Supporting Information

Overcoming Rigidity: Flexible aliphatic ligand backbones as a standard for the alkoxycarbonylation of alkenes

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1 General Information

All commercial reagents were ordered from Acros Organics, Alfa Aesar, Aldrich, TCI or Strem. Dry solvents were prepared according to standard procedures.[1] Air- and moisturesensitive syntheses were performed under argon atmosphere in heat gun vacuum dried glassware. To transfer reagents standard syringe techniques were used. Non-commercial ligands were prepared according to literature. Dtbpx was purchased from Abcr and was stored and used under Schlenk conditions. 1-Octene was distilled in the presence of sodium under argon. This procedure was used for all olefinic substrates, unless otherwise stated.

NMR spectra were recorded at 25 °C using Bruker Avance 300 (300 MHz) and 400 (400 MHz) NMR spectrometers. Chemical shifts δ (ppm) are given relative to residual solvent peaks: references for $CDCl_3$ were 7.26 ppm (^{1}H-NMR) and 77.16 ppm (^{13}C-NMR) and the references for DCM-d_2 were 5.32 ppm (^{1}H-NMR). Signals were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), and m (multiplet).

GC analyses were measured on an Agilent 7890 A with an HP5 (30 m) or an Agilent 8890 with an HP1 (50 m). Linear to branched ratios were determined by GC analysis of the crude reaction mixture.

1.1 General Procedures

1.1.1 General Procedure of Alkoxycarbonylation of Liquid Olefins (Section A)

A 50 mL schlenk flask was charged with palladium(II) bis(acetylacetonate) (0.04 mol%, 2.44 mg $Pd(acac)_2$), ligand (0.16 mol%), a magnetic stirring bar and MeOH (20 mL). The solution was stirred for at least 10 minutes under argon before *p*-toluenesulfonic acid monohydrate (0.4 mol%, 15.22 mg, $PTSA \cdot H_2O$) and the substrate (20 mmol) were added. The solution was transferred into a cycled 100 mL steel Autoclave via syringe. The autoclave was charged with 30 bar of CO and then heated to 80 °C. After 24 hours the reaction was stopped, and the autoclave was allowed the cool down and reach room temperature before releasing the pressure.

1.1.2 General Procedure of Alkoxycarbonylation of Challenging Liquid Olefins (Section B)

A 50 mL schlenk flask was charged with $Pd(acac)_2$ (0.08 mol%, 4.87 mg), ligand (0.32 mol%, 23.96 mg), a magnetic stirring bar and MeOH (20 mL). The solution was stirred for at least 10 minutes under argon before $PTSA \cdot H_2O$ (0.8 mol%, 30.44 mg) and the substrate (20 mmol) were added. The solution was transferred into a cycled 100 mL steel Autoclave via syringe. The autoclave was charged with 30 bar of CO and then heated to 120 °C. After 24 hours the reaction was stopped, and the autoclave was allowed to cool down and reach room temperature before releasing the pressure.

1.1.3 General Procedure of Alkoxycarbonylation of Liquid Olefins with a Short Reaction Time

A 50 mL schlenk flask was charged with $Pd(acac)_2$ (0.04 mol%, 2.44 mg), ligand (0.16 mol%), a magnetic stirring bar and MeOH (20 mL). The solution was stirred for at least 10 minutes under argon before $PTSA \cdot H_2O$ (0.4 mol%, 15.22 mg) and the substrate (20 mmol, 2.24 g, 3.14 mL) were added. At the same time, a placeholder autoclave was used to heat the metal block to the reaction temperature to keep the preheating period to a minimum. The solution was transferred into a cycled 100 mL steel Autoclave via syringe. The autoclave was charged with 30 bar of CO. Reaction autoclave and placeholder were exchanged for each other and the reaction was started. After 2 hours the reaction was stopped, the autoclave was allowed to cool down and reach room temperature before slowly releasing the pressure.

1.1.4 General Procedure of Alkoxycarbonylation of Ethylene

A 500 mL schlenk flask was charged with $Pd(acac)_2$ (0.00096 mol%, 1.98 mg), ligand (0.0138 mol%, 48.7 mg), a magnetic stirring bar and MeOH (200 mL). The solution was stirred for at least 10 minutes under argon before PTSA·H_2O (0.069 mol%, 123.68 mg) was added. The solution was then transferred into a cycled 450 mL steel Autoclave via cannula. The ethylene (682 mmol, 19.1 g) was then fed into the autoclave before the autoclave was charged with CO to gain a total pressure of 50 bar. The reaction temperature was then set to 80 °C for 48 hours. After the reaction was completed, the pressure slowly and carefully released.

1.1.5 General Procedure of Alkoxycarbonylation of 1-Butene

A 50 mL schlenk flask was charged with $Pd(acac)_2$ (0.04 mol%, 2.44 mg), ligand (0.16 mol%, 11.98 mg), a magnetic stirring bar and MeOH (20 mL). The solution was stirred for at least 10 minutes under argon before PTSA·H_2O (0.4 mol%, 15.22 mg) was added. Eventually, the solution was transferred via syringe into the cycled 100 mL steel autoclave.

1-Butene was added to the autoclave via recondensation from a weighed-out storage vessel using an IPA/dry ice bath. The autoclave was allowed to reach room temperature before charging it with 30 bar of CO and heating to 120 °C. After the reaction was completed, the autoclave was allowed to cool down and reach room temperature before releasing the pressure slowly.

1.1.6 General Procedure 1 for Isolation of the Products

To isolate the desired ester from the reaction mixture, the solvent was first removed using a rotary evaporator. The residue was then taken up in *n*-pentane and filtered through celite before the solvent was removed again to afford the product.

1.1.7 General Procedure 2 for Isolation of the Products

To isolate the desired compound, the crude reaction mixture was distilled under vacuum to afford the product. The specific pressures and temperatures for the corresponding products are mentioned below.

1.1.8 Procedure for Kinetic Profiling

A 100 mL schlenk flask was charged with $Pd(acac)_2$ (0.04 mol%, 9.75 mg), ligand (0.16 mol%), a magnetic stirring bar and MeOH (80 mL). The solution was stirred for at least 10 minutes under argon before $PTSA \cdot H_2O$ (0.4 mol%, 60.87 mg) was added. Afterwards the diisobutene (80 mmol, 8.98 g, 12.52 mL) mixture and the internal standard (mesitylene, 4 mL) were added. The solution was then transferred into a cycled 300 mL steel Autoclave via cannula. The autoclave was charged with 30 bar of CO and heated to 120 °C.

To take samples from the autoclave at regular intervals, the stirrer was stopped one minute before sampling. A few drops were then taken from the sampling port and discarded before the next few drops were used for GC analysis. The stirrer was then restarted until the next sampling took place. After 8 hours the reaction was stopped, the autoclave was allowed to cool down and reach room temperature before releasing the pressure slowly.

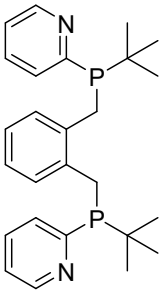
A blind experiment without mesitylene was performed showing no difference in yield compared to one with mesitylene showing the innocence of the chosen internal standard.

1.1.9 Up-Scaling Reaction for TON

Under an argon atmosphere, methyl methacrylate (21.3 mL, 200 mol, MMA) and methanol (190 mL) were added to a 500 mL Schlenk vessel and stirred overnight. $Pd(acac)_2$ (0.016 mmol, 4.87 mg) and **L3** (0.064 mmol, 23.96 mg,) as well as 10 mL methanol were stirred in a separate Schlenk flask. Once everything had dissolved, the contents of the Schlenk flask were added to the 500 mL Schlenk flask and further stirred for 30 minutes. $PTSA \cdot H_2O$ (0.16 mmol, 30.44 mg) was added and stirred for another five minutes. The reaction mixture was then transferred to a 450 mL autoclave under argon via cannula. The reaction mixture was first fed with 30 bar of CO before being heated to 80 °C. The reaction was kept stirring for 22.5 hours. Afterwards, the autoclave was cooled to room temperature and depressurized slowly.

2 Experimental Section

2.1 Synthesis of **L1**

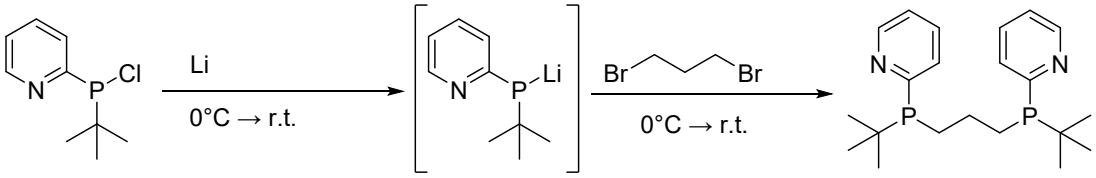


L1 was produced according to literature and the NMR data is in accordance with previously reported analytical values.[2]

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.85 – 8.69 (m, 2H), 7.62 – 7.43 (m, 2H), 7.25 – 7.16 (m, 2H), 7.14 – 7.04 (m, 2H), 6.88 – 6.80 (m, 2H), 6.77 – 6.69 (m, 2H), 4.03 – 3.87 (m, 2H), 3.32 – 3.21 (m, 2H), 1.10 (d, *J* = 11.8 Hz, 9H), 1.06 (d, *J* = 11.8 Hz, 9H).
^{13}C NMR {^{1}H} (75 MHz, CD_2Cl_2) δ 149.5, 134.6, 134.5, 132.6, 132.5, 132.1, 131.9, 125.2, 125.2, 123.0, 122.9, 30.4, 30.2, 27.7, 27.5, 27.3, 25.0, 24.9, 24.8, 24.7.
^{31}P NMR {^{1}H} (122 MHz, CD_2Cl_2) δ = 9.0, 12.0.

2.2 Synthesis routes of **L3**

2.2.1 Optimized synthesis of **L3**



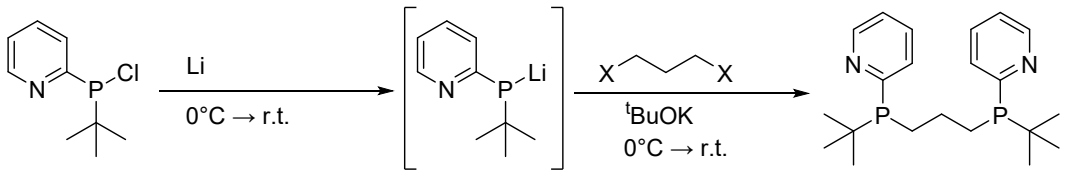
L3
90% yield, brown oil

For production of the material used in this study, the literature known synthesis[3] was adapted and simplified (further modifications can be found in sections **2.2.2.1** and **2.2.2.2**): Lithium (152 mmol, 1.05 g) was added slowly to the solution of 2-(tert-butylchlorophosphanyl)pyridine (60.8 mmol, 11.15 mL) and 10 mL THF under argon at 0 C, the solution slowly changed color from yellow to deep red. The mixture was then stirred for 24 hours at room temperature. The 1,3-dibromopropane (27.6 mmol, 2.89 mL) was then added (slowly) to the mixture at 0 °C under argon and stirred for a further 24 hours. Degassed water (4.0 mL) was added to quench the reaction, and the solvent was removed under vacuum. Degassed water (80 mL) and diethyl ether (200 mL) were added, and the organic phase was separated.

The aqueous phase was extracted three times with diethyl ether (3×40 mL) and the combined organic phases were dried over magnesium sulfate anhydrous, filtered and the solvent was removed under reduced pressure to afford the ligand as brown oil. The ligand was then dried azeotropically. To do this, the ligand was dissolved in toluene (40 mL). The solvent was removed in vacuo (9.25 mg, 90% yield).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.69 – 8.60 (m, 2H), 7.60 – 7.51 (m, 2H), 7.50 – 7.43 (m, 2H), 7.21 – 7.10 (m, 2H), 2.56 – 2.32 (m, 2H), 1.72 – 1.44 (m, 4H), 0.98 (d, *J* = 11.6 Hz, 9H), 0.94 (d, *J* = 11.5 Hz, 9H).
^{13}C NMR {^{1}H} (75 MHz, CD_2Cl_2) δ = 22.4, 22.5, 22.6, 22.7, 22.7, 22.9, 24.3, 24.4, 24.5, 24.6, 24.7, 24.8, 27.8, 28.0, 29.7, 29.7, 29.8, 29.9, 122.3, 122.8, 130.8, 130.8, 131.2, 131.3, 134.8, 134.9, 145.0, 150.0, 150.0, 150.1, 162.2, 162.3, 162.4, 162.5.
^{31}P NMR {^{1}H} (122 MHz, CD_2Cl_2) δ = 6.1, 6.3.

2.2.2 Synthesis of **L3** with Different Haloalkanes



15.2 mmol

L3
86-88% yield, brown oil

L3 was also synthesized with different haloalkanes adapting the synthesis known to literature.[3] Lithium (270 mg, 38 mmol) was added slowly to the solution of 2-(tert-butylchlorophosphanyl)pyridine in THF (30 mL) under argon at 0 °C, and the solution slowly became red. The mixture was allowed to reach room temperature and then left to stir for 24 hours. Then potassium tert-butoxide (1.8 g, 16 mmol) and 1,3-dihalopropane (0.67 mL, 6.9 mmol) were slowly added to the mixture at 0 °C under argon, and further stirred for 24 h. Degassed water (1.0 mL) was added to quench the reaction and the solvent was removed under vacuum. Degassed water (20 mL) and diethyl ether (50 mL) were added, and the organic phase was separated. The aqueous phase was extracted three times with diethyl ether (3×10 mL) and the combined organic phase was dried over magnesium sulfate anhydrous, filtered and the solvent was removed under reduced pressure to afford the ligand as brown oil.

2.2.2.1 1,3-dibromopropane as dihaloalkane

(2.28 g, 88% yield)

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.70 – 8.57 (m, 2H), 7.61 – 7.51 (m, 2H), 7.51 – 7.44 (m, 2H), 7.20 – 7.09 (m, 2H), 2.57 – 2.36 (m, 2H), 1.76 – 1.43 (m, 4H), 0.98 (d, *J* = 11.7 Hz, 9H), 0.95 (d, *J* = 11.5 Hz, 9H).
^{13}C NMR {^{1}H} (75 MHz, CD_2Cl_2) δ = 22.4, 22.5, 22.6, 22.7, 22.8, 22.9, 23.0, 24.1, 24.3, 24.4, 24.5, 24.6, 24.8, 27.8, 28.0, 29.7, 29.7, 29.8, 29.9, 30.2, 30.4, 30.5, 30.5, 122.3, 122.8, 125.6, 128.6, 129.4, 130.9, 131.3, 134.8, 150.1, 162.2, 162.3.
^{31}P NMR {^{1}H} (122 MHz, CD_2Cl_2) δ = 6.1, 6.3.

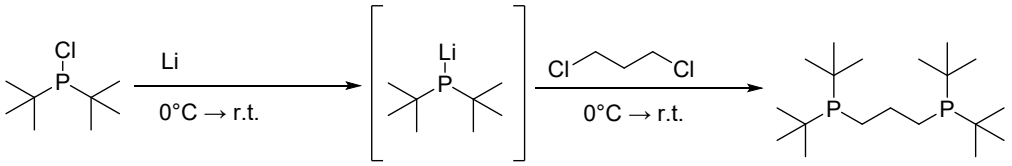
2.2.2.2 1,3-dichloropropane as dihaloalkane

(2.2 g, 86% yield)

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.85 – 8.69 (m, 2H), 7.62 – 7.43 (m, 2H), 7.25 – 7.16 (m, 2H), 7.14 – 7.04 (m, 2H), 6.88 – 6.80 (m, 2H), 6.77 – 6.69 (m, 2H), 4.03 – 3.87 (m, 2H), 3.32 – 3.21 (m, 2H), 1.10 (d, *J* = 11.8 Hz, 9H), 1.06 (d, *J* = 11.8 Hz, 9H).
^{13}C NMR {^{1}H} (75 MHz, CD_2Cl_2) δ = 21.6, 22.6, 24.8, 27.8, 27.9, 28.0, 29.7, 29.8, 122.8, 125.6, 128.6, 129.4, 130.8, 130.8, 131.2, 131.3, 134.8, 134.9, 150.0, 150.1.
^{31}P NMR (122 MHz, CD_2Cl_2) δ = 6.1, 6.3.

The NMR shifts of both ligands are according to literature. [3]

2.3 Synthesis of **L4**



27.7 mmol

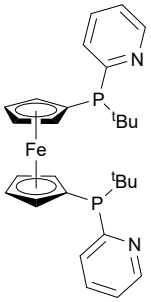
L4
76% yield, colourless liquid

L4 was prepared by adaption of a published method.[3] Lithium (540 mg, 38 mmol) was added slowly to the solution of di(tert-butyl) chlorophosphine (5.8 mL, 30.2 mmol) in THF (60 mL) under argon at 0 C, and the solution slowly became red. The mixture was stirred at room temperature overnight. The 1,3-dichloropropane (1.34 ml, 13.8 mmol) was added (slowly) to the mixture at 0 °C under argon, and the mixture was further stirred over 24 h. The solvent was removed in vacuo to afford the ligand as a white solid.

The product was then filtered through a plug of silica using Et_2O as an eluent. Afterwards the solvent was again removed in vacuo. The ligand was afforded as a colorless oil (3.5 g, 76 % yield). The NMR shifts match the literature.[4]

^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.75 – 1.63 (m, 2H), 1.53 – 1.44 (m, 4H), 1.11 (d, *J* = 10.6 Hz, 36 H).
^{13}C NMR {^{1}H} (101 MHz, CD_2Cl_2) δ 31.6 (d, *J* = 26.2 Hz), 31.4 (d, *J* = 21.1 Hz), 29.9 (d, *J* = 13.5 Hz), 23.9 (d, *J* = 13.5 Hz), 23. 7 (d, *J* = 13.5 Hz).
^{31}P NMR {^{1}H} (122 MHz, CD_2Cl_2) δ = 26.8.

2.4 Synthesis of **L5**



L5 was prepared according to literature and the NMR data is in accordance with the previously published values.[5]

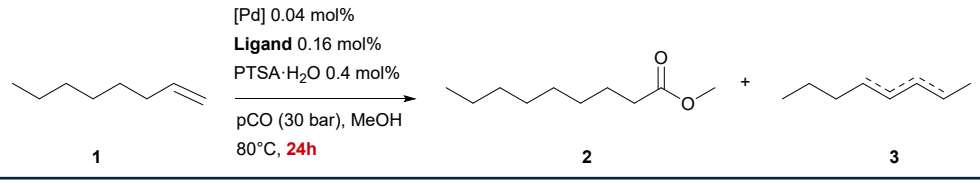
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.85 – 8.67 (m, 2H), 7.89 – 7.73 (m, 2H), 7.73 – 7.57 (m, 2H), 7.42 – 7.15 (m, 2H), 4.83 – 4.72 (m, 1H), 4.60 – 4.49 (m, 1H), 4.41 – 4.29 (m, 1H), 4.21 – 4.15 (m, 1H), 4.04 – 3.97 (m, 1H), 3.91 – 3.87 (m, 1H), 3.87 – 3.82 (m, 3H), 0.93 (d, *J* = 12.3 Hz, 9H), 0.90 (d, *J* = 12.4 Hz, 9H).

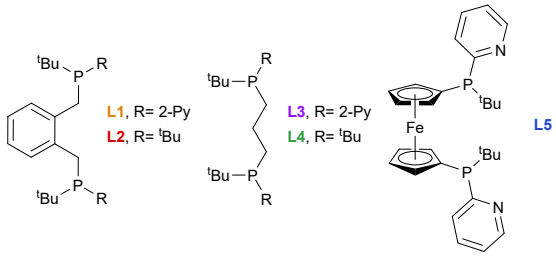
^{13}C NMR {^{1}H} (75 MHz, CD_2Cl_2) δ = 28.0, 28.2, 31.6, 31.7, 69.1, 71.5, 71.5, 71.6, 71.6, 72.4, 72.5, 73.4, 73.6, 73.7, 73.8, 73.9, 73.9, 77.1, 77.6, 77.7, 78.2, 123.1, 123.2, 131.8, 131.9, 132.3, 132.5, 134.9, 135.1, 149.7, 149.8, 149.9, 163.0, 163.2.

^{31}P NMR {^{1}H} (122 MHz, CD_2Cl_2) δ = 7.0.

2.5 Optimizations

To discuss differences in reactivity, reactions were started at different temperatures and reaction times. To determine the yields and n:iso-selectivity, mesitylene (1 mL) was added as an internal standard after the reaction was completed. The experiments in **Table 1** were set up according to **1.1.1**.





Entry	Ligand	Conv. [%]	Σ esters [%]	n:iso [%]	3 [%]
1	L1	97	91	70:30	4
2	L2	> 99	74	94:6	24
3	L3[a]	> 99	91	60:40	3
4	L4	31	3	> 99:1	18
5	L5	> 99	92	73:27	< 1

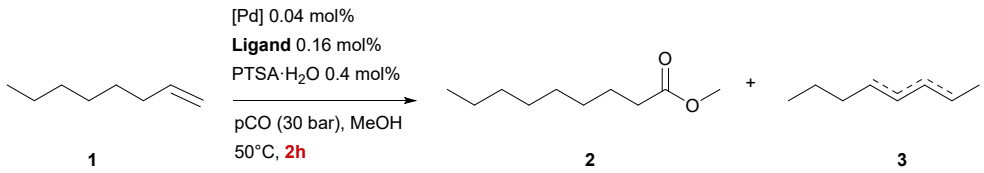
Table 1: Alkoxycarbonylation of 1-octene for 24 hours at 80 °C with **L1**-**L5**; [a] prepared according to **2.2.1**.

L3, mentioned in sections **2.2**, were compared to see whether the different synthesis routes produced different results (**Table 2**). The experiments in **Table 2** were set up according to **1.1.1**.

Entry	Synthesis	Conv. [%]	Σ esters [%]	*n*:iso [%]	3 [%]
1	**2.2.1**	> 99	91	60:40	3
2	**2.2.2.1**	> 99	98	59:41	< 1
3	**2.2.2.2**	> 99	97	59:41	1
4	*	> 99	93	60:40	< 1

Table 2: Alkoxycarbonylation of 1-octene for 24 hours at 80 °C with **L3** with different synthesis routes.* Ligand was prepared according to literature.[3]

The experiments in **Table 1** were set up according to **1.1.1** at 50 °C.

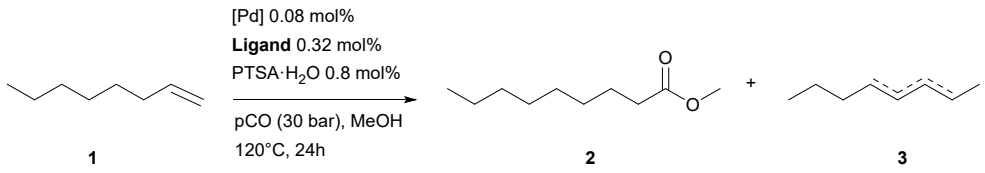


Entry	Ligand	Conv. [%]	Σ esters [%]	*n*:iso [%]	3 [%]
1	L1	92	25	87:13	52
2	L3	65	41	67:33	7
3	L5	> 99	3	63:34	84

Table 3: Alkoxycarbonylation of 1-octene for 2 hours at 50 °C with **L1**, **L3** and **L5**.

After the reaction was completed, the mixture was allowed to cool down. To determine the yield and the *n*:iso-selectivity via GC analysis an internal standard (mesitylene, 1 mL) was added.

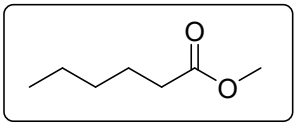
To enable a direct comparison of the Methoxycarbonylation of 1-octene and 2-octene, an experiment was conducted in accordance with **1.1.2**.



Entry	Ligand	Conv. [%]	Total Esters [%]	*n*:iso [%]	C8 [%]
1	L3	> 99	96	57:43	<1

Table 4: Alkoxycarbonylation of 1-octene with the conditions of Section **B**.

2.6 Analytical data



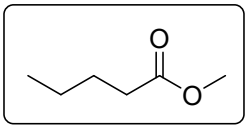
Methyl hexanoate (2a)

Compound **2a** was prepared according to general procedure **1.1.1** at 120 °C. Afterwards the product was isolated via general procedure **1.1.6** to afford compound as a clear liquid (1.56 g, 60% yield) the n/iso selectivity was determined by GC-analysis (*n*/iso selectivity: 63/37).

NMR of the *n*-ester:[6]

1H NMR (300 MHz, CDCl3) δ 3.62 (s, 3H), 2.26 (t, J = 7.5 Hz, 2H), 1.69 – 1.49 (m, 2H), 1.36 – 1.18 (m, 4H), 0.89 – 0.80 (m, 3H).

^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ = 14.0, 22.4, 24.7, 31.4, 34.1, 51.5, 174.4.



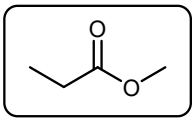
Methyl pentanoate (2b)

Compound **2b** was prepared according to general procedure **1.1.5**. Afterwards the product was isolated via general procedure **1.1.6** to afford the title compound as a clear liquid (1.49 g, 65% yield) the *n*/iso selectivity was determined by GC-analysis (*n*/iso: 62/38).

