Supplementary Material (ESI) for Chemical Communications

Synthesis of 4,5-Diheteroarylphenanthrenes and Their Dinuclear Ruthenium(II) Bis(2,2′:6′,2″-terpyridine) Complexes Possessing Severe Helical Twists

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Supplementary Information

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General Experimental Methods. All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. Commercially available chemicals were of reagent grade and were used as received without further purification. Diketone **4**,[1c] 1-ethynyl-2-iodobenzene (**3**),[4] 4-ethynylpyridine (**7a**),[6] 5-ethynyl-2,2′-bipyridine (**7b**),[7] 4′-ethynyl-2,2′:6′,2″-terpyridine (**7c**),[7a,8] 4′-ethoxy-2,2′:6′,2″-terpyridine (**11**),[8b] and 4′-chloro-2,2′:6′,2″-terpyridine (**12**)[8a,b] were prepared according to the reported procedures. Purification by column chromatography was performed using 32-63 μm silica gel. Melting points were uncorrected. High resolution mass spectra were obtained on a hybrid linear ion trap Fourier transform mass spectrometer system equipped with an ion source. UV−vis spectra of 2.5×10^{-5} M solutions of **2a**−**c** in dichloromethane and 1.0×10^{-5} M solutions of **13**, **14**, and $[Ru(4'\text{-}EtOtpy)_2](PF_6)_2$ in acetonitrile were recorded at room temperature. Emission spectra of 1.0×10^{-7} M solutions of **2a**−**c** in dichloromethane were recorded at room temperature upon excitation at 360 nm.

Propargylic Alcohol 5. To 6.00 g (26.3 mmol) of 1-ethynyl-2-iodobenzene (**3**) in 50 mL of THF under a nitrogen atmosphere at 0 °C was added 23.3 mL of a 1.2 M solution of LDA (28.0 mmol) in hexanes. After 30 min of stirring, a solution of 3.23 g of diketone **4** (13.1 mmol) in 40 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 h, 50 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/20% THF in hexanes, $R_f = 0.33$) to produce 8.73 g (12.5 mmol, 95%, 1:1 mixture of the *meso* and *rac* isomers) of **5** as a white solid: mp 227−228 °C; IR 3559, 757 cm^{-1}; ^1H NMR (mixture of the *meso* and *rac* isomers, $CDCl_3$, 600 MHz) δ 7.85 (2 H, dd, $J = 7.8$, 1.2 Hz), 7.71 (4 H, s), 7.48 (2 H, dd, *J* = 7.8, 1.2 Hz), 7.30 (2 H, td, *J* = 7.5, 1.2 Hz), 7.01 (2 H, td, *J* = 8.1, 1.8 Hz), 2.45 (2 H, br), 1.12 (18 H, s); ^{13}C NMR (mixture of the *meso* and *rac* isomers, $CDCl_3$, 150 MHz) δ 141.0, 138.8, 133.2, 129.52, 129.49, 127.7, 126.7, 100.4, 96.1, 87.6, 79.5, 40.0, 25.7; HRMS *m/z* calcd for $C_{32}H_{32}I_2O_2Na$ (MNa^+) 725.0384, found 725.0385.

Diiodide 6. To a mixture of **5** (8.4 g, 11.96 mmol) and triethylsilane (4.17 g, 35.9 mmol) in 200 mL of dichloromethane was added 1.09 g of trifluoroacetic acid (95.6 mmol). After 1 h of stirring at room temperature, 5.1 g (48.1 mmol) of sodium carbonate was added followed by 50 mL of water. The organic layer was separated, washed with brine and water, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by flash column chromatography (silica gel/10% diethyl ether in hexanes, R_f = 0.57) to provide 7.69 g (11.5 mmol, 96%, 1:1 mixture of the *meso* and *rac* isomers) of **6** as a white solid: mp 182−183 °C; IR 2219, 1462, 750 cm^{-1}; ^{1}H NMR (mixture of the *meso* and *rac* isomers, $CDCl_3$, 600 MHz) δ 7.83 (2 H, dd, *J* = 8.1, 1.2 Hz), 7.43 (2 H, dd, *J* = 7.8, 1.8 Hz), 7.38 (4 H, s), 7.26 (2 H, td, *J* = 7.5, 1.2 Hz), 6.96 (2 H, td, *J* = 7.8, 1.8 Hz), 3.68 (2 H, s), 1.08 (18 H, s); ^{13}C NMR (mixture of the *meso* and *rac* isomers, $CDCl_3$, 150 MHz) δ 138.6, 137.4, 133.0, 130.6, 129.1, 128.8, 127.6, 100.6, 95.7, 85.6, 50.3, 35.7, 27.9; HRMS *m/z* calcd for $C_{32}H_{33}I_2$ (MH^+) 671.0666, found 671.0665.

Tetraacetylene 8a. The following procedure for **8a** is representative for the preparation of tetraacetylenes **8a**−**c**. To a mixture of **6** (0.90 g, 1.34 mmol), $Pd(PPh_3)_2Cl_2$ (0.047 g, 0.067 mmol), and CuI (0.0064 g, 0.034 mmol) in 40 mL of triethylamine under a nitrogen atmosphere was added via cannula a solution of **7a** (0.29 g, 2.81 mmol) in 20 mL of triethylamine. The resulting mixture was heated to reflux for 24 h before it was allowed to cool to room temperature. The mixture was concentrated in vacuo. The black residue was dissolved in 100 mL of dichloromethane and then washed with brine and water. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/CH_2Cl_2:MeOH = 19:1, $R_f = 0.45$) provided 0.75 g (1.2 mmol, 90%, 1:1 mixture of the *meso* and *rac* isomers) of **8a** as a yellow solid with some fractions contained only the *meso* or the *rac* isomer: mp 183−185 °C; IR 2218, 1590, 1235, 821, 764 cm^{-1}; *meso*-**8a**: ^1H NMR ($CDCl_3$, 600 MHz) δ 8.55 (4 H, br s), 7.56 (2 H, dd, $J = 7.8, 1.2$ Hz), 7.53 (2 H, dd, $J = 7.8, 1.2$ Hz), 7.35 (2 H, td, $J = 7.8, 1.2$ Hz), 7.30 (2 H, td, $J = 7.8, 1.2$ Hz), 7.297−7.28 (8 H, m), 3.66 (2 H, s), 1.02 (18 H, s); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 148.0, 137.6, 133.2, 132.5, 132.4, 129.3, 129.0, 127.6, 126.8, 126.1, 124.0, 96.4, 95.1, 89.4, 82.2, 50.2, 35.5, 27.8. *rac*-**8a**: ^1H NMR ($CDCl_3$, 600 MHz) δ 8.50 (4 H, br s), 7.52 (2 H, d, $J = 7.8$ Hz), 7.46 (2 H, d, $J = 6.6$ Hz), 7.30−7.24 (12 H, m), 3.67 (2 H, s), 1.01 (18 H, s); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 149.4, 137.5, 132.3, 132.2, 131.6, 128.9, 128.8, 127.4, 126.7, 125.6, 124.3, 96.3, 93.3, 89.7, 82.1, 50.2, 35.5, 27.7; MS *m/z* 621 (MH^+), 254; HRMS *m/z* calcd for $C_{46}H_{41}N_2$ (MH^+) 621.3264, found 621.3261. Recrystallization of the separated *meso*-**8a** and *rac*-**8a** from CH_2Cl_2/MeOH produced crystals suitable for X-ray structure analyses.

Crystal data for *meso*-**8a**: $C_{46}H_{40}N_2$, $M = 620.80$, monoclinic, space group $P2_1/n$, colorless, $a = 12.4736(7)$ Å, $b = 5.9821(3)$ Å, $c = 24.7092(14)$ Å, $\beta = 100.789(1)°$, $V = 1811.17(17)$ Å^3, $Z = 2$, $D_c = 1.138$ g/cm^3, μ(Mo-Kα) = 0.66 cm^{-1}, $T = 293$ K, 4067 unique data with $R_{int} = 0.0432$. Final $R_1 = 0.0568$, w$R_2 = 0.1552$ for 2850 reflections with $I > 2\sigma(I)$, $GOF = 1.021$. CCDC number 750093.

Crystal data for *rac*-**8a**: $C_{46}H_{40}N_2$, $M = 620.80$, monoclinic, space group $P2_1/c$, colorless, $a = 13.002(1)$ Å, $b = 18.459(2)$ Å, $c = 15.624(1)$ Å, $\beta = 103.267(2)°$, $V = 3649.7(6)$ Å^3, $Z = 4$, $D_c = 1.130$ g/cm^3, μ(Mo-Kα) = 0.65 cm^{-1}, $T = 293$ K, 8186 unique data with $R_{int} = 0.0509$. Final $R_1 = 0.0538$, w$R_2 = 0.1427$ for 4978 reflections with $I > 2\sigma(I)$, $GOF = 1.010$. CCDC number 750094.

Tetraacetylene 8b. The same procedure was repeated as described for **8a** except that 0.27 g (1.5 mmol) of **7b** was treated with a mixture of **6** (0.50 g, 0.75 mmol), $Pd(PPh_3)_2Cl_2$ (0.028 g, 0.040 mmol), and CuI (0.0043 g, 0.023 mmol) in 50 mL of triethylamine. Purification by flash column chromatography (silica gel/CH_2Cl_2:MeOH =19:1, R_f = 0.52) furnished 0.49 g of **8b** (0.65 mmol, 86%, 1:1 mixture of the *meso* and *rac* isomers) as a yellow solid: mp 189−192 °C; IR 2210, 1739, 1217, 752 cm^{-1}; ^1H NMR (mixture of the *meso* and *rac* isomers, $CDCl_3$, 600 MHz) δ 8.76−8.66 (4 H, m), 8.50−8.43 (4 H, m), 7.89 (1 H, t, J = 7.2 Hz), 7.83 (1 H, t, J = 7.2 Hz), 7.81−7.77 (2 H, m), 7.54−7.51 (3 H, m), 7.48−7.46 (1 H, m), 7.39−7.34 (2 H, m), 7.32 and 7.31 (4 H, two singlets), 7.28−7.24 (4 H, m), 3.71 and 3.66 (2 H, two singlets), 1.01 (18 H, s); ^{13}C NMR (mixture of the *meso* and *rac* isomers, $CDCl_3$, 150 MHz) δ 154.3, 152.9, 151.7, 151.6, 147.9, 139.74, 139.72, 138.3, 137.54, 137.46, 132.29, 132.23, 132.19, 132.15, 128.99, 128.97, 128.53, 128.47, 127.4, 126.64, 126.59, 124.71, 124.67, 124.2, 122.1, 121.0, 96.29, 96.27, 93.38, 93.33, 89.3, 82.3, 82.1, 50.2, 35.51, 35.50, 27.8; MS *m/z* 775 (MH^+), 718; HRMS *m/z* calcd for $C_{56}H_{47}N_4$ (MH^+) 775.3795, found 775.3789.

Tetraacetylene 8c. The same procedure was repeated as described for **8a** except that 0.26 g (1.0 mmol) of **7c** was treated with a mixture of **6** (0.32 g, 0.48 mmol), $Pd(PPh_3)_2Cl_2$ (0.015 g, 0.021 mmol), and CuI (0.005 g, 0.026 mmol) in 50 mL of triethylamine. Purification by flash column chromatography (silica gel/CH_2Cl_2:MeOH = 9:1, R_f = 0.43) furnished 0.34 g of **8c** (0.37 mmol, 77%, 1:1 mixture of the *meso* and *rac* isomers) as a yellow solid: mp 251−253 °C; IR 2220, 1738, 1583, 1390, 788 cm^{-1}; ^1H NMR (mixture of the *meso* and *rac* isomers, $CDCl_3$, 600 MHz) δ 8.72 (4 H, d, J = 3.6 Hz), 8.60 (4 H, d, J = 8.4 Hz), 8.59 (4 H, s), 7.86 (4 H, t, J = 7.8 Hz), 7.54 (2 H, m), 7.43 (2 H, m), 7.34 (4 H, t, J = 6.3 Hz), 7.32 (4 H, s), 7.27−7.22 (4 H, m), 3.64 (2 H, s), 1.01 (18 H, s); ^{13}C NMR (mixture of the *meso* and *rac* isomers, $CDCl_3$, 150 MHz) δ 155.3, 155.2, 148.9, 137.3, 137.2, 133.4, 132.4, 132.2, 129.0, 128.6, 127.3, 126.8, 124.7, 124.0, 123.2, 121.4, 96.5, 93.2, 90.6, 82.1, 50.2, 35.5, 27.7; MS *m/z* 929 (MH^+), 872, 815; HRMS *m/z* calcd for $C_{66}H_{53}N_6$ (MH^+) 929.4326, found 929.4319.

4,5-Diheteroarylphenanthrene 2a. To 0.28 g (0.45 mmol) of **8a** in 30 mL of anhydrous toluene under a nitrogen atmosphere was added 1.0 mL of a 1.0 M solution of potassium *tert*-butoxide (1.0 mmol) in 2-methyl-2-propanol. The reaction mixture was then heated under reflux for 6 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 120 mL of dichloromethane were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. Flash column chromatograph (silica gel/CH_2Cl_2:MeOH =19:1, R_f = 0.33) provided 0.16 g (0.26 mmol, 58%) of **2a** as a yellow solid: mp >350 °C; IR 1594, 830, 741 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 8.33 (4 H, d, J = 5.4 Hz), 7.89 (2 H, s), 7.45 (2 H, d, J = 7.8 Hz), 7.13 (2 H, t, J = 7.5 Hz), 6.80 (2 H, t, J = 7.5 Hz), 6.63 (4 H, d, J = 6.0 Hz), 6.30 (2 H, d, J = 8.4 Hz), 4.45 (2 H, d, J = 21.0 Hz), 4.19 (2 H, d, J = 21.0 Hz), 1.83 (18 H, s); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 149.2, 147.3, 144.4, 141.4, 140.2, 139.8, 136.8, 132.1, 131.8, 130.2, 127.4 (br), 127.0, 125.7, 124.1, 122.6, 122.3, 39.7, 38.0, 33.3; HRMS *m/z* calcd for $C_{46}H_{41}N_2$ (MH^+) 621.3264, found 621.3263. Recrystallization of **2a** from CH_2Cl_2/MeOH produced a crystal suitable for X-ray structure analysis.

