Supplementary Material (ESI) for Chemical Communications

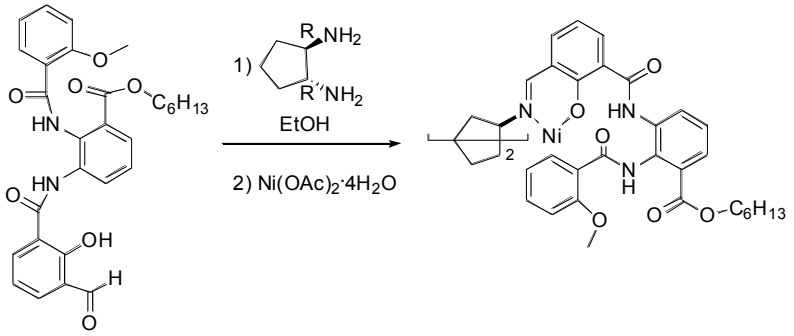
Interplay between Diamine Structure and Absolute Helicity in Ni-salen Metallofoldamers

Zhenzhen Dong[a], Shi Bai[a], Glenn P. A. Yap[a], Joseph M. Fox[a]*

Supporting Information

General Considerations All reactions were carried out in round bottomed flasks that were flame-dried under vacuum and cooled under nitrogen. Chromatography was performed on silica gel (ICN SiliTech 32-62D, 60Å). For ^{13}C NMR, multiplicities were distinguished using an APT pulse sequence: typical methylene and quaternary carbons appear 'up' (u); methine and methyl carbons 'down' (dn). FT-IR spectra were collected on a Thermo Electron Co. IR100 spectrometer using a Performer Attenuated Total Reflectance (ATR) probe with a ZnSe plate. X-ray quality crystals of **5** were grown from toluene/CH_2Cl_2. Circular Dichroism spectra were collected on a JASCO J-810 spectropolarimeter. Wavelength scans were recorded using a 2 nm date pitch and a 50 nm/min scan speed, and spectra were collected in 0.1 cm quartz cells. The spectra of the solutions of **4** ($6.8*10^{-4}$ M in CH_2Cl_2) and **5** ($4.0*10^{-4}$ M in CH_2Cl_2) were collected at 20 °C.

Ni-Salen 4

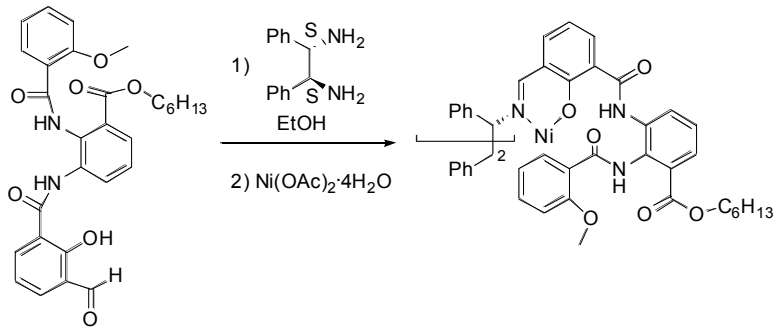


3 **4**

A solution of (1*R*,2*R*)-cyclopentane-1,2-diamine (0.002 g, 0.020 mmol) in EtOH (1.5 mL) was combined with aldehyde **3**[1] (0.021 g, 0.040 mmol) and heated to reflux for 4 h. The reaction mixture was cooled to rt and $Ni(OAc)_2{\cdot}4H_2O$ (7.5 mg, 0.030 mmol) was added. The mixture was then heated to reflux for another 4 h, and a dark orange precipitate was observed. The precipitate was filtered, washed with cold ethanol, and dried under vacuum to give the title product as a dark orange solid. The yield was 0.012 g (55%). The purity was measured to be ≥ 95% by ^{1}H NMR. mp: 162-170°C; $[\alpha]^{23}_D$ –500° (*c* 0.012, CH_2Cl_2); ^{1}H NMR (400MHz, $CDCl_3$, δ): 10.74 (s, 2H), 10.67 (s, 2H), 8.42 (d, J = 6.8 Hz, 2H), 8.23 (s, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.49 (dd, J = 7.6, 1.2 Hz, 2H), 7.34 (app t, J = 6.8 Hz, 2H), 7.18 (d, J =6.8 Hz, 2H), 6.97 (app t, J = 6.8 Hz, 2H), 6.85 (app t, J = 8.0 Hz, 2H), 6.75-6.69 (m, 4H), 6.62 (d, J = 8.0 Hz, 2H), 4.18 (t, J = 6.8 Hz, 4H), 3.23 (s, 6H), 2.95 (m, 2H), 2.09 (m, 2H), 1.72-1.65 (m, 6H), 1.41-1.25 (m, 12H), 1.17-1.12 (m, 2H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100MHz, $CDCl_3$, δ): 165.2 (u), 162.4 (u), 162.0 (u), 160.9 (u), 157.5 (dn), 157.0 (u), 137.4

(dn), 135.6 (dn), 133.9 (u), 132.6 (dn), 130.7 (dn), 127.8 (u), 126.0 (dn), 124.2 (dn), 123.7 (u), 123.6 (u), 123.3 (dn), 122.6 (u), 120.1 (u), 119.3 (dn), 114.6 (dn), 110.2 (dn), 74.1 (dn), 63.8 (u), 53.9 (dn), 30.5 (u), 27.5 (u), 24.7 (u), 22.0 (u), 21.5 (u), 18.2 (u), 13.0 (dn); IR (cm^{-1}): 2900, 1718, 1708, 1656, 1597, 1527, 1492, 1460, 1431, 1388, 1293, 1253, 1179, 1131, 1080, 1022, 893, 675; UV-vis (6.8×10^{-6} M in CH_2Cl_2) λ_{max}: 238, 262, 310, 418; HRMS (ESI+) m/z: [M+Na], calcd for $C_{63}H_{66}N_6NiO_{12}$: 1179.3990, found: 1179.3997.

Ni Salen 5

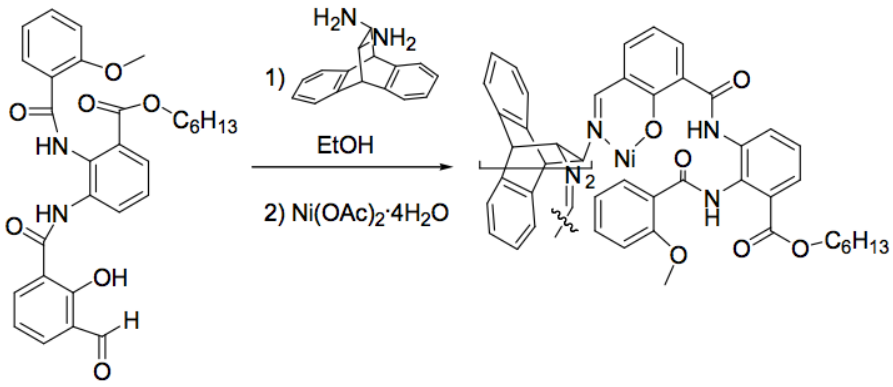


3 **5**

(1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (41 mg, 0.19 mmol) was dissolved in EtOH (10 mL), and 1.0 mL (4.1 mg of the diamine, 0.019 mmol) of this solution was combined with compound **3** (20 mg, 0.039 mmol) in EtOH (2 mL). The resulting solution was heated to reflux for 4 h. The reaction mixture was cooled and $Ni(OAc)_2{\cdot}4H_2O$ was added and heated for 4 h. Water (5 mL) was added to the crude mixture which was then allowed to stand for 16h at rt. The precipitates were filtered through glass wool, washed with ethanol and water, and

dried under vacuum to give the title compound as a dark orange solid. The yield was 21 mg (84%). The purity was measured to be 94% by ^{1}H NMR. mp: 135-140°C; $[\alpha]^{23}_{D}$ +550° (*c* 0.011, CH_2Cl_2); ^{1}H NMR (400MHz, $CDCl_3$, δ): 10.86 (s, 2H), 10.78 (s, 2H), 8.47-8.43(m, 4H), 7.57 (d, J = 8.0Hz, 2H), 7.55-7.52 (m, 4H), 7.24-7.32 (m, 6H), 7.28-7.20 (m, 2H), 6.98 (d, J = 7.6Hz, 2H), 6.90-6.86 (m, 6H), 6.70-6.67 (m, 6H), 4.20-4.15 (m, 4H), 4.10 (s, 2H), 3.26 (s, 6H), 1.73-1.66 (m, 4H), 1.42-1.26 (m, 12H), 0.89 (t, J = 7.4Hz, 6H); ^{13}C NMR (100MHz, $CDCl_3$, δ): 165.2 (u), 162.3 (u), 161.2 (u), 160.5 (dn), 159.8 (u), 157.2 (u), 138.1 (dn), 136.1 (dn), 133.8 (u), 133.1 (dn), 132.8 (u), 130.7 (dn), 128.6 (3C, dn), 128.0 (u), 127.8 (2C, dn), 126.5 (dn), 124.1 (dn), 123.9 (2C, u), 123.4 (dn), 122.5 (u), 120.1(u), 119.1 (dn), 114.6 (dn), 110.4 (dn), 76.6 (dn), 63.8 (u), 54.0 (dn), 30.5 (u), 27.5 (u), 24.7 (u), 21.5 (u), 13.0 (dn); IR (cm^{-1}): 3001, 2919, 2865, 1713, 1660, 1614, 1537, 1504, 1451, 1291, 1238, 1178, 1134, 1085, 1013, 751, 631; UV-vis (4.0×10^{-6} M in CH_2Cl_2) λ_{max}: 232, 260, 328, 416; HRMS (ESI+) m/z: [M+Na], calcd for $C_{72}H_{70}N_6NiO_{12}$: 1291.4303, found: 1291.4307.

