

Hydrogenation of carboxylic esters catalyzed by manganese catalysts supported by bidentate NHC-phosphine ligands

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1. General information:

All manipulations were carried out using Schlenk techniques under an atmosphere of dry argon or in an argon-filled glovebox (MBraun Unilabplus Eco. Dry and oxygen-free organic solvents (THF, Et₂O, CH₂Cl₂, toluene, pentane) were obtained using LabSolv (Innovative Technology) solvent purification system. Organic solvents used for column chromatography and water were degassed by argon bubbling during 15 min. Deuterated toluene, THF, and CD₂Cl₂ for NMR experiments were degassed prior to use and 2Me-THF for catalytic experiments was distilled and kept over 4Å molecular sieves. Liquid esters and CDCl₃ were passed through a short column of basic alumina, deoxygenated by three freeze-pump-thaw cycles. Column chromatography purification of organic substrates was performed on Organics Ultrapure silica gel (size 40-63 μm), KHBET₃ was purchased from Aldrich and used as received. *N*-mesitylimidazole,¹ *N*-isopropylimidazole,² imidazo[1,5-a]pyridine,³ 1-(2-chloroethyl)-3-(2,4,6-trimethylphenyl)-1*H*-imidazolium chloride,⁴ 1,3-bis(2,4,6-trimethylphenyl)-1*H*-imidazolium chloride,⁵ 1-[2-(diphenylphosphino)ethyl]-3-(2,4,6-trimethylphenyl)-1*H*-imidazolium chloride **L2.HCl**,⁴ 1-[2-(diphenylphosphino)ethyl]-3-methyl-1*H*-imidazolium hexafluorophosphate **L3.HPF₆**,⁶ 1-[2-(diphenylphosphino)ethyl]-3-isopropyl-1*H*-imidazolium hexafluorophosphate **L4.HPF₆**,⁶ [Me₂N(CH₂)₂IMes]PF₆ **L7.HPF₆**,⁷ complex **7**⁷ and complex **1**⁸ were prepared according to known methods. All other reagent grade chemicals purchased from commercial sources were used as received. IR spectra in solution were recorded in 0.1 mm CaF₂ cells using a Perkin Elmer Frontier FT-IR spectrometer and given in cm⁻¹. ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on Bruker Avance 300, Bruker Avance 400, and Avance III HD 400, and referenced against the residual signals of deuterated solvents (¹H and ¹³C), BF₃.OEt₂ (¹⁹F, external standard) and 85% H₃PO₄ (³¹P, external standard), respectively. When necessary, signal attribution in ¹³C spectra was based on decoupled ¹³C{³¹P, ¹H} and 2D ¹³C-¹H HMQC/HMBC experiments. High-resolution mass spectra (ESI positive mode) were obtained using a Xevo G2 QTof (Waters) spectrometer. Elemental analyses were carried out at the LCC-CNRS (Toulouse) using a Perkin Elmer 2400 series II analyzer. Non-stirred 'Autoclave Maxitech' autoclaves (50 mL) were used for the hydrogenation reactions. For mechanistic studies, Wilmad® quick pressure valve NMR tube 5mm diameter with thin wall were used.

2. Tables of optimization

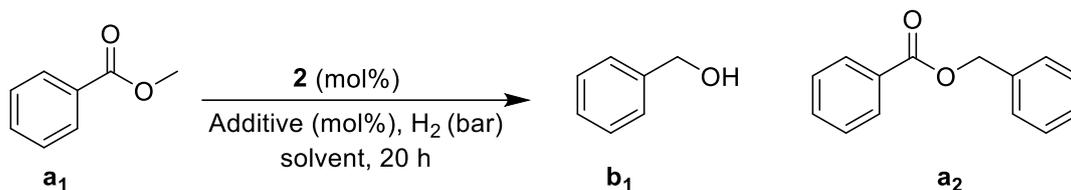


Table S1: Optimization of reaction parameters for the hydrogenation of methyl benzoate with complex 2.

Entry	[Mn] (mol%)	Base (mol%)	H ₂ (bar)	Temp. (°C)	Conversion ^[b] (%)	NMR Yield	
						b ₁	a ₂
1	2 (2)	^t BuOK (50)	50	120	>98	>98	-
2	2 (1)	^t BuOK (50)	50	120	68	57	11
3	2 (2)	^t BuOK (20)	50	120	>98	>98	-
4	2 (2)	^t BuOK (20)	50	100	>98	>98	-
5	2 (2)	^t BuOK (10)	50	100	96	89	7
6	2 (1)	^t BuOK (20)	50	100	>98	>98	-
7	2 (1)	^t BuOK (20)	50	80	70	55	15
8	2 (1)	-	50	100	0	0	-
9	2 (1)	^t BuOK (20)	30	100	89	83	6
10	2 (0.5)	^t BuOK (20)	50	100	94	92	2
11	2 (1)	^t BuOLi (20)	30	100	83	71	12
12	2 (1)	^t BuONa (20)	30	100	>98	30	70

[a] Experimental procedure: catalyst, THF (1.5 mL), ester (1 mmol) and additive were introduced under inert atmosphere in this order into an autoclave, the latter was then rapidly pressurized with H₂ to the required pressure and heated in an oil bath under stirring for 20 h at the indicated temperature.

[b] Conversions and yields were determined by ¹H NMR.

Table S2: Solvent screening for complex 2-catalysed hydrogenation of methyl benzoate.

Entry	Solvent	Time (h)	Conversion ^[b] (%)	NMR yield	
				b ₁	a ₂
1	THF	20	89	83	6
2	Toluene	20	91	78	13
3	Dioxane	20	0	0	0
4	CPME	20	81	48	33
5	2-Me-THF	20	>98	92	8
6	2-Me-THF	24	>98	>98	0

[a] Experimental procedure: catalyst **2** (1 mol%), solvent (1.5 mL), ester (methyl benzoate: 1 mmol) and base (^tBuOK: 20 mol%) were introduced under an inert atmosphere in this order into the autoclave, the latter was rapidly pressurized with H₂ to the required pressure (30 bar) and heated under stirring for 20 h at 100 °C.

[b] Conversions determined by ¹H NMR spectroscopy.

Table S3: Optimisation of reaction parameters for complex 2-catalysed hydrogenation of methyl benzoate in 2-Me-THF.

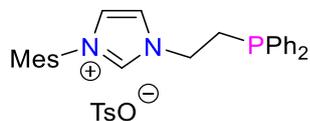
Entry	[Mn] (mol%)	Additive (mol%)	H ₂ (bar)	Conversion ^[b] (%)	NMR yield	
					b ₁	a ₂
1	2 (1)	^t BuOK (20)	30	>98	>98	0
2	2(1)	NaHBET ₃ (1)	30	74	41	33
3	2 (1)	LiHBET ₃ (1)	30	0	0	0
4	2 (1)	KHBET ₃ (1)	30	76	67	9
5	2 (0.1)	KHBET ₃ (5)	50	83	38	45
6	2 (0.1)	KHBET ₃ (10)	50	90	67	23
7	2 (0.2)	KHBET ₃ (10)	50	97	91	6
8	2 (0.5)	KHBET ₃ (10)	50	98	98 (96)	-

[a] Experimental procedure: An autoclave was loaded with an ester solution (1 mmol) in 2-Me-THF (1 mL) and a solution of **2** (0.5 mol%) which was prepared in 0.5 mL of 2-Me-THF and activated with a borohydride solution (1M in THF for LiHBET₃ and KHBET₃, 1M in toluene for NaHBET₃) for 30 min in that order, then the autoclave was immediately pressurised with hydrogen and kept under stirring for 24 h at 100 °C.

[b] Conversions determined by ¹H NMR spectroscopy. Isolated yield in parenthesis.

3. Synthesis of ligands:

Synthesis of [Ph₂P(CH₂)₂Im-Mes]OTs (L2.HOTs)



1-[2-(diphenylphosphino)ethyl]-3-(2,4,6-trimethylphenyl)-1*H*-imidazolium chloride (**L2.HCl**) (934 mg, 2.15 mmol) was dissolved in dichloromethane (20 mL), and then, sodium *p*-toluenesulfonate (625 mg, 3.22 mmol, 1.5 equiv.) was added. The mixture was stirred at room temperature for 3 h and filtered through celite. After concentration under vacuum (c.a. 5 mL), the product was precipitated by addition of diethyl ether (20 mL). The solid was washed with diethyl ether (3 × 20 mL). The resulting product was dried under vacuum to afford **L2.HOTs** as a white powder (1.20 g, 98%).

¹H NMR (400 MHz, CDCl₃, 25 °C) δ 9.83 (t, *J* = 1.5 Hz, 1H, NCHN), 7.65 (d, *J* = 8.0 Hz, 2H, CH_{OTs}), 7.59 (t, *J* = 1.7 Hz, 1H, CH_{Im}), 7.43-7.35 (m, 4H, CH_{Ph}), 7.35-7.28 (m, 6H, CH_{Ph}), 7.07 (t, *J* = 1.6 Hz, 1H, CH_{Im}), 7.00 (d, *J* = 8.0 Hz, 2H, CH_{OTs}), 6.93 (s, 2H, CH_{Mes}), 4.64 (dt, *J* = 11.6, 7.0 Hz, 2H, PPh₂CH₂), 2.75 (t, *J* = 7.0 Hz, 2H, NCH₂), 2.32 (s, 3H, CH₃), 2.28 (s, 3H, CH₃), 1.97 (s, 6H, CH₃).

¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C) δ 144.1 (s, C_{Ts}), 141.2 (s, C_{Ts}), 138.97 (s, NCHN), 138.90 (s, C_{Mes}), 136.5 (d, *J* = 9.7 Hz, C_{Ph}), 134.5 (s, C_{Mes}), 132.9 (d, *J* = 18.3 Hz, CH_{Ph}), 130.9 (s, C_{Mes}), 129.9 (s, CH_{Ts}), 129.4 (s, CH_{Ts}), 129.0 (d, *J* = 5.2 Hz, CH_{Ph}), 128.5 (s, CH_{Mes}), 126.1 (s, CH_{Ph}), 123.4 (s, CH_{Im}), 122.9 (s, CH_{Im}), 48.2 (d, *J* = 18.7 Hz, NCH₂), 29.6 (d, *J* = 14.4 Hz, Ph₂PCH₂), 21.4 (s, CH₃), 21.2 (s, CH₃), 17.7 (s, CH₃).

³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C) δ -23.22.

Elemental analysis: calcd (%) for C₃₃H₃₅N₂O₃PS: C, 69.45; H, 6.18; N, 4.91; found: C, 69.36; H, 6.39; N, 5.05

MS (ESI): *m/z*: calcd for C₂₆H₂₈N₂P⁺: 399.17.

Synthesis of [PCy₂P(CH₂)₂IMes]Cl (L5.HCl)



To a solution of LiPCy₂ (0.70 mmol in THF (5 mL)) was added a solution of 1-(2-chloroethyl)-3-(2,4,6-trimethylphenyl)-1*H*-imidazolium chloride (200 mg, 0.70 mmol) in THF (10 mL) at -78 °C via cannula. The mixture was then stirred at r.t. for 18 h. The solvent was removed under vacuum. Degassed methanol (2 mL) was added and the mixture was stirred for 10 min. The methanol was then removed under vacuum and the residue was crystallized in THF / Et₂O and washed two times with Et₂O to give **L5.HCl** as a white solid (273 mg, 87%). (LiPCy₂ was obtained by deprotonation of HPCy₂ (142 μL, 0.70 mmol) with 2 equivalents of *n*-BuLi (2.5 M solution in hexane, 560 μL, 1.4 mmol) in THF (5 mL) at -78 °C for 30 min).

¹H NMR (400 MHz, CDCl₃, 25 °C) δ 10.62 (s, 1H, NCHN_{Im}), 7.87 (s, 1H, CH_{Im}), 7.09 (s, 1H, CH_{Im}), 6.97 (s, 2H, CH_{Mes}), 4.98-4.74 (m, 2H, NCH₂), 3.80-3.63 (m, 2H, PCH₂), 2.32 (s, 3H, CH₃_{Mes}), 2.06 (s, 6H, CH₃_{Mes}), 1.88-1.52 (m, 13H, CH_{PCy₂}), 1.34-1.00 (m, 9H, CH_{PCy₂}).

¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C) δ 141.4 (s, C_{Mes}), 138.8 (s, CH_{Im}), 134.4 (s, C_{Mes}), 130.9 (s, C_{Mes}), 129.9 (s, CH_{Mes}), 123.5 (d, *J* = 5.6 Hz, CH_{Im}), 122.3 (s, CH_{Im}), 50.5 (d, *J* = 23.0 Hz, NCH₂), 33.0 (d, *J* = 11.1 Hz, CH_{Cy-*ipso*}), 30.1 (d, *J* = 14.1 Hz, CH₂_{Cy}), 28.8 (d, *J* = 7.5 Hz, CH₂_{Cy}), 27.2 (d, *J* = 11.7 Hz, CH₂_{Cy}), 27.1 (d, *J* = 7.7 Hz, CH₂_{Cy}), 26.4 (s, CH₂_{Cy}), 23.5 (d, *J* = 20.7 Hz, PCH₂), 21.2 (s, CH₃_{Mes}), 17.7 (s, CH₃_{Mes}).

³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C) δ -12.23.

HR-MS (ESI): *m/z*: calcd for C₂₆H₄₀N₂P⁺: 411.2929, found: 411.2925, ε_r = 1 ppm.

Synthesis of [PCy₂P(CH₂)₂IMes]OTs (L5.HOTs)



Compound **L5.HOTs** was prepared following the same method as for the synthesis of **L2.HOTs**. Starting from compound **L5.HCl** (500 mg, 1.12 mmol) and NaOTs (325 mg, 1.67 mmol, 1.50 eq), the compound **L5.HOTs** was obtained as an orange solid (632 mg, 97%) and used without purification in the next step.

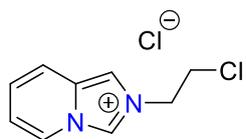
¹H NMR (400 MHz, CDCl₃, 25 °C) δ 9.80 (s, 1H, NCHN_{Im}), 7.77 (s, 1H, CH_{Im}), 7.68 (d, *J* = 7.8 Hz, 2H, CH_{OTos}), 7.12-6.99 (s, 3H, CH_{Im}+ CH_{OTos}), 6.95 (s, 2H, CH_{Mes}), 4.76-4.55 (m, 2H, NCH₂), 2.31 (s, 6H, CH_{3 Mes}+ CH_{3 OTos}), 2.05-1.87 (m, 8H, PCH₂+ CH_{3 Mes}), 1.79-0.96 (m, 22H, CH_{PCy2}).

¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C) δ 144.0 (s, C_{OTos}), 141.1 (s, C_{Mes}), 138.9 (s, C_{OTos}), 138.6 (s, 1H, CH_{Im}), 134.5 (s, C_{Mes}), 131.0 (s, C_{Mes}), 129.8 (s, CH_{Mes}), 128.5 (s, CH_{OTos}), 126.1 (s, CH_{OTos}), 123.6 (d, *J* = 4.5 Hz, CH_{Im}), 122.7 (s, CH_{Im}), 50.4 (d, *J* = 23.3 Hz, NCH₂), 32.9 (d, *J* = 11.3 Hz, CH_{Cy-ipso}), 30.0 (d, *J* = 14.1 Hz, CH_{2 Cy}), 28.7 (d, *J* = 7.5 Hz, CH_{2 Cy}), 27.2 (d, *J* = 11.7 Hz, CH_{2 Cy}), 27.1 (d, *J* = 7.9 Hz, CH_{2 Cy}), 26.4 (s, CH_{2 Cy}), 23.1 (d, *J* = 20.6 Hz, PCH₂), 21.4 (s, CH₃), 21.2 (s, CH₃), 17.6 (s, CH₃).

³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C) δ -12.84.

HR-MS (ESI): *m/z*: calcd for C₂₆H₄₀N₂P⁺: 411.2929, found: 411.2928, ε_r = 0.2 ppm.

Synthesis of $[\text{Cl}(\text{CH}_2)_2\text{IPy}]\text{Cl}$ (**L6(Cl)**).HCl



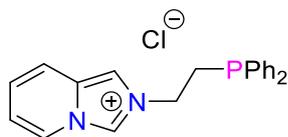
Imidazo[1,5-a]pyridine (1.50 g, 12.7 mmol) was dissolved in an excess of 1,2-dichloroethane (20 mL, 254.0 mmol, 20 equiv) and the solution was stirred under reflux for two days. 1,2-dichloroethane was then removed under vacuum. The residue was redissolved in dichloromethane. A viscous oil was obtained upon addition of Et₂O. The residue was triturated three times with Et₂O (3 x 15 mL) to afford **L6(Cl)**.HCl as a black viscous liquid (2.20 g, 80%).

¹H NMR (400 MHz, CDCl₃, 25 °C) δ 11.27 (s, 1H, NCHN), 8.84 (d, *J* = 7.1 Hz, 1H, CH_{IPy}), 8.43 (s, 1H, CH_{IPy}), 7.65 (d, *J* = 9.4 Hz, 1H, CH_{IPy}), 7.16 (dd, *J* = 9.4, 6.8 Hz, 1H, CH_{IPy}), 7.02 (t, *J* = 6.8 Hz, 1H, CH_{IPy}), 5.15 (t, *J* = 5.2 Hz, 2H, NCH₂CH₂Cl), 4.18 (t, *J* = 5.2 Hz, 2H, NCH₂CH₂Cl).

¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C) δ 129.7 (s, C_{IPy}), 127.7 (s, NCHN), 125.0 (s, CH_{IPy}), 124.6 (s, CH_{IPy}), 118.2 (s, CH_{IPy}), 117.8 (s, CH_{IPy}), 113.8 (s, CH_{IPy}), 52.6 (s, NCH₂CH₂Cl), 43.5 (s, NCH₂CH₂Cl).

HR-MS (ESI): *m/z*: calcd for C₉H₁₀N₂Cl⁺: 181.0533, found: 181.0537, *ε*r = 2.2 ppm

Synthesis of [Ph₂P(CH₂)₂IPy]Cl (L6.HCl)



2-(2-(Diphenylphosphino)ethyl)-imidazo[1,5-a]pyridinium chloride was synthesized by a method analogous to that for 1-[2-(diphenylphosphino)ethyl]-3-(2,4,6-trimethylphenyl)-1H-imidazolium chloride starting from 2-(2-chloroethyl)-imidazo[1,5-a]pyridinium chloride (450 mg, 2.07 mmol). Compound **L6.HCl** was obtained as a dark orange solid (628 mg, 82%).

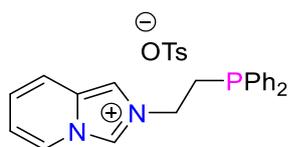
¹H NMR (400 MHz, CDCl₃, 25 °C) δ 11.42 (s, 1H, NCHN), 8.94 (d, *J* = 7.1 Hz, 1H, CH_{IPy}), 7.58 (s, 1H, CH_{IPy}), 7.42 (d, *J* = 9.4 Hz, 1H, CH_{IPy}), 7.39-7.31 (m, 4H, CH_{Ph}), 7.28-7.19 (m, 6H), 7.07 (dd, *J* = 9.4, 6.7 Hz, 1H, CH_{IPy}), 6.90 (t, *J* = 6.8 Hz, 1H, CH_{IPy}), 4.68 (dt, *J* = 11.0, 7.2 Hz, 2H, NCH₂), 2.82 (t, *J* = 7.1 Hz, 2H, PPh₂CH₂).

¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C) δ 135.9 (d, *J* = 11.6 Hz, C_{Ph}), 132.6 (d, *J* = 19.5 Hz, CH_{Ph}), 129.6 (s, C_{IPy}), 129.2 (s, CH_{Ph}), 128.6 (d, *J* = 7.1 Hz, CH_{Ph}), 127.3 (s, NCHN), 124.9 (s, CH_{IPy}), 124.7 (s, CH_{IPy}), 117.8 (s, CH_{IPy}), 117.2 (s, CH_{IPy}), 112.6 (s, CH_{IPy}), 49.1 (d, *J* = 22.6 Hz, NCH₂), 29.4 (d, *J* = 16.8 Hz, Ph₂PCH₂).

³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C) δ -21.47.

HR-MS (ESI): *m/z*: calcd for C₂₁H₂₀N₂P⁺: 331.1364, found: 331.1369, *ε*r = 1.5 ppm.

Synthesis of [Ph₂P(CH₂)₂IPy]OTs (L6.HOTs)



This ligand was prepared starting from **L6.HCl** (265 mg, 0.72 mmol) by following a method to that for the synthesis of **L2.HOTs**. Compound **L6.HOTs** was obtained as an orange solid (354 mg, 97%).

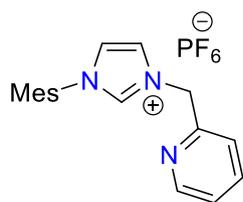
¹H NMR (400 MHz, CDCl₃, 25 °C) δ 10.66 (s, 1H, NCHN), 8.70 (d, *J* = 7.1 Hz, 1H, CH_{IPy}), 7.81 (d, *J* = 7.8 Hz, 2H, CH_{TS}), 7.62 (s, 1H, CH_{IPy}), 7.44-7.32 (m, 5H, CH_{IPy+Ph}), 7.28-7.19 (m, 6H, CH_{Ph}), 7.11 (d, *J* = 7.8 Hz, 2H, CH_{TS}), 7.03 (dd, *J* = 9.3, 6.6 Hz, 1H, CH_{IPy}), 6.86 (t, *J* = 7.1 Hz, 1H, CH_{IPy}), 4.61 (dt, *J* = 11.0, 7.2 Hz, 2H, NCH₂), 2.80 (t, *J* = 7.2 Hz, 2H, Ph₂PCH₂), 2.31 (s, 3H, CH₃_{TS}).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 143.8 (s, C_{TS}), 139.4 (s, C_{TS}), 136.11 (d, *J* = 11.8 Hz, C_{Ph}), 132.6 (d, *J* = 19.5 Hz, CH_{Ph}), 129.6 (s, C_{IPy}), 129.1 (s, CH_{Ph}), 128.7 (s, CH_{TS}), 128.5 (d, *J* = 7.0 Hz, CH_{Ph}), 127.1 (s, NCHN), 125.9 (s, CH_{TS}), 124.57 (s, CH_{IPy}), 124.53 (s, CH_{IPy}), 117.9 (s, CH_{IPy}), 117.2 (s, CH_{IPy}), 113.0 (s, CH_{IPy}), 49.0 (d, *J* = 22.7 Hz, NCH₂), 28.8 (d, *J* = 16.5 Hz, Ph₂PCH₂), 21.3 (s, CH₃_{TS}).

³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C) δ -21.36.

HR-MS (ESI): *m/z*: calcd for C₂₁H₂₀N₂P⁺: 331.1364, found: 331.1363, ε_r = 0.3 ppm.

Synthesis of [PyCH₂IMes]PF₆ (**L8.HPF₆**)



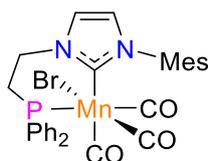
[PyCH₂IMes]PF₆ was synthesized by a method analogous to that for [Me₂N(CH₂)₂IMes]PF₆ **L7.HPF₆**. Mesityl imidazole (500 mg, 2.68 mmol) was added to suspension 2-(chloromethyl)pyridine hydrochloride (2,68 mmol) in 5 ml acetonitrile. The mixture was heated at 90 °C for 30 h. Upon cooling the solvent was removed under vacuum, the oily residue was redissolved in water (10 mL) and neutralized with saturated aqueous sodium carbonate solution till pH = 9. The aqueous solution was then extracted with ethyl acetate (2 x 15 mL) to remove unreacted organic materials. At this point imidazolium salt remains in aqueous phase. The aqueous phase was vigorously stirred with KPF₆ (1.5 equiv.) and extracted with dichloromethane (3 x 20 mL). The organic phase was dried over sodium sulfate, evaporated to dryness to produce **L8.HPF₆** as a brown oil. (680 mg, 60%). The spectroscopic data are in agreement with the one reported in the literature.⁹

4. Synthesis of complexes

General procedure A

To a stirred suspension of the precursor salt **LX.HX** in toluene or THF, a solution of KHMDS (1.1 eq, 0.5 M in toluene) was added at r.t. and then the resulting yellow suspension was sonicated during 5 min and stirred for additional 15 min. $[\text{Mn}(\text{CO})_5\text{Br}]$ (1 eq.) was added in one portion as a solid inducing a vigorous CO evolution. The resulting orange solution was stirred for 3 h at 60 °C and monitored by IR. After cooling the reaction mixture to r.t., filtration through Celite and evaporation of the solvent under vacuum, the crude product was crystallized in toluene or in a THF /pentane or in a THF / hexane mixture to afford the corresponding complex **CX** as a yellow powder.

Synthesis of $[(\text{MnBr}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{-Im-Mes}))]$ (**2**)



According to general procedure **A**, **L2.HOTs** (500 mg, 0.88 mmol) in toluene (40 mL) afforded complex **2** (490 mg, 90%) as a yellow powder. The crude reaction mixture was purified by column chromatography on basic alumina (eluent: toluene / THF : 2/1 then THF). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into the solution of complex **2** in THF at r.t.

^1H NMR (400 MHz, CD_2Cl_2 , 25 °C) δ 8.12-8.01 (m, 2H, CH_{Ph}), 7.55-7.29 (m, 8H, CH_{Ph}), 7.27 (br s, 1H, CH_{Im}), 7.02 (br s, 1H, CH_{Mes}), 6.93-6.92 (m, 2H, $\text{CH}_{\text{Im}} + \text{CH}_{\text{Mes}}$), 5.34-5.23 (m, 1H, NCH_2), 4.34 (ddt, $J = 31.7, 13.9, 4.3$ Hz, 1H, NCH_2), 3.01-2.86 (m, 1H, Ph_2PCH_2), 2.70-2.54 (m, 1H, Ph_2PCH_2), 2.34 (s, 3H, CH_3_{Mes}), 2.15 (s, 3H, CH_3_{Mes}), 1.79 (s, 3H, CH_3_{Mes}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2 , 25 °C) δ 222.3 (d, $J = 19.9$ Hz, Mn-CO), 219.1 (d, $J = 29.6$ Hz, Mn-CO), 217.1 (d, $J = 29.6$ Hz, Mn-CO), 188.0 (d, $J = 24.3$ Hz, Mn-CN₂), 139.9 (s, C_{Mes}), 137.9 (s, C_{Mes}), 137.1 (d, $J = 42.2$ Hz, C_{Ph}), 137.0 (s, C_{Mes}), 136.2 (s, C_{Mes}), 134.8 (d, $J = 9.5$ Hz, CH_{Ph}), 134.6 (d, $J = 35.8$ Hz, C_{Ph}), 131.4 (d, $J = 9.3$ Hz, CH_{Ph}), 130.8 (d, $J = 2.3$ Hz, CH_{Ph}) 130.0 (d, $J =$

2.1 Hz, CH_{Ph}), 129.6 (s, CH_{Mes}), 129.2 (s, CH_{Mes}), 128.9 (d, *J* = 8.9 Hz, CH_{Ph}), 128.7 (d, *J* = 9.3 Hz, CH_{Ph}), 125.0 (s, CH_{Im}), 123.2 (s, CH_{Im}), 47.3 (d, *J* = 3.4 Hz, NCH₂), 28.3 (d, *J* = 18.6 Hz, Ph₂PCH₂), 21.2 (s, CH_{3 Mes}), 18.9 (s, CH_{3 Mes}), 18.1 (s, CH_{3 Mes}).

³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C) δ 37.44.

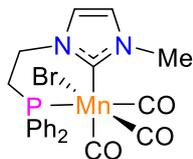
IR ν_{CO} (CH₂Cl₂): 2017, 1940, 1905 cm⁻¹.

IR ν_{CO} (solid, ATR) = 2005, 1925, 1907 cm⁻¹.

Elemental analysis: calcd (%) for C₂₉H₂₇BrMnN₂O₃P: C 56.42, H 4.41, N 4.54; found: C 56.24, H 4.36, N 4.52.

HR-MS (ESI): *m/z*: calcd for C₂₉H₂₇MnN₂O₃P⁺: 537.1140, found: 537.1149, ε_r = 1.7 ppm.

Synthesis of [(MnBr(CO)₃(Ph₂P(CH₂)₂-Im-Me)] (**3**)



According to general procedure **A**, **L3.HPF₆** (169 mg, 0.38 mmol) in toluene (20 mL) afforded complex **3** (173 mg, 88%) as a yellow powder. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of hexane into the solution of complex **3** in toluene at r.t.

¹H NMR (400 MHz, CDCl₃, 25 °C) δ 7.95-7.78 (m, 2H, CH_{Ph}), 7.49-7.31 (m, 8H, CH_{Ph}), 7.02 (s, 1H, CH_{Im}), 6.98 (s, 1H, CH_{Im}), 5.39-5.17 (m, 1H, NCH₂), 4.38-4.11 (m, 1H, NCH₂), 4.03 (s, 3H, NCH₃), 2.87-2.67 (m, 1H, Ph₂PCH₂), 2.54-2.47 (m, 1H, Ph₂PCH₂).

¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C) δ 223.5 (d, *J* = 16.6 Hz, Mn-CO), 219.5 (d, *J* = 27.7 Hz, Mn-CO), 218.0 (d, *J* = 23.1 Hz, Mn-CO), 186.3 (d, *J* = 23.5 Hz, Mn-CN₂), 136.6 (d, *J* = 41.2 Hz, C_{Ph}),

134.0 (d, $J = 40.4$ Hz, C_{PH}), 133.9 (d, $J = 9.2$ Hz, CH_{PH}), 131.5 (d, $J = 9.5$ Hz, CH_{PH}), 130.3 (d, $J = 2.2$ Hz, CH_{PH}), 129.9 (d, $J = 2.0$ Hz, CH_{PH}), 128.7 (d, $J = 8.9$ Hz, CH_{PH}), 128.4 (d, $J = 9.4$ Hz, CH_{PH}), 123.4 (s, CH_{Im}), 123.2 (s, CH_{Im}), 47.0 (d, $J = 3.4$ Hz, NCH₂), 39.2 (s, NCH₃), 28.2 (d, $J = 19.9$ Hz, PPh₂CH₂).

³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C) δ 38.95.

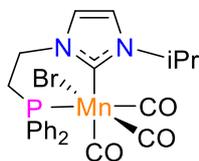
IR ν_{CO} (CH₂Cl₂): 2023, 1952, 1919 cm⁻¹.

IR ν_{CO} (solid, ATR) = 2005, 1925, 1907 cm⁻¹.

Elemental analysis: calcd (%) for C₂₁H₁₉BrMnN₂O₃P: C, 49.15; H, 3.73; N, 5.46; found: C, 49.50; H, 3.55; N, 5.30.

HR-MS (ESI): m/z: calcd for C₂₁H₁₉MnN₂O₃P⁺: 433.0514, found: 433.0519, ε = 1.2 ppm

Synthesis of [(MnBr(CO)₃(Ph₂P(CH₂)₂-Im-ⁱPr)] (4)



According to general procedure **A**, **L4.HPF₆** (0.170 g, 0.36 mmol) in THF (20 mL) afforded complex **4** (0.193 g, 98%) as a yellow powder (the crude product was purified by column chromatography on basic alumina (eluent: toluene / THF : 2/1). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of cyclohexane into a solution of complex **C3** in THF at r.t.

¹H NMR (400 MHz, CD₂Cl₂, 25 °C) δ 7.93-7.81 (m, 2H, CH_{PH}), 7.46-7.28 (m, 8H, CH_{PH}), 7.16-7.12 (m, 2H, CH_{Im}), 5.44-5.25 (m, 2H, NCH₂ + CH_{iPr}), 4.24 (ddt, $J = 29.3, 13.8, 4.6$ Hz, 1H, NCH₂), 2.82-2.70 (m, 1H, Ph₂PCH₂), 2.62-2.49 (m, 1H, Ph₂PCH₂), 1.54 (d, $J = 6.6$ Hz, 3H, CH_{3 iPr}), 1.36 (d, $J = 6.6$ Hz, 3H, CH_{3 iPr}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2 , 25 °C) δ 224.1 (d, $J = 18.9$ Hz, Mn-CO), 220.3 (d, $J = 29.6$ Hz, Mn-CO), 219.2 (d, $J = 22.3$ Hz, Mn-CO), 184.3 (d, $J = 24.5$ Hz, Mn-CN₂), 137.1 (d, $J = 41.3$ Hz, C_{Ph}), 134.8 (d, $J = 37.3$ Hz, C_{Ph}), 134.0 (d, $J = 9.2$ Hz, CH_{Ph}), 131.7 (d, $J = 9.5$ Hz, CH_{Ph}), 130.5 (d, $J = 2.4$ Hz, CH_{Ph}), 130.1 (d, $J = 2.1$ Hz, CH_{Ph}), 128.9 (d, $J = 9.0$ Hz, CH_{Ph}), 128.5 (d, $J = 9.3$ Hz, CH_{Ph}), 124.8 (s, CH_{Im}), 118.0 (s, CH_{Im}), 52.6 (s, CH_{iPr}), 47.3 (d, $J = 2.7$ Hz, NCH₂), 28.6 (d, $J = 20.8$ Hz, PPh₂CH₂), 24.1 (s, CH_{3 iPr}), 24.0 (s, CH_{3 iPr}).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , 25 °C) δ 38.72.

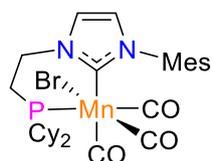
IR ν_{CO} (CD_2Cl_2): 2015, 1939, 1901 cm^{-1} .

IR ν_{CO} (solid, ATR) = 2004, 1927, 1891 cm^{-1} .

Elemental analysis: calcd (%) for $\text{C}_{23}\text{H}_{23}\text{BrMnN}_2\text{O}_3\text{P}$: C, 51.04; H, 4.28; N, 5.18; found: C, 50.68; H, 4.21; N, 4.94.

HR-MS (ESI): m/z : calcd for $\text{C}_{23}\text{H}_{23}\text{MnN}_2\text{O}_3\text{P}^+$: 461.0824, found: 461.0827, $\epsilon_r = 0.7$ ppm

Synthesis of [(MnBr(CO)₃(Cy₂P(CH₂)₂-Im-Mes)] (5)



According to general procedure **A**, **L5.HOTs** (200 mg, 0.34 mmol) in toluene (20 mL) afforded complex **5** (192 mg, 88%) as a yellow powder. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of dichloromethane into a solution of complex **5** in toluene at r.t.

^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 7.07 (d, $J = 1.6$ Hz, 1H, CH_{Im}), 7.00 (s, 1H, CH_{Mes}), 6.99 (s, 1H, CH_{Mes}), 6.83 (d, $J = 1.6$ Hz, 1H, CH_{Im}), 5.31-5.21 (m, 1H, NCH₂), 4.17-4.04 (m, 1H, NCH₂), 2.36-1.19 (m + s, 33H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25 °C) δ 223.9 (d, $J = 18.5$ Hz, Mn-CO), 219.0 (d, $J = 23.3$ Hz, Mn-CO), 216.2 (d, $J = 27.0$ Hz, Mn-CO), 188.9 (d, $J = 23.0$ Hz, Mn-CN₂), 139.2 (s, C_{Mes}), 138.0 (s, C_{Mes}), 136.6 (s, C_{Mes}), 135.4 (s, C_{Mes}), 129.4 (s, CH_{Mes}), 128.9 (s, CH_{Mes}), 124.4 (s, CH_{Im}), 122.6 (s, CH_{Im}), 47.4 (s, NCH₂), 37.2 (d, $J = 21.6$ Hz, CH_{cy}), 36.6 (d, $J = 16.9$ Hz, CH_{cy}), 29.3 (s, CH_{2 cy}), 28.5 (s, CH_{2 cy}), 27.8 (s, CH_{2 cy}), 27.6 (d, $J = 10.4$ Hz, CH_{2 cy}), 27.4 (d, $J = 9.7$ Hz, CH_{2 cy}), 27.06 (d, $J = 9.3$ Hz, CH_{2 cy}), 27.06 (s, CH_{2 cy}), 26.9 (d, $J = 10.6$ Hz, CH_{2 cy}), 26.3 (s, CH_{2 cy}), 25.9 (s, CH_{2 cy}), 21.2 (s, CH_{3 Mes}), 19.6 (d, $J = 14.6$ Hz, PCH₂), 18.9 (s, CH_{3 Mes}), 18.1 (s, CH_{3 Mes}).

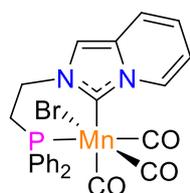
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25 °C) δ 36.69.

IR ν_{CO} (CH_2Cl_2): 2011, 1933, 1891 cm^{-1} .

Elemental analysis: calcd (%) for $\text{C}_{29}\text{H}_{39}\text{BrMnN}_2\text{O}_3\text{P}$: C, 55.34; H, 6.25; N, 4.45; found: C, 55.10; H, 6.57; N, 4.48.

HR-MS (ESI): m/z : calcd for $\text{C}_{29}\text{H}_{39}\text{MnN}_2\text{O}_3\text{P}^+$: 549.2079, found: 549.2074, $\epsilon_r = 0.9$ ppm.

Synthesis of $[(\text{MnBr}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{-IPy}))]$ (**6**)



According to general procedure **A**, **L6.HOTs** (245 mg, 0.49 mmol) in THF (25 mL) afforded complex **6** (232 mg, 86%) as a yellow powder. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of cyclohexane into the solution of complex **6** in THF at r.t.

^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 8.77 (d, $J = 7.5$ Hz, 1H, CH_{IPy}), 7.86 (br s, 2H, CH_{Ph}), 7.64-7.29 (m, 10H, 2 CH_{IPy} + 8 CH_{Ph}), 6.88 (br s, 1H, CH_{IPy}), 6.67 (br s, 1H, CH_{IPy}), 5.55 (br s, 1H, NCH₂), 4.48 (br s, 1H, NCH₂), 2.82 (br s, 1H, PPh₂CH₂), 2.63 (m, 1H, PPh₂CH₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25 °C) δ 223.2 (d, J = 18.7 Hz, Mn-CO), 219.3 (d, J = 27.1 Hz, Mn-CO), 218.1 (d, J = 22.7 Hz, Mn-CO), 177.4 (d, J = 24.7 Hz, Mn-CN₂), 136.3 (d, J = 41.2 Hz, C_{Ph}), 133.86 (d, J = 9.1 Hz, CH_{Ph}), 133.80 (d, J = 37.3 Hz, C_{Ph}), 131.9 (s, C_{IPy}), 131.6 (d, J = 9.6 Hz, CH_{Ph}), 130.3 (s, CH_{Ph}), 129.9 (s, CH_{Ph}), 128.72 (d, J = 8.1 Hz, CH_{Ph}), 128.68 (s, CH_{IPy}) 128.3 (d, J = 9.3 Hz, CH_{Ph}), 122.6 (s, CH_{IPy}), 117.8 (s, CH_{IPy}), 114.6 (s, CH_{IPy}), 113.3 (s, CH_{IPy}), 48.0 (s, NCH₂), 28.5 (d, J = 20.5 Hz, PPh₂CH₂).

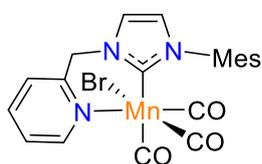
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25 °C) δ 39.67.

IR vco (CH_2Cl_2): 2016, 1940, 1904 cm^{-1} .

Elemental analysis: calcd (%) for $\text{C}_{24}\text{H}_{19}\text{BrMnN}_2\text{O}_3\text{P}$: C, 52.48; H, 3.49; N, 5.10; found: C, 53.08; H, 3.17; N, 4.86.

HR-MS (ESI): m/z : calcd for $\text{C}_{24}\text{H}_{19}\text{MnN}_2\text{O}_3\text{P}^+$: 469.0514, found: 469.0515, ϵ_r = 0.2 ppm.

Synthesis of [(MnBr(CO)₃(Py-CH₂-Im-Mes)] (**8**)



According to general procedure **A**, **L8.HPF₆** (365 mg, 0.86 mmol) in THF (40 mL) afforded complex **8** (310 mg, 73%) as a yellow powder. The crude product was purified by column chromatography on silica (size 40-63 μm) with eluent: toluene / THF: 2/1 and then THF.

^1H NMR (400 MHz, CD_2Cl_2 , 25 °C) δ 9.18 (d, J = 5.6 Hz, 1H, CH_{Py}), 7.83 (td, J = 7.7, 1.6 Hz, 1H, CH_{Py}), 7.47 (d, J = 7.7 Hz, 1H, CH_{Py}), 7.37 (d, J = 1.8 Hz, 1H, CH_{Im}), 7.30 (ddd, J = 7.4, 5.7, 1.6 Hz, 1H, CH_{Py}), 7.04-6.96 (m, 3H, CH_{Mes}, CH_{Im}), 6.48 (d, J = 15.2 Hz, 1H, CH₂), 5.07 (d, J = 15.2 Hz, 1H, CH₂), 2.35 (s, 3H, CH₃ Mes), 2.18 (s, 3H, CH₃ Mes), 2.01 (s, 3H, CH₃ Mes).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2 , 25 °C) δ 224.3 (s, Mn-CO), 222.9 (s, Mn-CO), 217.2 (s, Mn-CO), 193.7 (s, Mn-CN₂), 157.6 (s, C_q), 157.4 (s, CH_{Py}), 139.8 (s, C_q), 138.9 (s, CH_{Py}), 137.9 (s, C_q),

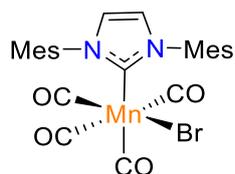
136.5 (s, C_q), 136.0 (s, C_q), 129.6 (s, CH_{Mes}), 129.1 (s, CH_{Mes}), 125.7 (s, CH_{Py}), 123.8 (s, CH_{Py}), 123.6 (s, CH_{Im}), 123.4 (s, CH_{Im}), 55.4 (s, CH₂), 21.3 (s, CH_{3 Mes}), 18.9 (s, CH_{3 Mes}), 18.0 (s, CH_{3 Mes}).

IR ν_{CO} (CH₂Cl₂): 2019, 1933, 1899 cm⁻¹.

Elemental analysis: calcd (%) for C₂₁H₁₉BrMnN₃O₃: C, 50.83; H, 3.86; N, 8.47; found : C, 51.97; H, 3.96; N, 8.54.

HR-MS (ESI): m/z: calcd for C₂₁H₁₉MnN₃O₃⁺: 416.0807, found: 416.0810, ϵ_r = 0.7 ppm.

Synthesis of [(MnBr(CO)₄(IMes))]



To a stirred suspension of 1,3-bis(2,4,6-trimethylphenyl)-1*H*-imidazolium chloride (248 mg, 0.72 mmol) in toluene, a solution of KHMDS (1.6 mL, 0.80 mmol, 1.1 eq., 0.5 M in toluene.) was added at r.t. and then the resulting yellow suspension was sonicated during 5 min and stirred for additional 3 h. After filtration through Celite, [Mn(CO)₅Br] (200 mg, 0.72 mmol, 1 eq.) was added in one portion, as a solid, inducing a vigorous CO evolution. The resulting orange solution was stirred for 18 h at r.t. and monitored by I.R. The crude product was crystallized in a toluene / hexane mixture affording complex [(MnBr(CO)₄(IMes))] as a yellow powder (250 mg, 62%).

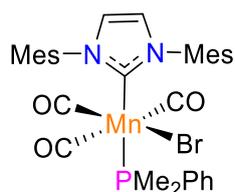
¹H NMR (400 MHz, CDCl₃, 25 °C) δ 7.14 (s, 2H, CH_{Im}), 7.04 (s, 4H, CH_{Mes}), 2.37 (s, 6H, CH_{3 Mes}), 2.19 (s, 12H, CH_{3 Mes}).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 219.5 (s, Mn-CO), 212.3 (s, Mn-CO), 207.8 (s, 2C, Mn-CO), 190.0 (s, Mn-CN₂), 140.8 (s, C_{Mes}), 137.4 (s, C_{Mes}), 137.0 (s, C_{Mes}), 129.7 (s, CH_{Mes}), 124.8 (s, CH_{Im}), 21.3 (s, CH_{3 Mes}), 18.4 (s, CH_{3 Mes}).

IR ν_{CO} (Toluene): 2078, 1997, 1934 cm^{-1} .

HR-MS (ESI): m/z : calcd for $\text{C}_{25}\text{H}_{24}\text{MnN}_2\text{O}_4^+$: 471.1117, found: 471.1122, $\epsilon_r = 1.1$ ppm.

Synthesis of **[(MnBr(CO)₃(PhMe₂P-Im(bisMes))]** (**11**)



To a stirred suspension of complex **[(MnBr(CO)₄(IMes))]** (50 mg, 0.09 mmol) in toluene (5 mL), PMe_2Ph (13 μL , 0.09 mmol, 1 equiv.) was added at r.t. and then the resulting yellow solution was stirred for 18 h at 70 °C. After cooling the reaction mixture to r.t. and evaporation of the solvent under vacuum, the crude product was crystallized in a toluene/hexane mixture affording complex **11** as a yellow powder (44 mg, 73%). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of hexane into a solution of complex **11** in THF at r.t.

^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 7.41-7.23 (m, 5H, CH_{Ph}), 7.05-6.98 (m, 6H, $\text{CH}_{\text{Im}} + \text{CH}_{\text{Mes}}$), 2.36 (s, 6H, CH_3_{Mes}), 2.21 (s, 12H, CH_3_{Mes}), 1.72 (d, $J = 8.7$ Hz, 6H, $\text{CH}_3_{\text{PMe}_2}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25 °C) δ 226.0 (br s, Mn-CO), 216.4 (d, $J = 24.2$ Hz, Mn-CO), 196.5 (d, $J = 15.0$ Hz, Mn-CN₂), 139.7 (s, C_{Mes}), 139.1 (d, $J = 38.4$ Hz, C_{Ph}), 138.2 (s, C_{Mes}), 137.3 (s, C_{Mes}), 129.4 (s, CH_{Mes}), 129.2 (d, $J = 8.1$ Hz, CH_{Ph}), 128.9 (d, $J = 2$ Hz, CH_{Ph}), 128.3 (d, $J = 8.8$ Hz, CH_{Ph}), 124.4 (s, CH_{Im}), 21.3 (s, CH_3_{Mes}), 18.6 (s, CH_3_{Mes}), 14.6 (d, $J = 28.9$ Hz, PCH_3). (Extra signals are observed at 141.6, 134.2, 130.6, and 130.2, which might be assigned to the minor isomer detected by IR.)

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25 °C) δ 26.85.

IR ν_{CO} (toluene): 1879, 1893, 1925, 1933, 2016, 2025 cm^{-1} . (Two isomers)

HR-MS (ESI): m/z : calcd for $\text{C}_{32}\text{H}_{35}\text{MnN}_2\text{O}_3\text{P}^+$: 581.1766, found: 581.1769, $\epsilon_r = 0.5$ ppm.

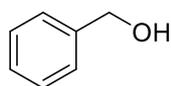
5. Catalytic hydrogenation of esters catalyzed by complex **2** and characterization of the resulting alcohols.

General procedure B for the hydrogenation reactions

Complex **2** (3.1 mg, 0.005 mmol, 0.5 mol%) was dissolved in 2-Me-THF (0.5 mL) and activated with KHBET_3 (0.1 mL, 1.0 M in THF, 0.1 mmol, 10 mol%) for 0.5 h. This solution was added to an autoclave previously charged under argon with a solution of ester (1 mmol) in 2-Me-THF (1 mL). Then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath at 100 °C for 24 hours. Once the reactor has cooled down and the hydrogen pressure has been released, the reaction mixture was diluted with ethyl acetate or CH_2Cl_2 (2.0 mL) and filtered through a small pad of silica (2 cm in a Pasteur pipette). The Pasteur pipette was then flushed with an additional volume of ethyl acetate or CH_2Cl_2 . The filtrate was evaporated under vacuum and the crude product was purified by column chromatography on silica (size 60-43 μm) using pentane/ethyl acetate mixtures as eluent to afford the corresponding alcohols. (Note: for specific conditions, see the main article Scheme 2.)

Spectroscopic characterization data of the alcohols

Benzyl alcohol **b1**¹⁰



According to general procedure **B**, methyl benzoate **a1** (125 μL , 1 mmol) gave the title compound **b1** as a colorless oil (103 mg, 96%)

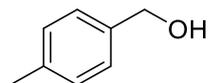
According to general procedure **B**, benzyl benzoate **a2** (190 μL , 1 mmol) gave the title compound **b1** after 24 h at 100 °C with 0.5 mol% as a colorless oil (186.1 mg, 86%).

According to general procedure **B**, ethyl benzoate **a3** (143 μ L, 1 mmol) gave the title compound **b1** after 48 h as a colorless oil (102 mg, 94%).

^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 7.57-7.33 (m, 5H), 4.70 (s, 2H), 3.45 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 140.9, 128.4, 127.4, 127.0, 64.8.

4-Tolylmethanol **b5**¹⁰



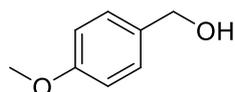
According to general procedure **B**, methyl 4-methylbenzoate **a5** (150mg, 1 mmol) gave the title compound **b5** as a white solid (118 mg, 97%).

According to general procedure **B** with 5 mol% of **2** at 120 $^\circ\text{C}$ for 48 h, ethylene bis(4-methylbenzoate) **a26** (149 mg, 0.5 mmol) gave the title compound **b5** as a white solid (100 mg, 82%).

^1H NMR (300 MHz, CDCl_3) δ 7.26 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 4.65 (s, 2H), 2.35 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.0, 137.4, 129.3, 127.2, 65.1, 21.2.

4-Methoxyphenylmethanol **b6**¹⁰



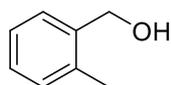
According to general procedure **B**, methyl 4-methoxybenzoate **a6** (166 mg, 1 mmol) gave the title compound **b6** as a yellow oil (110 mg, 80%).

According to general procedure **B**, ethyl 4-methoxybenzoate **a7** (162 μ L, 1 mmol) gave the title compound **b6** after 48 h as an orange oil (123 mg, 89%).

^1H NMR (300 MHz, CDCl_3) δ 7.33-7.27 (m, 2H), 6.91-6.83 (m, 2H), 4.60 (s, 2H), 3.81 (s, 3H), 1.80 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 159.3, 133.3, 128.8, 114.1, 65.1, 55.4.

2-Tolylmethanol **b8**¹⁰

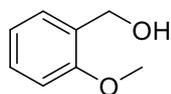


According to general procedure **B**, methyl 2-methylbenzoate **a8** (140 μ L, 1 mmol) gave the title compound **b8** as a colorless oil (83 mg, 68%).

^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 7.38-7.32 (m, 1H), 7.25-7.15 (m, 3H), 4.69 (s, 2H), 2.36 (s, 3H), 1.77 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 138.8, 136.2, 130.4, 127.9, 127.7, 126.2, 63.6, 18.7.

2-Methoxyphenylmethanol **b9**¹¹

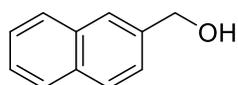


According to general procedure **B**, methyl 2-methoxybenzoate **a9** (143 μ L, 1 mmol) gave the title compound **b9** as a colorless oil (103 mg, 74%).

^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 7.31-7.25 (m, 2H), 6.95 (td, $J = 7.4, 1.0$ Hz, 1H), 6.91-6.87 (m, 1H), 4.69 (s, 2H), 3.87 (s, 3H), 2.35 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 157.6, 129.2, 129.1, 128.9, 120.8, 110.3, 62.3, 55.4.

2-Naphthylmethanol **b11**¹²

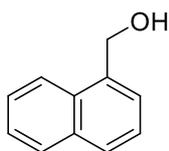


According to general procedure **B** with 1 mol% of **2**, methyl 2-naphthoate **a11** (186 mg, 1 mmol) gave the title compound **b11** after 48 h as a white solid (153 mg, 97%).

^1H NMR (400 MHz, CDCl_3) δ 7.87-7.78 (m, 4H), 7.52-7.44 (m, 3H), 4.84 (s, 2H), 2.09 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.4, 133.5, 133.0, 128.4, 128.0, 127.8, 126.3, 126.0, 125.5, 125.3, 65.5.

1-Naphthylmethanol **b12**¹³

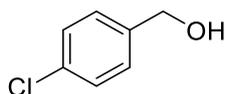


According to general procedure **B** with 1 mol% of **2**, methyl 1-naphthoate **a12** (159 μ L, 1 mmol) gave the title compound **b12** after 48 h as an orange oil (150 mg, 95%).

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 7.5 Hz, 1H), 7.88 (dd, J = 7.0, 2.1 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.59-7.39 (m, 4H), 5.09 (s, 2H), 2.36 (s, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 136.4, 133.9, 131.3, 128.7, 128.6, 126.4, 125.9, 125.5, 125.4, 123.7, 63.6.

4-Chlorophenylmethanol **b14**¹⁴

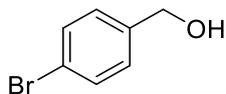


According to general procedure **B**, methyl 4-chlorobenzoate **a14** (170 mg, 1 mmol) gave the title compound **b14** as a white crystalline solid (135 mg, 95%).

¹H NMR (300 MHz, CDCl₃, 25 $^{\circ}$ C) δ 7.38-7.27 (m, 4H), 4.64 (s, 2H), 2.01 (s, 1H).

¹³C{¹H} NMR (75 MHz, CDCl₃, 25 $^{\circ}$ C) δ 139.4, 133.4, 128.8, 128.4, 64.6.

4-Bromophenylmethanol **b15**¹⁰

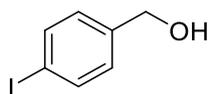


According to general procedure **B** with 1 mol% of **2**, methyl 4-bromobenzoate **a15** (215 mg, 1 mmol) gave the title compound **b15** as a white crystalline solid (172 mg, 92%).

¹H NMR (400 MHz, CDCl₃) δ 7.50-7.45 (m, 2H), 7.25-7.20 (m, 2H), 4.63 (s, 2H), 1.92 (s, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 139.9, 131.7, 128.7, 121.6, 64.7.

4-Iodophenylmethanol **b16**¹³

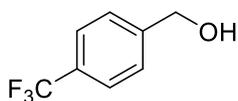


According to general procedure **B** with 1 mol% of **2**, methyl 4-iodobenzoate **a16** (262 mg, 1 mmol) gave the title compound **b16** as a white solid (68 mg, 29%).

^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 4.64 (s, 2H), 1.73 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 140.6, 137.7, 128.9, 93.1, 64.8.

4-(Trifluoromethyl)phenylmethanol **b17**¹⁵



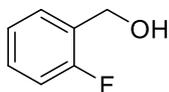
According to general procedure **B**, methyl 4-(trifluoromethyl) benzoate **a17** (161 μL , 1 mmol) gave the title compound **b17** as a colorless oil (108 mg, 61%).

^1H NMR (300 MHz, CDCl_3) δ 7.62 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 4.76 (s, 2H), 1.89 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 144.7 (q, $J = 1.5$ Hz), 129.8 (q, $J = 32.2$ Hz), 126.9, 125.5 (q, $J = 3.8$ Hz), 124.3 (q, $J = 272$ Hz), 64.2.

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, CDCl_3) δ -62.50.

2-Fluorophenylmethanol **b18**¹⁶



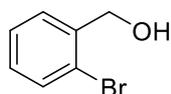
According to general procedure **B**, methyl 2-fluorobenzoate **a18** (127 μL , 1 mmol) gave the title compound **b18** as a pale-yellow oil (90 mg, 71%).

^1H NMR (400 MHz, CDCl_3 , 25°C) δ 7.41 (td, $J = 7.5, 1.8$ Hz, 1H), 7.32-7.23 (m, 1H), 7.14 (td, $J = 7.5, 1.2$ Hz, 1H), 7.07-7.02 (m, 1H), 4.75 (s, 2H), 1.99 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25 °C) δ 160.7 (d, $J_{\text{CF}} = 246.1$ Hz), 129.6-129.3 (2C, two signals merged), 127.9 (d, $J_{\text{CF}} = 14.7$ Hz), 124.4 (d, $J_{\text{CF}} = 3.6$ Hz), 115.4 (d, $J_{\text{CF}} = 21.2$ Hz), 59.5 (d, $J_{\text{CF}} = 4.4$ Hz).

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -119.86.

2-Bromophenylmethanol **b19**¹⁷

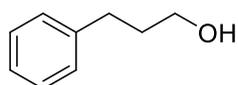


According to general procedure **B**, methyl 2-bromobenzoate **a19** (140 μL , 1 mmol) gave the title compound **b19** as a colorless oil (114 mg, 61%).

^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 7.55 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.50-7.47 (m, 1H), 7.33 (td, $J = 7.5, 1.2$ Hz, 1H), 7.20-7.13 (m, 1H), 4.75 (s, 2H), 2.07 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25 °C) δ 139.9, 132.7, 129.3, 129.1, 127.8, 122.7, 65.2.

3-Phenylpropan-1-ol **b20**¹⁶



According to general procedure **B** with 1 mol% of **2**, methyl 3-phenylpropanoate **a20** (157 μL , 1 mmol) gave the title compound **b20** after 48 h as a colorless oil (111 mg, 82%).

^1H NMR (400 MHz, CDCl_3) δ 7.35-7.27 (m, 2H), 7.23-7.19 (m, 3H), 3.68 (t, $J = 6.5$ Hz, 2H), 2.74-2.70 (m, 2H), 1.98 (s, 1H), 1.97-1.85 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 141.9, 128.50, 128.47, 125.9, 62.2, 34.3, 32.1.

Decan-1-ol **b21**¹⁸

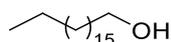


According to general procedure **B**, methyl decanoate **a21** (214 μ L, 1 mmol) gave the title compound **b21** after 48 h as a pale-yellow oil (142 mg, 90%).

^1H NMR (400 MHz, CDCl_3) δ 3.62 (t, J = 6.7 Hz, 2H), 1.60-1.49 (m, 3H, CH_2 + OH), 1.36-1.22 (m, 14H), 0.87 (t, J = 6.8 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 63.2, 32.9, 32.0, 29.75, 29.70, 29.57, 29.46, 25.88, 22.81, 14.2.

Octadecan-1-ol **b22**¹⁹

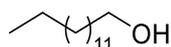


According to general procedure **B** with 1 mol% of **2**, methyl stearate **a22** (298 mg, 1 mmol) gave the title compound **b22** after 48 h as a white solid (203 mg, 75%).

^1H NMR (400 MHz, CDCl_3) δ 3.64 (t, J = 6.6 Hz, 2H), 1.62-1.52 (m, 2H), 1.38-1.19 (m, 31H, CH_2 + OH), 0.88 (t, J = 6.9 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 63.3, 33.0, 32.1, 29.85 (4C), 29.83 (2C), 29.81(2C), 29.77, 29.75, 29.59, 29.51, 25.9, 22.8, 14.3.

Tetradecan-1-ol **b23**¹⁹

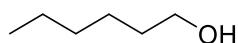


According to general procedure **B** with 1 mol% of **2**, isopropyl myristate **a23** (270 mg, 1 mmol) gave the title compound **b23** after 48 h as a colorless oil (120 mg, 56%).

^1H NMR (300 MHz, CDCl_3) δ 3.64 (t, J = 6.6 Hz, 2H), 1.59-1.52 (m, 2H), 1.44-1.16 (m, 23H, CH_2 + OH), 0.88 (t, J = 6.7 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 63.3, 33.0, 32.1, 29.82 (4C), 29.77, 29.75, 29.59, 29.51, 25.9, 22.8, 14.3.

Hexan-1-ol **b24**²⁰



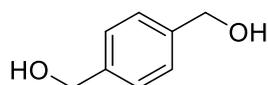
According to general procedure **B** with 1 mol% of **2**, hexyl hexanoate **a24** (200 mg, 1 mmol) gave the title compound **b24** after 48 h as a colorless oil (60 mg, 29%).

Polycaprolactone **a29** (100 mg, 0.8 mmol, Aldrich, $M_w = 14\ 000$) was introduced in the autoclave. The latter was flushed with argon. A solution of complex **2** (5 mol%) in 2-Me-THF/anisole (1/1 mL) was activated with KHBET_3 (10 mol%) for 30 min and transferred to the autoclave, which was immediately pressurized with H_2 (50 bar) and heated at 100 °C for 24 h. Then after cooling down, the pressure was released and the yellow solution was filtered over a small pad of silica in a pipette. The solution was collected in a round-bottom flask and 1,3,5-trimethoxy benzene (1/3 vs PLC) was added as internal standard for NMR analysis. RMN yield = 79%.

^1H NMR (400 MHz, CDCl_3) δ 3.63 (t, $J = 6.6$ Hz, 2H), 1.62-1.49 (m, 2H), 1.45 (br s, 1H), 1.40-1.21 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 63.2, 32.9, 31.8, 25.5, 22.8, 14.2.

1,4-Benzenedimethanol **b25**¹¹

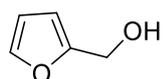


According to general procedure **B**, dimethyl terephthalate **a25** (194 mg, 1 mmol) was reduced with **2** (4 mol%) at 120 °C to give the title compound **b25** as a solid white (130 mg, 94%). Note: MeOH was used instead of EtOAc or CH_2Cl_2 in this case for solubility reason.

^1H NMR (300 MHz, CDCl_3) δ 7.37 (s, 4H), 4.69 (s, 4H), 1.65 (s, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 140.5, 127.4, 65.3.

2-Furanmethanol **b27**¹⁴



According to general procedure **B** with 1 mol% of **2**, ethyl 2-furoate **a27** (140 mg, 1 mmol) gave the title compound **b27** after 48 h as a dark orange oil (45 mg, 46%).

^1H NMR (400 MHz, CDCl_3) δ 7.38 (s, 1H), 6.32 (s, 1H), 6.27 (s, 1H), 4.57 (s, 2H), 2.46 (br s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.1, 142.6, 110.4, 107.8, 57.4.

6. Additional experiments

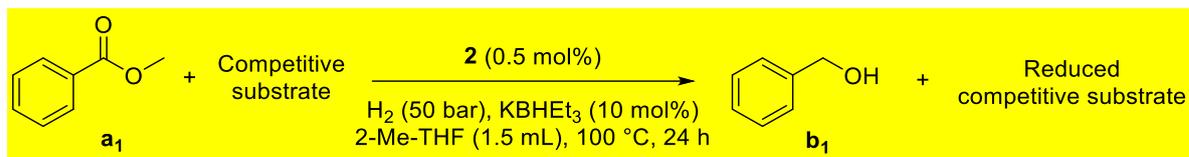


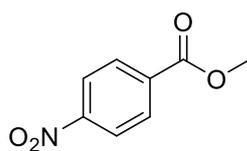
Table S4: Hydrogenation of methyl benzoate **a₁ in the presence of a competitive substrate with complex **2**.^[a]**

Competitive substrate	NMR conversion of a ₁	NMR yield of b ₁	Isolated yield of b ₁	NMR conversion of the competitive substrate
	60	52	48	0
	63	57	57	0
	13	7	4	0

[a] Experimental procedure: Complex **2** (3.1 mg, 0.005 mmol, 0.5 mol%) was dissolved in 2-Me-THF (0.5 mL) and activated with KBHET₃ (0.1 mL, 1.0 M in THF, 0.1 mmol, 10 mol%) for 0.5 h. This solution was added to an autoclave previously charged under argon with a solution of methyl benzoate **a**₁ (124 μL, 1 mmol) and the competitive substrate (1 mmol) in 2-Me-THF (1 mL). Then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath at 100 °C for 24 hours. Once the reactor has cooled down and the hydrogen pressure has been released, the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a small pad of silica (2 cm in a Pasteur pipette). The Pasteur pipette was then flushed with an additional volume of CH₂Cl₂. The filtrate was evaporated under vacuum and the crude product was purified by column chromatography on silica (size 60-43 μm) using pentane/ethyl acetate mixtures as eluent to afford the corresponding alcohols.

Table S5: Unsuccessful substrates.^[a]

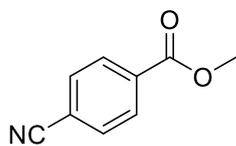
Substrate	NMR conversion of the ester (%)	NMR yield of the alcohol (%)	Remarks
	<2	<2	
	27	16	11 % of trans-esterified product



0

0

No reduction of the NO₂ group detected, only starting material was detected



0

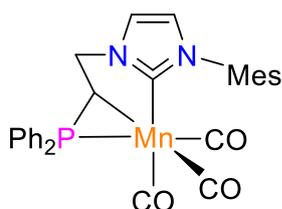
0

No reduction of the CN group detected, only starting material was detected)

[a] Experimental procedure: an autoclave was loaded with a solution of ester (1 mmol) in 2-Me-THF (1 mL) and a solution of **2** (0.5 mol%) in 2-Me-THF, which was first preactivated with KHBET₃ (10 mol%, 1M in THF) for 30 min, in this order. Then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath for 24 h at 100 °C. Crude mixture was analyzed by ¹H NMR.

7. Mechanistic studies

Synthesis of complex **12**



Complex **2** (224 mg, 0.36 mmol) was dissolved in THF (8 mL) and KHMDS (0.5 M solution in toluene, 1.09 mmol, 2.17 mL, 3 equiv.) was added. The mixture was stirred for 15 min at room temperature and concentrated in vacuum (until 2 mL). Deoxygenated *n*-hexane was added. The resulting solution was filtered with a cannula. The excess THF and *n*-hexane were removed in vacuum to afford a brown oily solid. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of *n*-hexane into the solution of complex **12** in toluene at r.t in a glove-box.

¹H NMR (400 MHz, THF-*d*₈) δ 7.95 – 6.88 (m, 14H, CH_{Im} + CH_{Ph} + CH_{Mes}), 6.69 (dt, *J*_{HP} = 12, *J*_{HH} = 18.3, 11.7 Hz, 1H, CH₂N), 5.90 (ddd, *J*_{HP} = 31.6, *J*_{HH} = 11.6, 2.2 Hz, 1H, CHP), 5.57 (ddd, *J*_{HP} = 18.2, *J*_{HH} = 18.3, 2.2 Hz, 1H, CH₂N), 2.31 (s, 6H, CH_{3Mes}), 1.96 (s, 3H, CH_{3Mes}).

Note: Satisfying ¹³C{¹H} NMR couldn't be recorded due to a low solubility of **12** in THF.

³¹P{¹H} NMR (162 MHz, THF-*d*₈) δ -12.7.

IR ν_{CO} (THF) = 1984, 1888 cm⁻¹.

HR-MS (ESI): m/z: calcd for [M+H]⁺ C₂₉H₂₇MnN₂O₃P⁺: 537.1140, found: 537.1143, ϵ_r = 0.6 ppm.

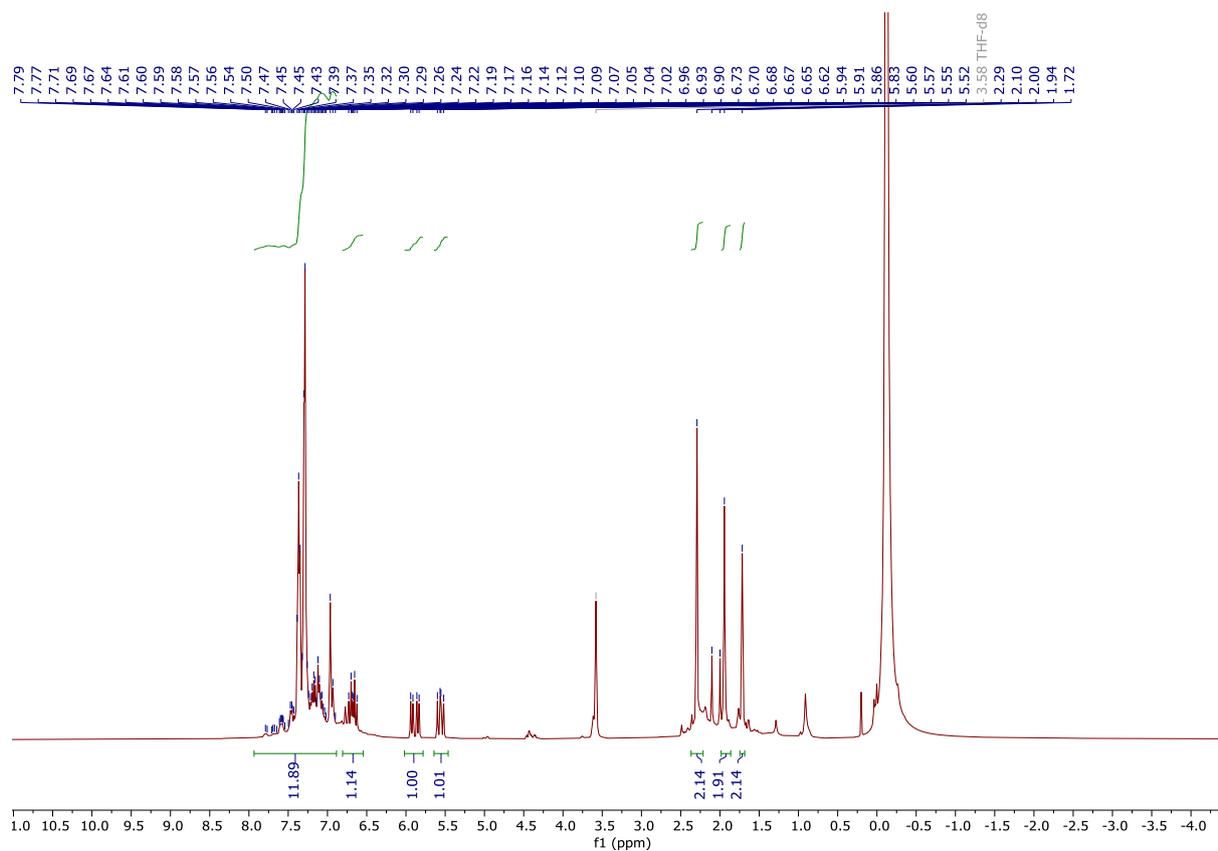


Figure S1: ¹H NMR spectrum of **12** in THF-*d*₈ recorded at 400 MHz.

--12.7

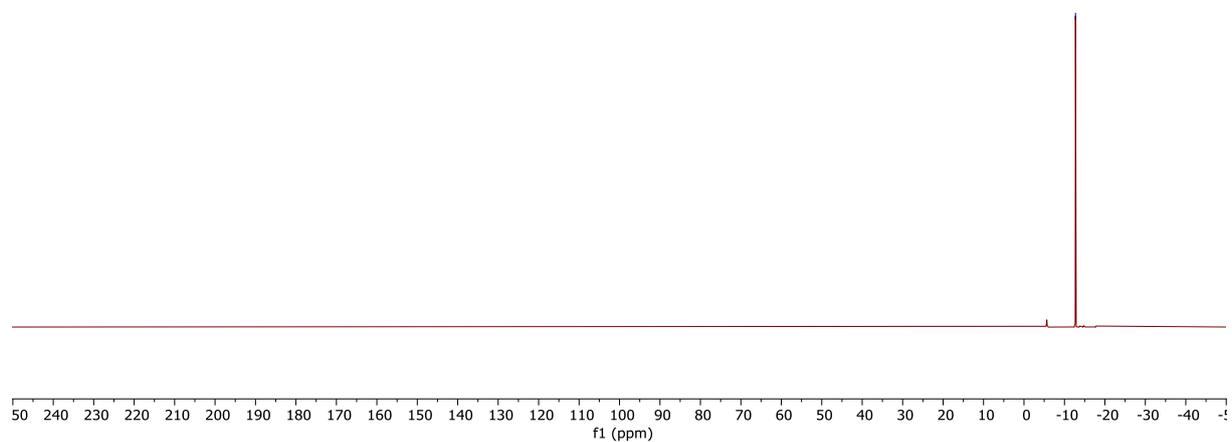
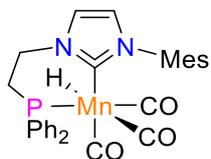


Figure S2: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **12** in THF- d_8 recorded at 162 MHz.

Synthesis of complex **13**



To a solution of complex **2** (200 mg, 0.32 mmol, 1 eq.) in degassed ethanol (20 mL), NaBH_4 (25 mg, 0.65 mmol, 2 eq.) was added and the reaction mixture was stirred at 80 °C for 3 h. The solvent was removed under vacuum and the resulting residue was dissolved in toluene (10 mL). The solution was washed with degassed water (3*12 mL), dried over Na_2SO_4 and filtered off to afford, after evaporation, **13** as a pale-yellow powder (142 mg, 0.26 mmol, 81%).

