

One-Handed Helical Double Stranded Polybisnorbornenes

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Supplementary Information

Experimental Section

Ferrocene-(*R,R*)-1,1'-diethyl bis[4-(4-aza-tricyclo[5.2.1.0^{2,6}]dec-4-yl)benzoate] (*RR*-6a). To a solution of **5a** (2.60 g, 10.3 mmol) in CH₂Cl₂ (43 mL) at 0 °C was added oxalyl chloride (2.1 mL, 24.3 mmol) and DMF (3 drops). The mixture was gradually warmed to rt and stirred for 1 h and evaporated in vacuo. Benzene was added to dissolve and the solvent was removed in vacuo to give the corresponding acid chloride **5b** which was used for the next reaction without further purification. To a mixture of **RR**-4a (0.64 g, 2.3 mmol), NEt₃ (1.90 mL, 13.8 mmol) and a trace amount of DMAP in CH₂Cl₂ (95 mL) was added the freshly prepared acid chloride described above in CH₂Cl₂ (47 mL) at 0 °C. The mixture was stirred at rt for 17 h. Saturated NaHCO₃ (110 mL) was added and the solution was washed with water, brine (100 mL x 3) and then dried (MgSO₄). The solvent was removed in vacuo and the residue was chromatography on silica gel (EtOAc/Hexane 3/7) to give the residue which was recrystallized three times from CH₂Cl₂/pentane (1/3) to get **RR**-6a as a light yellow solid (0.52 g, 30%): mp 185-186 °C; [α]_D²⁵ = - 124.2 (c = 0.01 g/mL, CHCl₃); IR: ν (cm⁻¹) 2965, 2859, 1696, 1634, 1606, 1524, 1474, 1380, 1333, 1178, 1098, 1040, 827, 749; ¹H NMR (300 MHz, CDCl₃): δ 1.50-1.63 (m, 10 H, including a doublet 6H, *J* = 6.5 Hz), 2.93-2.98 (m, 8 H), 3.08-3.09 (m, 4 H), 3.26-3.34 (m, 4 H), 4.11 (m, 4 H), 4.22 (d, *J* = 1.7 Hz, 2 H), 4.32 (d, *J* = 1.7 Hz, 2 H), 5.95 (q, *J* = 6.5 Hz, 2 H), 6.15 (s, 4 H), 6.37 (d, *J* = 8.9 Hz, 4 H), 7.88 (d, *J* = 8.9 Hz, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 21.0, 45.4, 46.6, 50.4, 52.1, 66.8, 67.9, 68.2, 68.8, 69.0, 89.8, 110.8, 116.7, 131.3, 135.8, 150.3, 166.4; MS (FAB) *m/z* (rel intensity): 748.4 (M⁺, 28), 564.3 (38), 494.4 (17), 460.3 (18), 402.4 (24), 334.3 (10); HRMS (FAB). Calcd.

$C_{46}H_{48}Fe^{56}N_2O_4$: 748.2964; Found: 748.2952.

SS-6a was obtained in 25% in a manner similar as that described above from **SS-4a**: mp 186-188 °C; $[\alpha]_D^{25} = +123.2$ (c = 0.01 g/ml, $CHCl_3$); IR: ν (cm^{-1}) 3091, 3056, 2963, 2849, 1692, 1605, 1527, 1473, 1380, 1332, 1270, 1178, 1097, 1069, 827, 769, 723, 489; 1H NMR (400 MHz, $CDCl_3$): δ 1.50-1.62 (m, 10 H, including a doublet 6H, $J = 6.5$ Hz), 2.94-2.98 (m, 8 H), 3.08-3.09 (m, 4 H), 3.26-3.31 (m, 4 H), 4.12 (m, 4 H), 4.22 (s, 2 H), 4.31 (s, 2 H), 5.98 (q, $J = 6.5$ Hz, 2 H), 6.15 (s, 4 H), 6.38 (d, $J = 8.8$ Hz, 4 H), 7.89 (d, $J = 8.8$ Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 45.4, 46.6, 50.4, 52.1, 66.8, 67.9, 68.2, 68.8, 69.0, 89.8, 110.8, 116.7, 131.3, 135.8, 150.3, 166.4; MS (FAB) m/z (rel intensity): 748.3 (M^+ , 32), 564.2 (41), 494.3 (17), 402.4 (24), 349.4 (38), 334.3(12); HRMS (FAB). Calcd. $C_{46}H_{48}Fe^{56}N_2O_4$: 748.2964; Found: 748.2964.

