

Reassembly Self-Sorting Triggered by Heterodimerization

Supplementary Information

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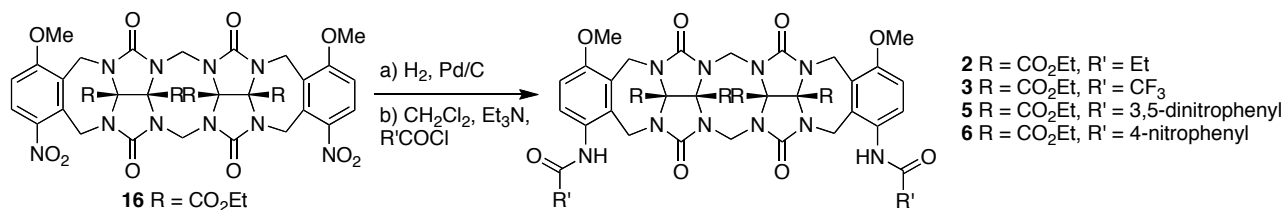
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Synthesis of molecular clips 1–15.

General Experimental Details. Starting materials were purchased from commercial suppliers and were used without further purification. Compounds **1**,¹ **4**,¹ **7**,² **10**,³ **16**,^{4,5} (\pm)-**17**,^{4,5} **18**,⁵ and (\pm)-**19**⁶ were synthesized according literatures. THF was distilled from sodium benzophenone ketyl, and dichloromethane and DMSO was distilled from CaH₂ immediately before use. NEt₃ was distilled from KOH immediately before use. TLC analysis was performed using precoated plates. Column chromatography was performed using silica gel (200-300 mesh) using eluents in the indicated v:v ratio. Melting points were determined using an XT-4 apparatus and not corrected. IR spectra were recorded on a PE-983 spectrophotometer as KBr pellets and were reported in cm⁻¹. NMR spectra were measured on Varian Mercury 400 and 600, and Bruker AVANCE-600, AM-400, DRX-400 instruments, operating at 400 or 600 MHz for ¹H and 100 or 150 MHz for ¹³C. Electron impact (EI) mass spectra were acquired using a Finnegan Trace MS spectrometer and some mass spectrometry was performed using a VG 7070E magnetic sector instrument by electron impact (EI) or by fast atom bombardment (FAB) using the indicated matrix. The matrix “magic bullet” is a 5:1 (w:w) mixture of dithiothreitol:dithioerythritol. Electrospray mass spectra (ESI-MS) were performed using a Waters Q-TOF II mass spectrometer.



Compound 2. A mixture of **16** (190 mg, 0.2 mmol) and 10% Pd/C (70 mg) in anhydrous DMF (10 mL) was stirred under H₂ (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anhydrous degassed CH₂Cl₂ (10 mL) and NEt₃ (0.5 mL, 4 mmol). This solution was added to a solution of propionyl chloride (52 μ L, 0.60 mmol) in anhydrous degassed CH₂Cl₂ (5 mL) at -78 °C. After 15 min, the cooling bath was removed, and stirring was continued at room temperature for 3 h. The reaction mixture was diluted with CHCl₃ (100 mL), washed with saturated aqueous NaHCO₃, dried over anhydrous MgSO₄, and concentrated. Flash chromatography (SiO₂, CHCl₃/MeOH, 50:1) gave slightly impure **2** (162 mg, 0.162 mmol, 81%). To get highest purity material, the solid was washed with EtOAc (2 mL), centrifuged, and the supernatant decanted yielding **2** as a white solid (152 mg, 0.152 mmol, 76%). Mp > 300 °C (dec.). TLC (CHCl₃/MeOH 20:1) R_f 0.25. IR (KBr, cm⁻¹): 3448m, 2982w, 1745s, 1669w, 1602w, 1559w, 1521w, 1457m, 1369w, 1258m, 1177w, 1130w, 1258m, 1018m, 954w. ¹H NMR (400 MHz, DMSO-*d*₆): 9.27 (s, 2H), 6.75-6.70 (m, 4H), 5.80 (d, *J* = 16.0, 2H), 5.22 (d, *J* = 16.0, 2H), 4.68 (d, *J* = 16.0, 2H), 4.52 (d, *J* = 16.0, 1H), 4.46 (d, *J* = 16.0, 1H), 4.25-4.05 (m, 12H), 3.72 (s, 6H), 2.40-2.30 (m, 4H), 1.23 (t, *J* = 7.0, 6H), 1.17 (t, *J* = 7.1, 6H), 1.12 (t, *J* = 7.5, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆): 172.8, 165.1, 164.1, 154.4, 154.1, 154.0, 133.2, 128.1, 126.6, 124.1, 111.2, 79.7,

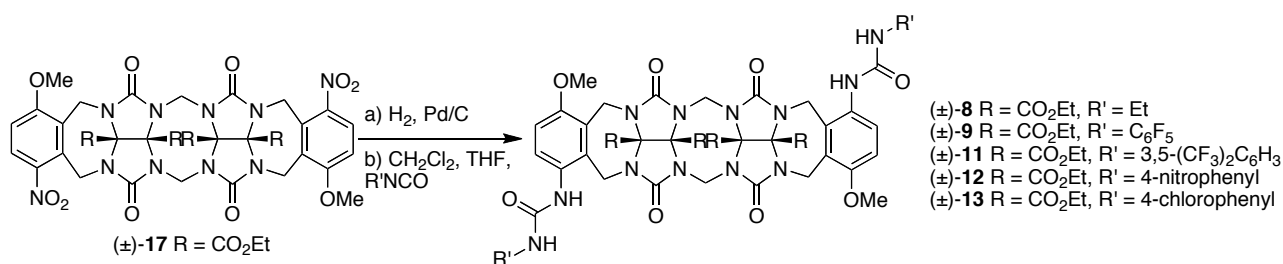
79.1, 78.5, 64.3, 63.7, 55.9, 47.2, 36.1, 28.7, 13.6, 13.5, 9.9 ppm (only 23 of the 24 expected resonances were observed). MS (FAB, magic bullet): m/z 1003.2 ($[M+1]^+$, 100), 1002.2 (M^+ , 60). HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{46}H_{54}N_{10}O_{16}Na$: 1025.3617; found: 1025.3601.

Compound 3. A mixture of **16** (190 mg, 0.2 mmol) and 10% Pd/C (70 mg) in anhydrous DMF (10 mL) was stirred under H_2 (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anhydrous degassed CH_2Cl_2 (10 mL) and NEt_3 (0.5 mL, 4 mmol). This solution was added to a solution of trifluoroacetic anhydride (126 mg, 0.60 mmol) in anhydrous degassed CH_2Cl_2 (5 mL) at $-78\text{ }^\circ C$. After 1 h, the cooling bath was removed, and stirring was continued at $0\text{ }^\circ C$ for 10 h. The reaction mixture was diluted with $CHCl_3$ (100 mL), washed with saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated. Flash chromatography (SiO_2 , $CHCl_3/MeOH$, 50:1) gave slightly impure **3** (171 mg, 0.158 mmol, 79%). To get highest purity material, the solid was washed with $EtOAc$ (2 mL), centrifuged, and the supernatant decanted yielding **3** as a white solid (132 mg, 0.122 mmol, 61%). Mp $> 300\text{ }^\circ C$ (dec.). TLC ($CHCl_3/MeOH$ 20:1) R_f 0.28. IR (KBr, cm^{-1}): 3854w, 3408m, 2984w, 1747s, 1601w, 1540m, 1457s, 1384m, 1371m, 1262s, 1160s, 1160s, 1084m, 1020m, 955w. 1H NMR (400 MHz, $DMSO-d_6$): 11.17 (s, 2H), 7.21 (d, $J = 8.8$, 2H), 7.01 (d, $J = 8.8$, 2H), 5.76 (d, $J = 16.0$, 2H), 5.74 (d, $J = 16.0$, 2H), 5.29 (d, $J = 16.0$, 2H), 4.64 (d, $J = 16.0$, 2H), 4.57 (d, $J = 16.0$, 1H), 4.41 (d, $J = 16.0$, 1H), 4.28-4.16 (m, 12H), 3.80 (s, 6H), 1.24-1.16 (m, 6H). ^{13}C NMR (100 MHz, $DMSO-d_6$): 164.8, 163.8, 155.8, 155.6, 154.3, 153.8, 134.0, 127.7, 125.3, 125.1, 116.1, 111.9, 79.9, 78.5, 64.5, 63.9, 56.2, 47.1, 47.1, 36.0, 13.6, 13.5 ppm (only 22 of the 23 expected resonances were observed). MS (FAB, magic bullet): m/z 1083.4 ($[M+1]^+$, 100), 1082.4 (M^+ , 20). HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{44}H_{44}F_6N_{10}O_{16}Na$: 1105.2739; found: 1105.2719.

Compound 5. A mixture of **16** (190 mg, 0.2 mmol) and 10% Pd/C (70 mg) in anhydrous DMF (10 mL) was stirred under H_2 (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anhydrous degassed CH_2Cl_2 (10 mL) and NEt_3 (0.5 mL, 4 mmol). This solution was added to a solution of 3,5-dinitrobenzoyl chloride (140 mg, 0.60 mmol) in anhydrous degassed CH_2Cl_2 (5 mL) at $-78\text{ }^\circ C$. After 15 min, the cooling bath was removed, and stirring was continued at room temperature for 3 h. The reaction mixture was diluted with $CHCl_3$ (100 mL), washed with saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated. Flash chromatography (SiO_2 , $CHCl_3/MeOH$, 50:1) gave slightly impure **5** (181 mg, 0.142 mmol, 71%). To get highest purity material, the solid was washed with $EtOAc$ (2 mL), centrifuged, and the supernatant decanted yielding **5** as a yellow solid (169 mg, 0.132 mmol, 66%). Mp $262-263\text{ }^\circ C$. TLC ($CHCl_3/MeOH$ 20:1) R_f 0.27. IR (KBr, cm^{-1}): 3383m, 2975m, 1761s, 1740s, 1665m, 1630w, 1600w, 1546m, 1458m, 1371m, 1346m, 1279s, 1179w, 1086s, 1050s, 1020m, 956w. 1H NMR (600 MHz, $DMSO-d_6$): 10.82 (br. s, 2H), 9.15 (s, 4H), 9.02 (s, 2H), 7.19 (br. s, 2H), 7.01 (br. s, 2H), 5.81 (d, $J = 16.0$ Hz, 1H), 5.71 (d, $J = 16.0$ Hz, 1H), 5.33 (d, $J = 16.0$ Hz, 2H), 4.79 (d, $J = 16.0$ Hz, 2H), 4.58 (d, $J = 16.0$ Hz, 1H), 4.40 (d, $J = 16.0$ Hz, 1H), 4.30 (d, $J = 16.0$ Hz, 2H), 4.28

(d, $J = 16.0$ Hz, 2H), 4.25-4.15 (m, 8H), 3.83 (s, 6H), 1.21 (t, $J = 6.6$ Hz, 6H), 1.19 (t, $J = 6.6$ Hz, 6H) ppm. ^{13}C NMR (150 MHz, DMSO- d_6): $\delta = 164.9, 163.9, 162.3, 155.0, 154.5, 153.9, 148.2, 136.6, 134.2, 129.5, 127.9, 127.8, 127.4, 124.6, 121.2, 79.9, 78.6, 64.4, 63.9, 56.1, 47.1, 36.0, 13.6, 13.5$ ppm (only 24 of the 26 expected resonances were observed). HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{54}\text{H}_{51}\text{N}_{14}\text{O}_{24}$: 1279.3195; found: 1279.3270.

Compound 6. A mixture of **16** (190 mg, 0.2 mmol) and 10% Pd/C (70 mg) in anhydrous DMF (10 mL) was stirred under H_2 (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anhydrous degassed CH_2Cl_2 (10 mL) and NEt_3 (0.5 mL, 4 mmol). This solution was added to a solution of 4-nitrobenzoyl chloride (112 mg, 0.60 mmol) in anhydrous degassed CH_2Cl_2 (5 mL) at -78°C . After 15 min, the cooling bath was removed, and stirring was continued at room temperature for 3 h. The reaction mixture was diluted with CHCl_3 (100 mL), washed with saturated aqueous NaHCO_3 , dried over anhydrous MgSO_4 , and concentrated. Flash chromatography (SiO_2 , $\text{CHCl}_3/\text{MeOH}$, 50:1) gave slightly impure **6** (211 mg, 0.178 mmol, 89%). To get highest purity material, the solid was washed with EtOAc (2 mL), centrifuged, and the supernatant decanted yielding **6** as a yellow solid (190 mg, 0.160 mmol, 80%). Mp $295\text{-}296^\circ\text{C}$. TLC ($\text{CHCl}_3/\text{MeOH}$ 20:1) R_f 0.31. IR (KBr, cm^{-1}): 3447m, 2983w, 1757s, 1669m, 1602m, 1527s, 1484m, 1456m, 1348m, 1264s, 1175w, 1082m, 1018m, 953w, 908m. ^1H NMR (600 MHz, DMSO- d_6): 10.16 (br. s, 2H), 8.31 (d, $J = 8.4$ Hz, 4H), 8.16 (d, $J = 8.4$ Hz, 4H), 6.90 (br. m, 2H), 6.75 (br. m, 2H), 5.85 (d, $J = 16.4$ Hz, 1H), 5.77 (d, $J = 16.4$ Hz, 1H), 5.35 (d, $J = 16.0$ Hz, 2H), 4.75 (d, $J = 16.0$ Hz, 2H), 4.61 (d, $J = 16.0$ Hz, 1H), 4.47 (d, $J = 16.4$ Hz, 1H), 4.30-4.20 (m, 12H), 3.78 (s, 6H), 1.25-1.15 (m, 12H) ppm. ^{13}C NMR (150 MHz, DMSO- d_6): $\delta = 164.9, 164.8, 163.9, 154.7, 153.9, 149.2, 139.9, 133.8, 129.1, 127.3, 126.9, 124.5, 123.6, 111.2, 79.8, 79.5, 64.5, 63.9, 55.9, 47.6, 47.3, 36.0, 13.6, 13.5$ ppm (only 24 of the 26 expected resonances were observed). HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{54}\text{H}_{53}\text{N}_{12}\text{O}_{20}$: 1189.3494; found: 1189.3499.



Compound (±)-8. A mixture of (±)-**17** (190 mg, 0.20 mmol) and 10% Pd/C (70 mg) in anh. DMF (20 mL) was stirred under H_2 (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anh. degassed $\text{CH}_2\text{Cl}_2/\text{THF}$ (3:1, v/v, 20 mL) and NEt_3 (5 mL). To this solution was added ethyl isocyanate (78 μL , 1.0 mmol) and stirring was continued at room temperature for 3 days. The reaction mixture was diluted with CHCl_3 (200 mL), washed with sat. aq. NaHCO_3 , dried over anh. MgSO_4 , and concentrated. Flash chromatography (SiO_2 ,

CHCl₃/MeOH, 50:1) gave slightly impure (±)-**8** (189 mg, 0.184 mmol, 92%). To get highest purity material, the solid was washed with EtOAc (2 mL), centrifuged, and the supernatant decanted yielding (±)-**8** as a white solid (166 mg, 0.162 mmol, 81%). Mp > 300 °C (dec.). TLC (CHCl₃/MeOH 20:1) *R_f* 0.41. IR (KBr, cm⁻¹): 3394m, 2977m, 2913m, 1747s, 1665s, 1599w, 1545m, 1457m, 1369w, 1260s, 1176w, 1084m, 1017m, 955w, 907m. ¹H NMR (600 MHz, DMSO-*d*₆): 7.67 (s, 2H), 7.07 (s, 2H), 6.76 (br. m, 2H), 6.38 (br. m, 2H), 5.79 (d, *J* = 16.2 Hz, 2H), 5.12 (d, *J* = 15.6 Hz, 2H), 4.78 (d, *J* = 16.2 Hz, 2H), 4.47 (d, *J* = 15.6 Hz, 2H), 4.26 (m, 4H), 4.21 (q, *J* = 7.2 Hz, 4H), 4.09 (q, *J* = 7.2 Hz, 4H), 3.64 (br. s, 6H), 3.07 (m, 4H), 1.22 (t, *J* = 7.2 Hz, 6H), 1.15 (t, *J* = 7.2 Hz, 6H), 1.05 (t, *J* = 7.2 Hz, 6H) ppm. ¹³C NMR (150 MHz, DMSO-*d*₆): 165.2, 164.1, 156.4, 154.1, 153.4, 132.4, 129.9, 126.9, 123.9, 111.5, 78.6, 78.6, 64.4, 63.6, 55.9, 47.2, 40.0, 36.2, 34.2, 15.5, 15.4, 13.5 (only 22 of the 23 expected resonances were observed). HRMS (ESI): *m/z* [M + H]⁺ calcd for C₅₆H₅₆N₁₃O₁₈: 1033.4015; found: 1033.4025; [M + Na]⁺ calcd for C₅₆H₅₆N₁₂O₁₈Na: 1055.3835; found: 1055.3783.

Compound (±)-**9**. A mixture of (±)-**17** (190 mg, 0.20 mmol) and 10% Pd/C (70 mg) in anh. DMF (20 mL) was stirred under H₂ (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anh. degassed CH₂Cl₂ (20 mL) and NEt₃ (5 mL). To this solution was added pentafluorophenyl isocyanate (130 μL, 1.0 mmol) and stirring was continued at room temperature for 1 day. The reaction mixture was diluted with CHCl₃ (200 mL), washed with sat. aq. NaHCO₃, dried over anh. MgSO₄, and concentrated. Flash chromatography (SiO₂, CHCl₃/MeOH, 50:1) gave slightly impure (±)-**9** (218 mg, 0.164 mmol, 82%). To get highest purity material, the solid was washed with EtOAc (2 mL), centrifuged, and the supernatant decanted yielding (±)-**9** as a white solid (197 mg, 0.148 mmol, 74%). Mp > 300 °C (dec.). TLC (CHCl₃/MeOH 20:1) *R_f* 0.52. IR (KBr, cm⁻¹): 3332m, 2986w, 1755s, 1688m, 1653w, 1601w, 1525s, 1458s, 1368m, 1262s, 1177w, 1132w, 1084m, 1018m, 954w, 908m. ¹H NMR (600 MHz, DMSO-*d*₆): 8.86 (br. s, 2H), 8.35 (br. s, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.84 (br. m, 2H), 5.82 (d, *J* = 15.6 Hz, 2H), 5.20 (d, *J* = 15.6 Hz, 2H), 4.85 (d, *J* = 15.6 Hz, 2H), 4.51 (d, *J* = 15.6 Hz, 2H), 4.34 (d, *J* = 15.6 Hz, 2H), 4.30-4.20 (m, 6H), 4.14 (q, *J* = 7.2 Hz, 4H), 3.68 (br. s, 6H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.20 (t, *J* = 7.2 Hz, 6H) ppm. ¹³C NMR (150 MHz, DMSO-*d*₆): δ = 165.1, 164.0, 154.7, 154.1, 153.9, 153.5, 142.7, 138.2, 137.1, 133.2, 128.4, 127.5, 124.4, 114.2, 111.6, 79.7, 78.6, 64.7, 63.7, 55.9, 47.4, 47.3, 36.1, 13.6, 13.5 ppm. HRMS (ESI): *m/z* [M + Na]⁺ calcd for C₅₄H₄₆F₁₀N₁₂O₁₆Na: 1331.2887; found: 1331.2892.

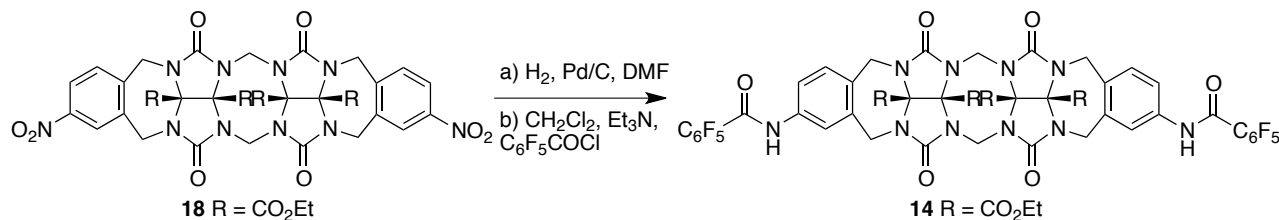
Compound (±)-**11**. A mixture of (±)-**17** (190 mg, 0.20 mmol) and 10% Pd/C (70 mg) in anh. DMF (20 mL) was stirred under H₂ (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anh. degassed CH₂Cl₂ (20 mL) and NEt₃ (5 mL). To this solution was added 3,5-bis(trifluoromethyl)phenyl isocyanate (172 μL, 1.0 mmol) and stirring was continued at room temperature for 5 hours. The reaction mixture was diluted with CHCl₃ (200 mL), washed with sat. aq. NaHCO₃, dried over anh. MgSO₄, and concentrated. Flash chromatography (SiO₂, CHCl₃/MeOH, 50:1) gave slightly impure (±)-**11** (187 mg, 0.134 mmol, 67%). To get highest

purity material, the solid was washed with EtOAc (2 mL), centrifuged, and the supernatant decanted yielding (\pm)-**11** as a white solid (168 mg, 0.120 mmol, 60%). Mp > 300 °C (dec.). TLC (CHCl₃/MeOH 20:1) *R_f* 0.33. IR (KBr, cm⁻¹): 3353m, 3120w, 2990w, 1757s, 1683m, 1624w, 1575m, 1518m, 1473s, 1389s, 1280s, 1180s, 1130s, 1086m, 959w, 945w, 908m. ¹H NMR (600 MHz, DMSO-*d*₆): 9.81 (s, 2H), 8.09 (s, 4H), 8.09 (br. s, 2H), 7.54 (s, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 7.2 Hz, 2H), 5.82 (d, *J* = 16.2 Hz, 2H), 5.25 (d, *J* = 15.6 Hz, 2H), 4.84 (d, *J* = 16.2 Hz, 2H), 4.53 (d, *J* = 16.2 Hz, 2H), 4.35 (d, *J* = 15.6 Hz, 2H), 4.30-4.15 (m, 10H), 3.54 (s, 6H), 1.24 (t, *J* = 7.2 Hz, 6H), 1.19 (t, *J* = 7.2 Hz, 6H) ppm. ¹³C NMR (150 MHz, DMSO-*d*₆): δ = 165.1, 164.0, 154.9, 154.0, 153.8, 142.1, 133.0, 132.9, 130.6 (q, *J*_{CF} = 30 Hz), 128.2, 127.6, 124.4, 123.3 (q, *J*_{CF} = 271 Hz), 117.6, 113.9, 111.6, 79.9, 78.7, 64.5, 63.8, 55.8, 47.4, 40.0, 36.1, 13.6, 13.6 ppm. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₅₈H₅₃F₁₂N₁₂O₁₆: 1401.3505; found: 1401.3551.

