Supporting Information

Iminyl Radical-Triggered 1,5-Hydrogen Atom Transfer/Heck-Type Coupling by Visible-Light Photoredox Catalysis

Li Chen, Li-Na Guo, Zhi-Yong Ma, Yu-Rui Gu, Junjie Zhang and Xin-Hua Duan*

Department of Chemistry, School of Science, Xi'an Key Laboratory of Sustainable Energy Material Chemistry, and MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an 710049, China

E-mail: duanxh@xjtu.edu.cn

Table of Contents

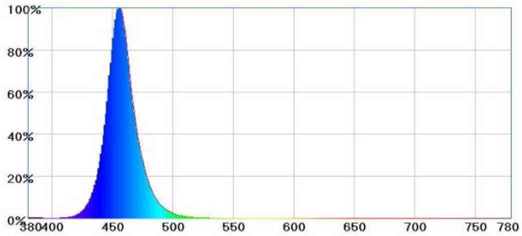
The Light Source and the Material of the Irradiation Vessel

Manufacturer：Xi 'an WATTECS experimental equipment co. LTD

Model：WP-VLH-1020

Broadband source：λ = 460-470 nm

Spectral distribution and intensity：



Material of the irradiation vessel：borosilicate reaction tube

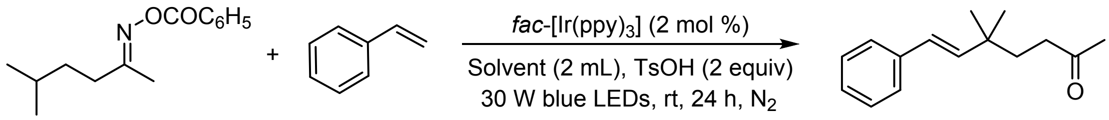
Distance from the light source to the irradiation vessel：2.0 cm

Not use any filters

(photographed by author Li-Na Guo)

Optimization of Oxime Esters 1a and Styrene 2a

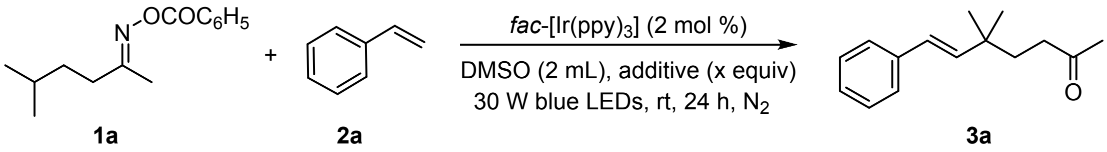
Screening of solvents[a]



entry	solvent	yield (%)[b]
1	MeCN	0
2	acetone	0
3	DCE	0
4	$PhCH_3$	0
5	THF	0
6	1,4-dioxane	trace
7	DMF	25
8	NMP	56
9	DMAc	61
10	DMSO	68
11	CH_3OH	0
12	HOAc	0

[a]Reaction conditions: 2.0 mol % *fac*-[Ir(ppy)$_3$], **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv) and TsOH (0.4 mmol, 2.0 equiv) in solvent (2.0 mL) were irradiated by 30 W blue light-emitting diodes (LEDs) for 24 h under N_2. [b]Yields of isolated product. HOAc = acetic acid. MeCN = acetonitrile. DMF = *N,N*-dimethylformamide. DMAc = dimethylacetamide. NMP = *N*-methyl pyrrolidone. DMSO = dimethyl sulfoxide. DCE = dichloroethane. THF = tetrahydrofuran.

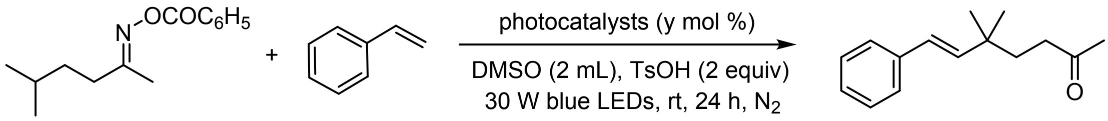
Screening of additives[a]



entry	additive	x	yield (%)[b]
1	TsOH	1.0	61
2	TfOH	1.0	52
3	MSA	1.0	59
4	HOAc	1.0	0
5	TFA	1.0	56
6	HCOOH	1.0	0
7	Benzoic acid	1.0	0
8	Ph(F_5)COOH	1.0	0
9	TsOH	0.5	25
10	TsOH	1.5	48
11	TsOH	2.0	68
12	TsOH	2.5	45
13	K_2CO_3	2.0	0
14	Cs_2CO_3	2.0	0
15	NaOAc	2.0	0
16	^{t}BuOK	2.0	0
17	Et_3N	2.0	0
18	KH_2PO_4	2.0	0
19	-	-	0

[a]Reaction conditions: 2.0 mol % *fac*-[Ir(ppy)$_3$], **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv) and additive (x equiv) in DMSO (2.0 mL) were irradiated by 30 W blue light-emitting diodes (LEDs) for 24 h under N_2. [b]Yields of isolated product. TsOH = 4-Methylbenzenesulfonic acid. TfOH = Trifluoromethanesulfonic acid. MSA = Methanesulfonic acid. TFA = Trifluoroacetic acid.

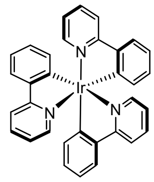
Screening of photocatalysts[a]



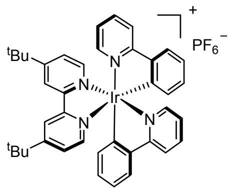
1a **2a** **3a**

entry	photocatalysts (y mol %)	yield (%)[b]
1	*fac*-[Ir(ppy)$_3$] (1 mol %)	73
2	*fac*-[Ir(ppy)$_3$] (2 mol %)	68
3	*fac*-[Ir(ppy)$_3$] (0.5 mol %)	$<$20
4	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2 mol %)	0
5	[Ir(dF(CF$_3$)ppy)$_2$(dtbpy)](PF$_6$) (2 mol %)	0
6	[Ru(bpy)$_3$]Cl$_2$ (2 mol %)	0
7	[Ru(bpy)$_3$](PF$_6$)$_2$ (2 mol %)	0
8	Cu(dap)$_2$Cl (2 mol %)	0
9	Eosin Y (2 mol %)	0
10	Rhodamine B (2 mol %)	0
11	Methylene blue (2 mol %)	0
12	Fluorescein (2 mol %)	0
13	Phenothiazine (2 mol %)	0
14	10-Methylphenothiazine (2 mol %)	0
15	4CzIPN (2 mol %)	0
16[c]	-	0

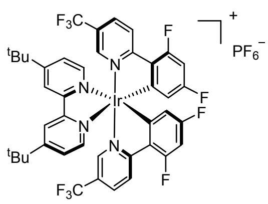
[a]Reaction conditions: y mol % photocatalysts, **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv) and TsOH (0.4 mmol, 2.0 equiv) in DMSO (2.0 mL) were irradiated by 30 W blue light-emitting diodes (LEDs) for 24 h under N_2. [b]Yields of isolated product. [c]The reaction was conducted in the absence of visible light or photocatalyst.



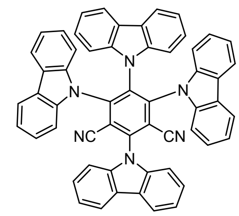
fac-Ir(ppy)$_3$



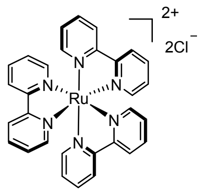
[Ir(ppy)$_2$dtbbpy]PF$_6$



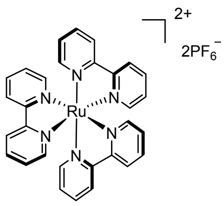
[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$)



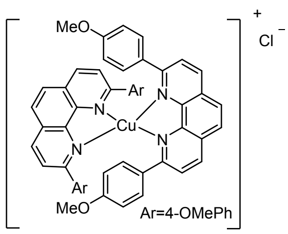
4CzIPN



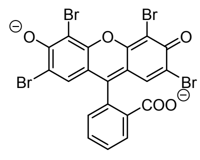
Ru(bpy)$_3$Cl$_2$



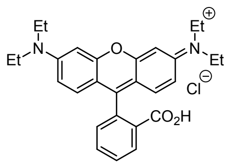
Ru(bpy)$_3$(PF$_6$)$_2$



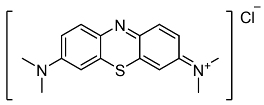
Cu(dap)$_2$Cl



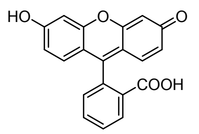
Eosin Y



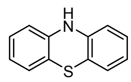
Rhodamine B



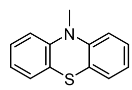
Methylene blue



Fluorescein

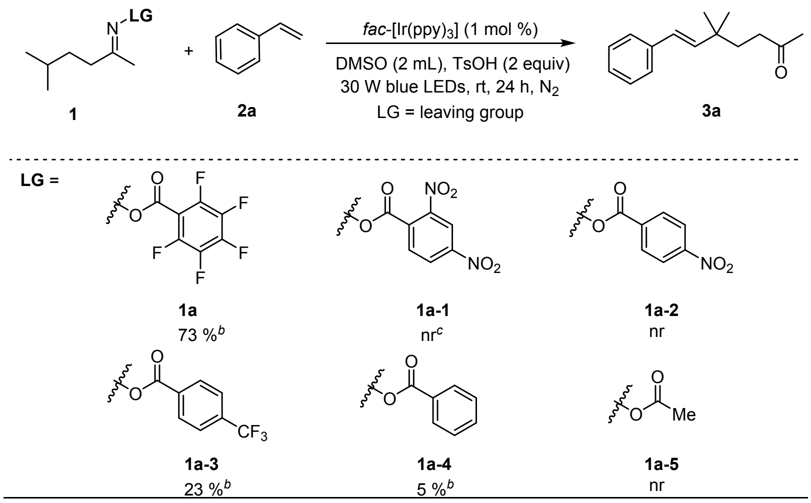


Phenothiazine



10-Methylphenothiazine

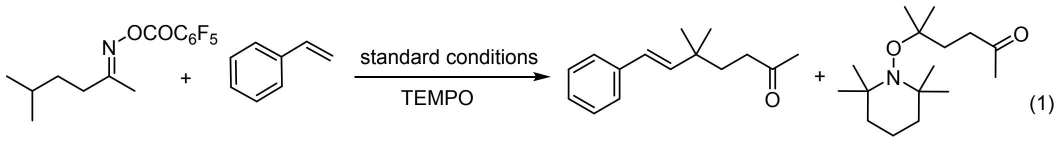
Screening of acyl oxime substrates[a]



[a]Reaction conditions: 1.0 mol % *fac*-[Ir(ppy)$_3$], **1** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), and TsOH (0.4 mmol, 2.0 equiv) in DMSO (2.0 mL) were irradiated by 30 W blue light-emitting diodes (LEDs) for 24 h under N$_2$. [b]Yields of isolated product. [c]nr = No reaction.

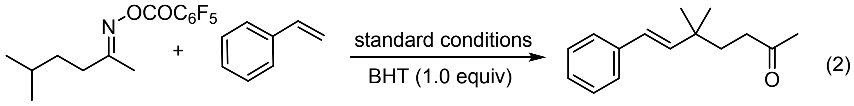
Investigation of the Reaction Mechanism

1. Radical Inhibiting Experiments



1a	2a		3a	5a
		0.5 equiv	34%	
		1.0 equiv	20%	
		3.0 equiv	0%	28%

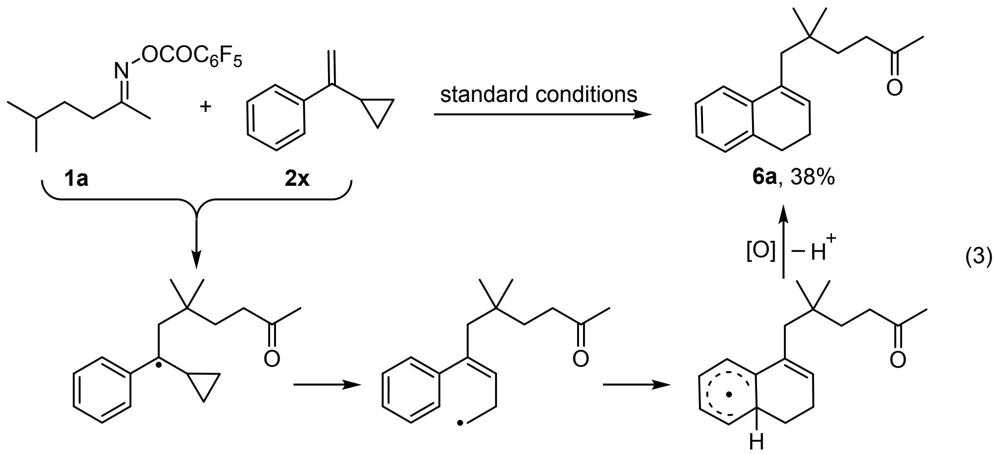
The addition of TEMPO obviously suppressed the reaction of **1a** with **2a** under the standard conditions. When 3.0 equiv of TEMPO was added, the yield of product **3a** was reduced to 0% and the corresponding TEMPO-adduct **5a** was isolated in 28% yield. This result indicates that a radical intermediate might be involved in this transformation.



1a **2a** **3a**, 0%

When 1.0 equiv of BHT was added to the reaction of **1a** with **2a** under the standard conditions, no desired product **3a** was observed. This result indicates that a radical intermediate might be involved in this transformation.

2. Radical Clock Experiment



Treatment of **1a** with **2x** under the standard conditions delivered the ring-expanded product **6a** in 38% isolated yield, which provides further evidence for a radical pathway.

3 Determination of the light intensity at 468 nm

The photon flux of the spectrophotometer was measured by ferrioxalate actinometry. The preparation of 0.15 M solution of ferrioxalate and buffered solution of phenanthroline was according to the literature procedures.[1] The fraction of light absorbed (f) by ferrioxalate solution was calculated using eq 1, where A is the measured absorbance at 468 nm (**Figure S1**, A= 0.411528). Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline. ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions. l is the path length (1.00 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). Where Φ is the quantum yield for the ferrioxalate actinometer (0.92 for a 0.15 M solution at λ =468 nm).[2] At 468 nm, photo flux was calculated to be 2.19×10^{-9} einstein s^{-1}.

$$f = 1 - 10^{-A} \tag{1}$$

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} \tag{2}$$

$$\text{photo flux} = \frac{\text{mol Fe}^{2+}}{\Phi \times t \times f} \tag{3}$$

Sample calculation:

$$f = 1 - 10^{-0.411528}$$

$$= 0.61232$$

$$\text{mol Fe}^{2+} = \frac{0.00235\text{L}^{-1} \times 0.522229}{1.000\text{ cm} \times 11100\text{L mol}^{-1}\text{cm}^{-1}}$$

$$= 1.11 \times 10^{-7}\text{ mol}$$

$$\text{photo flux} = \frac{1.11 \times 10^{-7}}{0.92 \times 90 \times 0.61232}$$

$$= 2.19 \times 10^{-9}\text{ einstein s}^{-1}$$

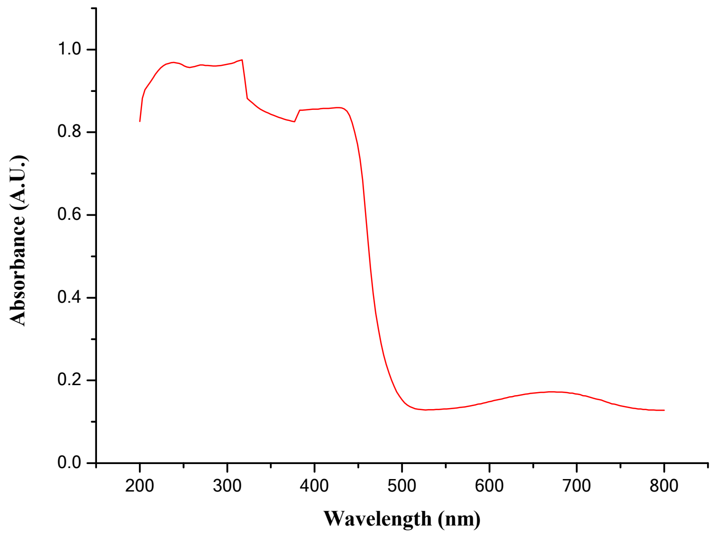
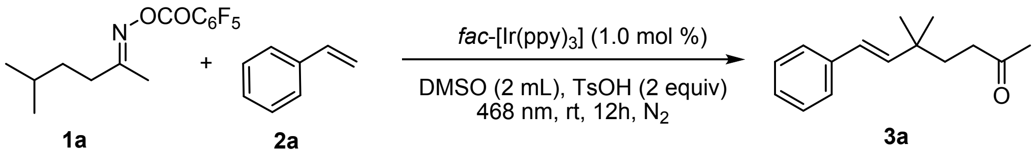


Figure S1. Absorbance of the ferrioxalate actinometer solution.

4 Determination of quantum yield:



A cuvette was pumped into the glovebox. The cuvette was charged with (*E*)-5-methylhexan-2-one *O*-perfluorobenzoyl oxime **1a** (0.2 mmol, 1.0 equiv), *fac*-[Ir(ppy)$_3$] (0.002 mmol, 1 mol %), TsOH (0.4 mmol, 2.0 equiv), styrene **2a** (0.4 mmol, 2.0 equiv) and 2.0 mL of DMSO. The cuvette sealed with a cap and septa, then stirred and irradiated (λ = 468 nm, slit width = 10.0 nm) for 43200 s (12 h). After irradiation, purification of the crude product by flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1), 8.7 mg of the **3a** (20%) was isolated.

By UV-Vis, all incident light is absorbed by the *fac*-[Ir(ppy)$_3$] photocatalyst under the reaction conditions (**Figure S2**, Absorbance = 0.612400). Therefore, fraction of light absorbed is 0.75588.

$$\text{Quantum Yield} = \frac{\text{numbers of moles of product}}{\text{flux } \times \text{f} \times \text{t}}$$

$$= \frac{8.7/216/1000}{2.19 \times 10^{-9} \times 0.75588 \times 43200}$$

$$= 0.56$$

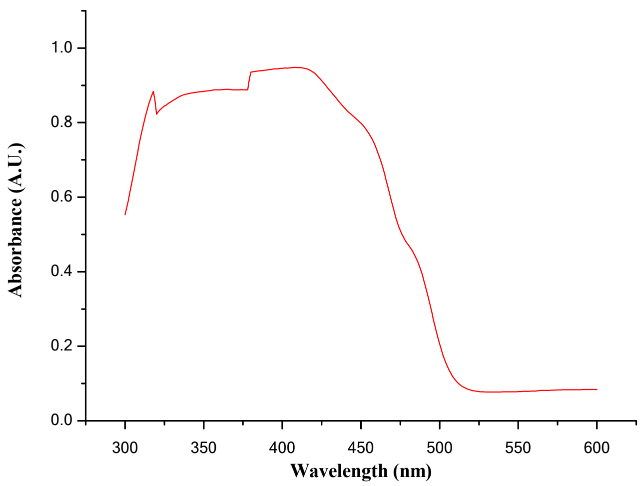
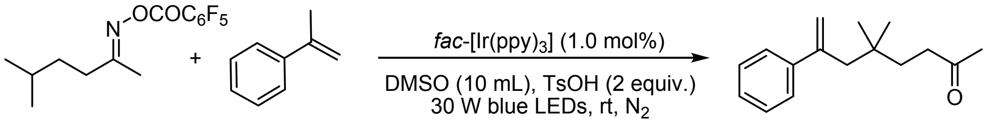


Figure S2. Absorbance of the *fac*-[Ir(ppy)$_3$] photocatalyst under the reaction conditions

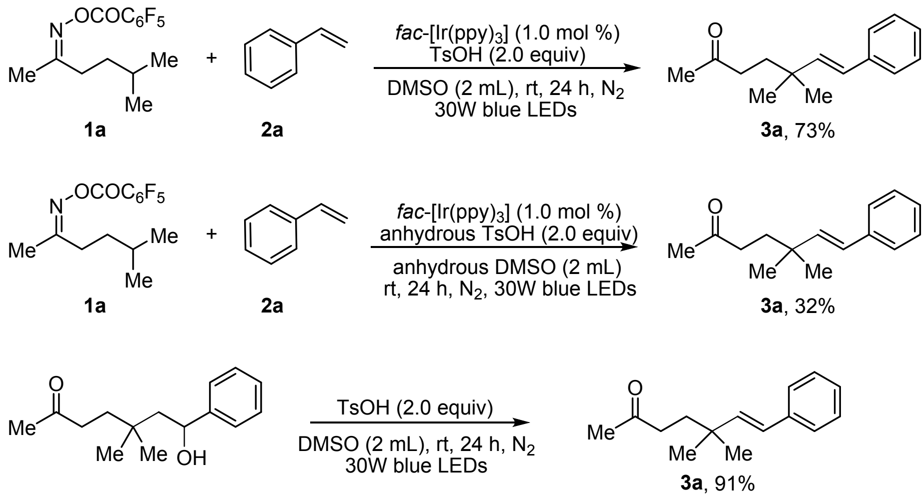
5 Scale up reaction



1a, 1.0 mmol **2o**, 2.0 mmol **3o**, 62%

A 50 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with **1a** (1.0 mmol, 1.0 equiv.), **2o** (2.0 mmol, 2.0 equiv.), *fac*-Ir(ppy)$_3$ (0.01 mmol, 1 mol%), TsOH (2.0 mmol, 2.0 equiv.). The flask was evacuated and backfilled with N_2 for 3 times. DMSO (10.0 mL, 0.1M) was then added with syringe under N_2. The mixture was then irradiated by a 30 W blue LEDs strips. After the reaction was complete (as judged by TLC analysis), then 10.0 mL H_2O was added and the mixture was stirred for 30 minutes at room temperature. The mixture was extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and concentrated in *vacuo*. Purification of the crude product by flash chromatography on silica gel (petroleum ether/ethyl acetate 30:1 to 20:1) to give the corresponding products in 62% (142.8 mg) yield.

6 Control experiment (using monohydrated PTSA and anhydrous PTSA)



When 2.0 equiv of anhydrous TsOH was used instead of monohydrated TsOH for the reaction of **1a** and **2a**, the desired product **3a** was observed in 32% yield. This result indicates that the crystalline water of TsOH had significant effect on the reaction and it might involve in reaction, serving as hydroxyl source to give corresponding alcohol.

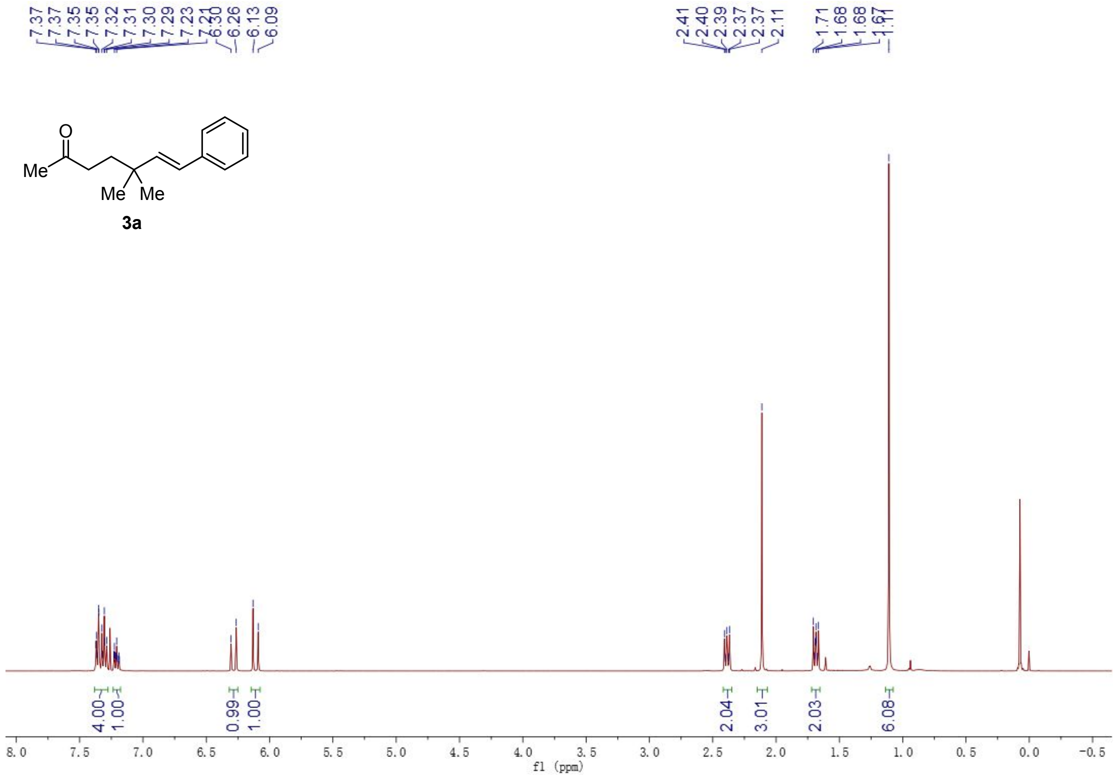
Furthermore, treatment of *γ*-hydroxyalkylation of alkyl ketone (corresponding alcohol as described in ref 7j) under the standard conditions delivered the **3a** in 91% isolated yield, which indicates that *γ*-hydroxyalkylation of alkyl ketone might also be intermediate in this transformation.

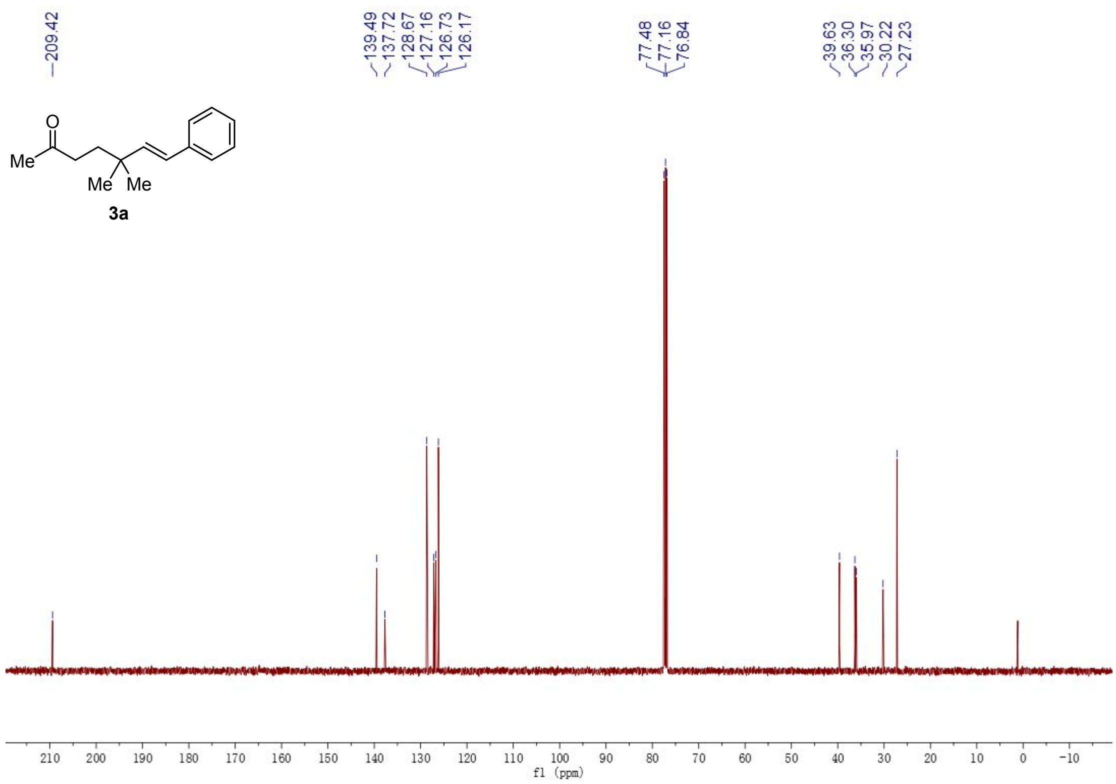
Reference

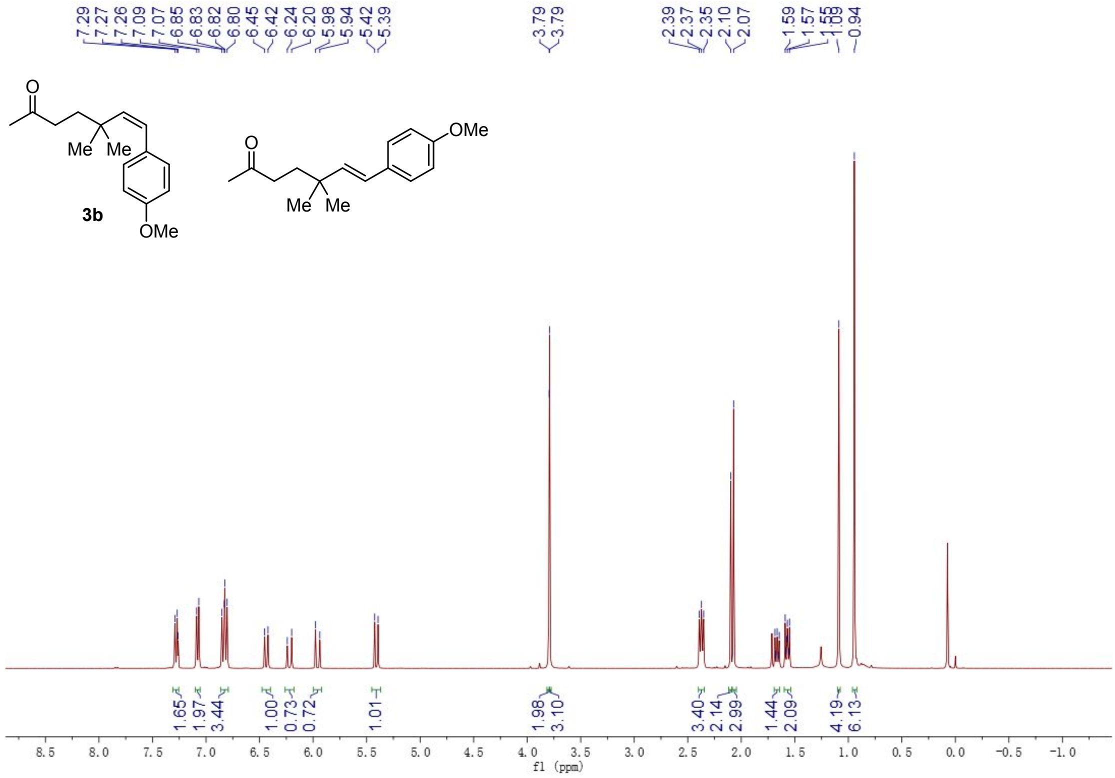
(1) Cismesia, M. A.; Yoon, T. P. Characterizing Chain Processes in Visible Light Photoredox Catalysis. *Chem. Sci.* **2015**, *6*, 5426−5434.

(2) Hatchard, C. G.; Parker, C. A. A New Sensitive Chemical Actinometer Ⅱ. Potassium Ferrioxalate as a Standard Chemical Actinometer. *Proc. R. Soc.* **1956**, *235*, 518−536.