Ni-salen 6

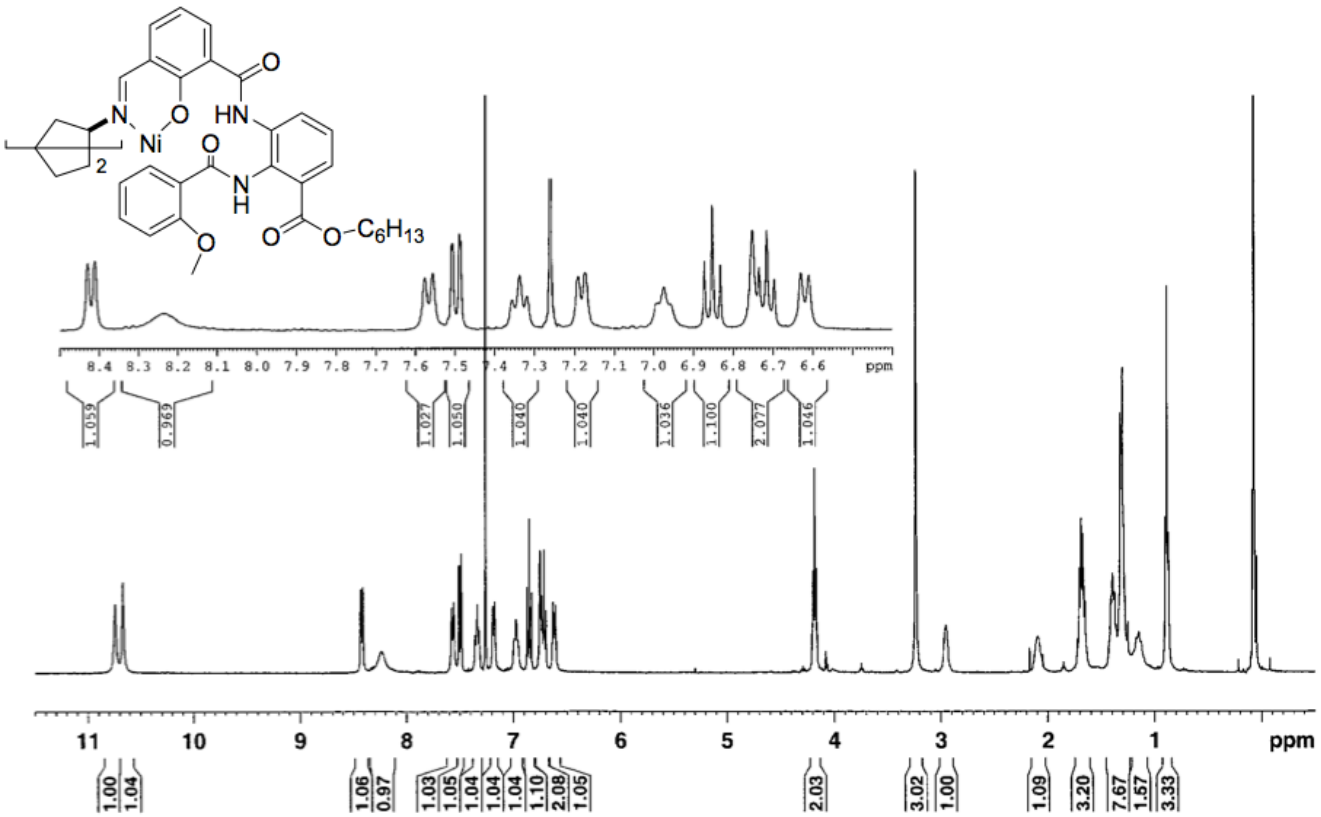


3 **6**

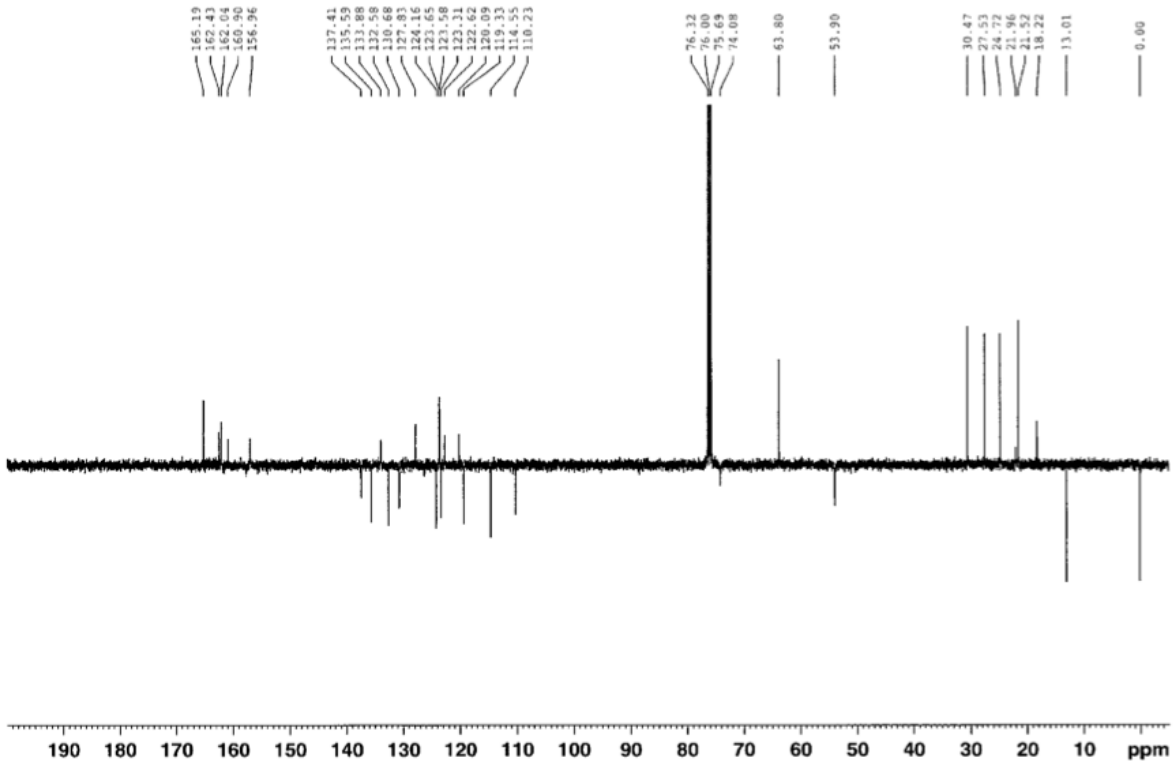
(11*R*, 12*R*)-9,10-dihydro-9,10-ethanoanthracene-11,12-diamine (9.1 mg, 0.038 mmol) was dissolved in EtOH (1 mL). This solution was combined with compound **3** (40 mg, 0.077 mmol) in EtOH (2 mL). The resulting solution was heated to reflux for 4 h. The reaction mixture was cooled and $Ni(OAc)_2.4H_2O$ (15.0 mg, 0.060 mmol) was added and heated for 4 h. Water (5 mL) was added to the crude mixture which was then allowed to stand for 16h at rt. The precipitates were filtered through glass wool, washed with ethanol and water, and S-3dried under vacuum to give the title compound as a dark orange solid. The yield was 0.028 g (57%). mp: 232-238°C; $[\alpha]^{23}_D$ –114° (*c* 0.011, CH_2Cl_2) ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 10.79-10.46 (m, 4H), 8.26 (dd, J= 7.6, 1.6Hz, 2H), 7.92-7.81 (m, 2H), 7.41-7.39 (m, 4H), 7.24-7.23 (m, 6H), 7.18-7.17 (m, 4H), 6.98 (s, 2H), 6.79 (app t, J= 8.0Hz, 2H), 6.68 (app t, J= 7.6Hz, 2H), 6.51-6.15 (m, 6H), 4.28 (s, 2H), 4.10 (s, 4H), 3.10 (s, 6H), 2.96 (s, 2H), 1.61-1.54 (m, 4H), 1.30-1.19 (m, 12H), 0.78 (t, J= 6.4Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2, δ: peaks were assigned using HMBC and HSQC): 166.4 (u), 163.5 (u), 166.3 (u), 162.0 (u), 158.2 (u), 155.0 (dn), 145.8 (u), 137.8 (dn), 136.8 (dn), 136.2 (u), 135.2 (u), 133.1 (dn), 132.4 (dn), 128.6 (u), 127.1 (dn), 127.0 (dn), 126.8 (dn), 126.3 (u), 125.1 (u), 125.0 (dn), 124.6 (u) ,124.2 (dn), 123.3 (u), 122.3 (dn), 121.0 (dn), 120.3 (dn), 115.6 (dn), 111.5 (dn), 75.1 (dn), 65.1 (u), 54.7 (dn), 42.7 (dn), 31.6 (u), 28.6 (u), 25.8 (u), 22.6 (u), 14.0 (dn); IR (cm^{-1}): 3655, 2920, 1712, 1659,

1633, 1553, 1536, 1503, 1481, 1461, 1433, 1293, 1135, 752; UV-vis ($6.2*10^{-6}$ M in CH_2Cl_2) λ_{max}: 236, 260, 316, 416; HRMS (ESI+) m/z: [M+Na], calcd for $C_{74}H_{70}N_6NiO_{12}$: 1315.4303, found: 1315.4294.

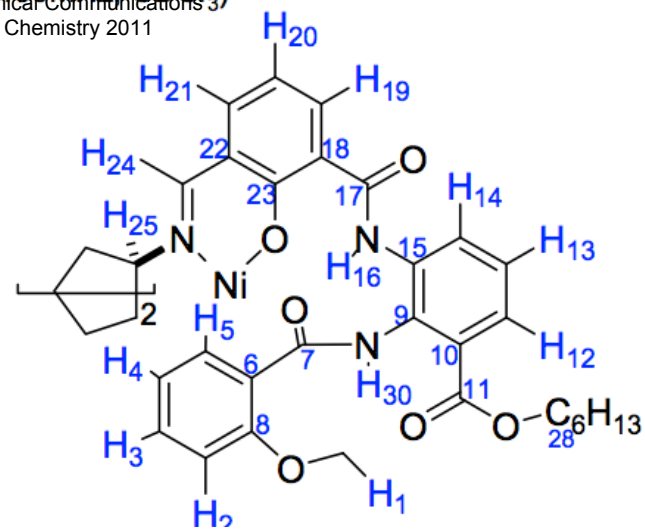
^{1}H NMR spectrum of **4** (400MHz, $CDCl_3$)



^{13}C NMR APT spectrum of **4** (100MHz, $CDCl_3$)



COSY spectrum of 4 (400MHz, $CDCl_3$)



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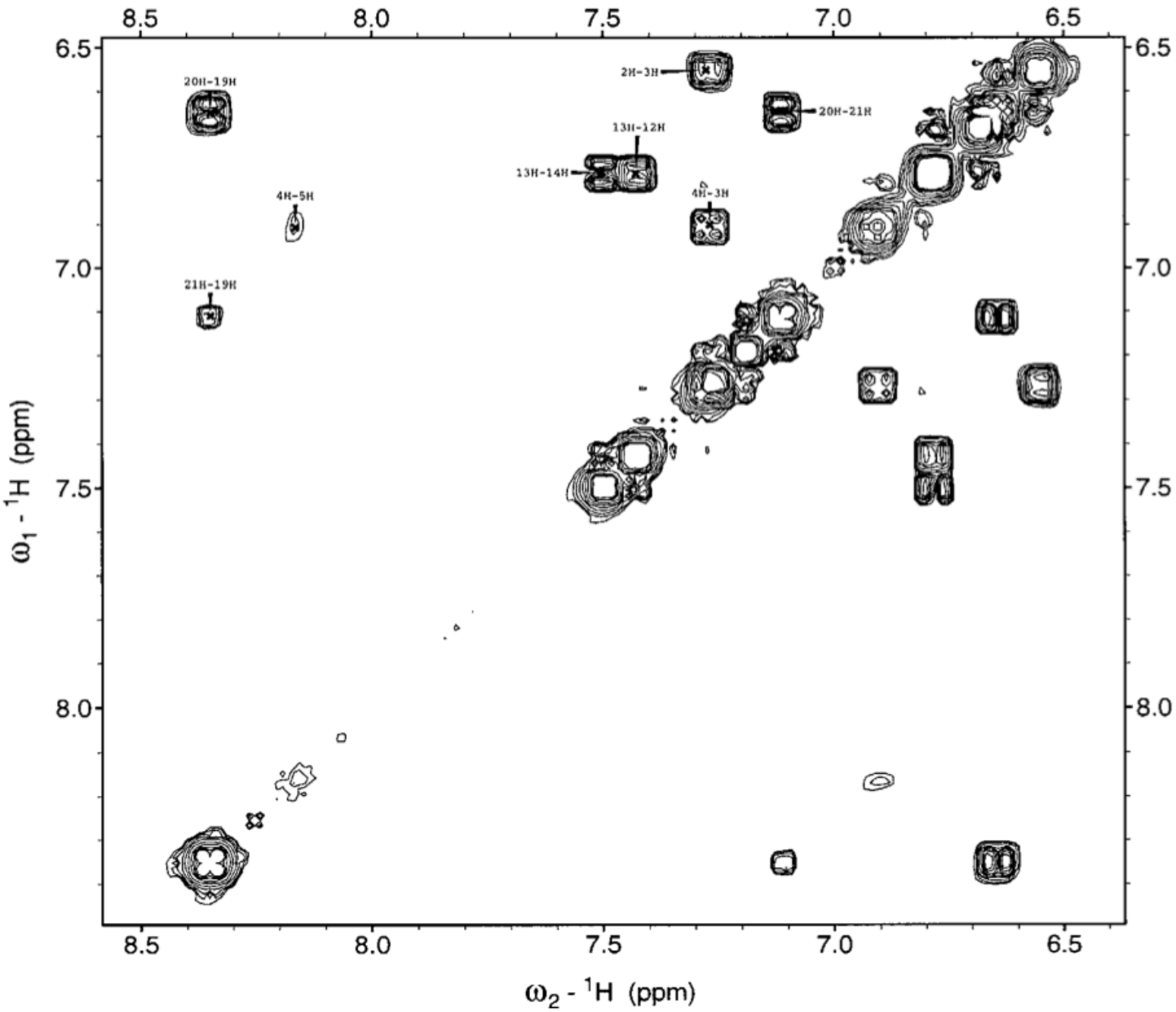
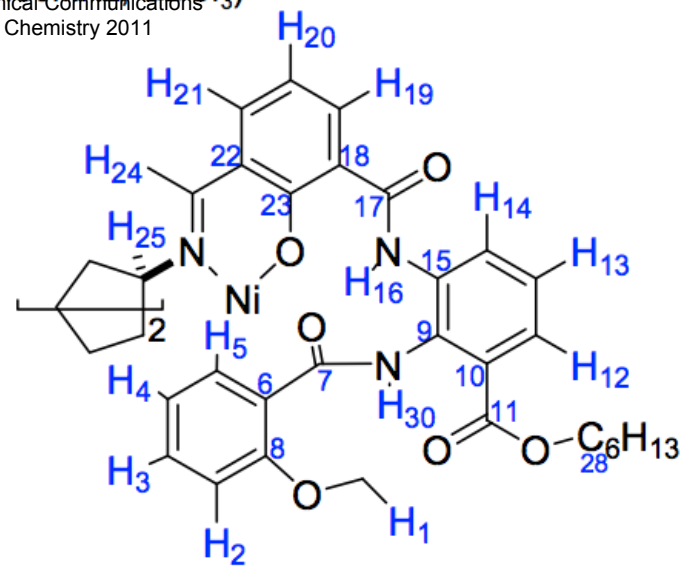