^1H NMR (400 MHz, THF- d_8): δ 7.77 – 7.72 (m, 2H, CH_{Ph}), 7.57-7.53 (m, 2H, CH_{Ph}), 7.39 – 7.26 (m, 7H, CH_{im} + CH_{Ph}), 6.95 (s, 1H, CH_{Mes}), 6.89 (s, 1H, CH_{im}), 6.88 (s, 1H, CH_{Mes}), 4.58-4.39 (m, 2H, N- CH_2), 2.37-2.32 (m, 2H, P- CH_2), 2.30 (s, 3H, CH_3 , Mes), 1.98 (s, 3H, CH_3 , Mes), 1.73 (s, 3H, CH_3 , Mes), -7.04 (d, $^2J_{\text{HP}} = 49.3$ Hz, 1H, Mn-H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, THF- d_8) δ 225.2 (d, $J = 24.4$ Hz, Mn-CO), 225.0 (d, $J = 18$ Hz, Mn-CO), 222.0 (d, $J = 15.6$ Hz, Mn-CO), 197.4 (d, $J = 25.0$ Hz, Mn-CN $_2$), 141.3 (d, $J = 41.6$ Hz, C_{Ph}), 141.1 (d, $J = 32.5$ Hz, C_{Ph}), 139.2 (s, C_{Mes}), 138.5 (s, C_{Mes}), 137.3 (s, C_{Mes}), 136.8 (s, C_{Mes}), 133.9 (d, $J = 10.4$ Hz, CH_{Ph}), 132.6 (d, $J = 10.4$ Hz, CH_{Ph}), 130.1 (d, $J = 2.2$ Hz, CH_{Ph}), 129.9 (d, $J = 1.9$ Hz, CH_{Ph}), 129.9 (s, CH_{Mes}), 129.8 (s, CH_{Mes}), 129.1 (d, $J = 8.6$ Hz, CH_{Ph}), 128.8 (d, $J = 9.1$ Hz, CH_{Ph}), 123.7 (s, CH_{im}), 123.1 (s, CH_{im}), 48.5 (d, $J = 4.3$ Hz, N- CH_2), 30.5 (d, $J = 23.5$ Hz, P- CH_2), 21.4 (s, CH_3 , Mes), 18.9 (s, CH_3 , Mes), 18.5 (s, CH_3 , Mes).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF- d_8) δ 65.4 ppm.

IR ν_{CO} (EtOH): 1986, 1905, 1890 cm^{-1} .

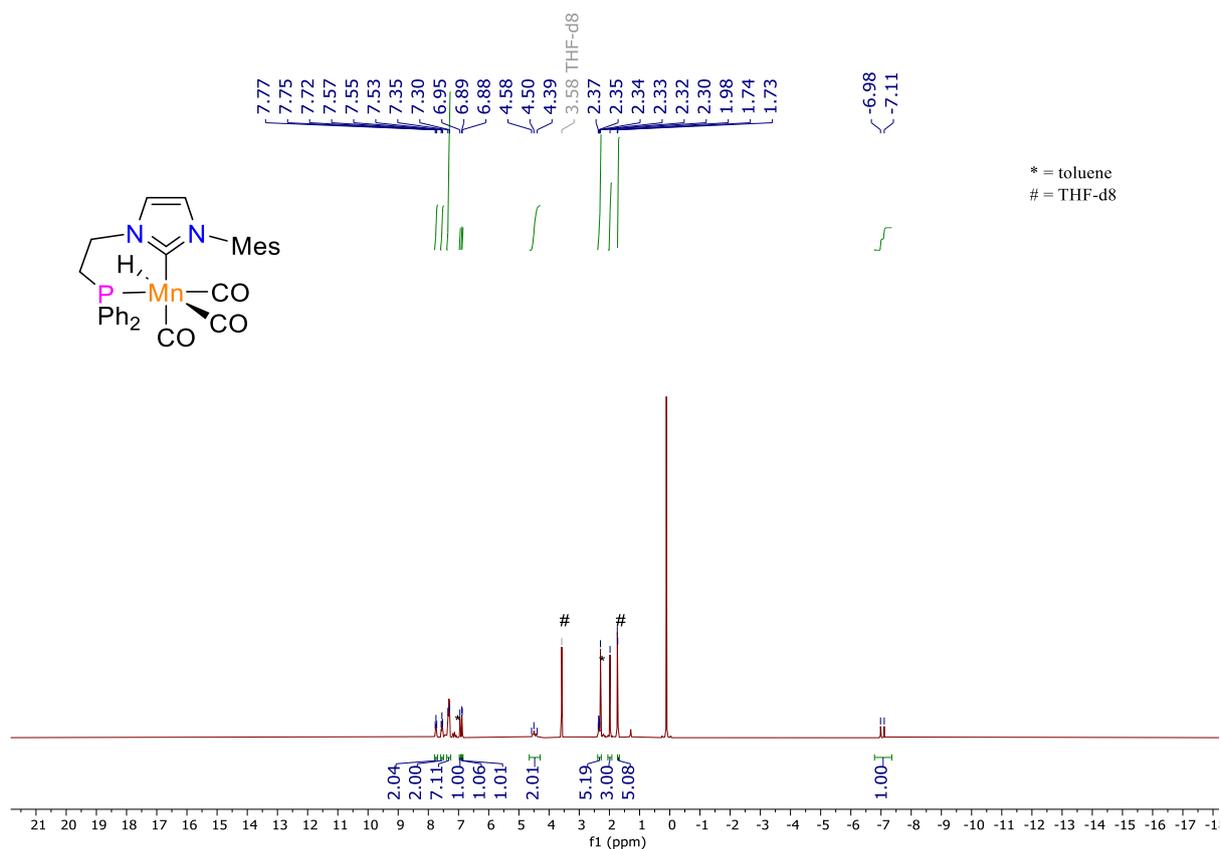


Figure S3: ¹H NMR spectrum of **13** in THF-*d*₈ recorded at 400 MHz.

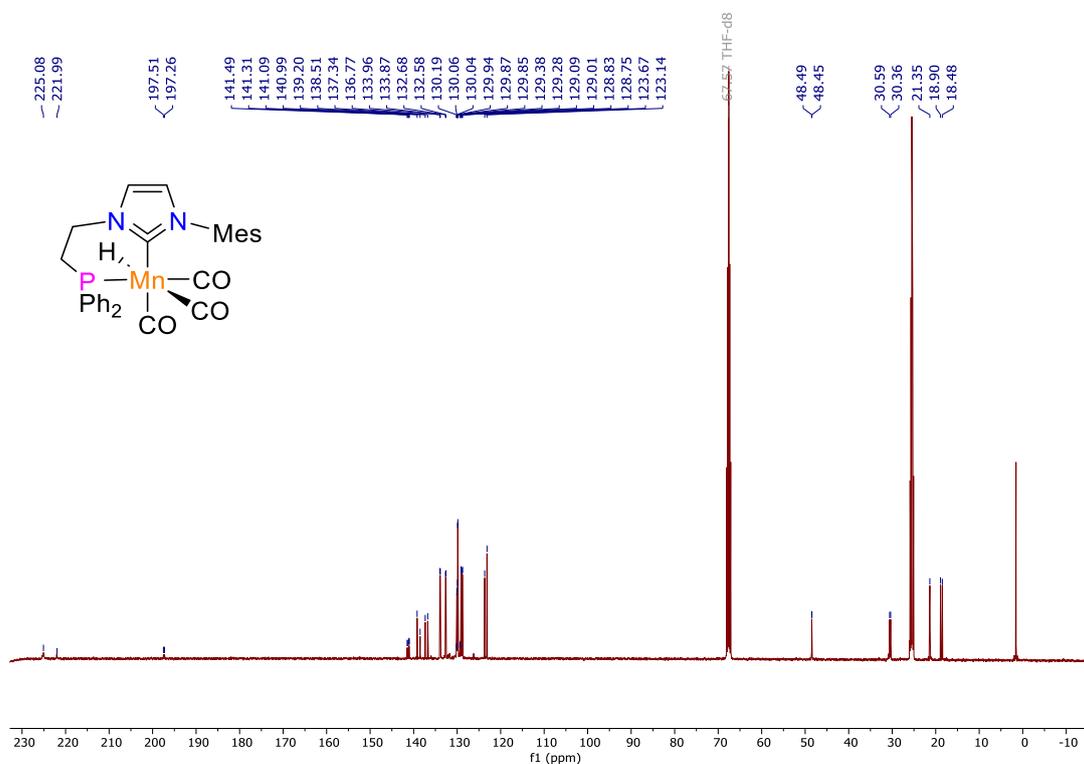


Figure S4: ¹³C{¹H} NMR spectrum of **13** in THF-*d*₈ recorded at 101 MHz.

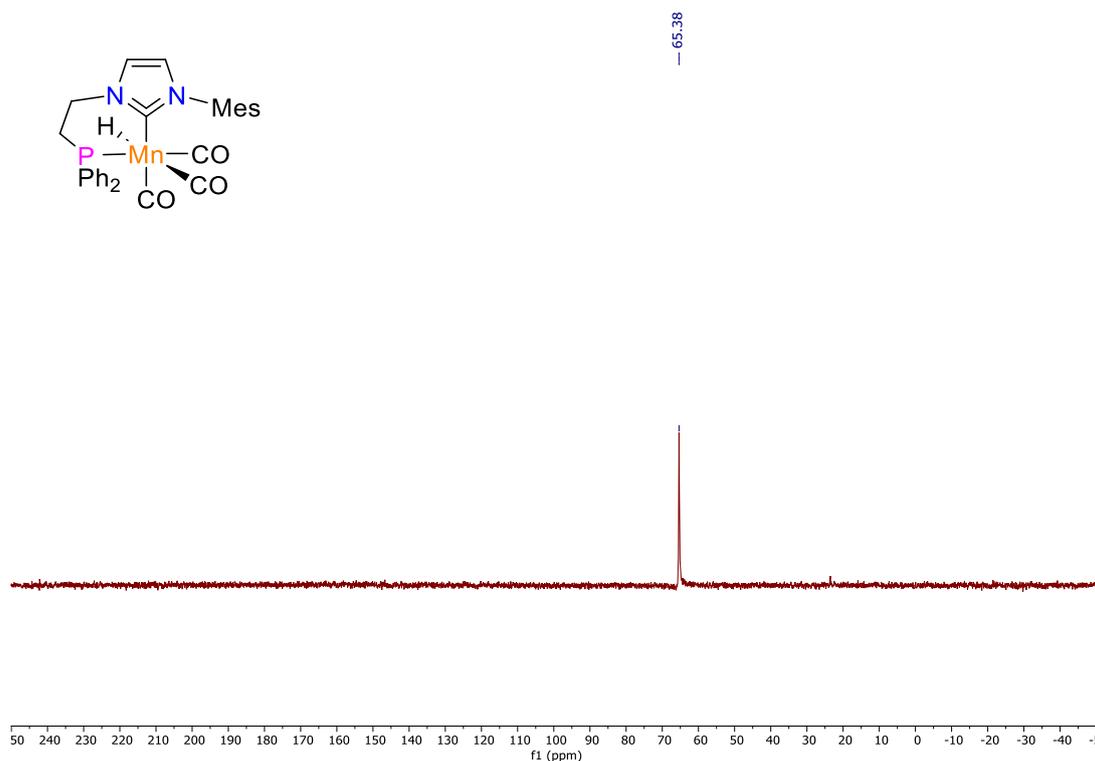
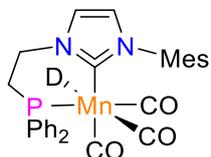


Figure S5: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **13** in $\text{THF-}d_8$ recorded at 162 MHz.

Synthesis of complex 13-D



To a solution of complex **2** (50 mg, 0.082 mmol, 1 eq.) in degassed ethanol (11 mL), NaBD_4 (7 mg, 0.17 mmol, 2.1 eq.) was added and the reaction mixture was stirred at 80 °C for 3 h. The solvent was removed under vacuum and the resulting residue was dissolved in toluene (5 mL). The solution was washed with degassed water (3*7 mL), dried over Na_2SO_4 and filtered off to afford, after evaporation, **13-D** as a pale-yellow powder (36.7 mg, 0.068 mmol, 83 %) with a purity of 95%.

^1H NMR (400 MHz, $\text{THF-}d_8$) δ 7.74 (t, $J = 9.8$ Hz, 2H, CHPh), 7.54 (d, $J = 8.4$ Hz, 2H, CHPh), 7.38 – 7.27 (m, 7H, $\text{CHIm} + \text{CHPh}$), 6.95 (s, 1H, CHMes), 6.89 (d, $J = 1.8$ Hz, 1H, CHIm), 6.88 (s, 1H, CHMes), 4.60 – 4.38 (m, 2H, N-CH_2), 2.40 – 2.31 (m, 2H, P-CH_2), 2.30 (s, 3H, CH_3 , Mes), 1.98 (s, 3H, CH_3 , Mes), 1.29 (s, 3H, CH_3 , Mes).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF- d_8) δ 66.7 ppm.

IR ν_{CO} (EtOH): 1986, 1905, 1889 cm^{-1} .

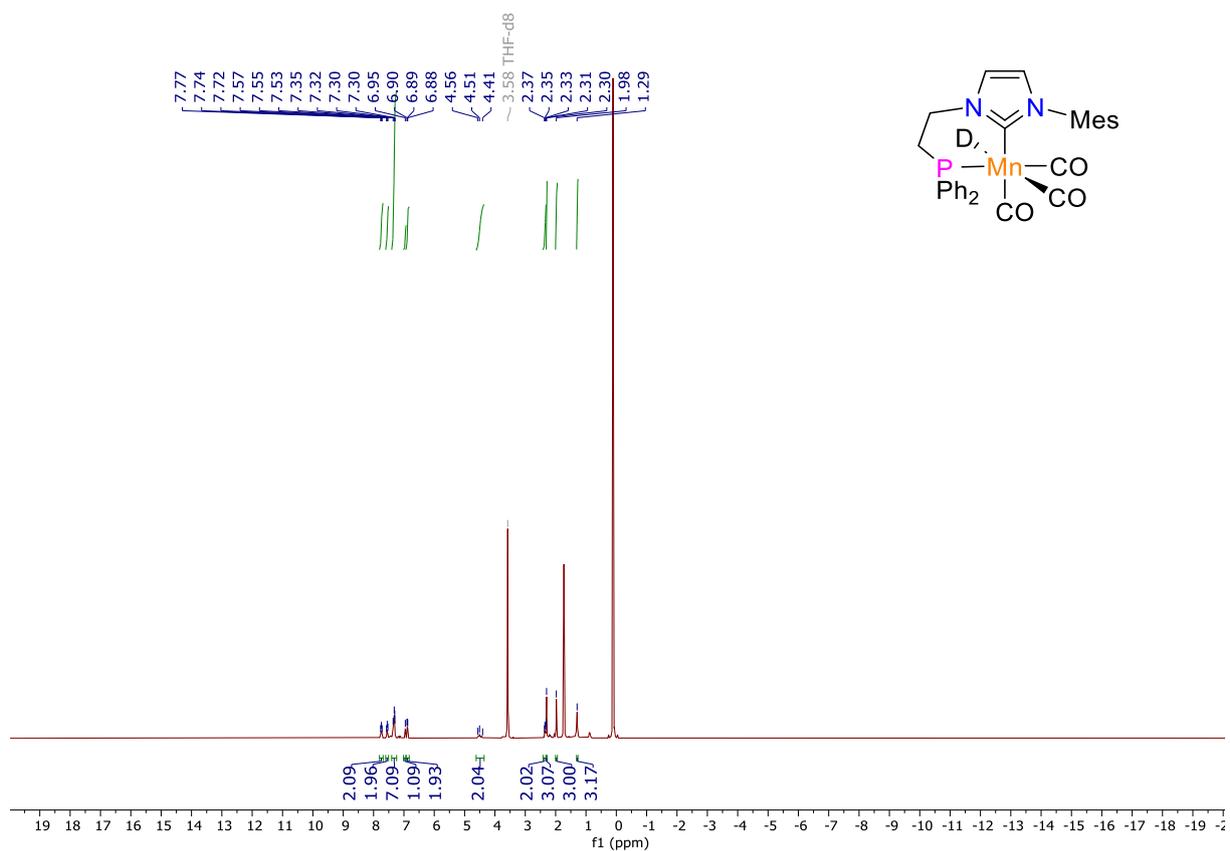


Figure S6: ^1H NMR spectrum of **13-D** in THF- d_8 recorded at 400 MHz.

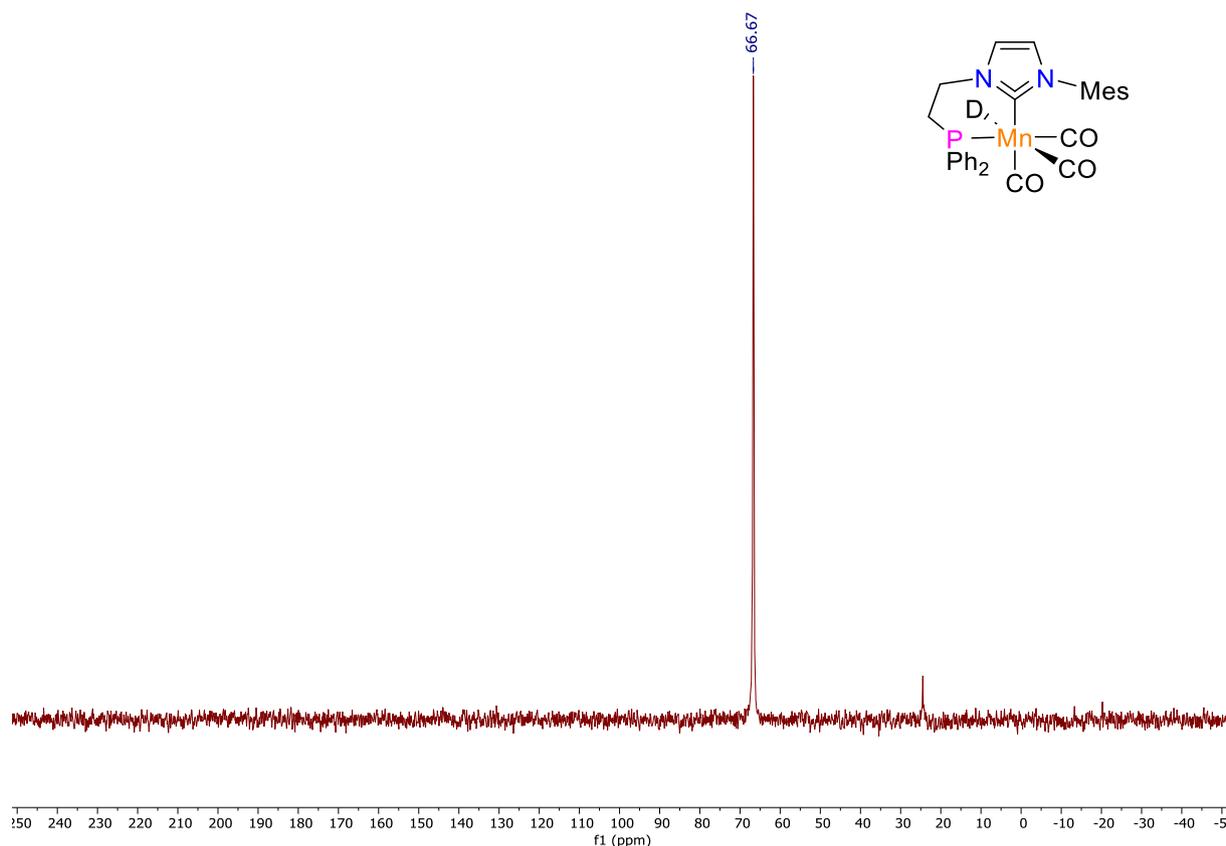


Figure S7: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **13-D** in $\text{THF-}d_8$ recorded at 162 MHz.

Study of the reactivity of complex **12**

Stability under H_2 of **12** generated in situ in an NMR tube

In an argon-filled glovebox, a solution of complex **2** (12.3 mg, 0.02 mmol) in $\text{THF-}d_8$ (0.5 mL) was filtered through a small pad of celite (2 cm in a Pasteur pipette) and transferred to a Wildmad NMR pressure tube. KHMDS (11.9 mg, 0.06 mmol) was added to the NMR tube, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figure S8) was recorded after 15 min at room temperature, showing full conversion to **12**. The NMR tube was pressurized with 4 bars of hydrogen and the reaction was monitored at room temperature by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Figure S9-11)

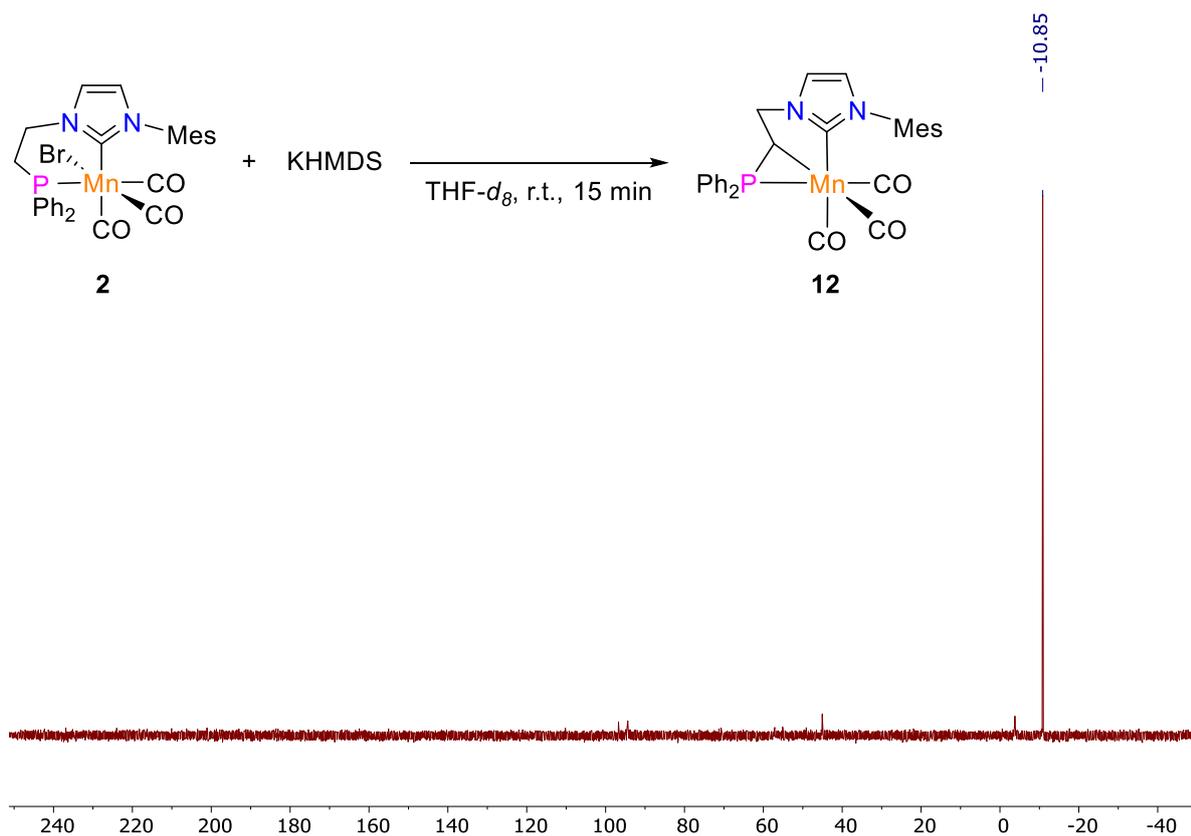


Figure S8: ³¹P{¹H} NMR spectrum of **12** generated *in situ* in THF-*d*₈ (after 15 min at room temperature without H₂ pressure) recorded at 162 MHz.

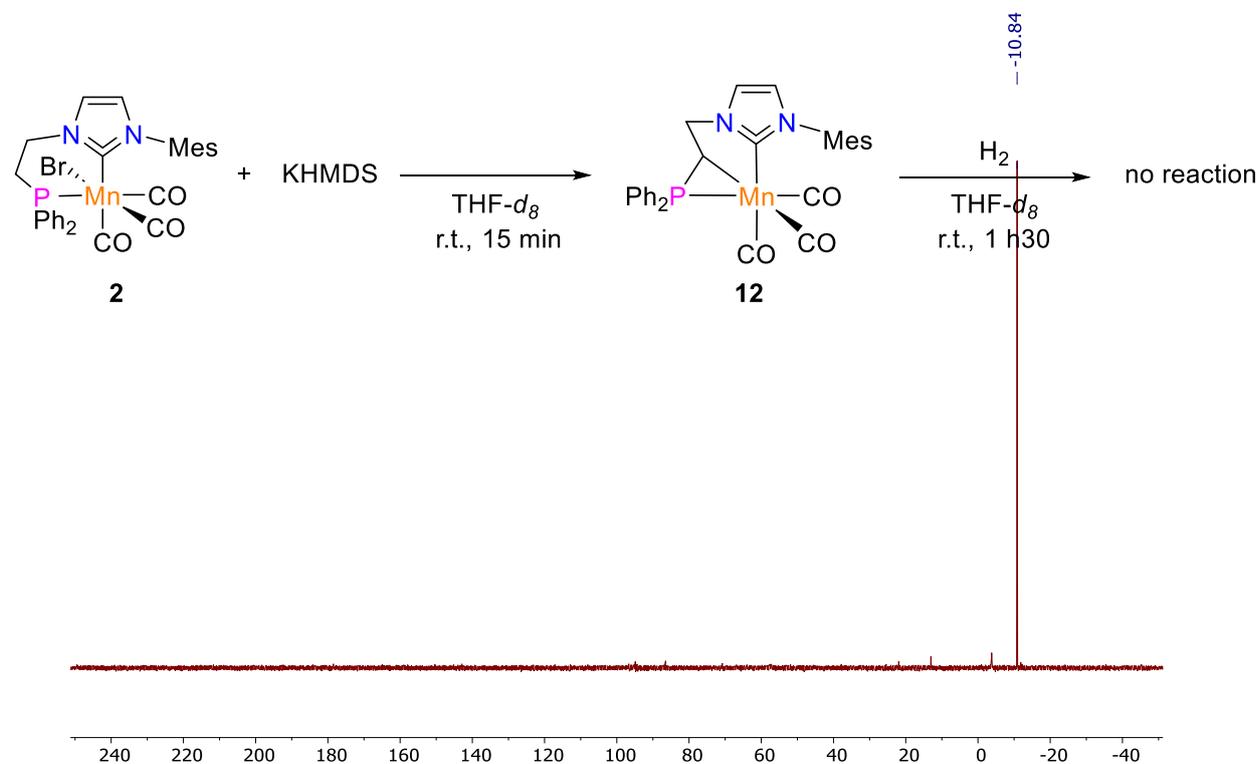


Figure S9: ³¹P{¹H} NMR spectrum of **12** generated *in situ* in THF-*d*₈ under H₂ pressure (4 bars) after 90 minutes at room temperature recorded at 162 MHz.

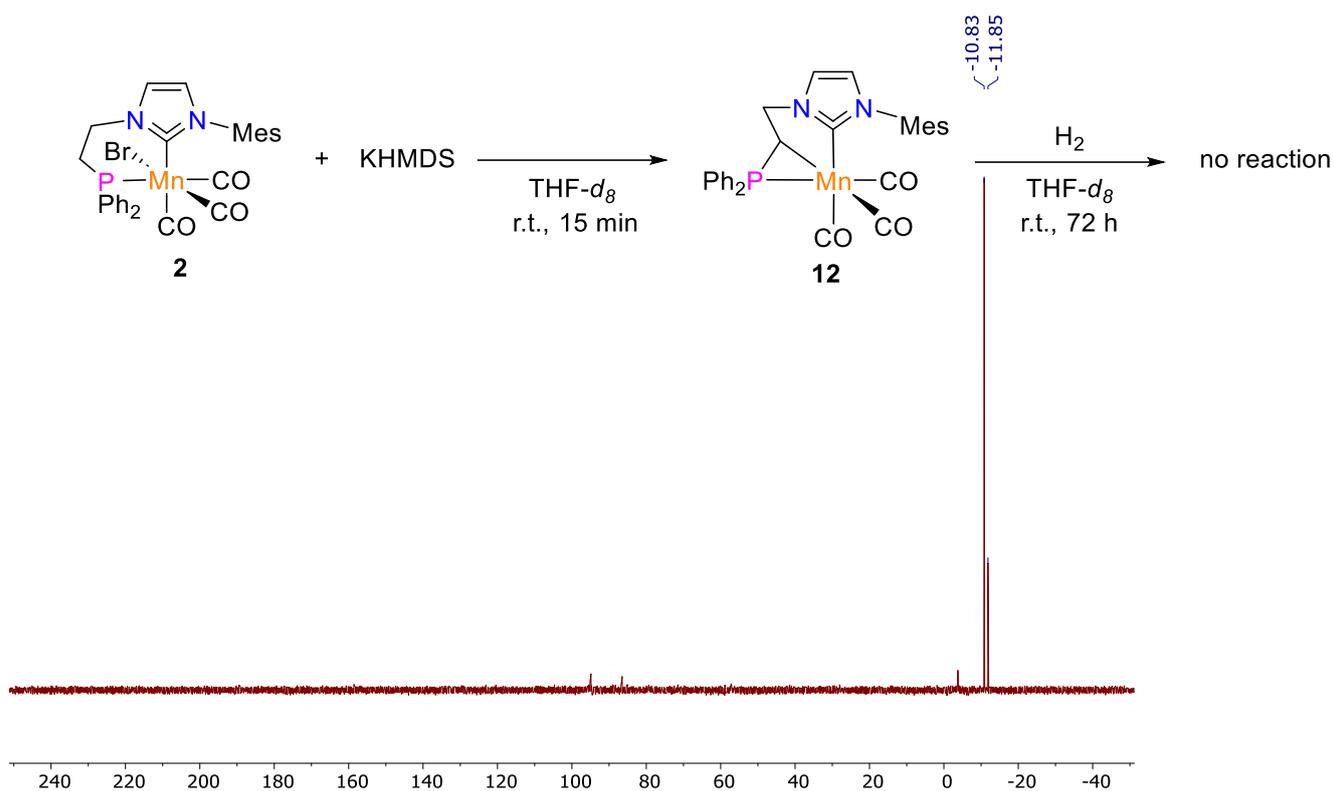


Figure S10: $^{31}P\{^1H\}$ NMR spectrum of **12** generated *in situ* in THF- d_8 under H_2 pressure (4 bars) after 72 h at room temperature recorded at 162 MHz.

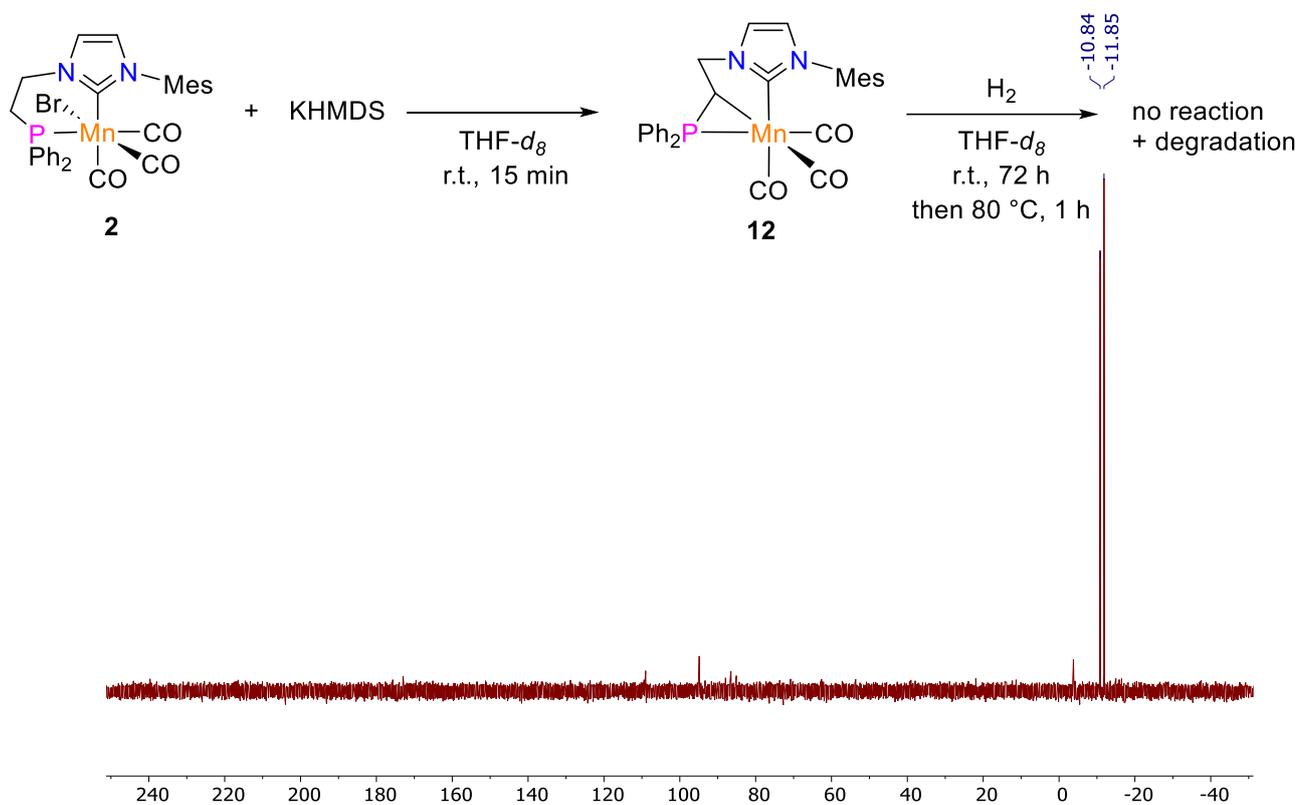


Figure S11: $^{31}P\{^1H\}$ NMR spectrum of **12** generated *in situ* in THF- d_8 under H_2 pressure (4 bars) after 72 h at room temperature and 1 h at 80 °C recorded at 162 MHz.

Stability of **12** under H₂

In a Schlenk tube, a solution of **12** (50 mg, 0.09 mmol) in THF (5 mL) was prepared under argon. Then, the solution was saturated with H₂ (bubbling of H₂, 1 atm) at room temperature. The solution was stirred under hydrogen atmosphere for an additional 30 minutes. The progress of the reaction was monitored by ³¹P{¹H} NMR using a capillary of C₆D₆ as internal reference.

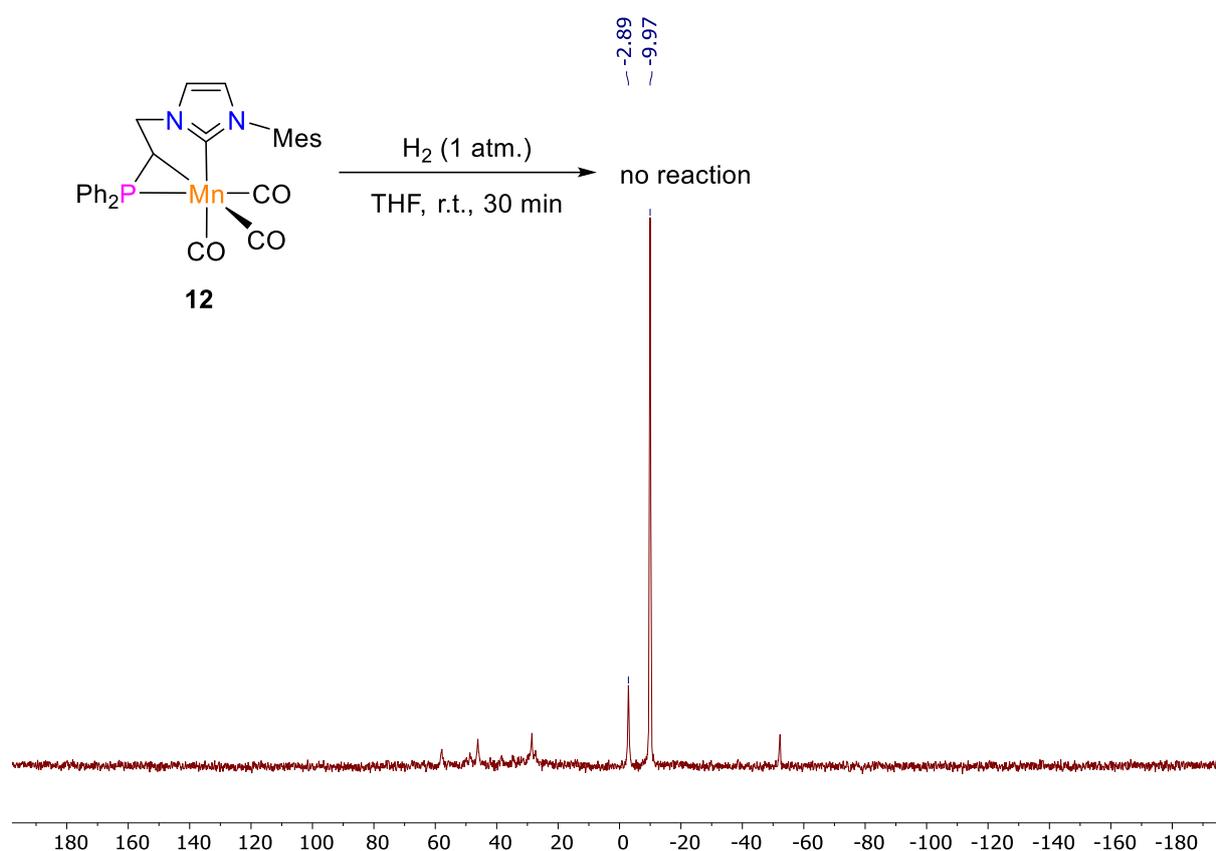
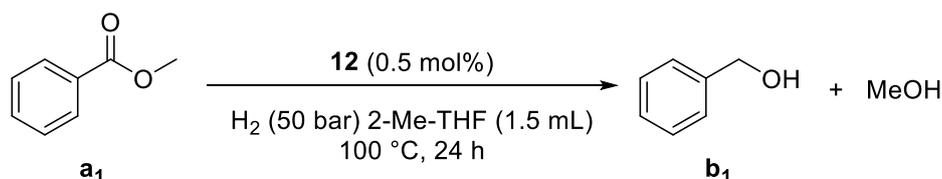


Figure S12: ³¹P{¹H} NMR spectrum of **12** under H₂ pressure (1 atm) after 30 min. at room temperature in THF with a capillary of C₆D₆ recorded at 162 MHz.

Hydrogenation of methyl benzoate **a**₁ catalyzed by complex **12** (generated in situ)



Under argon, an autoclave was charged with a solution of methyl benzoate **a**₁ (124 μL, 1.00 mmol) in 2-Me-THF (1 mL) and a solution of complex **12** previously generated in situ in an NMR tube (**2** (3.1 mg, 0.5 mol%) and KHMDS (3.0 mg, 1.5 mol%) in 0.5 mL THF-*d*₈). Then the autoclave was immediately

pressurized with hydrogen (50 bar) and kept under stirring in an oil bath at 100 °C for 24 h. Once the reactor has cooled down to room temperature and the pressure of hydrogen has been released, the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a small pad of Celite (2 cm in a Pasteur pipette). The Pasteur pipette was then flushed with an additional volume of CH₂Cl₂. The conversion and yield were determined by ¹H NMR (benzyl alcohol **b**₁ 2% and benzyl benzoate **a**₂ 3%)

Hydrogenation of methyl benzoate **a₁ catalyzed by complex **12** (isolated complex)**

Under argon, an autoclave was charged with a solution of methyl benzoate **a**₁ (124 μL, 1.00 mmol) in 2-Me-THF (0.5 mL) and a solution of complex **12** (2.7 mg, 0.5 mol%, 1 mL of 2-Me-THF). Then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath at 100 °C for 24 h. Once the reactor has cooled down to room temperature and the pressure of hydrogen has been released, the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a small pad of Celite (2 cm in a Pasteur pipette). The Pasteur pipette was then flushed with an additional volume of DCM. No conversion of methyl benzoate was observed according to the ¹H NMR spectrum.

Reactivity of **2 towards KHBET₃**

In an argon-filled glovebox, a solution of complex **2** (14.3 mg, 0.023 mmol) in THF-*d*₈ (0.4 mL) was filtered through a small pad of celite (2 cm in a Pasteur pipette) and transferred into a Wildmad NMR pressure tube. KHBET₃ (1M in THF, 115 μL, 0.115 mmol) was added to the NMR tube, and the reaction was monitored at room temperature by ¹H and ³¹P{¹H} NMR spectroscopy after 30 min (Figure S13-14). Then the mixture was then heated at 60 °C and monitored by ¹H and ³¹P{¹H} NMR spectroscopies after 1h20 (Figures S15-16).

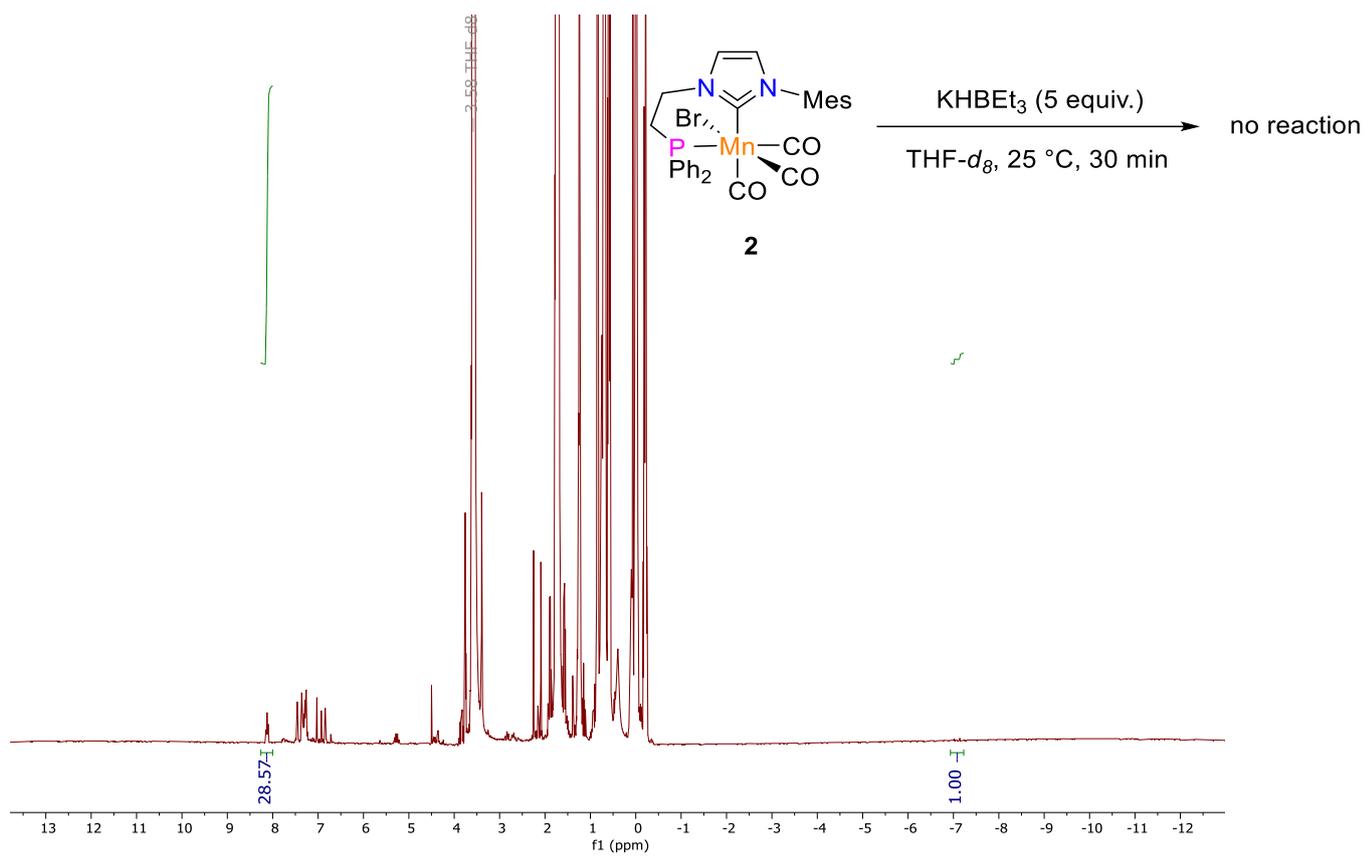


Figure S13: ^1H NMR monitoring of the reaction of **2** and KBHET_3 after 30 min at $25\text{ }^\circ\text{C}$ in $\text{THF-}d_8$ recorded at 400 MHz.

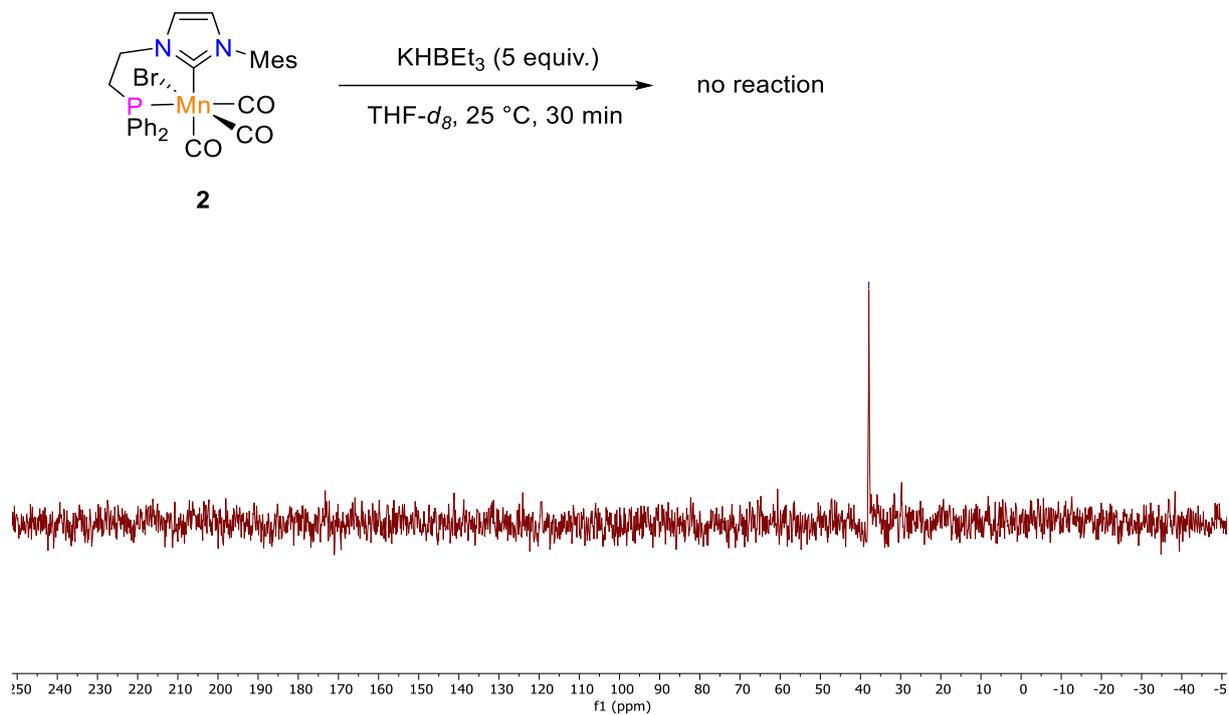


Figure S14: $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of the reaction of **2** and KHBET_3 after 30 min at 25 °C in $\text{THF-}d_8$ recorded at 162 MHz.

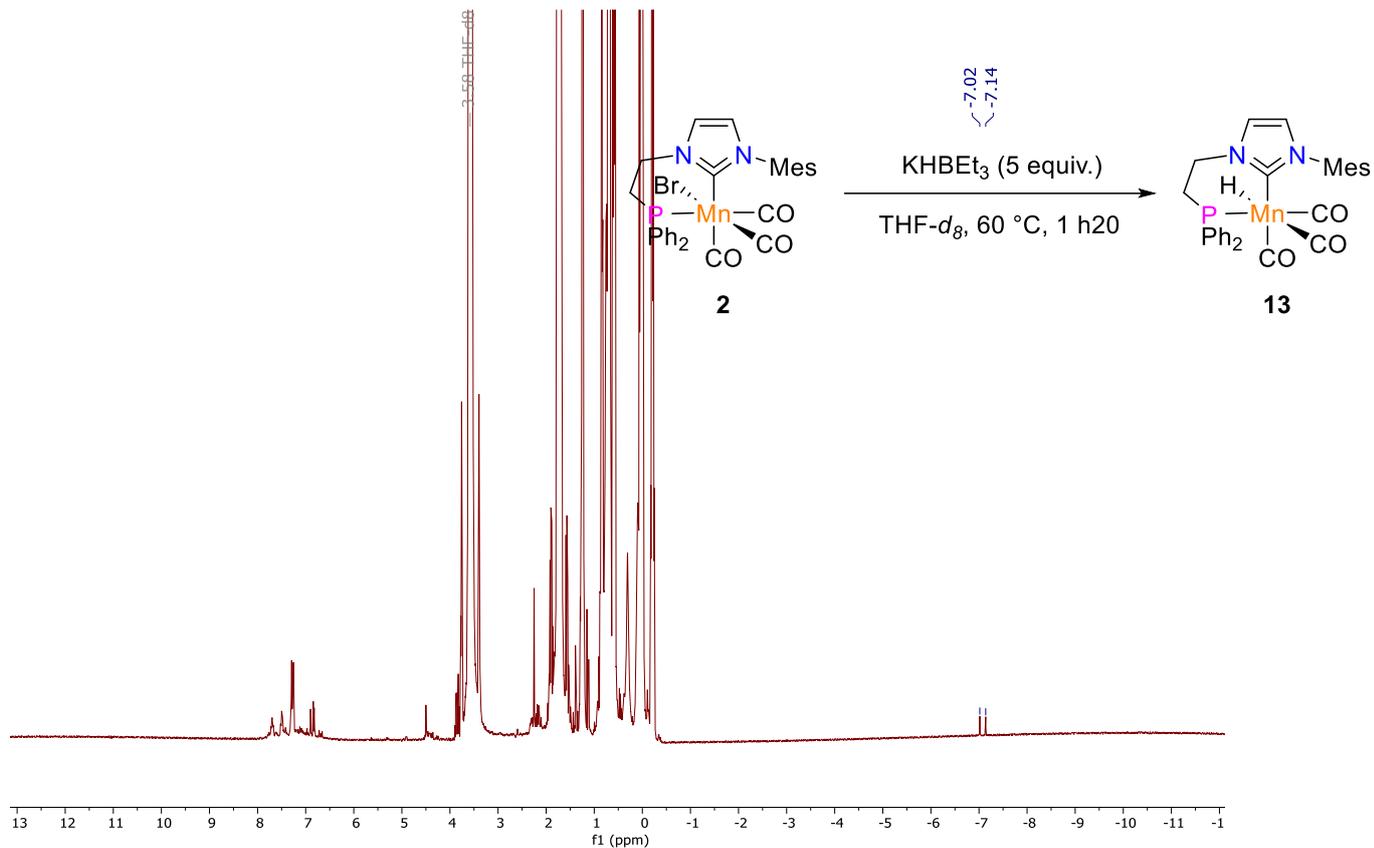


Figure S15: ^1H NMR monitoring of the reaction of **2** and KHBET_3 after 1 h20 min at 60 °C in $\text{THF-}d_8$ recorded at 400 MHz.

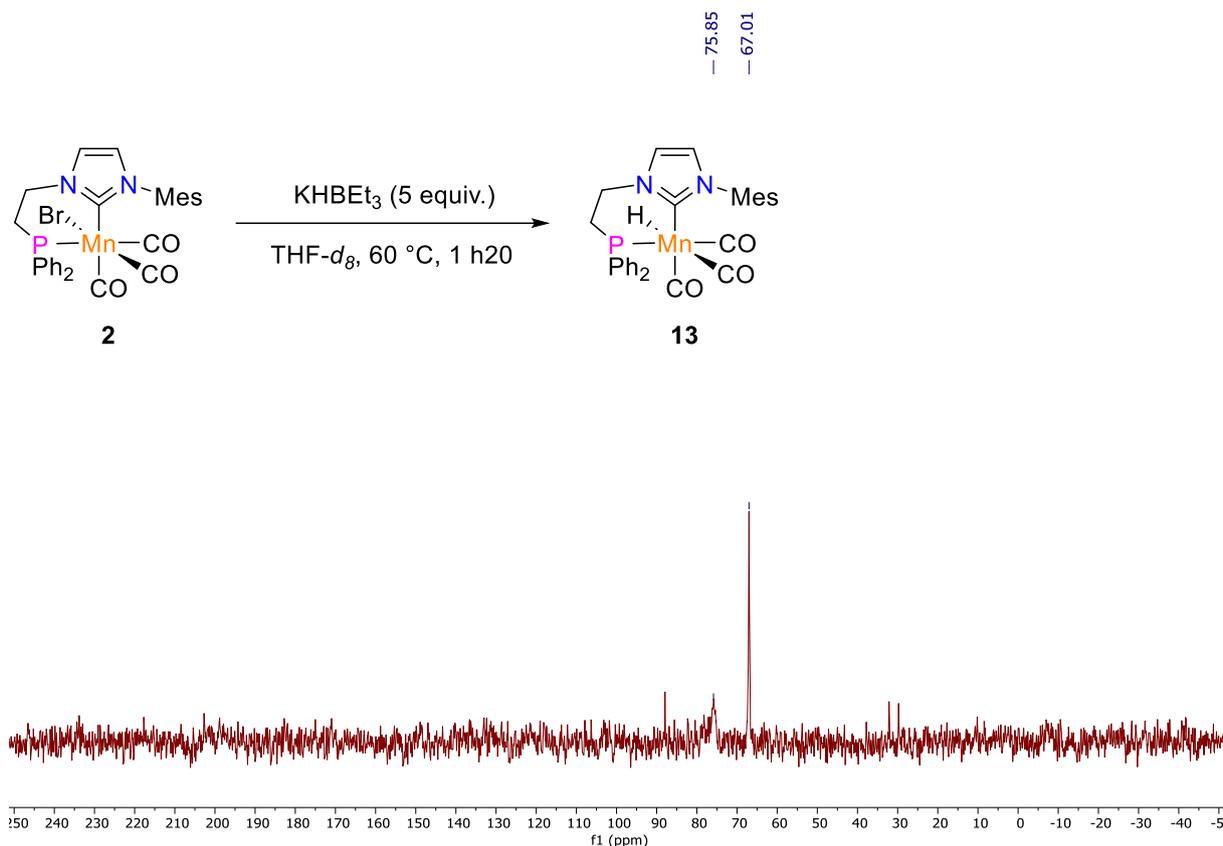
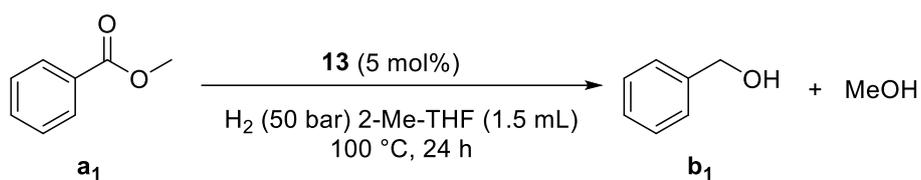


Figure S16: $^{31}\text{P}\{^1\text{H}\}$ monitoring of the reaction of **2** and KHBEt_3 after 1 h 20 min at 60 °C in $\text{THF-}d_8$ recorded at 162 MHz.

Hydrogenation of methyl benzoate **a1** catalyzed by complex **13**

Under argon, an autoclave was charged with a solution of methylbenzoate **a1** (124 μL , 1.00 mmol) in 2-Me-THF (0.5 mL) and a solution of complex **13** (26.9 mg, 5 mol%, 0.5 mL of 2-Me-THF). Then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath at 100 °C for 24 h. Once the reactor has cooled down to room temperature and the pressure of hydrogen has been released, the reaction mixture was diluted with EtOAc (2.0 mL) and filtered through a small pad of Celite (2 cm in a Pasteur pipette). The Pasteur pipette was then flushed with an additional volume of EtOAc. The conversion and yield were determined by ^1H NMR (benzyl alcohol **b1** 3% and benzyl benzoate **a2** 2%) (Figure S17).



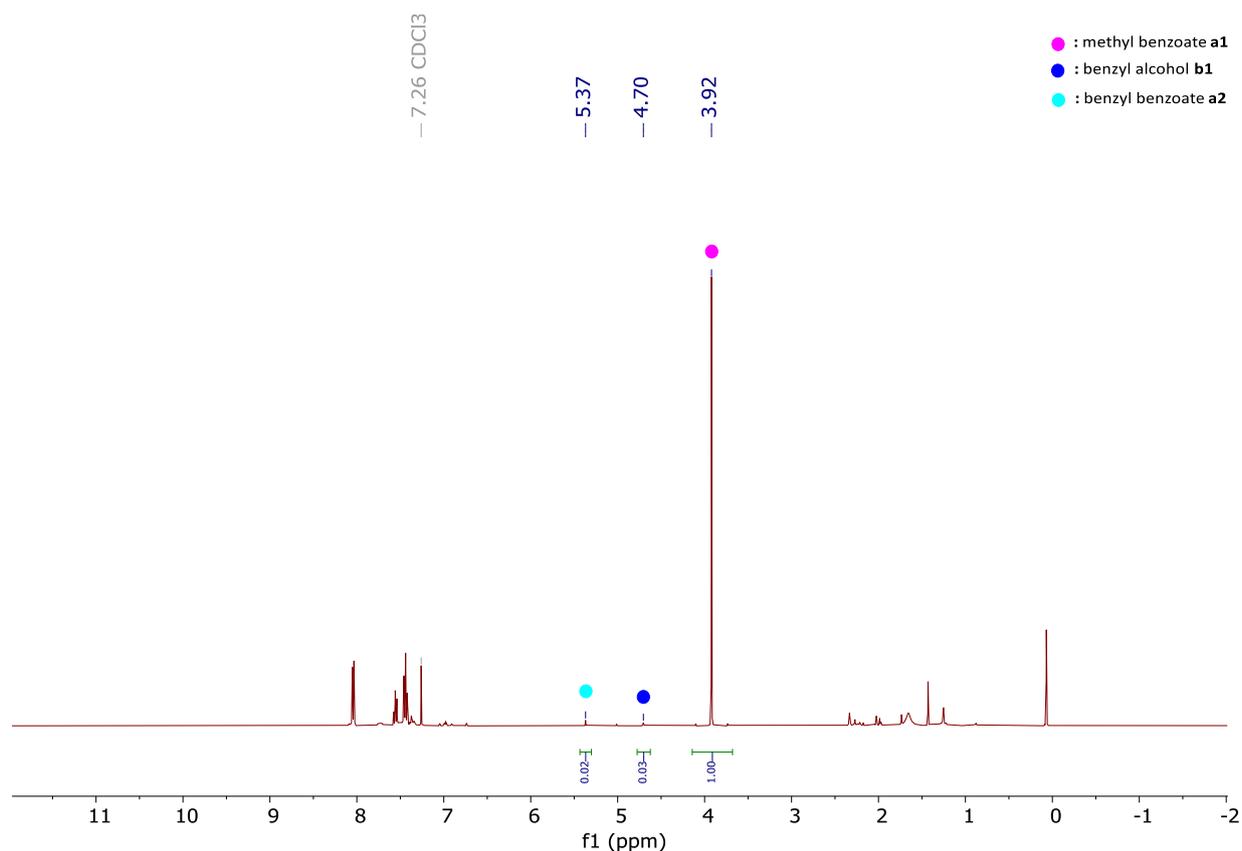


Figure S17: ^1H NMR spectrum of the crude reaction mixture after the hydrogenation of methyl benzoate catalyzed by **13** in CDCl_3 recorded at 400 MHz.

Reaction between **13** and acetophenone

In an argon-filled glovebox, a solution of complex **13** (14 mg, 0.026 mmol) in $\text{THF-}d_8$ (0.4 mL) was filtered through a small pad of celite (2 cm in a Pasteur pipette) and transferred to a Wildmad NMR pressure tube. Acetophenone (0.1 mL of a stock solution (15 μL in 0.5 mL of $\text{THF-}d_8$), 0.026 mmol, 1 equiv.) was added to the NMR tube. The NMR tube was pressurized to 4 bars of H_2 and the mixture stirred at r.t. for 22 h and then was heated at 80 $^\circ\text{C}$ in the dark for 24 h. No reaction between **13** and acetophenone was observed after 24 h according to the ^1H NMR spectrum (Figure S18).

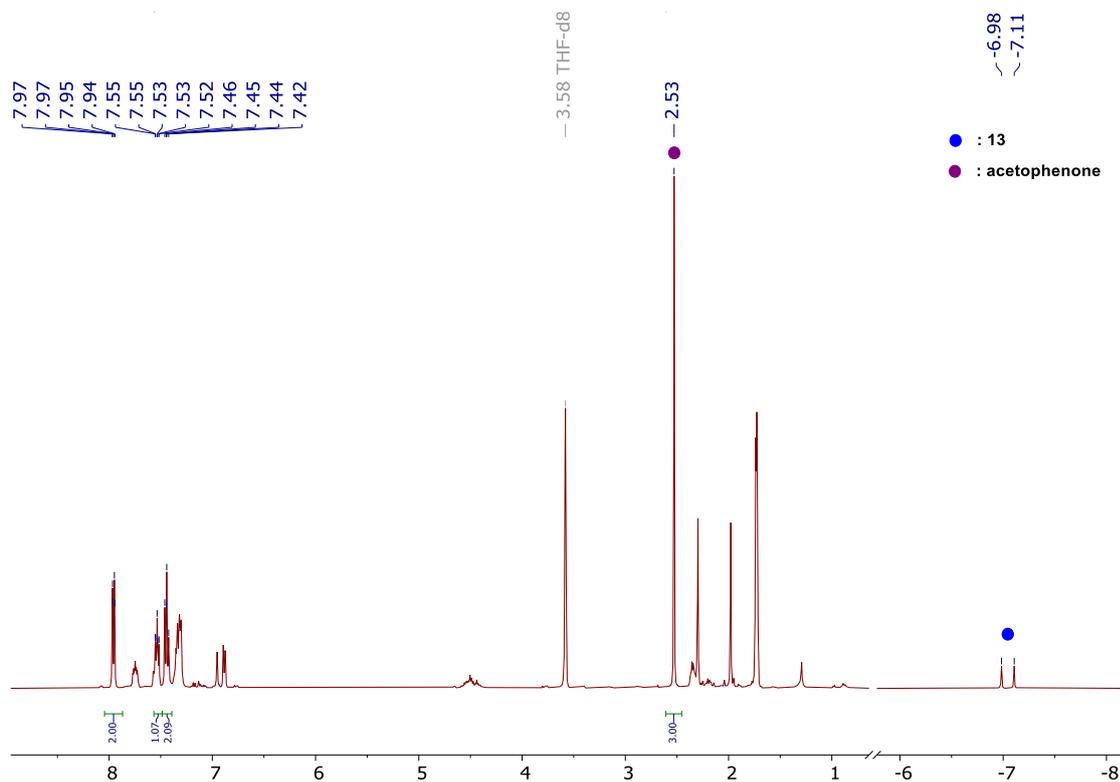
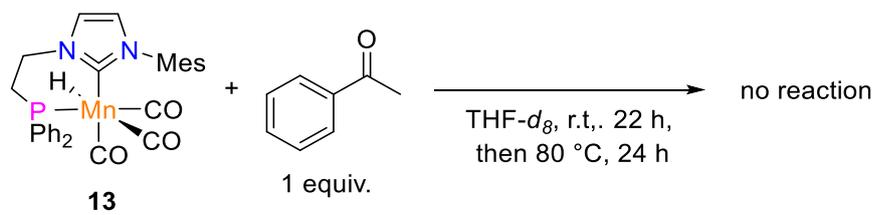


Figure S18: $^1\text{H NMR}$ monitoring of the reaction of **13** and acetophenone at 80 °C after 24 h in THF- d_8 recorded at 162 MHz.

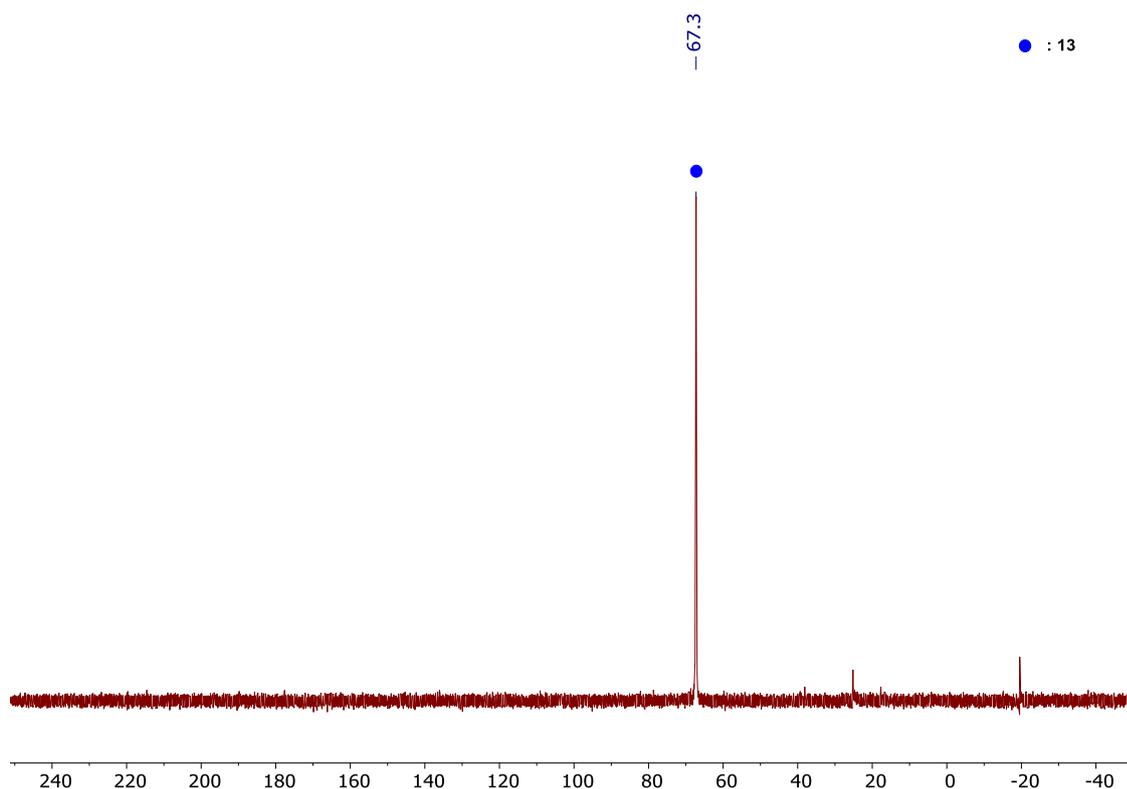


Figure S19: $^{31}\text{P}\{^1\text{H}\}$ monitoring of the reaction of **13** and acetophenone at 80 °C after 24 h in THF- d_8 recorded at 162 MHz.

Hydrogenation of methyl benzoate in the presence of **13** and KHBET_3

Under argon, an autoclave was charged with a solution of methyl benzoate (126 μL , 1 mmol) in 2-Me-THF (0.5 mL) and a solution of **13** (2.8 mg, 0.5 mol%) which was prepared in 2-Me-THF (0.5 mL) and activated with KHBET_3 (0.1 mL, 1.0 M in THF, 0.1 mmol, 10 mol%) for 30 min at r.t. in this order, then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath at 100 °C for 24 h. Once the reactor has cooled down to room temperature and the pressure of hydrogen has been released, the reaction mixture was diluted with CH_2Cl_2 (2.0 mL) and filtered through a small pad of Celite (2 cm in a Pasteur pipette). The Pasteur pipette was then flushed with an additional volume of CH_2Cl_2 . Methyl benzoate was converted in benzyl alcohol in 75% according to the ^1H NMR spectrum (Figure S20).

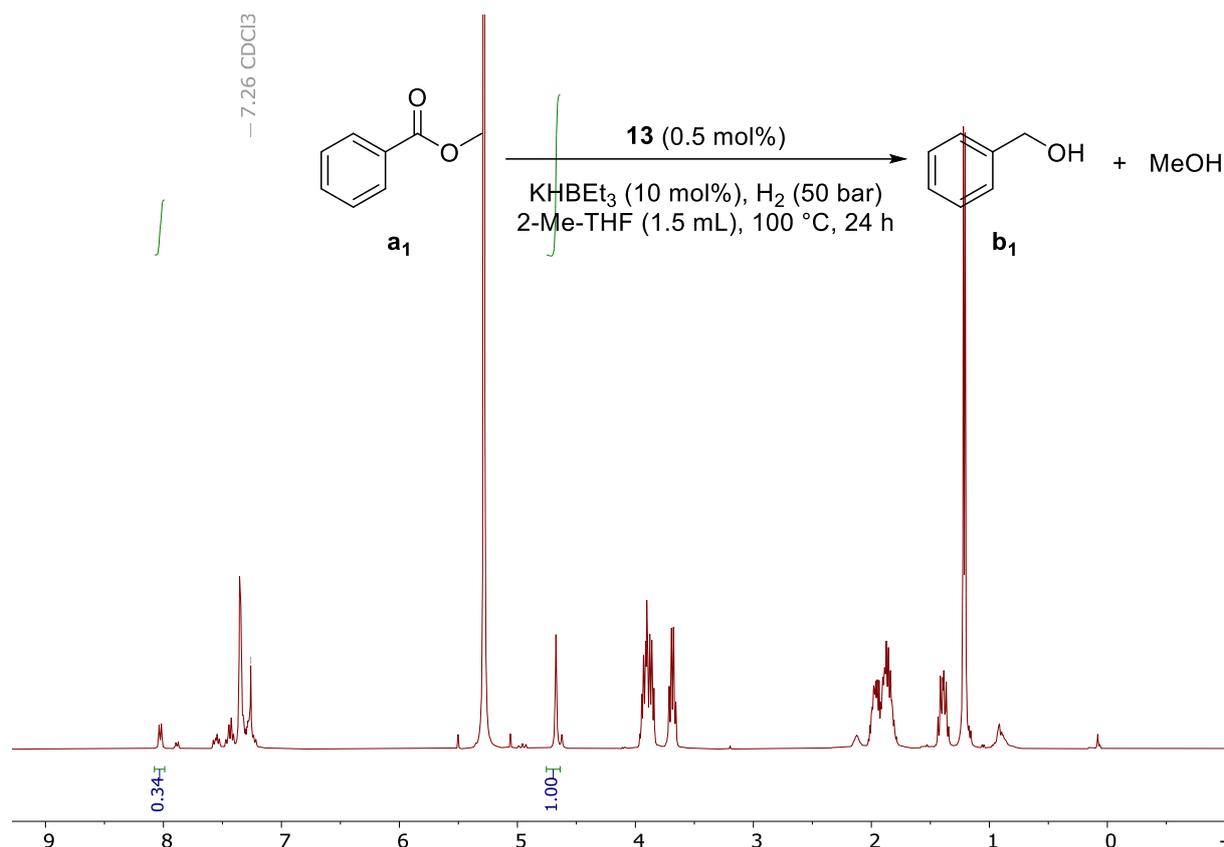


Figure S20: ^1H NMR spectrum of the crude mixture after hydrogenation of **a1** catalyzed by **13** in the presence of KHBET_3 in CDCl_3 recorded at 400 MHz.

Hydrogenation of methyl benzoate in the presence of **13** and Me_3NO

Under argon, an autoclave was charged with a solution of methyl benzoate (125 μL , 1 mmol) in 2-Me-THF (0.5 mL) and a solution of **13** (2.8 mg, 0.5 mol%) which was prepared in 2-Me-THF (0.5 mL) and reacted with Me_3NO (7.5 mg, 10 mol%) for 30 min at r.t. in this order, then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath at 100 $^\circ\text{C}$ for 24 h. Once the reactor has cooled down to room temperature and the pressure of hydrogen has been released, the reaction mixture was diluted with EtOAc (2.0 mL) and filtered through a small pad of Celite (2 cm in a Pasteur pipette). The Pasteur pipette was then flushed with an additional volume of EtOAc. No conversion of methyl benzoate was observed according to the ^1H NMR spectrum (Figure S21).

