Supporting Information

Iron catalyzed ketoalkylation and ketoalkylation/etherification of styrenes initiated by selective C-C bond cleavage

Meng-Ting Suo, Shuo Yang, Jun-Cheng Yang, Ze-Yu Liu, Jun-Jie Zhang, and Li-Na Guo*

Department of Chemistry, School of Chemistry, 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.

Email: guoln81@xjtu.edu.cn

Table of Contents

General Information

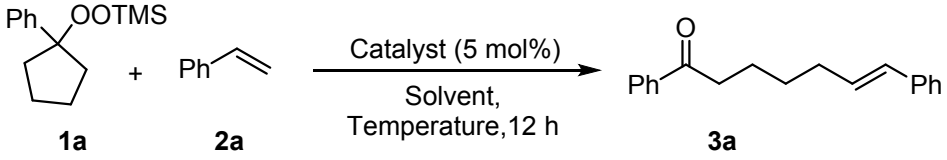
All reactions were conducted in 10mL oven-dried reaction tube under an atmosphere of nitrogen. Reactions were monitored by thin layer chromatography (TLC) and visualized using UV light or a basic DNP solution. Column chromatography was carried out on silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III-400 and Advance III-600 in solvents as indicated. Chemical shift are reported in parts per million from tetramethylsilane (TMS) with the solvent resonance as internal standard ($CDCl_3$: ^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.0). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are reported in cm^{-1}. High-resolution mass spectrometry (HRMS) spectra were obtained on a WATERS I-Class VION IMS Q-Tof. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification.

Starting Materials

All of cycloalkyl silyl peroxides **1** were prepared from the corresponding cycloalkyl alcohols according to the literature.[1,2] All of the NMR spectra of known compounds were in full accordance with the data in the literature.

Optimization of Reaction Conditions

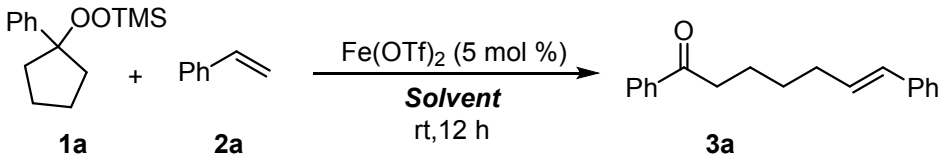
General Procedure for the Alkyl-Heck-type Coupling of Cyclopentyl Silyl Peroxide 1a with Styrene 2a



An 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with $Fe(OTf)_2$ (5 mol %). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cyclopentyl silyl peroxide **1a** (1.0 equiv.), styrene **2a** in solvent (See Table S1) was added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at specified temperature for 12 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether = 1:50) to give the product **3a** as colorless oil. The results are summarized as following.

Table S1. Optimization of the reaction of cyclopentyl silyl peroxide 1a with styrene 2a[a]

Solvent

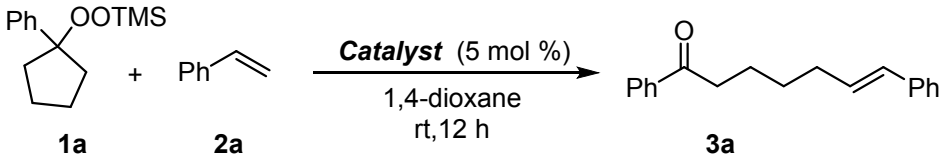


1a **2a** **3a**

Entry	Solvent	Yield (%)[b]
1	DMF	trace
2	DMAc	35
3	CH_3CN	41
4	DMSO	trace
5	THF	29
6	DME	30
7	MTBE	30
8	**1,4-dioxane**	**59**
9	DCE	8
10	Cyclohexane	28

[a]Reaction conditions: 5 mol % of $Fe(OTf)_2$, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.), solvent (1.0 mL), room temperature, for 12 h, under N_2.[b]Yields of isolated product of **3a**.

Catalyst

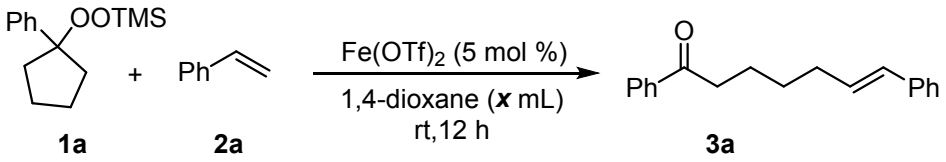


1a **2a** **3a**

Entry	Catalyst	Yield (%)[b]
1	**$Fe(OTf)_2$**	**59**
2	$Fe(OTs)_2$	trace
3	$FeBr_2$	trace
4	$Fe(OAc)_2$	trace
5	$FeSO_4•7H_2O$	trace
6	$Fe(OTf)_3$	56
7	$FeCl_3$	trace
8	$Fe(NO_3)_3•9H_2O$	trace
9	Cu(OTf)	51
10	$Cu(OTf)_2$	25
11	CuCl	trace
12	CuI	trace
13	$NiCl_2$•glyme	n.r.
14	$CoCl_2$	n.r.

[a]Reaction conditions: 5 mol % of catalyst, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.), 1,4-dioxane (1.0 mL), room temperature, for 12 h, under N_2. [b]Yields of isolated product of **3a**.

Concentration

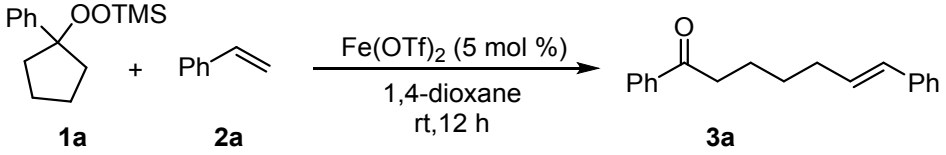


1a **2a** **3a**

Entry	Solvent/mL	Yield (%)[b]
1	1.0	59
2	**2.0**	**77**
3	5.0	73

[a]Reaction conditions: 5 mol % of $Fe(OTf)_2$, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.), 1,4-dioxane (***x*** mL), room temperature, for 12 h, under N_2.[b]Yields of isolated product of **3a**.

Ratio of 1a:2a

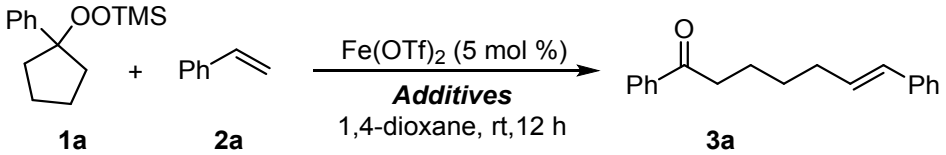


1a **2a** **3a**

Entry	**1a:2a**	Yield (%)[b]
1	1:1	57
2	**1:1.5**	**77**
3	1:2	81
4	1:3	84

[a]Reaction conditions: 5 mol % of $Fe(OTf)_2$, **1a** (0.2 mmol, 1.0 equiv.), **1a**:**2a** = 1:x, 1,4-dioxane (2.0 mL), room temperature, for 12 h, under N_2. [b]Yields of isolated product of **3a**.

Additives

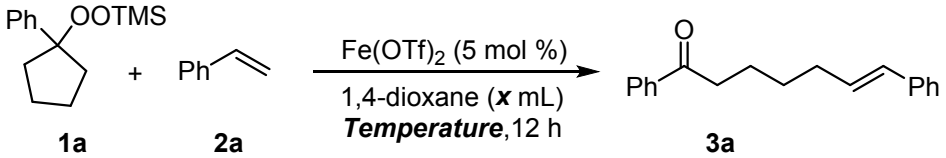


1a **2a** **3a**

Entry	Additives	Yield (%)[b]
1	**-**	**77**
2	TsOH	54
3	DABCO	n.r.
4	K_2CO_3	n.r.

[a]Reaction conditions: 5 mol % of $Fe(OTf)_2$, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.), 1,4-dioxane (2.0 mL), additives (0.4 mmol, 2.0 equiv.), room temperature, for 12 h, under N_2.[b]Yields of isolated product of **3a**.

Temperature



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

Entry	Temperature	Yield (%)[b]
1	r.t.	77
2	**40**	**84**
3	60	79
4	90	70

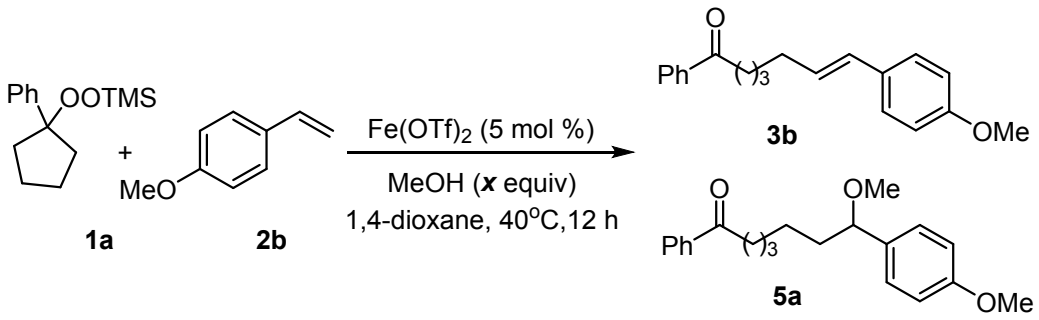
[a]Reaction conditions: 5 mol % of $Fe(OTf)_2$, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.), 1,4-dioxane (2.0 mL), temperature, for 12 h, under N_2.[b]Yields of isolated product of **3a**.

General Procedure for the Oxyalkylation of 4-Methoxystyrene 2b with Cyclopentyl Silyl Peroxide 1a and Methanol

An 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with 5 mol % of $Fe(OTf)_2$. Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cyclopentyl silyl peroxide **1a** (0.20 mmol, 1.0 equiv.), 4-methoxystyrene **2b** (0.30 mmol, 1.5 equiv.), methanol (See Table S2) in 1,4-dioxane (2.0 mL) was added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at 40 ^oC for 12 h. After that, the resulting mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether = 1:50) to give the product **5a** as colorless oil. The results are summarized as following.

Table S2. Optimization of the reaction of cyclopentyl silyl peroxide 1a with 4-Methoxystyrene 2b and methanol

Ratio of methanol [a]



Entry	Nucleophile (equiv.)	Yield (%)[b/c]
1	1.5	12/70
2	3.0	9/74
3	**5.0**	**trace/86**
4	10.0	trace/88

[a]Reaction conditions: 5 mol % of $Fe(OTf)_2$, **1a** (0.2 mmol, 1.0 equiv.), **2b** (0.3 mmol, 1.5 equiv.), 1,4-dioxane (2.0 mL), MeOH (**x** equiv.), 40°C, for 12 h, under N_2. [b]Yields of isolated product of **3b**. [c]Yields of isolated product of **5a**.

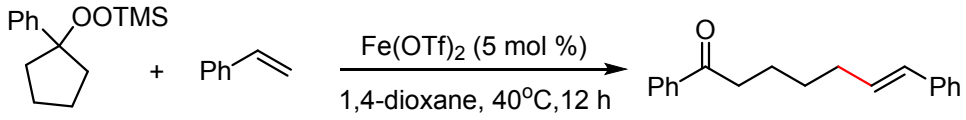
Representative Procedure for the Alkyl-Heck-type Couplings of Cycloalkyl Silyl Peroxides 1 with Olefins 2

An 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with $Fe(OTf)_2$ (5 mol %). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cycloalkyl silyl peroxide **1** (0.20 mmol, 1.0 equiv.), olefins **2** (0.30 mmol, 1.5 equiv.) in 1,4-dioxane (2 mL) was added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at 40 ^oC for 12 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether = 1:50) to give the product **3** or **4** in yields listed in Schemes 1 and 2.

Representative Procedure for the Oxyalkylation of Olefins 2 with Cycloalkyl Silyl Peroxides 1 and Nucleophiles

An 10 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with 5 mol % of $Fe(OTf)_2$. Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cycloalkyl silyl peroxides **1** (0.20 mmol, 1.0 equiv.), olefins **2** (0.30 mmol, 1.5 equiv.), nucleophiles (1.0 mmol, 5.0 equiv.) in 1,4-dioxane (2.0 mL) was added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at 40 ^oC for 12 h. After that, the resulting mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether = 1:50) to give the product **5** in yields listed in Scheme 3.

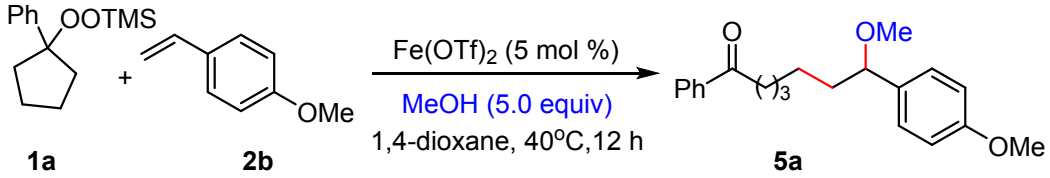
Larger Scale for the Reaction of Cyclopentyl Silyl Peroxide 1a with Styrene 2a



1a 2 mmol, 0.5 g | **2a** 3 mmol, 0.31 g | **3a** 0.42 g, 79%

An 100 mL oven-dried sealed tube equipped with a magnetic stirring bar was charged with $Fe(OTf)_2$ (5 mol %). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cyclopentyl silyl peroxide **1a** (2 mmol, 1.0 equiv, 0.50 g), styrene **2a** (3 mmol, 1.5 equiv, 0.31 g) in 1,4-dioxane (20 mL) was added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at 40°C for 24 h. After that, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether = 1:50) to obtain the product **3a** (0.42 g, 79%).

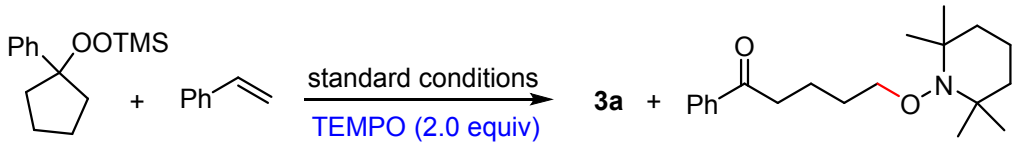
Larger Scale for the Reaction of Cyclopentyl Silyl Peroxide 1a with 4-Methoxystyrene 2b and Methanol



1a 2 mmol, 0.5 g **2b** 3 mmol, 0.40 g **5a** 0.5 g, 77%

An 100 mL oven-dried Schlenk-tube equipped with a magnetic stirrer was charged with $Fe(OTf)_2$ (5 mol %). Then, the tube was evacuated and backfilled with nitrogen for three times. Subsequently, a solution of cyclopentyl silyl peroxide **1a** (2 mmol, 1.0 equiv, 0.50 g), 4-methoxystyrene **2b** (3 mmol, 1.5 equiv, 0.40 g), methanol (10 mmol, 5.0 equiv, 0.32 g) in 1,4-dioxane (20 mL) was added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at 40 °C for 24 h. After that, the resulting mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether = 1:50) to obtain the product **5a** (0.50 g, 77%).

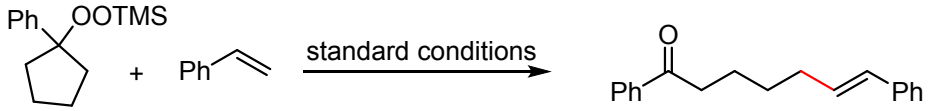
Investigation of the Reaction Mechanism



1a **2a** **3a**, 0% **6a**, 71%

When 2.0 equiv of TEMPO was added to the reaction of **1a** with **2a** under the standard conditions, no desired product **3a** was observed and the corresponding TEMPO-adduct **6a** was obtained in 71 % yield. These results indicate that a radical intermediate might be involved in this transformation.

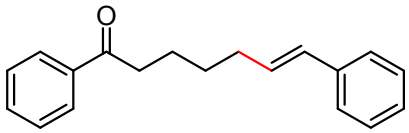
1-Phenyl-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentan-1-one (6a): (known compound)[1b,2]; Colorless oil; (71%, 45.0 mg); R_f = 0.3 (EtOAc/petroleum ether = 1:30); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.78 (t, *J* = 6.4 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.66 – 1.59 (m, 2H), 1.50 – 1.40 (m, 5H), 1.32 – 1.28 (m, 1H), 1.15 (s, 6H), 1.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 137.0, 132.8, 128.5, 128.0, 76.4, 59.6, 39.5, 38.6, 33.0, 28.4, 21.4, 20.1, 17.1 ppm.



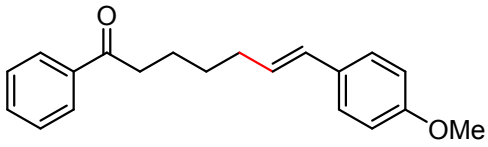
1a **2a** BHT (2.0 equiv) **3a**, 64%
BHT (4.0 equiv) **3a**, 15%

Moreover, when 2.0 equiv or 4.0 equiv of BHT was added to the reaction of **1a** with **2a**, both of them led to a decreased yield of **3a**. These results also support a radical pathway for this transformation.

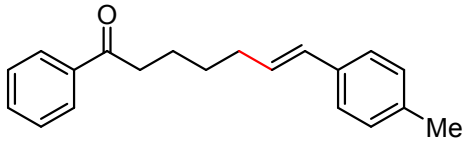
Characterization of Products 3



1,7-Diphenylhept-6-en-1-one (3a): (known compound)[b], Colorless oil; (84%, 44.5 mg); *E*/*Z* > 99:1; R_f = 0.45 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.54 – 7.49 (m, 1H), 7.44 – 7.40 (m, 2H), 7.33 – 7.22 (m, 4H), 7.19 – 7.13 (m, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 16.0, 6.8 Hz, 1H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.28 – 2.20 (m, 2H), 1.83 – 1.75 (m, 2H), 1.59 – 1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 137.7, 137.0, 132.9, 130.4, 130.1, 128.5, 128.4, 128.0, 126.8, 125.9, 38.4, 32.8, 29.0, 23.9 ppm.

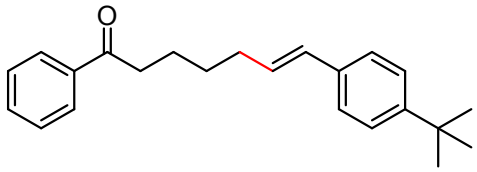


7-(4-Methoxyphenyl)-1-phenylhept-6-en-1-one (3b): Colorless oil; (76%, 44.7 mg); *E*/*Z* > 99:1; R_f = 0.41 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.08 (dt, *J* = 15.6, 7.2Hz, 1H), 3.80 (s, 3H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.23 – 2.28 (m, 2H), 1.85 – 1.78 (m, 2H), 1.61 – 1.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 158.6, 137.0, 132.9, 130.6, 129.5, 128.5, 128.3, 128.0, 127.0, 113.9, 55.2, 38.4, 32.8, 29.1, 23.9 ppm; IR (neat): υ_{max} 2923, 2853, 1725, 1682, 1603, 1508, 1453, 967, 741, 691 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}NaO_2$ $[M+Na]^+$, 317.1512, found 317.1510.

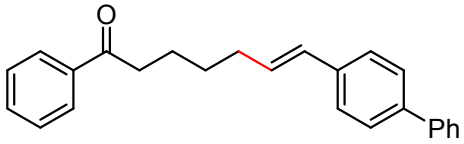


1-Phenyl-7-(*p*-tolyl)hept-6-en-1-one (3c): (known compound)[b], Faint yellow oil; (85%, 47.3 mg); *E*/*Z* > 99:1; R_f = 0.30 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 6.0 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.18 (dt, *J* =

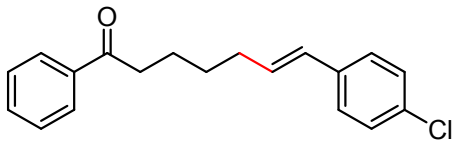
15.6, 6.8 Hz, 1H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.32 – 2.52 (m, 2H), 1.86 – 1.78 (m, 2H), 1.61 – 1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 137.0, 136.5, 135.0, 132.9, 130.0, 129.4, 129.1, 128.5, 128.0, 125.8, 38.4, 32.8, 29.1, 23.9, 21.1 ppm.



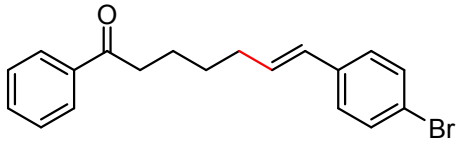
7-(4-(*tert*-Butyl)phenyl)-1-phenylhept-6-en-1-one (3d): Yellow oil; (76%, 48.7 mg); *E*/*Z* > 99:1; R_f = 0.34 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.28 (m, 4H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 15.6, 6.8 Hz, 1H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.29 – 2.23 (m, 2H), 1.85 – 1.76 (m, 2H), 1.62 – 1.54 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 149.8, 137.0, 135.0, 132.9, 129.8, 129.7, 128.5, 128.0, 125.6, 125.3, 38.4, 34.4, 32.8, 31.3, 29.1, 23.9 ppm; IR (neat): υ_{max} 2957, 2866, 1685, 1595, 1510, 1453, 1404, 839, 745, 693 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{28}NaO$ $[M+Na]^+$, 343.2032, found 343.2030.



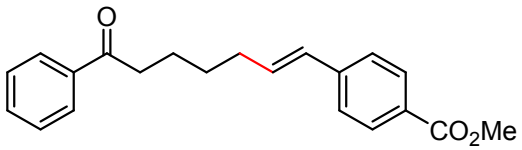
7-([1,1'-Biphenyl]-4-yl)-1-phenylhept-6-en-1-one (3e): White soild; (82%, 55.8 mg); mp: 99 – 102 °C; *E*/*Z* > 99:1; R_f = 0.25 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.62 – 7.58 (m, 2H), 7.58 – 7.53 (m, 3H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.45 – 7.40 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.28 (dt, *J* = 15.6, 6.6 Hz, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.34 – 2.28 (m, 2H), 1.86 – 1.82 (m, 2H), 1.63 – 1.58 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.3, 140.8, 139.6, 137.0, 136.8, 132.9, 130.7, 129.7, 128.7, 128.6, 128.0, 127.2, 127.1, 126.9, 126.3, 38.4, 32.9, 29.0, 23.9 ppm; IR (neat): υ_{max} 3029, 2927, 2861, 1674, 1590, 1451, 1409, 853, 753, 689 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{24}NaO$ $[M+Na]^+$ 363.1719, found 363.1717.



7-(4-Chlorophenyl)-1-phenylhept-6-en-1-one (3f): (known compound)[b], White solid; (73%, 42.8 mg); *E*/*Z* > 99:1; R_f = 0.31 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* =8.0 Hz, 2H), 7.26 – 7.27 (m, 4H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.28 (dt, *J* = 15.6, 6.6 Hz, 1H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.30 – 2.25 (m, 2H), 1.86 – 1.78 (m, 2H), 1.63 – 1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.2, 137.0, 136.2, 132.9, 132.3, 131.2, 129.0, 128.5, 128.0, 127.1, 38.3, 32.8, 28.9, 23.8 ppm.

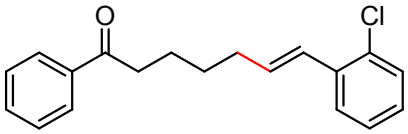


7-(4-Fromophenyl)-1-phenylhept-6-en-1-one (3g): (known compound)[b], White solid; (72%, 49.4 mg); *E*/*Z* > 99:1; R_f = 0.31 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.20 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.22 (dt, *J* = 16.0, 6.8 Hz, 1H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.29 – 2.23 (m, 2H), 1.84 – 1.76 (m, 2H), 1.60 – 1.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 136.9, 136.6, 133.0, 131.5, 131.3, 129.0, 128.6, 128.0, 127.5, 120.4, 38.3, 32.8, 28.8, 23.8 ppm.

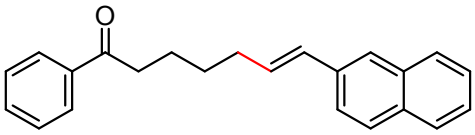


Methyl-4-(7-oxo-7-phenylhept-1-en-1-yl)benzoate (3h): Yellow oil; (77%, 49.6 mg); *E*/*Z* > 99:1; R_f = 0.25 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.58 – 7.52 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.17 (dt, *J* = 16.0, 6.8 Hz, 1H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 2.28 – 2.23 (m, 2H), 1.85 – 1.77 (m, 2H), 1.60 – 1.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 169.5, 149.5, 137.0, 135.6, 132.9, 130.7, 129.2, 128.6, 128.0, 126.8, 121.5, 38.4, 32.8, 29.0, 23.9, 21.1 ppm; IR (neat): υ_{max} 2932, 1760, 1683, 1593, 1505, 1447, 853, 747, 693 cm^{-1}; HRMS (ESI) calcd for

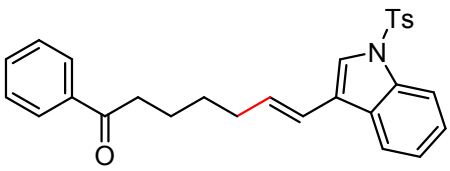
$C_{21}H_{22}NaO_3$ $[M+Na]^+$ 345.1461, found 345.1460.



7-(2-Chlorophenyl)-1-phenylhept-6-en-1-one (3i): Yellow oil; (77%, 46.1 mg); *E*/*Z* > 99:1; R_f = 0.38 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 15.6 Hz, 1H), 6.27 – 6.16 (m, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.35 – 2.30 (m, 2H), 1.87 – 1.79 (m, 2H), 1.64 – 1.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 137.0, 135.8, 133.4, 132.9, 132.5, 129.6, 128.6, 128.0, 127.9, 126.7, 126.6, 126.4, 38.4, 33.0, 28.9, 23.9 ppm; IR (neat): υ_{max} 3062, 2932, 1684, 1591, 1446, 970, 802, 751, 693 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{19}ClNaO$ $[M+Na]^+$ 321.1017, found 321.1016.

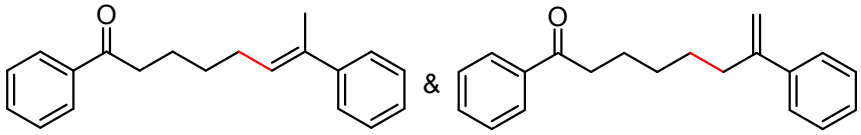


7-(Naphthalen-2-yl)-1-phenylhept-6-en-1-one (3j): Yellow oil; (81%, 50.1 mg); *E*/*Z* > 99:1; R_f = 0.33 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.78 – 7.75 (m, 3H), 7.67 (s, 1H), 7.59 – 7.53 (m, 2H), 7.48 – 7.39 (m, 4H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.36 (dt, *J* = 16.2, 6.6 Hz, 1H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.36 – 2.31 (m, 2H), 1.87 – 1.82 (m, 2H), 1.65 – 1.60 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.33, 137.01, 135.20, 133.68, 132.92, 132.65, 130.95, 130.27, 128.56, 128.04, 128.03, 127.81, 127.60, 126.09, 125.44, 125.36, 123.54, 38.42, 32.97, 29.05, 23.92 ppm; IR (neat): υ_{max} 3056, 2930, 2854, 1681, 1626, 1597, 1580, 1508, 1448, 1409, 811, 659 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}NaO$ $[M+Na]^+$ 337.1563, found 337.1559.



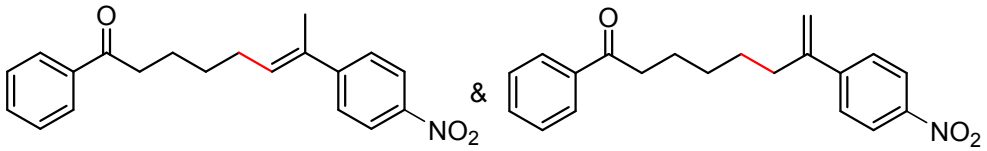
1-Phenyl-7-(1-tosyl-1H-indol-3-yl)hept-6-en-1-one (3k): Faint yellow oil; (28%,

25.6 mg); *E*/*Z* > 99:1; R_f = 0.23 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 3H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.51 (s, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.19 (m, 3H), 6.45 (d, *J* = 16.4 Hz, 1H), 6.32 – 6.23 (m, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 2.31 – 2.27 (m, 2H), 1.87 – 1.79 (m, 2H), 1.63 – 1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 144.9, 136.9, 135.1, 132.9, 132.1, 129.8, 129.2, 128.6, 128.0, 126.8, 124.7, 123.3, 122.8, 120.9, 120.5, 120.3, 113.7, 38.4, 33.3, 29.0, 23.8, 21.5 ppm; IR (neat): υ_{max} 3394, 2925, 2315, 1686, 1521, 756, 685 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}NNaO_3S$ $[M+Na]^+$480.1604, found 480.1609.



***l*-3l** 67 : ***t*-3l** 33

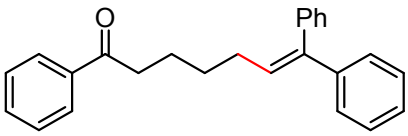
1,7-Diphenyloct-6-en-1-one (*l*-3l) and 1,7-diphenyloct-7-en-1-one (*t*-3l): (known compound)[b], Yellow oil; (98%, 54.5 mg); *l*/*t* = 67:33; R_f = 0.43 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 3H), 7.58 – 7.54 (m, 1.5H), 7.48 – 7.45 (m, 3H), 7.43 – 7.35 (m, 3H), 7.35 – 7.28 (m, 3H), 7.25 – 7.20 (m, 1.5H), 5.83 – 5.76 (m, 1H), 5.27 (d, *J* = 1.2 Hz, 0.5H), 5.06 (d, *J* = 1.2 Hz, 0.5H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 1H), 2.53 (t, *J* = 7.2 Hz, 1H), 2.30 – 2.24 (m, 2H), 2.05 (s, 3H), 1.87 – 1.81 (m, 2H), 1.79 – 1.71 (m, 1H), 1.61 – 1.51 (m, 3H), 1.48 – 1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.42, 200.35, 148.46, 143.87, 141.27, 137.01, 134.95, 132.89, 132.86, 128.54, 128.52, 128.22, 128.11, 128.07, 128.02, 127.25, 126.47, 126.09, 125.58, 112.23, 38.46, 35.13, 29.28, 28.93, 28.60, 27.99, 24.08, 15.81 ppm.



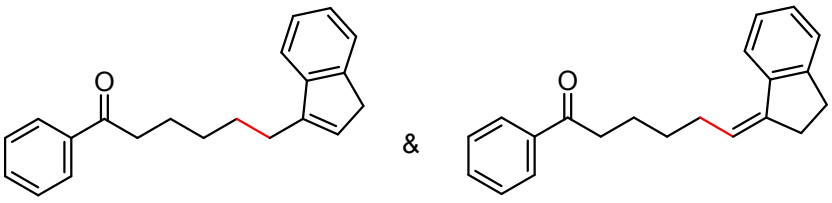
***l*-3m** 90 : ***t*-3m** 10

7-(4-Nitrophenyl)-1-phenyloct-6-en-1-one (*l*-3m) and 7-(4-Nitrophenyl)-1-phenyloct-7-en-1-one (*t*-3m): Yellow oil; (76%, 49.0 mg); *l*/*t* = 90:10; R_f = 0.42

(EtOAc/petroleum ether = 1:15); ***l*-3m:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.14 (m, 2H), 7.97 – 7.93 (m, 2H), 7.58 – 7.53 (m, 1H), 7.52 – 7.43 (m, 4H), 6.01 – 5.90 (m, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.33 – 2.27 (m, 2H), 2.07 (s, 3H), 1.87 – 1.77 (m, 2H), 1.65 – 1.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.1, 150.3, 146.2, 137.0, 133.6, 133.0, 132.3, 128.6, 128.0, 126.1, 123.5, 38.3, 29.0, 28.9, 24.0, 15.6 ppm; IR (neat): υ_{max} 3448, 2315, 1627, 1382, 746, 664 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}NO_3$ $[M+H]^+$ 324.1594, found 324.1589.



1,7,7-Triphenylhept-6-en-1-one (3n): Yellow oil; (76%, 51.8 mg); *E*/*Z* > 99:1; R_f = 0.35 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.41 (m, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 2H), 7.23 – 7.20 (m, 3H), 7.20 (m, 1H), 7.18 – 7.15 (m, 2H), 6.08 (t, *J* = 7.2 Hz, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.20 – 2.14 (m, 2H), 1.78 – 1.71 (m, 2H), 1.58 – 1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.27, 142.68, 141.91, 140.16, 137.01, 132.85, 129.88, 129.49, 128.51, 128.12, 128.03, 128.00, 127.18, 126.85, 126.79, 38.19, 29.43, 29.37, 23.72 ppm; IR (neat): υ_{max} 3451, 3060, 2935, 1682, 1592, 1494, 1449, 757, 698, 643 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{24}NaO$ $[M+Na]^+$ 363.1719, found 363.1717.

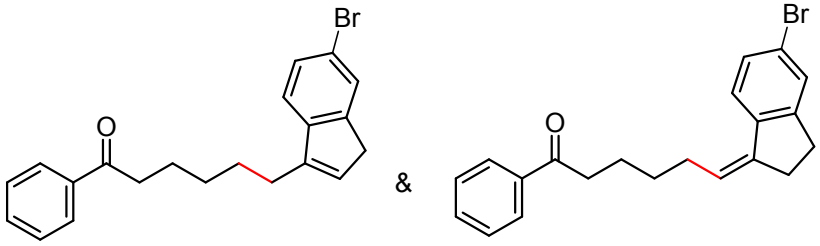


***endo*-3o** : ***exo*-3o**

89 : 11

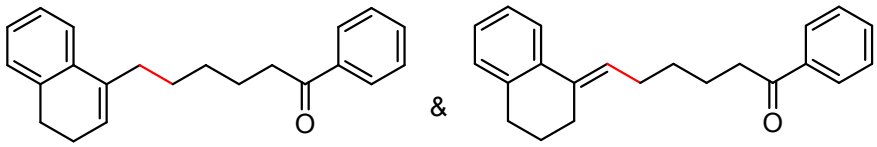
6-(1*H*-Inden-3-yl)-1-phenylhexan-1-one (*endo*-3o) and 6-(2,3-Dihydro-1H-inden-1-ylidene)-1-phenylhexan-1-one (*exo*-3o) : Yellow oil; (74%, 42.9 mg); *endo*: *exo* = 89:11; R_f = 0.34 (EtOAc/petroleum ether = 1:25); ***endo*-3o:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.48 – 7.45 (m, 3H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.21 (s, 1H), 3.33 (d, *J* = 1.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.60 – 2.56 (m, 2H), 1.84 – 1.79 (m, 2H), 1.79

– 1.73 (m, 2H), 1.55 – 1.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.5, 145.5, 144.5, 144.4, 137.1, 132.9, 128.5, 128.0, 127.8, 125.9, 124.4, 123.7, 118.9, 38.5, 37.7, 29.3, 27.8, 27.6, 24.2 ppm; IR (neat): υ_{max} 3062, 2935, 1682, 1593, 1453, 804, 693 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{22}NaO$ $[M+Na]^+$ 313.1563, found 313.1570.



***endo*-3p** 91 : ***exo*-3p** 9

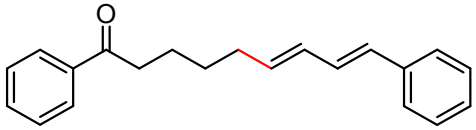
6-(6-Bromo-1*H*-inden-3-yl)-1-phenylhexan-1-one (*endo*-3p) and 6-(5-Bromo-2,3-dihydro-1H-inden-1-ylidene)-1-phenylhexan-1-one (*exo*-3p): Yellow oil; (71%, 52.4 mg); *endo*: *exo* = 91:9; R_f = 0.35 (EtOAc/petroleum ether = 1:20); ***endo*-3p:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.48 – 7.44 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.18 (s, 1H), 3.30 (s, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H), 1.84 – 1.76 (m, 2H), 1.76 – 1.68 (m, 2H), 1.54 – 1.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 146.6, 144.4, 143.9, 137.0, 132.9, 129.0, 128.5, 128.2, 128.0, 126.9, 120.1, 118.6, 38.5, 37.6, 29.2, 27.8, 27.4, 24.1 ppm; IR (neat): υ_{max} 3449, 2931, 1682, 1593, 1454, 803, 752, 691 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{21}BrNaO$ $[M+Na]^+$ 391.0668, found 391.0670.



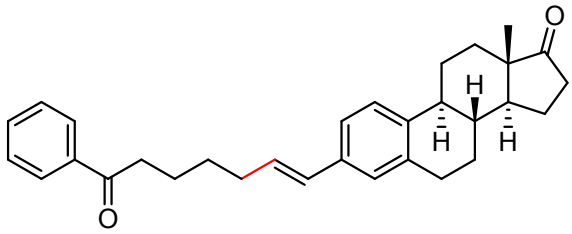
***endo*-3q** 92 : ***exo*-3q** 8

6-(3,4-Dihydronaphthalen-1-yl)-1-phenylhexan-1-one (*endo*-3q) and 6-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)-1-phenylhexan-1-one (*exo*-3q): Yellow oil; (83%, 50.5 mg); *endo*: *exo* = 92:8; R_f = 0.33 (EtOAc/petroleum ether = 1:25); ***endo*-3q:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.24 (m, 1H), 7.23 – 7.17 (m, 1H), 7.14 – 7.13 (m, 2H), 5.85 (t, *J* =

4.4 Hz, 1H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.76 – 2.70 (m, 2H), 2.48 – 2.44 (m, 2H), 2.27 – 2.21 (m, 2H), 1.82 – 1.75 (m, 2H), 1.63 – 1.56 (m, 2H), 1.51 – 1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.5, 137.1, 136.8, 136.3, 134.9, 132.8, 128.5, 128.0, 127.5, 126.5, 126.2, 124.8, 122.6, 38.5, 32.6, 29.2, 28.4, 28.2, 24.2, 23.1 ppm; IR (neat): υ_{max} 3059, 2933, 1683, 1592, 1450, 803, 750, 693 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{24}NaO$ $[M+Na]^+$ 327.1719, found 327.1716.



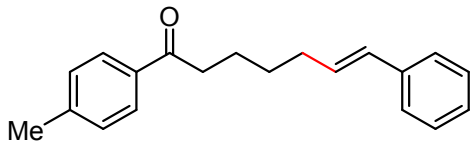
1,9-Diphenylnona-6,8-dien-1-one (3r): (known compound)[b], Colorless oil; (58%, 33.7 mg); *EE*/*ZE* = 2:1; R_f = 0.49 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 7.24 – 7.17 (m, 1H), 7.07 (dd, *J* = 15.1, 11.5 Hz, 0.34H), 6.75 (dd, *J* = 15.6, 10.4 Hz, 0.69H), 6.54 (d, *J* = 15.6 Hz, 0.32H), 6.45 (d, *J* = 15.7 Hz, 0.64H), 6.28 – 6.14 (m, 1H), 5.90 – 5.76 (m, 0.66H), 5.57 – 5.50 (m, 0.33H), 3.02 – 2.98 (m, 2H), 2.42 – 2.30 (m, 1H), 2.23 – 2.20 (m, 1H), 1.86 – 1.76 (m, 2H), 1.58 – 1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.3, 137.6, 137.0, 135.1, 132.9, 132.5, 132.2, 130.9, 130.2, 129.3, 129.1, 128.6, 128.5, 128.0, 127.4, 127.1, 126.3, 126.1, 124.3, 38.4, 38.3, 32.6, 29.3, 29.0, 27.8, 23.9, 23.9 ppm.



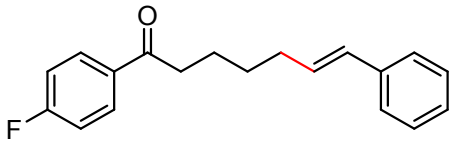
(8R,9S,13S,14S)-13-Methyl-3-(7-oxo-7-phenylhept-1-en-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (3s): Colorless oil; (59%, 52.0 mg); R_f = 0.15 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.08 (s, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.18 (dt, *J* = 15.6, 6.8 Hz 1H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.91 – 2.88 (m, 2H), 2.54 – 2.47 (m, 1H), 2.45 – 2.38 (m, 1H), 2.29 – 2.23 (m, 3H), 2.20 – 2.12 (m, 1H), 2.10 –

1.94 (m, 3H), 1.84 – 1.76 (m, 2H), 1.66 – 1.60 (m, 2H), 1.57 – 1.42 (m, 6H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 220.9, 200.3, 138.5, 137.0, 136.5, 135.4, 132.9, 129.9, 129.8, 128.5, 128.0, 126.5, 125.5, 123.4, 50.5, 48.0, 44.4, 38.4, 38.2, 35.8, 32.8, 31.6, 29.4, 29.1, 26.5, 25.7, 23.8, 21.6, 13.8 ppm; IR (neat): υ_{max} 3450, 2960, 1734, 1681, 1412, 803, 692 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{36}NaO_2$ $[M+Na]^+$ 463.2608, found 463.2606.

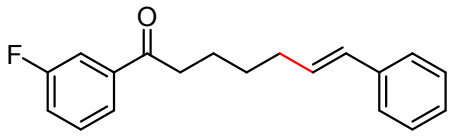
Characterization of Products 4



7-Phenyl-1-(*p*-tolyl)hept-6-en-1-one (4a): (known compound)[b], White solid; (88%, 48.9 mg); *E*/*Z* > 99:1; R_f = 0.36 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.26 (m, 2H), 7.24 (s, 1H), 7.22 – 7.16 (m, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.23 (dt, *J* = 16.0, 6.8 Hz, 1H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 2.31 – 2.23 (m, 2H), 1.84 – 1.76 (m, 2H), 1.61 – 1.52 (m, 2H); ^{13}C NMR (100 MHz,) δ = 200.0, 143.7, 134.5, 130.5, 130.1, 129.2, 128.4, 128.2, 126.8, 125.9, 38.3, 32.9, 29.0, 24.0, 21.6 ppm.

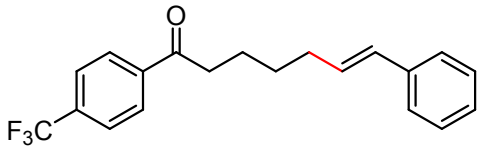


1-(4-Fluorophenyl)-7-phenylhept-6-en-1-one (4b): (known compound)[b], White solid; (85%, 48.1 mg); *E*/*Z* > 99:1; R_f = 0.43 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.13 – 7.10 (m, 2H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.23 (dt, *J* = 16.2, 6.6 Hz, 1H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.30 – 2.25 (m, 2H), 1.83 – 1.78 (m, 2H), 1.60 – 1.54 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.6, 165.6 (d, *J* = 252.0 Hz), 137.7, 133.4 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 9.0 Hz), 130.4, 130.2, 128.5, 126.9, 125.9, 115.6 (d, *J* = 21.8 Hz), 38.3, 32.8, 29.0, 23.8 ppm.

