

# **Supporting Information**

## **Ni-Catalyzed 1,2-Acyl Migration Reactions Triggered by C–C Bond Activation of Ketones**

Cheng Jiang,<sup>†§</sup> Hong Lu,<sup>†§</sup> Wen-Hua Xu,<sup>†</sup> Jianing Wu,<sup>†</sup> Tian-Yang Yu,<sup>†</sup> Peng-Fei Xu,<sup>‡</sup> Hao Wei\*<sup>†</sup>

<sup>†</sup>Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an 710069, China

<sup>‡</sup>State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

\*E-mail: haow@nwu.edu.cn

### **Table of Contents**

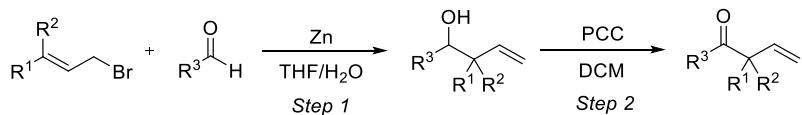
<b>1. General information .....</b>	<b>2</b>
<b>2. Experimental procedures .....</b>	<b>2</b>
<b>2.1 Preparation of substrates 1, 3a-3j.....</b>	<b>2</b>
<b>2.2 Preparation of substrates 3k and 3l .....</b>	<b>2</b>
<b>2.3 Experimental procedures of Ni-catalyzed 1,2-acyl migration reaction .....</b>	<b>3</b>
<b>2.4 Control experiments .....</b>	<b>3</b>
<b>2.5 Optimization details.....</b>	<b>4</b>
<b>3. Crystallographic Data .....</b>	<b>6</b>
<b>3.1 X-ray data for 2i (CCDC 1918052).....</b>	<b>6</b>
<b>3.2 X-ray data for 5o (CCDC 1918051).....</b>	<b>7</b>
<b>4. Computational studies .....</b>	<b>8</b>
<b>5. Spectral data.....</b>	<b>50</b>
<b>6. Copies of NMR spectra.....</b>	<b>79</b>
<b>7. References.....</b>	<b>192</b>

## 1. General information

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques unless otherwise noted. Column chromatography was carried out on silica gel (300–400 mesh) using a forced flow of eluent at 0.3–0.5 bar pressure. Flash column chromatography was carried out using silica gel (200–300 mesh) at increased pressure.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra were recorded on a WNMR-I spectrometer (400 MHz  $^1\text{H}$ , 100 MHz  $^{13}\text{C}$ ) and Bruker AVANCE HD III (600 MHz  $^1\text{H}$ , 125 MHz  $^{13}\text{C}$ ). The spectra were recorded in  $\text{CDCl}_3$  as the solvent at room temperature.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in ppm relative to either the residual solvent peak ( $^{13}\text{C}$ ) or TMS ( $^1\text{H}$ ) as an internal standard. HRMS were performed on Bruker Daltonics MicroTof-Q II mass spectrometer.

## 2. Experimental procedures

### 2.1 Preparation of substrates 1, 3a-3j



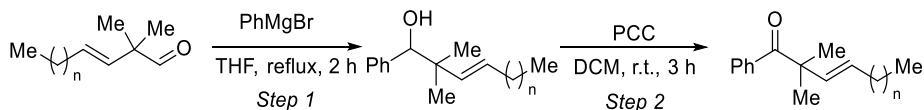
#### Step 1:<sup>1</sup>

**Method A:**<sup>1a</sup> To a solution of aldehyde (10.0 mmol) and brominated substance<sup>2</sup> (12.0 mmol) in THF/H<sub>2</sub>O (30.0 ml/30.0 ml), then Zinc powder (12.0 mmol) was added in portions at 0 °C. The reaction mixture was stirred at room temperature for 12 h. Then, the mixture was filtered and extracted with EtOAc (3×50 ml). The combined organic phase was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the alcohol.

**Method B:**<sup>1b</sup> To a solution of Cp<sub>2</sub>TiCl<sub>2</sub> (0.01 mmol) and Zinc powder (2.4 mmol) in THF (2.0 mmol), then a solution of aldehyde (1.0 mmol) and appropriate allyl bromide (2.4 mmol) in THF (2.0 mL) was added dropwise at RT under an atmosphere of N<sub>2</sub>. The reaction mixture was stirred until all starting material was consumed (monitored by TLC). Then, the mixture was diluted with saturated aqueous NH<sub>4</sub>Cl (10.0 mL) and EtOAc (10.0 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (3×10 ml). The combined organic phase was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the alcohol.

**Step 2:** To a solution of alcohol (10.0 mmol) in DCM (50.0 ml), then PCC (25.0 mmol) was added at room temperature and stirring 3 h. The consumption of alcohol was confirmed by TLC analysis. The reaction mixture was filtered and extracted with EtOAc (3×50 ml). The combined organic phase was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the ketone.

### 2.2 Preparation of substrates 3k and 3l



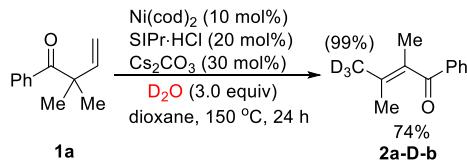
**Step 1:** A 100 mL round bottomed flask was charged with aldehyde (10.0 mmol), then the vessel was placed under vacuum and the atmosphere was exchanged with N<sub>2</sub> three times before adding THF (30.0 ml), PhMgBr (15.0 mmol) was added in portions at room temperature. Then, the mixture was heated to reflux for 2 h. The consumption of alcohol was confirmed by TLC analysis. The mixture was quenched with H<sub>2</sub>O, filtered and extracted with EtOAc (3×30 ml). The combined organic phase was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the ester.

**Step 2** same as Step 2 in **2.1**.

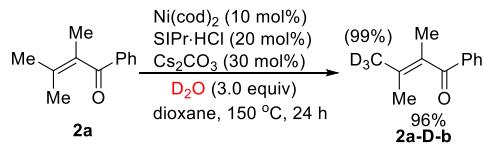
### 2.3 Experimental procedures of Ni-catalyzed 1,2-acyl migration reaction

To a dried sealed tube were added Ni(cod)<sub>2</sub> (0.02 mmol), SiPr-HCl (0.04 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.06 mmol), **1a** (0.2 mmol), dioxane (2.0 ml) in glovebox. The reaction mixture was stirred at 150 °C for 24 h and cooled to room temperature, the crude mixture was filtered through a pad of silica gel. The filtrate was then concentrated in vacuo to give a residue, which was purified by flash column chromatography over silica gel.

### 2.4 Control experiments



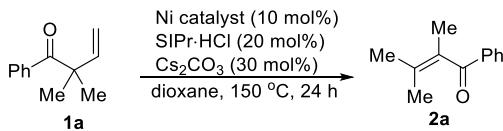
To a dried sealed tube were added Ni(cod)<sub>2</sub> (0.02 mmol), SiPr-HCl (0.04 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.06 mmol), **1a** (0.2 mmol), D<sub>2</sub>O (0.6 mmol) and dioxane (2.0 ml) in glovebox. The reaction mixture was stirred at 150 °C for 24 h and cooled to room temperature, the crude mixture was filtered through a pad of silica gel. The filtrate was then concentrated in vacuo to give a residue, which was purified by flash column chromatography over silica gel.



To a dried sealed tube were added Ni(cod)<sub>2</sub> (0.02 mmol), SiPr-HCl (0.04 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.06 mmol), **2a** (0.2 mmol), D<sub>2</sub>O (0.6 mmol) and dioxane (2.0 ml) in glovebox. The reaction mixture was stirred at 150 °C for 24 h and cooled to room temperature, the crude mixture was filtered through a pad of silica gel. The filtrate was then concentrated in vacuo to give a residue, which was purified by flash column chromatography over silica gel.

## 2.5 Optimization details

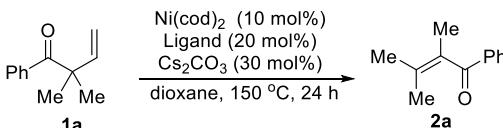
Table S1. Screening of nickel catalysts.<sup>a</sup>



Entry	Catalyst	Yield (%)
1	NiBr <sub>2</sub>	trace
2	Ni(PPh <sub>3</sub> )Cl <sub>2</sub>	trace
3	Ni(cod) <sub>2</sub>	76
4	Ni(N <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	13
5	Ni(dppf)Cl <sub>2</sub>	trace

<sup>a</sup>Standard conditions: **1a** (0.2 mmol), Ni catalyst (10 mol%), SiPr·HCl (20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (30 mol%) and dioxane (2.0 mL) at 150 °C in sealed tube.

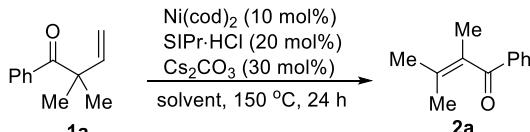
Table S2. Effect of the ligand utilized.<sup>a</sup>



Entry	Ligand	Yield (%)
1	SiPr·HCl	76
2	IPr·HCl	66
3	IPr <sup>Me</sup> ·HCl	46
4	IMes·HCl	31
5	PPh <sub>3</sub>	55
6	dppe	n.r.
7	1,10-phen	n.r.
8	Xantphos	n.r.

<sup>a</sup>Standard conditions: **1a** (0.2 mmol), Ni(cod)<sub>2</sub> (10 mol%), Ligand (20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (30 mol%) and dioxane (2.0 mL) at 150 °C in sealed tube.

Table S3. Effect of the solvent utilized.<sup>a</sup>

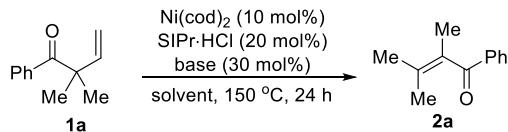


Entry	Solvent	Yield (%)
1	dioxane	76
2	toluene	52
3	dioxane/toluene	66
4	xylene	35
5	DMF	trace
6	NMP	trace

7	DMSO	n.r.
8	Ethylene glycol	n.r.
9	H <sub>2</sub> O	n.r.
10	EtOH	n.r.

<sup>a</sup>Standard conditions: **1a** (0.2 mmol), Ni(cod)<sub>2</sub> (10 mol%), SPr-HCl (20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (30 mol%) and solvent (2.0 mL) at 150 °C in sealed tube.

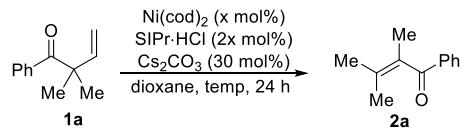
Table S4. Effect of the base utilized.<sup>a</sup>



Entry	base	Yield (%)
1	Cs <sub>2</sub> CO <sub>3</sub>	76
2	CsF	trace
3	K <sub>3</sub> PO <sub>4</sub>	trace
4	K <sub>2</sub> CO <sub>3</sub>	trace
5	NaOH	50
6	Na <sub>2</sub> CO <sub>3</sub>	trace
7	t-BuOK	n.r.
8	NaOEt	37
9	Without base	0

<sup>a</sup>Standard conditions: **1a** (0.2 mmol), Ni(cod)<sub>2</sub> (10 mol%), SPr-HCl (20 mol%), base (30 mol%) and dioxane (2.0 mL) at 150 °C in sealed tube.

Table S5. Screening of catalyst loadings and temperature.<sup>a</sup>



Entry	x (mol%)	temp (°C)	Yield (%)
1	10	150	76
2	5	150	44
3	10	120	46
4	10	160	69

<sup>a</sup>Standard conditions: **1a** (0.2 mmol), Ni(cod)<sub>2</sub> (10 mol%), SPr-HCl (20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (30 mol%) and dioxane (2.0 mL) at 150 °C in sealed tube.

### 3. Crystallographic Data

#### 3.1 X-ray data for **2i** (CCDC 1918052)

Single crystal of product **2i** was obtained through slow evaporation of a solution in diethyl ether-methanol at room temperature.

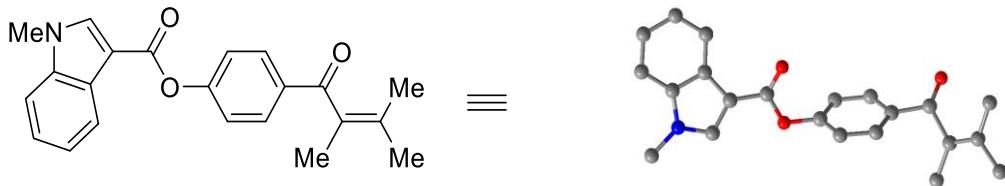


Table S6. Crystal data and structure refinement for **2i**

Empirical formula	C <sub>22</sub> H <sub>21</sub> NO <sub>3</sub>
Formula weight	344.40
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	11.3444(2)
b/Å	16.6403(3)
c/Å	10.0554(2)
α/°	90
β/°	103.695(2)
γ/°	90
Volume/Å <sup>3</sup>	1844.23(6)
Z	4
Density (calculated) g/cm <sup>3</sup>	1.240
μ/mm <sup>-1</sup>	0.639
F(000)	728.0
Crystal size/mm <sup>3</sup>	0.3 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection	8.022 to 134.16°
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 19, -12 ≤ l ≤ 7
Reflections collected	10184
Independent reflections	3280 [R <sub>int</sub> = 0.0428, R <sub>sigma</sub> = 0.0448]
Data/restraints/parameters	3280/0/258
Goodness-of-fit on F <sup>2</sup>	1.061
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0468, wR <sub>2</sub> = 0.1209
Final R indexes [all data]	R <sub>1</sub> = 0.0529, wR <sub>2</sub> = 0.1286
Largest diff. peak/hole / e Å <sup>-3</sup>	0.18/-0.24

### 3.2 X-ray data for **5o** (CCDC 1918051)

Single crystal of product **5o** was obtained through slow evaporation of a solution in ethyl acetate-petroleum ether at room temperature.

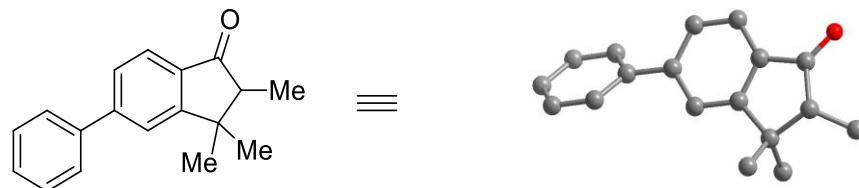
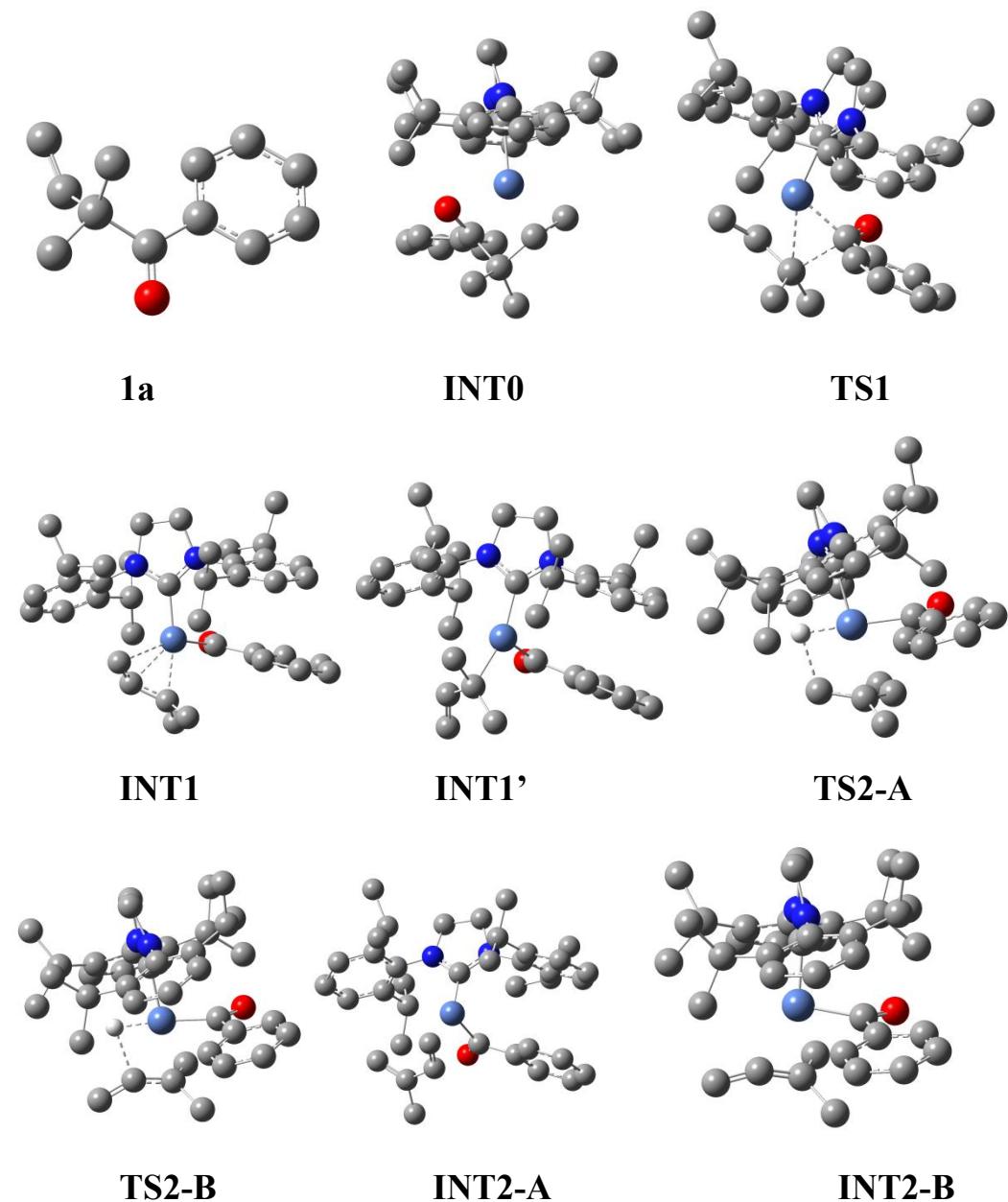


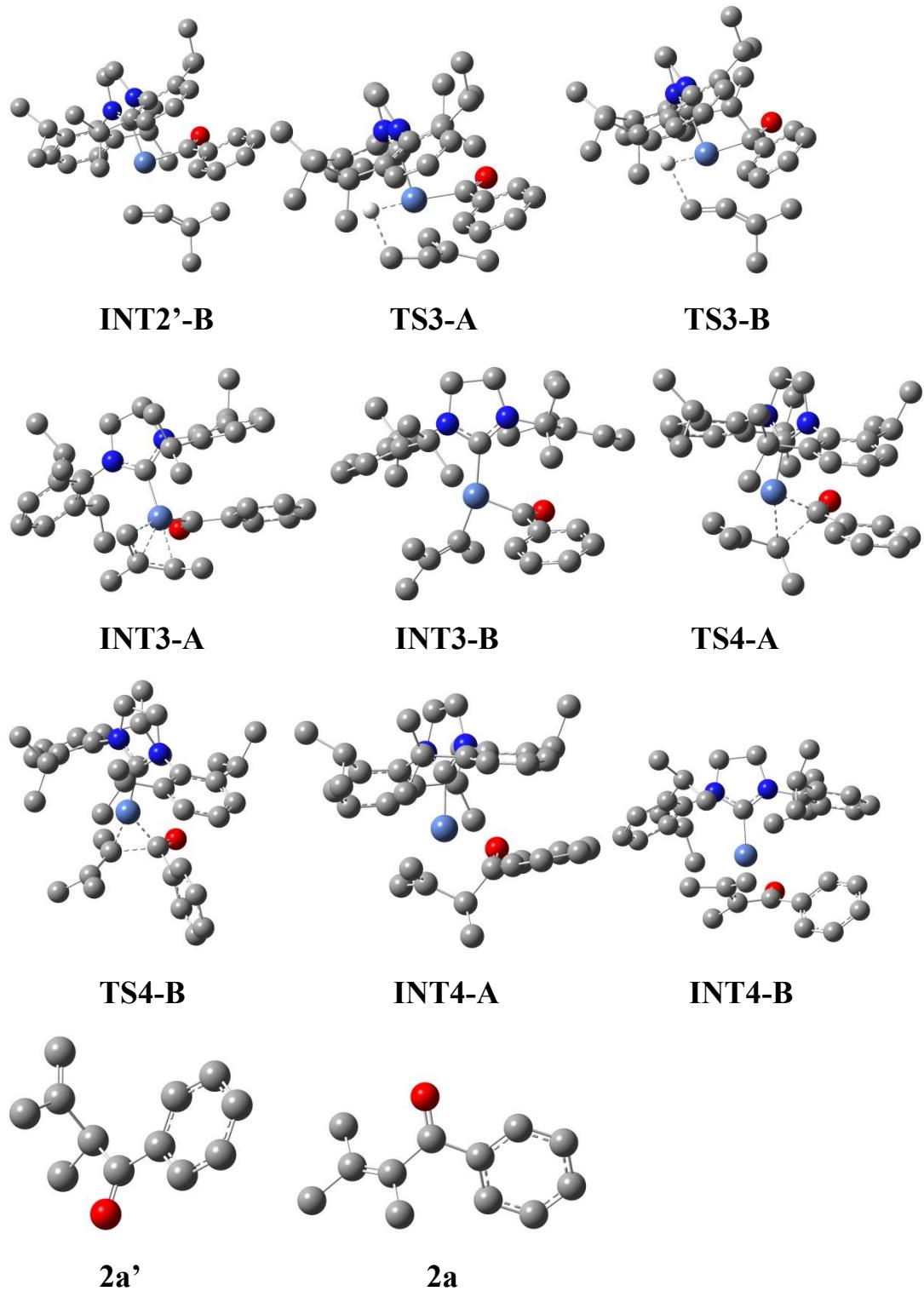
Table S7. Crystal data and structure refinement for **5o**

Empirical formula	C <sub>18</sub> H <sub>18</sub> O
Formula weight	250.32
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	11.5972(5)
b/Å	9.6059(4)
c/Å	13.0289(5)
α/°	90
β/°	107.205(4)
γ/°	90
Volume/Å <sup>3</sup>	1386.49(10)
Z	4
Density (calculated) g/cm <sup>3</sup>	1.199
μ/mm <sup>-1</sup>	0.558
F(000)	536.0
Crystal size/mm <sup>3</sup>	0.2 × 0.2 × 0.2
Radiation	CuKα ( $\lambda = 1.54184$ )
2Θ range for data collection	7.98 to 134.088°
Index ranges	-13 ≤ h ≤ 13, -11 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections collected	6988
Independent reflections	2419 [ $R_{\text{int}} = 0.0461$ , $R_{\text{sigma}} = 0.0529$ ]
Data/restraints/parameters	2419/0/175
Goodness-of-fit on F <sup>2</sup>	1.078
Final R indexes [I>=2σ (I)]	$R_1 = 0.0534$ , $wR_2 = 0.1404$
Final R indexes [all data]	$R_1 = 0.0628$ , $wR_2 = 0.1600$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.65/-0.28

#### 4. Computational studies

The geometries were optimized at the density functional B3LYP-D3<sup>3-5</sup> level of theory. The LANL2DZ type ECP<sup>6</sup> together with the valence basis functions were chosen only for the metal element and 6-31G(d)<sup>7</sup> for the rest. Solvation effects in 1,4-dioxane were treated by the implicit solvation model IEFPCM.<sup>8</sup> The free energies were obtained after vibrational frequency computations. Single-point energies based on the geometry structures obtained at the B3LYP level were obtained by M06L functional<sup>9</sup> using a higher level basis set, i.e., LANL2TZ(f) basis set and pseudopotential<sup>10,11</sup> for Ni and 6-311+G(d,p) basis set for all the other atoms. All calculations were performed with the Gaussian09 program.<sup>12</sup>





**Figure S1.** DFT optimized structures of transition states and key intermediates.<sup>13</sup>

## Cartesian Coordinates and Energies

26

**1a**

C	-4.3494671745	-6.1713055029	1.3359504964
O	-3.8125519846	-6.8065963493	2.2335959081
C	-5.6807734698	-5.5216195079	1.598201176
C	-6.2271267448	-4.4882635566	0.818546794
C	-6.4045919265	-5.9827940454	2.7128535837
C	-7.4662623234	-3.9360284808	1.146092842
H	-5.6751584738	-4.0934100316	-0.0246359938
C	-7.6459700557	-5.4396935083	3.0308374273
H	-5.9735978241	-6.7737761371	3.3173308662
C	-8.1810933899	-4.4124234153	2.2468737445
H	-7.8714358397	-3.1302872536	0.5401592833
H	-8.1966727554	-5.8138739488	3.8895032277
H	-9.1485072652	-3.9842374038	2.4953679483
C	-3.670904875	-6.1027034241	-0.0628540542
C	-2.398002032	-6.9795579082	-0.0208659976
H	-1.9097596184	-6.9572008069	-1.0004829863
H	-1.6917206141	-6.6201245988	0.7323840537
H	-2.6503660404	-8.0142207252	0.2305410113
C	-4.6331558	-6.6707153033	-1.1271861556
H	-5.5350791971	-6.0658648867	-1.2467790199
H	-4.1269924957	-6.7288147689	-2.0967597193
H	-4.9407657288	-7.685157134	-0.8510444537
C	-3.2184591321	-4.6789498808	-0.3493179184
H	-2.6274565127	-4.2302227726	0.4505944833
C	-3.4072957938	-3.9878445324	-1.4753941286
H	-3.9805171482	-4.3778009836	-2.3120933483
H	-2.9890269545	-2.9925292931	-1.5985469101

95

**INT0**

Ni	0.2633296169	-0.6642293576	-0.8250434719
C	0.594074945	0.6888505888	0.5432550017
C	1.834821665	1.6343522884	2.3263010516
C	0.4887545866	2.3637222547	2.2081706911
H	1.8912923104	1.0196359551	3.2314039498
H	2.6968092769	2.3058271353	2.3174349442
H	-0.0687527096	2.3864910754	3.1476252282
H	0.5985678503	3.394109536	1.8461606644
N	-0.2153065086	1.547749234	1.197927296
N	1.8137254476	0.7762692169	1.123122691

C	2.948819557	0.0074292025	0.7045335654
C	3.684066599	0.4419832406	-0.4250994992
C	3.3053031844	-1.1469711835	1.4274107756
C	4.8288254896	-0.2822604972	-0.7726892107
C	4.468174555	-1.8301453523	1.0448388538
C	5.2290210361	-1.3980604643	-0.0357992667
H	5.4185905692	0.0210763776	-1.6309926357
H	4.7708396682	-2.7166160914	1.5949709644
H	6.1282847378	-1.939017812	-0.3190439061
C	-1.5305250006	1.9001513398	0.7591100928
C	-1.6504091986	2.8413065611	-0.2892111526
C	-2.6584258664	1.3417324759	1.3914963462
C	-2.9330103595	3.2047639993	-0.7123977939
C	-3.9202250316	1.7439712469	0.9280262146
C	-4.063252884	2.6595507054	-0.1085687444
H	-3.0467829368	3.9247596526	-1.5183040347
H	-5.0552428603	2.94400151	-0.4499786967
C	2.461571888	-1.675924908	2.5803493119
H	1.5434020983	-1.0843998919	2.6270629308
C	3.2021158662	-1.5317040433	3.9236802958
H	2.5642413185	-1.8627132147	4.7518078562
H	4.1121972383	-2.1436722022	3.9358682964
H	3.5002365492	-0.4938004133	4.1134564515
C	2.0230247695	-3.1326998941	2.3416333133
H	1.4568063843	-3.2138719284	1.4102789232
H	2.8826040133	-3.8124085707	2.3009785902
H	1.3769040242	-3.464106899	3.163756288
C	3.221218497	1.6404851906	-1.2513584208
H	2.129420494	1.580905379	-1.3014051286
C	3.5934223949	2.9800782089	-0.5872390553
H	3.1607593057	3.0740495055	0.4117848767
H	4.6818709768	3.0795010357	-0.4955033576
H	3.2245077177	3.819215936	-1.1898614004
C	3.7332160961	1.6210948351	-2.7002148788
H	3.544773832	0.6562737062	-3.1831654211
H	3.2220075946	2.3979631294	-3.2801868509
H	4.8092961922	1.8248469598	-2.7596640289
C	-0.4327905305	3.4914603968	-0.9384793982
H	0.4671178422	3.0457157613	-0.5090961377
C	-0.3753200635	3.2214982639	-2.4514548421
H	-0.3822487717	2.1464544125	-2.6433784201
H	-1.2248297448	3.6746828781	-2.9759169052
H	0.5437753249	3.6423350113	-2.8778421801
C	-0.3864945134	5.0025236957	-0.6417097007

H	-1.2458095122	5.520646041	-1.083576296
H	-0.3995326522	5.198330904	0.4368014964
H	0.5252175559	5.4463137613	-1.0596651604
C	-0.9955639013	-2.2335258413	-0.9582252016
O	-0.3337836135	-2.4152204895	0.1289877385
C	-2.433482077	-1.8218473878	-0.8297863954
C	-3.0703062369	-0.8958977475	-1.6709362893
C	-3.1750794352	-2.3964546921	0.2163286823
C	-4.4164281547	-0.5814718324	-1.4934751893
H	-2.5016056443	-0.3881056762	-2.440547993
C	-4.5246318693	-2.0900091563	0.387885471
H	-2.6750905995	-3.0863929537	0.8882242297
C	-5.1531342282	-1.1852636064	-0.4719569158
H	-4.8848587752	0.153081	-2.1423591155
H	-5.0852125102	-2.5571465916	1.1937963843
H	-6.2037488356	-0.9414043624	-0.3379149876
C	-0.3783038938	-2.7624726127	-2.2889865232
C	0.2928546126	-4.1191368645	-2.0231241904
H	0.8650262427	-4.431938284	-2.9052163663
H	0.9698742118	-4.0512455629	-1.1680828412
H	-0.4585260025	-4.888136322	-1.8075939195
C	-1.3587385029	-2.902079815	-3.4607034972
H	-1.7799297529	-1.9470595058	-3.7796873779
H	-0.8354445742	-3.3354771738	-4.3210077813
H	-2.1919585666	-3.5626806178	-3.1938066054
C	0.6846979727	-1.6801408805	-2.4961790883
H	1.7253964683	-1.997979239	-2.3954696458
C	0.4306983149	-0.3522816913	-2.8540917457
H	-0.5416271379	-0.046895865	-3.2377963219
H	1.2531615859	0.2922263304	-3.1482206723
H	-4.8054195575	1.3117856805	1.3867453647
C	-2.6569973437	0.3853766506	2.5884500461
H	-3.5329370187	-0.2568460243	2.4297664818
C	-2.9113672482	1.1831054207	3.8862704914
H	-3.8212536376	1.7891030615	3.81510431
H	-3.0158892852	0.5028687469	4.7402170841
H	-2.0758619395	1.8614515554	4.0990207979
C	-1.4646288673	-0.5671201196	2.7740479515
H	-1.177880695	-1.0715136328	1.849035771
H	-0.5841691664	-0.0514487195	3.1702974695
H	-1.7443562626	-1.3335410626	3.5082424242

**TS1**

Ni	0.4658478284	-0.7086483422	-0.8667365096
C	0.4666501056	0.5947906476	0.4960196076
C	1.5339813306	1.7213177182	2.2904316868
C	0.1553037517	2.3451179218	2.0490755231
H	1.5781405372	1.1635785079	3.2327123408
H	2.3479909013	2.45169596	2.2813684053
H	-0.4483440236	2.4167881292	2.9555263293
H	0.2160837053	3.3434923994	1.5940267274
N	-0.4472551939	1.4018544683	1.0844207454
N	1.641405396	0.7975253711	1.1473331096
C	2.8911529663	0.2370216088	0.7249965782
C	3.7007269417	1.0038448719	-0.1379981249
C	3.2716838643	-1.0482252176	1.165535325
C	4.906506766	0.4459616625	-0.5794126819
C	4.4905447151	-1.5588951392	0.7022629792
C	5.2981550288	-0.8249868483	-0.1654458696
H	5.5407257578	1.0089809815	-1.2586091181
H	4.8121562332	-2.545492979	1.0199769575
H	6.2366981313	-1.2452834976	-0.5175667909
C	-1.7725992411	1.6566207237	0.6146530179
C	-1.935942255	2.4188638049	-0.5655106244
C	-2.875977164	1.2244592149	1.3783120022
C	-3.2345174641	2.7468203675	-0.9694444699
C	-4.1534111155	1.5949461159	0.9327599949
C	-4.3380576925	2.3504411972	-0.2191954233
H	-3.3812533533	3.3258684661	-1.877090826
H	-5.3416358147	2.6137860547	-0.5428614595
C	2.407052514	-1.841346616	2.1373508583
H	1.3780111587	-1.4889928776	2.0325284248
C	2.8719806839	-1.5906066388	3.5867823301
H	2.2108747639	-2.1031620027	4.2956576409
H	3.8910364976	-1.9689264581	3.73678248
H	2.8773062472	-0.5236614162	3.8353471397
C	2.382711511	-3.3474485237	1.8373726144
H	2.0703601818	-3.5299477857	0.8070569008
H	3.3574956515	-3.8196016983	2.0106498621
H	1.653869155	-3.8380200545	2.4907261305
C	3.2803688336	2.3870979319	-0.6211612703
H	2.3727128337	2.6735247769	-0.0824201687
C	4.34746202	3.4541313424	-0.3197233103
H	4.5945919977	3.4788893359	0.747963922
H	5.2748150589	3.2655231408	-0.8726143341

H	3.9845345831	4.4466973323	-0.6117127631
C	2.9155101709	2.3614819182	-2.1162932005
H	2.1218312939	1.6320982053	-2.2999918881
H	2.5674370946	3.3488903085	-2.4439461356
H	3.7821311845	2.0860881954	-2.729423952
C	-0.7548108049	2.9022916188	-1.4012579076
H	0.1691003929	2.6062068916	-0.900270828
C	-0.7388789807	2.2272446422	-2.7846686515
H	-0.598173852	1.1465861785	-2.6716547425
H	-1.6725715174	2.4060585213	-3.3305927795
H	0.0893020814	2.6126769346	-3.3901585934
C	-0.7339243206	4.4368306359	-1.5260134581
H	-1.6005541878	4.8113225027	-2.0829297793
H	-0.7393322257	4.9145718068	-0.5393821629
H	0.1687938689	4.7598743408	-2.0584554811
C	-0.8413870833	-2.0701467209	-0.3887824605
O	-0.3960463013	-2.696057662	0.5923768585
C	-2.3309705944	-1.8600906088	-0.4922779627
C	-2.906845441	-0.8883206496	-1.319358029
C	-3.1718997498	-2.6839888699	0.2726340767
C	-4.291459452	-0.761509917	-1.4087916036
H	-2.261259779	-0.2141553685	-1.8688215989
C	-4.5578774892	-2.5526934086	0.1940386134
H	-2.7132727666	-3.4207029121	0.9248114875
C	-5.1218461236	-1.5953609235	-0.6553093493
H	-4.7209509378	0.005602288	-2.04580099
H	-5.1991720421	-3.1990932616	0.7884011633
H	-6.2021680897	-1.4941351842	-0.7227821299
C	-0.0567977863	-2.6415889068	-2.0545703157
C	-0.0915769353	-4.1492045576	-1.79084894
H	0.3069669773	-4.6864708806	-2.6630928362
H	0.5062498191	-4.4064732297	-0.9140708312
H	-1.1177055947	-4.4916215136	-1.6153009876
C	-0.9154648266	-2.2721407526	-3.2607118338
H	-0.960735675	-1.1939812078	-3.4327384877
H	-0.4895749179	-2.7345058362	-4.1624753404
H	-1.9398453173	-2.6342031975	-3.143024592
C	1.3323379618	-2.1230752723	-2.1086957257
H	2.0588523528	-2.6488988683	-1.485800904
C	1.7786057436	-1.0273434823	-2.8087224579
H	1.1781604811	-0.5181175009	-3.5558737401
H	2.8128503245	-0.715559406	-2.7142709834
H	-5.0200400857	1.2600038322	1.4972635246
C	-2.8384139445	0.403244564	2.6737570257

H	-3.6965641404	-0.277074189	2.5863303271
C	-3.1161555938	1.3167062412	3.8880652435
H	-4.0413654614	1.8888430196	3.7603979031
H	-3.2052576867	0.7189001922	4.802966692
H	-2.3007019477	2.0348040409	4.0372665157
C	-1.623699317	-0.4974375331	2.9513170005
H	-1.3451151711	-1.1098183208	2.09299732
H	-0.7428274063	0.0697250515	3.2665886927
H	-1.8795315356	-1.1739127461	3.7764823261

95

**INT1**

Ni	0.2790887062	0.8790866741	0.7885362723
C	0.5975082306	-0.7289424922	-0.2645572299
C	1.7770276549	-2.2537309879	-1.6353614419
C	0.3529691025	-2.7706121616	-1.428069799
H	1.9507098563	-1.9052082291	-2.658944987
H	2.5419554943	-2.9914268884	-1.3903796661
H	-0.1583719749	-3.0128723752	-2.3613544413
H	0.3098434848	-3.6523746852	-0.7751771622
N	-0.290559354	-1.6255758244	-0.7559860561
N	1.8258035596	-1.109833994	-0.7002365825
C	3.0616462876	-0.4028497577	-0.5062182275
C	4.0480357444	-0.9457875777	0.3477103631
C	3.2865343223	0.8019336752	-1.2180292609
C	5.2621123011	-0.2509702964	0.4680631166
C	4.5182253811	1.4473562183	-1.0582390873
C	5.5037429961	0.9287137125	-0.2241655706
H	6.0268928215	-0.6494243454	1.1307947276
H	4.7084955035	2.3701366868	-1.5957659188
H	6.4523395976	1.4463299259	-0.1089220955
C	-1.688184311	-1.697764476	-0.4439435202
C	-2.0696321665	-2.2048833749	0.8202542189
C	-2.6467318634	-1.3373703886	-1.4144166251
C	-3.4307903693	-2.294738612	1.1226566804
C	-3.9989061432	-1.4379632289	-1.0499091847
C	-4.3935238608	-1.9037535416	0.1973947209
H	-3.7382392823	-2.6656563992	2.0964549063
H	-5.4488347061	-1.9550935439	0.4501444352
C	2.2554334513	1.3941153401	-2.1717372239
H	1.2662702528	1.0517477653	-1.870904492
C	2.5143011613	0.9241750395	-3.6170430385
H	1.7362508386	1.3101412176	-4.2858821484
H	3.4858492564	1.2874869739	-3.9750350698

H	2.5191625544	-0.1677102906	-3.699684446
C	2.1999204216	2.929094826	-2.1174759909
H	2.1049349443	3.2785158192	-1.0856386151
H	3.0884290272	3.3924439675	-2.5637077617
H	1.3197240238	3.2783933567	-2.6622141315
C	3.9649433483	-2.2333371626	1.1798537956
H	4.5318138242	-2.0025461096	2.0919222809
C	2.584712346	-2.7017147247	1.6618876904
H	1.9787441773	-1.8672620392	2.0204852464
H	2.0242296133	-3.2181305631	0.8789251274
H	2.7160460628	-3.415831015	2.4836226579
C	4.7238674973	-3.3849802182	0.4860803555
H	5.7515639782	-3.0944760829	0.2441207635
H	4.7594762141	-4.2656261773	1.1384942127
H	4.2354200641	-3.6821119585	-0.4489030853
C	-1.0483981817	-2.669792863	1.8495670321
H	-0.0609367898	-2.6137877931	1.3946208048
C	-1.0206583742	-1.7450179597	3.0780838415
H	-0.7527968711	-0.7279756164	2.7771157371
H	-1.9958518452	-1.7117469605	3.5783181534
H	-0.2757008978	-2.091488101	3.8045629081
C	-1.2761215308	-4.13654008	2.2586100893
H	-2.2268851077	-4.2687312782	2.7876201982
H	-1.2872333119	-4.7945273528	1.382020118
H	-0.4741399987	-4.4701143761	2.9278486893
C	-1.0469805522	1.7345567664	-0.2569362649
O	-0.6998987332	2.3781472848	-1.250193674
C	-2.5230264482	1.7168305108	0.0816311868
C	-2.9977661141	1.1020637991	1.2433011544
C	-3.437857101	2.3445496	-0.7794161819
C	-4.3562433925	1.1297501291	1.5597873916
H	-2.2931399218	0.589351827	1.887048526
C	-4.7970638936	2.3613710666	-0.4765667649
H	-3.0530445255	2.8126637592	-1.6804285297
C	-5.2587931288	1.7598027074	0.7006739645
H	-4.7115189038	0.6451729561	2.4653800215
H	-5.4997715003	2.8466683201	-1.1498476779
H	-6.3188720588	1.7776546047	0.9416203287
C	0.3029515677	2.6338438697	2.0721118465
C	-0.6101257349	2.4027416635	3.2634333987
H	-0.5595539002	1.3822567226	3.6530048642
H	-0.3378486783	3.0846161141	4.0857942107
H	-1.6520881684	2.6077414242	3.0006447326
H	-4.7548768632	-1.1331338323	-1.7690031315

C	-2.4010188334	-0.9177023964	-2.8707860644
H	-3.1792888929	-0.1700150621	-3.0760722939
C	-2.6822852468	-2.1195237186	-3.8015284958
H	-3.6760662452	-2.5438336404	-3.6242033951
H	-2.621660768	-1.8108785778	-4.8519369712
H	-1.9483632047	-2.9195088003	-3.6450423106
C	-1.0739332262	-0.2494531627	-3.2597614876
H	-0.8276031317	0.5838576362	-2.6046316181
H	-0.2329745837	-0.947199651	-3.2703128692
H	-1.1723872557	0.1429741564	-4.2794531162
C	1.6032203535	2.0349690747	2.0413253072
H	2.3345540561	2.4987328517	1.3754876647
C	1.9387270915	0.7873405659	2.5480513526
H	2.9165691885	0.3722727428	2.3432693518
H	1.3436589715	0.2913703522	3.3088204411
C	0.1463023584	4.0076003564	1.4515790605
H	-0.8993175236	4.1975830557	1.1851961537
H	0.4562608517	4.7981437618	2.1540906049
H	0.7367630103	4.105026896	0.5360395602

95

**INT1'**

Ni	-0.8933517186	-0.9765475313	-0.2399127024
C	-2.5244721632	-1.9850514477	0.0712790822
C	-4.4428765359	-3.1977394111	-0.5859880599
C	-4.3278076307	-3.2208435511	0.9436165414
H	-5.2839992919	-2.5861892088	-0.9288410802
H	-4.5333736145	-4.1926542867	-1.0280405561
H	-5.2455669499	-2.9124167298	1.4475335622
H	-4.0335819485	-4.2055310474	1.3312182843
N	-3.2368933694	-2.2530167055	1.1851418832
N	-3.1666465143	-2.5602724254	-0.9680514919
C	-2.6474646222	-2.5662452631	-2.3059057469
C	-1.949064682	-3.7122480878	-2.7410808707
C	-2.8193259753	-1.4310755215	-3.1290530224
C	-1.4067993489	-3.7009578429	-4.0321028133
C	-2.251300387	-1.4692400531	-4.4084726608
C	-1.5493291913	-2.5876745129	-4.8559312393
H	-0.8651443483	-4.570672628	-4.3930447729
H	-2.3564823658	-0.6119015596	-5.0645500978
H	-1.1152446191	-2.5909304976	-5.8522690387
C	-2.7742584436	-2.0194643153	2.519932061
C	-1.7216171704	-2.8241450607	3.014289658
C	-3.4006123372	-1.0406577349	3.3168603475

C	-1.2950283193	-2.6230356505	4.3306733606
C	-2.9283750903	-0.880762097	4.6281491355
C	-1.893607782	-1.6578143155	5.1350619895
H	-0.4837189073	-3.2266923004	4.7279363851
H	-1.5449053464	-1.5022006109	6.1523790688
C	-3.6418430649	-0.2324281922	-2.6693788122
H	-3.5709637766	-0.1730387096	-1.5807928813
C	-5.1210984376	-0.4372372053	-3.0597438157
H	-5.7373421577	0.3772821675	-2.6613286581
H	-5.2330062293	-0.4463260788	-4.1512385613
H	-5.5205396429	-1.3842683976	-2.6813589517
C	-3.1340634701	1.1138451178	-3.2055996366
H	-2.0928975324	1.2788259756	-2.9237133913
H	-3.2385239311	1.1896797553	-4.2951769166
H	-3.7239796519	1.9221352801	-2.7610541908
C	-1.8031892629	-4.9546942943	-1.8681072704
H	-2.1825835499	-4.7144625134	-0.8704600869
C	-2.6538272723	-6.1114062629	-2.4302292549
H	-3.7044599246	-5.8205810366	-2.5426989564
H	-2.2895027809	-6.4178439697	-3.4178344548
H	-2.6067949899	-6.9835441877	-1.7674053352
C	-0.3399190087	-5.3995434219	-1.6912840632
H	0.2704875217	-4.6050380088	-1.2530418035
H	-0.2914842107	-6.2701880925	-1.0264289346
H	0.1146501499	-5.6861564423	-2.646134383
C	-1.0493141009	-3.9057291088	2.1739506681
H	-1.5140048229	-3.9184173736	1.1855485625
C	0.4430549126	-3.6019054989	1.9522956385
H	0.5676018217	-2.6292060023	1.4661281563
H	0.9951213536	-3.5846981459	2.899052715
H	0.8972809514	-4.3648867776	1.3089980334
C	-1.2479316093	-5.3041536042	2.7875383777
H	-0.762524315	-5.3859717076	3.7668620775
H	-2.3119909943	-5.5300021135	2.9230839693
H	-0.8145011924	-6.0709179908	2.1340797959
C	-1.4042711801	0.69893418	0.3839301512
O	-2.0620240343	1.4678847559	-0.3116328674
C	-1.0842778112	1.1107571269	1.8068221808
C	-0.2077084317	0.3726052046	2.6081914273
C	-1.6909848041	2.2595545117	2.33912075
C	0.0751368029	0.7774344738	3.9120465938
H	0.2409784804	-0.5272775792	2.2023055986
C	-1.4245170261	2.6586358331	3.6471949564
H	-2.3683783794	2.8220853487	1.7039436149

C	-0.5343933026	1.9200833418	4.4353541284
H	0.755074462	0.1922795082	4.5250224297
H	-1.9029414168	3.5464108988	4.0539312056
H	-0.3219507992	2.232277057	5.4549121969
C	0.8029191975	-0.3731973418	-1.0170961369
C	1.87938438	0.1914503612	-0.102947225
H	2.0860105155	-0.4879033285	0.7309565862
H	2.8246372445	0.3609781388	-0.6439900894
H	1.5692632055	1.1475787977	0.3303140498
H	-3.3797642144	-0.1161144345	5.2551140005
C	-4.5932249496	-0.1577057743	2.9295513872
H	-4.4047331616	0.7965842041	3.4394164631
C	-5.8886316532	-0.7408864591	3.5366531935
H	-5.7916743216	-0.8972052275	4.6163014452
H	-6.7325196575	-0.0631844486	3.3610013232
H	-6.1362145175	-1.7082001089	3.0826755326
C	-4.8140795769	0.198811686	1.4505384321
H	-3.9058458007	0.5560475575	0.9662342172
H	-5.2046787762	-0.6399678291	0.8674014293
H	-5.5603337204	1.0009602862	1.3969997005
C	0.9200905564	-1.8671086579	-1.3183286399
H	0.0168022435	-2.4678040221	-0.9731003388
H	0.961877199	-2.1036599568	-2.386254573
H	1.757313075	-2.3382772059	-0.7957579892
C	0.4729690082	0.4367807196	-2.2033871901
H	-0.1271363168	-0.0796264649	-2.9545110998
C	0.7907136281	1.7221203721	-2.4334696013
H	0.4481775034	2.2315368819	-3.330049907
H	1.3656451115	2.3156179306	-1.7277331778

95

### TS2-A

Ni	0.3580066789	-0.6072605333	-0.9387042678
C	0.4040949403	0.65457373	0.4464819294
C	1.3848032822	1.9416291068	2.1640101692
C	0.0062475316	2.5186011058	1.8226086243
H	1.4055901013	1.4731682617	3.1537898367
H	2.18555003	2.682919997	2.1135169192
H	-0.6271069672	2.6655442065	2.6992379807
H	0.0697842809	3.4695726186	1.2766430777
N	-0.5507937893	1.4784697849	0.935498339
N	1.5510821241	0.9199408772	1.1137212722
C	2.8261880351	0.3454013538	0.7963364635
C	3.6660979298	1.0392557001	-0.1015498045

C	3.2072730133	-0.875749164	1.3891183143
C	4.9101327142	0.4743559209	-0.4057890802
C	4.4640593329	-1.3959513135	1.0549151279
C	5.306152259	-0.7334835128	0.1648223891
H	5.5779254267	0.9884532364	-1.0914270821
H	4.7863383487	-2.3348690756	1.4927769479
H	6.2757014424	-1.1582753204	-0.0825359898
C	-1.8815687239	1.6174835152	0.4267308077
C	-2.0657926193	2.2669836328	-0.8158581107
C	-2.9723668472	1.1641004442	1.197150253
C	-3.3712769463	2.4465260699	-1.2845548703
C	-4.2582881264	1.3695036264	0.6751556896
C	-4.4632961847	2.0021367959	-0.5450834861
H	-3.5326645482	2.9425369019	-2.2376045403
H	-5.472467403	2.1390306038	-0.9243609335
C	2.3136580222	-1.5844602707	2.3992673601
H	1.2833418885	-1.273741181	2.2105790148
C	2.7030895302	-1.1663660451	3.8326703345
H	2.0165869487	-1.6128079467	4.5619512714
H	3.7190815829	-1.5061844883	4.0701137996
H	2.6820827742	-0.0790744992	3.9649445378
C	2.3366340576	-3.1143937221	2.2654320543
H	2.0796072922	-3.4110129936	1.2477889903
H	3.313102885	-3.5361464021	2.5350939909
H	1.5908512017	-3.549400992	2.9391491073
C	3.2796782235	2.3882374698	-0.6970428984
H	2.230382227	2.5753245836	-0.4521216994
C	4.1237188738	3.5175617765	-0.0721556548
H	4.0398323858	3.5291113441	1.0205937477
H	5.1848029971	3.3923162418	-0.3186714919
H	3.8021080239	4.4950296495	-0.4512479051
C	3.3915038726	2.4196059065	-2.2314501086
H	2.7780656558	1.6334592645	-2.6802949218
H	3.0423857809	3.3868730919	-2.6128972399
H	4.4267092853	2.2869438051	-2.5665237232
C	-0.9006320244	2.8004745814	-1.6423888543
H	0.0318106156	2.5100610341	-1.1556968948
C	-0.8649275203	2.1729950915	-3.0466707846
H	-0.7972481719	1.0835858428	-2.9722164814
H	-1.7560008177	2.4308945335	-3.6309501254
H	0.0150678465	2.5270634272	-3.5966468609
C	-0.9305495666	4.3384557068	-1.7184888499
H	-1.8283834481	4.6962916703	-2.2361894455
H	-0.9237535862	4.7857569806	-0.7175485906

H	-0.0559461719	4.7103717128	-2.2658803037
C	-0.7797175004	-1.8895130402	-0.045550165
O	-0.3489836156	-2.6851957579	0.7916685963
C	-2.2735338586	-1.919427159	-0.3295838409
C	-2.8272459433	-1.1619406679	-1.3675986928
C	-3.121725172	-2.7114281882	0.4600957494
C	-4.1962796661	-1.2025462224	-1.6290322179
H	-2.1753920467	-0.5246637165	-1.9573144496
C	-4.4934067536	-2.7412395565	0.2167231857
H	-2.6768643681	-3.293556327	1.2619943151
C	-5.0329128881	-1.9904302798	-0.8348161465
H	-4.6125455634	-0.6042645127	-2.4347060538
H	-5.1450404784	-3.350862425	0.8384262597
H	-6.1024806048	-2.0156894428	-1.0286775187
C	0.8305874126	-2.1707373548	-2.5899467656
C	-0.4332121924	-2.6056210805	-3.3097359749
H	-0.9706823459	-1.750298769	-3.7300224661
H	-0.1803553444	-3.2851974565	-4.136745498
H	-1.1209409859	-3.1348480647	-2.6440413279
H	-5.1137386297	1.0075862791	1.2399262975
C	-2.9253464206	0.5084326995	2.5839594965
H	-3.7316104635	-0.2369414802	2.5601962751
C	-3.3077648596	1.5468597579	3.6623539953
H	-4.2651500428	2.0283324221	3.4368909118
H	-3.3869846143	1.0664020066	4.6448044362
H	-2.5495198669	2.3359744969	3.7362988236
C	-1.6655921386	-0.2590051317	3.0156098857
H	-1.3198113918	-0.9600630022	2.2572812257
H	-0.8348266556	0.4036689878	3.2726219582
H	-1.9054166557	-0.8342455408	3.9182618254
C	1.4620319766	-0.9722622748	-2.944282044
H	1.2593793143	0.4292461111	-1.7308060196
H	2.5221047858	-0.8307445259	-2.7639475399
H	1.0402159312	-0.3574459361	-3.7333071144
C	1.5342215711	-3.2173662424	-1.8196281092
H	0.9023645083	-4.0503404118	-1.5154083863
C	2.824241419	-3.2328622837	-1.4513683493
H	3.515065908	-2.4264022602	-1.6797449248
H	3.2249066802	-4.0538929033	-0.865187383

95

**TS2-B**

Ni	0.2809030912	-0.5194370527	-1.0068584649
C	0.4148764456	0.5539960034	0.5310681917

C	1.4881476595	1.6613631899	2.3174212352
C	0.0736939971	2.2285526473	2.1462892361
H	1.5970733453	1.0921683202	3.2461826009
H	2.2643794439	2.4291671092	2.2875909956
H	-0.4986164351	2.2439851967	3.0759322979
H	0.0741583987	3.2414491866	1.7223715029
N	-0.5192460363	1.288970408	1.1757592019
N	1.5982789485	0.7631067927	1.1523897631
C	2.8516883272	0.2059203374	0.7309337123
C	3.6547978617	0.9552074455	-0.1553692927
C	3.2526393172	-1.0558676196	1.219816467
C	4.8791517932	0.4075372713	-0.5551729611
C	4.4854160845	-1.5602266685	0.7867381939
C	5.2903107101	-0.8404982411	-0.0935269869
H	5.5168435133	0.9639311882	-1.2358354187
H	4.8205038344	-2.5290777383	1.1423545444
H	6.2425960423	-1.252415973	-0.4175988297
C	-1.8903859514	1.4277558834	0.7882134458
C	-2.1966430729	2.234284317	-0.3310714796
C	-2.8979975705	0.8087624564	1.5568974018
C	-3.5402928378	2.4019942948	-0.6816360932
C	-4.2270437803	1.007011736	1.1541981104
C	-4.5515055977	1.7916433786	0.0539839084
H	-3.7955681968	3.0186688688	-1.5387881663
H	-5.5911816083	1.9190936067	-0.2355852169
C	2.4131550155	-1.8283916421	2.2298524906
H	1.3765876378	-1.4983688207	2.1259190693
C	2.8907911528	-1.5176878127	3.6644737624
H	2.2407725169	-2.0072359913	4.3995316799
H	3.9129166276	-1.8867008237	3.815626144
H	2.8970562322	-0.4433009711	3.8757223407
C	2.4202014425	-3.3469431685	1.9958796133
H	2.123144086	-3.5829529355	0.9735911297
H	3.403019815	-3.7884386348	2.2013556893
H	1.697677463	-3.8226779178	2.6678366403
C	3.2448664637	2.3375786773	-0.64642305
H	2.1898638712	2.4803041237	-0.3963577438
C	4.0626059346	3.4325412956	0.0681830018
H	3.9679544306	3.3675464853	1.158122505
H	5.12806058	3.3401479701	-0.1747295286
H	3.7297617029	4.4293376604	-0.2454682617
C	3.3696916516	2.4845932672	-2.1728749808
H	2.840702112	1.6767437287	-2.6847686949
H	2.9389916374	3.4412799923	-2.4928676749

H	4.4170431442	2.4719535481	-2.4973031143
C	-1.1212397432	2.9505089677	-1.1400276889
H	-0.1423489584	2.6324697469	-0.7751315271
C	-1.1729303637	2.5613003806	-2.6264014293
H	-1.038829587	1.4823551278	-2.7423296788
H	-2.1217409871	2.8520866417	-3.0924084836
H	-0.364465497	3.0608830218	-3.1737819736
C	-1.2197151341	4.4771442709	-0.958305678
H	-2.1705996823	4.863355582	-1.3443095761
H	-1.152332818	4.7582151453	0.0993328676
H	-0.4083388784	4.979572268	-1.4986855779
C	-0.7302404318	-1.9559822888	-0.2223421204
O	-0.221667279	-2.8783535144	0.419894259
C	-2.2373836994	-1.9749108276	-0.4037781738
C	-2.8568967724	-1.1572768123	-1.3569470749
C	-3.0297361632	-2.8209593886	0.3867854934
C	-4.2395665189	-1.1932558488	-1.5332412404
H	-2.2460446567	-0.4849489684	-1.9534220899
C	-4.4146292393	-2.8422168909	0.2316214655
H	-2.5341933378	-3.452952815	1.1180160294
C	-5.0215850315	-2.0320522585	-0.7351027904
H	-4.7084255271	-0.553250481	-2.2755083056
H	-5.0237050957	-3.4923033362	0.8553918615
H	-6.101361929	-2.0512000681	-0.8607424724
C	0.7799359373	-1.9759304461	-2.7364218137
H	-5.019801257	0.5192685861	1.7155837457
C	-2.7177585747	-0.0194886134	2.8359107878
H	-3.4906786677	-0.7966388652	2.769106167
C	-3.0590903315	0.8485437552	4.0676247593
H	-4.0500124948	1.3055712155	3.9760058268
H	-3.0429078709	0.2412224804	4.9805115816
H	-2.3304543572	1.6588906799	4.1920171823
C	-1.3967879758	-0.7686555033	3.0714690048
H	-1.0804211635	-1.3426904918	2.2017275767
H	-0.5785100384	-0.1022130493	3.3572053232
H	-1.5407363823	-1.4711931846	3.9014784748
C	0.9304675902	-0.6934332787	-3.2033891503
C	1.0743460142	0.1177385683	-4.2397304767
H	0.9790293665	1.1946452041	-4.1689822725
H	1.3042851451	-0.3032600312	-5.2186689693
H	1.1196003738	0.5932459002	-1.8198043196
C	1.942526498	-2.6983761505	-2.0836943126
H	2.6935391277	-1.9982543764	-1.706527484
H	1.5844561819	-3.3033354314	-1.2446102759

H	2.4232459102	-3.3666967804	-2.8143792539
C	-0.3636549194	-2.8391666566	-3.2357549217
H	-0.0257288624	-3.4178846577	-4.1087123027
H	-0.6850531879	-3.5494999608	-2.4678339936
H	-1.2263088548	-2.2391196319	-3.5338879458

95

**INT2-A**

Ni	0.2797716893	-0.4140222994	-1.0512190545
C	0.3462071061	0.6689560387	0.4574505832
C	1.3187463989	1.8239468893	2.2678659759
C	-0.0808128254	2.389989117	1.9996823117
H	1.3727956334	1.2742543508	3.2138548399
H	2.0981000101	2.5895767754	2.2658059065
H	-0.7034344936	2.4404896906	2.8949036129
H	-0.0500677258	3.3873201821	1.5414120544
N	-0.6241580401	1.4179414349	1.0324469195
N	1.4953111373	0.8998316878	1.1322656629
C	2.7842776287	0.3765701722	0.7849833903
C	3.6130960819	1.1432435253	-0.0626272034
C	3.2042028843	-0.8556067556	1.3261883401
C	4.8875235414	0.6463544692	-0.3596230972
C	4.4936649812	-1.3016380224	1.0086543727
C	5.3275687344	-0.5632611229	0.1734074012
H	5.5459068169	1.2180073562	-1.0076479497
H	4.8468994525	-2.2432056625	1.4169318653
H	6.3226697396	-0.9310078839	-0.0635731577
C	-1.9728954105	1.5375897994	0.5654902368
C	-2.2191992647	2.3010764531	-0.5989176865
C	-3.0207249366	0.9380309986	1.2954228615
C	-3.538258689	2.4238243745	-1.0471816644
C	-4.321976441	1.0863728832	0.7917725603
C	-4.5847512584	1.8134637636	-0.3626921714
H	-3.7465103726	3.0058723824	-1.9404757368
H	-5.6037369478	1.9014721071	-0.7300092315
C	2.3173117344	-1.6676840949	2.2608634824
H	1.284662388	-1.346760062	2.1077676425
C	2.704564622	-1.4021346531	3.7300970281
H	2.0261435207	-1.9342649537	4.4076388287
H	3.7258794052	-1.7501923377	3.9297506269
H	2.6671248884	-0.3354265101	3.9780895905
C	2.3538710211	-3.174383685	1.9591143175
H	2.1036862974	-3.3592017355	0.9133770503
H	3.3341089309	-3.6136296267	2.1828838865

H	1.6098889393	-3.6890417217	2.5763913165
C	3.1814804699	2.495200998	-0.6166785908
H	2.1201469617	2.6265616285	-0.3897161244
C	3.9627567806	3.6377665896	0.0627076408
H	3.8539952466	3.6114298036	1.1531728391
H	5.0336392141	3.5663614647	-0.1623529471
H	3.6076036438	4.6123477338	-0.293313555
C	3.3246276581	2.5757074601	-2.1466429672
H	2.7621750199	1.7681075765	-2.623995265
H	2.9297637092	3.5320960571	-2.5107089275
H	4.3728714908	2.5096448327	-2.4610586119
C	-1.1092228298	3.0307936433	-1.3473231931
H	-0.1496379488	2.7309117106	-0.9227999597
C	-1.0618653449	2.6389584036	-2.8331123862
H	-0.9291267591	1.5583435701	-2.9296951215
H	-1.9741784601	2.9354342357	-3.364049656
H	-0.2115975947	3.1260266173	-3.3248301644
C	-1.2474015378	4.5560309408	-1.177960704
H	-2.1821003925	4.9215830109	-1.6197191017
H	-1.2470961403	4.8419679804	-0.1195045505
H	-0.4160199129	5.0726546137	-1.672704053
C	-0.7853451928	-1.801799775	-0.1978767888
O	-0.3409173078	-2.6253422347	0.6037585049
C	-2.2694557307	-1.8718909059	-0.5183403542
C	-2.8152814683	-1.1474215867	-1.5853755282
C	-3.1169357882	-2.6690135345	0.2665777101
C	-4.1778902929	-1.2237941689	-1.8740503066
H	-2.1671522864	-0.5071380708	-2.1780426782
C	-4.4817726119	-2.7336286006	-0.0055615123
H	-2.6765474379	-3.2284919758	1.0867110478
C	-5.0141925125	-2.0140553402	-1.0819426132
H	-4.5901217062	-0.6530445416	-2.7017498351
H	-5.1333788428	-3.3464583327	0.6129479951
H	-6.0785185722	-2.0657229291	-1.2976440559
C	0.5498684104	-2.1066268832	-2.6469084186
H	-5.1424141851	0.6077569911	1.32020364
C	-2.9227284452	0.1962967246	2.6355669843
H	-3.6798203422	-0.596218994	2.5667092996
C	-3.3652274295	1.1422236592	3.7749739027
H	-4.3535795127	1.5721305983	3.5813767155
H	-3.4052177615	0.6011625134	4.7279402098
H	-2.6593863572	1.9737744162	3.8912993689
C	-1.6151550619	-0.512041102	3.0225032727
H	-1.2298585805	-1.1465167408	2.2263040101

H	-0.8273815901	0.1863418787	3.3169538709
H	-1.8142887741	-1.1505110319	3.8920786745
C	0.7778492822	-0.8976404701	-3.2650449135
H	1.0425871234	0.784833122	-1.688374782
H	1.781387527	-0.5332117197	-3.4479528099
H	-0.0223613642	-0.3865960261	-3.7907299361
C	1.5968153308	-2.9788106522	-2.0630506006
C	2.8224181441	-2.5284210445	-1.7463693721
H	3.1049710992	-1.4852825707	-1.8518748003
H	3.5671851734	-3.1869098073	-1.3109265646
H	-0.4471201122	-2.5354692114	-2.7129160754
C	1.168950709	-4.400632964	-1.7929559405
H	0.3720646097	-4.4032409233	-1.0392577212
H	0.7730215073	-4.8808961923	-2.6975633394
H	1.998606899	-5.0059927688	-1.4153975733

95

**INT2-B**

Ni	0.2808142394	-0.3869478967	-1.0682660349
C	0.3971972269	0.5847855903	0.5124591667
C	1.4749110529	1.637367697	2.3288951533
C	0.0695110406	2.2298664694	2.1586736822
H	1.5717001342	1.0595434555	3.2537010619
H	2.2631955997	2.3940202477	2.3084276314
H	-0.5096487375	2.232714443	3.0842659495
H	0.0888870134	3.252342765	1.7591311048
N	-0.5313645536	1.3219056965	1.1640482926
N	1.5774147146	0.7497651153	1.156466765
C	2.8221800543	0.170688418	0.7381247322
C	3.6228459883	0.8802619731	-0.1831109307
C	3.2230029785	-1.0728300815	1.2726139851
C	4.8278435379	0.296411806	-0.5917447341
C	4.4391130394	-1.6113314867	0.8342985812
C	5.2304079021	-0.9412079988	-0.0954858491
H	5.4610664021	0.8206018919	-1.3014953233
H	4.7718121462	-2.5672487107	1.2257581897
H	6.1682220405	-1.3800363101	-0.4264636502
C	-1.9088102553	1.4606251868	0.7966825165
C	-2.2373986037	2.3011966302	-0.2905018205
C	-2.9024821904	0.8039595063	1.5535110201
C	-3.5855404481	2.4548808125	-0.6303526945
C	-4.2366976097	0.9885936946	1.161264251
C	-4.5814169247	1.7994639343	0.086620231
H	-3.8559676072	3.0963446471	-1.4643347002

H	-5.6246533111	1.9150162615	-0.1951811225
C	2.4107823808	-1.7817457123	2.3490095052
H	1.3824573936	-1.4171440589	2.2841636387
C	2.9731874489	-1.432562081	3.7441727658
H	2.3439624716	-1.8647974786	4.5315218781
H	3.986513333	-1.8369480302	3.8594325183
H	3.0331955847	-0.3514168556	3.9080961064
C	2.3577495429	-3.3079066629	2.1771489657
H	1.9760245967	-3.5733673968	1.1909067719
H	3.3405399664	-3.7709188961	2.3267433229
H	1.6783608416	-3.7353474998	2.9234851709
C	3.246014506	2.268100229	-0.685075323
H	2.2034577443	2.4495572326	-0.4116989376
C	4.1175614755	3.3399868111	0.0006362011
H	4.0407254726	3.2882387051	1.093015327
H	5.1744727011	3.2089637613	-0.2612976598
H	3.8129655618	4.3446796775	-0.316716789
C	3.3374599628	2.3916645256	-2.2155687118
H	2.7442420038	1.6112605959	-2.6994201692
H	2.9522953183	3.3680185848	-2.5345262685
H	4.3731276154	2.3170967126	-2.5684655183
C	-1.1804025504	3.0672741904	-1.0763237646
H	-0.1950155965	2.749297925	-0.730903229
C	-1.2386949796	2.7337381389	-2.5757839326
H	-1.1214171989	1.656974686	-2.7249266749
H	-2.1841264622	3.0533107367	-3.0299689183
H	-0.4229876414	3.2395101041	-3.1065782639
C	-1.3034162946	4.583478065	-0.8340296423
H	-2.2663456527	4.9676098346	-1.1914032495
H	-1.2257004221	4.8242523068	0.2328801399
H	-0.5086853938	5.1212015112	-1.3651391176
C	-0.671312328	-1.879491362	-0.2776888013
O	-0.1538230217	-2.7983779273	0.3637471159
C	-2.1797108054	-1.9155666078	-0.4510738661
C	-2.8121769118	-1.112191593	-1.4089210148
C	-2.9605705028	-2.7604542682	0.3516863593
C	-4.1959850966	-1.1596058179	-1.5743120433
H	-2.2116675384	-0.4435903733	-2.0203722207
C	-4.3464232004	-2.7928295462	0.2073589447
H	-2.4546739203	-3.3824069464	1.0844162832
C	-4.9662074467	-1.9955979902	-0.7618177575
H	-4.6748319584	-0.530557132	-2.3195650229
H	-4.9463451202	-3.4414521577	0.8414990448
H	-6.0467886782	-2.0226134276	-0.8786204552

C	0.8436924065	-2.0046006696	-2.720325434
H	-5.0175880897	0.4705431217	1.7119525831
C	-2.7078464755	-0.0462674608	2.8160956609
H	-3.4670284987	-0.8353074799	2.7344789213
C	-3.0646853199	0.7949233934	4.0622768045
H	-4.0645882162	1.2335752169	3.9795387197
H	-3.0345506159	0.1736199062	4.9653889257
H	-2.3520554255	1.6177282341	4.1978781049
C	-1.3748788556	-0.775495865	3.0428355864
H	-1.0445950585	-1.3289729833	2.1652458416
H	-0.5709527284	-0.0989631386	3.3446606438
H	-1.5085273208	-1.4947194721	3.8602221366
C	0.8005630367	-0.7769044294	-3.282687842
C	0.8683711137	0.1042576626	-4.261005891
H	0.6254503074	1.151180572	-4.128235409
H	1.1923292061	-0.2138387699	-5.2528639063
H	0.9430857353	0.8987015071	-1.6048762782
C	2.0966601668	-2.4997781971	-2.0261180696
H	2.808533028	-1.6902914001	-1.8472675462
H	1.8303409681	-2.9500839615	-1.0646305885
H	2.5770952845	-3.2697852591	-2.6471851942
C	-0.2185280916	-3.0426347263	-3.0294395794
H	0.1341472562	-3.6572285475	-3.8700798246
H	-0.3837564133	-3.7023542356	-2.1736976412
H	-1.1693884701	-2.5844282885	-3.3087878864

95

**INT2'-B**

Ni	0.3249576405	-0.8532461155	-0.5851729397
C	0.5655257252	0.7398607564	0.3605268728
C	1.6832083685	2.3025175349	1.7167499546
C	0.3862616374	2.9254997839	1.1950338568
H	1.6303950889	2.053963915	2.7838723302
H	2.5621388673	2.9276123621	1.5464666721
H	-0.2151619848	3.3935015551	1.9751688004
H	0.5657296643	3.6645495224	0.4022076752
N	-0.3015658292	1.7487014431	0.6262253139
N	1.7539054053	1.0631580241	0.9198848278
C	3.000586433	0.3988001134	0.6762370789
C	3.8780715889	0.9708770609	-0.2720813486
C	3.3296904396	-0.7727079744	1.3828513105
C	5.1200949045	0.3601300883	-0.4717703665
C	4.586552658	-1.347315419	1.1455424941
C	5.4777729873	-0.7866338322	0.2355596163

H	5.8120793803	0.7813991755	-1.1960023352
H	4.8669690517	-2.2477098672	1.6845576789
H	6.4486916747	-1.2465784028	0.0701571634
C	-1.6038602063	1.8870955567	0.0417545656
C	-1.6965648564	2.1280197777	-1.3506406675
C	-2.7522452348	1.8212496516	0.858455039
C	-2.9667512244	2.2432910516	-1.9230143616
C	-3.9998198133	1.9269280176	0.2234288152
C	-4.1147792989	2.1264858563	-1.1459034646
H	-3.0565721921	2.4251401883	-2.9900650893
H	-5.0968848994	2.1927553758	-1.6061586357
C	2.371047204	-1.4277422394	2.3647382406
H	1.4122170422	-0.909704575	2.317607772
C	2.899762302	-1.327625264	3.8071492781
H	2.1789856644	-1.766618426	4.5068881642
H	3.8512615372	-1.8616143988	3.9233262445
H	3.0659384304	-0.2832727447	4.0982872254
C	2.0810893078	-2.8869530386	1.9707309761
H	1.6767805907	-2.9331793777	0.9543426734
H	2.9826294419	-3.5104231875	2.0202384129
H	1.3292202814	-3.3097459112	2.6436246227
C	3.5040172103	2.1982956559	-1.0954432707
H	2.4937646426	2.5048559567	-0.8122381592
C	4.4482070561	3.3827024683	-0.8174099948
H	4.4734958879	3.6363114484	0.2489070848
H	5.4746386428	3.1524195217	-1.1257970788
H	4.1236707409	4.2704683416	-1.3731741535
C	3.4535444359	1.870907123	-2.5997026045
H	2.7552477552	1.0488831293	-2.7858518844
H	3.1182334672	2.7478090949	-3.1674776343
H	4.4401060724	1.5815307338	-2.9802995907
C	-0.4709634541	2.3209847844	-2.2380963956
H	0.4199318805	2.0586577966	-1.6673907817
C	-0.4856880961	1.3848111751	-3.4574612875
H	-0.579667156	0.3458511638	-3.1304577085
H	-1.3110434273	1.6138212023	-4.1415289615
H	0.4520570878	1.4801208716	-4.0167100928
C	-0.3358687737	3.7934837645	-2.6707315886
H	-1.1894482352	4.1074155728	-3.2833754332
H	-0.287012512	4.4614337774	-1.8027360371
H	0.5765050988	3.934740219	-3.2631308682
C	-1.0173588956	-1.47143914	0.6750174785
O	-0.7772799561	-1.7751506743	1.8479632499
C	-2.4712814581	-1.5026759269	0.2386302964

C	-2.8313519659	-1.3209441996	-1.1015764238
C	-3.4812881417	-1.7095114845	1.191225121
C	-4.1715598205	-1.3461363715	-1.4884683837
H	-2.0520203593	-1.1555195325	-1.8398742571
C	-4.8212933973	-1.7278568668	0.8122742625
H	-3.1842770176	-1.8563158681	2.2253291805
C	-5.1692457743	-1.5475732322	-0.5317280457
H	-4.4383727167	-1.1980213792	-2.5316661613
H	-5.5974905156	-1.8855482763	1.5575730832
H	-6.2146769501	-1.5615476158	-0.8301317115
C	0.249566023	-3.0013385568	-1.5522419293
H	-4.8991282698	1.8414283492	0.827812203
C	-2.8169594429	1.7301649	2.3896281353
H	-3.6976125201	1.1049280813	2.5893362863
C	-3.1229744205	3.1322696908	2.9648692693
H	-4.0194359393	3.5688103652	2.5121416396
H	-3.2769715691	3.0750814528	4.0490741733
H	-2.2900174198	3.8219846128	2.7804571599
C	-1.664542328	1.0839538701	3.1735408457
H	-1.3646331537	0.1220917149	2.7616402274
H	-0.7817195486	1.726061793	3.232864696
H	-2.0034333775	0.9199875021	4.2041456202
C	0.9522969775	-2.1675638898	-2.3544585444
H	1.3325486456	-0.134120325	-1.530991218
H	2.0400413978	-2.1583889394	-2.3417283905
H	0.4844760308	-1.6308875194	-3.1778409895
C	-0.2406344306	-4.1872854452	-1.2314477838
C	-0.9696763476	-4.5821377215	0.0281391362
H	-2.0510428653	-4.6352286443	-0.1568497083
H	-0.6477971748	-5.5838355507	0.3404115767
H	-0.7975522747	-3.8910454133	0.8489685932
C	-0.0881420121	-5.3134274432	-2.244217582
H	0.4066024941	-4.9803718873	-3.1603149329
H	0.4929198963	-6.1393609895	-1.8116084993
H	-1.0740695037	-5.7208652767	-2.507960699

95

**TS3-A**

Ni	0.3012637169	-0.5402891952	-0.9535397631
C	0.3615259844	0.602384446	0.5293163083
C	1.3328352037	1.7843310133	2.3232830826
C	-0.0768491372	2.3285344294	2.0631049764
H	1.3995081529	1.2361412943	3.2692360575
H	2.1012788442	2.5606347556	2.3160404012

H	-0.6923728852	2.3764344898	2.9633248303
H	-0.064613373	3.3228656154	1.5975210185
N	-0.6139153203	1.3421079857	1.1059608426
N	1.513446212	0.8605389317	1.187642336
C	2.8003732889	0.3380993007	0.8298775734
C	3.6213798018	1.1096528361	-0.0204890082
C	3.2166248544	-0.9056058973	1.3473973128
C	4.8867395211	0.6067661781	-0.3447540333
C	4.4948954421	-1.3599316106	0.9988907625
C	5.3220364324	-0.6162331663	0.1610715822
H	5.5403280613	1.1817776025	-0.994684733
H	4.8448396763	-2.3124986601	1.3831487409
H	6.3084740686	-0.9911315145	-0.0995787074
C	-1.9594886558	1.4572186084	0.6289646821
C	-2.1962715084	2.203169186	-0.5488493202
C	-3.012758133	0.8703526809	1.3605321472
C	-3.5132553512	2.3320790212	-1.0008846753
C	-4.3116084443	1.0216474746	0.8514574317
C	-4.5662065702	1.7393718572	-0.3106583181
H	-3.714798558	2.901884827	-1.9035520362
H	-5.5835705002	1.8312354418	-0.6813973412
C	2.3365528428	-1.7181859036	2.2884884972
H	1.3012006062	-1.4061571964	2.1342015643
C	2.7245786597	-1.4372094533	3.7549528679
H	2.0486961997	-1.9652581493	4.4381474773
H	3.7472325382	-1.7805659007	3.9558893853
H	2.684776904	-0.3685770744	3.9936523169
C	2.3807674072	-3.2276459611	2.0032290858
H	2.1293846166	-3.4275597232	0.9604100894
H	3.3637807183	-3.6591501174	2.2301180811
H	1.6415086168	-3.7380252785	2.6295906683
C	3.188974169	2.4724938686	-0.547809074
H	2.1299486386	2.6036280009	-0.3084341301
C	3.9797126204	3.5999845405	0.1460235965
H	3.8812441061	3.5528344135	1.2366255107
H	5.0480494047	3.5284903191	-0.0906541973
H	3.6249289379	4.5824414862	-0.1879454065
C	3.3187811424	2.5855563367	-2.0769318231
H	2.7504891523	1.79225737	-2.5708196183
H	2.9264716778	3.5519748605	-2.4162343932
H	4.3635487894	2.520703993	-2.4023818652
C	-1.0762443818	2.8972472743	-1.3161539171
H	-0.1201593211	2.5890908049	-0.8893531553
C	-1.0441249418	2.4692288297	-2.7927759541

