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SUPPLEMENTARY MATERIAL TO

Stereoselective synthesis of (–)-tetrahydropyrenophorol

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SPECTRAL DATA FOR THE SYNTHESIZED COMPOUNDS

*(*R*)-5-(4-Methoxybenzyloxy)-1-(2-vinyl-1,3-dithian-2-yl)pentan-2-ol* ***(3)***. Anal. calcd. for $C_{19}H_{28}O_3S_2$: C, 61.92; H, 7.66; S, 17.40 %. Found: C, 61.89; H, 7.72; S, 17.35 %; FTIR (neat, cm^{-1}): 3429, 2971, 1619, 1436, 1267, 1023, 941, 771; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.21 (2H, *d*, *J* = 8.3 Hz), 6.81 (2H, *d*, *J* = 8.3 Hz), 5.91–5.73 (1H, *m*), 5.04–4.88 (2H, *m*), 4.51 (2H, *s*), 3.94–3.82 (1H, *m*), 3.70 (3H, *s*), 3.47 (2H, *t*, *J* = 6.3 Hz), 2.88–2.78 (4H, *m*), 1.93–1.79 (2H, *m*), 1.74–1.61 (3H, *m*), 1.51–1.28 (3H, *m*); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 159.3, 135.6, 129.8, 129.4, 119.1, 113.7, 79.2, 72.4, 69.7, 55.6, 54.2, 50.6, 36.7, 31.3, 27.3, 24.2; ESIMS: 391 $(M+Na)^+$; $[\alpha]_D$ (*c*: 0.6 mol/L, $CHCl_3$): +18.8.

*(*R*)-*tert*-Butyl(5-(4-methoxybenzyloxy)-1-(2-vinyl-1,3-dithian-2-yl)pentan-2--yloxy)di-phenylsilane* ***(6)***. Anal. calcd. for $C_{35}H_{46}O_3S_2Si$: C, 69.26; H, 7.64; S, 10.57 %. Found: C, 69.23; H, 7.70; S, 10.52 %; FTIR (neat, cm^{-1}): 3069, 2931, 2858, 1612, 1512, 1427, 1373, 1246, 1104, 1076, 701; ^{1}H-NMR (300 MHz, $CDCl_3$, δ /): 7.70–7.45 (4H, *m*), 7.41–7.34 (6H, *m*), 7.23 (2H, *d*, *J* = 8.4 Hz), 6.83 (2H, *d*, *J* = 8.4 Hz), 5.85–5.75 (1H, *m*), 5.09–4.95 (2H, *m*), 4.49 (2H, *s*), 3.85–3.75 (1H, *m*), 3.69 (3H, *s*), 3.51 (2H, *t*, *J* = 6.1 Hz), 2.91–2.80 (4H, *m*), 1.91–1.81 (2H, *m*), 1.77–1.65 (2H, *m*), 1.57–1.33 (4H, m), 0.91 (9H, s); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 159.1, 135.3, 134.6, 132.7, 129.9, 129.5, 129.1, 127.3, 119.0, 113.6, 79.6, 79.1, 72.3, 55.5, 53.9, 50.1, 35.6, 32.4, 27.6, 26.3, 24.3, 18.9; ESIMS: 629 $(M+Na)^+$; $[\alpha]_D$ (*c*: 1.1 mol/L, $CHCl_3$): +36.9.

*(*S*)-1-(2-((*R*)-2-(*tert*-Butyldiphenylsilyloxy)-5-(4-methoxybenzyloxy)pentyl)--1,3-dithian-2-yl)ethane-1,2-diol* ***(7)***. Data for major isomer. Anal. calcd. for $C_{35}H_{48}O_5S_2Si$: C, 65.58; H, 7.55; S, 10.01 %. Found: C, 65.53; H, 7.45; S, 10.05 %; FTIR (neat, cm^{-1}): 3448, 3057, 2930, 2851, 1610, 1513, 1465, 1247, 1079,

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936, 704; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.75–7.61 (4H, *m*), 7.49–7.31 (6H, *m*), 7.19 (2H, *d*, *J* = 8.1 Hz), 6.79 (2H, *d*, *J* = 8.1 Hz), 4.59 (1H, *d*, *J* =11.2 Hz), 4.40 (1H, *d*, *J* =11.2 Hz), 4.04–3.91 (2H, *m*), 3.88–3.74 (2H, *m*), 3.68 (3H, *s*), 3.49 (2H, *t*, *J* = 6.2 Hz), 2.93–2.79 (4H, *m*), 1.89–1.77 (2H, *m*), 1.73–1.61 (2H, *m*), 1.54–1.31 (4H, *m*), 0.93 (9H, *s*); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 159.0, 134.3, 132.8, 130.1, 129.8, 129.0, 127.5, 114.1, 79.9, 79.0, 72.3, 71.6, 66.4, 55.1, 49.3, 35.2, 32.0, 28.2, 26.1, 24.2, 19.0; ESIMS: 641 $(M+H)^+$; $[\alpha]_D$ (*c*: 0.9 mol/L, $CHCl_3$): +69.6.

