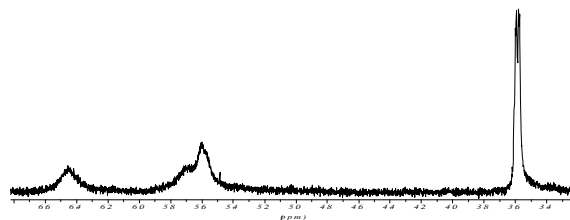
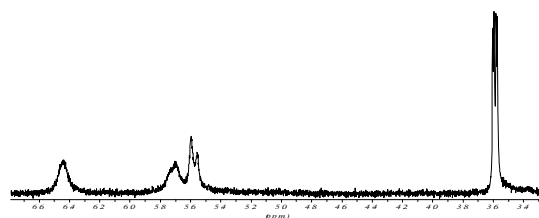


Supporting Information

a)



b)



c)

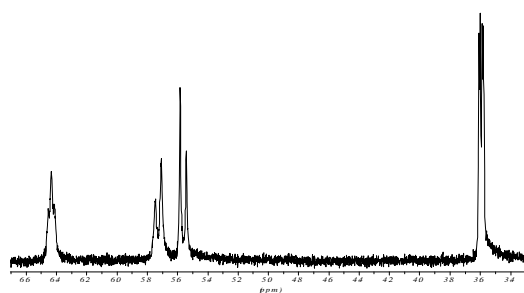
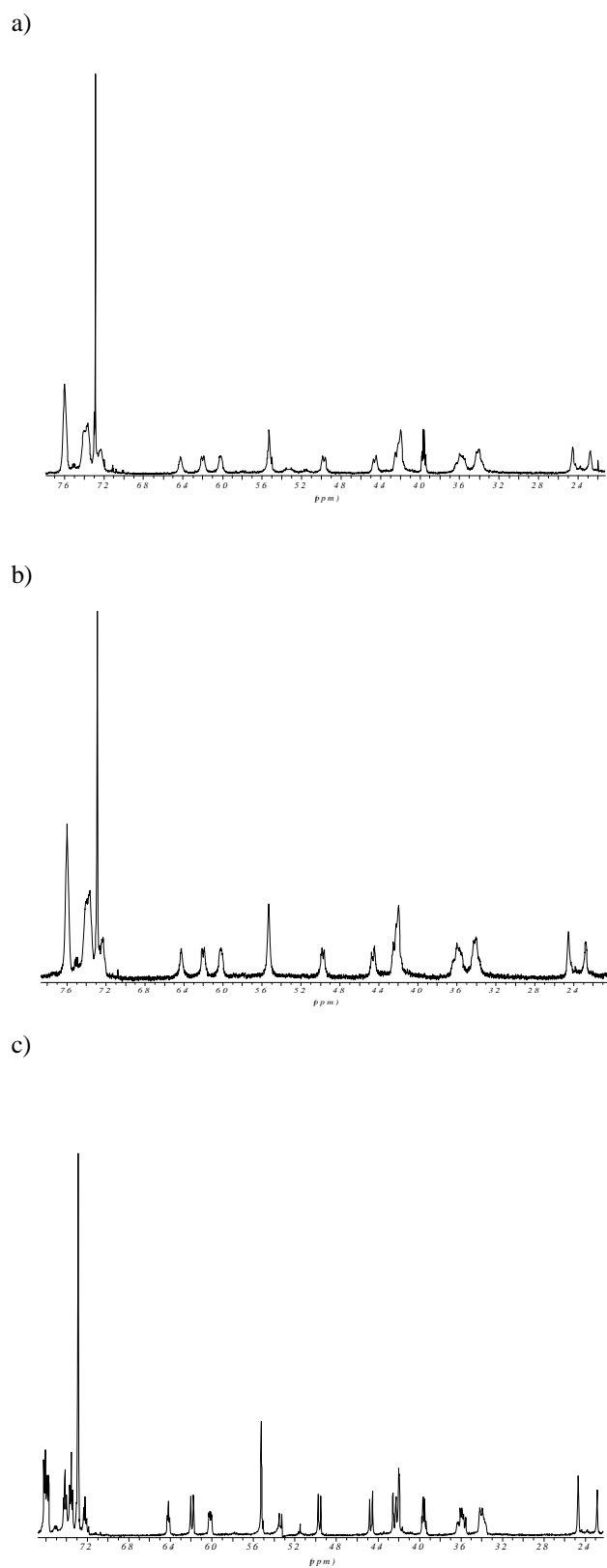
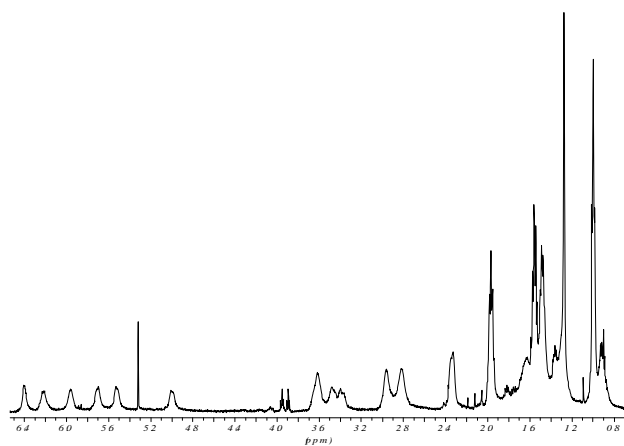


Figure S1: <sup>1</sup>H NMR spectra of compound 3a registered at different temperatures: a) 298 K; b) 303 K; c) 323 K.

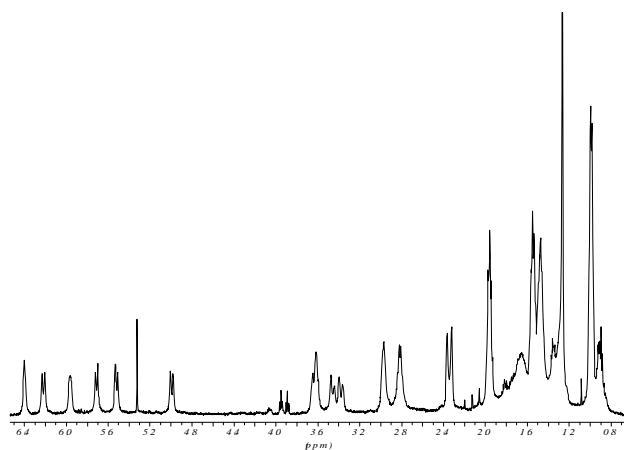


**Figure S2:  $^1\text{H}$  NMR spectra of compound 3b registered at different temperatures: a) 298 K; b) 288 K; c) 278 K.**

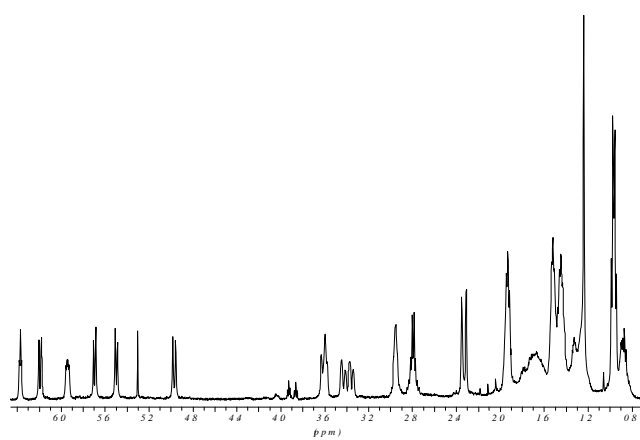
a)



b)

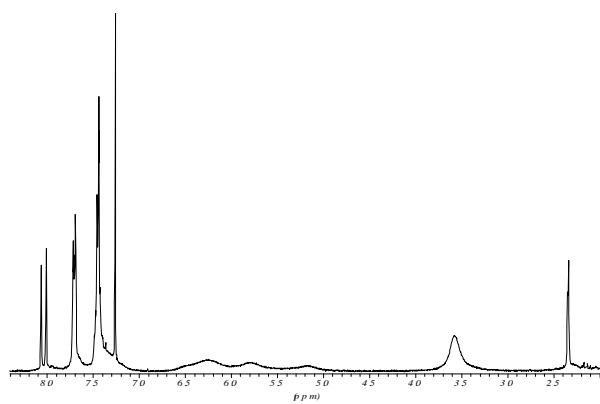


c)

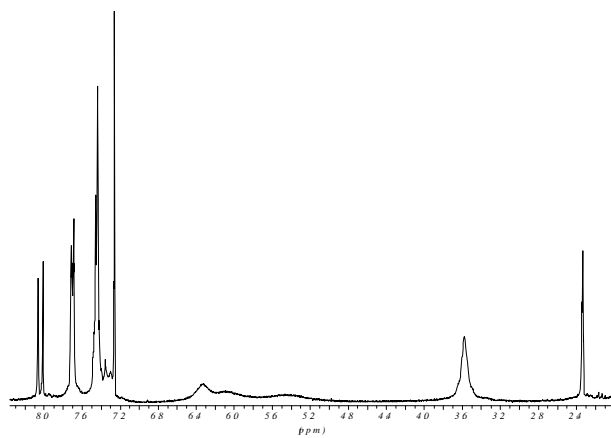


**Figure S3: <sup>1</sup>H NMR spectra of compound 3c registered at different temperatures: a) 298 K; b) 288 K; c) 278 K.**

