Heteroligated Pt^{II} Weak-Link Approach Complexes Using Hemilabile *N*-Heterocyclic Carbene-Thioether and Phosphino-Thioether Ligands

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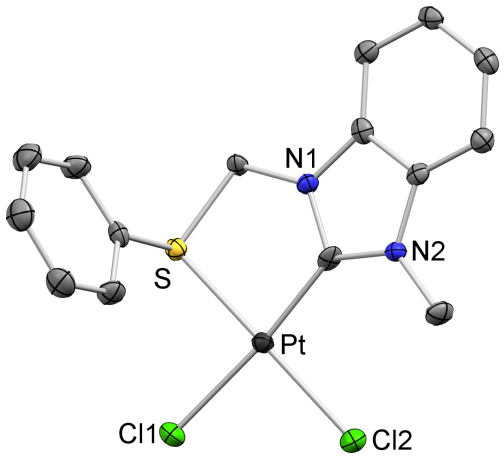
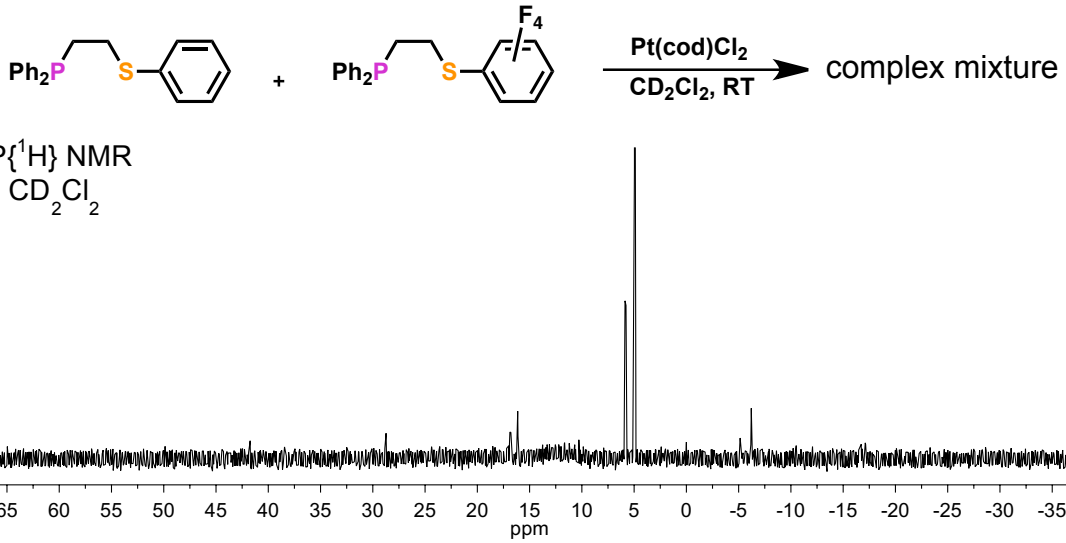
Structure of Monoligated Complex 2 determined by single crystal X-ray diffraction

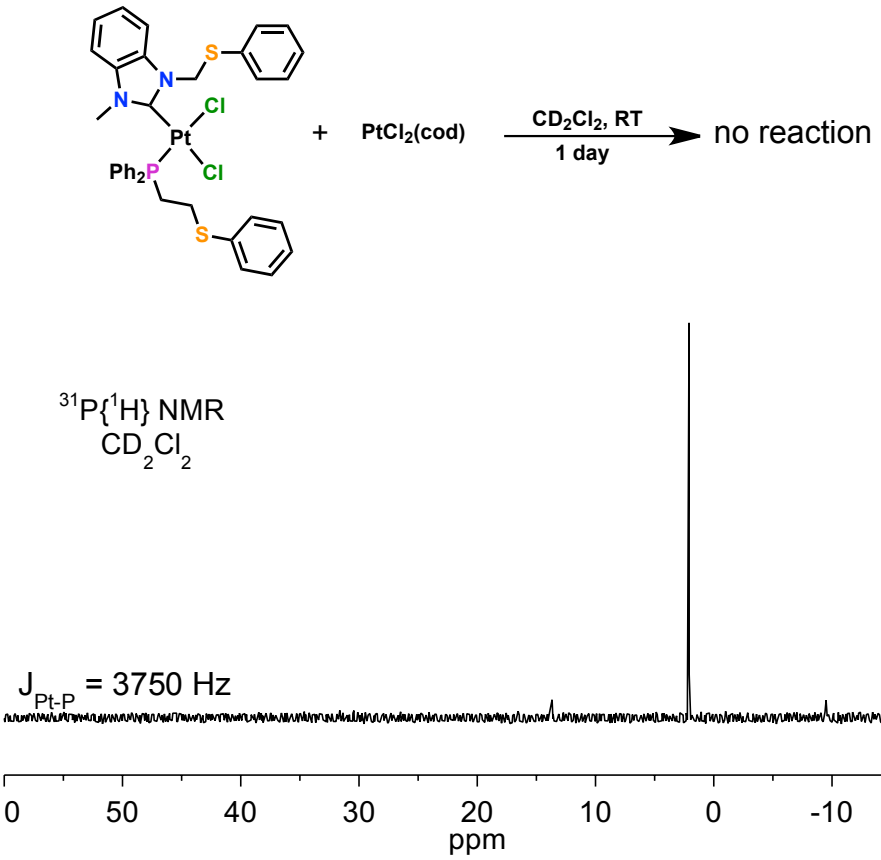


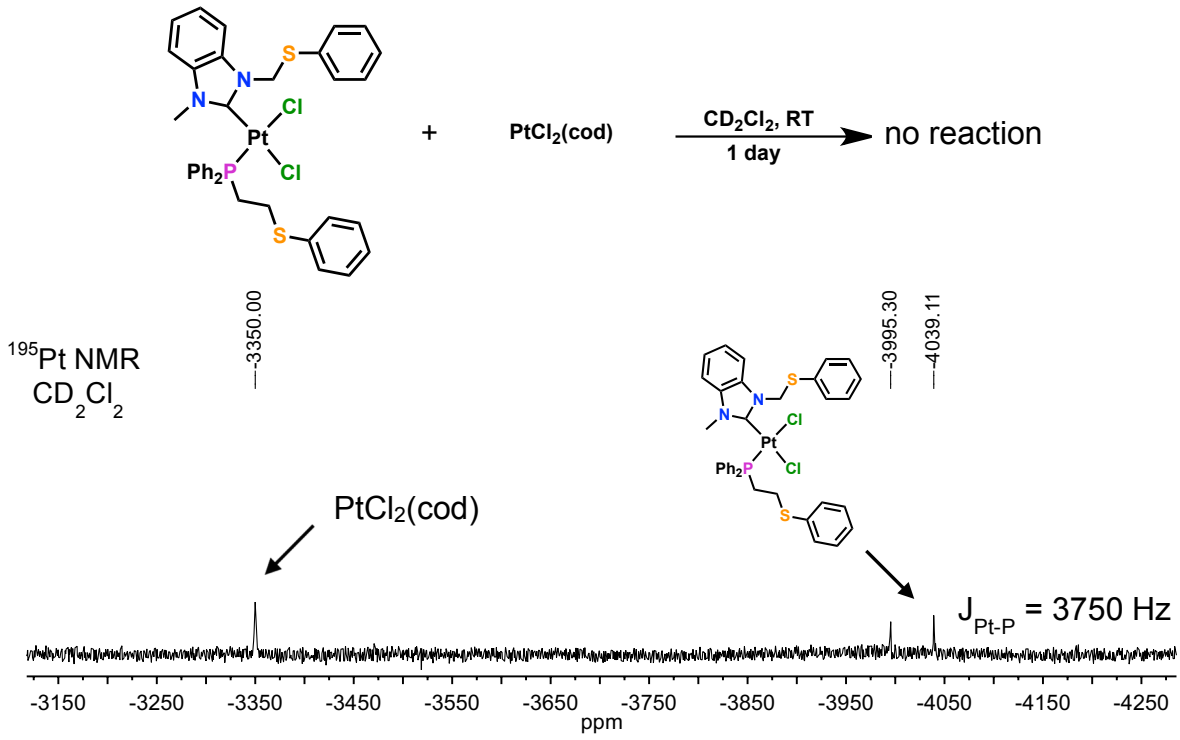
$^{31}P\{^{1}H\}$ NMR spectrum of ligand scrambling in WLA complexes with P,X ligands in CD_2Cl_2



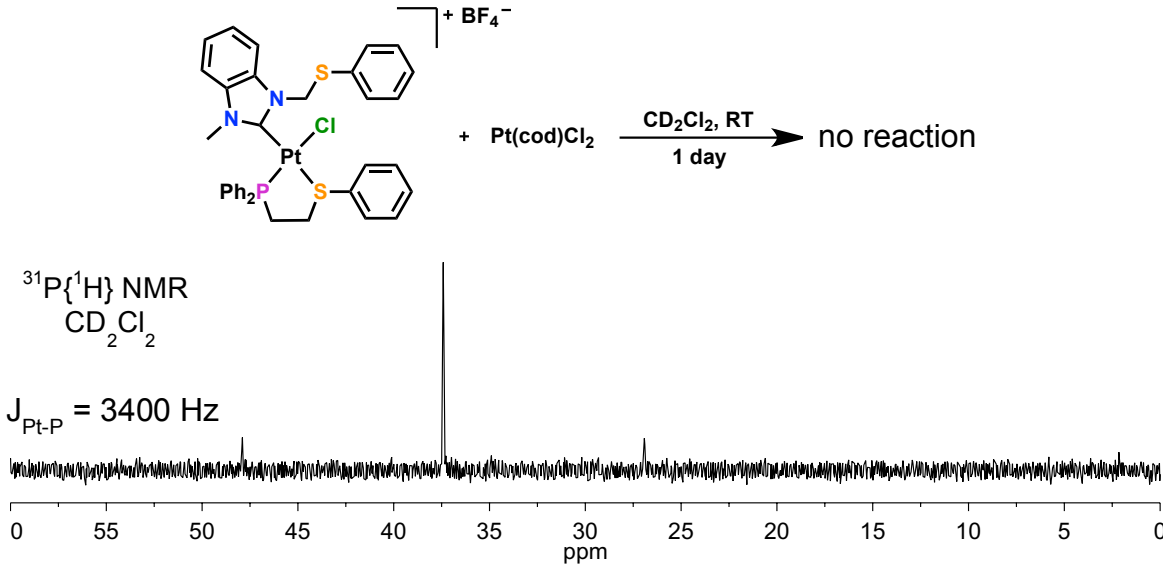
The complex mixture likely comprises the two homoligated species (i.e. $[(\kappa^2\text{-}Ph_2PCH_2CH_2S\text{-}C_6H_5)(\kappa^1\text{-}Ph_2PCH_2CH_2S\text{-}C_6H_5)PtCl]^+BF_4^-$ and $[(\kappa^2\text{-}Ph_2PCH_2CH_2S\text{-}C_6HF_4)(\kappa^1\text{-}Ph_2PCH_2CH_2S\text{-}C_6HF_4)PtCl]^+BF_4^-$) the desired heteroligated species, $[(\kappa^2\text{-}Ph_2PCH_2CH_2S\text{-}C_6H_5)(\kappa^1\text{-}Ph_2PCH_2CH_2S\text{-}C_6HF_4)PtCl]^+BF_4^-$.