NMR data of the isolated product:[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23 (t, 2H), 1.65 – 1.44 (m, 2H), 1.34 – 1.18 (m, 2H), 0.82 (s, 3H).

^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ = 13.6, 22.2, 27.0, 33.8, 51.3, 174.2.

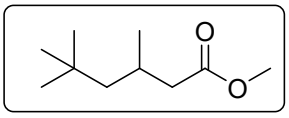


Methylpropionate (2c)

Compound **2c** was prepared according to general procedure **1.1.4**. Afterwards the yield was determined by GC-analysis using mesitylene (40 mL) as an internal standard (> 99% yield).

The product was identified by comparison with a sample of the pure substance, which is commercially available. This compound and mesitylene, which was used as an internal standard, were then used to perform GC calibration in order to determine the yield.

Retention times: methylpropionate: 3.95 min, mesitylene: 20.44 min. Reference retention times: purchased methlpropionate and mesitylene: methylpropionate: 3.90 min, mesitylene: 20.32 min.



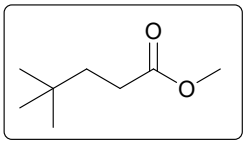
Methyl-3,5,5-trimethylhexanoate (2d)

Compound **2d** was prepared according to general procedure **1.1.1** with 80 mmol of substrate instead of 20 mmol at 120 °C for 20 hours in a 300 mL steel autoclave. Afterwards the product was isolated at 70 °C and 19 mbar via general procedure **1.1.7** to afford the title compound as a clear liquid (11.3 g, 82% yield).

NMR data of the isolated product:[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.56 (s, 0H), 2.28 – 2.14 (m, 1H), 2.11 – 1.86 (m, 1H), 1.21 – 1.09 (m, 1H), 1.09 – 0.95 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.81 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ = 22.7, 27.0, 29.9, 31.0, 43.8, 50.5, 51.1, 173.4.



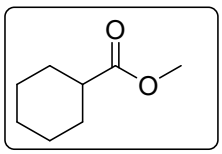
Methyl-4,4-dimethylpentanoate (2e)

Compound **2e** was prepared according to general procedure **1.1.1** at 120 °C. Afterwards the product was isolated via general procedure **1.1.6** to afford the title compound as a clear liquid (1.88 g, 65% yield).

NMR data of the isolated product:[9]

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.45 (s, 3H), 2.13 – 2.02 (m, 2H), 1.42 – 1.28 (m, 2H), 0.70 (s, 9H).

^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ = 28.7, 29.6, 29.8, 38.4, 51.0, 174.2.

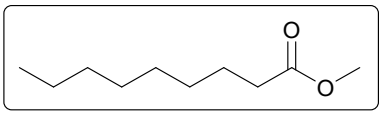


Methyl cyclohexanecarboxylate (2f)

Compound **2f** was prepared according to general procedure **1.1.1** at 120 °C. Afterwards the product was isolated via general procedure **1.1.6** to afford the title compound as a clear liquid (2.59 g, 90% yield).

NMR data of the isolated product:[10]

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.63 (s, 3H), 2.34 – 2.21 (m, 1H), 1.95 – 1.81 (m, 2H), 1.80 – 1.68 (m, 2H), 1.67 – 1.56 (m, 1H), 1.53 – 1.33 (m, 2H), 1.33 – 1.14 (m, 3H).
^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ = 25.6, 25.9, 29.1, 43.2, 51.5, 176.7.

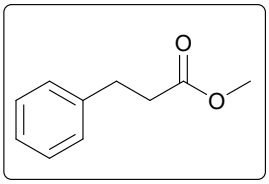


Methyl nonanoate (2g)

Compound **2g** was prepared according to general procedure **1.1.2** from 2-octene. The yield and the *n*/iso selectivity was determined by GC analysis by adding mesitylene (1 mL) as an internal standard. (92% yield; *n*/iso selectivity: 54/46). The product was identified by comparison with a sample of the pure substance, which is commercially available. This compound and mesitylene, which was used as an internal standard, were then used to perform GC calibration in order to determine the yield.

Retention times: methyl nonanoate: 28.421 min, iso-esters: 27.241 min, 26.806 min, 26.569 min, mesitylene: 23.084 min.

Reference retention times: purchased methyl nonanoate (28.38 min), 2-octene (18.80 min), and mesitylene (23.07 min).



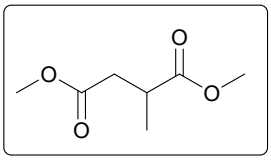
Methyl 3-phenylpropionate (2h)

Compound **2h** was prepared according to general procedure **1.1.2**. Afterwards the product was isolated via general procedure **1.1.6** to afford compound to afford the title compound as a clear liquid (3.22 g, 98% yield) the *n*/iso selectivity was determined by GC analysis. (*n*/iso selectivity: 53/47).

NMR data of the isolated product mixture:[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.11 (m, 5H, *n* & iso), 3.68 (q, *J* = 7.2 Hz, 3H, iso), 3.561 (s, 3H, *n*), 3.60 (s, 3H, iso), 2.91 (t, 2H, *n*), 2.59 (t, 2H, *n*), 1.46 (d, *J* = 7.2 Hz, 3H, iso).

^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ = 18.4, 30.9, 35.7, 45.4, 51.5, 51.92, 126.3, 127.1, 127.5, 128.3, 128.5, 128.6, 140.5, 140.6, 173.2, 174.9.

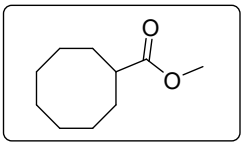


Methyl 2-methylsuccinate (2i)

Compound **2i** was prepared according to general procedure **1.1.2** with 40 mmol of substrate (without further purifications mentioned above in section **1**). Afterwards the product was isolated at 92 °C at 26 mbar via general procedure **1.1.7** to afford the title compound as a clear liquid (6.0 g, 93% yield).

NMR data of the isolated product:[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.66 (s, 3H), 3.00 – 2.82 (m, 1H), 2.73 (dd, *J* = 16.5, 8.1 Hz, 1H), 2.39 (dd, *J* = 16.5, 6.1 Hz, 1H), 1.20 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 175.8, 172.4, 52.0, 51.8, 4.5, 35.8, 17.1.

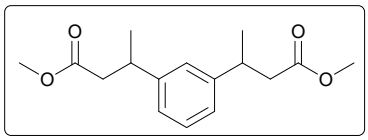


Methyl cyclooctanecarboxylate (2j)

Compound **2j** was prepared according to general procedure **1.1.2**. Afterwards the product was isolated via general procedure **1.1.6** to afford the title compound as a clear liquid (3.14 g, 92% yield).

NMR data of the isolated product:[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 3H), 2.56 – 2.42 (m, 1H), 1.91 – 1.77 (m, 2H), 1.74 – 1.61 (m, 4H), 1.59 – 1.36 (m, 8H).
^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ = 25.3, 26.2, 26.8, 28.8, 43.6, 51.6, 177.8.

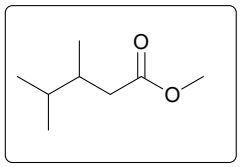


dimethyl 3,3'-(1,3-phenylene)dibutyrate (2k)

Compound **2k** was prepared according to general procedure **1.1.2**. Afterwards the product was isolated via general procedure **1.1.6** to afford the title compound as a clear liquid (10.38 g, 93% yield).

NMR data of the isolated product mixture:[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.17 (m, 1H), 7.06 (d, *J* = 6.9 Hz, 3H), 3.62 (s, 6H), 3.35 – 3.17 (m, 2H), 2.70 – 2.46 (m, 4H), 1.29 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 173.0, 146.1, 128.8, 125.5, 124.8, 51.6, 42.9, 36.6, 21.8.

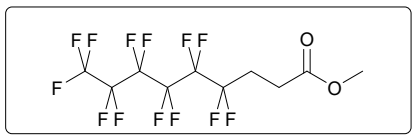


Methyl-3,4-dimethylpentanoate (2l)

Compound **2l** was prepared according to general procedure **1.1.2** with 0. 8 mol% of $Pd(acac)_2$, 3.2 mol% of **L3**, 8 mol% PTSA·H_2O. Afterwards the product was isolated via general procedure **1.1.6** to afford the title compound as a light yellow liquid (2.61 g, 91% yield).

NMR data of the isolated product:[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 2.34 (dd, *J* = 14.7, 5.2 Hz, 1H), 2.06 (dd, *J* = 14.7, 9.2 Hz, 1H), 1.92 – 1.79 (m, 1H), 1.63 – 1.50 (m, 9H), 0.89 – 0.80 (m, 8H).
^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 174.34, 51.51, 39.12, 36.02, 32.19, 19.92, 18.37, 15.95.



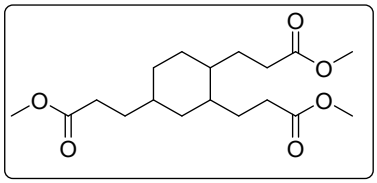
methyl 2,2,3,3-tetrahydroperfluorononanoate (2m)

Compound **2m** was prepared according to general procedure **1.1.2** with 40 mmol of substrate (without further purifications mentioned above in section **1**). Afterwards the product was isolated via general procedure **1.1.6** to afford the title compound as a clear liquid (7.68 g, 95% yield).

NMR data of the isolated product:[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (s, 3H), 2.68 – 2.59 (m, 2H), 2.59 – 2.36 (m, 2H).

^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 171.7 52.4, 27.0, 26.7, 26.4, 25.4.



Trimethyl 3,3',3''-(cyclohexane-1,2,4-triyl)tripropionate (2n)

Compound **2n** was prepared according to general procedure **1.1.2** with 40 mmol substrate at 80 °C. Aafter 8 hours the temperature was raised to 100 °C. Afterwards the product was isolated at 165 °C under 10^{-3} bar via general procedure **1.1.7** to afford the title compound as isomeric mixture of the triple carbonylated compound as a clear liquid (9.57 g, 70% yield).

NMR data of the isolated triple carbonylated products:[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 – 3.63 (m), 2.45 – 2.11 (m), 1.93 (m), 1.72 (m), 1.63 – 1.29 (m), 1.15 – 0.75 (m), 0.60 (m). (21H in total)

^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 174.5, 174.5, 174.5, 174.5, 174.4, 51.6, 51.6, 40.7, 40.6, 40.5, 40.4, 38.2, 37.5, 37.0, 36.5, 36.1, 35.6, 35.2, 33.8, 32.8, 32.5, 32.4, 32.4, 32.3, 32.3, 32.2, 32.1, 32.1, 32.0, 31.9, 31.8, 31.7, 31.7, 31.3, 31.1, 31.1, 31.0, 30.8, 30.3, 29.1, 28.6, 28.4, 28.3, 28.2, 28.0, 28.0, 27.0, 26.5, 25.0, 20.7, 19.7.

2.7 Kinetic Profiling

To investigate the kinetics of the methoxycarbonylation of diisobutene, two kinetic experiments were conducted, enabling a comparison between **L1** and **L3**. These experiments were set up according to **1.1.8**. Afterwards the yield of the components were determined by GC analysis

The conversion of the two diisobutene isomers, TMP1 and TMP2, to the desired ester (Methyl-3,5,5-trimethylhexanoate) and the non-desired side product (2-methoxy-2,3,3-trimethyl-butane) were examined.

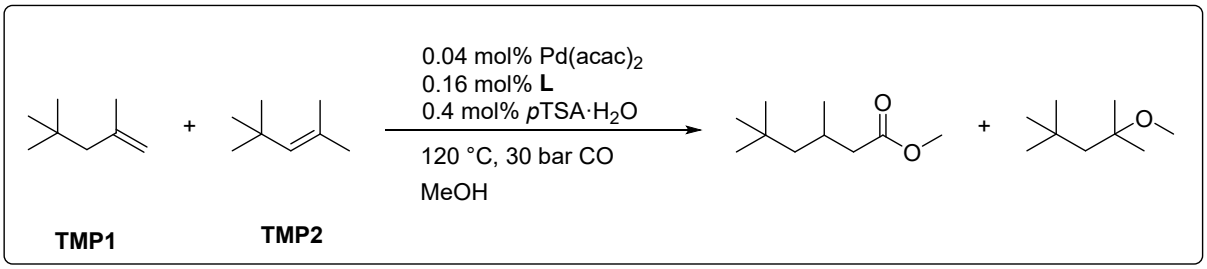


Figure 1: Palladium-catalyzed methoxycarbonylation of diisobutene with **L1** and **L3**.
Reaction conditions: diisobutene (80 mmol), $Pd(acac)_2$ (9.75 mg, 0.04 mol%), L (0.16 mol%, **L1**: 55.87 mg, **L3**: 47.93 mg), PTSA·H_2O (0.4 mol%, 60.87 mg), MeOH (80 mL), CO (30 bar), 120 °C, 24 h.

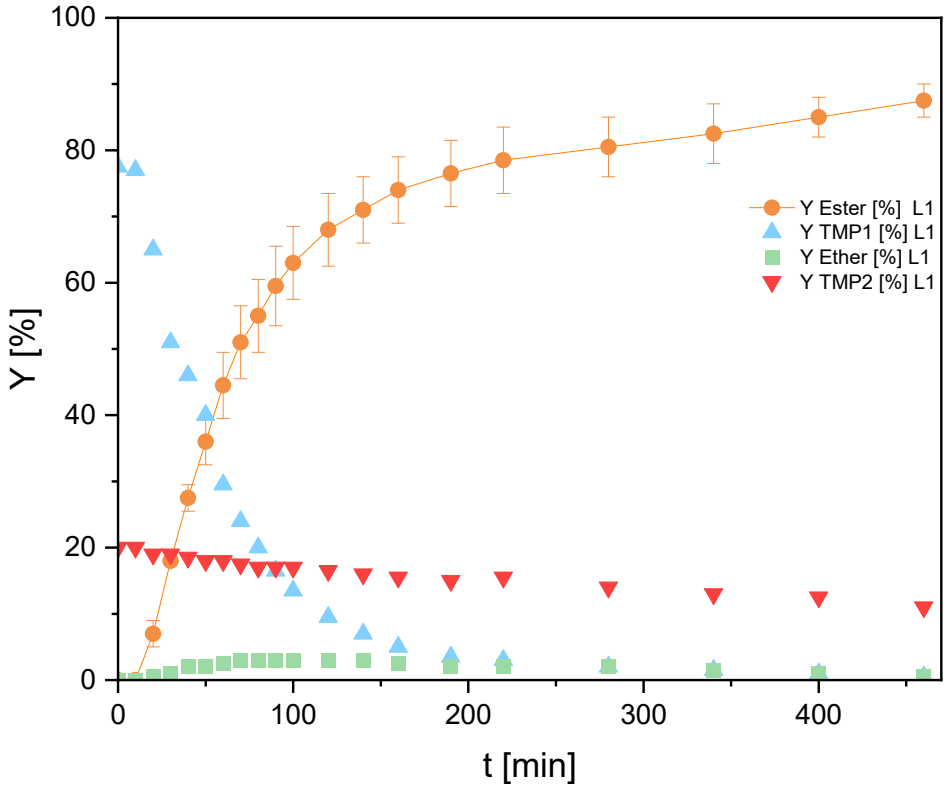


Figure 2: Kinetic profile of the methoxycarbonylation of diisobutene with **L1** over 8 hours.

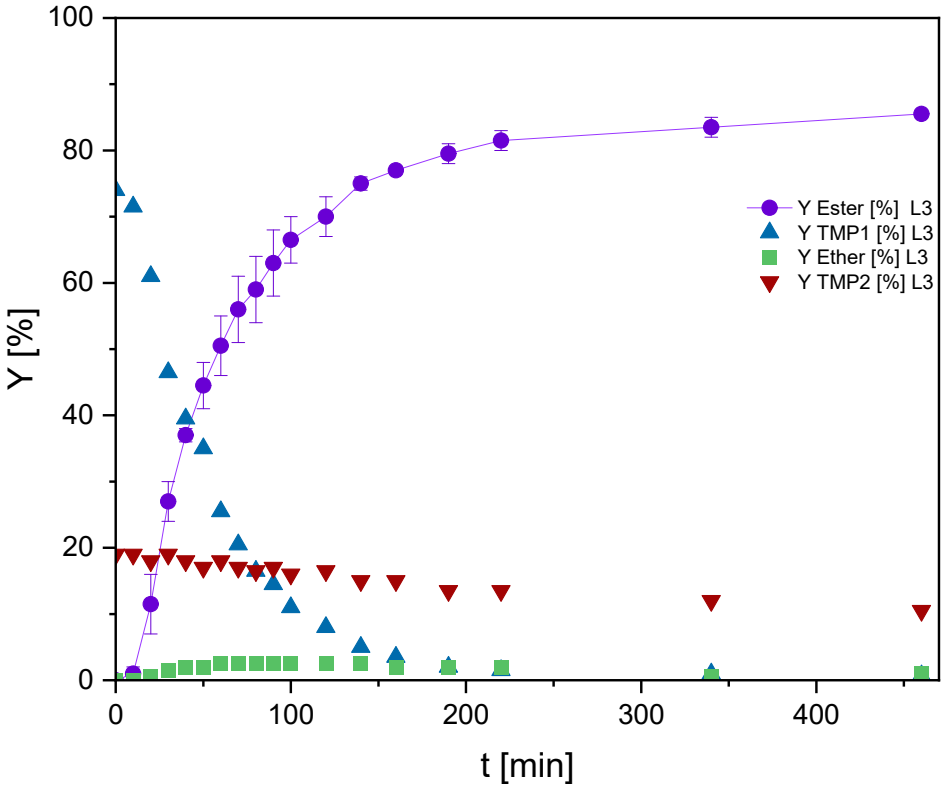


Figure 3: Kinetic profile of the methoxycarbonylation of diisobutene with **L3** over 8 hours.

2.8 Up-Scaling

To show the industrial relevance we decided to scale up the Methoxycarbonylation of MMA to Methyl 2-methylsuccinate. The compound was prepared according to **1.1.9** after around 5 hours and 40 minutes CO was refilled to reach a total pressure of 35 bar.

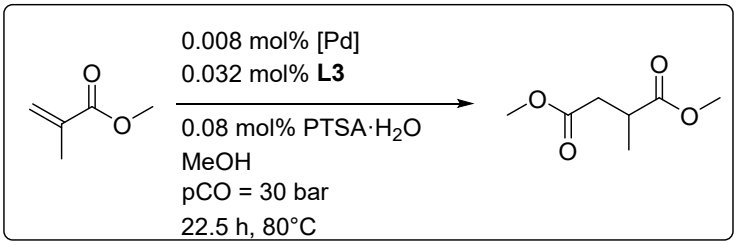


Figure 4: Palladium-catalyzed methoxycarbonylation of MMA with **L3**.

Reaction conditions: diisobutene (200 mmol, 21.3 mL), $Pd(acac)_2$ (0.016 mol%, 4.87 mg), **L3** (0.064 mol%,23.96 mg), PTSA·H_2O (0.16 mol%, 30.44 mg), MeOH (190 mL), CO (30 bar), 80 °C, 22.5 h.

After the reaction was completed the product was isolated was isolated via general procedure **1.1.7** at 92 °C and 26 mbar to afford the title compound as a clear liquid (31.17 g, 97% yield).

NMR data of the isolated product: [12]

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.66 (s, 3H), 3.00 – 2.82 (m, 1H), 2.73 (dd, *J* = 16.5, 8.1 Hz, 1H), 2.39 (dd, *J* = 16.5, 6.1 Hz, 1H), 1.20 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ 175.82, 172.40, 52.04, 51.83, 37.51, 35.82, 17.12.

2.9 References

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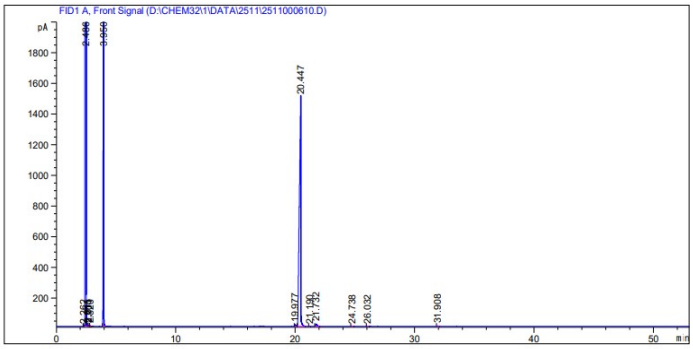
2.10 GC spectra

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   2.262 BB    0.0135    1.37577    1.83913  0.00138
   2   2.486 BB S  0.1040 7.80827e4  1.34045e4  78.18718
   3   2.615 BV X  0.0135    2.32024    2.84204  0.00232
   4   2.701 VV X  0.0269    8.04666    4.24870  0.00806
   5   2.820 VB X  0.0218    2.65658    1.82451  0.00266
   6   3.950 BB    0.0402 8809.14844 2902.11255  8.82093

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   7  19.977 BB    0.0698   53.96663   11.04497  0.05404
   8  20.447 BB    0.1060 1.27483e4 1492.75476 12.76538
   9  21.190 BB    0.0572    7.48386    2.04049  0.00749
  10  21.732 BB    0.1046  114.61897   14.95944  0.11477
  11  24.738 BB    0.0937   11.20137    1.68180  0.01122
  12  26.032 BB    0.0839   12.34588    2.00308  0.01236
  13  31.908 BB    0.0840   12.19585    2.19611  0.01221

Totals :                  9.98664e4  1.78441e4

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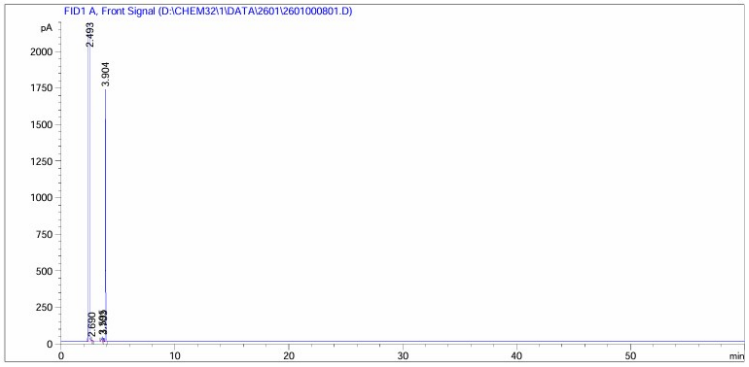
Figure 5: GC spectrum of **2c** with the internal standard mesitylene as reference.

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
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   2   2.690 BB X  0.0257    7.23913    4.20729  0.00843
   3   3.595 BV    0.1021  192.59909   26.57796  0.22437
   4   3.703 VB    0.0291   44.65442   22.92253  0.05202
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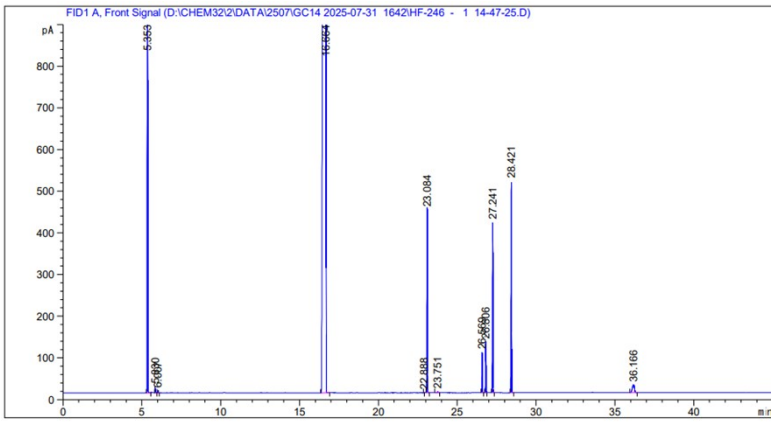
Figure 6: GC spectrum of methylpropionat as reference for **2c**.