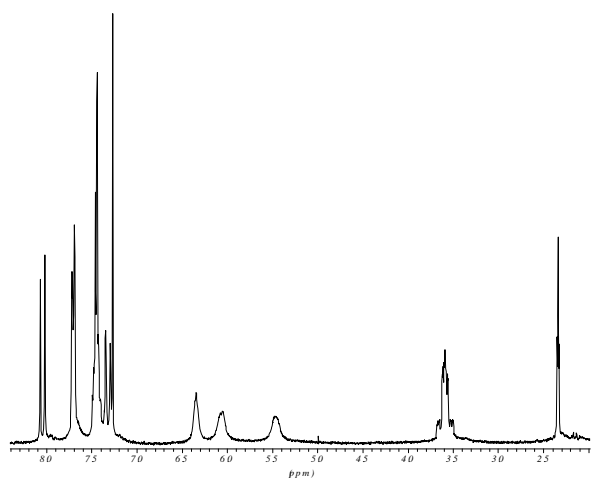
a)



b)



c)



**Figure S4: <sup>1</sup>H NMR spectra of compound 3d registered at different temperatures: a) 298K; b) 303K; c) 323K**

**2:**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{S}_2\text{C}$ , 298 K, 500 MHz):  $\delta = 4.99$  (d,  $^2\text{J} = 11.3$  Hz, 1 H,  $\text{CH}_2\text{-N}$ ), 4.87 (dd,  $^3\text{J} = 7.8$ ,  $^3\text{J} = 4.8$  Hz, 1 H,  $\text{CH-N}$ ), 4.77 (d,  $^2\text{J} = 11.3$  Hz, 1 H,  $\text{CH}_2\text{-N}$ ), 3.49 (ddd,  $^2\text{J} = 16.7$ ,  $^3\text{J} = 7.8$ ,  $^4\text{J} = 2.7$  Hz, 1 H,  $\text{CH}_2$ ), 3.24 (ddd,  $^2\text{J} = 16.7$ ,  $^3\text{J} = 4.8$ ,  $^4\text{J} = 2.7$  Hz, 1 H,  $\text{CH}_2$ ), 2.22 (t,  $^4\text{J} = 2.7$  Hz, 1 H, CH) ppm ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{S}_2\text{C}$ , 298 K, 75 MHz):  $\delta = 156.0, 154.5, 154.0, 151.9, 147.6, 147.56, 147.54, 147.53, 147.1, 146.9, 146.8, 146.76, 146.71, 146.7, 146.6, 146.57, 146.54, 146.5, 146.4, 146.0, 145.97, 145.96, 145.9, 145.86, 145.82, 145.8, 145.78, 145.72, 145.7, 145.69, 145.66, 145.1, 144.9, 144.8, 144.79, 143.7, 143.5, 143.2, 143.15, 143.14, 143.0, 142.9, 142.7, 142.67, 142.64, 142.53, 142.5, 142.4, 142.3, 142.2, 140.8, 140.7, 140.5, 140.4, 137.7, 136.4, 136.16, 136.11, 81.4, 77.0, 75.1, 72.7, 72.0, 62.6, 30.58$  ppm; FTIR (KBr):  $\nu = 1508, 1461, 1425, 526$   $\text{cm}^{-1}$ ; MS (ESI): 802.1  $[\text{M}+\text{H}]^+$ .

**3a:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 323 K, 300 MHz):  $\delta = 7.92\text{-}7.89$  (m, 2 H, Ar-H), 7.57-7.55 (m, 3 H, Ar-H), 6.42 (br t, 1 H,  $\text{CH-N}$ ), 5.71 (d,  $^2\text{J} = 12$  Hz, 1 H,  $\text{CH}_2\text{-N}$ ), 5.54 (d,  $^2\text{J} = 12$  Hz, 1 H,  $\text{CH}_2\text{-N}$ ), 3.58 (dd,  $^3\text{J} = 6.4$ ,  $^4\text{J} = 2.6$  Hz, 2 H,  $\text{CH}_2$ ), 2.33 (t,  $^4\text{J} = 2.6$  Hz, 1 H, CH) ppm ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K, 75 MHz):  $\delta = 170.1$  (CO), 154.7, 154.2, 152.4, 150.1, 147.42, 147.4, 146.4, 146.39, 146.38, 146.2, 146.1, 145.76, 145.7, 145.68, 145.6, 145.5, 145.44, 145.4, 145.3, 144.65, 144.6, 144.5, 144.44, 144.4, 143.2, 143.1, 142.8, 142.77, 142.7, 142.4, 142.3, 142.2, 142.17, 142.12, 142.1, 141.9, 141.8, 141.7, 140.33, 140.3, 139.9, 138.1, 136.9, 135.3, 130.9, 129.0, 128.8 (2 C), 128.3 (2C), 128.2, 125.3, 80.2, 73.5, 70.6, 65.4, 29.9 ppm; FTIR (KBr):  $\nu = 1641, 1400, 526$   $\text{cm}^{-1}$ .

**3b:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 278 K, 500 MHz, mixture of rotamers, 1:1):  $\delta = 6.39, 5.98$  (br t, br m, 1 H), 6.27, 4.93 (d, d,  $^2\text{J} = 12.4$  Hz, 1 H), 5.49 (br s, 2 H), 4.43, 4.21 (d, d,  $^2\text{J} = 14.6$  Hz, 1 H), 4.17, 3.93 (br s, br m, 1 H), 3.54, 3.37 (br m, br m, 2 H), 2.44, 2.25 (br s, br s, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K, 125 MHz, mixture of rotamers):  $\delta = 170.2$  (CO), 169.6 (CO), 149.5, 147.4, 146.36, 146.3, 146.2, 146.1, 146.0, 145.66, 145.6, 145.4, 145.37, 145.3, 145.2, 144.6, 144.5, 144.4, 143.1, 143.0, 142.7, 142.2, 142.1, 142.0, 141.8, 141.7, 140.2, 139.8, 135.1, 134.9, 129.1, 127.7, 127.5, 96.1, 74.2, 73.7, 73.0, 72.6, 70.3, 69.5, 66.4, 64.4, 58.3, 42.8, 42.4, 29.7, 25.7 ppm; FTIR (KBr):  $\nu = 1641, 1400, 526$   $\text{cm}^{-1}$ .

**3c:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 278 K, 500 MHz, mixture of rotamers):  $\delta = 6.37, 5.94$  (br t, br m, 1 H), 6.19, 4.96 (d, d,  $^2\text{J} = 12.6$  Hz, 1 H), 5.69, 5.49 (d, d,  $^2\text{J} = 11.5$  Hz, 1 H), 3.89, 3.61 (m, br m, 1 H), 3.42, 3.35 (br d, br d, 1 H), 2.95 (m, 1 H), 2.79 (m, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K, 125 MHz, mixture of rotamers):  $\delta = 164.2, 152.3, 150.3, 149.5, 147.44, 147.4, 147.39, 146.6, 146.45, 146.4, 146.35, 146.3, 146.2, 146.1, 145.7, 145.66, 145.6, 145.53, 145.5, 145.44, 145.4, 145.37, 145.3, 144.73, 144.7, 144.6, 144.57, 144.5,$

144.48, 144.4, 143.2, 143.1, 142.77, 142.7, 142.1, 141.9, 141.7, 140.3, 139.8, 96.1, 74.4, 73.5, 73.1, 72.9, 72.7, 72.5, 70.3, 66.4, 31.6, 29.6, 22.6, 14.0 ppm; FTIR (KBr):  $\nu = 1655, 1410, 526 \text{ cm}^{-1}$ .

**3d**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 323 K, 500 MHz):  $\delta = 8.04$  (d,  $^3J = 15.4 \text{ Hz}$ , 1 H,  $\text{CH}=\text{CH}$ ), 7.72-7.69 (m, 2 H, Ar-H), 7.48-7.42 (m, 3 H, Ar-H), 7.32 (d,  $^3J = 15.4 \text{ Hz}$ , 1 H,  $\text{CH}=\text{CH}$ ), 6.34 (br m, 1 H), 6.05 (br m, 1 H), 5.46 (br m, 1 H), 3.67-3.35 (br m, 2 H,  $\text{CH}_2$ ), 2.34 (t,  $^4J = 2.5 \text{ Hz}$ , 1 H,  $\text{CH}=\text{C}$ ) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 298 K, 50 MHz):  $\delta = 165.0$  (CO), 154.2, 152.5, 149.8, 147.3, 147.2, 146.3, 146.27, 146.2, 146.1, 146.08, 146.0, 145.6, 145.5, 145.4, 145.35, 145.3, 145.25, 145.2, 144.6, 144.5, 144.4, 144.3, 144.2, 143.1, 143.0, 142.7, 142.6, 142.3, 142.14, 142.1, 142.05, 142.03, 142.02, 142.0, 141.97, 141.7, 141.6, 140.2, 140.1, 139.7, 134.9, 130.1, 128.9 (2 C), 128.1 (2 C), 117.1, 80.1, 77.2, 73.6, 69.7, 65.8, 29.9 ppm; FTIR (KBr):  $\nu = 1652, 1400, 526 \text{ cm}^{-1}$ .