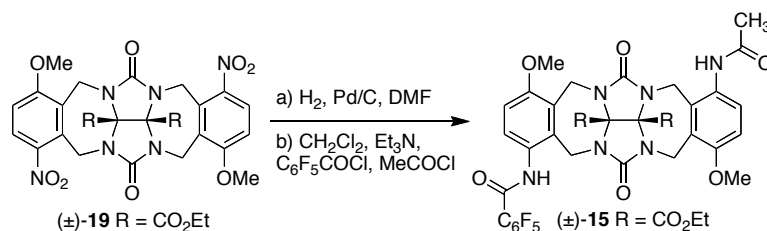
Compound (\pm)-**12**. A mixture of (\pm)-**17** (190 mg, 0.20 mmol) and 10% Pd/C (70 mg) in anh. DMF (20 mL) was stirred under H₂ (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anh. degassed CH₂Cl₂ (20 mL) and NEt₃ (5 mL). To this solution was added 4-nitrophenyl isocyanate (164 mg, 1.0 mmol) and stirring was continued at room temperature for 6 hours. The reaction mixture was diluted with CHCl₃ (200 mL), washed with sat. aq. NaHCO₃, dried over anh. MgSO₄, and concentrated. Flash chromatography (SiO₂, CHCl₃/MeOH, 50:1) gave slightly impure (\pm)-**12** (197 mg, 0.162 mmol, 81%). To get highest purity material, the solid was washed with EtOAc (2 mL), centrifuged, and the supernatant decanted yielding (\pm)-**12** as a yellow solid (183 mg, 0.150 mmol, 75 %). Mp > 300 °C (dec.). TLC (CHCl₃/MeOH 20:1) *R_f* 0.24. IR (KBr, cm⁻¹): 3355m, 2981w, 1756s, 1598m, 1557m, 1508s, 1460m, 1368w, 1330s, 1301m, 1256s, 1177m, 1112m, 1083m, 1017m, 956w, 908m. ¹H NMR (600 MHz, DMSO-*d*₆): 9.82 (s, 2H), 8.16 (d, *J* = 9.3 Hz, 4H), 8.16 (br. s, 2H), 7.67 (d, *J* = 9.3 Hz, 4H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 5.82 (d, *J* = 15.6 Hz, 2H), 5.22 (d, *J* = 15.6 Hz, 2H), 4.84 (d, *J* = 16.2 Hz, 2H), 4.52 (d, *J* = 16.2 Hz, 2H), 4.36 (d, *J* = 15.6 Hz, 2H), 4.29 (d, *J* = 15.6 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 4H), 4.14 (q, *J* = 7.2 Hz, 4H), 3.39 (s, 6H), 1.24 (t, *J* = 7.2 Hz, 6H), 1.17 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (150 MHz, DMSO-*d*₆): 165.1, 164.0, 154.9, 154.2, 154.0, 153.3, 146.6, 140.9, 132.9, 128.4, 127.7, 125.1, 124.4, 117.3, 111.8, 79.8, 78.7, 64.5, 63.9, 56.0, 47.4, 36.2, 13.7, 13.6 ppm (only 24 of the 25 expected resonances were observed). HRMS (ESI): *m/z* [M + H]⁺ calcd for C₅₄H₅₅N₁₄O₂₀: 1219.3712; found: 1219.3730.

Compound (\pm)-**13**. A mixture of (\pm)-**17** (190 mg, 0.20 mmol) and 10% Pd/C (70 mg) in anh. DMF (20 mL) was stirred under H₂ (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anh. degassed CH₂Cl₂ (20 mL) and NEt₃ (5 mL). To this solution was added 4-chlorophenyl isocyanate (128 μL, 1.0 mmol) and stirring was continued at room temperature for 1 day. The reaction mixture was diluted with CHCl₃ (200 mL), washed with sat. aq. NaHCO₃, dried over anh. MgSO₄, and concentrated. Flash chromatography (SiO₂, CHCl₃/MeOH, 50:1) gave slightly impure (\pm)-**13** (224 mg, 0.184 mmol, 92%). To get highest purity material, the

solid was washed with EtOAc (2 mL), centrifuged, and the supernatant decanted yielding (\pm)-**13** as a white solid (199 mg, 0.164 mmol, 82%). Mp > 300 °C (dec.). TLC (CHCl₃/MeOH 20:1) R_f 0.40. IR (KBr, cm⁻¹): 3352m, 2983w, 1750s, 1676m, 1597m, 1539m, 1490m, 1457m, 1433m, 1397w, 1366w, 1247s, 1715w, 1086m, 1017m, 909m. ¹H NMR (600 MHz, DMSO-*d*₆): 9.18 (s, 2H), 7.96 (s, 2H), 7.46 (d, J = 8.7 Hz, 4H), 7.30 (d, J = 8.7 Hz, 4H), 7.22 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.81 (d, J = 15.6 Hz, 2H), 5.19 (d, J = 15.6 Hz, 2H), 4.83 (d, J = 15.6 Hz, 2H), 4.50 (d, J = 15.6 Hz, 2H), 4.35 (d, J = 15.6 Hz, 2H), 4.31 (d, J = 15.6 Hz, 2H), 4.21 (q, J = 7.2 Hz, 4H), 4.11 (q, J = 7.2 Hz, 4H), 3.71 (s, 6H), 1.23 (t, J = 7.2 Hz, 6H), 1.15 (t, J = 7.2 Hz, 6H) ppm. ¹³C NMR (150 MHz, DMSO-*d*₆): 165.5, 164.4, 155.4, 154.3, 154.2, 139.4, 133.1, 129.3, 128.9, 127.9, 125.5, 124.6, 119.9, 112.1, 80.0, 79.1, 64.8, 64.1, 56.5, 56.4, 47.6, 36.5, 13.9 ppm (only 24 of the 25 expected resonances were observed). HRMS (ESI): m/z [M + Na]⁺ calcd for C₅₄H₅₄Cl₂N₁₂O₁₆Na: 1219.3050; found: 1219.2983.



Compound **14**. A mixture of **18** (178 mg, 0.2 mmol) and 10% Pd/C (70 mg) in anhydrous DMF (10 mL) was stirred under H₂ (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anhydrous degassed CH₂Cl₂ (10 mL) and NEt₃ (0.5 mL, 4 mmol). This solution was added to a solution of pentafluorobenzoyl chloride (86 μ L, 0.60 mmol) in anhydrous degassed CH₂Cl₂ (5 mL) at -78 °C. After 15 min, the cooling bath was removed, and stirring was continued at room temperature for 3 h. The reaction mixture was diluted with CHCl₃ (100 mL), washed with saturated aqueous NaHCO₃, dried over anhydrous MgSO₄, and concentrated. Flash chromatography (SiO₂, CHCl₃/MeOH, 50:1) gave **14** (197 mg, 0.172 mmol, 81%). To get highest purity material, the solid was washed with EtOAc (2 mL), centrifuged, and the supernatant decanted yielding **14** as a white solid (177 mg, 0.146 mmol, 73%). Mp > 300 °C (dec.). TLC (CHCl₃/MeOH 20:1) R_f 0.29. IR (KBr, cm⁻¹): 3443w, 2986w, 1752s, 1686m, 1655w, 1602w, 1552m, 1520s, 1501s, 1455s, 1426s, 1367w, 1331m, 1387m, 1252s, 1171w, 1098w, 1018m, 993m, 910m. ¹H NMR (400 MHz, DMSO-*d*₆): 11.01 (s, 2H), 7.62 (d, J = 1.6 Hz, 2H), 7.45 (dd, J = 8.2 and 1.6 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.82 (d, J = 16.4 Hz, 2H), 4.70-4.45 (m, 10H), 4.30-4.15 (m, 8H), 1.25 (t, J = 7.2 Hz, 6H), 1.21 (t, J = 7.2 Hz, 6H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): 165.0, 164.1, 154.8, 154.2, 154.0, 143.2 (J_{CF} = 247 Hz), 141.5 (J_{CF} = 263 Hz), 137.1 (J = 267 Hz), 137.6, 137.1, 132.5, 130.3, 120.5, 118.8, 112.3 (J_{CF} = 21 Hz), 79.9, 78.5, 64.4, 63.9, 47.4, 47.3, 44.9, 44.2, 13.6, 13.5 ppm. HRMS (ESI): m/z [M + Na]⁺ calcd for C₅₂H₄₀F₁₀N₁₀O₁₄Na: 1241.2458; found: 1241.2403.



Compound (\pm)-**15**. A mixture of **19** (128 mg, 0.2 mmol) and 10% Pd/C (50 mg) in anhydrous DMF (10 mL) was stirred under H₂ (15-20 psi) at room temperature for 6 h. The reaction mixture was filtered under Ar and concentrated under high vacuum at room temperature. The residue was dissolved in a mixture of anhydrous degassed CH₂Cl₂ (10 mL) and NEt₃ (0.5 mL, 4 mmol). This solution was added to a solution of pentafluorobenzoyl chloride (13 μ L, 0.09 mmol) in anhydrous degassed CH₂Cl₂ (5 mL) at -78 °C. After 15 min, the cooling bath was removed, and stirring was continued at room temperature for 1 h. Then, the mixture was cooled to -78 °C and added to a solution of acetyl chloride (11 μ L, 0.15 mmol) in anhydrous degassed CH₂Cl₂ (5 mL) at -78 °C. After 15 min, the cooling bath was removed, and stirring was continued at room temperature for 2 h. The reaction mixture was diluted with CHCl₃ (100 mL), washed with saturated aqueous NaHCO₃, dried over anhydrous MgSO₄, and concentrated. Flash chromatography (SiO₂, CHCl₃/MeOH, 50:1) gave **15** (93 mg, 0.114 mmol, 57%). To get highest purity material, the solid was washed with EtOAc (2 mL), centrifuged, and the supernatant decanted yielding (\pm)-**15** as a white solid 80 mg, 0.098 mmol, 49 %). Mp 267-268 °C. TLC (CHCl₃/MeOH 20:1) *R_f* 0.35. IR (KBr, cm⁻¹): 3311m, 2984w, 1759m, 1744m, 1705s, 1680s, 1652w, 1599w, 1502s, 1469m, 1446m, 1429m, 1367w, 1327m, 1267s, 1138w, 1105w, 1073m, 1041w, 1023w, 994m, 960w, 918w. ¹H NMR (400 MHz, DMSO-*d*₆): 10.58 (s, 1H), 9.40 (s, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 5.28 (d, *J* = 16.0 Hz, 1H), 5.22 (d, *J* = 16.0 Hz, 1H), 4.80 (d, *J* = 16.0 Hz, 1H), 4.69 (d, *J* = 16.0 Hz, 1H), 4.30-4.10 (m, 8H), 3.77 (s, 3H), 3.70 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 6H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 168.8, 165.2, 156.4, 155.5, 155.3, 155.1, 154.1, 143.3 (d, *J*_{CF} = 241 Hz), 141.3 (d, *J*_{CF} = 240 Hz), 136.9 (d, *J*_{CF} = 250 Hz), 134.6, 133.8, 128.9, 126.9, 126.6, 125.8, 125.3, 112.3, 111.7, 111.3, 79.9, 63.4, 56.2, 56.1, 35.9, 22.9, 13.7 ppm (only 27 of the 35 expected resonances were observed). HRMS (ESI): *m/z* [M + Na]⁺ calcd for C₃₇H₃₃F₅N₆O₁₀Na: 839.2071; found: 839.2068. X-ray crystal structure.

References:

1. Wu, A. X.; Mukhopadhyay, P.; Chakraborty, A.; Fettingner, J. C.; Isaacs, L. *J. Am. Chem. Soc.* **2004**, *126*, 10035-10043.
2. Wu, A. X.; Chakraborty, A.; Fettingner, J. C.; Flowers, R. A.; Isaacs, L. *Angew. Chem. Int. Ed.* **2002**, *41*, 4028-4031.
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4. Mukhopadhyay, P.; Wu, A. X.; Isaacs, L. *J. Org. Chem.* **2004**, *69*, 6157-6164.
5. Ghosh, S.; Wu, A. X.; Fettingner, J. C.; Zavalij, P. Y.; Isaacs, L. *J. Org. Chem.* **2008**, *73*, 5915-5925.
6. Wang, Z. G.; Zhou, B. H.; Chen, Y. F.; Yin, G. D.; Li, Y. T.; Wu, A. X.; Isaacs, L. *J. Org. Chem.* **2006**, *71*, 4502-4508.

Characterization of Homodimers by ^1H NMR

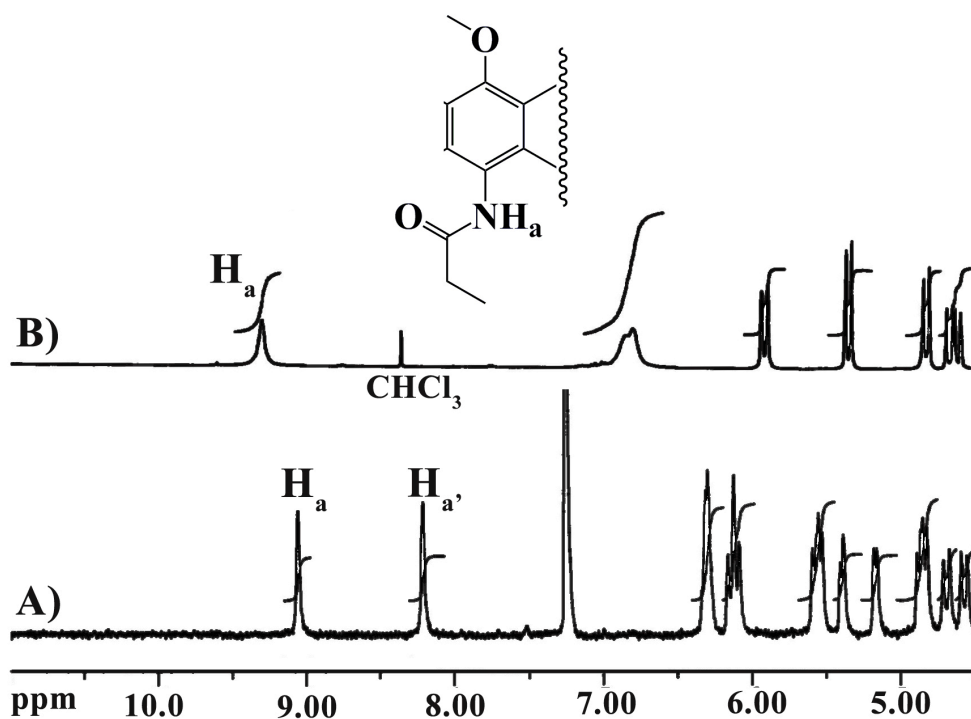


Figure S1. Portion of the ^1H NMR (400 MHz, room temperature) spectrum recorded for (A) dimer $2\cdot 2$ in CDCl_3 (20 mM), and (B) monomer 2 in $\text{DMSO-}d_6$.

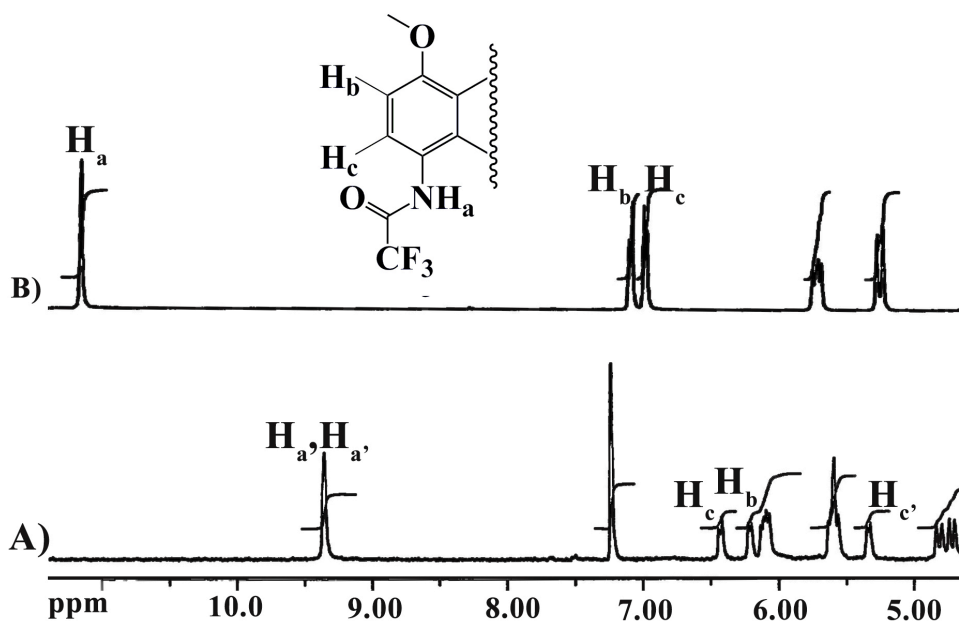


Figure S2. Portion of the ^1H NMR (400 MHz, room temperature) spectrum recorded for (A) dimer $3\cdot 3$ in CDCl_3 (20 mM), and (B) monomer 3 in $\text{DMSO-}d_6$.

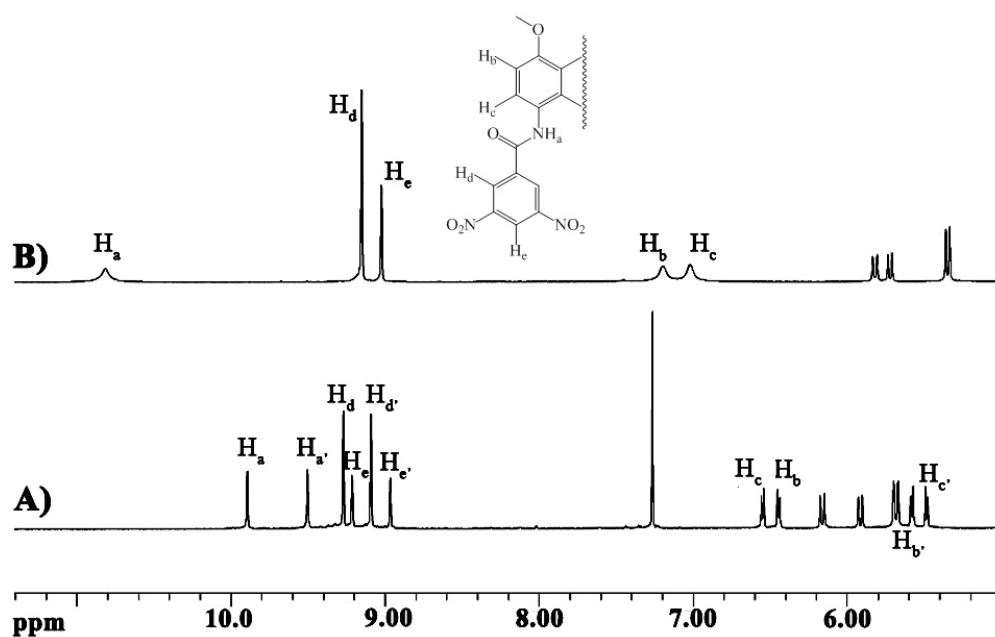


Figure S3. Portion of the ¹H NMR (600 MHz, room temperature) spectrum recorded for A) dimer 5•5 in CDCl₃ (20 mM), and B) monomer 5 in DMSO-*d*₆.

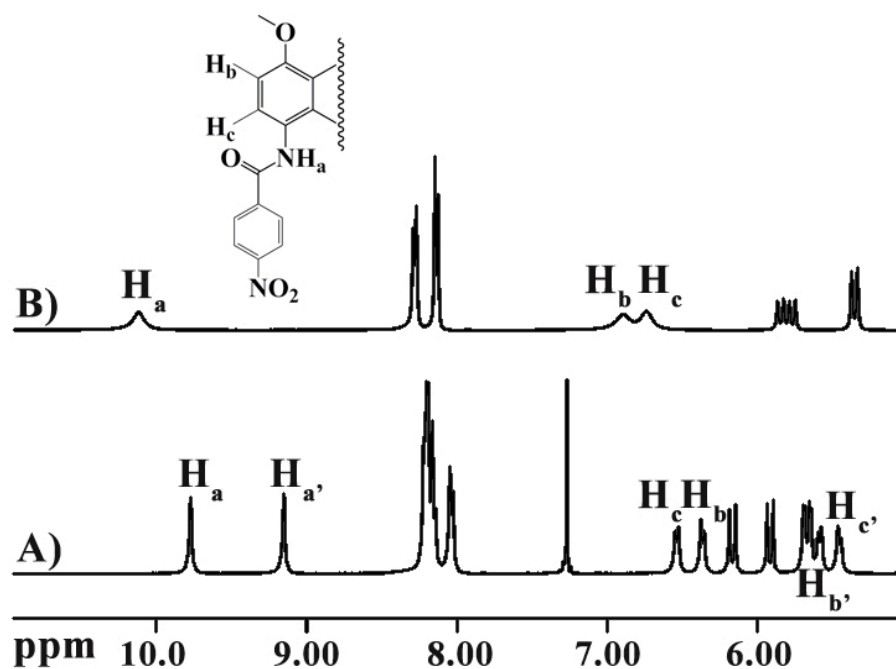


Figure S4. Portion of the ¹H NMR (600 MHz, room temperature) spectrum recorded for (A) dimer 6•6 in CDCl₃ (20 mM), and (B) monomer 6 in DMSO-*d*₆.

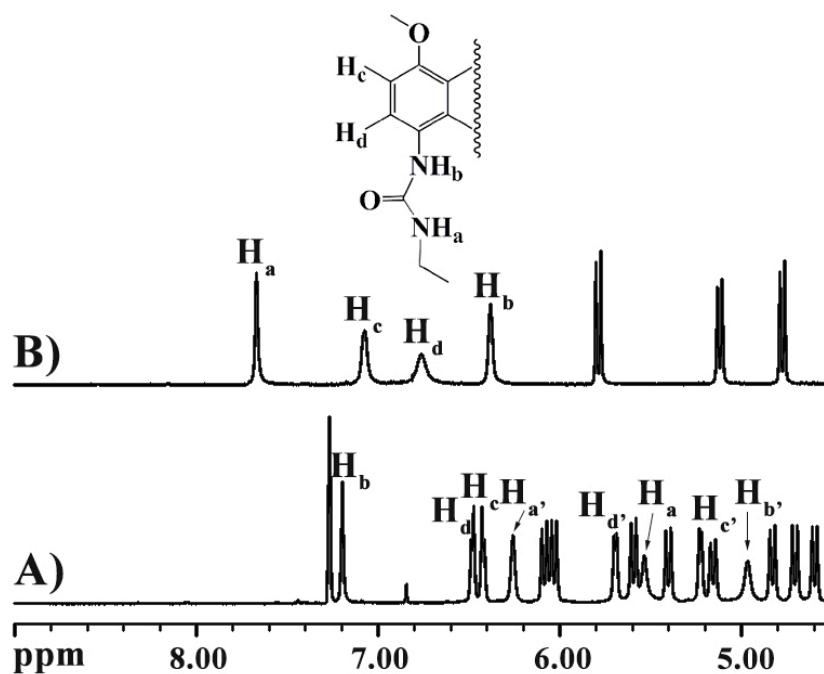


Figure S5. Portion of the ¹H NMR (600 MHz, room temperature) spectrum recorded for (A) dimer (+)-8•(-)-8 in CDCl₃ (20 mM), and (B) monomer (±)-8 in DMSO-*d*₆.

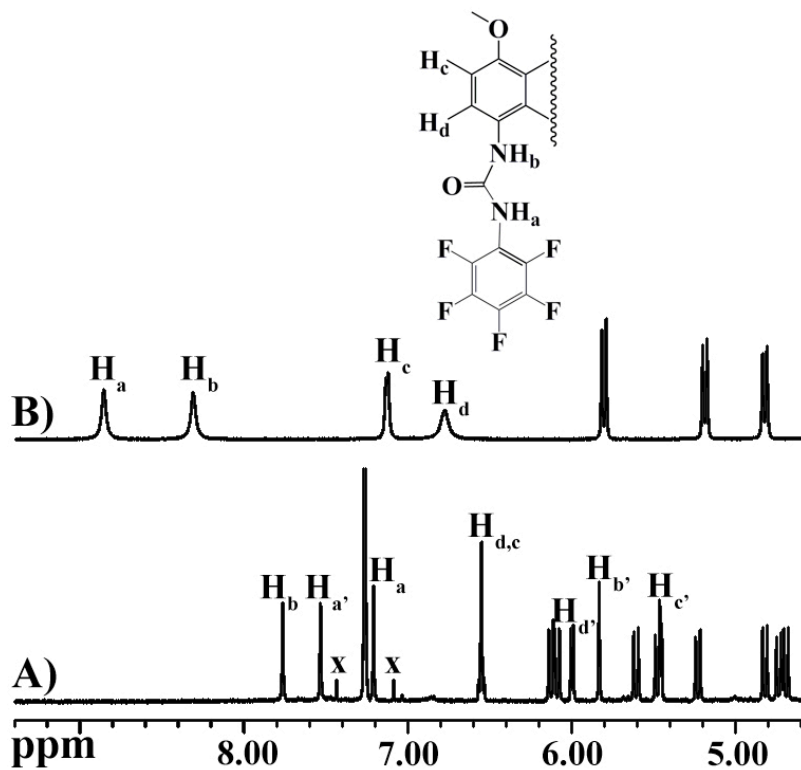


Figure S6. Portion of the ¹H NMR (600 MHz, room temperature) spectrum recorded for (A) dimer (+)-9•(-)-9 in CDCl₃ (5 mM), and (B) monomer (±)-9 in DMSO-*d*₆. x = ¹³CHCl₃.