Polymer RR-7a. Under nitrogen atmosphere, a solution of $(Cy_3P)_2Cl_2Ru=CHPh$ (5 mg, 0.006 mmol) in CH_2Cl_2 (2 mL) was added to **RR-6a** (45 mg, 0.06 mmol) in CH_2Cl_2 (6 mL). The mixture was stirred at rt for 2 h, quenched with ethyl vinyl ether (2 mL). The solvent was removed in vacuo and the residue was poured into Et_2O (50 mL). The solid was collected and washed with Et_2O to afford **RR-7a** as a brown yellow solid (40 mg, 88%): $M_n = 16,300$; $M_w = 23,200$; PDI = 1.4.; IR: ν (cm^{-1}) 2937, 2840, 1698, 1605, 1524, 1480, 1379, 1335, 1179, 1070, 950, 827, 767; 1H NMR (400 MHz, CD_2Cl_2): δ 1.15-1.95 (br, 10 H), 2.40-3.55 (br, 16 H), 3.80-4.45 (br, 8 H), 5.050-5.65 (br, 4 H), 5.65-6.05 (br, 2 H), 6.20-6.85 (br, 4 H), 7.60-8.15 (br, 4 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 21.2, 37.1, 45.3, 47.4, 50.1, 67.4, 69.3, 90.4, 112.0, 118.0, 126.5, 129.1, 131.7, 151.6, 166.5. (Peaks at 126.5 and 129.1 belong to the end groups of the polymer).

Polymer SS-7a was obtained in 88% in a manner similar as that described above from **RR-6a**; $M_n = 17,600$; $M_w = 26,100$; PDI = 1.5; IR: ν (cm^{-1}) 2923, 2844, 1701, 1605, 1527, 1483, 1382, 1331, 1272, 1180, 1100, 1069, 964, 827, 770, 736, 698; 1H NMR (400 MHz, CD_2Cl_2): δ 1.15-1.95 (br, 10 H), 2.45-3.55 (br, 16 H), 3.85-4.45 (br, 8 H), 5.10-5.65 (br, 4 H), 5.70-6.05 (br, 2 H), 6.25-6.85 (br, 4 H), 7.60-8.15 (br, 4 H);

^{13}C NMR (125 MHz, CD_2Cl_2): δ 21.2, 37.1, 45.3, 47.4, 50.1, 67.4, 69.3, 90.4, 112.0, 118.0, 131.7, 151.6, 166.5. (Peaks at 126.5 and 129.1 belong to the end groups of the polymer).