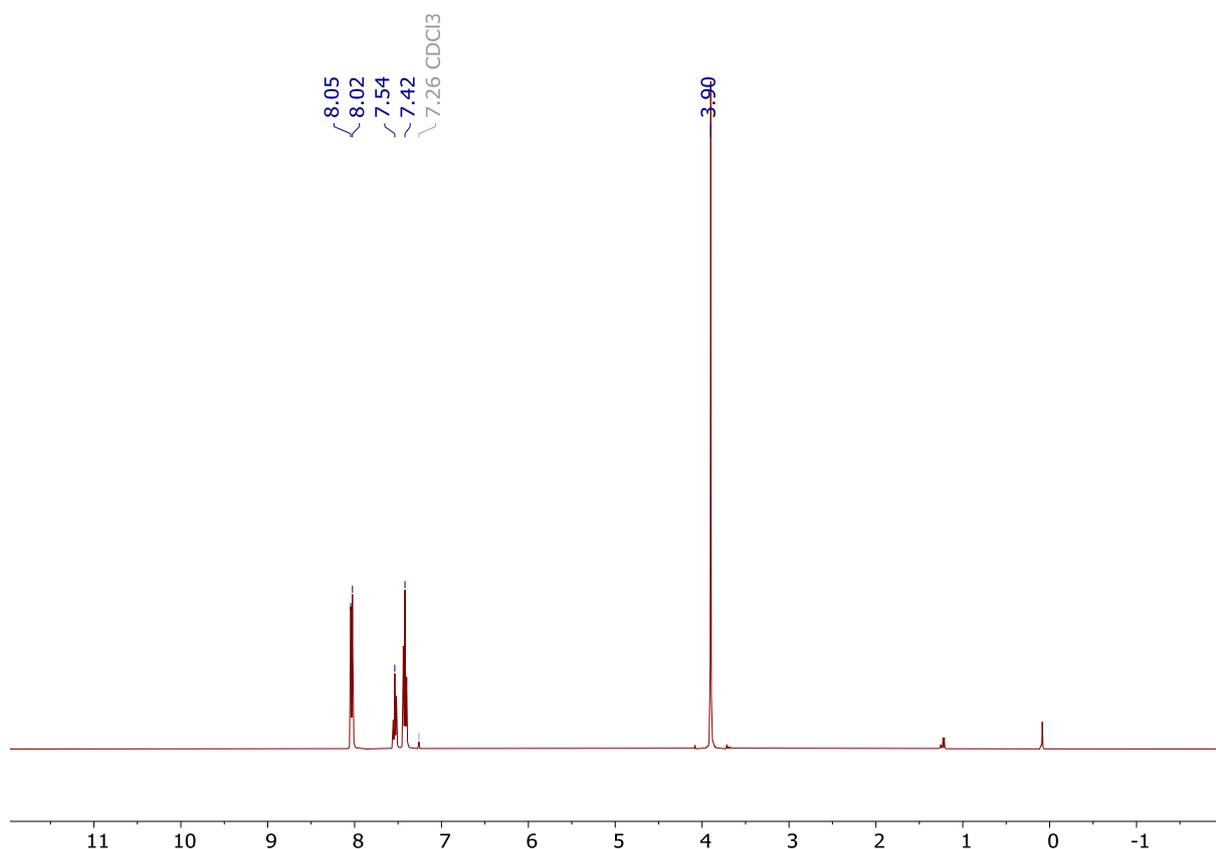


Figure S21: ^1H NMR spectrum of the crude mixture after hydrogenation of **a1** catalyzed by **13** in the presence of Me_3NO in CDCl_3 recorded at 400 MHz.

Irradiation of complex **13** at 365 nm

In an argon-filled glovebox, a solution of complex **13** (13.0 mg, 0.024 mmol) in $\text{THF-}d_8$ (0.4 mL) was filtered through a small pad of celite (2 cm in a Pasteur pipette) and transferred to a Wildmad NMR pressure tube. The solution was irradiated at 365 nm, and the reaction was monitored at room temperature by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy after 3 h and then after a night. (Figure S22-23).

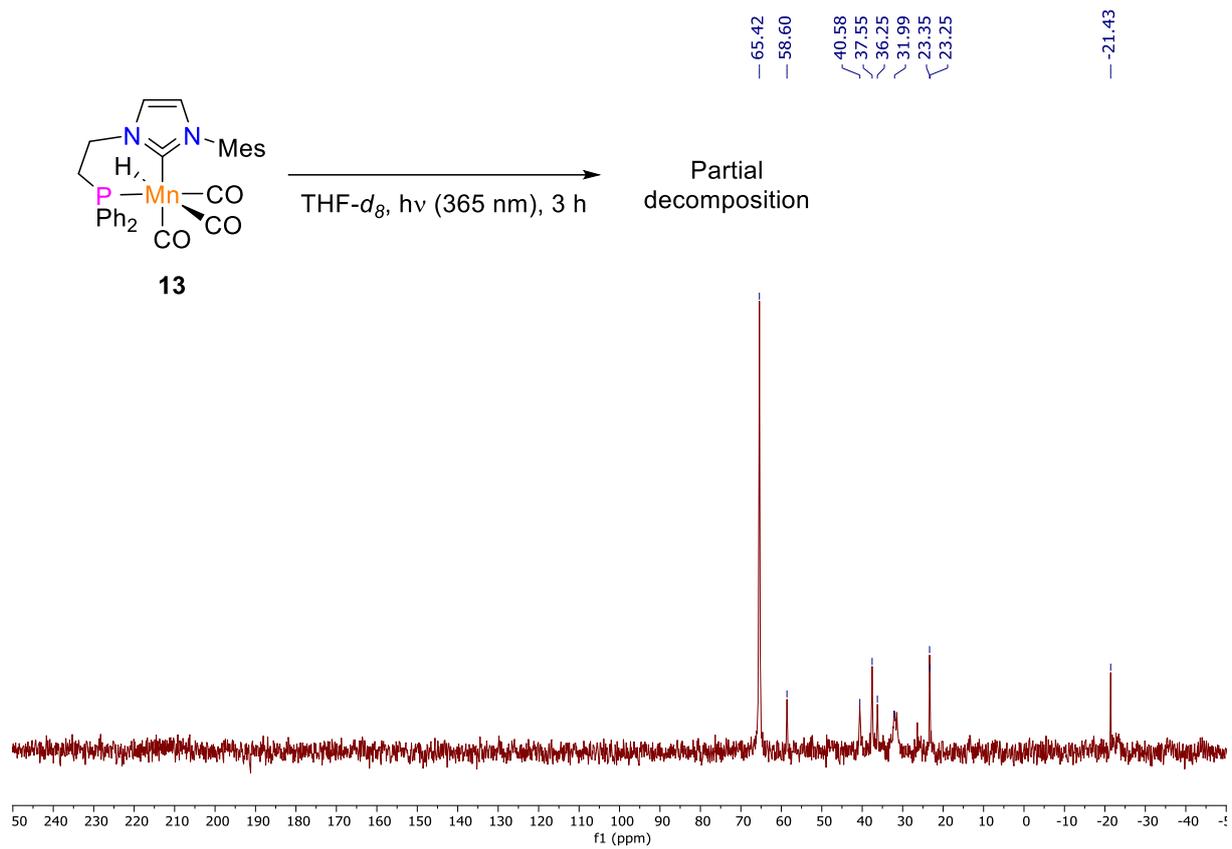


Figure S22: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a solution of **13** after 3 h of irradiation at 365 nm in THF-*d*₈ recorded at 162 MHz.

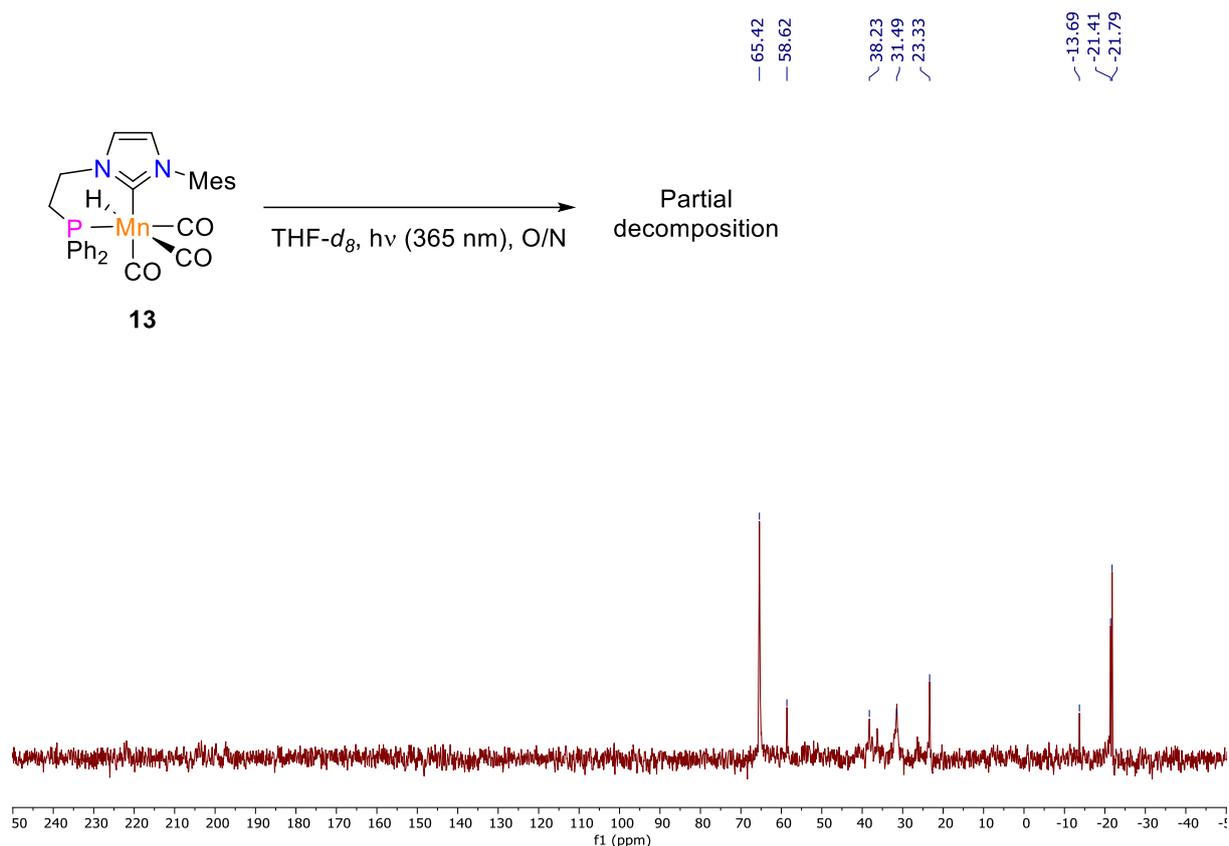
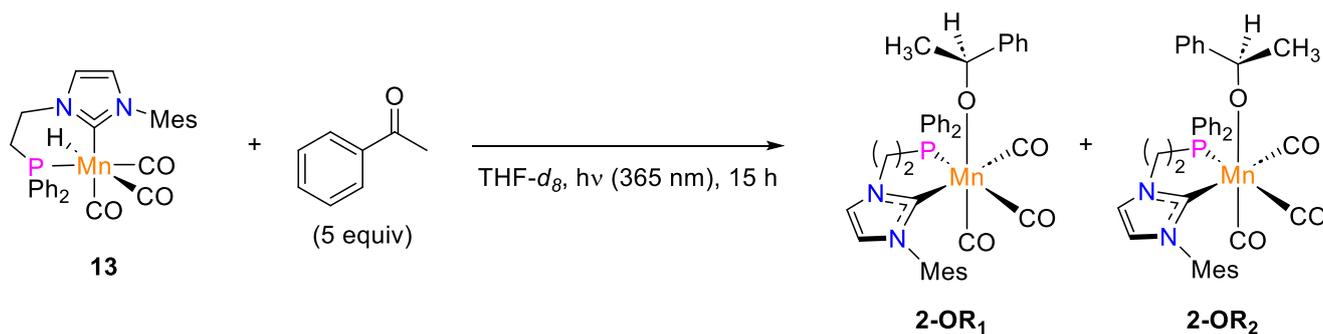


Figure S23: $^{31}\text{P}\{^1\text{H}\}$ NMR of a solution of **13** after 18 h of irradiation at 365 nm in THF- d_8 recorded at 162 MHz.

Irradiation of complex **13** at 365 nm in the presence of acetophenone



In an argon-filled glovebox, a solution of complex **13** (10.8 mg, 0.020 mmol) in THF- d_8 (0.4 mL) was filtered through a small pad of celite (2 cm in a Pasteur pipette) and transferred to a Wildmad NMR pressure tube. Acetophenone (12 μL , 0.1 mmol) was added to the NMR tube. The solution was irradiated at 365 nm for 15 h, and the reaction was monitored at room temperature by ^1H , $^{31}\text{P}\{^1\text{H}\}$ $^1\text{H}/^1\text{H}$ COSY NMR spectroscopy. (Figure S24-27)

After irradiation, the solvent was evaporated and the IR spectrum of the mixture was recorded in toluene.

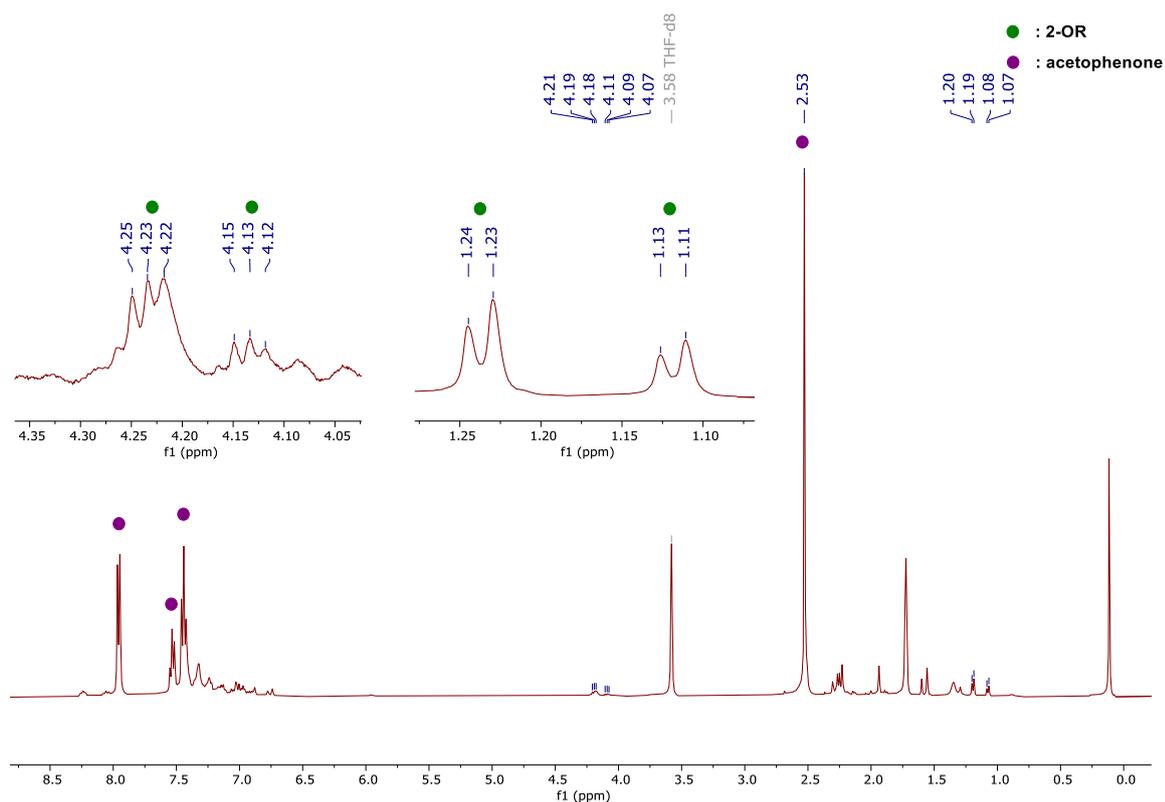


Figure S24: ^1H NMR spectrum of a solution of **13** in the presence of acetophenone after 15 h under irradiation in $\text{THF-}d_8$ recorded at 400 MHz.

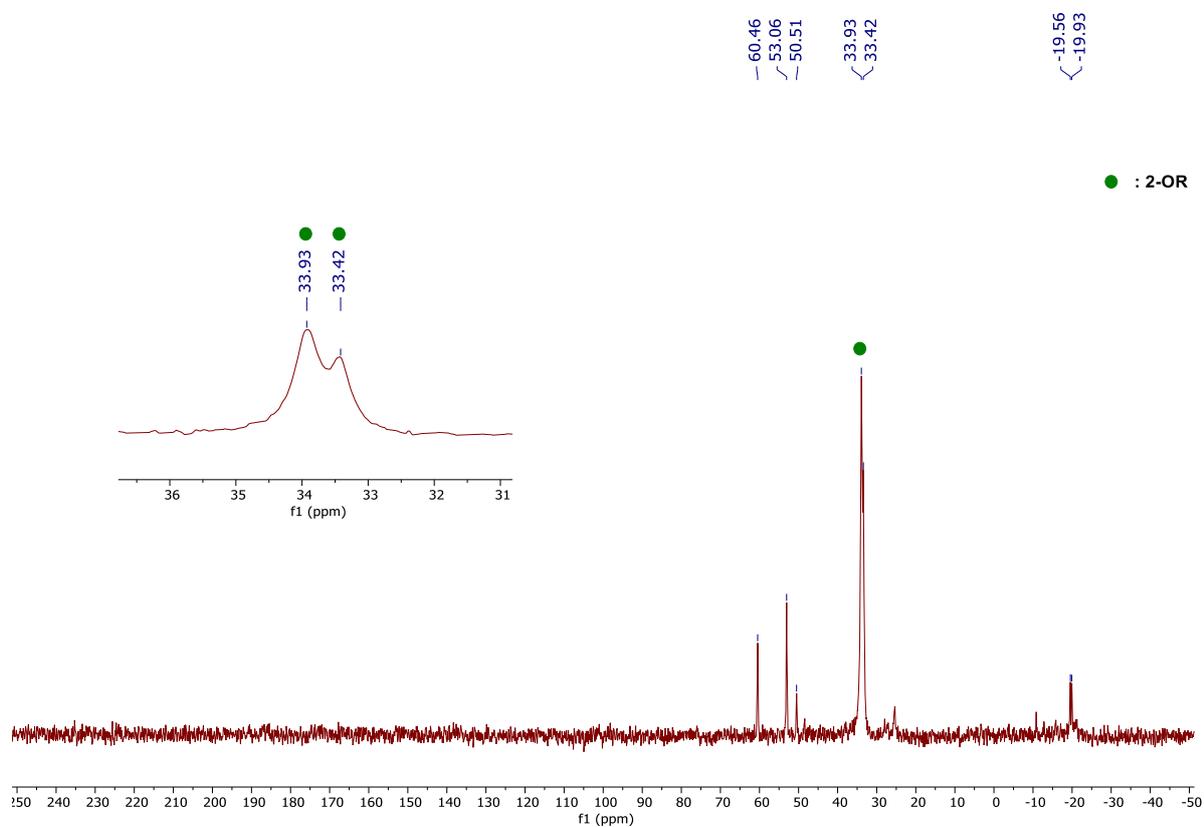


Figure S25: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a solution of **13** in the presence of acetophenone after 15 h under irradiation in $\text{THF-}d_8$ recorded at 162 MHz.

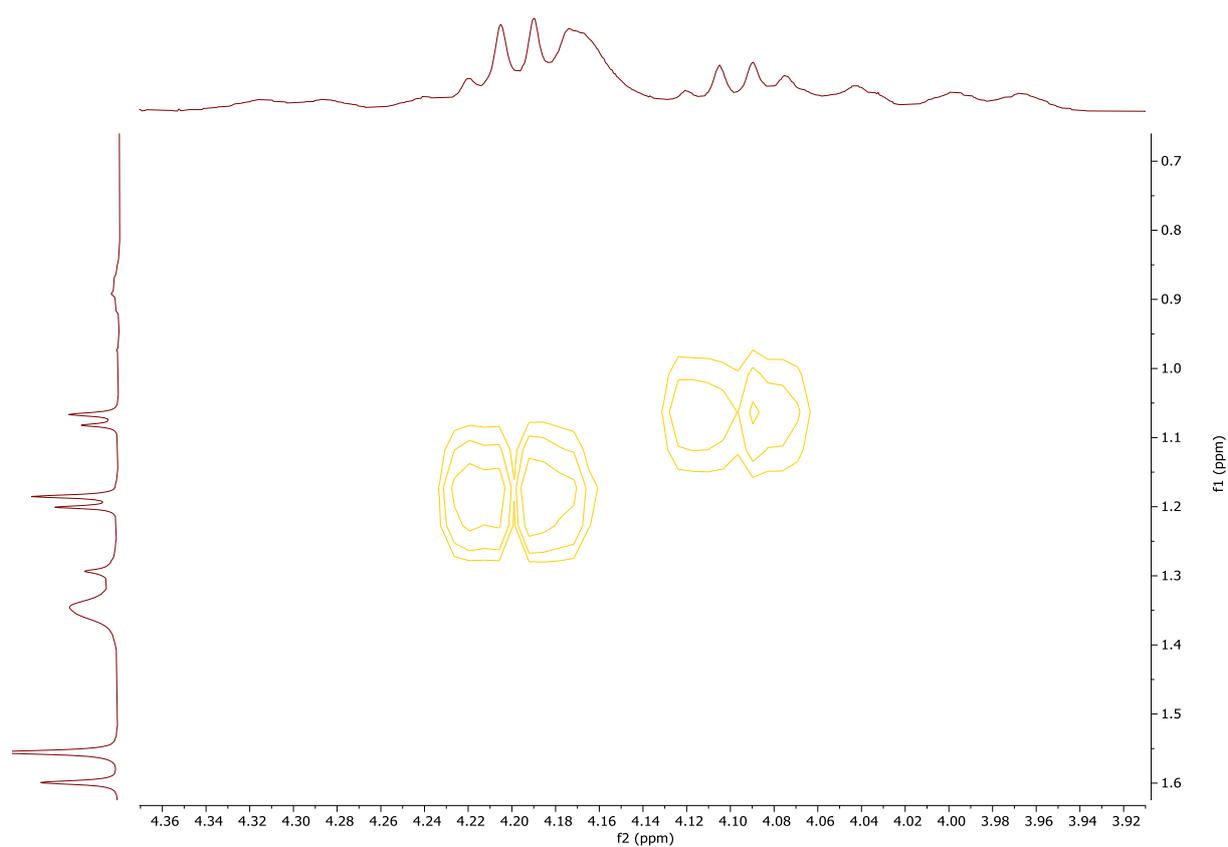


Figure S26: Zoom of $^1\text{H}/^1\text{H}$ COSY NMR spectrum of a solution of **13** in the presence of acetophenone after 15 h under irradiation in $\text{THF-}d_8$ recorded at 400 MHz.

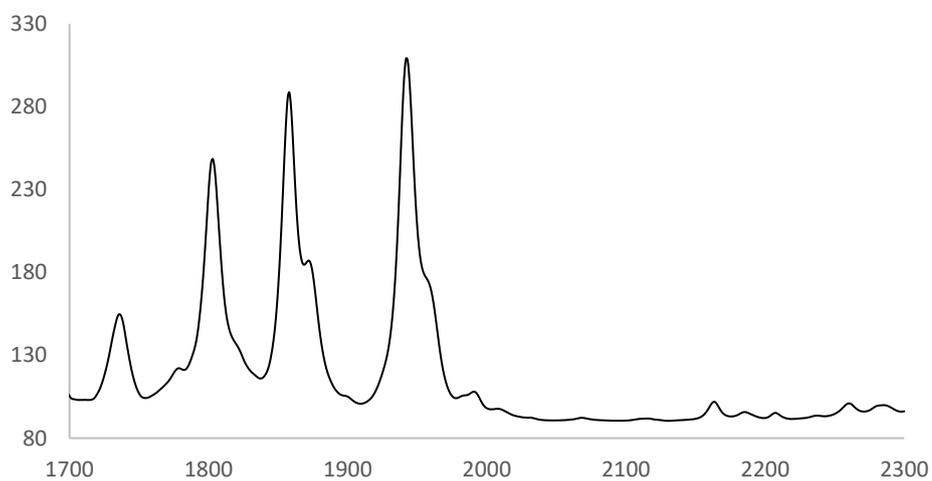


Figure S27: IR spectrum of a solution of **13** in the presence of acetophenone after 15 h of irradiation recorded in toluene.

Irradiation of complex **13-D** at 365 nm in the presence of acetophenone

In an argon-filled glovebox, a solution of complex **13-D** (10.5 mg, 0.02 mmol) in THF-*d*₈ (0.4 mL) was filtered through a small pad of celite (2 cm in a Pasteur pipette) and transferred to a Wildmad NMR pressure tube. Acetophenone (11 μL, 0.1 mmol) was added to the NMR tube. The solution was irradiated at 365 nm during 7 h and the reaction was monitored by ¹H and ³¹P{¹H} NMR spectroscopy. (Figure S28-29)

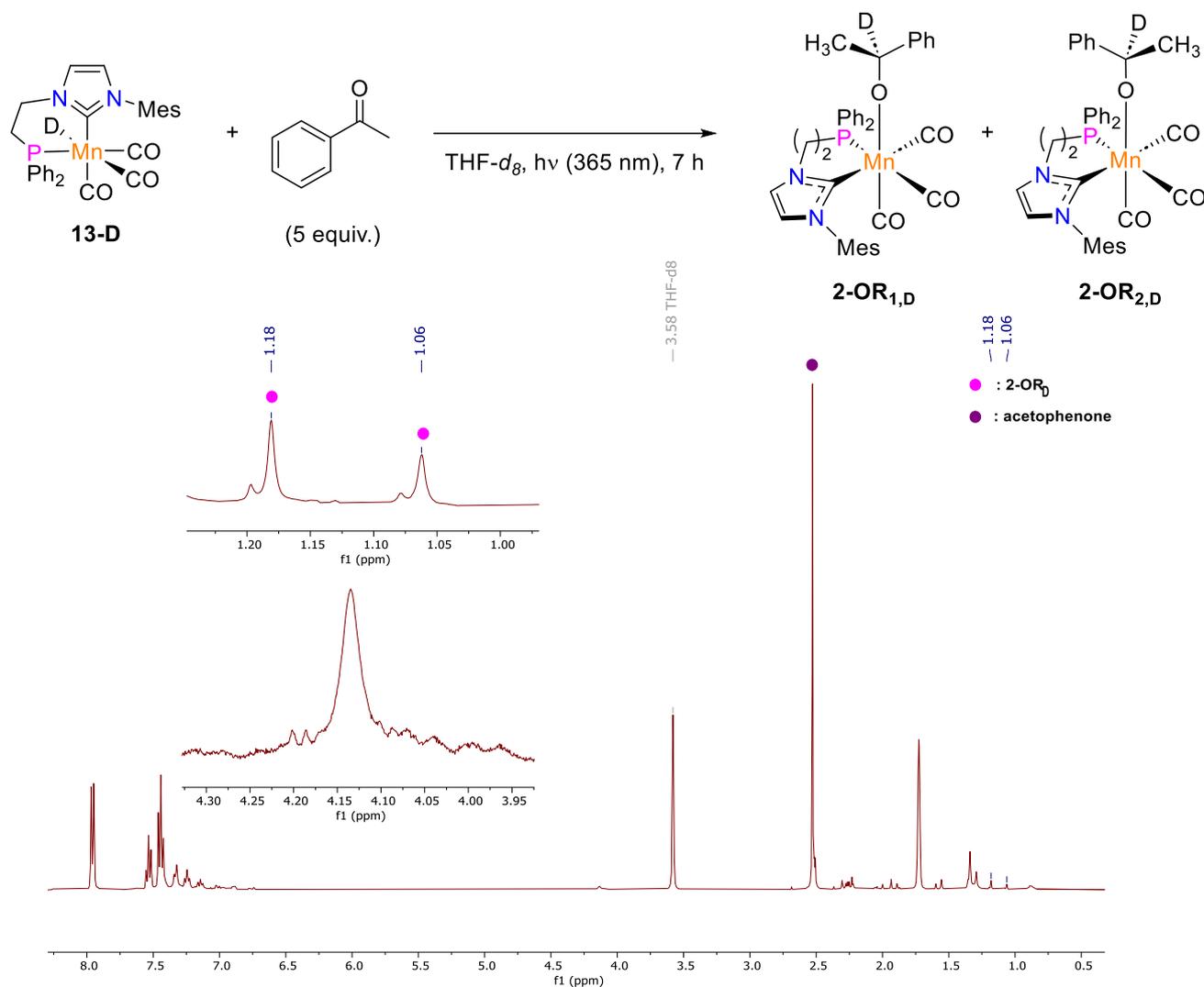


Figure S28: ¹H NMR spectrum of a solution of **13-D** in the presence of acetophenone after 7 h under irradiation in THF-*d*₈ recorded at 400 MHz.

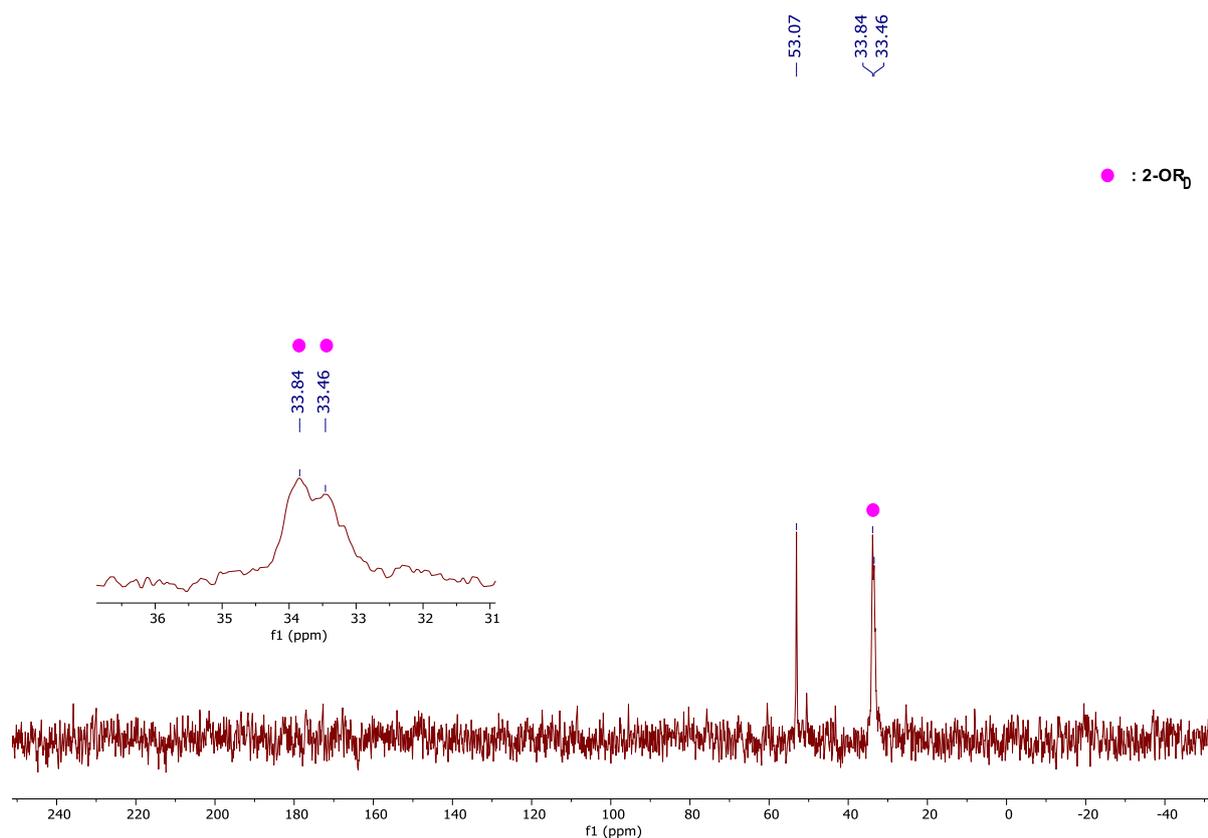
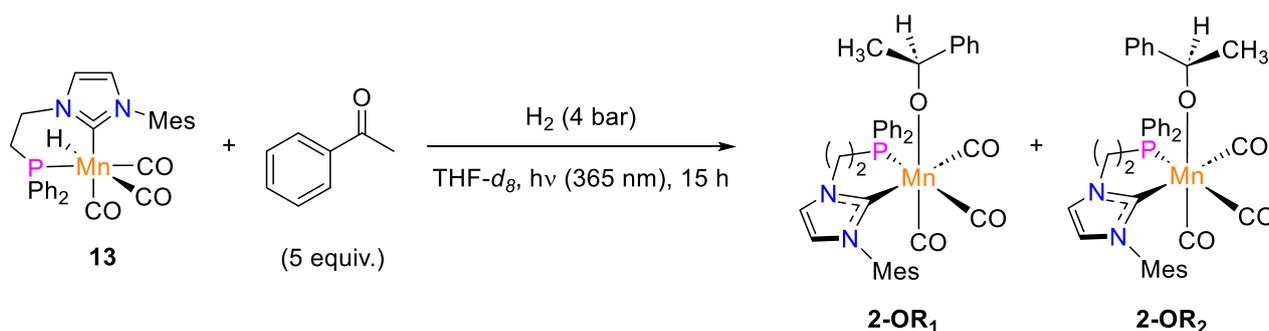


Figure S29: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a solution of **13-D** in the presence of acetophenone after 7 h under irradiation in $\text{THF-}d_8$ recorded at 162 MHz.

Irradiation of complex **13** at 365 nm in the presence of acetophenone and H_2

In an argon-filled glovebox, a solution of complex **13** (10.8 mg, 0.020 mmol) in $\text{THF-}d_8$ (0.4 mL) was filtered through a small pad of celite (2 cm in a Pasteur pipette) and transferred to a Wildmad NMR pressure tube. Acetophenone (12 μL , 0.1 mmol) was added to the NMR tube and the latter was pressurized under 4 bar of H_2 . The solution was irradiated at 365 nm during 15 h and the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. (Figure S30) The mixture was then heated at 80 $^\circ\text{C}$ during 24 h and the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded (Figure S31). Acetophenone was converted in 1-phenylethanol in 83% according to ^1H NMR spectrum (Figure S32).



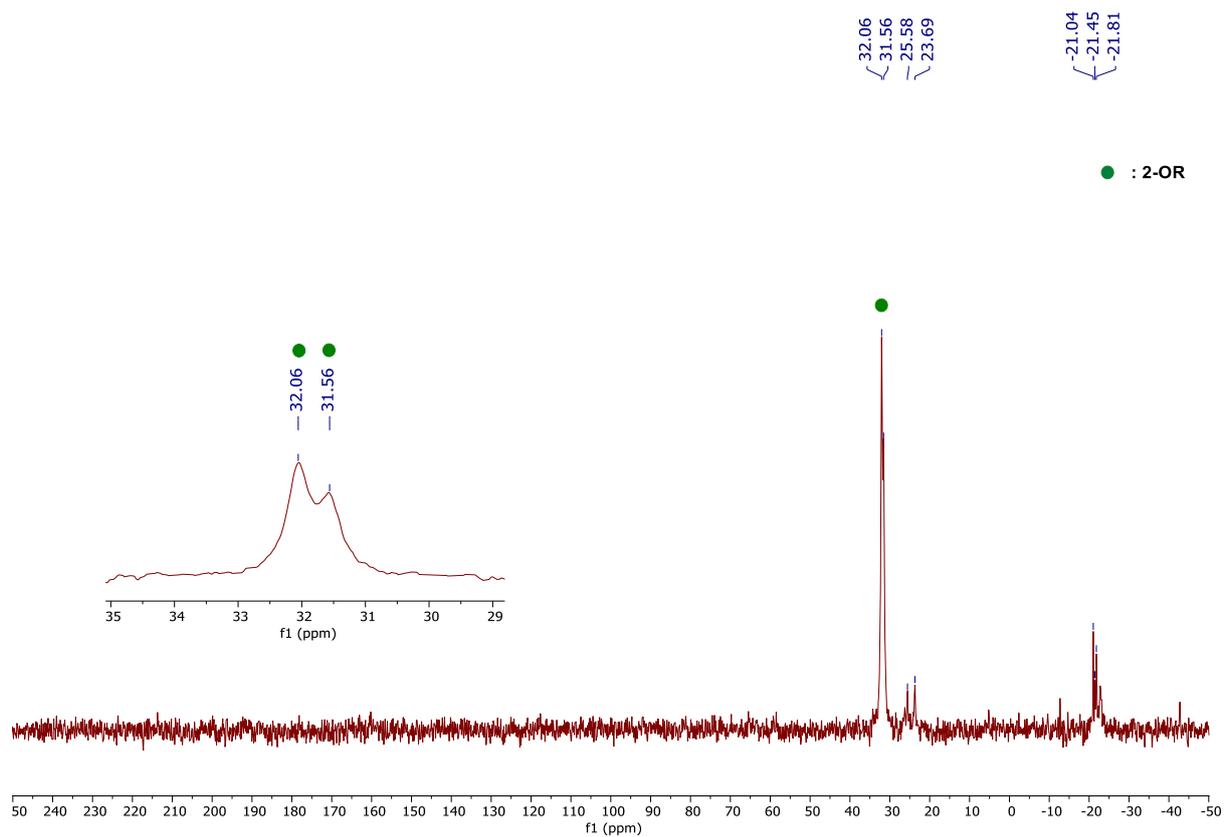


Figure S30: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a solution of **13** in the presence of acetophenone under H_2 pressure after 15 h under irradiation in $\text{THF-}d_8$ recorded at 162 MHz.

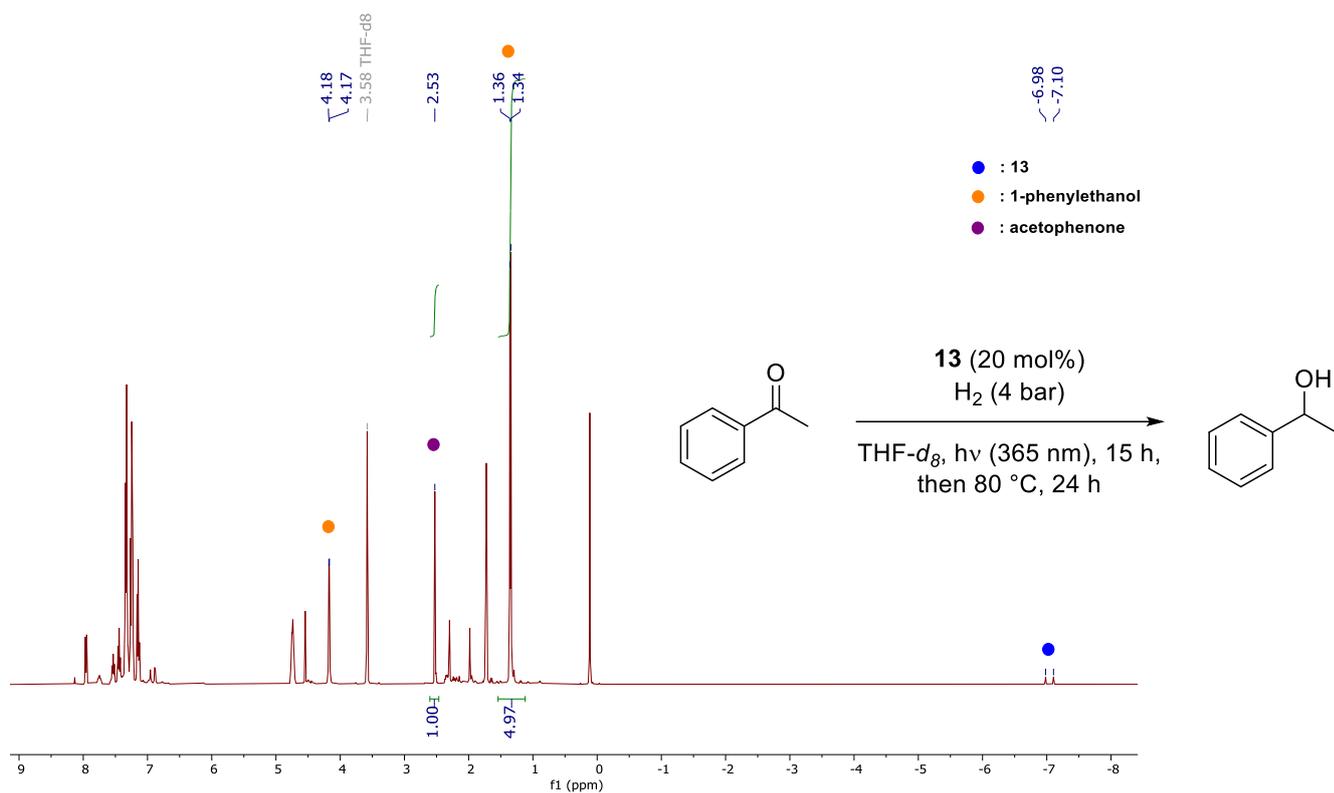


Figure S31: 1H NMR spectrum of a solution of **13** in the presence of acetophenone under H_2 pressure after 15 h under irradiation followed by 24 h at 80 °C in THF- d_8 recorded at 400 MHz.

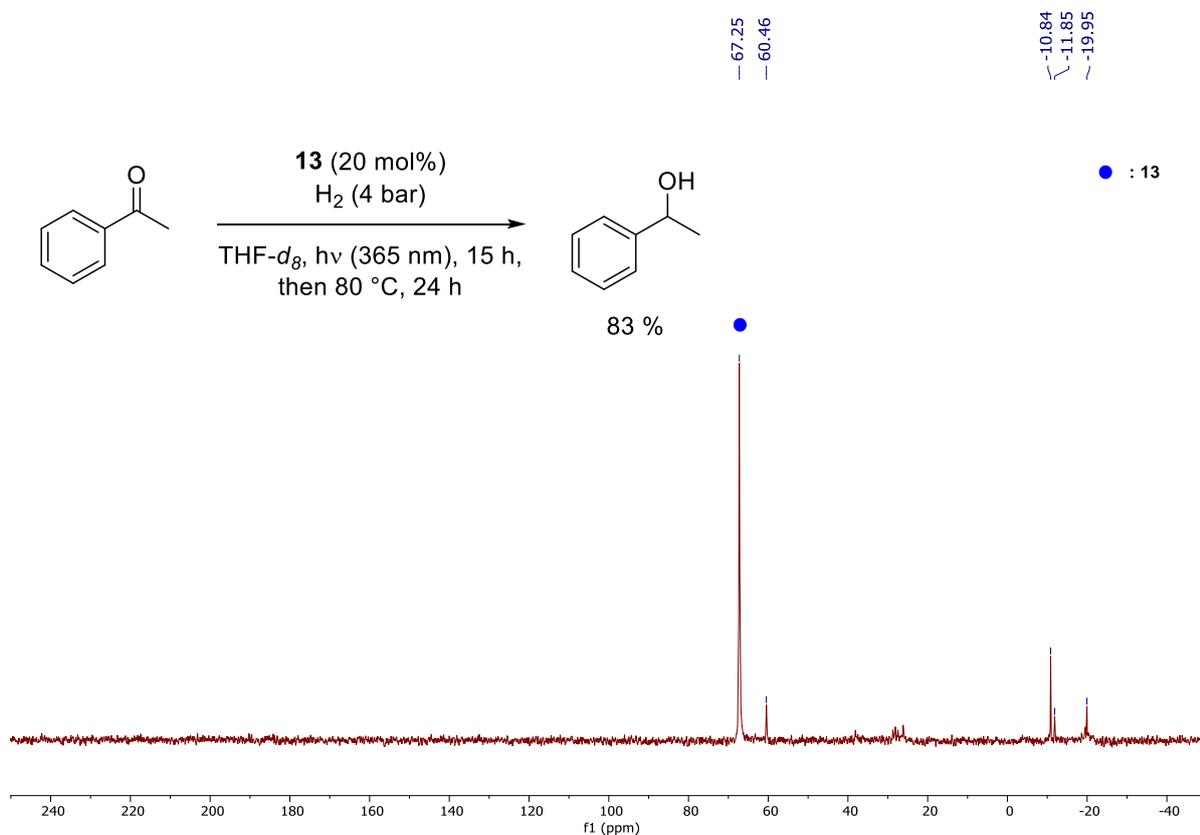


Figure S32: $^{31}P\{^1H\}$ NMR spectrum of a solution of **13** in the presence of acetophenone under H_2 pressure after 15 h under irradiation followed by 24 h at 80 °C in THF- d_8 recorded at 162 MHz.

8. Single-crystal X-Ray diffraction

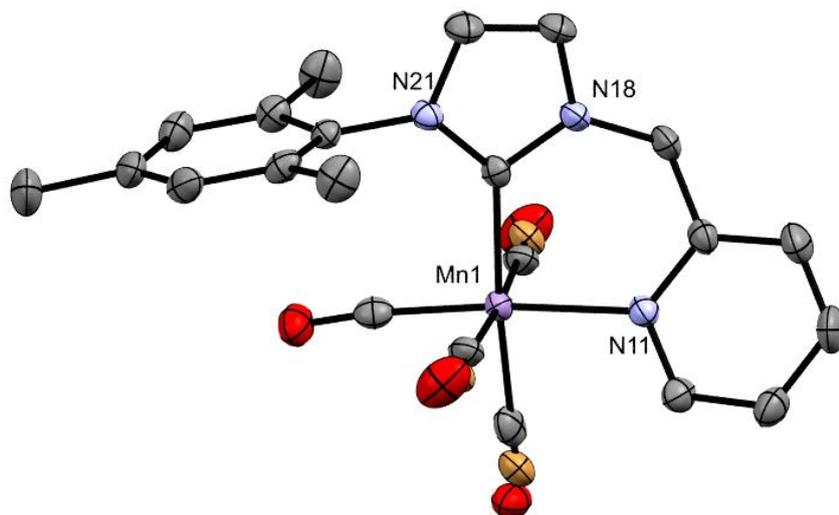
Single crystals suitable for X-ray diffraction were coated with paratone oil and mounted onto the goniometer. The X-ray crystallographic data were obtained at low temperature from diffractometers (Bruker Apex2 (MoK α radiation source) or Oxford-Diffraction Gemini (CuK α)), equipped with an Oxford Cryosystem. The structures have been solved by direct methods using SHELXT or SUPERFLIP and refined by means of least-square procedures on F or F² using CRYSTALS or SHELXL. The scattering factors for all the atoms were used as listed in the International Tables for X-ray Crystallography. Absorption correction was performed using a multi-scan procedure. All non-hydrogen atoms were refined anisotropically excepting for complex **6** (THF molecules were isotropically refined). The H atoms were usually located in a difference map, but those attached to carbon atoms were systematically repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry and Uiso (H) (in the range 1.2-1.5 times Ueq of the parent atom), after which the positions were refined with riding constraints. Crystallographic information for all the complexes are gathered in Tables S6 and S7; the CIF files are also available from The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif) under the references CCDC-2284587 to 2284596.

Tables S6 Crystal and structure refinements data for complexes 2-6

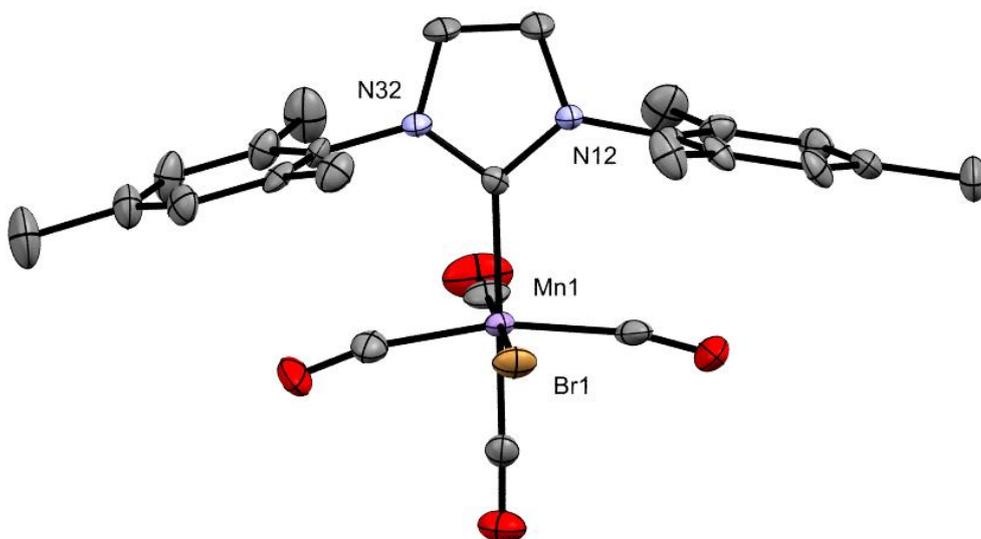
	2	3	4	5	6
Formula	C ₂₉ H ₂₇ Br Mn N ₂ O ₃ P	C ₂₈ H ₂₇ Br Mn N ₂ O ₃ P	C ₂₃ H ₂₃ Br Mn N ₂ O ₃ P	C ₃₆ H ₄₇ Br Mn N ₂ O ₃ P	C ₂₈ H ₂₇ Br Mn N ₂ O ₄ P
M _w (g mol ⁻¹)	617.35	605.34	541.25	721.59	621.34
T(K)	110	110	150	110	110
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group	P 2 ₁ /n	P -1	P 2 ₁ /c	P -1	P -1
a (Å)	14.76210(2)	10.7028(16)	15.24086(12)	7.96450(4)	13.21080(2)
b (Å)	8.286200(17)	10.7643(15)	7.99267(6)	15.09920(5)	13.99510(3)
c (Å)	22.21010(3)	11.9004(17)	19.54312(18)	15.18570(5)	15.14720(3)
α (°)	90	76.194(5)	90	91.343(4)	102.534(2)
β (°)	101.156(2)	80.986(5)	99.6421(8)	99.654(4)	101.224(2)
γ (°)	90	84.523(5)	90	104.457(4)	91.462(2)
V (Å ³)	2665.44(2)	1312.6(3)	2347.02(3)	1739.24(5)	2674.75(4)
Z	4	2	4	2	4
ρ _{calcd.} (g cm ⁻³)	1.538	1.532	1.532	1.378	1.543
μ (mm ⁻¹)	2.089 (Mo Kα)	2.119 (Mo Kα)	7.434 (Cu Kα)	1.611 (Mo Kα)	2.084 (Mo Kα)
Collected reflns	71134	88604	43705	58714	134100
Unique reflns	8144	8046	4527	11097	15098
R _{int}	0.048	0.046	0.067	0.056	0.074
Nb of parameters	334	325	281	397	617
Nb of reflns(I ≥ 2σ)	7058	7393	4422	8725	11686
Refinement on	F	F ²	F ²	F ²	F ²
Final R, wR (I ≥ 2σ)	0.0252, 0.0277	0.0222, 0.0557	0.0382, 0.1024	0.0389, 0.0961	0.0475, 0.1134
R, wR (all data)	0.0330, 0.0648	0.0252, 0.0577	0.0387, 0.1031	0.0488, 0.1037	0.0661, 0.1267
Δρ _{min} / Δρ _{max}	-0.27/0.44	-0.67/0.59	-1.10/1.13	-1.05/1.28	-1.25/2.04
GOF	1.0046	0.9956	1.0055	0.9952	0.9933
CCDC Dep. Number	2284589	2284590	2284591	2284592	2284593

Table S7: Crystal and structures refinements data for complexes **8-13**

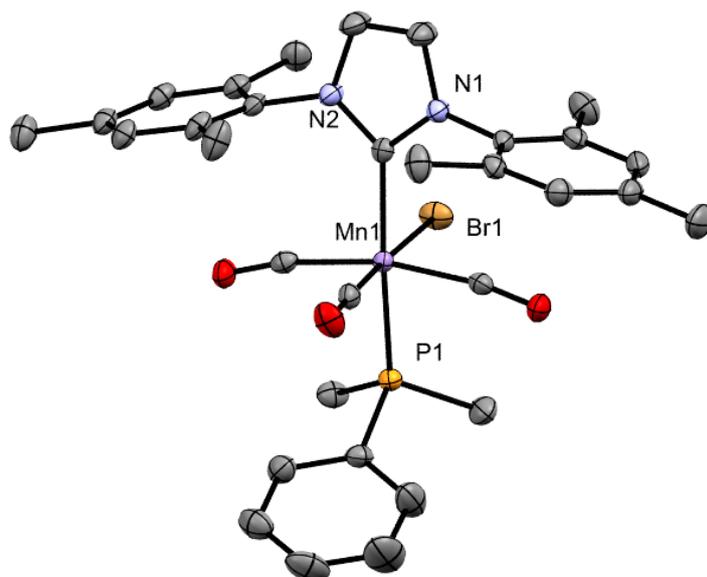
	8	[(MnBr(CO)4(IMes))]	11	12	13
Formula	C ₂₁ H ₁₉ Br Mn N ₃ O ₃ , C H ₂ Cl ₂	C ₂₅ H ₂₄ Br Mn N ₂ O ₄	C ₃₂ H ₃₅ Br Mn N ₂ O ₃ P	C ₂₉ H ₂₆ Mn N ₂ O ₃ P	C ₂₉ H ₂₈ Mn N ₂ O ₃ P
M _w (g mol ⁻¹)	581.17	551.31	661.45	536.44	538.45
T(K)	150	150	150	150	100
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	C 2/c	P 2 ₁ /c	P -1	P 2 ₁ /n	P 2 ₁ /c
<i>a</i> (Å)	39.293(4)	17.4000(16)	9.3638(3)	11.90620(17)	8.84370(2)
<i>b</i> (Å)	7.7798(7)	17.479(2)	9.3661(3)	8.36695(11)	20.54320(3)
<i>c</i> (Å)	16.0842(15)	8.4854(8)	19.2653(6)	26.3978(4)	14.77250(3)
∠ (°)	90	90	98.502(3)	90	90
∠ (°)	104.265(3)	100.926(3)	94.519(3)	90.6523(12)	107.054(2)
∠ (°)	90	90	111.269(3)	90	90
V (Å ³)	4765.2(8)	2533.9(5)	1541.06(9)	2629.54(6)	2565.82(3)
Z	8	4	2	4	4
ρ _{calcd.} (g cm ⁻³)	1.620	1.445	1.425	1.355	1.394
μ (mm ⁻¹)	2.484 (Mo Kα)	2.130 (Mo Kα)	5.767 (Cu Kα)	4.923 (Cu Kα)	0.611 (Mo Kα)
Collected reflns	36601	25902	30188	40133	86315
Unique reflns	5464	5817	5984	5110	7217
<i>R</i> _{int}	0.0508	0.120	0.043	0.047	0.044
Nb of parameters	311	304	361	325	329
Nb of reflns (<i>I</i> ≥ 2σ)	4600	3867	5533	4749	6444
Refinement on	F ²	F ²	F ²	F ²	F
Final <i>R</i> , <i>wR</i> (<i>I</i> ≥ 2σ)	0.0585, 0.1303	0.0582, 0.1027	0.0279, 0.0664	0.0341, 0.1067	0.0300, 0.0347
<i>R</i> , <i>wR</i> (all data)	0.0723, 0.1376	0.1073, 0.1162	0.0309, 0.0694	0.0369, 0.1139	0.0351, 0.0433
Δρ _{min} / Δρ _{max}	-1.14/0.88	-0.44/0.10	-0.39/0.34	-0.50/0.58	-0.30/0.46
GOF	1.120	1.062	0.9917	0.9735	1.0008
CCDC Dep. Number	2284596	2284595	2284594	2284587	2284588



Complex 8



$[(MnBr(CO)_4(IMes))]$



Complex 11

Figure S33: Perspective views of complexes **8**, $[(\text{MnBr}(\text{CO})_4)(\text{IMes})]$ and **11** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms were omitted for clarity.

9. Computational section

8.1 Full Computational details

All calculations have been performed with the Gaussian 16 suite of programs (revision C01)¹ and a custom script developed in the laboratory was utilized to interface with the xtb software (v. 6.4.1).²

All geometry optimisations were performed with an 2-layered ONIOM³ QM/QM' approach: the high level corresponds to DFT (PBE0⁴ hybrid functional) with a triple- ζ def2-TZVP(-f)⁵ basis set for all atoms, except the Mn center for which a relativistic effective core potential from the Stuttgart group⁶ and its associated basis set have been used. The low level corresponds to the semi-empirical tight-binding GFN2-xTB⁷ method. A recent study has shown that such approach leads to a substantial reduction in computational costs while maintaining a high level of accuracy.⁸ This QM:QM' approach defines here the 'BS1 level'.

The nature of the extrema, as minima or transition states, was confirmed by analytical frequency calculations at the BS1 level. IRC calculations have been performed, followed by geometry optimizations, in order to connect the different minima with their respective transition states. This BS1 level was also used for the statistical mechanics calculations of the thermal and entropic effects which were carried out using the rigid rotor/harmonic oscillator approximation at room temperature and 1 atm.

Single point calculations were carried out with 'BS2 level', which is defined as follows. The same hybrid functional (PBE0) has been used, including the D3BJ Grimme correction for dispersion effects (D3 correction with Becke-Johnson damping)⁹, with a quadruple-zeta def2-QZVPP basis set for all atoms⁵ except the Mn center for which a relativistic effective core potential from the Stuttgart group⁶ and its associated basis set have been used. The solvent effects (THF) were included with the IEFPCM solvation model.¹⁰

The reported Gibbs energies for all species were calculated at 298.15 K and 1 atm as follows:

$$G^{THF,PBE0-D3BJ,BS2} = E_{SCRF}^{THF,PBE0-D3BJ,BS2} + G_{correction}^{gas,PBE0,BS1 //GFN2-xTB} + RT \ln(24.45)$$

The last term is related to the free energy change associated with a standard-state concentration change (vs. an ideal gaz).¹¹

NBO analysis were carried out with the NBO7 program¹² (BS2 level).

Calculations of ¹H NMR shieldings, σ , and related chemical shifts, δ , were performed within the gauge-including atomic orbital (GIAO) framework at the BS2 level.

The ¹H shielding of the reference compound (TMS) has been computed using the same protocol, leading to a value of 31.5 ppm.

8.2 Coordinates for the optimized structures of all extrema

C2

Mn	7.104628	4.120282	14.125036
Br	9.235468	4.739903	12.832319
P	8.212176	3.318504	15.990439
C	7.322524	2.242487	13.315576
C	6.996663	0.326733	12.144903
C	8.196011	0.231386	12.747032
C	9.564698	1.652084	14.241536
C	9.223493	1.797421	15.708996
C	7.132417	5.770715	14.861059
C	5.525492	3.809585	14.874717

C	6.277162	4.875622	12.695584
C	9.404463	4.354922	16.903899
C	9.775239	4.013852	18.205267
C	10.732351	4.752462	18.877311
C	11.336556	5.836276	18.253161
C	10.980064	6.172858	16.958468
C	10.017470	5.435922	16.282369
C	7.026909	2.826630	17.284669
C	6.434125	1.568174	17.284072
C	5.419508	1.265188	18.178082
C	4.978134	2.219886	19.079768
C	5.552714	3.482086	19.077676
C	6.566212	3.784971	18.184782
C	5.233539	2.015532	11.993177
C	4.064659	1.740052	12.694671
C	2.870350	2.211645	12.166182
C	2.826674	2.906865	10.965288
C	4.013040	3.111340	10.271432
C	5.232346	2.673455	10.764902
C	4.075956	0.917888	13.945435
C	1.533700	3.450228	10.440361
C	6.504467	2.901655	10.010649
N	6.479733	1.550163	12.503951
N	8.375902	1.397606	13.451055
O	7.117156	6.816148	15.323791
O	4.485150	3.691741	15.345551
O	5.758494	5.474133	11.874288
H	6.467733	-0.347576	11.494553
H	8.934834	-0.551202	12.732644
H	10.236319	0.805931	14.088539
H	10.045706	2.552842	13.855110

H	10.136345	1.886234	16.299208
H	8.683864	0.917007	16.060026
H	9.303463	3.172681	18.700741
H	11.008086	4.482972	19.890379
H	12.086282	6.415816	18.779618
H	11.451714	7.013402	16.463262
H	9.765811	5.684100	15.258110
H	6.744643	0.812668	16.572006
H	4.969789	0.279139	18.164769
H	4.183606	1.984041	19.777782
H	5.207143	4.238776	19.772194
H	7.003600	4.776756	18.186936
H	1.949500	2.027332	12.710268
H	3.993417	3.644268	9.326317
H	3.200831	1.135707	14.556889
H	4.962884	1.101646	14.549867
H	4.060488	-0.148666	13.699126
H	1.511008	3.437988	9.349232
H	1.397188	4.488097	10.758732
H	0.681212	2.877831	10.809265
H	6.331801	3.562866	9.162074
H	7.278801	3.348922	10.638706
H	6.908895	1.959661	9.628804

C13

Mn	8.506246	5.997237	5.540064
P	8.447119	3.893379	4.749756
C	6.767383	6.388783	4.586783
C	4.664643	7.083871	4.071210
C	5.077987	6.293258	3.065899
C	7.117547	4.972520	2.576435

C	7.329050	3.655290	3.300050
C	9.565640	6.580955	4.212196
C	8.565803	7.546511	6.451853
C	9.789931	5.420428	6.644977
C	5.600452	7.938696	6.155496
C	5.104783	7.378505	7.327221
C	4.996066	8.202674	8.440109
C	5.343281	9.545568	8.393857
C	5.804969	10.070668	7.193146
C	5.943419	9.285201	6.060256
C	4.701702	5.940240	7.383506
C	5.217565	10.417948	9.605172
C	6.488149	9.850411	4.786673
C	10.045751	3.279729	4.106863
C	10.426549	3.493196	2.785298
C	11.678578	3.103023	2.337667
C	12.571508	2.499770	3.208802
C	12.204822	2.290655	4.529754
C	10.952359	2.677819	4.976014
C	7.956029	2.498481	5.821965
C	7.956316	1.198036	5.317487
C	7.578665	0.135080	6.118132
C	7.206371	0.358015	7.437857
C	7.213260	1.645275	7.948152
C	7.584430	2.712750	7.141761
N	5.696853	7.132457	4.983661
N	6.354452	5.892117	3.389571
O	10.261422	6.975434	3.383139
O	8.727938	8.481403	7.095537
O	10.567439	5.037484	7.399266
H	7.542866	5.526206	6.686656

H	3.744305	7.619635	4.225220
H	4.587691	5.986379	2.158084
H	8.067200	5.442155	2.314247
H	6.558577	4.818373	1.651529
H	6.371869	3.286501	3.674742
H	7.739358	2.902823	2.624201
H	4.629302	7.779293	9.369739
H	6.088532	11.117057	7.142103
H	5.549322	5.297385	7.133599
H	4.343997	5.679118	8.379584
H	3.905008	5.722281	6.666875
H	5.052155	9.824965	10.505462
H	6.119766	11.015548	9.752467
H	4.379066	11.113131	9.503374
H	7.422922	9.356120	4.510176
H	5.795031	9.711760	3.952979
H	6.686107	10.916640	4.893417
H	9.752550	3.975674	2.087820
H	11.957703	3.277853	1.305061
H	13.551641	2.196119	2.860120
H	12.897921	1.823836	5.219801
H	10.677649	2.506248	6.009770
H	8.271986	1.012712	4.296549
H	7.582124	-0.871693	5.716473
H	6.917053	-0.475827	8.067237
H	6.932352	1.824136	8.979581
H	7.590939	3.725588	7.527750

12

O	-0.843651	-1.076193	-3.185680
O	1.167491	2.445393	-2.866679

C	-0.521092	-0.460433	-2.271948
C	0.758548	1.706142	-2.090784
Mn	0.042751	0.559702	-0.902313
P	2.081928	0.092449	-0.125970
C	1.121106	1.257780	0.794067
C	2.677002	-1.228104	0.972800
C	3.621967	0.810763	-0.757693
C	0.527878	0.780952	2.094063
H	1.487319	2.279144	0.845759
C	3.571640	-0.932668	2.001163
C	2.212350	-2.528000	0.830246
C	3.801186	2.185588	-0.875986
C	4.631020	-0.043911	-1.199205
N	-0.330437	-0.356987	1.815542
H	1.271266	0.470258	2.840708
H	-0.082399	1.575077	2.539391
C	3.987248	-1.926031	2.871837
H	3.947917	0.079665	2.111231
C	2.627457	-3.525106	1.701568
H	1.519153	-2.751471	0.030474
C	4.971759	2.695895	-1.415539
H	3.024035	2.868117	-0.553633
C	5.800541	0.467537	-1.736537
H	4.504394	-1.118224	-1.113849
C	-0.713717	-0.610276	0.546167
C	-0.908491	-1.219950	2.713304
C	3.513435	-3.224219	2.724203
H	4.684179	-1.689429	3.668740
H	2.259844	-4.538389	1.579198
C	5.974252	1.839919	-1.845675
H	5.098425	3.769529	-1.501391

H	6.578523	-0.209001	-2.073416
N	-1.576287	-1.653078	0.667419
C	-1.701653	-2.037575	1.990795
H	-0.705538	-1.189848	3.770595
H	3.840076	-4.001107	3.407038
H	6.888917	2.241291	-2.268031
C	-2.422361	-2.168540	-0.364397
H	-2.342646	-2.850365	2.288214
C	-3.677090	-1.580567	-0.535048
C	-2.013011	-3.253747	-1.132778
C	-4.501587	-2.081304	-1.532637
C	-4.137764	-0.454682	0.337986
C	-2.877121	-3.725268	-2.112373
C	-0.669929	-3.885196	-0.953940
C	-4.116461	-3.145284	-2.338645
H	-5.476519	-1.626233	-1.680615
H	-4.148904	-0.746547	1.392551
H	-3.485579	0.415770	0.251952
H	-5.147005	-0.146743	0.061244
H	-2.562702	-4.566739	-2.722708
H	0.096672	-3.286133	-1.456029
H	-0.396228	-3.968982	0.099838
H	-0.653202	-4.882733	-1.396464
C	-5.006489	-3.637563	-3.439159
H	-6.061069	-3.485757	-3.197820
H	-4.799760	-3.096794	-4.368916
H	-4.847442	-4.700425	-3.635008
C	-1.339625	1.662332	-0.703367
O	-2.188029	2.418814	-0.532683

I E_SCRF=-1901.205349 Hcorr=0.513291 Gcorr=0.408713

Mn	-0.078126	-1.006803	-0.662320
P	-1.876322	-0.079769	0.491743
C	0.837562	-1.081965	1.147269
C	2.384986	-1.013155	2.813354
C	1.222877	-1.450932	3.342926
C	-1.131855	-1.745580	2.501527
C	-1.926537	-0.527865	2.180747
C	0.606017	0.545818	-1.216094
C	1.126154	-2.061427	-1.411087
C	-1.135558	-1.176925	-2.075013
C	3.082742	-0.222362	0.602795
C	4.011761	-1.031228	-0.048586
C	4.930421	-0.431260	-0.898715
C	4.949594	0.940947	-1.090468
C	4.050337	1.728682	-0.384767
C	3.116080	1.168767	0.470574
C	4.056117	-2.508836	0.200502
C	5.916937	1.571142	-2.048657
C	2.178669	2.025851	1.264995
C	-1.805653	1.750051	0.379964
C	-1.414225	2.500854	1.479423
C	-1.233831	3.867198	1.361524
C	-1.440230	4.488759	0.141135
C	-1.828388	3.741515	-0.961861
C	-2.006505	2.377716	-0.845559
C	-3.566077	-0.403541	-0.182834
C	-4.584989	0.535973	-0.016270
C	-5.896330	0.209588	-0.303517
C	-6.219888	-1.062299	-0.747087
C	-5.217127	-2.011954	-0.885582
C	-3.907812	-1.690502	-0.595612

N	2.129104	-0.797390	1.478120
N	0.308723	-1.493566	2.323270
O	1.020690	1.530820	-1.661130
O	1.857061	-2.783557	-1.942913
O	-1.826414	-1.308044	-2.991619
H	-0.726288	-2.358140	-0.157131
H	3.352231	-0.840404	3.253963
H	0.968696	-1.722631	4.353727
H	-1.265602	-2.029178	3.550594
H	-1.332780	-2.642293	1.888997
H	-2.889798	-0.461671	2.684559
H	5.641166	-1.053857	-1.425097
H	4.071044	2.802316	-0.511554
H	3.066253	-2.896289	0.428947
H	4.438746	-3.030961	-0.672617
H	4.712324	-2.723353	1.047281
H	6.761089	0.912478	-2.241796
H	5.416350	1.770161	-2.996606
H	6.287337	2.518364	-1.660128
H	1.154168	1.664138	1.181737
H	2.451738	2.005484	2.322206
H	2.205973	3.054917	0.915498
H	-1.260834	1.981832	2.418971
H	-0.928613	4.451993	2.220864
H	-1.294028	5.557269	0.045197
H	-1.983093	4.229817	-1.915528
H	-2.299074	1.777833	-1.700724
H	-4.340163	1.530760	0.335061
H	-6.675049	0.952975	-0.180811
H	-7.246936	-1.315318	-0.976862
H	-5.464943	-3.010192	-1.224025

H -3.128874 -2.434671 -0.697490

|| E_SCRF=-2285.939220 Hcorr=0.658407 Gcorr=0.531243

O 1.252608 2.160443 -2.090748

O -2.002435 -0.768520 -2.530006

C 0.799658 1.301546 -1.456295

C -1.193813 -0.433520 -1.777233

H -0.771877 -1.136207 0.242847

C -1.834554 -4.048663 0.305485

H -0.715901 -4.839872 -1.328396

O -3.301429 -4.790915 -1.382917

C -0.678383 -4.546194 -0.290147

H 1.396400 -4.992904 -0.050859

C 0.498188 -4.631707 0.428091

H 1.443346 -4.319013 2.325849

C 0.525483 -4.247108 1.758412

H -0.601509 -3.464404 3.401376

C -0.623910 -3.765484 2.362794

H -2.683808 -3.264642 2.117757

C -1.796586 -3.652236 1.639197

H -4.519885 -2.990723 0.719613

C -3.074544 -3.966463 -0.519789

H -3.446609 -1.886607 -0.140466

C -4.005778 -2.820953 -0.232843

H -4.745439 -2.741832 -1.028461

C 1.045484 -1.332005 -1.213893

O 1.638290 -2.203526 -1.690018

Mn 0.034314 -0.034327 -0.564822

P -1.516363 1.336793 0.519666

C 1.124454 0.115584 1.146438

C -1.709113 0.992230 2.224583

C	-1.157351	3.144985	0.472380
C	-3.151402	1.297059	-0.320184
N	2.474421	0.248298	1.326344
N	0.650529	0.095135	2.413152
C	-0.806860	-0.059627	2.735697
H	-1.777741	1.881349	2.852771
C	0.135075	3.539525	0.806838
C	-2.135292	4.123788	0.312877
C	-3.298553	1.793769	-1.611282
C	-4.231326	0.700693	0.313794
C	2.815315	0.296049	2.660298
C	3.454099	0.139484	0.305138
C	1.652550	0.205198	3.341318
H	-0.849771	-0.120960	3.828626
H	-1.044785	-1.048040	2.331199
C	0.462833	4.872196	0.928088
H	0.879830	2.770299	0.970258
C	-1.808092	5.461958	0.442155
H	-3.152620	3.835878	0.083565
C	-4.516988	1.697606	-2.253480
H	-2.445535	2.250138	-2.101669
C	-5.450323	0.599221	-0.332532
H	-4.081101	0.330331	1.321504
H	3.834777	0.401145	2.993051
C	3.934981	-1.137050	-0.006570
C	3.995786	1.271584	-0.300732
H	1.455416	0.222398	4.400694
C	-0.511219	5.844025	0.739855
H	1.477139	5.163311	1.171846
H	-2.574183	6.216022	0.309562
C	-5.593685	1.098259	-1.616209

H	-4.632365	2.083504	-3.258015
H	-6.291869	0.129927	0.161509
C	4.881510	-1.267764	-1.007745
C	3.468587	-2.330910	0.770383
C	4.942040	1.097324	-1.302984
C	3.607185	2.657753	0.113610
H	-0.259028	6.892219	0.833419
H	-6.545085	1.018057	-2.125967
C	5.374425	-0.160849	-1.685297
H	5.239902	-2.253750	-1.268966
H	2.383607	-2.334309	0.861589
H	3.778588	-3.249199	0.278836
H	3.893108	-2.311271	1.776772
H	5.346703	1.972539	-1.792948
H	2.808742	3.030585	-0.526292
H	3.257865	2.679360	1.144063
H	4.456717	3.332416	0.015413
C	6.359622	-0.331899	-2.803217
H	7.056417	-1.140026	-2.587353
H	5.829538	-0.582240	-3.722509
H	6.920659	0.584514	-2.973604

TS II-III E_SCRF= Hcorr= Gcorr=

O	-0.186001	2.287904	-1.867412
O	-1.482939	-1.205496	-2.946658
C	-0.152606	1.286127	-1.288688
C	-0.982950	-1.061508	-1.928565
H	-0.342456	-1.893725	0.311483
C	1.177399	-3.398434	0.235217
H	1.506790	-4.020192	-1.758425
O	-0.650463	-3.201743	-1.328549

C	1.963417	-3.923834	-0.783676
H	3.873657	-4.693668	-1.360867
C	3.274112	-4.294968	-0.553151
H	4.842097	-4.459674	0.903501
C	3.818630	-4.162968	0.712956
H	3.466950	-3.530084	2.728741
C	3.045184	-3.642941	1.737496
H	1.161510	-2.836259	2.313996
C	1.737675	-3.258346	1.499752
H	-1.127213	-4.859174	0.706195
C	-0.281331	-3.068423	-0.089664
H	-0.970358	-3.610435	1.962340
C	-1.209238	-3.786322	0.909111
H	-2.238623	-3.480790	0.715652
C	1.427775	-0.688569	-1.230462
O	2.384614	-0.930945	-1.820391
Mn	-0.124683	-0.257476	-0.459652
P	-2.210161	0.238757	0.580782
C	0.738312	0.476415	1.244281
C	-2.203168	-0.021551	2.305071
C	-2.743334	1.994748	0.394948
C	-3.605208	-0.653927	-0.217428
N	1.844175	1.259963	1.408108
N	0.307734	0.281950	2.509580
C	-0.927346	-0.517613	2.848691
H	-2.690896	0.758500	2.888486
C	-1.818725	2.973153	0.750145
C	-4.051366	2.380273	0.116287
C	-3.966893	-0.374986	-1.531054
C	-4.255785	-1.662730	0.478071
C	2.088232	1.531371	2.734564