*(*S*)-1-(2-((*R*)-2-(*tert*-Butyldiphenylsilyloxy)-5-(4-methoxybenzyloxy)pentyl)--1,3-dithian-2-yl)ethanol (**8**)*. Anal. calcd. for $C_{35}H_{48}O_4S_2Si$: C, 67.26; H, 7.74; S, 10.26 %. Found: C, 67.23; H, 7.55; S, 10.15 %; FTIR (neat, cm^{-1}): 3383, 3032, 2863, 1614, 1451, 1366, 974, 714; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.75–7.63 (4H, *m*), 7.51–7.39 (6H, *m*), 7.23 (2H, *d*, *J* = 8.3 Hz), 6.83 (2H, *d*, *J* = 8.3 Hz), 4.49 (2H, *s*), 4.09–4.01 (1H, *m*), 3.90–3.82 (1H, *m*), 3.71 (3H, *s*), 3.51 (2H, *t*, *J* = 6.0 Hz), 2.93–2.81 (4H, *m*), 1.98–1.98 (2H, *m*), 1.81–1.70 (2H, *m*), 1.51–1.33 (4H, *m*), 1.22 (3H, *d*, *J* = 6.3 Hz), 0.93 (9H, *s*); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 159.2, 134.1, 132.0, 129.9, 129.7, 129.0, 127.6, 113.8, 79.7, 79.0, 72.3, 71.0, 69.8, 55.2, 48.8, 35.0, 31.9, 28.1, 26.0, 24.1, 19.1, 18.4; ESIMS: 625 $(M+H)^+$; $[\alpha]_D$ (*c*: 0.8 mol/L, $CHCl_3$): +145.9.

tert-*Butyl((*R*)-1-(2-((*S*)-1-(*tert*-butyldimethylsilyloxy)ethyl)-1,3-dithian-2-yl)--5-(4-methoxybenzyloxy)pentan-2-yloxy)diphenylsilane (**9**)*. Anal. calcd. for $C_{41}H_{62}O_4S_2Si_2$: C, 66.62; H, 8.45; S, 8.68 %. Found: C, 66.57; H, 8.55; S, 8.65 %; FTIR (neat, cm^{-1}): 3021, 2932, 1612, 1511, 1444, 1386, 1164, 1037, 712; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.66–7.52 (4H, *m*), 7.49–7.34 (6H, *m*), 7.21 (2H, *d*, *J* = 8.2 Hz), 6.81 (2H, *d*, *J* = 8.2 Hz), 4.47 (2H, *s*), 3.88–3.77 (1H, *m*), 3.72 (3H, *s*), 3.75–3.65 (1H, *m*), 3.54 (2H, *t*, *J* = 6.3 Hz), 2.89–2.70 (4H, *m*), 1.93–1.78 (3H, *m*), 1.59–1.36 (5H, *m*), 1.19 (3H, *d*, *J* = 6.1 Hz), 0.91 (9H, *s*), 0.88 (9H, *s*), 0.14 (3H, *s*), 0.08 (3H, *s*); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 159.4, 134.3, 132.1, 129.7, 129.0, 128.7, 127.3, 113.6, 80.1, 79.2, 72.8, 71.3, 70.4, 55.0, 48.6, 35.3, 32.0, 28.3, 26.1, 25.8, 24.1, 19.3, 18.5, 18.3, –4.1, –4.5; ESIMS: 739 $(M+H)^+$; $[\alpha]_D$ (*c*: 0.6 mol/L, $CHCl_3$): +117.8.

*(4*R*,7*S*)-7-(*tert*-Butyldimethylsilyloxy)-4-(*tert*-butyldiphenylsilyloxy)octan-1--ol (**10**)*. Anal. calcd. for $C_{30}H_{50}O_3Si_2$: C, 69.98; H, 9.79 %. Found: C, 69.89; H, 9.85 %; FTIR (neat, cm^{-1}) 3443, 3039, 2932, 2859, 1615, 1513, 1465, 1247, 1077, 936, 701; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.65–7.55 (4H, *m*), 7.39–7.29 (6H, *m*), 3.72–3.61 (1H, *m*), 3.51 (2H, *t*, *J* = 6.1 Hz), 3.50–3.41 (1H, *m*), 1.72–1.50 (6H, *m*), 1.48–1.32 (2H, *m*), 1.26 (3H, *d*, *J* = 6.2 Hz), 0.94 (9H, *s*), 0.87 (9H, *s*), 0.17 (3H, *s*), 0.03 (3H, *s*); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 135.3, 133.0, 130.1, 128.3, 80.1, 73.1, 71.9, 62.6, 51.3, 36.4, 34.7, 28.6, 26.2, 25.9, 24.2, 19.3, 18.6, 18.4, –4.2, –4.8; ESIMS: 515 $(M+H)^+$; $[\alpha]_D$ (*c*: 0.8 mol/L, $CHCl_3$): +52.6.

