, *J* = 7.1 Hz), 6.24 (dt, 1H, *J* = 16.2, 2.2 Hz), 6.89 (d, 2H, *J* = 16.2 Hz), 6.94 (dd, 1H, *J* = 5.1, 3.6 Hz), 7.13 (dd, 1H, *J* = 3.6, 1.2 Hz), 7.18 (dd, 1H, *J* = 5.1, 1.2 Hz), 7.45 (d, 2H, *J* = 8.4 Hz), 7.56 (d, 2H, *J* = 8.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 18.9, 18.9, 27.6, 74.4, 80.0, 93.1, 93.3, 111.4, 123.9, 124.0 (q, $^1J_{F–C}$ = 272 Hz), 125.6 (q, $^3J_{F–C}$ = 3.8 Hz), 126.1, 126.1, 126.8, 129.8 (q, $^2J_{F–C}$ = 32.4 Hz), 131.1, 138.7, 139.8; MS (MALDI-TOF) *m/z* 344 (M^+). Anal. Calcd for $C_{20}H_{15}F_3S$: C, 69.75; H, 4.39. Found: C, 69.76; H, 4.50.

4f: Yield 73%; White solid; Mp; 82-83 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.87 (tt, 2H, *J* = 7.1, 7.1 Hz), 2.55 (td, 2H, *J* = 7.1, 2.2 Hz), 2.59 (t, 2H, *J* = 7.1 Hz), 3.91 (s, 3H), 6.26 (dt, 1H, *J* = 16.2, 2.2 Hz), 6.89 (d, 2H, *J* = 16.2 Hz), 6.94 (dd, 1H, *J* = 5.1, 3.6 Hz), 7.13 (dd, 1H, *J* = 3.6, 1.2 Hz), 7.18 (dd, 1H, *J* = 5.1, 1.2 Hz), 7.41 (d, 2H, *J* = 8.4 Hz), 7.98 (d, 2H, *J* = 8.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 19.0, 19.0, 27.7, 52.1, 74.4, 80.2, 93.1, 93.3, 111.3, 123.8, 125.8, 126.0, 126.7, 129.5, 129.9, 131.1, 139.1, 140.7, 166.6; MS (MALDI-TOF) *m/z* 334 (M^+); Anal. Calcd for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.43. Found: C, 75.37; H, 5.45.

Synthesis of Enediynes 4g,h. Typical Procedure: A mixture of **3c** (520 mg, 2.0 mmol), 2-iodo-5-methoxythiophene (480 mg, 2.0 mmol), $PdCl_2(PPh_3)$ (42 mg, 0.060 mmol), CuI (5.7 mg, 0.030 mmol), triethylamine (1.5 mL), and toluene (4.5 mL) was stirred at room temperature. After 24 h, a fluffy precipitate was formed. The suspension was treated with

saturated aq. NH_4Cl (10 mL) and extracted with Et_2O (15 mL × 2). The combined organic extracts were washed with water (20 mL), saturated aq. $NaHCO_3$ (20 mL), brine (20 mL), and dried over anhydrous Na_2SO_4. After removal of the volatile components under reduced pressure, the residue was subjected to silica gel column chromatography (hexane/AcOEt = 30/1) to afford **4g** (R_f = 0.4) as a yellow solid (200 mg, 27%).

4g: Yield 27%; Mp 32–33 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.85 (tt, 2H, *J* = 7.0, 7.0 Hz), 2.48–2.60 (m, 4H), 3.87 (s, 3H), 6.02 (d, 1H, *J* = 3.9 Hz), 6.24 (m, 1H), 6.78 (d, 1H, *J* = 3.9 Hz), 6.88 (d, 2H, *J* = 16.2 Hz), 7.44 (d, 2H, *J* = 8.4 Hz), 7.56 (d, 2H, *J* = 8.4 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 18.9, 18.9, 27.7, 60.2, 74.9, 80.0, 90.7, 93.4, 103.6, 110.2, 111.5, 125.6 (q, $^3J_{F–C}$ = 3.8 Hz), 126.2, 129.6, 129.8 (q, $^2J_{F–C}$ = 32.4 Hz), 138.7, 139.9, 165.9; MS (MALDI-TOF) *m/z* 374 (M^+); Anal. Calcd for $C_{21}H_{17}F_3OS$: C, 67.36; H, 4.58. Found: C, 67.12; H, 4.56. CF_3 carbon could not be detected clearly in the ^{13}C NMR.

4h: Yield 21%; Yellow solid; Mp 48–49 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.84 (tt, 2H, *J* = 7.0, 7.0 Hz), 2.45–2.64 (m, 4H), 3.87 (s, 3H), 3.91 (s, 3H), 6.02 (d, 1H, *J* = 3.9 Hz), 6.25 (m, 1H), 6.78 (d, 1H, *J* = 3.9 Hz), 6.89 (d, 2H, *J* = 16.2 Hz), 7.41 (d, 2H, *J* = 8.3 Hz), 7.98 (d, 2H, *J* = 8.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 18.9, 18.9, 27.7, 52.1, 60.1, 74.9, 80.2, 90.7, 93.4, 103.6, 110.2, 111.4, 125.9, 129.5, 129.6, 130.0, 139.1, 140.8, 165.9, 166.7; MS (MALDI-TOF) *m/z* 364 (M^+); Anal. Calcd for $C_{22}H_{20}O_3S$: C, 72.50; H, 5.53. Found: C, 72.23; H, 5.32.

Synthesis of Enediyne 4i. To a solution of **3b** (520 mg, 3.0 mmol) in THF (3 mL) was added a hexane solution of *n*-BuLi (1.59 M, 1.9 mL, 3.0 mmol) at 0 °C. After 10 min of stirring, a THF solution (3 mL) of anhydrous zinc chloride (410 mg, 3.0mmol) was added to the solution, and the resulting mixture was stirred for an additional 15 min at room temperature. A solution of 9-(bromomethylene)-9*H*-fluorene (770 mg, 3.0 mmol) in THF (10 mL) and Pd $(PPh_3)_4$ (170 mg, 0.15 mmol) were added to the above solution at 0 °C. The mixture was then stirred for 16 h at room temperature. Diethyl ether (50 mL) and 3% HCl aq (30 mL) were poured into the reaction mixture, and the aqueous phase was extracted with Et_2O (15 mL × 2). The combined organic extracts were washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After removal of the volatile components under reduced pressure, the residue was subjected to silica gel column chromatography (hexane/CH_2Cl_2 = 3/1) to afford **4i** (R_f = 0.6) as a yellow semisolid (650 mg, 62%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.99 (tt, 2H, *J* = 6.9, 6.9 Hz), 2.68 (t, 2H, *J* = 6.8 Hz), 2.79 (td, 2H, *J* = 6.9, 2.7 Hz), 6.58 (t, 1H, *J* = 2.7 Hz), 6.95 (dd, 1H, *J* = 5.1, 3.6 Hz), 7.15 (dd, 1H, *J* = 3.6, 1.2 Hz), 7.19 (dd, 1H, *J* = 5.1, 1.2 Hz), 7.22–7.42 (m, 5H), 7.60–7.72 (m, 3H), 8.50 (d, 1H, *J* = 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 19.0, 19.5, 27.5, 74.6, 80.4, 92.9, 101.8, 104.5, 119.6, 119.7, 120.0, 123.8, 124.5, 126.1, 126.8, 127.0, 127.3, 128.8, 129.0, 131.2, 137.0, 138.3, 139.1, 140.5, 143.5; MS (MALDI-TOF) *m/z* 350 (M^+) Anal. Calcd for $C_{25}H_{18}S$: C, 85.67; H, 5.18. Found: C, 85.37; H, 5.34.

Spectroscopic and Analytical Data for 2-Alkenyl-5-arylphospholes 5b–i:

2-Phenyl-5-[4-(trifluoromethyl)styryl]phosphole 5b: Yield 58%; Yellow solid; Mp 167–168 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.37 (tt, 2H, J = 7.2, 7.2 Hz), 2.54–2.87 (m, 3H), 2.93-3.07 (m, 1H), 6.62 (d, 1H, J = 15.6 Hz), 7.11 (dd, 1H, J = 15.6 Hz, $^{3}J_{P–H}$ = 15.6 Hz), 7.15 (m, 1H), 7.20–7.30 (m, 5H), 7.41 (d, 2H, J = 8.3 Hz), 7.40–7.50 (m, 4H), 7.49 (d, 2H, J = 8.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 27.2 (d, J_{P-C} = 1.7 Hz), 29.2, 29.4, 124.2 (q, $^{1}J_{F–C}$ = 270 Hz), 125.3 (q, $^{3}J_{F–C}$ = 3.8 Hz), 125.8 (d, $J_{P–C}$ = 17.3 Hz), 126.1, 126.4, 127.4 (d, $J_{P–C}$ = 9.9 Hz), 127.5 (d, $J_{P–C}$ = 10.7 Hz), 128.4 (d, $J_{P–C}$ = 1.6 Hz), 128.4 (q, $^{2}J_{F–C}$ = 32.2 Hz), 128.7 (d, $J_{P–C}$ = 8.3 Hz), 129.4 (d, $J_{P–C}$ = 1.7 Hz), 133.1 (d, $J_{P–C}$ = 12.3 Hz), 133.3 (d, $J_{P–C}$ = 18.9 Hz), 135.5, 136.5 (d, $J_{P–C}$ = 18.2 Hz), 138.3, 141.2, 154.0 (d, $J_{P–C}$ = 9.1 Hz), 159.3 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ + 27.6; UV/Vis (THF) λ_{max} (ε) 405 (27800); Fluorescence (THF) λ_{em} (ϕ_f/%) 504 (0.20); MS (MALDI-TOF) m/z 446 (M^+); Anal. Calcd for $C_{28}H_{22}F_3P$: C, 75.33; H, 4.97. Found: C, 75.22; H, 5.01.

