

Rethinking Basic Concepts – Hydrogenation of Alkenes Catalyzed by Bench-Stable Alkyl Mn(I) Complexes

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1. General Information

All reactions were performed under an inert atmosphere of argon by using Schlenk techniques or in a MBraun inert-gas glovebox. The solvents were purified according to standard procedures. The deuterated solvents were purchased from Aldrich and dried over 3 Å molecular sieves. Complexes *fac*-[Mn(dpre)(CO)₃(Br)] (dpre = 1,2-bis(di-*n*-propylphosphino)ethane) (**1**),¹ *fac*-[Mn(dippe)(CO)₃(Br)] (dippe = 1,2-bis(di-*iso*-propylphosphino)ethane) (**2**)² *fac*-[Mn(dippe)(CO)₃(H)] (**7**)² [Mn(CO)₅(CH₃)] (**8**)³ and *fac*-[Mn(bipy)(CO)₃(CH₃)] (**9**)⁴ were synthesized according to literature. ¹H and ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on Bruker AVANCE-250, AVANCE-400, and AVANCE-600 spectrometers. ¹H and ¹³C{¹H} NMR spectra were referenced internally to residual protio-solvent, and solvent resonances, respectively, and are reported relative to tetramethylsilane (δ = 0 ppm). ³¹P{¹H} NMR spectra were referenced externally to H₃PO₄ (85%) (δ = 0 ppm). Hydrogenation reactions were carried out in a Roth steel autoclave using a Tecsis manometer.

High resolution-accurate mass data mass spectra were recorded on a hybrid Maxis Qq-aoTOF mass spectrometer (Bruker Daltonics, Bremen, Germany) fitted with an ESI-source. Measured accurate mass data of the [M]⁺ ions for confirming calculated elemental compositions were typically within ± 5 ppm accuracy. The mass calibration was done with a commercial mixture of perfluorinated trialkyl-triazines (ES Tuning Mix, Agilent Technologies, Santa Clara, CA, USA).

GC-MS analysis was conducted on a ISQ LT Single quadrupole MS (Thermo Fisher) directly interfaced to a TRACE 1300 Gas Chromatographic systems (Thermo Fisher), using a Rxi-5Sil MS (30 m, 0.25mm ID) cross-bonded dimethyl polysiloxane capillary column

2. Synthesis

fac-[Mn(dpre)(CO)₃(CH₃)] (3). To a solution of *fac*-[Mn(dpre)(CO)₃(Br)] (**9**) (500mg, 1.11 mmol) in anhydrous THF (30 mL) liquid Na/K alloy (2:3, 110 mg, 3.33 mmol) was added and stirred for 24 h. The solution was filtrated *via* a syringe filter and methyl iodide (1 mL) was added and the mixture was stirred for 10 min. The solvent was removed under vacuum and the residue was extracted with CH₂Cl₂ (15 mL) giving an orange solution. Upon removal of the solvent a yellow oily residue was obtained which was dissolved in boiling anhydrous MeOH (10 mL) and the flask was stored in the freezer resulting in the crystallization of an off-white solid. Yield: 293 mg (64%) off-white solid. ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 1.72 – 1.33 (*m*, 14H), 1.33–1.19 (*m*, 3H), 1.19 – 0.93 (*m*, 7H), 0.87 (*t*, J = 6.9 Hz, 6H), 0.80 (*t*, J = 6.2 Hz, 7H), -0.70 (*t*, J = 9.0 Hz, 3H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 31.4 (*vt*, J = 12.1 Hz), 24.6 (*vd*, J = 10.1 Hz), 23.9 (*vt*, J = 20.2 Hz), 17.3 (*vd*, J = 64.6 Hz), 15.7 (*vd*, J = 12.1 Hz), -16.8 (*vt*, J = 18.2 Hz), (CO not observed). ³¹P{¹H} NMR (δ , 162 MHz, C₆D₆, 20 °C): 78.7 (*s*). ATR-IR (solid, cm⁻¹): 1974 (ν_{CO}), 1888 (ν_{CO}), 1853 (ν_{CO}). HRMS (TOF ESI+): *m/z* calculated for C₁₇H₃₁MnO₃P₂ [M-CH₃]⁺: 401.1202, found 401.1199.

fac-[Mn(dpre)(CO)₃(CH₂CH₃)] (4). This compound was prepared in analogous fashion to **5** with *fac*-[Mn(dpre)(CO)₃(Br)] (**9**) (500mg, 1.11 mmol) and ethyl bromide (1 mL) as starting materials. The crude product was extracted with *n*-pentane (20 mL). Insoluble materials were removed via filtrated over silica. The solvent was removed under vacuum giving colorless oil which solidified after about 1 week at -30°C. Yield: 55 mg (12 %) flesh colored solid. ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 1.76 (*t*, J = 7.7 Hz, 3H), 1.64 – 1.20 (*m*, 15H), 1.20–1.06 (*m*, 3H), 1.06 – 0.82 (*m*, 7H), 0.74 (*t*, J = 7.2 Hz, 6H), 0.69 (*t*, J = 6.9 Hz, 6H), 0.07 – -0.06 (*m*, 2H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 32.5, 31.9 (*vt*, J = 12.1 Hz), 30.5, 24.5 (*vm*), 24.2, 24.0, 22.1, 17.7,

16.3 (*vm*), 0.2 (*vt*, *J* = 16.1 Hz), (CO not observed). $^{31}\text{P}\{\text{H}\}$ NMR (δ , 162 MHz, C₆D₆, 20 °C): 76.9 (*s*). ATR-IR (solid, cm⁻¹): 1964 (ν_{CO}), 1888 (ν_{CO}), 1853 (ν_{CO}). HRMS (TOF ESI+): *m/z* calculated for C₁₇H₃₁MnO₃P₂ [M-C₂H₅]⁺: 401.1202, found 401.1202

***fac*-[Mn(dpre)(CO)₃(CH₂CH₂CH₃)] (5).** This compound was prepared in analogous fashion to **7** with *fac*-[Mn(dpre)(CO)₃(Br)] (**9**) (500mg, 1.11 mmol) and propyl bromide (5 mL) as starting materials. Complex **9** was obtained as colorless oil which solidified after 2 h at room temperature. Yield: 145 mg (32 %) colorless solid. ^1H NMR (δ , 400 MHz, CD₂Cl₂, 20 °C): 2.01 – 1.46 (*m*, 23H), 1.16 (*q*, *J* = 6.9 Hz, 12H), 1.06 (*t*, *J* = 7.1 Hz, 3H), 0.00 (*quin*, *J* = 16.8, 9.0 Hz, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (δ , 101 MHz, CD₂Cl₂, 20 °C): 31.4 (*vd*, *J* = 12.1 Hz), 30.9, 24.2 (*vd*, *J* = 8.0 Hz), 24.1, 23.9 (*vd*, *J* = 6.2 Hz), 23.8, 17.5, 17.2, 15.8 (*vt*, *J* = 10.1 Hz), 11.0 (*vt*, *J* = 15.1 Hz), (CO not observed). $^{31}\text{P}\{\text{H}\}$ NMR (δ , 162 MHz, CD₂Cl₂, 20 °C): 76.9 (*s*). ATR-IR (solid, cm⁻¹): 1967 (ν_{CO}), 1888 (ν_{CO}), 1853 (ν_{CO}). HRMS (TOF ESI+): *m/z* calculated for C₁₇H₃₁MnO₃P₂ [M-C₃H₇]⁺: 401.1202, found 401.1205

***fac*-[Mn(dippe)(CO)₃(CH₂CH₂CH₃)] (6).** This compound was prepared in analogous fashion to **5** with *fac*-[Mn(dippe)(CO)₃(Br)] (**10**) (300mg, 0.62 mmol) and propyl bromide (5 mL) as starting materials. The crude product was extracted with *n*-pentane (30 mL). Upon removal of the solvent under vacuum, a yellow oil was obtained which was recrystallized from *n*-pentane. Yield: 185 mg (67 %) pale yellow solid. ^1H NMR (δ , 400 MHz, CD₂Cl₂, 20 °C): 2.47 – 2.03 (*m*, 7H), 1.98 – 1.52 (*m*, 13H), 1.52 – 1.07 (*m*, 33H), 0.93 (*t*, *J* = 7.1 Hz, 2H), 0.10 (*quin*, *J* = 17.0 Hz, *J* = 8.5 Hz, 2H)). $^{13}\text{C}\{\text{H}\}$ NMR (δ , 101 MHz, CD₂Cl₂, 20 °C): 30.1, 27.9 (*vt*, *J* = 9.0 Hz), 24.0 (*vt*, *J* = 18.2 Hz), 21.6, 19.8 (*vd*, *J* = 10.1 Hz), 19.3, 18.4, 9.5 (*vt*, *J* = 15.1 Hz), (CO not observed). $^{31}\text{P}\{\text{H}\}$ NMR (δ , 162 MHz, CD₂Cl₂, 20 °C): 90.9 (*s*). ATR-IR (solid, cm⁻¹): 1964 (ν_{CO}), 1878 (ν_{CO}), 1858 (ν_{CO}). HRMS (TOF ESI+): *m/z* calculated for C₁₇H₃₁MnO₃P₂ [M-C₃H₇]⁺: 401.1202, found 401.1200.

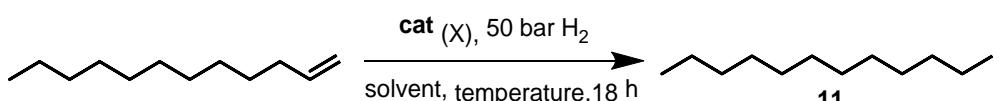
***fac*-[Mn(dpre)(CO)₃(H)] (10).** A microwave vial was charged with Mn₂(CO)₁₀ (300 mg, 0.77 mmol), 1,2-bis(dipropylphosphino)ethane (404 mg, 1.54 mmol) and anhydrous *n*-pentanol (350 μL). The mixture was heated to 140 °C for 5 h. All volatiles were removed under vacuum affording a red oil. Anhydrous MeOH (3 mL) was added and the yellow solution was placed in the freezer giving a yellow solution and a colorless precipitate. The suspension was centrifuged and the mother liquor was decanted. The solid was washed three times with MeOH (1 mL) and the solid was dried under vacuum. Yield: 80 mg (14 %) colorless solid. ^1H NMR (δ , 400 MHz, C₆D₆, 20 °C): 1.56 – 0.85 (*m*, 25H), 0.76 (*t*, *J* = 6.9 Hz, 6H), 0.70 (*t*, *J* = 6.0 Hz, 6H), -9.25 (*t*, *J* = 48.6 Hz, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (δ , 101 MHz, C₆D₆, 20 °C): 224.6, 221.2, 32.6 (*vm*), 25.1 (*vt*, *J* = 13.1 Hz), 16.8 (*vd*, *J* = 6.1 Hz), 15.0 (*vm*). $^{31}\text{P}\{\text{H}\}$ NMR (δ , 162 MHz, C₆D₆, 20 °C): 86.8 (*s*). ATR-IR (solid, cm⁻¹): 1976 (ν_{CO}), 1873 (ν_{CO}), 1737 (ν_{MnH}). HRMS (TOF ESI+): *m/z* calculated for C₁₇H₃₁MnO₃P₂ [M-H]⁺: 401.1202, found 401.1196.

3. General procedure for the hydrogenation of alkenes

Inside an argon-flushed glovebox the substrate and the catalyst were mixed with anhydrous solvent (5 mL) and transferred into a steel autoclave, which was three times evacuated and flushed with argon prior to use. The autoclave was then flushed three times with hydrogen, 50 bar of H₂ pressure were applied and the autoclave was placed in an oil bath (40–100 °C), if heating was required. The reaction was carried for 18 to 24 h. The autoclave was then cooled in an ice bath for 10 min and depressurized. The products were filtrated over a short plug of silica, transferred to a round bottom flask and the solvent was removed under vacuum. Methyl benzoate was added as standard and the samples were analyzed by ^1H NMR spectroscopy or the conversion determined by GC-MS for all substrates, which were not isolated.

4. Table of optimization reactions

Table S1. Catalyst Screening for the Synthesis of Dodecane from 1-Dodecene^a



entry	catalyst	X (mol%)	solvent	T (°C)	yield (%) ^b
1	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₃)] (3)	2	toluene	100	99
2	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₃)] (4)	2	toluene	100	99
3	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (5)	2	toluene	100	99
4	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	2	toluene	100	99
5	<i>fac</i> -[Mn(dippe)(CO) ₃ (H)] (7)	4	toluene	100	
6	[Mn(CO) ₅ (CH ₃)] (8)	4	toluene	100	
7	<i>fac</i> -[Mn(bipy)(CO) ₃ (CH ₃)] (9)	4	toluene	100	
8	<i>fac</i> -[Mn(dpre)(CO) ₃ (H)] (10)	4	toluene	100	
9	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₃)] (3)	2	toluene	60	
10	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₃)] (4)	2	toluene	60	99
11	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (5)	2	toluene	60	99
12	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	2	toluene	60	99
13	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₃)] (3)	2	Et ₂ O	60	99
14	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₃)] (4)	2	Et ₂ O	60	99
15	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (5)	2	Et ₂ O	60	99
16	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	2	Et ₂ O	60	99
17	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₃)] (3)	2	Et ₂ O	40	
18	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₃)] (4)	2	Et ₂ O	40	99
19	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (5)	2	Et ₂ O	40	99
20	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	2	Et ₂ O	40	99
21	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₃)] (4)	2	Et ₂ O	25	
22	<i>fac</i> -[Mn(dpre)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (5)	2	Et ₂ O	25	
23	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	2	Et ₂ O	25	99
24	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	2	THF	25	99
25	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	2	DME	25	99
26	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	2	MeOH	25	<5
27	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	2	CH ₂ Cl ₂	25	<5
28	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	1	Et ₂ O	25	87
29	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	1	THF	25	82
30	<i>fac</i> -[Mn(dippe)(CO) ₃ (CH ₂ CH ₂ CH ₃)] (6)	1	DME	25	84

^aReaction conditions: 1-dodecene (0.56 mmol), 50 bar H₂, 5 mL solvent, 18 h. ^bYield determined by ¹H-NMR analysis using methyl benzoate as standard.

5. Preliminary Mechanistic studies

Reaction of Complex 6 with hydrogen gas

A microwave vial was charged with 20 mg of complex **6** and dissolved in 0.6 mL THF-*d*₈. A stirring bar was added and the vial was closed. The sample was placed in steel autoclave, which was three times evacuated and flushed with Argon. The septum was penetrated with a needle. The autoclave was three times flushed with hydrogen gas and a pressure of 50 bar hydrogen was applied. The reaction was run for 24 h before the pressure was released. The content of the vial was quickly transferred to NMR under argon and NMR analysis was performed.

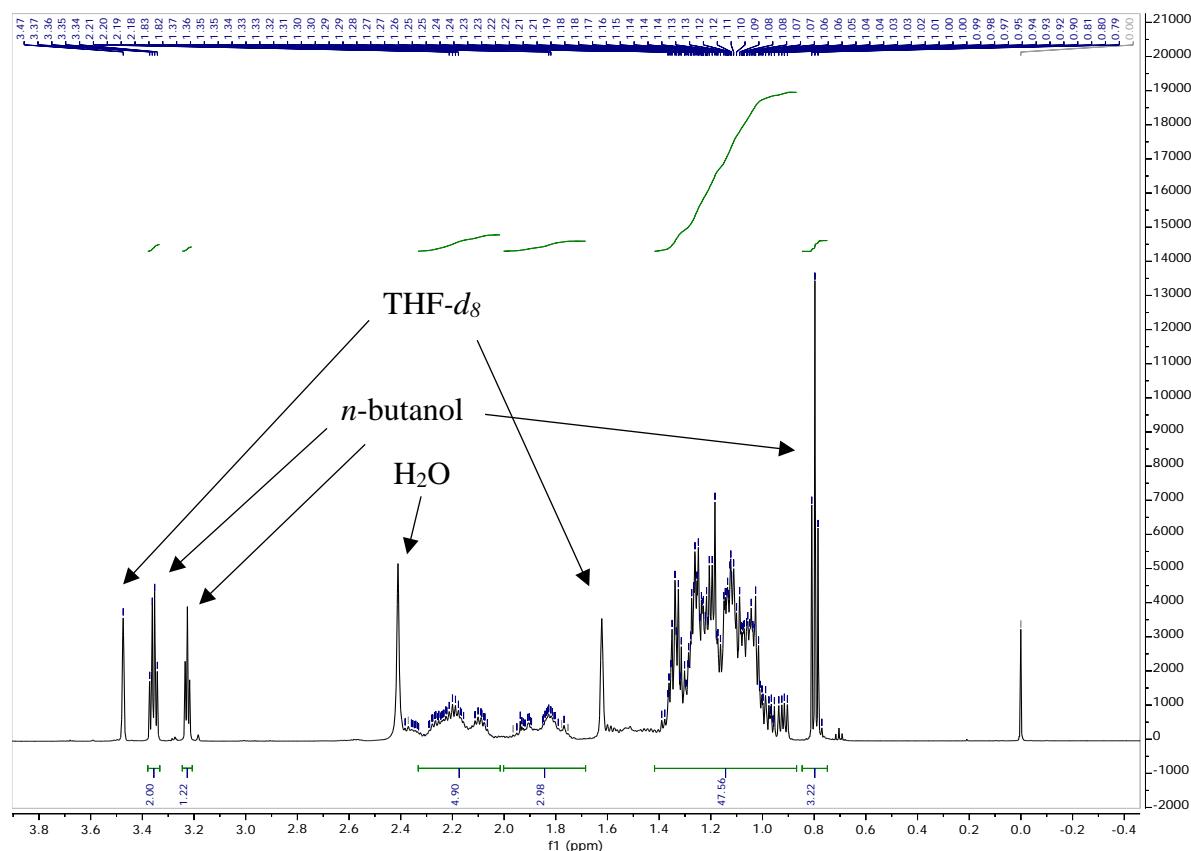


Figure S1. ¹H NMR (600 MHz, THF-*d*₈, 20 °C) of reaction of complex **6** with hydrogen gas at 50 bar after 24 h.

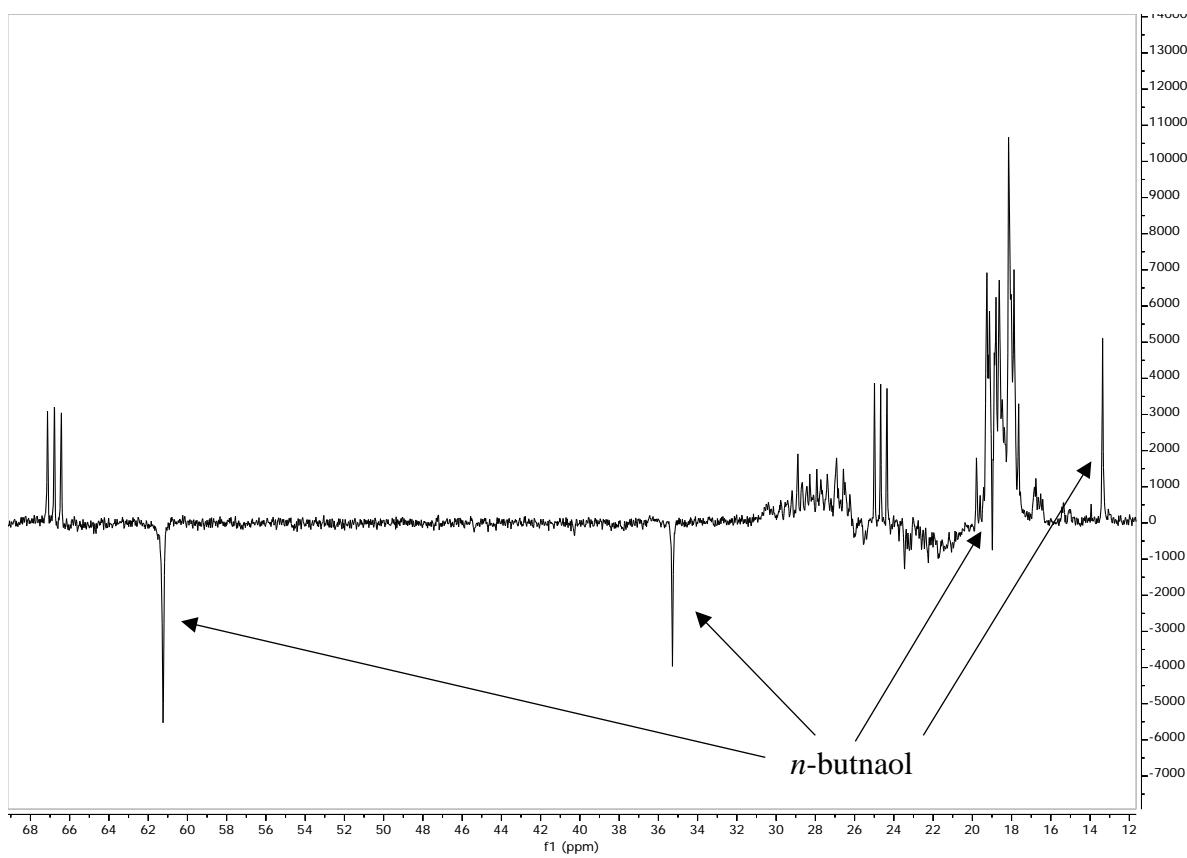


Figure S2. DEPT135 (63 MHz, THF-*d*₈, 20 °C) of reaction of complex **6** with hydrogen gas at 50 bar after 24 h.

Reaction of complex 6 with hydrogen gas and 3 equiv of (4-methyl)-styrene

A microwave vial was charged with 20 mg of complex **6**, (4-methyl)-styrene (3 eq.) and dissolved in 0.6 mL THF-*d*₈. A stirring bar was added and the vial was closed. The sample was placed in steel autoclave, which was three times evacuated and flushed with Argon. The septum was penetrated with a needle. The autoclave was three times flushed with hydrogen gas and a pressure of 50 bar hydrogen was applied. The reaction was run for 2 h before the pressure was released. The content of the vial was quickly transferred to NMR under argon and NMR analysis was performed.

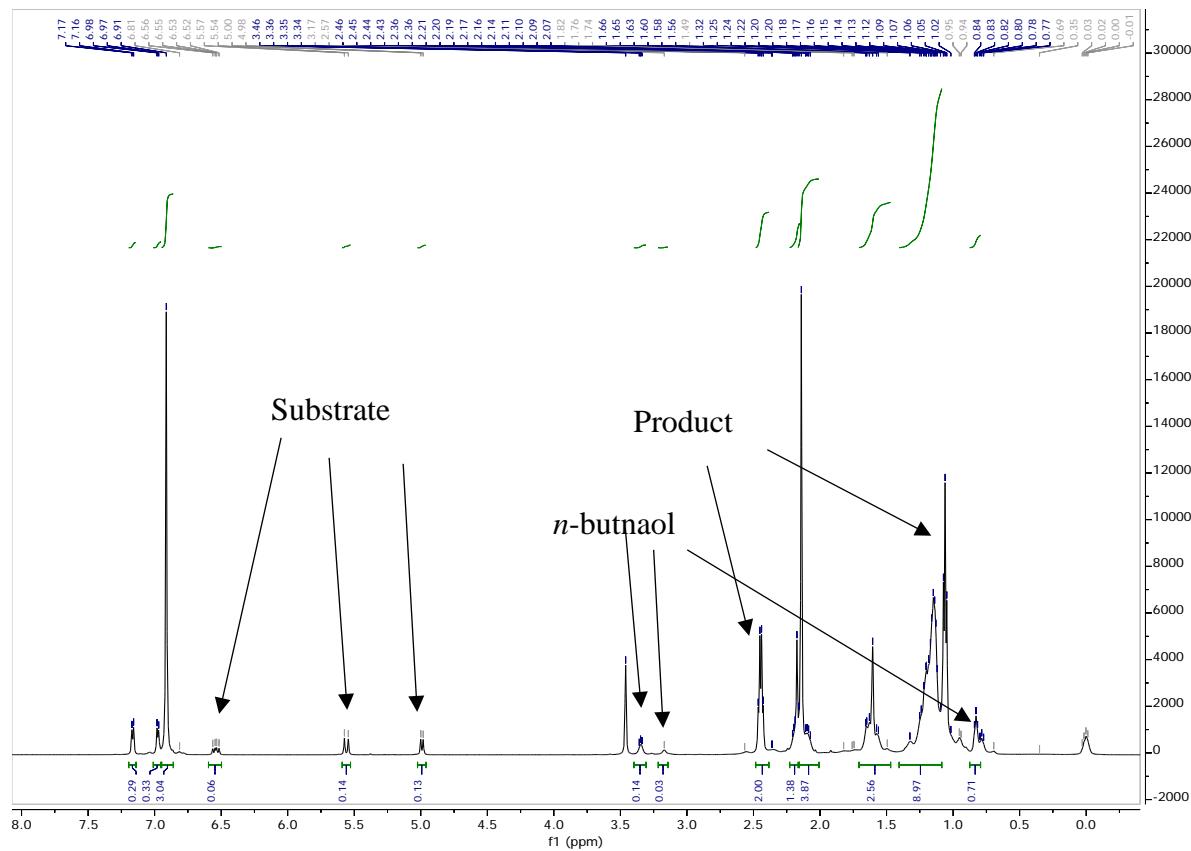


Figure S3. ¹H NMR (600 MHz, THF-*d*₈, 20 °C) of reaction of complex **6** with hydrogen gas at 50 bar and 3 equiv. of (4-methyl)styrene after 2 h.