4,5-Diheteroarylphenanthrene 2b. To 0.26 g (0.33 mmol) of **8b** in 30 mL of anhydrous toluene under a nitrogen atmosphere was added 0.7 mL of a 1.0 M solution of potassium *tert*-butoxide (0.7 mmol) in 2-methyl-2-propanol. The reaction mixture was then heated under reflux for 6 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 120 mL of dichloromethane were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. Flash column chromatograph (silica gel/CH_2Cl_2:MeOH =19:1, R_f =

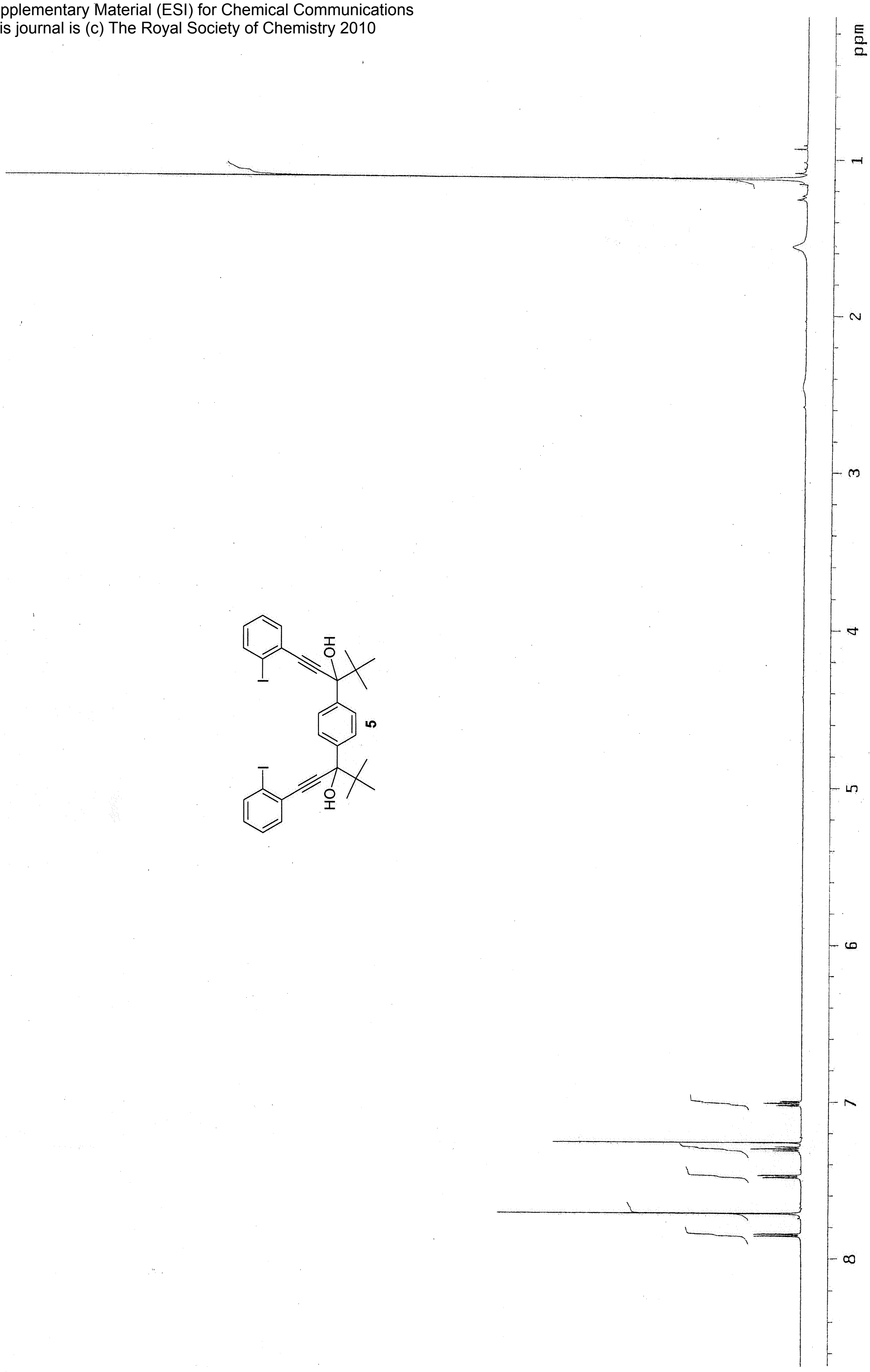
0.4) provided 0.14 g (0.17 mmol, 53%) of **2b** as a yellow solid: mp >350 °C; IR 1707, 1458, 746 cm^{-1}; ^{1}H NMR (CDCl$_3$, 600 MHz) δ 8.70 (2 H, d, *J* = 3.6 Hz), 8.47 (2 H, br s), 8.20 (2 H, br s), 7.93 (2 H, s), 7.89 (4 H, br s), 7.40 (2 H, d, *J* = 7.2 Hz), 7.35 (2 H, t, *J* = 5.4 Hz), 7.06–7.02 (4 H, m), 6.72 (2 H, t, *J* = 7.8 Hz), 6.29 (2 H, d, *J* = 7.8 Hz), 4.43 (2 H, d, *J* = 21.0 Hz), 4.19 (2 H, d, *J* = 21.0 Hz), 1.85 (18 H, s); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 155.6, 148.6, 144.4, 141.1, 140.2, 137.8, 137.5, 135.7, 132.2, 131.0, 130.3, 126.7, 125.9, 124.1, 123.8, 122.5, 122.4, 122.0, 121.2, 39.9, 38.0, 33.4; MS *m/z* 775 (MH$^+$), 760; HRMS *m/z* calcd for $C_{56}H_{47}N_4$ (MH$^+$) 775.3795, found 775.3788.

4,5-Diheteroarylphenanthrene 2c. To 0.32 g (0.34 mmol) of **8c** in 30 mL of anhydrous toluene under a nitrogen atmosphere was added 0.7 mL of a 1.0 M solution of potassium *tert*-butoxide (0.7 mmol) in 2-methyl-2-propanol. The reaction mixture was then heated under reflux for 6 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 120 mL of dichloromethane were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. Flash column chromatograph (silica gel/CH$_2$Cl$_2$:MeOH = 9:1, R_f = 0.32) provided 0.15 g (0.16 mmol, 48%) of **2c** as a yellow solid: mp >350 °C; IR 1583, 1565, 1466, 793, 735 cm^{-1}; ^{1}H NMR (CDCl$_3$, 60 °C, 600 MHz) δ 8.44 (4 H, br), 8.40 (4 H, br), 7.91 (4 H, br), 7.90 (2 H, s), 7.68 (4 H, br), 7.32 (2 H, d, *J* = 7.2 Hz), 7.10 (4 H, br), 6.97 (2 H, t, *J* = 7.2 Hz), 6.70 (2 H, d, *J* = 7.8 Hz), 6.59 (2 H, t, *J* = 7.5 Hz), 4.18 (2 H, d, *J* = 21.0 Hz), 4.13 (2 H, d, *J* = 21.0 Hz), 1.88 (18 H, s); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 155 (very br), 148.4 (br), 148.2 (br), 144.4, 141.0 (br), 140.0, 137 (very br), 136.5, 132.5 (very br), 132.0, 126.6, 126.0 (br), 125.8, 123.9, 123.3 (br), 122.3, 122.2, 121.1 (br), 39.6, 38.1, 33.3; HRMS *m/z* calcd for $C_{66}H_{53}N_6$ (MH$^+$) 929.4325, found 929.4319. Recrystallization of **2c** from CH$_2$Cl$_2$/MeOH produced a crystal suitable for X-ray structure analysis. The crystal lattice was also found to contain two molecules of CH_2Cl_2.

[Cl_3Ru(2c)RuCl_3] (10). To a suspension of 0.066 g of $RuCl_3 \cdot 3H_2O$ (0.25 mmol) and 15 mL of ethanol was added 0.110 g of **2c** (0.118 mmol). The reaction mixture was heated to reflux for 16 h before it was allowed to cool to room temperature. The dark brown precipitate was collected by filtration, washed thoroughly with methanol, water, and diethyl ether, and dried in vacuo to yield 0.146 g of **10** (92%) as a dark brown solid: mp >350 °C; IR 1599, 1469, 790, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 14.40 (2 H, s), 14.28 (2 H, s), 13.82 (2 H, s), 10.17 (2 H, s), 7.75 (2 H, d, J = 21.0 Hz), 7.26 (2 H, s), 4.83 (2 H, d, J = 21.0 Hz), 4.51 (2 H, s), 1.24 (2 H, s), 0.59 (18 H, s), −1.53 (2 H, s), −2.75 (2 H, s), −3.64 (2 H, s), −7.02 (2 H, s), −9.35 (2 H, s), −9.80 (2 H, s), −32.35 (2 H, s), −35.56 (2 H, s); HRMS *m/z* calcd for $C_{66}H_{52}Cl_6N_6Ru_2$ (M^+) 1342.0471, found 1342.0531.

[(4′-EtOtpy)Ru(2c)Ru(4′-EtOtpy)](PF_6)$_4$ (13). A mixture of **10** (0.084 g, 0.062 mmol), 4′-EtOtpy (0.035 g, 0.126 mmol), and *N*-ethylmorpholine (0.043 g, 0.37 mmol) in 7 mL of methanol was heated under reflux for 1 h before it was allowed to cool to room temperature. The mixture was filtered and the filtrate was treated with an excess of NH_4PF_6 (0.10 g, 0.62 mmol) in 10 mL of methanol to give a brown precipitate. The brown precipitate was collected by filtration, washed with water, methanol, and diethyl ether, and dried in vacuo to produce 0.102 g (0.045 mmol, 73%) of **13** as a brown solid. The ^1H NMR spectrum of the brown solid showed the presence of a small amount of the homoleptic species [Ru(4′-EtOtpy)$_2$](PF_6)$_2$. The brown solid was further purified by flash column chromatography (silica gel/acetonitrile:saturated aqueous potassium nitrate:water = 7:1:0.5, R_f = 0.48). The main brown band was collected followed by the addition of excess NH_4PF_6. The solution was further concentrated in *vacuo* to induce precipitation. The precipitate was collected and washed with a small amount of methanol, dried in *vacuo*, to produce a more homogeneous sample of **13** as a light brown solid: mp >350 °C; IR 1615, 1213, 826, 787 cm^{-1}; ^{1}H NMR (CD$_3$CN, 600 MHz) δ 8.48 (4 H, br s), 8.33 (2 H, s), 8.31 (4 H, s), 7.82 (4 H, br s), 7.64 (2 H, d, *J* =7.2 Hz), 7.39 (2 H, td, *J* = 7.2, 1.2 Hz), 7.33 (2 H, d, *J* = 8.4 Hz), 7.15 (4 H, br s), 7.02 (2 H, t, *J* = 7.8 Hz), 4.61 (4 H, q, *J* = 7.2 Hz), 4.46 (2 H, d, *J* = 21.6 Hz), 4.30 (2 H, d, *J* = 21.6 Hz), 1.97 (18 H, s) 1.64 (6 H, t, *J* = 7.2 Hz); ^{13}C NMR (CD$_3$CN, 150 MHz) δ 167.7, 156.6, 153.9, 147.2, 145.9, 144.3, 142.8, 139.3, 138.9, 137.5, 134.3, 133.8, 131.3, 129.4, 128.9, 127.9, 126.6, 124.6, 122.6, 112.3, 67.2, 40.4, 39.3, 33.9, 14.8; HRMS *m/z* calcd for $C_{100}H_{82}F_{24}N_{12}O_2P_4Ru_2$ (M$^+$) 2266.3338, found 2266.3423.

[(4′-Cltpy)Ru(2c)Ru(4′-Cltpy)](PF$_6$)$_4$ (14). A mixture of **10** (0.025 g, 0.019 mmol), 4′-Cltpy (**12**) (0.010 g, 0.038 mmol), and *N*-ethylmorpholine (0.014 g, 0.12 mmol) in 5 mL of methanol was heated under reflux for 1 h before it was allowed to cool to room temperature. The mixture was filtered and the filtrate was treated with an excess of NH$_4$PF$_6$ (0.033 g, 0.20 mmol) in 10 mL of methanol to give a brown precipitate. The brown precipitate was collected by filtration, washed with water, methanol, and diethyl ether, and dried in vacuo to produce 0.028 g (0.013 mmol, 68%) of **14** as a brown solid: ^{1}H NMR (CD$_3$CN, 600 MHz) δ 8.87 (4 H, s), 8.50 (4 H, m), 8.34 (2 H, s), 7.9–7.85 (4 H, br), 7.65 (2 H, d, *J* = 7.8 Hz), 7.40 (2 H, t, *J* = 6.6 Hz), 7.36 (2 H, d, *J* = 8.4 Hz), 7.19 (4 H, t, *J* = 6.0 Hz), 7.04 (2 H, t, *J* = 7.2 Hz), 4.46 (2 H, d, *J* = 21.6 Hz), 4.30 (2 H, d, *J* = 21.6 Hz), 1.96 (18 H, s); HRMS *m/z* calcd for $C_{96}H_{72}Cl_2N_{12}Ru_2$ (M – 4 PF$_6$)$^+$ 1666.3467, found 1666.3552. The ^{1}HNMR spectrum showed that the sample contains minor amount of the homoleptic species [Ru(4′-Cltpy)$_2$](PF$_6$)$_2$.