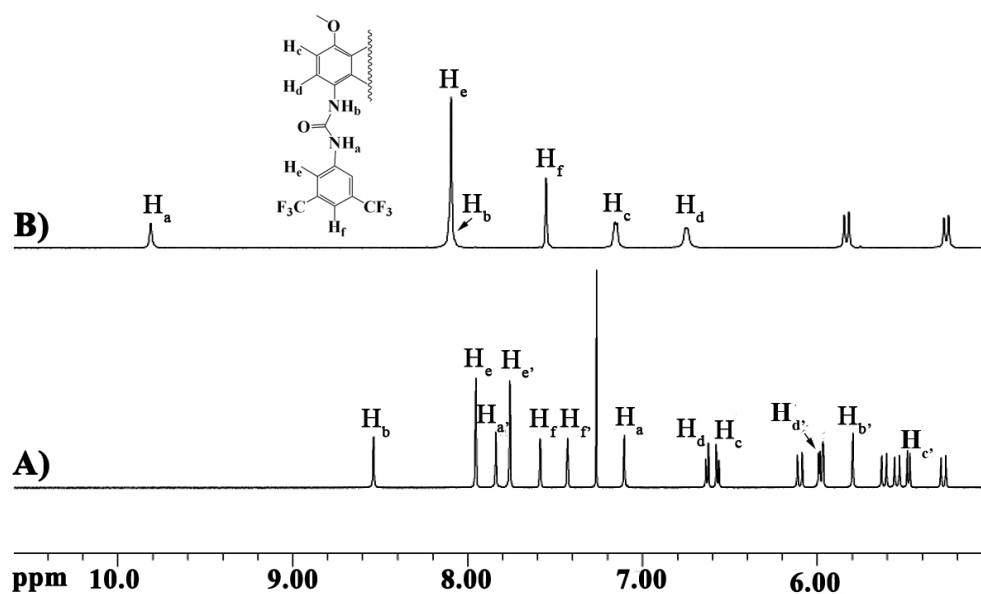


Figure S7. Portion of the ¹H NMR (600 MHz, room temperature) spectrum recorded for A) dimer (+)-11•(-)-11 in CDCl₃ (20 mM), and B) monomer (±)-11 in DMSO-*d*₆.

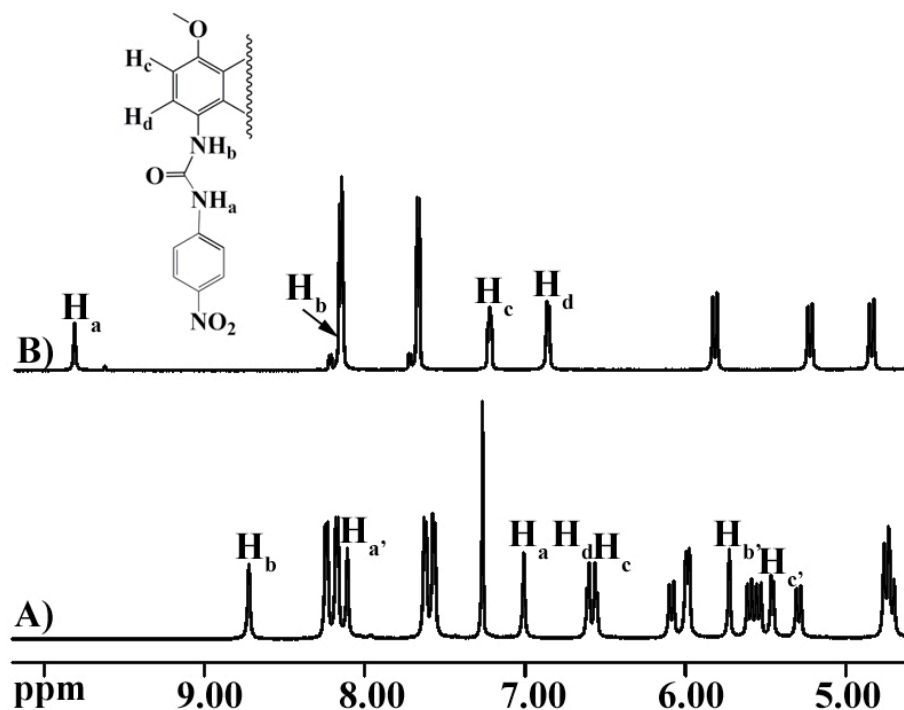


Figure S8. Portion of the ¹H NMR (600 MHz, room temperature) spectrum recorded for (A) dimer (+)-12•(-)-12 in CDCl₃ (20 mM), and (B) monomer (±)-12 in DMSO-*d*₆.

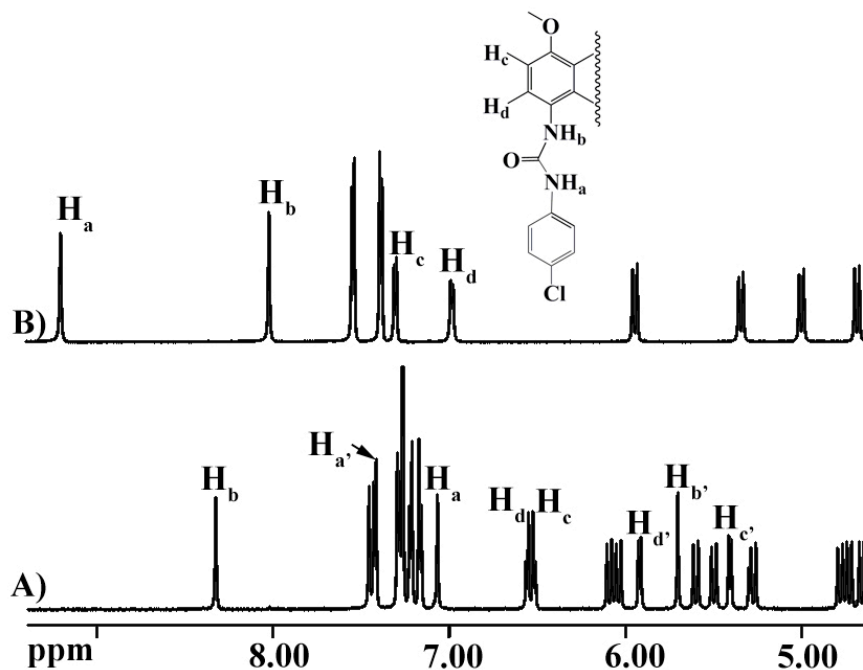


Figure S9. Portion of the ¹H NMR (600 MHz, room temperature) spectrum recorded for (A) dimer (+)-13•(-)-13 in CDCl₃ (20 mM), and (B) monomer (±)-13 in DMSO-*d*₆.

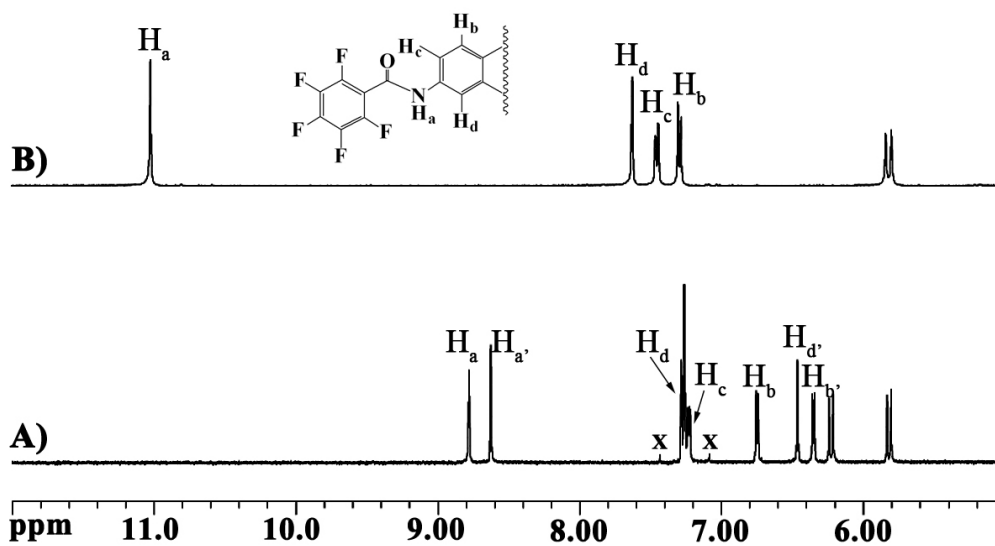


Figure S10. Portion of the ¹H NMR spectrum (400 MHz, room temperature) recorded for (A) dimer 14•14 in CDCl₃ (5 mM), and (B) monomer 14 in DMSO-*d*₆. x = ¹³CHCl₃.

Characterization of homodimers by x-ray crystallography

X-ray Crystallographic Data for **3** and (\pm)-**13**. Crystal data for **3**·(ClCH₂CH₂Cl): C₄₆H₄₈Cl₂F₆N₁₀O₁₆, $M_r = 1181.84$, Monoclinic, space group $C2/c$, $a = 31.260(11)$, $b = 13.333(5)$, $c = 27.209(10)$ Å, $Z = 8$, $V = 10504(6)$ Å³, $D_c = 1.495$ g cm⁻³, $\mu = 0.224$ mm⁻¹, $\theta_{\max} = 25.00^\circ$, $F(000) = 4880$, reflections collected/unique, 36605/9236 ($R_{\text{int}} = 0.0878$), final R indices [$I > 2\sigma(I)$] $R_1 = 0.0705$, $wR_2 = 0.1929$, R indices (all data) $R_1 = 0.1271$, $wR_2 = 0.2233$, GOF = 0.998 for all data. Crystal data for (\pm)-**13**·(CH₂Cl₂)₂·(CH₃OH): C₅₇H₆₂Cl₆N₁₂O₁₇, $M_r = 1399.89$, Triclinic, space group $P-1$, $a = 14.4991(10)$, $b = 15.5113(11)$, $c = 116.0201(11)$ Å, $Z = 2$, $V = 3161.4(4)$ Å³, $D_c = 1.471$ g cm⁻³, $\mu = 0.351$ mm⁻¹, $\theta_{\max} = 25.50^\circ$, $F(000) = 1452$, reflections collected/unique, 20709/11641 ($R_{\text{int}} = 0.1005$), final R indices [$I > 2\sigma(I)$] $R_1 = 0.0746$, $wR_2 = 0.2021$, R indices (all data) $R_1 = 0.0843$, $wR_2 = 0.2108$, GOF = 1.078 for all data. CCDC-782748 (**3**) and CCDC-782746 ((\pm)-**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (t44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

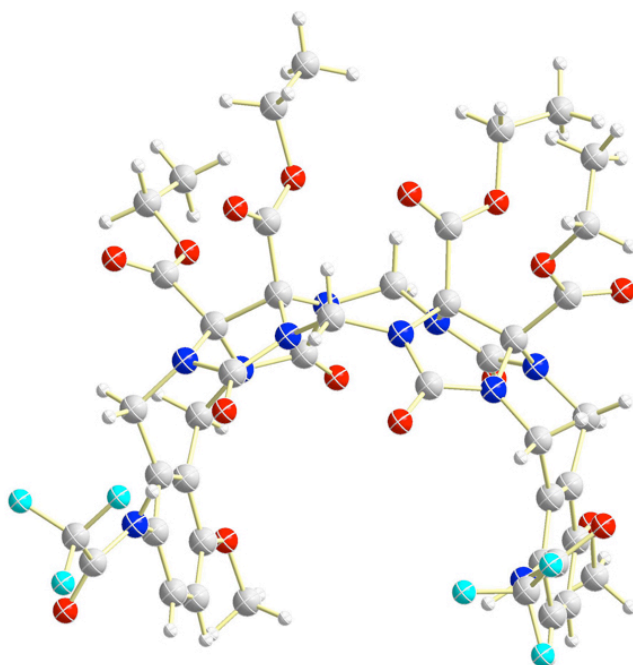


Figure S11. The crystal structure of **3**. Solvating ClCH₂CH₂Cl has been removed for clarity. Some of the CO₂Et groups adopt two orientations in the crystal; here, the major orientation component is depicted. C, grey; H, white; N, blue; O, red; Cl, green.

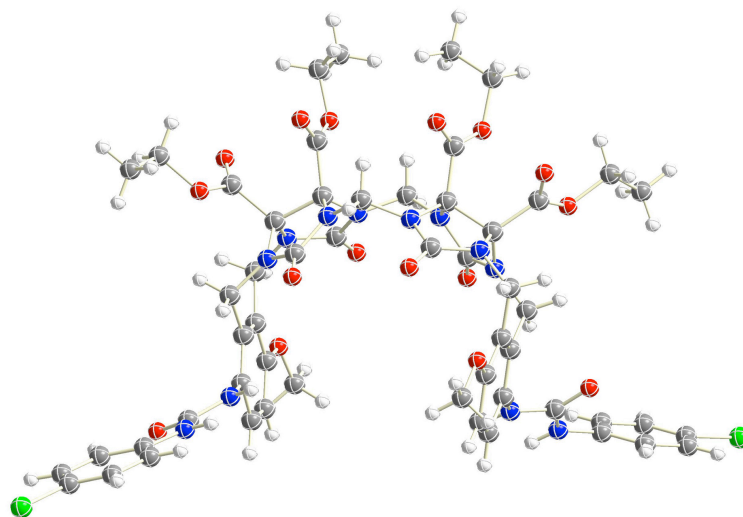


Figure S12. The crystal structure of (±)-**13**. Solvating CH_2Cl_2 and CH_3OH have been removed for clarity. Some of the CO_2Et groups adopt two orientations in the crystal; here, the major orientation component is depicted. C, gray; H, white; N, blue; O, red; Cl, green.

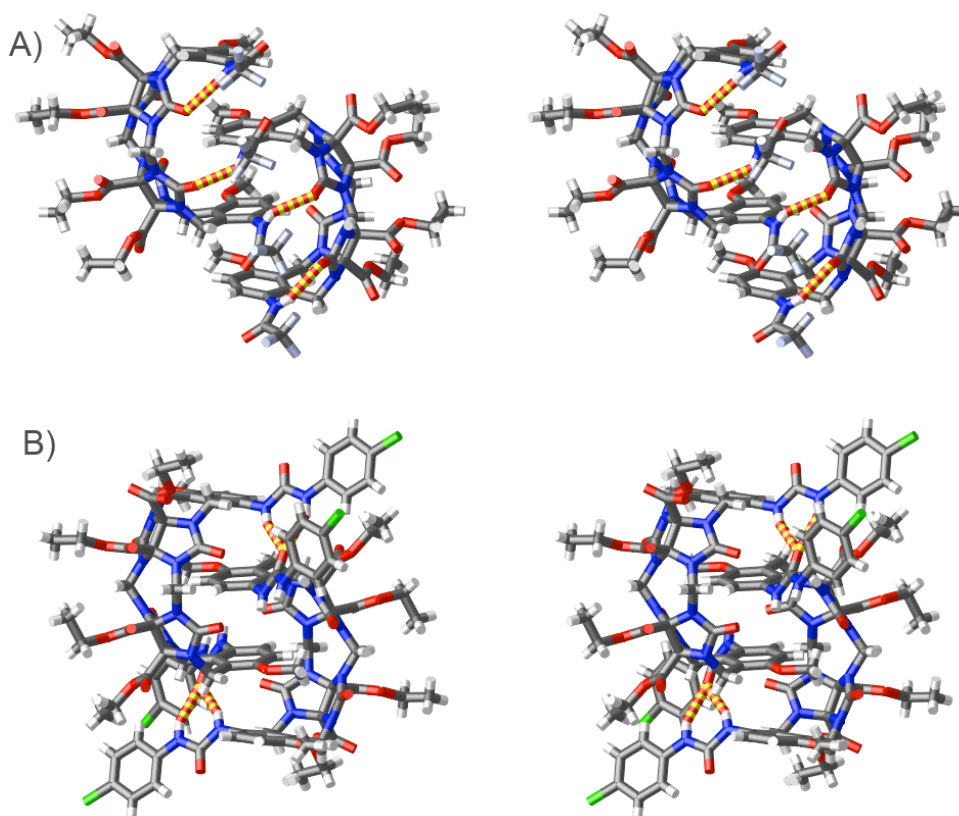


Figure S13. Stereoviews of the molecular structures of (A) **3•3**, and (B) (+)-**13•(-)-13** in the crystal. Solvating $\text{ClCH}_2\text{CH}_2\text{Cl}$, CH_2Cl_2 and CH_3OH have been removed for clarity. Some of the CO_2Et groups adopt two orientations in the crystal; here, the major orientation component is depicted. C, gray; H, white; N, blue; O, red; Cl, green; F, light-blue; and H-bonds, yellow dot-line.

Tabulation of heterodimerization equilibrium constants and related ^1H NMR spectra.

Table S1. Heterodimer Equilibrium Constants, K_{eq} , and Heterodimer Mole Fractions (χ_{AB}) for Binary Mixtures of **1–13**.^{a)}

Entry Number	Clip A	Clip B	K_{eq}	$\chi_{\text{AB}} / \%$
1	1	2	4.7	52.0
2 ^{b)}	1	4	562.9/576.6 ^{c)}	92.2/92.3 ^{c)}
3	1	5	26.9	72.2
4	1	6	38.9	75.7
5	2	4	139.7	85.5
6	3	7	9.6	60.8
7	(±)- 8	(±)- 9	19.27	68.7
8	(±)- 8	(±)- 10	7.8	58.3
9	(±)- 8	(±)- 11	534.4/539.8 ^{c)}	92.0/92.1 ^{c)}
10	(±)- 8	(±)- 12	126.6	84.9
11	(±)- 8	(±)- 13	6.1	55.2
12	(±)- 10	(±)- 13	5.0	52.7
13	(±)- 11	(±)- 12	16.2	66.8

a) 20 mM, CDCl_3 , 600 MHz, room temperature. b) Reported in reference 3d. c) 5 mM, $\text{C}_6\text{D}_5\text{CD}_3/\text{CDCl}_3$ (5:1, v:v), 600 MHz, room temperature.

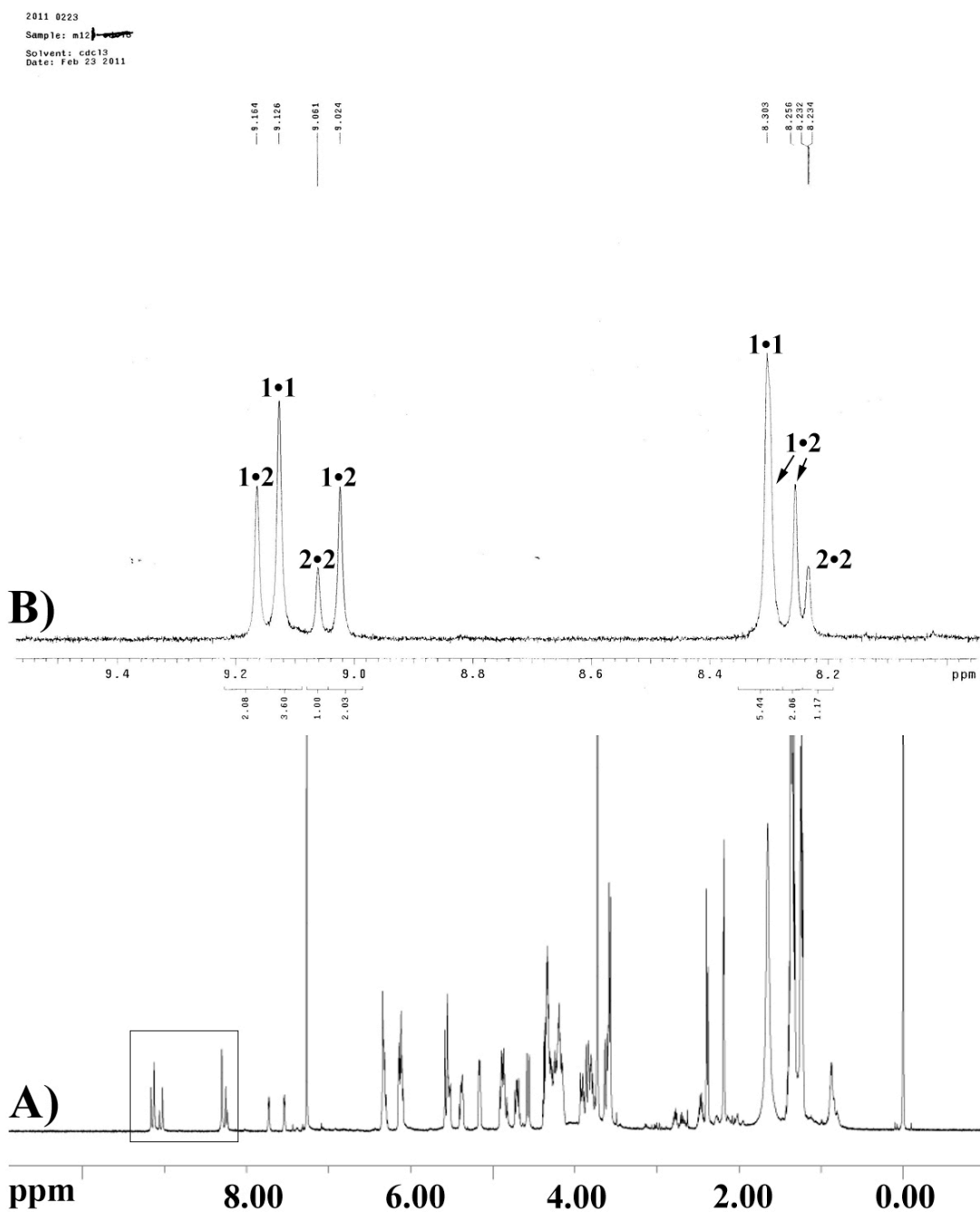


Figure S14. The ^1H NMR spectra (600 MHz, 2 mM, RT, CDCl_3) recorded for the heterodimerization of **1** and **2**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 1)