HSQC spectrum of **4** (400MHz, $CDCl_3$)



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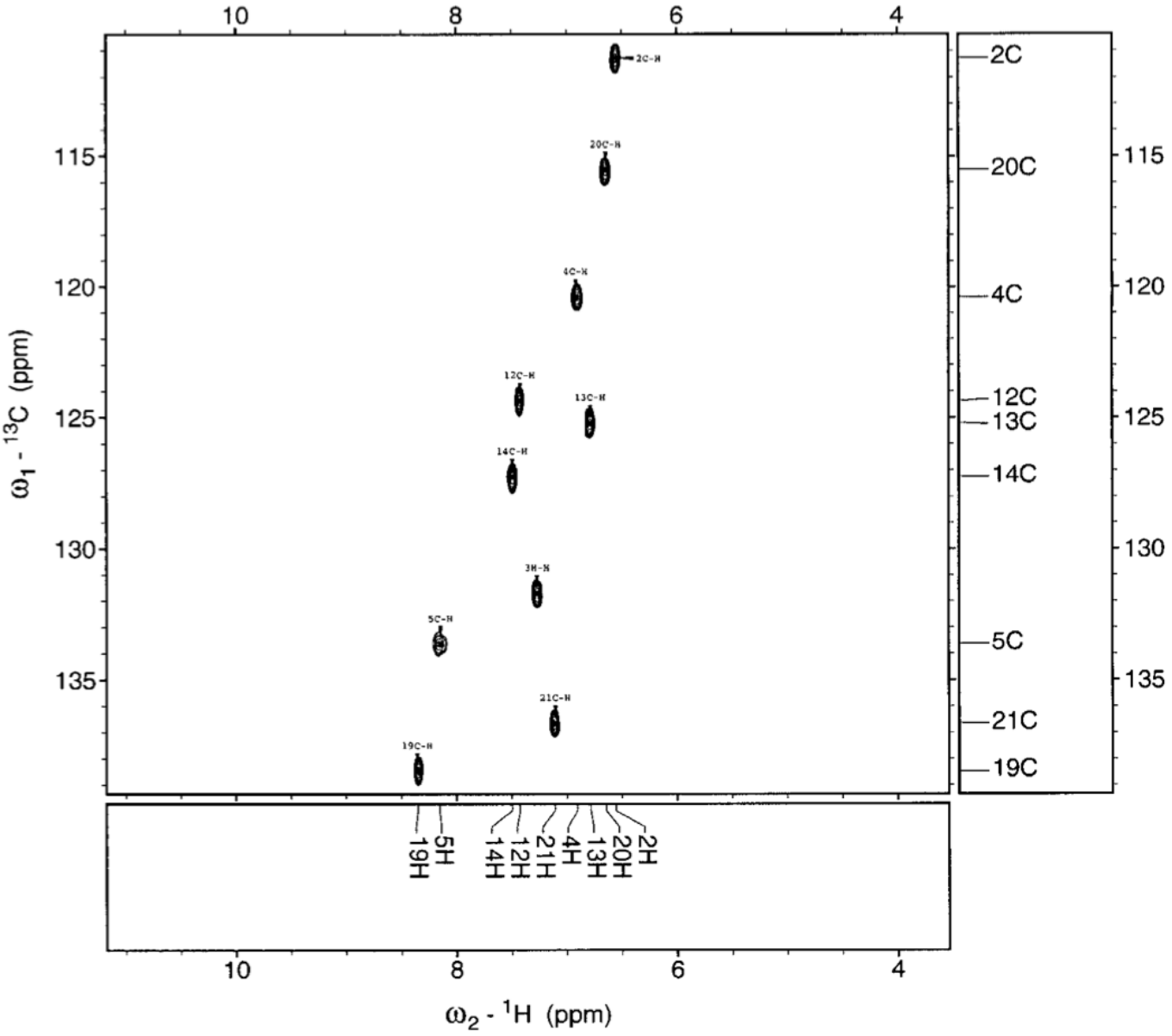
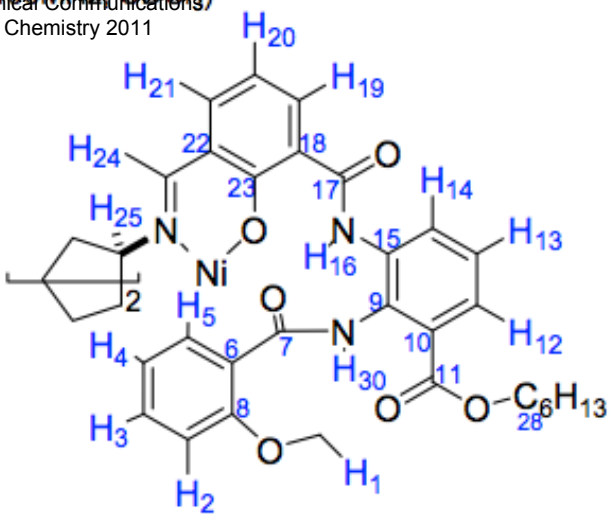


HMBC spectrum of **4** (400MHz, $CDCl_3$)



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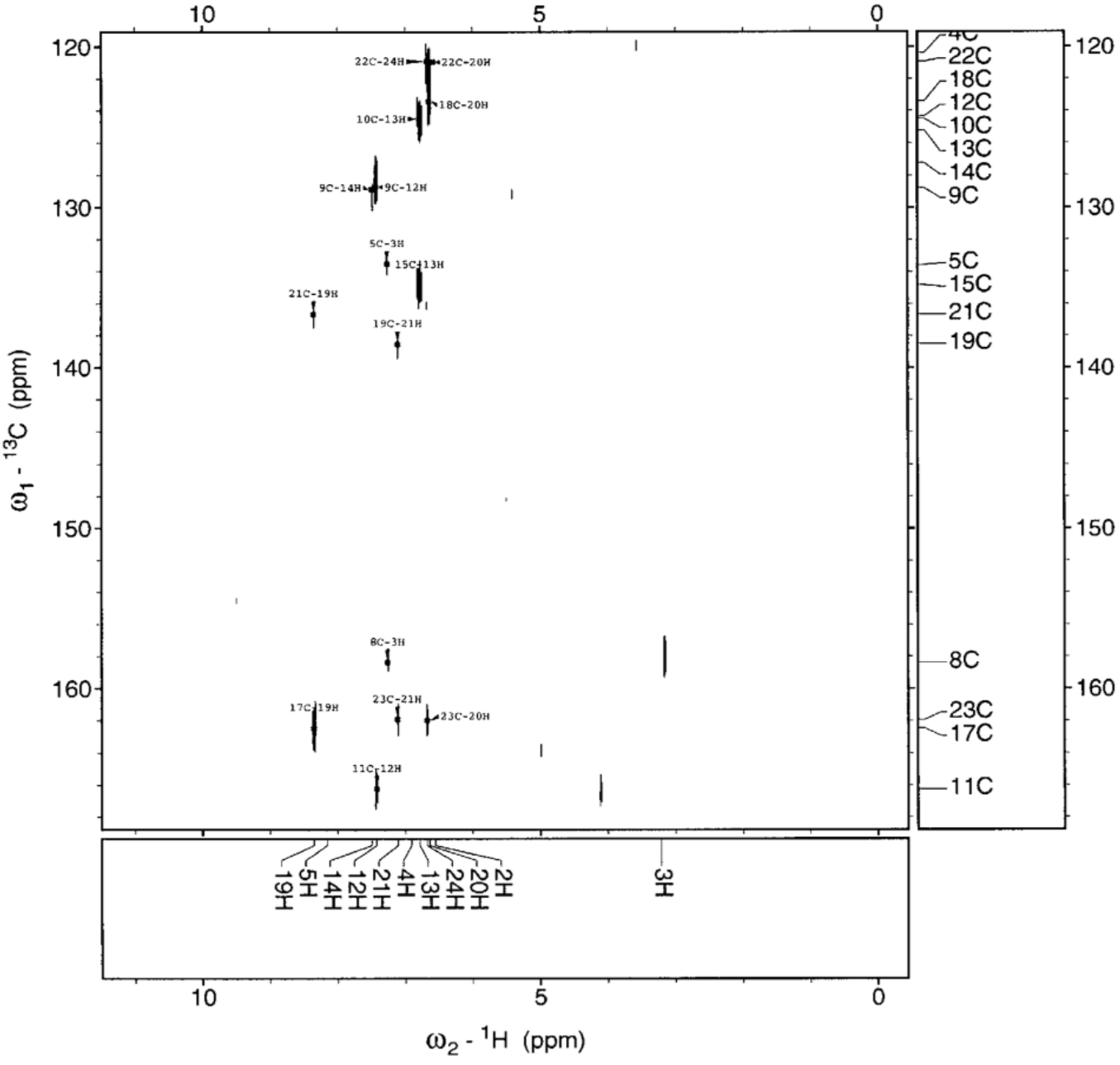
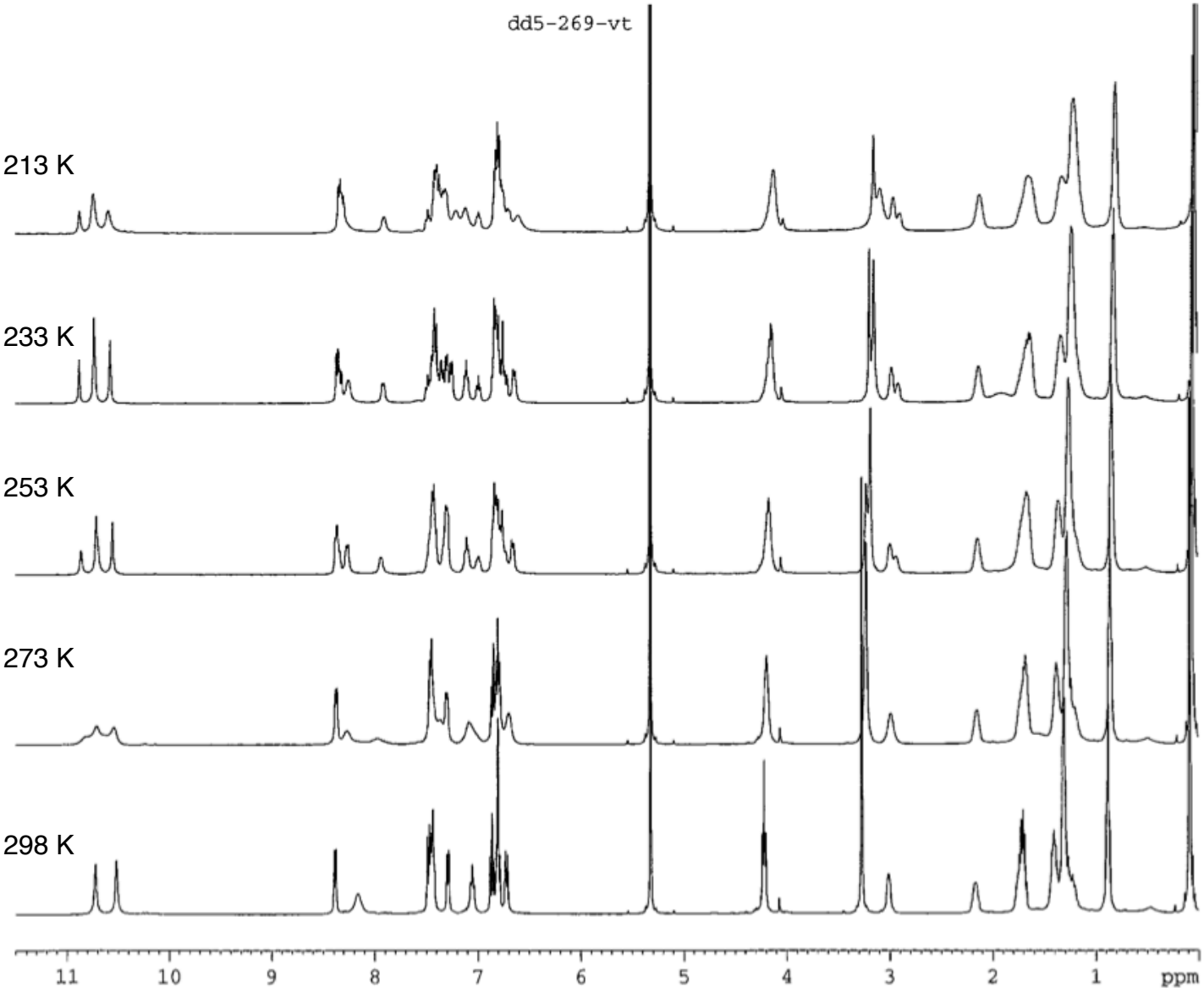
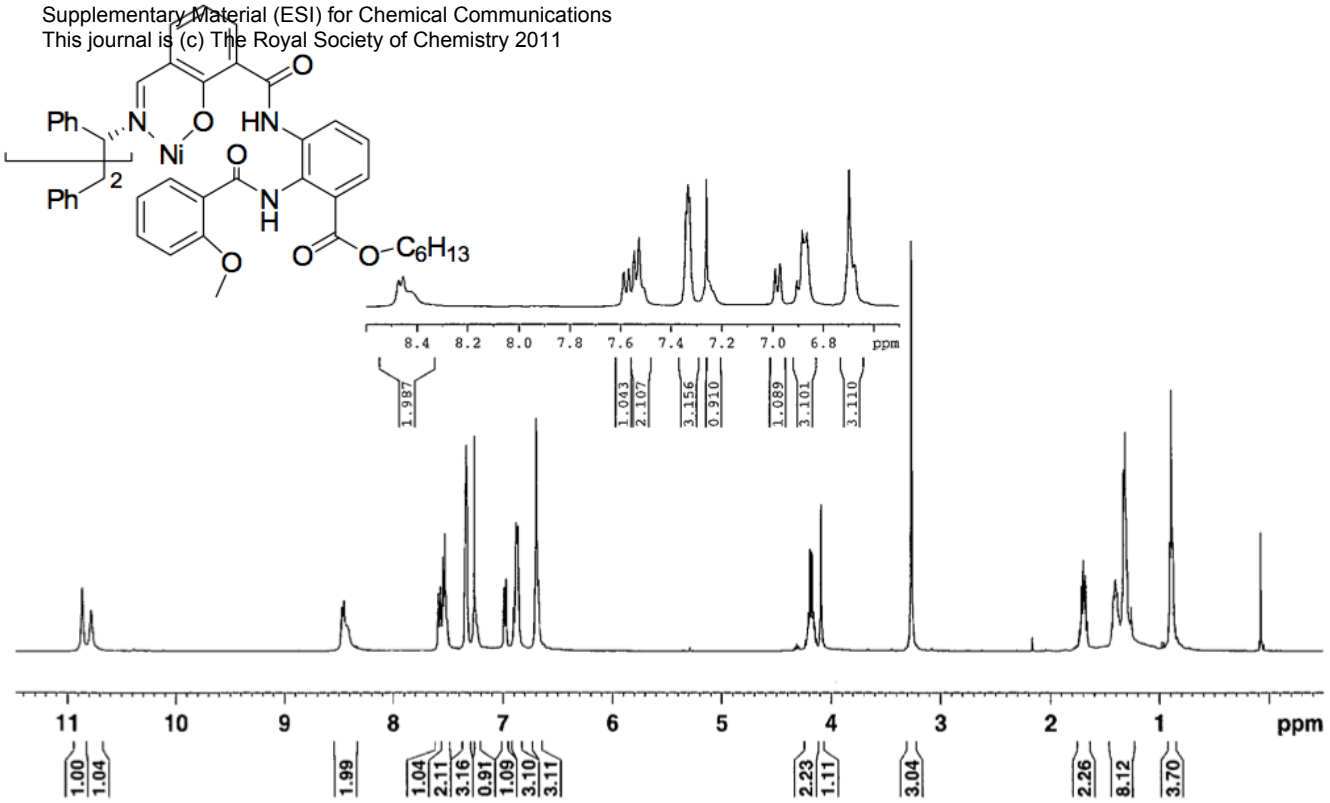