H	-0.9639213078	1.3815060261	-2.8655389922
H	-1.9424051227	2.7920776306	-3.331879587
H	-0.173279843	2.9067855964	-3.2948614402
C	-1.1829436346	4.4282840223	-1.18353159
H	-2.113692237	4.8006802437	-1.6278402613
H	-1.1693821318	4.7399636703	-0.1325594725
H	-0.34529422	4.9163194327	-1.6964388577
C	-0.7944484598	-1.8973479885	-0.1320749075
O	-0.3627257102	-2.7212667705	0.6758586859
C	-2.2745508566	-1.956102919	-0.4682486461
C	-2.8033929222	-1.2306303257	-1.542316168
C	-3.1366441526	-2.7416440595	0.3126002775
C	-4.1641279864	-1.2936130354	-1.8426838098
H	-2.141181245	-0.601982308	-2.1317521627
C	-4.4995603302	-2.7936648512	0.0281871336
H	-2.7093517267	-3.3024515788	1.1387950401
C	-5.015374491	-2.0723611866	-1.0551023491
H	-4.5630507384	-0.7221526556	-2.6764410317
H	-5.1626368414	-3.3979774405	0.6428573329
H	-6.0782553106	-2.1141029543	-1.2799800428
C	0.6479151673	-2.0017412209	-2.6699297138
H	-5.1365326812	0.5527959118	1.381708963
C	-2.9200187456	0.1352422052	2.7043715616
H	-3.6817001053	-0.6532268172	2.6386931556
C	-3.3574011151	1.0877549942	3.8400681968
H	-4.3429058581	1.5231212713	3.6439813708
H	-3.4018252001	0.5500526476	4.7947022072
H	-2.6465290255	1.9152172003	3.9546166436
C	-1.6160262041	-0.579485171	3.0922596489
H	-1.2365211945	-1.219847878	2.2976870319
H	-0.8230376234	0.1154486877	3.3811766717
H	-1.8173909002	-1.2127549084	3.9650796371
C	1.0937090996	-0.759136015	-3.1266679929
H	1.1519138744	0.5675367601	-1.7704247987
H	2.1550262147	-0.5561639189	-3.2177296448
H	0.4452557048	-0.1479967336	-3.7450327262
C	1.5315727426	-3.0485652132	-2.1099938053
C	2.7970230032	-2.8136515589	-1.7190896444
H	3.2432500059	-1.8241853667	-1.7434035371
H	3.4137007676	-3.6077803482	-1.3091827693
H	-0.3647612969	-2.3067285986	-2.9224750614
C	0.8976049598	-4.4114956596	-1.9660667717
H	0.070671104	-4.3595528537	-1.2481390861
H	0.4857056246	-4.7639578645	-2.9211080979

H	1.6155003221	-5.154155922	-1.6047202062
---	--------------	--------------	---------------

95

**TS3-B**

Ni	0.2974593895	-0.8950006118	-0.5446814116
C	0.5475101012	0.7240030859	0.3724341866
C	1.679338975	2.3050591923	1.6961148636
C	0.3727649403	2.9181375533	1.1857001741
H	1.6422910542	2.0683961153	2.7665898478
H	2.5538955904	2.9308479562	1.5066382227
H	-0.2200225262	3.3903525364	1.9699139386
H	0.5382523393	3.6510578297	0.384042613
N	-0.3176350034	1.7338111445	0.63529974
N	1.7418221904	1.0567579022	0.9123725873
C	2.9824351029	0.3811164854	0.6693918886
C	3.8568174749	0.9361609064	-0.2916218711
C	3.3053486971	-0.7885881253	1.3824329722
C	5.0917310269	0.31255544	-0.4961534844
C	4.5555467662	-1.3756844576	1.1405056169
C	5.4447666322	-0.8307825725	0.218899284
H	5.7813612277	0.720841224	-1.2300128852
H	4.8322445639	-2.2740084813	1.6847062884
H	6.4102159829	-1.3009142369	0.0502307622
C	-1.6217162917	1.8646984797	0.0537383632
C	-1.7199107379	2.0837848214	-1.3416673154
C	-2.7659569478	1.8120751482	0.8765243802
C	-2.9923667781	2.2007546531	-1.908537376
C	-4.0161928529	1.9198639368	0.2475253797
C	-4.1368973824	2.1048182635	-1.1234477486
H	-3.0868805691	2.3658555116	-2.9779630087
H	-5.1209144871	2.1729268154	-1.5792701011
C	2.3483320071	-1.4288972371	2.3762777354
H	1.3879115986	-0.914220727	2.3211129576
C	2.8793369131	-1.3001533967	3.8157197987
H	2.1617011055	-1.7288203365	4.5249648384
H	3.8330648434	-1.8285969117	3.9389941178
H	3.0426650384	-0.2500788437	4.0873731868
C	2.0610841378	-2.896201514	2.0105885872
H	1.6530373602	-2.9631968497	0.9967077871
H	2.9640991649	-3.5165681334	2.0705892871
H	1.3116427215	-3.3064968169	2.6934627783
C	3.485035755	2.1572822019	-1.1255400898
H	2.4808566809	2.4770279723	-0.8351472572
C	4.4429954932	3.3361807926	-0.8728917391

H	4.4815916786	3.6027922093	0.1898154795
H	5.4639190047	3.0923587122	-1.189001872
H	4.1207640663	4.2197703678	-1.4365412016
C	3.4151162611	1.8116312276	-2.6249677626
H	2.707045246	0.9943098296	-2.7947840598
H	3.0826295638	2.6843666184	-3.2005999818
H	4.394395616	1.5068343353	-3.0120991637
C	-0.4983908183	2.2430434339	-2.2414625438
H	0.3953406302	1.9988900828	-1.6667159526
C	-0.5243111247	1.2621280222	-3.4255147248
H	-0.6174479982	0.2356366355	-3.0601758034
H	-1.3560919491	1.4665962588	-4.1094881739
H	0.4080868478	1.3361386124	-3.9970374879
C	-0.3590251227	3.6983700337	-2.726817067
H	-1.2147490185	3.9957170148	-3.3446027511
H	-0.3005696445	4.3955621314	-1.8826586066
H	0.5500636797	3.8139207282	-3.3297060251
C	-1.052574249	-1.5133451388	0.6974336102
O	-0.8111808228	-1.8429308342	1.8626596808
C	-2.5082117893	-1.5225394239	0.2641858208
C	-2.8664085044	-1.3661110404	-1.0791816588
C	-3.5198275695	-1.6874606153	1.2229916055
C	-4.2075158083	-1.3766475792	-1.4640080747
H	-2.0829683256	-1.2404168625	-1.8210549292
C	-4.860634682	-1.6877673103	0.8462865048
H	-3.2244377363	-1.8172423495	2.2598594604
C	-5.2073803709	-1.5340180133	-0.5012946933
H	-4.4730770133	-1.2518038977	-2.5106225835
H	-5.6384615428	-1.8114427154	1.5963167853
H	-6.2534295818	-1.5349331874	-0.7979238371
C	0.3394016284	-2.9354005363	-1.5882995289
H	-4.9127718663	1.8461988812	0.8574464242
C	-2.8196889109	1.7257619993	2.4079905299
H	-3.7048708071	1.1096334115	2.615683992
C	-3.1073697924	3.1306617403	2.9852170065
H	-4.0030386335	3.575272417	2.5387177272
H	-3.2542241412	3.0752182761	4.0705054752
H	-2.2696288455	3.8128379495	2.7948097103
C	-1.6667241694	1.0665702245	3.1806758359
H	-1.3800776013	0.1024585093	2.7640248308
H	-0.7765090673	1.6991234922	3.2324551791
H	-1.9975612823	0.9035910653	4.2140130469
C	1.1511648748	-2.1225964682	-2.3276723751
H	1.3521770228	-0.2496994185	-1.5378701054

H	2.2319971964	-2.1449205552	-2.2027421378
H	0.7910638091	-1.60468808	-3.2142253326
C	-0.1785809632	-4.1397798378	-1.390778643
C	-1.0664212591	-4.5722459295	-0.2499525813
H	-2.1199174764	-4.5776146397	-0.5606064813
H	-0.8146740778	-5.5977169628	0.0497973761
H	-0.971560323	-3.9263587666	0.6198819726
C	0.1061149586	-5.2329020696	-2.4097385506
H	0.7112761774	-4.8701292959	-3.2450062121
H	0.6321815914	-6.0728311055	-1.9349787727
H	-0.8350622624	-5.6353583027	-2.8103582744

95

**INT3-A**

Ni	-0.1229415391	-0.8997061235	0.9580354167
C	-0.5385587746	0.4250068066	-0.3796336381
C	-1.7135569932	1.4294129493	-2.1686065733
C	-0.4566335157	2.246259618	-1.8846788526
H	-1.6408248131	0.8613884041	-3.1027363843
H	-2.6228641393	2.0312032913	-2.1977017248
H	0.1449868882	2.4364984314	-2.773977965
H	-0.6791484258	3.2080681872	-1.4078011559
N	0.2616840465	1.3694182825	-0.9357293124
N	-1.7298198569	0.4996053675	-1.0210735665
C	-2.9504481121	-0.1358752771	-0.6220476897
C	-3.8460935053	0.6001486303	0.1871844435
C	-3.2555026156	-1.4264125694	-1.0973749984
C	-5.0455439492	-0.016024561	0.5613873252
C	-4.4757055523	-1.9929818938	-0.7044163911
C	-5.3556977283	-1.303802139	0.1267760044
H	-5.751613686	0.5225018839	1.187185037
H	-4.7386889258	-2.9871345588	-1.0515405358
H	-6.2927704889	-1.7656645344	0.42658438
C	1.5511797396	1.7752683099	-0.4685865026
C	1.6477529128	2.4360229834	0.7837589613
C	2.6786820509	1.5856347282	-1.2942757967
C	2.9024597107	2.897018268	1.1935287201
C	3.9097828346	2.0755534556	-0.8292695768
C	4.0286225731	2.7233630144	0.3921180068
H	3.0016741671	3.4067030181	2.1464169344
H	4.9977005605	3.0838495365	0.7268825939
C	-2.3329419	-2.1525923111	-2.067480267
H	-1.3311364962	-1.7312548215	-1.9626676482
C	-2.8189076161	-1.9256015034	-3.5146996202

H	-2.122644783	-2.3822289552	-4.2280382497
H	-3.8072228732	-2.3776804728	-3.6665624004
H	-2.9046432535	-0.8601448926	-3.7552923772
C	-2.1983495949	-3.6554250432	-1.7825072771
H	-1.8481243184	-3.827632883	-0.7633941229
H	-3.1432963091	-4.1918783867	-1.9330661614
H	-1.455721561	-4.0880122421	-2.4605147926
C	-3.5869320463	2.056280435	0.5709845424
H	-2.5556774306	2.3007440076	0.3002693132
C	-4.5247772454	2.9837930146	-0.2320041388
H	-4.4552476245	2.8038399825	-1.3103210221
H	-5.5692632251	2.8210864567	0.0591160473
H	-4.2809131292	4.0359281162	-0.042776171
C	-3.7332909355	2.3513521842	2.074526094
H	-3.0167468487	1.7823654798	2.6705282165
H	-3.5536156544	3.4171194306	2.2597165357
H	-4.7406513541	2.1201479658	2.4388496774
C	0.4273642034	2.7070258993	1.6618017531
H	-0.3472371957	1.9807663167	1.4077314904
C	0.7160802977	2.5274868868	3.1620395567
H	1.195715019	1.5645490878	3.3617017726
H	1.3676157593	3.316367331	3.554891633
H	-0.2210864396	2.5691881678	3.7285094277
C	-0.1342238653	4.1202856155	1.4052196841
H	0.6039354209	4.884610985	1.6770445638
H	-0.3950612867	4.2726014056	0.3532019458
H	-1.0367114739	4.2877629838	2.0055455508
C	1.1019803582	-1.8869187265	-0.1015422445
O	0.6450483944	-2.710565023	-0.9002004231
C	2.6085480238	-1.7558999602	-0.0100061883
C	3.2029550283	-0.8312549449	0.8540256698
C	3.4303029758	-2.5692491562	-0.8069693573
C	4.5919755949	-0.7264926744	0.9395315431
H	2.5653837502	-0.1746851571	1.4363036374
C	4.8171727159	-2.4616329055	-0.7346689507
H	2.9511333223	-3.2754469541	-1.4787007028
C	5.4015505069	-1.541150336	0.1450400271
H	5.0385119873	0.004510292	1.6074779208
H	5.4471494086	-3.0930269492	-1.356844287
H	6.4840459446	-1.458073281	0.205030553
C	0.2661989932	-2.2128293185	2.5204159393
C	1.2920787422	-1.6321517387	3.4710650673
H	1.1940856221	-0.5495195661	3.588953237
H	1.1853366127	-2.0815885505	4.470473061

H	2.3077407506	-1.8379107844	3.1231951993
C	-1.1012816079	-1.8171192213	2.4962014706
C	-1.4530450244	-0.4621807866	2.5897460388
H	-0.8608346032	0.2460792649	3.1616714307
H	-2.4868834641	-0.1894315328	2.4221051595
H	4.7963807517	1.917313955	-1.4379776516
C	2.7370460658	0.9121009118	-2.6745541114
H	3.6663549923	0.3271401983	-2.6452809959
C	2.9184044293	1.983342442	-3.7738881082
H	3.7729654502	2.6362216719	-3.5682263311
H	3.0783034369	1.5060350996	-4.7478930504
H	2.0291271211	2.6200514379	-3.8560851318
C	1.6427155232	-0.0832663125	-3.0926661044
H	1.4230559242	-0.8223102139	-2.3252932207
H	0.7070911846	0.4071035138	-3.3735255807
H	1.9947386424	-0.6220631033	-3.9808462391
C	-2.1439190878	-2.8287326439	2.0728616646
H	-1.7135558921	-3.5872043626	1.4123400143
H	-2.5307969183	-3.3437095593	2.9628475487
H	-2.9846368788	-2.3582369114	1.5586570906
H	0.449109594	-3.2572383935	2.2694213812

95

**INT3-B**

Ni	0.0003593928	1.0354595862	0.2120618518
C	0.3318492336	-0.7309620824	-0.5488405305
C	1.7835434524	-2.2357479804	-1.6673165906
C	0.3281816383	-2.6809514976	-1.8870348416
H	2.2641729743	-1.8923131918	-2.5904169503
H	2.4124134564	-3.0126529908	-1.2215441981
H	0.0570329307	-2.7416390601	-2.9439796305
H	0.1080281139	-3.6469023422	-1.4210519315
N	-0.4413069545	-1.6074011248	-1.2202125199
N	1.6176976928	-1.1036580204	-0.7364577182
C	2.7494786684	-0.446821981	-0.1503610441
C	3.2207925699	-0.9163488231	1.0952776384
C	3.3747612482	0.6112210599	-0.8387553522
C	4.3449582937	-0.29275114	1.6454374618
C	4.5010268463	1.1999838262	-0.2486250634
C	4.983052712	0.7525544523	0.9778786101
H	4.7267420063	-0.6205880574	2.6069158791
H	5.0031559537	2.0175315942	-0.7574854733
H	5.8569502277	1.2229161585	1.4208827703
C	-1.8682003824	-1.7105349959	-1.1056862468

C	-2.3901721946	-2.4858977892	-0.0440830182
C	-2.7048776095	-1.0896779936	-2.0539812128
C	-3.7783828179	-2.6224548829	0.0582527608
C	-4.0893516795	-1.2482175315	-1.8930437854
C	-4.6258849436	-2.0035709033	-0.8557290804
H	-4.1991434903	-3.2126268299	0.8668944629
H	-5.7034306948	-2.1070959148	-0.758289439
C	2.8695565754	1.1046104936	-2.1872692925
H	1.9121808898	0.6145696025	-2.3845914069
C	3.8451063394	0.7169028513	-3.3148047876
H	3.4502762425	1.0311598214	-4.2880980531
H	4.8184581579	1.2018219514	-3.1730379623
H	4.0153965566	-0.365728763	-3.3467345047
C	2.6005139581	2.6197057488	-2.1802892617
H	1.9319579604	2.8850033618	-1.3565899615
H	3.5284085842	3.193679518	-2.0702795592
H	2.1322554597	2.9214606396	-3.124508427
C	2.4916074291	-2.0267318949	1.8428586587
H	1.9464299978	-2.6254395054	1.1043763088
C	3.4357286685	-2.9798775881	2.5931132778
H	4.2192490017	-3.3712387541	1.9345346654
H	3.9224535297	-2.4874436726	3.442639561
H	2.8671939702	-3.8270459912	2.993130772
C	1.4425494302	-1.4254014584	2.7984692035
H	0.7038659983	-0.8335188572	2.2491135576
H	0.9114725539	-2.2171520852	3.3379386057
H	1.9237374678	-0.7711626715	3.5351941196
C	-1.4975578623	-3.2197454085	0.9534922547
H	-0.4625644089	-2.9064985749	0.7890955678
C	-1.8361022692	-2.8795411084	2.4150646097
H	-1.7208469125	-1.8125601336	2.6117595402
H	-2.8641900724	-3.1595944614	2.6683691831
H	-1.1688522093	-3.4293692799	3.0893869566
C	-1.5732646889	-4.7434346836	0.7245675374
H	-2.5818846609	-5.1184460432	0.9347229662
H	-1.3319812491	-5.0129724035	-0.3100214489
H	-0.8747074906	-5.267039024	1.3882791433
C	-1.7992059627	1.1730088109	0.5142565725
O	-2.5812380487	1.471244781	-0.3741919841
C	-2.3011236709	0.7901562619	1.879898068
C	-1.5055355366	0.91856669	3.0248251782
C	-3.6029862589	0.2787058837	1.9948857898
C	-2.0014724115	0.5331990037	4.2714432368
H	-0.5097749099	1.3350448972	2.9268113152

C	-4.0926440506	-0.1169852656	3.2377113623
H	-4.203141469	0.1815905814	1.0968620737
C	-3.2926105799	0.008468079	4.3787023026
H	-1.381112407	0.6414622507	5.1572587867
H	-5.0962112725	-0.526853702	3.3194959567
H	-3.6751195809	-0.3008459279	5.3480254887
H	-4.7554669406	-0.7631454018	-2.6022442315
C	-2.2621269523	-0.3097051199	-3.2951421647
H	-3.0789223286	0.39818527	-3.485022765
C	-2.2025405387	-1.2575894295	-4.512408115
H	-3.1459854166	-1.7982937454	-4.6453846512
H	-1.9966228996	-0.6921760747	-5.4292470555
H	-1.4059051718	-2.0017876912	-4.3930461825
C	-0.9847923665	0.5390938516	-3.2098940526
H	-0.9653851548	1.1319416188	-2.2928977489
H	-0.0791110925	-0.0730223881	-3.2493304017
H	-0.9546334718	1.2221447928	-4.0676317035
C	0.1384547565	2.9057612518	0.5480731233
C	1.1039309439	3.3354932101	1.3955512762
C	-0.6030681462	3.8762807481	-0.3559798228
H	-1.1755999727	4.6230278822	0.2138658202
H	0.0839743181	4.4297466302	-1.0122532285
H	-1.3159913975	3.3488435071	-0.9950300449
C	1.8927978749	2.42823718	2.3159333314
H	1.7416665199	2.702838874	3.3717237818
H	1.628149176	1.3741783375	2.2004200959
H	2.970733302	2.5106000976	2.1199326669
C	1.5584076638	4.7806368331	1.4911698509
H	2.5897390233	4.8887756671	1.1203311297
H	0.9271362987	5.4708638435	0.9268160566
H	1.5717283108	5.1162506012	2.5388646267

95

#### TS4-A

Ni	0.2793921664	-0.5654574231	-0.994307945
C	0.4295421432	0.4945797649	0.5517404623
C	1.5221357155	1.3577459683	2.4710301529
C	0.1580690387	2.0359689547	2.3205792922
H	1.5569332508	0.6782897776	3.3301890743
H	2.3518146947	2.0656336809	2.5538053565
H	-0.4394770533	2.009717221	3.2338617607
H	0.2414059042	3.0809628614	1.9919527553
N	-0.4682732451	1.2315829531	1.2531640456
N	1.6111079862	0.5907722113	1.2148804627

C	2.8579865562	0.0470831789	0.7679289522
C	3.6980687289	0.8713727705	-0.0101219283
C	3.2335536152	-1.2585853249	1.1467114473
C	4.9266002189	0.3498194373	-0.4318969053
C	4.4843113753	-1.7249260369	0.7212749032
C	5.3200513261	-0.9352781247	-0.0655223628
H	5.5832049126	0.9557909856	-1.0496052846
H	4.8048757575	-2.723335363	1.0016790302
H	6.281099142	-1.3227671101	-0.3936110696
C	-1.7937593144	1.5597832956	0.8278378689
C	-1.9535262824	2.4873174268	-0.2279559101
C	-2.900017351	1.0219723782	1.5169305211
C	-3.2508239498	2.8558801577	-0.5986895813
C	-4.1771605654	1.4247757385	1.0982296063
C	-4.3583849474	2.3293240821	0.0590539593
H	-3.393678965	3.5686000697	-1.4062482416
H	-5.3618335524	2.6165832617	-0.244052182
C	2.3332002719	-2.1330610475	2.0093604903
H	1.3155277682	-1.740863332	1.9403819417
C	2.787131256	-2.0820153316	3.4825244248
H	2.1014973695	-2.6587200102	4.1144968751
H	3.7918936985	-2.5090211072	3.5930094027
H	2.8221785072	-1.0558193689	3.8648712385
C	2.2722297352	-3.5887077979	1.5190986025
H	1.9605147422	-3.6324071418	0.4733205553
H	3.2352580497	-4.1014674235	1.6321004838
H	1.5274575355	-4.1399462514	2.1017060052
C	3.2842912483	2.281228335	-0.4150449488
H	2.4082803119	2.5591268766	0.1787218576
C	4.3786750302	3.3233503991	-0.1270331275
H	4.6930812149	3.2915664923	0.9224784482
H	5.2673373773	3.1635144395	-0.7481300207
H	4.0045263979	4.3309059389	-0.3433268699
C	2.8497920006	2.3151780032	-1.8910304314
H	2.0164678779	1.6263764275	-2.0584030182
H	2.5284379661	3.3244062258	-2.1763681653
H	3.6773202117	2.0221388157	-2.5489926512
C	-0.768517959	3.1321800741	-0.9396821194
H	0.1512956925	2.6796884927	-0.5632318541
C	-0.7975269181	2.8634517838	-2.4532367027
H	-0.7584158499	1.7873839886	-2.641954395
H	-1.6996048769	3.2724475783	-2.9226221631
H	0.0718999174	3.3220522999	-2.9380981216
C	-0.6990446053	4.642326233	-0.6428125601

H	-1.5766993465	5.1669669561	-1.0385318085
H	-0.6551338175	4.8354350162	0.435465742
H	0.1926476181	5.0817671887	-1.1063416441
C	-0.8424626741	-2.0409349321	-0.4570790371
O	-0.5122458128	-2.8078673974	0.4596062112
C	-2.3201548567	-1.7310671026	-0.6399285907
C	-2.7985796479	-0.7643573839	-1.5358612287
C	-3.2463610171	-2.4567181257	0.1228701485
C	-4.1656978699	-0.5406918192	-1.6804258083
H	-2.0926227408	-0.1705177132	-2.1075270754
C	-4.6162236251	-2.2311929974	-0.0135015165
H	-2.86576016	-3.1975677946	0.8184692426
C	-5.0805219771	-1.2760284024	-0.9215824412
H	-4.5168508609	0.2222587109	-2.3691703568
H	-5.3219955291	-2.8037146097	0.5836810575
H	-6.1473488616	-1.0982946769	-1.0312558645
C	0.0528207518	-2.5062279786	-2.1233770589
C	-1.048040438	-3.0057666207	-3.0531029099
H	-1.6454055942	-2.1898323954	-3.4659068058
H	-0.5959180418	-3.5498236296	-3.893677979
H	-1.7317445939	-3.6827178852	-2.5315774523
C	1.0199854948	-1.5309151556	-2.6981177034
C	0.6278115625	-0.4182387968	-3.4016327179
H	-0.4022868722	-0.2649081539	-3.7070792367
H	1.3599447565	0.2747553423	-3.8012496868
H	-5.0457690096	1.0044655782	1.5985828458
C	-2.87288612	0.0804860809	2.7283395213
H	-3.7157911603	-0.6032297539	2.5602820248
C	-3.1916547493	0.8802427204	4.0118027461
H	-4.1262641694	1.4432412298	3.9172219172
H	-3.2827841122	0.2042069357	4.8704131261
H	-2.3936366327	1.5988713951	4.2355849296
C	-1.6487035924	-0.8189831851	2.9615943153
H	-1.3392919148	-1.3569408799	2.0660631805
H	-0.7868731767	-0.2653499931	3.3452756806
H	-1.9116977355	-1.5635094971	3.7236828827
C	2.4905961318	-1.8081176801	-2.4599489926
H	2.8275756861	-2.6308711274	-3.1058142663
H	3.1073476445	-0.92843886	-2.6644644834
H	2.6733911808	-2.1097703077	-1.4244271284
H	0.5895416059	-3.3349896843	-1.664288196

**TS4-B**

Ni	0.1895991335	0.8031350887	-0.0744810371
C	0.5802152031	-1.0552732011	-0.0051355304
C	2.0995937889	-2.8499074555	0.3010120691
C	0.6907090255	-3.4187670723	0.0541211556
H	2.8478781376	-3.2437457044	-0.3930384285
H	2.455469489	-3.0227802776	1.3249467318
H	0.6241512368	-3.9644667062	-0.8929113928
H	0.3462540194	-4.0785099153	0.8559395611
N	-0.1403443227	-2.1972127356	-0.0026145203
N	1.8841629735	-1.4092551636	0.0794533443
C	2.9582945536	-0.4604393621	0.0940803654
C	3.298033562	0.1872840613	1.2994116989
C	3.640745959	-0.2026176973	-1.1128510792
C	4.348022455	1.1139823985	1.2709042141
C	4.6764256076	0.7376085859	-1.0921392046
C	5.0305489944	1.3890146336	0.0882519797
H	4.630467703	1.6289129925	2.1848427565
H	5.2046418256	0.9725156195	-2.0112920285
H	5.8382494905	2.1162239357	0.0848225156
C	-1.567121782	-2.2560712924	0.0948630803
C	-2.1331303994	-2.1828432015	1.3887014977
C	-2.3664275321	-2.3868099478	-1.0595932274
C	-3.5265506393	-2.2146262028	1.5097419533
C	-3.7576208617	-2.4227804991	-0.8785780253
C	-4.33610142	-2.3364211673	0.3832719733
H	-3.9824599638	-2.1351341717	2.4919842739
H	-5.4176232862	-2.3548844386	0.4880779209
C	3.2238404667	-0.8666672849	-2.4180796521
H	2.5695887692	-1.7086661284	-2.1729022292
C	4.4194997725	-1.4293906435	-3.2055558432
H	4.0633658764	-1.979457426	-4.0842378855
H	5.0808834357	-0.6332184512	-3.5660615844
H	5.0189232291	-2.1122190809	-2.5920365462
C	2.3948852211	0.1095556709	-3.2741139245
H	1.50182365	0.4509050194	-2.7433327893
H	2.9912816925	0.9914259635	-3.5393523078
H	2.07437634	-0.3762782095	-4.2037095656
C	2.5554119312	-0.0799216016	2.6024451763
H	1.7274653425	-0.7615201955	2.3868480524
C	3.46918541	-0.7639311556	3.6357072494
H	3.8827424065	-1.7000301251	3.2424646266
H	4.3107772011	-0.1169407396	3.9100419185

H	2.9095255098	-0.99321007	4.5504216558
C	1.9347392327	1.2102695786	3.1684615708
H	1.2656869621	1.6672387728	2.4320224044
H	1.3555164388	0.9902048002	4.0723699682
H	2.7045624546	1.9442737838	3.433461918
C	-1.2693792735	-2.0203610382	2.6350609916
H	-0.2338840888	-2.2500626637	2.3654622364
C	-1.2928272141	-0.558337121	3.1168919014
H	-0.9039124229	0.1055359544	2.3378611303
H	-2.3147805375	-0.2420820145	3.3579490494
H	-0.6749669446	-0.4365323115	4.0145303252
C	-1.6667321643	-2.988633967	3.7627823076
H	-2.660969793	-2.7630853246	4.1644256751
H	-1.6730793536	-4.0274191818	3.4134314356
H	-0.9543362221	-2.9090655865	4.5921841092
C	-0.8937915014	1.8040505518	-1.2447292557
O	-0.5634570762	1.8114997089	-2.4451620459
C	-2.3640807639	2.0149265797	-0.9401881419
C	-3.1223001505	1.0627363774	-0.2535096343
C	-2.9886281012	3.1768329181	-1.4130189892
C	-4.4853646307	1.2704920519	-0.0315612309
H	-2.6360545196	0.1672493439	0.1144598921
C	-4.345467527	3.395858757	-1.1739798784
H	-2.3989940199	3.9082275591	-1.9589883427
C	-5.0991900718	2.4406542594	-0.4831360758
H	-5.0603076623	0.5145234085	0.496064628
H	-4.8177519718	4.3080422806	-1.5307499402
H	-6.1579198667	2.6085395577	-0.3018450632
H	-4.395670462	-2.5081510886	-1.7545360603
C	-1.8678927029	-2.5407242485	-2.4983685705
H	-2.6870347772	-2.1561858883	-3.1200893399
C	-1.7177156289	-4.036130621	-2.85099958
H	-2.6453646492	-4.5863736347	-2.658061948
H	-1.461048528	-4.1538125308	-3.9105214221
H	-0.9232088913	-4.5058652536	-2.2599042976
C	-0.618666874	-1.747321035	-2.9114232861
H	-0.6585126974	-0.7097680122	-2.5728883563
H	0.3029676367	-2.1934232018	-2.5280123927
H	-0.5465320325	-1.7454646358	-4.0055979936
C	0.2811277124	2.7520116401	-0.1973703136
C	-0.1335745644	3.4570015386	0.8892827789
C	1.488246844	3.1665417839	-1.0139522517
H	1.4553364611	4.2234456275	-1.3132890715
H	2.4126235936	3.0020096169	-0.4471996444

H	1.5368262565	2.5745665901	-1.9283262901
C	-1.2785124822	3.0788651362	1.7966191306
H	-2.0770789019	3.8326166994	1.7485718755
H	-1.7081953505	2.1085499946	1.5615199191
H	-0.9276294622	3.0511977496	2.8381655403
C	0.5889204298	4.6998319034	1.3638792205
H	1.2197050182	4.4550879809	2.2315341924
H	1.2325771513	5.1460544686	0.6033219327
H	-0.1283515146	5.4592637405	1.7030153149

95

**INT4-A**

Ni	0.3510605494	-0.6164501969	-0.8971515437
C	0.5200306355	0.6184215403	0.6027547996
C	1.5968276734	1.5395866683	2.5054337412
C	0.2089560321	2.1751000997	2.3566872597
H	1.655981995	0.8709964998	3.372106952
H	2.4051570476	2.2727975514	2.5794142795
H	-0.3888326224	2.1173098099	3.2688898686
H	0.2574175257	3.2262251631	2.041143612
N	-0.3872350222	1.3581620639	1.280678944
N	1.7005671355	0.7608360755	1.2565739586
C	2.926404445	0.1464124414	0.8403038385
C	3.8022988676	0.9000760243	0.0303176983
C	3.2319414943	-1.1682496357	1.2503241358
C	4.9827959403	0.2894815211	-0.4083734775
C	4.4339187873	-1.7288601326	0.7993618624
C	5.2954760581	-1.0149611315	-0.0297474513
H	5.6664680957	0.8373597191	-1.0496477154
H	4.6976442833	-2.738478975	1.0986701229
H	6.2178534768	-1.4735564257	-0.3768352534
C	-1.7265216596	1.6140681784	0.8481062892
C	-1.9300660539	2.5737554207	-0.1692554215
C	-2.8053736235	0.9626466993	1.4799748456
C	-3.2426229236	2.8703294843	-0.5521084563
C	-4.0995814882	1.3004686459	1.0573875207
C	-4.323321182	2.2411784348	0.05865708
H	-3.4184625825	3.6034495816	-1.3345871614
H	-5.3385641135	2.4750650862	-0.2512332429
C	2.3250178888	-1.9439189118	2.1969839176
H	1.3374997644	-1.4765898454	2.1717096288
C	2.8702270902	-1.8573045388	3.6379614731
H	2.1840180173	-2.3481814429	4.3384338317
H	3.844821838	-2.3557180029	3.7117689501

H	3.006418808	-0.819497842	3.9622229164
C	2.1310287458	-3.41252497	1.7861355627
H	1.7231784273	-3.4801102047	0.7758485835
H	3.0664609853	-3.9818830318	1.8438920334
H	1.4138657165	-3.8894962796	2.4643008877
C	3.4589471791	2.323953663	-0.3925657507
H	2.7118693484	2.7102651372	0.3087323608
C	4.6656205545	3.275570191	-0.3419052599
H	5.1583453406	3.2472978681	0.6366403741
H	5.4139460801	3.0278646249	-1.1033641122
H	4.3378468142	4.3041001802	-0.5324257731
C	2.8018006531	2.3265058796	-1.7842185893
H	1.8972097667	1.7125012436	-1.776074809
H	2.5317738397	3.3468464857	-2.0832506223
H	3.4888275999	1.9201853057	-2.5371546142
C	-0.7743151555	3.3010553772	-0.8468215955
H	0.1633846137	2.9249447053	-0.430738221
C	-0.7389731882	2.9994534209	-2.3546144425
H	-0.6325783118	1.9232707972	-2.5121081263
H	-1.6525380003	3.3415334629	-2.8551120244
H	0.1128302459	3.5025219699	-2.8265633591
C	-0.8262973211	4.8162317326	-0.576374847
H	-1.726139713	5.2700430523	-1.0081709207
H	-0.8300369289	5.0290351729	0.499235576
H	0.0447129108	5.3126467255	-1.0211209758
C	-0.9728220119	-2.3523935698	-1.0668245618
O	-0.3605302231	-2.6229526851	0.0093089902
C	-2.4105080071	-1.938007268	-0.9953260578
C	-3.0153241524	-1.0326689601	-1.8817281137
C	-3.1957964491	-2.5157286853	0.016441971
C	-4.3728974609	-0.7377085911	-1.7773433621
H	-2.413244139	-0.5281655247	-2.6274140928
C	-4.5572349919	-2.2311295501	0.1118489876
H	-2.7205374389	-3.1958769455	0.7154763972
C	-5.1523187733	-1.3451438691	-0.789605114
H	-4.8198148903	-0.0188776302	-2.4583170221
H	-5.1532685557	-2.7001890222	0.8906954742
H	-6.2121762166	-1.1169298427	-0.7138083931
C	-0.2811500092	-2.7724143497	-2.3878165836
C	-1.1608354577	-2.9999831063	-3.6199833796
H	-1.6101544187	-2.0768002676	-3.9926844444
H	-0.5531543657	-3.4217516268	-4.4287642495
H	-1.9738590792	-3.7003652018	-3.3970562652
C	0.8104557288	-1.7081136038	-2.5389816764

C	0.51183535	-0.4104133209	-2.9645754639
H	-0.4635388185	-0.1632885132	-3.3782540937
H	1.3136229502	0.2563158127	-3.269638049
H	-4.9455324187	0.7975623592	1.5181829097
C	-2.7224133639	-0.0448015465	2.6315746148
H	-3.5540531571	-0.7378384067	2.4483651136
C	-3.0186494559	0.6626651309	3.9718480856
H	-3.9684696791	1.2074556842	3.9378976172
H	-3.069565934	-0.0685953608	4.787668074
H	-2.2307015855	1.3842703812	4.2194357364
C	-1.4655591089	-0.9210421842	2.7532367336
H	-1.1629526531	-1.3542673374	1.797513487
H	-0.6152315854	-0.3687946369	3.1648328614
H	-1.6800959934	-1.7431075087	3.4482248369
C	2.2436002347	-2.165305122	-2.3750592519
H	2.5269402565	-2.8523998063	-3.1877538951
H	2.9380865292	-1.3194069648	-2.3763922355
H	2.3794081861	-2.7036426455	-1.4301960962
H	0.2055507776	-3.7233808514	-2.1393036273

95

**INT4-B**

Ni	0.037131135	0.8481281899	-0.3688084976
C	0.6079514585	-0.9367297992	0.0738328605
C	2.0998705666	-2.7621138661	0.3500926637
C	0.6565345951	-3.2796690523	0.4145048105
H	2.6232629279	-3.0890307332	-0.5572457227
H	2.7035232338	-3.0532730634	1.2142094303
H	0.463143004	-4.100868646	-0.2787955369
H	0.3725360117	-3.6066005797	1.4234813213
N	-0.1207267503	-2.0801879836	0.0403166175
N	1.8909627608	-1.3017875302	0.3163834342
C	2.9873427721	-0.3790146721	0.3065950978
C	3.461211727	0.1080971079	1.5421335552
C	3.5539641227	0.0094723502	-0.922211923
C	4.4808539155	1.0651016746	1.5191347348
C	4.561549734	0.9834380375	-0.8960972569
C	5.0135278183	1.5135719587	0.3099536029
H	4.85947998	1.4737134314	2.4504951038
H	5.0031376258	1.3190192803	-1.8304104396
H	5.7945405544	2.2694041509	0.310821374
C	-1.5522480041	-2.1522460635	-0.0134147741
C	-2.2729951444	-1.9593967531	1.1865263799
C	-2.2065691756	-2.4682541806	-1.2238725534

C	-3.6663577853	-2.0806311898	1.1588192927
C	-3.6063109347	-2.5734944024	-1.1946587803
C	-4.3328607307	-2.3903770535	-0.0226093905
H	-4.2346891929	-1.9184217582	2.0699346116
H	-5.4161530592	-2.4773919168	-0.033554235
C	3.1455942774	-0.6390353948	-2.239648772
H	2.4225046088	-1.4247464591	-2.015340575
C	4.3567836959	-1.3118129896	-2.914247629
H	4.0353227963	-1.8597677751	-3.8077652812
H	5.1041213285	-0.5739144234	-3.2281764219
H	4.8492572286	-2.0183353454	-2.2358725885
C	2.4420758621	0.3347656088	-3.1980704074
H	1.4946243741	0.6803540782	-2.7771442438
H	3.0682246833	1.2091692591	-3.4121930909
H	2.223948379	-0.1660930565	-4.1487836438
C	2.8440620656	-0.3753169535	2.8504134442
H	2.4660222234	-1.3894530435	2.6799918475
C	3.85014568	-0.456991093	4.0087317821
H	4.7351447641	-1.0419195076	3.7338936401
H	4.1863044231	0.5366626239	4.3266575827
H	3.3799514769	-0.9319675003	4.8773864115
C	1.6296116095	0.4895225131	3.2331459482
H	0.9273937855	0.5624064949	2.3977945353
H	1.1089011783	0.0620582788	4.0988607278
H	1.94993799	1.5038453371	3.498192018
C	-1.5886371029	-1.578552054	2.4931167485
H	-0.506495112	-1.5960548148	2.3395402816
C	-1.9578870823	-0.133961923	2.8660990705
H	-1.6821152058	0.5335510819	2.0477109976
H	-3.0345279974	-0.0291021503	3.0438467321
H	-1.4260458423	0.1846436018	3.7698330936
C	-1.9072755712	-2.5642359002	3.630573356
H	-2.9736971678	-2.5605717763	3.8835130837
H	-1.6318865252	-3.5900196047	3.3585276117
H	-1.3521477094	-2.2883668588	4.5350270054
C	-1.3190235325	2.0678828818	-1.2929000199
O	-1.2086292367	1.2723619631	-2.2883163301
C	-2.6707243247	2.2390739045	-0.6776047637
C	-3.5043874089	1.1201841962	-0.5396287992
C	-3.1421064662	3.5007321739	-0.2900103614
C	-4.7775241691	1.2576079287	0.0096822528
H	-3.1327904135	0.1509955913	-0.8516677442
C	-4.4243843481	3.6414722276	0.2420877426
H	-2.4920722555	4.3646737861	-0.4009645143

C	-5.2416728894	2.5181891829	0.4005306815
H	-5.4040057076	0.3788018357	0.1339229901
H	-4.7850039818	4.6241967142	0.5349272651
H	-6.2374436924	2.6257222633	0.8232222278
H	-4.1304378331	-2.8037671874	-2.1189992171
C	-1.5467060767	-2.7619517383	-2.573660857
H	-2.2899214255	-2.4514878344	-3.3197661194
C	-1.3524106078	-4.2825866552	-2.753560052
H	-2.2897308104	-4.8281098979	-2.5984377535
H	-0.9880163151	-4.5032271248	-3.7640090273
H	-0.6162259262	-4.6738797364	-2.0414596815
C	-0.2584602934	-2.0021205846	-2.917425898
H	-0.3372101788	-0.9426540295	-2.6639689772
H	0.6076946986	-2.4202974707	-2.3982622656
H	-0.0680462168	-2.0897002331	-3.9939728039
C	-0.1079765213	2.7855007969	-0.8482395436
C	0.2820406937	2.8343568878	0.5141782997
C	0.8619323762	3.214862015	-1.9351864144
H	0.9990014738	4.3047131299	-1.8926546017
H	1.8511777887	2.7603459607	-1.8344106073
H	0.4682976993	2.9429852472	-2.9158068254
C	-0.6566431662	2.9887994899	1.6964147679
H	-0.7914302745	4.061240282	1.9156159845
H	-1.6431919747	2.5637848775	1.5379675831
H	-0.2263897677	2.5309828613	2.5916482023
C	1.6766748118	3.3463880036	0.8335823689
H	1.9444488632	3.1108178816	1.8669501194
H	2.4458429796	2.9112412979	0.1932578621
H	1.7246361496	4.4419729203	0.7245047846

27

**2a'**

C	1.4189270568	-1.5563553419	2.2337962362
O	0.3491545688	-1.980595533	2.6513135351
C	2.1082010848	-2.2365302107	1.0891907892
C	3.3390914222	-1.805059501	0.5673704673
C	1.4804603801	-3.3571940737	0.5176135594
C	3.9258609908	-2.4813710397	-0.5028111486
H	3.8535289232	-0.9571517591	1.0035528904
C	2.0658018226	-4.029683891	-0.5507039838
H	0.5303546065	-3.6808878251	0.9295991119
C	3.2915967965	-3.5919393608	-1.0641614779
H	4.8794973811	-2.1414027931	-0.8968895791
H	1.570570519	-4.8937773203	-0.9849514015

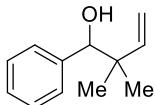
H	3.7505788315	-4.1161379566	-1.898148185
C	2.0734580744	-0.3303239222	2.8934875497
C	1.0565487538	0.4103134294	3.7789028263
H	0.6948397871	-0.2299527758	4.5873261435
H	1.5237457532	1.2993985695	4.2131813558
H	0.1858990095	0.7170240045	3.19075206
C	3.3104942165	-0.7360987921	3.6963410993
C	4.4444490676	-0.0319834866	3.6142395671
H	5.3166259935	-0.2846294573	4.2122198358
H	4.5407750716	0.824932404	2.9509035133
C	3.1674957425	-1.9330818972	4.6044523828
H	3.0140107059	-2.8505576353	4.0209712172
H	4.056734373	-2.0716927637	5.2262616609
H	2.2965727515	-1.8345161442	5.2636350696
H	2.3953171259	0.3492982532	2.094412625

27

**2a**

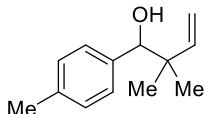
C	1.1149725476	-0.9415075435	1.6917911686
O	-0.0150060983	-1.2777625884	2.0370671485
C	1.9978200299	-1.9253701431	0.9781194255
C	3.3954748029	-1.8022883779	0.9708622464
C	1.4036444723	-3.0346809038	0.3565081675
C	4.1849480804	-2.768228977	0.3463332762
H	3.8646217873	-0.960267818	1.4710401066
C	2.1904266923	-3.9915065791	-0.2797112549
H	0.3225360817	-3.1263759079	0.3856944559
C	3.5834381979	-3.8597984137	-0.2854884926
H	5.2670377551	-2.6705822206	0.3536458844
H	1.7224287215	-4.8419295353	-0.767993582
H	4.1980642487	-4.6083605288	-0.7783411711
C	1.6482637066	0.4366522133	1.9588900567
C	1.5555692484	0.987365741	3.1896549941
C	2.2467733164	1.1700047933	0.765362609
H	1.6825554444	2.0846567531	0.5483859648
H	3.2924534401	1.4586992047	0.9269803747
H	2.2171482014	0.5509564663	-0.1349772341
C	0.9758070233	0.2939624162	4.3994715091
H	1.6558507661	0.4029891194	5.2550249109
H	0.0307896935	0.7743039178	4.6876347695
H	0.7698284159	-0.7643206872	4.2418131846
C	2.0667885336	2.3762566708	3.4892557897
H	1.2829729148	2.9668159766	3.9827014042
H	2.9071734919	2.3283295727	4.1960064413
H	2.3985624044	2.9254858088	2.6062832862

## 5. Spectral data



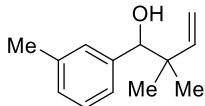
### 2,2-dimethyl-1-phenylbut-3-en-1-ol (1a')

Prepared from 1-bromo-3-methylbut-2-ene (1.79 g, 12.0 mmol) and benzaldehyde (1.06 g, 10.0 mmol), method A. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (1.0 g, 58% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32 – 7.25 (m, 5H), 5.94 – 5.89 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.15 (d,  $J$  = 10.2 Hz, 1H), 5.09 (d,  $J$  = 17.4 Hz, 1H), 4.43 (s, 1H), 1.96 (s, 1H), 1.01 (s, 3H), 0.96 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.3, 140.9, 127.9, 127.7, 127.6, 114.0, 80.9, 42.4, 24.7, 21.3. HRMS (ESI) m/z calculated for  $\text{C}_{12}\text{H}_{16}\text{ONa}$  [M+Na]<sup>+</sup> 199.1093, found 199.1077.



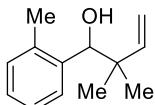
### 2,2-dimethyl-1-(p-tolyl)but-3-en-1-ol (1b')

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-methylbenzaldehyde (0.12 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.17 g, 87% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.19 (d,  $J$  = 7.8 Hz, 1H), 7.12 (d,  $J$  = 7.8 Hz, 1H), 5.94 – 5.89 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.13 – 5.12 (m, 1H), 5.09 (d,  $J$  = 17.4 Hz, 1H), 4.40 (d,  $J$  = 2.4 Hz, 1H), 2.34 (s, 3H), 1.96 (d,  $J$  = 2.4 Hz, 1H), 1.00 (s, 3H), 0.96 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.0, 137.9, 136.6, 127.9, 127.5, 113.2, 80.4, 41.9, 24.1, 21.2, 20.9.  $\text{C}_{13}\text{H}_{18}\text{ONa}$  [M+Na]<sup>+</sup> 213.1250, found 213.1239.



### 2,2-dimethyl-1-(m-tolyl)but-3-en-1-ol (1c')

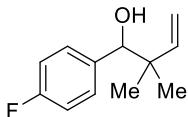
Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 3-methylbenzaldehyde (0.12 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.16 g, 85% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.20 – 7.18 (m, 1H), 7.10 – 7.07 (m, 3H), 5.94 – 5.89 (dd,  $J$  = 10.8 Hz,  $J$  = 18.0 Hz, 1H), 5.14 – 5.13 (m, 1H), 5.09 – 5.06 (m, 1H), 4.39 (d,  $J$  = 1.8 Hz, 1H), 2.35 (s, 3H), 2.02 (d,  $J$  = 1.8 Hz, 1H), 1.01 (s, 3H), 0.96 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.2, 140.7, 136.9, 128.4, 128.1, 127.3, 124.9, 113.7, 80.6, 42.1, 24.5, 21.5, 21.0. HRMS (ESI) m/z calculated for  $\text{C}_{13}\text{H}_{18}\text{ONa}$  [M+Na]<sup>+</sup> 213.1250, found 213.1238.



### 2,2-dimethyl-1-(o-tolyl)but-3-en-1-ol (1d')

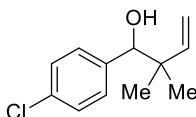
Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 2-methylbenzaldehyde (0.12 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.15 g, 81% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44 (d,  $J$  = 7.2 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.12 – 7.10 (m, 1H), 5.96 – 5.92 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.13 – 5.11 (m, 1H), 5.09 – 5.06 (m, 1H), 4.78 (s, 1H), 2.34 (s, 3H), 1.93 (s, 1H),

1.05 (s, 3H), 1.03 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.1, 139.5, 135.7, 130.1, 127.7, 127.1, 125.3, 113.5, 75.2, 43.1, 24.1, 21.3, 20.3. HRMS (ESI) m/z calculated for  $\text{C}_{13}\text{H}_{18}\text{ONa} [\text{M}+\text{Na}]^+$  213.1250, found 213.1241.



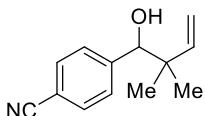
### **1-(4-fluorophenyl)-2,2-dimethylbut-3-en-1-ol (1e')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-fluorobenzaldehyde (0.13 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.17 g, 87% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.26 – 7.24 (m, 2H), 7.00 – 6.97 (m, 2H), 5.90 – 5.86 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.15 – 5.13 (m, 1H), 5.08 – 5.05 (m, 1H), 4.40 (s, 1H), 2.11 (d,  $J$  = 1.8 Hz, 1H), 0.98 (s, 3H), 0.93 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.3, 160.8, 144.7, 136.4, 129.2, 129.1, 114.3, 114.1, 113.8, 79.9, 42.1, 24.2, 20.9. HRMS (ESI) m/z calculated for  $\text{C}_{12}\text{H}_{15}\text{FONa} [\text{M}+\text{Na}]^+$  217.0999, found 217.0977.



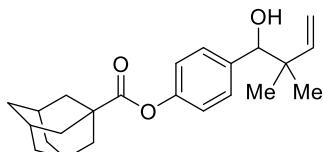
### **1-(4-chlorophenyl)-2,2-dimethylbut-3-en-1-ol (1f')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-chlorobenzaldehyde (0.14 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.18 g, 83% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27 (d,  $J$  = 8.4 Hz, 2H), 7.21 (d,  $J$  = 9.0 Hz, 2H), 5.89 – 5.84 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 4.37 (s, 1H), 2.14 (s, 1H), 0.98 (s, 3H), 0.93 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.6, 139.2, 133.0, 129.1, 127.6, 114.1, 79.9, 42.1, 24.2, 20.9. HRMS (ESI) m/z calculated for  $\text{C}_{12}\text{H}_{15}\text{ClONa} [\text{M}+\text{Na}]^+$  233.0703, found 233.0682.



### **4-(1-hydroxy-2,2-dimethylbut-3-en-1-yl)benzonitrile (1g')**

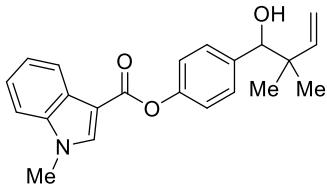
Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-formylbenzonitrile (0.26 g, 2.0 mmol), method A. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 15/1) afforded the desired product as a colorless oil (0.20 g, 50% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (d,  $J$  = 8.4 Hz, 2H), 7.42 (d,  $J$  = 9.0 Hz, 2H), 5.88 – 5.84 (dd,  $J$  = 10.2 Hz,  $J$  = 18.0 Hz, 1H), 5.18 – 5.16 (m, 1H), 5.09 – 5.06 (m, 1H), 4.47 (d,  $J$  = 0.6 Hz, 1H), 2.25 (d,  $J$  = 2.4 Hz, 1H), 1.01 (s, 3H), 0.95 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.1, 144.1, 131.2, 128.5, 118.9, 114.7, 111.1, 79.8, 42.3, 24.1, 20.9. HRMS (ESI) m/z calculated for  $\text{C}_{13}\text{H}_{15}\text{NONa} [\text{M}+\text{Na}]^+$  224.1046, found 224.1044.



### **4-(1-hydroxy-2,2-dimethylbut-3-en-1-yl)phenyl (3r,5r,7r)-adamantane-1-carboxylate (1h')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-formylphenyl (3r,5r,7r)-adamantane-1-carboxylate (0.28 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 15/1) afforded the desired product as a white semisolid (0.28 g, 78% yield).

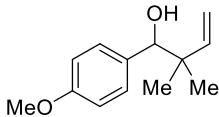
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.92 – 5.88 (dd, *J* = 10.8 Hz, *J* = 17.4 Hz, 1H), 5.14 (d, *J* = 10.8 Hz, 1H), 5.14 (d, *J* = 17.4 Hz, 1H), 4.31 (s, 1H), 2.08 – 2.02 (m, 10H), 1.79 – 1.74 (m, 6H), 1.00 (s, 3H), 0.95 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 176.2, 150.4, 144.9, 138.0, 128.6, 120.6, 113.9, 80.2, 42.2, 40.9, 39.0, 38.7, 37.2, 36.4, 28.2, 27.9, 24.4, 20.9. HRMS (ESI) m/z calculated for C<sub>23</sub>H<sub>30</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 377.2087, found 377.2115.



**4-(1-hydroxy-2,2-dimethylbut-3-en-1-yl)phenyl 1-methyl-1H-indole-3-carboxylate (1i')**

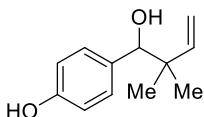
Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-formylphenyl 1-methyl-1H-indole-3-carboxylate (0.28 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 10/1) afforded the desired product as a white semisolid (0.29 g, 84% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.24 – 8.23 (m, 1H), 7.92 (s, 1H), 7.38 – 7.29 (m, 5H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.95 – 5.90 (dd, *J* = 10.8 Hz, *J* = 18.0 Hz, 1H), 5.15 – 5.13 (m, 1H), 5.09 – 5.07 (m, 1H), 4.45 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 3H), 2.11 (d, *J* = 3.0 Hz, 1H), 1.03 (s, 3H), 0.99 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 163.0, 150.2, 144.9, 137.9, 137.3, 136.1, 128.7, 126.7, 123.0, 122.2, 121.6, 121.0, 133.8, 109.8, 106.0, 80.2, 42.2, 33.5, 24.3, 21.0. HRMS (ESI) m/z calculated for C<sub>22</sub>H<sub>23</sub>NONa [M+Na]<sup>+</sup> 372.1570, found 372.1597.



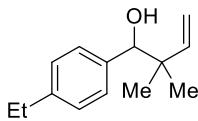
**1-(4-methoxyphenyl)-2,2-dimethylbut-3-en-1-ol (1j')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-methoxybenzaldehyde (0.14 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 15/1) afforded the desired product as a colorless oil (0.17 g, 83% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.94 – 5.89 (dd, *J* = 10.8 Hz, *J* = 17.4 Hz, 1H), 5.14 – 5.12 (m, 1H), 5.09 – 5.06 (m, 1H), 4.39, (s, 1H), 3.80 (s, 3H), 1.98 (s, 1H), 0.99 (s, 3H), 0.95 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 158.9, 145.2, 132.9, 128.8, 113.7, 112.9, 80.3, 55.2, 42.3, 24.5, 20.9. HRMS (ESI) m/z calculated for C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 229.1190, found 229.1195.



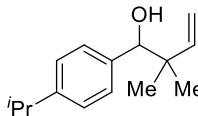
**4-(1-hydroxy-2,2-dimethylbut-3-en-1-yl)phenol (1k')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-hydroxybenzaldehyde (0.12 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.17 g, 89% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 5.93 – 5.88 (dd, *J* = 10.8 Hz, *J* = 17.4 Hz, 1H), 5.15 – 5.13 (m, 1H), 5.09 – 5.06 (m, 1H), 4.89 (s, 1H), 4.39 (d, *J* = 2.4 Hz, 1H), 1.99 (d, *J* = 2.4 Hz, 1H), 0.99 (s, 3H), 0.94 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 154.89, 145.2, 133.0, 129.3, 114.4, 113.9, 80.3, 42.3, 24.5, 20.9. HRMS (ESI) m/z calculated for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 215.1043, found 215.1022.



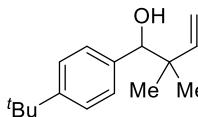
**1-(4-ethylphenyl)-2,2-dimethylbut-3-en-1-ol (1l')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-ethylbenzaldehyde (0.14 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.17 g, 82% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.18 (d,  $J$  = 7.8 Hz, 2H), 7.12 (d,  $J$  = 7.8 Hz, 2H), 5.91 – 5.87 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.10 – 5.08 (m, 2H), 5.05 – 5.02 (m, 2H), 4.34 (s, 1H), 2.64 – 2.60 (q,  $J$  = 7.8 Hz, 2H), 2.14 (s, 1H), 1.22 (t,  $J$  = 7.8 Hz, 3H), 3.05 (s, 3H), 3.17 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.2, 143.2, 138.1, 127.7, 126.9, 113.4, 80.5, 42.1, 28.4, 24.3, 21.1, 15.5. HRMS (ESI) m/z calculated for  $\text{C}_{14}\text{H}_{20}\text{ONa}$  [M+Na]<sup>+</sup> 227.1406, found 227.1405.



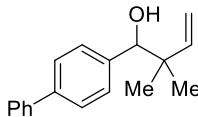
**1-(4-isopropylphenyl)-2,2-dimethylbut-3-en-1-ol (1m')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-isopropylbenzaldehyde (0.15 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.18 g, 83% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.22 (d,  $J$  = 8.4 Hz, 2H), 7.17 (d,  $J$  = 7.8 Hz, 2H), 5.95 – 5.99 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.14 (d,  $J$  = 10.8 Hz, 1H), 5.14 (d,  $J$  = 17.4 Hz, 1H), 4.40 (d,  $J$  = 2.4 Hz, 1H), 2.92 – 2.87 (m, 1H), 1.97 (d,  $J$  = 3.0 Hz, 1H), 1.25 (s, 3H), 1.24 (s, 3H), 1.01 (s, 3H), 0.96 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.9, 145.3, 138.2, 127.7, 125.6, 113.6, 80.6, 42.2, 33.7, 24.5, 24.0, 23.9, 21.1. HRMS (ESI) m/z calculated for  $\text{C}_{15}\text{H}_{22}\text{ONa}$  [M+Na]<sup>+</sup> 241.1563, found 241.1568.



**1-(4-(tert-butyl)phenyl)-2,2-dimethylbut-3-en-1-ol (1n')**

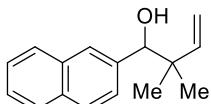
Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 4-(tert-butyl)benzaldehyde (0.16 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.20 g, 85% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33 (d,  $J$  = 8.4 Hz, 2H), 7.22 (d,  $J$  = 8.4 Hz, 2H), 5.94 – 5.90 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.14 – 5.12 (m, 1H), 5.09 – 5.06 (m, 1H), 4.40 (d,  $J$  = 1.8 Hz, 1H), 2.00 (d,  $J$  = 3.0 Hz, 1H), 1.31 (s, 9H), 1.01 (s, 3H), 0.94 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 145.3, 137.8, 127.4, 124.4, 113.6, 80.5, 42.2, 34.4, 31.4, 24.5, 21.1. HRMS (ESI) m/z calculated for  $\text{C}_{16}\text{H}_{24}\text{ONa}$  [M+Na]<sup>+</sup> 255.1719, found 255.1723.



**1-([1,1'-biphenyl]-4-yl)-2,2-dimethylbut-3-en-1-ol (1o')**

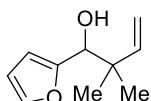
Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and [1,1'-biphenyl]-4-carbaldehyde (0.18 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a white semisolid (0.20 g, 81% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 (d,  $J$  = 7.2 Hz, 2H), 7.54 (d,  $J$  = 8.4 Hz, 2H), 7.23 (t,  $J$  = 7.8 Hz, 2H), 7.36 – 7.32 (m, 3H),

5.96 – 5.91 (dd,  $J$  = 10.8 Hz, 1H), 5.17 – 5.15 (m, 1H), 5.11 – 5.08 (m, 1H), 4.46 (d,  $J$  = 2.4 Hz, 1H), 2.09 (d,  $J$  = 2.4 Hz, 1H), 3.03 (s, 3H), 2.97 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.1, 140.8, 140.2, 139.8, 128.7, 128.2, 127.2, 127.0, 126.2, 113.9, 80.4, 42.3, 24.5, 21.0. HRMS (ESI) m/z calculated for  $\text{C}_{18}\text{H}_{20}\text{ONa} [\text{M}+\text{Na}]^+$  275.1406, found 275.1415.



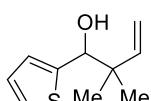
### **2,2-dimethyl-1-(naphthalen-2-yl)but-3-en-1-ol (1p')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 2-naphthaldehyde (0.16 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 15/1) afforded the desired product as a white semisolid (0.18 g, 80% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.82 – 7.81 (m, 2H), 7.77 (d,  $J$  = 8.4 Hz, 1H), 7.72 (s, 1H), 7.47 – 7.42 (m, 3H), 5.97 – 5.92 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.16 (d,  $J$  = 10.8 Hz, 1H), 5.09 (d,  $J$  = 17.4 Hz, 1H), 4.57 (d,  $J$  = 2.4 Hz, 1H), 2.18 (d,  $J$  = 2.4 Hz, 1H), 1.05 (s, 3H), 0.99 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.1, 138.4, 132.9, 132.7, 127.9, 127.5, 126.9, 126.6, 126.1, 125.9, 125.7, 113.9, 80.7, 42.5, 24.5, 21.2. HRMS (ESI) m/z calculated for  $\text{C}_{16}\text{H}_{18}\text{ONa} [\text{M}+\text{Na}]^+$  249.1249, found 249.1252.



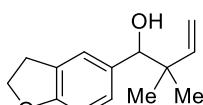
### **1-(furan-2-yl)-2,2-dimethylbut-3-en-1-ol (1q')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and furan-2-carbaldehyde (0.10 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a yellow oil (0.13 g, 78% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35 – 7.34 (m, 1H), 6.33 – 6.32 (m, 1H), 6.23 (d,  $J$  = 3.0 Hz, 1H), 5.95 – 5.90 (dd,  $J$  = 10.8 Hz,  $J$  = 18.0 Hz, 1H), 5.15 – 5.09 (m, 2H), 4.42 (d,  $J$  = 5.4 Hz, 1H), 2.08 (d,  $J$  = 5.4 Hz, 1H), 1.07 (s, 3H), 1.03 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.7, 144.3, 141.5, 113.9, 109.9, 107.4, 74.9, 42.2, 23.7, 22.1. HRMS (ESI) m/z calculated for  $\text{C}_{10}\text{H}_{14}\text{O}_2\text{Na} [\text{M}+\text{Na}]^+$  189.0886, found 189.0824.



### **2,2-dimethyl-1-(thiophen-2-yl)but-3-en-1-ol (1r')**

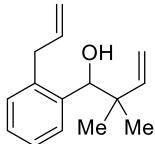
Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and thiophene-2-carbaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a yellow oil (0.13 g, 72% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.24 – 7.23 (m, 1H), 6.97 – 6.94 (m, 2H), 5.99 – 5.95 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.18 – 5.16 (m, 1H), 5.14 (d,  $J$  = 17.4 Hz, 1H), 4.71 (d,  $J$  = 3.0 Hz, 1H), 2.14 (d,  $J$  = 3.6 Hz, 1H), 1.08 (s, 3H), 1.04 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.5, 126.0, 125.4, 124.4, 114.3, 77.4, 42.2, 24.3, 21.5.



### **1-(2,3-dihydrobenzofuran-5-yl)-2,2-dimethylbut-3-en-1-ol (1s')**

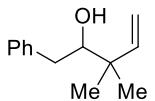
Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 2,3-dihydrobenzofuran-5-carbaldehyde (0.15 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum

ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.18 g, 82% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.13 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 5.93 – 5.89 (dd, *J* = 10.8 Hz, *J* = 17.4 Hz, 1H), 5.13 (d, *J* = 10.8 Hz, 1H), 5.07 (d, *J* = 17.4 Hz, 1H), 4.54 (t, *J* = 9.0 Hz, 2H), 4.35 (d, *J* = 1.8 Hz, 1H), 3.19 – 3.17 (m, 2H), 2.06 (d, *J* = 2.4 Hz, 1H), 0.99 (s, 3H), 0.95 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 159.4, 145.3, 132.9, 127.6, 126.1, 124.1, 113.5, 108.0, 80.5, 71.2, 42.2, 29.7, 24.5, 20.9. HRMS (ESI) m/z calculated for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 241.1199, found 241.1196.



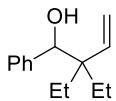
### **1-(2-allylphenyl)-2,2-dimethylbut-3-en-1-ol (1t')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 2-allylbenzaldehyde (0.15 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.18 g, 83% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.48 – 7.46 (m, 1H), 7.24 – 7.19 (m, 2H), 7.15 – 7.14 (m, 1H), 5.99 – 5.92 (m, 2H), 5.13 – 5.06 (m, 3H), 5.01 – 4.98 (m, 1H), 4.82 (s, 1H), 3.61 – 3.57 (m, 1H), 3.36 – 3.32 (m, 1H), 1.81 (br, 1H), 1.06 (s, 3H), 1.04 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 145.2, 139.3, 137.6, 137.3, 129.4, 128.0, 127.4, 125.9, 115.9, 113.6, 75.1, 42.9, 37.3, 24.4, 21.7 HRMS (ESI) m/z calculated for C<sub>15</sub>H<sub>20</sub>ONa [M+Na]<sup>+</sup> 239.1406, found 239.1408.



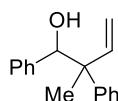
### **3,3-dimethyl-1-phenylpent-4-en-2-ol (1u')**

Prepared from 1-bromo-3-methylbut-2-ene (0.36 g, 2.4 mmol) and 2-phenylacetaldehyde (0.12 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.16 g, 82% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.29 – 7.27 (m, 2H), 7.20 – 7.19 (m, 3H), 5.93 – 5.89 (dd, *J* = 10.8 Hz, *J* = 18.0 Hz, 1H), 5.11 – 5.07 (m, 2H), 3.47 (d, *J* = 10.8 Hz, 1H), 2.87 (d, *J* = 13.8 Hz, 1H), 2.45 – 2.41 (m, 1H), 1.59 (s, 1H), 1.09 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 145.2, 139.8, 129.2, 128.4, 126.2, 113.0, 79.2, 41.4, 38.3, 22.7.



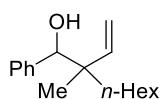
### **2,2-diethyl-1-phenylbut-3-en-1-ol (3a')**

Prepared from 1-bromo-3-ethylpent-2-ene (0.43 g, 2.4 mmol) and benzaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.18 g, 87% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.25 – 7.23 (m, 2H), 7.21 – 7.18 (m, 3H), 5.65 – 5.59 (dd, *J* = 10.8 Hz, *J* = 18.0 Hz, 1H), 5.22 – 5.20 (m, 1H), 4.97 – 4.94 (m, 1H), 4.48 (s, 1H), 2.23 (s, 1H), 1.76 – 1.70 (m, 1H), 1.54 – 1.48 (m, 1H), 1.32 – 1.26 (m, 1H), 1.10 – 1.04 (m, 1H), 0.87 – 0.84 (m, 3H), 0.73 – 0.71 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 141.5, 141.4, 127.8, 127.2, 127.1, 115.8, 77.2, 47.2, 24.5, 22.9, 7.7, 7.5. HRMS (ESI) m/z calculated for C<sub>14</sub>H<sub>20</sub>ONa [M+Na]<sup>+</sup> 227.1406, found 227.1401.



**2-methyl-1,2-diphenylbut-3-en-1-ol (3b')**

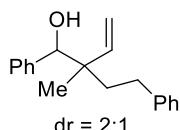
Prepared from (*Z*)-(4-bromobut-2-en-2-yl)benzene (0.51 g, 2.4 mmol) and benzaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.17 g, 73% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.37 – 7.36 (m, 2H), 7.32 – 7.29 (m, 2H), 7.23 – 7.22 (m, 1H), 7.21 – 7.18 (m, 3H), 7.10 – 7.09 (m, 2H), 6.57 – 6.52 (dd, *J* = 10.8 Hz, *J* = 17.4 Hz, 1H), 5.32 – 5.30 (m, 1H), 5.10 (d, *J* = 18.0 Hz, 1H), 5.05 (s, 1H), 2.09 (br, 1H), 1.28 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 144.9, 142.0, 140.0, 128.2, 127.9, 127.4, 127.2, 127.1, 126.5, 115.5, 80.2, 50.2, 20.6. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 261.1249, found 261.1210.



dr = 1.2:1

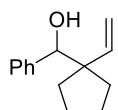
**2-methyl-1-phenyl-2-vinyloctan-1-ol (3c')**

Prepared from (*Z*)-1-bromo-3-methylnon-2-ene (0.26 g, 1.2 mmol) and benzaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.13 g, 80% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.37 – 7.26 (m, 12H), 5.87 – 5.82 (m, 1H), 5.79 – 5.74 (m, 1H), 5.29 – 5.25 (m, 1H), 5.18 – 5.16 (m, 1H), 5.09 – 5.06 (m, 1H), 5.00 – 4.97 (m, 1H), 4.44 – 4.42 (m, 2H), 2.03 – 2.01 (m, 2H), 1.57 – 1.56 (m, 2H), 1.32 – 1.16 (m, 20H), 1.05 – 1.04 (m, 3H), 0.89 – 0.85 (m, 8H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 144.2, 142.9, 141.3, 140.6, 128.1, 127.8, 127.5, 127.4, 127.3, 127.3, 115.6, 114.9, 80.8, 80.0, 45.9, 45.3, 37.7, 36.5, 31.9, 30.1, 30.0, 24.0, 22.6, 19.1, 16.4, 14.1. HRMS (ESI) m/z calculated for C<sub>11</sub>H<sub>13</sub>ONa [M+Na]<sup>+</sup> 269.1875, found 269.1875.



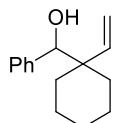
**2-methyl-2-phenethyl-1-phenylbut-3-en-1-ol (3d')**

Prepared from (*Z*)-(5-bromo-3-methylpent-3-en-1-yl)benzene (0.29 g, 1.2 mmol) and benzaldehyde (0.11 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.20 g, 76% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.29 – 7.23 (m, 20H), 7.17 – 7.11 (m, 9H), 5.95 – 5.85 (m, 3H), 5.34 – 5.32 (m, 2H), 5.25 – 5.23 (m, 1H), 5.16 – 5.13 (m, 2H), 5.08 – 5.05 (m, 1H), 4.48 – 4.45 (m, 3H), 2.51 – 2.47 (m, 6H), 2.08 – 2.05 (m, 3H), 1.75 – 1.67 (m, 3H), 1.61 – 1.56 (m, 3H), 1.34 (s, 3H), 1.00 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 143.6, 142.9, 142.8, 142.6, 141.1, 140.4, 128.3, 128.2, 128.0, 127.8, 127.6, 127.5, 127.5, 127.4, 125.6, 125.6, 116.2, 115.3, 80.8, 80.1, 46.0, 45.4, 39.5, 38.3, 30.6, 30.6, 18.9, 16.5. HRMS (ESI) m/z calculated for C<sub>19</sub>H<sub>22</sub>ONa [M+Na]<sup>+</sup> 289.1563, found 289.1563.



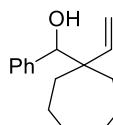
**phenyl(1-vinylcyclopentyl)methanol (3e')**

Prepared from (2-bromoethylidene)cyclopentane (0.42 g, 2.4 mmol) and benzaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.15 g, 73% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.30 – 7.23 (m, 5H), 5.79 – 5.74 (dd,  $J$  = 10.8 Hz,  $J$  = 18.0 Hz, 1H), 5.18 (d,  $J$  = 10.8 Hz, 1H), 5.04 (d,  $J$  = 17.4 Hz, 1H), 4.52 (s, 1H), 2.11 (br, 1H), 1.83 – 1.80 (m, 1H), 1.73 – 1.68 (m, 1H), 1.60 – 1.50 (m, 5H), 1.41 – 1.38 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.7, 141.7, 127.5, 127.3, 114.9, 80.2, 55.2, 34.1, 33.1, 23.4, 23.3. HRMS (ESI) m/z calculated for  $\text{C}_{14}\text{H}_{18}\text{ONa} [\text{M}+\text{Na}]^+$  225.1249, found 225.1255.



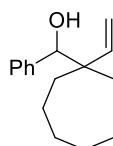
### **phenyl(1-vinylcyclohexyl)methanol (3f')**

Prepared from (2-bromoethylidene)cyclohexane (0.45 g, 2.4 mmol) and benzaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.17 g, 79% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.28 – 7.26 (m, 2H), 7.24 – 7.21 (m, 3H), 5.55 – 5.51 (dd,  $J$  = 10.8 Hz,  $J$  = 18.0 Hz, 1H), 5.38 (d,  $J$  = 10.8 Hz, 1H), 5.09 (d,  $J$  = 18.0 Hz, 1H), 4.31 (s, 1H), 2.22 (s, 1H), 1.90 – 1.87 (m, 1H), 1.53 – 1.51 (m, 2H), 1.49 – 1.44 (m, 2H), 1.39 – 1.25 (m, 4H), 1.13 – 1.09 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.8, 140.8, 127.9, 127.3, 127.2, 117.3, 80.9, 45.6, 32.7, 31.3, 26.3, 22.0, 21.9. HRMS (ESI) m/z calculated for  $\text{C}_{15}\text{H}_{20}\text{ONa} [\text{M}+\text{Na}]^+$  239.1406, found 239.1410.



### **phenyl(1-vinylcycloheptyl)methanol (3g')**

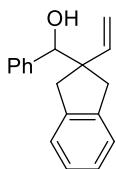
Prepared from (2-bromoethylidene)cycloheptane (0.49 g, 2.4 mmol) and benzaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.16 g, 71% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.29 – 7.22 (m, 5H), 5.77 – 5.73 (dd,  $J$  = 10.8 Hz,  $J$  = 18.0 Hz, 1H), 5.26 (d,  $J$  = 10.8 Hz, 1H), 5.06 (d,  $J$  = 17.4 Hz, 1H), 4.36 (s, 1H), 2.15 (s, 1H), 1.79 – 1.69 (m, 2H), 1.49 – 1.31 (m, 10H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.9, 141.1, 128.0, 127.3, 127.2, 115.2, 80.1, 48.7, 34.6, 33.1, 30.2, 30.0, 22.8, 22.5. HRMS (ESI) m/z calculated for  $\text{C}_{16}\text{H}_{22}\text{ONa} [\text{M}+\text{Na}]^+$  253.1562, found 253.1569.



### **phenyl(1-vinylcyclooctyl)methanol (3h')**

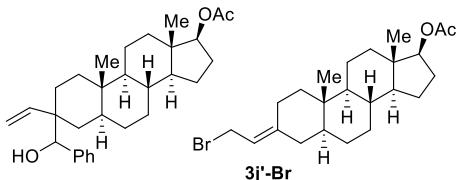
Prepared from (2-bromoethylidene)cyclooctane (0.52 g, 2.4 mmol) and benzaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.17 g, 71% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.29 – 7.23 (m, 5H), 5.75 – 5.69 (dd,  $J$  = 11.4 Hz,  $J$  = 18.0 Hz, 1H), 5.28 – 5.26 (m, 1H), 5.05 – 5.02 (m, 1H), 4.46 (s, 1H), 2.07 (s, 1H), 1.86 – 1.82 (m, 1H), 1.77 – 1.73 (m, 1H), 1.62 – 1.44 (m, 9H), 1.41 – 1.26 (m, 2H), 0.89 – 0.83 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.2, 141.4, 127.9, 127.4,

127.3, 115.8, 79.0, 48.4, 29.7, 29.2, 28.9, 27.9, 25.2, 22.8, 22.6. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>24</sub>ONa [M+Na]<sup>+</sup> 267.1719, found 267.1728.



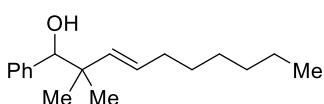
### **phenyl(2-vinyl-2,3-dihydro-1H-inden-2-yl)methanol (3i')**

Prepared from 2-(2-bromoethylidene)-2,3-dihydro-1H-indene (0.54 g, 2.4 mmol) and benzaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.20 g, 79% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.28 – 7.21 (m, 5H), 7.13 – 7.12 (m, 1H), 7.09 – 7.07 (m, 3H), 5.94 – 5.89 (dd, J = 10.8 Hz, J = 17.4 Hz, 1H), 5.05 – 5.03 (m, 1H), 4.94 – 4.91 (m, 1H), 4.61 (s, 1H), 3.27 (d, J = 15.6 Hz, 1H), 3.03 (d, J = 15.6 Hz, 1H), 2.96 (d, J = 15.6 Hz, 1H), 2.66 (d, J = 15.6 Hz, 1H), 2.29 (br, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 141.9, 141.7, 141.4, 140.4, 127.6, 127.5, 127.4, 126.2, 126.1, 124.4, 124.1, 114.9, 79.0, 55.5, 40.9, 39.9. HRMS (ESI) m/z calculated for C<sub>18</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 273.1249, found 273.1221.



