Supporting Information

Cross-Coupling of Alkenyl and Aryl Carboxylate with Grignard Reagent via Fe Catalyzed C-O Bond Activation

Bi-Jie Li,[1] Li Xu,[1,2] Zhen-Hua Wu,[1] Bing-Tao Guan,[1] Bi-Qin Wang[2] and Zhang-Jie Shi*[1,3]

[1]Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Green Chemistry Center, Peking University, Beijing 100871, and [2] Department of Chemistry, Sichuan Normal University, Chengdu, Sichuan, 410061, and [3] State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Table of contents

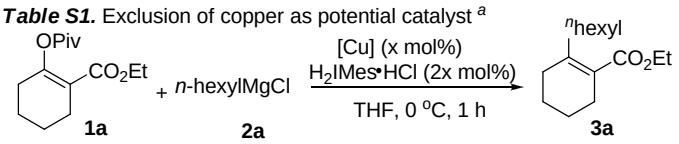
Table	Page
General	S2-3
Preparation and characterization of starting materials	S4-S7
Characterization of products	S7-S12
References	S13
NMR Spectrum of starting materials **1a-3l**	S14-S25
NMR Spectrum of products **3a-3w**	S26-S46

General. All the reactions were carried out under nitrogen atmosphere using standard Schlenk technique. $FeCl_2$ (98% purity) was purchased from Strem and *n*-hexylmagnesium chloride (2.0 M in THF) was purchased from Aldrich without further purification. THF was distilled over sodium using benzophenone as indicator. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) was registered on Bruker spectrometers and ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) was registered on Varian spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh. IR, GC, MS, and HRMS were performed by the State-authorized Analytical Center in Peking University.

General procedure for the cross coupling of alkenyl pivalate with Grignard reagent via Fe catalysis: To an oven dried Schlenk tube was added ethyl 2-(pivaloyloxy)cyclohex-1-enecarboxylate **1a** (127 mg, 0.50 mmol), carbene ligand (3.4 mg, 0.01 mmol, or LiCl (127 mg, 3.0 mmol)). The tube was evacuated and refilled with N_2, and this process was repeated for 3 times. Then 0.63 mL of a solution of $FeCl_2$ in THF (1 mg/1 mL) was added into the tube via syringe. The mixture was cooled down to 0 ℃ in an ice-water bath before 0.5 mL of *n*-hexylmagnesium chloride (2.0 M in THF) was added during 5-10 seconds. After being stirred at that temperature for an hour, the reaction was quenched by saturated aqueous NH_4Cl. 40 mL EtOAc was added and the organic layer was separated and dried over magnesium sulfate. After removal of the solvent, the residue was applied to flash column chromatography eluting with ethyl acetate and petroleum ether.

Exclusion of copper contaminant as potential catalyst or co-catalyst: in light of the recent event that copper contaminant in iron salt may play a role in catalyzing certain reactions,[1] we have carefully examined our system and performed the following control experiments. First, various copper(I) and copper(II) salts were tested to see whether they could catalyze the reaction. However, none of them showed any catalytic reactivity at either low or high catalyst loading (Table S1). Secondly, various copper(I) and copper(II) salts were added to the iron catalyzed reaction of 2-naphthyl pivalate, which has an incomplete conversion, to see whether copper could play the role as co-catalyst to promote the efficiency. Again, it turned out that copper salts inhibited the reaction to various extent rather than improving the yield. None of them could promote the efficiency (Table S2). Based on these control experiments, we concluded that copper contaminant did not function as catalyst or co-catalyst in the current catalytic system.

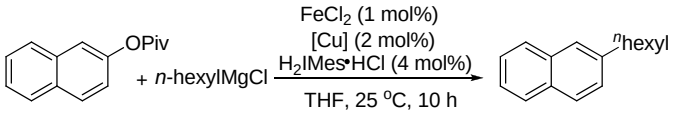
Table S1. Exclusion of copper as potential catalyst [a]



Entry	[Cu]	x	Yield(%)[b]
1	$Cu(acac)_2$	1.0	0
2	$CuCl_2$	1.0	0
3	CuF_2	1.0	0
4	$Cu(OTf)_2$	1.0	0
5	CuI	1.0	0
6	CuBr	1.0	0
7	CuCl	1.0	0
8	Cu_2O	1.0	0
9	$Cu(acac)_2$	10.0	0
10	$CuCl_2$	10.0	0
11	CuF_2	10.0	0
12	$Cu(OTf)_2$	10.0	0
13	CuI	10.0	0
14	CuBr	10.0	0
15	CuCl	10.0	0
16	Cu_2O	10.0	0

[a] Reaction condition: 0.5 mmol of **1a**, 1.0 mmol of **2a**, x mol% of copper catalyst, 2x mol% of ligand. [b] Determined by GC.

Table S2. Exclusion of copper as potential co-catalyst [a]

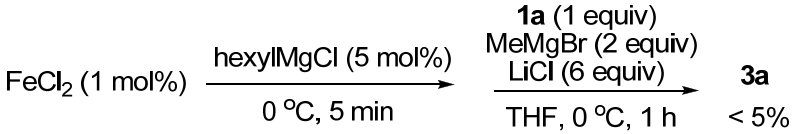


Entry	[Cu]	Yield(%)[b]
1	-	40
2	$CuCl_2$	14
3	CuF_2	<5
4	$Cu(OTf)_2$	26
5	CuI	<5
6	CuBr	<5
7	CuCl	17
8	Cu_2O	34
9	$Cu(acac)_2$	24

[a] Reaction condition: 0.5 mmol of **1k**, 1.0 mmol of **2a**, 1 mol% of $FeCl_2$, 2 mol% of copper salt, 4 mol% of ligand. [b] Determined by GC with tetradecane as internal standard.

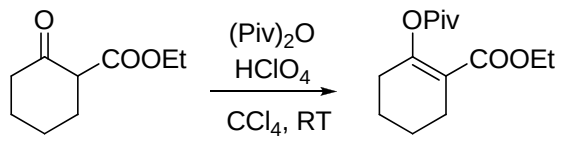
Attempts to cross couple methyl Grignard reagent with alkenyl carboxylate:

Since the reaction worked well for long-chain Grignard reagent but not MeMgBr, we performed the following reaction in an attempt to activate the catalyst by catalytic amount of hexylMgCl. However, no desired product was observed. The reason is unclear at present.



Preparation of alkenyl pivalate substrates:

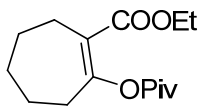
Typical procedure for the synthesis of ethyl 2-(pivaloyloxy)cyclohex-1-enecarboxylate (1a)



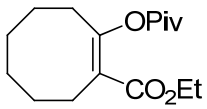
To a solution of 3.40 g (20 mmol) of ethyl 2-oxocyclohexanecarboxylate and 11.18 g (60 mmol) of trimethylacetic anhydride in 20 mL of carbon tetrachloride was added a drop of perchloric acid and the mixture was stirred for 3 h at room temperature. Dichloromethane (10mL) was added and the organic layer was washed with water, then saturated $NaHCO_3$ solution, and dried over Na_2SO_4. Removal of the solvent, followed by chromatographic purification (silica gel, petroleum ether/ethyl acetate= 100/1) afforded the product.

ethyl 2-(pivaloyloxy)cyclohex-1-enecarboxylate (1a)[2], 78%. **H NMR ($CDCl_3$, 200 MHz)**: δ 4.19-4.11 (q, 2 H, *J*=7.0 Hz), 2.41-2.37 (m, 2 H), 2.22-2.18 (m, 2 H), 1.73-1.63 (m, 4 H), 1.29-1.21 (m, 12 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 157.78, 165.72, 154.74, 118.02, 60.14, 38.79, 28.59, 26.97, 25.28, 21.95, 21.67, 14.22. **IR** (cm^{-1}): ν 2939, 1749, 1721, 1124. **MS** ($C_{14}H_{22}O_4$): 254 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 277.14158, Found: 277.14103.

.

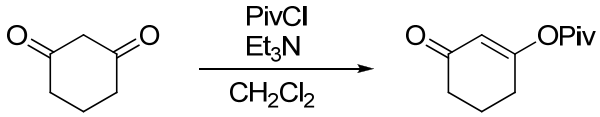


Ethyl 2-oxocycloheptanecarboxylate (1b): follow the procedure for **1a**, 61%. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 4.19-4.11 (q, 2 H, *J*=6.8 Hz), 2.44-2.39 (m, 2 H), 2.34-2.29 (m, 2 H), 1.71-1.57 (m, 6 H), 1.30-1.11 (m, 12 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 176.16, 167.03, 158.40, 122.85, 60.43, 38.66, 34.94, 31.37, 27.76, 26.92, 26.00, 24.20, 14.22. **IR** (cm^{-1}): ν 2927, 1745, 1719, 1127. **MS** ($C_{15}H_{24}O_4$): 268 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 291.15723, Found: 291.15668



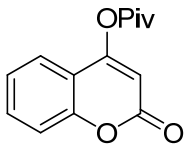
Ethyl 2-oxocyclooctanecarboxylate (**1c**): follow the procedure for **1a**, 77%. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 4.19-4.11 (q, 2 H, *J*=6.8 Hz), 2.44-2.39 (m, 2 H), 2.34-2.29 (m, 2 H), 1.71-1.57 (m, 6 H), 1.22 (s, 9 H). 1.17 (t, 3 H, *J* = 2.4 Hz). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 175.98, 166.09, 156.39, 119.91, 60.08, 38.76, 32.18, 29.84, 28.07, 27.43, 26.94, 26.61, 25.43, 14.19. **IR** (cm^{-1}): ν 2929, 1749, 1718, 1119. **MS** ($C_{16}H_{26}O_4$): 282 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 305.17288, Found: 305.17233.

Typical procedure for the synthesis of 3-oxocyclohex-1-enyl pivalate (1e)[3]

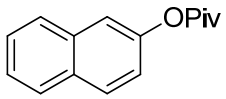


To a solution of 1,3-cyclohexadione (20 mmol) and NEt_3 (40 mmol) in 30 mL CH_2Cl_2 was added PivCl (30 mmol) at 0 ℃. Then the reaction was stirred at room temperature for an additional 3 h. the organic layer was washed with water, saturated NH_4Cl and dried. Removal of the solvent, followed by chromatographic purification (silica gel, petroleum ether/ethyl acetate= 20/1) afforded the product.

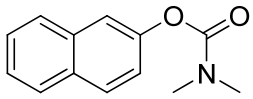
.**3-oxocyclohex-1-enyl pivalate (1e),** 89%. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 5.68 (s, 1 H), 2.37-2.33 (m, 2 H), 2.26-2.20 (m, 2 H), 1.93-1.87 (m, 2 H), 1.08 (s, 9 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 198.85, 174.67, 170.01, 116.96, 38.87, 36.30, 27.78, 26.43, 20.84. **IR** (cm^{-1}): ν 2975, 1753, 1679, 1121, 1094. **MS** ($C_{11}H_{16}O_3$): 196 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 219.09971, Found: 219.09917.



2-oxo-2H-chromen-4-yl pivalate (1d): starting from 4-hydroxycoumarin, follow the procedure for **1e**, 70%. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 7.63-7.55 (m, 2 H), 7.40-7.30 (m, 2 H), 6.48(s, 1 H), 1.48 (s, 9 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 174.16, 161.37, 158.71, 153.49, 132.61, 124.26, 122.43, 116.93, 115.63, 104.78, 39.95, 26.90. **IR** (cm^{-1}): ν 2975, 1770, 1728, 1377, 1088. **MS** ($C_{14}H_{14}O_4$): 246 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 269.07898, Found: 269.07843

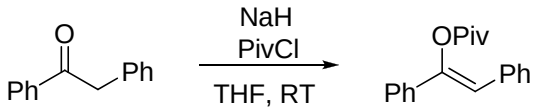


2-naphthyl pivalate (**1k):** starting from 2-naphthol, follow the procedure for **1e**, 96%. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 7.83 (t, 3 H, *J* = 8.8 Hz), 7.53-7.45 (m, 3 H), 7.23-7.18 (m, 1 H), 1.39 (s, 9 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 177.15, 148.74, 133.76, 131.33, 129.23, 127.69, 127.50, 126.42, 125.48, 121.10, 118.32, 39.07, 27.12. **IR** (cm^{-1}): ν 2972, 1747, 1479, 1464, 1131. **MS** ($C_{15}H_{16}O_2$): 228 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 251.10480, Found: 251.10425



naphthalen-2-yl dimethylcarbamate (**1l**): starting from 2-naphthol, follow the literature procedure, [4] recrystallized from EtOAc/hexane, 80%. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 7.88-7.80 (m, 3 H), 7.62 (d, 1 H, *J* = 2.2 Hz), 7.53-7.44 (m, 2 H), 7.34, (d, 1 H, *J* = 2.2 Hz), 7.29 (d, 1 H, *J* = 2.6 Hz), 3.14 (s, 3 H), 3.05(s, 3 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: 175.53, 175.14, 136.68, 134.29, 129.00, 128.67, 128.35, 127.27, 127.17, 126.15, 115.04, 111.79, 38.76, 27.13, 26.96. **IR** (cm^{-1}): ν 2970, 1718, 1388, 1379. 1210. **MS** ($C_{13}H_{13}NO_2$): 215 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 238.08440, Found: 238.08385.

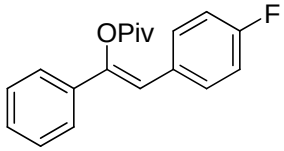
Typical procedure for the synthesis of (Z)-1,2-diphenylvinyl pivalate (1f)[5]



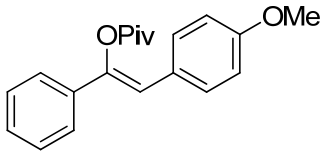
A mineral oil suspension of NaH (70%, 1.03 g, 30 mmol) was placed in a dry 100-ml flask under N_2, and THF (30 ml) was added into the flask. To this suspension, deoxybenzoin (3.92g, 20 mmol) in THF (15 mL) was added dropwise. The resulting mixture was stirred at room temperature for 2

h. Pivaloyl chloride (6.0 g, 50 mmol) in 10 mL THF was added, and the resulting solution was stirred for an additional 3 h before quenching with water (10 mL). The aqueous layer was extracted with ethyl acetate, and the combined organic layer were washed with 5% HCl, water, and brine before being dried over anhydrous $MgSO_4$. After removal of solvent, the residue was recrystallized from ethyl acetate and petroleum ether.

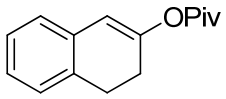
(Z)-1,2-diphenylvinyl pivalate (1f): 89%. The product was obtained as a single isomer based on ^{1}H NMR, ^{13}C NMR and GC analysis. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 7.53-7.25 (m, 10 H), 6.69 (s, 1 H), 1.32 (s, 9 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 175.73, 146.95, 136.12, 134.31, 128.76, 128.54, 128.46, 128.20, 127.42, 124.82, 117.13, 39.04, 27.21. **IR** (cm^{-1}): ν 2976, 1742, 1447, 1107. **MS** ($C_{19}H_{20}O_2$): 280 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 313.13610, Found: 313.13555.



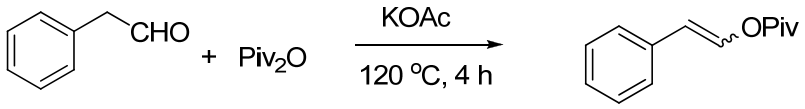
(Z)-2-(4-fluorophenyl)-1-phenylvinyl pivalate (**1g**): follow the procedure for **1f**, 80%. The product was obtained as a single isomer based on ^{1}H NMR, ^{13}C NMR and GC analysis. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 7.56-7.49 (m, 4 H), 7.41-7.30 (m, 3 H), 7.13-7.05 (m, 2 H), 6.64(s, 1 H), 1.37 (s, 9 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 175.73, (165.25, 160.31, J_0 = 247 Hz), 146.06, 134.13, (132.45, 132.38, J_3 = 3.5 Hz), 128.71, 128.24, 127.51, (126.80, 126.64, J_2 = 8 Hz), 117.08, (115.77, 115.34, J_1 = 22 Hz), 39.04, 27.15. **IR** (cm^{-1}): ν 2973, 1743, 1510, 1107. **MS** ($C_{19}H_{19}FO_2$): 298 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 321.12668, Found: 321.12613.



(Z)-2-(4-methoxyphenyl)-1-phenylvinyl pivalate (**1h**): follow the procedure for **1f**, 70%. The product was obtained as a single isomer based on ^{1}H NMR, ^{13}C NMR and GC analysis. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 7.39-7.34 (m, 4 H), 7.27-7.16 (m, 3 H), 6.84-6.78 (m, 2 H), 6.49(s, 1 H), 1.27 (s, 9 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 175.77, 159.87, 146.79, 134.55, 128.64, 128.17, 127.15, 126.23, 115.48, 114.00, 55.24, 39.07, 27.23. **IR** (cm^{-1}): ν 2973, 1748, 1608, 1503, 1105. **MS** ($C_{20}H_{22}O_3$): 310 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 333.14666, Found: 333.14612.

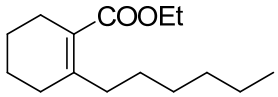


3,4-dihydronaphthalen-2-yl pivalate (**1j**): starting from 2-tetralone, follow the procedure for **1f**, 96%. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 7.19-7.12 (m, 3 H), 7.05-7.01 (m, 3 H), 6.23 (s, 1 H), 3.02 (t, 2 H, J = 8.2 Hz), 2.51 (t, 2 H, J = 8.2 Hz), 1.33 (s, 9 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 176.59, 151.16, 133.21, 133.10, 127.10, 126.59, 126.46, 126.01, 114.32, 38.87, 28.49, 27.01, 26.15. **IR** (cm^{-1}): ν 2974, 1743, 1480, 1278, 1118. **MS** ($C_{15}H_{18}O_2$): 230 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 253.12045, Found: 253.11990.

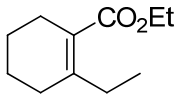


A mixture of phenylacetaldehyde (10 mmol), pivalic anhydride (20 mmol) and KOAc (2 mmol) was stirred at 120 ℃ for 4 h. After cooled to room temperature, the mixture was diluted with 50 mL EtOAc. The organic layer was washed twice with saturated Na_2CO_3, water and dried. Evaporation of the solvent followed by purification by flash chromatography afforded the product. **Styryl pivalate** (**1i**): 40%. The product was obtained as a *E*/*Z* = 2/1 mixure as deduced from ^{1}H NMR. **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 7.77 (d, 1 H, *J* = 12.8 Hz), 7.51 (d, 1 H, *J* = 7.4 Hz), 7.28-7.14 (m, 7 H), 6.34 (d, 0.85 H, *J* = 12.8 Hz, *E* isomer), 5.64 (d, 0.39 H, *J* = 7.4 Hz, *Z* isomer), 1.26 (s, 4.8 H) , 1.21 (s, 9 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 175.53, 175.14, 136.68, 134.29, 129.00, 128.67, 128.35, 127.27, 127.17, 126.15, 115.04, 111.79, 38.76, 27.13, 26.96. **IR** (cm^{-1}): ν 2920, 1740, 1211. **MS** ($C_{13}H_{16}O_2$): 204 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 227.10480, Found: 227.10425.

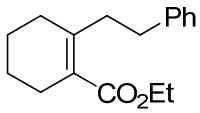
Characterization of products



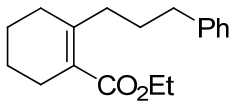
ethyl 2-hexylcyclohex-1-enecarboxylate (3a). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.175 (q, 2 H, *J* = 7.2 Hz), 2.323-2.266 (m, 4 H), 2.129-2.113 (m, 2 H). 1.602-1.586 (m, 4 H), 1.446-1.409 (m, 2 H), 1.308-1.271 (m, 9 H), 0.881 (t, 3 H, *J* = 7.2 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 169.22, 148.79, 124.33, 59.74, 35.44, 31.71, 31.08, 29.54, 28.62, 26.47, 22.56, 22.31, 22.30, 14.22, 14.00. **MS** ($C_{15}H_{26}O_2$): 238 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 239.20111, Found: 239.20020. **IR** (cm^{-1}): ν 2927, 2857, 1711, 1224.



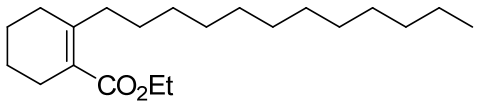
ethyl 2-ethylcyclohex-1-enecarboxylate(3d). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.174 (q, 2 H, *J* = 7.4 Hz), 2.346-2.291 (m, 2 H), 2.259-2.241 (m, 2 H), 2.117-2.111 (m, 2 H), 1.611-1.579 (m, 4 H), 1.303-1.248 (m, 3 H), 1.039 (t, 3 H, *J* = 7.6 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 169.24, 150.12, 124.06, 59.83, 30.48, 29.67, 28.47, 26.43, 22.33, 14.25, 13.03. **MS** ($C_{11}H_{18}O_2$): 182 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 205.12045, Found: 205.11934. **IR** (cm^{-1}): ν 2919, 2845, 1712, 1226.



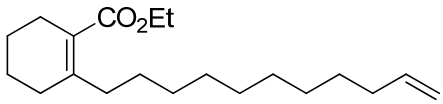
ethyl 2-phenethylcyclohex-1-enecarboxylate(3e)[6]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.288-7.151 (m, 5 H), 4.173 (q, 2 H, *J* = 7.4 Hz), 2.773-2.732 (m, 2 H), 2.644-2.604 (m, 2 H), 2.289 (s, 2 H), 2.127-2.118 (m, 2 H), 1.607-1.575 (m, 4 H), 1.271 (t, 3 H, *J* = 6.4 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 169.81, 148.30, 142.18, 128.35, 128.21, 128.19, 125.71, 125.12, 59.86, 37.63, 35.03, 31.57, 26.47, 22.26, 14.29. **MS** ($C_{17}H_{22}O_2$): 258 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 259.16980, Found: 259.16899. **IR** (cm^{-1}): ν 2934, 2842, 1710, 1226.



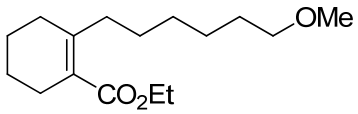
ethyl 2-(3-phenylpropyl)cyclohex-1-enecarboxylate(3f). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.269-7.217 (m, 2 H), 7.178-7.130 (m, 3 H), 4.137 (q, 2 H, *J* = 7.2 Hz), 2.626 (t, 2 H, *J* = 6.8 Hz), 2.378 (t, 2 H, *J* = 7.6 Hz), 2.266 (s, 2 H), 2.092 (s, 2 H), 1.804-1.635 (m, 2 H), 1.579-1.564 (m, 4 H), 1.255 (t, 3 H, *J* = 6.4 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 169.01, 148.17, 142.32, 128.25, 128.10, 125.53, 124.75, 59.72, 36.02, 35.13, 30.99, 30.30, 26.42, 22.23, 22.20, 14.19. **MS** ($C_{18}H_{24}O_2$): 272 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 273.18546, Found: 273.18458. **IR** (cm^{-1}): ν 2934, 2845, 1707, 1225.



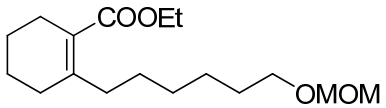
ethyl 2-dodecylcyclohex-1-enecarboxylate(3g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.168 (q, 2 H, *J* = 6.8 Hz), 2.2937 (q, 4 H, *J* = 7.6 Hz), 2.109 (s, 2 H), 1.589 (t, 2 H, *J* = 3.2 Hz), 1.439-1.405 (m, 2 H), 1.300-1.258 (m, 23H), 0.8771 (t, 3 H, *J* = 6.8 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 169.13, 148.86, 124.30, 59.71, 35.46, 31.87, 31.12, 29.89, 29.63, 29.62, 29.60, 29.58, 29.52, 29.31, 28.68, 26.46, 22.63, 22.32, 22.31, 14.22, 14.02. **MS** ($C_{21}H_{38}O_2$): 322 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 323.29501, Found: 323.29424. **IR** (cm^{-1}): ν 2923, 2853, 1713, 1225.



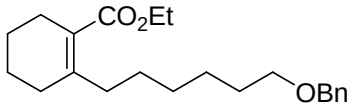
ethyl 2-(undec-10-enyl)cyclohex-1-enecarboxylate(3h). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.852-5.750 (m, 1 H), 5.010-4.9031 (m, 2 H), 4.170 (q, 2 H, *J* = 7.2 Hz), 2.321-2.265 (m, 4 H), 2.115-2.109 (m, 2 H), 2.060-2.007 (m, 2 H), 1.619-1.556 (m, 4 H), 1.427-1.303 (m, 3 H), 1.285-1.268 (m, 14 H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 169.12, 148.80, 139.06, 124.31, 113.99, 59.70, 35.43, 33.73, 31.09, 29.85, 29.47, 29.41, 29.06, 28.86, 28.64, 26.44, 22.30, 22.29, 14.22. **MS** ($C_{20}H_{34}O_2$): 306 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 307.26371, Found: 307.26286. **IR** (cm^{-1}): ν 2925, 2853, 1711, 1225.



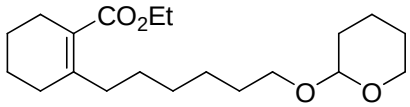
ethyl 2-(6-methoxyhexyl)cyclohex-1-enecarboxylate(3i). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.171 (q, 2 H, *J* = 7.4 Hz), 3.360 (t, 2 H, *J* = 5.8 Hz), 3.324 (s, 3 H), 2.328-2.264 (m, 4 H), 2.110 (d, 2 H, *J* = 2.7 Hz), 1.599-1.575 (m, 6 H), 1.457-1.443 (m, 2 H), 1.347-1.321 (m, 4 H), 1.306-1.269 (m, 3 H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 169.13, 148.70, 124.37, 72.78, 59.72, 58.39, 35.31, 31.05, 29.63, 29.49, 28.53, 26.42, 25.94, 22.27, 22.25, 14.20. **MS** ($C_{16}H_{28}O_3$): 268 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 291.19361, Found: 291.19281. **IR** (cm^{-1}): ν 2930, 2849, 1710, 1226.