2-Thienyl-5-styrylphosphole 5c: Yield 62%; Yellow solid; Mp 148–149 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.27–2.50 (m, 2H), 2.55-2.75 (m, 2H), 2.75–2.95 (m, 2H), 6.60 (d, 1H, J = 15.6 Hz), 6.90 (m, 1H), 6.96 (m, 1H), 7.00 (dd, 1H, J = 15.6 Hz, $^{3}J_{P–H}$ = 15.6 Hz), 7.12–7.17 (m, 2H), 7.23–7.35 (m, 7H), 7.48–7.55 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 27.2 (d, $J_{P–C}$ = 1.3 Hz), 28.8, 29.2 (d, $J_{P–C}$ = 1.3 Hz), 123.5 (d, $J_{P–C}$ = 17.4 Hz), 124.4 (d,

J_{P-C} = 1.9 Hz), 124.4 (d, J_{P-C} = 8.0 Hz), 126.2, 127.1, 127.5, 128.5, 128.8 (d, J_{P-C} = 8.1 Hz), 129.2 (d, J_{P-C} = 10.6 Hz), 129.6 (d, J_{P-C} = 1.3 Hz), 130.9 (d, J_{P-C} = 2.5 Hz), 133.6 (d, J_{P-C} = 12.4 Hz), 133.6 (d, J_{P-C} = 19.8 Hz), 135.6 (d, J_{P-C} = 1.9 Hz), 137.8, 140.4 (d, J_{P-C} = 23.0 Hz), 153.4 (d, J_{P-C} = 8.8 Hz), 157.7 (d, J_{P-C} = 8.1 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ + 29.6; UV/Vis (THF) λ_{max} (ε) 417 (27100); Fluorescence (THF) λ_{em} (ϕ_f/%) 516 (4.3); MS (MALDI-TOF) *m/z* 384 (M^+); Anal. Calcd for $C_{25}H_{21}PS$: C, 78.10; H, 5.51. Found: C, 77.87; H, 5.50.

2-Thienyl-5-(4-chlorostyryl)phosphole 5d: Yield 65%; Yellow solid; Mp 172–173 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25–2.50 (m, 2H), 2.55-3.00 (m, 4H), 6.53 (d, 1H, *J* = 16.0 Hz), 6.90 (m, 1H), 6.96 (m, 1H), 6.97 (dd, 1H, *J* = 16.0 Hz, $^{3}J_{P-C}$ = 16.0 Hz), 7.15 (m, 1H), 7.18–7.32 (m, 7H), 7.48–7.55 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 27.3 (d, J_{P-C} = 1.6 Hz), 28.8, 29.3, 123.9 (d, J_{P-C} = 17.3 Hz), 124.4 (d, J_{P-C} = 8.3 Hz), 124.4 (d, J_{P-C} = 1.6 Hz), 127.2, 127.4, 127.5 (d, J_{P-C} = 10.7 Hz), 128.6, 128.7 (d, J_{P-C} = 8.2 Hz), 129.6 (d, J_{P-C} = 1.7 Hz), 131.2 (d, J_{P-C} = 2.4 Hz), 132.4, 133.3 (d, J_{P-C} = 12.4 Hz), 133.5 (d, J_{P-C} = 19.8 Hz), 135.1 (d, J_{P-C} = 2.5 Hz), 136.2, 140.2 (d, J_{P-C} = 23.1 Hz), 153.2 (d, J_{P-C} = 9.0 Hz), 158.1 (d, J_{P-C} = 8.2 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ + 29.5; UV/Vis (THF) λ_{max} (ε) 420 (31100); Fluorescence (THF) λ_{em} (ϕ_f/%) 522 (2.3); MS (MALDI-TOF) *m/z* 419 (M^+); Anal. Calcd for $C_{25}H_{20}ClPS$: C, 71.68; H, 4.81. Found: C, 71.39; H, 4.83.

2-Thienyl-5-[4-(trifluoromethyl)styryl]phosphole 5e: Yield 66%; Yellow solid; Mp

155–156 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.28–2.52 (m, 2H), 2.52-2.78 (m, 2H), 2.78–3.00 (m, 2H), 6.58 (d, 1H, J = 15.6 Hz), 6.91 (m, 1H), 6.98 (m, 1H), 7.08 (dd, 1H, J = 15.6 Hz, $^{3}J_{P-H}$ = 15.6 Hz), 7.17 (m, 1H), 7.25–7.35 (m, 3H), 7.39 (d, 2H, J = 8.3 Hz), 7.48 (d, 2H, J = 8.3 Hz), 7.45–7.55 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 27.3 (d, J_{P-C} = 1.6 Hz), 28.8, 29.2, 124.0 (q, $^{1}J_{F-C}$ = 272 Hz), 124.7 (d, J_{P-C} = 5.0 Hz), 124.8, 125.4 (q, $^{3}J_{F-C}$ = 3.8 Hz), 125.8 (d, J_{P-C} = 18.0 Hz), 126.1, 127.2 (d, J_{P-C} = 10.6 Hz), 127.6, 128.5 (q, $^{2}J_{F-C}$ = 32.3 Hz), 128.8 (d, J_{P-C} = 8.7 Hz), 129.8 (d, J_{P-C} = 1.2 Hz), 132.0 (d, J_{P-C} = 2.5 Hz), 133.3 (d, J_{P-C} = 13.1 Hz), 133.6 (d, J_{P-C} = 20.5 Hz), 134.9 (d, J_{P-C} = 1.8 Hz), 140.2 (d, J_{P-C} = 23.0 Hz), 141.2, 153.2 (d, J_{P-C} = 8.1 Hz), 159.4 (d, J_{P-C} = 8.7 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ + 29.5; UV/Vis (THF) λ_{max} (ε) 421 (30300); Fluorescence (THF) λ_{em} (ϕ_f/%) 545 (0.27); MS (MALDI-TOF) *m/z* 452 (M^+); Anal. Calcd for $C_{26}H_{20}F_3PS$: C, 69.02; H, 4.46. Found: C, 69.19; H, 4.41.

2-Thienyl-5-[4-(methoxycarbonyl)styryl]phosphole 5f: Yield 59%; Yellow solid; Mp 183–184 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29–2.50 (m, 2H), 2.59-2.77 (m, 2H), 2.78–2.97 (m, 2H), 3.89 (s, 3H), 6.59 (d, 1H, J = 15.6 Hz), 6.91 (m, 1H), 6.98 (m, 1H), 7.11 (dd, 1H, J = 15.6 Hz, $^{3}J_{P-H}$ = 15.6 Hz), 7.17 (m, 1H), 7.26–7.34 (m, 3H), 7.36 (d, 2H, J = 8.1 Hz), 7.48–7.56 (m, 2H), 7.91 (d, 2H, J = 8.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 27.3, 28.7, 29.2, 51.9, 124.6 (d, J_{P-C} = 5.7 Hz), 124.6 125.7, 125.8, 127.4, 127.5 (d, J_{P-C} = 10.7 Hz), 128.0, 128.7 (d, J_{P-C} = 8.2 Hz), 129.6 (d, J_{P-C} = 1.6 Hz), 129.7, 131.9 (d, J_{P-C} = 2.5

Hz), 133.1 (d, J_{P-C} = 12.3 Hz), 133.5 (d, J_{P-C} = 20.6 Hz), 134.9 (d, J_{P-C} = 1.7 Hz), 140.0 (d, J_{P-C} = 23.1 Hz), 142.1, 153.0 (d, J_{P-C} = 8.3 Hz), 159.2 (d, J_{P-C} = 8.3 Hz), 166.7; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ + 29.3; UV/Vis (THF) λ_{max} (ε) 428 (33400); Fluorescence (THF) λ_{em} (ϕ_f/%) 552 (0.25); MS (MALDI-TOF) *m/z* 442 (M^+); Anal. Calcd for $C_{27}H_{23}O_2PS$: C, 73.28; H, 5.24. Found: C, 72.91; H, 5.13.

2-(5-Methoxythienyl)-5-[4-(trifluoromethyl)styryl]phosphole 5g: Yield 58%; Orange solid; Mp 162–163 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25–2.48 (m, 2H), 2.55-2.70 (m, 2H), 2.72–2.88 (m, 2H), 3.84 (s, 3H), 6.01 (d, 1H, *J* = 4.2 Hz), 6.53 (d, 1H, *J* = 15.6 Hz), 6.63 (d, 1H, *J* = 4.2 Hz), 7.06 (dd, 1H, *J* = 15.6 Hz, ^{3}J(P,H) = 15.6 Hz), 7.25–7.33 (m, 3H), 7.38 (d, 2H, *J* = 8.4 Hz), 7.47 (d, 2H, *J* = 8.3 Hz), 7.45–7.55 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 27.3 (d, J_{P-C} = 1.7 Hz), 28.9, 28.9, 69.1, 104.4, 122.8 (q, $^{1}J_{F-C}$ = 271 Hz), 122.9 (d, J_{P-C} = 9.1 Hz), 125.3 (q, $^{3}J_{F-C}$ = 3.8 Hz), 125.8 (d, J_{P-C} = 17.3 Hz), 125.9, 126.4 (d, J_{P-C} = 10.7 Hz), 126.9 (d, J_{P-C} = 24.8 Hz), 128.2 (q, $^{2}J_{F-C}$ = 32.3 Hz), 128.7 (d, J_{P-C} = 8.3 Hz), 129.6, 132.7 (d, J_{P-C} = 2.5 Hz), 133.4 (d, J_{P-C} = 1.6 Hz), 133.4 (d, J_{P-C} = 19.8 Hz), 133.6 (d, J_{P-C} = 12.4 Hz), 141.3, 150.5 (d, J_{P-C} = 8.3 Hz), 159.6 (d, J_{P-C} = 8.3 Hz), 166.3 (d, J_{P-C} = 2.5 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ + 28.7; UV/Vis (THF) λ_{max} (ε) 441 (30900); Fluorescence (THF) λ_{em} (ϕ_f/%) 613 (0.17); MS (MALDI-TOF) *m/z* 483 (M^+); Anal. Calcd for $C_{27}H_{22}F_3OPS$: C, 67.21; H, 4.60. Found: C, 66.96; H, 4.56.