Variable temperature

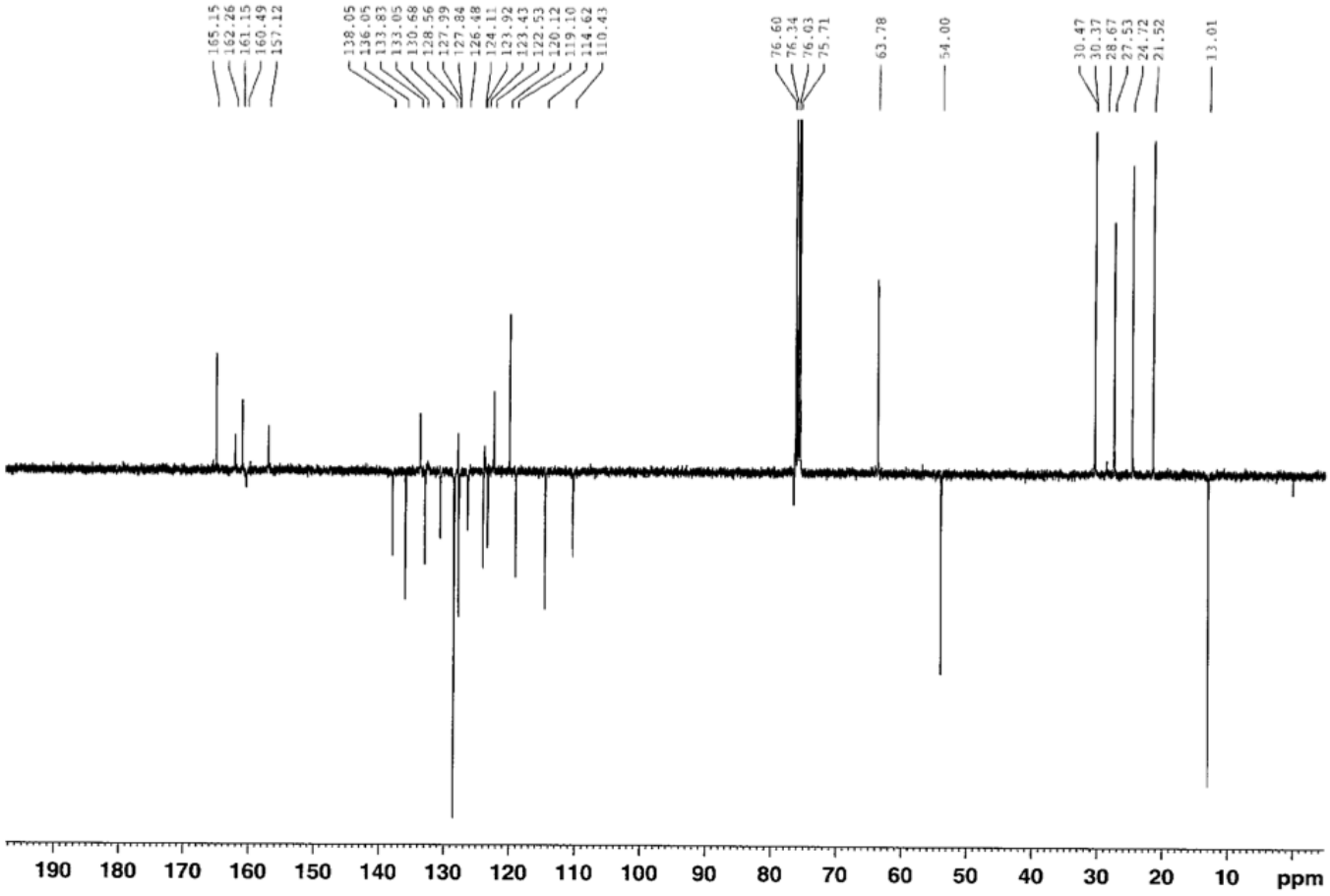
^{1}H NMR spectrum of **4** (400MHz, $CDCl_3$)



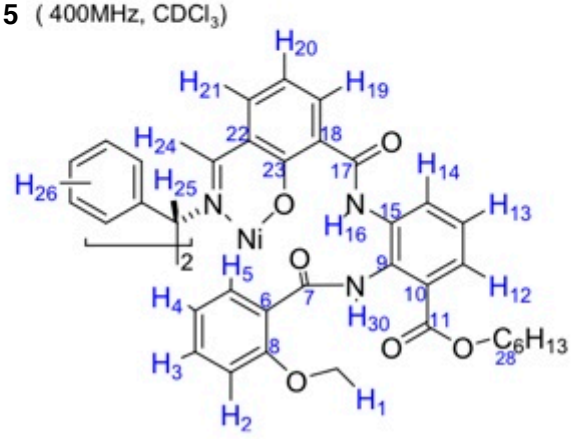
^{1}H NMR spectrum of **5** (400MHz, $CDCl_3$)



^{13}C NMR APT spectrum of **5** (100MHz, $CDCl_3$)



COSY spectrum of **5** (400MHz, $CDCl_3$)