Ferrocene-(*R,R*)- α,α' -dibenzyl bis[4-(4-aza-tricyclo[5.2.1.0^{2,6}]dec-4-yl)benzoate] (*RR*-6b). To a solution of **5a** (5.00 g, 20.0 mmol) in CH_2Cl_2 (86 mL) at 0 °C was added oxalyl chloride (6.1 mL, 48.0 mmol) and DMF (3 drops). The mixture was gradually warmed to rt and stirred for 1 h and evaporated in vacuo. Benzene was added to dissolve and the solvent was removed in vacuo to give **5b** which was used for the next reaction without further purification. To a mixture of **RR**-4b (1.79 g, 4.5 mmol), NEt_3 (3.8 mL, 27.0 mmol) and a trace amount of DMAP in CH_2Cl_2 (180 mL) was added the freshly prepared acid chloride described above in CH_2Cl_2 (90 mL) at 0 °C. The mixture was stirred at rt for 17 h. Saturated NaHCO_3 (220 mL) was added and the solution was washed with water, brine (100 mL x 3) and then dried (MgSO_4). The solvent was removed in vacuo and the residue was chromatography on silica gel (EtOAc/Hexane 1/1) to give the residue which was recrystallized three times from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (1/3) to get **RR**-6b as a light yellow solid (0.66 g, 17%): mp 175-176 °C; $[\alpha]_{\text{D}}^{21} = -37.0$ ($c = 0.01$ g/mL, CHCl_3); IR: ν (cm^{-1}) 3064, 3031, 2965, 2850, 1693, 1643, 1604, 1524, 1473, 1382, 1316, 1268, 1176, 1098, 1042, 970, 872, 826, 795, 765, 723, 698, 664, 429, 412, 404; ^1H NMR (400 MHz, CDCl_3): δ 1.48 (d, $J = 8.0$ Hz, 2 H), 1.59 (d, $J = 8.0$ Hz, 2 H), 2.93-2.96 (m, 8 H), 3.07 (brs, 4 H), 3.25-3.27 (m, 4 H), 4.07 (s, 6 H), 4.35 (s, 2 H), 6.14 (s, 4H), 6.38 (d, $J = 8.4$ Hz, 4 H), 6.81 (s, 2 H), 7.22-7.30 (m, 6 H), 7.38-7.40 (m, 4 H), 7.94 (d, $J = 8.4$ Hz, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 45.3, 46.6, 50.4, 52.0, 67.7, 68.5, 69.2, 69.3, 73.2, 89.4, 110.9, 116.2, 126.9, 127.6, 128.1, 131.4, 135.7, 141.0, 150.4, 165.8; MS (FAB) m/z (rel intensity): 872.4 (M^+ , 22), 770.3 (3), 618.4 (19), 564.3 (33), 497.3 (4), 464.3 (38), 460.3 (14), 360.3 (4); HRMS (FAB). Calcd. $\text{C}_{56}\text{H}_{52}\text{Fe}^{56}\text{N}_2\text{O}_4$: 872.3277; Found: 872.3277.

SS-6b was obtained in 15% in a manner similar as that described above from **SS**-4b: mp 173-174 °C; $[\alpha]_{\text{D}}^{20} = +39.0$ ($c = 0.01$ g/mL, CHCl_3); IR: ν (cm^{-1}) 3063, 2964, 2850, 1697, 1604, 1524, 1474, 1381, 1317, 1267, 1177, 1098, 1042, 970, 827, 767, 723, 698,

504; ^1H NMR (400 MHz, CDCl_3): δ 1.49 (d, $J = 8.0$ Hz, 2 H), 1.60 (d, $J = 8.0$ Hz, 2 H), 2.93-2.96 (m, 8 H), 3.07 (brs, 4 H), 3.25-3.27 (m, 4 H), 4.07 (s, 6 H), 4.35 (s, 2 H), 6.14 (s, 4H), 6.39 (d, $J = 8.4$ Hz, 4 H), 6.81 (s, 2 H), 7.22-7.30 (m, 6 H), 7.38-7.40 (m, 4 H), 7.96 (d, $J = 8.4$ Hz, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 45.3, 46.6, 50.4, 52.0, 67.7, 68.5, 69.2, 69.3, 73.2, 89.4, 110.9, 116.2, 126.9, 127.6, 128.1, 131.4, 135.7, 141.0, 150.4, 165.8; MS (FAB) m/z (rel intensity): 872.2 (M^+ , 48), 618.3 (27), 564.3 (80), 492.4(17), 464.3 (100), 462.3 (12), 425.4(11), 396.3(27), 391.5(26), 349.5(61); HRMS (FAB). Calcd. $\text{C}_{56}\text{H}_{52}\text{Fe}^{56}\text{N}_2\text{O}_4$: 872.3277; Found: 872.3264; Anal. Calcd: C 77.06, H 6.00, N 3.21; found: C 76.74, H 6.01, N 3.25.