### **Compound 3j'**

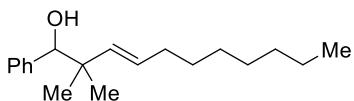
Prepared from **3j'-Br** (1.04 g, 2.4 mmol) and benzaldehyde (0.11 g, 1.0 mmol), method B. Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a white semisolid (0.31 g, 67% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.30 – 7.28 (m, 2H), 7.26 – 7.22 (m, 3H), 5.53 – 5.48 (m, 1H), 5.39 – 5.36 (m, 1H), 5.29 (s, 3H), 5.09 – 5.07 (m, 1H), 4.56 – 4.53 (m, 1H), 4.29 – 4.27 (m, 1H), 2.09 – 2.08 (m, 1H), 2.02 (s, 3H), 1.69 – 1.55 (m, 4H), 1.49 – 1.34 (m, 6H), 1.27 – 1.13 (m, 6H), 1.05 – 0.95 (m, 2H), 0.89 – 0.85 (m, 1H), 0.75 (s, 3H), 0.67 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 171.2, 142.3, 141.9, 140.7, 128.0, 127.9, 127.4, 127.3, 117.3, 82.9, 81.8, 54.3, 53.4, 50.8, 46.3, 42.6, 41.7, 36.9, 36.1, 35.4, 35.2, 34.3, 31.5, 28.7, 27.5, 26.4, 23.5, 21.2, 20.4, 12.1, 11.9. HRMS (ESI) m/z calculated for C<sub>30</sub>H<sub>24</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 473.3026, found 473.3025.



### **(E)-2,2-dimethyl-1-phenyldec-3-en-1-ol (3k')**

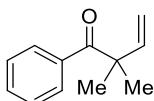
Prepared from PhMgBr (4.5 mL, 4.5 mmol, 1 M in THF) and (E)-2,2-dimethyldec-3-enal (0.55 g, 3.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.55 g, 70% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.27 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.18 (m, 1H), 5.38 – 5.33 (m, 1H), 5.27 – 5.24 (m, 1H), 4.44 (s, 1H), 2.35 (s, 1H), 2.13 – 2.09 (m, 2H), 1.32 – 1.26 (m, 8H), 1.04 (s, 6H), 0.89 – 0.87 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 140.9, 135.2, 132.2, 127.7, 127.2, 127.0, 80.9, 42.2, 31.6, 30.1, 28.9, 28.5, 25.8, 23.9, 22.5, 13.9. HRMS (ESI) m/z calculated for C<sub>18</sub>H<sub>28</sub>ONa [M+Na]<sup>+</sup> 283.2032,

found 283.2040.



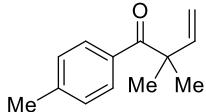
**(E)-2,2-dimethyl-1-phenylundec-3-en-1-ol (3l')**

Prepared from PhMgBr (4.5 mL, 4.5 mmol, 1 M in THF) and (*E*)-2,2-dimethylundec-3-enal (0.59 g, 3.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1) afforded the desired product as a colorless oil (0.54 g, 65% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.27 – 7.22 (m, 4H), 7.20 – 7.18 (m, 1H), 5.38 – 5.33 (m, 1H), 5.26 – 5.24 (m, 1H), 4.44 (s, 1H), 2.34 (s, 1H), 2.13 – 2.09 (m, 2H), 1.31 – 1.27 (m, 10H), 1.04 (s, 6H), 0.89 – 0.37 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 140.9, 135.2, 132.2, 127.7, 127.2, 127.0, 80.9, 42.3, 31.7, 30.2, 29.2, 29.1, 28.5, 25.8, 23.9, 22.5, 13.9. HRMS (ESI) m/z calculated for C<sub>19</sub>H<sub>30</sub>ONa [M+Na]<sup>+</sup> 297.2189, found 297.2207.



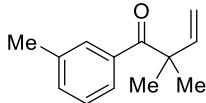
**2,2-Dimethyl-1-phenylbut-3-en-1-one (1a)**

Prepared from 2,2-dimethyl-1-(p-tolyl)but-3-en-1-ol (1.76 g, 10.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **1a** as a colorless oil (1.26 g, 72% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 6.21 – 6.16 (dd, *J* = 10.8 Hz, *J* = 17.4 Hz, 1H), 5.25 – 5.19 (m, 2H), 1.39 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 204.5, 143.8, 137.0, 131.6, 129.2, 127.9, 113.9, 50.1, 25.9. HRMS (ESI) m/z calculated for C<sub>12</sub>H<sub>14</sub>ONa [M+Na]<sup>+</sup> 197.0937, found 197.0923.



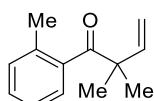
**2,2-Dimethyl-1-(p-tolyl) but-3-en-1-one (1b)**

Prepared from 2,2-dimethyl-1-phenylbut-3-en-1-ol (0.19 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **1b** as a colorless oil (0.14 g, 75% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.21 – 6.16 (dd, *J* = 10.8 Hz, *J* = 17.4 Hz, 1H), 5.23 – 5.17 (m, 2H), 2.36 (s, 3H), 1.39 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 203.8, 144.1, 142.3, 134.1, 129.6, 128.5, 113.7, 49.9, 26.1, 21.4. HRMS (ESI) m/z calculated for C<sub>13</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 211.1093, found 211.1112.



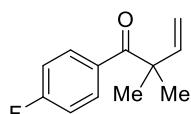
**2,2-Dimethyl-1-(m-tolyl) but-3-en-1-one (1c)**

Prepared from 2,2-dimethyl-1-(m-tolyl)but-3-en-1-ol (0.19 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **1c** as a colorless oil (0.15 g, 77% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.67 – 7.65 (m, 2H), 7.27 – 7.23 (m, 2H), 6.22 – 6.14 (m, 1H), 5.24 – 5.18 (m, 2H), 2.36 (s, 3H), 1.38 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 204.9, 143.9, 137.7, 137.3, 132.3, 129.7, 127.7, 126.4, 113.9, 50.2, 26.1, 21.4. HRMS (ESI) m/z calculated for C<sub>13</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 211.1093, found 211.1091.



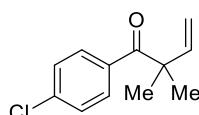
**2,2-Dimethyl-1-(o-tolyl) but-3-en-1-one (**1d**)**

Prepared from 2,2-dimethyl-1-(o-tolyl)but-3-en-1-ol (0.19 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **1d** as a colorless oil (0.13 g, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.23 – 7.11 (m, 4H), 6.05 – 5.98 (m, 1H), 5.18 – 5.12 (m, 2H), 2.22 (s, 3H), 1.31 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 210.6, 142.4, 140.3, 134.2, 130.6, 128.8, 125.2, 124.5, 113.9, 51.2, 24.3, 19.8. HRMS (ESI) m/z calculated for C<sub>13</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 211.1093, found 211.1093.



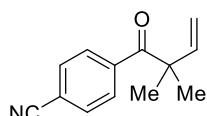
**1-(4-Fluorophenyl)-2,2-dimethylbut-3-en-1-one (**1e**)**

Prepared from 1-(4-fluorophenyl)-2,2-dimethylbut-3-en-1-ol (0.20 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **1e** as a colorless oil (0.13 g, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.98 – 7.95 (m, 2H), 7.07 – 7.03 (m, 2H), 6.21 – 6.14 (dd, J = 10.8 Hz, J = 17.6 Hz, 1H), 5.26 – 5.21 (m, 2H), 1.39 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 202.6, 163.5 (d, J = 251.8 Hz), 143.7, 132.8 (d, J = 2.5 Hz), 132.0 (d, J = 8.4 Hz), 115.0, 114.8, 114.1, 49.9, 26.0. HRMS (ESI) m/z calculated for C<sub>12</sub>H<sub>13</sub>OFNa [M+Na]<sup>+</sup> 215.0843, found 215.0841.



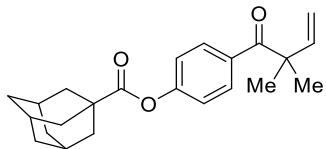
**1-(4-Chlorophenyl)-2,2-dimethylbut-3-en-1-one (**1f**)**

Prepared from 1-(4-chlorophenyl)-2,2-dimethylbut-3-en-1-ol (0.21 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **1f** as a colorless oil (0.15 g, 73% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.86 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.19 – 6.12 (dd, J = 10.4 Hz, J = 17.6 Hz, 1H), 5.25 – 5.20 (m, 2H), 1.38 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 202.9, 143.5, 137.9, 134.9, 130.8, 128.1, 114.3, 49.9, 25.9. HRMS (ESI) m/z calculated for C<sub>12</sub>H<sub>13</sub>OClNa [M+Na]<sup>+</sup> 231.0547, found 231.0539.



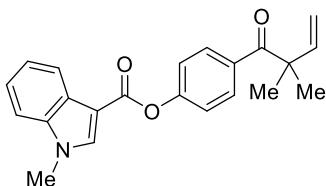
**4-(2,2-Dimethylbut-3-enoyl) benzonitrile (**1g**)**

Prepared from 4-(1-hydroxy-2,2-dimethylbut-3-en-1-yl)benzonitrile (0.20 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 30/1) afforded the desired product **1g** as a colorless oil (0.12 g, 62% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.94 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 6.18 – 6.11 (dd, J = 10.8 Hz, J = 17.6 Hz, 1H), 5.28 – 5.23 (m, 2H), 1.39 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 203.4, 142.7, 140.6, 131.8, 129.4, 117.9, 115.1, 114.8, 50.2, 25.5. HRMS (ESI) m/z calculated for C<sub>13</sub>H<sub>13</sub>ONNa [M+Na]<sup>+</sup> 222.0889, found 222.0890.



**4-(2,2-Dimethylbut-3-enoyl) phenyl (3r,5r,7r)-adamantane-1-carboxylate (1h)**

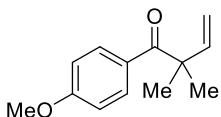
Prepared from 4-(1-hydroxy-2,2-dimethylbut-3-en-1-yl)phenyl (3r,5r,7r)-adamantane-1-carboxylate (0.18 g, 0.5 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 40/1) afforded the desired product **1h** as a white solid (0.12 g, 70% yield). M.P.: 60–62 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.97 (d,  $J$  = 8.4 Hz, 2H), 7.07 (d,  $J$  = 8.4 Hz, 2H), 6.22 – 6.15 (m, 1H), 5.25 – 5.19 (m, 2H), 2.18 – 2.07 (m, 2H), 2.06 – 1.99 (m, 6H), 1.97 – 1.83 (m, 1H), 1.81 – 1.69 (m, 1H), 1.39 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.9, 175.6, 153.7, 143.8, 133.8, 131.0, 121.0, 114.1, 55.7, 50.0, 41.0, 38.6, 36.3, 34.9, 27.8, 26.0, 25.4, 24.6. HRMS (ESI) m/z calculated for  $\text{C}_{23}\text{H}_{28}\text{O}_3\text{Na}$   $[\text{M}+\text{Na}]^+$  375.1931, found 375.1930



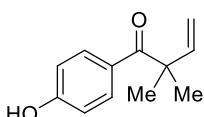
**4-(2,2-Dimethylbut-3-enoyl) phenyl 1-methyl-1H-indole-3-carboxylate (1i)**

Prepared from 4-(1-hydroxy-2,2-dimethylbut-3-en-1-yl)phenyl 1-methyl-1H-indole-3-carboxylate (0.17 g, 0.5 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 40/1) afforded the desired product **1i** as a yellow solid (0.13 g, 72% yield). M.P.: 82–84 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.21 – 8.19 (m, 1H), 8.01 (d,  $J$  = 8.4 Hz, 2H), 7.90 (s, 1H), 7.34 – 7.30 (m, 3H), 8.01 (d,  $J$  = 8.8 Hz, 2H), 6.22 – 6.15 (dd,  $J$  = 10.8 Hz,  $J$  = 17.6 Hz, 1H), 5.26 – 5.19 (m, 2H), 3.80 (s, 3H), 1.40 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.1, 162.4, 153.6, 144.3, 143.7, 137.2, 136.3, 133.6, 132.1, 131.0, 126.6, 123.1, 122.3, 121.4, 114.6, 114.0, 113.4, 109.9, 105.3, 49.9, 33.4, 26.0. HRMS (ESI) m/z calculated for  $\text{C}_{22}\text{H}_{21}\text{O}_3\text{NNa}$   $[\text{M}+\text{Na}]^+$  370.1414, found 370.1395.

**1-(4-Methoxyphenyl)-2,2-dimethylbut-3-en-1-one (1j)**



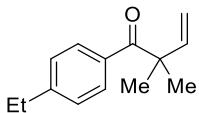
Prepared from 1-(4-methoxyphenyl)-2,2-dimethylbut-3-en-1-ol (0.21 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 40/1) afforded the desired product **1j** as a colorless oil (0.16 g, 78% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.97 (d,  $J$  = 8.8 Hz, 2H), 6.87 (d,  $J$  = 8.8 Hz, 2H), 6.23 – 6.16 (m, 1H), 5.25 – 5.17 (m, 2H), 3.84 (s, 3H), 1.39 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.3, 162.4, 144.4, 131.9, 129.1, 113.5, 113.0, 55.3, 49.8, 26.3. HRMS (ESI) m/z calculated for  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$  227.1043, found 227.1043.



**1-(4-Hydroxyphenyl)-2,2-dimethylbut-3-en-1-one (1k)**

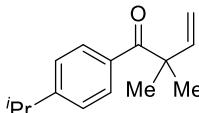
Prepared from 4-(1-hydroxy-2,2-dimethylbut-3-en-1-yl)phenol (0.19 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 40/1) afforded the desired product **1k** as a colorless oil (0.15 g, 76% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 – 7.91 (m, 2H), 6.82 – 6.81

(m, 2H), 6.22 – 6.17 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.96 (s, 1H), 5.24 (d,  $J$  = 18.0 Hz, 1H), 5.20 (d,  $J$  = 10.8 Hz, 1H), 1.40 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.0, 159.1, 144.3, 132.4, 129.2, 114.7, 113.7, 49.9, 26.3. HRMS (ESI) m/z calculated for  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{Na}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 213.0886, found 213.0887.



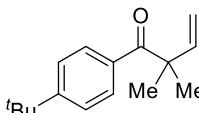
### **1-(4-Ethylphenyl)-2,2-dimethylbut-3-en-1-one (1l)**

Prepared from 1-(4-ethylphenyl)-2,2-dimethylbut-3-en-1-ol (0.20 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **1l** as a colorless oil (0.15 g, 76% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $J$  = 8.0 Hz, 2H), 7.19 (d,  $J$  = 8.0 Hz, 2H), 6.23 – 6.16 (dd,  $J$  = 10.8 Hz,  $J$  = 17.6 Hz, 1H), 5.25 – 5.18 (q, 2H), 2.70 – 2.64 (q,  $J$  = 7.6 Hz, 2H), 1.39 (s, 6H), 1.24 (t,  $J$  = 7.6 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.9, 148.5, 144.1, 134.3, 129.7, 127.4, 113.8, 49.9, 28.8, 26.1, 15.1. HRMS (ESI) m/z calculated for  $\text{C}_{14}\text{H}_{18}\text{ONa}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 225.1250, found 225.1251.



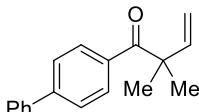
### **1-(4-Isopropylphenyl)-2,2-dimethylbut-3-en-1-one (1m)**

Prepared from 1-(4-isopropylphenyl)-2,2-dimethylbut-3-en-1-ol (0.22 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **1m** as a colorless oil (0.16 g, 73% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J$  = 8.0 Hz, 2H), 7.24 (d,  $J$  = 8.0 Hz, 2H), 6.23 – 6.16 (dd,  $J$  = 10.8 Hz,  $J$  = 17.6 Hz, 1H), 5.25 – 5.18 (m, 2H), 2.95 – 2.89 (m, 1H), 1.39 (s, 6H), 1.25 (s, 3H), 1.24 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.8, 153.0, 144.1, 134.3, 129.7, 125.9, 113.7, 49.9, 34.0, 26.1, 23.6. HRMS (ESI) m/z calculated for  $\text{C}_{15}\text{H}_{20}\text{ONa}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 239.1406, found 239.1420.



### **1-(4-(tert-Butyl) phenyl)-2,2-dimethylbut-3-en-1-one (1n)**

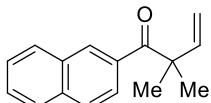
Prepared from 1-(4-(tert-butyl)phenyl)-2,2-dimethylbut-3-en-1-ol (0.23 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **1n** as a colorless oil (0.17 g, 74% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 (d,  $J$  = 8.4 Hz, 2H), 7.39 (d,  $J$  = 8.4 Hz, 2H), 6.24 – 6.16 (dd,  $J$  = 10.8 Hz,  $J$  = 17.6 Hz, 1H), 5.26 – 5.18 (m, 2H), 1.40 (s, 6H), 1.32 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.7, 155.2, 144.1, 133.9, 129.5, 124.8, 113.7, 49.9, 34.9, 31.0, 26.1. HRMS (ESI) m/z calculated for  $\text{C}_{16}\text{H}_{22}\text{ONa}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 253.1563, found 253.1583.



### **1-([1,1'-Biphenyl]-4-yl)-2,2-dimethylbut-3-en-1-one (1o)**

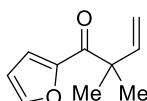
Prepared from 1-([1,1'-biphenyl]-4-yl)-2,2-dimethylbut-3-en-1-ol (0.25 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **1o** as a white solid (0.18 g, 74% yield). M.P.: 60–64 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99 (d,  $J$  = 7.6 Hz, 2H), 7.60 (d,  $J$  = 7.6 Hz, 4H), 7.45 (t,  $J$  = 7.6 Hz, 2H), 7.39 – 7.35 (m, 1H), 6.26 (dd,  $J$  = 10.4 Hz,  $J$  =

18.0 Hz, 1H), 5.28 – 5.21 (m, 2H), 1.43 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.9, 144.4, 143.9, 140.0, 135.5, 130.0, 128.9, 128.0, 127.2, 126.6, 114.1, 50.1, 26.1. HRMS (ESI) m/z calculated for  $\text{C}_{18}\text{H}_{18}\text{ONa} [\text{M}+\text{Na}]^+$  273.1250, found 273.1250.



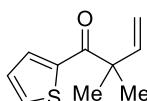
**2,2-Dimethyl-1-(naphthalen-2-yl) but-3-en-1-one (1p)**

Prepared from 2,2-dimethyl-1-(naphthalen-2-yl)but-3-en-1-ol (0.23 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **1p** as a colorless oil (0.18 g, 80% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.46 (s, 1H), 7.96 – 7.94 (m, 1H), 7.88 (d,  $J$  = 8.0 Hz, 1H), 7.81 – 7.78 (m, 2H), 7.55 – 7.47 (m, 2H), 6.30 – 6.23 (dd,  $J$  = 10.4 Hz,  $J$  = 17.6 Hz, 1H), 5.32 – 5.23 (m, 2H), 1.45 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.3, 143.9, 134.6, 134.1, 132.1, 130.6, 129.4, 127.9, 127.5, 126.4, 125.5, 114.0, 50.2, 26.1. HRMS (ESI) m/z calculated for  $\text{C}_{16}\text{H}_{16}\text{ONa} [\text{M}+\text{Na}]^+$  247.1093, found 247.1093.



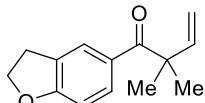
**1-(Furan-2-yl)-2,2-dimethylbut-3-en-1-one (1q)**

Prepared from 1-(furan-2-yl)-2,2-dimethylbut-3-en-1-ol (0.17 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **1q** as a yellow oil (0.12 g, 72% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (br, 1H), 7.22 (br, 1H), 6.47 (dd,  $J$  = 1.2 Hz, 1H), 6.22 (dd,  $J$  = 7.2 Hz,  $J$  = 15.6 Hz, 1H), 5.22 – 5.15 (m, 2H), 1.41 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.7, 151.7, 145.4, 142.9, 118.9, 113.9, 111.6, 49.1, 24.7. HRMS (ESI) m/z calculated for  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{Na} [\text{M}+\text{Na}]^+$  187.0730, found 187.0719.



**2,2-Dimethyl-1-(thiophen-2-yl) but-3-en-1-one (1r)**

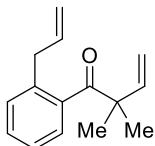
Prepared from 2,2-dimethyl-1-(thiophen-2-yl)but-3-en-1-ol (0.18 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **1r** as a yellow oil (0.14 g, 75% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81 (d,  $J$  = 3.6 Hz, 1H), 7.54 (d,  $J$  = 5.4 Hz, 1H), 7.06 – 7.04 (m, 1H), 6.22 (dd,  $J$  = 10.8 Hz,  $J$  = 18.0 Hz, 1H), 5.31 (d,  $J$  = 17.4 Hz, 1H), 5.24 (d,  $J$  = 10.8 Hz, 1H), 1.42 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.1, 143.6, 142.5, 133.4, 132.7, 127.5, 114.2, 49.9, 25.6. HRMS (ESI) m/z calculated for  $\text{C}_{10}\text{H}_{12}\text{OSNa} [\text{M}+\text{Na}]^+$  203.0501, found 203.0499.



**1-(2,3-Dihydrobenzofuran-5-yl)-2,2-dimethylbut-3-en-1-one (1s)**

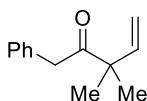
Prepared from 1-(2,3-dihydrobenzofuran-5-yl)-2,2-dimethylbut-3-en-1-ol (0.22 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **1s** as a colorless oil (0.17 g, 77% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 – 7.84 (m, 2H), 6.72 (d,  $J$  = 9.0 Hz, 1H), 6.22 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.23 (d,  $J$  = 17.4 Hz, 1H), 5.19 (d,  $J$  = 10.8 Hz, 1H), 4.62 (t,  $J$  = 8.4 Hz, 2H), 3.22 (t,  $J$  = 9.0 Hz, 2H), 1.39 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):

$\delta$  202.4, 163.2, 144.6, 131.6, 129.4, 127.1, 126.9, 113.4, 108.3, 71.9, 49.8, 29.1, 26.4. HRMS (ESI) m/z calculated for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 239.1043, found 239.1052.



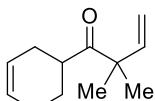
**1-(2-Allylphenyl)-2,2-dimethylbut-3-en-1-one (1t)**

Prepared from 1-(2-allylphenyl)-2,2-dimethylbut-3-en-1-ol (0.22 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **1t** as a colorless oil (0.15 g, 71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.32 – 7.27 (m, 2H), 7.25 – 7.24 (m, 1H), 7.17 – 7.15 (m, 1H), 6.06 – 6.01 (m, 1H), 5.93 – 5.86 (m, 1H), 5.20 – 5.15 (m, 2H), 5.06 – 5.02 (m, 2H), 3.31 – 3.30 (m, 2H), 1.33 – 1.32 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  210.6, 142.9, 140.1, 137.0, 136.9, 130.1, 129.2, 125.8, 125.2, 116.3, 114.0, 59.9, 51.2, 37.6, 24.8. HRMS (ESI) m/z calculated for C<sub>15</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 237.1250, found 237.1251.



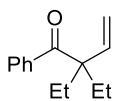
**3,3-Dimethyl-1-phenylpent-4-en-2-one (1u)**

Prepared from 3,3-dimethyl-1-phenylpent-4-en-2-ol (0.19 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **1u** as a colorless oil (0.10 g, 53% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.30 – 7.28 (m, 2H), 7.25 – 7.22 (m, 1H), 7.15 – 7.14 (m, 2H), 5.98 – 5.94 (dd, *J* = 10.8 Hz, *J* = 17.4 Hz, 1H), 5.24 (d, *J* = 3.0 Hz, 1H), 5.21 (d, *J* = 3.0 Hz, 1H), 3.76 (s, 2H), 1.28 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  209.9, 142.2, 134.8, 129.6, 128.3, 126.6, 114.8, 51.3, 43.9, 23.5. HRMS (ESI) m/z calculated for C<sub>13</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 211.1093, found 211.1094.



**1-(Cyclohex-3-en-1-yl)-2,2-dimethylbut-3-en-1-one (1v)**

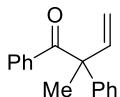
Prepared from 1-(cyclohex-3-en-1-yl)-2,2-dimethylbut-3-en-1-ol (0.18 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **1v** as a colorless oil (0.10 g, 57% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.97 (dd, *J* = 10.8 Hz, *J* = 17.2 Hz, 1H), 5.68 (br, 2H), 5.21 – 5.17 (m, 2H), 3.03 – 2.98 (m, 1H), 2.17 (br, 1H), 2.13 – 2.05 (m, 2H), 1.98 – 1.93 (m, 1H), 1.78 – 1.67 (m, 1H), 1.63 – 1.53 (m, 1H), 1.25 – 1.23 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  216.1, 141.8, 126.2, 125.8, 114.8, 51.4, 41.3, 30.9, 28.9, 26.2, 24.7, 23.1. HRMS (ESI) m/z calculated for C<sub>12</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 201.1250, found 201.1247.



**2,2-Diethyl-1-phenylbut-3-en-1-one (3a)**

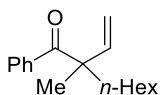
Prepared from 2,2-diethyl-1-phenylbut-3-en-1-ol (0.20 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **3a** as a colorless oil (0.16 g, 78% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.90 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.46 (m, 1H), 7.40 – 7.36 (m, 2H), 6.13 – 6.06 (m, 1H), 5.37 – 5.21 (m, 2H), 1.99 – 1.85 (m, 4H), 0.78 (t, *J* = 7.4 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  210.6, 142.9, 140.1, 137.0, 136.9, 130.1, 129.2, 125.8, 125.2, 116.3, 114.0, 59.9, 51.2, 37.6, 24.8. HRMS (ESI) m/z calculated for C<sub>15</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 237.1250, found 237.1251.

NMR (100 MHz, CDCl<sub>3</sub>): δ 204.7, 141.6, 138.0, 131.4, 128.8, 127.8, 115.6, 57.3, 26.4, 7.9. HRMS (ESI) m/z calculated for C<sub>14</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 225.1250, found 225.1250.



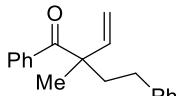
### **2-Methyl-1,2-diphenylbut-3-en-1-one (3b)**

Prepared from 2-methyl-1,2-diphenylbut-3-en-1-ol (0.24 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **3b** as a colorless oil (0.18 g, 78% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.54 – 7.53 (m, 2H), 7.37 – 7.32 (m, 3H), 7.28 – 7.23 (m, 3H), 7.22 – 7.21 (m, 2H), 6.64 – 6.59 (dd, J = 10.8 Hz, J = 17.4 Hz, 1H), 5.30 – 5.28 (m, 1H), 5.17 – 5.14 (m, 1H), 1.67 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 200.8, 144.4, 140.9, 136.2, 131.8, 130.0, 128.9, 127.9, 126.9, 126.4, 116.5, 58.5, 25.9. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 259.1093, found 259.1092.



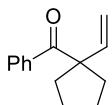
### **2-Methyl-1-phenyl-2-vinyloctan-1-one (3c)**

Prepared from 2-methyl-1-phenyl-2-vinyloctan-1-ol (0.12 g, 0.5 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **3c** as a colorless oil (94.1 mg, 77% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.84 – 7.82 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 – 7.34 (m, 2H), 6.23 – 6.16 (dd, J = 10.8 Hz, J = 17.6 Hz, 1H), 5.23 – 5.17 (m, 2H), 1.93 – 1.86 (m, 1H), 1.76 – 1.69 (m, 1H), 1.35 (s, 3H), 1.27 – 1.20 (m, 8H), 1.07 (br, 1H), 0.88 – 0.81 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 204.9, 143.4, 137.8, 131.4, 128.9, 127.9, 114.6, 53.7, 38.9, 31.5, 29.8, 24.0, 22.8, 22.5, 13.9. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>24</sub>ONa [M+Na]<sup>+</sup> 267.1719, found 267.1709.



### **2-Methyl-2-phenethyl-1-phenylbut-3-en-1-one (3d)**

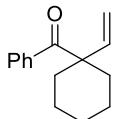
Prepared from 2-methyl-2-phenethyl-1-phenylbut-3-en-1-ol (0.13 g, 0.5 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **3d** as a colorless oil (97.8 mg, 74% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89 (d, J = 7.2 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.40 – 7.36 (m, 2H), 7.24 – 7.20 (m, 2H), 7.16 – 7.12 (m, 1H), 7.05 – 7.03 (m, 2H), 6.24 – 6.17 (dd, J = 10.8 Hz, J = 17.2 Hz, 1H), 5.29 – 5.23 (m, 2H), 2.62 – 2.55 (m, 1H), 2.43 – 2.35 (m, 1H), 2.25 – 2.17 (m, 1H), 2.09 – 2.01 (m, 1H), 1.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 204.4, 142.8, 142.2, 137.6, 131.6, 128.9, 128.3, 128.2, 127.9, 125.8, 115.1, 53.6, 41.2, 30.8, 22.9. HRMS (ESI) m/z calculated for C<sub>19</sub>H<sub>20</sub>ONa [M+Na]<sup>+</sup> 287.1406, found 287.1403.



### **Phenyl(1-vinylcyclopentyl) methanone (3e)**

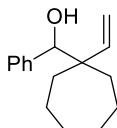
Prepared from phenyl(1-vinylcyclopentyl)methanol (0.20 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **3e** as a colorless oil (0.15 g, 74% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.91 – 7.89 (m, 2H), 7.48 – 7.45

(m, 1H), 7.39 – 7.37 (m, 2H), 6.21 – 6.16 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.14 (d,  $J$  = 10.8 Hz, 1H), 5.07 (d,  $J$  = 17.4 Hz, 1H), 2.34 – 2.30 (m, 2H), 1.91 – 1.87 (m, 2H), 1.70 – 1.64 (m, 2H), 1.63 – 1.55 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.7, 143.6, 136.2, 131.9, 129.8, 127.9, 114.4, 61.7, 36.7, 24.7. HRMS (ESI) m/z calculated for  $\text{C}_{14}\text{H}_{16}\text{ONa} [\text{M}+\text{Na}]^+$  223.1093, found 223.1082.



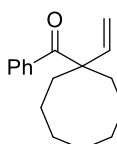
### Phenyl(1-vinylcyclohexyl) methanone (3f)

Prepared from phenyl(1-vinylcyclohexyl)methanol (0.22 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **3f** as a colorless oil (0.17 g, 78% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76 – 7.75 (m, 2H), 7.45 – 7.43 (m, 1H), 7.35 (t,  $J$  = 7.8 Hz, 2H), 6.14 – 6.10 (dd,  $J$  = 10.8 Hz, 1H), 5.27 (d,  $J$  = 10.8 Hz,  $J$  = 18.0 Hz, 1H), 5.21 (d,  $J$  = 18.0 Hz, 1H), 2.18 – 2.15 (m, 2H), 1.65 – 1.61 (m, 2H), 1.56 – 1.50 (m, 2H), 1.48 – 1.44 (m, 1H), 1.37 – 1.31 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  205.5, 142.7, 138.2, 131.1, 128.7, 127.8, 116.1, 54.3, 35.0, 25.8, 22.7. HRMS (ESI) m/z calculated for  $\text{C}_{15}\text{H}_{18}\text{ONa} [\text{M}+\text{Na}]^+$  237.1250, found 237.1236.



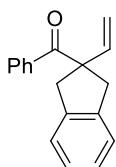
### Phenyl(1-vinylcycloheptyl) methanone (3g)

Prepared from phenyl(1-vinylcyclohexyl)methanol (0.23 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **3g** as a colorless oil (0.17 g, 73% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81 (d,  $J$  = 7.6 Hz, 2H), 7.45 – 7.42 (m, 1H), 7.37 – 7.33 (m, 2H), 6.15 – 6.08 (dd,  $J$  = 10.8 Hz,  $J$  = 17.6 Hz, 1H), 5.21 (d,  $J$  = 10.8 Hz, 1H), 5.15 (d,  $J$  = 17.6 Hz, 1H), 2.25 – 2.19 (m, 2H), 1.83 – 1.78 (m, 2H), 1.61 – 1.43 (m, 8H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.7, 143.8, 138.1, 131.2, 129.1, 127.8, 114.6, 57.4, 36.8, 30.0, 23.4. HRMS (ESI) m/z calculated for  $\text{C}_{16}\text{H}_{20}\text{ONa} [\text{M}+\text{Na}]^+$  251.1406, found 251.1402



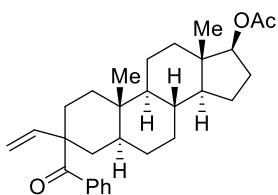
### Phenyl(1-vinylcyclooctyl) methanone (3h)

Prepared from phenyl(1-vinylcyclooctyl)methanol (0.23 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **3h** as a colorless oil (0.17 g, 72% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 – 7.78 (m, 2H), 7.44 – 7.42 (m, 1H), 7.34 (t,  $J$  = 7.8 Hz, 2H), 6.05 – 6.00 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.29 (d,  $J$  = 10.8 Hz, 1H), 5.24 (d,  $J$  = 18.0 Hz, 1H), 2.24 – 2.20 (m, 2H), 1.91 – 1.86 (m, 2H), 1.55 – 1.58 (m, 1H), 1.53 – 1.49 (m, 5H), 1.48 – 1.41 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  205.6, 142.9, 138.8, 131.0, 128.7, 127.8, 115.4, 57.8, 30.8, 28.3, 25.2, 22.4. HRMS (ESI) m/z calculated for  $\text{C}_{17}\text{H}_{22}\text{ONa} [\text{M}+\text{Na}]^+$  265.1563, found 265.1553.



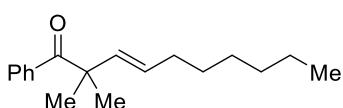
**Phenyl(2-vinyl-2,3-dihydro-1H-inden-2-yl) methanone (3i)**

Prepared from phenyl(1-vinylcyclooctyl)methanol (0.25 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **3i** as a colorless oil (0.20 g, 82% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 – 7.93 (m, 2H), 7.53 – 7.50 (m, 1H), 7.42 (d,  $J$  = 7.8 Hz, 2H), 7.19 – 7.18 (m, 2H), 7.16 – 7.14 (m, 2H), 6.31 – 6.27 (dd,  $J$  = 10.8 Hz,  $J$  = 17.4 Hz, 1H), 5.16 (d,  $J$  = 3.0 Hz, 1H), 5.14 (d,  $J$  = 3.6 Hz, 1H), 3.71 (d,  $J$  = 15.6 Hz, 2H), 3.28 (d,  $J$  = 15.6 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.9, 142.3, 140.6, 136.2, 132.3, 129.7, 128.1, 126.7, 124.4, 115.0, 61.9, 43.1. HRMS (ESI) m/z calculated for  $\text{C}_{18}\text{H}_{16}\text{ONa} [\text{M}+\text{Na}]^+$  271.1099, found 271.1114.



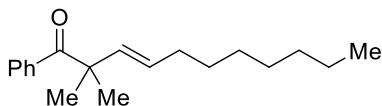
**Compound (3j)**

Prepared from **3j'** (0.22 g, 0.5 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 20/1) afforded the desired product **3j** as a white solid (0.16 g, 71% yield). M.P.: 134–137 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73 – 7.72 (d,  $J$  = 7.8 Hz, 2H), 7.43 (t,  $J$  = 7.8 Hz, 1H), 7.37 – 7.35 (m, 2H), 6.24 – 6.20 (dd,  $J$  = 10.8 Hz,  $J$  = 18.0 Hz, 1H), 5.36 (d,  $J$  = 10.2 Hz, 1H), 5.22 (d,  $J$  = 18.0 Hz, 1H), 4.59 – 4.56 (m, 1H), 2.18 – 2.11 (m, 1H), 2.03 (s, 3H), 2.02 – 1.98 (m, 1H), 1.81 – 1.76 (m, 1H), 1.73 – 1.66 (m, 4H), 1.64 – 1.62 (m, 1H), 1.64 – 1.62 (m, 1H), 1.61 – 1.59 (m, 1H), 1.49 – 1.42 (m, 1H), 1.41 – 1.34 (m, 2H), 1.31 – 1.18 (m, 5H), 1.15 – 1.10 (m, 1H), 1.05 – 0.99 (m, 1H), 0.94 – 0.87 (m, 1H), 0.77 (s, 6H), 0.73 – 0.68 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 204.9, 171.2, 140.6, 137.5, 131.1, 128.9, 127.8, 117.9, 82.9, 54.4, 53.8, 50.8, 42.6, 41.5, 37.2, 36.9, 35.6, 35.2, 34.3, 31.5, 29.8, 28.6, 27.5, 23.5, 21.2, 20.4, 12.1, 11.9. HRMS (ESI) m/z calculated for  $\text{C}_{30}\text{H}_{40}\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$  471.2870, found 471.2883.



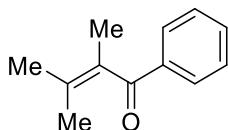
**(E)-2,2-Dimethyl-1-phenyldec-3-en-1-one (3k)**

Prepared from (E)-2,2-dimethyl-1-phenyldec-3-en-1-ol (0.25 g, 1.0 mmol). Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1) afforded the desired product **3k** as a colorless oil (0.17 g, 71% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 (d,  $J$  = 7.6 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.44 (d,  $J$  = 7.6 Hz, 2H), 5.83 (d,  $J$  = 11.2 Hz, 1H), 5.35 – 5.28 (m, 1H), 1.74 – 1.72 (m, 2H), 1.41 (s, 7H), 1.13 – 1.08 (m, 2H), 1.02 – 1.01 (m, 5H), 0.74 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.9, 135.5, 135.1, 132.9, 132.0, 129.9, 127.7, 47.9, 31.3, 28.6, 28.2, 28.0, 28.0, 22.4, 13.9. HRMS (ESI) m/z calculated for  $\text{C}_{18}\text{H}_{26}\text{ONa} [\text{M}+\text{Na}]^+$  281.1876, found 281.1867.



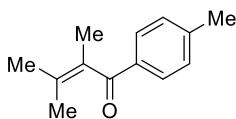
**(E)-2,2-Dimethyl-1-phenylundec-3-en-1-one (3l)**

Prepared from (*E*)-2,2-dimethyl-1-phenylundec-3-en-1-one (0.27 g, 1.0 mmol). Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1) afforded the desired product **3l** as a colorless oil (0.20 g, 74% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.45 (m, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 5.82 (dd, *J* = 11.2 Hz, 1H), 5.35 – 5.28 (m, 1H), 1.74 – 1.73 (m, 2H), 1.45 (s, 7H), 1.27 – 1.17 (m, 3H), 1.09 (br, 4H), 1.02 (br, 4H), 0.83 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 204.9, 135.6, 135.2, 132.9, 131.9, 129.9, 127.7, 47.9, 31.7, 29.04, 29.01, 28.9, 28.2, 28.1, 22.5, 14.0. HRMS (ESI) m/z calculated for C<sub>19</sub>H<sub>28</sub>ONa [M+Na]<sup>+</sup> 295.2032, found 295.2020.



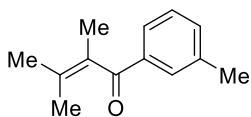
**2,3-Dimethyl-1-phenylbut-2-en-1-one (2a)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.88 – 7.87 (m, 2H), 7.56 – 7.54 (m, 1H), 7.47 – 7.44 (m, 2H), 1.88 (s, 3H), 1.83 (s, 3H), 1.60 – 1.61 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 201.5, 136.8, 133.5, 132.9, 129.7, 129.3, 128.6, 22.3, 20.1, 16.5. HRMS (ESI) m/z calculated for C<sub>12</sub>H<sub>14</sub>ONa [M+Na]<sup>+</sup> 197.0937, found 197.0938.



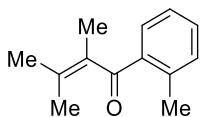
**2,3-Dimethyl-1-(p-tolyl) but-2-en-1-one (2b)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.87 (s, 3H), 1.82 (s, 3H), 1.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.5, 143.9, 134.2, 132.8, 129.8, 129.5, 129.4, 22.3, 21.7, 20.0, 16.6. HRMS (ESI) m/z calculated for C<sub>13</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 211.1093, found 211.1108.



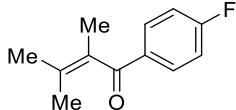
**2,3-Dimethyl-1-(m-tolyl) but-2-en-1-one (2c)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.70 (s, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.37 – 7.31 (m, 2H), 2.40 (s, 3H), 1.87 (s, 3H), 1.83 (s, 3H), 1.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.7, 138.4, 136.8, 133.7, 133.2, 129.8, 129.5, 128.4, 126.7, 22.3, 21.2, 20.1, 16.6. HRMS (ESI) m/z calculated for C<sub>13</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 211.1093, found 211.1088.



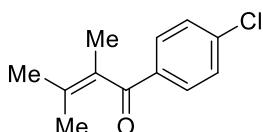
**2,3-Dimethyl-1-(o-tolyl) but-2-en-1-one (2d)**

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (d,  $J$  = 7.6 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.25 – 7.19 (m, 2H), 2.50 (s, 3H), 1.84 (s, 3H), 1.83 (s, 3H), 1.67 – 1.63 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.0, 138.5, 138.2, 137.6, 131.7, 131.5, 131.0, 129.9, 125.7, 22.4, 21.3, 20.7, 16.5. HRMS (ESI) m/z calculated for  $\text{C}_{13}\text{H}_{16}\text{ONa} [\text{M}+\text{Na}]^+$  211.1093, found 211.1088.



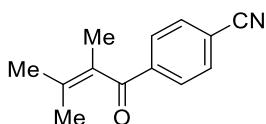
### 1-(4-Fluorophenyl)-2,3-dimethylbut-2-en-1-one (2e)

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 – 7.89 (m, 2H), 7.13 (t,  $J$  = 8.4 Hz, 2H), 1.88 (s, 3H), 1.83 (s, 3H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.1, 167.0, 164.5 (d,  $J$  = 253.2 Hz), 133.6, 133.2, 131.9 (d,  $J$  = 9.2 Hz), 129.4, 115.9, 115.6 (d,  $J$  = 21.7 Hz), 22.4, 20.1, 16.5. HRMS (ESI) m/z calculated for  $\text{C}_{12}\text{H}_{13}\text{OFNa} [\text{M}+\text{Na}]^+$  215.0843, found 215.0847.



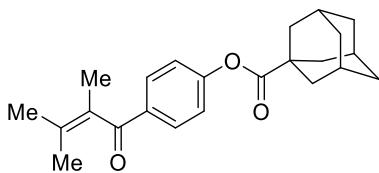
### 1-(4-Chlorophenyl)-2,3-dimethylbut-2-en-1-one (2f)

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.82 – 7.80 (m, 2H), 7.44 – 7.42 (m, 2H), 1.87 (s, 3H), 1.83 (s, 3H), 1.60 (d,  $J$  = 1.2 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.2, 139.4, 135.3, 134.2, 130.7, 129.3, 128.9, 22.4, 20.2, 16.5. HRMS (ESI) m/z calculated for  $\text{C}_{12}\text{H}_{13}\text{OCINa} [\text{M}+\text{Na}]^+$  231.0547, found 231.0541.



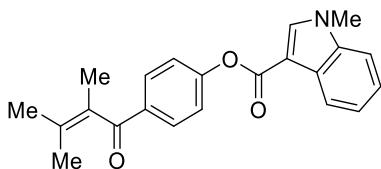
### 4-(2,3-Dimethylbut-2-enoyl) benzonitrile (2g)

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 40/1). Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d,  $J$  = 8.0 Hz, 2H), 7.78 (d,  $J$  = 7.6 Hz, 2H), 1.88 (s, 3H), 1.87 (s, 3H), 1.62 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.7, 140.3, 136.5, 132.5, 129.5, 128.8, 118.0, 115.9, 22.6, 20.5, 16.4. HRMS (ESI) m/z calculated for  $\text{C}_{13}\text{H}_{13}\text{ONa} [\text{M}+\text{Na}]^+$  222.0889, found 222.0888.



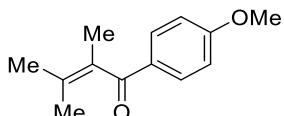
### 4-(2,3-Dimethylbut-2-enoyl) phenyl adamantane-1-carboxylate (2h)

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 40/1). White solid. M.P.: 65–67 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91 (d,  $J$  = 8.4 Hz, 2H), 7.15 (d,  $J$  = 8.4 Hz, 2H), 2.09 (br, 3H), 2.06 (br, 6H), 1.87 (br, 3H), 1.83 (br, 3H), 1.78 (br, 6H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.4, 175.6, 154.9, 134.1, 133.5, 130.9, 129.6, 121.8, 41.2, 38.7, 36.4, 27.9, 22.4, 20.1, 16.5. HRMS (ESI) m/z calculated for  $\text{C}_{23}\text{H}_{28}\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$  375.1931, found 375.1921.



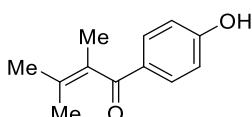
**4-(2,3-Dimethylbut-2-enoyl) phenyl 1-methyl-1H-indole-3-carboxylate (2i)**

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 40/1). Yellow solid. M.P.: 81–85 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.23 – 8.21 (m, 1H), 7.97 – 7.95 (m, 3H), 7.40 – 7.30 (m, 5H), 3.86 (s, 3H), 1.90 (s, 3H), 1.83 (s, 3H), 1.63 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.6, 162.3, 154.8, 137.3, 136.3, 133.8, 133.3, 130.9, 129.5, 126.7, 123.2, 122.4, 122.2, 121.5, 109.9, 105.5, 33.5, 22.4, 20.0, 16.5. HRMS (ESI) m/z calculated for  $\text{C}_{22}\text{H}_{21}\text{O}_3\text{NNa}$  [M+Na]<sup>+</sup> 370.1414, found 370.1408.



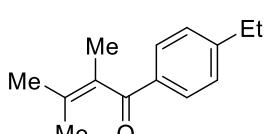
**1-(4-Methoxyphenyl)-2,3-dimethylbut-2-en-1-one (2j)**

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 40/1). Colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 – 7.85 (m, 2H), 6.95 – 6.92 (m, 2H), 3.87 (s, 3H), 1.87 (s, 3H), 1.81 (s, 3H), 1.59 (dd,  $J$  = 1.2 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.5, 163.6, 132.1, 131.7, 129.9, 129.7, 113.8, 55.4, 22.3, 19.9, 16.6. HRMS (ESI) m/z calculated for  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Na}$  [M+Na]<sup>+</sup> 227.1043, found 227.1043.



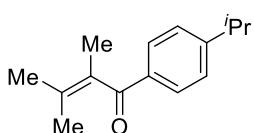
**1-(4-Hydroxyphenyl)-2,3-dimethylbut-2-en-1-one (2k)**

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.09 (br, 1H), 7.84 (d,  $J$  = 8.4 Hz, 2H), 6.95 (d,  $J$  = 8.4 Hz, 2H), 1.88 (s, 3H), 1.80 (s, 3H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.2, 161.6, 132.9, 132.3, 129.4, 128.7, 115.7, 22.4, 19.9, 16.7. HRMS (ESI) m/z calculated for  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{Na}$  [M+Na]<sup>+</sup> 213.0886, found 213.0887.



**1-(4-Ethylphenyl)-2,3-dimethylbut-2-en-1-one (2l)**

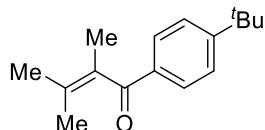
Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.82 (d,  $J$  = 8.0 Hz, 2H), 7.29 (d,  $J$  = 8.0 Hz, 2H), 2.73 – 2.68 (q,  $J$  = 7.6 Hz, 2H), 1.88 (s, 3H), 1.82 (s, 3H), 1.60 (s, 3H), 1.26 (t,  $J$  = 7.6 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.4, 149.9, 134.3, 132.7, 129.8, 129.6, 128.1, 28.9, 22.3, 19.9, 16.6, 15.1. HRMS (ESI) m/z calculated for  $\text{C}_{14}\text{H}_{18}\text{ONa}$  [M+Na]<sup>+</sup> 225.1250, found 225.1248.



**1-(4-Isopropylphenyl)-2,3-dimethylbut-2-en-1-one (2m)**

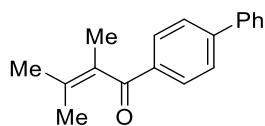
Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (400

MHz, CDCl<sub>3</sub>): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.93 – 2.86 (m, 1H), 1.80 (s, 3H), 1.75 (s, 3H), 1.53 (s, 3H), 1.21 (s, 3H), 1.19 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.4, 154.5, 134.5, 132.7, 129.9, 129.6, 126.7, 34.2, 23.6, 22.3, 19.9, 16.6. HRMS (ESI) m/z calculated for C<sub>15</sub>H<sub>20</sub>ONa [M+Na]<sup>+</sup> 239.1406, found 239.1420.



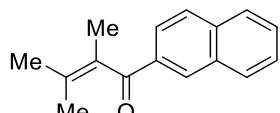
### **1-(4-(tert-Butyl) phenyl)-2,3-dimethylbut-2-en-1-one (2n)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 1.88 (s, 3H), 1.83 (s, 3H), 1.61 (s, 3H), 1.34 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.4, 156.7, 133.9, 132.7, 129.8, 129.3, 125.5, 35.1, 31.1, 22.3, 19.9, 16.6. HRMS (ESI) m/z calculated for C<sub>16</sub>H<sub>22</sub>ONa [M+Na]<sup>+</sup> 253.1563, found 253.1578.



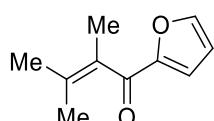
### **1-([1,1'-Biphenyl]-4-yl)-2,3-dimethylbut-2-en-1-one (2o)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). White semisolid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.46 (m, 2H), 7.41 – 7.38 (m, 1H), 1.91 (s, 3H), 1.85 (s, 3H), 1.64 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 201.2, 145.7, 140.0, 135.5, 133.4, 129.9, 129.8, 128.9, 128.1, 127.3, 127.2, 22.4, 20.1, 16.6. HRMS (ESI) m/z calculated for C<sub>18</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 273.1250, found 273.1250.



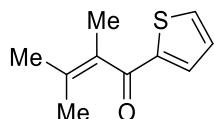
### **2,3-Dimethyl-1-(naphthalen-2-yl) but-2-en-1-one (2p)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.35 (br, 1H), 8.00 – 7.94 (m, 2H), 7.91 – 7.86 (m, 2H), 7.61 – 7.52 (m, 2H), 1.96 (s, 3H), 1.89 (s, 3H), 1.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.7, 135.7, 134.1, 133.5, 132.7, 131.4, 129.8, 129.5, 128.5, 128.4, 127.8, 126.6, 124.6, 22.5, 20.2, 16.7. HRMS (ESI) m/z calculated for C<sub>16</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 247.1093, found 247.1090.



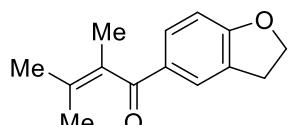
### **1-(Furan-2-yl)-2,3-dimethylbut-2-en-1-one (2q)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.62 – 7.61 (m, 1H), 7.09 (d, *J* = 3.6 Hz, 1H), 6.53 – 6.52 (dd, *J* = 1.8 Hz, *J* = 3.6 Hz, 1H), 1.91 (s, 3H), 1.81 (s, 3H), 1.69 (d, *J* = 1.2 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 188.7, 152.6, 146.8, 135.2, 129.1, 119.1, 112.2, 22.3, 20.4, 16.3. HRMS (ESI) m/z calculated for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 187.0730, found 187.0731.



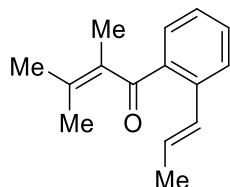
**2,3-Dimethyl-1-(thiophen-2-yl) but-2-en-1-one (2r)**

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.66 (d,  $J$  = 4.8 Hz, 1H), 7.59 (d,  $J$  = 4.2 Hz, 1H), 7.12 (t,  $J$  = 3.6 Hz, 1H), 1.93 (s, 3H), 1.81 (s, 3H), 1.67 (d,  $J$  = 1.2 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.9, 144.2, 134.2, 133.7, 133.1, 129.9, 128.1, 22.5, 19.9, 16.6. HRMS (ESI) m/z calculated for  $\text{C}_{10}\text{H}_{12}\text{OSNa} [\text{M}+\text{Na}]^+$  203.0501, found 203.0499.



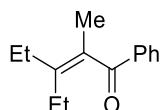
**1-(2,3-Dihydrobenzofuran-5-yl)-2,3-dimethylbut-2-en-1-one (2s)**

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (m, 1H), 7.71 – 7.69 (m, 1H), 6.80 (d,  $J$  = 7.8 Hz, 1H), 4.66 (t,  $J$  = 9.0 Hz, 2H), 3.25 (t,  $J$  = 8.4 Hz, 2H), 1.87 (s, 3H), 1.81 (s, 3H), 1.59 (d,  $J$  = 1.2 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.5, 164.5, 131.8, 131.7, 130.0, 129.9, 127.8, 126.4, 109.1, 72.2, 28.9, 22.3, 19.9, 16.7. HRMS (ESI) m/z calculated for  $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Na} [\text{M}+\text{Na}]^+$  239.1043, found 239.1049.



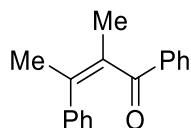
**(E)-2,3-Dimethyl-1-(2-(prop-1-en-1-yl) phenyl) but-2-en-1-one (2t)**

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.53 – 7.51 (m, 1H), 7.44 – 7.37 (m, 2H), 7.25 – 7.21 (m, 1H), 6.83 – 6.80 (m, 1H), 6.21 – 6.14 (m, 1H), 1.87 (d,  $J$  = 6.0 Hz, 3H), 1.83 (s, 6H), 1.70 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.4, 139.4, 137.8, 131.6, 130.9, 130.5, 129.2, 129.1, 128.3, 126.8, 126.5, 22.6, 21.7, 18.7, 16.5. HRMS (ESI) m/z calculated for  $\text{C}_{15}\text{H}_{18}\text{ONa} [\text{M}+\text{Na}]^+$  237.1250, found 237.1251.



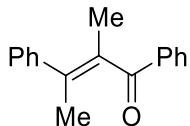
**3-Ethyl-2-methyl-1-phenylpent-2-en-1-one (4a)**

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91 (d,  $J$  = 8.0 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.48 – 7.44 (m, 2H), 2.25 – 2.19 (q,  $J$  = 7.2 Hz, 2H), 1.98 – 1.92 (q,  $J$  = 7.2 Hz, 2H), 1.87 (s, 3H), 1.12 (t,  $J$  = 7.2 Hz, 3H), 0.91 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.7, 143.5, 136.7, 133.0, 129.3, 129.0, 128.6, 26.4, 23.5, 15.9, 12.9, 12.5. HRMS (ESI) m/z calculated for  $\text{C}_{14}\text{H}_{18}\text{ONa} [\text{M}+\text{Na}]^+$  225.1250, found 225.1250.



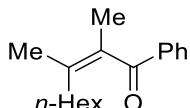
**(Z)-2-Methyl-1,3-diphenylbut-2-en-1-one (Z-4b)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.59 (m, 1H), 7.53 – 7.50 (m, 2H), 7.43 – 7.39 (m, 2H), 7.32 – 7.30 (m, 3H), 1.89 (s, 3H), 1.85 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.1, 141.9, 136.5, 136.1, 133.3, 132.0, 129.2, 128.8, 128.3, 127.8, 127.0, 22.4, 17.9. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 259.1093, found 259.1090.



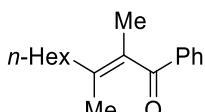
**(E)-2-Methyl-1,3-diphenylbut-2-en-1-one (E-4b)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.33 – 7.31 (m, 1H), 7.23 – 7.20 (m, 2H), 7.07 – 7.03 (m, 4H), 7.00 – 6.98 (m, 1H), 2.22 (s, 3H), 2.12 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.45, 142.6, 138.5, 136.9, 132.9, 132.3, 129.2, 128.1, 127.9, 127.8, 127.1, 20.5, 17.8. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 259.1093, found 259.1092.



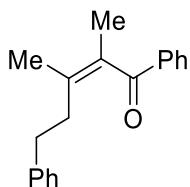
**(Z)-2,3-Dimethyl-1-phenylnon-2-en-1-one (Z-4c)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.88 – 7.86 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.53 (m, 1H), 7.47 – 7.43 (m, 2H), 1.91 (t, *J* = 7.6 Hz, 2H), 1.86 (s, 3H), 1.80 (s, 3H), 1.35 – 1.32 (m, 2H), 1.19 – 1.10 (m, 6H), 0.80 (t, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.6, 137.6, 136.9, 132.9, 129.8, 129.3, 128.5, 36.0, 31.5, 29.1, 28.0, 22.4, 17.5, 16.7, 13.9. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>24</sub>ONa [M+Na]<sup>+</sup> 267.1719, found 267.1708.



**(E)-2,3-Dimethyl-1-phenylnon-2-en-1-one (E-4c)**

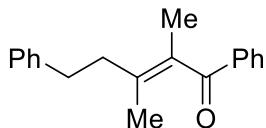
Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.44 (m, 2H), 2.18 (t, *J* = 7.2 Hz, 2H), 1.88 (s, 3H), 1.58 (s, 3H), 1.53 – 1.47 (m, 2H), 1.35 (br, 5H), 1.26 – 1.23 (m, 1H), 0.92 – 0.91 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.8, 137.2, 136.8, 132.9, 129.3, 128.6, 128.5, 33.9, 31.8, 29.4, 27.6, 22.6, 20.2, 16.2, 14.1. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>24</sub>ONa [M+Na]<sup>+</sup> 267.1719, found 267.1706.



**(Z)-2,3-Dimethyl-1,5-diphenylpent-2-en-1-one (Z-4d)**

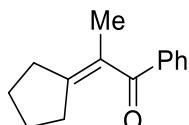
Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.45 – 7.41 (m, 2H), 7.18 – 7.08 (m,

3H), 6.96 – 6.94 (d,  $J$  = 7.2 Hz, 2H), 2.67 – 2.63 (m, 2H), 2.26 – 2.22 (m, 2H), 1.88 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.3, 141.7, 136.9, 136.6, 132.9, 130.9, 129.3, 128.6, 128.3, 128.2, 125.8, 38.3, 34.6, 17.7, 16.7. HRMS (ESI) m/z calculated for  $\text{C}_{19}\text{H}_{20}\text{ONa} [\text{M}+\text{Na}]^+$  287.1406, found 287.1398.



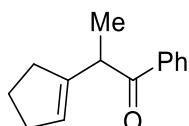
#### (E)-2,3-Dimethyl-1,5-diphenylpent-2-en-1-one (E-4d)

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70 (d,  $J$  = 7.2 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.4 (t,  $J$  = 7.6 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.32 (d,  $J$  = 6.4 Hz, 3H), 2.85 (t,  $J$  = 7.6 Hz, 2H), 2.53 (t,  $J$  = 7.6 Hz, 2H), 1.77 (s, 3H), 1.61 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.6, 141.6, 136.4, 135.2, 133.0, 130.9, 129.4, 128.6, 128.5, 128.4, 126.1, 35.5, 33.6, 19.9, 16.2. HRMS (ESI) m/z calculated for  $\text{C}_{19}\text{H}_{20}\text{ONa} [\text{M}+\text{Na}]^+$  287.1406, found 287.1410.



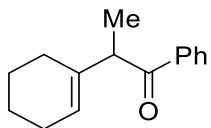
#### 2-Cyclopentylidene-1-phenylpropan-1-one (C2-4e)

Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J$  = 7.2 Hz, 2H), 7.53 – 7.51 (m, 1H), 7.45 – 7.42 (m, 2H), 2.41 – 2.39 (m, 2H), 2.11 – 2.09 (m, 2H), 1.93 (s, 3H), 1.72 – 1.68 (m, 2H), 1.61 – 1.57 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.5, 138.2, 132.3, 129.0, 128.5, 126.6, 33.1, 31.9, 27.2, 25.5, 17.6. HRMS (ESI) m/z calculated for  $\text{C}_{14}\text{H}_{16}\text{ONa} [\text{M}+\text{Na}]^+$  223.1093, found 223.1084.



#### 2-(Cyclopent-1-en-1-yl)-1-phenylpropan-1-one (C3-4e)

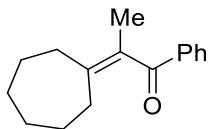
Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 – 7.96 (m, 2H), 7.55 – 7.51 (m, 1H), 7.46 – 7.42 (m, 2H), 5.49 (br, 1H), 4.29 – 4.23 (m, 2H), 2.35 – 2.20 (m, 4H), 1.87 – 1.78 (m, 2H), 1.35 (d,  $J$  = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.0, 143.6, 136.8, 132.7, 128.4, 126.9, 43.5, 33.3, 32.5, 23.2, 15.9. HRMS (ESI) m/z calculated for  $\text{C}_{14}\text{H}_{16}\text{ONa} [\text{M}+\text{Na}]^+$  223.1093., found 223.1081.



#### 2-(Cyclohex-1-en-1-yl)-1-phenylpropan-1-one (4f)

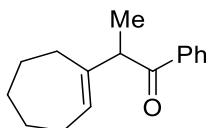
Flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 50/1). Colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (d,  $J$  = 11.4 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.44 – 7.40 (m, 2H), 5.58 (br, 1H), 4.02 – 3.97 (m, 1H), 2.06 – 1.88 (m, 4H), 1.62 – 1.54 (m, 2H), 1.50 – 1.47 (m, 2H), 1.30 (d,  $J$  = 10.2 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.3, 137.7, 136.9, 132.6, 128.3, 128.2, 124.7, 49.2,

26.4, 25.3, 22.8, 22.1, 15.9. HRMS (ESI) m/z calculated for C<sub>15</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 237.1250, found 237.1252.



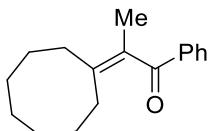
**2-Cycloheptylidene-1-phenylpropan-1-one (C2-4g)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.9 (d, *J* = 7.2 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.48 – 7.44 (m, 2H), 2.42 – 2.39 (m, 2H), 2.14 (br, 2H), 1.86 (s, 3H), 1.70 – 1.68 (m, 2H), 1.59 (br, 2H), 1.48 (br, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.8, 142.1, 136.8, 132.9, 129.6, 129.4, 128.6, 33.3, 31.6, 29.9, 28.8, 27.8, 26.7, 16.1. HRMS (ESI) m/z calculated for C<sub>16</sub>H<sub>20</sub>ONa [M+Na]<sup>+</sup> 251.1406, found 251.1399.



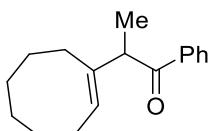
**2-(Cyclohept-1-en-1-yl)-1-phenylpropan-1-one (C3-4g)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.99 – 7.98 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.43 – 7.40 (m, 2H), 5.79 (t, *J* = 6.6 Hz, 1H), 4.09 – 4.05 (m, 1H), 2.17 – 2.13 (m, 1H), 2.09 – 2.05 (m, 3H), 1.68 – 1.63 (m, 2H), 1.43 – 1.39 (m, 4H), 1.28 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 201.3, 144.3, 136.9, 132.5, 130.1, 128.5, 128.2, 51.4, 32.5, 30.3, 28.4, 26.8, 26.7, 15.9. HRMS (ESI) m/z calculated for C<sub>16</sub>H<sub>20</sub>ONa [M+Na]<sup>+</sup> 251.1406, found 251.1397.



**2-Cyclooctylidene-1-phenylpropan-1-one (C2-4h)**

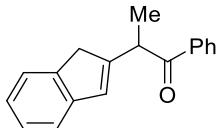
Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.89 – 7.87 (m, 2H), 7.56 – 7.53 (m, 1H), 7.47 – 7.44 (m, 2H), 2.38 – 2.36 (m, 2H), 2.10 – 2.08 (m, 2H), 1.88 (s, 3H), 1.74 – 1.72 (m, 2H), 1.57 – 1.53 (m, 6H), 1.47 – 1.43 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 201.8, 142.3, 136.8, 132.9, 129.9, 129.3, 128.6, 33.5, 30.4, 27.4, 26.9, 26.3, 26.1, 25.1, 16.5. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>22</sub>ONa [M+Na]<sup>+</sup> 265.1563, found 265.1556.



**(E)-2-(Cyclooct-1-en-1-yl)-1-phenylpropan-1-one (C3-4h)**

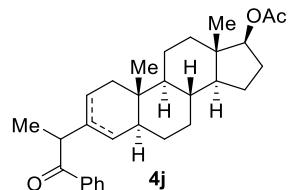
Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.99 – 7.97 (m, 2H), 7.52 – 7.49 (m, 1H), 7.43 – 7.40 (m, 2H), 5.58 – 5.55 (m, 1H), 4.16 – 4.12 (m, 1H), 2.23 – 2.15 (m, 2H), 2.09 – 2.05 (m, 2H), 1.52 – 1.49 (m, 1H), 1.43 – 1.40 (m, 2H), 1.37 – 1.32 (m, 8H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 201.5, 140.1, 137.2, 132.5, 128.4, 128.3,

128.2, 49.7, 29.4, 29.3, 27.7, 26.4, 26.1, 26.0, 16.7. HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>22</sub>ONa [M+Na]<sup>+</sup> 265.1563., found 265.1550.  
found 271.1114.



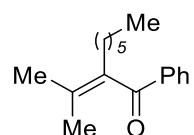
### **2-(1H-inden-2-yl)-1-phenylpropan-1-one (4i)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.01 – 8.00 (m, 2H), 7.53 – 7.50 (m, 1H), 7.44 – 7.41 (m, 2H), 7.36 – 7.35 (m, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H), 7.12 – 7.10 (td, J = 1.2 Hz, J = 7.2 Hz, 1H), 6.67 – 6.66 (s, 1H), 4.71 – 4.67 (q, J = 6.6 Hz, 1H), 3.44 – 3.30 (m, 2H), 1.52 (d, J = 6.6 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 200.2, 148.4, 144.7, 143.1, 136.5, 132.9, 128.9, 128.6, 128.5, 126.4, 124.3, 123.5, 120.6, 43.6, 39.3, 17.5. HRMS (ESI) m/z calculated for C<sub>18</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup> 271.1093, found 271.1114.



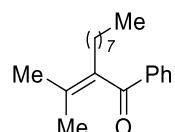
### **Compound (4j)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 20/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.97 – 7.94 (m, 4H), 7.53 – 7.49 (m, 2H), 7.44 – 7.40 (m, 4H), 5.52 – 5.51 (m, 1H), 5.48 – 5.47 (m, 1H), 4.58 – 4.54 (m, 2H), 4.05 – 3.95 (m, 2H), 2.18 – 2.08 (m, 2H), 2.02 (s, 6H), 1.96 – 1.89 (m, 2H), 1.78 – 1.75 (m, 2H), 1.73 – 1.59 (m, 8H), 1.47 – 1.39 (m, 8H), 1.34 – 1.28 (m, 6H), 1.26 – 1.22 (m, 7H), 1.19 – 1.08 (m, 4H), 1.02 – 0.93 (m, 2H), 0.89 – 0.81 (m, 3H), 0.76 (s, 3H), 0.75 (s, 3H), 0.68 – 0.62 (m, 5H), 0.51 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 201.4, 201.2, 171.2, 136.9, 136.5, 136.2, 132.6, 128.4, 128.3, 123.9, 123.6, 82.9, 53.7, 50.7, 49.2, 48.7, 42.5, 41.7, 41.6, 40.1, 36.9, 35.3, 34.5, 34.4, 31.5, 31.2, 30.9, 29.7, 28.4, 27.5, 23.5, 21.2, 20.5, 16.0, 15.9, 12.0, 11.9, 11.6, 11.4. HRMS (ESI) m/z calculated for C<sub>30</sub>H<sub>40</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 471.2870, found 471.2865.



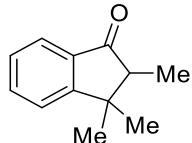
### **Phenyl-2-(propan-2-ylidene) nonan-1-one (4k)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.90 – 7.88 (m, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.43 (m, 2H), 2.31(t, J = 7.6 Hz, 2H), 1.84 (s, 3H), 1.56 (s, 3H), 1.32 – 1.31 (m, 4H), 1.27 – 1.23 (m, 6H), 0.84 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.8, 137.5, 135.2, 132.9, 132.6, 129.3, 128.6, 31.5, 30.9, 29.3, 28.6, 22.7, 22.5, 19.9, 14.0. HRMS (ESI) m/z calculated for C<sub>18</sub>H<sub>26</sub>ONa [M+Na]<sup>+</sup> 281.1876, found 281.1878.



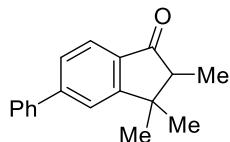
**Phenyl-2-(propan-2-ylidene) undecan-1-one (4l)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.90 – 7.88 (m, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.43 (m, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.84 (s, 3H), 1.56 (s, 3H), 1.35 – 1.30 (m, 2H), 1.29 – 1.22 (m, 12H), 0.85 (t, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 201.3, 137.5, 135.2, 132.9, 132.6, 129.3, 128.5, 32.6, 31.8, 30.0, 29.6, 29.3, 29.2, 28.6, 22.7, 22.6, 19.9, 14.0. HRMS (ESI) m/z calculated for C<sub>19</sub>H<sub>28</sub>ONa [M+Na]<sup>+</sup> 295.2032, found 295.2016.



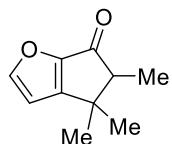
**2,3,3-trimethyl-2,3-dihydro-1H-inden-1-one (5a)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.73 (d, *J* = 7.2 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.35 (m, 1H), 2.48 (q, *J* = 7.4 Hz, 1H), 1.46 (s, 3H), 1.22 (d, *J* = 7.2 Hz, 3H), 1.14 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 207.9, 162.7, 134.7, 134.5, 127.3, 123.5, 123.3, 54.7, 41.8, 27.7, 26.9, 9.6. HRMS (ESI) m/z calculated for C<sub>12</sub>H<sub>14</sub>ONa [M+Na]<sup>+</sup> 197.0937, found 197.0935.



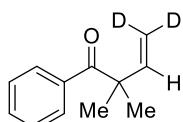
**2,3,3-trimethyl-5-phenyl-2,3-dihydro-1H-inden-1-one (5o)**

Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). White solid. M.P.: 90–94 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.68 (br, 1H), 7.64 – 7.63 (m, 2H), 7.59 – 7.58 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.42 – 7.40 (m, 1H), 2.55 – 2.51 (q, *J* = 7.2 Hz, 1H), 1.50 (s, 3H), 1.24 (d, *J* = 7.2 Hz, 3H), 1.20 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 207.4, 163.3, 147.8, 140.6, 133.4, 128.9, 128.2, 127.5, 126.8, 123.9, 121.9, 55.0, 41.9, 27.8, 26.9, 9.7. HRMS (ESI) m/z calculated for C<sub>18</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 273.1250, found 273.1250.



**4,4,5-trimethyl-4H-cyclopenta[b]furan-6(5H)-one (5q)**

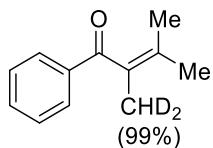
Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.72 (d, *J* = 1.8 Hz, 1H), 6.47 (d, *J* = 1.8 Hz, 1H), 2.73 – 2.70 (m, 1H), 1.36 (s, 3H), 1.21 (d, *J* = 7.8 Hz, 3H), 1.19 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 190.3, 163.8, 153.3, 152.3, 107.7, 58.9, 36.9, 27.9, 25.1, 10.7. HRMS (ESI) m/z calculated for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 187.0730, found 187.0722.



**1a-D-b**

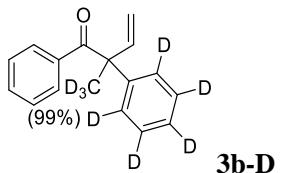
Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>): δ 7.88 – 7.86 (m, 2H), 7.47– 7.43 (m, 1H), 7.39 – 7.34 (m, 2H), 6.18 – 6.16 (m, 1H), 1.39 (s, 6H). HRMS (ESI) m/z calculated for C<sub>12</sub>H<sub>12</sub>D<sub>2</sub>ONa[M+Na]<sup>+</sup> 199.1062, found 199.1054.



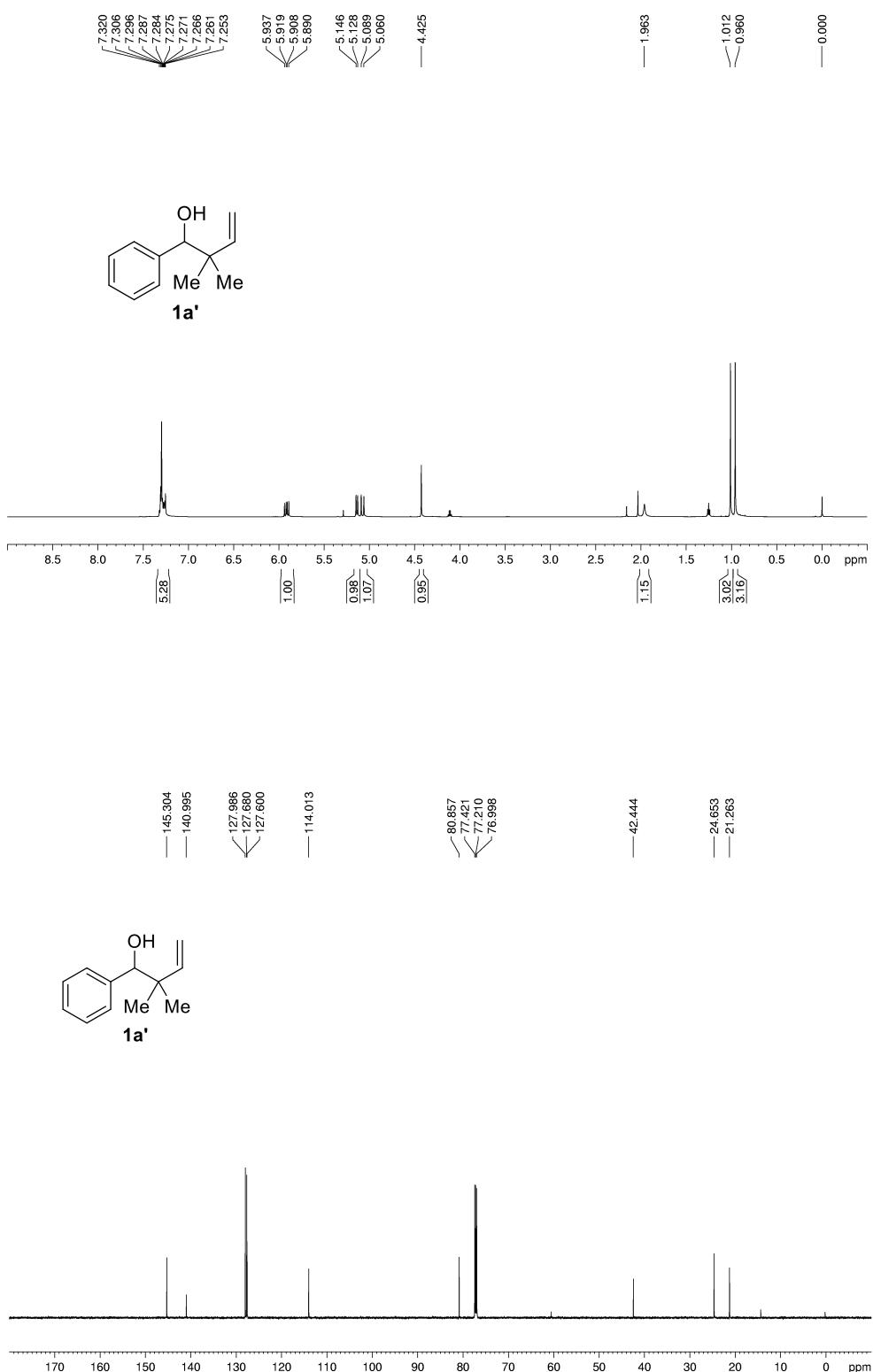
**2a-D-b**

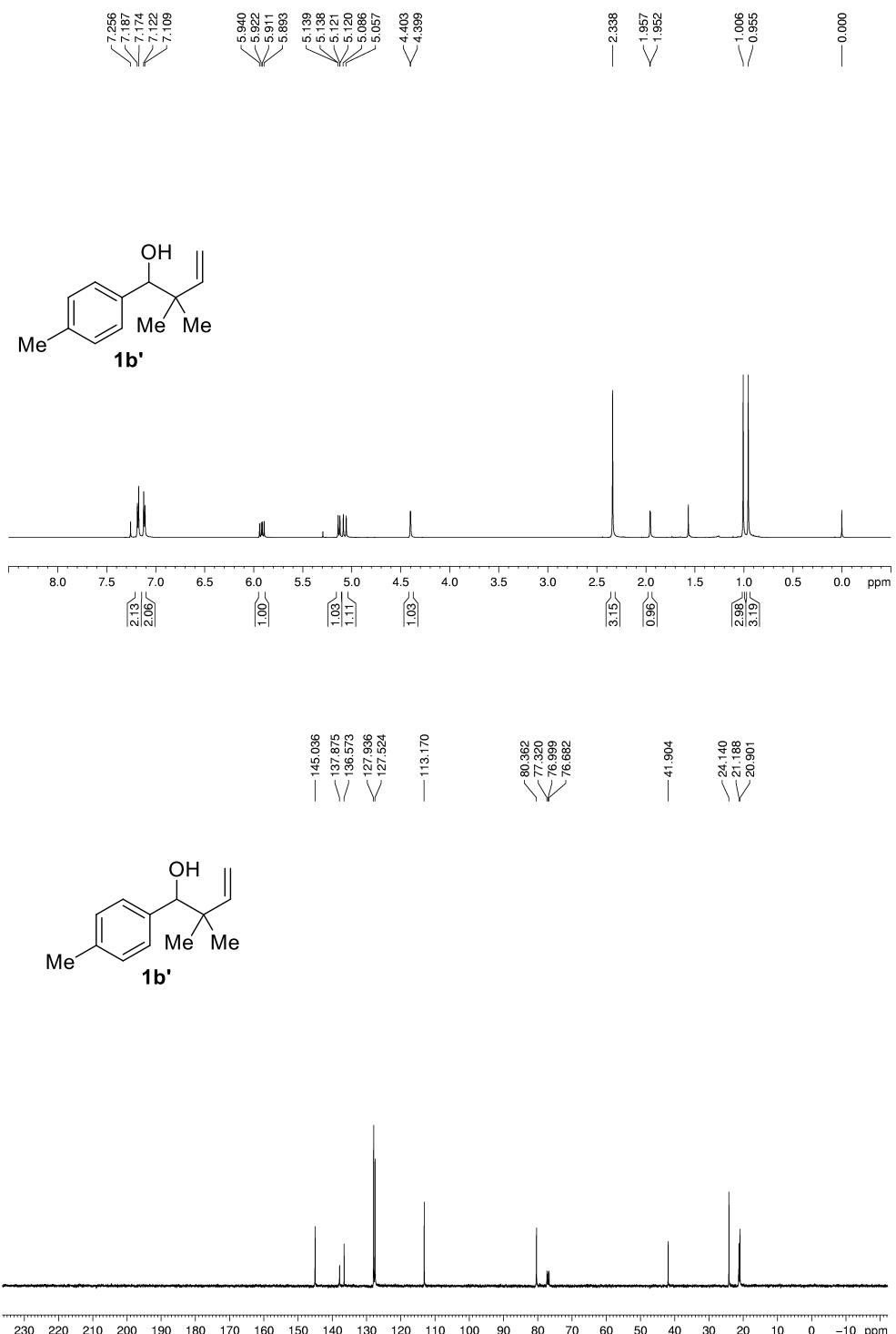
Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89 – 7.86 (d, J = 7.6 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.45 (t, J = 7.6 Hz, 2H), 1.85 (s, 1H), 1.83 (s, 3H), 1.61(s, 3H). HRMS (ESI) m/z calculated for C<sub>12</sub>H<sub>12</sub>D<sub>2</sub>ONa[M+Na]<sup>+</sup> 199.1062, found 199.1063.