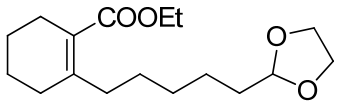
ethyl 2-(6-(methoxymethoxy)hexyl)cyclohex-1-enecarboxylate(3j). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.566 (s, 2 H), 4.124 (t, 2 H, *J* = 6.4 Hz), 3.468 (t, 2 H, *J* = 6.6 Hz), 3.309 (s, 3 H), 2.284-2.217 (m, 4 H), 2.067-2.061 (m, 2 H), 1.562-1.531 (m, 6 H), 1.337-1.287 (m, 5 H), 1.259-1.223 (m, 4 H). **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 169.10, 148.64, 124.40, 96.26, 67.69, 59.71, 54.93, 35.30, 31.05, 29.58, 28.53, 26.42, 26.02, 22.26, 22.25, 14.21. **MS** ($C_{17}H_{30}O_4$): 298 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 321.20418, Found: 321.20317. **IR** (cm^{-1}): ν 2938, 2853, 1707, 1225.



ethyl 2-(6-(benzyloxy)hexyl)cyclohex-1-enecarboxylate(3k). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.361-7.349 (m, 4 H), 7.305-7.283 (m, 1 H), 4.517 (s, 2 H), 4.189 (q, 2 H, *J* = 7.2 Hz), 3.485 (t, 2 H, *J* = 6.8 Hz), 2.356-2.293 (m, 4 H), 2.132-2.126 (m, 2 H), 1.665-1.596 (m, 6 H), 1.491-1.247 (m, 6 H), 1.236-1.211 (m, 3 H). **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 169.04, 148.69, 138.58, 128.17, 127.43, 127.29, 124.33, 72.69, 70.32, 59.67, 35.29, 31.03, 29.60, 28.51, 26.40, 25.98, 22.24, 22.22, 14.19. **MS** ($C_{22}H_{32}O_3$): 344 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 367.22491, Found: 367.22405. **IR** (cm^{-1}): ν 2930, 2856, 1709, 1226.

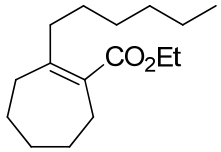


ethyl 2-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)cyclohex-1-enecarboxylate(3l). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.568 (d, 1 H, *J* = 4.0 Hz), 4.171 (q, 2 H, *J* = 7.2 Hz), 3.886-3.839 (m, 1 H), 3.756-3.698 (m, 1 H), 3.520-3.469 (m, 1 H), 3.406-3.348 (m, 1 H), 2.298 (q, 4 H, *J* = 7.6 Hz), 2.115 (s, 2 H), 1.847-1.800 (m, 1 H), 1.742-1.681 (m, 1 H), 1.599-1.518 (m, 10 H), 1.378-1.307 (m, 5 H), 1.307-1.271 (m, 4 H). **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 169.08, 148.65, 124.33, 98.66, 67.46, 62.13, 59.67, 35.29, 31.03, 30.64, 29.61, 29.58, 29.44, 28.53, 26.39, 26.04, 25.39, 22.24, 22.22, 14.18. **MS** ($C_{20}H_{34}O_4$): 338 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 361.23548, Found: 361.23429. **IR** (cm^{-1}): ν 2932, 2857, 1710, 1226.

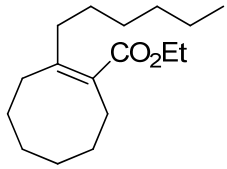


ethyl 2-(5-(1,3-dioxolan-2-yl)pentyl)cyclohex-1-enecarboxylate(3m). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.836 (t, 1 H, *J* = 4.8 Hz), 4.169 (q, 2 H, *J* = 7.1 Hz), 3.963-3.942 (m, 2 H), 3.857-3.835 (m, 2 H), 2.329-2.261 (m, 4 H), 2.111-2.104 (m, 2 H), 1.677-1.637 (m, 2 H), 1.604-1.574 (m, 4 H), 1.452-1.305 (m, 6 H), 1.287 (t, 3 H, *J* = 7.1 Hz). **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 169.09, 148.53, 124.39, 104.51, 64.69, 59.71, 35.23, 33.73, 31.03, 29.66, 28.47, 26.40, 23.87, 22.24, 22.22, 14.19. **MS** ($C_{17}H_{28}O_4$): 296 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 319.18853, Found: 319.18766.

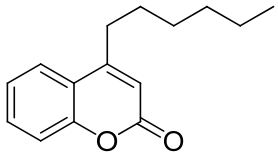
IR (cm^{-1}): ν 2930, 2858, 1708, 1226.



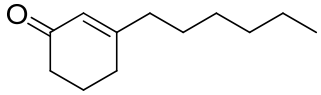
ethyl 2-hexylcyclohept-1-enecarboxylate(3n). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.169 (q, 2 H, *J* = 7.2 Hz), 2.412 (t, 2 H, *J* = 5.2 Hz), 2.284 (q, 4 H, *J* = 8.0 Hz), 1.766-1.737 (m, 2 H), 1.534-1.417 (m, 6 H), 1.306-1.258 (m, 9 H), 0.882 (t, 3 H, *J* = 6.5 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 170.29, 153.66, 130.52, 59.85, 36.99, 35.29, 32.39, 31.71, 30.14, 29.44, 27.88, 26.61, 25.71, 22.54, 14.22, 13.98. **MS** ($C_{16}H_{28}O_2$): 252 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 253.21676, Found: 253.21598. **IR** (cm^{-1}): ν 2924, 2853, 1710, 1197.



(E)-ethyl 2-hexylcyclooct-1-enecarboxylate(3o). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.170 (q, 2 H, *J* = 7.2 Hz), 2.386 (t, 2 H, *J* = 6.8 Hz), 2.308-2.246 (m, 4 H), 1.540 (s, 4 H), 1.474 (d, 6 H, *J* = 2.7 Hz), 1.339-1.209 (m, 9 H), 0.885 (t, 3 H, *J* = 7.2 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 169.57, 151.43, 127.26, 59.67, 34.98, 32.55, 31.73, 29.83, 29.73, 29.02, 28.70, 28.37, 26.66, 26.25, 22.58, 14.23, 13.99. **MS** ($C_{17}H_{30}O_2$): 266 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 267.23241, Found: 267.23145. **IR** (cm^{-1}): ν 2925, 2855, 1710, 1197.

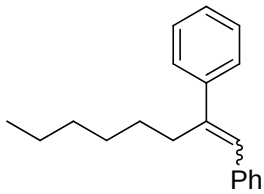


4-hexyl-2H-chromen-2-one(3p)[7]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.651-7.628 (m, 1 H), 7.541-7.499 (m, 1 H), 7.343-7.276 (m, 2 H), 6.280 (s, 1 H), 2.767 (t, 2 H, *J* = 7.6 Hz), 1.720-1.662 (m, 2 H), 1.482-1.411 (m, 2 H), 1.378-1.323 (m, 4 H), 0.917 (t, 3 H, *J* = 2.4 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 160.79, 156.17, 153.50, 131.37, 124.15, 123.98, 119.09, 117.02, 113.58, 31.51, 31.34, 28.91, 27.86, 22.35, 13.85. **MS** ($C_{15}H_{18}O_2$): (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 231.13850, Found: 231.13742. **IR** (cm^{-1}): ν 2934, 2845, 1716, 1177.

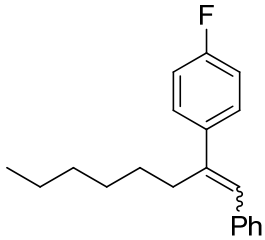


3-hexylcyclohex-2-enone(3q)[8]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.871 (s, 1 H), 2.357 (t, 2 H, *J* = 6.4 Hz), 2.283 (t, 2 H, *J* = 6.0 Hz), 2.205 (m, 2 H), 2.015-1.951 (m, 2 H), 1.513-1.476 (m, 2 H), 1.308-1.253 (m, 6 H), 0.894 (t, 3 H, *J* = 2.6 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 199.91, 166.70, 125.61, 38.04, 37.33, 31.54, 29.64, 28.88, 26.86, 22.71, 22.48, 13.98. **MS** ($C_{12}H_{20}O$): 180 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 181.15924, Found: 181.15859. **IR** (cm^{-1}): ν 2926, 1672, 1456,

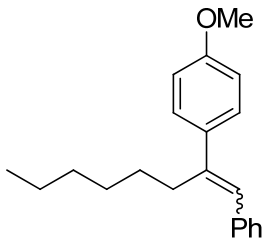
1191.



oct-1-ene-1,2-diyldibenzene (*Z:E*=2:1) (3r), the major isomer was determined by comparison of NMR with literature report.[9] **^{1}H NMR (CDCl$_3$, 400 MHz)**: δ 7.456-7.452 (m, 2 H), 7.434-7.147 (m, 8 H), 7.051-7.009 (m, 1 H), 6.915-6.895 (m, 1 H), 6.685 (s, 1 H), 6.418 (s, 1 H), 2.691 (t, 2 H, *J* = 7.8 Hz), 2.471 (t, 1 H, *J* = 7.3 Hz), 1.418-1.206 (m, 12 H), 0.864-0.812 (m, 4 H). **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 143.53, 143.38, 143.13, 138.34, 128.95, 128.74， 128.73, 128.52, 128.42, 128.29, 128.19, 128.03, 127.75, 127.07, 126.75, 126.58, 126.44, 126.08, 125.99, 40.70, 31.68, 31.51, 30.17, 29.30, 28.86, 28.66, 27.87, 22.62, 22.57, 14.07, 14.01. **MS** ($C_{20}H_{24}$): 264 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 287.17757, Found: 287.17686. **IR** (cm^{-1}): ν 2927, 1652, 1457, 1074.

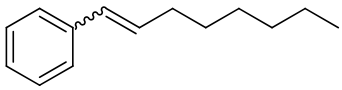


1-fluoro-4-(1-phenyloct-1-en-2-yl)benzene (3s), the ratio of isomer was determined by analogy of NMR with **3r** and **3t**. **^{1}H NMR (CDCl$_3$, 400 MHz)**: δ 7.482-7.376 (m, 5 H), 7.358-7.302 (m, 1 H), 7.357-7.025(m, 5 H), 6.700 (s, 0.8 H), 6.500 (s, 0.4 H), 2.728 (t, 2 H, *J* = 7.6 Hz), 2.522 (t, 2 H, *J* = 6.8 Hz), 1.465-1.259 (m, 10 H), 0.955-0.866 (m, 3 H). **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ (163.33, 160.88, J_0 = 245 Hz, trans), (163.00,160.56, J_0 = 244 Hz, cis), 142.36, (139.12, 139.09, J_3 = 3 Hz, cis), 138.15, 137.37, (137.15, 137.12, J_3 = 3 Hz, trans), (130.20, 130.12, J_2 = 8 Hz, trans), 128.96, 128.71, 128.23, (128.14, 128.06, J_2 = 8 Hz, cis), 127.85, 126.54, 126.14, (115.48, 115.27, J_1 = 21 Hz, cis), (115.20, 114.99, J_1 = 21 Hz, trans), 40.57, 31.66, 31.50, 30.27, 29.24, 28.81, 28.58, 27.82, 22.60, 22.56, 14.06, 14.00. **MS** ($C_{20}H_{23}F$): 282 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 305.16815, Found: 305.16737. **IR** (cm^{-1}): ν 2927, 2849, 1507, 1231.

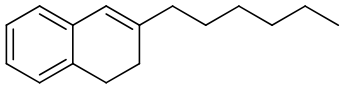


1-methoxy-4-(1-phenyloct-1-en-2-yl)benzene(3t), the minor isomer was determined by comparison of NMR with literature report.[10] **^{1}H NMR (CDCl$_3$, 400 MHz)**: δ 7.330-7.218 (m, 6 H), 7.168-7.129 (m, 1 H), 7.025-6.955 (m, 3 H), 6.878-6.810 (m,3 H), 6.753-6.732 (m, 1 H), 6.566 (s, 1 H), 6.315 (s, 0.5 H), 3.740 (s, 3 H), 3.712 (s, 2 H), 2.589 (t, 2 H, *J* = 7.7 Hz), 2.379 (t, 1 H, *J* =

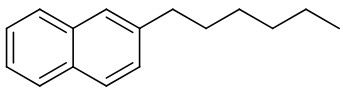
7.3 Hz), 1.350-1.145 (m, 13 H), 0.811-0.748 (m, 5 H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 158.89, 158.46, 143.10, 142.76, 138.55, 137.82, 135.49, 133.49, 129.67, 128.96, 128.74, 128.19, 127.79, 127.61, 126.74, 126.28, 125.88, 125.79, 113.85, 113.71, 55.27, 55.13, 40.73, 31.71, 31.56, 30.15, 29.36, 28.88, 28.77, 27.96, 22.64, 22.61, 14.10, 14.05. **MS** ($C_{21}H_{26}O$): 294 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 295.20619, Found: 295.20539. **IR** (cm^{-1}): ν 2927, 1606, 1510, 1245.



oct-1-enylbenzene (3u), a mixture of E:Z = 2:1 isomer, as deduced from ^{1}H NMR.[11] **^{1}H NMR ($CDCl_3$, 200 MHz)**: δ 7.35-7.10 (m, 7.5 H), 6.43-6.33 (m, 1.4 H), 6.24, 6.16 (dt, 1 H, *J* = 15.8, 6.4 Hz, *tran* isomer), 5.68, 5.62 (dt, 1 H, *J* = 11.8, 5.4 Hz, *cis* isomer), 2.31 (dt, 0.88 H, *J* = 7.0, 1.0 Hz, *cis* isomer), 2.19 (t, 2 H, *J* = 6.8 Hz, *tran* isomer), 1.44-1.26 (m, 14 H), 0.91-0.83 (m, 5 H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 137.96, 133.19, 131.15, 129.71, 128.72, 128.69, 128.41, 128.04, 126.69, 126.35, 125.88, 33.05, 31.76, 29.95, 29.36, 29.02, 28.91, 28.64, 22.63, 14.07, 14.04. **MS** ($C_{14}H_{20}$): 188 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 189.16433, Found: 189.16378. **IR** (cm^{-1}): ν 2924, 1494, 1468, 962.



3-hexyl-1,2-dihydronaphthalene (3v). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.26-7.07 (m, 4 H), 6.33 (s, 1 H), 2.91 (t, 2 H, *J* = 8.8 Hz), 2.39-2.27 (m, 4 H), 1.62-1.60 (m, 2 H), 1.52-1.44 (m, 6 H), 1.04 (m, 6 H), 0.878 (t, 3 H, *J* = 8.8 Hz). **^{13}C NMR ($CDCl_3$, 50 MHz)**: 142.35, 135.02, 134.36, 127.05, 126.32, 125.87, 125.23, 122.05, 37.46, 31.77, 29.04, 28.22, 27.52, 27.32, 22.62, 14.08. **MS** ($C_{16}H_{22}$): 214 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 215.17998, Found: 215.17943. **IR** (cm^{-1}): ν 2926, 2855, 1485, 1452.



2-hexylnaphthalene(3w)[12] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.776-7.716 (m, 3 H), 7.579 (s, 1 H), 7.427-7.355 (m, 2 H), 7.311-7.290 (d, 1 H, *J* = 8.4 Hz), 2.737 (t, 2 H, *J* = 7.5 Hz), 1.713-1.639 (m, 2 H), 1.386-1.296 (m, 6 H), 0.878 (t, 3 H, *J* = 6.8 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 140.43, 133.65, 131.93, 127.69, 127.57, 127.42, 127.38, 126.25, 125.76, 124.94, 36.12, 31.77, 31.34, 29.03, 22.62, 14.01. **MS** ($C_{16}H_{20}$): 212 (M^+). **IR** (cm^{-1}): ν 2927, 1600, 1508, 1269.

References:

1 Buchwald, S. L.; Bolm, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 5586.

2 Ohta, H.; Kobayashi, N.; Sugai, T. *Agric. Biol. Chem.* **1990**, *54*, 489.

3 Lin, S.-W.; Lin, Y.-L.; Lin, T.-C.; Yang, D.-Y. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1297.

4 Perjgssy, A.; Jones, R. G.; McClair, S. L. Wilkins, J. M. *J. Org. Chem.* **1983**, *48*, 1266.

5 Ruberu, S. R.; Fox, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 6310.

6 Schiess, P.; Suter, C. *Helv. Chim. Acta* **1971**, *54*, 2636.

7 Cao, H.; Xiao, W.-J. *Can. J. Chem.* **2005**, *83*, 826.

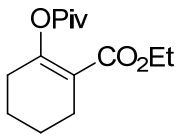
8 Kozikowski, A. P.; Jung, S. H. *J. Org. Chem.* **1986**, *51*, 3400.

9 McKinley, N. F.; O'Shea, D. F. *J. Org. Chem.* **2006**, *71*, 9552.

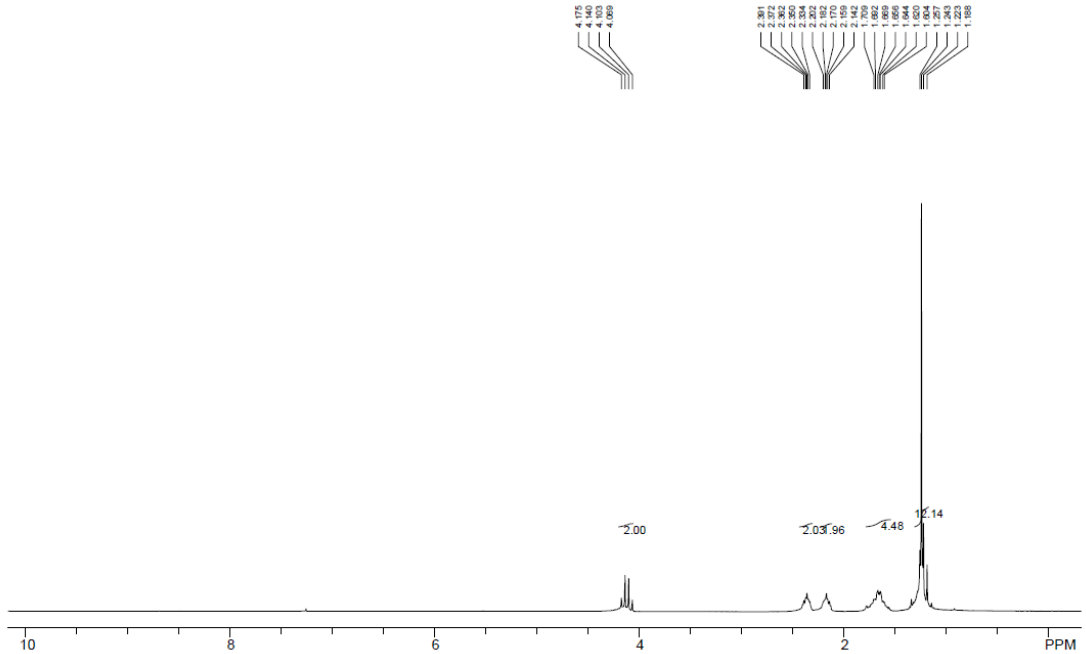
10 Yamanoi, S.; Seki, K.; Matsumoto, T.; Suzuki, K. *J. Organomet. Chem.* **2001**, *624*, 143.

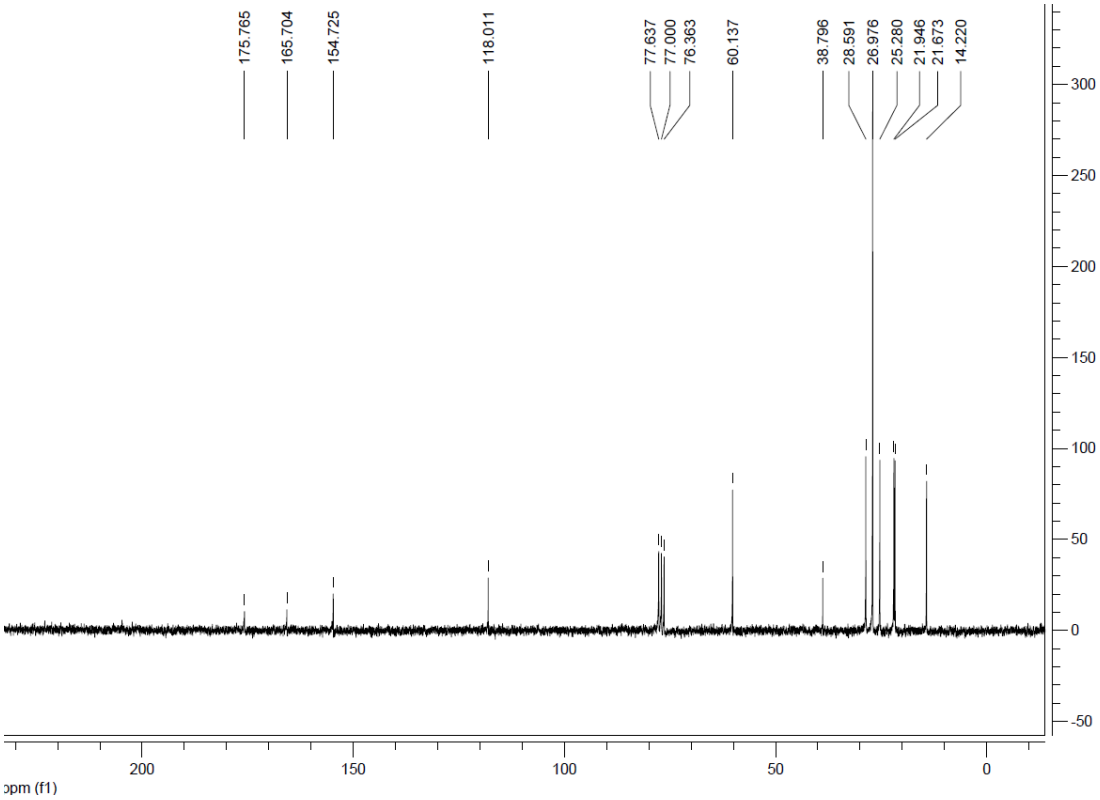
11 (a) Bellucci, G.; Chmppe, C.; Cordoni. A. *Tetrahedron: Asymmetry* **1996**, *7*, 197.
(b) Wang, Z.; Zhang, G.; Guzei, I.; Verkade, J, G. *J. Org. Chem.* **2001**, *66* 3521.

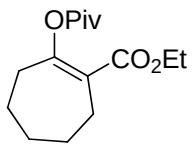
12 Akira, S.; Satoshi, S.; Kanji, S; Shigeo, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1626.



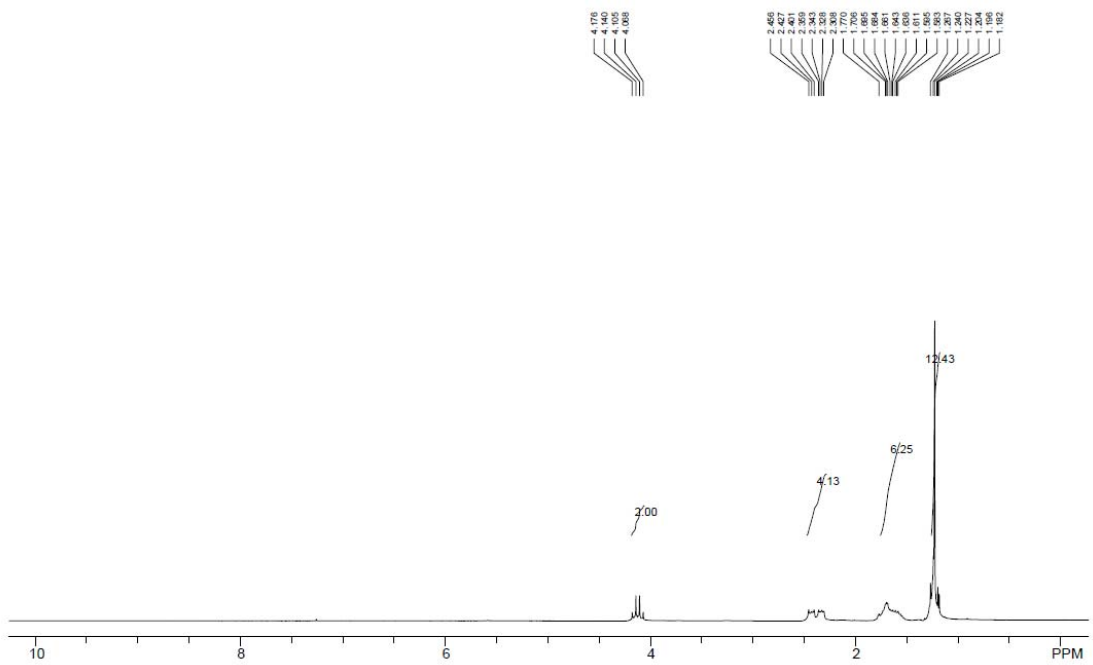
ethyl 2-(pivaloyloxy)cyclohex-1-enecarboxylate (1a)

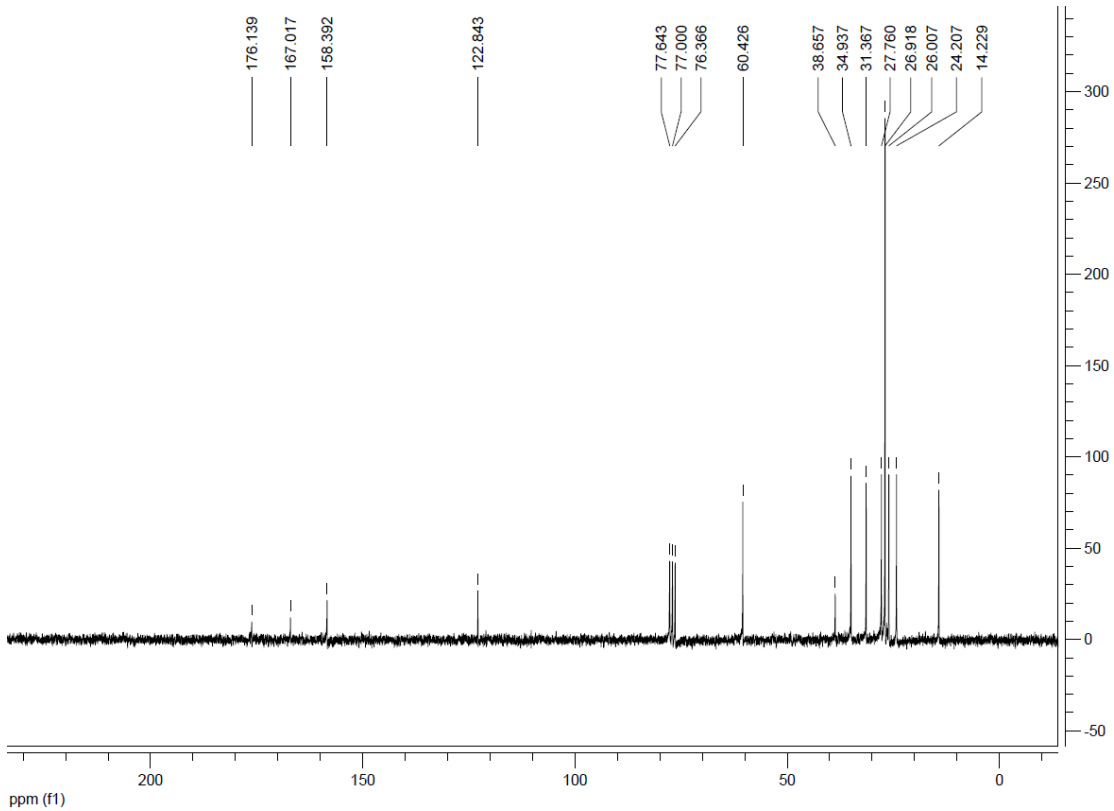


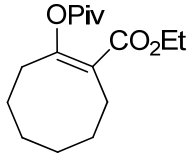




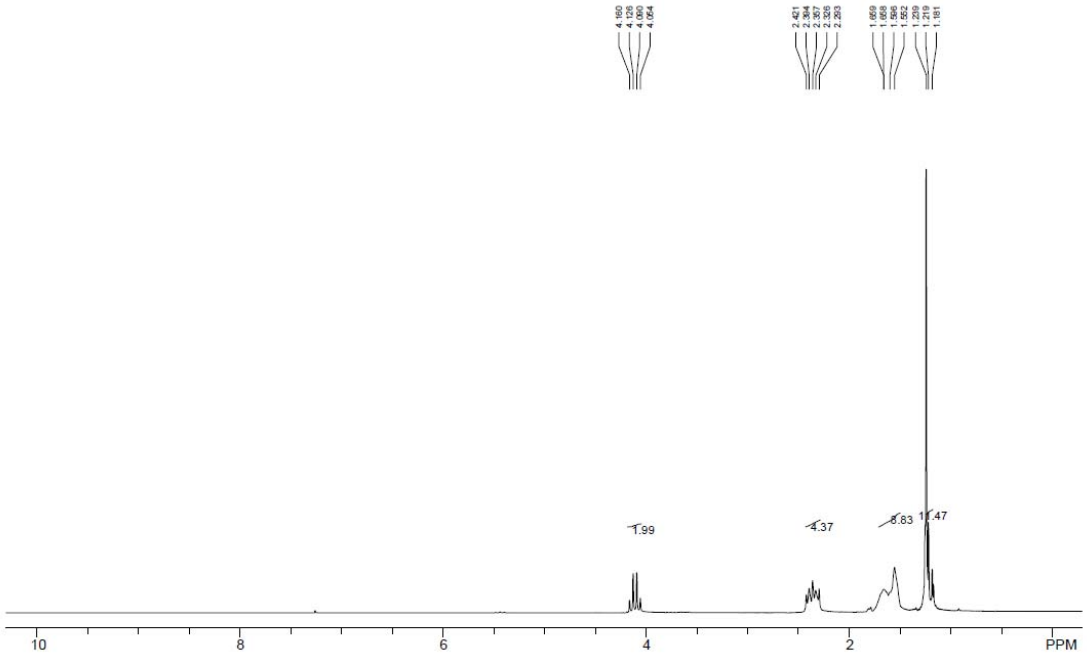
ethyl 2-(pivaloyloxy)cyclohept-1-enecarboxylate (1b)