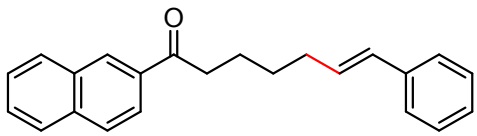


1-(3-Fluorophenyl)-7-phenylhept-6-en-1-one (4c): (known compound)[b], Colorless oil; (93%, 52.5 mg); *E*/*Z* > 99:1; R_f = 0.50 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 1H), 7.66 – 7.63 (m, 1H), 7.43 (td, *J* = 7.8, 5.4 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* =7.8 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 16.2, 6.6 Hz, 1H), 2.98 (t, *J* =

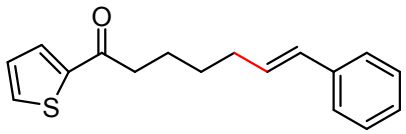
7.2 Hz, 2H), 2.30 – 2.26 (m, 2H), 1.84 – 1.78 (m, 2H), 1.61 – 1.55 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.92 (d, *J* = 2.1 Hz), 162.85 (d, *J* = 246.3 Hz), 139.08 (d, *J* = 5.9 Hz), 137.68, 130.31, 130.21 (d, *J* = 17.6 Hz), 130.18, 128.45, 126.86, 125.91, 123.76 (d, *J* = 2.6 Hz), 119.91 (d, *J* = 21.1 Hz), 114.76 (d, *J* = 22.1 Hz), 38.53, 32.79, 28.92, 23.70 ppm.



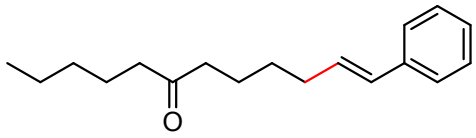
7-Phenyl-1-(4-(trifluoromethyl)phenyl)hept-6-en-1-one (4d): (known compound)[b], White solid; (85%, 55.0 mg); *E*/*Z* > 99:1; R_f = 0.39 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 6.21 (dt, *J* = 15.6, 7.2 Hz, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.30 – 2.23 (m, 2H), 1.84 – 1.79 (m, 2H), 1.60 – 1.55 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 199.21, 139.60, 137.66,134.24 (q, *J* = 32.7 Hz), 130.27, 130.24, 128.48, 128.35, 126.91, 125.91, 125.65 (q, *J* = 4.1 Hz), 124.77 (q, *J* = 270.8 Hz), 38.70, 32.78, 28.89, 23.62 ppm.



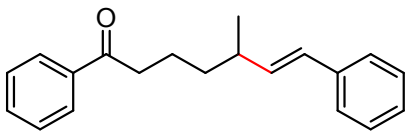
1-(Naphthalen-2-yl)-7-phenylhept-6-en-1-one (4e): Yellow oil; (62%, 39.0 mg); *E*/*Z* > 99:1; R_f = 0.33 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.06 – 8.03 (m, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.64 – 7.52 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.25 (dt, *J* = 15.6, 6.4 Hz, 1H), 3.14 (t, *J* = 7.2 Hz, 2H), 2.34 – 2.28 (m, 2H), 1.92 – 1.83 (m, 2H), 1.65 – 1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.30, 137.70, 135.48, 134.28, 132.49, 130.46, 130.12, 129.62, 129.51, 128.45, 128.39, 128.34, 127.73, 126.82, 126.69, 125.90, 123.90, 38.47, 32.85, 29.02, 24.04 ppm; IR (neat): υ_{max} 3025, 2931, 2858, 1947, 1679, 1630, 1591, 814, 746, 697 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}NaO$ $[M+Na]^+$ 337.1563, found 337.1571.



7-Phenyl-1-(thiophen-2-yl)hept-6-en-1-one (4f): Yellow oil; (55%, 29.8 mg); *E*/*Z* > 99:1; R_f = 0.35 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 1H), 7.65 – 7.59 (m, 1H), 7.34 – 7.30 (m, 2H), 7.30 – 7.27 (m, 2H), 7.14 – 7.11 (m, 1H), 7.14 – 7.09 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.6, 6.8 Hz 1H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.30 – 7.24 (m, 2H), 1.87 – 1.78 (m, 2H), 1.62 – 1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.3, 144.4, 137.7, 133.4, 131.7, 130.3, 130.1, 128.4, 128.0, 126.8, 125.9, 39.2, 32.8, 28.9, 24.3 ppm; IR (neat): υ_{max} 3024, 2931, 2859, 1662, 1509, 1449, 1415, 1234, 1062, 967, 598 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{18}NaOS$ $[M+Na]^+$ 293.0971, found 293.0970.

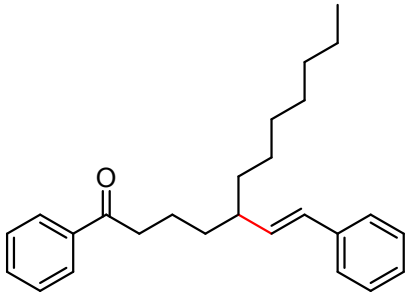


9-(3-Methoxyphenyl)non-8-en-3-one (4g): Colorless oil; (78%, 40.3 mg); *E*/*Z* > 99:1; R_f = 0.45 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.20 (dt, *J* = 15.6, 6.6 Hz, 1H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.25 – 2.20 (m, 2H), 1.66 – 1.61 (m, 2H), 1.60 – 1.54 (m, 2H), 1.50 – 1.44 (m, 2H), 1.34 – 1.29 (m, 2H), 1.28 – 1.24 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 211.4, 137.7, 130.4, 130.1, 128.4, 126.8, 125.9, 42.8, 42.6, 32.8, 31.4, 28.9, 23.5, 23.4, 22.4, 13.9 ppm; IR (neat): υ_{max} 3023, 2931, 2862, 1712, 1454, 1413, 968, 746, 695 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{26}NaO$ $[M+Na]^+$ 281.1876, found 281.1879.

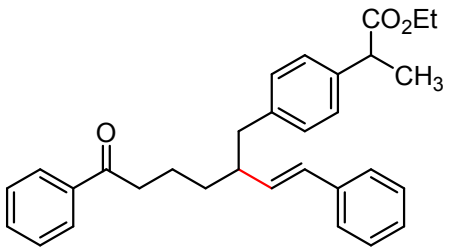


5-Methyl-1,7-diphenylhept-6-en-1-one (4h): (known compound)[b], Colorless oil; (89%, 49.6 mg); *E*/*Z* > 99:1; R_f = 0.43 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 2H), 7.57 – 7.53 (m, 1H), 7.46 – 7.43 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 15.6 Hz,

1H), 6.11 (dd, *J* = 15.6, 7.8 Hz, 1H), 3.03 – 2.93 (m, 2H), 2.39 – 2.34 (m, 1H), 1.82 – 1.76 (m, 2H), 1.52 – 1.45 (m, 2H), 1.12 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.36, 137.72, 136.99, 136.31, 132.87, 128.53, 128.43, 128.40, 128.02, 126.82, 125.97, 38.60, 37.24, 36.62, 22.24, 20.66 ppm.

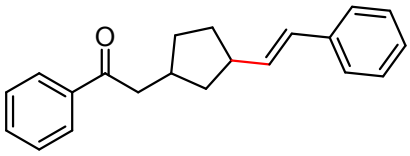


1-Phenyl-5-styryldodecan-1-one (4i): Yellow oil; (83%, 60.2 mg); *E*/*Z* > 99:1; R_f = 0.41 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 15.6 Hz, 1H), 5.97 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.01 – 2.91 (m, 2H), 2.20 – 2.14 (m, 1H), 1.84 – 1.77 (m, 1H), 1.76 – 1.69 (m, 1H), 1.58 – 1.52 (m, 1H), 1.48 – 1.38 (m, 2H), 1.33 – 1.32 (m, 2H), 1.29 – 1.22 (m, 9H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.4, 137.7, 137.0, 135.2, 132.9, 129.9, 128.5, 128.4, 128.0, 126.8, 126.0, 43.4, 38.7, 35.5, 35.1, 31.9, 29.7, 29.3, 27.3, 22.7, 22.3, 14.1 ppm; IR (neat): υ_{max} 2921, 1680, 1450, 966, 879, 753, 686 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{34}NaO$ $[M+Na]^+$ 385.2502, found 385.2497.

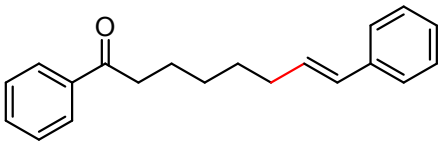


Ethyl-2-(4-(6-oxo-6-phenyl-2-styrylhexyl)phenyl)propanoate (4j): (known compound)[b], Colorless oil; (79%, 71.8 mg); *E*/*Z* > 99:1; dr = 1:1; R_f = 0.17 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.40 (m, 2H), 7.30 – 7.27 (m, 4H), 7.20 – 7.18 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.02 (dd, *J* = 16.0, 8.8 Hz, 1H), 4.15 – 4,05 (m, 2H), 3.69 – 3.63 (m, 1H), 2.99 – 2.87 (m, 2H), 2.71 (d, *J* = 6.8 Hz, 2H), 2.52

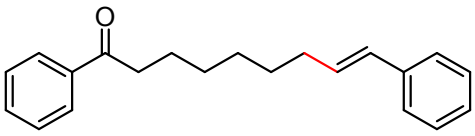
– 2.44 (m, 1H), 1.86 –1.78 (m, 1H), 1.75 – 1.66 (m, 1H), 1.63 – 1.58 (m, 1H), 1.56 – 1.50 (m, 1H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.20 – 1.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.28, 174.72, 174.70, 138.99, 138.16, 138.13, 137.60, 136.99, 133.99, 132.89, 130.36, 129.50, 128.54, 128.43, 128.03, 127.21, 126.93, 126.04, 60.63, 45.17, 45.14, 44.87, 41.76, 38.59, 34.10, 29.69, 22.22, 18.55, 18.50, 14.09 ppm.



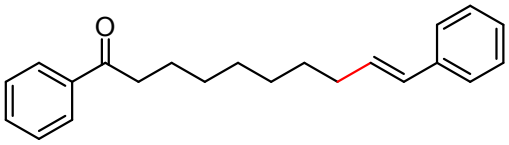
1-Phenyl-2-(3-styrylcyclopentyl)ethan-1-one (4k): (known compound)[b], Colorless oil; (78%, 45.3 mg); *E*/*Z* > 99:1; dr = 1:1; R_f = 0.55 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.37 (dd, *J* = 16.0, 2.8 Hz, 1H), 6.21 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.07 – 3.03 (m, 2H), 2.81 – 2.50 (m, 2H), 2.12 – 2.18 (m, 0.54H), 2.09 – 1.88 (m, 2H), 1.86 – 1.78 (m, 0.56H), 1.60 – 1.46 (m, 1H), 1.44 – 1.25 (m, 1.44H), 1.19 – 1.09 (m, 0.56H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.0, 137.7, 137.1, 135.3, 135.1, 132.9, 128.5, 128.4, 128.1, 128.0, 126.8, 125.9, 45.3, 45.0, 43.5, 42.3, 40.6, 38.9, 35.8, 34.7, 33.3, 32.9, 31.9, 31.7 ppm.



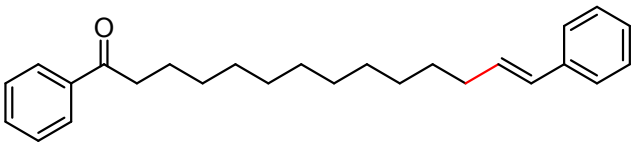
1,8-Diphenyloct-7-en-1-one (4l): (known compound)[b], White soild; (44%, 24.5 mg); *E*/*Z* > 99:1; R_f = 0.44 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.22 (dt, *J* = 15.6, 7.2 Hz, 1H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.26 – 2.21 (m, 2H), 1.81 – 1.76 (m, 2H), 1.56 – 1.51 (m, 2H), 1.48 – 1.43 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.46, 137.82, 137.03, 132.89, 130.81, 129.92, 128.55, 128.45, 128.04, 126.79, 125.90, 38.54, 32.84, 29.18, 28.89, 24.17 ppm.



1,9-Diphenylnon-8-en-1-one (4m): (known compound)[b], Colorless oil; (80%, 46.8 mg); *E*/*Z* > 99:1; R_f = 0.43 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.57 – 7.54 (m, 1H), 7.48 – 7.45 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 16.2 Hz, 1H), 6.23 (dt, *J* = 16.2, 6.6 Hz, 1H), 2.98 (t, *J* = 7.8 Hz, 2H), 2.24 – 2.20 (m, 2H), 1.79 – 1.73 (m, 2H), 1.53 – 1.46 (m, 2H), 1.45 – 1.38 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.49, 137.85, 137.04, 132.84, 130.97, 129.79, 128.52, 128.43, 128.01, 126.73, 125.87, 38.54, 32.92, 29.17, 29.15, 28.98, 24.24 ppm.



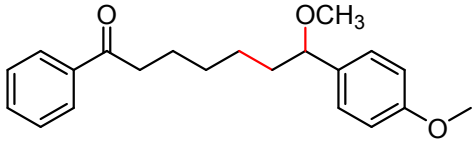
1,10-Diphenyldec-9-en-1-one (4n): (known compound)[b], White soild; (70%, 42.9 mg); *E*/*Z* > 99:1; R_f = 0.49 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 2H), 7.57 – 7.53 (m, 1H), 7.48 – 7.44 (m, 2H), 7.35 – 7.27 (m, 4H), 7.21 – 7.17 (m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.22 (dt, *J* = 16.0, 6.8 Hz, 1H), 2.99 – 2.95 (m, 2H), 2.23 – 2.18 (m, 2H), 1.77 – 1.71 (m, 2H), 1.49 – 1.44 (m, 2H), 1.38 – 1.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.6, 137.9, 137.0, 132.9, 131.1, 129.7, 128.5, 128.4, 128.0, 126.7, 125.9, 38.6, 33.0, 29.3, 29.0, 24.3 ppm.



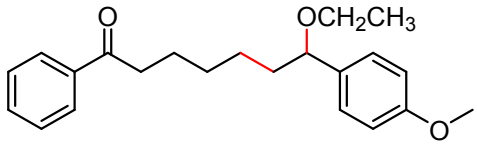
1,14-Diphenyltetradec-13-en-1-one (4o): White soild; (77%, 55.8 mg); mp: 73 – 75 ^{o}C; *E*/*Z* > 99:1; R_f = 0.50 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.23 (dt, *J* = 16.0, 6.8 Hz, 1H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.23 – 2.17 (m, 2H), 1.78 – 1.70 (m, 2H), 1.48 – 1.43 (m, 2H), 1.37 – 1.26 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.6, 137.9, 137.0, 132.8, 131.2, 129.6, 128.5, 128.4, 128.0, 126.7, 125.9, 38.6,

33.0, 29.6, 29.5, 29.4, 29.2, 24.3 ppm; IR (neat): υ_{max} 2921, 2851, 1684, 1456, 736, 690 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{34}NaO$ $[M+Na]^+$ 385.2502, found 385.2497.

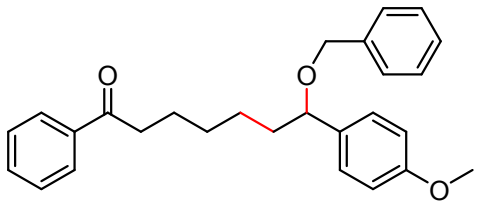
Characterization of Products 5



7-Methoxy-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5a): Colorless oil; (86%, 56.2 mg); R_f = 0.25 (EtOAc/petroleum ether = 1:25); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.58 – 7.50 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.90 – 6.86 (m, 2H), 4.03 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 3.17 (s, 3H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.59 (m, 4H), 1.45 – 1.23 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 159.0, 137.0, 134.3, 132.8, 128.5, 128.0, 127.8, 113.7, 83.5, 56.3, 55.2, 38.5, 37.9, 29.2, 25.6, 24.2 ppm; IR (neat): υ_{max} 2934, 2856, 1684, 1607, 1510, 1454, 831, 748, 694 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{26}NaO_3$ $[M+Na]^+$ 349.1774, found 349.1775.

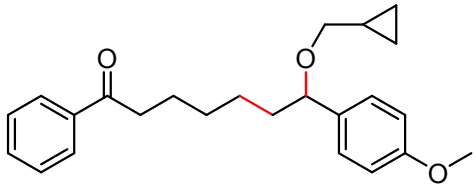


7-Ethoxy-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5b): Colorless oil; (81%, 55.1 mg); R_f = 0.28 (EtOAc/petroleum ether = 1:25); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.57 – 7.52 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.18 (m, 2H), 6.89 – 6.85 (m, 2H), 4.13 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 3.39 – 3.30 (m, 1H), 3.30 – 3.29 (m, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 1.83 – 1.59 (m, 4H), 1.47 – 1.33 (m, 3H), 1.31 – 1.22 (m, 1H), 1.15 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 158.8, 137.0, 135.1, 132.8, 128.5, 128.0, 127.7, 113.6, 81.6, 63.7, 55.2, 38.5, 38.1, 29.2, 25.7, 24.2, 15.3 ppm; IR (neat): υ_{max} 2934, 2861, 1684, 1607, 1510, 1453, 830, 751, 693 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{28}NaO_3$ $[M+Na]^+$ 363.1931, found 363.1930.

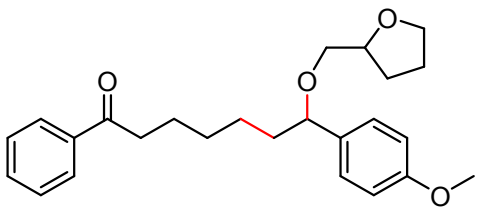


7-(Benzyloxy)-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5c): Yellow oil; (93%,

74.8 mg); R_f = 0.40 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.35 – 7.28 (m, 5H), 7.26 – 7.24 (s, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.27 – 4.20 (m, 2H), 3.83 (s, 3H), 2.92 (t, *J* = 7.2 Hz, 2H), 1.94 – 1.82 (m, 1H), 1.76 – 1.64 (m, 3H), 1.51 – 1.44 (m, 1H), 1.40 – 1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 159.0, 138.7, 136.9, 134.5, 132.8, 128.5, 128.3, 128.0, 127.9, 127.8, 127.4, 113.7, 80.8, 70.1, 55.2, 38.5, 38.1, 29.1, 25.7, 24.2 ppm; IR (neat): υ_{max} 2933, 2857, 1683, 1608, 1509, 1453, 804, 746, 695 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{30}NaO_3$ $[M+Na]^+$ 425.2087, found 425.2090.

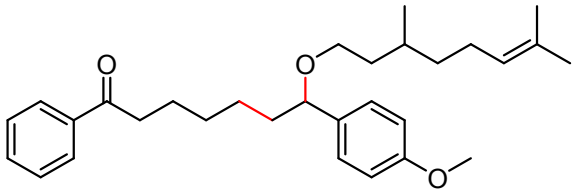


7-(Cyclopropylmethoxy)-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5d): Yellow oil; (86%, 62.9 mg); R_f = 0.35 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.86 (m, 2H), 7.58 – 7.50 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.18 (m, 2H), 6.88 – 6.84 (m, 2H), 4.16 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 3.11 (dd, *J* = 10.0, 6.8Hz, 1H), 3.04 (dd, *J* = 10.0, 6.8Hz, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.91 – 1.77 (m, 1H), 1.75 – 1.67 (m, 2H), 1.64 – 1.56 (m, 1H), 1.50 – 1.34 (m, 3H), 1.32 – 1.25 (m, 1H), 1.07 – 0.96 (m, 1H), 0.53 – 0.42 (m, 2H), 0.15 – 0.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.5, 158.8, 137.0, 135.0, 132.8, 128.5, 128.0, 127.7, 113.6, 81.4, 73.2, 55.2, 38.5, 38.3, 29.2, 25.8, 24.2, 10.7, 3.1, 2.9 ppm; IR (neat): υ_{max} 3072, 2005, 2935, 1685, 1607, 1510, 1455, 830, 750, 693 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{30}NaO_3$ $[M+Na]^+$ 389.2087, found 389.2082.

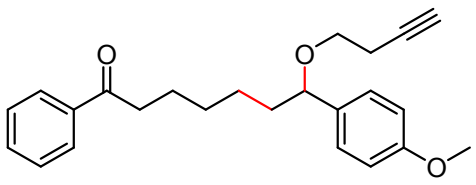


7-(4-Methoxyphenyl)-1-phenyl-7-((tetrahydrofuran-2-yl)methoxy)heptan-1-one (5e): Faint yellow oil; (78%, 61.8 mg); dr = 1:1; R_f = 0.32 (EtOAc/petroleum ether =

1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.20 – 4.15 (m, 1H), 4.05 – 3.95 (m, 1H), 3.87 – 3.81 (m, 1H), 3.80 (s, 3H), 3.77 – 3.70 (m, 1H), 3.30 (dd, *J* = 10.0, 6.0 Hz, 0.5H), 3.27 – 3.22 (m, 1H), 3.19 (dd, *J* = 10.0, 4.4 Hz, 0.5H), 2.95 – 2.89 (m, 2H), 1.92 – 1.79 (m, 4H), 1.74 – 1.66 (m, 2H), 1.64 – 1.57 (m, 2H), 1.45 – 1.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.46, 158.89, 137.01, 134.74, 134.70, 132.83, 128.50, 128.01, 127.90, 127.81, 113.63, 82.34, 82.31, 78.10, 77.82, 71.27, 71.16, 68.26, 68.22, 55.20, 38.49, 38.09, 37.99, 29.17, 28.32, 28.13, 25.70, 25.61, 25.43, 24.20 ppm; IR (neat): υ_{max} 3029, 2935, 2861,1728, 1684, 1592, 1452, 756, 698 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{32}NaO_4$ $[M+Na]^+$ 419.2193, found 419.2197.

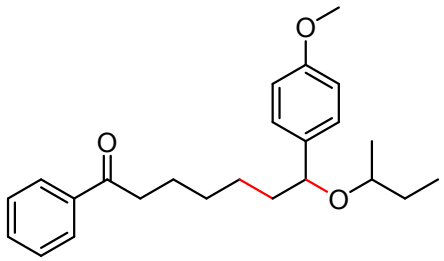


7-((3,7-Dimethyloct-6-en-1-yl)oxy)-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5f): Yellow oil; (78%, 70.3 mg); dr = 1:1; R_f = 0.33 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.07 – 5.05 (m, 1H), 4.10 (t, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 3.34 – 3.26 (m, 1H), 3.25 – 3.16 (m, 1H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.02 – 1.84 (m, 2H), 1.79 – 1.50 (m, 12H), 1.43 – 1.22 (m, 6H), 1.15 – 0.97 (m, 1H), 0.84 – 0.78 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.46, 158.77, 136.96, 135.19, 135.16, 132.84, 131.05, 130.99, 128.50, 128.00, 127.70, 127.66, 124.84, 124.83, 113.57, 81.84, 81.71, 66.80, 55.18, 38.48, 38.19, 37.17, 37.02, 36.89, 36.79, 29.50, 29.45, 29.17, 25.75, 25.71, 25.44, 25.40, 24.20, 19.51, 19.46, 17.60 ppm; IR (neat): υ_{max} 2925, 2859, 1727, 1685, 1608, 1510, 1453, 805, 752, 693 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{42}NaO_3$ $[M+Na]^+$ 473.3036, found 473.3039.

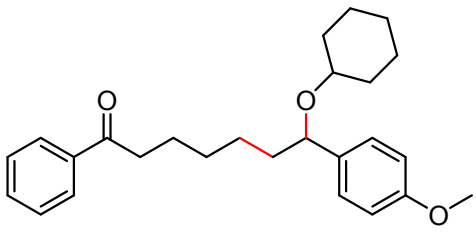


7-(But-3-yn-1-yloxy)-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5g): Faint

yellow oil; (80%, 58.3 mg); R_f = 0.35 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 – 7.43 (m, 2H), 7.22 – 7.19 (m, 2H), 6.91 – 6.81 (m, 2H), 4.24 – 4.11 (m, 1H), 3.80 (s, 3H), 3.46 – 3.39 (m, 1H), 3.38 – 3.31 (m, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.48 – 2.32 (m, 2H), 1.94 (t, *J* = 2.8 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.76 – 1.66 (m, 2H), 1.65 – 1.60 (m, 1H), 1.52 – 1.42 (m, 1H), 1.43 – 1.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.5, 159.0, 137.0, 134.5, 132.9, 128.5, 128.0, 127.8, 113.7, 82.0, 81.5, 69.1, 66.5, 55.2, 38.5, 38.0, 29.1, 25.7, 24.2, 19.9 ppm; IR (neat): υ_{max} 2934, 2861, 2237, 1684, 1607, 1511, 1454, 828, 751, 692 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{28}NaO_3$ $[M+Na]^+$ 387.1931, found 387.1928.

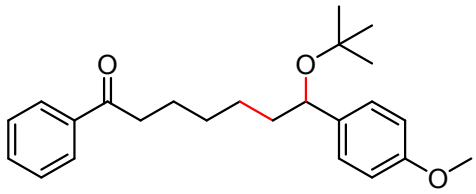


7-(*sec*-Butoxy)-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5h): Yellow oil; (62%, 45.7 mg); dr = 1:1; R_f = 0.23 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.19 (m, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 4.24 (dd, *J* = 12.4, 5.6 Hz, 1H), 3.80 (s, 3H), 3.31 – 3.23 (m, 0.5H), 3.22 – 3.13 (m, 0.5H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.82 – 1.66 (m, 3H), 1.61 – 1.51 (m, 2H), 1.50 – 1.27 (m, 5H), 1.09 (d, *J* = 6.0 Hz, 1.5H), 0.97 (d, *J* = 6.0 Hz, 1.5H), 0.88 (t, *J* = 7.6 Hz, 1.5H), 0.76 (t, *J* = 7.6 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.5, 158.7, 137.0, 136.1, 132.8, 128.5, 128.0, 127.9, 127.7, 120.1, 113.5, 113.4, 104.9, 79.4, 78.3, 73.9, 73.0, 55.2, 38.6, 38.5, 30.3, 29.2, 28.1, 25.9, 24.2, 20.3, 18.6, 10.2, 9.3, 8.0 ppm; IR (neat): υ_{max} 2932, 2866, 1684, 1611, 1455, 830, 752, 693 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{32}NaO_3$ $[M+Na]^+$ 391.2244, found 391.2239.

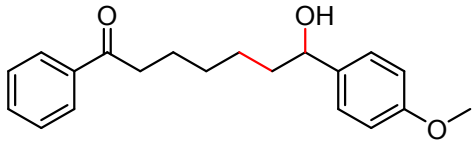


7-(Cyclohexyloxy)-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5i): Faint yellow

oil; (50%, 39.5 mg); R_f = 0.30 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.32 – 4.28 (m, 1H), 3.80 (s, 3H), 3.15 – 3.05 (m, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.75 – 1.67 (m, 6H), 1.43 – 1.34 (m, 2H), 1.30 – 1.25 (m, 7H), 1.15 – 1.09 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.5, 158.6, 136.2, 132.8, 128.5, 128.0, 127.6, 113.5, 78.2, 74.5, 55.2, 38.8, 38.5, 33.6, 31.5, 29.2, 26.0, 25.8, 24.4, 24.3, 24.1 ppm; IR (neat): υ_{max} 2929, 2857, 1685, 1610, 1510, 1454, 804, 752, 695 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{34}NaO_3$ $[M+Na]^+$ 417.2400, found 417.2401.

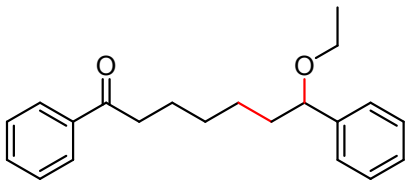


7-(*tert*-Butoxy)-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5j): Yellow oil; (35%, 25.8 mg); R_f = 0.35 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.38 – 4.34 (m, 1H), 3.79 (s, 3H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.75 – 1.66 (m, 2H), 1.56 – 1.43 (m, 2H), 1.41 – 1.34 (m, 2H), 1.28 – 1.25 (m, 2H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.5, 158.2, 139.1, 137.0, 132.8, 128.5, 128.0, 127.0, 113.4, 73.9, 73.8, 55.2, 40.3, 38.5, 29.3, 28.8, 26.1, 24.3 ppm; IR (neat): υ_{max} 2966, 1684, 1608, 1509, 1455, 815, 749, 694 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{32}NaO_3$ $[M+Na]^+$ 391.2244, found 391.2239.

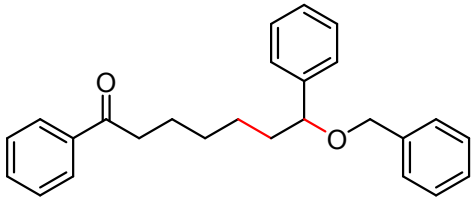


7-Hydroxy-7-(4-methoxyphenyl)-1-phenylheptan-1-one (5k): Yellow oil; (84%, 52.4 mg); R_f = 0.20 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.58 – 7.51 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.27 – 7.23 (m, 2H), 6.89 – 6.84 (m, 2H), 4.61 (t, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 2.94 (t, *J* = 7.6 Hz, 2H), 1.94 (s, 1H), 1.85 – 1.77 (m, 1H), 1.74 – 1.70 (m, 2H), 1.51 – 1.20 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 158.9, 136.9, 132.9, 128.5, 128.0, 127.1, 113.7, 74.1, 55.2,

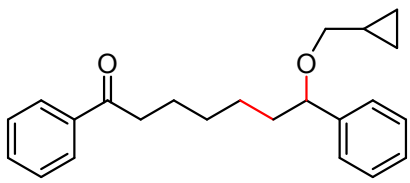
38.7, 38.4, 29.1, 25.7, 24.1 ppm; IR (neat): υ_{max} 2966, 1684, 1608, 1509, 1455, 815, 749, 694 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{24}NaO_3$ $[M+Na]^+$ 335.1618, found 335.1617.



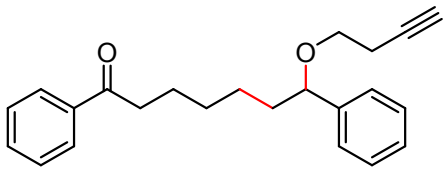
7-Ethoxy-1,7-diphenylheptan-1-one (5l): Colorless oil; (46%, 28.5 mg); R_f = 0.34 (EtOAc/petroleum ether = 1:20); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.88 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.26 (m, 5H), 4.19 (t, *J* =6.0 Hz, 1H), 3.41 – 3.33 (m, 1H), 3.32 – 3.25 (m, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.86 – 1.76 (m, 1H), 1.76 – 1.67 (m, 2H), 1.67 – 1.60 (m, 1H), 1.52 – 1.44 (m, 1H), 1.43 – 1.34 (m, 2H), 1.33 – 1.26 (m, 1H), 1.17 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.5, 143.2, 137.6, 132.9, 128.5, 128.3, 128.0, 127.3, 126.5, 82.1, 64.1, 38.5, 38.2, 29.2, 25.7, 24.2, 15.3 ppm; IR (neat): υ_{max} 2966, 2929, 1684, 1523, 1458, 756, 696 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{26}NaO_2$ $[M+Na]^+$ 333.1825, found 333.1860.



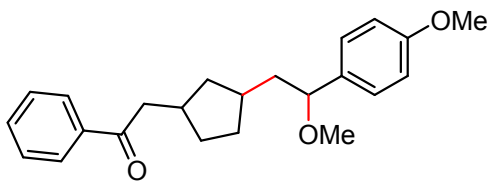
7-(Benzyloxy)-1,7-diphenylheptan-1-one (5m): Colorless oil; (48%, 35.7 mg); R_f = 0.33 (EtOAc/petroleum ether = 1:20); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.88 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.39 – 7.28 (m, 10H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.30 (dd, *J* = 7.6, 6.0 Hz, 1H), 4.25 (d, *J* = 11.6 Hz, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.94 – 1.81 (m, 1H), 1.76 – 1.64 (m, 3H), 1.55 – 1.46 (m, 1H), 1.41 – 1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 142.6, 138.6, 137.0, 132.9, 128.5, 128.4, 128.3, 128.0, 127.8, 127.5, 127.4, 126.8, 81.3, 70.4, 38.5, 38.2, 29.1, 25.7, 24.2 ppm; IR (neat): υ_{max} 3030, 2934, 2859, 1684, 1592, 1494, 1452, 802, 746, 697 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{28}NaO_2$ $[M+Na]^+$ 395.1982, found 395.1979.



7-(Cyclopropylmethoxy)-1,7-diphenylheptan-1-one (5n): Yellow oil; (54%, 36.3 mg); R_f = 0.35 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.26 (m, 3H), 4.21 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.14 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.07 (dd, *J* = 10.0, 6.4 Hz, 1H), 2.94 (t, *J* = 7.2 Hz, 2H), 1.90 – 1.79 (m, 1H), 1.76 – 1.67 (m, 2H), 1.66 – 1.60 (m, 1H), 1.56 – 1.44 (m, 1H), 1.42 – 1.35 (m, 2H), 1.34 – 1.26 (m, 1H), 1.09 – 0.98 (m, 1H), 0.54 – 0.43 (m, 2H), 0.15 – 0.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.5, 143.1, 137.0, 132.9, 128.5, 128.3, 128.0, 127.3, 126.5, 81.8, 73.5, 38.5, 38.3, 29.2, 25.8, 24.2, 10.7, 3.1, 2.9 ppm; IR (neat): υ_{max} 3013, 2934, 2858, 1684, 1592, 1453, 1410, 802, 746, 697 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{28}NaO_2$ $[M+Na]^+$ 359.1982, found 359.1975.

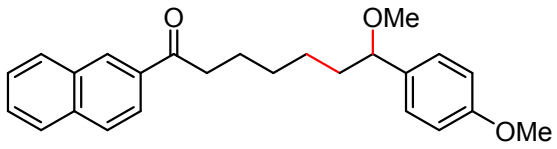


7-(But-3-yn-1-yloxy)-1,7-diphenylheptan-1-one (5o): Faint yellow oil; (50%, 33.4 mg); R_f = 0.30 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.59 – 7.51 (m, 1H), 7.49 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 3H), 4.25 – 4.21 (m, 1H), 3.48 – 3.41 (m, 1H), 3.40 – 3.34 (m, 1H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.50 – 2.35 (m, 2H), 1.94 (t, *J* = 2.4 Hz, 1H), 1.88 – 1.77 (m, 1H), 1.75 – 1.64 (m, 2H), 1.65 – 1.60 (m, 1H), 1.55 – 1.43 (m, 1H), 1.42 – 1.35 (m, 2H), 1.34 – 1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 142.5, 137.0, 132.9, 128.5, 128.3, 128.0, 127.5, 126.5, 82.4, 81.5, 69.1, 66.7, 38.5, 38.1, 29.1, 25.7, 24.2, 19.9 ppm; IR (neat): υ_{max} 3013, 2959, 2245, 1682, 1591, 1450, 802, 694 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{26}NaO_2$ $[M+Na]^+$ 357.1825, found 357.1819.



2-(3-(2-Methoxy-2-(4-methoxyphenyl)ethyl)cyclopentyl)-1-phenylethan-1-one (5p): Faint yellow oil; (81%, 56.9 mg); dr = 1:1; R_f = 0.33 (EtOAc/petroleum ether =

1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 – 7.43 (m, 2H), 7.21 – 7.17 (m, 2H), 6.89 – 6.86 (m, 2H), 4.03 (t, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 3.15 (s, 3H), 2.99 (d, *J* = 6.9 Hz, 1H), 2.95 (d, *J* = 7.1 Hz, 1H), 2.56 – 2.47 (m, 0.5H), 2.43 – 2.34 (m, 0.5H), 1.96 – 1.78 (m, 4H), 1.59 – 1.40 (m, 2H), 1.30 – 1.22 (m, 2H), 1.20 – 1.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.24, 159.01, 137.21, 134.45, 132.84, 128.52, 128.06, 127.91, 127.86, 113.71, 82.84, 82.78, 82.72, 56.29, 55.22, 45.27, 45.18, 44.85, 44.77, 40.53, 38.56, 38.48, 36.44, 35.85, 35.73, 35.19, 35.14, 34.65, 34.56, 33.01, 32.85, 32.77, 31.58, 31.45, 31.39 ppm; IR (neat): υ_{max} 2931, 2856, 1683, 1463, 1447, 1209, 1034, 831, 694, 574 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{28}NaO_3$ $[M+Na]^+$ 375.1931, found 375.1924.



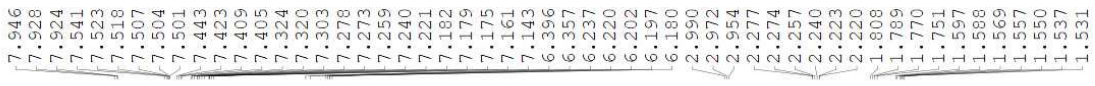
7-Methoxy-7-(4-methoxyphenyl)-1-(naphthalen-2-yl)heptan-1-one (5q): Faint yellow oil; (63%, 47.4 mg); R_f = 0.28 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.03 – 8.00 (m, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.64 – 7.51 (m, 2H), 7.21 – 7.18 (m, 2H), 6.89 – 6.86 (m, 2H), 4.04 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 3.18 (s, 3H), 3.07 (t, *J* = 7.6 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.71 – 1.54 (m, 2H), 1.42 – 1.38 (m, 2H), 1.35 – 1.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 159.0, 135.5, 134.4, 134.3, 132.5, 129.6, 129.5, 128.4, 128.3, 127.8, 127.7, 126.7, 123.9, 83.5, 56.3, 55.2, 38.5, 37.9, 29.2, 25.7, 24.4 ppm; IR (neat): υ_{max} 2931, 1670, 1610, 1510, 1244, 1173, 1086, 827, 748, 476 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{28}NaO_3$ $[M+Na]^+$ 399.1931, found 399.1918.

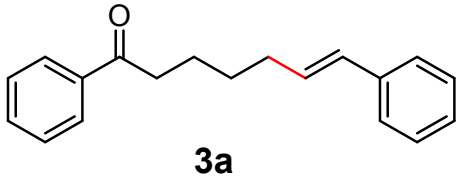
References

(1) (a) R. Sakamoto, S. Sakurai and K. Maruoka, *Chem.-Eur. J.*, **2017**, *23*, 9030; (b) R. Sakamoto, T. Kato, S. Sakurai and K. Maruoka, *Org. Lett*., **2018,** *20*, 1400; (c) T. Seihara, S. Sakurai, T. Kato, R. Sakamoto and Maruoka, K. *Org. Lett*., **2019**, *21*, 2477; (d) P. C. Too, Y. L. Tnay and S. Chiba, *Beilstein J. Org. Chem.*, 2013, **9**, 1217.

(2) P. Gao, H. Wu, J.-C. Yang and L.-N. Guo, *Org. Lett*., **2019**, *21*, 7104.