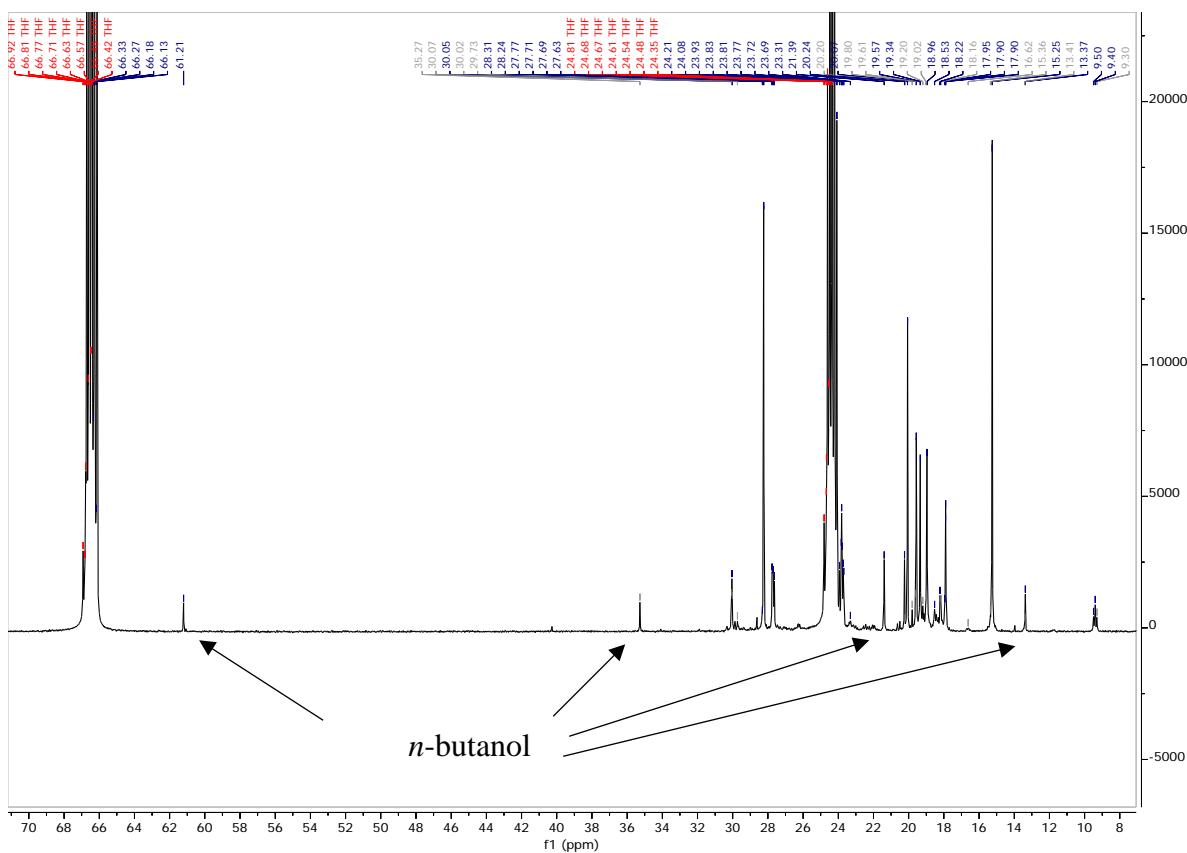


Figure S4. ¹H NMR (151 MHz, THF-*d*8, 20 °C) of reaction of complex **6** with hydrogen gas at 50 bar and 3 equiv. (4-methyl)styrene after 2h.

Hydrogenation of (4-methyl)-styrene in the presence of PMe₃ (20 mol%)

To a solution of **6** (5 mg, 2 mol%) and (4-methyl)-styrene (1 equiv) in THF-*d*₈ (0.6 mL), 1 mL of a 1 M THF solution of PMe₃ (20 mol%) was added. The sample was placed in steel autoclave, which was three times evacuated and flushed with Argon. The autoclave was three times flushed with hydrogen gas and a pressure of 50 bar hydrogen was applied. The reaction was run for 18 h before the pressure was released. The content was vial was quickly transferred to NMR under argon and NMR analysis was performed. No conversion to alkane could be detected.

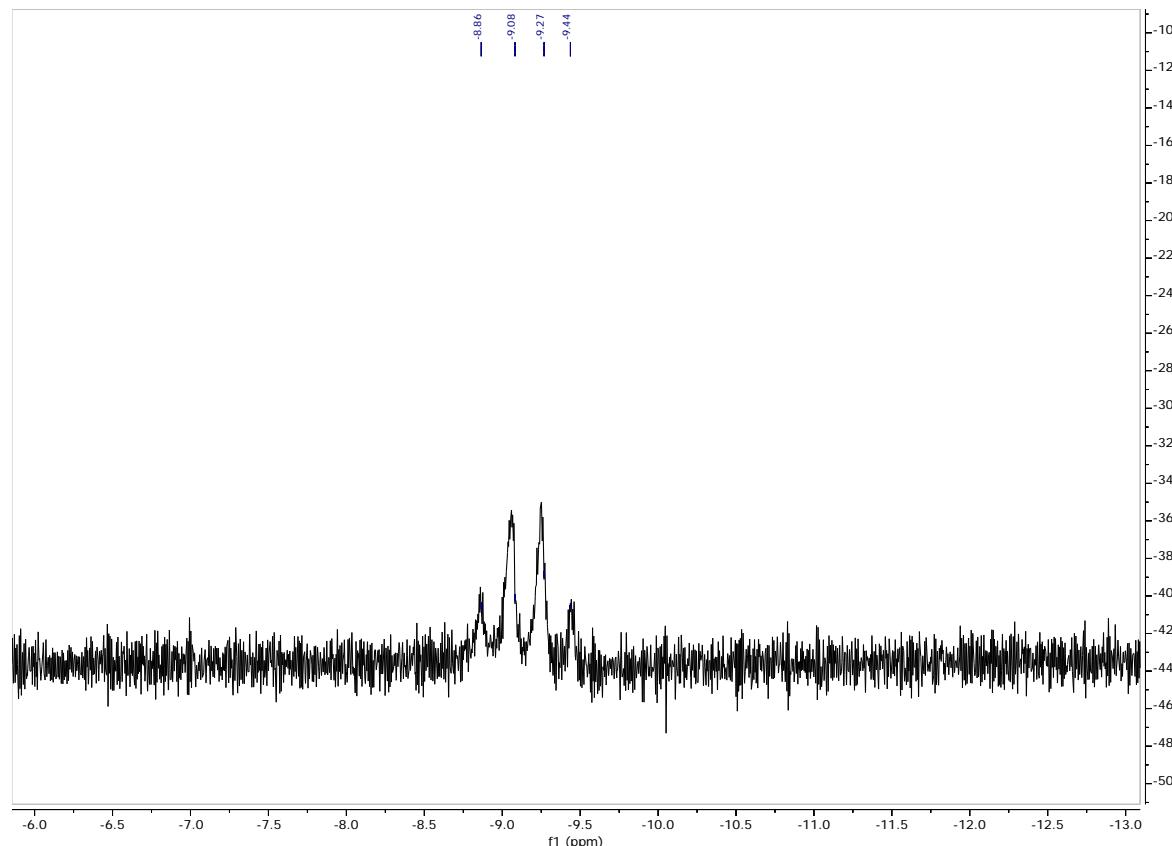


Figure S5. ¹H NMR (250 MHz, THF-*d*₈, 20 °C) of reaction of complex **6** (2 mol%) with hydrogen gas at 50 bar and 1 equiv of (4-methyl)styrene after 18h in the presence of 20 mol% PMe₃ (only hydride region displayed).

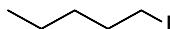
6. Characterization of Organic Products

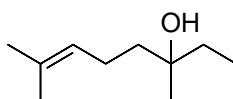
 **Dodecane⁵** (**11**), colorless liquid, 95 mg (99%). ¹H NMR (δ , 400 MHz, CDCl₃, 20 °C): 1.25 (s, 21H), 0.87 (t, J = 6.4 Hz, 6H). ¹³C{¹H} NMR (δ , 101 MHz, CDCl₃, 20 °C): 32.0, 29.7, 29.7, 29.4, 22.7, 14.1.

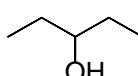
 **Decane⁶** (**12**), pale yellow liquid, 79 mg (99%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 1.28 (s, 16H), 0.90 (t, J = 6.9 Hz, 6H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 32.0, 29.8, 29.5, 22.7, 14.0.

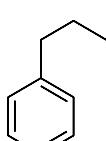
 **Hexadecane⁷** (**13**), pale yellow liquid, 125 mg (99%) ¹H NMR (400 MHz, C₆D₆) δ = 1.29 (s, 31H), 0.91 (t, J = 6.8 Hz, 6H). ¹³C NMR (101 MHz, C₆D₆) δ = 32.0, 29.9, 29.8, 29.8, 29.5, 22.8, 14.0.

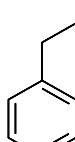
 **Octadecane⁸** (**14**), pale yellow oil, which solidified upon standing, 139 mg (99%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 1.27 (s, 34H), 0.91 (t, J = 7.3 Hz, 6H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 32.0, 29.9, 29.8, 29.8, 29.5, 22.8, 14.0.

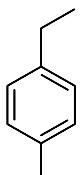
 **1-Bromopentane⁹** (**15**) pale yellow liquid, 84 mg (99%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 3.00 (t, J = 6.9 Hz, 2H), 1.63 – 1.47 (q, J = 14.5 Hz, 7.7 Hz, 2H), 1.24 – 1.02 (m, 4H), 0.75 (t, J = 7.2 Hz, 3H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 33.2, 32.4, 30.1, 21.7, 13.6.

 **rac-3,7-Dimethyloct-6-en-3-ol⁵** (**16**), pale yellow liquid, 88 mg (99%). ¹H NMR (δ , 400 MHz, CD₂Cl₂, 20 °C): 5.12 (t, J = 7.4 Hz, 2H), 2.01 (q, J = 7.2 Hz, 2H), 1.67 (s, 4H), 1.61 (s, 3H), 1.52 – 1.35 (m, 5H), 1.11 (s, 3H), 0.87 (t, J = 7.6 Hz, 3H). ¹³C{¹H} NMR (δ , 101 MHz, CD₂Cl₂, 20 °C): 131.3, 124.6, 72.5, 41.2, 34.2, 26.1, 25.4, 22.6, 17.3, 8.0.

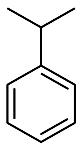
 **3-Pentanol¹⁰** (**17**), pale yellow liquid, 49 mg (99%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 3.46 (s, 1H), 3.39 – 3.24 (m, 1H), 1.39 (q, J = 7.5 Hz, 4H), 0.9 (t, J = 7.7 Hz, 6H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 73.9, 29.6, 9.8.

 **Propylbenzene¹¹** (**18**), pale yellow liquid, 67 mg (99%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 7.20 – 7.10 (m, 2H), 7.10 – 6.98 (m, 3H), 2.43 (t, J = 7.5 Hz, 2H), 1.52 (h, J = 14.8, 7.4 Hz, 2H), 0.84 (t, J = 6.6 Hz, 3H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 142.3, 128.3, 128.1, 125.6, 38.0, 24.5, 13.5.

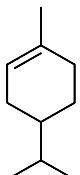
 **Ethylbenzene¹²** (**19**), pale yellow liquid, 60 mg (99%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 7.20 – 7.11 (m, 2H), 7.10 – 7.00 (m, 3H), 2.45 (q, J = 7.6 Hz, 2H), 1.16 – 1.01 (t, J = 7.4 Hz, 3H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 143.9, 128.2, 124.7, 125.6, 28.9, 15.5.



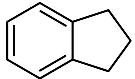
1-ethyl-4methyl-benzene¹³ (20), colorless liquid, 67 mg (99%). ¹H NMR (δ , 400 MHz, CD₂Cl₂, 20 °C): 7.24-7.08 (*m*, 4H), 2.65 (*q*, *J* = 7.6 Hz, 2H), 2.35 (*s*, 3H), 1.26 (*t*, *J* = 7.6 Hz, 3H). ¹³C{¹H} NMR (δ , 101 MHz, CD₂Cl₂, 20 °C): 141.3, 135.0, 129.0, 127.6, 28.4, 20.7, 15.6.



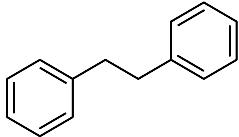
Cymene¹⁴ (23), colorless liquid, 68 mg (99%). ¹H NMR (δ , 400 MHz, CD₂Cl₂, 20 °C): 7.42 – 7.12 (*m*, 5H), 2.91 (*hept*, *J* = 6.7 Hz, 1H), 1.26 (*d*, *J* = 6.9 Hz, 6H). ¹³C{¹H} NMR (δ , 101 MHz, CD₂Cl₂, 20 °C): 149.0, 128.2, 126.4, 125.7, 34.1, 23.8.



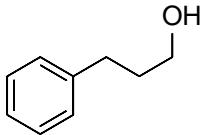
rac-4-Isopropyl-1-methylcyclohex-1-ene¹⁵ (26), colorless liquid, 94 mg (94%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 5.38 (*s*, 1H), 1.95-1.81 (*m*, 4H), 1.75-1.59 (*m*, 7H), 1.45 – 0.97 (*m*, 5H), 0.80 (*dd*, *J* = 6.7, 2.9 Hz, 9H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 133.2, 121.1, 40.0, 32.2, 30.7, 29.0, 26.5, 23.3, 19.8.



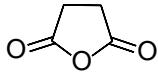
2,3-Dihydro-1H-indene¹⁶ (27), pale yellow liquid, 68 mg (99%). ¹H NMR (δ , 400 MHz, CD₂Cl₂, 20 °C): 7.32 – 7.20 (*m*, 2H), 7.14-7.11 (*m*, 2H), 2.93 (*t*, *J* = 7.4 Hz, 4H), 2.08 (*p*, *J* = 7.5 Hz, 1H). ¹³C{¹H} NMR (δ , 101 MHz, CD₂Cl₂, 20 °C): 144.2, 125.9, 124.2, 32.8, 25.4.



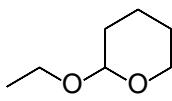
1,2-Diphenylethane¹² (28, 29), colorless solid, 101 mg (99%). ¹H NMR (δ , 400 MHz, CD₂Cl₂, 20 °C): 7.46-7.27 (*m*, 10H), 3.04 (*s*, 4H). ¹³C{¹H} NMR (δ , 101 MHz, CD₂Cl₂, 20 °C): 142.0, 128.6, 128.4, 126.0, 38.0.



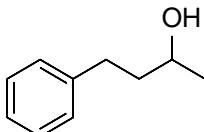
3-Phenylpropane-1-ol¹⁷ (30), pale yellow oil, 76 mg (99%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 7.32 – 7.12 (*m*, 3H), 7.12 – 6.97 (*m*, 3H), 3.50 – 3.28 (*m*, 2H), 2.53 (*t*, *J* = 7.4 Hz, 2H), 1.95 (*s*, 1H), 1.77 – 1.57 (*m*, 2H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 142.0, 128.4, 128.3, 125.7, 61.6, 34.3, 32.0.



Dihydrofuran-2,5-dion¹⁸ (31), colorless solid, 57 mg (99%). ¹H NMR (δ , 400 MHz, DMSO-d₆, 20 °C): 2.89 (*s*, 4H). ¹³C{¹H} NMR (δ , 101 MHz, DMSO-d₆, 20 °C): 174.1, 29.2.



2-Ethoxytetrahydro-2H-pyran^{19,20} (32), colorless liquid, 73 mg (99%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 4.53 (*t*, J=3.7 Hz, 1H), 3.84 – 3.67 (*m*, 2H), 3.40 – 3.17 (*m*, 2H), 1.45 – 1.15 (*m*, 10H), 1.09 (*t*, J = 7.1 Hz, 3H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 98.1, 62.4, 61.2, 30.8, 29.9, 25.6, 19.3, 15.1.



rac-4-Phenylbutane-2-ol²¹ (34), pale yellow oil, 84 mg (99%). ¹H NMR (δ , 400 MHz, C₆D₆, 20 °C): 7.57 – 6.61 (*m*, 4H), 3.66 – 3.42 (*m*, 1H), 2.72 – 2.36 (*m*, 2H), 2.27 (*s*, 1H), 1.72 – 1.40 (*m*, 2H), 0.99 (*d*, J = 6.1 Hz, 3H). ¹³C{¹H} NMR (δ , 101 MHz, C₆D₆, 20 °C): 142.3, 128.4, 128.3, 125.7, 66.6, 40.9, 32.1, 23.4.

7. X-ray Structure Determination

X-ray diffraction data of **8** (CCDC 1920413) were collected at $T = 100$ K in a dry stream of nitrogen on a Bruker Kappa APEX II diffractometer system using graphite-monochromatized Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) and fine sliced φ - and ω -scans. Data were reduced to intensity values with SAINT and an absorption correction was applied with the multi-scan approach implemented in SADABS.²² The structure was solved by the dual-space approach implemented in SHELXT²³ and refined with SHELXL.²⁴ Non-hydrogen atoms were refined anisotropically. The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms.

8. Computational Details

The computational results presented have been achieved in part using the Vienna Scientific Cluster (VSC). All calculations were performed using the GAUSSIAN 09 software package²⁵ without symmetry constraints. The optimized geometries were obtained with the PBE0 functional. That functional uses a hybrid generalized gradient approximation (GGA), including 25 % mixture of Hartree-Fock²⁶ exchange with DFT²⁷ exchange-correlation, given by Perdew, Burke and Ernzerhof functional (PBE).²⁸ The basis set used for the geometry optimizations (basis b1) consisted of the Stuttgart/Dresden ECP (SDD) basis set²⁹ to describe the electrons of iron, and a standard 6-31G(d,p) basis set³⁰ for all other atoms. Transition state optimizations were performed with the Synchronous Transit-Guided Quasi-Newton Method (STQN) developed by Schlegel *et al.*³¹ following extensive searches of the Potential Energy Surface. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profiles. The electronic energies (E_{b1}) obtained at the PBE0/b1 level of theory were converted to free energy at 298.15 K and 1 atm (G_{b1}) by using zero point energy and thermal energy corrections based on structural and vibration frequency data calculated at the same level.