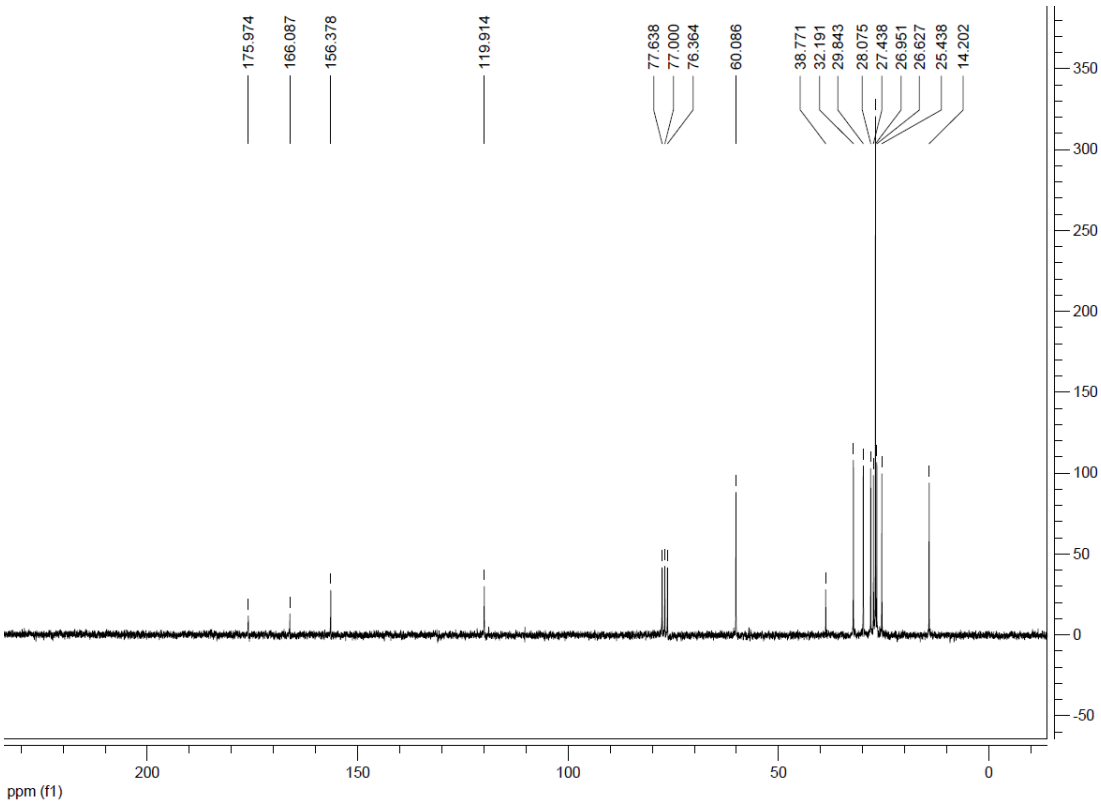


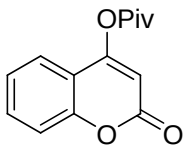




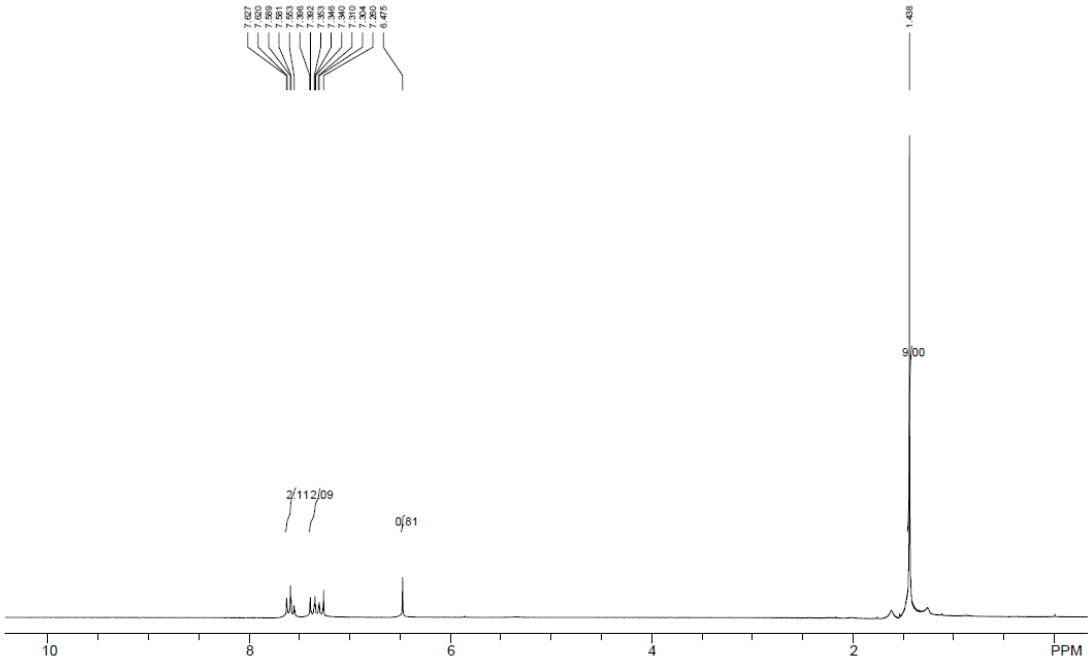
(Z)-ethyl 2-(pivaloyloxy)cyclooct-1-enecarboxylate (1c)

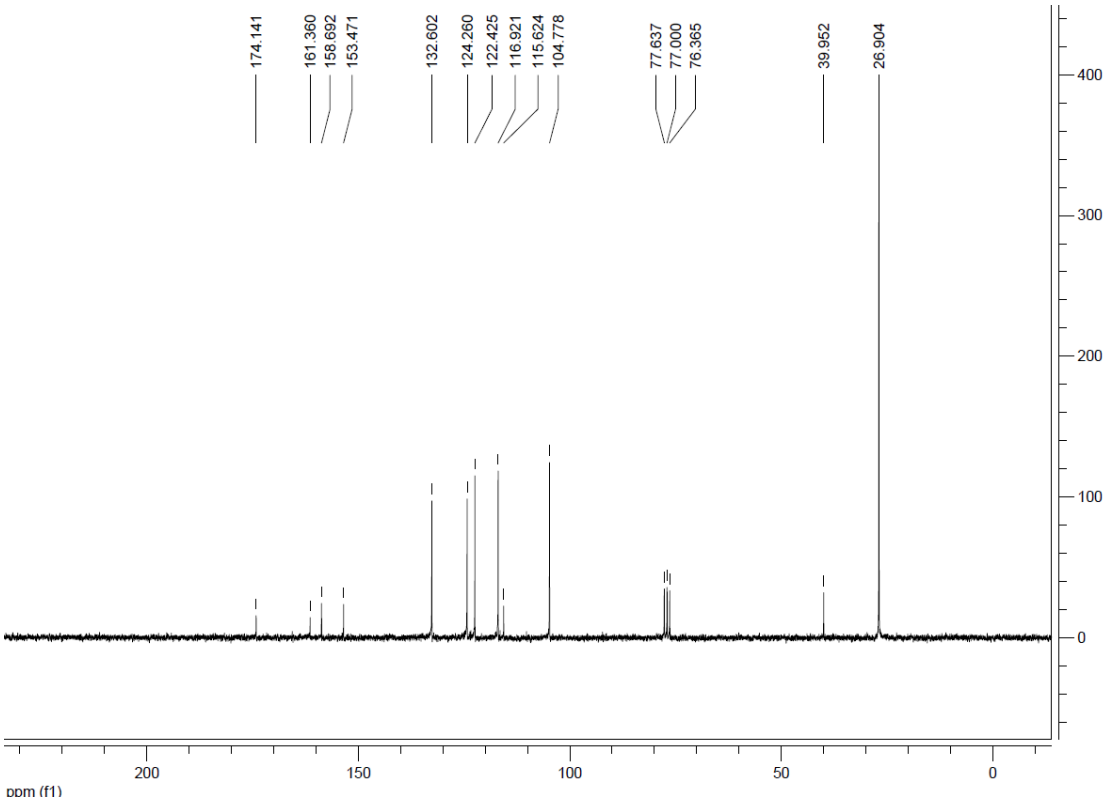


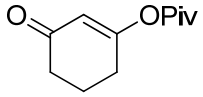




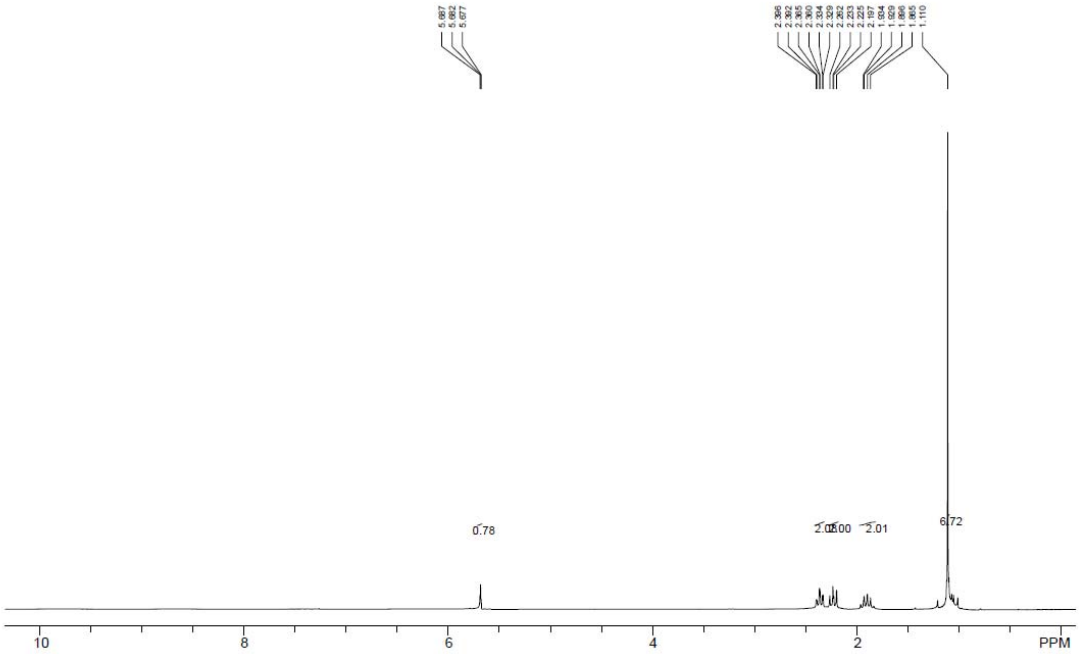
2-oxo-2H-chromen-4-yl pivalate (1d)

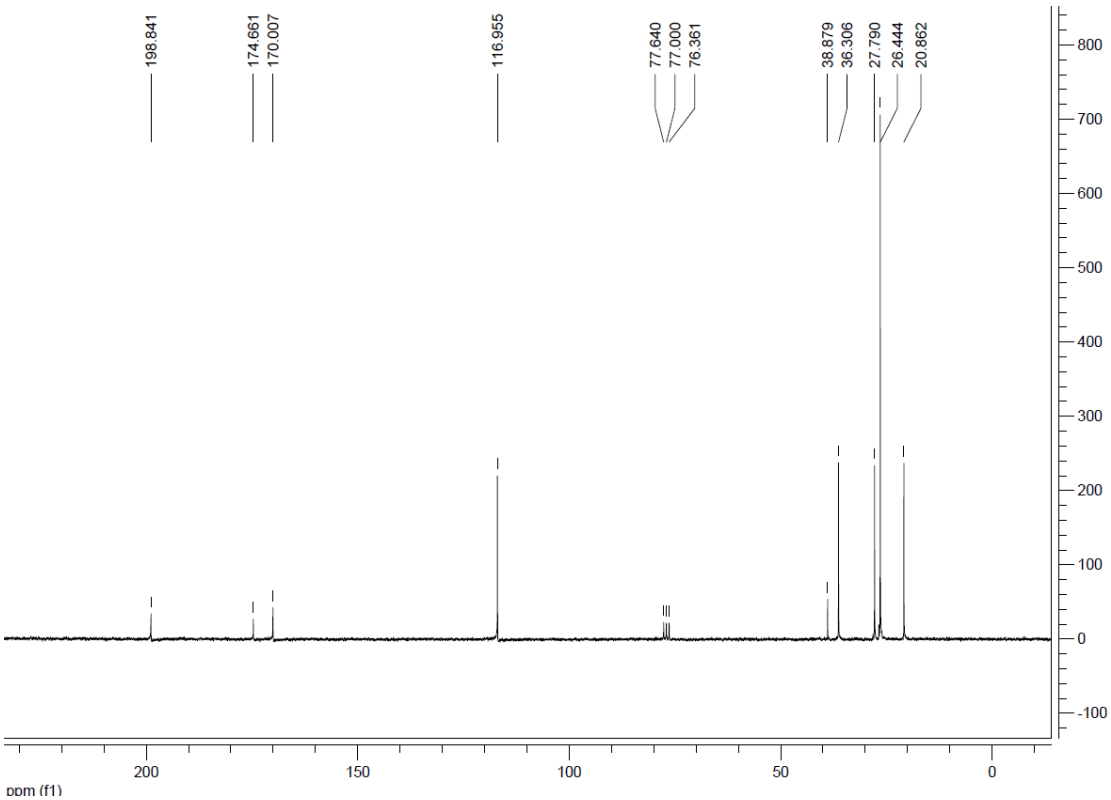


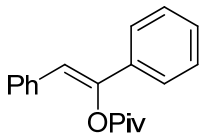




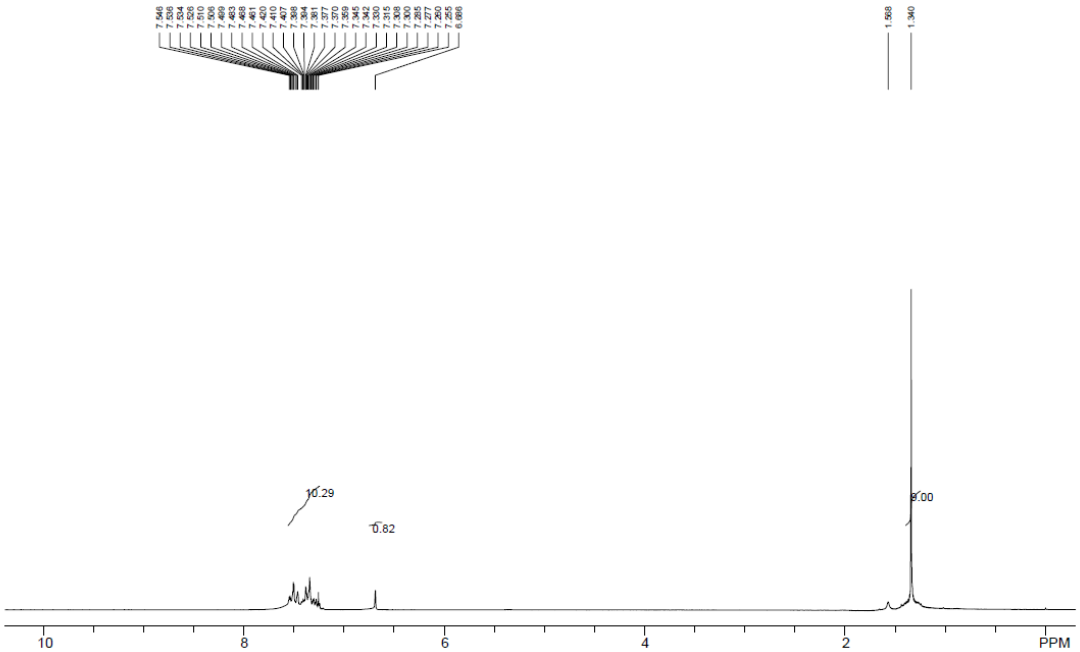
3-oxocyclohex-1-enyl pivalate (1e)

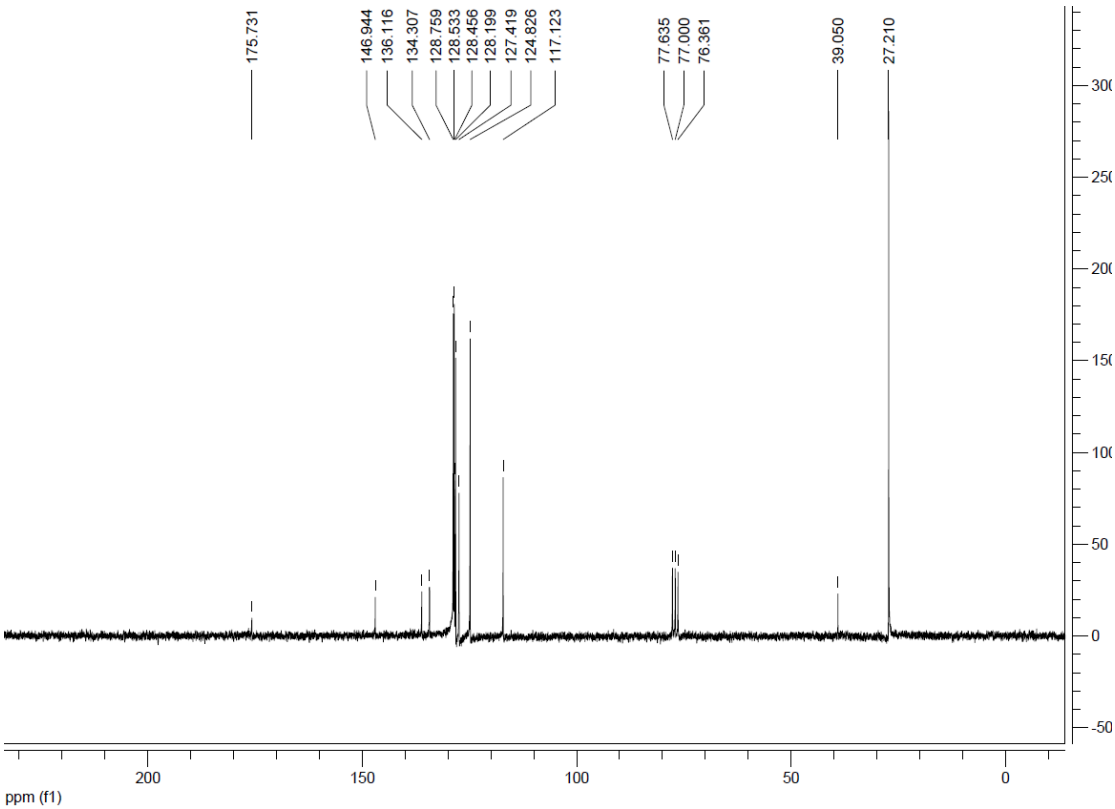


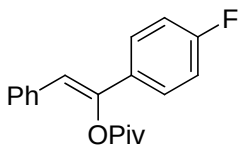




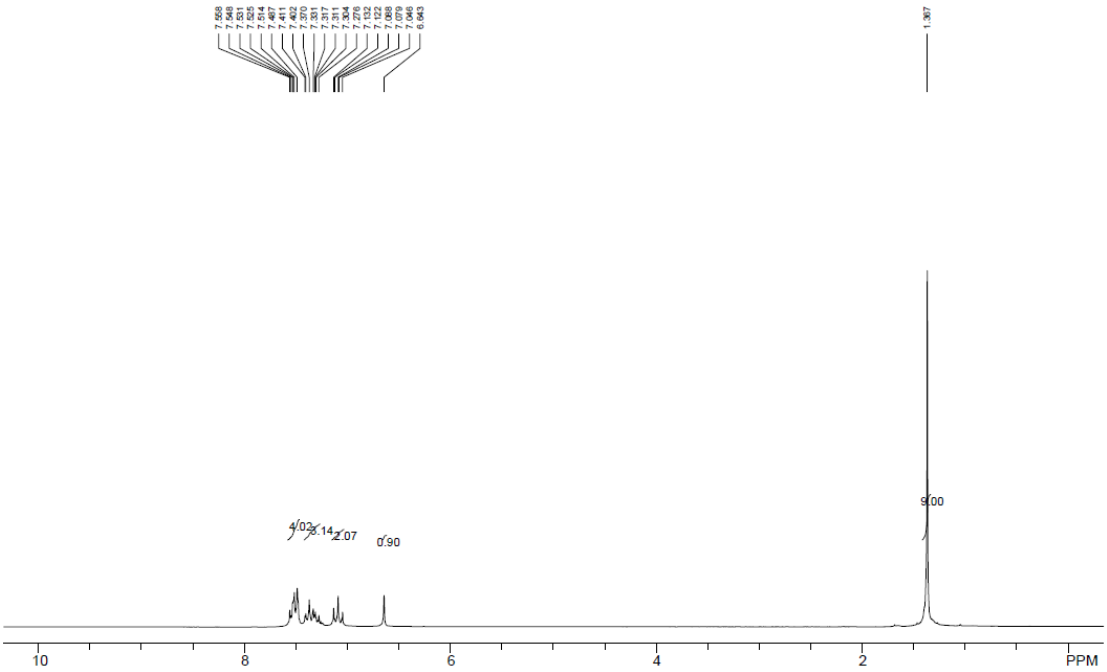
(Z)-1,2-diphenylvinyl pivalate (1f)

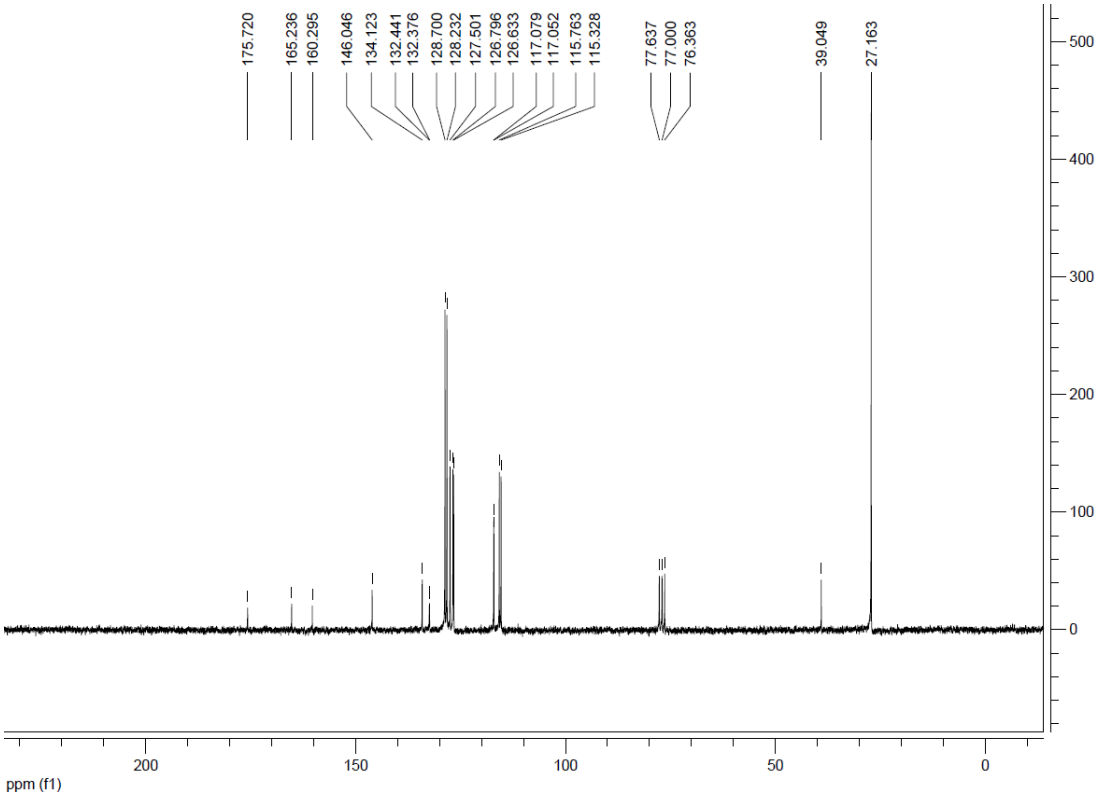


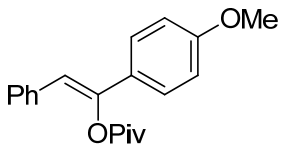




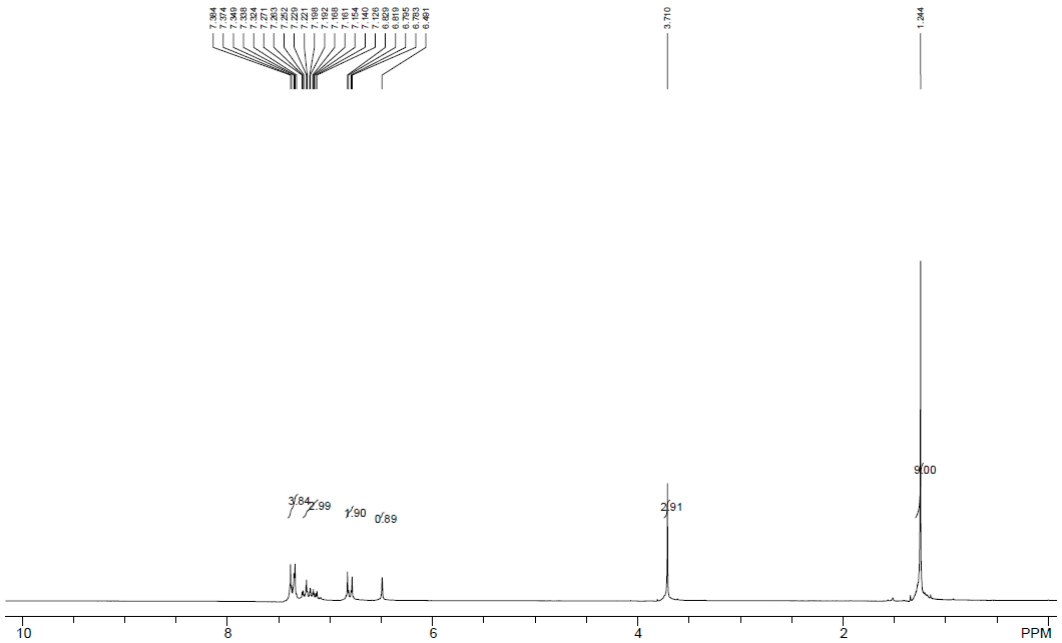
(Z)-1-(4-fluorophenyl)-2-phenylvinyl pivalate (1g)