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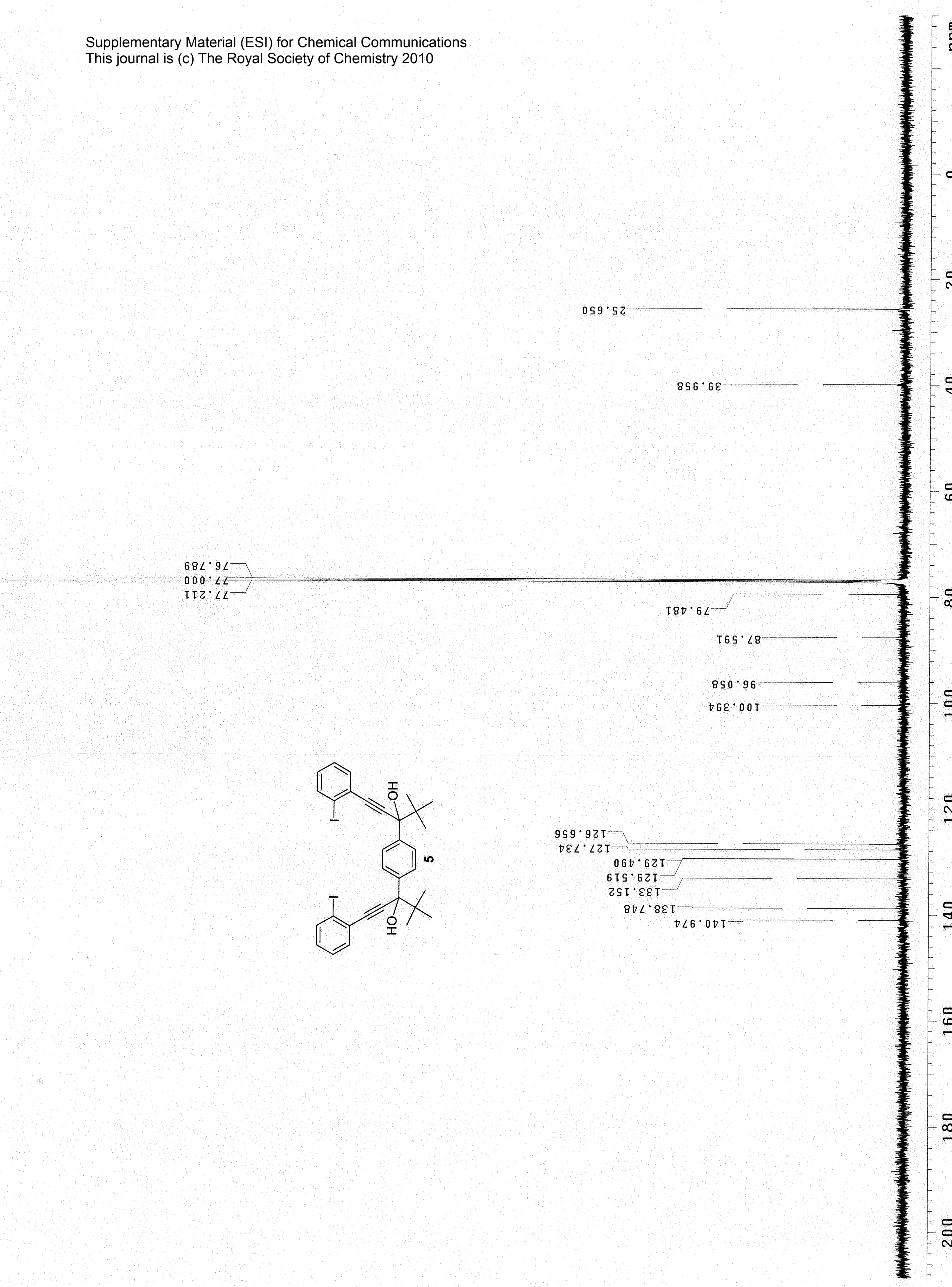
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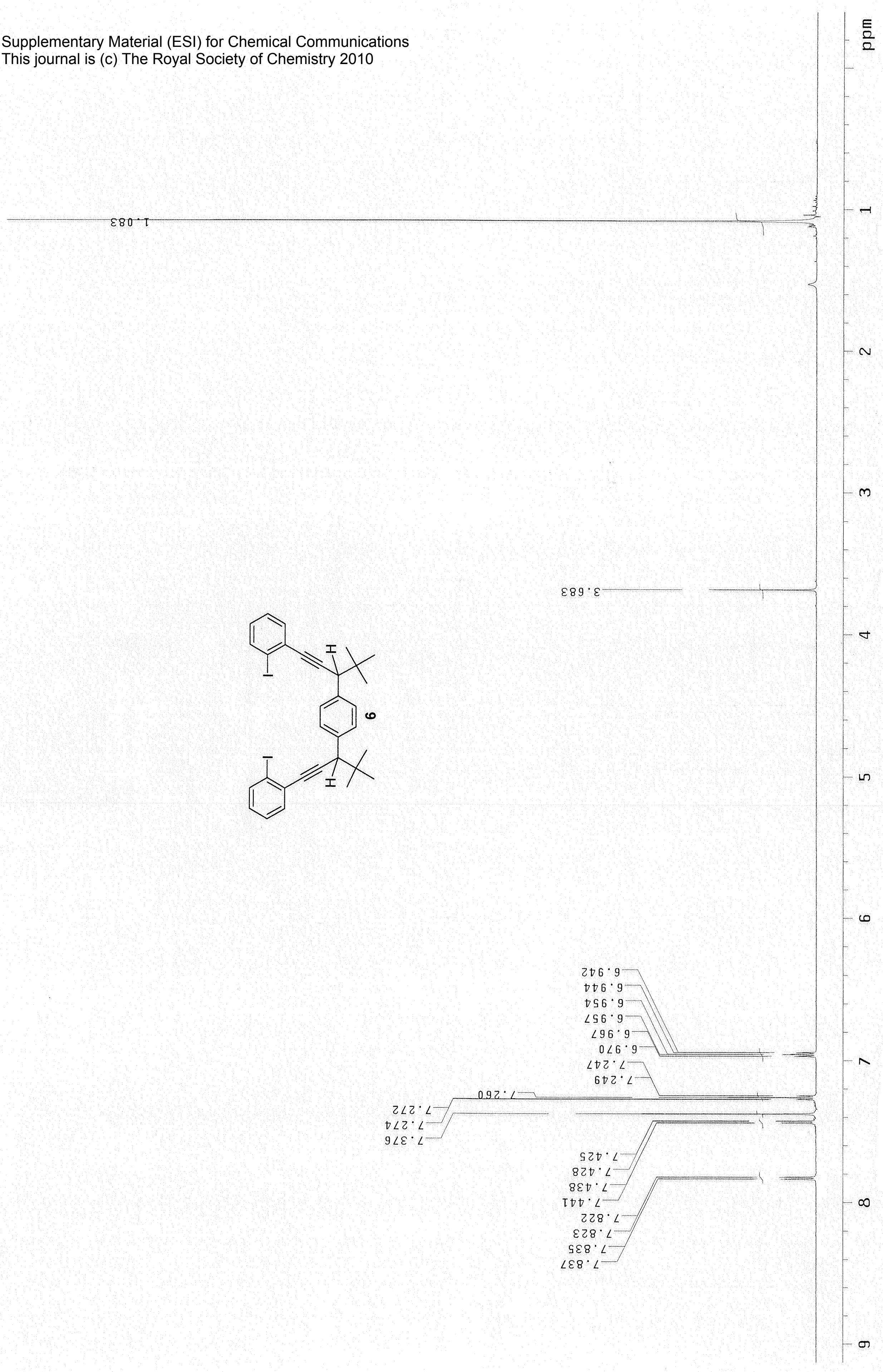
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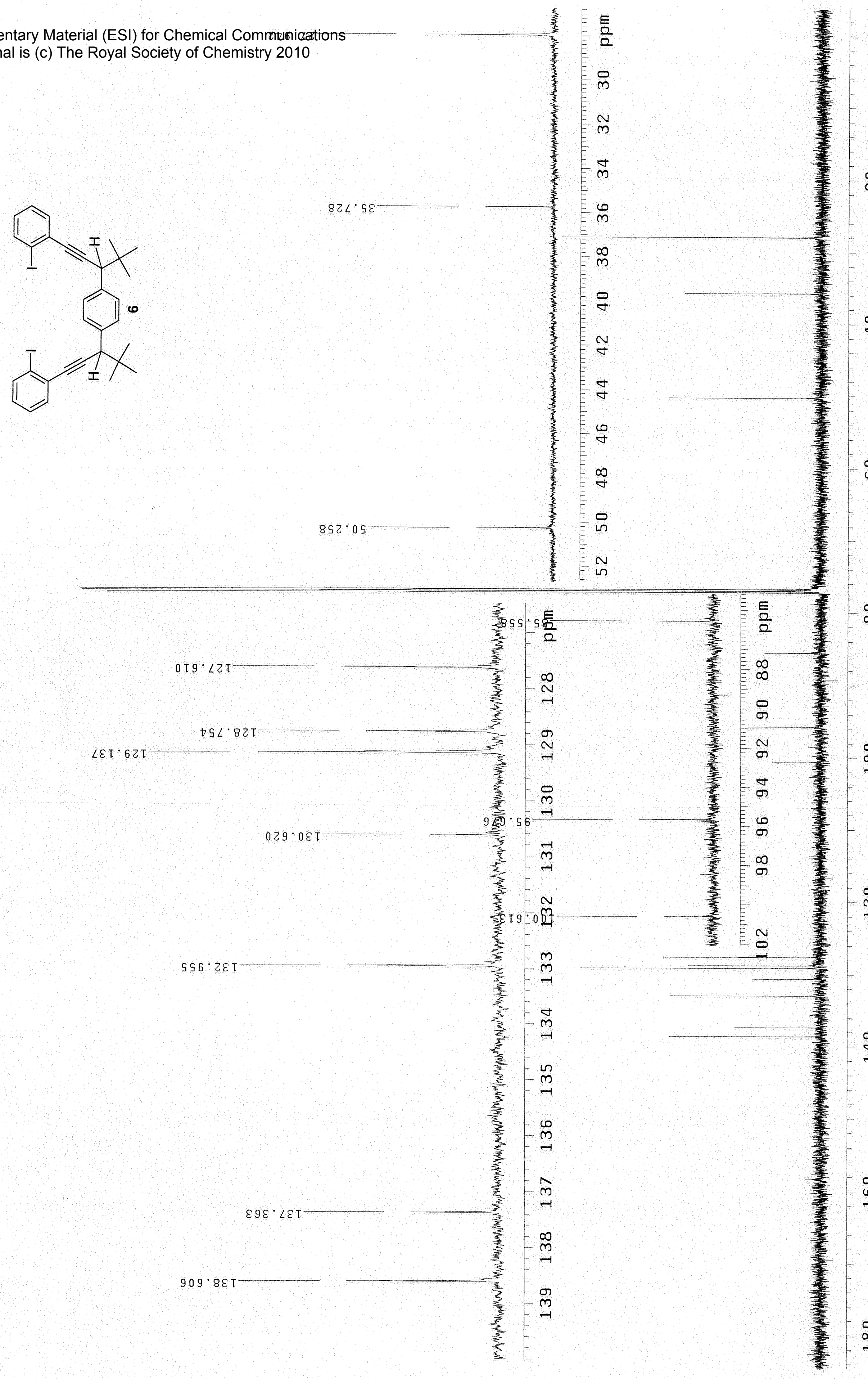
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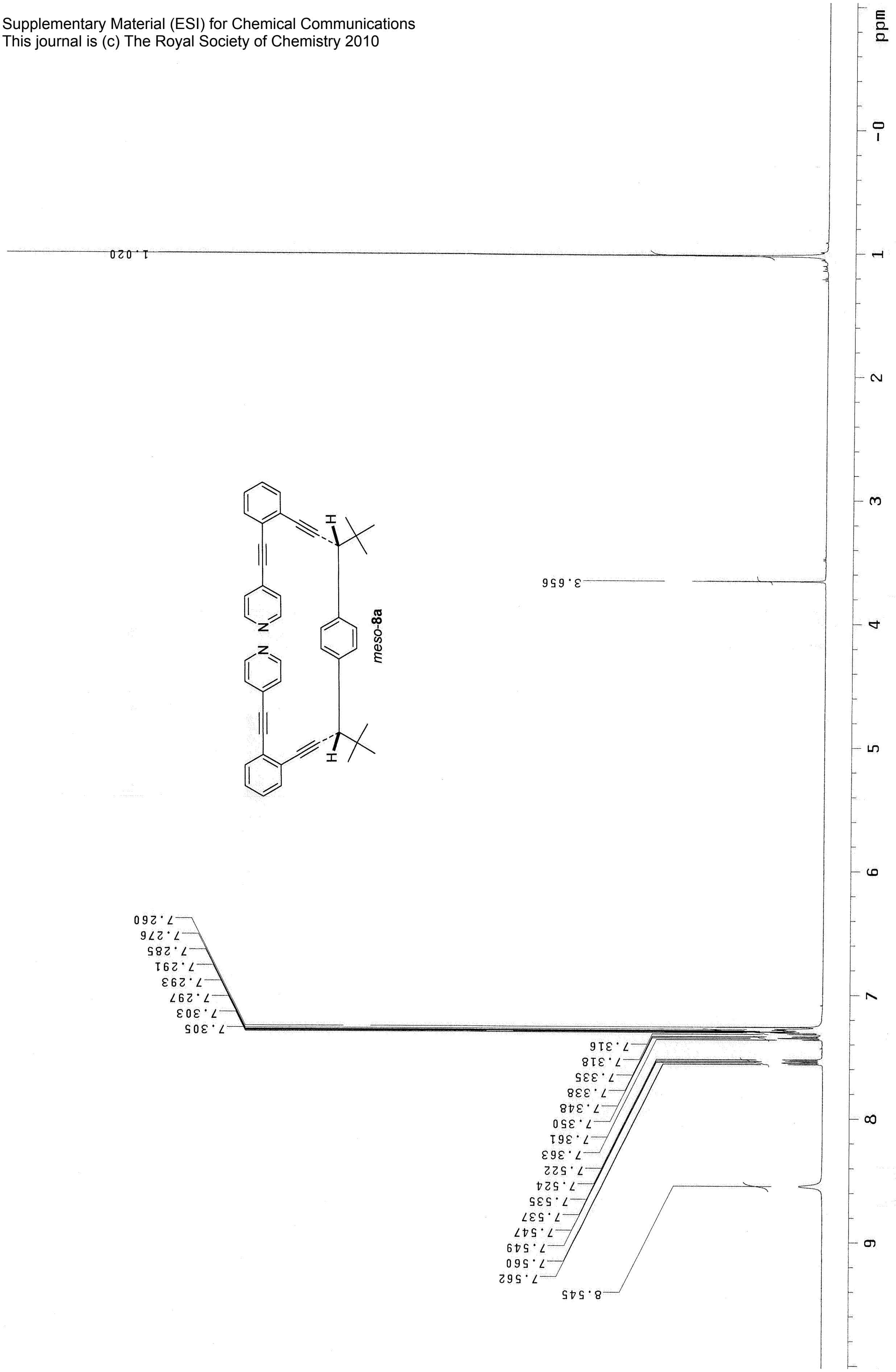
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2
3
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7
8
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1.020
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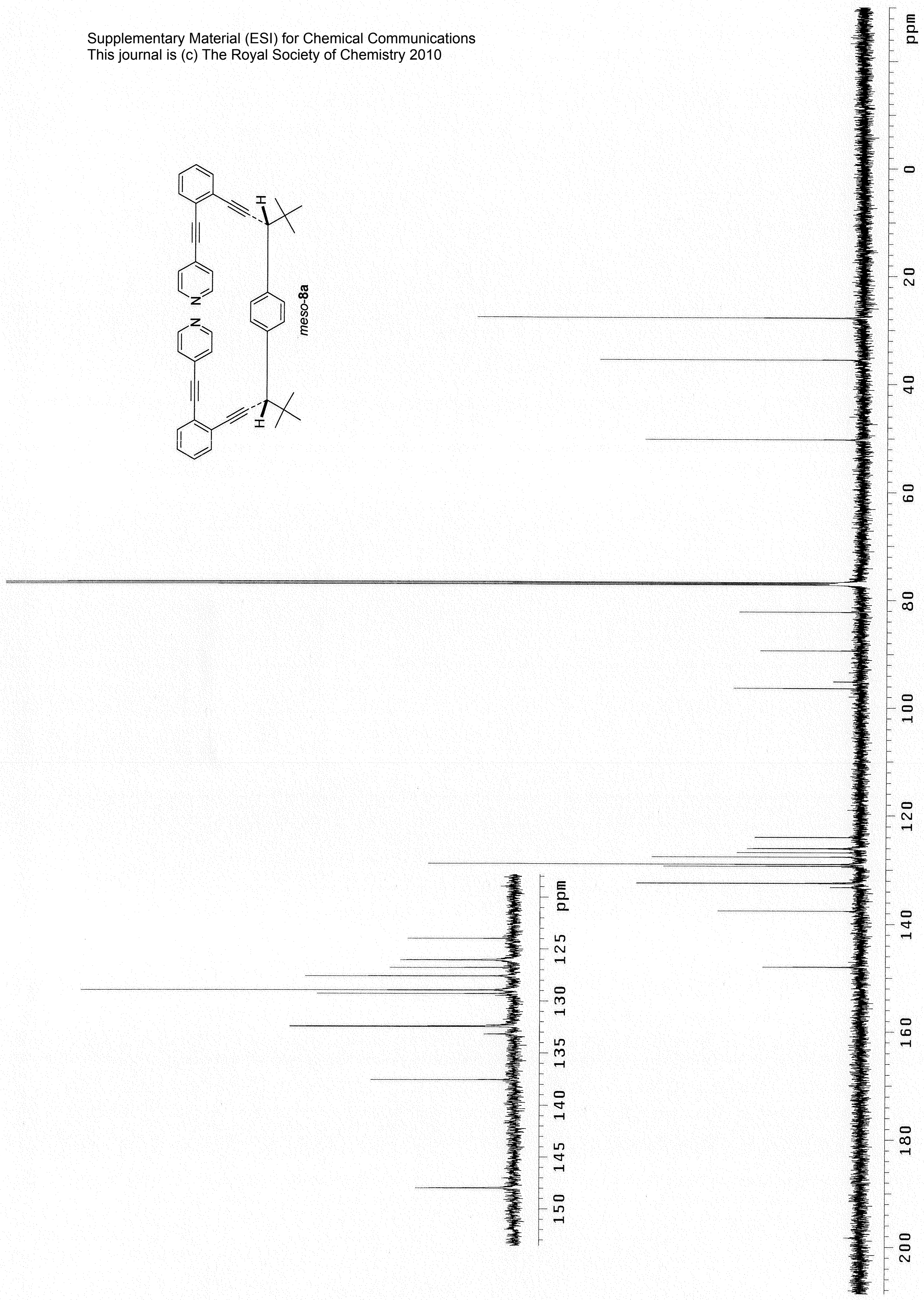
7.260
7.276
7.285
7.291
7.293
7.297
7.303
7.305
7.316
7.318
7.335
7.338
7.348
7.350
7.361
7.363
7.522
7.524
7.535
7.537
7.547
7.549
7.560
7.562
8.545
N
N
H
H
meso-8a