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Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
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   2   5.830 BB    0.0224   22.93399   15.40419  0.04615
   3   6.007 BB    0.0258   10.09391    5.94245  0.02031
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Peak RetTime Type  Width     Area      Height     Area
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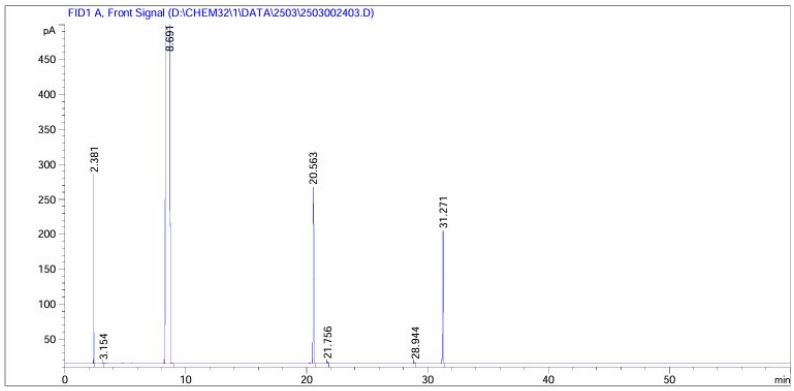
----|-------|----|-------|----------|----------|--------|
   4  16.664 BB    0.1165 4.17020e4  4441.27686 83.92305
   5  22.888 BV    0.0293    2.39440    1.31272  0.00482
   6  23.084 BB    0.0331  908.27472  438.90192  1.82785
   7  23.751 BB    0.0468    8.42949    2.67153  0.01696
   8  26.569 BB    0.0310  183.16370   97.16166  0.36861
   9  26.806 VV    0.0318  239.60881  122.81001  0.48220
  10  27.241 BB    0.0323  854.25317  409.58331  1.71914
  11  28.421 BB    0.0342 1098.33325  507.83185  2.21034
  12  36.166 BB    0.1208  179.48738   18.72248  0.36121