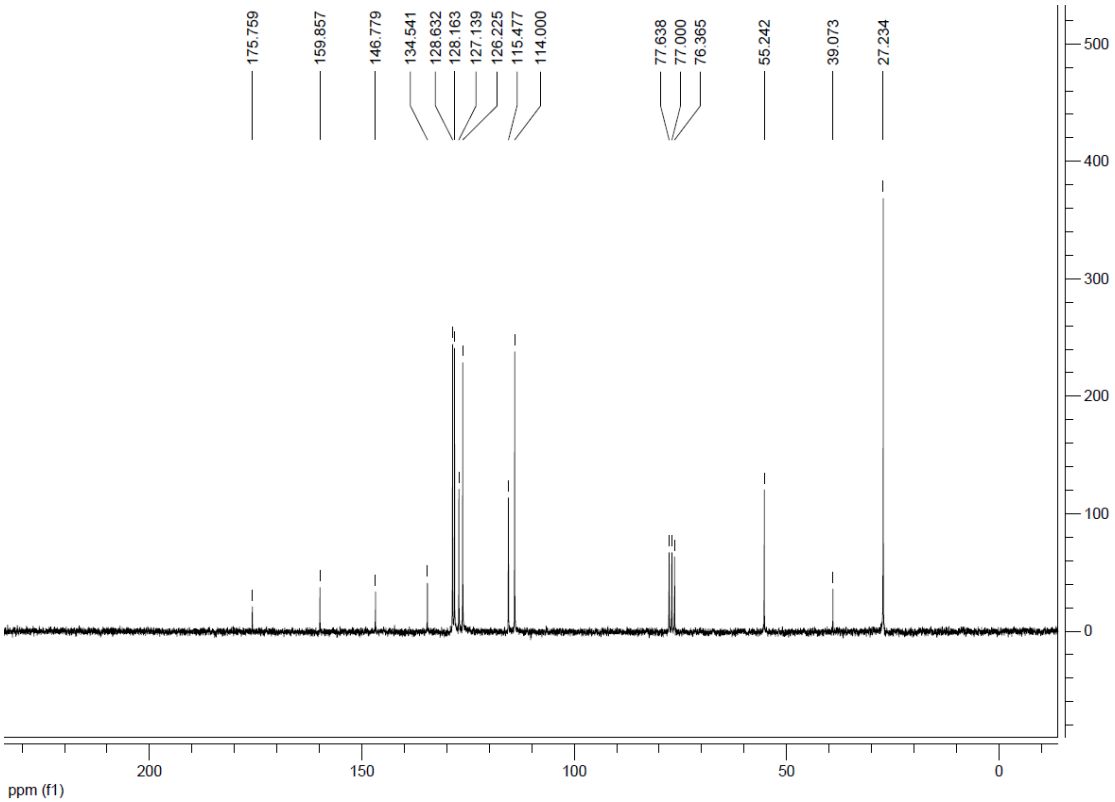


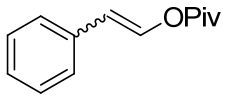




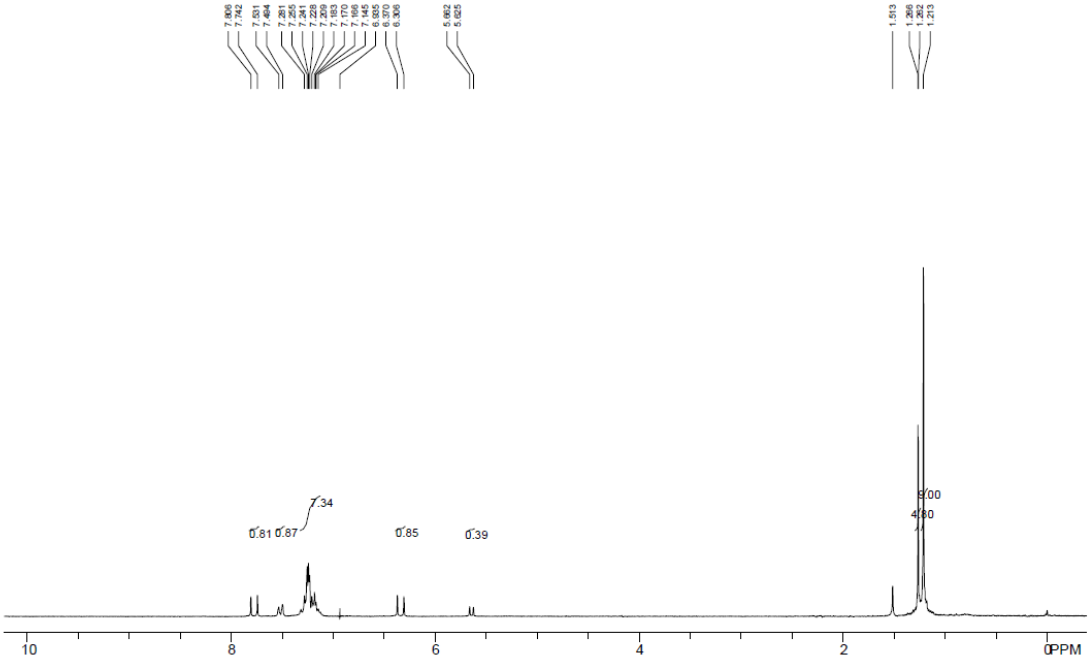
(Z)-1-(4-methoxyphenyl)-2-phenylvinyl pivalate (1h)

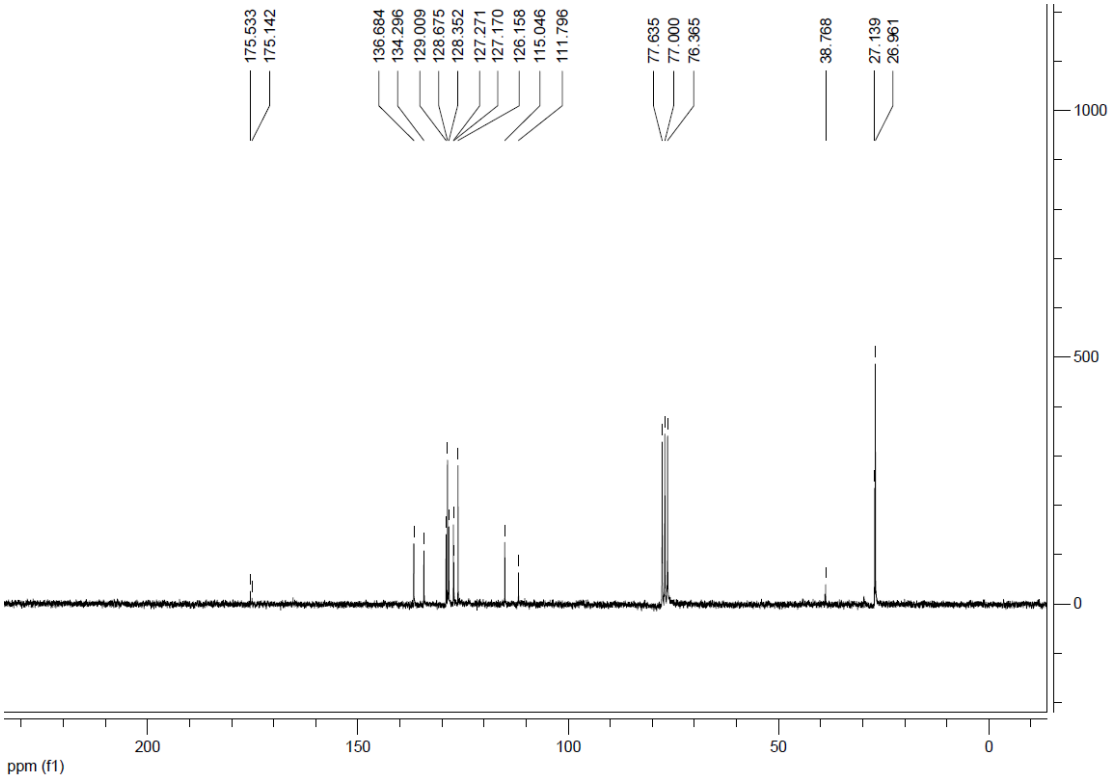


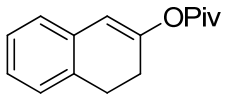




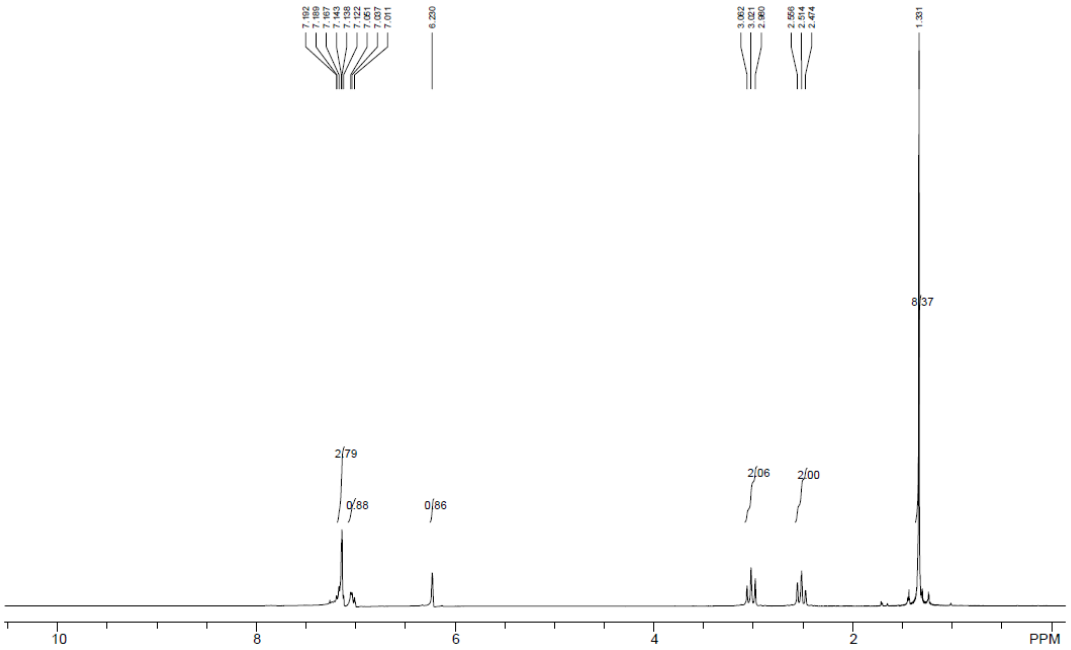
styryl pivalate (1i)

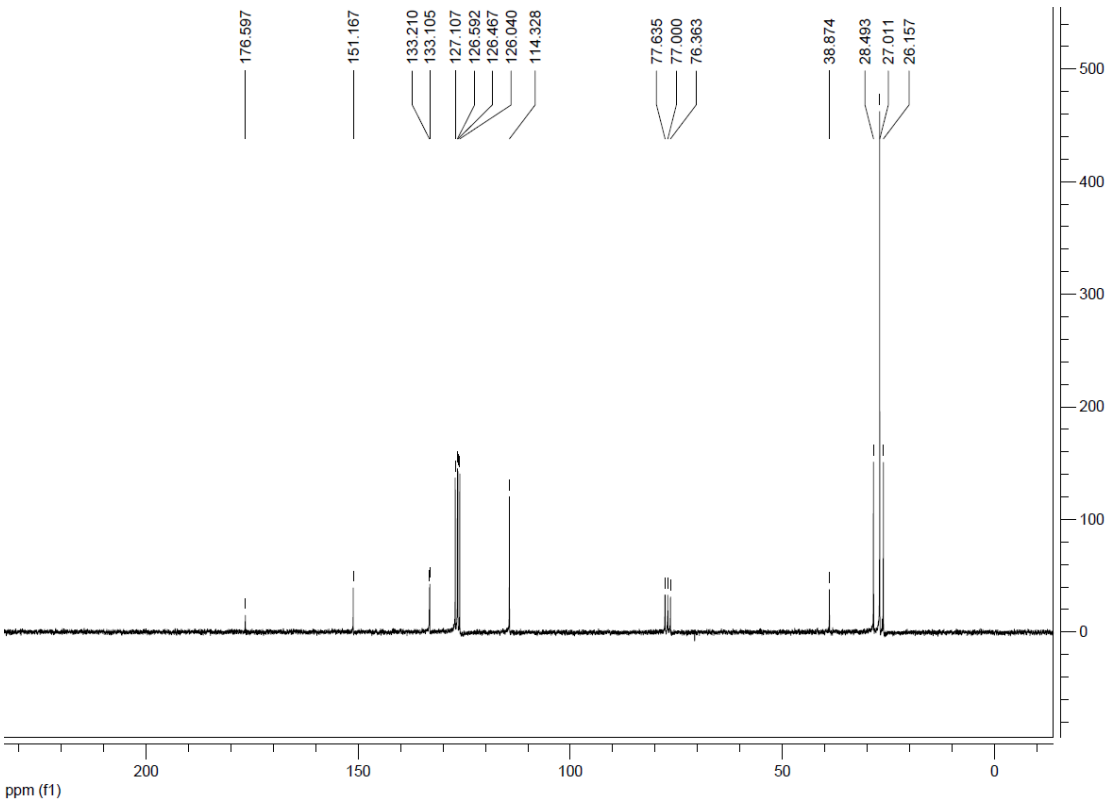


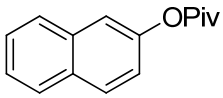




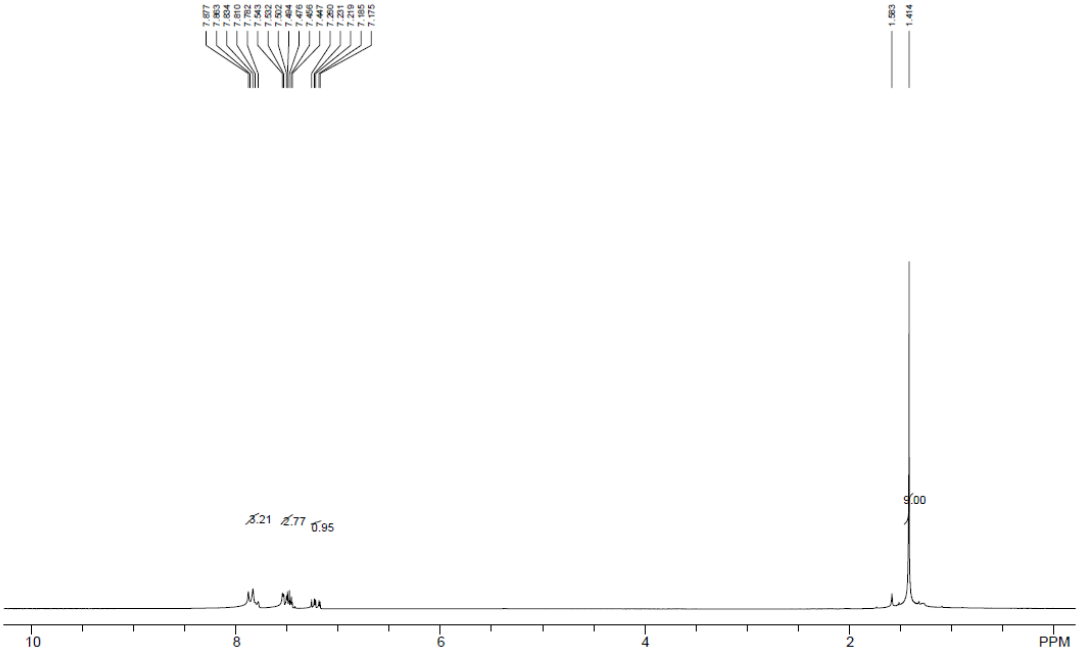
3,4-dihydronaphthalen-2-yl pivalate (1j)

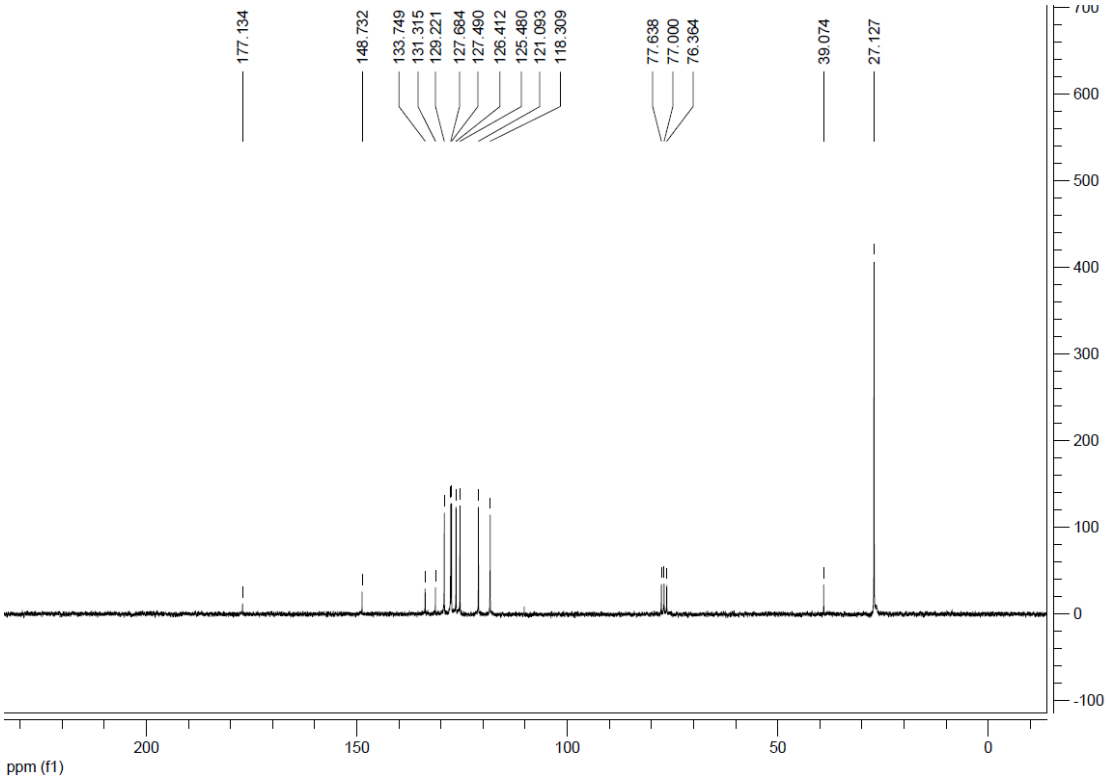


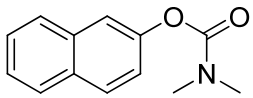




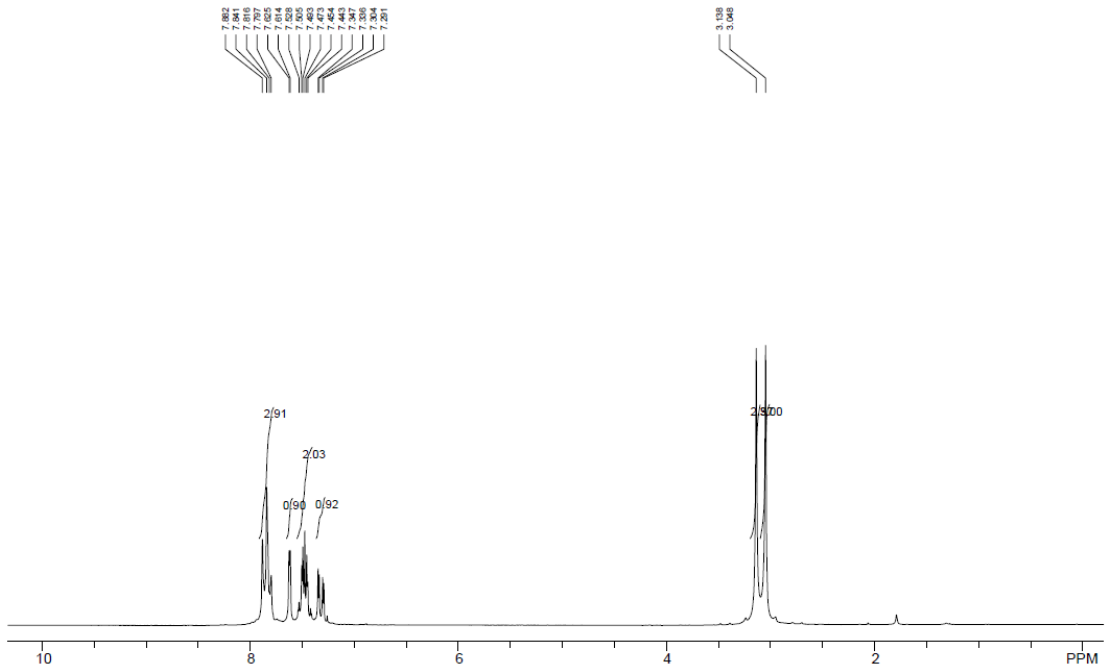
naphthalen-2-yl pivalate (1k)

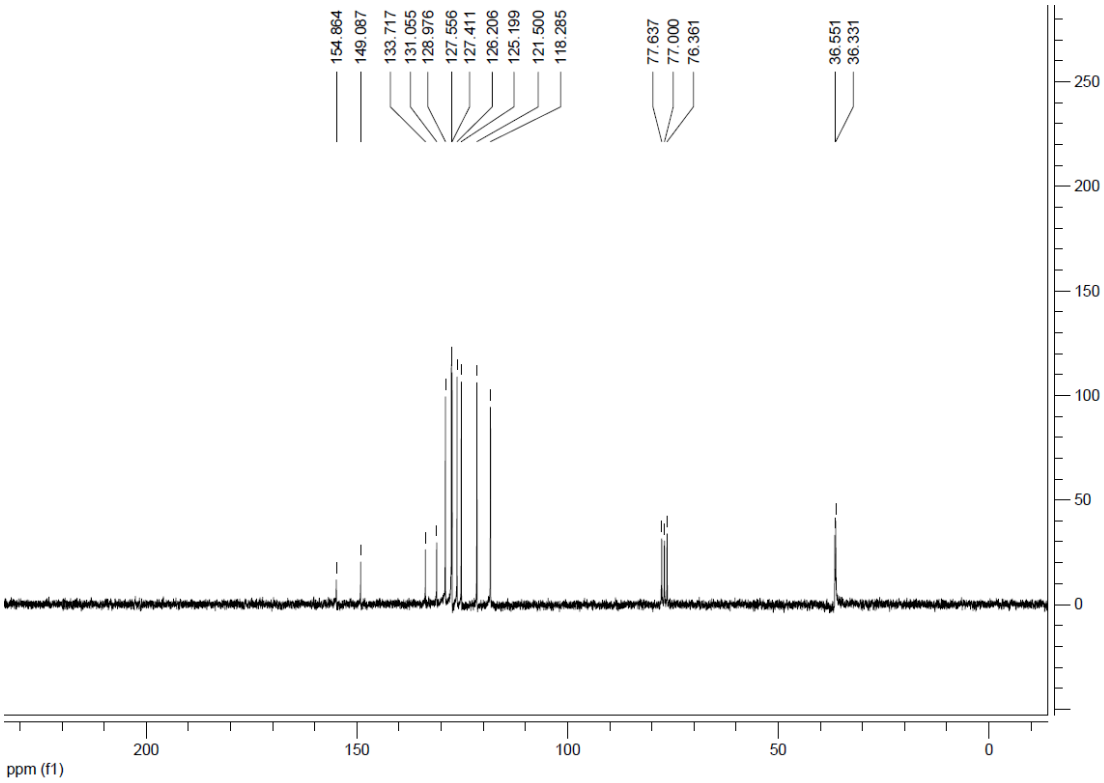


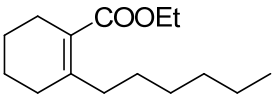




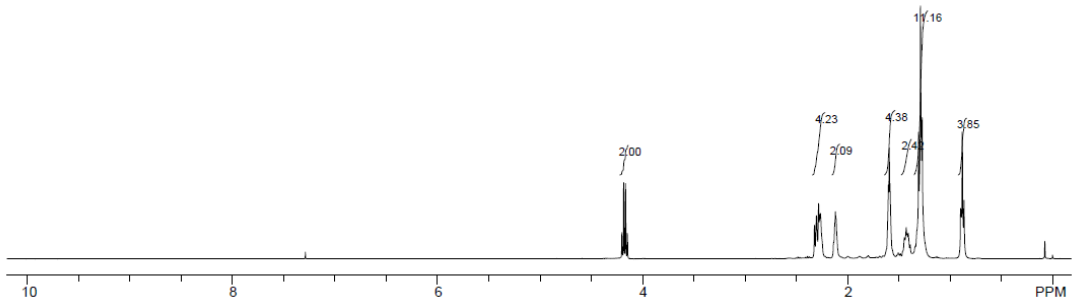
naphthalen-2-yl dimethylcarbamate (1l)