meso-**8a**

N
N
H
H
ppm
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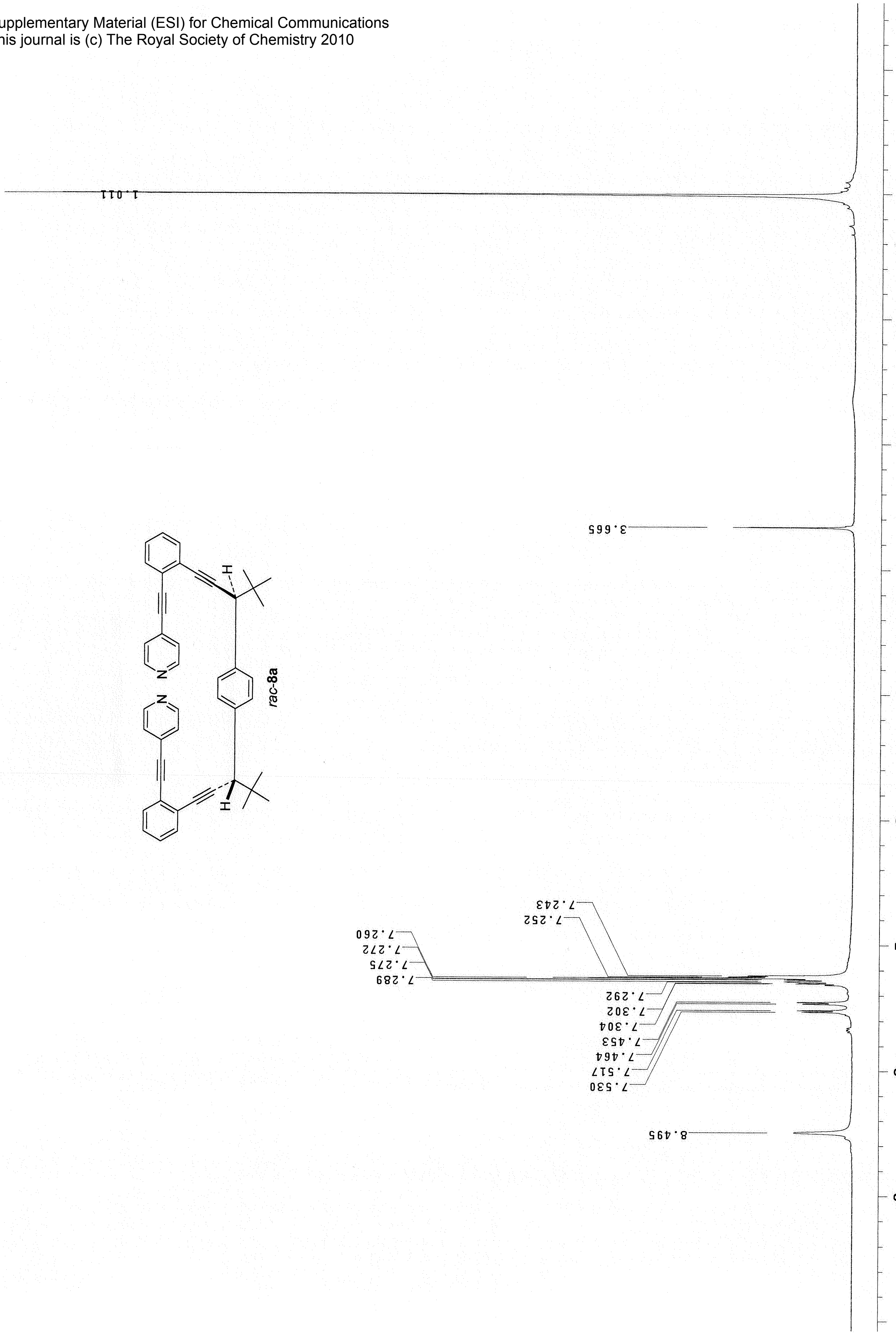
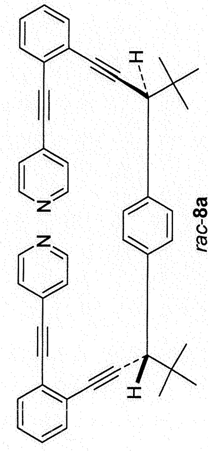
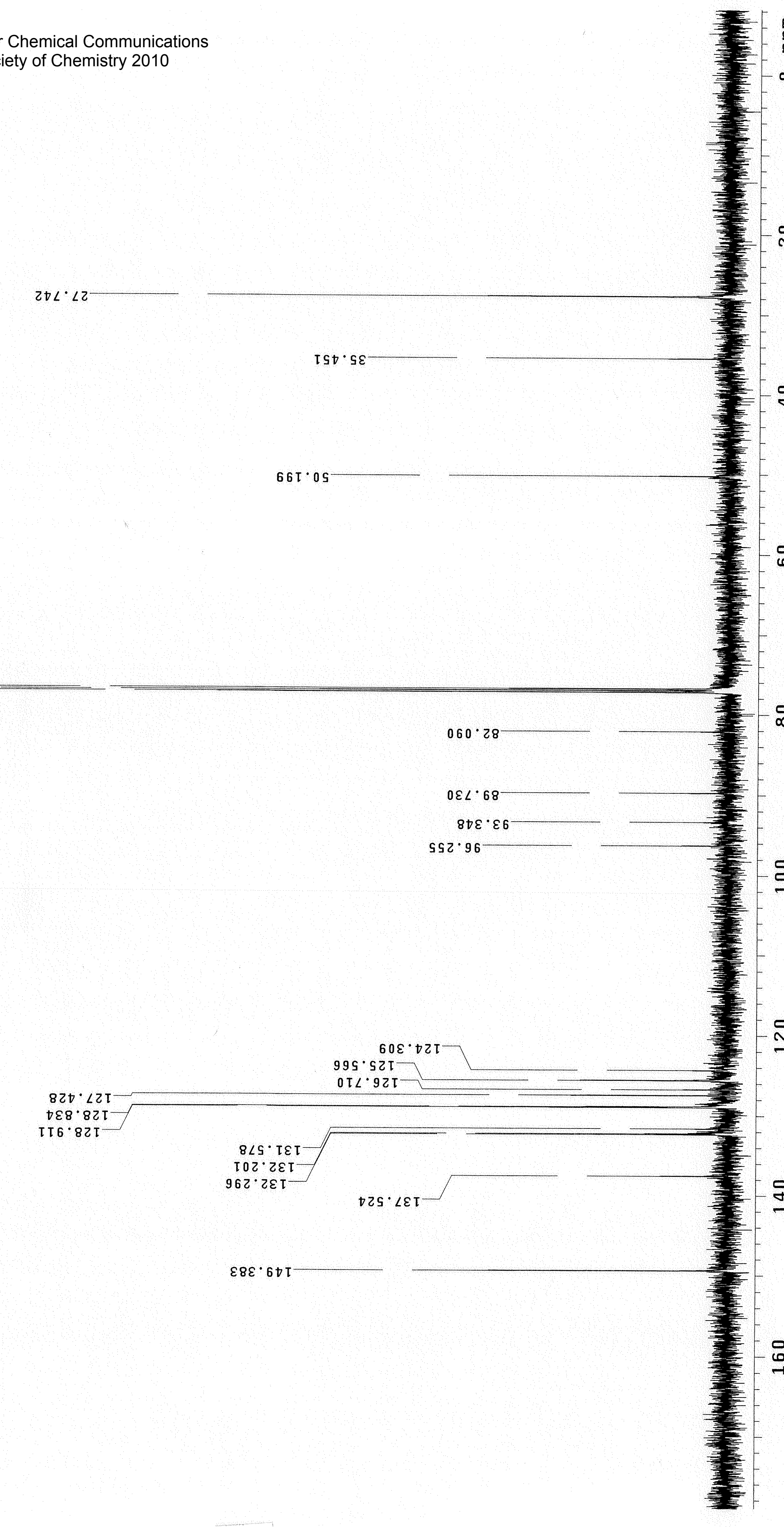
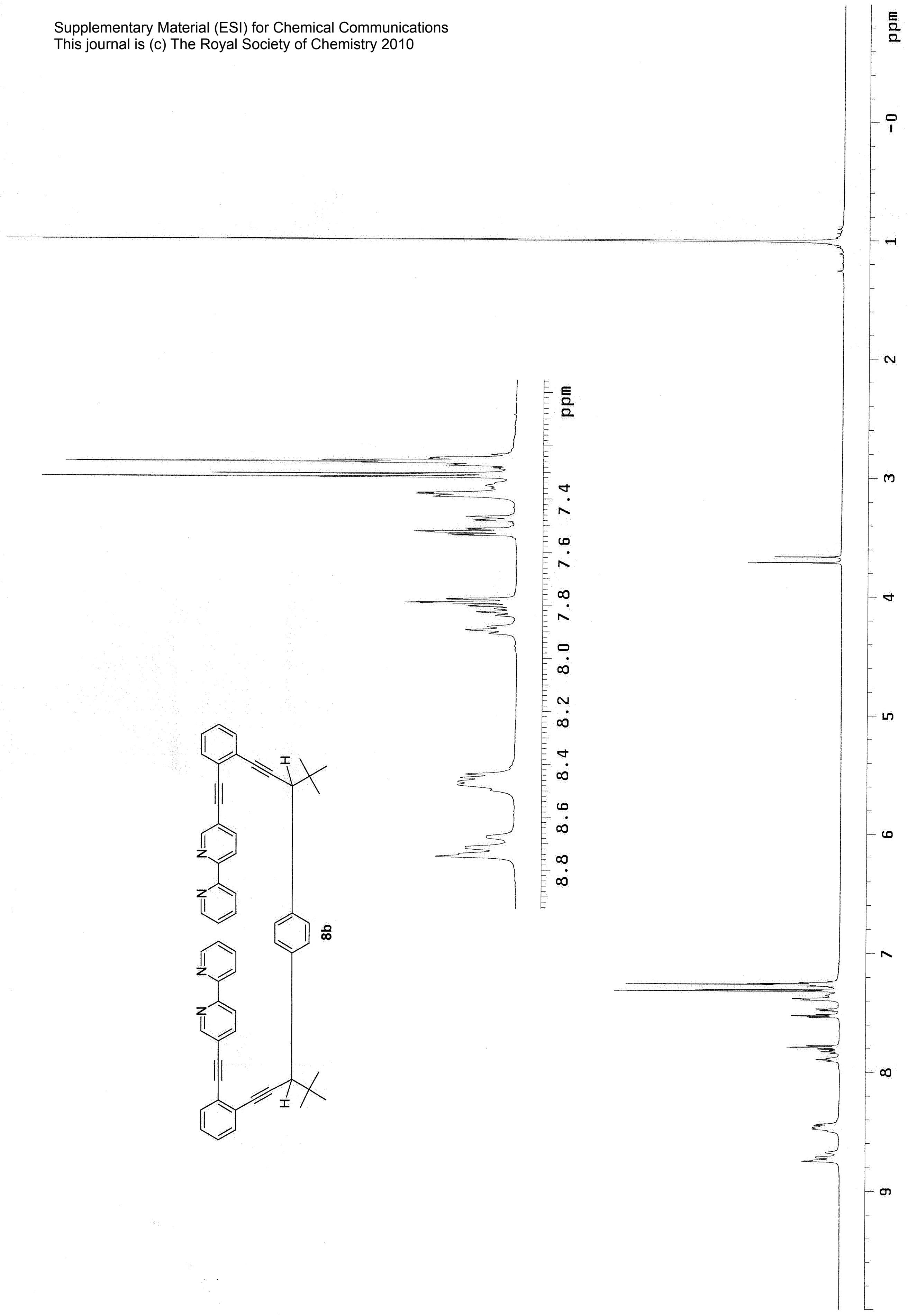
60
80
100
120
140
160
180
200
ppm
125
130
135
140
145
150


N
N
H
H
rac-8a
1.011
3.665
7.243
7.252
7.260
7.272
7.275
7.289
7.292
7.302
7.304
7.453
7.464
7.517
7.530
8.495
0
1
2
3
4
5
6
7
8
9
ppm

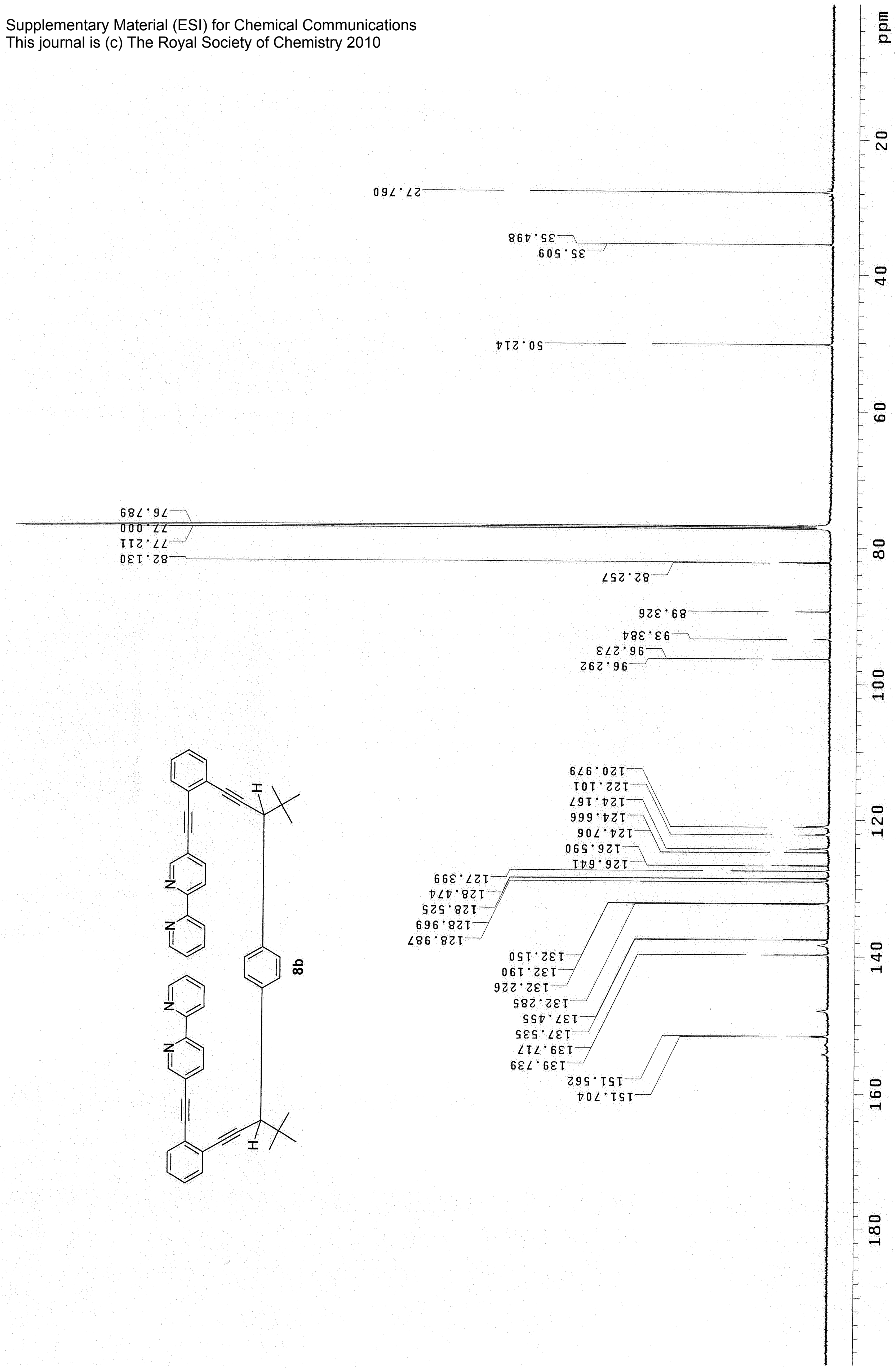

N
N
H
H

rac-8a


27.742
35.451
50.199
76.785
77.000
77.211
82.090
89.730
93.348
96.255
124.309
125.566
126.710
127.428
128.834
128.911
131.578
132.201
132.296
137.524
149.383
ppm
0
20
40
60
80
100
120
140
160



8b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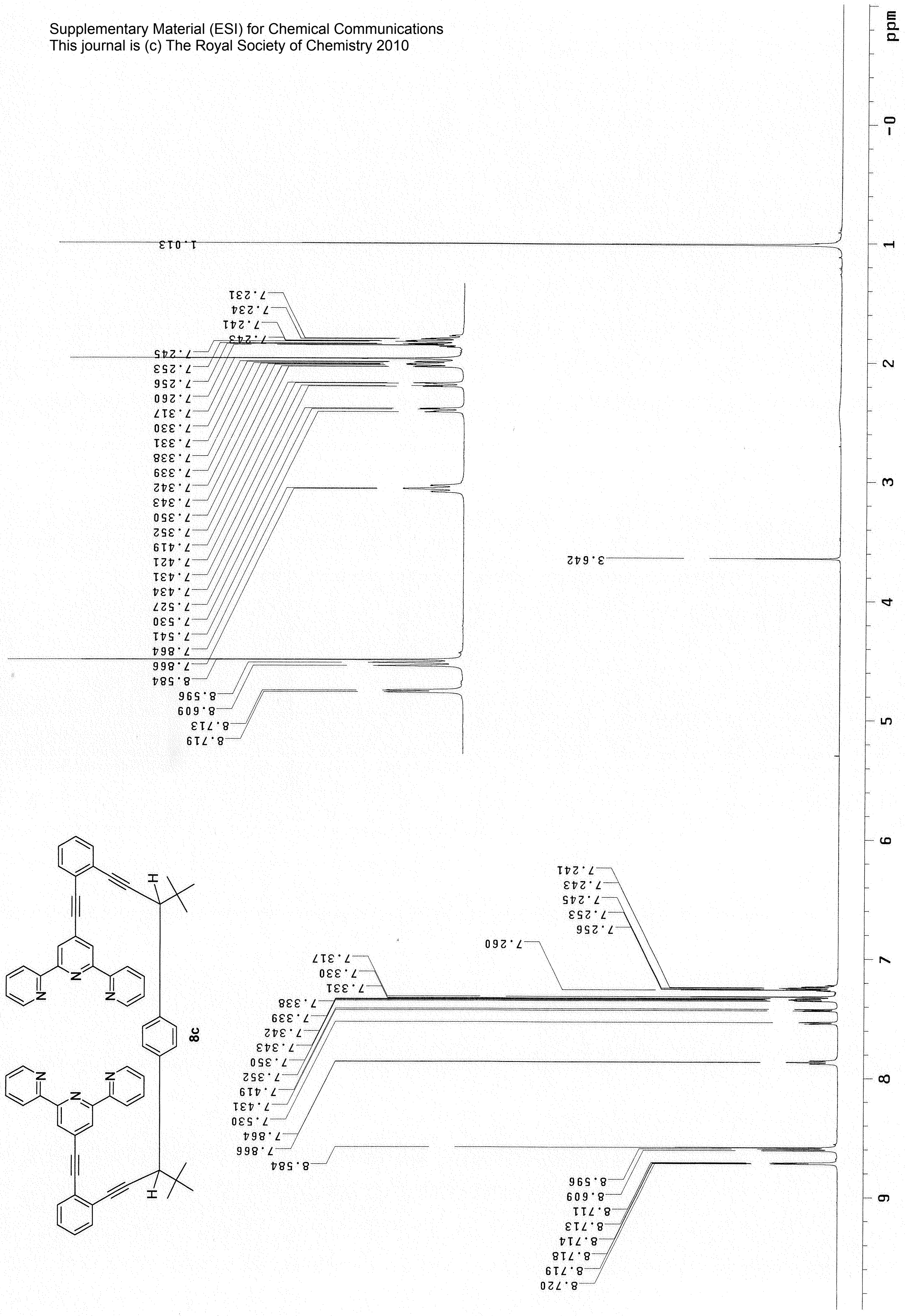
35.498
35.509
50.214
76.789
77.000
77.211
82.130
82.257
89.326
93.384
96.273
96.292
120.979
122.101
124.167
124.666
124.706
126.590
126.641
127.399
128.474
128.525
128.969
128.987
132.150
132.190
132.226
132.285
137.455
137.535
139.717
139.739
151.562
151.704
8b
ppm
20
40
60
80
100
120
140
160
180