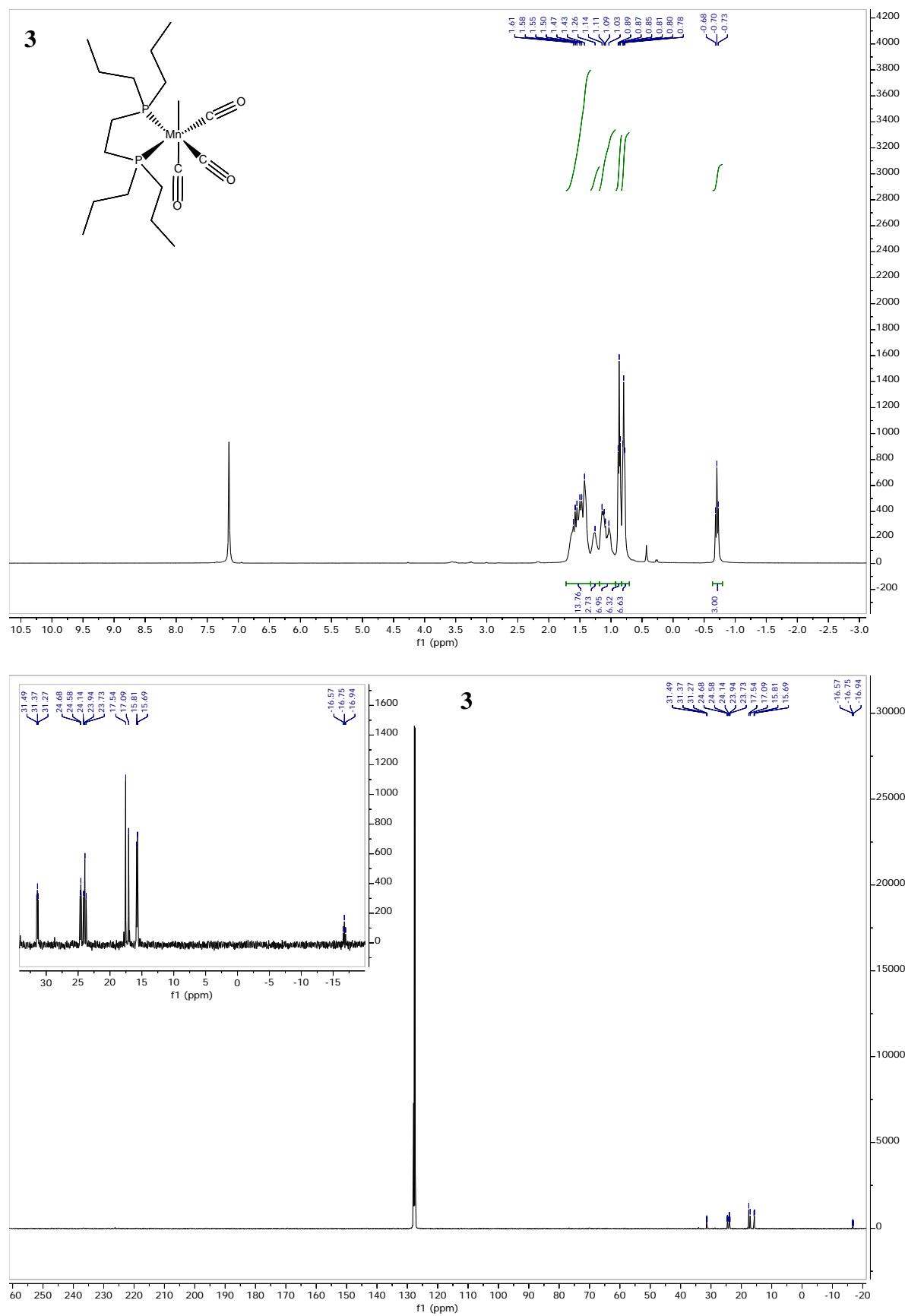
9. References

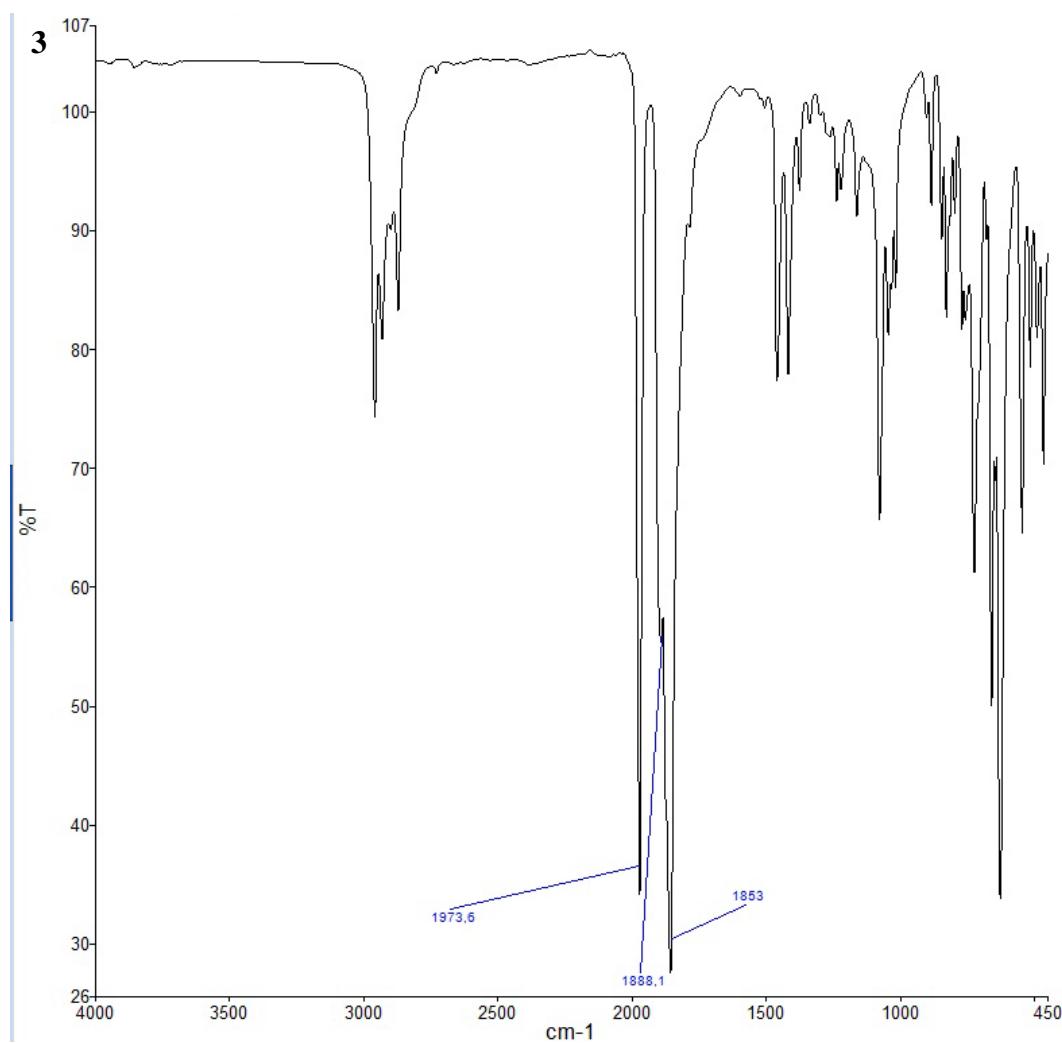
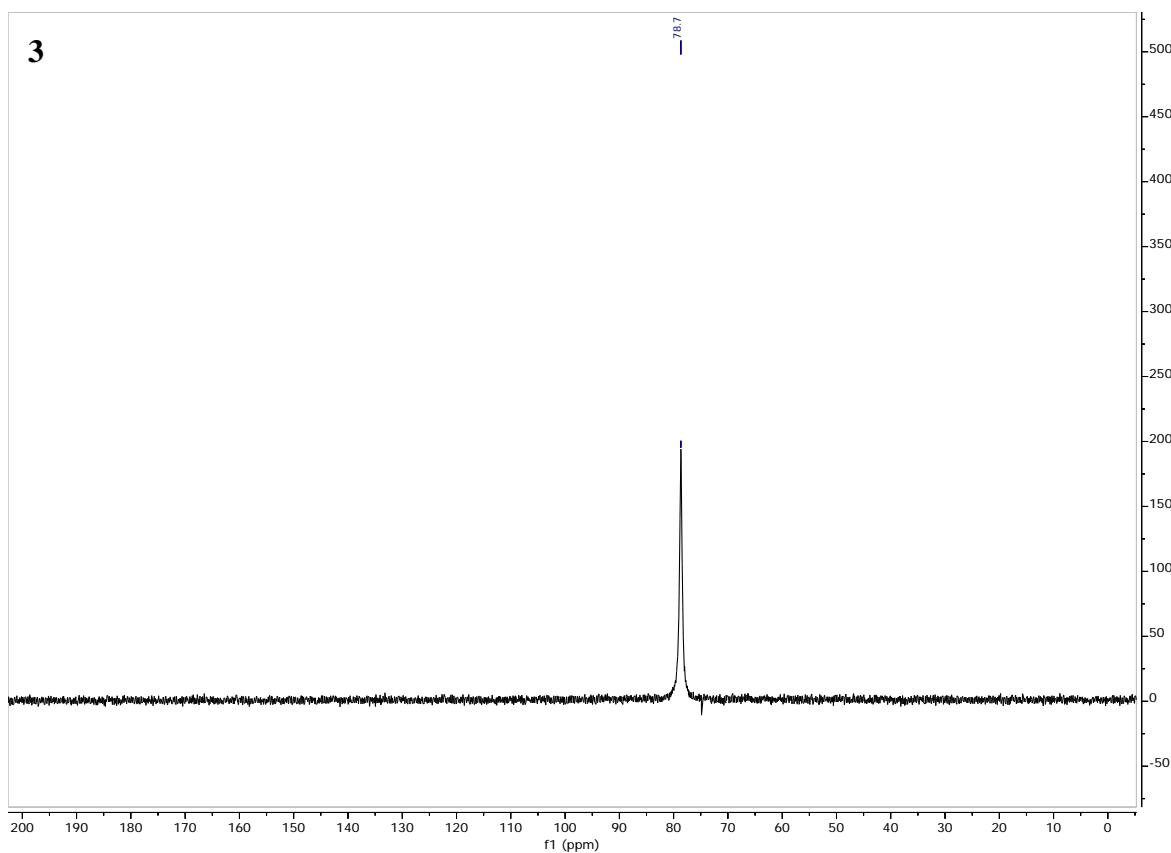
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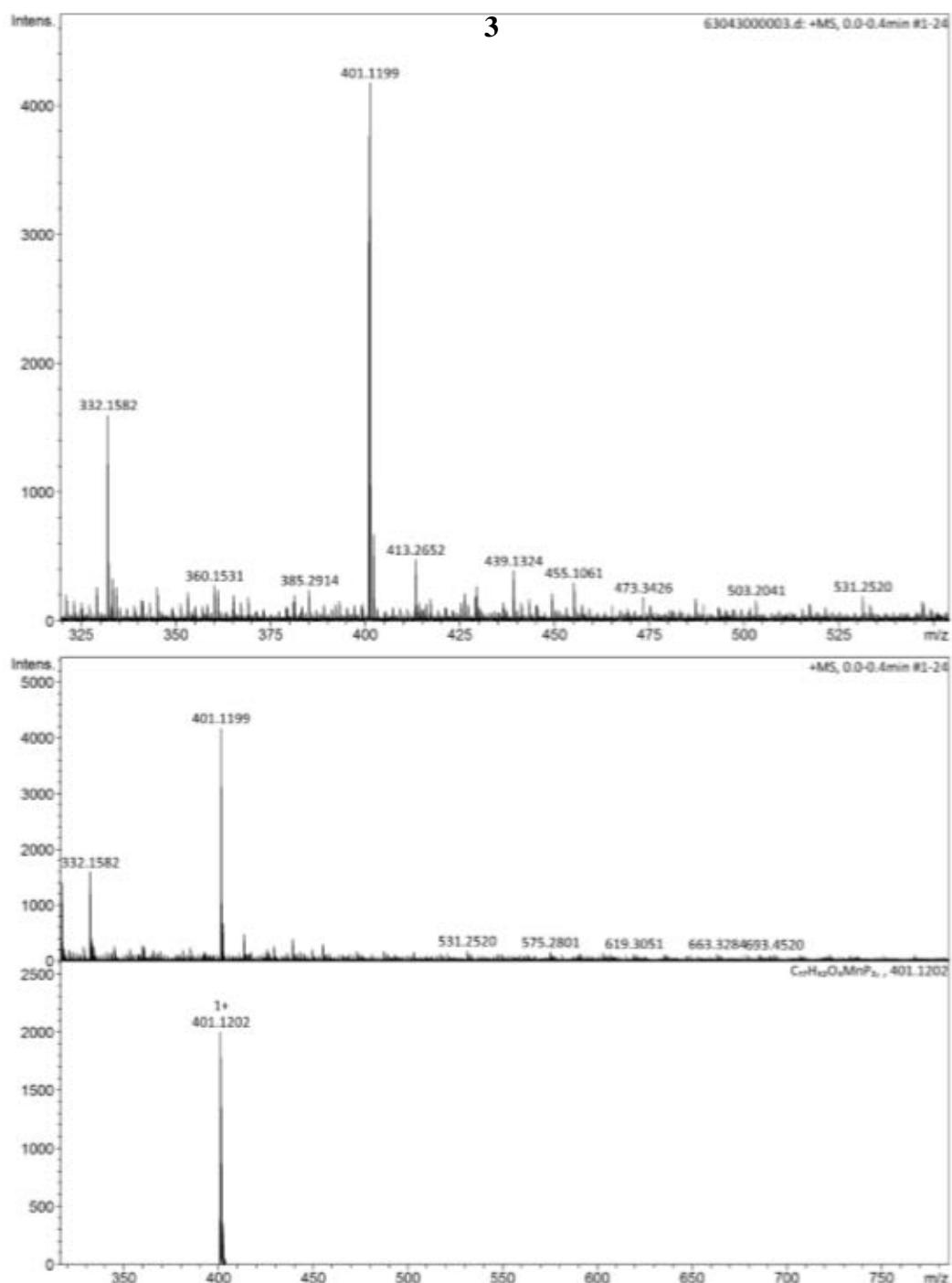
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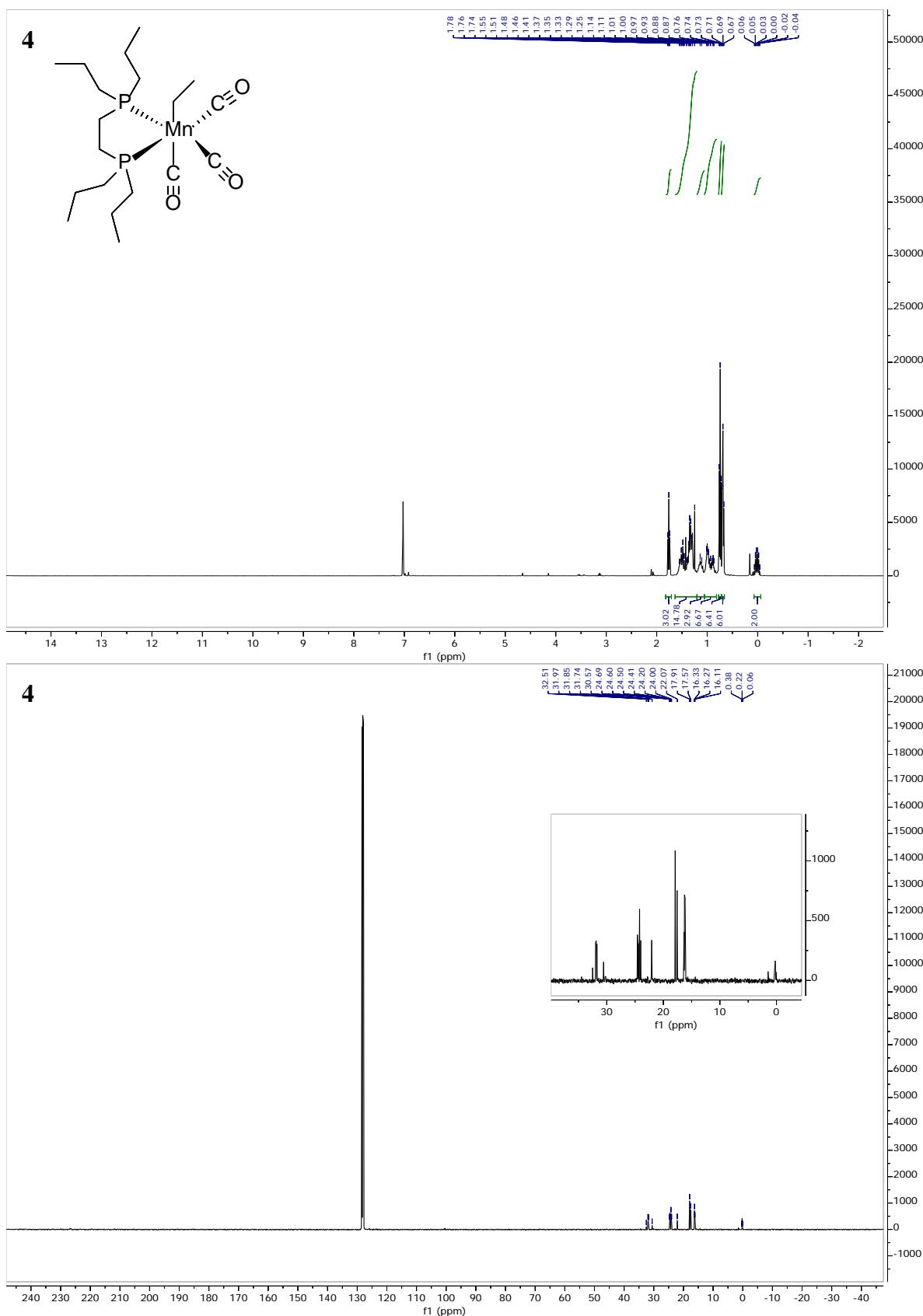
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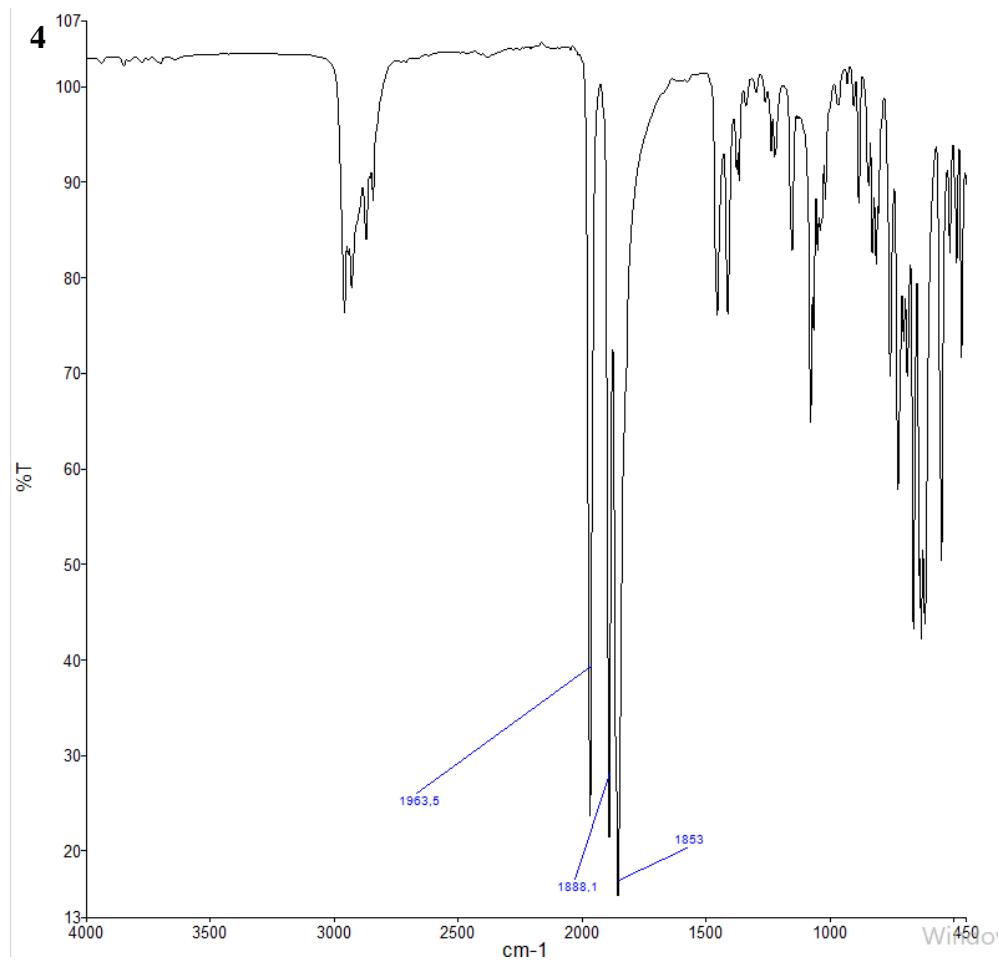
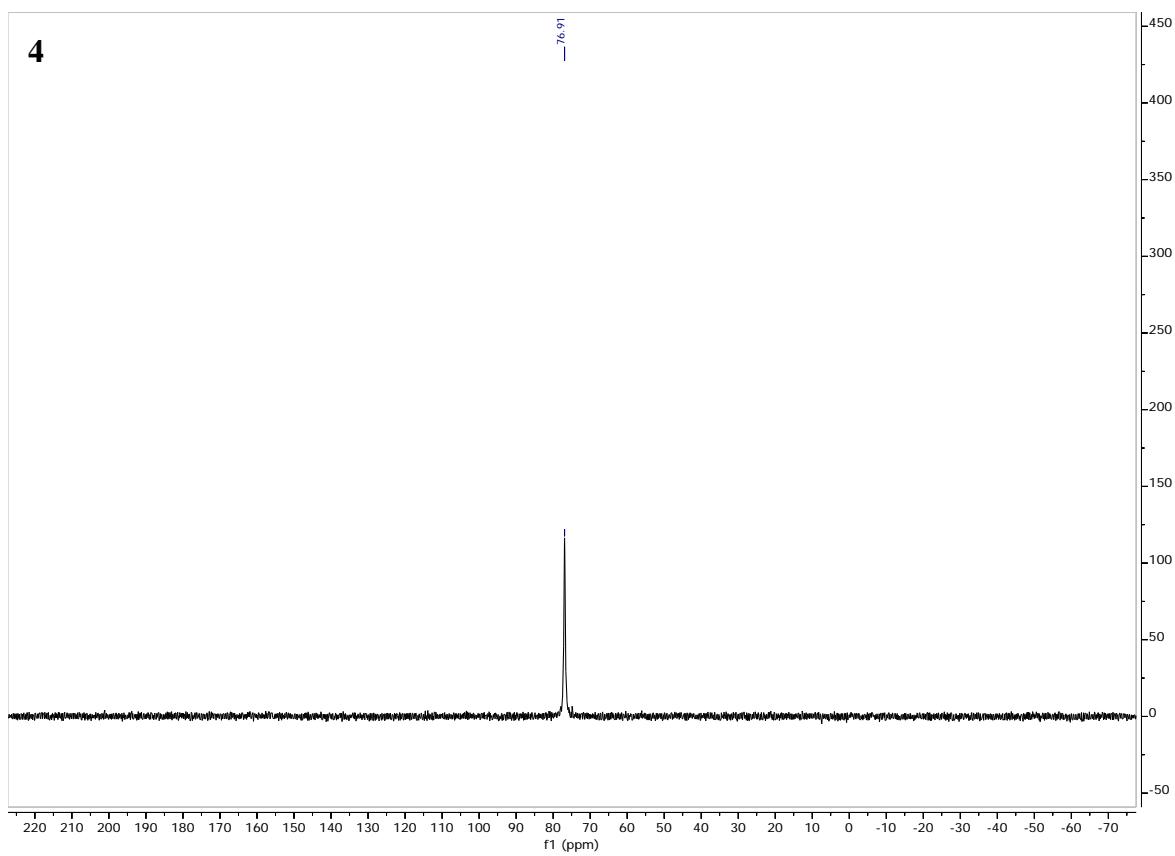
10. NMR Spectra of All Complexes and Organic Products

