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Supporting Information

Straightforward α-Allylation of Carbonyl Compounds with Alkenes via α-Carbonyl Radical Intermediates

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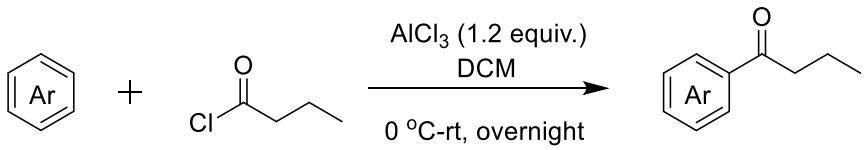
General Information

All reactions were conducted under nitrogen atmosphere. Unless otherwise noted, chemical reagents were purchased from commercial suppliers (Sigma-Aldrich, J&K Chemicals, Acros Organics, Alfa Aesar, Adamas-beta®, Innochem, Aladdin, TCI, Accela, Sinocompound, Laajoo, Bidepharm, Energy Chemicals and 3A Chemicals) and were used without further purification. Dioxane and toluene were distilled from Na and stored under nitrogen. DMF, DMSO, CH_3CN, DCE and chlorobenzene were distilled over CaH_2 and stored under nitrogen atmosphere. GC data were recorded on Agilent 8860. Flash chromatography was performed with Sepaflash columns produced by Santai Technologies. ^1H NMR (400 MHz), ^{13}C NMR (101 MHz), ^{19}F NMR (377 MHz) spectra were recorded in $CDCl_3$ solutions using a Bruker AVANCE 400 spectrometer. Calibration was done using tetramethylsilane (0 ppm) or residual undeuterated solvent $CDCl_3$ (7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR). HRMS were performed by the Shanghai Mass Spectrometry Center in Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences (Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS, Operation Mode: ESI Positive Ion Mode, ESI Negative Ion Mode, Dart positive or FI Positive Ion Mode, Analyzer Type: TOF).

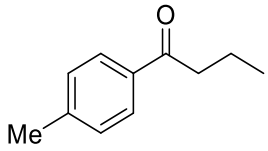
Synthesis and characterization of the starting materials

General procedure A for synthesis of the aryl butyl ketones (1c, 1d, 1e,1l, 1p) (Friedel-Crafts Acylation)



A dried 150 mL round bottom flask was charged with a magnetic stirbar and anhydrous aluminum trichloride (1.2 equiv.) in DCM (20 mL). The flask was cooled to 0 °C in an ice bath followed by dropwise addition of acid chloride (1.2 equiv.). Then the reaction mixture was stirred at 0 °C for 10 minutes. A solution of arene in DCM (20 mL DCM, 20 mmol arene 1.0 equiv.) was added dropwise during 10 minutes. After addition, the solution was gradually warmed to room temperature and stirred until completion of the reaction (monitored by TLC). The reaction mixture was quenched by adding ice cold water (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with dilute HCl (25 mL, 2N), sodium carbonate solution (25 mL, saturated solution) and finally with water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (0 - 5% EtOAc in petroleum ether) to afford the product.

1-(4-methylphenyl) butan-1-one (1c)

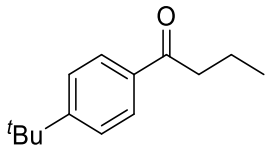


Following the **general procedure A** with toluene (1.84 g, 20 mmol), butyryl chloride (2.56 g, 24 mmol), aluminum trichloride (3.20 g, 24 mmol). The reaction mixture was stirred at room temperature for overnight. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound **1c** as a yellow oil. The characterization data are in accordance with the literature[1].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.93 – 2.88 (m, 2H), 2.39 (s, 3H), 1.76 (m, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 143.4, 134.5, 129.1, 128.1, 40.3, 21.5, 17.8, 13.8.

1-(4-(tert-butyl) phenyl) butan-1-one (1d)

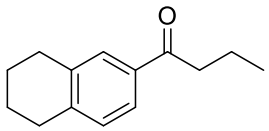


Following the **general procedure A** with tert-butylbenzene (2.68 g, 20 mmol), butyryl chloride (2.56 g, 24 mmol), aluminum trichloride (3.20 g, 24 mmol). The reaction mixture was stirred at room temperature for overnight. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound **1d** as a pink oil. The characterization data are in accordance with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.73 (m, 2H), 7.51 – 7.42 (m, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 1.77 (m, *J* = 7.4 Hz, 2H), 1.34 (s, 9H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 156.5, 134.5, 128.0, 125.4, 40.4, 35.0, 31.0, 17.8, 13.9.

1-(5,6,7,8-tetrahydronaphthalen-2-yl) butan-1-one (1e)

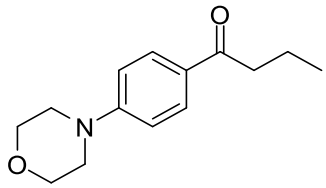


Following the **general procedure A** with tetralin (2.64 g, 20 mmol), butyryl chloride (2.56 g, 24 mmol), aluminum trichloride (3.20 g, 24 mmol). The reaction mixture was stirred at room temperature for overnight. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound as a yellow oil. The characterization data are in accordance with the literature[3].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dq, *J* = 4.4, 2.0 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.81 (q, *J* = 5.5, 5.0 Hz, 4H), 1.81 (p, *J* = 3.3 Hz, 4H), 1.75 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 142.8, 137.3, 134.6, 129.2, 128.9, 125.1, 40.4, 29.6, 29.4, 22.9, 22.8, 17.9, 13.9.

1-(4-morpholinophenyl)-3-methylpropan-1-one (1l)

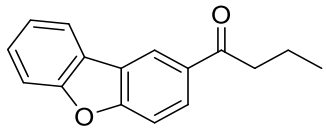


Following the **general procedure A** with 4-phenylmorpholine (3.26 g, 20 mmol), butyryl chloride (2.56 g, 24 mmol), aluminum trichloride (3.20 g, 24 mmol). The reaction mixture was stirred at room temperature for overnight. Purification by silica gel flash chromatography (20% EtOAc in petroleum ether) gave the title compound **1l** as a light-yellow solid. The characterization data are in accordance with the literature[1].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.85 (t, *J* = 4.9 Hz, 4H), 3.33 – 3.25 (m, 4H), 2.86 (t, *J* = 7.4 Hz, 2H), 1.75 (p, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8 154.0, 130.0, 128.0, 113.3, 66.5, 47.5, 39.9, 18.1, 13.9.

1-dibenzofuran-2-yl-butan-1-one (1p)



Following the **general procedure A** with dibenzofuran (3.36 g, 20 mmol), butyryl chloride (2.56 g, 24 mmol), aluminum trichloride (3.20 g, 24 mmol). The reaction mixture was stirred at room temperature for overnight. Purification by silica gel flash chromatography (20% EtOAc in petroleum ether) gave the title compound **1p** as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 3.03 (t, *J* = 7.3 Hz, 2H), 1.83 (h, *J* = 7.4 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 158.6, 156.7, 132.3, 127.8, 127.6, 124.4, 123.7 123.2, 121.1, 120.8, 111.8, 111.4, 40.5, 17.9, 13.9.

Synthesis of the aryl butyl ketones(1k)

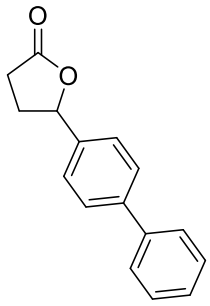
1k

Under the nitrogen atmosphere, 4-hydroxybutyrophenone (3.28 g, 20 mmol) was added to a 250 mL round bottom flask, then 20 mL DCM, DMAP (0.05 equiv.), Et_3N (1.5 equiv.) was added in turn. Five minutes later, Acetyl Chloride (1.73 g, 22 mmol, 1.1 equiv.) was added dropwise and the reaction mixture was stirred at room temperature overnight. The reaction mixture was quenched with saturated brine. The crude mixture was extracted with DCM three times and dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (0 - 10 % EtOAc in petroleum ether) to afford the *p*-acetoxy-butyrophenon **(1k)** as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.21 – 7.13 (m, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 1.75 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 168.8, 154.1, 134.6, 129.6, 121.7, 40.4, 21.1, 17.7, 13.8.

5-([1,1'-biphenyl]-4-yl) dihydrofuran-2(3H)-one (4a)

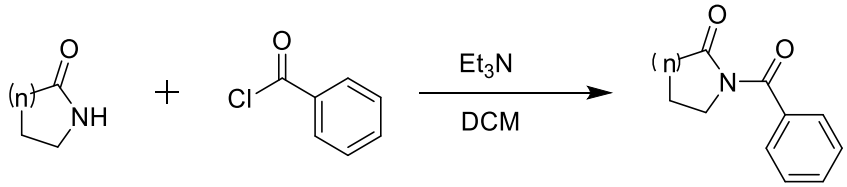


The compound **4a** was prepared by literature procedure[4].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 10.7, 7.8 Hz, 4H), 7.49 – 7.34 (m, 5H), 5.56 (dd, *J* = 8.2, 5.8 Hz, 1H), 2.74 – 2.62 (m, 3H), 2.24 (ddd, *J* = 12.1, 8.3, 3.6 Hz, 1H).

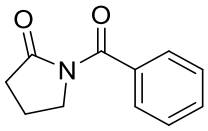
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 141.3, 140.3, 138.2, 128.8, 127.5, 127.4, 127.0, 125.7, 81.0, 30.8, 28.9.

General procedure B for synthesis of the 1-benzoyl-lactam(6a-6c)



The lactam (20.0 mmol, 1.0 equiv.) was dissolved in 50 mL of dichloromethane. Triethylamine (40 mmol, 2.0 equiv.) and benzoyl chloride (20 mmol, 1.0 equiv.) were added at 0 °C. After addition, the mixture was reacted at room temperature for overnight. The reaction was quenched with 20 mL of saturated aqueous ammonium chloride solution and extracted with ethyl acetate (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (10 % EtOAc in petroleum ether) to afford the product.

1-benzoylpyrrolidin-2-one (6a)

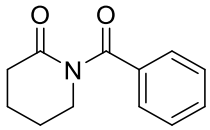


Following the **general procedure B** with 2-pyrrolidinone (1.70 g, 20 mmol), benzoyl chloride (2.81 g, 20 mmol). The reaction mixture was stirred at room temperature for overnight. Purification by silica gel flash chromatography (10 % EtOAc in petroleum ether) gave the title compound as a white solid. The characterization data are in accordance with the literature[5].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 3.95 (t, *J* = 7.1 Hz, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 2.13 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 170.6, 134.3, 131.8, 128.8, 127.7, 46.5, 33.2, 17.6.

1-benzoylpiperidin-2-one (6b)

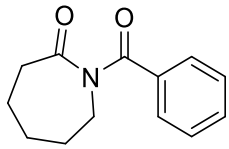


Following the **general procedure B** with 2-piperidone (1.98 g, 20 mmol), benzoyl chloride (2.81 g, 20 mmol). The reaction mixture was stirred at room temperature for overnight. Purification by silica gel flash chromatography (10 % EtOAc in petroleum ether) gave the title compound as a white solid. The characterization data are in accordance with the literature[6].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 3.78 (t, *J* = 5.7 Hz, 2H), 2.55 (t, *J* = 6.4 Hz, 2H), 1.95 (m, *J* = 8.1, 4.4 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 173.4, 136.0, 131.4, 128.0, 127.8, 46.0, 34.5, 22.7, 21.3.

N-Benzoylcaprolactam (6c)

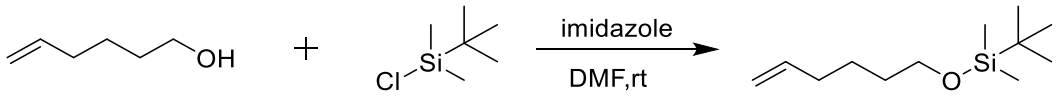


Following the **general procedure B** with epsilon-caprolactam (2.26 g, 20 mmol), benzoyl chloride (2.81 g, 20 mmol). The reaction mixture was stirred at room temperature for overnight. Purification by silica gel flash chromatography (10 % EtOAc in petroleum ether) gave the title compound as a white solid. The characterization data are in accordance with the literature[6].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 3.95 (s, 2H), 2.72 – 2.65 (m, 2H), 1.82 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 174.0, 136.5 131.2, 128.0, 127.5, 45.0, 38.6, 29.4, 29.0, 23.6.

Synthesis of the tert-butyl(5-hexenyloxy) dimethyl silane (2i)



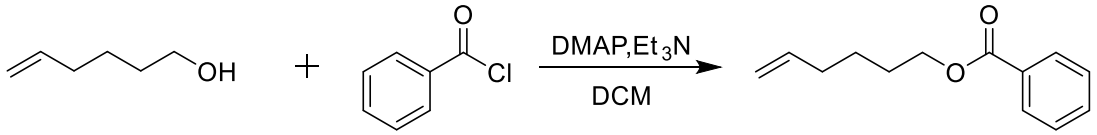
2i

To a stirred solution of 5-hexen-l-ol (1.0 g, 10 mmol) in DMF (50 mL) at room temperature was added imidazole (1.02 g, 15 mmol) and tert-butyl-dimethyl-silyl chloride (1.81 g, 12 mmol). The reaction mixture was allowed to stir at room temperature for overnight. The mixture was then diluted with EtOAc (150 mL), washed with water (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (petroleum ether) to give the tert-butyl (5-hexenyloxy) dimethyl silane (**2i**) as a colorless oil. The characterization data are in accordance with the literature[7].

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (m, *J* = 17.1, 10.6, 6.6 Hz, 1H), 4.97 (dd, *J* = 24.4, 13.8 Hz, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.06 (q, *J* = 7.3 Hz, 2H), 1.52 (q, *J* = 7.7, 7.0 Hz, 2H), 1.47 – 1.39 (m, 2H), 0.90 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 114.4, 63.1, 33.5, 32.3, 26.0, 25.2, 18.4, -5.3.

Synthesis of the benzoic acid hex-5-enyl ester (2j)



2j

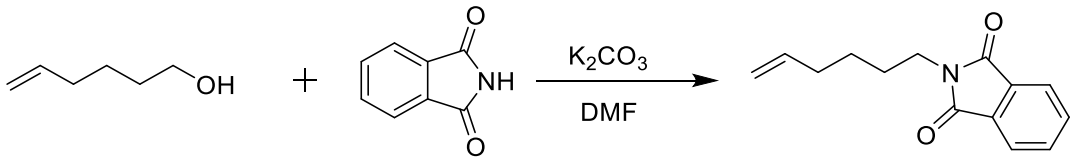
The 5-hexen-l-ol (1.0 g, 10 mmol) was dissolved in 50 mL of dichloromethane. DMAP (244 mg, 2 mmol, 0.2 equiv.), triethylamine (20 mmol, 2.0 equiv.) and benzoyl chloride (1.69 g,12 mmol, 1.2 equiv.) were added at 0°C. After addition, the mixture was reacted at room temperature for overnight. The reaction was quenched with 20 mL of saturated aqueous ammonium chloride solution and extracted with ethyl acetate (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (10% EtOAc in petroleum ether) to give the benzoic acid hex-5-enyl ester **(2j)** as a colorless oil. The characterization data are in accordance with the

literature[8].

^{1}H NMR (400 MHz, $CDCl_3$ δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 5.90 – 5.71 (m, 1H), 5.01 (dd, *J* = 23.1, 13.7 Hz, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.13 (q, *J* = 7.3 Hz, 2H), 1.78 (p, *J* = 6.8 Hz, 2H), 1.55 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 138.2, 132.7, 130.4, 129.4, 128.2, 114.8, 64.7, 33.2, 28.1, 25.2.

Synthesis of the N-(5-hexenyl) phthalimide (2k)



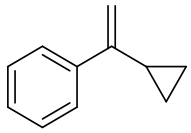
2k

To a solution of phthalimide (2.94 g, 20 mmol) and 5-bromo-1-pentene (3.2 mL, 24 mmol) in anhydrous DMF (30 mL) was added K_2CO_3 (3.31 g, 24 mmol) under N_2 atmosphere at room temperature (25 °C) and the mixture was stirred for 4 h at 65 °C (monitored by TLC). After being cooled to room temperature, saturated aqueous NH_4Cl was added and the mixture was extracted with EtOAc. The combined organic layer was washed with brine. The organic phase was collected and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the crude product was purified by flash column chromatography (hexane/EtOAc = 5:1) to give the *N*-(5-hexenyl) phthalimide **(2k)** as a colorless oil. The characterization data are in accordance with the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.68 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.75 (m, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 – 4.86 (m, 2H), 3.66 (t, *J* = 7.3 Hz, 2H), 2.07 (q, *J* = 7.1 Hz, 2H), 1.66 (p, *J* = 7.9 Hz, 2H), 1.41 (p, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 138.2, 133.8, 132.1, 123.1, 114.8, 37.7, 33.2, 27.9, 26.0.

Synthesis of the α-cyclopropylstyrene (2v)



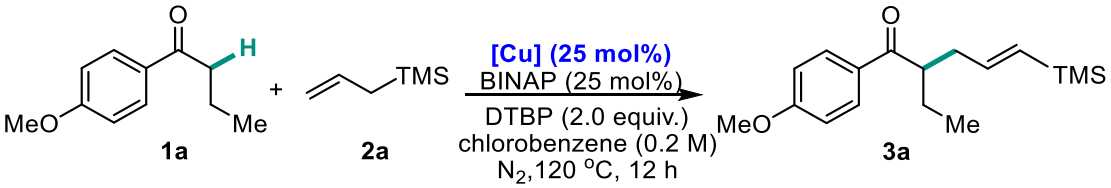
The compound **2v** was prepared by literature procedure[10].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H), 7.43 (dd, *J* = 8.3, 6.4 Hz, 2H), 7.40 – 7.34 (m, 1H), 5.38 (s, 1H), 5.03 (s, 1H), 1.74 (ddd, *J* = 13.7, 8.2, 5.3 Hz, 1H), 0.95 – 0.89 (m, 2H), 0.71 – 0.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 141.6, 128.1, 127.4, 126.1, 109.0, 15.1, 6.7.

Optimization of Reaction Conditions

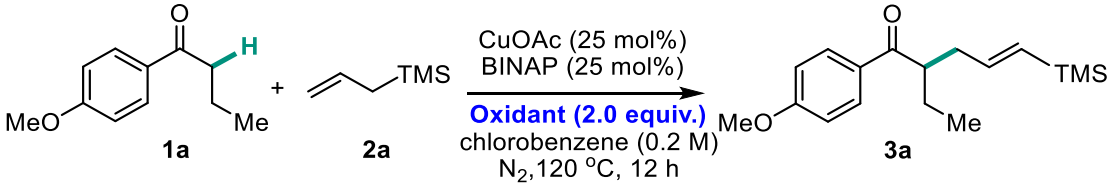
Table S1. Optimization of [Cu][a]



Entry	[**Cu**] (25 mol%)	Yield (%) [b]
1	CuOAc	77(75)
2	CuCl	17
3	CuBr	11
4	CuI	trace
5	CuCN	14
6	Cu_2S	0
7	Cu_2O	0
8	CuOTf	trace
9	Cu $(OAc)_2$	41
10[c]	Cu $(OAc)_2$	0
11[d]	Cu $(OAc)_2$	0
12[e]	Cu $(OAc)_2$	12
13[f]	Cu $(OAc)_2$	31
14	$Cu(acac)_2$	14
15	Cu $(PPh_3)_3Cl$	9
16	$Cu(C_8H_{15}O_2)_2$	46
17	Cu $(TFA)_2$	10
18	CuTc	31
19	CPT[g]	5

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (1.0 mmol), [**Cu**] (0.1 mmol), BINAP (0.1 mmol), DTBP (0.8 mmol), chlorobenzene (2.0 mL). [b]Yield is determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard. [c]Ligand = 1,10-phenanthroline (25 mmol%), Oxidant = TEMPO (2.0 equiv.). [d]Ligand = Bpy (25mmol%), Oxidant = TEMPO (2.0 equiv.). [e]Ligand = 1,10-phenanthroline (25 mmol%). [f]Ligand = $CyPPh_2$ (25mmol%). [g]CPT = Copper Pyrithione.

Table S2. Optimization of Oxidant[a]

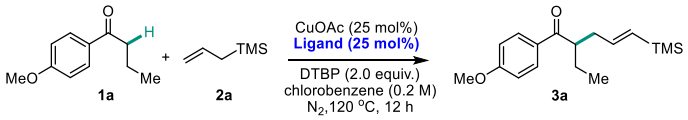


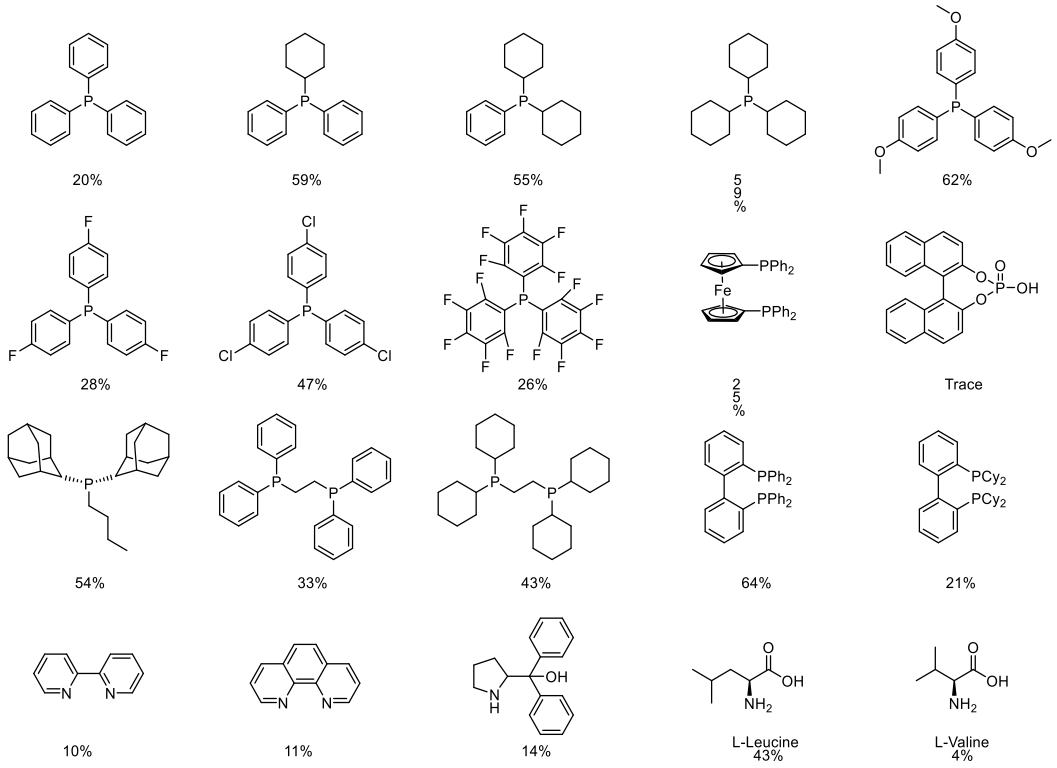
Entry	Oxidant (2.0 eq)	Yield (%) [b]
1	BPO	Trace
2	TBPB	Trace
3	TBHP	Trace
4	DCP	14
5	TEMPO	0

6	$Mn(OAc)_3$	22
7	AgOAc	35
8	DDQ	0
9	$PhI(OAc)_2$	Trace
10	$K_2S_2O_8$	0

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (1.0 mmol), CuOAc (0.1 mmol), BINAP (0.1 mmol), oxidant (0.8 mmol), chlorobenzene (2.0 mL). [b]Yield is determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

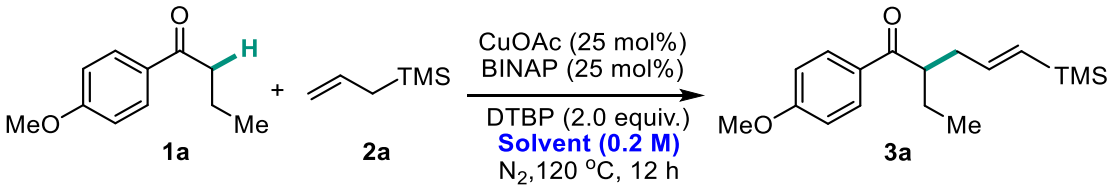
Table S3. Optimization of Ligand[a, b]





[a]Reaction conditions: **1a** (0.4 mmol), **2a** (1.0 mmol), CuOAc (0.1 mmol), Ligand (0.1 mmol), DTBP (0.8 mmol), Chlorobenzene (2.0 mL). [b]Yield is determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

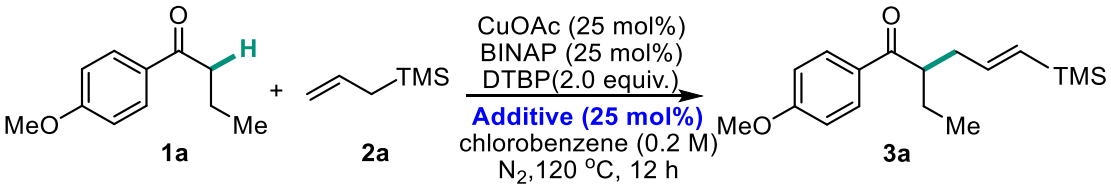
Table S4. Optimization of Solvent[a]



Entry	Solvent (0.2 M)	Yield (%) [b]
1	toluene	63
2	DMF	trace
3	DMSO	7
4	DCE	11
5	*o*-DCB	60
6	dioxane	8

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (1.0 mmol), CuOAc (0.1 mmol), BINAP (0.1 mmol), DTBP (0.8 mmol), solvent (2.0 mL). [b]Yield is determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

Table S5. Optimization of Additive[a]



Entry	Additive (25 mol%)	Yield (%) [b]
1	H_2O	30
2	HOAc	53
3	KOAc	41
4	TBAB[c]	55

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (1.0 mmol), CuOAc (0.1 mmol), BINAP (0.1 mmol), DTBP (0.8 mmol), Chlorobenzene (2.0 mL). [b]Yield is determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard. [c]TBAB=Tetrabutylammonium bromide.

Synthesis and Characterization of the Products

I General procedure for *α*-alkylation of aryl ketones

In a nitrogen-filled glovebox, a 20 mL Schlenk tube equipped with a stir bar was charged with CuOAc (12.3 mg, 0.1 mmol, 0.25 equiv.) and BINAP (62.3 mg, 0.1 mmol, 0.25 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then aryl ketone (0.4 mmol, 1.0 equiv.) (lactone or lactam was conducted with 0.2 mmol scale), olefine (1.0 mmol, 2.5 equiv.), DTBP (0.8 mmol, 2.0 equiv.) and chlorobenzene (2.0 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow (if the substituted ketone was solid, it was added to the tube in the glove box). The reaction mixture was stirred at 100 - 120 ^{o}C for 12 - 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of EtOAc, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure and the crude product was purified by flash chromatography on silica gel to provide the corresponding product.