^{1}H NMR and ^{13}C{^{1}H} NMR Spectra of Products 3



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7.27
7.26
7.09
7.07
6.85
6.83
6.82
6.80
6.45
6.42
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6.20
5.98
5.94
5.42
5.39
3.79
3.79
2.39
2.37
2.35
2.10
2.07
1.59
1.57
1.55
1.09
0.94
3b
OMe
Me
Me
1.65
1.97
3.44
1.00
0.73
0.72
1.01
1.98
3.10
3.40
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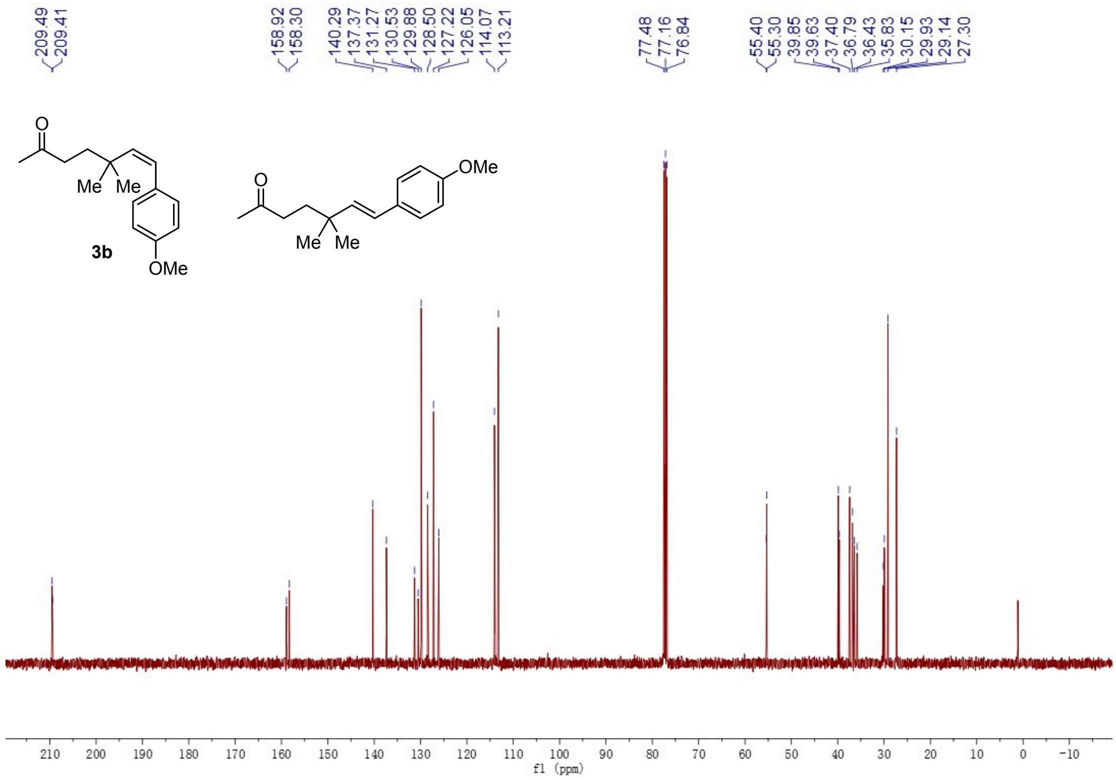
4.19
6.13
f1 (ppm)


209.49
209.41
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39.85
39.63
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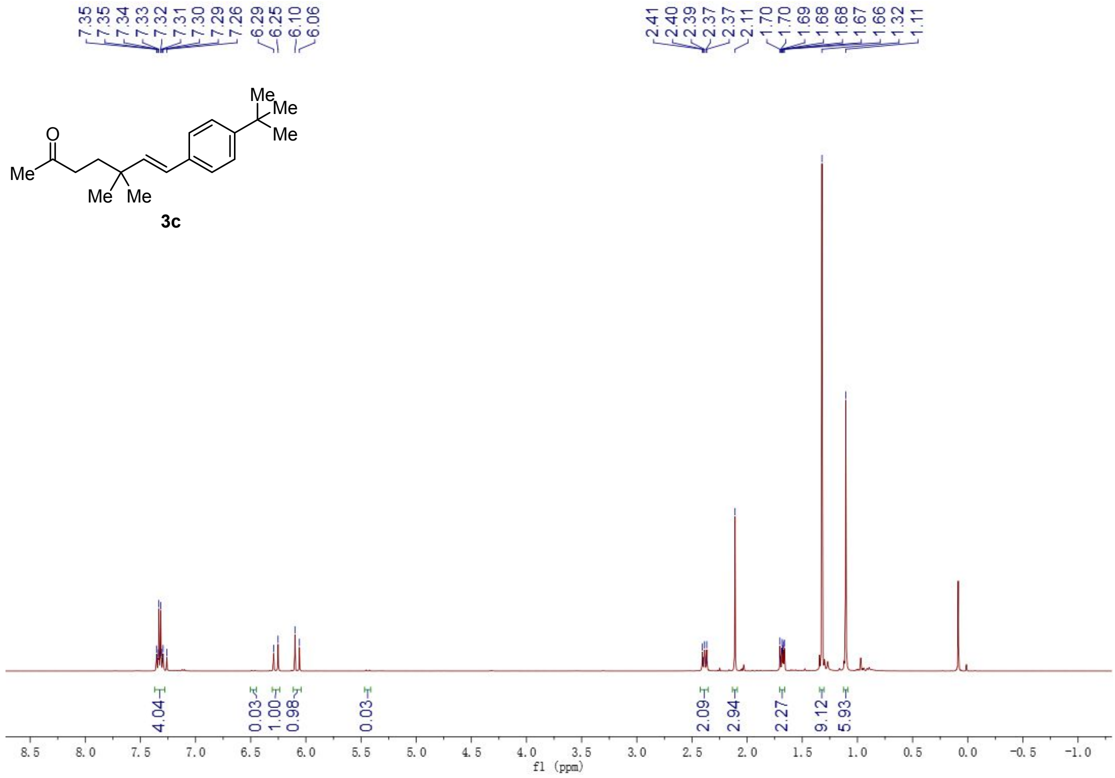
29.93
29.14
27.30
3b
OMe
Me
Me
f1 (ppm)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2.41
2.40
2.39
2.37
2.37
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1.70
1.70
1.69
1.68
1.68
1.67
1.66
1.32
1.11
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0.03
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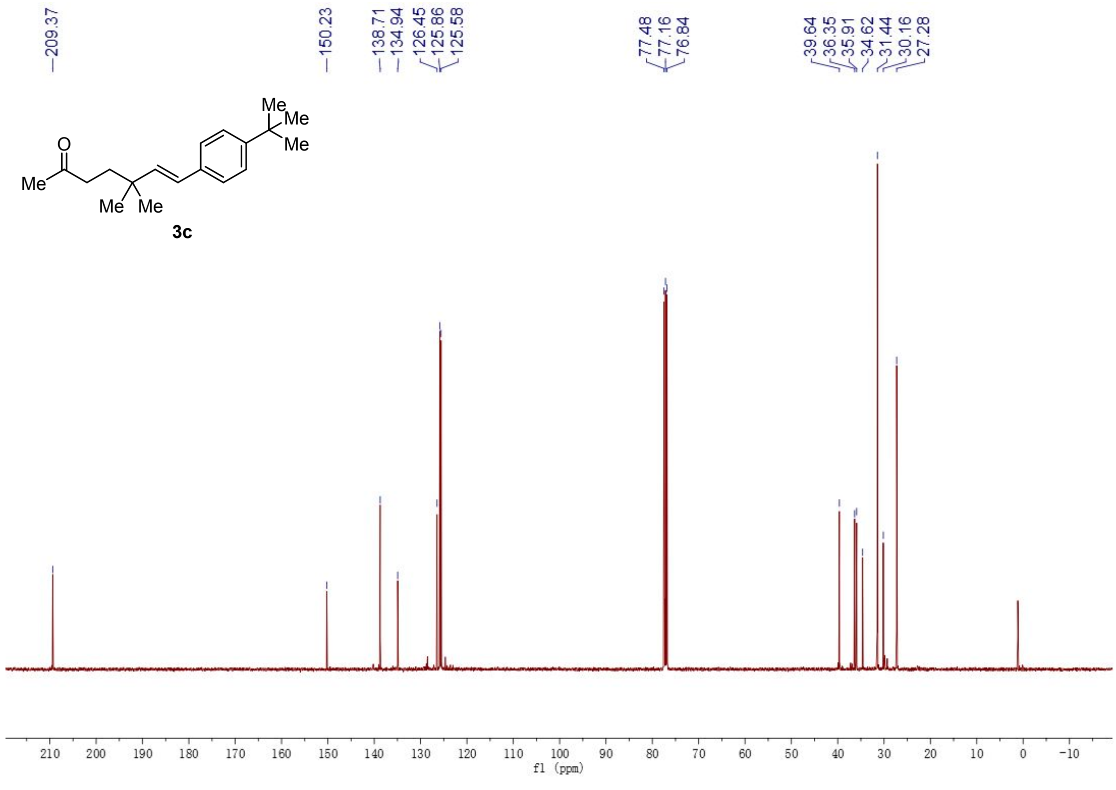
2.94
2.27
9.12
5.93
f1 (ppm)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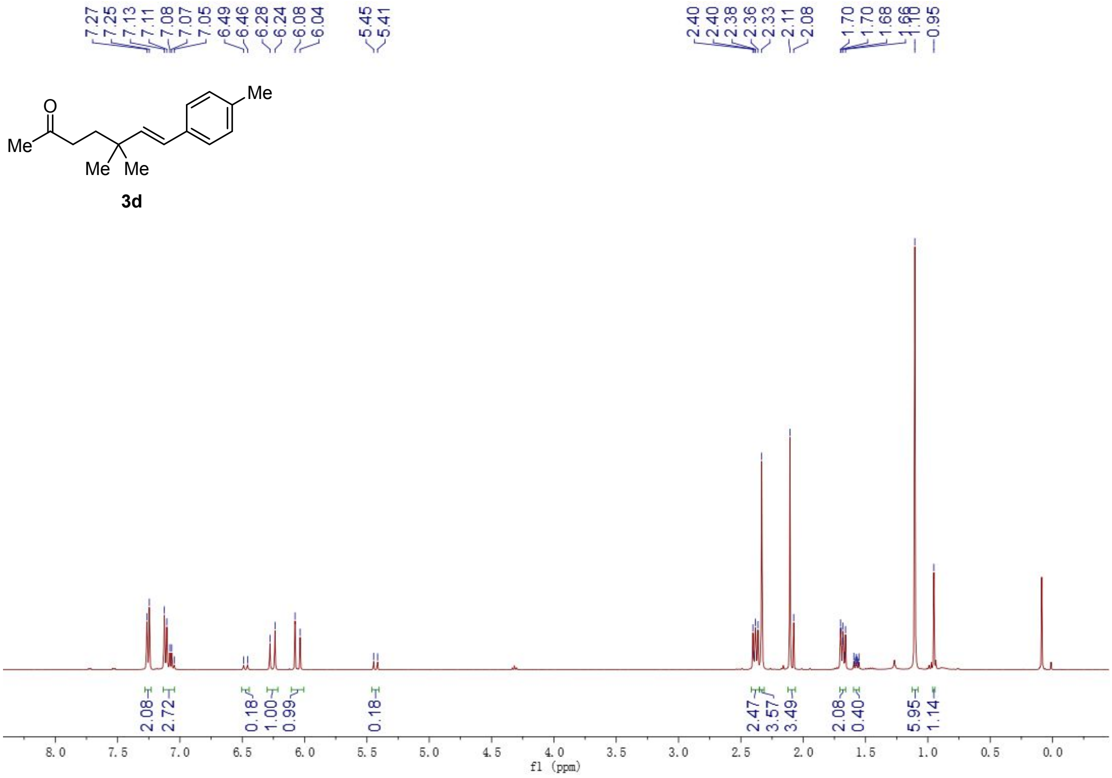
f1 (ppm)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2.40
2.40
2.38
2.36
2.33
2.11
2.08
1.70
1.70
1.68
1.66
1.10
0.95
Me
O
Me
Me Me
3d
2.08
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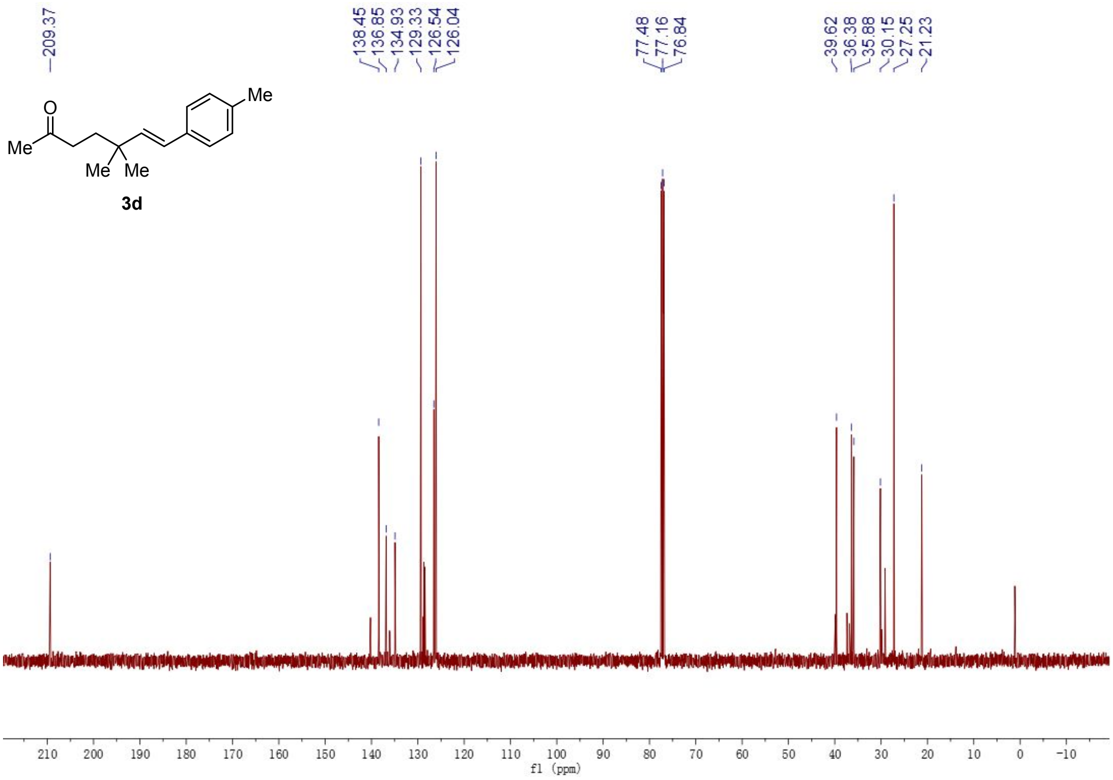
f1 (ppm)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134.93
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126.54
126.04
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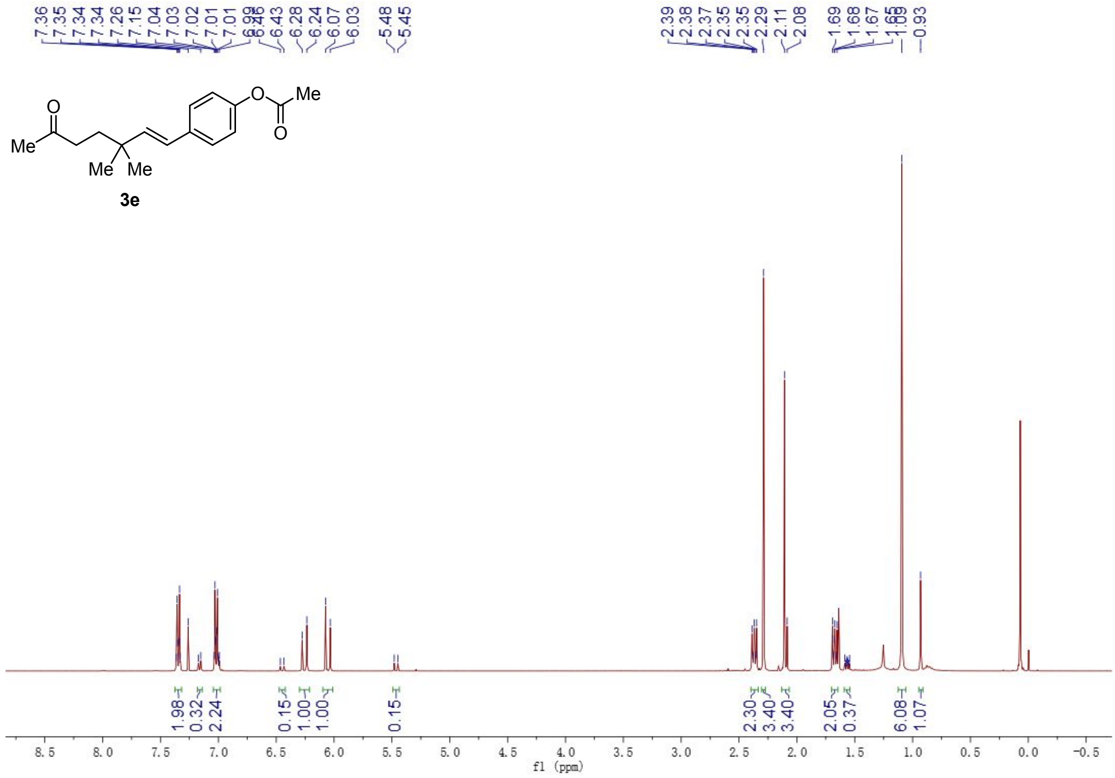
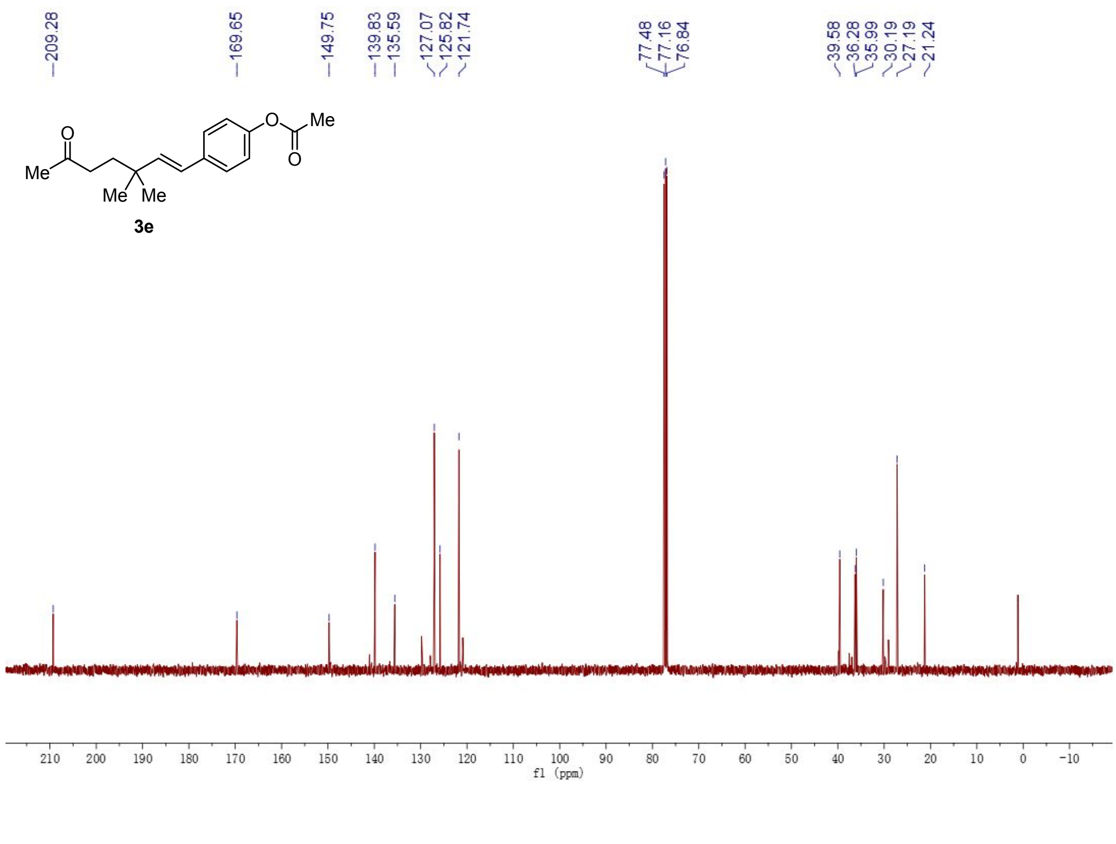
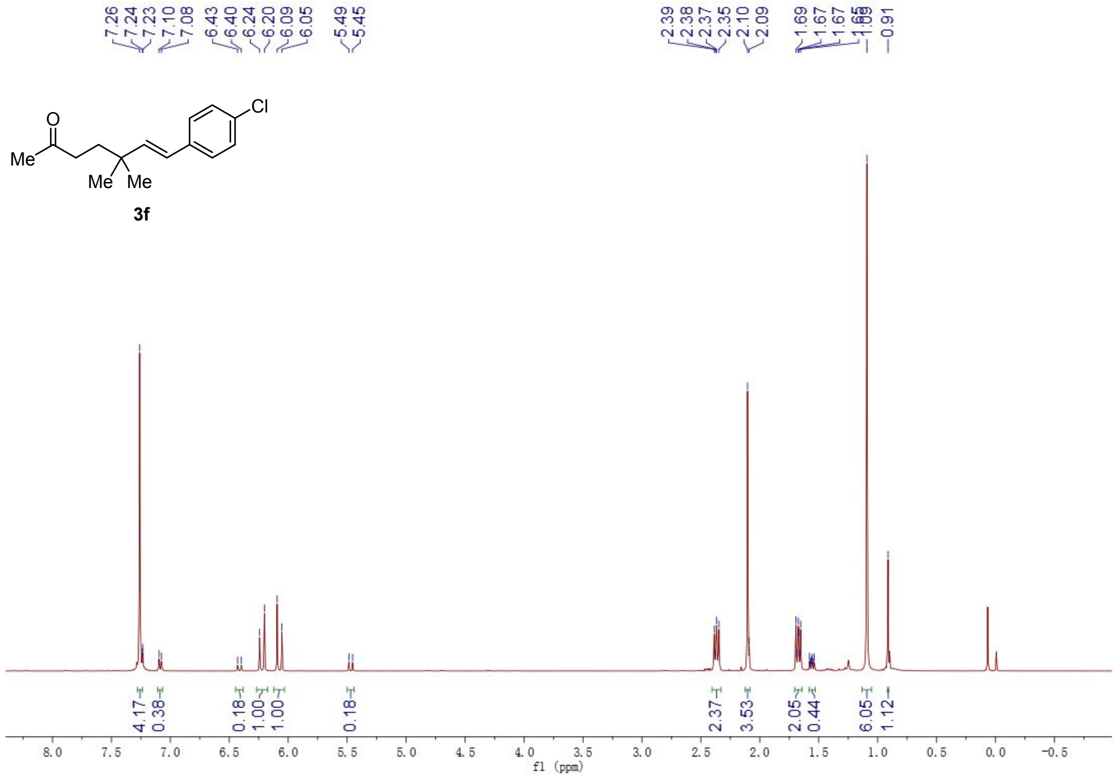
35.88
30.15
27.25
21.23
Me
O
Me
Me Me
3d
f1 (ppm)



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5.45
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2.38
2.37
2.35
2.10
2.09
1.69
1.67
1.67
1.65
0.91
Cl
O
Me
Me
Me
3f
4.17
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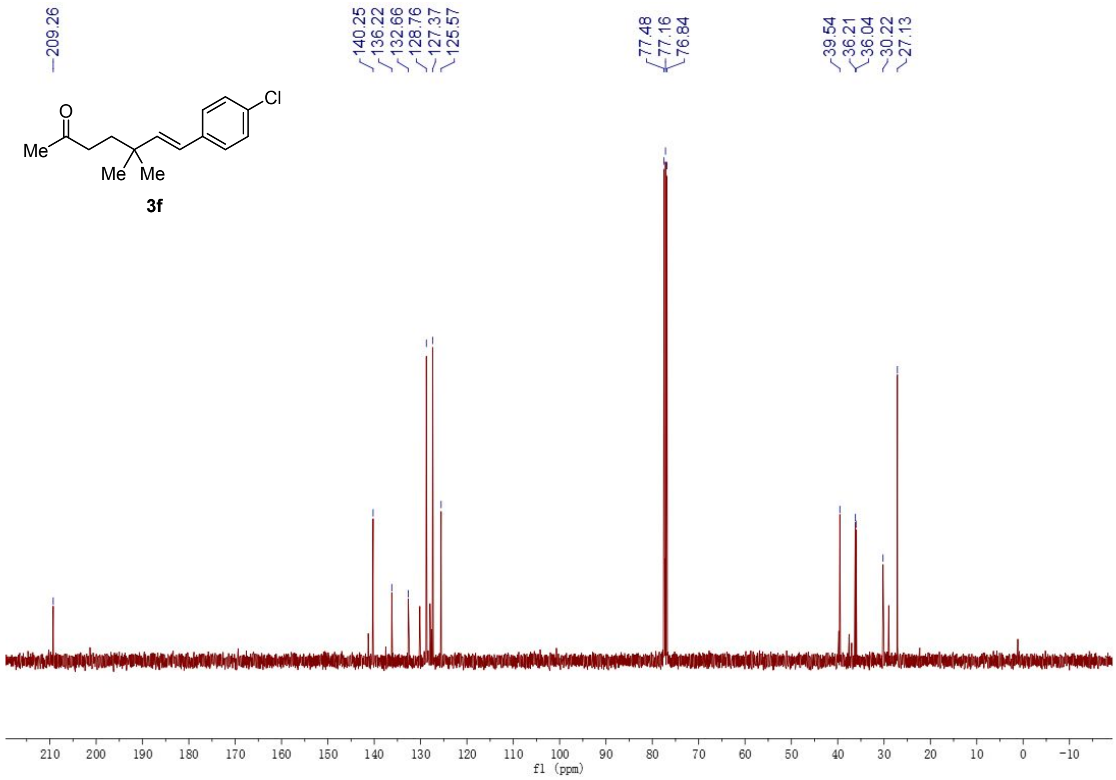
1.12
f1 (ppm)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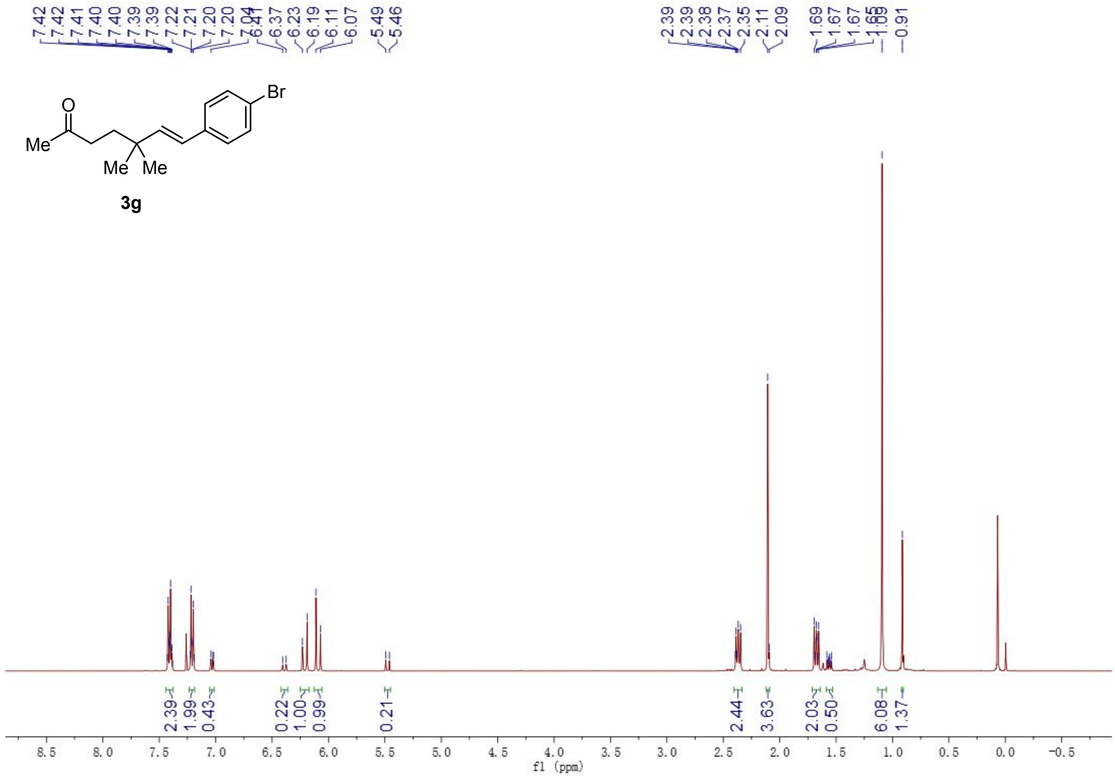
27.13
Cl
O
Me
Me
Me
3f
f1 (ppm)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2.39 2.39 2.38 2.37 2.35 2.11 2.09 1.69 1.67 1.67 0.91
Br
O
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Me Me
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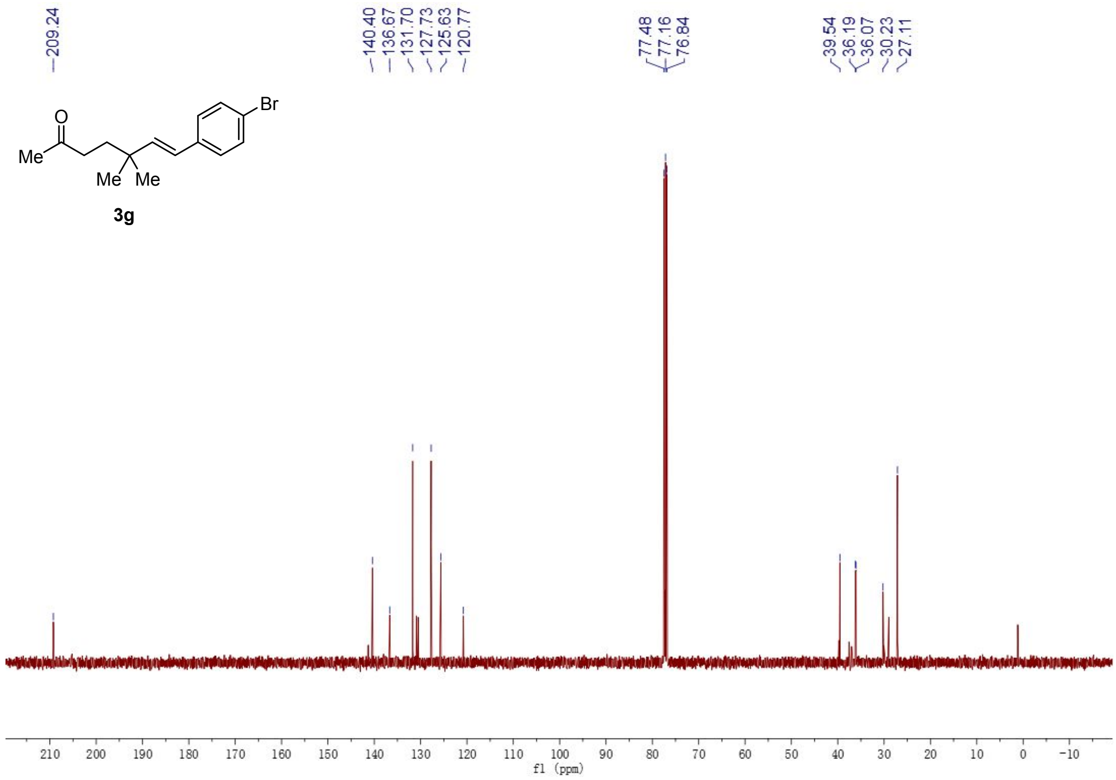
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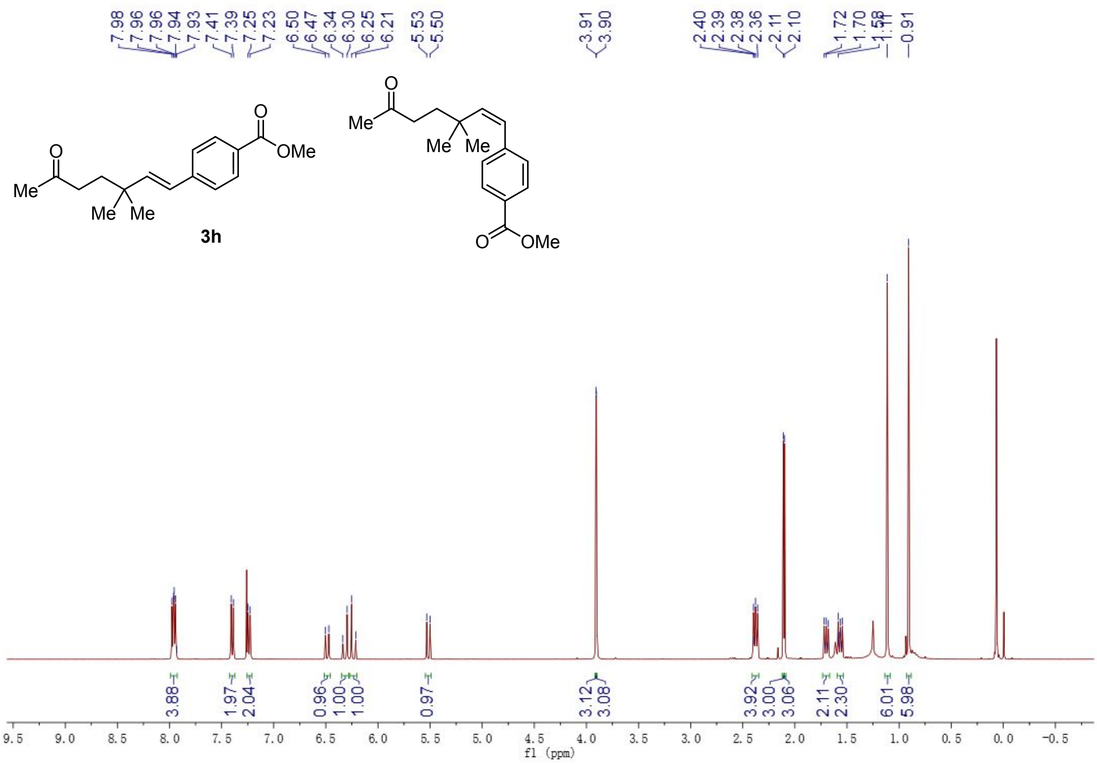
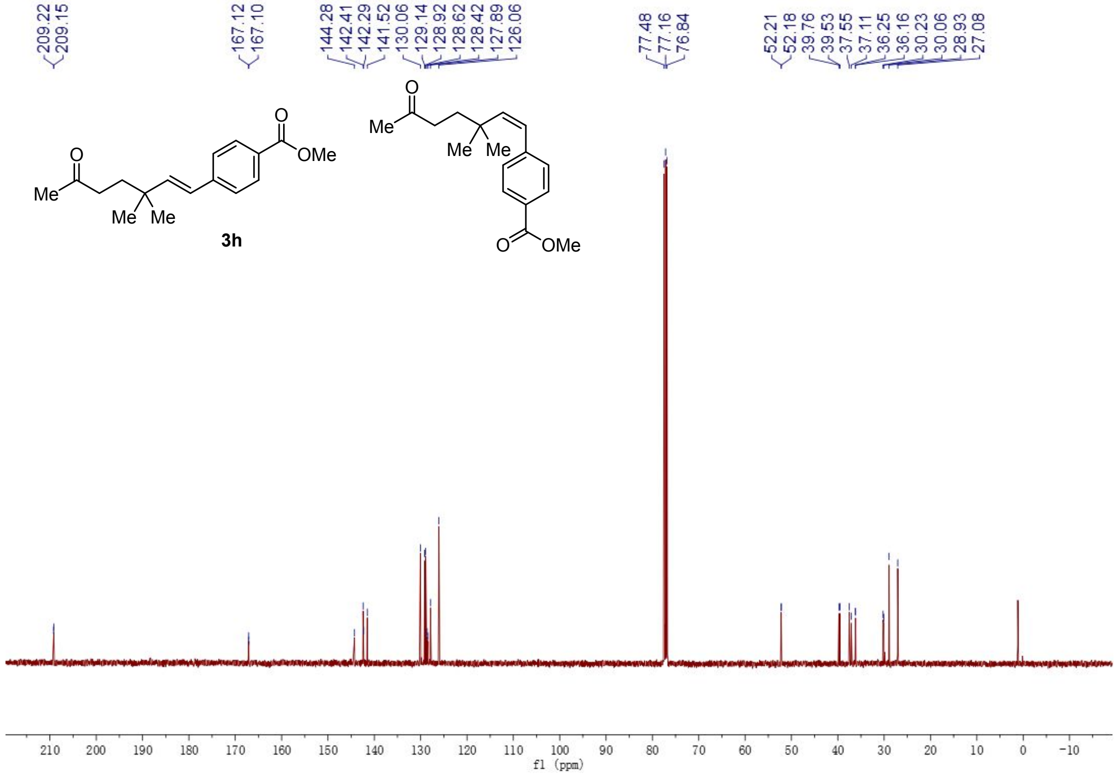
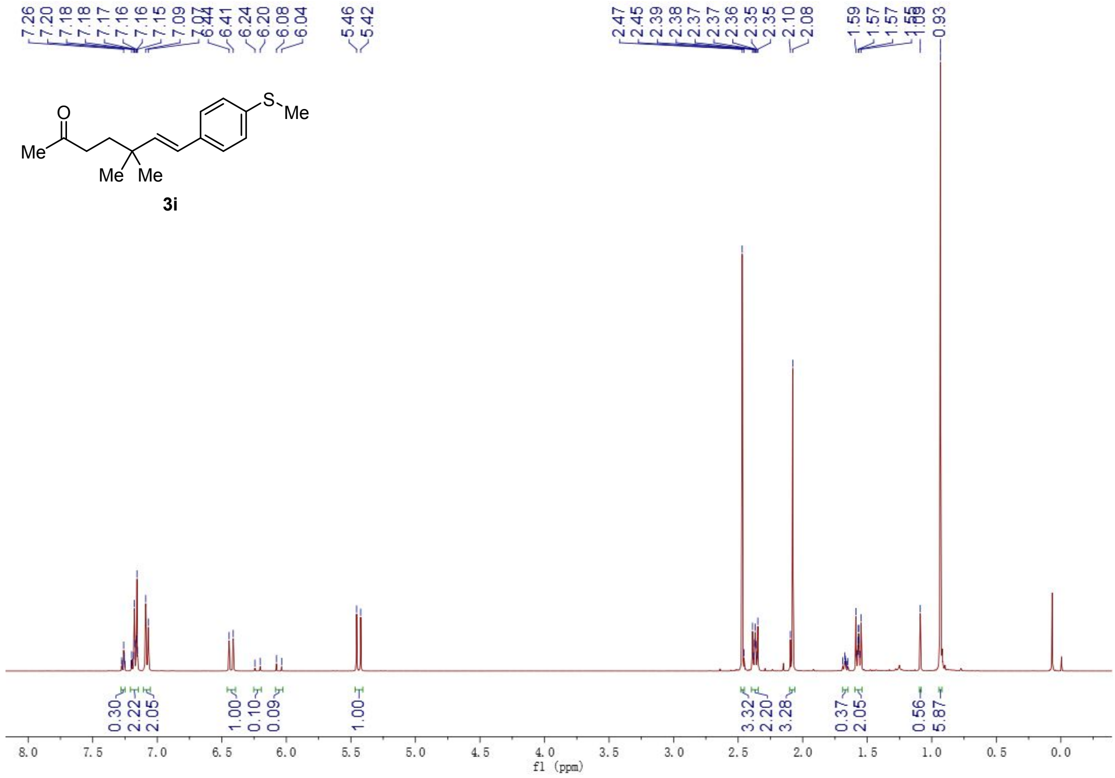
Me Me
3g
f1 (ppm)