*(4*S*,7*S*)-7-(*tert-*Butyldimethylsilyloxy)-4-*(tert-*butyldiphenylsilyloxy)octanoic acid (**11**)*. Anal. calcd. for $C_{30}H_{48}O_4Si_2$: C, 68.13; H, 9.15 %. Found: C, 68.09; H, 9.25 %; FTIR (neat, cm^{-1}): 3532, 3031, 2930, 2857, 1718, 1609, 1239, 1097, 711; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.64–7.48 (4H, *m*), 7.43–7.30 (6H, *m*), 3.71–3.58 (1H, *m*), 3.52–3.39 (1H, *m*), 2.49–2.33 (2H, *m*), 1.66–1.39 (6H, *m*), 1.11 (3H, *d*, *J* = 6.3 Hz), 0.98 (9H, *s*), 0.91 (9H, *s*), 0.14 (3H, *s*), 0.08 (3H, *s*); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 179.3, 136.1, 132.7, 130.1, 127.9, 79.6, 67.8, 37.3, 32.1, 30.8, 30.1, 26.1, 25.8, 24.2, 19.3, 18.4, –4.1, –4.4;. ESIMS: 529 $(M+H)^+$; $[\alpha]_D$ (*c*: 0.42 mol/L, $CHCl_3$): +22.24

*(4*S*,7*S*)-4-(*tert-*Butyldiphenylsilyloxy)-7-hydroxyoctanoic acid (**2**)*. Anal. calcd. for $C_{24}H_{34}O_4Si$: C, 69.52; H, 8.27 %. Found: C, 69.49; H, 8.35 %; FTIR (neat, cm^{-1}): 3451, 2927, 2857, 1720, 1612, 1514, 1360, 1041, 777; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.68–7.58 (4H, *m*), 7.43–7.31 (6H, *m*), 3.69–3.57 (1H, *m*), 3.44–3.39 (m, 1H), 2.36 (2H, *t*, *J* = 6.6 Hz), 1.71–1.31 (6H, *m*), 1.21 (3H, d, *J* = 6.0 Hz), 0.94 (9H, *s*); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 178.3, 135.6, 133.0, 129.9, 128.1, 80.3, 68.3, 37.7, 32.1, 21.6, 28.7, 26.4, 24.2, 19.0; ESIMS: 415 $(M+ H)^+$; $[\alpha]_D$ (*c*: 0.6 mol/L, $CHCl_3$): +75.6.

*(5*S*,8*R*,13*S*,16*R*)-5,13-Bis(*tert-*butyldiphenylsilyloxy)-8,16-dimethyl-1,9-di-oxacyclo-hexadecane-2,10-dione (**12**)*. Anal. calcd. for $C_{48}H_{64}O_6Si_2$: C, 72.68; H, 8.13 %. Found: C, 72.63; H, 8.25 %; FTIR (neat, cm^{-1}): 3416, 3068, 2932, 2859, 1727, 1608, 1527, 1462, 1427, 1273, 1105, 918, 702; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.71–7.60 (8H, *m*), 7.43–7.31 (12H, *m*), 4.99–4.85 (2H, *m*), 3.69–3.61 (2H, *m*), 2.56 (4H, *t*, *J* = 7.1 Hz), 1.77–1.54 (8H, *m*), 1.51–1.32 (4H, *m*), 1.18 (6H, *d*, *J* = 6.2 Hz), 1.01 (18H, *s*); ^{13}C-NMR (75 MHz , $CDCl_3$, δ / ppm): 174.3, 135.0, 133.1, 129.7, 127.6, 80.2, 73.4, 38.0, 32.3, 30.7, 28.6, 26.7, 20.3, 19.2; ESIMS: 793 $(M+ H)^+$; $[\alpha]_D$ (*c*: 1.03 mol/L, $CHCl_3$): –15.7.

*(–)-Tetrahydropyrenophorol (**1**)*. FTIR (neat, cm^{-1}): m.p.: 126–128 °C; 3420, 2985, 2844, 1730, 1701, 1335, 1260, 1164, 1065; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 5.05–4.95 (2H, *m*), 3.59–3.47 (2H, *m*), 2.51–2.28 (4H, *m*), 1.99–1.77 (4H, *m*), 1.80–1.64 (4H, *m*), 1.58–1.42 (2H, *m*), 1.38–1.28 (2H, *m*), 1.23 (6H, *d*, *J* = 6.6 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 173.7, 69.6, 68.9, 33.2, 31.3, 30.9, 30.9, 19.8; ESIMS: 317 $(M+ H)^+$; $[\alpha]_D^{25}$ (*c*: 0.3, $CHCl_3$): −64.7. Lit:[12] $[\alpha]_D$ (*c*: 0.14 mol/L, $CHCl_3$): –68.

^{1}H-NMR AND ^{13}C-NMR SPECTRA OF THE SYNTHESIZED COMPOUNDS

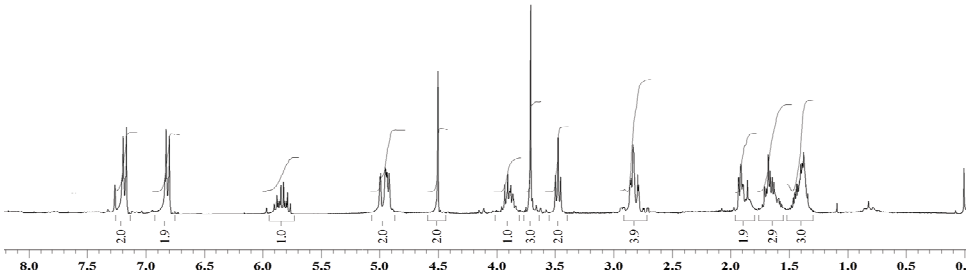

Fig. S-1. ^{1}H-NMR spectrum of compound **3**.