General procedure for the PK reaction: a solution of **3a-d** (0.05 mmol) in dry toluene (45 ml) at room temperature was stirred with powdered 4Å molecular sieves (7 g per mmol of **3a-d**; oven dried for 4 h at 120°C) under argon atmosphere for 15 min, 0.05 mmol of  $\text{Co}_2(\text{CO})_8$  was added in one portion and the mixture was stirred at 60°C. After 2-3 h, the reaction was filtered off over celite and the solvent was evaporated under vacuum. Flash chromatography using neutral silica-gel ( $\text{CH}_2\text{Cl}_2/\text{cyclohexane}$ : 1/1) afforded the pure product **5a-d** in a 95-98% yield.

**5a**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 298 K, 500 MHz):  $\delta = 7.75$ -7.74 (m, 2 H; Ar-H), 7.59-7.55 (m, 3 H; Ar-H), 6.92 (s, 1 H;  $\text{CH}=\text{C}$ ), 5.34 (d,  $^3J = 5.6 \text{ Hz}$ , 1 H;  $\text{CH}-\text{N}$ ), 5.28 (d,  $^2J = 11.5 \text{ Hz}$ , 1 H;  $\text{CH}_2-\text{N}$ ), 4.87 (d,  $^2J = 11.5 \text{ Hz}$ , 1 H;  $\text{CH}_2-\text{N}$ ), 4.64 (d,  $^2J = 14.6 \text{ Hz}$ , 1 H;  $\text{CH}_2$ ), 3.76 (dd,  $^2J = 14.6$ ,  $^3J = 5.6 \text{ Hz}$ , 1 H;  $\text{CH}_2$ ) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ , 298 K, TMS):  $\delta = 202.2$  (CO), 184.5 ( $\text{C}=\text{CH}$ ), 173.7 (CO-N), 150.6, 149.15, 149.13, 149.09, 149.08, 148.4, 148.34, 148.33, 147.63, 147.62, 147.5, 147.4, 146.9, 146.7, 146.6, 146.5, 146.3, 146.0, 145.7, 145.5, 145.4, 145.3, 145.05, 145.03, 144.85, 144.84, 144.7, 144.6, 144.5 (2 C), 144.4, 144.33, 144.3 (2 C), 144.1, 143.8, 143.76, 143.7, 143.67, 143.65, 143.63, 143.0, 142.8, 142.6, 142.5, 142.4, 141.9, 141.7, 141.6, 141.1, 140.7, 138.7, 138.5, 135.7, 135.6, 135.3, 135.0, 131.65 (Ar-C), 129.17 (2 C, Ar-C), 127.91 (2C, Ar-C), 126.05 ( $\text{C}=\text{CH}$ ), 73.95 ( $\text{C}_{\text{sp}^3}-\text{C}_{60}$ ), 73.56 ( $\text{C}_{\text{sp}^3}-\text{C}_{60}$ ), 72.08 ( $\text{CH}-\text{N}$ ), 70.10 ( $\text{C}_{\text{sp}^3}-\text{C}_{60}$ ), 64.26 ( $\text{C}_{\text{sp}^3}-\text{C}_{60}$ ), 62.99 ( $\text{CH}_2-\text{N}$ ), 33.68 ppm ( $\text{CH}_2$ ); FTIR (KBr):  $\nu = 1718, 1637, 526 \text{ cm}^{-1}$ ; HRMS (MALDI-TOF): Calcd for  $[\text{C}_{73}\text{H}_{11}\text{NO}_2]^+$  933.07892; found 933.07811.

**5b**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 298 K, 500 MHz):  $\delta = 7.47$ -7.41 (m, 4 H, Ar-H), 7.37-7.34 (m, 1 H, Ar-H), 6.81 (d,  $^4J = 1.5 \text{ Hz}$ , 1 H,  $\text{CH}=\text{C}$ ), 5.28 (d,  $^2J = 11.0 \text{ Hz}$ , 1 H,  $\text{CH}_2-\text{N}$ ), 5.25 (d,  $^3J = 6.3 \text{ Hz}$ , 1 H,  $\text{CH}-\text{N}$ ), 5.02 (d,  $^2J = 11.0 \text{ Hz}$ , 1 H,  $\text{CH}_2-\text{N}$ ), 4.82 (d,  $^2J = 14.9 \text{ Hz}$ , 1 H,  $\text{CH}_2$ ), 3.99 (AB sist., 2 H,  $\text{CH}_2-\text{CO}$ ), 3.67 (ddd,  $^2J =$

14.9,  $^3J = 6.3$ ,  $^4J = 1.5$  Hz, 1 H, CH<sub>2</sub>) ppm;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 298 K, 125 MHz):  $\delta = 201.9$  (CO), 184.2 (C=CH), 172.9 (CO-N), 150.5, 149.2, 149.15, 149.14, 149.1, 148.4, 148.37, 148.3, 147.6, 147.46, 147.44, 147.1, 146.9, 146.7, 146.5, 146.4, 146.1, 145.9, 145.45, 145.4, 145.3, 145.06, 145.0, 144.84, 144.8, 144.7, 144.63, 144.6, 144.5, 144.34, 144.3, 144.25, 144.2, 143.8, 143.7, 143.67, 143.65, 143.61, 143.6, 143.1, 142.8, 142.7, 142.6, 142.4, 141.9, 141.7, 140.9, 140.8, 138.6, 138.5, 135.3, 135.2, 134.9, 133.6, 129.1 (2C, Ar-C), 129.0, 128.96 (2C, Ar-C), 128.2, 127.5 (Ar-C), 126.1 (C=CH), 74.0 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 73.7 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 73.0 (CH-N), 69.8 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 63.9 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 60.6 (CH<sub>2</sub>-N), 43.7 (CH<sub>2</sub>-CO), 33.8 ppm (CH<sub>2</sub>). FTIR (KBr):  $\nu = 1718, 1637, 524\text{ cm}^{-1}$ ; FAB:  $m/z: 947\text{ [M}^+]$ .

**5c:**  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 298 K, 500 MHz):  $\delta = 6.84$  (d,  $^4J = 1.5$  Hz, 1 H; CH=C), 5.24 (d,  $^2J = 11.1$  Hz, 1 H; CH<sub>2</sub>-N), 5.23 (d,  $^3J = 6.3$  Hz, 1 H; CH-N), 5.06 (d,  $^2J = 11.1$  Hz, 1 H; CH<sub>2</sub>-N), 4.72 (d,  $^2J = 14.8$  Hz, 1 H; CH<sub>2</sub>), 3.68 (ddd,  $^2J = 14.8$ ,  $^3J = 6.3$ ,  $^4J = 1.5$  Hz, 1 H; CH<sub>2</sub>), 2.74-2.49 (m, 2 H; CH<sub>2</sub>-CO), 1.86-1.81 (m, 2 H; CH<sub>2</sub>), 1.51-1.45 (m, 4 H; 2 CH<sub>2</sub>), 1.01-0.97 (m, 3 H; CH<sub>3</sub>) ppm;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 298 K, 125 MHz):  $\delta = 202.0$  (CO), 184.4 (C=CH), 175.4 (CO-N), 150.7, 149.2, 149.17, 149.14, 149.1, 148.5, 148.4, 148.3, 147.7, 147.5, 147.4, 147.0, 146.9, 146.7, 146.6, 146.5, 146.4, 146.2, 146.1, 145.5 (2 C), 145.3, 145.1, 145.0, 144.85, 144.84, 144.8, 144.7, 144.6, 144.5, 144.4, 144.34, 144.3, 144.26, 144.2, 144.0, 143.73, 143.7, 143.65, 143.6, 143.58, 143.1, 142.8, 142.7, 142.6, 142.4, 141.9, 141.8, 141.6, 141.0, 140.8, 138.7, 138.6, 135.3, 135.0, 134.9, 126.1 (C=CH), 74.1 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 73.87 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 72.96 (CH-N), 69.71 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 63.88 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 60.64 (CH<sub>2</sub>-N), 36.34 (CH<sub>2</sub>-CO), 34.24 (CH<sub>2</sub>), 31.55 (CH<sub>2</sub>), 24.51 (CH<sub>2</sub>), 22.55 (CH<sub>2</sub>), 14.02 ppm (CH<sub>3</sub>); FTIR (KBr):  $\nu = 1718, 1637, 524\text{ cm}^{-1}$ ; FAB:  $m/z: 927\text{ [M}^+]$ .