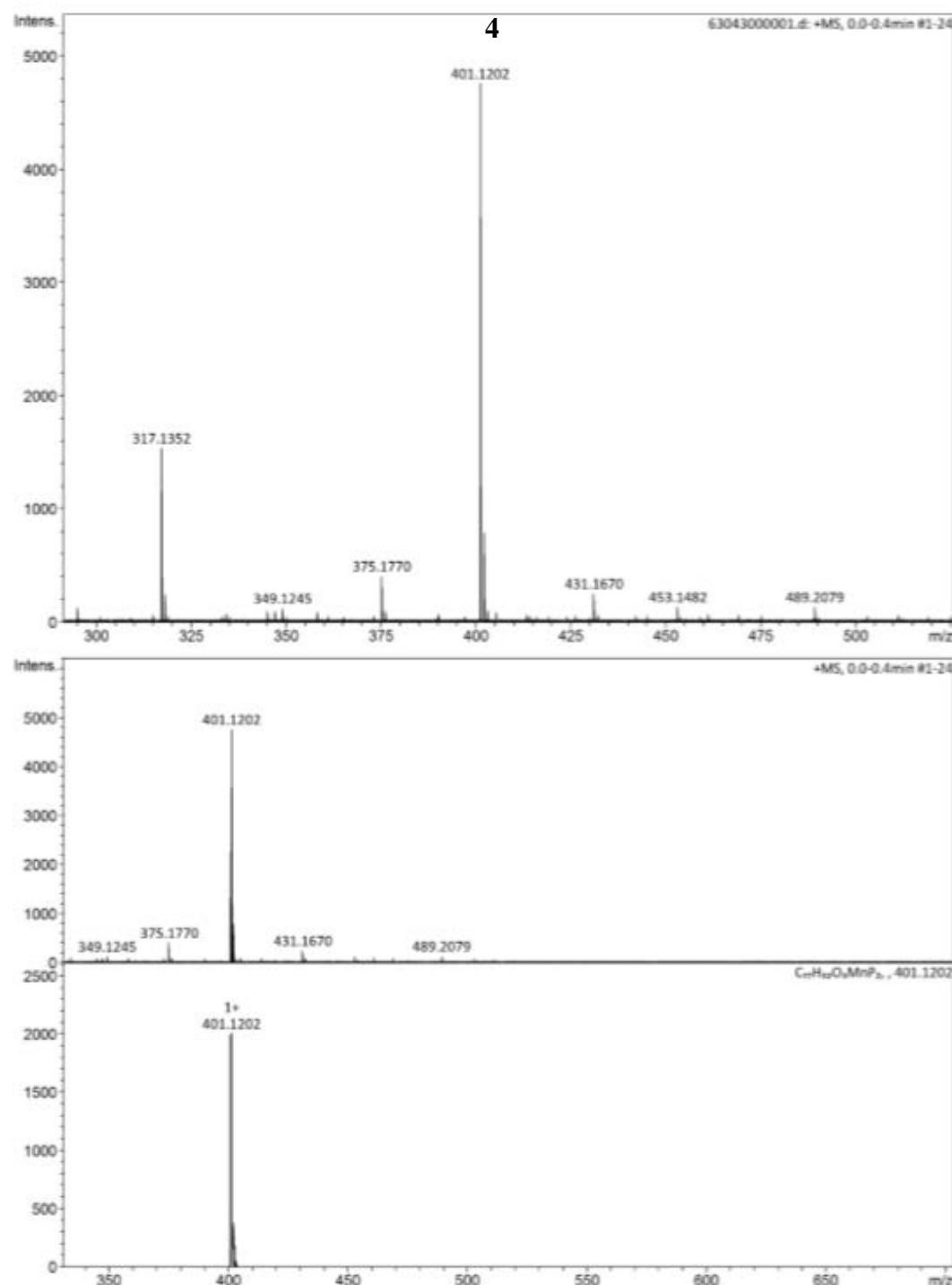


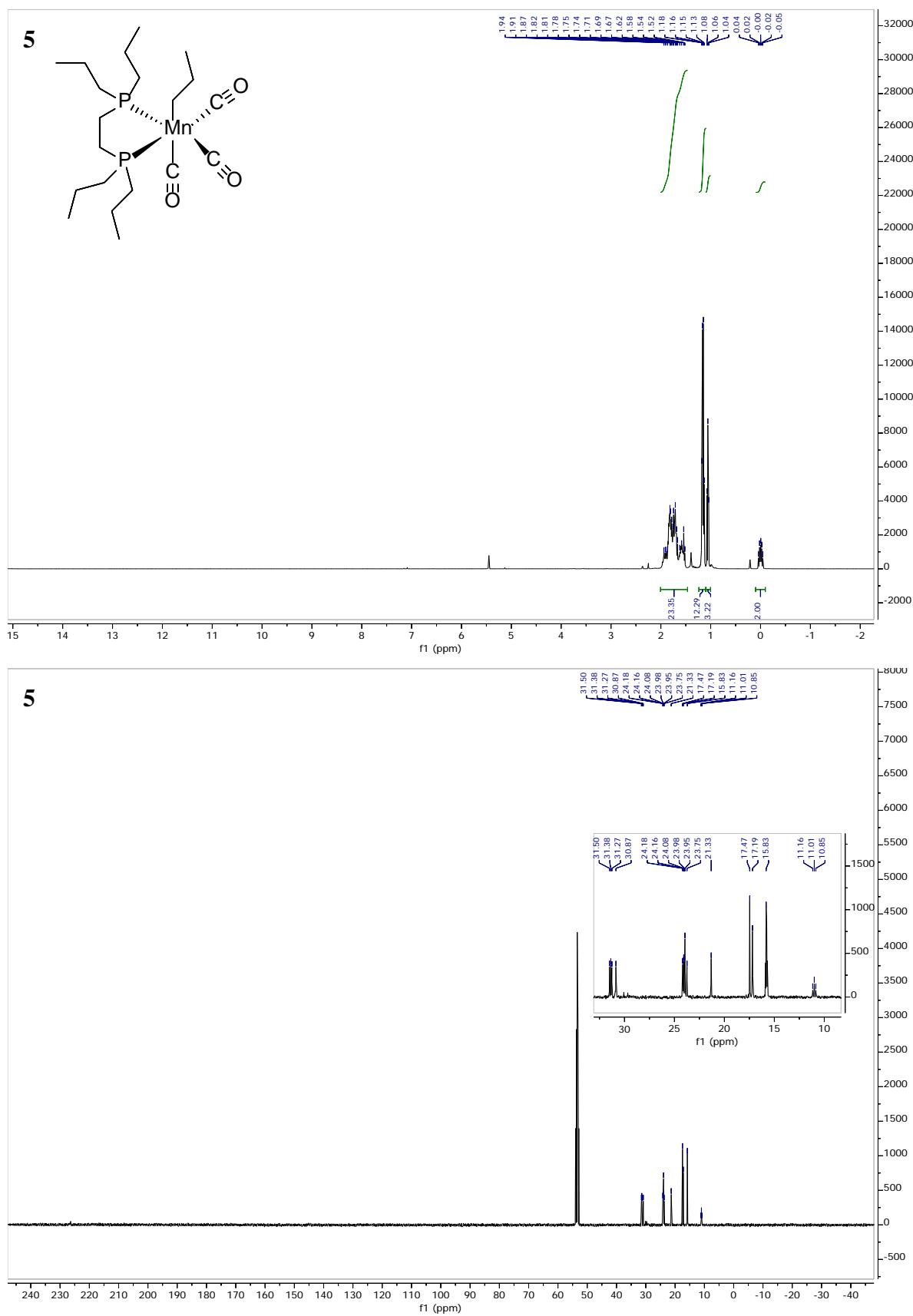


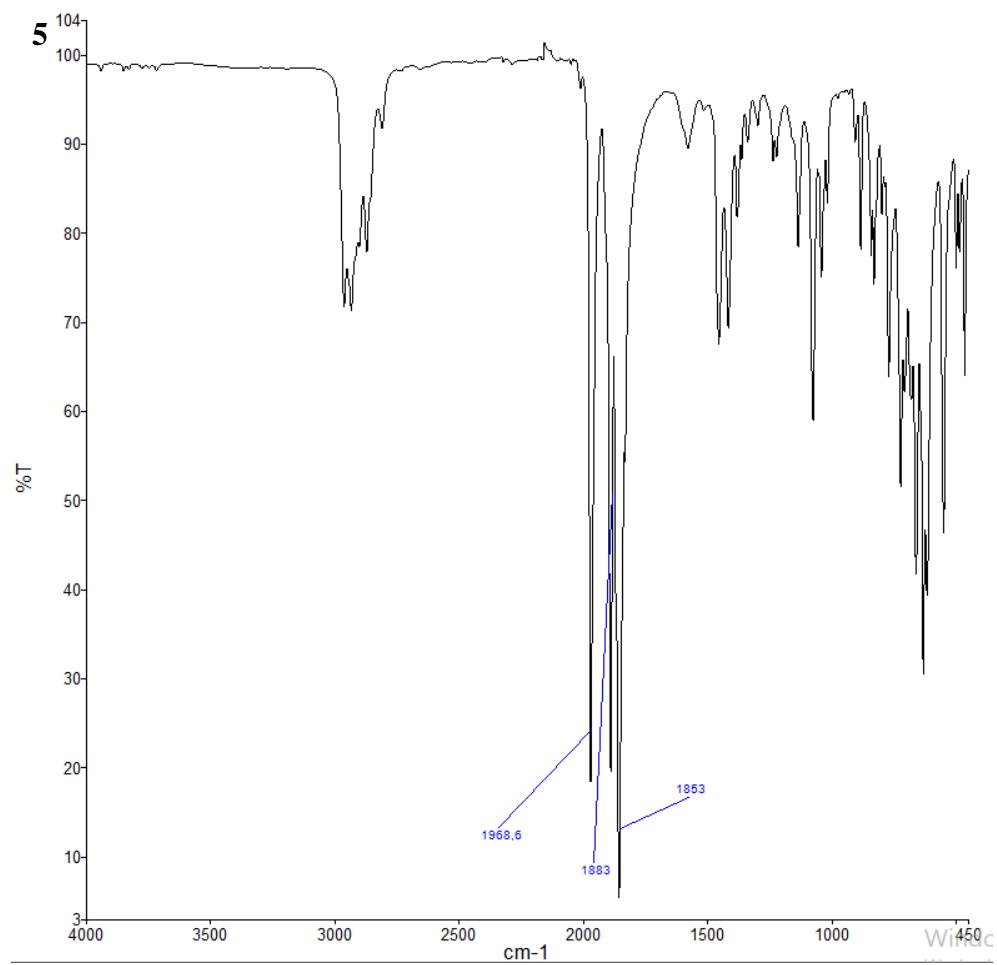
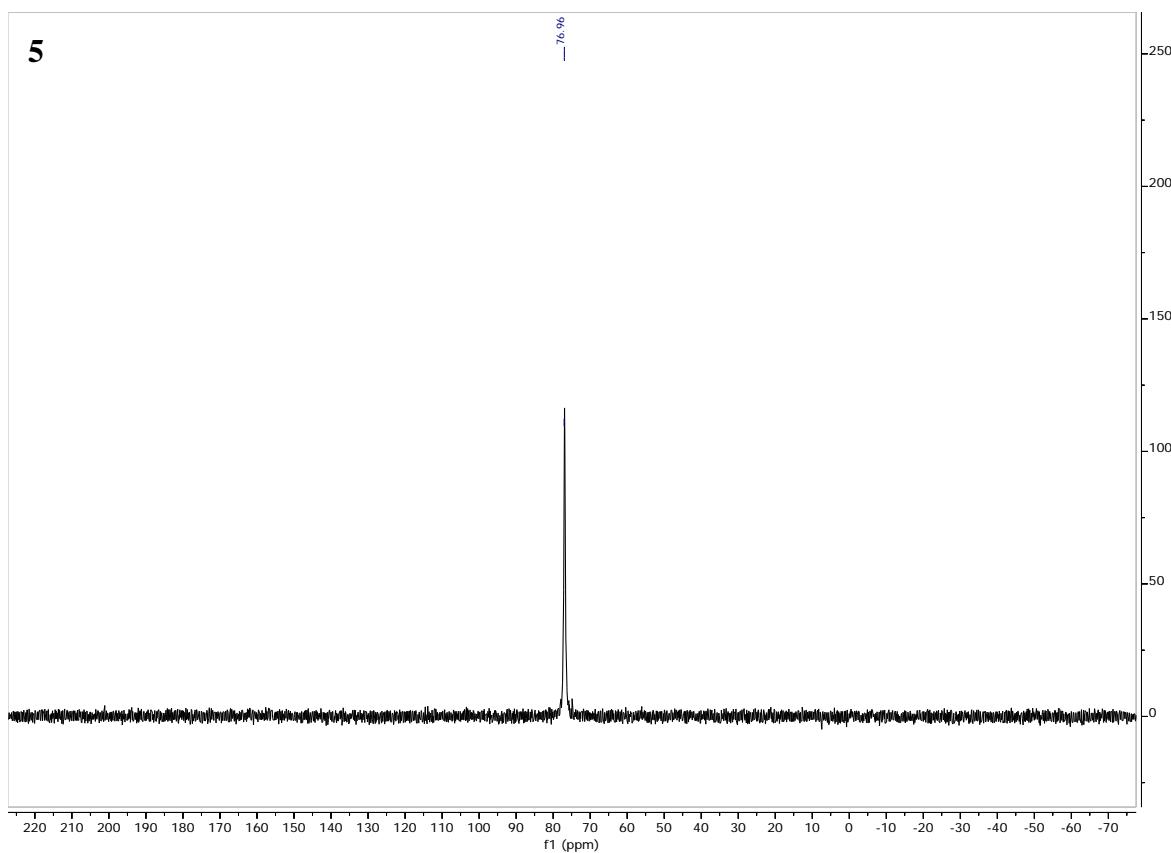


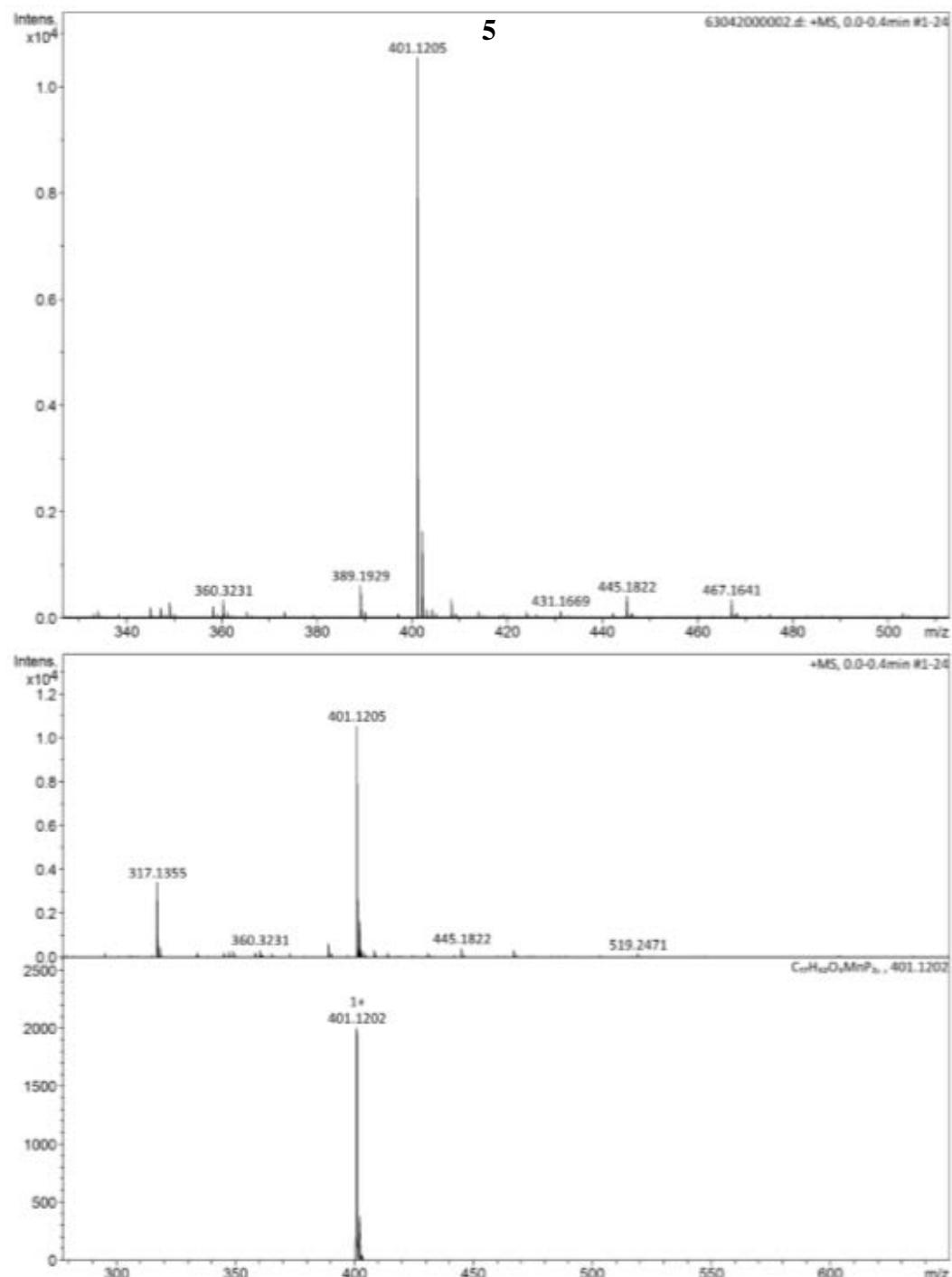


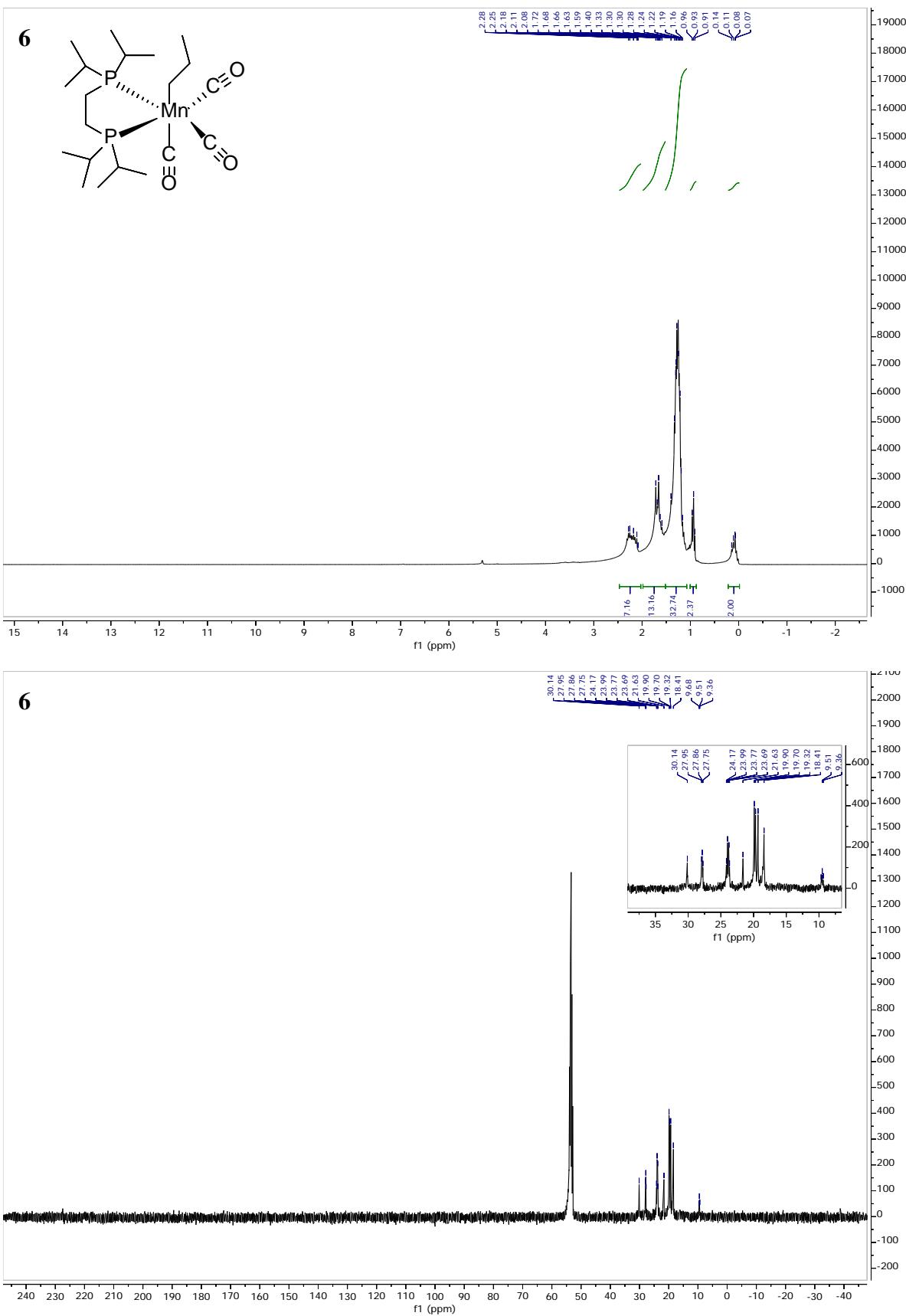


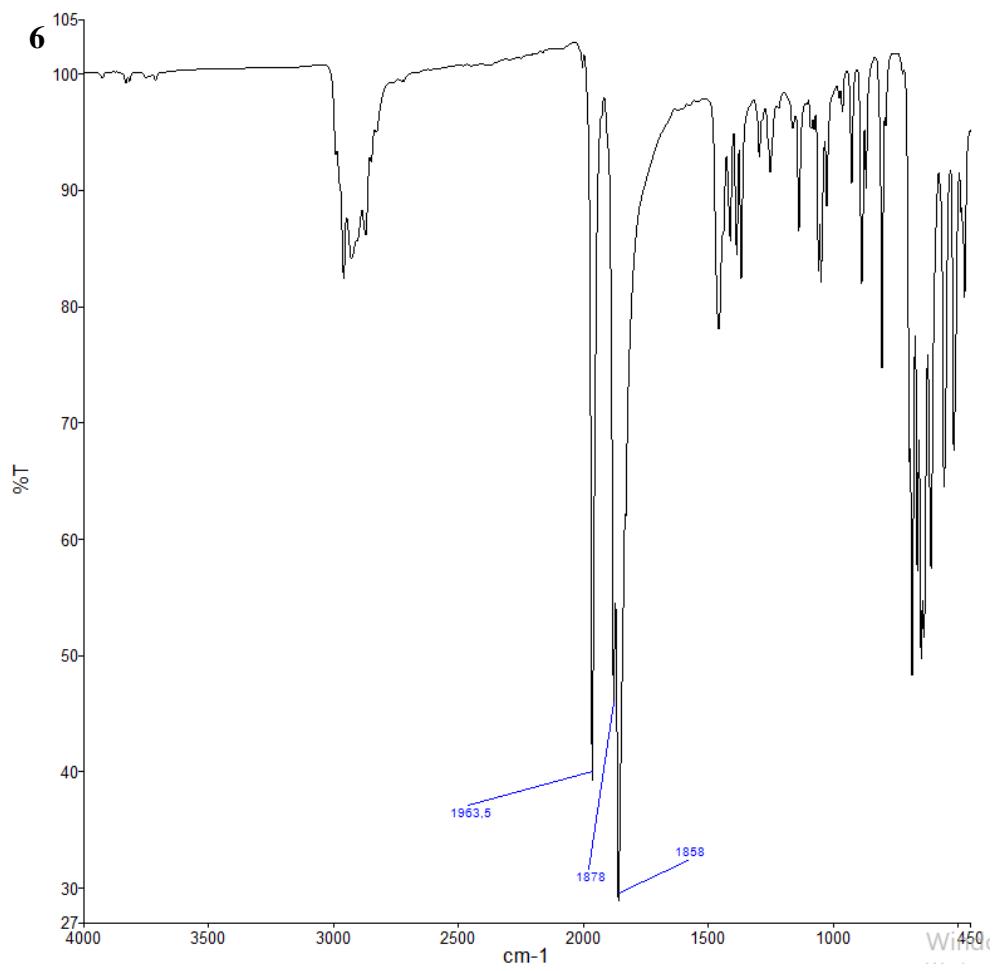
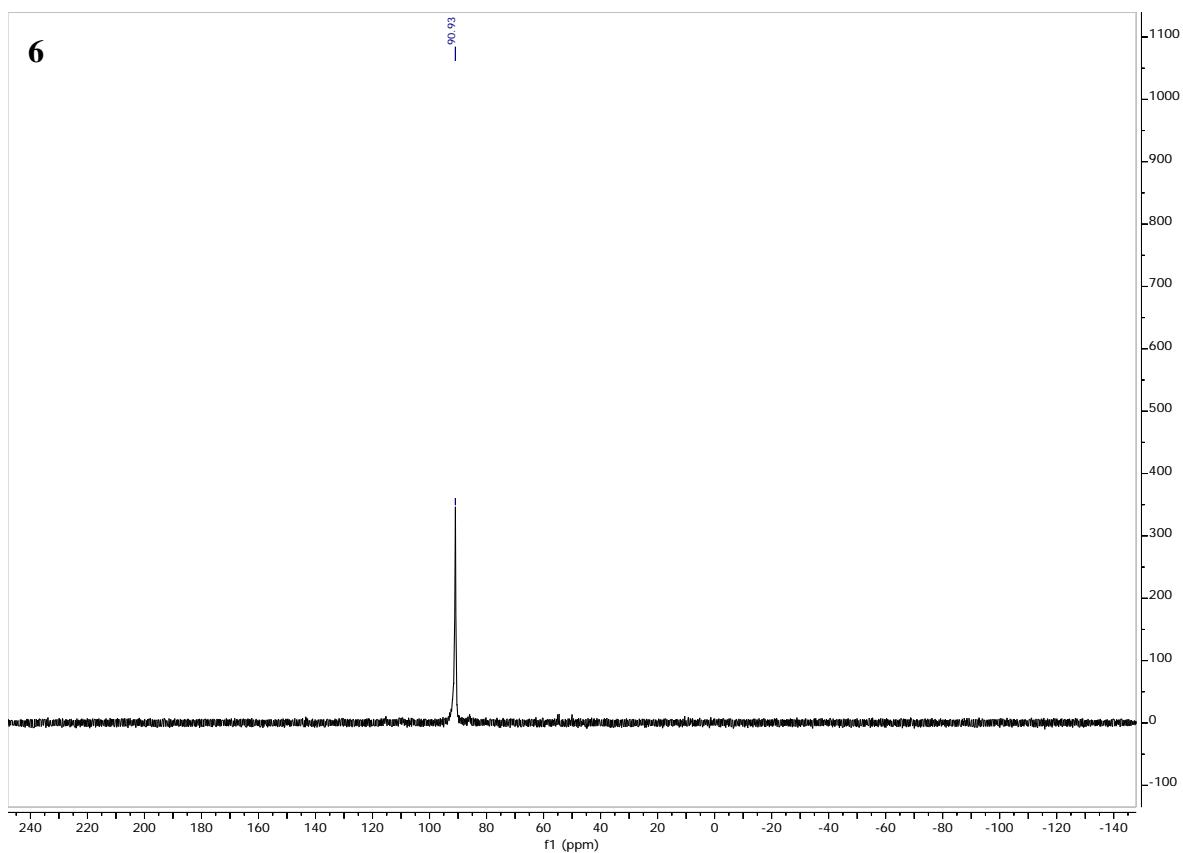