II General procedure for *α*-alkylation of aryl ketones

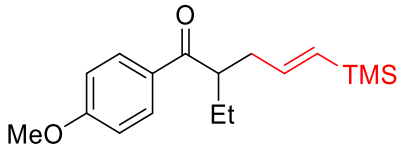
In a nitrogen-filled glovebox, a 20 mL Schlenk tube equipped with a stir bar was charged with CuOAc (12.3 mg, 0.1 mmol, 0.25 equiv.), BINAP (62.3 mg, 0.1 mmol, 0.25 equiv.) and AgOAc (200.3 mg, 1.2 mmol, 3.0 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then aryl ketone (0.4 mmol, 1.0 equiv.), olefine (1.0 mmol, 2.5 equiv.) and dioxane (2.0 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow (if the substituted ketone was solid, it was added to the tube in the glove box). The reaction mixture was stirred at 100 - 120 ^{o}C for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of EtOAc. followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure and the crude product was purified by flash chromatography on silica gel to provide the corresponding product.

III General procedure for *α*-alkylation of aryl ketones

In a nitrogen-filled glovebox, a 20 mL Schlenk tube equipped with a stir bar was charged

with CuOAc (12.3 mg, 0.1 mmol, 0.25 equiv.), BINAP (62.3 mg,0.1 mmol, 0.25 equiv.) and Ag_2CO_3 (220.6 mg, 0.8 mmol, 2.0 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then aryl ketone (0.4 mmol,1.0 equiv.), olefine (1.0 mmol, 2.5 equiv.), HOAc (24.0 mg, 0.4 mmol) and dioxane (2.0 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow (if the the substituted ketone was solid, it was added to the tube in the glove box). The reaction mixture was stirred at 100 - 120 °C for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of EtOAc, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure and the crude product was purified by flash chromatography on silica gel to provide the corresponding product.

(*E*)-2-ethyl-1-(4-methoxyphenyl)-5-(trimethylsilyl) pent-4-en-1-one (3a)



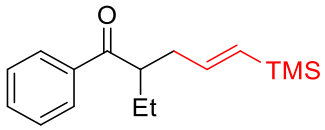
Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound **3a** as a yellow oil (87.4 mg, 75% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 5.92 (dt, *J* = 18.4, 6.6 Hz, 1H), 5.62 (d, *J* = 18.5 Hz, 1H), 3.83 (s, 3H), 3.39 (dq, *J* = 12.8, 6.4, 5.2 Hz, 1H), 2.57 – 2.46 (m, 1H), 2.28 (dt, *J* = 13.8, 6.7 Hz, 1H), 1.76 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.55 (ddd, *J* = 13.3, 7.5, 5.4 Hz, 1H), 0.84 (t, *J* = 7.4 Hz, 3H), -0.06 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.3, 163.3, 144.0, 132.2, 130.7, 130.4, 113.6, 55.3, 46.9, 39.3, 25.0, 11.9, -1.4.

HRMS (Dart positive) M = $C_{17}H_{26}O_2Si$: calculated $(M+H)^+$ m/z 291.1773; found $(M+H)^+$ m/z 291.1774.

(*E*)-2-Ethyl-1-phenyl-5-trimethylsilanyl-pent-4-en-1-one (3b)



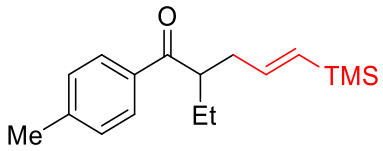
Following the **general procedure (I)** with butyrophenone (59.3 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 24 h. Purification by silica gel flash chromatography (0 - 1% EtOAc in petroleum ether) gave the title compound **3b** as a pale-yellow oil (73.9 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.57 – 7.51 (m, 1H), 7.48 – 7.42 (m, 2H), 5.92 (dt, *J* = 18.5, 6.6 Hz, 1H), 5.64 (dt, *J* = 18.4, 1.4 Hz, 1H), 3.51 – 3.42 (m, 1H), 2.53 (dddd, *J* = 13.9, 7.7, 6.3, 1.4 Hz, 1H), 2.37 – 2.28 (m, 1H), 1.81 (dt, *J* = 13.6, 7.6 Hz, 1H), 1.64 – 1.53 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 143.7, 137.7, 132.7, 132.5, 128.5, 128.2, 47.3, 39.2, 24.9, -1.4.

HRMS (Dart positive) M = $C_{16}H_{24}OSi$: calculated $(M+H)^+$ m/z 261.1669; found $(M+H)^+$ m/z 261.1669.

(*E*)-2-Ethyl-1-(p-tolyl)-5-(trimethylsilyl) pent-4-en-1-one (3c)



Following the **general procedure (I)** with 1-(4-methylphenyl) butan-1-one (64.9 mg, 0.4 mmol), allyl-trimethyl-silane (114.3mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (0 – 1 % EtOAc in petroleum ether) gave the title compound **3c** as a pale-yellow oil (73.5 mg, 67% yield).

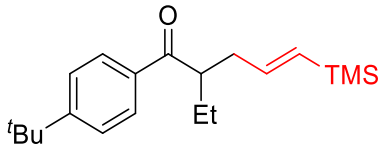
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 6.6 Hz, 2H), 7.24 (s, 2H), 5.93 (dt, *J* = 18.4, 6.5 Hz, 1H), 5.64 (dd, *J* = 18.6, 1.7 Hz, 1H), 3.43 (dt, *J* = 12.6, 6.7 Hz, 1H), 2.52 (dt, *J* = 13.9,

6.9 Hz, 1H), 2.40 (s, 3H), 2.30 (dt, *J* = 13.8, 6.6 Hz, 1H), 1.79 (dt, *J* = 13.8, 7.1 Hz, 1H), 1.57 (h, *J* = 7.5 Hz, 1H), 0.86 (t, *J* = 7.4 Hz, 3H), -0.04 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 143.9, 143.5, 135.2, 132.4, 129.2, 128.3, 47.2, 39.2, 25.0, 21.5, 11.8, -1.4.

HRMS (Dart positive) M = $C_{17}H_{26}OSi$: calculated $(M+H)^+$ m/z 275.1826; found $(M+H)^+$ m/z 275.1825.

(*E*)-1-(4-(tert-butyl) phenyl)-2-ethyl-5-(trimethylsilyl) pent-4-en-1-one (3d)



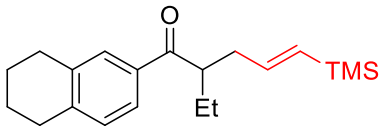
Following the **general procedure (I)** with 1-(4-(tert-butyl) phenyl) butan-1-one (81.7 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 ºC for 12 h. Purification by silica gel flash chromatography (0 - 1% EtOAc in petroleum ether) gave the title compound **3d** as a colorless oil (81.2 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 5.92 (dt, *J* = 18.4, 6.6 Hz, 1H), 5.63 (d, *J* = 18.5 Hz, 1H), 3.45 (p, *J* = 6.9 Hz, 1H), 2.51 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.31 (dt, *J* = 13.7, 6.6 Hz, 1H), 1.81 (dp, *J* = 14.9, 7.5 Hz, 1H), 1.57 (dp, *J* = 13.8, 7.2 Hz, 1H), 1.34 (s, 9H), 0.87 (t, *J* = 7.4 Hz, 3H), -0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 156.4, 144.0, 135.1, 132.3, 128.2, 125.5, 47.2, 39.3, 35.0, 31.1, 24.9, 11.8, -1.4.

HRMS (positive) M = $C_{20}H_{32}OSi$: calculated $(M+H)^+$ m/z 317.2295.; found $(M+H)^+$ m/z 317.2292.

(*E*)-2-ethyl-1-(5,6,7,8-tetrahydronaphthalen-2-yl)-5-(trimethylsilyl) pent-4-en-1-one (3e)



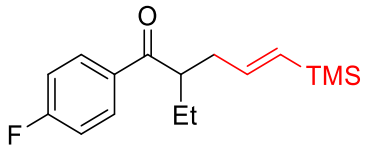
Following the **general procedure (I)** with 1-(5,6,7,8-tetrahydronaphthalen-2-yl) butan-1-one (80.9 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **3e** as a pale-yellow oil (80.7 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.4 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 1H), 5.93 (dt, *J* = 18.5, 6.6 Hz, 1H), 5.64 (d, *J* = 18.1 Hz, 1H), 3.42 (p, *J* = 6.5 Hz, 1H), 2.82 (s, 4H), 2.52 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.29 (dt, *J* = 13.7, 6.6 Hz, 1H), 1.85 – 1.73 (m, 5H), 1.58 (dq, *J* = 14.0, 7.2 Hz, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 144.1, 142.9, 137.4, 135.2, 132.3, 129.3, 129.1, 125.3, 47.1, 39.2, 29.6, 29.4, 25.0, 23.0, 22.8, 11.8, -1.3.

HRMS (Dart positive) M = $C_{20}H_{30}OSi$: calculated $(M+H)^+$ m/z 315.2139; found $(M+H)^+$ m/z 315.2137.

(*E*)-2-ethyl-1-(4-fluorophenyl)-5-(trimethylsilyl) pent-4-en-1-one (3f)



Following the **general procedure (I)** with 1-(4-fluorophenyl) butan-1-one (66.5 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 1% EtOAc in petroleum ether) gave the title compound **3f** as a pale-yellow oil (56.0 mg, 50% yield).

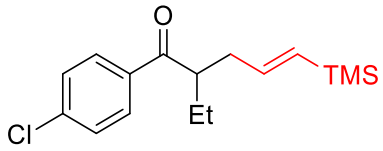
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (td, *J* = 7.0, 5.1, 2.9 Hz, 2H), 7.16 – 7.08 (m, 2H), 5.91 (dd, *J* = 17.8, 8.4 Hz, 1H), 5.63 (dd, *J* = 18.4, 3.0 Hz, 1H), 3.42 (d, *J* = 7.3 Hz, 1H), 2.56 – 2.43 (m, 1H), 2.32 (q, *J* = 7.1 Hz, 1H), 1.85 – 1.69 (m, 1H), 1.64 – 1.50 (m, 1H), 0.86 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 166.9(d, *J*=253 Hz), 143.6, 134.1(d, *J*=2.77 Hz), 132.7, 130.8 (d, *J*=9.14 Hz), 115.7(d, *J*=21.6 Hz), 47.3, 39.2, 25.0, 11.8, -1.4.

^{19}F NMR (300 MHz, $CDCl_3$) δ -105.67.

HRMS (Dart positive) M = $C_{16}H_{23}FOSi$: calculated $(M+H)^+$ m/z 279.1575; found $(M+H)^+$ m/z 279.1575.

(*E*)-1-(4-chlorophenyl)-2-ethyl-5-(trimethylsilyl) pent-4-en-1-one (3g)



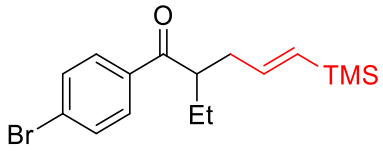
Following the **general procedure (I)** with 4-*n*butanoylchlorobenzene (73.1 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **3g** as a colorless oil (76.3 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.45 – 7.41 (m, 2H), 5.96 – 5.79 (dt, *J*=18.5,6.7 Hz,1H), 5.63 (dt, *J* = 18.5, 1.4 Hz, 1H), 3.47 – 3.28 (m, 1H), 2.50 (dddd, *J* = 14.0, 7.7, 6.3, 1.4 Hz, 1H), 2.35 – 2.23 (m, 1H), 1.78 (dt, *J* = 13.7, 7.5 Hz, 1H), 1.63 – 1.50 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H), -0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 143.5, 139.3, 136.0, 132.8, 129.6, 128.9, 47.4, 39.1, 24.9, 11.7, -1.4.

HRMS (FI positive) M = $C_{16}H_{23}ClOSi$: calculated $(M)^+$ m/z 294.1201; found $(M)^+$ m/z 294.1204.

(*E*)-1-(4-bromophenyl)-2-ethyl-5-(trimethylsilyl) pent-4-en-1-one (3h)



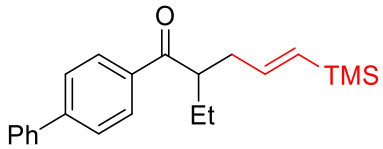
Following the **general procedure (I)** with 1-(4-bromophenyl)-1-butanone (90.8 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 ºC for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **3h** as a colorless oil (68.8 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.3 Hz, 2H), 7.59 (d, *J* = 6.3 Hz, 2H), 5.90 (dt, *J* = 18.6, 6.6 Hz, 1H), 5.63 (d, *J* = 18.4 Hz, 1H), 3.39 (p, *J* = 5.7 Hz, 1H), 2.50 (dt, *J* = 14.4, 7.6 Hz, 1H), 2.31 (dt, *J* = 13.8, 6.6 Hz, 1H), 1.79 (dq, *J* = 15.0, 7.4 Hz, 1H), 1.58 (dq, *J* = 13.4, 7.2 Hz, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 143.4, 136.4, 132.8, 131.8, 129.7, 127.9, 47.4, 39.1, 24.9, 11.7, -1.4.

HRMS (Dart positive) M = $C_{16}H_{23}BrOSi$: calculated $(M+H)^+$ m/z 339.0774; found $(M+H)^+$ m/z 339.0774.

(*E*)-1-([1,1'-biphenyl]-4-yl)-2-ethyl-5-(trimethylsilyl) pent-4-en-1-one(3i)



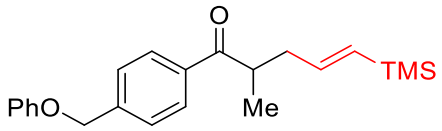
Following the **general procedure (I)** with 1-([1,1'-biphenyl]-4-yl) butan-1-one (89.7 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 ºC for 12 h. Purification by silica gel flash chromatography (0 - 1% EtOAc in petroleum ether) gave the title compound **3i** as a yellow oil (77.5 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.5 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.43 – 7.37 (m, 1H), 5.97 (dt, *J* = 18.3, 6.5 Hz, 1H), 5.68 (d, *J* = 18.6 Hz, 1H), 3.51 (p, *J* = 6.6 Hz, 1H), 2.57 (dt, *J* = 13.9, 7.0 Hz, 1H), 2.36 (dt, *J* = 13.8, 6.6 Hz, 1H), 1.85 (dt, *J* = 14.6, 7.2 Hz, 1H), 1.63 (td, *J* = 13.9, 13.2, 6.2 Hz, 1H), 0.91 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 145.5 143.8, 139.9, 136.4, 132.6, 128.9, 128.8, 128.1, 127.2, 127.2, 47.4, 39.3, 25.0, 11.8, -1.3.

HRMS (Dart positive) M = $C_{22}H_{28}OSi$: calculated $(M+H)^+$ m/z 337.1982; found $(M+H)^+$ m/z 337.1982.

(*E*)-2-methyl-1-(4-(phenoxymethyl) phenyl)-5(trimethylsilyl)pent-4-en-1-one (3j)



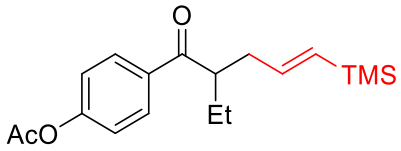
Following the **general procedure (I)** with 1-(4-phenoxymethyl-phenyl)-propan-1-one (96.1 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 ºC for 12 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound **3j** as a yellow oil (121 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.46 – 7.35 (m, 5H), 7.05 – 7.00 (m, 2H), 6.03 – 5.92 (dt, *J* = 18.4, 6.3 Hz,1H), 5.68 (dt, *J* = 18.5, 1.4 Hz, 1H), 5.14 (s, 2H), 3.51 (h, *J* = 6.7 Hz, 1H), 2.59 (dtd, *J* = 13.9, 6.1, 1.5 Hz, 1H), 2.23 (dtd, *J* = 14.3, 7.3, 1.3 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H), -0.02 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 162.4, 143.9, 136.2, 132.6, 130.6, 129.7, 128.7, 128.2, 127.4, 114.6, 70.1, 40.8, 39.9, 17.0, -1.3.

HRMS (Dart positive) M = $C_{22}H_{28}O_2Si$: calculated $(M+H)^+$ m/z 353.1931; found $(M+H)^+$ m/z 395.1931.

(*E*)-4-(2-ethyl-5-(trimethylsilyl) pent-4-enoyl) phenyl acetate (3k)



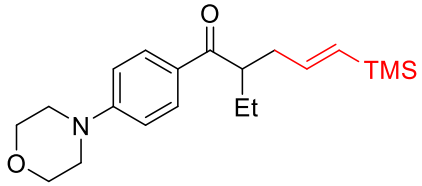
Following the **general procedure (I)** with p-acetoxy-butyrophenon (82.5 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound **3k** as a pale-yellow oil (76.5 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.22 – 7.15 (m, 2H), 5.91 (dt, *J* = 18.4, 6.6 Hz, 1H), 5.64 (dt, *J* = 18.4, 1.4 Hz, 1H), 3.42 (dt, *J* = 13.8, 7.4 Hz, 1H), 2.52 (dddd, *J* = 13.9, 7.6, 6.2, 1.5 Hz, 1H), 2.32 (s, 4H), 1.85 – 1.74 (m, 1H), 1.63 – 1.52 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H), -0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 168.8, 154.1, 143.6, 135.1, 132.7, 129.8, 121.7, 47.3, 39.0, 24.9, 21.1, 11.7, -1.4.

HRMS (Dart positive) M = $C_{18}H_{26}O_3Si$: calculated $(M+H)^+$ m/z 319.1724; found $(M+H)^+$ m/z319.1723.

(*E*)-2-ethyl-1-(4-morpholinophenyl)-5-(trimethylsilyl) pent-4-en-1-one (3l)



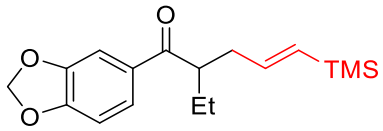
Following the **general procedure (I)** with 1-(4-morpholinophenyl)-3-methylpropan-1-one (46.7 mg, 0.2 mmol), allyl-trimethyl-silane (57.1 mg, 0.5 mmol), DTBP (58.5 mg, 0.4 mmol), CuOAc (6.2 mg, 0.05 mmol), BINAP (31.1 mg, 0.05 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave the title compound **3l** as a pale-yellow oil (26.6 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.0 Hz, 2H), 6.87 (d, *J* = 6.9 Hz, 2H), 5.93 (dt, *J* = 18.6, 6.7 Hz, 1H), 5.63 (d, *J* = 18.3 Hz, 1H), 3.85 (t, *J* = 3.9 Hz, 4H), 3.37 (q, *J* = 6.8 Hz, 1H), 3.29 (t, *J* = 4.0 Hz, 4H), 2.51 (dt, *J* = 13.9, 6.9 Hz, 1H), 2.28 (dt, *J* = 13.9, 6.8 Hz, 1H), 1.76 (dq, *J* = 15.1, 7.4, 6.8 Hz, 1H), 1.55 (dp, *J* = 13.9, 7.0, 6.5 Hz, 1H), 0.85 (td, *J* = 7.5, 1.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 154.1, 144.2, 132.1, 130.2, 128.5, 113.3, 66.5, 47.5, 46.7, 39.4, 25.1, 11.8, -1.3.

HRMS (Dart positive) M = $C_{20}H_{31}NO_2Si$: calculated $(M+H)^+$ m/z 346.2197; found $(M+H)^+$ m/z 346.2194.

(*E*)-1-(benzo[d][1,3] dioxol-5-yl)-2-ethyl-5-(trimethylsilyl) pent-4-en-1-one (3m)



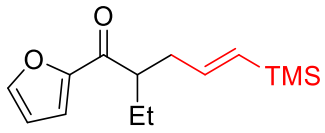
Following the **general procedure (I)** with 1-(benzo[d] [1,3] dioxol-5-yl) butan-1-one (76.9 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 ºC for 12 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave the title compound **3m** as a yellow oil (48.7 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.42 (s, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.03 (s, 2H), 5.91 (dt, *J* = 18.4, 6.6 Hz, 1H), 5.63 (d, *J* = 18.5 Hz, 1H), 3.34 (dq, *J* = 12.7, 6.4, 5.9 Hz, 1H), 2.49 (dt, *J* = 13.9, 6.6 Hz, 1H), 2.28 (dt, *J* = 13.7, 6.6 Hz, 1H), 1.77 (dp, *J* = 14.8, 7.4 Hz, 1H), 1.55 (dp, *J* = 13.7, 6.7 Hz, 1H), 0.85 (t, *J* = 7.4 Hz, 3H), -0.04 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 151.6, 148.2, 132.6, 132.4, 124.3, 108.1, 107.8, 101.8, 47.1, 39.4, 25.1, 11.8, -1.3.

HRMS (Dart positive) M = $C_{17}H_{24}O_3Si$: calculated $(M+H)^+$ m/z 305.1567; found $(M+H)^+$ m/z 305.1567.

(*E*)-2-ethyl-1-(furan-2-yl)-5-(trimethylsilyl) pent-4-en-1-one (3n)



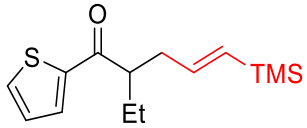
Following the **general procedure (II)** with 1-(furan-2-yl) butan-1-one (55.3 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (5% EtOAc in petroleum ether) gave the title compound **3n** as a yellow oil (47.6 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.16 (d, *J* = 3.6 Hz, 1H), 6.52 (dt, *J* = 3.3, 1.6 Hz, 1H), 5.91 (dt, *J* = 18.4, 6.6 Hz, 1H), 5.63 (d, *J* = 18.5 Hz, 1H), 3.19 (q, *J* = 6.7 Hz, 1H), 2.49 (dt, *J* = 14.4, 7.2 Hz, 1H), 2.30 (dt, *J* = 13.5, 6.5 Hz, 1H), 1.77 (dt, *J* = 14.5, 7.8 Hz, 1H), 1.56 (dt, *J* = 14.1, 6.5 Hz, 1H), 0.86 (d, *J* = 7.5 Hz, 3H), -0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 152.0, 146.9, 144.4, 132.2, 117.3, 111.5, 48.4, 37.0, 24.8, 10.4, -1.4.

HRMS (Dart positive) M = $C_{14}H_{22}O_2Si$: calculated $(M+H)^+$ m/z 251.1462; found $(M+H)^+$ m/z 251.1462.

(*E*)-2-ethyl-1-(thiophen-2-yl)-5-(trimethylsilyl) pent-4-en-1-one (3o)



Following the **general procedure (II)** with 1-(thiophen-2-yl) butan-1-one (61.7 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (5% EtOAc in petroleum ether) gave the title compound **3o** as a yellow oil (51.9 mg, 49% yield).

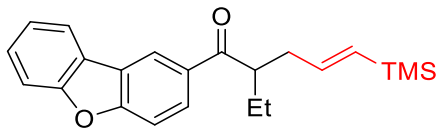
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 3.8 Hz, 1H), 7.63 (d, *J* = 4.9 Hz, 1H), 7.15 – 7.11 (m, 1H), 5.93 (dt, *J* = 18.5, 6.7 Hz, 1H), 5.65 (d, *J* = 18.5 Hz, 1H), 3.23 (h, *J* = 7.4 Hz, 1H),

2.52 (dt, *J* = 14.3, 7.2 Hz, 1H), 2.33 (dt, *J* = 13.5, 6.6 Hz, 1H), 1.81 (dp, *J* = 15.0, 7.5 Hz, 1H), 1.57 (dd, *J* = 13.1, 7.3 Hz, 1H), 0.89 (t, *J* = 7.5 Hz, 3H), -0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 145.1, 143.3, 133.4, 132.4, 131.3, 127.7, 49.4, 39.4, 25.0, 11.6, -1.7.

HRMS-ESI (Dart positive) M = $C_{14}H_{22}OSSi$: calculated $(M+H)^+$ m/z 267.1233; found $(M+H)^+$ m/z 267.1234.

(*E*)-1-(dibenzo [b, d] furan-2-yl)-2-ethyl-5-(trimethylsilyl) pent-4-en-1-one (3p)



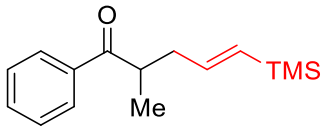
Following the **general procedure (II)** with 1-(dibenzo[b,d]furan-2-yl)butan-1-one (47.7 mg, 0.2 mmol), allyl-trimethyl-silane (57.1 mg, 0.5 mmol), DTBP (58.5 mg, 0.4 mmol), CuOAc (6.2 mg, 0.05 mmol), BINAP (31.1 mg, 0.05 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 ºC for 12 h. Purification by silica gel flash chromatography (0 - 20% EtOAc in petroleum ether) gave the title compound **3p** as a yellow oil (32.0 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.61 (dd, *J* = 8.2, 4.0 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 5.99 (dt, *J* = 18.7, 6.6 Hz, 1H), 5.69 (d, *J* = 18.6 Hz, 1H), 3.60 (p, *J* = 6.9 Hz, 1H), 2.61 (dt, *J* = 13.9, 6.9 Hz, 1H), 2.39 (dt, *J* = 13.8, 6.7 Hz, 1H), 1.88 (dp, *J* = 15.2, 7.6 Hz, 1H), 1.67 (dt, *J* = 13.9, 7.0 Hz, 1H), 0.97 – 0.89 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 158.8, 156.9, 143.8, 133.1, 132.7, 127.9, 127.9, 124.59, 123.8, 123.3, 121.5, 120.9, 111.9, 111.6, 47.5, 39.4, 25.2, 11.8, -1.3.

HRMS-ESI (Dart positive) M = $C_{22}H_{26}O_2Si$: calculated $(M+H)^+$ m/z 351.1775; found $(M+H)^+$ m/z 351.1773.

(*E*)-2-methyl-1-phenyl-5-(trimethylsilyl) pent-4-en-1-one (3q)



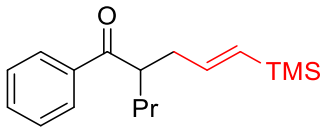
Following the **general procedure (I)** with propiophenone (53.7 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **3q** as a pale-yellow oil (71.7 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.97 (dt, *J* = 18.6, 6.6 Hz, 1H), 5.67 (d, *J* = 17.4 Hz, 1H), 3.55 (h, *J* = 7.1 Hz, 1H), 2.59 (dt, *J* = 13.6, 6.2 Hz, 1H), 2.24 (dt, *J* = 14.6, 7.4 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 3H), -0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 143.6, 136.6, 132.8, 132.8, 128.6, 128.3, 40.7, 40.3, 16.9, -1.3.