NMR spectra of competition experiments: Fully open tweezer complex 4 + $PtCl_2(cod)$



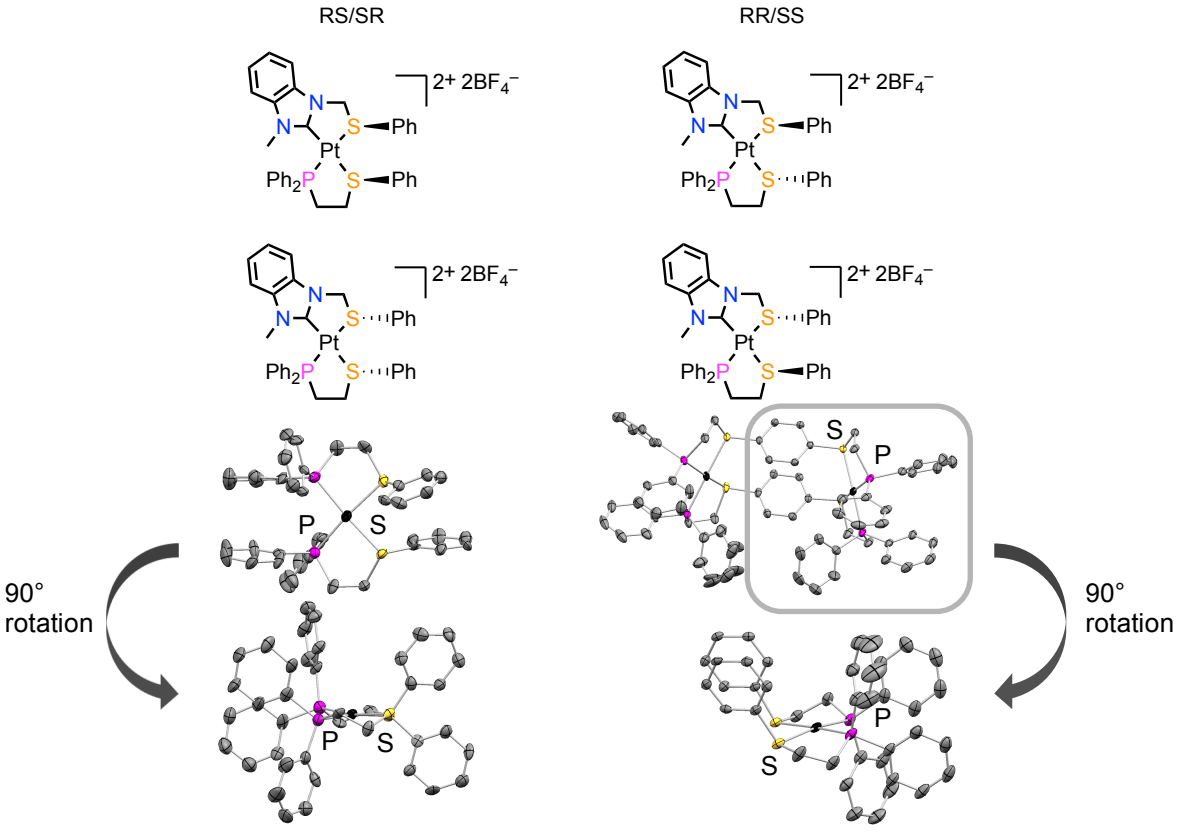


NMR spectra of competition experiments: Semiopen tweezer complex 5 + $PtCl_2(cod)$

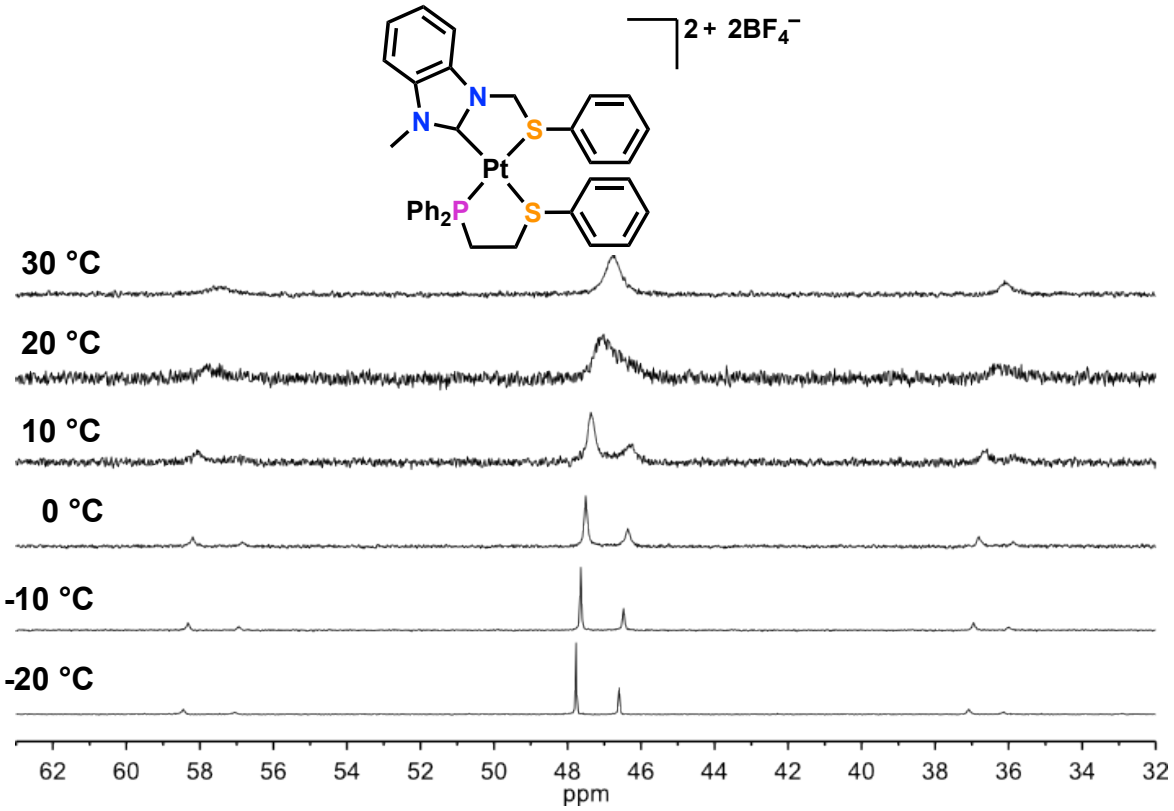


Depiction of the Possible Diastereomers of Closed Tweezer Complex 7

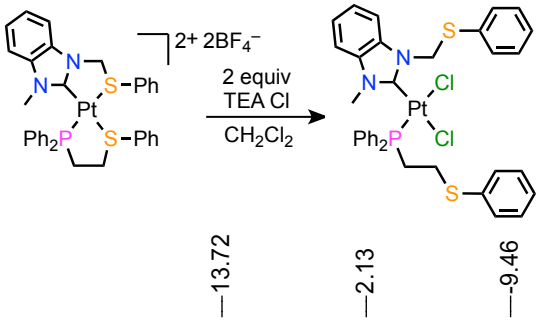
The left-hand column depicts the RR and SS enantiomer pair, and the right-hand column depicts the RS and SR enantiomer pair. In the case of the RR/SS stereoisomers, the substituents on the thioethers extend on opposite sides of the square planar Pt^{II} center (crystal structure from *Inorg. Chem.*, 2013, **52**, 5876). On the other hand, in the case of the RS/SR stereoisomers, the substituents on the thioethers extend on the same side of the square planar Pt^{II} center (crystal structure from *Inorg. Chem.*, 2013, **52**, 5876).



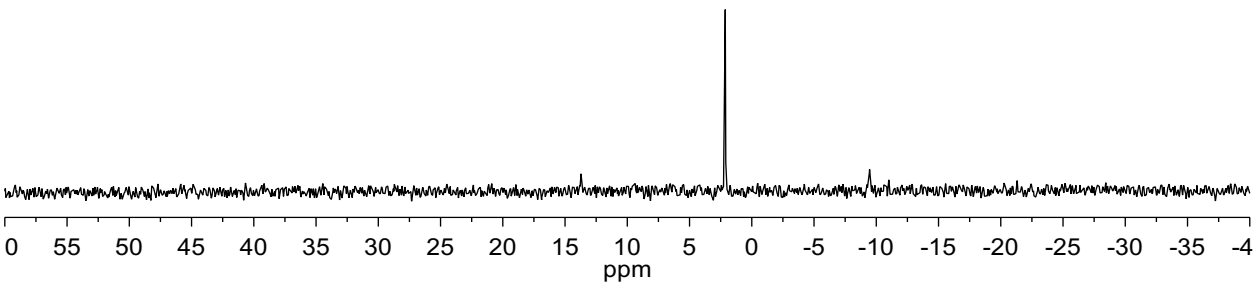
Variable Temperature $^{31}P\{^{1}H\}$ NMR Spectra of Closed Tweezer Complex 7 in CD_2Cl_2



$^{31}P\{^{1}H\}$ NMR spectrum of fully open tweezer complex 4 from closed tweezer complex 7



$^{31}P\{^{1}H\}$ NMR
CD_2Cl_2



Synthesis of all compounds

General Methods/Instrument Details. The syntheses of platinum(II) complexes and all manipulations were done under ambient conditions. All solvents were anhydrous grade, purchased from Sigma-Aldrich, and used as received unless otherwise noted. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. The P,S–phenylene–S,P ligand[1] and the P,S–Ph ligand[2] were prepared according to literature procedures or adaptations thereof. All other chemicals were purchased from Aldrich Chemical Co. and were used as received. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ^{1}H NMR spectra were referenced internally to residual protons in the deuterated solvents (dichloromethane-d_2 = δ 5.32; nitromethane-d_3 = δ 4.33; methanol-d_4 = δ 3.31). ^{31}P{^{1}H} NMR spectra were referenced to an external 85% H_3PO_4 standard (δ 0). Electrospray ionization (ESI) mass spectra were recorded on an Agilent 6120 LC-TOF instrument in positive ion mode. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ. It should be noted that the inability to obtain accurate elemental analysis in Pt-containing complexes results is known in the literature. This is likely due to incomplete combustion and the formation of platinum hydroxide and/or platinum carbides as byproducts, thus decreasing the experimental values of the carbon and hydrogen content, as observed experimentally in some samples (*Inorg. Chem.*, **1993**, *32*, 1951).

Synthesis of Ligand 1. To an oven-dried flask equipped with a stir bar, 5 g chloromethylphenyl sulfide was added. It was dissolved in 10 mL acetone that had been dried over molecular sieves). 4.165 g 1-methylbenzimidazole was then dissolved in 20 mL dried acetone and was slowly added to the solution of the chloromethylphenyl sulfide. The resulting solution was refluxed overnight. The white precipitate was filtered, thoroughly washed with acetone, and dried (isolated yields = 54%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 11.77 – 11.28 (s, 1H), 7.86 – 7.06 (m, 9H), 6.30 – 6.04 (s, 2H), 4.18 – 4.03 (s, 3H). HRMS (ESI+) *m/z* Calcd for $[M - Cl^-]^+$: 255.0950. Found: 255.0964

Synthesis of Monoligated Complex 2. $PtCl_2$(cod) (0.17 mmol, 64.3 mg, 1 equiv) was added to a solution of imidazolium salt **1** (0.17 mmol, 50.0 mg, 1 equiv) in dichloromethane (10 mL). After 10 minutes, Ag_2O (0.086 mmol, 19.9 mg, 0.5 equiv) was added and the reaction mixture was shielded from light and stirred overnight. The solvent was reduced to ca. 1 mL *in vacuo* and 10 mL of hexanes was added, precipitating a pale yellow solid. The solid was filtered and washed with diethyl ether (5 mL) to afford monoligated complex **2** (isolated yields = 54%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.90 – 7.12 (m, 9H), 5.68 – 5.46 (d, J = 12.1 Hz, 1H), 5.12 – 4.90 (d, $J_{H–H}$ = 12.0 Hz, $J_{H–Pt}$ = 48 Hz, 1H), 4.39 – 4.33 (s, 3H). ^{195}Pt NMR (86 MHz, CD_2Cl_2) δ -3464.52. Anal. Calcd for $C_{15}H_{14}Cl_2N_2PtS$: C 34.62, H 2.71, N 5.38. Found: C 34.90, H 2.64, N 5.25. HRMS (ESI+) *m/z* Calcd for $[M - Cl^-]^+$: 485.0198. Found: 485.0200. Single crystals suitable for X-ray diffraction studies were obtained by layering diethyl ether over a dichloromethane solution of complex **2**.

Synthesis of Fully Open Tweezer Complex 4. A solution of ligand **3** (0.023 mmol, 12.8 mg, 1 equiv) in dichloromethane (2 mL) was added in a dropwise manner to a suspension of monoligated complex **2** (0.045 mmol, 23.6 mg, 2 equiv) in dichloromethane (2 mL). After 20 minutes, hexanes (10 mL) was added, precipitating the fully open tweezer complex **4** as an off-

white solid. (*in situ* yields (by $^{31}P\{^{1}H\}$ NMR spectroscopy) = 100%, isolated yields > 95%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.65 – 6.97 (m, 23H), 6.75 – 6.68 (d, J = 8.2 Hz, 1H), 6.09 – 6.01 (d, J = 13.7 Hz, 1H), 5.75 – 5.67 (d, J = 13.7 Hz, 1H), 3.71 – 3.66 (s, 2H), 3.55 – 3.41 (m, 1H), 3.38 – 3.24 (m, 1H), 3.12 – 2.87 (m, 2H). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ 2.18 (s, $J_{P–Pt}$ = 3750 Hz). Anal. Calcd for $C_{35}H_{33}Cl_2N_2PPtS_2$: C 49.88, H 3.95, N 3.32. Found: C 50.01, H 4.20, N 3.23. HRMS (ESI+) *m/z* Calcd for $[M – Cl^–]^+$: 807.1149. Found: 807.1155.