Polymer *RR-7b*. Under nitrogen atmosphere, a solution of $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHPh}$ (5 mg, 0.006 mmol) in CH_2Cl_2 (4 mL) was added to ***RR-6b*** (50 mg, 0.06 mmol) in CH_2Cl_2 (6 mL). The mixture was stirred at rt for 2 h, quenched with ethyl vinyl ether (2 mL), The solvent was removed in vacuo and the residue was poured into Et_2O (50 mL). The solid was collected and washed with Et_2O to afford ***RR-7b*** as a brown yellow solid (46 mg, 92%): $M_n = 15,000$; $M_w = 19,800$; PDI = 1.3; IR: ν (cm^{-1}) 3031, 2940, 2851, 1697, 1639, 1605, 1523, 1477, 1383, 1311, 1267, 1217, 1177, 1098, 1042, 970, 831, 770, 701, 505, 432; ^1H NMR (400 MHz, CDCl_3): δ 1.10-2.05 (br, 4 H), 2.35-3.65 (br, 16 H), 3.70-4.55 (br, 8 H), 4.80-5.75 (br, 4 H), 6.30-6.95 (br, 6 H), 7.00-7.60 (br, 10 H), 7.75-8.25 (br, 4 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 37.0, 45.5, 47.3, 50.1, 69.1, 73.9, 90.4, 112.0, 117.4, 127.3, 128.2, 128.8, 131.9, 142.0, 151.7, 166.1;

Polymer *SS-7b* was obtained in 69% in a manner similar as that described above from ***SS-6b*** as starting material.; $M_n = 16,400$; $M_w = 23,700$; PDI = 1.4; IR: ν (cm^{-1}) 3098, 3063, 3025, 2938, 2850, 1699, 1605, 1520, 1479, 1381, 1313, 1266, 1177, 1097, 1042, 965, 826, 766, 722, 697, 502; ^1H NMR (500 MHz, CD_2Cl_2): δ 1.10-2.05 (br, 4 H), 2.35-3.65 (br, 16 H), 3.90-4.55 (br, 8 H), 5.00-5.75 (br, 4 H), 6.30-6.95 (br, 6 H), 6.95-7.55 (br, 10 H), 7.75-8.25 (br, 4 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 37.0, 45.5, 47.3, 50.1, 69.1, 73.8, 90.4, 112.0, 117.4, 127.3, 128.2, 128.8, 131.9, 142.0, 151.7, 166.1; Anal. Calcd: C 77.06, H 6.00, N 3.21; found: C 75.62, H

6.03, N 3.17.

Methanolysis of *RR-7b*. Under nitrogen atmosphere, a mixture of *RR-7b* (118 mg, 0.14 mmol) in CHCl_3 (20 mL), 10% aq NaOH (4 mL) and MeOH (10 mL) was stirred at rt for 24 h. CH_2Cl_2 was added. The organic layer was separated and washed with H_2O . The organic layer was dried (MgSO_4) and the solvent was removed in vacuo and the residue was chromatography with EtOAc/Hexane (5/9.5) to give **7b** as a light yellow solid (40 mg, 70%): mp 106-108 °C (lit.⁵: 104-106 °C); $[\alpha]_{\text{D}}^{23} = + 64.0$ ($c = 0.01$ g/mL, EtOH); lit.⁵: $[\alpha]_{\text{D}}^{19} = + 87.0$ ($c = 0.11$ g/mL, EtOH); The aqueous layer was acidified with 1N HCl and then yield grayish white **9** (30 mg, 44 %) which was used for the next reaction without further analyze. A mixture of MeI (0.11 mL, 1.8 mmol) was added a solution of **9** (30 mg, 0.12mmol) and CsF (27 mg, 0.18 mmol) suspension in DMF (2 mL) at rt for 24 h. Saturated NaHCO_3 aqueous solution (5 mL) was added and extracted with CH_2Cl_2 . The solution was washed with water and then dried (MgSO_4). The solvent was removed in vacuo and the residue was precipitate with Et_2O to give **10** as a grayish white solid (23 mg, 72%): ^1H NMR (400 MHz): δ 1.28-1.45 (br, 1 H), 1.72-1.95 (br, 1H), 2.62-2.83 (br, 2H), 2.83-3.00 (br, 2H), 3.11-3.35 (br, 4 H), 3.72-3.92 (br, 3 H), 5.25-5.48 (br, 2 H), 6.38-6.58 (br, 2 H), 7.76-7.94 (br, 2H). (126.0, 128.5 belong to the end group of the polymer). ^{13}C NMR (100 MHz): δ 35.6, 36.1, 44.5, 46.4, 49.4, 51.4, 111.4, 116.9, 131.3, 131.6, 150.8, 167.4; GPC (THF): M_n , 5500; M_w , 6600; PDI, 1.2.