ppm
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3
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5
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8
9
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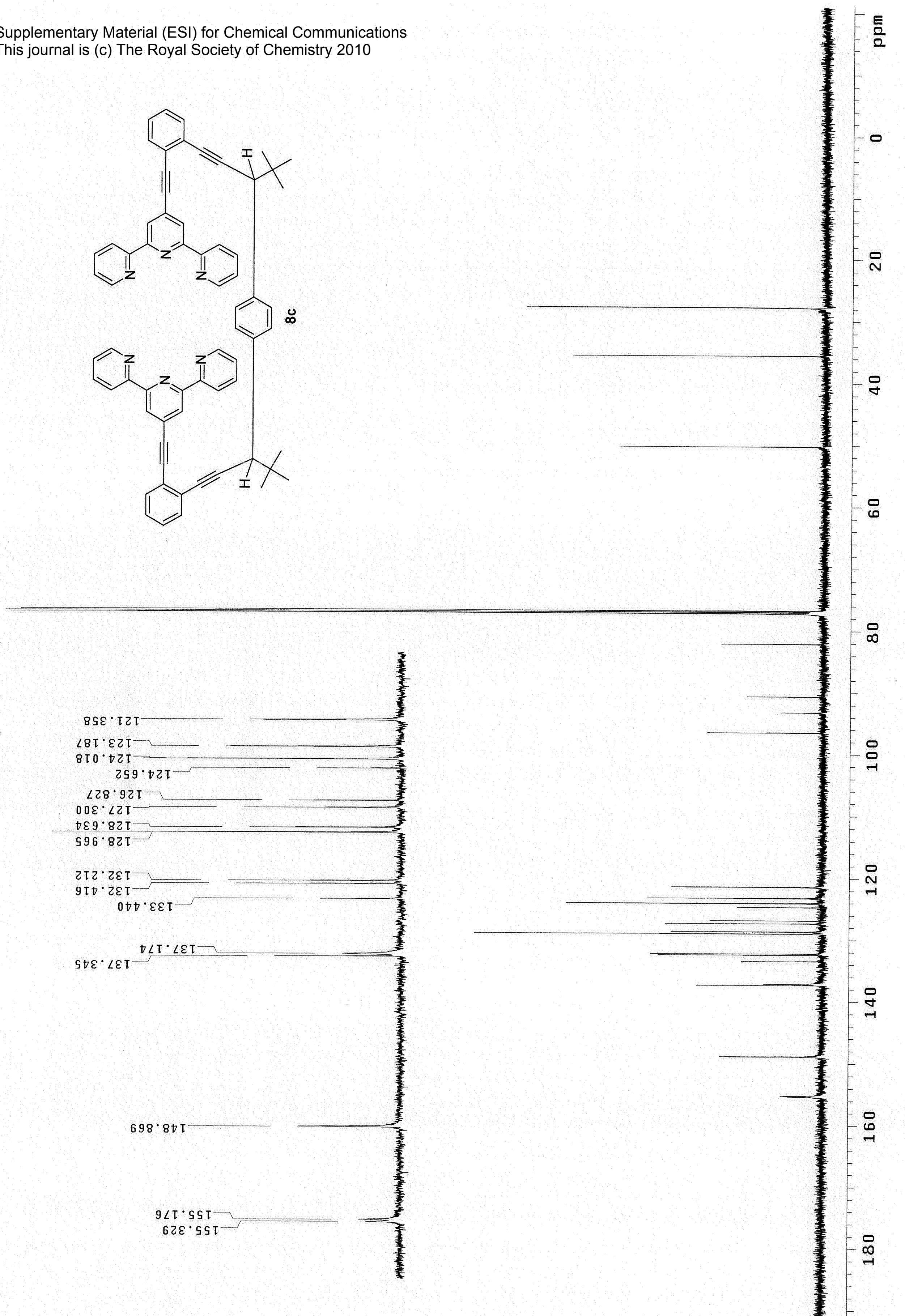
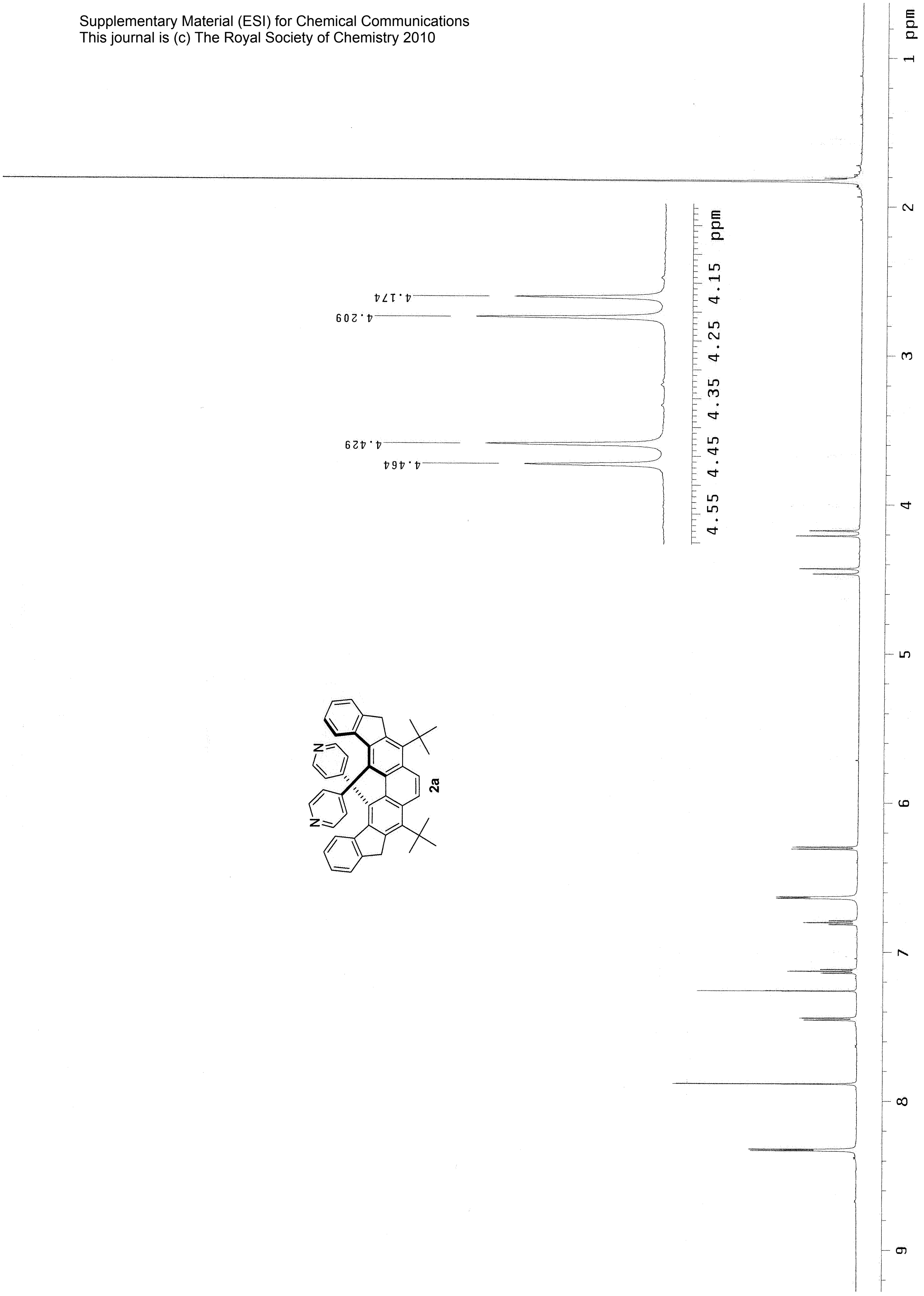
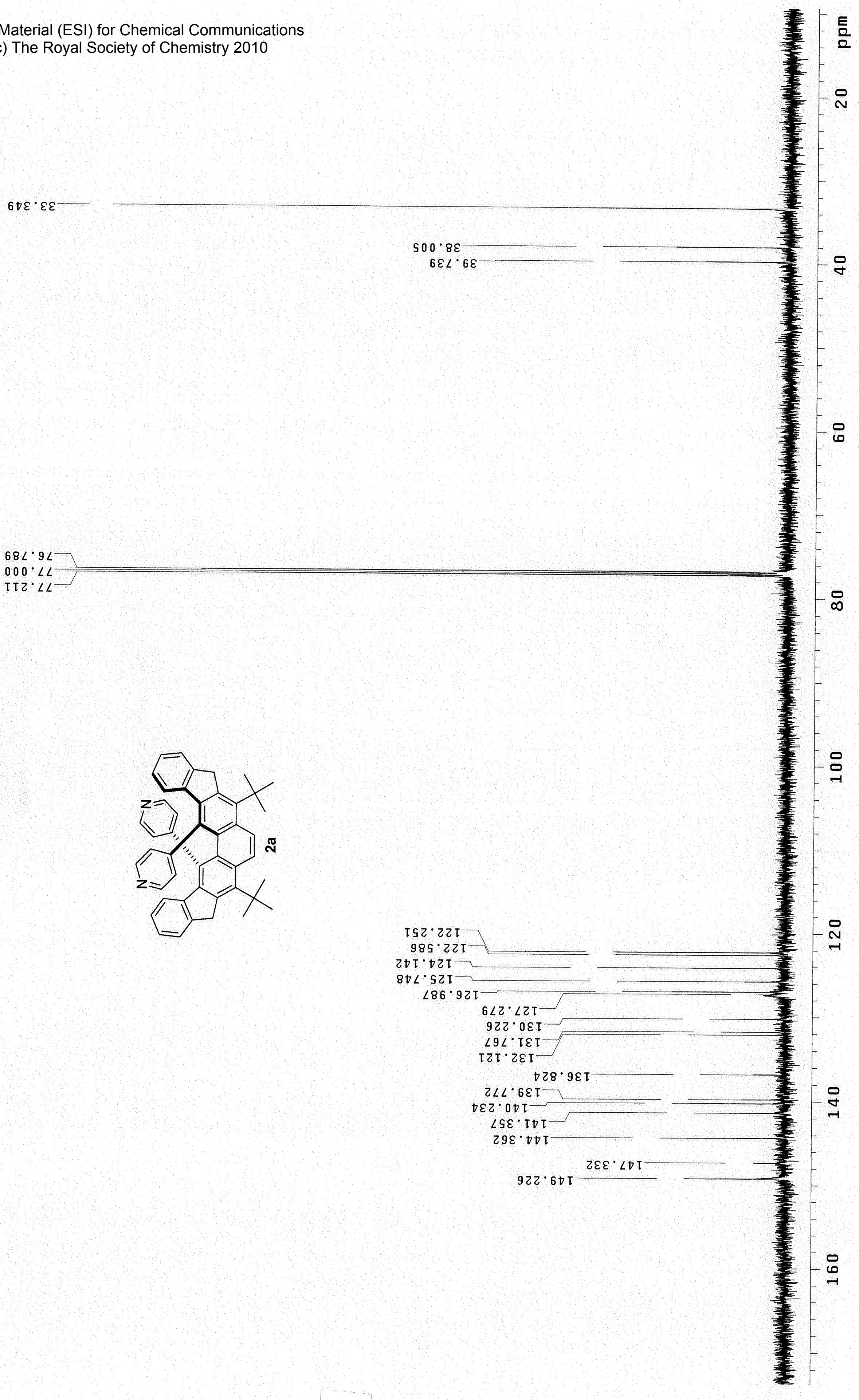
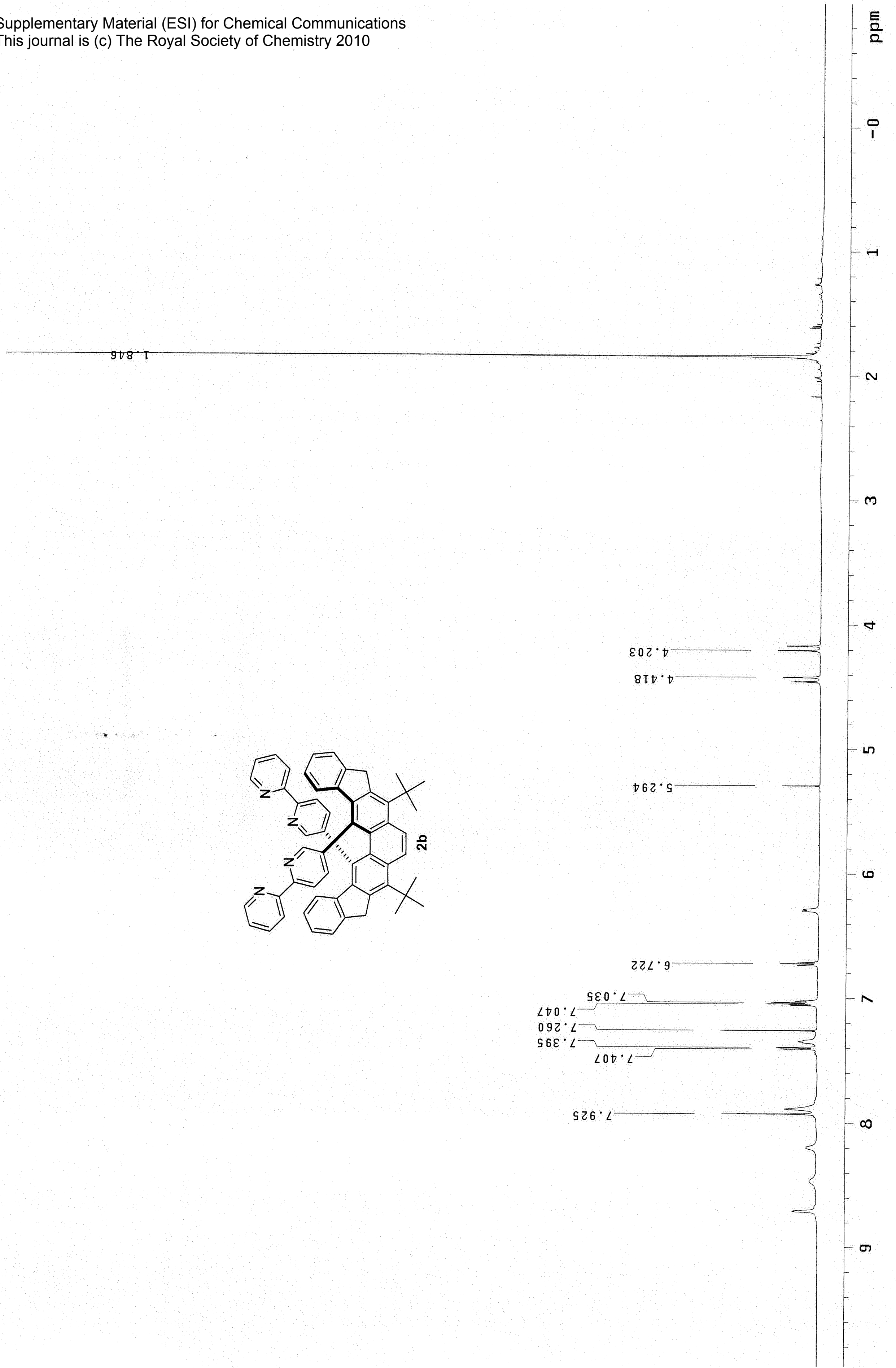
3.642
7.231
7.234
7.241
7.243
7.245
7.253
7.256
7.260
7.317
7.330
7.331
7.338
7.339
7.342
7.343
7.350
7.352
7.419
7.421
7.431
7.434
7.527
7.530
7.541
7.864
7.866
8.584
8.596
8.609
8.711
8.713
8.714
8.718
8.719
8.720
H
N
8c