Totals :                  4.96908e4  8271.55891

=====================================================================
                        *** End of Report ***
```

Figure 7: GC spectrum of **2g** with the internal standard mesitylene as reference.




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.381 BB    0.0139  228.64221  269.03516  0.54819
   2   3.154 BB    0.0220    1.49488    1.06234  0.00358
   3   8.691 BB    0.1702 3.97431e4  2831.18896 95.28751
   4  20.563 BB    0.0643 1009.15546  252.02127  2.41954
   5  21.756 BB    0.0588    8.78811    2.35412  0.02107
   6  28.944 BB    0.0570    7.44268    2.03955  0.01784
   7  31.271 BB    0.0575  709.98853  188.83484  1.70226

Totals :                  4.17086e4  3546.53624

=====================================================================
                        *** End of Report ***
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Figure 8: GC spectrum of methyl nonanoate as reference for **2g**.

2.11 NMR spectra

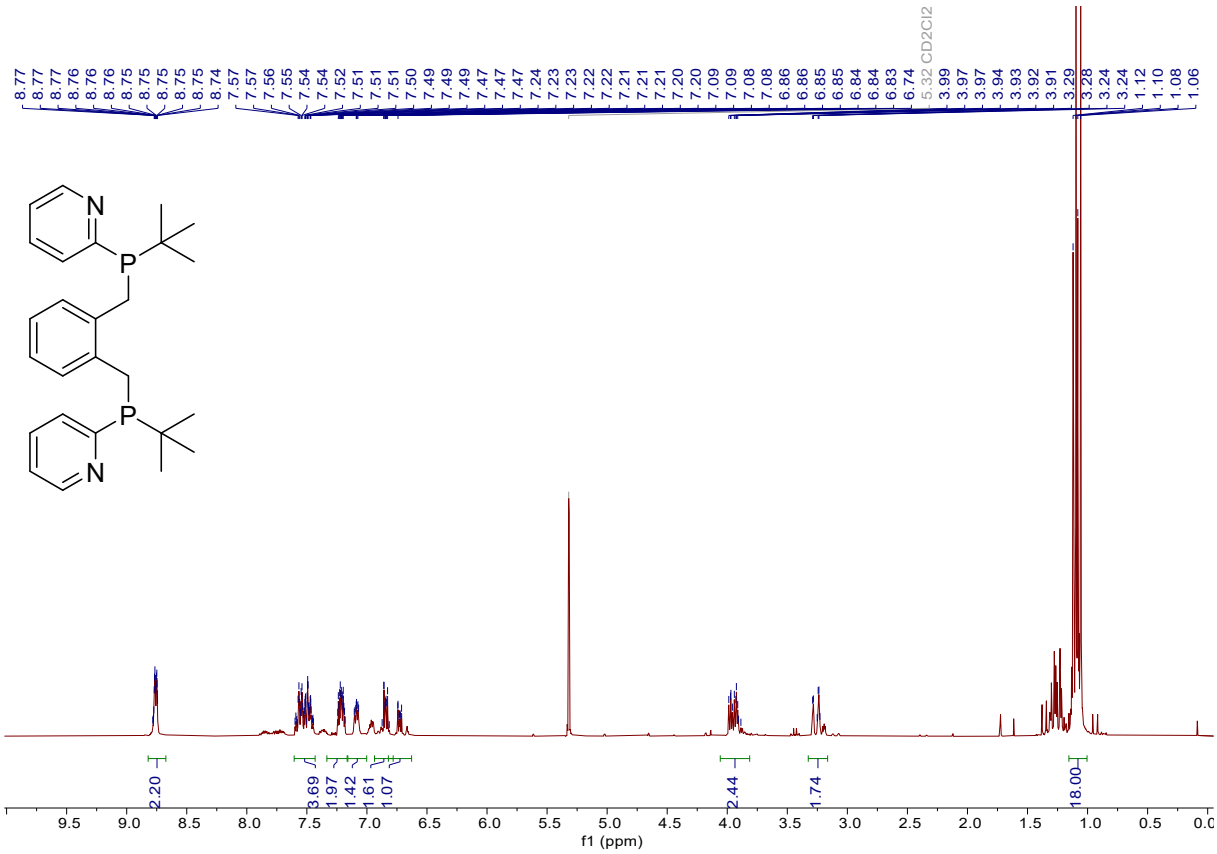

Figure 9: ^{1}H NMR spectrum of **L1** in DCM-d_2.

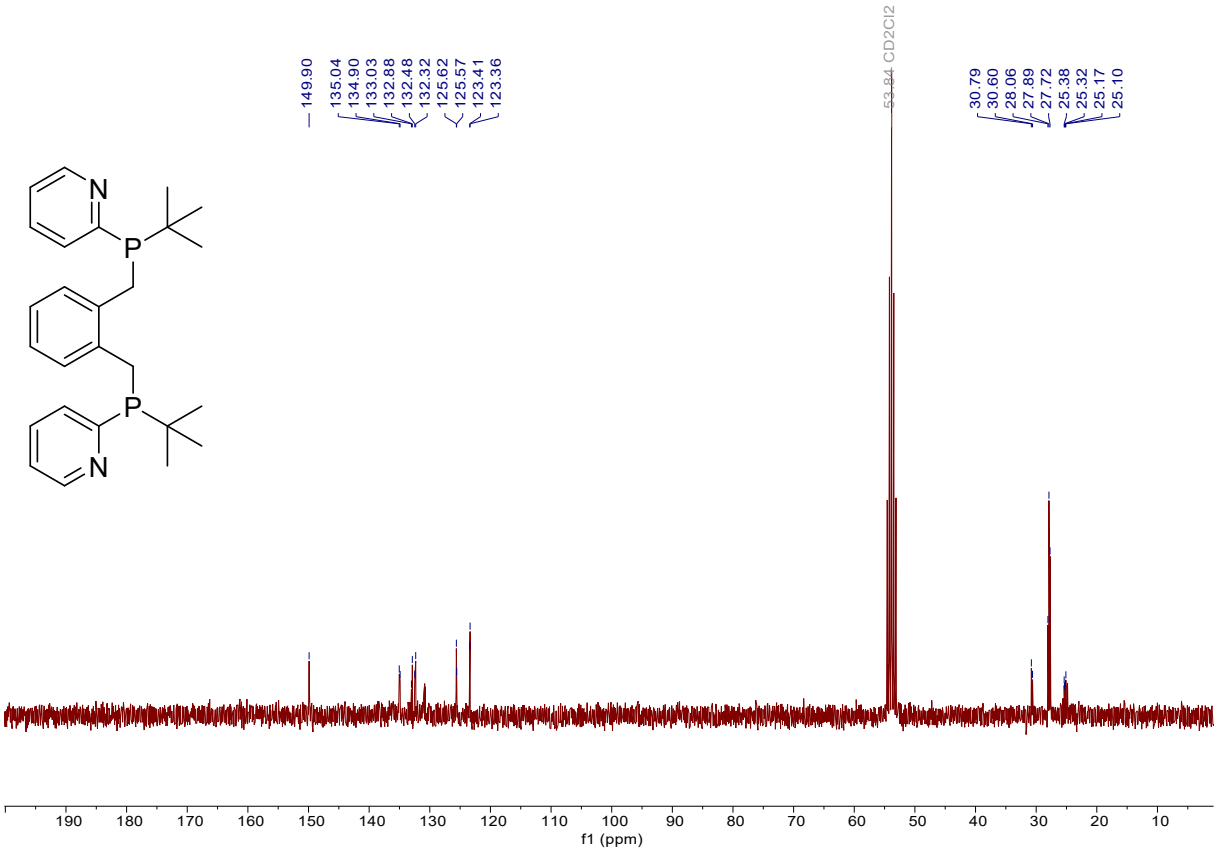