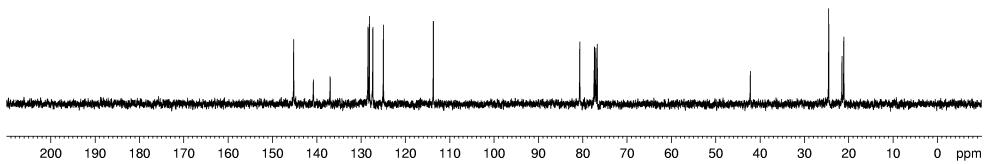
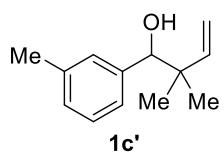
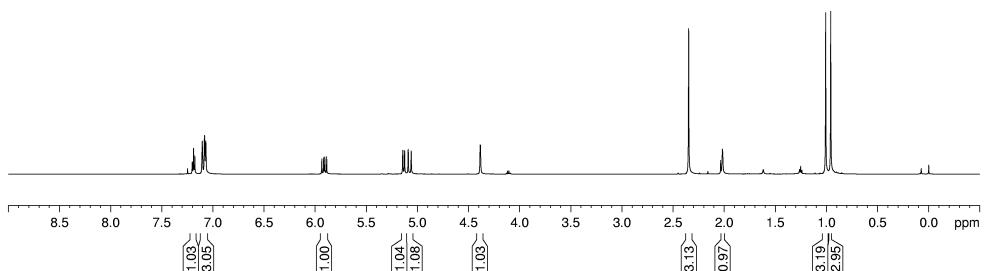
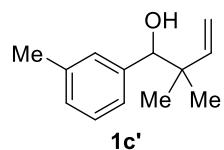


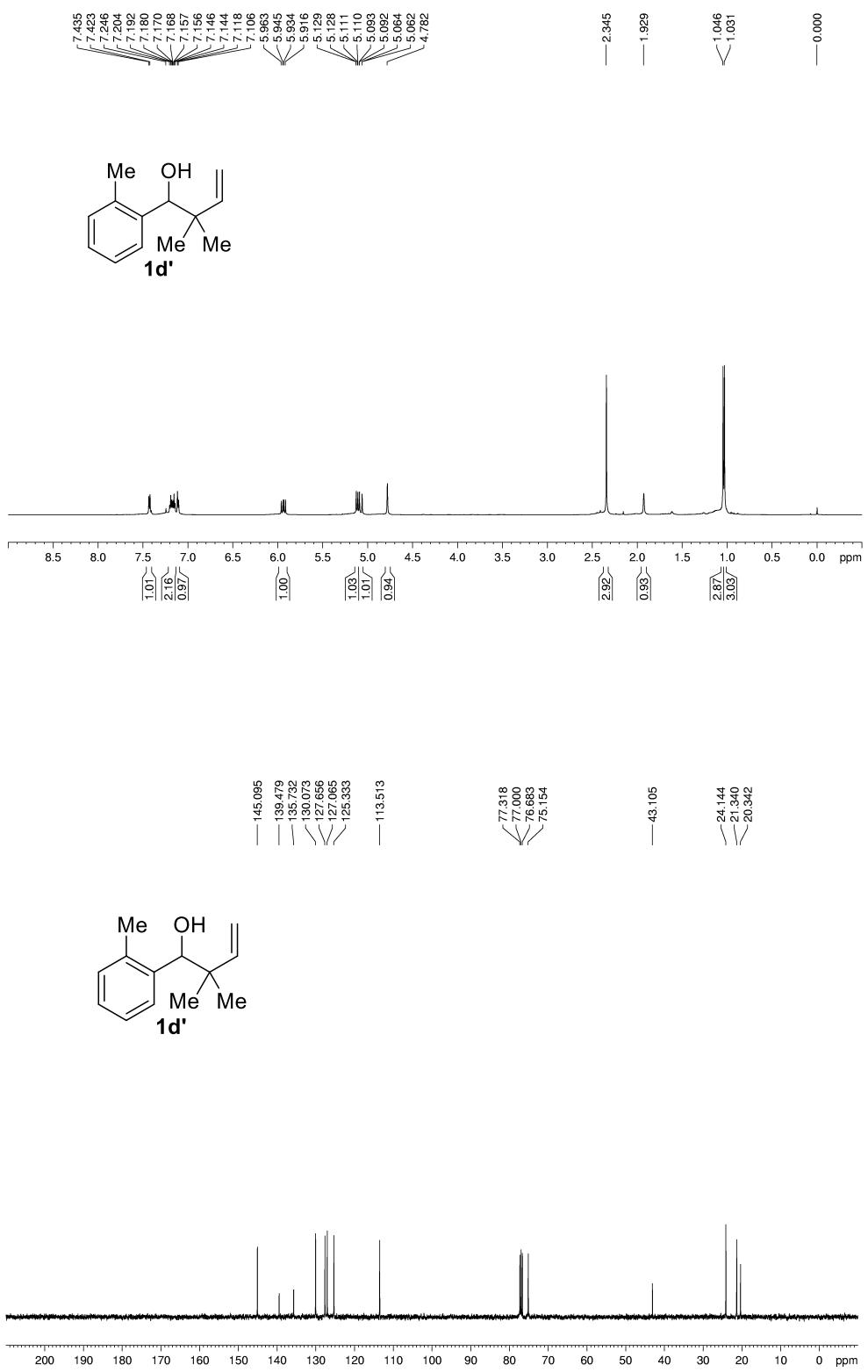
Flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 50/1). Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.54 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.23 (t, J = 7.8 Hz, 2H), 6.64 – 6.59 (dd, J = 10.8 Hz, J = 17.4 Hz, 1H), 5.31 (d, J = 10.8 Hz, 1H), 5.17 (d, J = 17.4 Hz, 1H). HRMS (ESI) m/z calculated for C<sub>17</sub>H<sub>8</sub>D<sub>8</sub>ONa[M+Na]<sup>+</sup> 267.1601, found 267.1598.

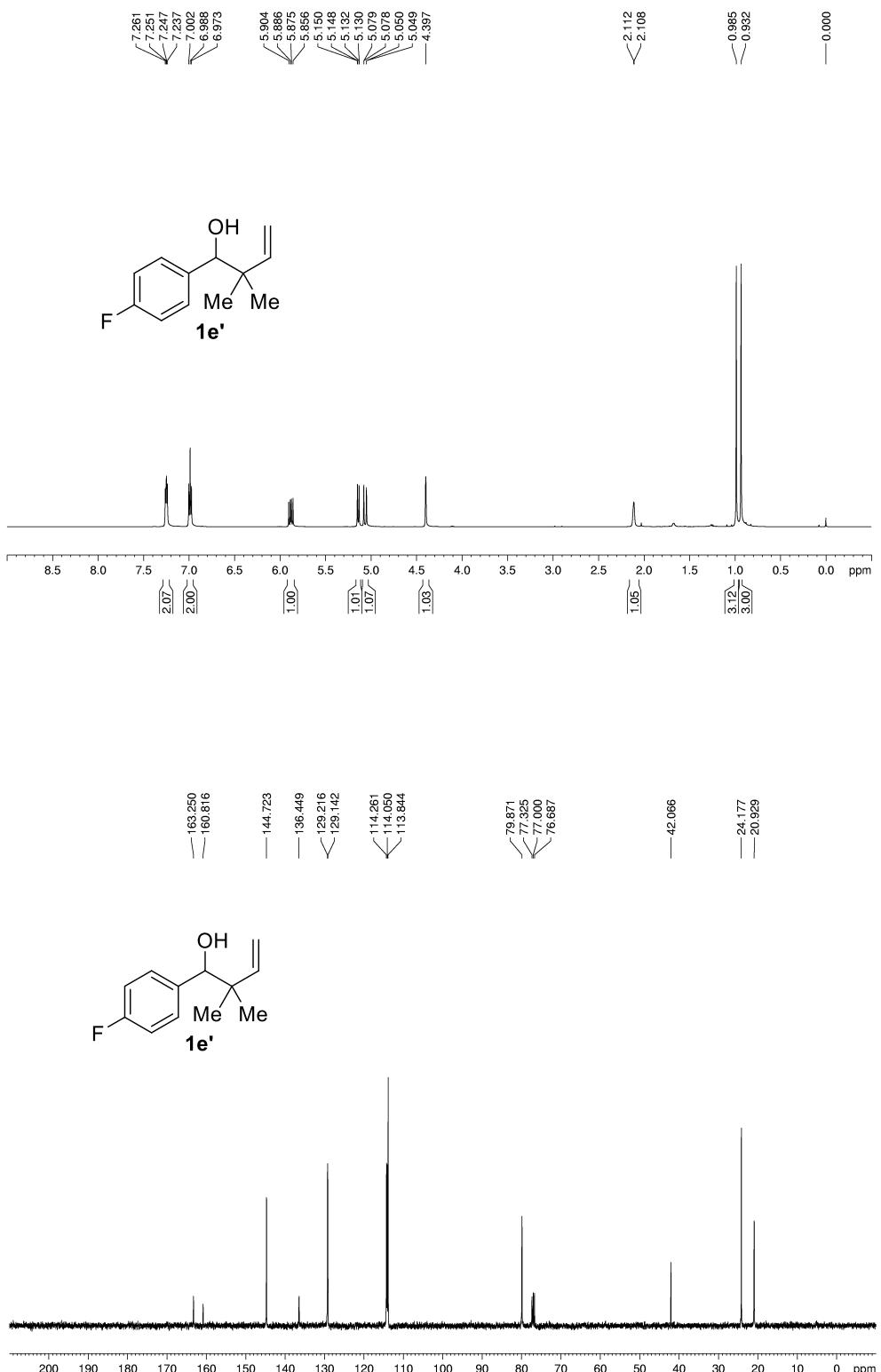
## 6. Copies of NMR spectra

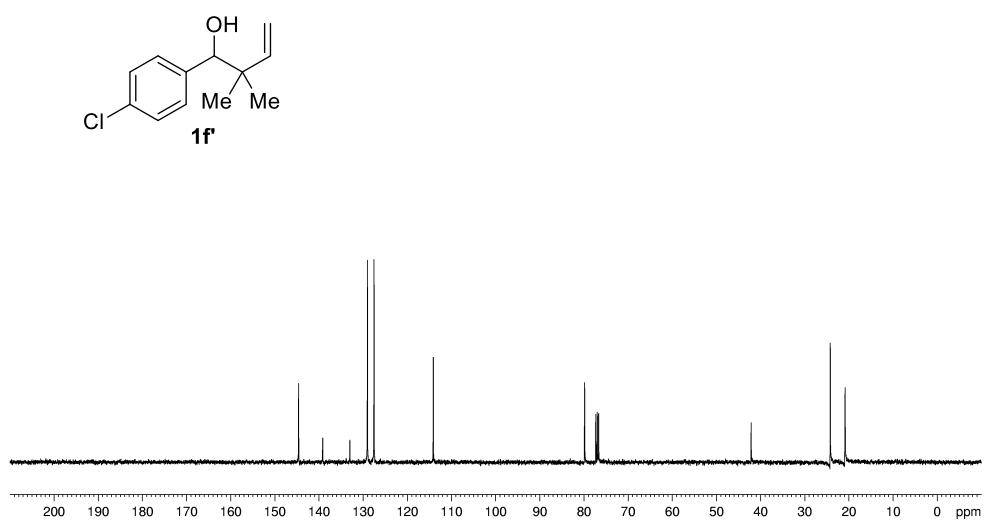
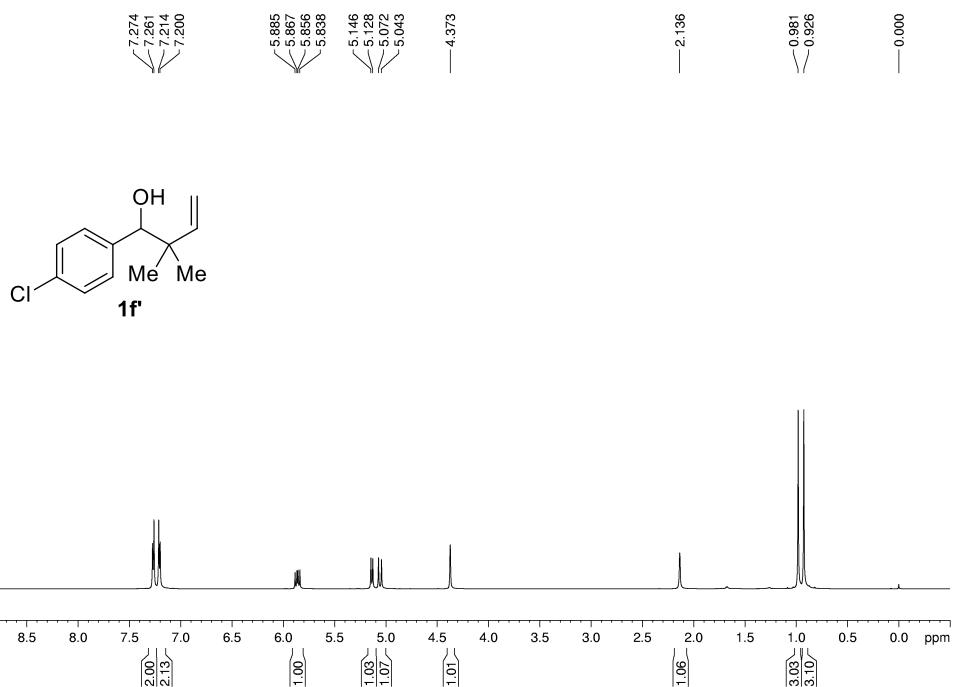


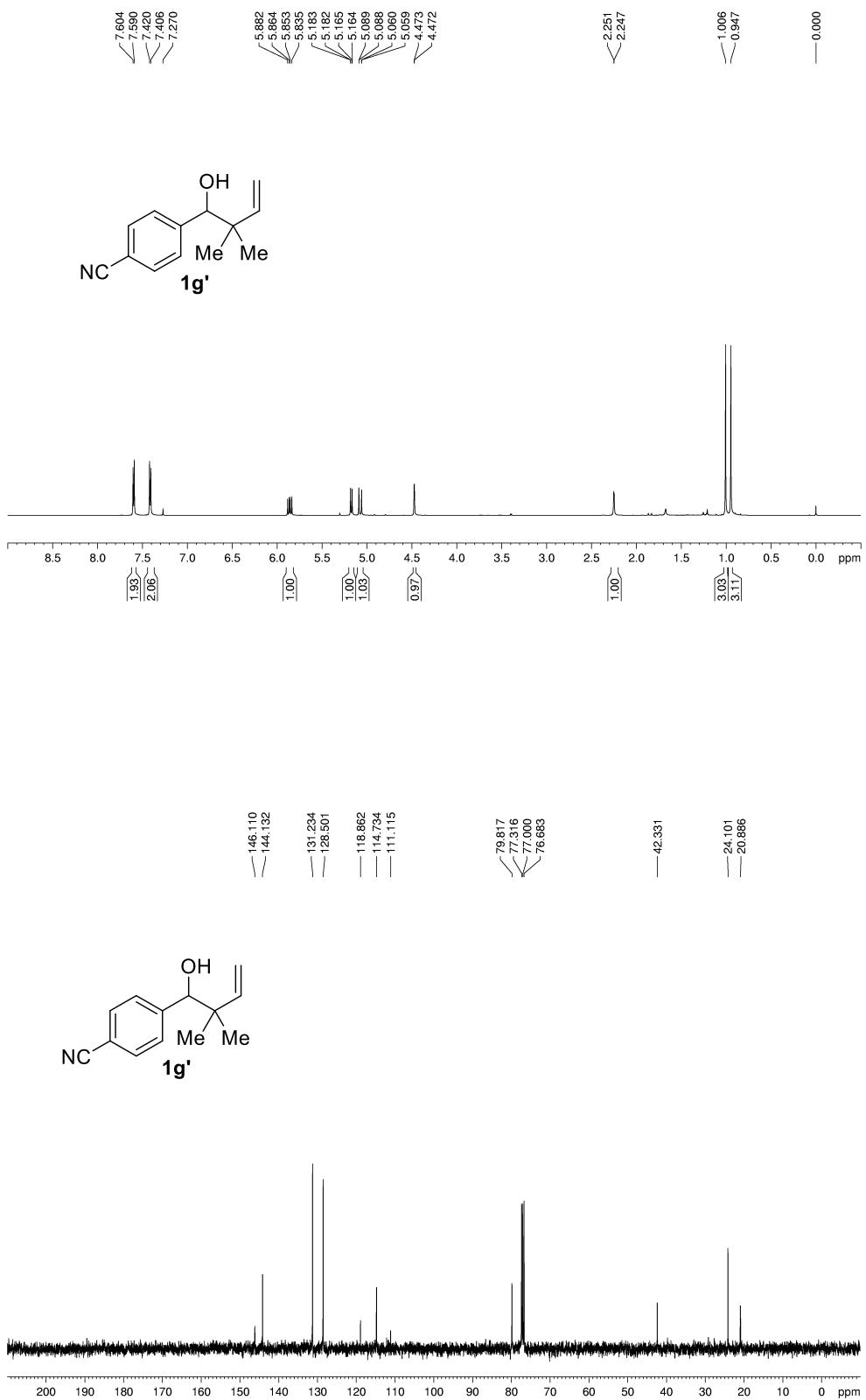


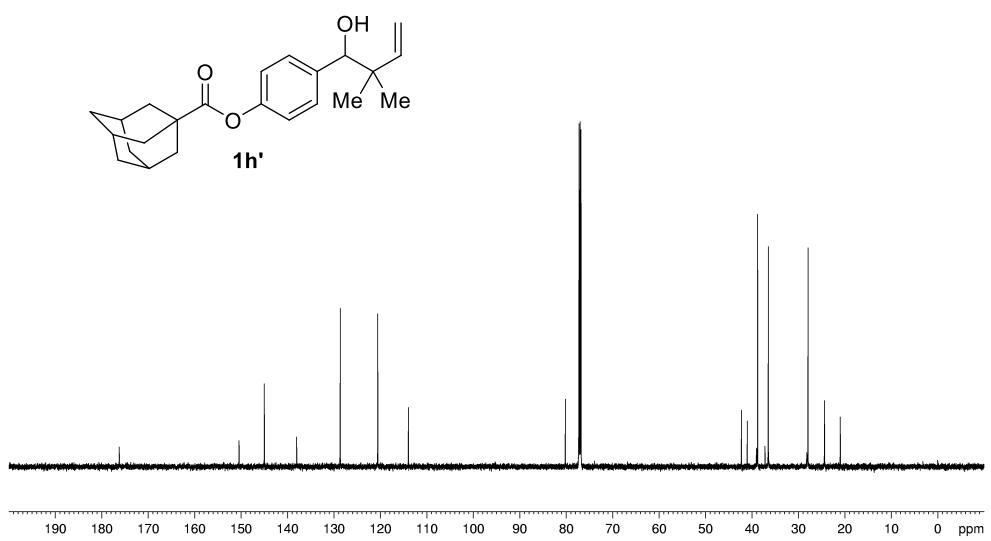
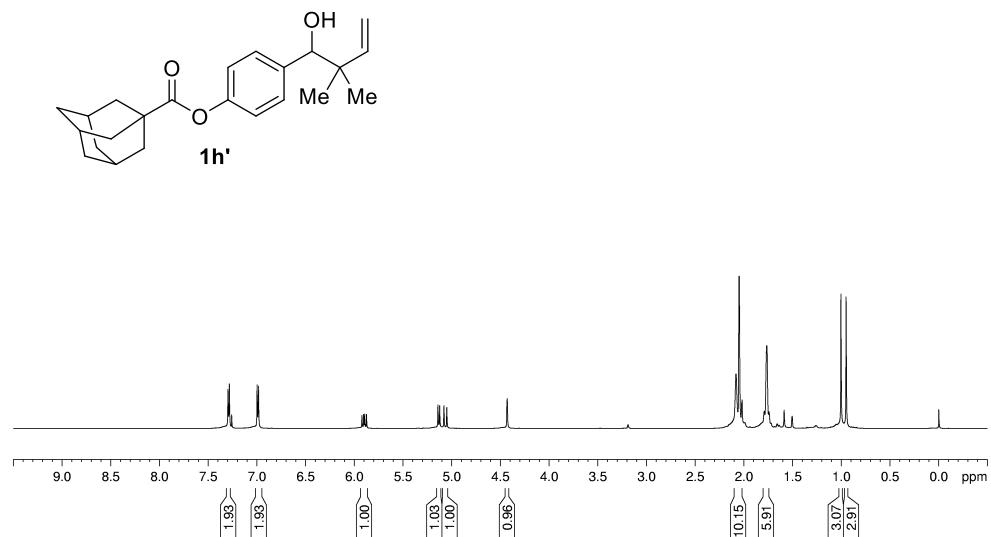


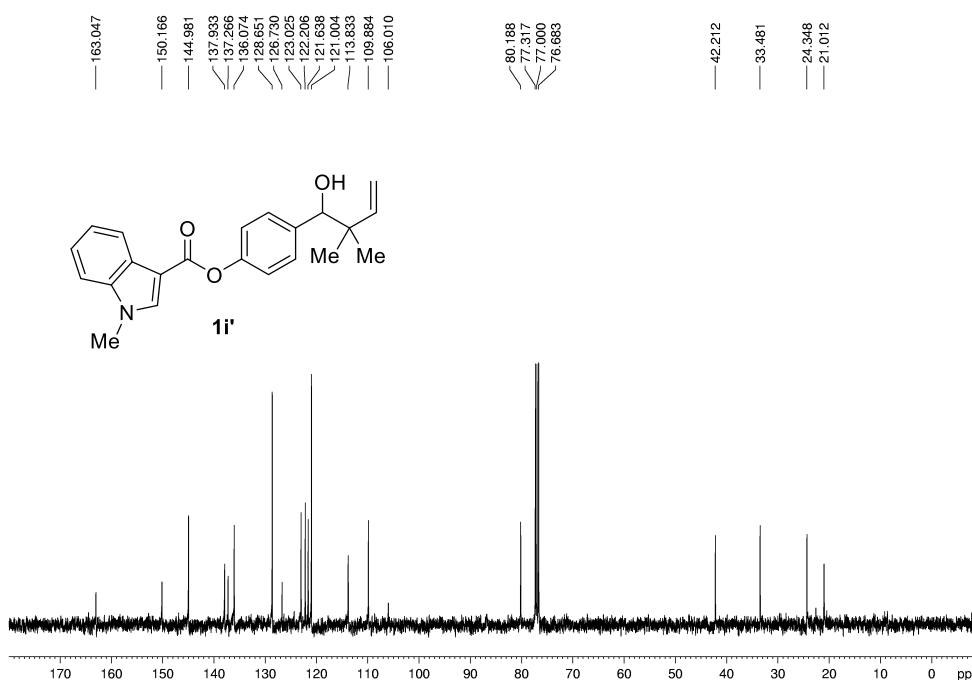
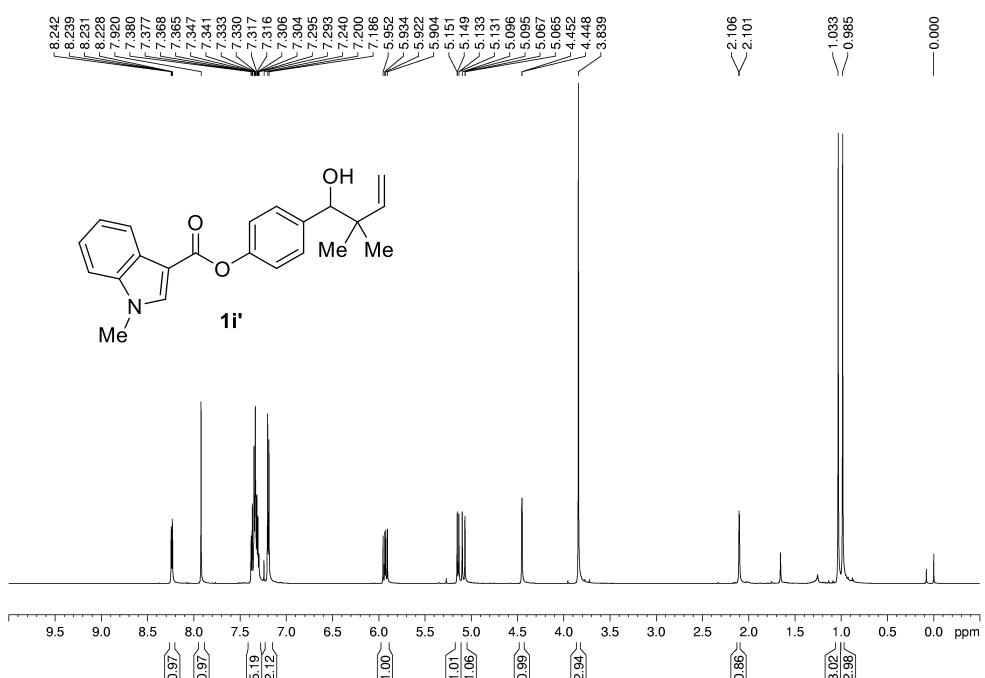


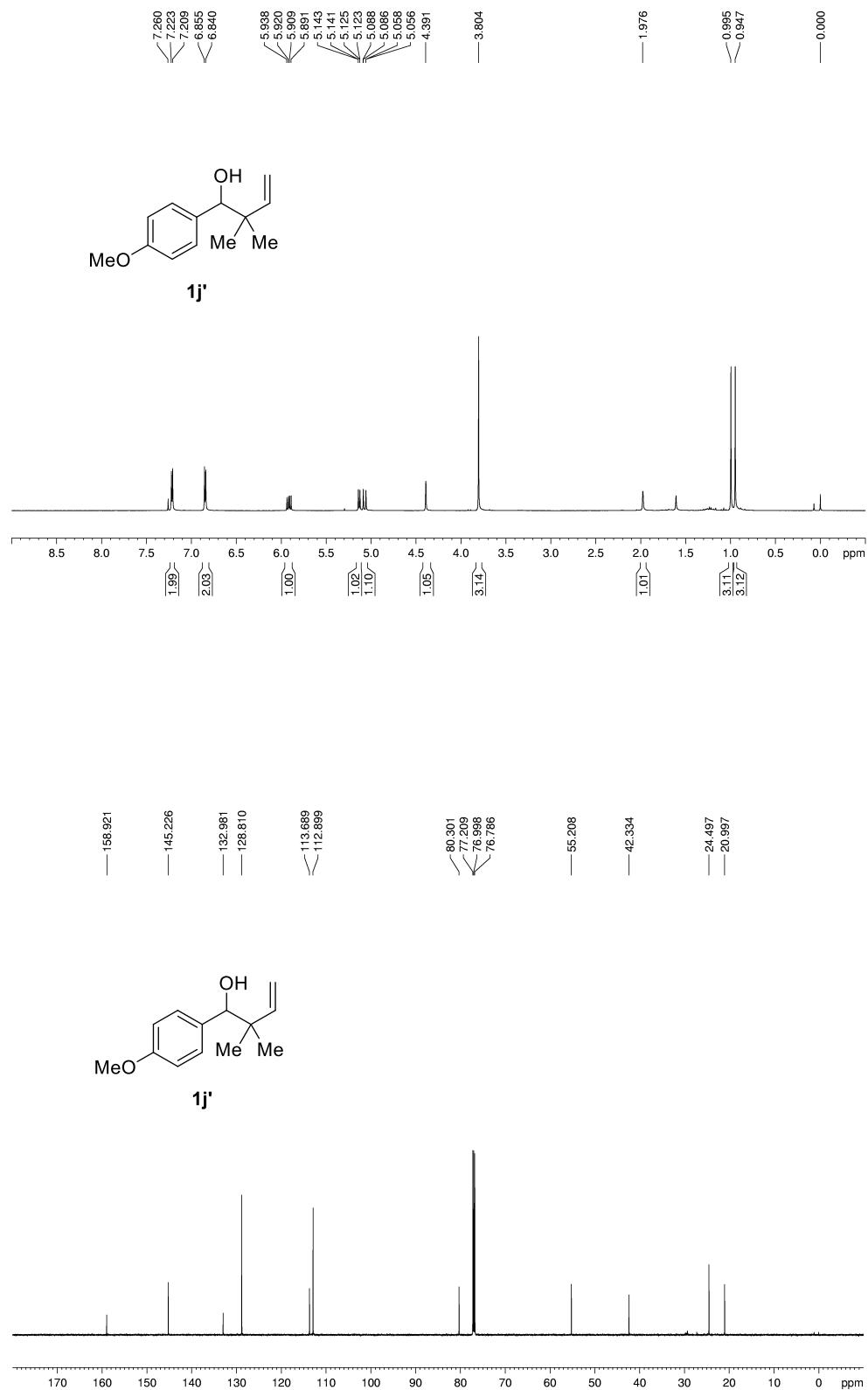


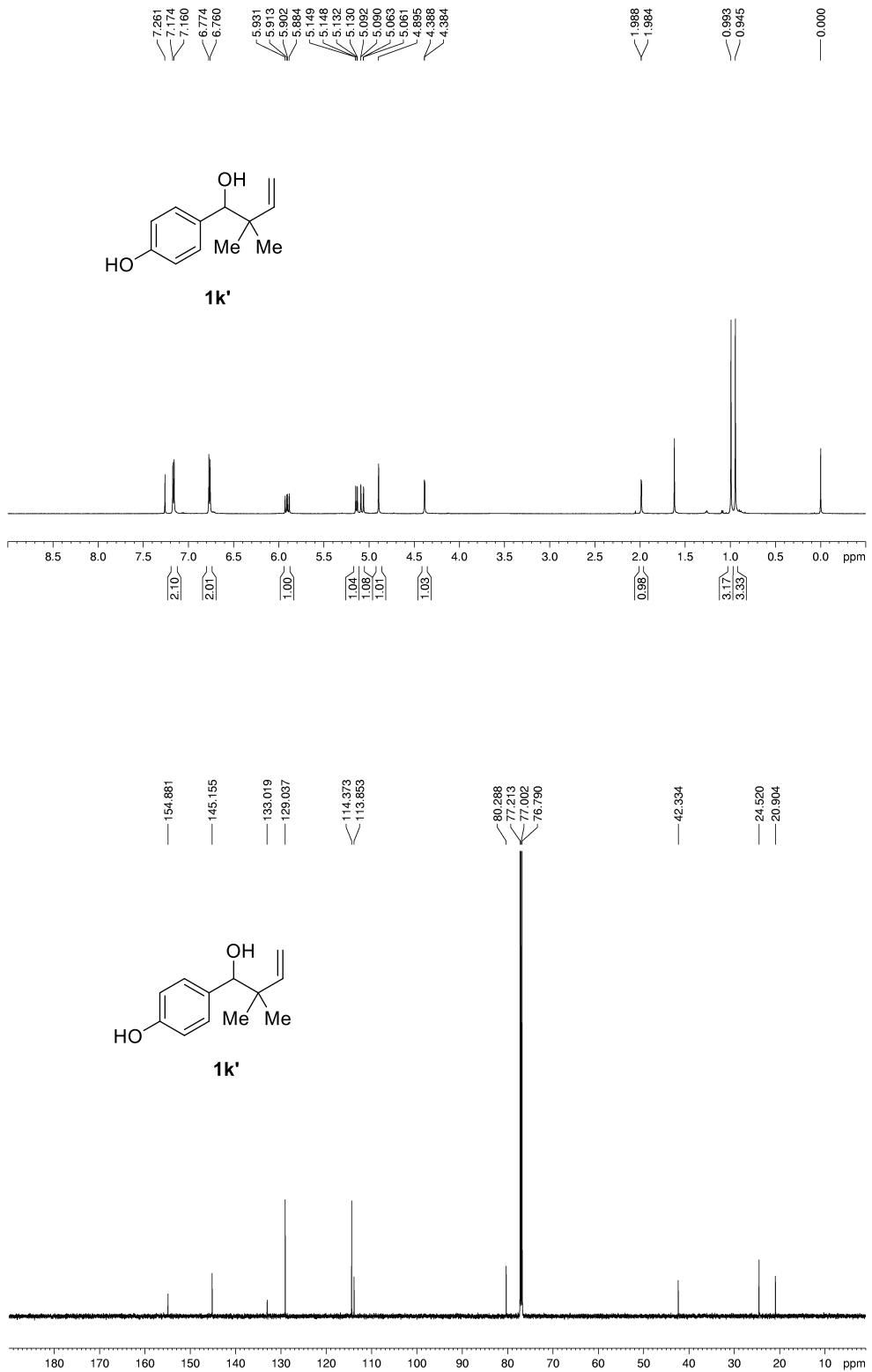


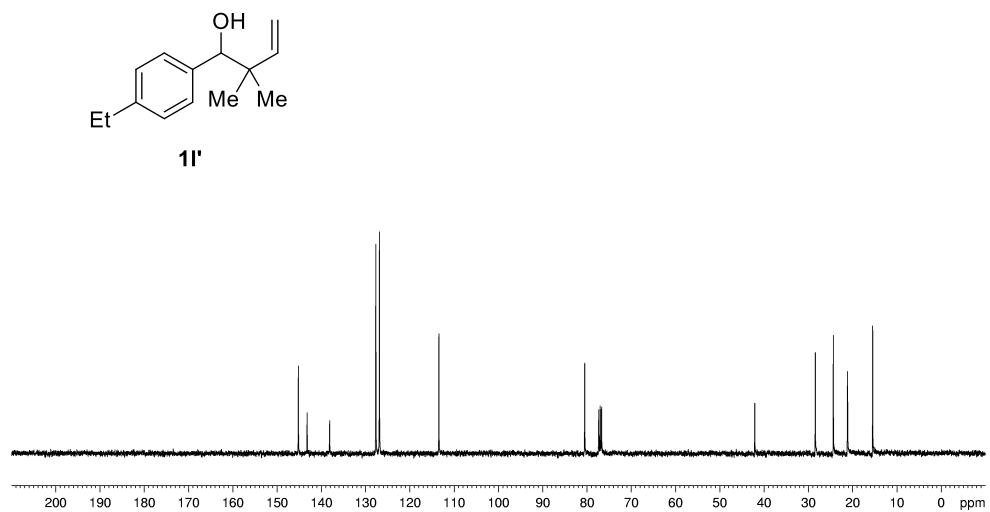
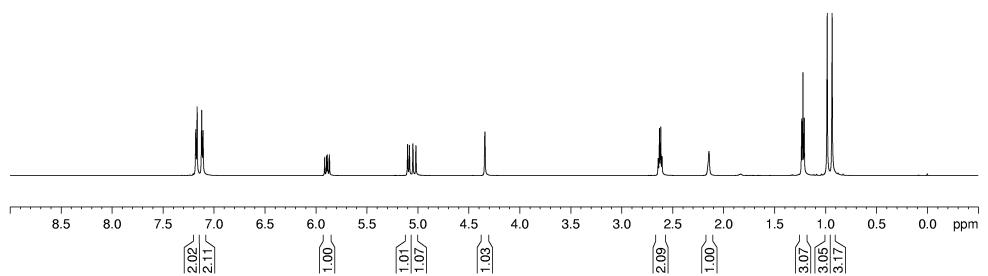
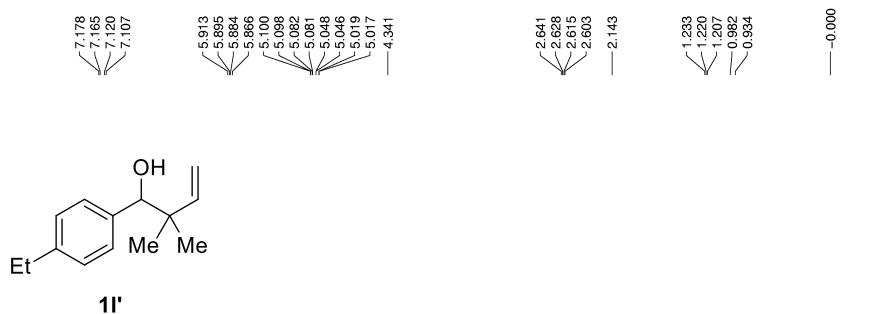


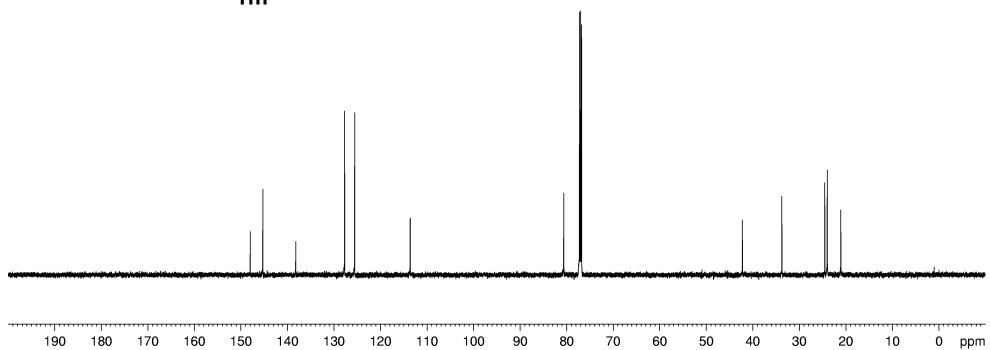
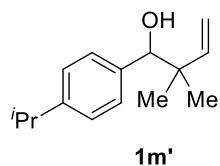
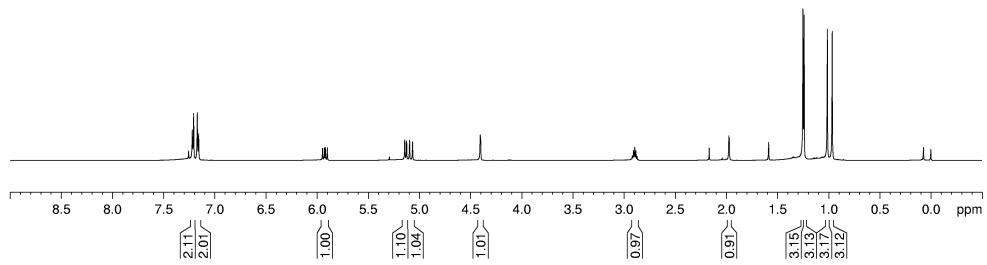
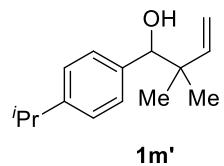


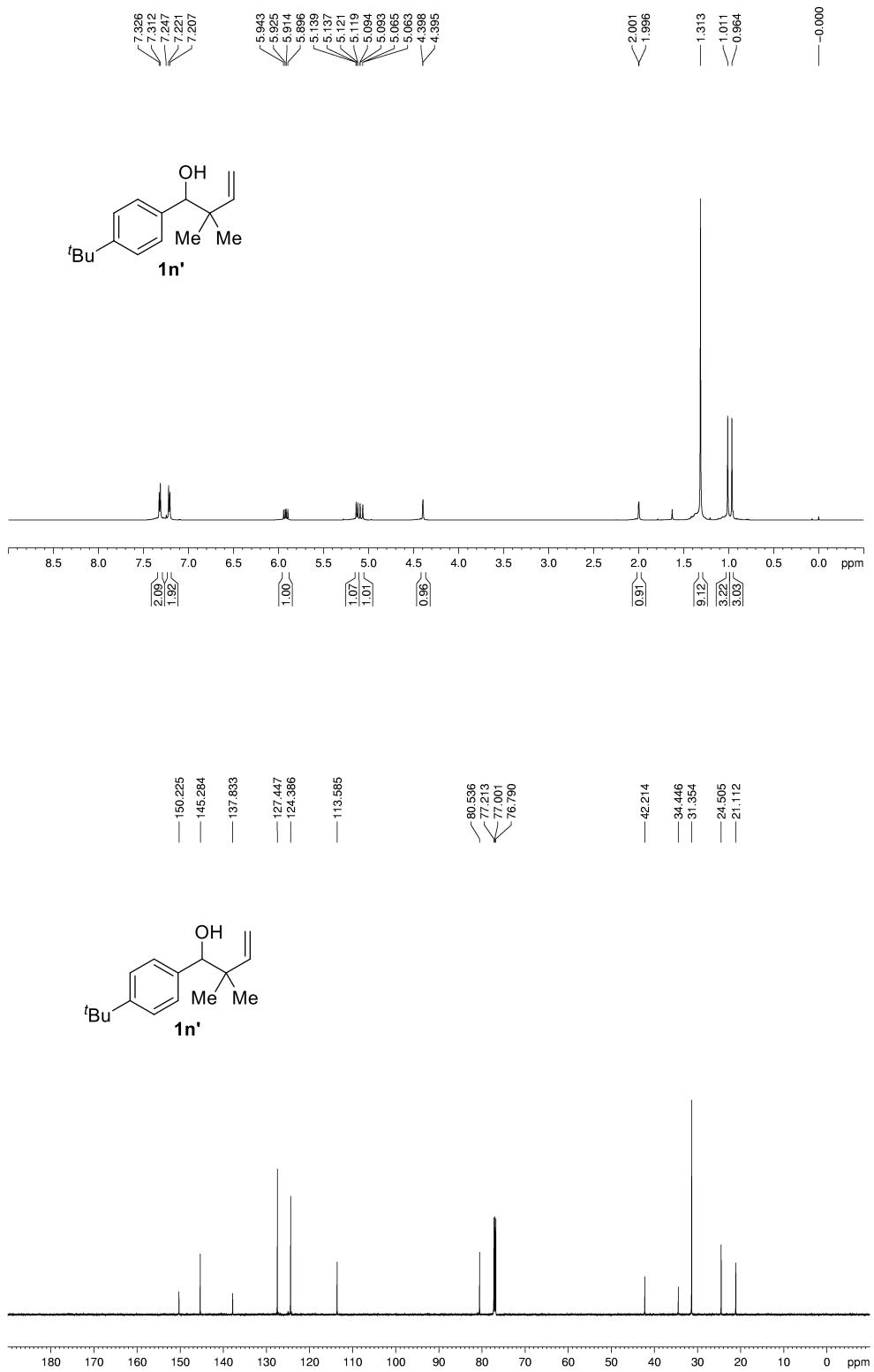


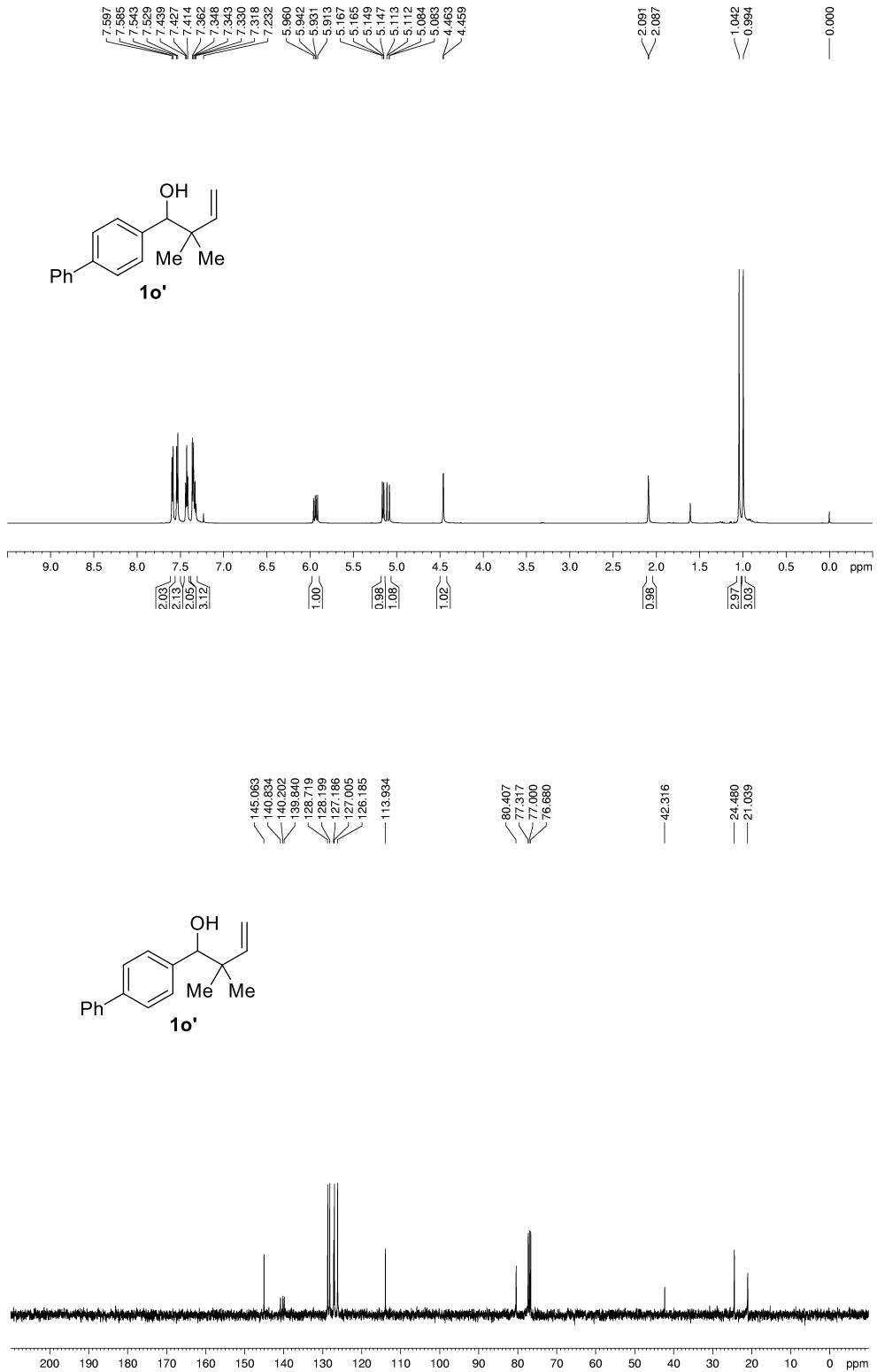


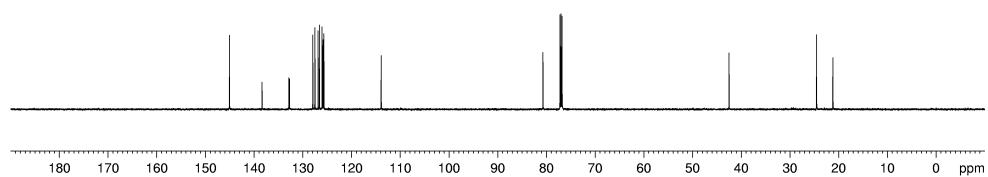
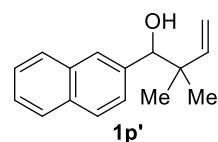
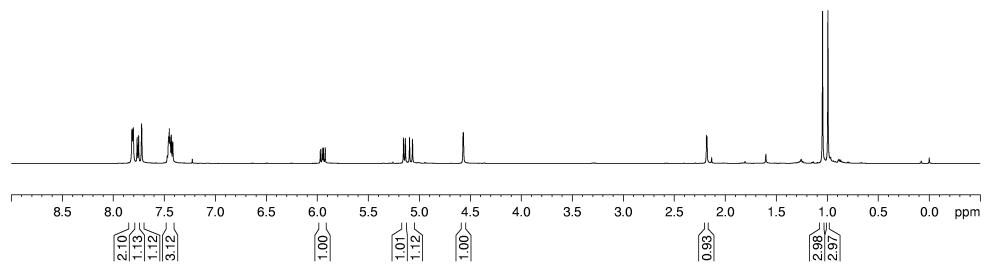
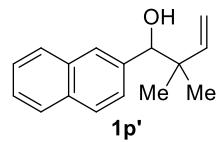


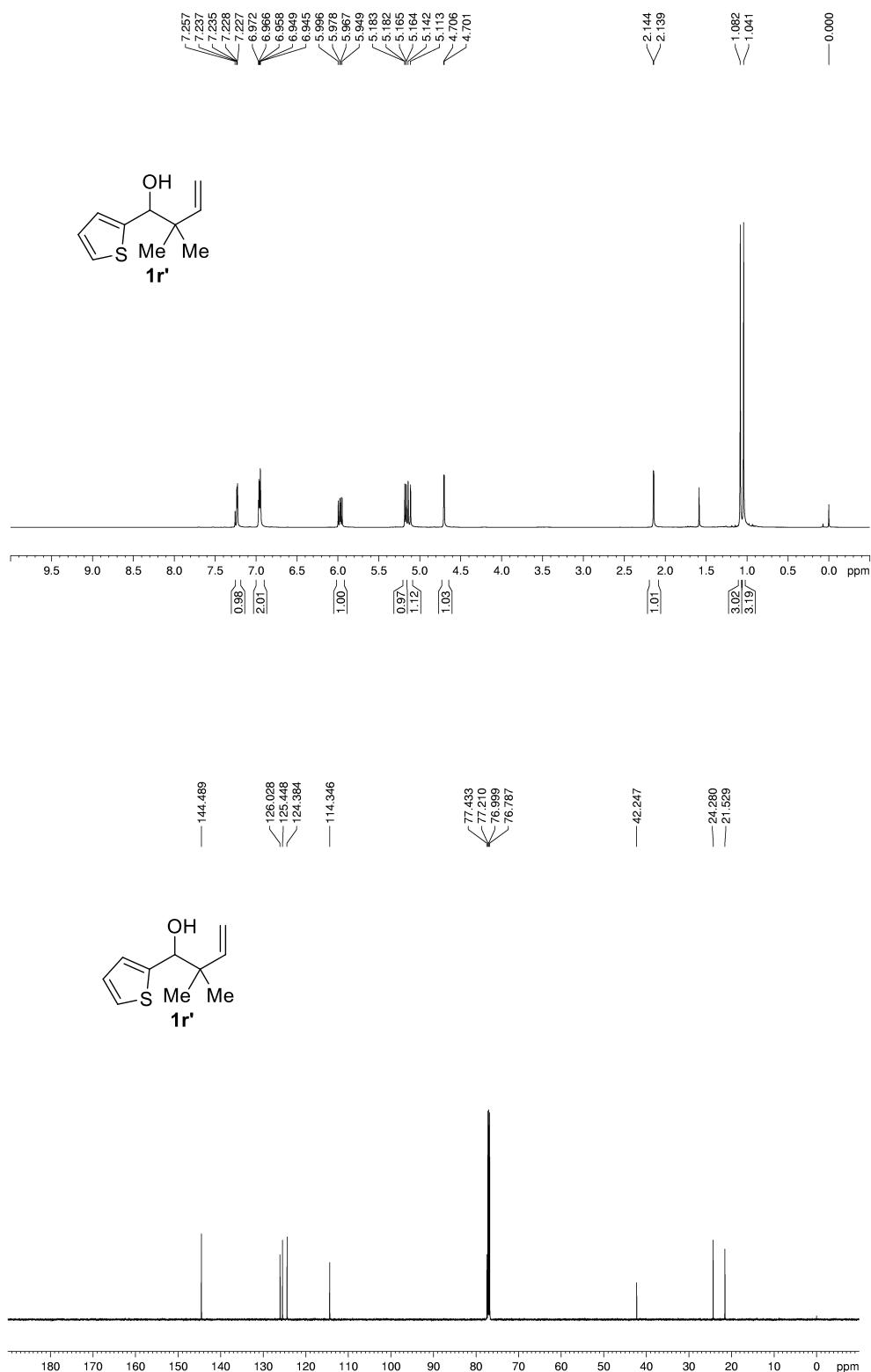


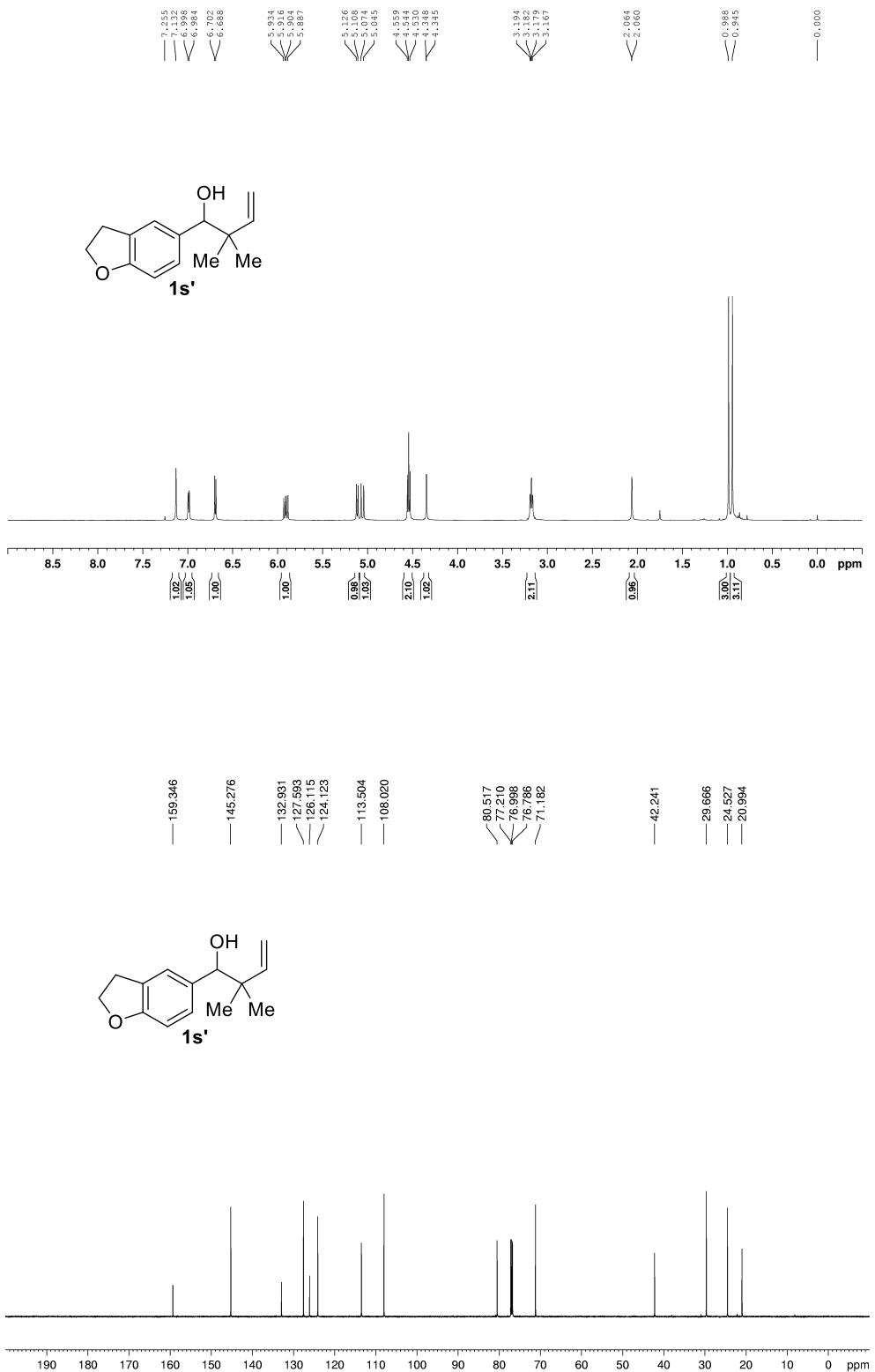


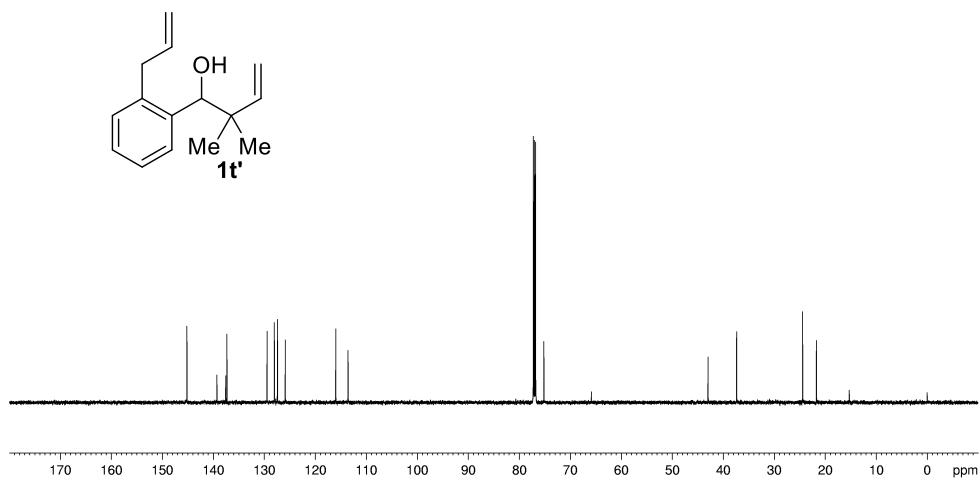
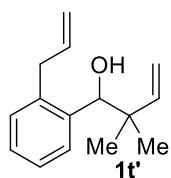
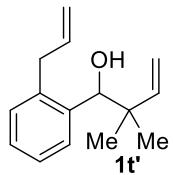


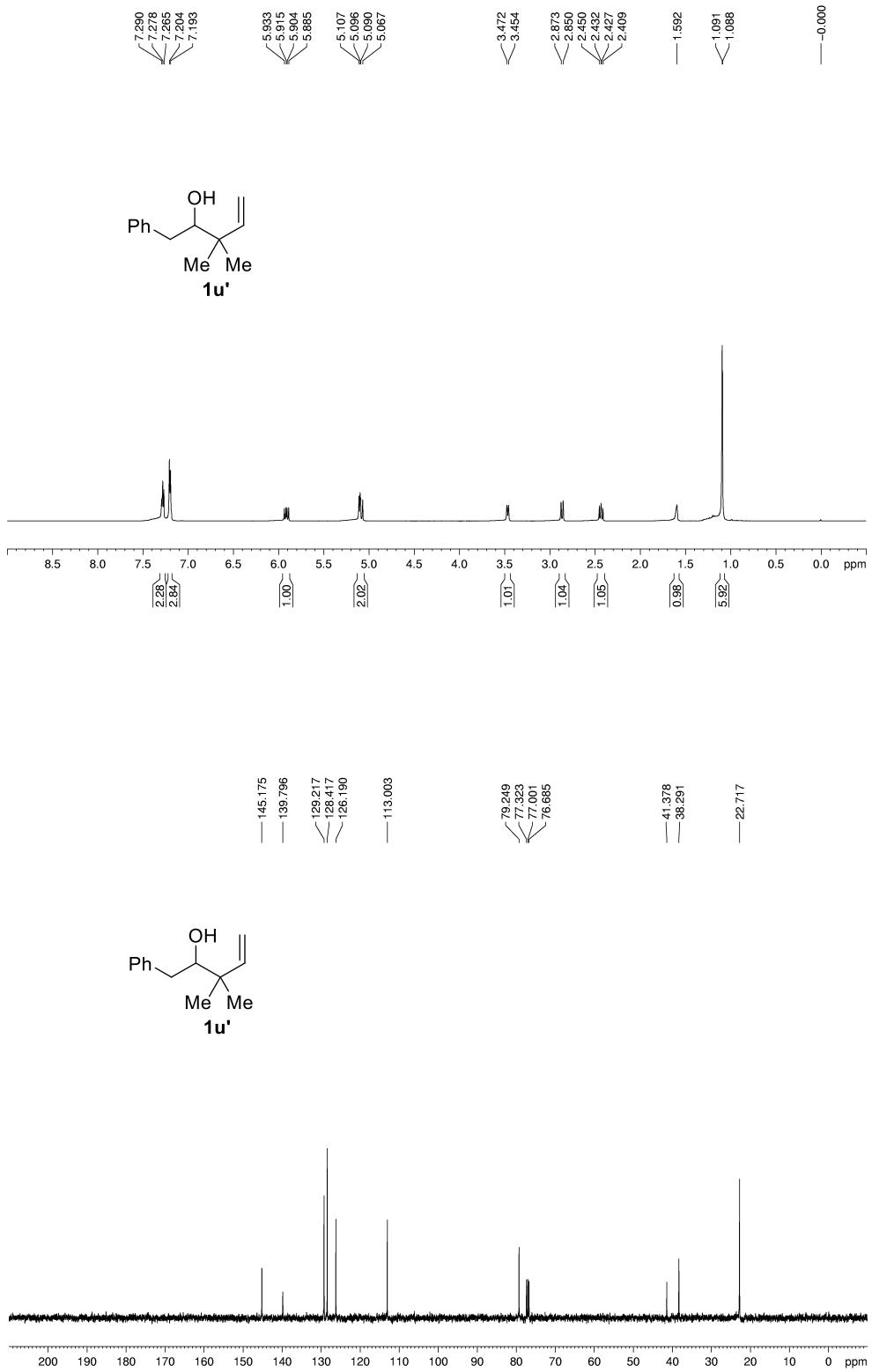


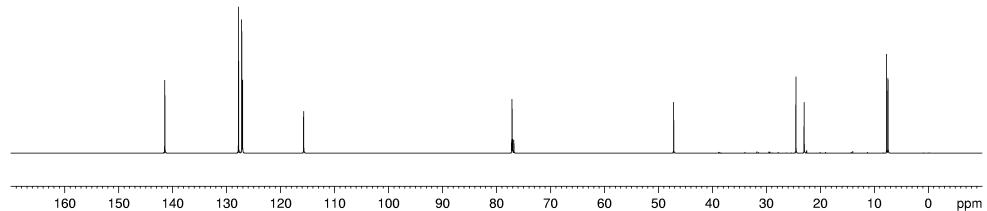
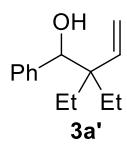
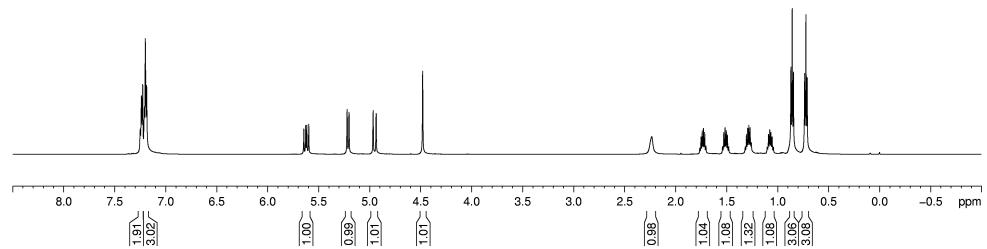
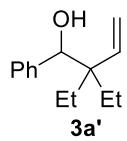


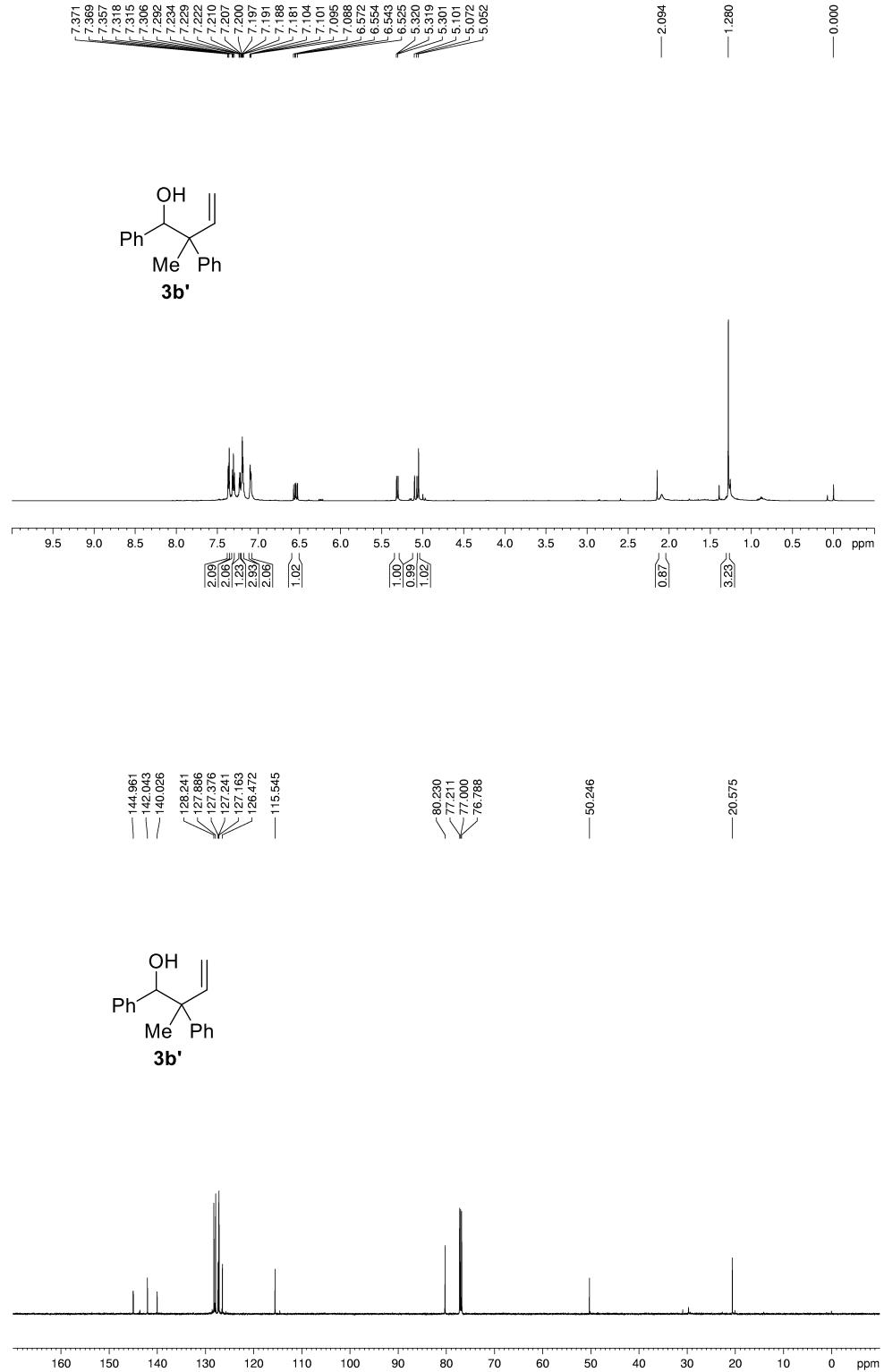


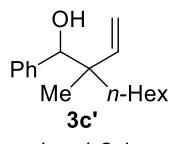
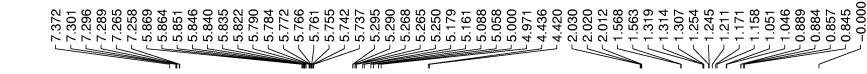




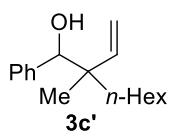
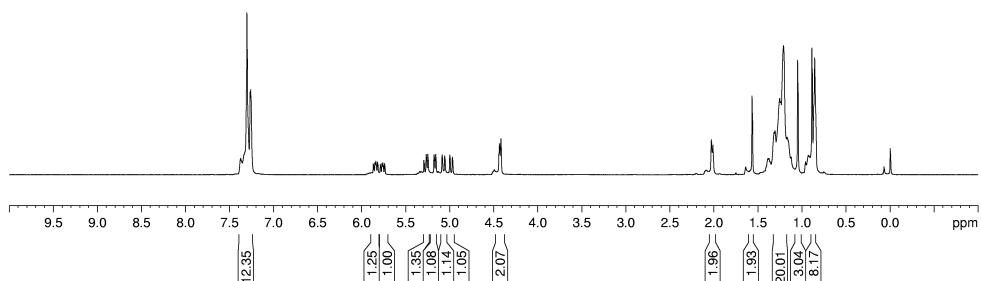




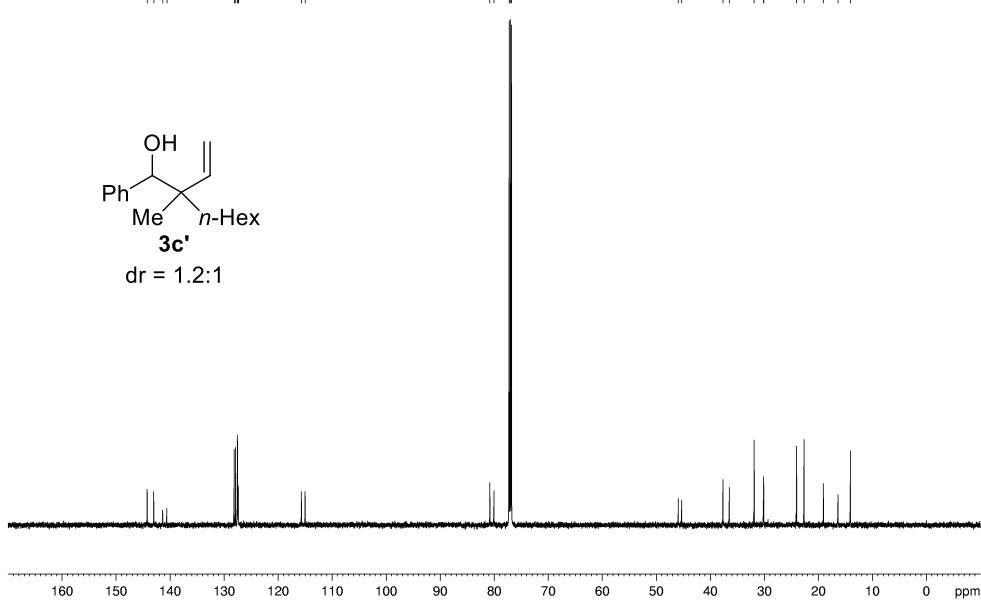


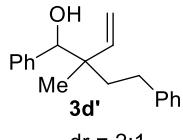


$$dr = 1.2:1$$

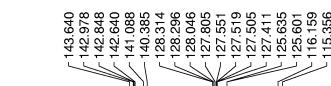
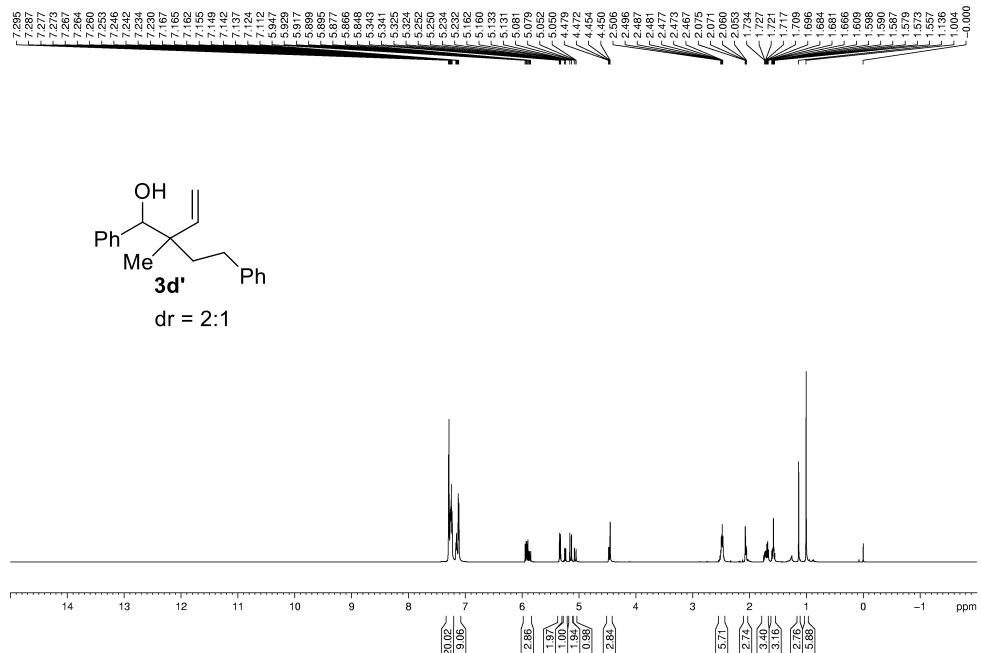


$$dr = 1.2:1$$



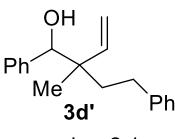


$$dr = 2:1$$

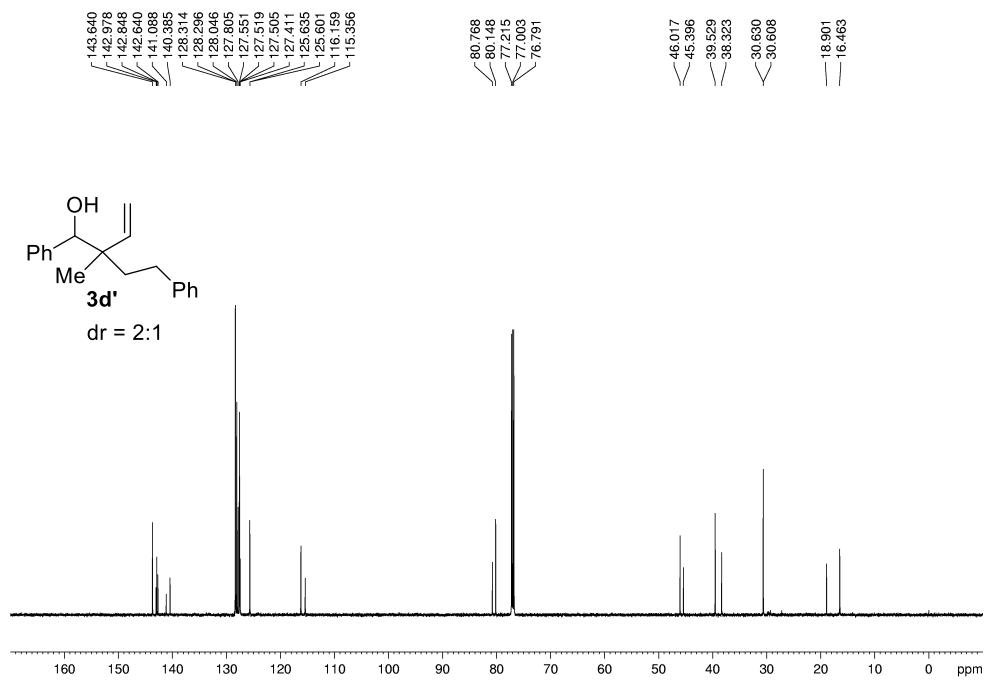


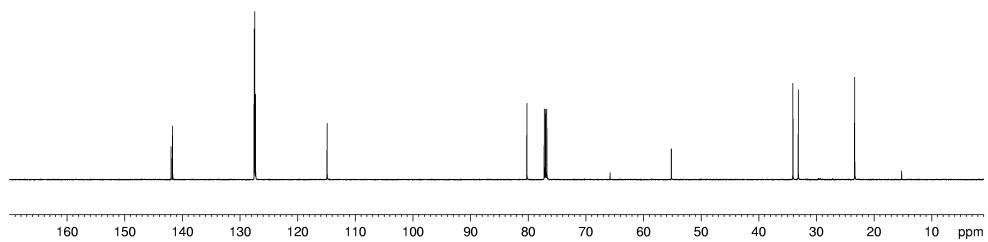
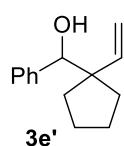
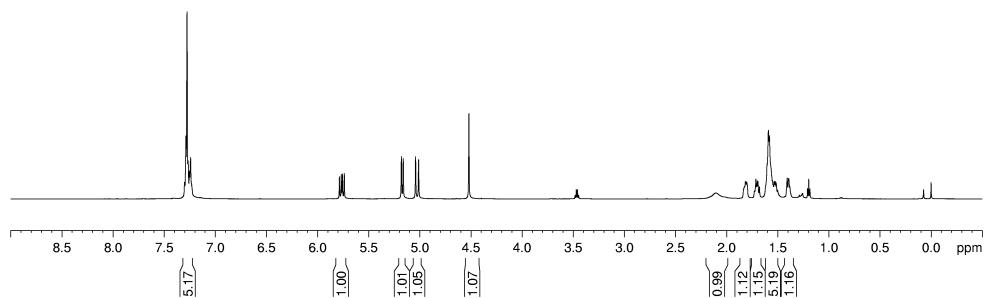
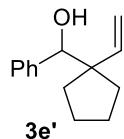
✓ 80.768  
✓ 80.148  
✓ 77.215  
✓ 77.003  
✓ 76.791