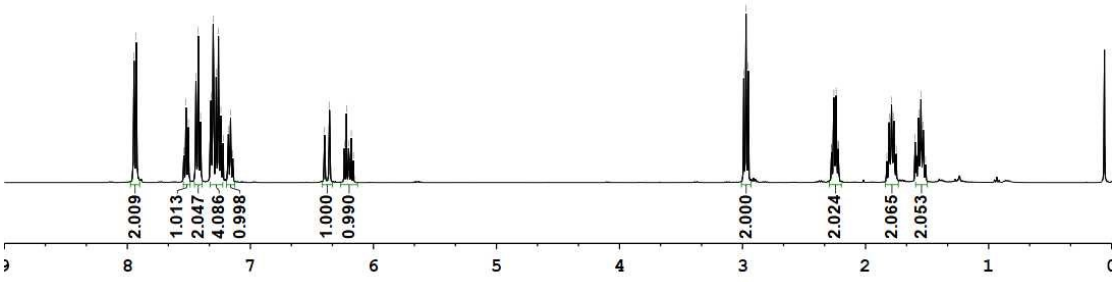
^{1}H NMR and ^{13}C NMR Spectra of the Products 3

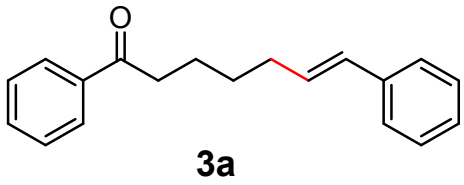




3a

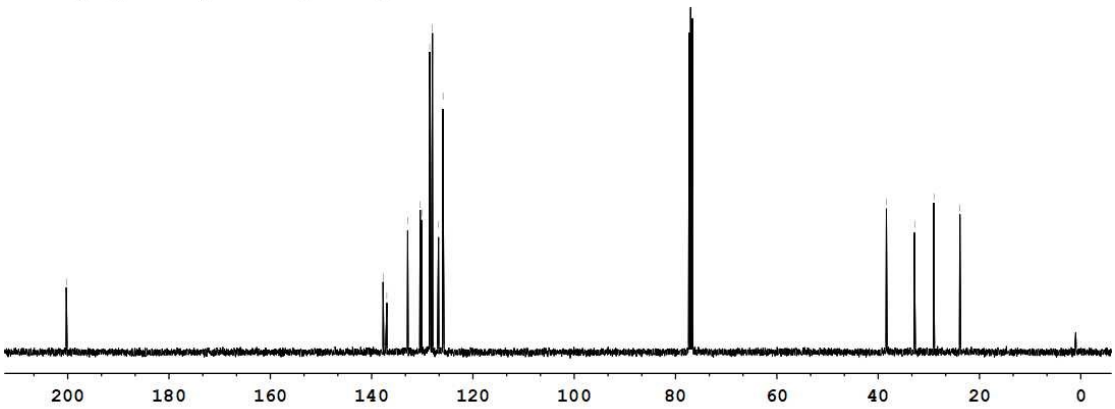
^{1}H NMR (400 MHz, $CDCl_3$)

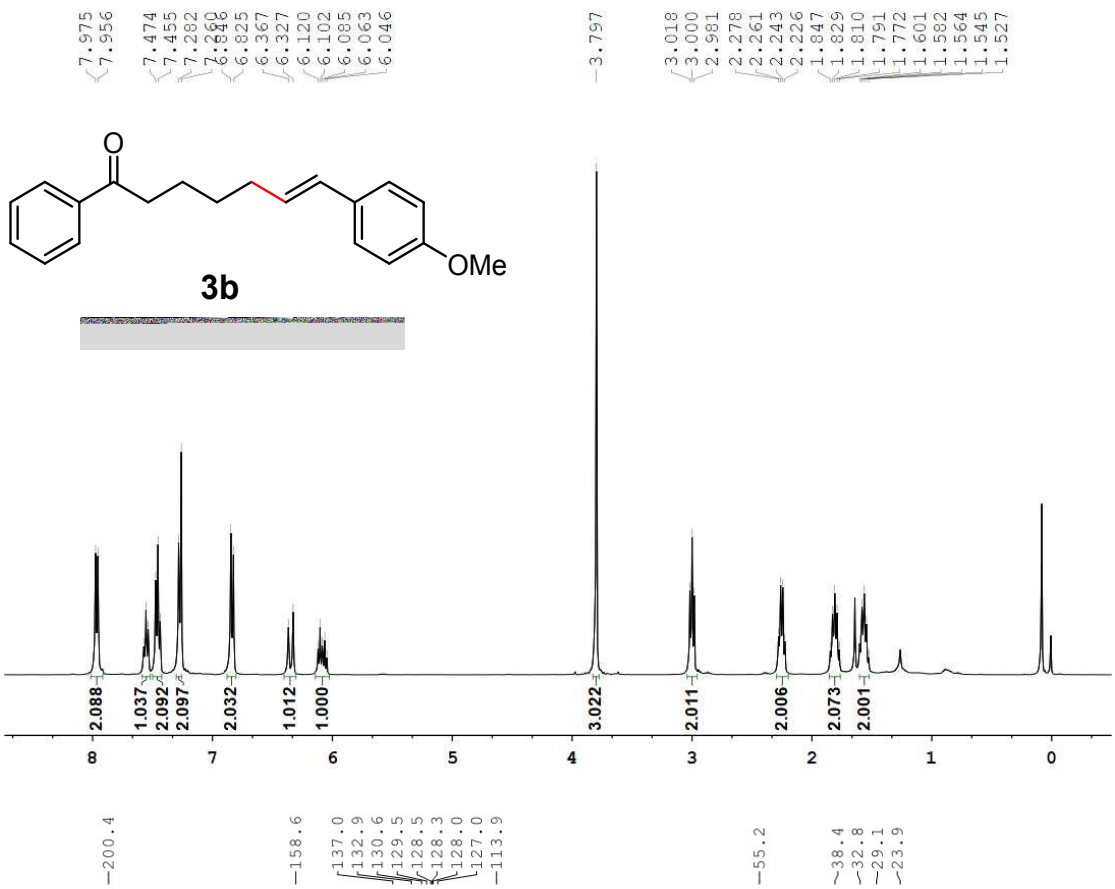


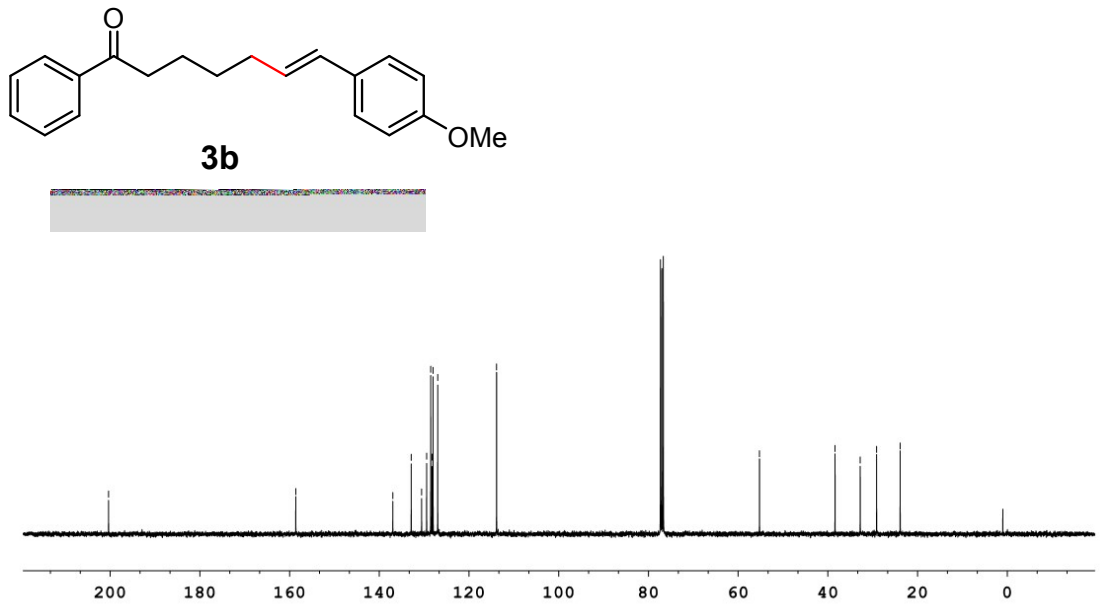


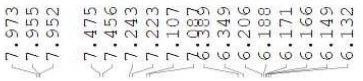
3a

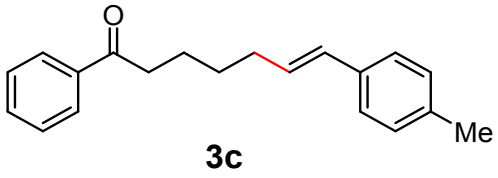
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)




7.975
7.956
7.474
7.455
7.282
6.825
6.367
6.327
6.120
6.102
6.085
6.063
6.046
3.797
3.018
3.000
2.981
2.278
2.261
2.243
2.226
1.847
1.829
1.810
1.791
1.772
1.601
1.582
1.564
1.545
1.527
O
OMe
3b
2.088
1.037
2.092
2.097
2.032
1.012
1.000
3.022
2.011
2.006
2.073
2.001
8
7
6
5
4
3
2
1
0

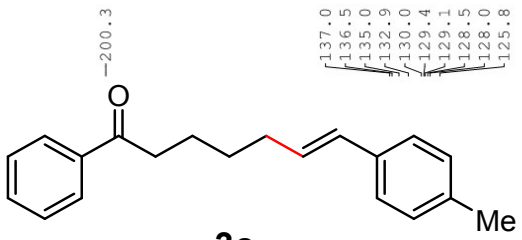

200.4
158.6
137.0
132.9
130.6
129.5
128.5
128.3
128.0
127.0
113.9
55.2
38.4
32.8
29.1
23.9
O
OMe
3b
200
180
160
140
120
100
80
60
40
20
0



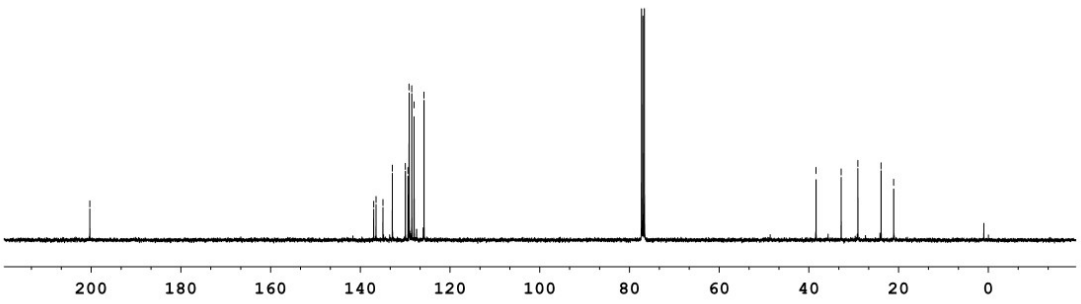


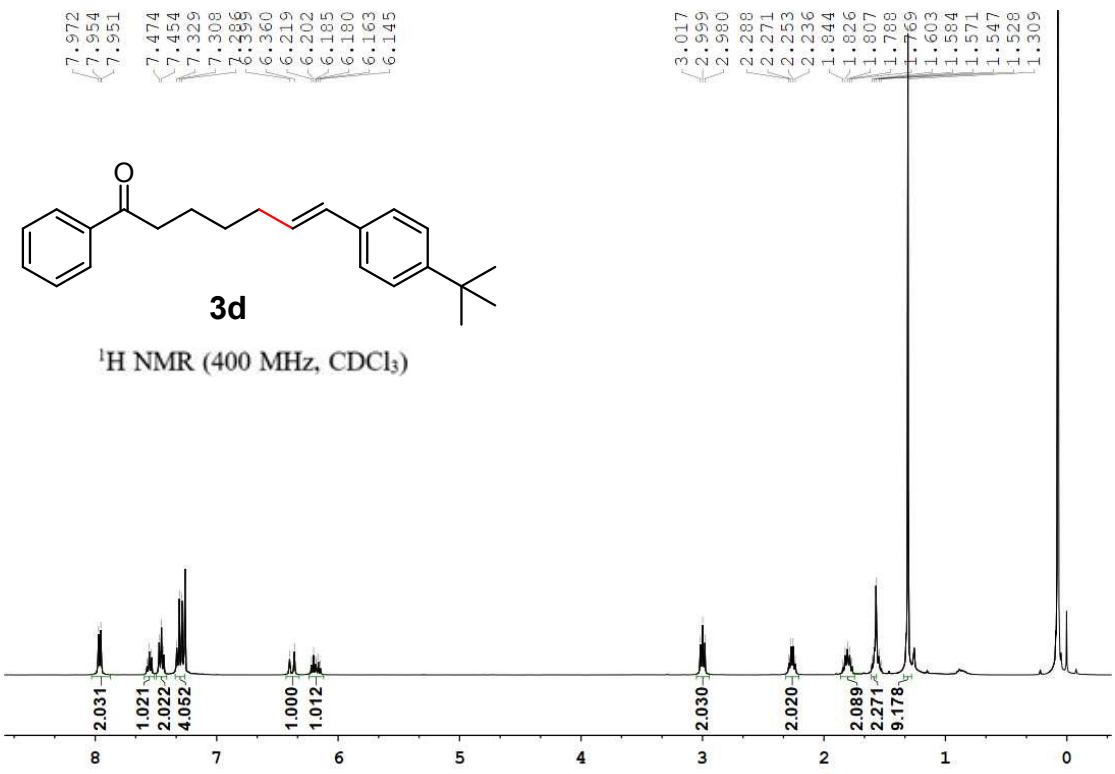
3c

^{1}H NMR (400 MHz, $CDCl_3$)



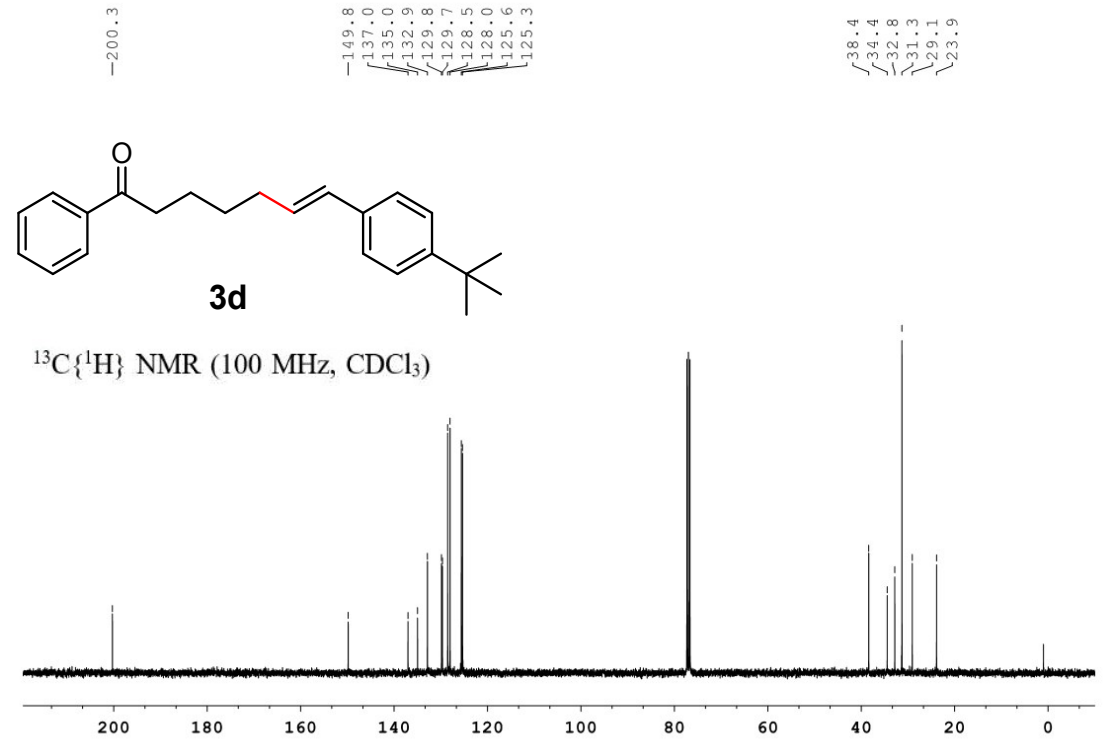
3c





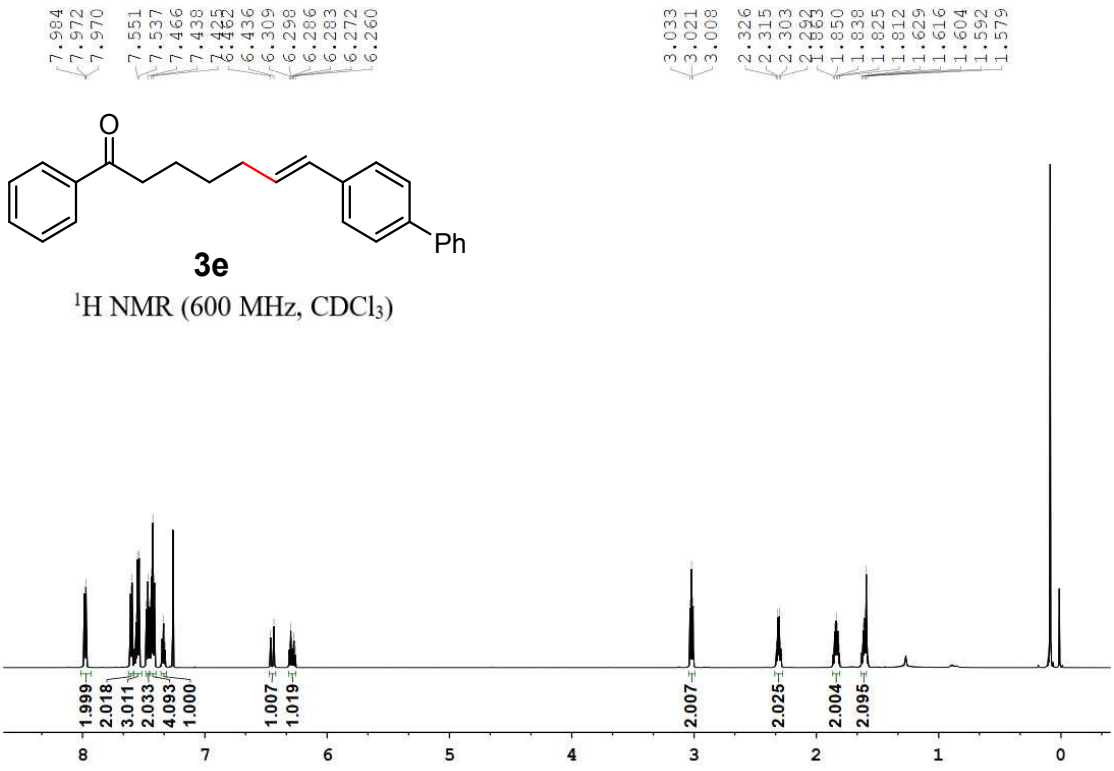
3d

^{1}H NMR (400 MHz, $CDCl_3$)



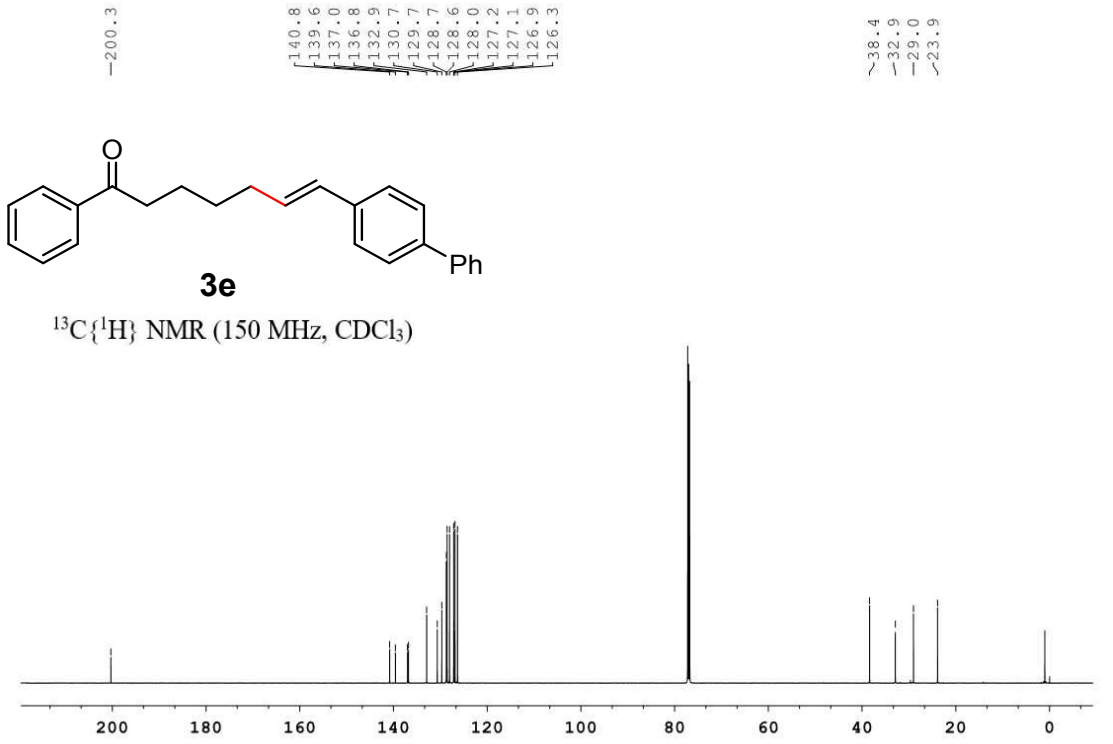
3d

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



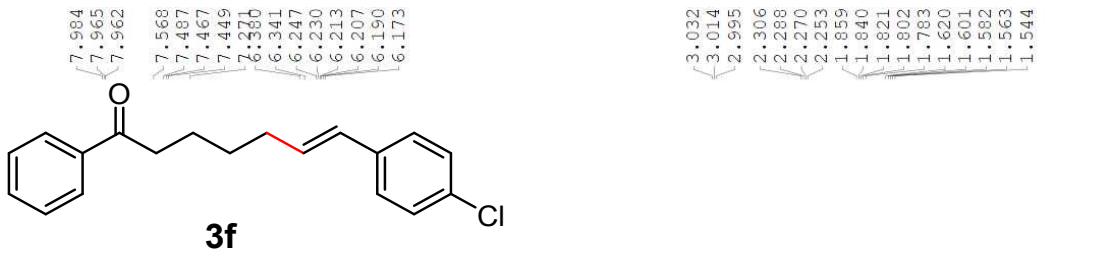
3e

^{1}H NMR (600 MHz, $CDCl_3$)



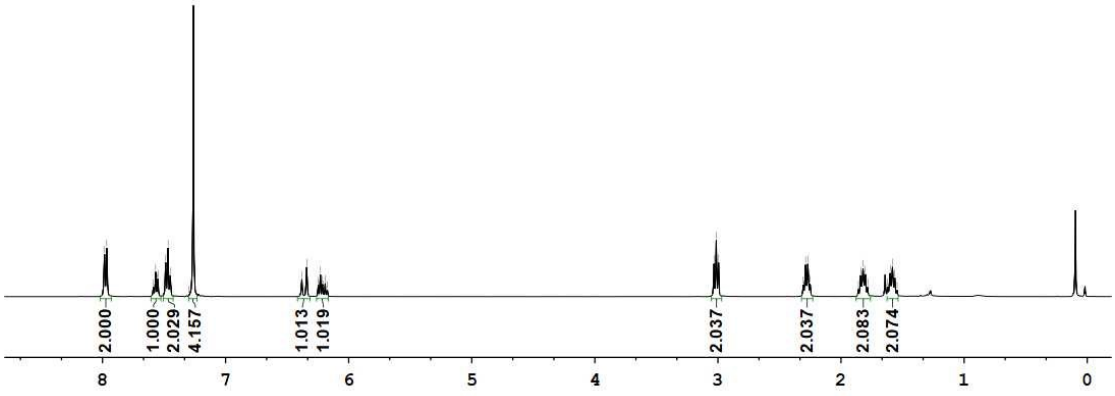
3e

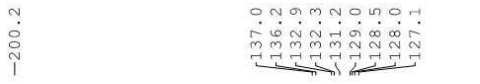
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$)

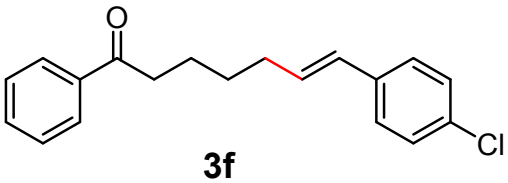


3f

^{1}H NMR (400 MHz, $CDCl_3$)

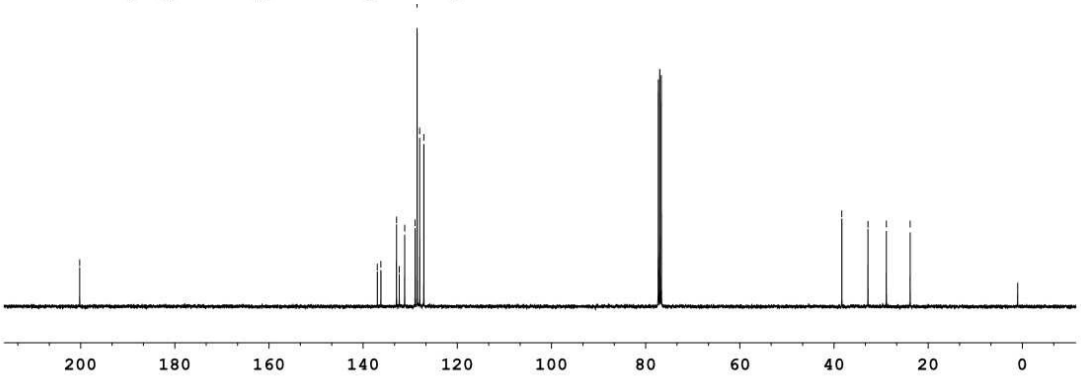


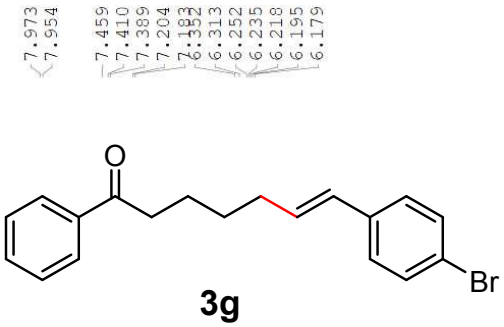




3f

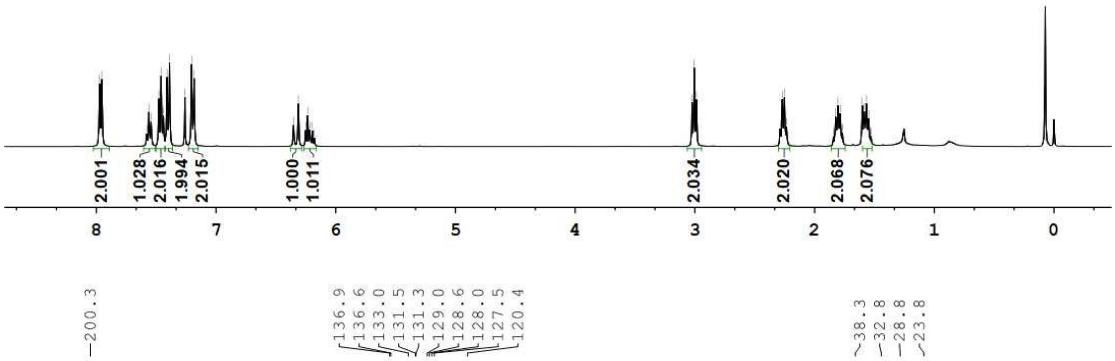
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

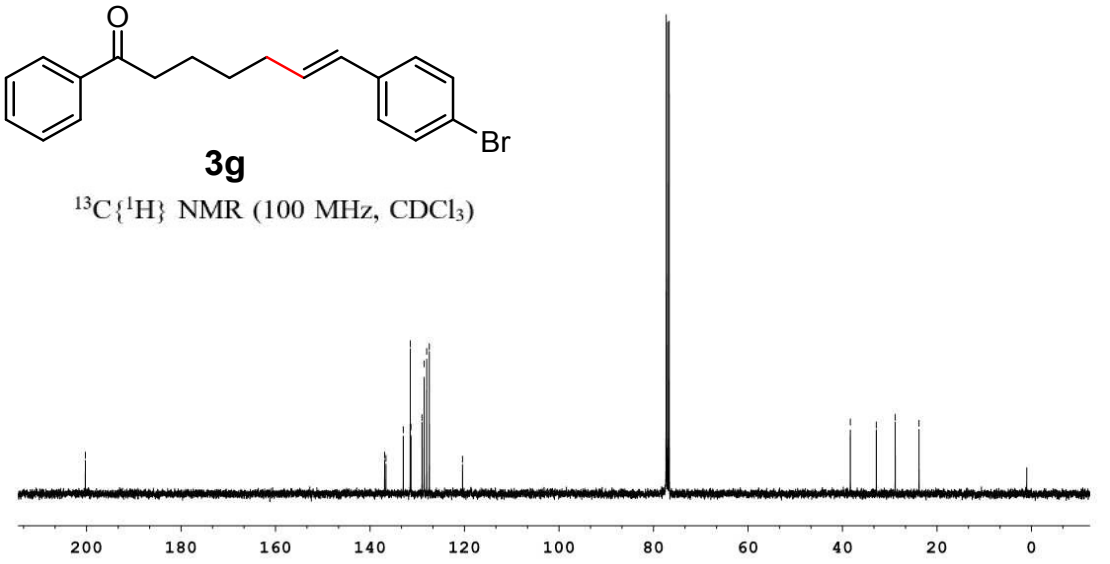




3g

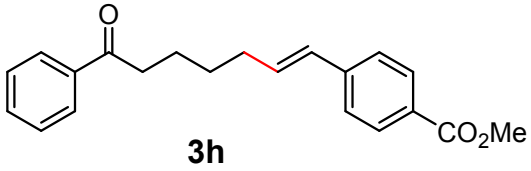
^{1}H NMR (400 MHz, $CDCl_3$)





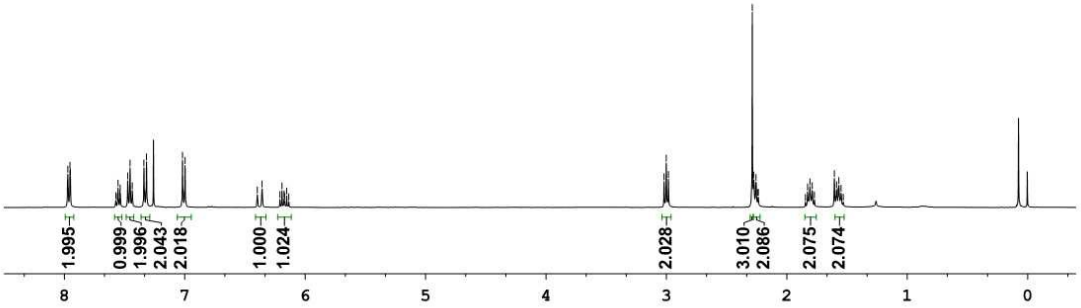
3g

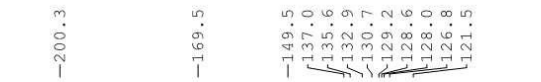
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

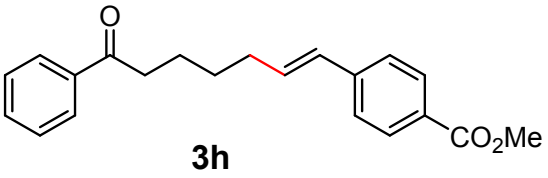


3h

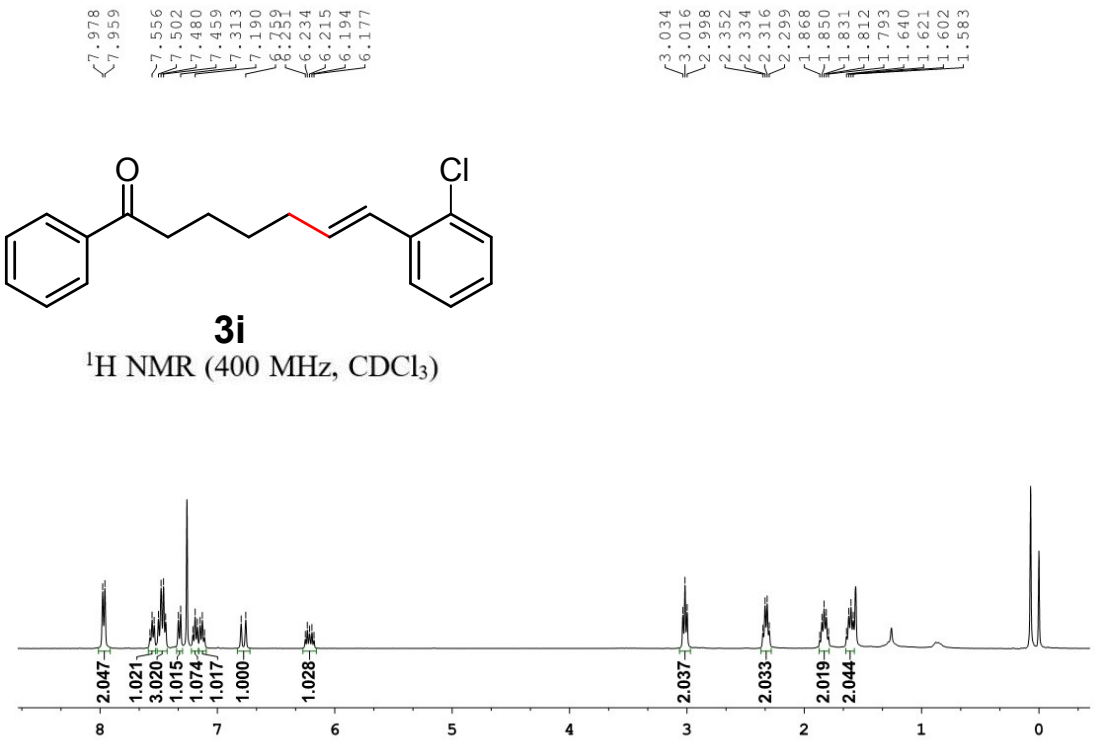
^{1}H NMR (400 MHz, $CDCl_3$)

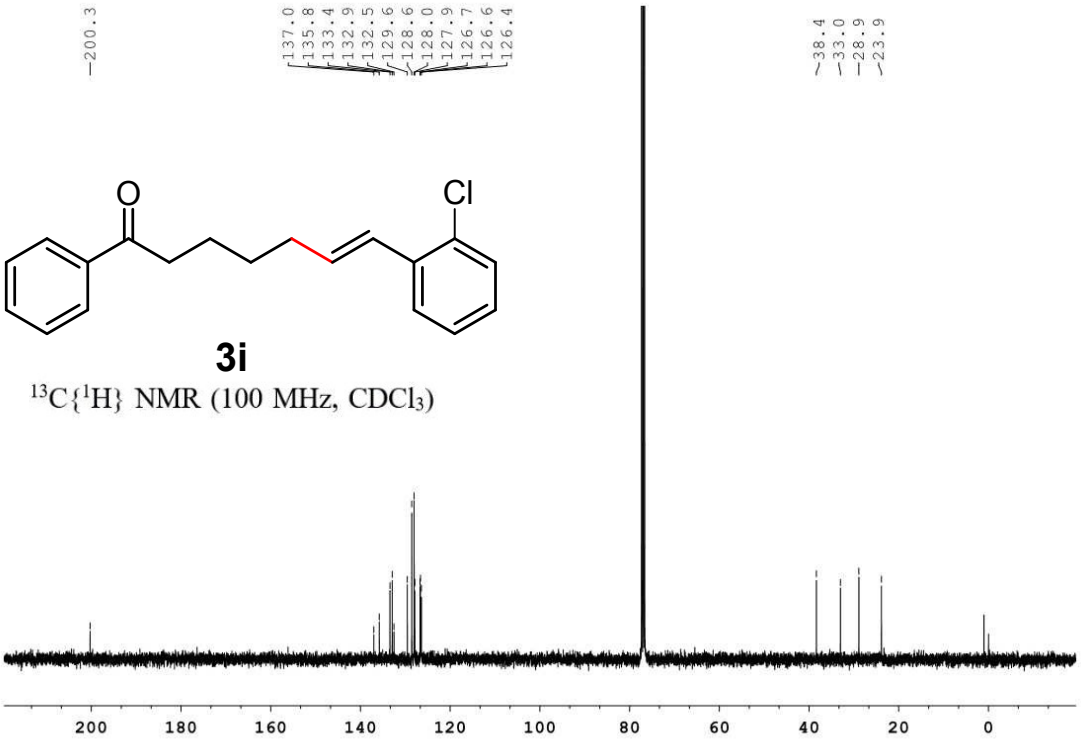


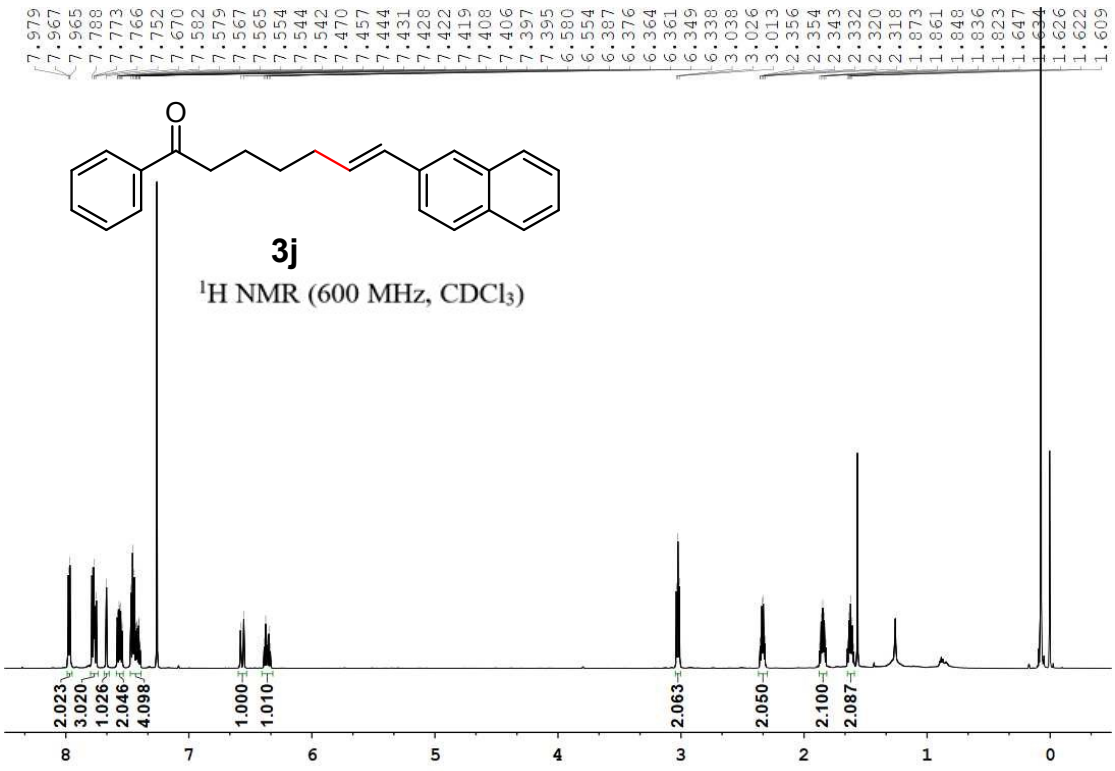




3h

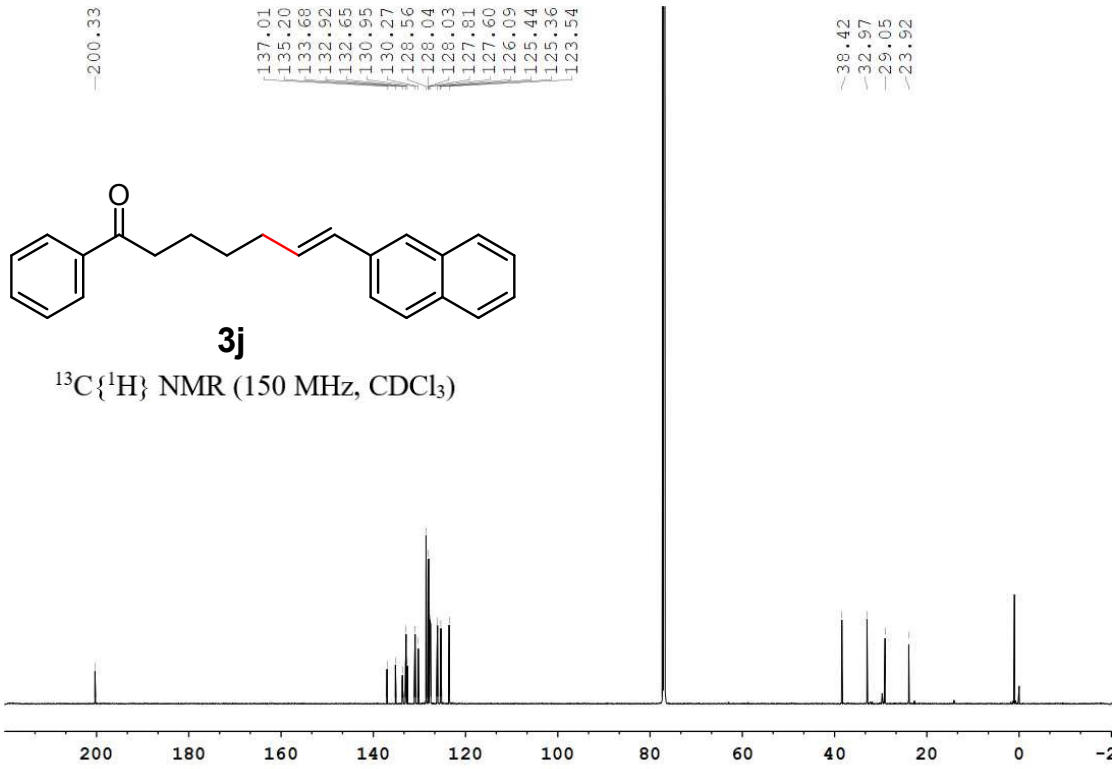

7.978
7.959
7.556
7.502
7.480
7.459
7.313
7.190
6.259
6.251
6.234
6.215
6.194
6.177
3.034
3.016
2.998
2.352
2.334
2.316
2.299
1.868
1.850
1.831
1.812
1.793
1.640
1.621
1.602
1.583
O
Cl
3i
1H NMR (400 MHz, CDCl3)
2.047
1.021
3.020
1.015
1.074
1.017
1.000
1.028
2.037
2.033
2.019
2.044
8
7
6
5
4
3
2
1
0


200.3
137.0
135.8
133.4
132.9
132.5
129.6
128.6
128.0
127.9
126.7
126.6
126.4
38.4
33.0
28.9
23.9
O
Cl
3i
13C{1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0



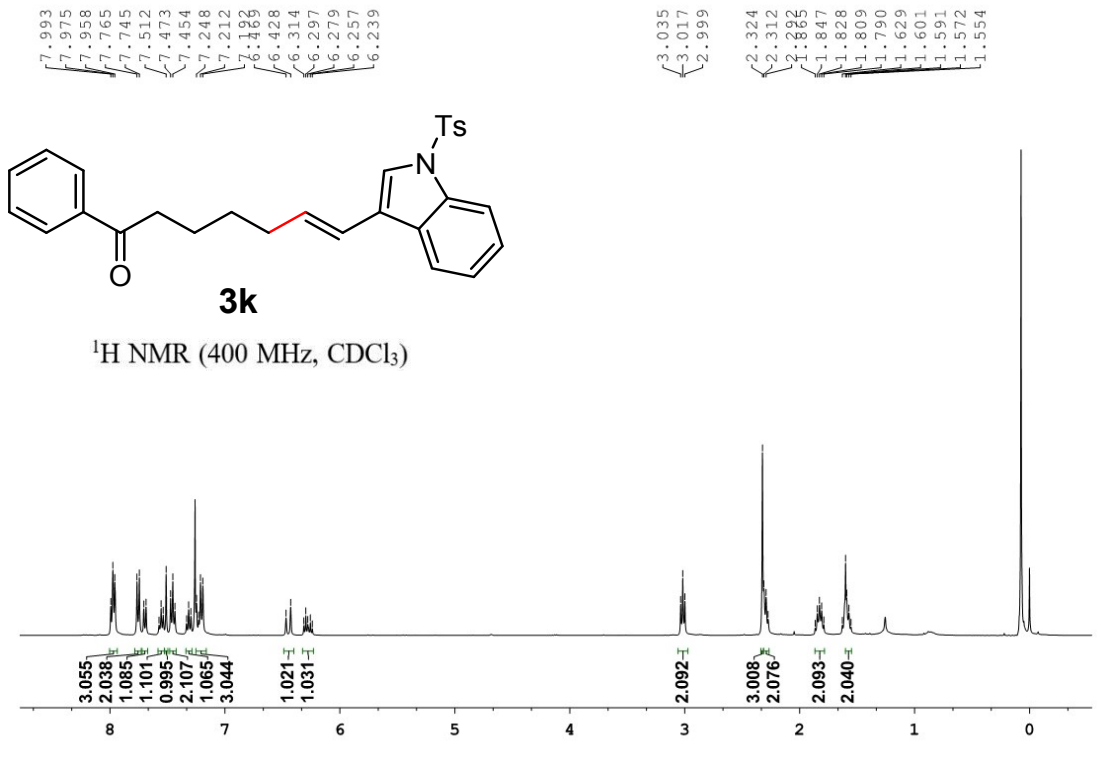
3j

^{1}H NMR (600 MHz, $CDCl_3$)