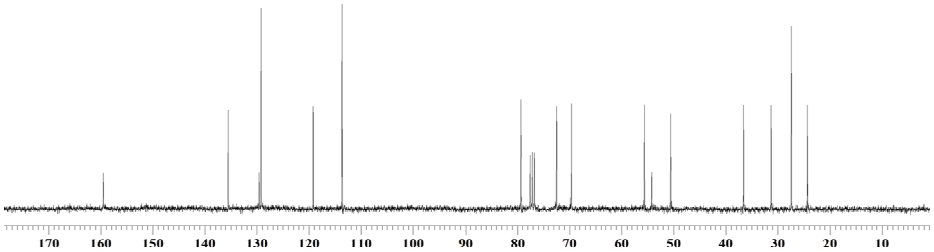

Fig. S-2. ^{13}C-NMR spectrum of compound **3**.

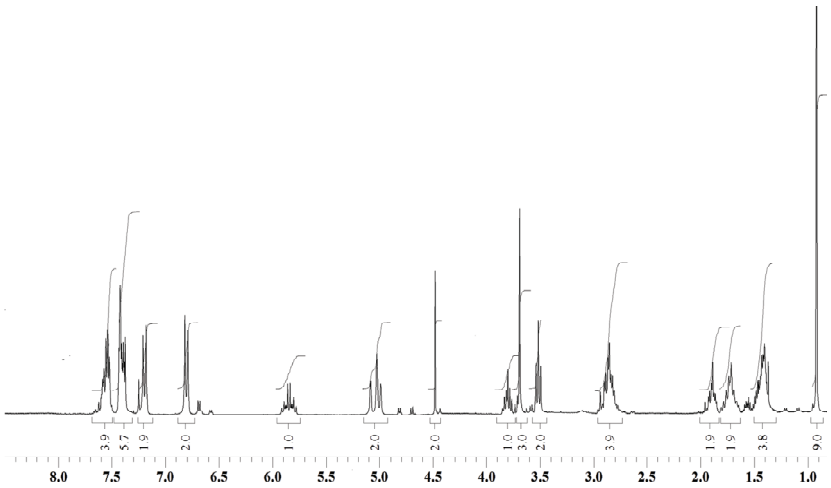

Fig. S-3. ^{1}H-NMR spectrum of compound **6**.

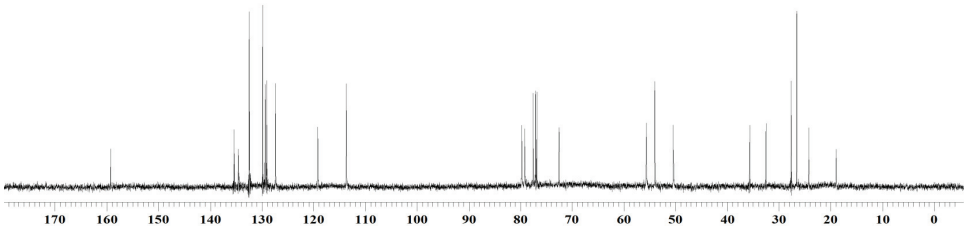

Fig. S-4. ^{13}C-NMR spectrum of compound **6**.

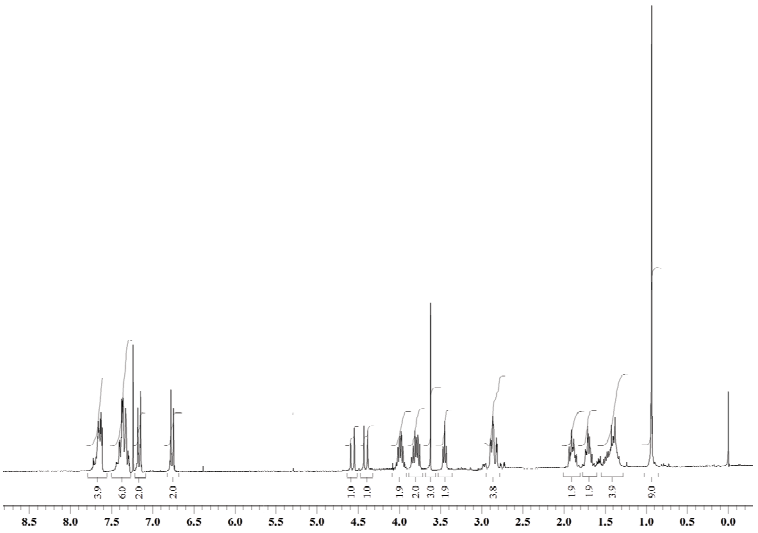

Fig. S-5. ^{1}H-NMR spectrum of compound **7**.