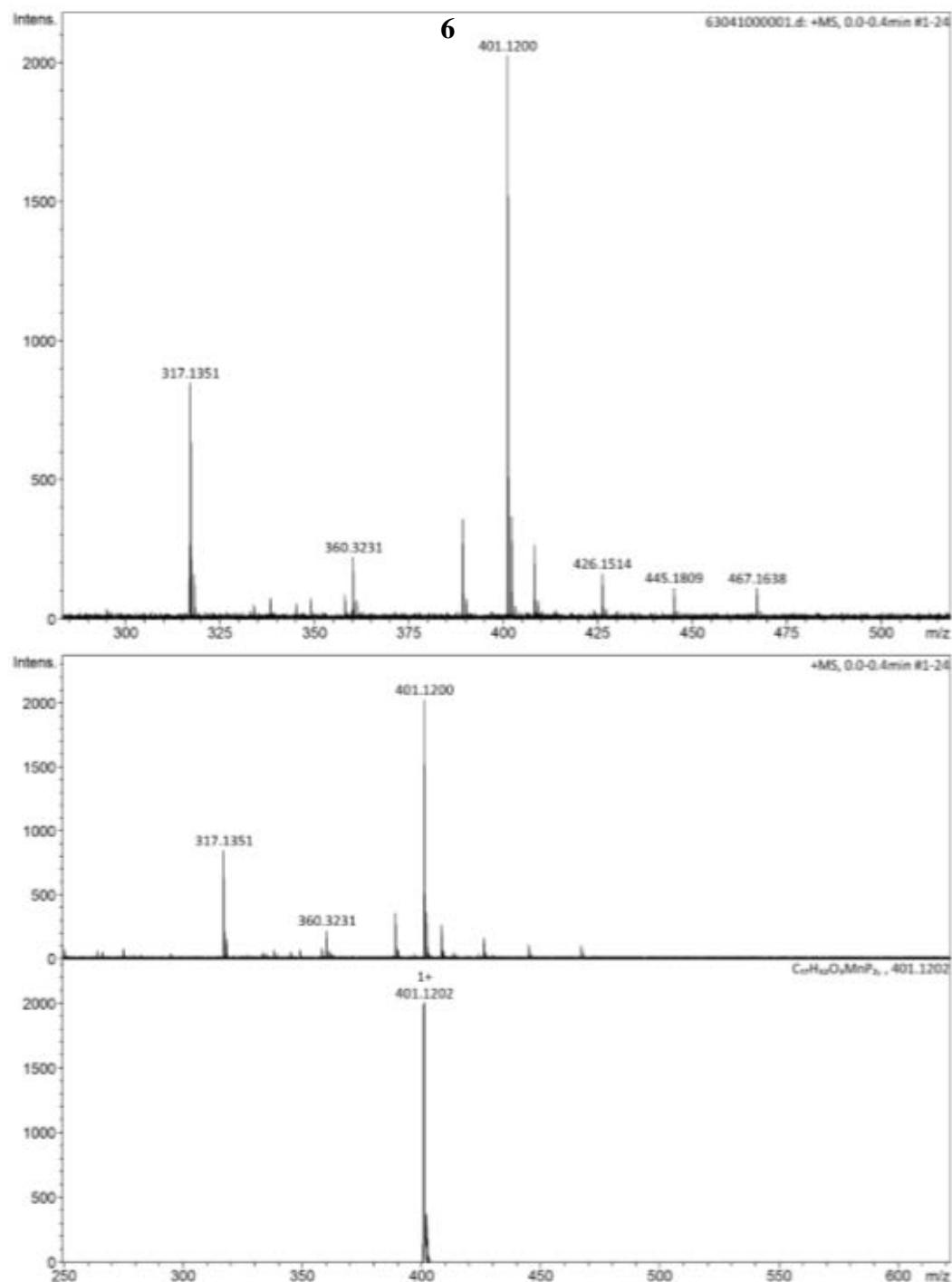


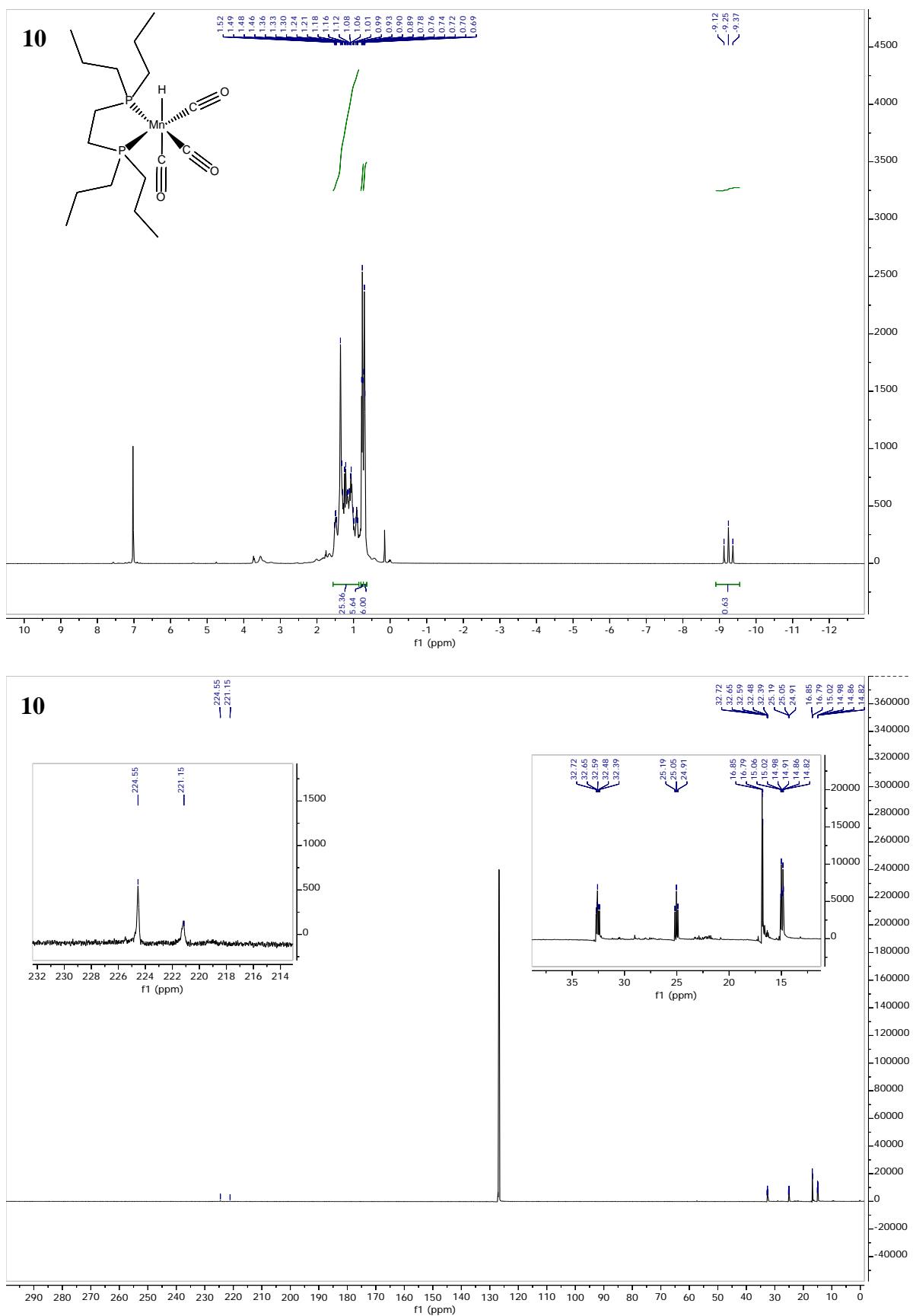


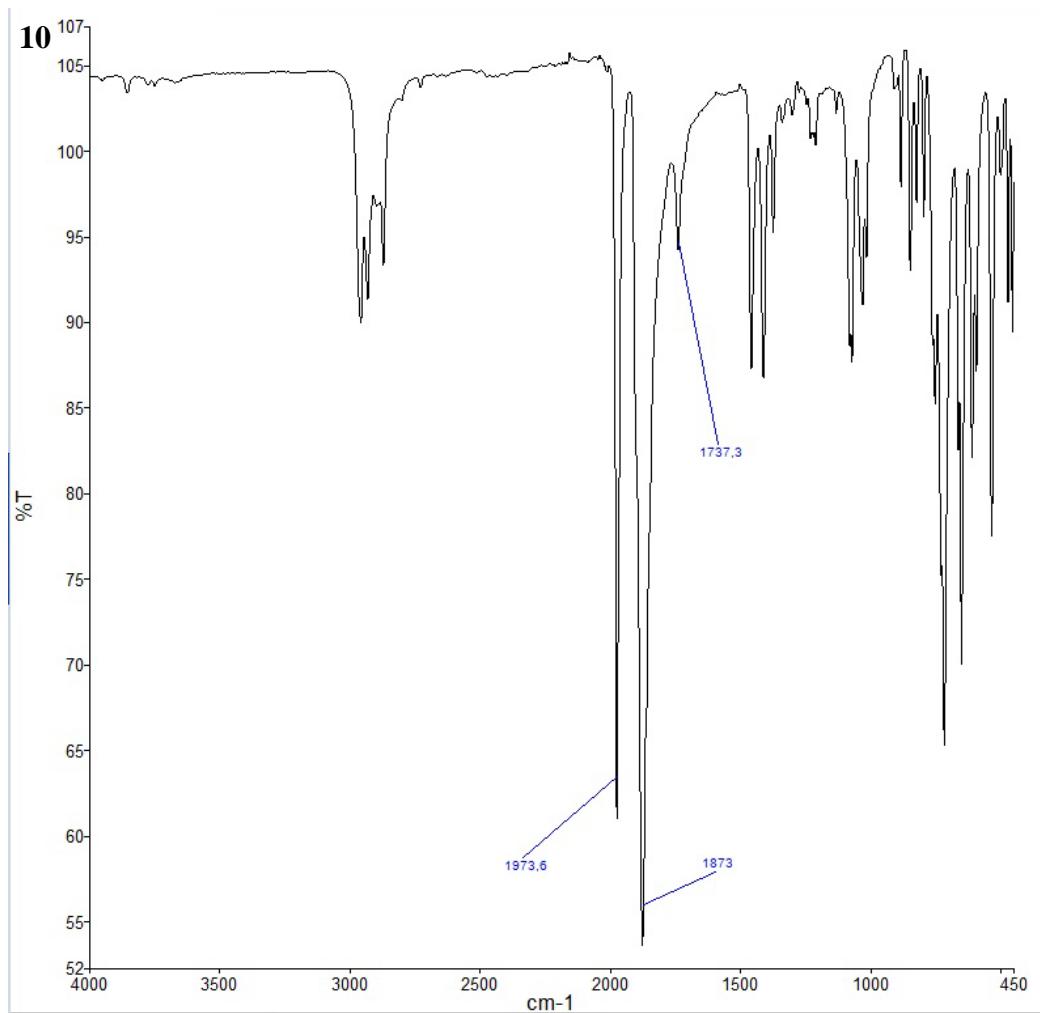
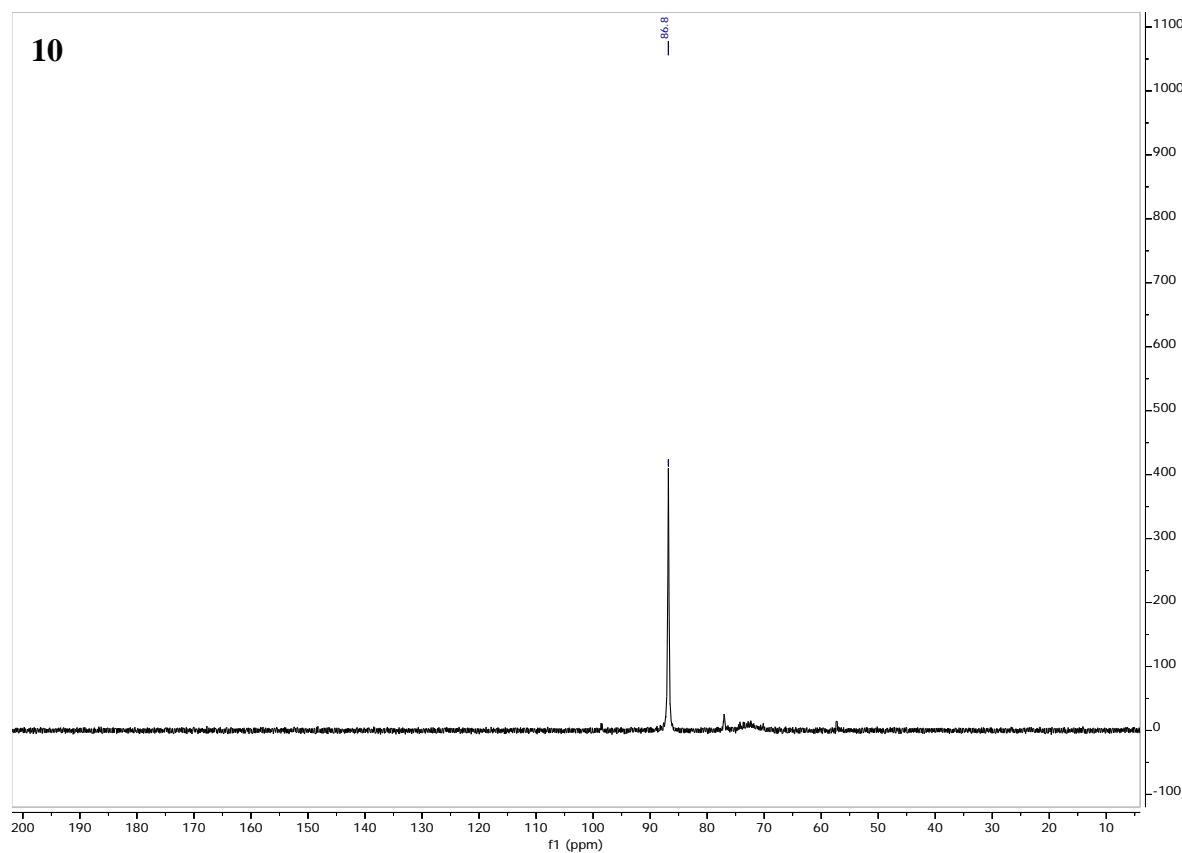


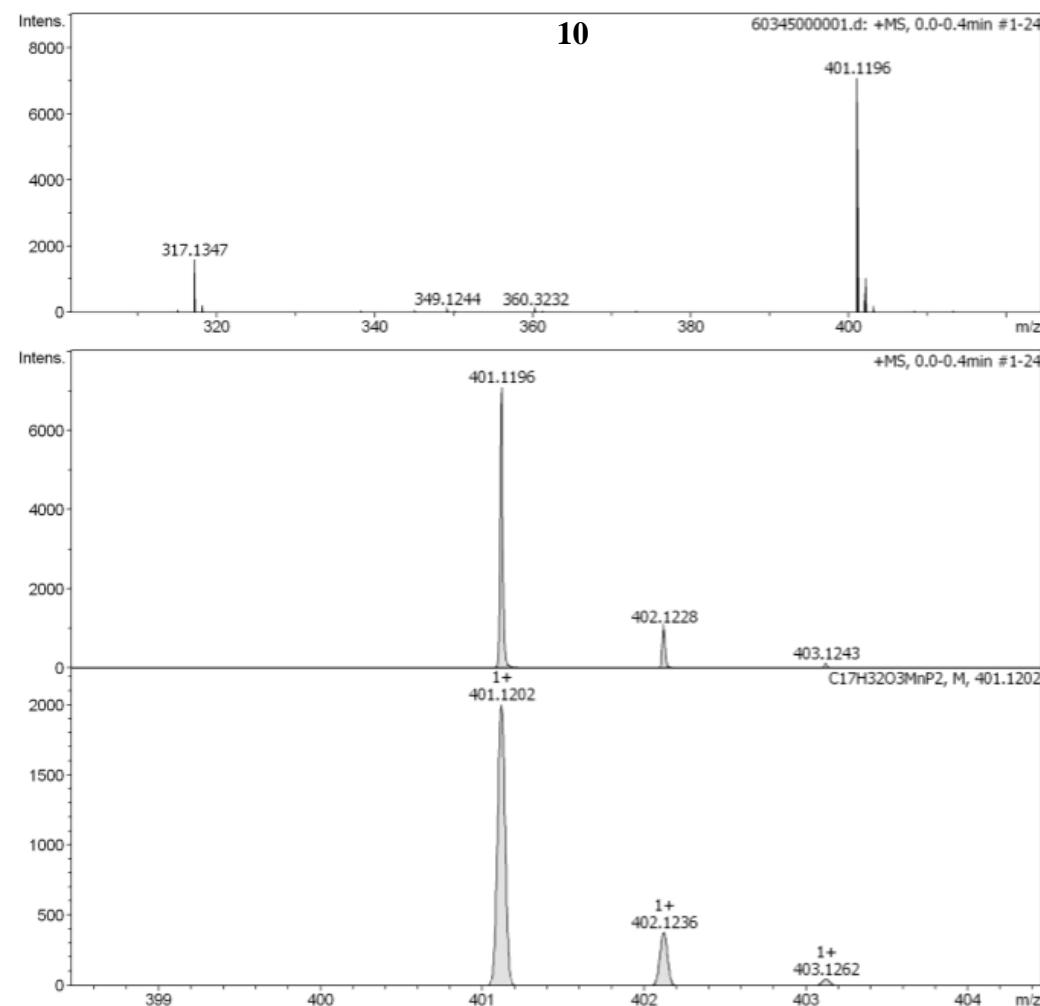


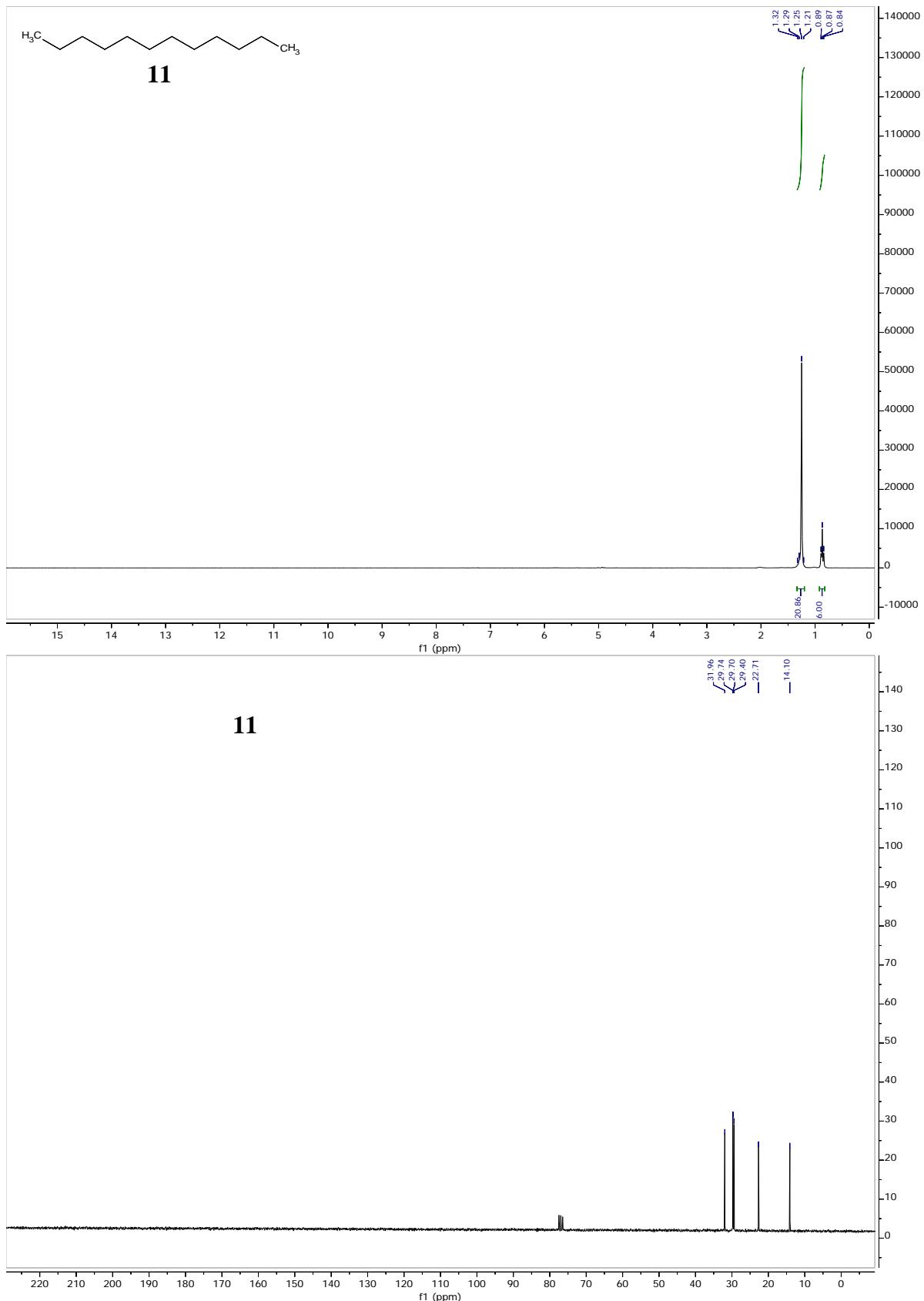


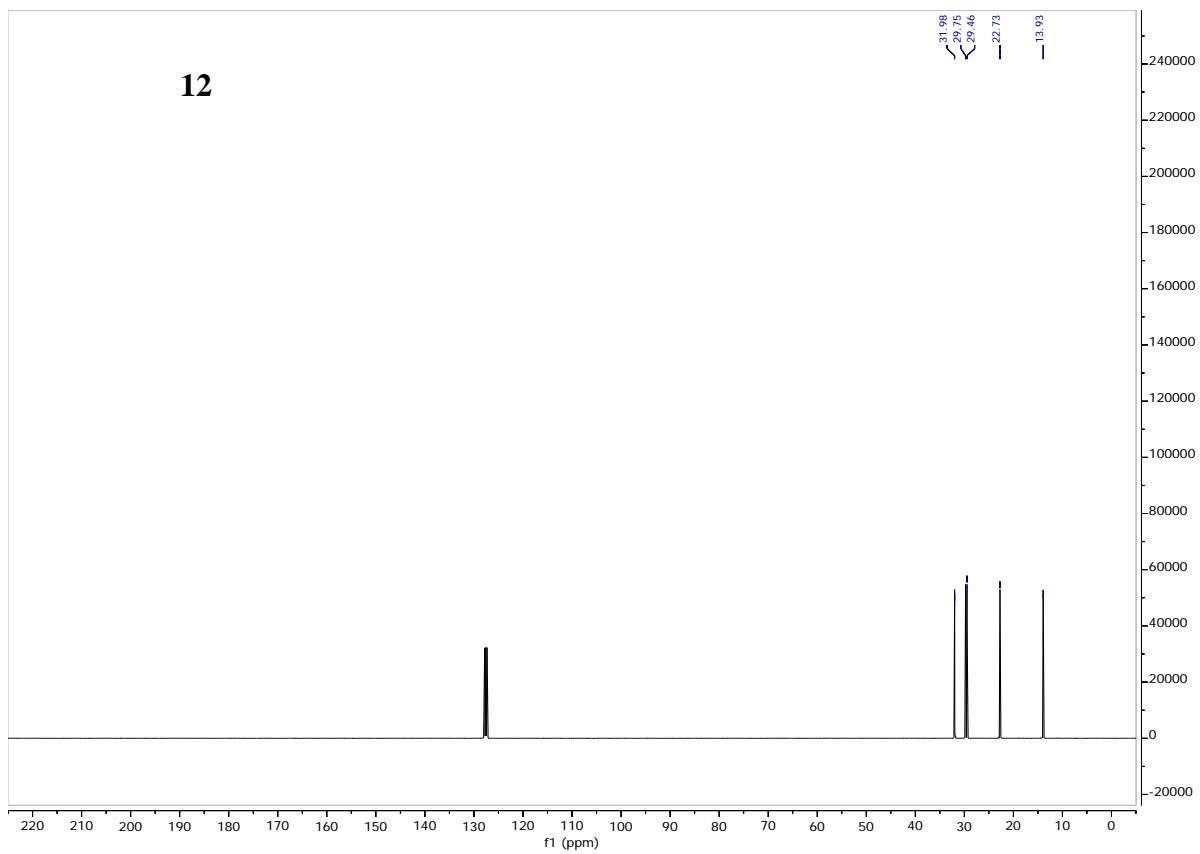
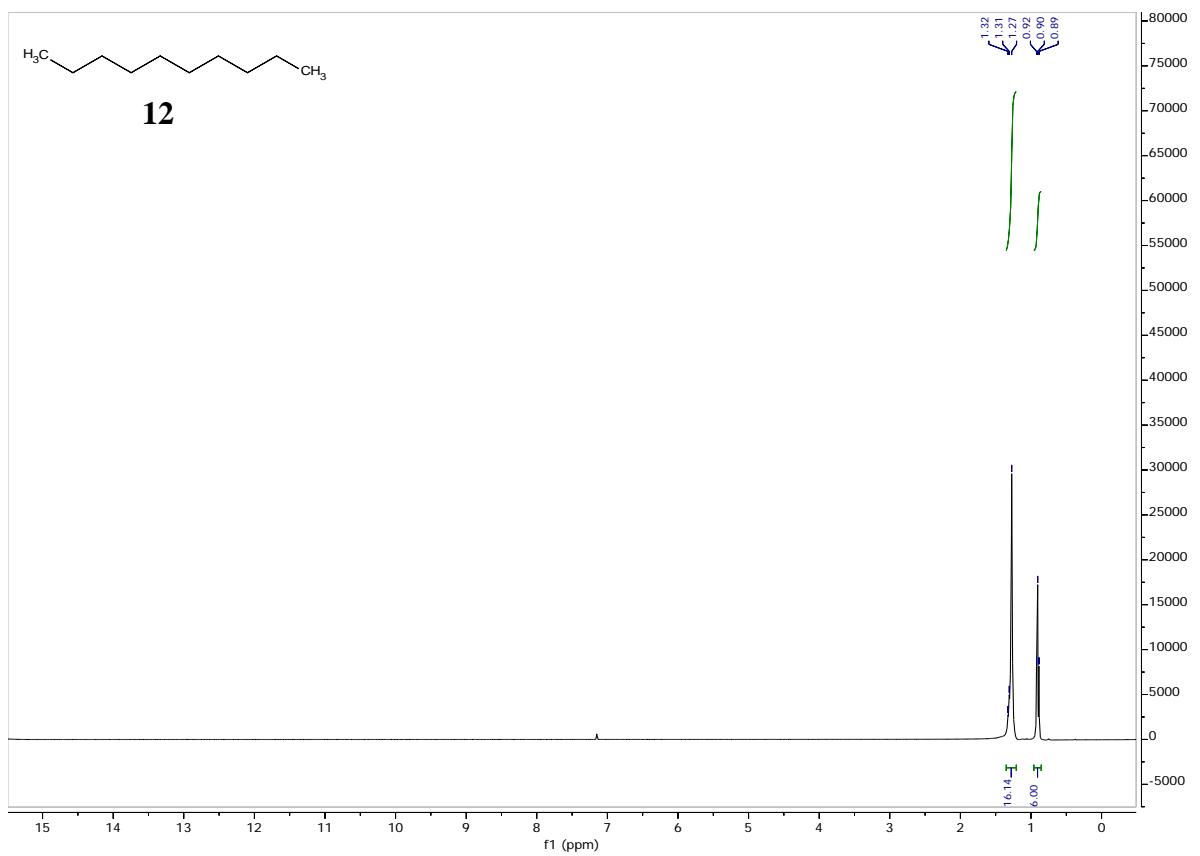