2-(5-Methoxythienyl)-5-[4-(methoxycarbonyl)styryl]phosphole 5h: Yield 60 %; Reddish

orange solid; Mp 210 °C (dec); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25–2.50 (m, 2H), 2.55–2.72 (m, 2H), 2.74–2.90 (m, 2H), 3.84 (s, 3H), 3.88 (s, 3H), 6.01 (d, 1H, J = 4.0 Hz), 6.54 (d, 1H, J = 15.8 Hz), 6.63 (d, 1H, J = 4.0 Hz), 7.09 (dd, 1H, J = 15.8 Hz, $^{3}J_{P–H}$ = 15.8 Hz), 7.25–7.35 (m, 3H), 7.35 (d, 2H, J = 8.4 Hz), 7.45–7.58 (m, 2H); 7.90 (d, 2H, J = 8.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 27.3, 28.8, 28.8 (d, $J_{P–C}$ = 1.6 Hz), 51.9, 60.0, 104.3, 122.8 (d, $J_{P–C}$ = 9.1 Hz), 125.6, 125.9 (d, $J_{P–C}$ = 17.4 Hz), 126.8 (d, $J_{P–C}$ = 9.9 Hz), 127.0 (d, $J_{P–C}$ = 23.9 Hz), 127.8, 128.7 (d, $J_{P–C}$ = 8.3 Hz), 129.5 (d, $J_{P–C}$ = 1.6 Hz), 129.7, 132.7 (d, $J_{P–C}$ = 2.4 Hz), 133.4 (d, $J_{P–C}$ = 19.8 Hz), 133.5 (d, $J_{P–C}$ = 12.4 Hz), 133.4, 142.3, 150.5 (d, $J_{P–C}$ = 8.2 Hz), 159.7 (d, $J_{P–C}$ = 8.2 Hz), 166.2 (d, $J_{P–C}$ = 3.3 Hz), 166.7; ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ + 28.6; UV/Vis (THF) λ_{max} (ε) 450 (36600); Fluorescence (THF) λ_{em} (ϕ_f/%) 622 (0.13); MS (MALDI-TOF) *m/z* 472 (M^+); Anal. Calcd for $C_{28}H_{25}O_3PS$: C, 71.17; H, 5.33. Found: C, 71.45; H, 5.51.

2-Thienyl-5-[(9*H*-fluoren-9-ylidene)methyl]phosphole 5i: Yield 61%; Reddish orange solid; Mp 116–117 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25–2.45 (m, 3H), 2.50–2.70 (m, 1H), 2.70–2.88 (m, 1H), 2.90–3.05 (m, 1H), 6.95 (m, 1H), 7.03 (m, 1H), 7.15–7.35 (m, 8H), 7.42–7.50 (m, 3H), 7.63–7.72 (m, 3H), 8.02 (d, 1H, J = 7.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 28.9, 29.6, 29.9, 119.4, 119.5, 120.0, 122.0 (d, $J_{P–C}$ = 13.9 Hz), 124.5 (d, $J_{P–C}$ = 8.3 Hz), 125.0, 125.0, 126.6, 126.7, 127.4, 127.6, 127.8, 128.6 (d, $J_{P–C}$ = 8.3 Hz), 129.4, 132.4 (d, $J_{P–C}$ = 13.2 Hz), 133.2 (d, $J_{P–C}$ = 4.1 Hz), 133.4 (d, $J_{P–C}$ = 18.1 Hz), 134.3

(d, J_{P-C} = 2.5 Hz), 135.3 (d, J_{P-C} = 7.5 Hz), 136.8, 138.4, 139.6, 139.9 (d, J_{P-C} = 22.2 Hz), 140.7, 152.7 (d, J_{P-C} = 9.9 Hz), 160.4 (d, J_{P-C} = 10.7 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ + 39.3; UV/Vis (THF) λ_{max} (ε) 437 (22400); MS (MALDI-TOF) *m/z* 458 (M^+); Anal. Calcd for $C_{31}H_{23}PS$: C, 81.20; H, 5.06. Found: C, 81.09; H, 5.06.

TABLE S1. Solvatochromism of Absorption and Fluorescence Maxima of **5c**,**e**–**h**, **6**.

	π*[a]	**5c**	**5e**	**5f**	**5g**	**5h**	**6**
cyclohexane	0.00	416; 507	418; 521	424; 528	437; 572	443; 580	432; 542
Et_2O	0.27	414; 513	418; 536	424; 544	437; 595	443; 608	432; 549
dioxane	0.55	417; 515	421; 536	428; 544	440; 599	448; 612	435; 556
THF	0.58	417; 516	421; 545	428; 552	441; 613	450; 622	438; 558
$CHCl_3$	0.58	420; 519	423; 544	431; 557	442; 610	453; 625	435; 555
acetone	0.71	415; 519	419; 548	426; 563	438; 621	447; 636	434; 563
MeCN	0.75	415; 517	418; 548	425; 569	438; 628	445; 646	433; 566
CH_2Cl_2	0.82	419; 520	422; 545	431; 568	441; 617	452; 636	436; 561
DMF	0.88	419; 521	423; 552	431; 573	443; 632	453; 650	438; 567

[a] Kamlet–Taft solvatochromic parameter.[5]

[5] Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

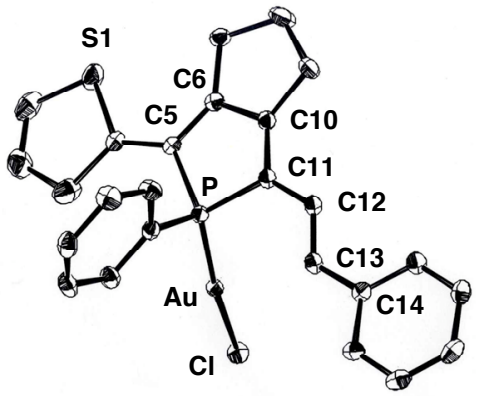

FIGURE S1. ORTEP diagram of **6** (50% probability ellipsoids). Selected bond lengths (Å) and bond angles (°): Au–Cl, 2.3171(6); Au–P, 2.2351(7); P–C5, 1.821(3); P–C11, 1.818(3); P–C20, 1.808(3); C5–C6, 1.355(5); C6–C10, 1.460(3); C10–C11, 1.354(5); C11–C12, 1.445(3); C12–C13, 1.345(5); C13–C14, 1.472(3); C5–P–C11, 93.40(16); C5–P–C20, 106.20(14); C11–P–C20, 107.69(13); Au–P–C5, 111.82(7); Au–P–C11, 116.26(9); Au–P–C20, 118.29(13); P–Au–Cl, 171.08(4).

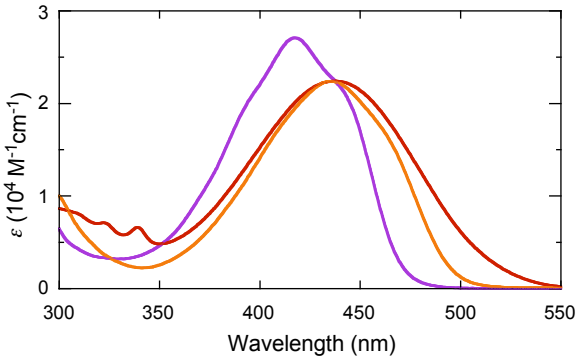

Figure S2. UV-vis absorption spectra of **5c** (purple), **5i** (red), and **6** (orange) in THF.