C	2.754691	1.650466	0.389223
C	1.108161	0.909421	3.426309
H	-0.946100	-0.546670	3.942806
H	-0.683331	-1.523829	2.500853
C	-2.168599	4.305768	0.772515
H	-0.815706	2.660692	1.010049
C	-4.404580	3.718217	0.145662
H	-4.794237	1.632635	-0.125990
C	-4.970015	-1.104489	-2.138186
H	-3.453810	0.416395	-2.064985
C	-5.255736	-2.396334	-0.134022
H	-3.961319	-1.844913	1.505097
H	2.920524	2.135395	3.055716
C	3.809170	0.784993	0.080262
C	2.667224	2.907976	-0.205494
H	0.911934	0.867384	4.485079
C	-3.467706	4.685951	0.463323
H	-1.433924	5.056129	1.035015
H	-5.423338	4.007838	-0.078832
C	-5.611611	-2.118668	-1.443145
H	-5.250782	-0.890487	-3.160838
H	-5.758320	-3.188434	0.406537
C	4.707491	1.153398	-0.906126
C	3.980961	-0.497124	0.833933
C	3.586247	3.237223	-1.193800
C	1.635156	3.913559	0.202507
H	-3.747276	5.730895	0.480464
H	-6.389598	-2.695185	-1.926301
C	4.592751	2.365590	-1.572350
H	5.510043	0.477470	-1.164740
H	3.046934	-1.055109	0.870333

H	4.731104	-1.124844	0.361299
H	4.290818	-0.294059	1.861096
H	3.506491	4.201850	-1.675680
H	0.763032	3.831304	-0.444055
H	1.315210	3.759946	1.230769
H	2.033941	4.922068	0.105006
C	5.544694	2.718030	-2.675970
H	6.549295	2.364633	-2.450889
H	5.220733	2.241972	-3.601527
H	5.574143	3.793165	-2.838831

III E_SCRF=-2285.833409 Hcorr=0.663256 Gcorr=0.541081

O	0.026554	-1.995785	-2.109785
O	1.347941	1.360268	-2.765286
C	0.018649	-1.099076	-1.374274
C	0.977638	1.447678	-1.623883
H	0.724244	1.839708	0.769972
C	-0.691710	3.386832	0.296275
H	-0.651535	4.054534	-1.727441
O	1.235584	2.729486	-1.035398
C	-1.233259	4.016002	-0.818319
H	-2.919137	5.031003	-1.647382
C	-2.503477	4.559076	-0.768438
H	-4.234307	4.926757	0.441496
C	-3.241367	4.500302	0.401083
H	-3.277416	3.833727	2.436912
C	-2.704699	3.887434	1.520546
H	-1.033845	2.844851	2.347120
C	-1.439458	3.332053	1.468161
H	1.685377	4.717752	0.609978
C	0.715587	2.839092	0.260765

H	1.287322	3.842780	2.102785
C	1.642905	3.729026	1.075267
H	2.647884	3.304870	1.090038
Mn	0.043056	0.278360	-0.324373
P	2.136025	-0.420090	0.564970
C	2.538414	-2.184851	0.211716
C	3.576368	0.430719	-0.192224
C	0.956945	0.129261	2.972503
C	1.552339	-3.129453	0.482907
C	3.820086	-2.627413	-0.104640
C	3.829208	0.278763	-1.551709
C	4.358815	1.289988	0.566105
N	-0.303135	-0.594610	2.583677
H	1.034805	-0.001035	4.056386
H	0.702821	1.185123	2.810053
C	1.819154	-4.478379	0.391966
H	0.568002	-2.777501	0.761058
C	4.089111	-3.981978	-0.189406
H	4.607367	-1.909385	-0.291581
C	4.859950	0.984791	-2.139447
H	3.199602	-0.381785	-2.134017
C	5.389122	1.997852	-0.026366
H	4.144022	1.377069	1.626002
C	-0.786210	-0.595573	1.317525
C	-1.101617	-1.303633	3.443236
C	3.092940	-4.912487	0.050633
H	1.037146	-5.200818	0.588229
H	5.087729	-4.315109	-0.443454
C	5.638020	1.846727	-1.380272
H	5.053730	0.874424	-3.197573
H	5.998647	2.670615	0.565213

N	-1.927343	-1.340577	1.427797
C	-2.136305	-1.779310	2.715756
H	-0.864940	-1.419640	4.488255
H	3.306622	-5.970853	-0.020701
H	6.439094	2.405562	-1.847317
C	-2.905346	-1.510934	0.411385
H	-2.983381	-2.386624	2.989287
C	-3.905524	-0.540841	0.294426
C	-2.932231	-2.659541	-0.377461
C	-4.880304	-0.696377	-0.675139
C	-3.920648	0.639350	1.216757
C	-3.924224	-2.775477	-1.342380
C	-1.936409	-3.763223	-0.204303
C	-4.889350	-1.798711	-1.517731
H	-5.642237	0.062809	-0.782787
H	-2.982084	1.186389	1.136936
H	-4.732372	1.316088	0.963207
H	-4.038210	0.318186	2.253361
H	-3.934501	-3.653368	-1.973322
H	-1.069078	-3.571984	-0.834335
H	-1.600626	-3.835653	0.827889
H	-2.370686	-4.715850	-0.502309
C	-5.921139	-1.920153	-2.599173
H	-5.592172	-1.364114	-3.477083
H	-6.063477	-2.959011	-2.889037
H	-6.875074	-1.506644	-2.276727
C	-1.460483	0.810974	-1.082682
O	-2.402389	1.126514	-1.677593
C	2.208304	-0.285383	2.307942
H	2.756944	-1.076811	2.817186

TS III-IV E_SCRF=-2285.816413 Hcorr=0.661805 Gcorr=0.537507

O	0.303563	-1.530945	-2.399189
O	1.119159	2.373181	-1.753507
C	0.188778	-0.862011	-1.454314
C	0.705626	1.805920	-0.791064
H	-0.847700	2.042088	1.636088
C	-1.432796	3.628421	0.351235
H	-0.013905	4.522570	-0.968603
O	0.793610	2.626462	0.482382
C	-1.060002	4.432443	-0.717045
H	-1.722405	5.695470	-2.307268
C	-2.021680	5.082760	-1.468409
H	-4.114505	5.451201	-1.744161
C	-3.362267	4.946481	-1.153039
H	-4.785639	4.038133	0.164812
C	-3.739058	4.153727	-0.082686
H	-3.079156	2.873113	1.495877
C	-2.778886	3.498619	0.665092
H	0.472410	4.775618	1.922758
C	-0.381468	2.939880	1.195093
H	-0.837494	4.139930	2.944259
C	0.027935	3.865010	2.332242
H	0.772376	3.376854	2.966013
Mn	0.041824	0.164491	-0.078093
P	2.278671	-0.388525	0.524066
C	2.883191	-1.953784	-0.233399
C	3.500965	0.823676	-0.111766
C	1.236479	-0.452920	3.019705
C	2.053866	-3.068655	-0.151953
C	4.181965	-2.117558	-0.706417
C	3.653343	0.981876	-1.485298

C	4.193667	1.646860	0.763063
N	0.033752	-1.272615	2.594581
H	1.378203	-0.701541	4.076581
H	0.864816	0.578653	2.981392
C	2.487748	-4.306285	-0.575355
H	1.056918	-2.937311	0.246934
C	4.619109	-3.361528	-1.126191
H	4.849425	-1.267481	-0.750397
C	4.515257	1.943683	-1.972592
H	3.076778	0.353908	-2.153921
C	5.050806	2.614679	0.271331
H	4.043433	1.507856	1.827158
C	-0.539224	-1.133235	1.377692
C	-0.598565	-2.221037	3.354189
C	3.776219	-4.457963	-1.069942
H	1.825875	-5.161270	-0.522097
H	5.629272	-3.477199	-1.498860
C	5.214804	2.760405	-1.096006
H	4.635323	2.071330	-3.040109
H	5.590830	3.261127	0.952652
N	-1.565917	-2.032272	1.410734
C	-1.618739	-2.706359	2.609900
H	-0.270703	-2.477441	4.348427
H	4.120610	-5.428104	-1.403331
H	5.882604	3.520409	-1.482189
C	-2.611490	-2.109477	0.452034
H	-2.358374	-3.462408	2.816574
C	-3.725137	-1.284083	0.635194
C	-2.569271	-3.028360	-0.593976
C	-4.770036	-1.357528	-0.268607
C	-3.775276	-0.330764	1.791272

C	-3.635598	-3.067866	-1.482428
C	-1.410743	-3.956762	-0.776252
C	-4.732456	-2.234814	-1.342964
H	-5.624772	-0.707866	-0.142152
H	-2.904023	0.323783	1.763354
H	-4.671754	0.282272	1.744217
H	-3.763502	-0.867974	2.741439
H	-3.598604	-3.765189	-2.307762
H	-0.636371	-3.455089	-1.355109
H	-0.985316	-4.250878	0.180979
H	-1.717872	-4.849781	-1.316959
C	-5.852266	-2.260726	-2.339951
H	-5.705733	-1.463925	-3.069103
H	-5.879246	-3.208601	-2.872960
H	-6.812367	-2.099061	-1.852937
C	-1.572024	0.580171	-0.670503
O	-2.578810	0.828015	-1.186459
C	2.473806	-0.640928	2.245788
H	3.070393	-1.508915	2.524671

IV E_SCRF=-2285.830910 Hcorr=0.662528 Gcorr=0.540603

P	-0.929756	1.323882	0.423159
O	1.807206	1.365532	-2.156826
O	-1.385120	-1.009389	-2.619207
C	1.289823	0.640314	-1.409541
C	-0.952777	-1.038120	-1.495256
H	-3.073870	-2.175891	-1.919042
C	-2.811775	-2.519339	-0.912085
Mn	0.483188	-0.442936	-0.337558
C	-1.153046	1.316812	2.159918
C	-0.444303	0.224828	2.848276

H	-1.097677	2.289297	2.647992
N	1.043774	0.110544	2.597777
H	-0.536100	0.306867	3.936263
H	-0.818200	-0.768560	2.572378
C	1.547953	-0.157148	1.371268
C	2.028372	0.254542	3.539122
N	2.895700	-0.181282	1.588614
C	3.208942	0.067274	2.906082
H	1.813027	0.484598	4.569854
H	4.225043	0.095204	3.263898
C	1.465744	-1.742748	-1.018761
O	2.092955	-2.542802	-1.575389
O	-1.633824	-1.835099	-0.515313
C	-3.950008	-2.206482	0.026651
H	-5.451148	-2.431836	-1.480209
C	-5.259304	-2.229263	-0.435376
H	-7.327631	-2.001734	0.056436
C	-6.311461	-1.984215	0.427372
H	-6.889807	-1.504884	2.434103
C	-6.066392	-1.704871	1.761551
H	-4.564633	-1.443661	3.265004
C	-4.763827	-1.672812	2.227160
H	-2.695407	-1.893839	1.721918
C	-3.713509	-1.928873	1.364928
H	-2.238920	-4.366060	0.059643
H	-3.448972	-4.568719	-1.221347
C	-2.547418	-4.019050	-0.930470
H	-1.751249	-4.251559	-1.641565
C	-0.262405	2.997985	0.041958
C	-2.551697	1.378296	-0.438491
C	1.067301	3.247190	0.371065

C	-1.057735	4.057463	-0.385141
C	-2.586832	1.532542	-1.820726
C	-3.729569	1.181855	0.267126
C	1.604739	4.508891	0.235920
H	1.669972	2.422673	0.728403
C	-0.518549	5.325230	-0.515460
H	-2.099586	3.887229	-0.621377
C	-3.796717	1.485771	-2.484451
H	-1.656707	1.670945	-2.358408
C	-4.940377	1.139190	-0.399953
H	-3.670851	1.065287	1.342563
C	0.811891	5.556979	-0.212597
H	2.644629	4.685010	0.479581
H	-1.144067	6.141580	-0.854698
C	-4.973247	1.284969	-1.776526
H	-3.826372	1.594844	-3.560291
H	-5.858912	0.984309	0.151689
H	1.230467	6.549103	-0.319453
H	-5.919087	1.239767	-2.301768
C	3.862821	-0.640271	0.655561
C	4.125932	-2.012822	0.611506
C	4.587286	0.251480	-0.132027
C	5.085291	-2.482329	-0.268252
C	3.373610	-2.953624	1.504126
C	5.537322	-0.259987	-1.006003
C	4.361270	1.728289	-0.055335
C	5.788033	-1.618560	-1.096263
H	5.280994	-3.544361	-0.319270
H	3.679321	-3.981122	1.324073
H	3.544207	-2.713020	2.554831
H	2.303872	-2.869355	1.308847

H	6.088102	0.425629	-1.634798
H	3.551325	2.002360	-0.729930
H	4.084999	2.034315	0.951368
H	5.256668	2.268090	-0.357247
C	6.785679	-2.154123	-2.079749
H	7.310331	-3.016964	-1.673241
H	6.267767	-2.470279	-2.985245
H	7.512705	-1.392446	-2.353006

V E_SCRF=-2287.014833 Hcorr=0.680849 Gcorr=0.557363

P	-0.461794	1.541986	0.729851
O	2.091294	0.578062	-1.969050
O	-1.259102	-0.112107	-2.237342
C	1.442607	0.163753	-1.110234
C	-1.100311	-0.660552	-1.163723
H	-3.415345	-0.609245	-2.066685
C	-3.299912	-1.563689	-1.542624
Mn	0.422230	-0.556746	0.137947
C	-0.193836	1.935256	2.408667
C	0.131423	0.781001	3.289628
H	-0.822438	2.698850	2.864190
N	1.428023	0.170663	2.931967
H	0.230041	1.114835	4.327289
H	-0.582391	-0.065389	3.315341
C	1.704605	-0.300933	1.689389
C	2.543640	0.208956	3.729355
N	3.038194	-0.568658	1.760565
C	3.571387	-0.260411	2.990789
H	2.515395	0.576012	4.741666
H	4.613248	-0.401103	3.224081
C	0.968010	-2.132300	-0.437417

O	1.295065	-3.146555	-0.893731
O	-2.142177	-1.499961	-0.721290
C	-4.507482	-1.803936	-0.674497
H	-3.446402	-2.969991	0.757242
C	-4.410605	-2.573663	0.476657
H	-5.437560	-3.404553	2.159715
C	-5.526178	-2.811723	1.259023
H	-7.628837	-2.476363	1.504920
C	-6.756129	-2.292249	0.892693
H	-7.819751	-1.116077	-0.545488
C	-6.862283	-1.529434	-0.258290
H	-5.825836	-0.676018	-1.924317
C	-5.744352	-1.284997	-1.034863
H	-2.313130	-2.488533	-3.216901
H	-3.011735	-3.642817	-2.062145
C	-3.166703	-2.684659	-2.565831
H	-4.070443	-2.759228	-3.180315
C	0.300339	2.851715	-0.301759
C	-2.265853	1.760269	0.372044
C	1.142304	3.785982	0.285665
C	0.139330	2.838920	-1.685197
C	-2.793043	2.852456	-0.314502
C	-3.152301	0.895939	1.013570
C	1.806523	4.714604	-0.495117
H	1.262429	3.757825	1.362054
C	0.804326	3.768649	-2.460801
H	-0.488011	2.082098	-2.138098
C	-4.160532	3.037291	-0.398210
H	-2.126043	3.555116	-0.795448
C	-4.515646	1.082465	0.935285
H	-2.770794	0.058160	1.584601

C	1.635452	4.708656	-1.869348
H	2.461778	5.443933	-0.034253
H	0.684456	3.757726	-3.536017
C	-5.029572	2.152296	0.217669
H	-4.553693	3.882922	-0.949562
H	-5.185013	0.392187	1.432252
H	2.157735	5.432156	-2.482976
H	-6.099838	2.296304	0.148294
C	3.828370	-0.991573	0.663692
C	4.069098	-2.349286	0.462774
C	4.399109	-0.022058	-0.162999
C	4.847109	-2.730171	-0.619197
C	3.515349	-3.363180	1.418436
C	5.171328	-0.443330	-1.233409
C	4.195198	1.433526	0.127041
C	5.389035	-1.790572	-1.483239
H	5.022777	-3.782109	-0.797539
H	3.603701	-4.365186	1.007367
H	4.053409	-3.323846	2.367706
H	2.464930	-3.158779	1.617829
H	5.600426	0.295923	-1.894991
H	3.143247	1.644226	0.317021
H	4.761959	1.726627	1.013091
H	4.518402	2.041248	-0.713474
C	6.182659	-2.221741	-2.681053
H	5.523916	-2.290967	-3.546912
H	6.964999	-1.500765	-2.910418
H	6.634961	-3.198321	-2.520414
H	-0.450344	-1.605890	1.142482
H	-0.757967	-0.869297	1.315551

TS V_VI E_SCRF=-2286.991455 Hcorr=0.678102 Gcorr=0.550337

P	-0.387789	1.711358	0.606402
O	2.199974	0.646083	-1.999999
O	-1.480240	-0.421442	-2.344385
C	1.495944	0.235901	-1.184509
C	-0.948216	-0.529438	-1.332104
H	-3.194194	-2.275087	-1.898109
C	-3.268088	-2.473862	-0.803217
Mn	0.371698	-0.454546	-0.009727
C	-0.198036	2.015945	2.310665
C	0.032846	0.814480	3.154485
H	-0.826087	2.783166	2.758455
N	1.321871	0.167867	2.829598
H	0.093942	1.096968	4.209746
H	-0.712948	0.001652	3.094932
C	1.625349	-0.292823	1.594140
C	2.402321	0.127959	3.671204
N	2.936012	-0.636824	1.708123
C	3.432250	-0.386199	2.965751
H	2.350990	0.477355	4.688591
H	4.453629	-0.592460	3.236704
C	0.897943	-2.093925	-0.472647
O	1.217401	-3.129795	-0.860429
O	-2.366679	-1.715946	-0.118371
C	-4.713732	-2.185354	-0.421716
H	-5.520454	-2.651560	-2.347828
C	-5.747264	-2.341136	-1.335895
H	-7.854343	-2.215397	-1.691361
C	-7.057498	-2.094441	-0.967974
H	-8.378985	-1.486492	0.607059
C	-7.353697	-1.684845	0.321761

H	-6.553364	-1.195070	2.246646
C	-6.329690	-1.522642	1.239411
H	-4.211686	-1.634611	1.569439
C	-5.021675	-1.772996	0.867785
H	-2.027586	-4.245700	-0.916293
H	-3.142158	-4.228154	0.460224
C	-3.041194	-3.981149	-0.601384
H	-3.758919	-4.585598	-1.170194
C	0.597372	2.947672	-0.331256
C	-2.099498	2.210012	0.129200
C	1.627350	3.634014	0.295812
C	0.388049	3.117097	-1.696001
C	-2.392569	3.570677	0.037837
C	-3.139521	1.285960	0.107057
C	2.440287	4.486884	-0.428495
H	1.762388	3.482021	1.360974
C	1.198659	3.969932	-2.418013
H	-0.412455	2.567059	-2.176875
C	-3.699097	3.994932	-0.108946
H	-1.584794	4.292279	0.076460
C	-4.443590	1.716566	-0.047081
H	-2.923769	0.225468	0.172313
C	2.226587	4.654845	-1.786391
H	3.243942	5.021567	0.062588
H	1.037853	4.101081	-3.479911
C	-4.729486	3.069167	-0.155964
H	-3.917530	5.053291	-0.187831
H	-5.243544	0.988900	-0.085040
H	2.863643	5.318501	-2.356731
H	-5.752656	3.402012	-0.275647
C	3.736475	-1.154697	0.659741

C	3.871359	-2.535196	0.516871
C	4.427664	-0.267566	-0.166408
C	4.658120	-3.018183	-0.516981
C	3.209125	-3.467785	1.486466
C	5.203080	-0.790786	-1.189213
C	4.362567	1.208506	0.080278
C	5.312242	-2.159369	-1.387897
H	4.753758	-4.086663	-0.650546
H	3.172350	-4.475444	1.081708
H	3.764834	-3.489447	2.426215
H	2.193032	-3.142642	1.702781
H	5.725536	-0.113928	-1.850342
H	3.346012	1.522352	0.309886
H	4.997821	1.474767	0.927629
H	4.699617	1.758538	-0.793869
C	6.114063	-2.700646	-2.533901
H	5.477987	-2.784225	-3.415371
H	6.942033	-2.038166	-2.777807
H	6.505252	-3.689726	-2.304690
H	-0.590205	-0.990699	1.305663
H	-1.084193	-1.346184	0.734155

VI E_SCRF=-2287.047298 Hcorr=0.682733 Gcorr=0.558058

P	2.157015	0.148246	0.355005
O	0.968643	-3.232400	-0.809491
O	1.901015	0.200839	-3.392070
C	0.685746	-2.109759	-0.852164
C	1.300864	-0.063791	-2.444261
H	-0.580036	3.993554	-1.631491
C	-1.631668	3.794315	-1.372947
Mn	0.312976	-0.380233	-1.002788

C	1.832419	1.336154	1.591627
C	0.434653	1.810702	1.621673
H	2.256650	1.089431	2.565161
N	-0.634191	0.758240	1.660824
H	0.243824	2.436751	2.498864
H	0.175970	2.402664	0.740092
C	-0.808893	-0.165254	0.687468
C	-1.559680	0.631495	2.662226
N	-1.889048	-0.876335	1.127209
C	-2.364090	-0.401135	2.330099
H	-1.564348	1.280644	3.521765
H	-3.210127	-0.842098	2.831058
C	-1.078768	-0.694983	-2.059100
O	-1.911659	-0.955614	-2.816913
O	-1.985483	2.483737	-1.737044
C	-1.805419	4.058184	0.110324
H	-3.410985	2.676190	0.300048
C	-2.796456	3.395014	0.820146
H	-3.751718	3.112821	2.712259
C	-2.980559	3.641381	2.168179
H	-2.316357	4.753032	3.875967
C	-2.177452	4.561032	2.820472
H	-0.556448	5.945737	2.624762
C	-1.190122	5.231298	2.117621
H	-0.224895	5.496492	0.226781
C	-1.005242	4.981423	0.769940
H	-2.382743	4.602952	-3.226359
H	-3.572977	4.554274	-1.914934
C	-2.523354	4.748062	-2.152508
H	-2.298276	5.788463	-1.901067
C	2.866021	-1.274780	1.287708

C	3.597958	0.647094	-0.671663
C	1.972587	-2.043439	2.029124
C	4.231078	-1.501808	1.443334
C	4.221329	-0.265007	-1.517542
C	4.014077	1.970237	-0.660549
C	2.417286	-3.050656	2.857015
H	0.914522	-1.828741	1.941155
C	4.678594	-2.507595	2.281875
H	4.943849	-0.892022	0.904459
C	5.260467	0.144558	-2.329300
H	3.877262	-1.293526	-1.532780
C	5.050574	2.380888	-1.479234
H	3.502570	2.653582	0.007180
C	3.779125	-3.292404	2.982499
H	1.707766	-3.651590	3.412184
H	5.742263	-2.680536	2.390240
C	5.676483	1.467742	-2.311459
H	5.747420	-0.564731	-2.986159
H	5.373849	3.414386	-1.472610
H	4.133907	-4.082568	3.631167
H	6.487167	1.786457	-2.954115
C	-2.569509	-1.888024	0.399182
C	-3.617630	-1.505370	-0.445889
C	-2.270350	-3.234866	0.597279
C	-4.282657	-2.483602	-1.165026
C	-4.032411	-0.070051	-0.545080
C	-2.957782	-4.184341	-0.148413
C	-1.253377	-3.683736	1.601917
C	-3.945109	-3.824893	-1.049258
H	-5.077940	-2.192785	-1.837022
H	-4.932186	0.024133	-1.148486

H	-4.228943	0.337432	0.447706
H	-3.247421	0.528792	-1.006961
H	-2.709782	-5.228754	-0.015419
H	-0.283569	-3.813284	1.124090
H	-1.144024	-2.958406	2.405901
H	-1.544797	-4.641900	2.030355
C	-4.646082	-4.857303	-1.881396
H	-4.227040	-4.861414	-2.887833
H	-4.522954	-5.851481	-1.457024
H	-5.708916	-4.634987	-1.962112
H	0.207662	1.214385	-1.060336
H	-1.251170	1.882268	-1.487448

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acetophenone E_SCRF=-384.624583 Hcorr=0.143996 Gcorr=0.105322

C	0.196795	0.324455	0.100852
O	1.403363	0.391433	0.202023
C	-0.513574	-1.005000	0.043811
H	-1.221363	-1.097989	0.873210
H	-1.079180	-1.098690	-0.888285
H	0.223671	-1.804280	0.103830
C	-0.630381	1.565586	0.028878
C	-2.019651	1.551241	-0.081546
C	0.032542	2.792138	0.075649
C	-2.723236	2.740058	-0.143299
H	-2.558932	0.617520	-0.119539
C	-0.673306	3.977241	0.013570
H	1.109002	2.787906	0.161343
C	-2.054529	3.952924	-0.096187
H	-3.799980	2.721921	-0.228739
H	-0.149631	4.920952	0.050563
H	-2.610519	4.877631	-0.145014

H2 E_SCRF=-1.169224 Hcorr=0.013364 Gcorr=0.001581

H 0.000000 0.000000 0.000000

H 0.000000 0.000000 0.746100

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1-Phenylethanol E_SCRF=-385.2826045 Hcorr=0.168109 Gcorr=0.128096

H -1.519751 2.898811 2.131073

C 0.342100 3.727826 2.762848

H 1.995829 2.448564 3.191541

O -0.115781 1.381481 2.273444

C 1.682142 3.467933 3.017774

H 3.643319 4.286567 3.245060

C 2.602910 4.499848 3.047462

H 2.908945 6.609812 2.850892

C 2.191209 5.803057 2.827319

H 0.530211 7.085106 2.403126

C 0.855743 6.069679 2.576129

H -1.105800 5.246369 2.342547

C -0.064034 5.036903 2.541952

H -0.318644 2.049769 4.809907

C -0.665315 2.597885 2.758062

H -1.620482 3.232297 4.584373

C -1.154565 2.336150 4.168095

H -1.887634 1.526475 4.171007

H 0.280198 1.555466 1.415383

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MethylBenzoate E_SCRF=-459.818289446 Hcorr=0.149674 Gcorr=0.109914

C -1.410532 0.099009 0.001658

O -0.214007 -0.058699 0.006488

O -1.999105 1.312556 -0.002748

C -2.400437 -1.007982 0.000114

C -3.772327 -0.770444 -0.000085
C -1.923703 -2.316949 -0.000479
C -4.653242 -1.835930 -0.000786
H -4.136699 0.244744 0.000483
C -2.809775 -3.376984 -0.001342
H -0.856229 -2.477917 -0.000241
C -4.174897 -3.136967 -0.001431
H -5.717711 -1.653191 -0.000775
H -2.438892 -4.391109 -0.001869
H -4.868132 -3.965347 -0.001949
C -1.091798 2.411363 -0.001382
H -0.454676 2.384037 -0.886293
H -1.711061 3.305615 -0.004796
H -0.460370 2.386823 0.887668

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TS_II_III (substrat: methylbenzoate) E_SCRF=-2361.000208 Hcorr=0.665692 Gcorr=0.540447

O -0.169515 -2.503296 -1.849653
O 1.483357 0.820983 -2.976089
C -0.081539 -1.503617 -1.272006
C 1.026960 0.776303 -1.923396
H 0.504795 1.593736 0.387404
C -0.654736 3.357782 0.099916
H -0.819900 3.670987 -1.991977
O 1.263954 2.703041 -1.205101
C -1.307555 3.811069 -1.037892
H -3.050842 4.763060 -1.830406
C -2.545031 4.419861 -0.938065
H -4.102141 5.072579 0.383745
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H -2.939311 4.292025 2.414791
C -2.481850 4.154881 1.443117

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H	5.578562	2.812496	0.355501
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C 2.214653 4.321472 0.755772

H 1.520375 5.172358 0.655580

H 2.900980 4.529833 1.580652

H 2.777898 4.224051 -0.176955

8.3 References of the computational section

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10. NMR Spectra of the ligands and complexes

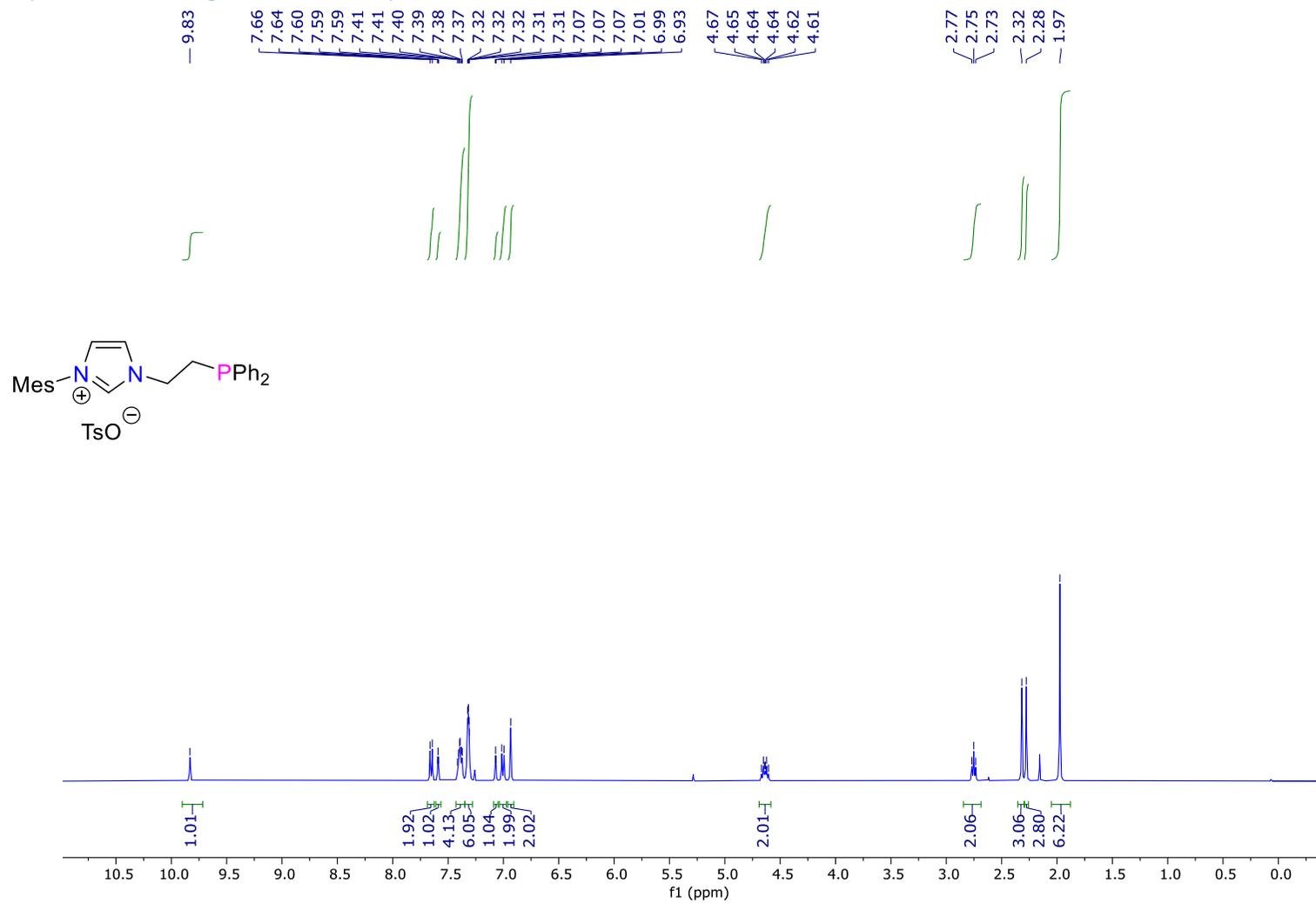


Figure S34: ^1H NMR spectrum of **L2.HOTs** in CDCl_3 recorded at 400 MHz.

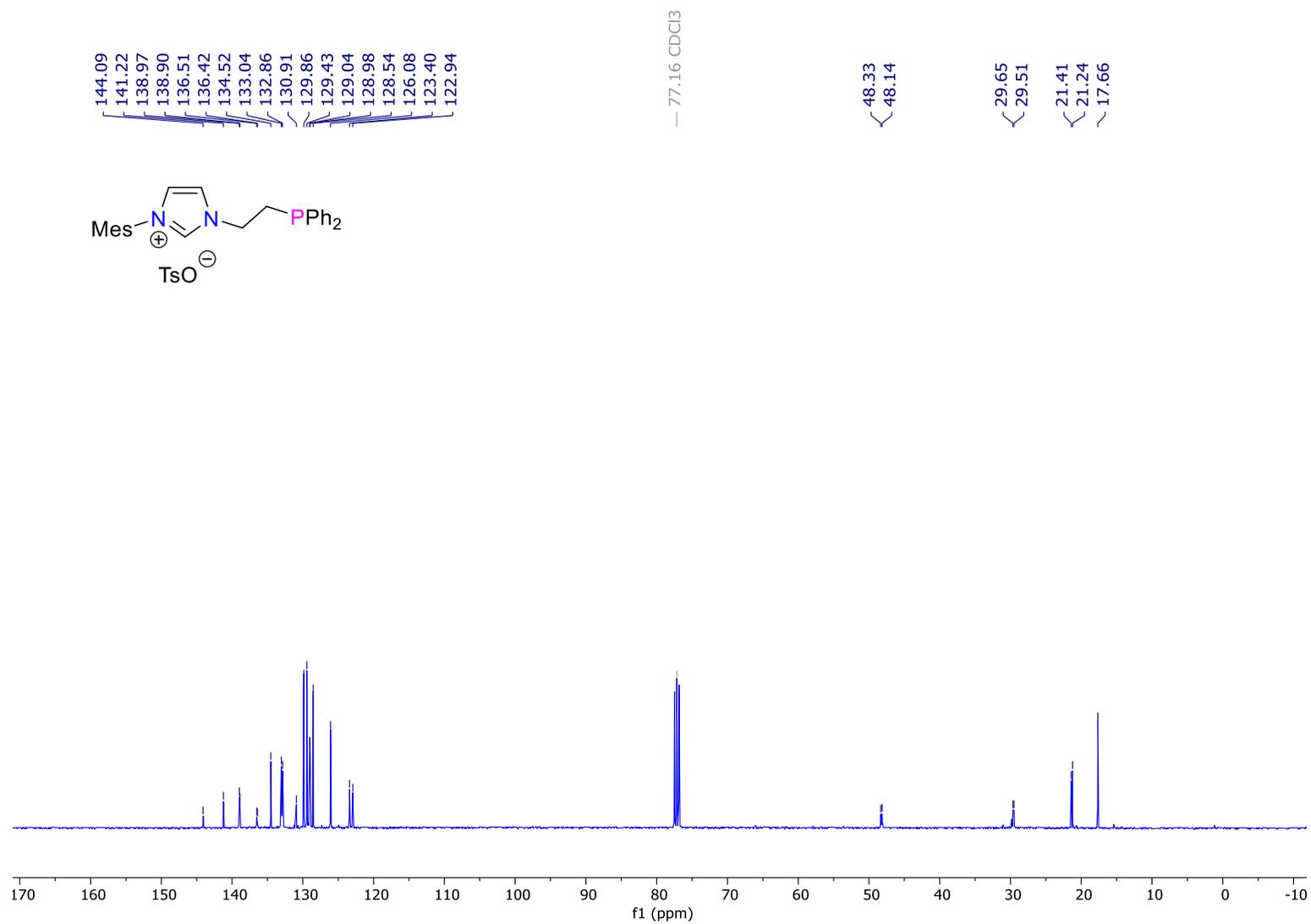


Figure S35: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **L2.HOTs** in CDCl_3 recorded at 101 MHz.

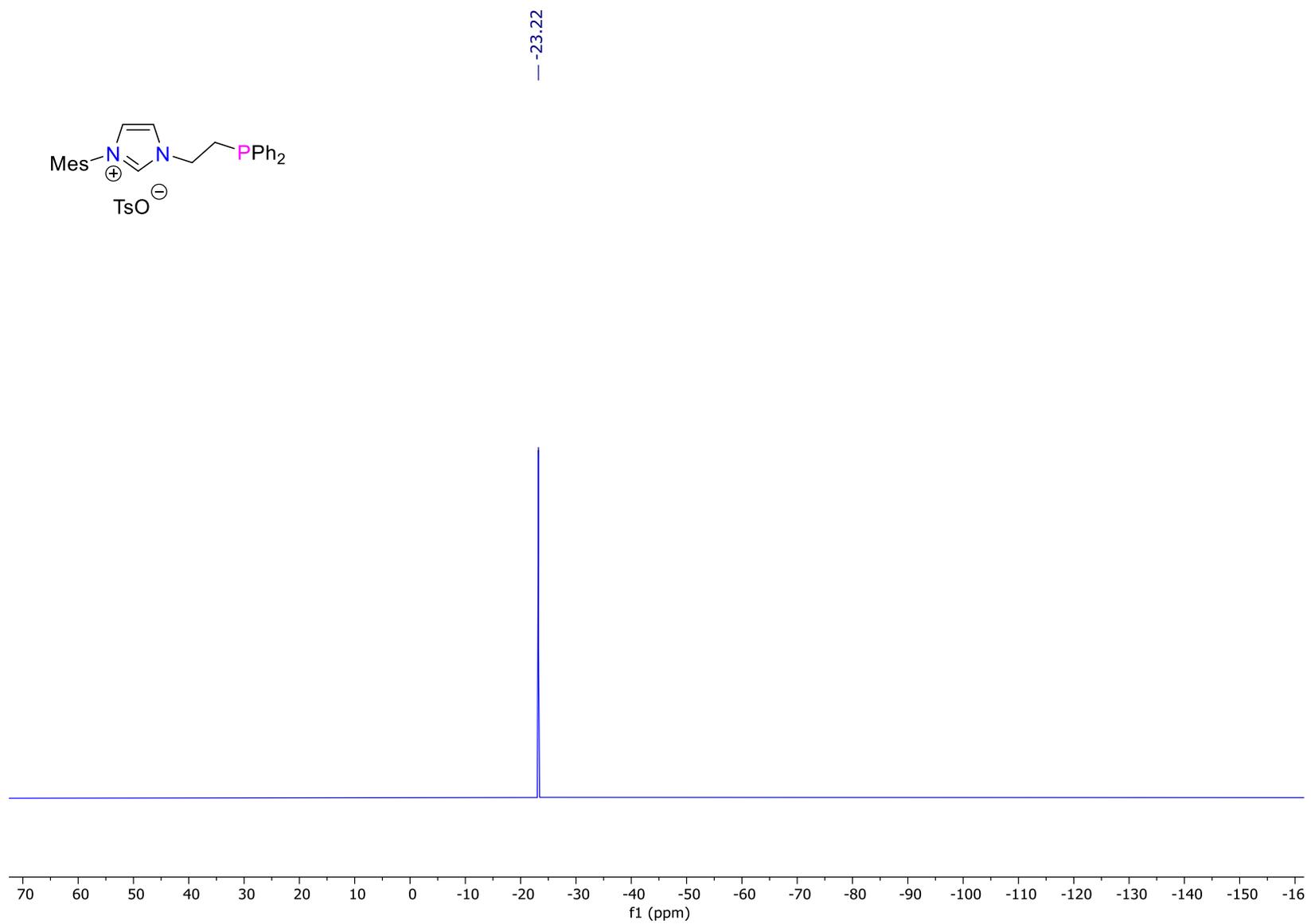


Figure S36: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **L2.HOTs** in CDCl_3 recorded at 162 MHz.

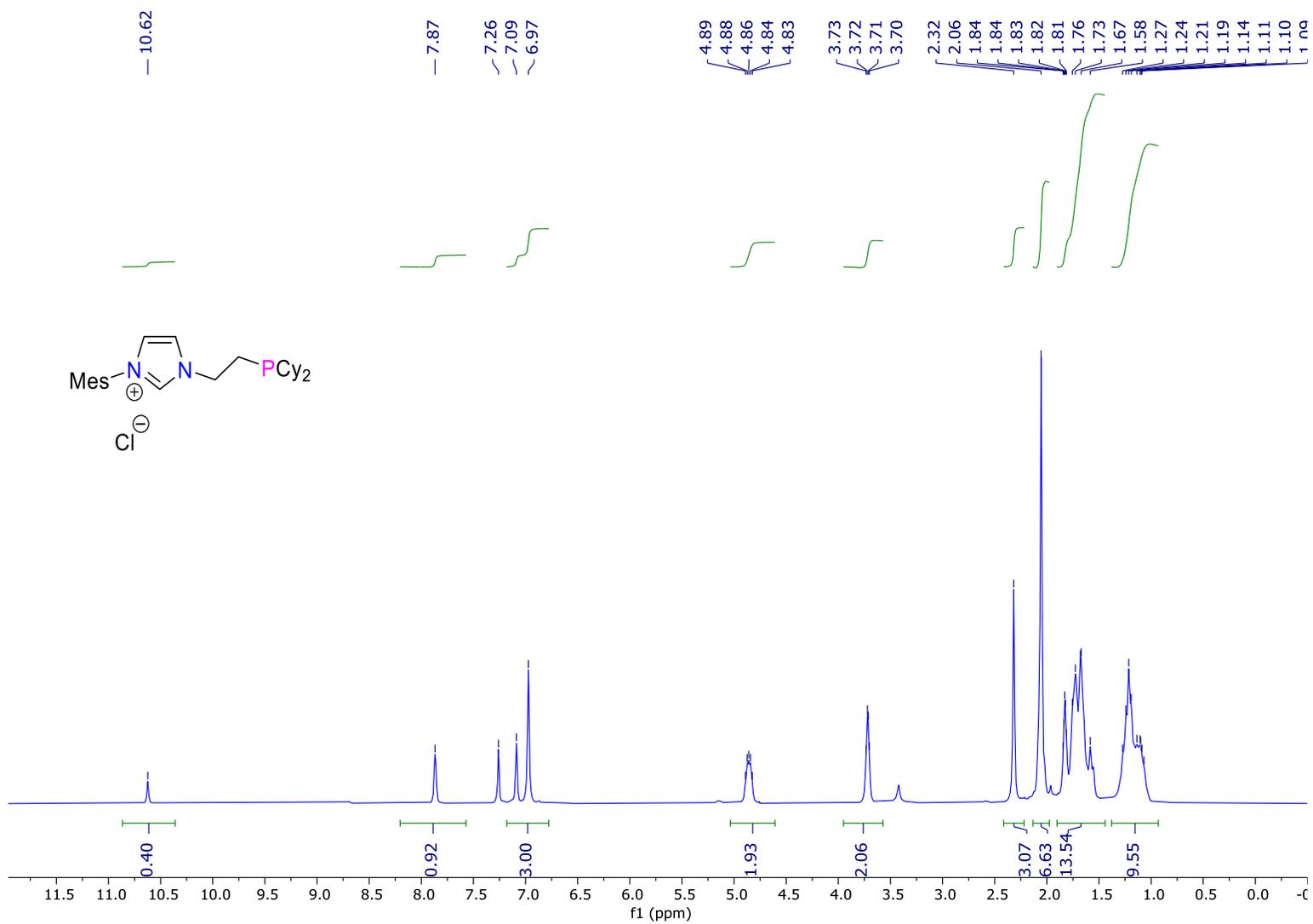


Figure S37: ^1H NMR spectrum of **L5.HCl** in CDCl_3 recorded at 400 MHz.

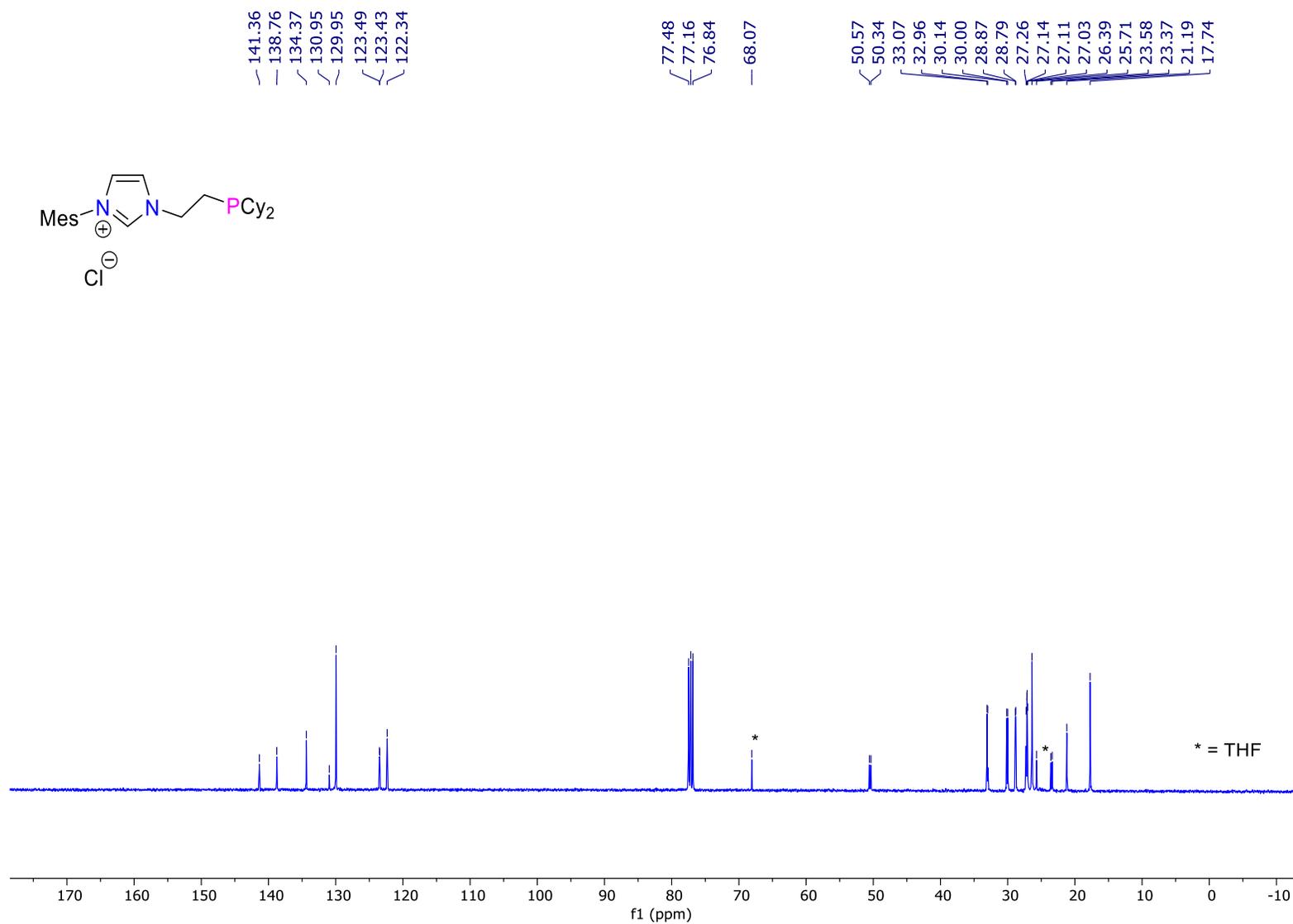


Figure S38: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **L5.HCl** in CDCl_3 recorded at 101 MHz.

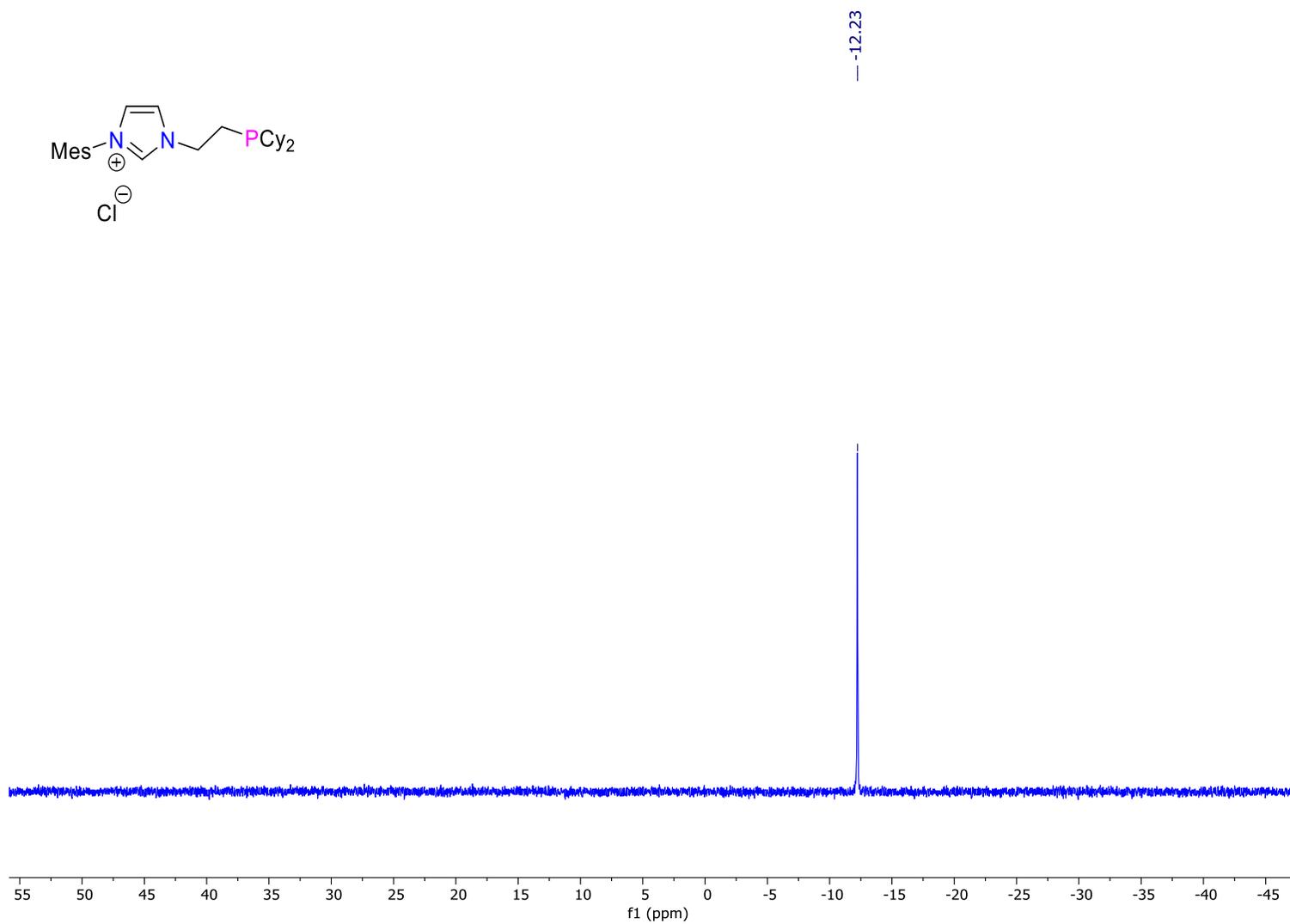


Figure S39: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **L5.HCl** in CDCl_3 recorded at 162 MHz.

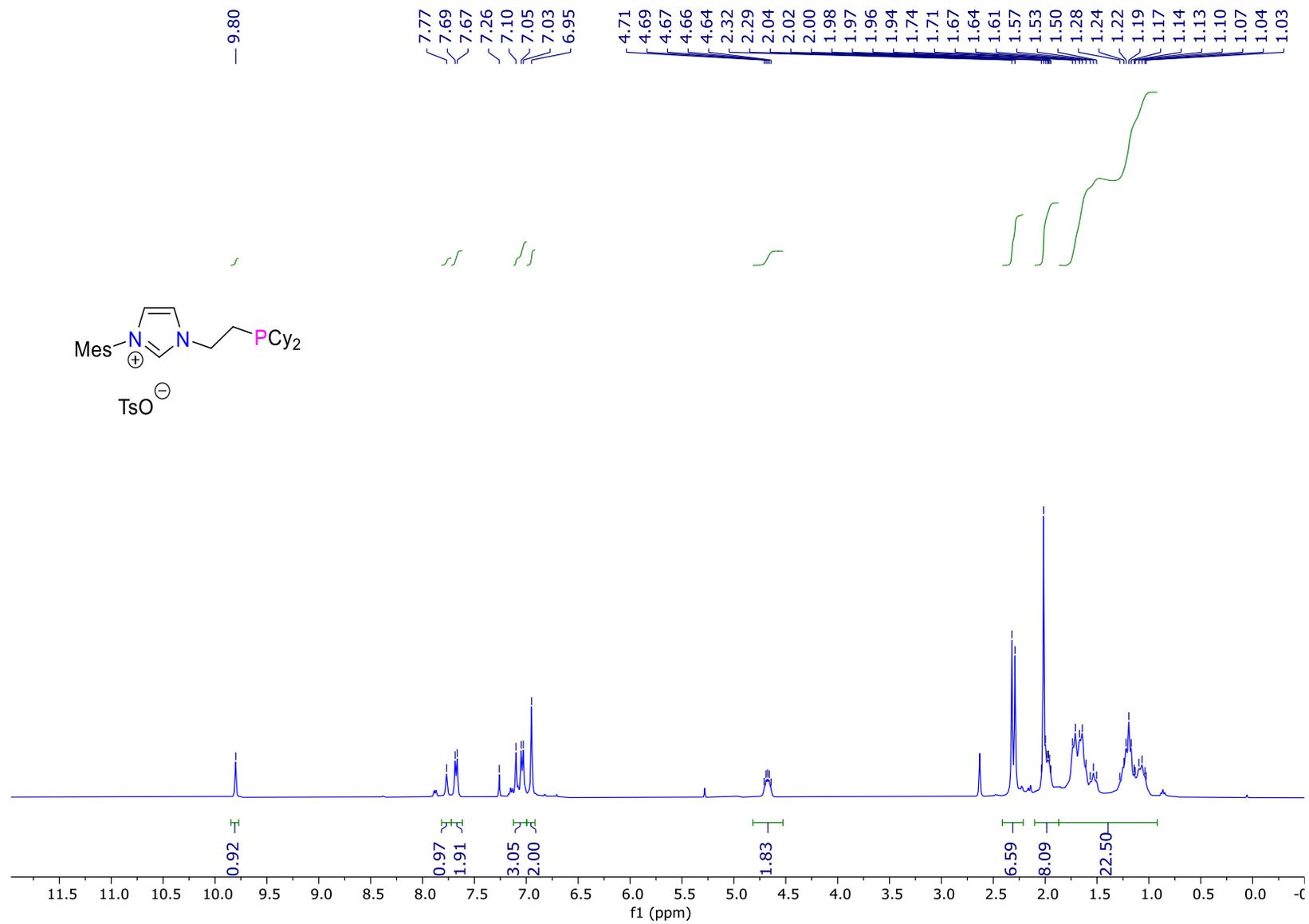


Figure S40: ¹H NMR spectrum of L5.HOTs in CDCl₃ recorded at 400 MHz.

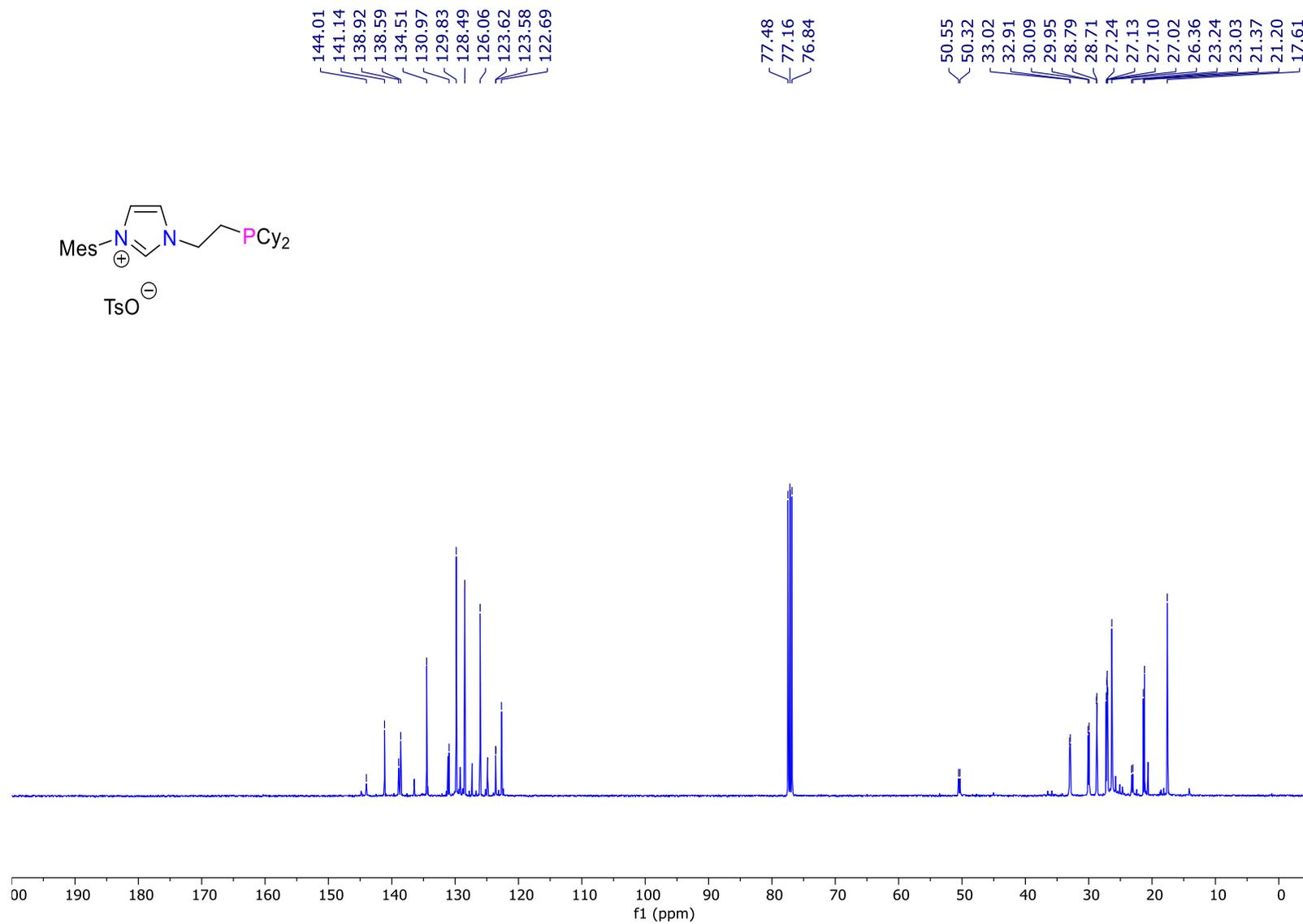


Figure S41: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **L5.HOTs** in CDCl_3 recorded at 101 MHz.

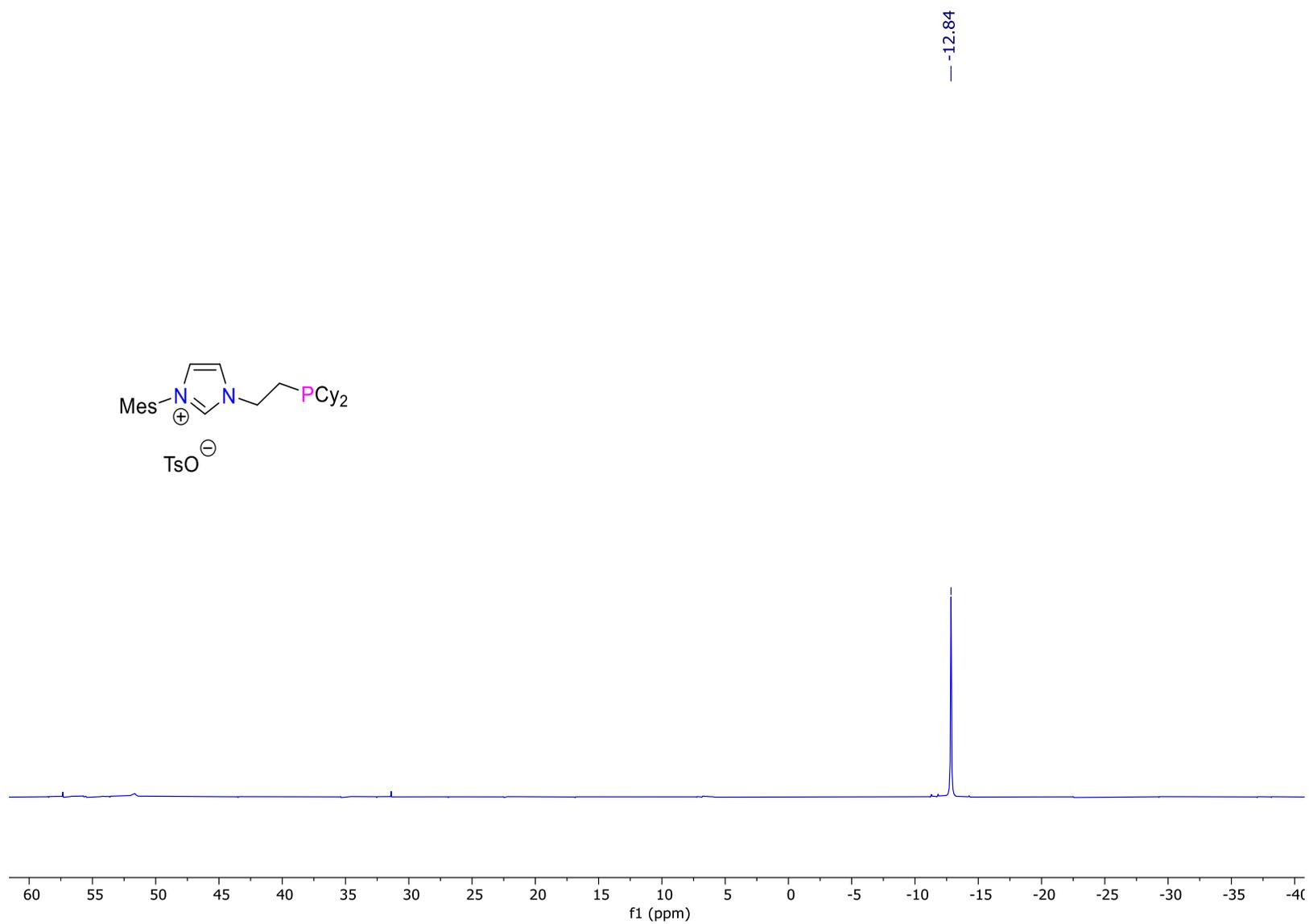


Figure S42: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **L5.HOTs** in CDCl_3 recorded at 162 MHz.

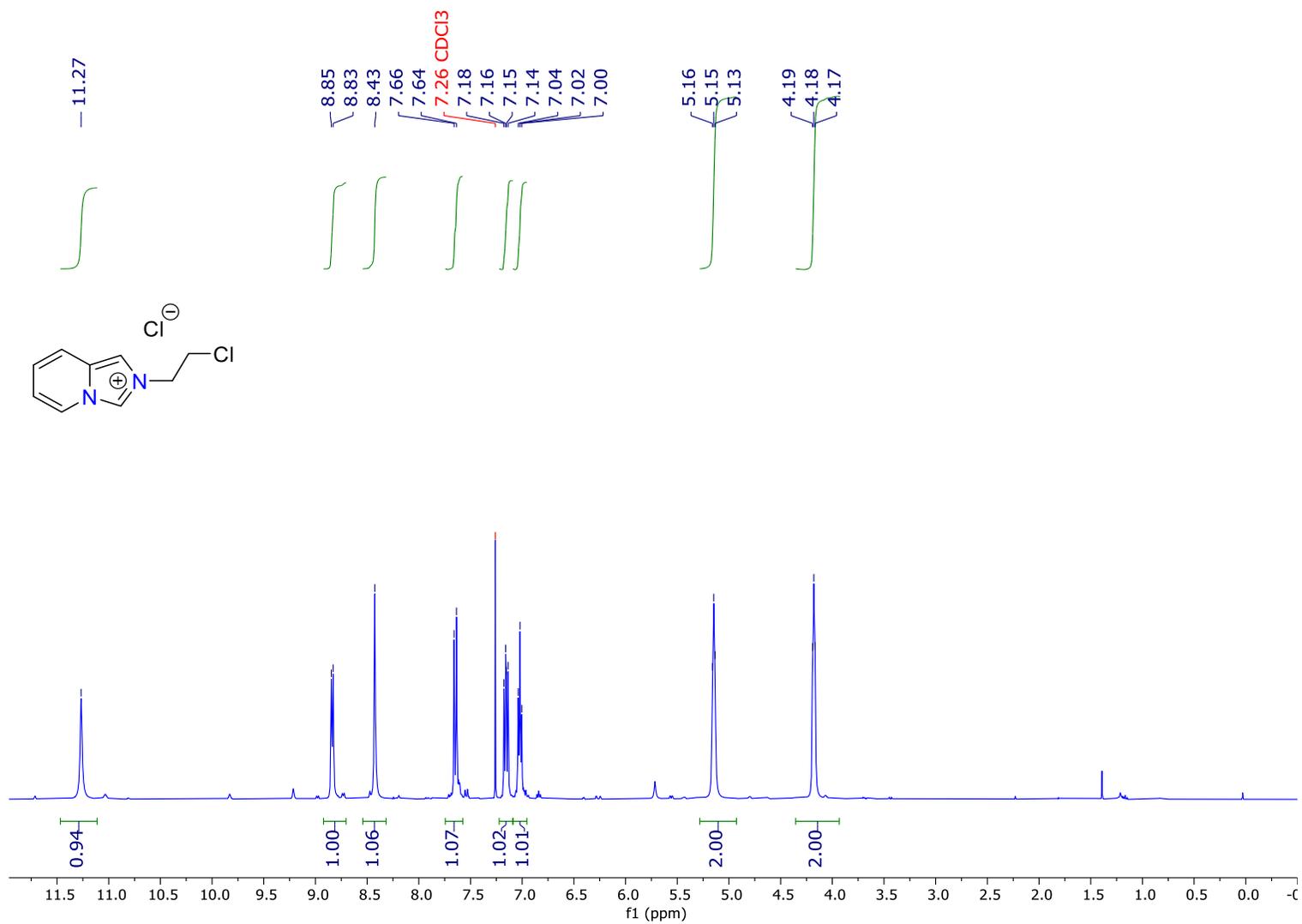


Figure S43: ¹H NMR spectrum of **L6(Cl).HCl** in CDCl₃ recorded at 400 MHz.

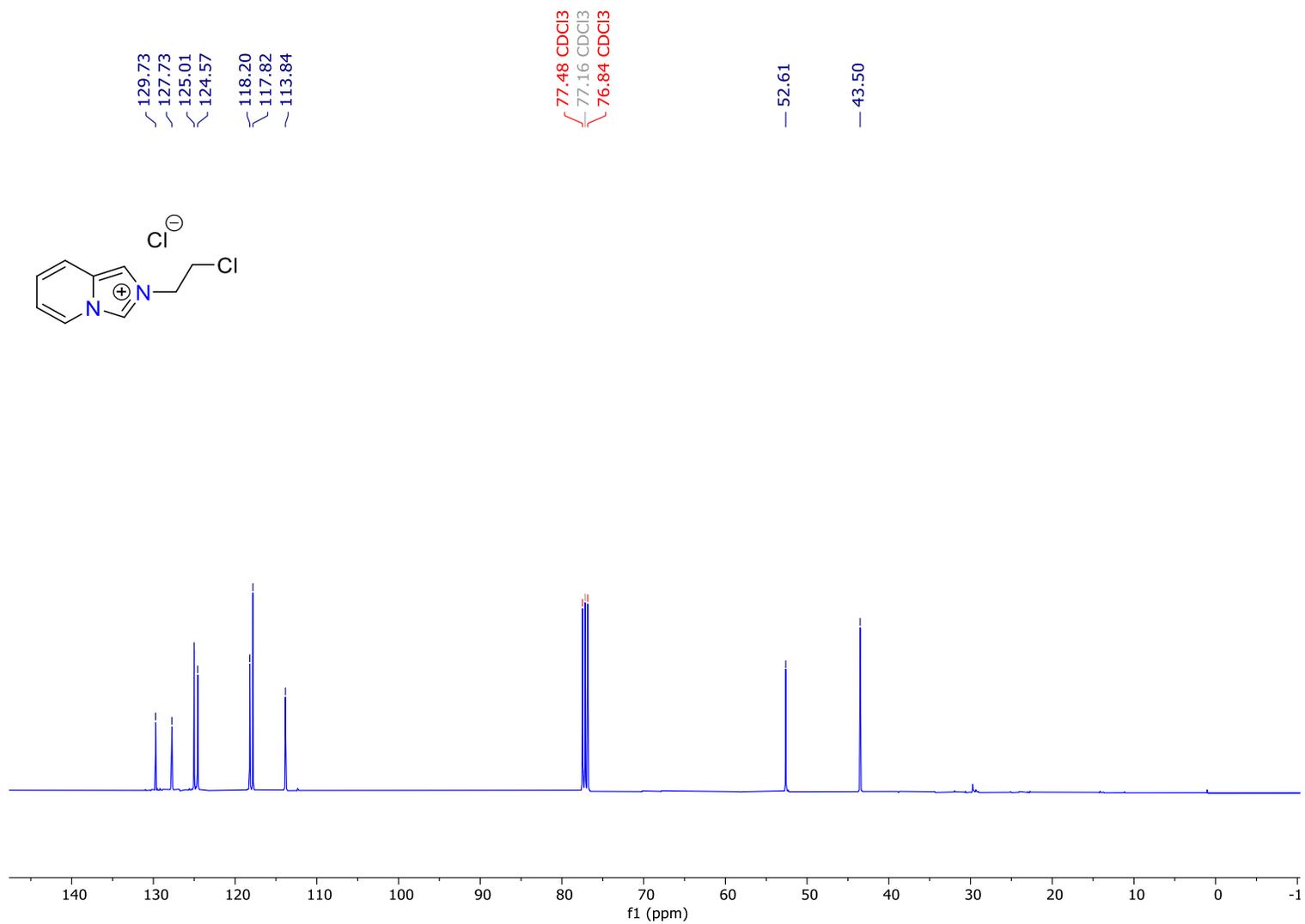


Figure S44: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of L6(Cl).HCl in CDCl_3 recorded at 101 MHz.

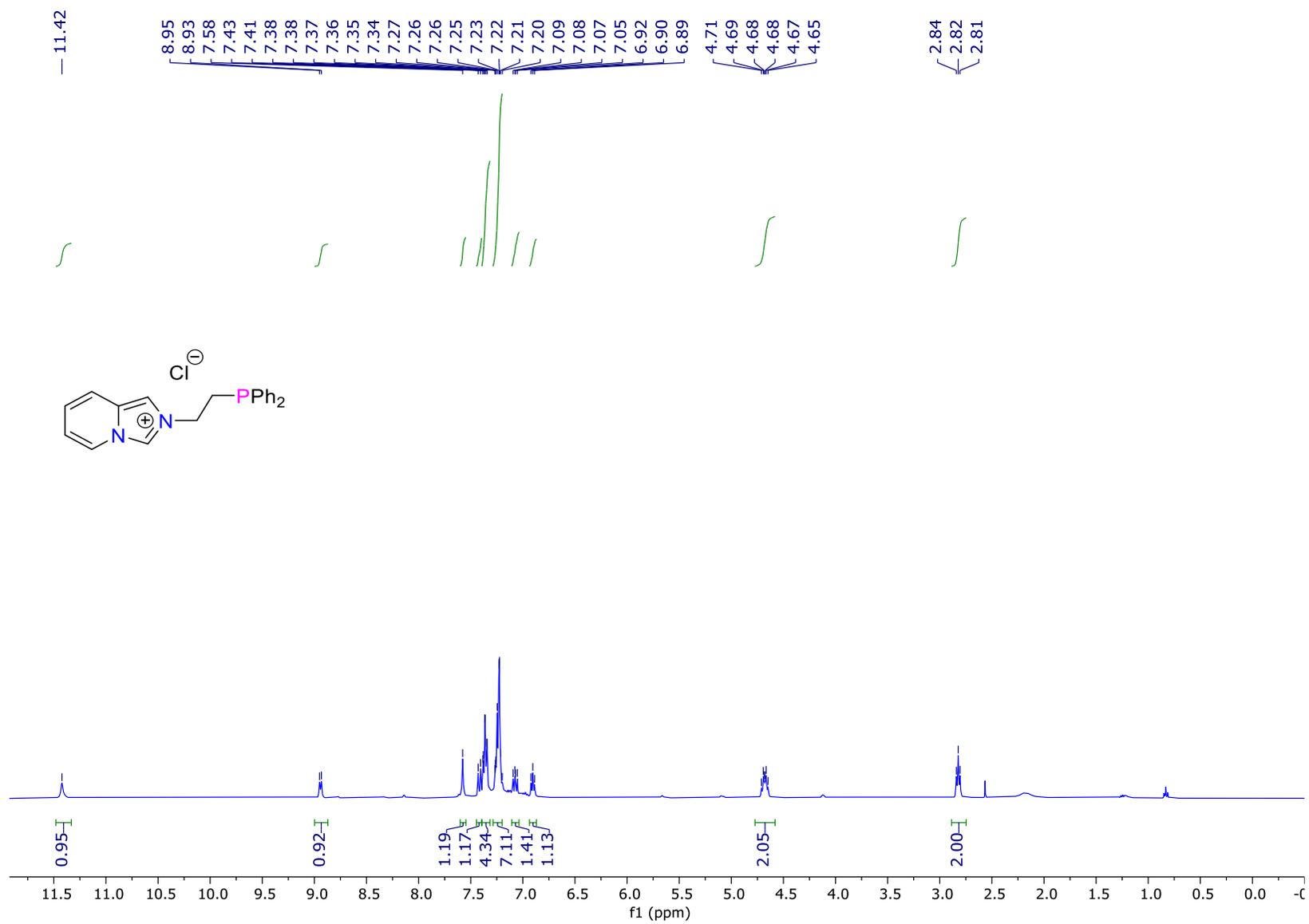


Figure S45: ¹H NMR spectrum of L6.HCl in CDCl₃ recorded at 400 MHz.