Synthesis of Semiopen Tweezer Complex 5. Excess $NaBF_4$ (0.149 mmol, 16.6 mg, 3 equiv) was added to a solution of fully open complex **4** (0.037 mmol, 59.8 mg, 1 equiv) in methanol (2 mL). After 20 minutes, a large amount of precipitate was observed. The solution was filtered and the precipitate was washed with hexanes (10 mL) to yield semiopen tweezer complex **5** as an off-white solid. Alternatively, to a solution of fully open complex **4** (0.0063 mmol, 5.3 mg, 1 equiv), $AgBF_4$ (0.0063 mmol, 1.22 mg, 1 equiv) was added. The resulting mixture was shielded from light and allowed to stir overnight. The mixture was then filtered through celite and hexanes (10 mL) was added, precipitating the semiopen tweezer complex **5** as an off-white solid (*in situ* yields (by $^{31}P\{^{1}H\}$ NMR spectroscopy) = 100%, isolated yields > 95%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.11 – 7.99 (m, 2H), 7.77 – 7.13 (m, 21H), 6.87 – 6.77 (d, J = 8.2 Hz, 1H), 5.56 – 5.17 (bs, 2H), 3.95 – 3.53 (s, 3H), 3.41 – 2.82 (m, 4H). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ 37.47 (s, $J_{P–Pt}$ = 3400 Hz). Anal. Calcd for $C_{35}H_{33}BClF_4N_2PPtS_2$: C 47.02, H 3.72, N 3.13. Found: C 45.76, H 3.78, N 2.46. HRMS (ESI+) *m/z* Calcd for $[M – BF_4^–]^+$: 807.1149 Found: 807.1162. Single crystals suitable for X-ray diffraction studies were obtained by layering pentane over a dichloromethane solution of complex **5**.

Synthesis of Semiopen Tweezer Complex 6. The fully open complex **4** (0.015 mmol, 12.6 mg, 1 equiv) was dissolved in CD_3OD (2 mL) (*in situ* yields (by $^{31}P\{^{1}H\}$ NMR spectroscopy) = 100%). $^{31}P\{^{1}H\}$ NMR (162 MHz, MeOD) δ 37.51 (s, $J_{P–Pt}$ = 3430 Hz). HRMS (ESI+) *m/z* Calcd for $[M – Cl^–]^+$: 807.1149. Found: 807.1158.

Synthesis of Fully Closed Tweezer Complex 7. A solution of ligand **3** (0.043 mmol, 13.9 mg, 1 equiv) in dichloromethane (2 mL) was added in a dropwise manner to a suspension of monoligated complex **2** (0.043 mmol, 22.5 mg, 1 equiv) in dichloromethane (2 mL). After 20 minutes, $AgBF_4$ (0.086 mmol, 16.8 mg, 2 equiv) was added and the reaction mixture was shielded from light and stirred overnight. The mixture was then filtered through celite. Hexanes (10 mL) was added, precipitating the fully closed tweezer complex **7** as an off-white solid. (*in situ* yields (by $^{31}P\{^{1}H\}$ NMR spectroscopy) = 100%, isolated yields > 95%). Closed tweezer complex **7** can also be synthesized directly from semiopen triple layer complex **5** by adding 1 equiv AgBF4 to a solution of complex **5** in CH_2Cl_2. The resulting mixture is then treated in the same manner as described above. ^{1}H NMR (400 MHz, CD_3NO_2) δ 8.75 – 6.90 (m, 24H), 6.20 – 5.71 (m, 2H), 3.85 – 2.47 (s, 7H). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ 46.77 (bs, $J_{P–Pt}$ = 3460 Hz). Anal. Calcd for $C_{35}H_{33}B_2F_8N_2PPtS_2$: C 44.46, H 3.52, N 2.96. Found: C 43.82, H 3.18, N 2.46. HRMS (ESI+) *m/z* Calcd for $[M – 2BF_4^– + Cl^–]^+$: 807.1149. Found: 807.1159. Single crystals suitable for X-ray diffraction studies were obtained by layering diethyl ether over a dichloromethane solution of complex **7**.

Synthesis of Fully Open Triple Layer Complex 11. A solution of the P,S-phenylene-S,P ligand[1] (0.023 mmol, 12.8 mg, 1 equiv) in dichloromethane (2 mL) was added in a dropwise

manner to a suspension of monoligated complex **2** (0.045 mmol, 23.6 mg, 2 equiv) in dichloromethane (2 mL). After 20 minutes, hexanes (10 mL) was added, precipitating the fully open triple-decker complex **4** as an off-white solid. (*in situ* yields (by $^{31}P\{^{1}H\}$ NMR spectroscopy) = 100%, isolated yields > 95%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.64 – 6.97 (m, 42H), 6.74 – 6.67 (d, J = 8.2 Hz, 2H), 6.09 – 6.01 (d, J = 13.6 Hz, 2H), 5.75 – 5.67 (d, J = 13.1 Hz, 2H), 3.71 – 3.66 (s, 6H), 3.58 – 3.44 (m, 2H), 3.41 – 3.25 (m, 2H), 3.13 – 2.88 (m, 4H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 2.29 (s, $J_{P–Pt}$ = 3750 Hz). Anal. Calcd for $C_{64}H_{60}Cl_4N_4P_2Pt_2S_4$: C 47.82, H 3.76, N 3.49. Found: C 47.94, H 3.62, N 3.32. HRMS (ESI+) *m/z* Calcd for $[M - Cl^-]^+$: 1571.1511. Found: 1571.1522.

Synthesis of Semiopen Triple Layer Complex 12. Excess $NaBF_4$ (0.149 mmol, 16.6 mg, 4 equiv) was added to a solution of fully open complex **12** (0.037 mmol, 59.8 mg, 1 equiv) in methanol (2 mL). After 20 minutes, hexanes (10 mL) was added, precipitating the semiopen triple-decker complex **13** as an off-white solid. (*in situ* yields (by $^{31}P\{^{1}H\}$ NMR spectroscopy) = 100%, isolated yields > 95%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.50 – 6.45 (m, 42H), 5.76 – 5.40 (s, 4H), 4.21 – 2.67 (m, 14H). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ 38.00 (bs, $J_{P–Pt}$ = 3370 Hz), 37.86 (bs, $J_{P–Pt}$ = 3380 Hz). Anal. Calcd for $C_{64}H_{60}B_2Cl_2F_8N_4P_2Pt_2S_4$: C 44.95, H 3.54, N 3.28. Found: C 43.79, H 3.25, N 3.09. HRMS (ESI+) *m/z* Calcd for $[M - BF_4^-]^+$: 1623.1867. Found: 1623.1841.

Synthesis of Fully Closed Triple Layer Complex 13. A solution of the P,S-phenylene-S,P (0.022 mmol, 12.3 mg, 1 equiv) in dichloromethane (2 mL) was added in a dropwise manner to a suspension of monoligated complex **2** (0.043 mmol, 22.6 mg, 2 equiv) in dichloromethane (2 mL). After 20 minutes, $AgBF_4$ (0.086 mmol, 16.9 mg, 4 equiv) was added and the reaction mixture was shielded from light and stirred overnight. The mixture was then filtered through celite. Hexanes (10 mL) was added, precipitating the fully closed triple-decker complex **13** as an off-white solid. (*in situ* yields (by $^{31}P\{^{1}H\}$ NMR spectroscopy) = 100%, isolated yields > 95%). Closed triple layer complex **13** can also be synthesized directly from semiopen triple layer complex **12** by adding 1 equiv AgBF4 to a solution of complex **12** in CH_2Cl_2. The resulting mixture is then treated in the same manner as described above. ^{1}H NMR (400 MHz, CD_3NO_2) δ 8.62 – 6.99 (m, 42H), 6.25 – 5.71 (bs, 4H), 3.60 – 3.47 (s, 6H), 3.46 – 2.55 (m, 8H). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_3NO_2) δ 50.43 (bs, $J_{P–Pt}$ = 3360 Hz). Anal. Calcd for $C_{64}H_{60}B_4F_{16}N_4P_2Pt_2S_4$: C 42.40, H 3.34, N 3.09. Found: 37.24, H 2.96, N 2.53. HRMS (ESI+) *m/z* Calcd for $[M - 3BF_4^- + 2Cl^-]^+$: 1623.1867. Found: 1623.1868.

Synthesis of Fully Open Tweezer Complex 4 from Fully Closed Tweezer Complex 7. To a solution of fully closed complex **7** (0.023 mmol, 21.47 mg, 1 equiv) in dichloromethane-d_2 (1 mL), tetraethylammonium chloride (0.045 mmol, 7.52 mg, 2 equiv) in dichloromethane-d_2 (0.5 mL) was added. The solution was stirred for 5 minutes, resulting in the synthesis of fully open tweezer complex **4** (*in situ* yields (by $^{31}P\{^{1}H\}$ NMR spectroscopy) = 100%).

X-ray Crystallography. Single crystals were mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated Mo Kα or Cu Kα radiation. Data were collected using Bruker APEXII detector and processed using APEX2 from Bruker. All structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were

included in idealized positions, but not refined. Their positions were constrained relative to their parent atom.