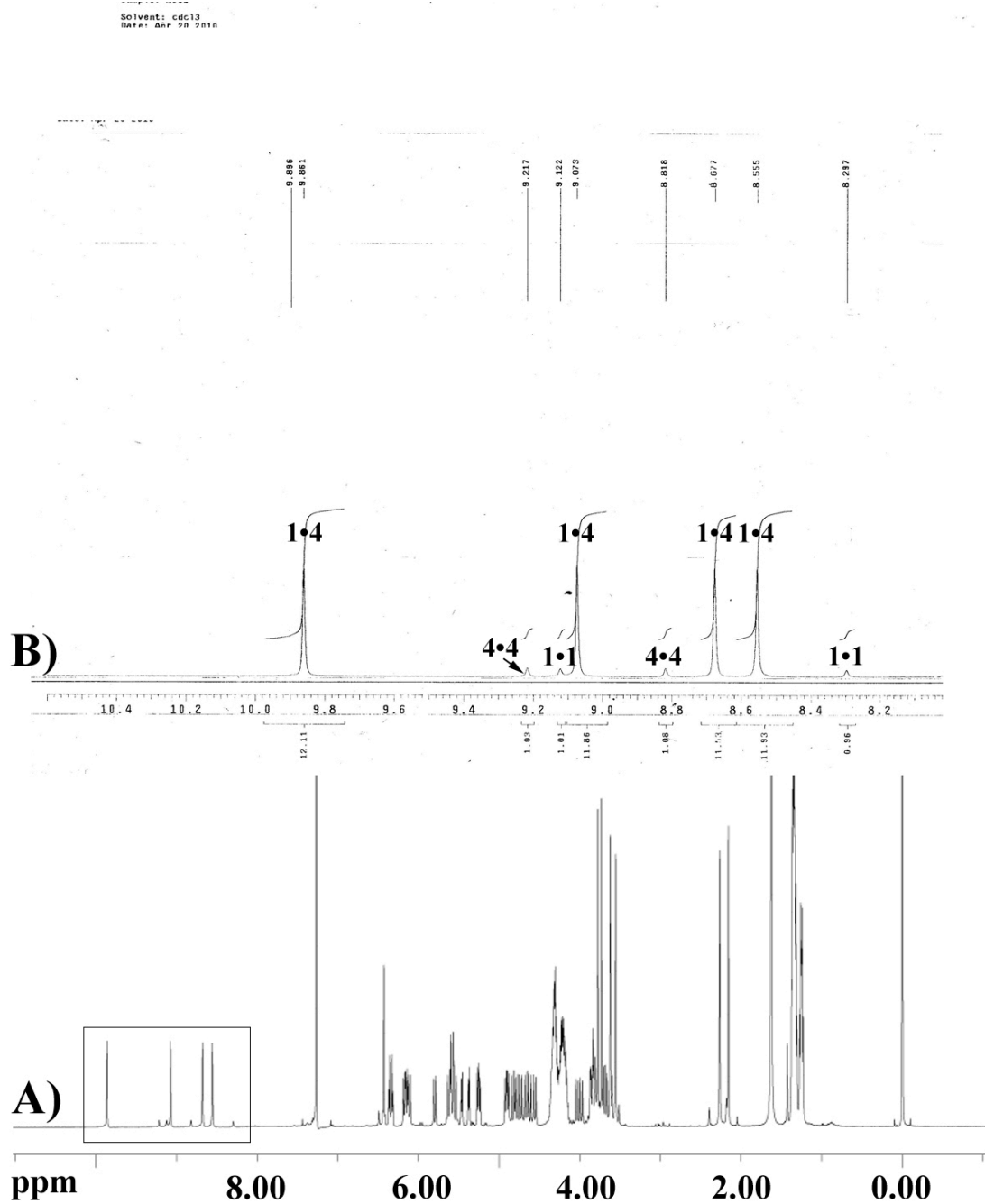


Figure S15. The ^1H NMR spectra (600 MHz, 5 mM, RT, CDCl_3) recorded for the heterodimerization of **1** and **4**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 2)

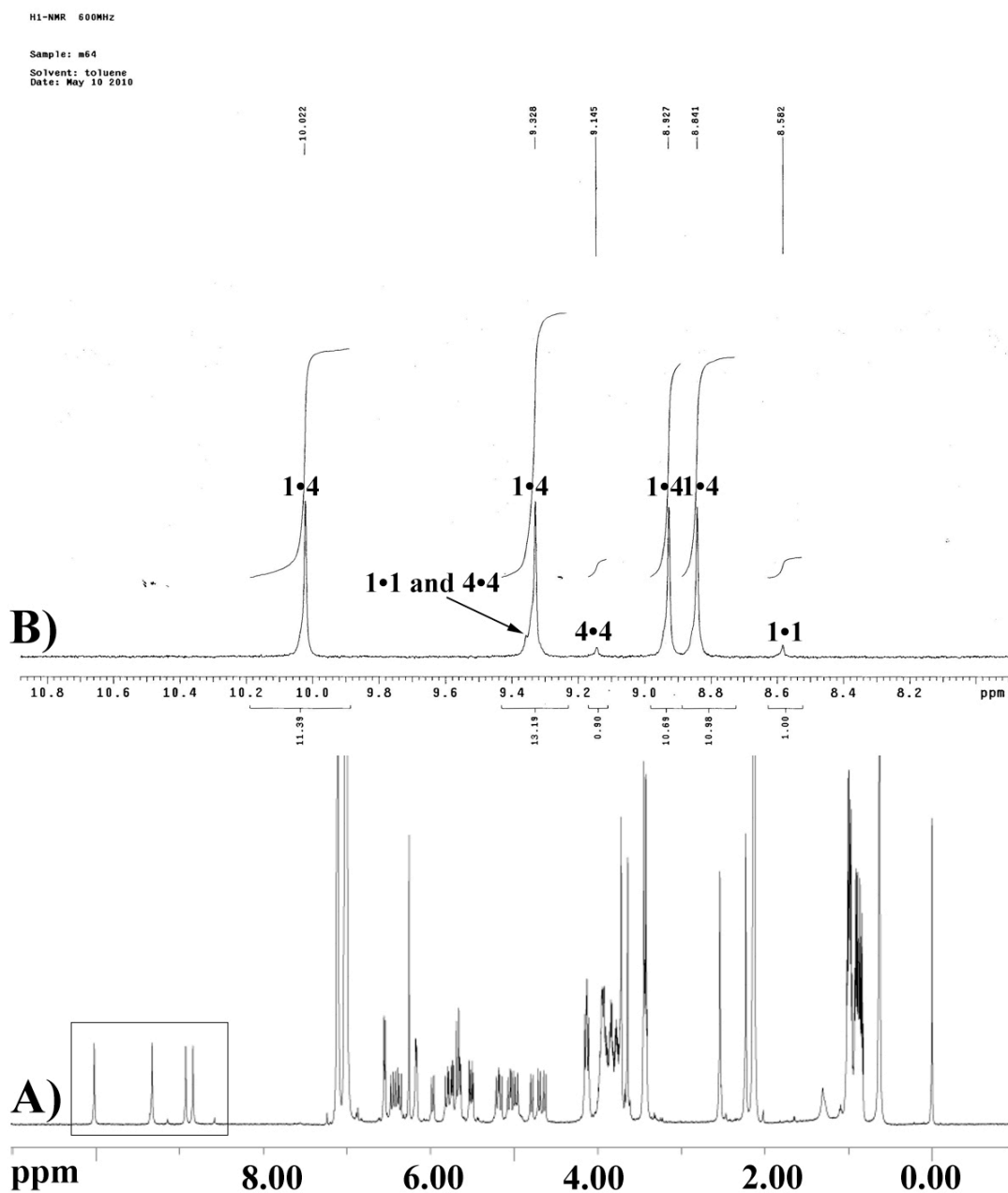


Figure S16. The ^1H NMR spectra (600 MHz, 5 mM, RT, $\text{C}_6\text{D}_5\text{CD}_3/\text{CDCl}_3 = 5:1$ (v:v)) recorded for the heterodimerization of **1** and **4**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 2)

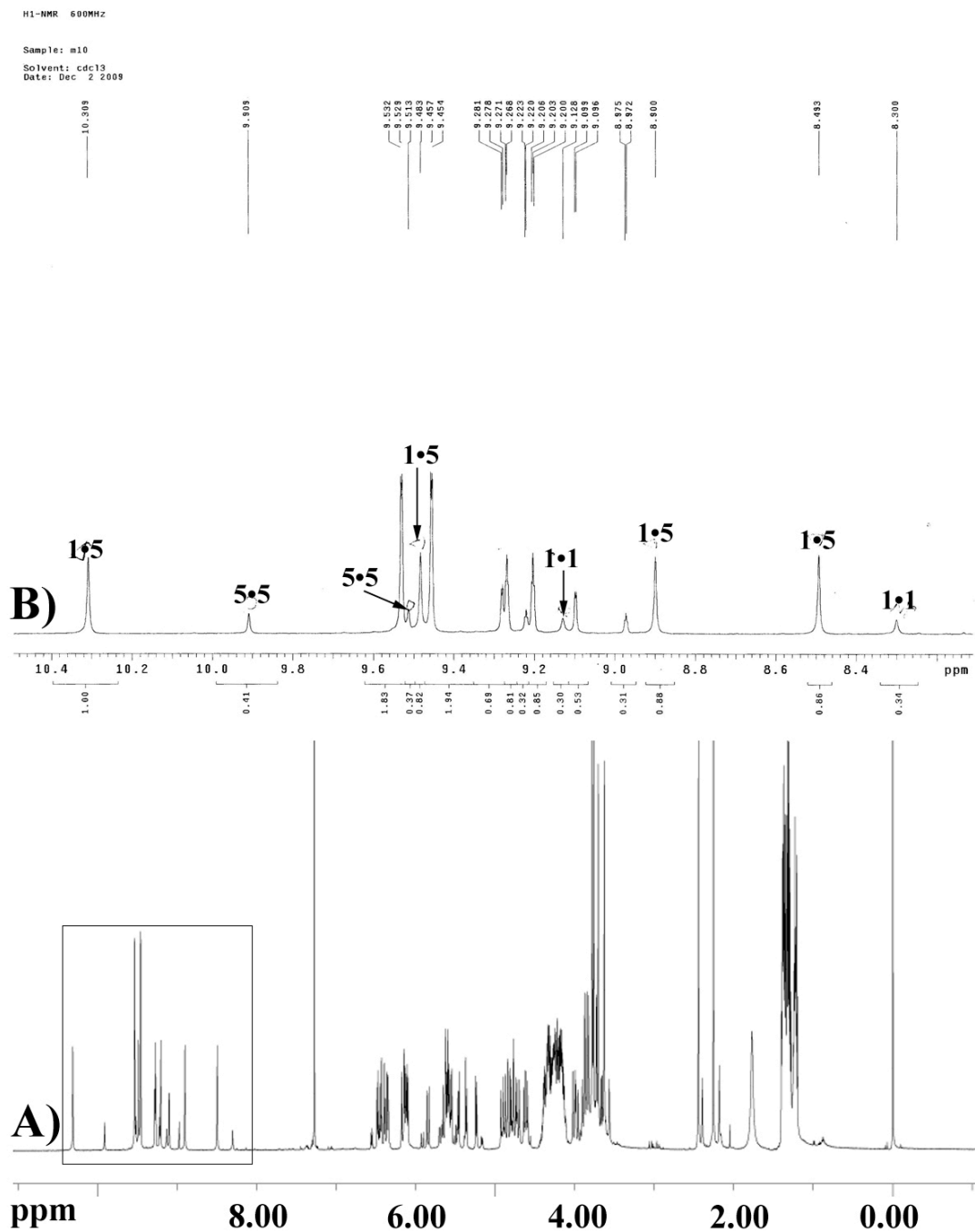


Figure S17. The ^1H NMR spectra (600 MHz, 20 mM, RT, CDCl_3) recorded for the heterodimerization of **1** and **5**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 3)

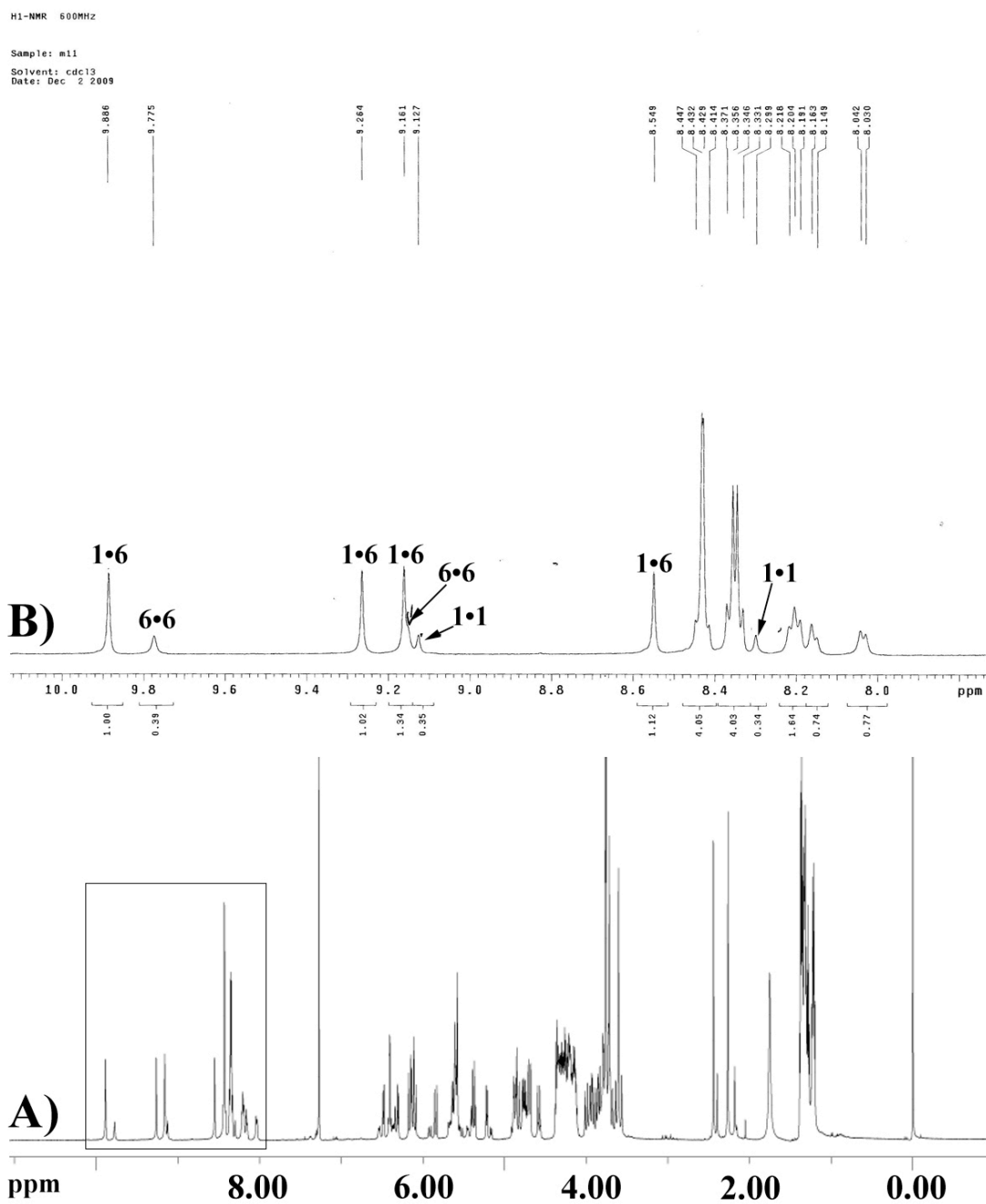


Figure S18. The ^1H NMR spectra (600 MHz, 20 mM, RT, CDCl_3) recorded for the heterodimerization of **1** and **6**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 4)

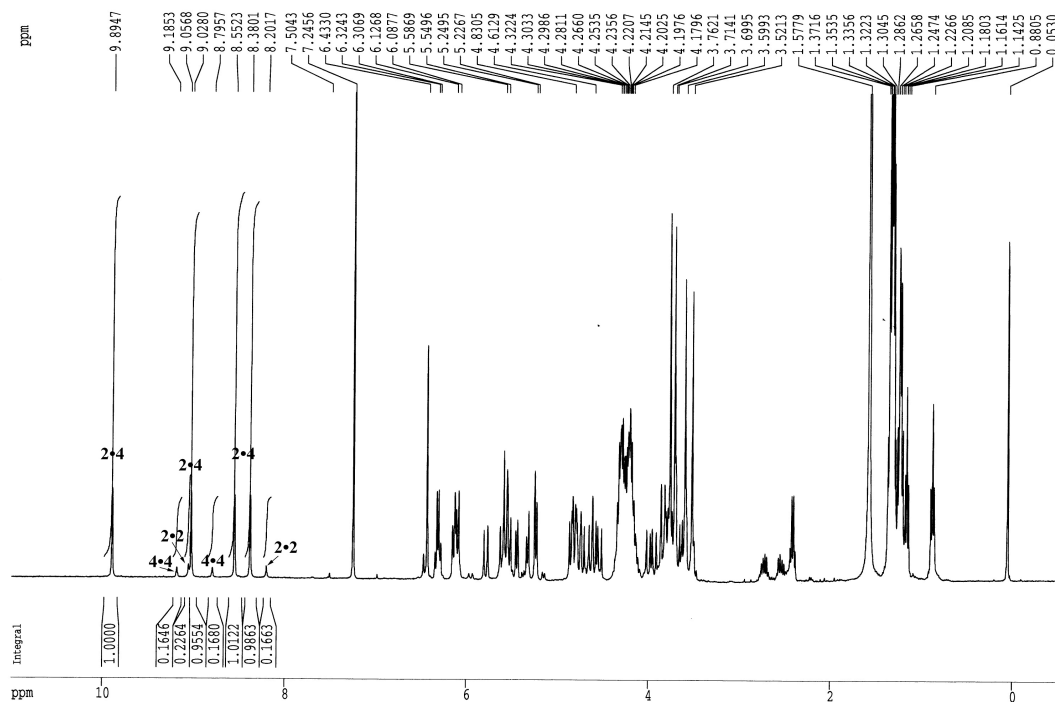


Figure S19. The ^1H NMR spectra (400 MHz, 20 mM, RT, CDCl_3) recorded for the heterodimerization of **2** and **4**. (Table 1, entry 5)

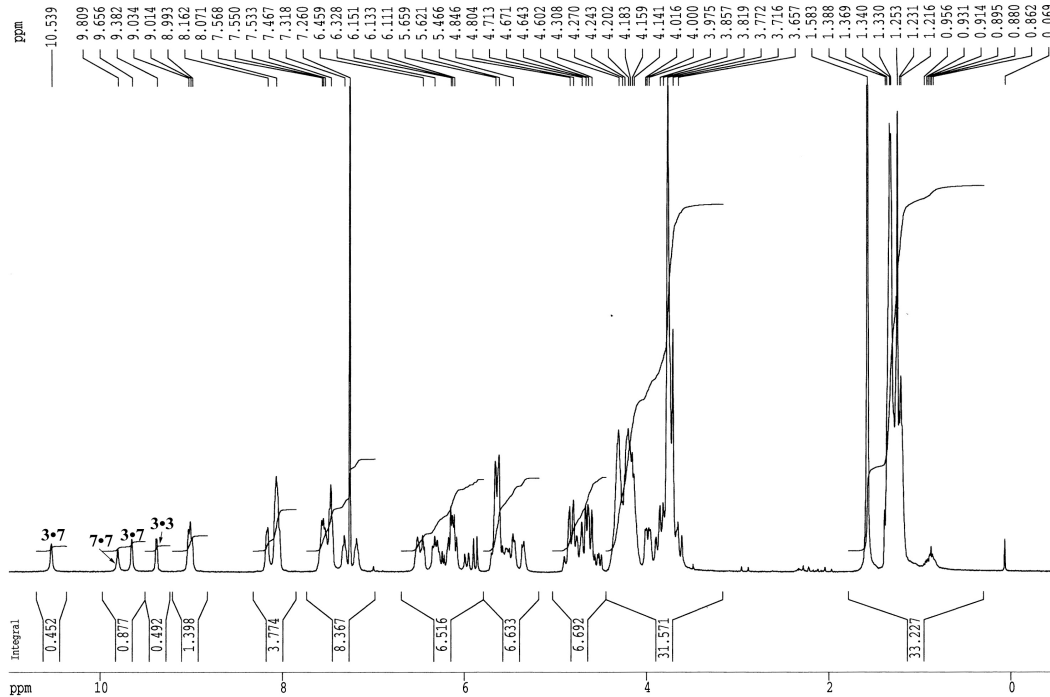


Figure S20. The ^1H NMR spectra (400 MHz, 20 mM, RT, CDCl_3) recorded for the heterodimerization of **3** and **7**. In this spectrum, the two NH singlets of **3**•**3** were overlapped (Table 1, entry 6)

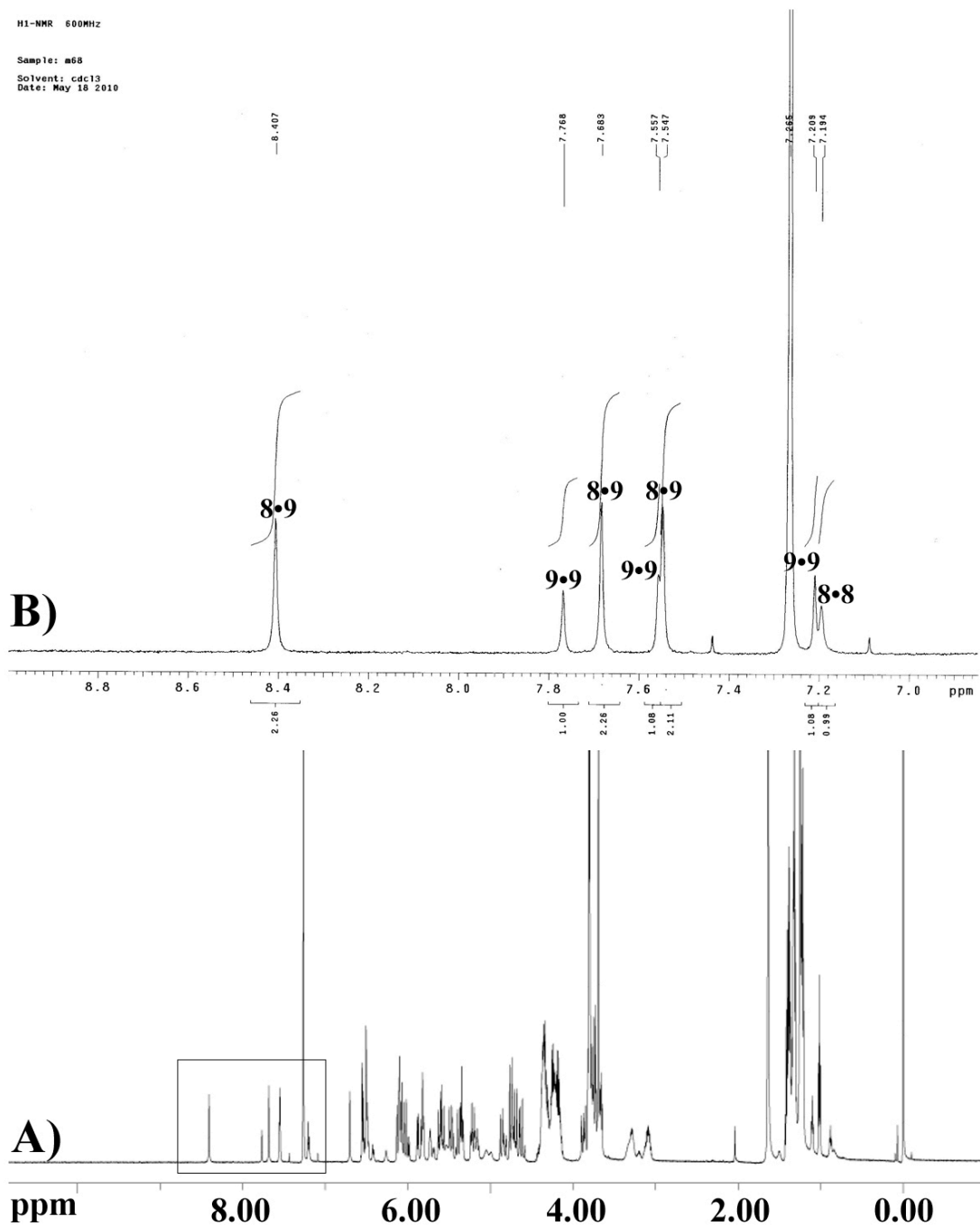


Figure S21. The ^1H NMR spectra (600 MHz, 5 mM, RT, CDCl_3) recorded for the heterodimerization of **8** and **9**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 7)