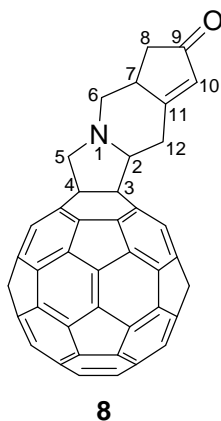
**5d:**  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 298 K, 500 MHz):  $\delta = 7.93$  (d,  $^3J = 15.4$  Hz, 1 H, CH=CH), 7.67-7.65 (m, 2 H, Ar-H), 7.46-7.44 (m 3 H, Ar-H), 7.02 (d,  $^3J = 15.4$  Hz, 1 H CH=CH), 6.87 (d,  $^4J = 1.5$  Hz, 1 H, CH=C), 5.50 (d,  $^2J = 10.9$  Hz, 1 H, CH<sub>2</sub>-N), 5.42 (d,  $^3J = 6.5$  Hz, 1 H CH-N), 5.20 (d,  $^2J = 10.9$  Hz, 1 H, CH<sub>2</sub>-N), 4.67 (d,  $^2J = 15.1$  Hz, 1 H, CH<sub>2</sub>), 3.77 (ddd,  $^2J = 15.1$ ,  $^3J = 6.5$ ,  $^4J = 1.5$  Hz, 1 H CH<sub>2</sub>) ppm;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 298 K, 125 MHz):  $\delta = 202.0$  (C=O), 184.4 (C=CH), 168.4 (CO-N), 150.7, 149.23, 149.2, 149.13, 149.1, 148.42, 148.4, 148.37, 147.7, 147.5, 147.3, 146.9, 146.7, 146.6, 146.5, 146.4, 146.3, 146.2, 145.5, 145.45, 145.4, 145.1, 145.0, 144.9, 144.83, 144.8, 144.7, 144.6, 144.5, 144.4, 144.35, 144.3, 144.24, 144.2, 143.9, 143.7, 143.67, 143.6, 143.1, 142.8, 142.7, 142.6, 142.4, 141.9, 141.8, 141.6, 140.9, 140.8, 138.7, 135.4, 134.9, 134.8, 134.5, 130.5, 129.0, 128.3, 126.3 (C=CH), 118.3 (CH=CH), 74.2 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 74.0 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>),

73.3 (CH-N), 69.5 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 63.8 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 60.8 (CH<sub>2</sub>-N), 34.5 ppm (CH<sub>2</sub>); FTIR (KBr):  $\nu$  = 1716, 1654, 1375, 524 cm<sup>-1</sup>; FAB: m/z: 960 [M+1<sup>+</sup>]; 959 [M<sup>+</sup>].

6: <sup>1</sup>H NMR (CDCl<sub>3</sub>/S<sub>2</sub>C, 298 K, 200 MHz):  $\delta$  = 6.35 (m, 1 H, CH=CH<sub>2</sub>), 5.59 (ddd, <sup>3</sup>J = 17.09, <sup>2</sup>J = 2.9, <sup>4</sup>J = 1.6 Hz, 1 H, CH=CH<sub>2</sub>), 5.43 (br d, 1 H, C=CH<sub>2</sub>), 4.86 (d, <sup>2</sup>J = 9.7 Hz, 1 H, CH<sub>2</sub>-N), 4.36 (ddt, <sup>2</sup>J = 13.7, <sup>3</sup>J = 5.1, <sup>4</sup>J = 1.6 Hz, 1 H, N-CH<sub>2</sub>-C=), 4.30 (br t, 1 H, CH-N), 4.14 (d, <sup>2</sup>J = 9.7 Hz, 1 H, CH<sub>2</sub>-N), 3.56 (br dd, 1 H, N-CH<sub>2</sub>-C=), 3.51 (ddd, <sup>2</sup>J = 17.3, <sup>3</sup>J = 5.3, <sup>4</sup>J = 2.7 Hz, 1 H, CH<sub>2</sub>), 3.24 (ddd, <sup>2</sup>J = 17.3, <sup>3</sup>J = 6.1, <sup>4</sup>J = 2.7 Hz, 1 H, CH<sub>2</sub>), 2.19 (t, <sup>4</sup>J = 2.7 Hz, 1 H, CH) ppm ; <sup>13</sup>C NMR (CDCl<sub>3</sub>/S<sub>2</sub>C, 298 K, 50 MHz):  $\delta$  = 155.9, 154.1, 153.8, 151.7, 147.2, 147.1, 146.9, 146.5, 146.3, 146.26, 146.2, 146.16, 146.1, 146.06, 146.0, 145.96, 145.9, 145.88, 145.8, 145.6, 145.5, 145.46, 145.4, 145.3, 145.2, 145.18, 145.1, 144.7, 144.5, 144.33, 144.3, 144.0, 143.9, 142.9, 142.6, 142.57, 142.5, 142.1, 142.07, 141.9, 141.8, 141.6, 140.9, 140.2, 140.1, 139.6, 137.7, 137.2, 136.2, 135.9, 135.6, 135.5, 118.8, 81.7, 75.0, 73.5, 72.6, 69.1, 66.5, 29.9 ppm; FTIR (KBr):  $\nu$  = 1712, 524 cm<sup>-1</sup>; MS (ESI): 842.3 [M+H]<sup>+</sup>.

7: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 500 MHz):  $\delta$  = 6.81 (d, <sup>4</sup>J = 1.6 Hz, 1H, CO-CH=), 6.15 (m, 1 H, CH=CH<sub>2</sub>), 5.48 (ddd, <sup>3</sup>J = 17.1, <sup>2</sup>J = 2.6, <sup>4</sup>J = 1.7 Hz, 1 H, CH=CH<sub>2</sub>), 5.36 (ddd, <sup>3</sup>J = 10.0, <sup>2</sup>J = 2.6, <sup>4</sup>J = 1.6 Hz, 1 H, CH=CH<sub>2</sub>), 4.58 (d, <sup>2</sup>J = 9.6 Hz, 1 H, CH<sub>2</sub>-N), 4.06 (d, <sup>3</sup>J = 4.6 Hz, 1 H, CH-N), 3.89 (d, <sup>2</sup>J = 9.6 Hz, 1 H, CH<sub>2</sub>-N), 3.86 (ddt, <sup>2</sup>J = 13.9, <sup>3</sup>J = 5.0, <sup>4</sup>J = 1.6 Hz, 1 H, CH<sub>2</sub>-CH=), 3.72 (d, <sup>2</sup>J = 13.9 Hz, 1 H, CH<sub>2</sub>), 3.54 (ddd, <sup>2</sup>J = 13.9, <sup>3</sup>J = 4.6, <sup>4</sup>J = 1.6 Hz, 1 H, CH<sub>2</sub>), 3.29 (br dd, <sup>2</sup>J = 13.9, <sup>3</sup>J = 7.4 Hz, 1 H, CH<sub>2</sub>-CH=) ppm ; <sup>13</sup>C NMR (CDCl<sub>3</sub>/S<sub>2</sub>C, 298 K, 125 MHz):  $\delta$  = 202.2 (CO), 184.1 (C=CH), 152.6, 150.3, 149.6, 149.2, 149.1, 149.0, 148.6, 148.34, 148.3, 148.1, 147.9, 147.3, 146.9, 146.6, 146.45, 146.4, 146.2, 145.9, 145.4, 145.3, 145.1, 145.0, 144.9, 144.85, 144.8, 144.7, 144.6, 144.5, 144.4, 144.3, 144.2, 144.16, 144.1, 13.65, 143.6, 143.5, 143.0, 142.8, 142.7, 142.6, 142.3, 141.9, 141.8, 141.7, 140.9, 138.5, 138.2, 137.7, 136.3, 135.5, 134.7, 134.5, 134.2, 130.8, 129.0, 128.2, 126.5 (C=CH), 125.3, 118.5 (CH=CH<sub>2</sub>), 77.3 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 73.9 (CH-N), 73.0 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 71.1 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 66.5 (CH<sub>2</sub>-N), 64.9 (C<sub>sp<sup>3</sup></sub>-C<sub>60</sub>), 55.0 (CH<sub>2</sub>-CH=), 33.4 ppm (CH<sub>2</sub>); FTIR (KBr):  $\nu$  = 1712, 524 cm<sup>-1</sup>; HRMS (MALDI-TOF): Calcd for [C<sub>69</sub>H<sub>12</sub>NO]<sup>+</sup> ([M+1]<sup>+</sup>) 870.09134; found 870.09094.