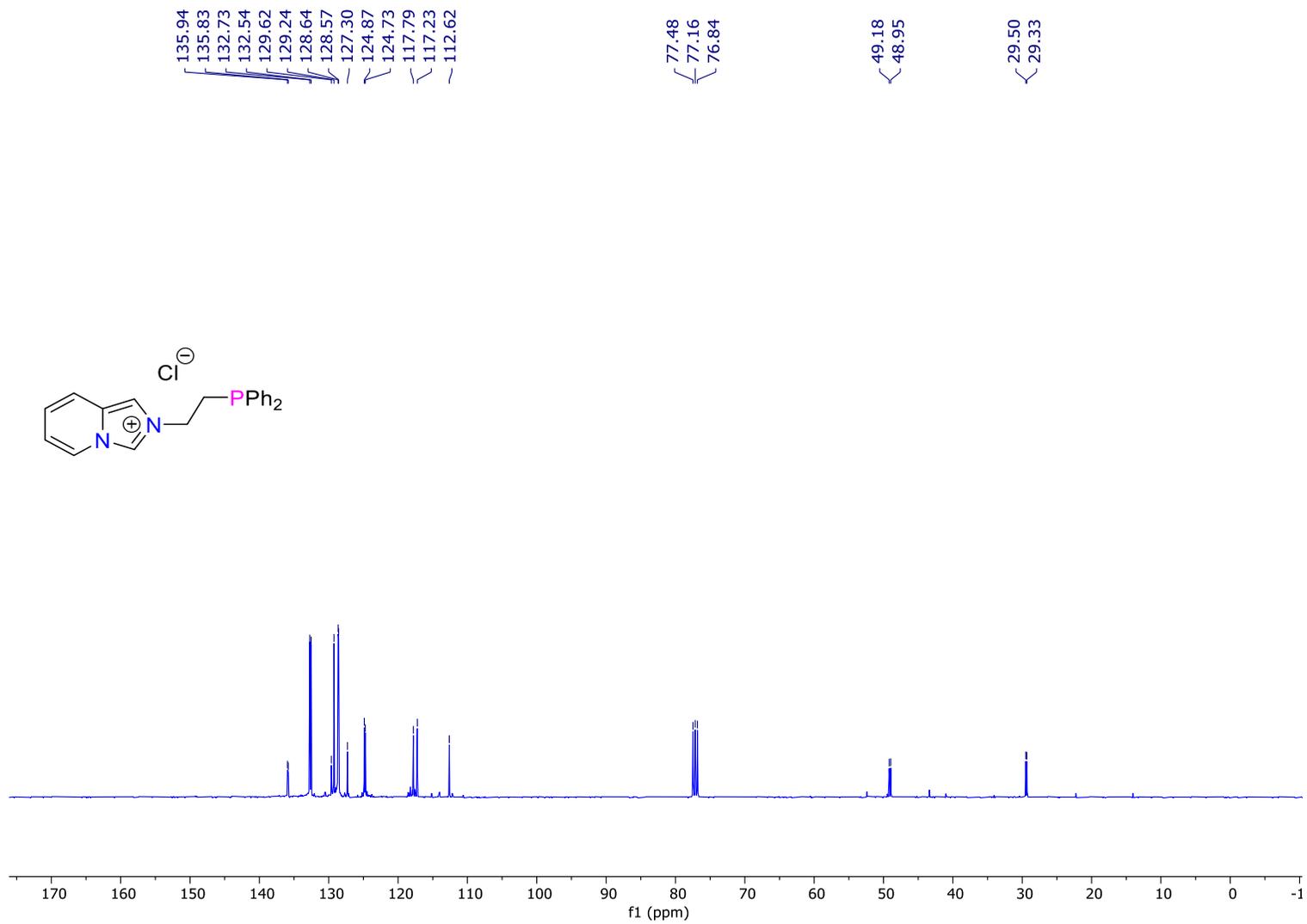


Figure S46: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **L6.HCl** in CDCl_3 recorded at 101 MHz.

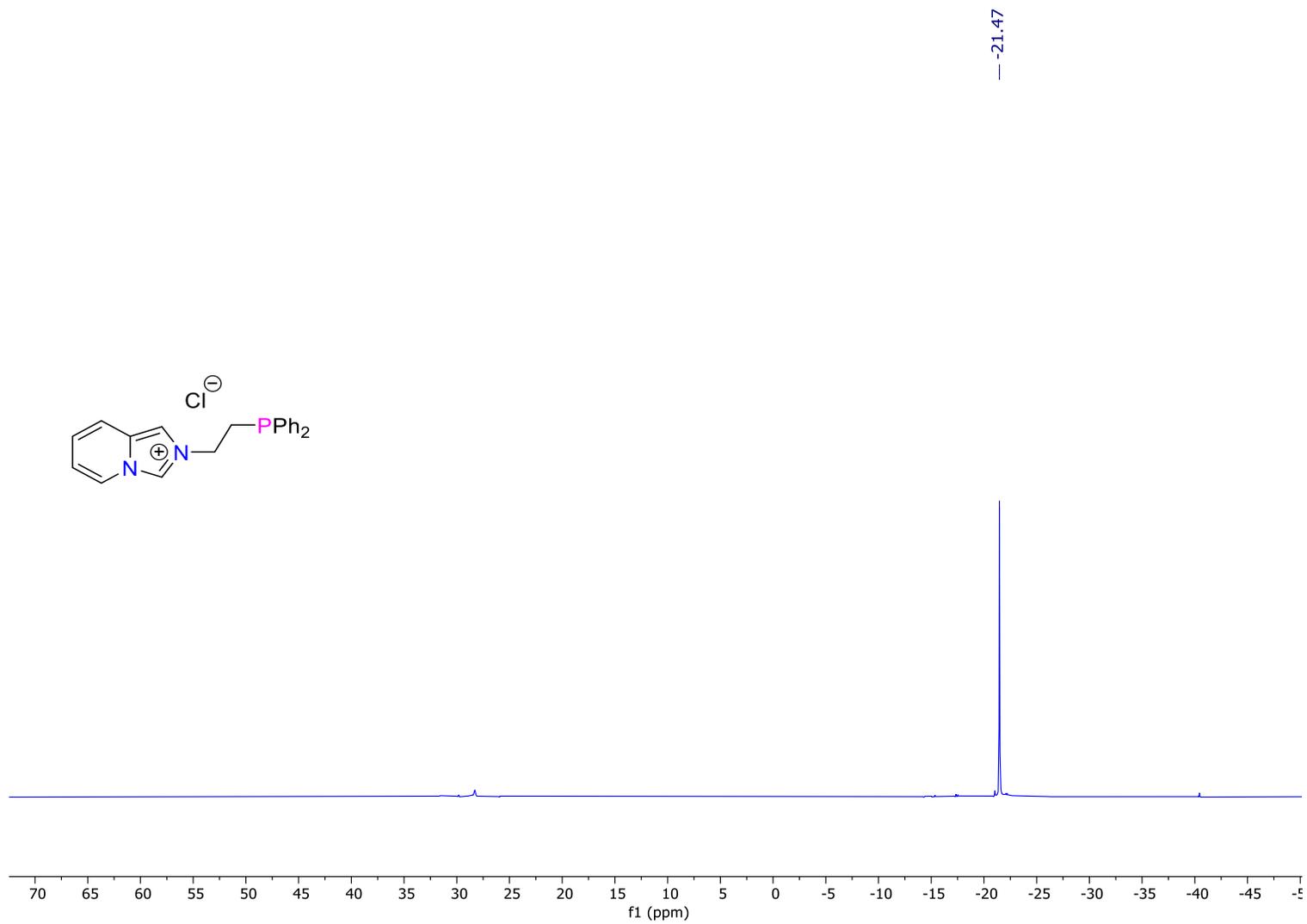


Figure S47: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **L6.HCl** in CDCl_3 recorded at 162 MHz.

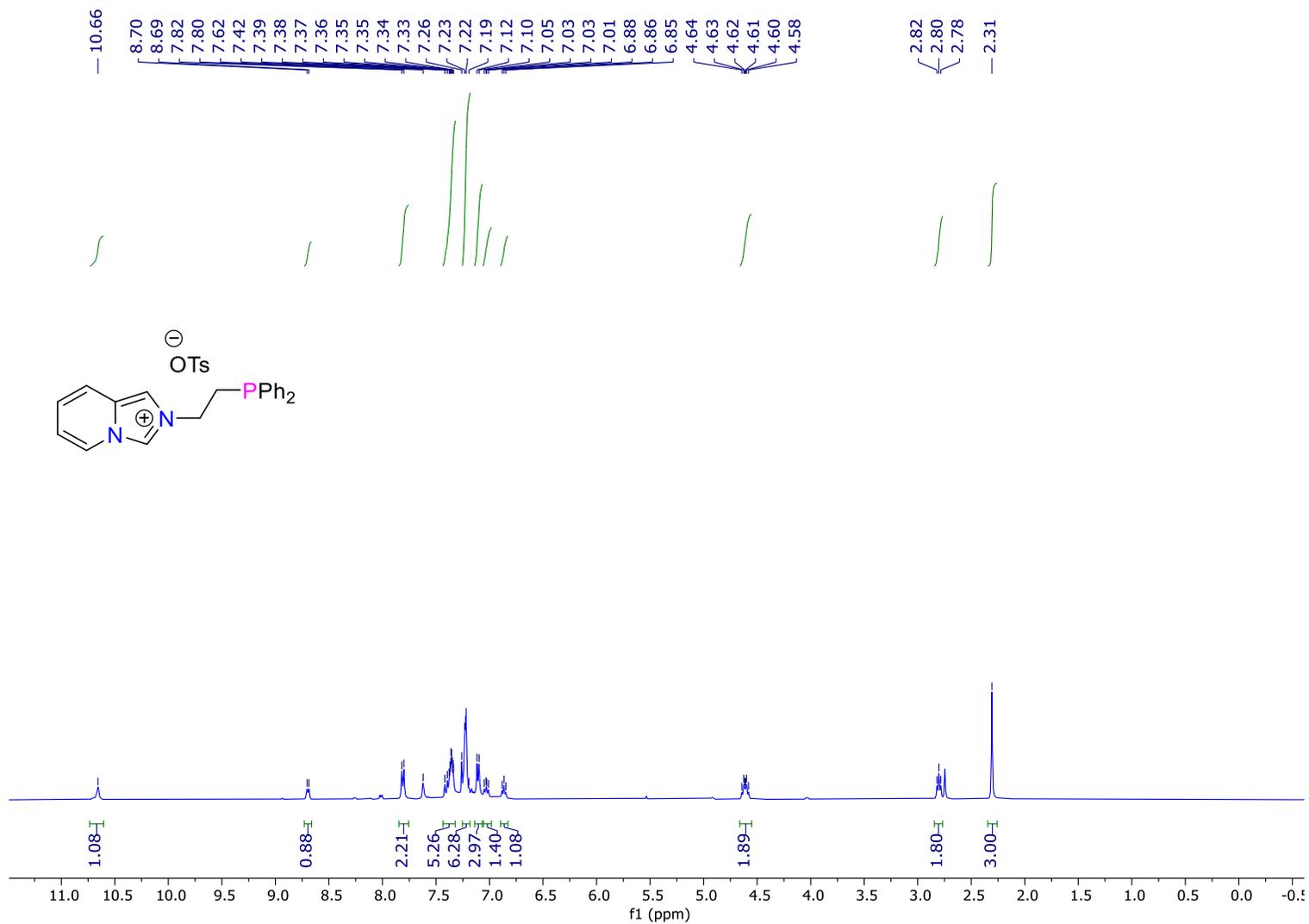


Figure S48: ¹H NMR spectrum of L6.HOTs in CDCl₃ recorded at 400 MHz.

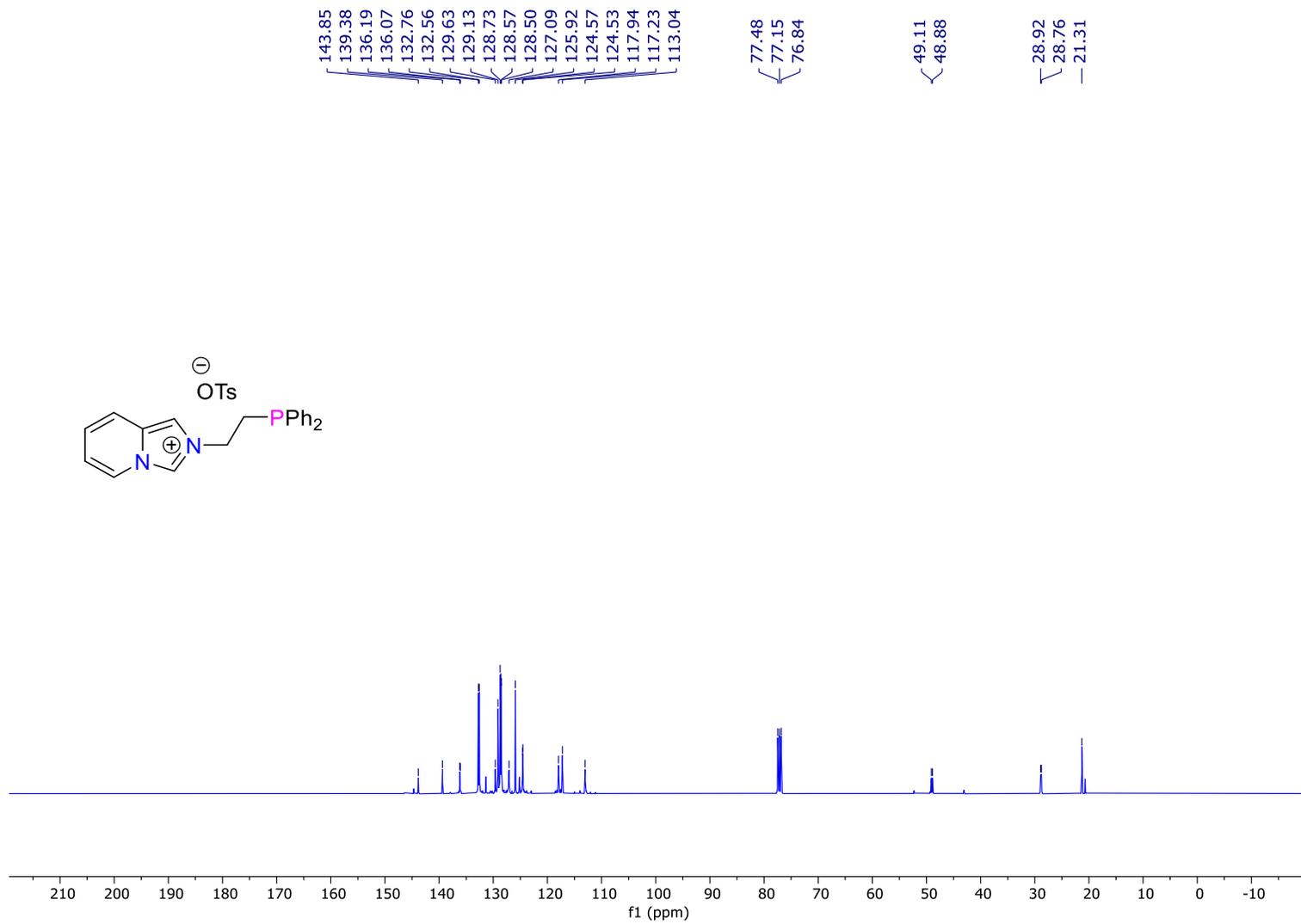


Figure S49: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **L6.HOTs** in CDCl_3 recorded at 101 MHz.

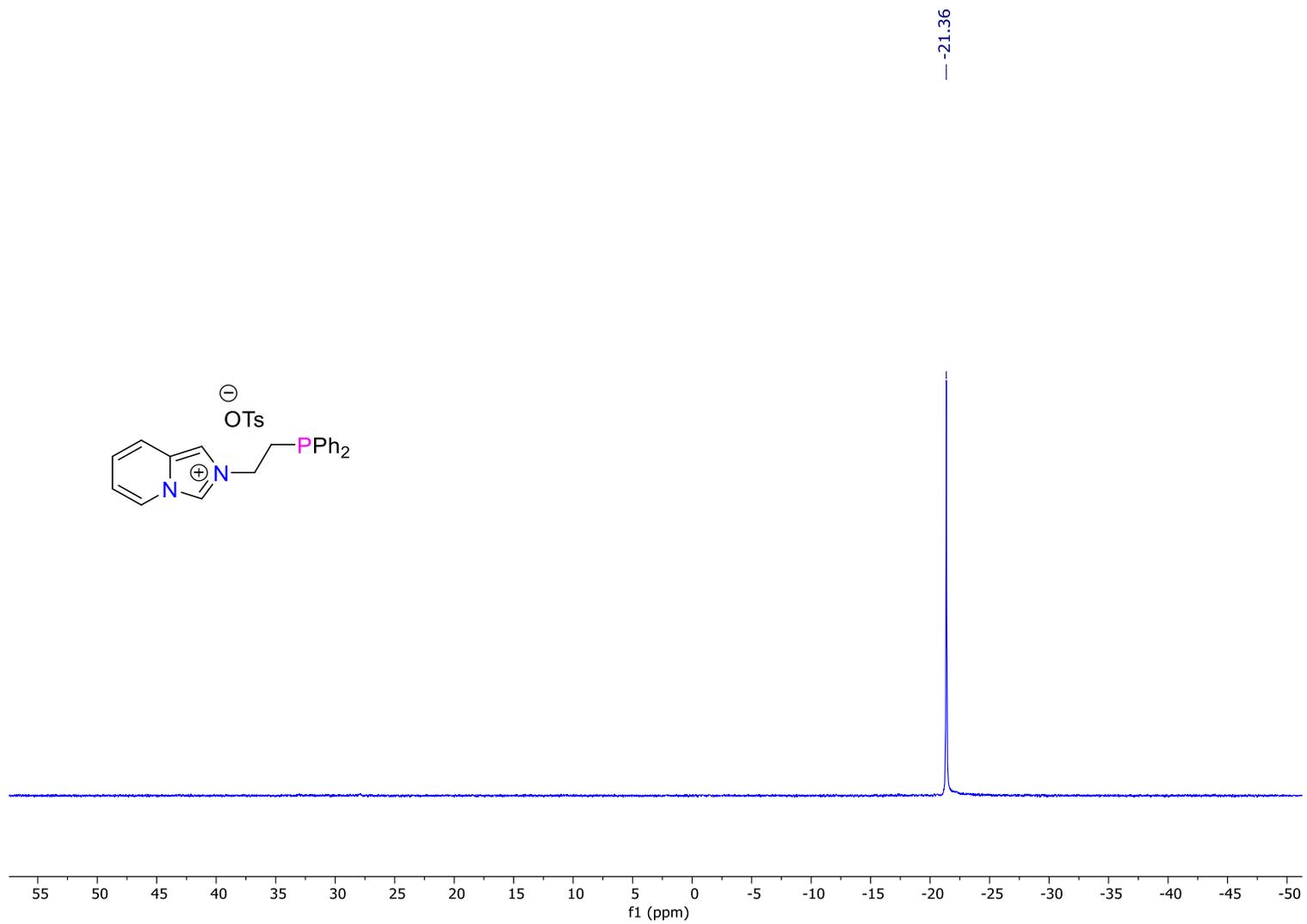


Figure S50: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **L6.HOTs** in CDCl_3 recorded at 162 MHz.

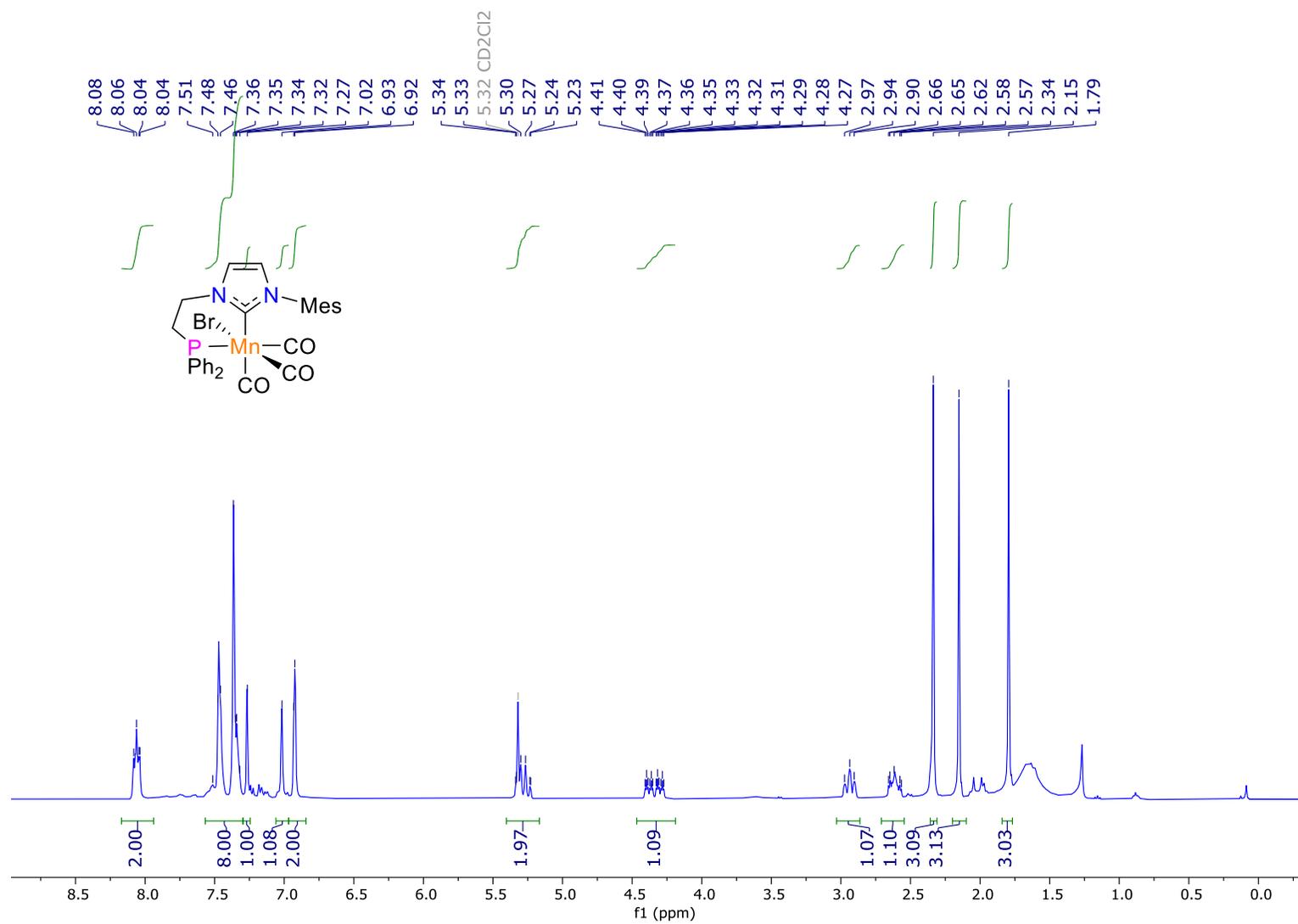


Figure S51: ¹H NMR spectrum of complex **2** in CDCl₃ recorded at 400 MHz.

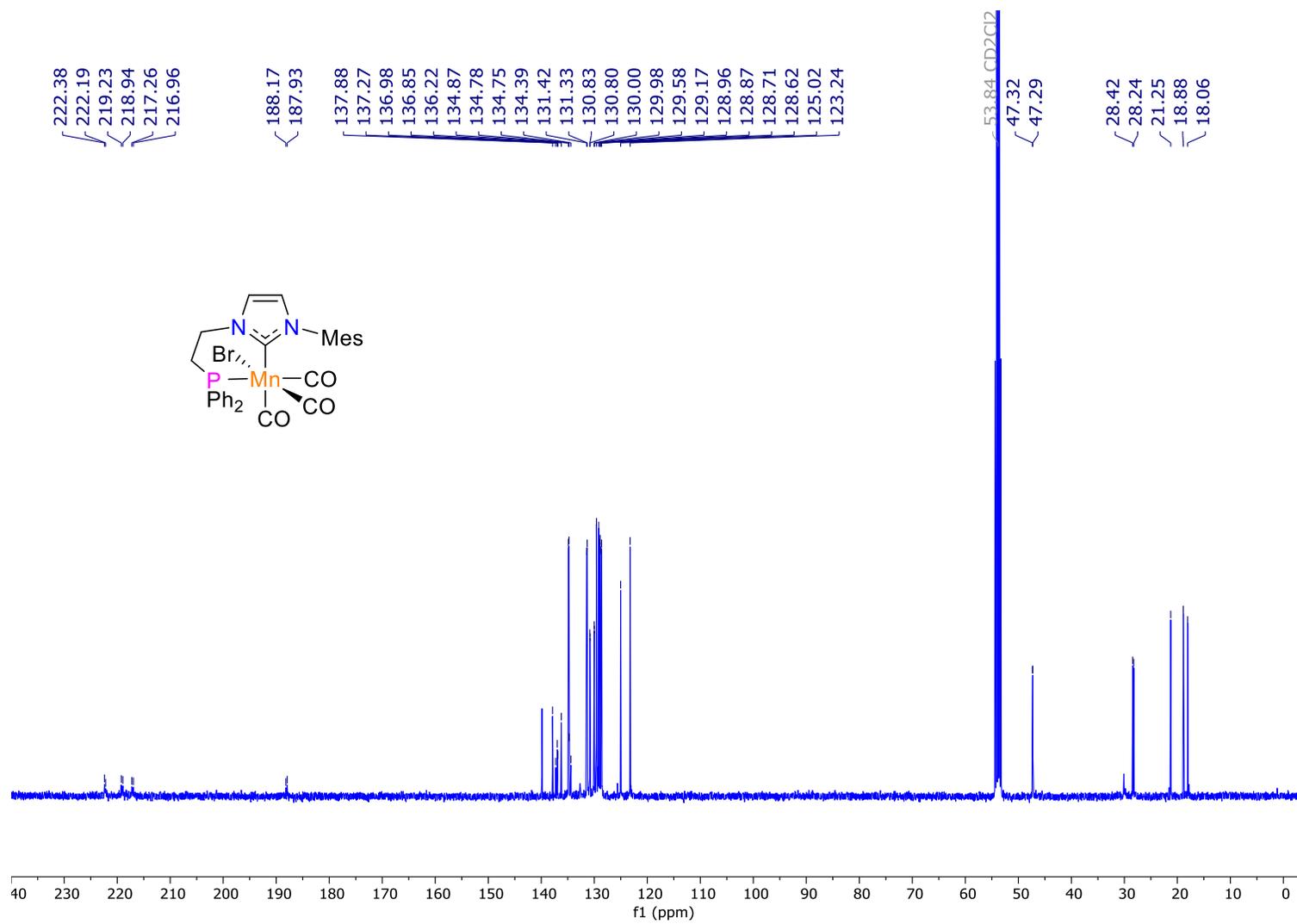


Figure S52: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **2** in CDCl_3 recorded at 101 MHz.

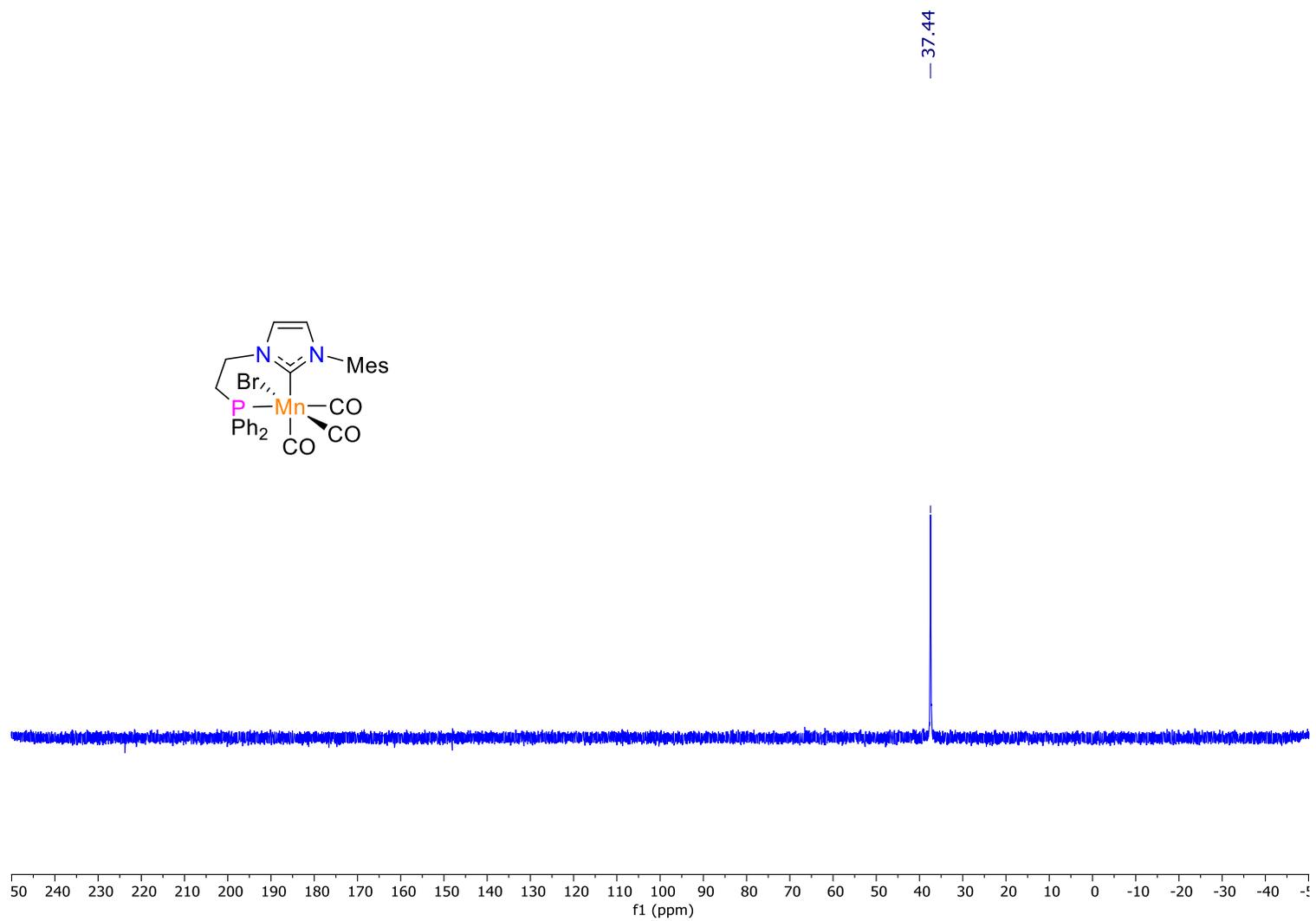


Figure S53: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **2** in CDCl_3 recorded at 162 MHz.

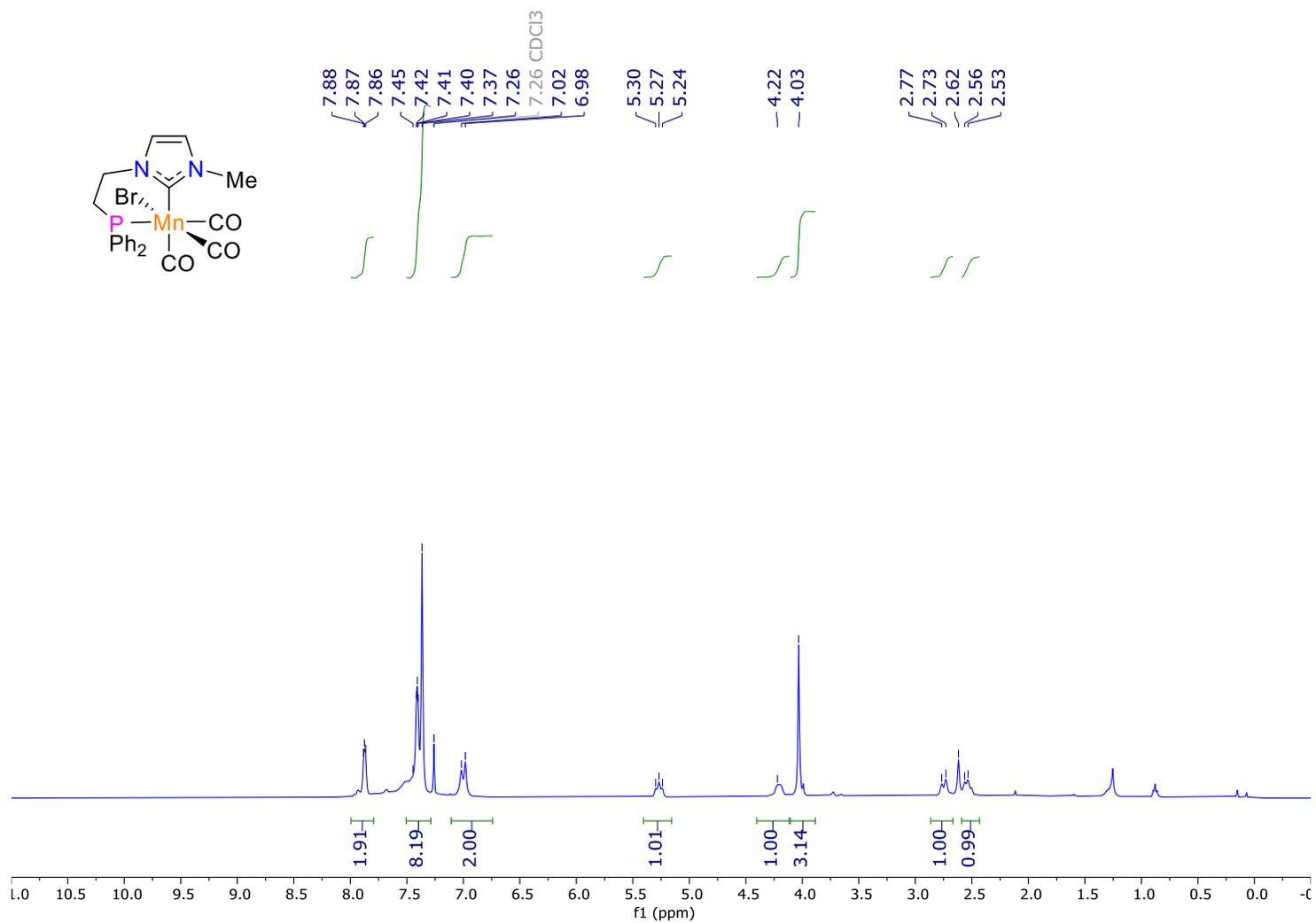


Figure S54: ¹H NMR spectrum of complex **3** in CDCl₃ recorded at 400 MHz.

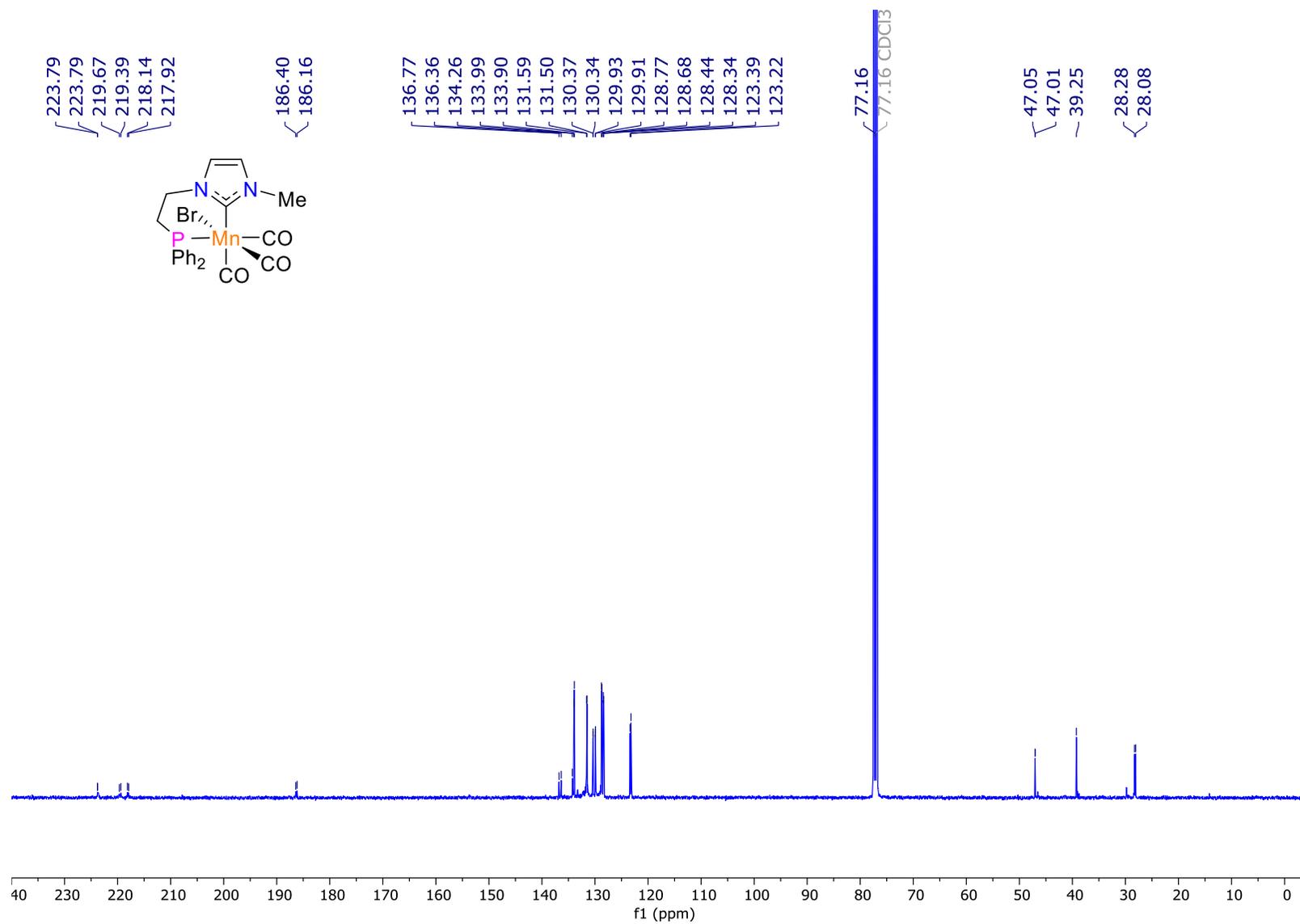


Figure S55: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 3 in CDCl_3 recorded at 101 MHz.

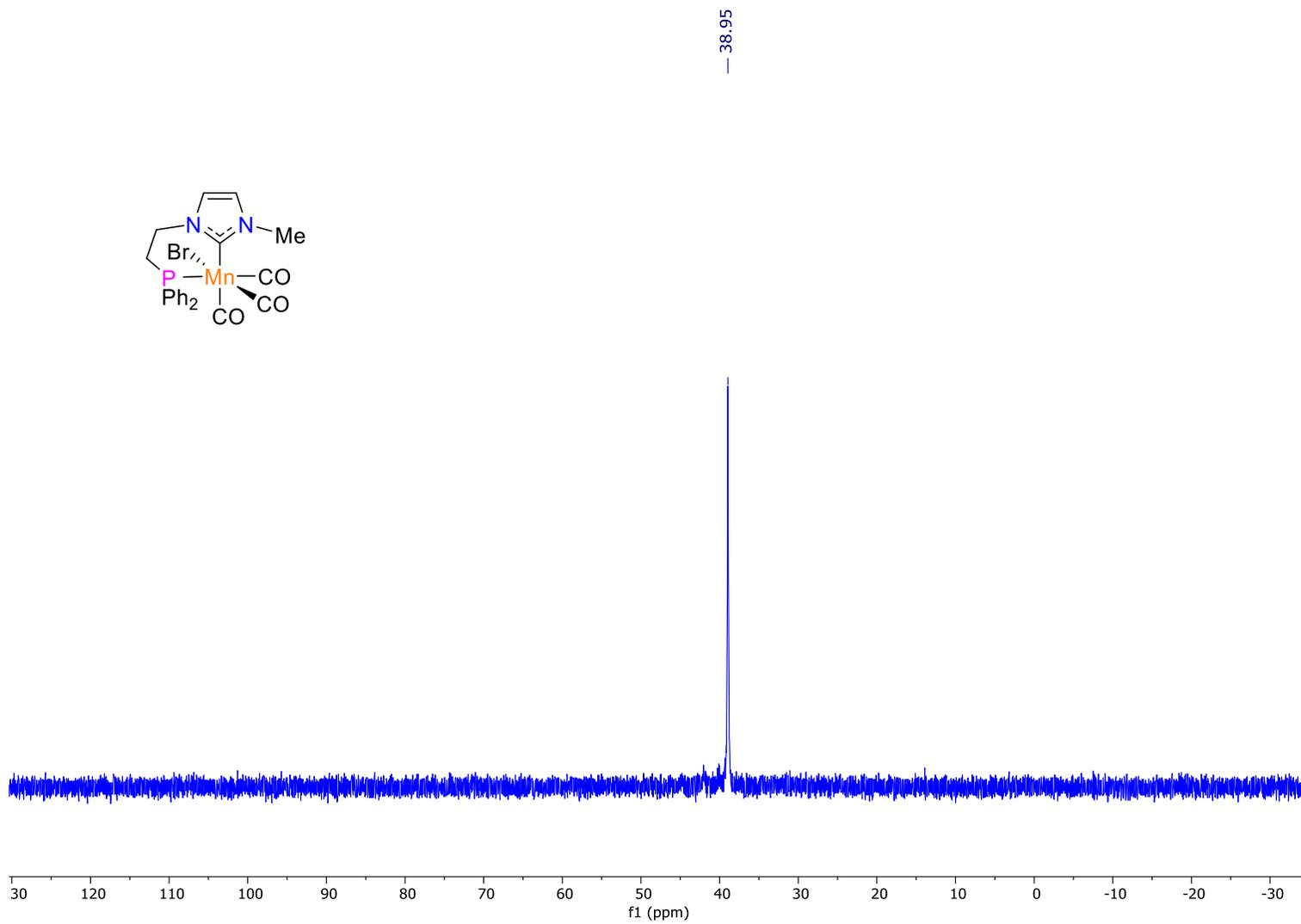


Figure S56: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **3** in CDCl_3 recorded at 162 MHz.

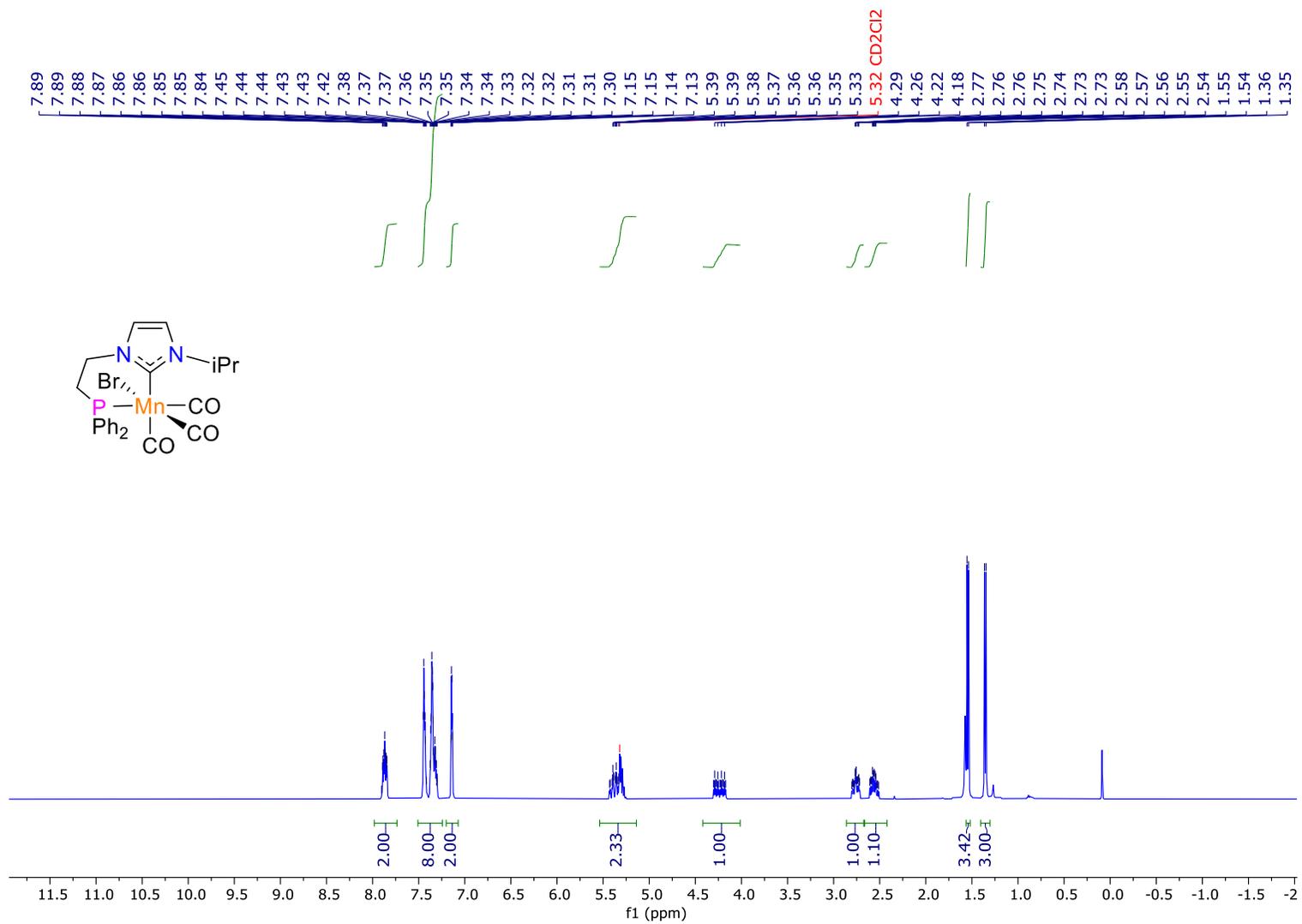


Figure S57: ¹H NMR spectrum of complex 4 in CDCl₃ recorded at 400 MHz.

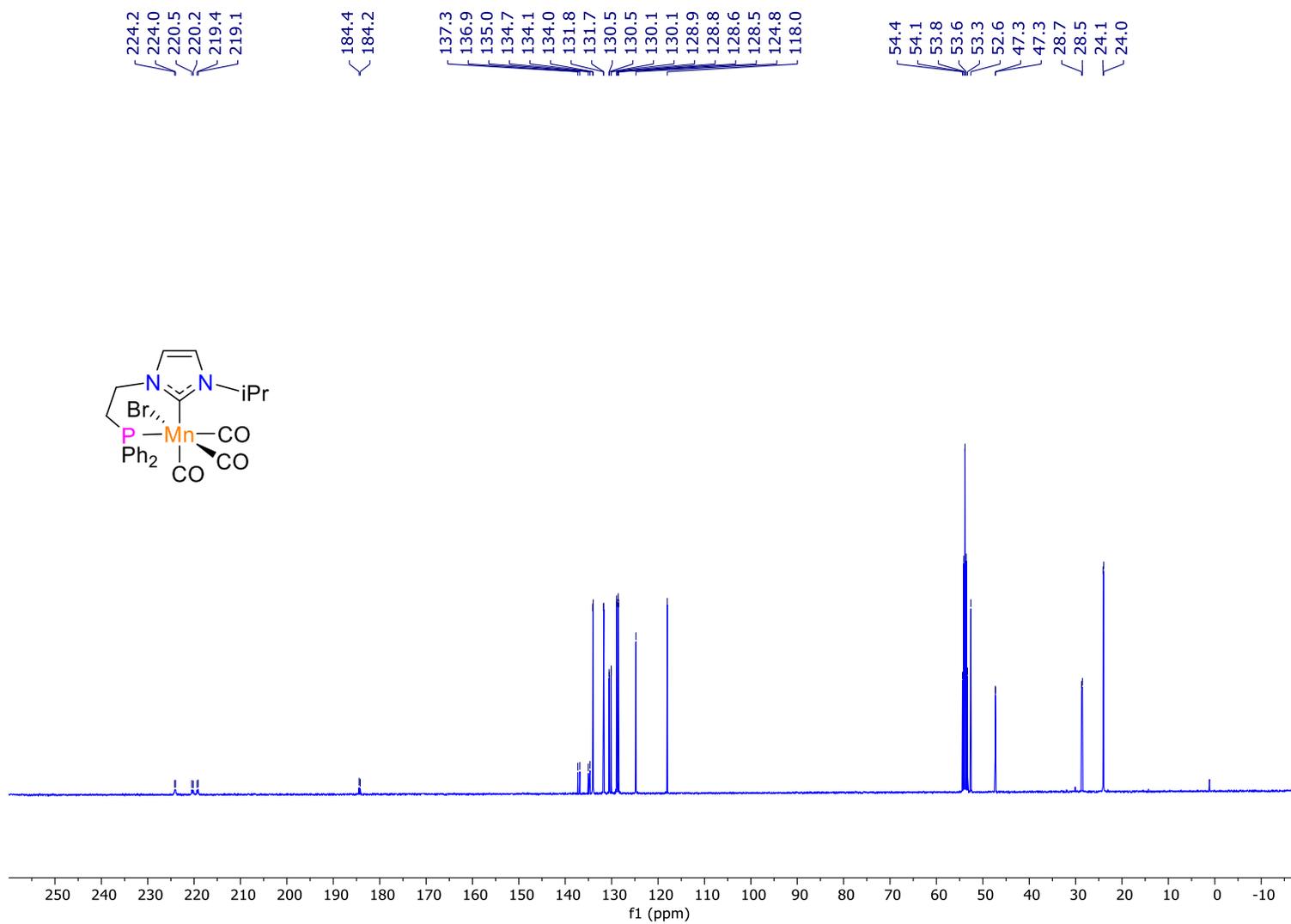


Figure S58: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 4 in CDCl_3 recorded at 101 MHz.

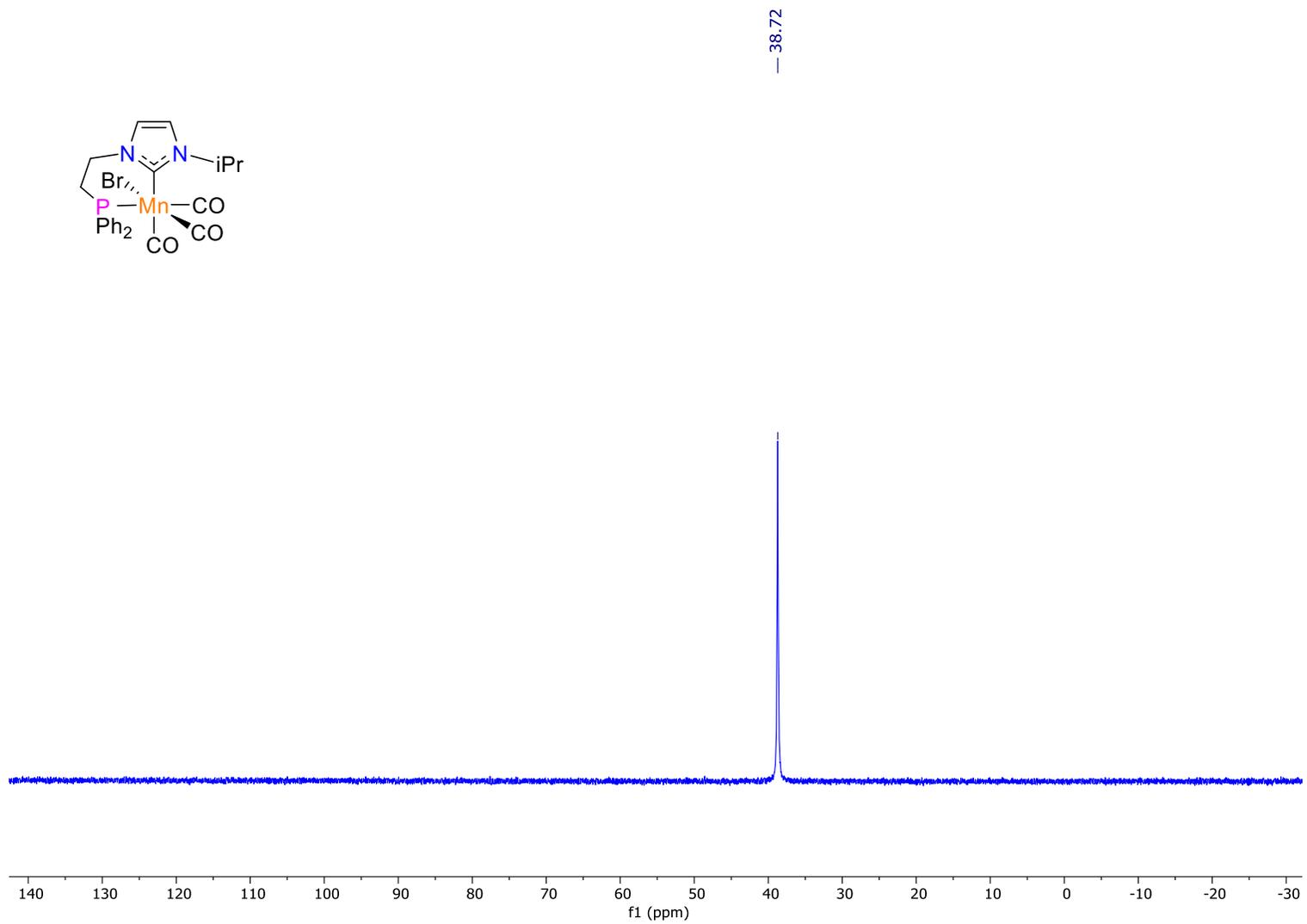


Figure S59: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **4** in CDCl_3 recorded at 162 MHz.

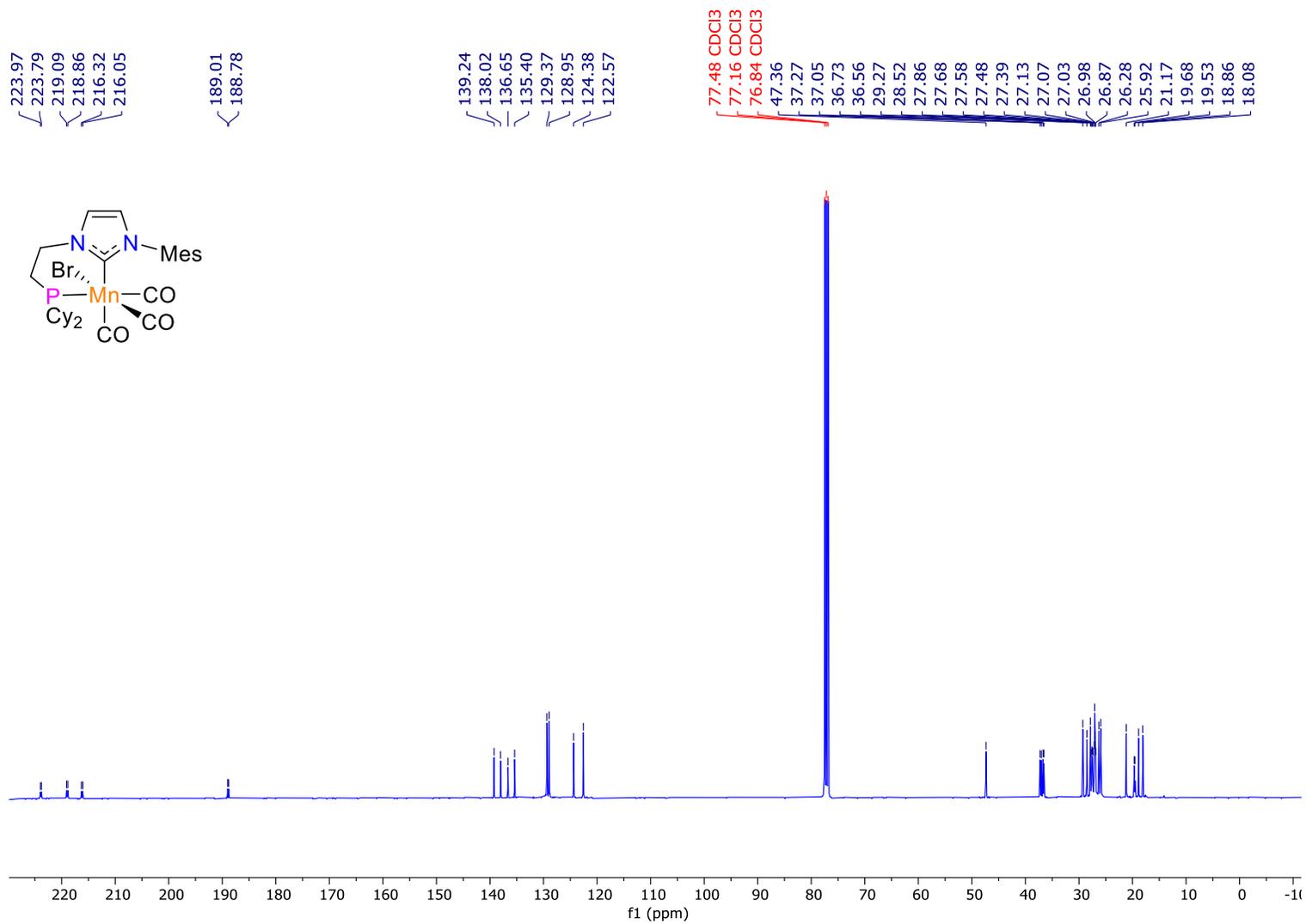


Figure S61: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 5 in CDCl_3 recorded at 101 MHz.

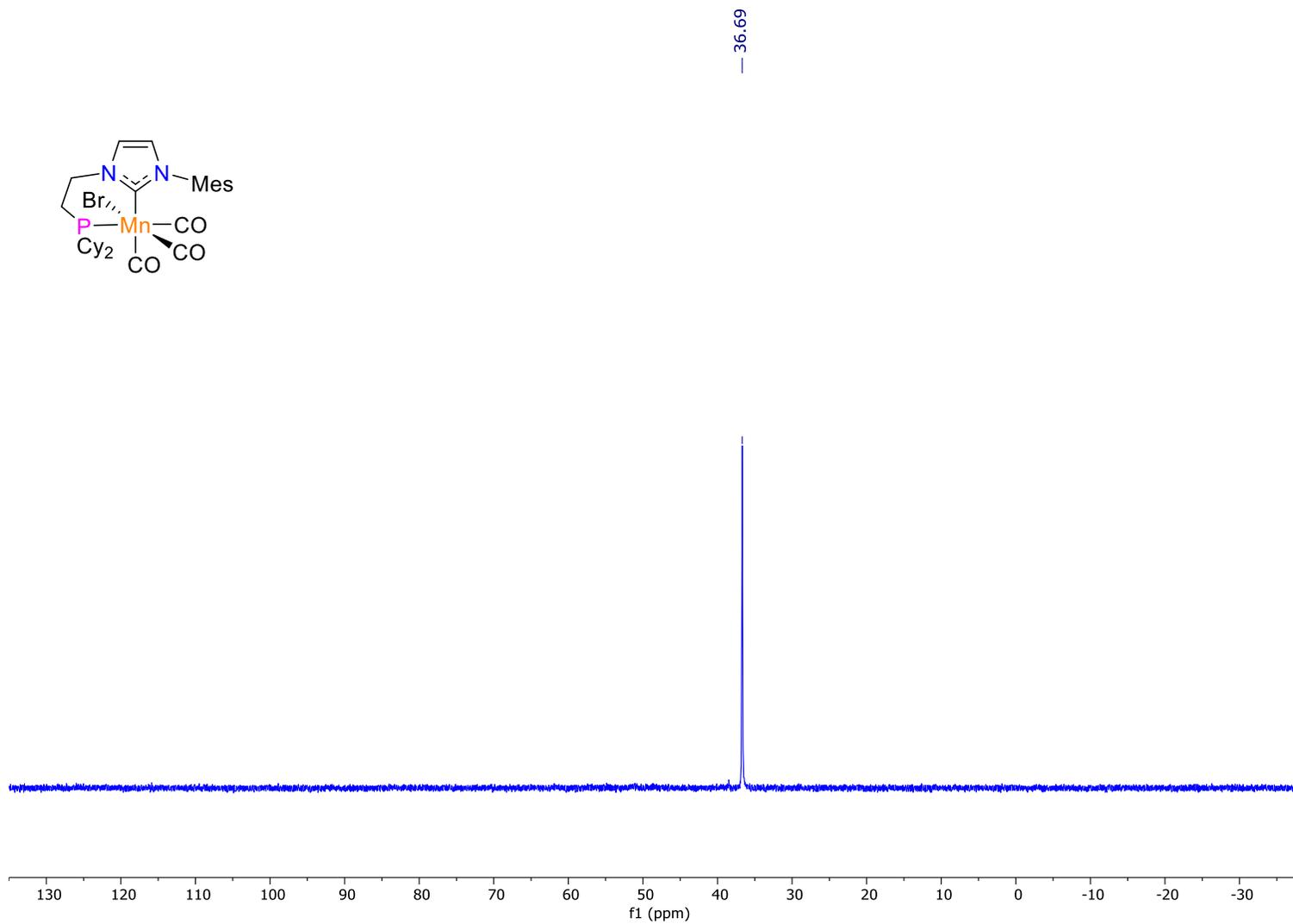
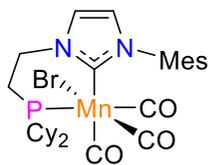


Figure S62: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex 5 in CDCl_3 recorded at 162 MHz.

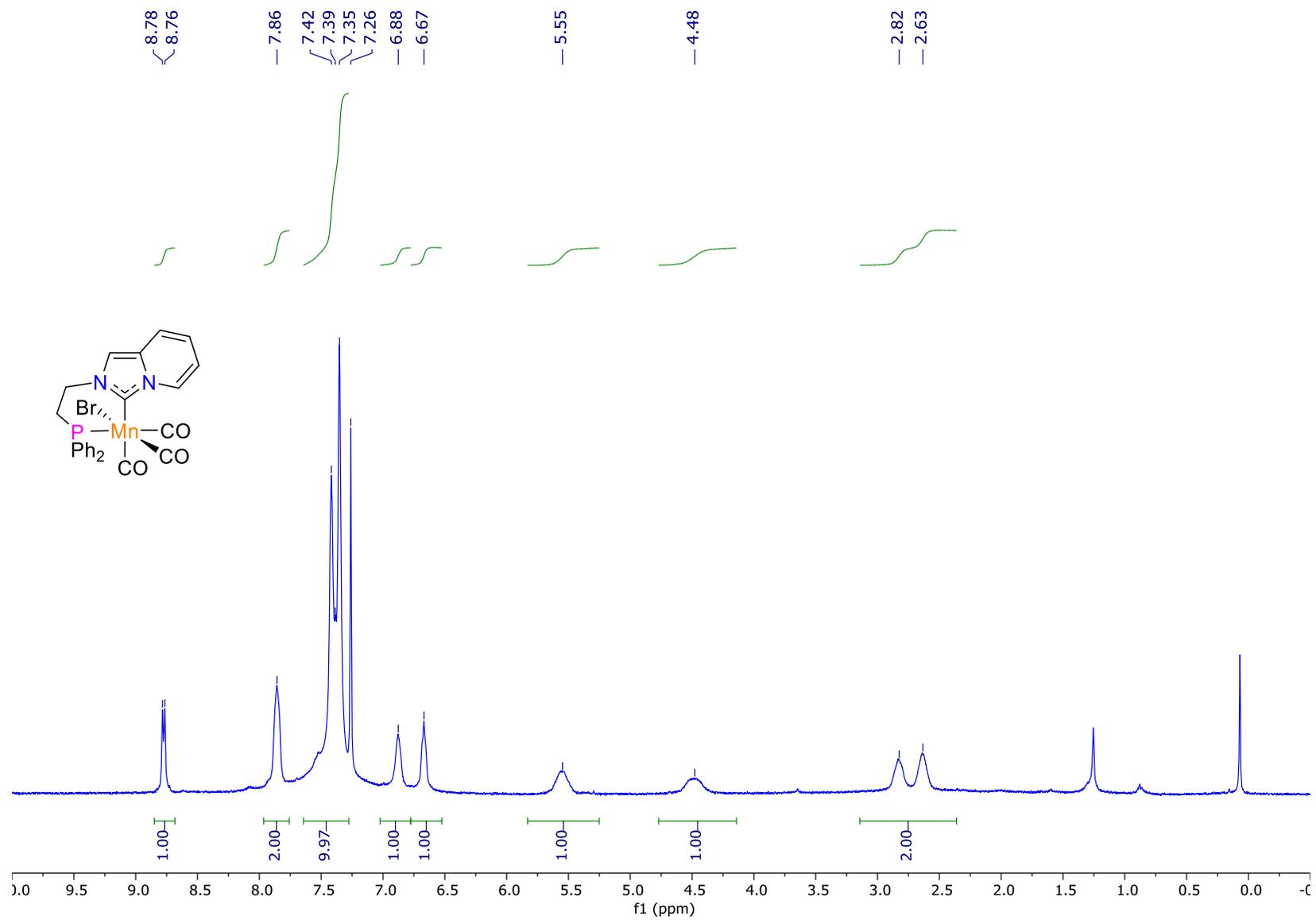


Figure S63: ¹H NMR spectrum of complex **6** in CDCl₃ recorded at 400 MHz.

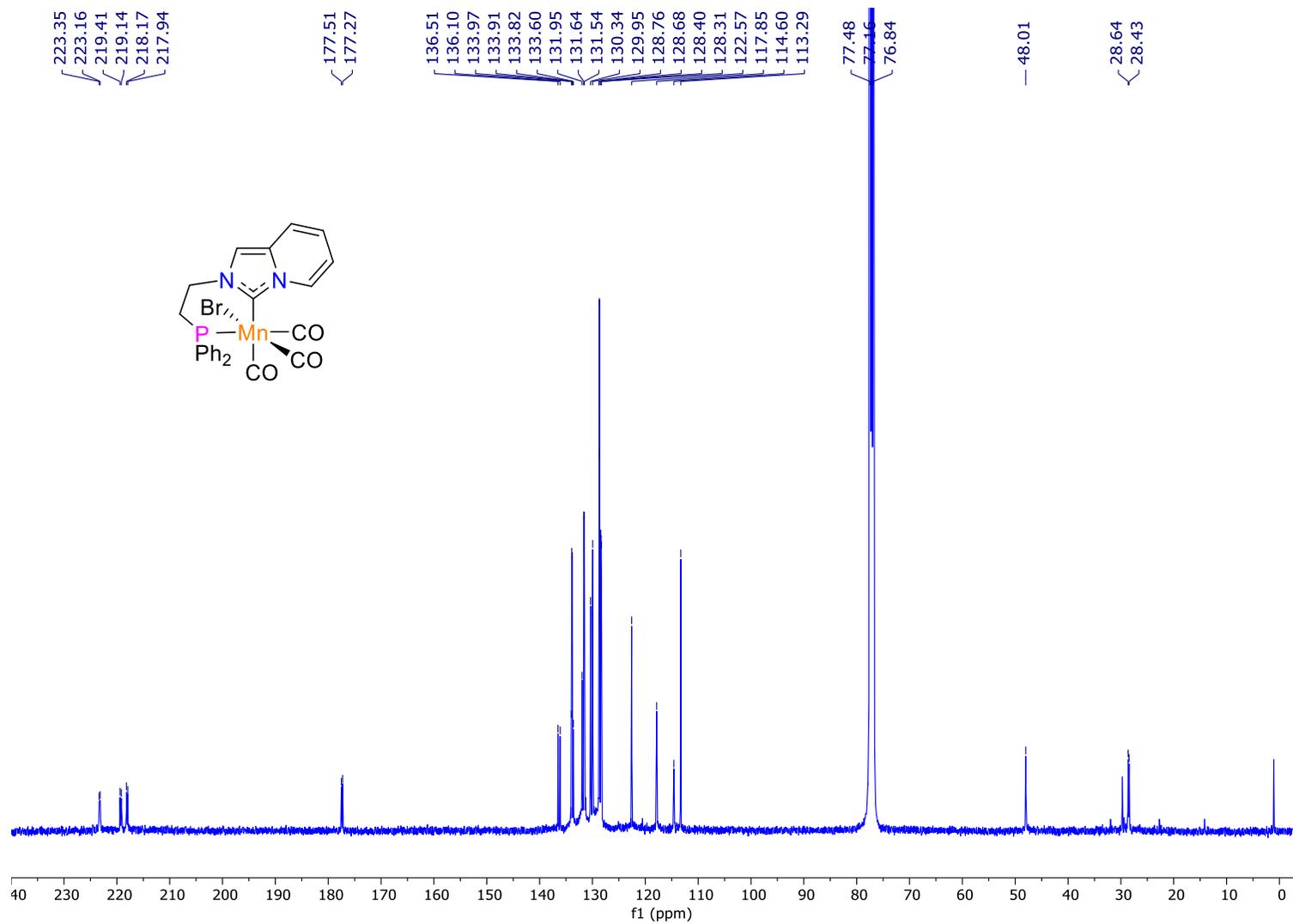


Figure S64: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 6 in CDCl_3 recorded at 101 MHz.

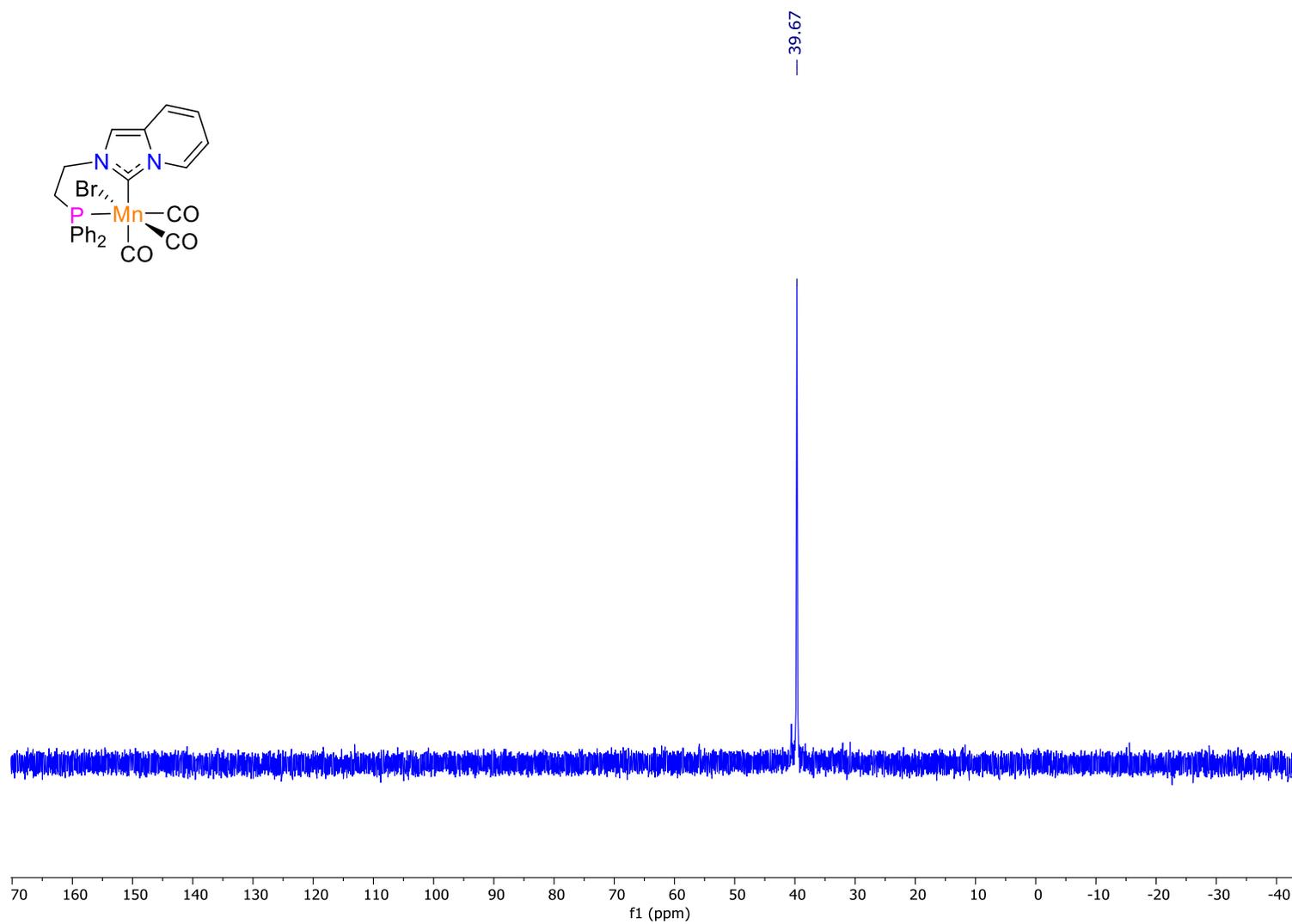


Figure S65: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex 6 in CDCl_3 recorded at 162 MHz.