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2.47 2.45 2.39 2.38 2.37 2.37 2.36 2.35 2.35 2.10 2.08 1.59 1.57 1.57 1.55 1.09 0.93
S
Me
O
Me
Me Me
3i
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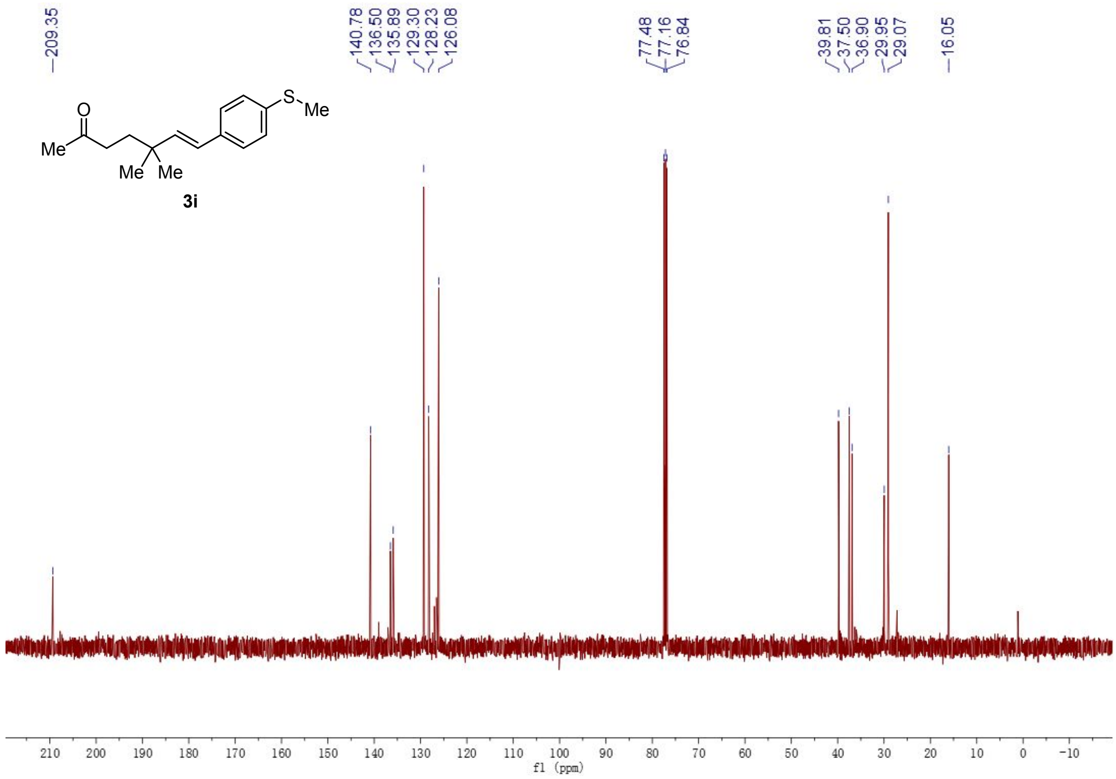
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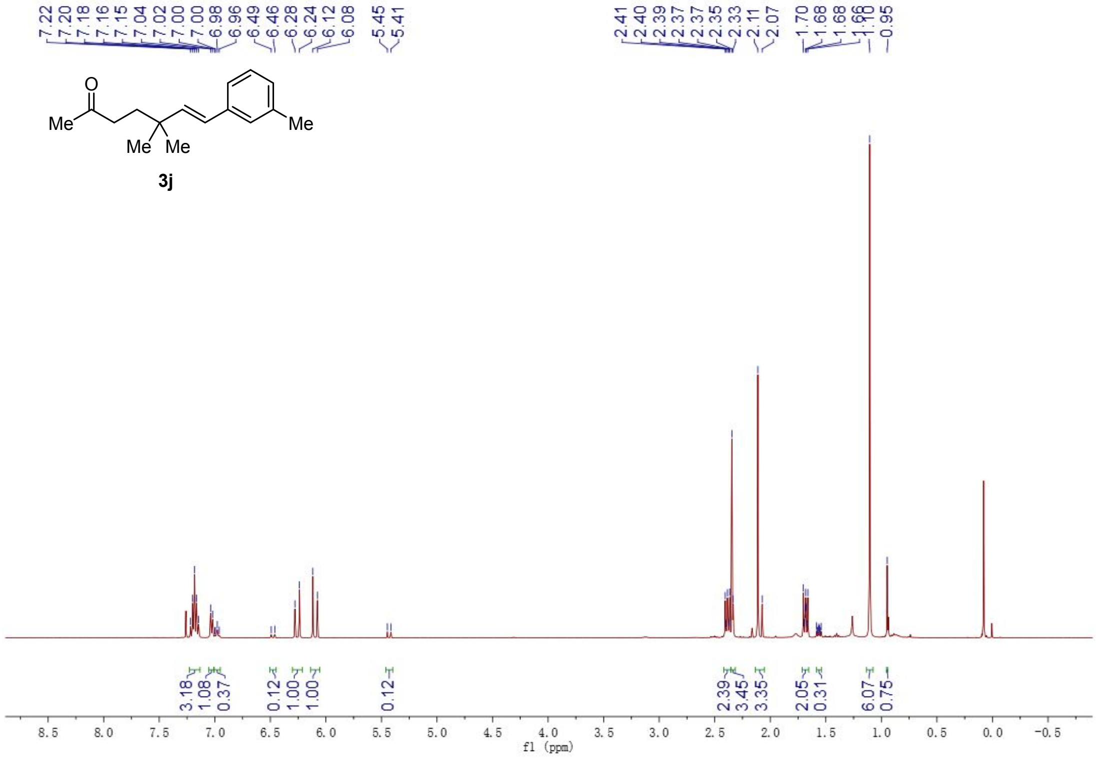
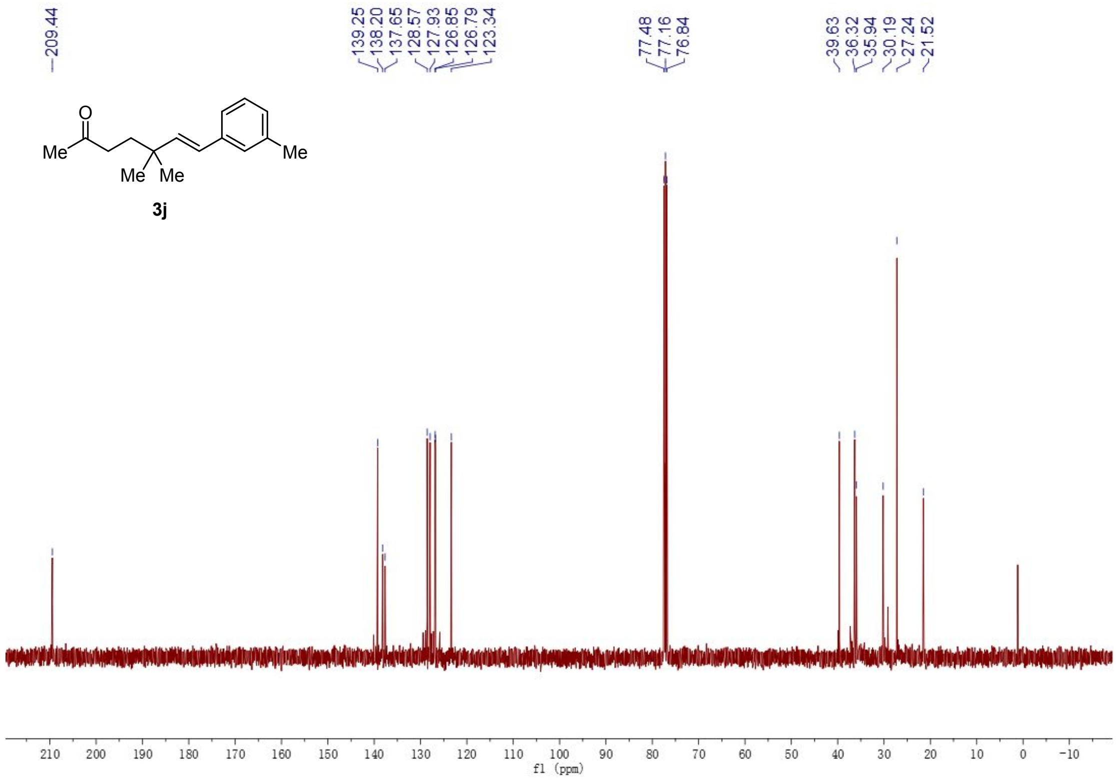
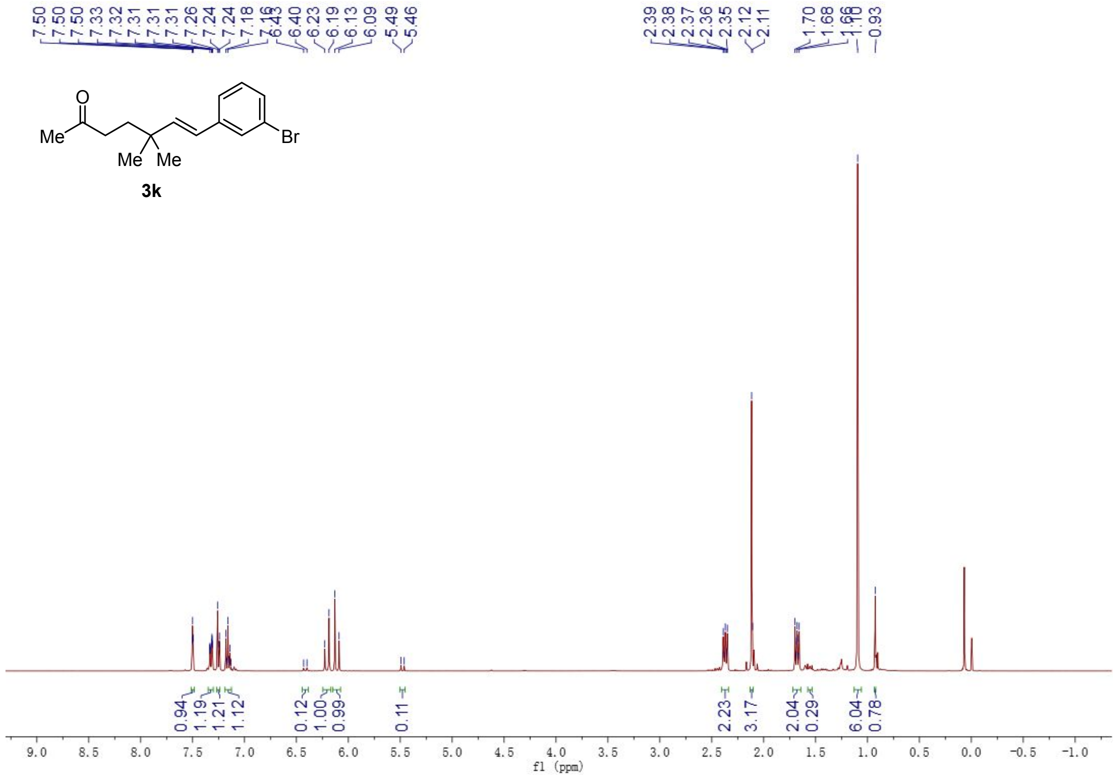
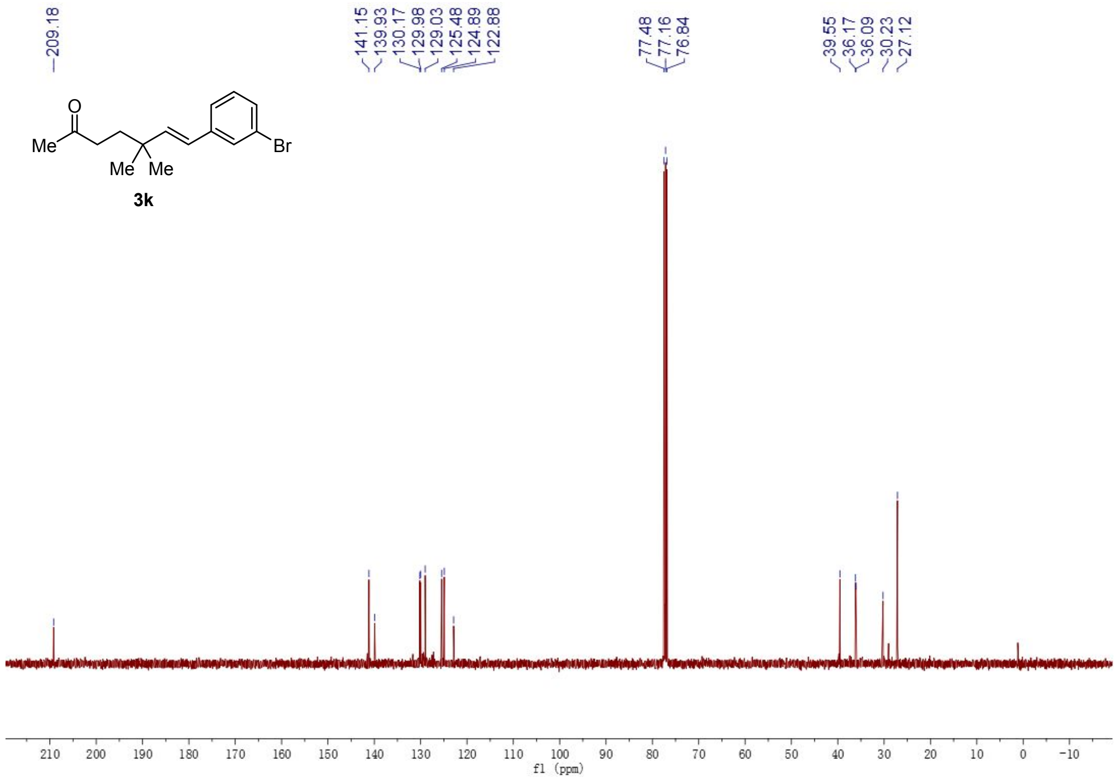
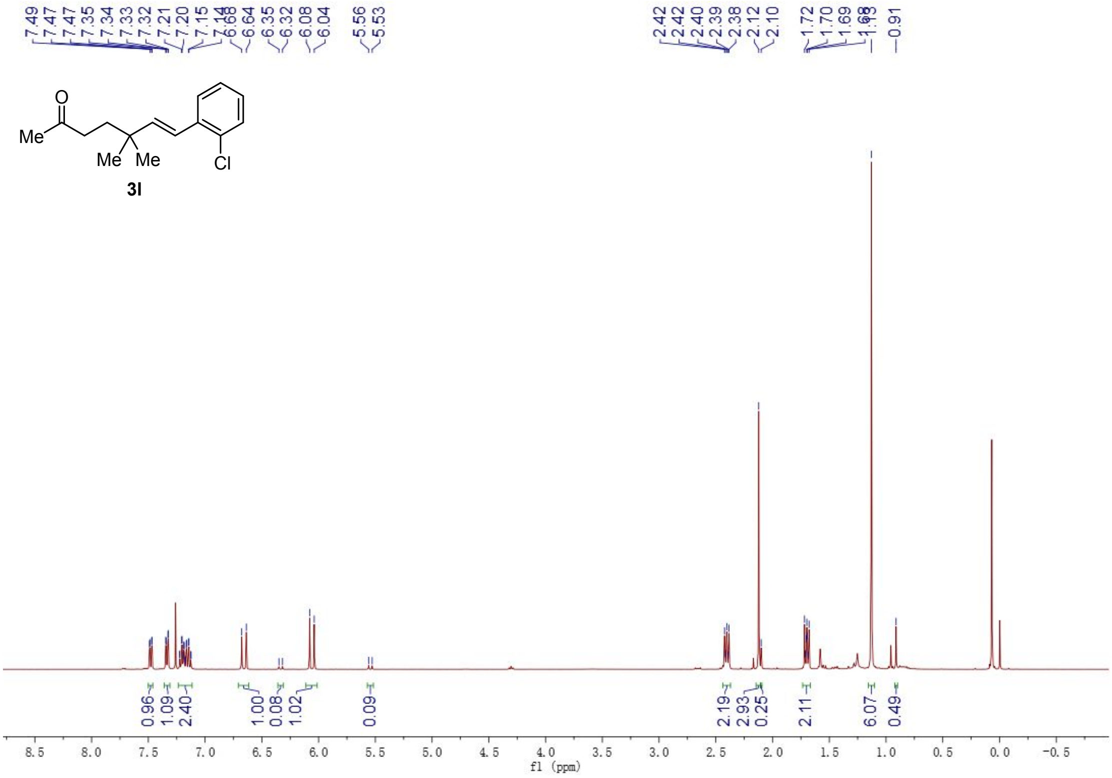
Me
O
Me
Me Me
3i
f1 (ppm)







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6.08
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2.42
2.42
2.40
2.39
2.38
2.12
2.10
1.72
1.70
1.69
1.68
1.13
0.91
O
Me
Me
Me
Cl
3l
0.96
1.09
2.40
1.00
0.08
1.02
0.09
2.19
2.93
0.25
2.11
6.07
0.49
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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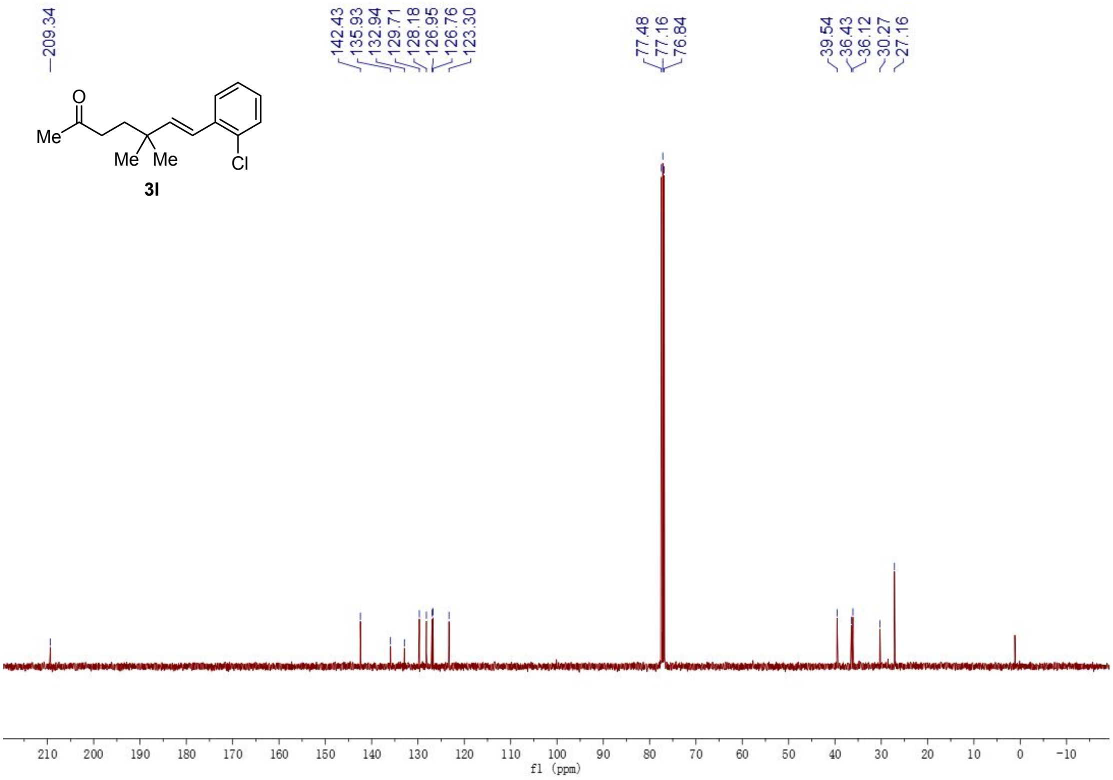
0.0
-0.5
f1 (ppm)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36.43
36.12
30.27
27.16
O
Me
Me
Me
Cl
3l
210
200
190
180
170
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100
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80
70
60
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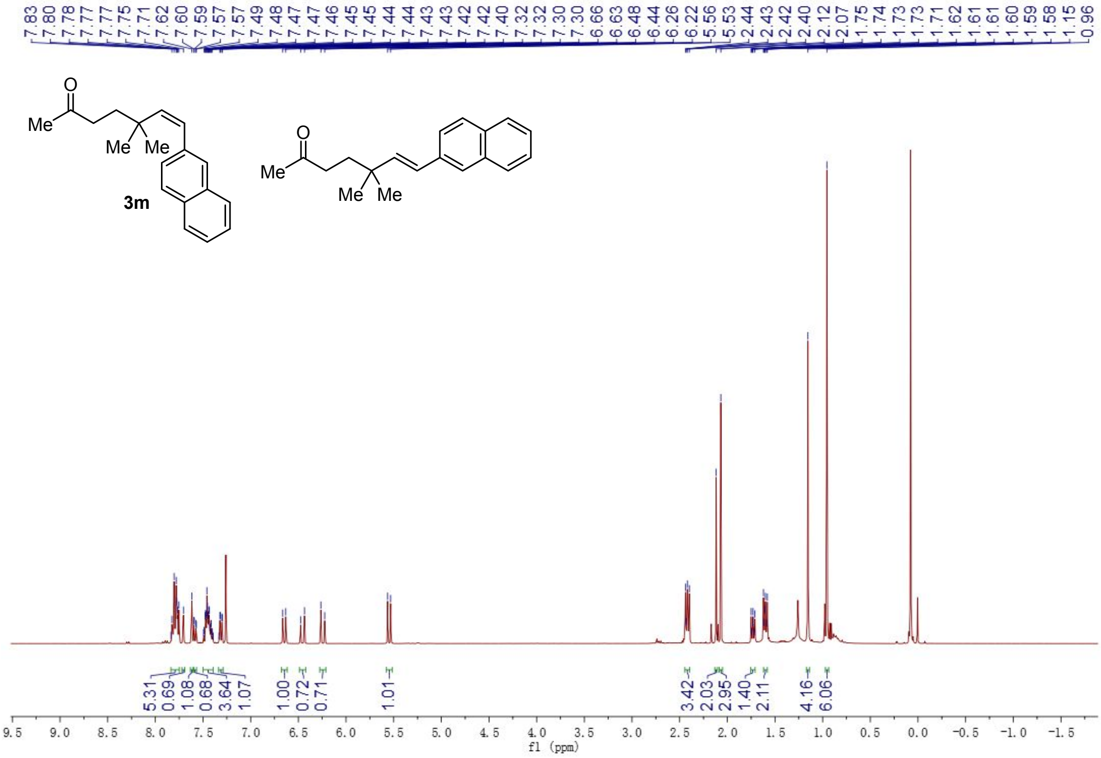
40
30
20
10
0
-10
f1 (ppm)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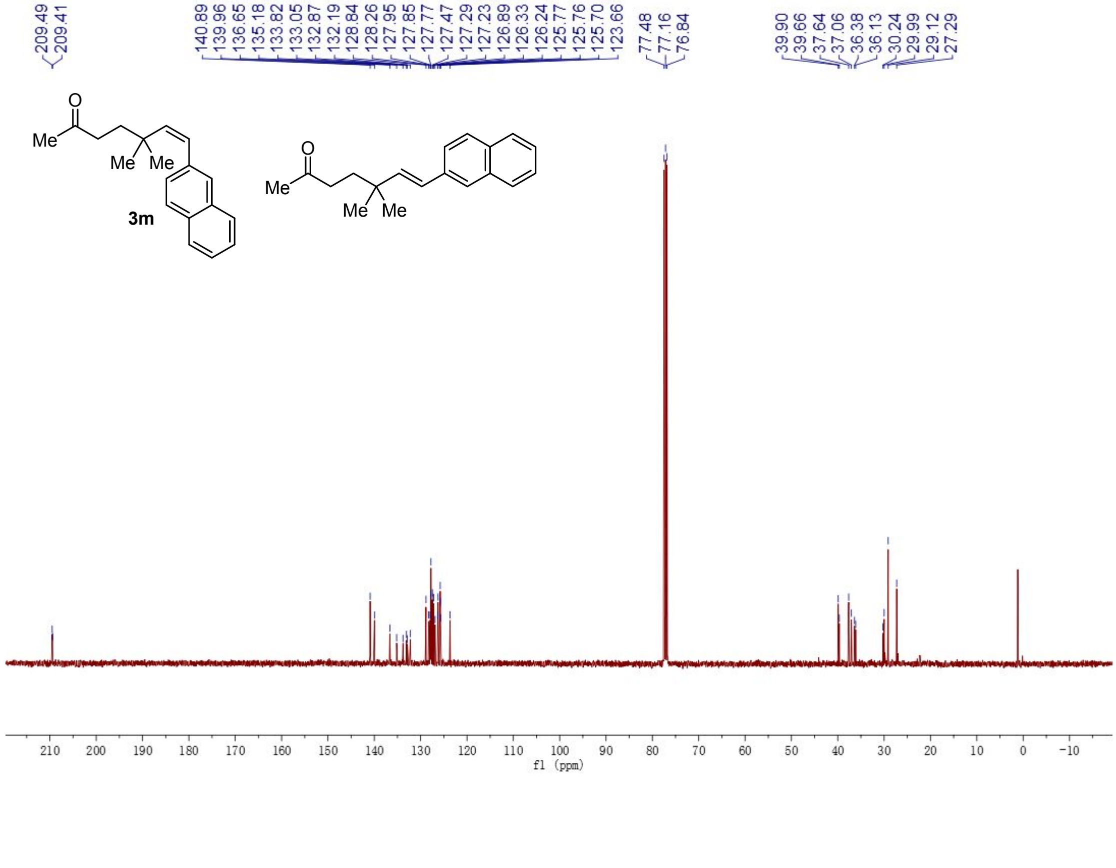
Me
Me Me
3m
5.31 0.69 1.08 0.68 3.64 1.07 1.00 0.72 0.71 1.01 3.42 2.03 2.95 1.40 2.11 4.16 6.06
f1 (ppm)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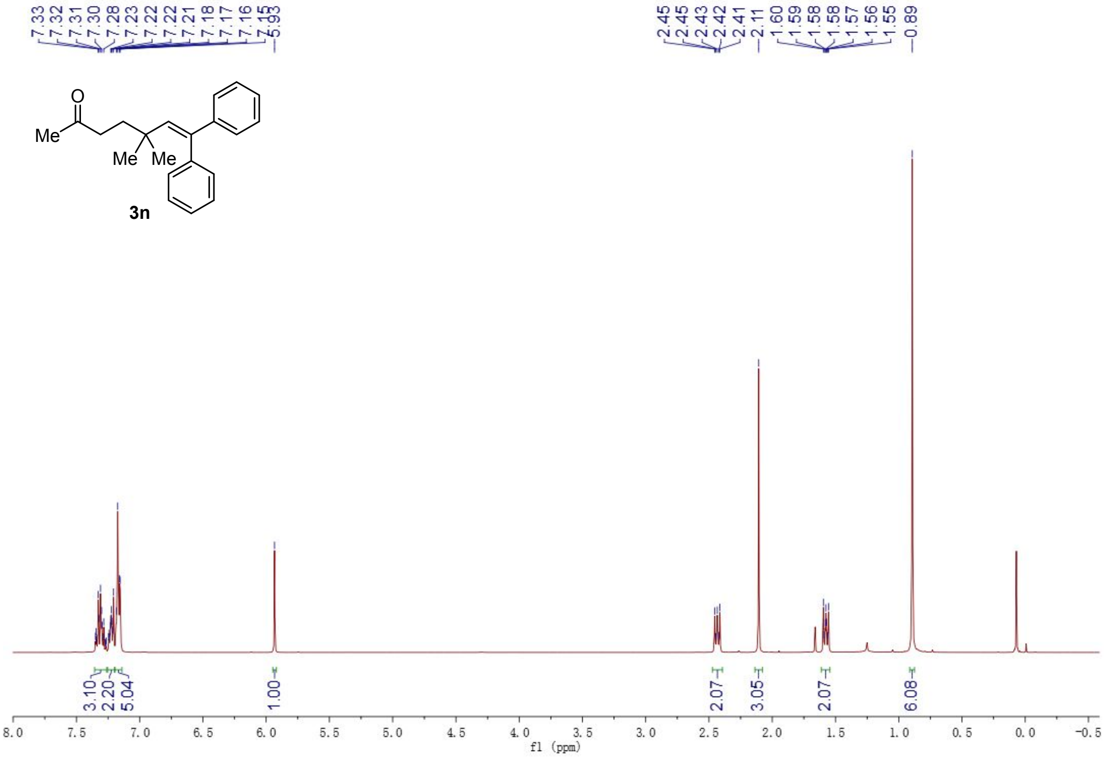
77.48 77.16 76.84
39.90 39.66 37.64 37.06 36.38 36.13 30.24 29.99 29.12 27.29
Me
Me Me
3m
f1 (ppm)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2.45
2.43
2.42
2.41
2.11
1.60
1.59
1.58
1.58
1.57
1.56
1.55
0.89
Me
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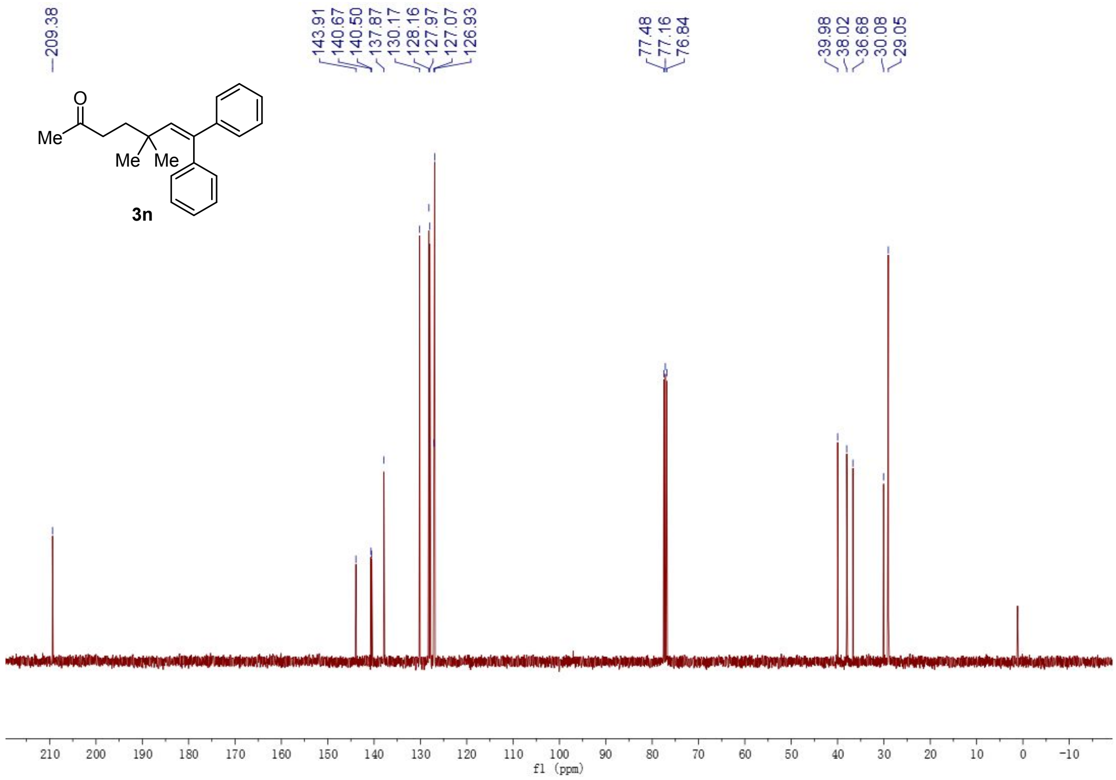
Me
Me
3n
3.10
2.20
5.04
1.00
2.07
3.05
2.07
6.08
fl (ppm)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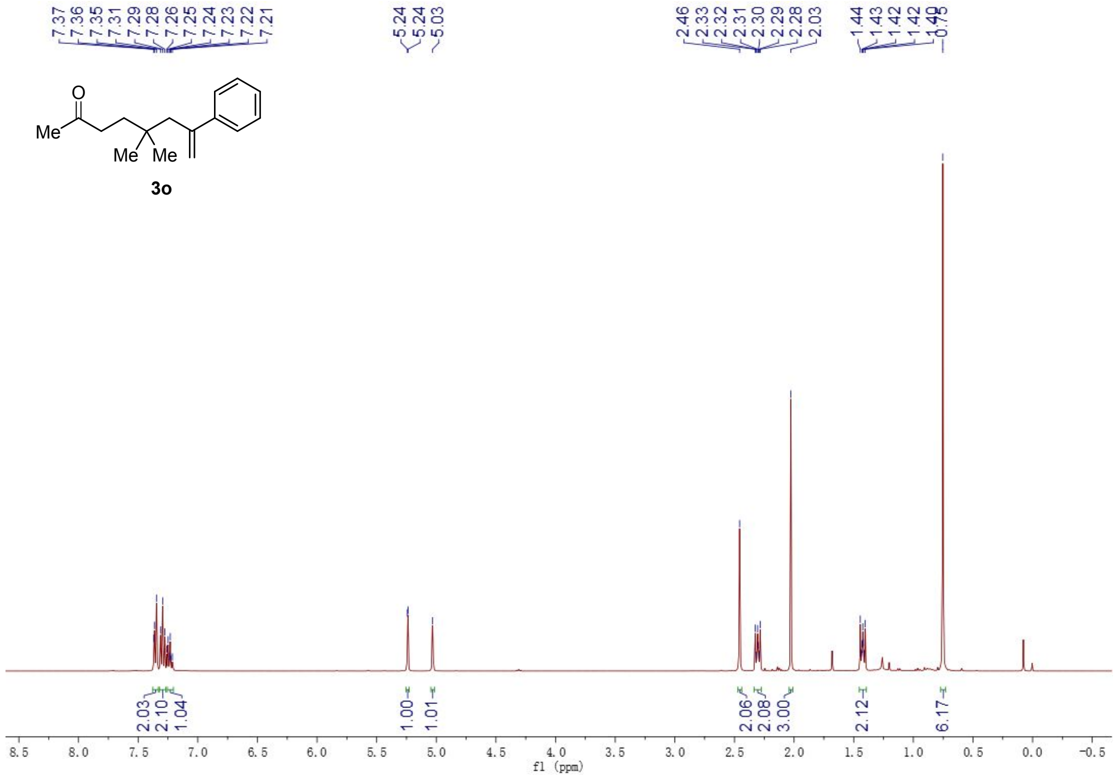
36.68
30.08
29.05
Me
O
Me
Me
3n
fl (ppm)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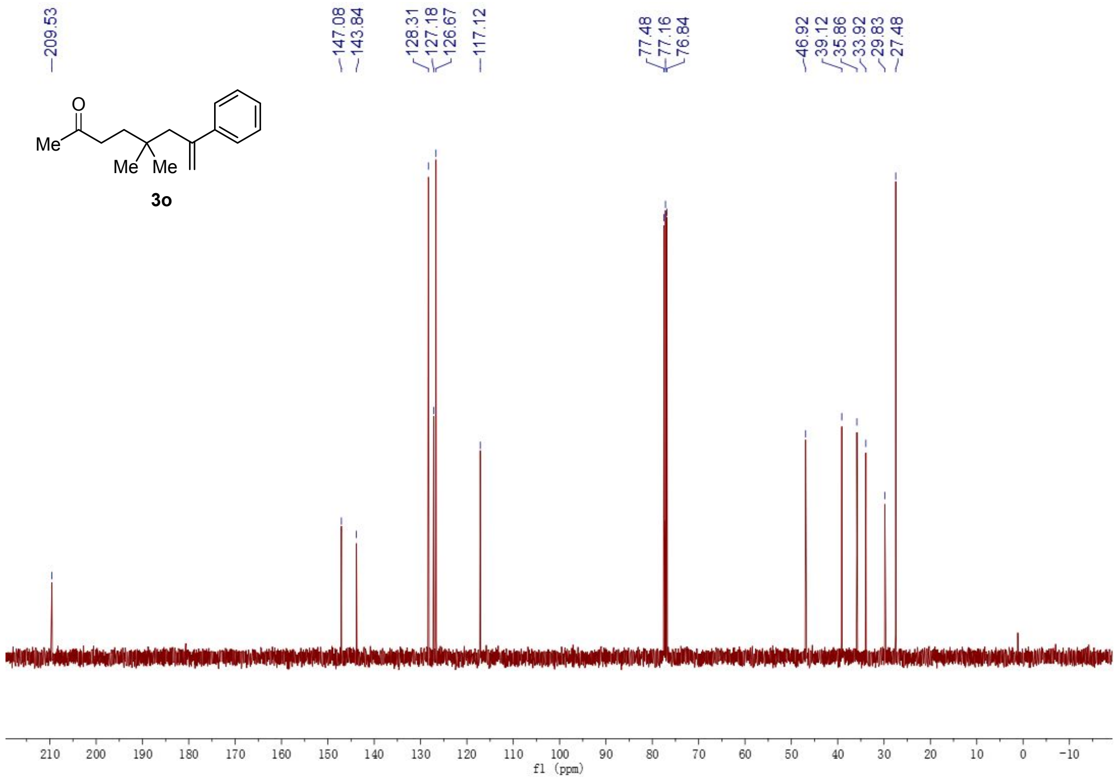
5.24 5.24 5.03
2.46 2.33 2.32 2.31 2.30 2.29 2.28 2.03
1.44 1.43 1.42 1.42 1.40 0.75
O
Me
Me Me
3o
2.03 2.10 1.04
1.00 1.01
2.06 2.08 3.00
2.12
6.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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117.12
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46.92 39.12 35.86 33.92 29.83 27.48
O
Me
Me Me
3o
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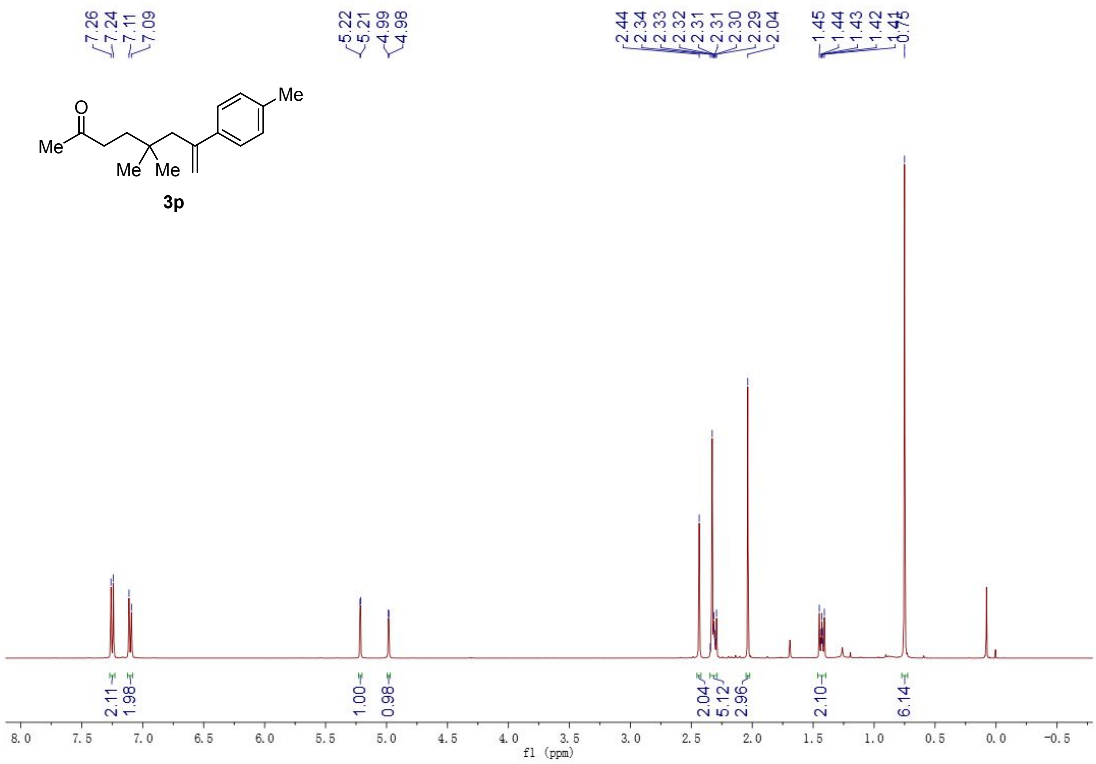
f1 (ppm)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2.31
2.31
2.30
2.29
2.04
1.45
1.44
1.43
1.42
1.41
0.75
O
Me
Me
Me
Me
3p
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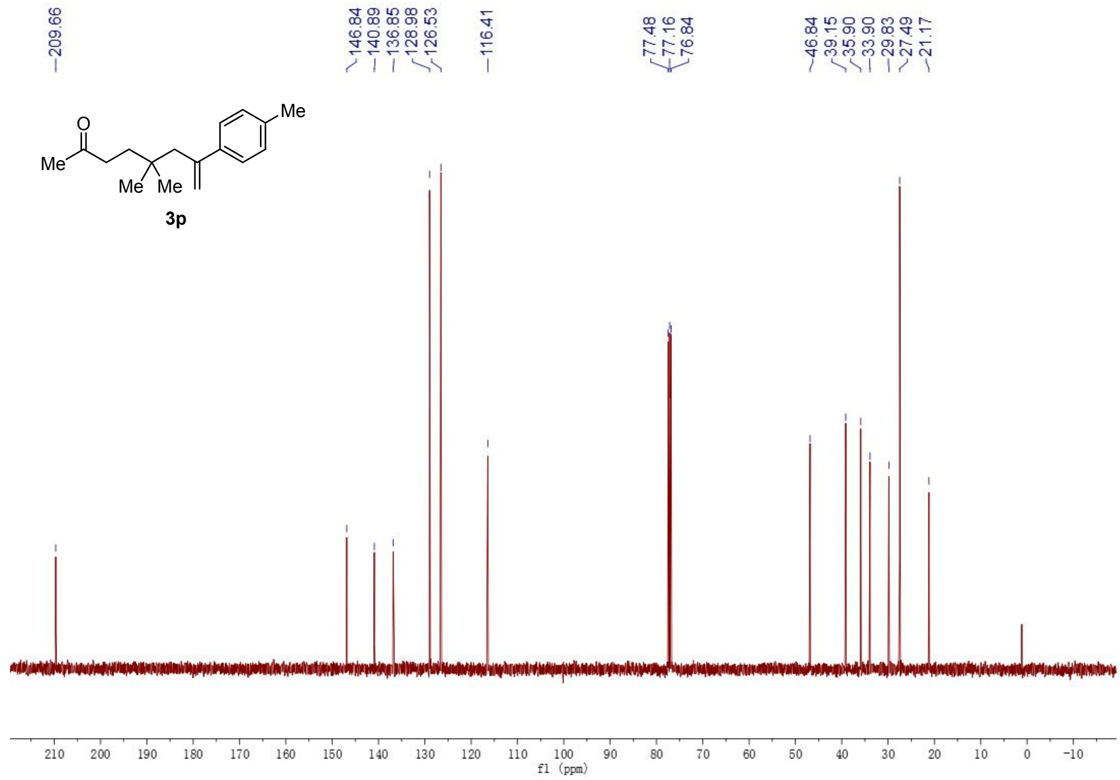
1.00
0.98
2.04
5.12
2.96
2.10
6.14
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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29.83
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Me
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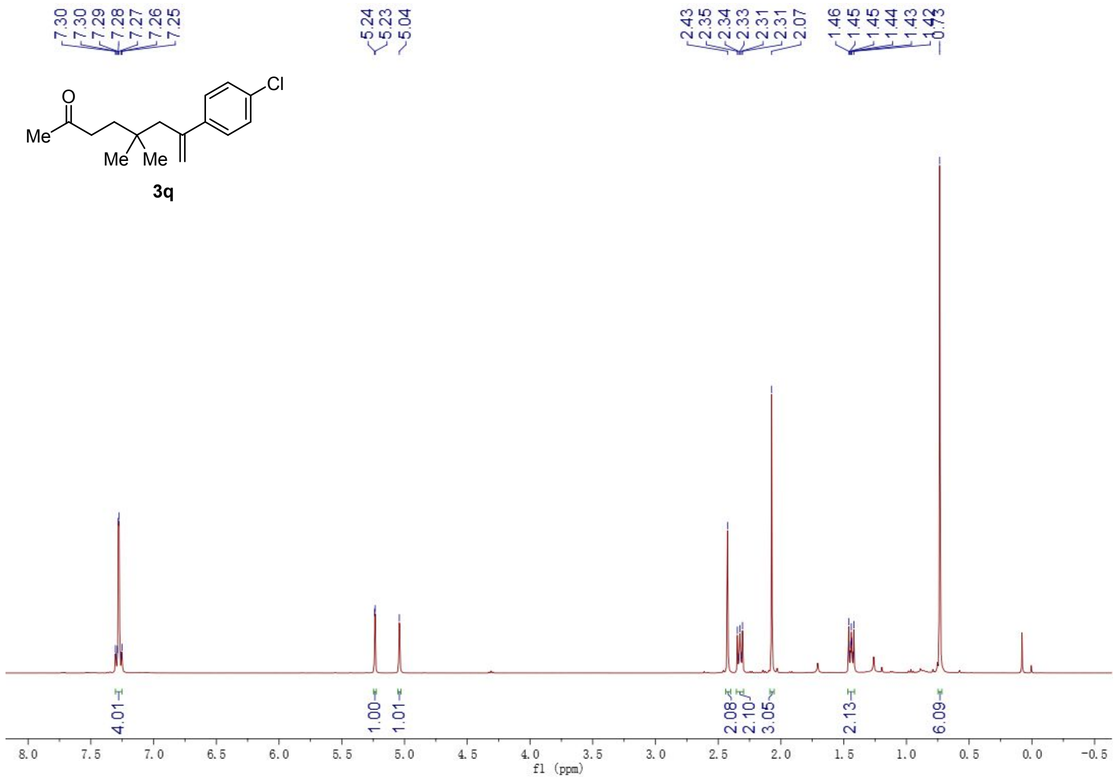
f1 (ppm)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2.43 2.35 2.34 2.33 2.31 2.31 2.07
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Cl
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Me Me
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1.01
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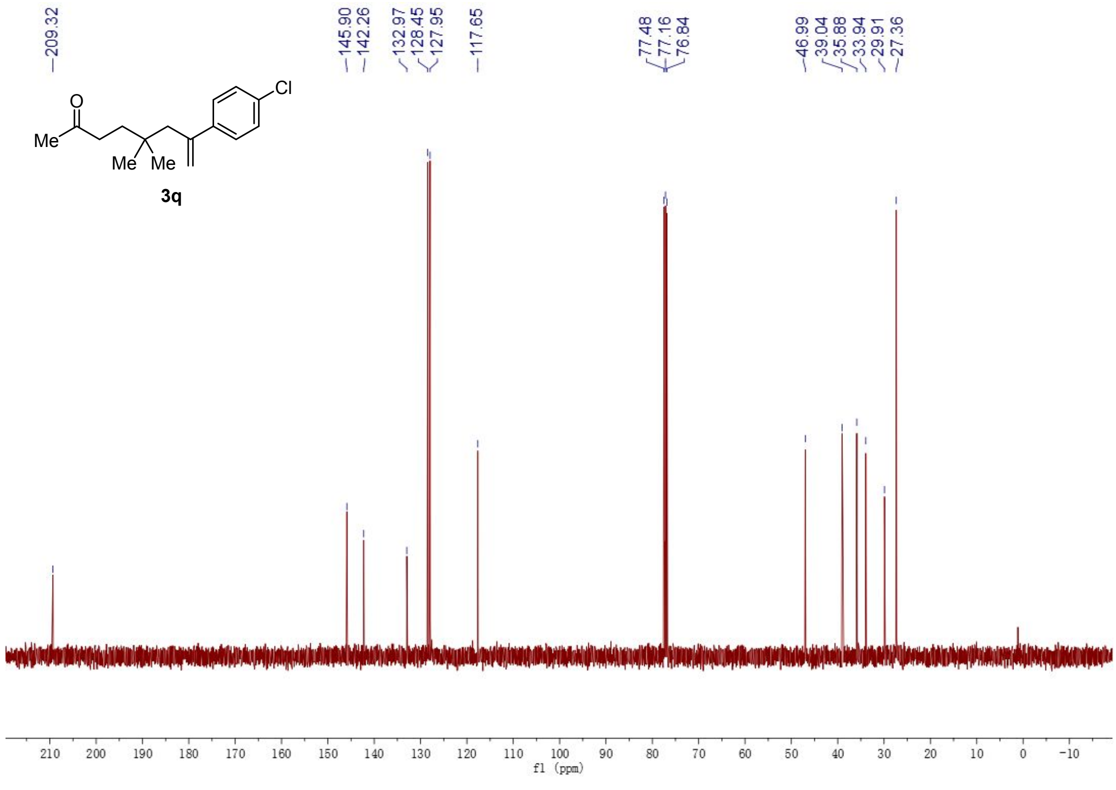
2.10
3.05
2.13
6.09
f1 (ppm)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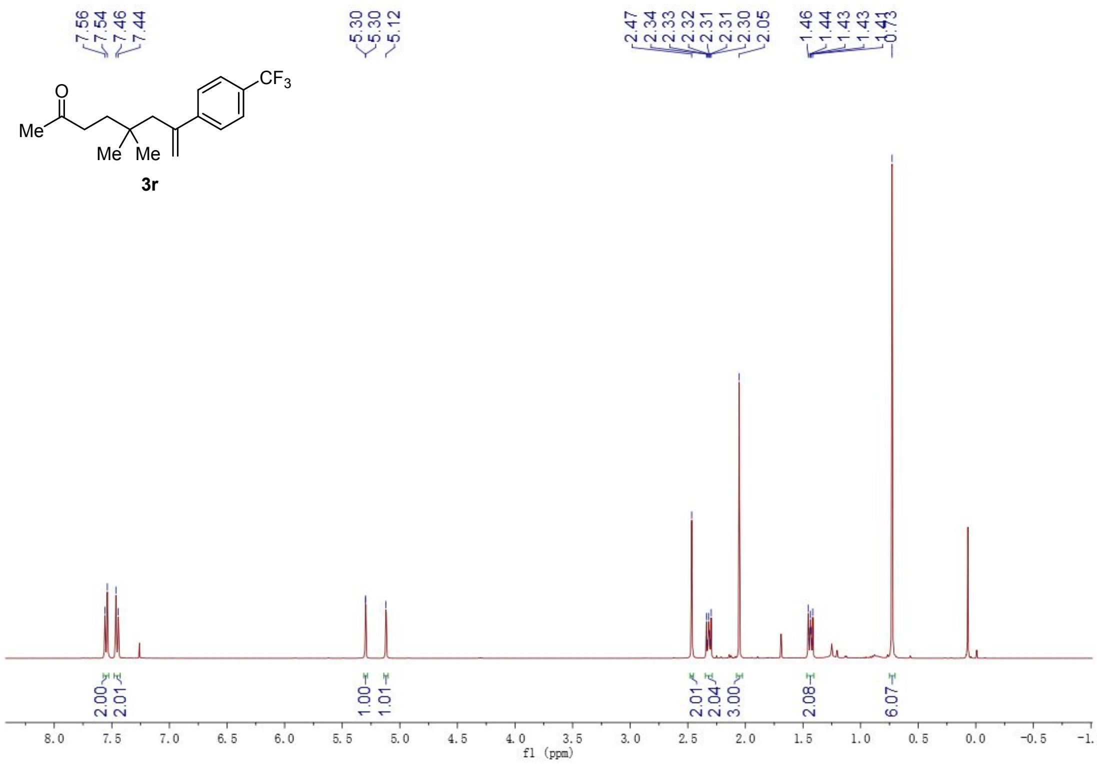
46.99 39.04 35.88 33.94 29.91 27.36
Cl
O
Me
Me Me
3q
f1 (ppm)