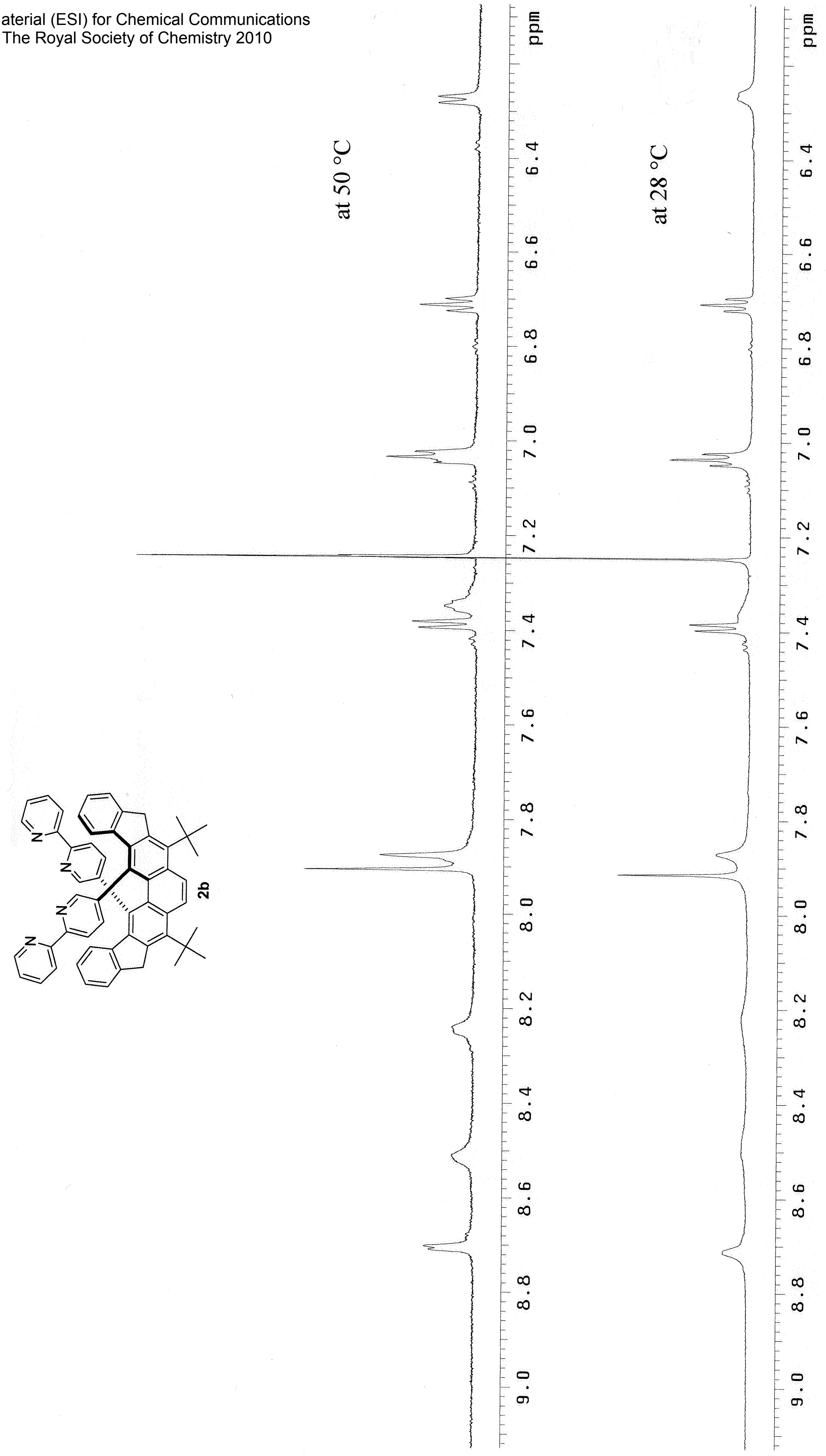

8c
N
N
N
N
N
N
H
H
121.358
123.187
124.018
124.652
126.827
127.300
128.634
128.965
132.212
132.416
133.440
137.174
137.345
148.869
155.176
155.329
ppm
0
20
40
60
80
100
120
140
160
180



2a


33.349
38.005
39.739
76.789
77.000
77.211
122.251
122.586
124.142
125.748
126.987
127.279
130.226
131.767
132.121
136.824
139.772
140.234
141.357
144.362
147.332
149.226
2a
N
N
ppm
20
40
60
80
100
120
140
160


1.846
4.203
4.418
5.294
6.722
7.035
7.047
7.260
7.395
7.407
7.925
2b
ppm
0
1
2
3
4
5
6
7
8
9


2b
N
N
N
N
at 50 °C
at 28 °C
ppm
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
9.0

Supplementary Material (ESI) for Chemical Communications
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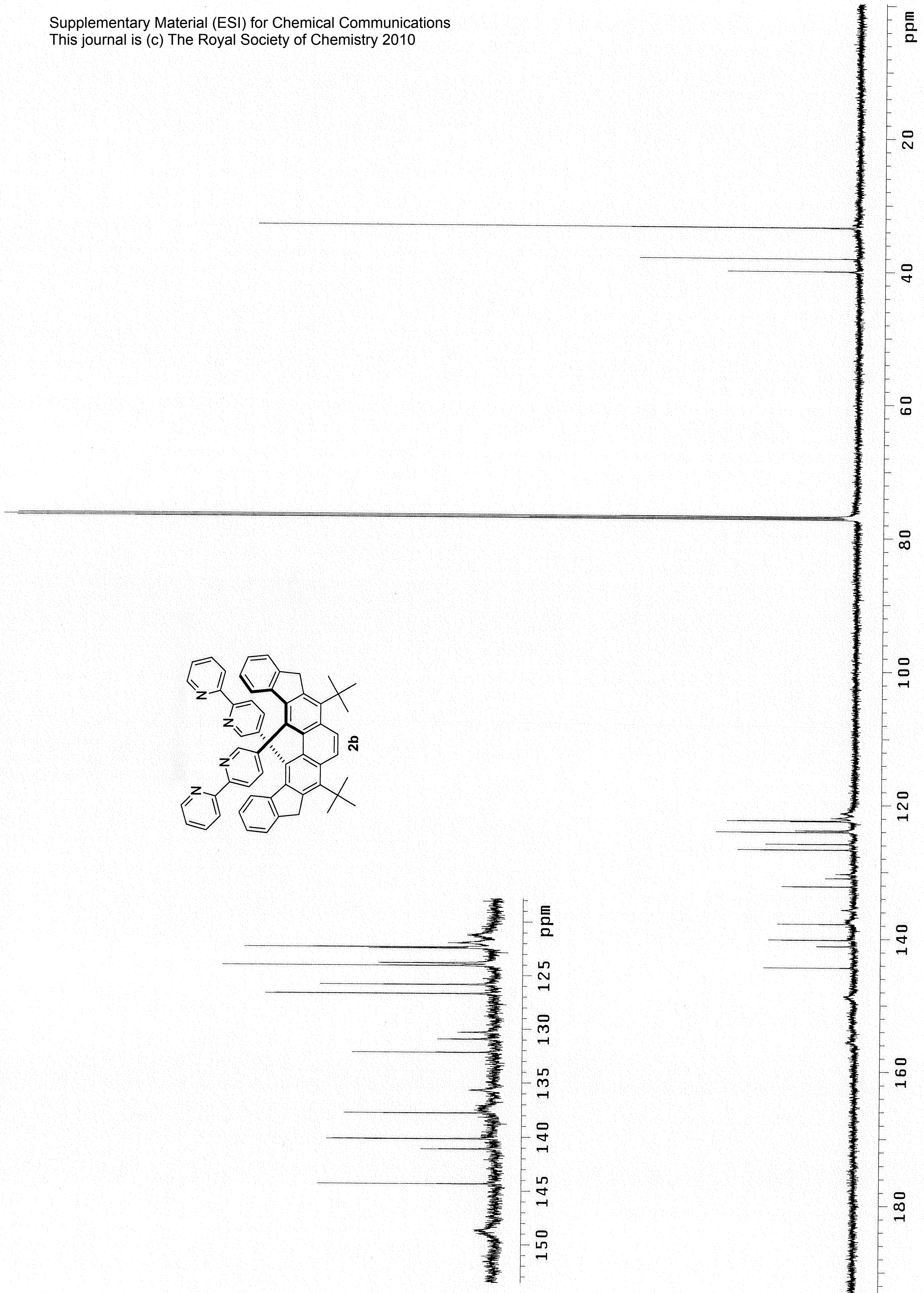
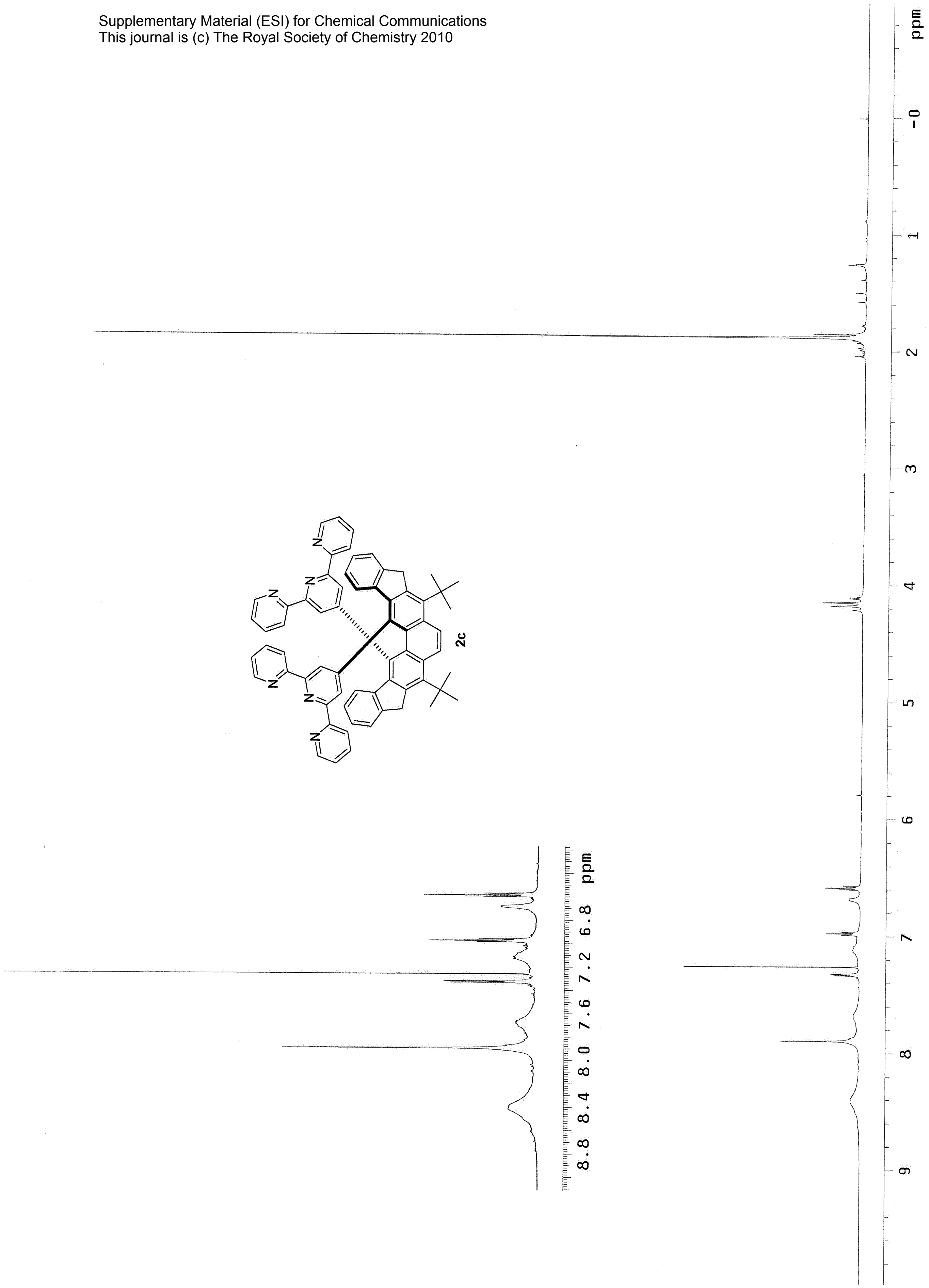
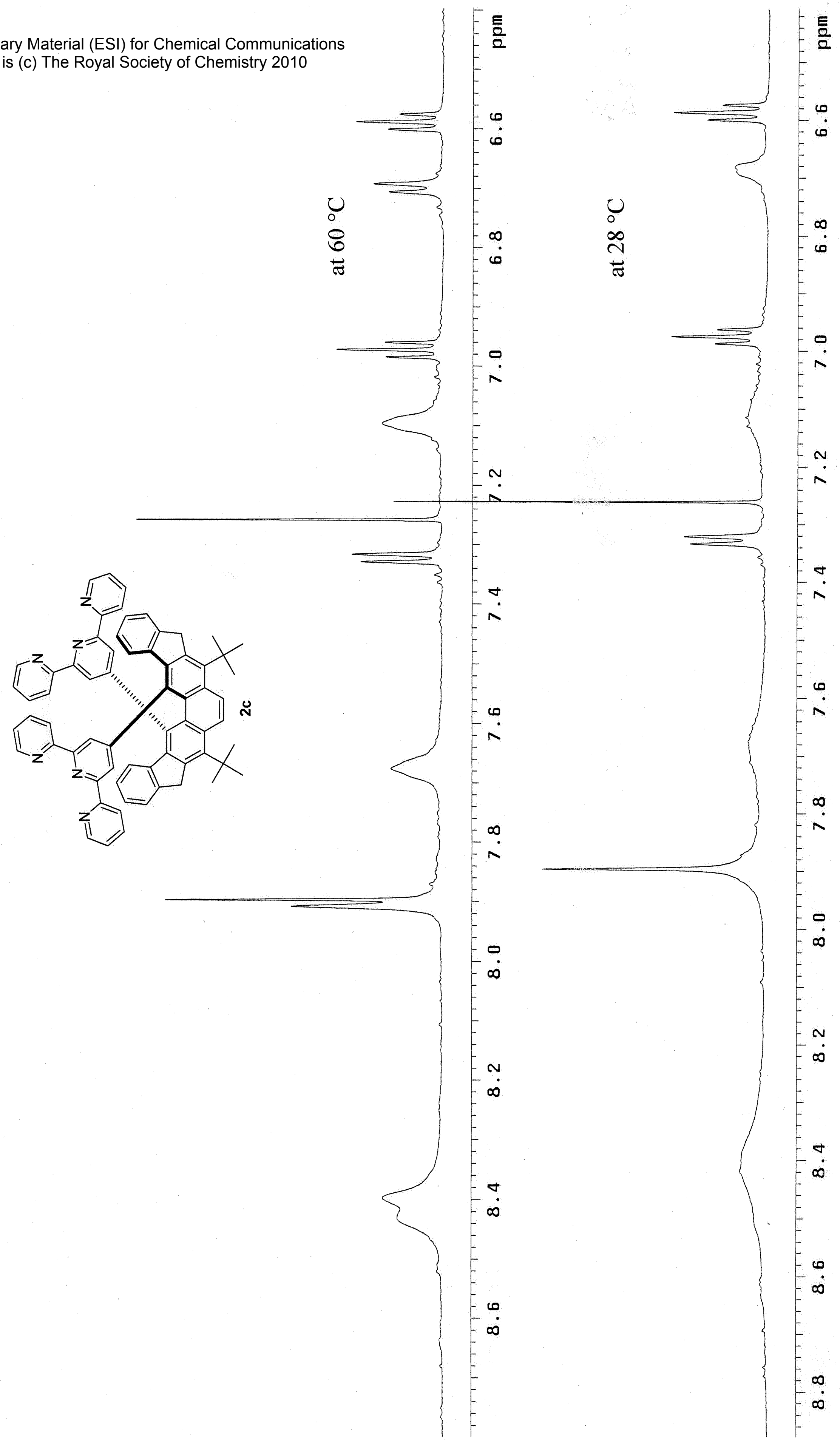
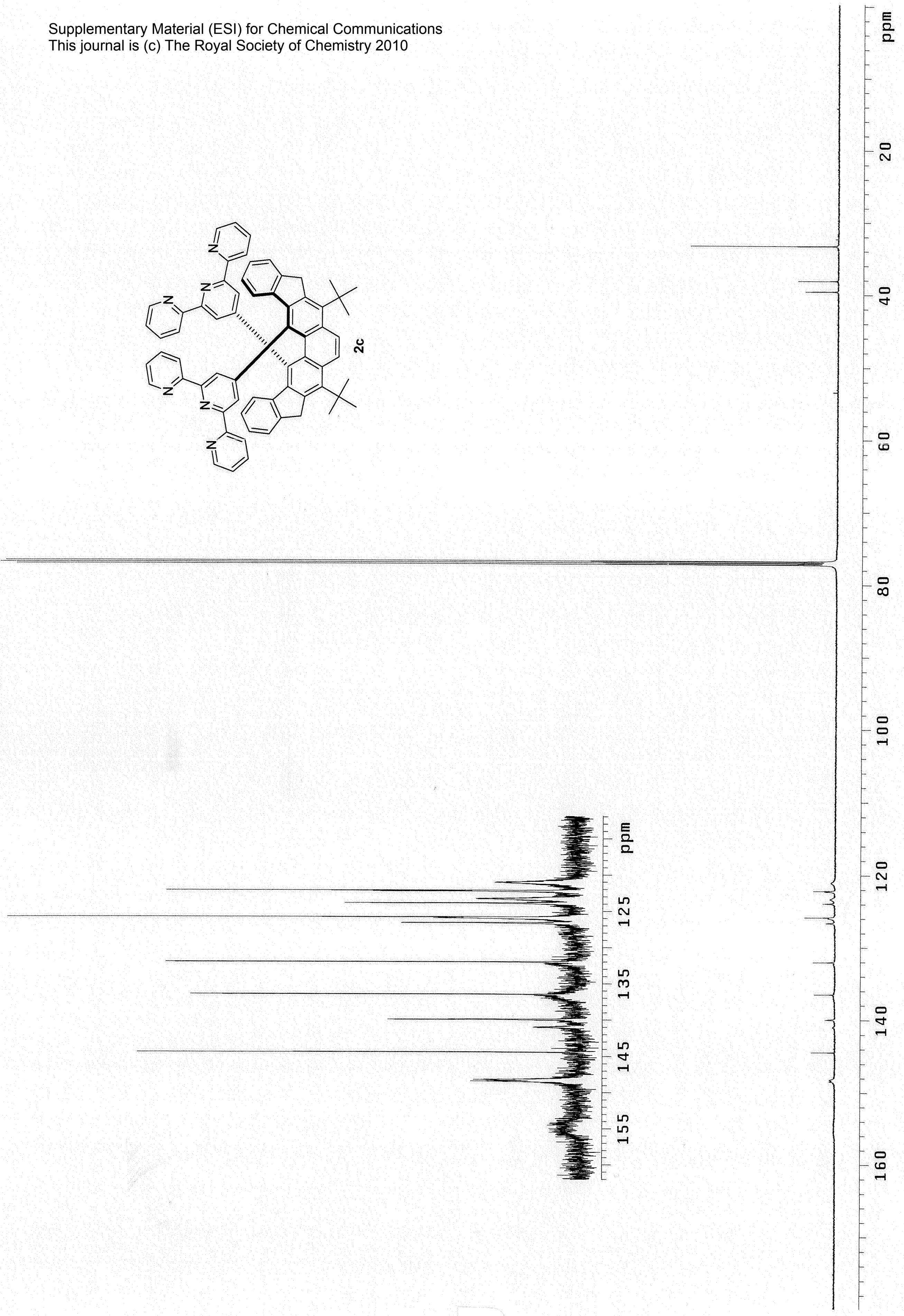