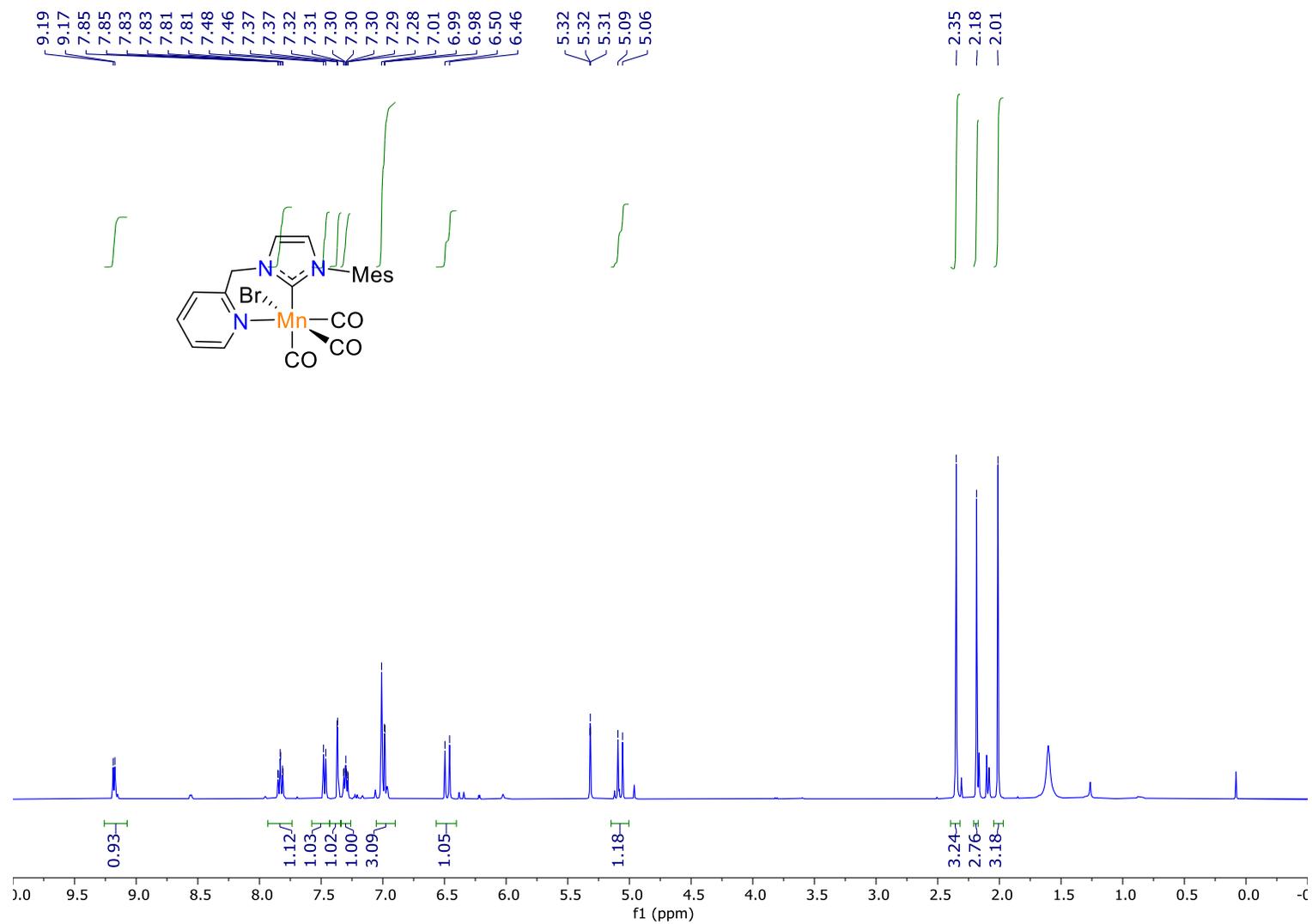


Figure S66: ¹H NMR spectrum of complex **8** in CDCl₃ recorded at 400 MHz.

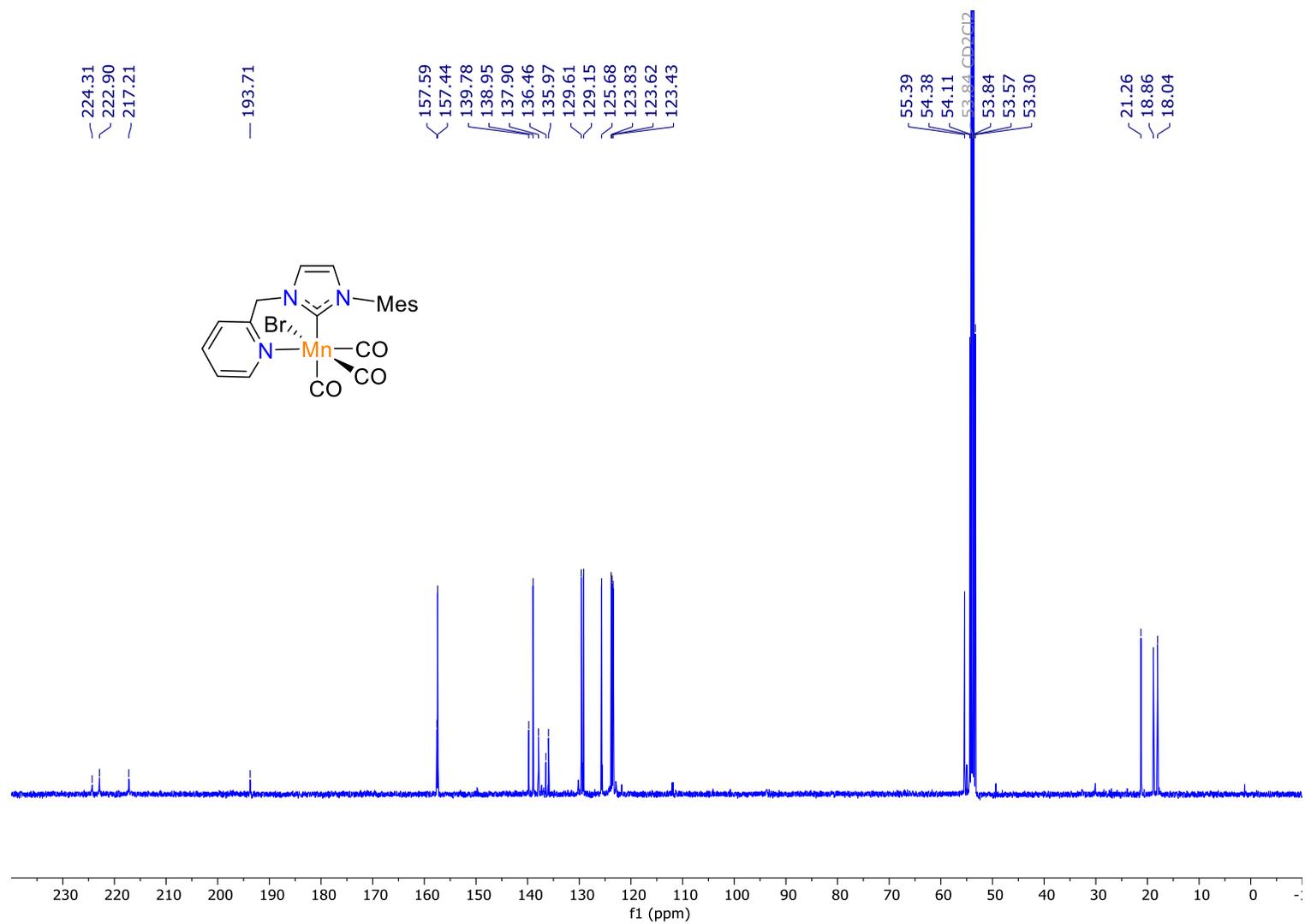


Figure S67: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 8 in CDCl_3 recorded at 101 MHz.

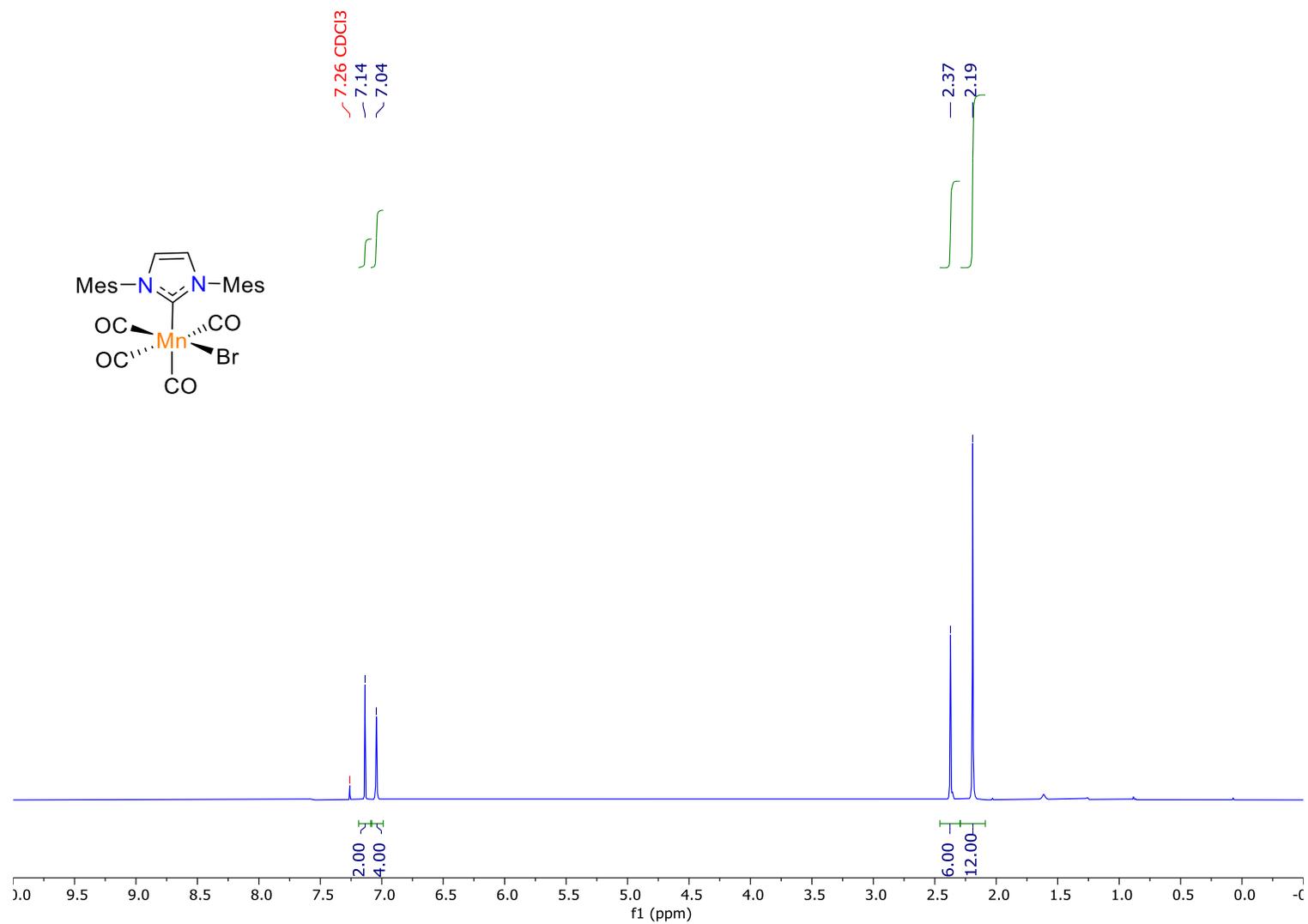


Figure S68: ^1H NMR spectrum of complex $[(\text{MnBr}(\text{CO})_4(\text{IMes}))]$ in CDCl_3 recorded at 400 MHz.

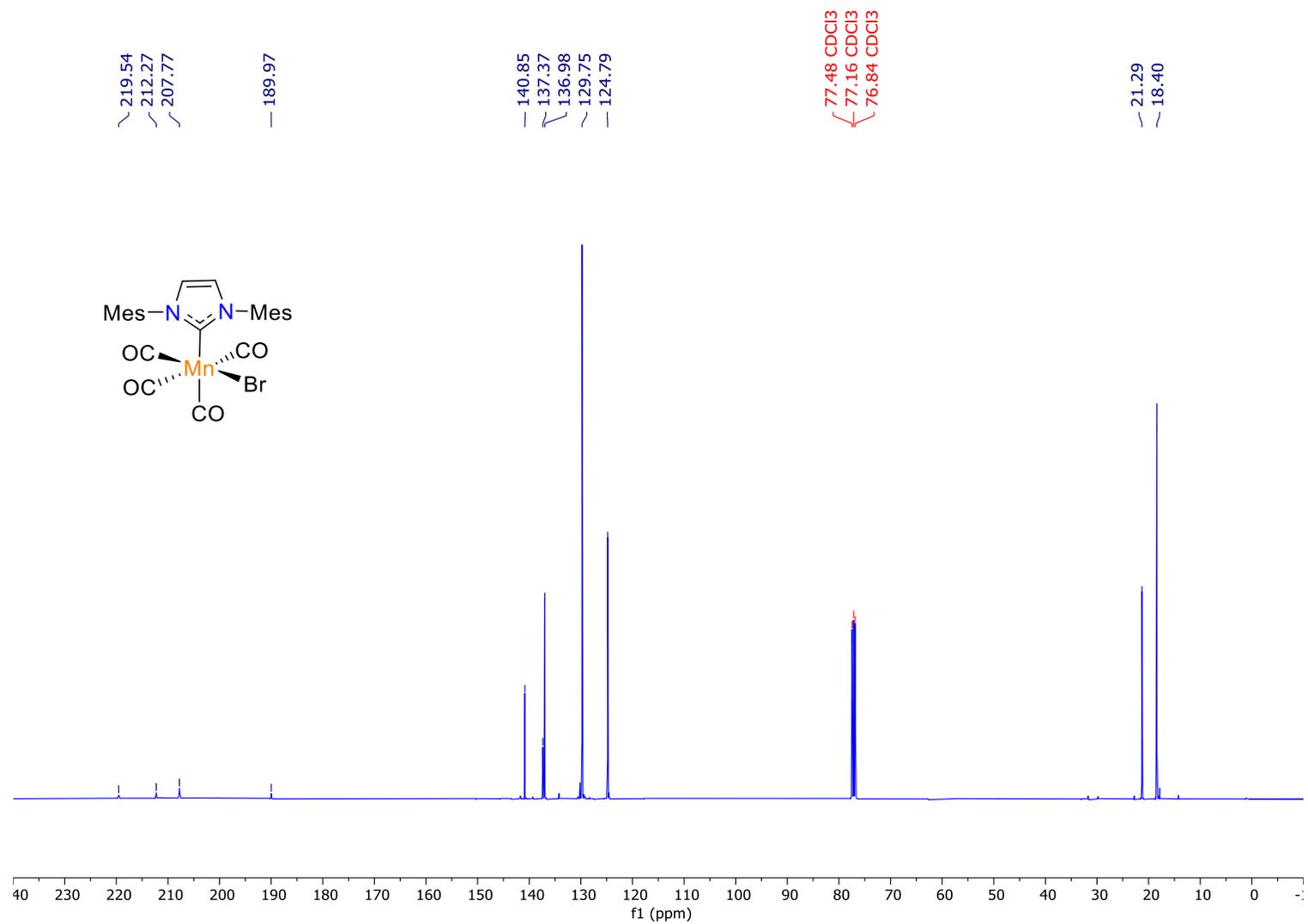


Figure S69: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex $[(\text{MnBr}(\text{CO})_4(\text{IMes}))]$ in CDCl_3 recorded at 101 MHz.

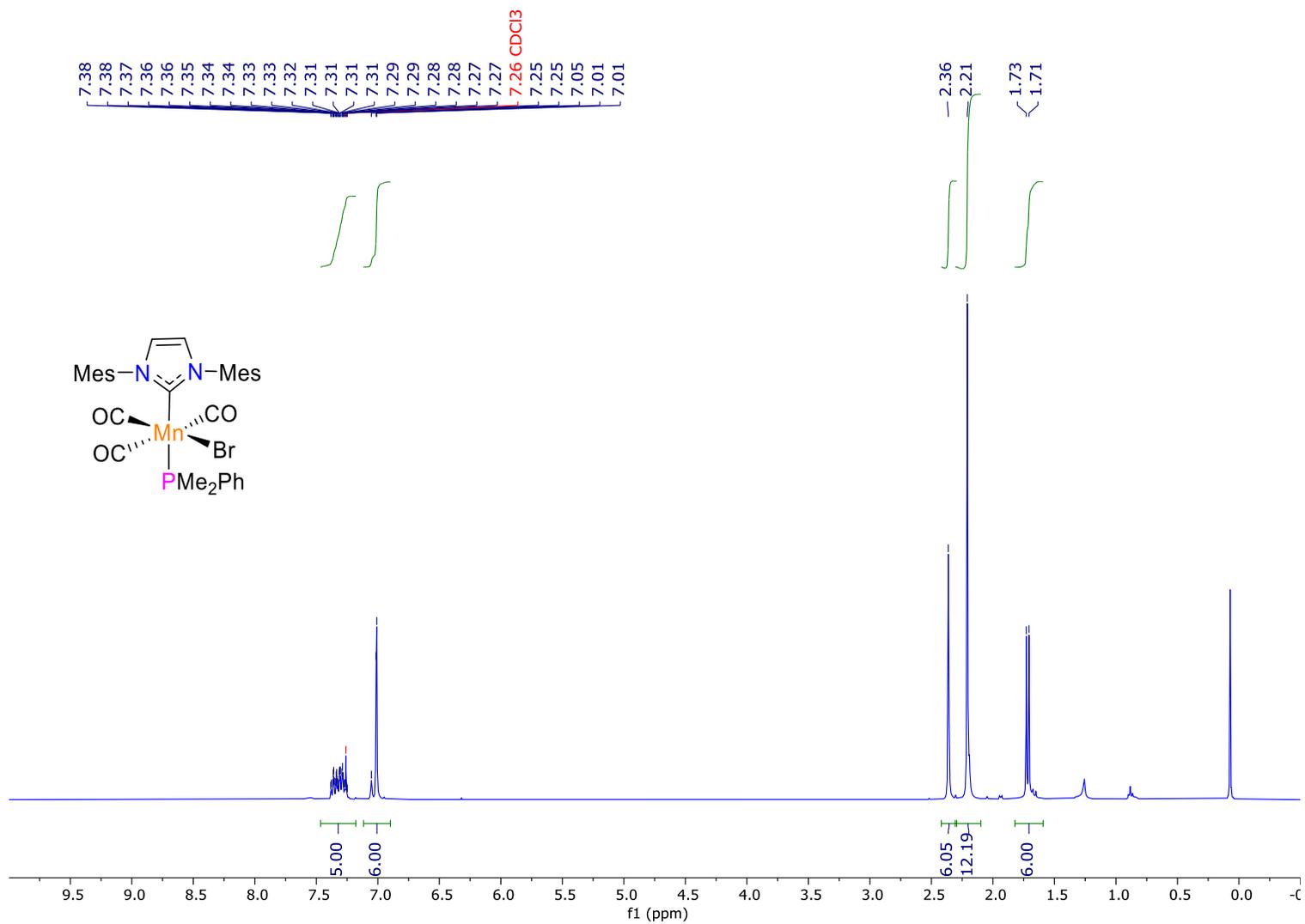


Figure S70: ¹H NMR spectrum of complex **11** in CDCl₃ recorded at 400 MHz.

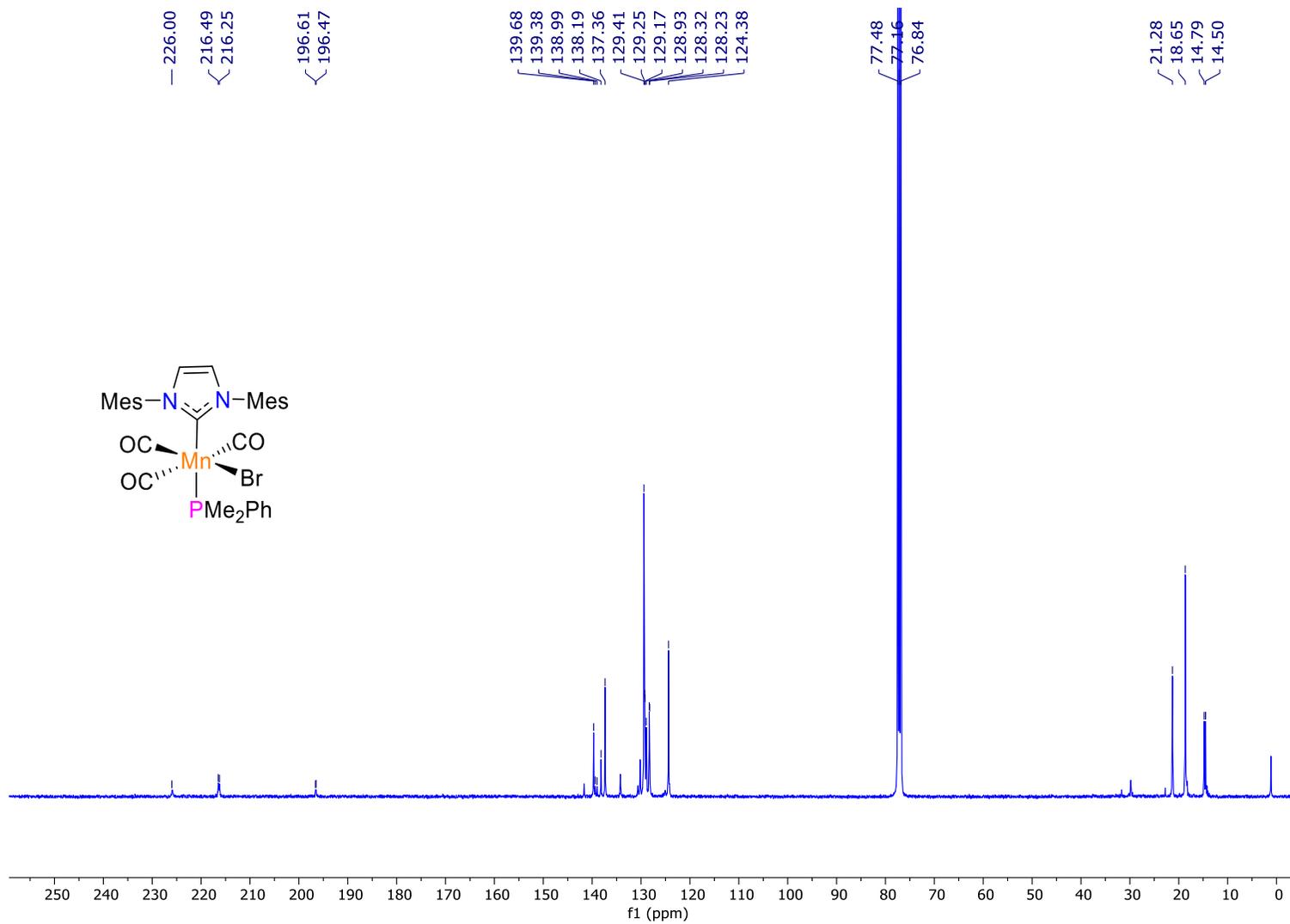


Figure S71: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **11** in CDCl_3 recorded at 101 MHz.

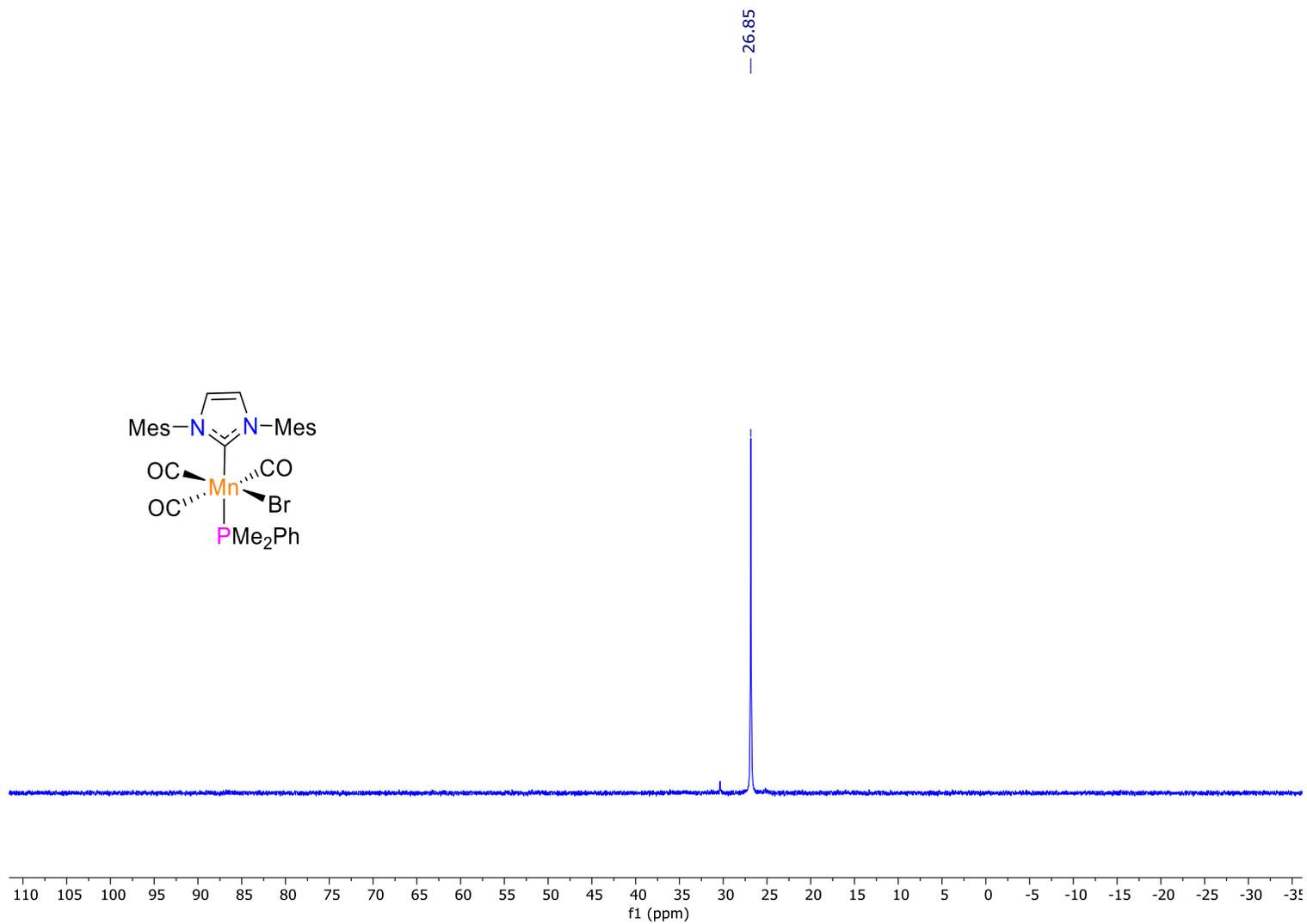


Figure S72: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **11** in CDCl_3 recorded at 162 MHz.

11. NMR spectra of the products of catalysis

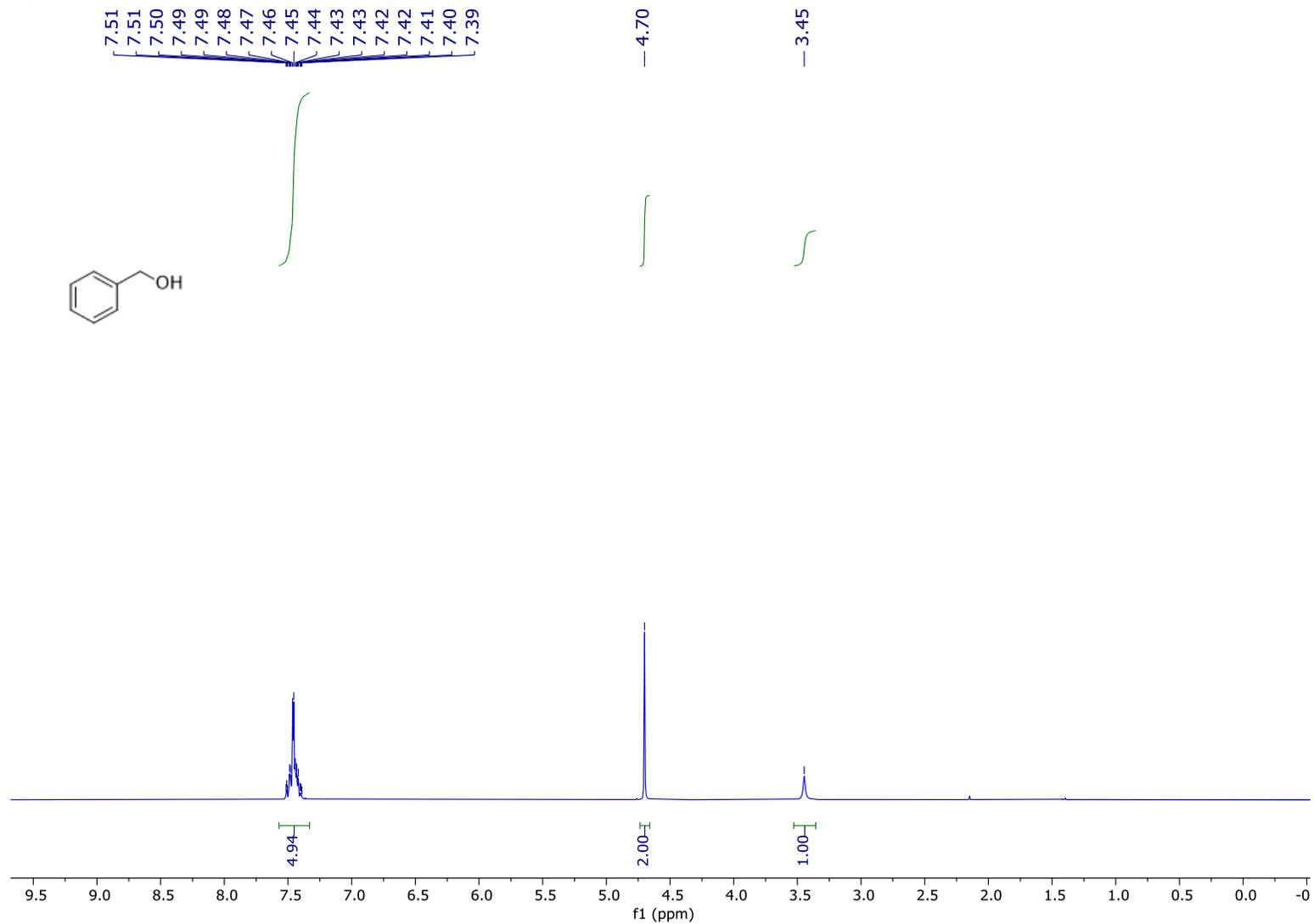


Figure S73: ¹H NMR spectrum of **b1** in CDCl₃ recorded at 300 MHz.

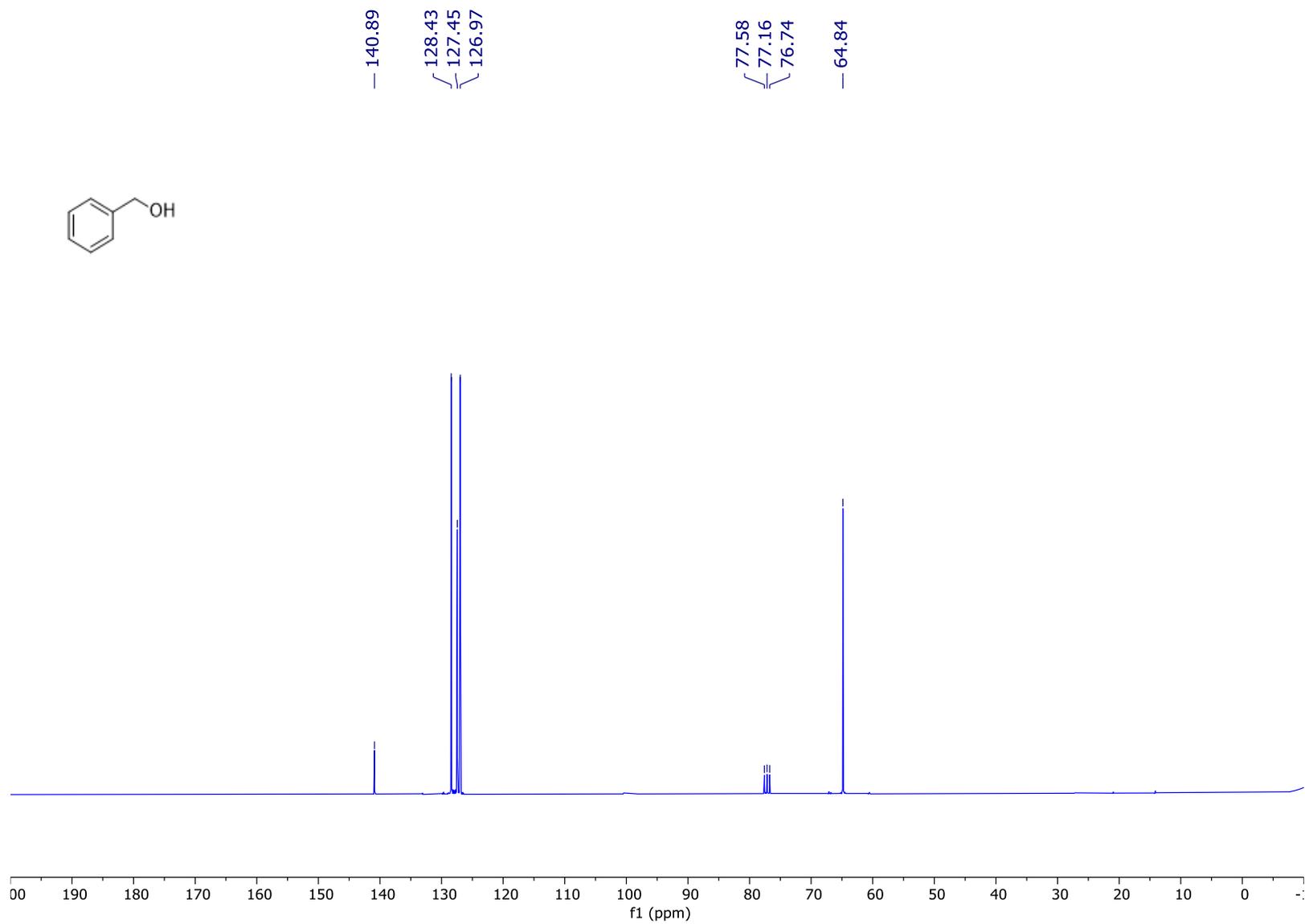


Figure S74: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b1** in CDCl_3 recorded at 75 MHz.

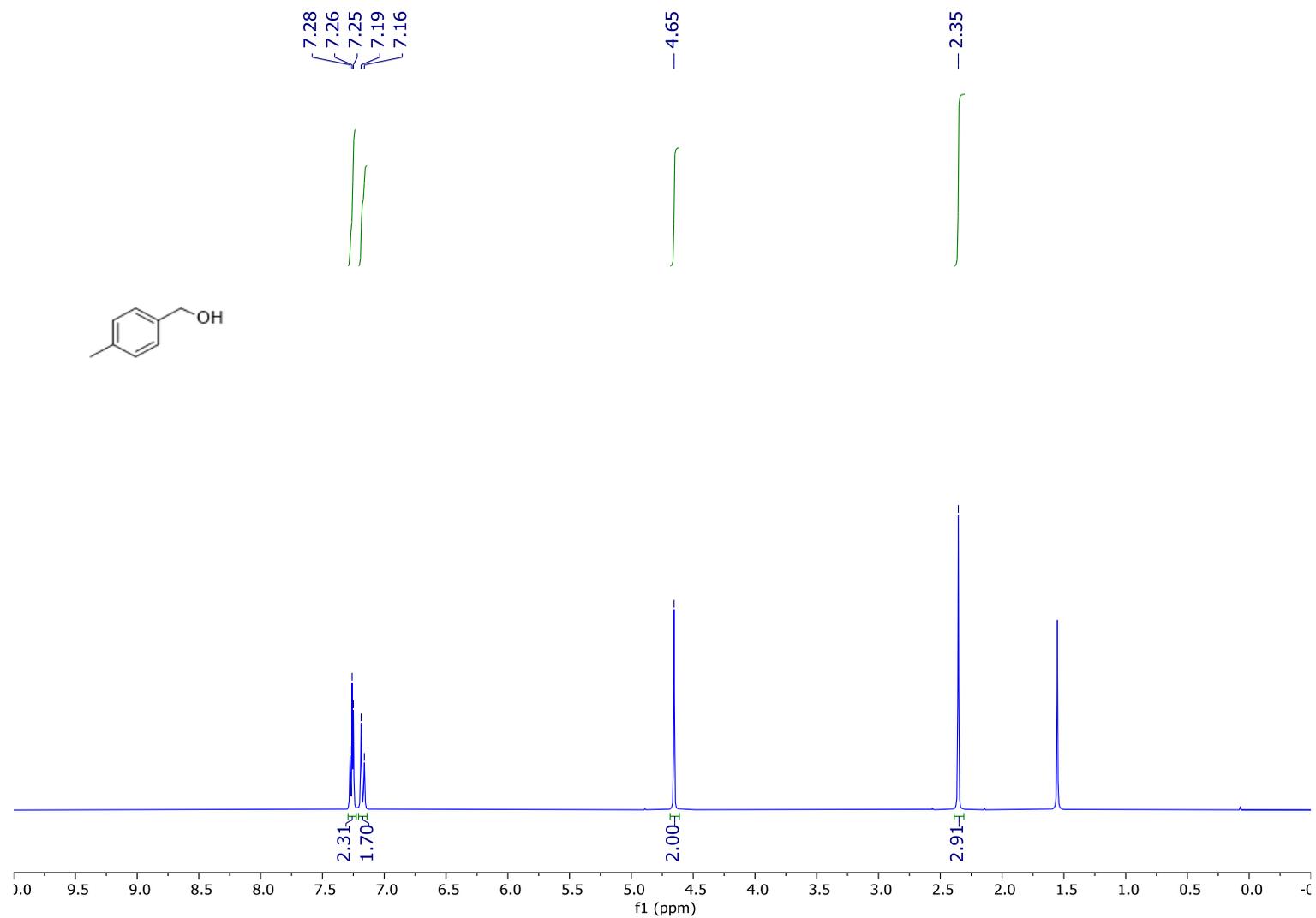


Figure S75: ¹H NMR spectrum of **b5** in CDCl₃ recorded at 300 MHz.

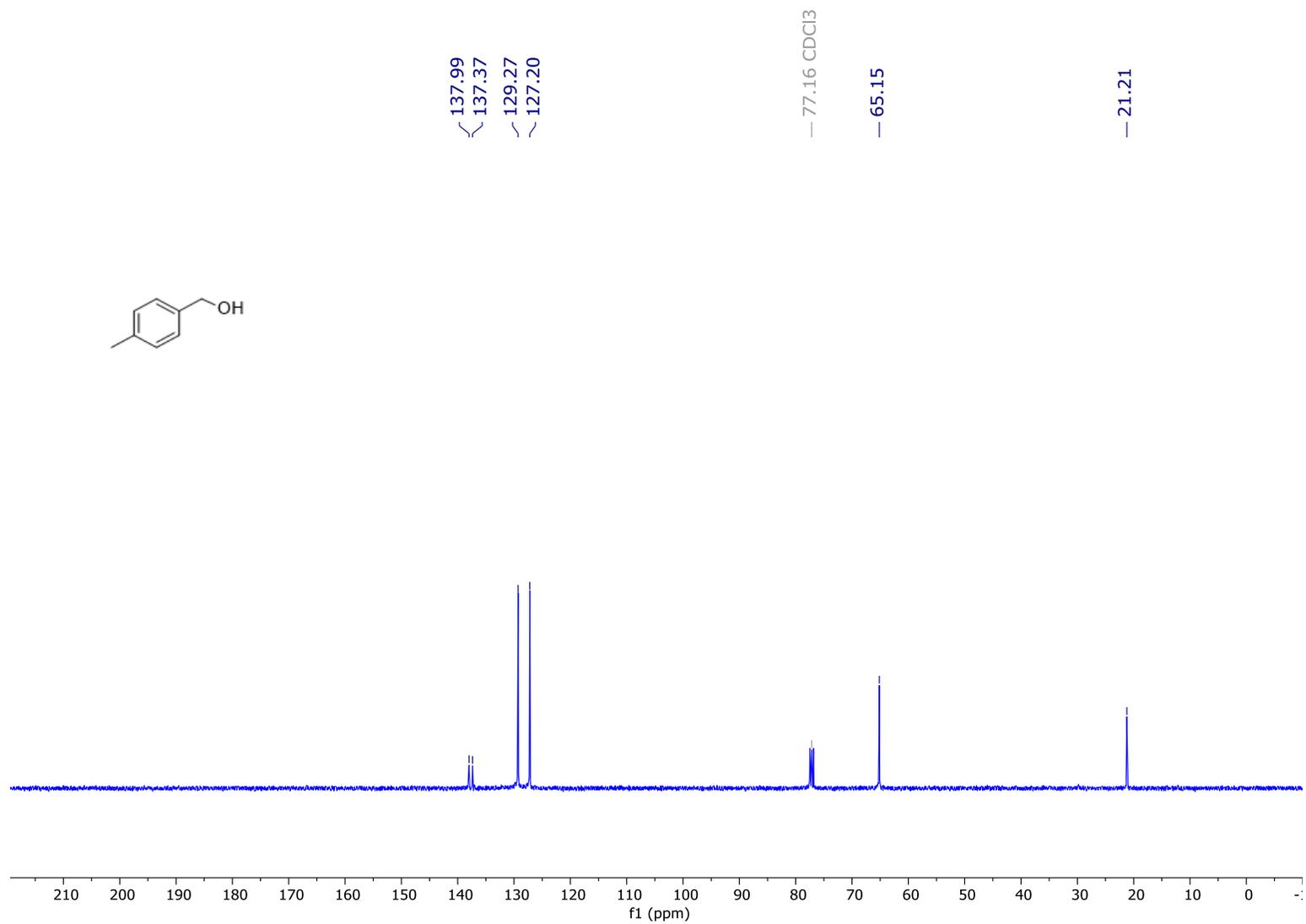


Figure S76: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b5** in CDCl_3 recorded at 75 MHz.

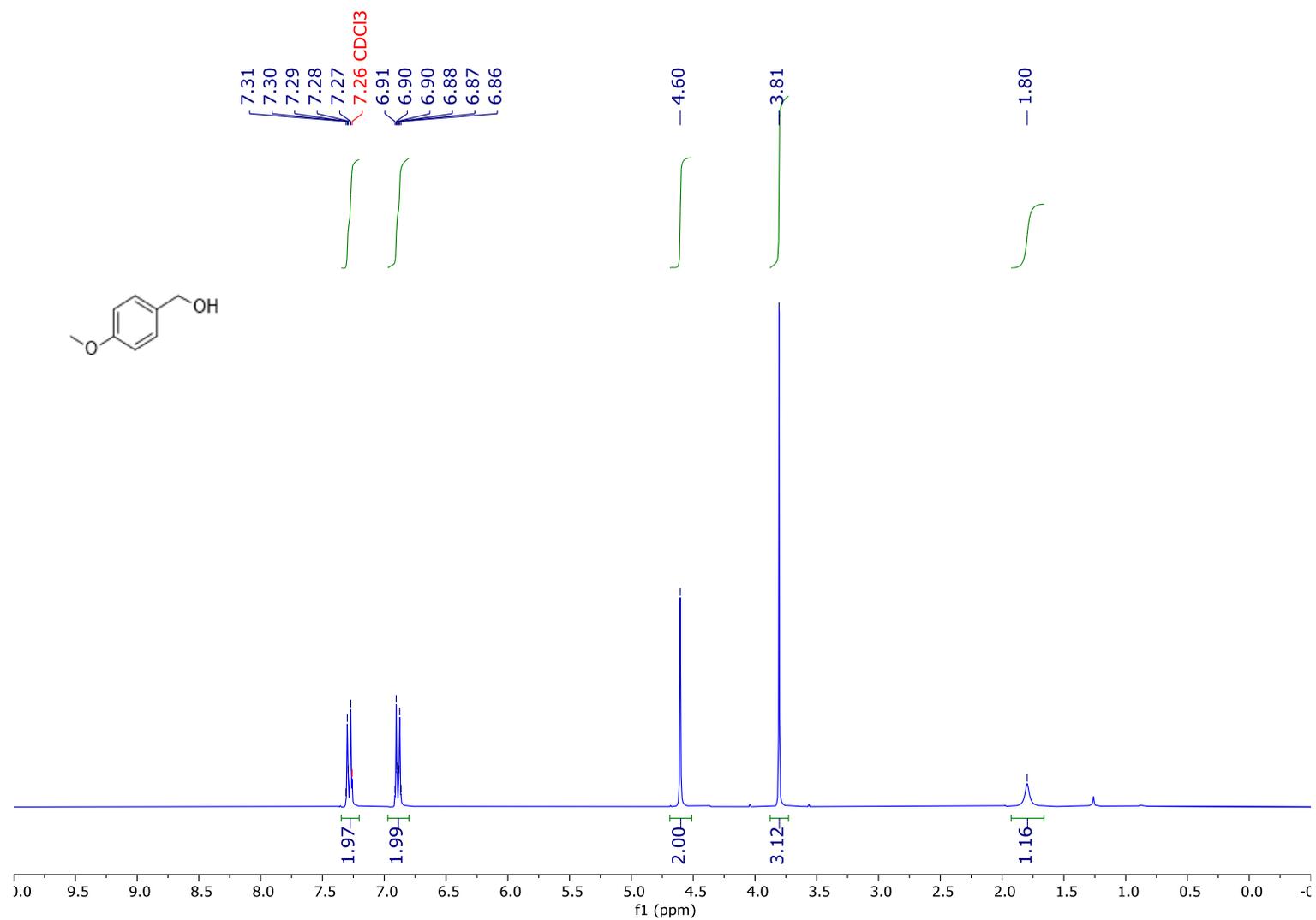


Figure S77: ¹H NMR spectrum of **b6** in CDCl₃ recorded at 300 MHz.

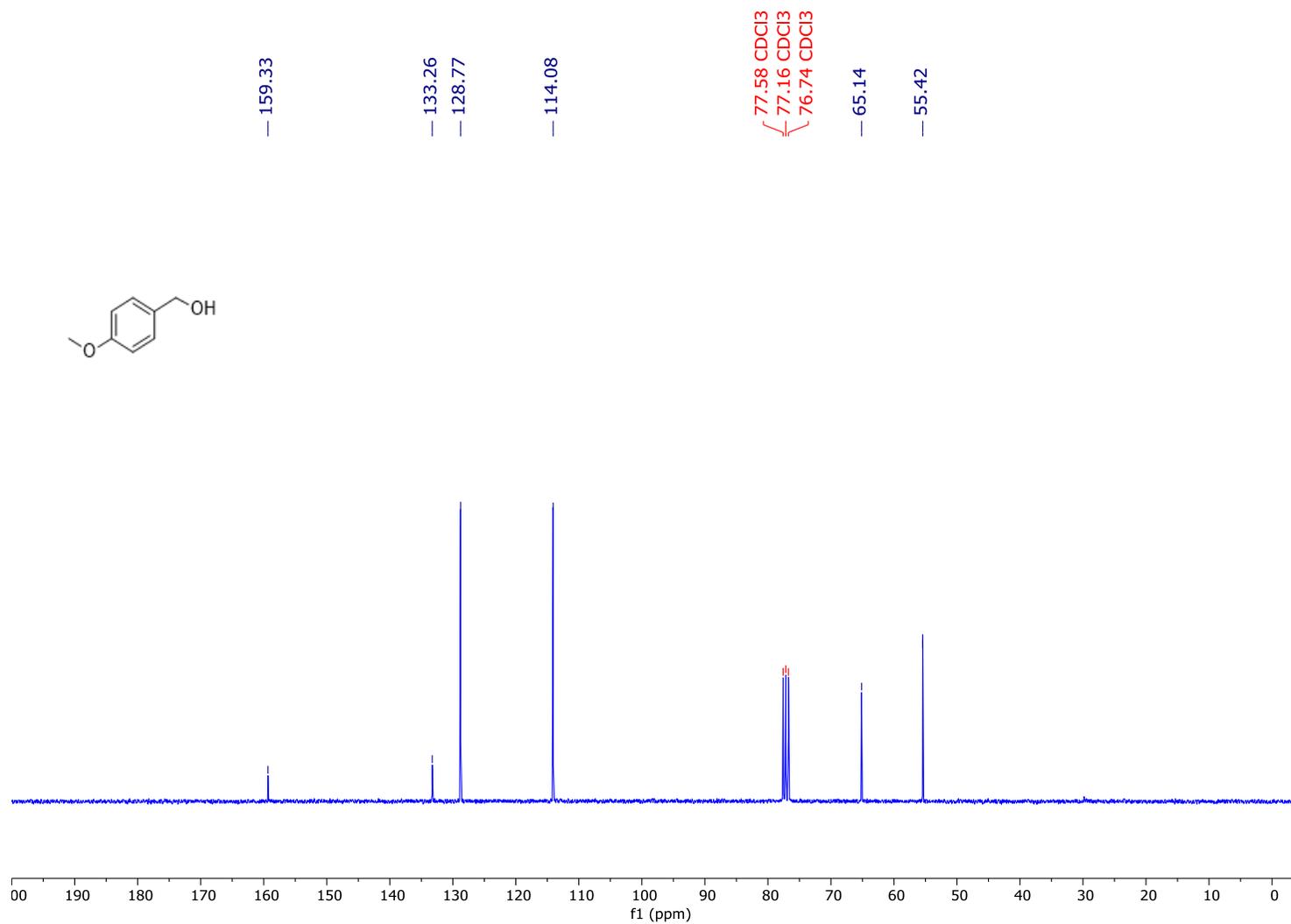
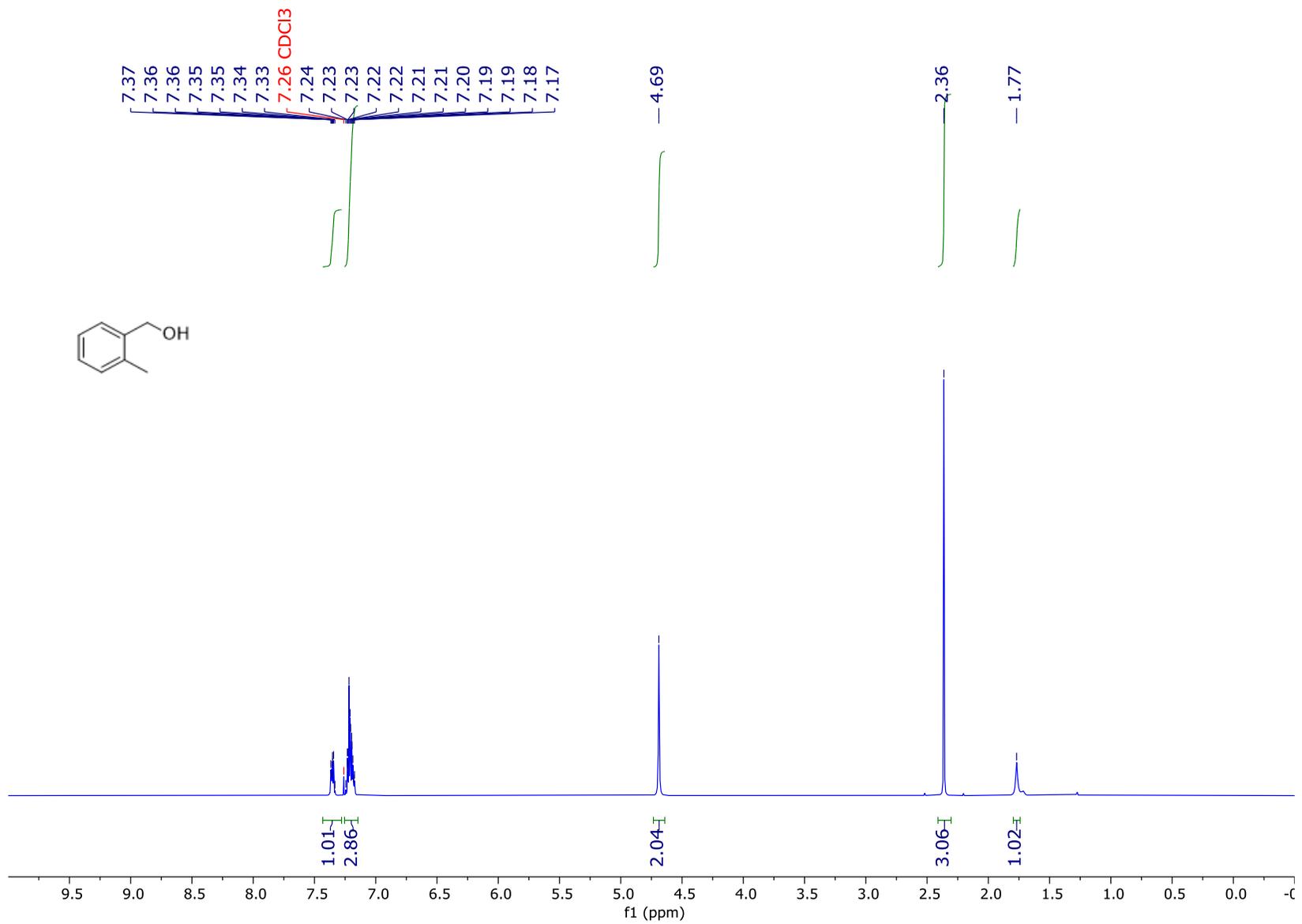


Figure S78: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b6** in CDCl_3 recorded at 75 MHz.



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Figure S79: ^{13}C NMR spectrum of **b8** in CDCl_3 recorded at 400 MHz

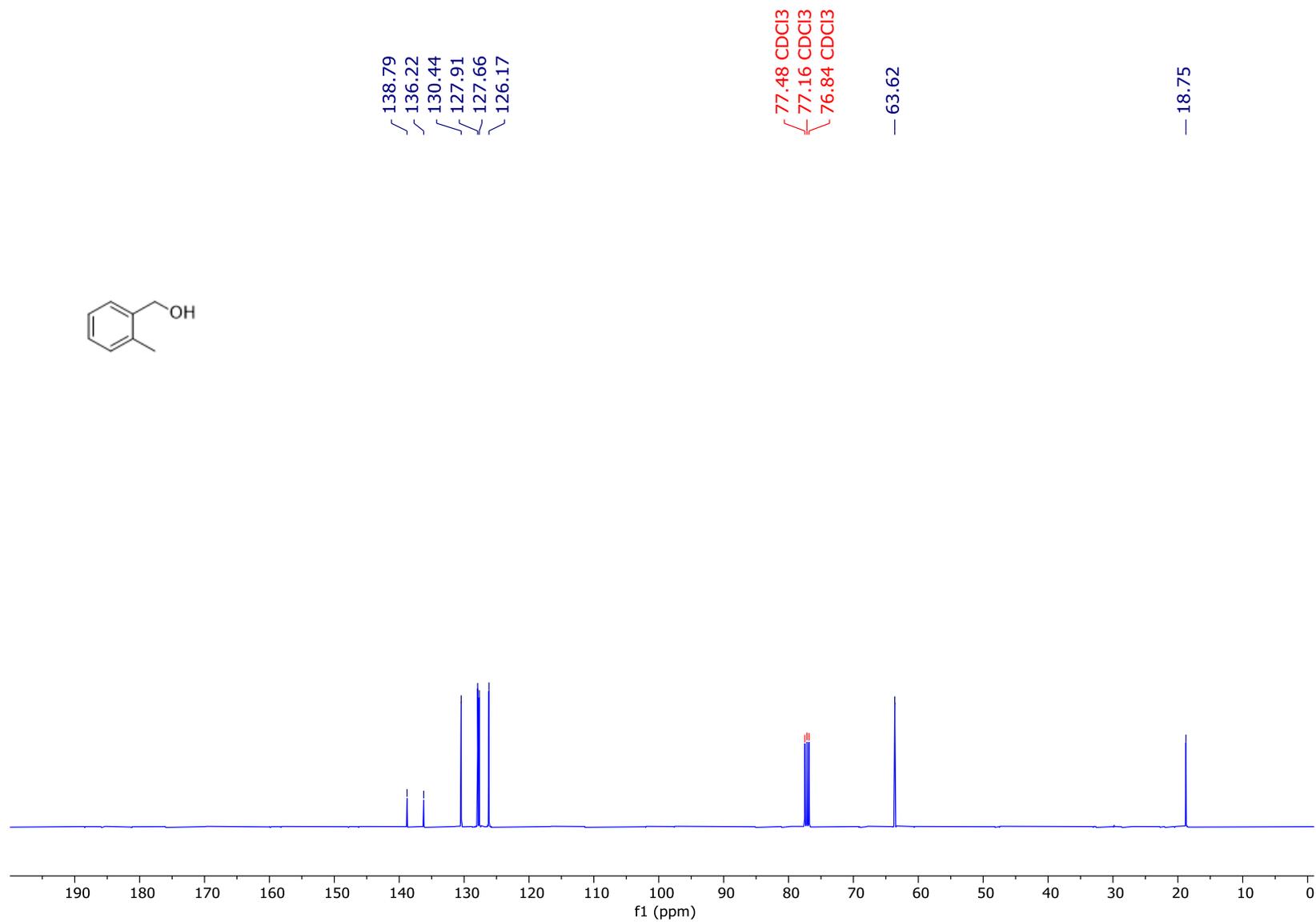


Figure S80: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b8** in CDCl_3 recorded at 101 MHz.

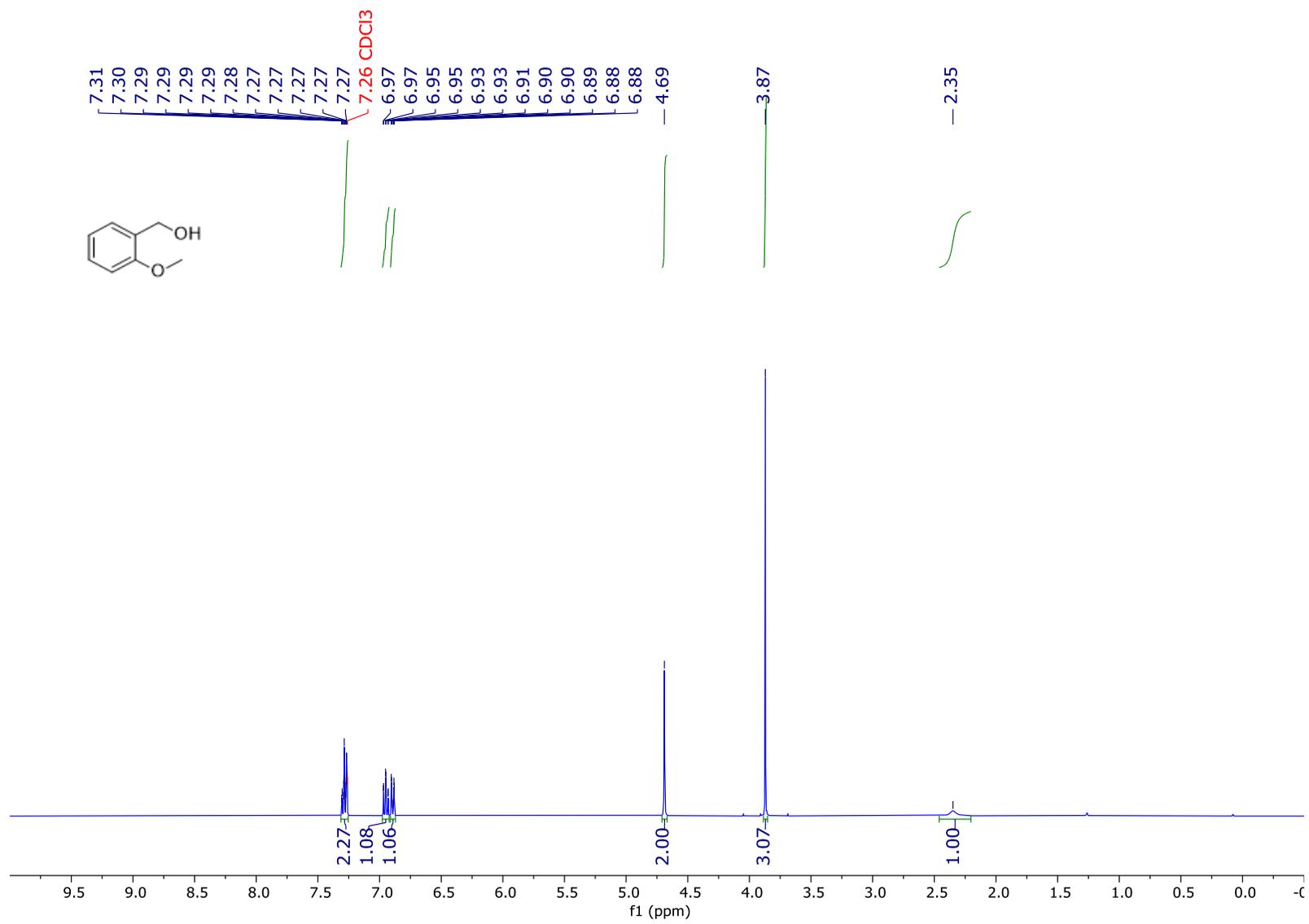


Figure S81: ^1H NMR spectrum of **b9** in CDCl_3 recorded at 400 MHz.

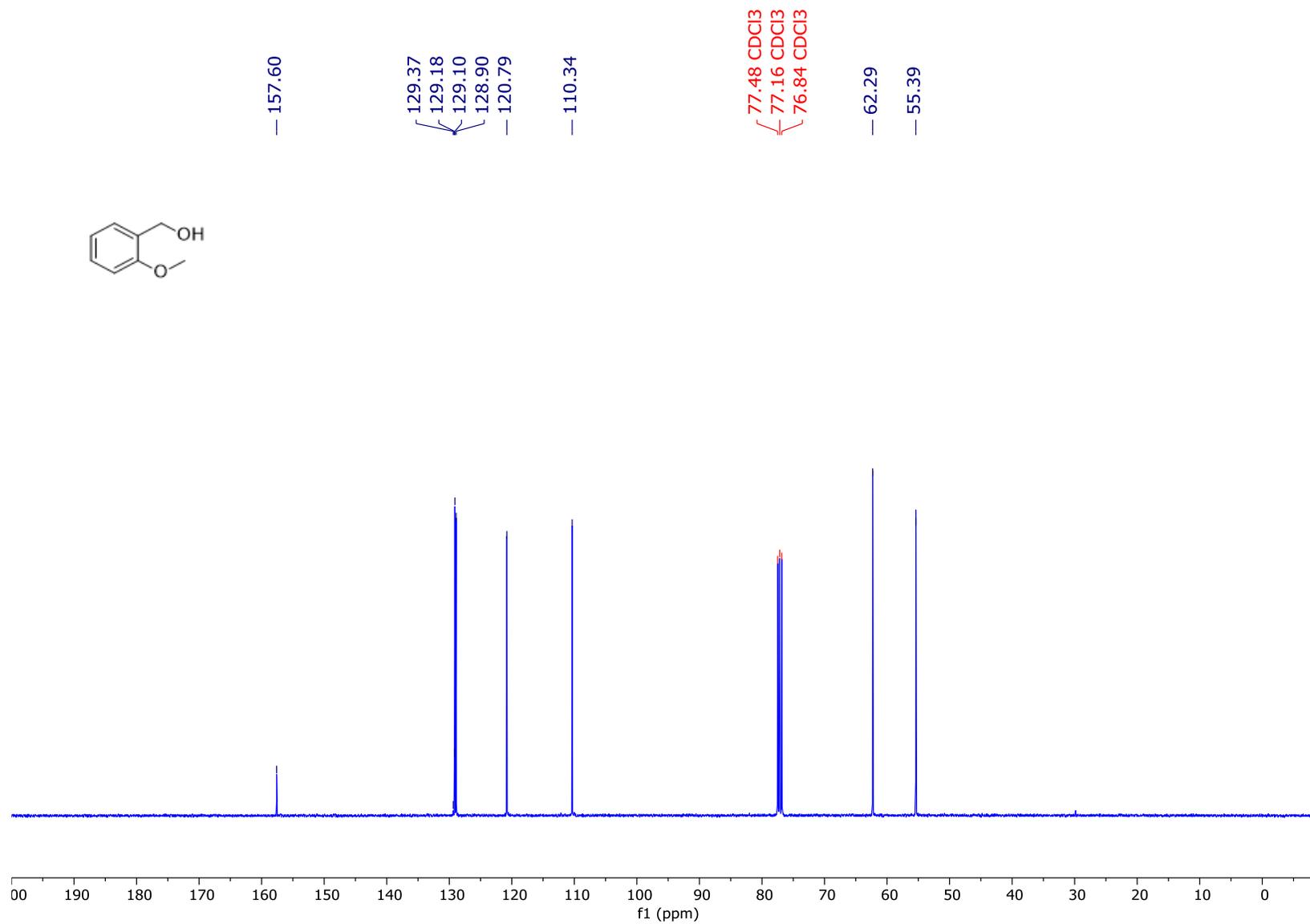


Figure S82: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b9** in CDCl_3 recorded at 101 MHz.

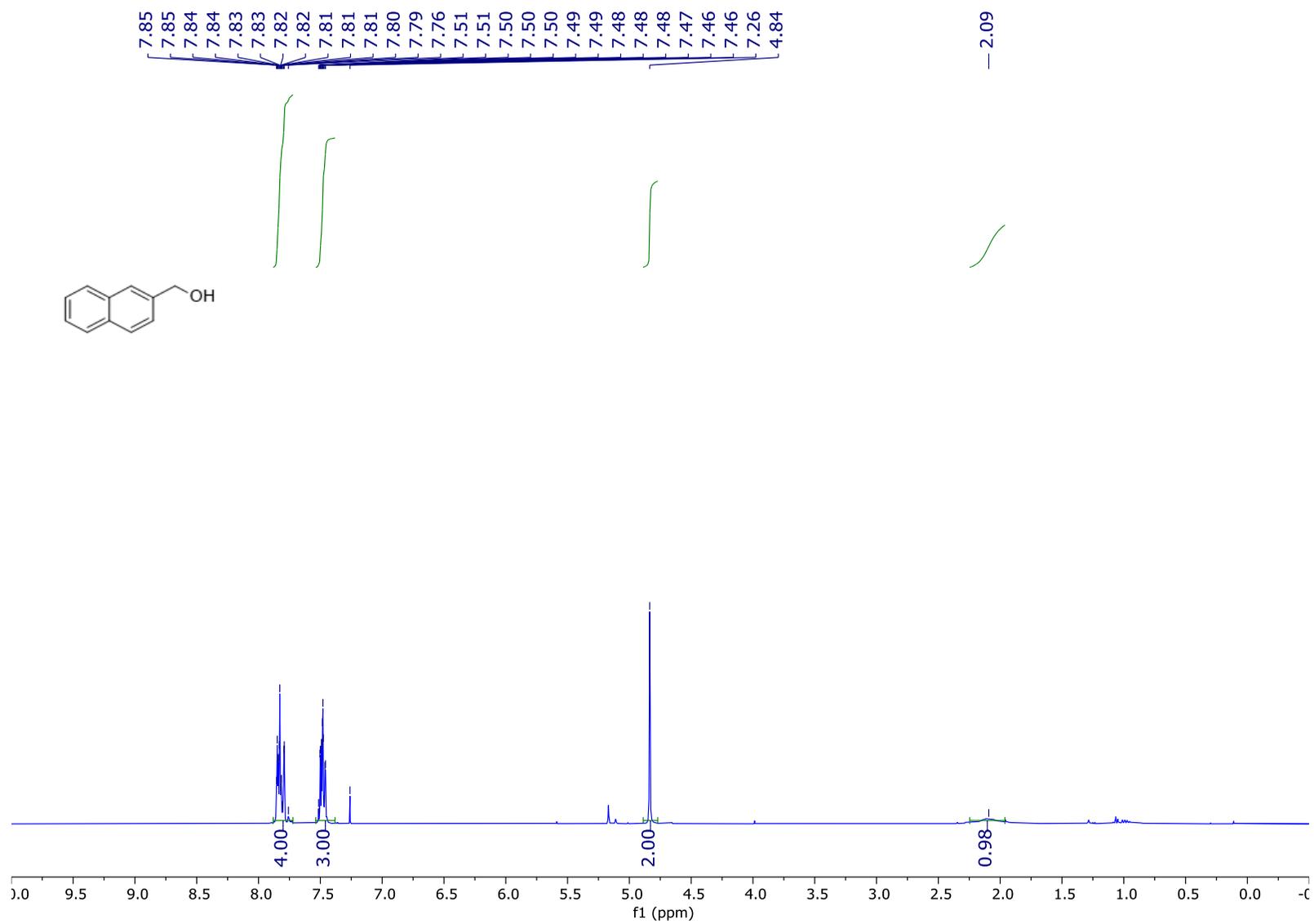


Figure S83: ^1H NMR spectrum of **b11** in CDCl_3 recorded at 400 MHz.

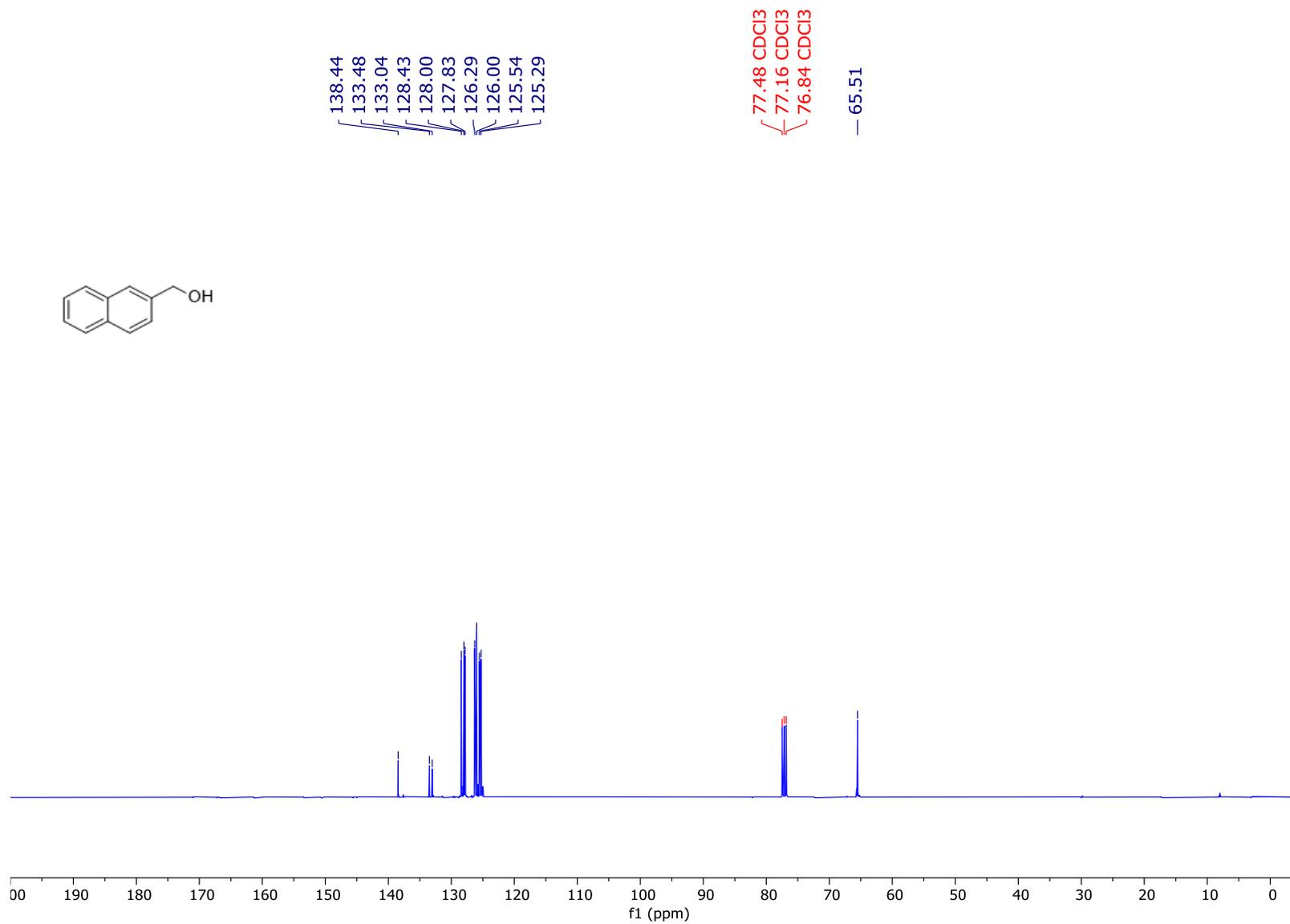


Figure S84: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b11** in CDCl_3 recorded at 101 MHz.