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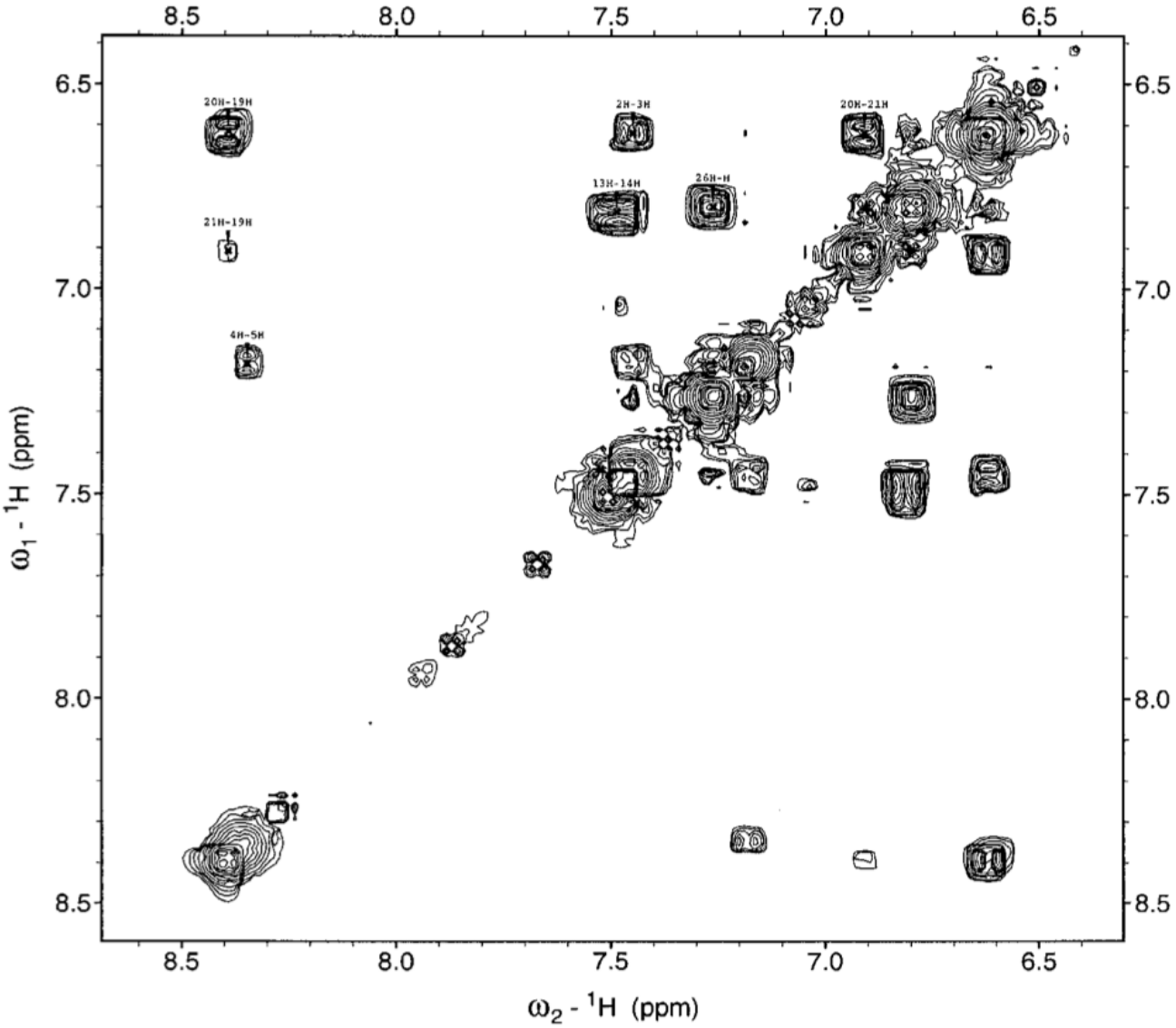
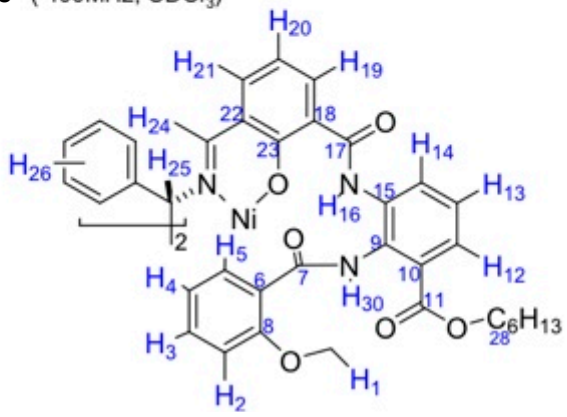


HSQC spectrum of **5** (400MHz, $CDCl_3$)



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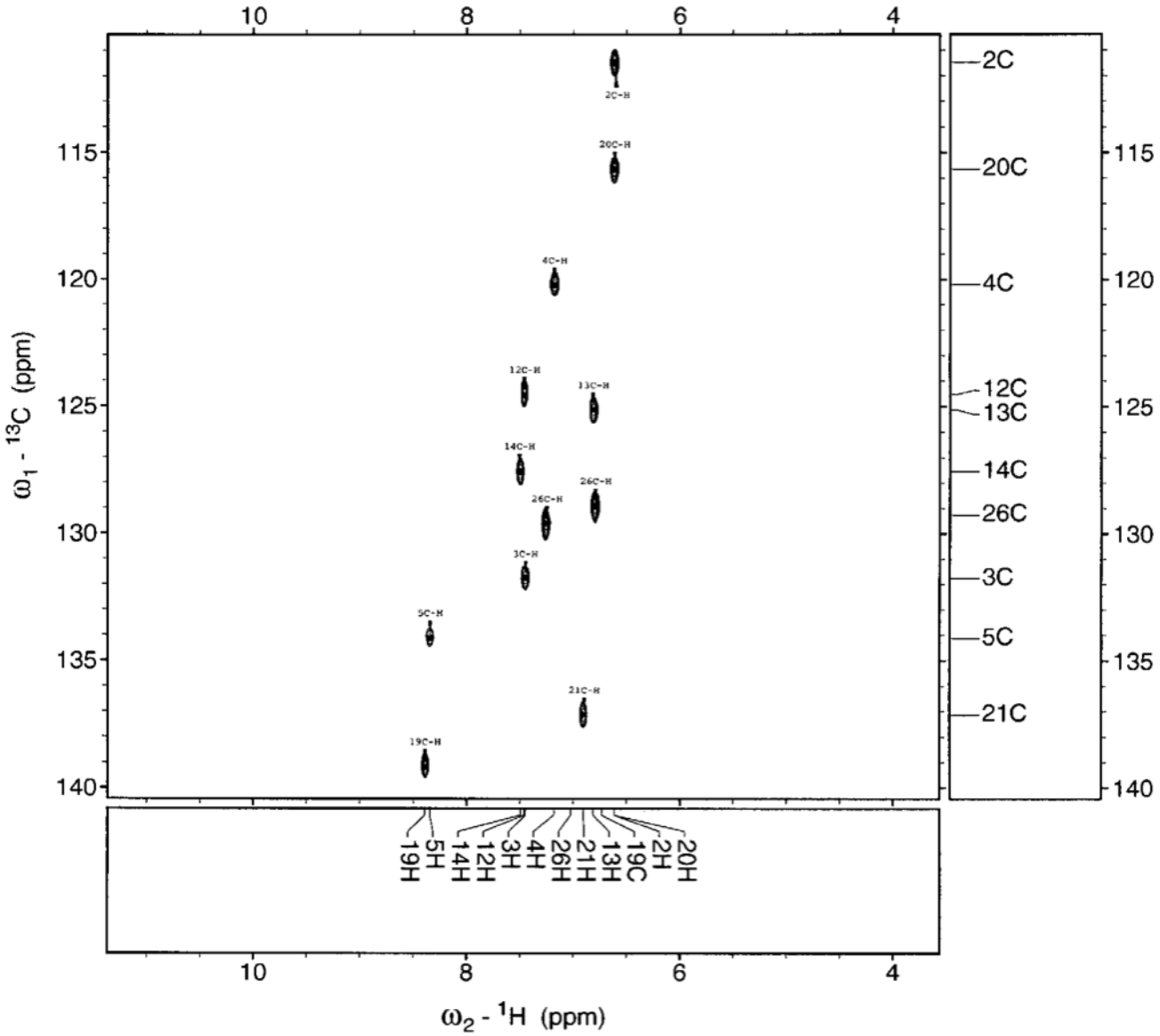
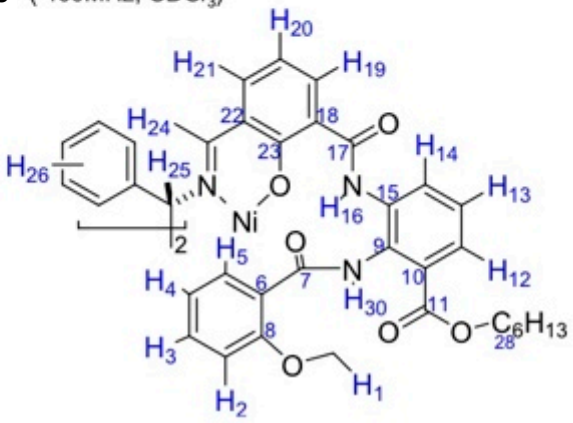


HMBC spectrum of **5** (400MHz, $CDCl_3$)



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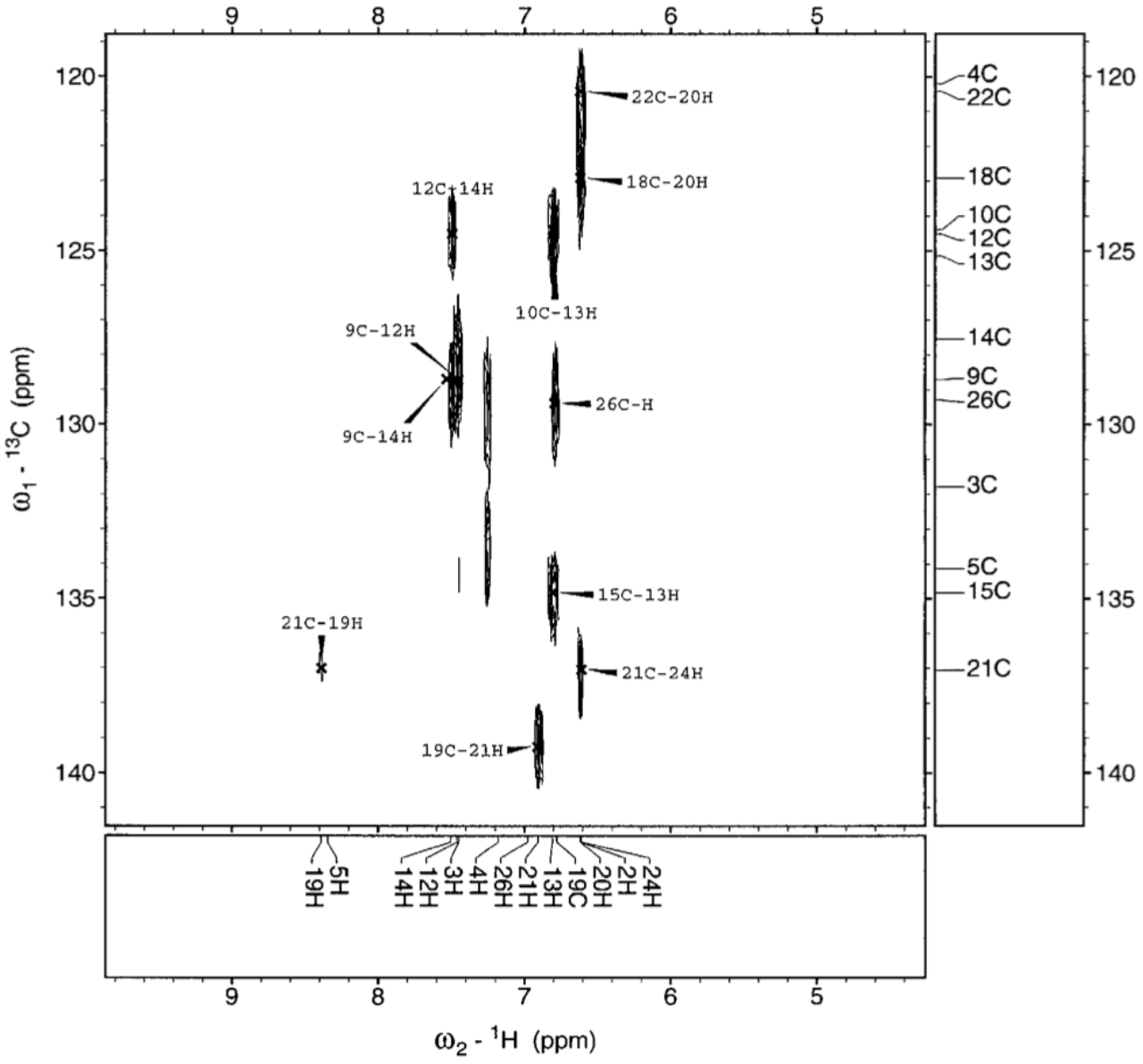
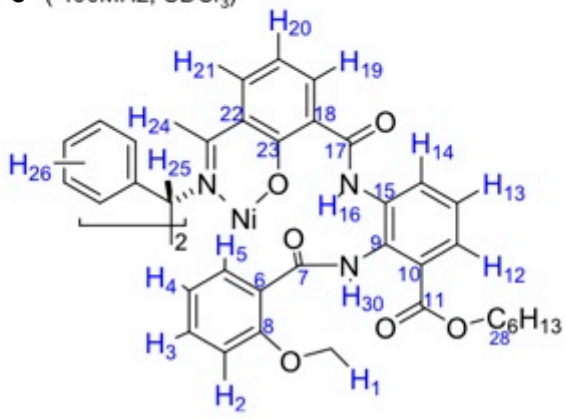