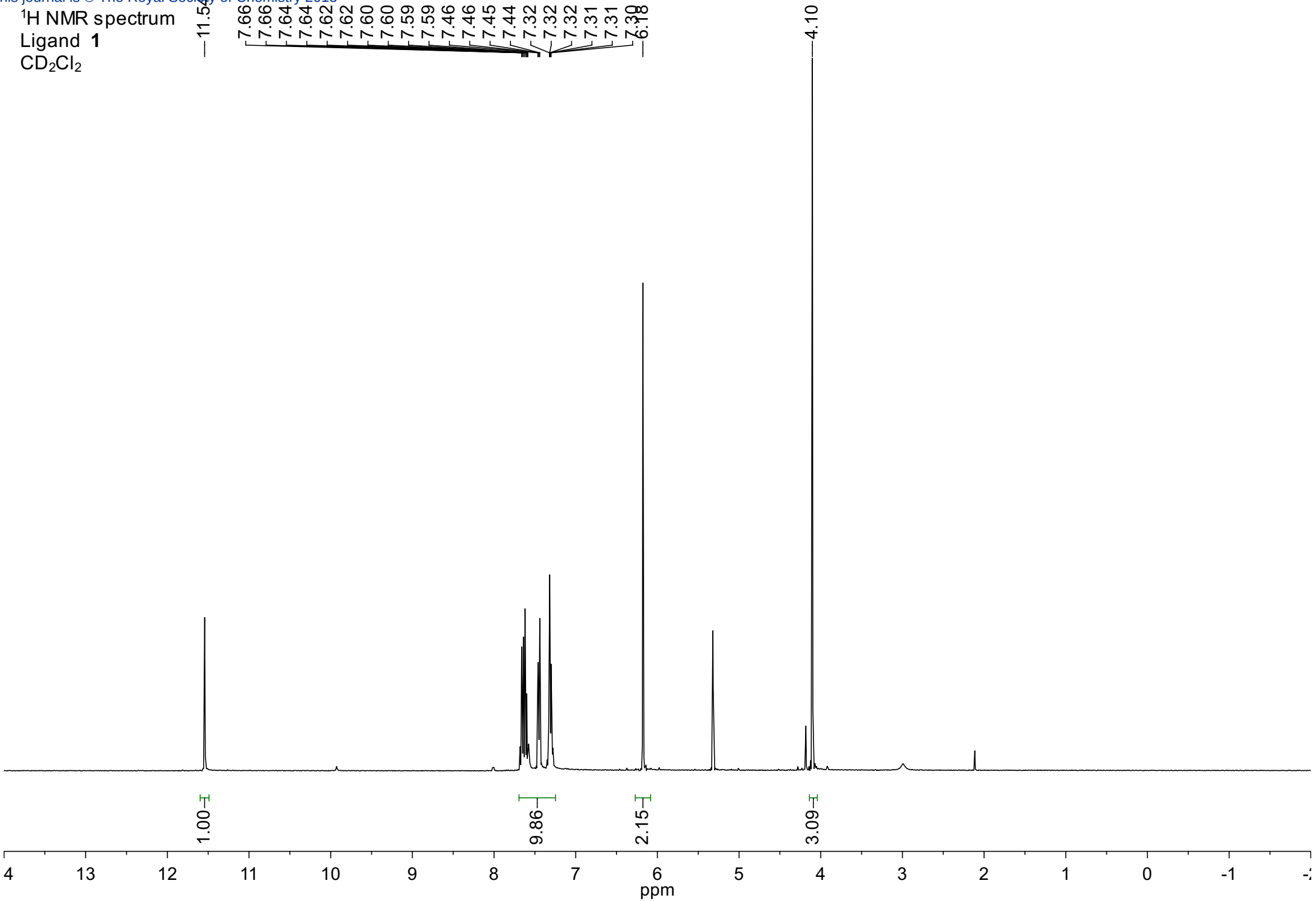
Crystal Data and Structure Refinement

	2	**5**	**7**
formula	$C_{31}H_{30}Cl_6N_4Pt_2S_2$	$C_{35}H_{33}BClF_4N_2PPtS_2$	$C_{35}H_{33}B_2F_8N_2PPtS_2$
FW	1125.59	894.07	945.43
color, habit	Colorless block	Colorless block	Colorless block
cryst dimens [mm]	0.173 x 0.135 x 0.059	0.239 x 0.202 x 0.061	0.311 x 0.153 x 0.118
cryst syst	Triclinic	Triclinic	Monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	9.6661(3)	9.4153(5)	10.2950(3)
b [Å]	13.0872(4)	12.0408(7)	9.8283(3)
c [Å]	15.6977(5)	16.6958(10)	34.0318(11)
α [deg]	111.0290(10)	102.425(3)	90
β [deg]	90.5750(10)	100.136(3)	94.6700(10)
γ [deg]	108.6830(10)	104.304(2)	90
V [Å^3]	1738.24(9)	1737.82(17)	3431.99(18)
Z	2	2	4
ρ_{calcd}	2.151	1.709	1.830
radiation (λ, D [Å])	Cu Kα (1.54178)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ [mm^{-1}]	0.5894	4.330	4.331
T [K]	100(2)	100(2)	100(2)
F(000)	1068	880	1856
min/max transmn	0.4320/0.7526	0.5894/0.5894	0.3193/0.7460
2θ range [deg]	9.76 to 126.66	2.58 to 60.44	4.314 to 60.072
reflns collected	12847	56611	36515
R_{int}	0.0259	0.0340	0.0438
data/retraints/params	5716/0/408	10237/0/425	10001/0/461
final R indices [$I^2 > 2\sigma(I)$]	R_1 = 0.0377, wR_2 = 0.0966	R_1 = 0.0243, wR_2 = 0.0510	R_1 = 0.0380, wR_2 = 0.0823
R indices [all data]	R_1 = 0.0384, wR_2 = 0.0971	R_1 = 0.0313, wR_2 = 0.0546	R_1 = 0.0398, wR_2 = 0.0829
GOF (F^2)	1.166	1.058	1.285
largest diff peak/hole [e Å^{-3}]	3.220/-1.453	0.972/-0.989	2.637/-1.903

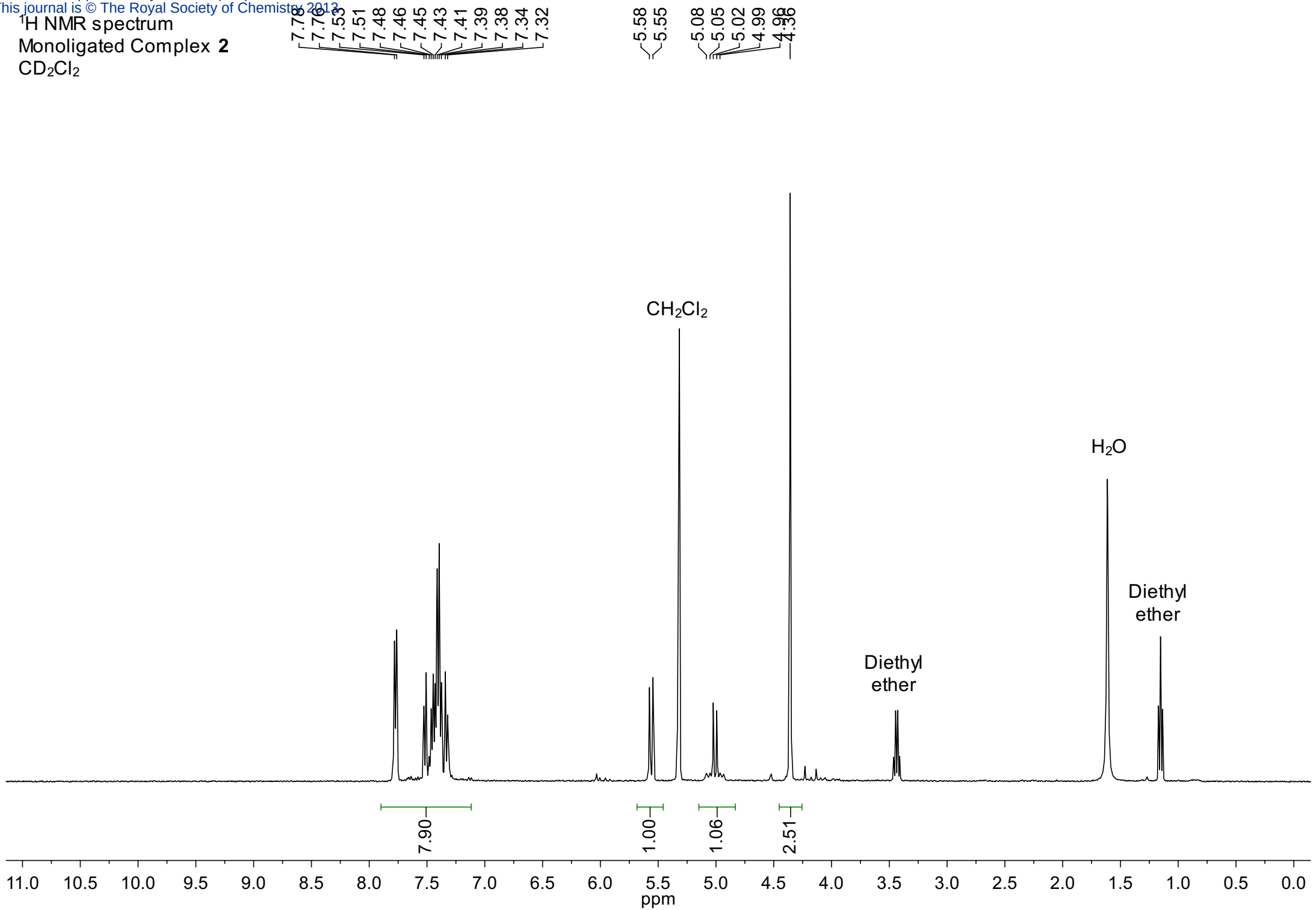
References

1. Farrell, J. R.; Mirkin, C. A.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *Angew. Chem. Int. Ed.* **1998,** *37,* 465.
2. P. A. Ulmann, A. M. Brown, M. V. Ovchinnikov, C. A. Mirkin, A. G. DiPasquale and A. L. Rheingold, *Chem.--Eur. J.*, 2007, **13**, 4529-4534

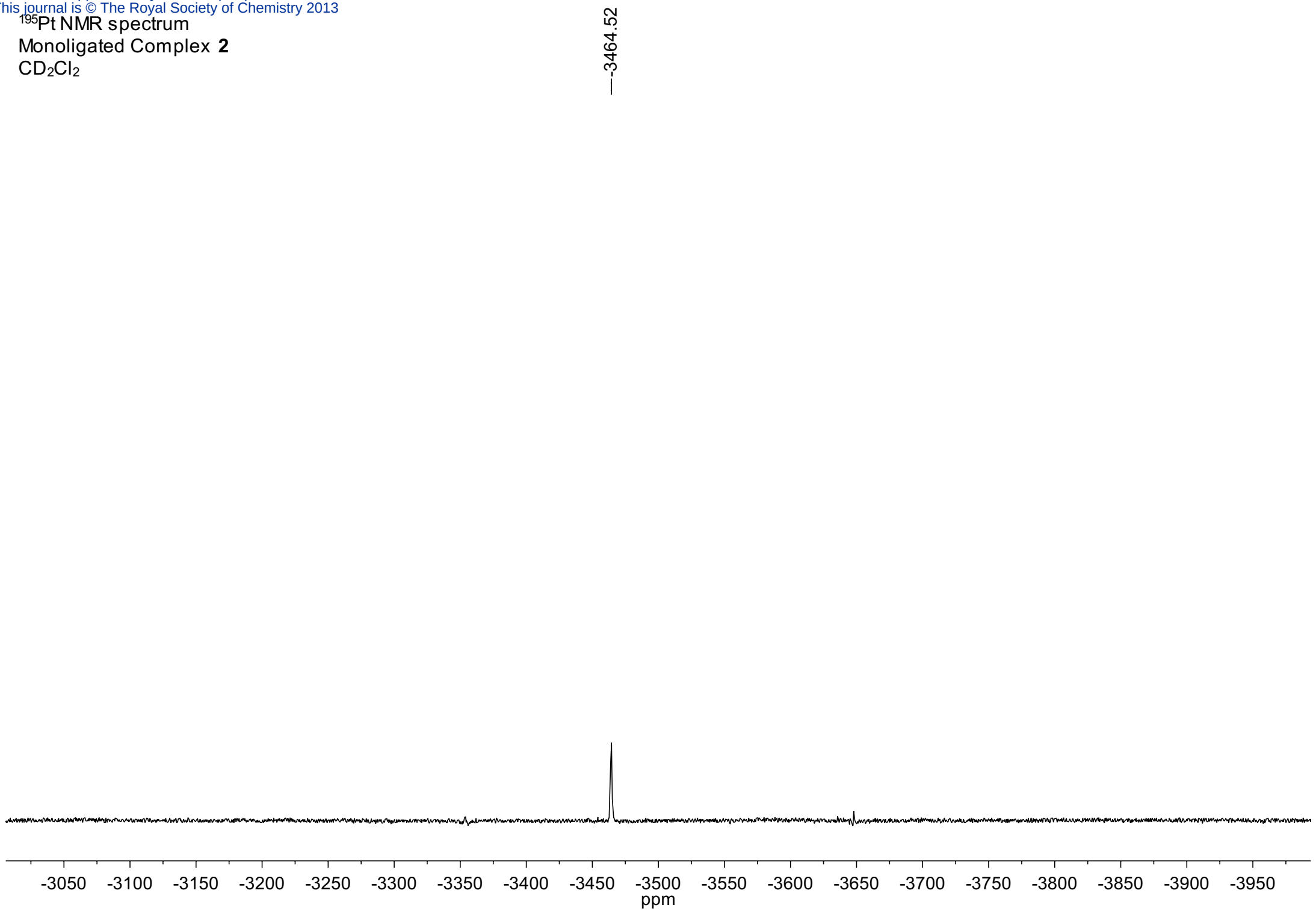
^{1}H NMR spectrum
Ligand **1**
CD_2Cl_2