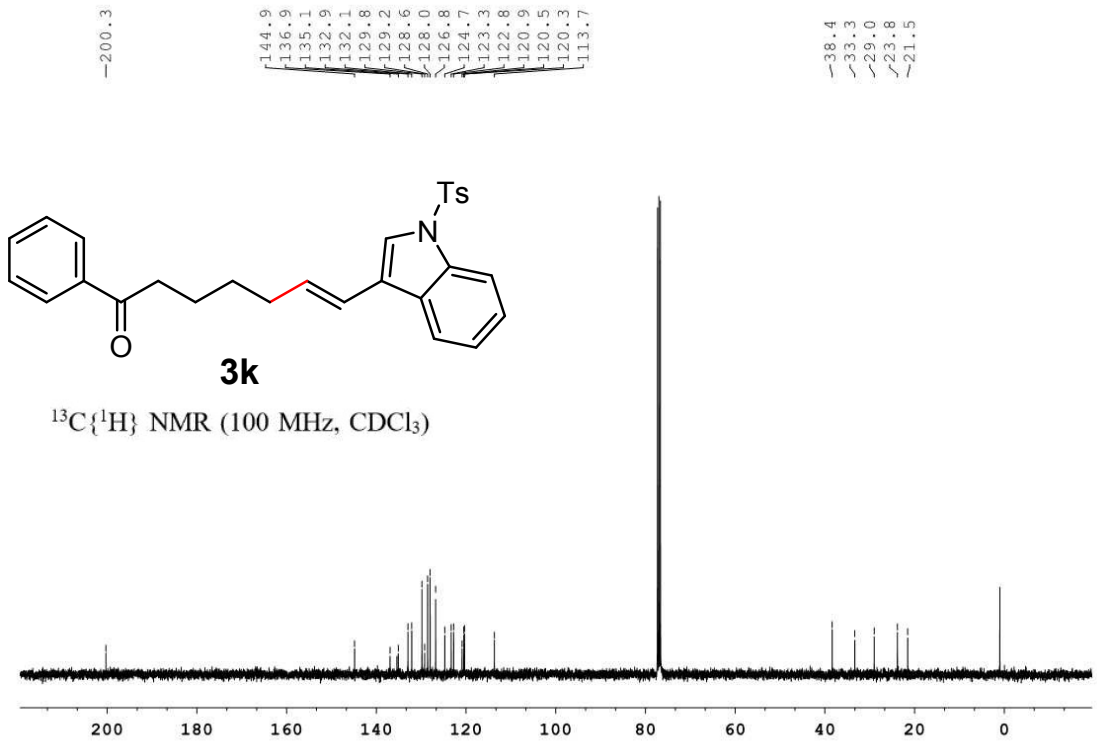
3j

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)



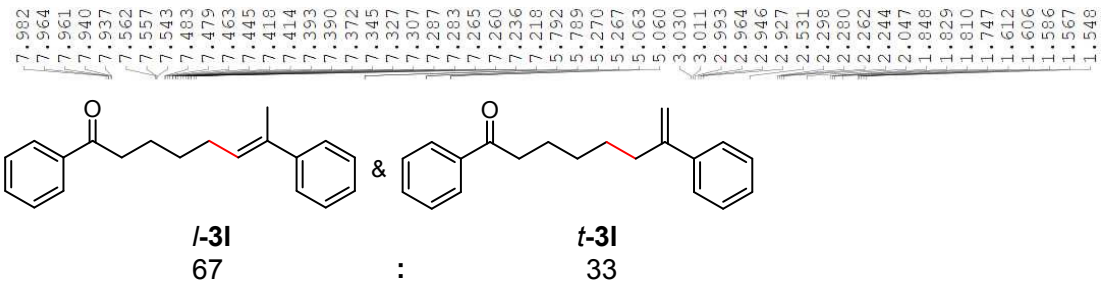
3k

^{1}H NMR (400 MHz, $CDCl_3$)



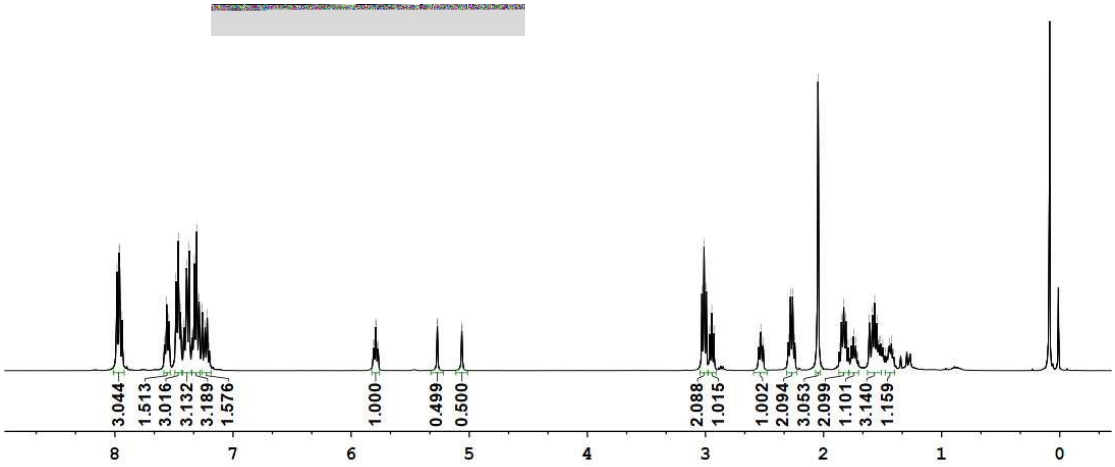
3k

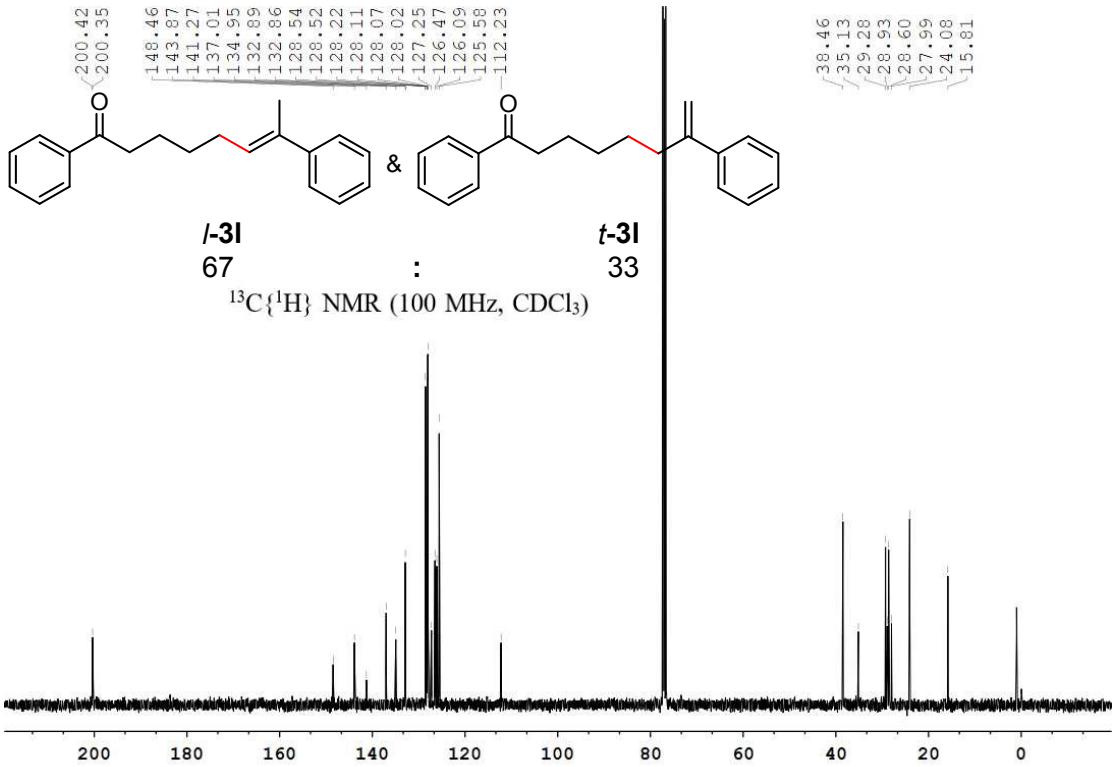
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



***l*-3l** : ***t*-3l**

67 : 33

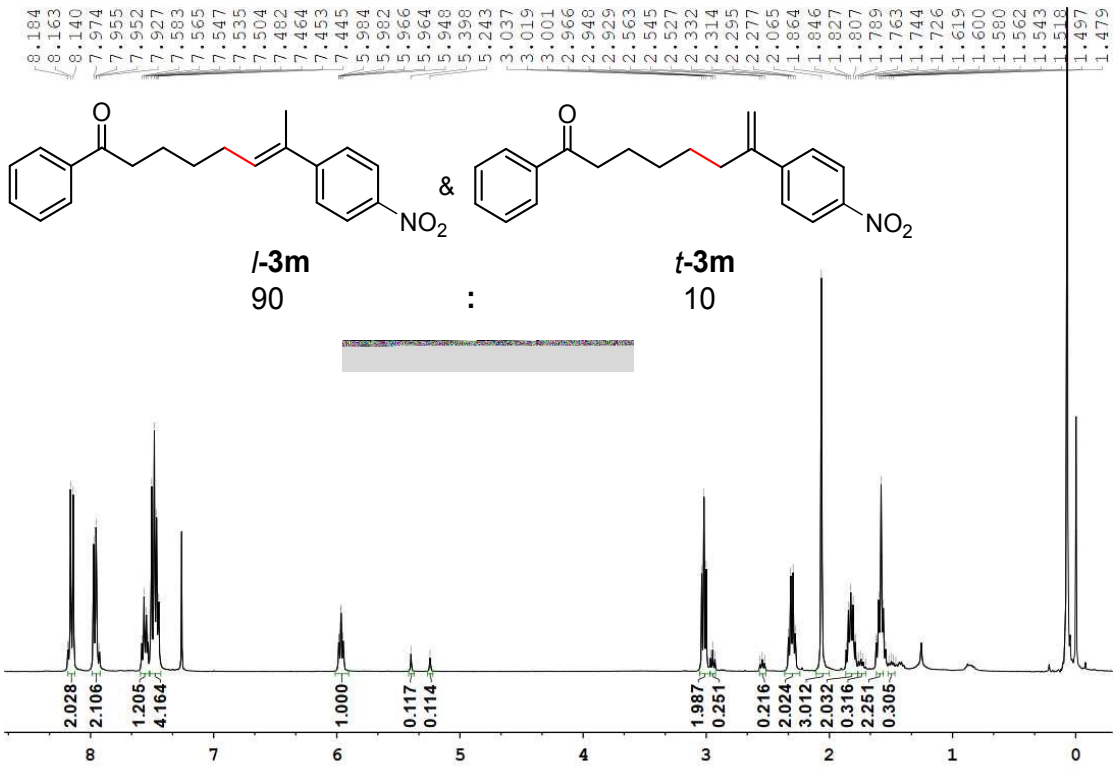


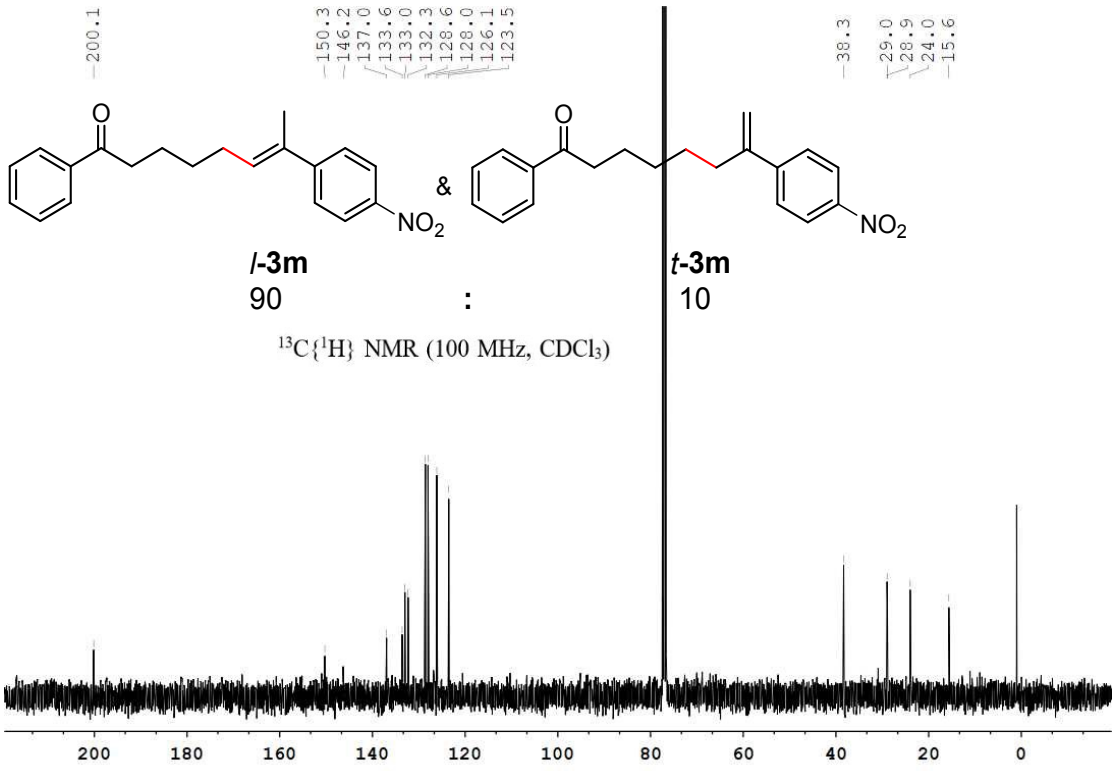


***l*-3l** : ***t*-3l**

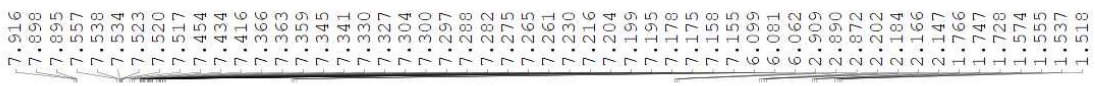
67 : 33

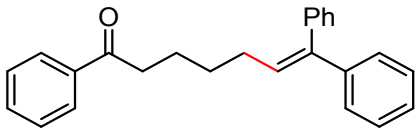
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



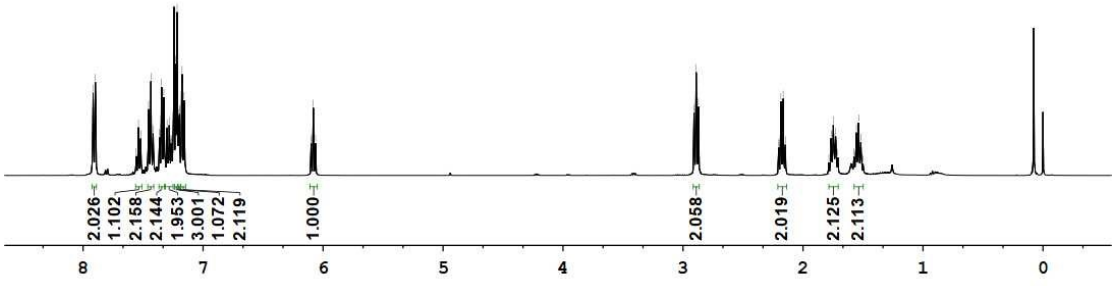


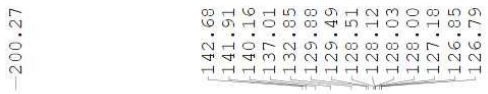
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

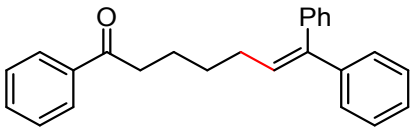

7.916
7.898
7.895
7.557
7.538
7.534
7.523
7.520
7.517
7.454
7.434
7.416
7.366
7.363
7.359
7.345
7.341
7.330
7.327
7.304
7.300
7.297
7.288
7.282
7.275
7.265
7.261
7.230
7.216
7.204
7.199
7.195
7.178
7.175
7.158
7.155
6.099
6.081
6.062
2.909
2.890
2.872
2.202
2.184
2.166
2.147
1.766
1.747
1.728
1.574
1.555
1.537
1.518


O
Ph

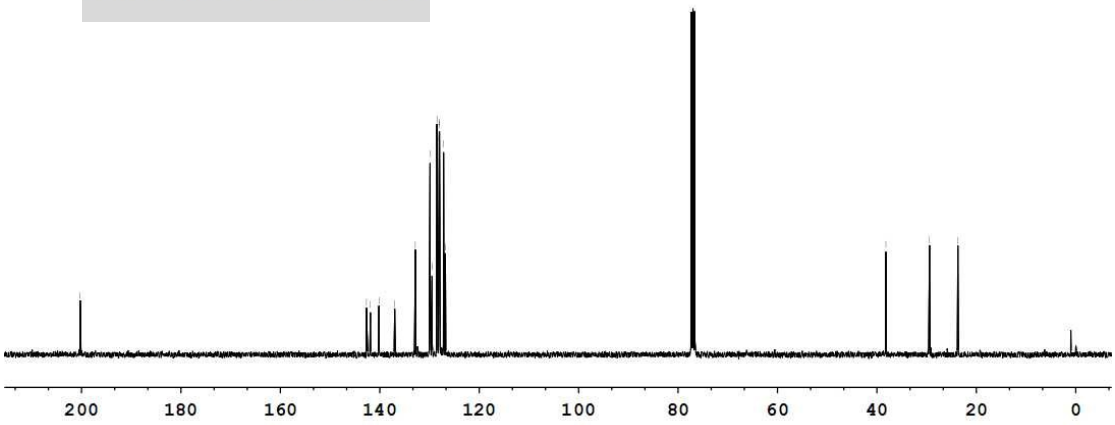
3n

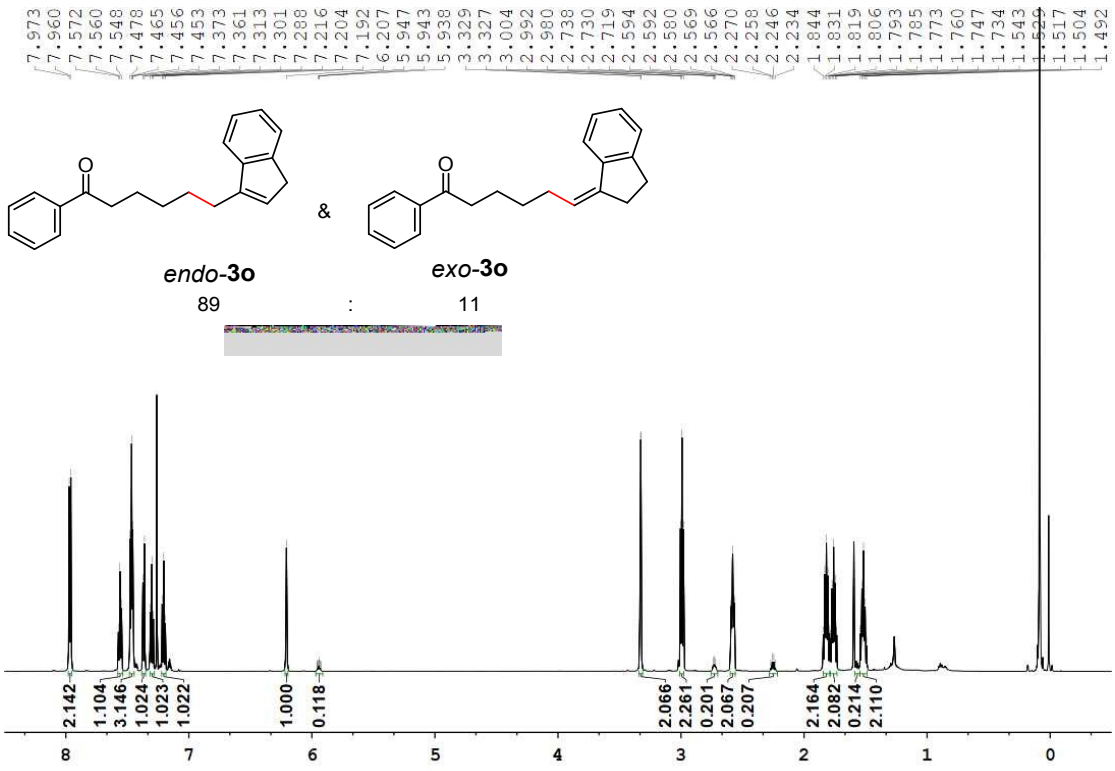

2.026
1.102
2.158
2.144
1.953
3.001
1.072
2.119
1.000
2.068
2.019
2.125
2.113
8
7
6
5
4
3
2
1
0

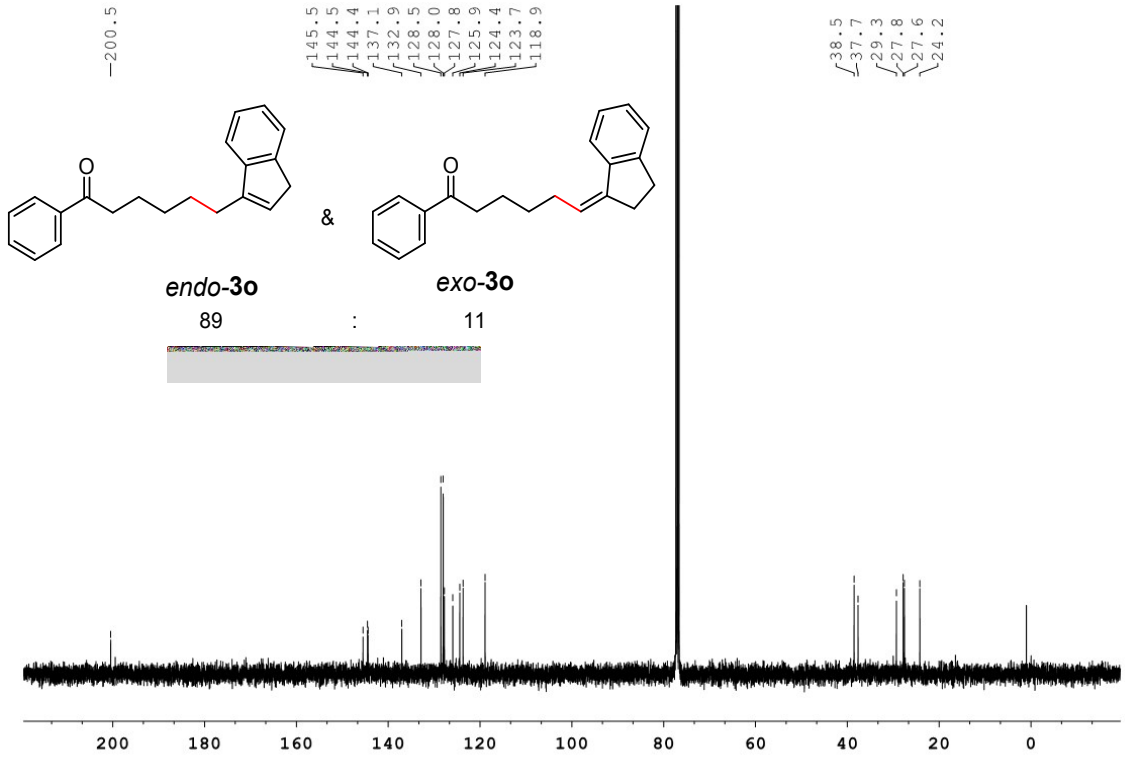

200.27
142.68
141.91
140.16
137.01
132.85
129.88
129.49
128.51
128.12
128.03
128.00
127.18
126.85
126.79
38.19
29.43
29.37
23.72

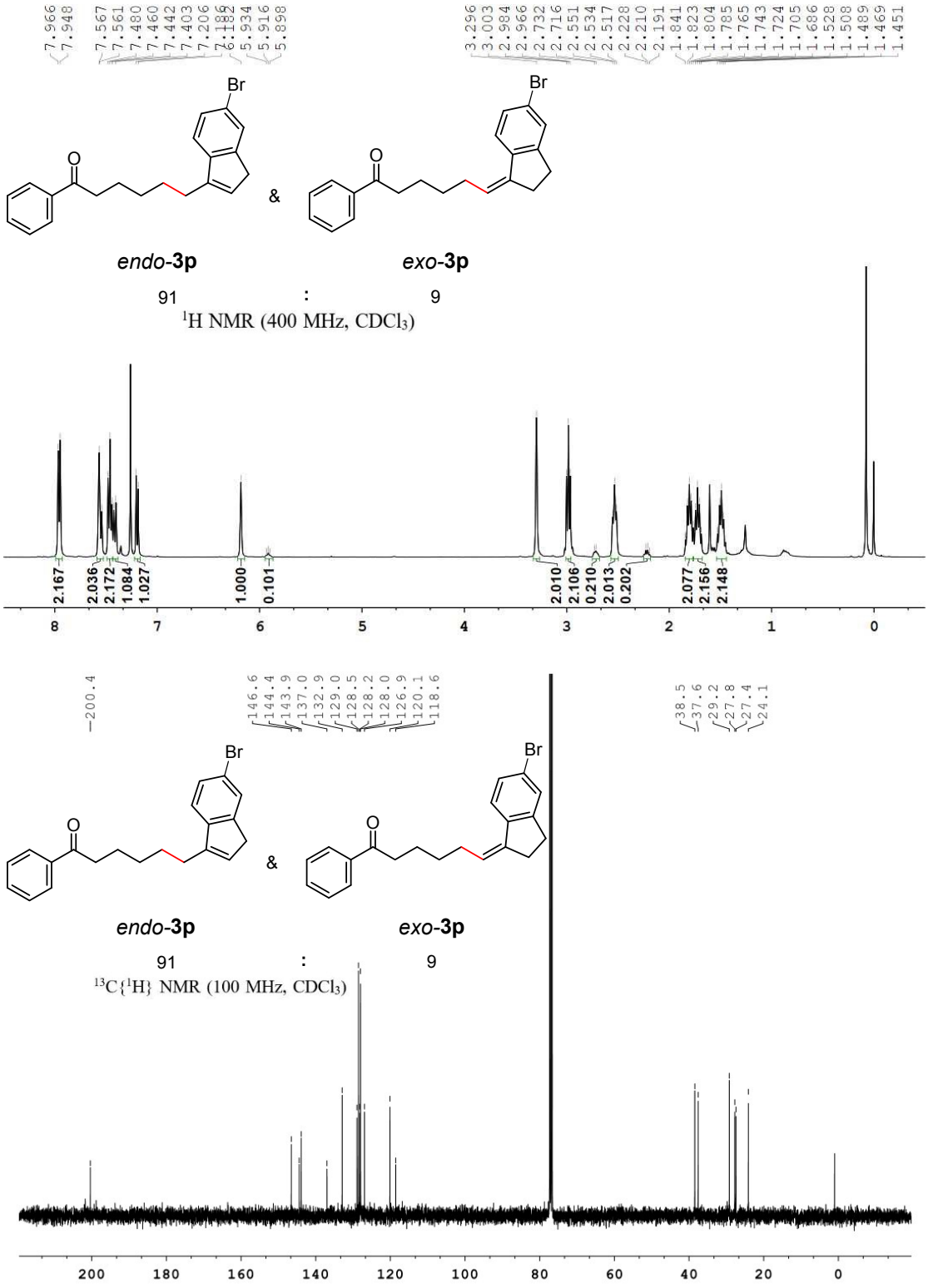

O
Ph

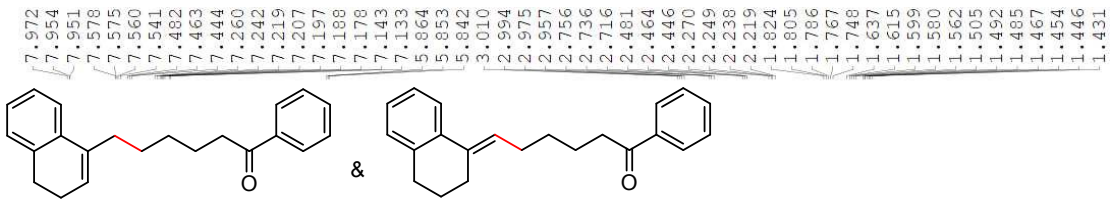
3n


200
180
160
140
120
100
80
60
40
20
0


7.973
7.960
7.572
7.560
7.548
7.478
7.465
7.456
7.453
7.373
7.361
7.313
7.301
7.288
7.216
7.204
7.192
6.207
5.947
5.943
5.938
3.329
3.327
3.004
2.992
2.980
2.738
2.730
2.719
2.594
2.592
2.580
2.569
2.566
2.270
2.258
2.246
2.234
1.844
1.831
1.819
1.806
1.793
1.785
1.773
1.760
1.747
1.734
1.543
1.529
1.517
1.504
1.492
&
endo-3o
exo-3o
89 : 11
2.142
1.104
3.146
1.024
1.023
1.022
1.000
0.118
2.066
2.261
0.201
2.067
0.207
2.164
2.082
0.214
2.110
8
7
6
5
4
3
2
1
0


200.5
145.5
144.5
144.4
137.1
132.9
128.5
128.0
127.8
125.9
124.4
123.7
118.9
38.5
37.7
29.3
27.8
27.6
24.2
&
endo-3o
exo-3o
89 : 11
200
180
160
140
120
100
80
60
40
20
0

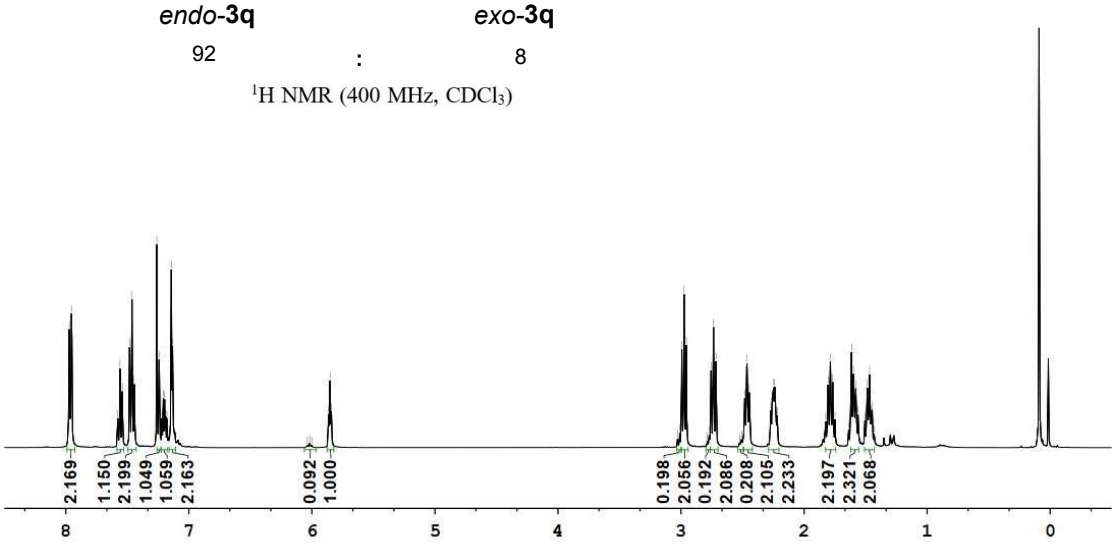

7.966
7.948
7.567
7.561
7.480
7.460
7.442
7.403
7.206
7.186
6.182
5.934
5.916
5.898
3.296
3.003
2.984
2.966
2.732
2.716
2.551
2.534
2.517
2.228
2.210
2.191
1.841
1.823
1.804
1.785
1.765
1.743
1.724
1.705
1.686
1.528
1.508
1.489
1.469
1.451
Br
O
&
Br
O
endo-3p
exo-3p
91 : 9
1H NMR (400 MHz, CDCl3)
2.167
2.036
2.172
1.084
1.027
1.000
0.101
2.010
2.106
0.210
2.013
0.202
2.077
2.156
2.148
8
7
6
5
4
3
2
1
0
200.4
146.6
144.4
143.9
137.0
132.9
129.0
128.5
128.2
128.0
126.9
120.1
118.6
38.5
37.6
29.2
27.8
27.4
24.1
Br
O
&
Br
O
endo-3p
exo-3p
91 : 9
13C{1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0

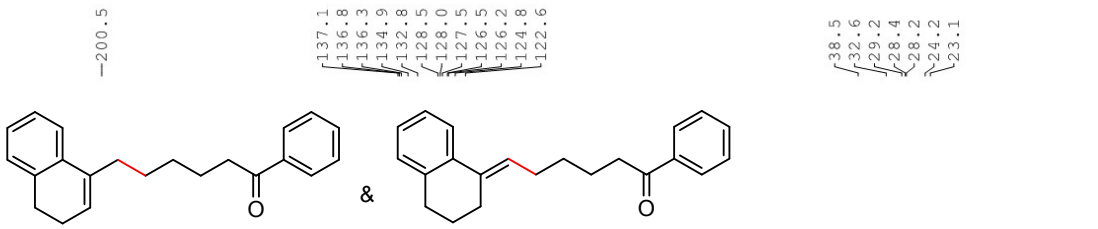


***endo*-3q** : ***exo*-3q**

92 : 8

^{1}H NMR (400 MHz, $CDCl_3$)