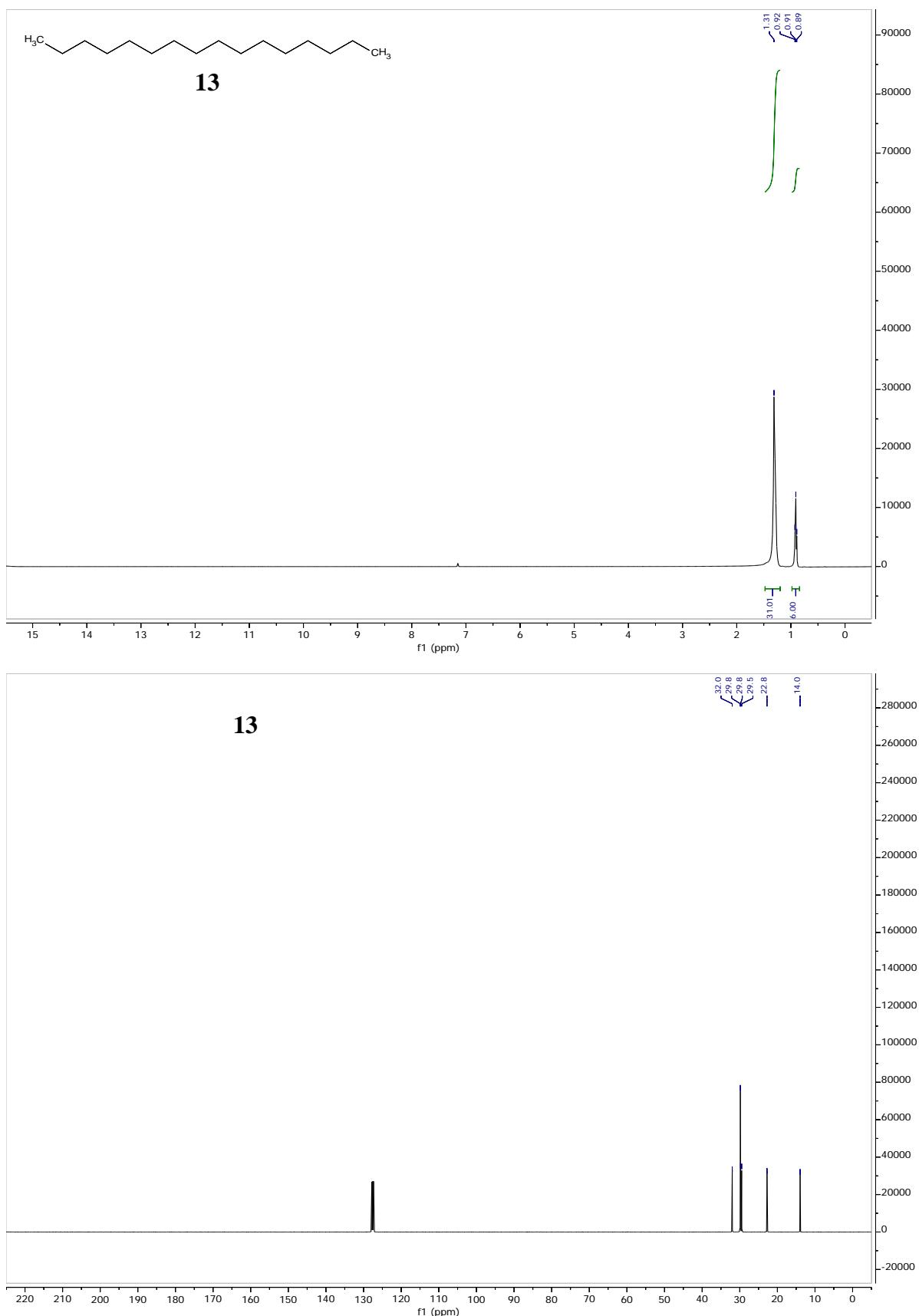


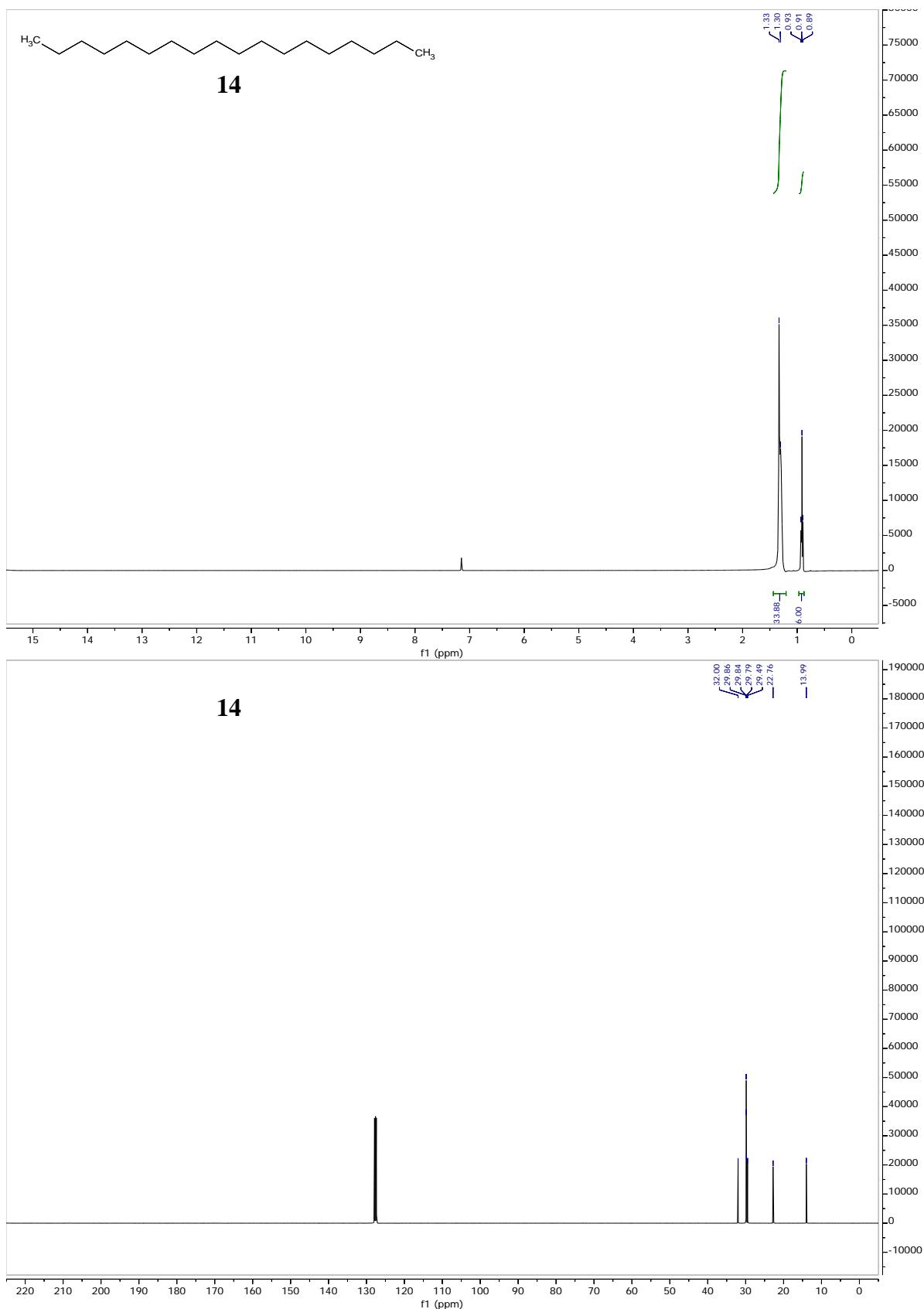


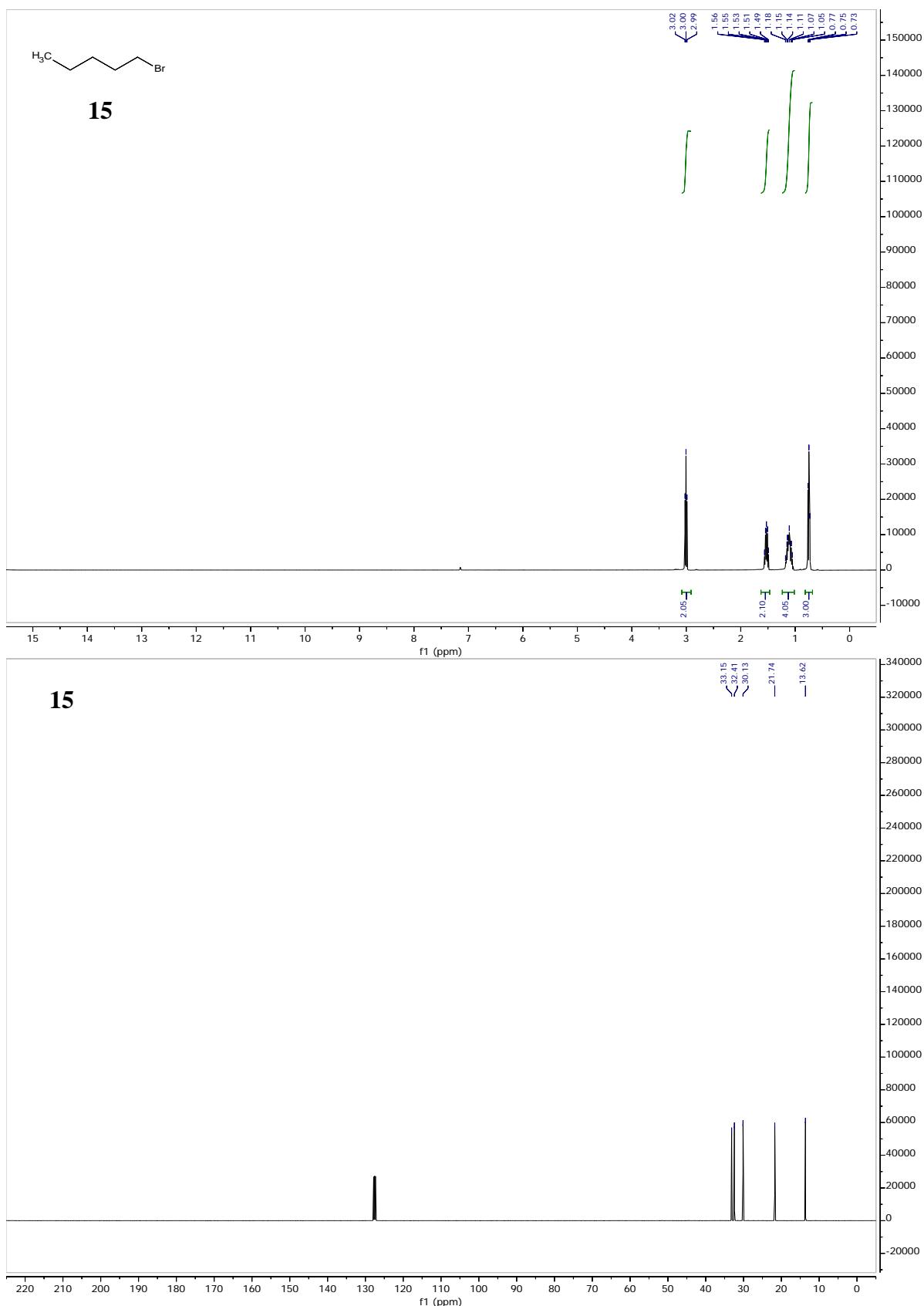


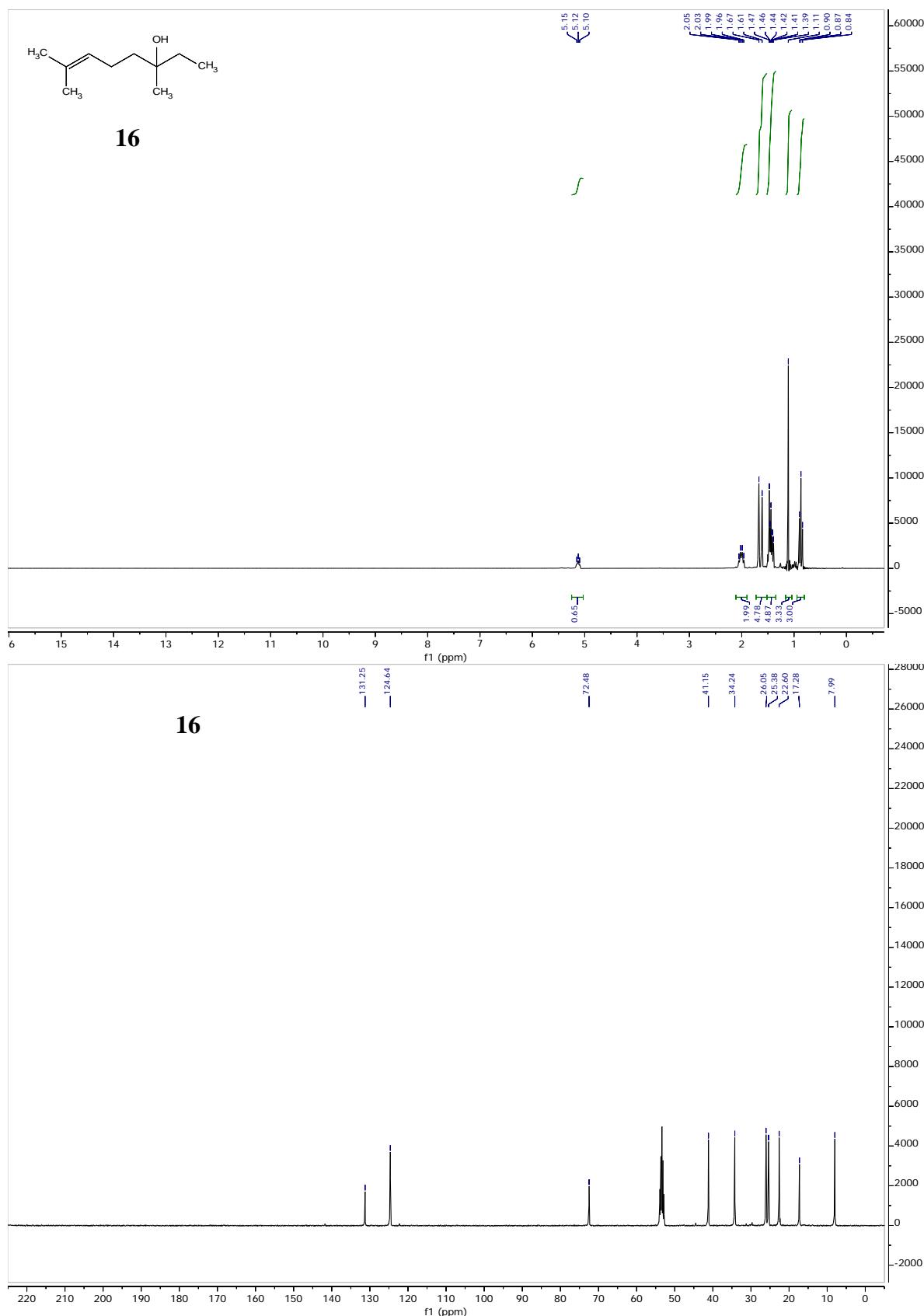


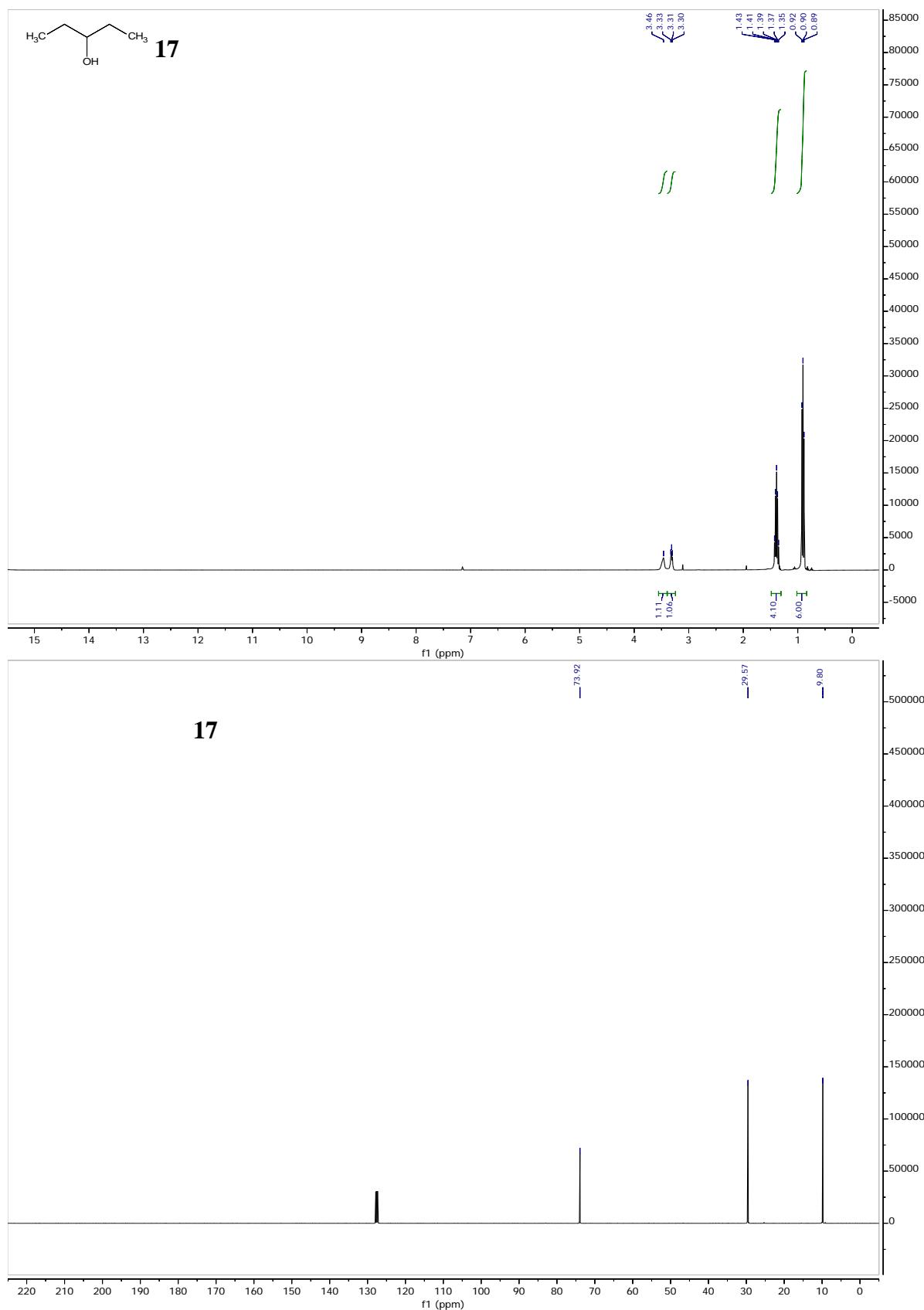


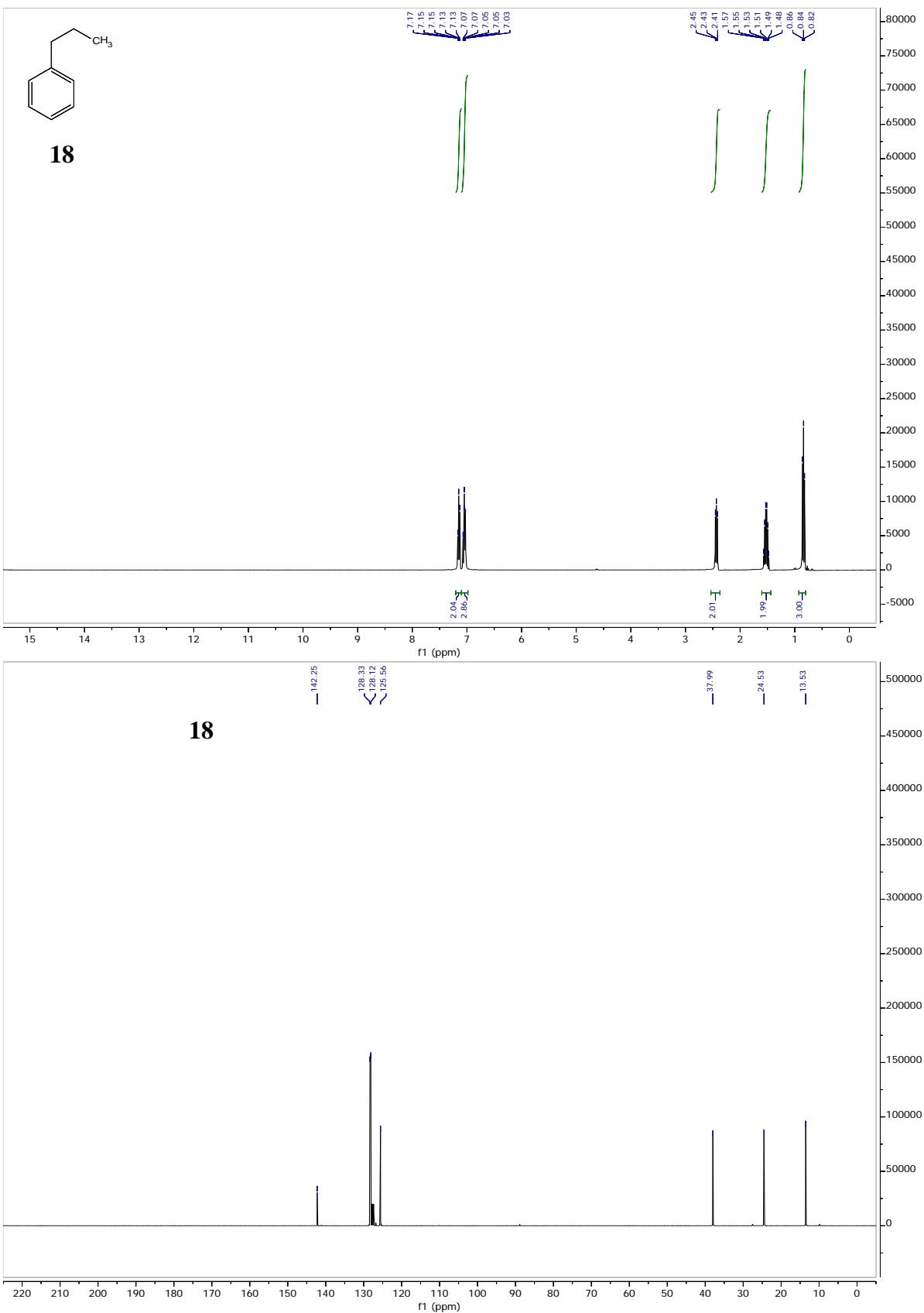


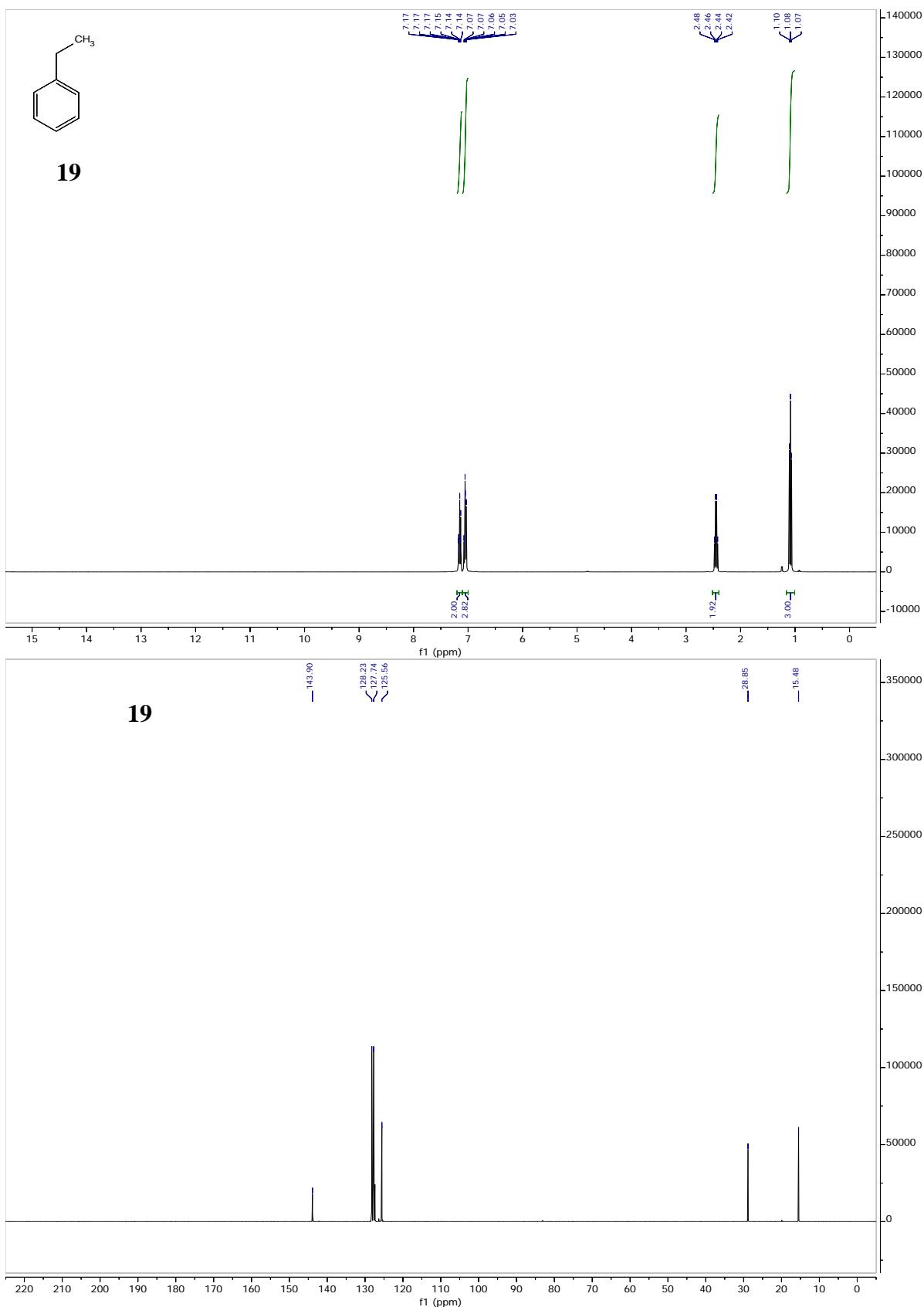


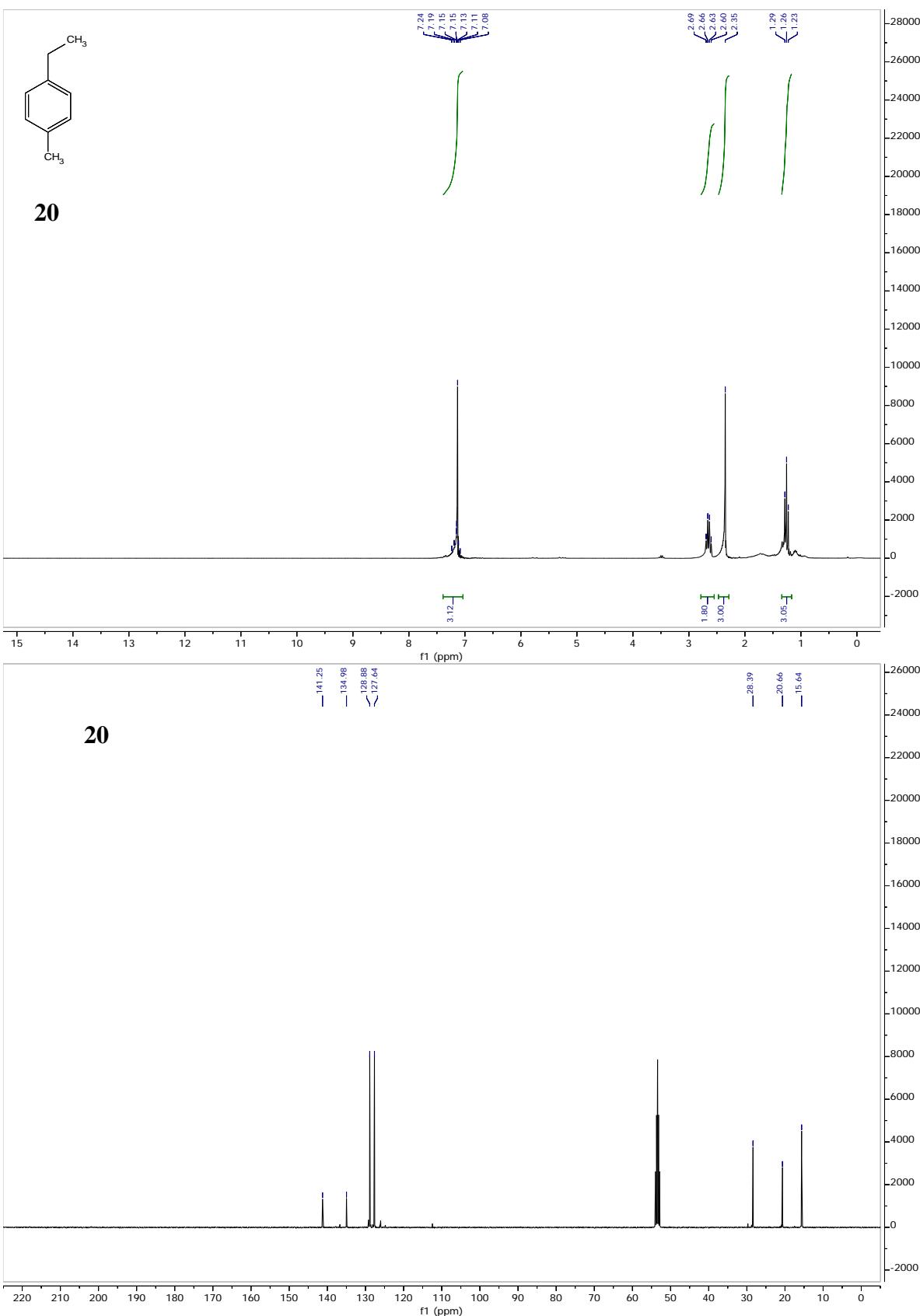


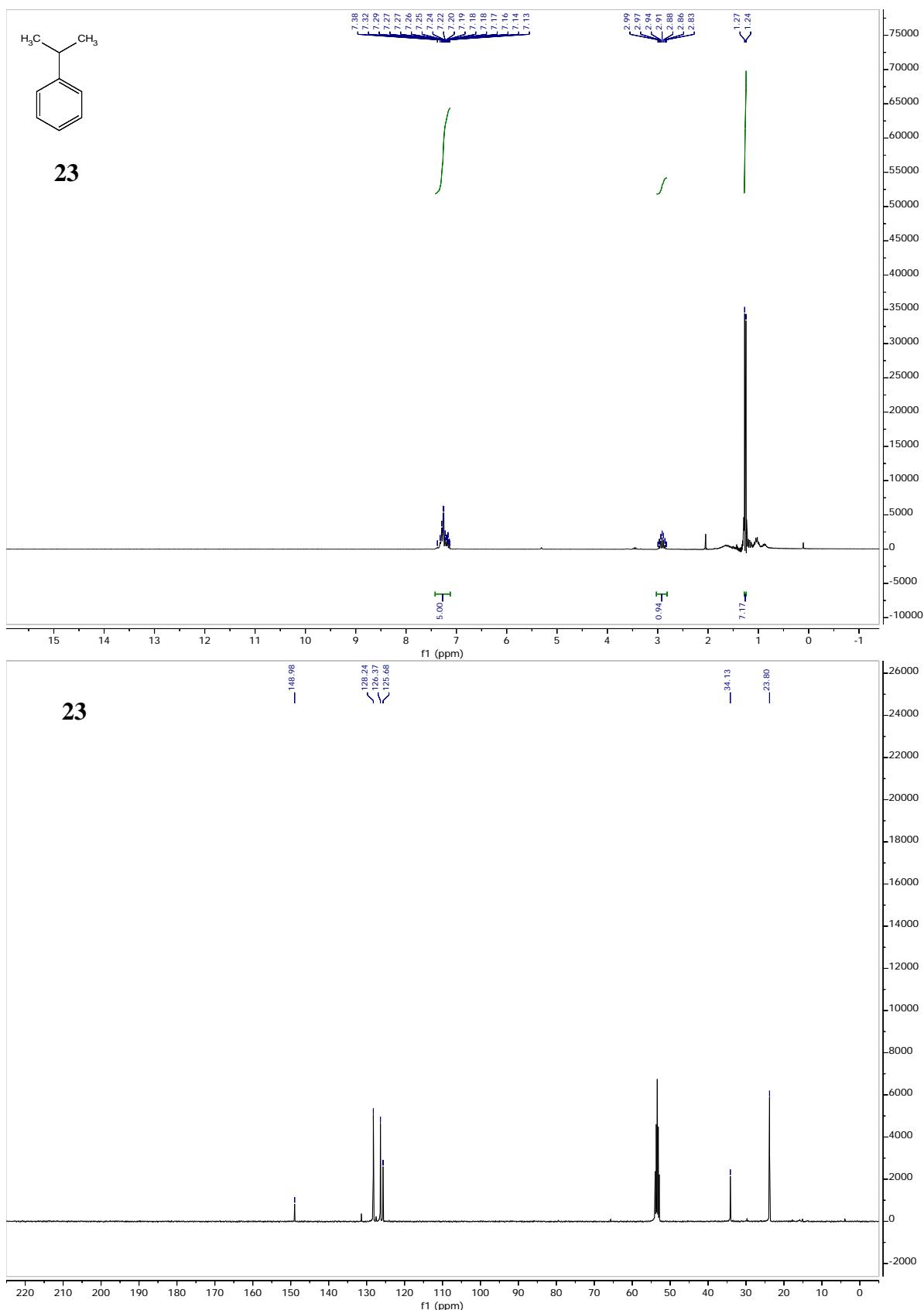


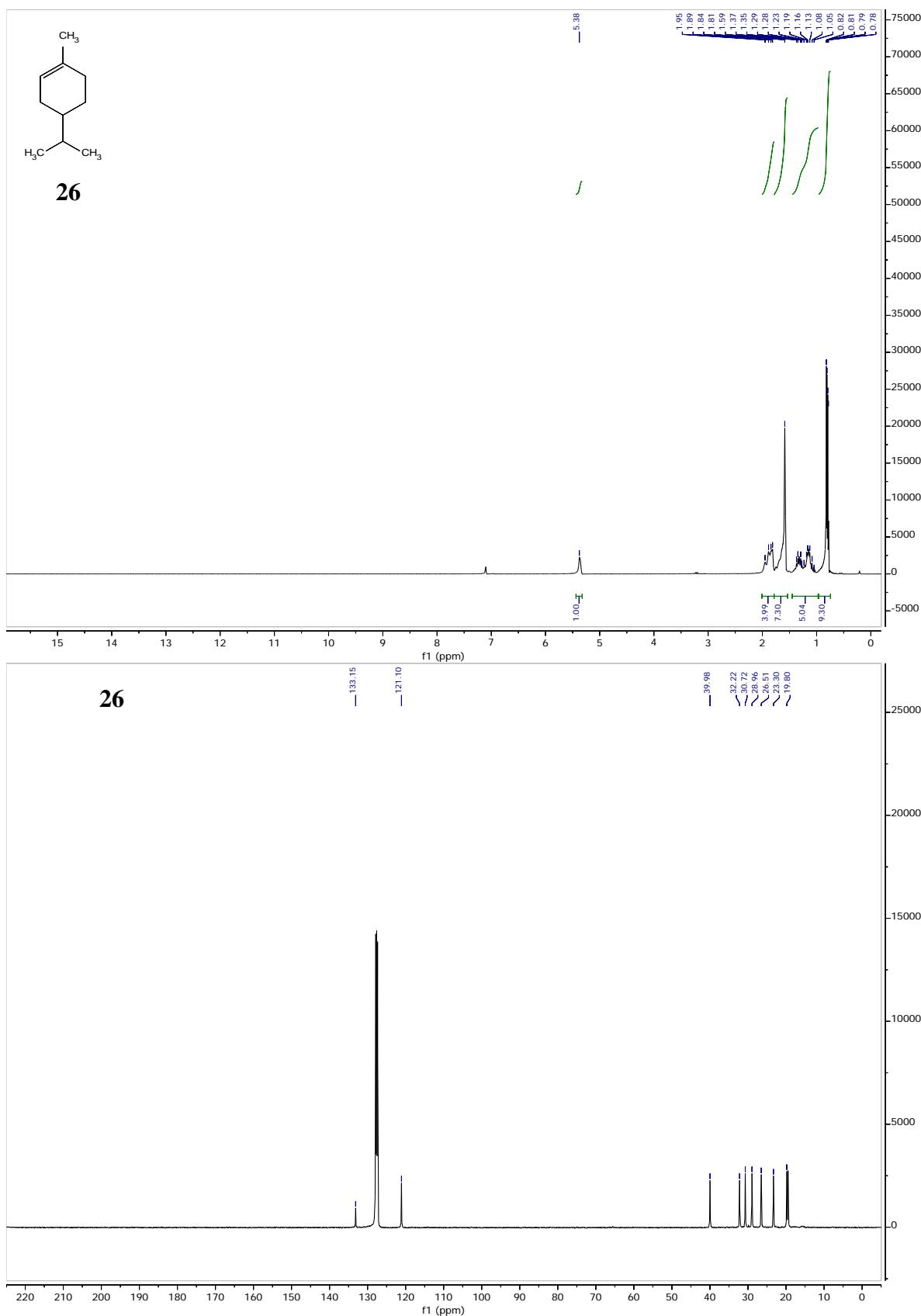


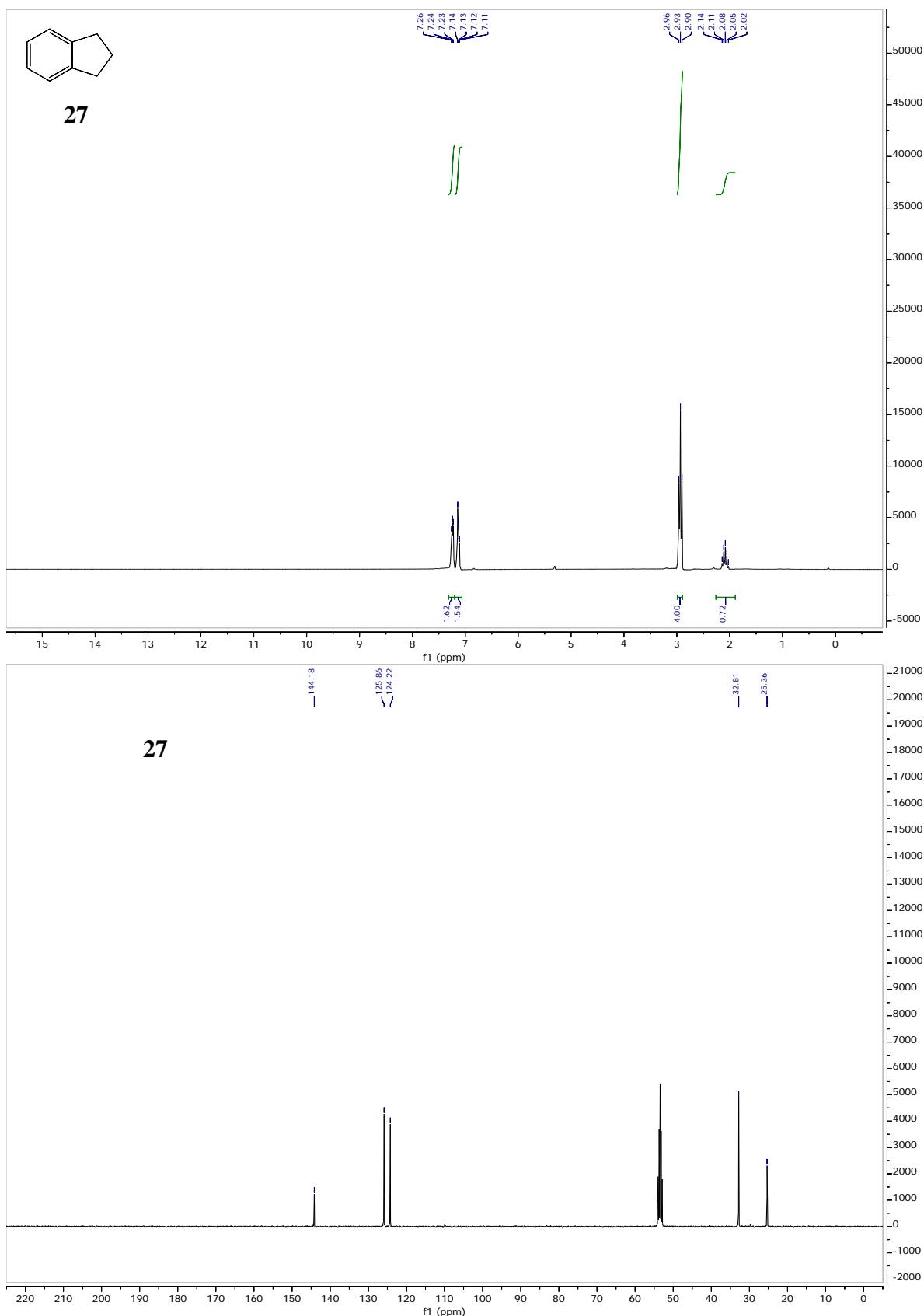


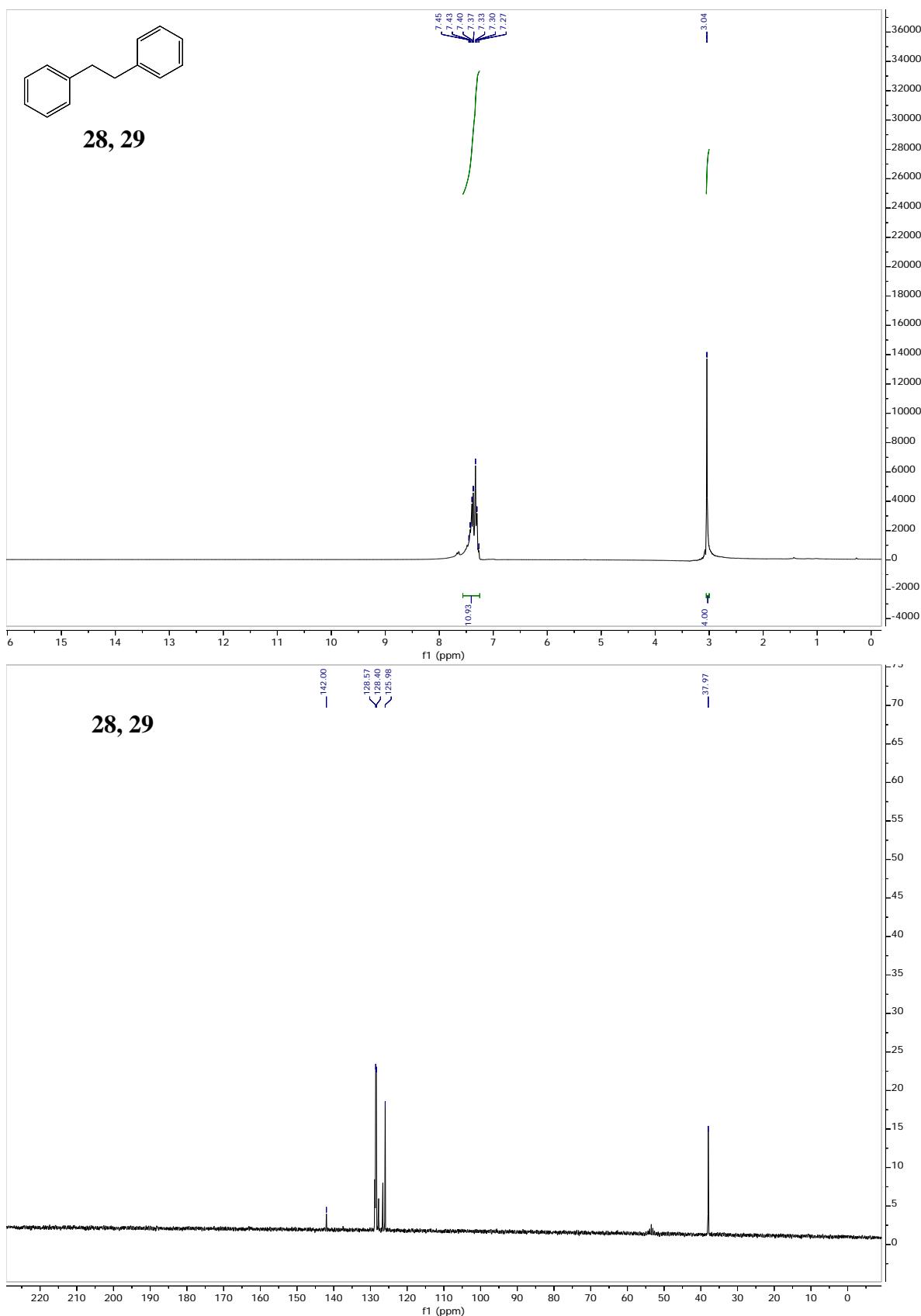


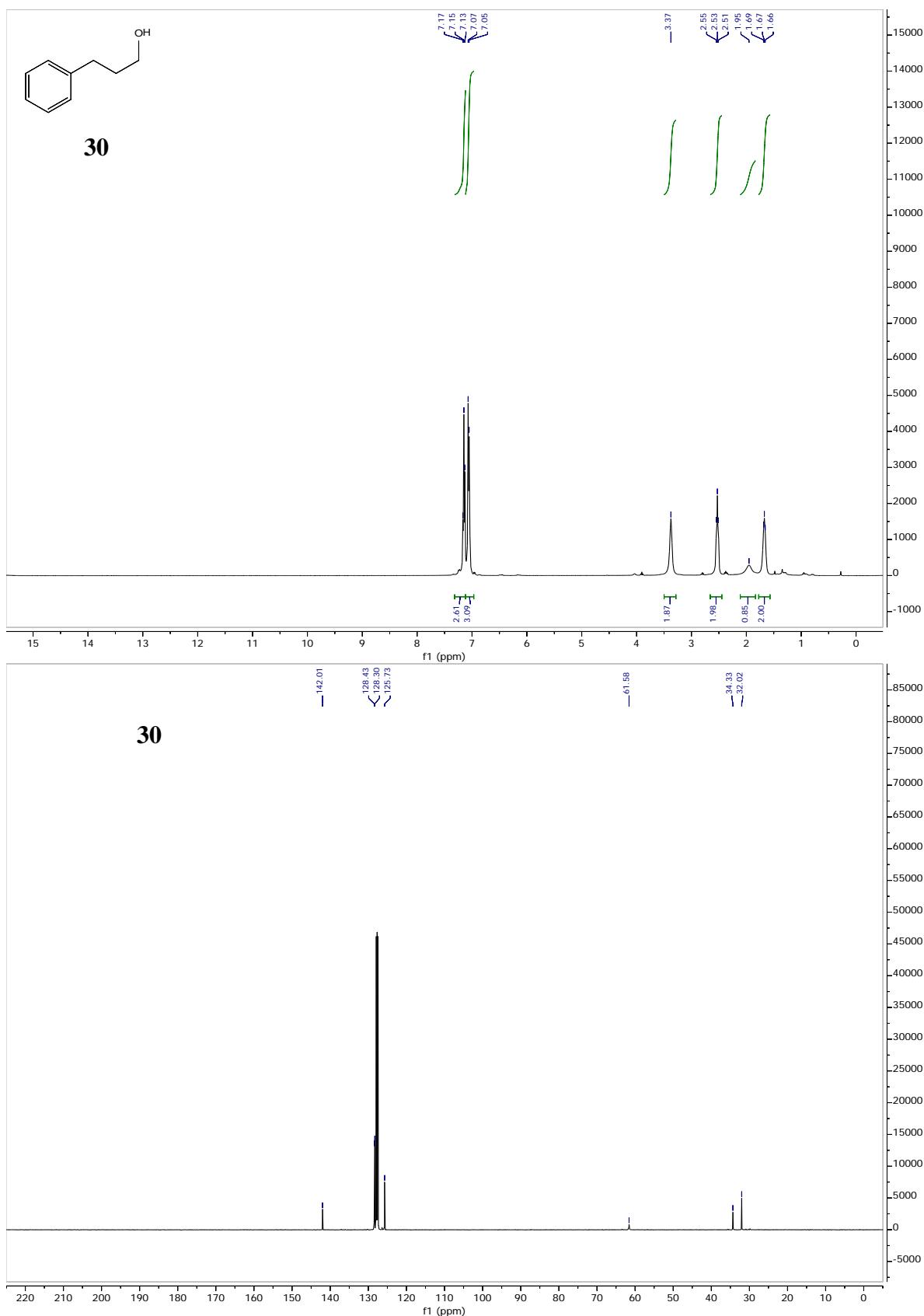