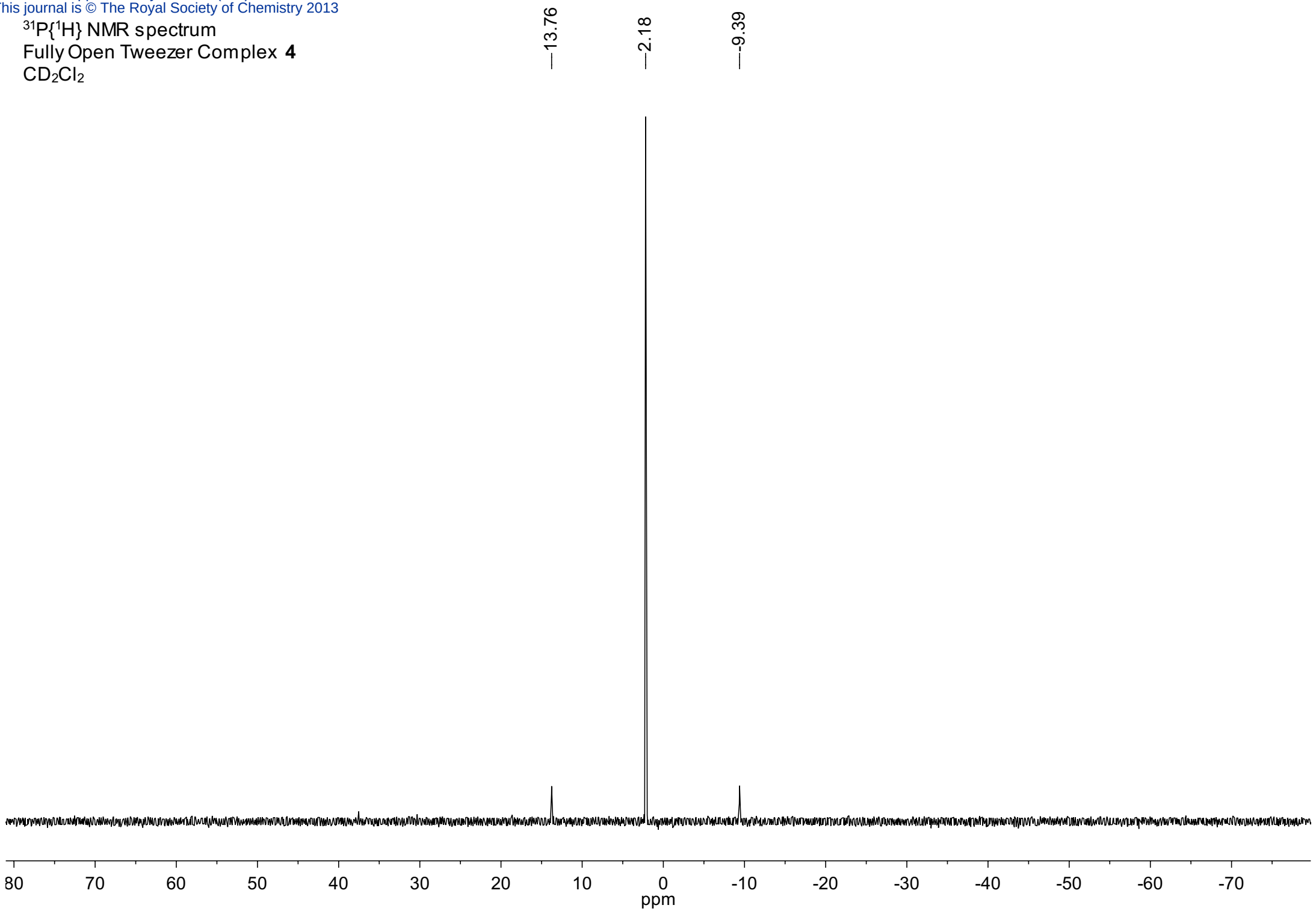
^{1}H NMR spectrum
Monoligated Complex **2**
CD_2Cl_2