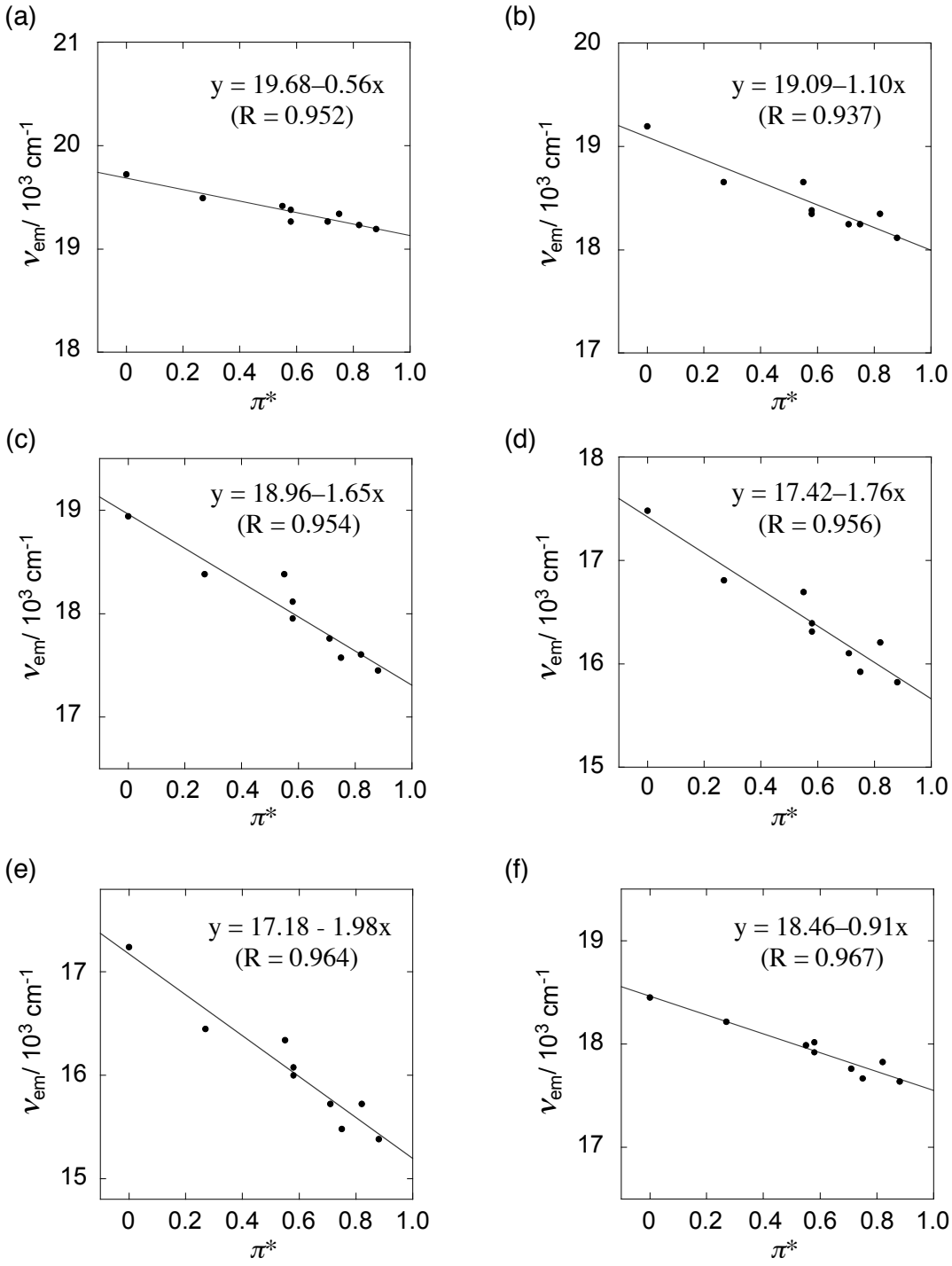

Figure S3. Kamlet–Taft analyses for the fluorescence spectra of of 2-aryl-5-styrylphospholes **5c**,**e**–**h**, **6**. (a) **5c**, (b) **5e**, (c) **5f**, (d) **5g**, (e) **5h**, (f) **6**.

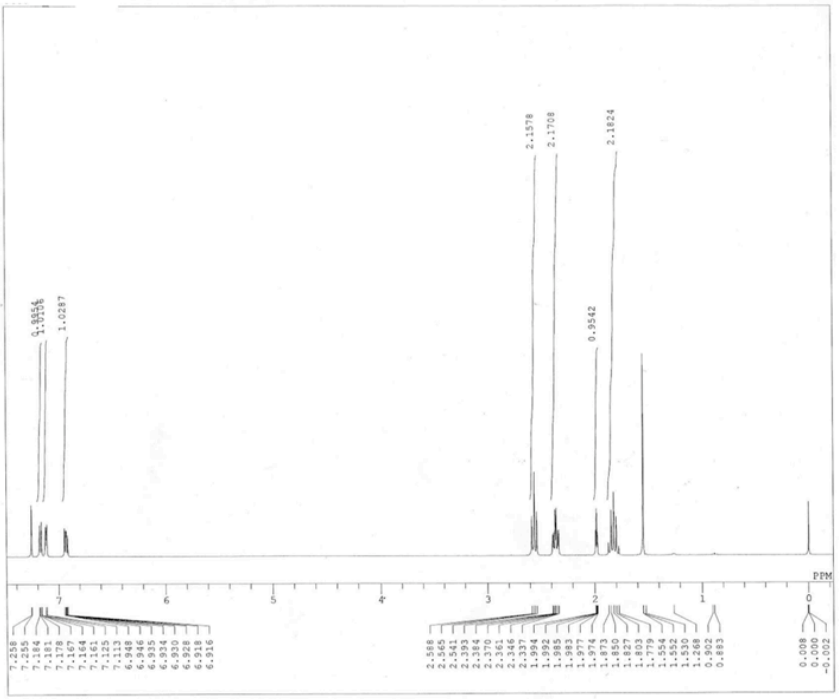

Figure S4. ^{1}H NMR spectrum of 3b in $CDCl_3$ (400 MHz).

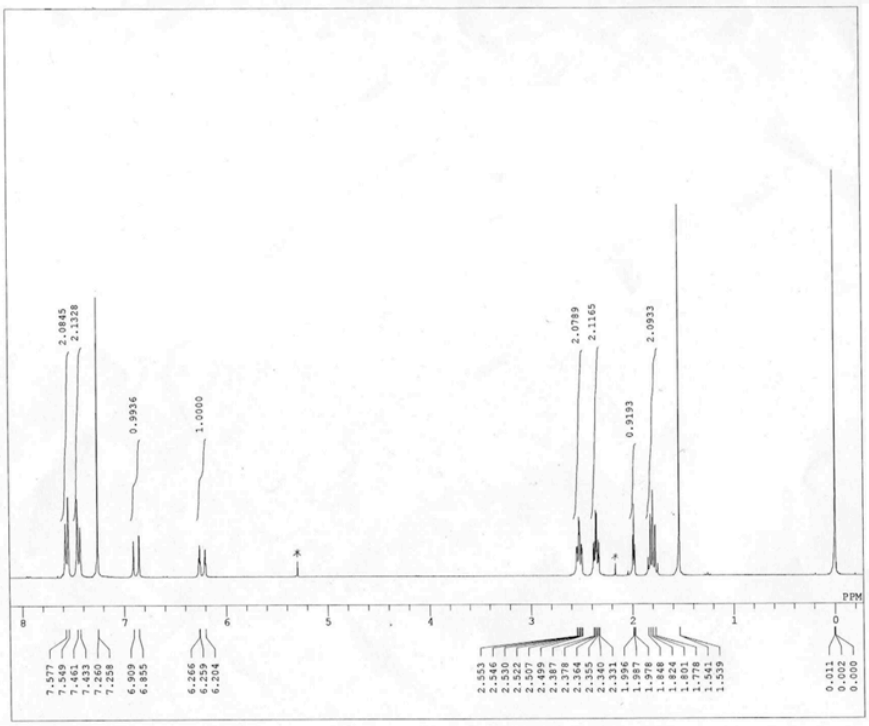

Figure S5. ^{1}H NMR spectrum of 3c in $CDCl_3$ (300 MHz).

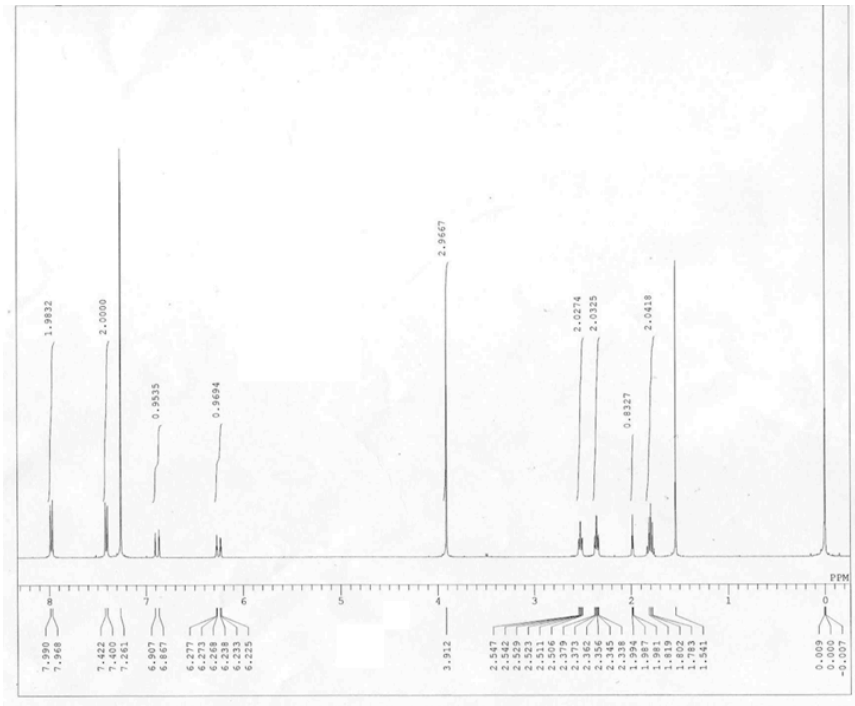

Figure S6. ^{1}H NMR spectrum of 3d in $CDCl_3$ (300 MHz).

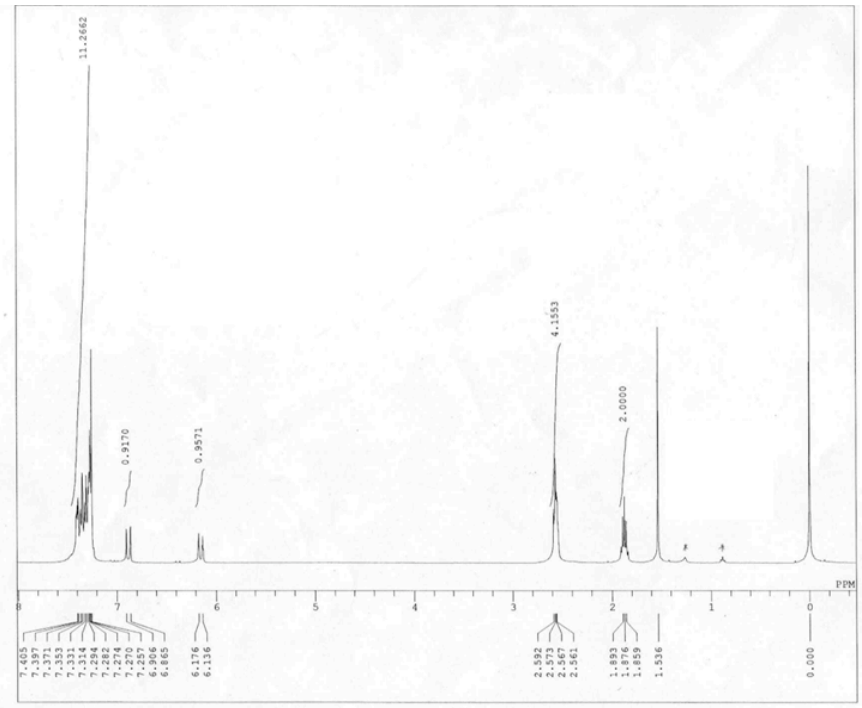

Figure S7. ^{1}H NMR spectrum of 4a in $CDCl_3$ (300 MHz).