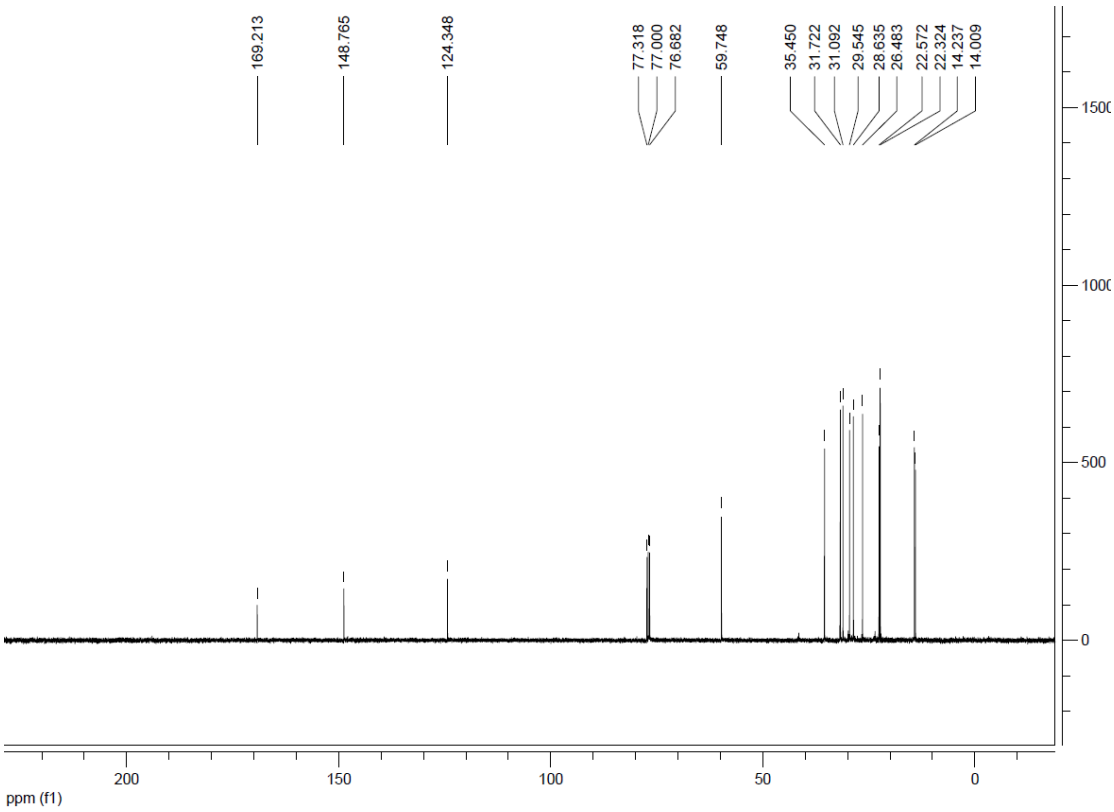


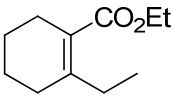




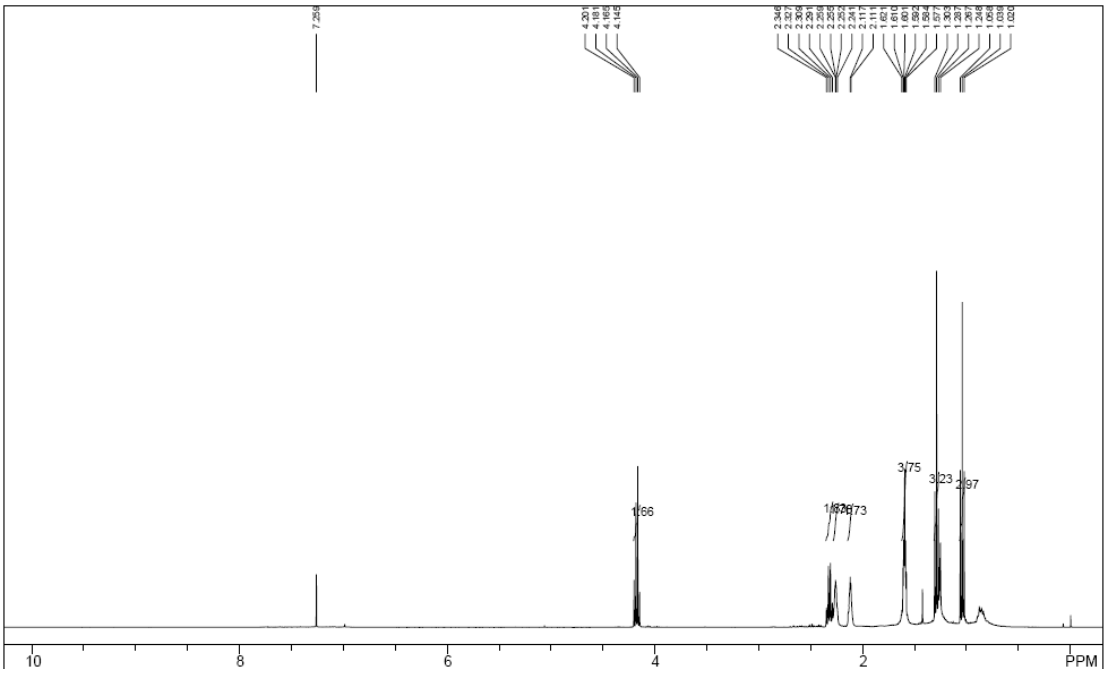
ethyl 2-hexylcyclohex-1-enecarboxylate (3a)

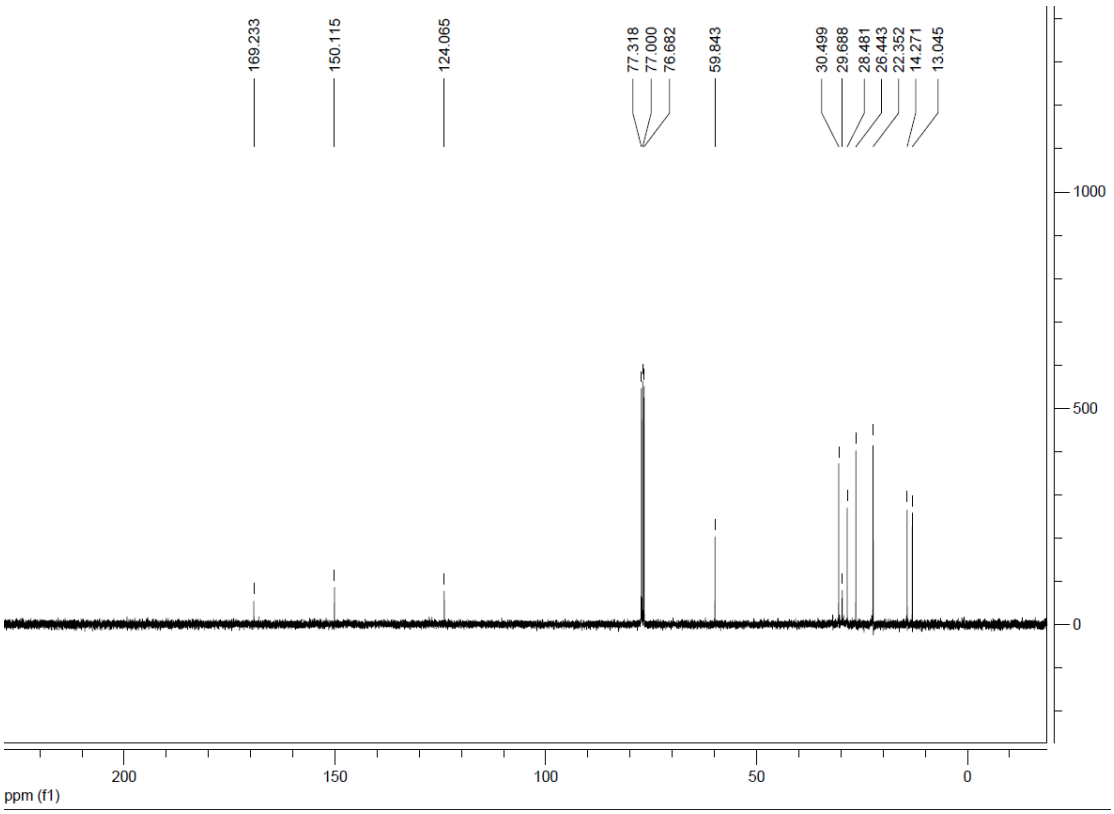


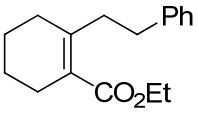




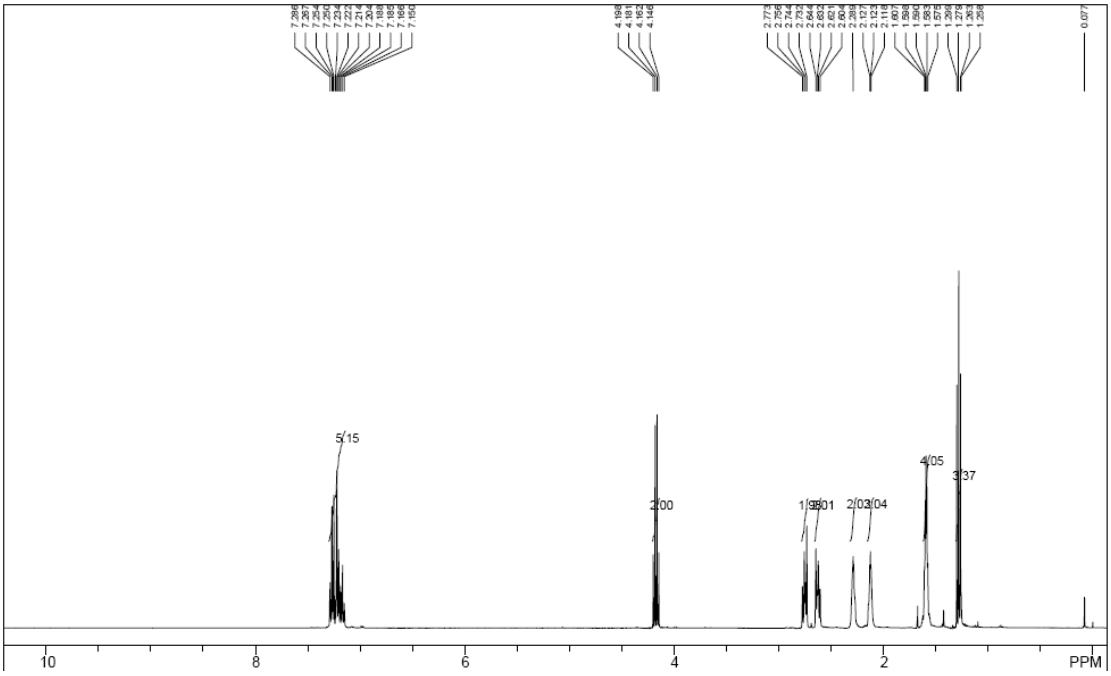
ethyl 2-ethylcyclohex-1-enecarboxylate(3d)

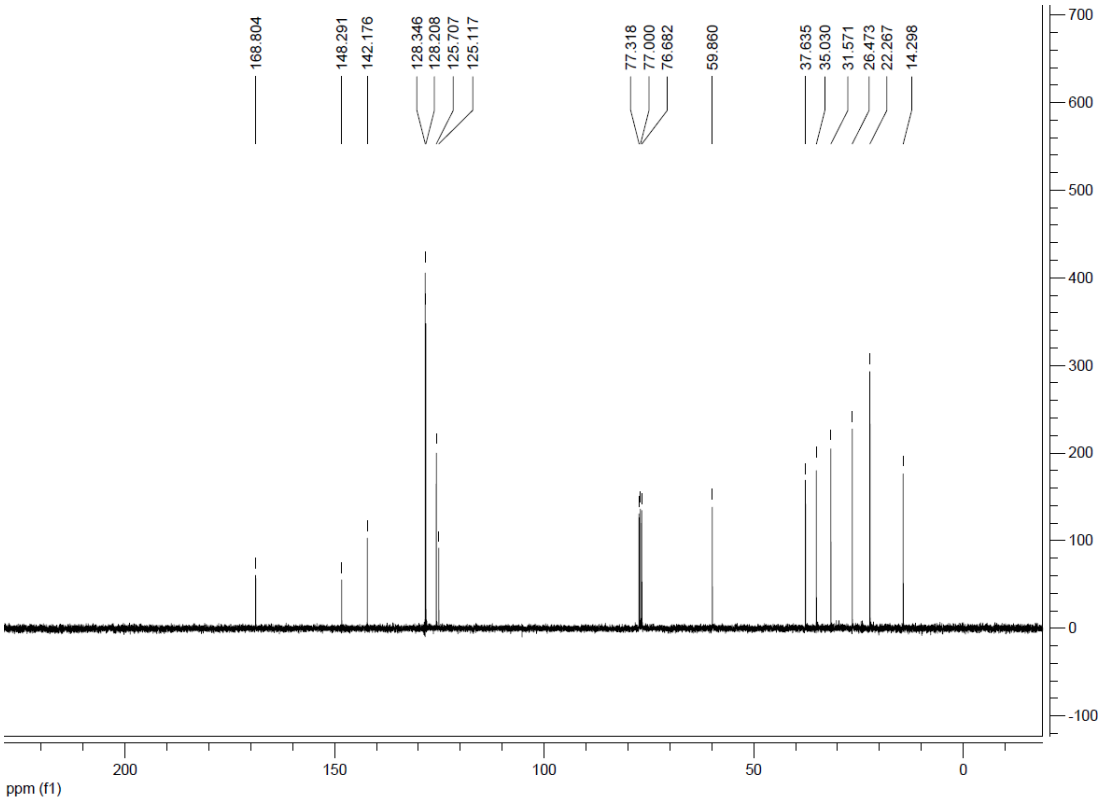


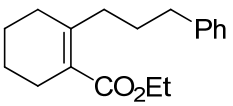




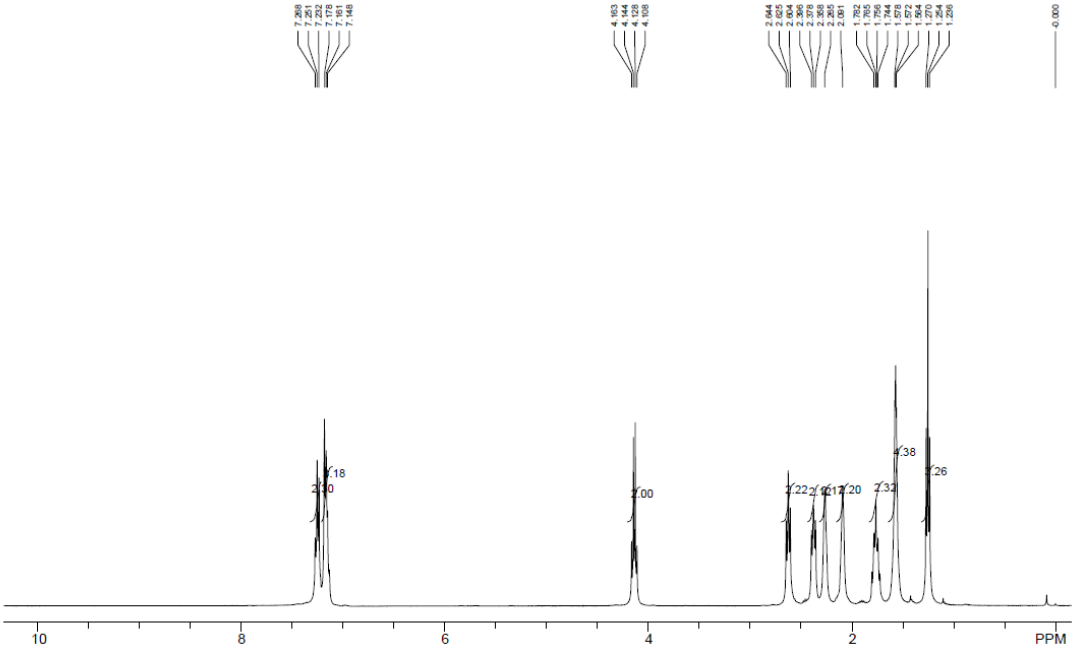
ethyl 2-phenethylcyclohex-1-enecarboxylate(3e)

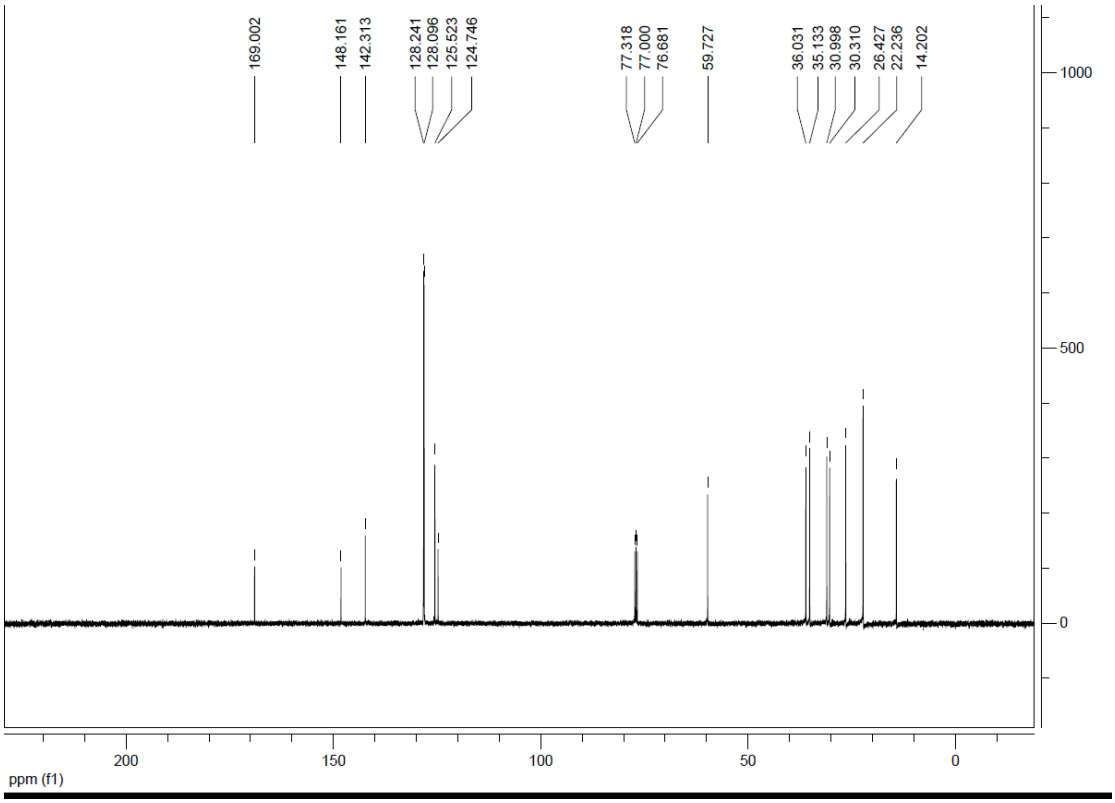


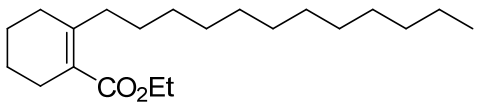




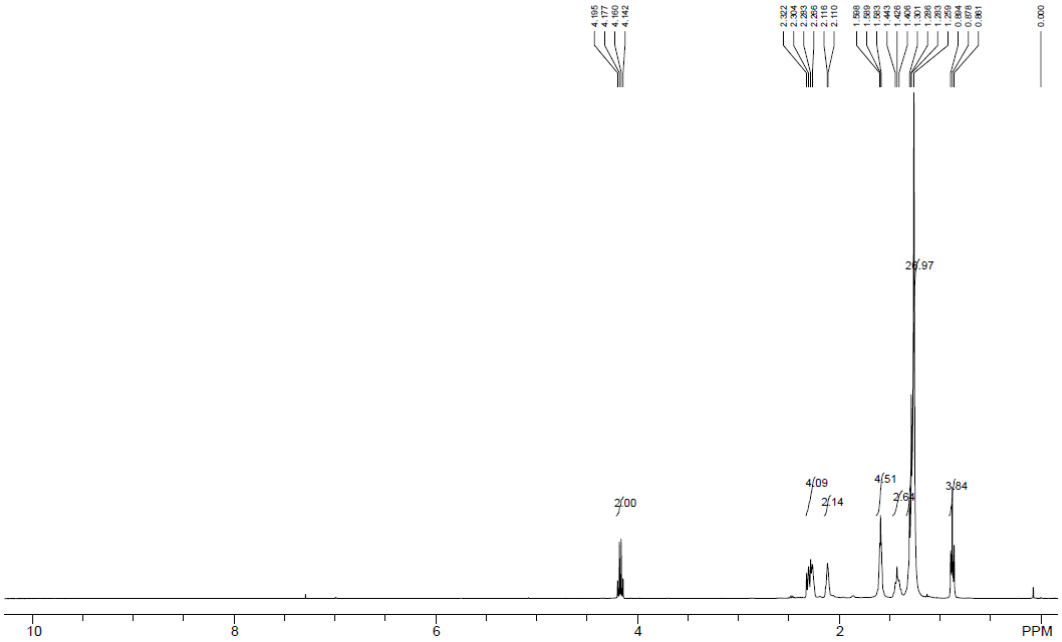
ethyl 2-(3-phenylpropyl)cyclohex-1-enecarboxylate(3f)

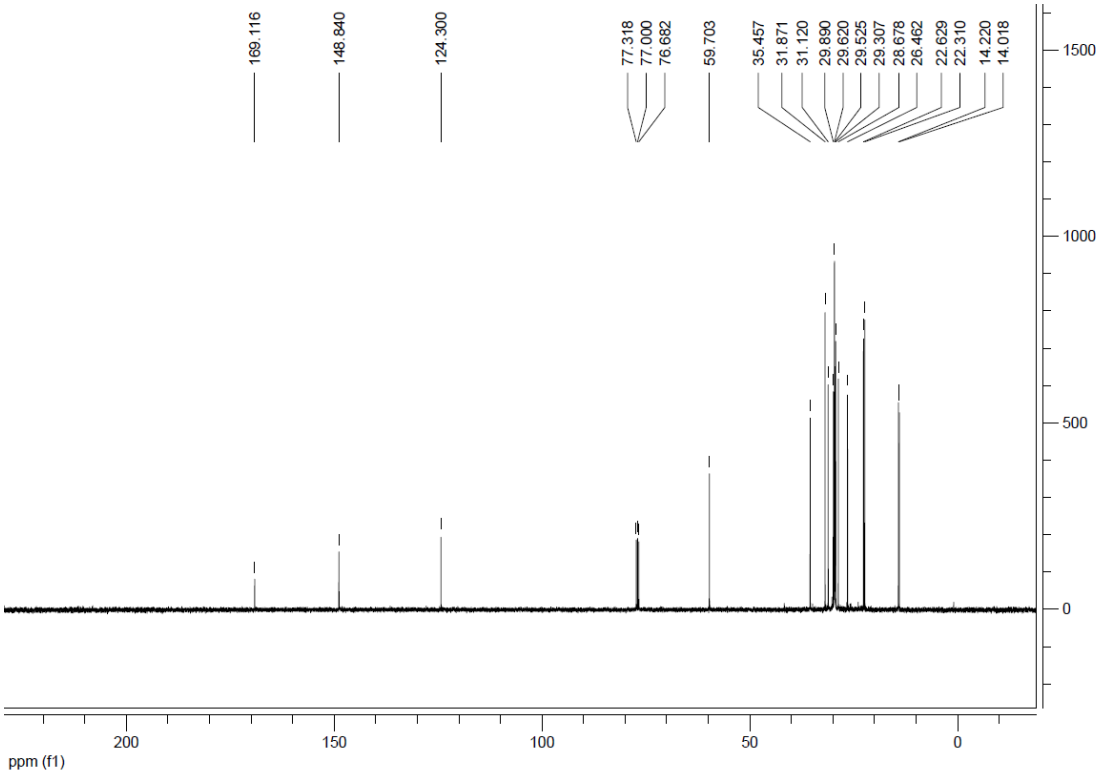


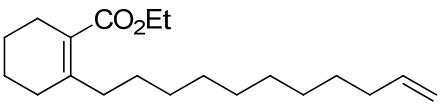




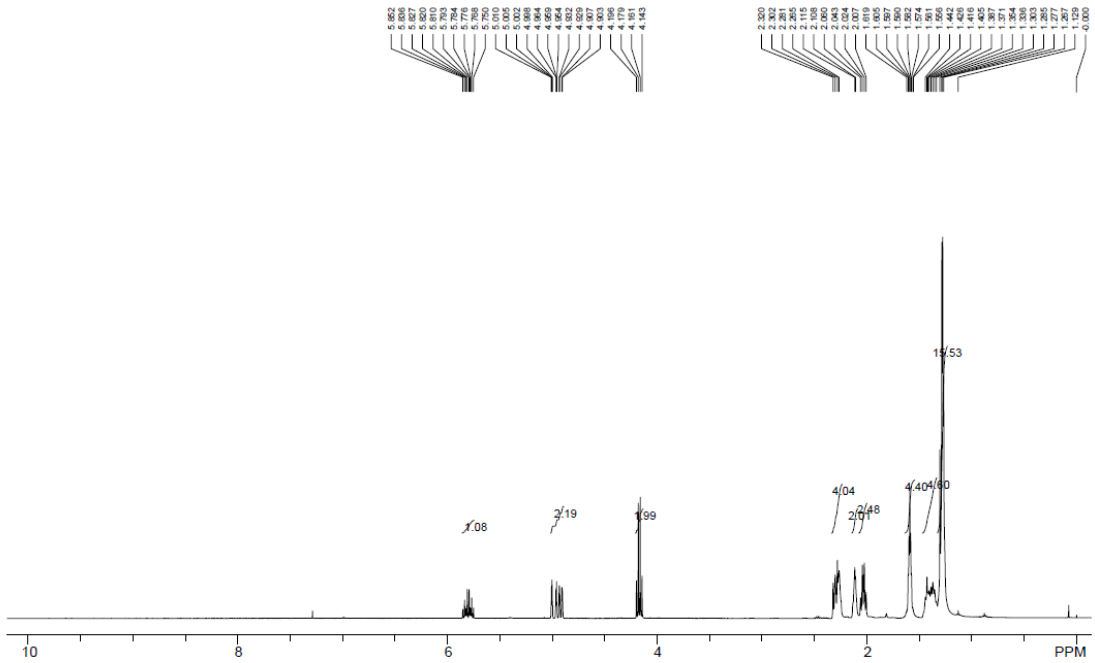
ethyl 2-dodecylcyclohex-1-enecarboxylate(3g)