HRMS (Dart positive) M = $C_{15}H_{22}OSi$: calculated $(M+H)^+$ m/z 247.1517; found $(M+H)^+$ m/z 247.1517.

(*E*)-1-phenyl-2-propyl-5-(trimethylsilyl) pent-4-en-1-one (3r)



Following the **general procedure (I)** with valerophenone (64.9 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **3r** as a pale-yellow oil (77.9 mg, 71% yield).

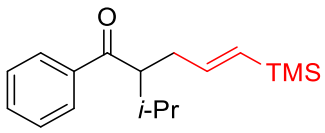
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 5.92 (dt, *J* = 17.7, 6.3 Hz, 1H), 5.63 (d, *J* = 18.5 Hz, 1H), 3.53 (p, *J* = 7.1, 6.6 Hz, 1H), 2.52 (dt, *J* = 14.1, 7.2 Hz, 1H), 2.31 (dt, *J* = 13.8, 6.5 Hz, 1H), 1.77 (dq, *J* = 16.2, 9.0,

8.0 Hz, 1H), 1.49 (dt, *J* = 14.9, 7.1 Hz, 1H), 1.30 (dt, *J* = 15.5, 7.7 Hz, 2H), 0.87 (t, *J* = 6.8 Hz, 3H), -0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.1, 143.8, 137.7, 132.8, 132.5, 128.5, 128.2, 45.7, 39.7, 34.2, 20.6, 14.2, -1.4.

HRMS (Dart positive) M = $C_{17}H_{26}OSi$: calculated $(M+H)^+$ m/z 275.1826; found $(M+H)^+$ m/z 275.1826.

(*E*)-2-isopropyl-1-phenyl-5-(trimethylsilyl) pent-4-en-1-one (3s)



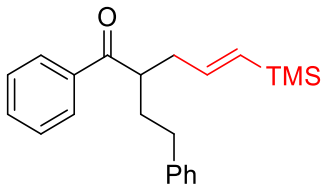
Following the **general procedure (I)** with 3-methyl-1-phenylbutan-1-one (64.9 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **3s** as a pale-yellow oil (55.6 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.87 (dt, *J* = 18.5, 6.6 Hz, 1H), 5.61 (d, *J* = 18.5 Hz, 1H), 3.34 (ddd, *J* = 10.5, 7.1, 4.2 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.44 – 2.35 (m, 1H), 2.07 (h, *J* = 6.8 Hz, 1H), 0.97 – 0.90 (m, 6H), -0.12 (d, *J* = 1.4 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 144.2, 138.6, 132.7, 132.2, 128.5, 128.2, 52.5, 36.7, 30.6, 21.3, 19.6, -1.5.

HRMS (Dart positive) M = $C_{17}H_{26}OSi$: calculated $(M+H)^+$ m/z 275.1826; found $(M+H)^+$ m/z 275.1824.

(*E*)-2-phenethyl-1-phenyl-5-(trimethylsilyl) pent-4-en-1-one (3t)



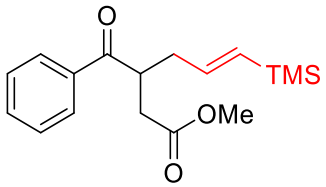
Following the **general procedure (I)** with 1,4-diphenylbutan-1-one (89.7 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **3t** as a yellow oil (89.5 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.0 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.93 (dt, *J* = 18.4, 6.5 Hz, 1H), 5.67 (d, *J* = 18.6 Hz, 1H), 3.71 – 3.27 (m, 1H), 2.68 (ddd, *J* = 14.9, 9.6, 5.8 Hz, 1H), 2.56 (h, *J* = 6.6 Hz, 2H), 2.38 (dt, *J* = 13.8, 6.8 Hz, 1H), 2.19 (td, *J* = 14.3, 8.7 Hz, 1H), 1.94 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 143.3, 141.7, 137.4, 132.9, 132.9, 128.5, 128.4, 128.3, 128.2, 125.9, 44.9, 39.7, 33.4, 33.2, -1.9.

HRMS (Dart positive) M = $C_{22}H_{28}OSi$: calculated $(M+H)^+$ m/z 337.1982; found $(M+H)^+$ m/z 337.1982.

methyl (*E*)-3-benzoyl-6-(trimethylsilyl) hex-5-enoate (3u)



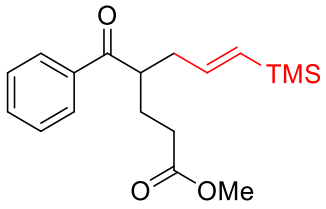
Following the **general procedure (I)** with methyl 3-benzoylpropionic acid methyl ester (76.9 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound **3u** as a yellow oil (84.9 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.57 – 7.52 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.86 (dt, *J* = 18.4, 6.7 Hz, 1H), 5.65 (dt, *J* = 18.4, 1.3 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.61 (s, 3H), 2.94 (dd, *J* = 17.0, 9.6 Hz, 1H), 2.55 – 2.45 (m, 2H), 2.23 (dt, *J* = 14.1, 7.5 Hz, 1H), -0.04 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 172.9, 141.9, 136.5, 134.1, 133.0, 128.6, 128.4, 51.7, 41.8, 39.5, 35.0, -1.5.

HRMS (Dart positive) M = $C_{17}H_{24}O_3Si$: calculated $(M+H)^+$ m/z 305.1567; found $(M+H)^+$ m/z 305.1564.

methyl (*E*)-4-benzoyl-7-(trimethylsilyl) hept-6-enoate (3v)



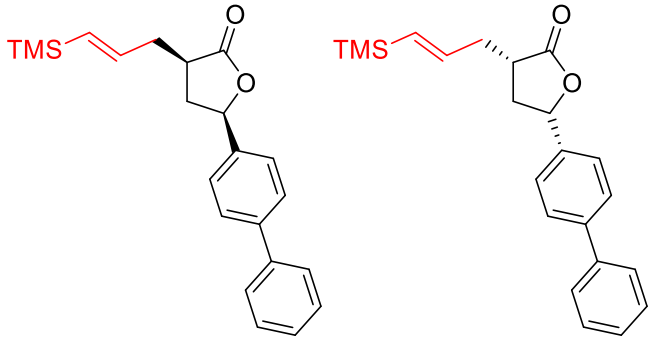
Following the **general procedure (I)** with methyl 4-benzoylbutyrate (82.5 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 ºC for 12 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave the title compound **3v** as a pale-yellow oil (79.5mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.59 – 7.50 (m, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 5.88 (dt, *J* = 18.5, 6.6 Hz, 1H), 5.64 (d, *J* = 18.5 Hz, 1H), 3.61 (s, 4H), 2.51 (dt, *J* = 14.0, 6.8 Hz, 1H), 2.30 (dddd, *J* = 32.6, 23.8, 15.8, 7.3 Hz, 3H), 2.11 (dq, *J* = 15.3, 7.4 Hz, 1H), 1.87 (dq, *J* = 14.1, 7.2, 6.8 Hz, 1H), -0.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 173.6, 142.8, 137.2, 133.2, 133.0, 128.6, 128.2, 51.5, 44.6, 39.7, 31.4, 26.4, -1.5.

HRMS (Dart positive) M = $C_{18}H_{26}O_3Si$: calculated $(M+H)^+$ m/z 319.1724; found $(M+H)^+$ m/z 319.1724.

[3*R*,5*R*(*S*)]-5-([1,1'-biphenyl]-4-yl)-3-((*E*)-3-(trimethylsilyl) allyl) dihydrofuran-2(3H)-one (5a)



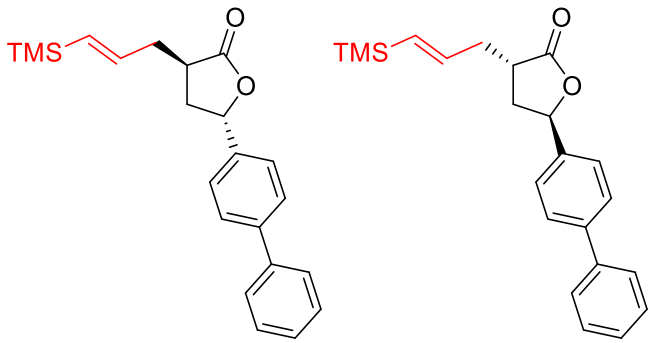
Following the **general procedure (I)** with 5-([1,1'-biphenyl]-4-yl) dihydrofuran-2(3H)-one (95.3 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 ºC for 12 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave a pair of enantiomers of the title compound **5a** as a yellow solid (28.4 mg, 20% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.58 (m, 4H), 7.49 – 7.35 (m, 5H), 6.01 (dt, *J* = 18.5, 6.5 Hz, 1H), 5.78 (dt, *J* = 18.4, 1.4 Hz, 1H), 5.42 (dd, *J* = 10.6, 5.9 Hz, 1H), 2.98 – 2.88 (m, 1H), 2.81 – 2.72 (m, 2H), 2.44 – 2.35 (m, 1H), 2.00 – 1.90 (m, 1H), 0.07 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 141.9, 141.5, 140.4, 138.1, 134.1, 128.8, 127.5, 127.4, 127.1, 126.0, 79.3, 40.7, 37.2, 36.9, -1.3.

HRMS (Dart positive) M = $C_{22}H_{26}O_2Si$: calculated $(M+H)^+$ m/z351.1775; found $(M+H)^+$ m/z 351.1772.

[3*R*,5*S*(*R*)]-5-([1,1'-biphenyl]-4-yl)-3-((*E*)-3-(trimethylsilyl) allyl) dihydrofuran-2(3H)-one (5a')



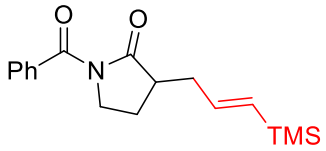
Following the **general procedure (I)** with 5-([1,1'-biphenyl]-4-yl) dihydrofuran-2(3H)-one (95.3 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave a pair of enantiomers of the title compound **5a'**as a yellow solid (30.9 mg, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.48 – 7.43 (m, 2H), 7.41 – 7.35 (m, 3H), 6.00 (dt, *J* = 18.4, 6.4 Hz, 1H), 5.82 (dt, *J* = 18.4, 1.4 Hz, 1H), 5.59 (dd, *J* = 7.8, 5.1 Hz, 1H), 2.85 (tdd, *J* = 9.1, 7.5, 4.5 Hz, 1H), 2.72 (dddd, *J* = 14.4, 6.0, 4.5, 1.4 Hz, 1H), 2.52 – 2.35 (m, 3H), 0.09 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 141.7, 141.1, 140.3, 138.8, 134.3, 128.8, 127.5, 127.41, 127.0, 125.5, 78.6, 38.3, 37.4, 35.6, -1.3.

HRMS-ESI (Dart positive) M = $C_{22}H_{26}O_2Si$: calculated $(M+H)^+$ m/z 351.1775; found $(M+H)^+$ m/z 351.1772.

(*E*)-1-benzoyl-3-(3-(trimethylsilyl) allyl) pyrrolidin-2-one (7a)



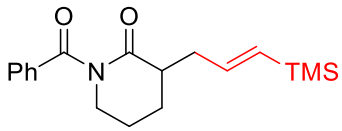
Following the **general procedure (I)** with 1-benzoylpyrrolidin-2-one (37.8 mg, 0.2 mmol), allyl-trimethyl-silane (57.1 mg, 0.5 mmol), DTBP (58.5 mg, 0.4 mmol), CuOAc (6.2 mg, 0.05 mmol), BINAP (31.1 mg, 0.05 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave the title compound **7a** as a pale-yellow oil (13.1 mg, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 5.98 (dt, *J* = 18.5, 6.5 Hz, 1H), 5.78 (d, *J* = 18.5 Hz, 1H), 3.96 (ddd, *J* = 11.5, 8.4, 3.1 Hz, 1H), 3.80 (ddd, *J* = 11.4, 9.1, 7.2 Hz, 1H), 2.81 – 2.60 (m, 2H), 2.36 – 2.24 (m, 2H), 1.84 (dq, *J* = 13.0, 9.1 Hz, 1H), 0.07 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 170.7, 142.1, 134.3, 134.0, 131.8, 128.8, 127.7, 44.5, 43.5, 37.3, 23.4, -1.3.

HRMS (Dart positive) M = $C_{17}H_{23}NO_2Si$: calculated $(M+H)^+$ m/z 302.1571; found $(M+H)^+$ m/z 302.1571.

(*E*)-2-benzoyl-6-(3-(trimethylsilyl) allyl) cyclohexan-1-one (7b)



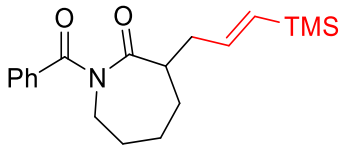
Following the **general procedure (I)** with 1-benzoylpiperidin-2-one (40.6 mg, 0.2 mmol), allyl-trimethyl-silane (57.1 mg, 0.5 mmol), DTBP (58.5 mg, 0.4 mmol), CuOAc (6.2 mg, 0.05 mmol), BINAP (31.1 mg, 0.05 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave the title compound **7b** as a pale-yellow oil (23.5 mg, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 5.96 (dt, *J* = 18.4, 6.6 Hz, 1H), 5.73 (d, *J* = 18.5 Hz, 1H), 3.90 – 3.74 (m, 2H), 2.70 (dt, *J* = 14.0, 5.2 Hz, 1H), 2.61 (dq, *J* = 14.3, 5.2 Hz, 1H), 2.35 – 2.25 (m, 1H), 2.06 (tq, *J* = 10.7, 5.7 Hz, 2H), 1.93 (dtd, *J* = 13.8, 9.7, 9.1, 5.9 Hz, 1H), 1.69 – 1.60 (m, 1H), 0.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 174.6, 143.2, 136.2, 133.5, 131.4, 128.1, 127.7, 46.0, 43.4, 37.9, 26.6, 21.8, -1.3.

HRMS (Dart positive) M = $C_{18}H_{25}NO_2Si$: calculated $(M+H)^+$ m/z 316.1727; found $(M+H)^+$ m/z 316.1727.

(*E*)-1-benzoyl-3-(3-(trimethylsilyl) allyl) azepan-2-one (7c)



Following the **general procedure (I)** with 2-benzoylcycloheptan-1-one (43.3 mg, 0.2 mmol), allyl-trimethyl-silane (57.1 mg, 0.5 mmol), DTBP (58.5 mg, 0.4 mmol), CuOAc (6.2 mg, 0.05 mmol), BINAP (31.1 mg, 0.05 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 -

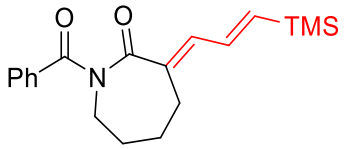
10% EtOAc in petroleum ether) gave the title compound **7c** as a pale-yellow oil (27.0 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 6.2 Hz, 1H), 7.40 – 7.35 (m, 2H), 6.00 (dt, *J* = 18.6, 6.2 Hz, 1H), 5.70 (d, *J* = 18.7 Hz, 1H), 4.54 (dd, *J* = 15.0, 5.2 Hz, 1H), 3.48 (dd, *J* = 15.1, 10.6 Hz, 1H), 2.87 (dd, *J* = 10.8, 5.6 Hz, 1H), 2.62 (dt, *J* = 12.9, 6.5 Hz, 1H), 2.16 – 1.96 (m, 3H), 1.85 (d, *J* = 15.5 Hz, 1H), 1.67 – 1.42 (m, 3H), 0.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 174.5, 144.1, 136.8, 132.4, 131.3, 128.1, 127.6, 45.5, 44.5, 39.2, 30.5, 28.7, 28.6, -1.2.

HRMS (Dart positive) M = $C_{19}H_{27}NO_2Si$: calculated $(M+H)^+$ m/z 330.1884; found $(M+H)^+$ m/z 330.1884.

(*E*)-1-benzoyl-3-((E)-3-(trimethylsilyl) allylidene) azepan-2-one (7c')



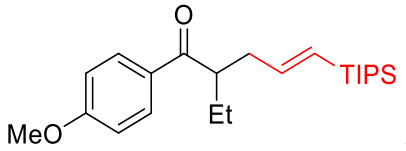
Following the **general procedure (I)** with 2-benzoylcycloheptan-1-one (43.3 mg, 0.2 mmol), allyl-trimethyl-silane (57.1 mg, 0.5 mmol), DTBP (58.5 mg, 0.4 mmol), CuOAc (6.2 mg, 0.05 mmol), BINAP (31.1 mg, 0.05 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 ^oC for 12 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave the title compound **7c'**as a pale-yellow oil (11.1 mg, 17% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 6.9, 1.6 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 6.87 – 6.75 (m, 2H), 6.42 – 6.26 (m, 1H), 4.05 – 3.84 (m, 2H), 2.73 (dd, *J* = 7.6, 3.9 Hz, 2H), 1.92 (q, *J* = 5.8 Hz, 2H), 1.85 (p, *J* = 5.7 Hz, 2H), 0.12 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 172.5, 145.5, 140.7, 137.0, 136.1, 135.5, 131.0, 128.2, 127.5, 44.0, 28.6, 28.0, 27.8, -1.6.

HRMS (Dart positive) M = $C_{19}H_{25}NO_2Si$: calculated $(M+H)^+$ m/z 328.1727; found $(M+H)^+$ m/z 328.1727.

(*E*)-2-ethyl-1-(4-methoxyphenyl)-5-(tri-iso-propylsilyl) pent-4-en-1-one (8a)



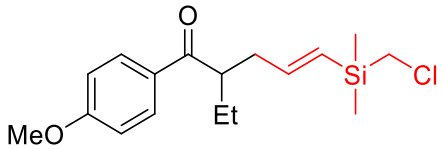
Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), allyl-tri-isopropyl-silane (198.4 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound **8a** as a yellow oil (104.9 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 6.95 – 6.90 (m, 2H), 5.97 (dt, *J* = 18.7, 6.6 Hz, 1H), 5.52 (dt, *J* = 18.8, 1.4 Hz, 1H), 3.86 (s, 3H), 3.44 (ddd, *J* = 13.4, 7.7, 5.7 Hz, 1H), 2.57 (dddd, *J* = 13.8, 7.6, 6.2, 1.5 Hz, 1H), 2.39 – 2.29 (m, 1H), 1.79 (dt, *J* = 13.7, 7.5 Hz, 1H), 1.65 – 1.53 (m, 1H), 1.03 (dd, *J* = 6.5, 2.3 Hz, 3H), 0.94 (d, *J* = 4.1 Hz, 18H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 163.3, 145.9, 130.7, 130.5, 126.3, 113.7, 55.4, 46.9, 40.1, 25.1, 18.5, 11.8, 10.7.

HRMS (Dart positive) M = $C_{23}H_{38}O_2Si$: calculated $(M+H)^+$ m/z 375.2714; found $(M+H)^+$ m/z 375.2711.

(*E*)-5-((chloromethyl)dimethyl silyl)-2-ethyl-1-(4-methoxyphenyl) pent-4-en-1-one (8b)



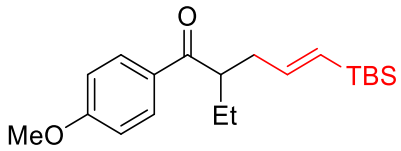
Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), allyl (Chloromethyl)dimethyl-silane (148.7 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound **8b** as a yellow oil (82.7 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 6.95 – 6.89 (m, 2H), 6.04 (dt, *J* = 18.6, 6.7 Hz, 1H), 5.61 (dt, *J* = 18.6, 1.4 Hz, 1H), 3.85 (s, 3H), 3.41 (tt, *J* = 7.7, 5.7 Hz, 1H), 2.67 (d, *J* = 1.2 Hz, 2H), 2.54 (dddd, *J* = 14.1, 7.8, 6.3, 1.5 Hz, 1H), 2.32 (dt, *J* = 12.8, 6.5 Hz, 1H), 1.83 – 1.71 (m, 1H), 1.62 – 1.49 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.07 (s, 6H).

^{13}C NMR (101 MHz, C $CDCl_3$) δ 202.0, 163.3, 147.1, 130.5, 130.4, 127.8, 113.7, 55.4, 46.6, 39.3, 30.4, 25.1, 11.7, -4.6, -4.6.

HRMS (Dart positive) M = $C_{17}H_{25}ClO_2Si$: calculated $(M+H)^+$ m/z 325.1385; found $(M+H)^+$ m/z 325.1385.

(*E*)-5-(tert-butyl dimethyl silyl)-2-ethyl-1-(4-methoxyphenyl) pent-4-en-1-one (8c)



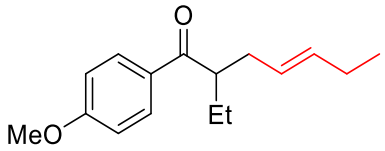
Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), allyl tert-butyl-dimethyl-silane (156.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the title compound **8c** as a yellow oil (88.3 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 6.96 – 6.90 (m, 2H), 5.94 (dt, *J* = 18.5, 6.6 Hz, 1H), 5.62 (dt, *J* = 18.5, 1.4 Hz, 1H), 3.86 (s, 3H), 3.42 (ddd, *J* = 13.4, 7.7, 5.9 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.36 – 2.27 (m, 1H), 1.84 – 1.72 (m, 1H), 1.63 – 1.51 (m, 1H), 0.86 (s, 3H), 0.77 (s, 9H), -0.09 (d, *J* = 8.1 Hz, 6H).

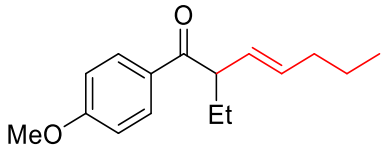
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 163.3, 145.3, 130.7, 130.5, 129.4, 113.7, 55.43, 46.9, 39.6, 26.3, 25.1, 16.3, 11.8, -6.2.

HRMS (Dart positive) M = $C_{20}H_{32}O_2Si$: calculated $(M+H)^+$ m/z 333.2244; found $(M+H)^+$ m/z 333.2243.

(*E*)-2-ethyl-1-(4-methoxyphenyl) hept-4-en-1-one (8d)



(*E*)-2-ethyl-1-(4-methoxyphenyl) hept-3-en-1-one(8d')



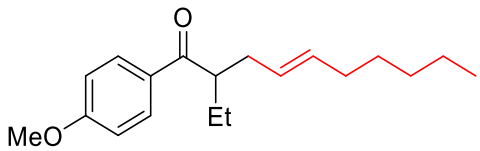
Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), 1-pentene (140.2 mg, 1.6 mmol, 4.0 equiv.), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 ºC for 24 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the mixture of **8d** and **8d'** as a yellow oil (41.1 mg, 42% yield, **8d:8d'** = 3.5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.87 (m, 2H), 6.98 – 6.89 (m, 2H), 5.57 – 5.19 (m, 2H), 3.87 (d, *J* = 8.3 Hz, 3H), 3.35 (h, *J* = 7.1 Hz, 1H), 2.41 (dq, *J* = 13.9, 6.8 Hz, 1H), 2.19 (dq, *J* = 13.9, 7.0 Hz, 1H), 1.93 (h, *J* = 7.6 Hz, 2H), 1.78 (dq, *J* = 15.0, 7.6 Hz, 1H), 1.58 (dq, *J* = 13.6, 7.2 Hz, 1H), 0.96 – 0.82 (m, 6H).

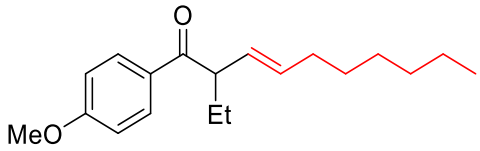
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 163.2, 134.2, 133.4, 130.7, 130.5, 126.2, 126.0, 113.6, 55.4, 47.5, 47.4, 35.1, 29.7, 25.5, 24.9, 20.5, 14.2, 13.7, 11.8

HRMS (Dart positive) M = $C_{16}H_{22}O_2$: calculated $(M+H)^+$ m/z 247.1693; found $(M+H)^+$ m/z 247.1693.

(*E*)-2-ethyl-1-(4-methoxyphenyl) dec-4-en-1-one (8e)



(*E*)-2-ethyl-1-(4-methoxyphenyl) dec-3-en-1-one (8e')



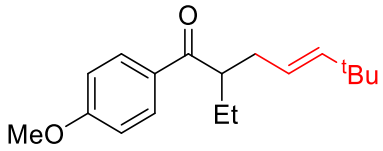
Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), 1-octene (112.2 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 24 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the mixture of **8e** and **8e'** as a yellow oil (55.3 mg, 48% yield, **8d:8d'** = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.87 (m, 2H), 6.96 – 6.87 (m, 2H), 5.46 – 5.24 (m, 2H), 3.85 (s, 3H), 3.39 – 3.27 (m, 1H), 2.45 – 2.34 (m, 1H), 2.17 (dq, *J* = 12.4, 6.5, 5.8 Hz, 1H), 1.89 (q, *J* = 6.5 Hz, 2H), 1.76 (dt, *J* = 13.6, 7.6 Hz, 1H), 1.61 – 1.51 (m, 1H), 1.26 – 1.15 (m, 6H), 0.84 (q, *J* = 7.3 Hz, 6H).

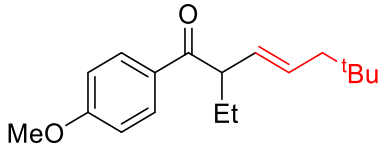
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 163.3, 163.2, 132.7, 131.8, 130.7, 130.4, 127.1, 126.5, 113.6, 55.3, 47.5, 35.1, 32.4, 31.4, 31.2, 29.2, 29.0, 25.0, 24.9, 22.5, 22.4, 14.0, 13.9, 11.8, 11.7.

HRMS (Dart positive) M = $C_{19}H_{28}O_2$: calculated $(M+H)^+$ m/z 289.2162; found $(M+H)^+$ m/z 289.2162.

(*E*)-2-ethyl-1-(4-methoxyphenyl)-6,6-dimethylhept-4-en-1-one (8f)



(*E*)-2-ethyl-1-(4-methoxyphenyl)-6,6-dimethylhept-3-en-1-one (8f')



Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), 4,4-dimethylpent-1-ene (98.2 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 24 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the mixture of **8e** and **8e'**as a pale-yellow oil (49.4 mg, 45% yield, **8d:8d'** = 2.2:1).