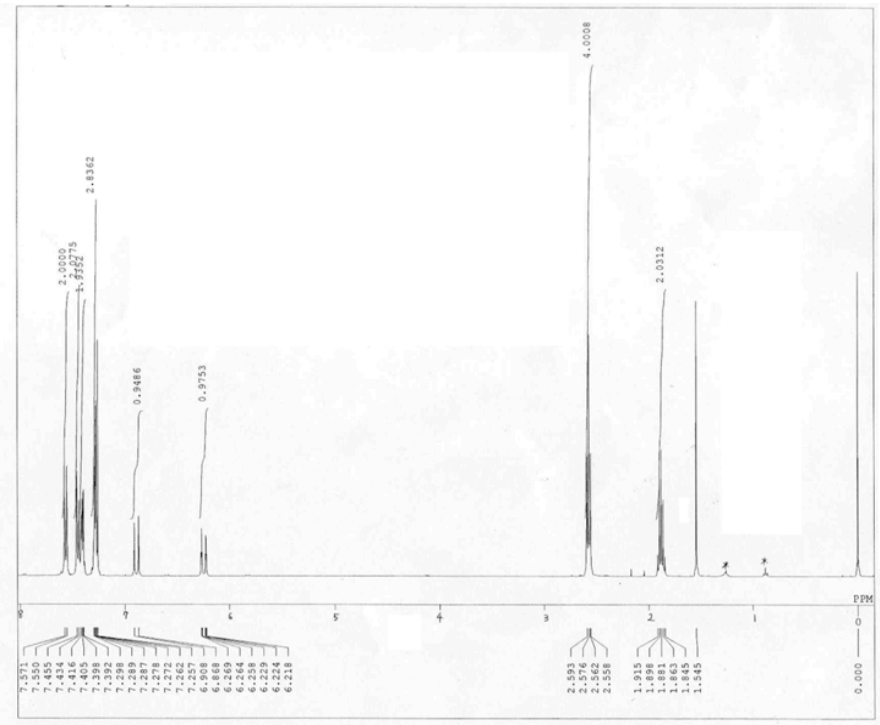

Figure S8. ^{1}H NMR spectrum of 4b in $CDCl_3$ (400 MHz).

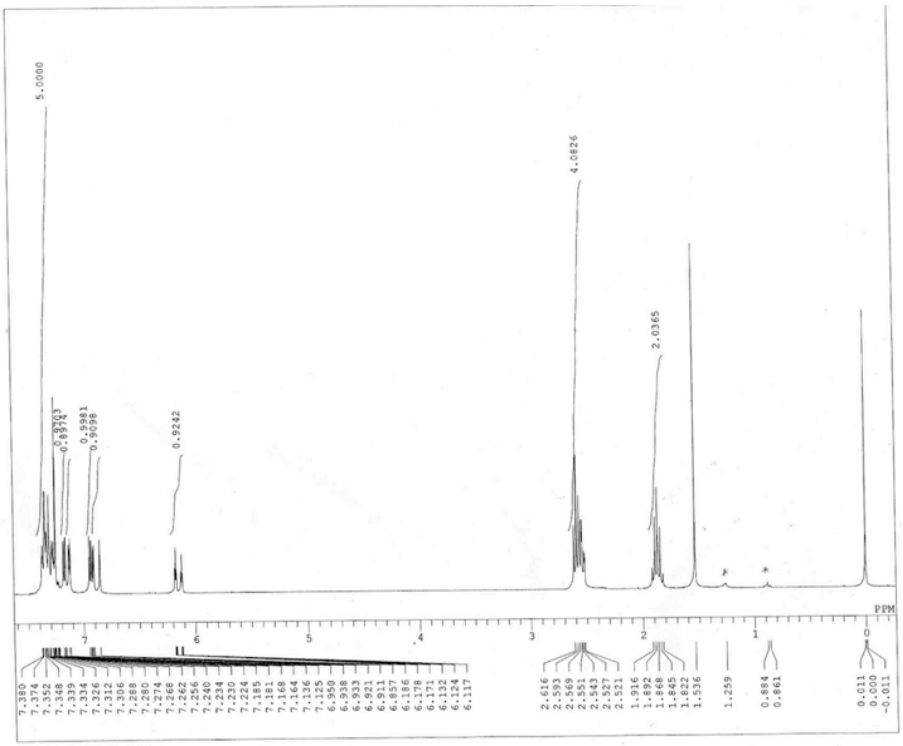

Figure S9. ^{1}H NMR spectrum of 4c in $CDCl_3$ (300 MHz).

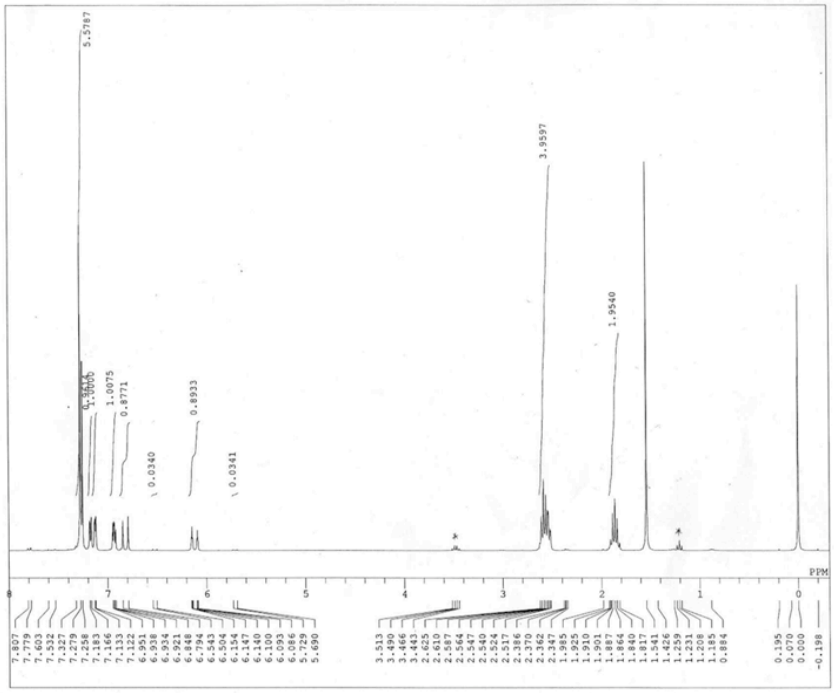

Figure S10. ^{1}H NMR spectrum of 4d in $CDCl_3$ (400 MHz).

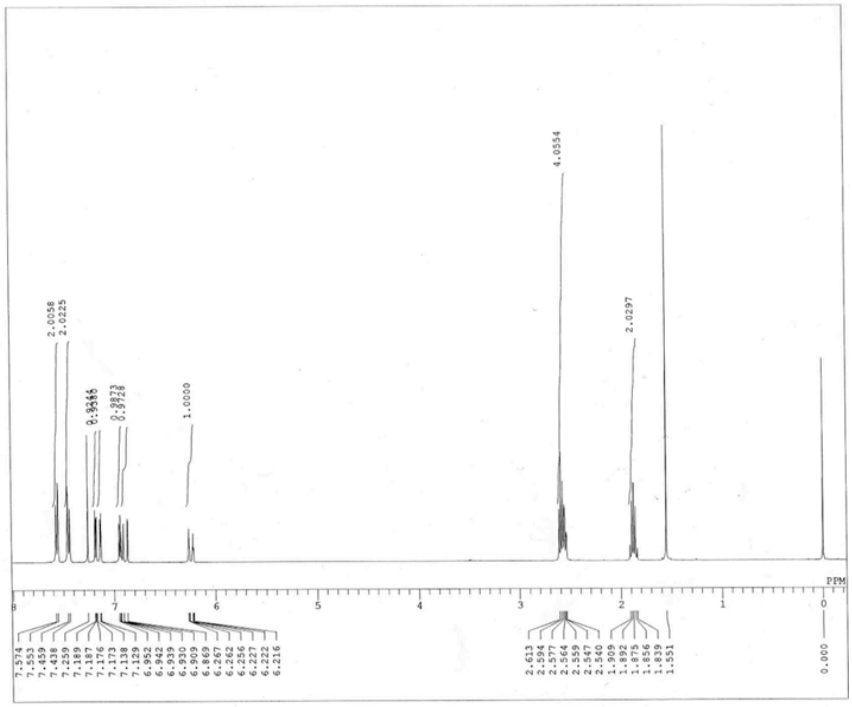

Figure S11. ^{1}H NMR spectrum of 4e in $CDCl_3$ (400 MHz).