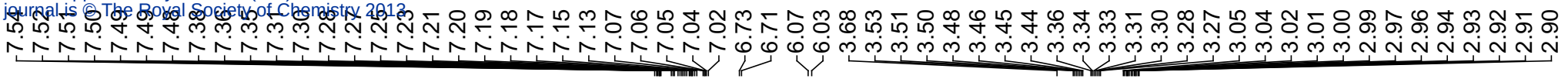


^{195}Pt NMR spectrum
Monoligated Complex **2**
CD_2Cl_2

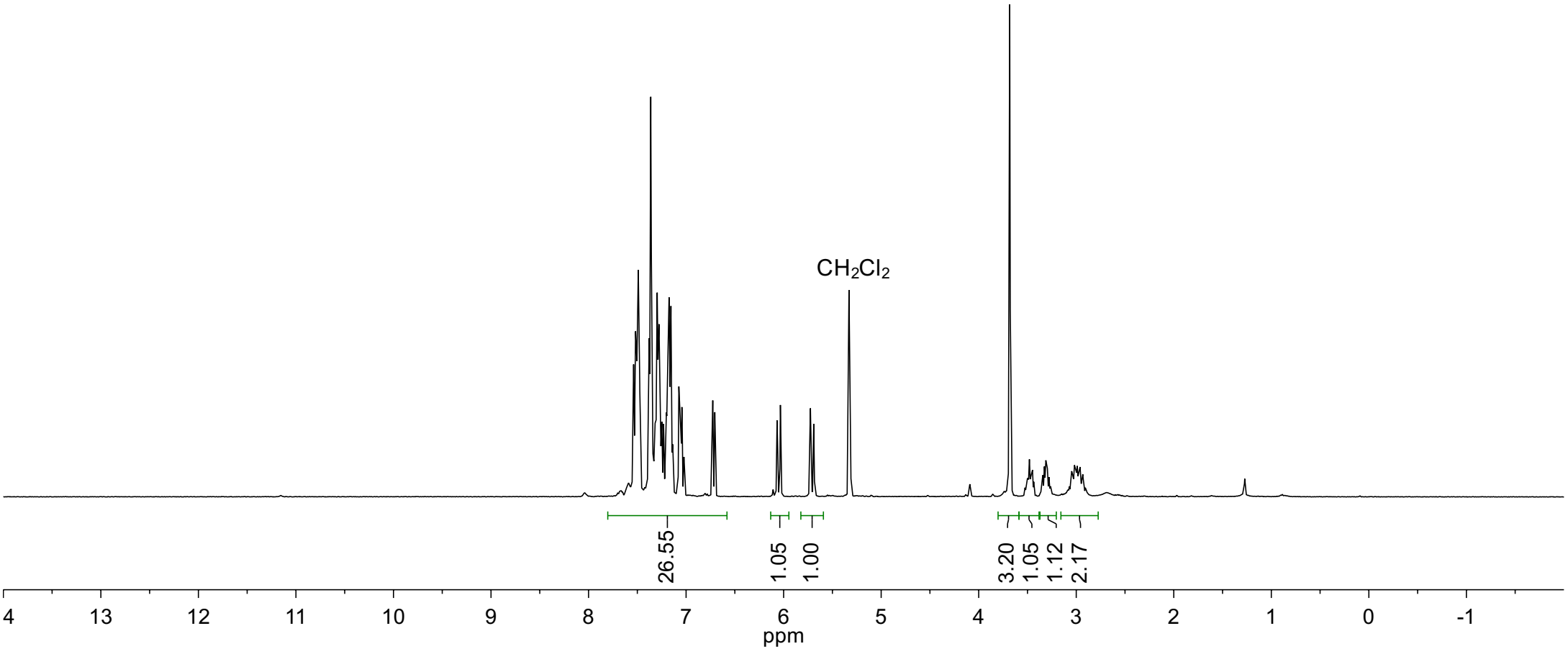


$^{31}P\{^{1}H\}$ NMR spectrum
Fully Open Tweezer Complex **4**
CD_2Cl_2

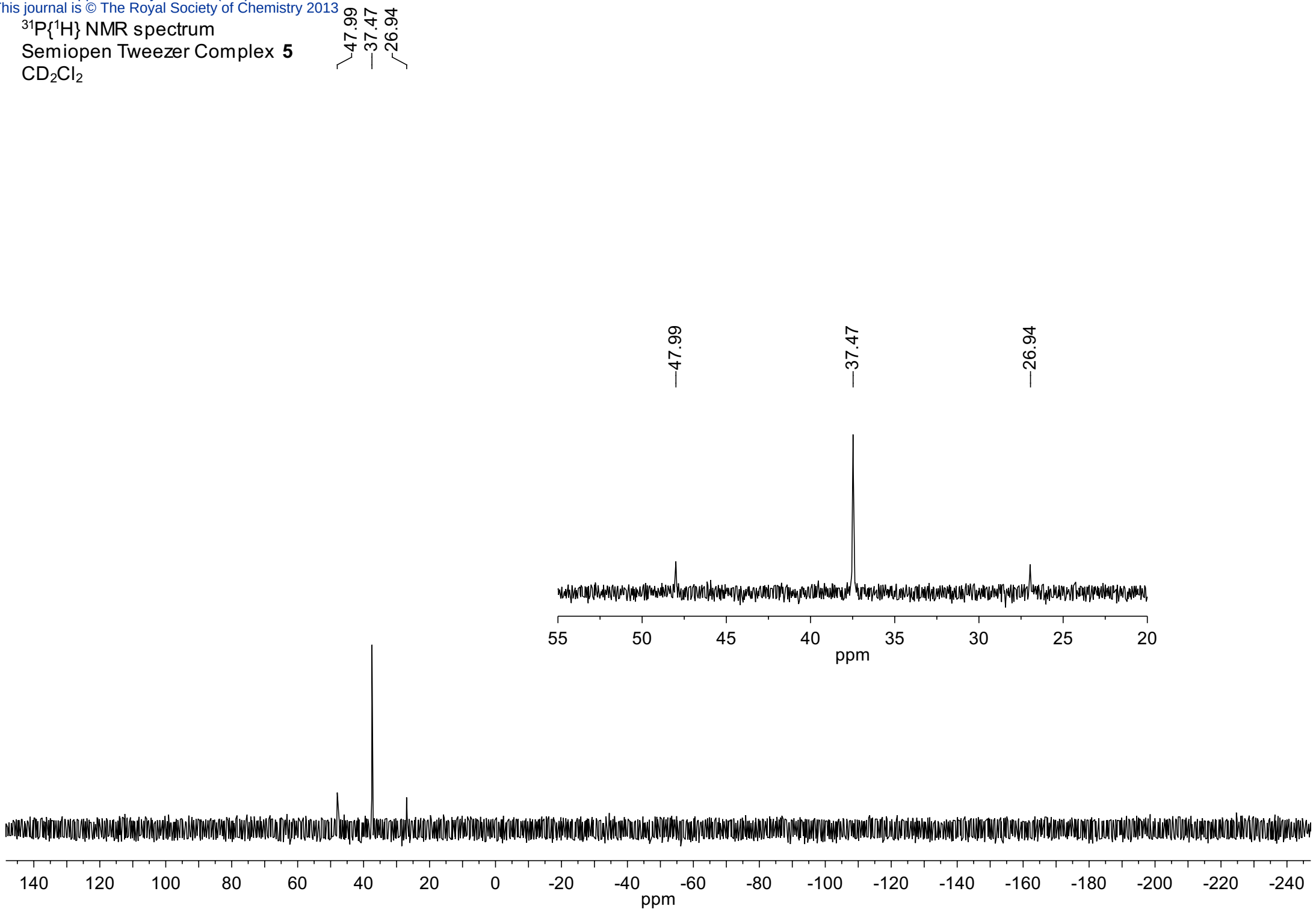


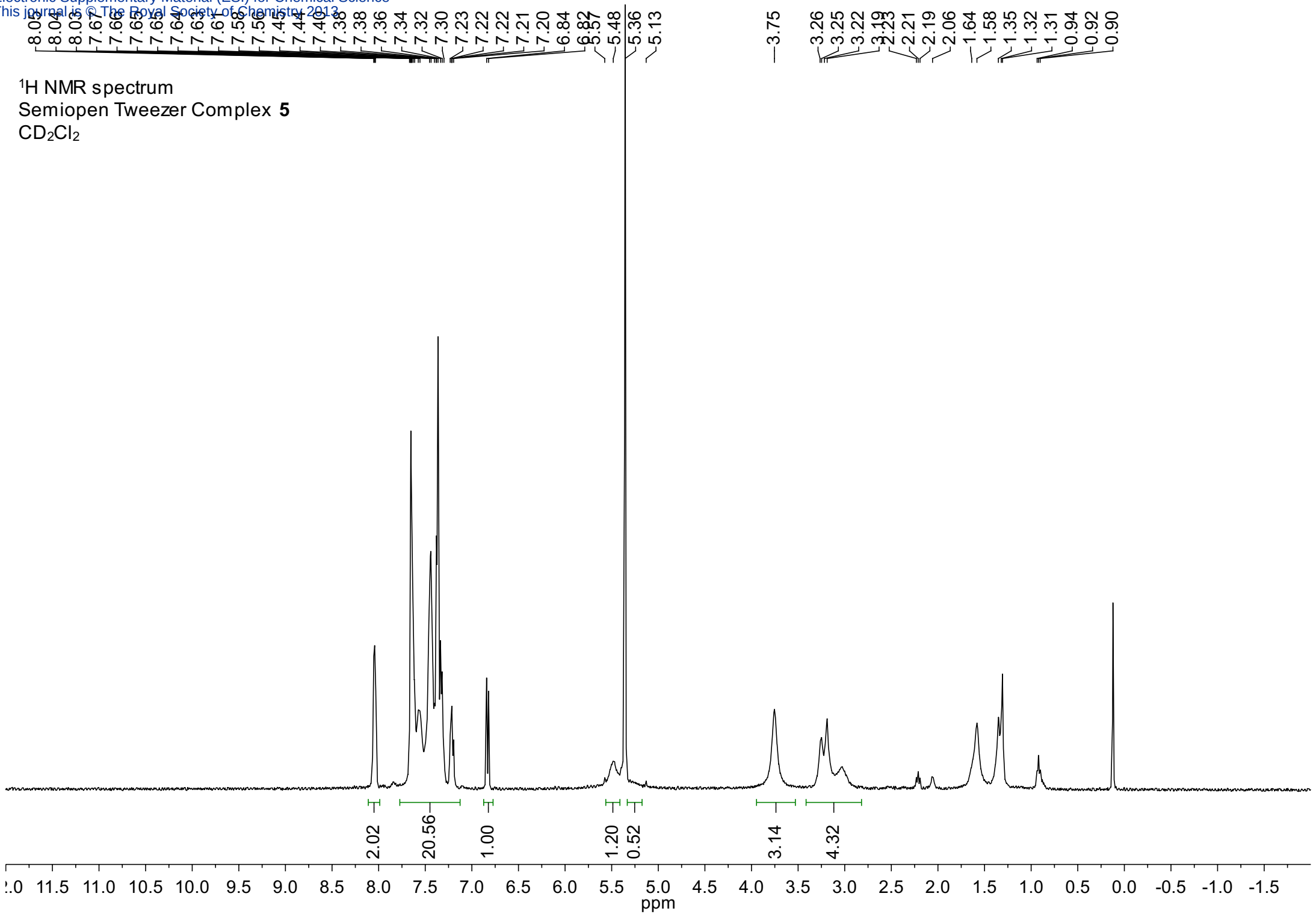


^{1}H NMR spectrum
Fully Open Tweezer Complex **4**
CD_2Cl_2



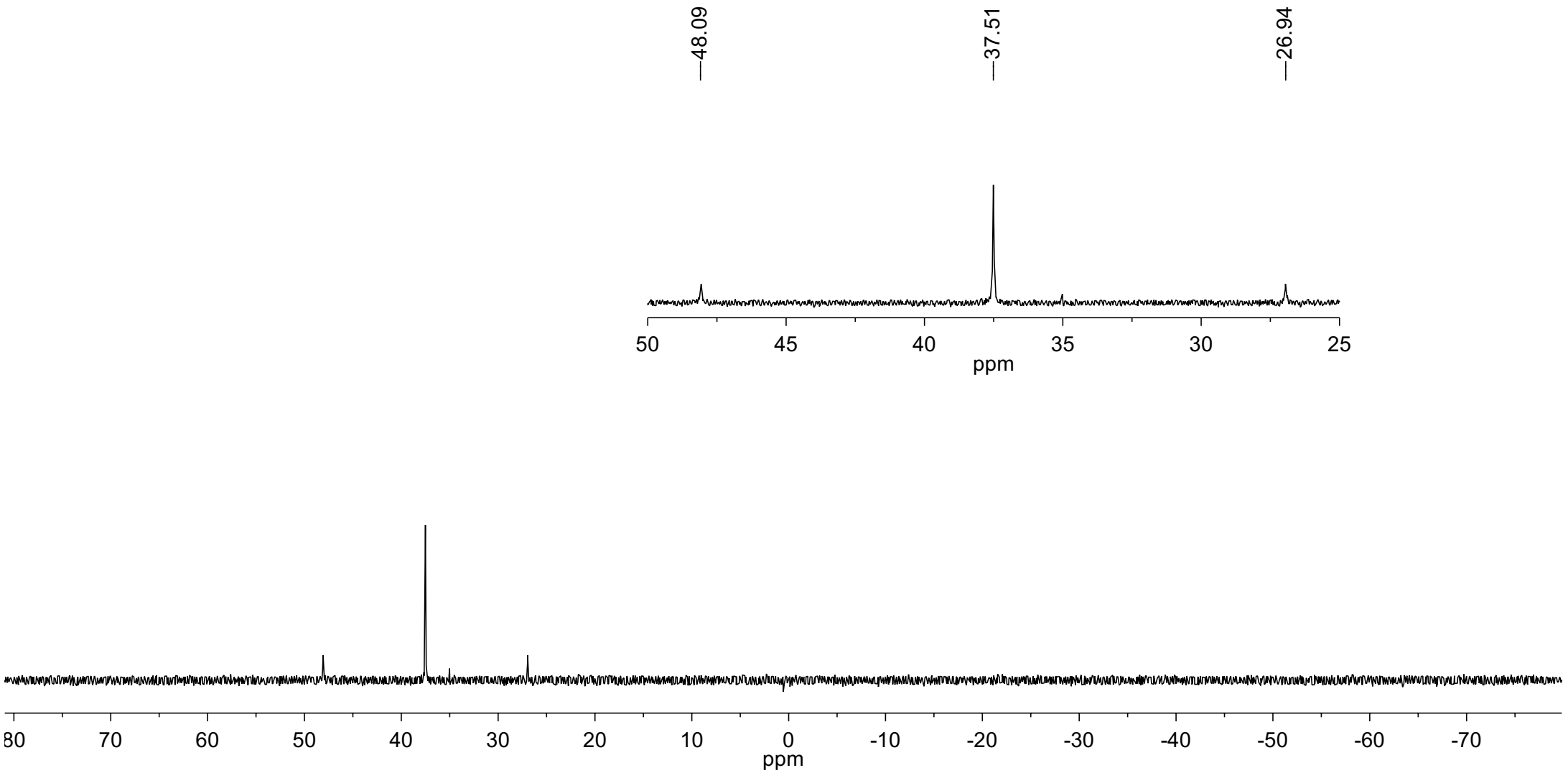
$^{31}P\{^{1}H\}$ NMR spectrum
Semiopen Tweezer Complex **5**
CD_2Cl_2



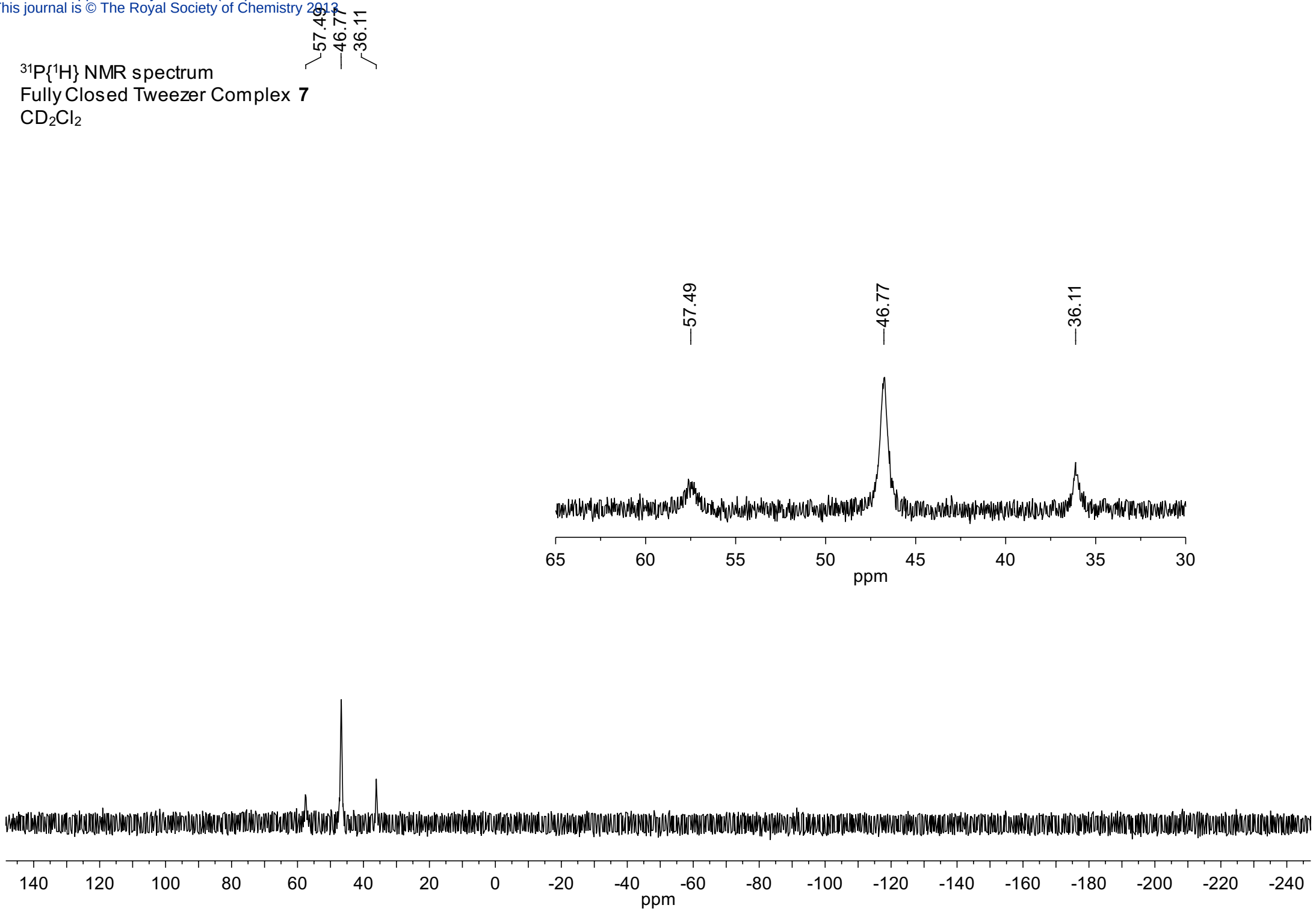


^{1}H NMR spectrum
Semiopen Tweezer Complex **5**
CD_2Cl_2

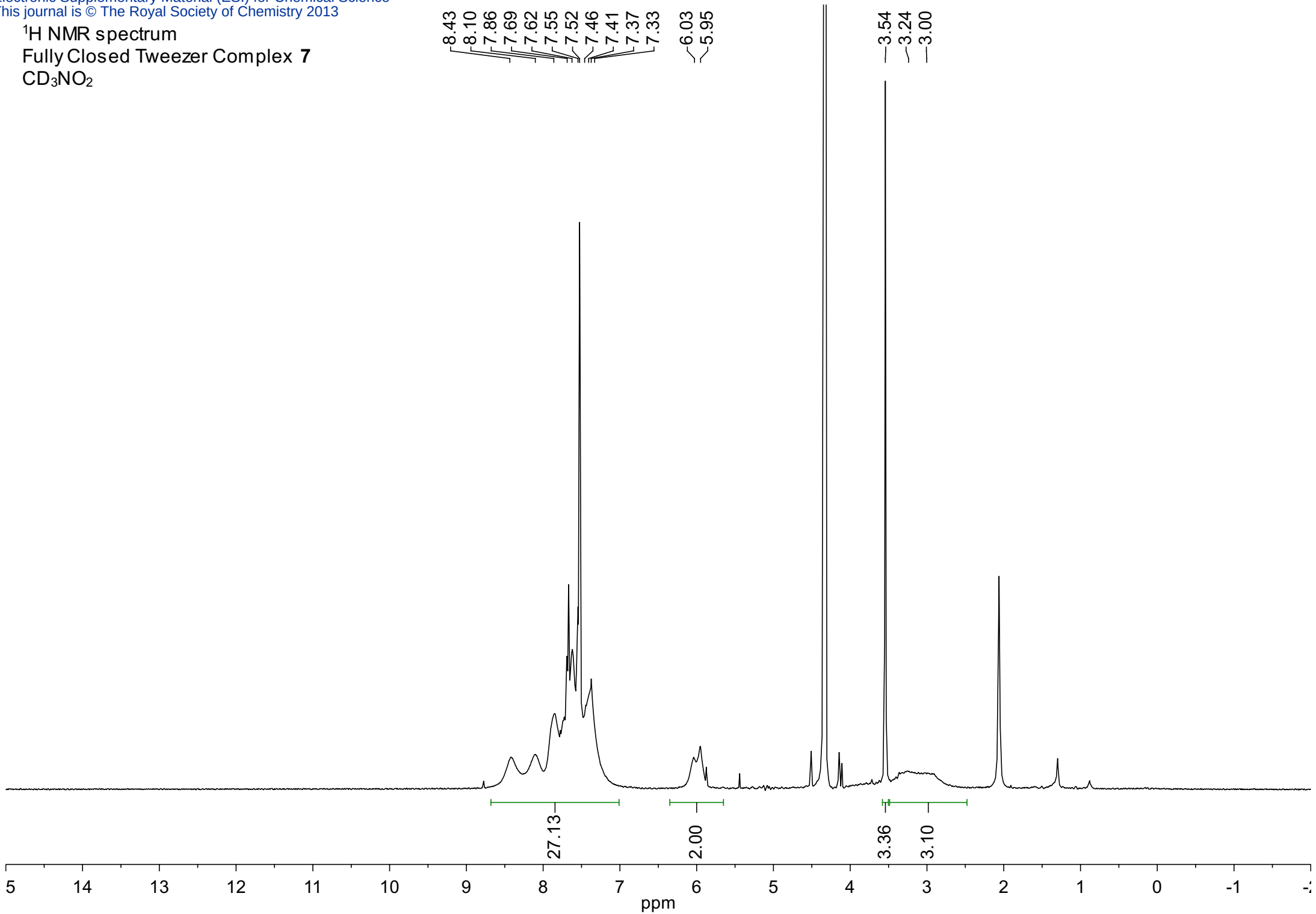
$^{31}P\{^{1}H\}$ NMR spectrum
Semiopen Tweezer Complex **6**
CD_3OD