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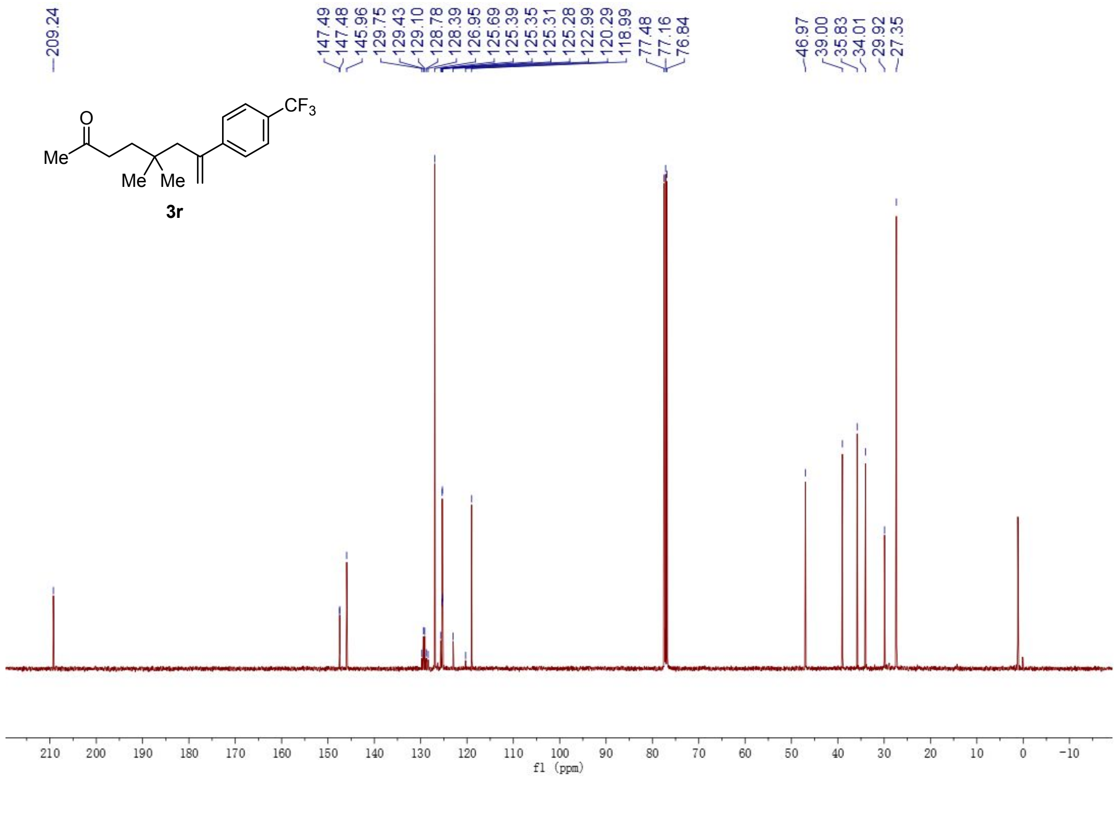

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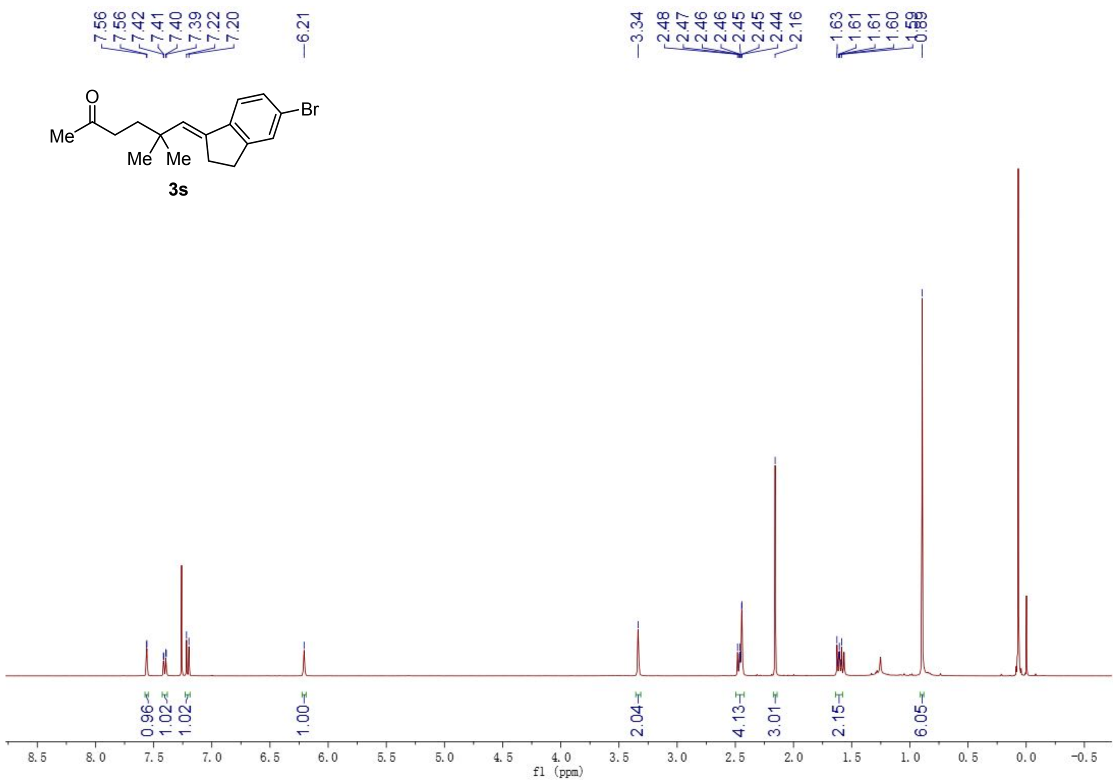

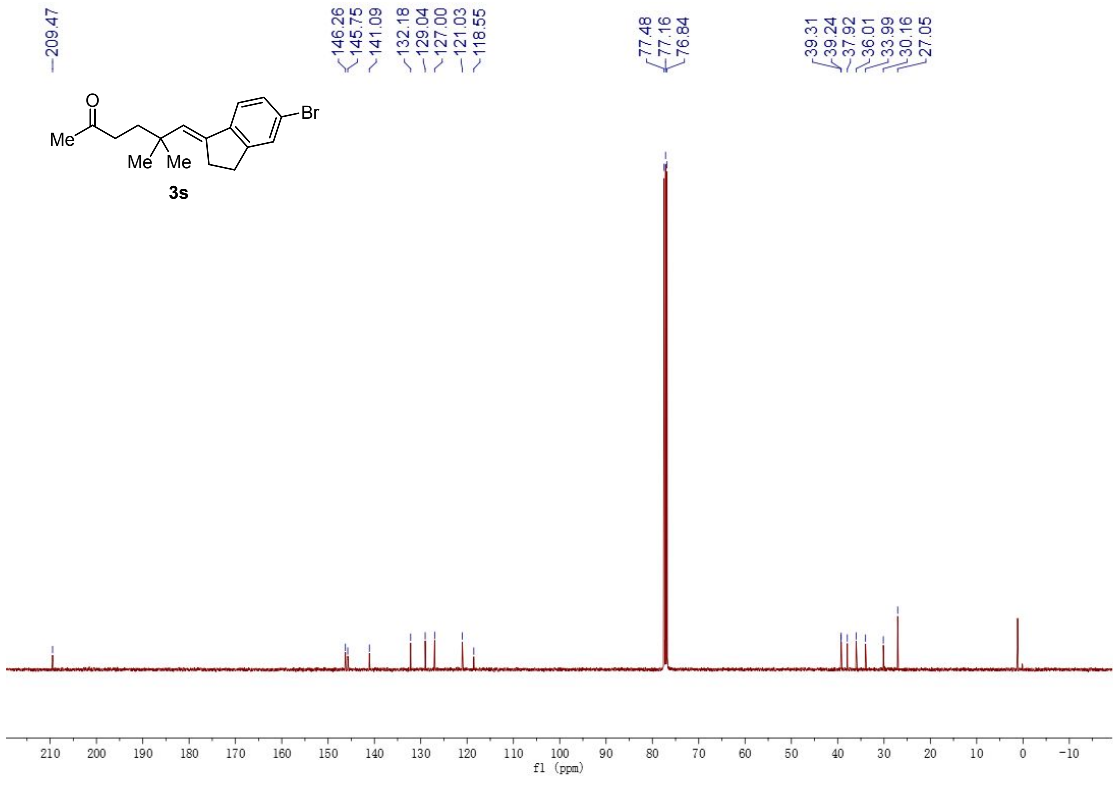

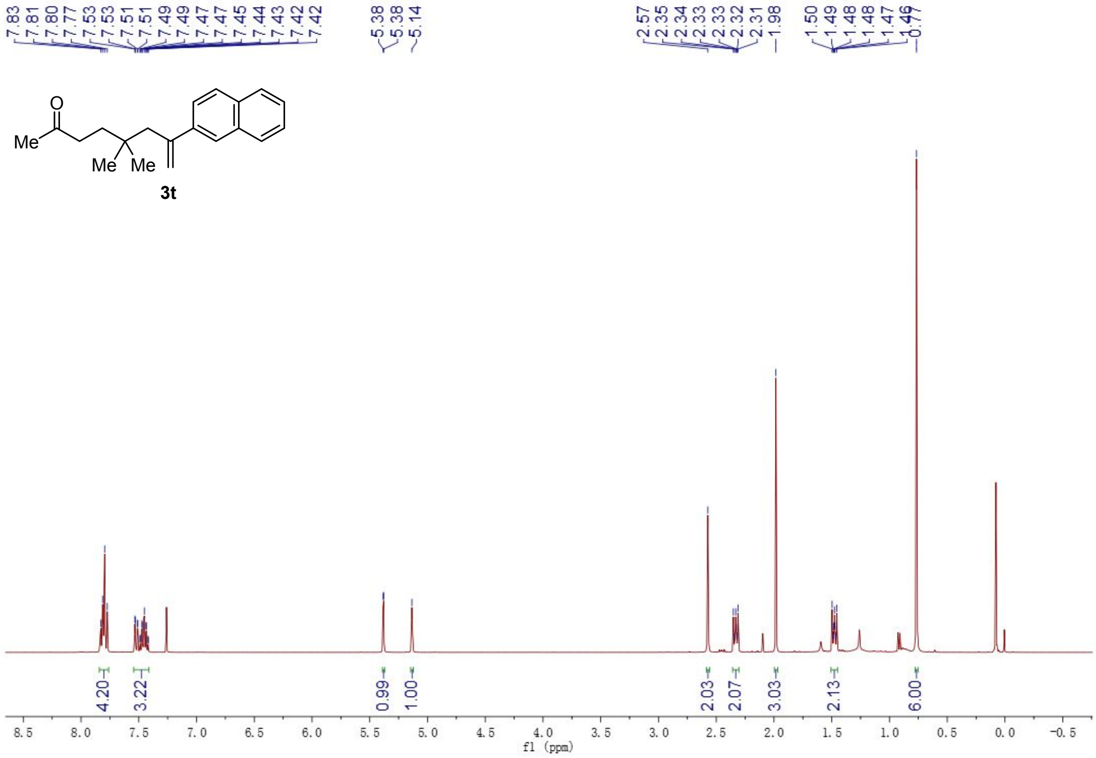

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5.38 5.38 5.14
2.57 2.35 2.34 2.33 2.33 2.32 2.31 1.98
1.50 1.49 1.48 1.48 1.47 1.46 0.77
Me
O
Me Me
3t
4.20 3.22 0.99 1.00 2.03 2.07 3.03 2.13 6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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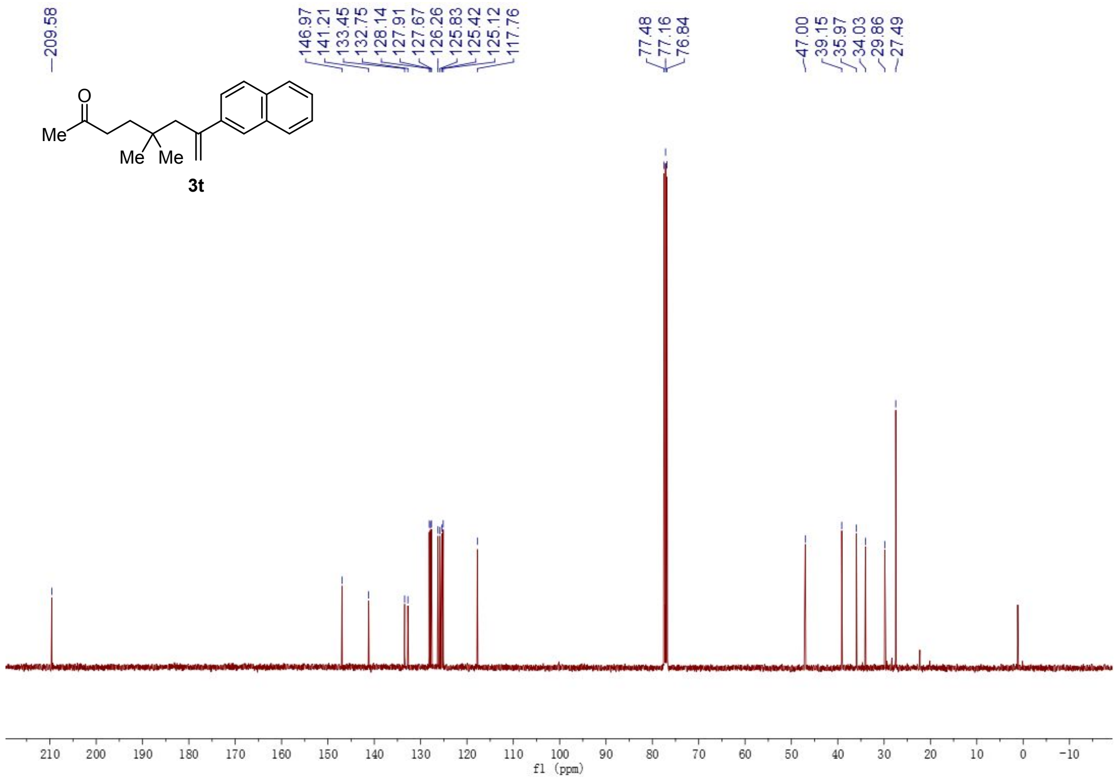

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77.48 77.16 76.84
47.00 39.15 35.97 34.03 29.86 27.49
Me
O
Me Me
3t
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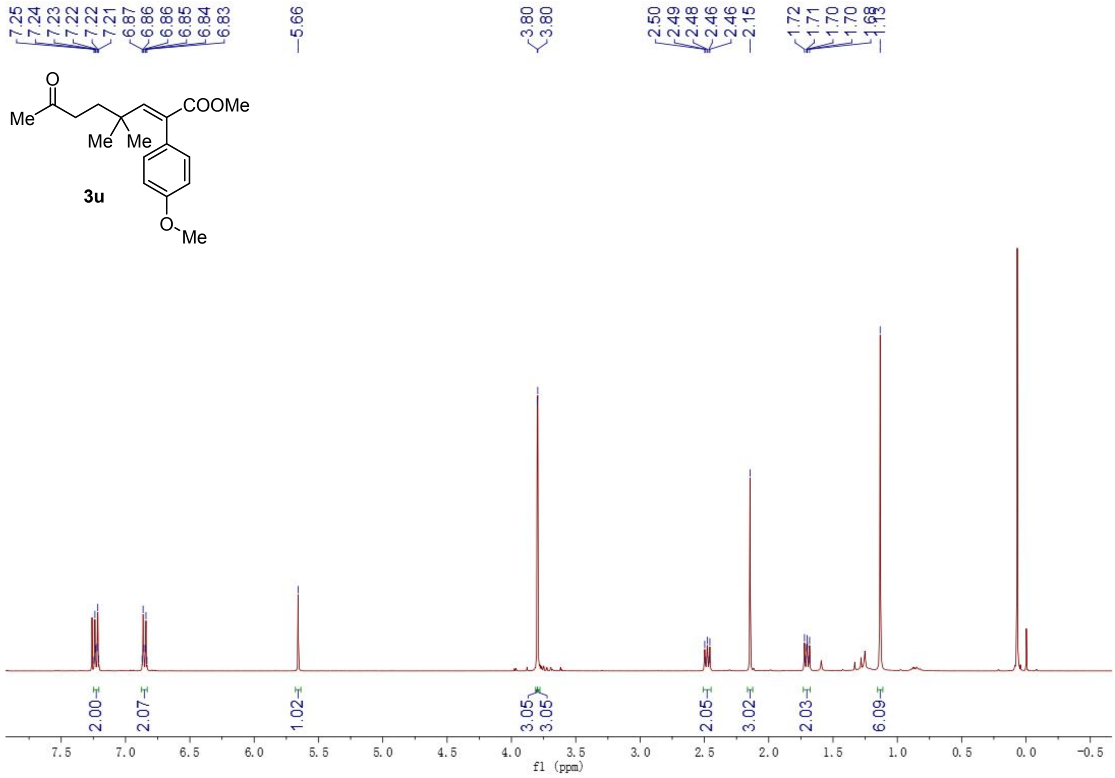
f1 (ppm)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1.72 1.71 1.70 1.70 1.68 1.13
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Me Me
3u
O
Me
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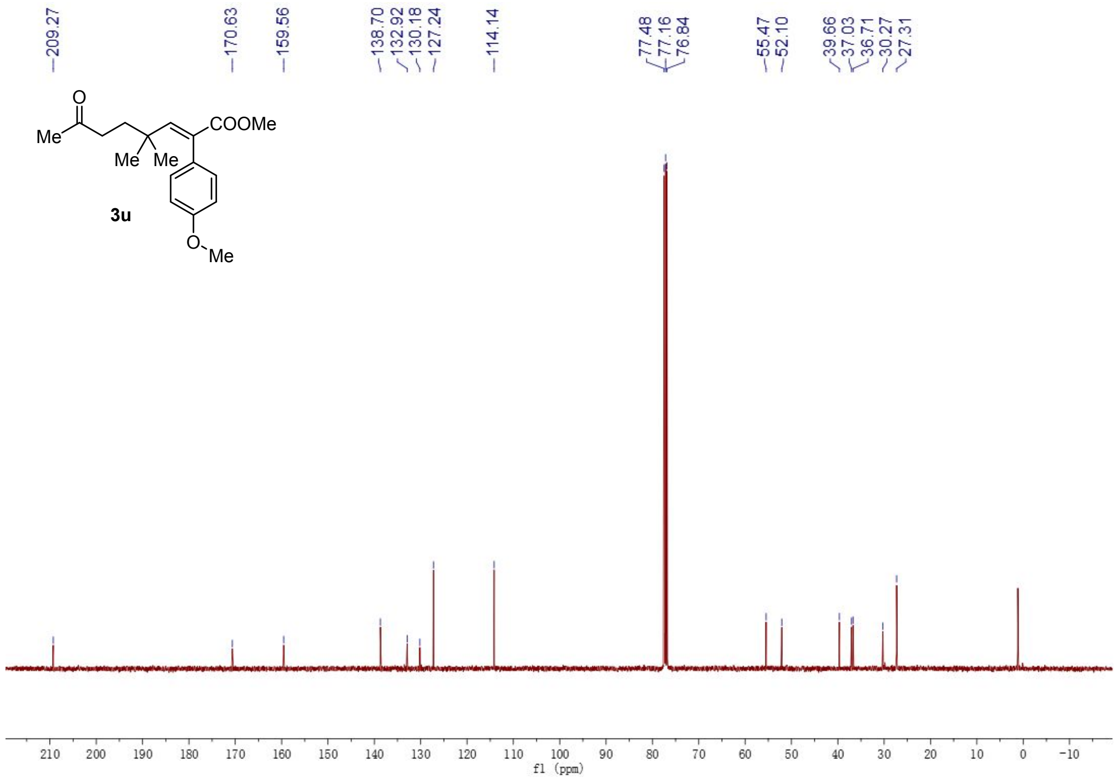
f1 (ppm)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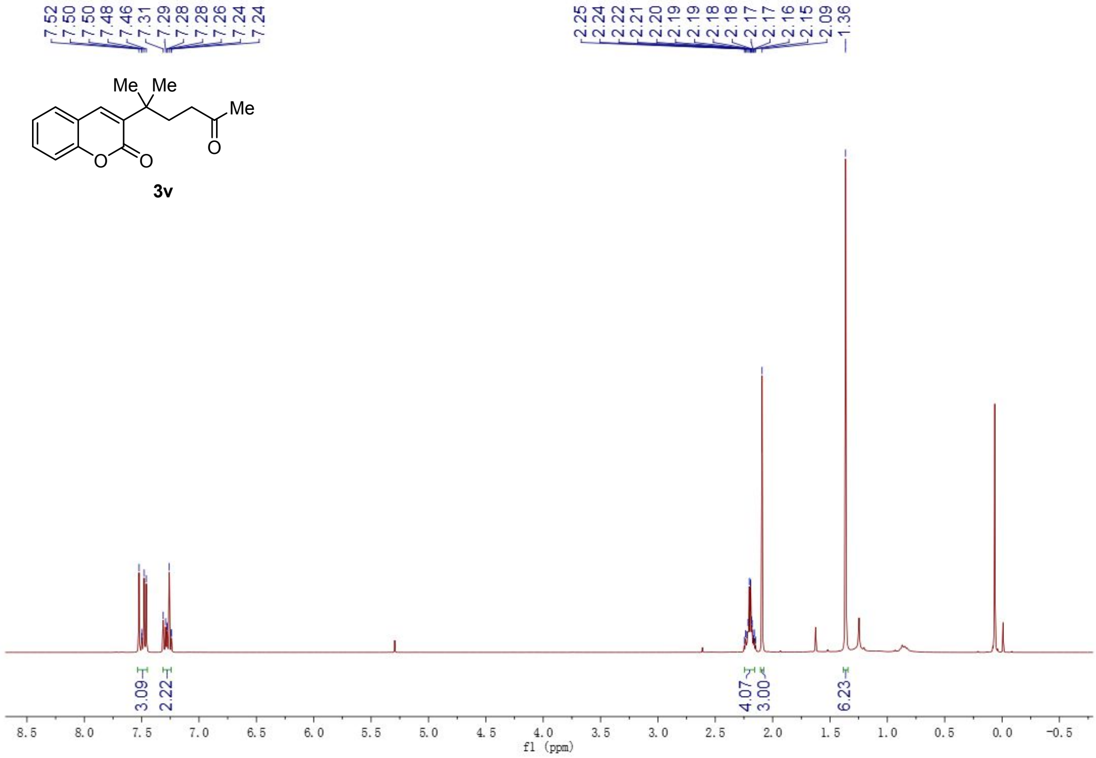
COOMe
Me
Me Me
3u
O
Me
f1 (ppm)