Figure 10: ^{13}C {^{1}H} NMR spectrum of **L1** in DCM-d_2.

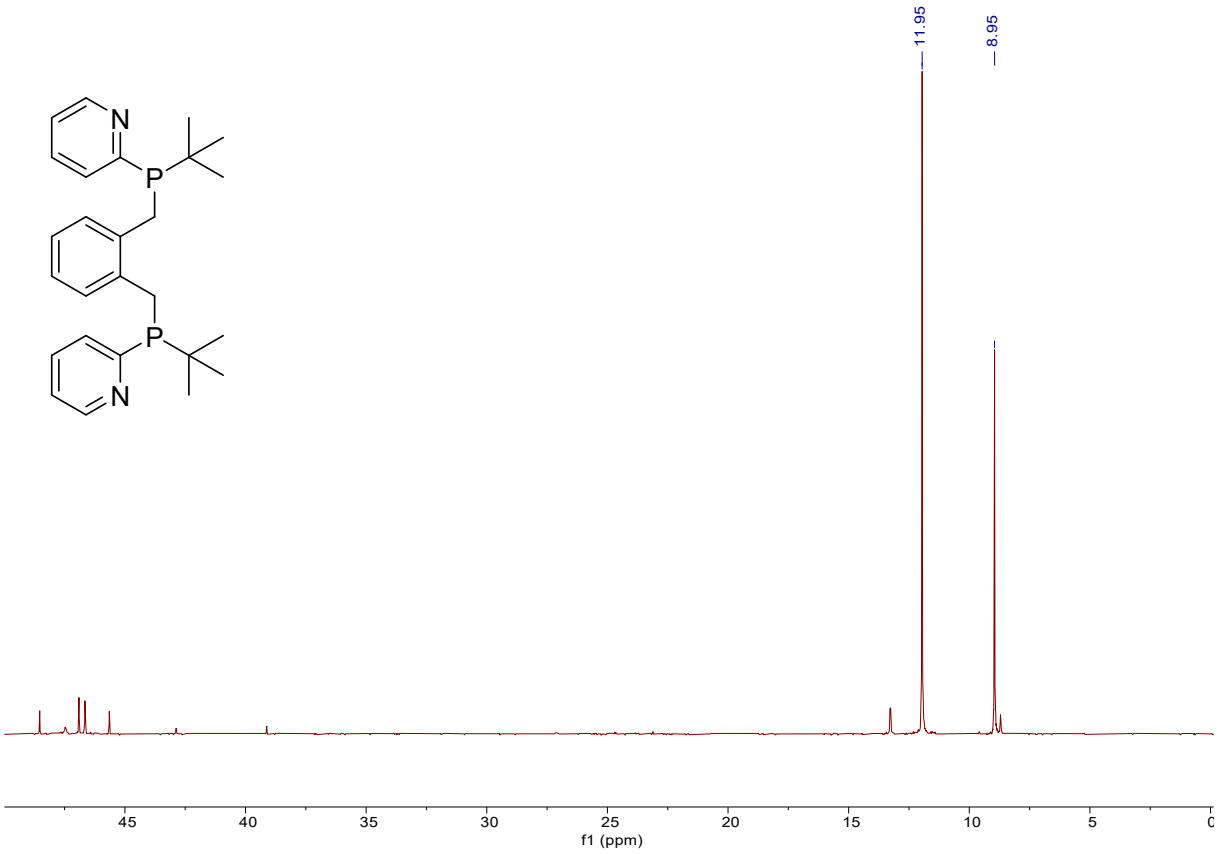

Figure 11: ^{31}P {^{1}H} NMR spectrum of **L1** in DCM-d_2.

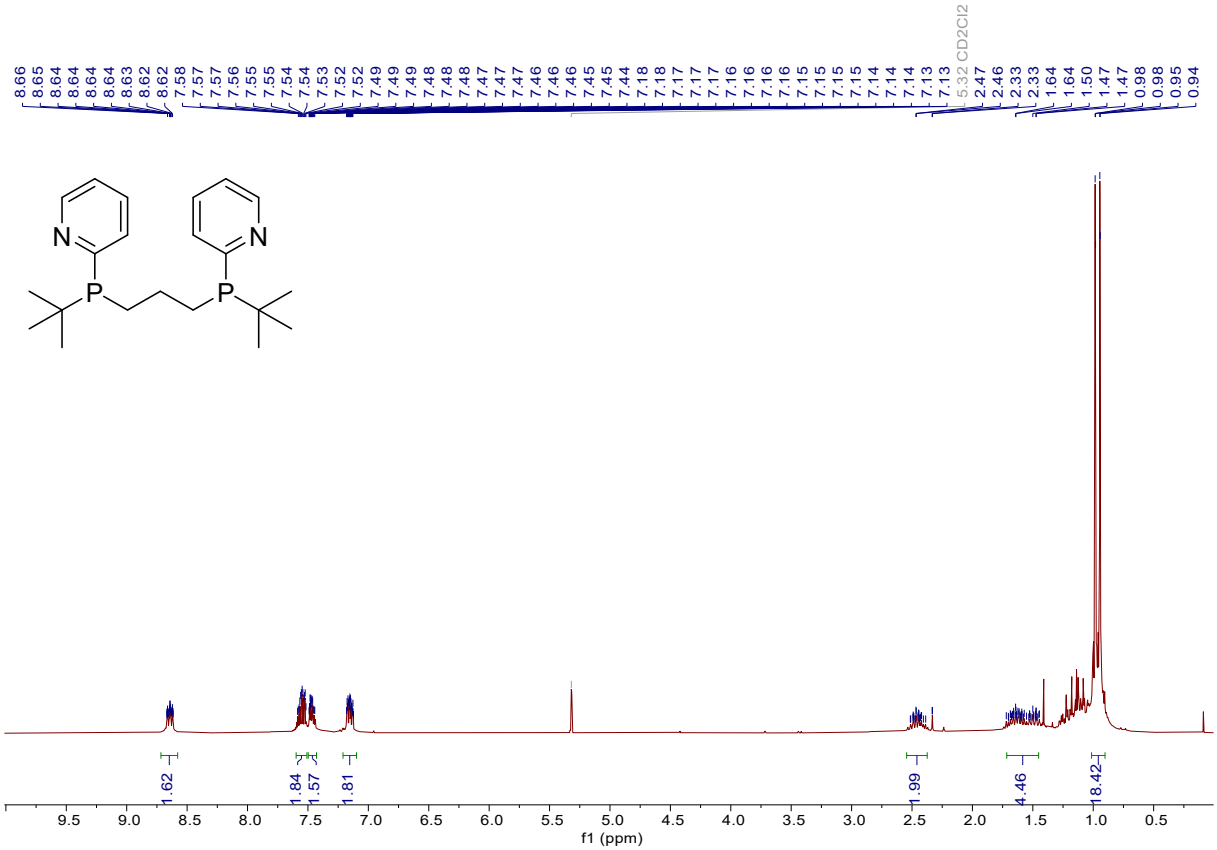

Figure 12: ^{1}H NMR spectrum of **L3** in DCM-d_2; section **2.2.1**.

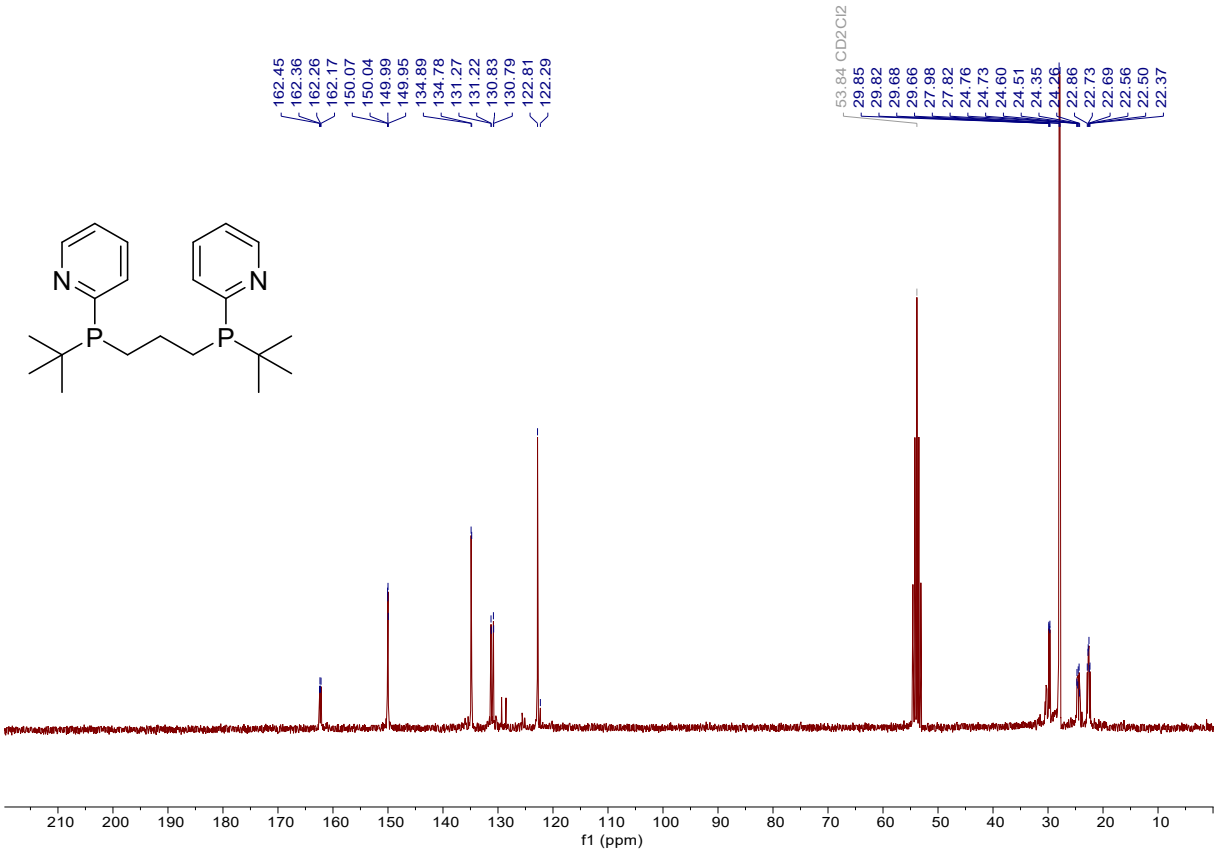

Figure 13: ^{13}C {^{1}H} NMR spectrum of **L3** in DCM-d_2; section **2.2.1**.

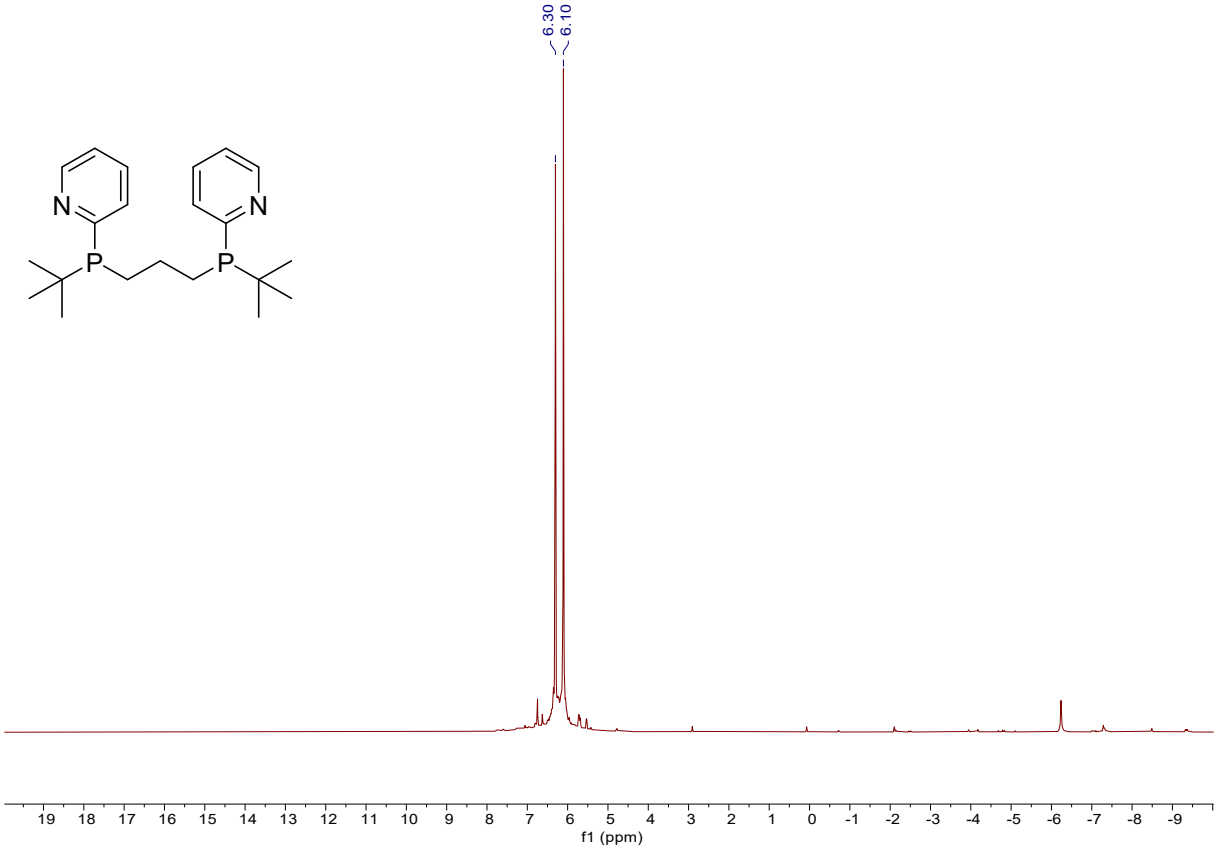

Figure 14: ^{31}P {^{1}H} NMR spectrum of **L3** in DCM-d_2; section **2.2.1**.

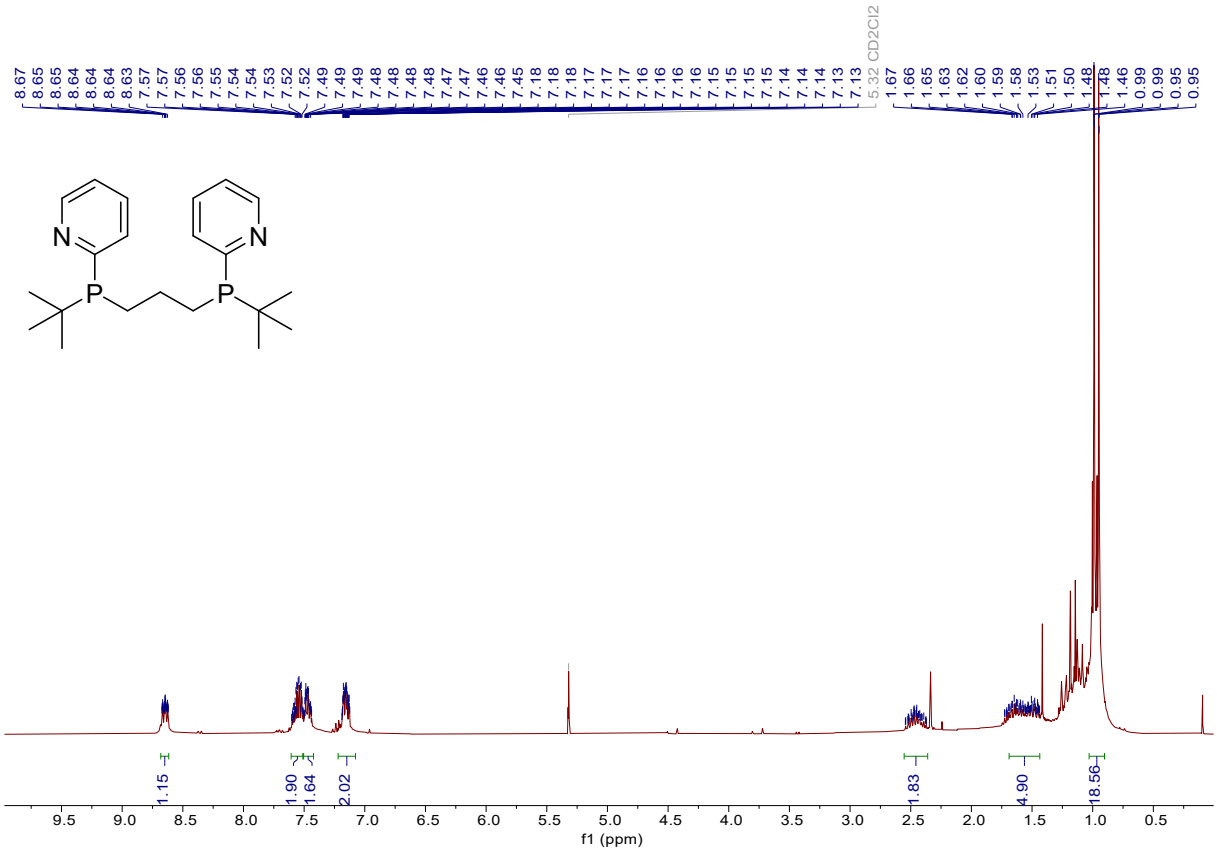

Figure 15: ^{1}H NMR spectrum of **L3** in DCM-d_2; section **2.2.2.1**.

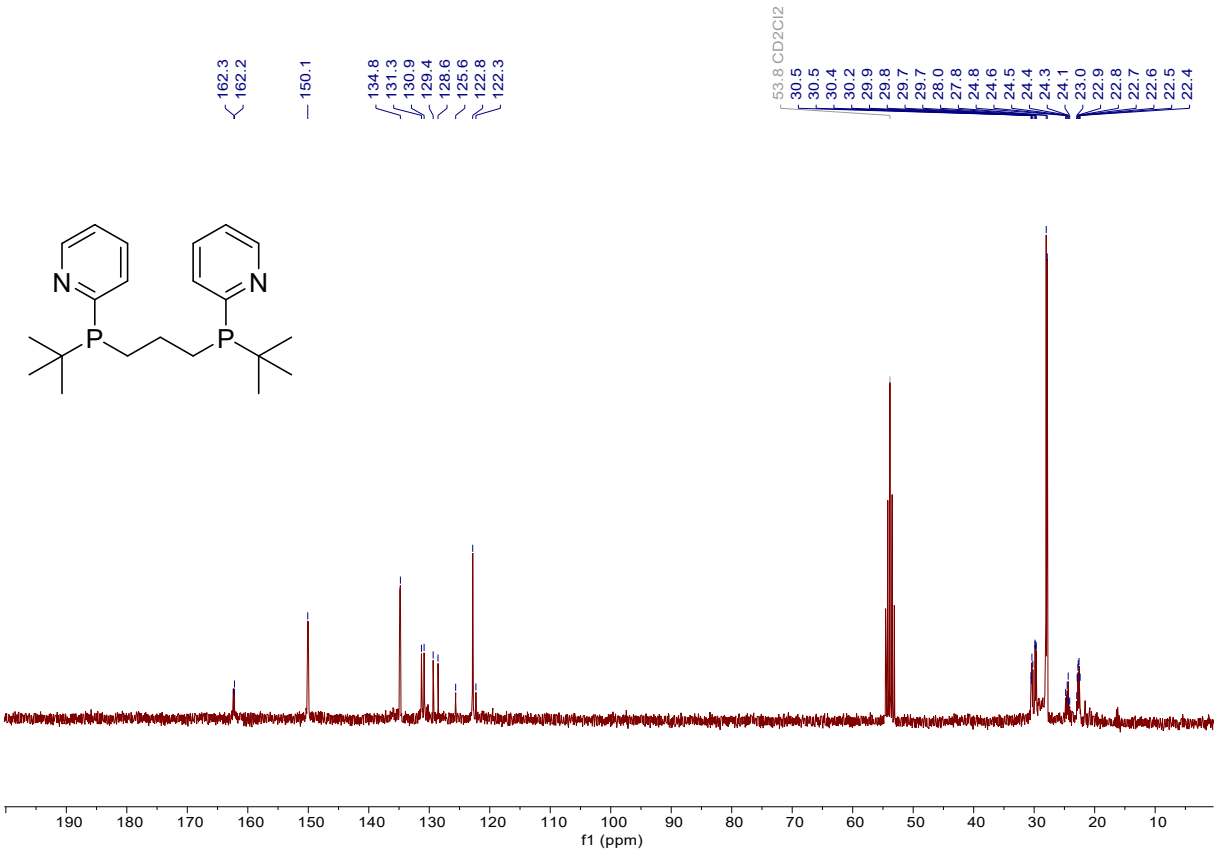

Figure 16: ^{13}C {^{1}H} NMR spectrum of **L3** in DCM-d_2; section **2.2.2.1**.

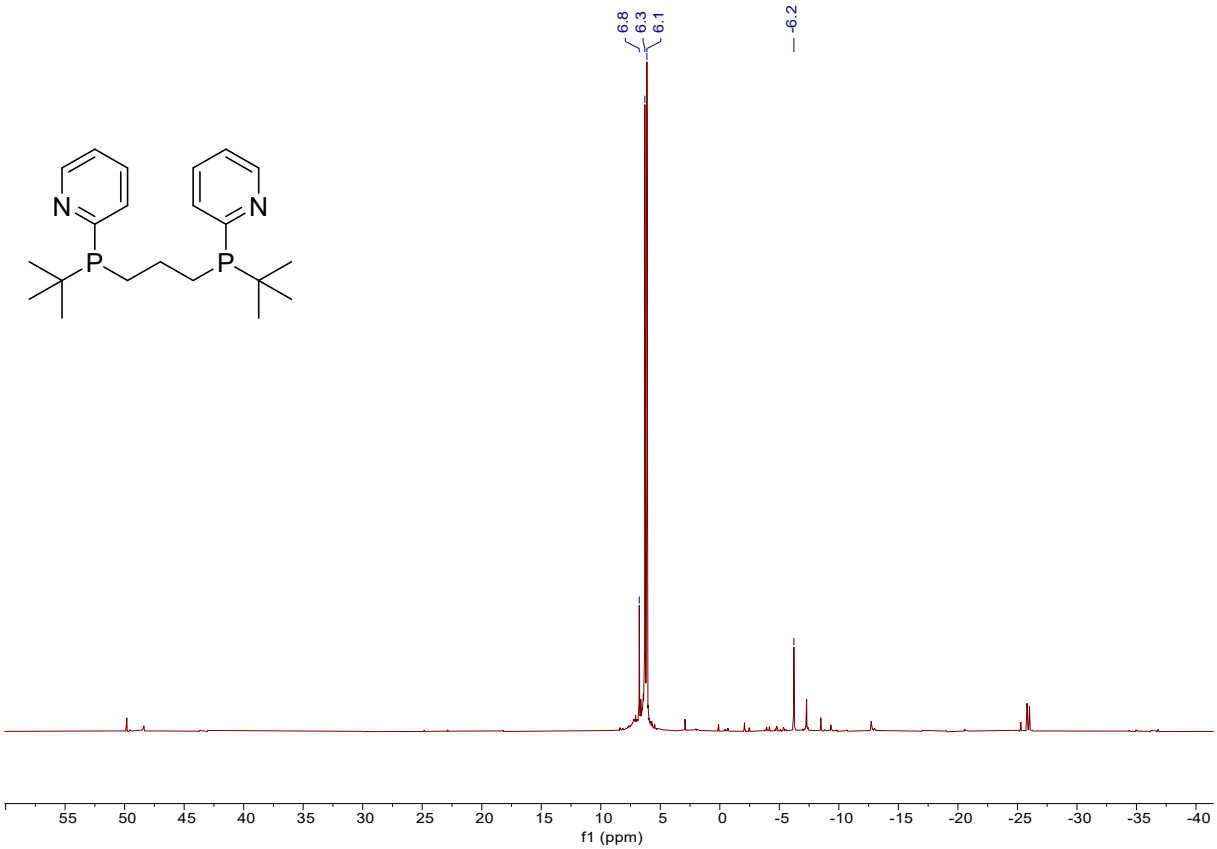

Figure 17: ^{31}P {^{1}H} NMR spectrum of **L3** in DCM-d_2; section **2.2.2.1**.

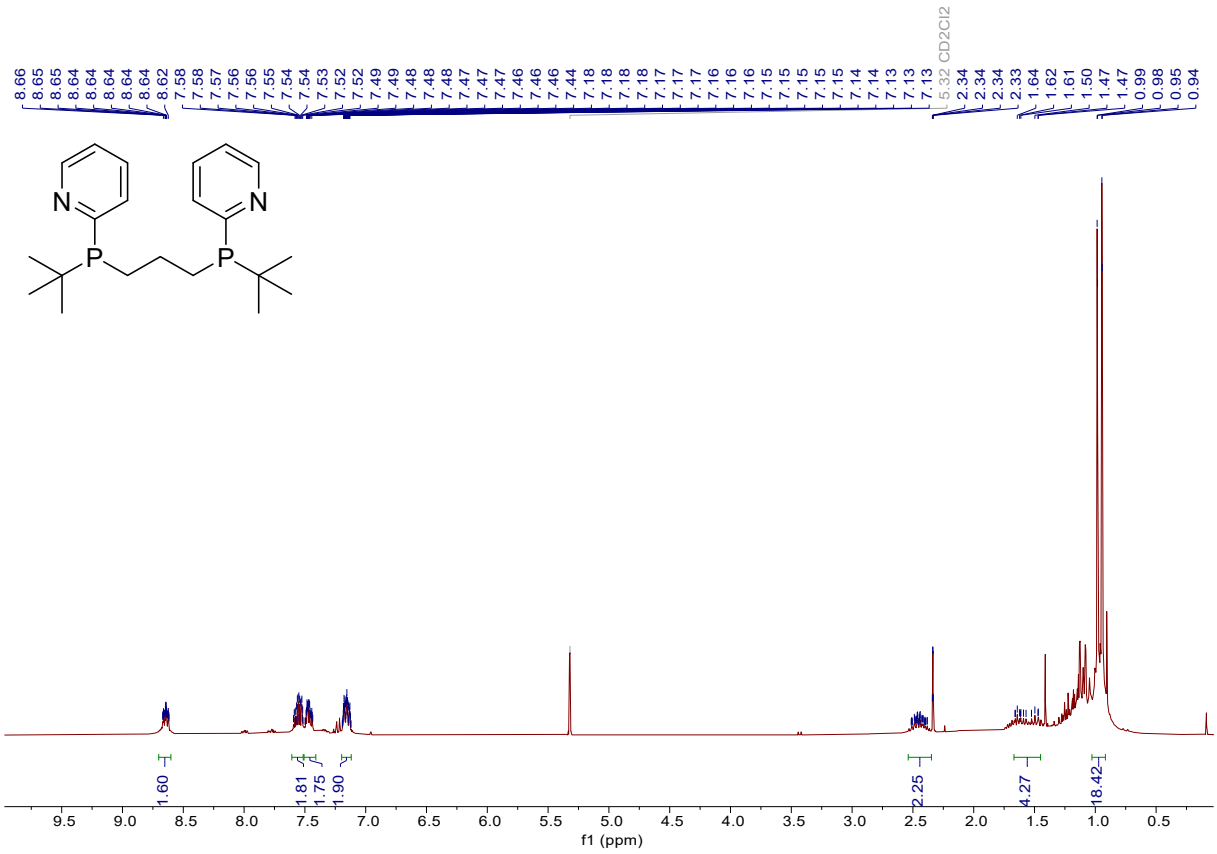

Figure 18: ^{1}H NMR spectrum of **L3** in DCM-d_2; section **2.2.2.2**.

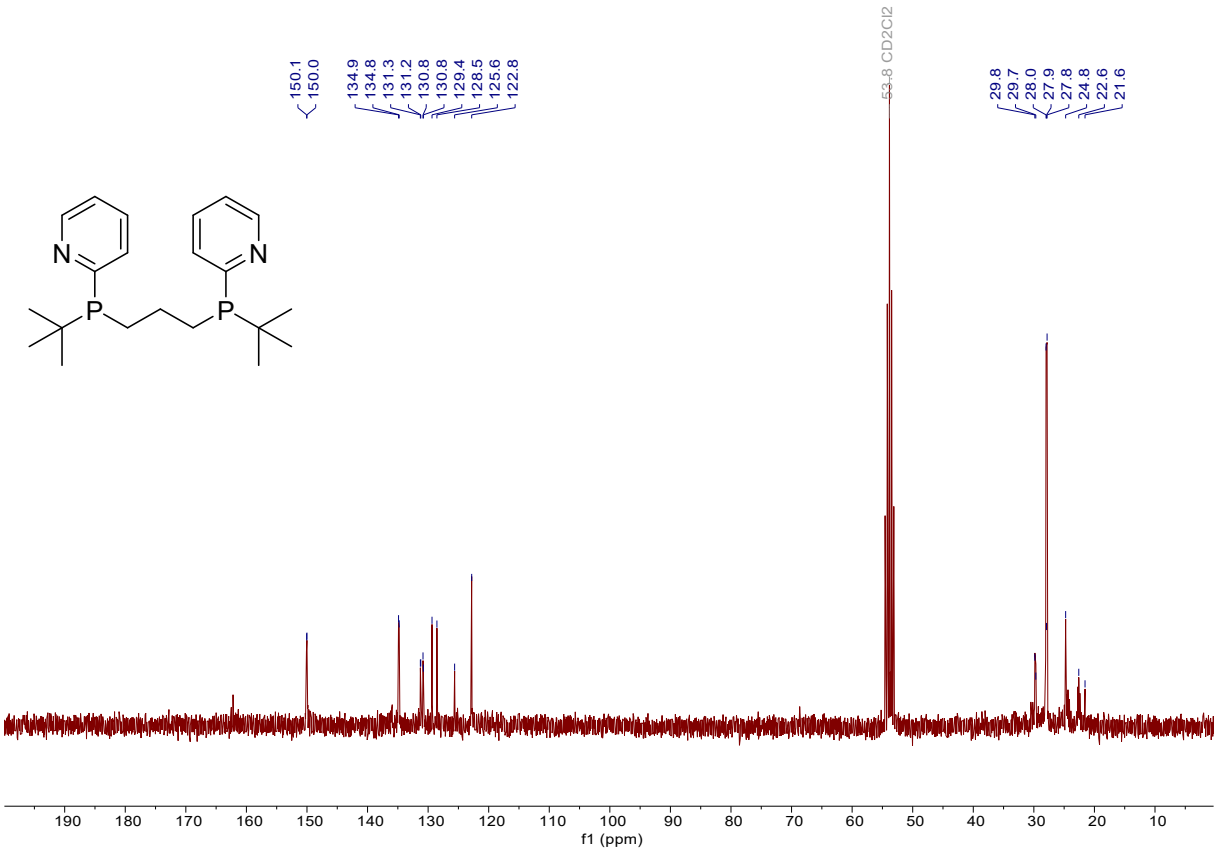

Figure 19: ^{13}C {^{1}H} NMR spectrum of **L3** in DCM-d_2; section **2.2.2.2**.