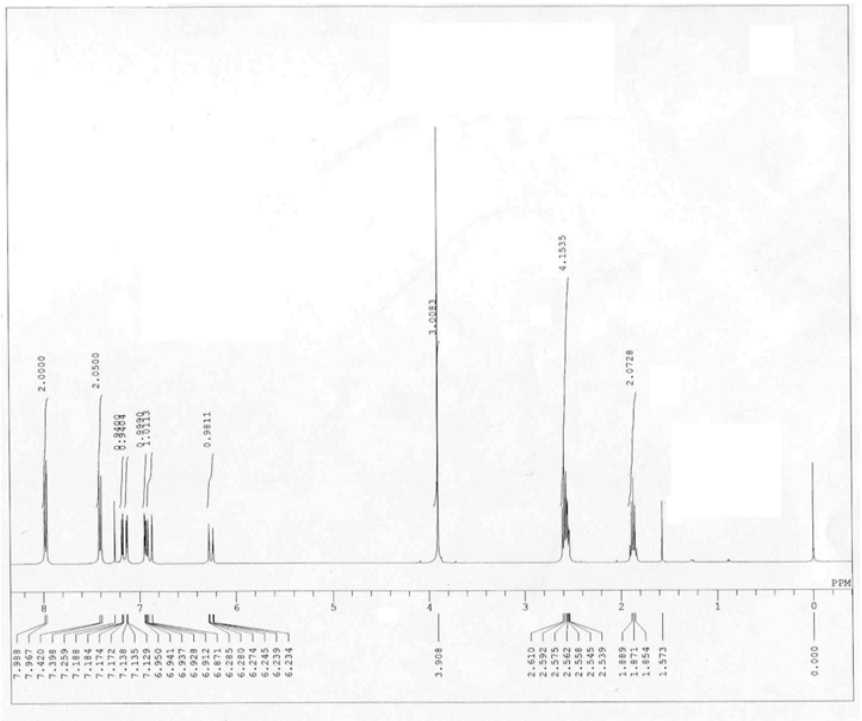

Figure S12. ^{1}H NMR spectrum of 4f in $CDCl_3$ (400 MHz).

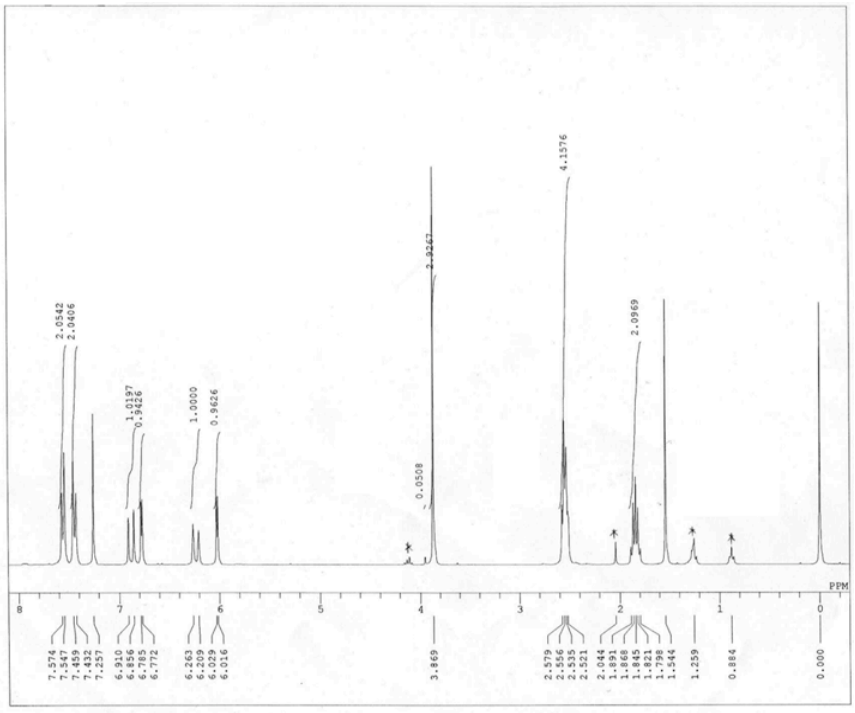

Figure S13. ^{1}H NMR spectrum of 4g in $CDCl_3$ (300 MHz).

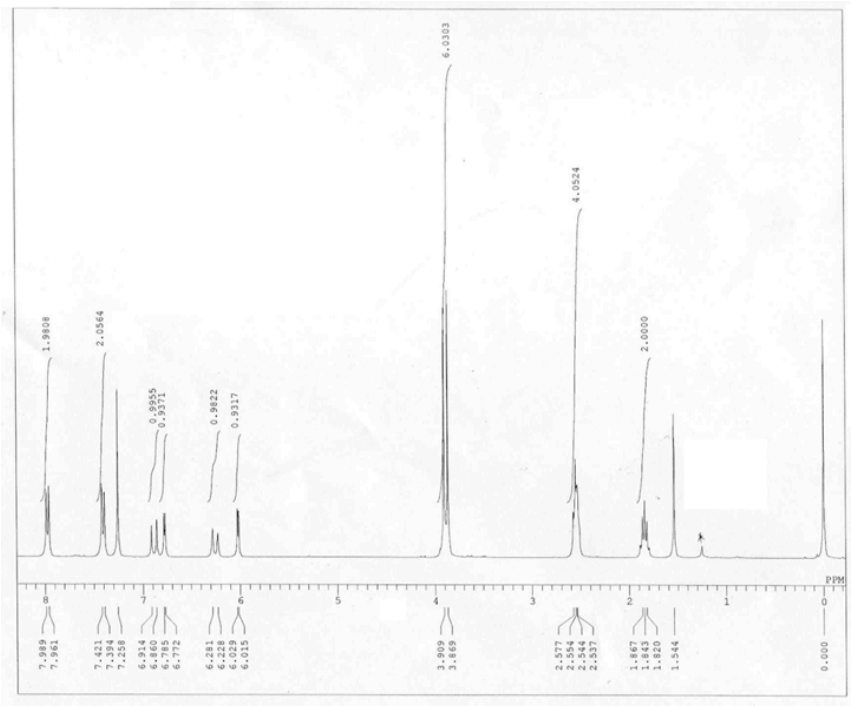

Figure S14. ^{1}H NMR spectrum of 4h in $CDCl_3$ (300 MHz).

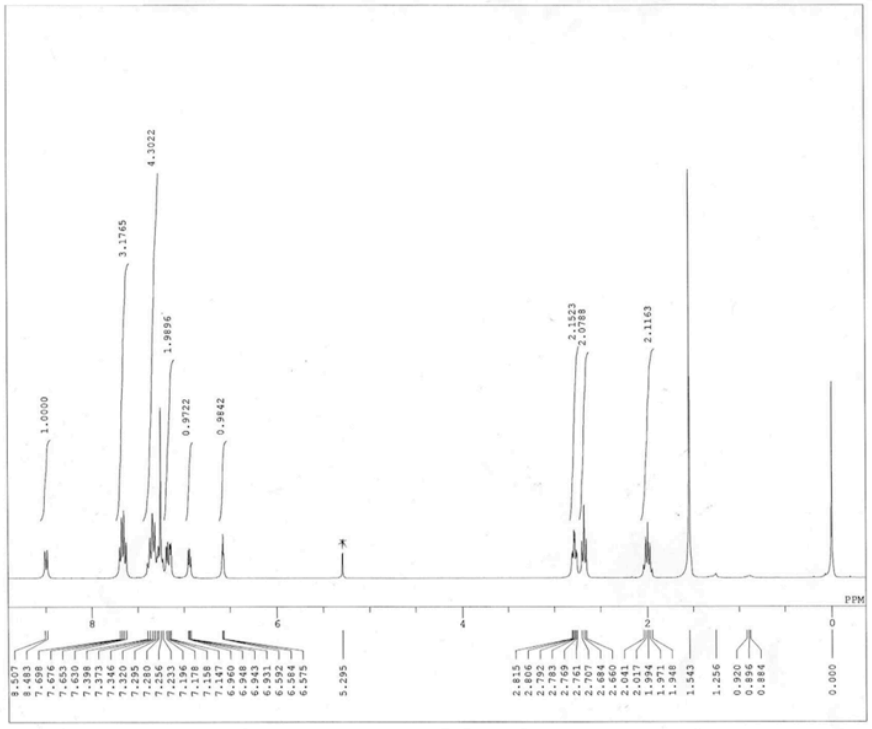

Figure S15. ^{1}H NMR spectrum of 4i in $CDCl_3$ (300 MHz).

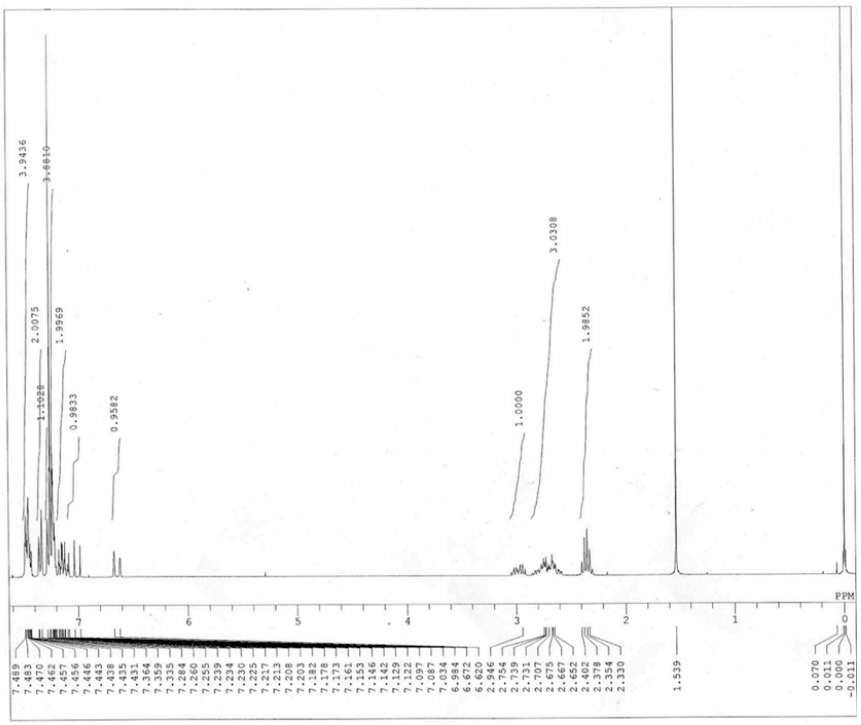

Figure S16. ^{1}H NMR spectrum of 5a in $CDCl_3$ (300 MHz).