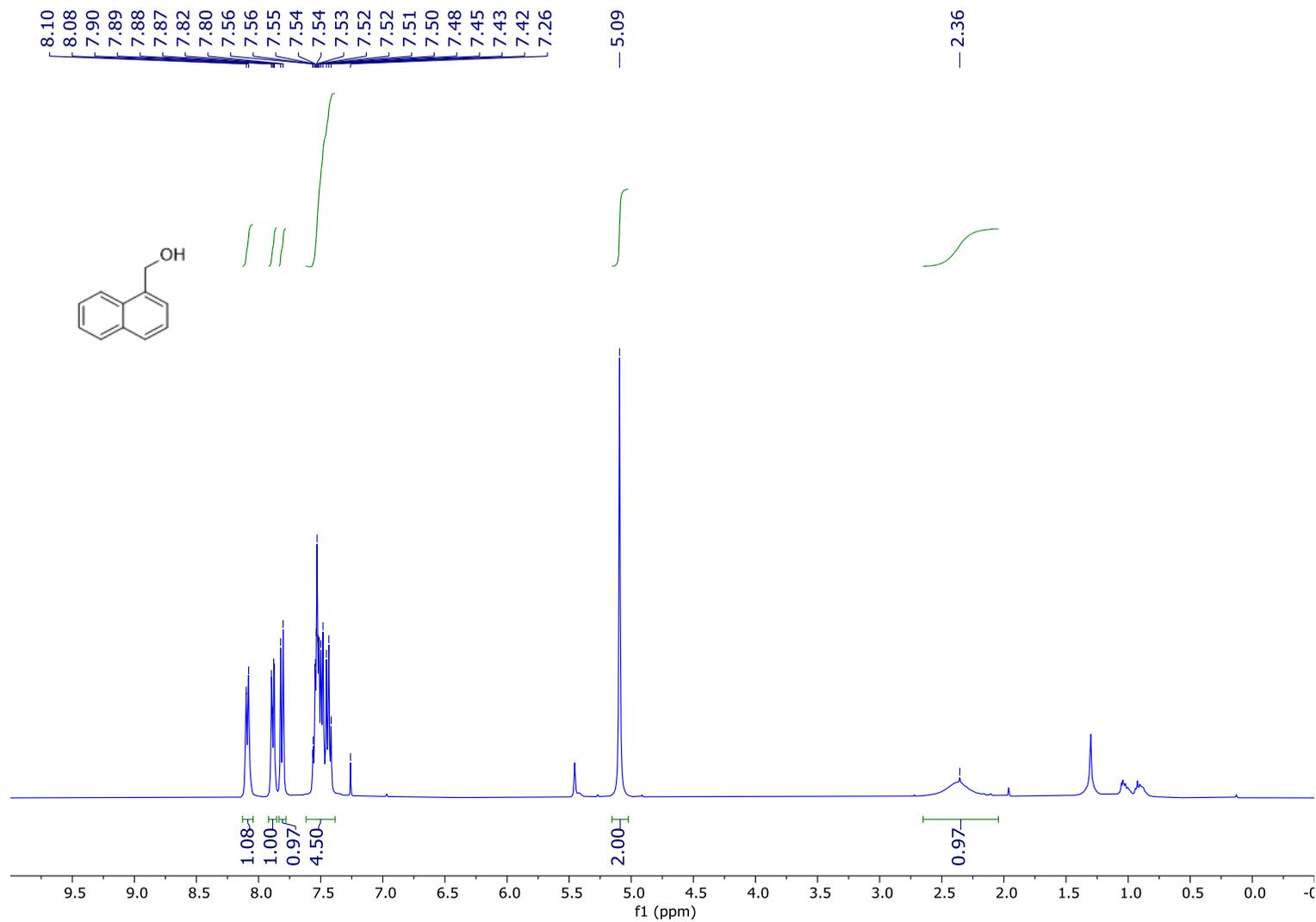


Figure S85: ^1H NMR spectrum of **b12** in CDCl_3 recorded at 400 MHz.

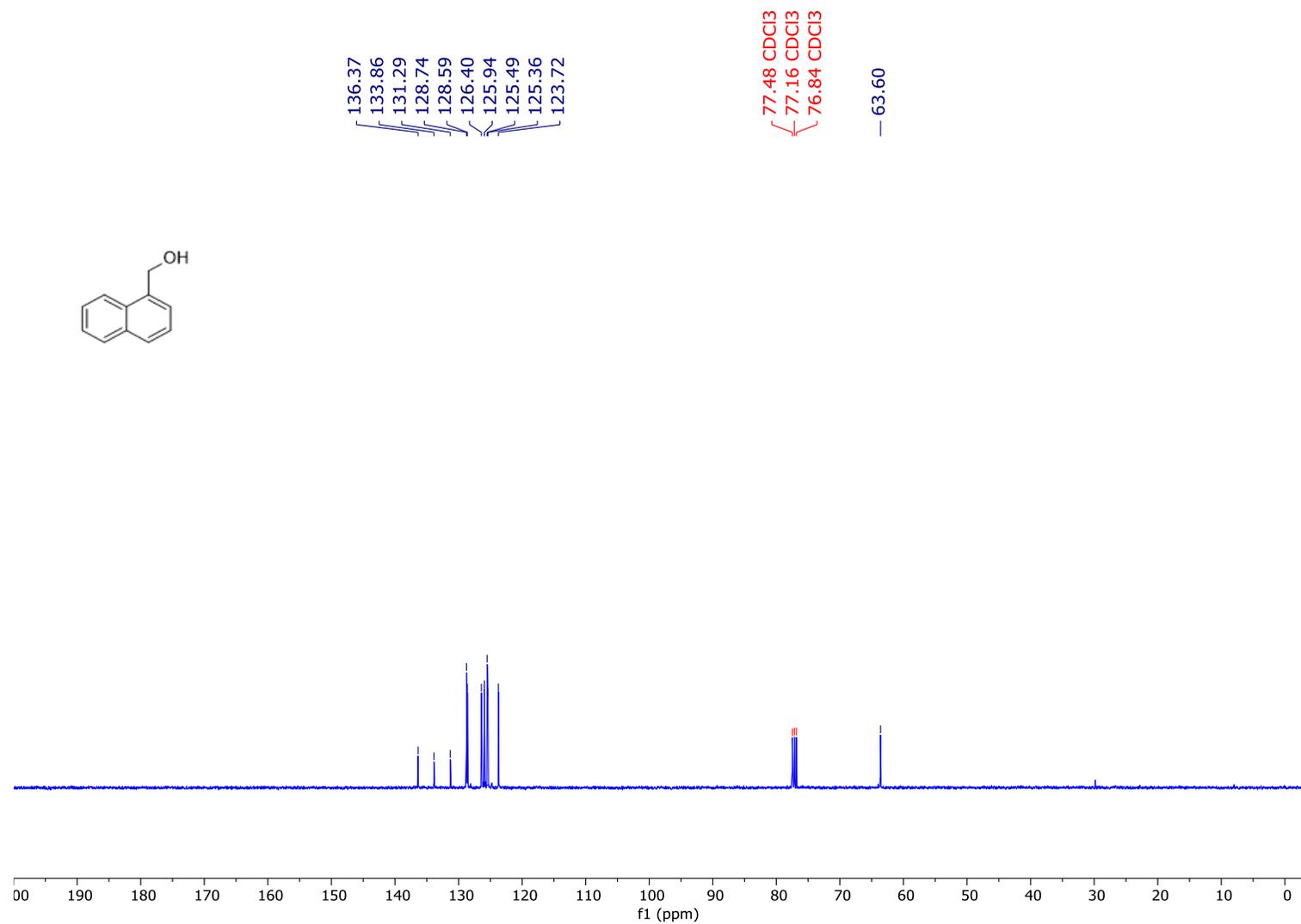


Figure S86: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b12** in CDCl_3 recorded at 101 MHz.

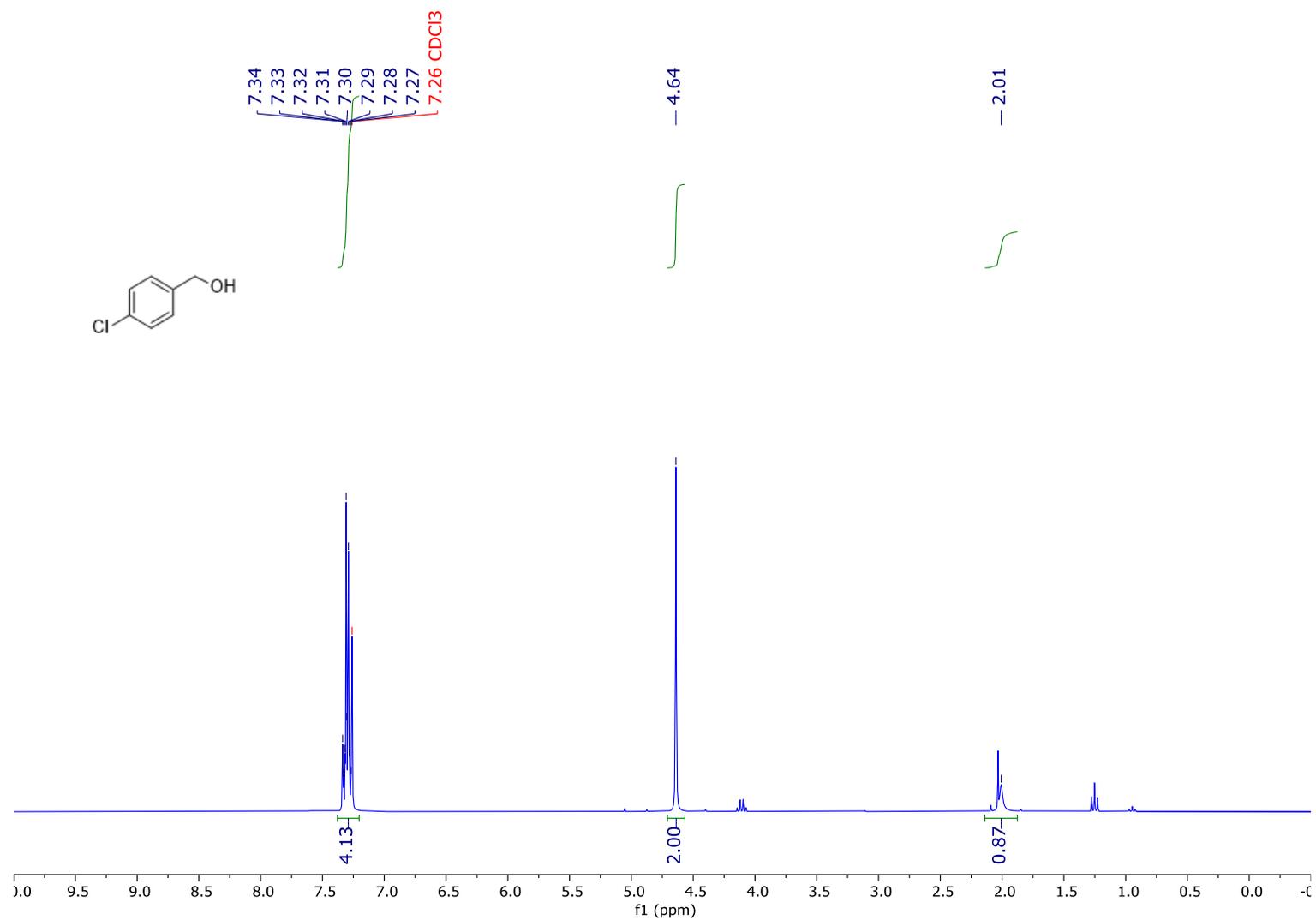


Figure S87: ¹H NMR spectrum of **b14** in CDCl₃ recorded at 300 MHz.

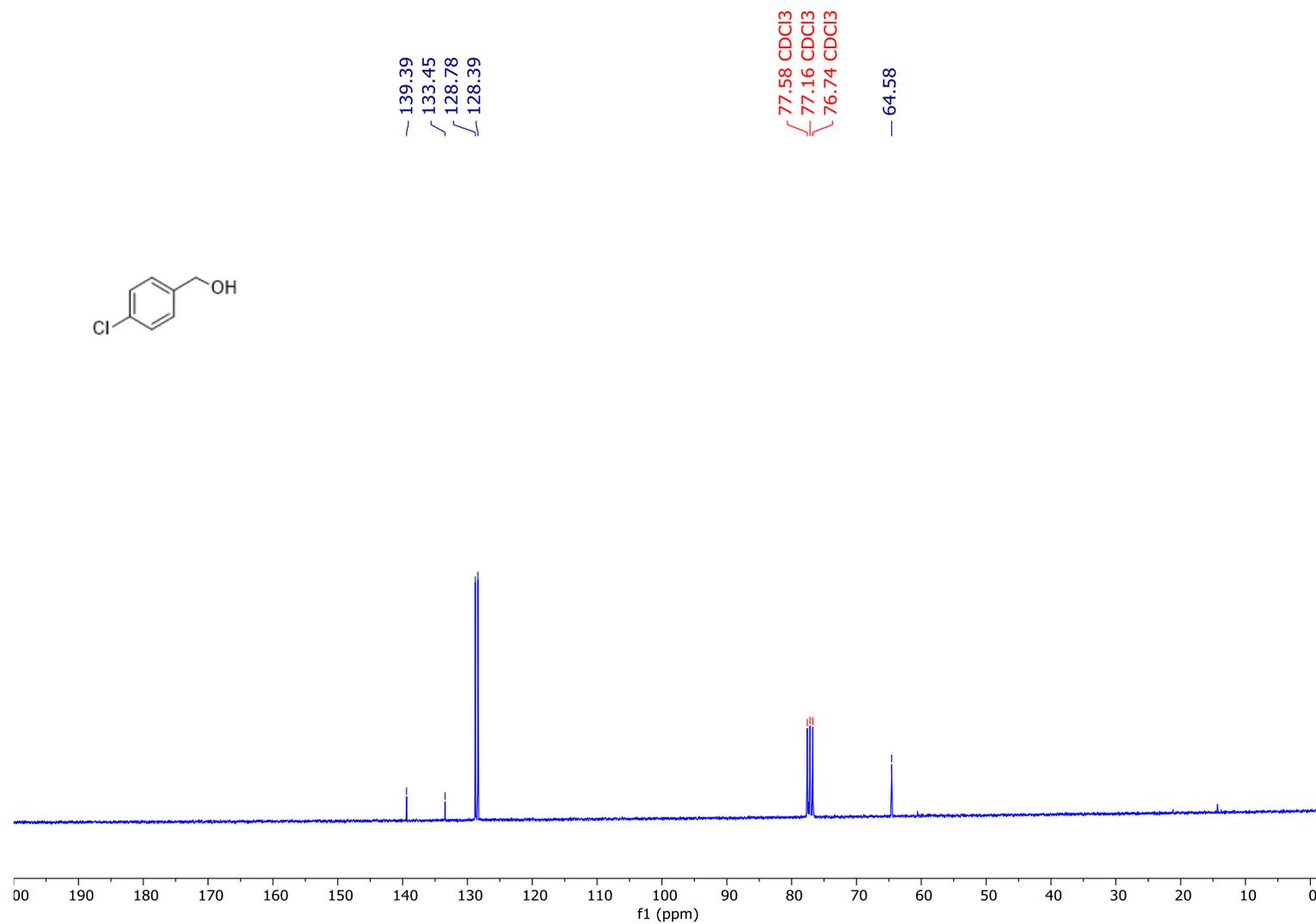


Figure S88: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b14** in CDCl_3 recorded at 75 MHz.

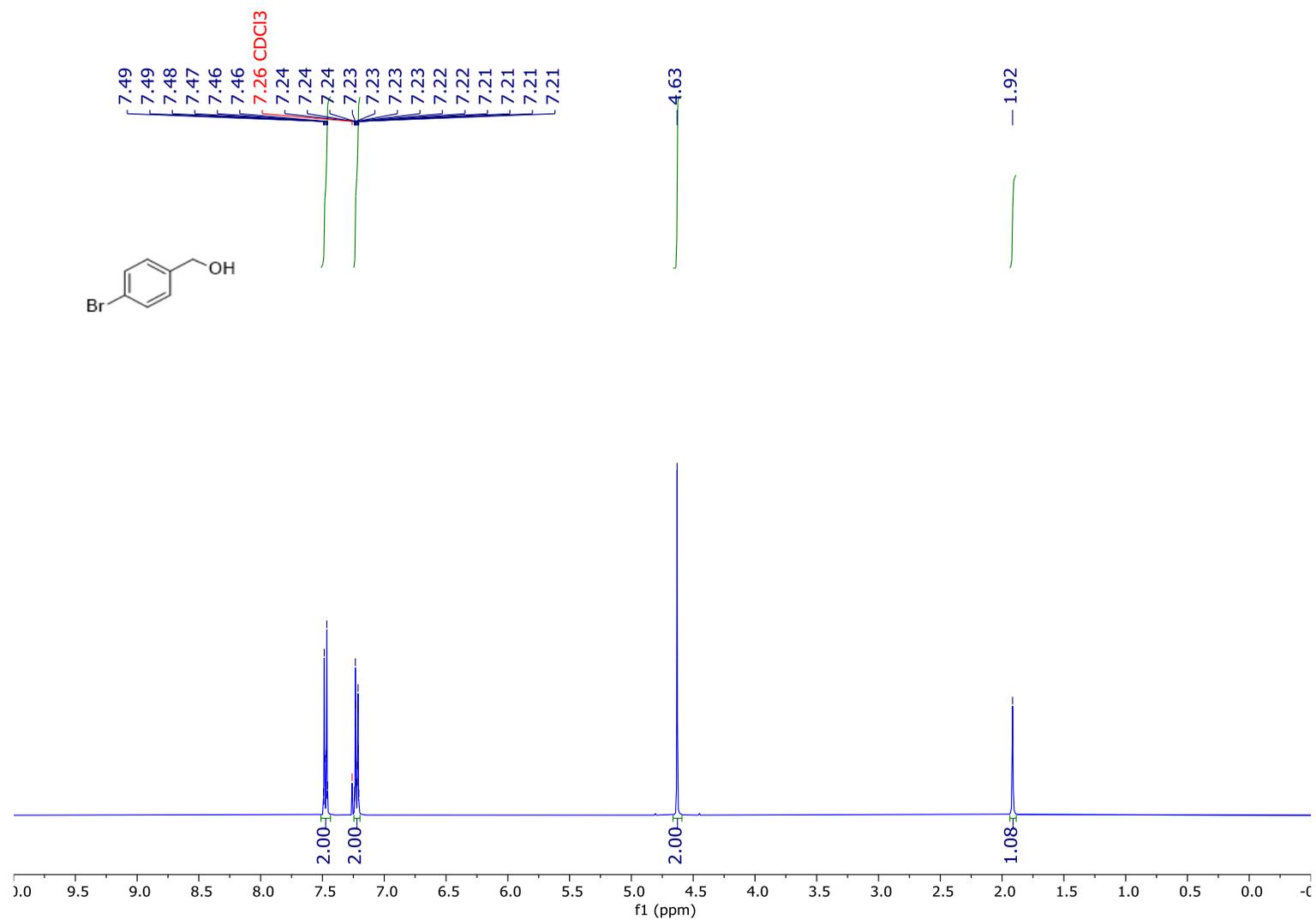


Figure S89: ¹H NMR spectrum of **b15** in CDCl₃ recorded at 400 MHz.

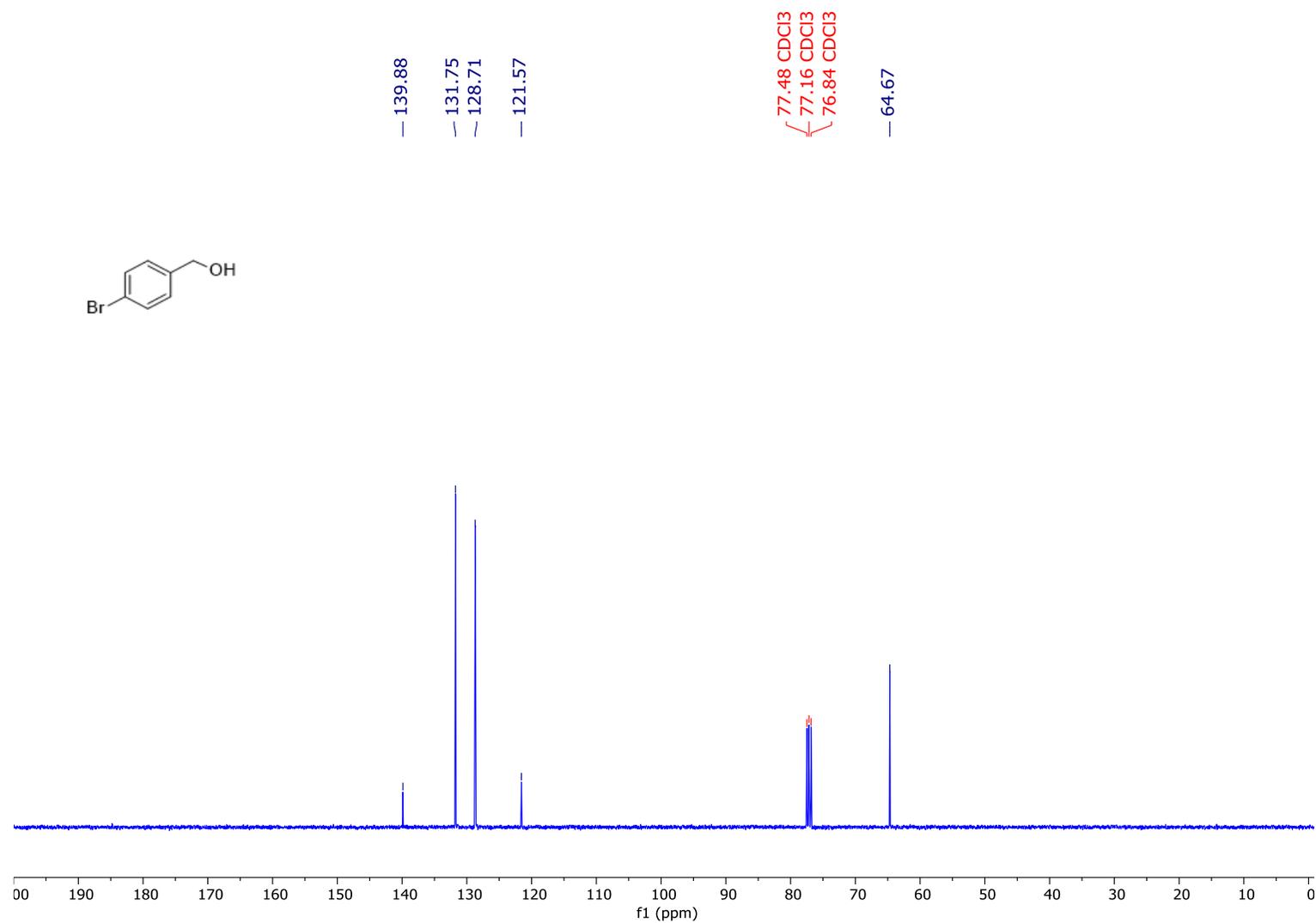


Figure S90: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b15** in CDCl_3 recorded at 101 MHz.

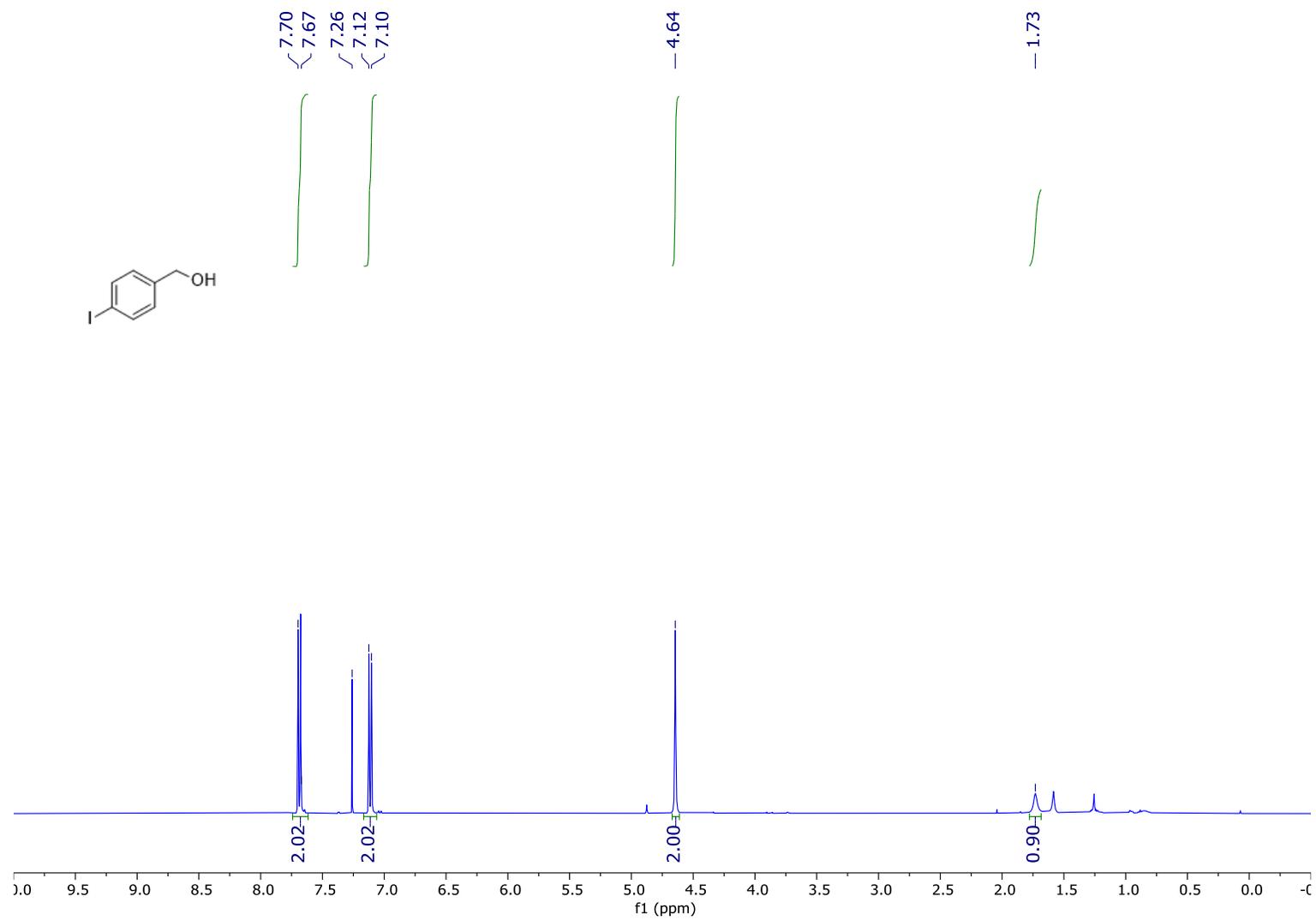


Figure S91: ¹H NMR spectrum of **b16** in CDCl₃ recorded at 400 MHz.

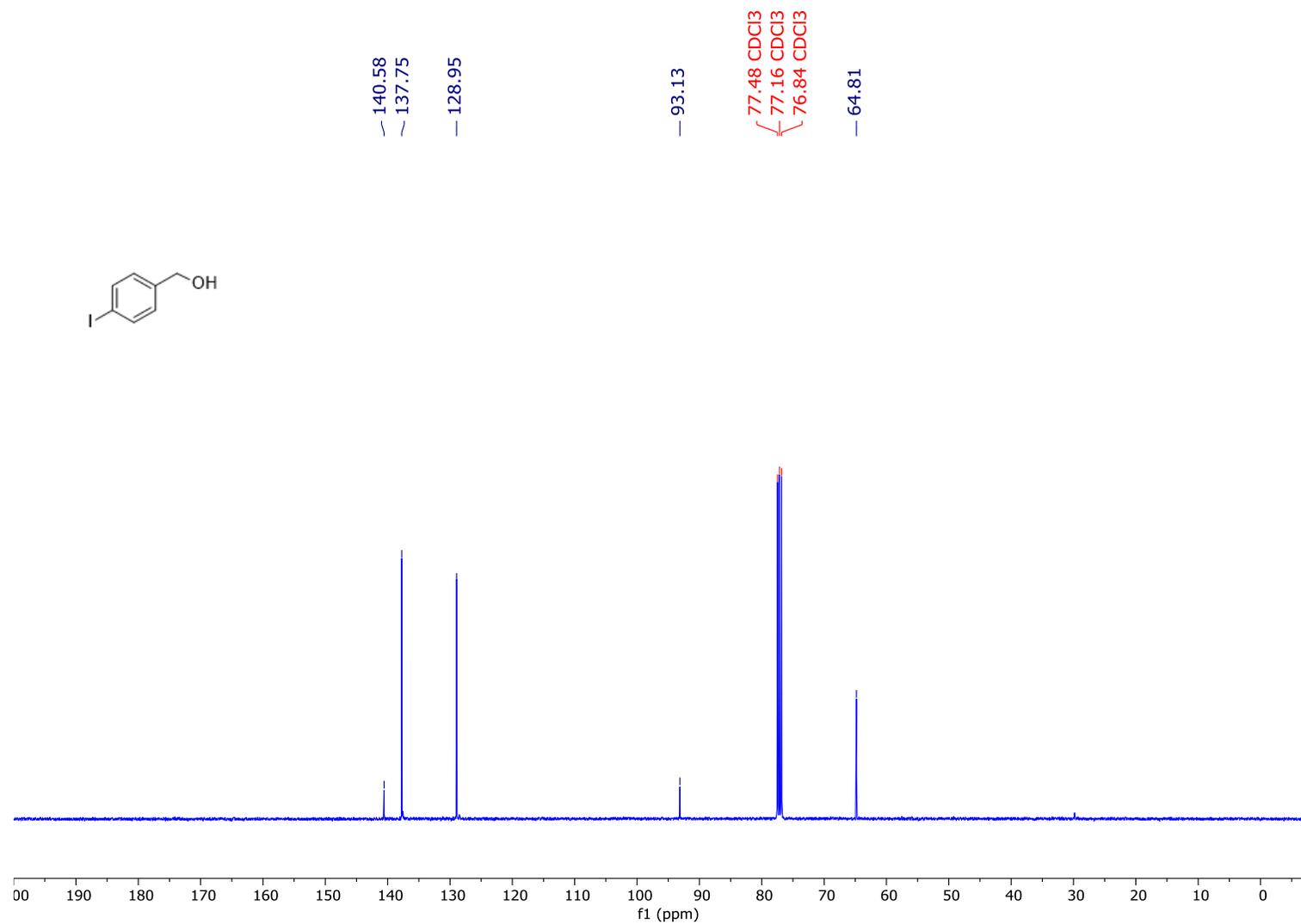


Figure S92: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b16** in CDCl_3 recorded at 101 MHz.

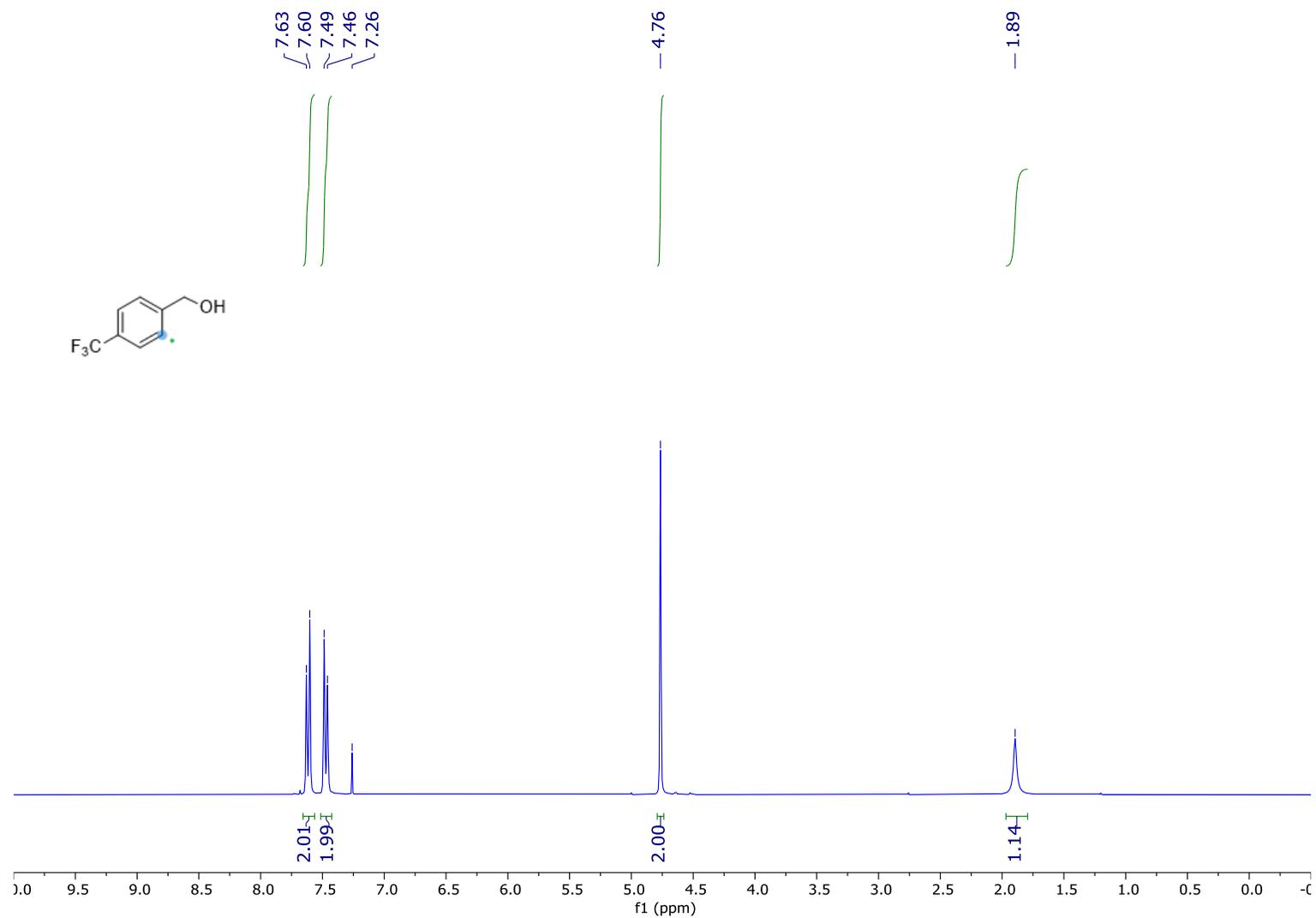


Figure S93: ¹H NMR spectrum of **b17** in CDCl₃ recorded at 300 MHz.

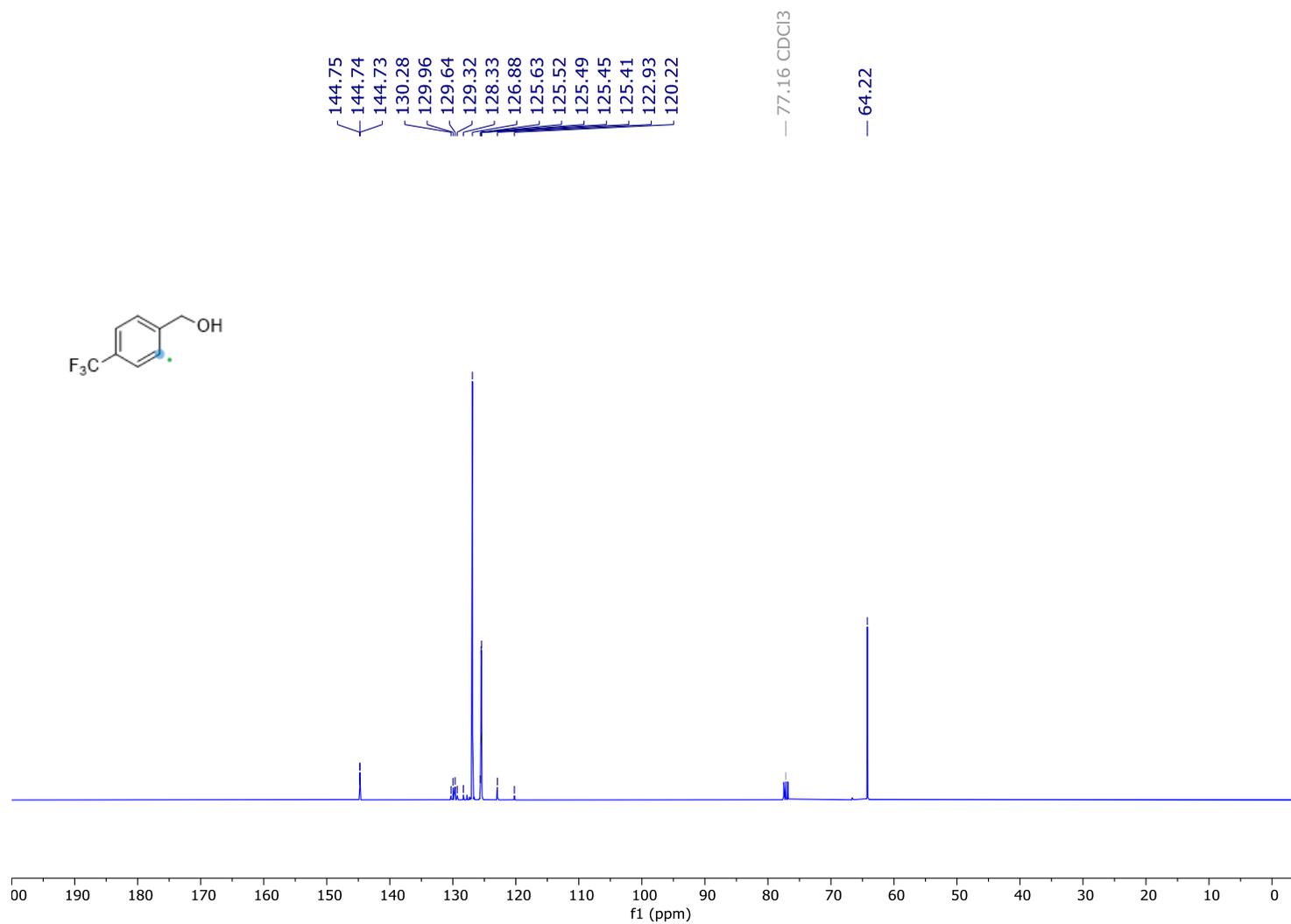


Figure S94: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b17** in CDCl_3 recorded at 101 MHz.

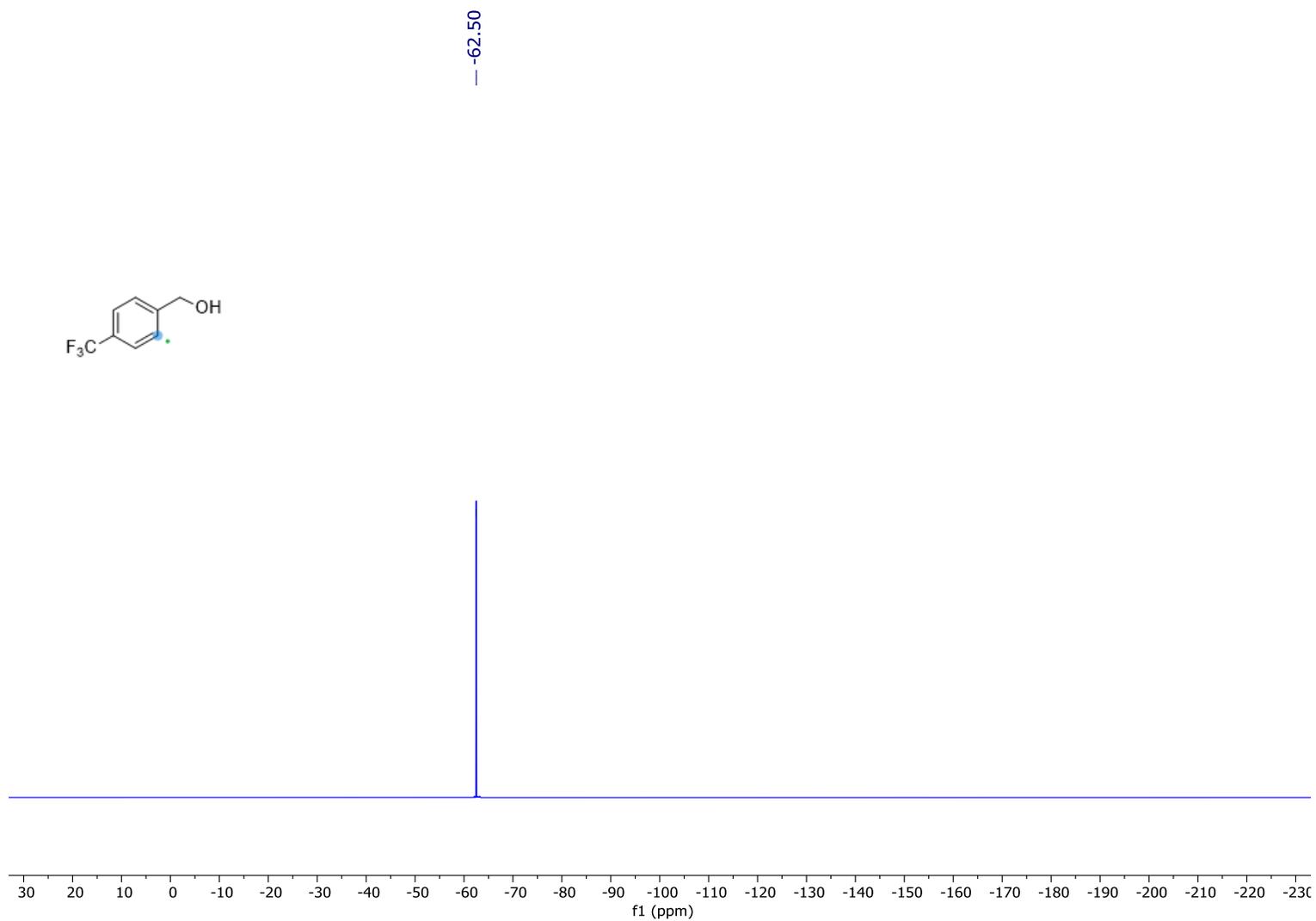


Figure S95: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **b17** in CDCl_3 recorded at 282 MHz.

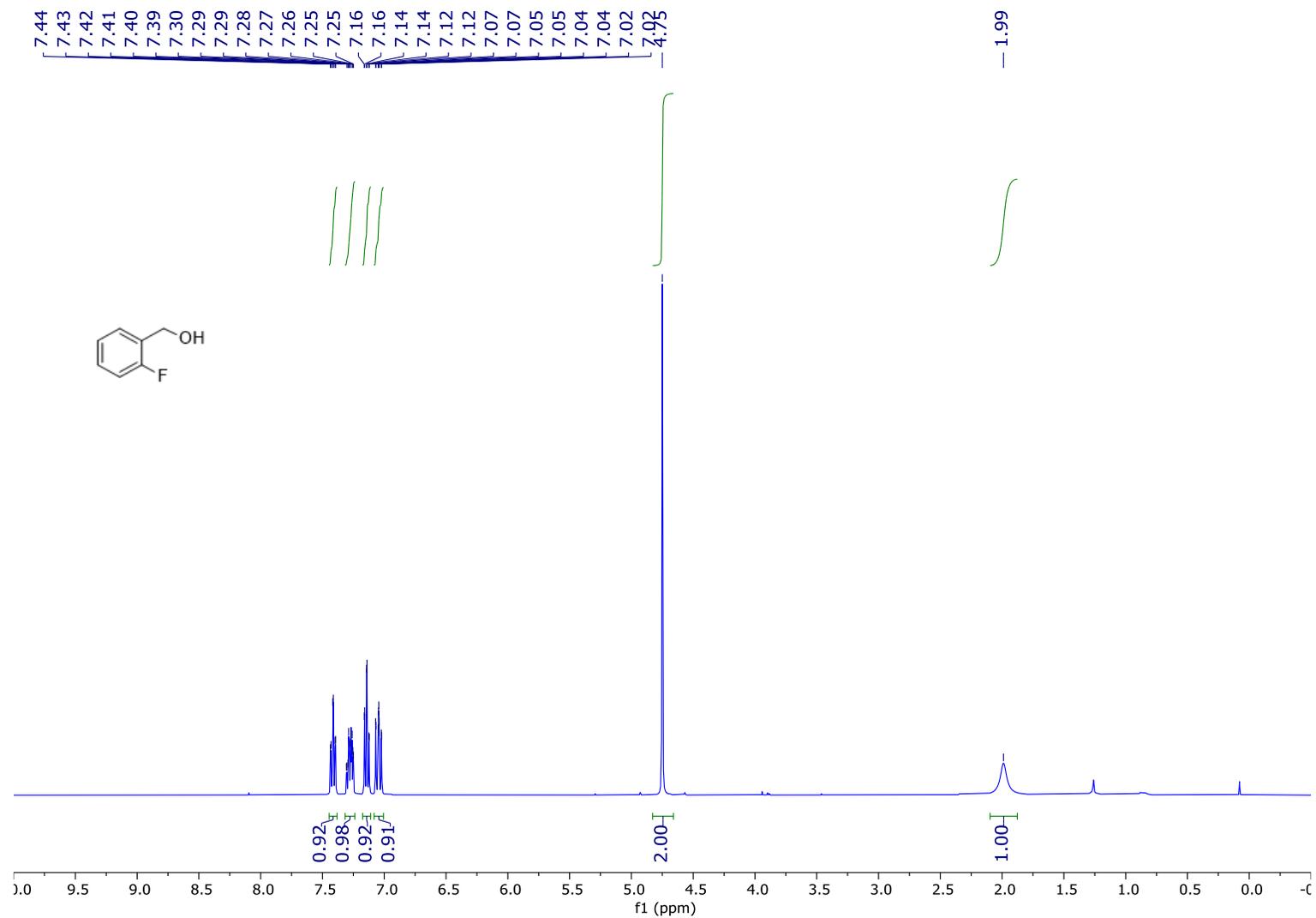


Figure S96: ^1H NMR spectrum of **b18** in CDCl_3 recorded at 400 MHz.

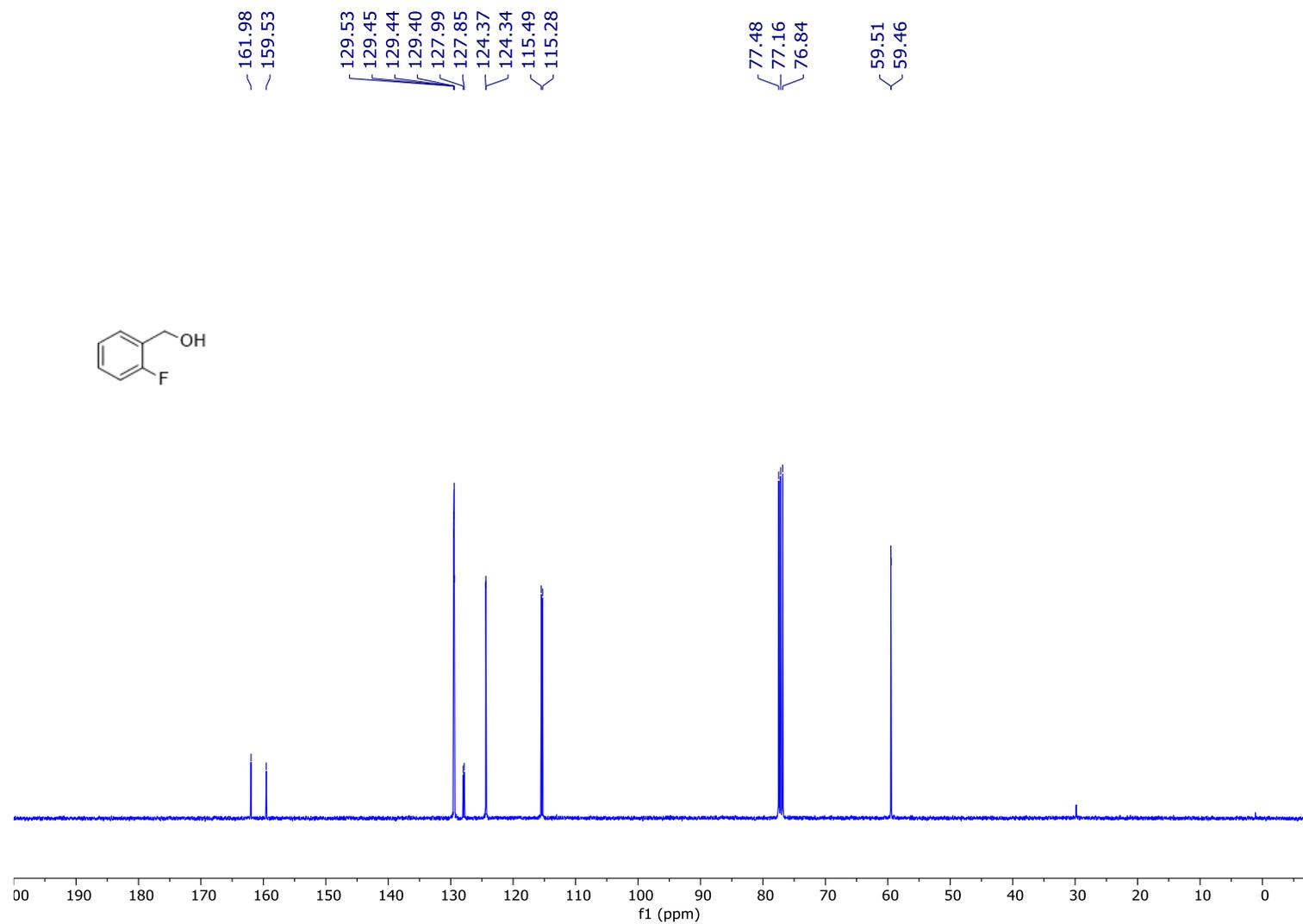


Figure S97: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b18** in CDCl_3 recorded at 101 MHz.

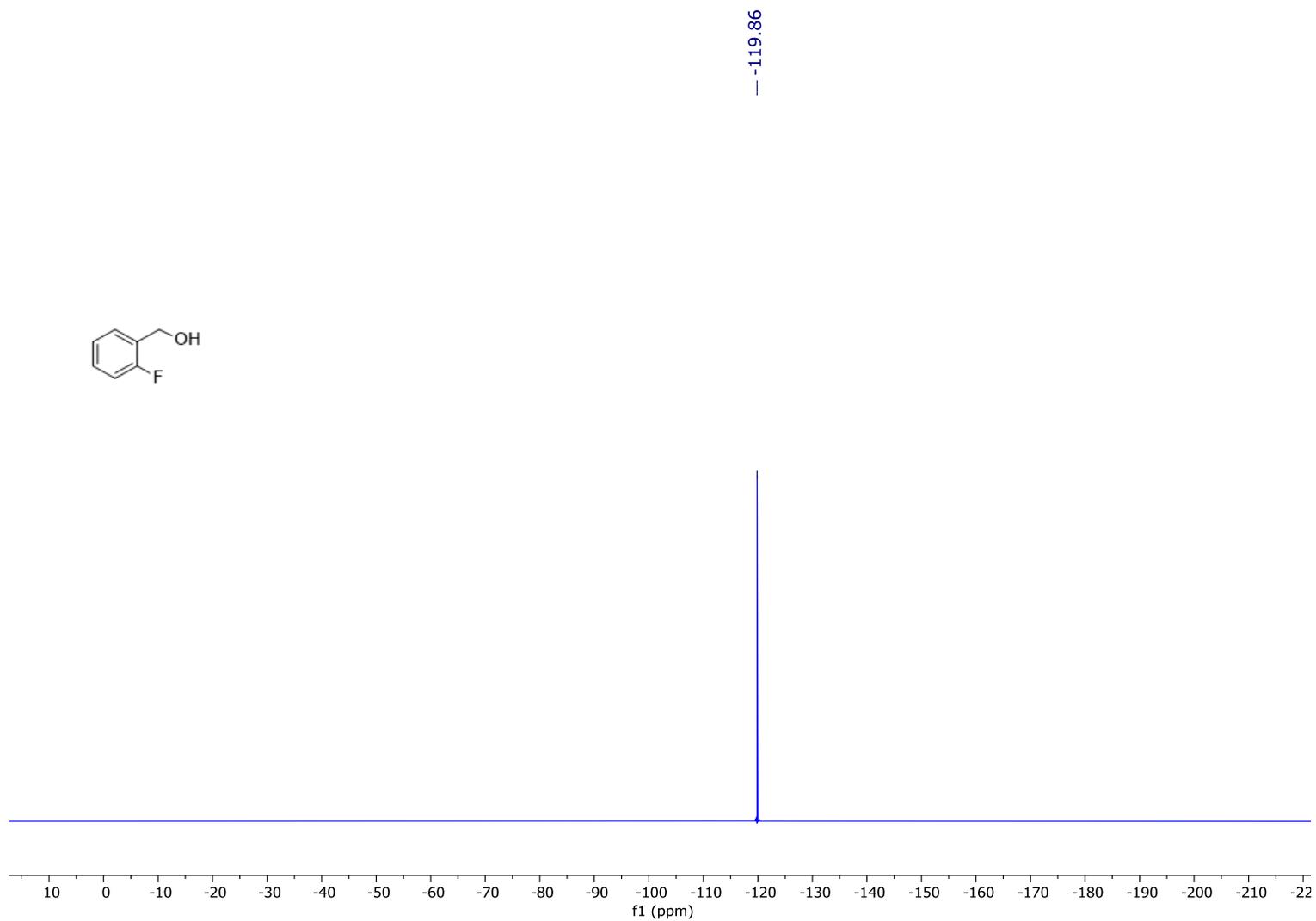


Figure S98: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **b18** in CDCl_3 recorded at 376 MHz.

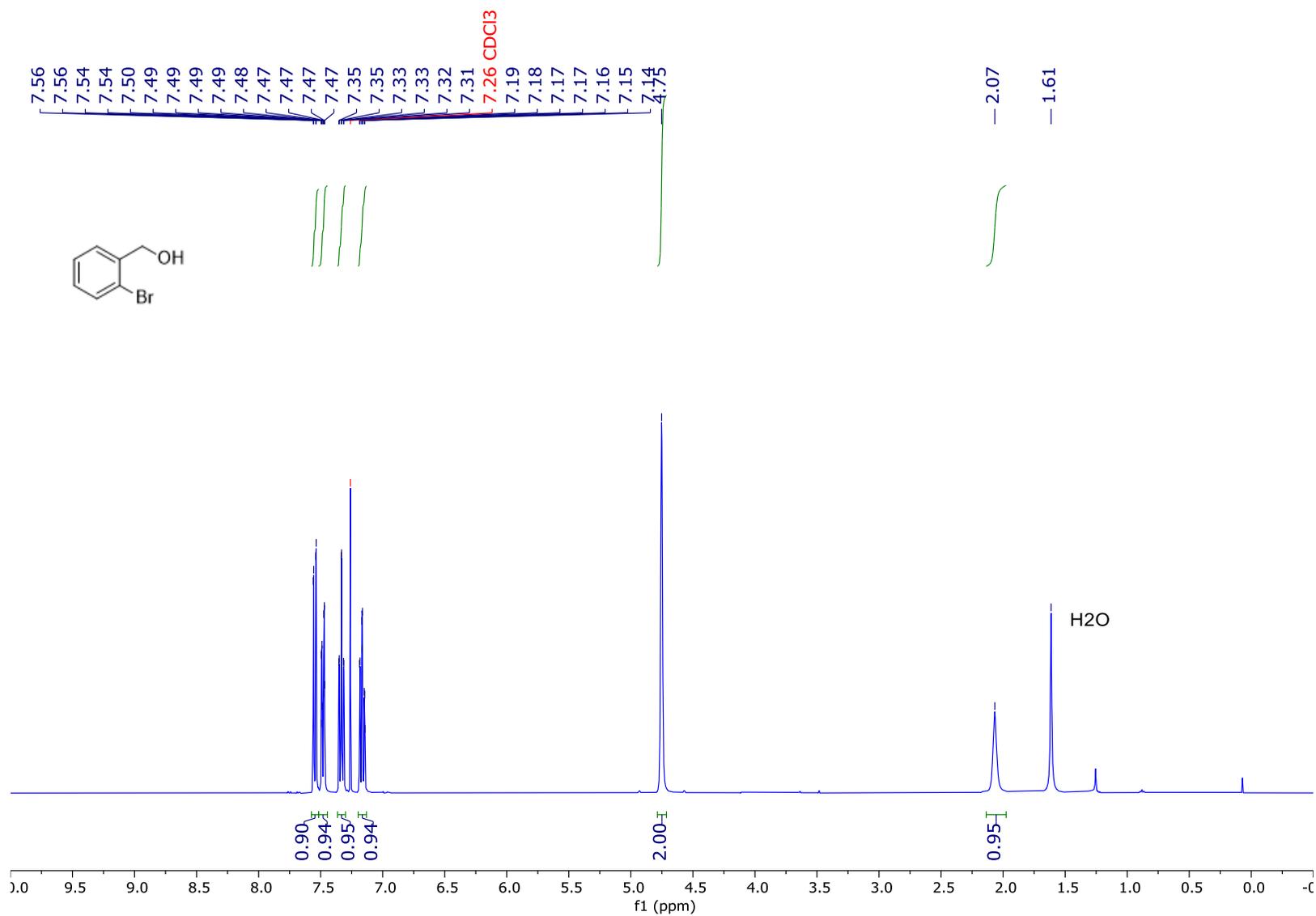


Figure S99: ¹H NMR spectrum of **b19** in CDCl₃ recorded at 400 MHz.

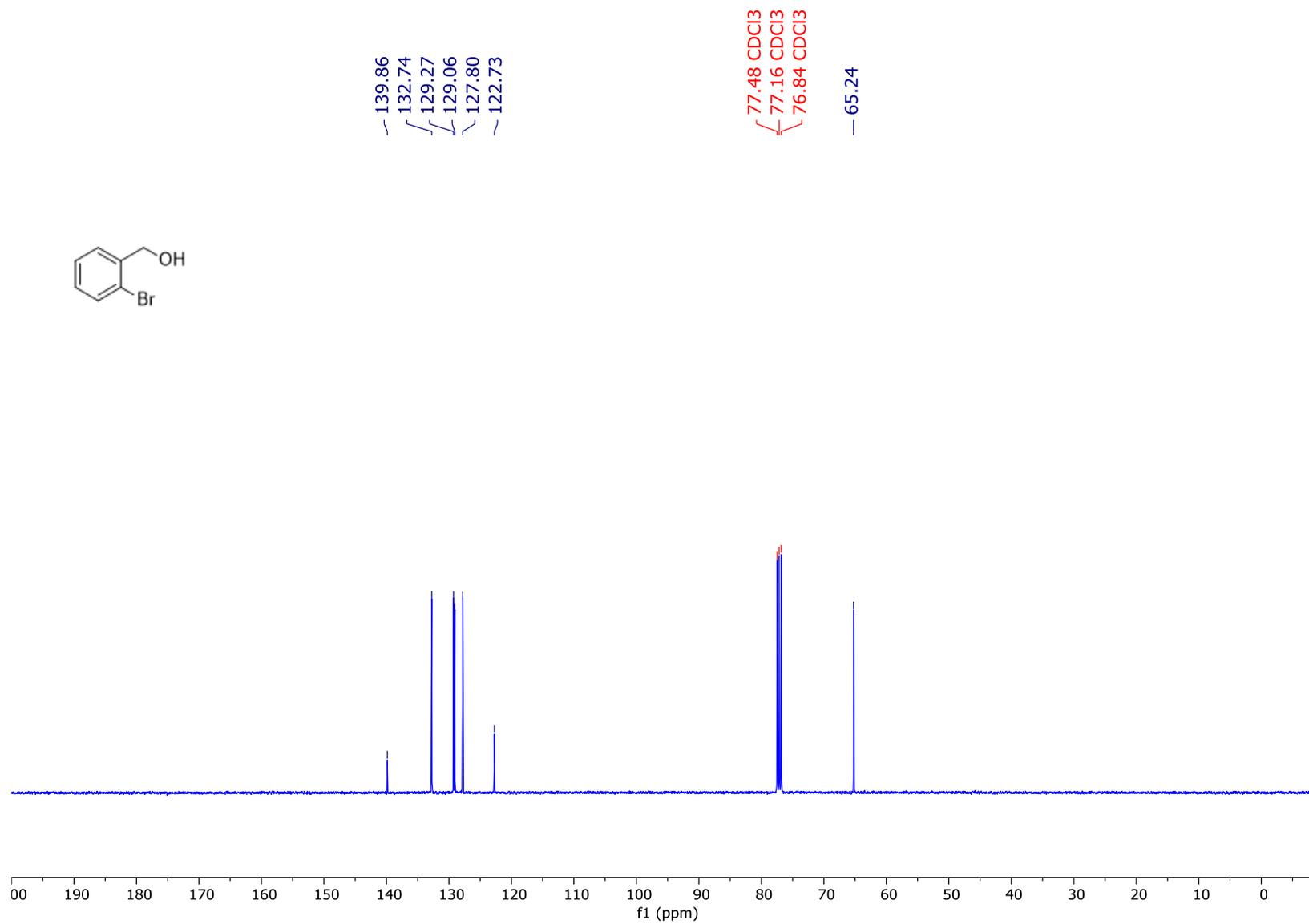


Figure S100: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b19** in CDCl_3 recorded at 101 MHz.

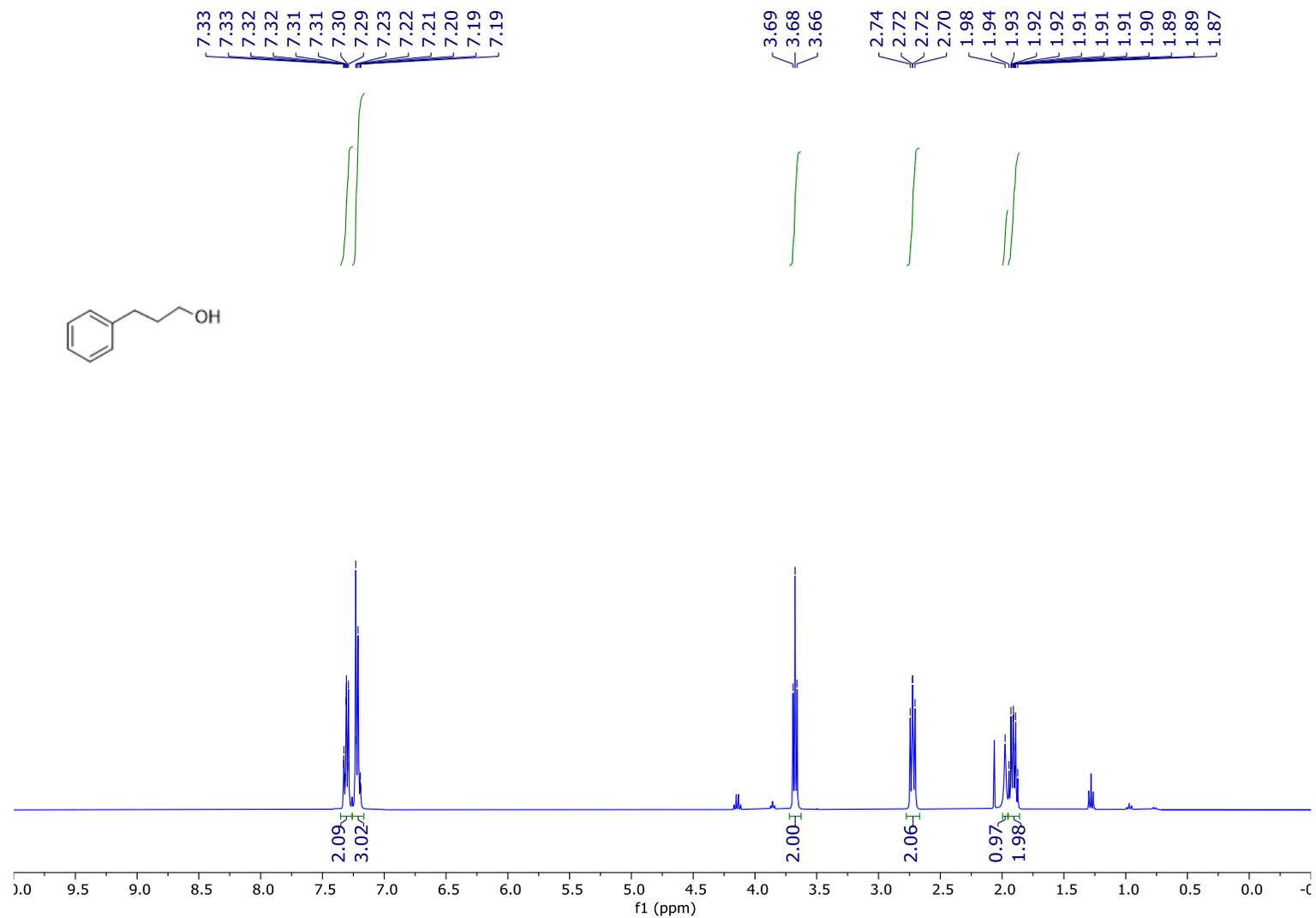


Figure S101: ¹H NMR spectrum of **b20** in CDCl₃ recorded at 400 MHz.

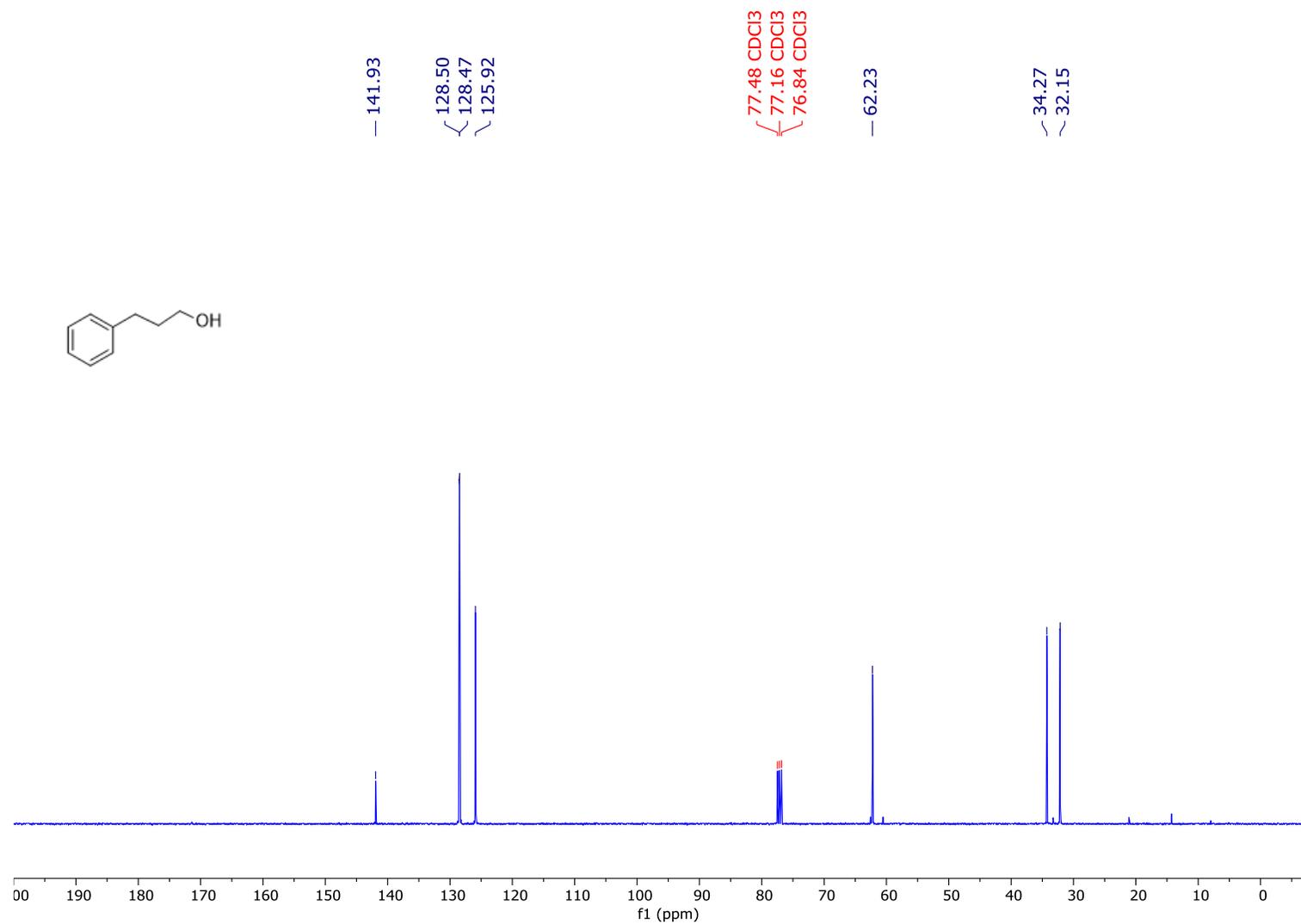


Figure S102: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b20** in CDCl_3 recorded at 101 MHz.

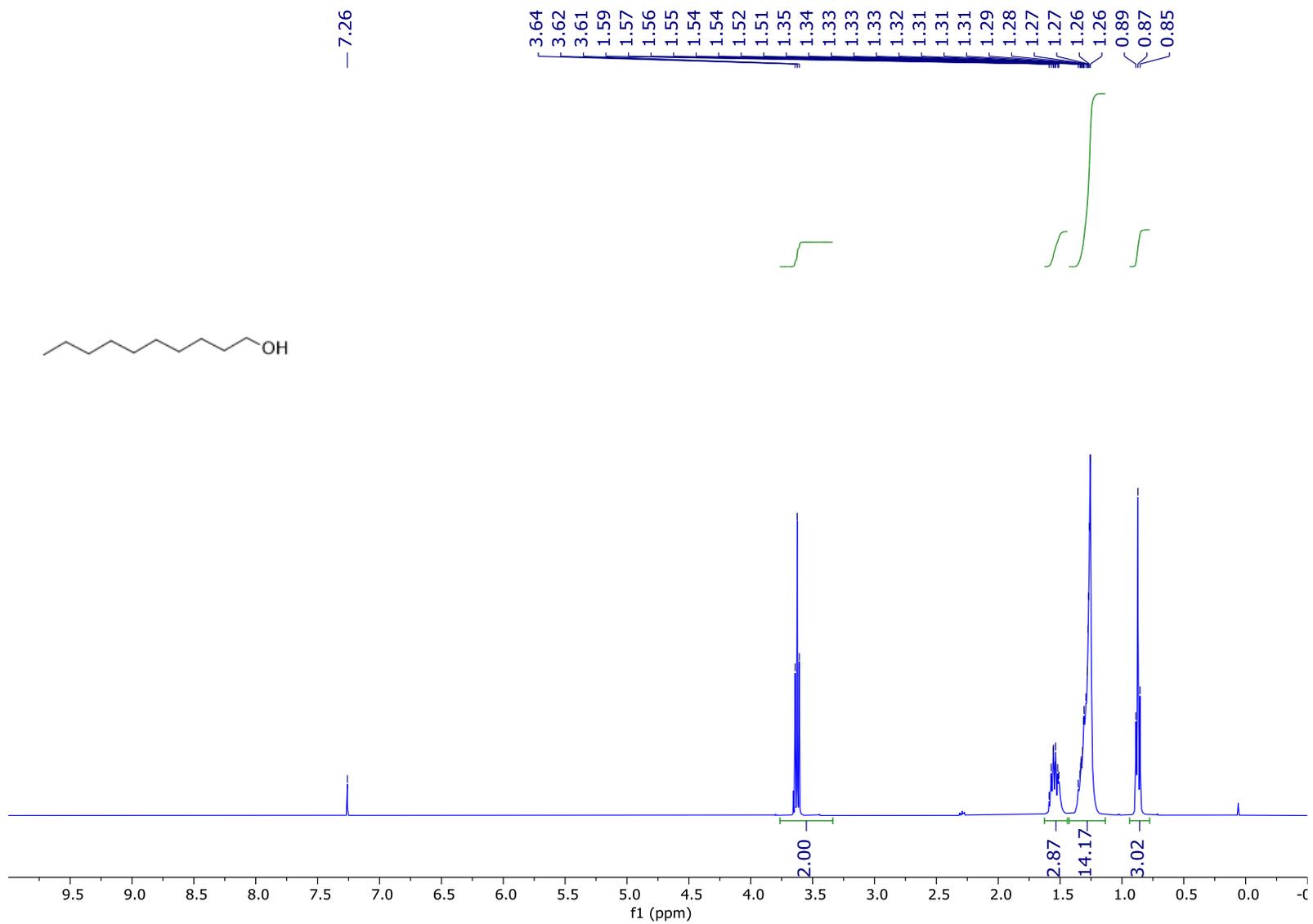


Figure S103: ¹H NMR spectrum of **b21** in CDCl₃ recorded at 400 MHz.