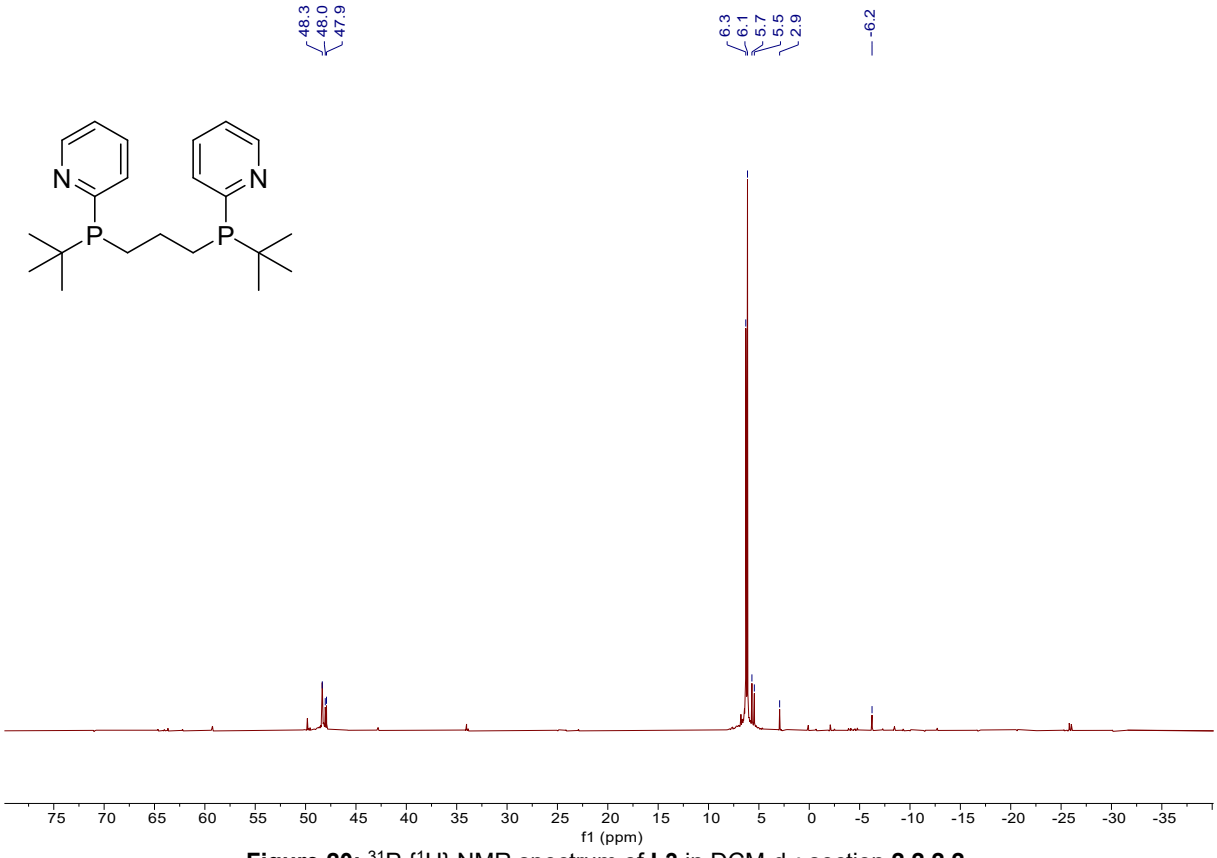

Figure 20: ^{31}P {^{1}H} NMR spectrum of **L3** in DCM-d_2; section **2.2.2.2**.

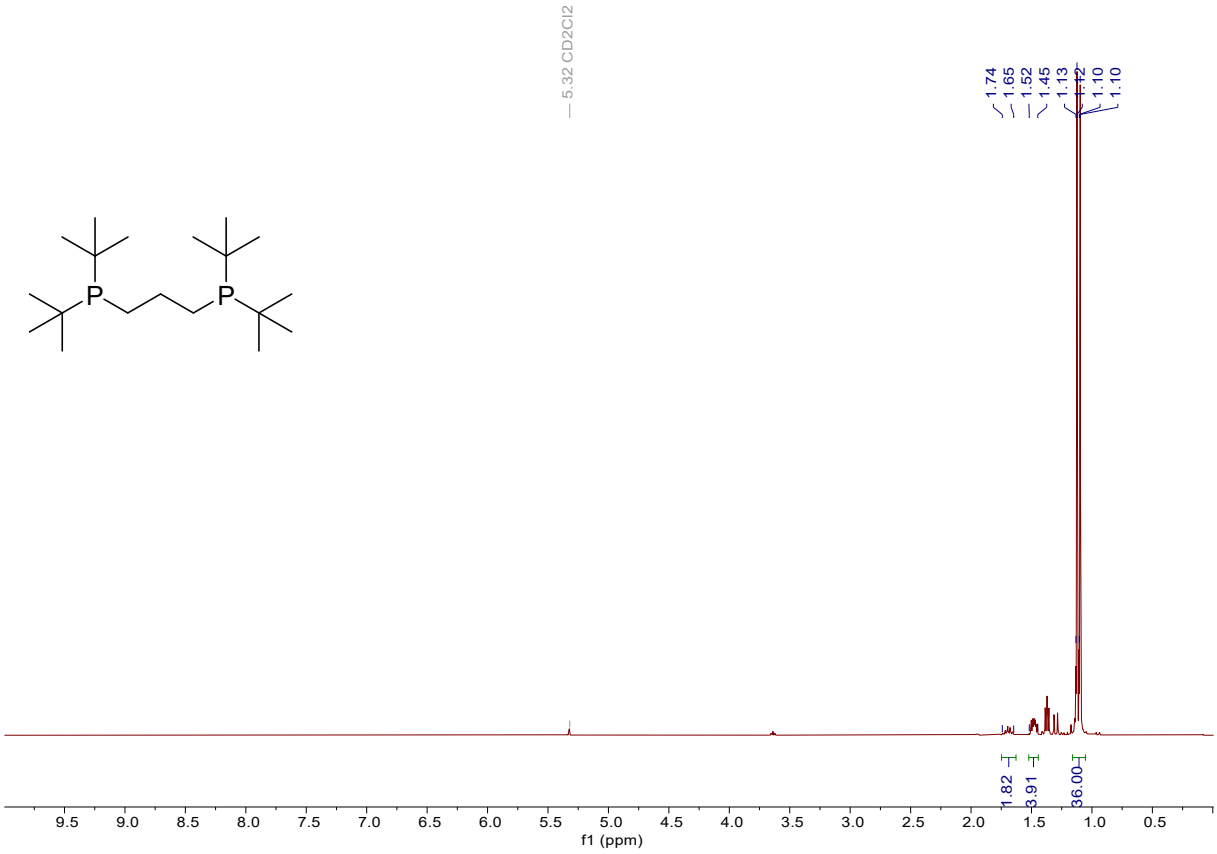

Figure 21: ^{1}H NMR spectrum of **L4** in DCM-d_2.

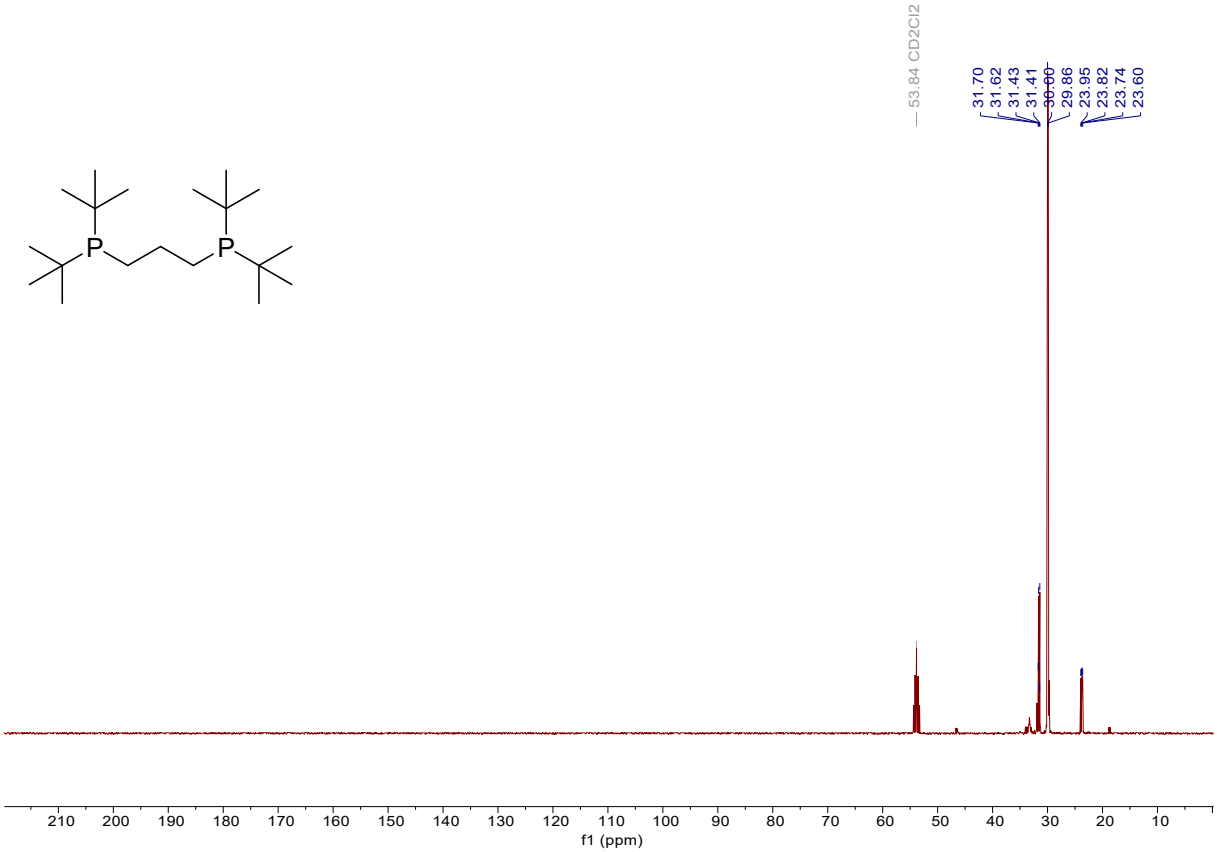

Figure 22: ^{13}C {^{1}H} NMR spectrum of **L4** in DCM-d_2.

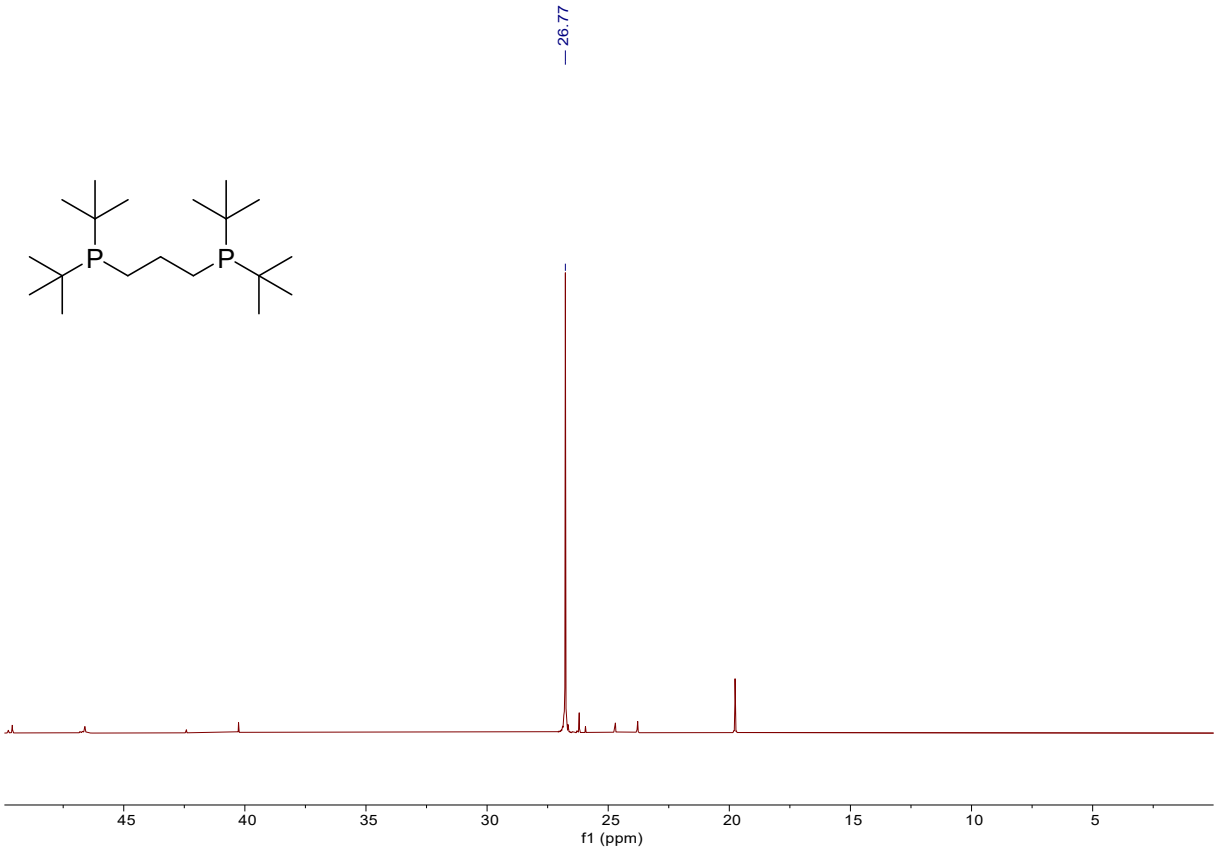

Figure 23: ^{31}P {^{1}H} NMR spectrum of **L4** in DCM-d_2.

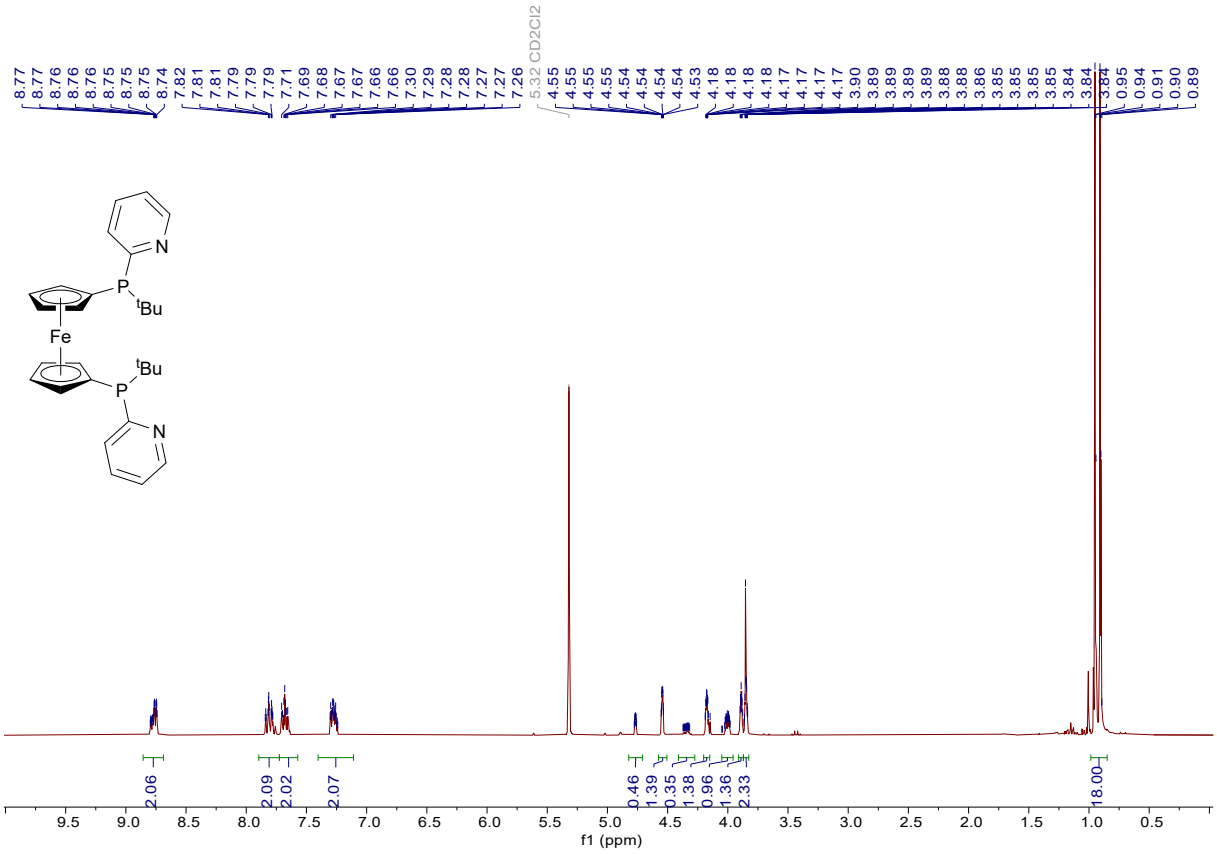

Figure 24: ^{1}H NMR spectrum of **L5** in DCM-d_2.

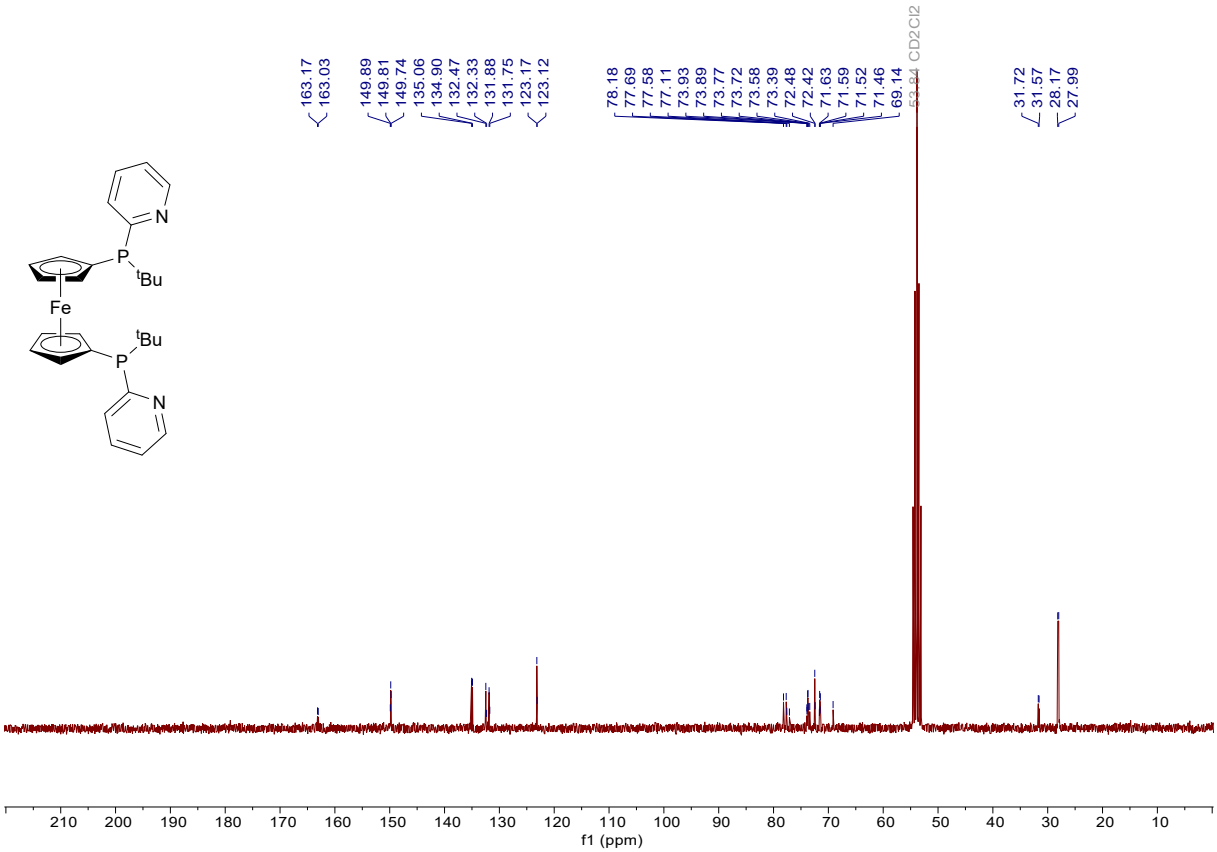

Figure 25: ^{13}C {^{1}H} NMR spectrum of **L5** in DCM-d_2.

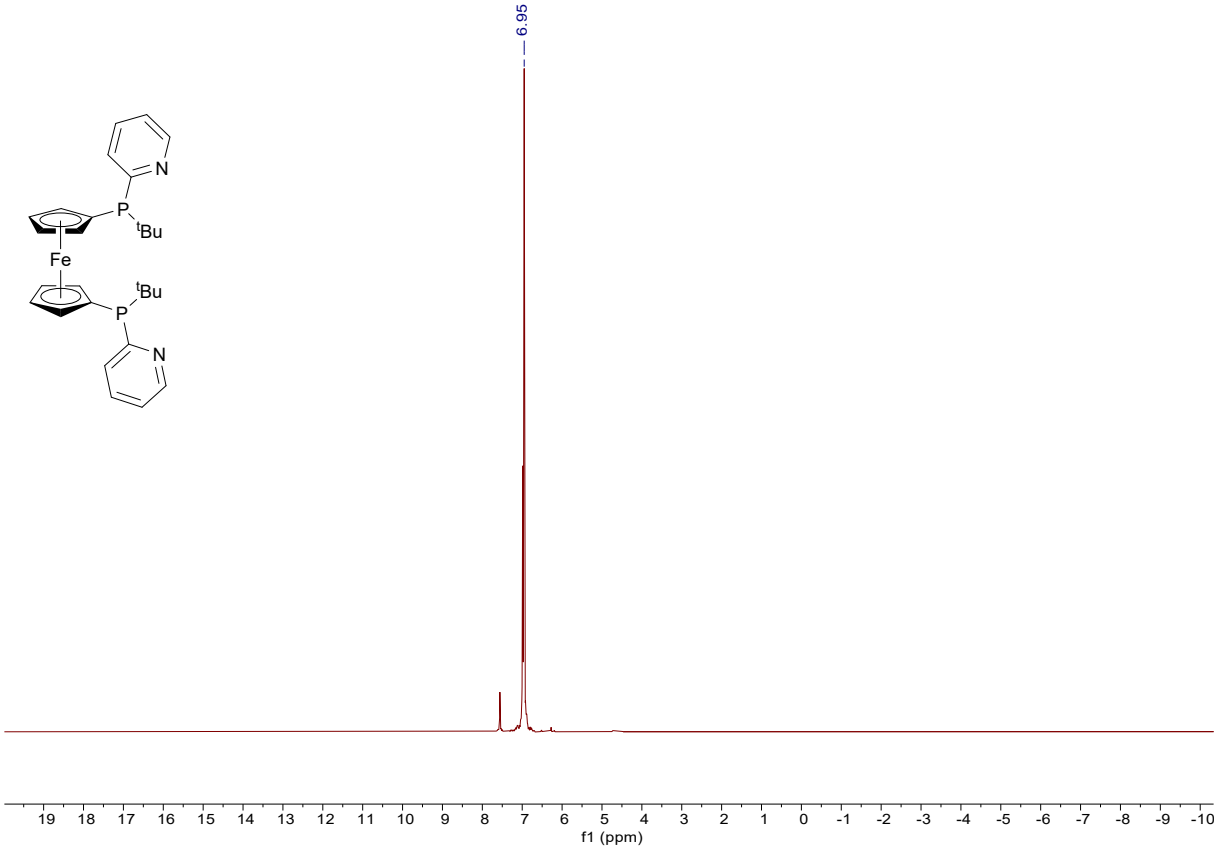

Figure 26: ^{31}P {^{1}H} NMR spectrum of **L5** in DCM-d_2.

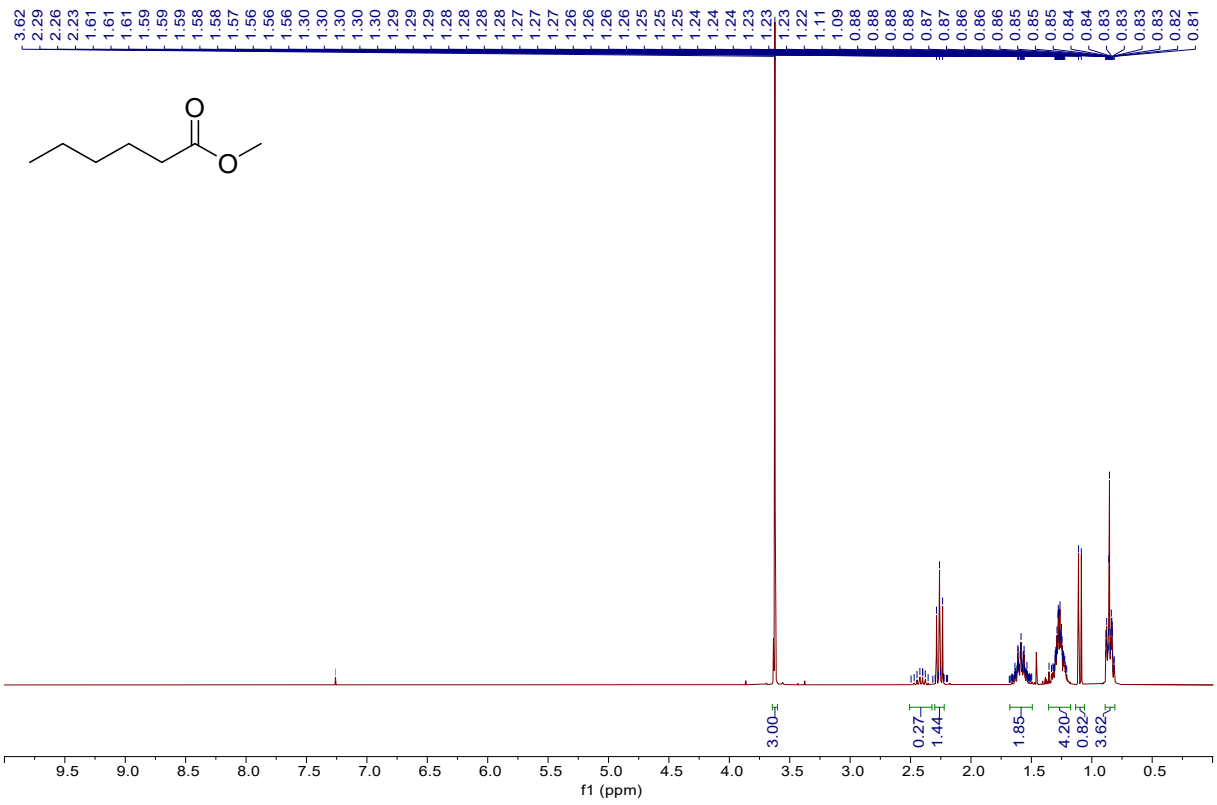

Figure 27: ^{1}H NMR spectrum of **2a** in $CDCl_3$.

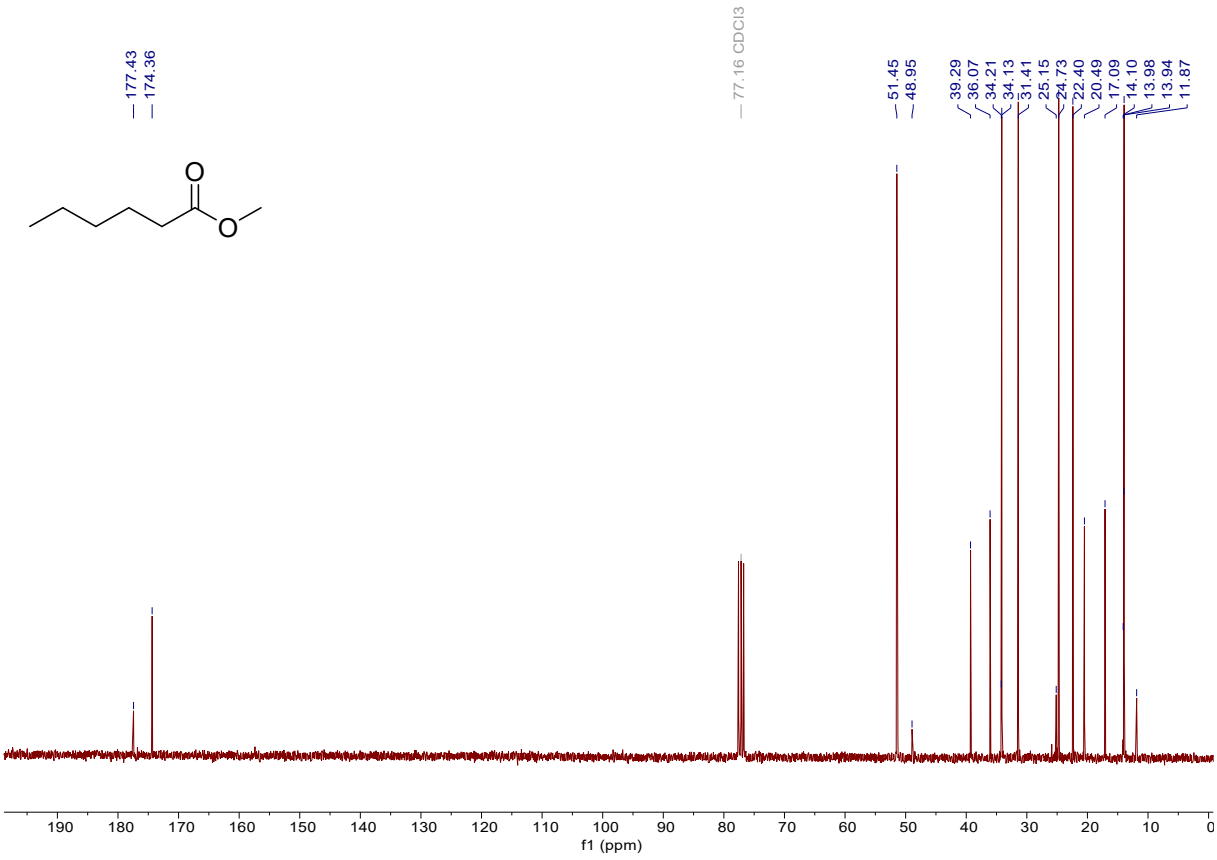

Figure 28: ^{13}C {^{1}H} NMR spectrum of **2a** in $CDCl_3$.

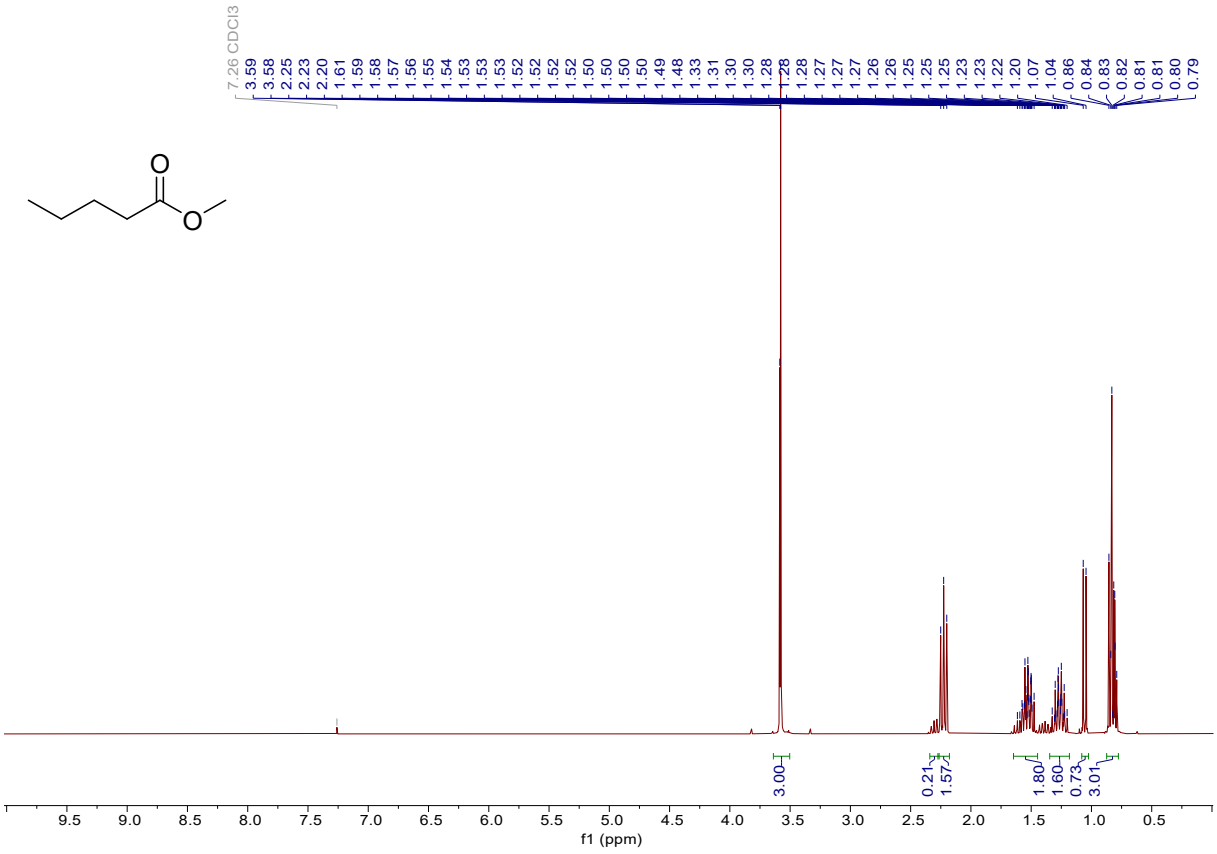

Figure 29: ^{1}H NMR spectrum of **2b** in $CDCl_3$.

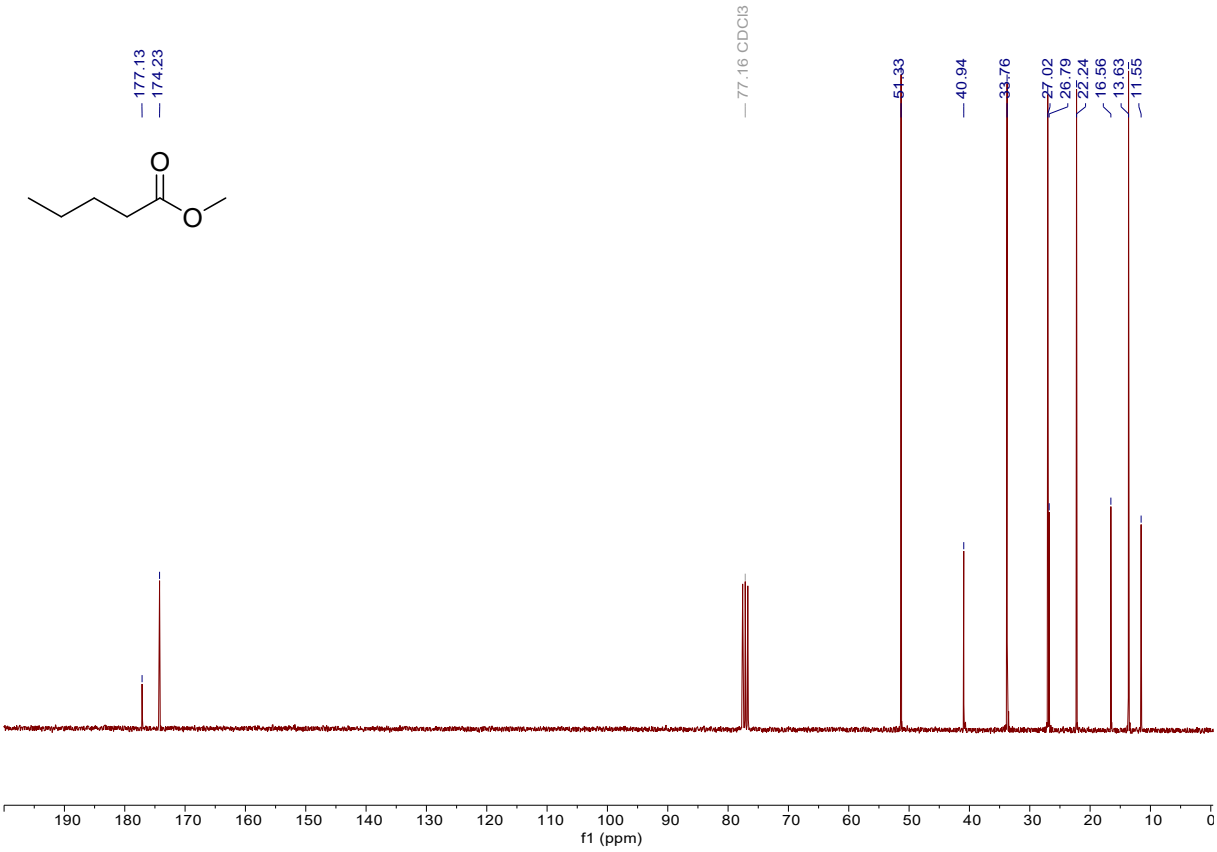

Figure 30: ^{13}C {^{1}H} NMR spectrum of **2b** in $CDCl_3$.