**Alatory numbering of compound 8 for spectroscopical assignment**

**8:**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{S}_2\text{C}$ , 298 K, 500 MHz):  $\delta$  = 6.19 (s, 1 H, H-10), 4.86 (d,  $^2\text{J}$  = 9.1 Hz, 1 H, H-5), 4.12 (d,  $^2\text{J}$  = 9.1 Hz, 1 H, H-5), 4.04 (dd,  $^2\text{J}$  = 10.5,  $^3\text{J}$  = 6.0 Hz, 1 H, H-6), 3.89 (dd,  $^3\text{J}$  = 11.5,  $^3\text{J}$  = 3.1 Hz, 1 H, H-2), 3.81 (dd,  $^2\text{J}$  = 13.0,  $^3\text{J}$  = 3.1 Hz, 1 H, H-12), 3.47 (m, 1 H, H-7), 3.25 (br t, 1 H, H-12), 2.78 (dd,  $^2\text{J}$  = 18.5,  $^3\text{J}$  = 6.6 Hz, 1 H, H-8), 2.47 (br t, 1 H, H-6), 2.27 (dd,  $^2\text{J}$  = 18.5,  $^3\text{J}$  = 2.5 Hz, 1 H, H-8) ppm ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{S}_2\text{C}$ , 298 K, 125 MHz):  $\delta$  = 207.7 (CO), 179.1 ( $\underline{\text{C}}=\text{CH}$ ), 156.0, 153.7, 153.1, 152.2, 147.8, 147.7, 146.86, 146.83, 146.77, 146.75, 146.7, 146.68, 146.61, 146.6, 146.52, 146.5 (2 C), 146.14, 146.1, 146.03, 146.0, 145.9, 145.85, 145.82 (2 C), 145.8, 145.73, 145.7, 145.2, 145.0, 144.85, 144.8, 143.6, 143.5, 143.22, 143.2, 143.14, 143.1, 142.64, 142.6 (2 C), 142.54, 142.5, 142.48, 142.44, 142.4, 142.24, 142.2, 140.8, 140.74, 140.7, 140.4, 138.1, 136.8, 136.6, 136.2, 129.7 (2 C), 128.7, 75.4 (C-2), 74.7 ( $\text{C}_{\text{sp}^3}\text{-C}_{60}$ ), 70.3 ( $\text{C}_{\text{sp}^3}\text{-C}_{60}$ ), 67.8 (C-5), 59.1 (C-6), 40.9 (C-7), 39.8 (C-8), 35.6 ppm ( $\text{CH}_2$ ); IR (KBr):  $\nu$  = 1706, 1624, 526  $\text{cm}^{-1}$ ; HRMS (MALDI-TOF): Calcd for  $[\text{C}_{69}\text{H}_{12}\text{NO}]^+$  ( $[\text{M}+1]^+$ ) 870.09134; found 870.09117.