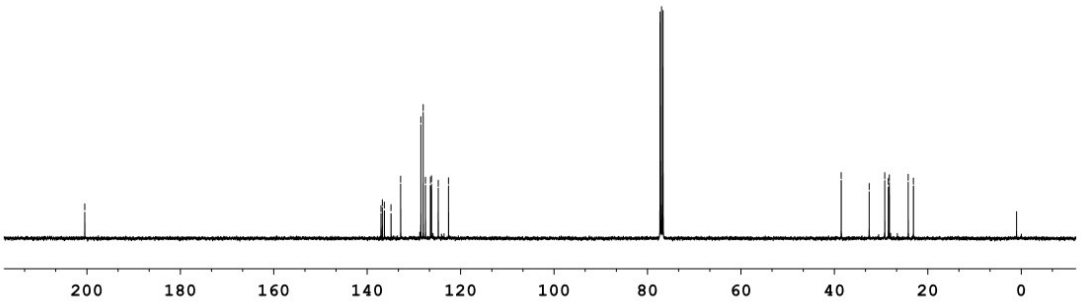


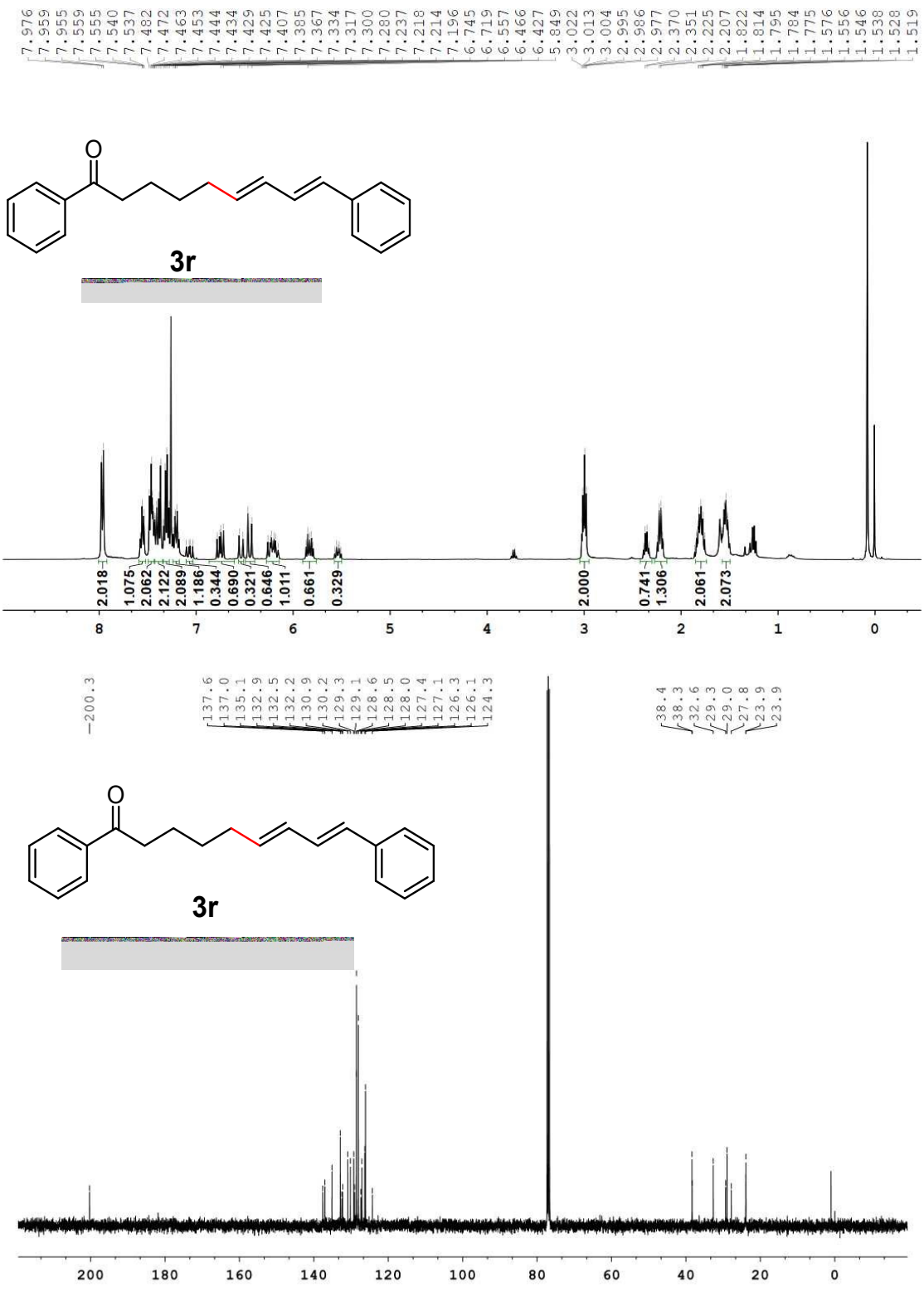


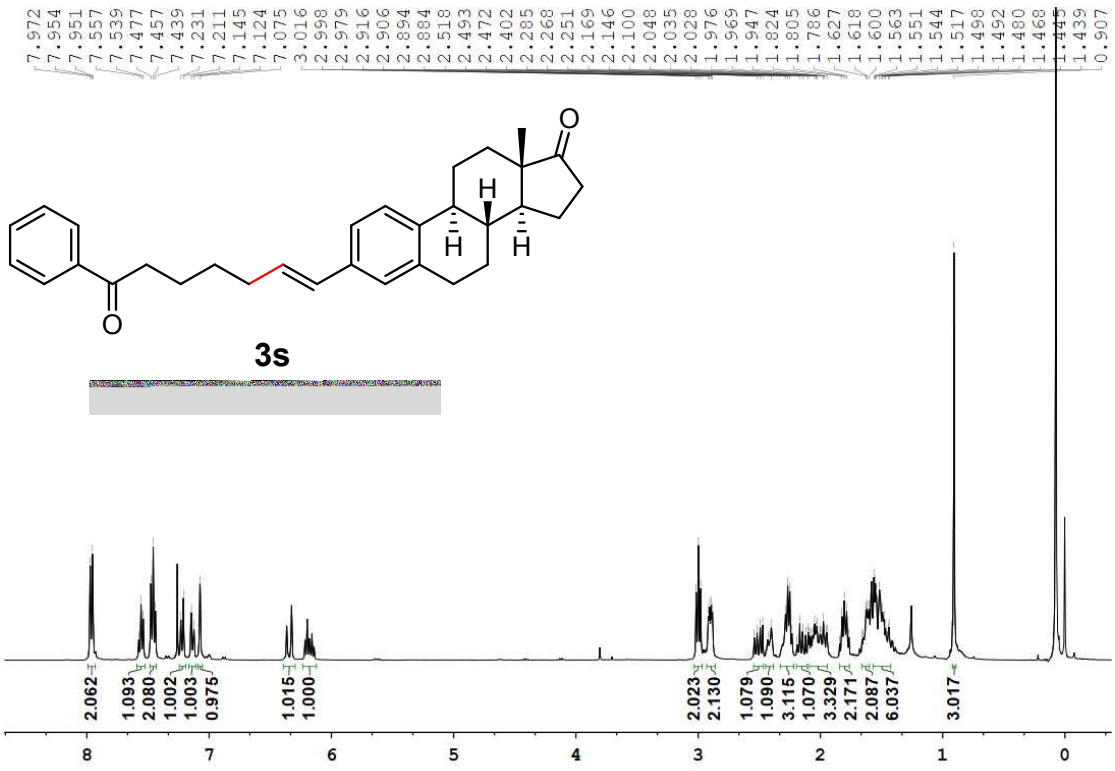
***endo*-3q** : ***exo*-3q**

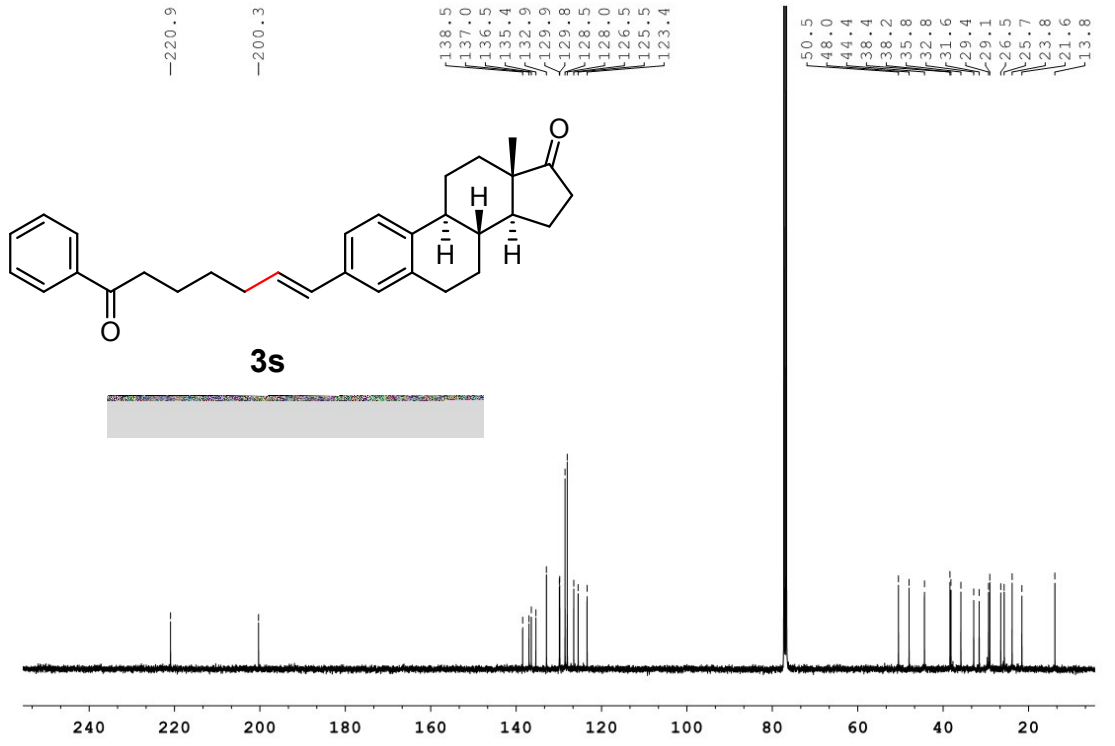
92 : 8

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

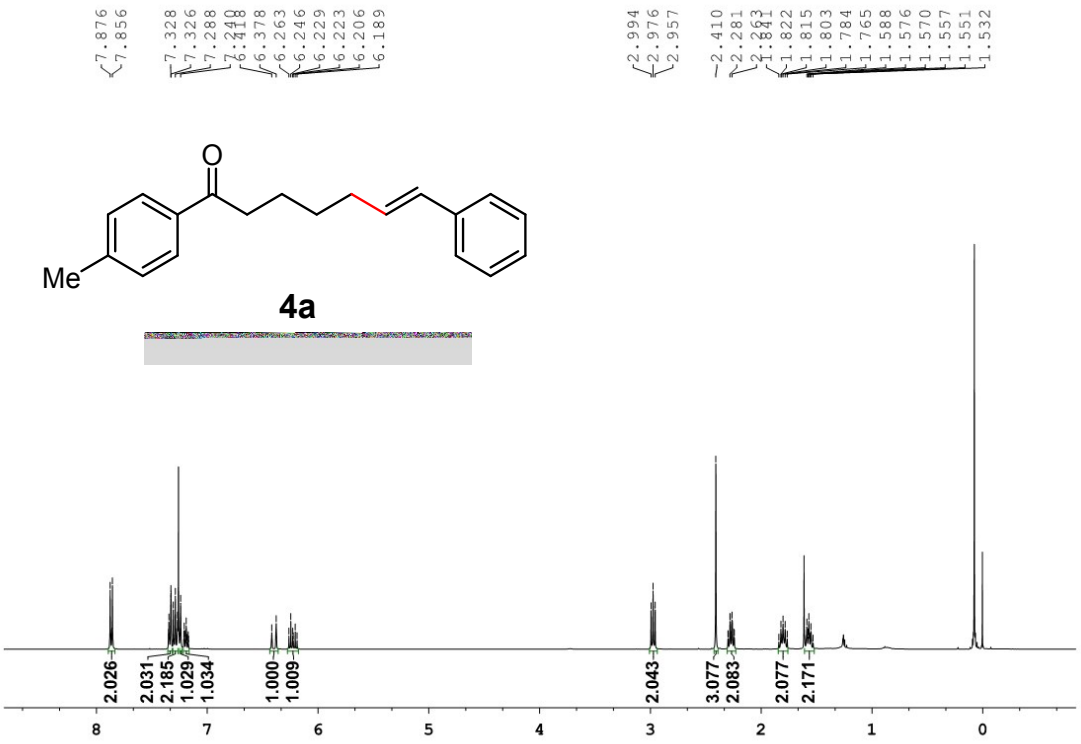


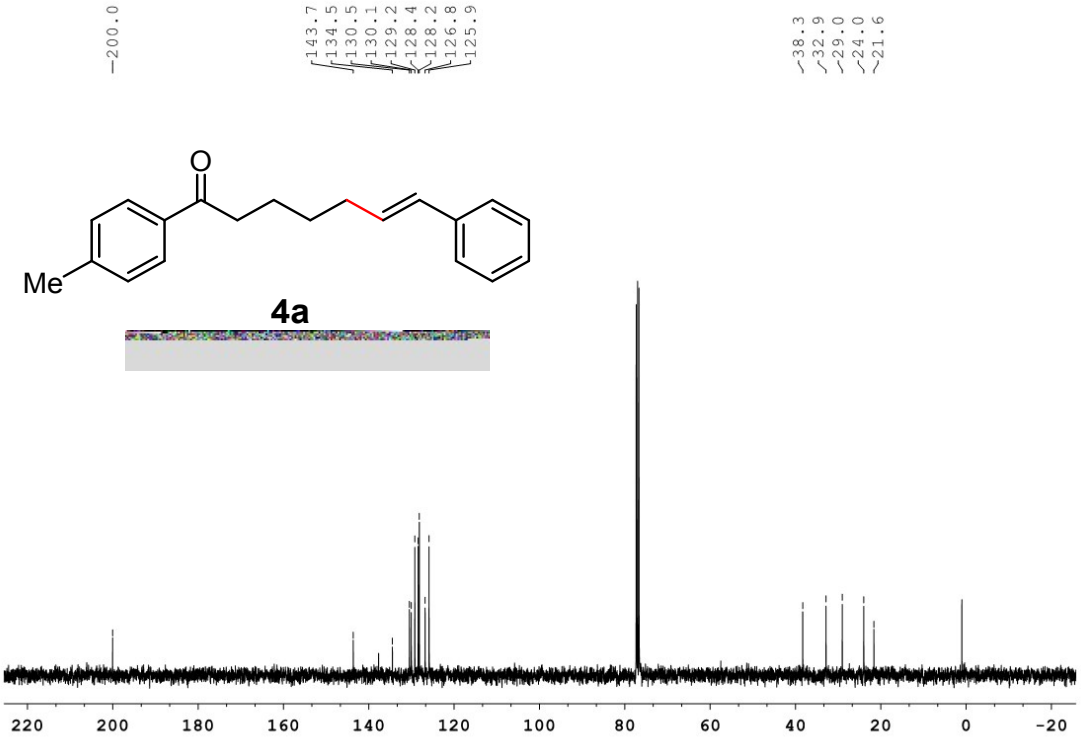

7.976
7.959
7.955
7.559
7.555
7.540
7.537
7.482
7.472
7.463
7.453
7.444
7.434
7.429
7.425
7.407
7.385
7.367
7.334
7.317
7.300
7.280
7.237
7.218
7.214
7.196
6.745
6.719
6.557
6.466
6.427
5.849
3.022
3.013
3.004
2.995
2.986
2.977
2.370
2.351
2.225
2.207
1.822
1.814
1.795
1.784
1.775
1.576
1.556
1.546
1.538
1.528
1.519
O
3r
2.018
1.075
2.062
2.122
2.089
1.186
0.344
0.690
0.321
0.646
1.011
0.661
0.329
2.000
0.741
1.306
2.061
2.073
8
7
6
5
4
3
2
1
0
200.3
137.6
137.0
135.1
132.9
132.5
132.2
130.9
130.2
129.3
129.1
128.6
128.5
128.0
127.4
127.1
126.3
126.1
124.3
38.4
38.3
32.6
29.3
29.0
27.8
23.9
23.9
O
3r
200
180
160
140
120
100
80
60
40
20
0

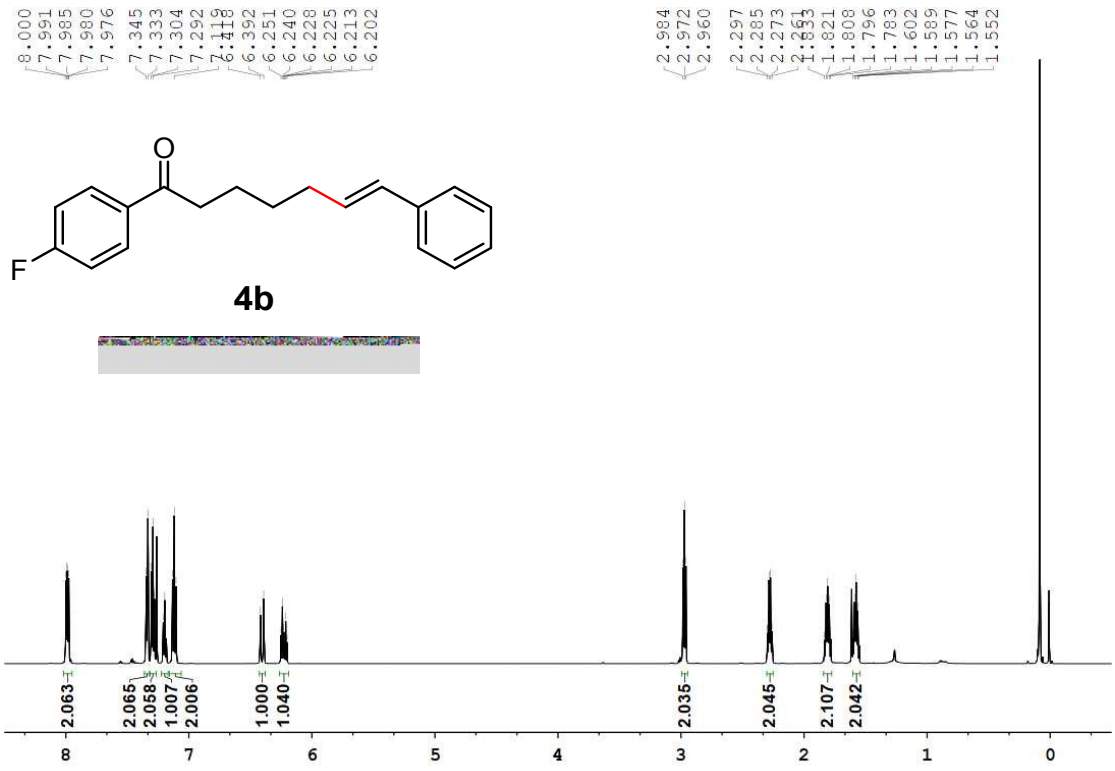

7.972
7.954
7.951
7.557
7.539
7.477
7.457
7.439
7.231
7.211
7.145
7.124
7.075
3.016
2.998
2.979
2.916
2.906
2.894
2.884
2.518
2.493
2.472
2.402
2.285
2.268
2.251
2.169
2.146
2.100
2.048
2.035
2.028
1.976
1.969
1.947
1.824
1.805
1.786
1.627
1.618
1.600
1.563
1.551
1.544
1.517
1.498
1.492
1.480
1.468
1.445
1.439
0.907
O
H
H
H
O
3s
2.062
1.093
2.080
1.002
1.003
0.975
1.015
1.000
2.023
2.130
1.079
1.090
3.115
1.070
3.329
2.171
2.087
6.037
3.017
8
7
6
5
4
3
2
1
0

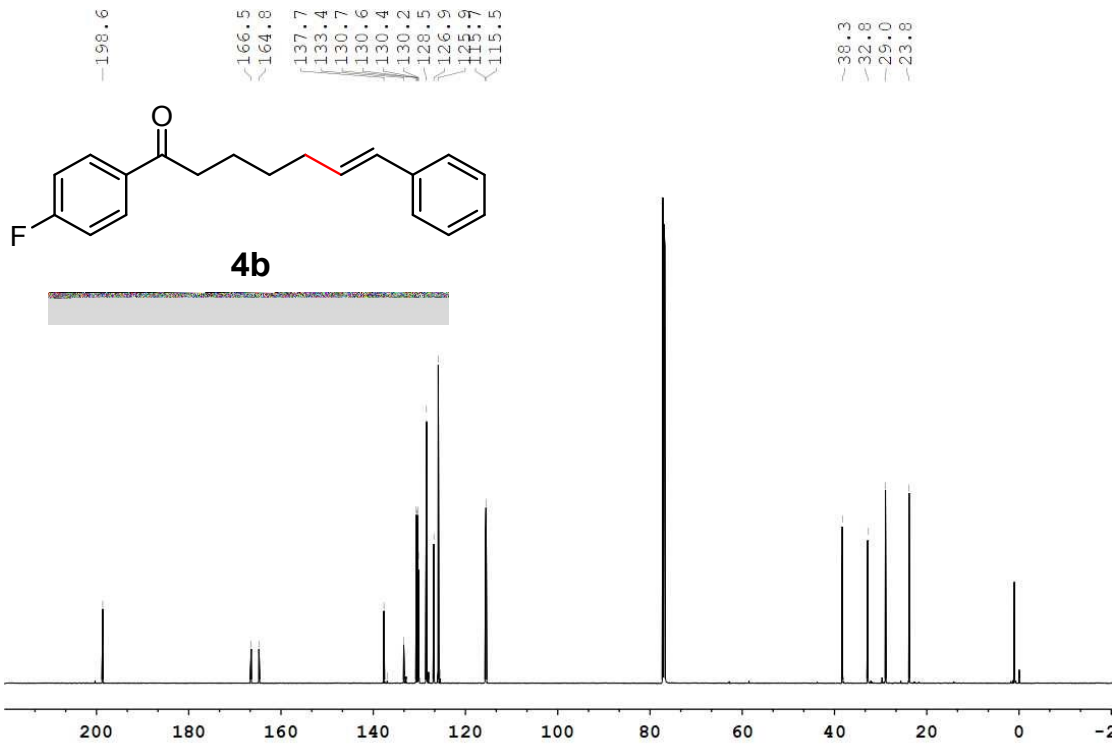

220.9
200.3
138.5
137.0
136.5
135.4
132.9
129.9
129.8
128.5
128.0
126.5
125.5
123.4
50.5
48.0
44.4
38.4
38.2
35.8
32.8
31.6
29.4
29.1
26.5
25.7
23.8
21.6
13.8
O
H
H
H
O
3s
240
220
200
180
160
140
120
100
80
60
40
20

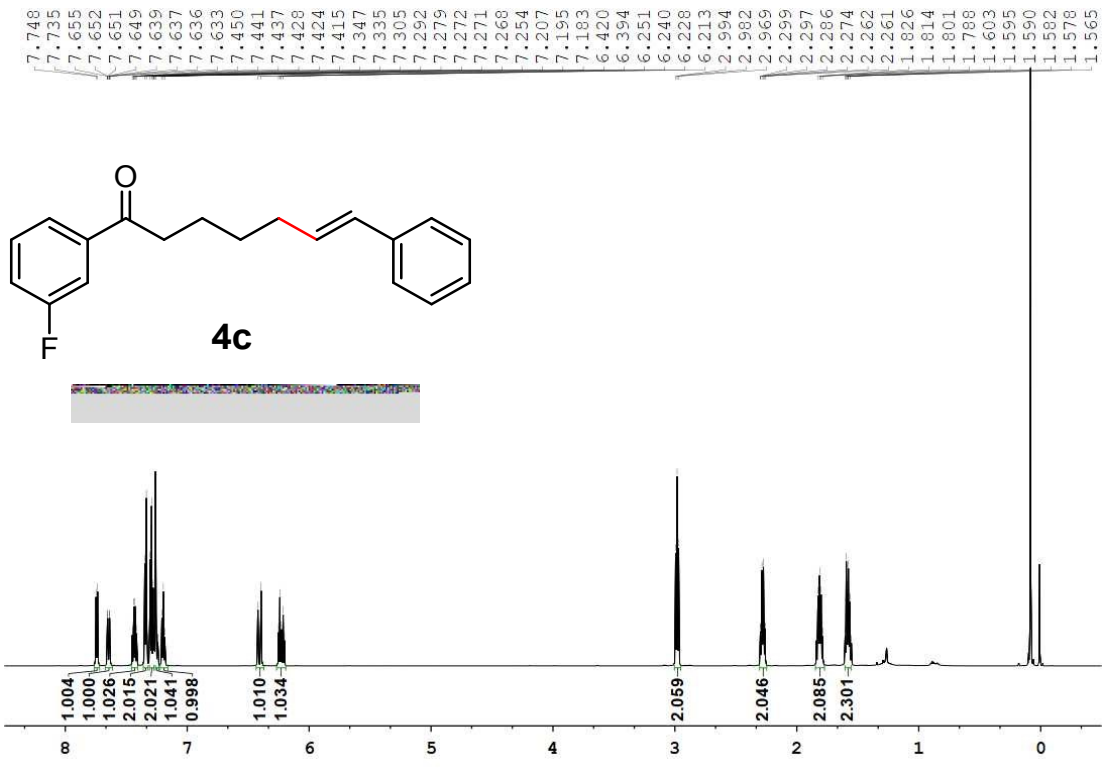
^{1}H NMR and ^{13}C NMR Spectra of the Products 4

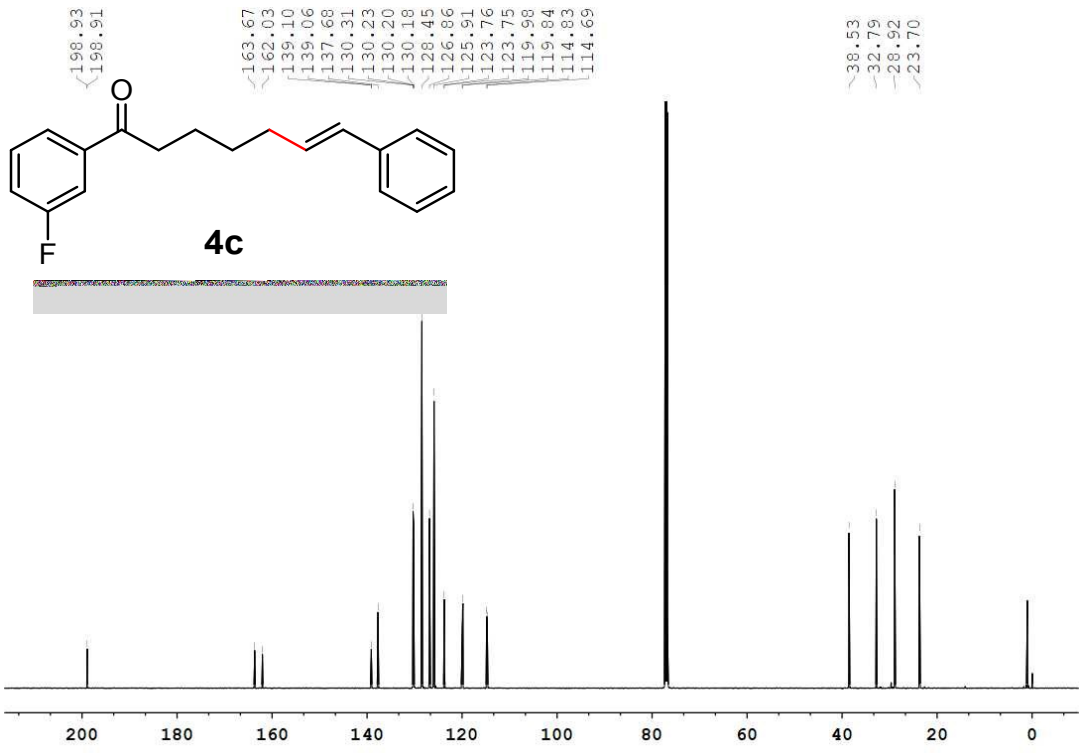


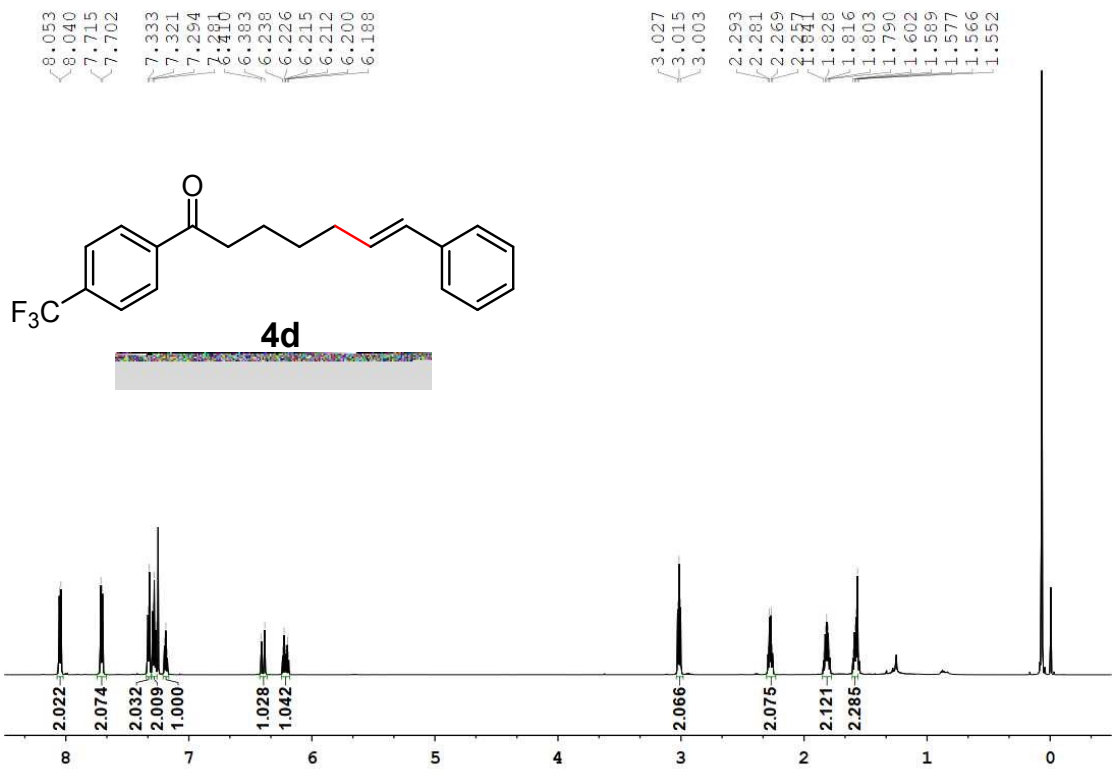


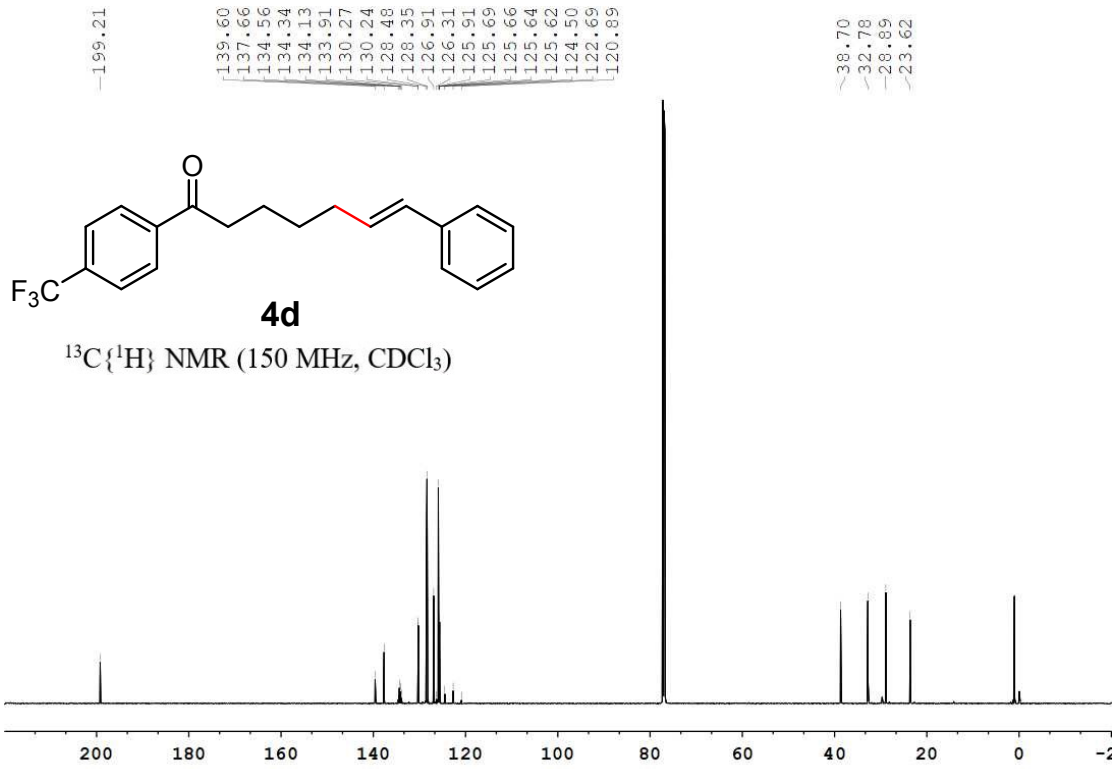

8.000
7.991
7.985
7.980
7.976
7.345
7.333
7.304
7.292
6.392
6.251
6.240
6.228
6.225
6.213
6.202
2.984
2.972
2.960
2.297
2.285
2.273
2.261
1.821
1.808
1.796
1.783
1.602
1.589
1.577
1.564
1.552
O
F
4b
2.063
2.065
2.058
1.007
2.006
1.000
1.040
2.035
2.045
2.107
2.042
8
7
6
5
4
3
2
1
0


198.6
166.5
164.8
137.7
133.4
130.7
130.6
130.4
130.2
128.5
126.9
125.7
115.5
38.3
32.8
29.0
23.8
O
F
4b
200
180
160
140
120
100
80
60
40
20
0

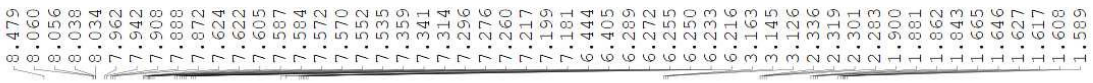

7.748
7.735
7.655
7.652
7.651
7.649
7.639
7.637
7.636
7.633
7.450
7.441
7.437
7.428
7.424
7.415
7.347
7.335
7.305
7.292
7.279
7.272
7.271
7.268
7.254
7.207
7.195
7.183
6.420
6.394
6.251
6.240
6.228
6.213
2.994
2.982
2.969
2.299
2.297
2.286
2.274
2.262
2.261
1.826
1.814
1.801
1.788
1.603
1.595
1.590
1.582
1.578
1.565
O
F
4c
1.004
1.000
1.026
2.015
2.021
1.041
0.998
1.010
1.034
2.059
2.046
2.085
2.301
8
7
6
5
4
3
2
1
0

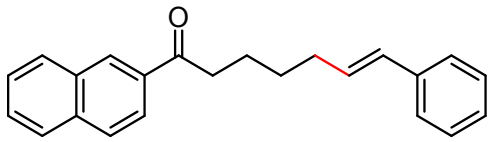

198.93
198.91
163.67
162.03
139.10
139.06
137.68
130.31
130.23
130.20
130.18
128.45
126.86
125.91
123.76
123.75
119.98
119.84
114.83
114.69
38.53
32.79
28.92
23.70
O
F
4c
200
180
160
140
120
100
80
60
40
20
0



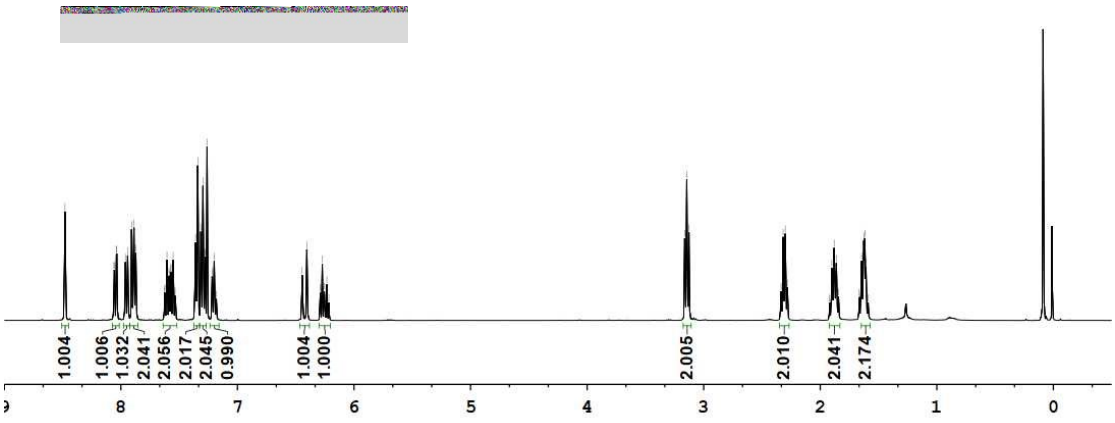


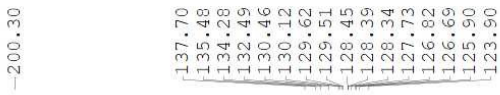
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

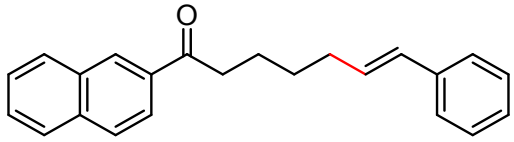




4e

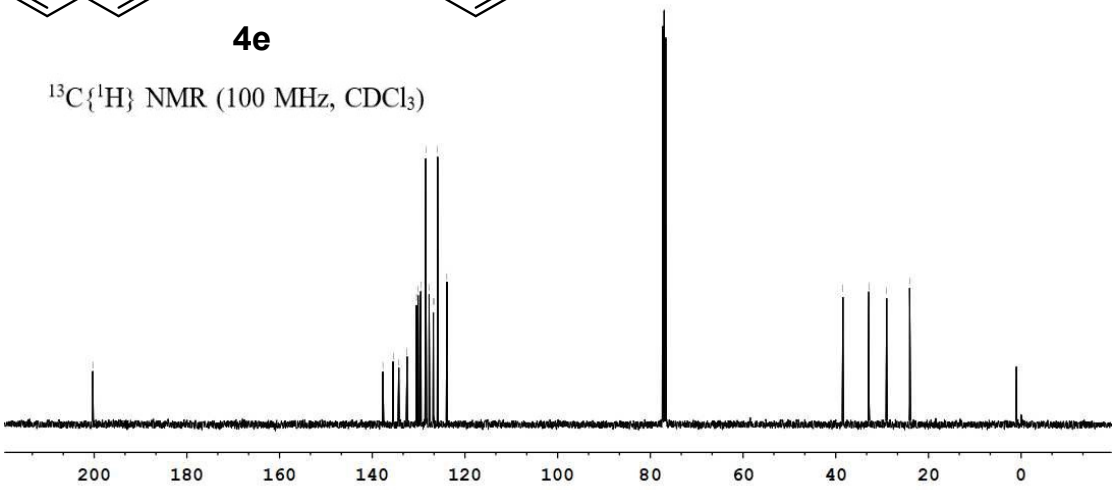


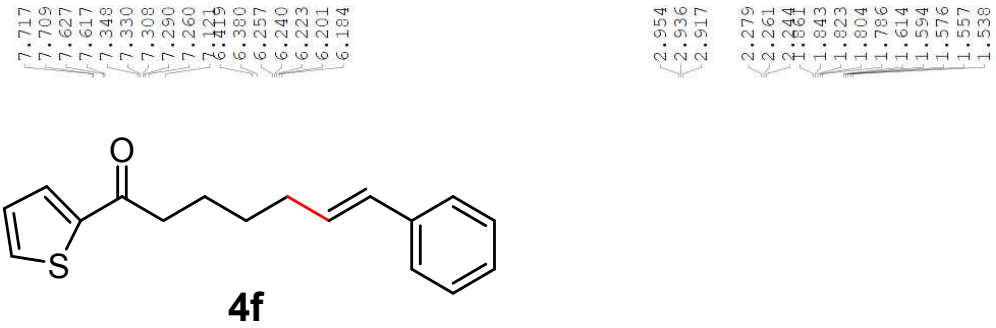




4e

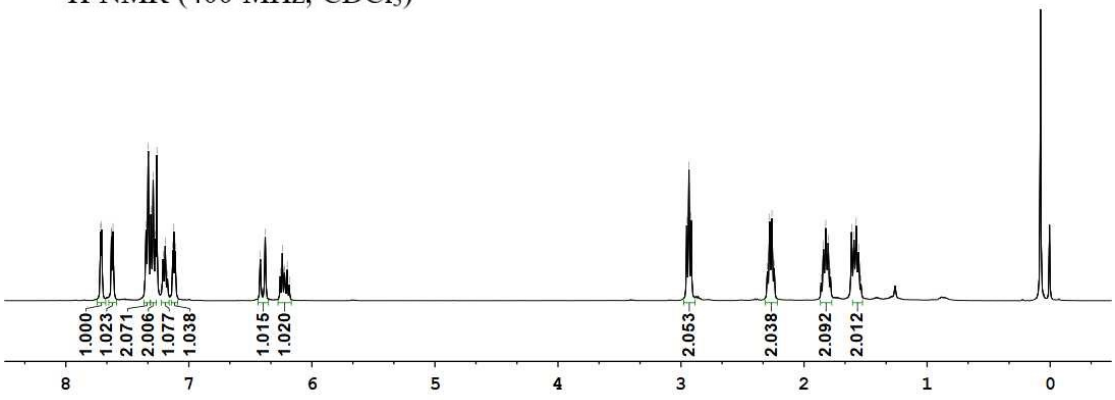
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

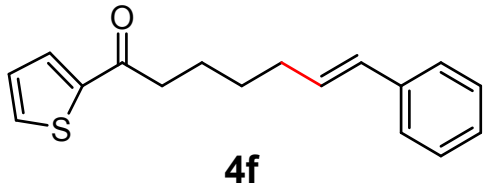




4f

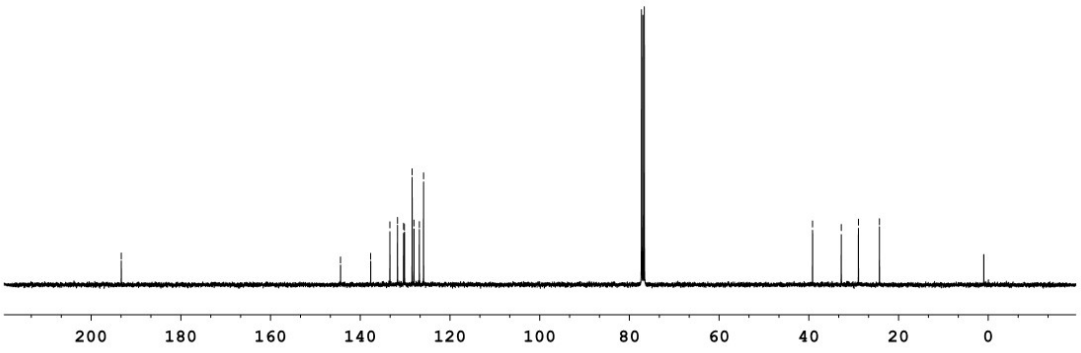
^{1}H NMR (400 MHz, $CDCl_3$)

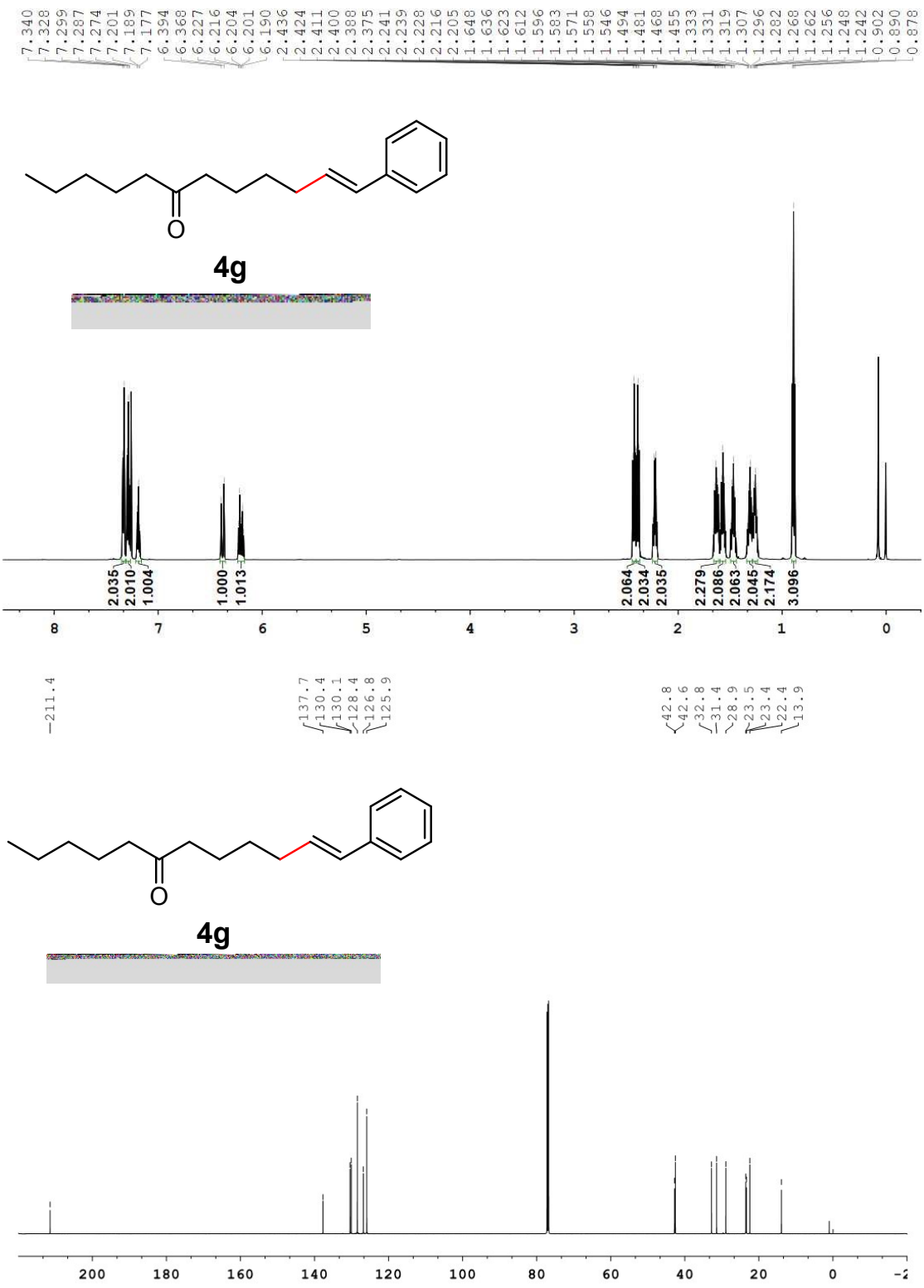


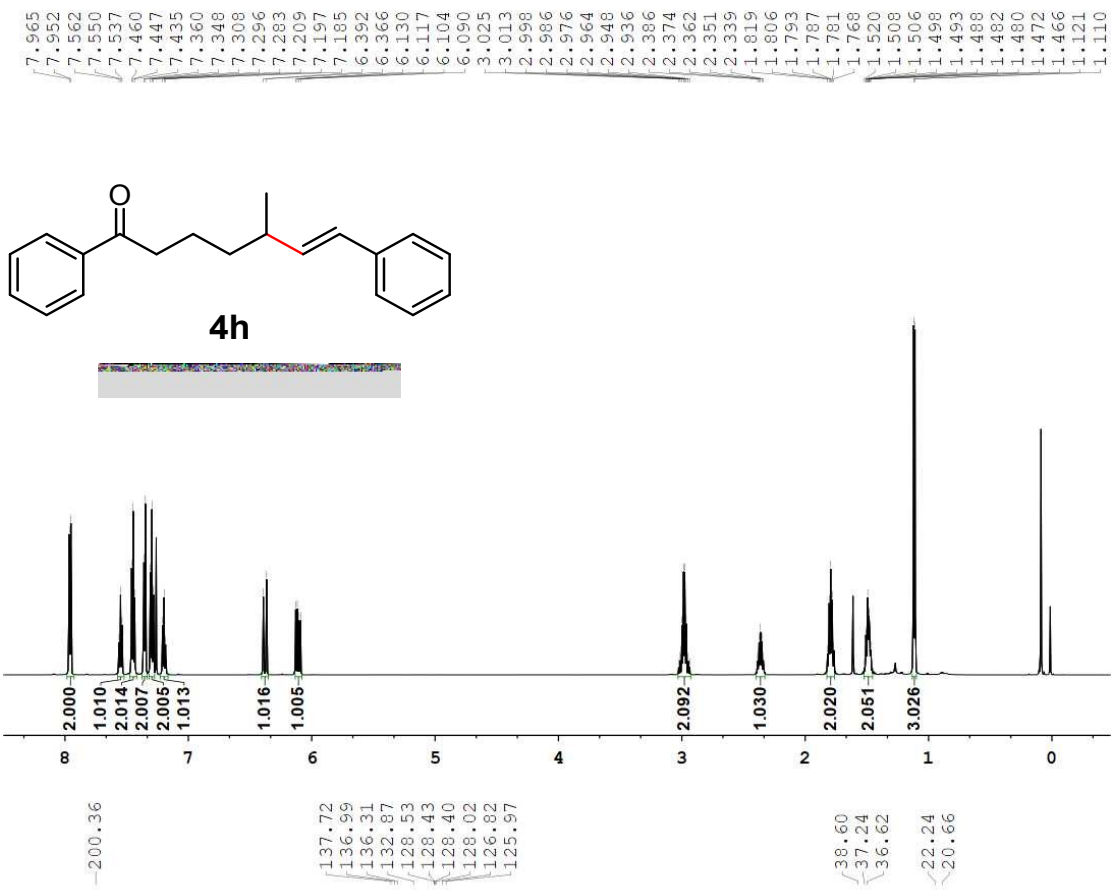


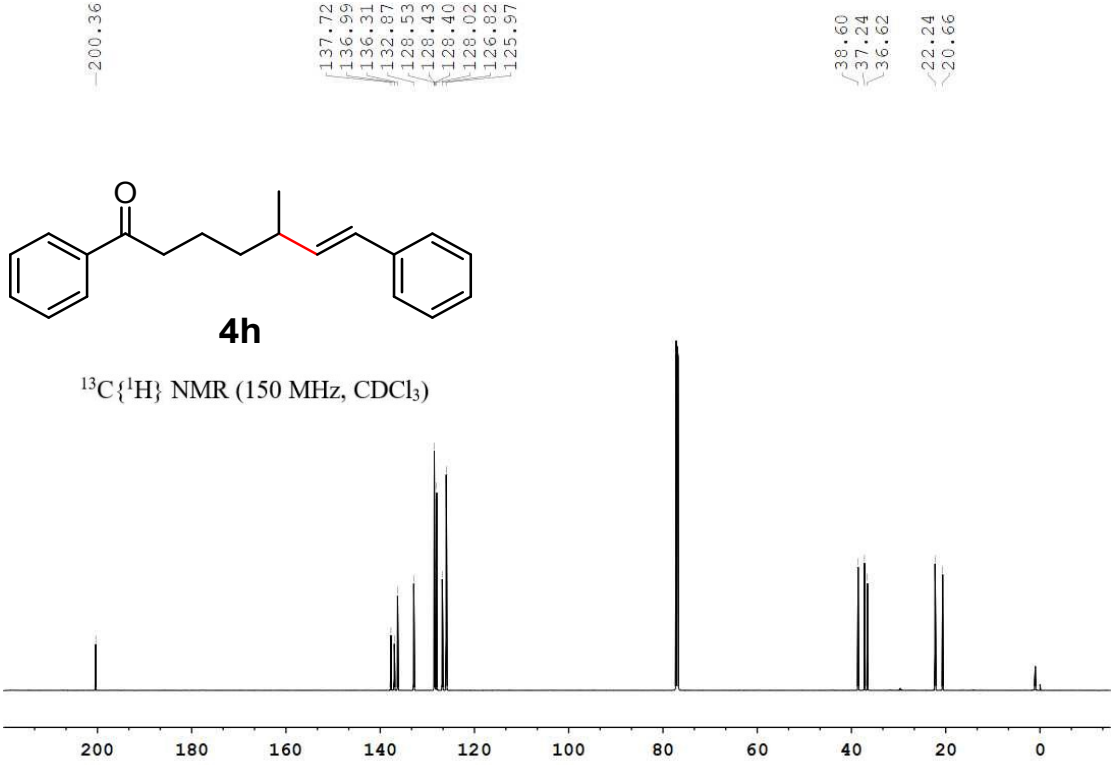
4f

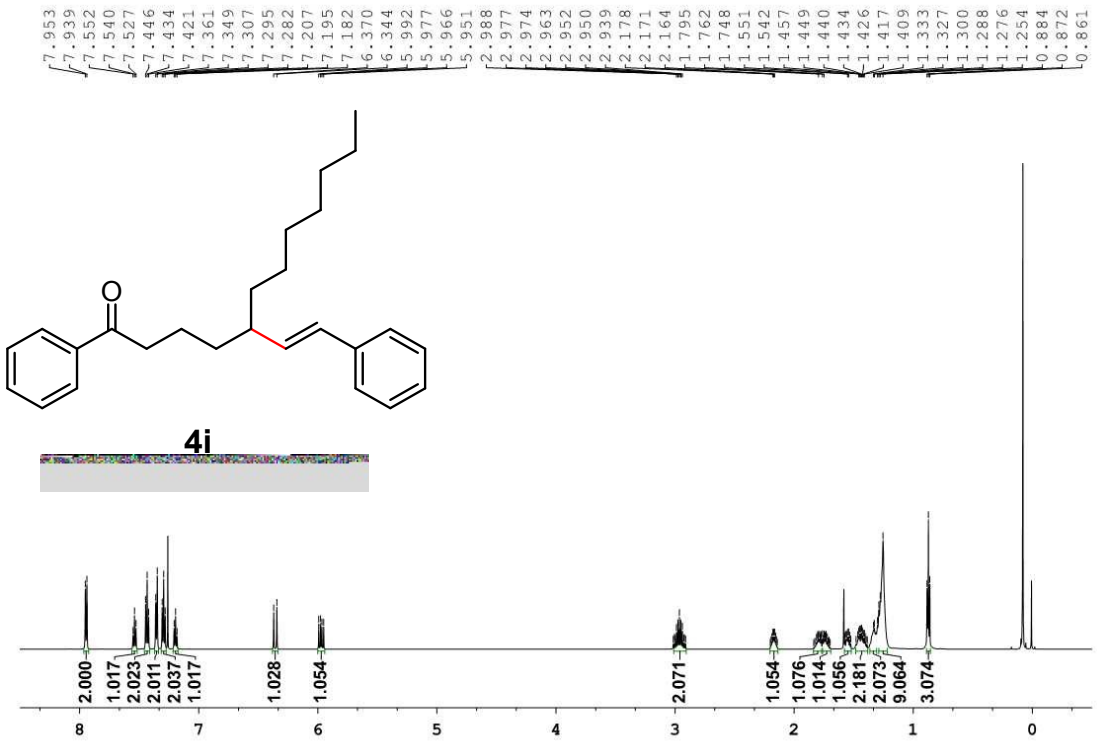
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