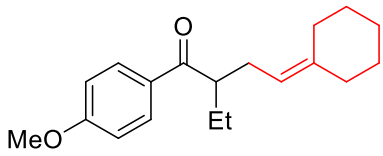
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dq, *J* = 9.9, 2.6 Hz, 2H), 6.97 – 6.86 (m, 2H), 5.42 (dt, *J* = 15.4, 1.3 Hz, 1H), 5.26 – 5.16 (m, 1H), 3.85 (s, 3H), 3.33 (tt, *J* = 7.7, 5.6 Hz, 1H), 2.42 – 2.30 (m, 1H), 2.18 (dddd, *J* = 13.6, 7.4, 6.2, 1.2 Hz, 1H), 1.77 (dt, *J* = 13.5, 7.6 Hz, 1H), 1.63 – 1.47 (m, 1H), 0.93 – 0.80 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 200.5, 163.3, 163.2, 143.6, 131.1, 130.9, 130.5, 130.4, 130.0, 129.9, 128.9, 121.7, 113.6, 113.6, 55.4, 47.7, 47.0, 41.7 35.5, 32.7, 30.9, 29.5, 29.3, 26.3, 24.9, 11.9, 11.8.

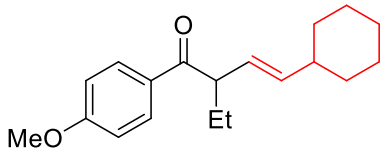
HRMS (Dart positive) (**8f**) M = $C_{18}H_{26}O_2$: calculated $(M+H)^+$ m/z 275.2006; found $(M+H)^+$ m/z 275.2006.

HRMS (Dart positive) (**8f'**) M = $C_{18}H_{26}O_2$: calculated $(M+H)^+$ m/z 275.2006; found $(M+H)^+$ m/z 275.2005.

4-cyclohexylidene-2-ethyl-1-(4-methoxyphenyl) butan-1-one (8g)



(*E*)-4-cyclohexyl-2-ethyl-1-(4-methoxyphenyl) but-3-en-1-one(8g')



Following the **general procedure (II)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), vinyl cyclohexane (110.2 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the mixture of **8j** and **8j'** as a pale-yellow oil (35.6 mg, 31% yield, **8g:8g'** = 10:1).

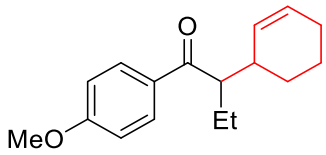
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 6.94 – 6.91 (m, 2H), 5.01 (t, *J* = 7.5 Hz, 1H), 3.86 (s, 3H), 3.40 – 3.19 (m, 1H), 2.37 (dt, *J* = 14.2, 7.1 Hz, 1H), 2.21 (dt, *J* = 14.3, 7.2 Hz, 1H), 2.08 (t, *J* = 5.9 Hz, 2H), 1.98 (t, *J* = 5.9 Hz, 2H), 1.77 (dq, *J* = 15.3, 7.7 Hz, 2H), 1.62 – 1.53 (m, 2H), 1.43 (d, *J* = 6.2 Hz, 4H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 163.2, 141.3, 130.7, 130.7, 130.5, 130.4, 118.4, 113.7 113.6, 55.4, 47.8, 47.4, 37.1, 29.8, 28.7, 28.5, 27.7, 26.8, 24.9, 11.9.

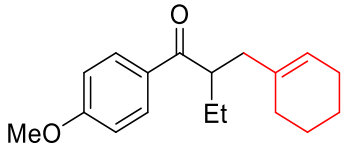
HRMS (Dart positive) (**8g**) M = $C_{19}H_{26}O_2$: calculated $(M+H)^+$ m/z 287.2006; found $(M+H)^+$ m/z 287.2005.

HRMS (Dart positive) (**8g'**) M = $C_{19}H_{26}O_2$: calculated $(M+H)^+$ m/z 287.2006; found $(M+H)^+$ m/z 287.2006.

2-(cyclohex-2-en-1-yl)-1-(4-methoxyphenyl) butan-1-one (8h)



2-(cyclohex-1-en-1-yl)-1-(4-methoxyphenyl) butan-1-one (8h')



Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), cyclohexene (82.1 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the mixture of **8h** and **8h'** as a pale-yellow oil (45.4 mg, 44% yield, **8h:8h'** = 1:1.6).

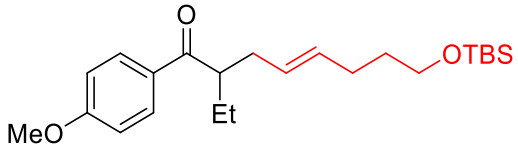
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 6.97 – 6.91 (m, 2H), 5.73 (s, 1H), 5.66 (dq, *J* = 10.0, 3.4 Hz, 1H), 5.46 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.87 (s, 4H), 3.28 (ddd, *J* = 9.8, 7.5, 3.7 Hz, 1H), 2.62 – 2.46 (m, 1H), 1.95 (t, *J* = 2.6 Hz, 2H), 1.87 – 1.78 (m, 1H), 1.71 (ddd, *J* = 12.2, 6.8, 3.3 Hz, 2H), 1.35 (d, *J* = 15.5 Hz, 3H), 0.81 (td, *J* = 7.4, 4.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 202.7, 163.3, 163.2, 131.7, 131.4, 130.5, 130.4, 130.1, 128.7, 128.6, 128.2, 113.7, 113.7, 55.4, 52.1, 51.5, 38.1, 37.6, 31.5, 31.4, 30.1, 27.7, 26.0, 25.2, 25.1, 22.6, 21.9, 21.7, 21.4, 12.1.

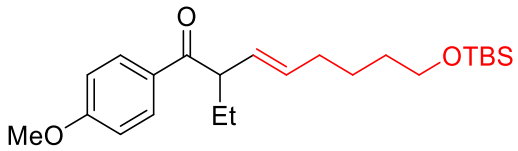
HRMS (Dart positive) (**8h**) M = $C_{17}H_{22}O_2$: calculated $(M+H)^+$ m/z 259.1693; found $(M+H)^+$ m/z 259.1693.

HRMS (Dart positive) (**8h'**) M = $C_{17}H_{22}O_2$: calculated $(M+H)^+$ m/z 259.1693; found $(M+H)^+$ m/z 259.1692.

(*E*)-8-((tert-butyldimethylsilyl) oxy)-2-ethyl-1-(4-methoxyphenyl) oct-4-en-1-one(8i)



(*E*)-8-((tert-butyldimethylsilyl) oxy)-2-ethyl-1-(4-methoxyphenyl) oct-3-en-1-one (8i')



Following the **general procedure (III)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), tert-butyl(5-hexenyloxy) dimethyl silane (214.4 mg, 1.0 mmol), Ag_2CO_3 (200.3 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol), HOAc (24.0 mg, 0.4 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 ºC for 24 h. Purification by silica gel flash chromatography (0 - 5% EtOAc in petroleum ether) gave the mixture of **8i** and **8i'** as a yellow oil (59.3 mg, 38% yield, **8i:8i'** = 4:1).

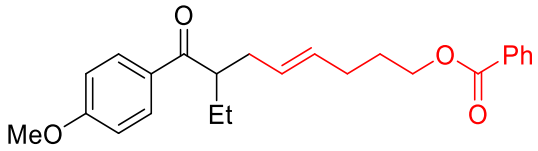
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 8.9, 2.2 Hz, 2H), 6.92 (dq, *J* = 7.2, 2.8 Hz, 2H), 5.55 – 5.25 (m, 2H), 3.84 (d, *J* = 2.1 Hz, 3H), 3.55 (dtd, *J* = 19.2, 6.6, 2.0 Hz, 2H), 3.32 (q, *J* = 6.1, 5.5 Hz, 1H), 2.40 (dt, *J* = 14.2, 7.1 Hz, 1H), 2.17 (dt, *J* = 12.9, 6.5 Hz, 1H), 2.10 – 1.85 (m, 2H), 1.83 – 1.64 (m, 1H), 1.51 (dtt, *J* = 19.1, 12.3, 6.6 Hz, 3H), 0.85 (qd, *J* = 7.6, 6.7, 2.1 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 163.2, 132.0, 131.0, 130.6, 130.5, 130.4, 127.5, 127.0, 113.6, 113.6, 62.6, 62.5, 55.3, 52.0, 47.4, 47.3, 35.0, 32.7, 32.4, 29.7, 28.7, 25.9, 25.0, 24.9, 23.5, 18.2, 11.8, 11.7, -5.4, -5.3.

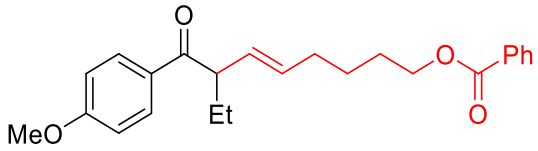
HRMS (Dart positive) (**8i**) M = $C_{23}H_{38}O_3Si$: calculated $(M+H)^+$ m/z 391.2663; found $(M+H)^+$ m/z 391.2661.

HRMS (Dart positive) (**8i'**) M = $C_{23}H_{38}O_3Si$: calculated $(M+H)^+$ m/z 391.2663; found $(M+H)^+$ m/z 391.2663.

(*E*)-7-(4-methoxybenzoyl) non-4-en-1-yl benzoate (8j)



(*E*)-7-(4-methoxybenzoyl) non-5-en-1-yl benzoate (8j')



Following the **general procedure (II)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), benzoic acid hex-5-enyl ester (204.3 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 ºC for 24 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave the mixture of **8j** and **8j'** as a yellow oil (50.7 mg, 33% yield, **8j:8j'** = 3.6:1).

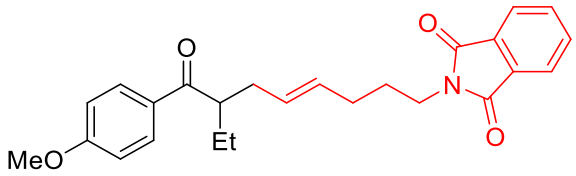
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.98 – 7.89 (m, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 6.94 – 6.85 (m, 2H), 5.42 (ttt, *J* = 14.9, 10.0, 5.2 Hz, 2H), 4.25 (dt, *J* = 24.1, 6.6 Hz, 2H), 3.82 (d, *J* = 3.5 Hz, 3H), 3.41 – 3.28 (m, 1H), 2.44 (tt, *J* = 13.0, 6.0 Hz, 1H), 2.25 – 2.15 (m, 1H), 2.07 (q, *J* = 6.8 Hz, 2H), 1.74 (td, *J* = 15.1, 13.4, 6.9 Hz, 3H), 1.54 (td, *J* = 13.6, 7.8 Hz, 1H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 202.2, 166.5, 166.4, 163.3, 163.2, 132.7, 132.7, 130.9, 130.5, 130.4, 129.9, 129.4, 129.3, 128.4, 128.2, 127.9, 113.6, 64.3, 64.2, 55.3, 47.2, 47.1, 35.0, 29.6, 28.8, 28.4, 28.3, 25.1, 25.0, 23.6, 11.7, 11.6.

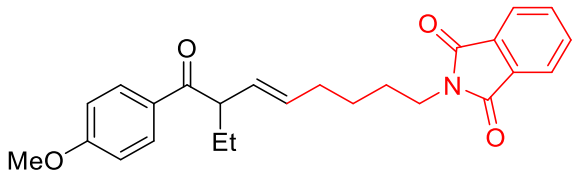
HRMS (Dart positive) (**8j**) M = $C_{24}H_{28}O_4$: calculated $(M+H)^+$ m/z 381.2060; found $(M+H)^+$ m/z 381.2059.

HRMS (Dart positive) (**8j'**) M = $C_{24}H_{28}O_4$: calculated $(M+H)^+$ m/z 381.2060; found $(M+H)^+$ m/z 381.2058.

(*E*)-2-(7-(4-methoxybenzoyl) non-5-en-1-yl) isoindoline-1,3-dione (8k)



(*E*)-2-(7-(4-methoxybenzoyl) non-4-en-1-yl) isoindoline-1,3-dione (8k')



Following the **general procedure (II)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), *N*-(5-hexenyl) phthalimide (229.3 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0-15% EtOAc in petroleum ether) gave the mixture of **8k** and **8k'** as a yellow oil (46.7 mg, 29% yield, **8k:8k'** = 2.4:1).

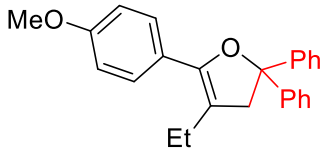
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.79 (t, *J* = 3.7 Hz, 2H), 7.67 (q, *J* = 4.5 Hz, 2H), 6.89 (t, *J* = 7.0 Hz, 2H), 5.36 (dq, *J* = 11.7, 6.3, 5.8 Hz, 2H), 3.82 (d, *J* = 7.3 Hz, 3H), 3.59 (dt, *J* = 27.0, 7.8 Hz, 2H), 3.32 (p, *J* = 6.7 Hz, 1H), 2.38 (ddd, *J* = 26.6, 12.9, 6.5 Hz, 1H), 2.17 – 1.91 (m, 3H), 1.78 – 1.57 (m, 3H), 1.52 (p, *J* = 6.7, 5.9 Hz, 1H), 0.81 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 202.1, 168.2, 163.2, 163.1, 133.8, 133.7, 132.0, 131.9, 130.8, 130.5, 130.4, 120., 128.3, 127.7, 123.0, 123.0, 122.9, 113.6, 113.5, 55.3, 55.2, 47.2, 47.1, 37.5, 37.4, 34.9, 29.7, 29.6, 28.3, 28.0, 25.0, 24.8, 11.7, 11.6.

HRMS (Dart positive) (8k) M = $C_{25}H_{27}NO_2$: calculated $(M+H)^+$ m/z 406.2013; found $(M+H)^+$ m/z 406.2012.

HRMS (Dart positive) (8k') M = $C_{25}H_{27}NO_2$: calculated $(M+H)^+$ m/z 406.2013; found $(M+H)^+$ m/z 406.2013.

4-ethyl-5-(4-methoxyphenyl)-2,2-diphenyl-2,3-dihydrofuran (9a)



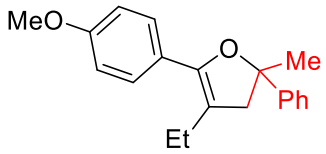
Following the **general procedure (II)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), 1,1-diphenylethylene (180.3 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0-2% EtOAc in petroleum ether) gave the title compound **9a** as a white solid (99.7 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.8, 1.5 Hz, 2H), 7.51 (dt, *J* = 8.2, 1.4 Hz, 4H), 7.33 (t, *J* = 7.7 Hz, 4H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 3.51 (s, 2H), 2.35 (q, *J* = 7.4 Hz, 2H), 1.08 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 146.9, 146.2, 128.4, 128.1, 126.9, 126.0, 125.8, 124.63, 113.6, 109.3, 87.5, 55.2, 48.8, 20.2, 13.1

HRMS (FI positive) M = $C_{25}H_{24}O_2$: calculated $(M)^+$ m/z 356.1771; found $(M)^+$ m/z 356.1773.

4-ethyl-5-(4-methoxyphenyl)-2-methyl-2-phenyl-2,3-dihydrofuran (9b)



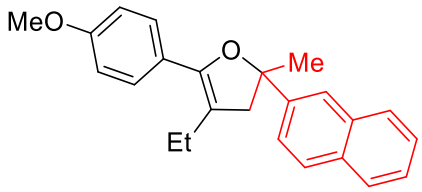
Following the **general procedure (II)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), 2-phenyl-1-propene (118.2 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9b** as a colorless oil. The product was easily decomposed on the column. (GC yield:64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 3.04 – 2.92 (m, 2H), 2.30 (dp, *J* = 21.9, 7.2 Hz, 2H), 1.71 (s, 3H), 1.05 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 148.4, 146.1, 128.4, 128.2, 126.6, 125.0, 124.5, 113.6, 109.03, 84.0, 55.3, 49.1, 29.5, 20.2, 13.2.

HRMS (Dart positive) M = $C_{20}H_{22}O_2$: calculated $(M+H)^+$ m/z 295.1693; found $(M+H)^+$ m/z 295.1693.

4-ethyl-5-(4-methoxyphenyl)-2-methyl-2-(naphthalen-2-yl)-2,3-dihydrofuran (9c)



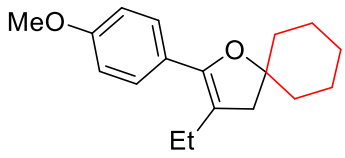
Following the **general procedure (II)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), 2-isopropenylnaphthalene (168.2 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9c** as a colorless oil. The product was easily decomposed on the column and 60% of GC yield was determined using *n*-dodecane as an internal standard.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 3H), 7.58 (d, *J* = 8.9 Hz, 3H), 7.46 (td, *J* = 7.3, 6.5, 4.1 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.07 (q, *J* = 15.2 Hz, 2H), 2.32 (qq, *J* = 15.2, 7.8 Hz, 2H), 1.81 (s, 3H), 1.07 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.1, 146.2, 145.6, 133.1, 132.3, 130.6, 128.5, 128.1, 128.1, 127.5, 126.0, 125.6, 123.6, 122.6, 113.6, 109.1, 84.1, 55.3, 49.0, 29.4, 20.2, 13.2.

HRMS (Dart positive) M = $C_{24}H_{24}O_2$: calculated $(M+H)^+$ m/z 345.1849; found $(M+H)^+$ m/z 345.1849.

3-ethyl-2-(4-methoxyphenyl)-1-oxaspiro [4.5] dec-2-ene (9d)



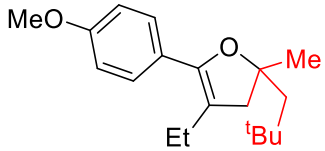
Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), methylene cyclohexane (96.2 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9d** as a pale-yellow oil. The product was easily decomposed on the column and 61% of GC yield was determined using *n*-dodecane as an internal standard.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 6.91 – 6.86 (m, 2H), 3.81 (s, 3H), 2.53 (s, 2H), 2.29 (q, *J* = 7.5 Hz, 2H), 1.84 – 1.74 (m, 4H), 1.63 (d, *J* = 11.2 Hz, 2H), 1.47 (td, *J* = 13.9, 12.3, 7.0 Hz, 4H), 1.08 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 145.9, 128.4, 125.4, 113.4, 108.8, 82.8, 55.2, 45.4, 37.2, 25.4, 23.1, 20.4, 13.2.

HRMS (FI positive) M = $C_{18}H_{24}O_2$: calculated $(M)^+$ m/z 272.1771; found $(M)^+$ m/z 272.1772.

4-ethyl-5-(4-methoxyphenyl)-2-methyl-2-neopentyl-2,3-dihydrofuran (9e)



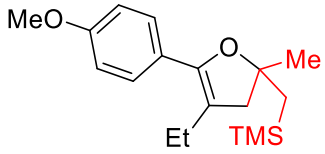
Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), 2,4,4-trimethyl-1-pentene (112.2 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL).The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9e** as a yellow oil. The product was easily decomposed on the column and 60% of GC yield was determined using *n*-dodecane as an internal standard.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.76 (d, *J* = 15.2 Hz, 1H), 2.46 (d, *J* = 15.2 Hz, 1H), 2.28 (dt, *J* = 11.2, 7.4 Hz, 2H), 1.79 (d, *J* = 14.5 Hz, 1H), 1.69 (d, *J* = 14.5 Hz, 1H), 1.41 (s, 3H), 1.25 (s, 3H), 1.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 145.6, 128.3, 125.5, 113.5, 108.9, 84.1, 55.3, 53.6, 48.4, 31.4, 29.7, 28.3, 20.3, 13.2.

HRMS (FI positive) M = $C_{19}H_{28}O_2$: calculated $(M)^+$ m/z 288.2089; found $(M)^+$ m/z 288.2087.

((4-ethyl-5-(4-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl) methyl) trimeth-yl silane (9f)



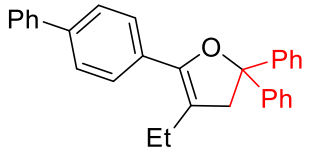
Following the **general procedure (I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), trimethyl(2-methylallyl) silane (128.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 ºC for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9f** as a pale-yellow oil. The product was easily decomposed on the column and 47% of GC yield was determined using *n*-dodecane as an internal standard.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 6.90 – 6.84 (m, 2H), 3.81 (s, 3H), 2.66 (d, J = 14.9 Hz, 1H), 2.51 (d, J = 15.1 Hz, 1H), 2.29 (q, J = 7.6 Hz, 2H), 1.41 (s, 3H), 1.26 (s, 2H), 1.07 (t, J = 7.5 Hz, 3H), 0.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 145.8, 128.3, 125.5, 113.4, 109.0, 83.8, 55.2, 48.4, 31.7, 29.7, 20.4, 13.2.

HRMS (Dart positive) M = $C_{18}H_{28}O_2Si$: calculated $(M+H)^+$ m/z 305.1931; found $(M+H)^+$ m/z 305.1932.

5-([1,1'-biphenyl]-4-yl)-4-ethyl-2,2-diphenyl-2,3-dihydrofuran (9g)



Following the **general procedure (II)** with 4-phenylbutyrophenone (89.7 mg, 0.4 mmol),

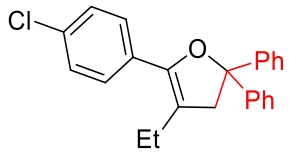
1,1-diphenylethylene (180.3 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9g** as a white solid (99.1 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.52 (dd, *J* = 7.8, 4.2 Hz, 4H), 7.42 (d, *J* = 7.7 Hz, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.23 (q, *J* = 7.6 Hz, 5H), 7.13 (t, *J* = 6.3 Hz, 2H), 3.44 (s, 2H), 2.31 (q, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 146.2, 140.7, 140.5, 130.9, 128.8, 128.2, 127.4, 127.3, 127.0, 126.9, 126.8, 125.8, 111.4, 87.7, 49.0, 20.3, 13.0.

HRMS (Dart positive) M = $C_{30}H_{26}O$: calculated $(M+H)^+$ m/z 403.2056; found $(M+H)^+$ m/z 403.2054.

5-(4-chlorophenyl)-4-ethyl-2,2-diphenyl-2,3-dihydrofuran (9h)



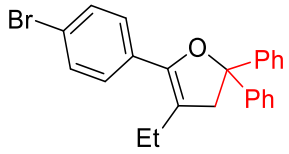
Following the **general procedure (II)** with 1-(4-chlorophenyl) butan-1-one (73.1 mg, 0.4 mmol), 1,1-diphenylethylene (180.3 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9h** as a pale-yellow oil (105.2 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.70 – 7.64 (m, 4H), 7.55 – 7.48 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 3H), 7.40 – 7.34 (m, 2H), 3.68 (s, 2H), 2.49 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 145.4, 133.4, 130.3, 128.3, 128.3, 128.2, 127.0, 125.7, 111.7, 87.8, 48.8, 20.2, 12.9.

HRMS (Dart positive) M = $C_{24}H_{21}ClO$: calculated $(M+H)^+$ m/z 361.1354; found $(M+H)^+$ m/z 361.1354.

5-(4-bromophenyl)-4-ethyl-2,2-diphenyl-2,3-dihydrofuran (9i)



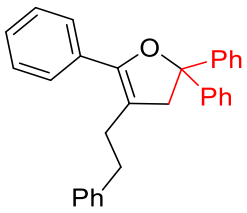
Following the **general procedure (II)** with 4'-bromobutyrophenone (90.8 mg, 0.4 mmol), 1,1-diphenylethylene (180.3 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9i** as a yellow oil (114.8 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 5.0 Hz, 8H), 7.42 (d, *J* = 7.0 Hz, 4H), 7.34 (t, *J* = 7.8 Hz, 2H), 3.64 (s, 2H), 2.45 (q, *J* = 7.1, 6.7 Hz, 2H), 1.19 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 145.5, 131.3, 130.8, 128.6, 128.2, 127.0, 125.7, 121.6, 111.9, 87.8, 48.8, 20.2, 12.9.

HRMS (Dart positive) M = $C_{24}H_{21}BrO$: calculated $(M+H)^+$ m/z 405.0849; found $(M+H)^+$ m/z 405.0844.

4-phenethyl-2,2,5-triphenyl-2,3-dihydrofuran (9j)



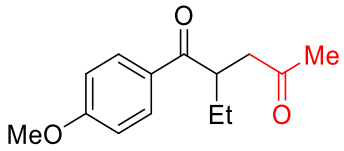
Following the g**eneral procedure (II)** with 1,4-diphenylbutan-1-one (89.7 mg, 0.4 mmol), 1,1-diphenylethylene (180.3 mg, 1.0 mmol), AgOAc (200.3 mg, 1.2 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and dioxane (2.0 mL). The reaction mixture was stirred at 120 °C for 24 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9j** as a white solid (101.4 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.4, 5.5 Hz, 6H), 7.45 – 7.36 (m, 7H), 7.34 – 7.23 (m, 5H), 7.14 (d, *J* = 6.5 Hz, 2H), 3.58 (s, 2H), 2.85 (t, *J* = 7.7 Hz, 2H), 2.70 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.90, 146.67, 141.50, 131.69, 128.43, 128.33, 128.15, 128.13, 127.92, 127.11, 126.98, 125.90, 125.82, 108.55, 87.84, 49.36, 34.67, 29.06.

HRMS (FI positive) M = $C_{30}H_{26}O$: calculated $(M)^+$ m/z 402.1978; found $(M)^+$ m/z 402.1981.

2-ethyl-1-(4-methoxyphenyl) pentane-1,4-dione(9k)



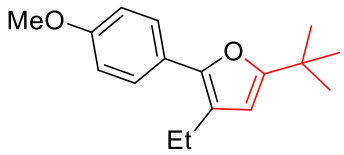
Following the **general procedure I** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), trimethyl(prop-1-en-2-yloxy)-silane (130.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 ºC for 12 h. Purification by silica gel flash chromatography (0 - 20% EtOAc in petroleum ether) gave the title compound **9k** as a pale-yellow oil (28.2 mg, 30% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 2H), 6.95 – 6.90 (m, 2H), 3.84 (s, 4H), 3.12 (dd, *J* = 18.0, 9.2 Hz, 1H), 2.55 (dd, *J* = 18.0, 4.3 Hz, 1H), 2.14 (s, 3H), 1.76 – 1.64 (m, 1H), 1.49 (dp, *J* = 14.6, 7.3 Hz, 1H), 0.85 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 201.6, 163.3, 130.6, 129.6, 113.7, 55.4, 44.6, 42.0, 30.1, 25.5, 11.5.