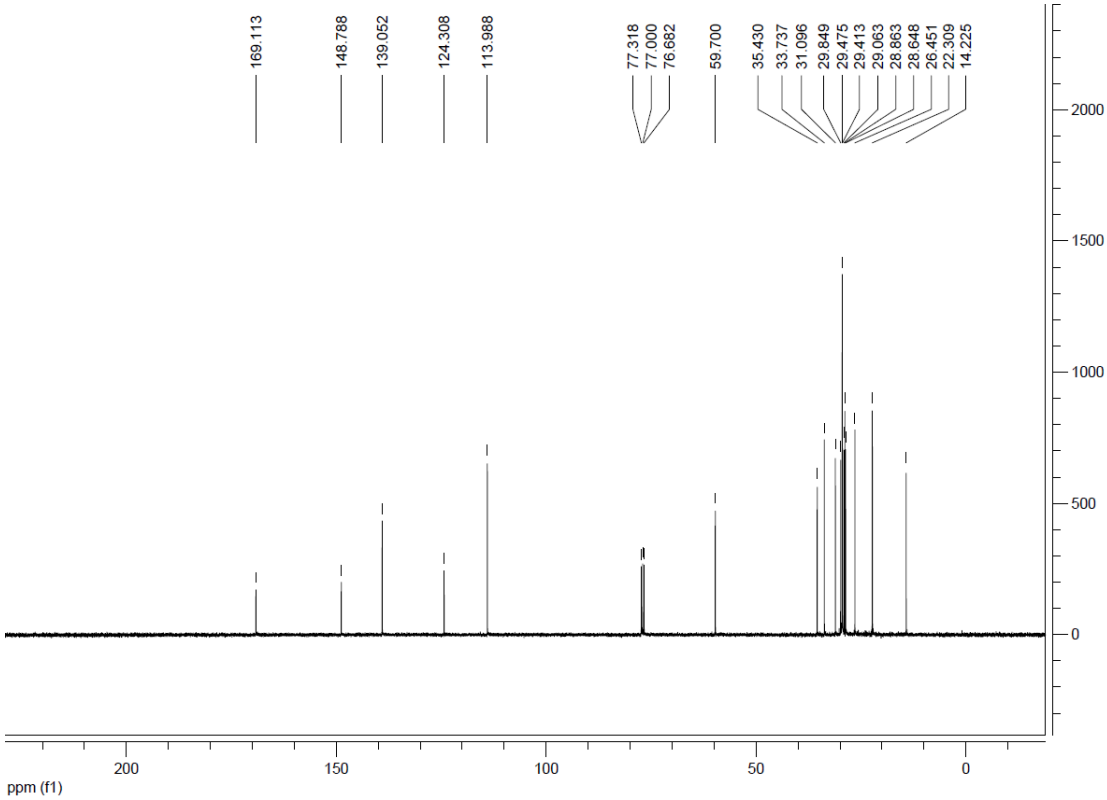


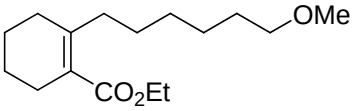




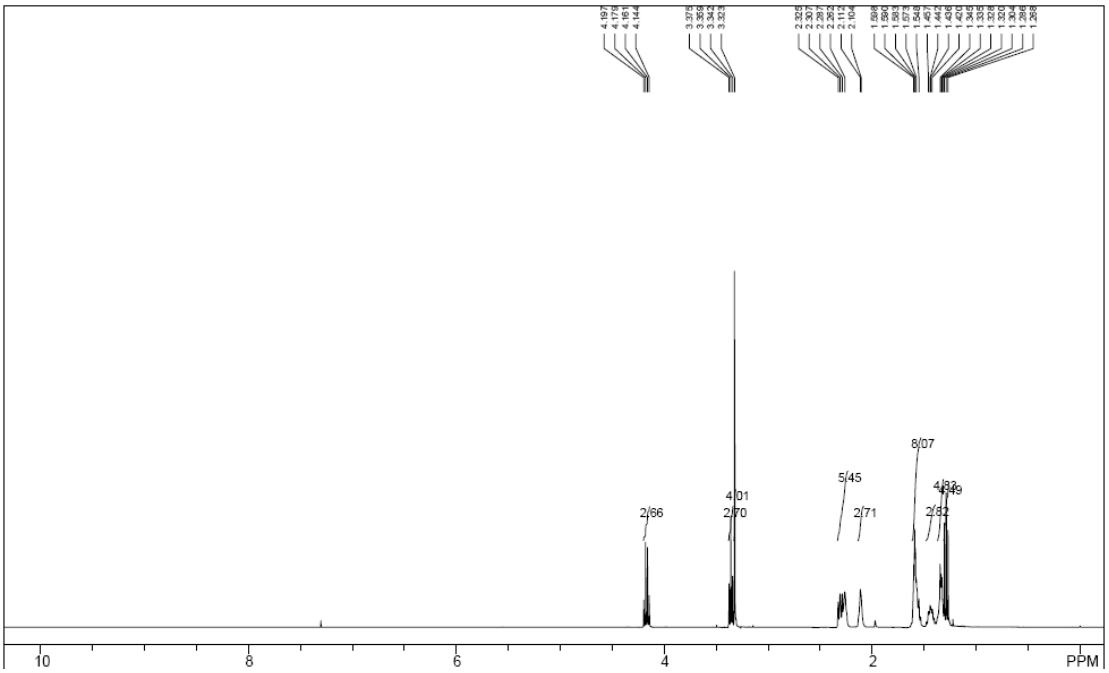
ethyl 2-(undec-10-enyl)cyclohex-1-enecarboxylate(3h)

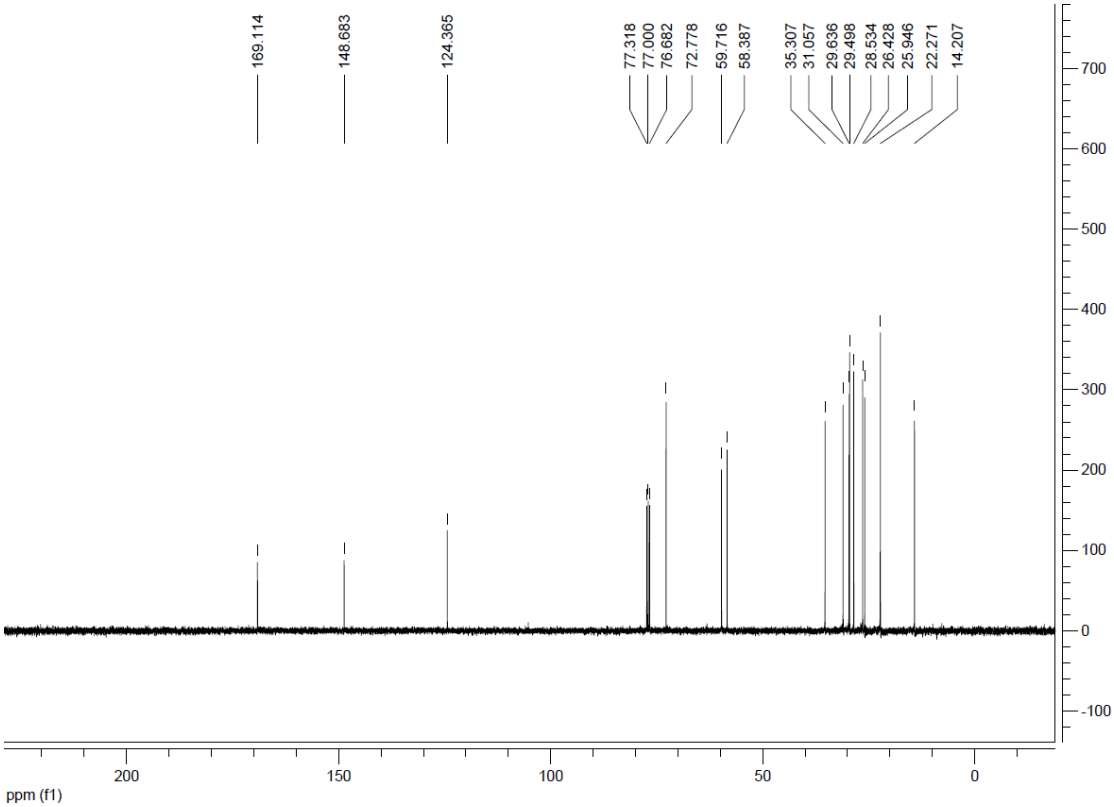


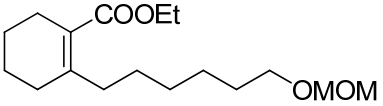




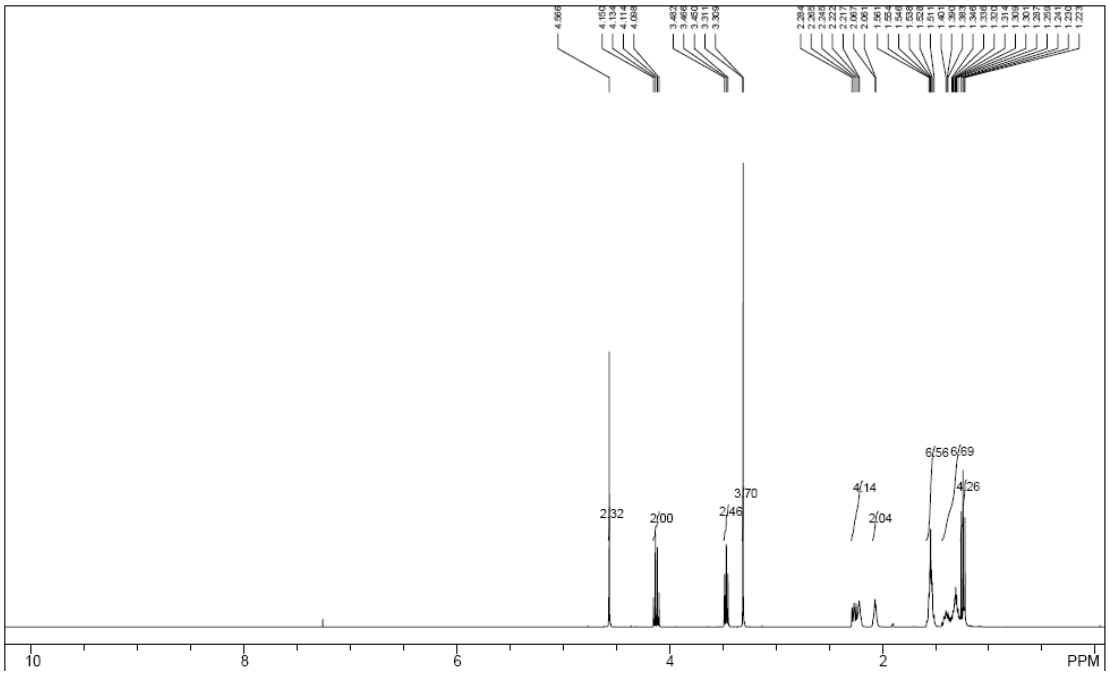
ethyl 2-(6-methoxyhexyl)cyclohex-1-enecarboxylate(3i)

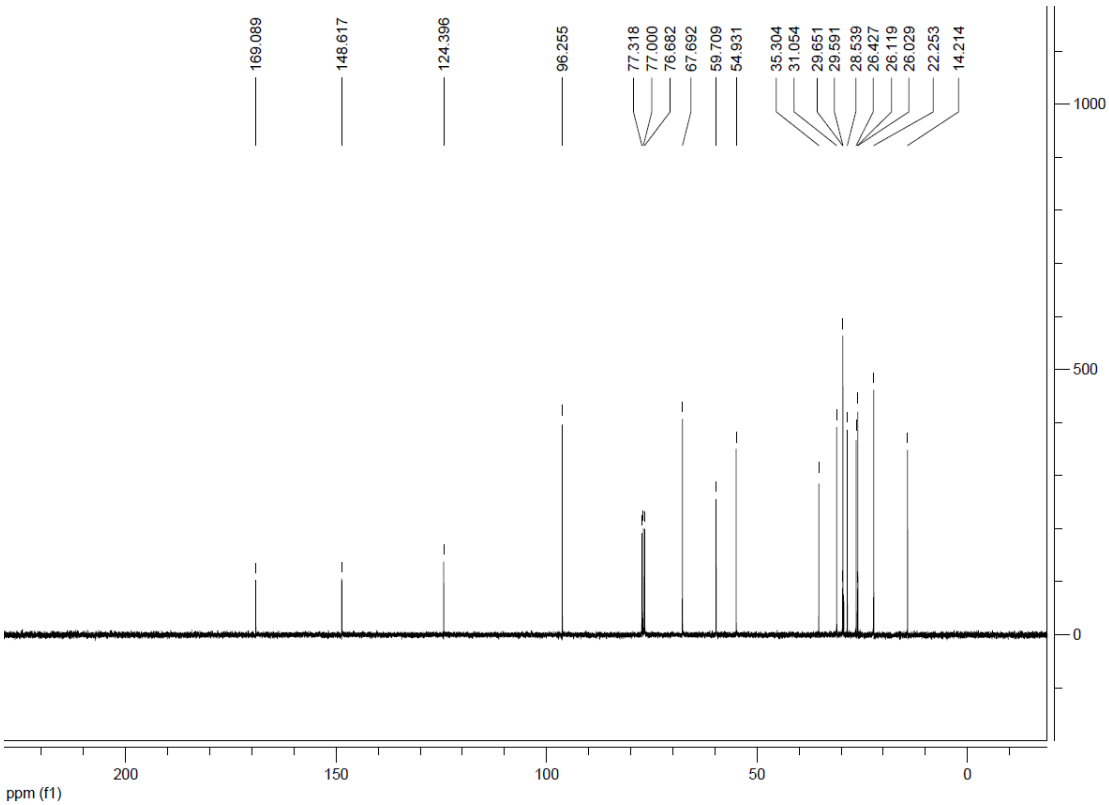


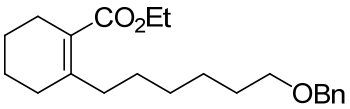




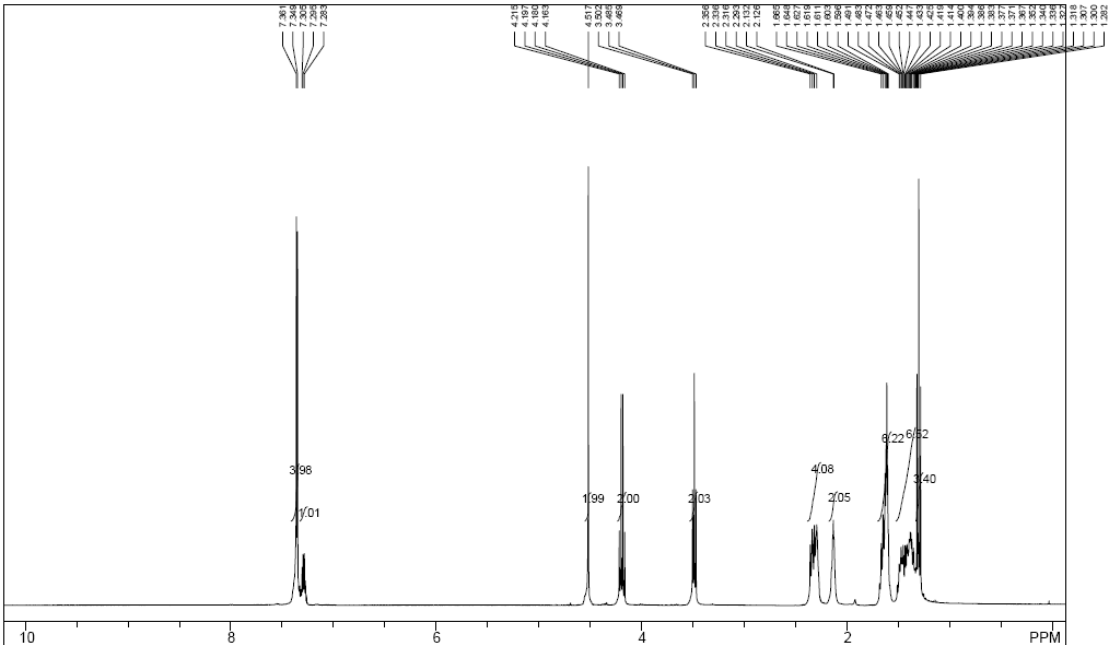
ethyl 2-(6-(methoxymethoxy)hexyl)cyclohex-1-enecarboxylate(3j)

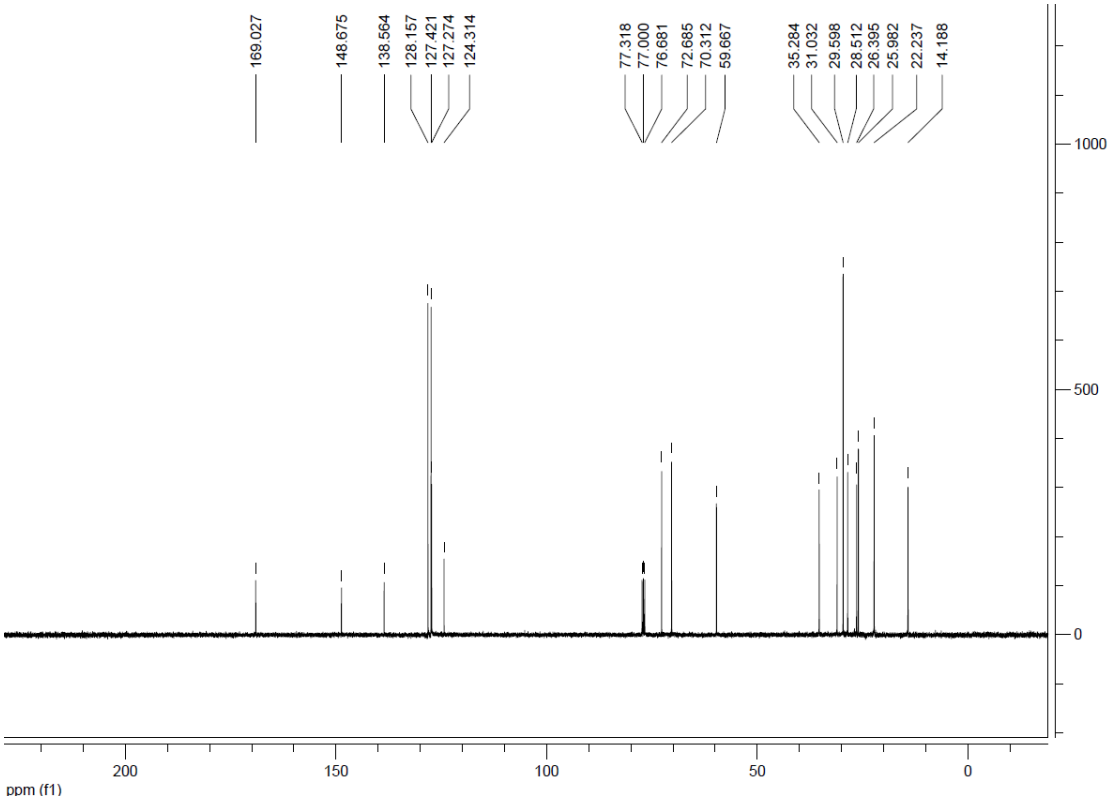


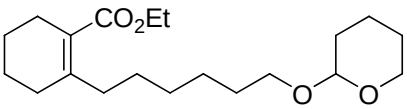




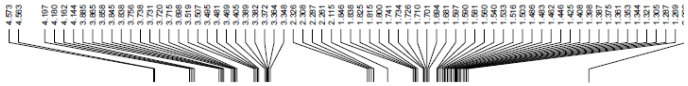
ethyl 2-(6-(benzyloxy)hexyl)cyclohex-1-enecarboxylate(3k)

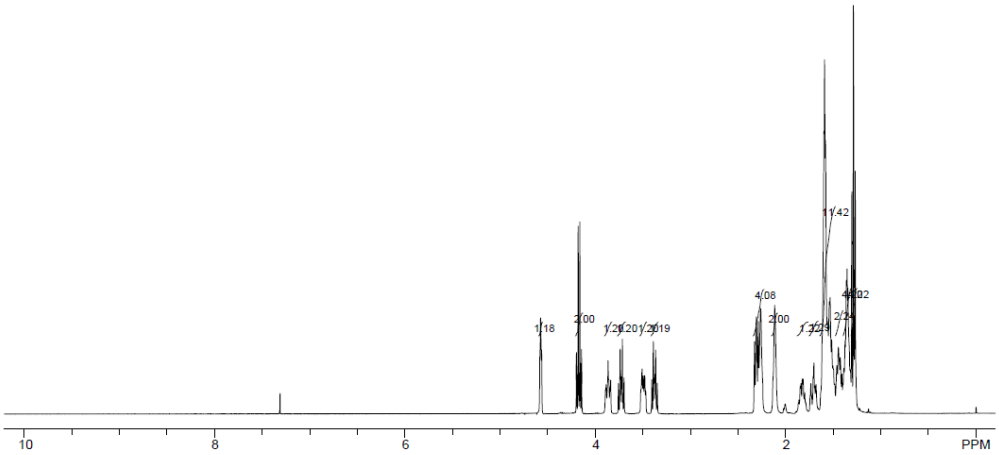


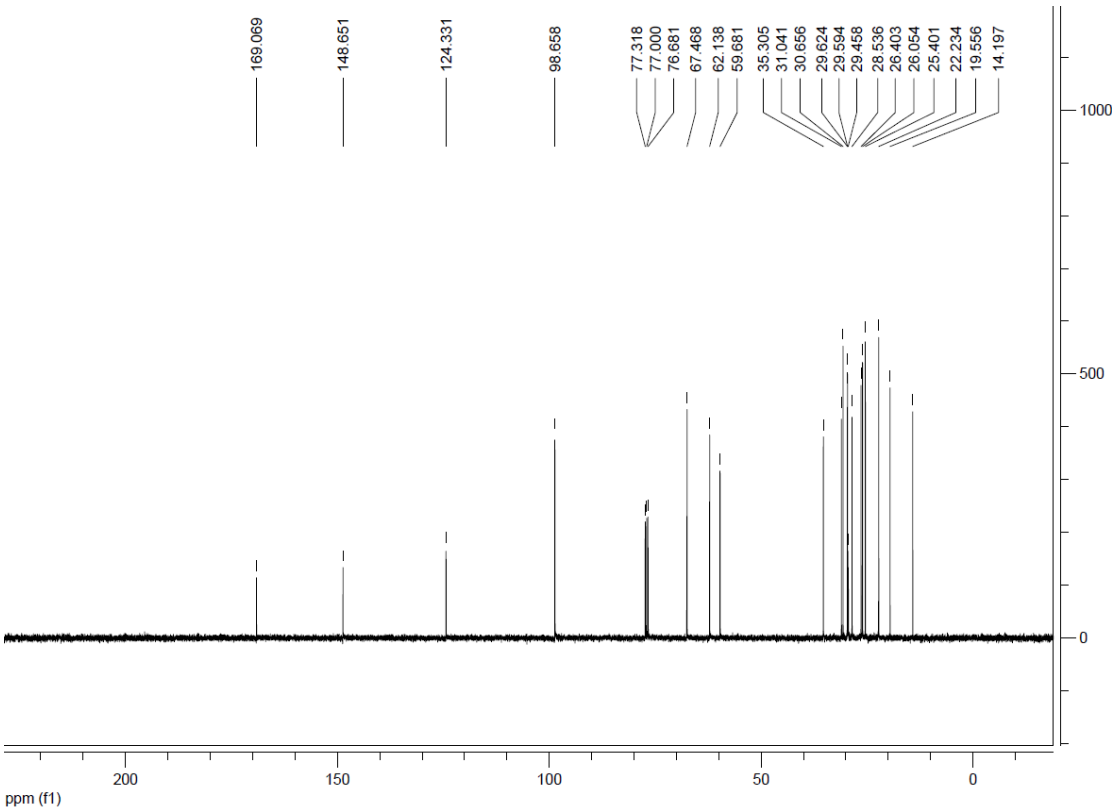


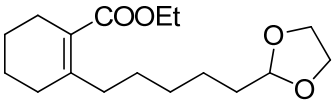


ethyl 2-(6-(tetrahydro-2H-pyran-2-yloxy)hexyl)cyclohex-1-enecarboxylate(3l)

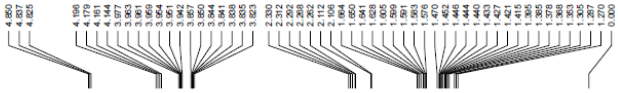


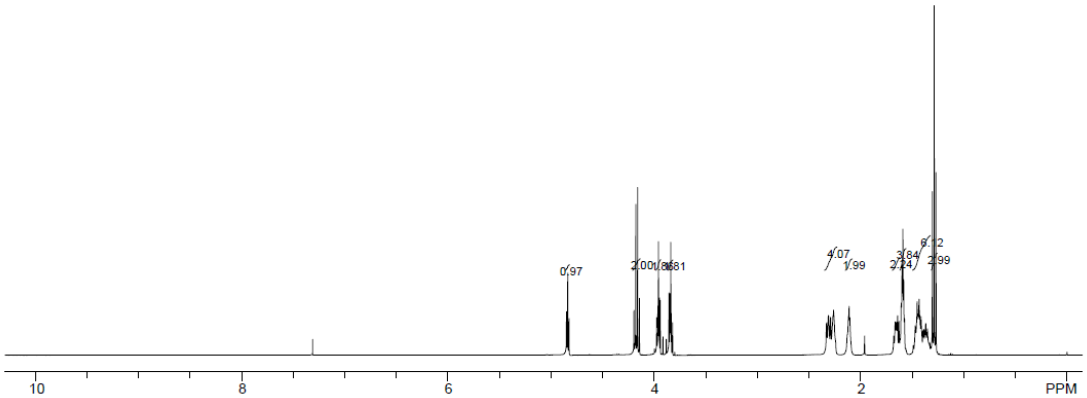


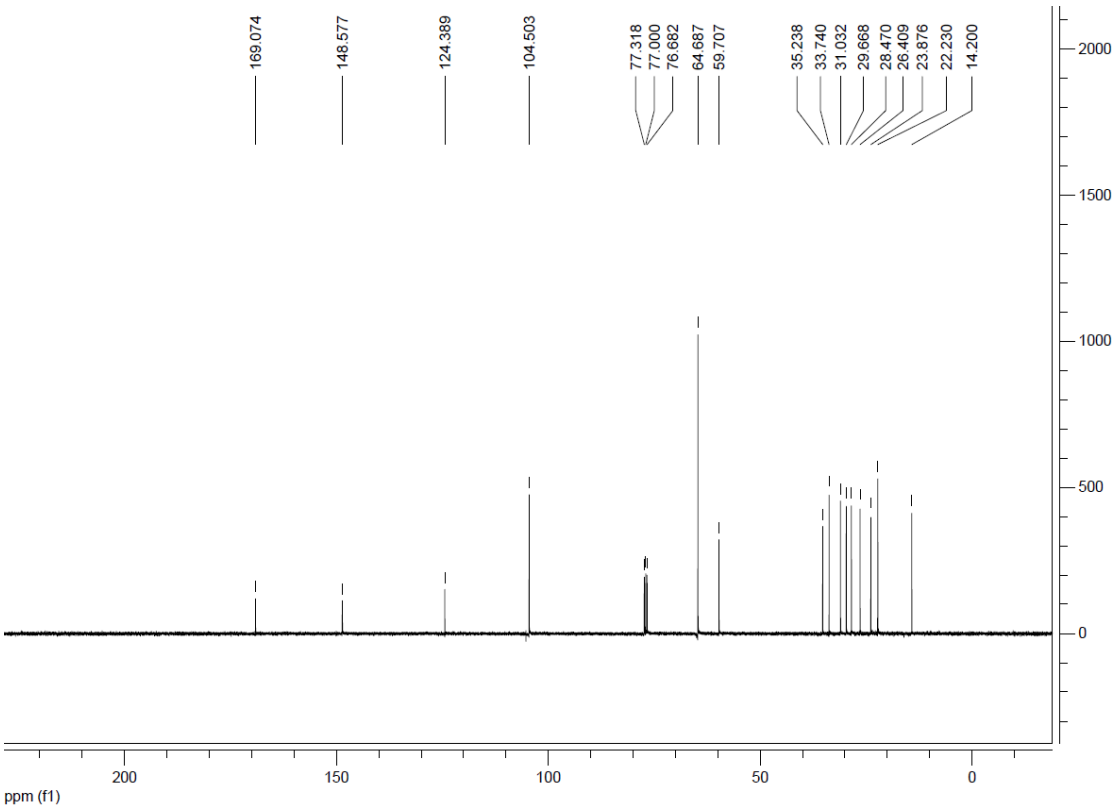


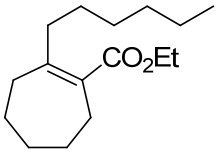


ethyl 2-(5-(1,3-dioxolan-2-yl)pentyl)cyclohex-1-enecarboxylate(3m)