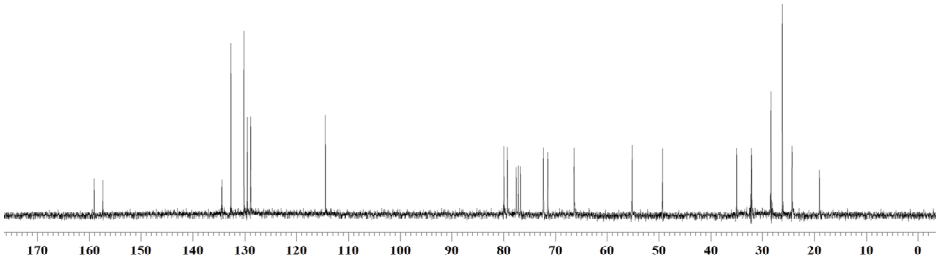

Fig. S-6. ^{13}C-NMR spectrum of compound **7**.

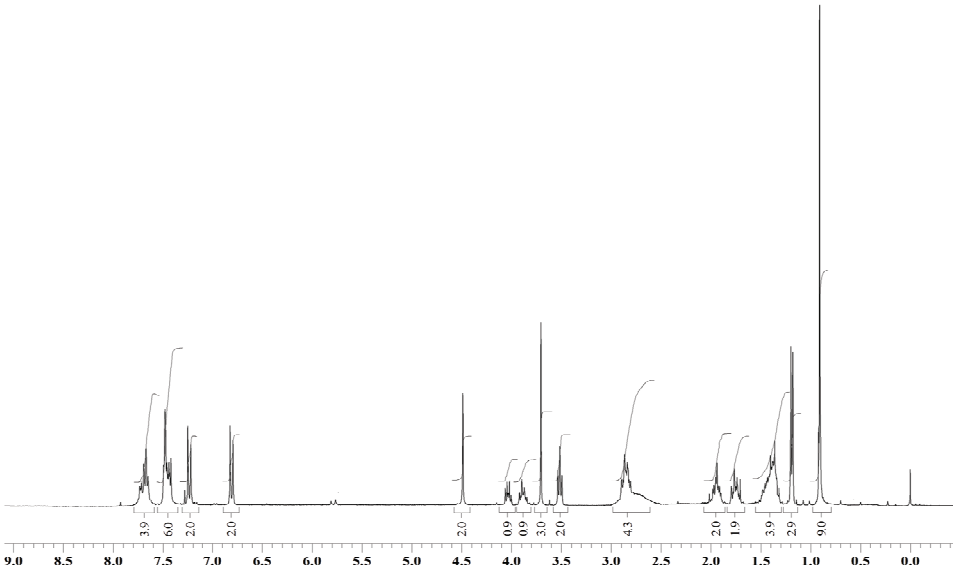

Fig. S-7. ^{1}H-NMR spectrum of compound **8**.

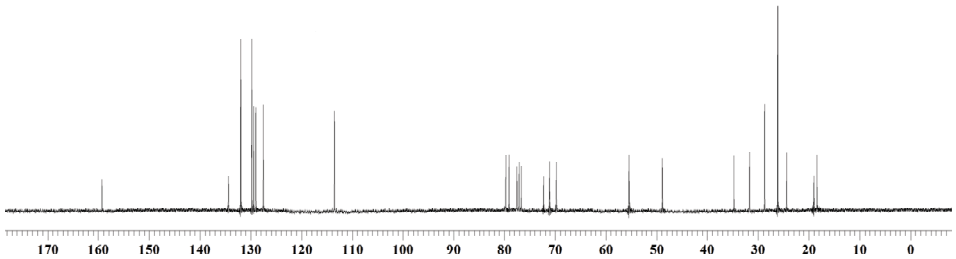

Fig. S-8. ^{13}C-NMR spectrum of compound **8**.

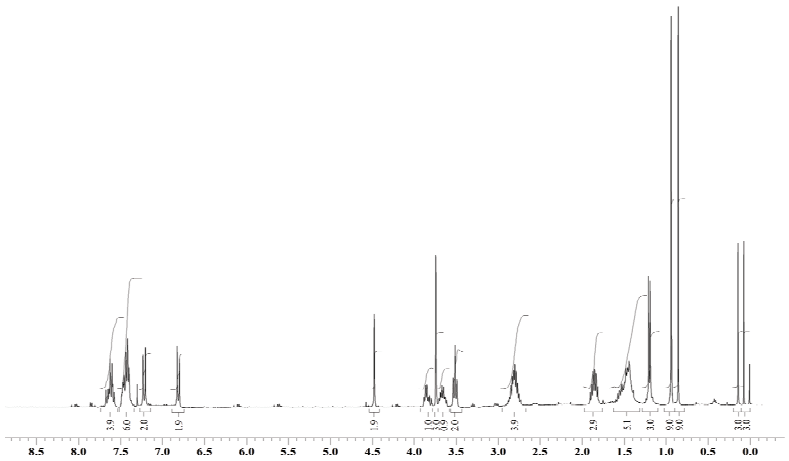

Fig. S-9. ^{1}H-NMR spectrum of compound **9**.