HRMS (Dart positive) M = $C_{14}H_{18}O_3$: calculated $(M+H)^+$ m/z 235.1329; found $(M+H)^+$ m/z 235.1327.

5-(tert-butyl)-3-ethyl-2-(4-methoxyphenyl) furan (9l)



Following the **general procedure I** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), (1-tert-butylvinyloxy)-trimethyl-silane (172.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0

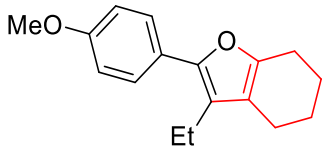
mL). The reaction mixture was stirred at 120 °C for 12 h. The reaction was quench with hydrochloric acid after finished. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9l** as a colorless oil (51.0 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.00 – 6.94 (m, 2H), 5.99 (s, 1H), 3.85 (s, 3H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.36 (s, 9H), 1.27 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 158.1, 145.8, 126.6, 125.3, 121.8, 113.9, 105.1, 55.2, 32.6, 29.1, 19.2, 14.5.

HRMS (Dart positive) M = $C_{17}H_{22}O_2$: calculated $(M+H)^+$ m/z 259.1693; found $(M+H)^+$ m/z 259.1690

3-ethyl-2-(4-methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran (9m)



Following the **general procedure I** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), (cyclohex-1-en-1-yloxy)-trimethyl-silane (170.3 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **9m** as a colorless oil (19.2 mg, 19% yield).

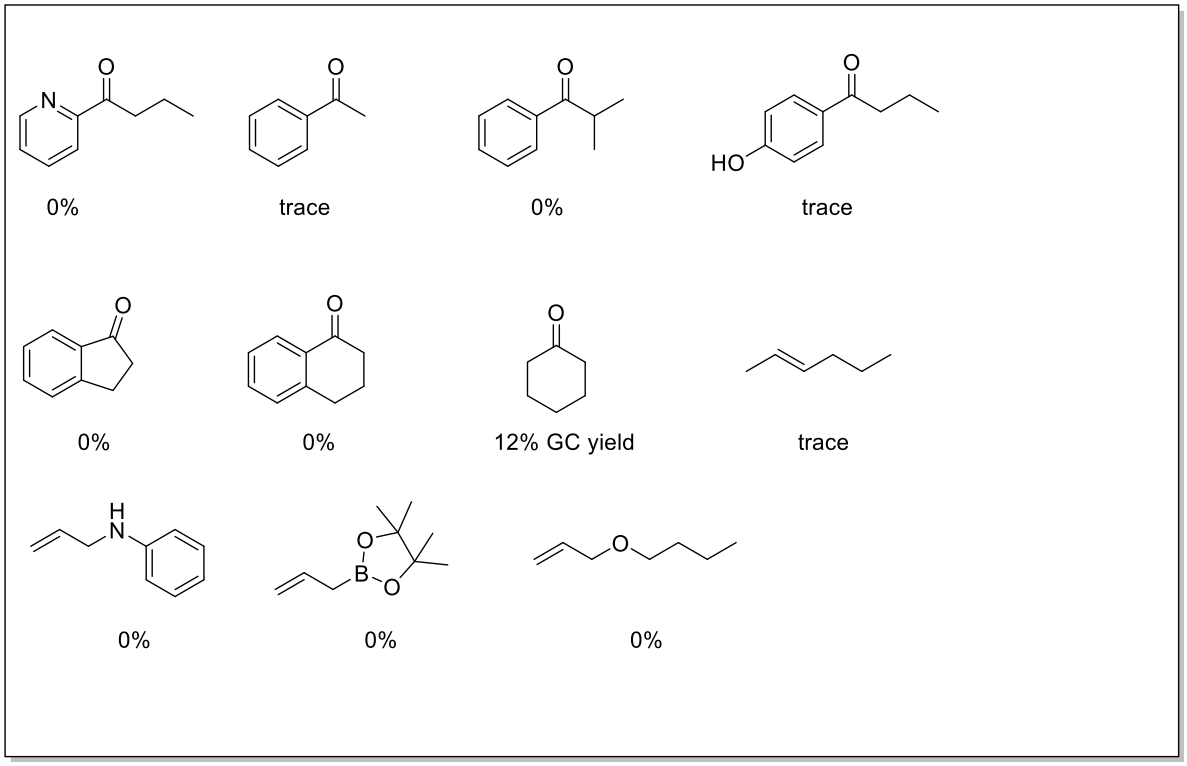
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 6.96 – 6.92 (m, 2H), 3.84 (s, 3H), 2.64 (tt, *J* = 6.3, 1.9 Hz, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.42 (tt, *J* = 6.0, 1.9 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.78 (pd, *J* = 5.6, 4.7, 2.3 Hz, 2H), 1.21 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 149.1, 146.2, 126.7, 125.2, 121.1, 119.2, 113.9, 55.2, 23.2, 23.0, 23.0, 20.8, 17.6, 14.5.

HRMS-ESI (Dart positive) M = $C_{17}H_{20}O_2$: calculated $(M+H)^+$ m/z 257.1536; found $(M+H)^+$ m/z 257.1534.

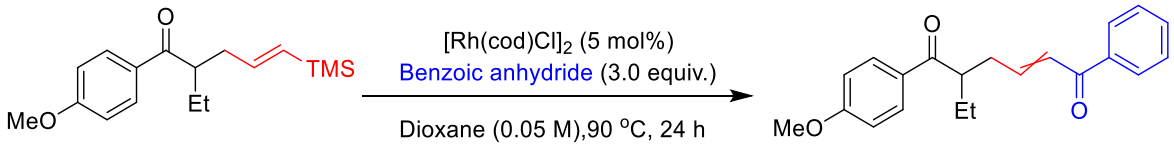
Examples of non-reactive substrate

Table S6. Unsuccessful Example



Synthetic Applications

I. Acylation with Benzoic Anhydride (Narasaka Acylation)

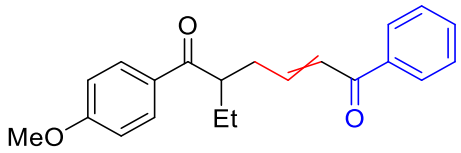


3a **10**

In a nitrogen-filled glovebox, a 20 mL Schlenk tube equipped with a stir bar was charged with $[Rh(COD)Cl]_2$ (5.0 mg, 0.01 mmol, 0.05 equiv.) and benzoic anhydride (135.7 mg, 0.6 mmol, 3.0 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then **3a** (58.1 mg, 0.2 mmol, 1.0 equiv.) and dioxane (4.0 mL) were added in turn to the Schlenk tube through the rubber septum using syringes and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 90 °C for 24

h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of EtOAc, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and then purified by flash chromatography on silica gel to provide the corresponding product **10** (57.3 mg, 89% yield, E: Z = 4:1).

(E/Z)5-ethyl-6-(4-methoxyphenyl)-1-phenylhex-2-ene-1,6-dione (10)

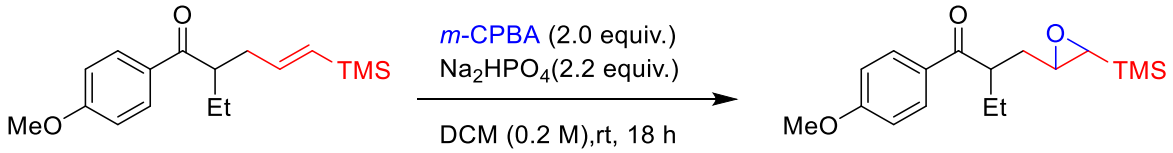


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.02 – 6.91 (m, 3H), 6.86 (d, *J* = 15.4 Hz, 1H), 3.85 (s, 3H), 3.55 (p, *J* = 6.7 Hz, 1H), 2.78 (dt, *J* = 14.7, 7.3 Hz, 1H), 2.50 (dt, *J* = 14.1, 6.6 Hz, 1H), 1.83 (dp, *J* = 14.7, 7.4 Hz, 1H), 1.64 (dp, *J* = 14.0, 7.1 Hz, 1H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 190.6, 163.5, 146.8, 137.6, 132.6, 130.5, 130.1, 129.9, 128.5, 128.4, 127.5, 113.8, 55.4, 46.0, 34.6, 25.6, 11.5.

HRMS (Dart positive) M = $C_{21}H_{22}O_3$: calculated $(M+H)^+$ m/z 323.1642; found $(M+H)^+$ m/z 323.1642.

II. Epoxidation with *m*-CPBA (Prilezhaev Epoxidation)

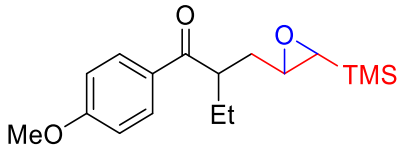


3a **11**

In a nitrogen-filled glovebox, a 20 mL Schlenk tube equipped with a stir bar was charged with 3-chloroperbenzoic acid (*m*-CPBA) (69.0 mg, 0.4 mmol, 2.0 equiv.), Na_2HPO_4 (62.5 mg, 0.44 mmol, 2.2 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then **3a** (58.1 mg, 0.2 mmol, 1.0 equiv.) and DCM (1.0 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at room temperature for 18 h. Upon reaction finished, the reaction mixture was diluted with 10 mL of EtOAc, followed by filtration through a pad of silica gel. The filtrate was concentrated

under reduced pressure, and then purified by flash chromatography on silica gel to provide the corresponding product **11** (47.1 mg, 77% yield).

1-(4-methoxyphenyl)-2-((3-(trimethylsilyl) oxiran-2-yl) methyl) butan-1-one (11)

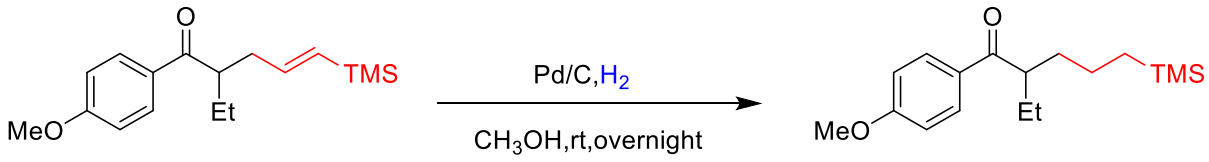


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 6.90 – 6.84 (m, 2H), 3.77 (s, 3H), 3.56 – 3.47 (m, 1H), 2.62 (ddd, *J* = 6.8, 4.5, 3.4 Hz, 1H), 2.10 (ddd, *J* = 14.0, 9.5, 4.6 Hz, 1H), 1.91 (d, *J* = 3.4 Hz, 1H), 1.73 (dt, *J* = 14.6, 7.2 Hz, 1H), 1.64 – 1.45 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H), -0.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 163.5, 130.5, 113.8, 55.4, 54.5, 52.4, 44.6, 36.22 26.4, 11.6, -3.9.

HRMS (Dart positive) M = $C_{17}H_{26}O_3Si$: calculated $(M+H)^+$ m/z 307.1724; found $(M+H)^+$ m/z 307.1724.

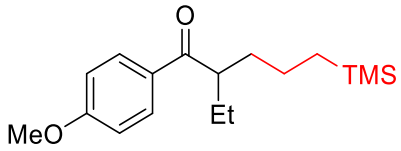
III. Catalytic hydrogenation



3a **12**

In a nitrogen-filled glovebox, a 20 mL Schlenk tube equipped with a stir bar was charged with Pd/C (10.0 mg, 0.01 mmol, 0.05 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then the tube was evacuated and backfilled with H_2 for three times. Then, **3a** (58.1 mg, 0.2 mmol, 1.0 equiv.) and CH_3OH (2.0 mL) were added in turn to the Schlenk tube through the rubber septum using syringes. The reaction mixture was stirred at room temperature for 12 h under an atmosphere of H_2 in a balloon. Upon reaction finished, the reaction mixture was diluted with 10 mL of EtOAc, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and then purified by flash chromatography on silica gel to provide the corresponding product **12** (56.0 mg, 96% yield).

2-ethyl-1-(4-methoxyphenyl)-5-(trimethylsilyl) pentan-1-one (12)

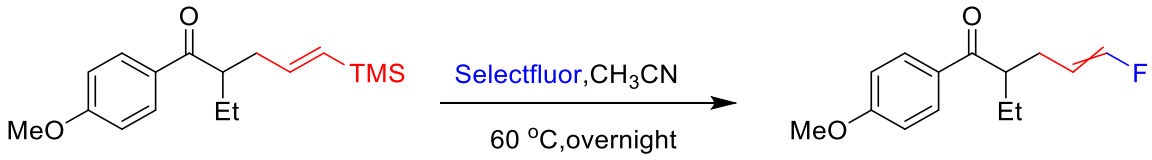


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.37 – 3.27 (m, 1H), 1.82 – 1.71 (m, 2H), 1.56 – 1.44 (m, 2H), 1.28 – 1.22 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H), 0.54 – 0.38 (m, 2H), -0.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 163.3, 130.9, 130.4, 113.7, 55.4, 47.0, 36.0, 25.5, 22.0, 16.9, 12.0, -1.7.

HRMS (Dart positive) M = $C_{17}H_{28}O_2Si$: calculated $(M+H)^+$ m/z 293.1931; found $(M+H)^+$ m/z 293.1931.

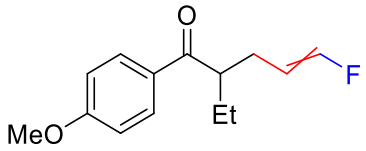
IV. Fluorination with selectfluor



3a **13**

In a nitrogen-filled glovebox, a 20 mL Schlenk tube equipped with a stir bar was charged with selectfluor (132.0 mg, 0.4 mmol, 2.0 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then **3a** (58.1 mg, 0.2 mmol, 1.0 equiv.) and CH_3CN (2.0 mL) were added in turn to the schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 60 °C for 12 h. Upon reaction finished, the reaction mixture was diluted with 10 mL of EtOAc, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and then purified by flash chromatography on silica gel to provide the corresponding product **13** (39.6 mg, 84% yield, E: Z = 1.3:1).

2-ethyl-5-fluoro-1-(4-methoxyphenyl) pent-4-en-1-one (13)



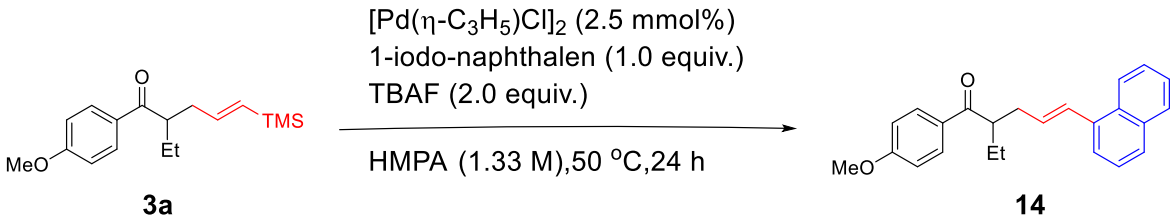
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.58(d, *J* =13.2 Hz,0.26 H), 6.53(d, *J* =4.6 Hz, 0.19 H), 6.37(d, *J* =11.1 Hz, 0.26 H), 6.31 (d, *J* =4.6 Hz ,0.19 H), 5.35 – 5.21 (m, 0.53 H), 4.80 – 4.64 (m, 0.4 H), 3.86 (s, 3H), 3.36 (dq, *J* = 20.1, 6.9 Hz, 1H), 2.38 (ddt, *J* = 29.8, 14.2, 6.9 Hz, 1H), 2.10 (dt, *J* = 15.2, 7.1 Hz, 1H), 1.78 (tt, *J* = 14.4, 7.2 Hz, 1H), 1.57 (tt, *J* = 12.7, 6.2 Hz, 1H), 0.87 (q, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 201.3, 163.5, 163.5, 150.9, 149.8, 148.3, 147.3, 130.54, 130.5, 130.3, 130.26, 113.8, 113.8, 109.1, 109.0, 108.4, 108.3, 55.5, 47.1, 47.1, 46.8, 27.1, 27.0, 25.3, 25.2, 24.8, 24.7, 11.6, 11.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.68, -129.09.

HRMS (Dart positive) M = $C_{14}H_{17}FO_2$: calculated $(M+H)^+$ m/z 237.1285; found $(M+H)^+$ m/z 237.1285.

V. Hiyama coupling

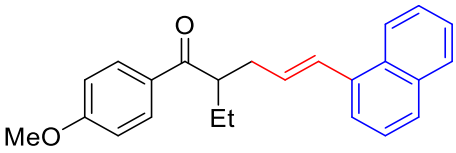


3a **14**

In a nitrogen-filled glovebox, a 20 mL Schlenk tube equipped with a stir bar was charged with allylpalladium chloride dimer (1.8 mg, 0.005 mmol, 0.025 equiv.) and TBAF (104.6 mg, 0.4 mmol, 2.0 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then **3a** (58.1 mg, 0.2 mmol, 1.0 equiv.) ,1-iodonaphthalene (50.8 mg, 0.2 mmol, 1.0 equiv.) and HMPA (0.15 mL) were added in turn to the schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 50 °C for 24 h. Upon reaction finished, the reaction mixture was diluted with 10 mL of EtOAc, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and then purified by flash

chromatography on silica gel to provide the corresponding product **14** (33.0 mg, 48% yield).

(*E*)-2-ethyl-1-(4-methoxyphenyl)-5-(naphthalen-1-yl) pent-4-en-1-one (14)

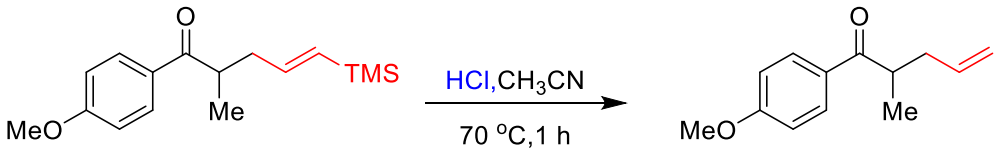


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 3H), 7.82 (dd, *J* = 6.3, 3.3 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.47 (dt, *J* = 6.4, 3.4 Hz, 2H), 7.40 (dt, *J* = 15.1, 7.5 Hz, 2H), 7.13 (d, *J* = 15.5 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.17 (dt, *J* = 15.0, 7.2 Hz, 1H), 3.86 (s, 3H), 3.58 (p, *J* = 7.1 Hz, 1H), 2.79 (dt, *J* = 14.8, 7.3 Hz, 1H), 2.56 (dt, *J* = 13.9, 6.8 Hz, 1H), 1.91 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.72 (dd, *J* = 13.8, 6.9 Hz, 1H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 163.4, 135.3, 133.5, 131.2, 131.0, 130.5, 130.5, 129.0, 128.3, 127.4, 125.8, 125.6, 125.5, 123.9, 123.6, 113.8, 55.4, 47.3, 35.8, 25.3, 11.8.

HRMS (ESI positive) M = $C_{24}H_{24}NaO_2$: calculated $(M+Na)^+$ m/z 367.1669; found $(M+Na)^+$ m/z 367.1670.

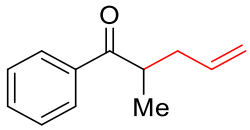
VI. Hydrolysis reaction



3q **15**

In a 20 mL tube equipped with a stir bar, **3q** (55.3 mg, 0.2 mmol, 1.0 equiv.), CH_3CN (2.0 mL) and conc. HCl (aq. 100 uL) were added in turn to the tube using syringes. The reaction mixture was stirred at 70 °C for 1 h. Upon reaction finished, the reaction mixture was quench with 1 N HCl (aq.) and extracted with DCM, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and then purified by flash chromatography on silica gel to provide the corresponding product **15**(31.6 mg, 91% yield). The characterization data are in accordance with the literature[11].

1-(4-methoxyphenyl)-2-methylpent-4-en-1-one (15)

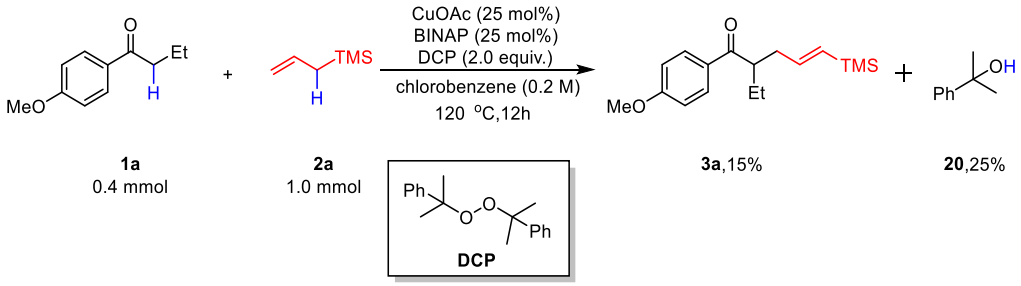


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.46 (tt, *J* = 6.7, 1.5 Hz, 2H), 5.85 – 5.71 (m, 1H), 5.10 – 4.96 (m, 2H), 3.54 (h, *J* = 6.9 Hz, 1H), 2.56 (dtt, *J* = 14.2, 6.4, 1.4 Hz, 1H), 2.24 – 2.16 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 136.4, 135.7, 132.9, 128.6, 128.1, 116.7, 40.3, 37.5, 17.0

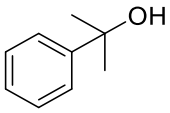
Experimental Procedure for Mechanism Studies

A. Activation of DCP



Following the general procedure **(I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), allyl-trimethyl-silane (114.3 mg, 1.0 mmol), DCP (216.3 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 120 °C for 12 h. Purification by silica gel flash chromatography (0 - 10% EtOAc in petroleum ether) gave the pale -yellow oil product **20** (13.6 mg) and the yellow oil product **3a** (17.2 mg) in 25% and 15% yield, respectively. The characterization data are in accordance with the literature[12].

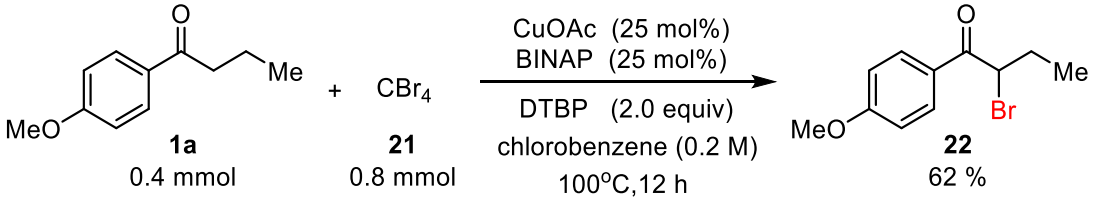
2-phenylpropan-2-ol (20)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.35 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 2.18 (s, 1H), 1.55 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 128.1, 126.6, 124.3, 72.4, 31.6.

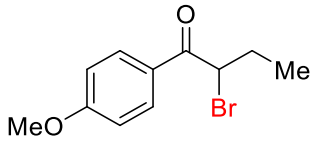
B. Radical-trapping experiment



In a nitrogen-filled glovebox, a 20 mL schlenk tube equipped with a stir bar was charged with CuOAc (12.3 mg, 0.1 mmol, 0.25 equiv.), BINAP (62.3 mg, 0.1 mmol, 0.25 equiv.) and

CBr_4 **(21)** (265.3 mg, 0.8 mmol, 2.0 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), DTBP (117.0 mg, 0.8 mmol, 2.0 equiv.) and chlorobenzene (2.0 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 100 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of EtOAc. followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and then purified by flash chromatography on silica gel to provide the corresponding product **22** as a colorless oil (63.9 mg, 62% yield). The characterization data are in accordance with the literature[13].

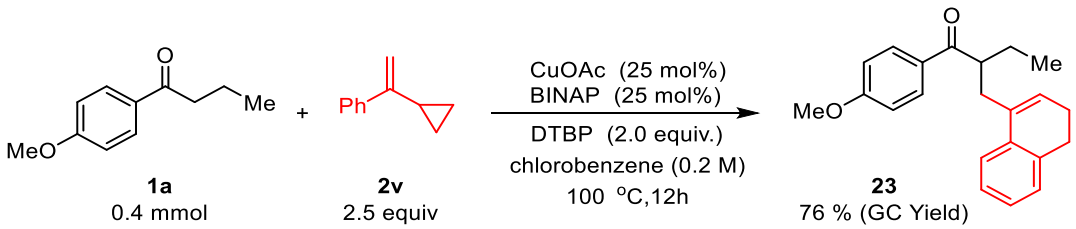
2-bromo-1-(4-methoxyphenyl) butan-1-one (22)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 6.96 – 6.90 (m, 2H), 5.04 (dd, *J* = 7.8, 6.4 Hz, 1H), 3.85 (s, 3H), 2.15 (ddq, *J* = 34.5, 14.6, 7.4 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 163.8, 131.1, 127.2, 113.9, 55.4, 49.0, 26.9, 12.1.

C. Radical clock experiment



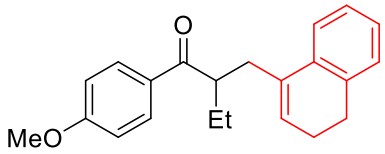
1a
0.4 mmol

2v
2.5 equiv

23
76 % (GC Yield)

Following the general procedure **(I)** with 1-(4-methoxyphenyl)-1-butanone (71.3 mg, 0.4 mmol), *α*-cyclopropyl styrene (144.2 mg, 1.0 mmol), DTBP (117.0 mg, 0.8 mmol), CuOAc (12.3 mg, 0.1 mmol), BINAP (62.3 mg, 0.1 mmol) and chlorobenzene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. Purification by silica gel flash chromatography (0 - 2% EtOAc in petroleum ether) gave the title compound **23** as a pale -yellow oil in 76% GC yield.

2-((3,4-dihydronaphthalen-1-yl) methyl)-1-(4-methoxyphenyl) butan-1-one (23)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.26 (dd, *J* = 13.7, 5.7 Hz, 2H), 7.16 (td, *J* = 7.2, 1.5 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.84 – 6.79 (m, 2H), 5.79 (t, *J* = 4.6 Hz, 1H), 3.83 (s, 3H), 3.61 (tt, *J* = 8.1, 5.6 Hz, 1H), 2.80 (dd, *J* = 14.1, 8.2 Hz, 1H), 2.70 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.36 (ddd, *J* = 15.7, 10.0, 7.0 Hz, 1H), 2.15 – 1.98 (m, 2H), 1.89 – 1.73 (m, 1H), 1.69 – 1.63 (m, 1H), 0.86 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4, 163.3, 137.1, 134.5, 134.0, 131.2, 130.4, 127.7, 127.2, 126.7, 126.3, 122.4, 113.5, 55.4, 45.4, 35.8, 28.1, 25.9, 22.9, 11.9.