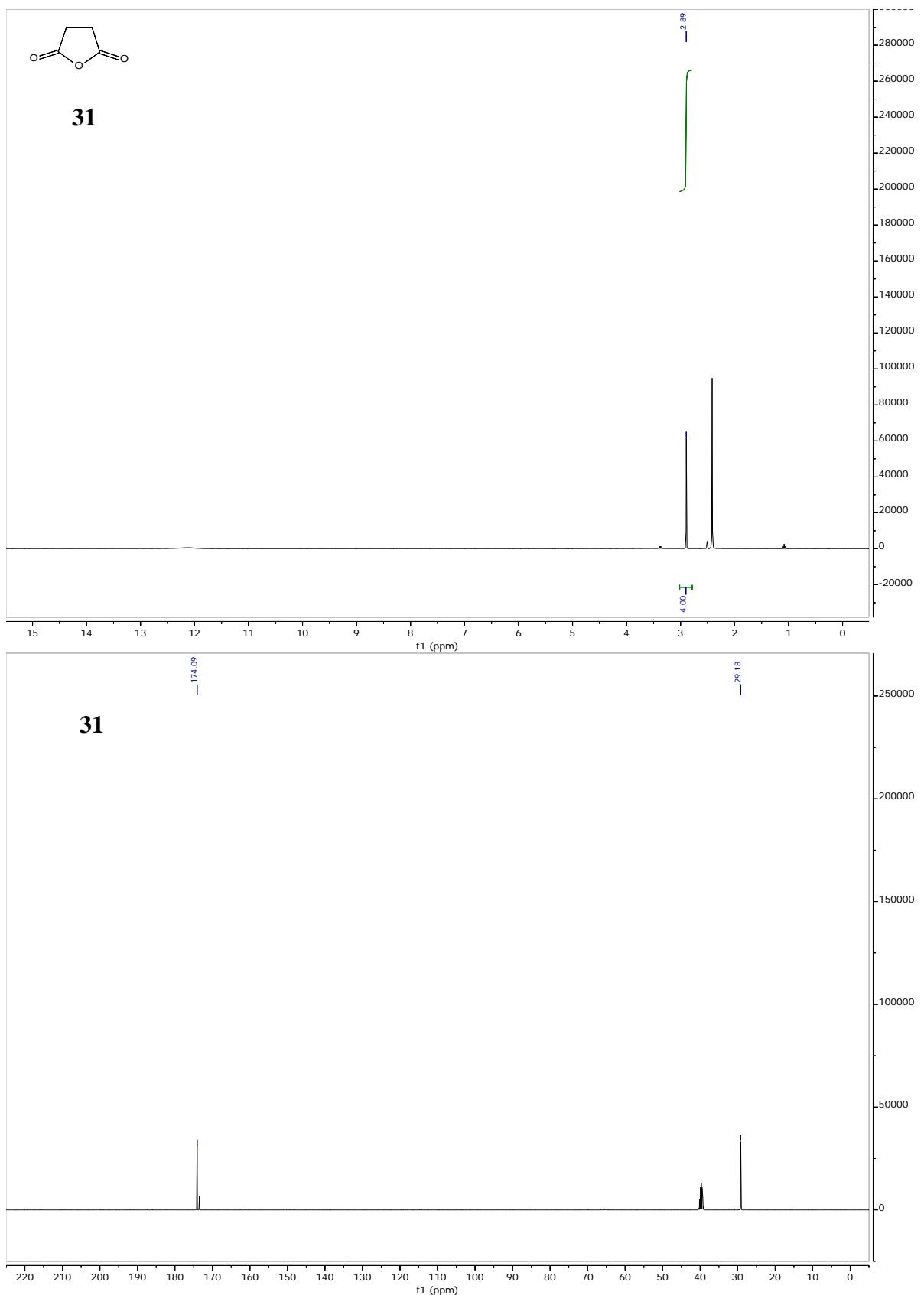


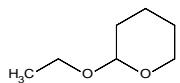




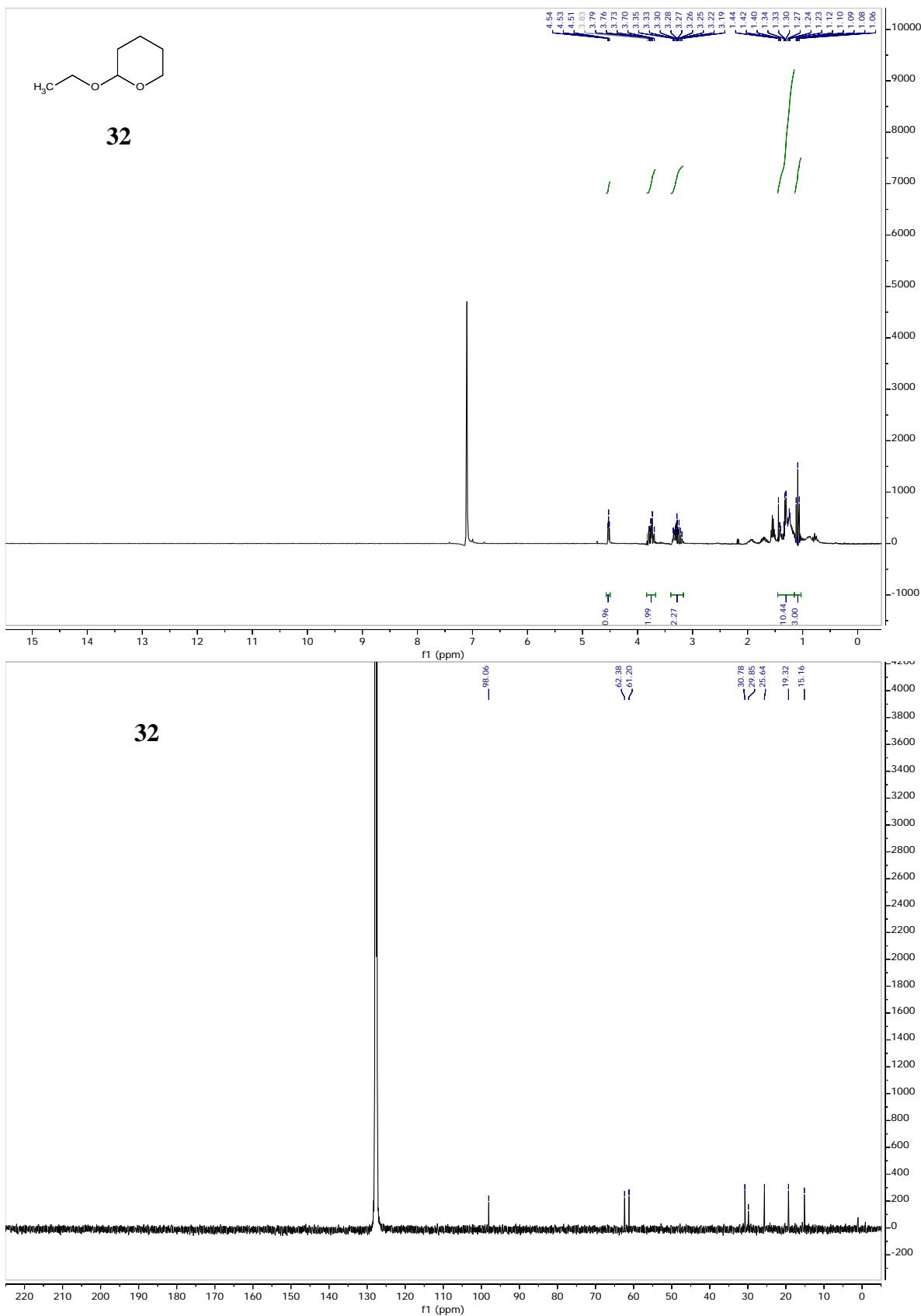


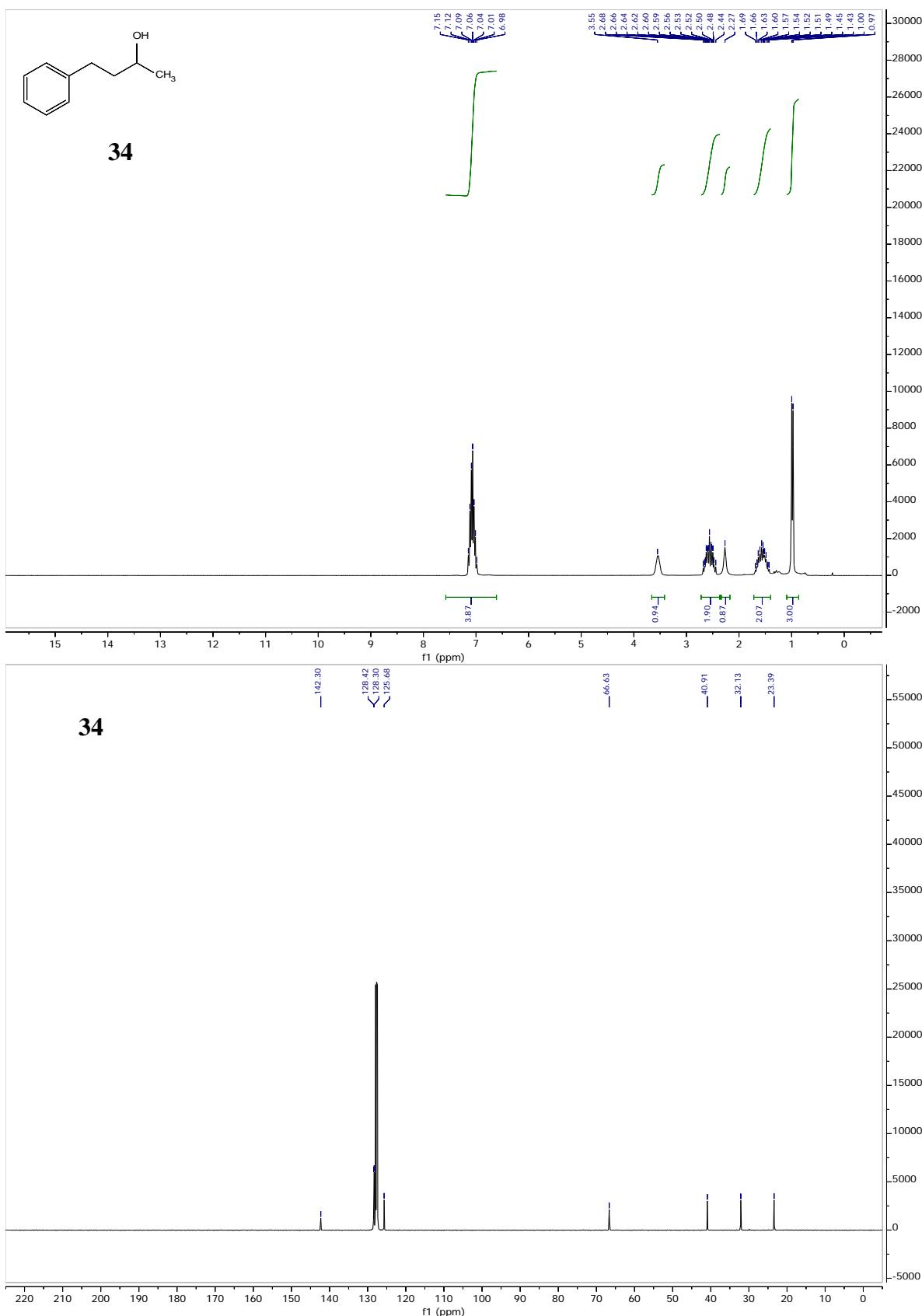






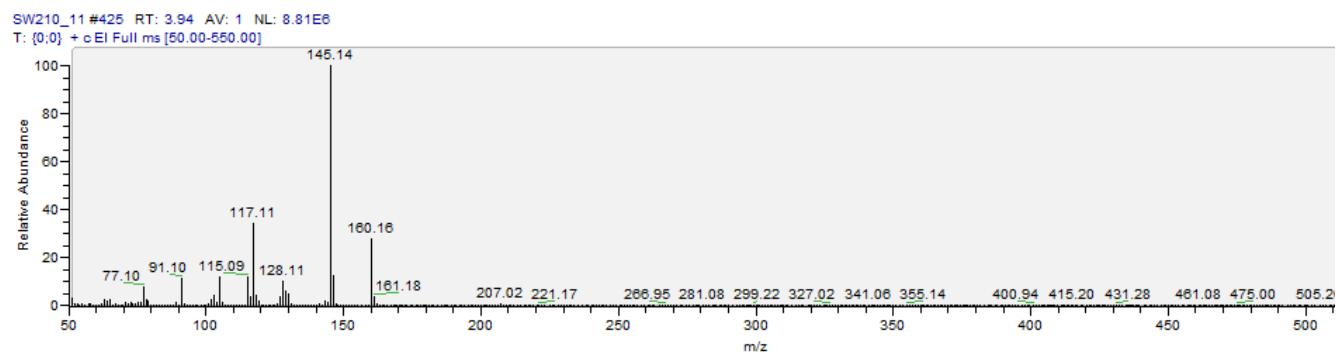
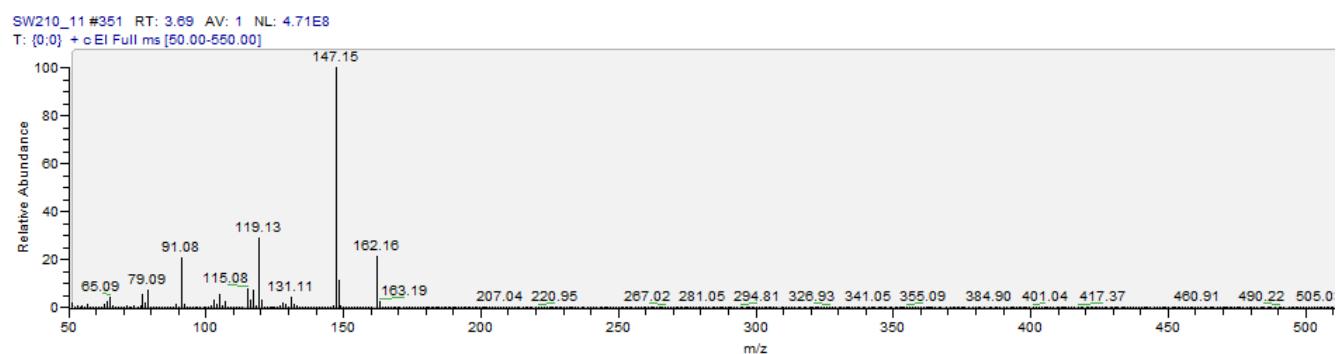
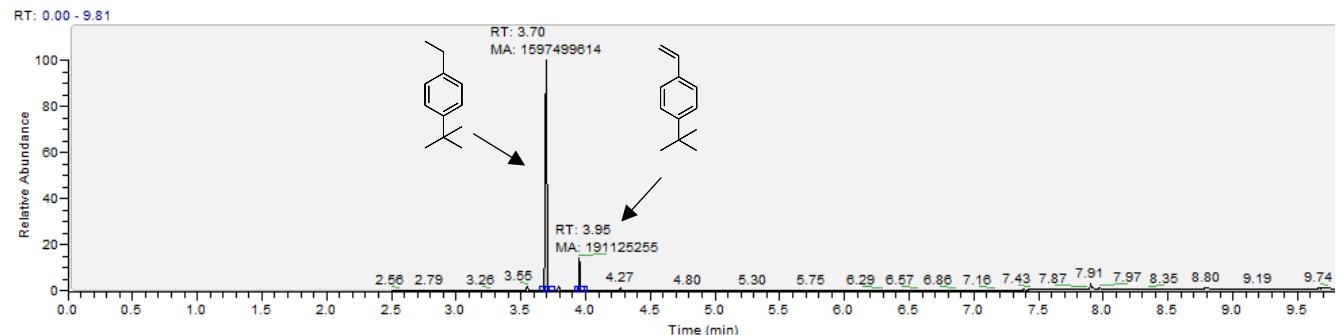
32



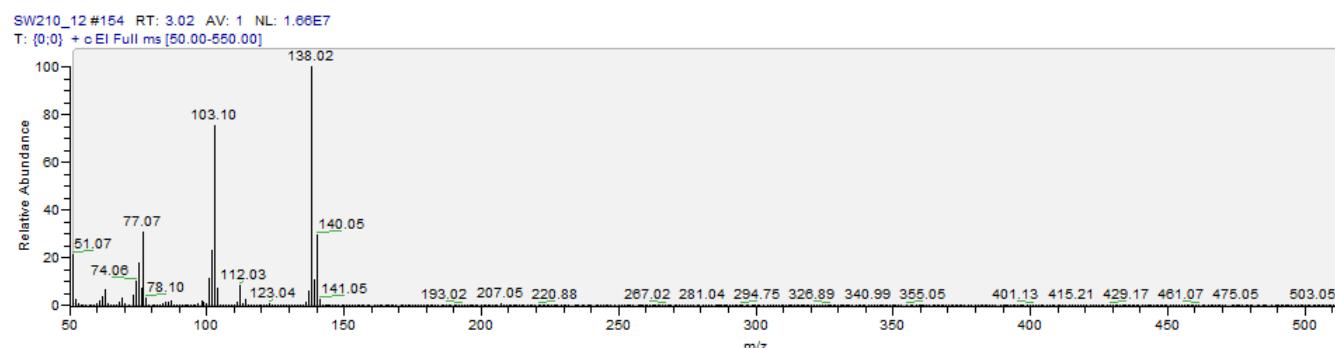
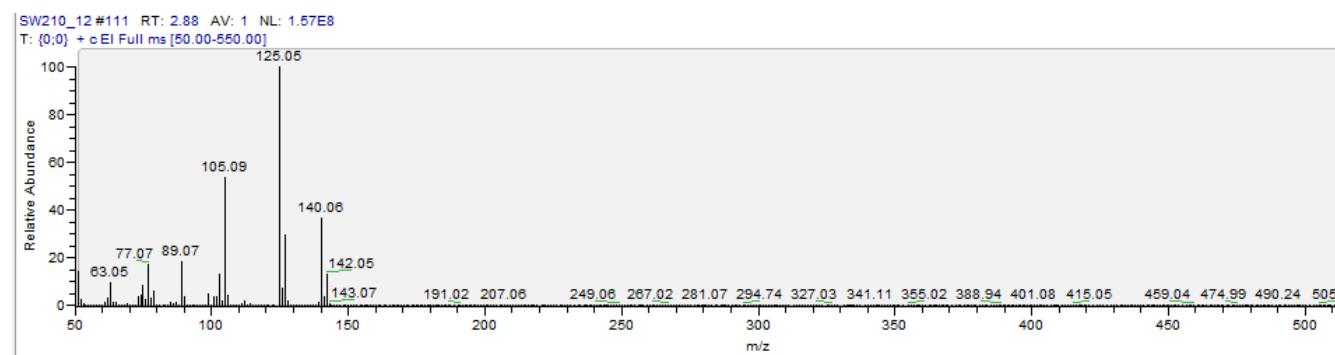
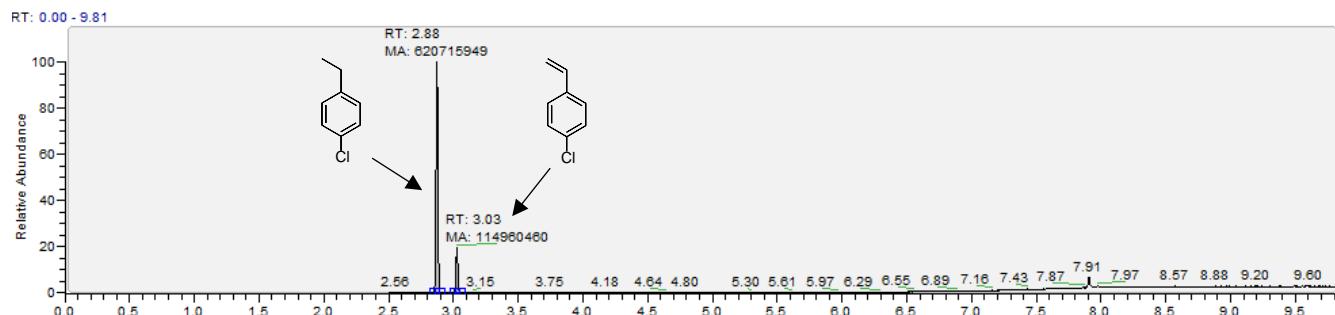


11. GC Traces and ^1H NMR analysis of substrates which were not isolated

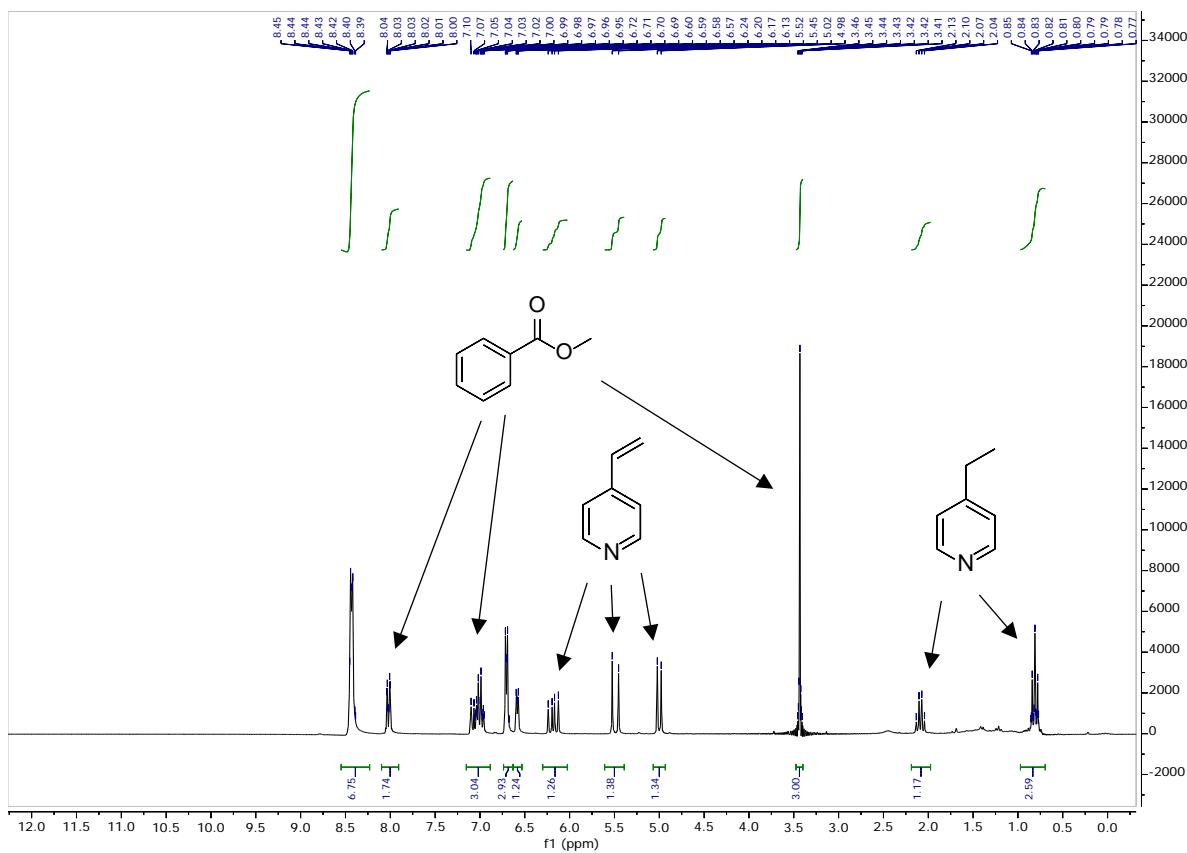