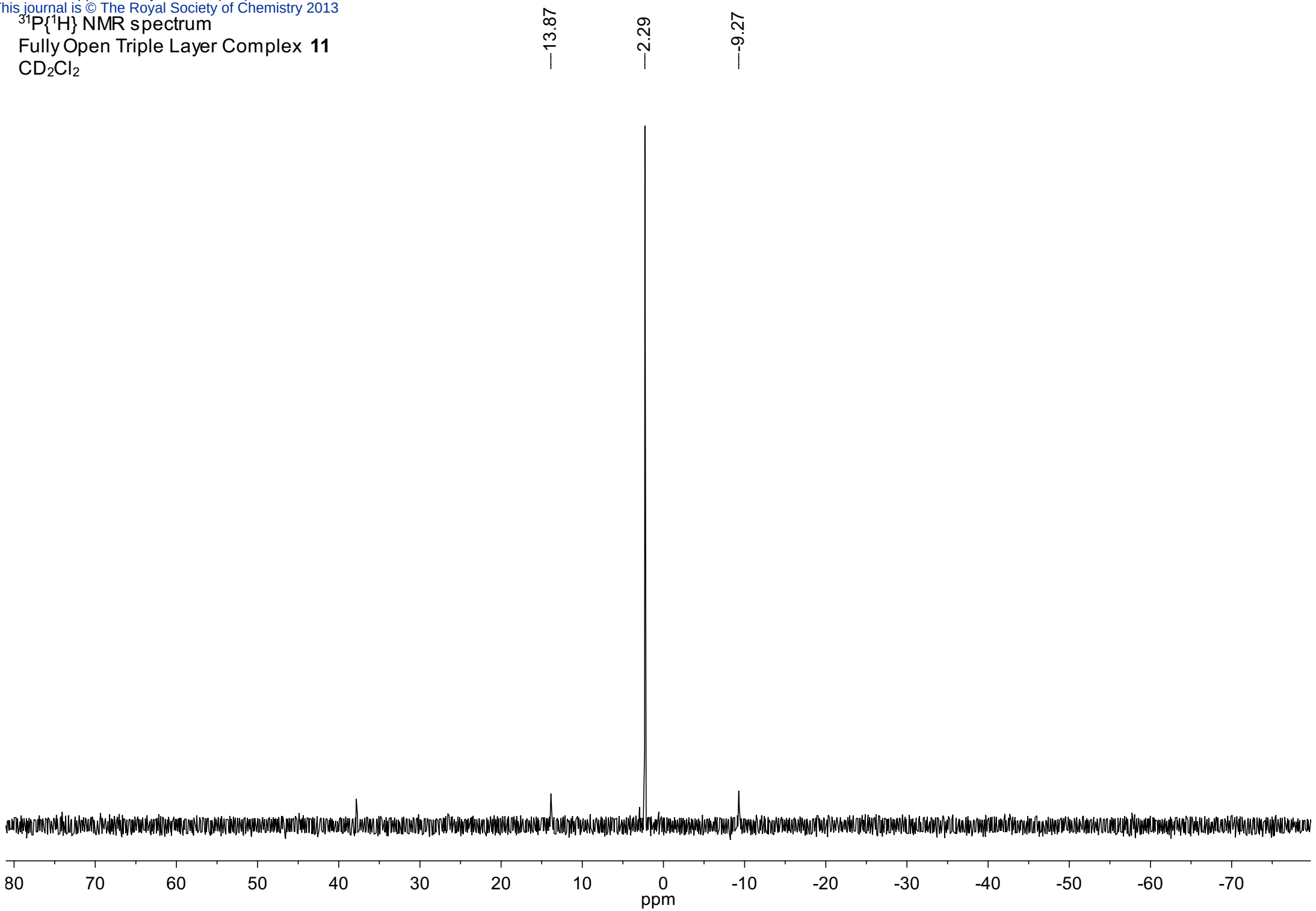
$^{31}P\{^{1}H\}$ NMR spectrum
Fully Closed Tweezer Complex **7**
CD_2Cl_2