Circular dichroism measurements. CD spectra were taken on a JASCO J-815 spectropolarimeter in a 1.0 cm cell. All spectroscopic experiments were conducted at 25 °C. Stock solutions containing monomers or polymers in CHCl_3 (Spectrometric grade) were prepared. The absorbances of monomers **6** and the corresponding polymers **7** were adjusted to be the same for the CD measurements.

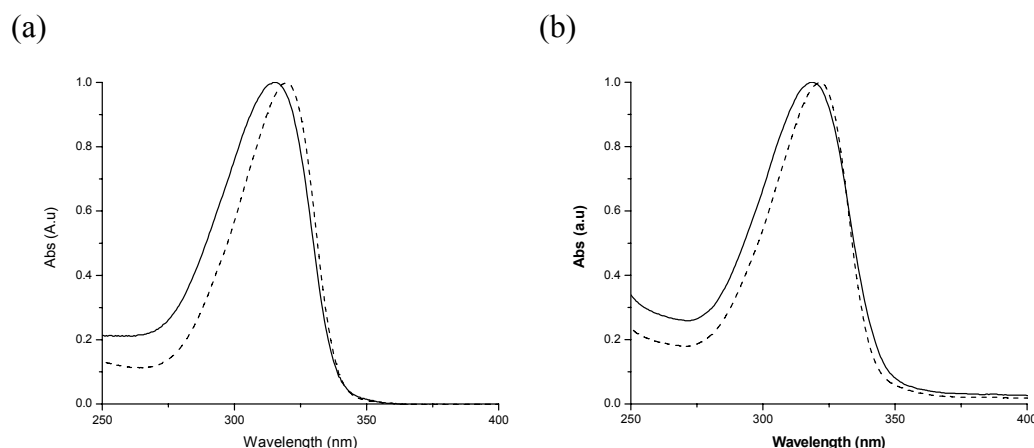


Figure S1 Absorption spectra of (a) **6a** (dotted line) and **7a** (solid line) and (b) **6b** (dotted line) and **7b** (solid line)