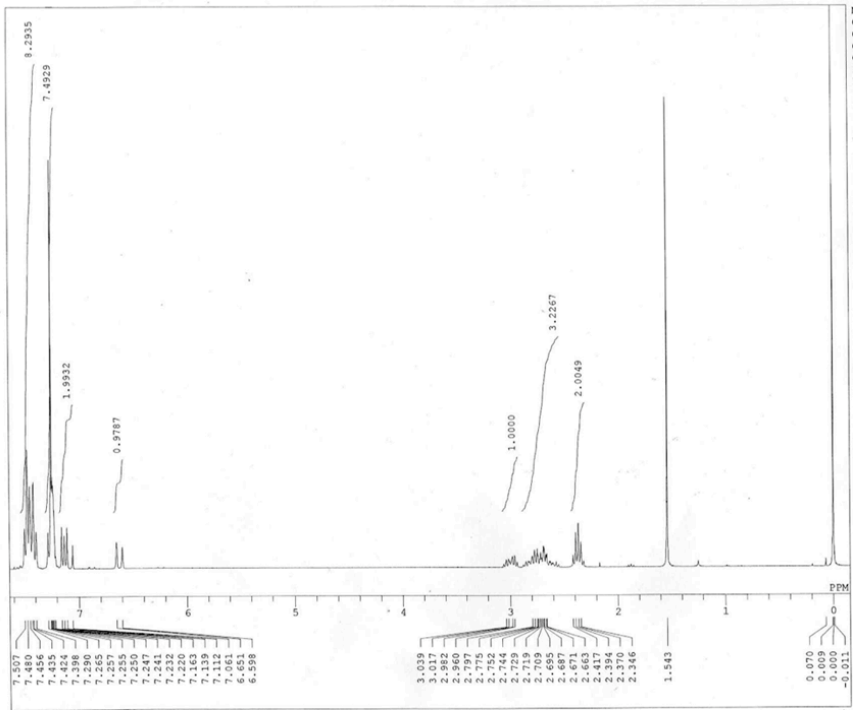

Figure S17. ^{1}H NMR spectrum of 5b in $CDCl_3$ (300 MHz).

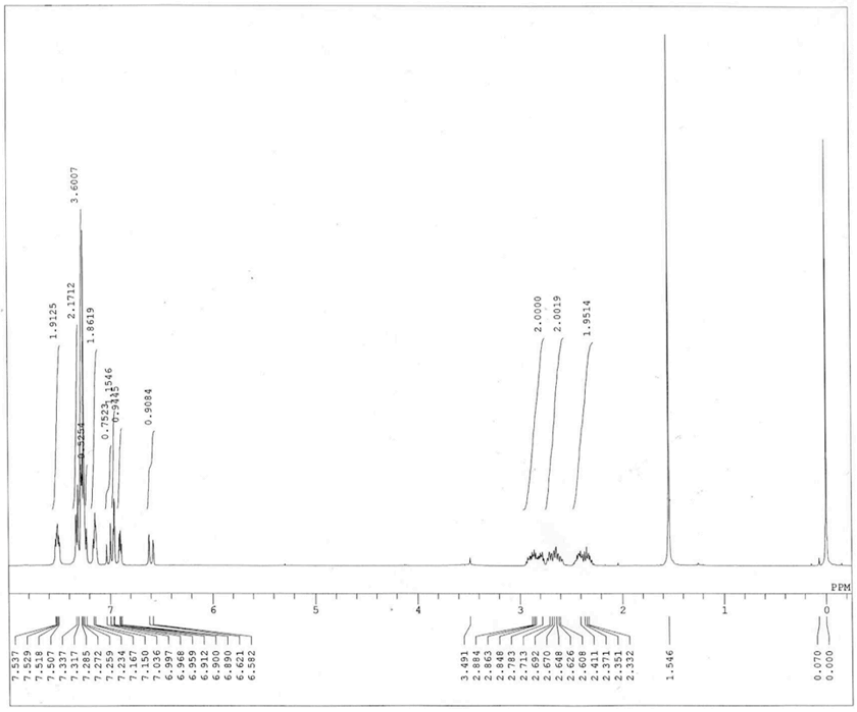

Figure S18. ^{1}H NMR spectrum of 5c in $CDCl_3$ (400 MHz).

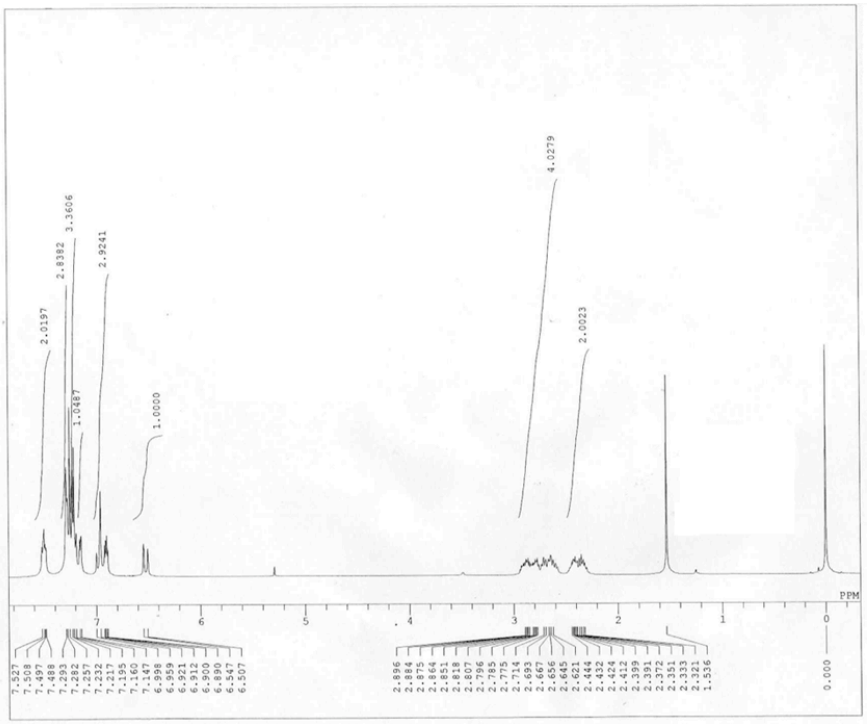

Figure S19. ^{1}H NMR spectrum of 5d in $CDCl_3$ (400 MHz).

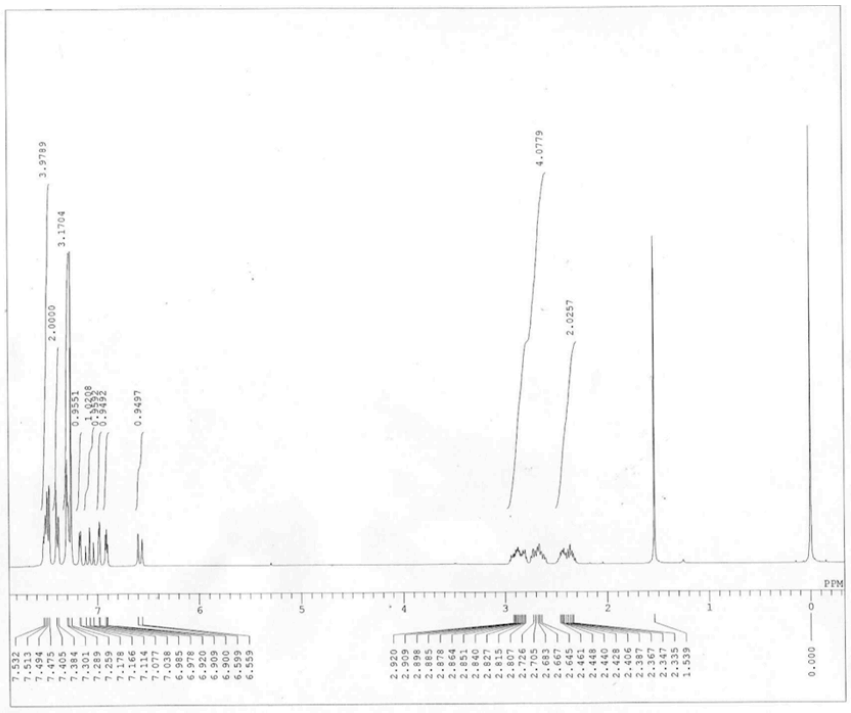

Figure S20. ^{1}H NMR spectrum of 5e in $CDCl_3$ (300 MHz).

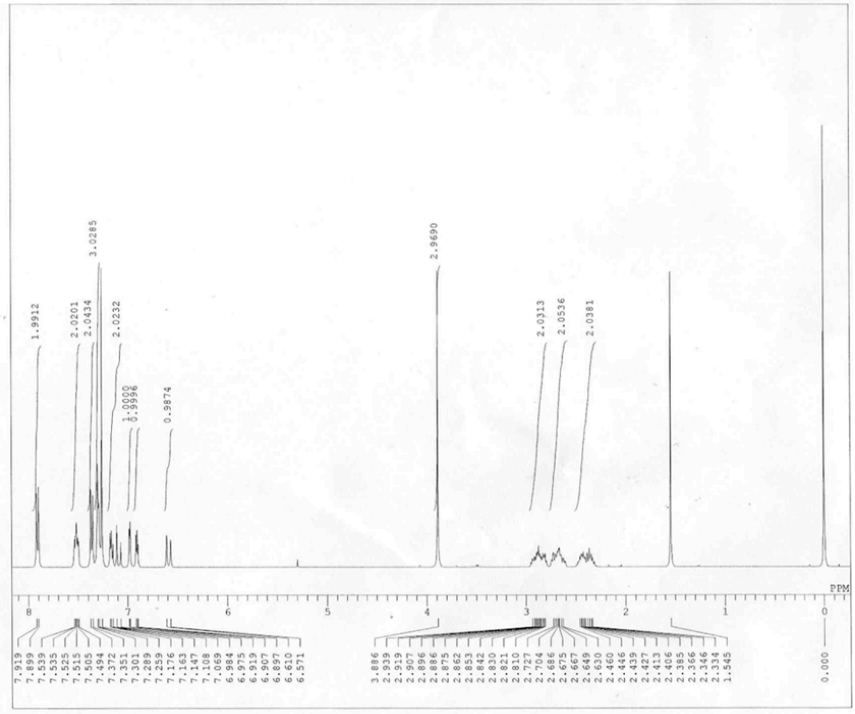

Figure S21. ^{1}H NMR spectrum of 5f in $CDCl_3$ (400 MHz).