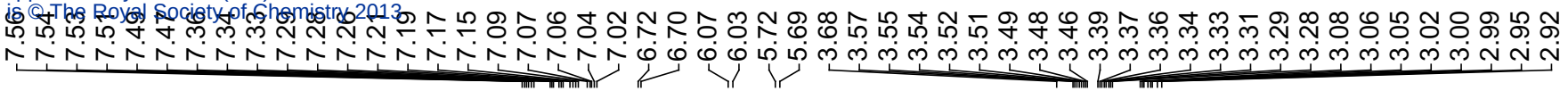


^{1}H NMR spectrum
Fully Closed Tweezer Complex **7**
CD_3NO_2

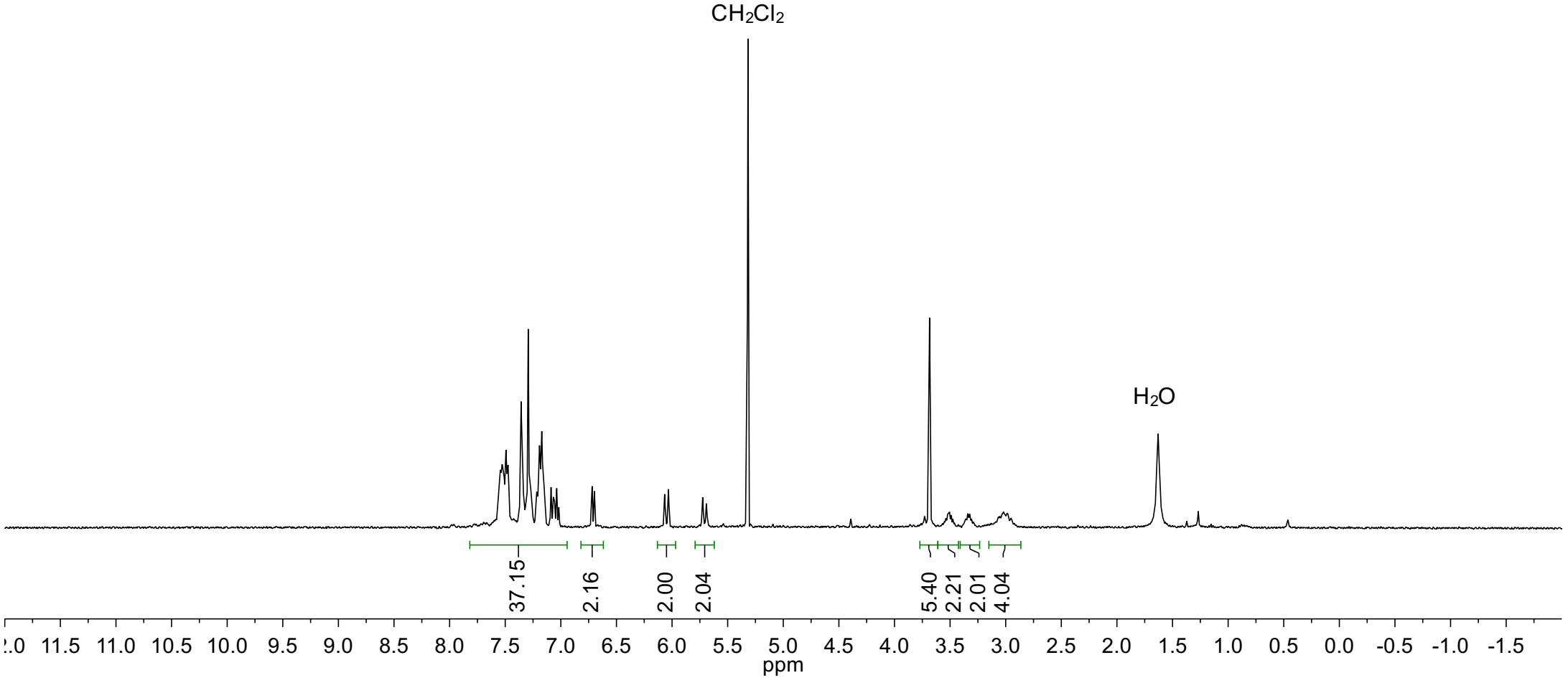


$^{31}P\{^{1}H\}$ NMR spectrum
Fully Open Triple Layer Complex **11**
CD_2Cl_2

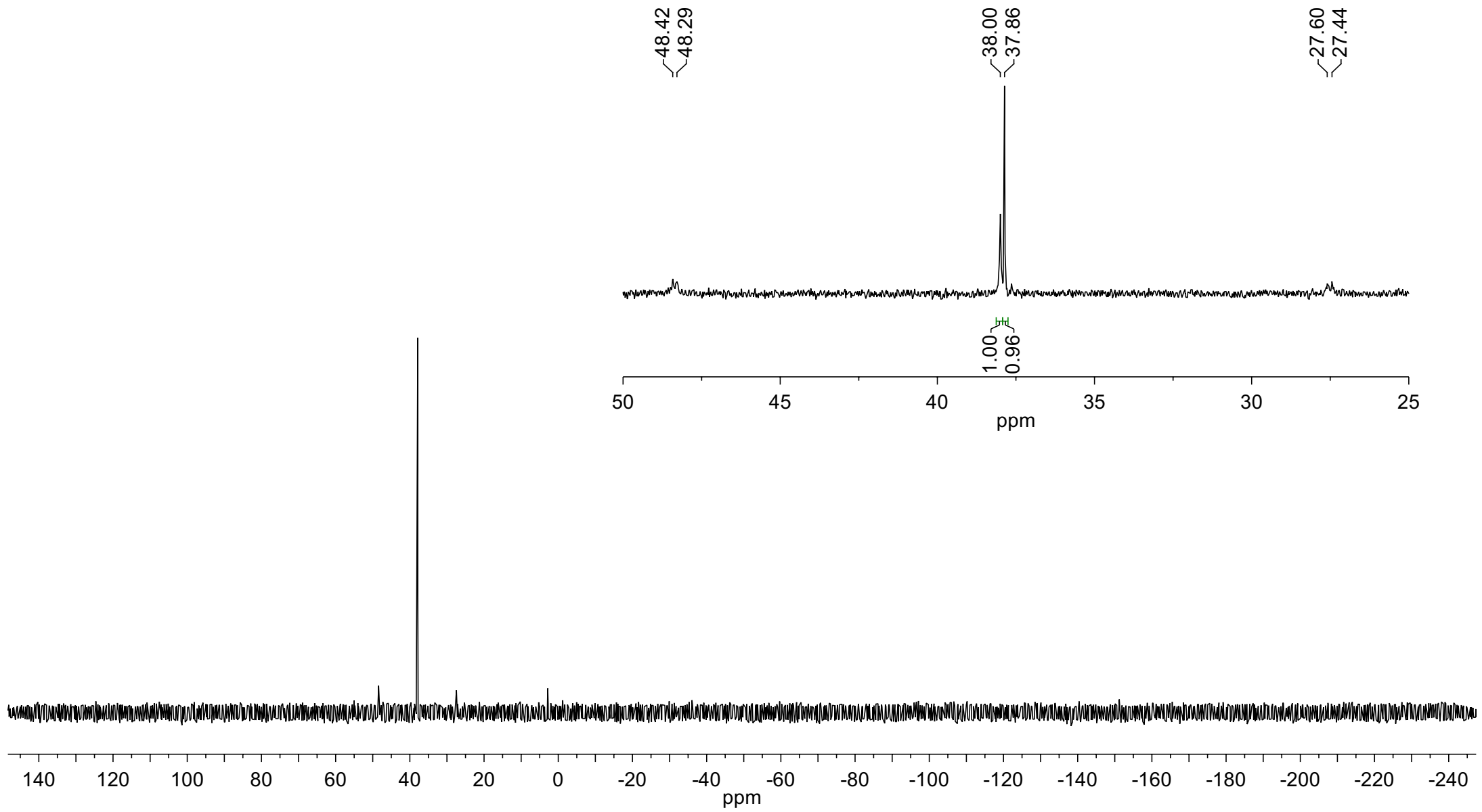


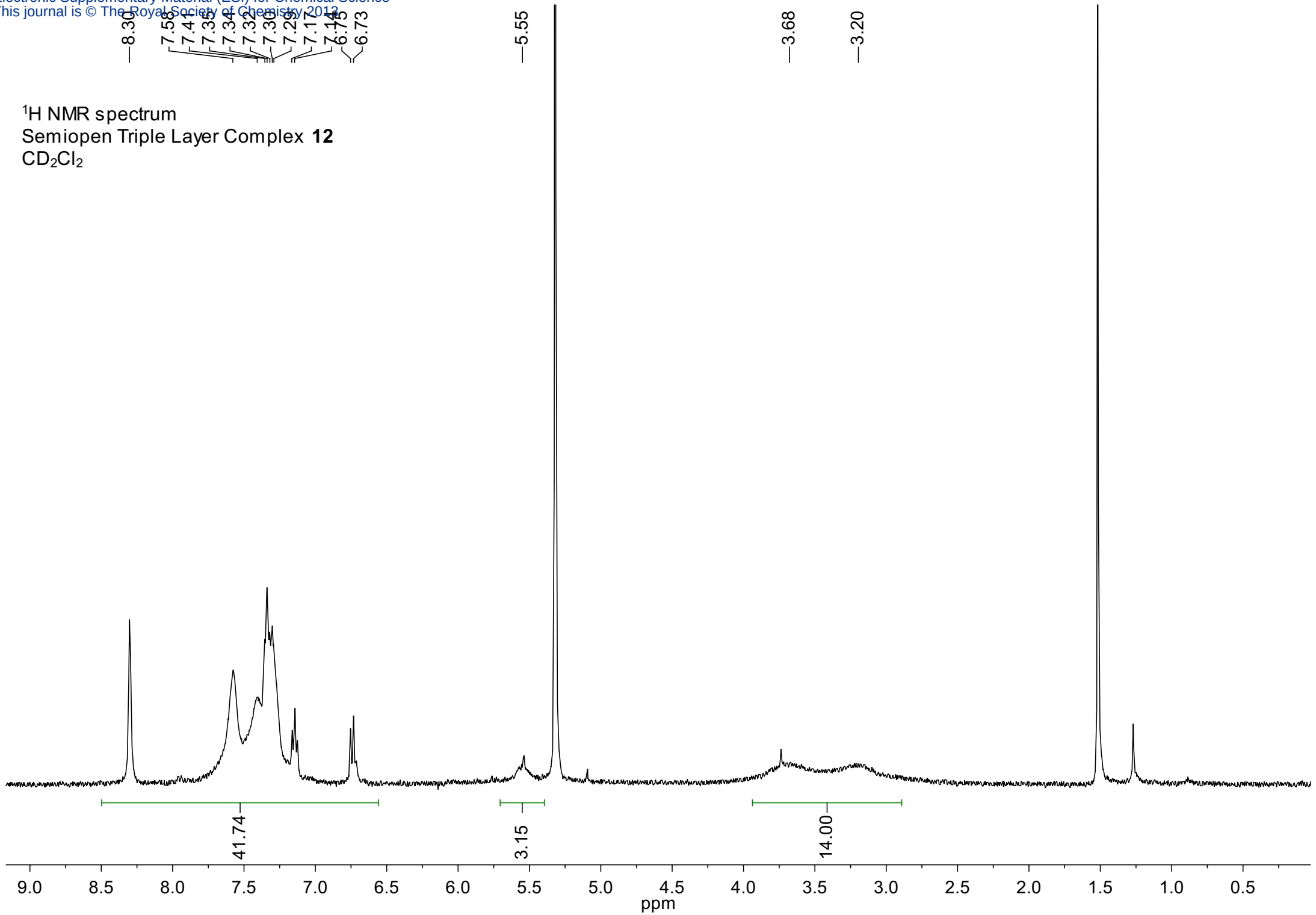


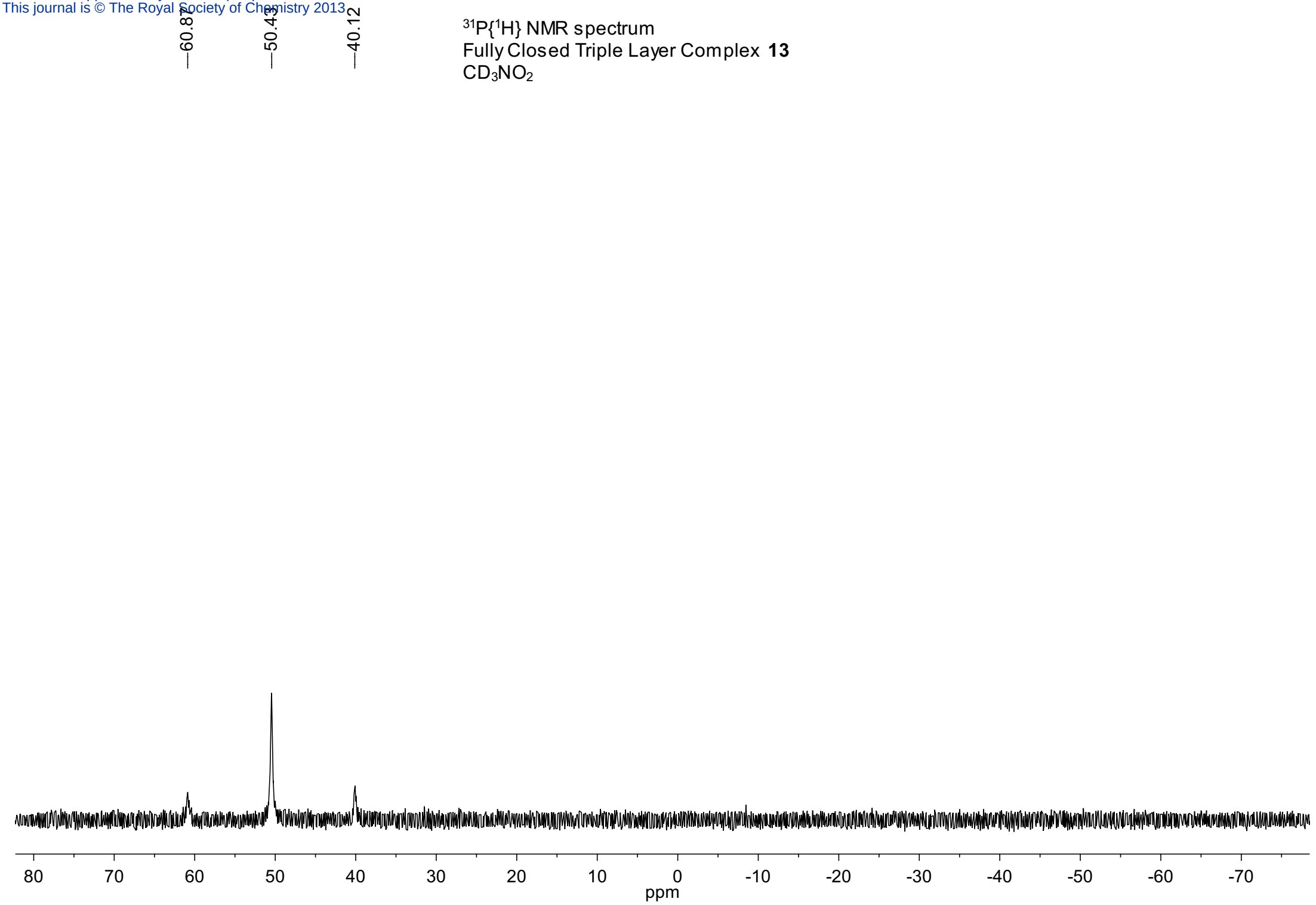
^{1}H NMR spectrum
Fully Open Triple Layer Complex **11**
CD_2Cl_2

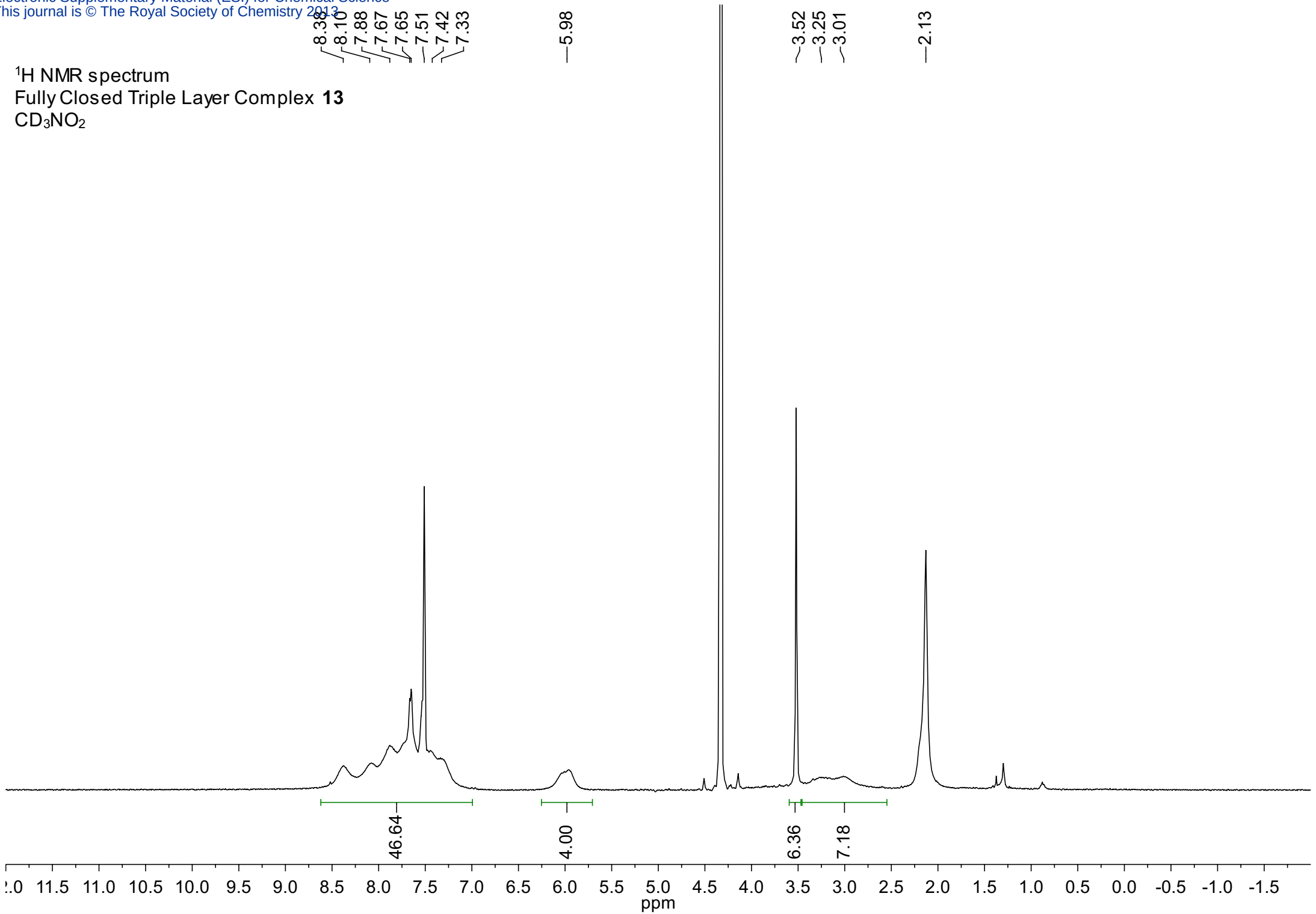


$^{31}P\{^{1}H\}$ NMR spectrum
Semiopen Triple Layer Complex **12**
CD_2Cl_2









^{1}H NMR spectrum
Fully Closed Triple Layer Complex **13**
CD_3NO_2