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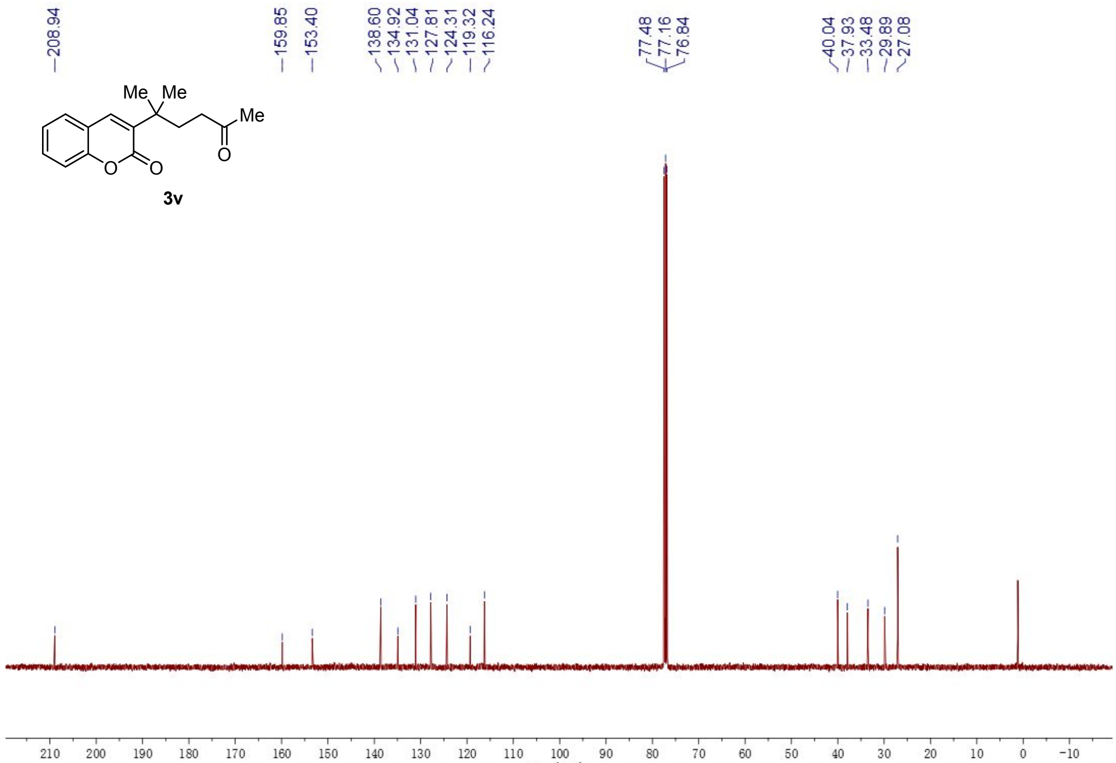
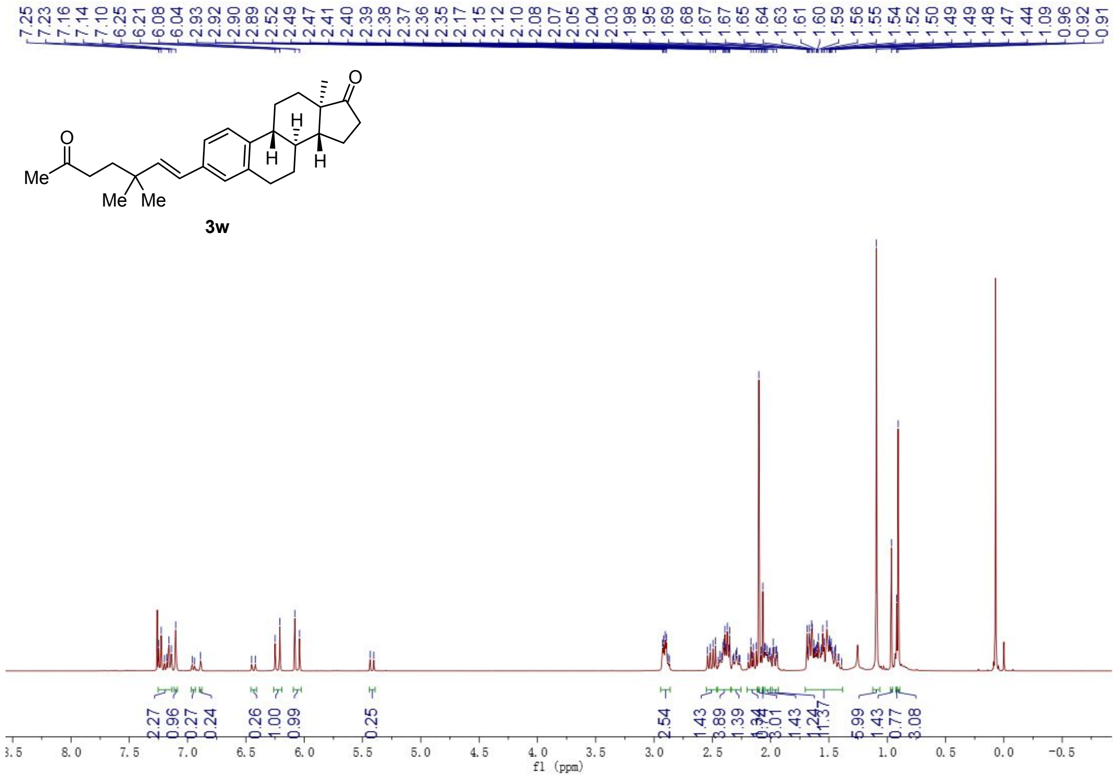


3v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0.91
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H
H
H
Me
Me
Me
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0.99
0.25
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3.01
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1.24
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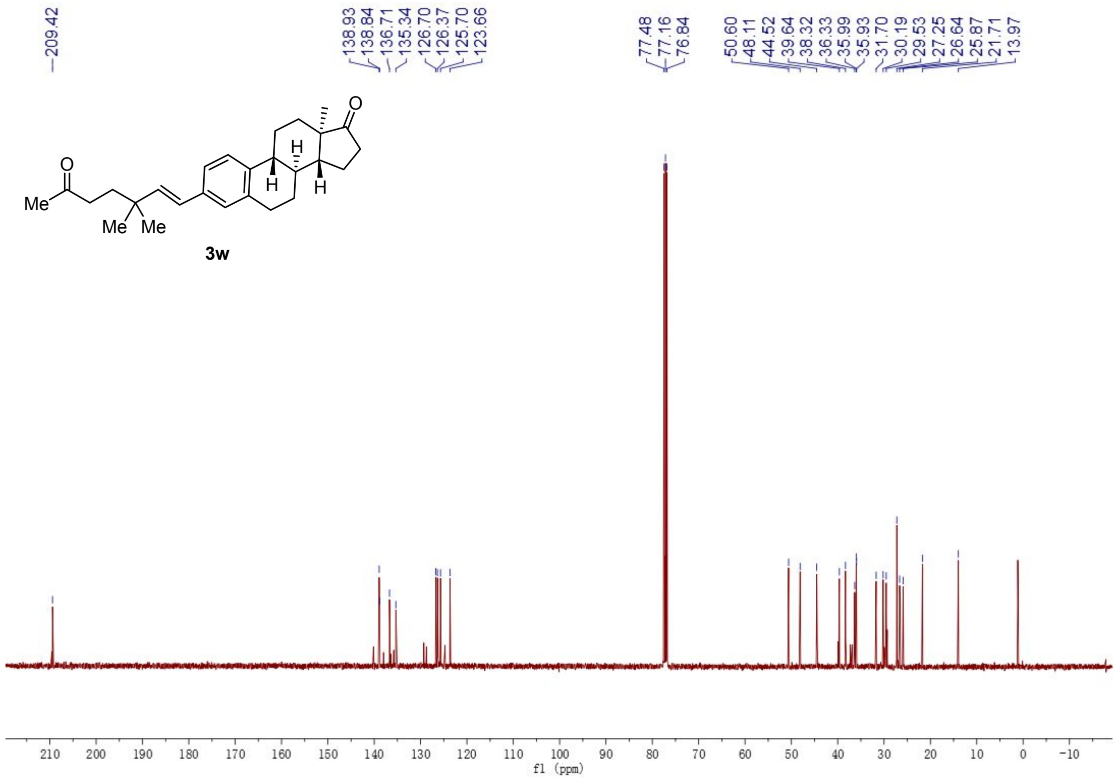
3.08
f1 (ppm)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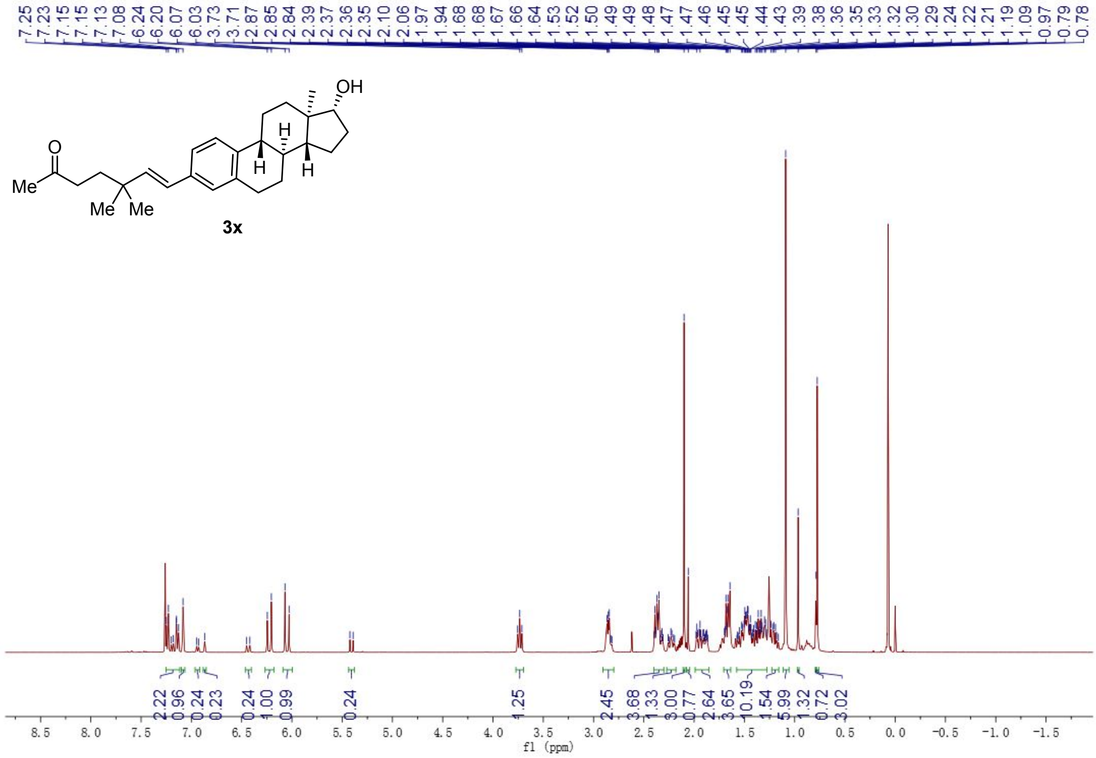
39.64
38.32
36.33
35.99
35.93
31.70
30.19
29.53
27.25
26.64
25.87
21.71
13.97
O
H
H
H
Me
Me
Me
3w
f1 (ppm)



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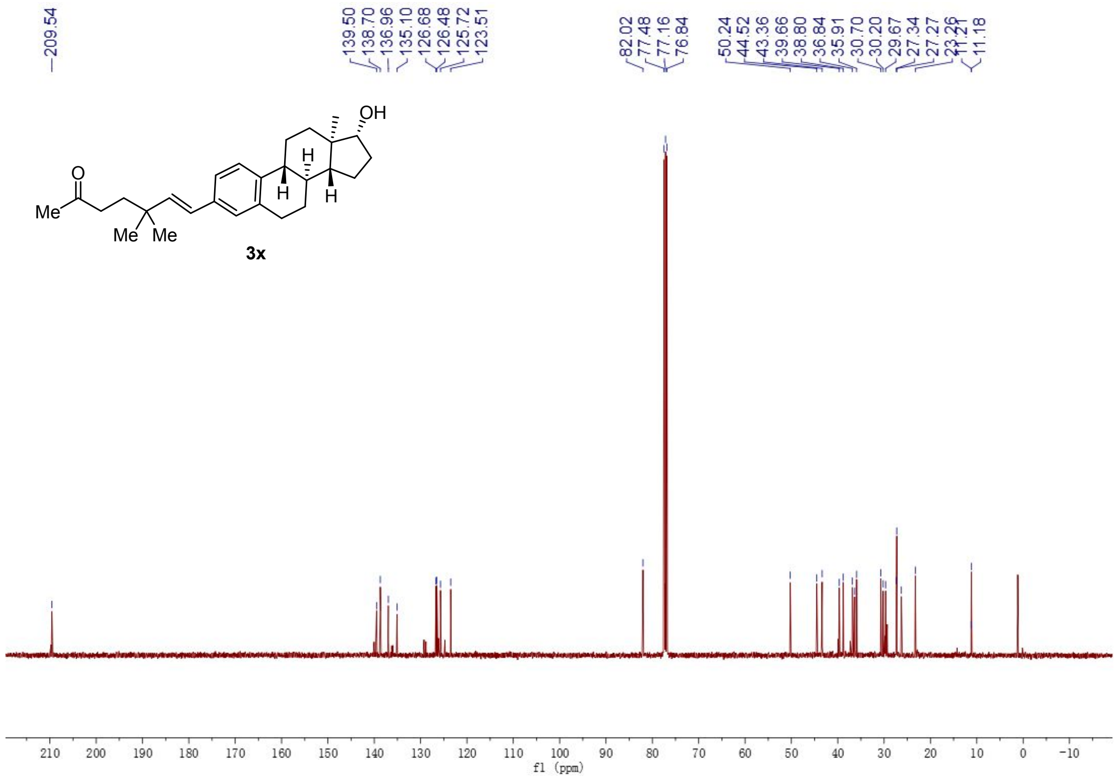
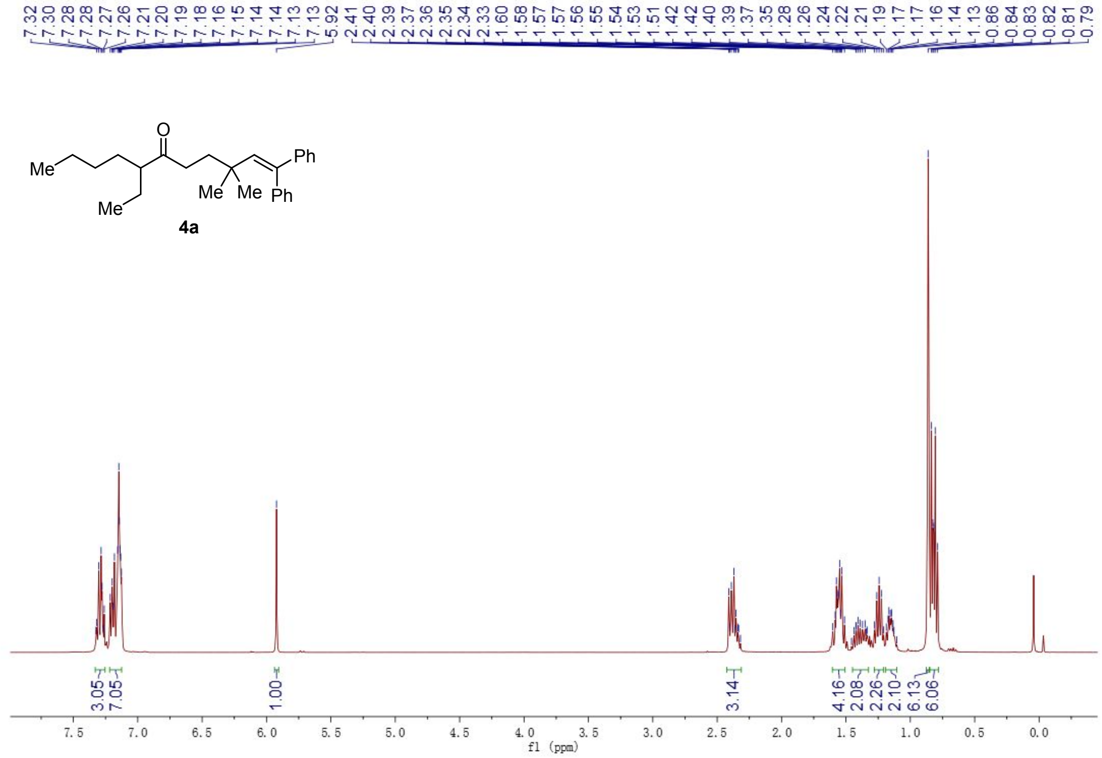
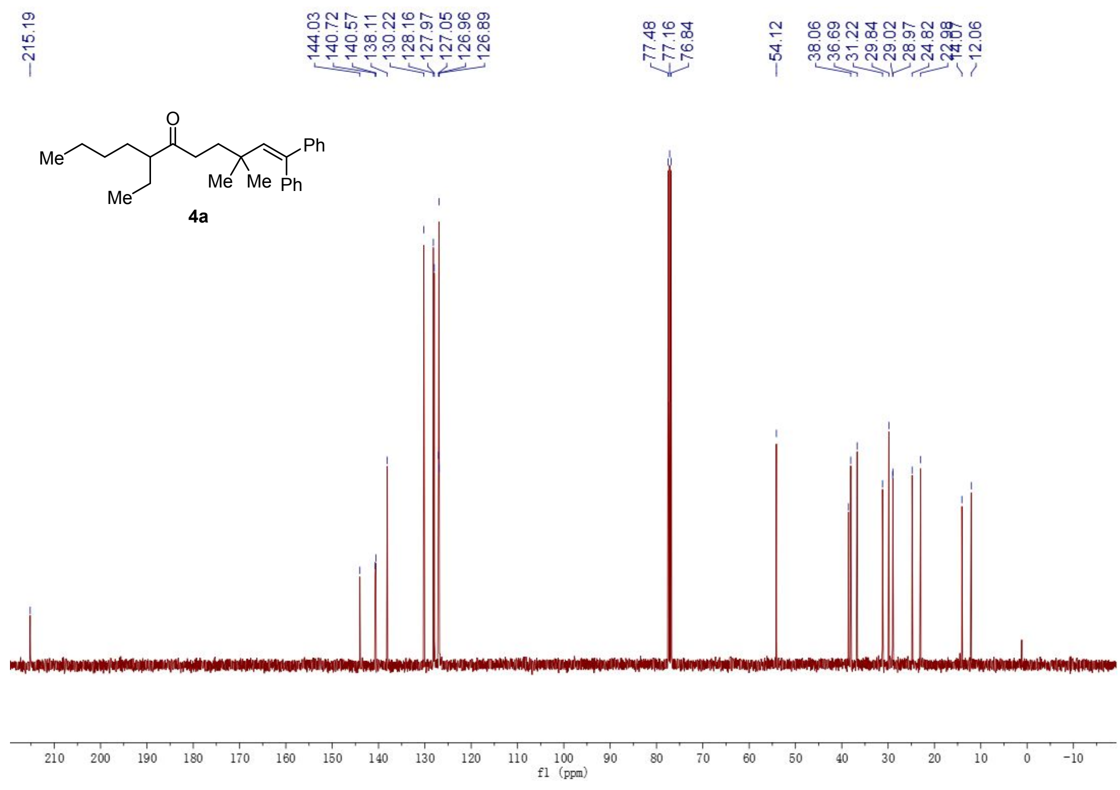
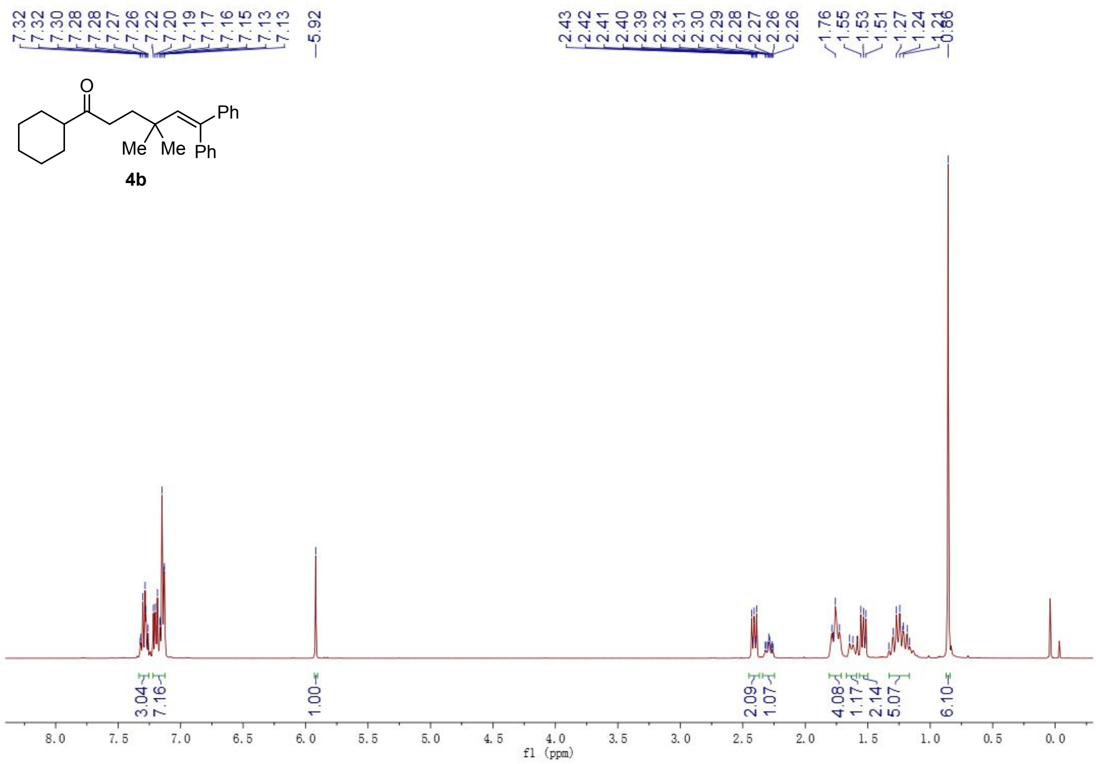


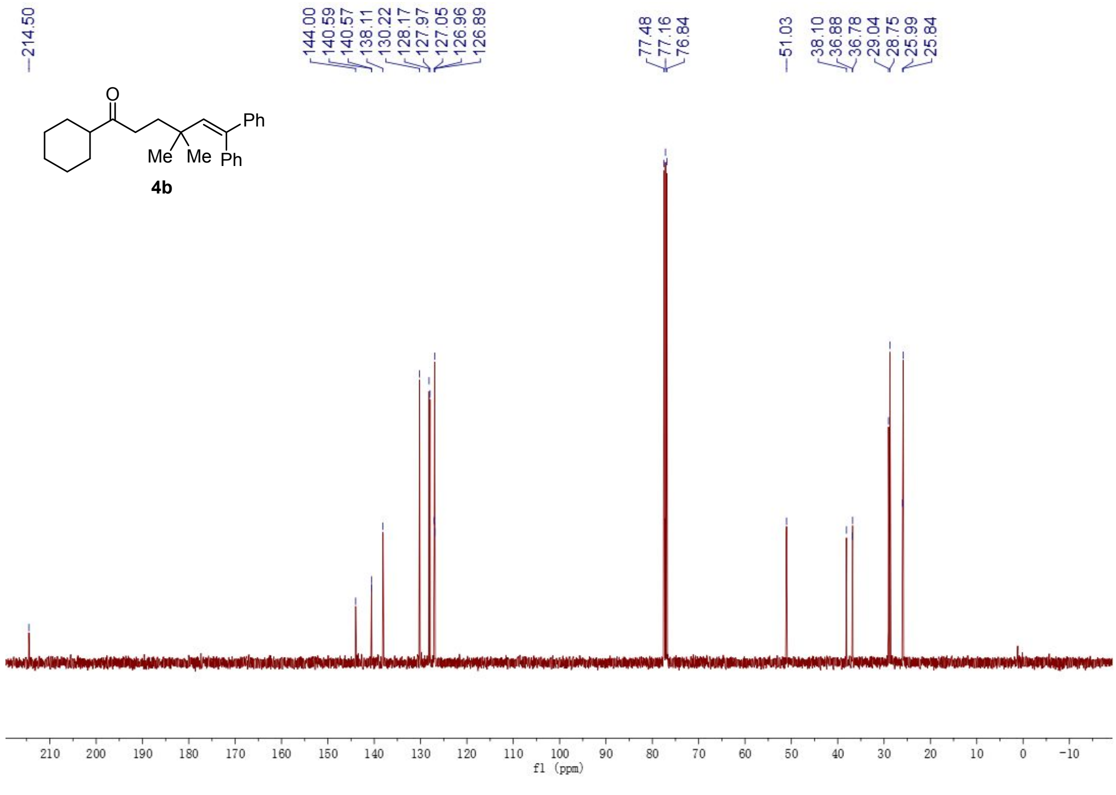
3x

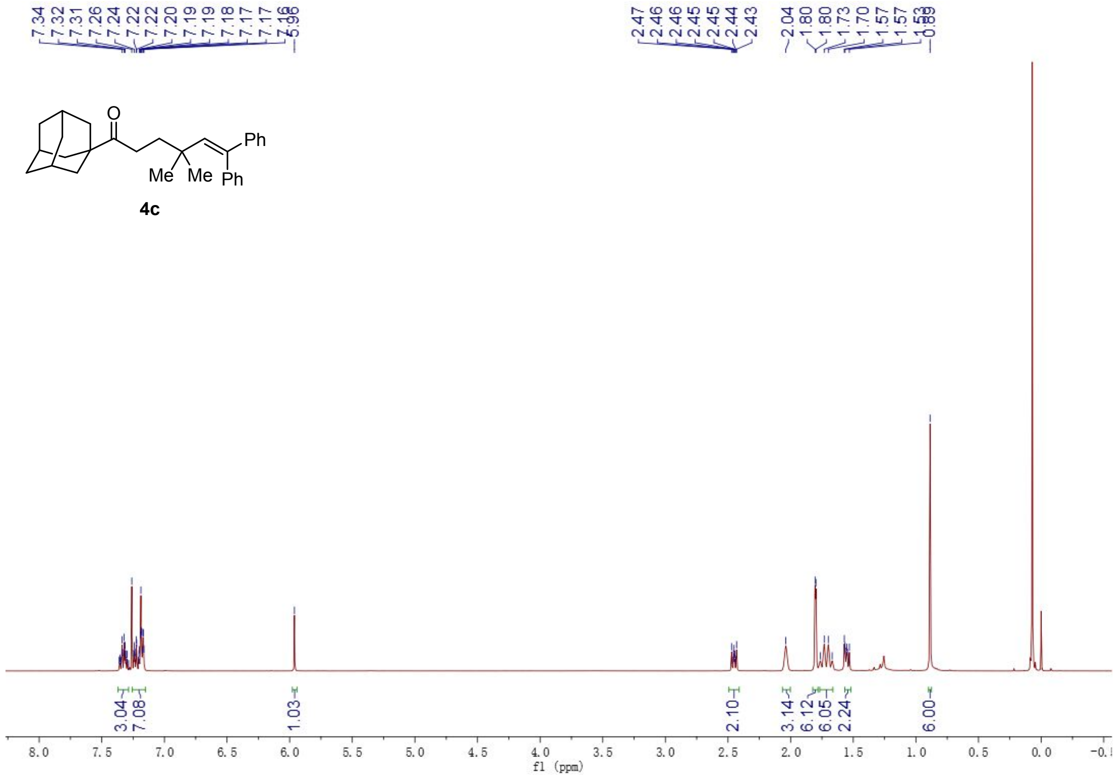
^{1}H NMR and ^{13}C{^{1}H} NMR Spectra of Products 4