HRMS-ESI (Dart positive) M = $C_{22}H_{24}O_2$: calculated $(M+H)^+$ m/z 321.1849; found $(M+H)^+$ m/z 321.1849.

X-ray Crystallograph Data

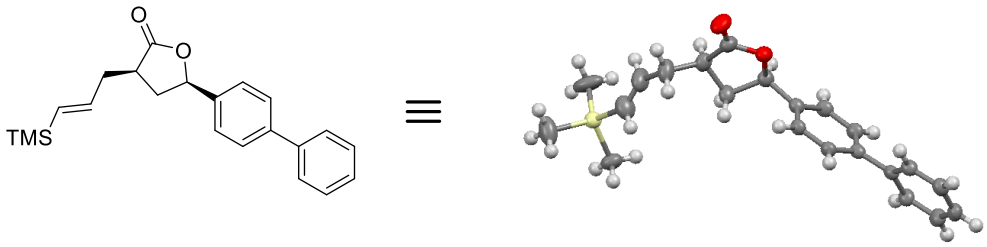


Figure S1 X-Ray structure of product **5a (CCDC 2264697)**

Table S7. Crystal data of **5a**

Identification code	**5a**
Empirical formula	C22 H26 O2 Si
Formula weight	350.52
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 6.2304(2) Å α=90.00° b = 24.1124(10) Å β= 90.00° c = 27.5082(13) Å γ = 90.00°
Volume	4132.6(3) $Å^3$
Z	8
Density (calculated)	1.127 Mg/m^3
Absorption coefficient	1.079 mm^{-1}
F(000)	1504
Crystal size	0.38 x 0.05x 0.05 mm^3
Theta range for data collection	2.44 to 70.00°.
Index ranges	-4<=h<=7, -29<=k<=27, -33<=l<=33
Reflections collected	14882

Independent reflections	7364 [R(int) = 0.0340]
Completeness to theta = 70.00°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9480 and 0.6846
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7364 / 80 / 451
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0595, wR2 = 0.1652
R indices (all data)	R1 = 0.0741, wR2 = 0.1766
Largest diff. peak and hole	0.474 and -0.200 e.$Å^{-3}$

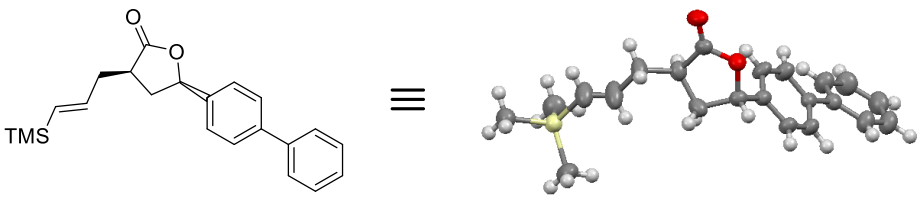


Figure S2 X-Ray structure of product **5a' (CCDC 2255820)**

Table S8. Crystal data of **5a'**

Identification code	**5a'**
Empirical formula	C22 H26 O2 Si
Formula weight	350.52
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 5.80280(10) Å α= 90.00° b = 10.05640(10) Å β= 90.00° c = 35.0886(6) Å γ = 90.00°
Volume	2047.61(5) $Å^3$
Z	4

Density (calculated)	1.137 Mg/m^3
Absorption coefficient	1.089 mm^{-1}
F(000)	752
Crystal size	0.32 x 0.26 x 0.20 mm^3
Theta range for data collection	2.52 to 71.99°.
Index ranges	-6<=h<=7, -12<=k<=12, -43<=l<=43
Reflections collected	51911
Independent reflections	3991 [R(int) = 0.1252]
Completeness to theta = 71.99°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8117 and 0.7220
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3991 / 3 / 227
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1610
R indices (all data)	R1 = 0.0601, wR2 = 0.1646
Largest diff. peak and hole	0.482 and -0.332 $e.Å^{-3}$

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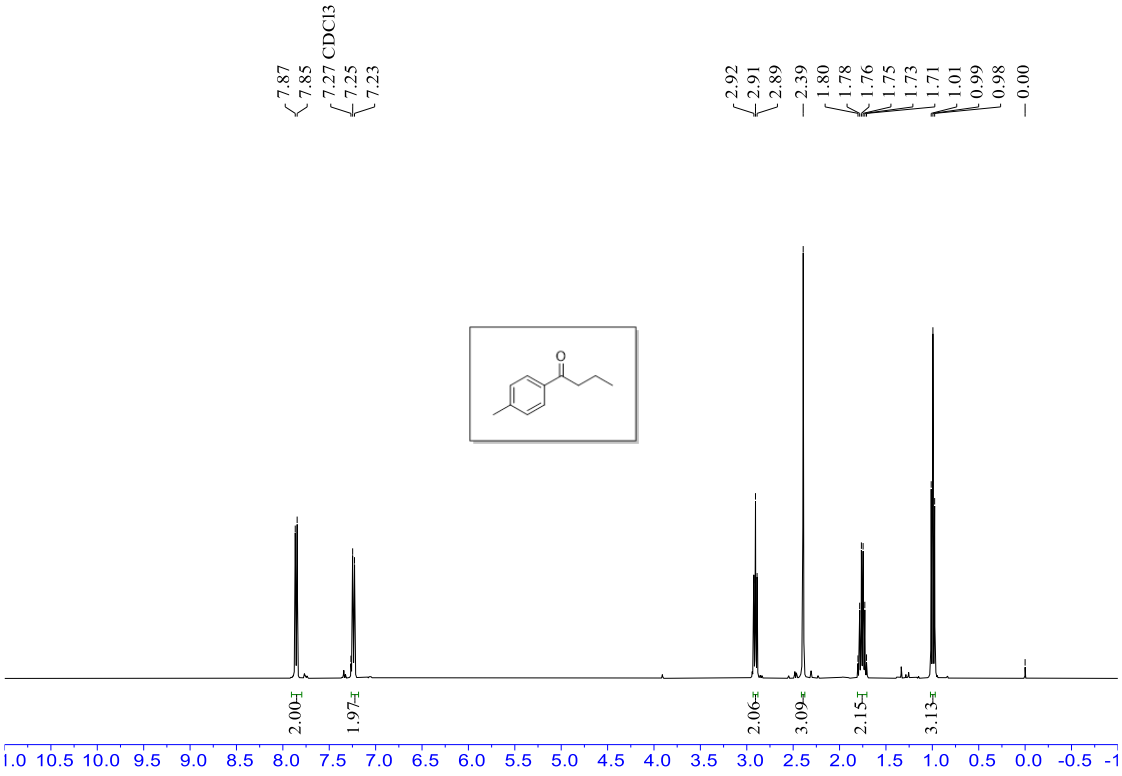
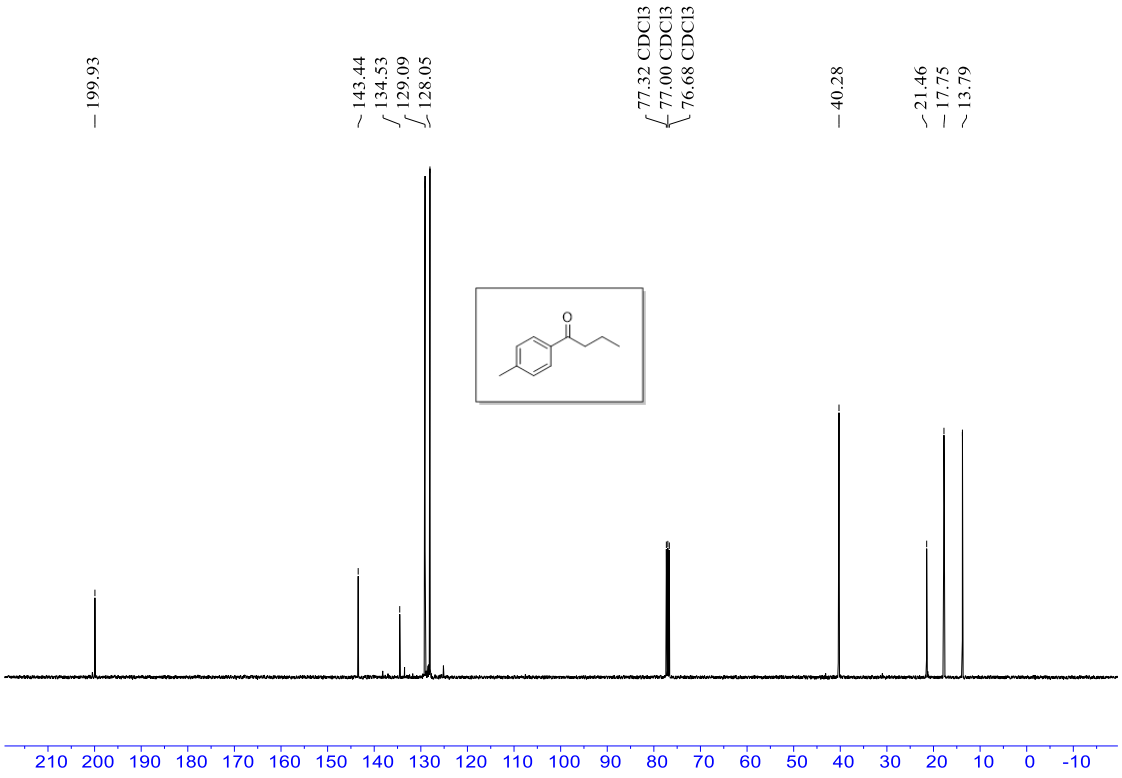
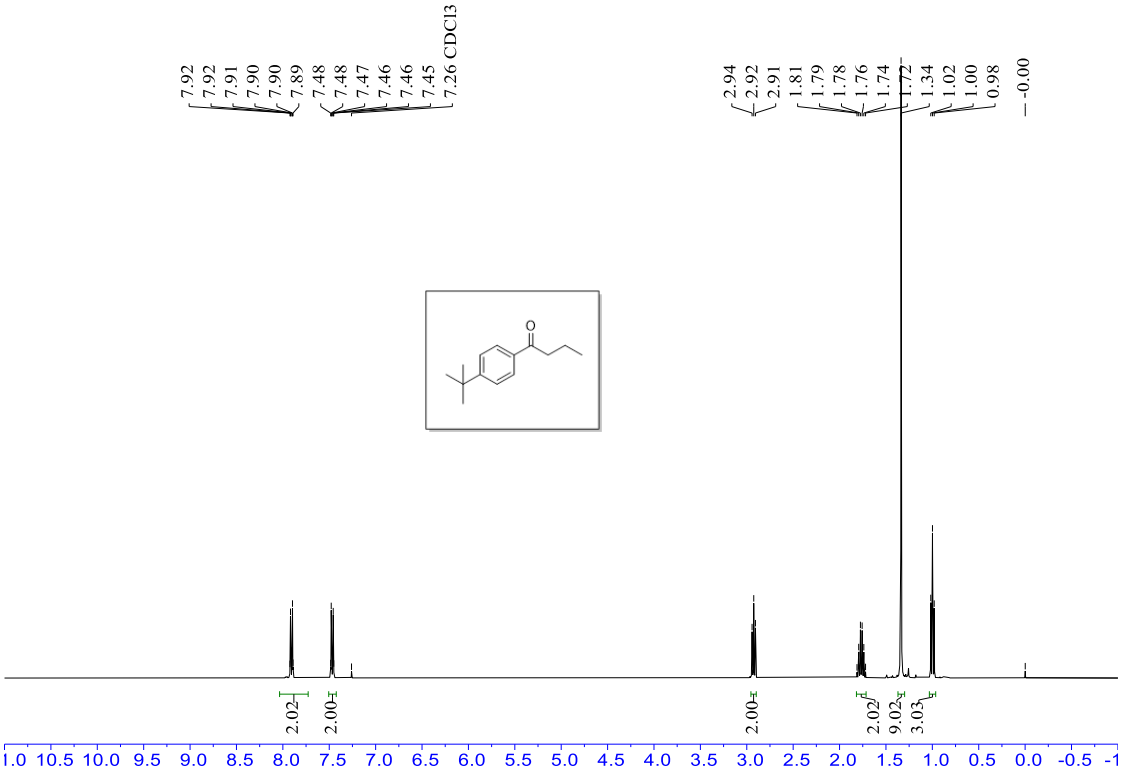
NMR Spectra



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1c**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **1c**



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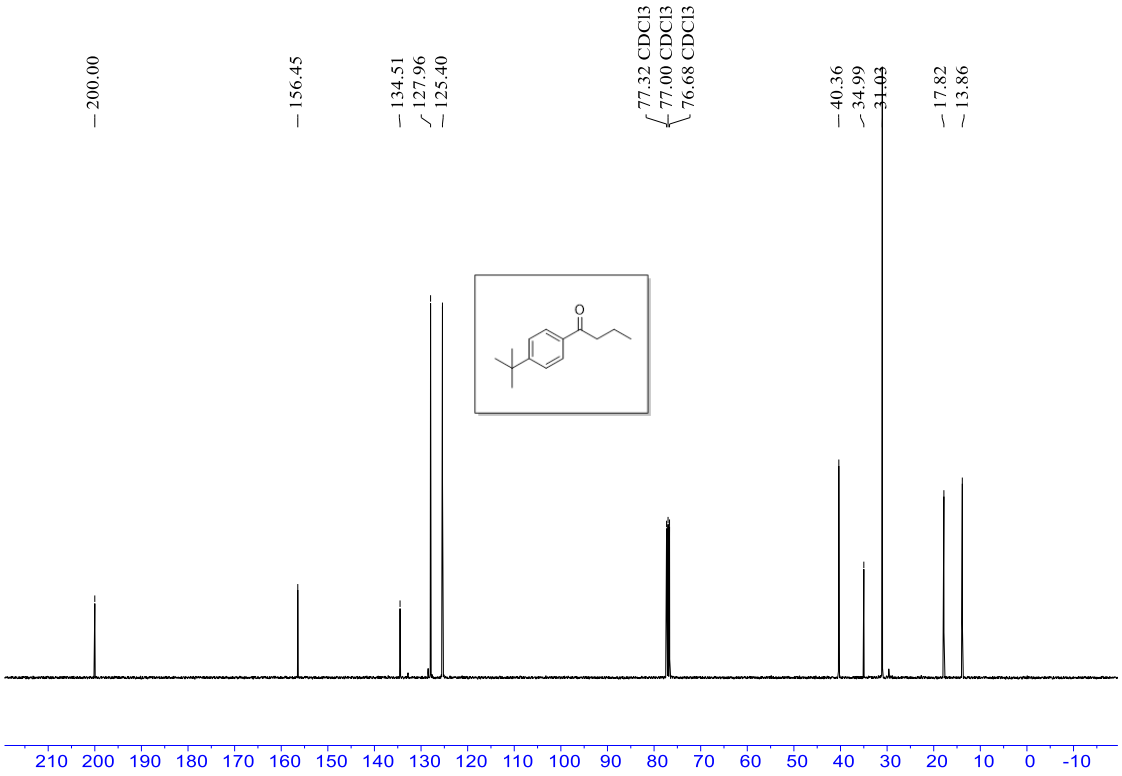
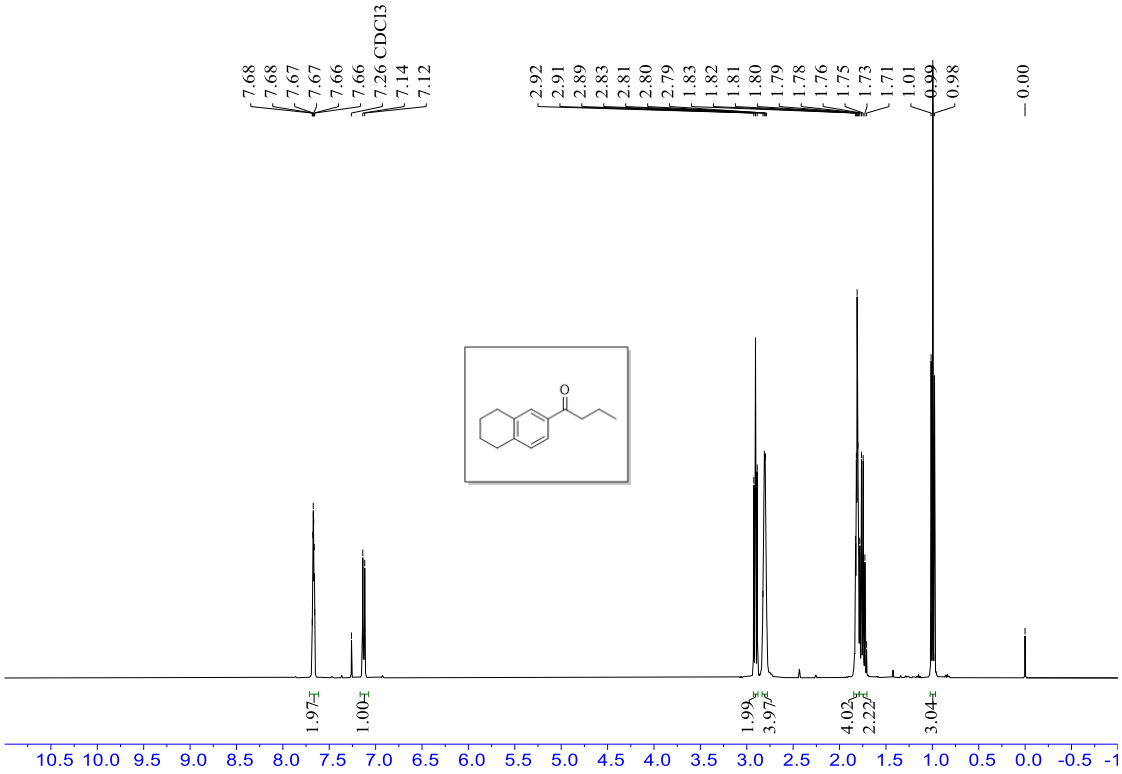
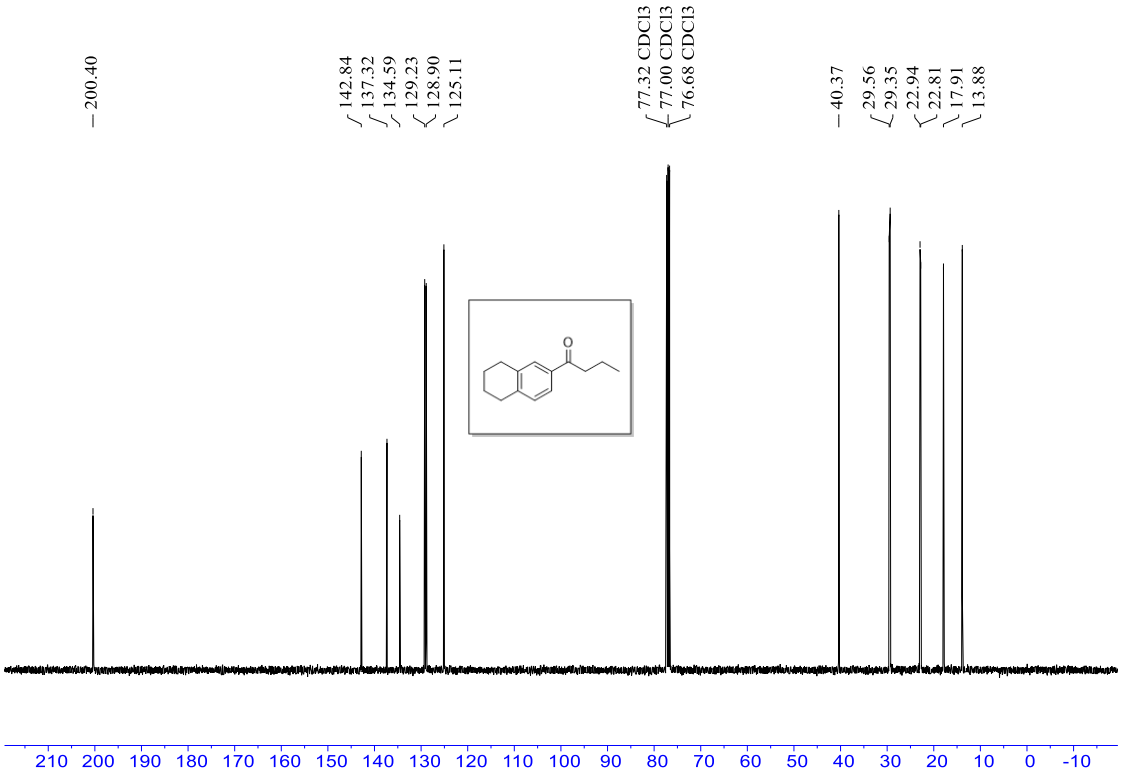


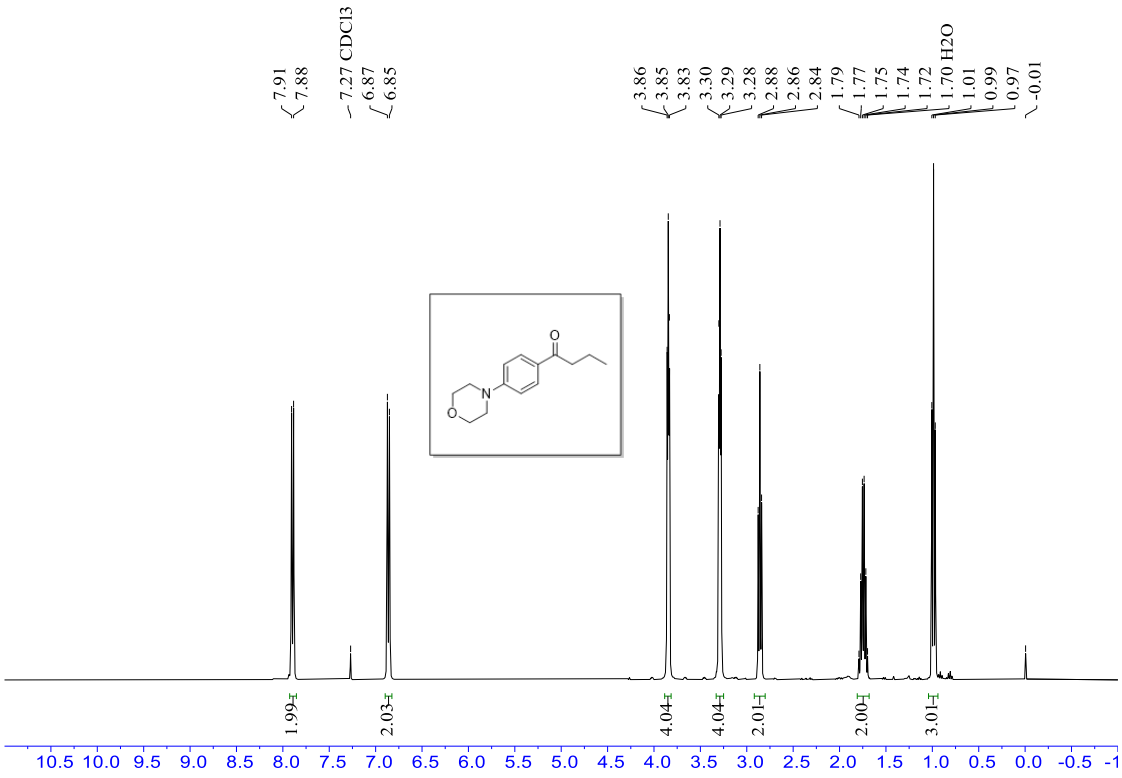
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **1d**



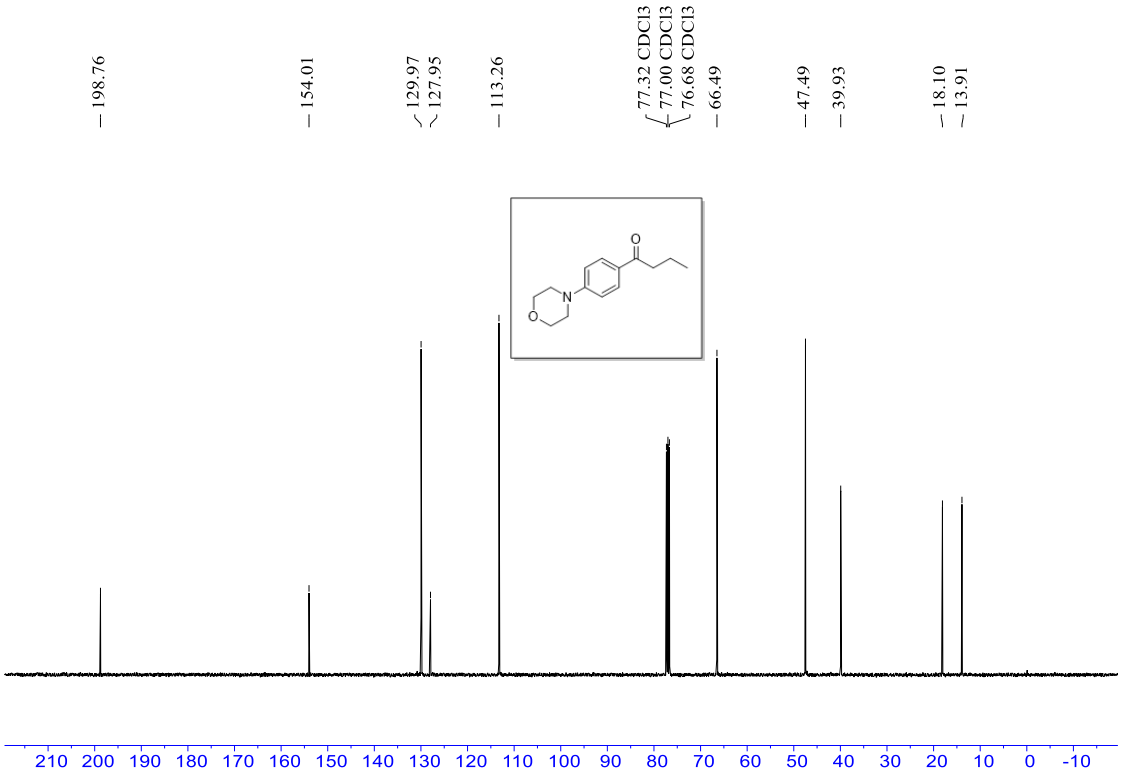
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1e**