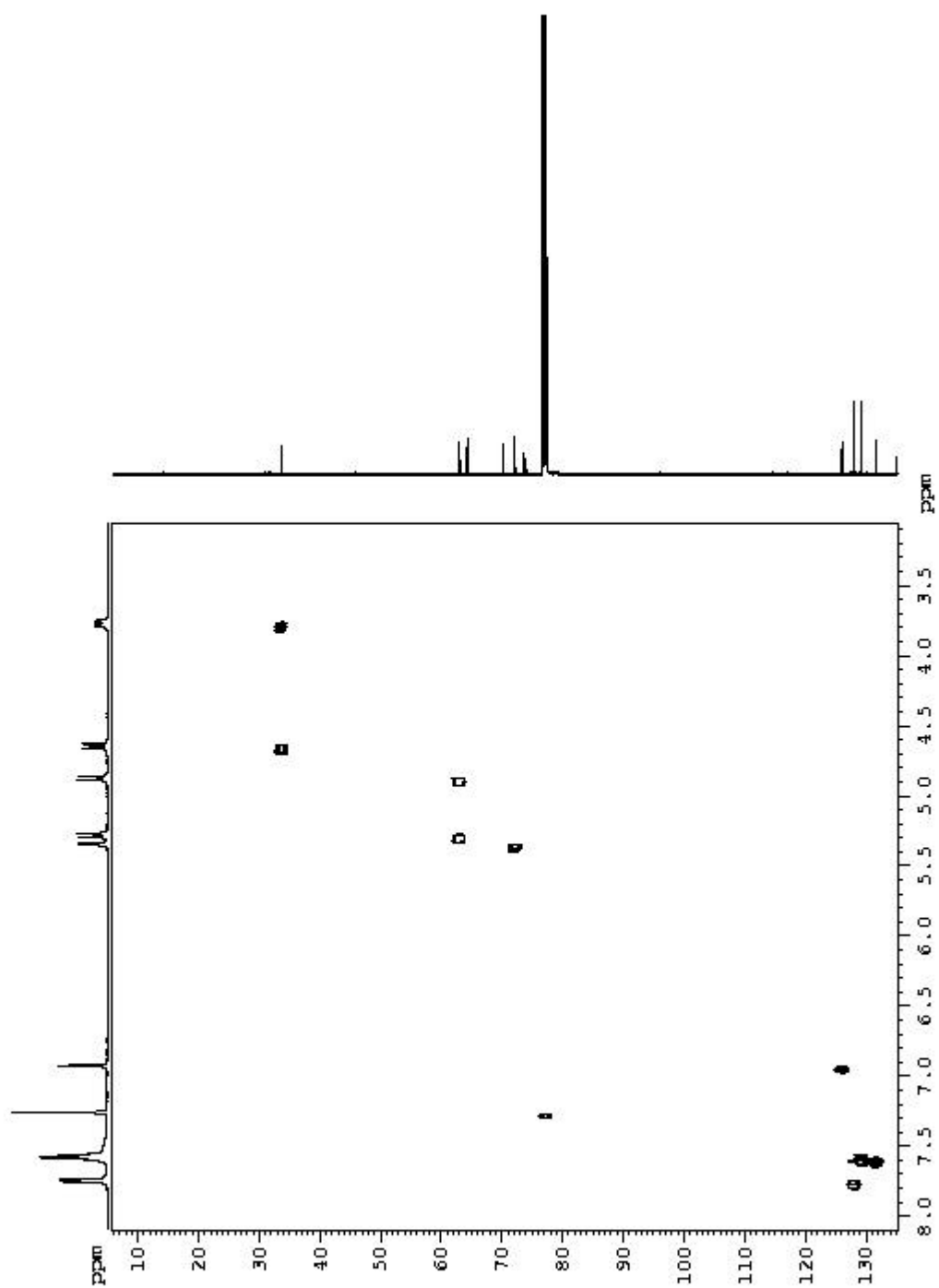


Figure S5: HMQC of compound 5a

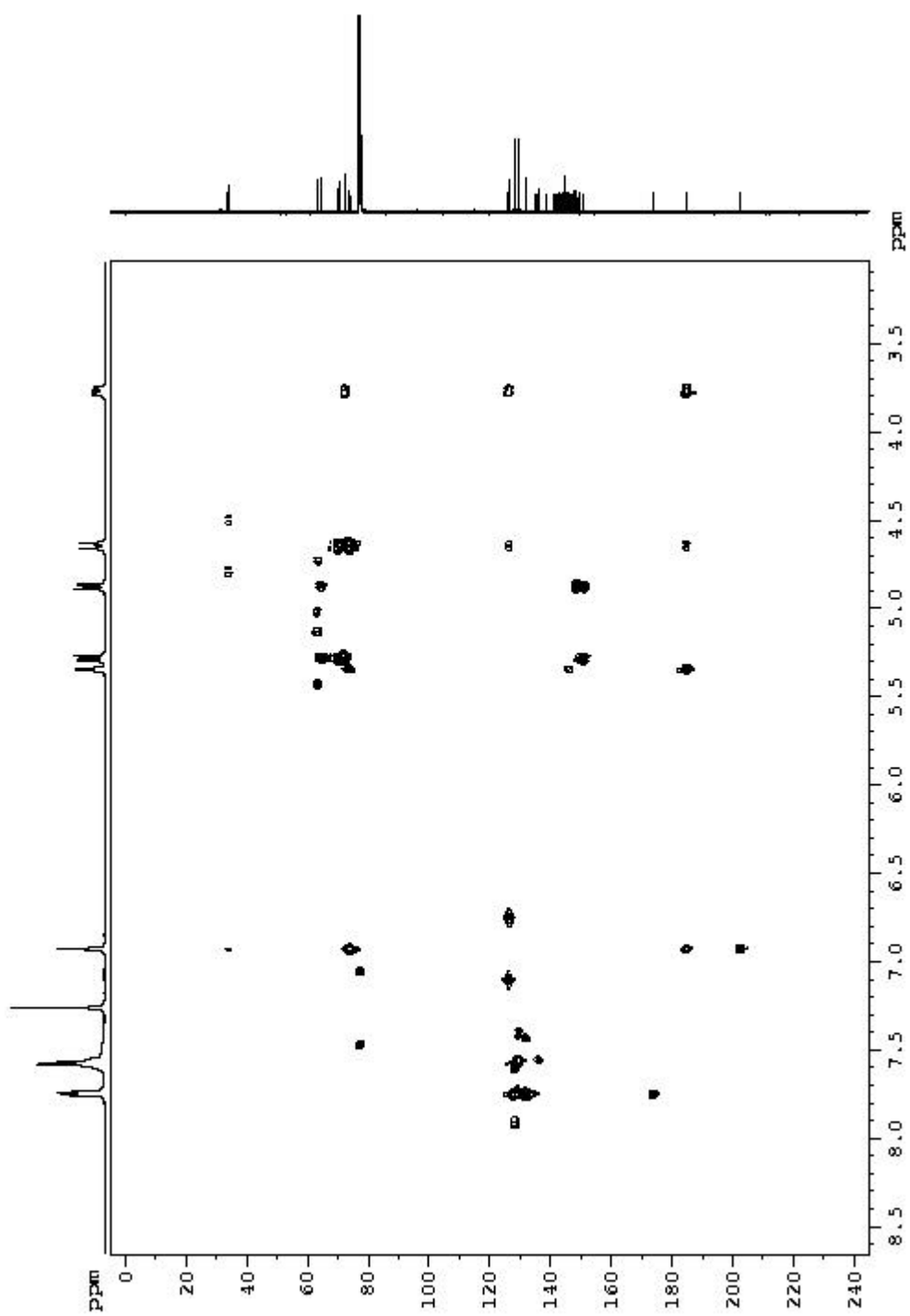


Figure S6: HMBC of compound 5a

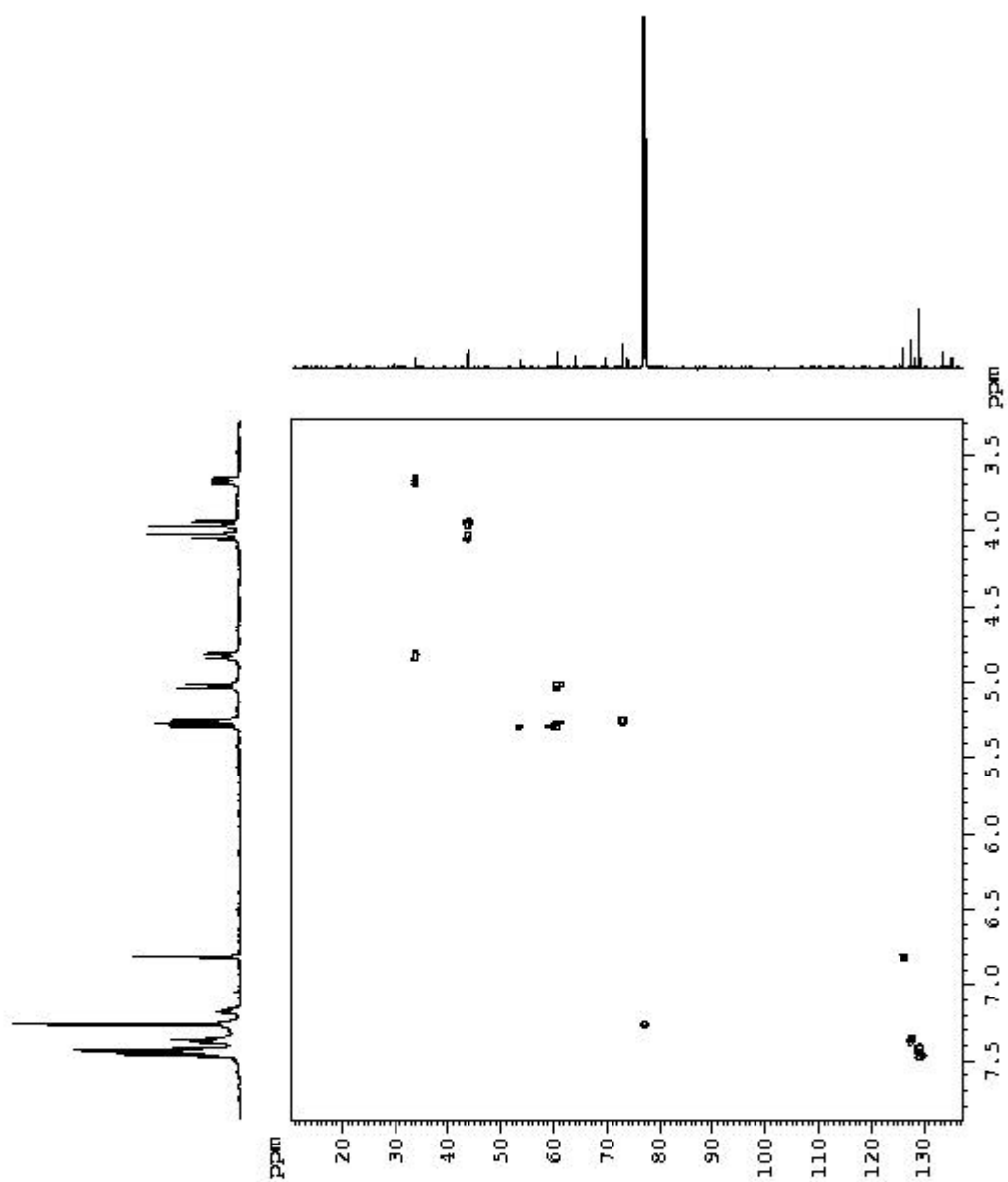


Figure S7: HMQC of compound 5b

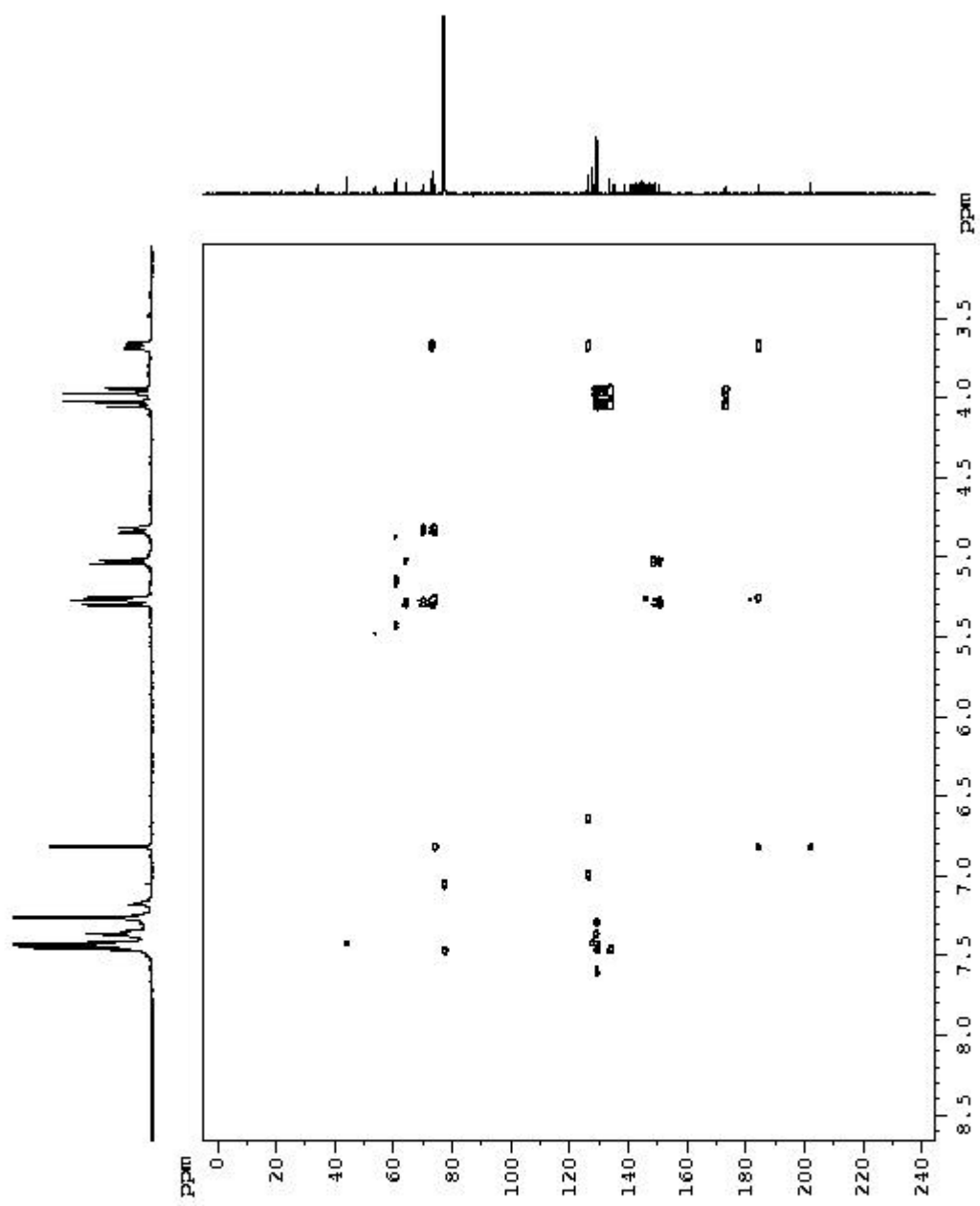