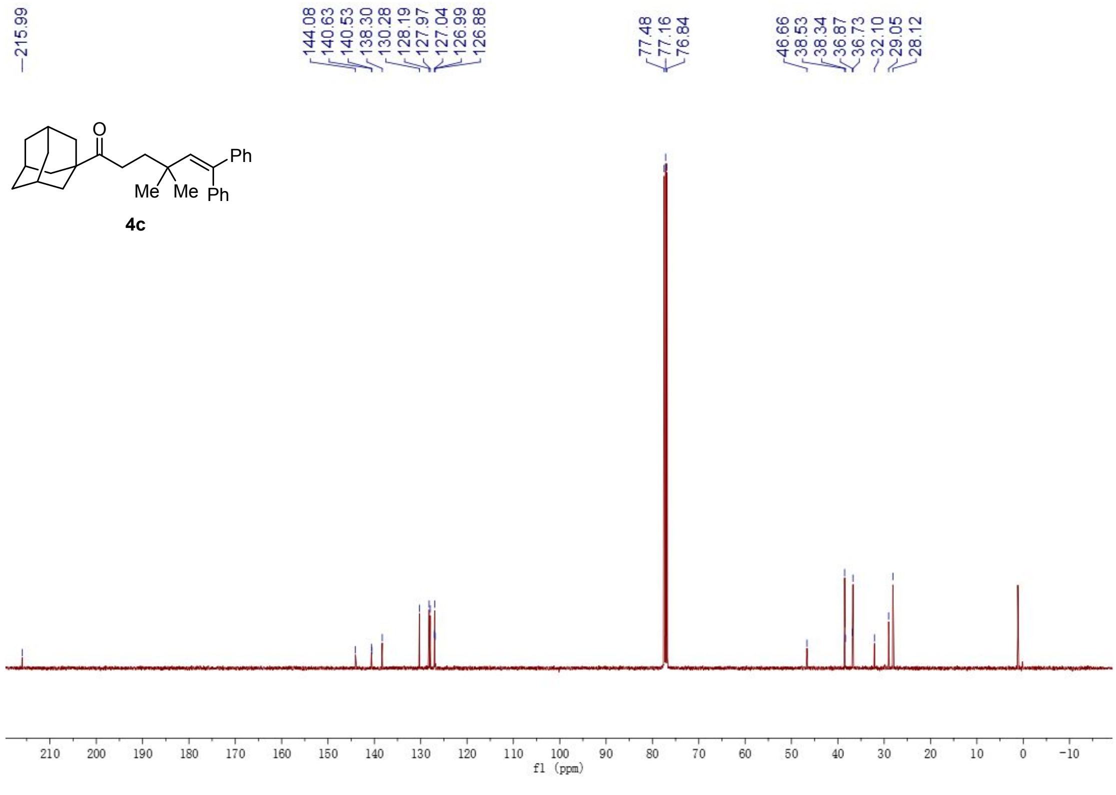


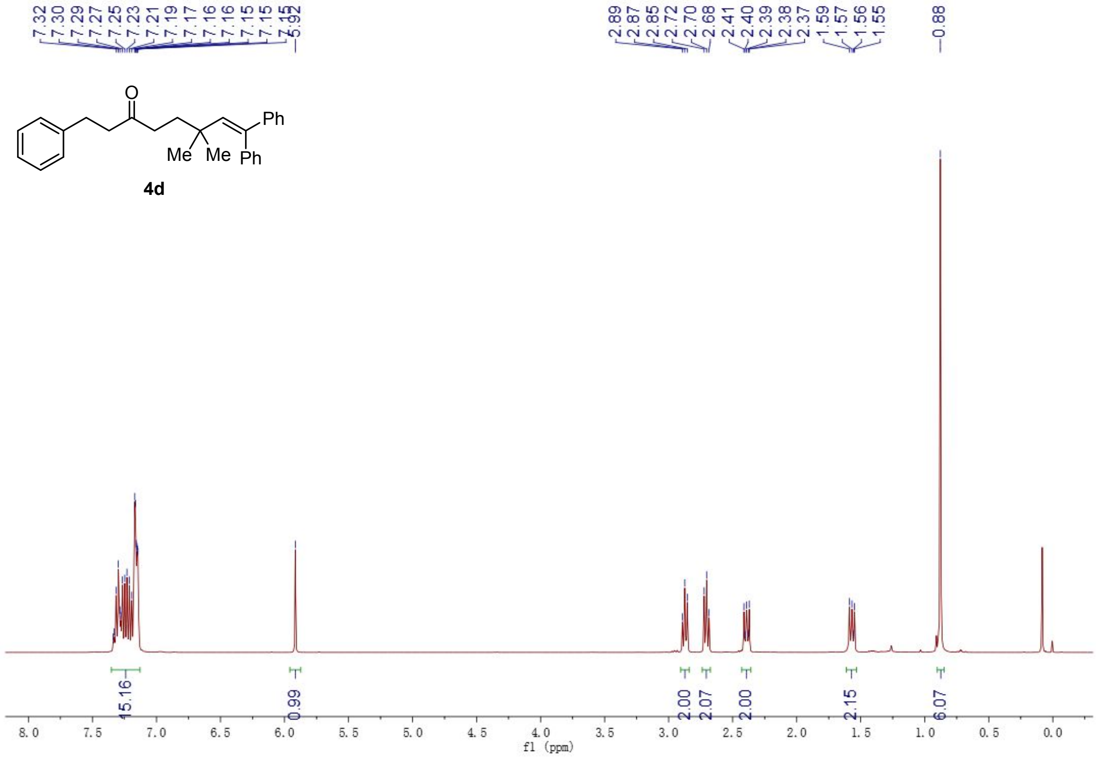








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2.38
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1.59
1.57
1.56
1.55
0.88
O
Ph
Me Me Ph
4d
15.16
0.99
2.00
2.07
2.00
2.15
6.07
8.0
7.5
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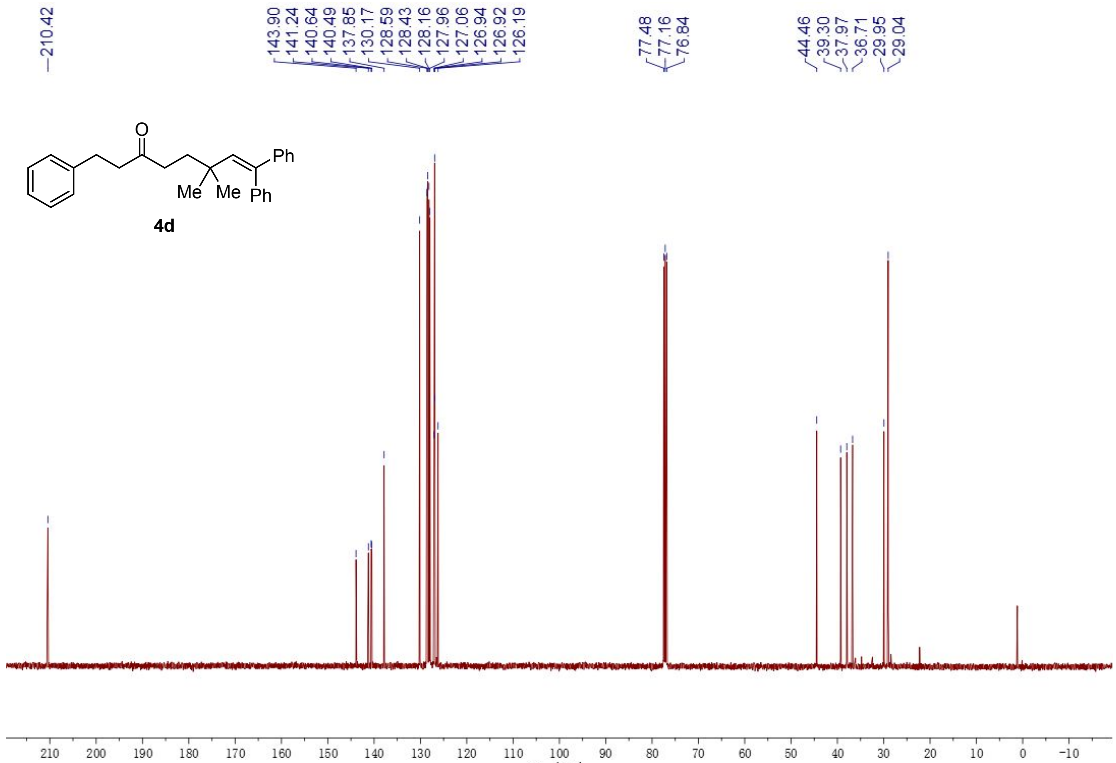
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O
Ph
Me Me Ph
4d
210
200
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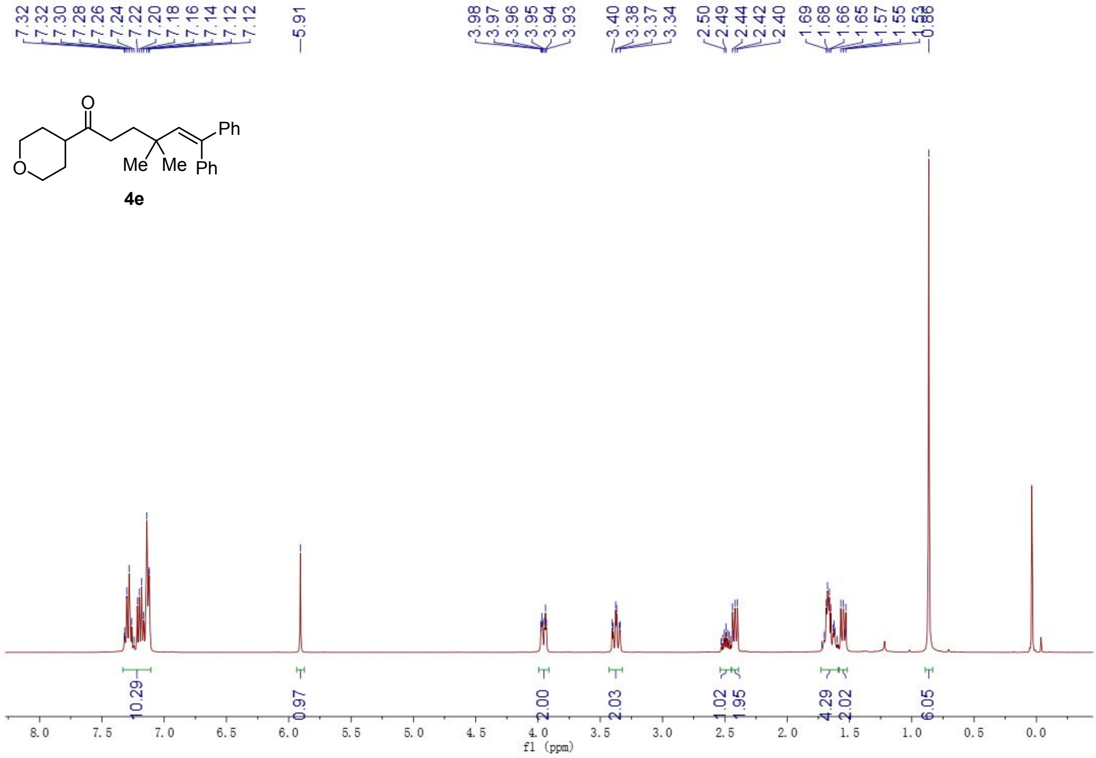
f1 (ppm)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Me
Ph
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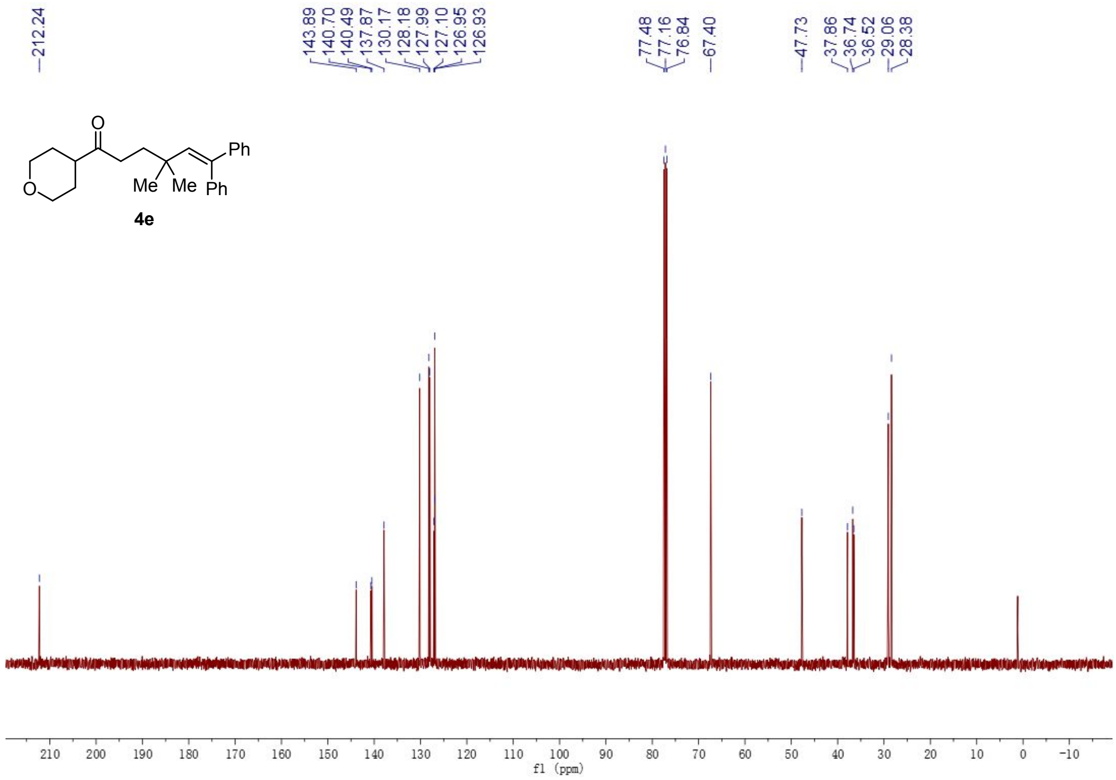
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47.73
37.86
36.74
36.52
29.06
28.38
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Ph
Me
Me
Ph
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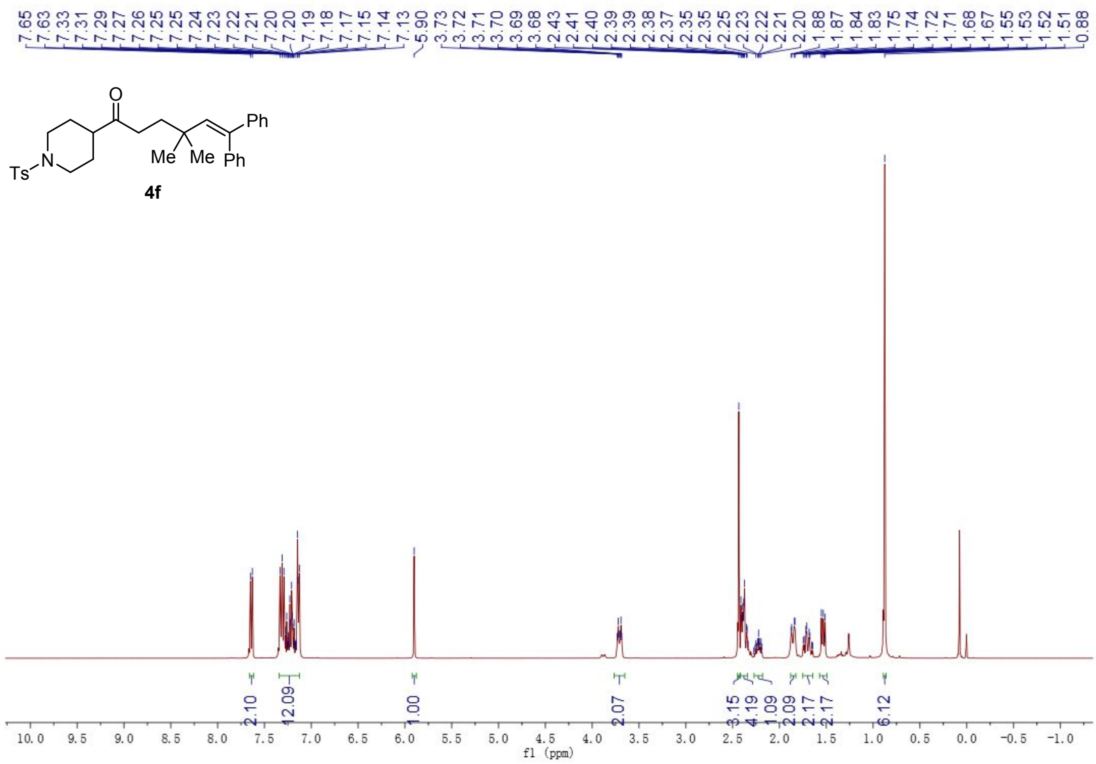
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7.14
7.13
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3.70
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3.68
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2.37
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2.25
2.23
2.22
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2.20
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1.87
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1.75
1.74
1.72
1.71
1.68
1.67
1.55
1.53
1.52
1.51
0.88
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Ph
Ts
N
Me
Me
Ph
4f
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3.15
4.19
1.09
2.09
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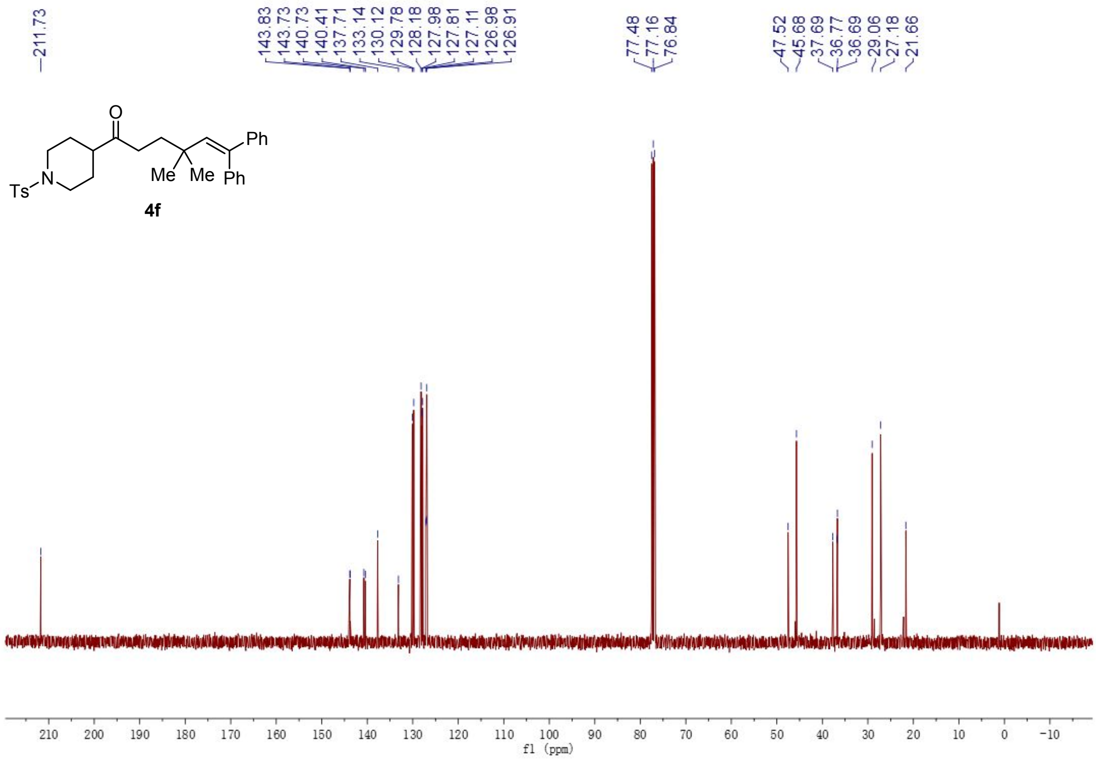
f1 (ppm)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77.16
76.84
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21.66
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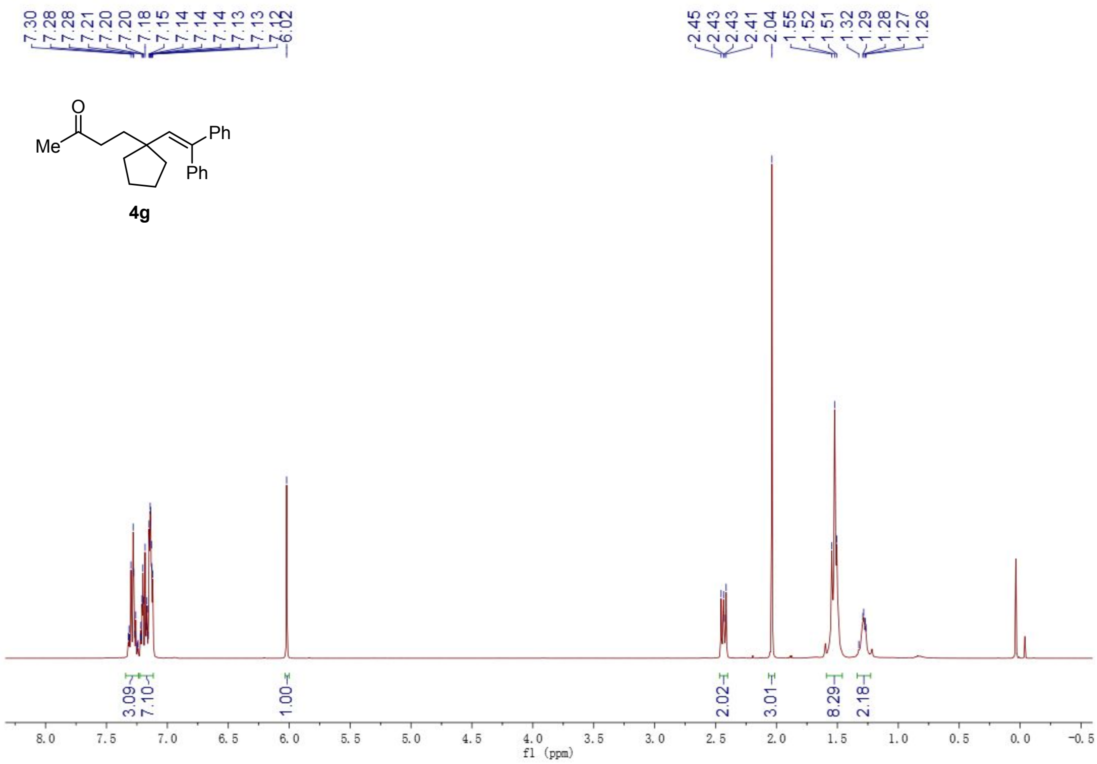
Ts
N
Me
Me
Ph
4f
f1 (ppm)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O
Me
Ph
Ph
4g
3.09 7.10 1.00 2.02 3.01 8.29 2.18
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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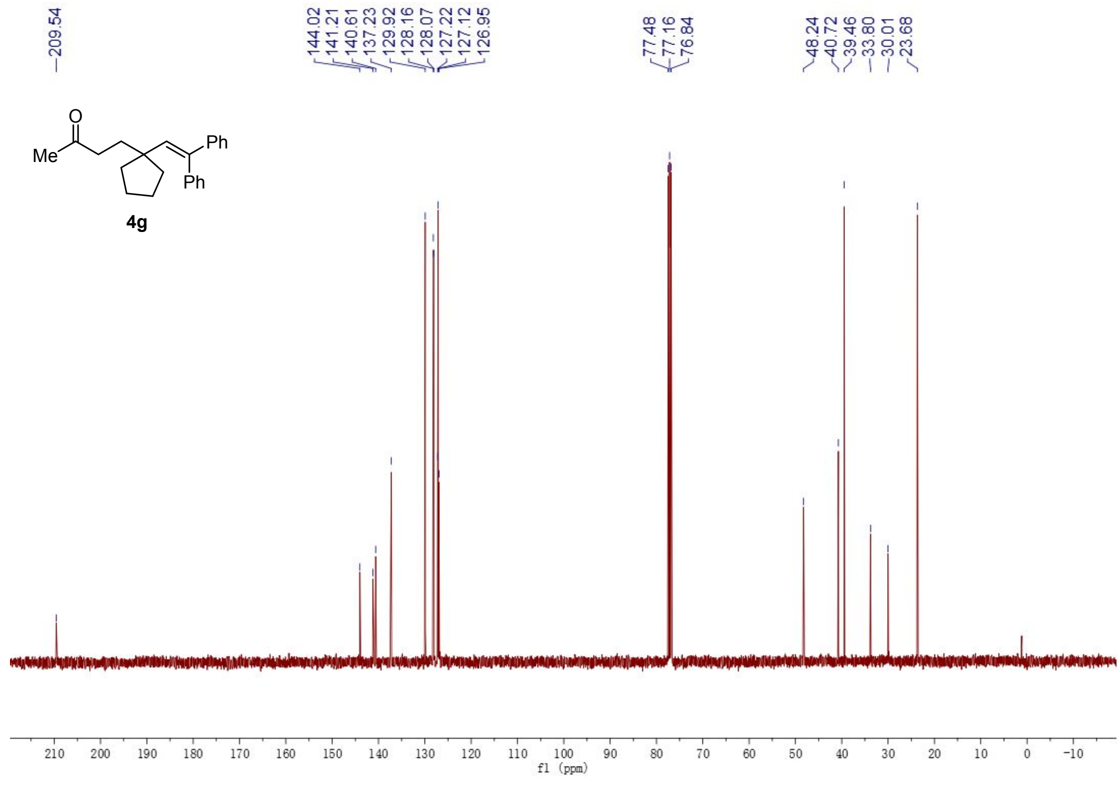
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77.48 77.16 76.84
48.24 40.72 39.46 33.80 30.01 23.68
O
Me
Ph
Ph
4g
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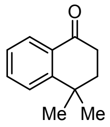
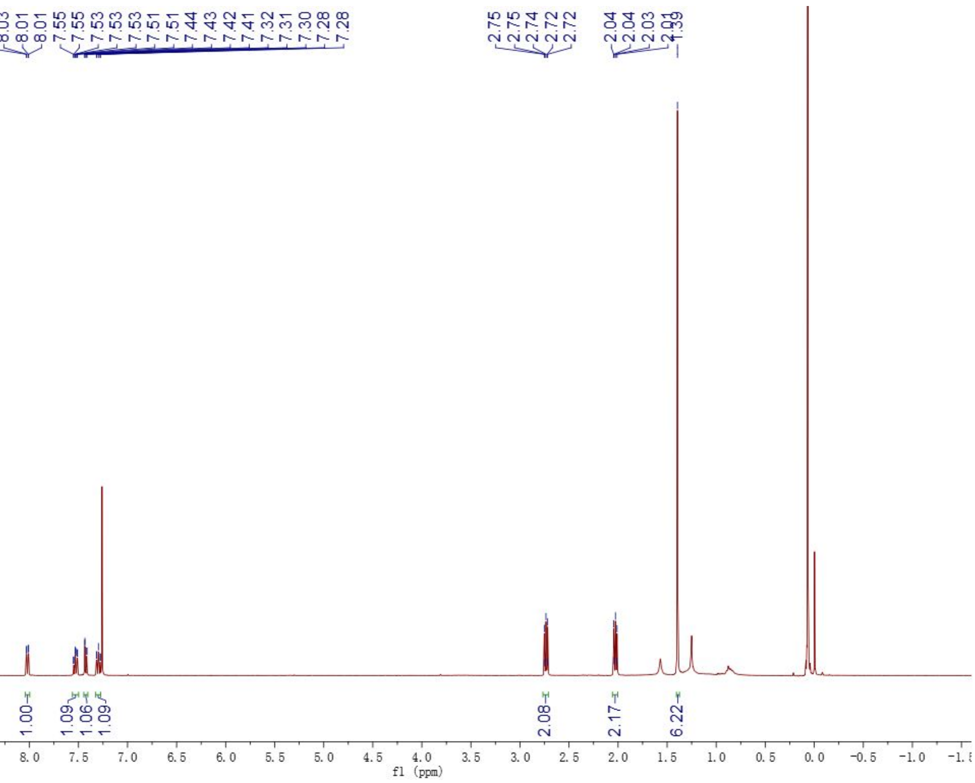


O
Me Me

4h'



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2.75 2.75 2.74 2.72 2.72 2.04 2.04 2.03 2.01 1.39
1.00 1.09 1.06 1.09 2.08 2.17 6.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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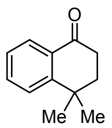
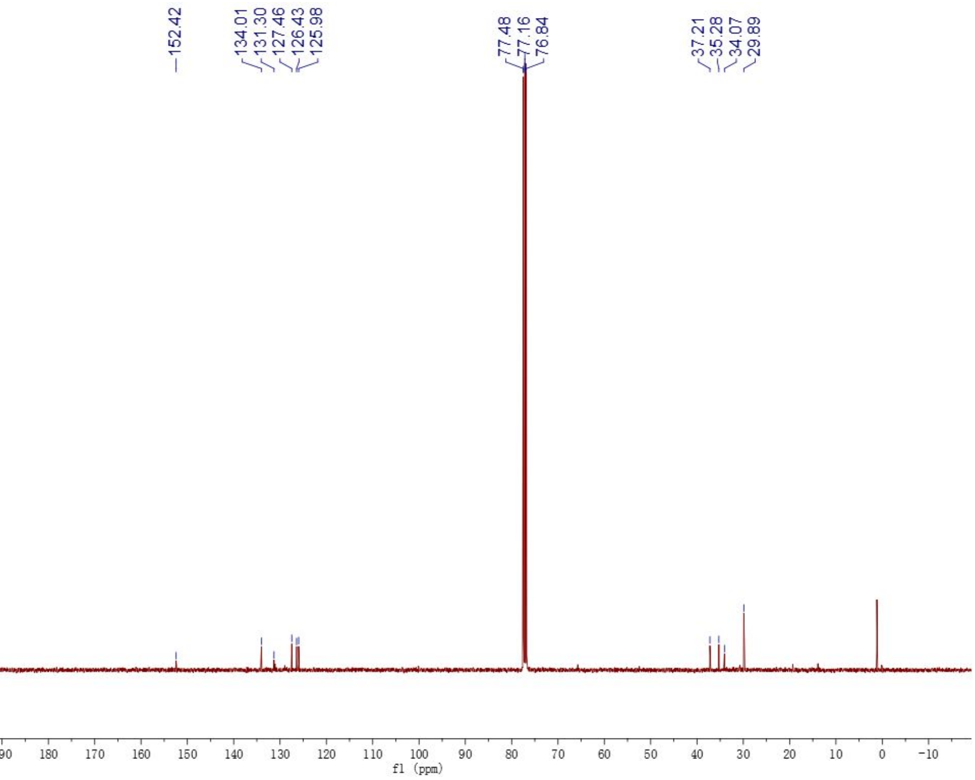


O
Me Me

4h'



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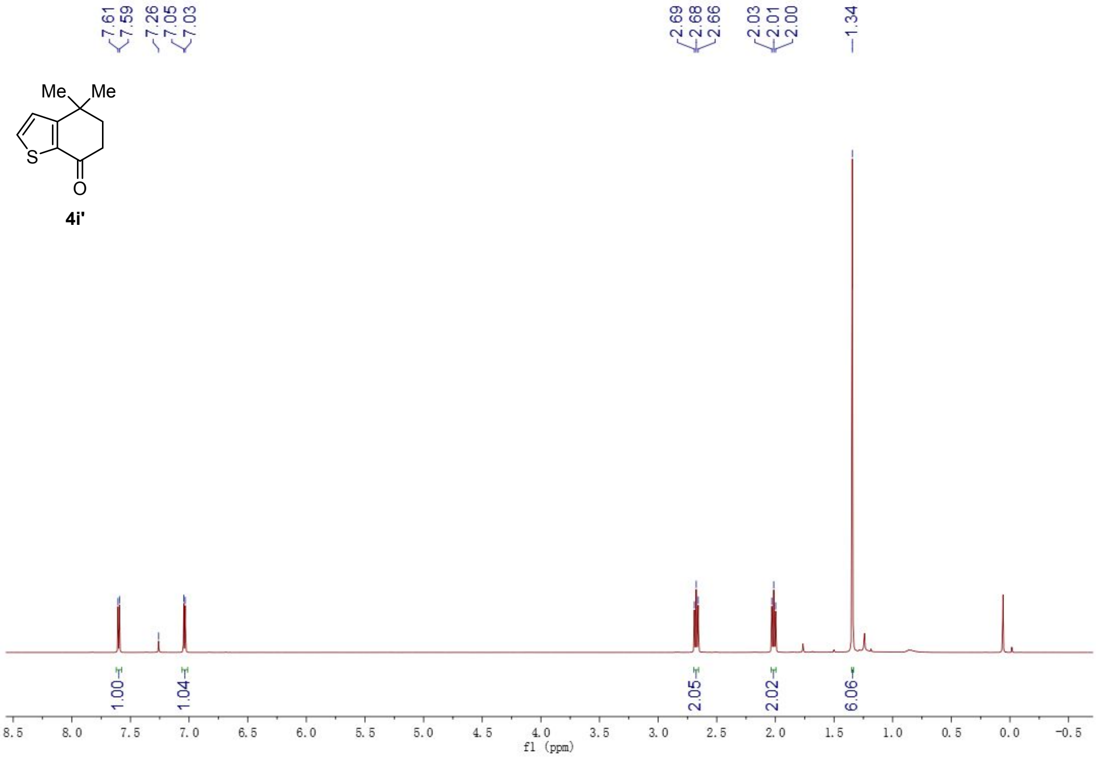
77.48 77.16 76.84
37.21 35.28 34.07 29.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.01
2.00
1.34
Me
Me
S
O
4i'
1.00
1.04
2.05
2.02
6.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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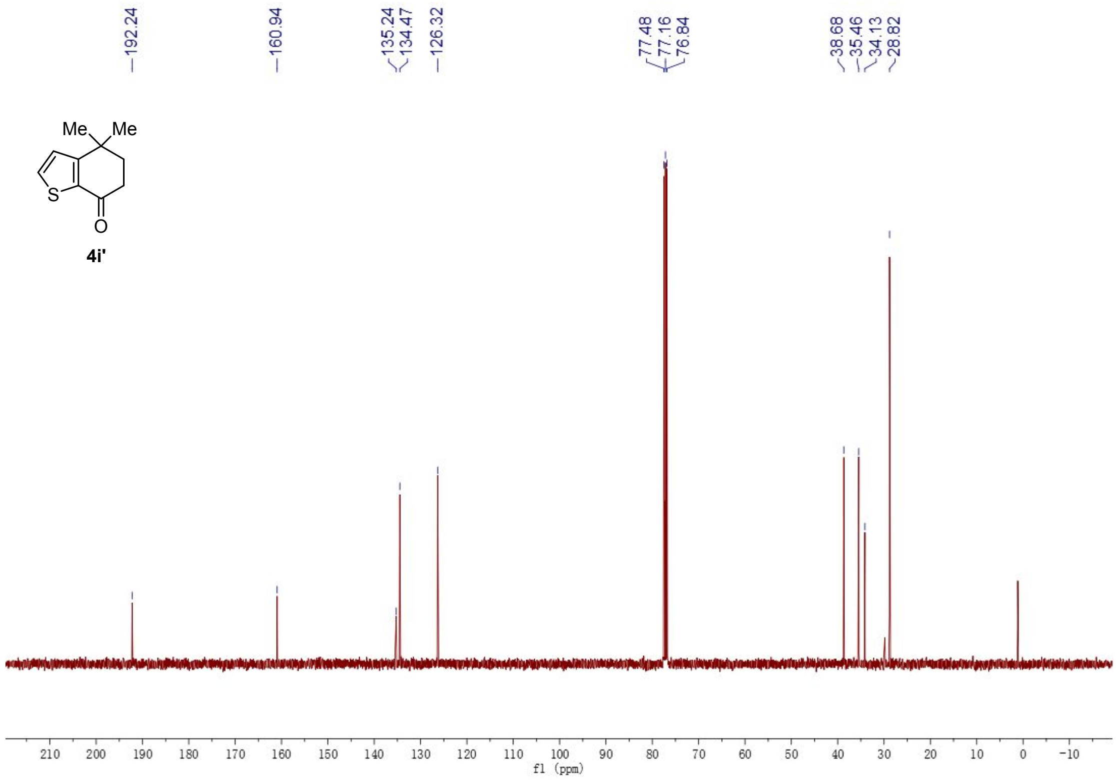
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Me
S
O
4i'
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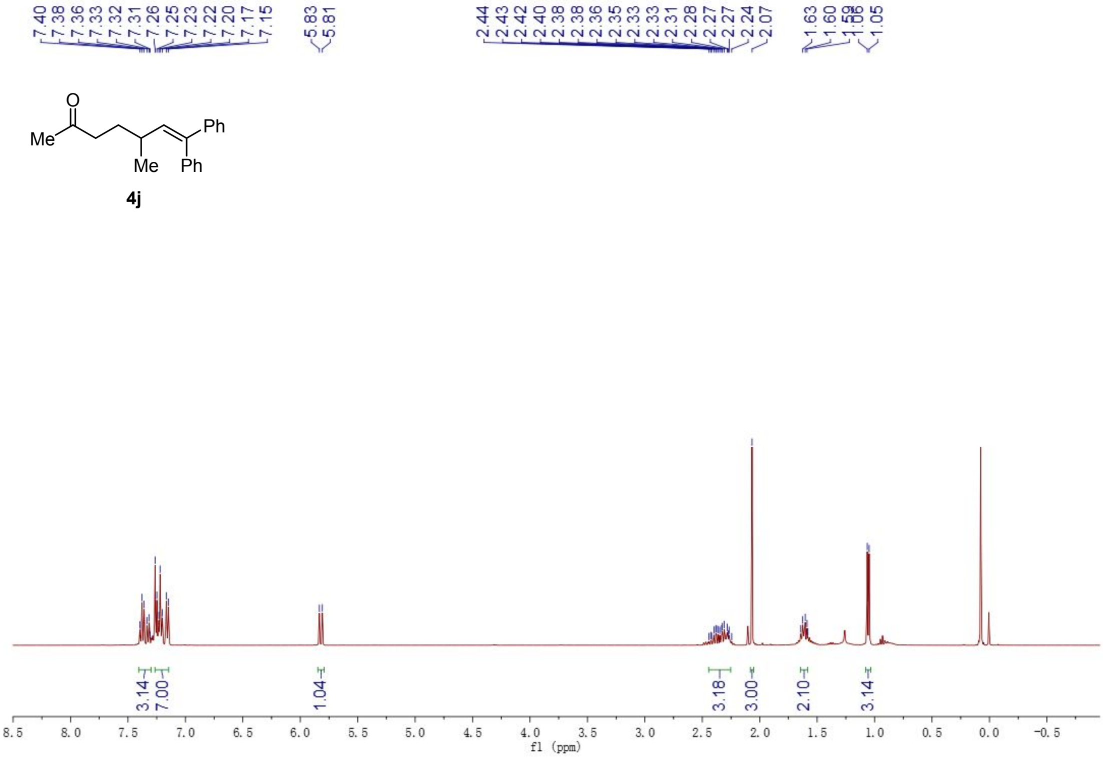
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2.33
2.31
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2.27
2.27
2.24
2.07
1.63
1.60
1.59
1.05
O
Me
Me
Ph
Ph
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7.00
1.04
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3.00
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7.0
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6.0
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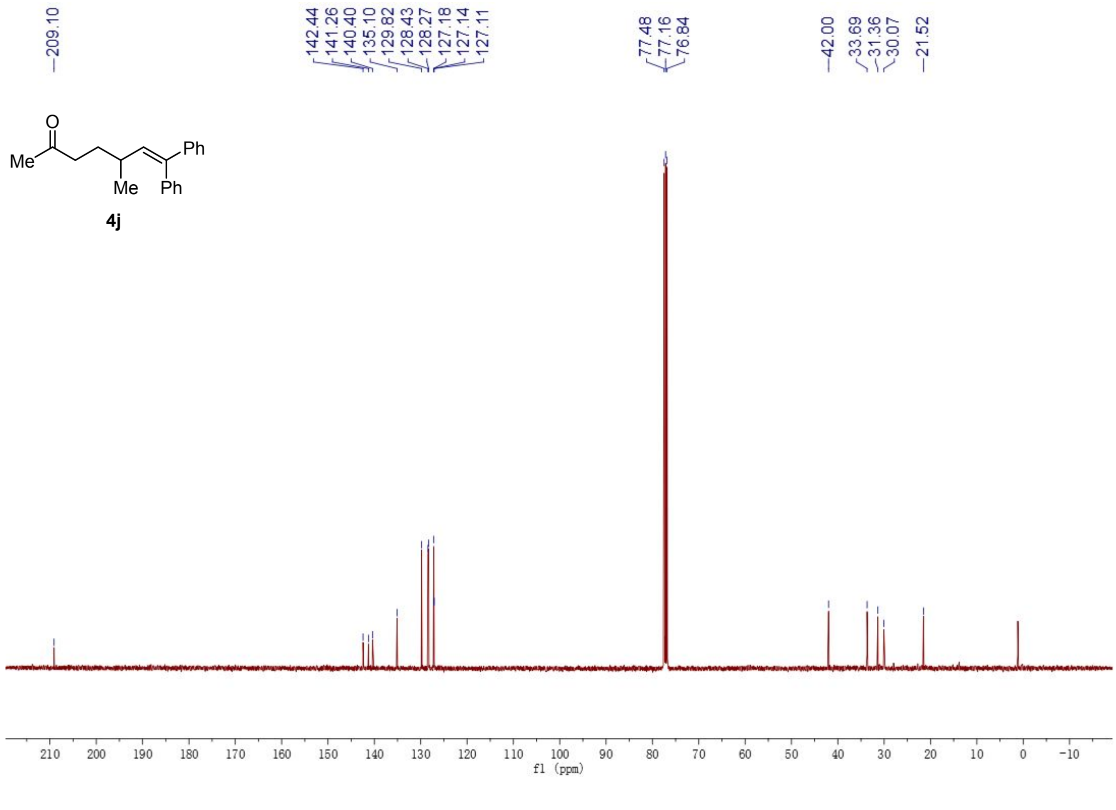
f1 (ppm)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76.84
42.00
33.69
31.36
30.07
21.52
O
Me
Me
Ph
Ph
4j
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180
170
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0
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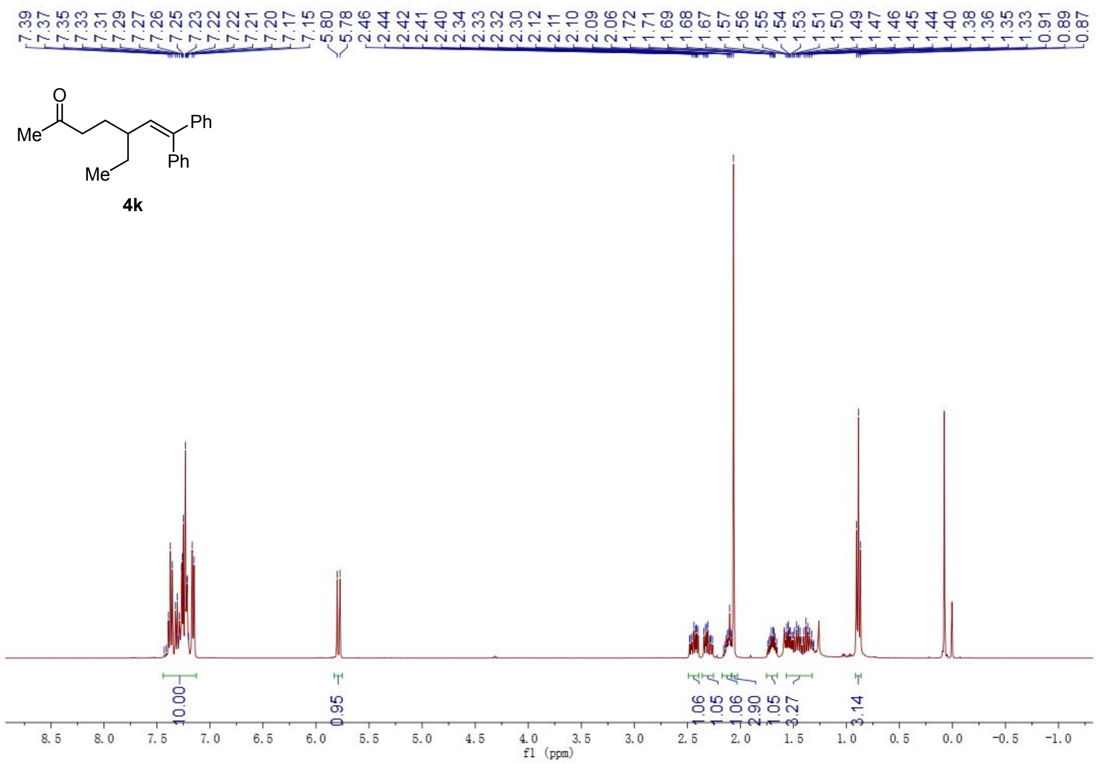
f1 (ppm)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O
Me
Ph
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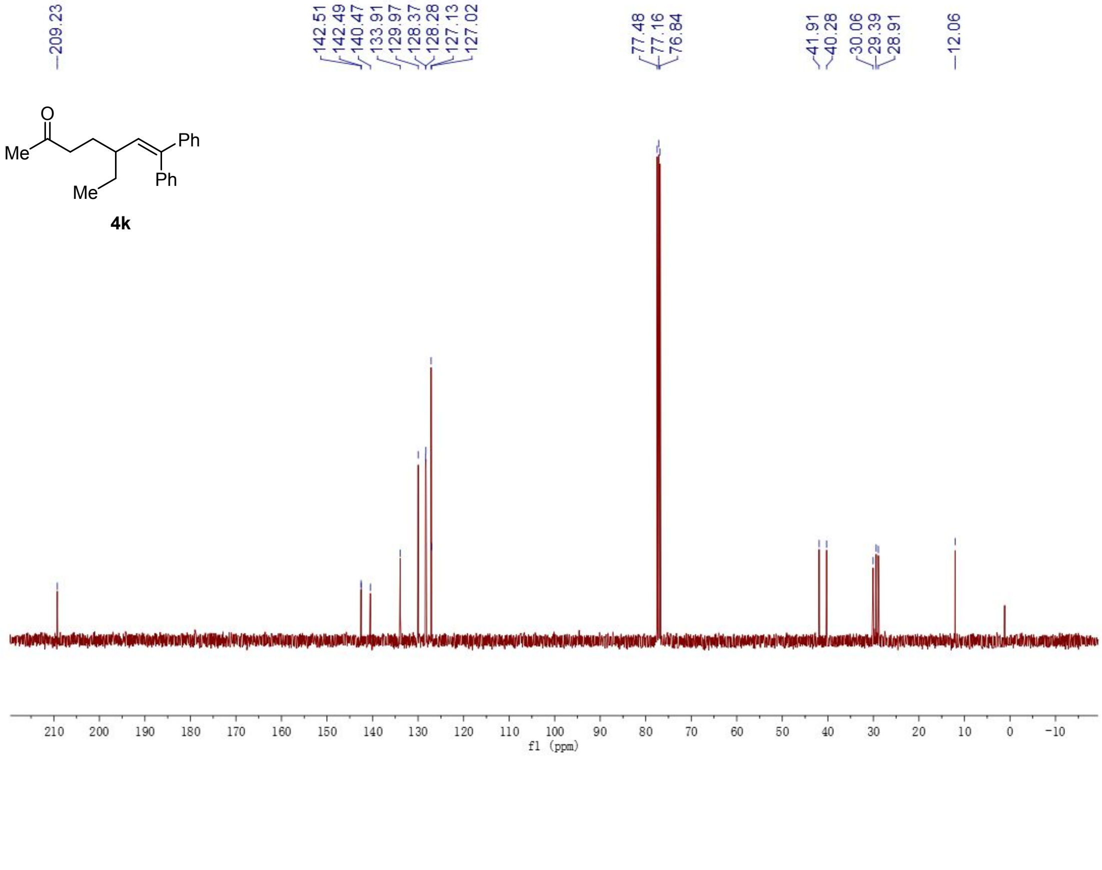
fl (ppm)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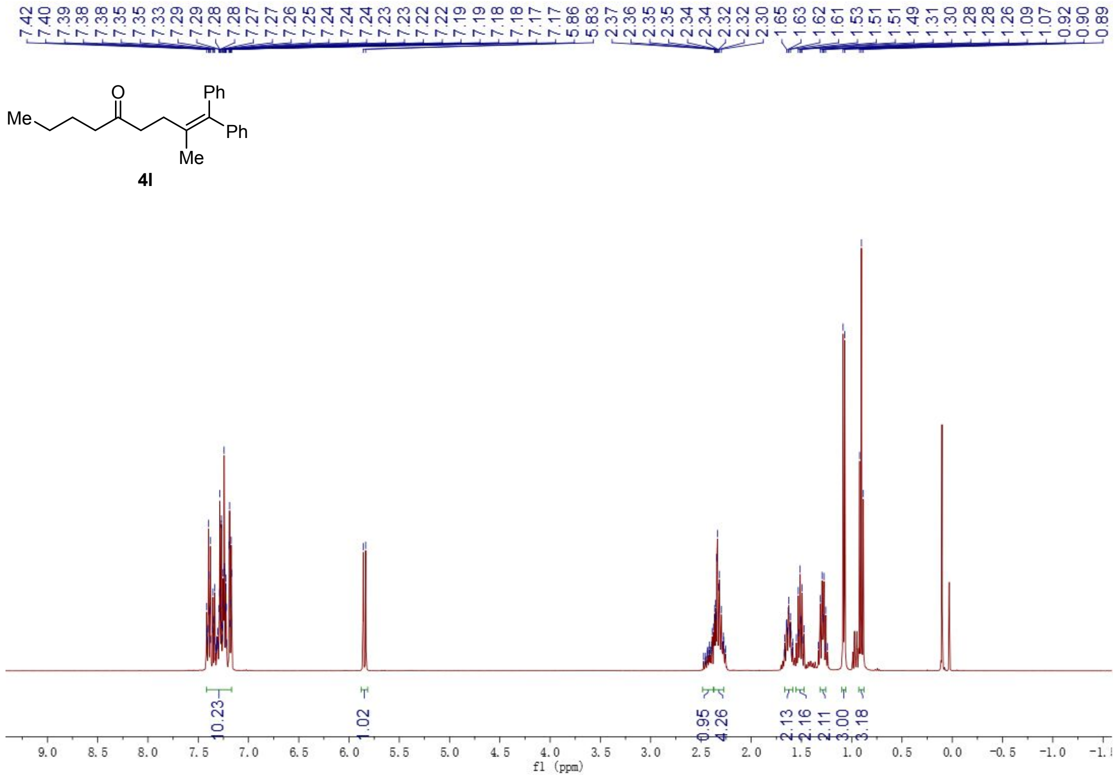
fl (ppm)