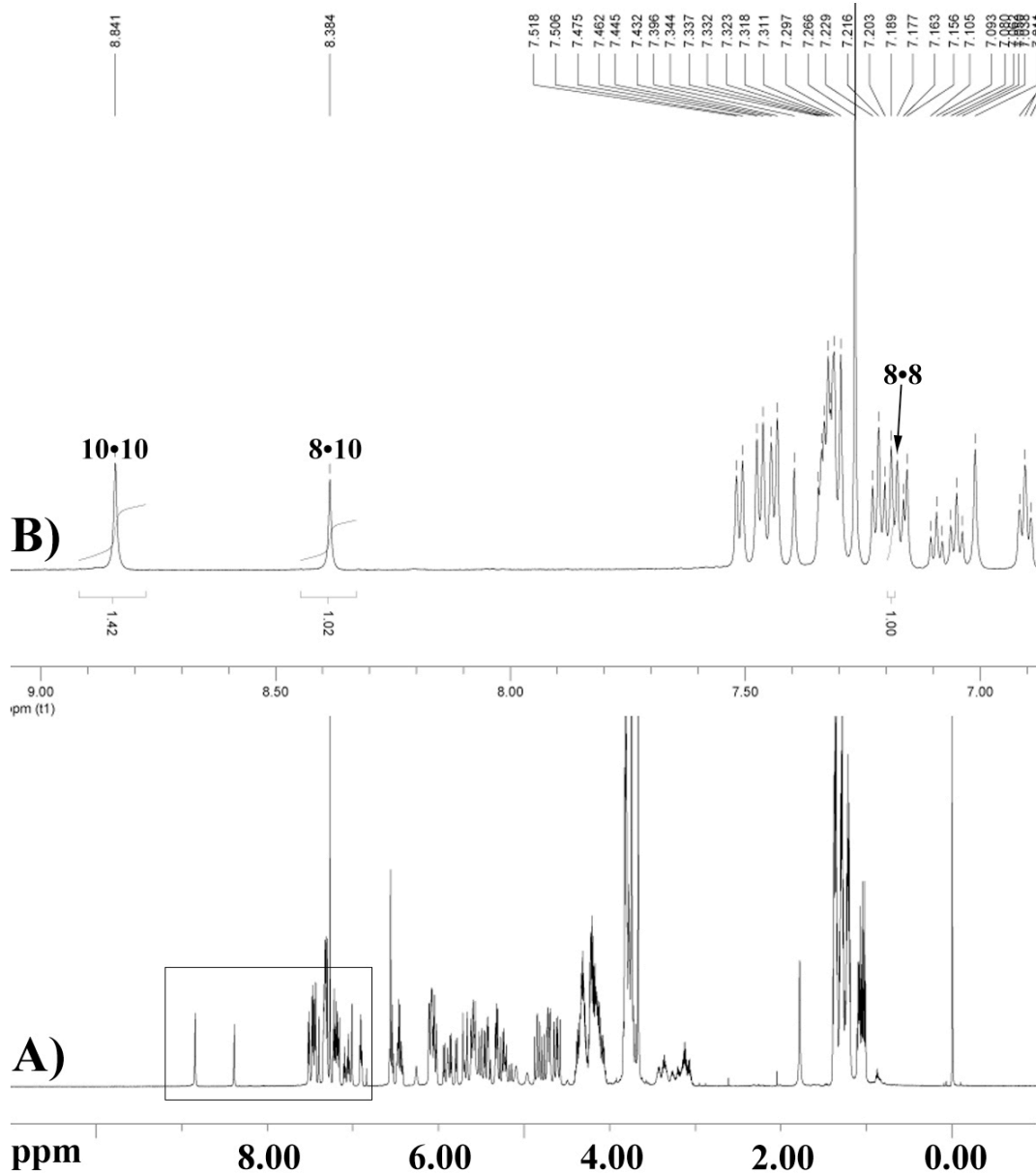


Figure S22. The ^1H NMR spectra (600 MHz, 5 mM, RT, CDCl_3) recorded for the heterodimerization of **8** and **10**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 8)

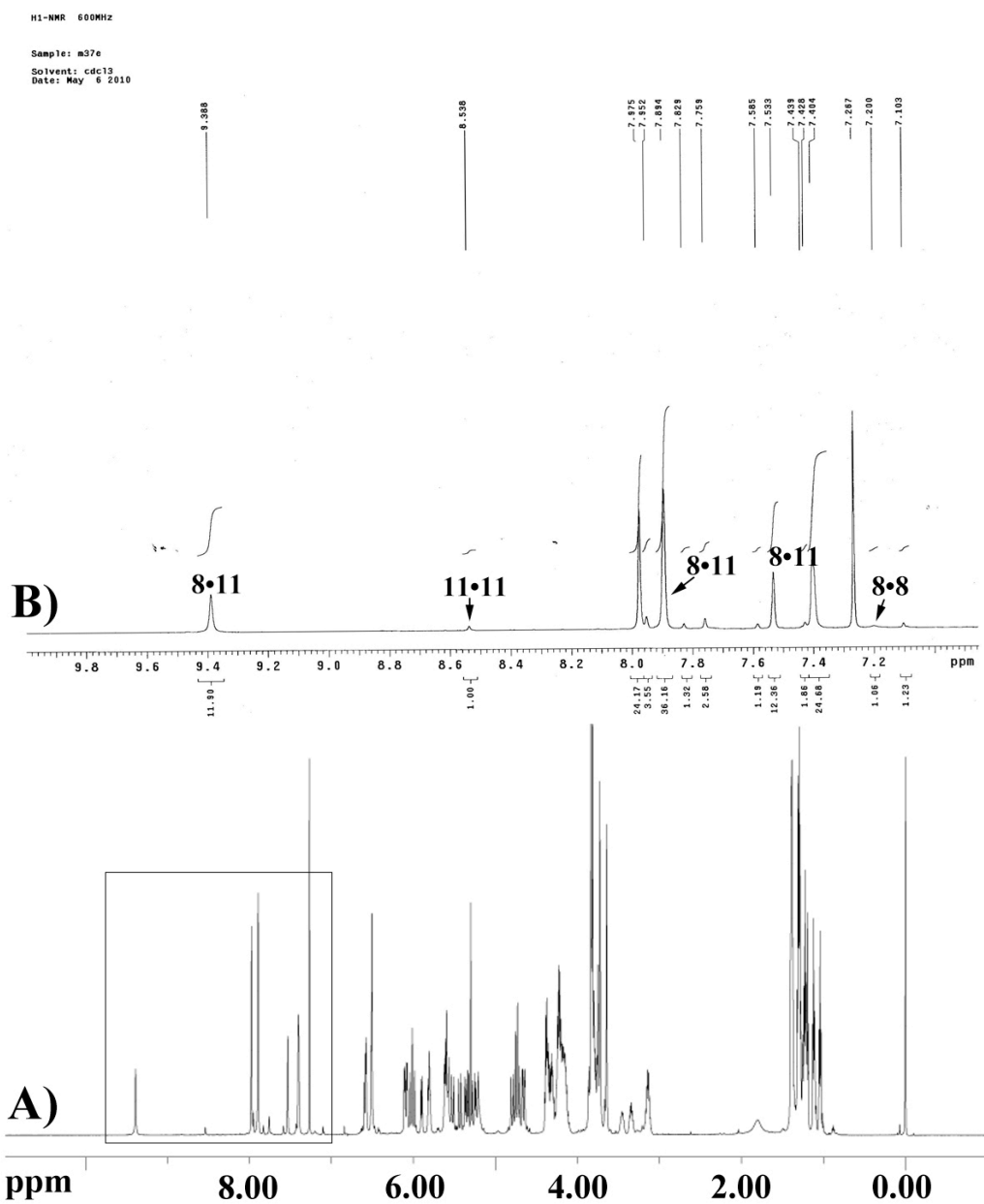


Figure S23. The ^1H NMR spectra (600 MHz, 20 mM, RT, CDCl_3) recorded for the heterodimerization of **8** and **11**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 9)

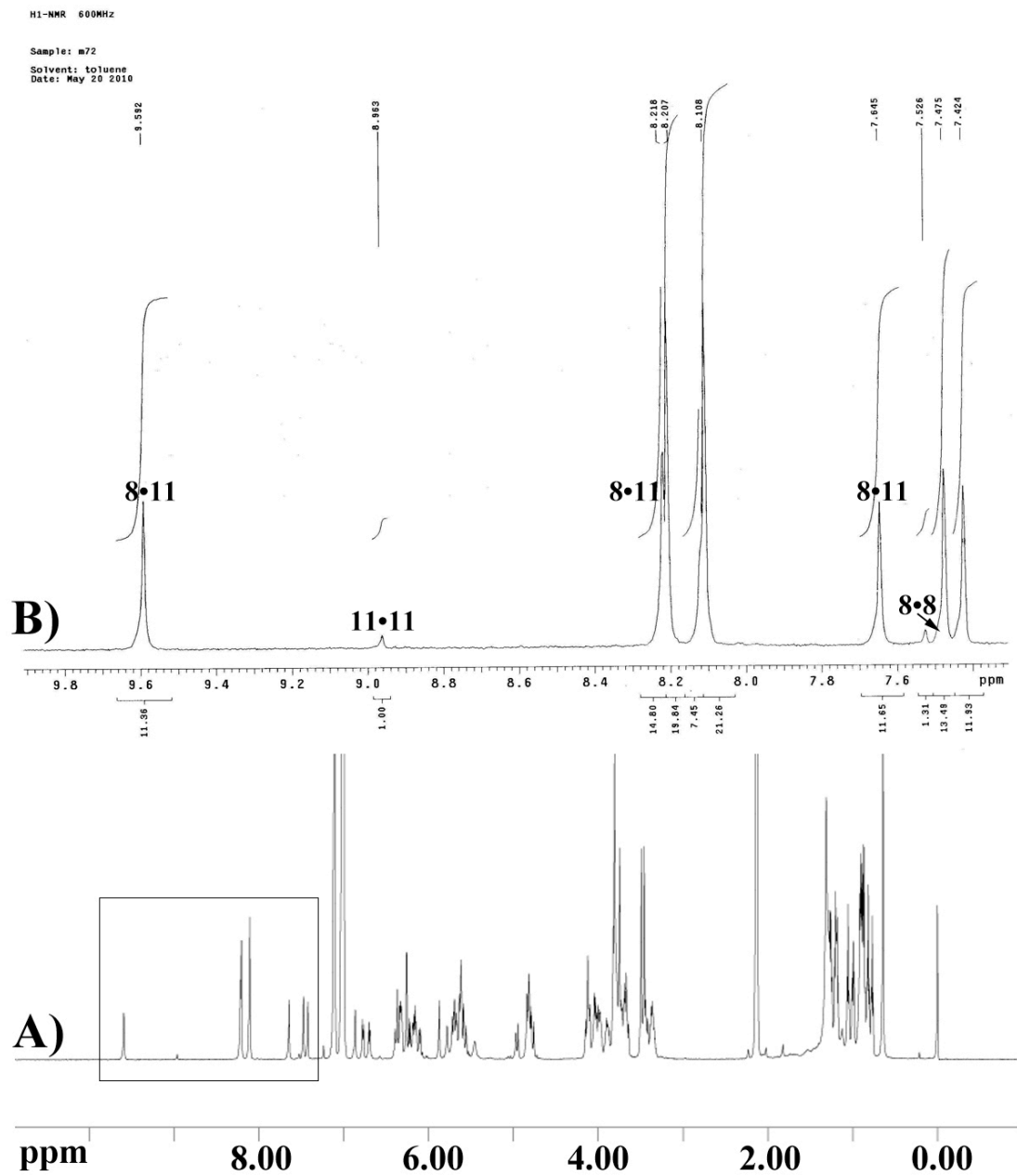


Figure S24. The ^1H NMR spectra (600 MHz, 5 mM, RT, $\text{C}_6\text{D}_5\text{CD}_3/\text{CDCl}_3 = 5:1$ (v:v)) recorded for the heterodimerization of **8** and **11**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 9)

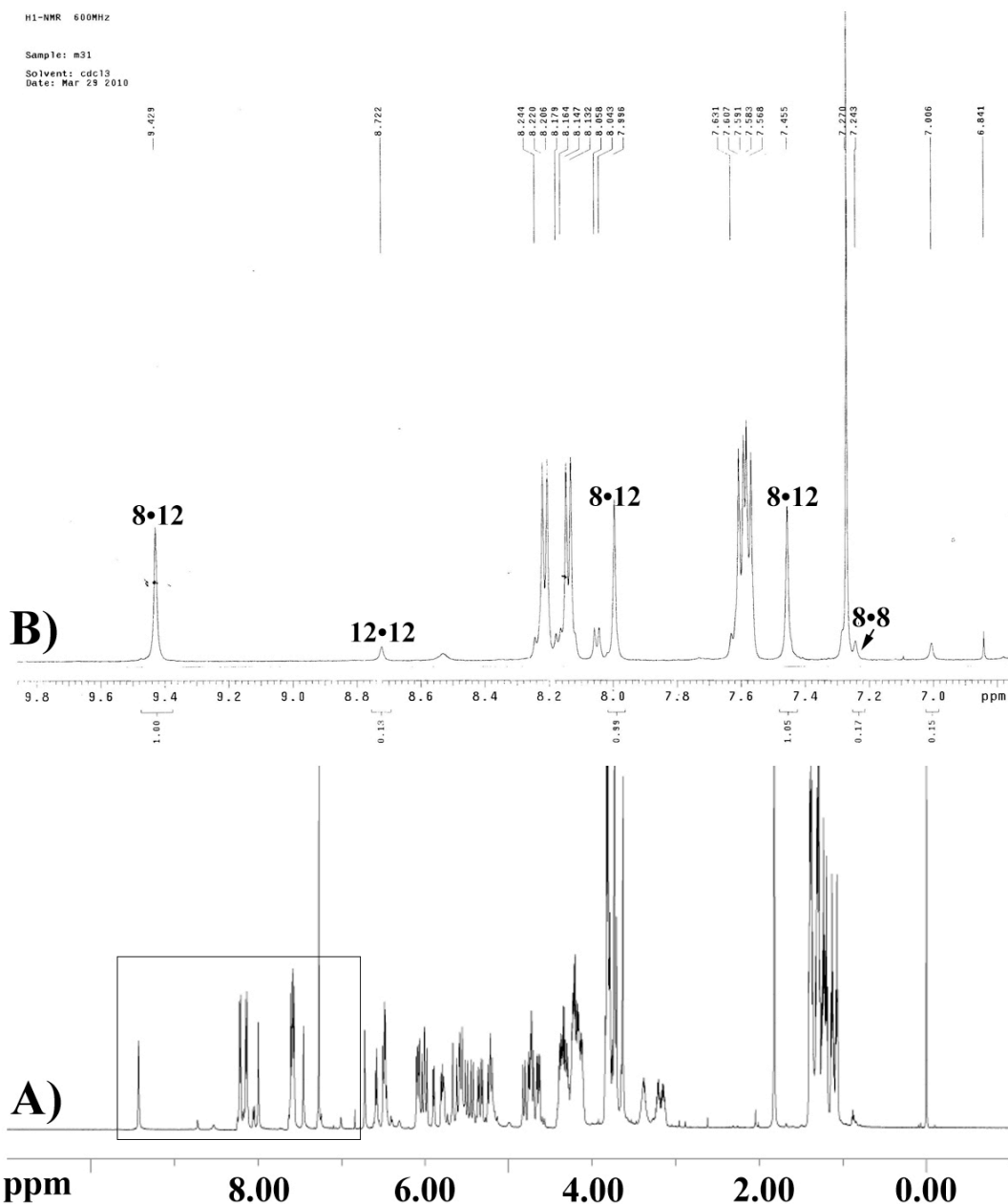


Figure S25. The ^1H NMR spectra (600 MHz, 20 mM, RT, CDCl_3) recorded for the heterodimerization of **8** and **12**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 10)

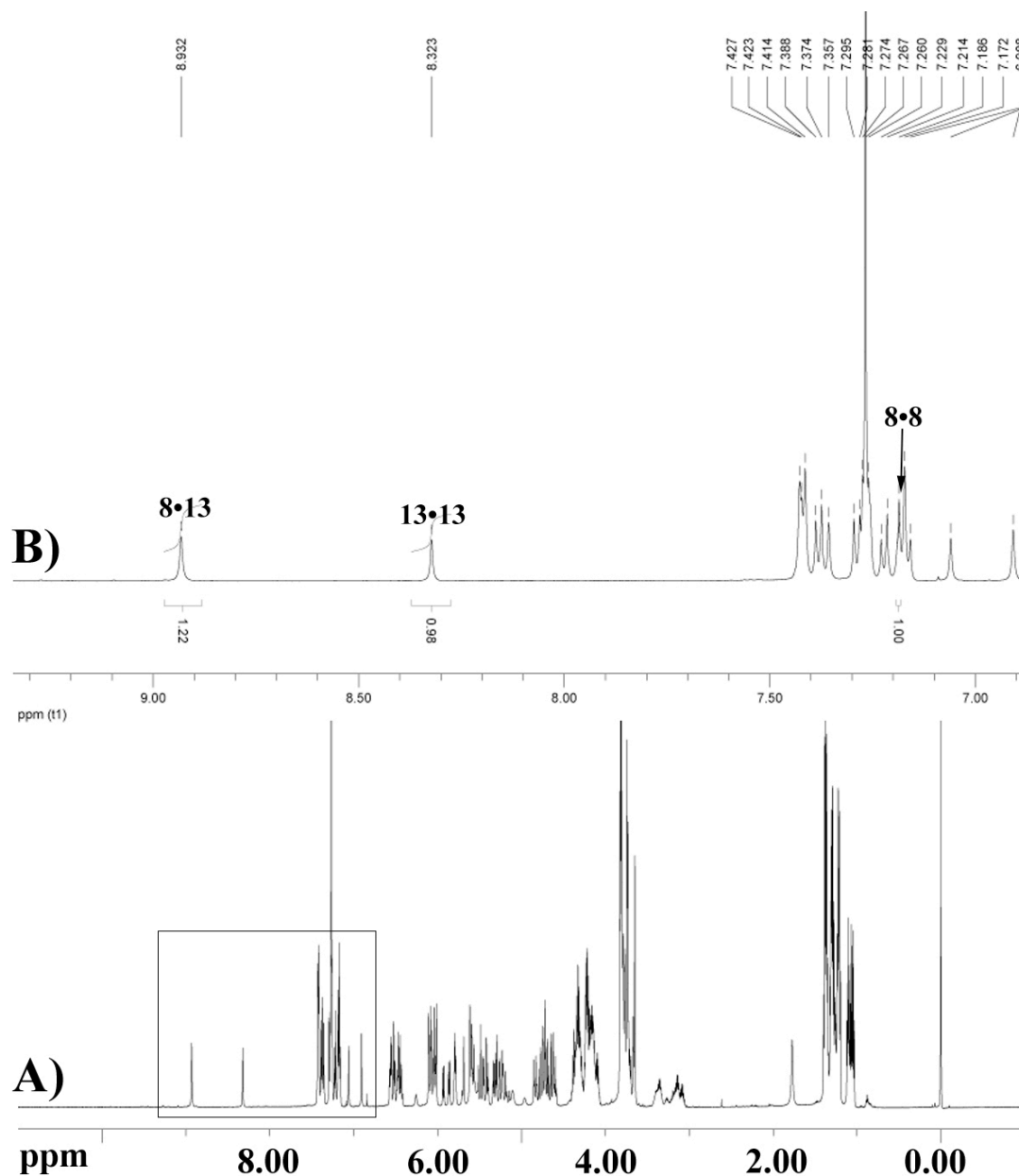


Figure S26. The ^1H NMR spectra (600 MHz, 20 mM, RT, CDCl_3) recorded for the heterodimerization of **8** and **13**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 11)

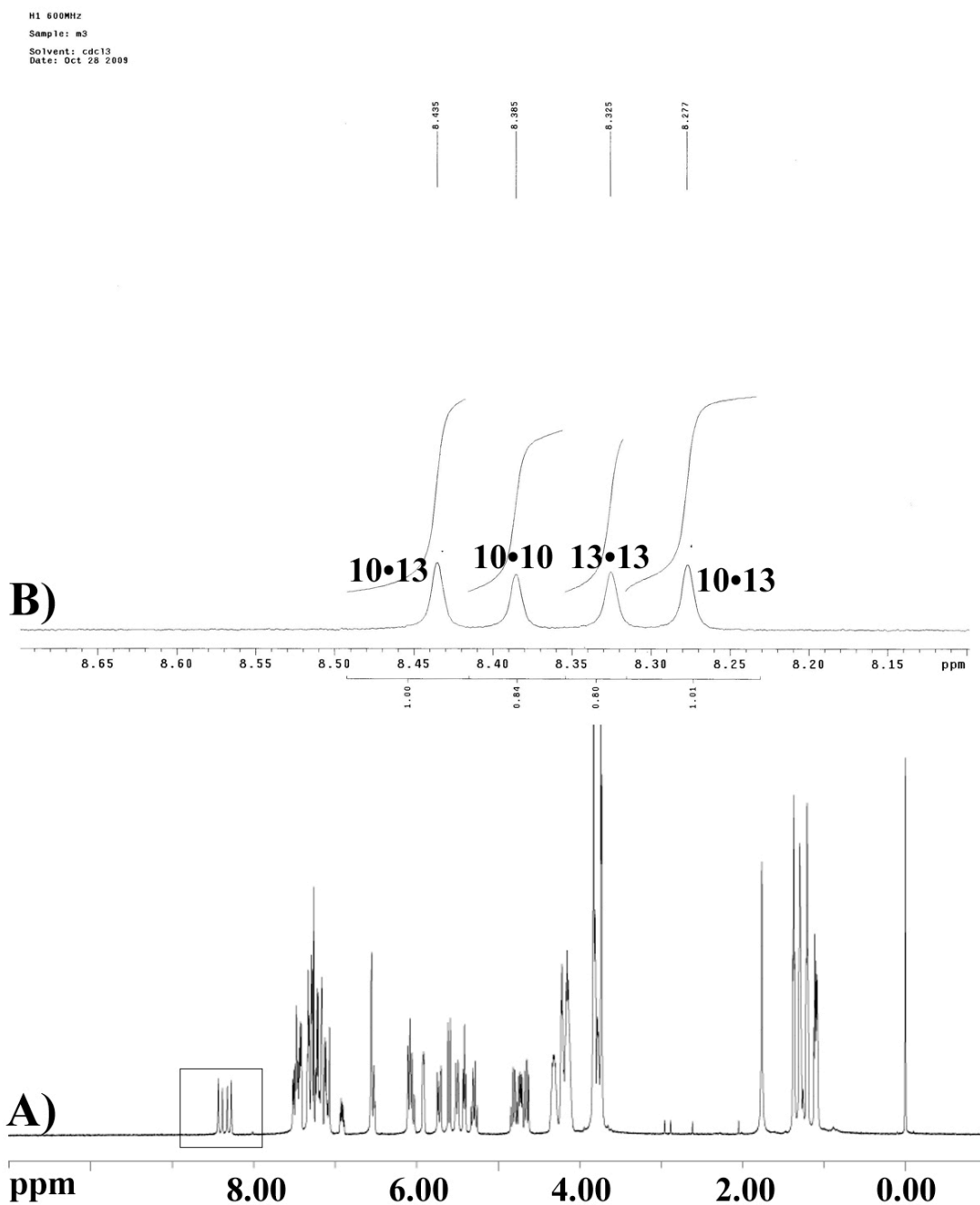


Figure S27. The ^1H NMR spectra (600 MHz, 20 mM, RT, CDCl_3) recorded for the heterodimerization of **10** and **13**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 12)