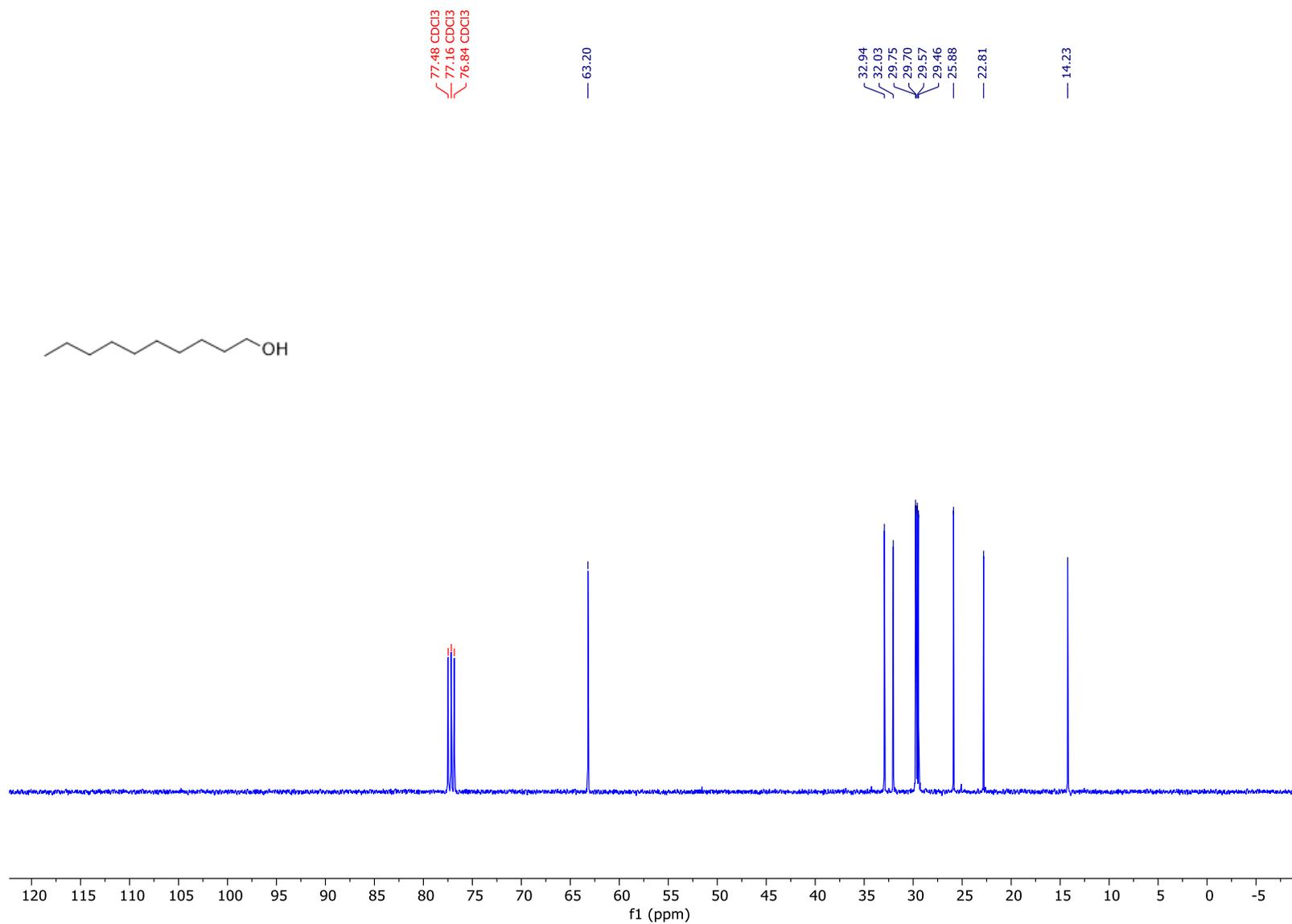


Figure S104: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b21** in CDCl_3 recorded at 101 MHz.

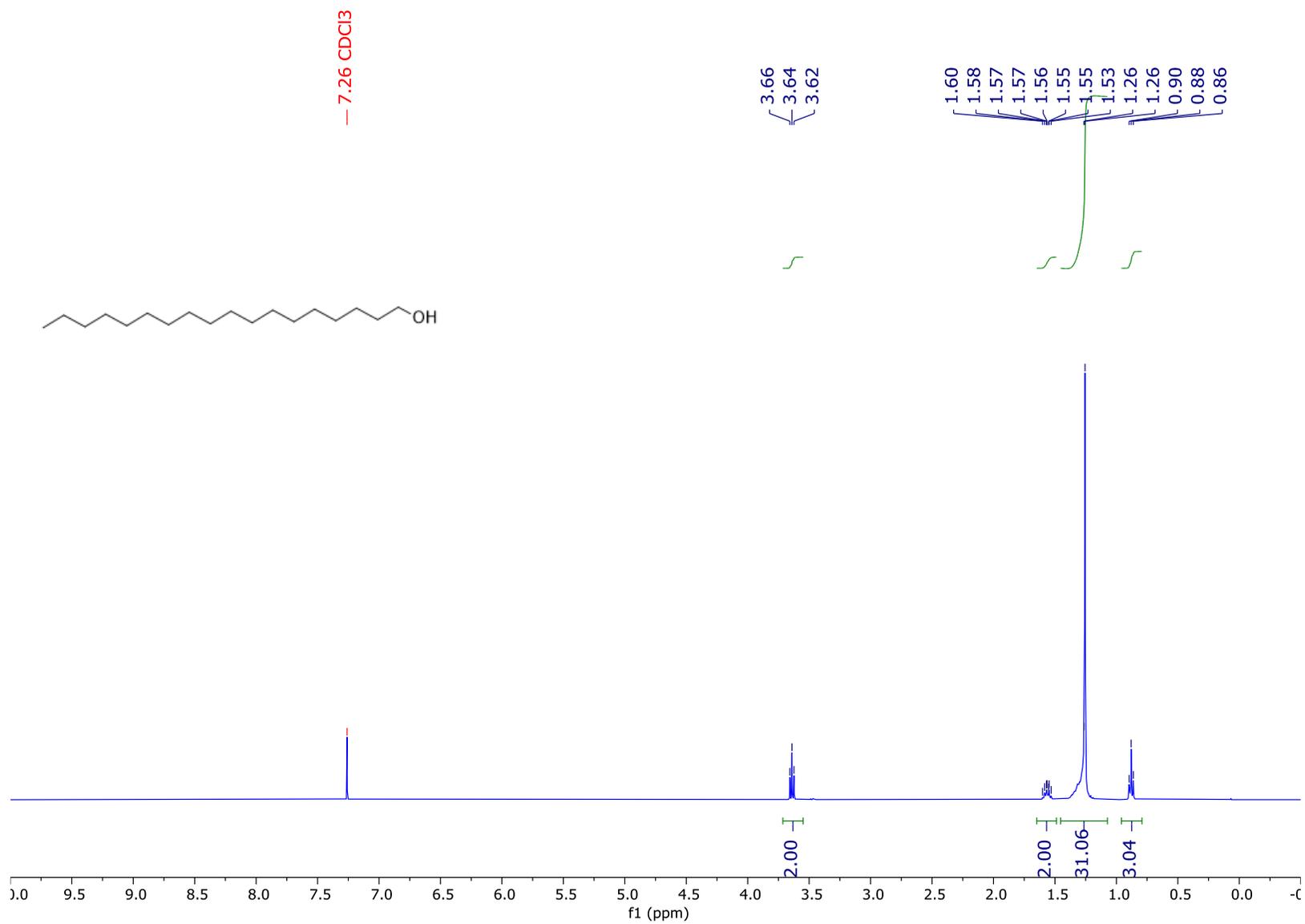


Figure S105: ^1H NMR spectrum of **b22** in CDCl_3 recorded at 400 MHz.

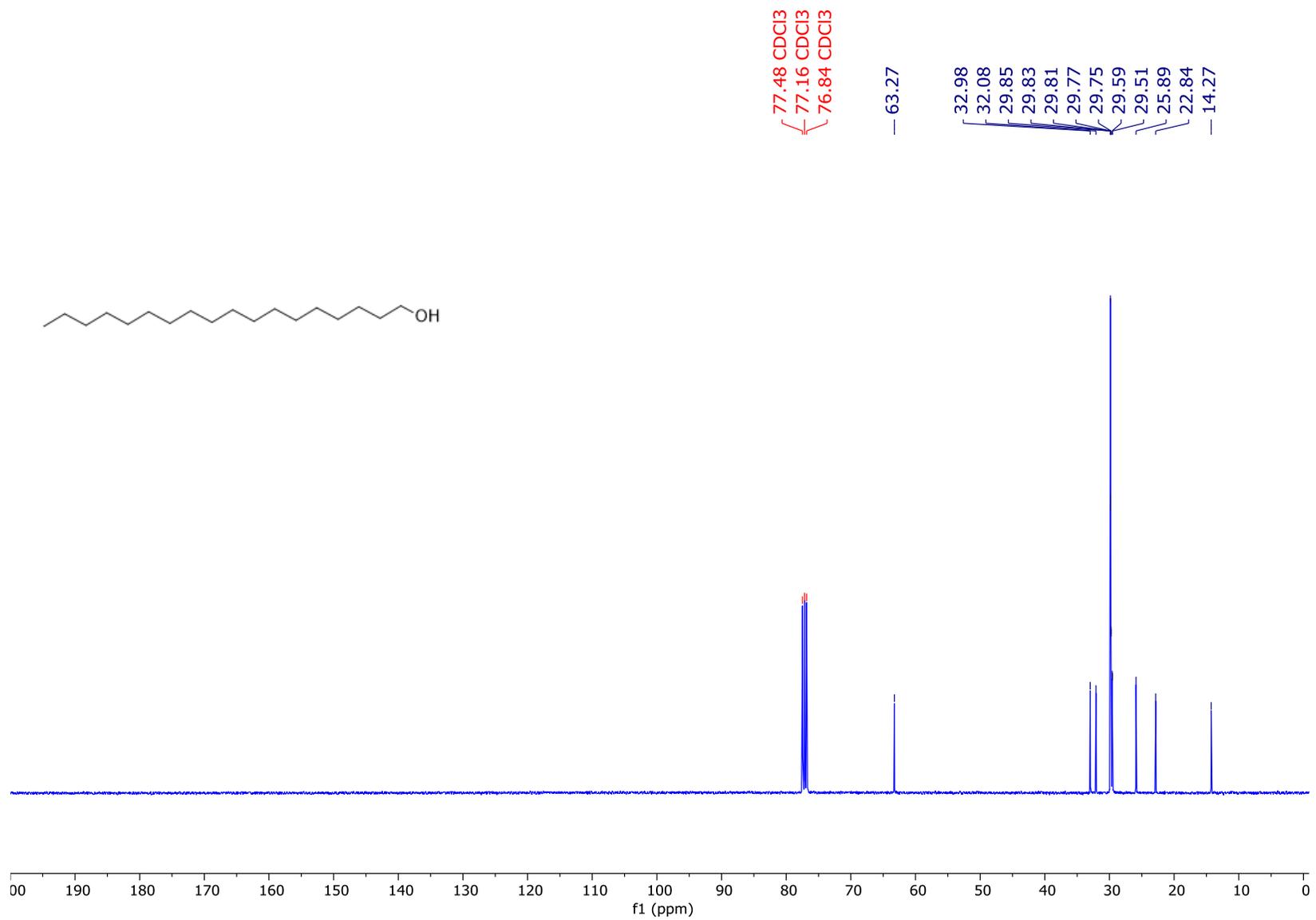


Figure S106: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b22** in CDCl_3 recorded at 101 MHz.

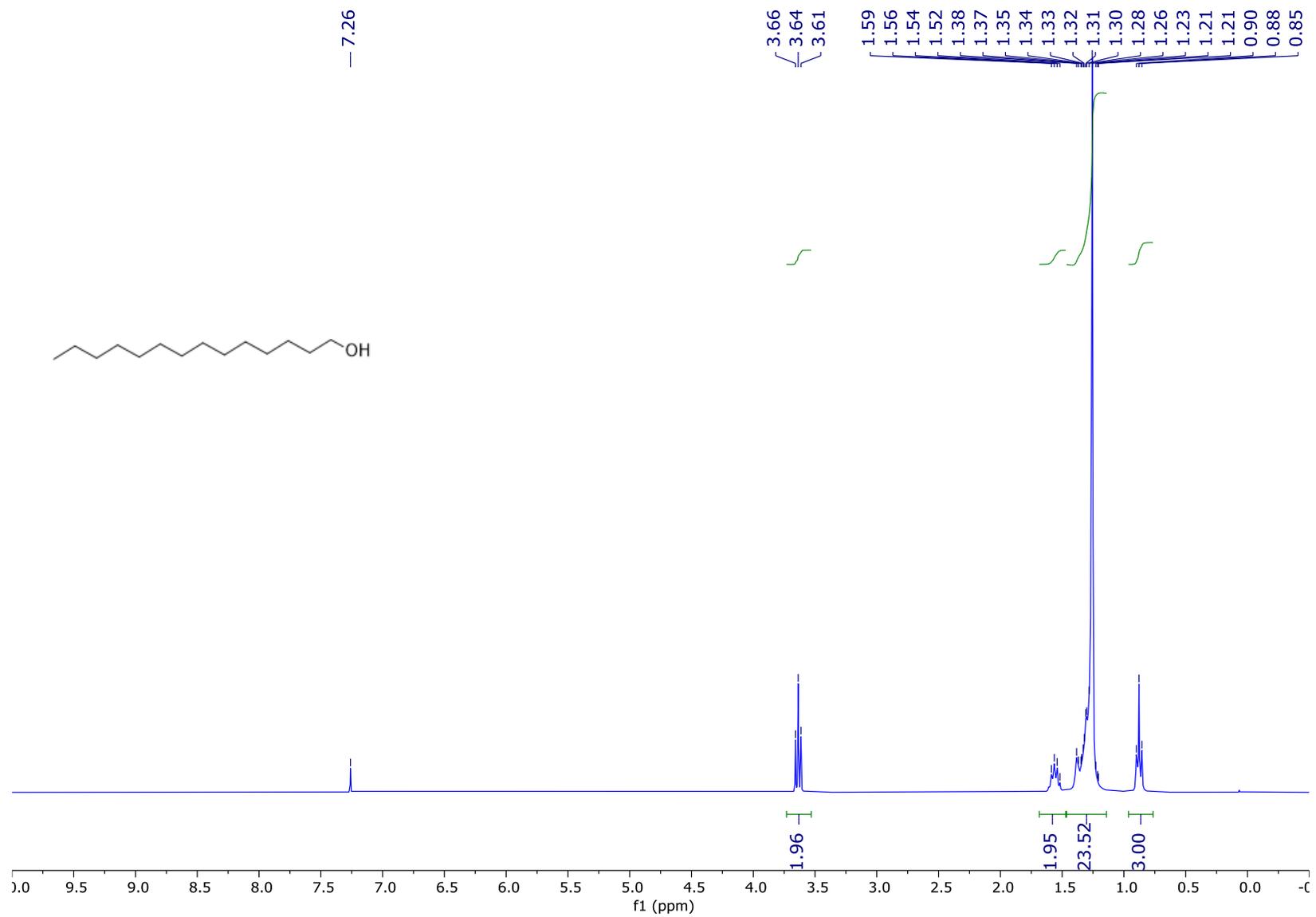


Figure S107: ¹H NMR spectrum of **b23** in CDCl₃ recorded at 300 MHz.

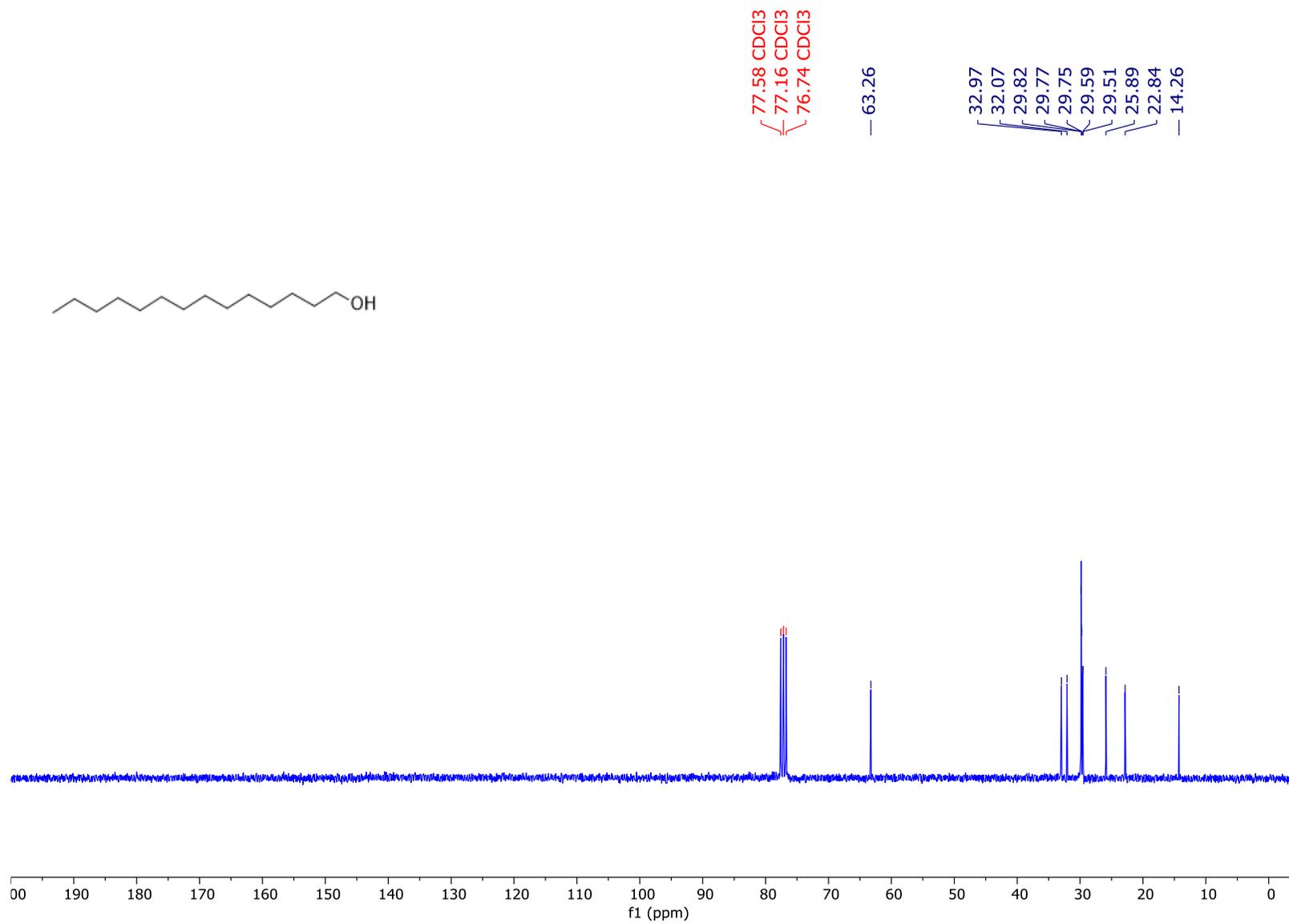


Figure S108: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b23** in CDCl_3 recorded at 75 MHz.

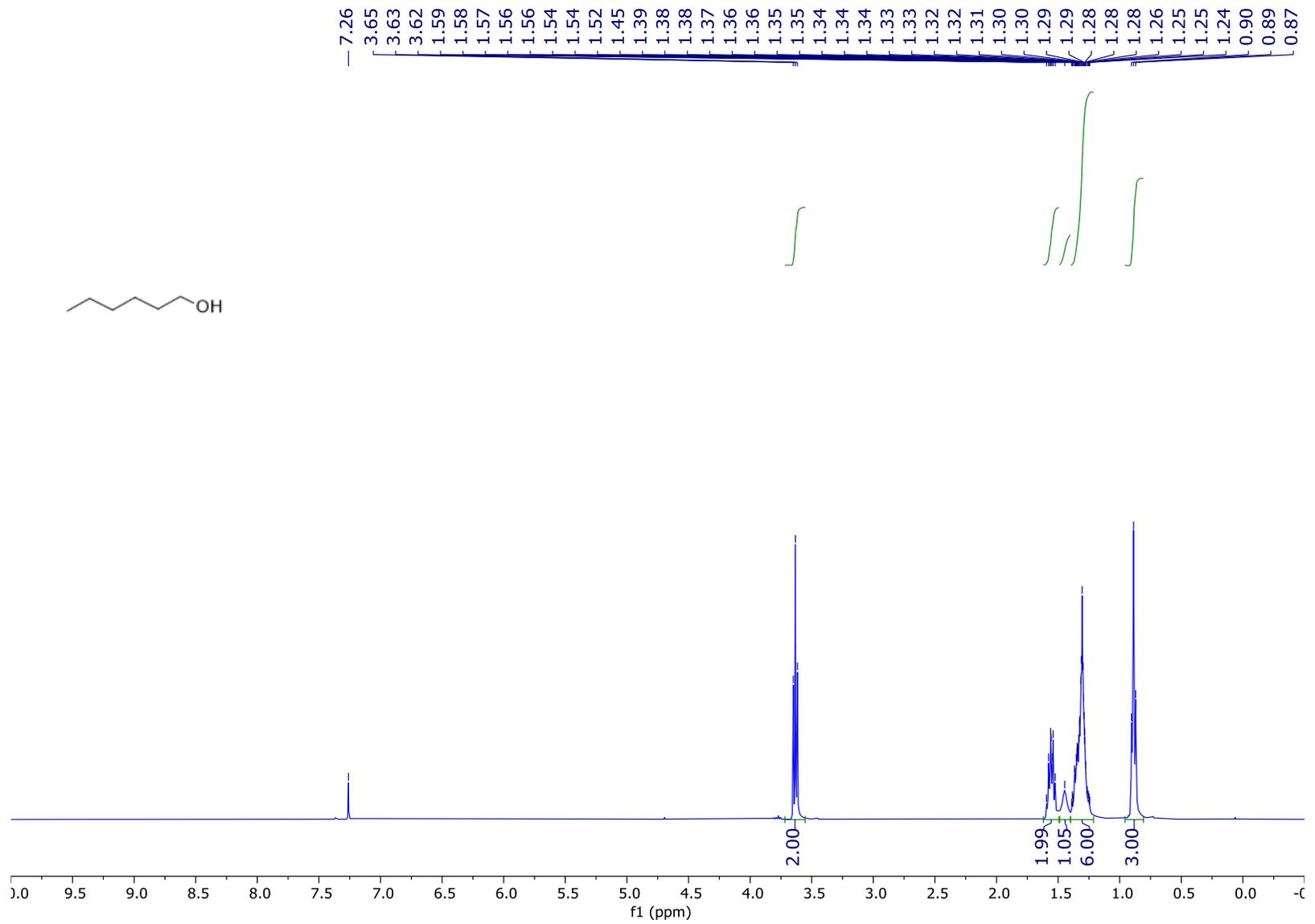


Figure S109: ¹H NMR spectrum of **b24** in CDCl₃ recorded at 400 MHz.

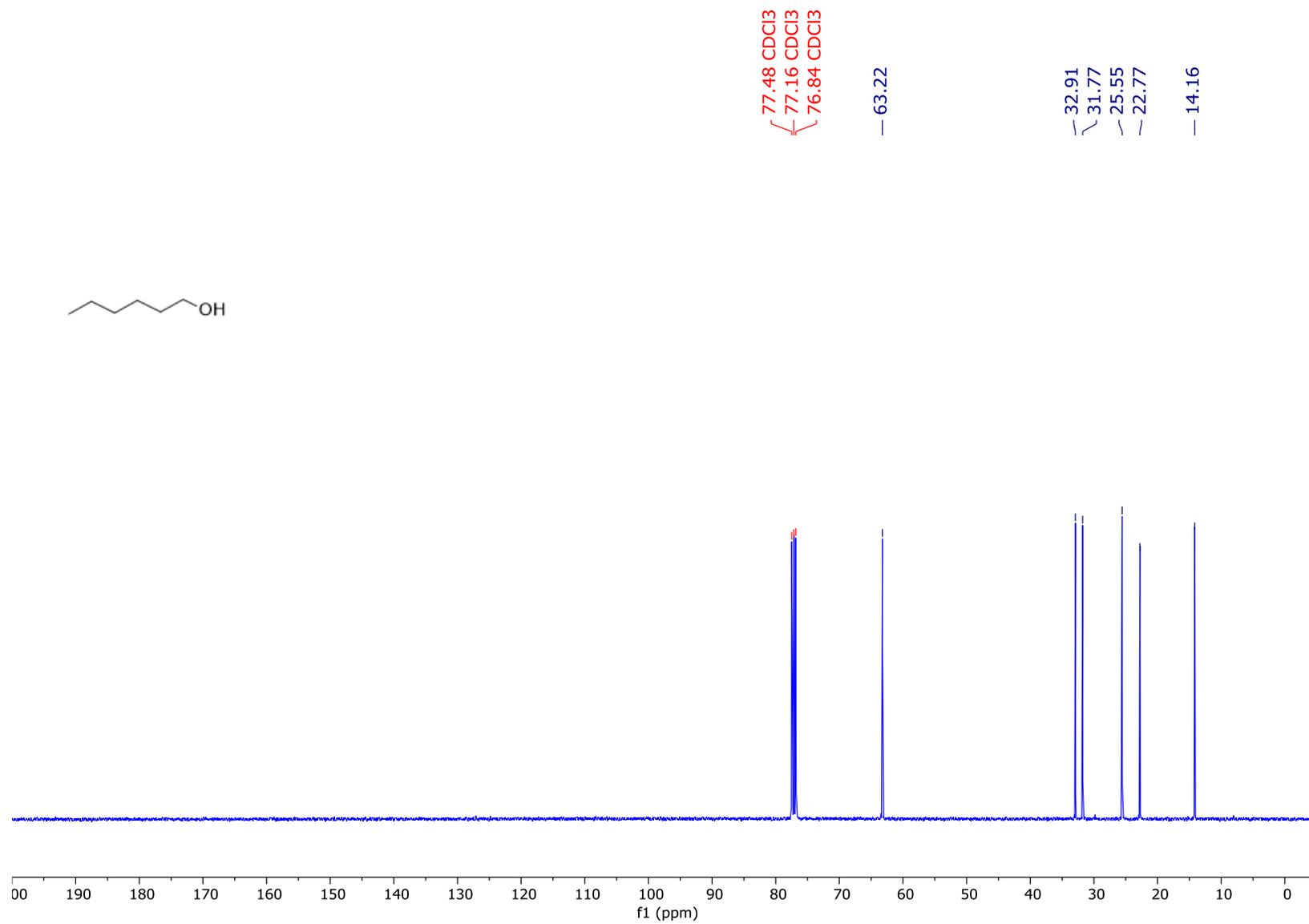


Figure S110: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b24** in CDCl_3 recorded at 101MHz.

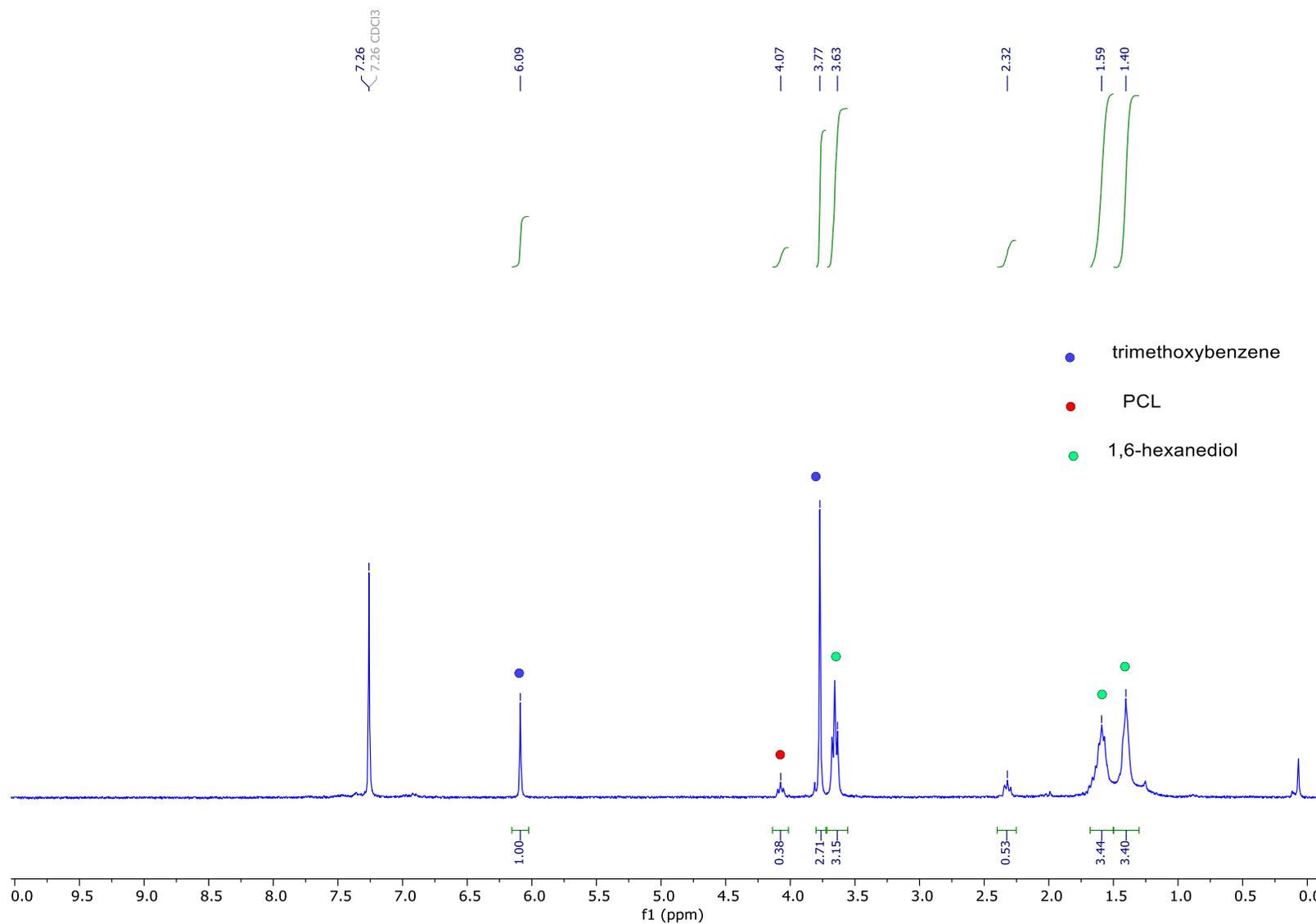


Figure S111: ¹H NMR spectrum of the crude mixture after hydrogenation of PCL in CDCl₃ recorded at 400 MHz.

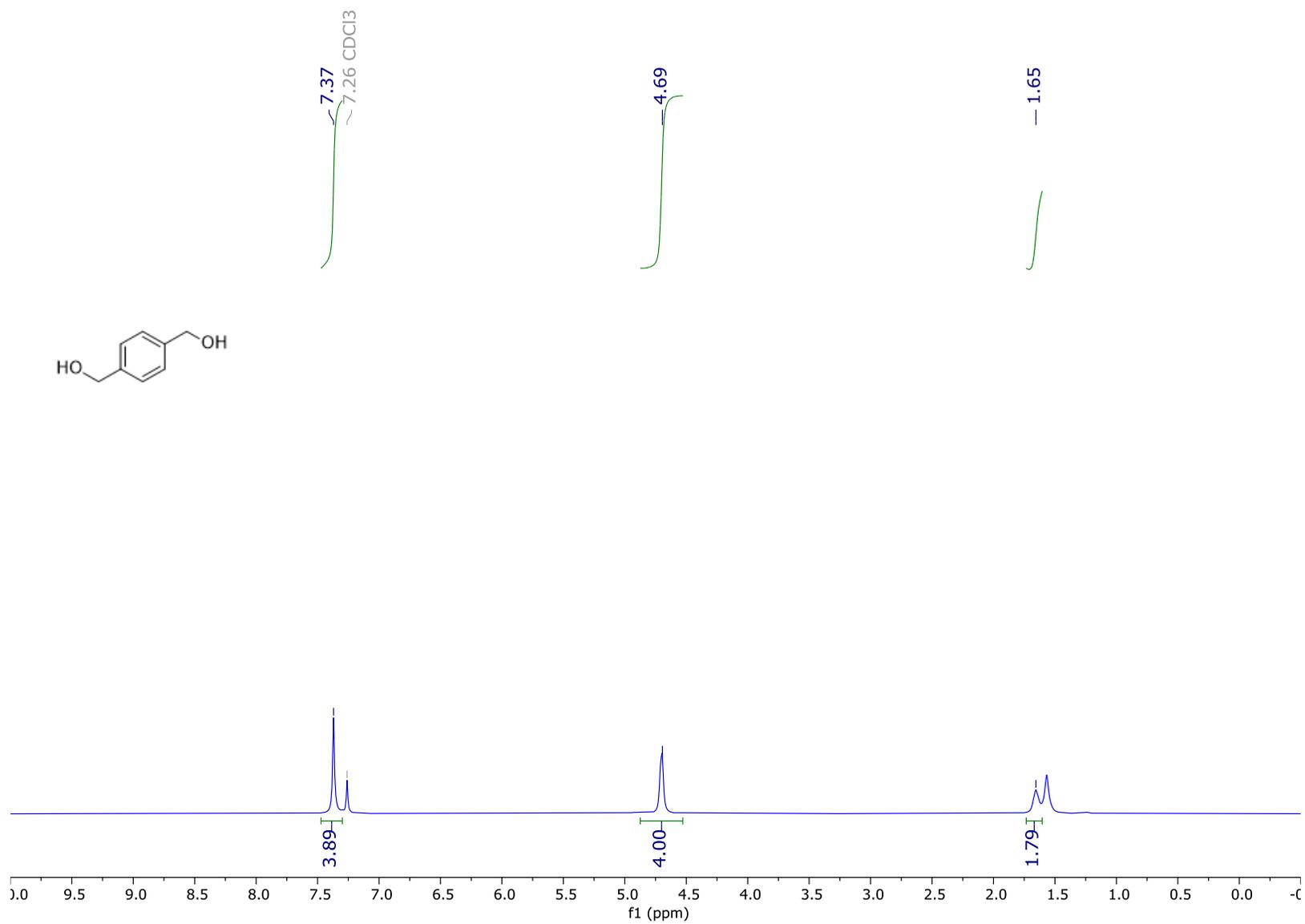


Figure S112: ¹H NMR spectrum of **b25** in CDCl₃ recorded at 300 MHz.

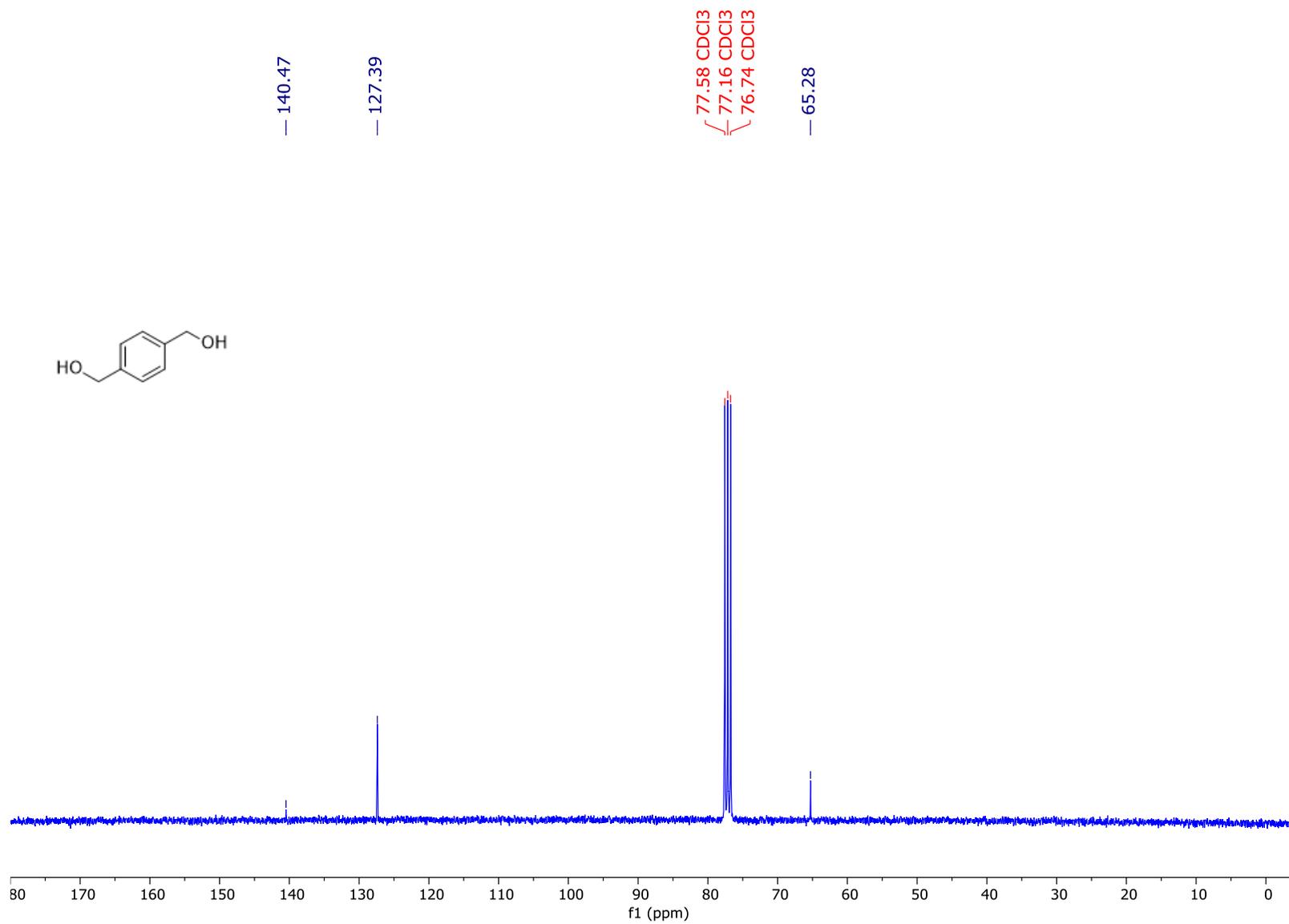


Figure S113: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b25** in CDCl_3 recorded at 75 MHz.

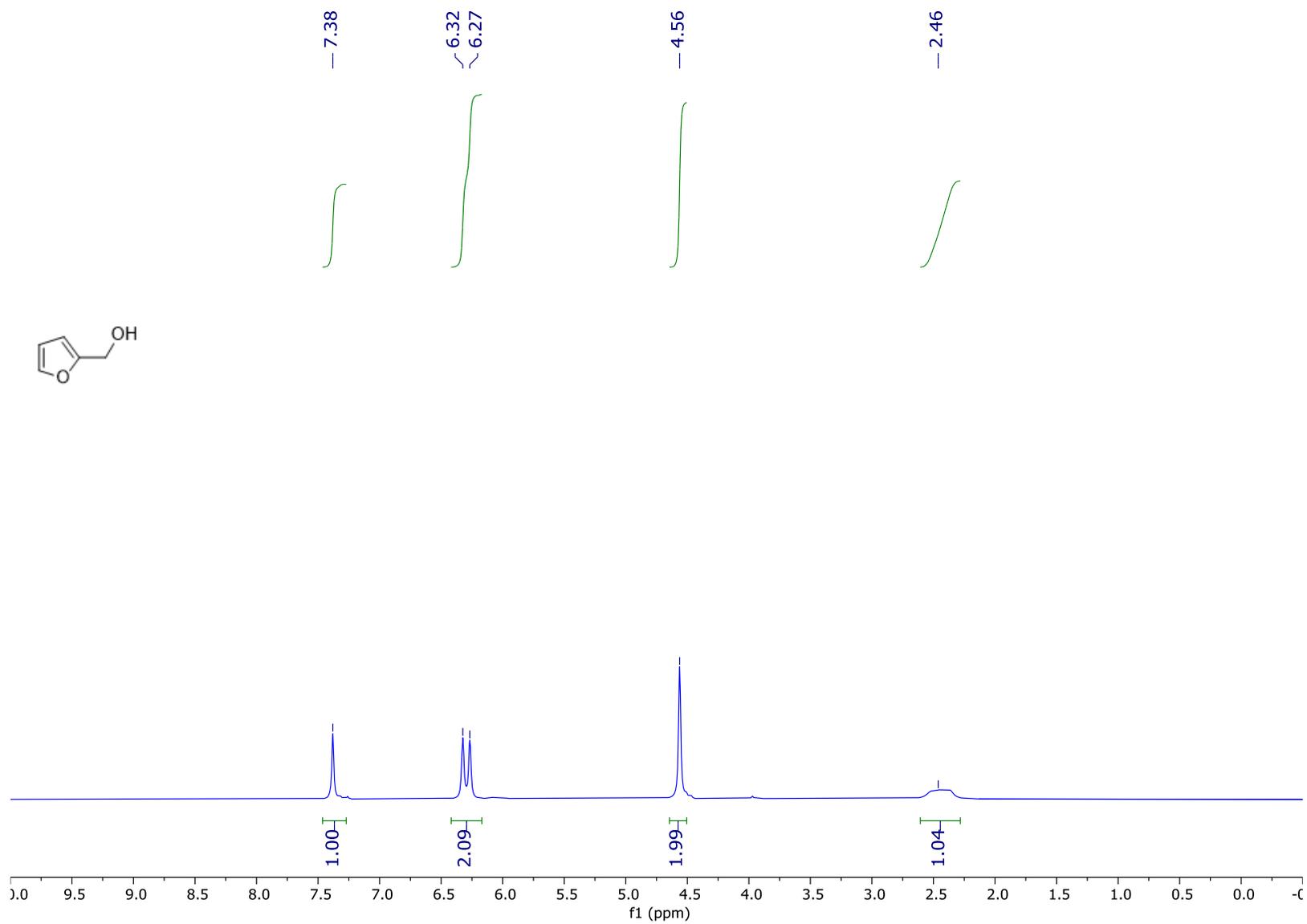


Figure S114: ¹H NMR spectrum of **b27** in CDCl₃ recorded at 400 MHz.

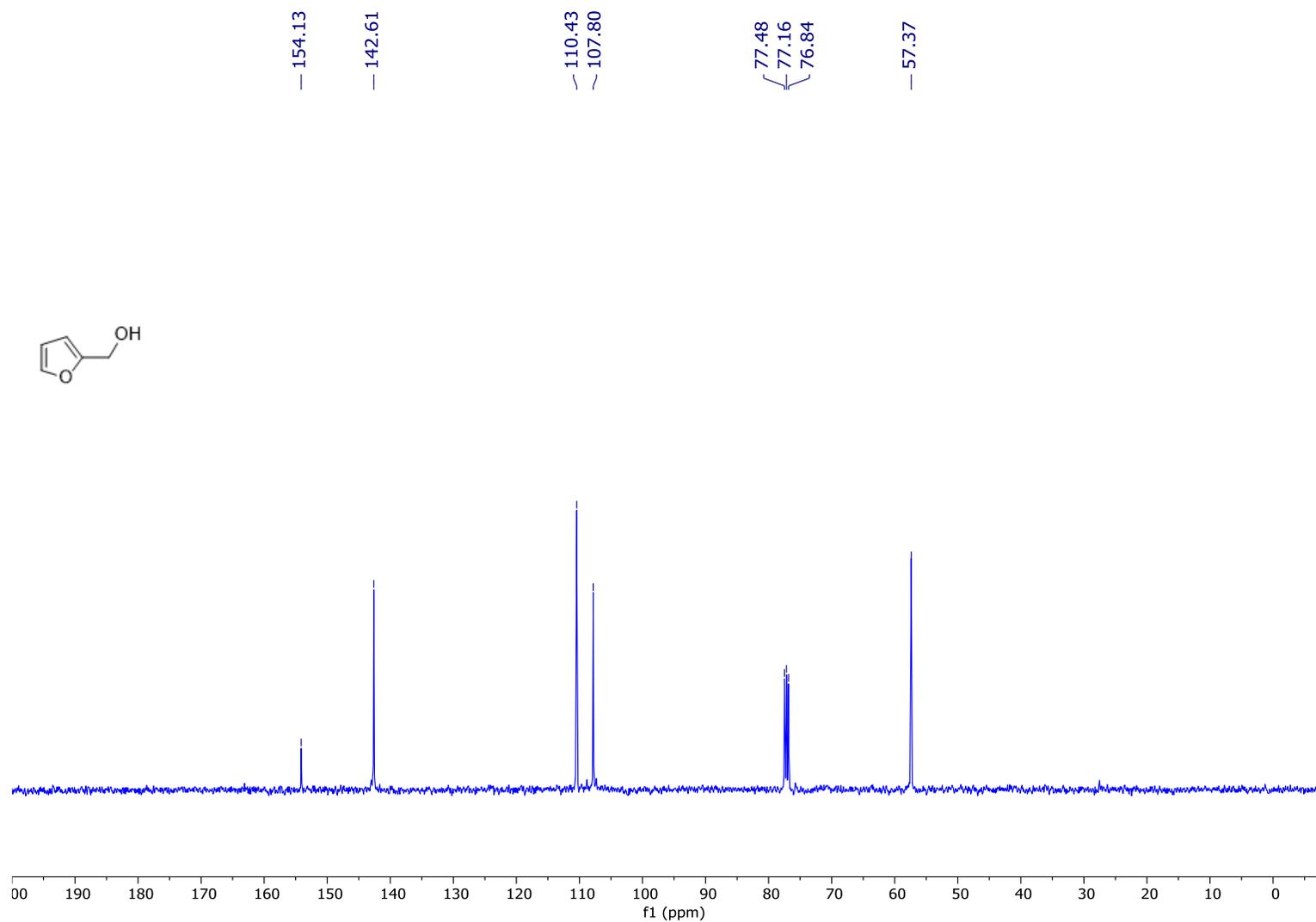


Figure S115: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **b27** in CDCl_3 recorded at 101 MHz.

12. IR spectra of the complexes

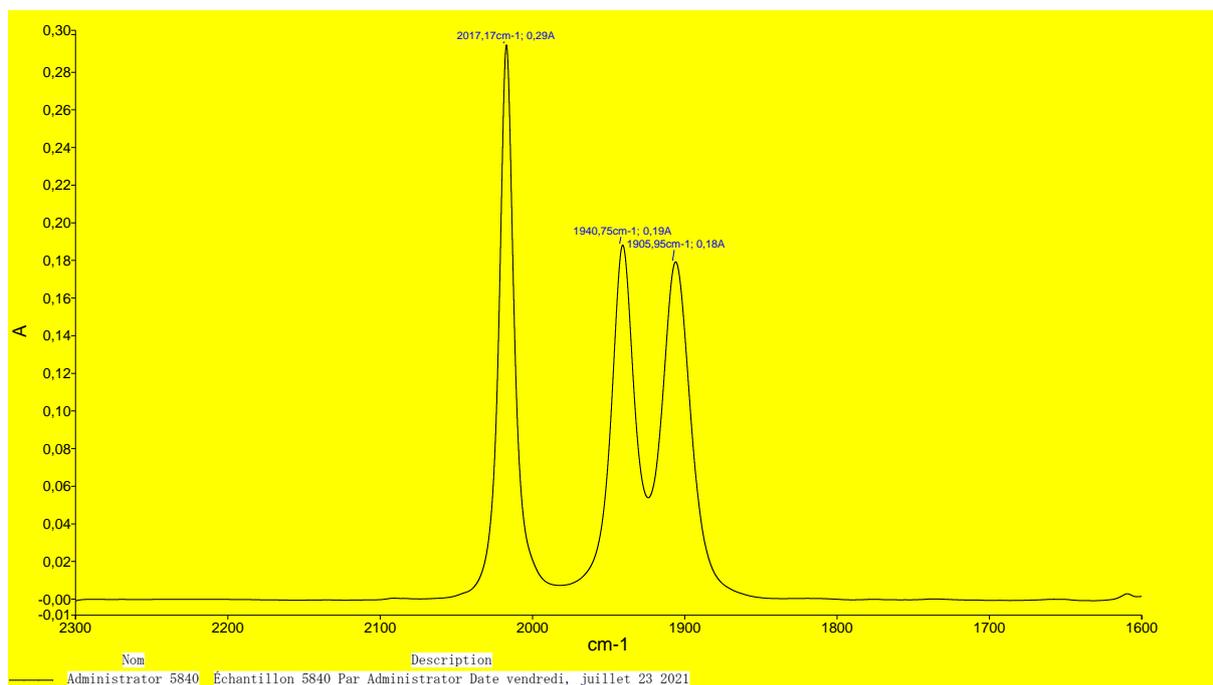


Figure S116: IR spectrum of complex **2** in CH_2Cl_2 .

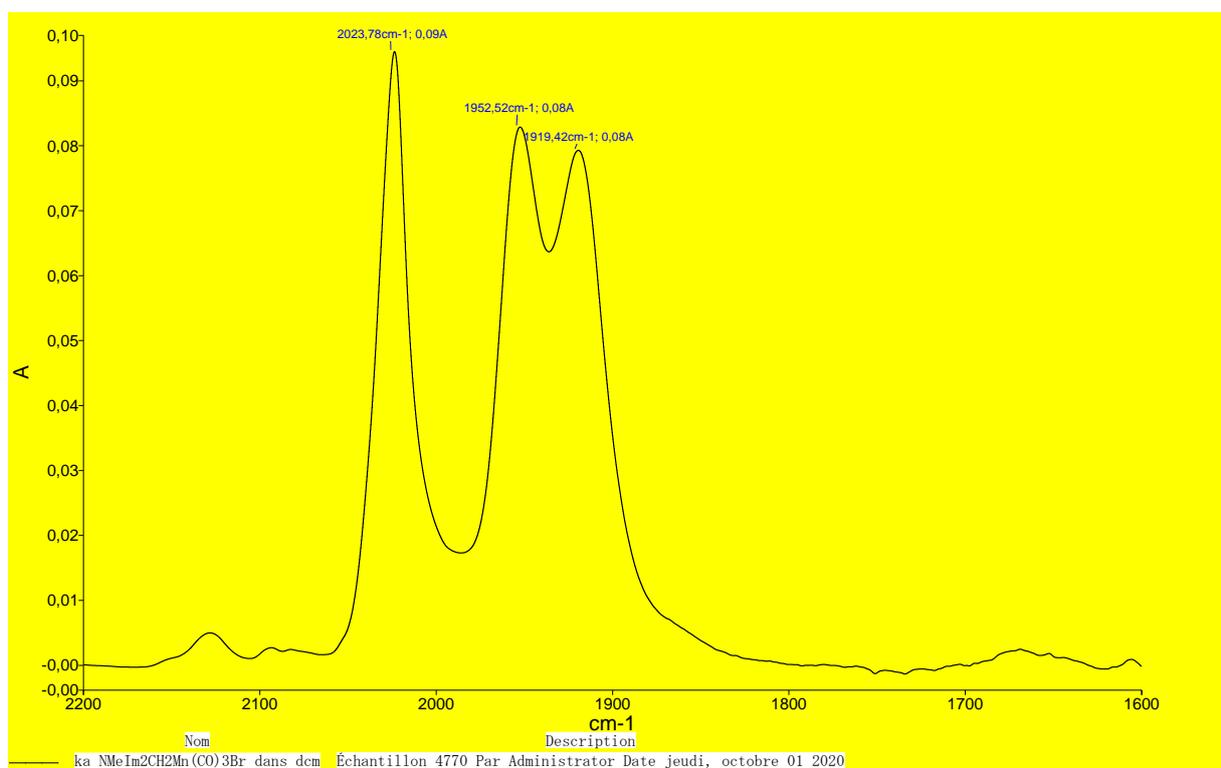


Figure S117: IR spectrum of complex **3** in CH_2Cl_2 .

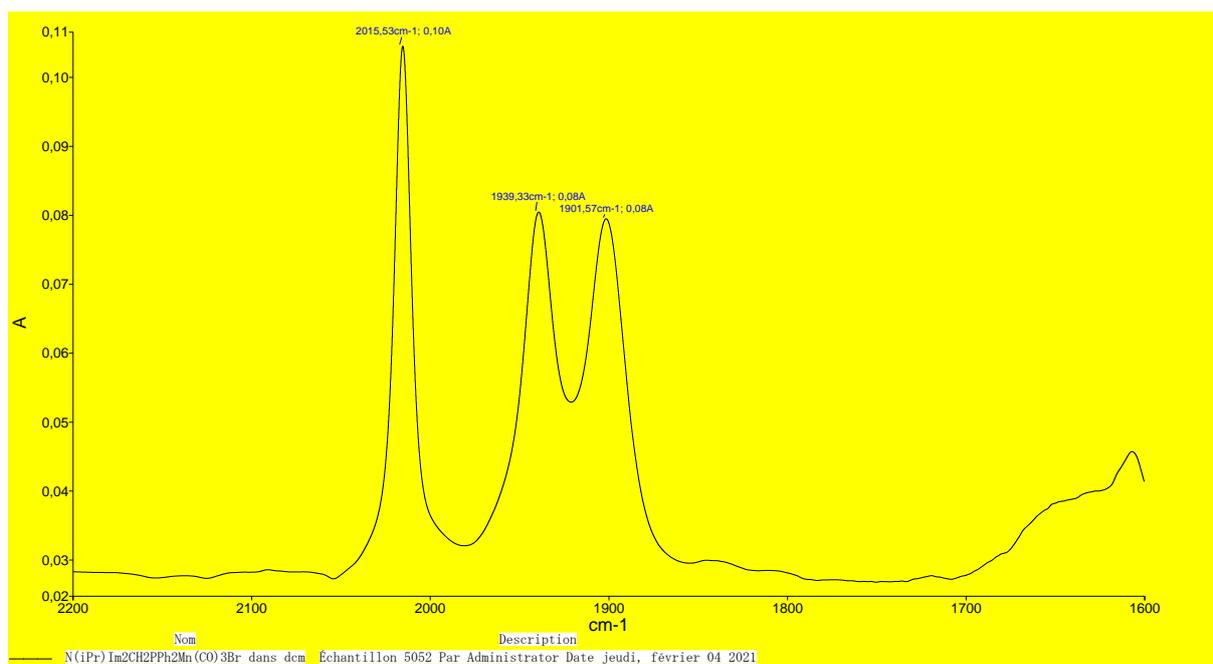


Figure S118: IR spectrum of complex 4 in CH_2Cl_2 .

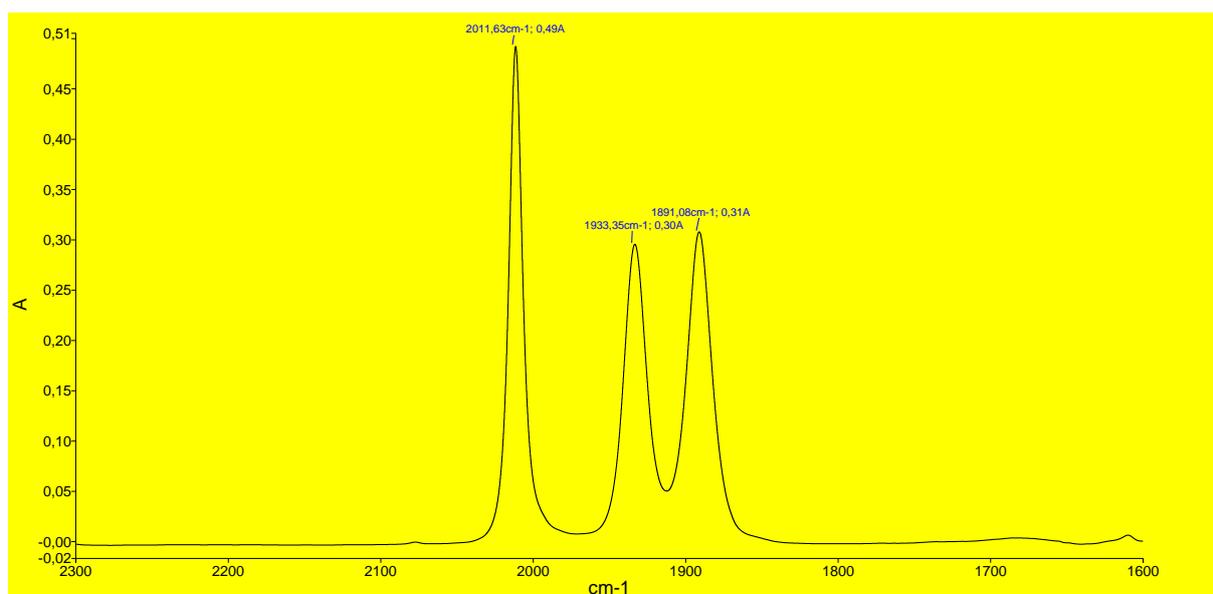


Figure S119: IR spectrum of complex 5 in CH_2Cl_2 .

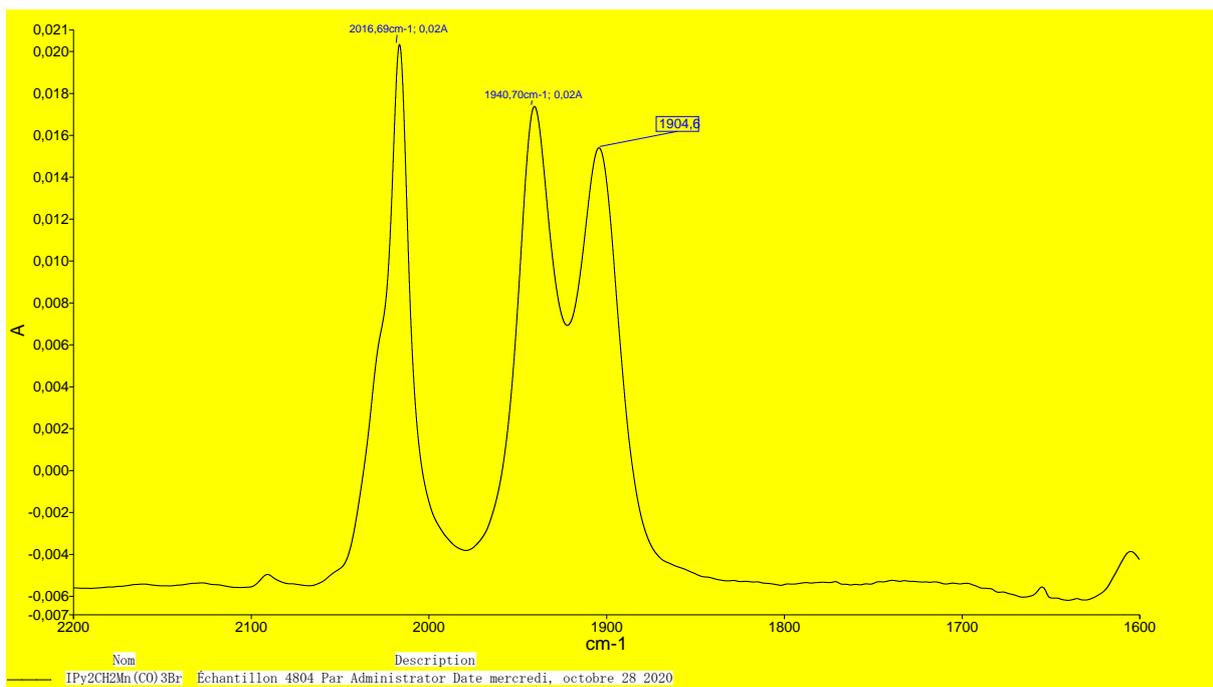


Figure S120: IR spectrum of complex **6** in CH₂Cl₂.

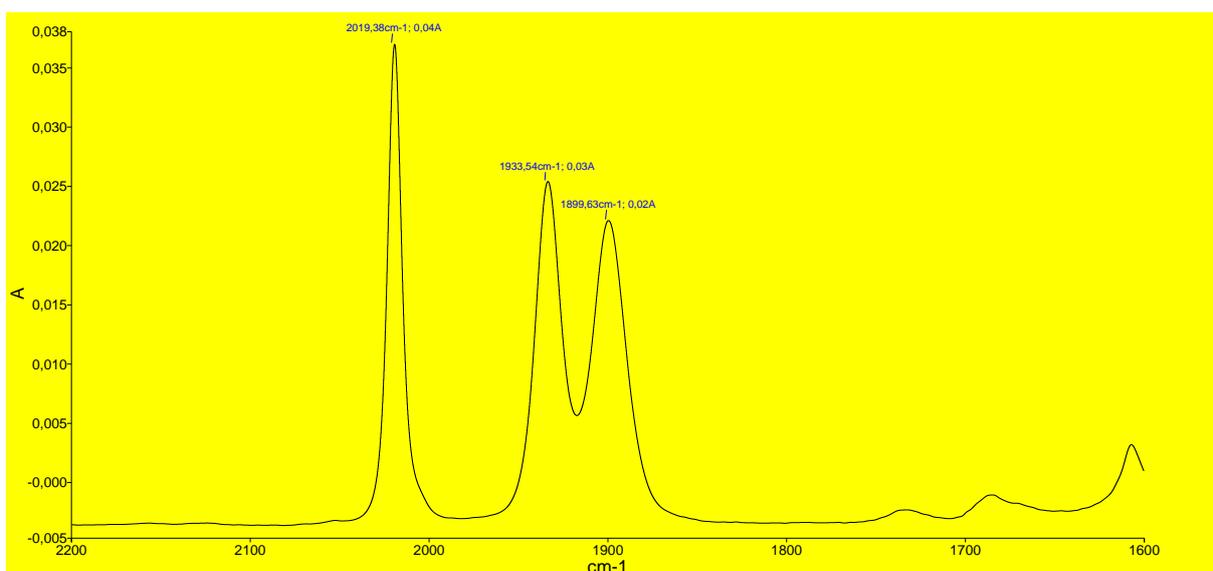


Figure S121: IR spectrum of complex **8** in CH₂Cl₂.

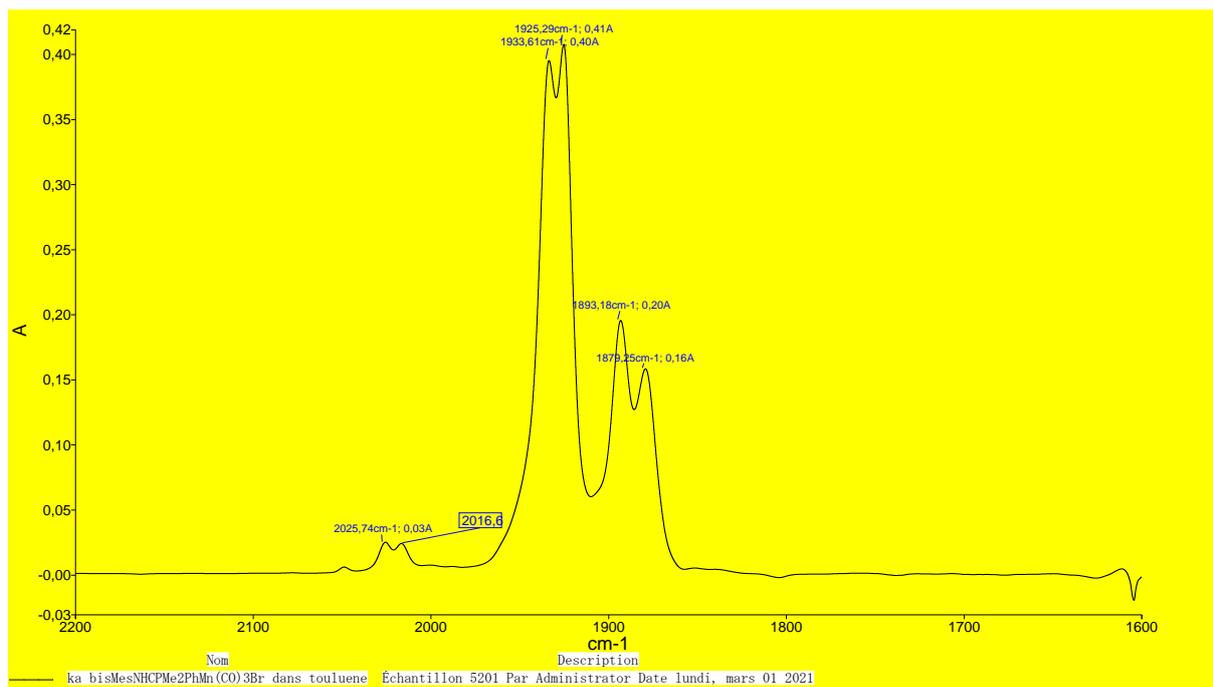


Figure S122: IR spectrum of complex **11** in CH₂Cl₂.

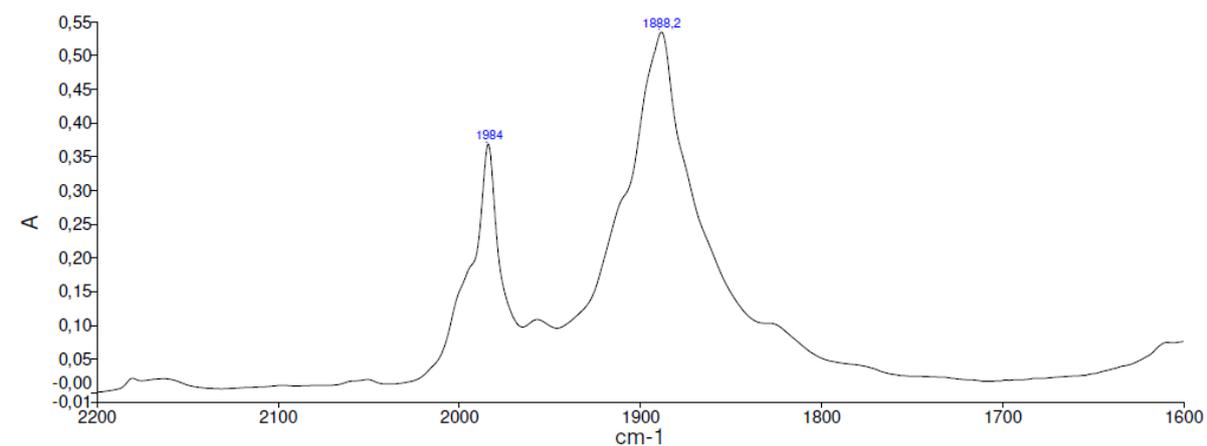


Figure S123: IR spectrum of complex **12** in THF.

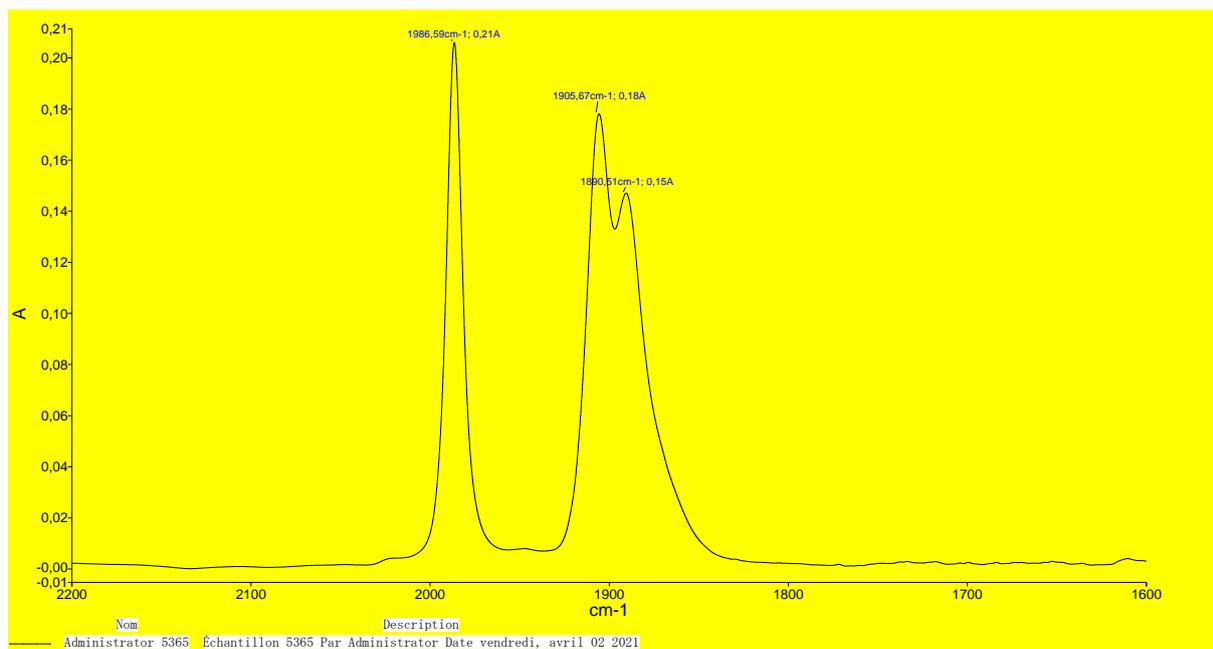


Figure S124: IR spectrum of complex **13** in EtOH.

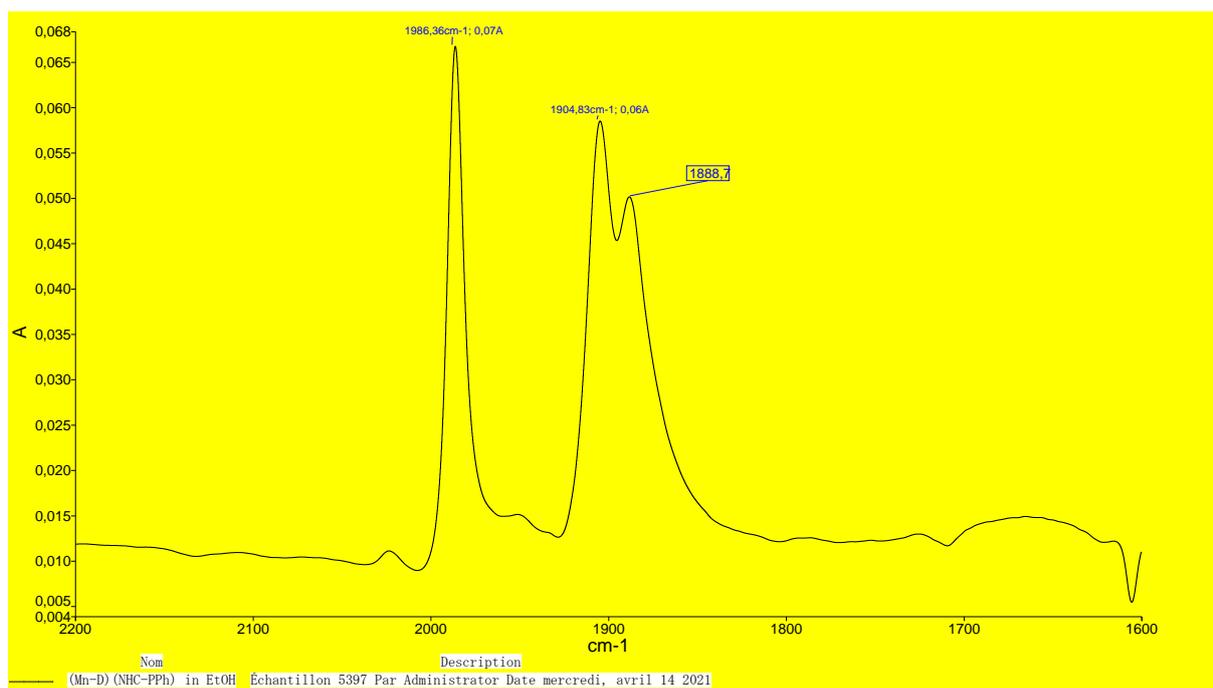


Figure S125: IR spectrum of complex **13-D** in EtOH.

13. References

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