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Ph
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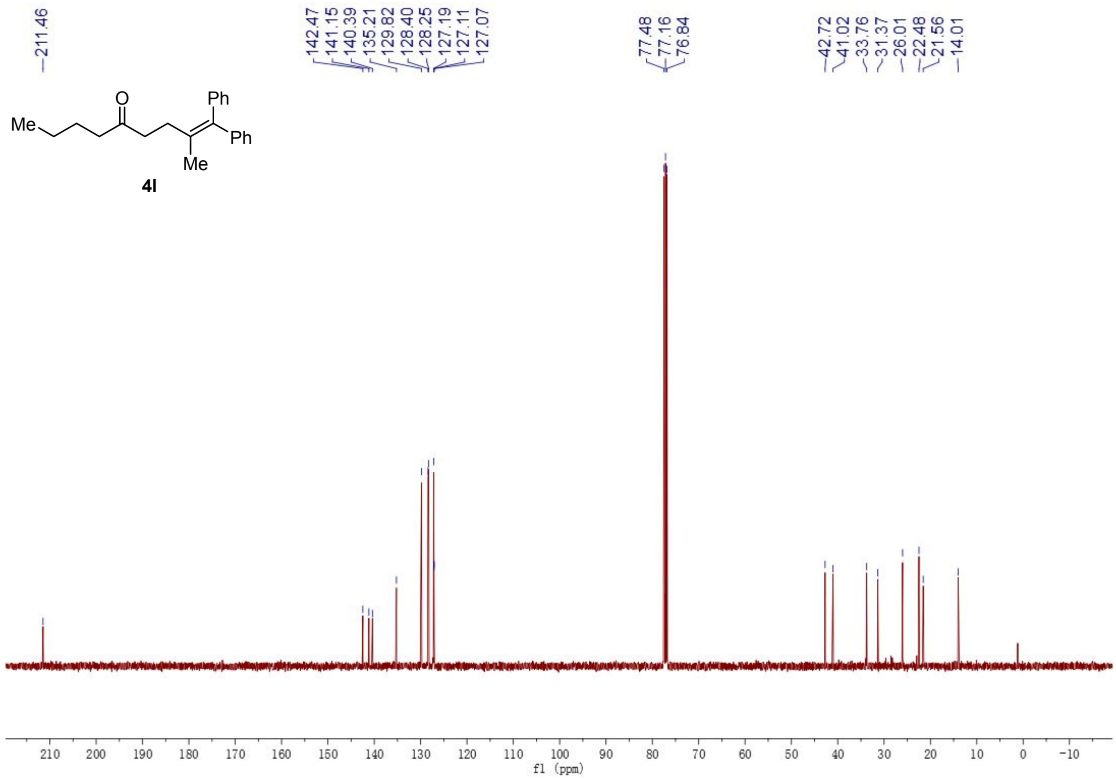

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77.48 77.16 76.84
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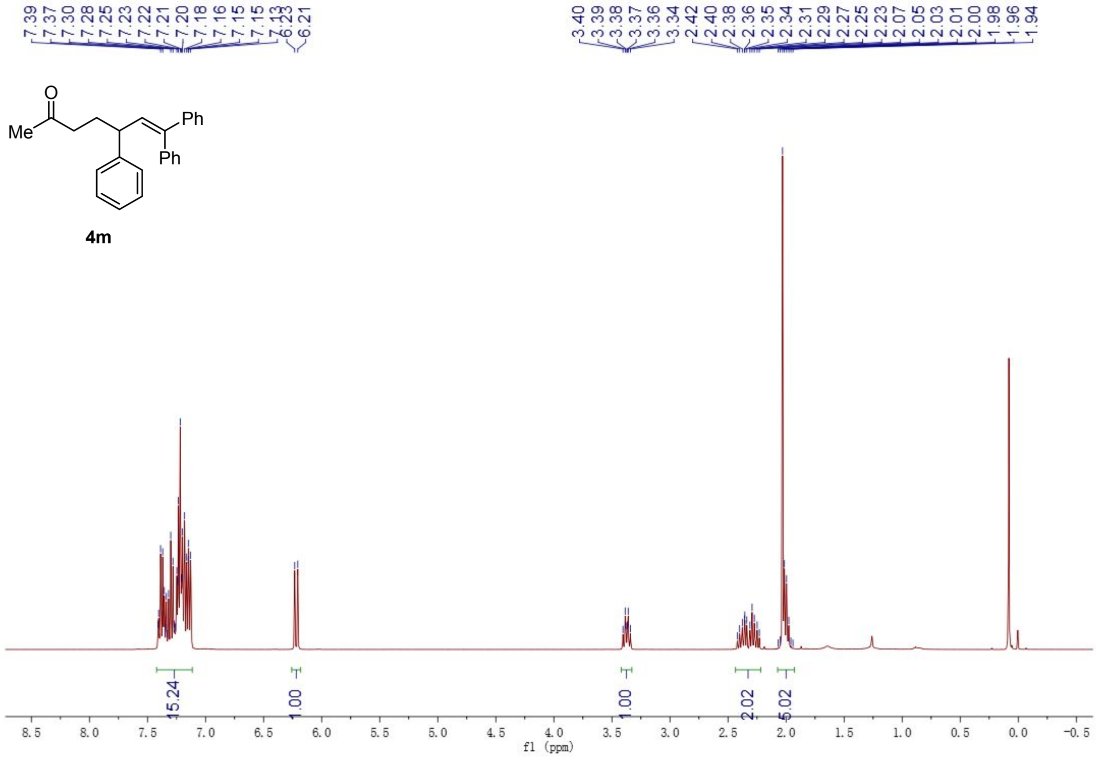
4l
f1 (ppm)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O
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Ph
Ph
4m
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1.00
1.00
2.02
5.02
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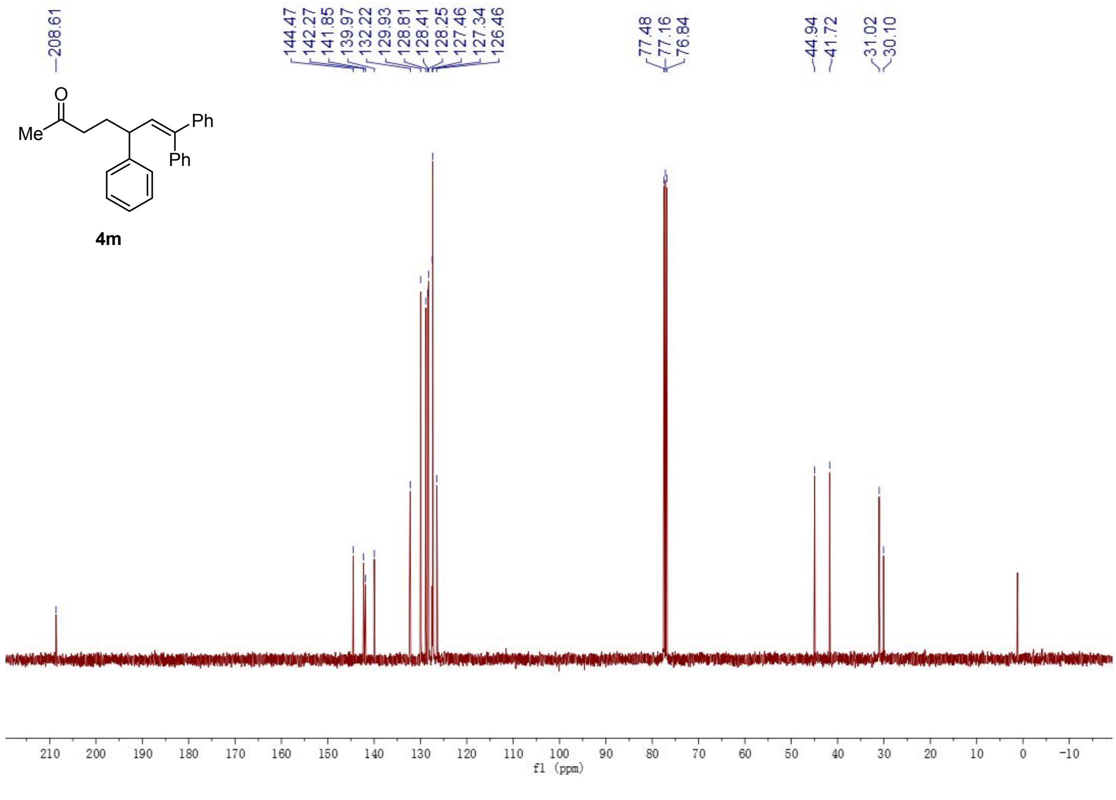
f1 (ppm)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77.48 77.16 76.84
44.94 41.72
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O
Me
Ph
Ph
4m
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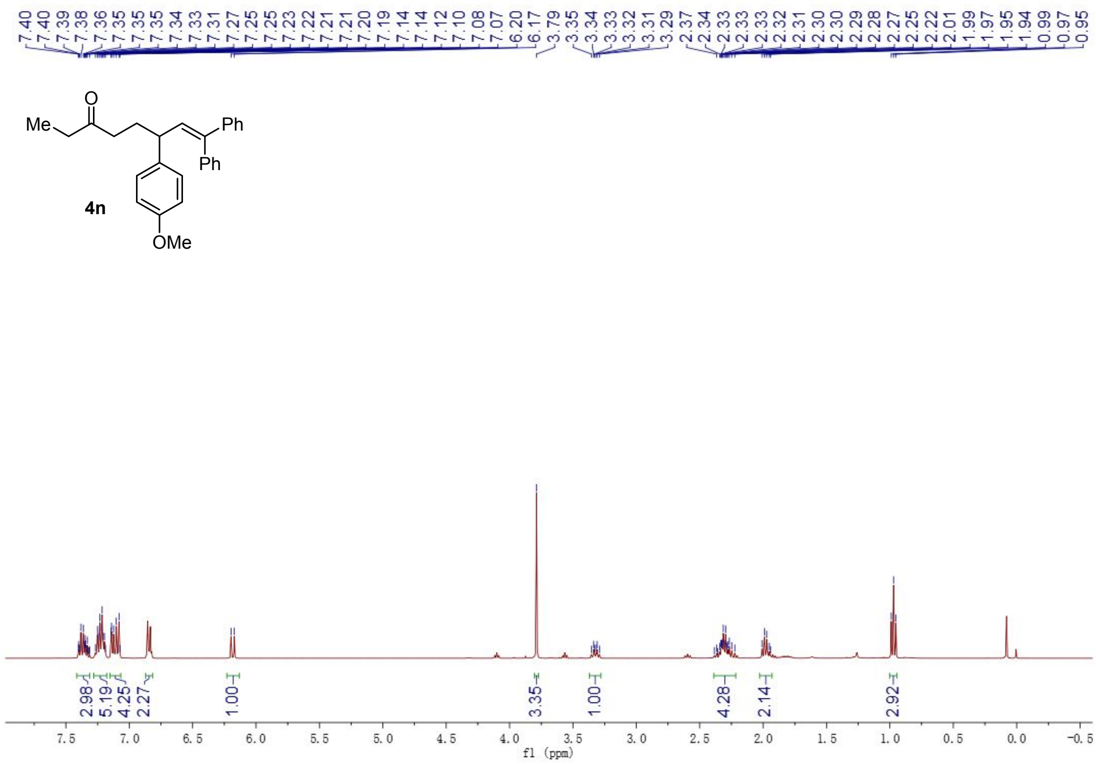
f1 (ppm)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0.5
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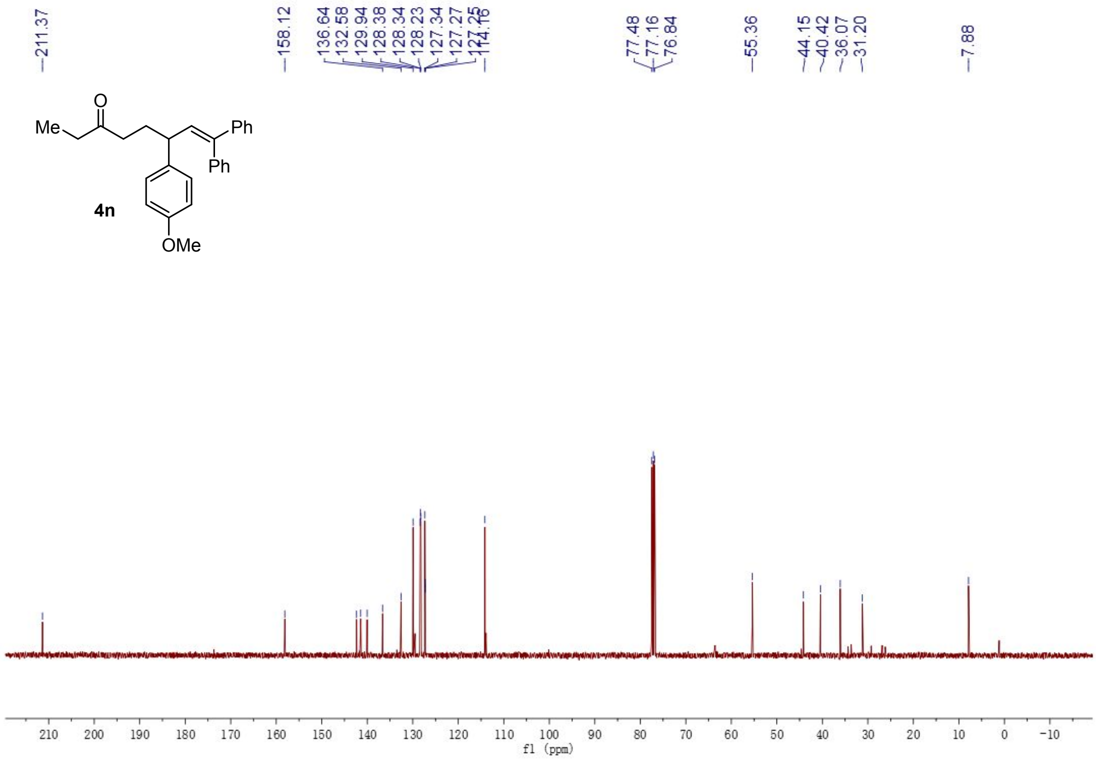
f1 (ppm)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77.16
76.84
55.36
44.15
40.42
36.07
31.20
7.88
Me
O
Ph
Ph
4n
OMe
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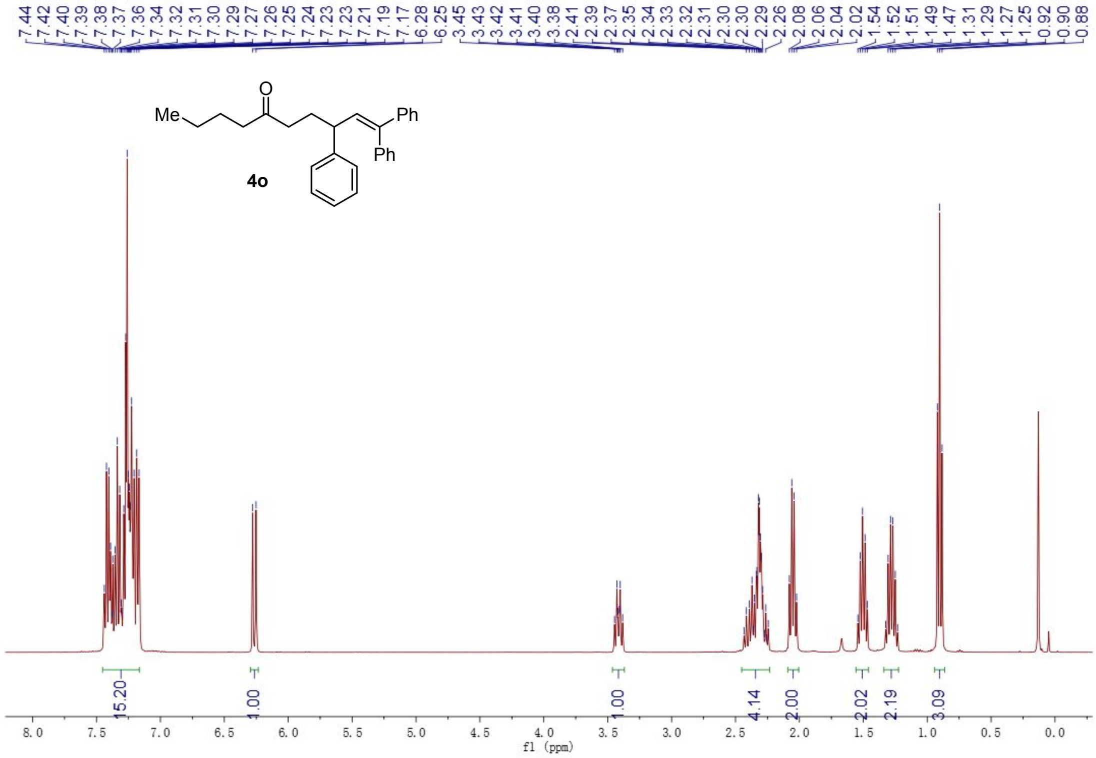
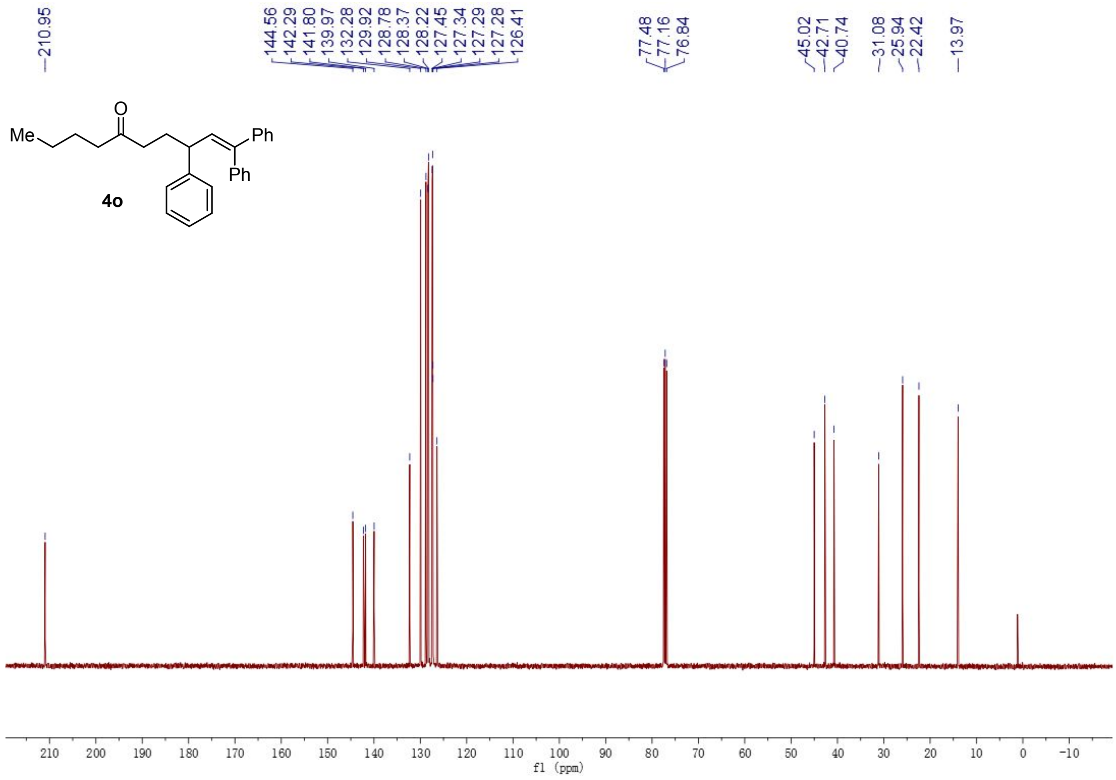
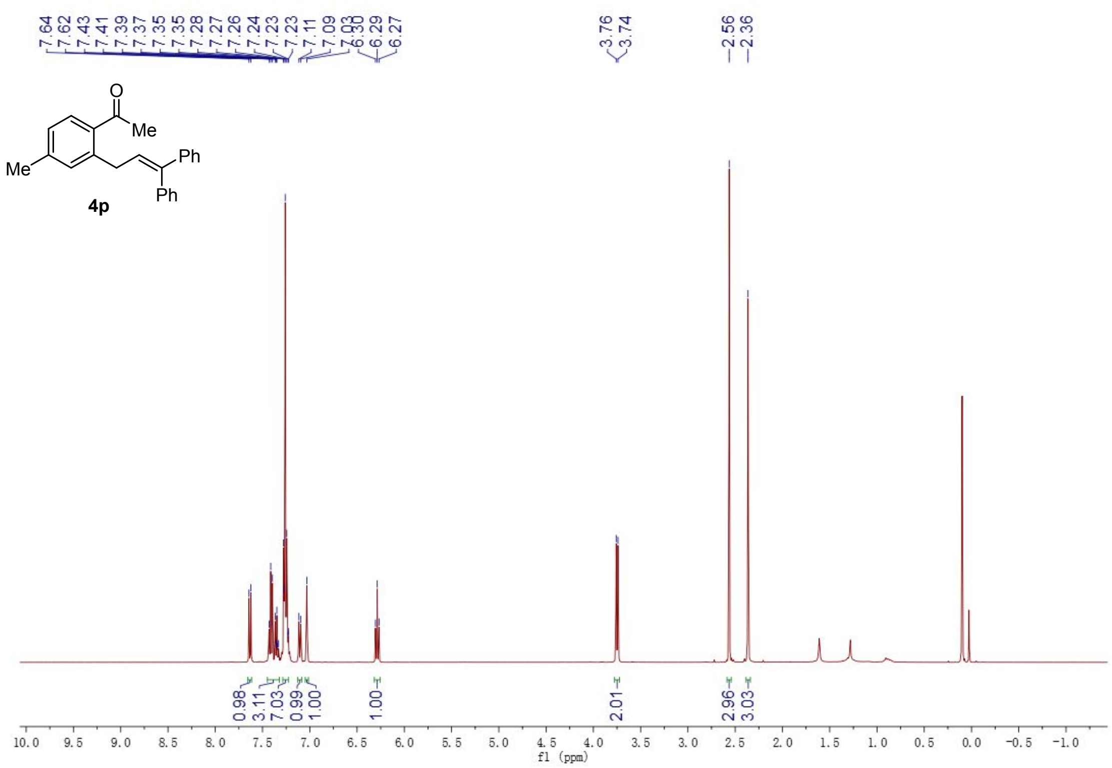
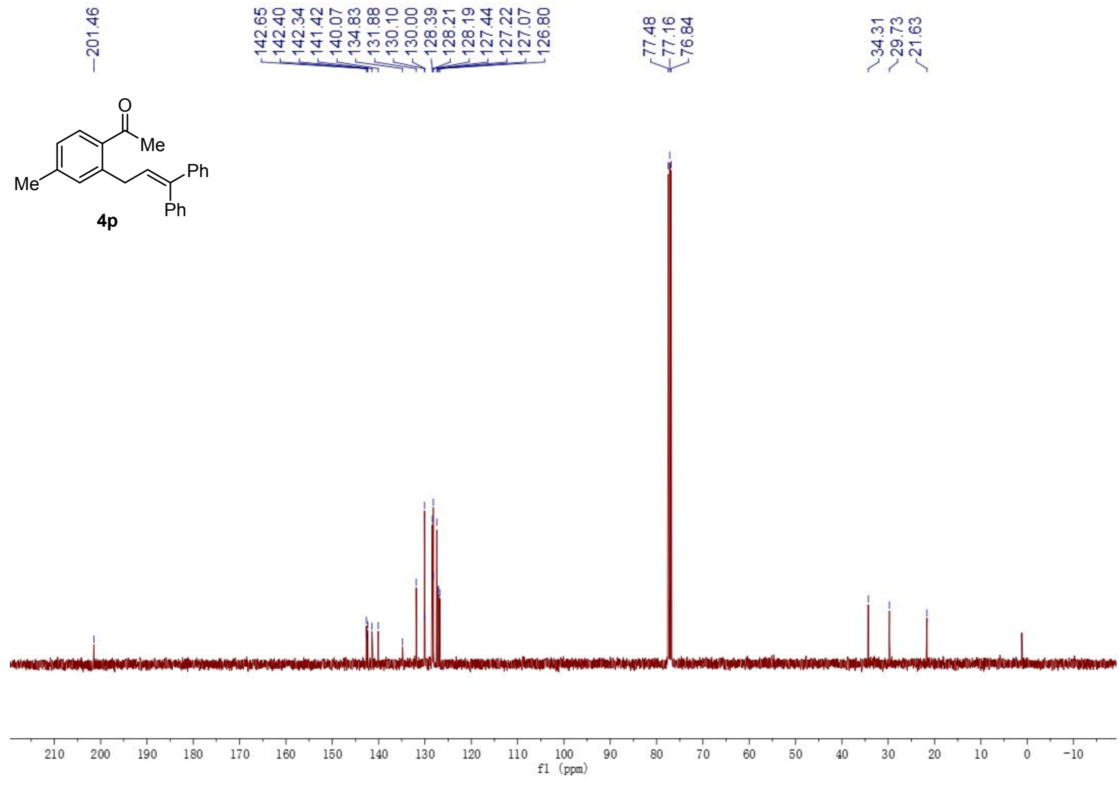
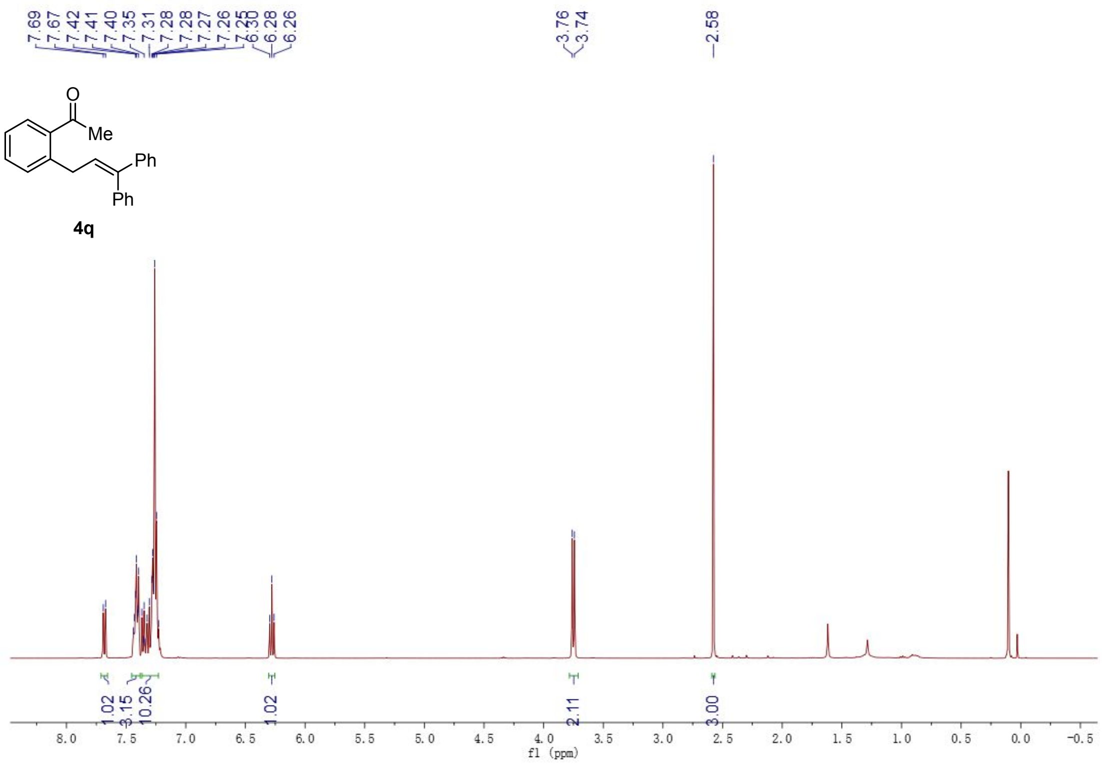
0
-10
f1 (ppm)


7.44 7.42 7.40 7.39 7.38 7.37 7.36 7.34 7.32 7.31 7.30 7.29 7.27 7.26 7.25 7.24 7.23 7.23 7.21 7.19 7.17 6.28 6.25 3.45 3.43 3.42 3.41 3.40 3.38 2.41 2.39 2.37 2.35 2.34 2.33 2.32 2.31 2.30 2.30 2.29 2.26 2.08 2.06 2.04 2.02 1.54 1.52 1.51 1.49 1.47 1.31 1.29 1.27 1.25 0.92 0.90 0.88
Me
O
Ph
Ph
4o
15.20
1.00
1.00
4.14
2.00
2.02
2.19
3.09
f1 (ppm)

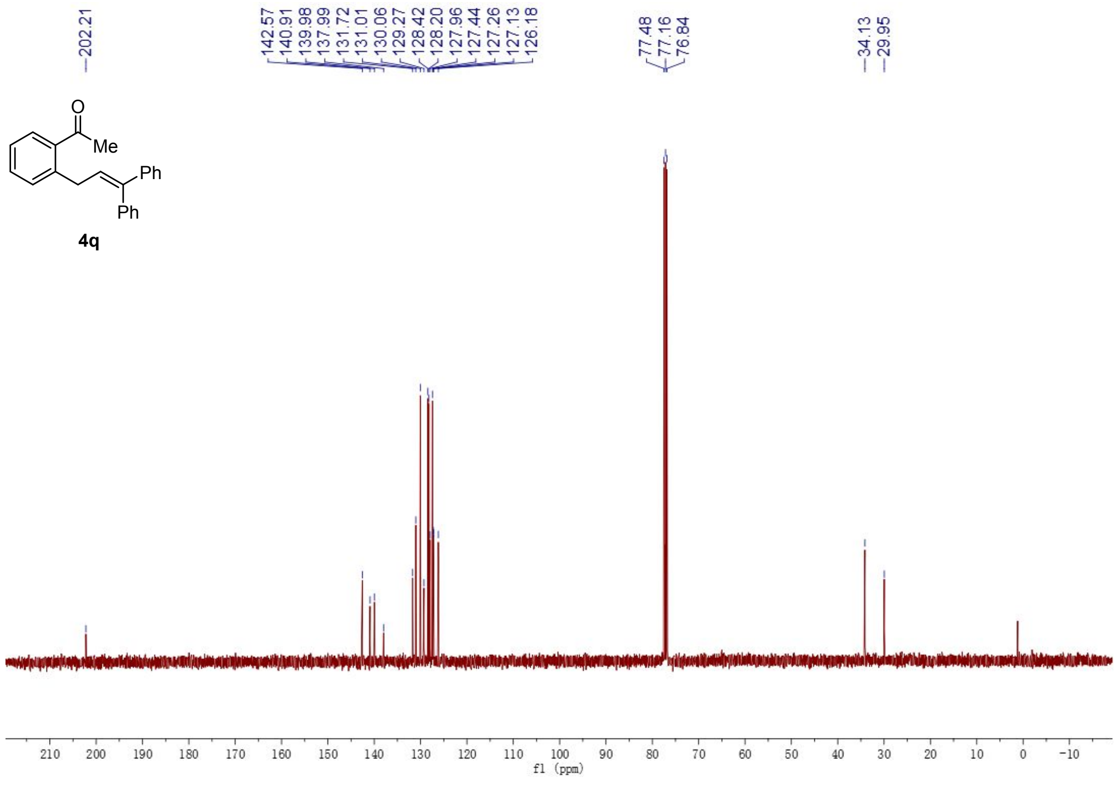

210.95
144.56 142.29 141.80 139.97 132.28 129.92 128.78 128.37 128.22 127.45 127.34 127.29 127.28 126.41
77.48 77.16 76.84
45.02 42.71 40.74
31.08 25.94 22.42
13.97
Me
O
Ph
Ph
4o
f1 (ppm)


7.64 7.62 7.43 7.41 7.39 7.37 7.35 7.35 7.28 7.27 7.26 7.24 7.23 7.23 7.11 7.09 7.03 6.30 6.29 6.27
3.76 3.74
2.56 2.36
Me
Me
Ph
Ph
4p
0.98 3.11 7.03 0.99 1.00
1.00
2.01
2.96 3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