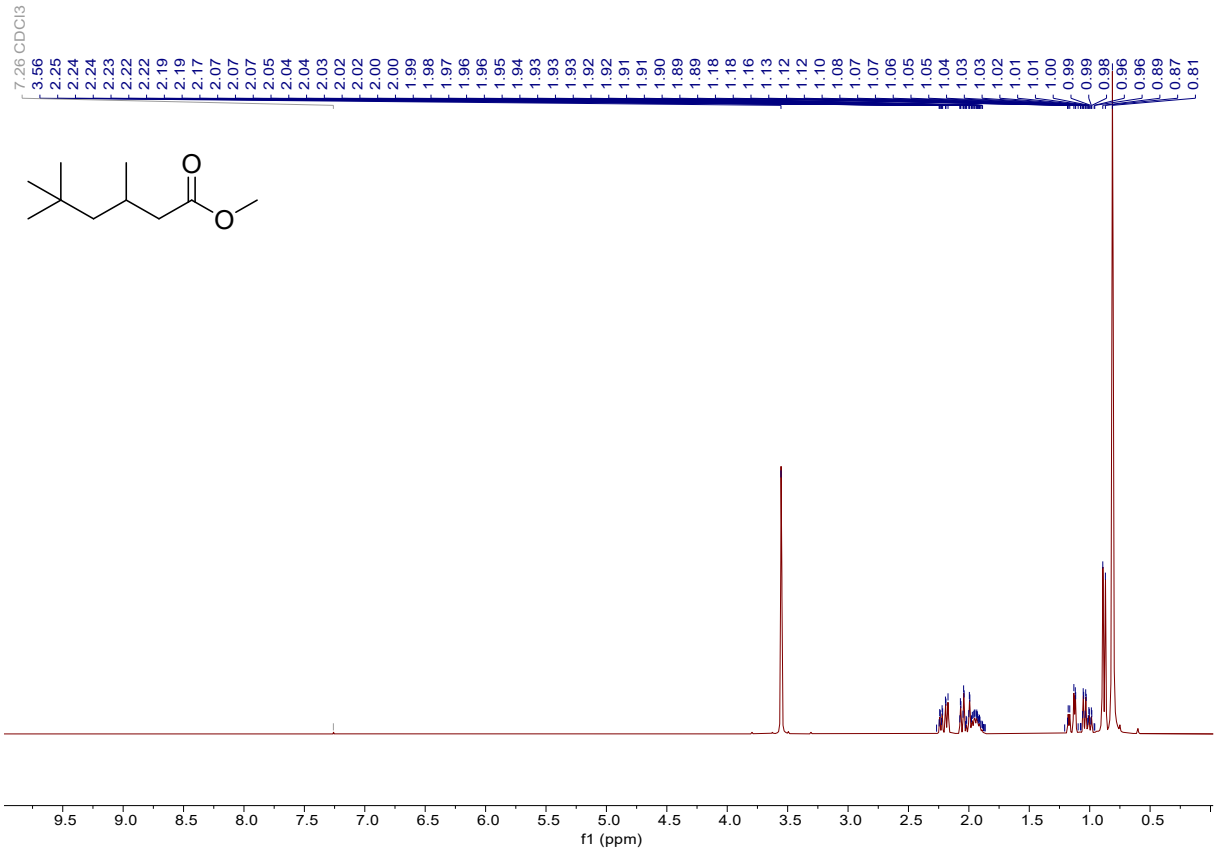

Figure 31: ^{1}H NMR spectrum of **2d** in $CDCl_3$.

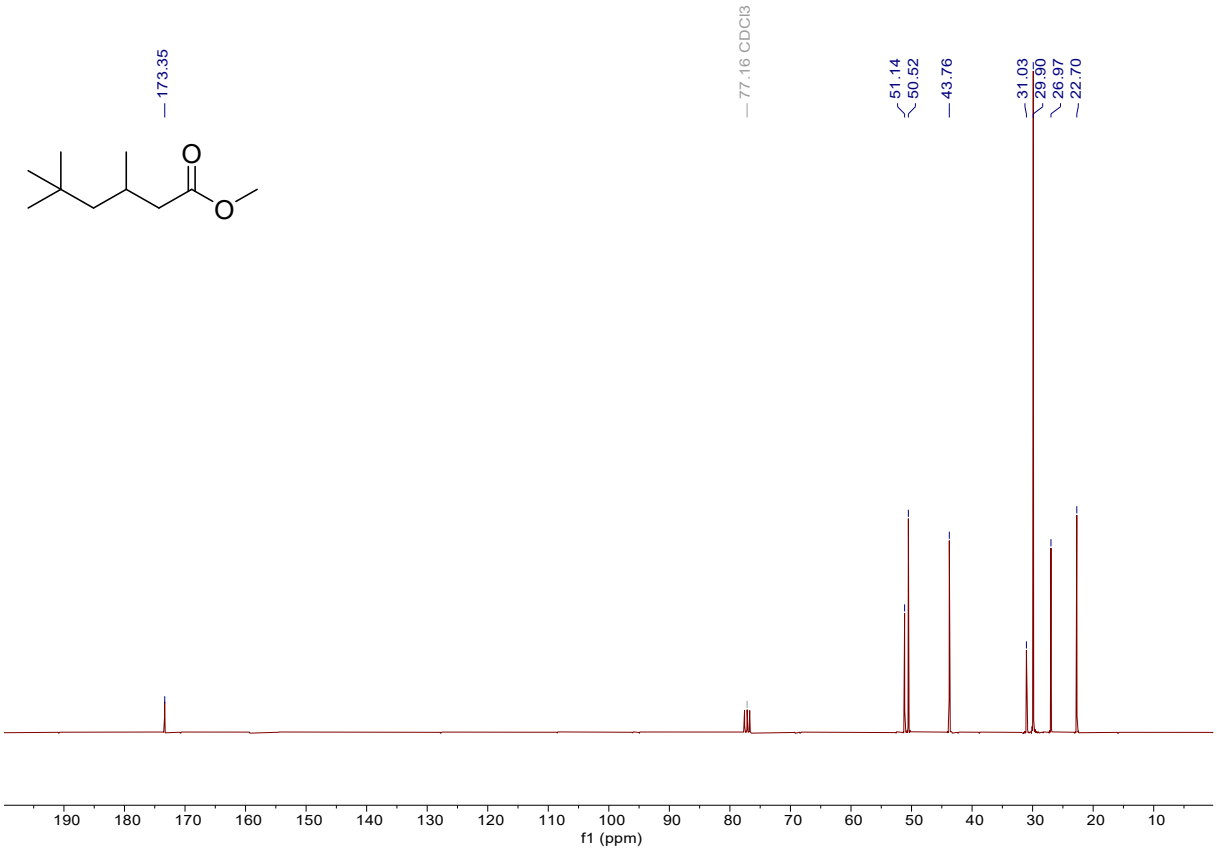

Figure 32: ^{13}C {^{1}H} NMR spectrum of **2d** in $CDCl_3$.

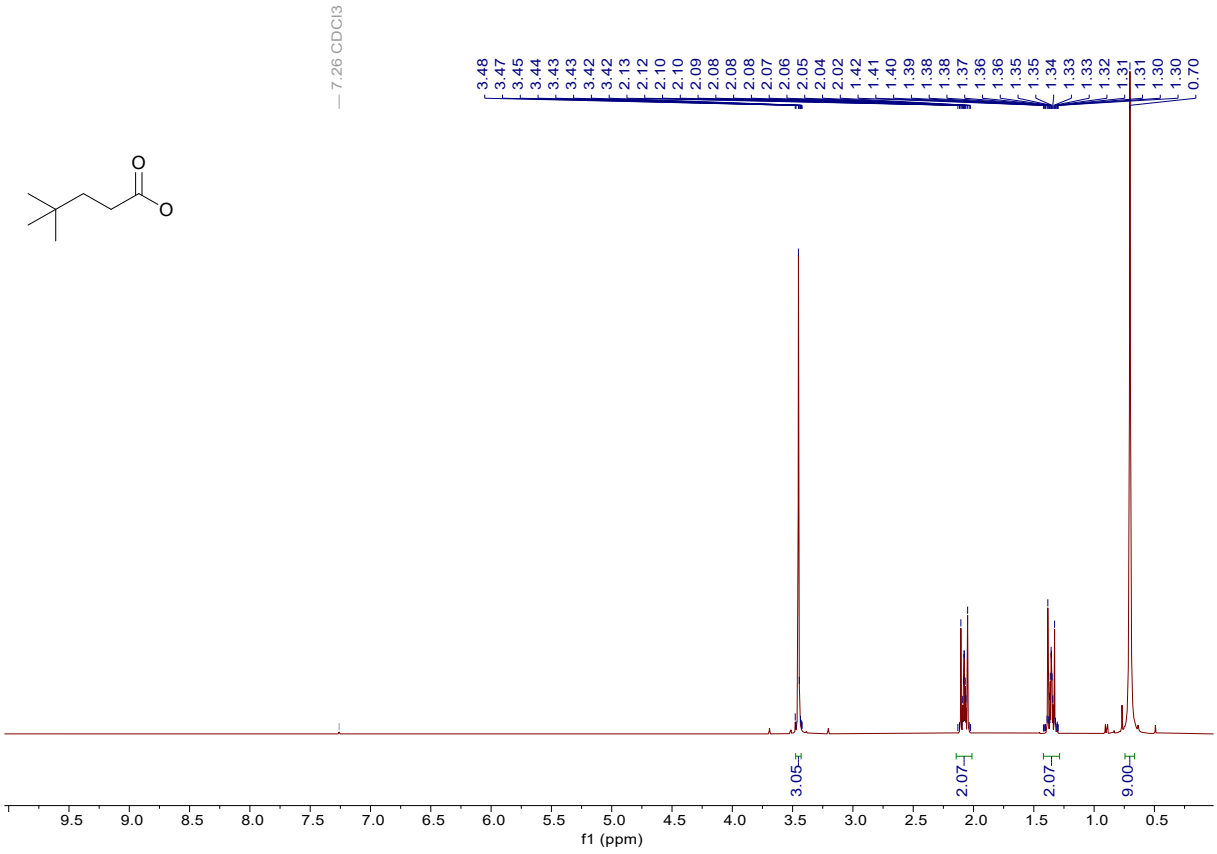

Figure 33: ^{1}H NMR spectrum of **2e** in $CDCl_3$

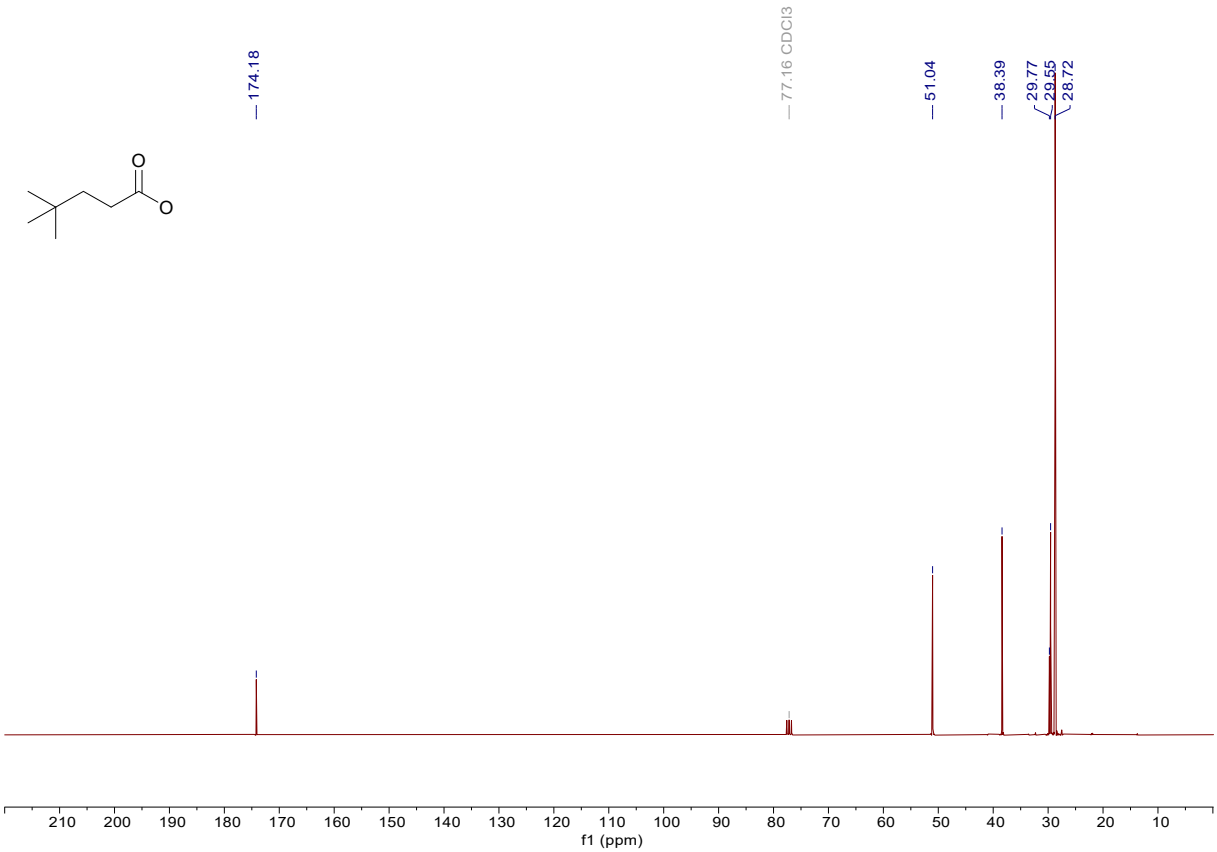

Figure 34: ^{13}C {^{1}H} NMR spectrum of **2e** in $CDCl_3$.

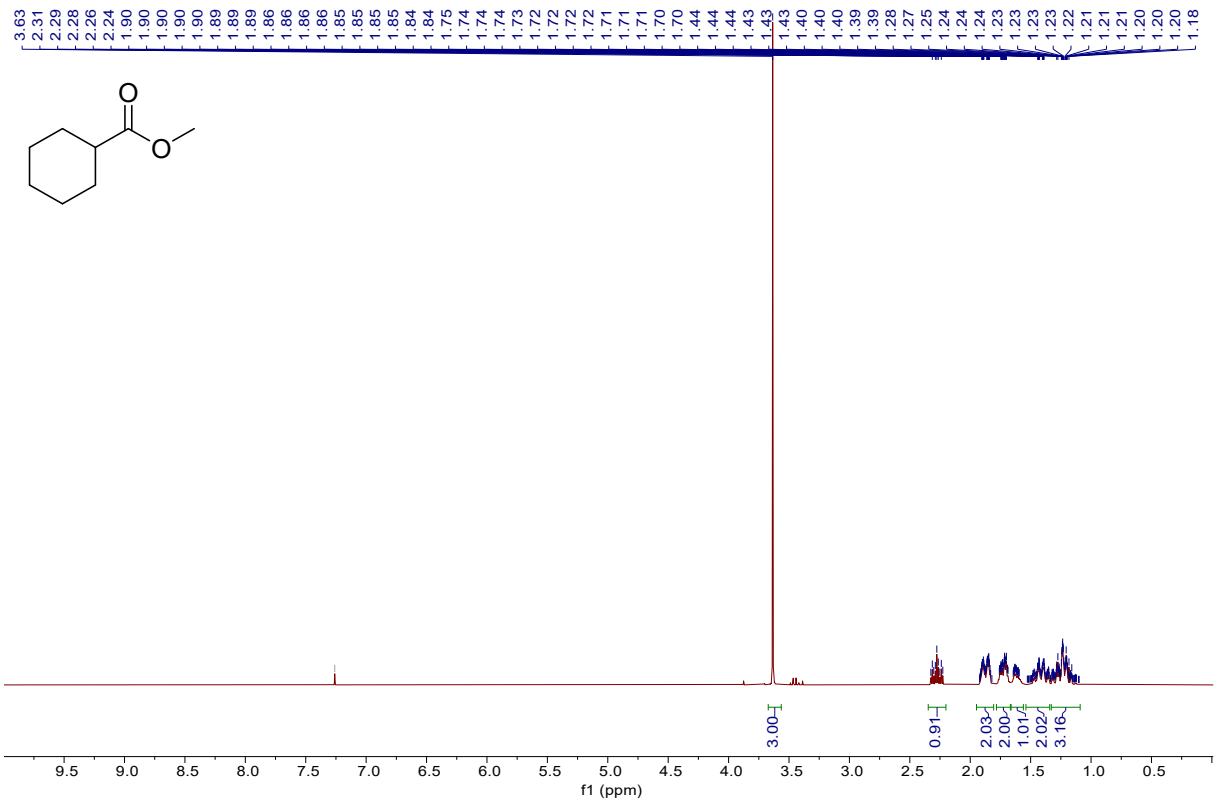

Figure 35: ^{1}H NMR spectrum of **2f** in $CDCl_3$.

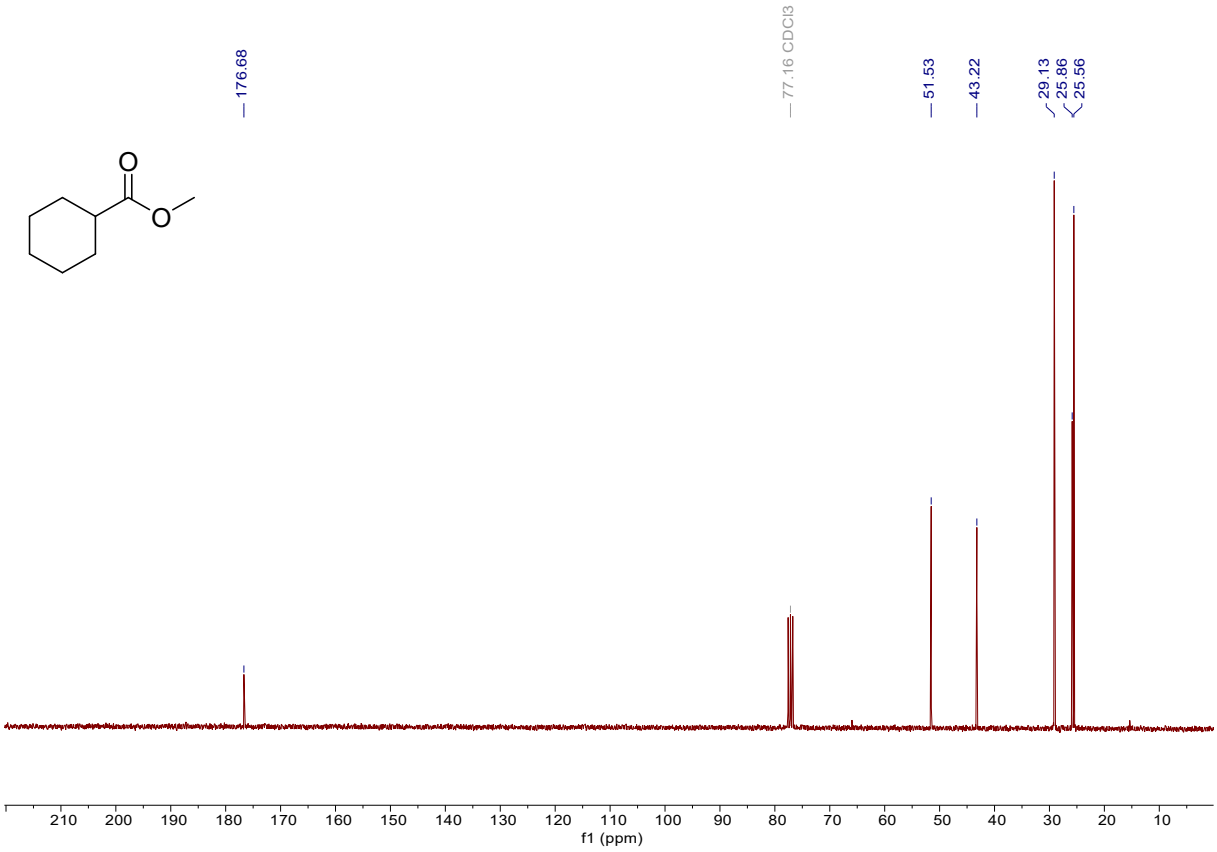

Figure 36: ^{13}C {^{1}H} NMR spectrum of **2f** in $CDCl_3$.

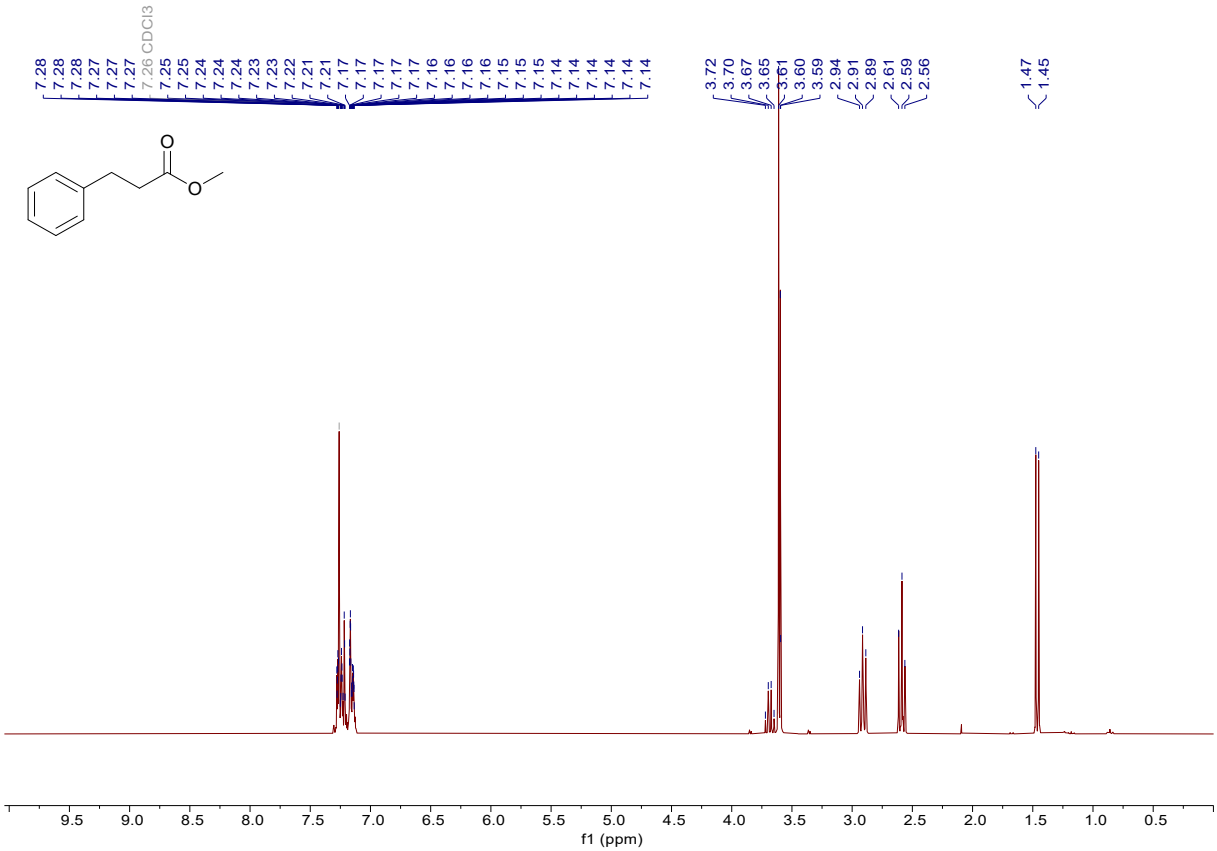

Figure 37: ^{1}H NMR spectrum of **2h** in $CDCl_3$.

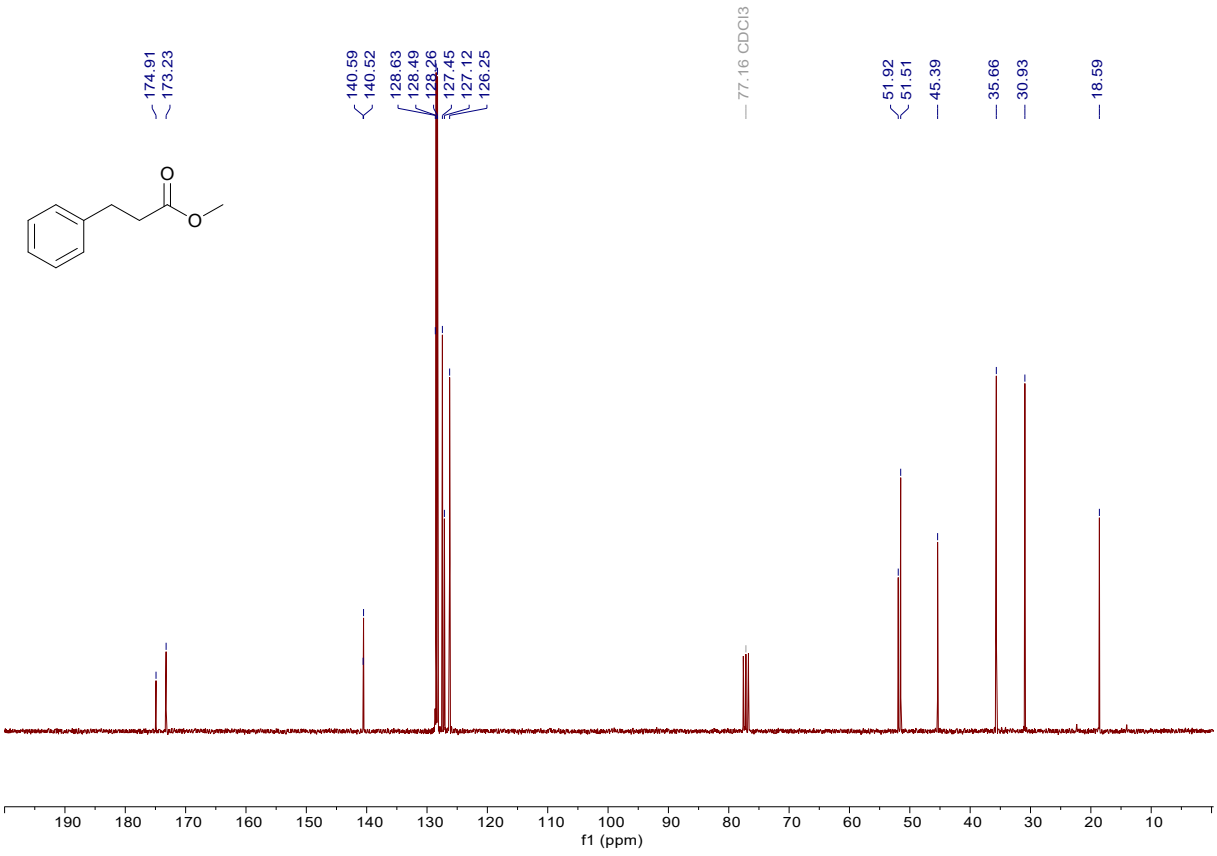

Figure 38: ^{13}C {^{1}H} NMR spectrum of **2h** in $CDCl_3$.

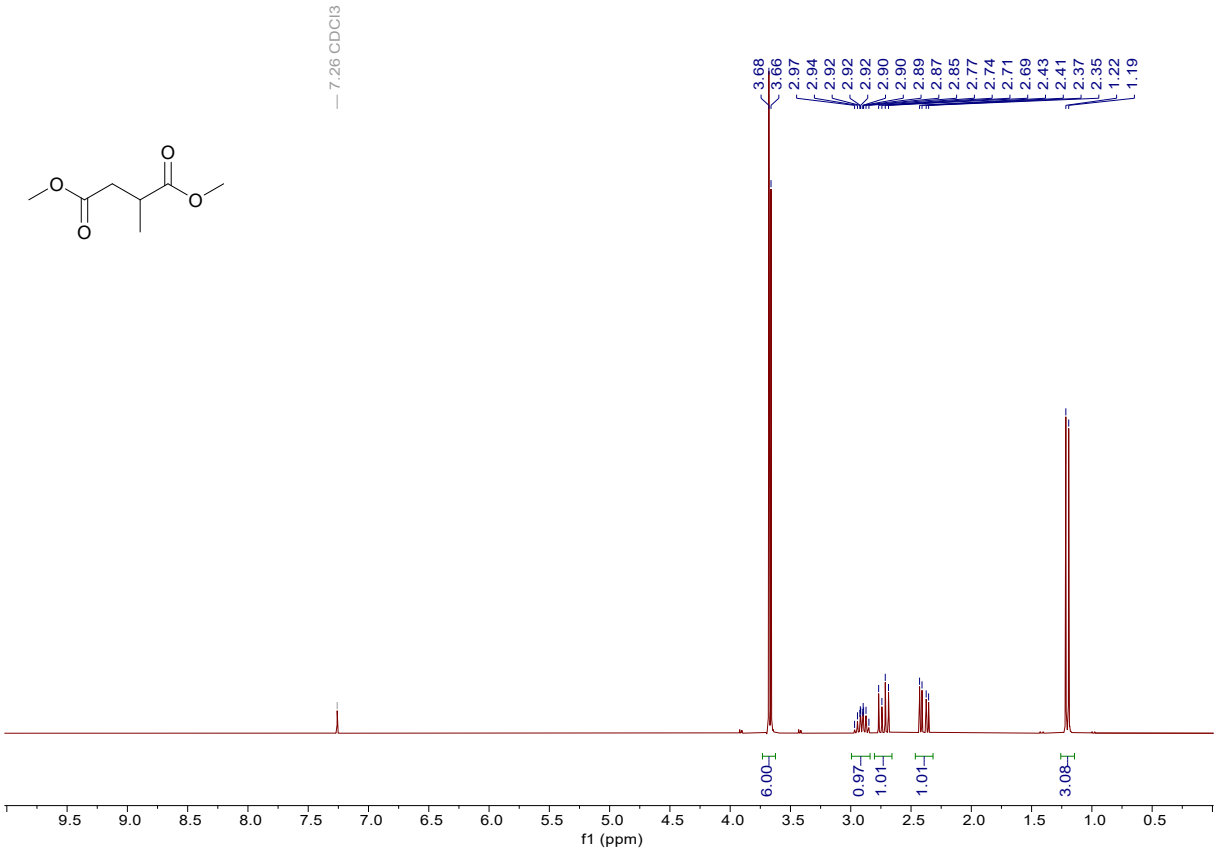

Figure 39: ^{1}H NMR spectrum of **2i** in $CDCl_3$.

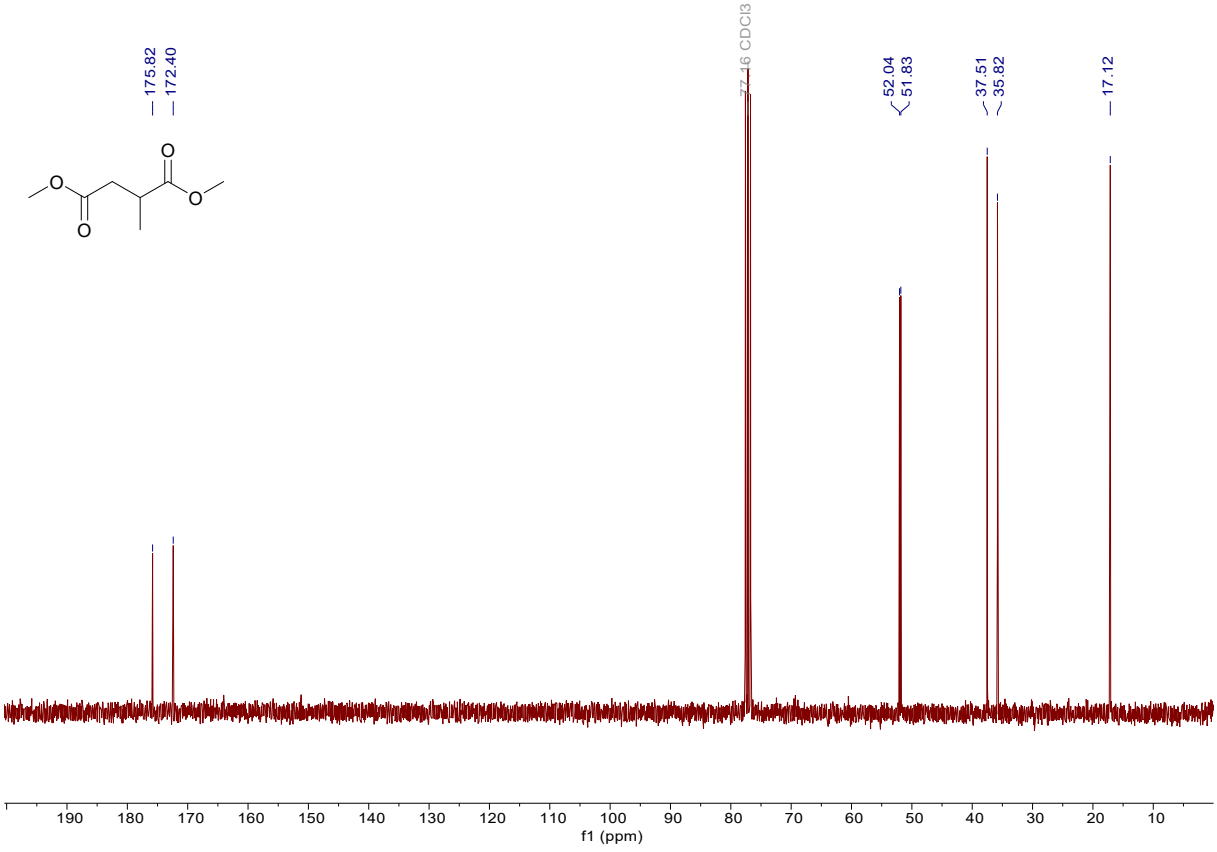

Figure 40: ^{13}C {^{1}H} NMR spectrum of **2i** in $CDCl_3$.

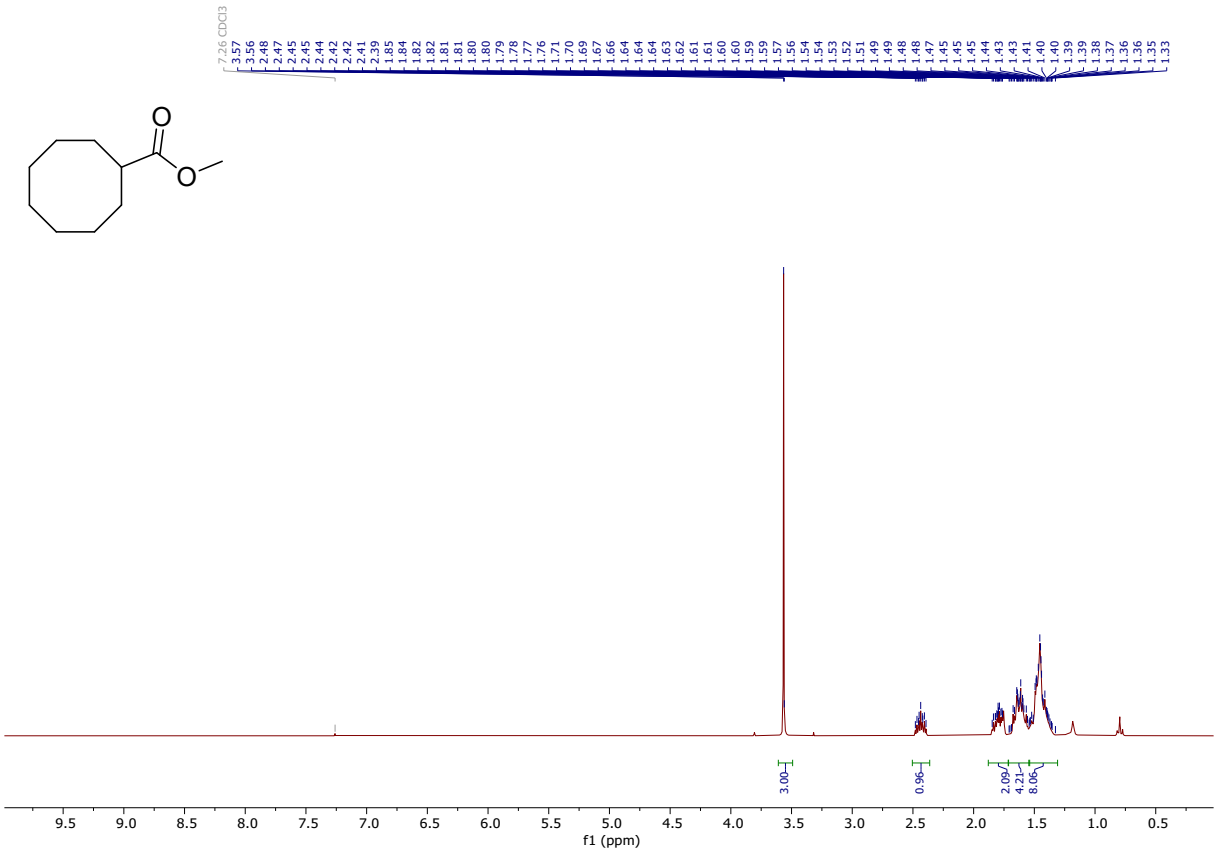

Figure 41: ^{1}H NMR spectrum of **2j** in $CDCl_3$.

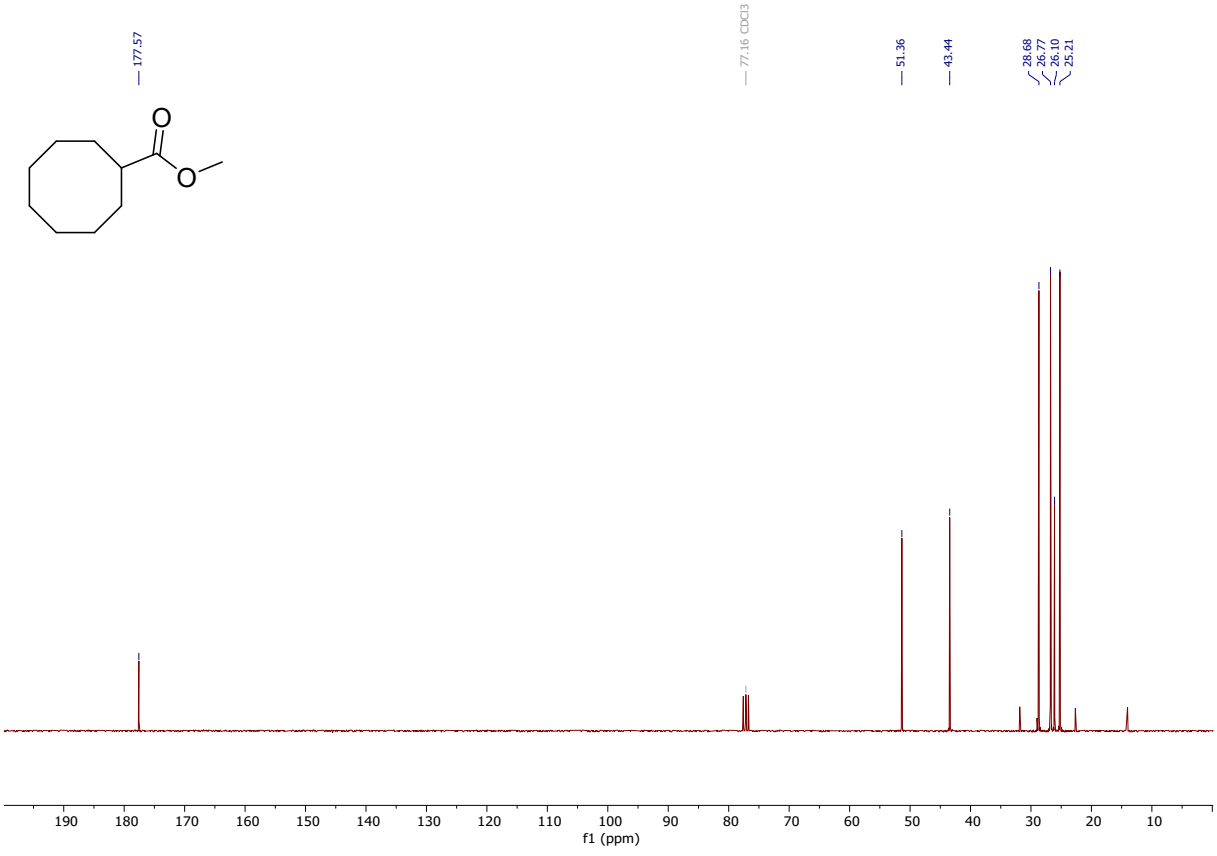