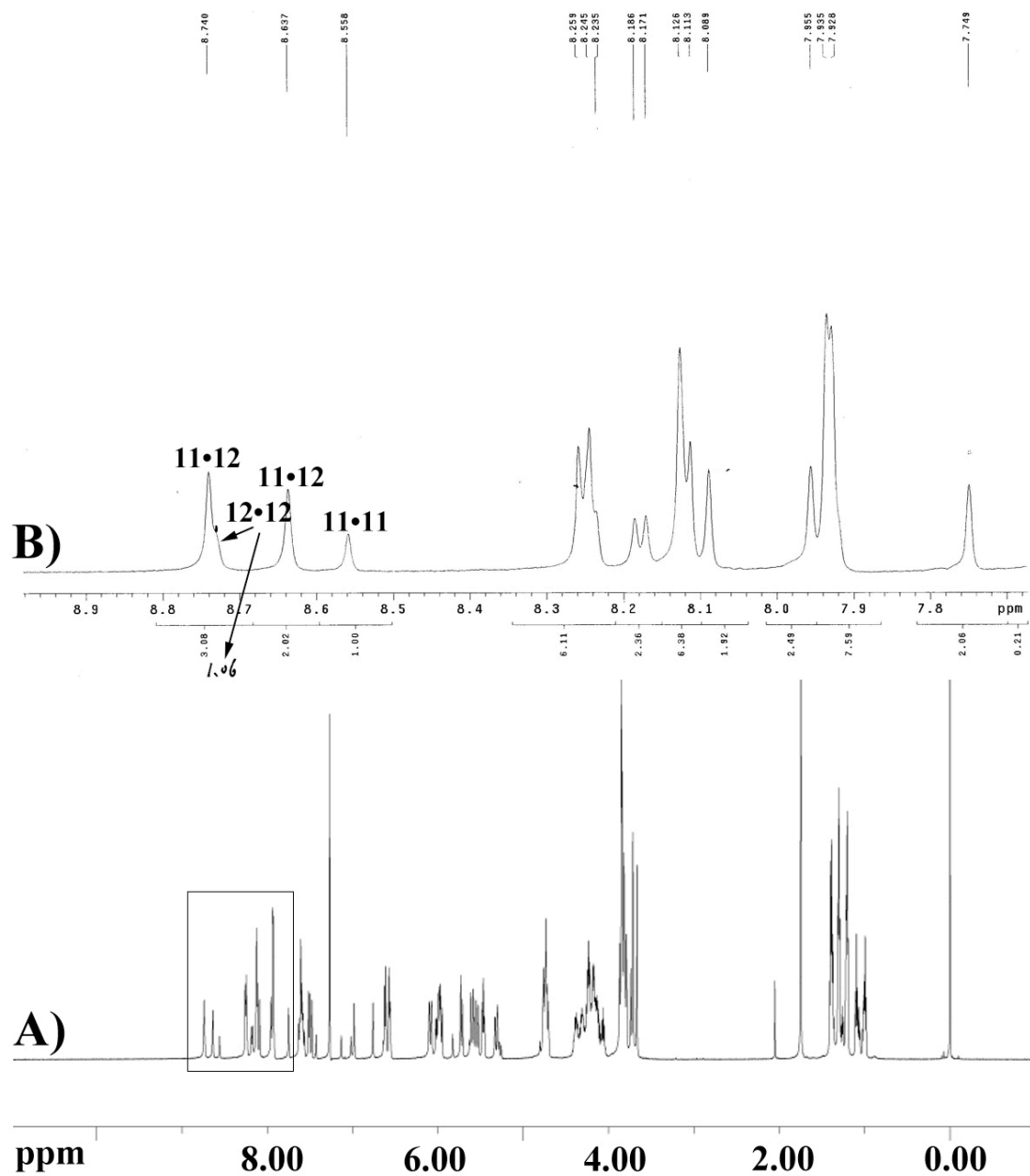


Figure S28. The ^1H NMR spectra (600 MHz, 20 mM, RT, CDCl_3) recorded for the heterodimerization of **11** and **12**: (A) full spectrum, and (B) expanded region of spectrum. (Table 1, entry 13)

Influence of Solvent on the heterodimerization process

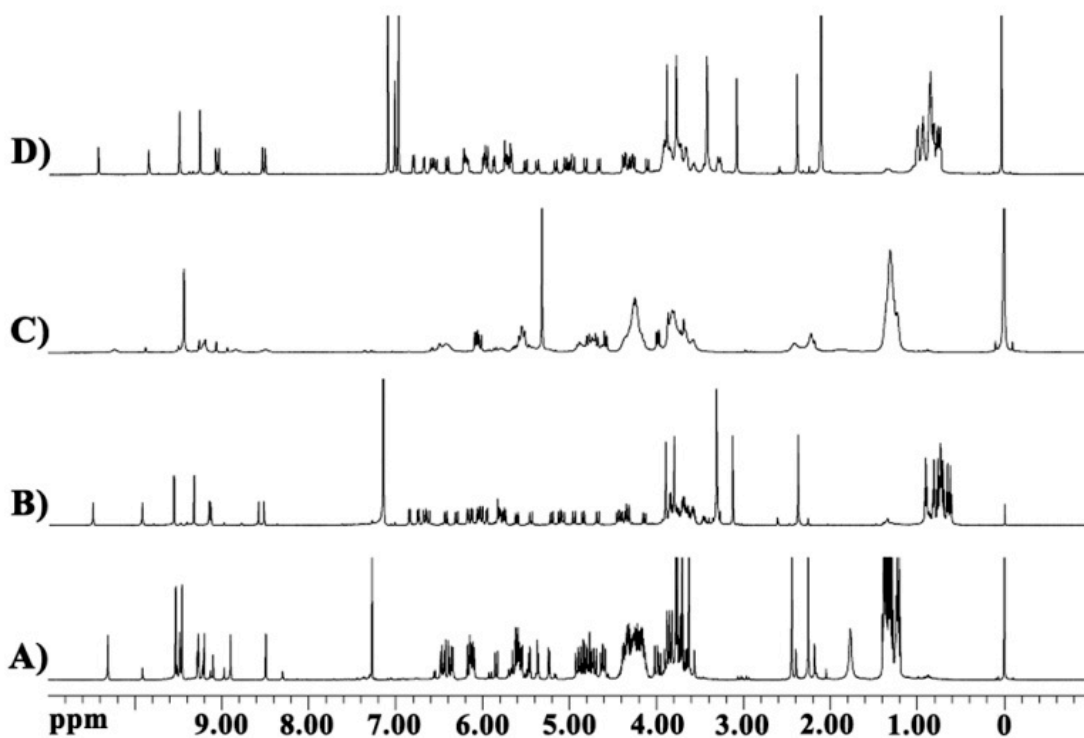


Figure S29. ^1H NMR spectra recorded for $1\cdot 5$ (20 mM, 600 MHz, room temperature) in A) CDCl_3 ($K_{\text{eq}} = 50.2$, $\chi_{1\cdot 5} = 0.779$), B) C_6D_6 (193.4, 0.874), C) CD_2Cl_2 (ill-defined aggregates), D) $\text{C}_6\text{D}_5\text{CD}_3$ (407.2, 0.901).

Characterization of heterodimers by ESI-MS.

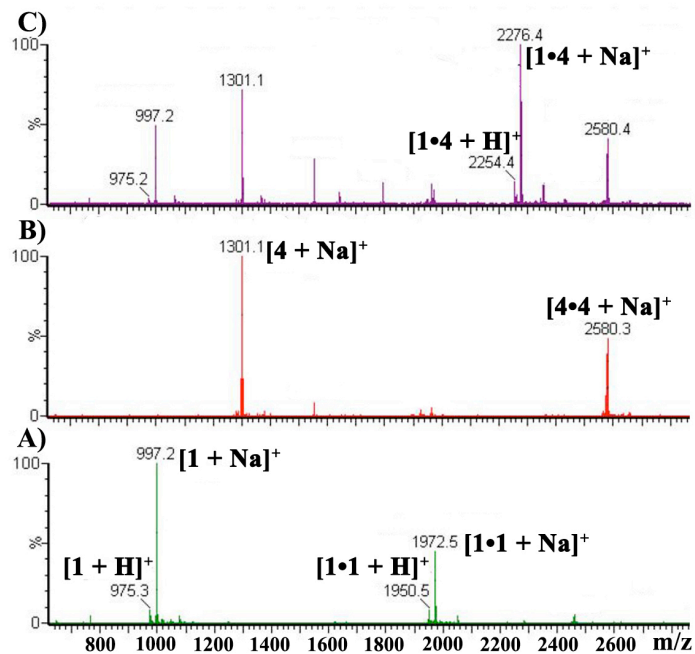


Figure S30. ESI-MS spectra of (A) **1** (20 μ M), (B) **4** (20 μ M), and (C) 1:1 mixture of **1** and **4** (20 μ M in each component) in methanol.

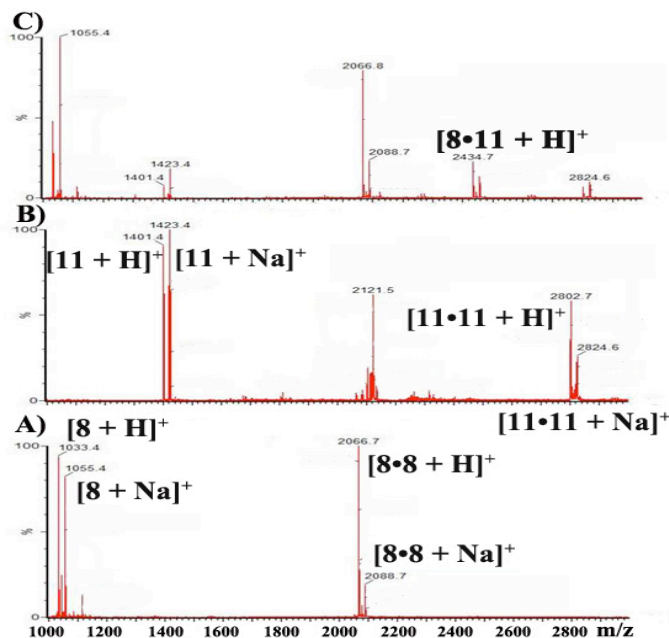


Figure S31. ESI-MS spectra of (A) (\pm)-**8** (20 μ M), (B) (\pm)-**11** (20 μ M), and (C) 1:1 mixture of (\pm)-**8** and (\pm)-**11** (20 μ M, respectively) in methanol. The peak at m/z 2121.5 corresponds to a doubly charged trimer ($[11_3 + K + H]^{2+}$).

Details of the X-ray structure of (\pm)-**15**

Crystal data for (\pm)-**15**·(CHCl₃)₃: C₄₀H₃₆Cl₉F₅N₆O₁₀, $M_r = 1174.80$, Triclinic, space group $P-1$, $a = 10.5648(10)$, $b = 15.5841(14)$, $c = 16.8119(15)$ Å, $Z = 2$, $V = 2444.4(4)$ Å³, $D_c = 1.596$ g cm⁻³, $\mu = 0.596$ mm⁻¹, $\theta_{\max} = 27.50^\circ$, $F(000) = 1192$, reflections collected/unique, 28452/10910 ($R_{\text{int}} = 0.0845$), final R indices [$I > 2\sigma(I)$] $R_1 = 0.0567$, $wR_2 = 0.1414$, R indices (all data) $R_1 = 0.0834$, $wR_2 = 0.1534$, GOF = 0.955 for all data. CCDC-782747 ((\pm)-**15**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (t44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

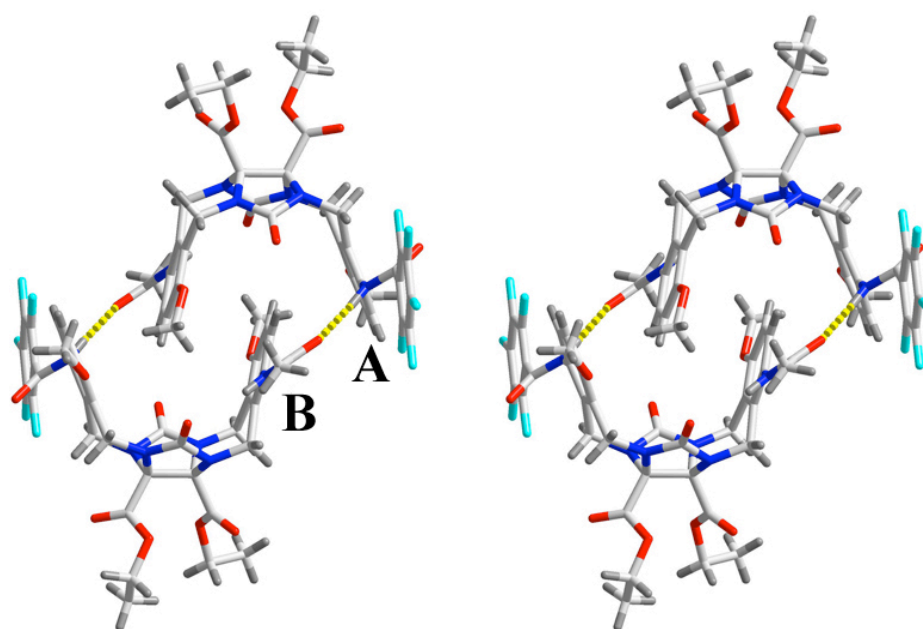


Figure S32. Stereoview of the molecular structure of (+)-**15**·(-)-**15** in the crystal. C, gray; H, white; N, blue; O, red; F, light-blue; and hetero H-bonds, yellow dot-line. To highlight the hetero H-bond, the pentafluorophenyl amide and the methyl amide groups are labelled **A** and **B**, respectively.

Variable Temperature and dilution experiments for the four component self sorting system comprising 1•4 and 8•11 monitored by ^1H NMR

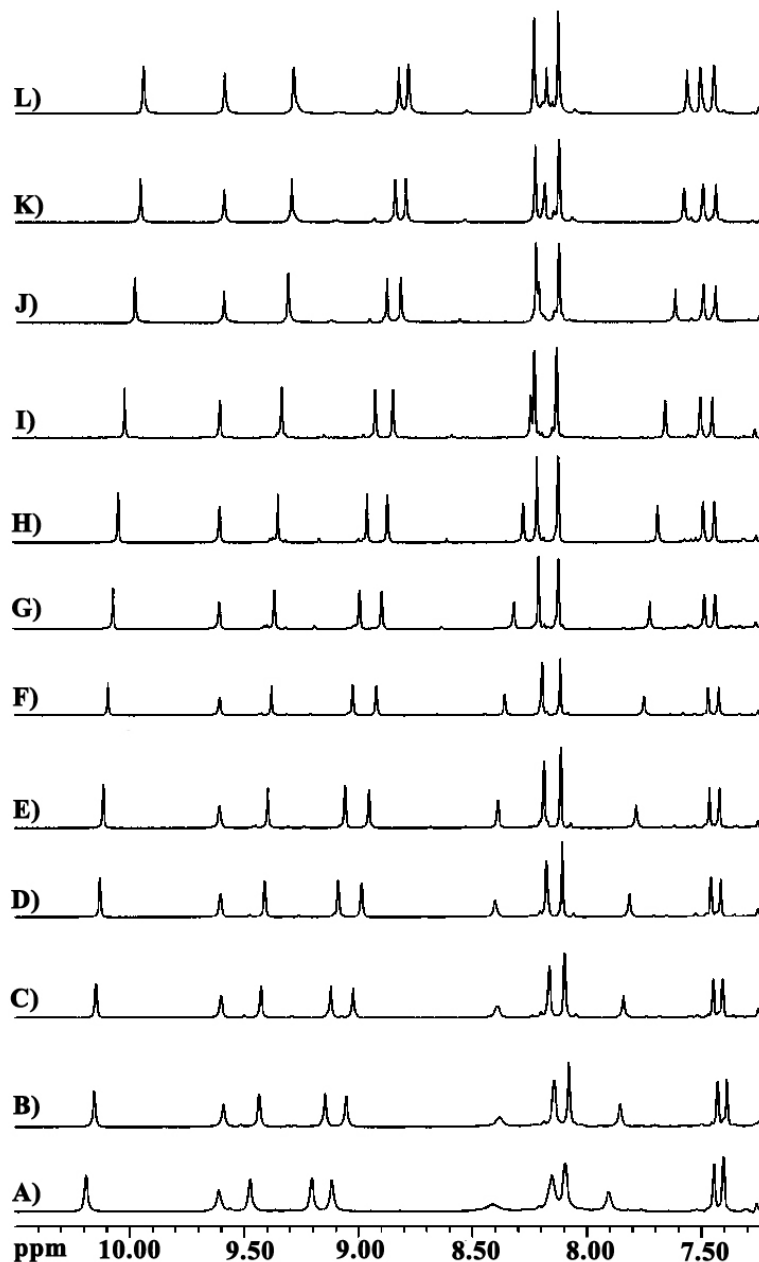


Figure S33. Portion of the ^1H NMR spectrum recorded for the self-sorted mixture of **1•4** and **8•11** ($\text{C}_6\text{D}_5\text{CD}_3/\text{CDCl}_3 = 5:1$, v/v, 600 MHz, 5 mM) at: A) 218 K, B) 228 K, C) 238 K, D) 248 K, E) 258 K, F) 268 K, G) 278 K, H) 288 K, I) 298 K, J) 308 K, K) 318 K, L) 323 K. The resonances at 10.1, 9.5, 9.2, 9.1, 8.4, and 7.9 ppm which shift upfield at higher temperatures correspond to the H-bonding N-H groups. The peaks corresponding to homodimers appear to get smaller at lower temperature which would suggest the heterodimerization is enthalpically driven. We did not quantify the mole fraction as a function of temperature because of the peak broadening and the limited dynamic range of the NMR which makes quantification of such small peaks challenging.

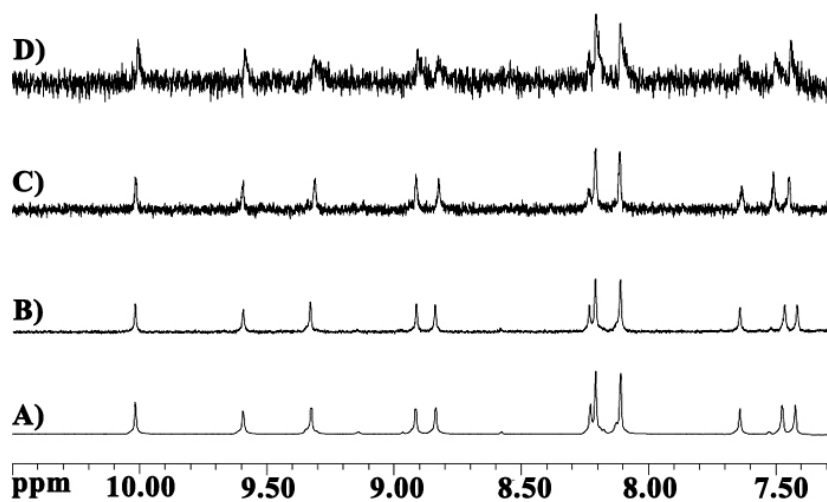
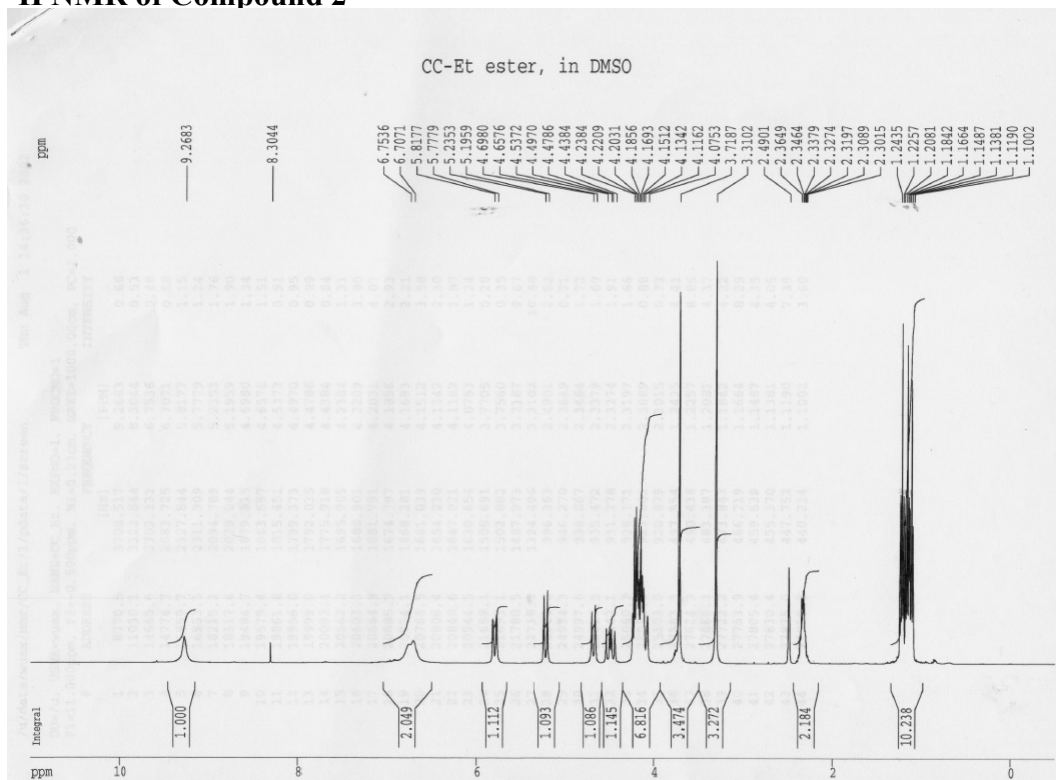


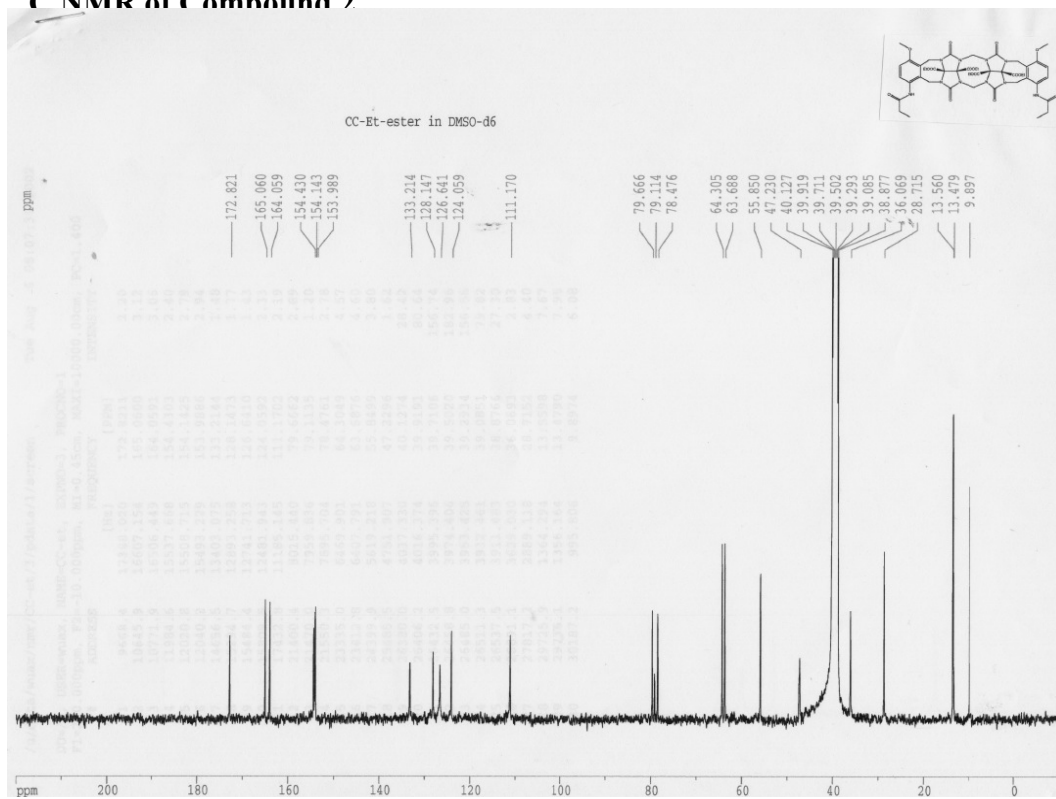
Figure S34. Portion of the ¹H NMR spectrum recorded for the self-sorted mixture comprising **1•4** and **8•11** ($C_6D_5CD_3/CDCl_3 = 5:1$, v/v, 600 MHz, room temperature) upon dilution: (A) 5 mM, (B) 1 mM, (C) 50 μ M, and (D) 25 μ M.