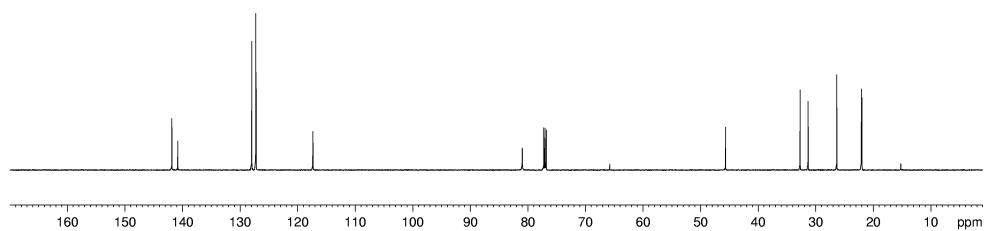
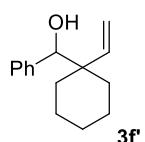
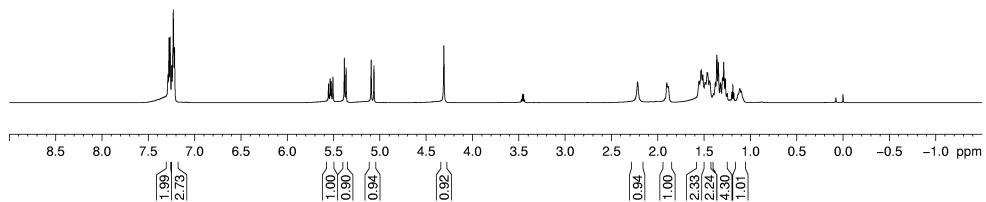
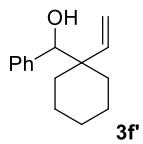
— 18.901  
— 16.463

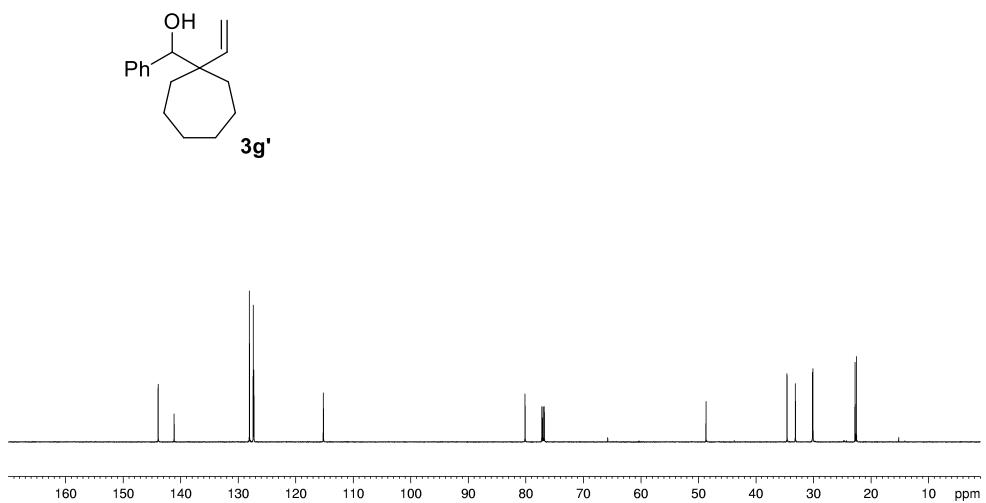
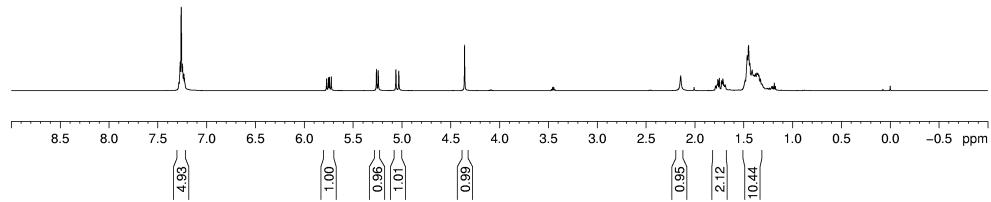
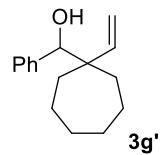


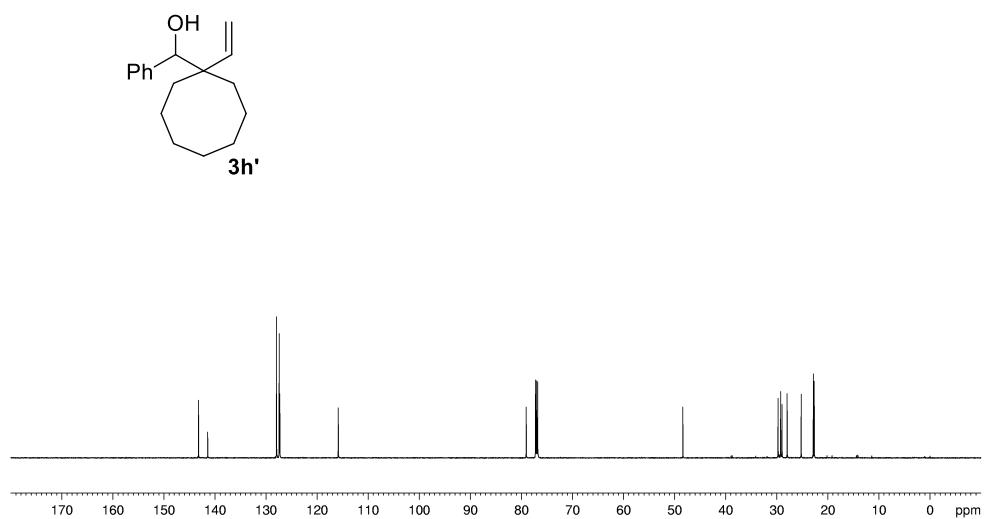
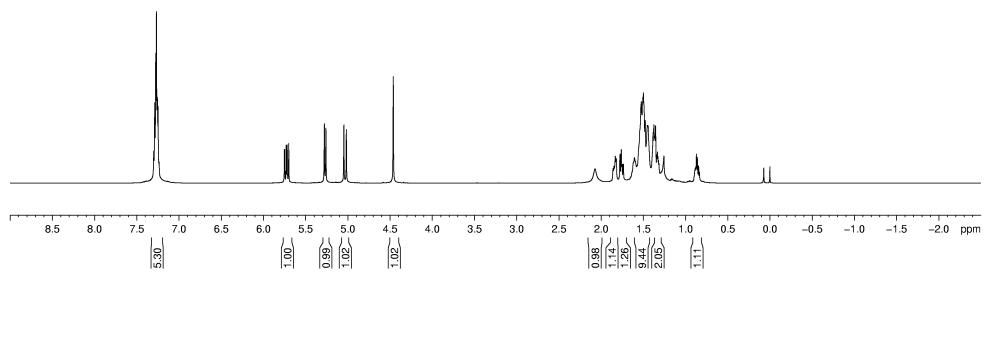
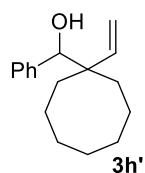
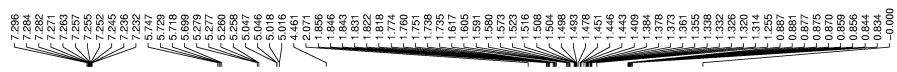
$$dr = 2:1$$

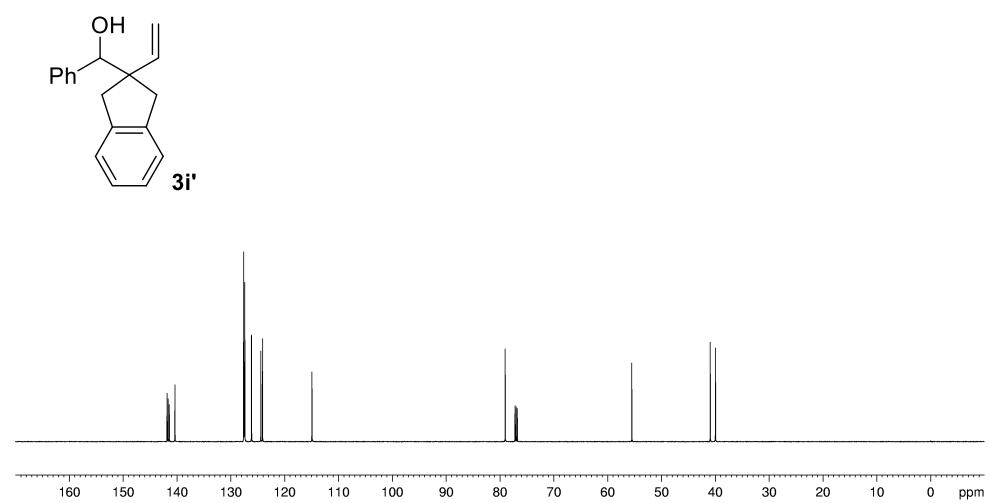
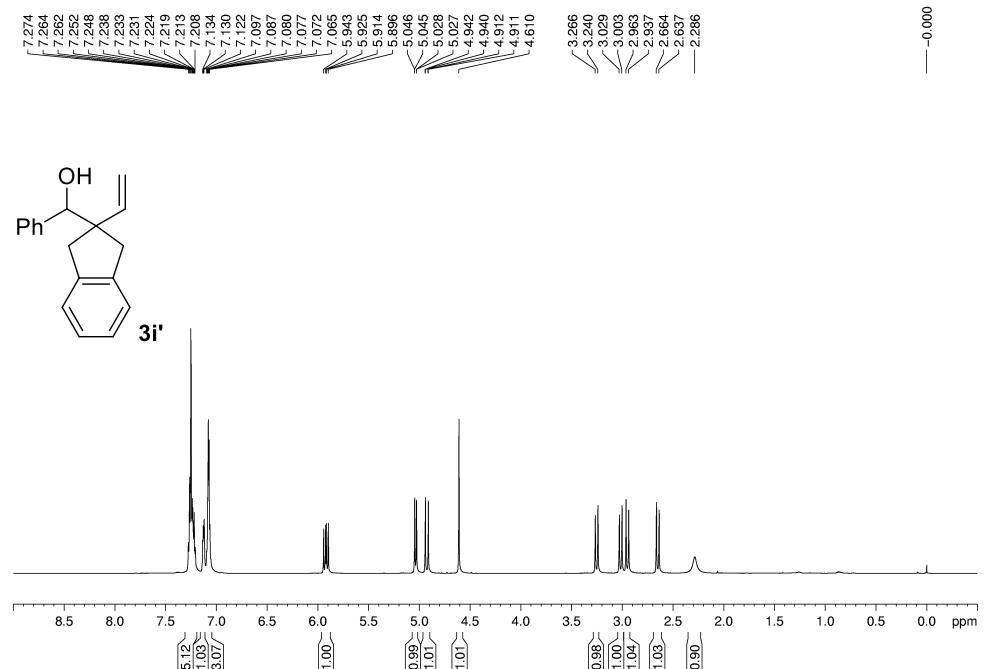


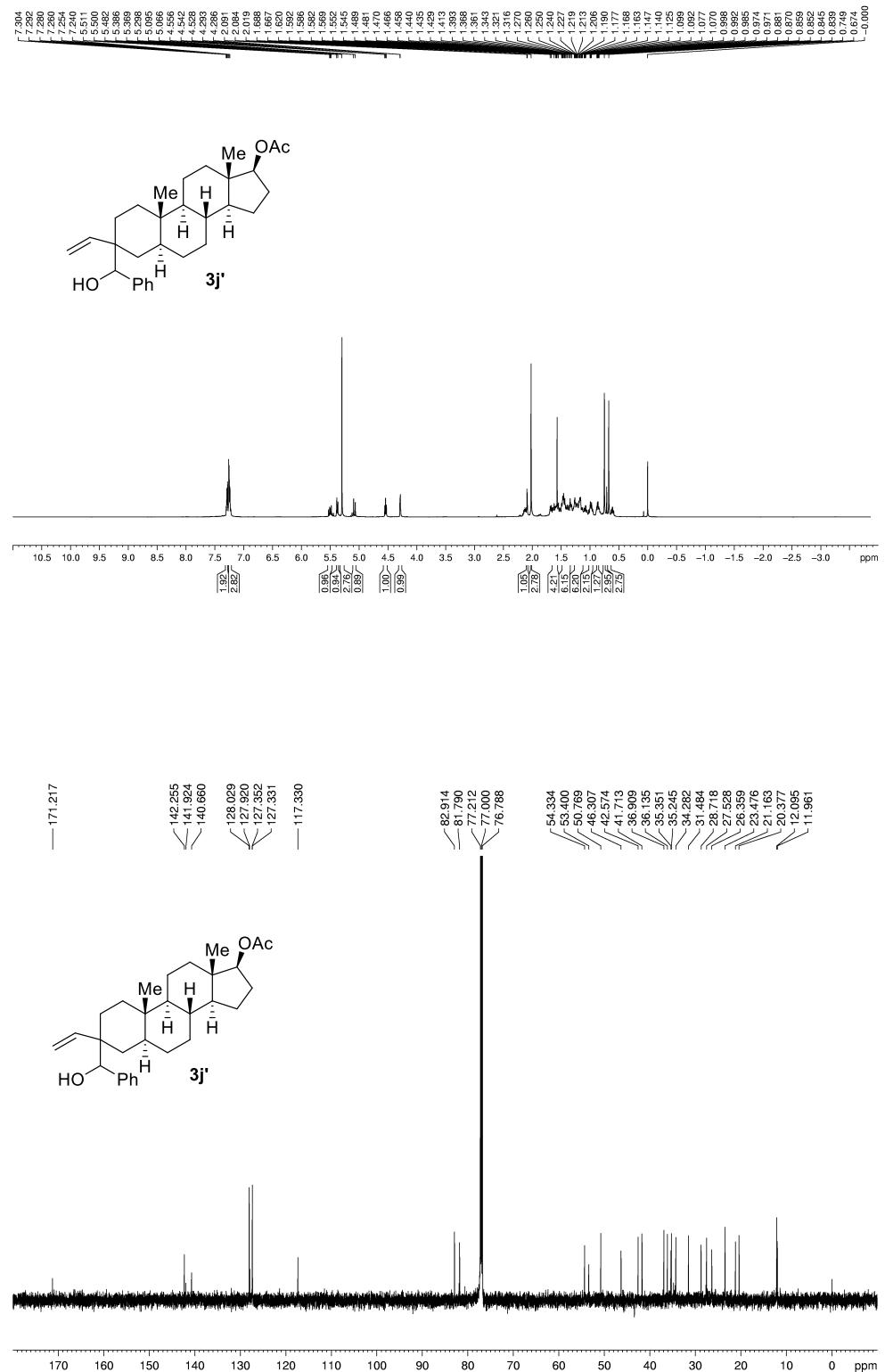


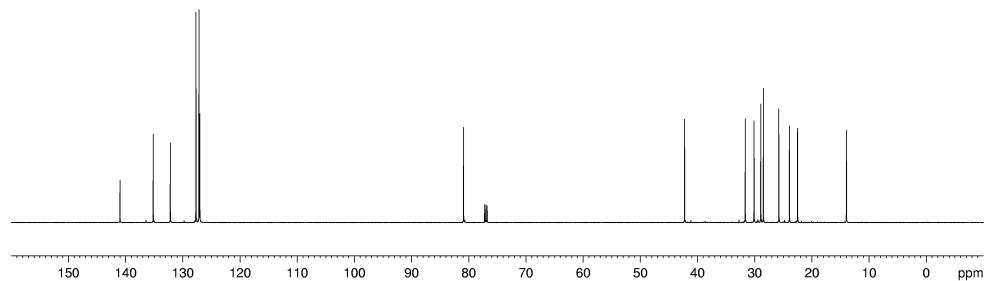
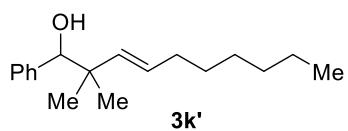
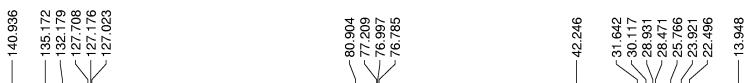
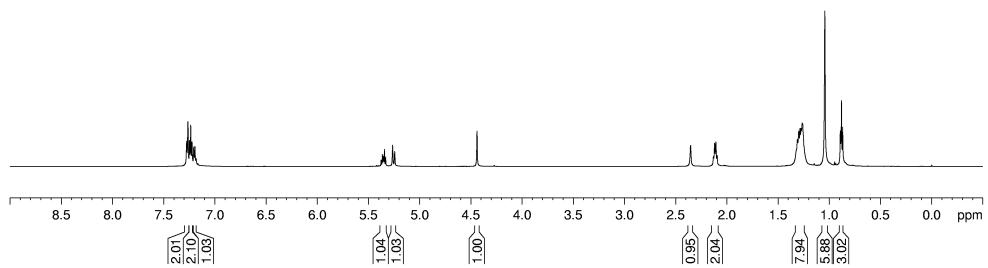
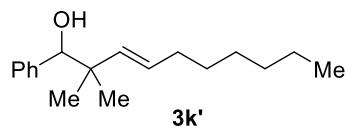


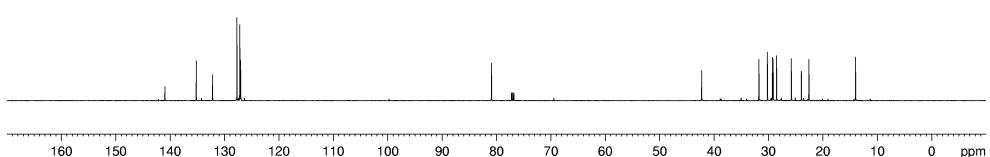
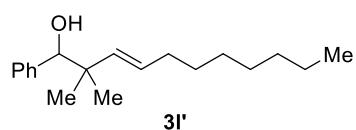
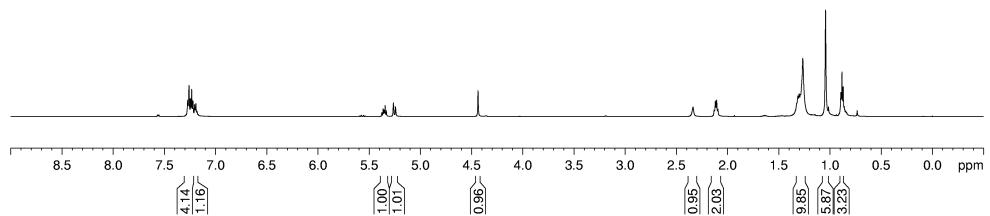
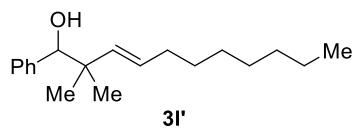


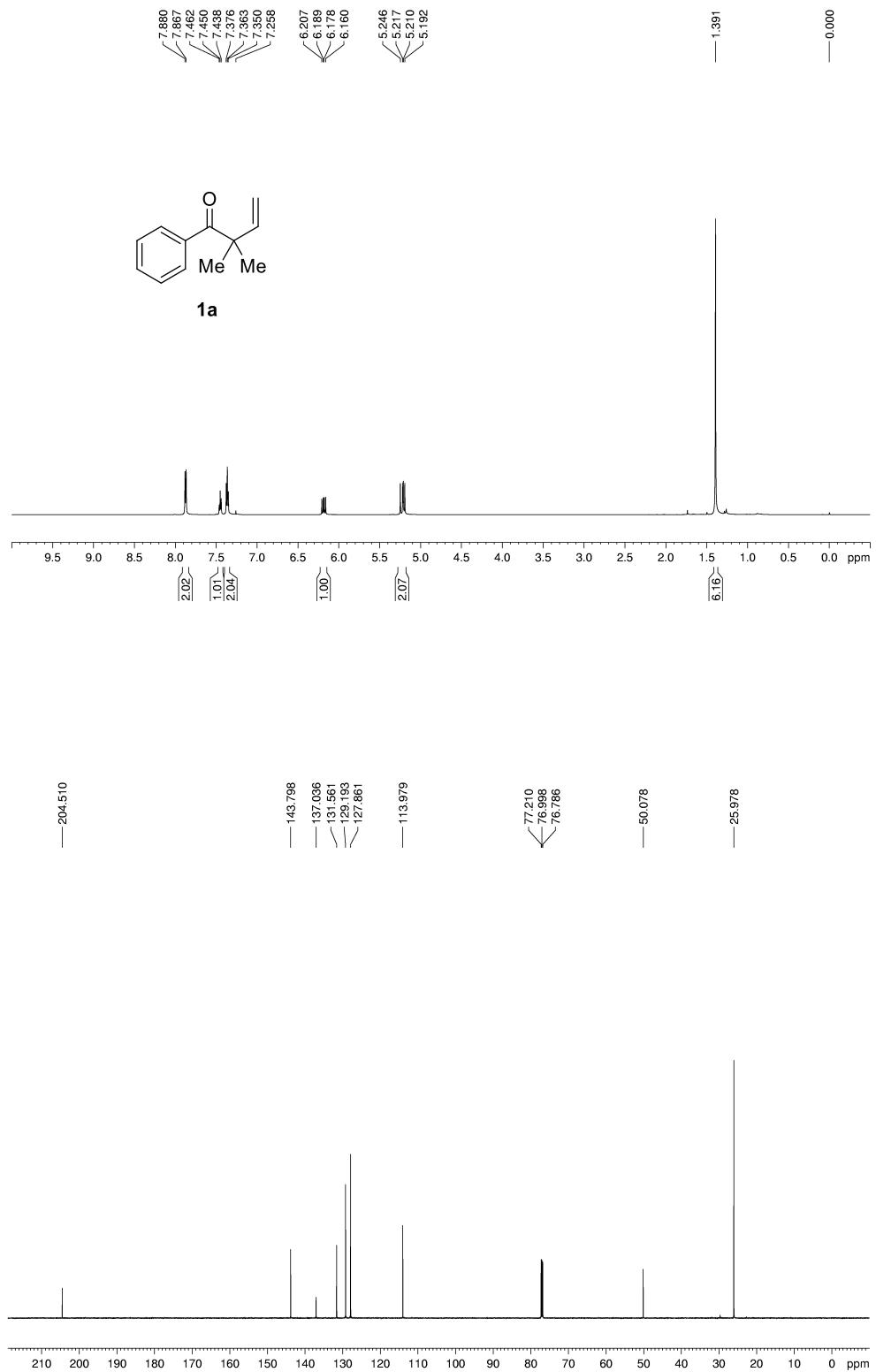


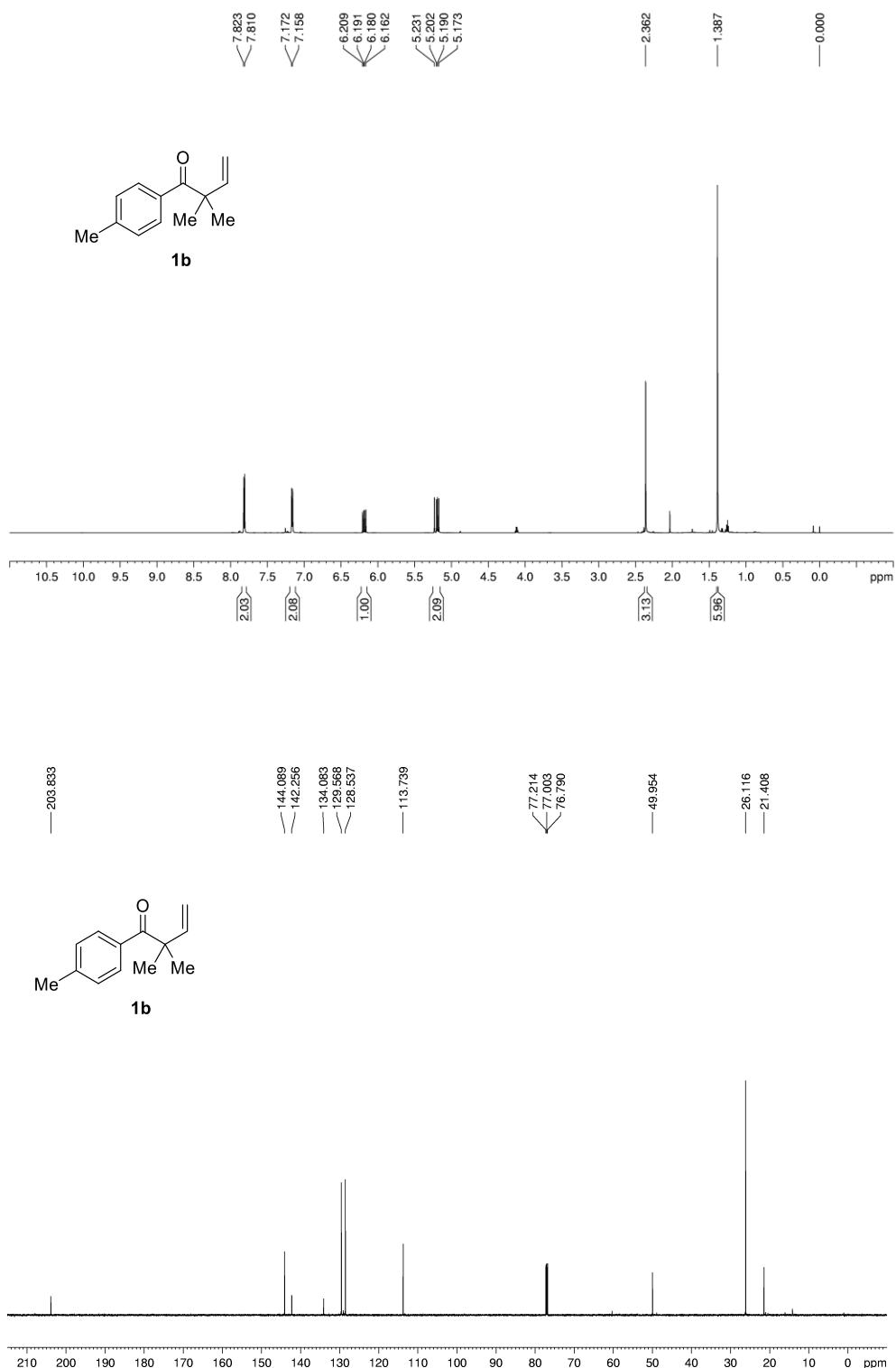


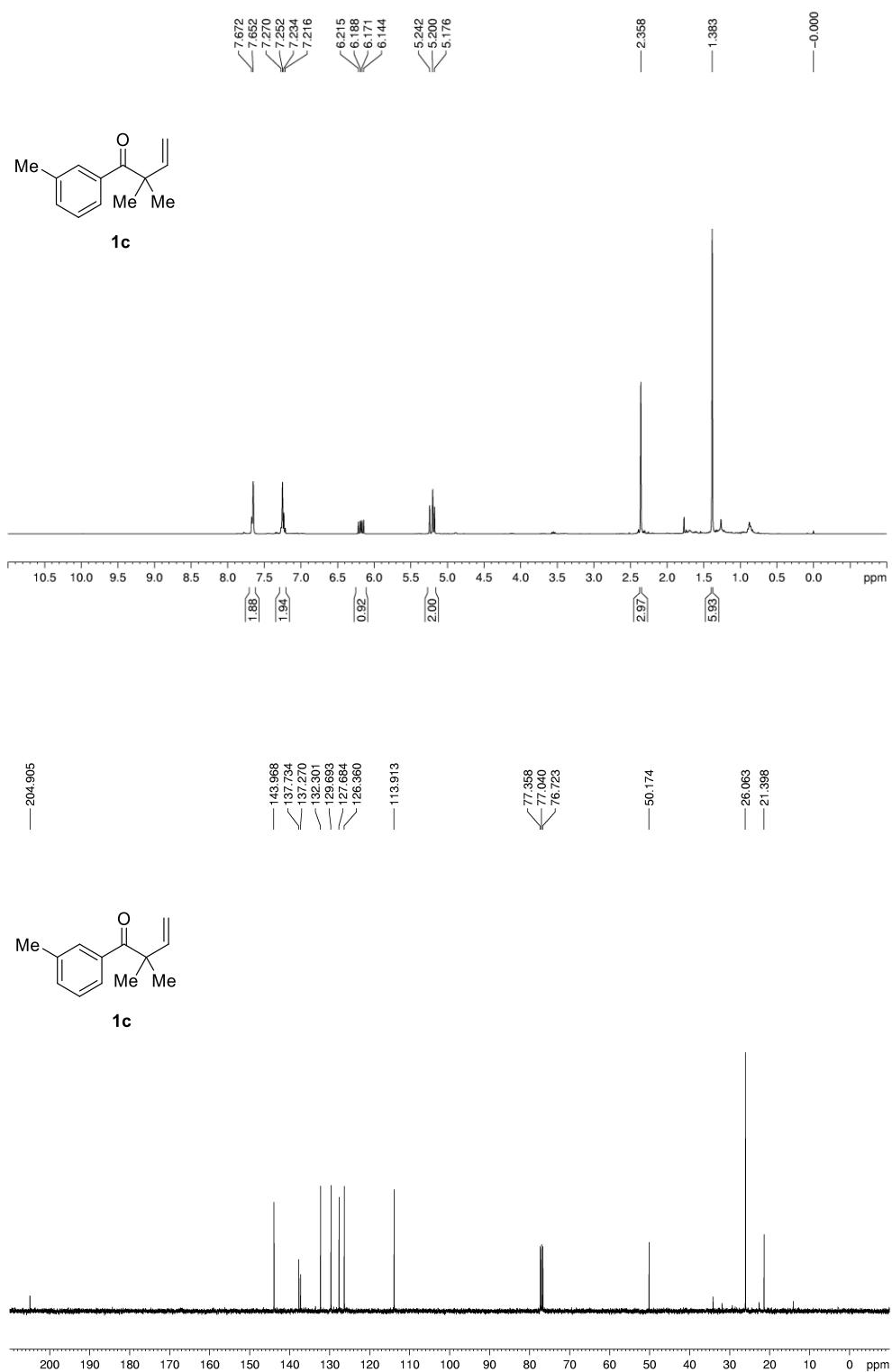


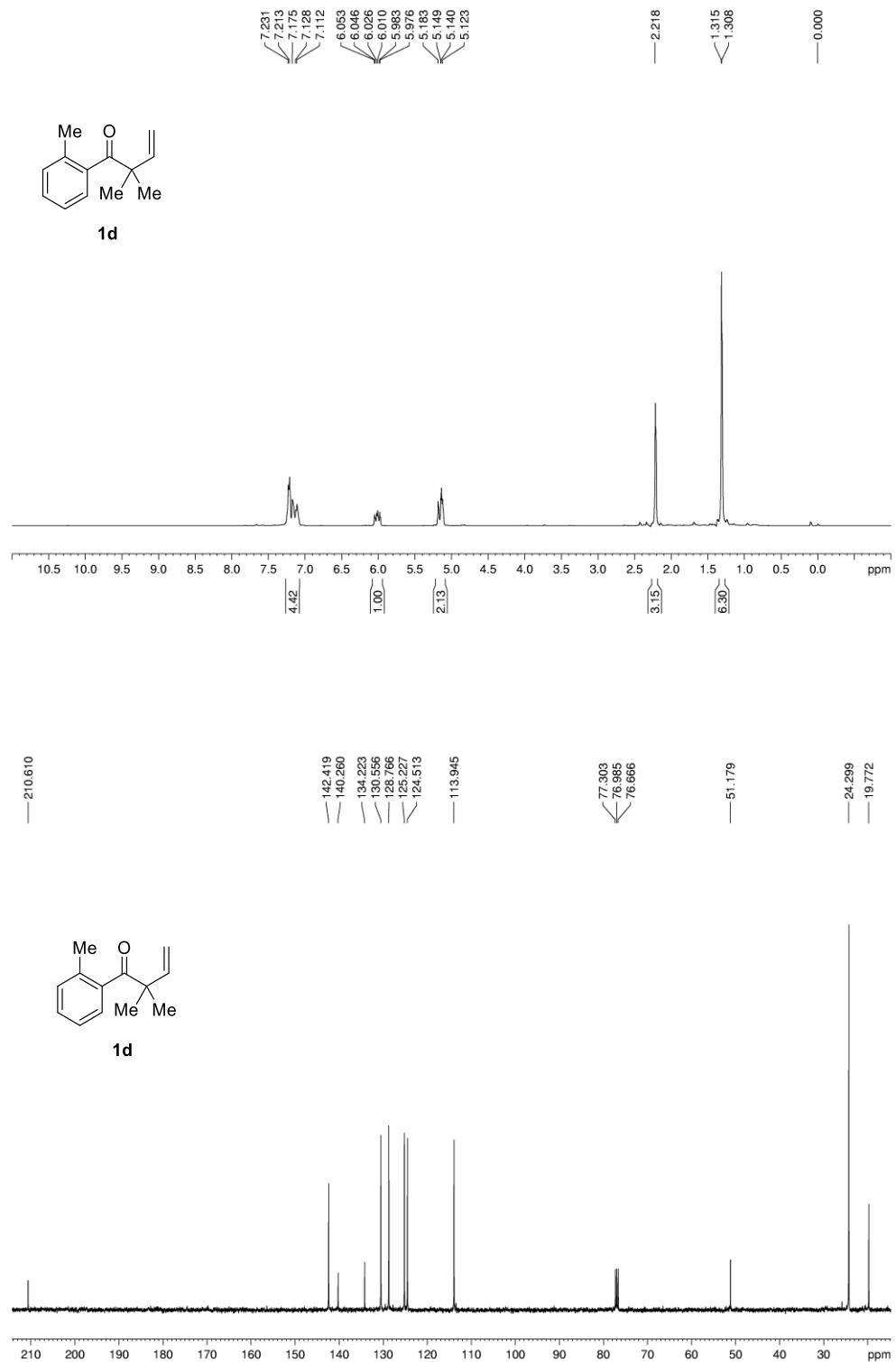


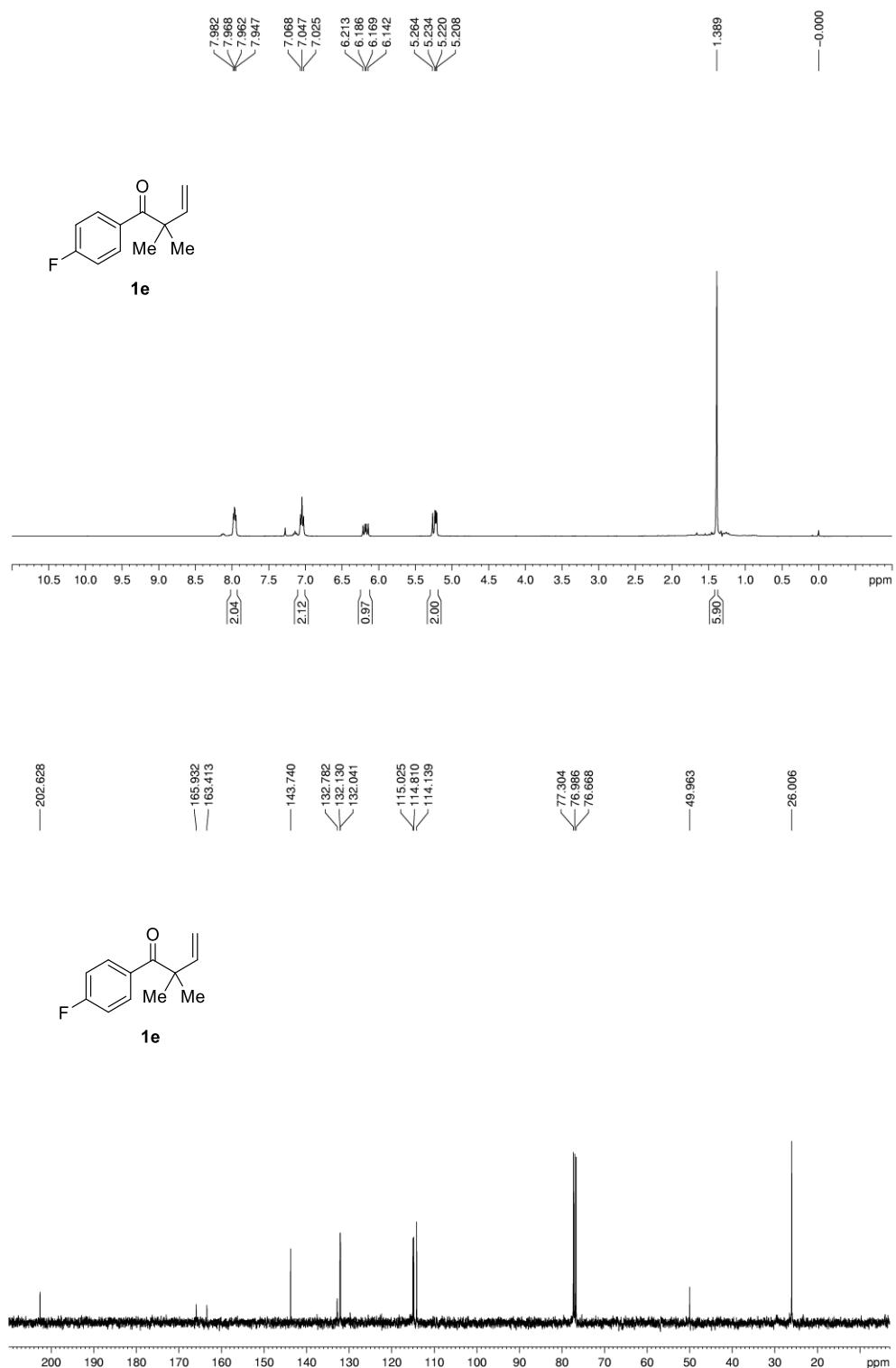


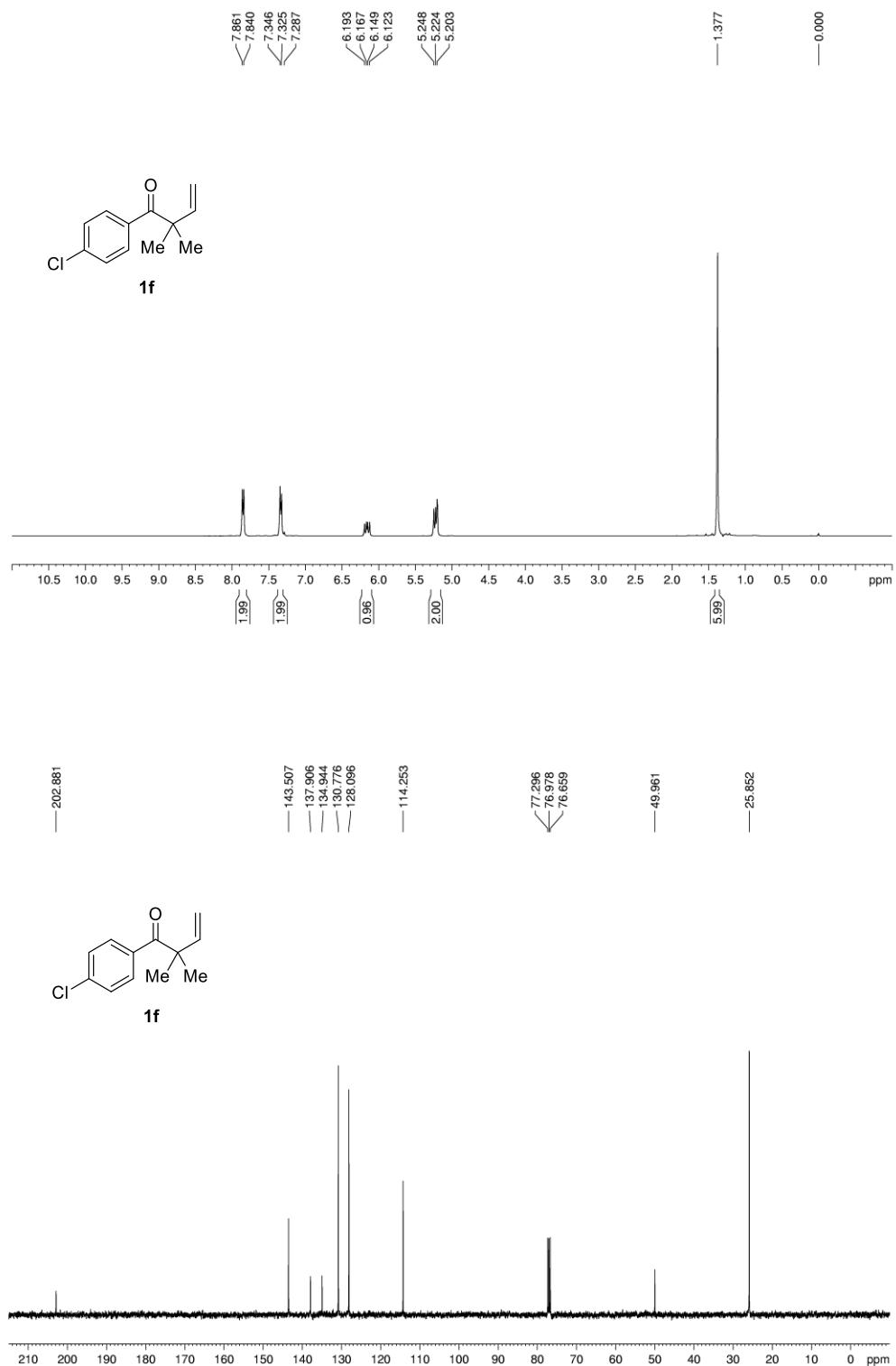


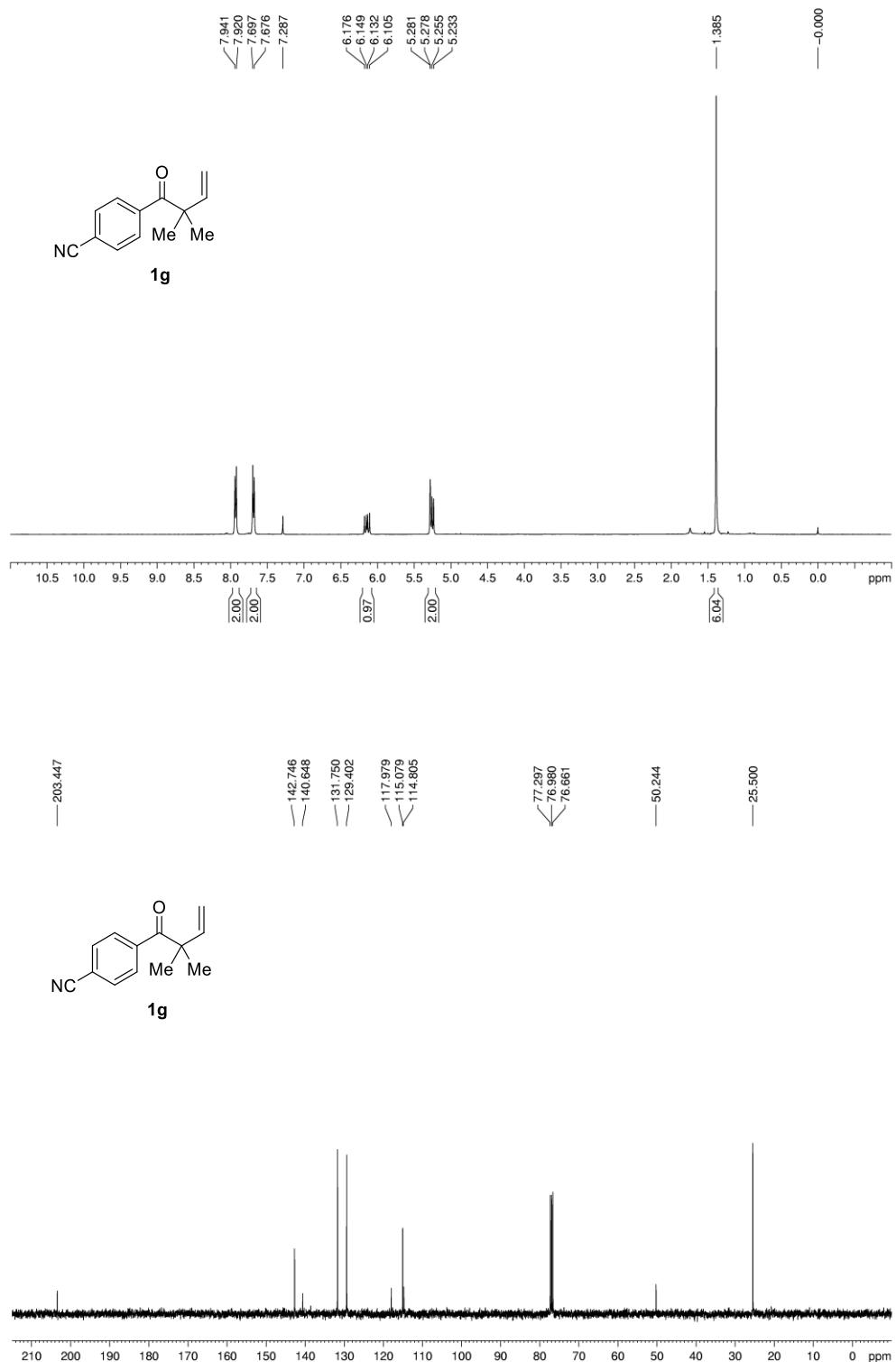


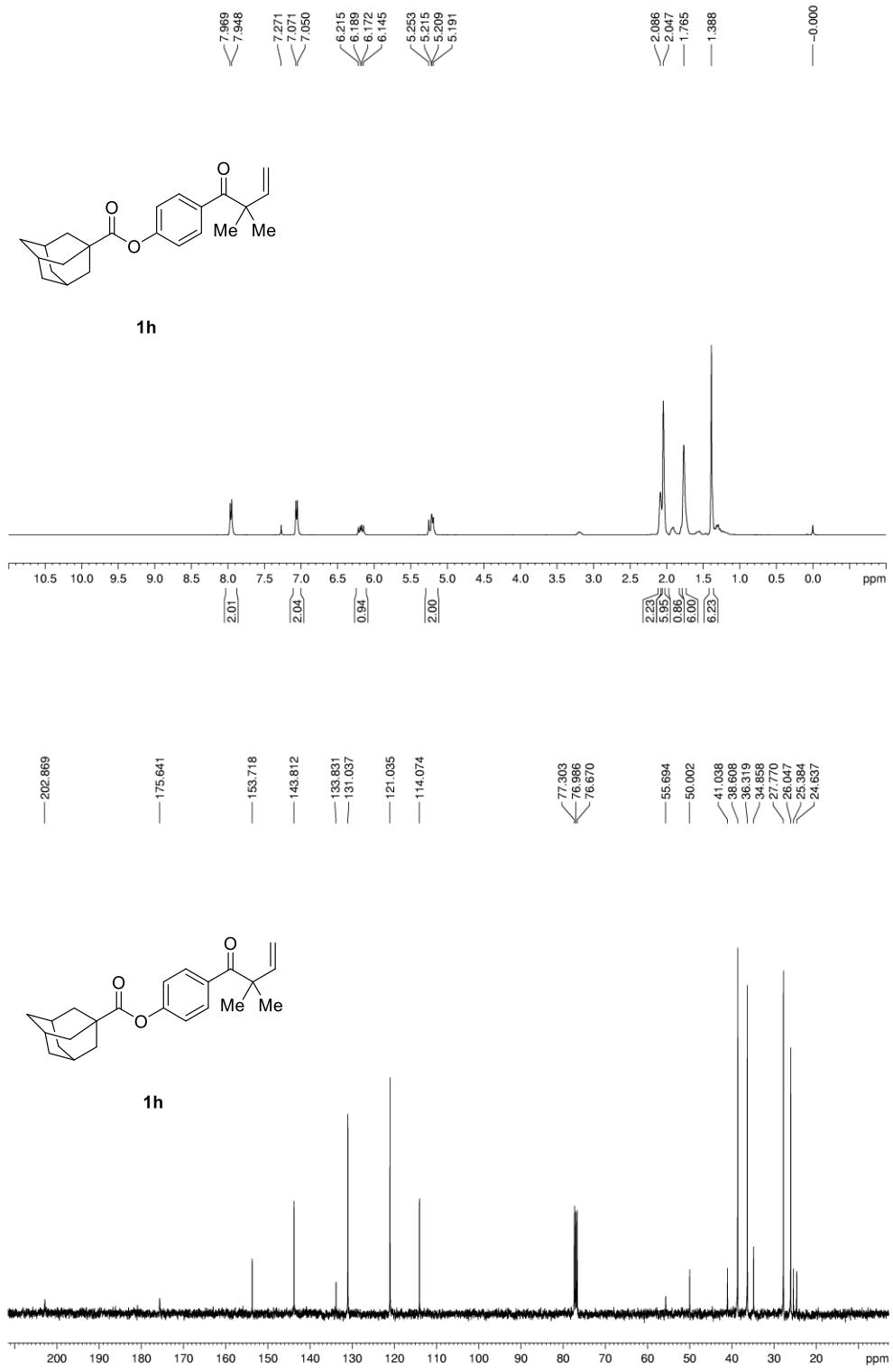


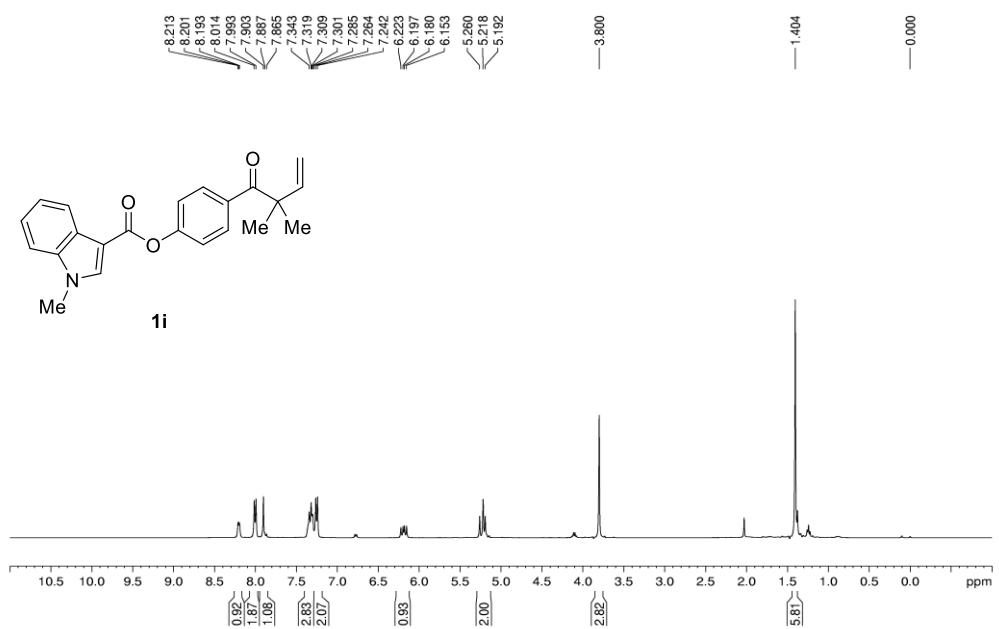


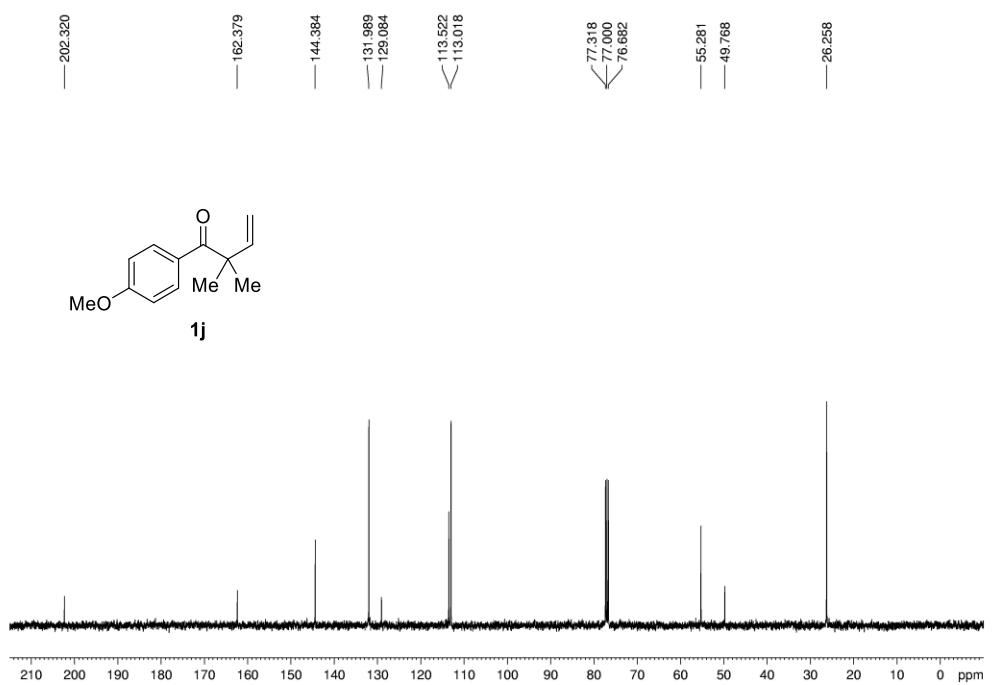
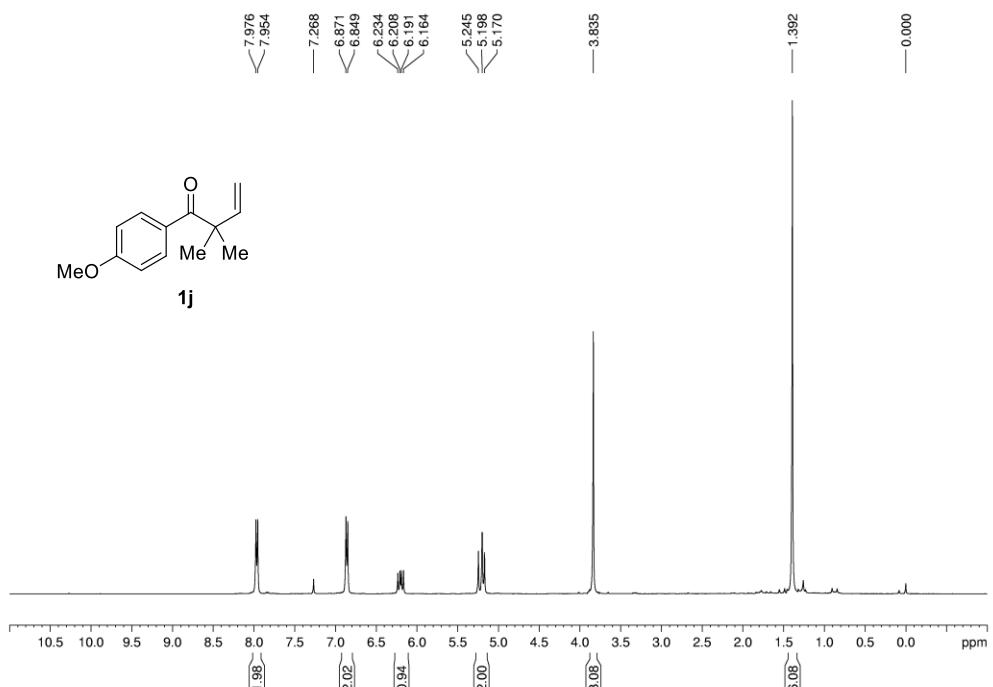


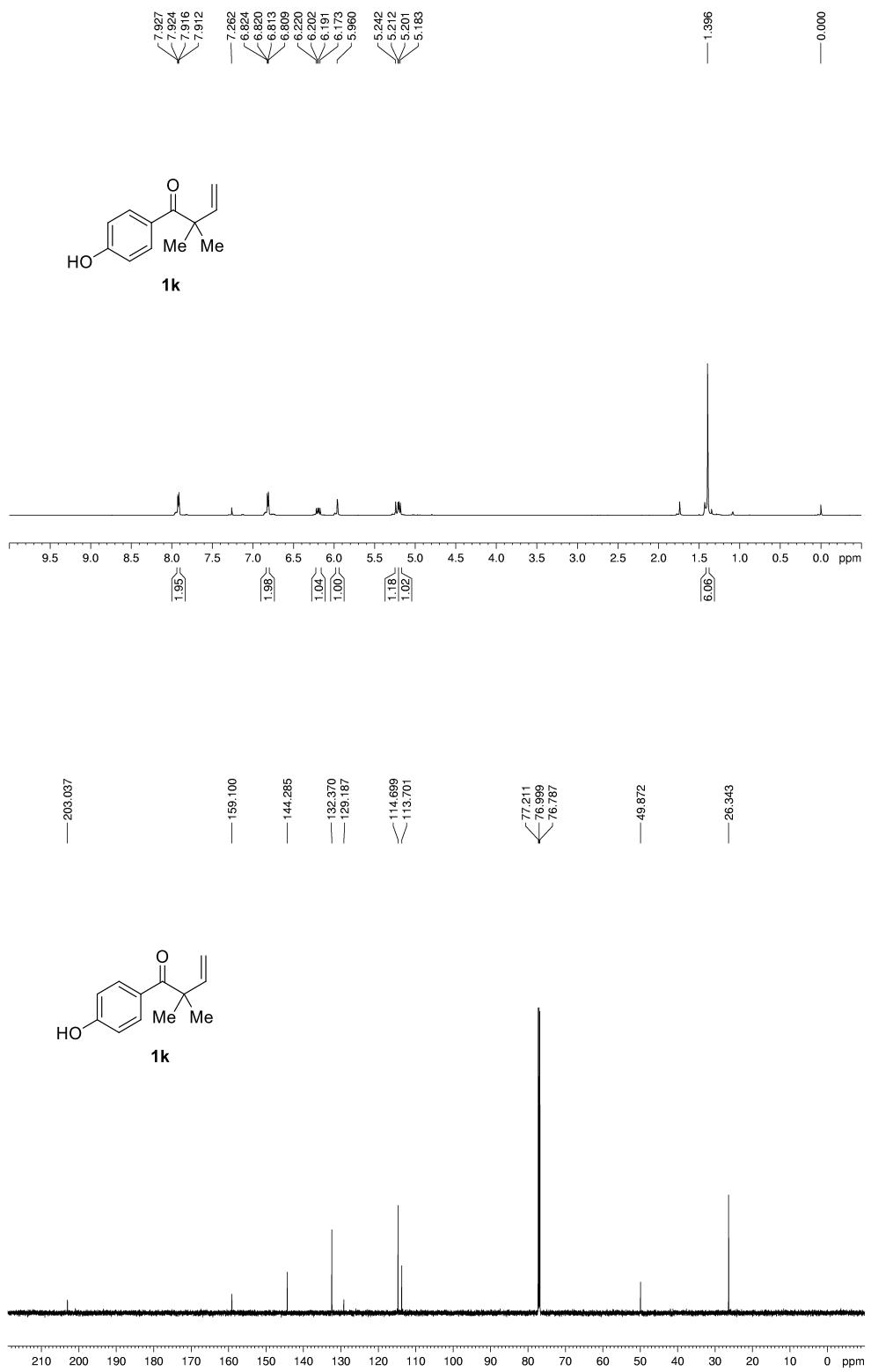


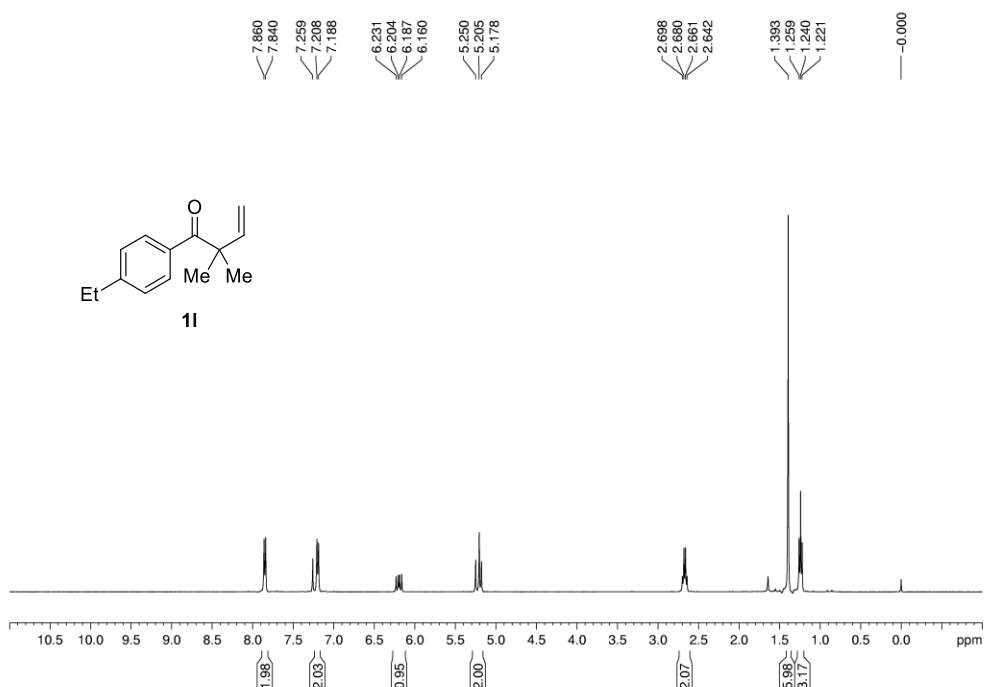




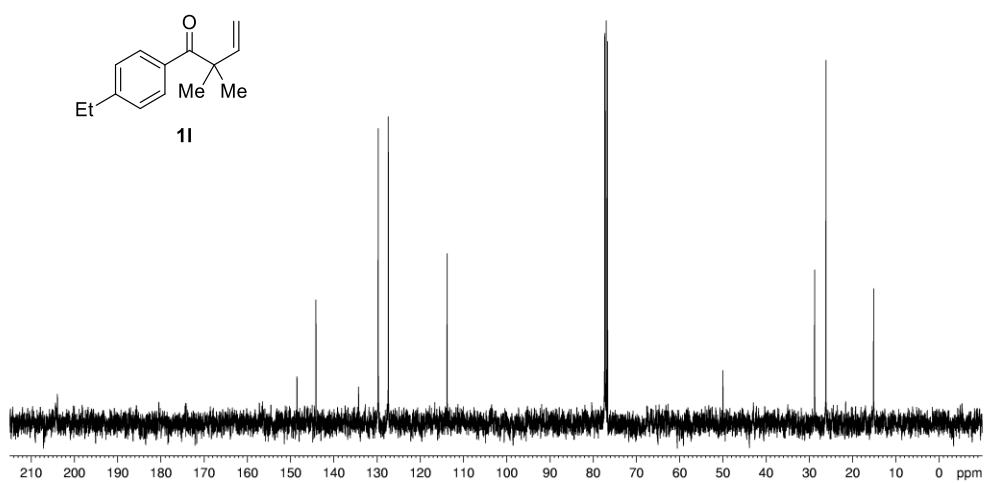


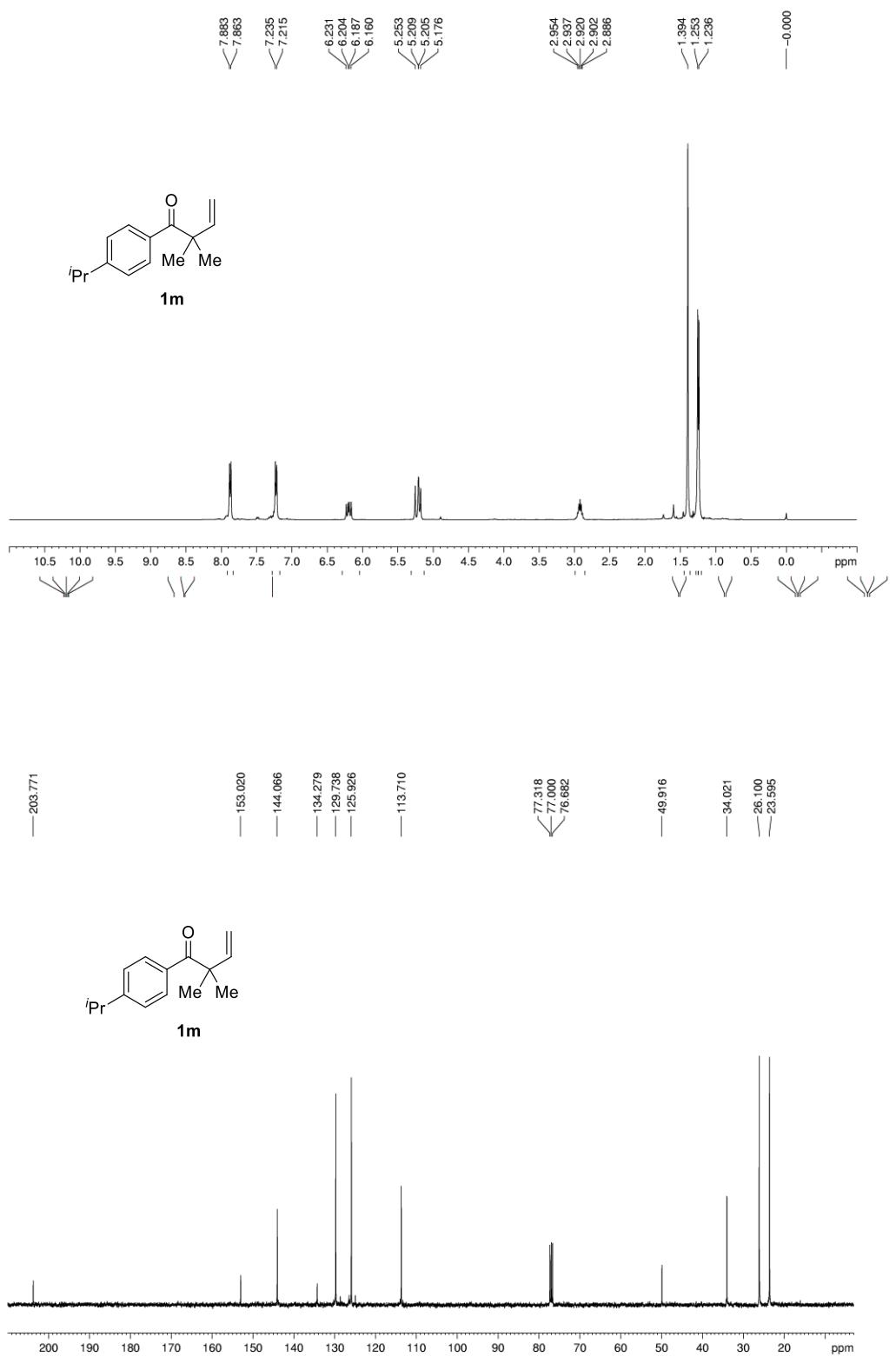


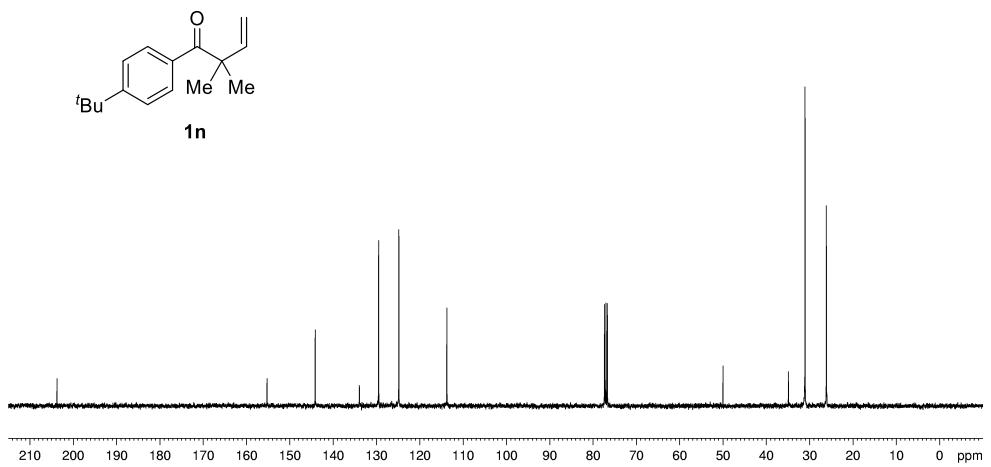
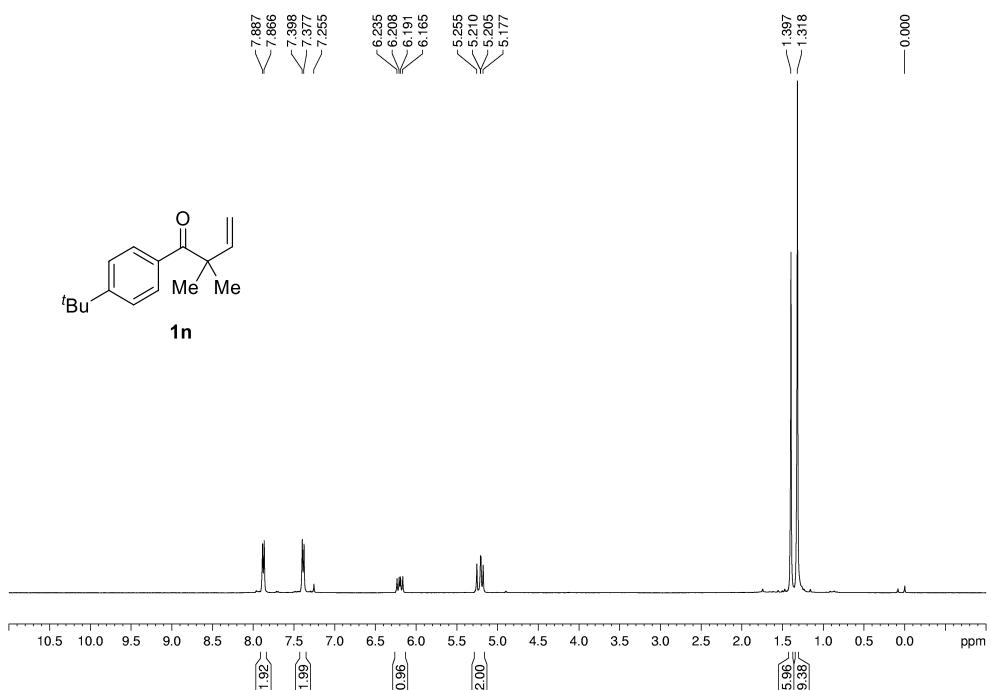


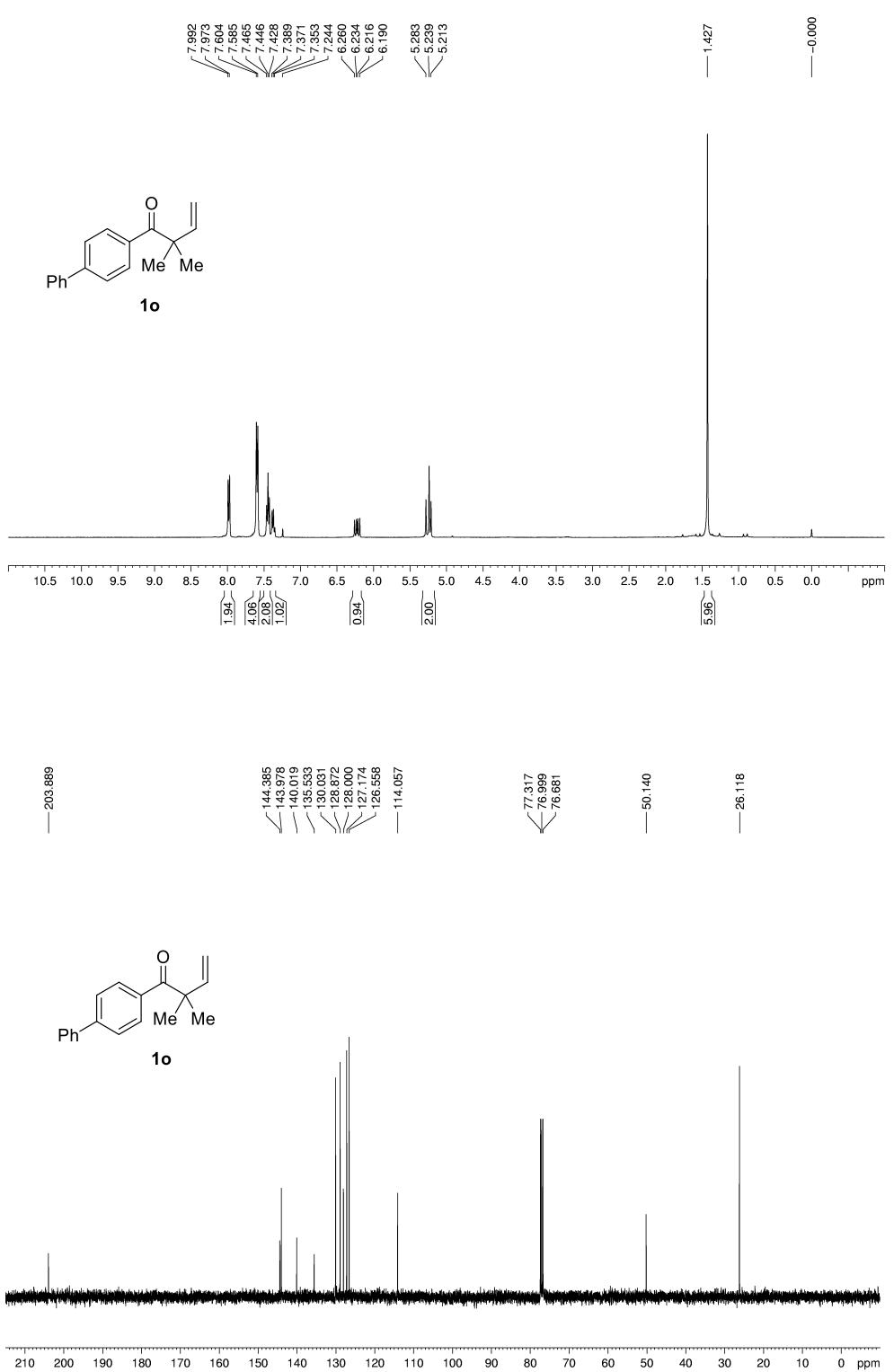


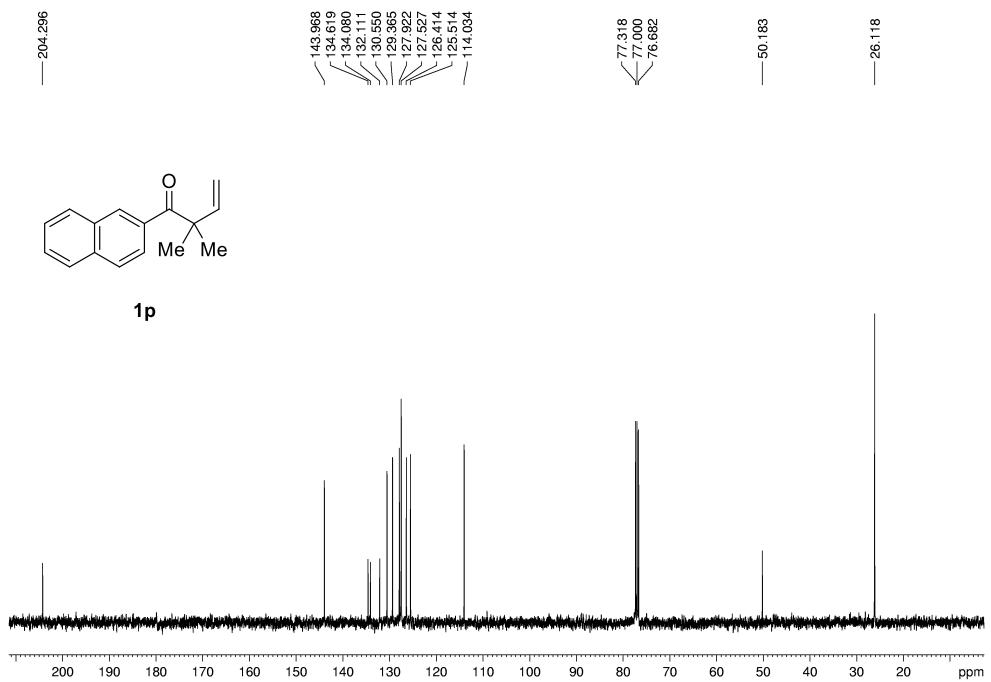
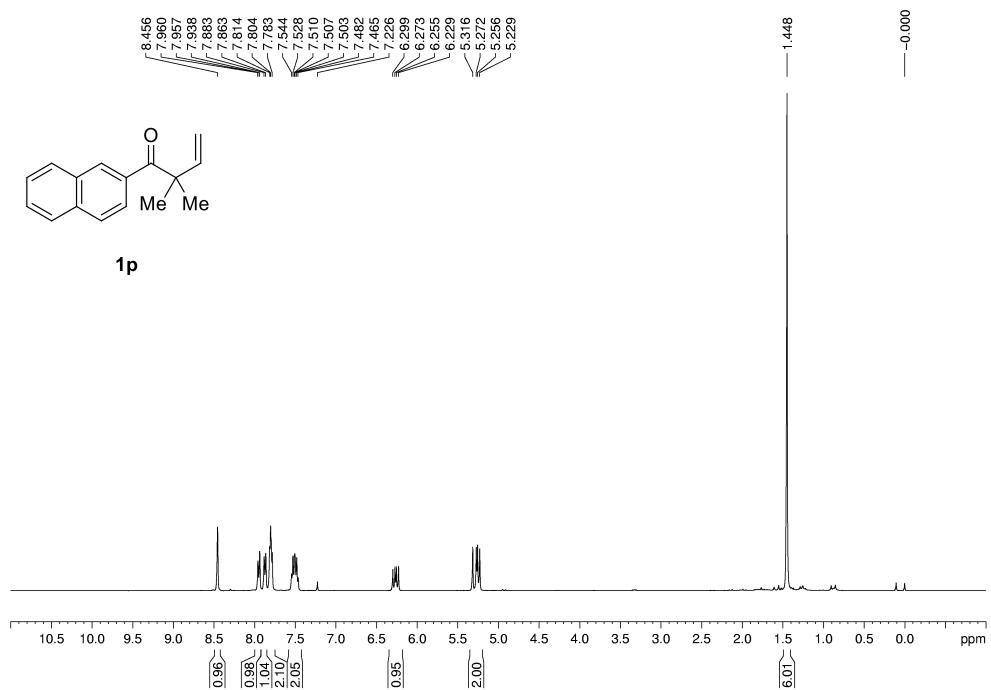
— 203.928  
 — 148.513  
 — 144.133  
 — 134.280  
 — 129.722  
 — 127.384  
 — 113.770