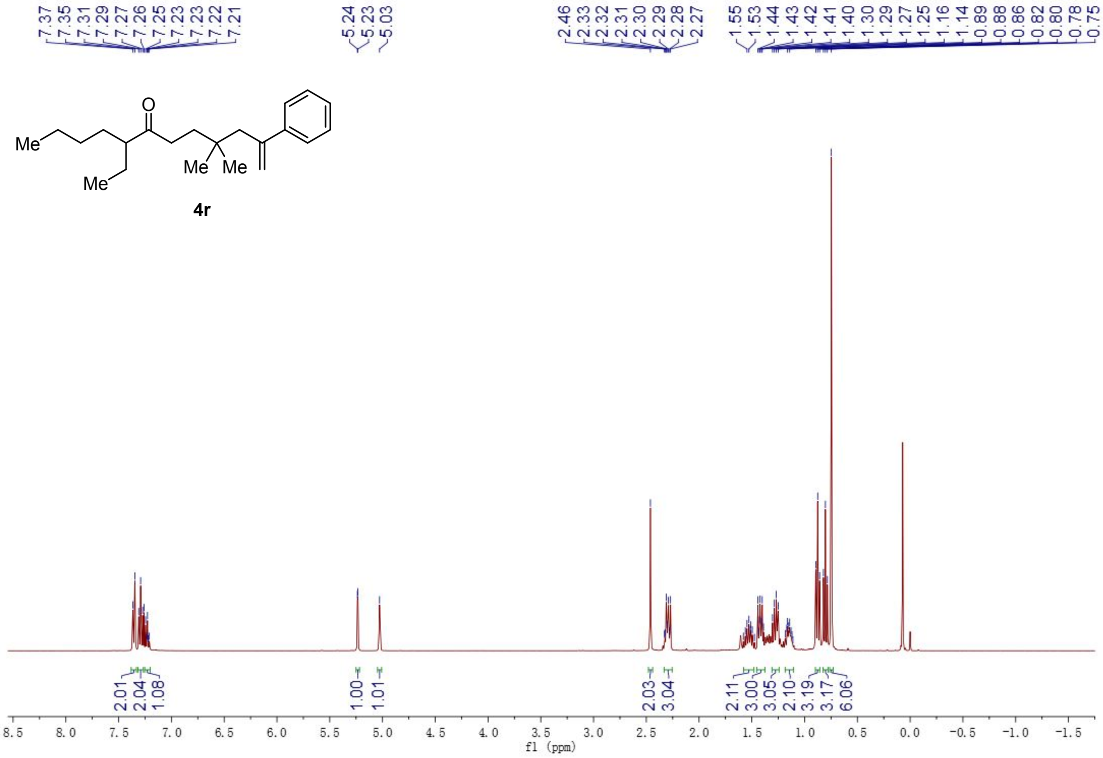

201.46
142.65 142.40 142.34 141.42 140.07 134.83 131.88 130.10 130.00 128.39 128.21 128.19 127.44 127.22 127.07 126.80
77.48 77.16 76.84
34.31 29.73 21.63
Me
Me
Ph
Ph
4p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

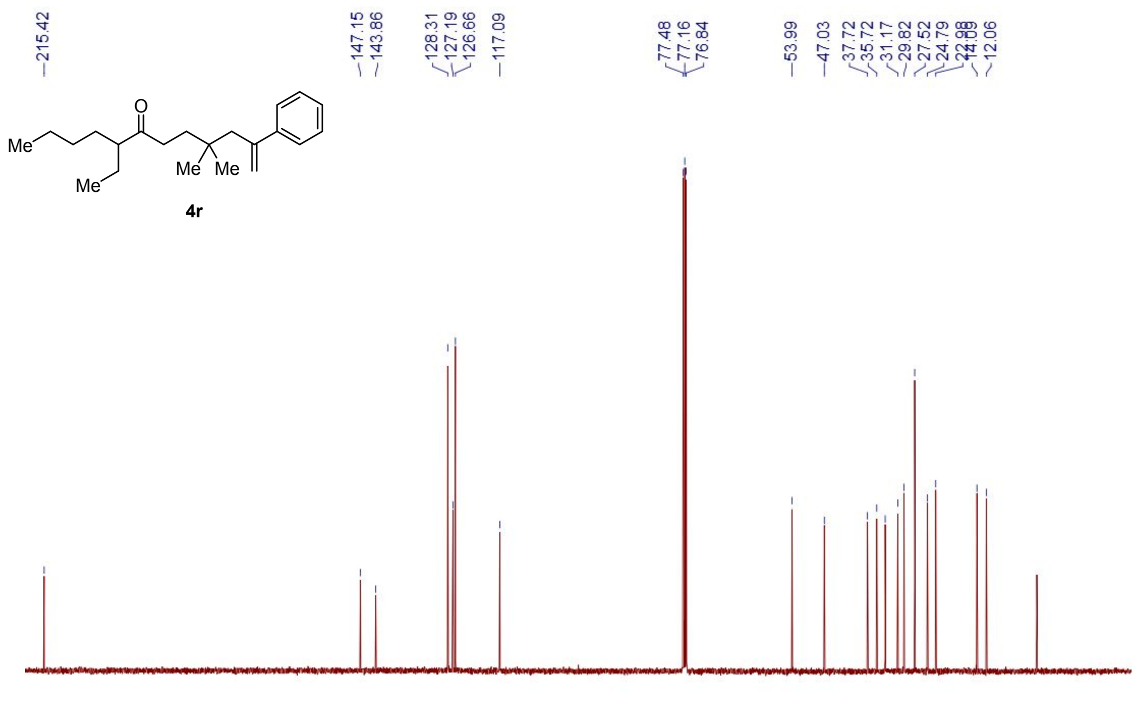

7.69
7.67
7.42
7.41
7.40
7.35
7.31
7.28
7.28
7.27
7.26
7.25
6.30
6.28
6.26
3.76
3.74
2.58
O
Me
Ph
Ph
1.02
3.15
10.26
1.02
2.11
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

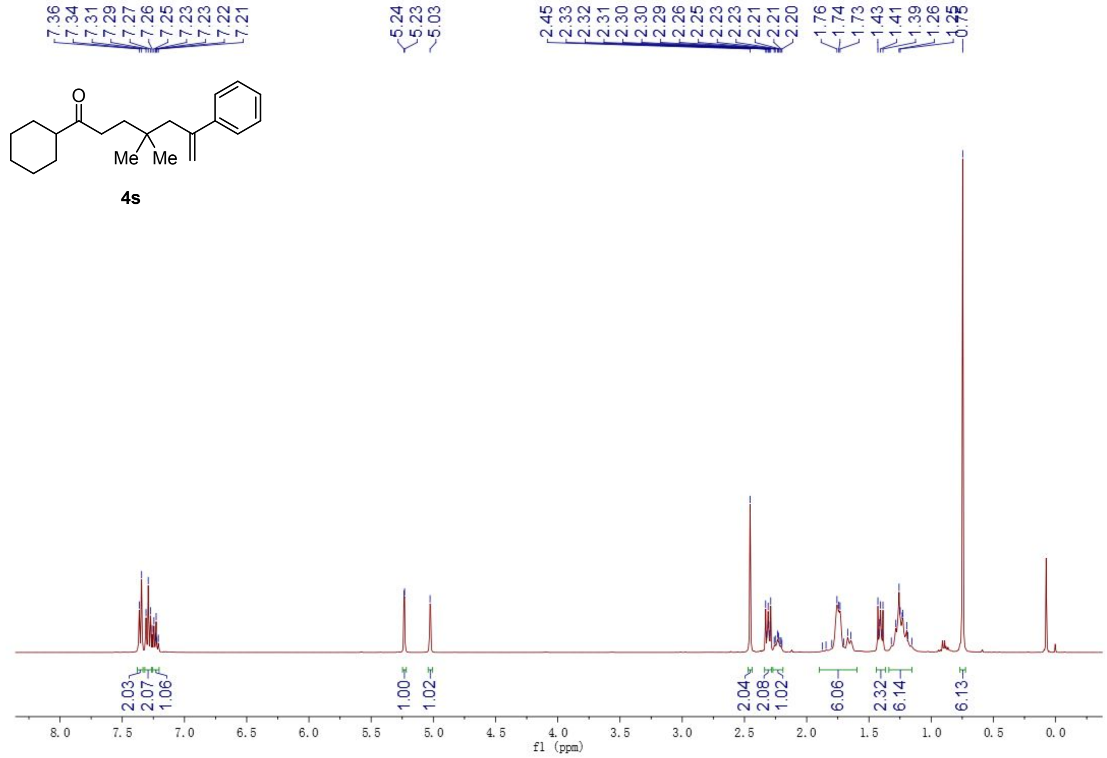
4q

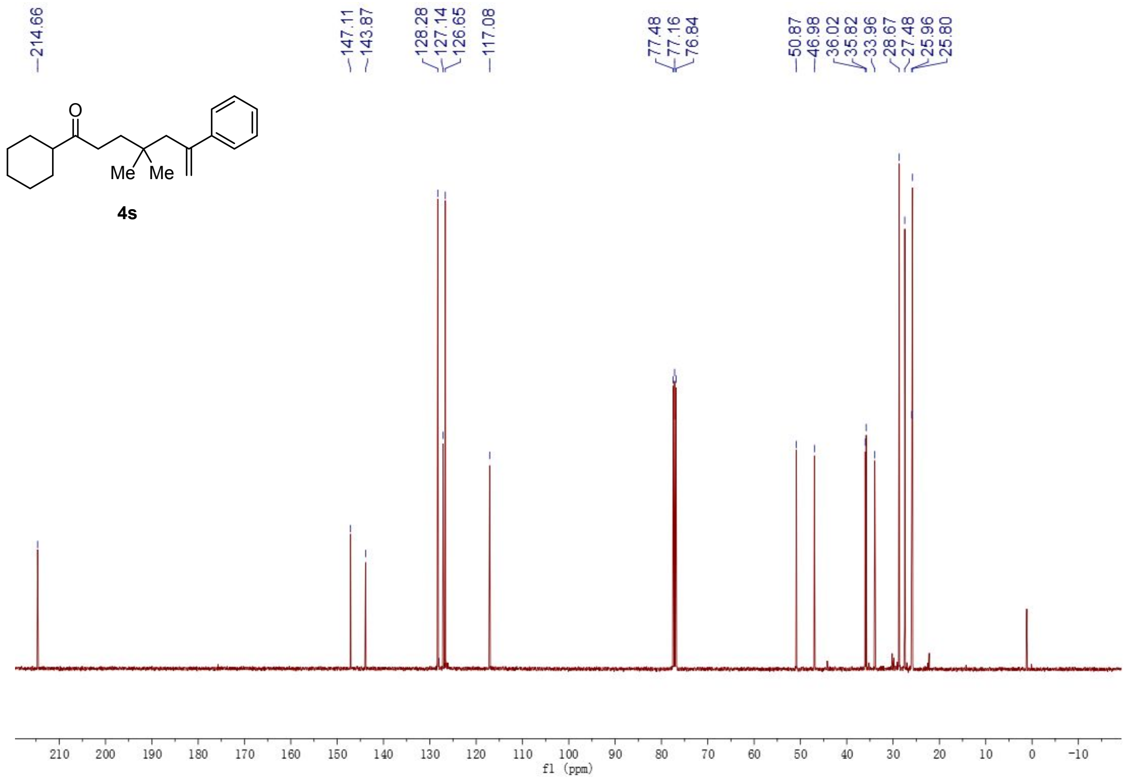

202.21
142.57
140.91
139.98
137.99
131.72
131.01
130.06
129.27
128.42
128.20
127.96
127.44
127.26
127.13
126.18
77.48
77.16
76.84
34.13
29.95
O
Me
Ph
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

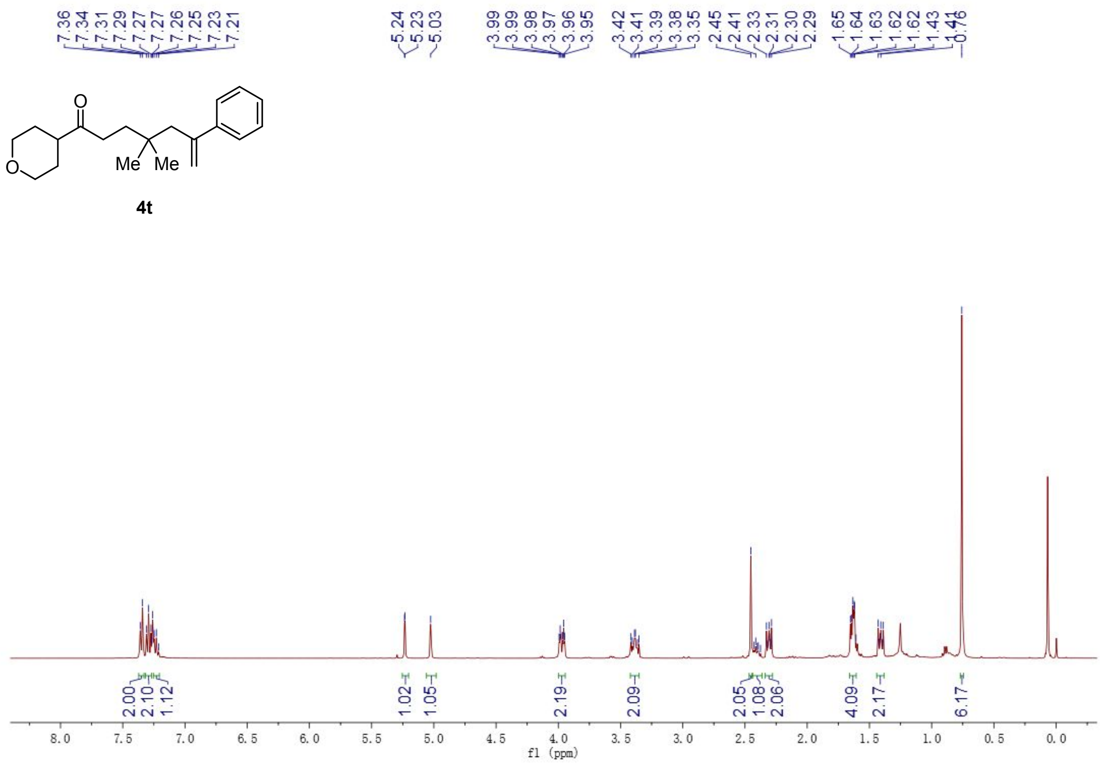
4q

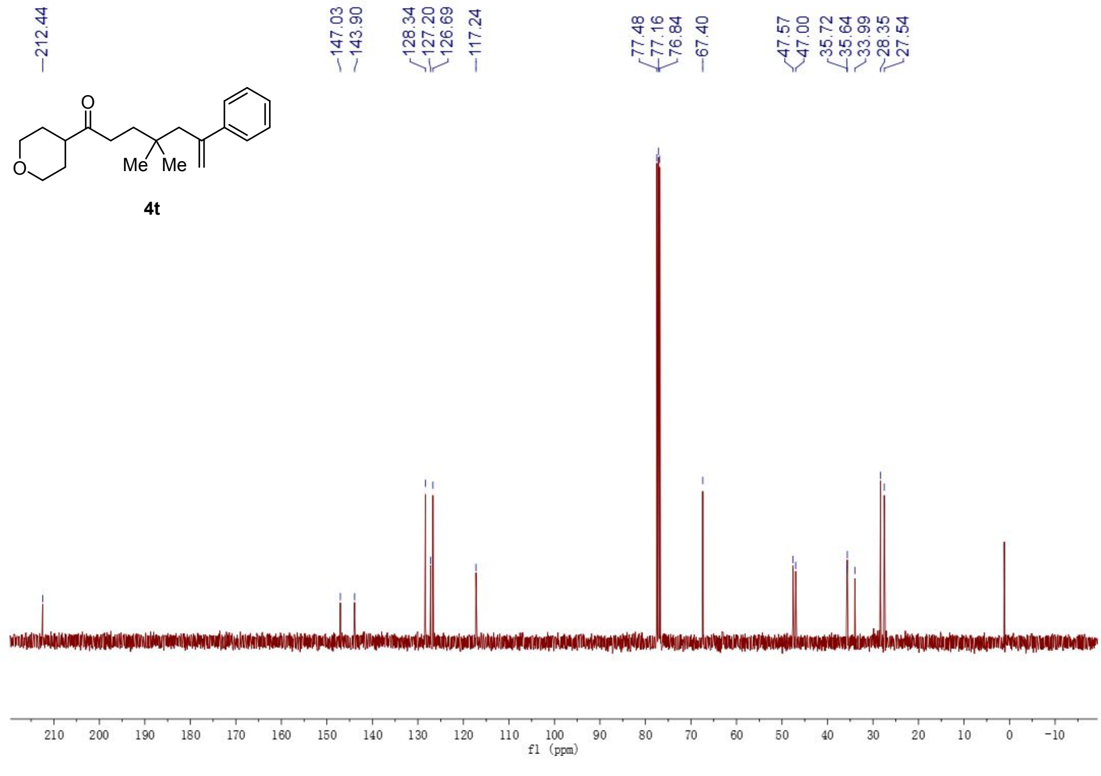


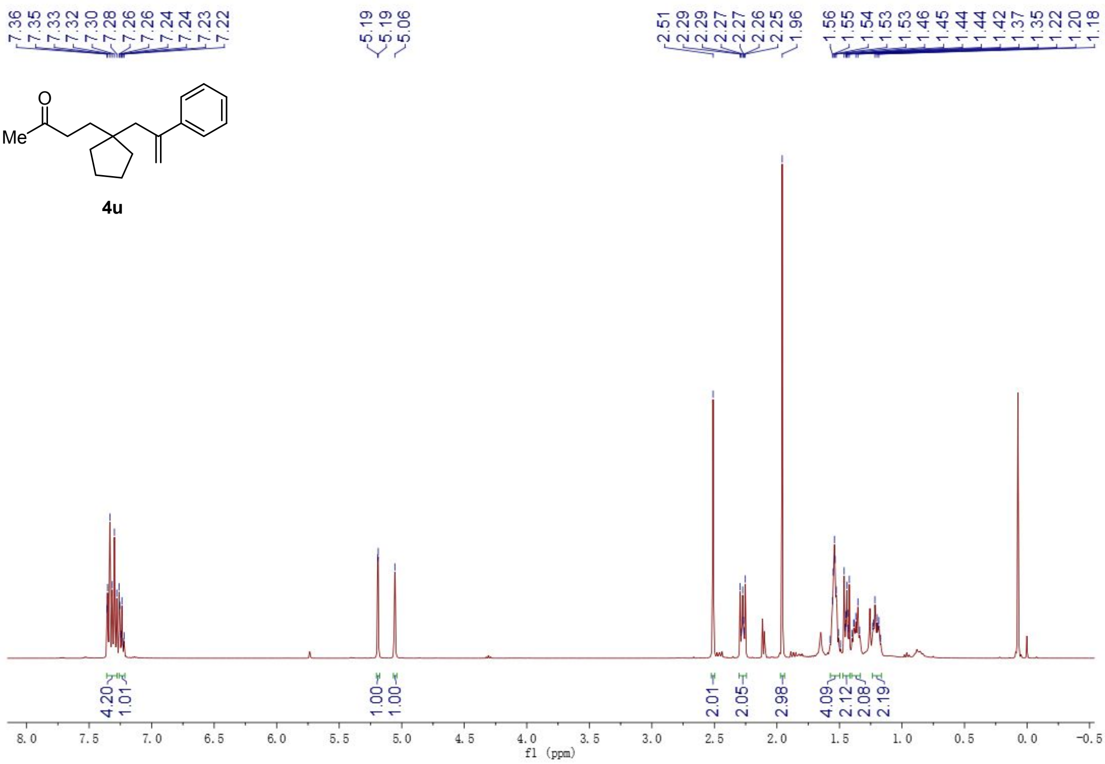


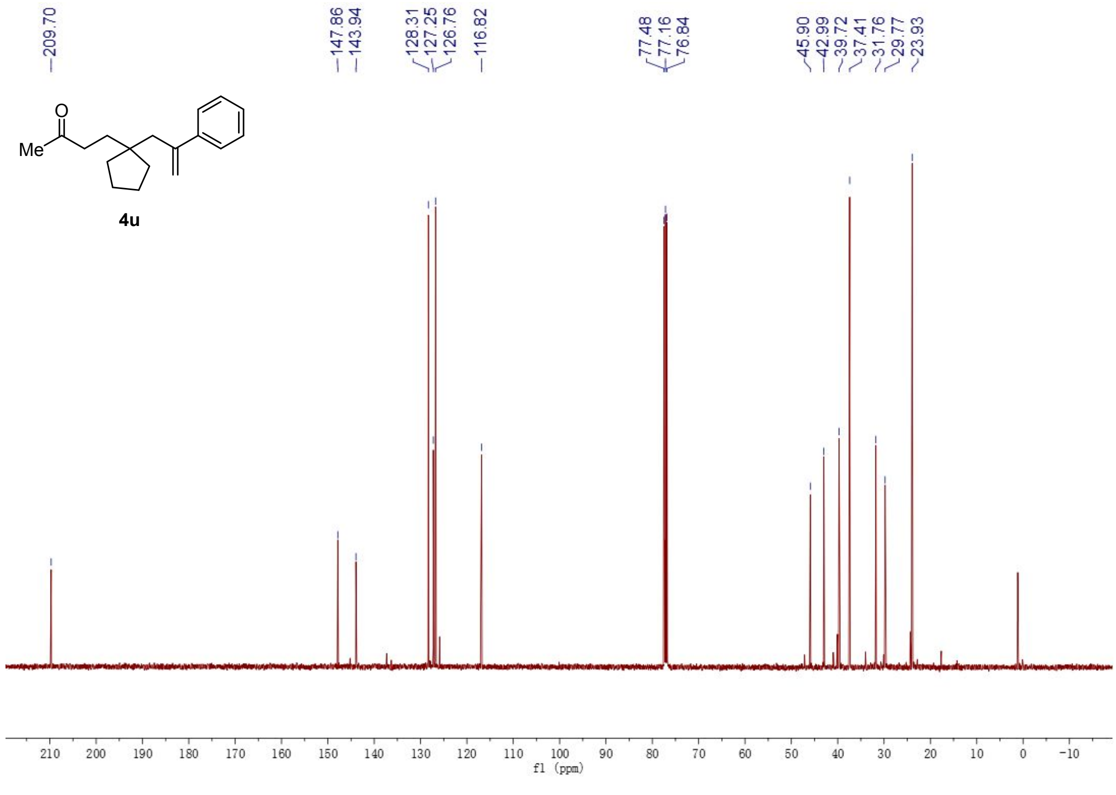

7.36 7.34 7.31 7.29 7.27 7.26 7.25 7.23 7.23 7.22 7.21
5.24 5.23 5.03
2.45 2.33 2.32 2.31 2.30 2.30 2.29 2.26 2.25 2.23 2.23 2.21 2.21 2.20
1.76 1.74 1.73 1.43 1.41 1.39 1.26 1.25 0.75
O
Me Me
4s
2.03 2.07 1.06 1.00 1.02 2.04 2.08 1.02 6.06 2.32 6.14 6.13
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


214.66
147.11 143.87
128.28 127.14 126.65 117.08
77.48 77.16 76.84
50.87 46.98 36.02 35.82 33.96 28.67 27.48 25.96 25.80
O
Me Me
4s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

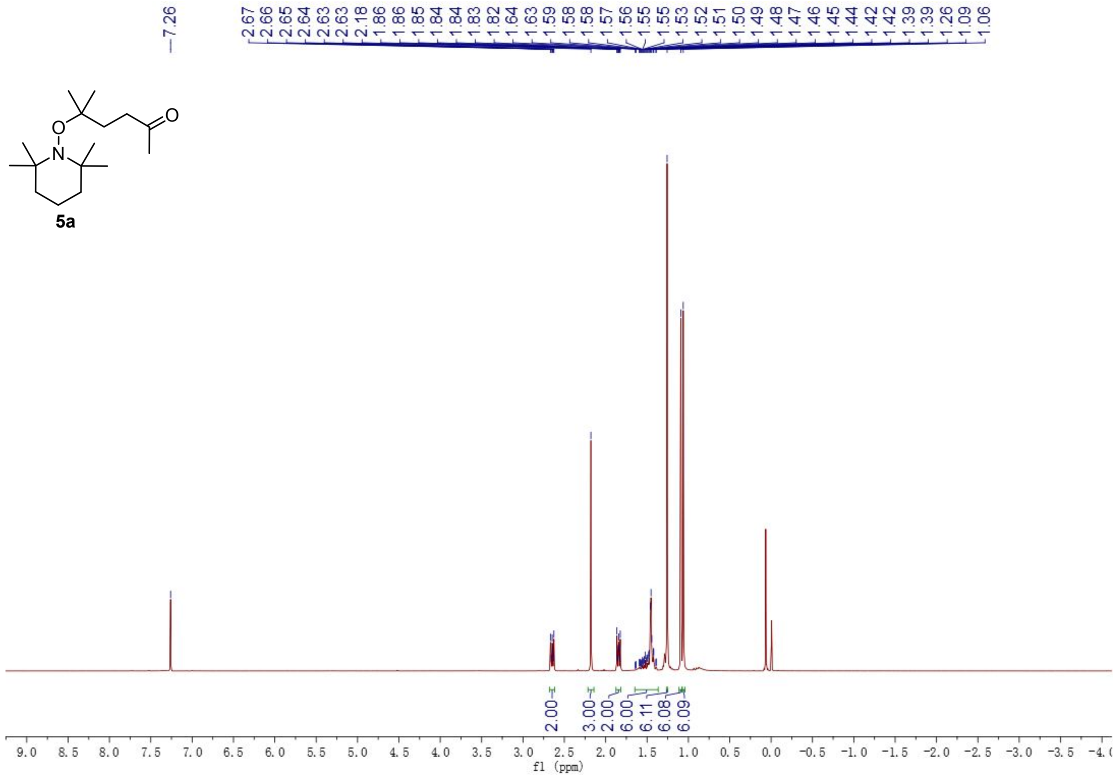

7.36 7.34 7.31 7.29 7.27 7.26 7.25 7.23 7.21
5.24 5.23 5.03
3.99 3.99 3.98 3.97 3.96 3.95
3.42 3.41 3.39 3.38 3.35
2.45 2.41 2.33 2.31 2.30 2.29
1.65 1.64 1.63 1.62 1.62 1.43 1.41 0.76
O
O
Me Me
4t
2.00 2.10 1.12 1.02 1.05 2.19 2.09 2.05 1.08 2.06 4.09 2.17 6.17
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


212.44
147.03 143.90
128.34 127.20 126.69
117.24
77.48 77.16 76.84
67.40
47.57 47.00
35.72 35.64 33.99
28.35 27.54
O
O
Me Me
4t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

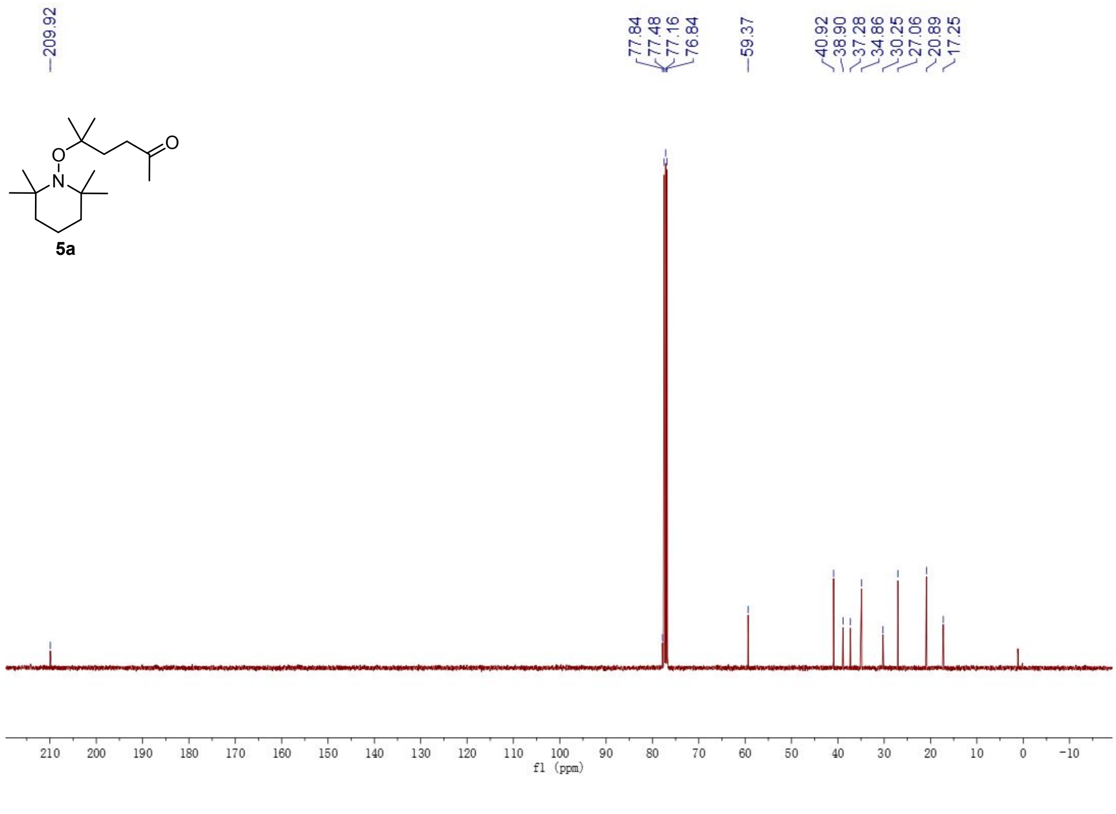

7.36 7.35 7.33 7.32 7.30 7.28 7.26 7.26 7.24 7.24 7.23 7.22
5.19 5.19 5.06
2.51 2.29 2.29 2.27 2.27 2.26 2.25 1.96
1.56 1.55 1.54 1.53 1.53 1.46 1.45 1.44 1.44 1.42 1.37 1.35 1.22 1.20 1.18
Me
O
4u
4.20 1.01 1.00 1.00 2.01 2.05 2.98 4.09 2.12 2.08 2.19
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


209.70
147.86 143.94
128.31 127.25 126.76
116.82
77.48 77.16 76.84
45.90 42.99 39.72 37.41 31.76 29.77 23.93
Me
O
4u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

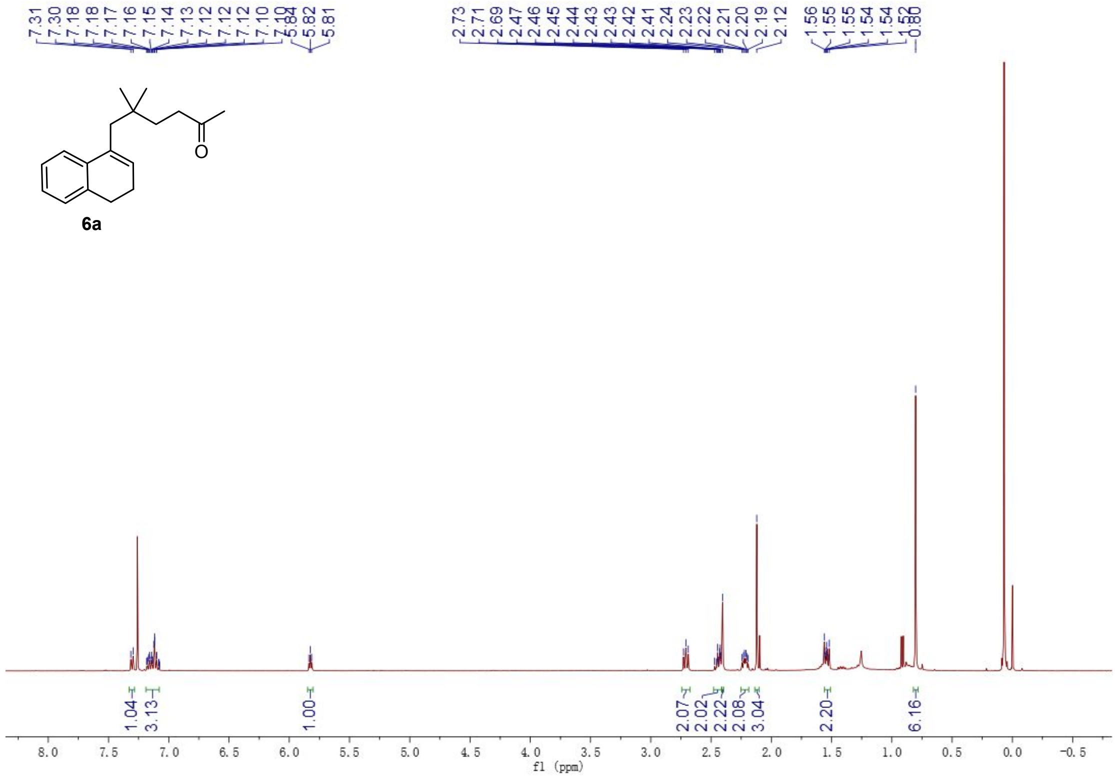
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR Spectra of Products 5a and 6a

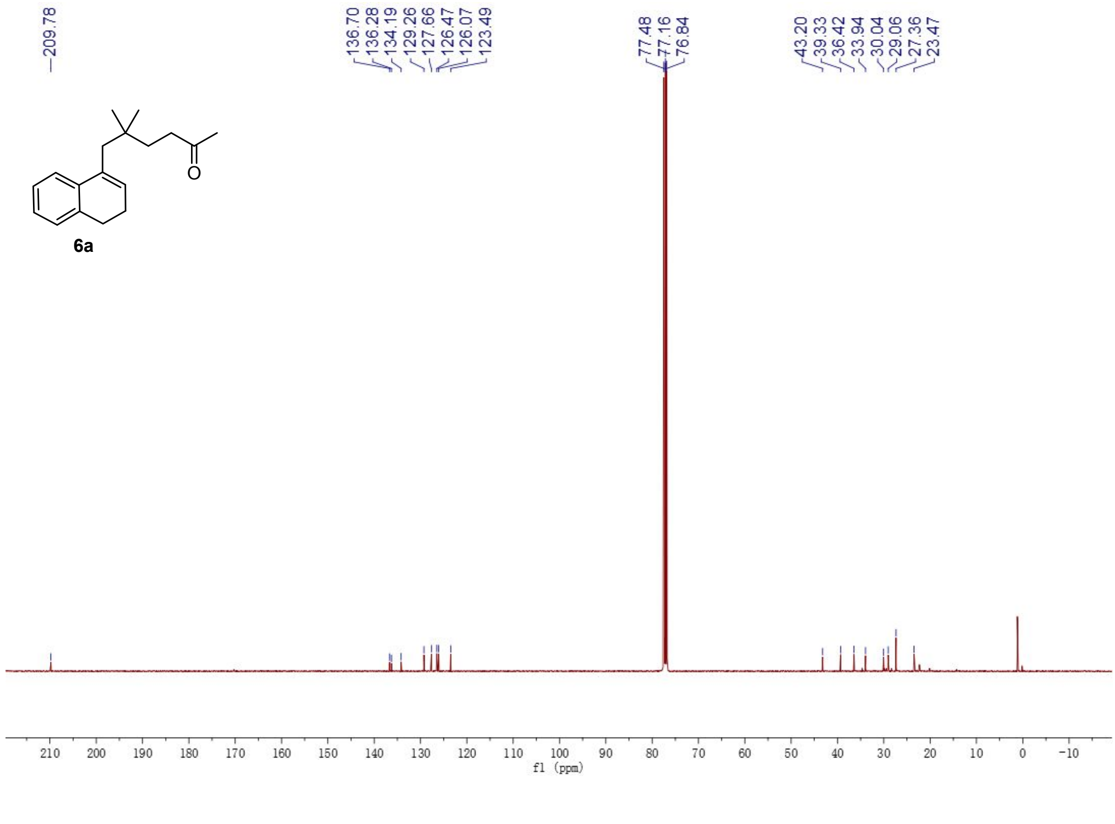


5a



5a


7.31
7.30
7.18
7.17
7.16
7.15
7.14
7.13
7.12
7.12
7.12
7.10
7.10
5.84
5.82
5.81
2.73
2.71
2.69
2.47
2.46
2.45
2.44
2.43
2.43
2.42
2.41
2.24
2.23
2.22
2.22
2.21
2.20
2.19
2.12
1.56
1.55
1.55
1.54
1.54
1.52
0.80
O
6a
1.04
3.13
1.00
2.07
2.02
2.22
2.08
3.04
2.20
6.16
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


209.78
136.70
136.28
134.19
129.26
127.66
126.47
126.07
123.49
77.48
77.16
76.84
43.20
39.33
36.42
33.94
30.04
29.06
27.36
23.47
O
6a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)