¹H and ¹³C NMR Spectra for all new compounds

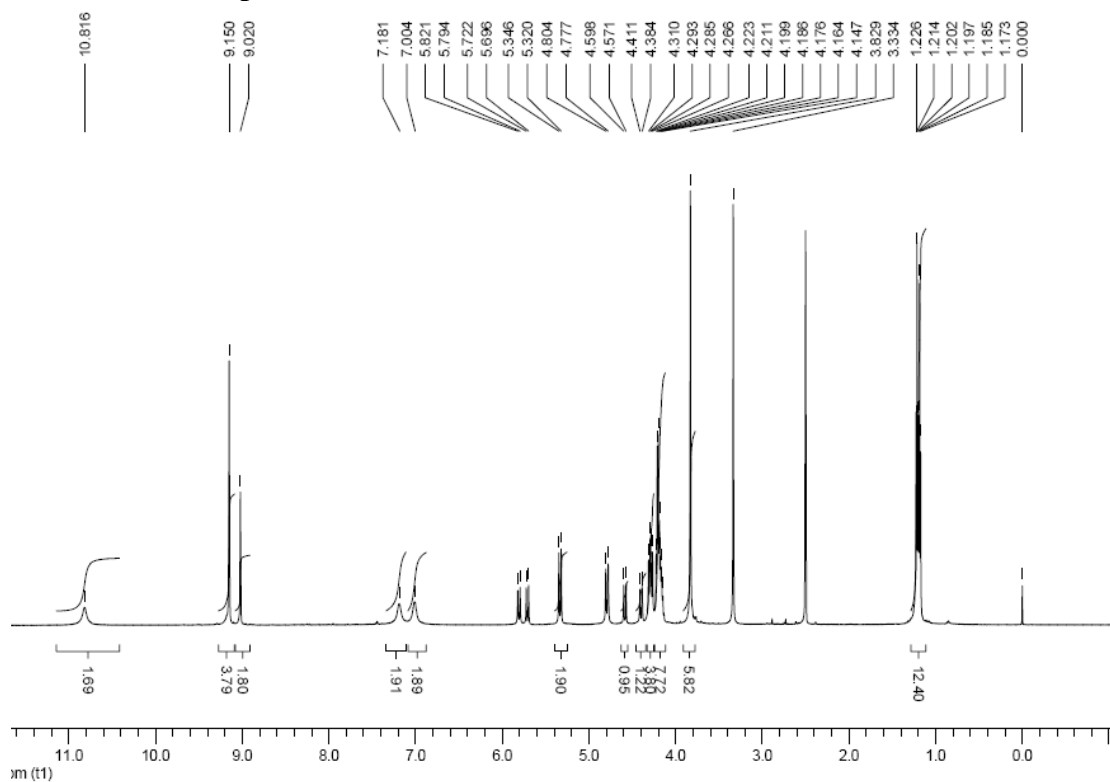
¹H NMR of Compound 2



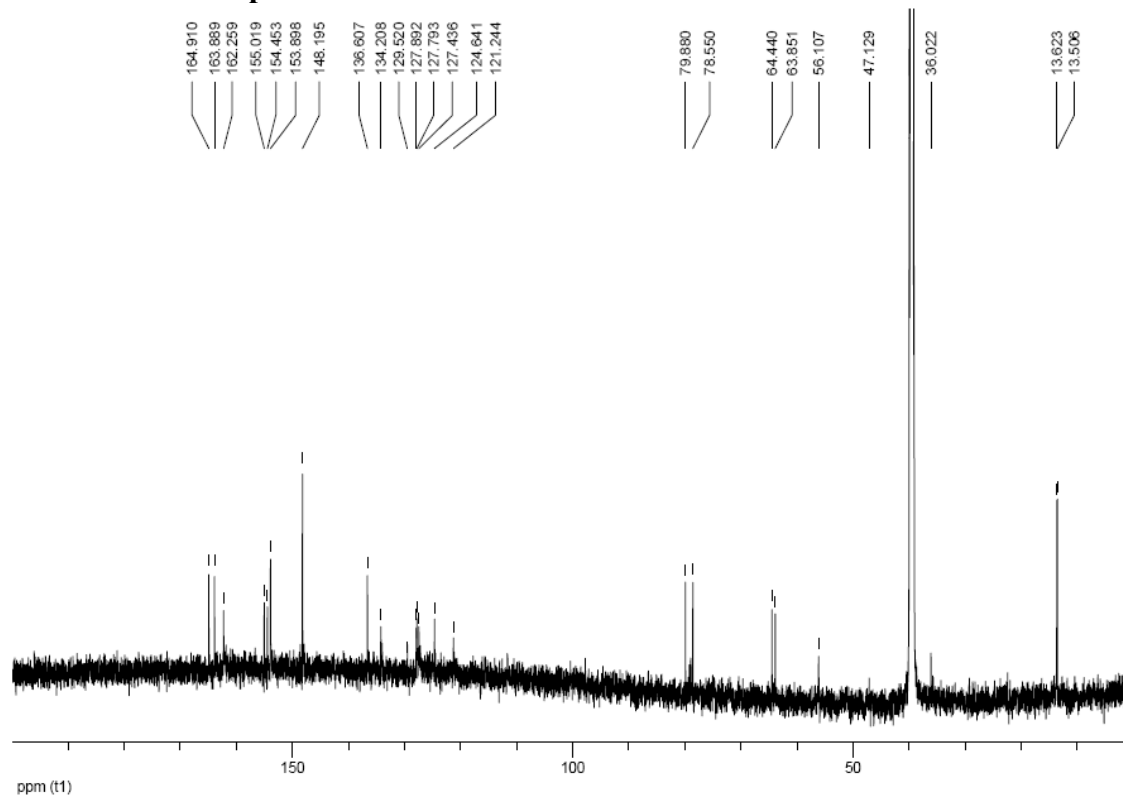
¹³C NMR of Compound 2



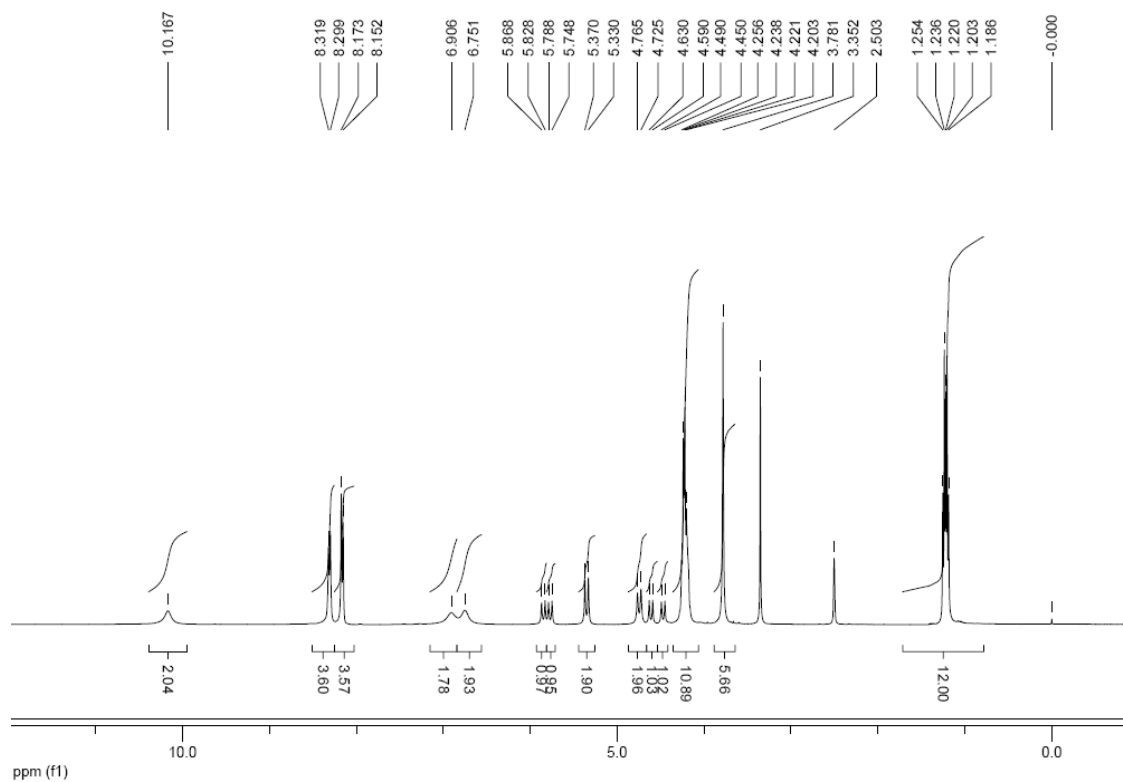
¹H NMR of Compound 5



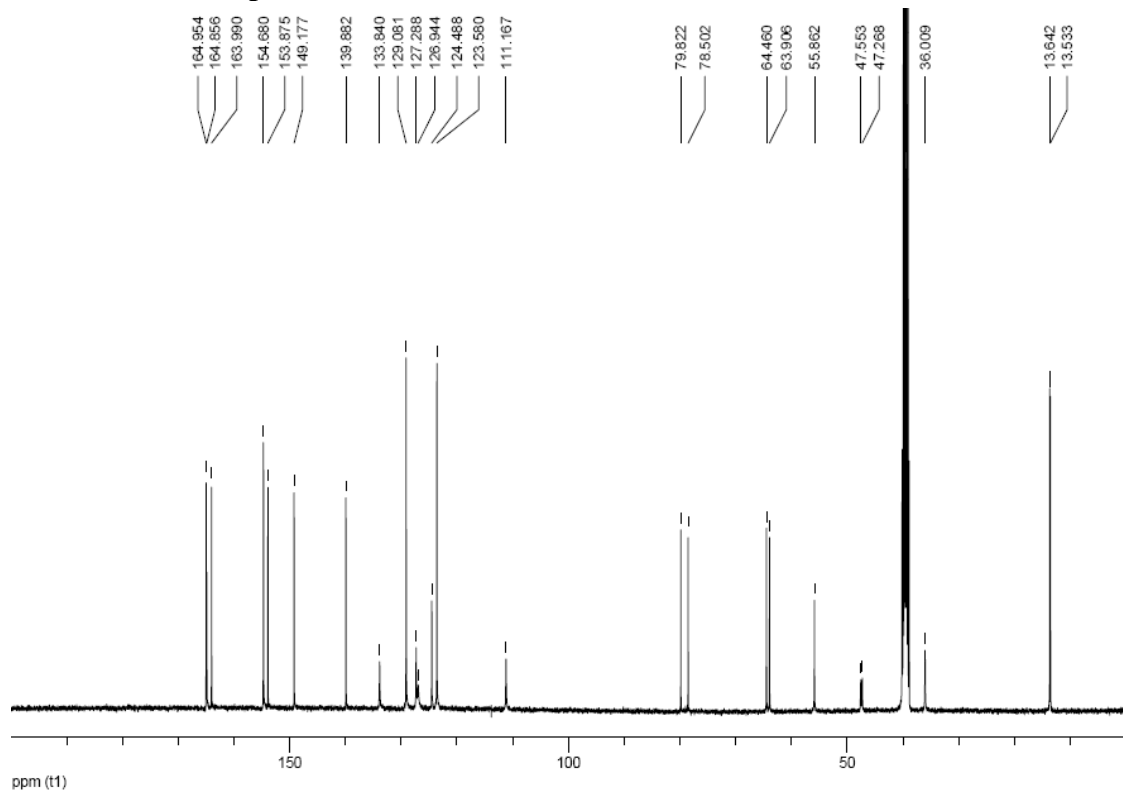
¹³C NMR of Compound 5



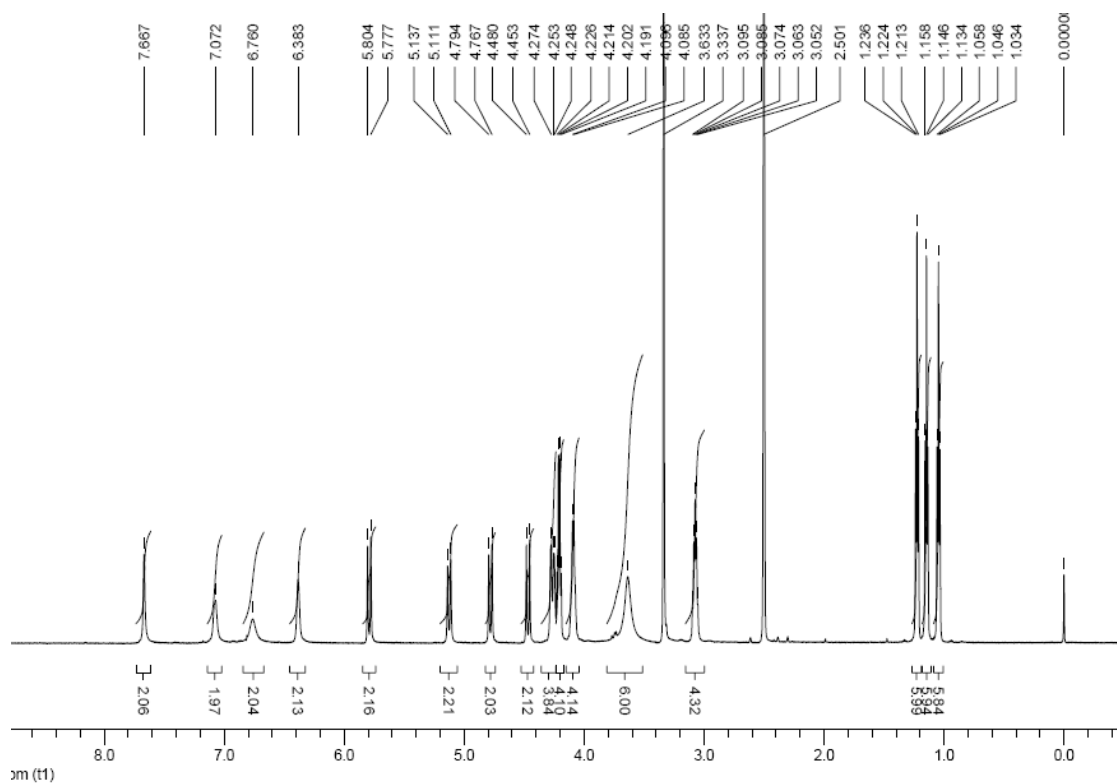
¹H NMR of Compound 6



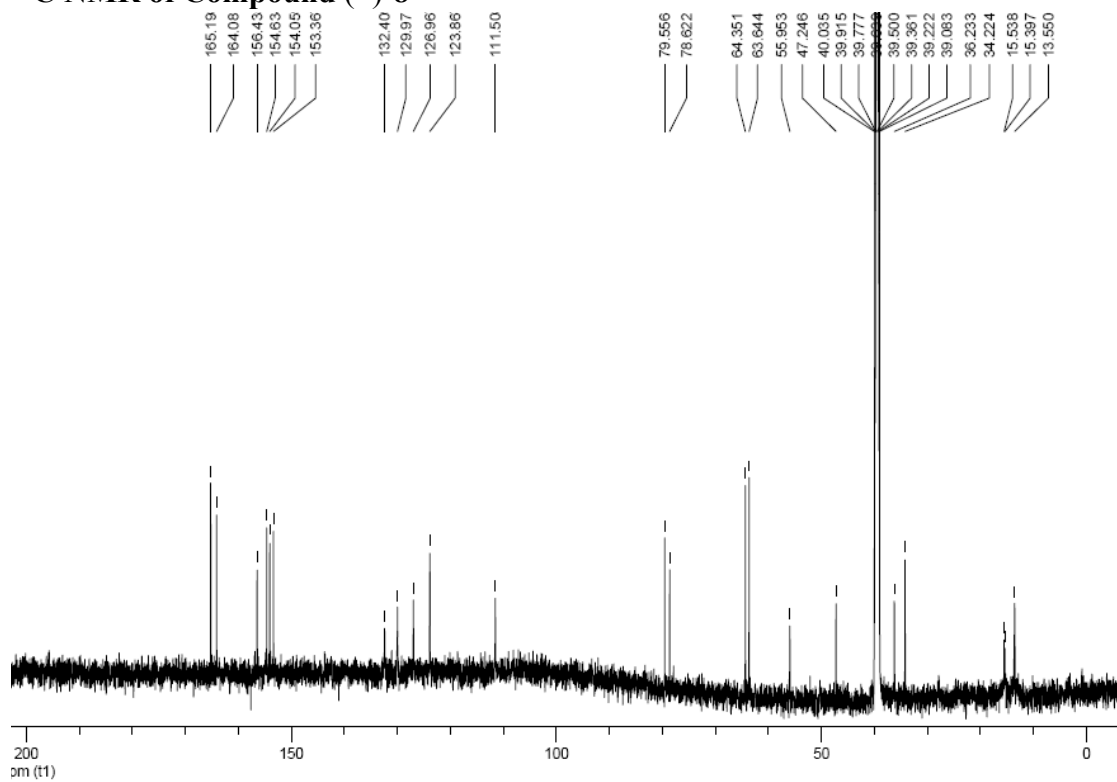
¹³C NMR of Compound 6



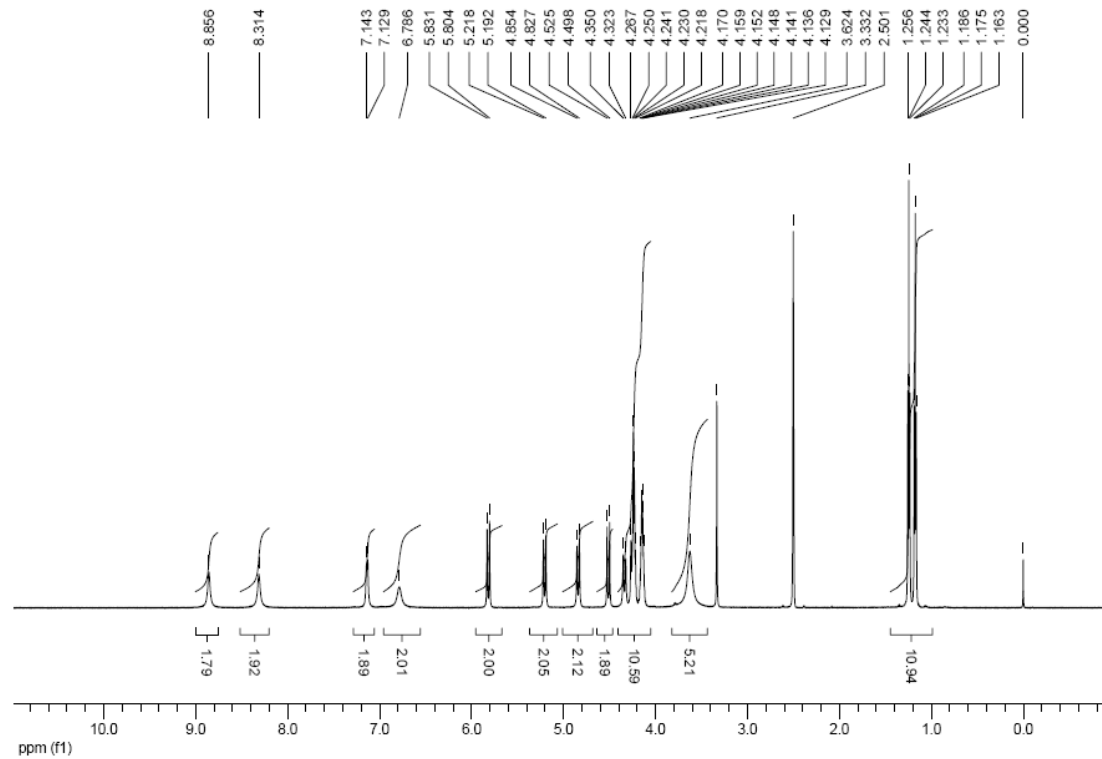
¹H NMR of Compound (±)-8



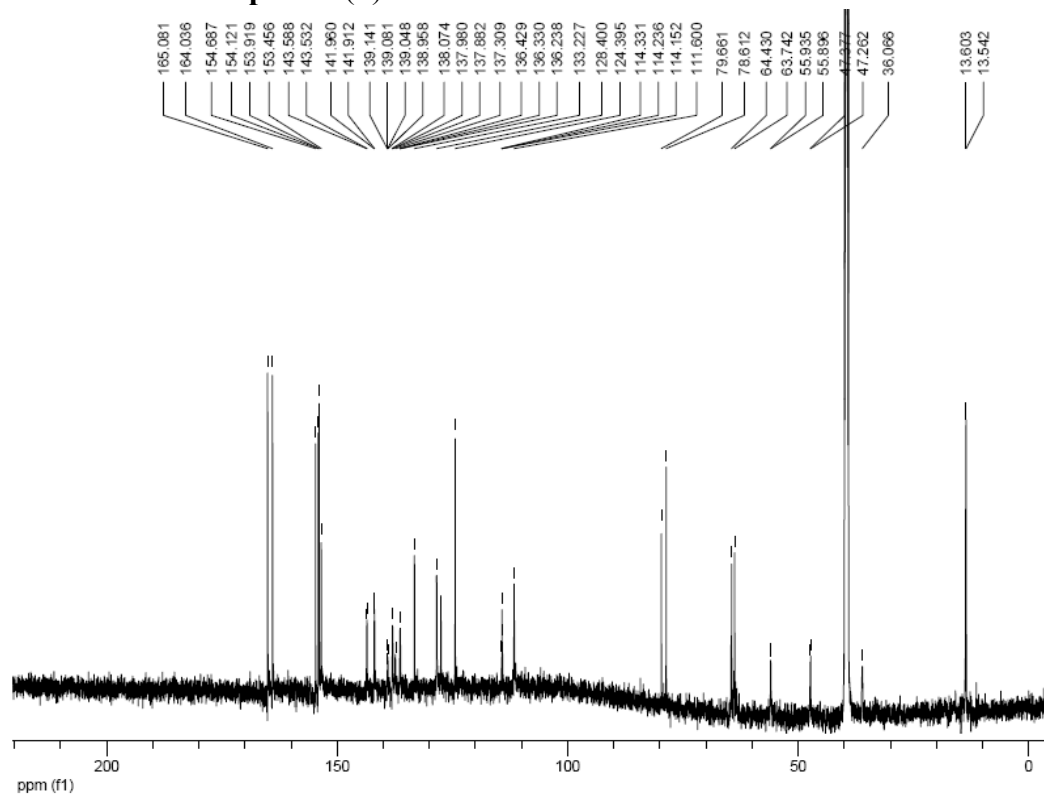
¹³C NMR of Compound (±)-8



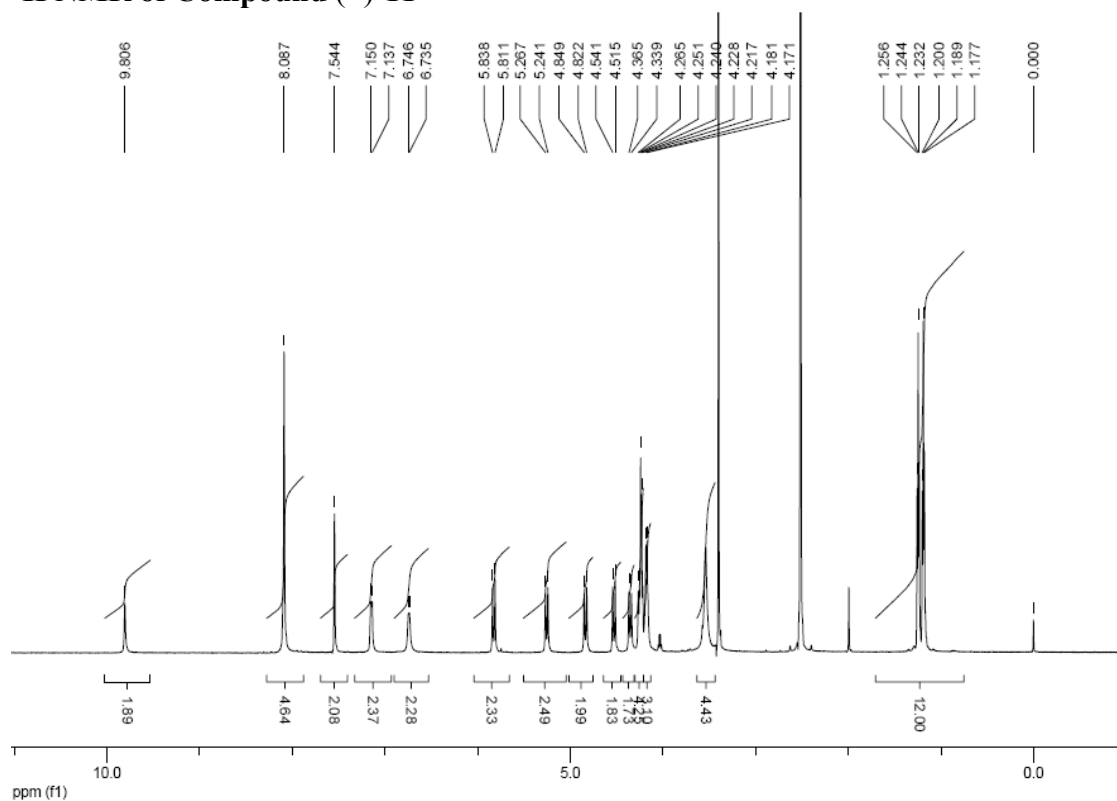
¹H NMR of Compound (±)-9