NOESY spectrum of **5** (400MHz, $CDCl_3$)



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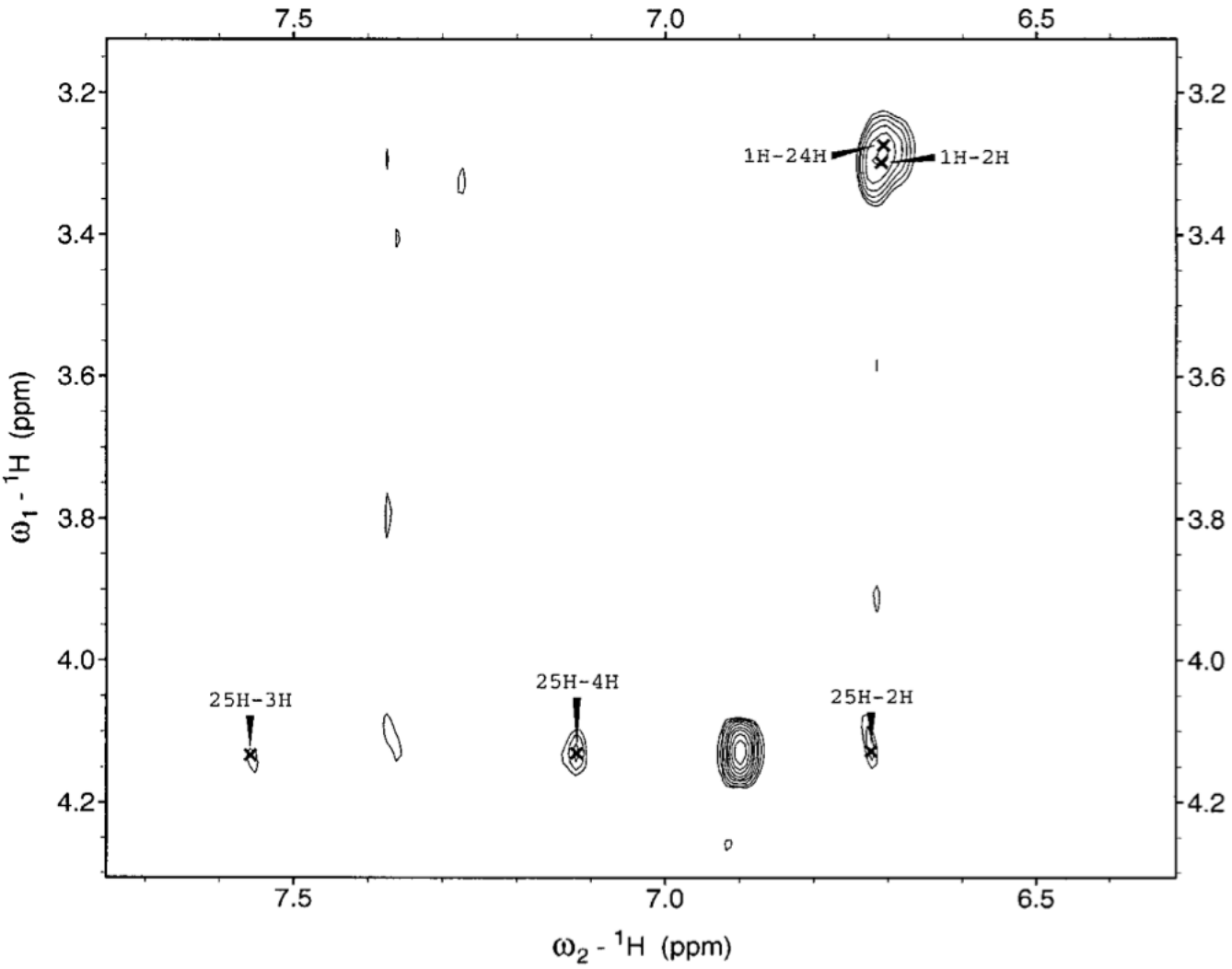
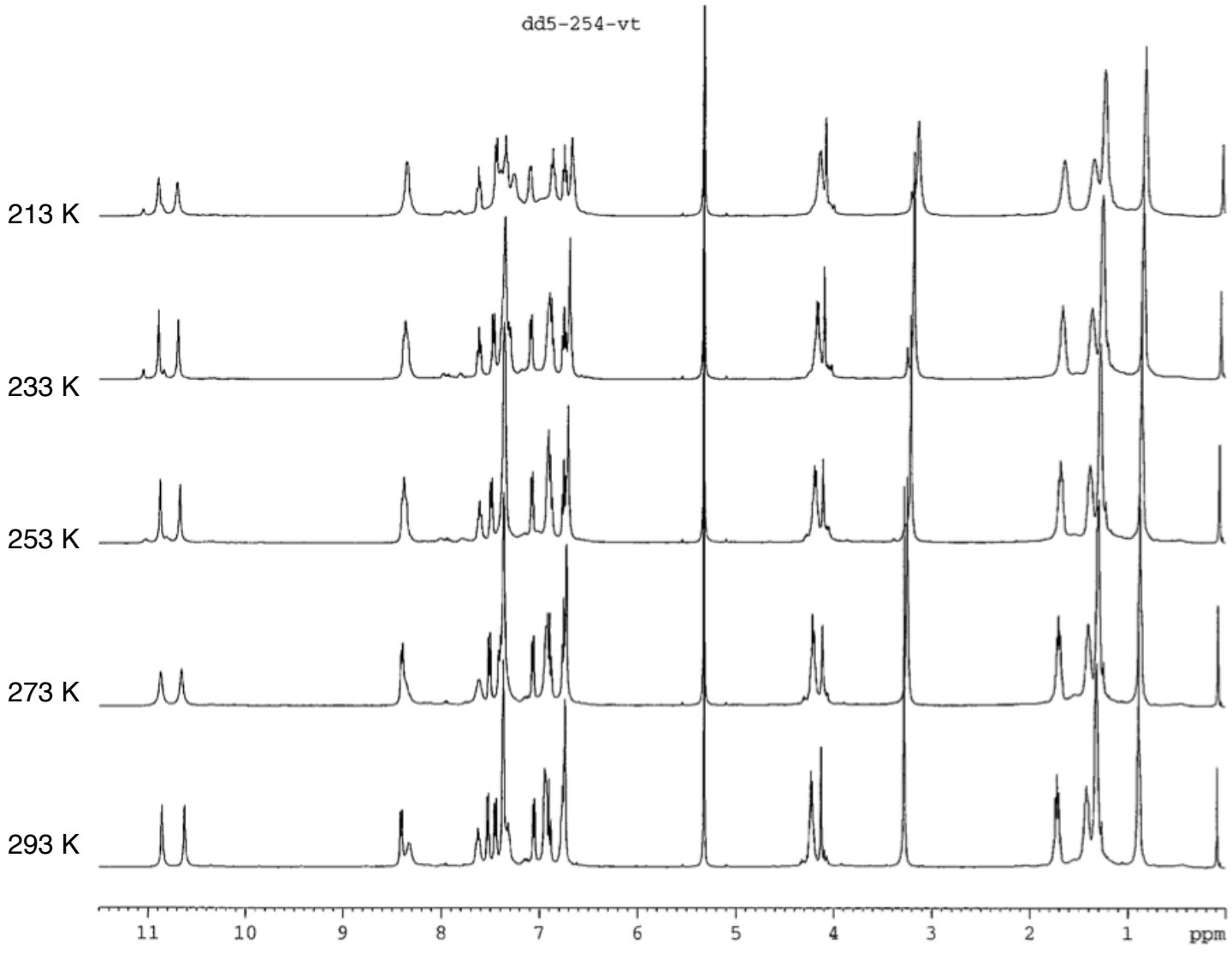
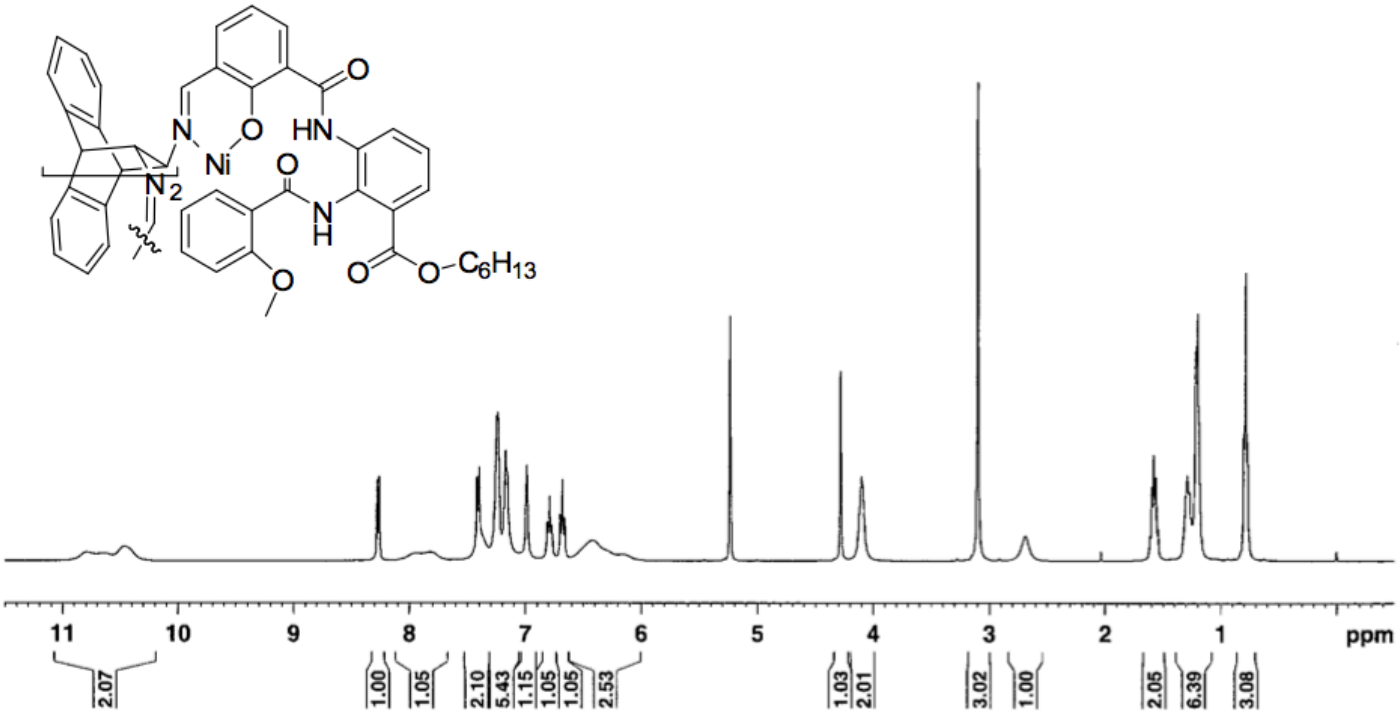