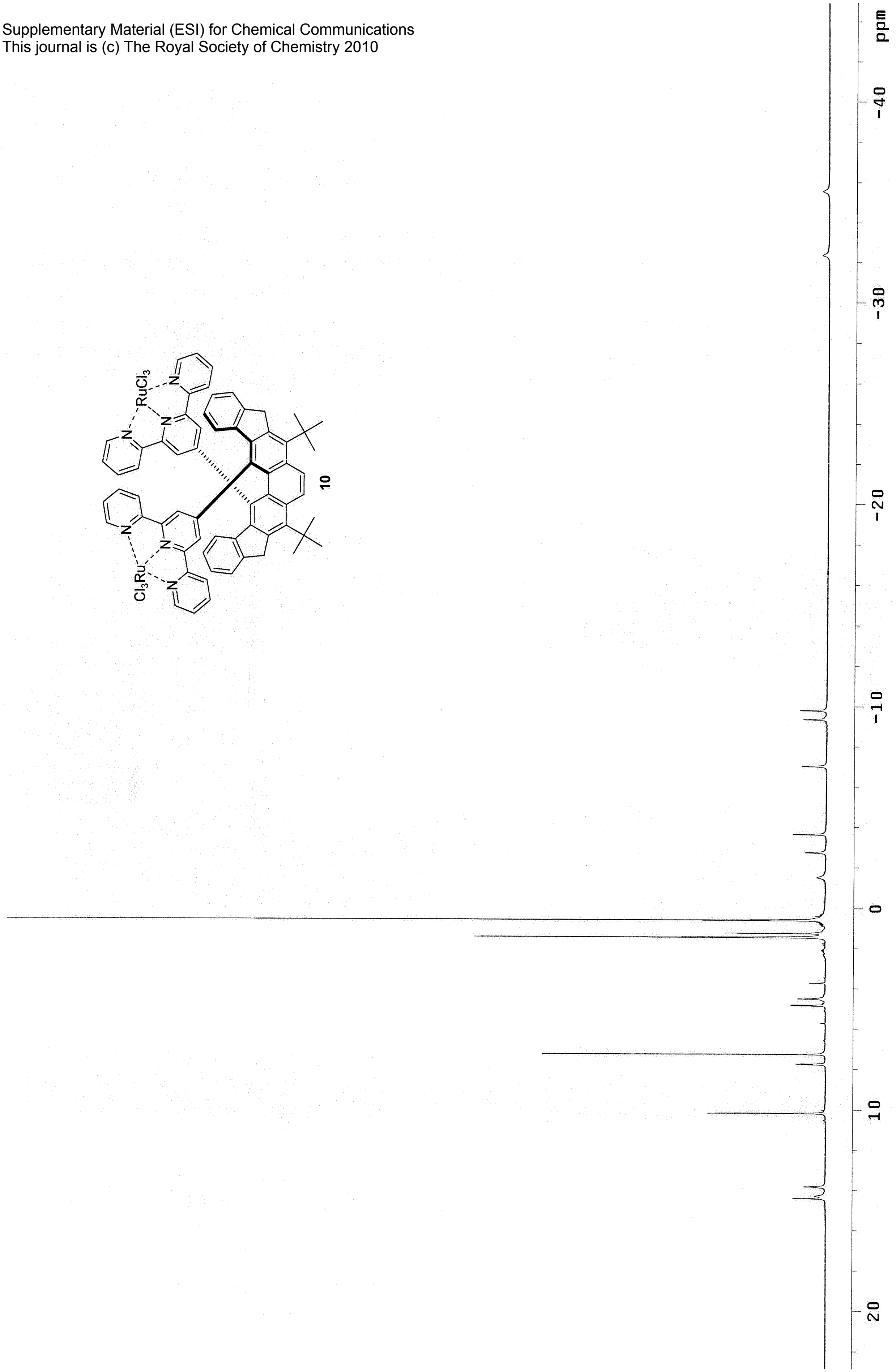
2b


2c
N
N
N
N
N
N
ppm
0
1
2
3
4
5
6
7
8
9
8.8 8.4 8.0 7.6 7.2 6.8 ppm

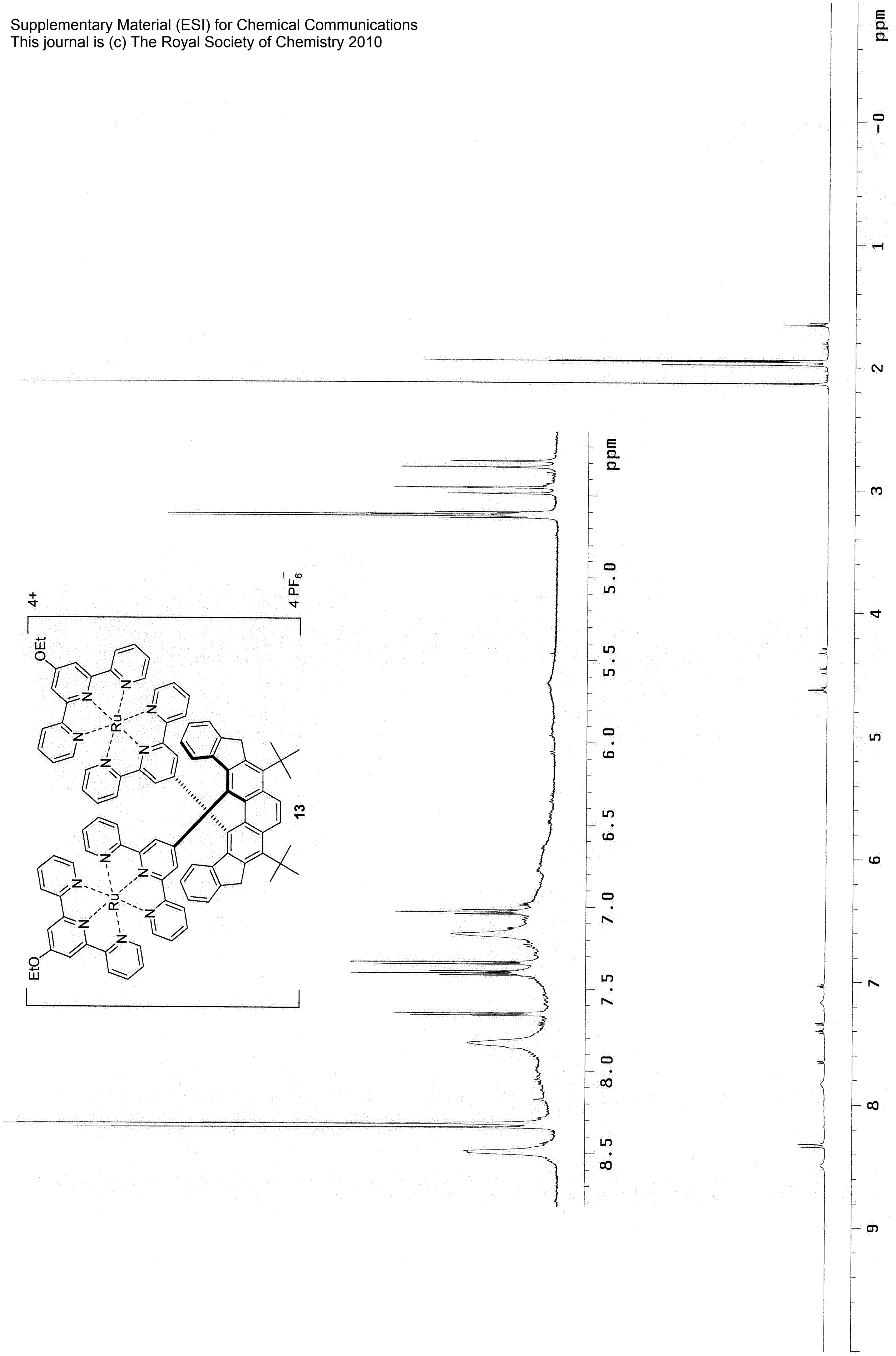

ppm
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
at 60 °C
at 28 °C
2c
N

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2010

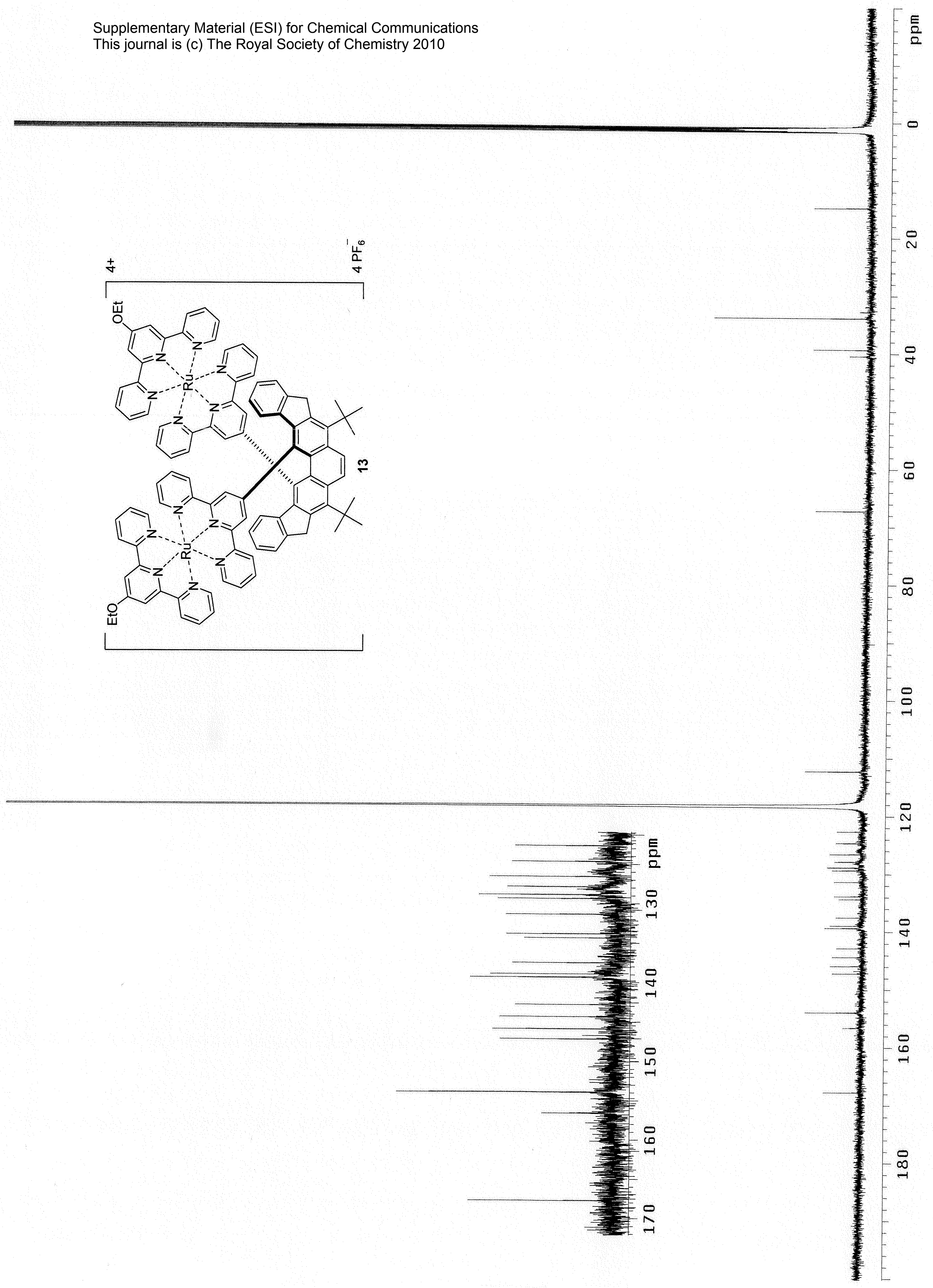

2c



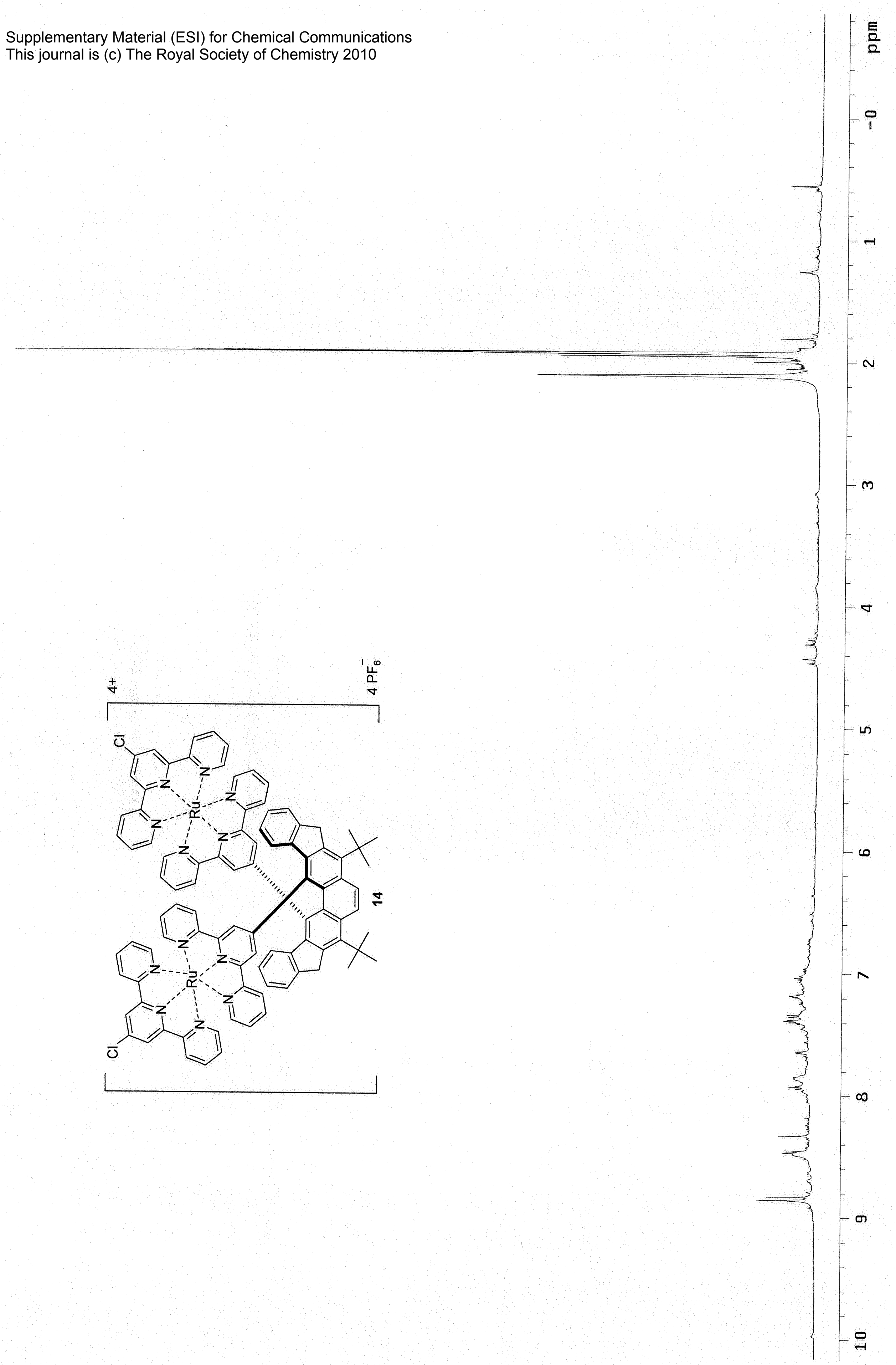
10



13


ppm
0
20
40
60
80
100
120
140
160
180
130
140
150
160
170
ppm
EtO
OEt
4+
4 PF$_6^-$
Ru
N

13



14

CCDC 750093

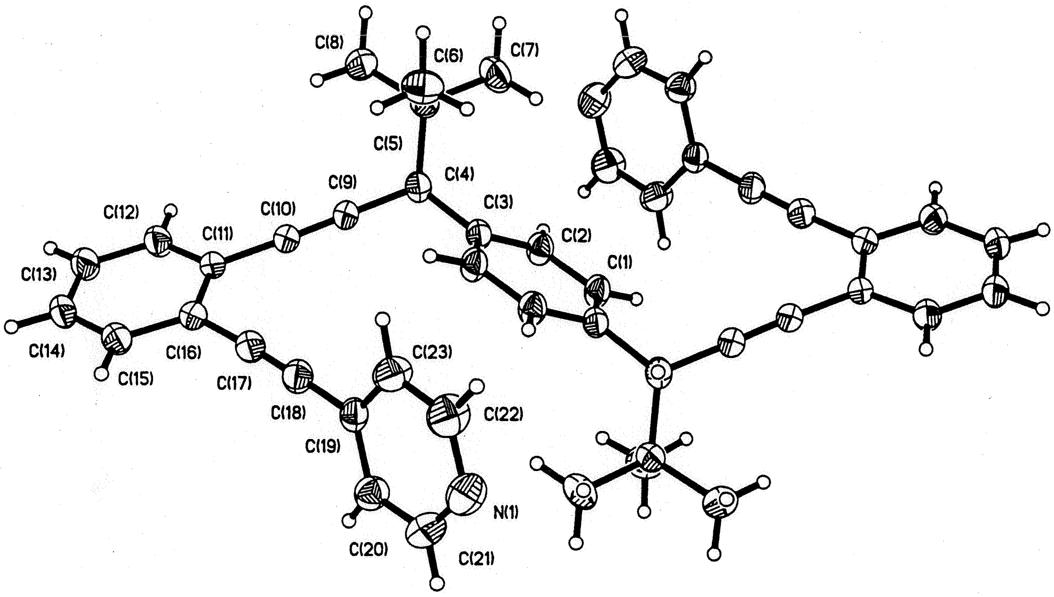


Figure S1. ORTEP Drawing of the Crystal Structure of *meso*-**8a**. The structure is constrained by a crystallographic center of symmetry in the crystal lattice. The thermal ellipsoids are scaled to enclose 30% probability.

CCDC 750094

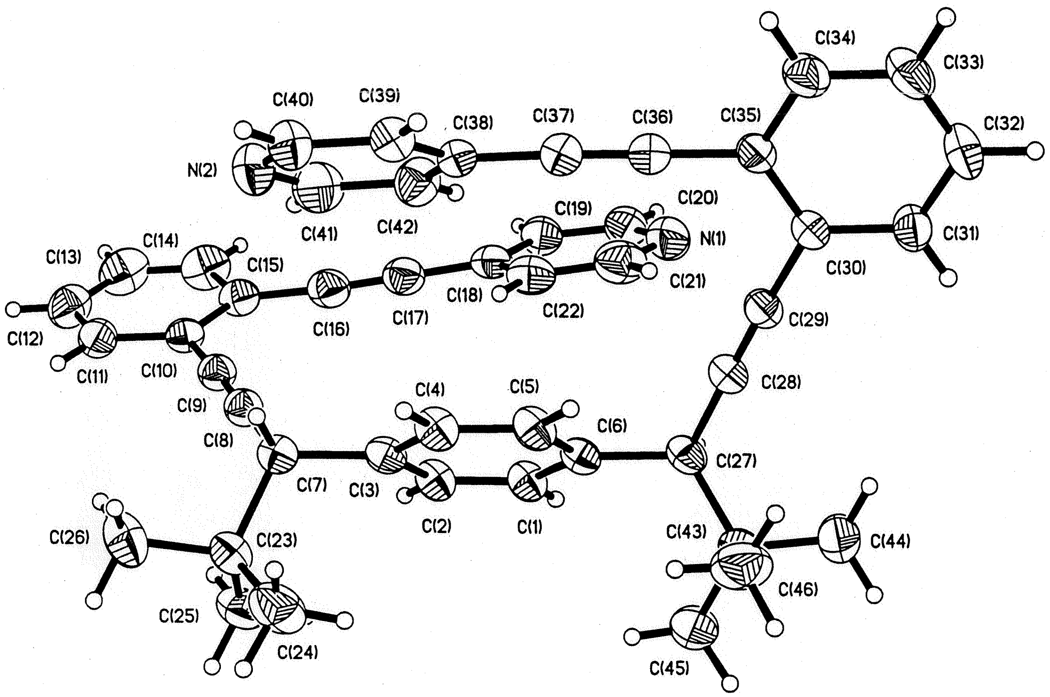