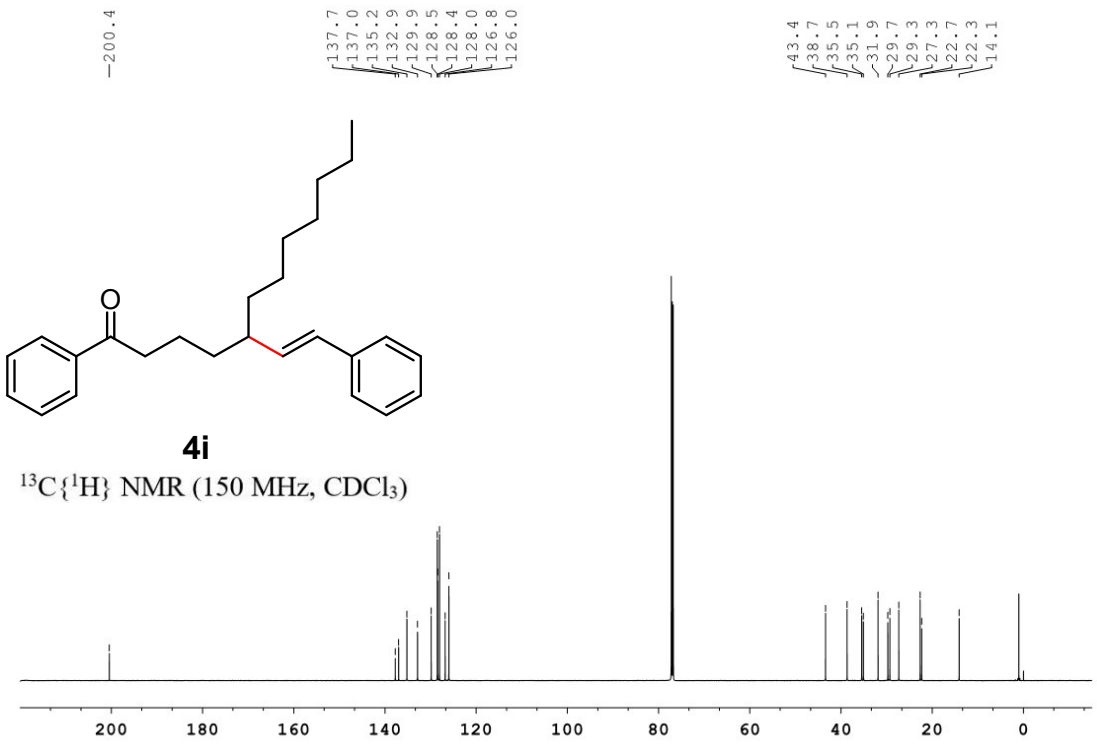



7.340
7.328
7.299
7.287
7.274
7.201
7.189
7.177
6.394
6.368
6.227
6.216
6.204
6.201
6.190
2.436
2.424
2.411
2.400
2.388
2.375
2.241
2.239
2.228
2.216
2.205
1.648
1.636
1.623
1.612
1.596
1.583
1.571
1.558
1.546
1.494
1.481
1.468
1.455
1.333
1.331
1.319
1.307
1.296
1.282
1.268
1.262
1.256
1.248
1.242
0.902
0.890
0.878
O
4g
2.035
2.010
1.004
1.000
1.013
2.064
2.034
2.035
2.279
2.086
2.063
2.045
2.174
3.096
8
7
6
5
4
3
2
1
0
211.4
137.7
130.4
130.1
128.4
126.8
125.9
42.8
42.6
32.8
31.4
28.9
23.5
23.4
22.4
13.9
O
4g
200
180
160
140
120
100
80
60
40
20
0

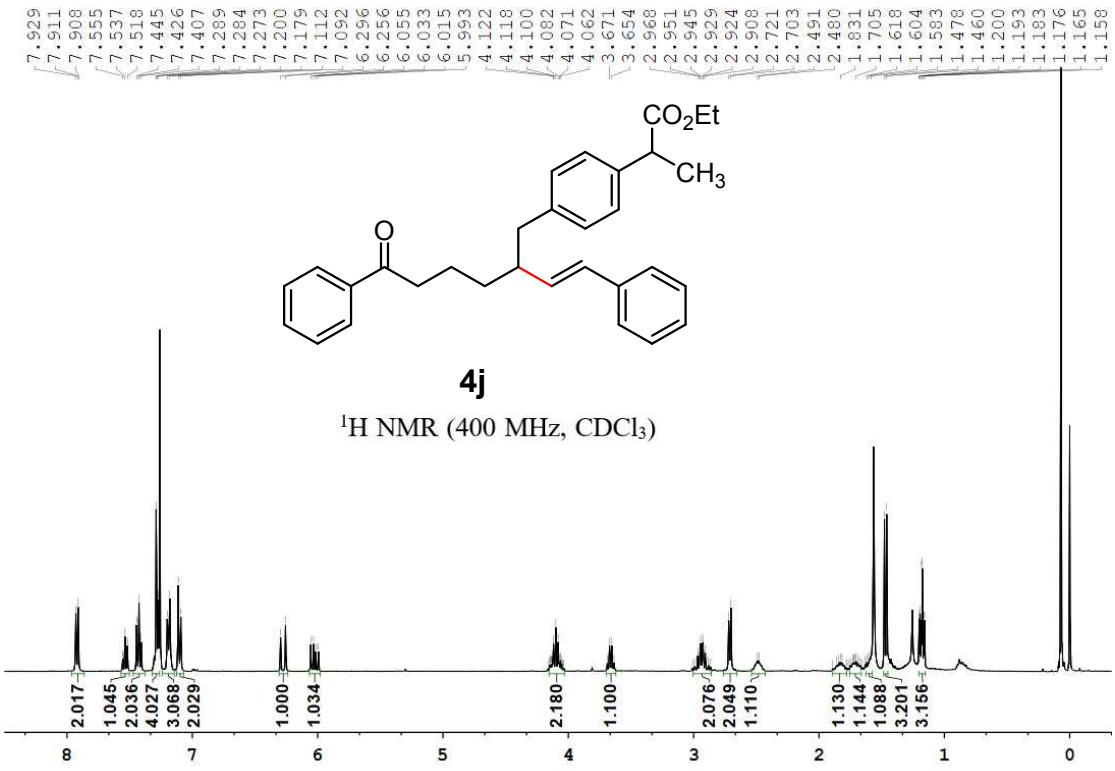

7.965
7.952
7.562
7.550
7.537
7.460
7.447
7.435
7.360
7.348
7.308
7.296
7.283
7.209
7.197
7.185
6.392
6.366
6.130
6.117
6.104
6.090
3.025
3.013
2.998
2.986
2.976
2.964
2.948
2.936
2.386
2.374
2.362
2.351
2.339
1.819
1.806
1.793
1.787
1.781
1.768
1.520
1.508
1.506
1.498
1.493
1.488
1.482
1.480
1.472
1.466
1.121
1.110
O
4h
2.000
1.010
2.014
2.007
2.005
1.013
1.016
1.005
2.092
1.030
2.020
2.051
3.026
8
7
6
5
4
3
2
1
0


200.36
137.72
136.99
136.31
132.87
128.53
128.43
128.40
128.02
126.82
125.97
38.60
37.24
36.62
22.24
20.66
O
4h
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)
200
180
160
140
120
100
80
60
40
20
0



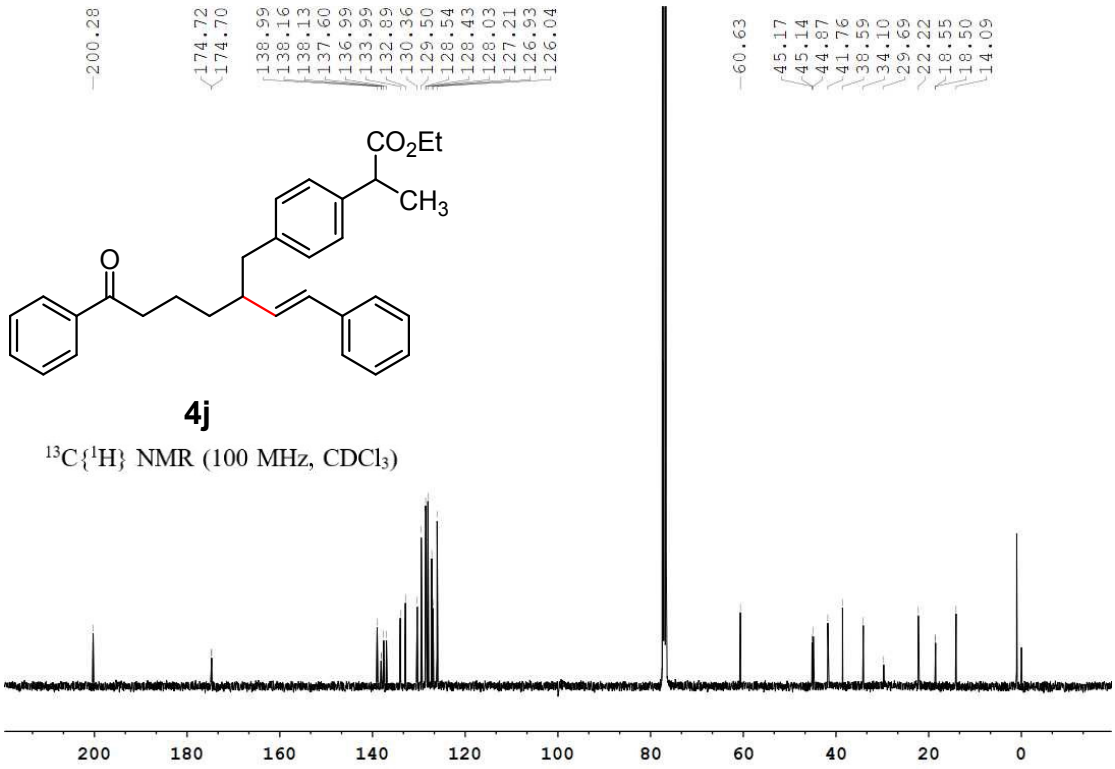


$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)



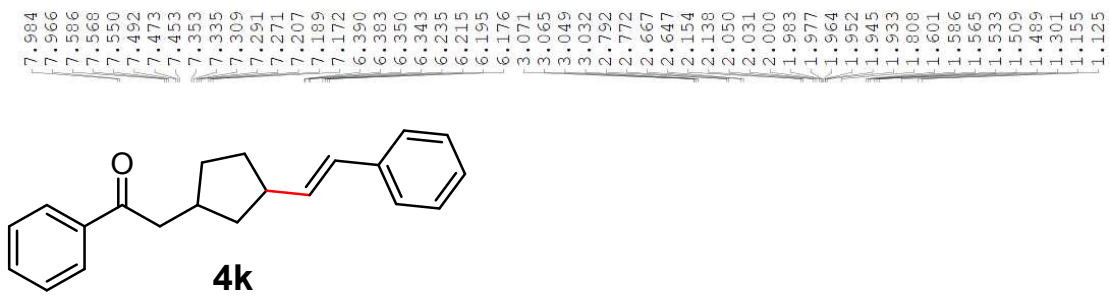
4j

^{1}H NMR (400 MHz, $CDCl_3$)



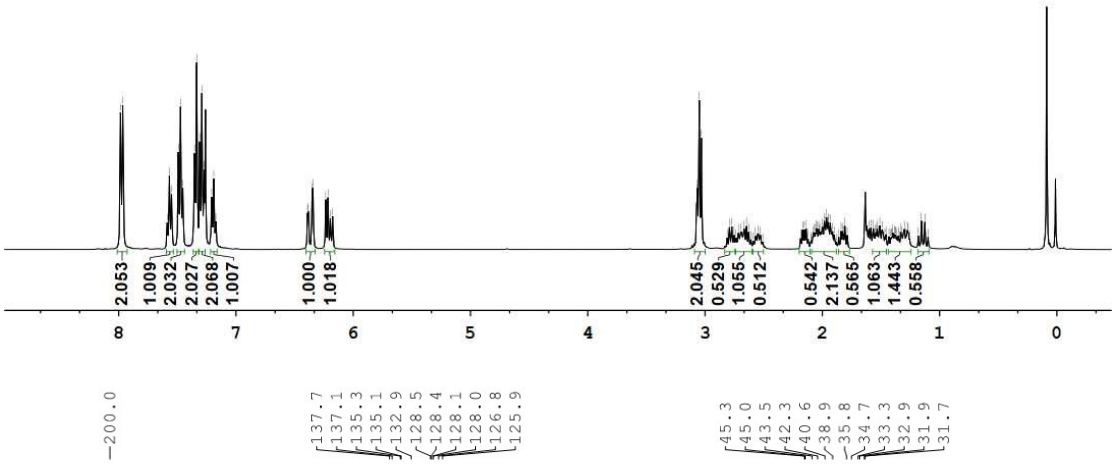
4j

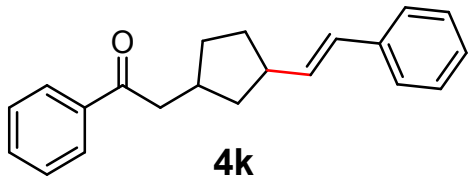
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



4k

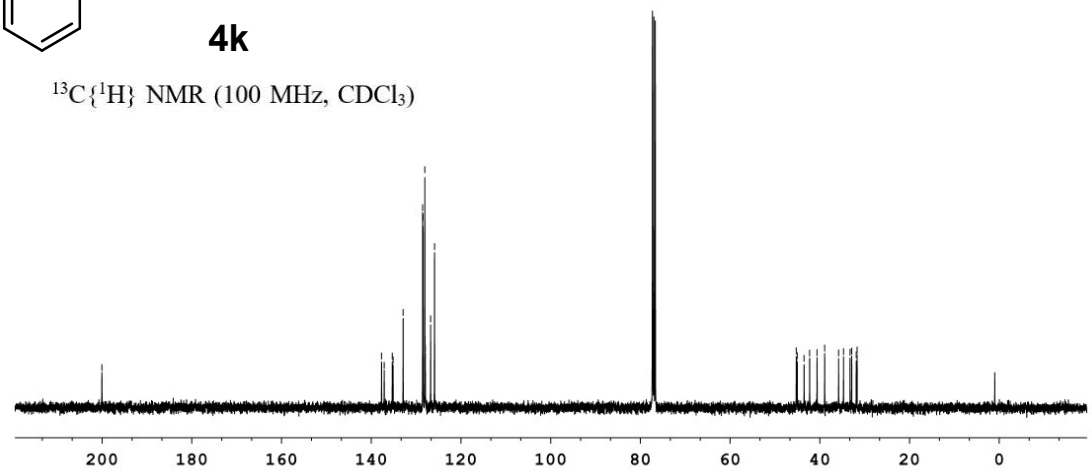
^{1}H NMR (400 MHz, $CDCl_3$)

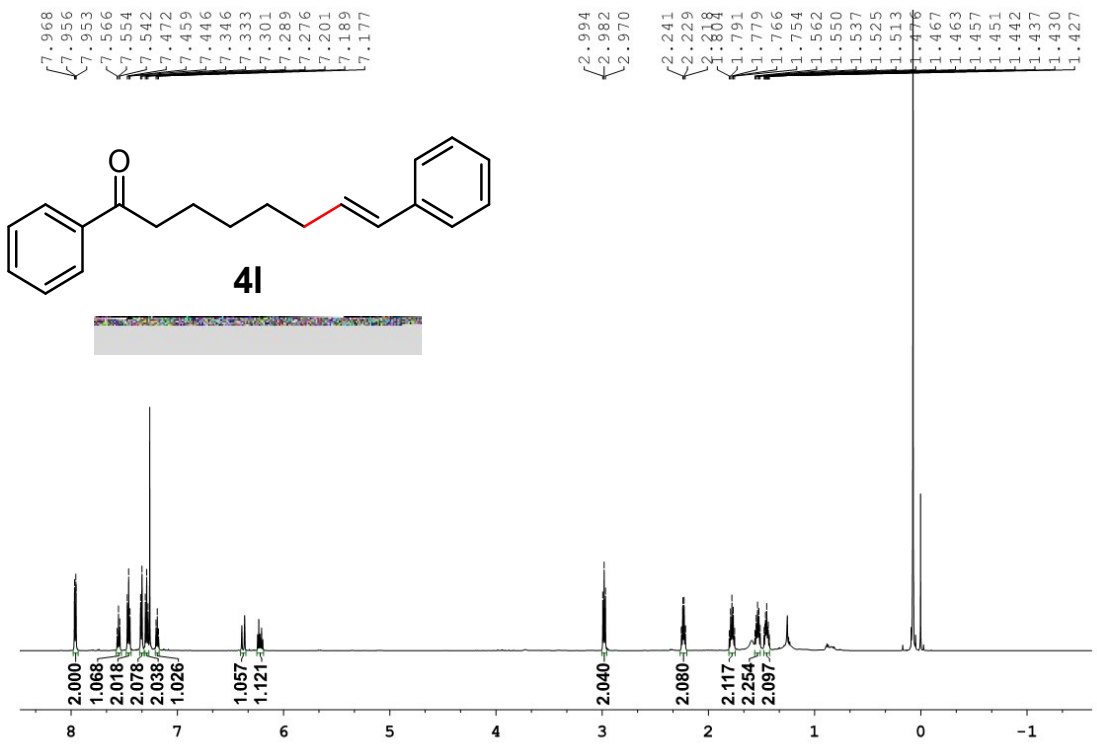


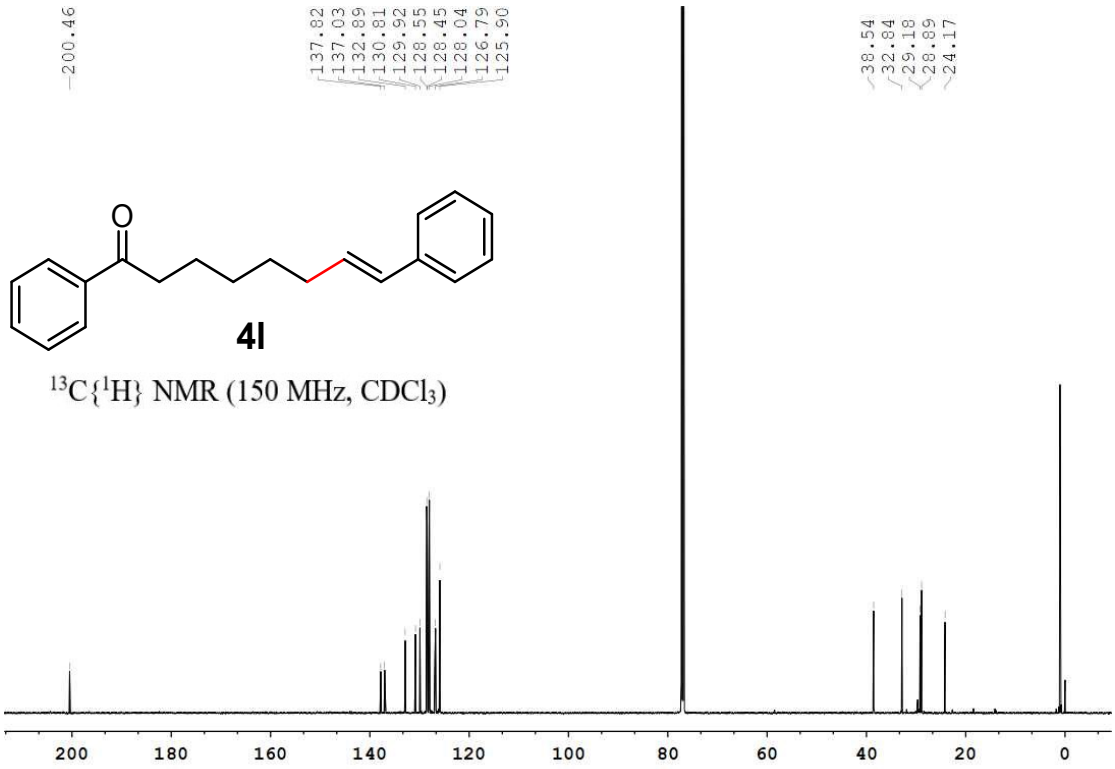


4k

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

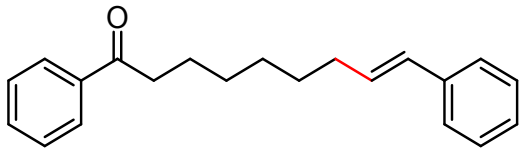




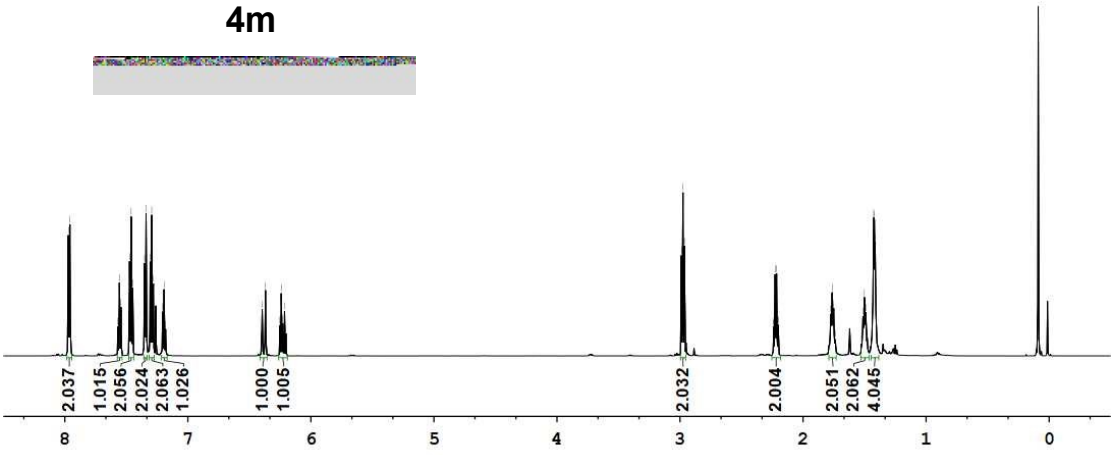


$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)

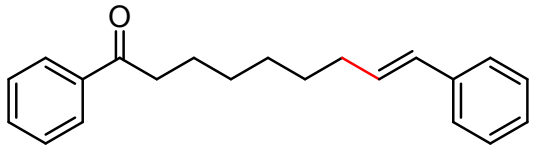

7.971
7.959
7.957
7.474
7.461
7.340
7.306
6.369
6.252
6.241
6.229
6.226
6.214
6.203
2.989
2.976
2.964
2.227
2.215
2.204
1.775
1.763
1.751
1.739
1.525
1.513
1.501
1.490
1.478
1.426
1.420
1.414


O

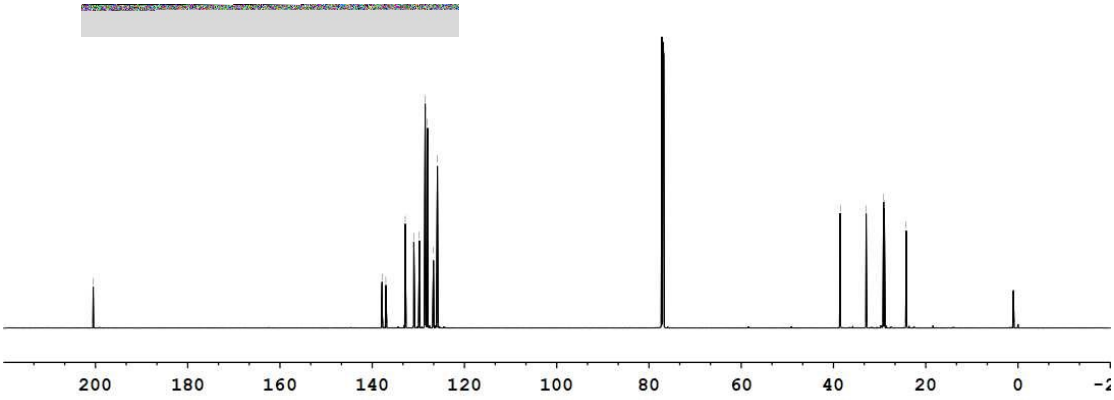
4m

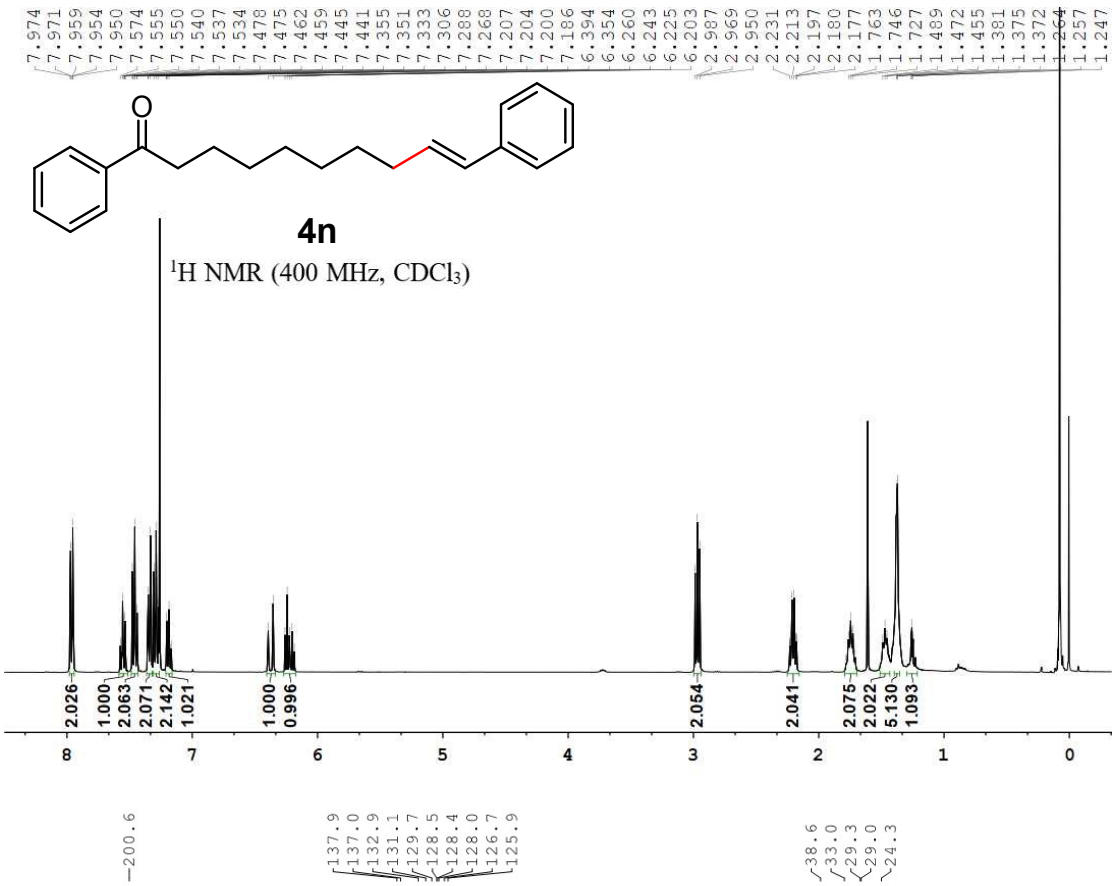

2.037
1.015
2.056
2.024
2.063
1.026
1.000
1.005
2.032
2.004
2.051
2.062
4.045
8
7
6
5
4
3
2
1
0

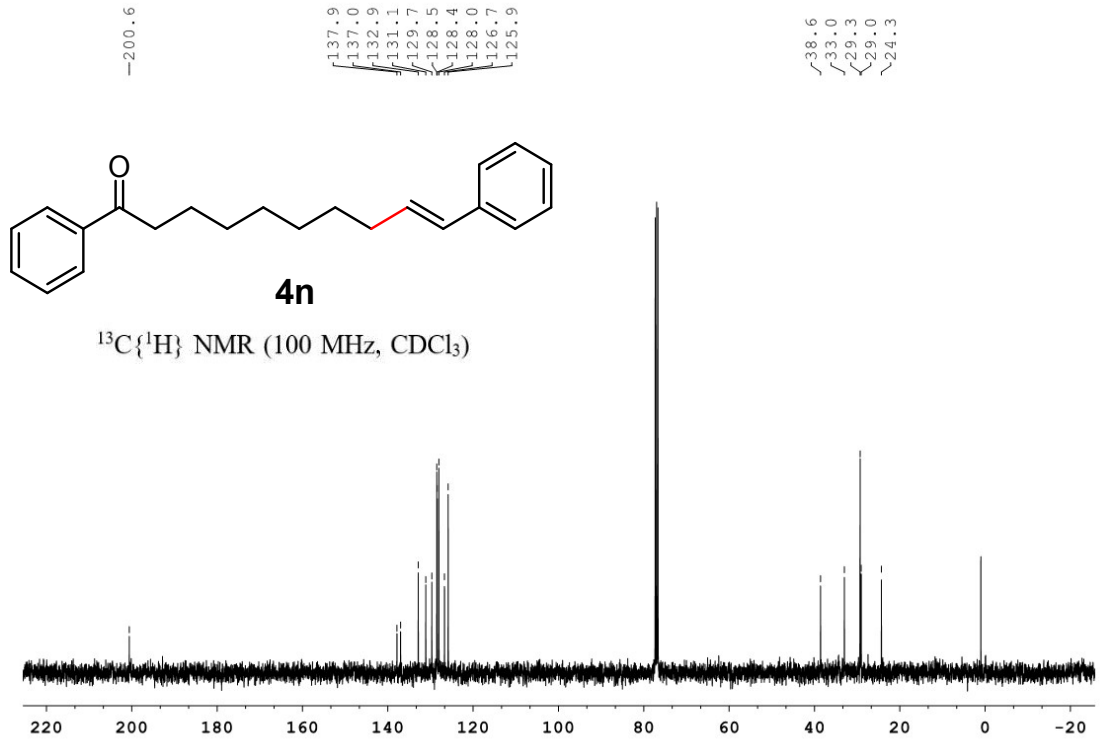

200.49
137.85
137.04
132.84
130.97
129.79
128.52
128.43
128.01
126.73
125.87
38.54
32.92
29.17
29.15
28.98
24.24

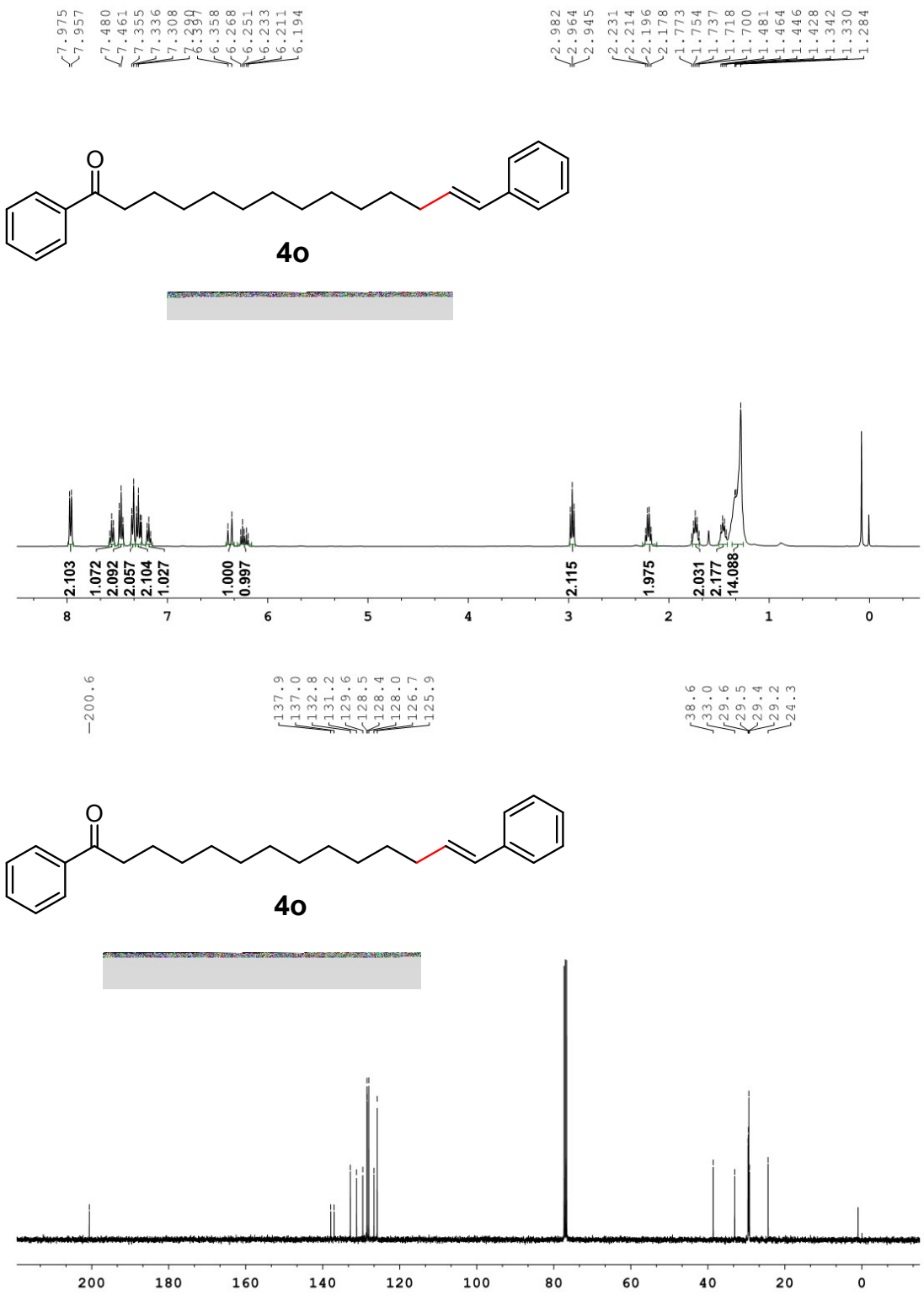

O

4m

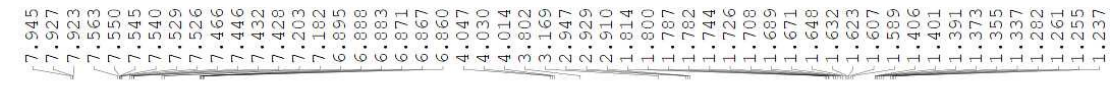

200
180
160
140
120
100
80
60
40
20
0

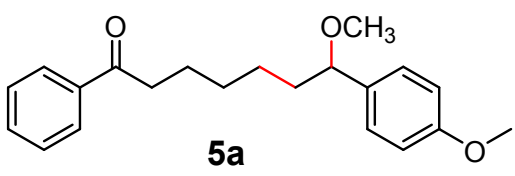

7.974
7.971
7.959
7.954
7.950
7.574
7.555
7.550
7.540
7.537
7.534
7.478
7.475
7.462
7.459
7.445
7.441
7.355
7.351
7.333
7.306
7.288
7.268
7.207
7.204
7.200
7.186
6.394
6.354
6.260
6.243
6.225
6.203
2.987
2.969
2.950
2.231
2.213
2.197
2.180
2.177
1.763
1.746
1.727
1.489
1.472
1.455
1.381
1.375
1.372
1.264
1.257
1.247
O
4n
1H NMR (400 MHz, CDCl3)
2.026
1.000
2.063
2.071
2.142
1.021
1.000
0.996
2.054
2.041
2.075
2.022
5.130
1.093
8
7
6
5
4
3
2
1
0


200.6
137.9
137.0
132.9
131.1
129.7
128.5
128.4
128.0
126.7
125.9
38.6
33.0
29.3
29.0
24.3
O
4n
13C{1H} NMR (100 MHz, CDCl3)
220
200
180
160
140
120
100
80
60
40
20
0
-20


7.975
7.957
7.480
7.461
7.355
7.336
7.308
6.358
6.268
6.251
6.233
6.211
6.194
2.982
2.964
2.945
2.231
2.214
2.196
2.178
1.773
1.754
1.737
1.718
1.700
1.481
1.464
1.446
1.428
1.342
1.330
1.284
O
4o
2.103
1.072
2.092
2.057
2.104
1.027
1.000
0.997
2.115
1.975
2.031
2.177
14.088
8
7
6
5
4
3
2
1
0
200.6
137.9
137.0
132.8
131.2
129.6
128.5
128.4
128.0
126.7
125.9
38.6
33.0
29.6
29.5
29.4
29.2
24.3
O
4o
200
180
160
140
120
100
80
60
40
20
0

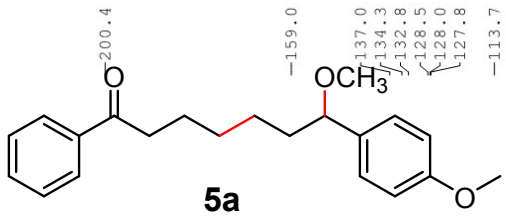
^{1}H NMR and ^{13}C NMR Spectra of the Products 5