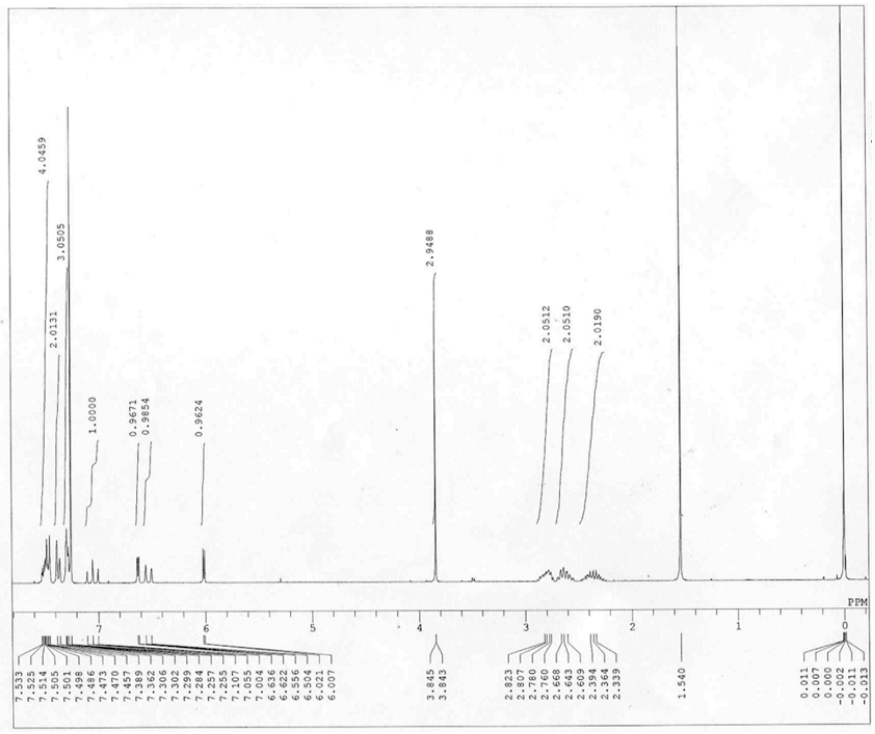

Figure S22. ^{1}H NMR spectrum of 5g in $CDCl_3$ (300 MHz).

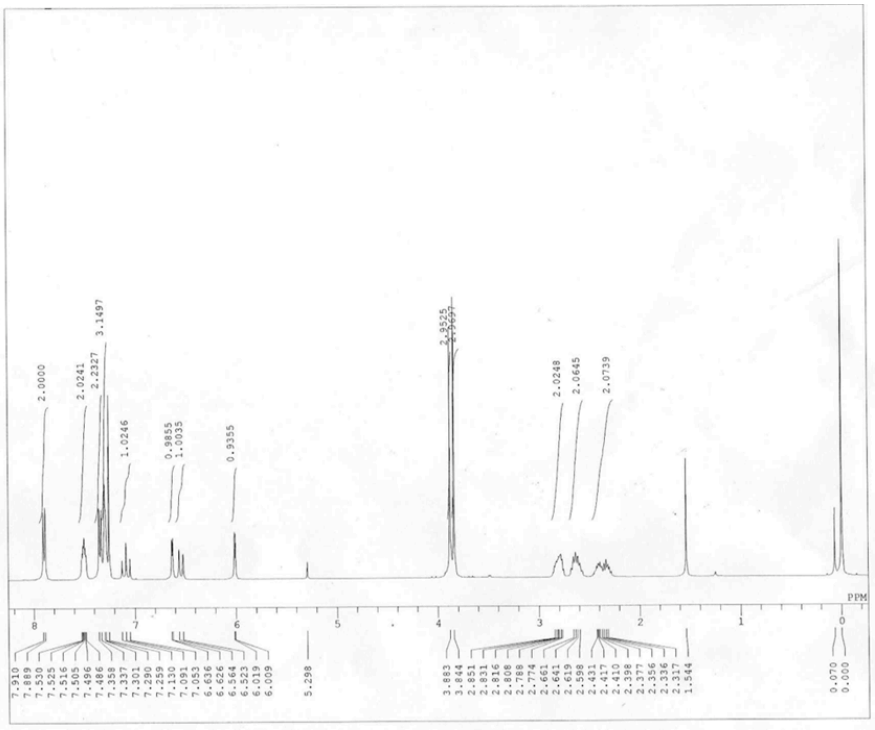

Figure S23. ^{1}H NMR spectrum of 5h in $CDCl_3$ (400 MHz).

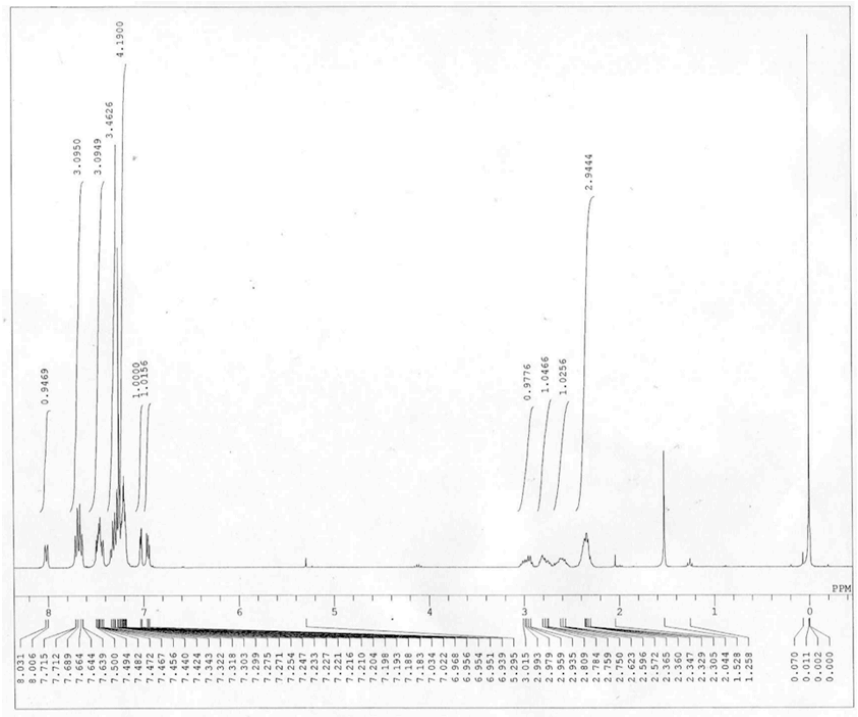

Figure S24. ^{1}H NMR spectrum of 5i in $CDCl_3$ (400 MHz).

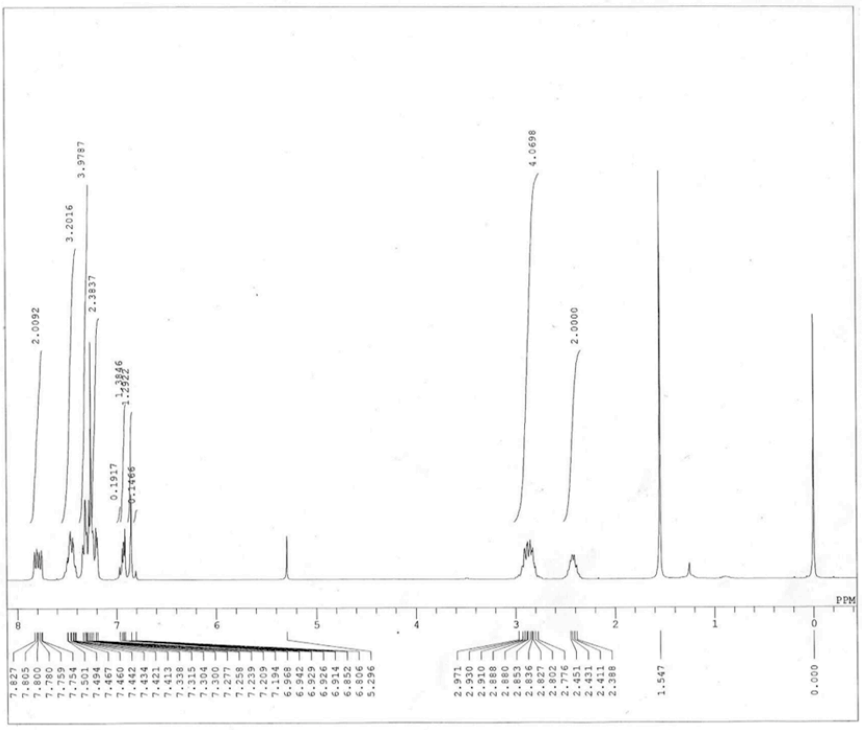

Figure S25. ^{1}H NMR spectrum of 6 in $CDCl_3$ (400 MHz).