Figure S8: HMBC of compound 5b

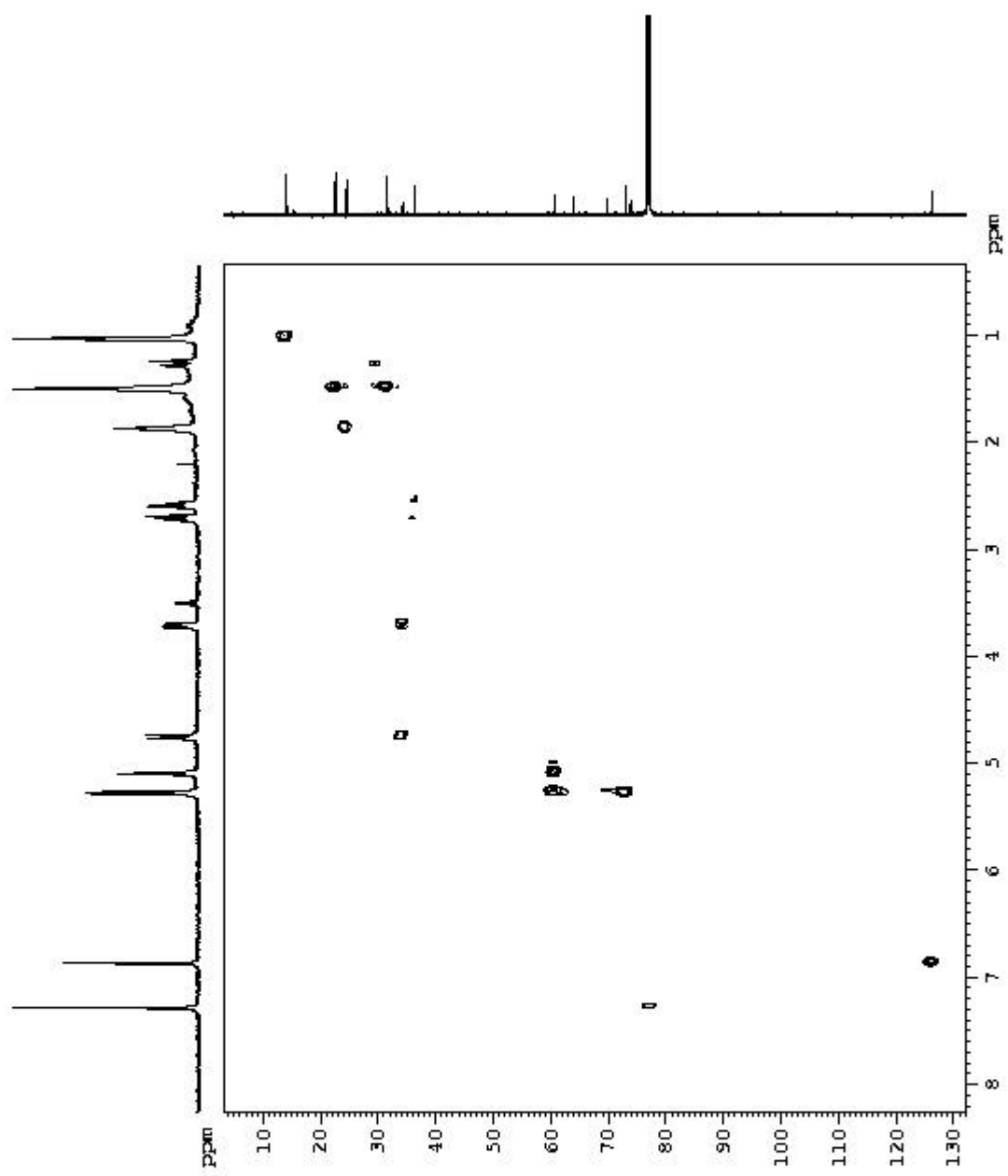


Figure S9: HMQC of compound 5c

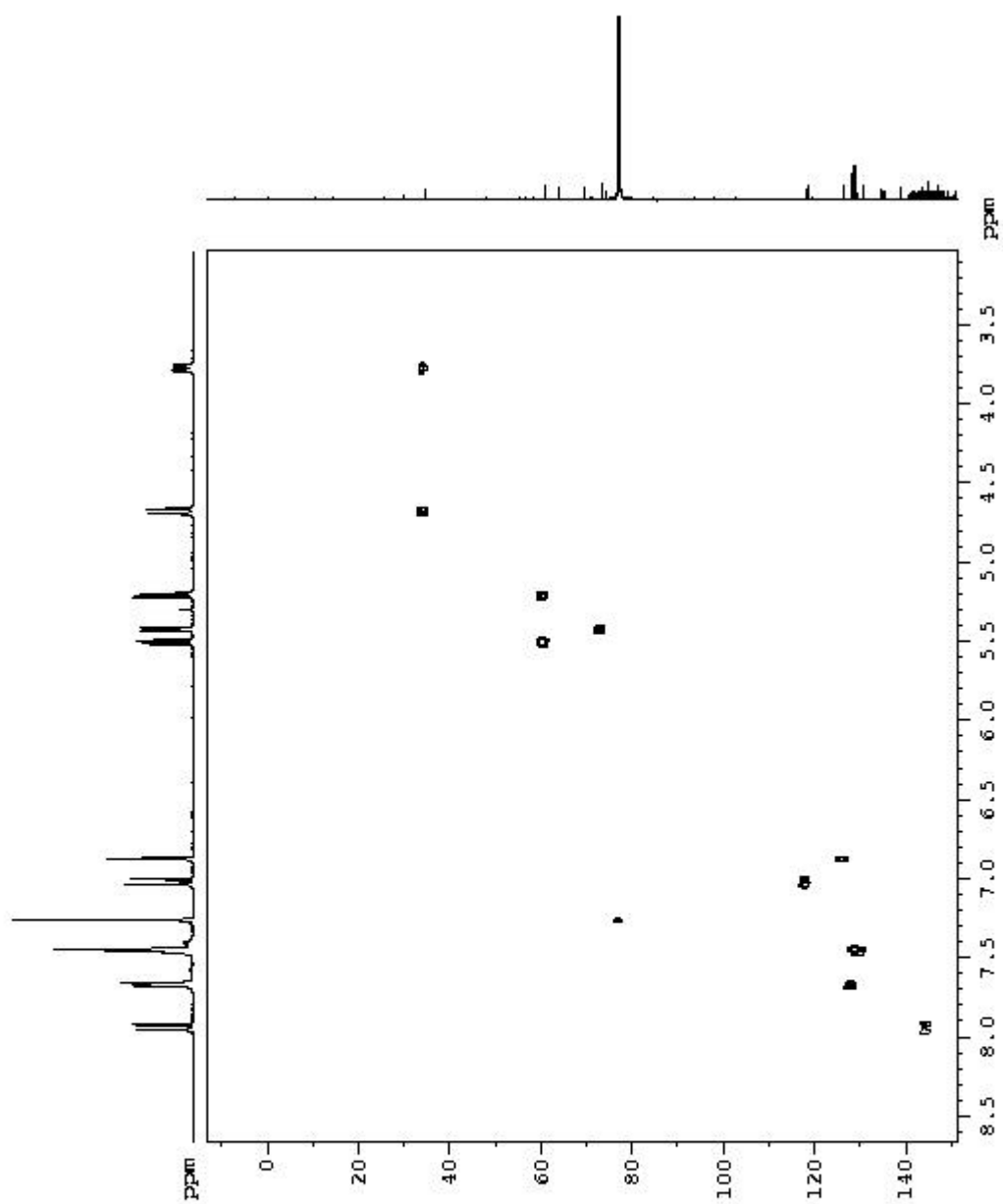


Figure S10: HMQC of compound 5d

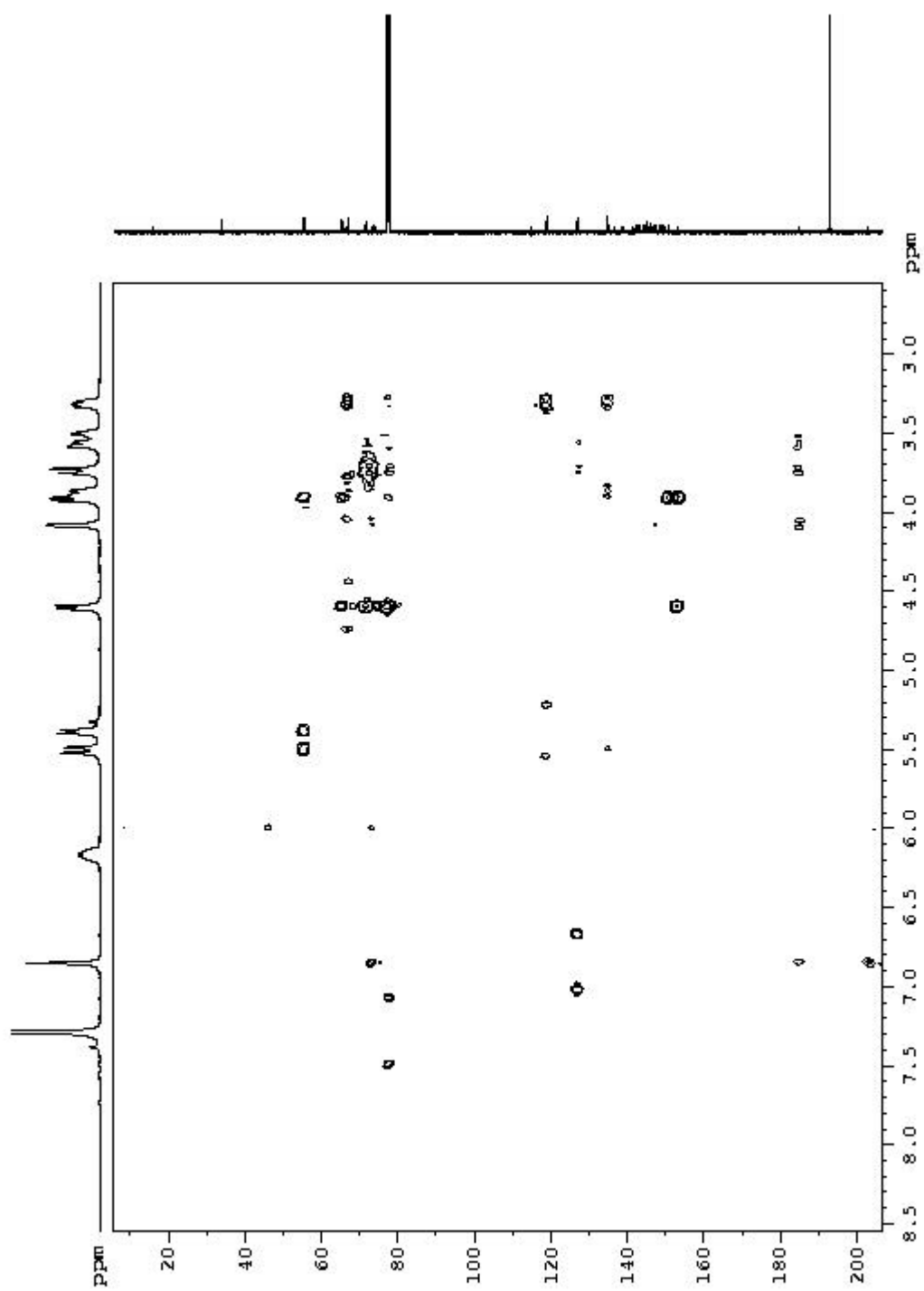