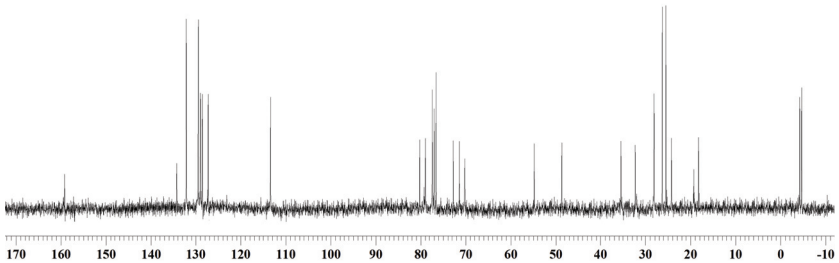

Fig S-10. ^{13}C-NMR spectrum of compound **9**.

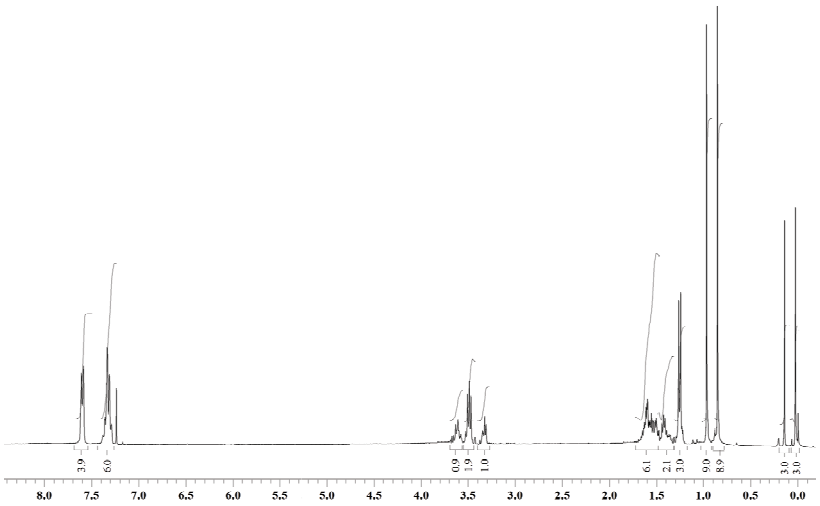

Fig. S-10. ^{1}H-NMR spectrum of compound **10**.

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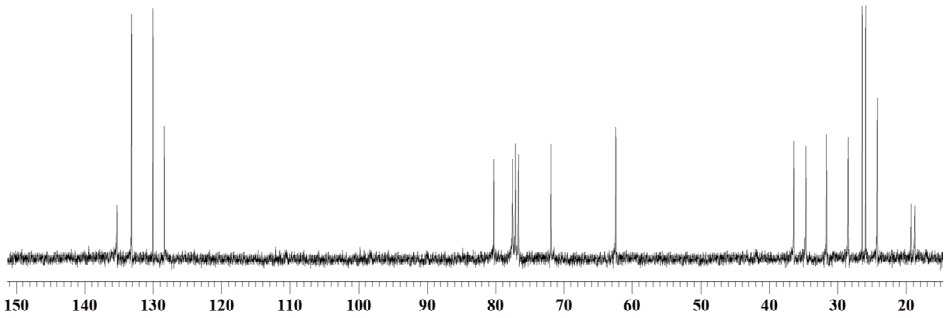

Fig. S-11. ^{13}C-NMR spectrum of compound **10**.

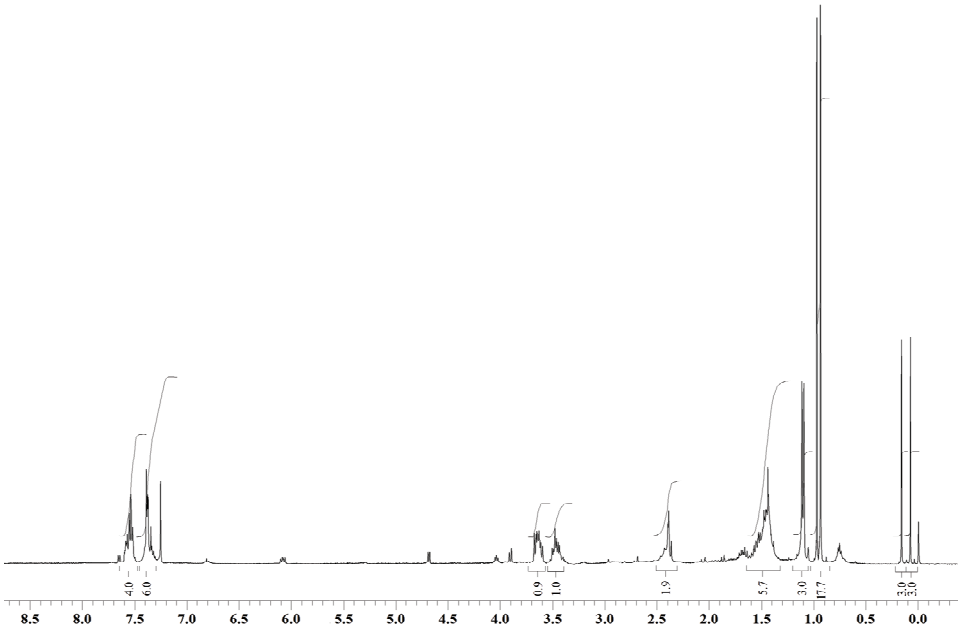

Fig. S-12. ^{1}H-NMR spectrum of compound **11**.