Variable temperature

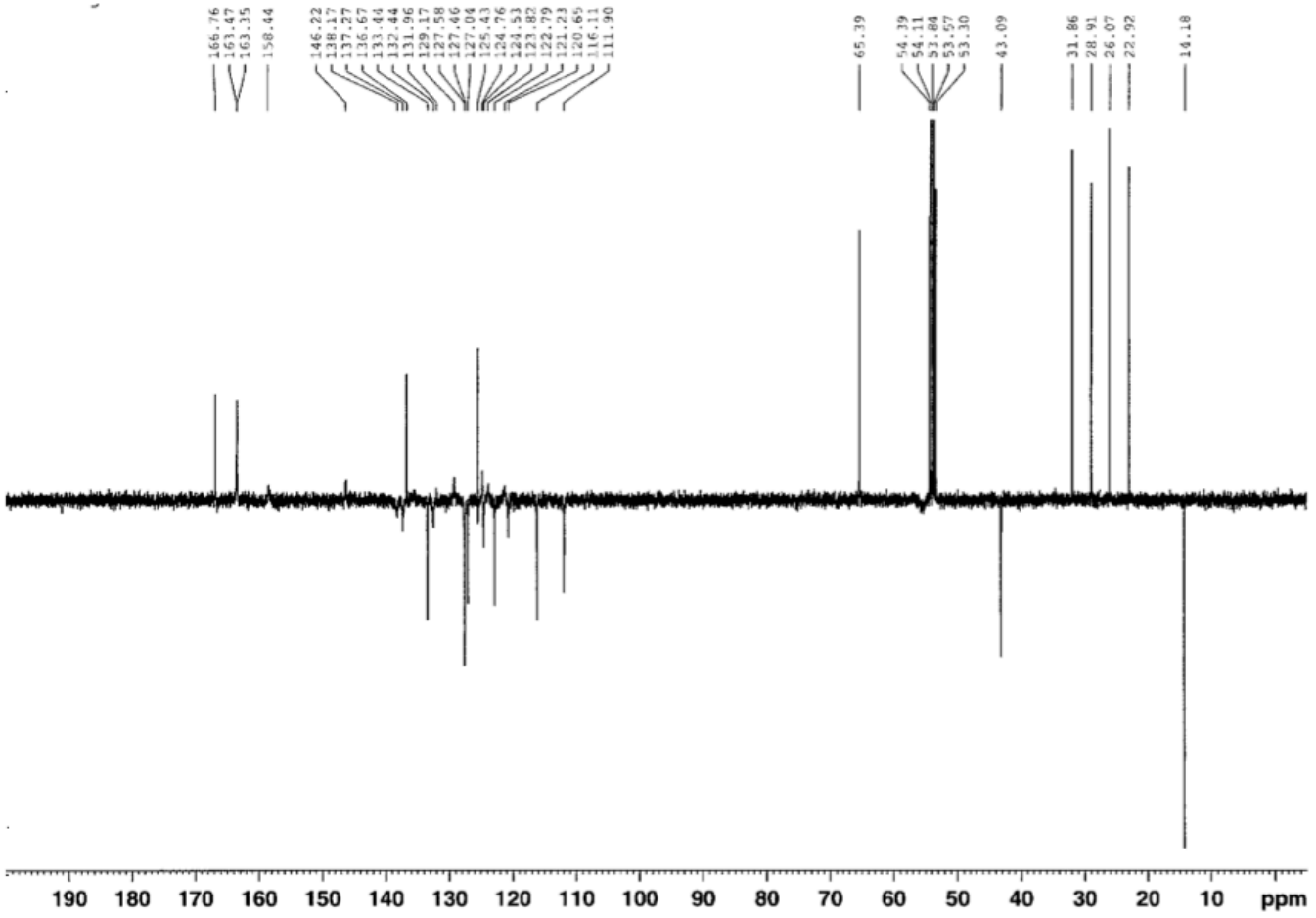
^{1}H NMR spectrum of **5** (400MHz, $CDCl_3$)



^{1}H NMR spectrum of **6** (400MHz, CD_2Cl_2)

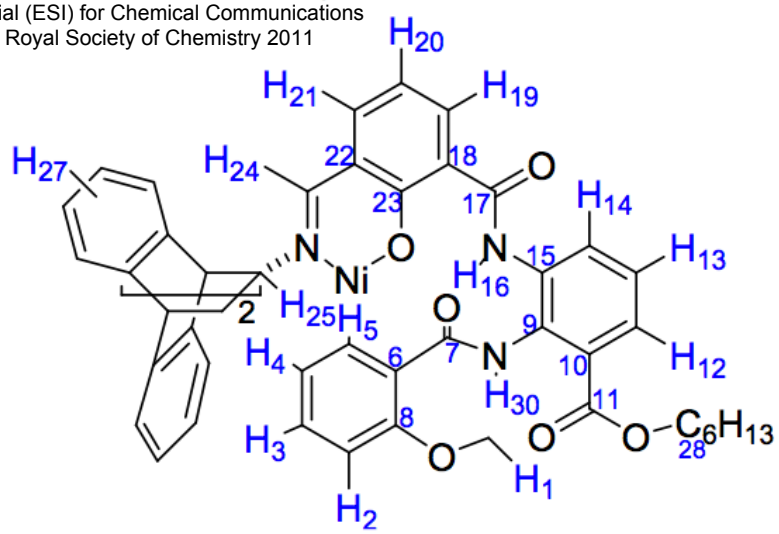


^{13}C NMR APT spectrum of **6** (100MHz, CD_2Cl_2)



COSY spectrum of **6** (400MHz, $CDCl_3$)

Supplementary Material (ESI) for Chemical Communications



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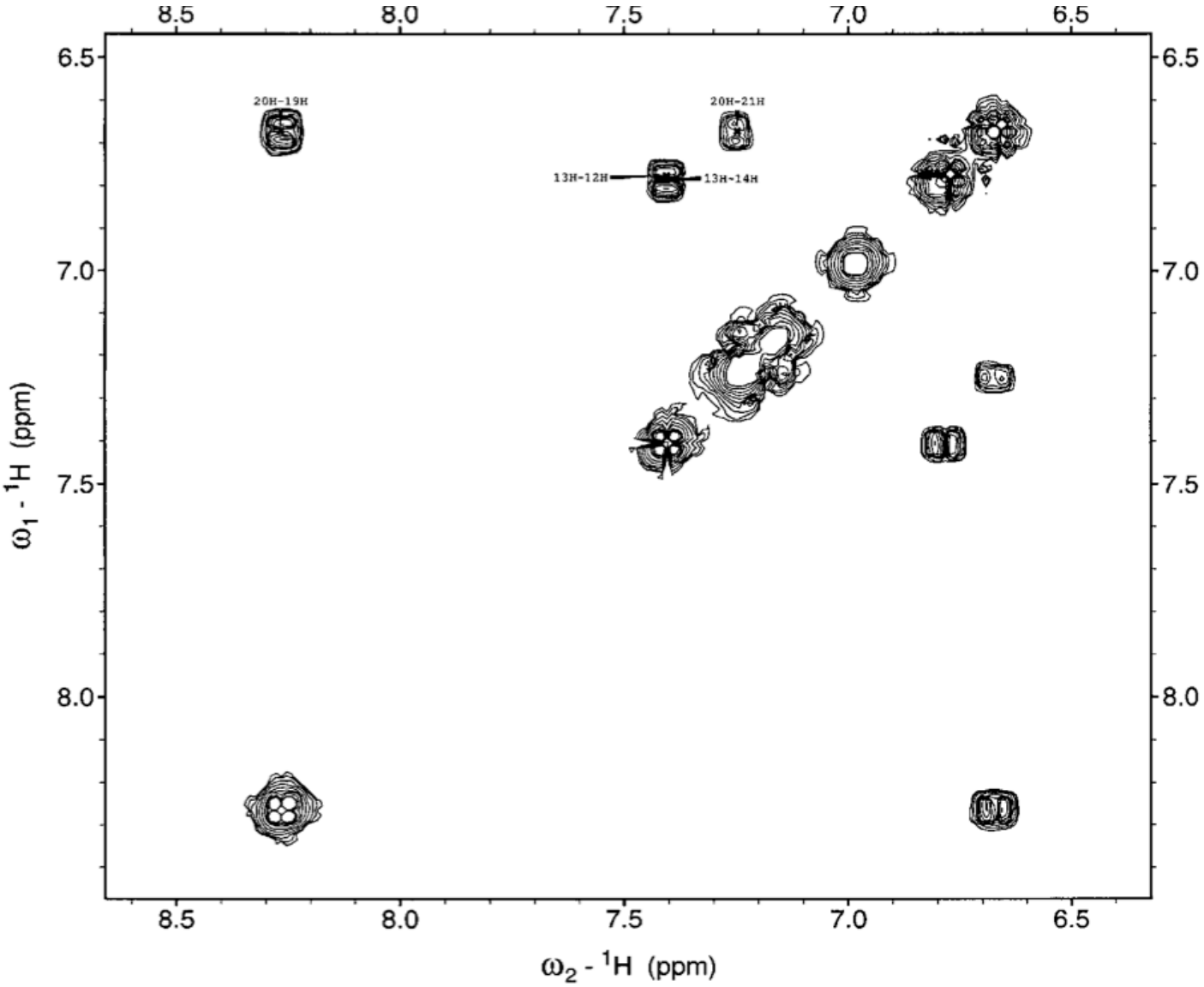
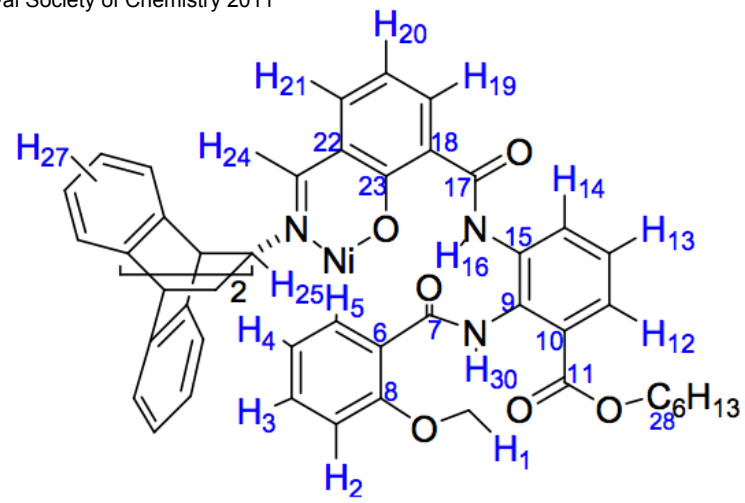


HSQC spectrum of **6** (400MHz, $CDCl_3$)