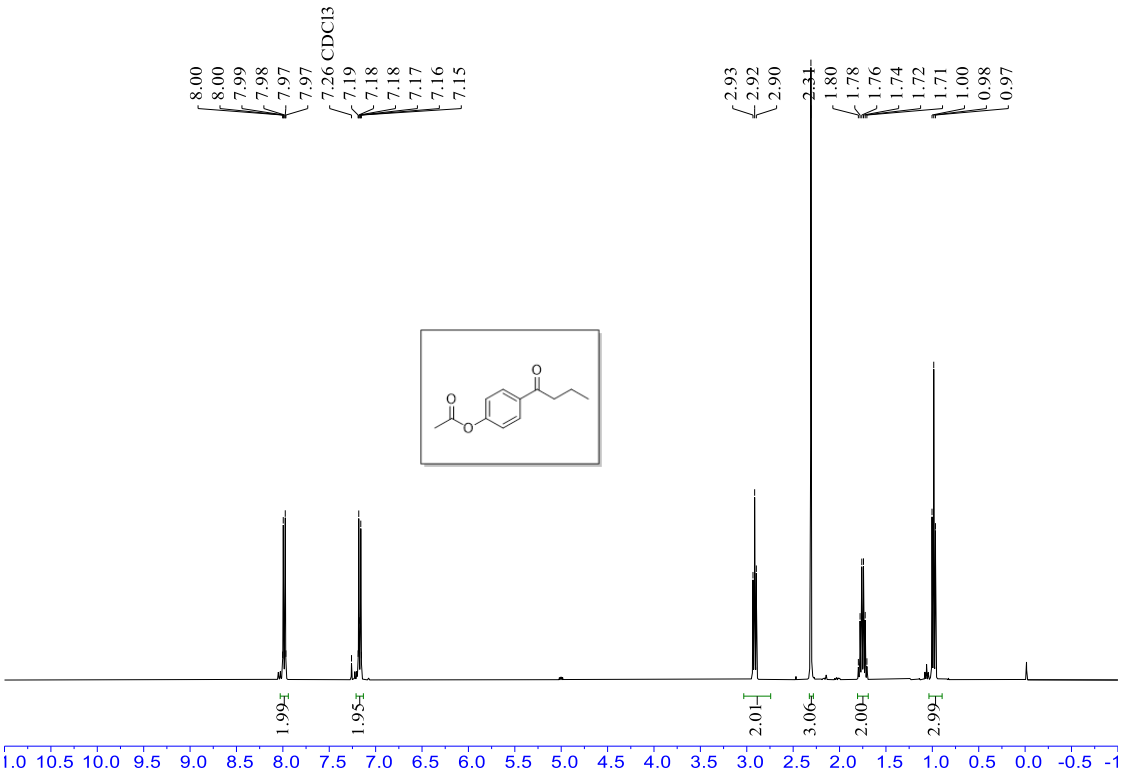
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **1e**



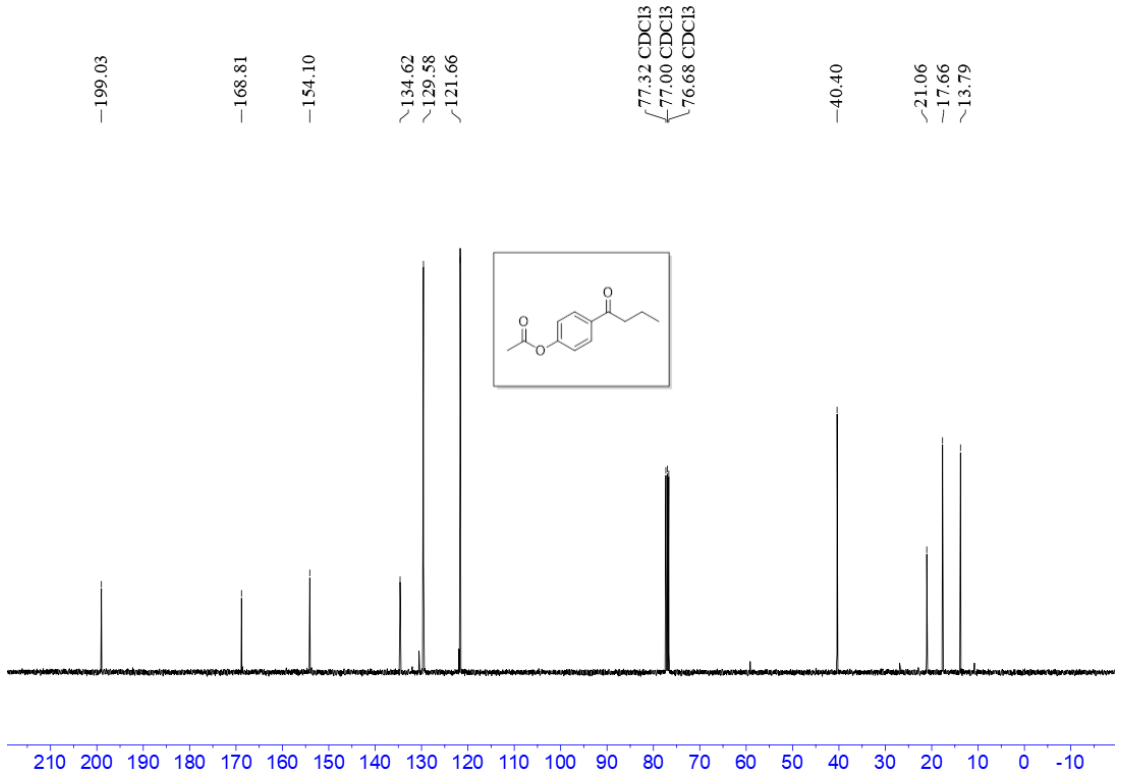
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1l**



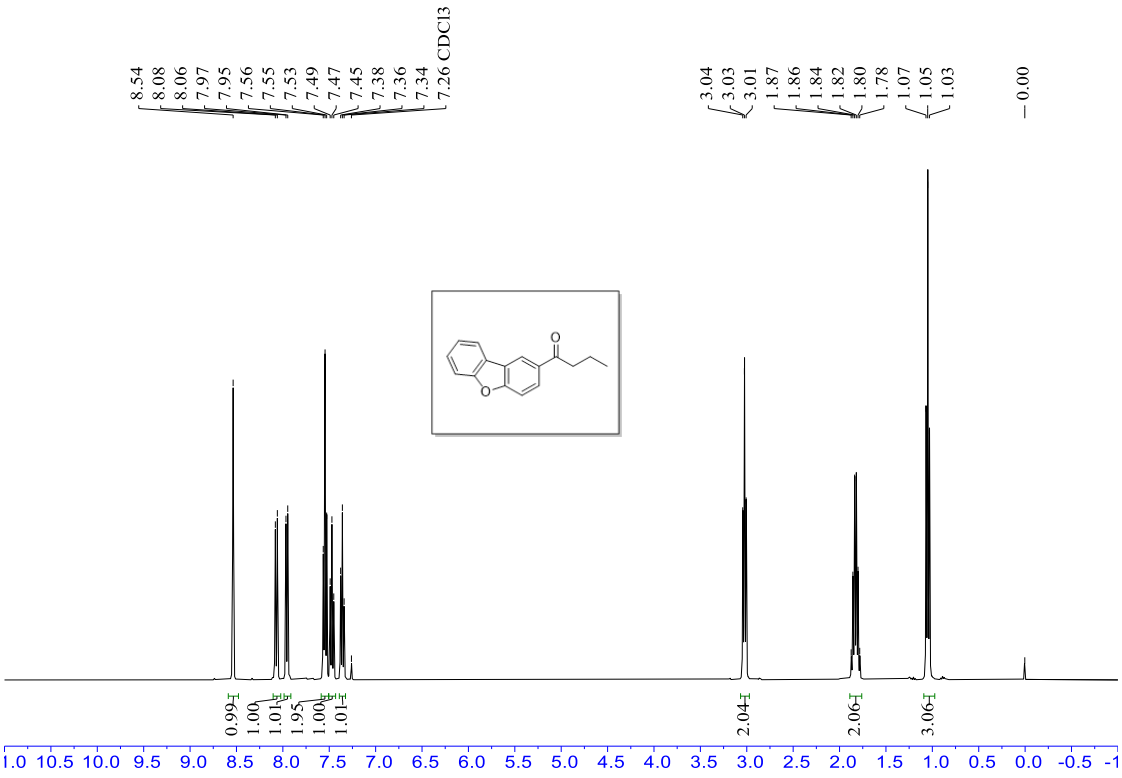
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **1l**



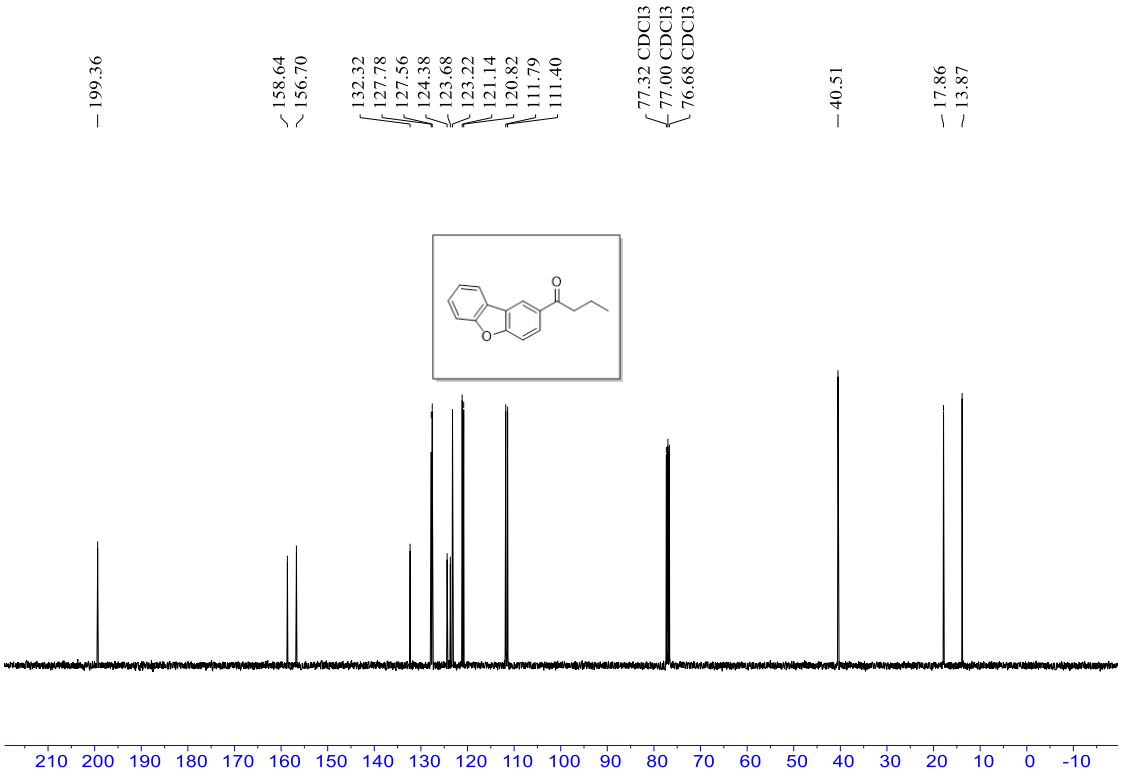
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1k**



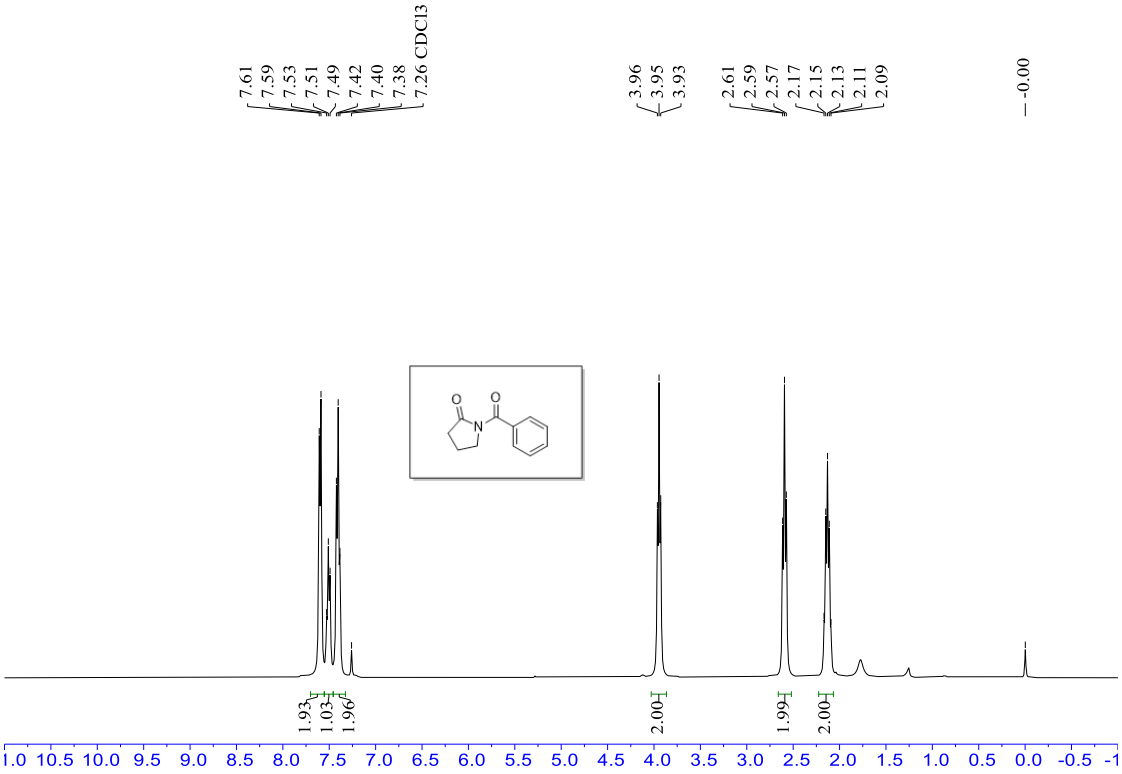
^{13}C NMR (101MHz, $CDCl_3$) spectrum for **1k**



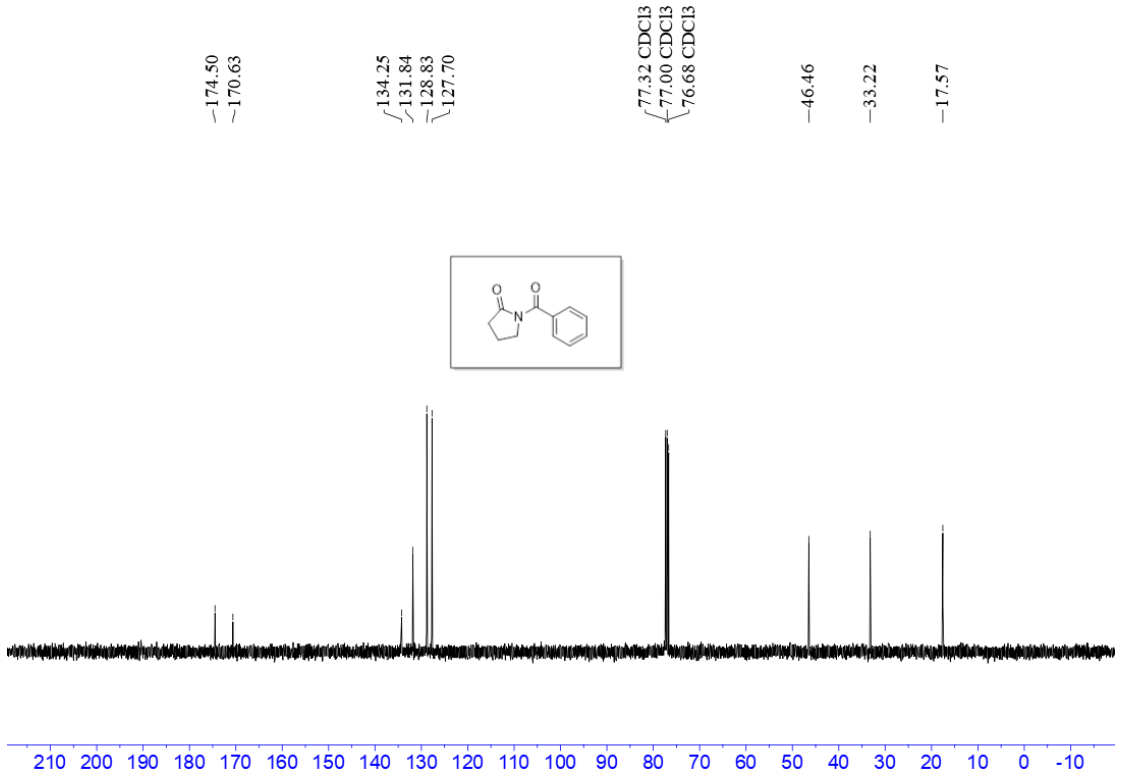
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **1p**



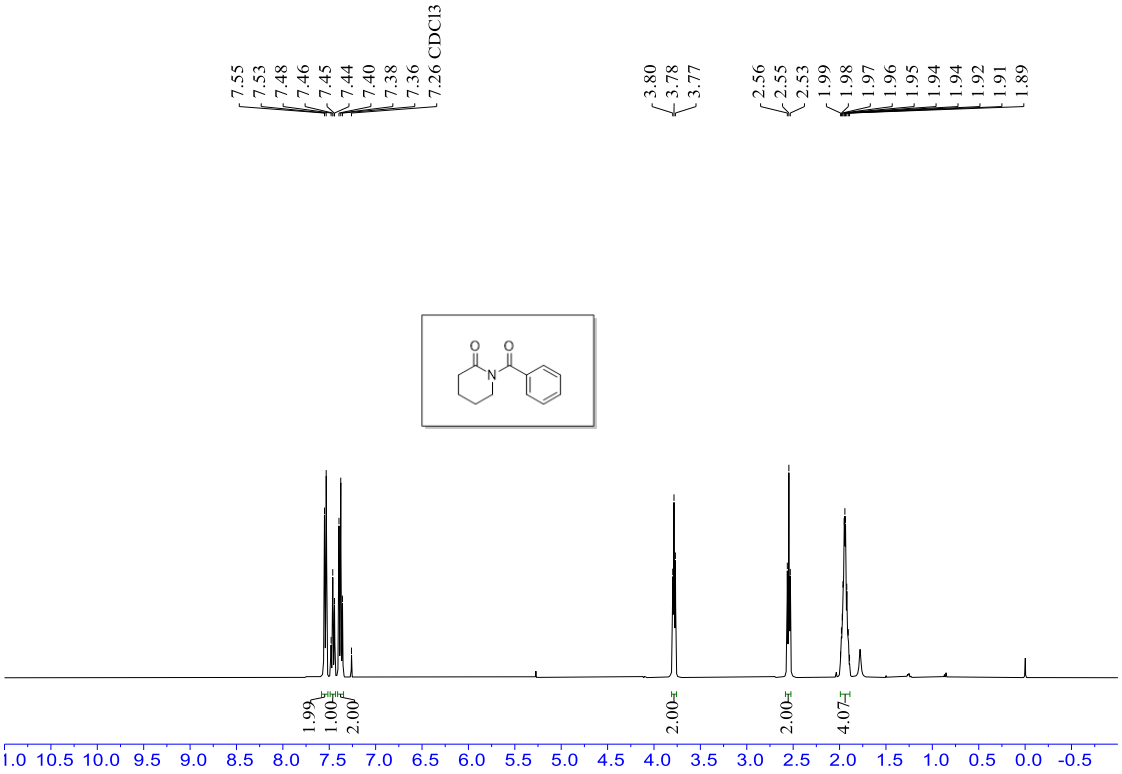
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **1p**



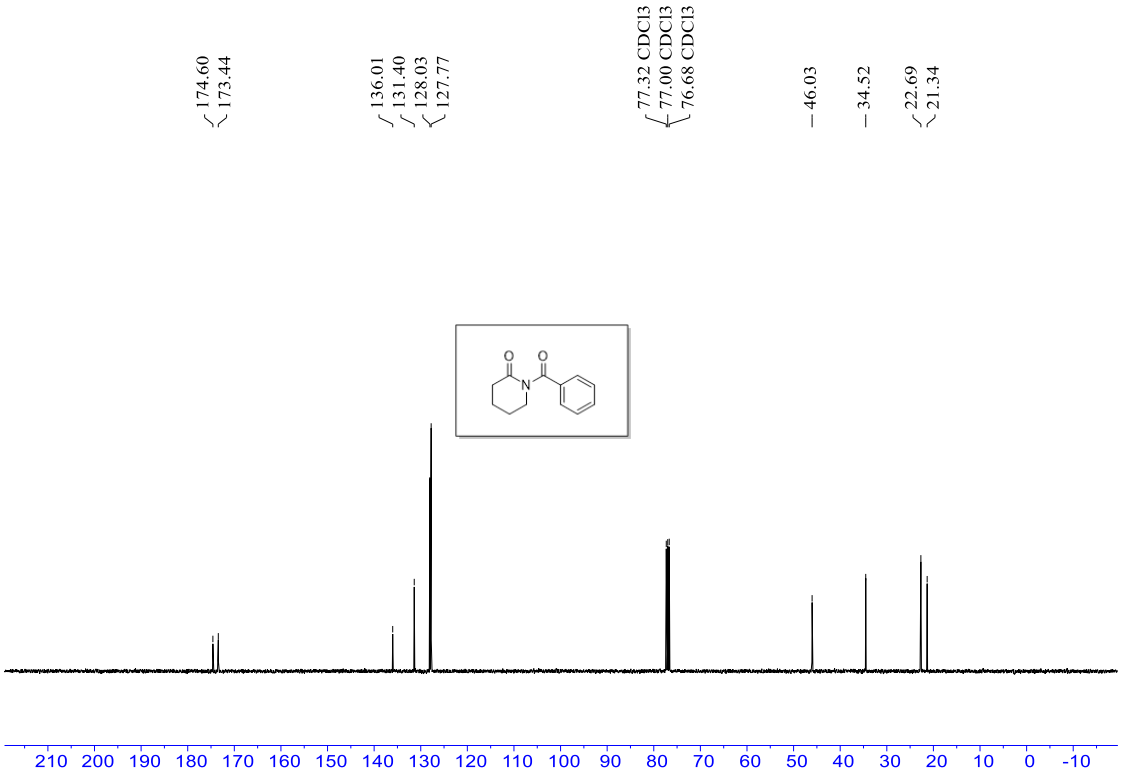
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **6a**



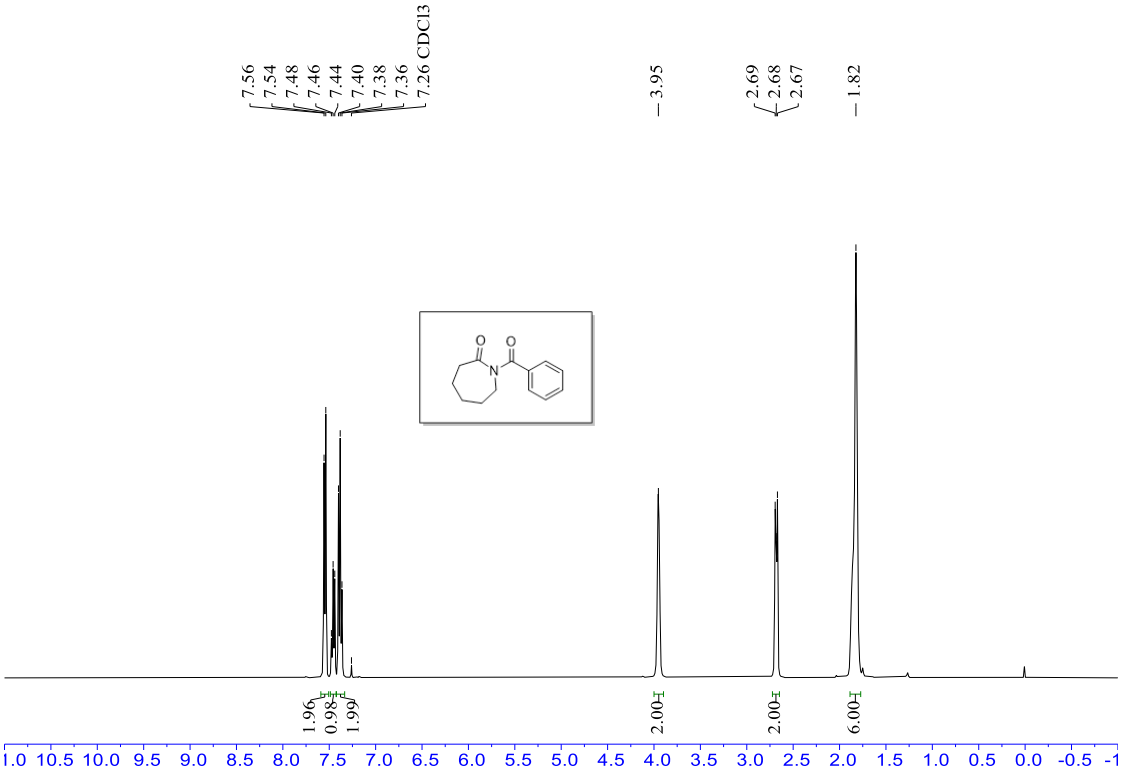
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **6a**