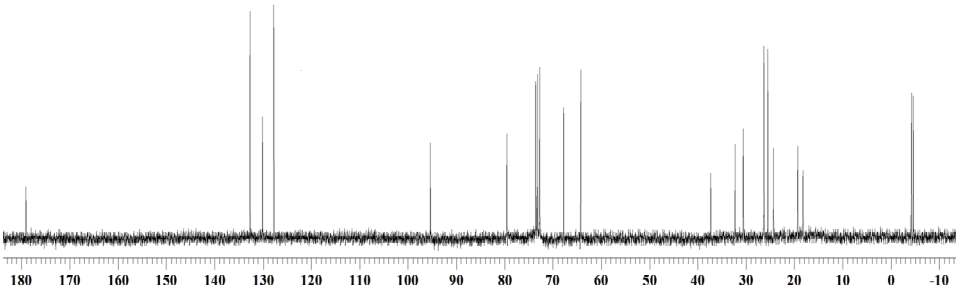

Fig. S-13. ^{13}C-NMR spectrum of compound **11**.

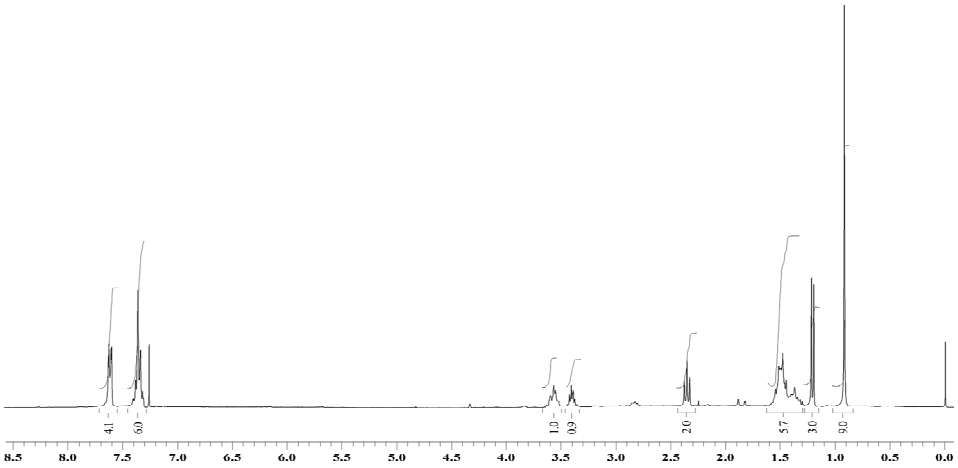

Fig. S-14. ^{1}H-NMR spectrum of compound **2**.

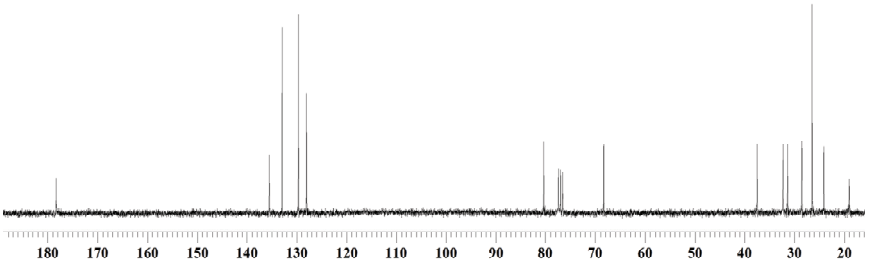

Fig. S-15. ^{13}C-NMR spectrum of compound **2**.

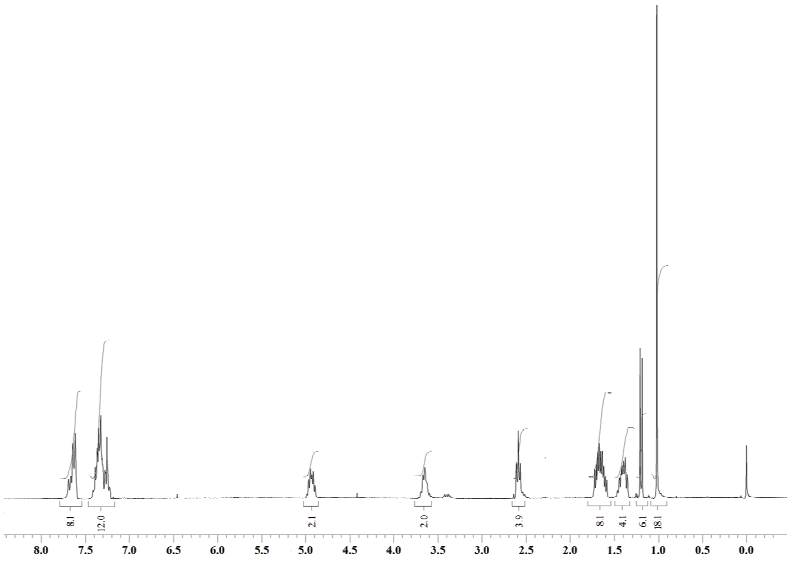

Fig. S-16. ^{1}H-NMR spectrum of compound **12**.