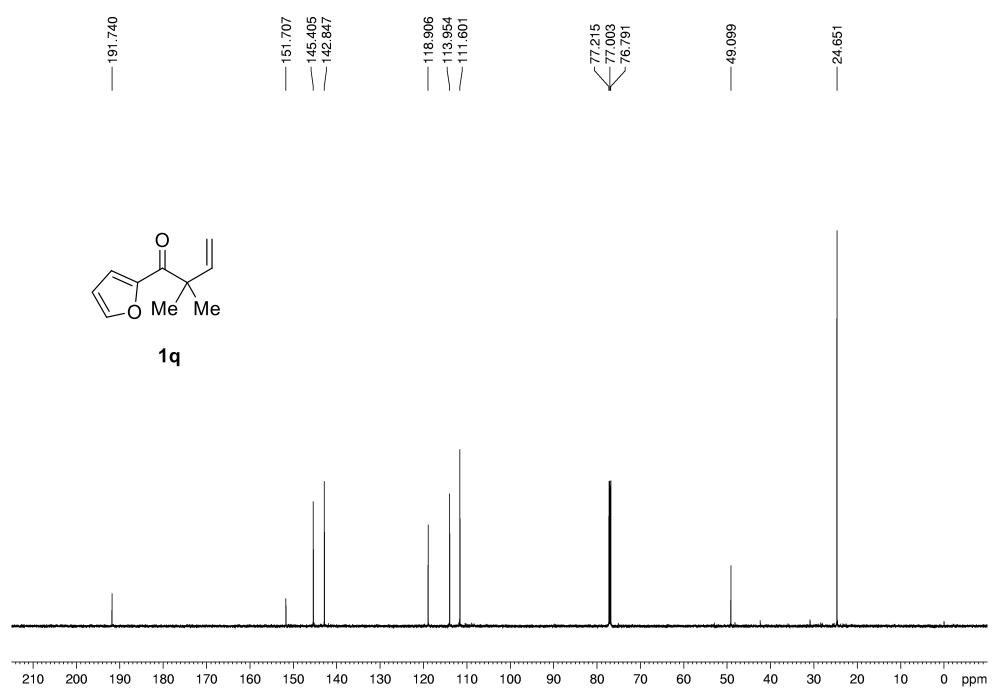
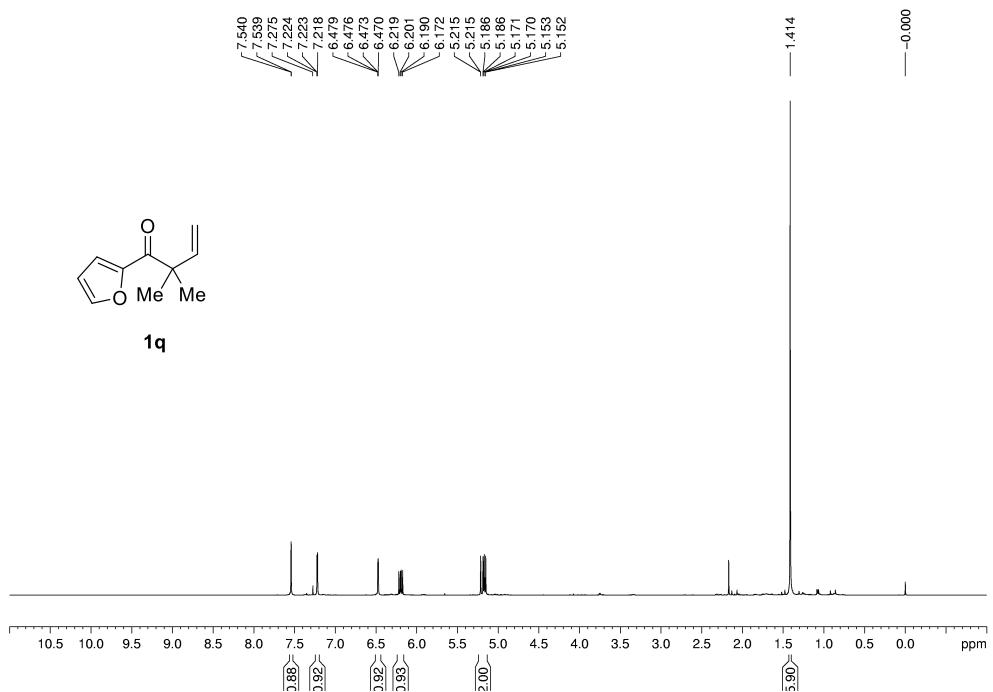


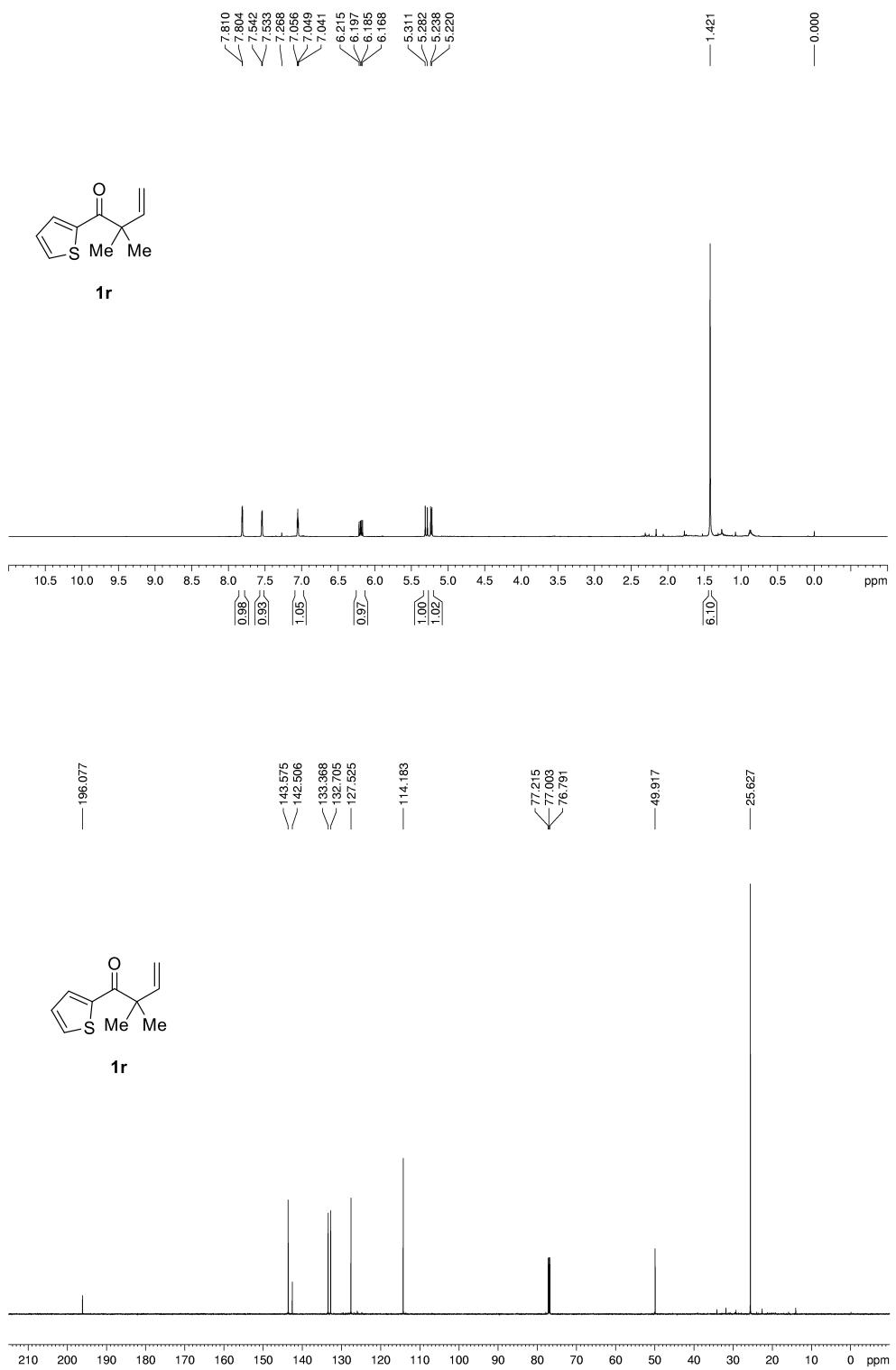


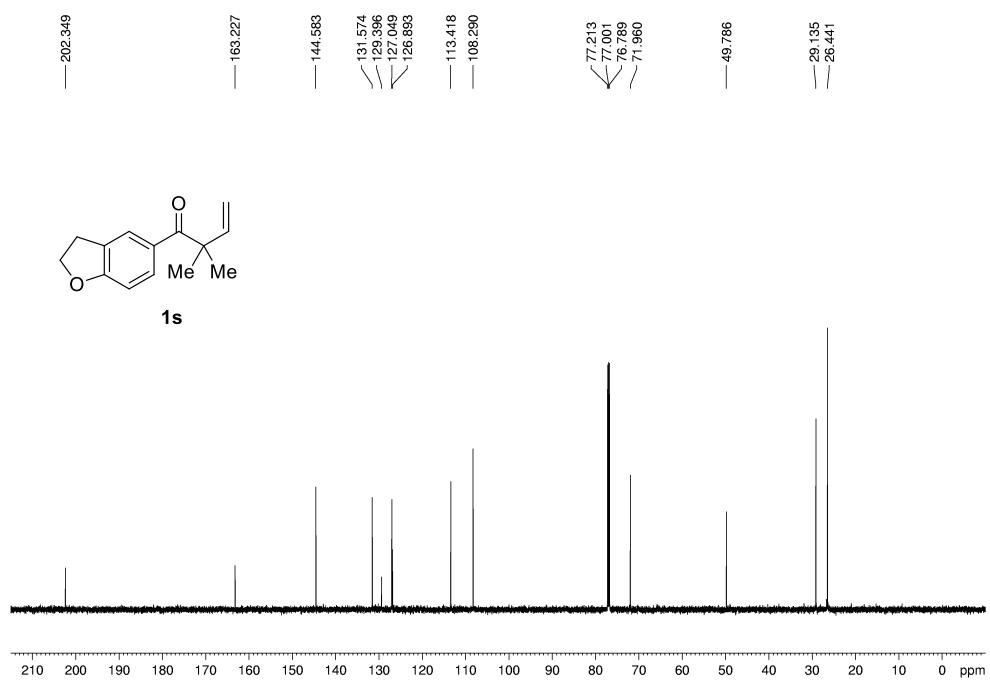
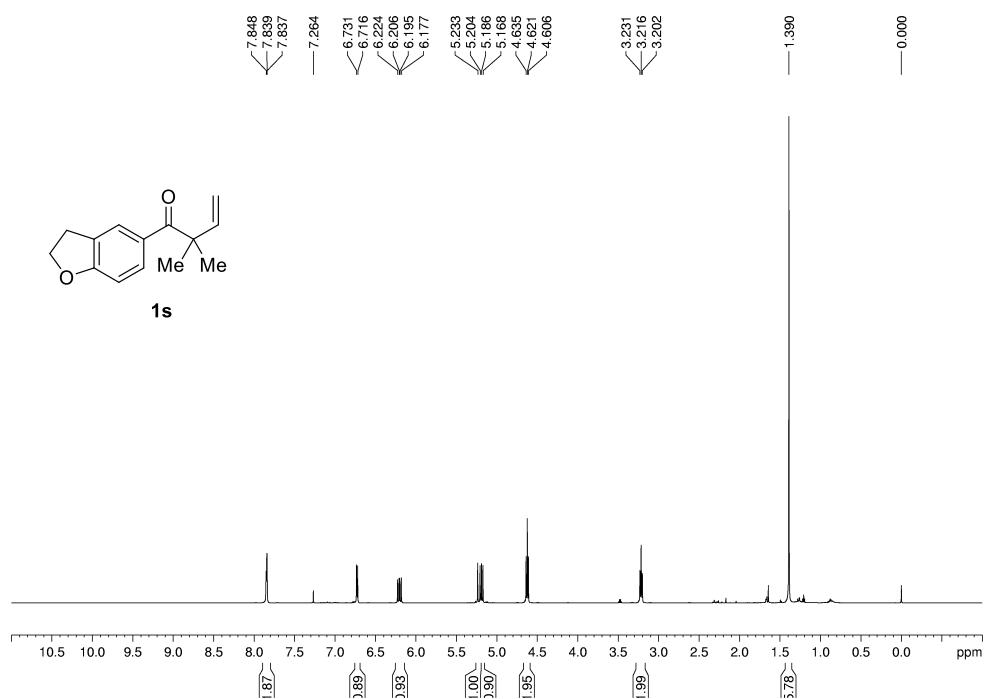


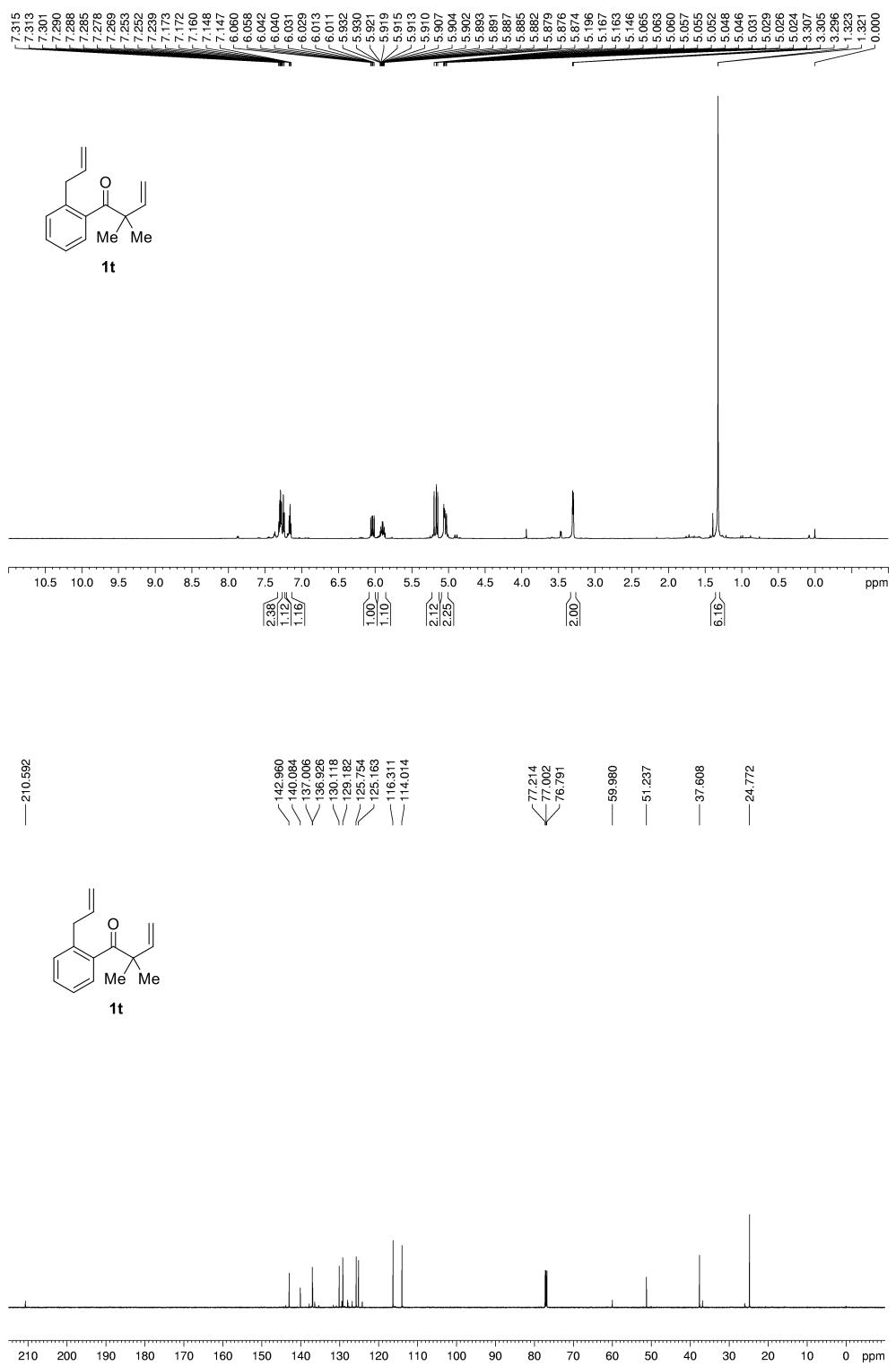


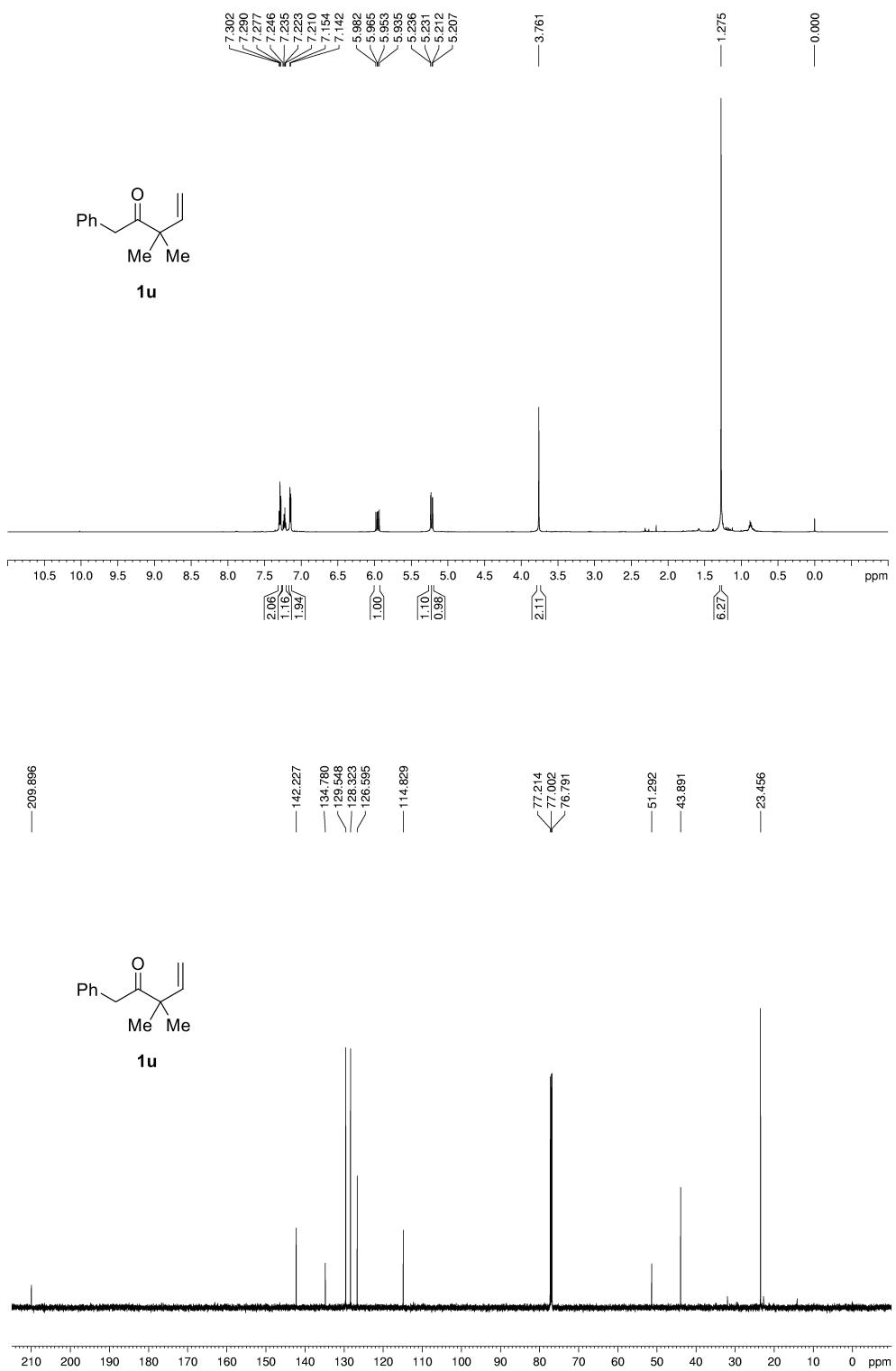


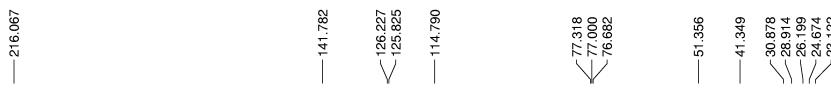
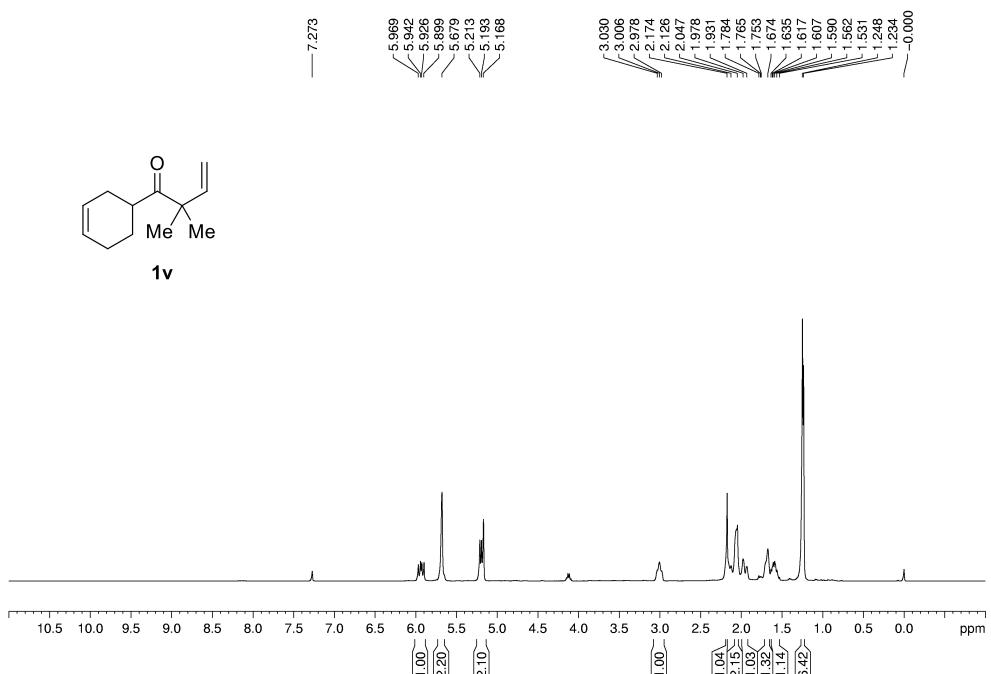


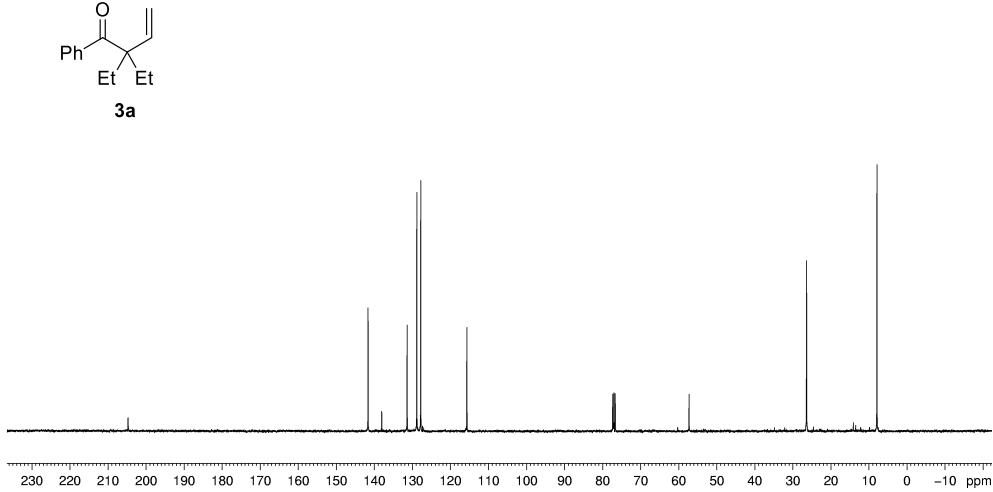
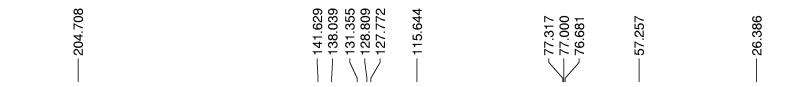
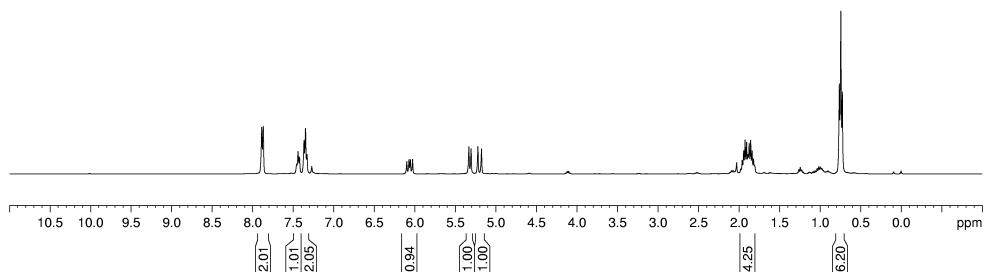
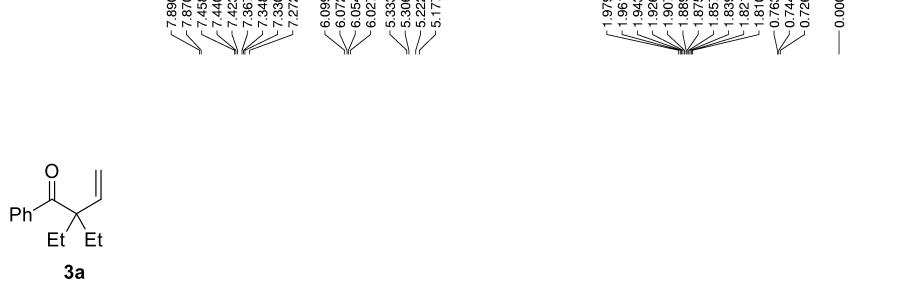


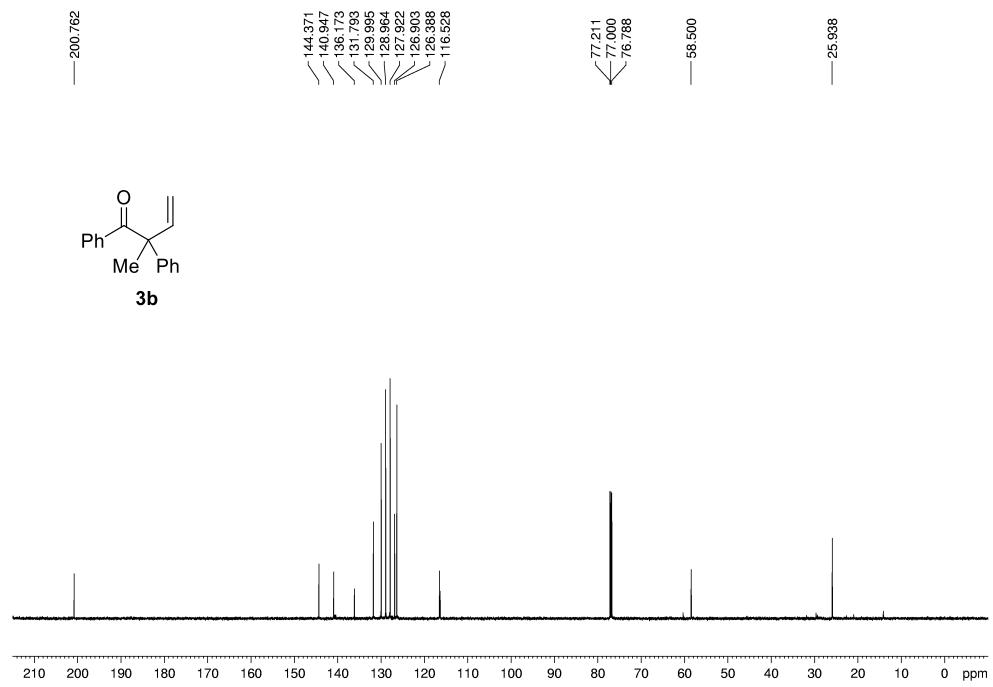
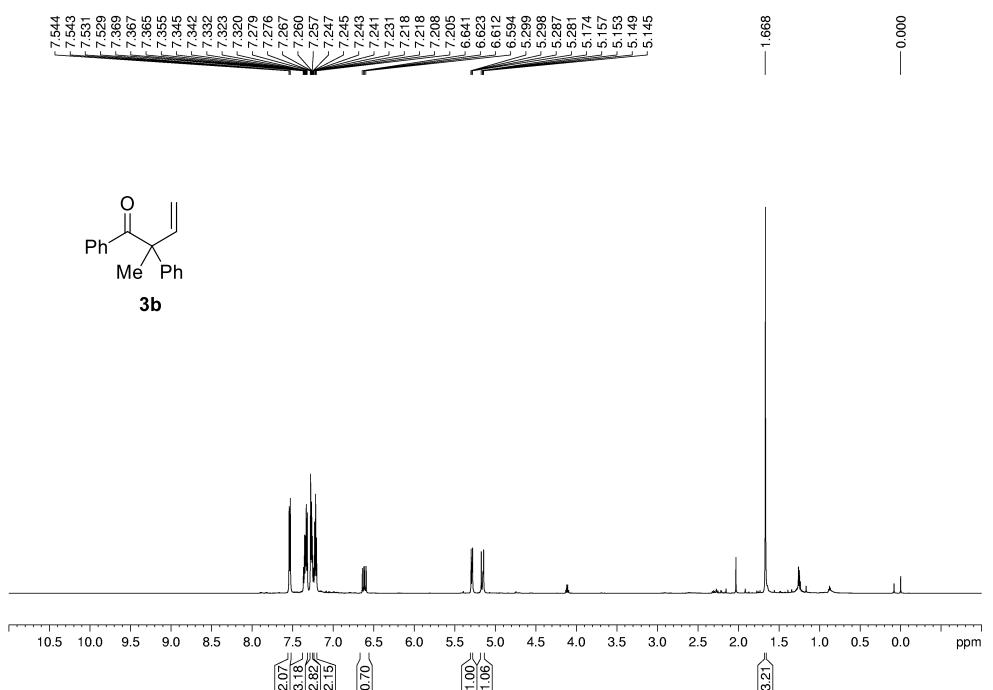


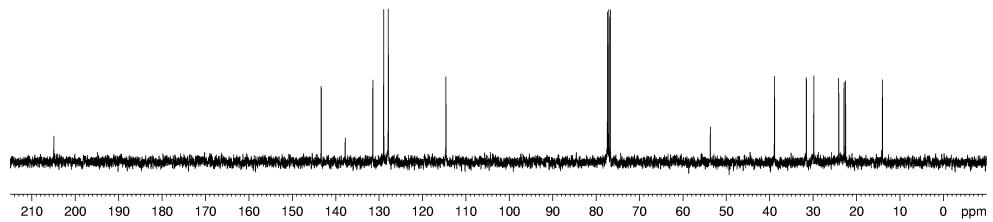
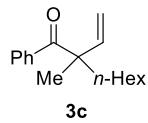
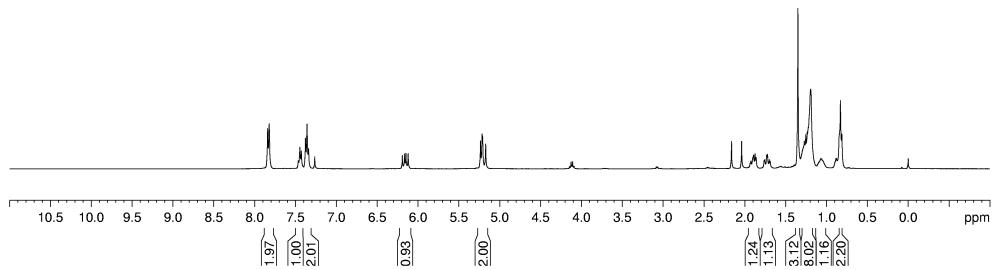
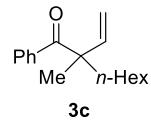


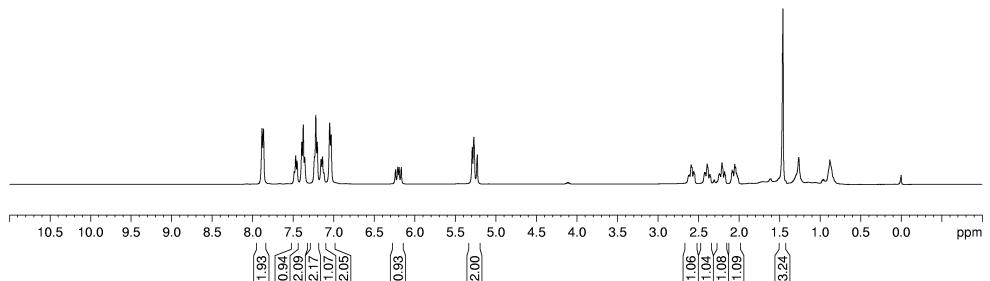
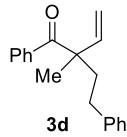




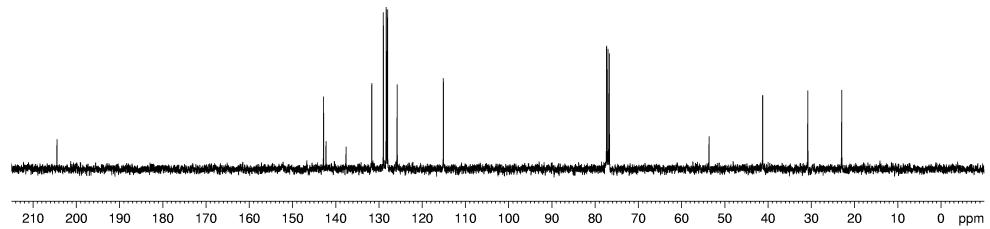
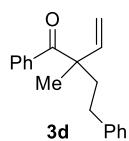


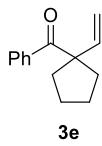




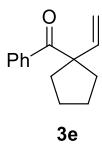
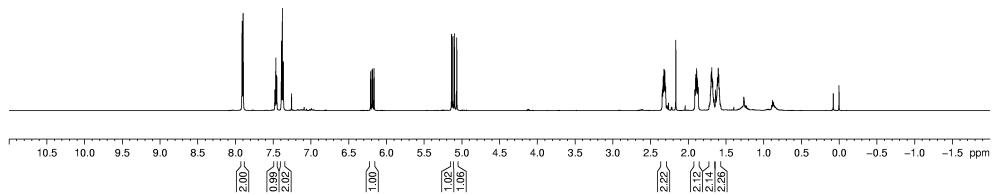


— 204.393

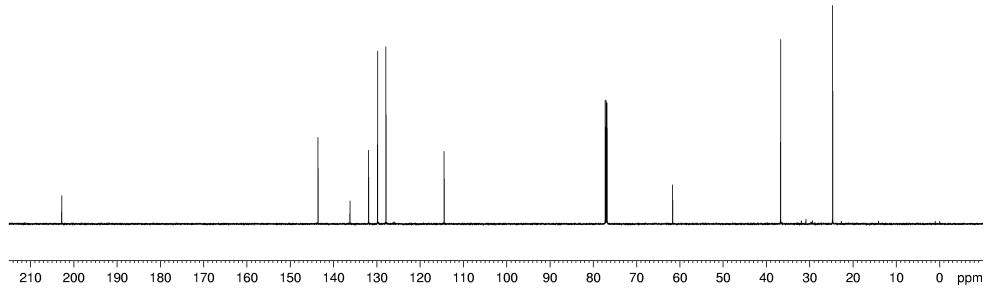


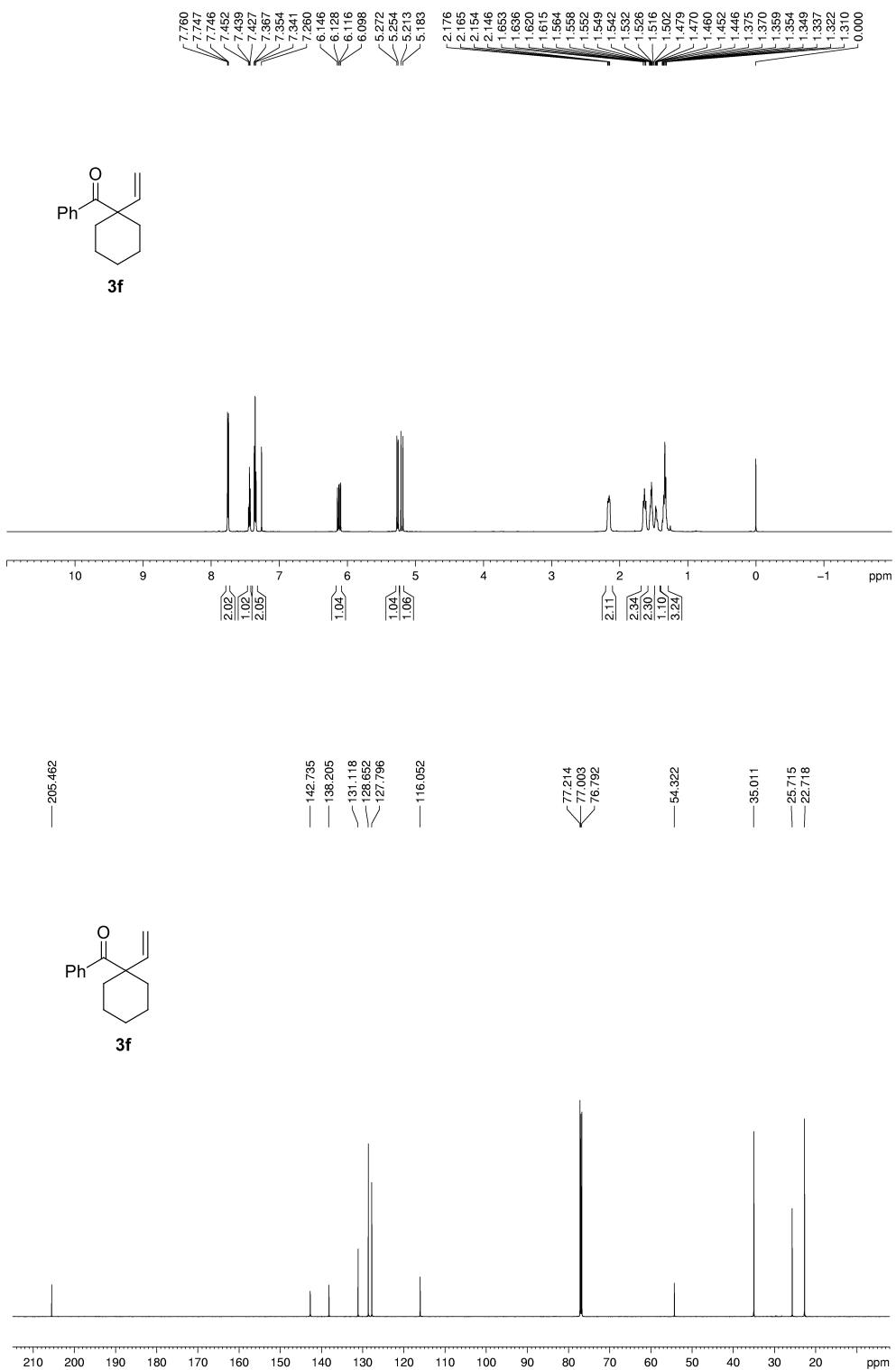


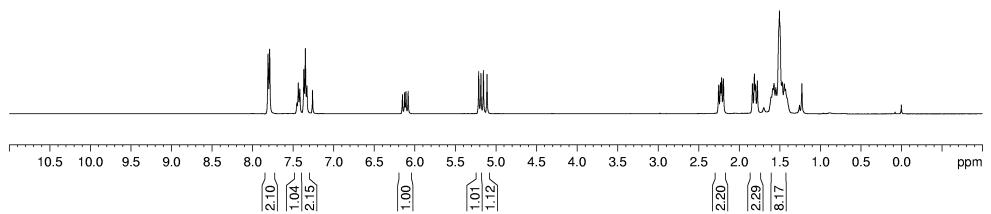
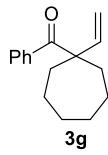
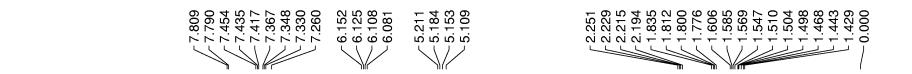
3e



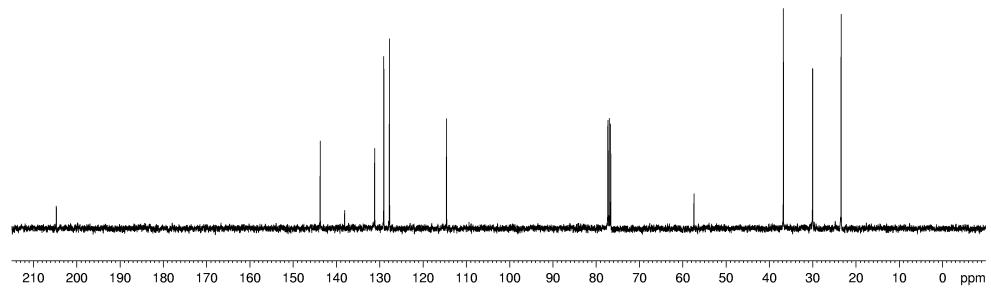
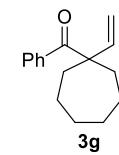
3e

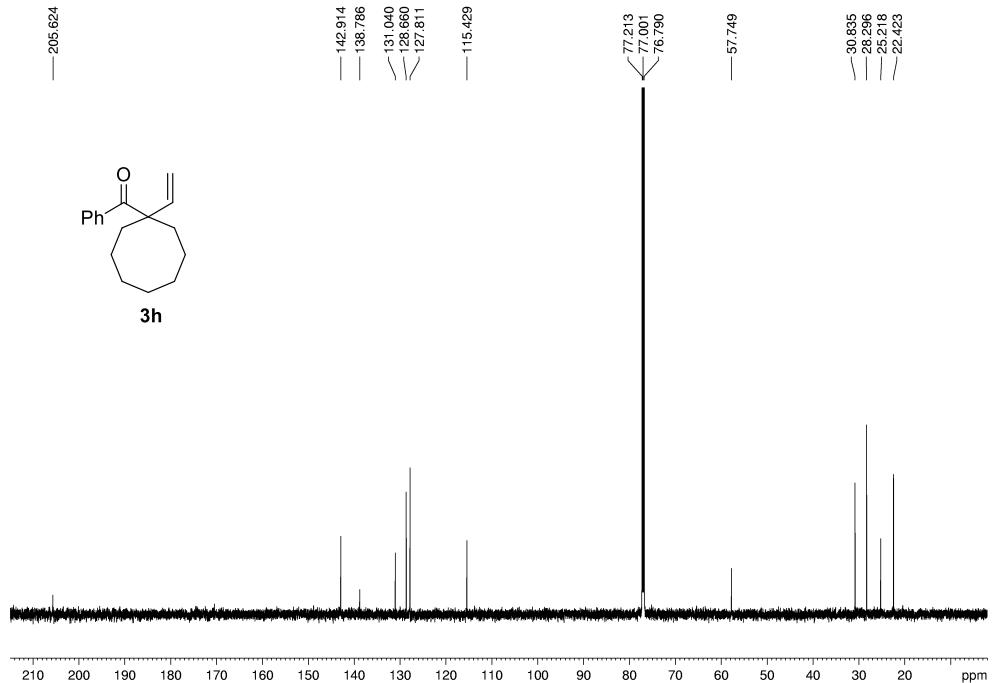
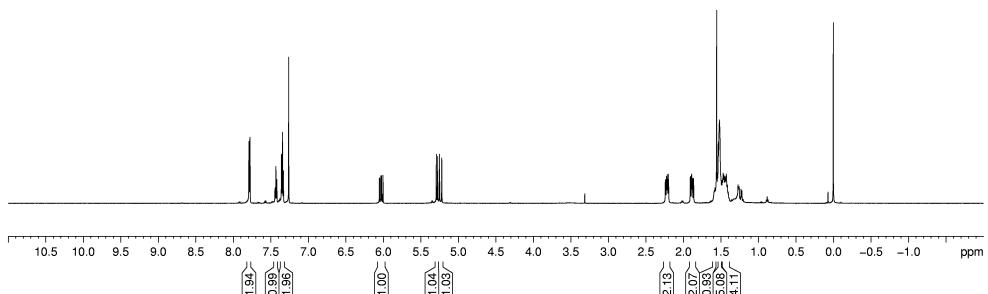
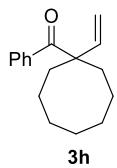
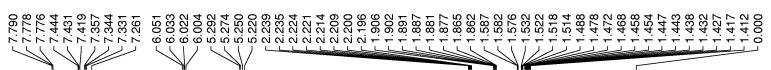


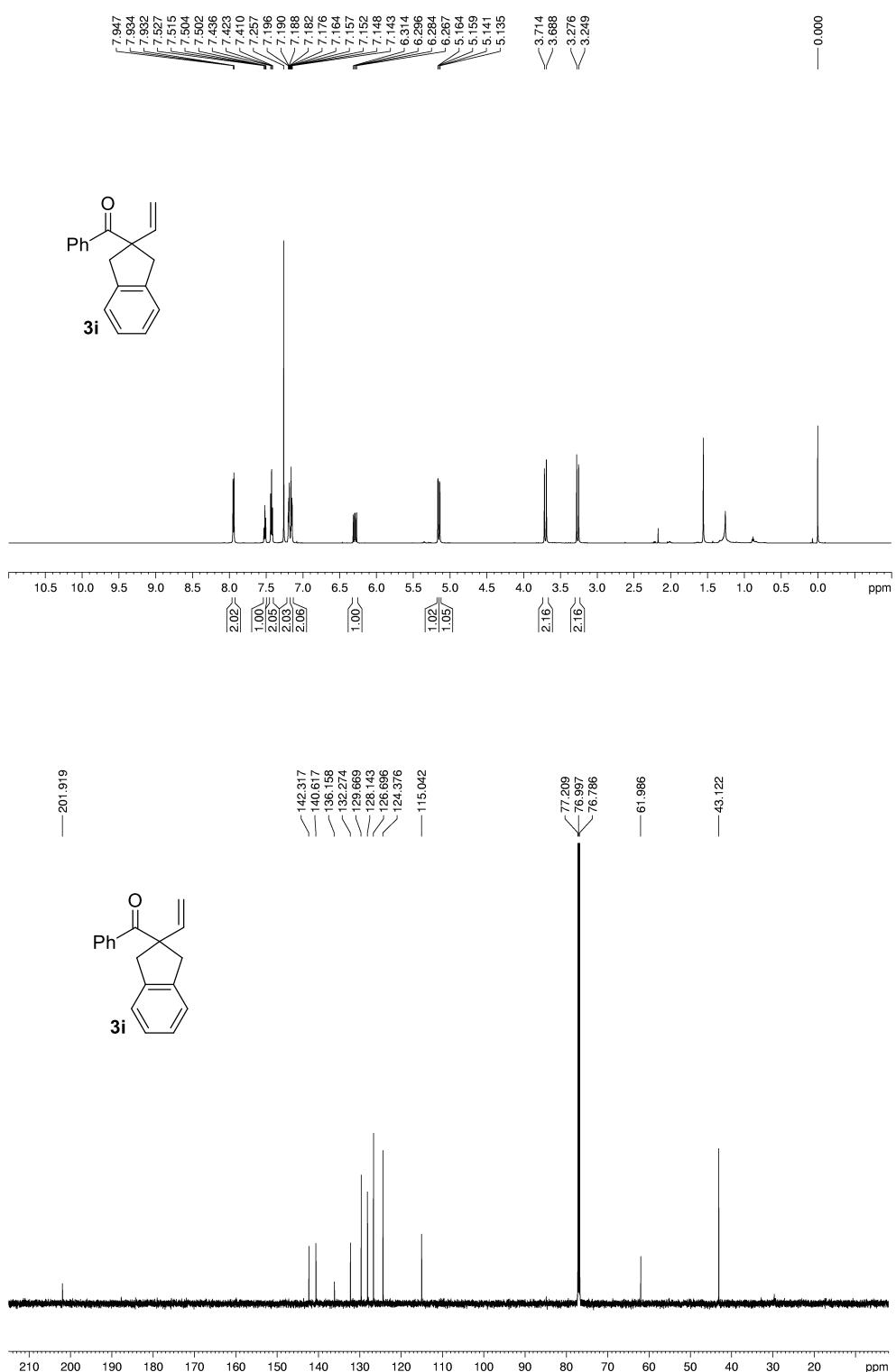


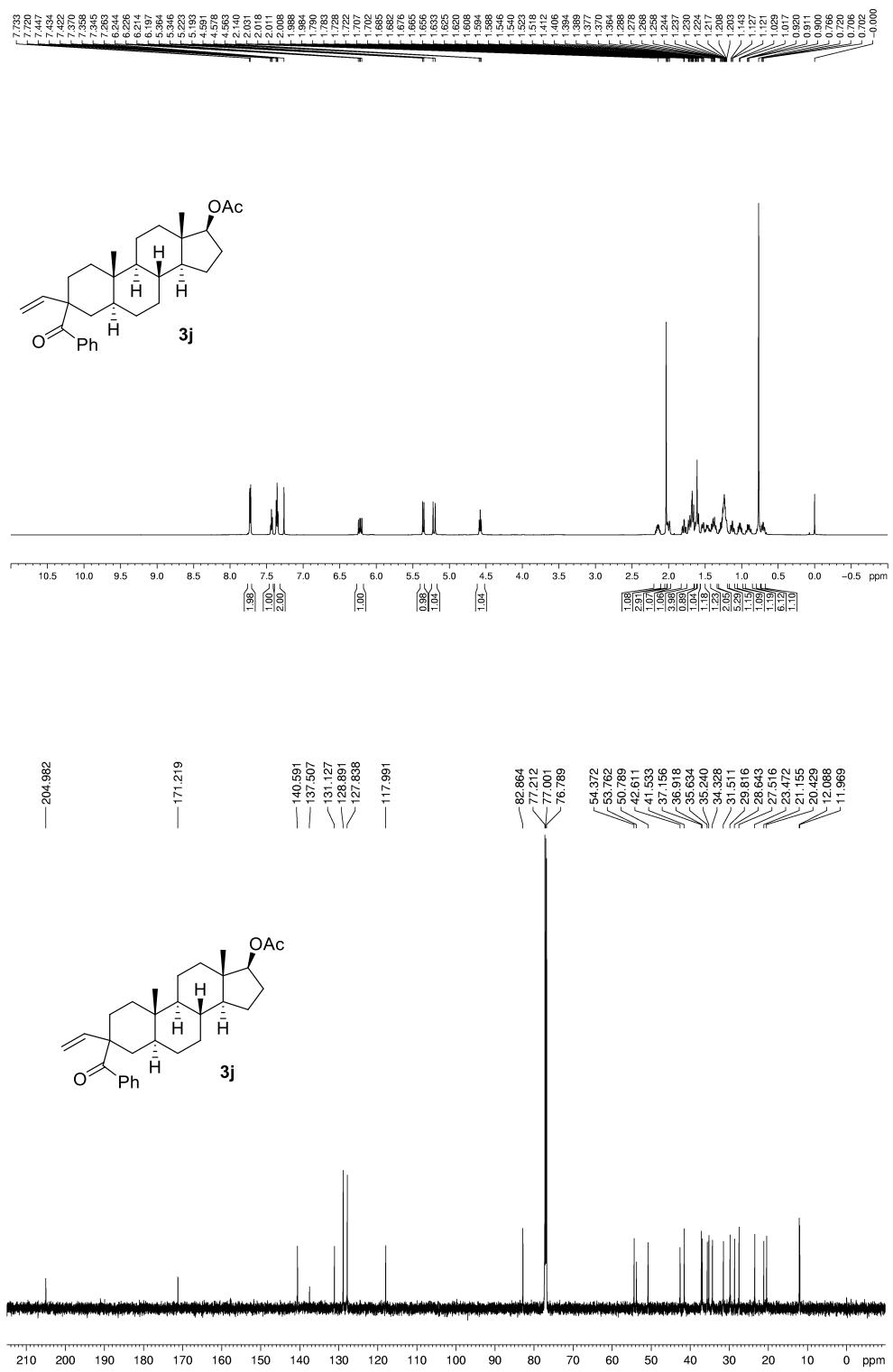


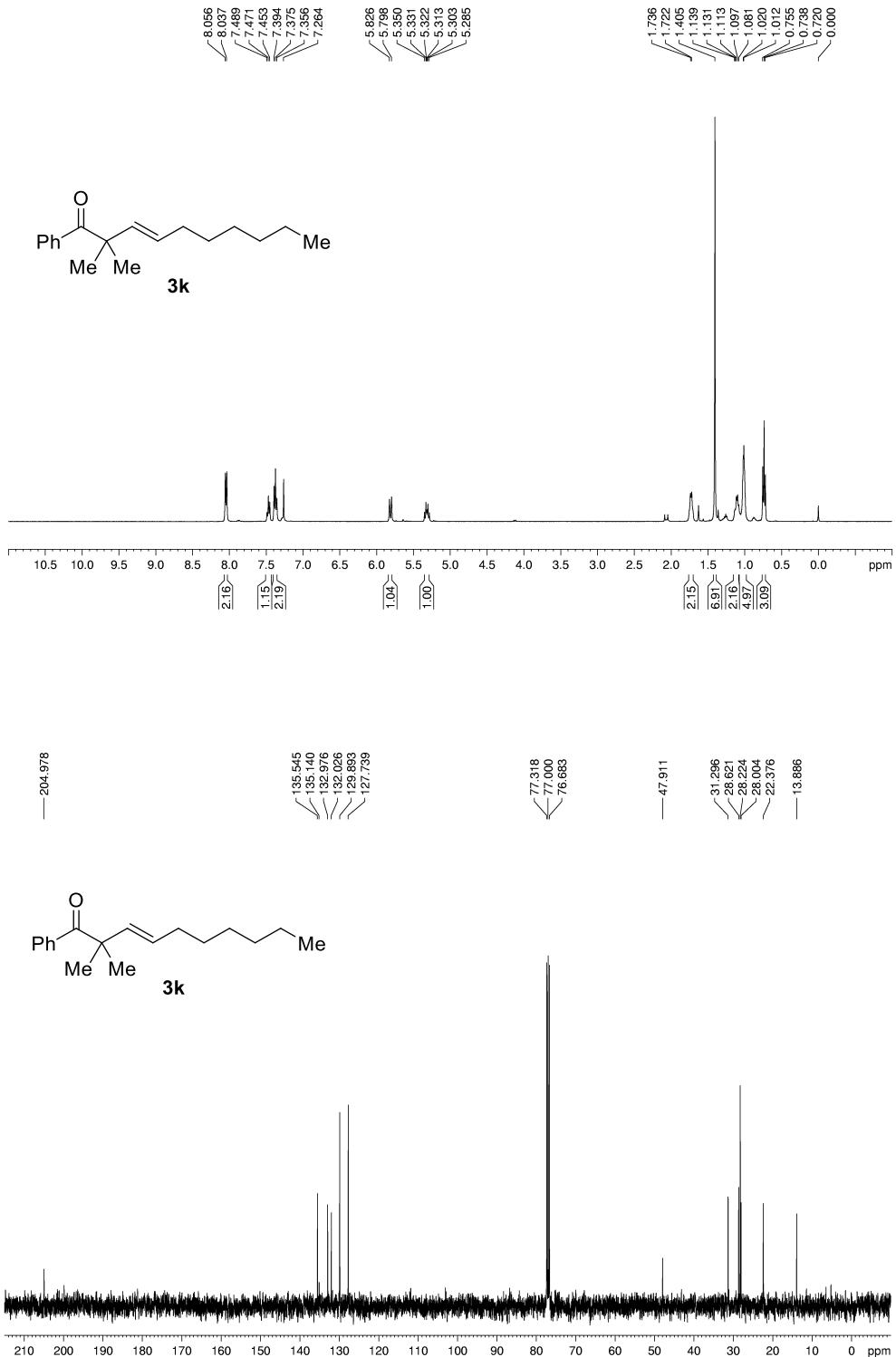
— 204.729  
 — 143.767  
 — 138.120  
 — 131.187  
 — 129.082  
 — 127.772  
 — 114.582  
 — 57.423  
 — 36.778  
 — 30.014  
 — 23.436

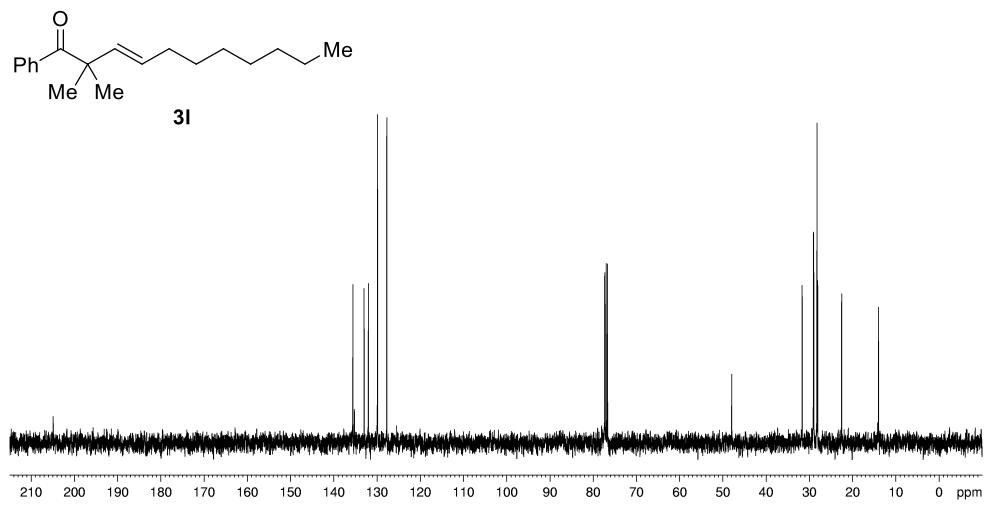
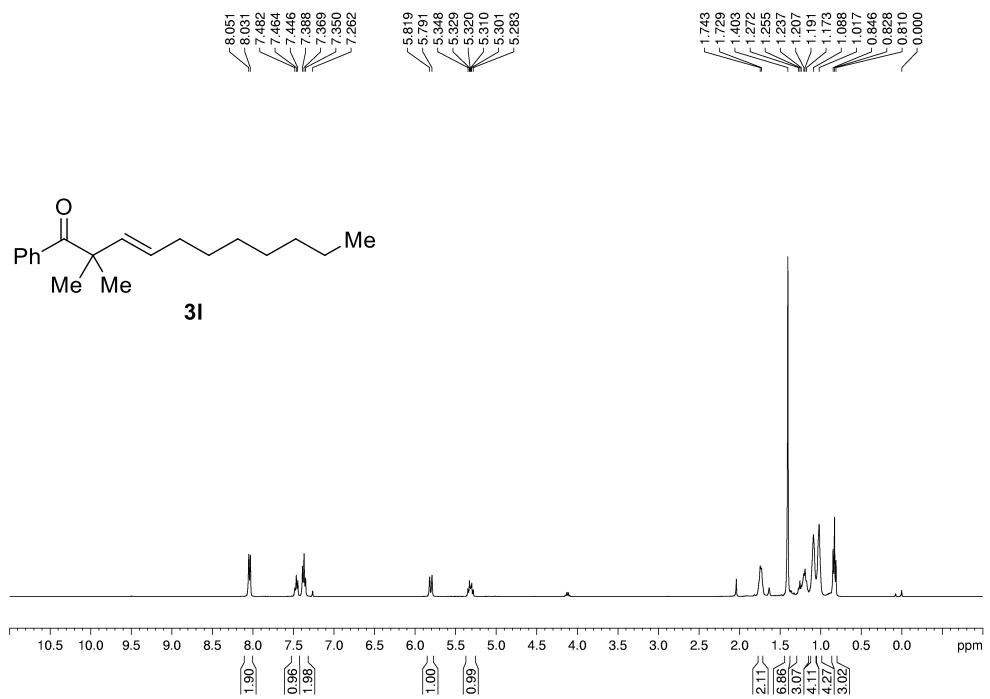


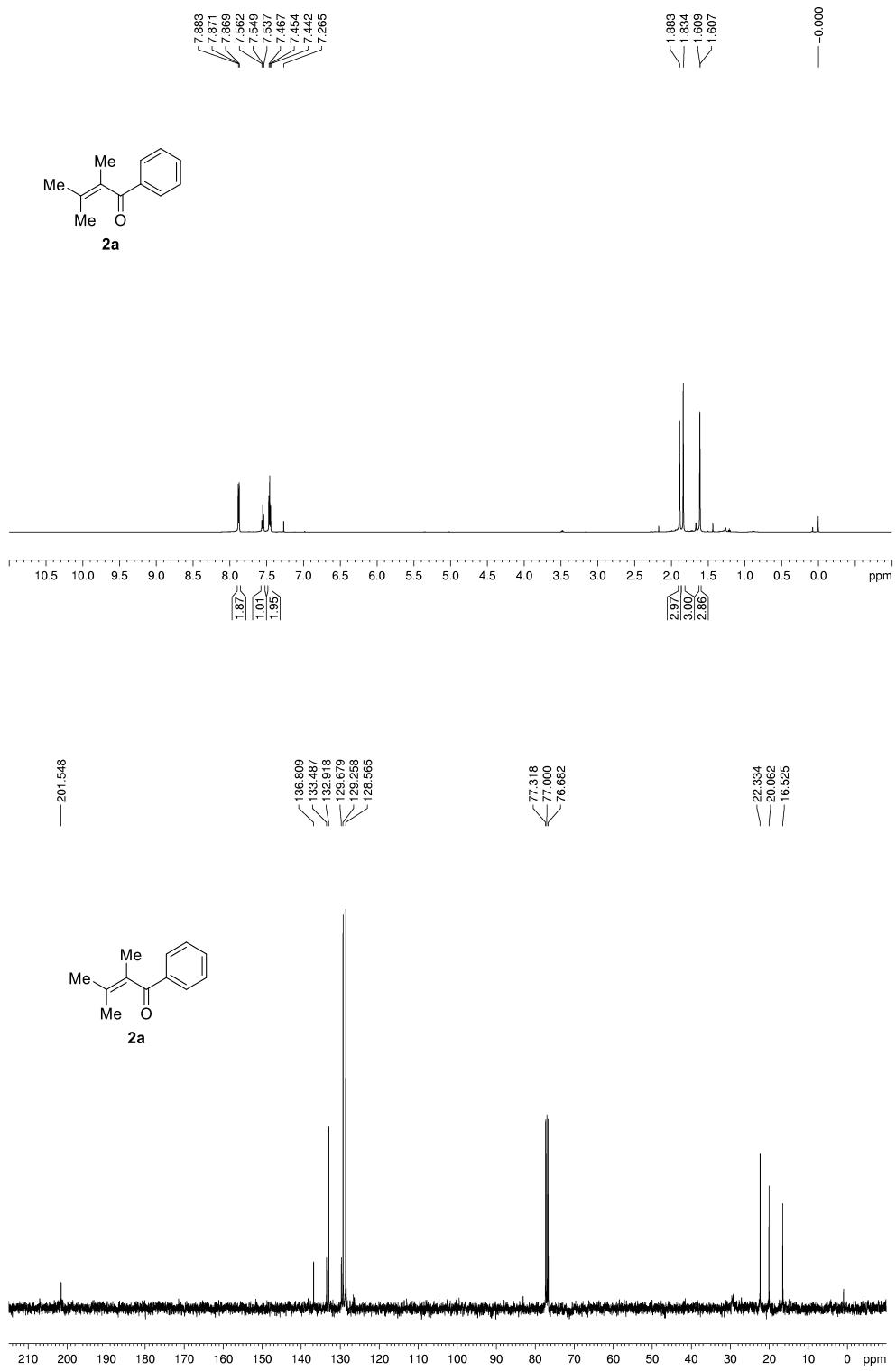


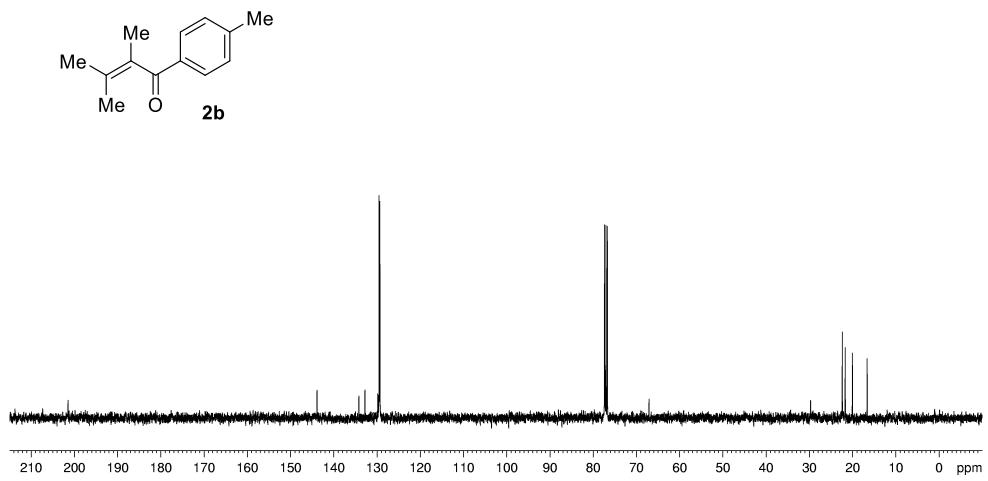
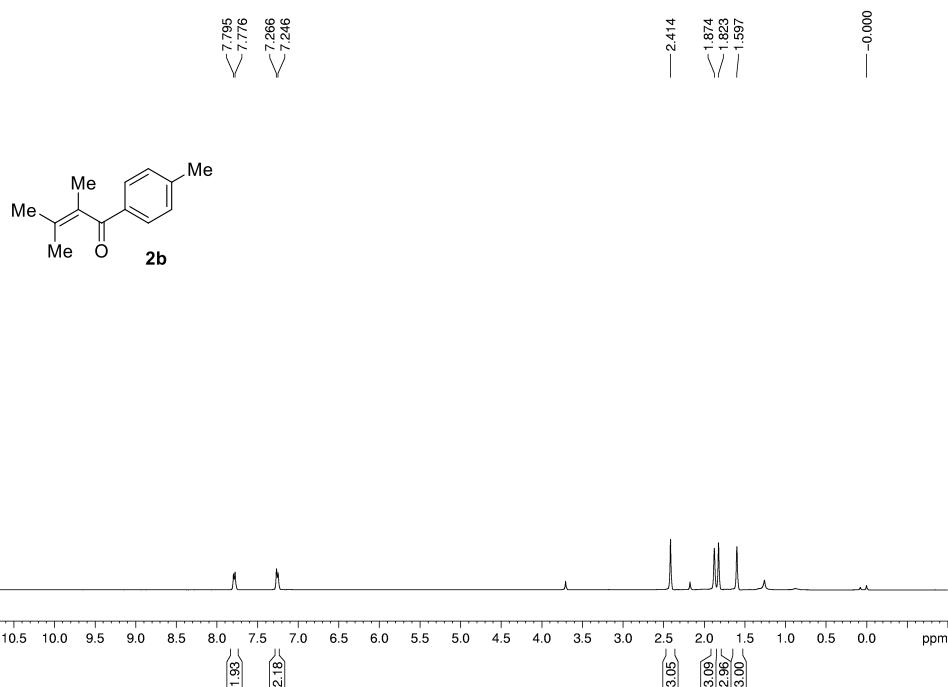


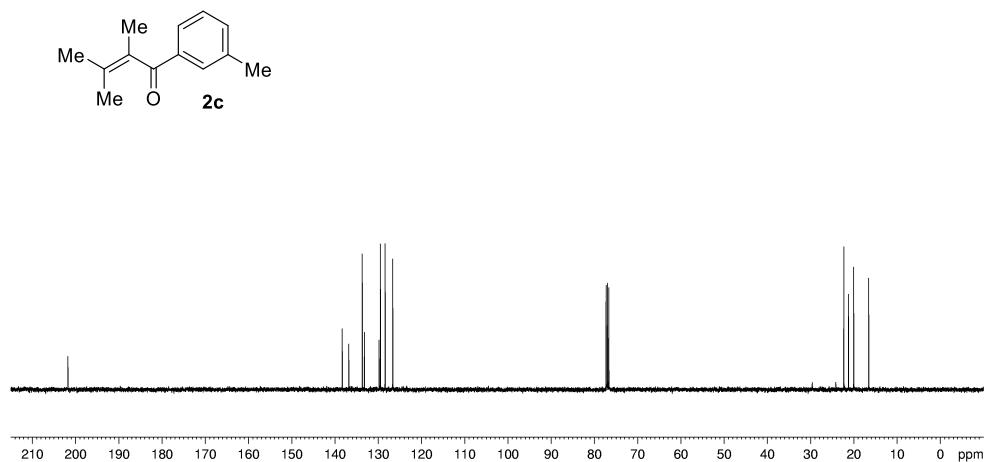
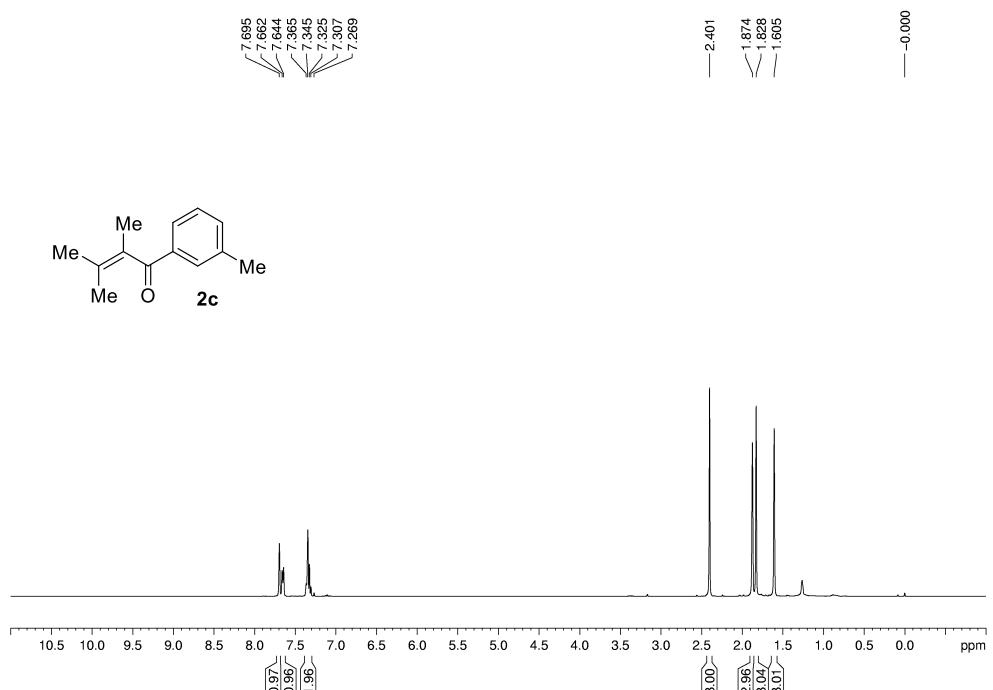


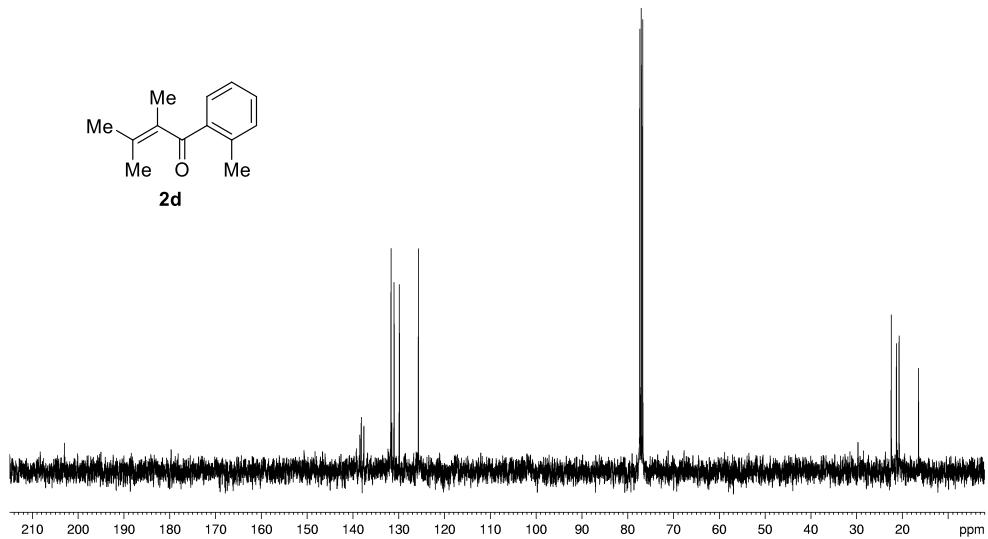
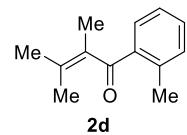
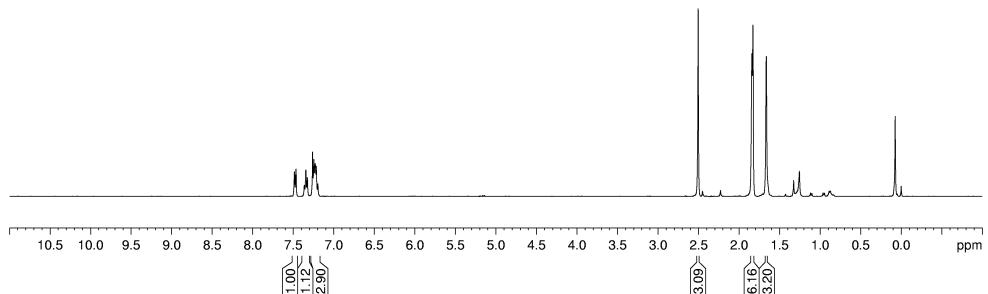
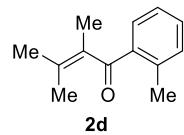