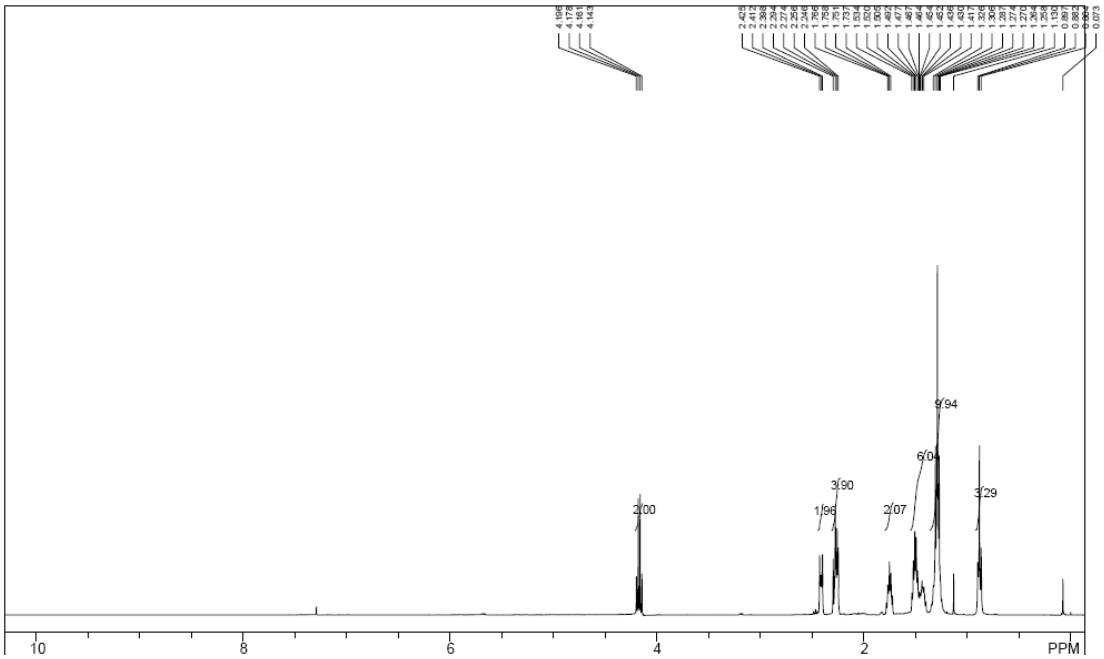


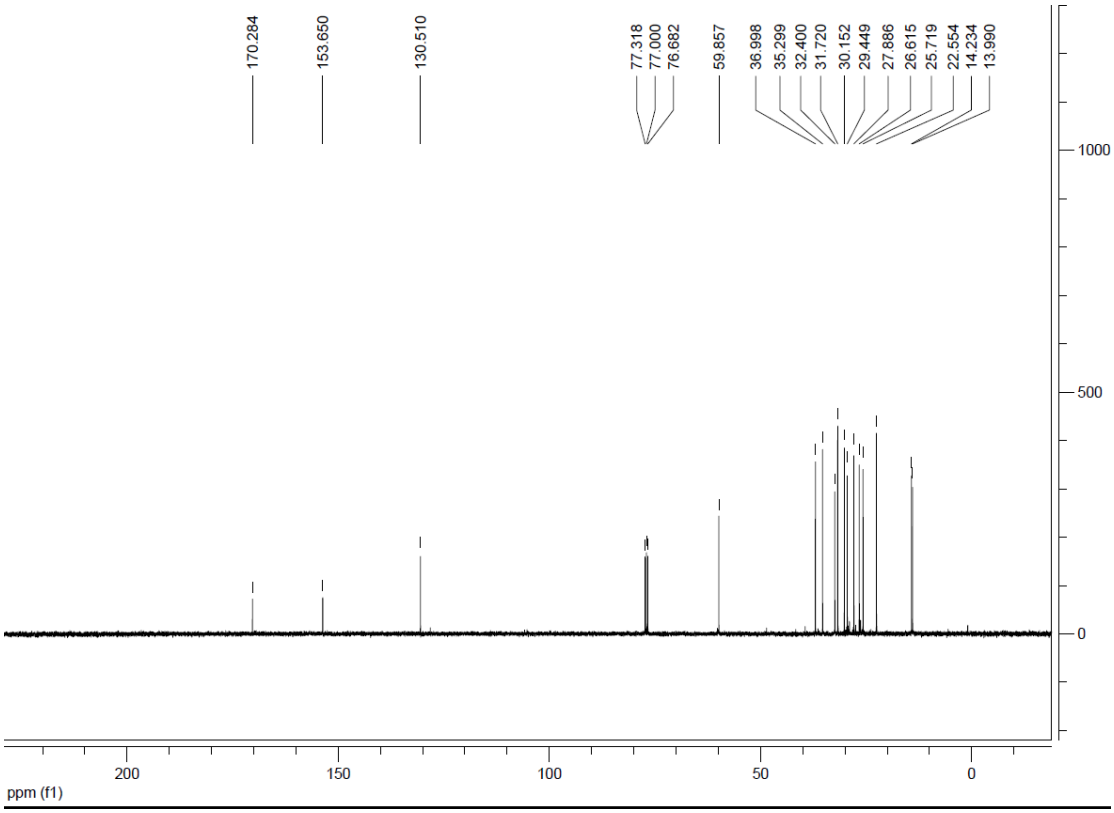


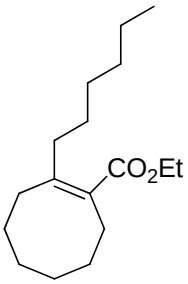




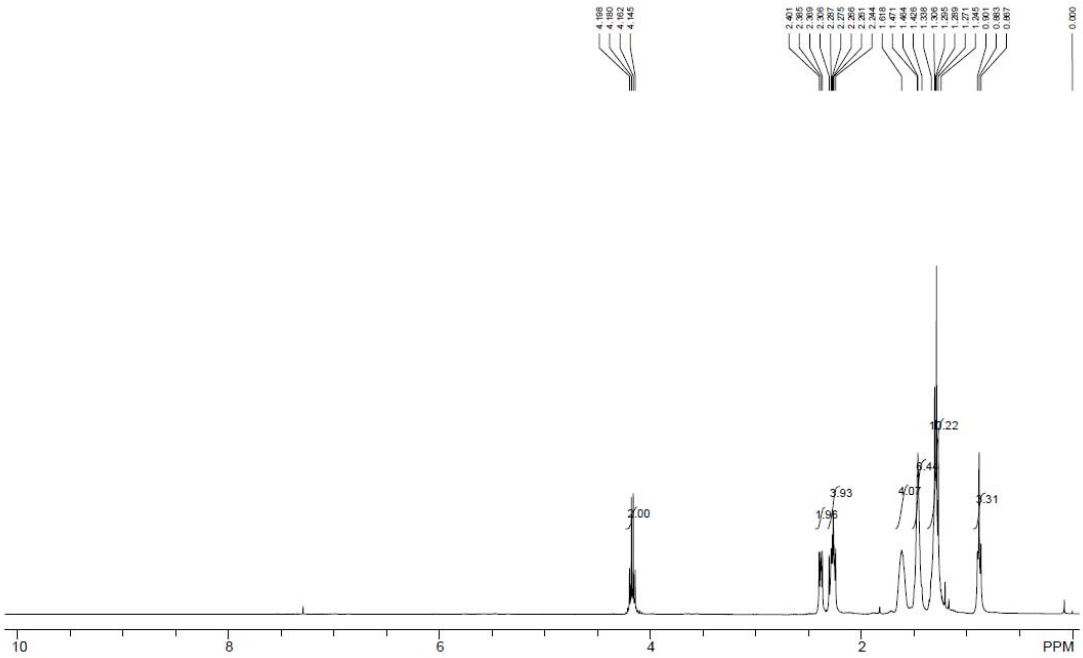
ethyl 2-hexylcyclohept-1-enecarboxylate(3n)

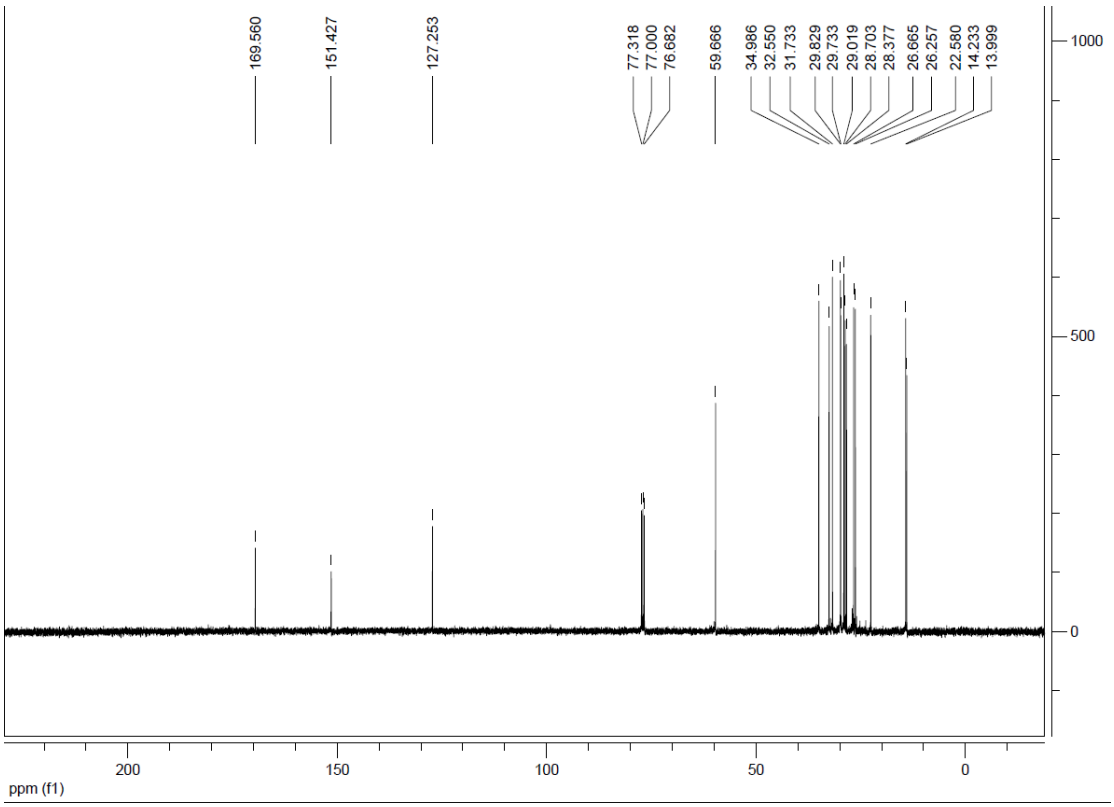


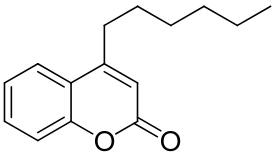




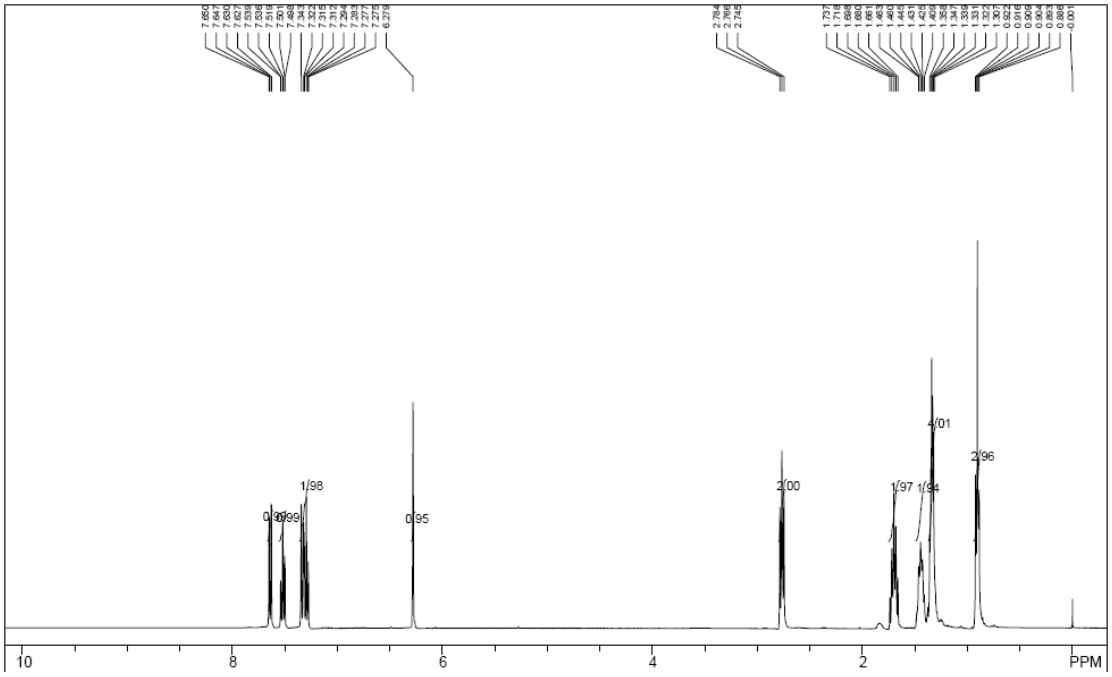
(E)-ethyl 2-hexylcyclooct-1-enecarboxylate(3o)

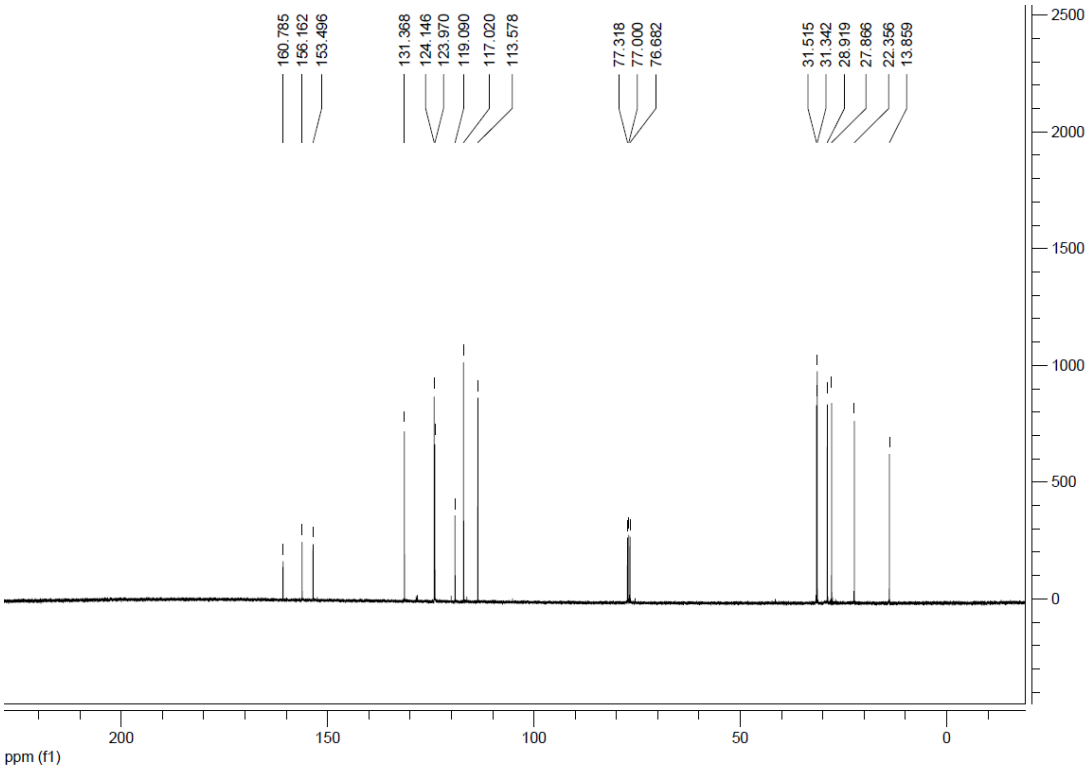


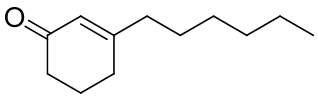




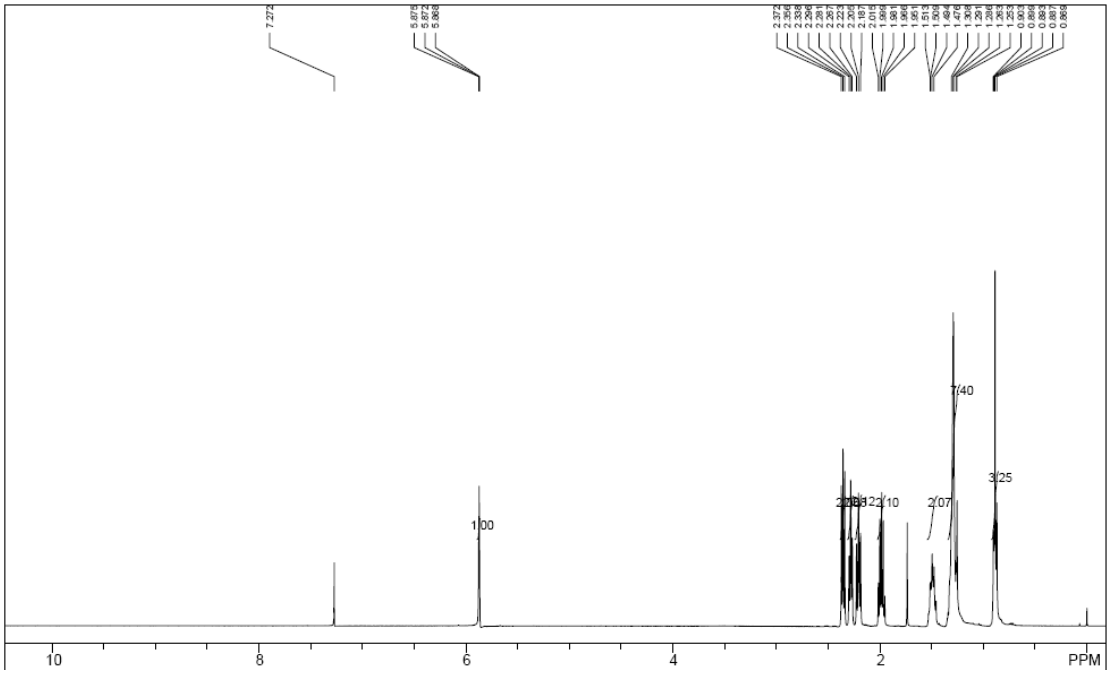
4-hexyl-2H-chromen-2-one(3p)

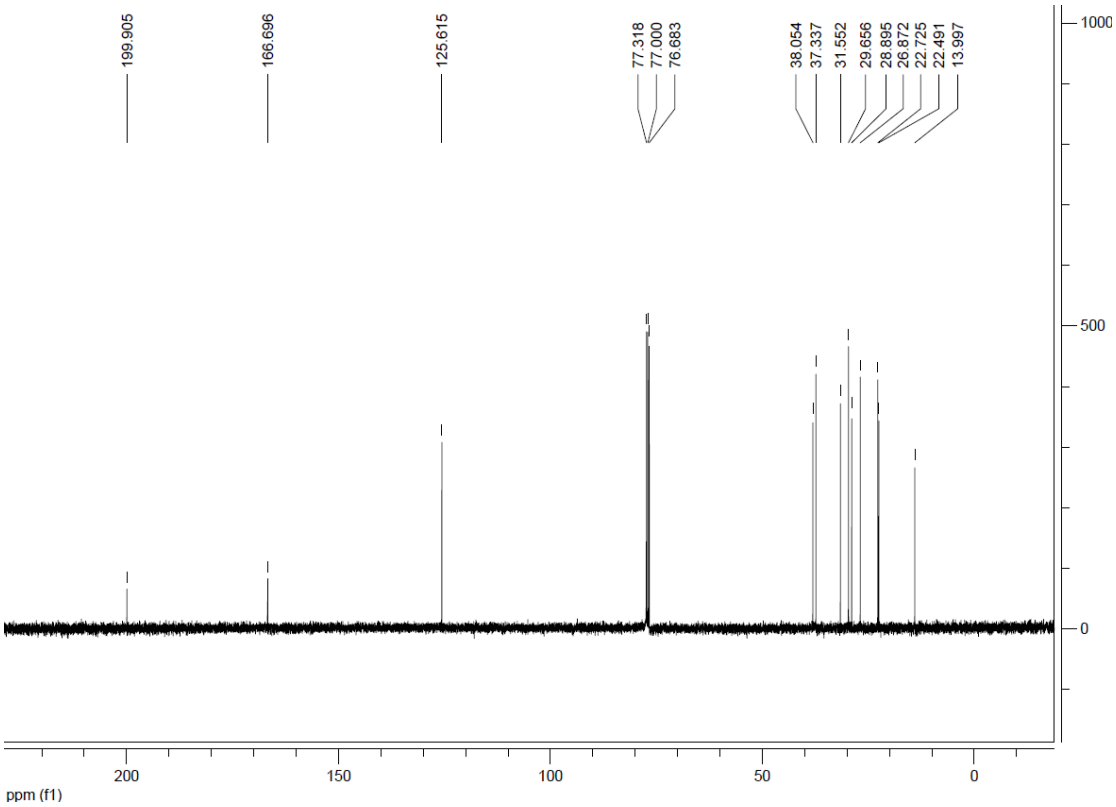


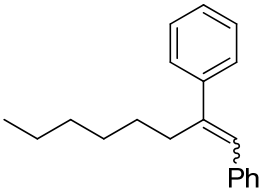




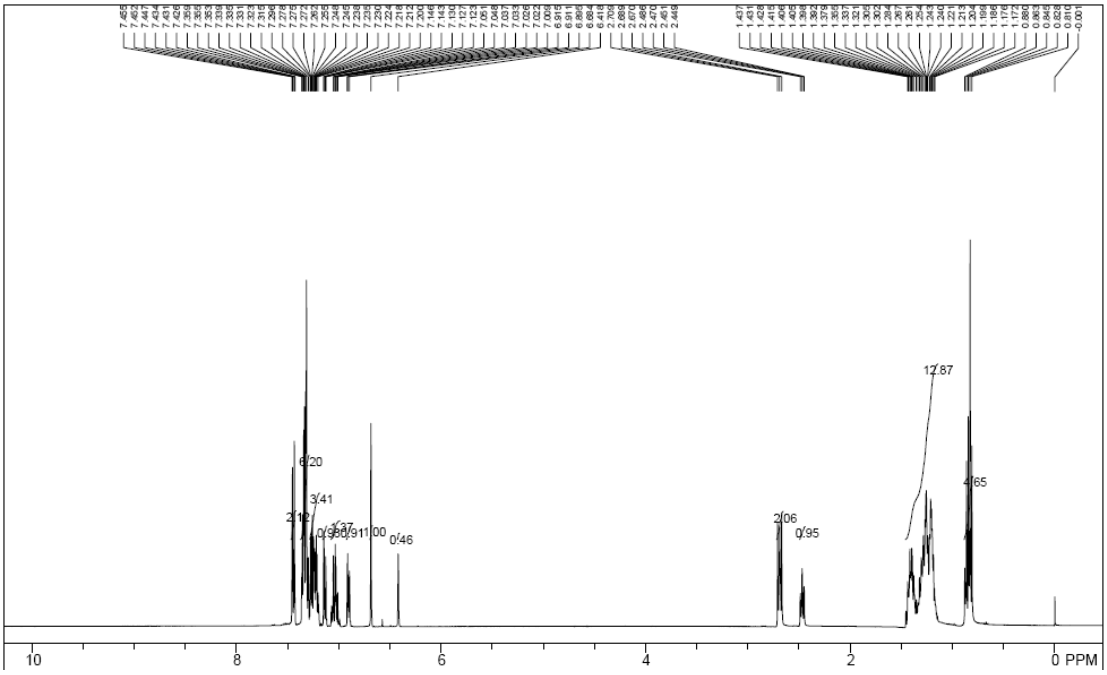
3-hexylcyclohex-2-enone(3q)