Figure 42: ^{13}C {^{1}H} NMR spectrum of **2j** in $CDCl_3$.

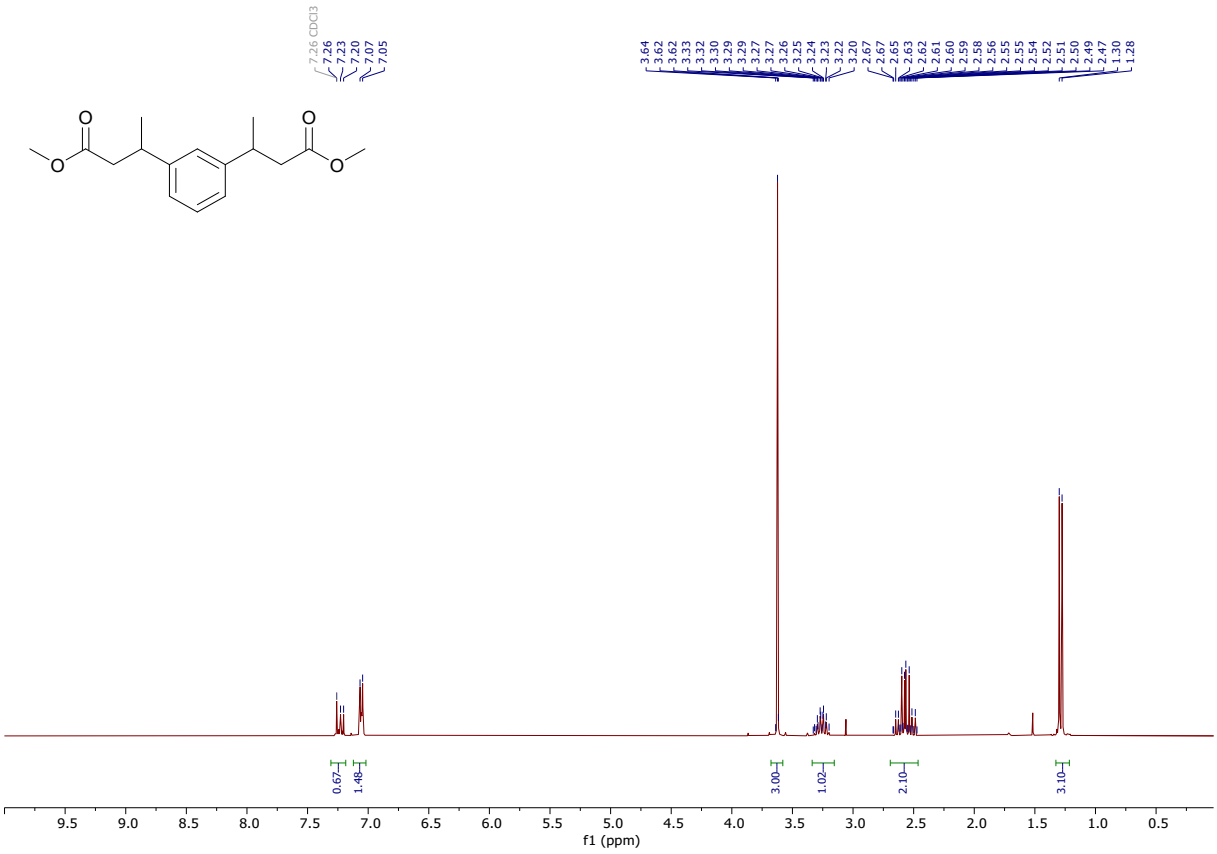

Figure 43: ^{1}H NMR spectrum of **2k** in $CDCl_3$.

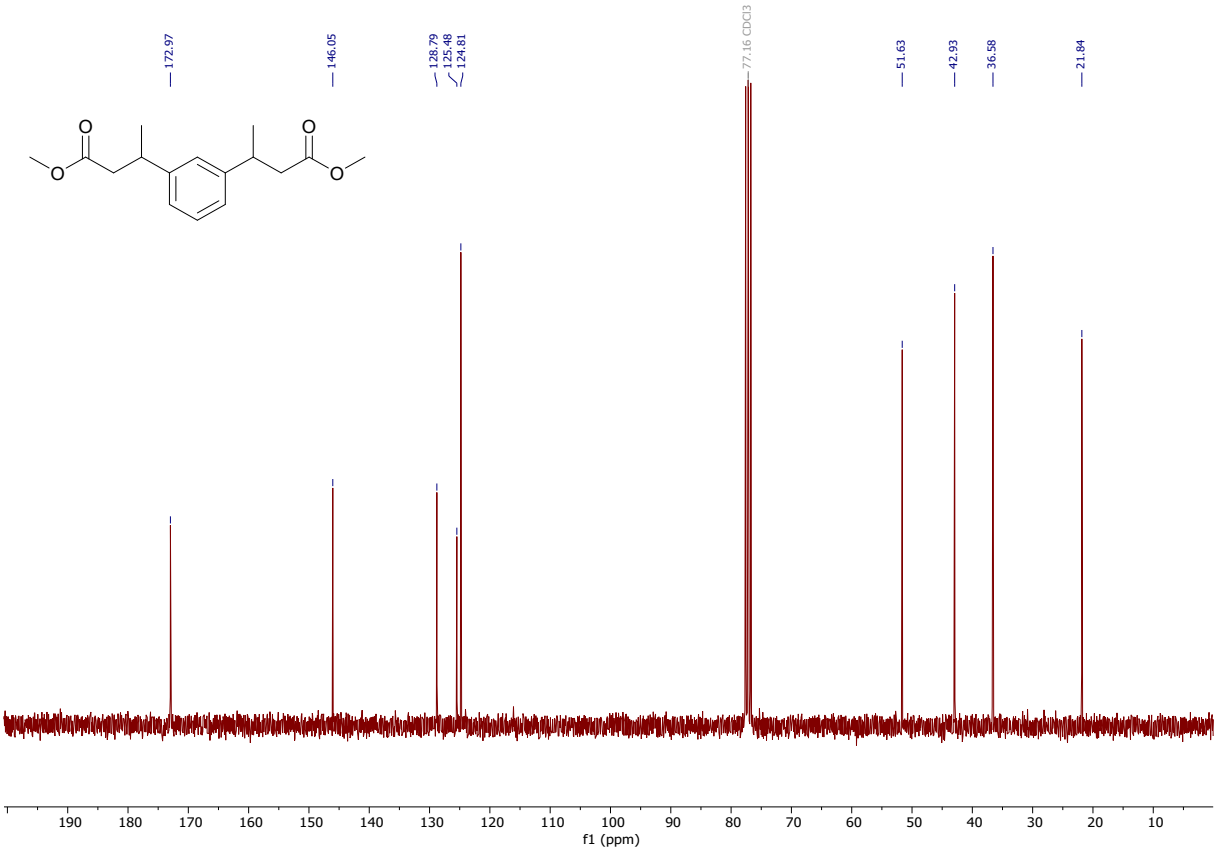

Figure 44: ^{13}C {^{1}H} NMR spectrum of **2k** in $CDCl_3$.

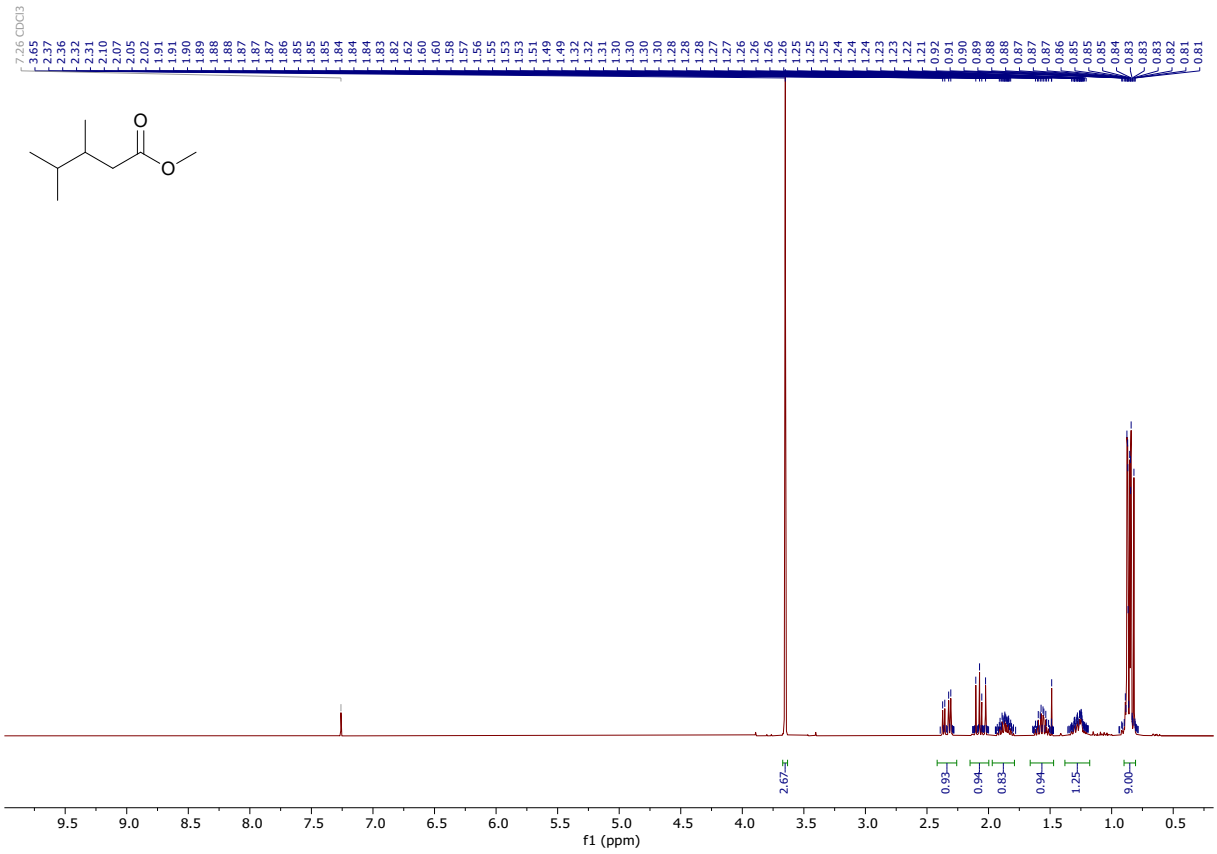

Figure 45: ^{1}H NMR spectrum of **2l** in $CDCl_3$.

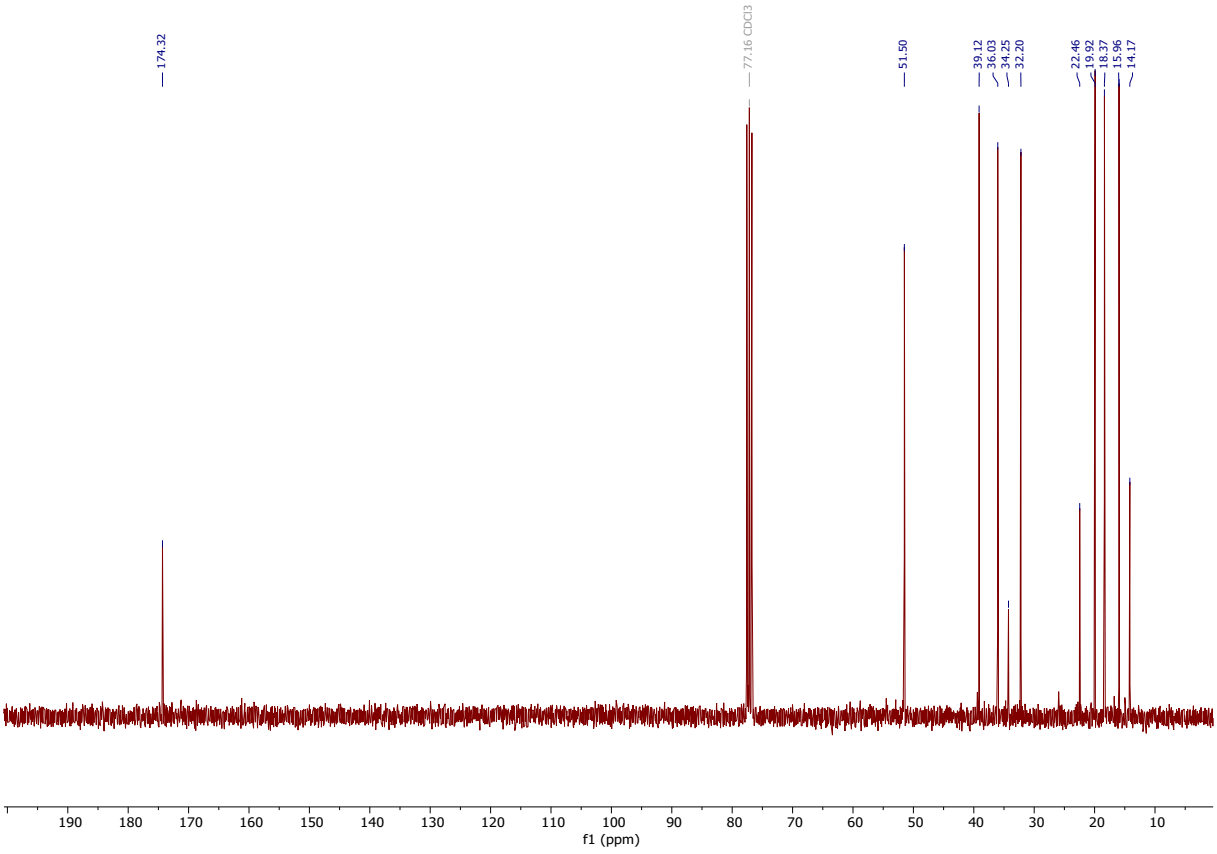

Figure 46: ^{13}C {^{1}H} NMR spectrum of **2l** in $CDCl_3$.

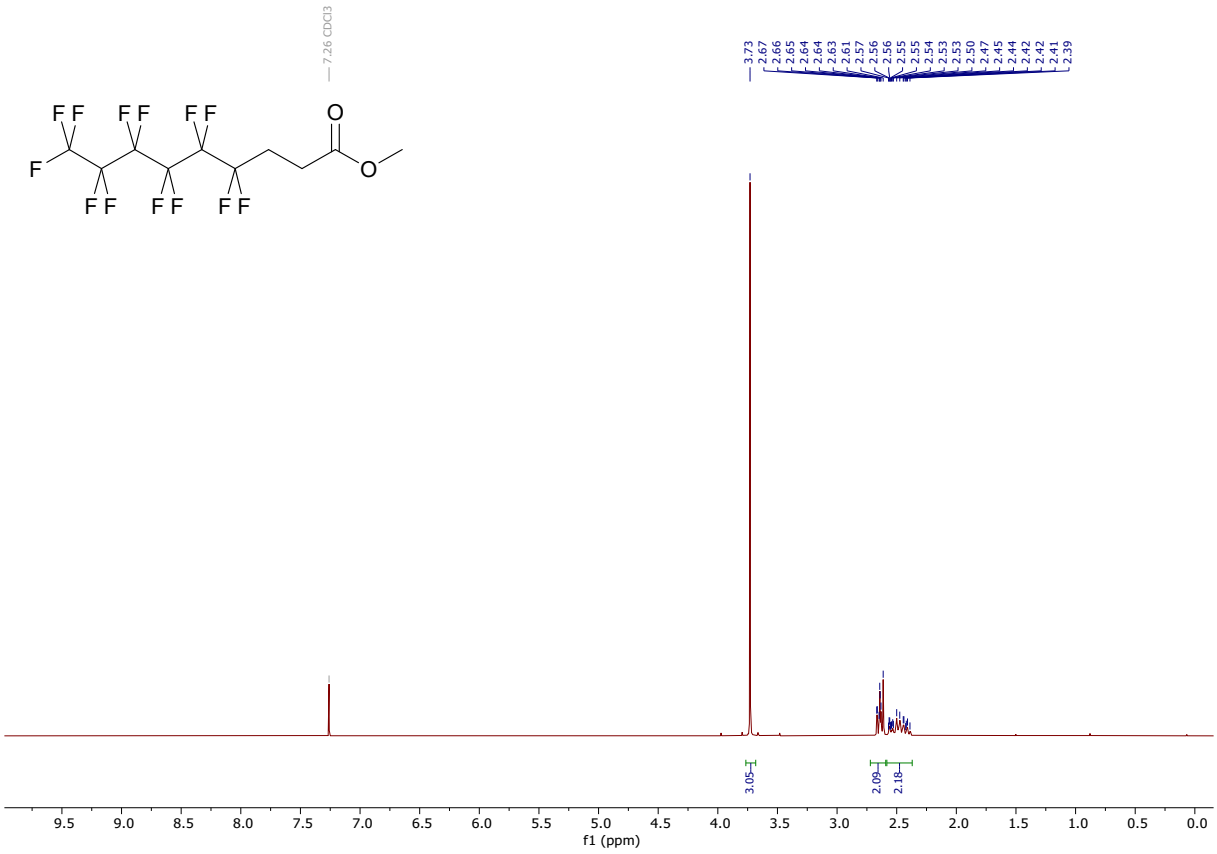

Figure 47: ^{1}H NMR spectrum of **2m** in $CDCl_3$.

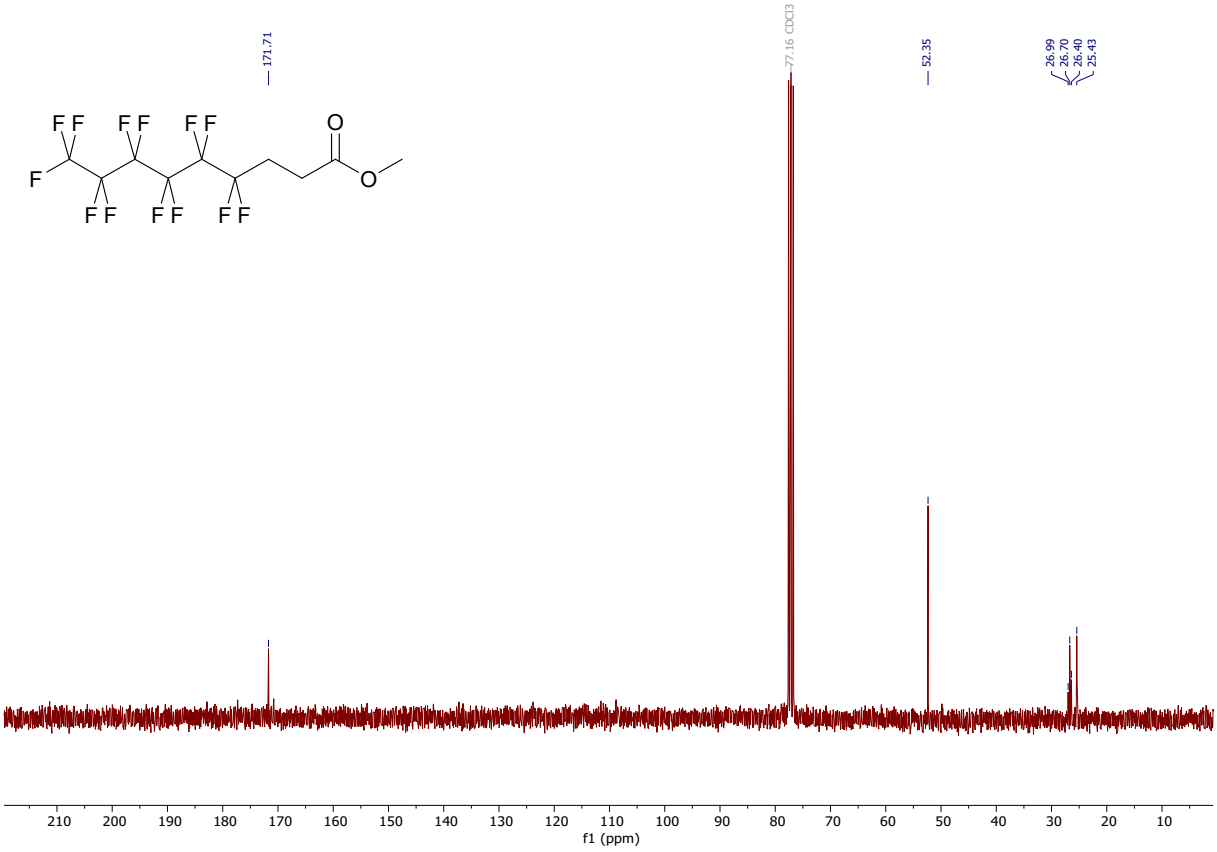

Figure 48: ^{13}C {^{1}H} NMR spectrum of **2m** in $CDCl_3$.

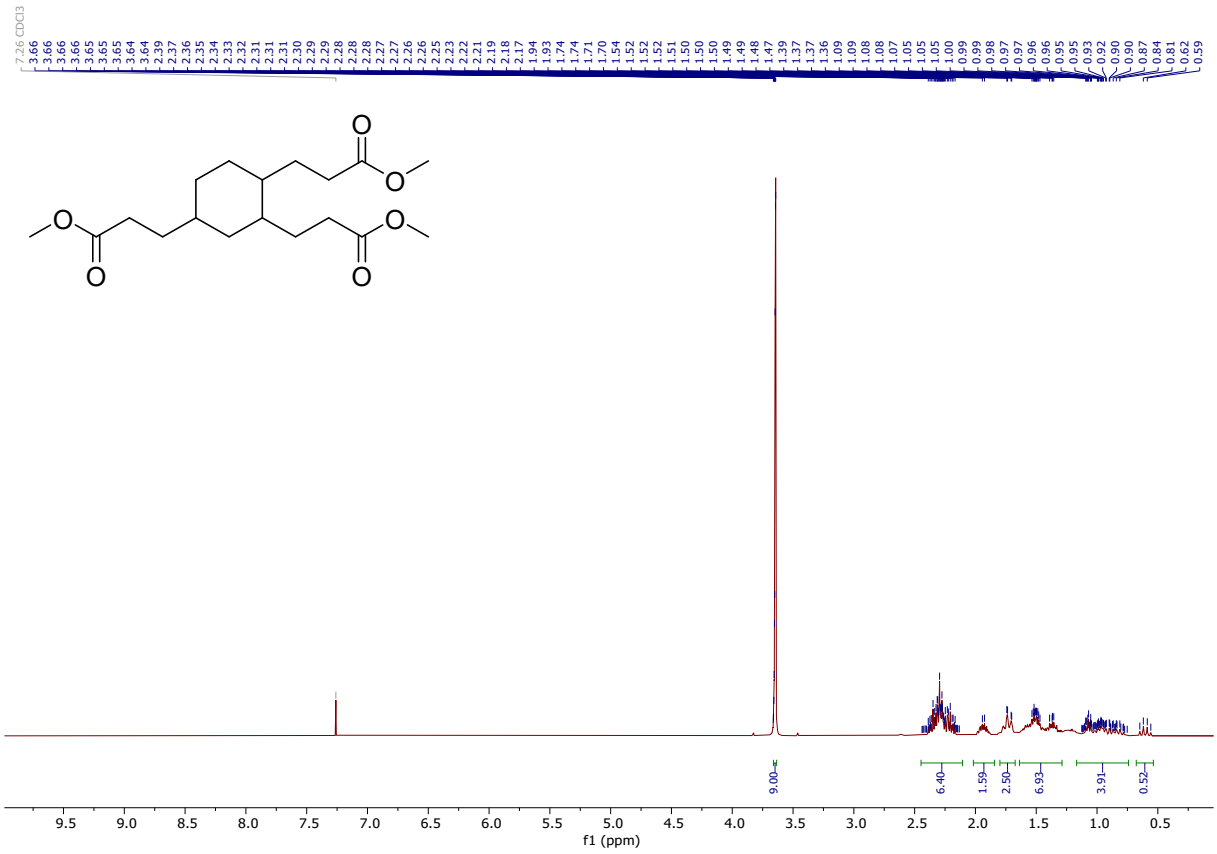

Figure 49: ^{1}H NMR spectrum of **2n** in $CDCl_3$.

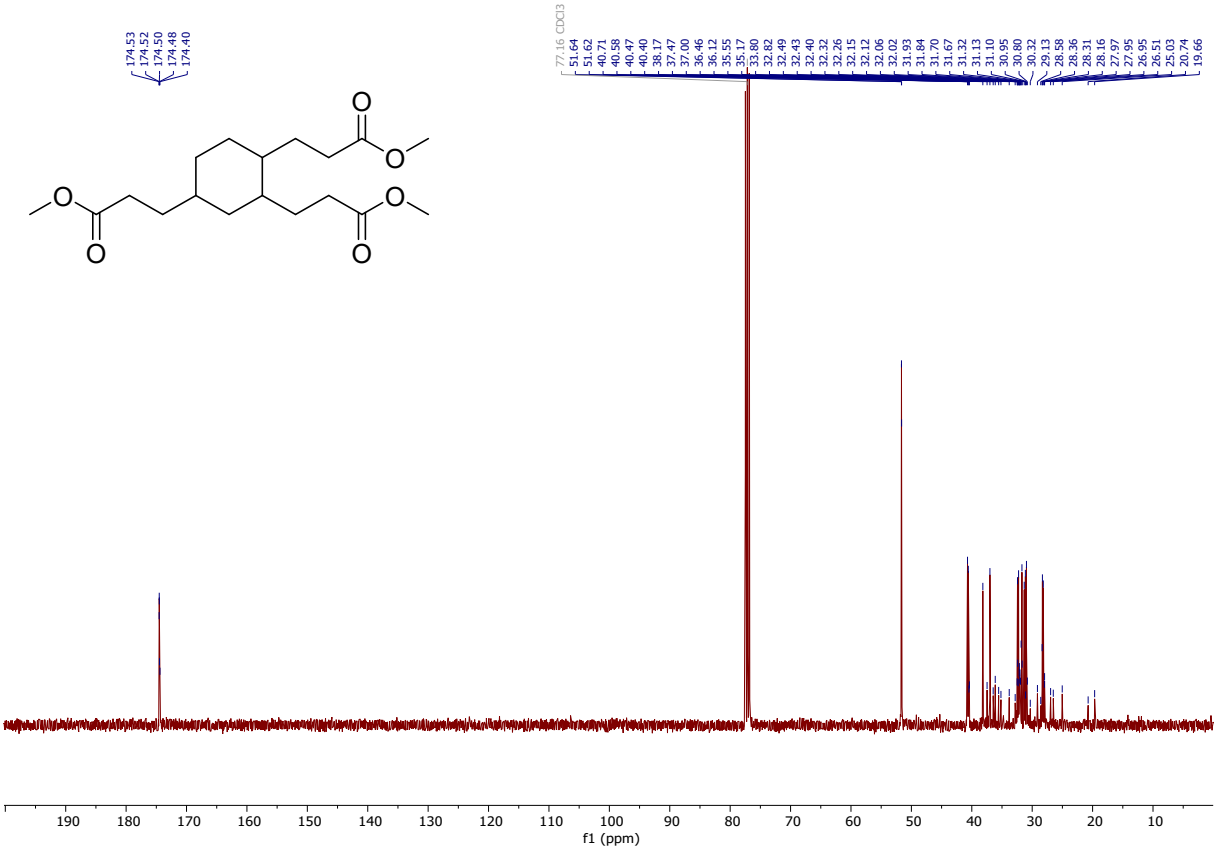

Figure 50: ^{13}C {^{1}H} NMR spectrum of **2n** in $CDCl_3$.

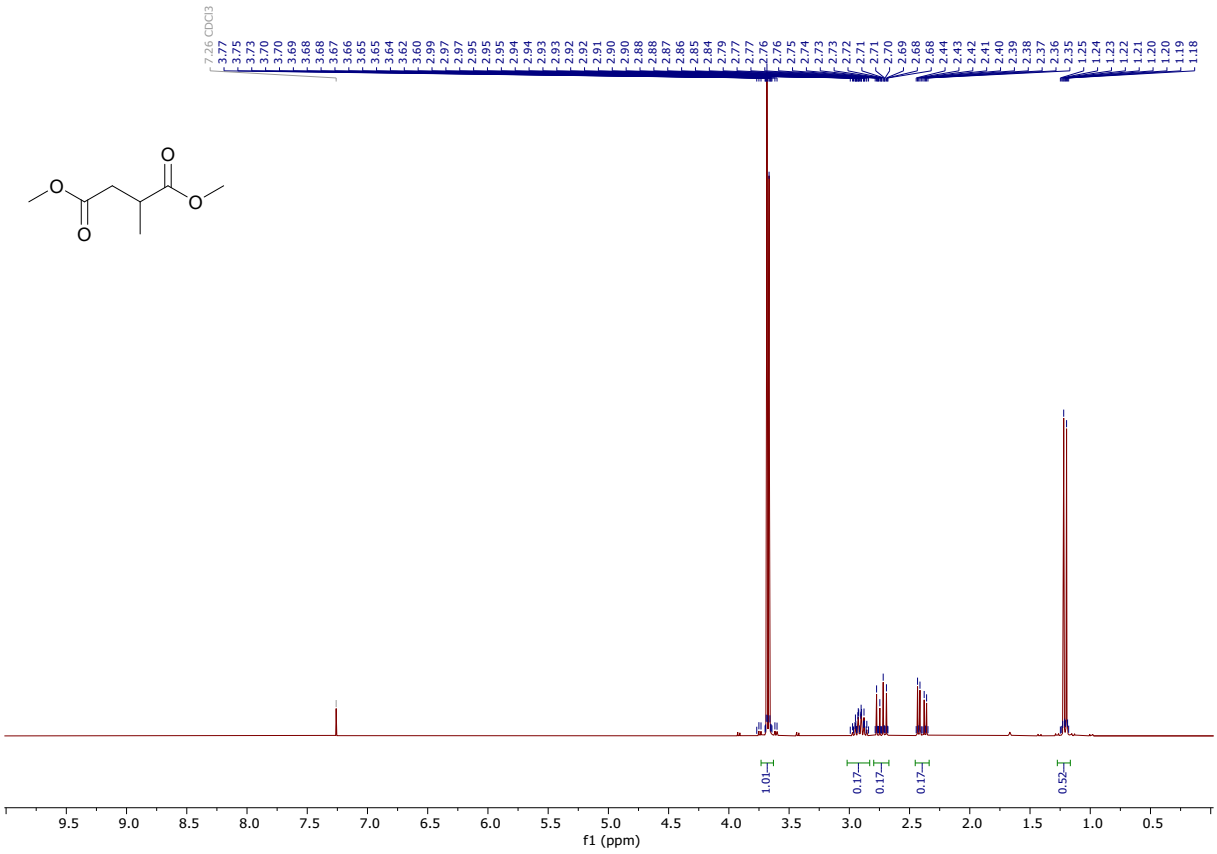

Figure 51: ^{1}H NMR spectrum of Methyl 2-methylsuccinate after the scale-up reaction in $CDCl_3$.

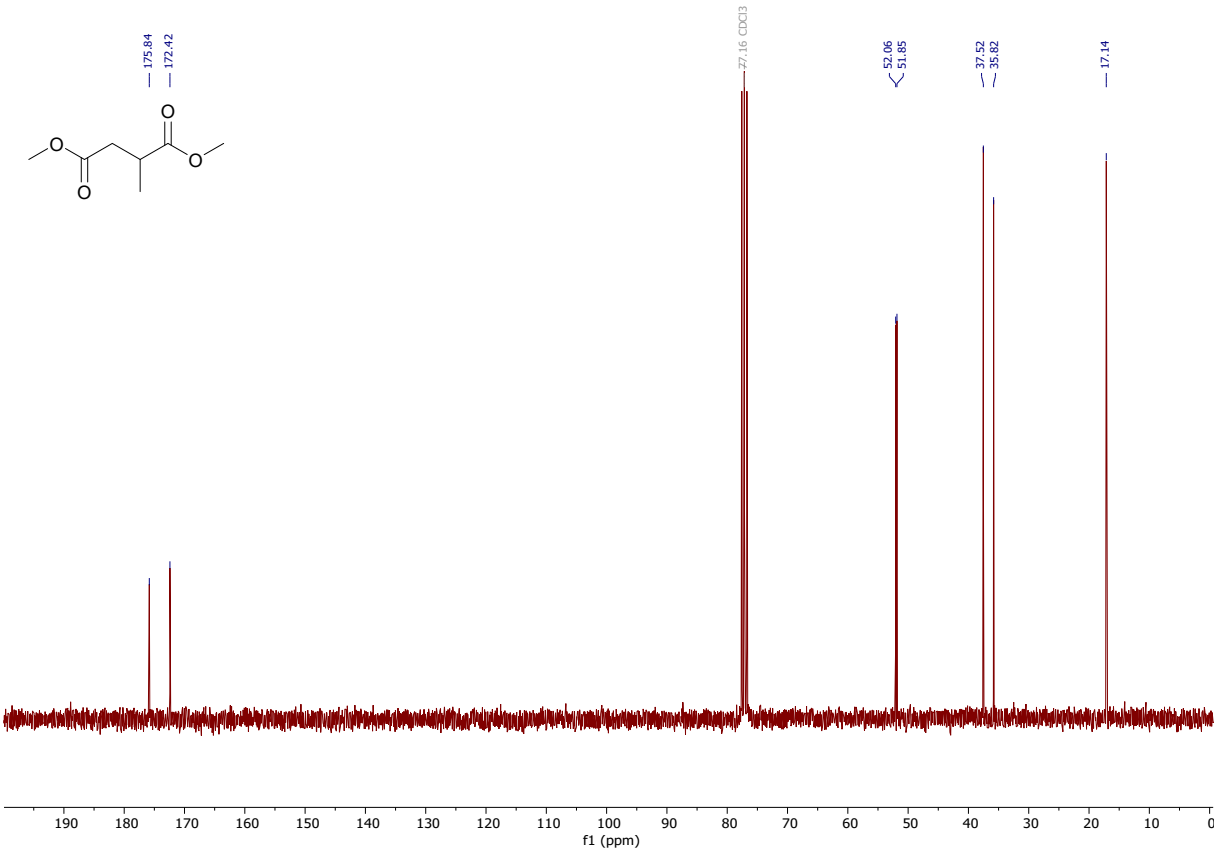

Figure 52: ^{13}C {^{1}H} NMR spectrum of Methyl 2-methylsuccinate after the scale up reaction in $CDCl_3$.