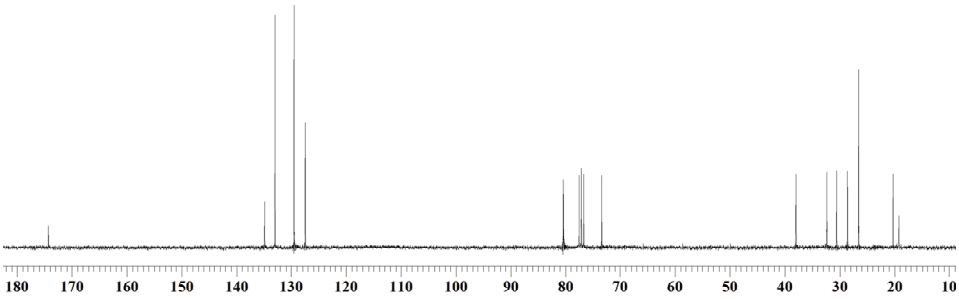

Fig. S-17. ^{13}C-NMR spectrum of compound **12**.

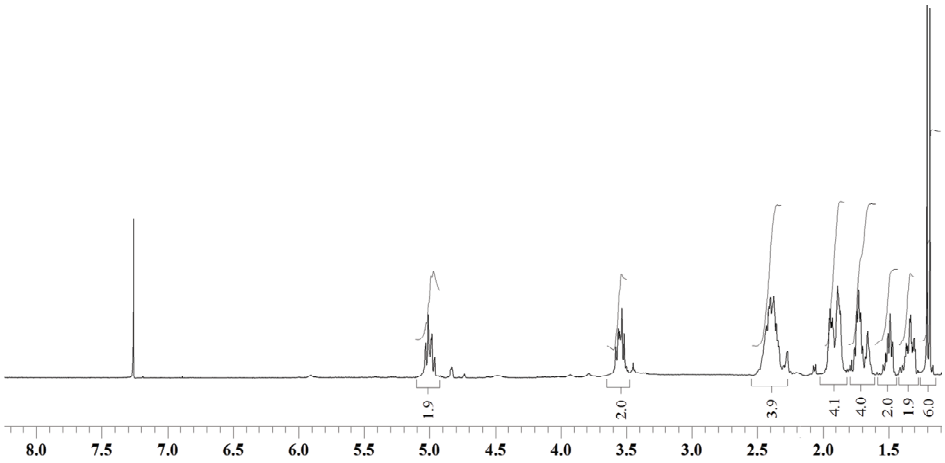

Fig. S-18. ^{1}H-NMR spectrum of compound **1**.

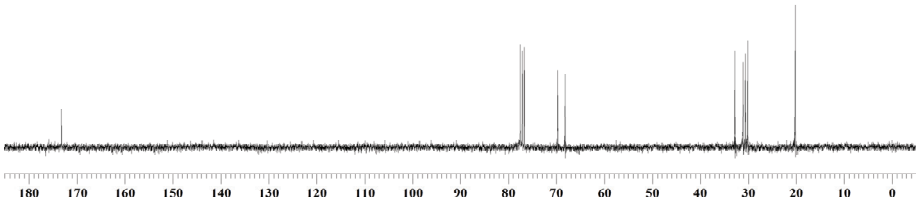

Fig. S-19. ^{13}C-NMR spectrum of compound **1**.

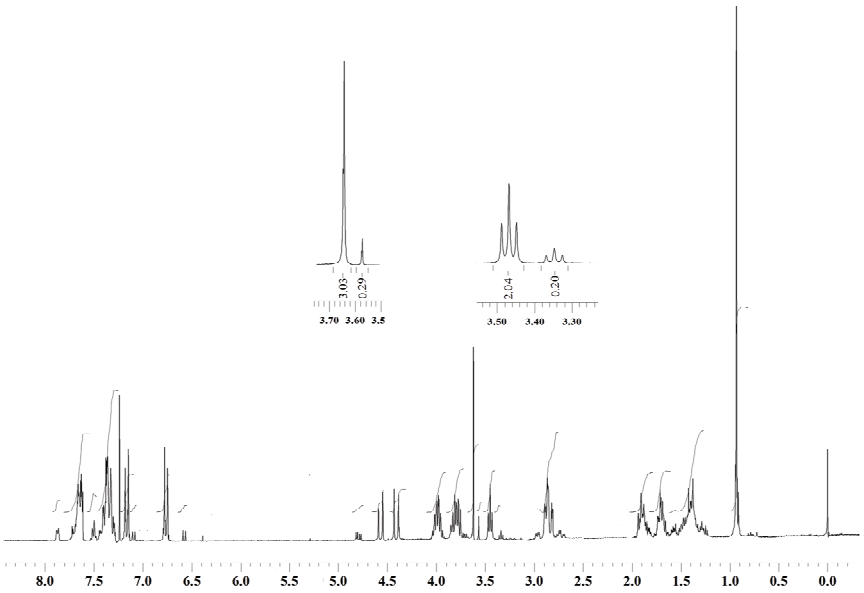

Fig. S-20. Crude ^{1}H-NMR spectrum of **7**.