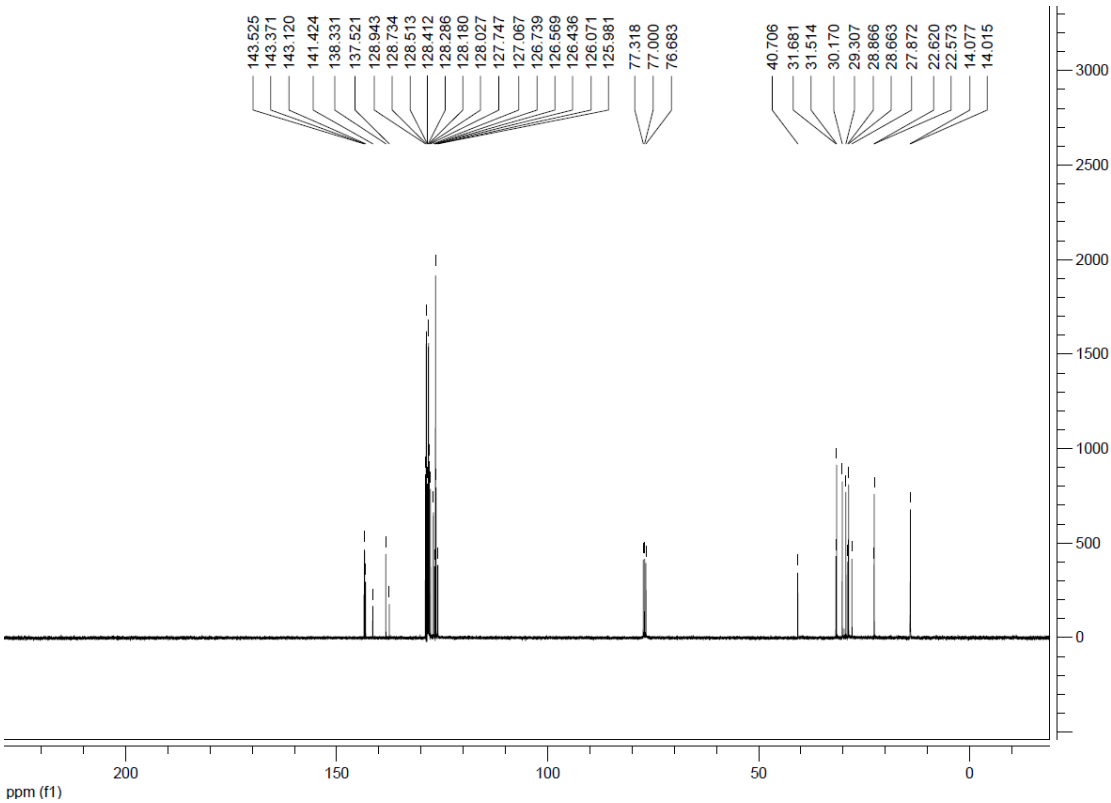


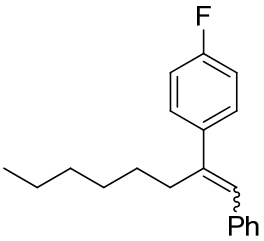




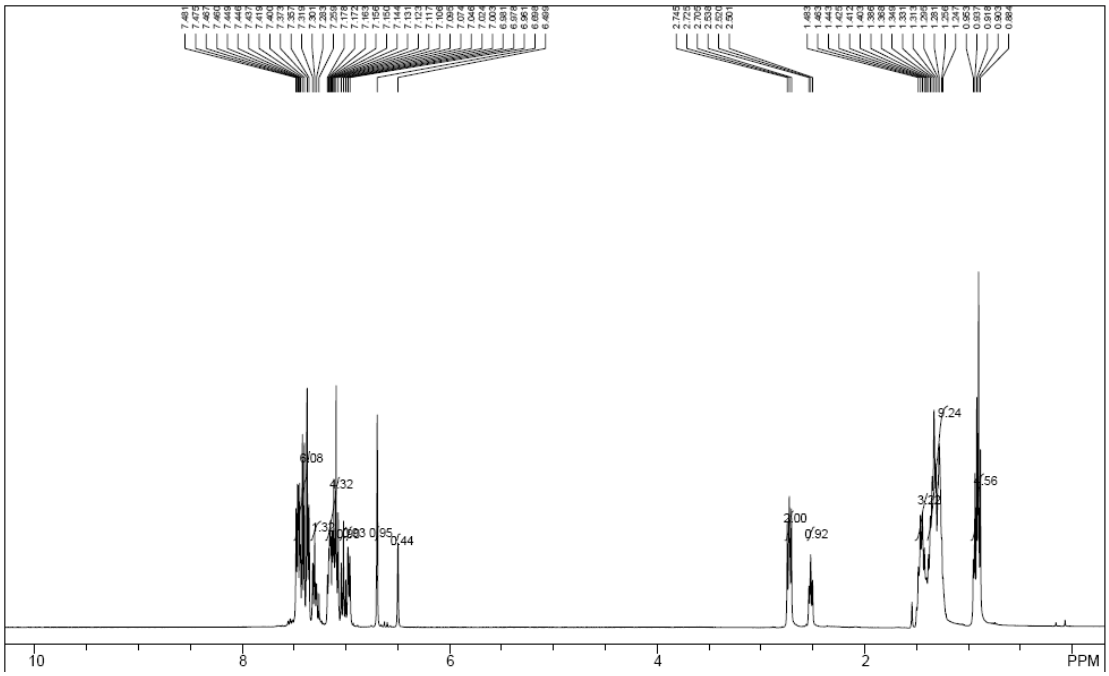
oct-1-ene-1,2-diyldibenzene(3r)

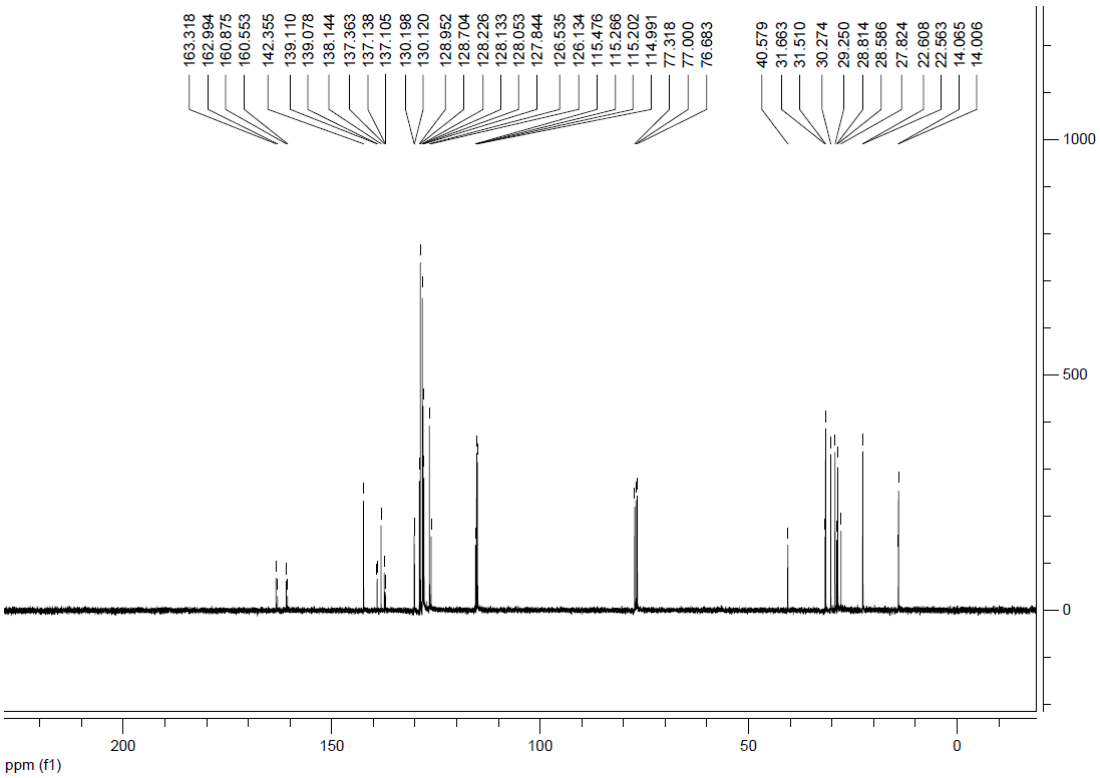


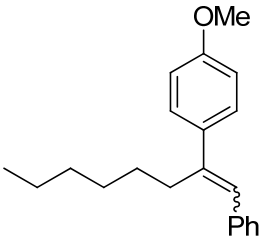




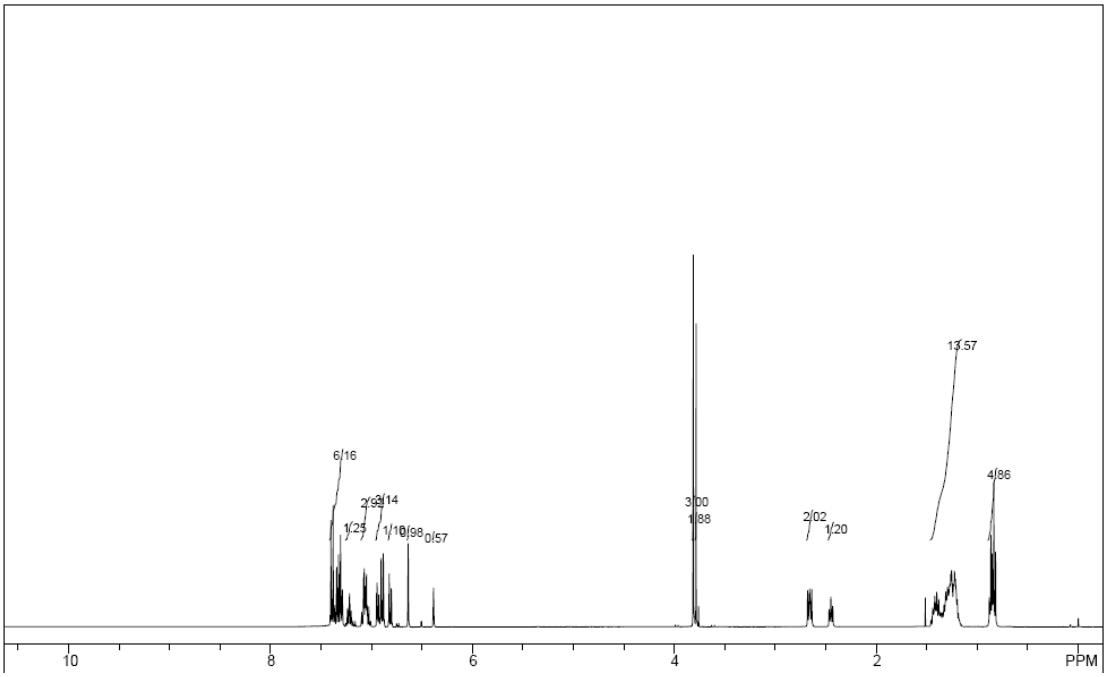
1-fluoro-4-(1-phenyloct-1-en-2-yl)benzene(3s)

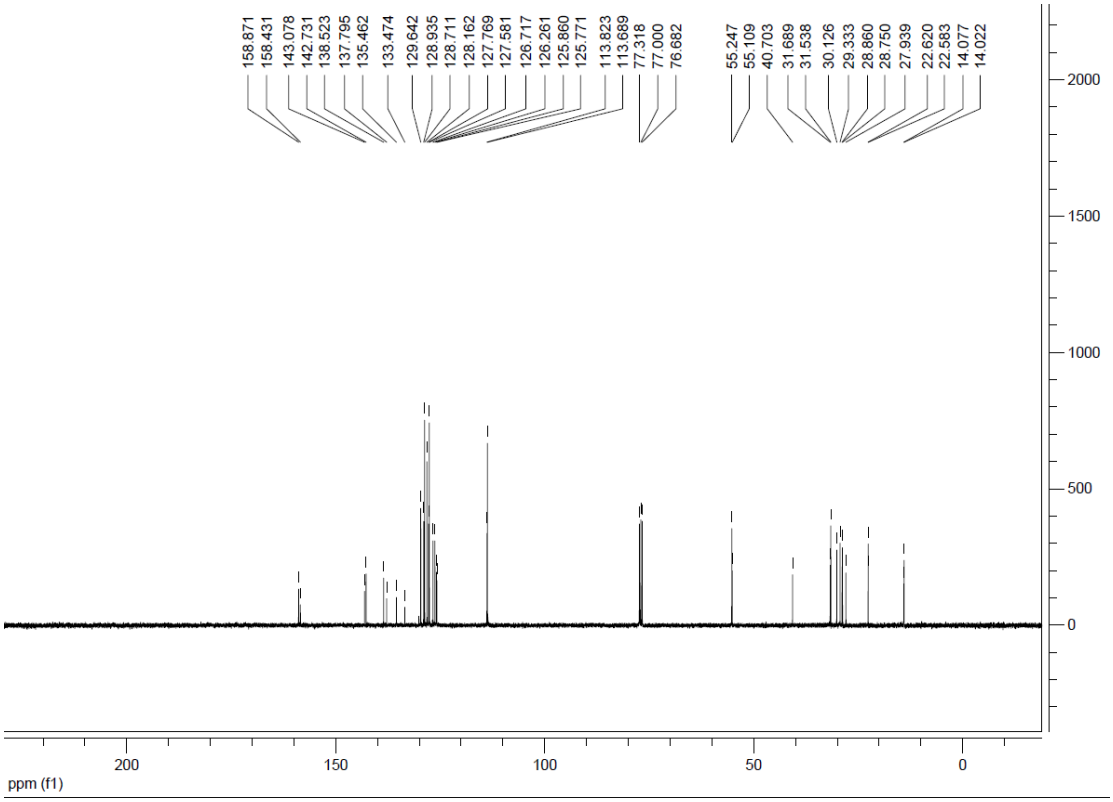


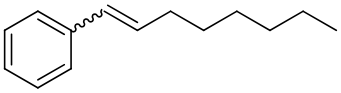




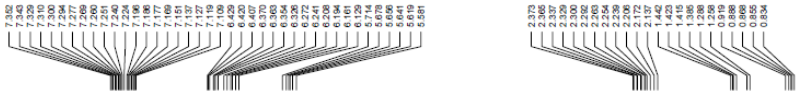
1-methoxy-4-(1-phenyloct-1-en-2-yl)benzene(3t)

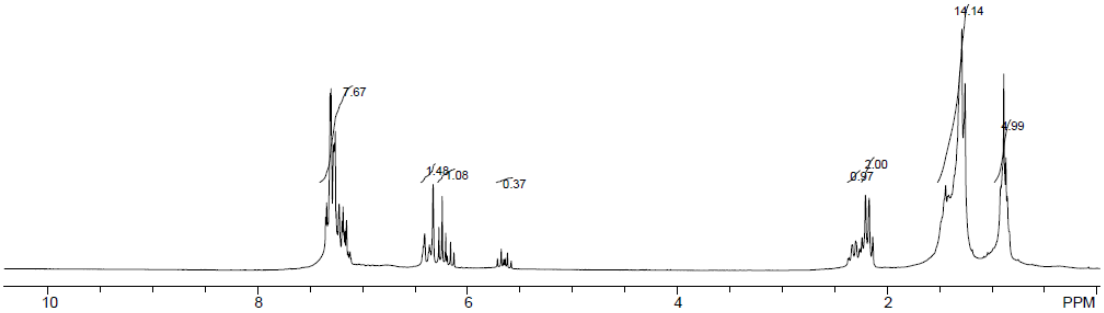


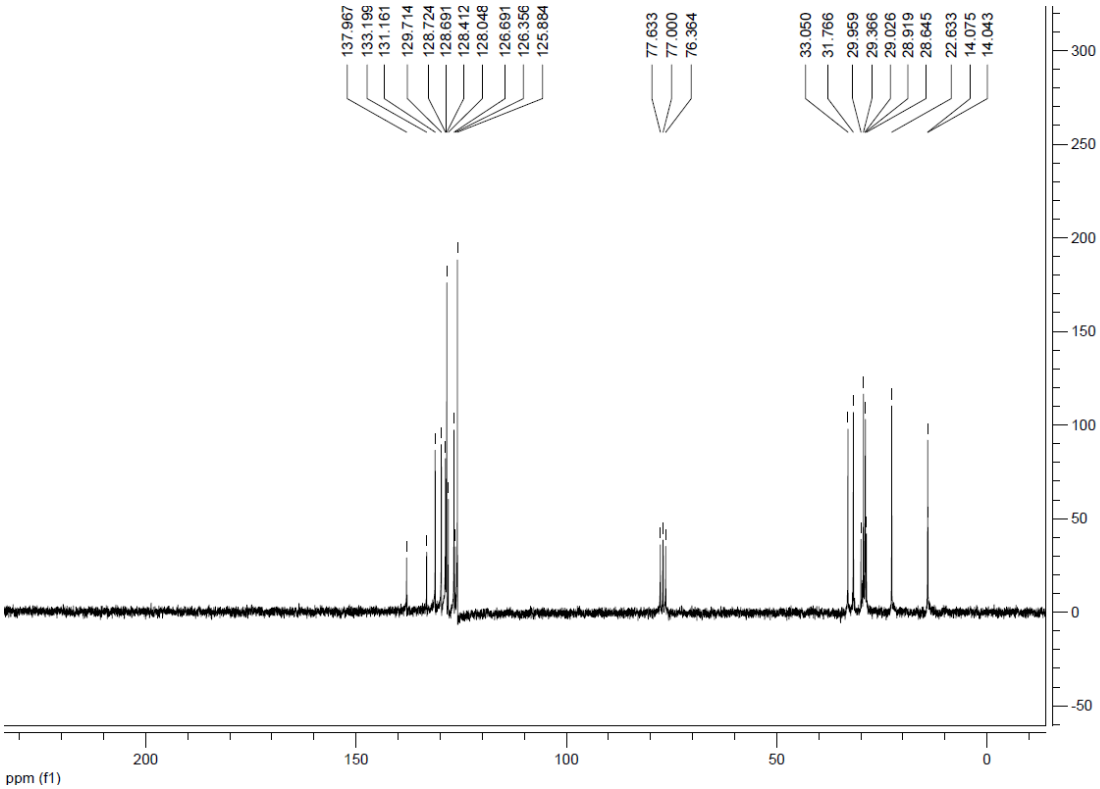


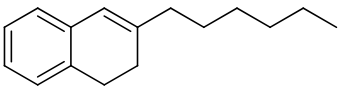


oct-1-enylbenzene (3u)

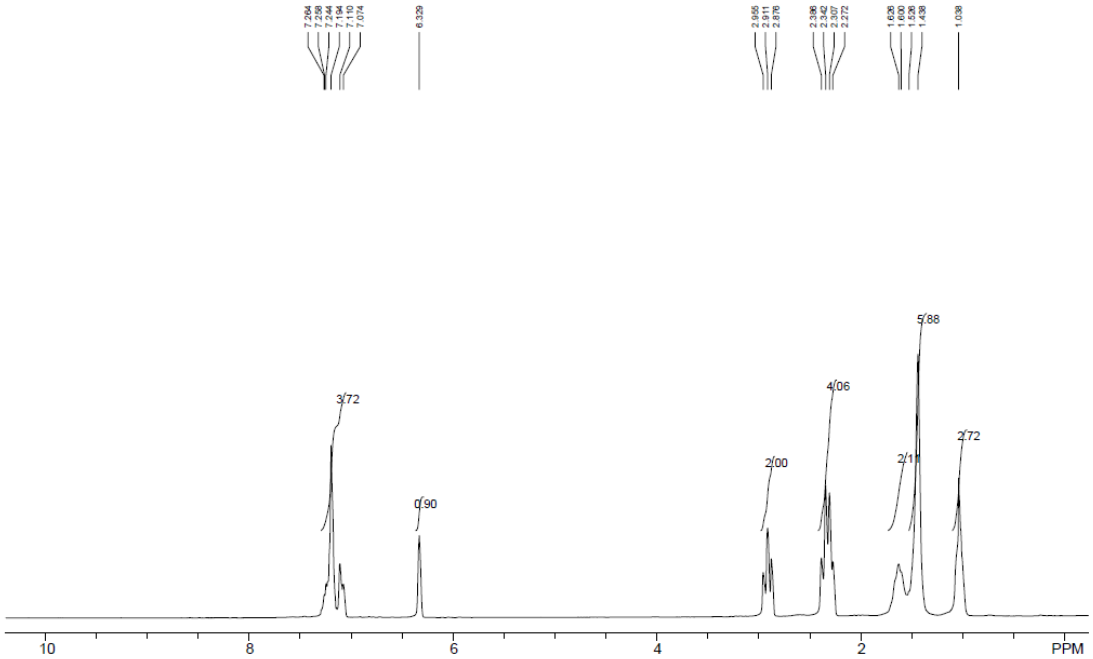


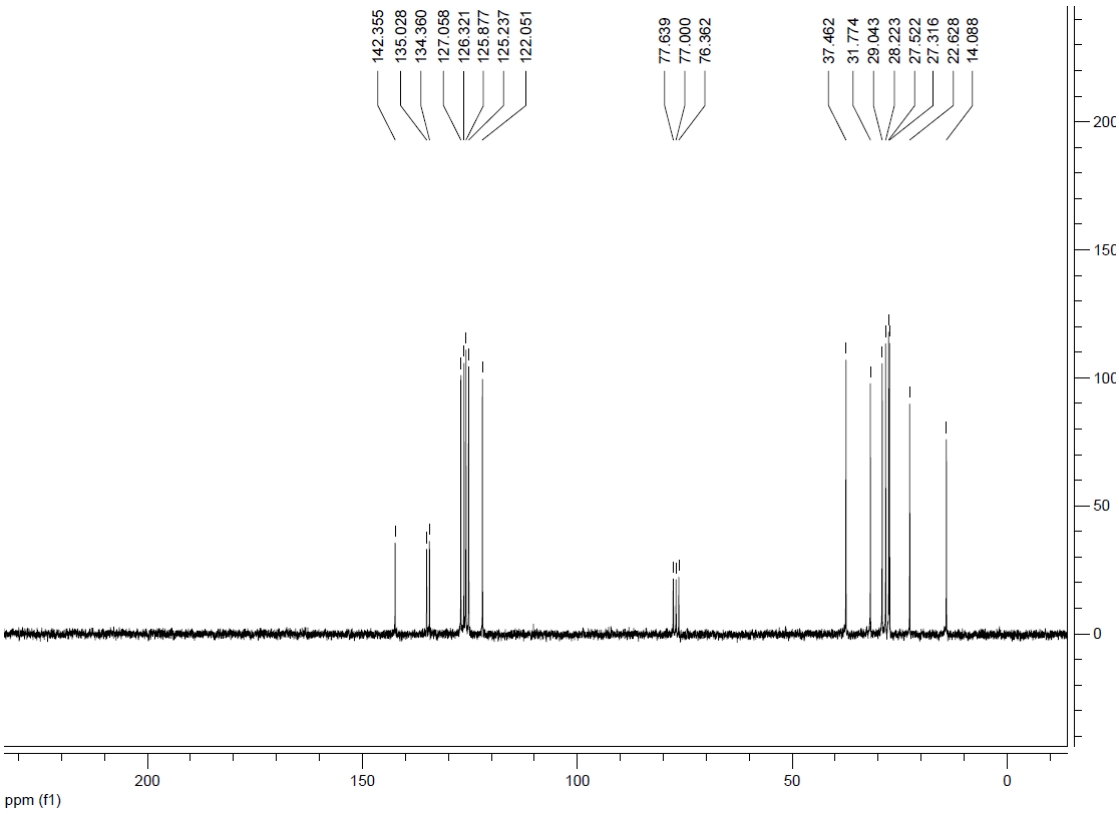


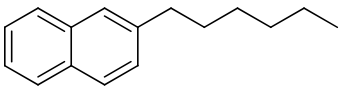
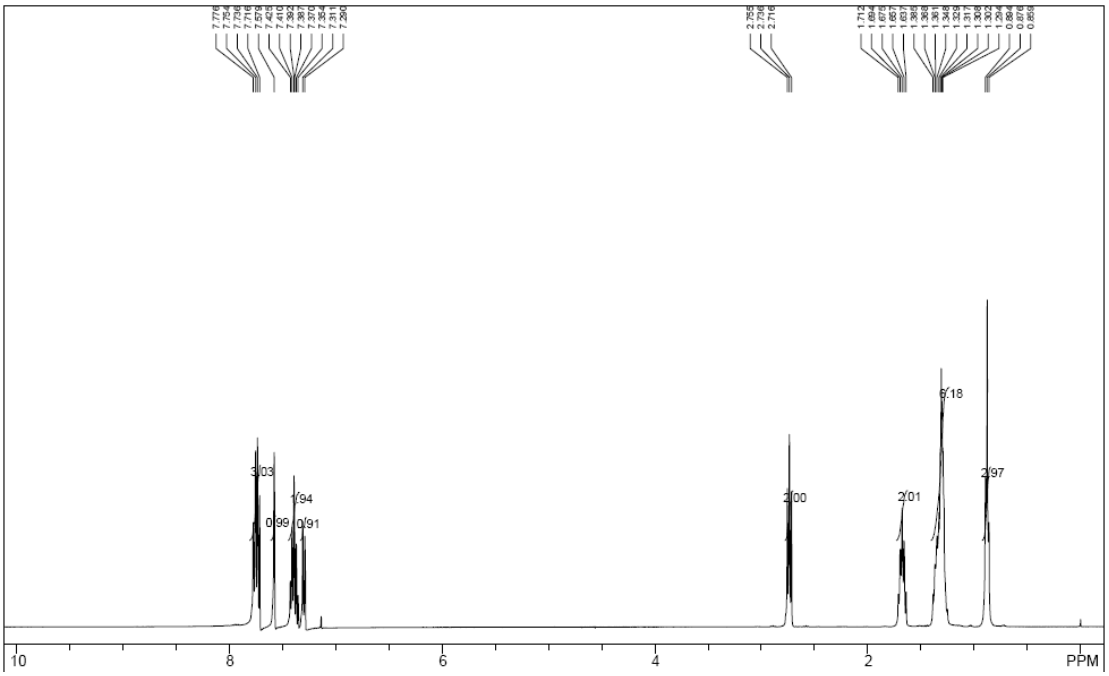
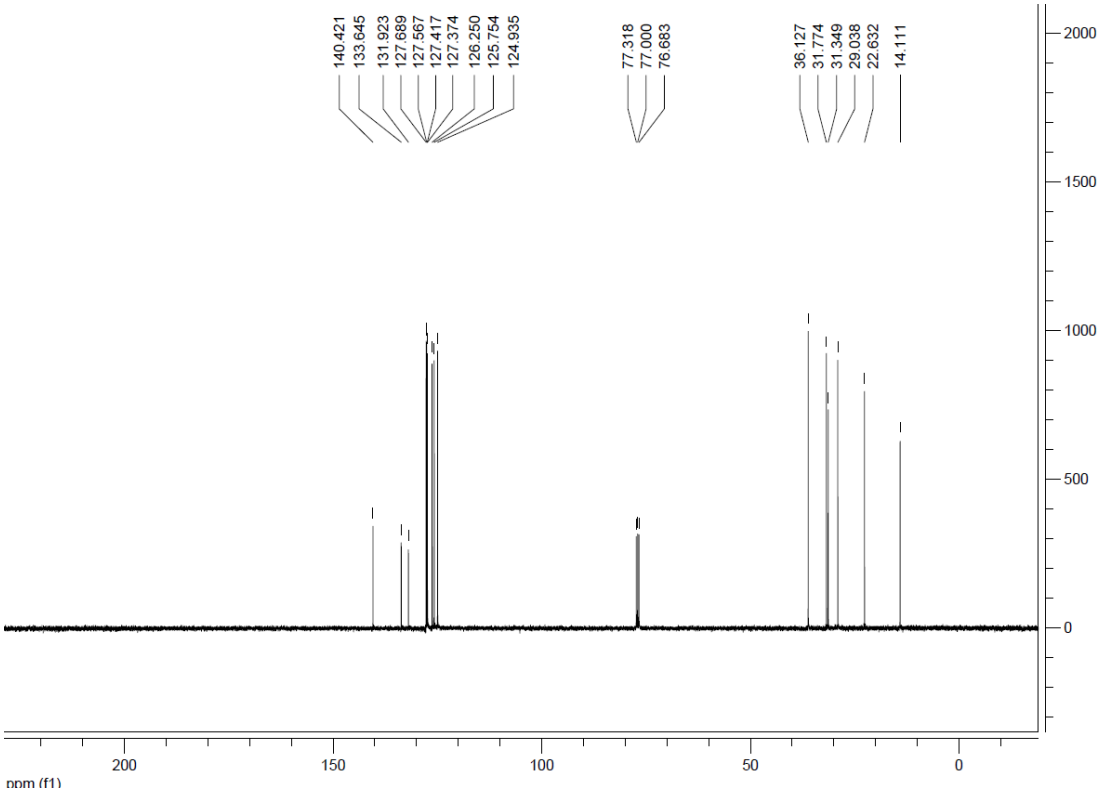




3-hexyl-1,2-dihydronaphthalene (3v)







2-hexylnaphthalene(3w)