4-*tert*-butylstyrene as substrate (**21**)

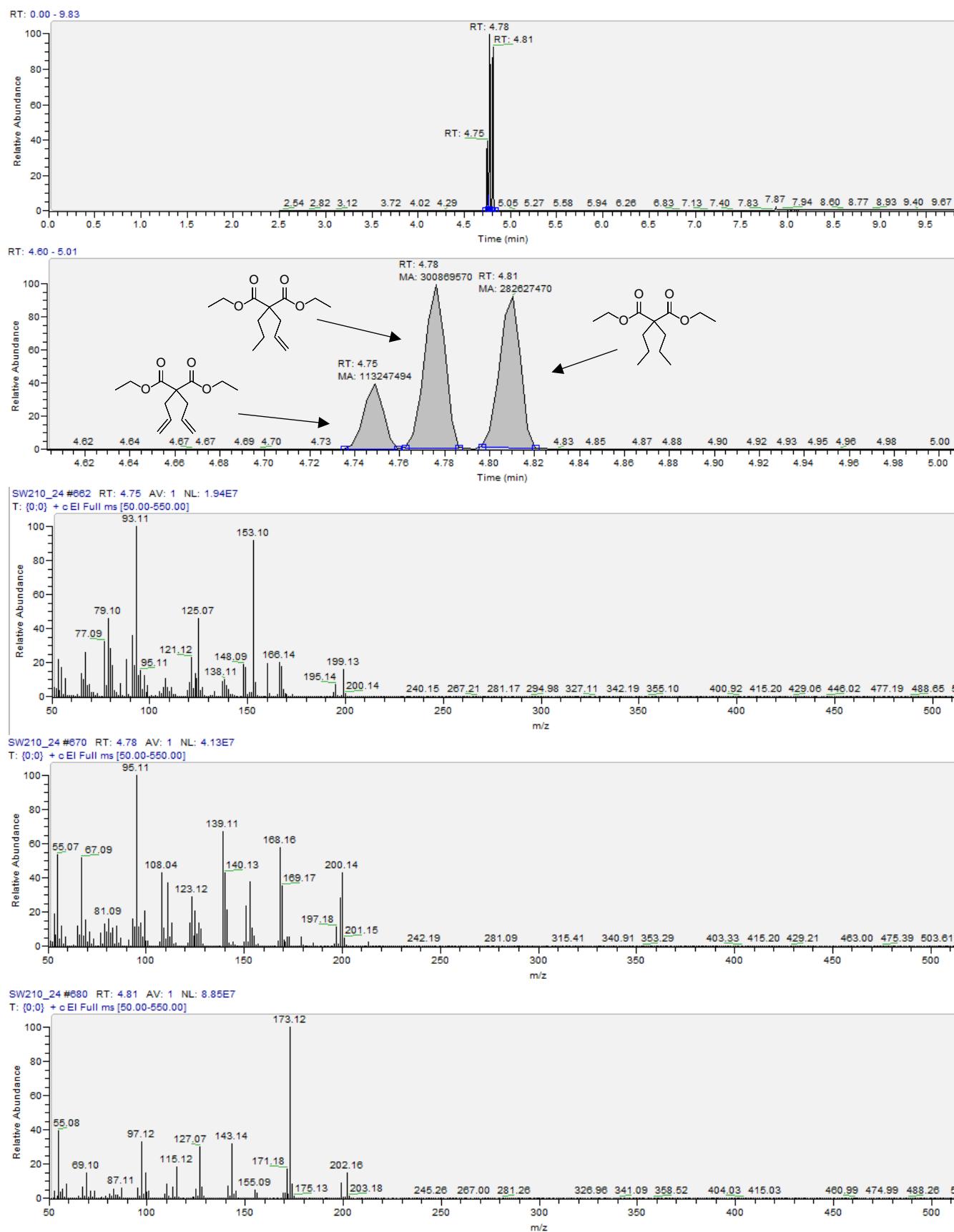


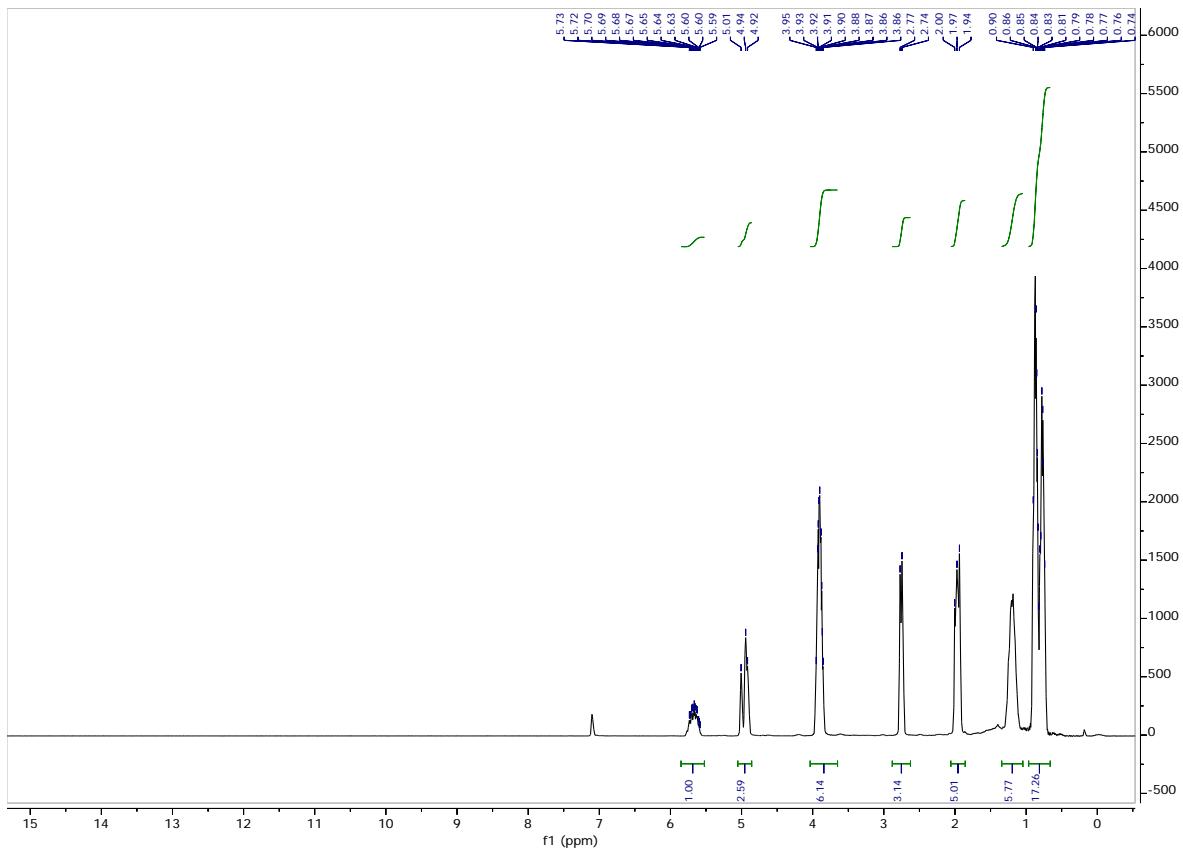
4-Chlorostyrene as substrate (22)

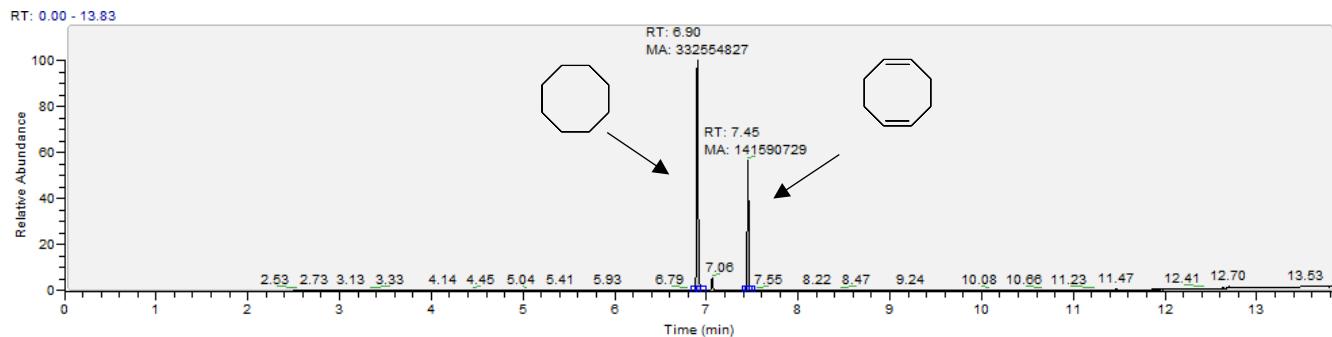


4-Vinylpyridine as substrate (24**)**



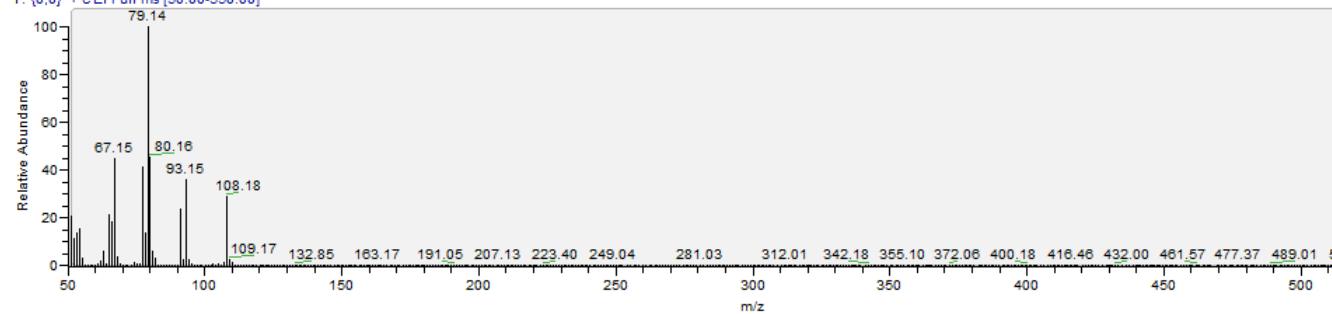
Diethyl 2,2-diallylmalonate as substrate (**25**)



1,5-Cyclooctadiene as substrate (**33**)

SW195_57 #1294 RT: 6.90 AV: 1 NL: 5.31E7

T: {0,0} + c El Full ms [50.00-550.00]



SW195_57 #1454 RT: 7.44 AV: 1 NL: 1.03E7

T: {0,0} + c El Full ms [50.00-550.00]