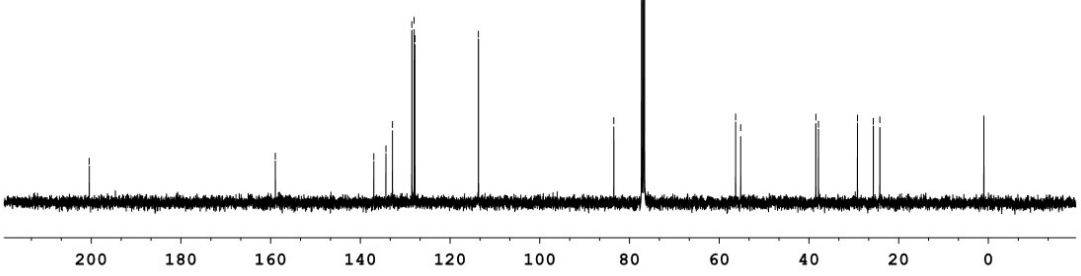
5a

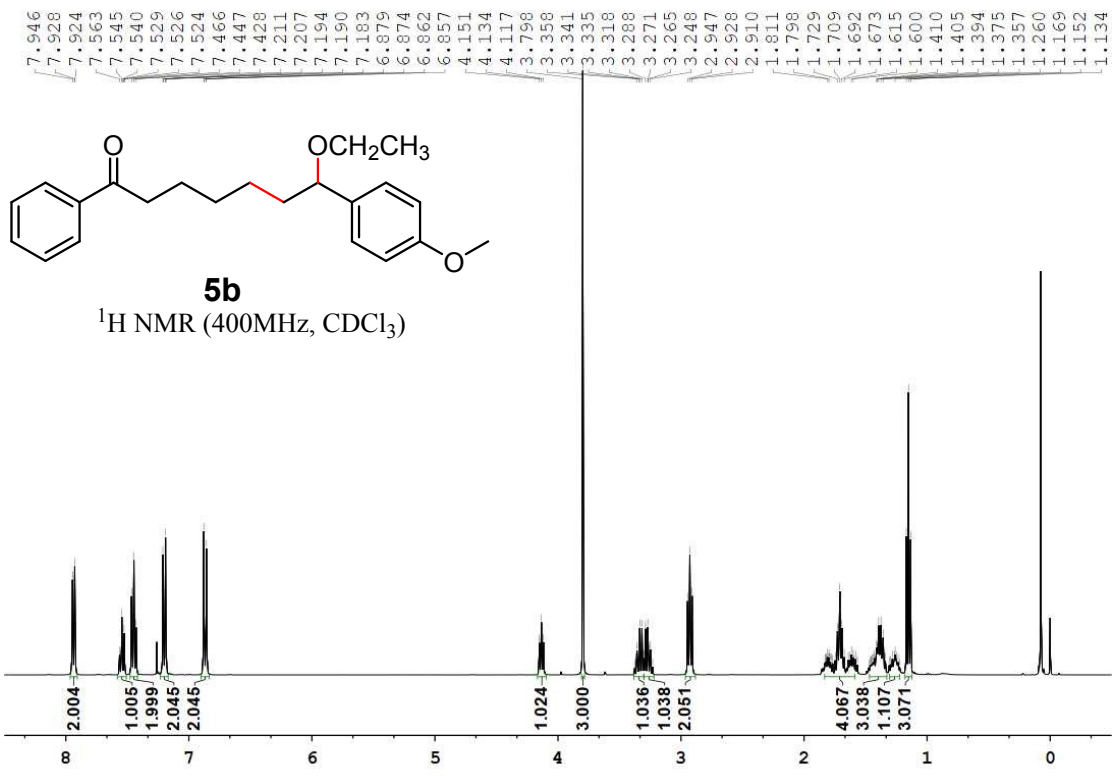
^{1}H NMR (400MHz, $CDCl_3$)



5a

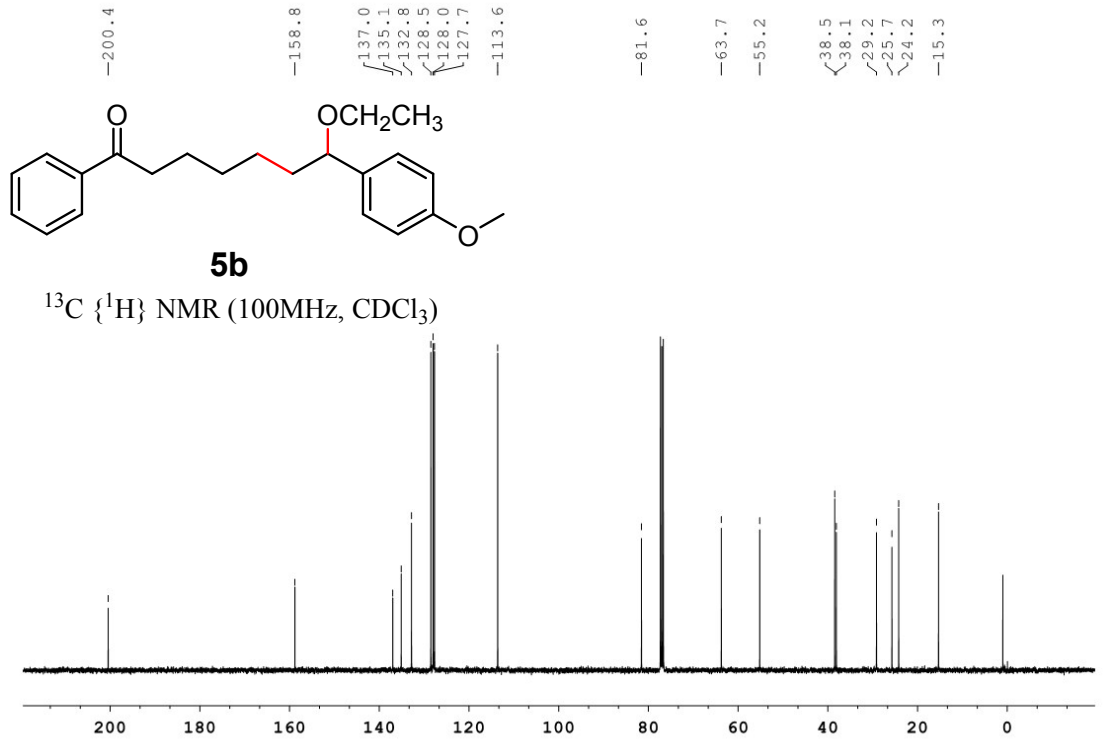
^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)





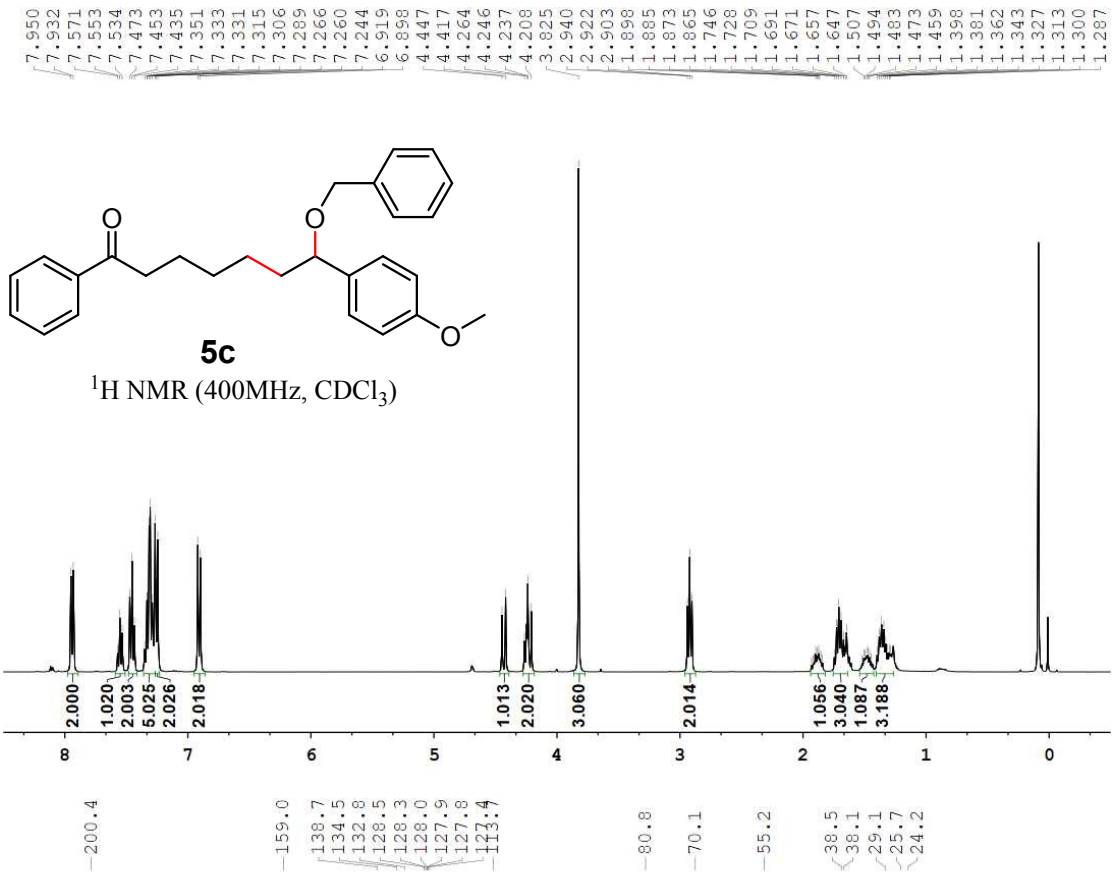
5b

^{1}H NMR (400MHz, $CDCl_3$)

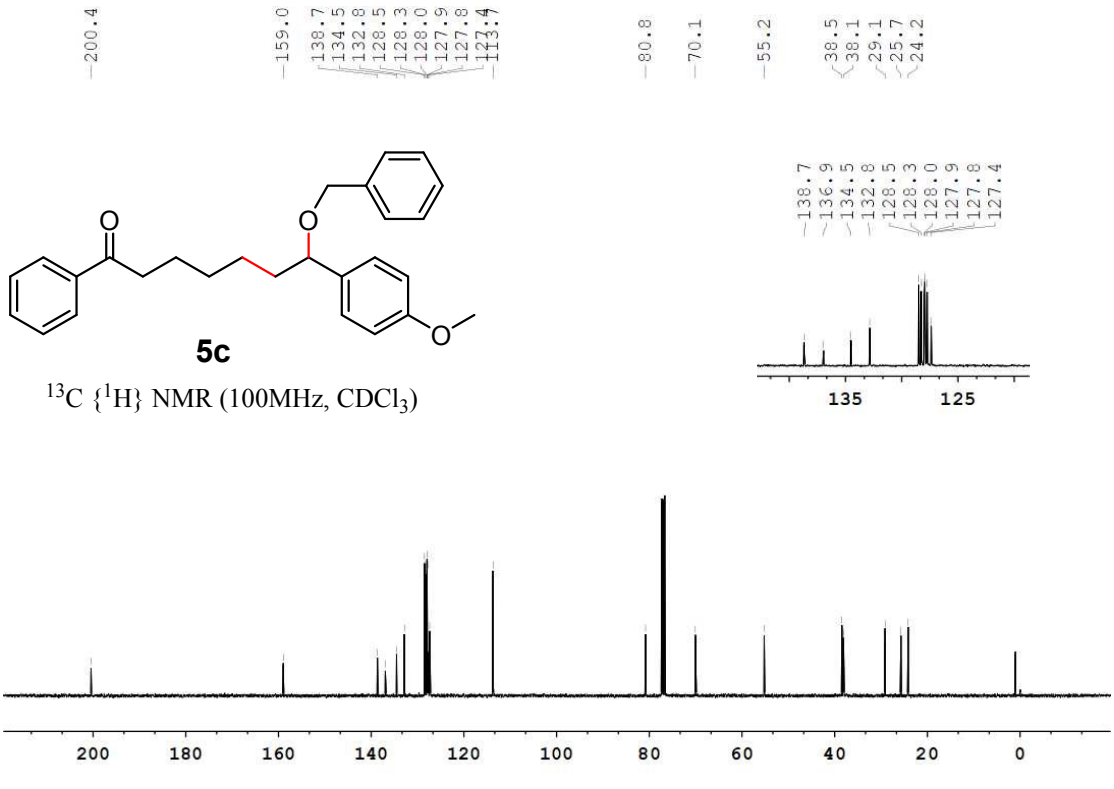


5b

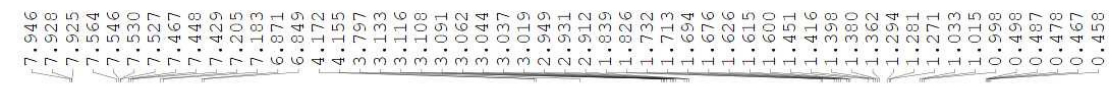
^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)

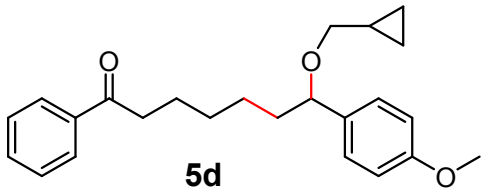


^{1}H NMR (400MHz, $CDCl_3$)



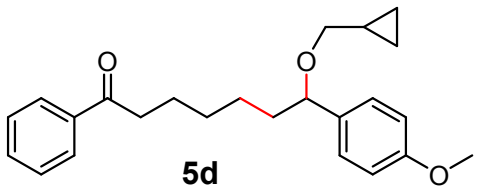
^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)





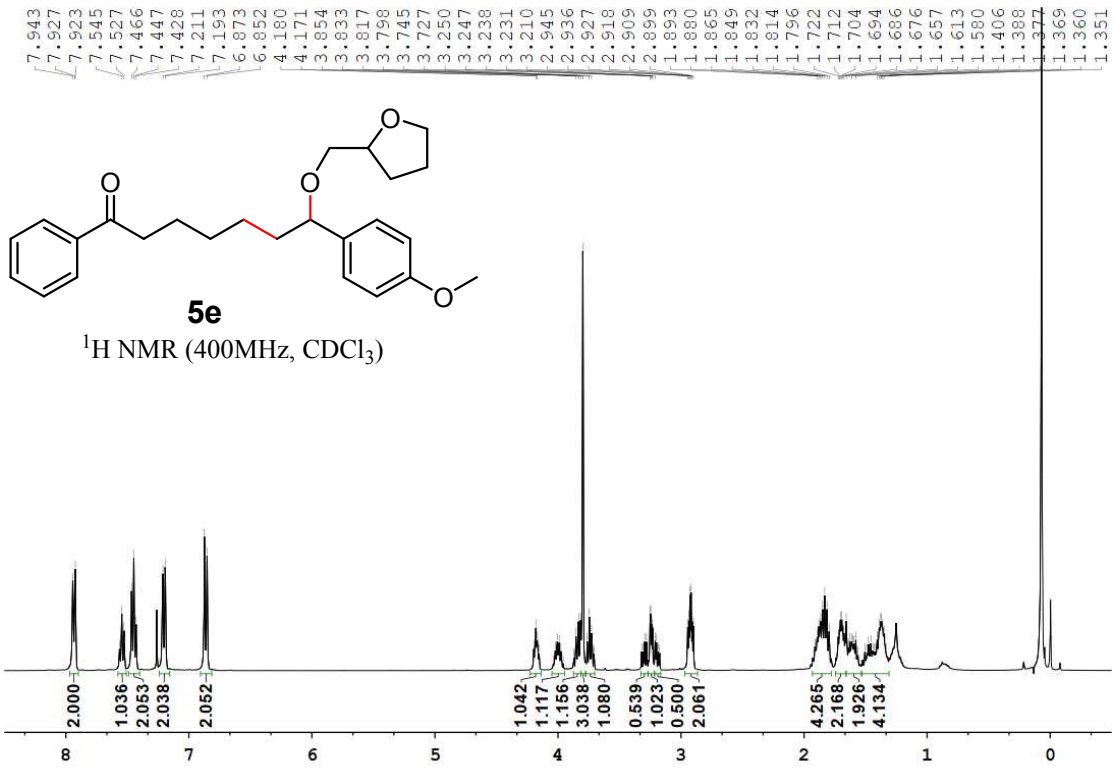
5d

^{1}H NMR (400MHz, $CDCl_3$)



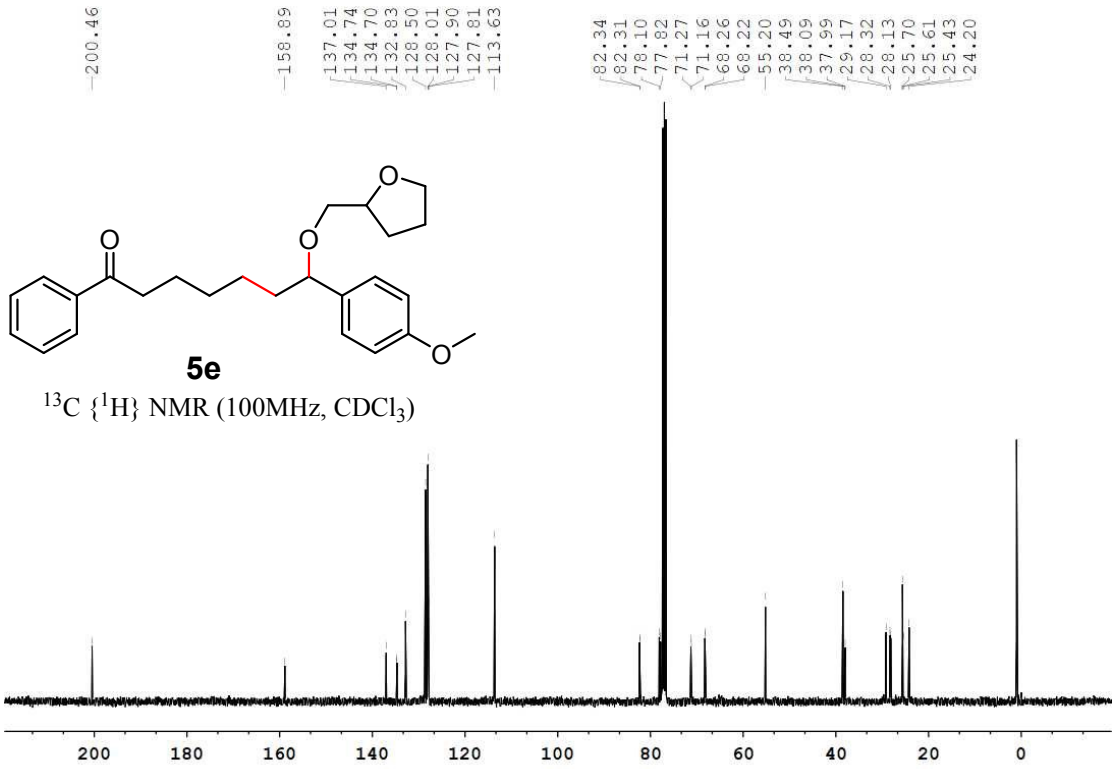
5d

^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)



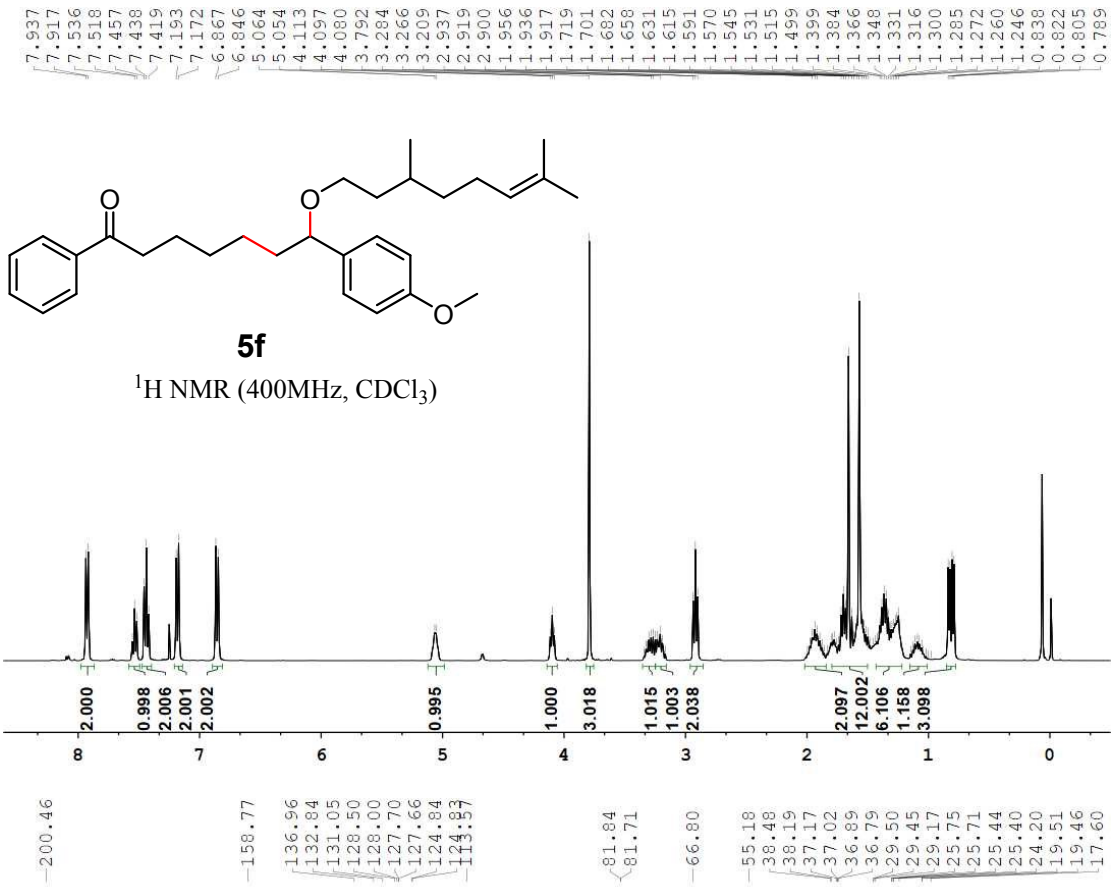
5e

^{1}H NMR (400MHz, $CDCl_3$)

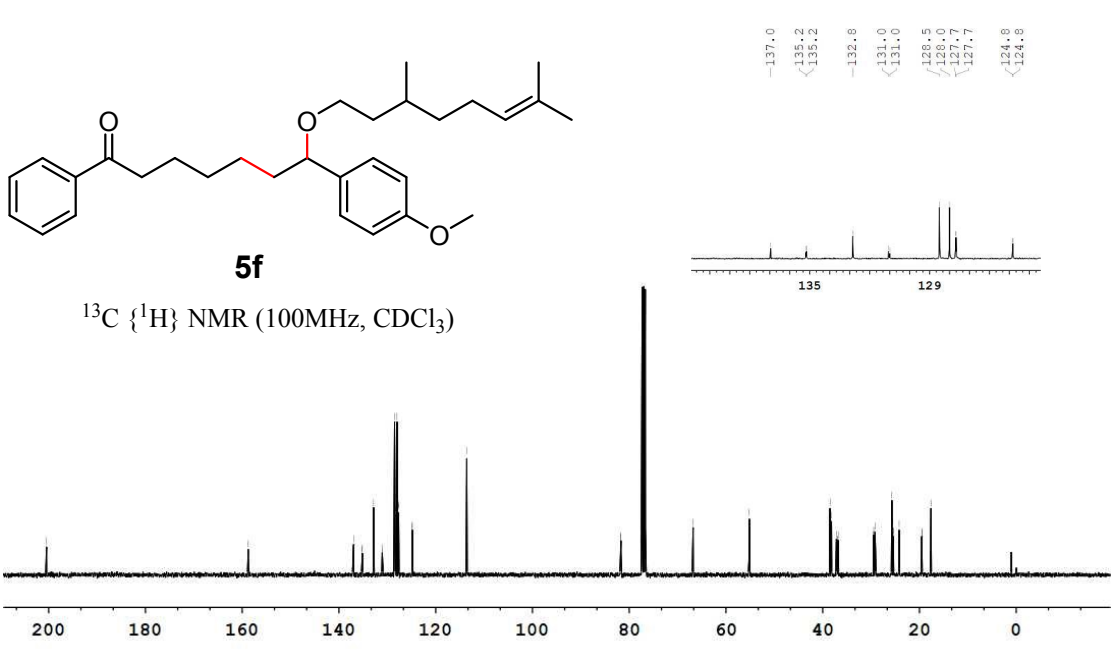


5e

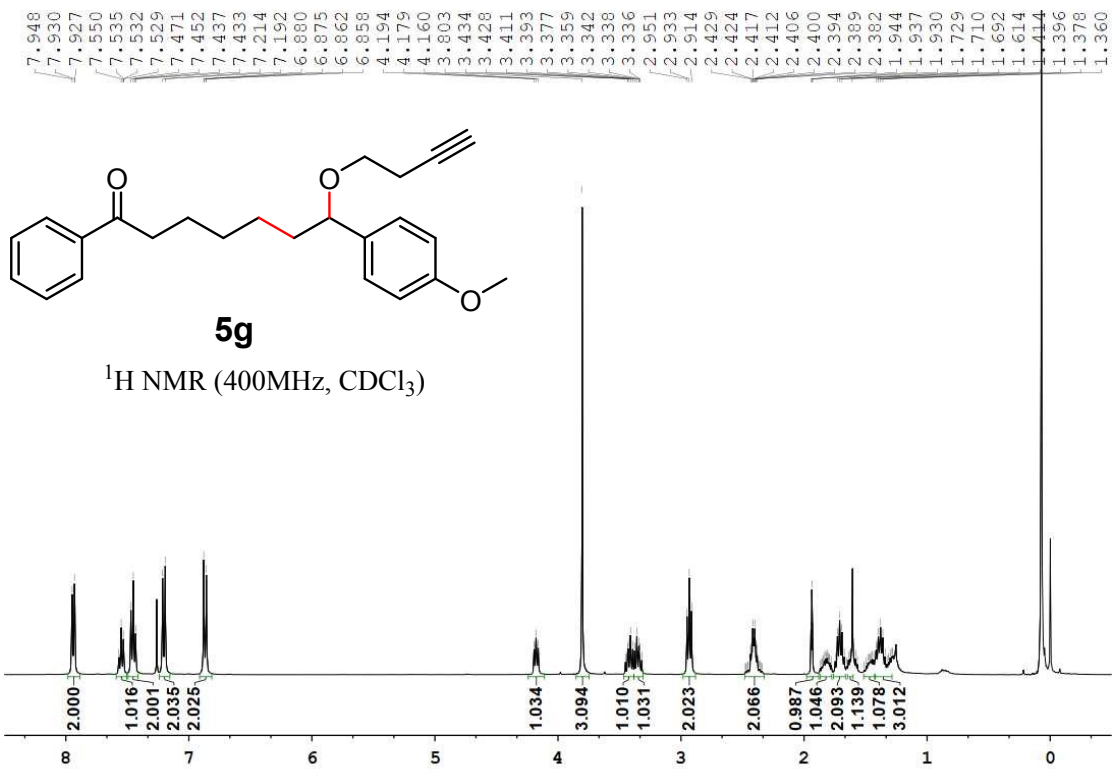
^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)



^{1}H NMR (400MHz, $CDCl_3$)

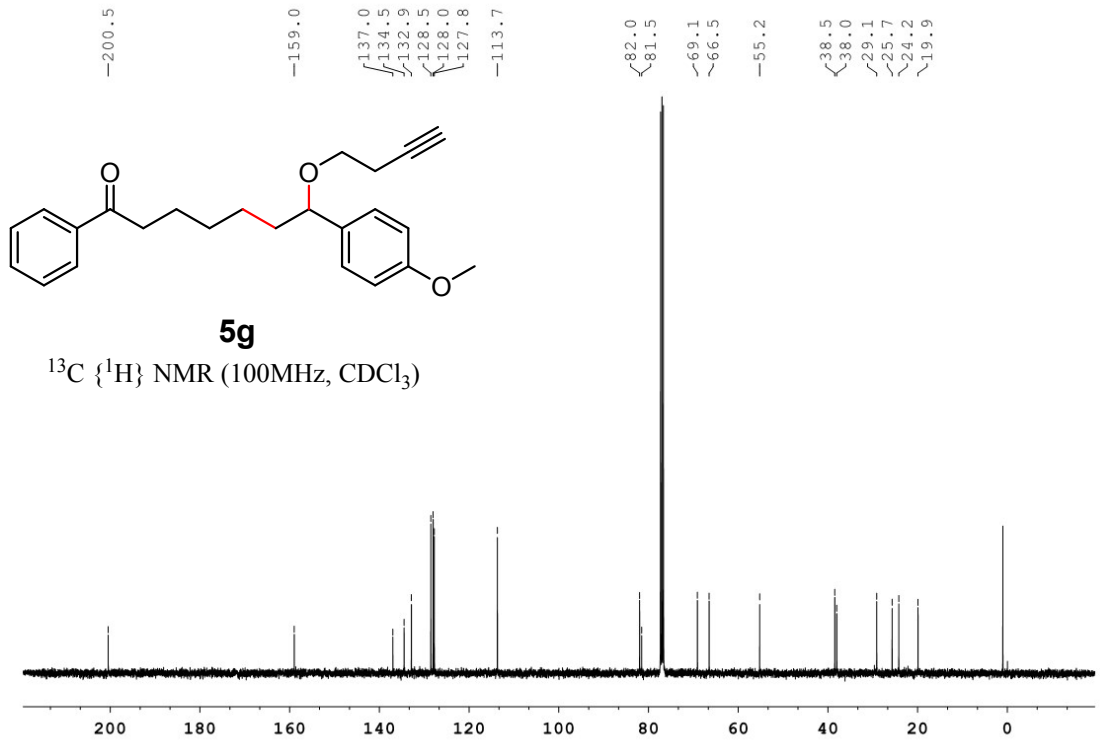


^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)



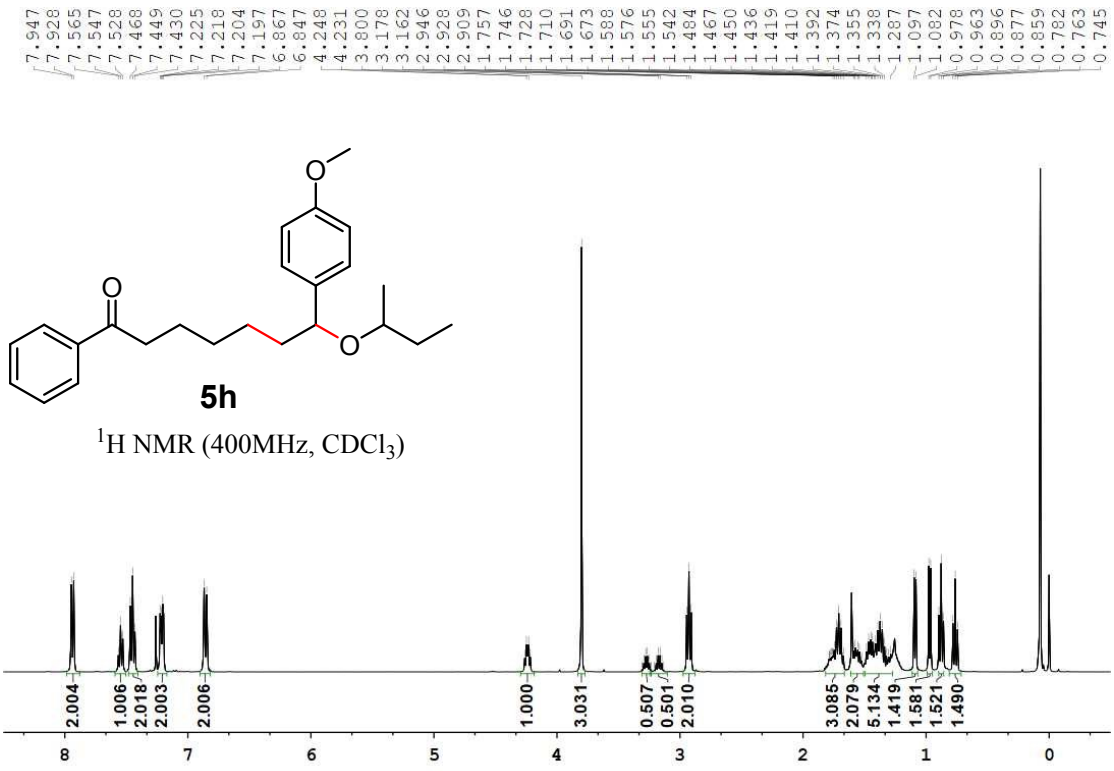
5g

^{1}H NMR (400MHz, $CDCl_3$)

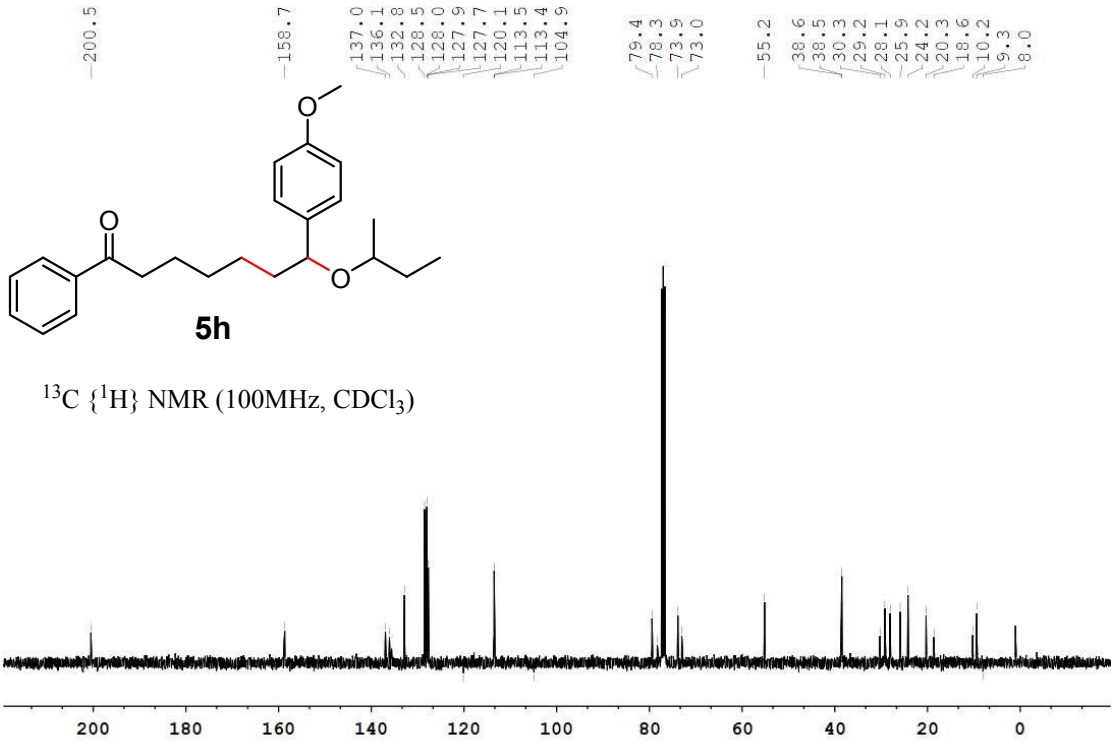


5g

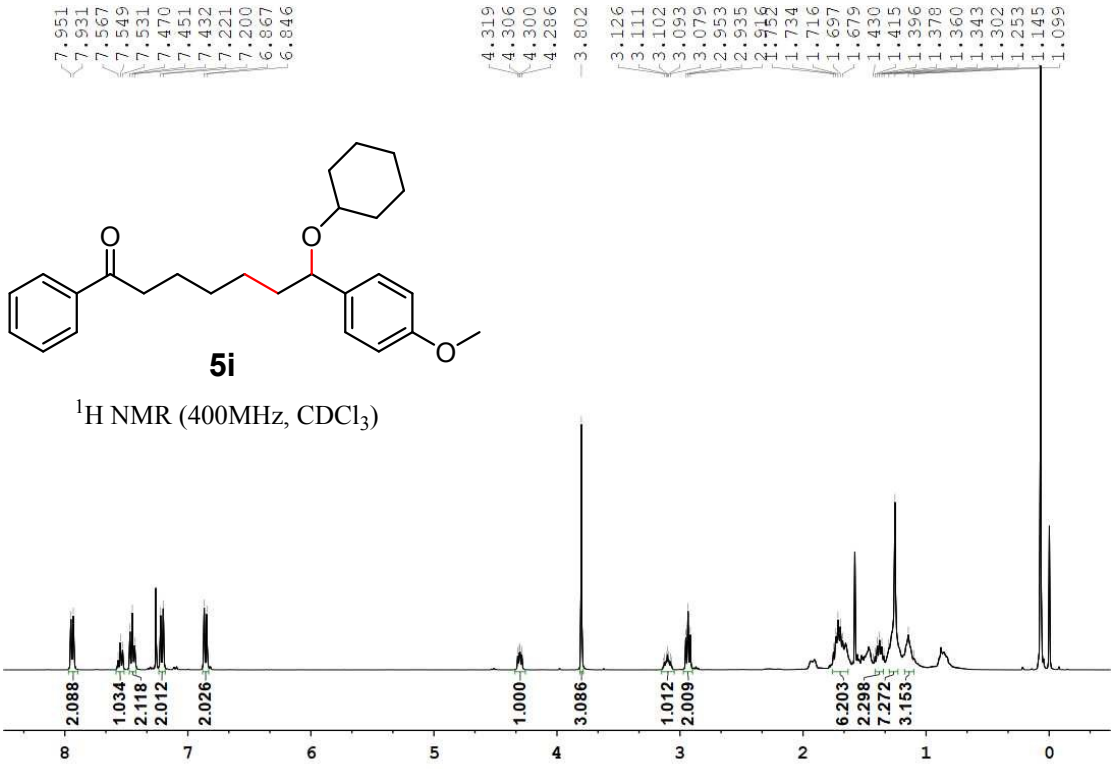
^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)



^{1}H NMR (400MHz, $CDCl_3$)

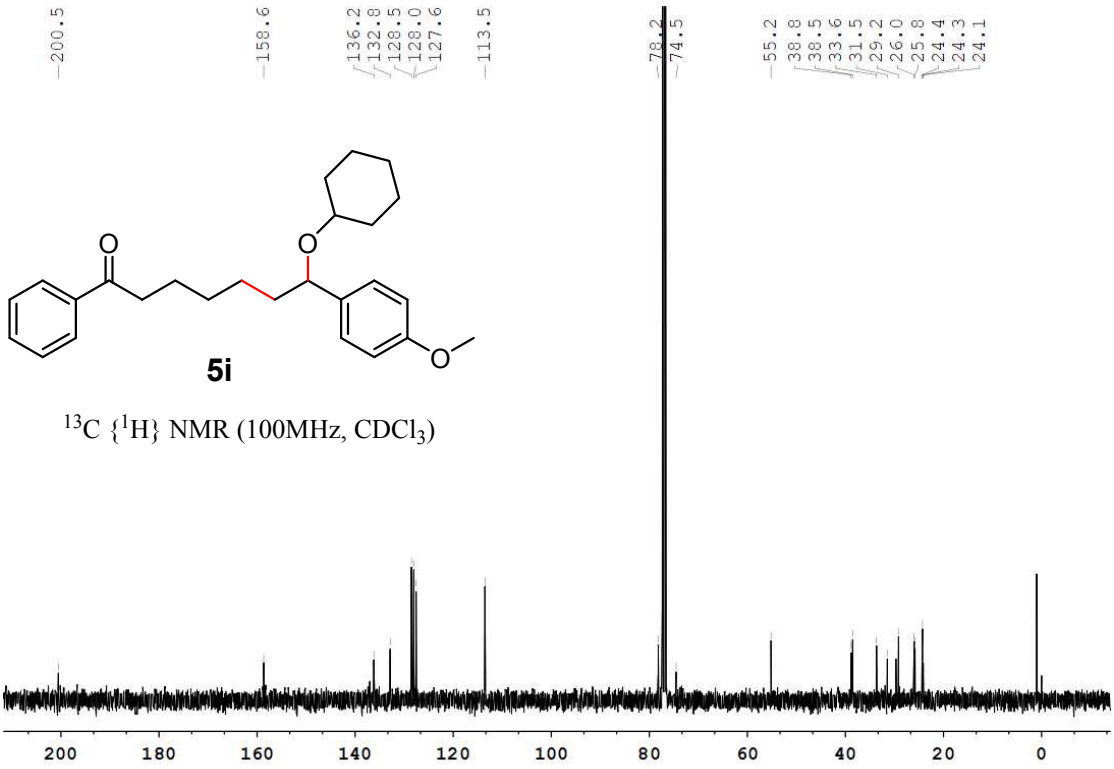


^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)



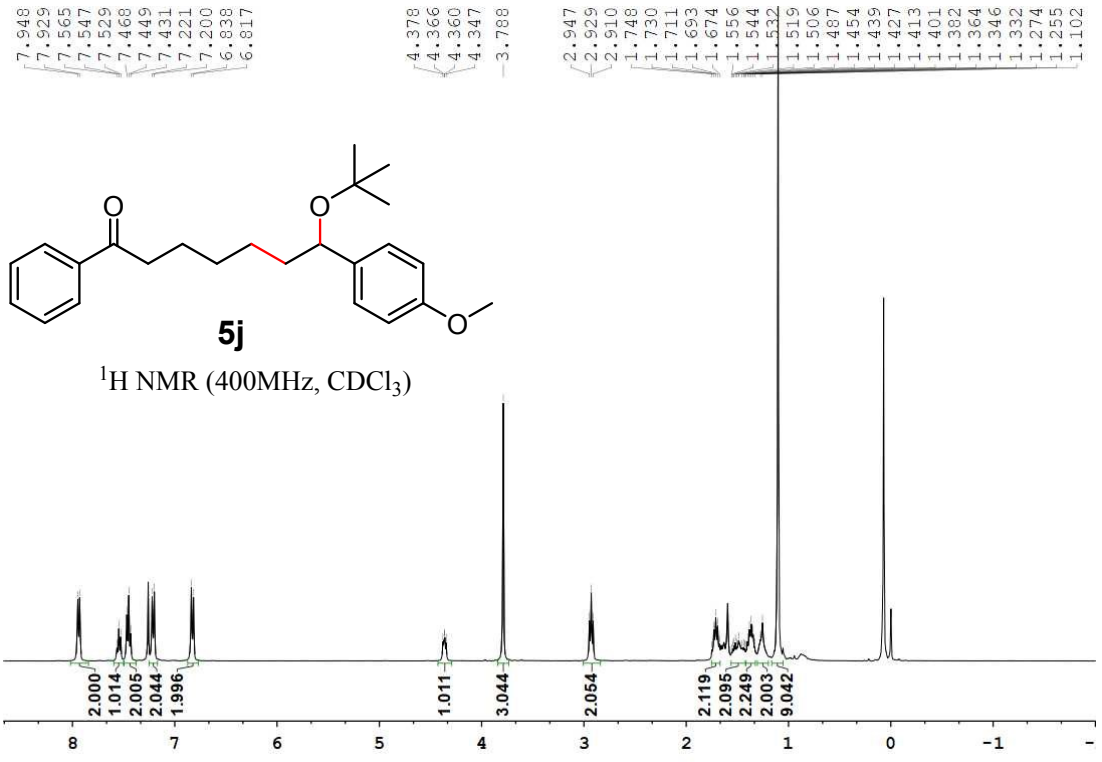
5i

^{1}H NMR (400MHz, $CDCl_3$)