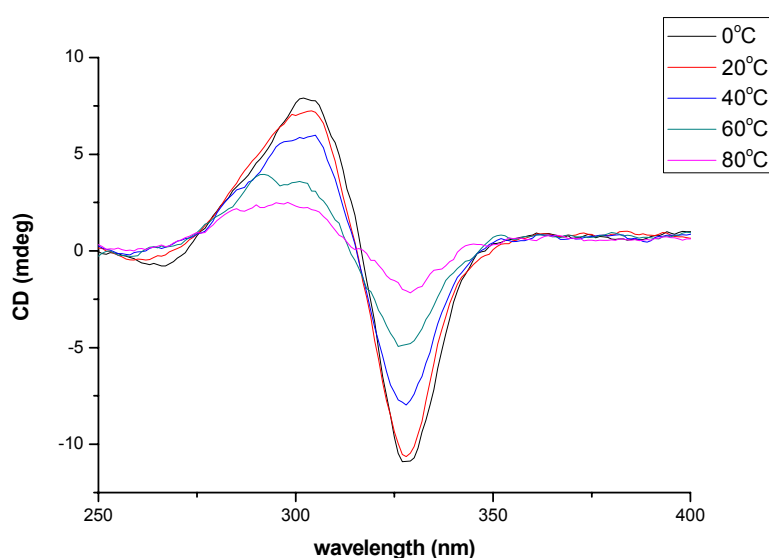


Figure S2 CD curves of **SS-7b** in CH₂Cl₂ (21 mg/L, or 2.4×10^{-5} M monomer units) measured at different temperatures.

Characterization by SPM (scanning probe microscopy). Measurements of STM (Scanning Tunneling Microscopy) were carried out with a NanoScope IIIa controller equipped with a Quadrex and a low current converter suitable for operation under conditions of high tunneling impedance (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA, USA). The typical bias voltage and tunneling current for STM imaging ranged from 0.15 to 1.5 V and from 10 to 300 pA, respectively. Commercially available Pt/Ir tips (PT, Nanotips, Digital Instruments) were employed. The microscope was housed in a chamber where dry N₂ was purging throughout the

experiments and the humidity was lower than 2%.

The deposition solution was 0.1- μ M **3** in CHCl_3 or $\text{C}_2\text{H}_4\text{Cl}_2$. Samples for SPM characterization were prepared by placing a drop of the deposition solution on freshly cleaved HOPG (highly oriented pyrolytic graphite, MikroMasch, Spain) with a Pasteur pipette. To remove trace amount of solvent, the sample was subjected to vacuum dry (~ 30 min, 120 mTorr) prior to imaging.

Molecular mechanics and dynamics simulations. The three dimensional structures of polymers *RR-7d* and *SS-7d* were constructed using a molecular modeling procedure, both the optimal interactions in a pair of monomers and the tacticity of polymerization^[7] (by varying both the monomer conformation and tacticity of the backbone of polymer) being considered. Molecular dynamics simulations were carried out to explore the global conformations and molecular interaction mechanism of polymers *RR-7d* and *SS-7d* using universal force field.^[19] With an extensive exploration of potential surface, isotactic polymers *RR-7d* and *SS-7d* with double bonds in trans configuration would be more stable in the supercoil structures than in helix or ladder structures. The relevant structural parameters (Table S1) are closely matched with the STM image of polymers *RR-7d* and *SS-7d* (Figure 1). It is noteworthy that the counter-clockwise oriented stacking of the chiral monomeric units leading to the secondary structures of *RR-7d* would be relatively more stable than the clockwise one by 3.7 kcal/mol per monomer (Figure S2). In a similar manner, *SS-7d* would preferentially have the clockwise supercoil structure.

Table S1. Structural parameters of optimized polymers *RR-7d* and *SS-7d*

	<i>RR</i>	<i>SS</i>
Stereochemistry	Isotactic_syn	Isotactic_syn
Chiral sense	counter-clockwise	clockwise
Mean number per turn	12	12
Fe-Fe distance	~ 7.0 Å	~ 7.0 Å
Project distance to Z axis	~ 4.2 Å	~ 4.2 Å
Pitch per turn	~ 51 Å	~ 51 Å
Diameter	~ 31 Å	~ 31 Å

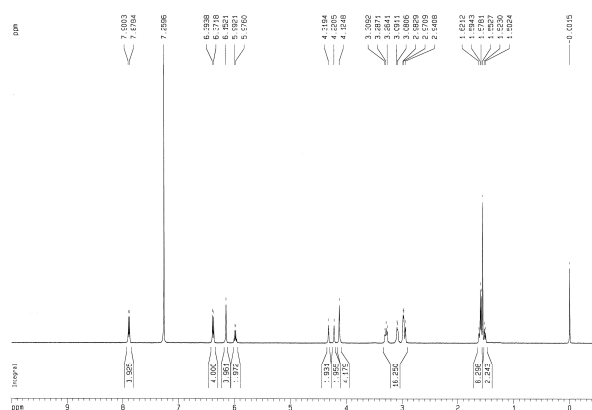


Figure S3. ¹H NMR spectrum of **6a**.