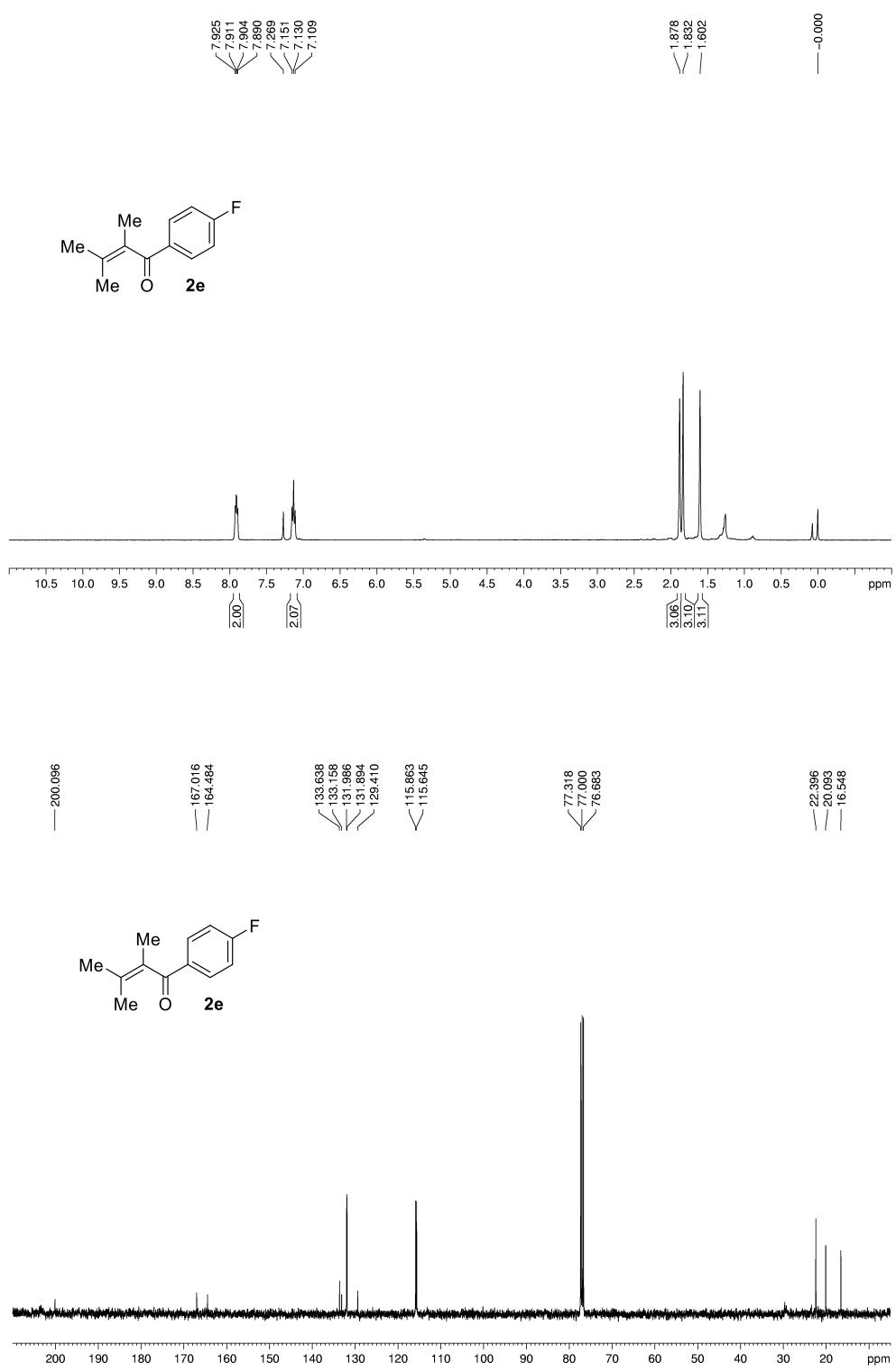


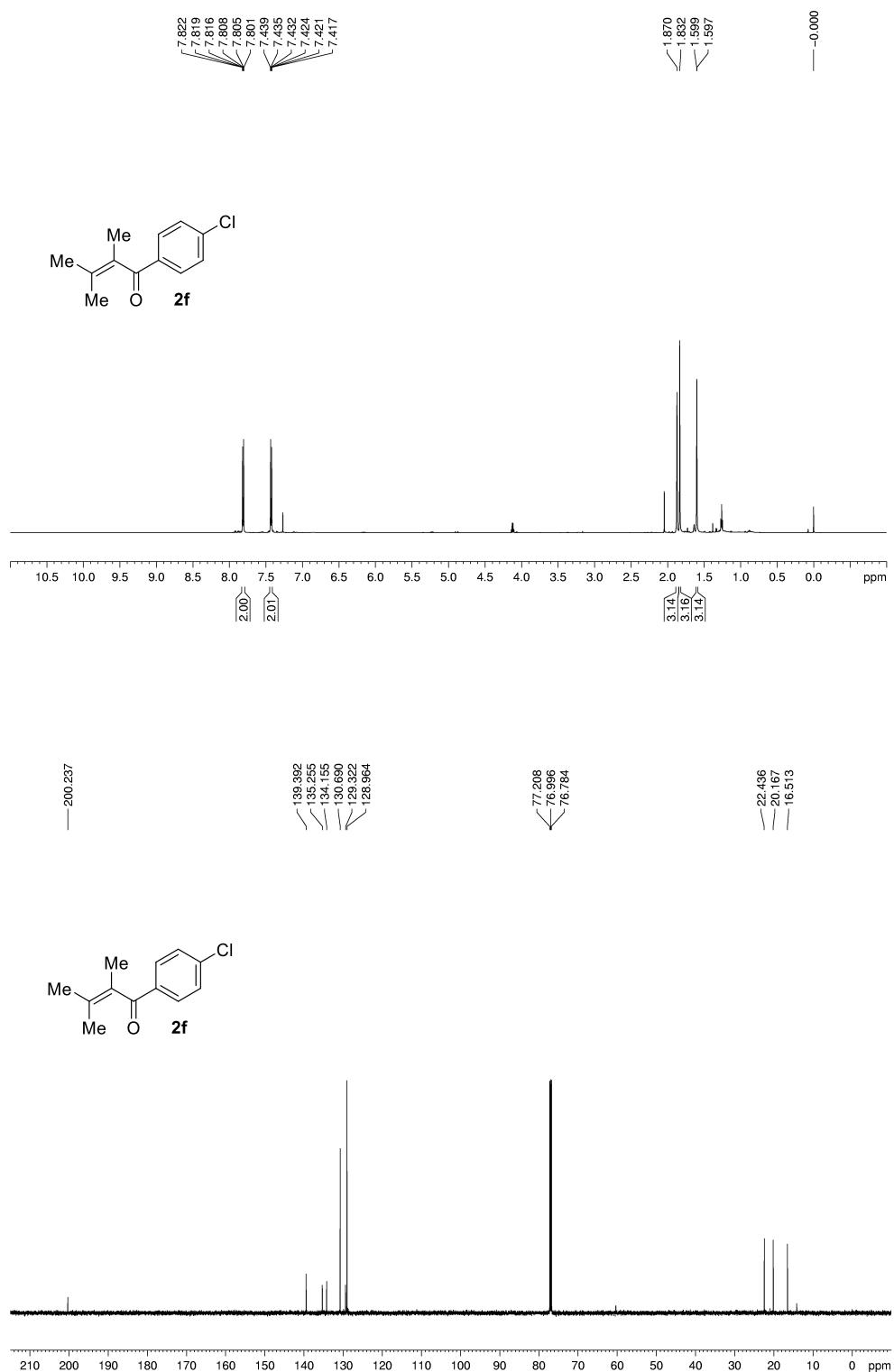


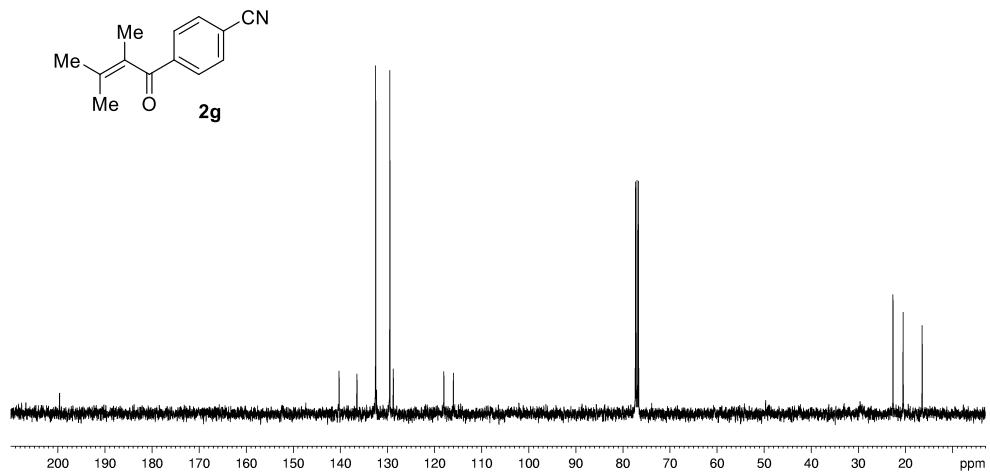
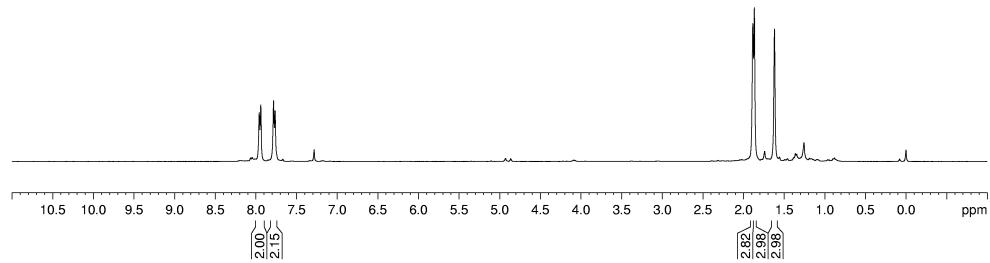
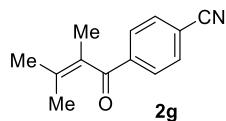


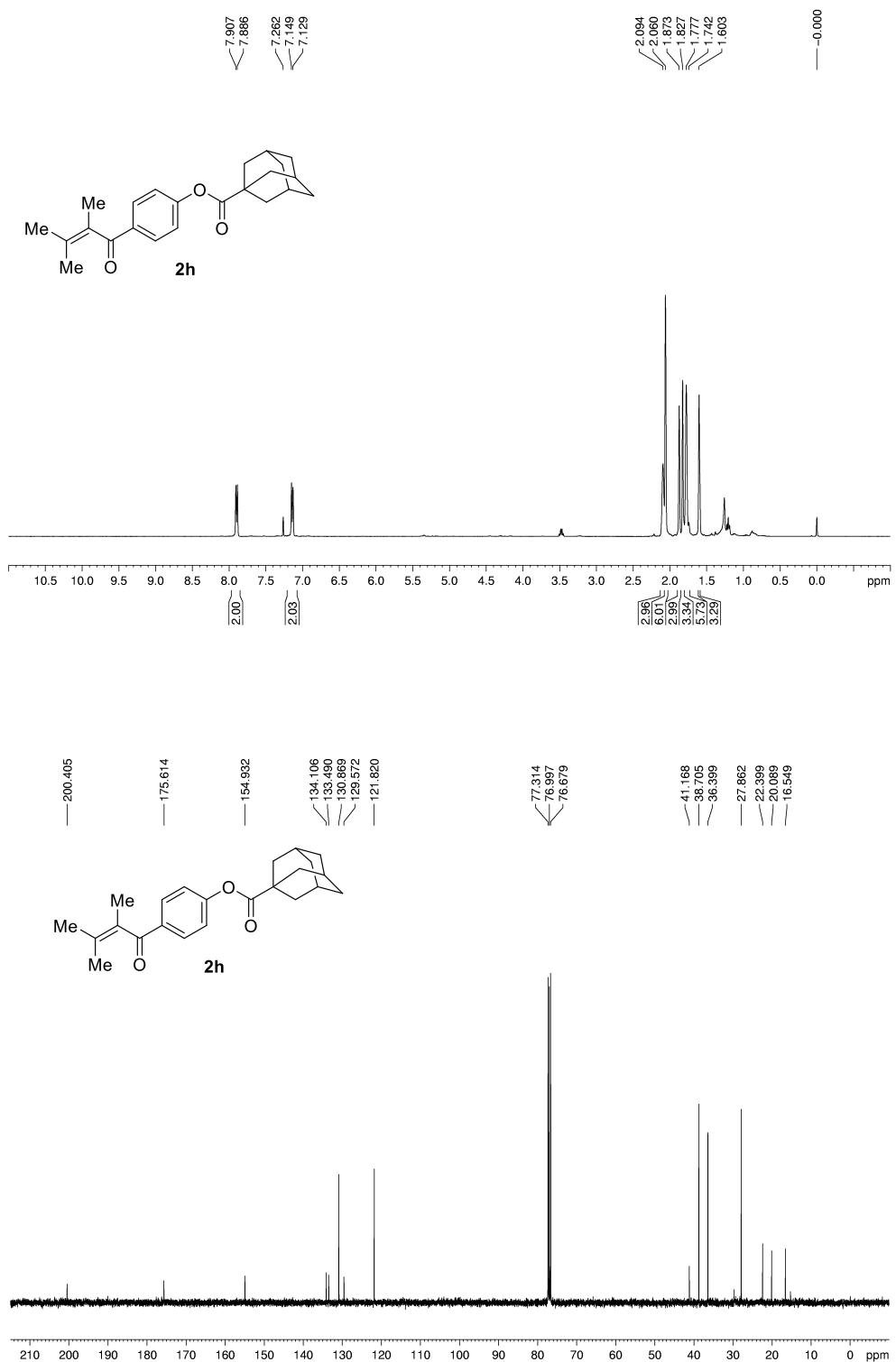


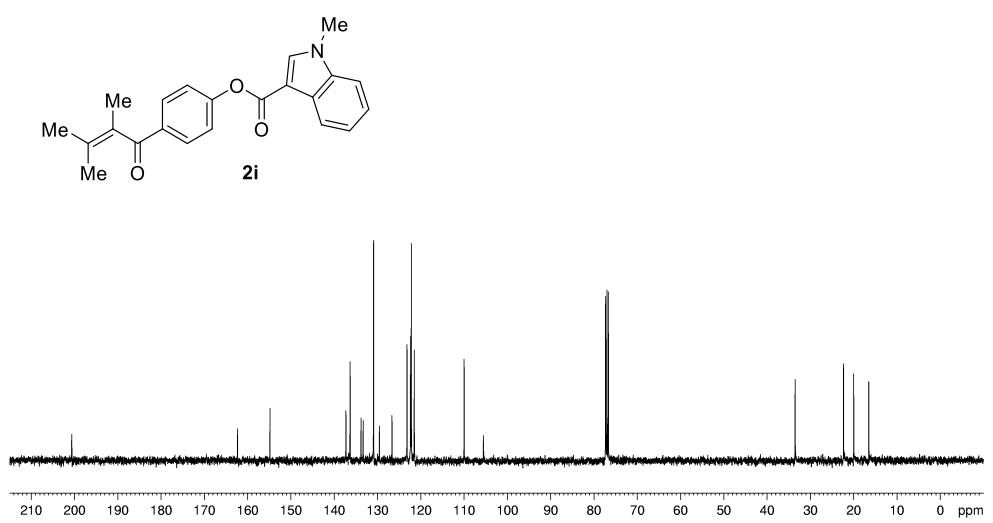
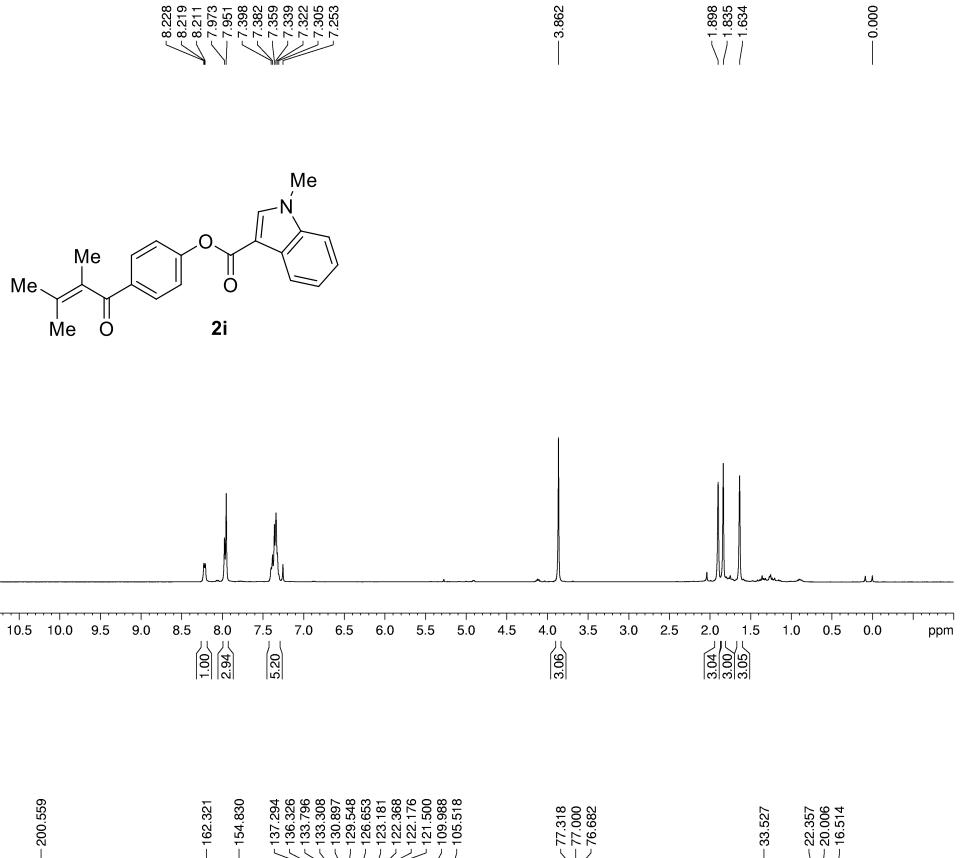


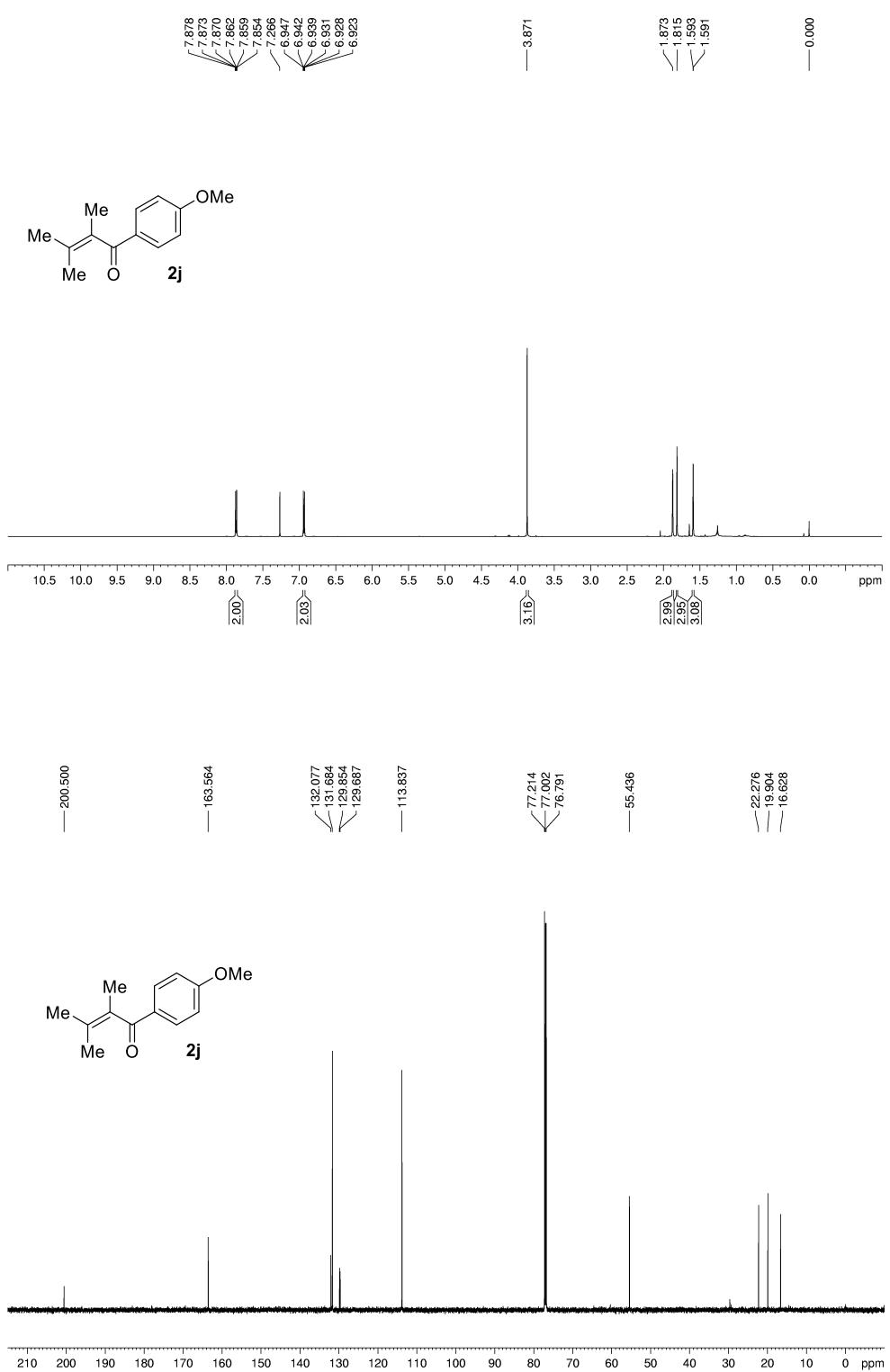


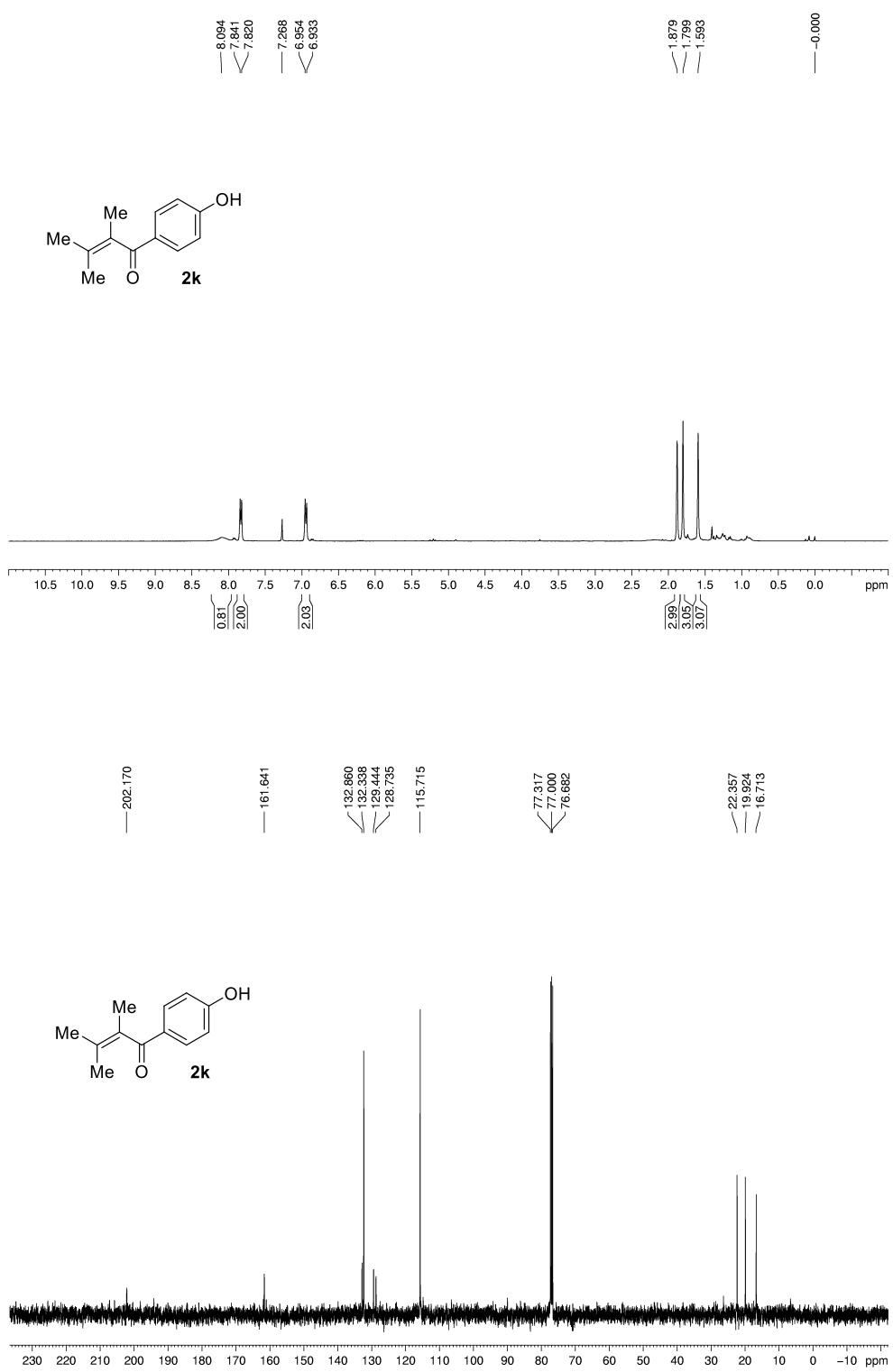


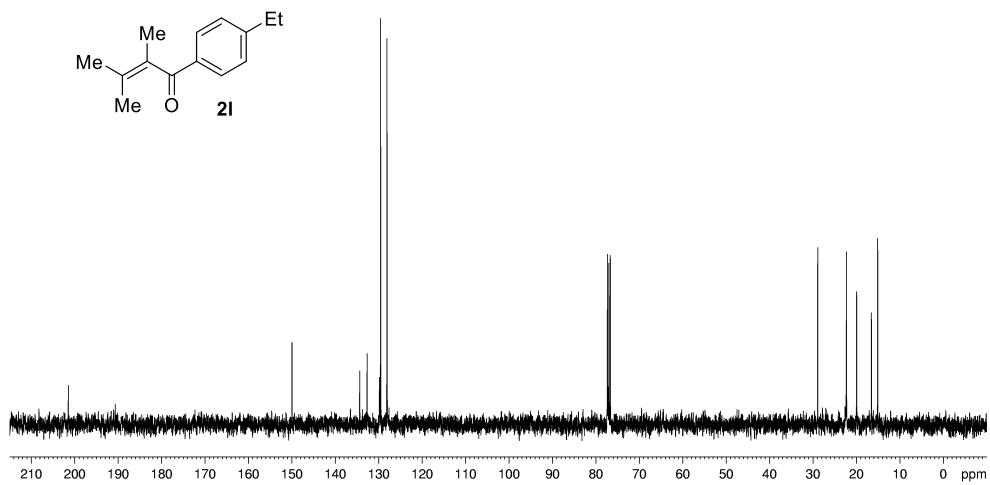
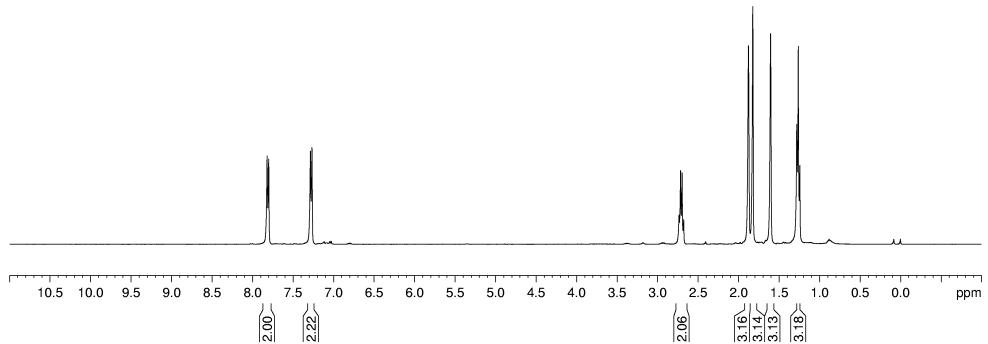
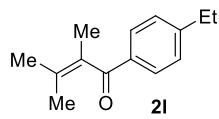


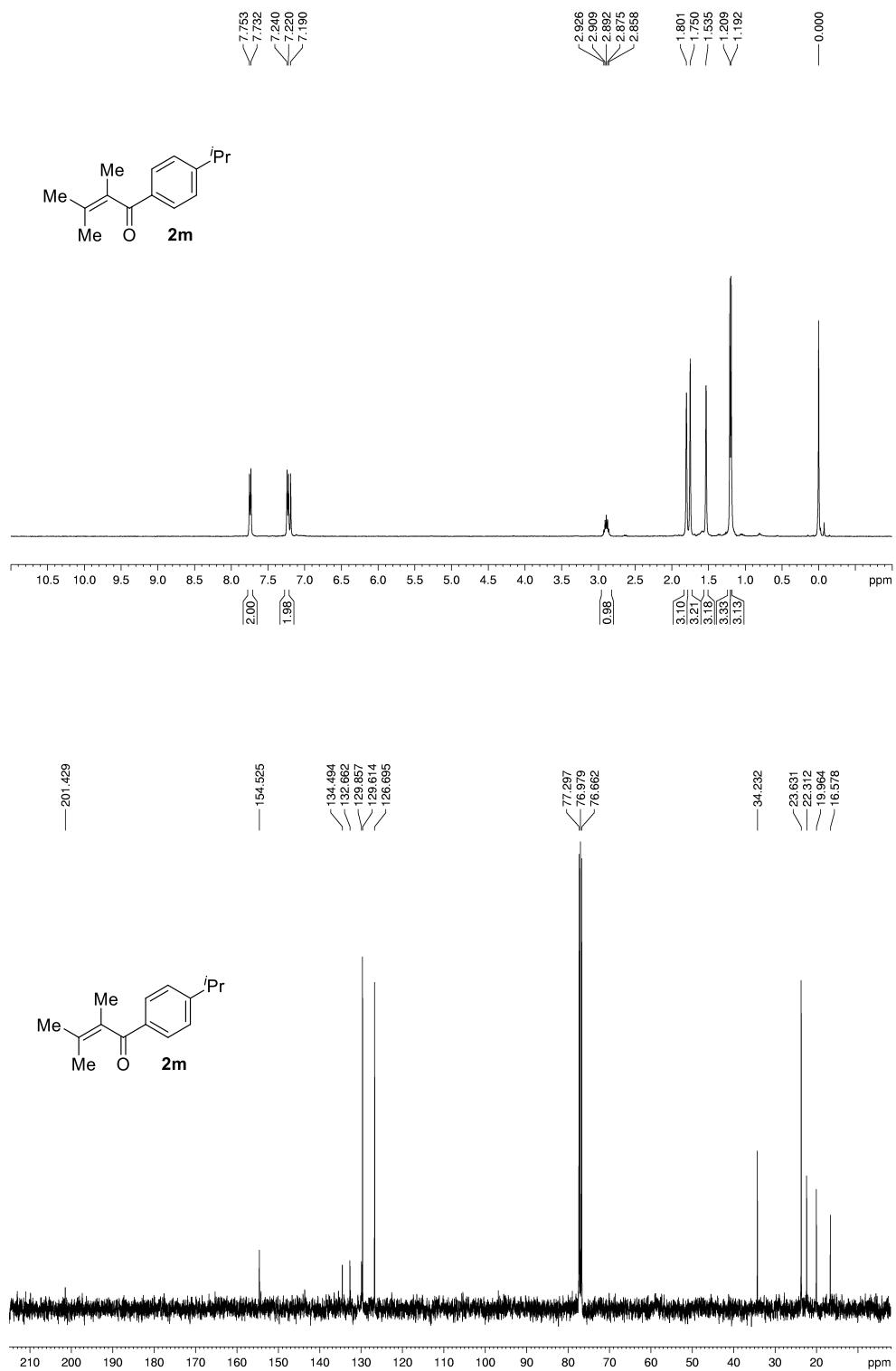


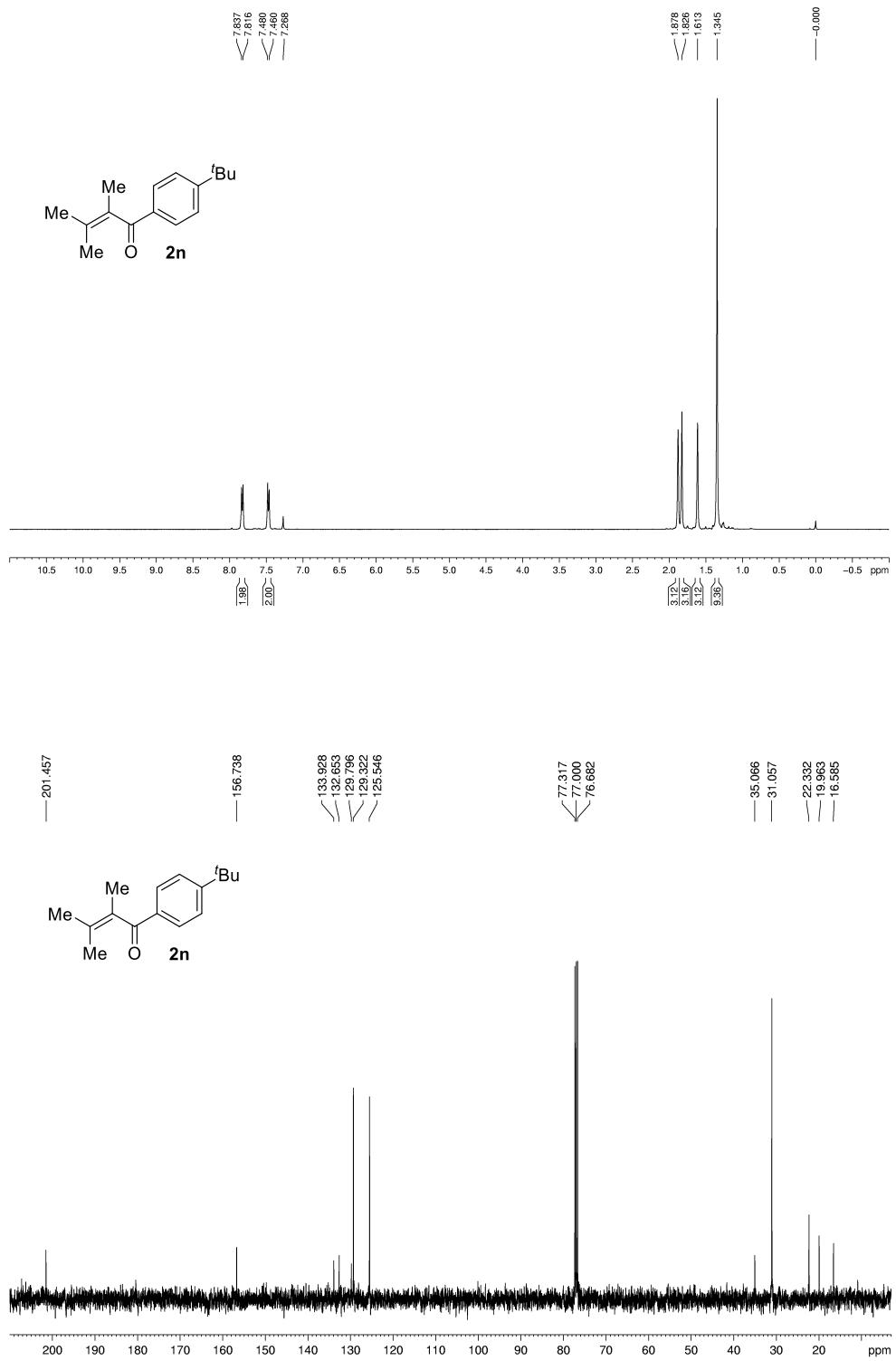


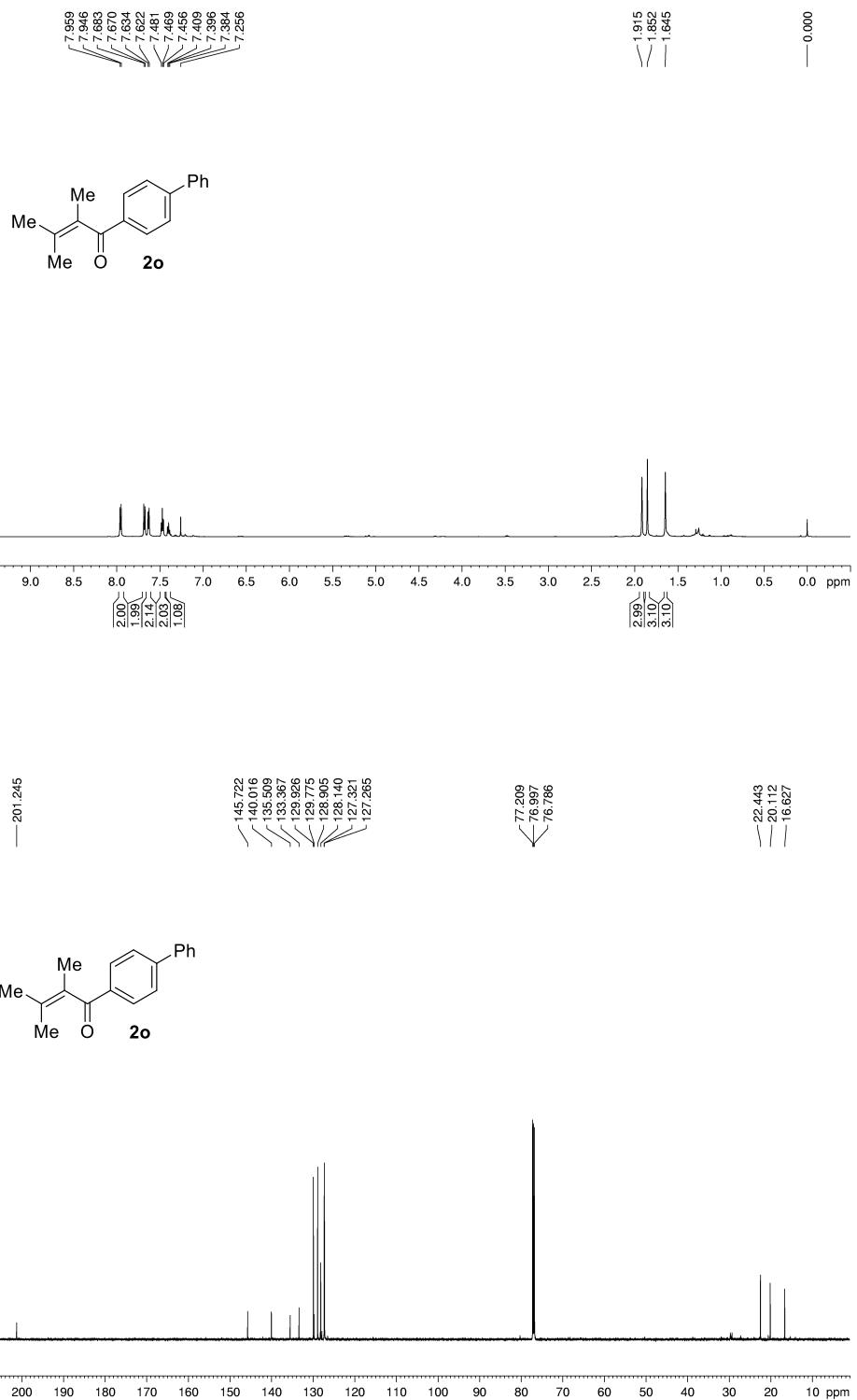


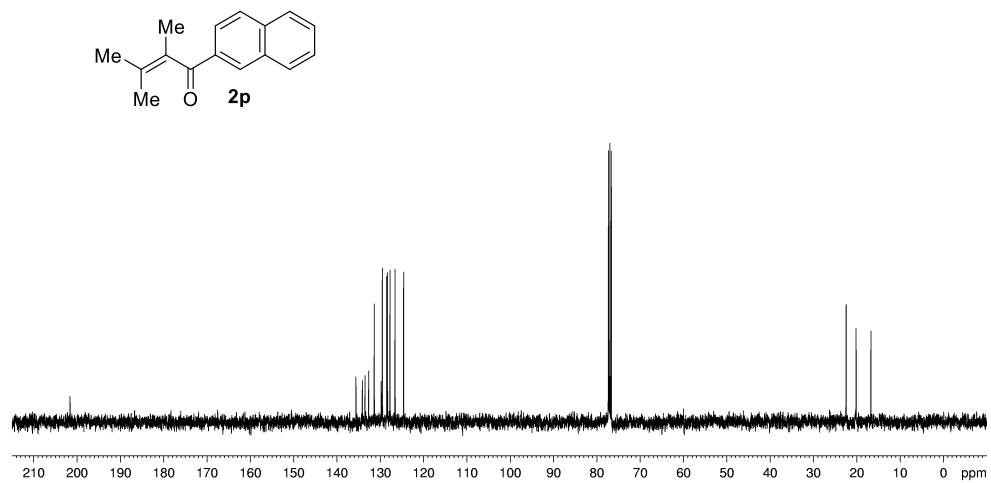
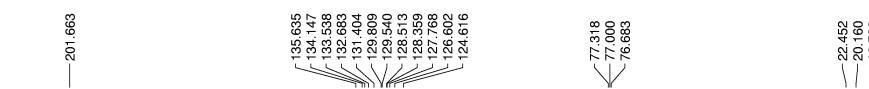
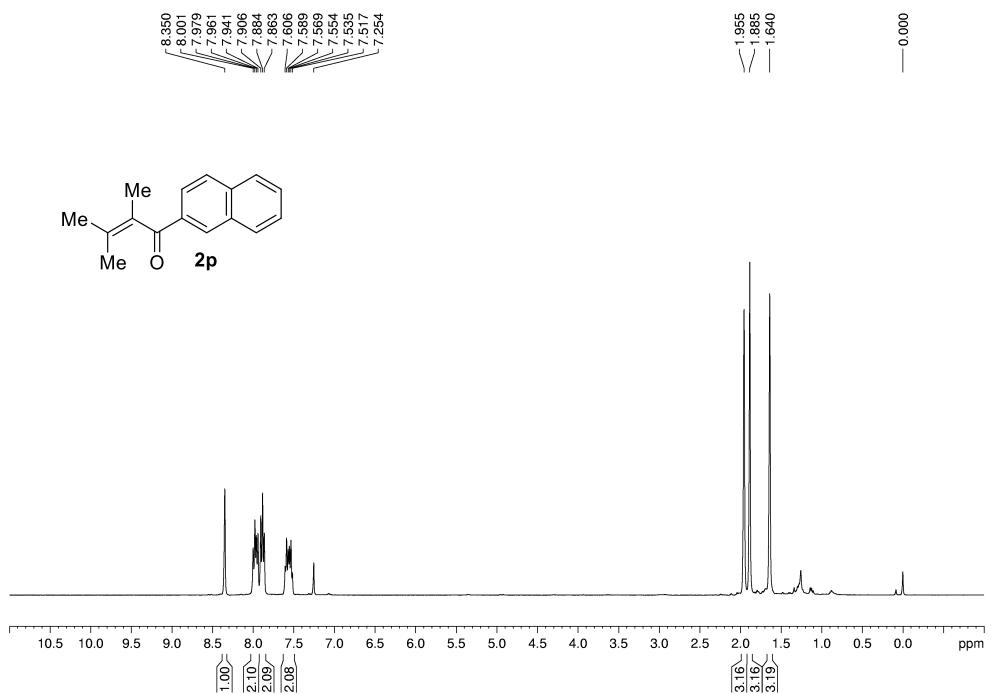


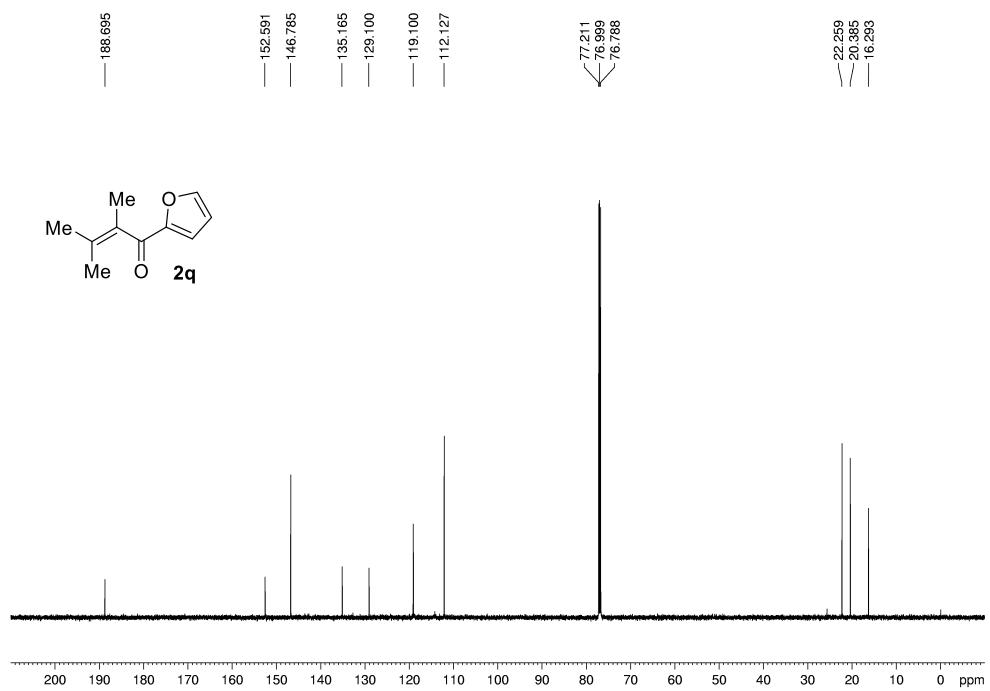
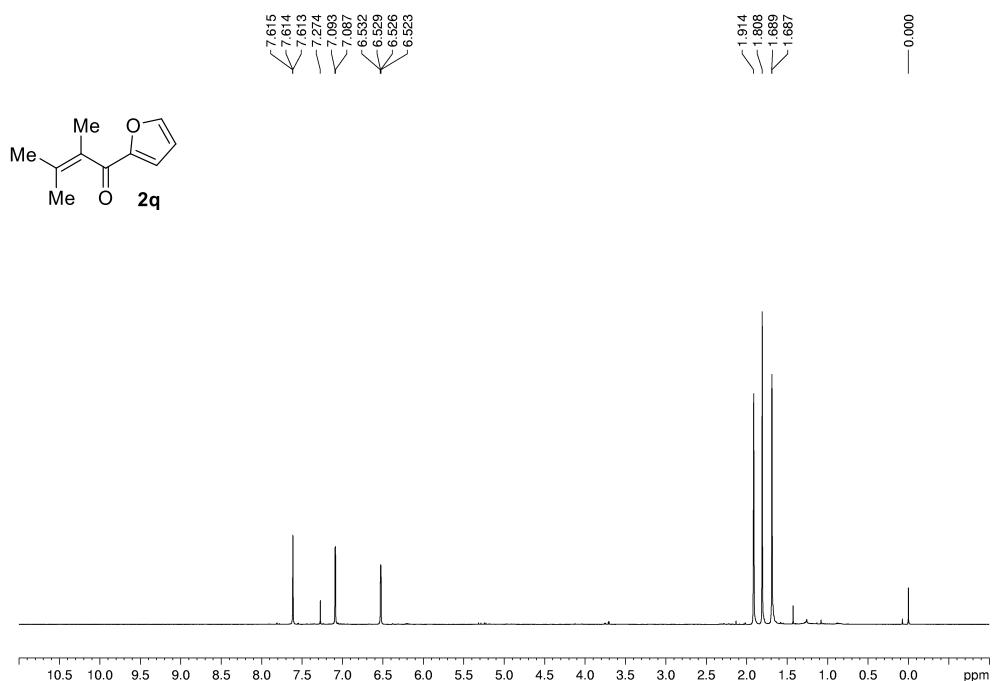






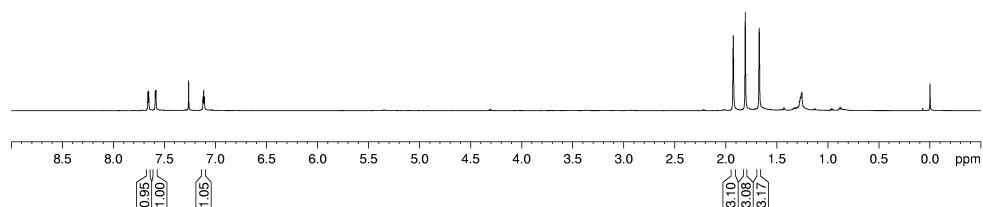
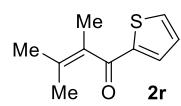






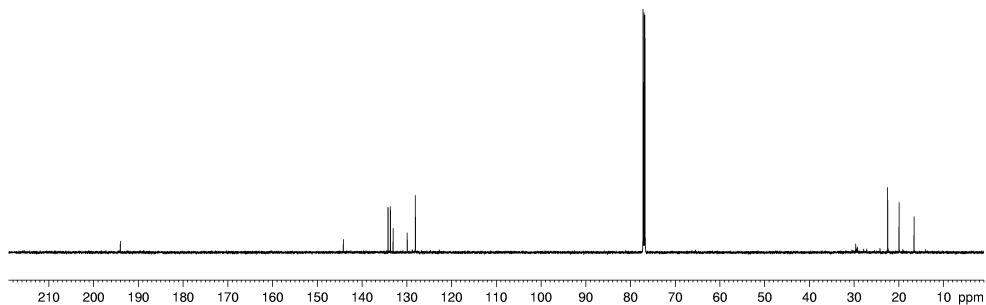
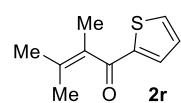
7.663  
7.655  
7.590  
7.584  
7.284  
7.124  
7.116  
7.110

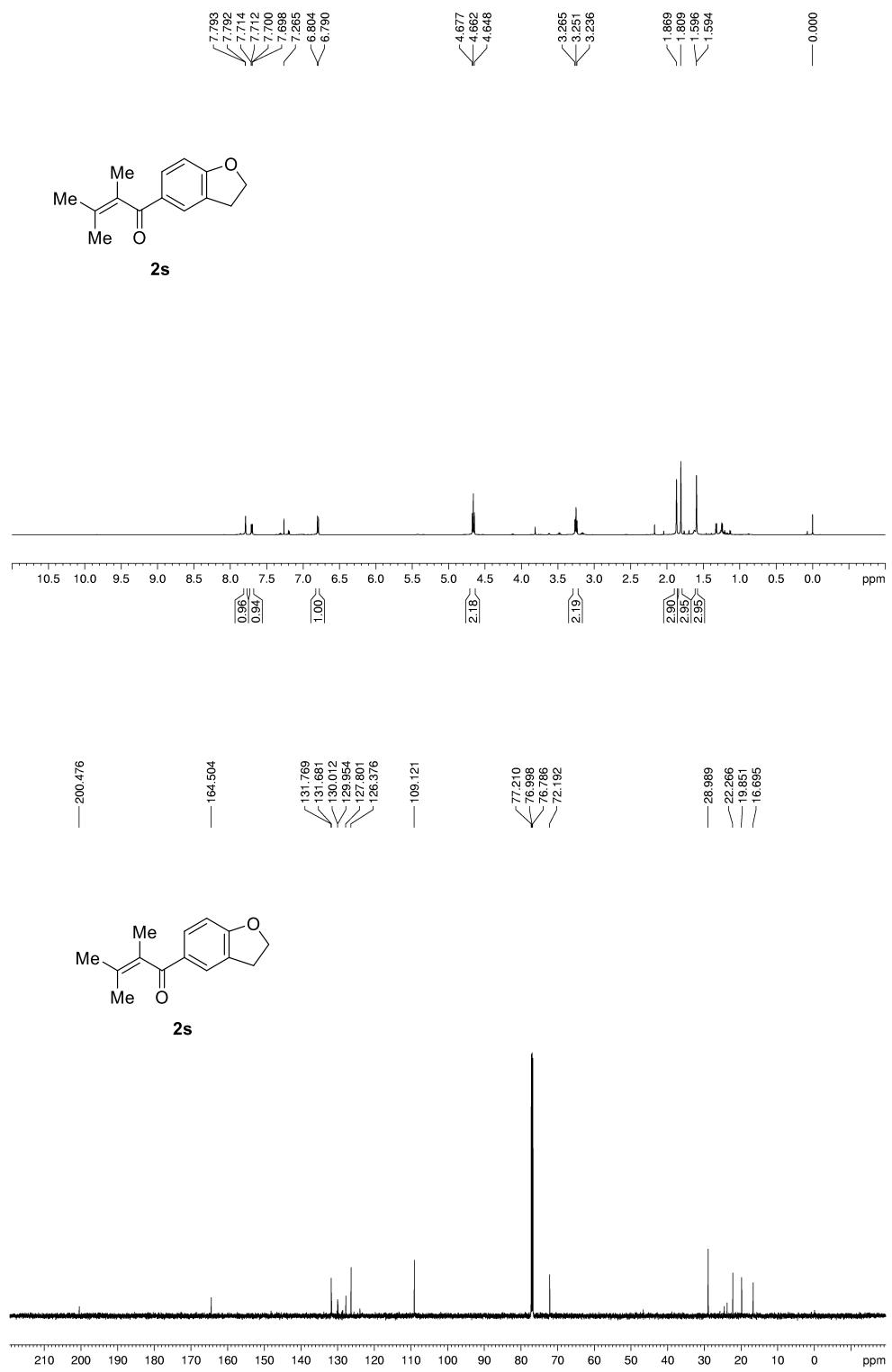
— 1.928  
— 1.810  
— 1.673  
— -0.000

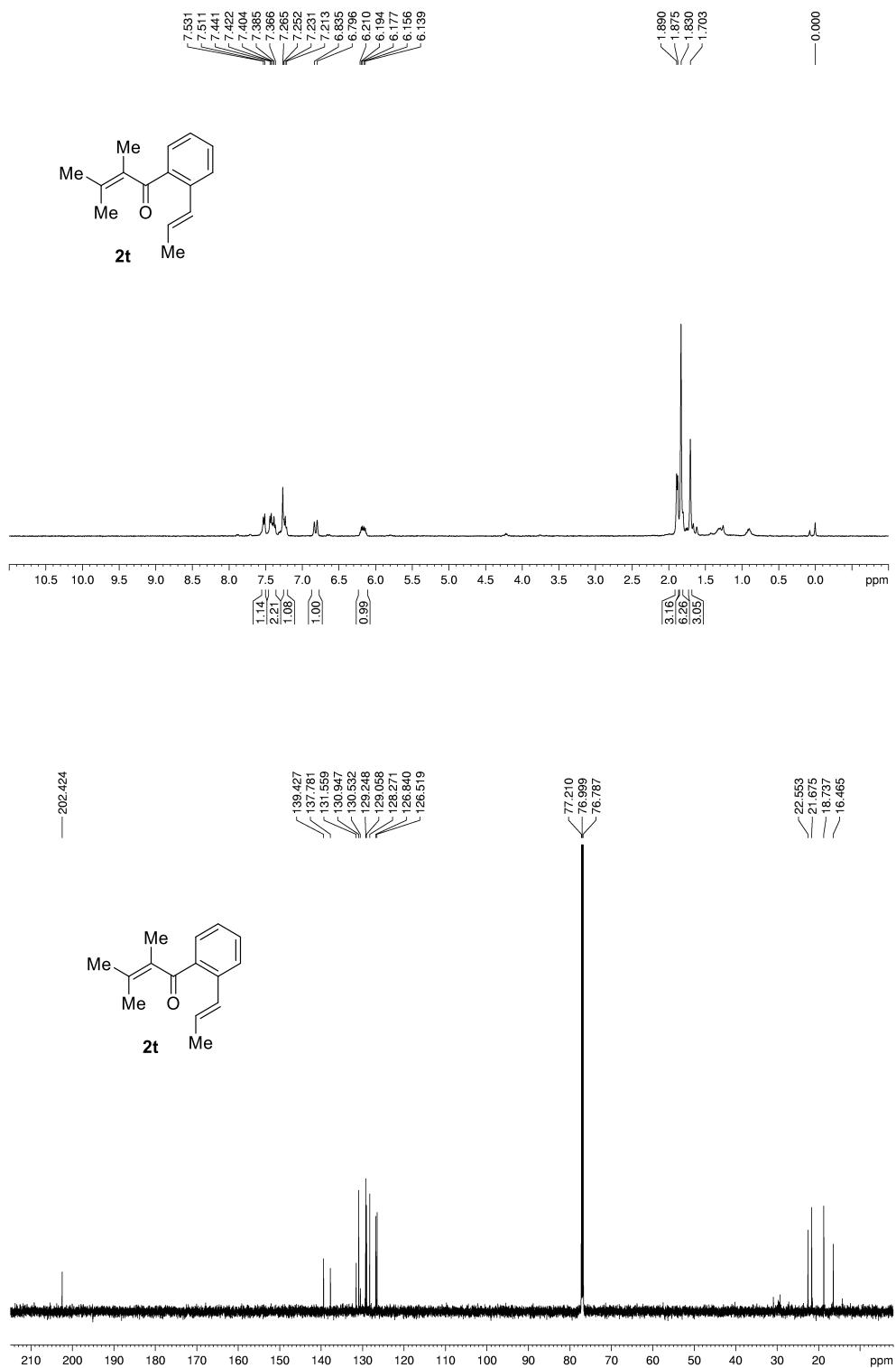


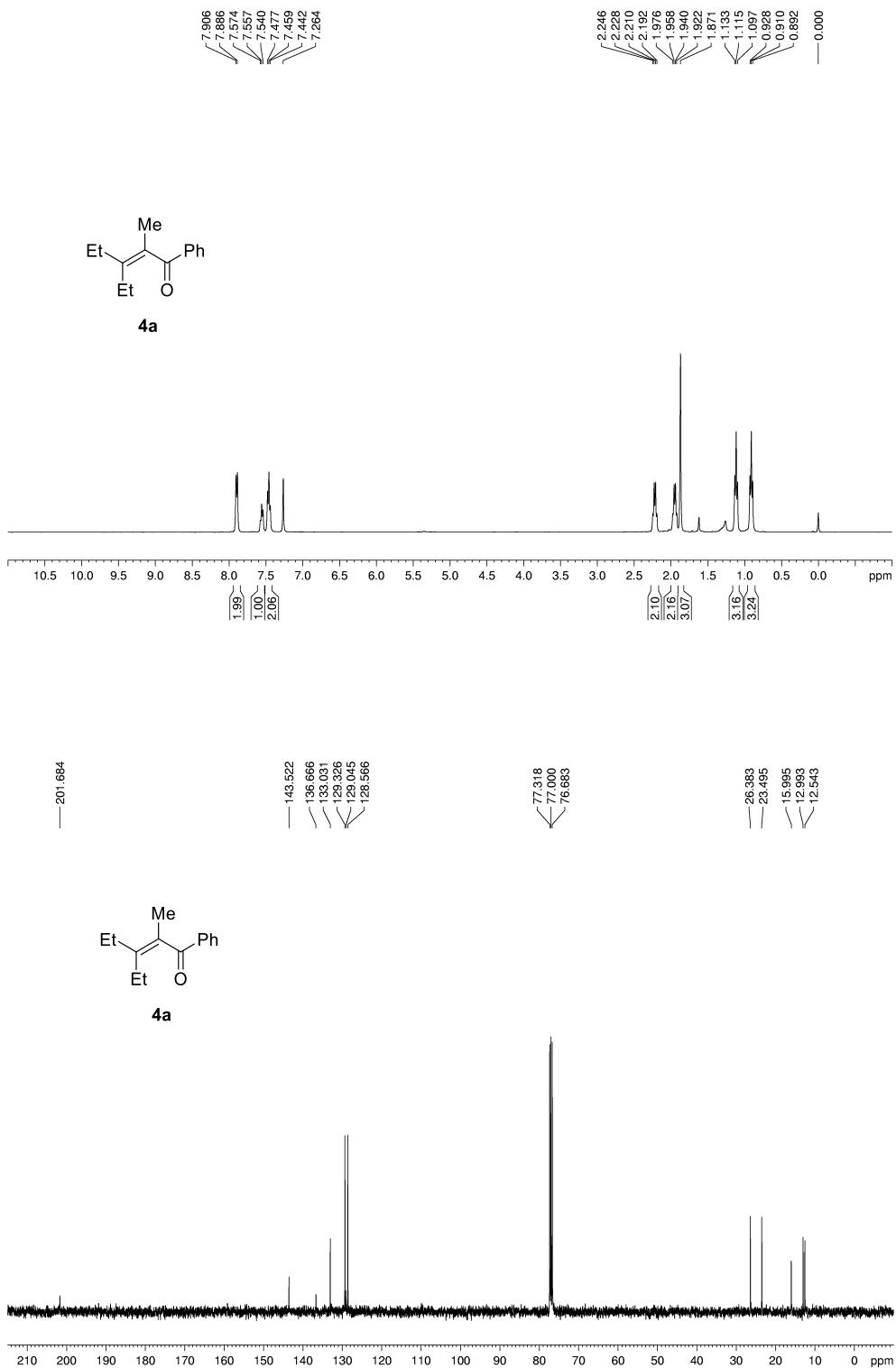
— 133.991  
— 144.207  
— 134.210  
— 133.687  
— 133.069  
— 129.940  
— 129.116

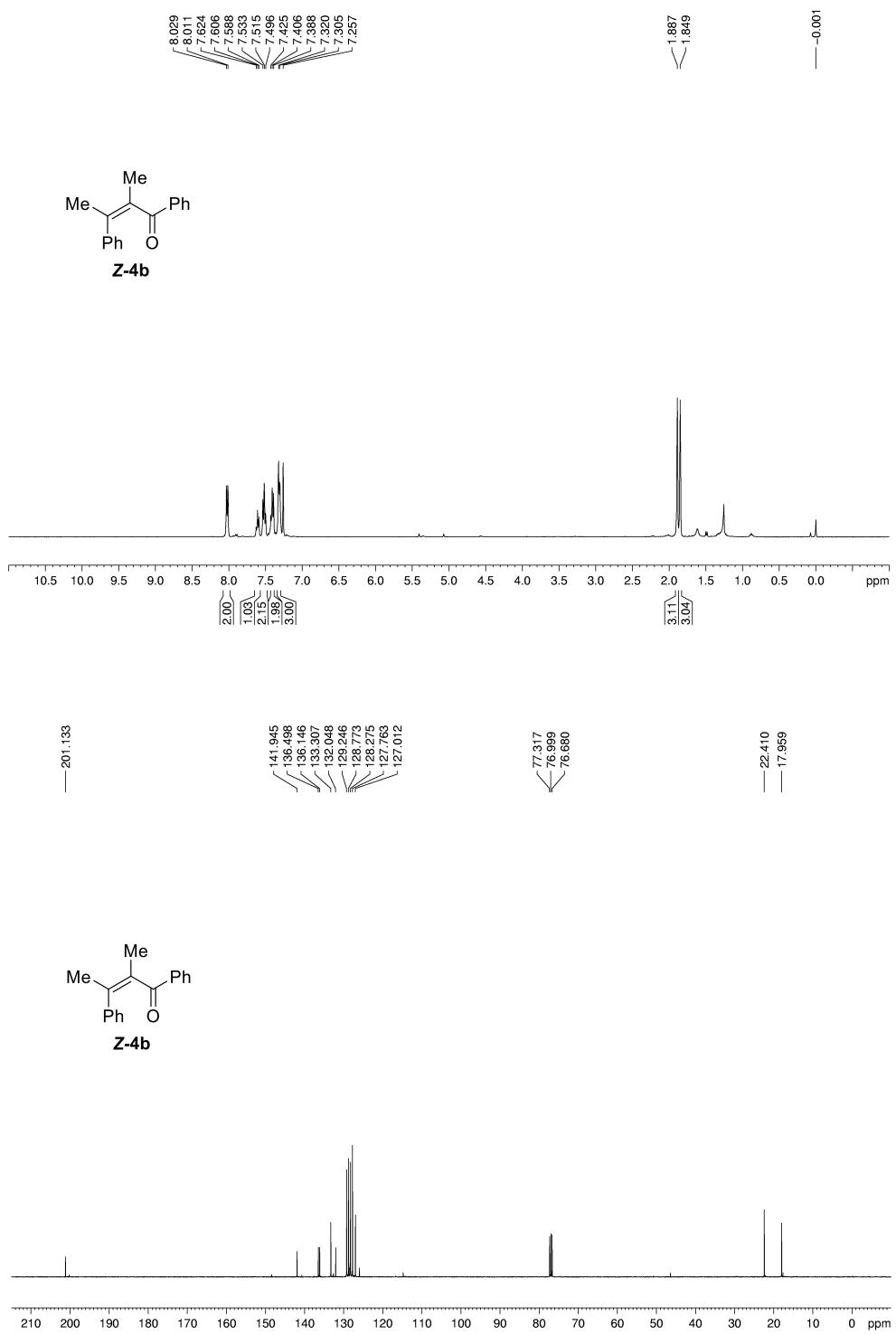
— 22.535  
— 19.991  
— 16.632

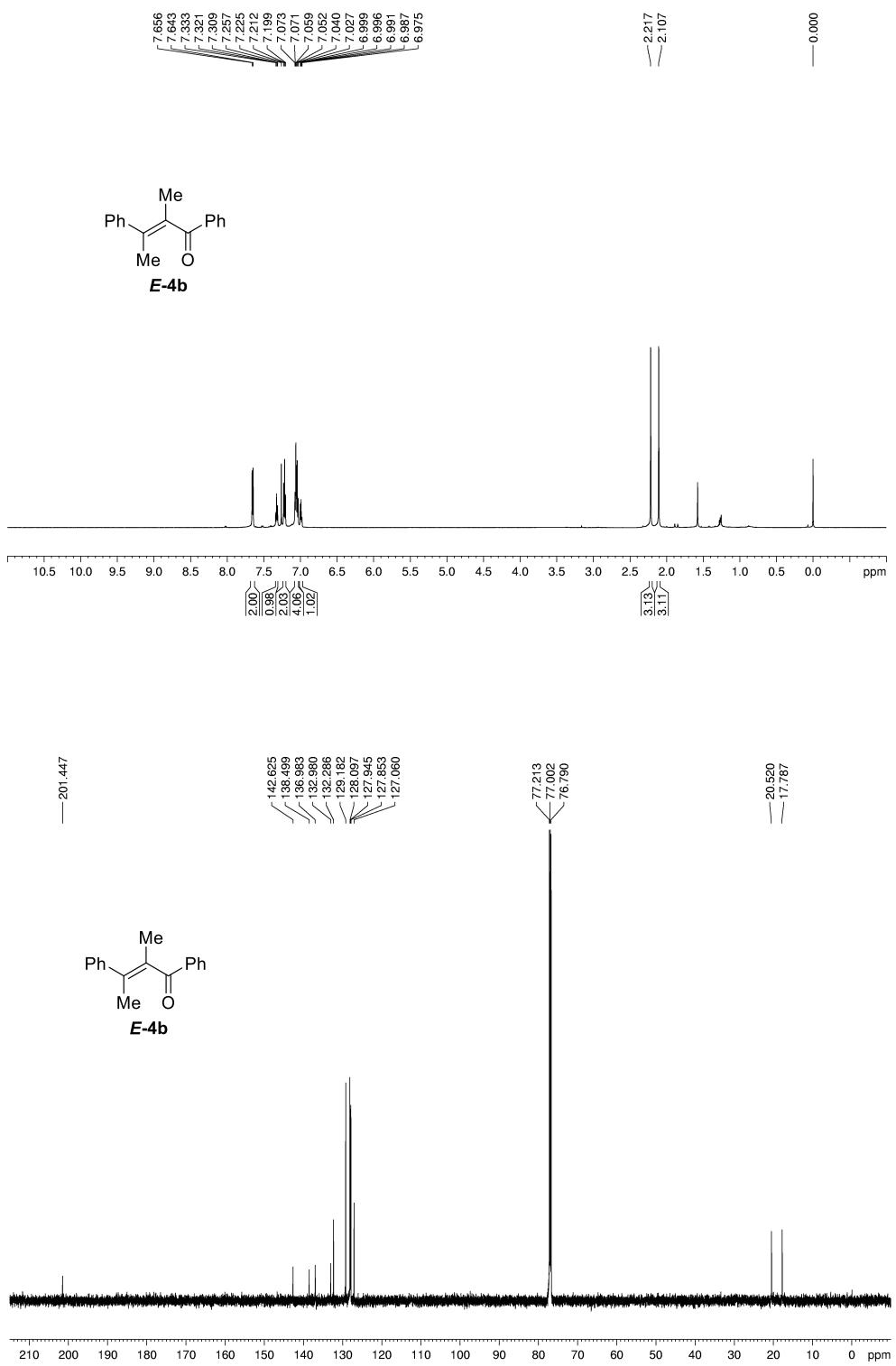


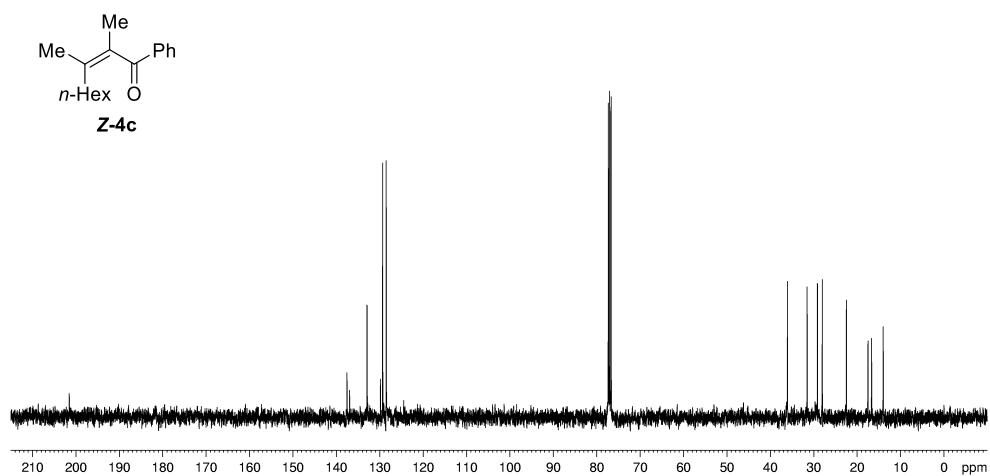
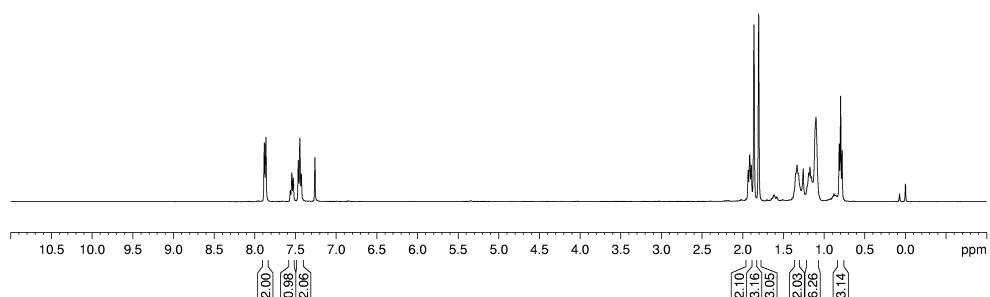


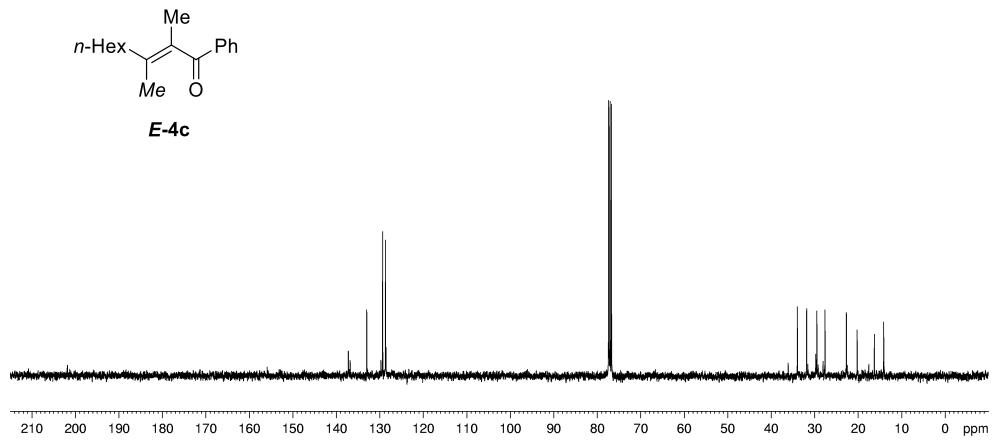
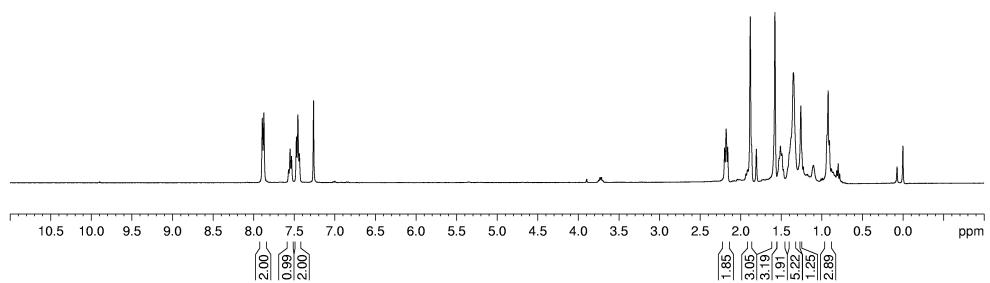
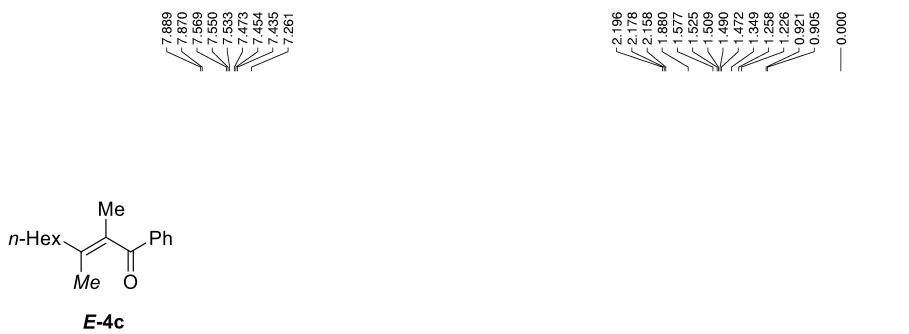


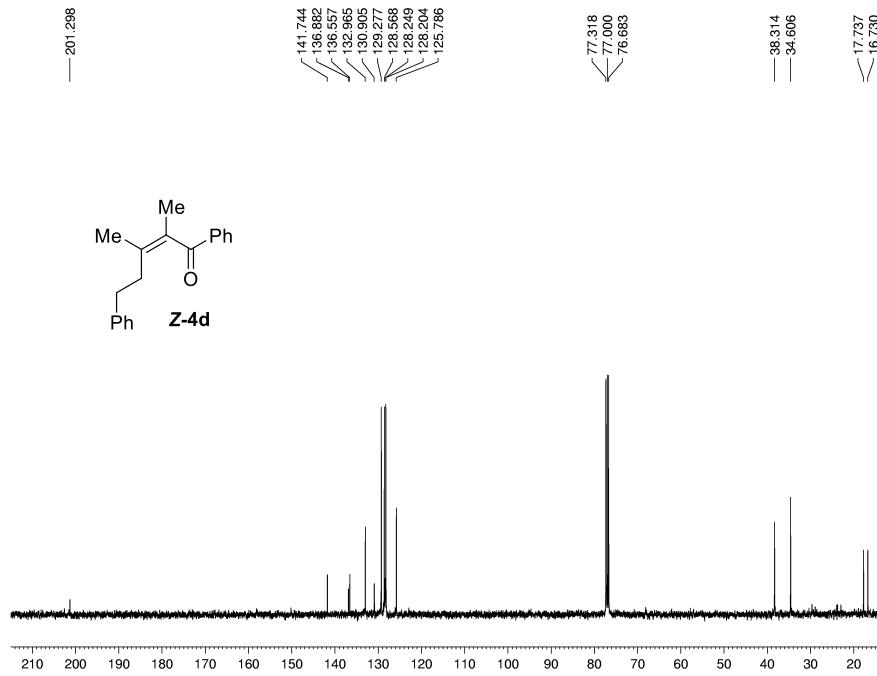
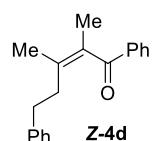
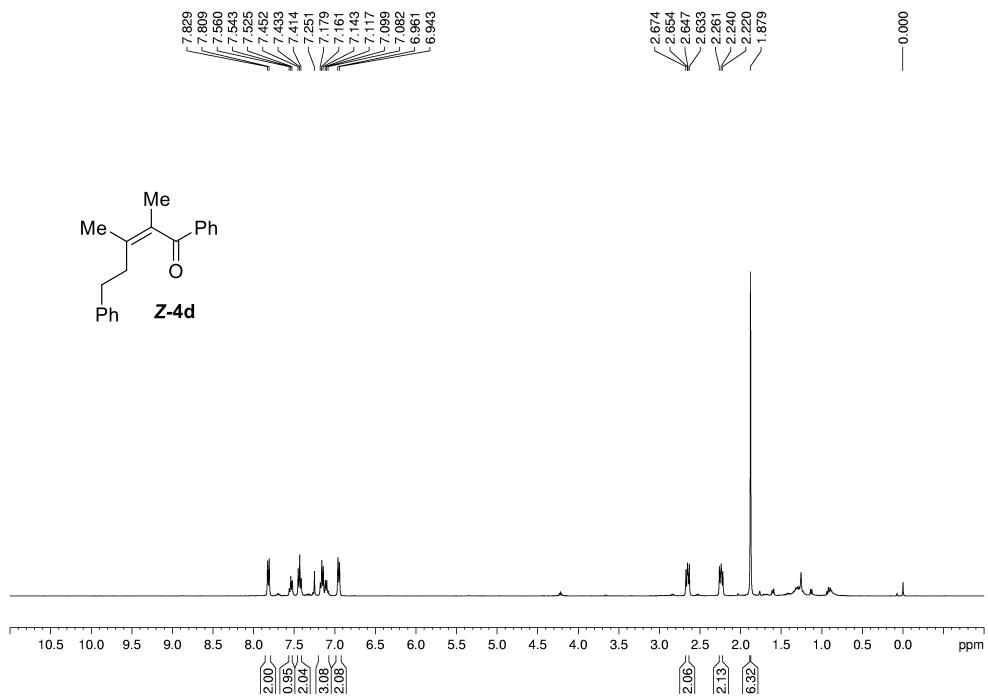
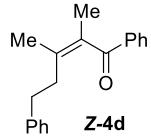


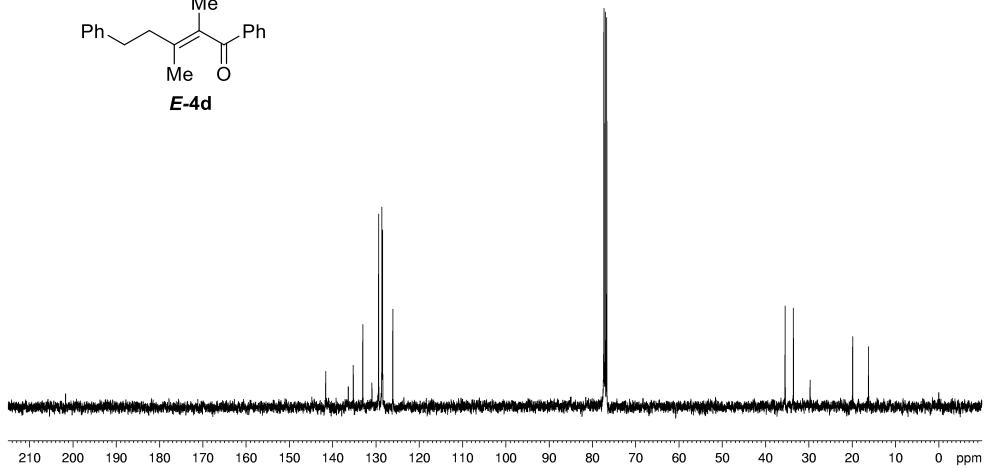
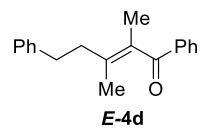
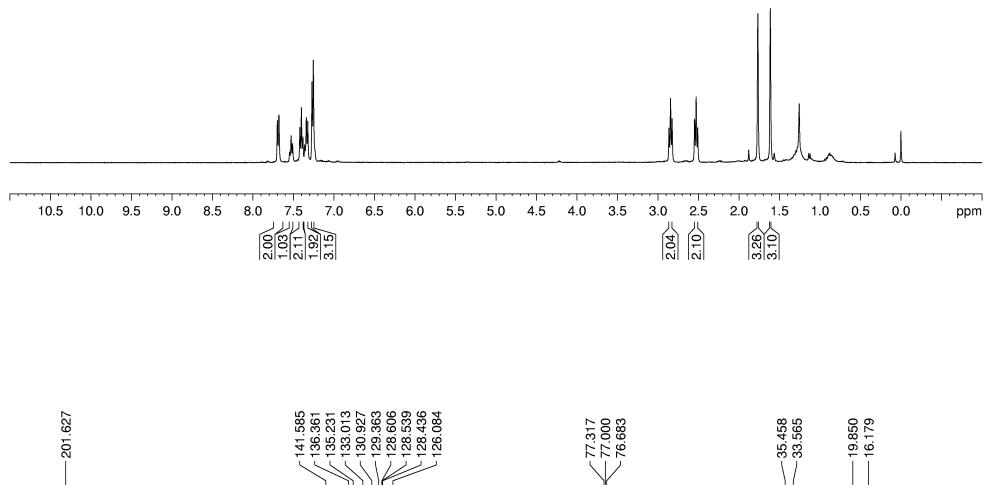
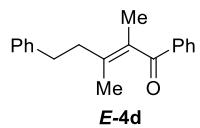