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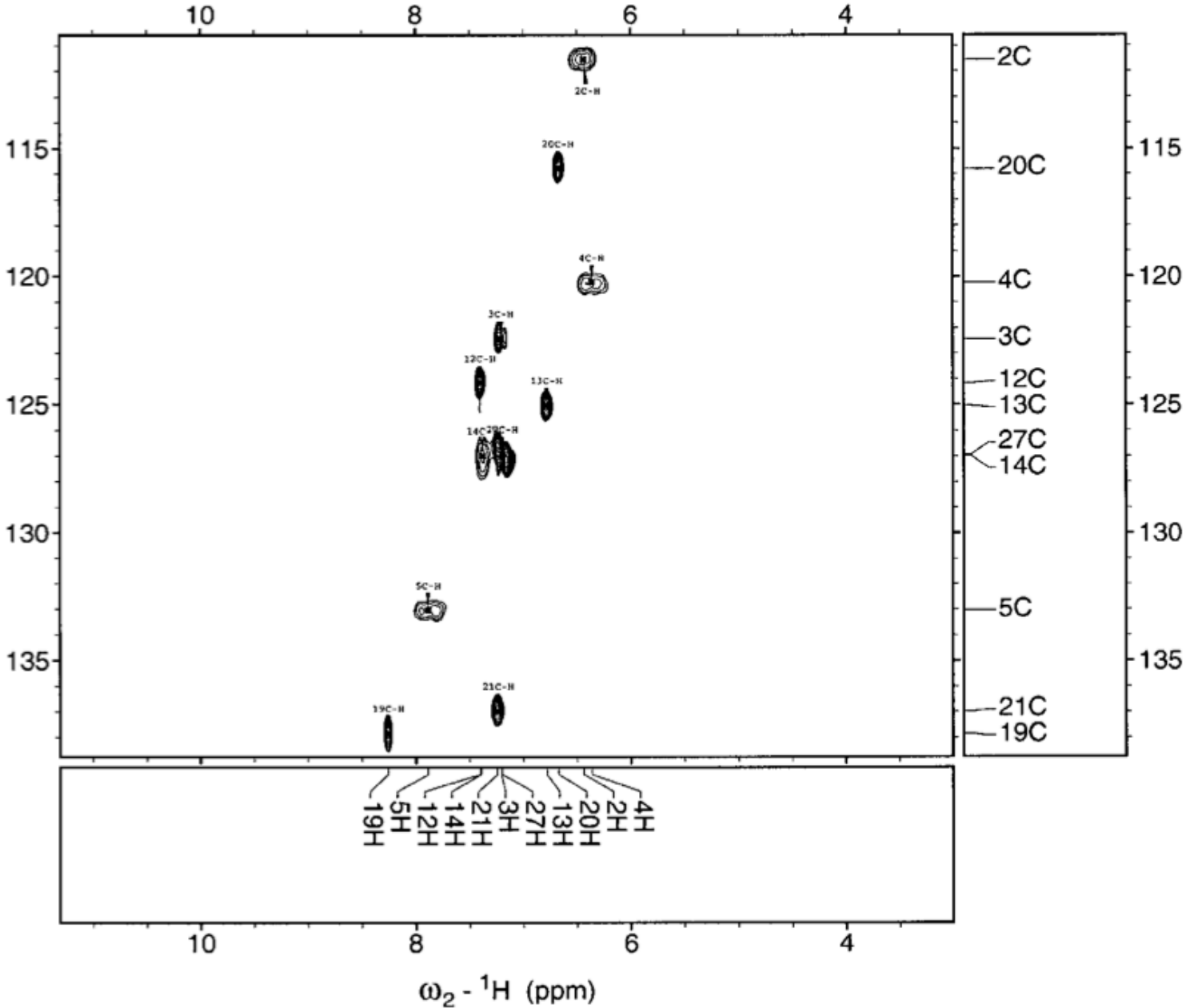
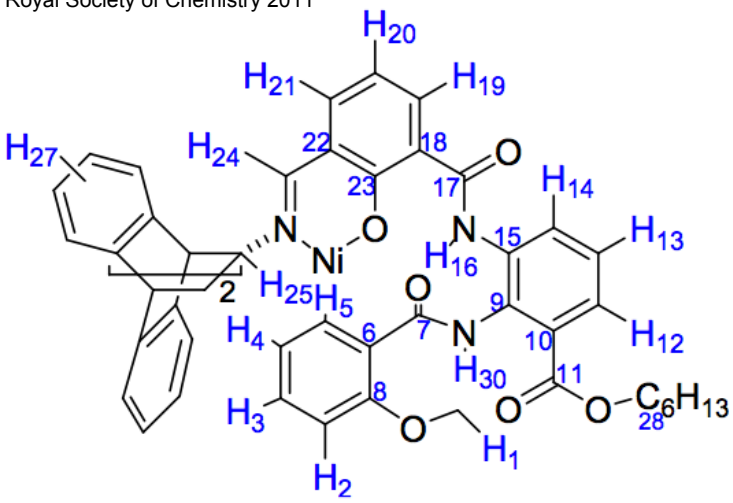


HSQC spectrum of **6** (400MHz, $CDCl_3$)



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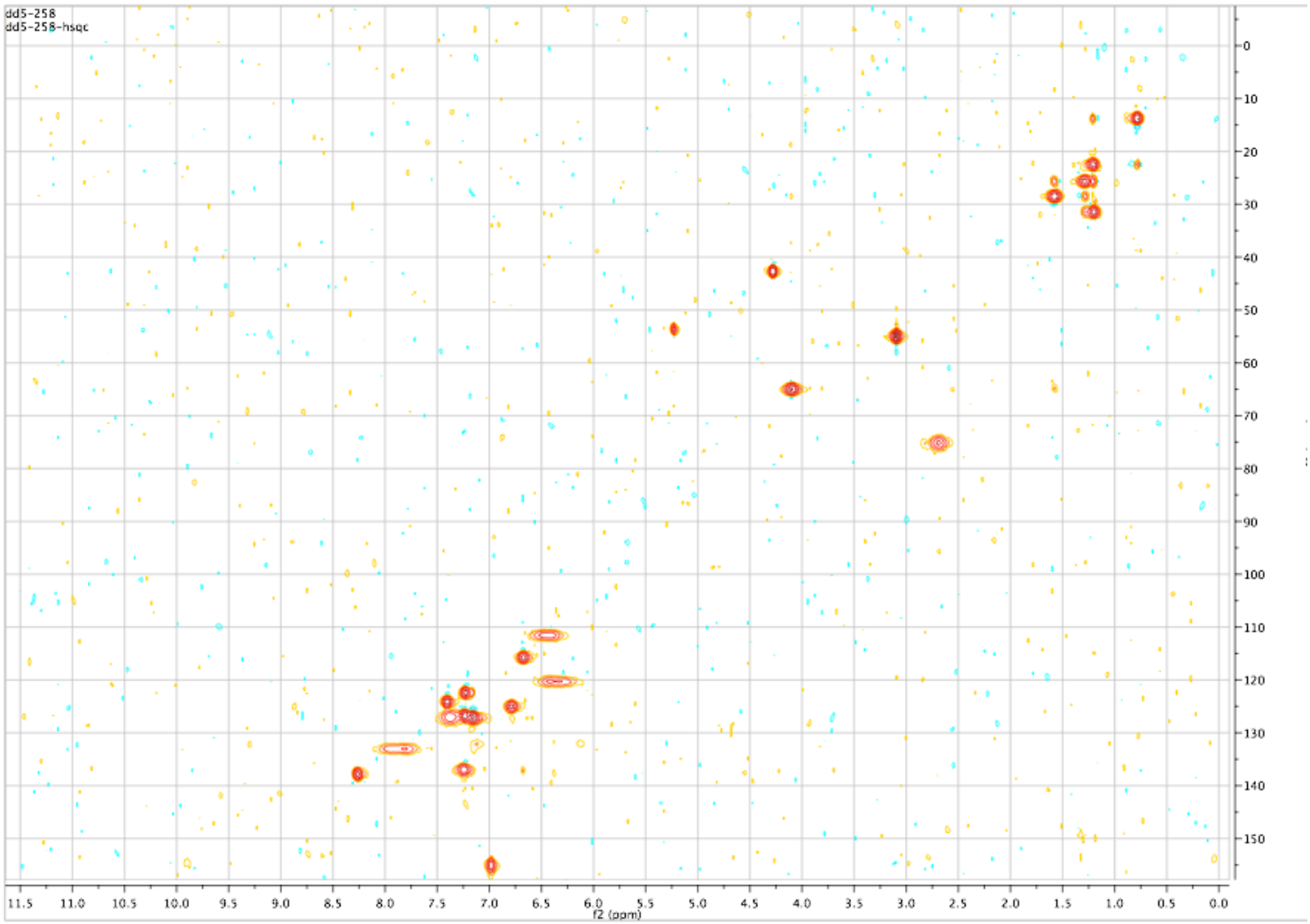
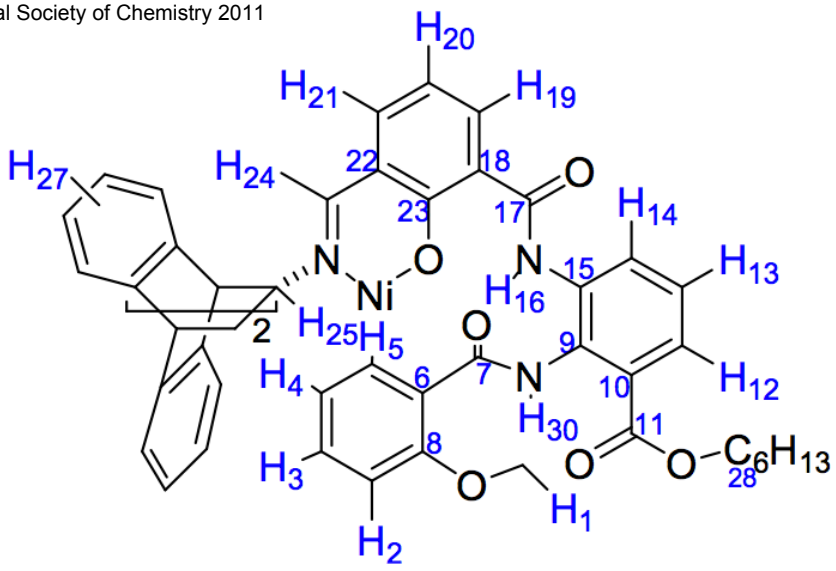
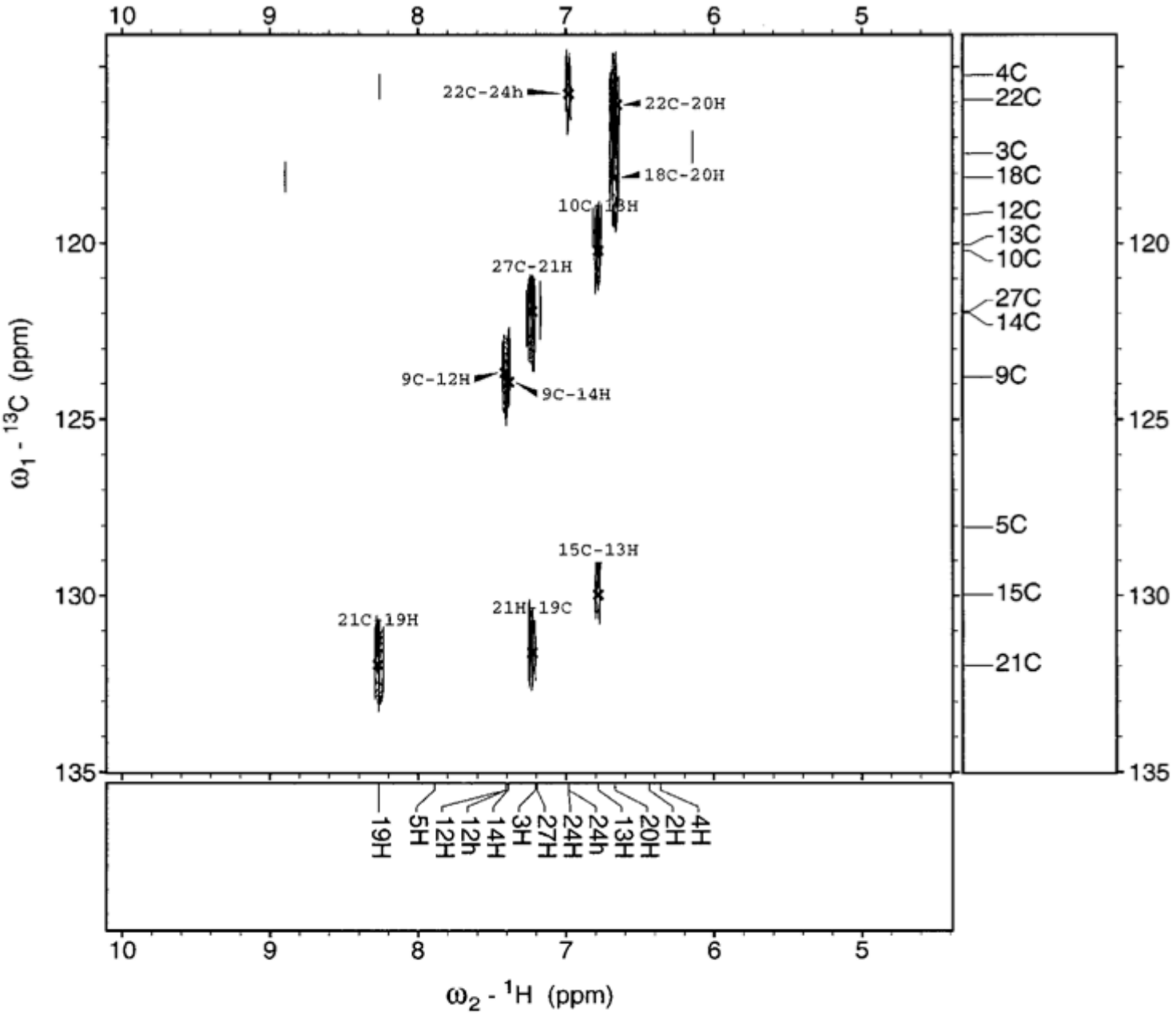


HMBC spectrum of **6** (400MHz, $CDCl_3$)





Variable temperature

^{1}H NMR spectrum of **6** (400MHz, CD_2Cl_2)