Figure S2. ORTEP Drawing of the Crystal Structure of *rac*-**8a**. The thermal ellipsoids are scaled to enclose 30% probability.

CCDC 750096

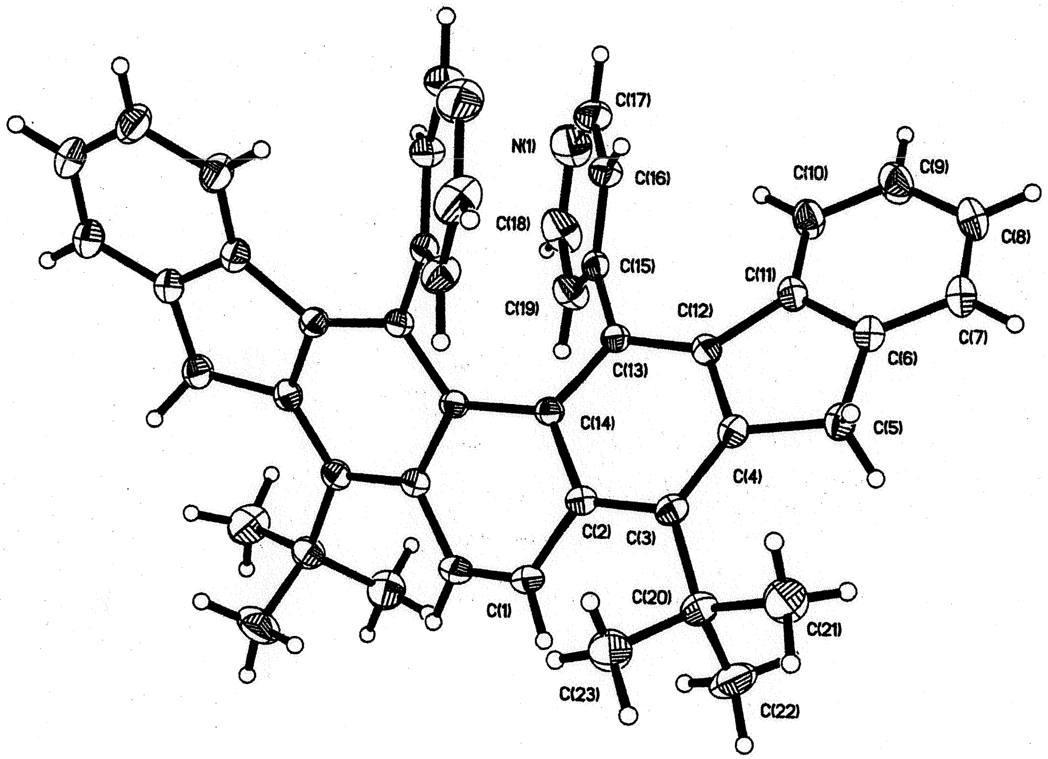


Figure S3. ORTEP Drawing of the Crystal Structure of **2a**. The thermal ellipsoids are scaled to enclose 30% probability.

CCDC 750095

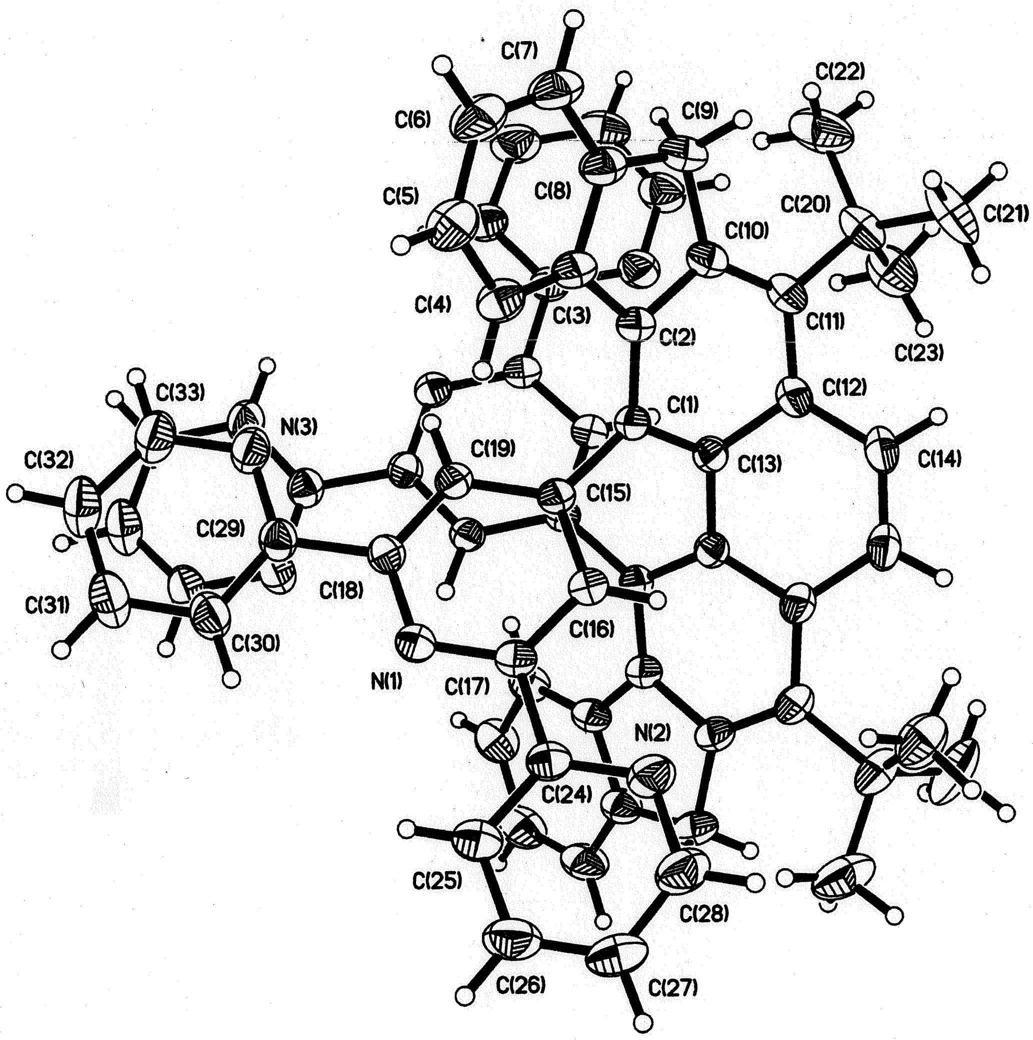
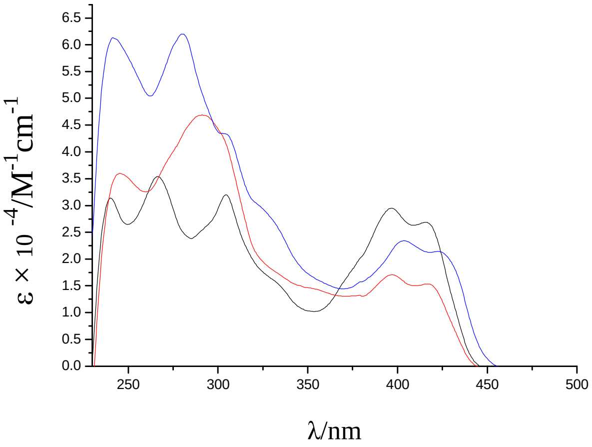


Figure S4. ORTEP Drawing of the Crystal Structure of **2c**. The structure is constrained by a crystallographic two-fold rotation axis. The thermal ellipsoids are scaled to enclose 30% probability.

(a)



(b)

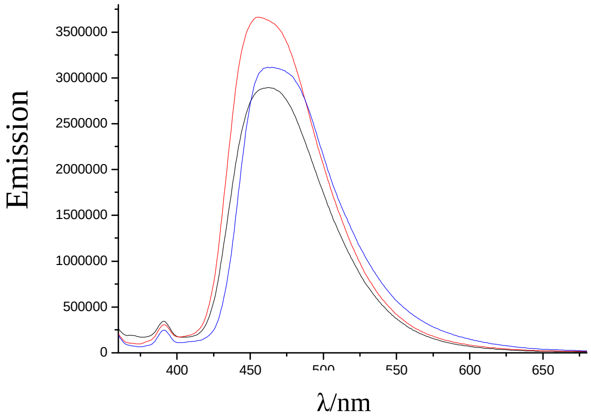


Figure S5. (a) UV−vis absorption spectra and (b) luminescence spectra of **2a** (black), **2b** (red), and **2c** (blue) in dichloromethane at room temperature.