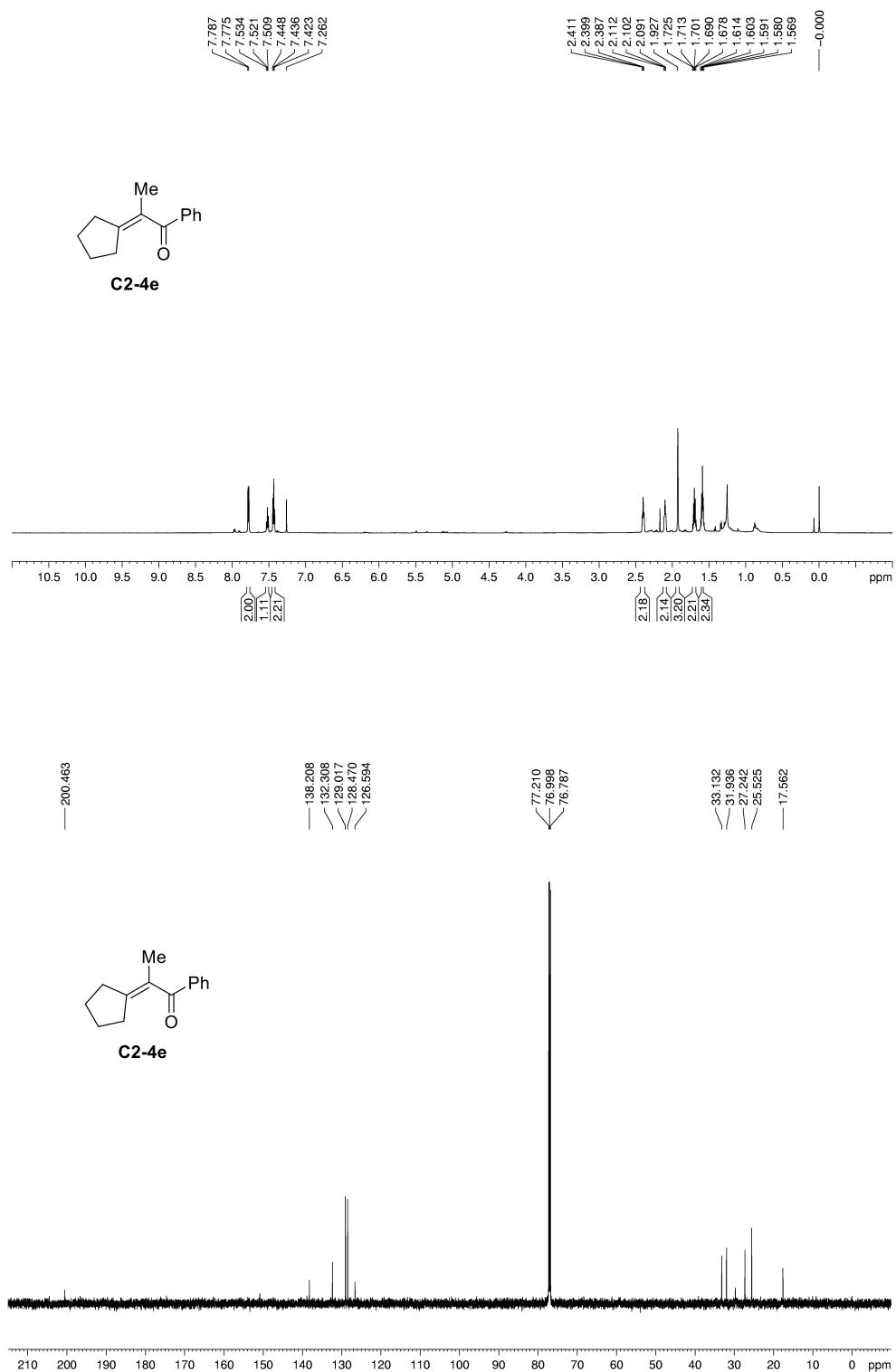


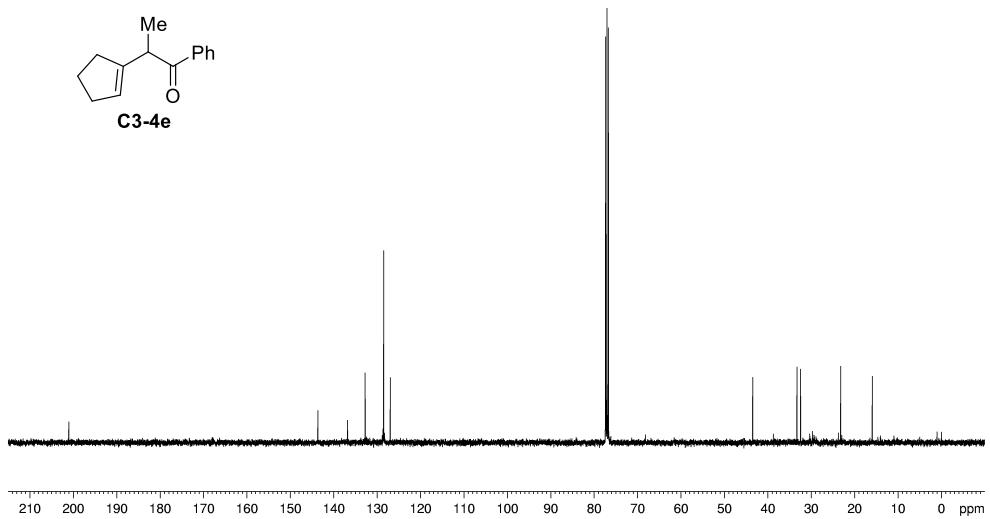
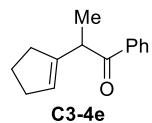
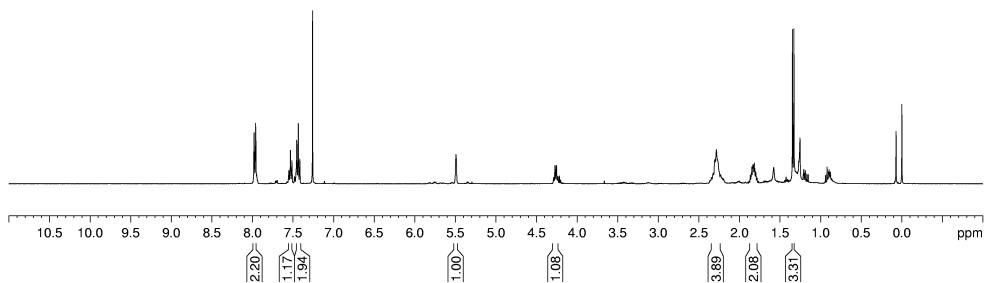
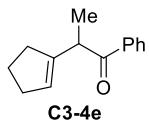
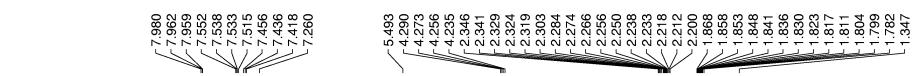


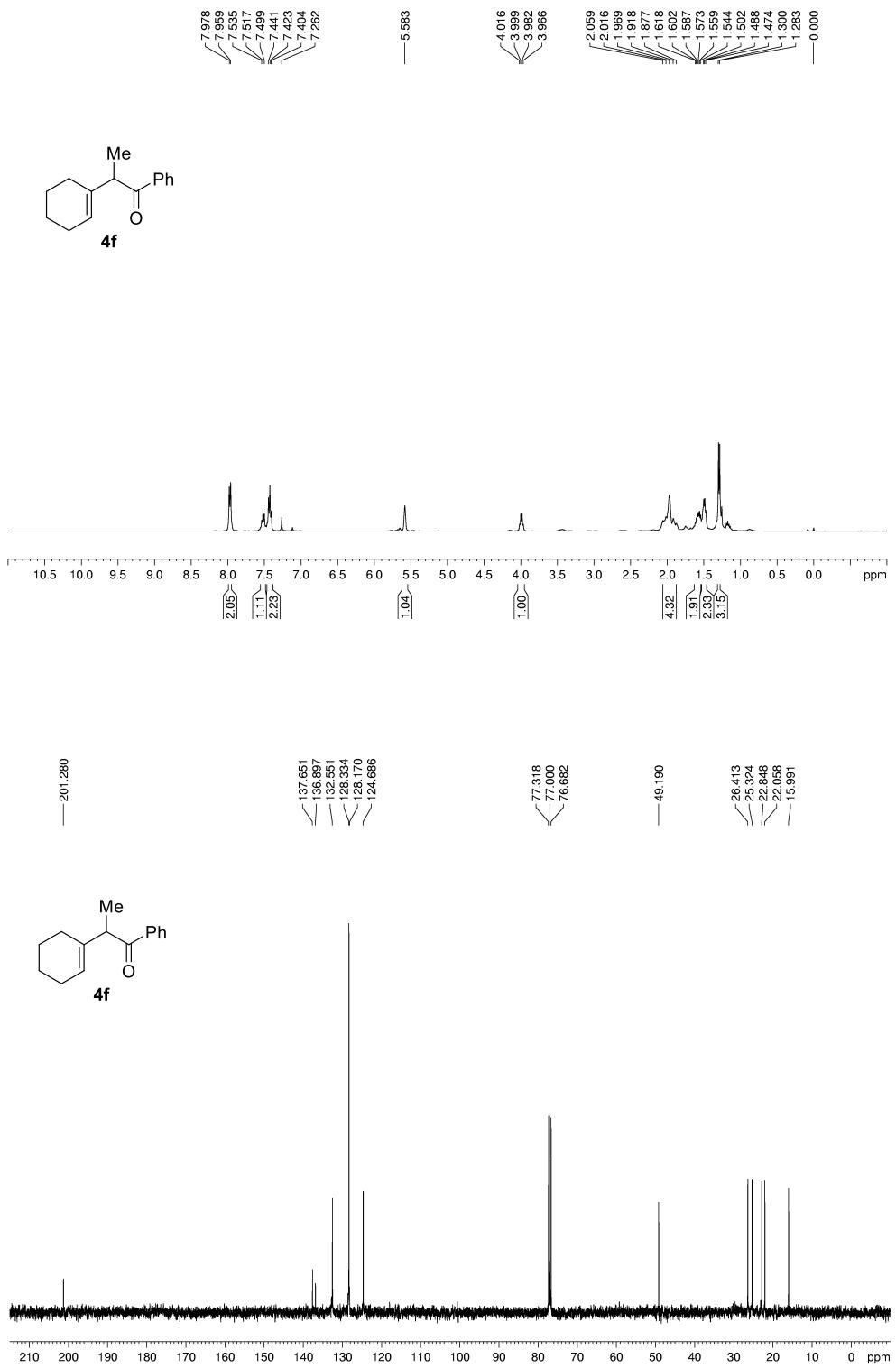


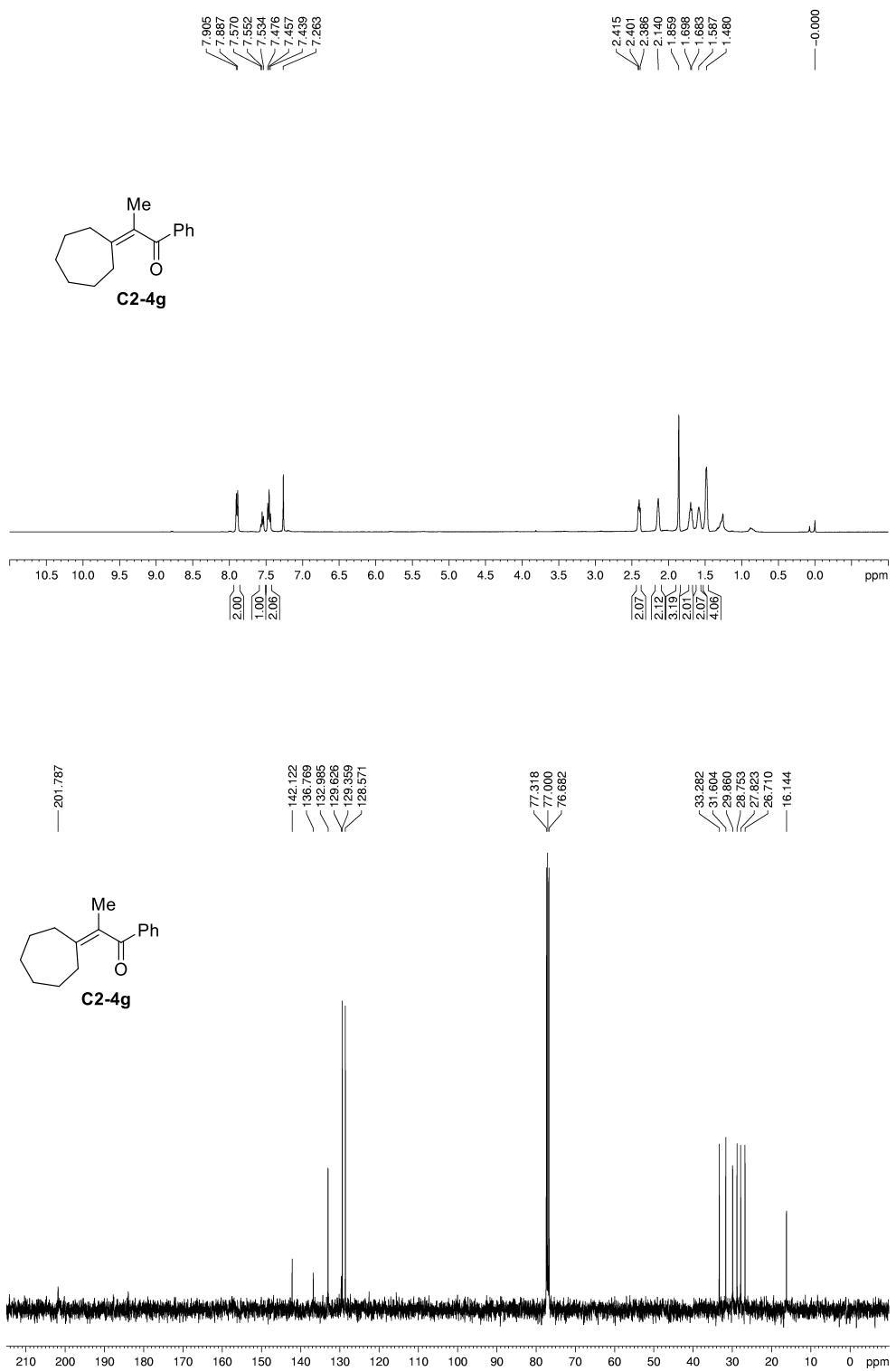


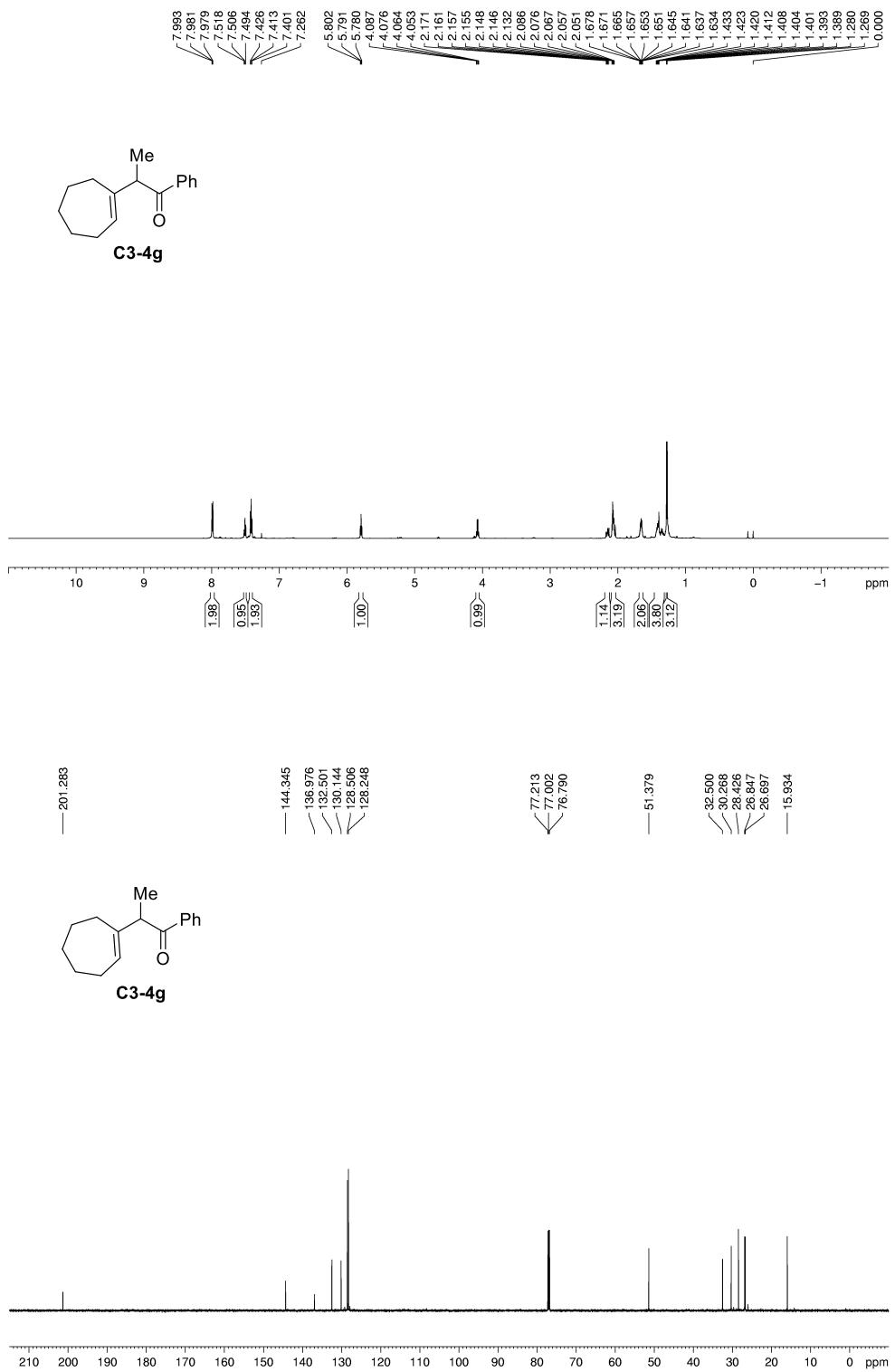


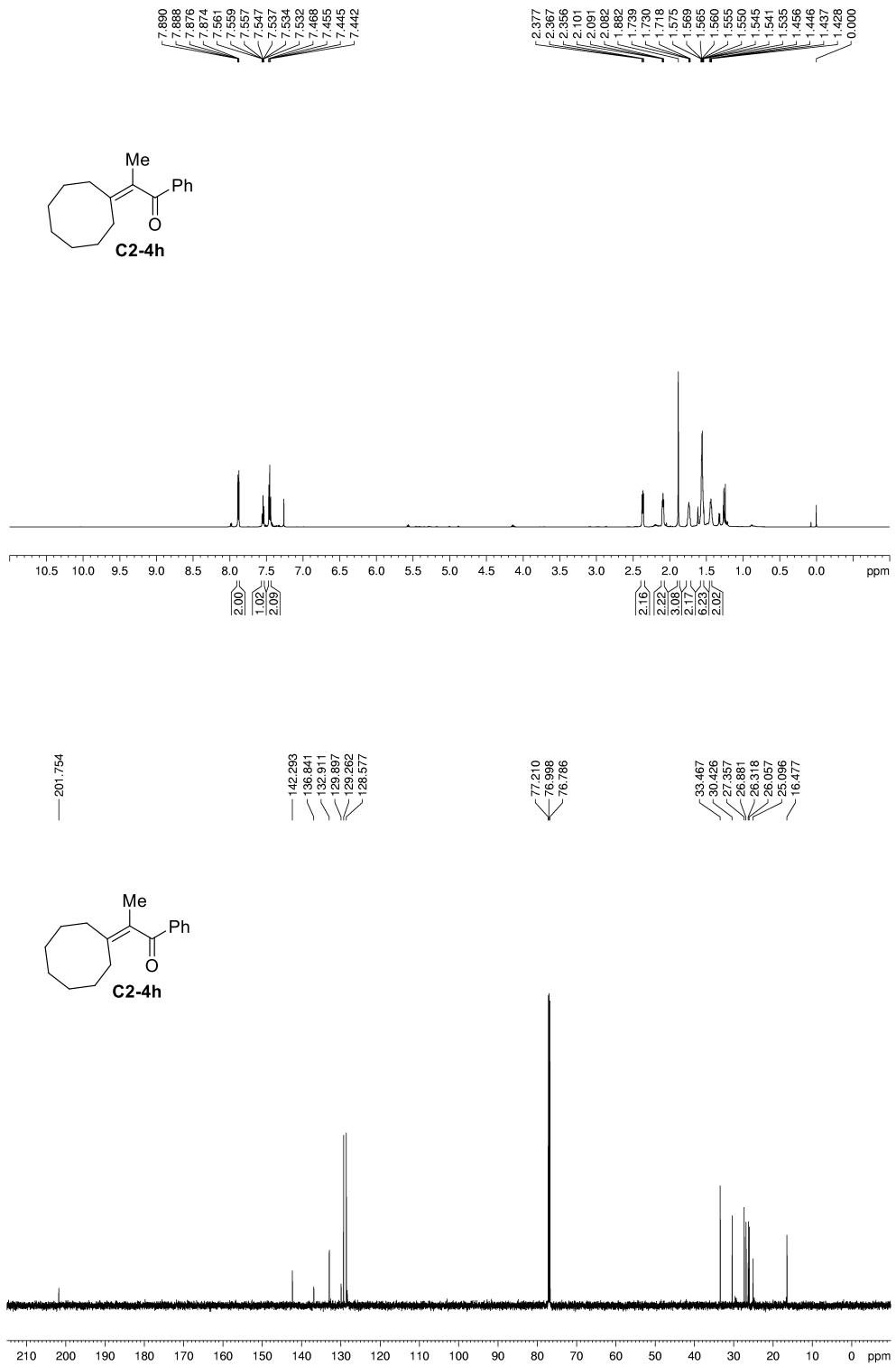


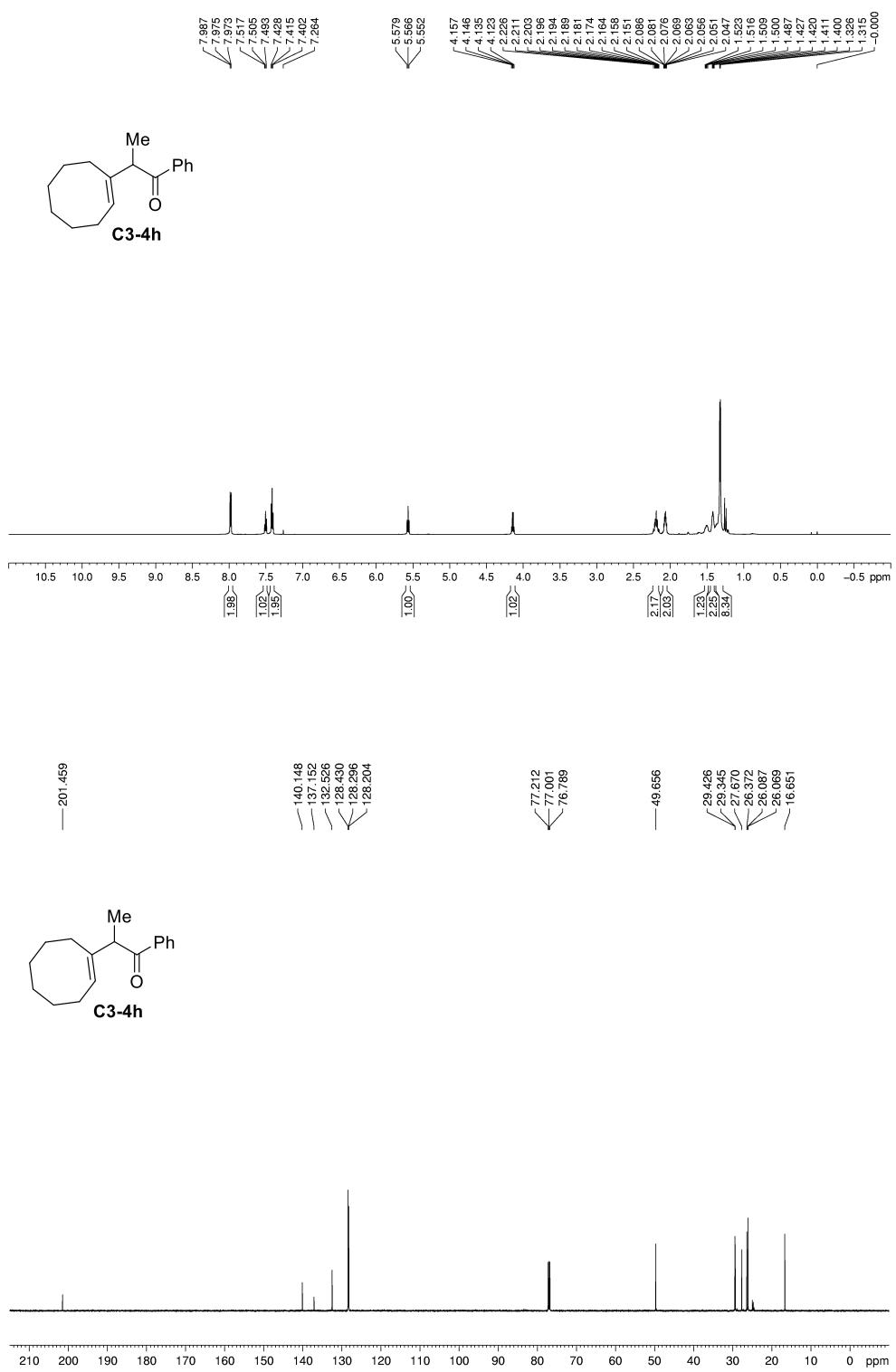


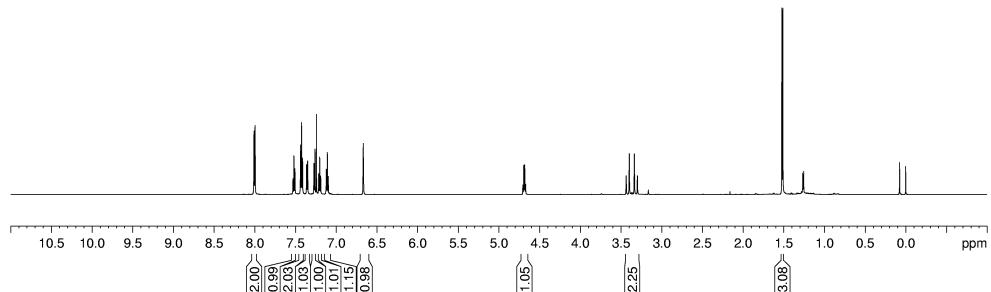
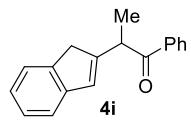
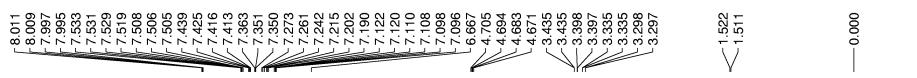




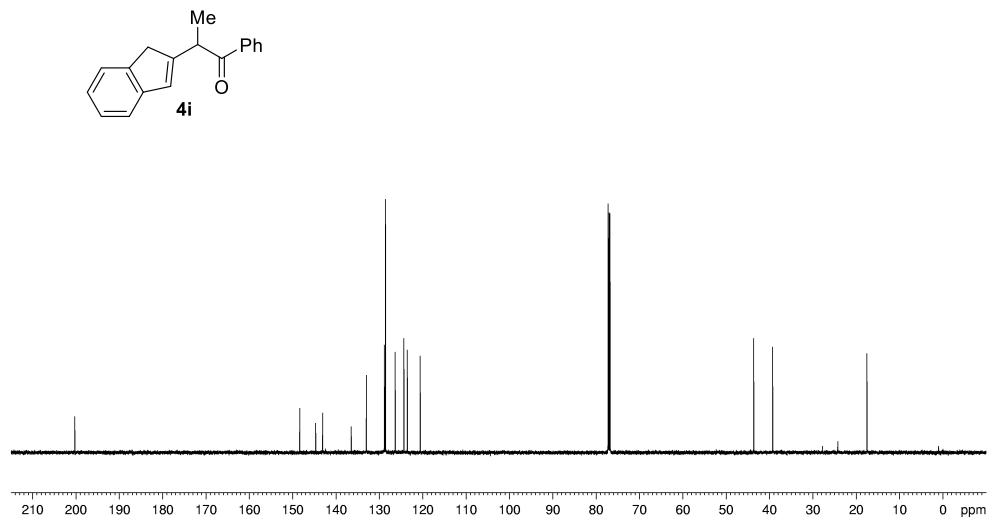


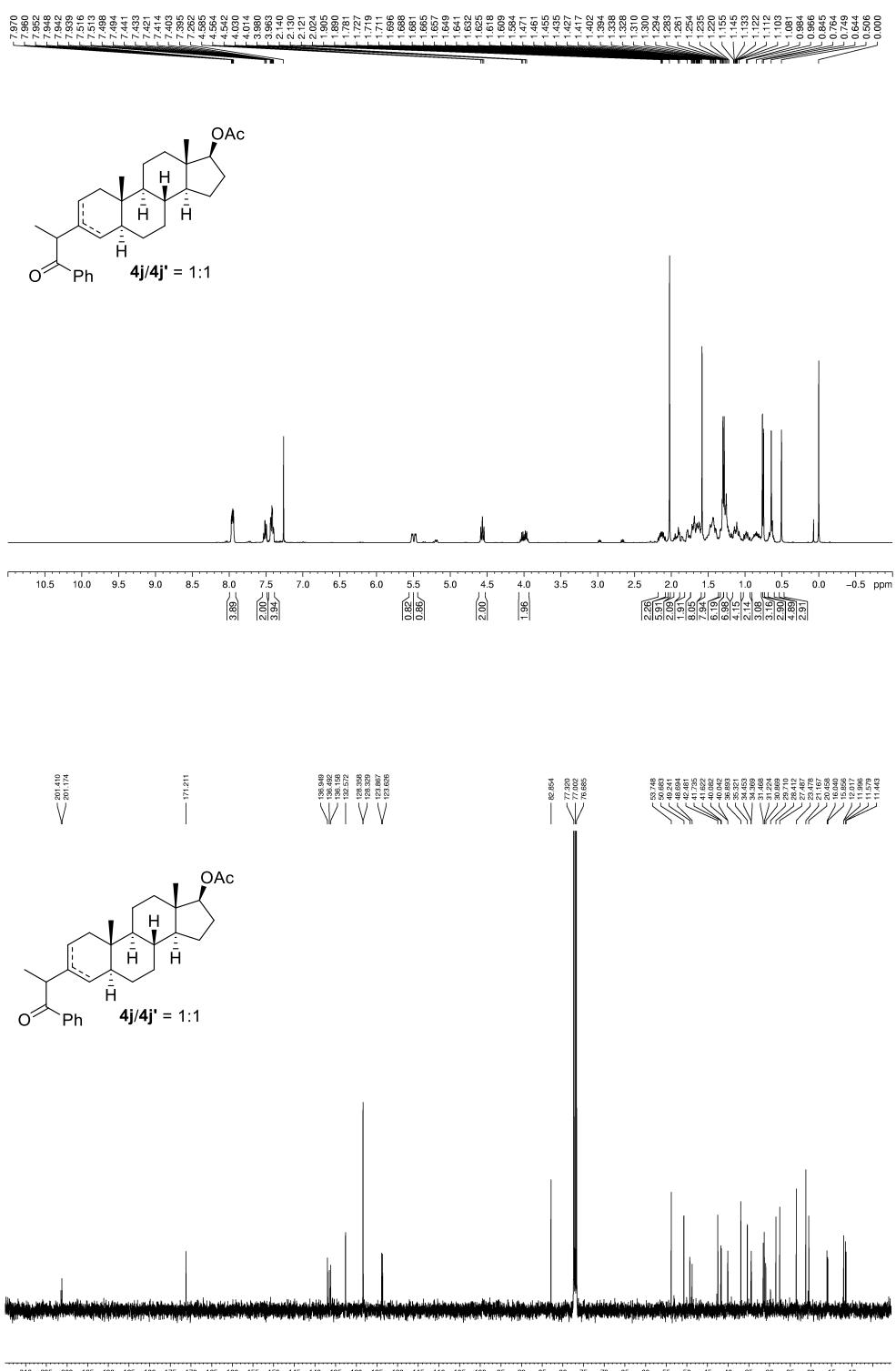


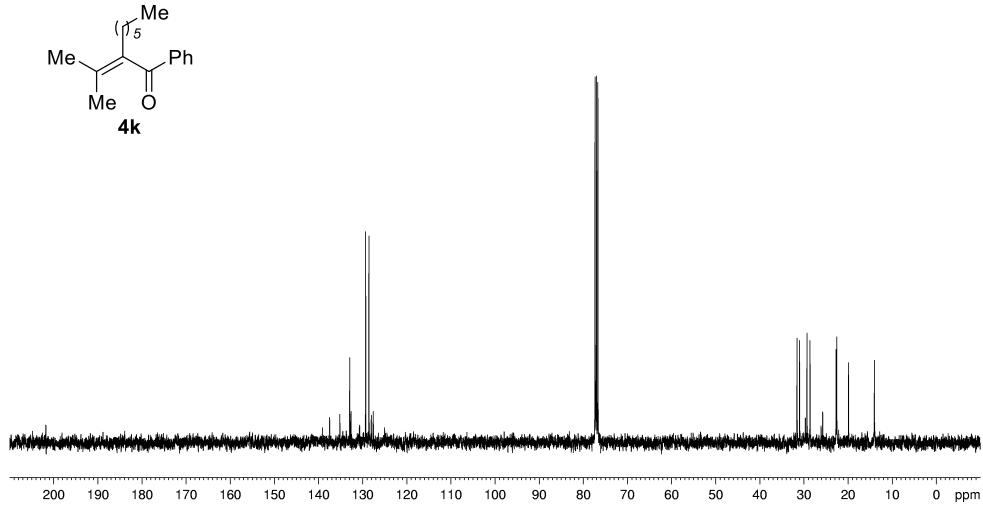
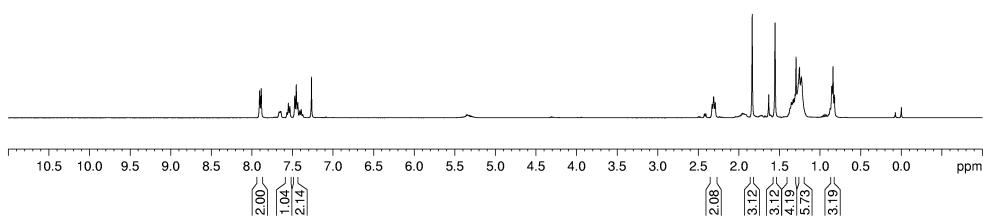


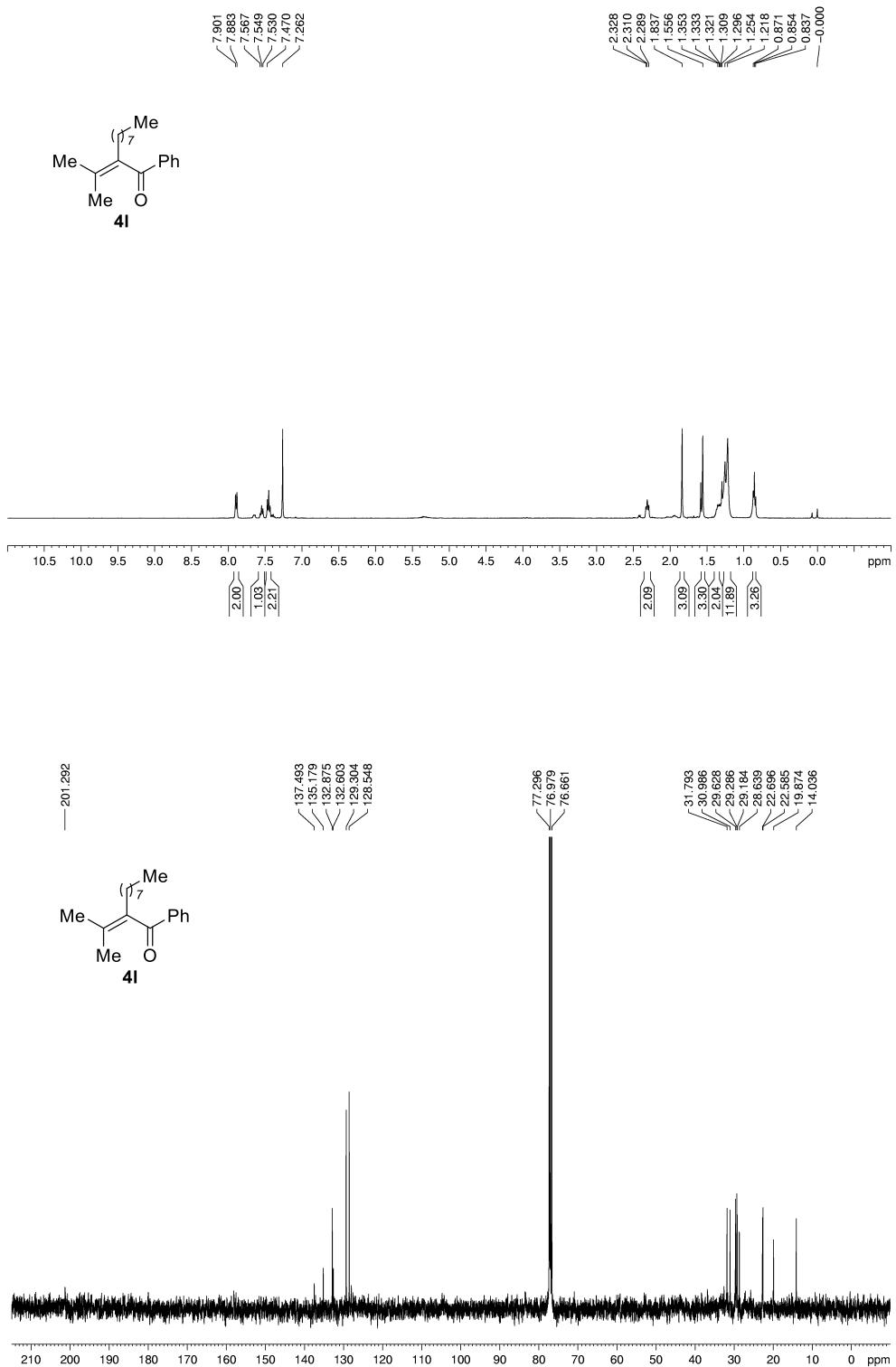


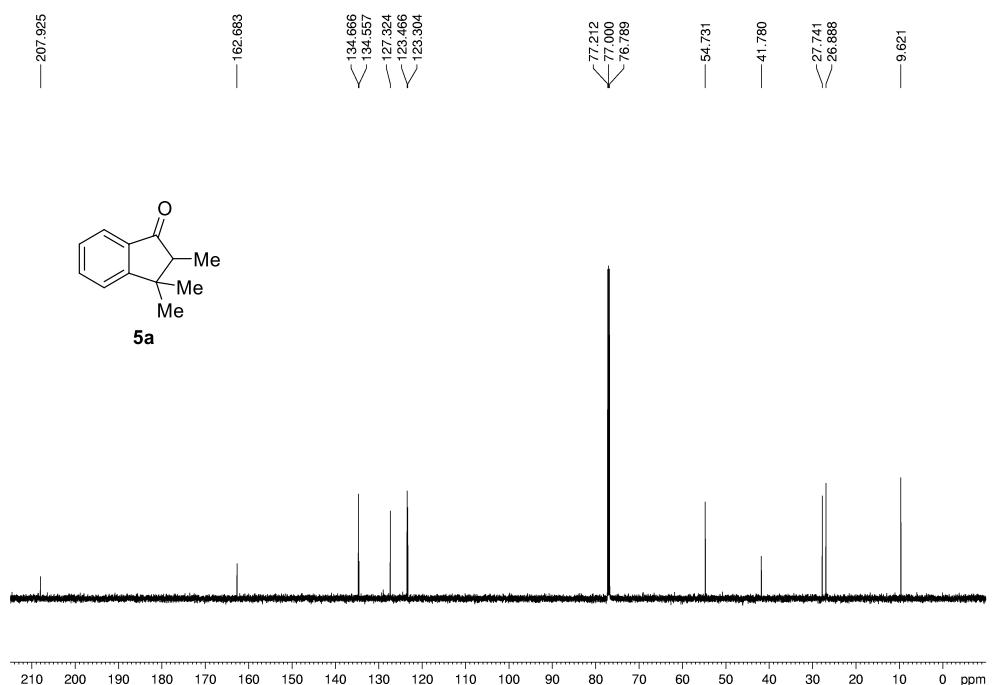
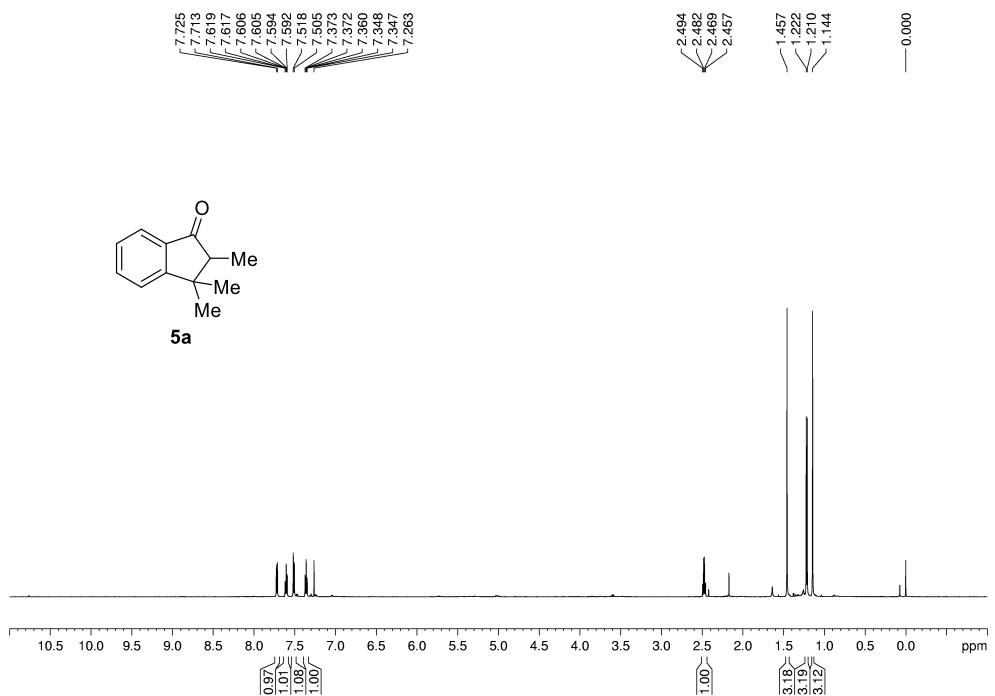
— 200.207  
<sup>1</sup>H NMR chemical shifts (δ, ppm): 148.374, 144.889, 143.079, 136.515, 132.995, 132.99, 128.554, 128.598, 128.587, 126.352, 124.340, 123.546, 120.584.

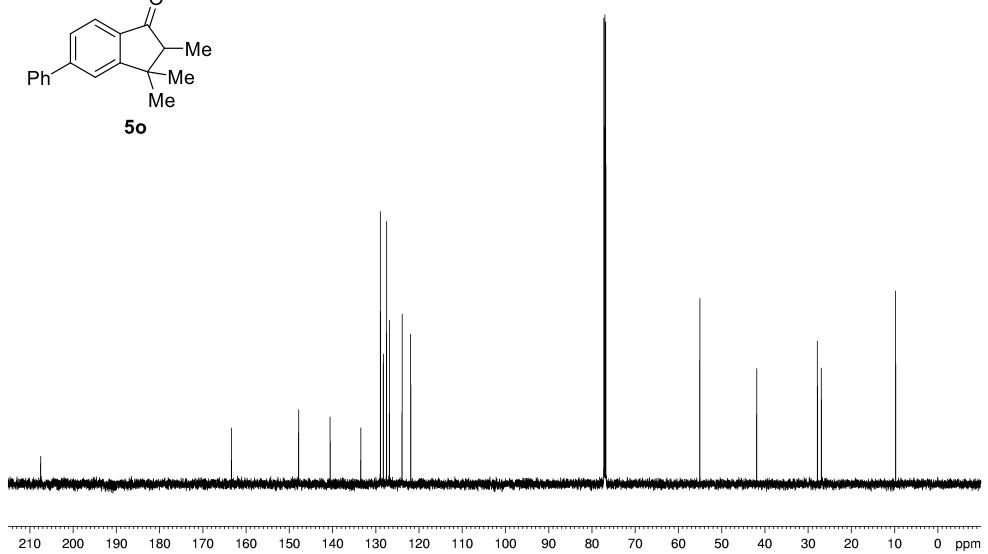
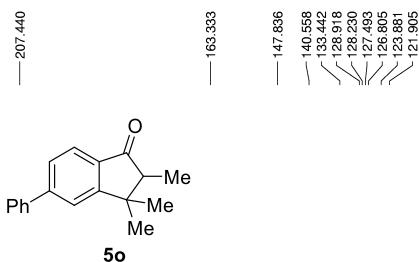
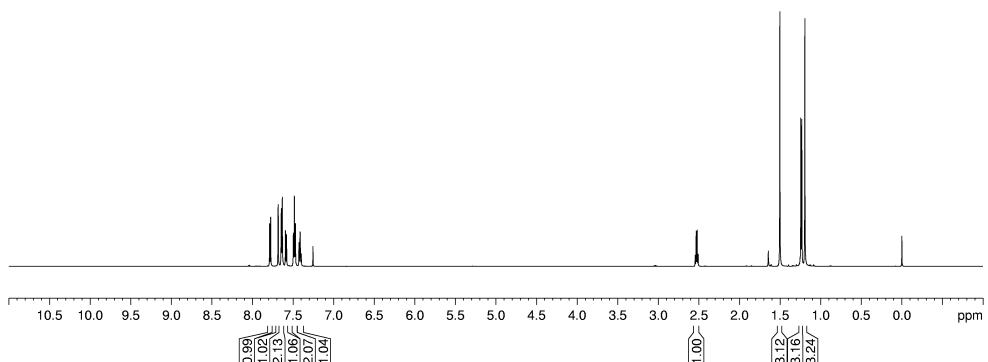
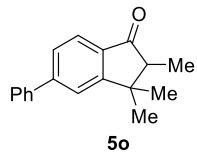


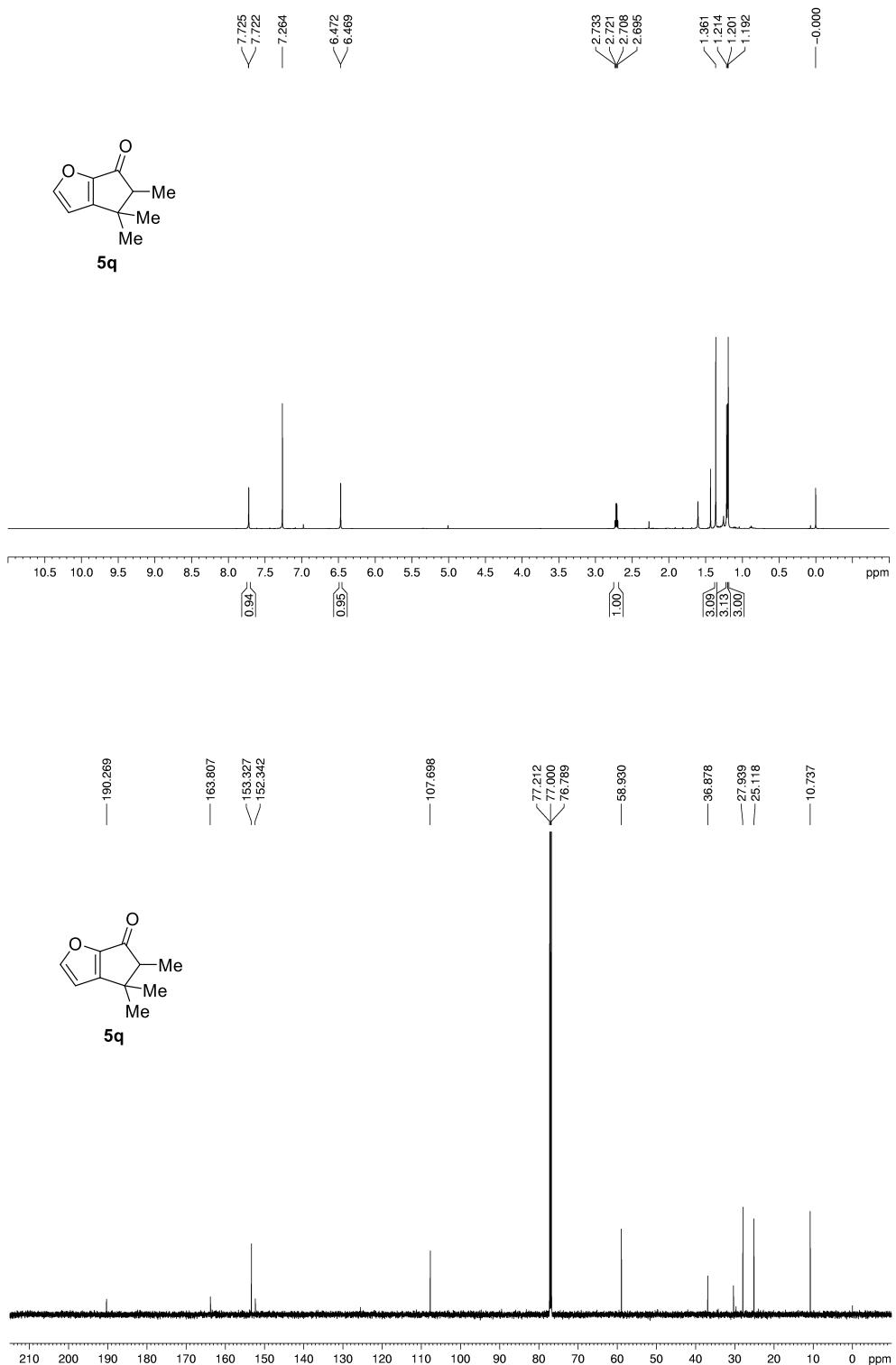


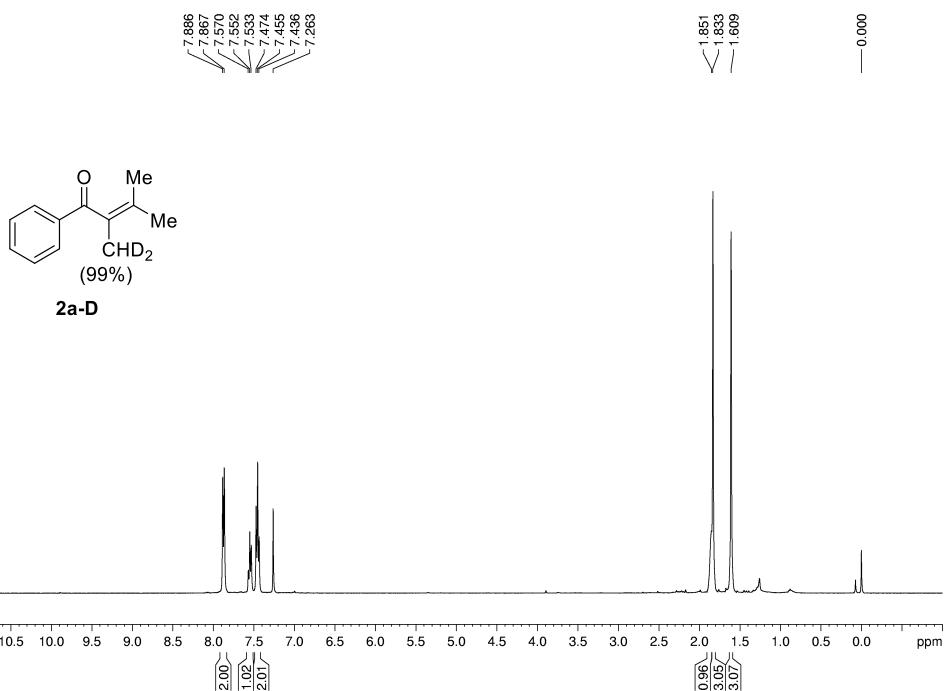
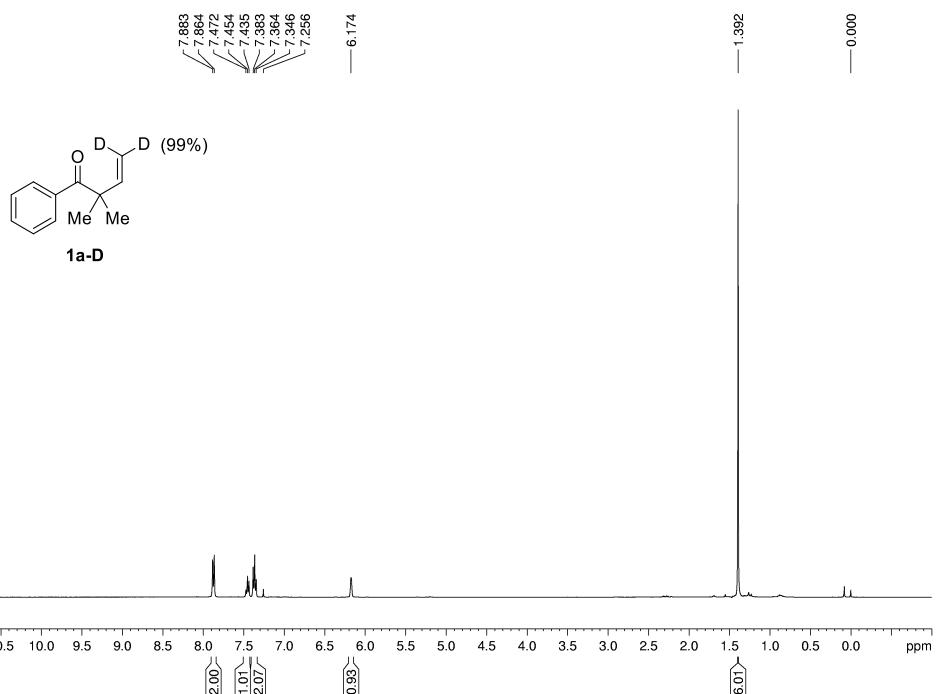


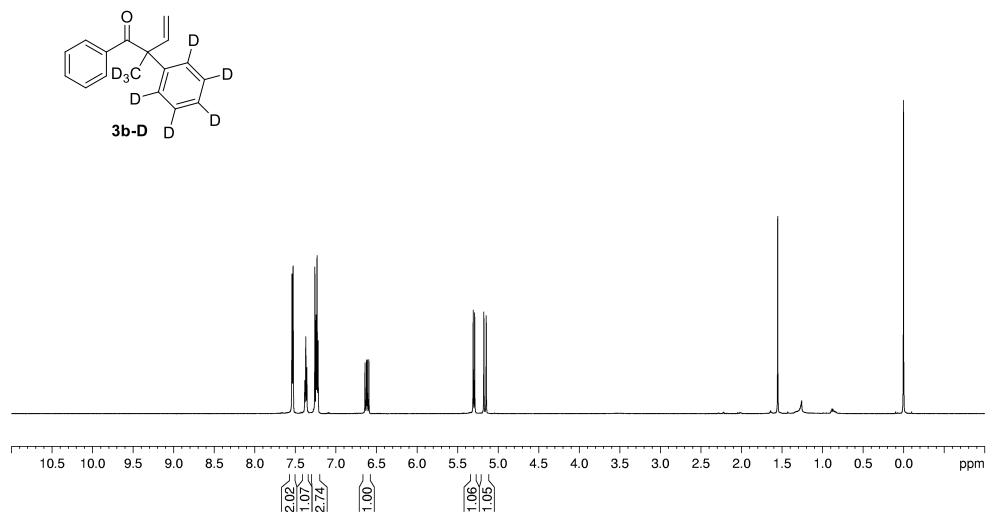
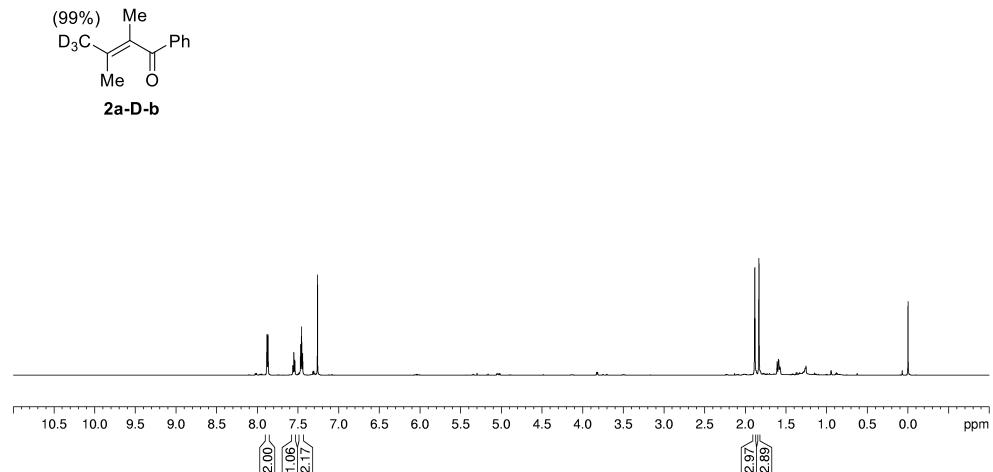


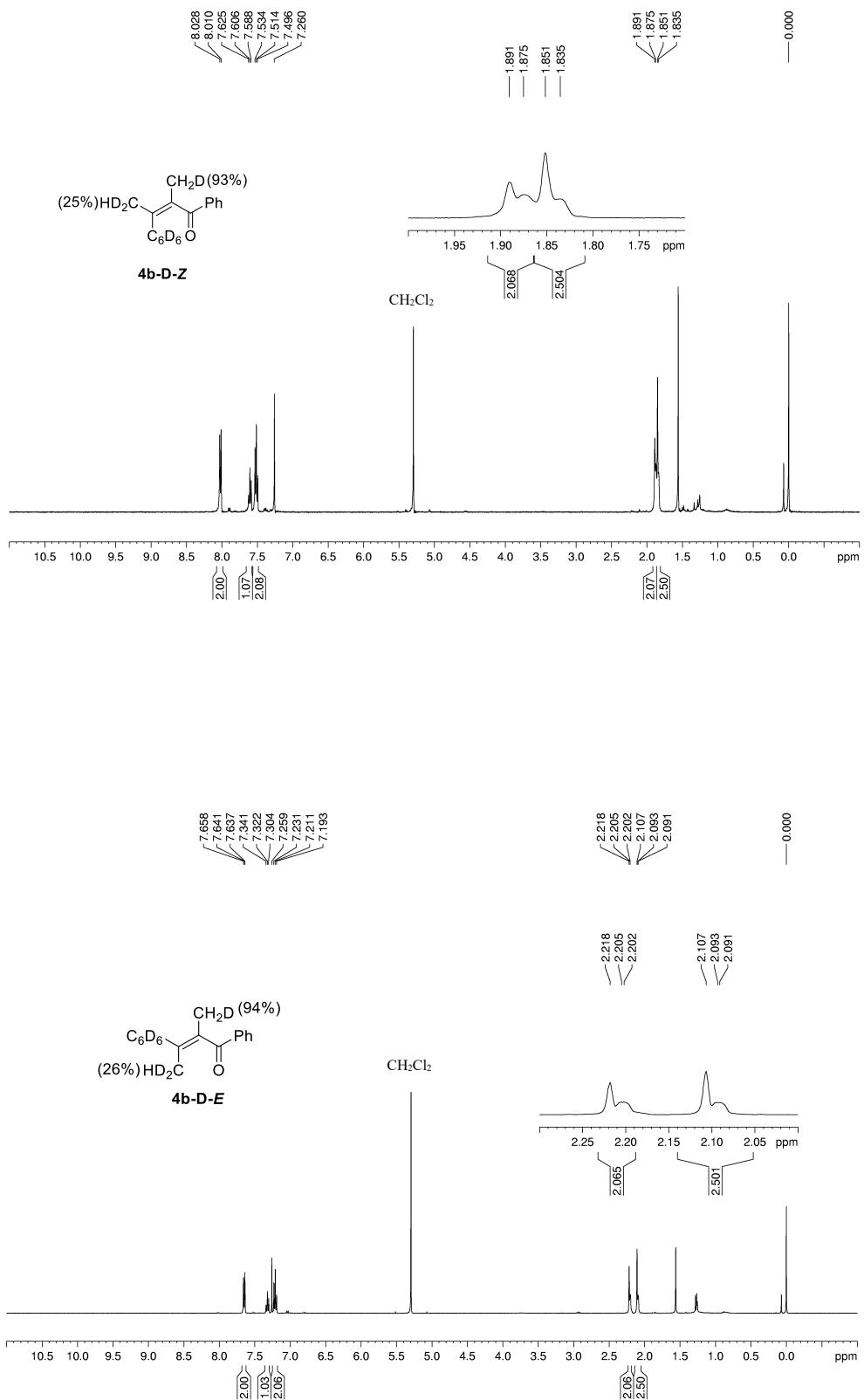






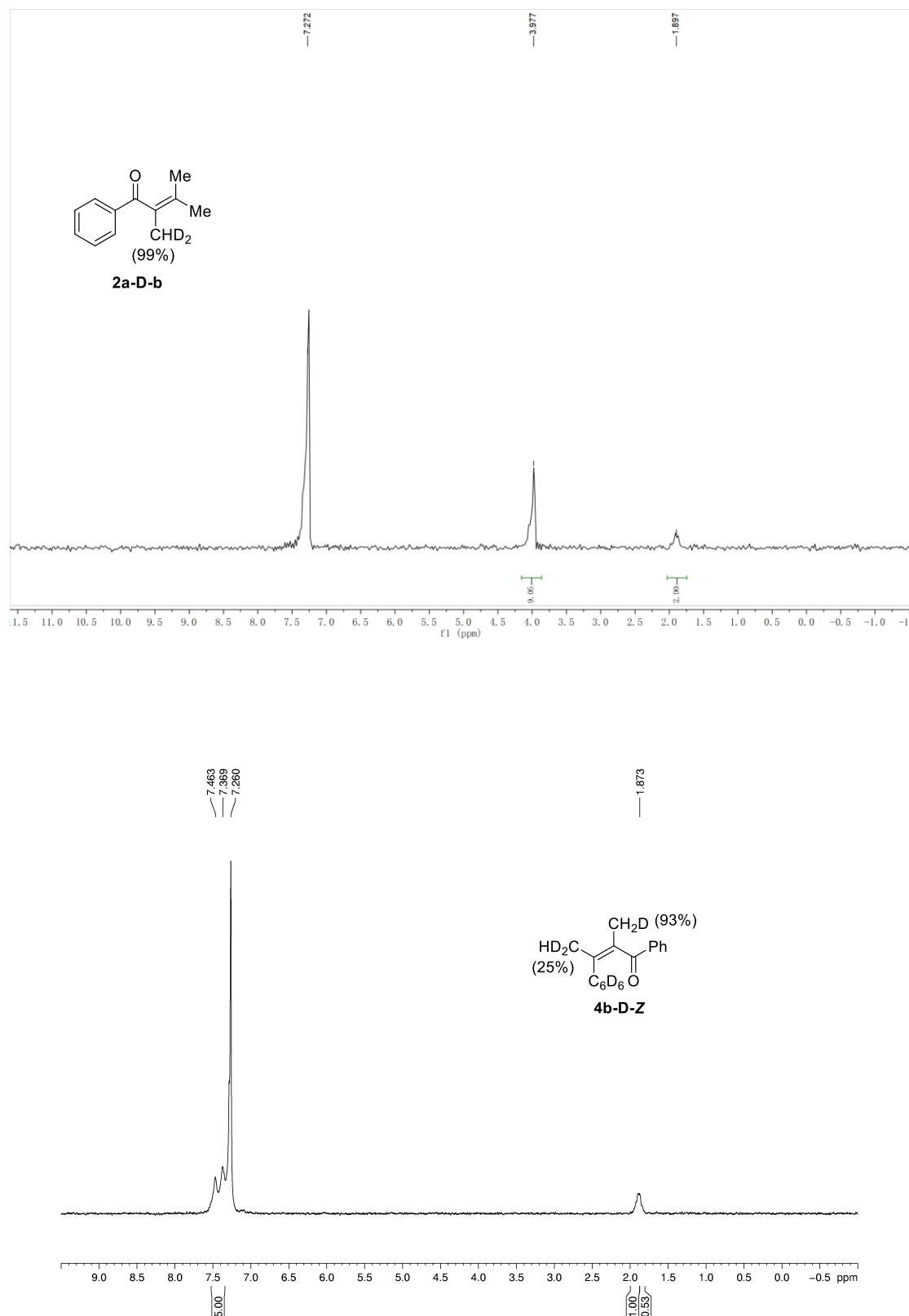


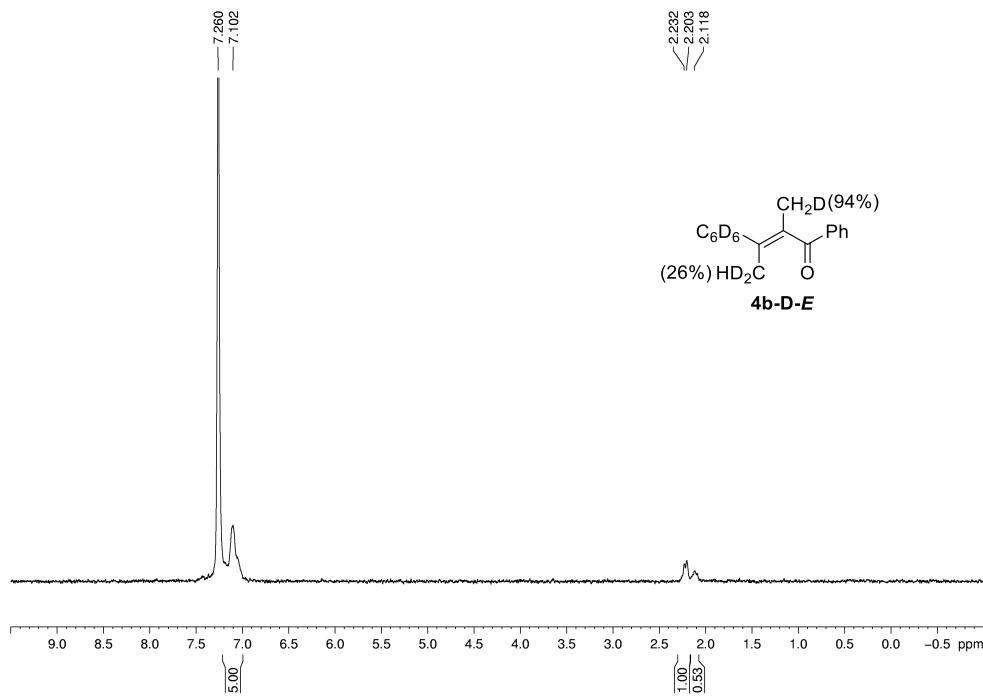




## <sup>2</sup>H NMR spectroscopy

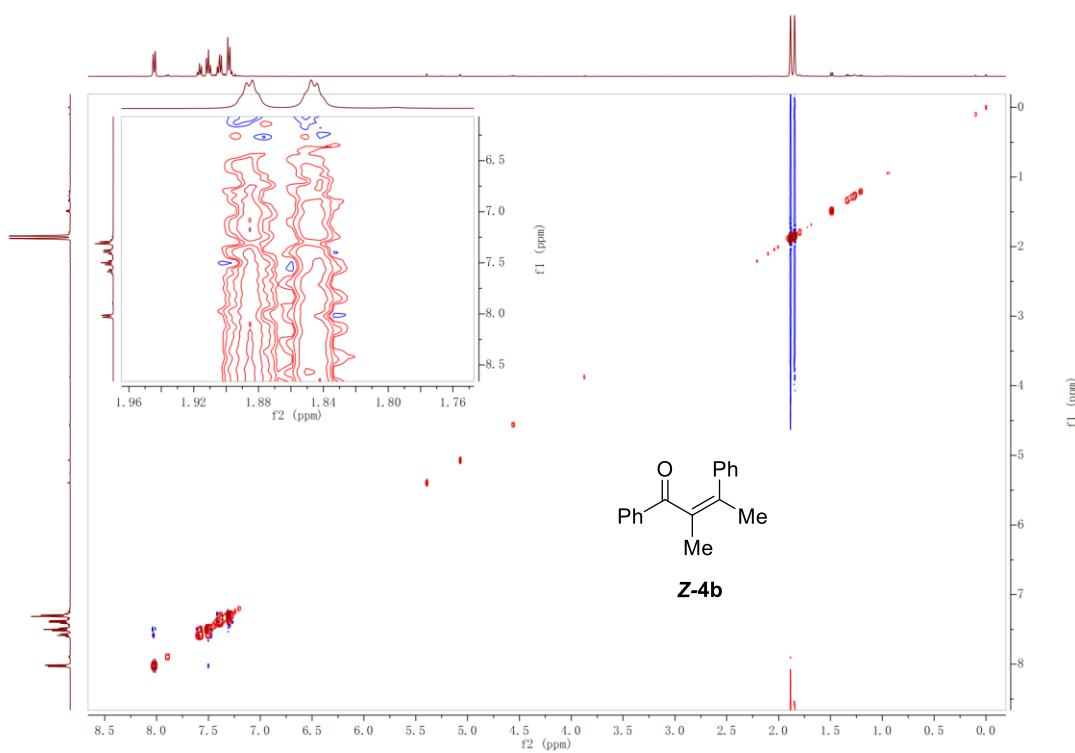
The <sup>2</sup>H NMR spectroscopy was measured with methyl 2-naphthoate-d3 as an internal standard (3.0 equiv) as an internal standard.



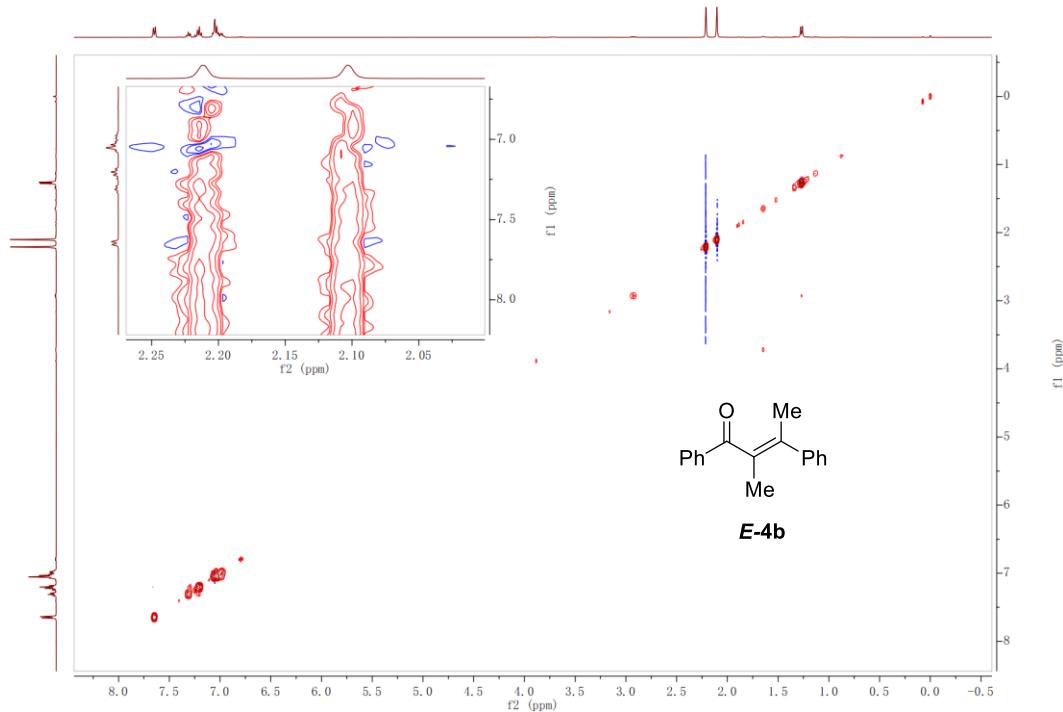


### NOESY

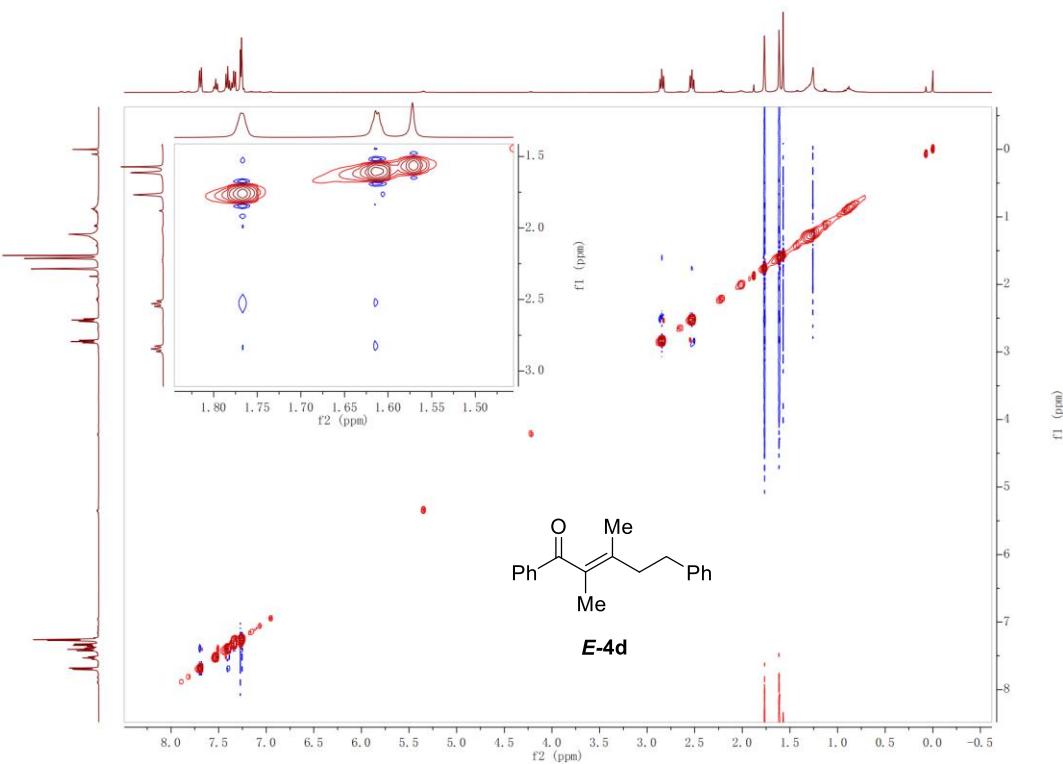
Z-4b



**E-4b**



**E-4d**



## 7. References

- (1) (a) Chen, F.; Zhu, F.-F.; Zhang, M.; Liu, R.-H.; Yu, W.; Han, B. Iminoxy Radical-Promoted Oxycyanation and Aminocyanation of Unactivated Alkenes: Synthesis of Cyano-Featured Isoxazolines and Cyclic Nitrones. *Org. Lett.* **2017**, *19*, 3255–3258. (b) Fleury, L. M.; Kosal, A. D.; Masters, J. T.; Ashfeld, B. L. Cooperative Titanocene and Phosphine Catalysis: Accelerated C–X Activation for the Generation of Reactive Organometallics. *J. Org. Chem.* **2013**, *78*, 253–269.
- (2) Yang, W.; Chen, C.; Chan, K. S. Hydrodebromination of Allylic and Benzylic Bromides with Water Catalyzed by a Rhodium Porphyrin Complex. *Dalton Trans.* **2018**, *47*, 12879–12883.
- (3) Becke, A. D. Density-functional Exchange-energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A*, **1988**, *38*, 3098–3100.
- (4) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-energy Formula Into a Functional of the Electron Density. *Phys. Rev. B*, **1988**, *37*, 785–789.
- (5) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (6) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for the Transition Metal Atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270–283.
- (7) Hariharan P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theoret. chim. Acta*, **1973**, *28*, 213–222.
- (8) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105*, 2999–3094.
- (9) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2006**, *125*, 194101.
- (10) Ehlers, A.W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. A Set of f-Polarization Functions for Pseudo-potential Basis Sets of the Transition Metals Sc–Cu, Y–Ag and La–Au. *Chem. Phys. Lett.*, **1993**, *208*, 111–114.
- (11) Roy, L. E.; Hay, P. J.; Martin. R. L. Distance in Zigzag Polyhex Nanotorus. *J. Chem. Theory Comput.* **2008**, *7*, 1029–1031.
- (12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.;

Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Gaussian 09, D. J. Fox., revision e.01. Gaussian, Inc., Wallingford CT, **2013**.

(13) Except for the hydrogen migration transition species, all hydrogens were omitted for clarity.