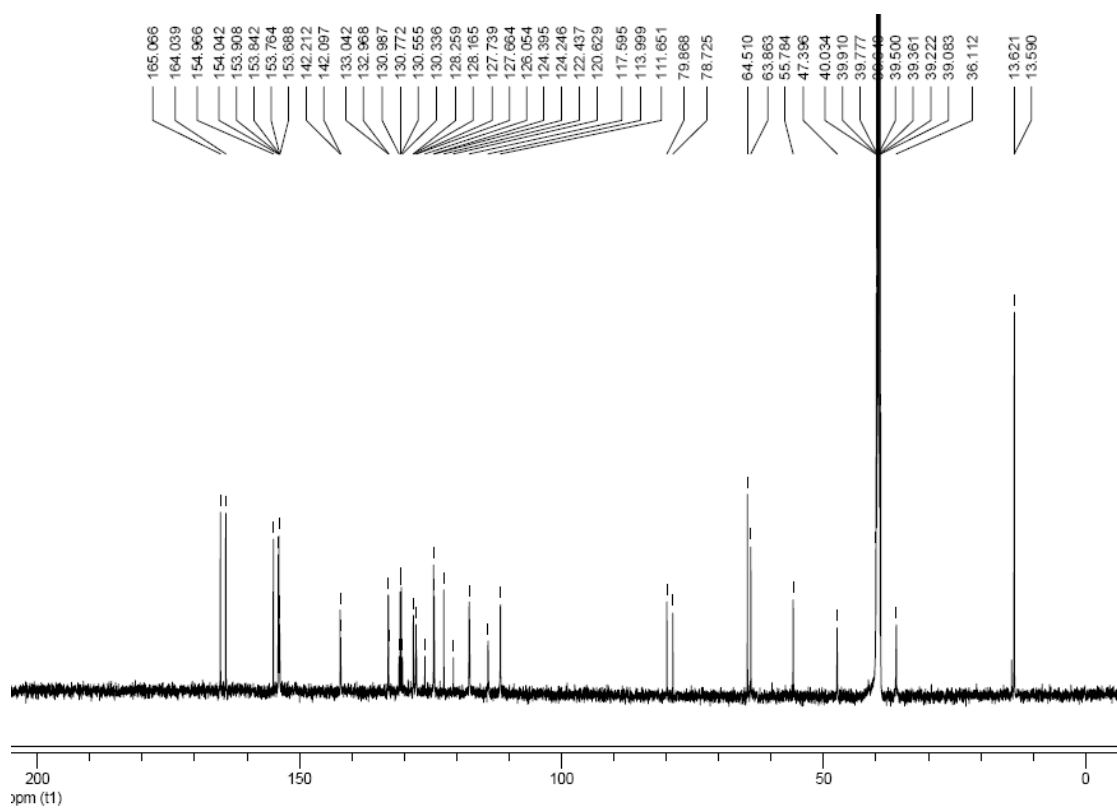
¹³C NMR of Compound (±)-9



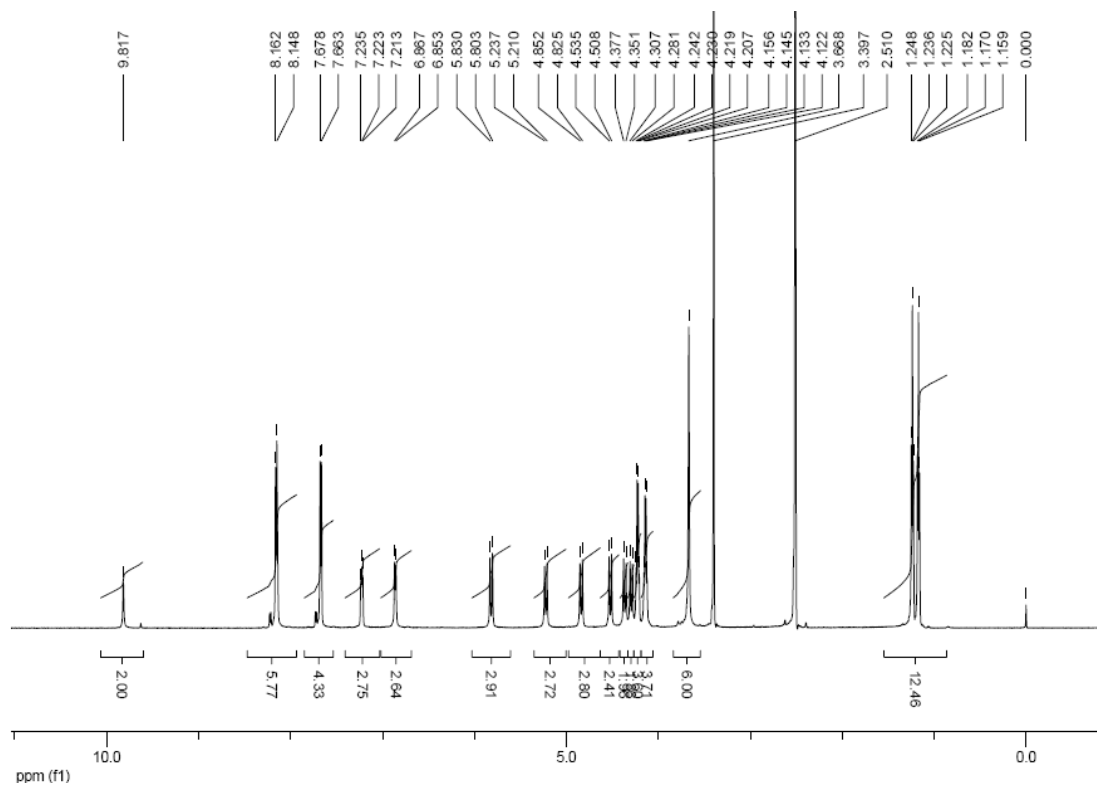
¹H NMR of Compound (±)-11



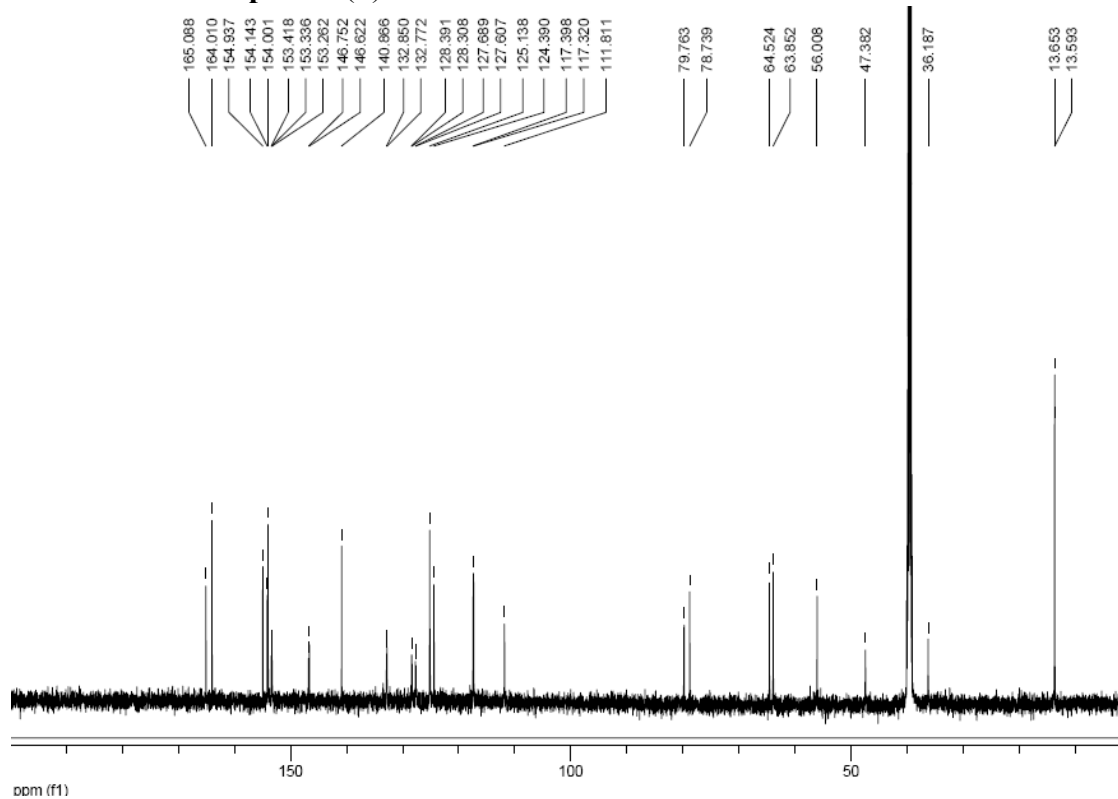
¹³C NMR of Compound (±)-11



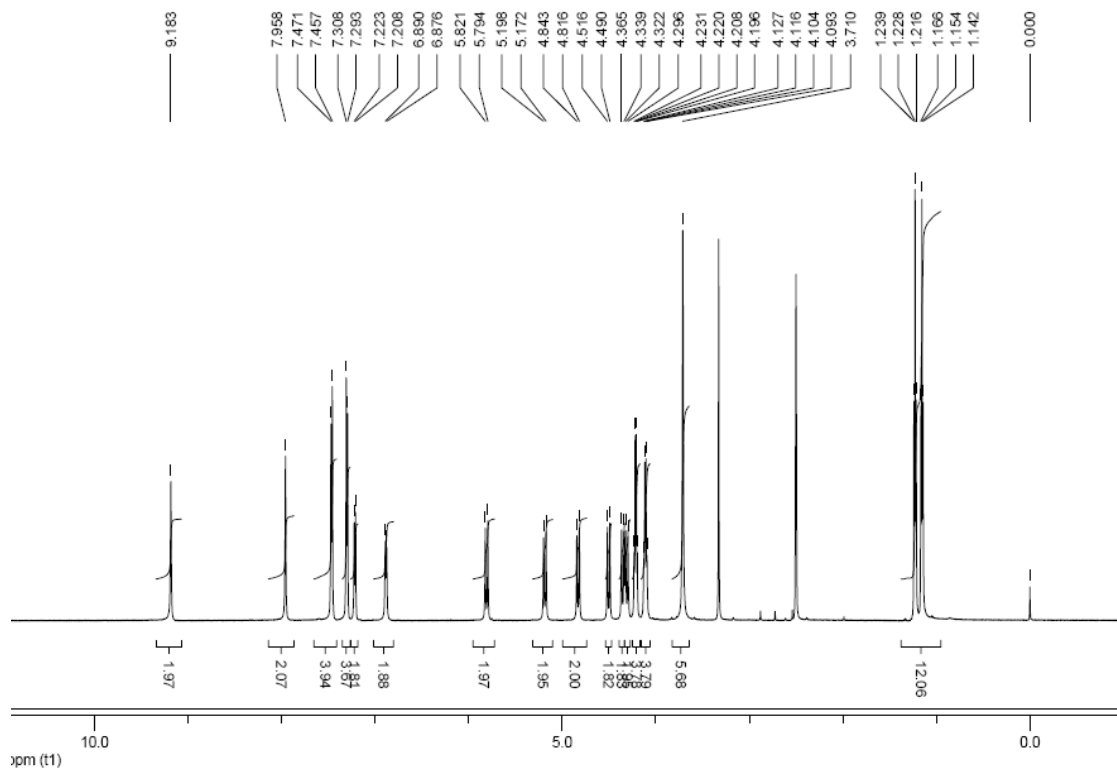
¹H NMR of Compound (±)-12



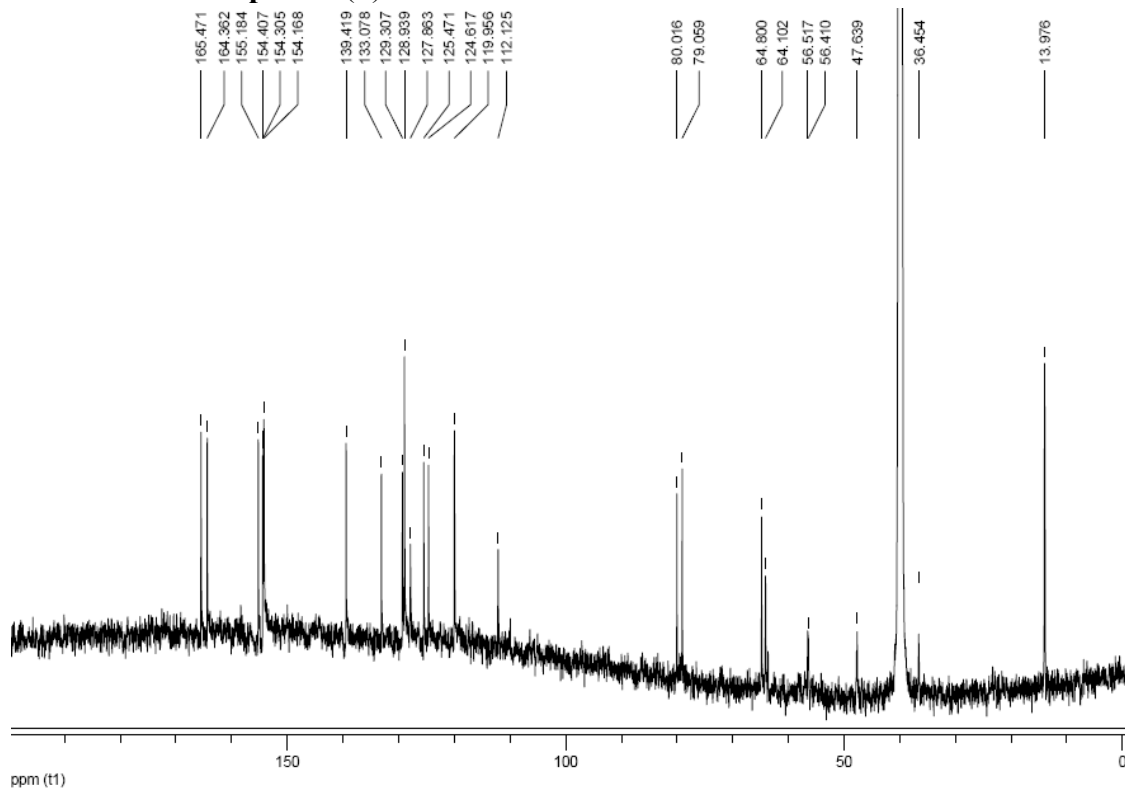
¹³C NMR of Compound (±)-12



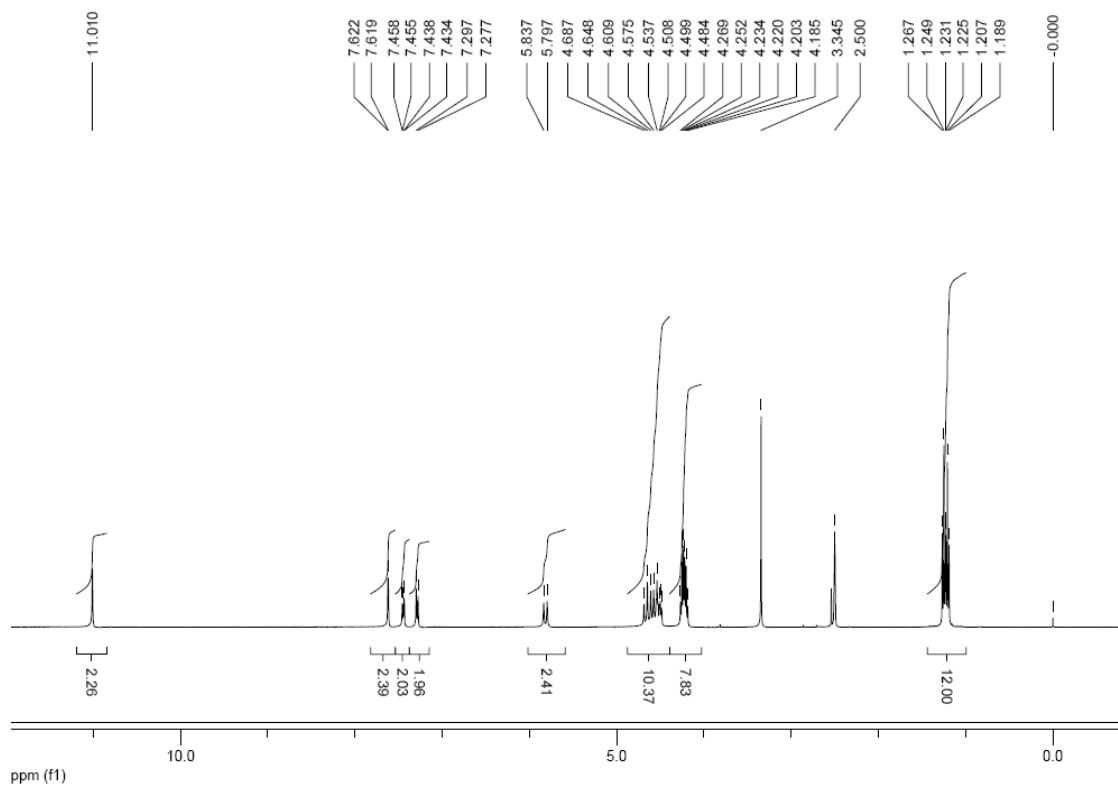
¹H NMR of Compound (±)-13



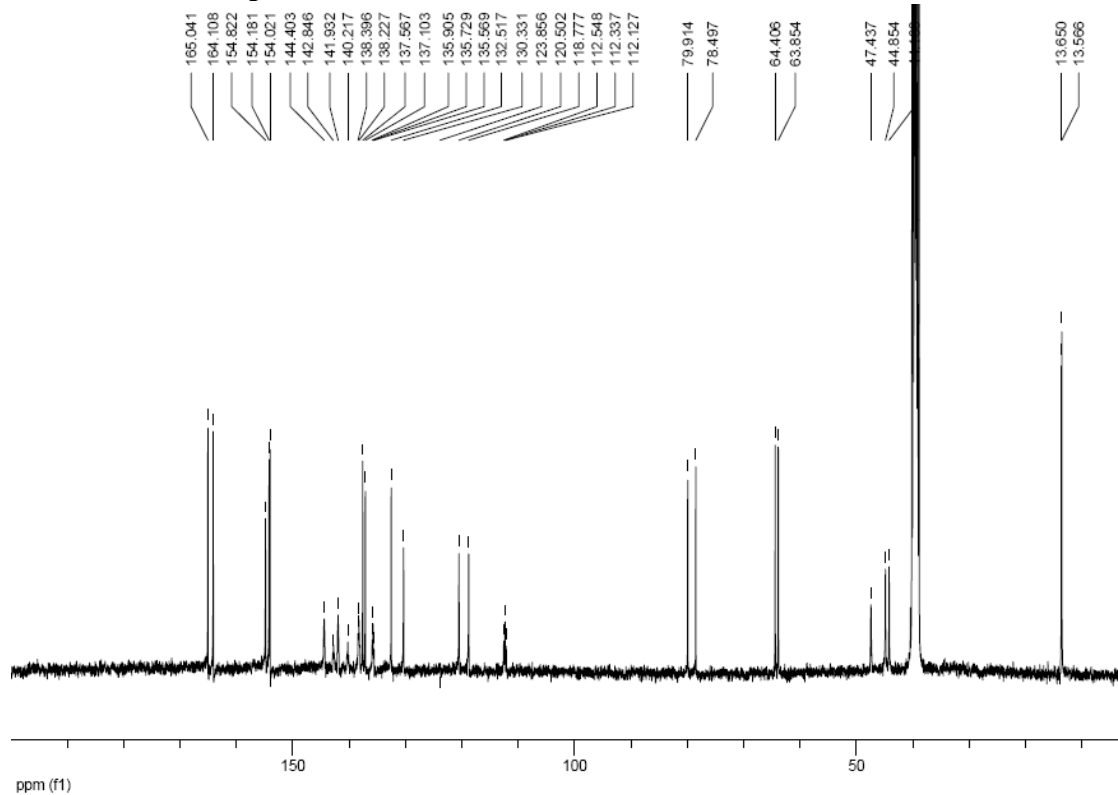
¹³C NMR of Compound (±)-13



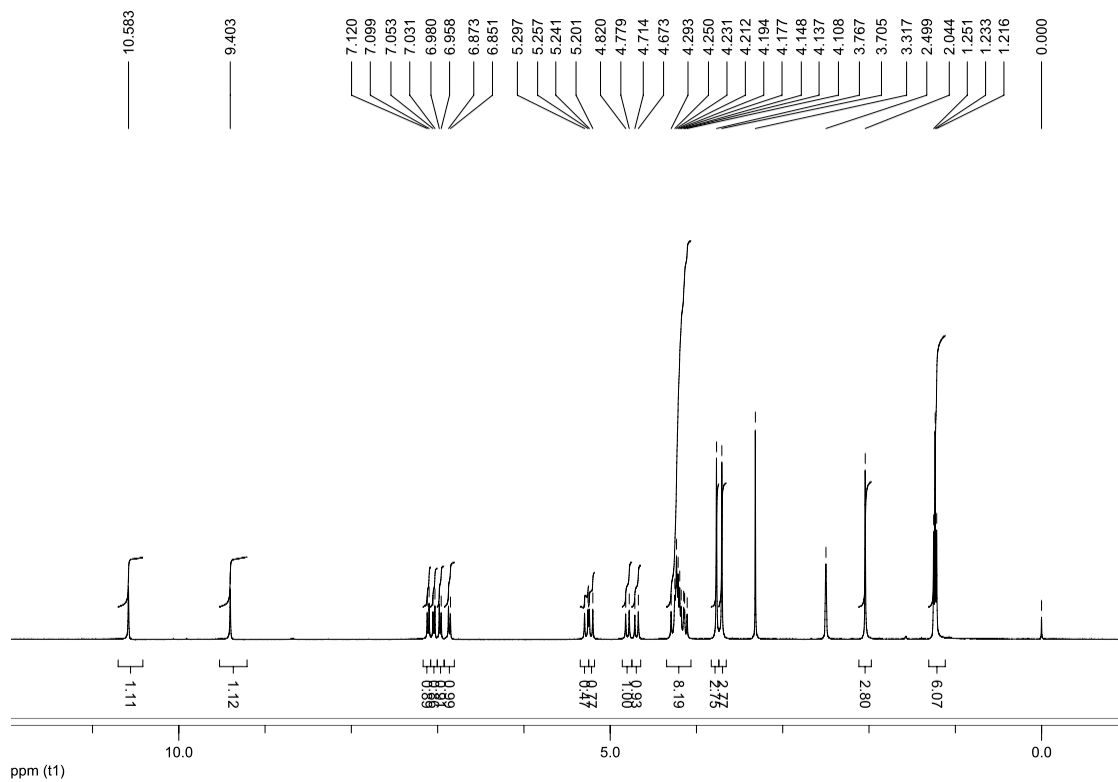
¹H NMR of Compound 14



¹³C NMR of Compound 14



¹H NMR of Compound 15



¹³C NMR of Compound 15