Figure S11: HMBC of compound 7



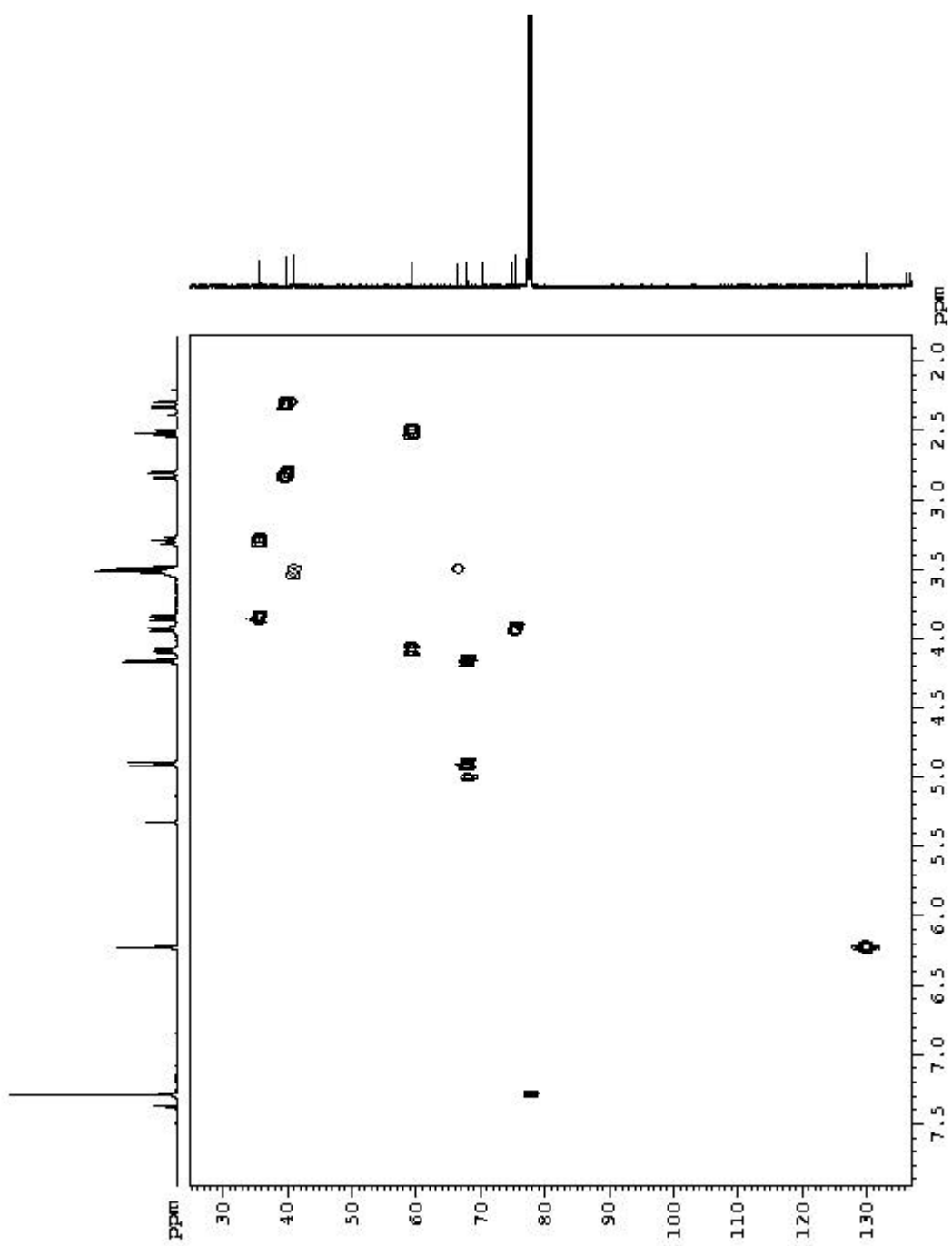


Figure S12: HMQC of compound 8

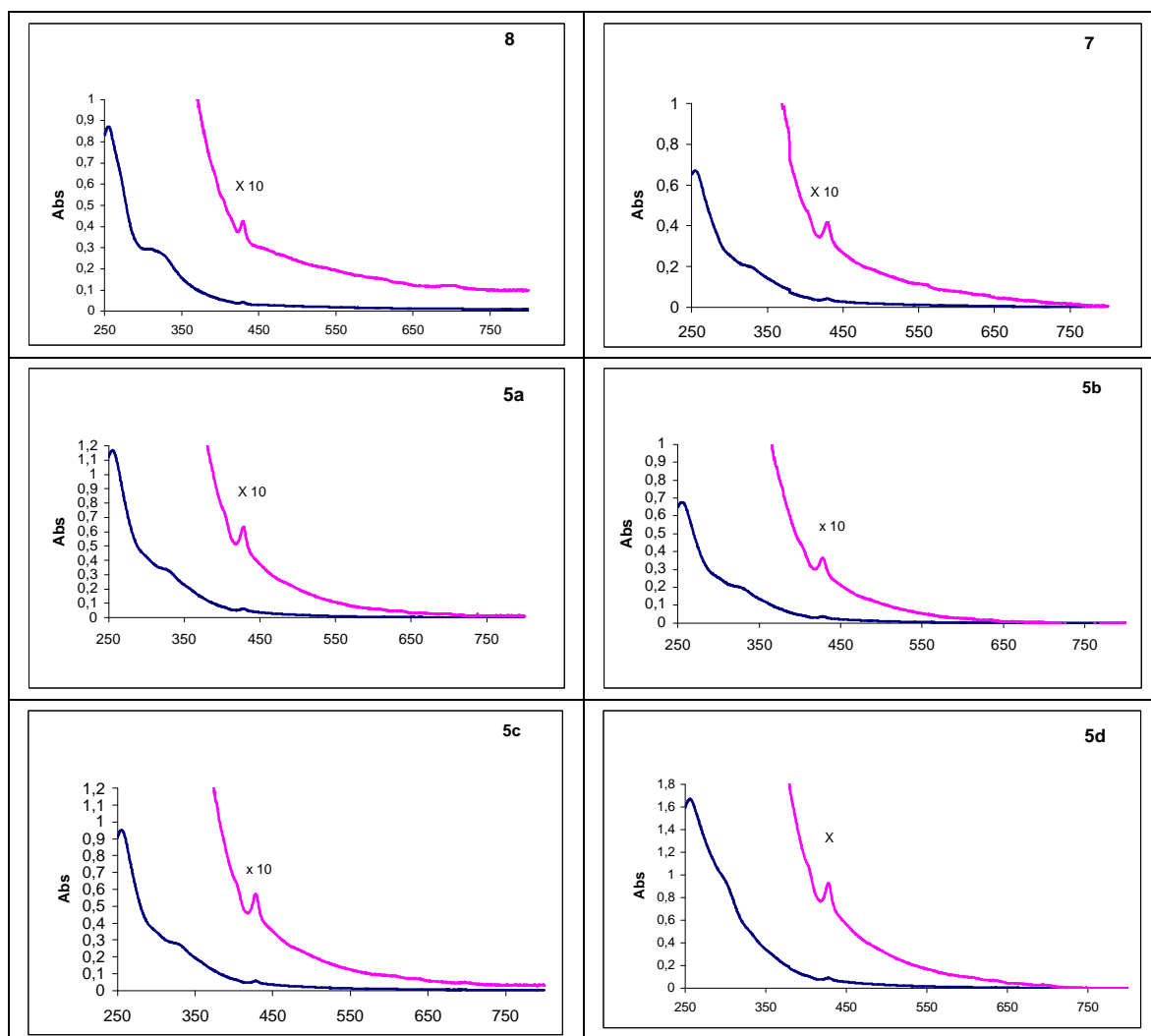


Figure S13: UV-vis spectra of the compounds 5a-d, 7 and 8 in  $\text{CH}_2\text{Cl}_2$  ( $1 \times 10^{-5}$  M).