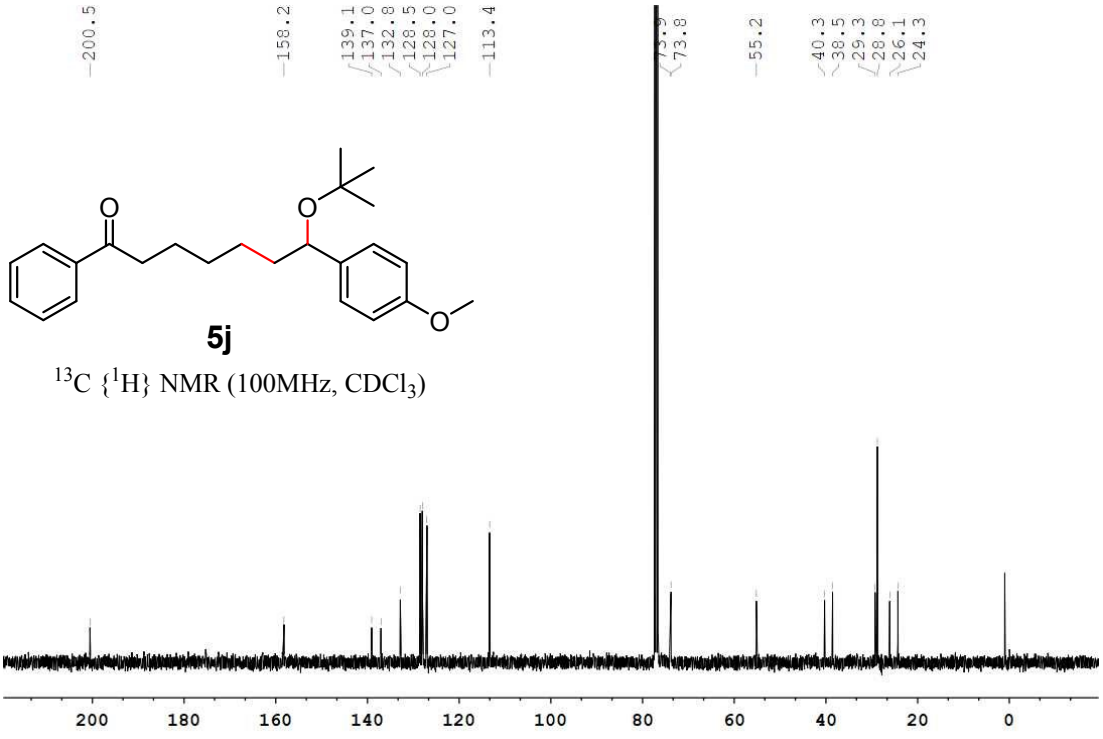
5i

^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)



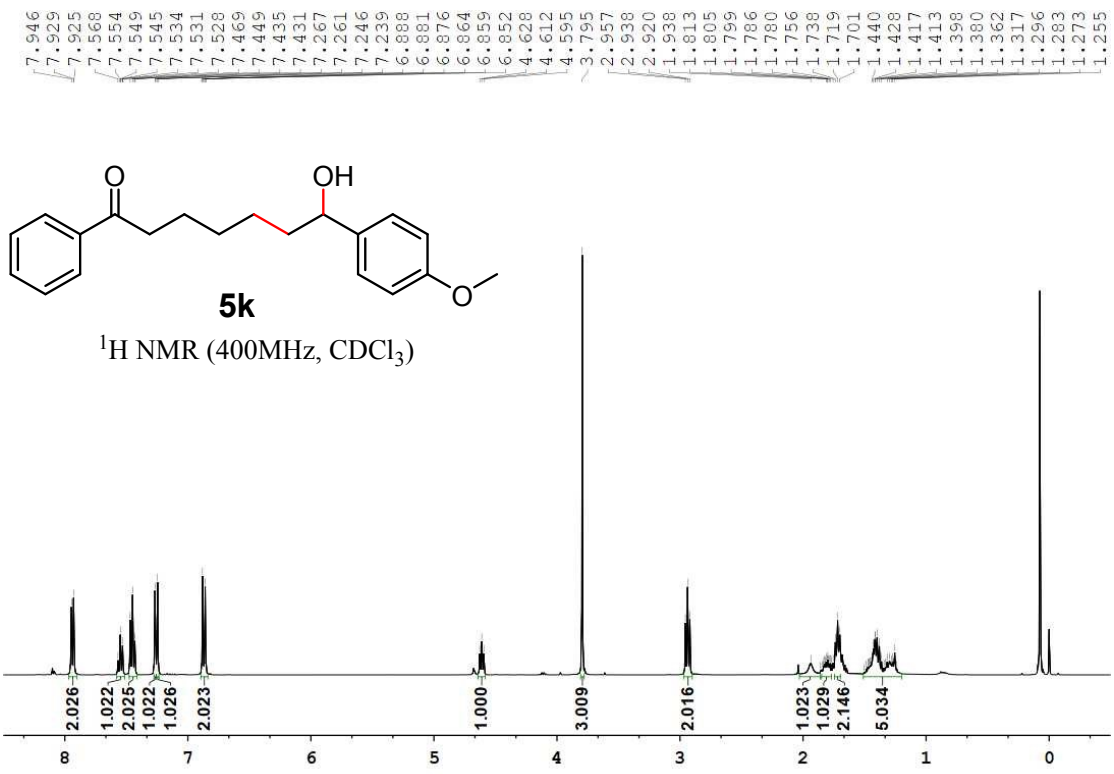
5j

^{1}H NMR (400MHz, $CDCl_3$)

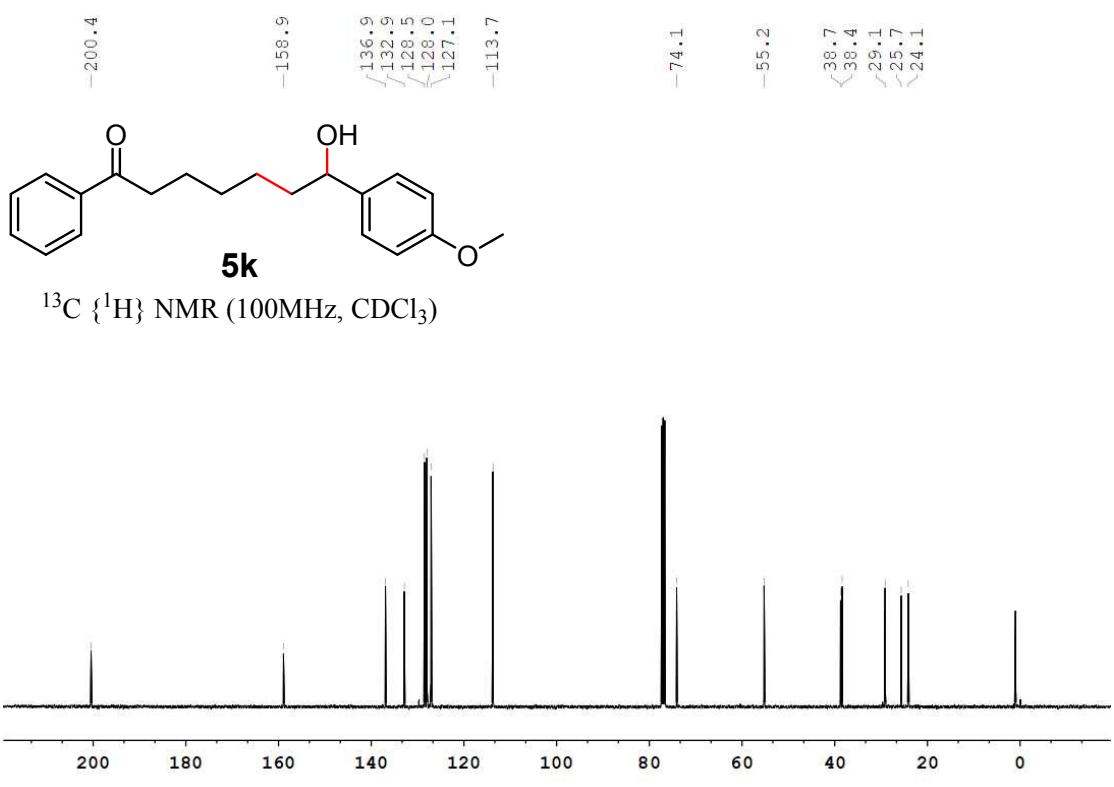


5j

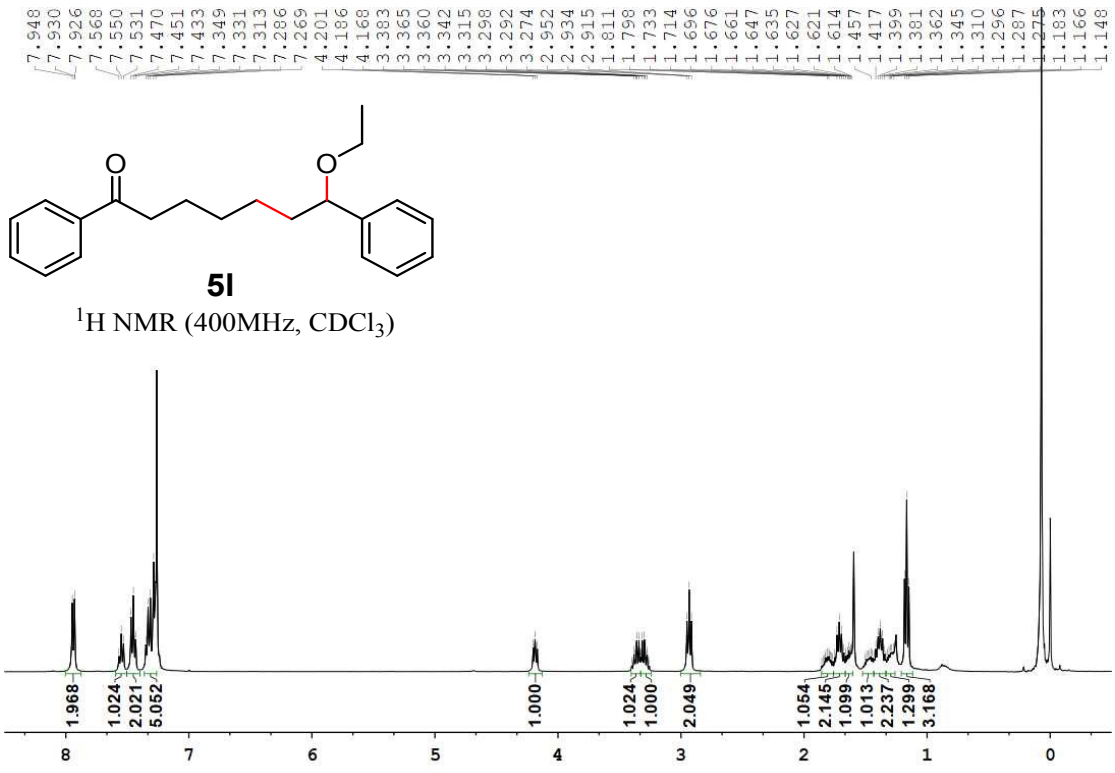
^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)



^{1}H NMR (400MHz, $CDCl_3$)

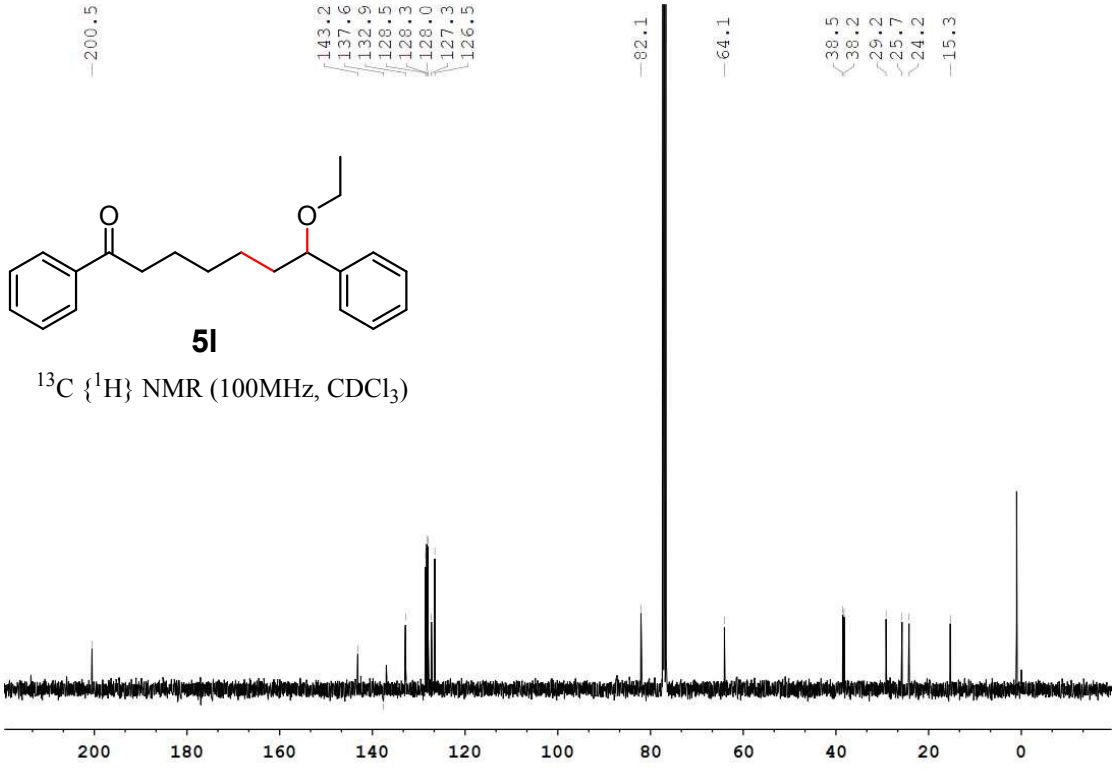


^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)



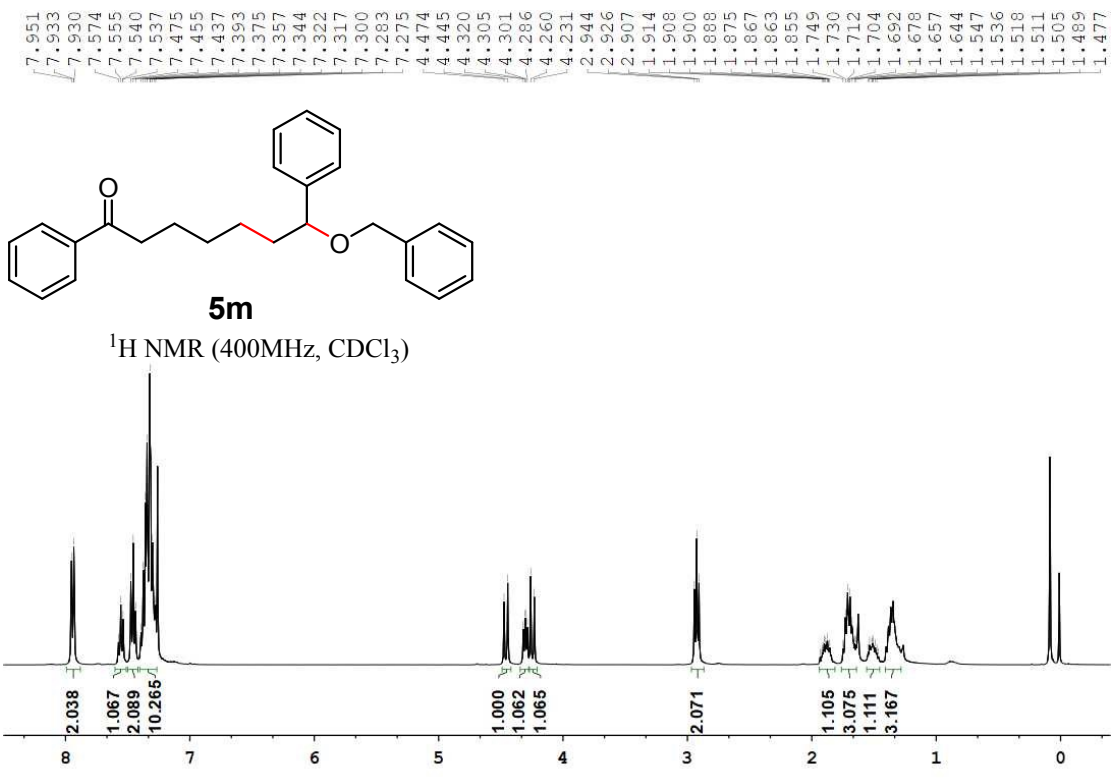
5l

^{1}H NMR (400MHz, $CDCl_3$)

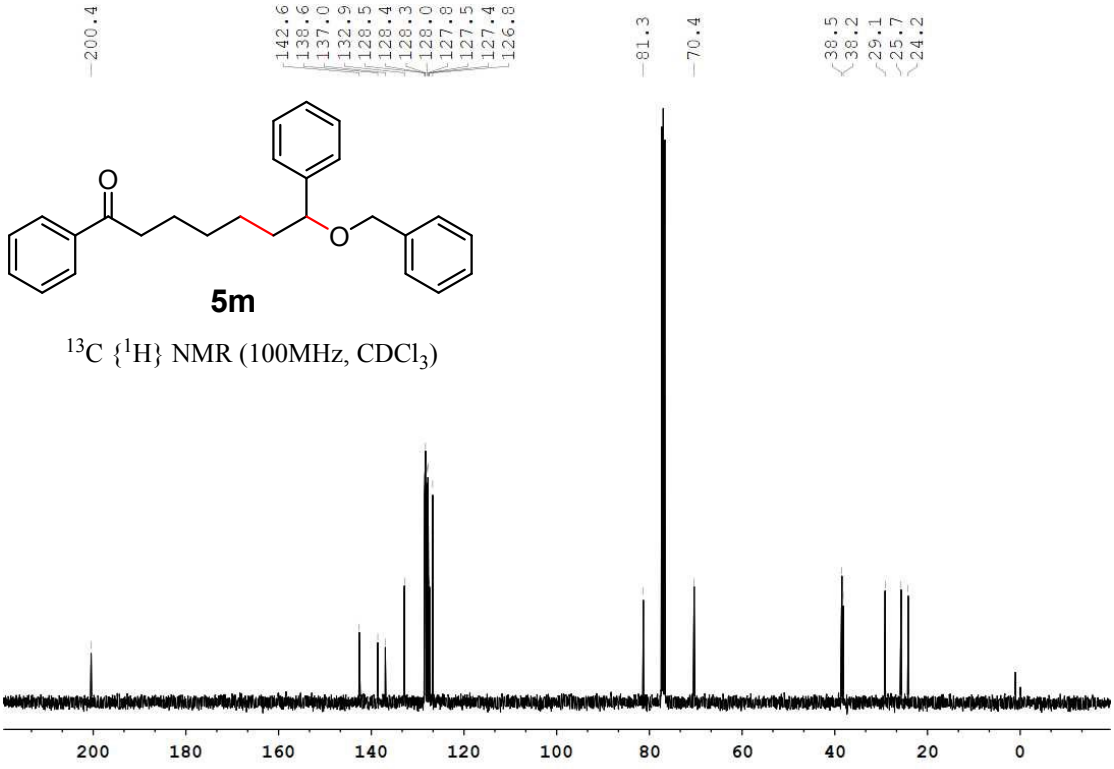


5l

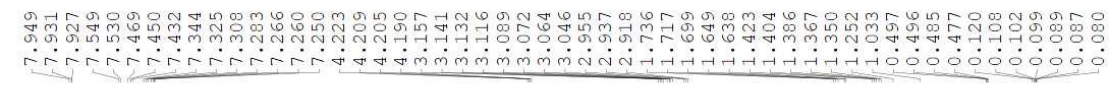
^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)

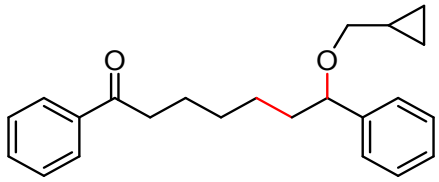


^{1}H NMR (400MHz, $CDCl_3$)



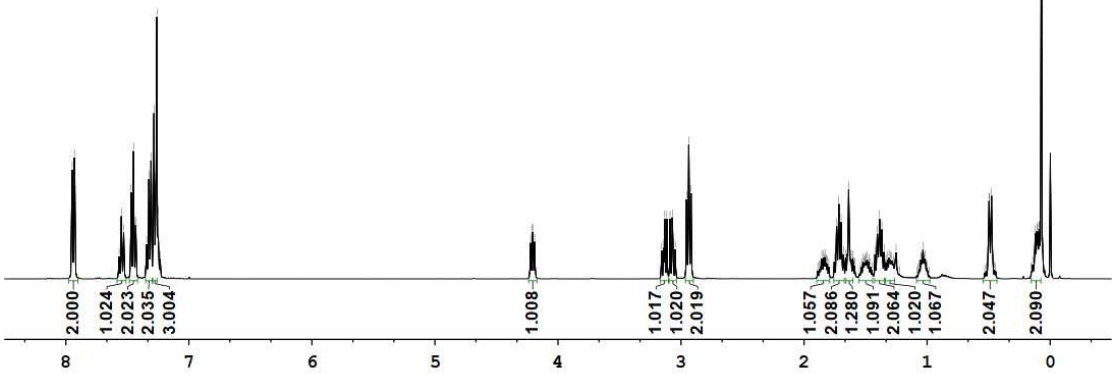
^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)

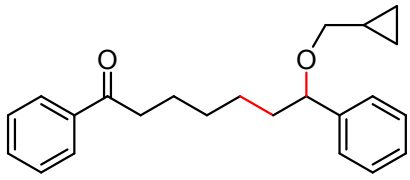




5n

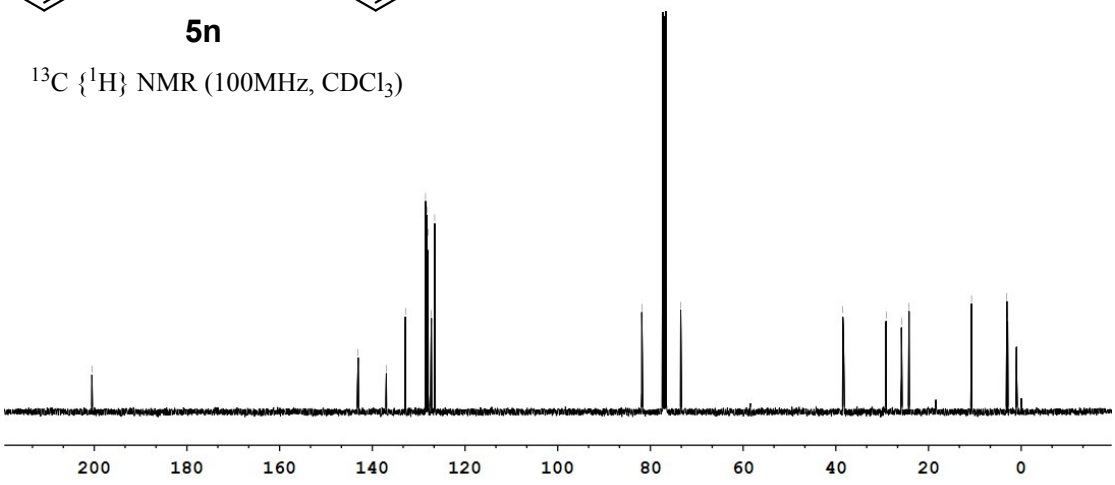
^{1}H NMR (400MHz, $CDCl_3$)

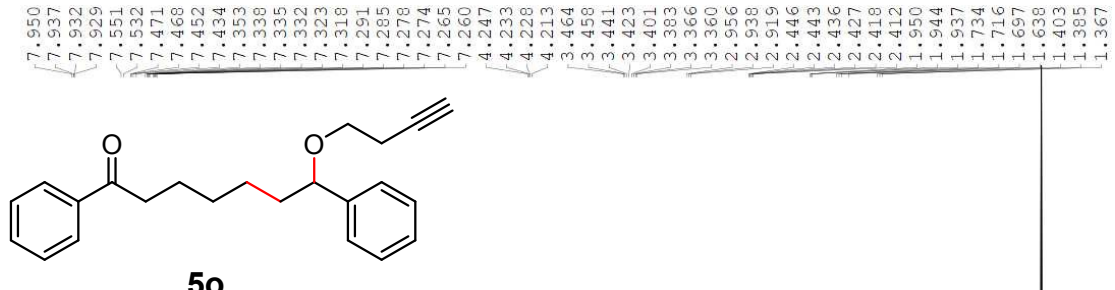




5n

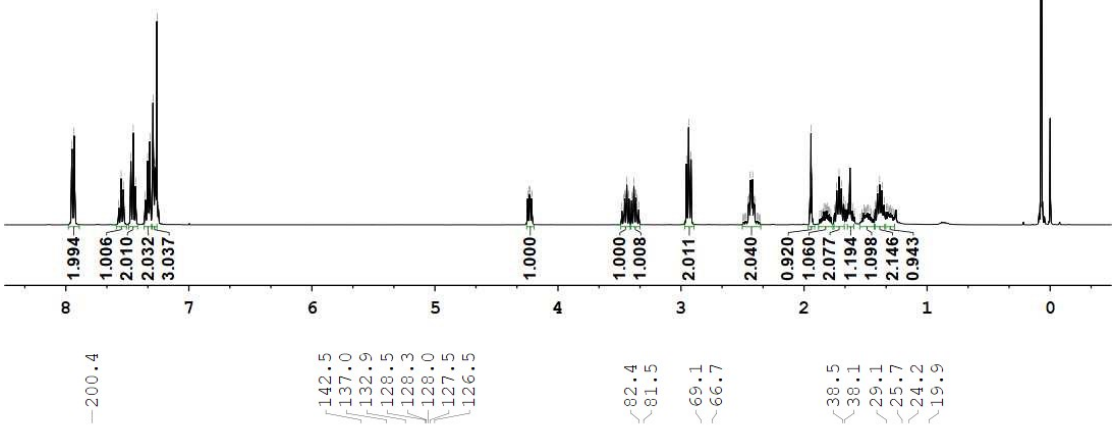
^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)

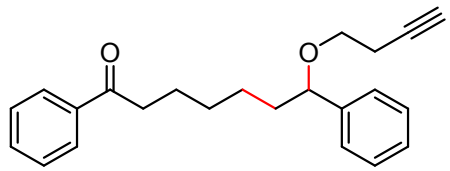




5o

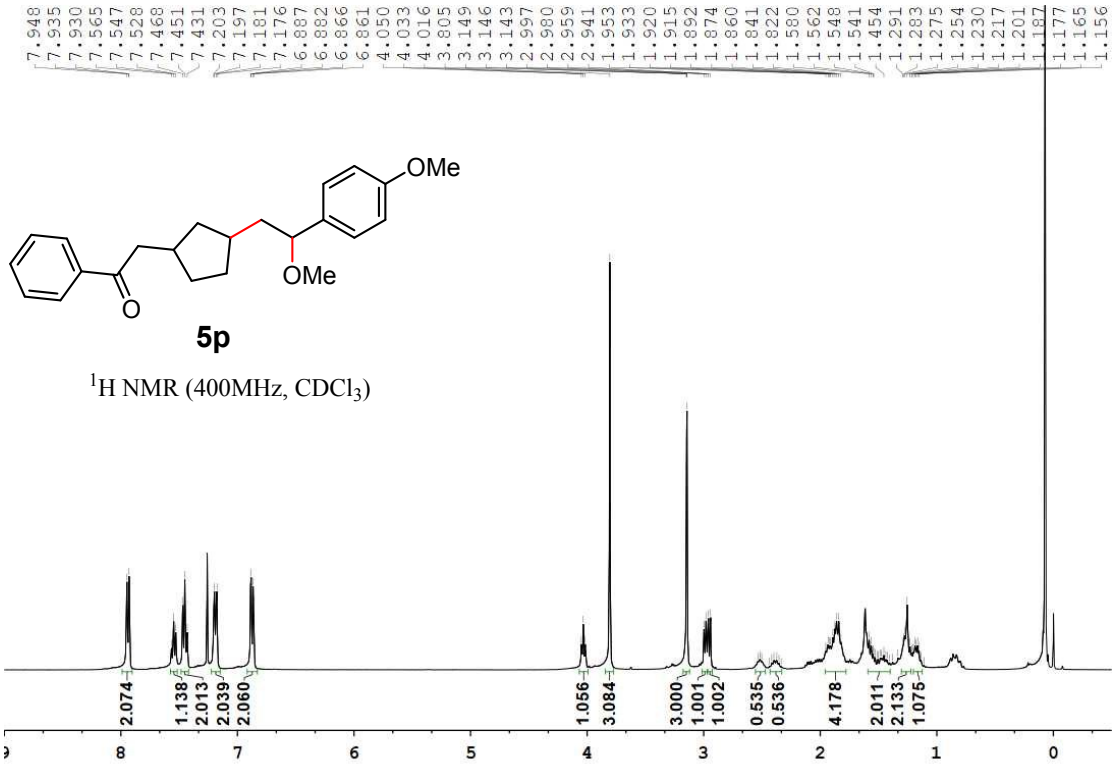
^{1}H NMR (400MHz, $CDCl_3$)





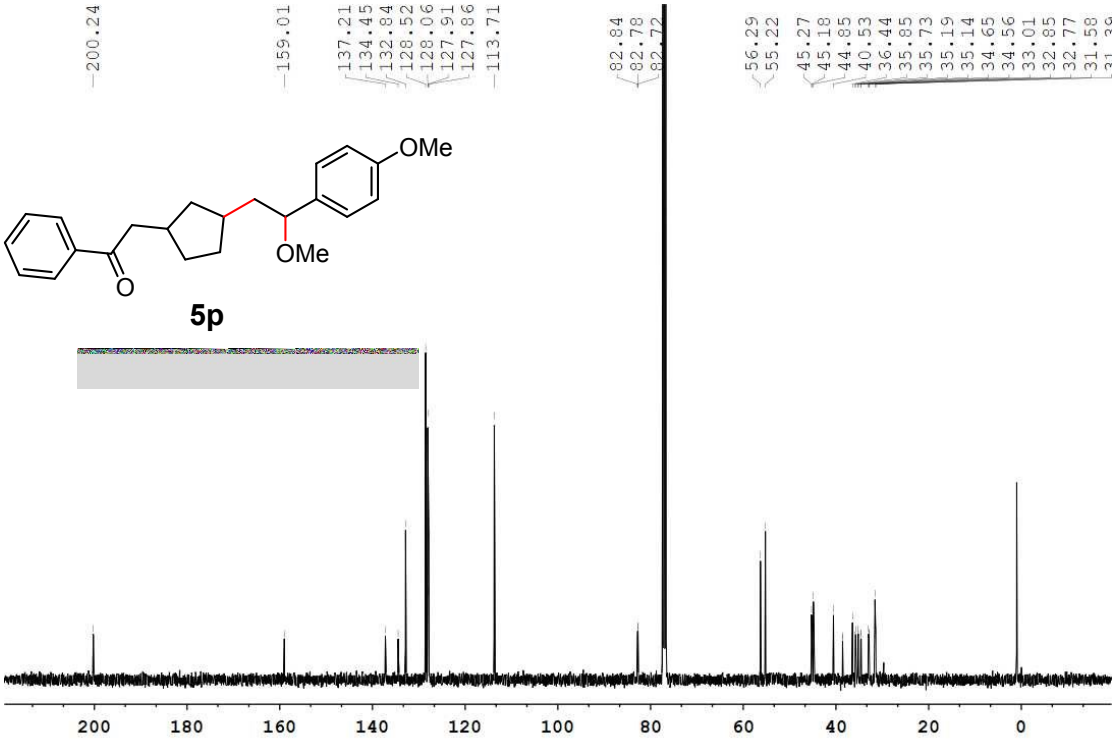
5o

^{13}C {^{1}H} NMR (100MHz, $CDCl_3$)

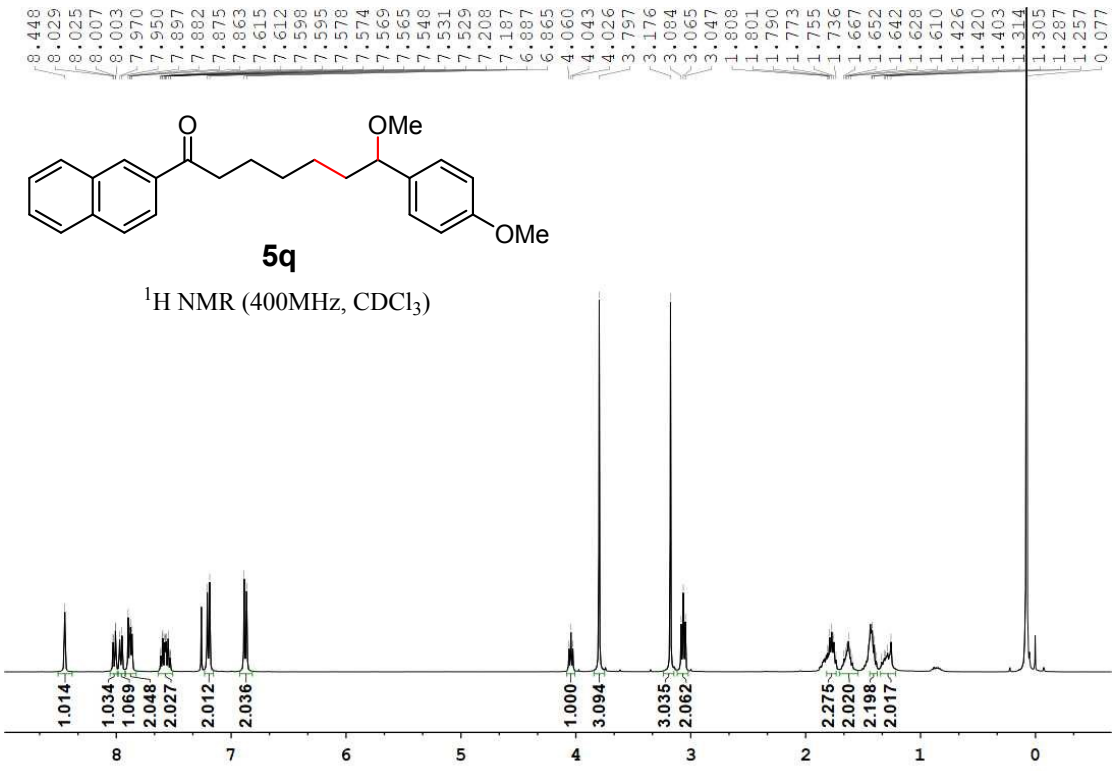


5p

^{1}H NMR (400MHz, $CDCl_3$)

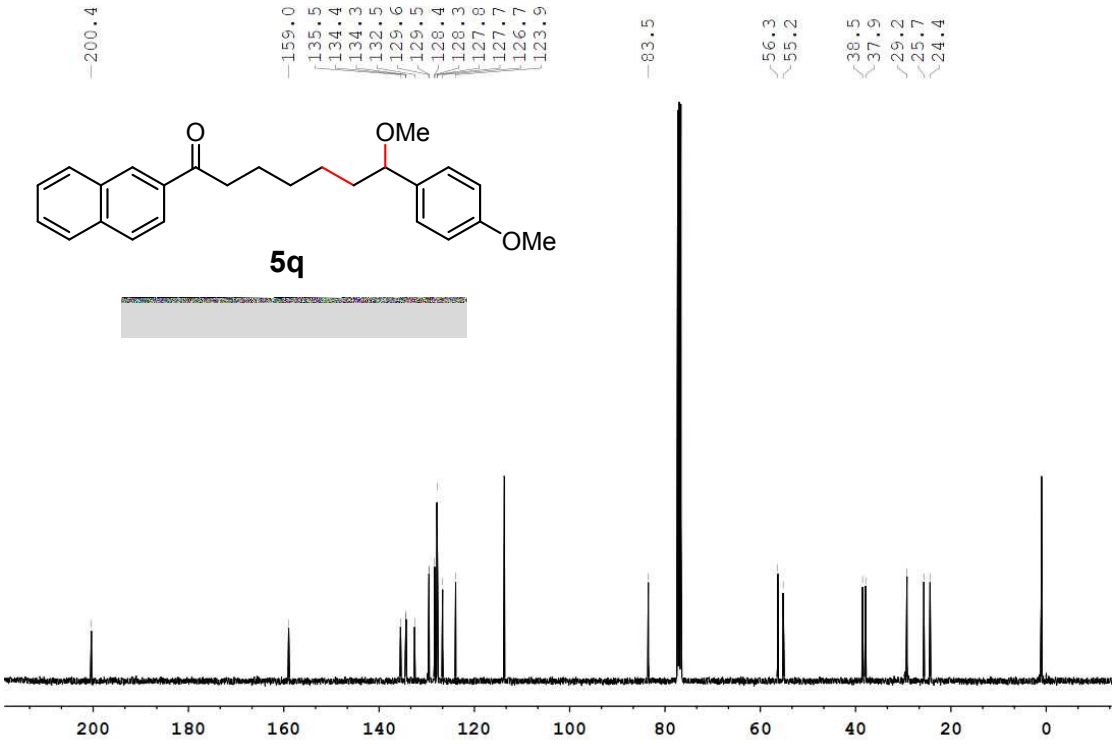


5p

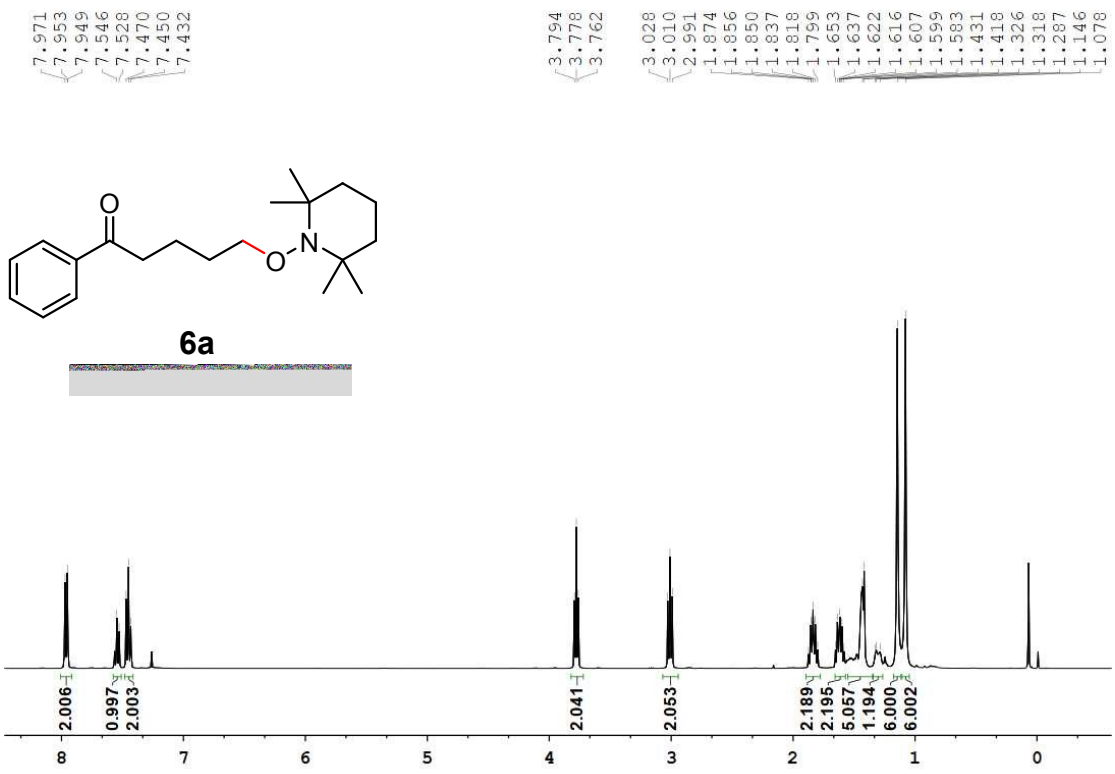


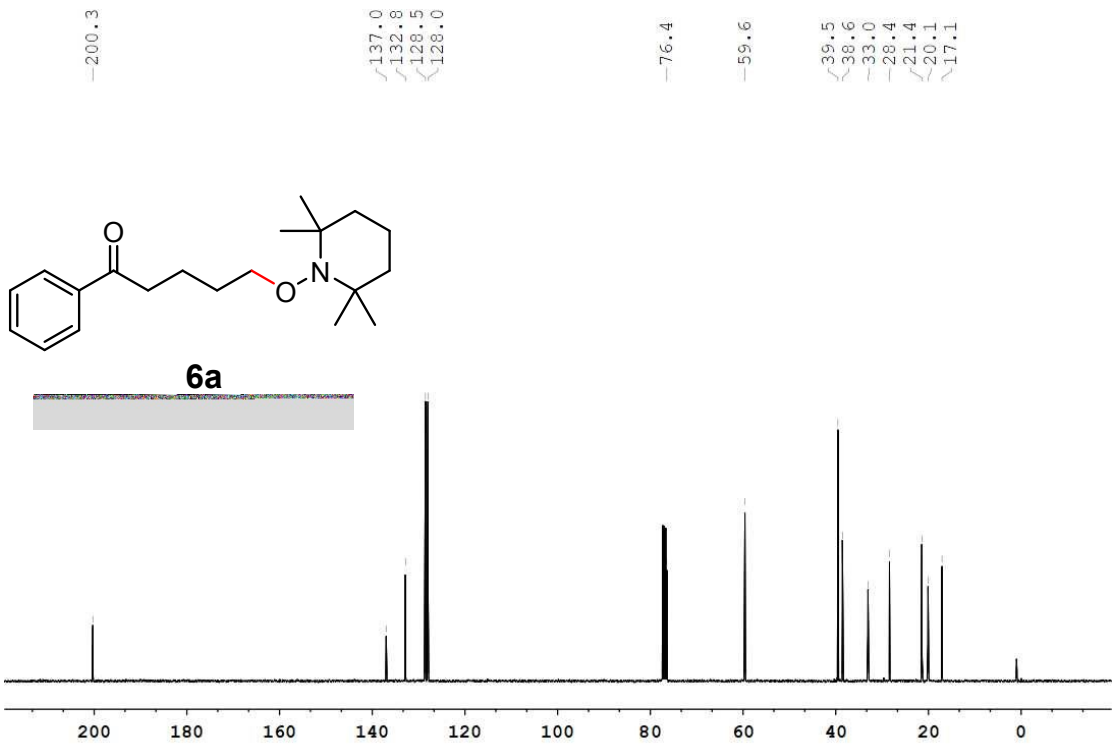
5q

^{1}H NMR (400MHz, $CDCl_3$)



5q


7.971
7.953
7.949
7.546
7.528
7.470
7.450
7.432
3.794
3.778
3.762
3.028
3.010
2.991
1.874
1.856
1.850
1.837
1.818
1.799
1.653
1.637
1.622
1.616
1.607
1.599
1.583
1.431
1.418
1.326
1.318
1.287
1.146
1.078
O
N
O
6a
2.006
0.997
2.003
2.041
2.053
2.189
2.195
5.057
1.194
6.000
6.002
8
7
6
5
4
3
2
1
0


200.3
137.0
132.8
128.5
128.0
76.4
59.6
39.5
38.6
33.0
28.4
21.4
20.1
17.1
O
N
O
6a
200
180
160
140
120
100
80
60
40
20
0