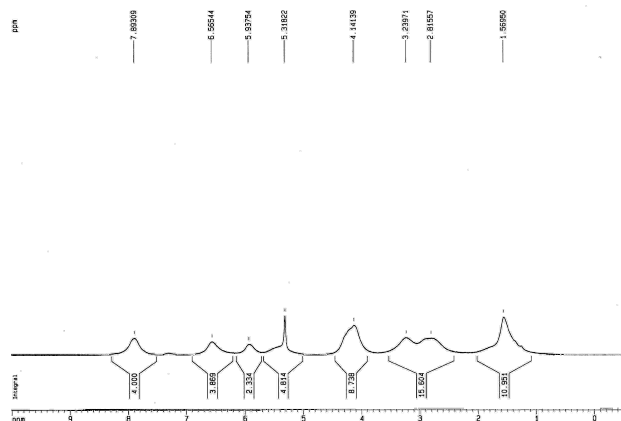


Figure S4. ^1H NMR spectrum of **7a**.

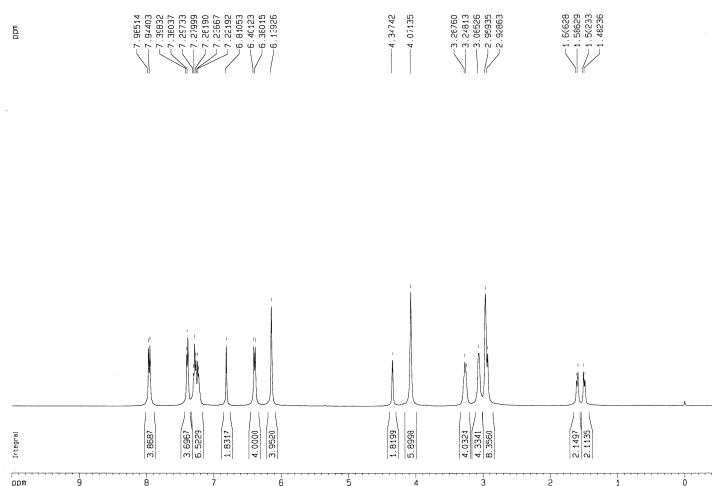


Figure S5. ^1H NMR spectrum of **6b**.

(a)

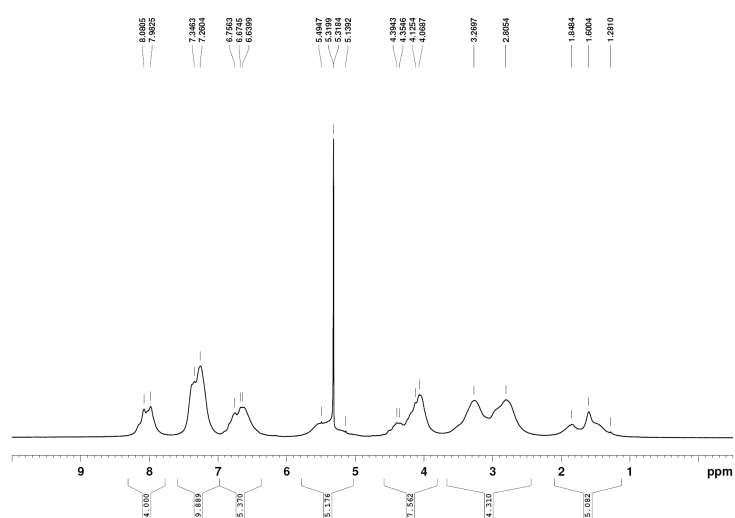


Figure S6. ^1H NMR spectrum of **7b**.