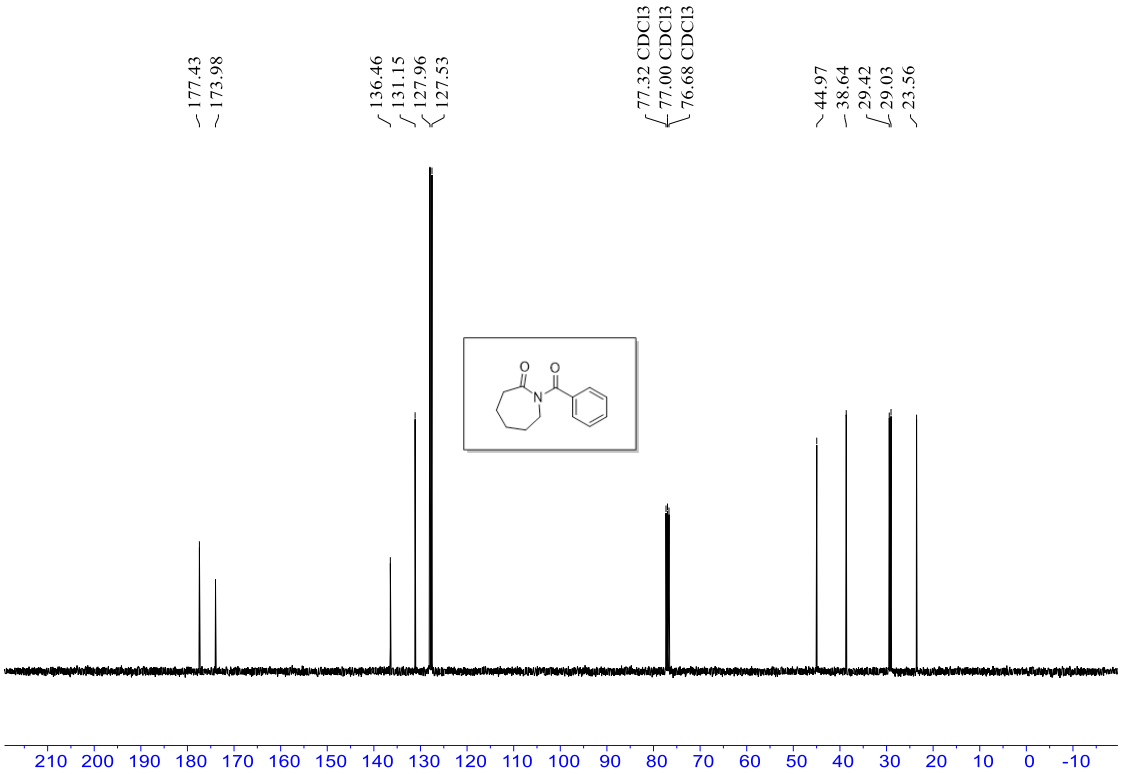
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **6b**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **6b**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **6c**



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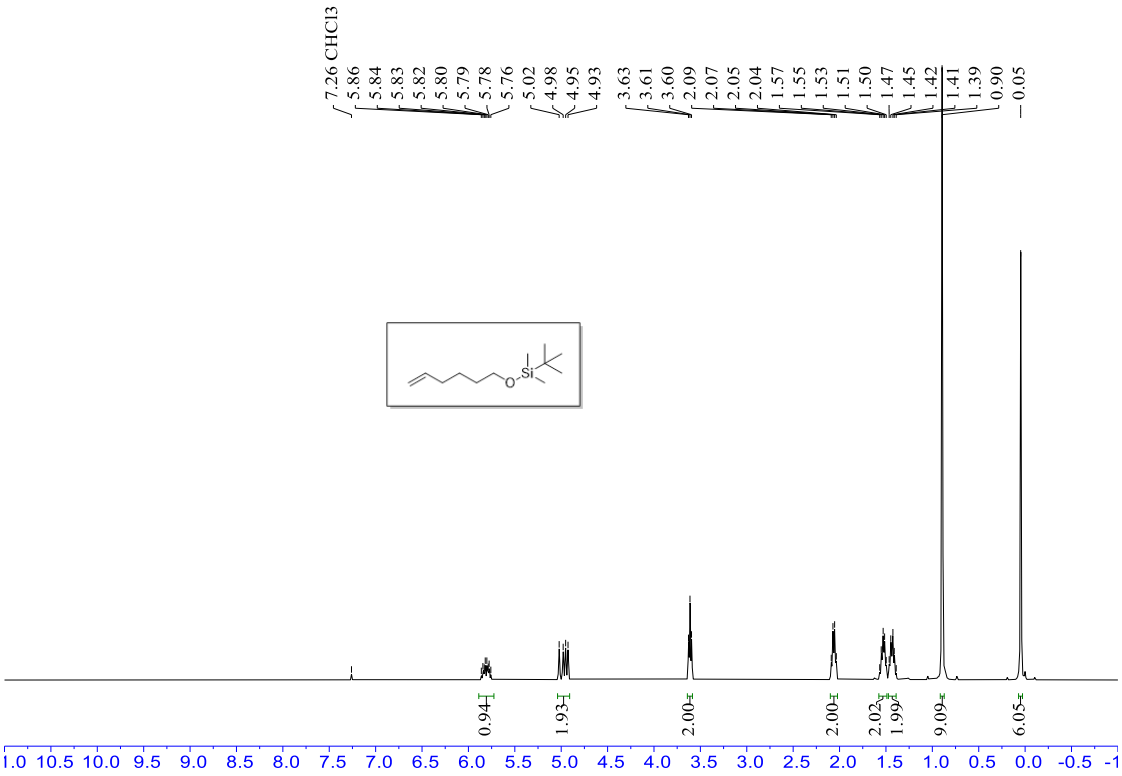
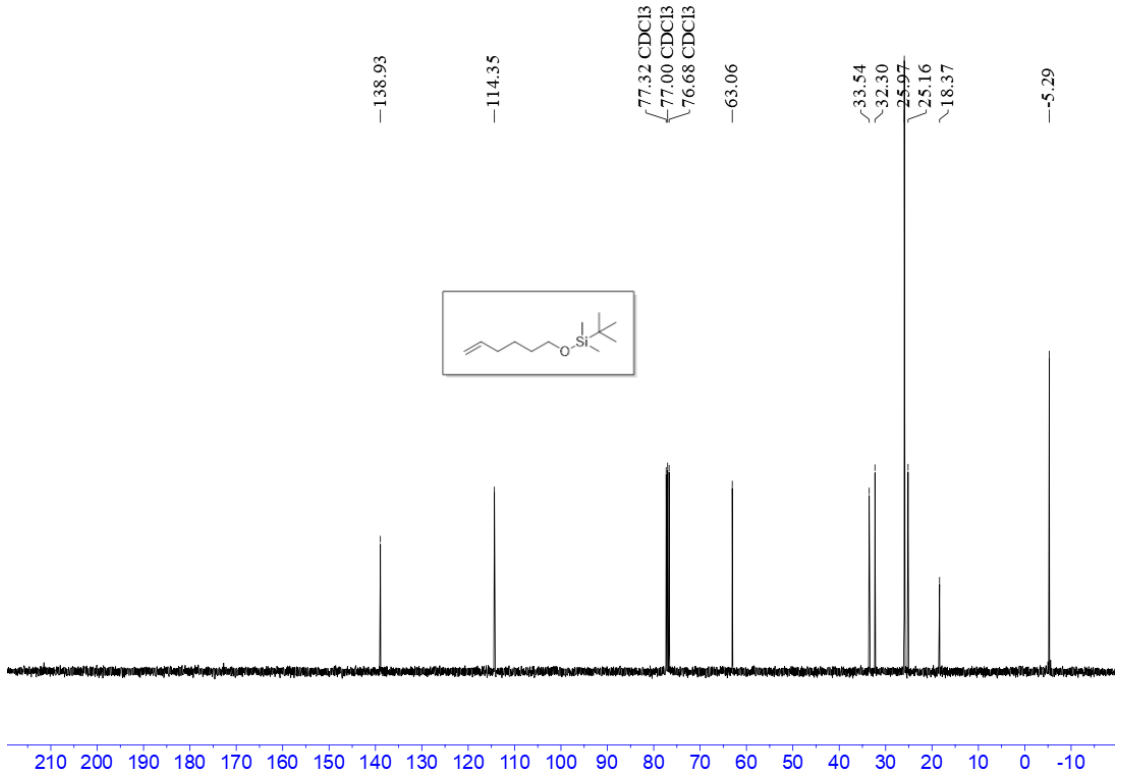
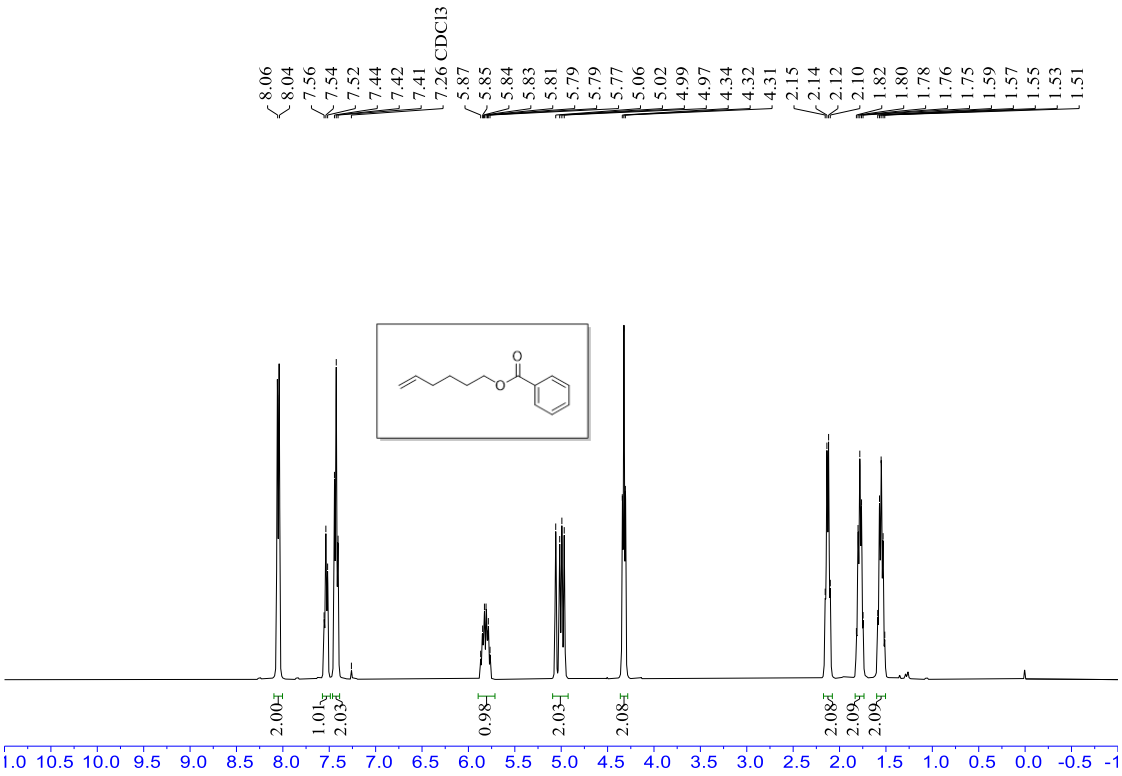


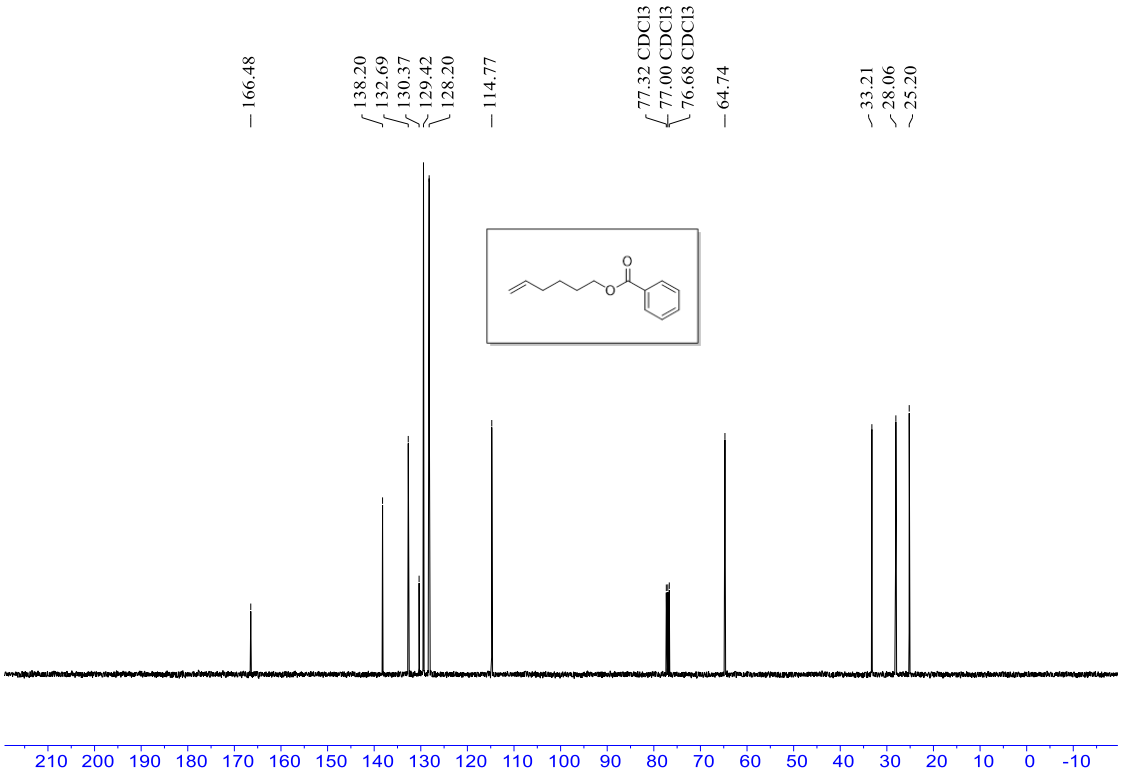
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2i**



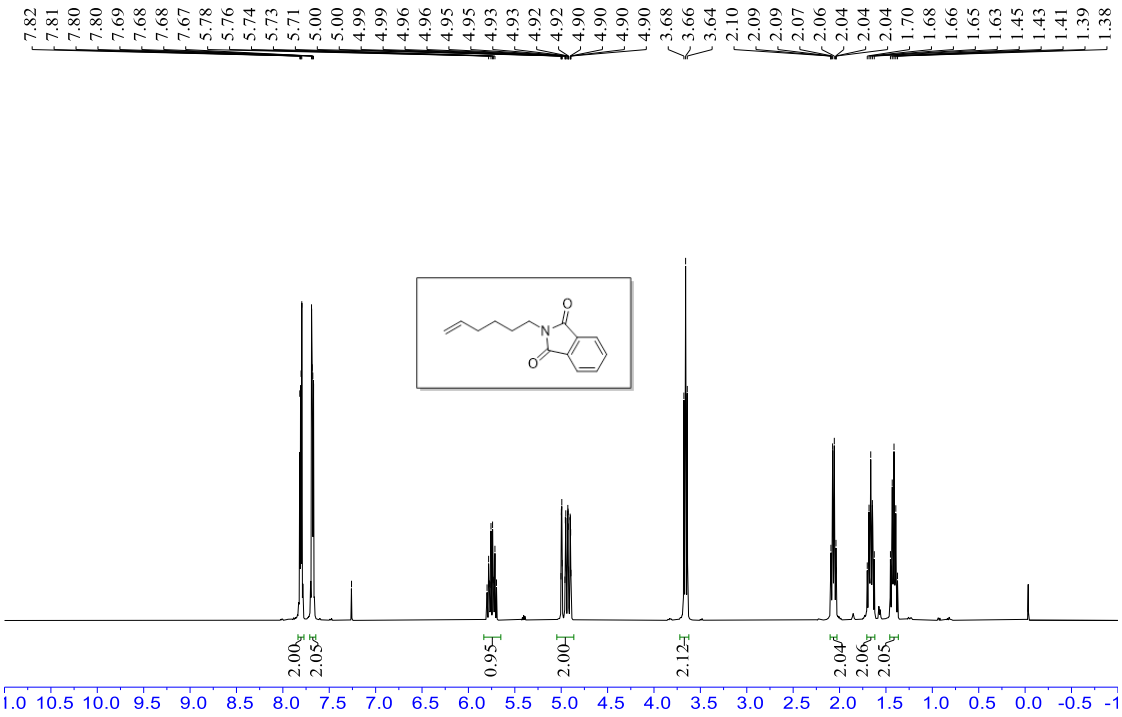
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2i**



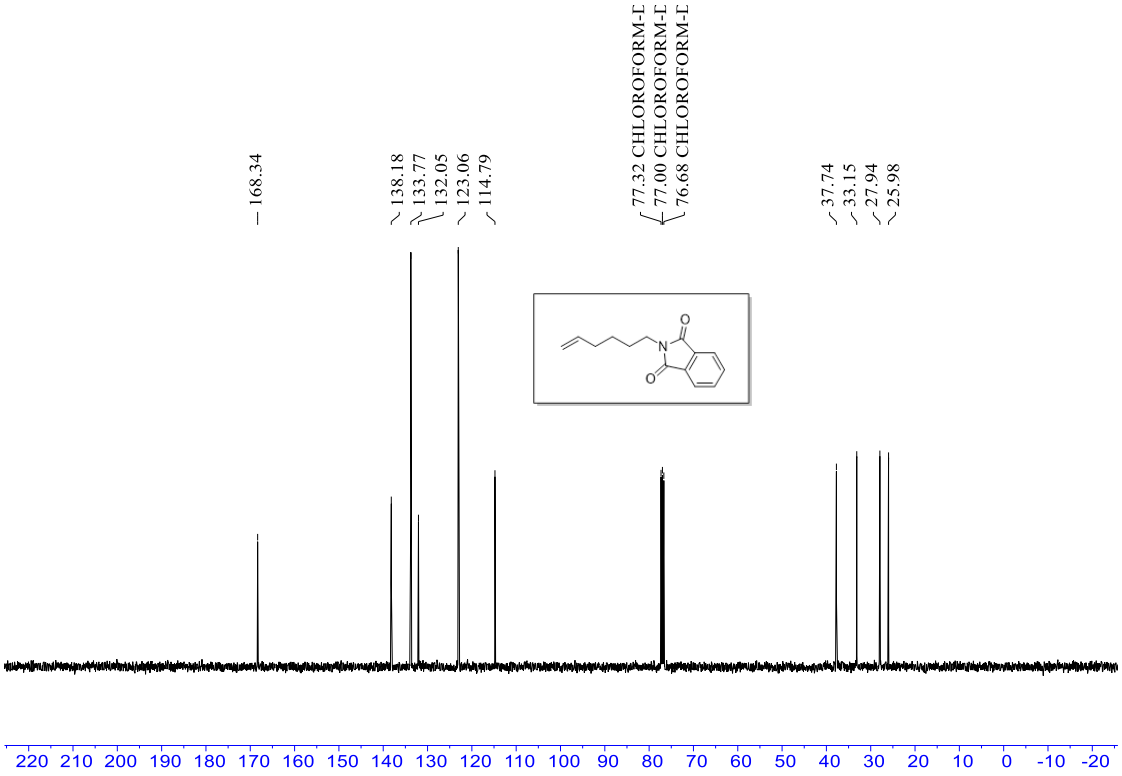
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2j**



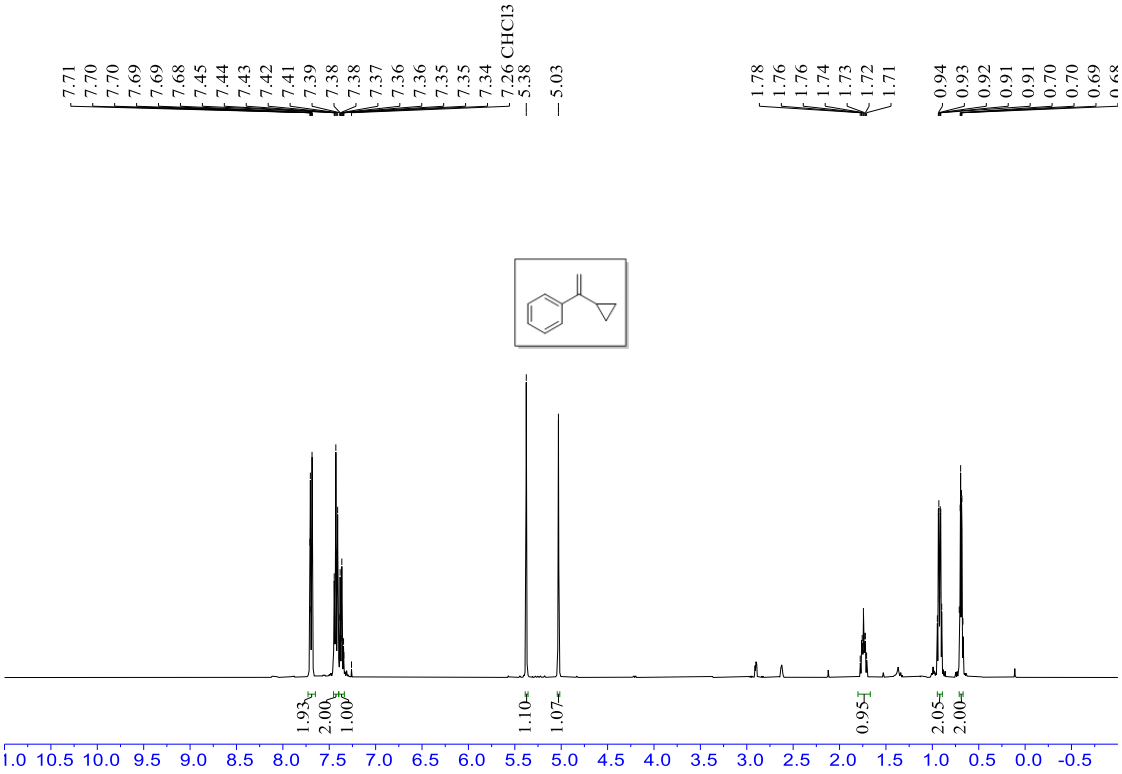
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2j**



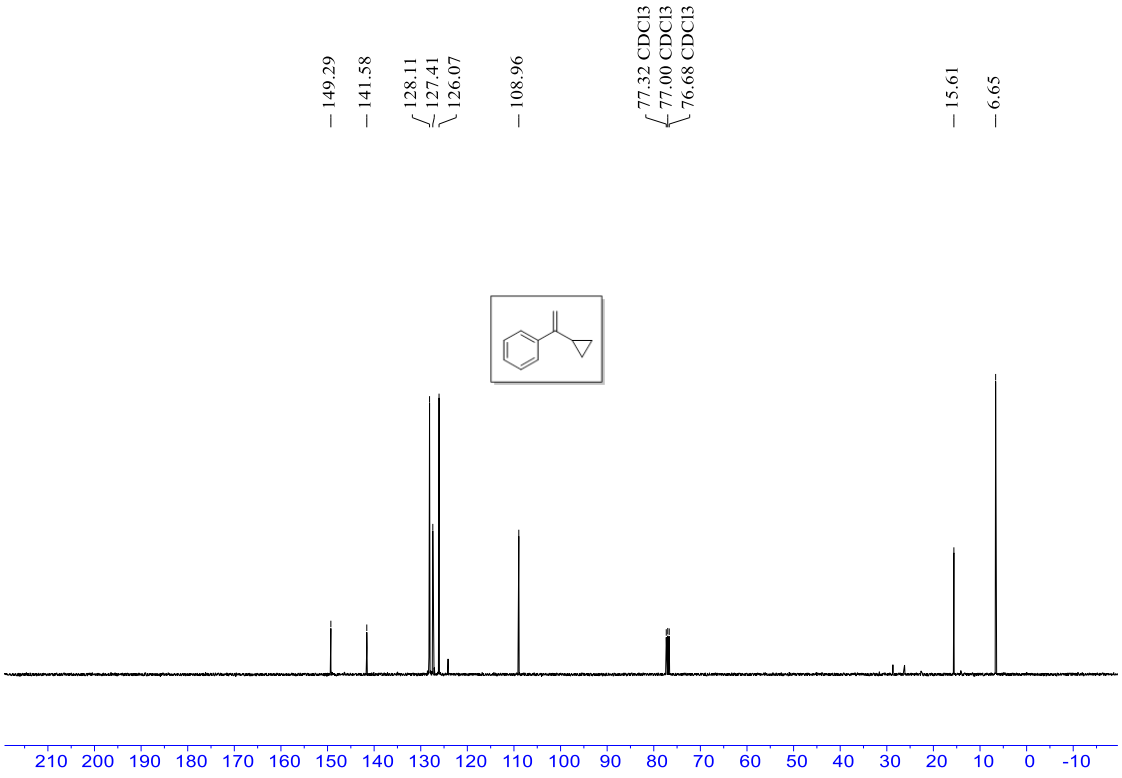
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2k**



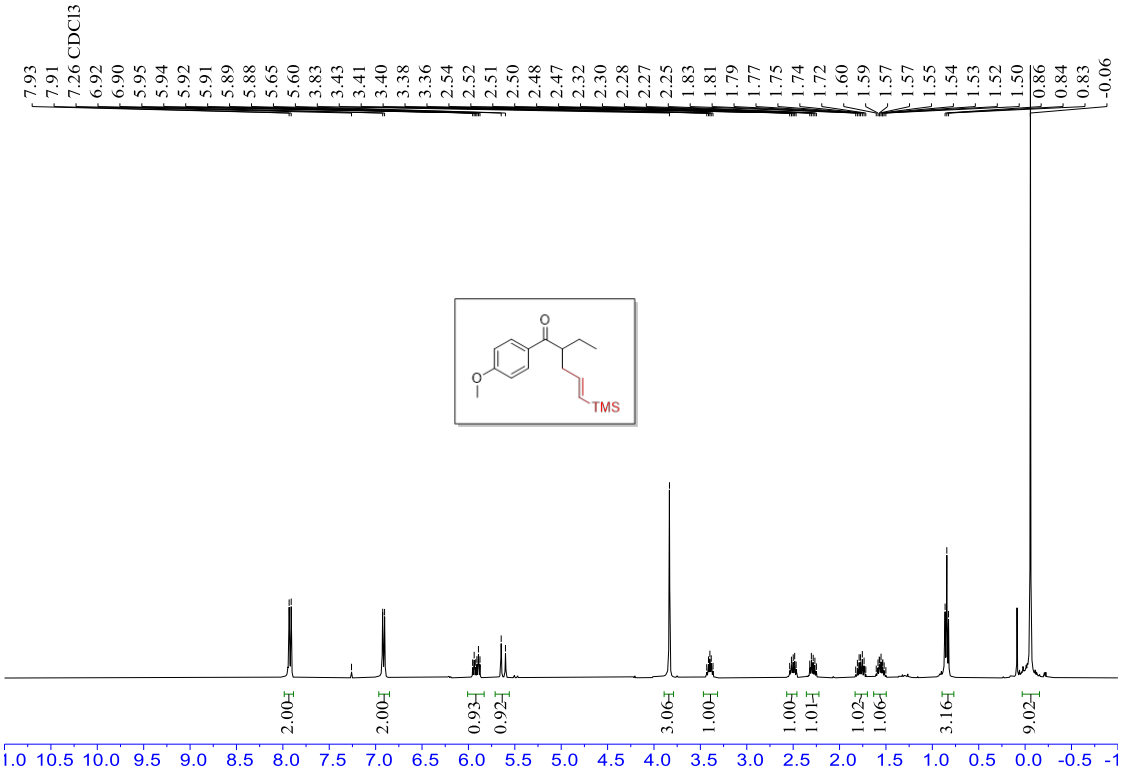
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2k**



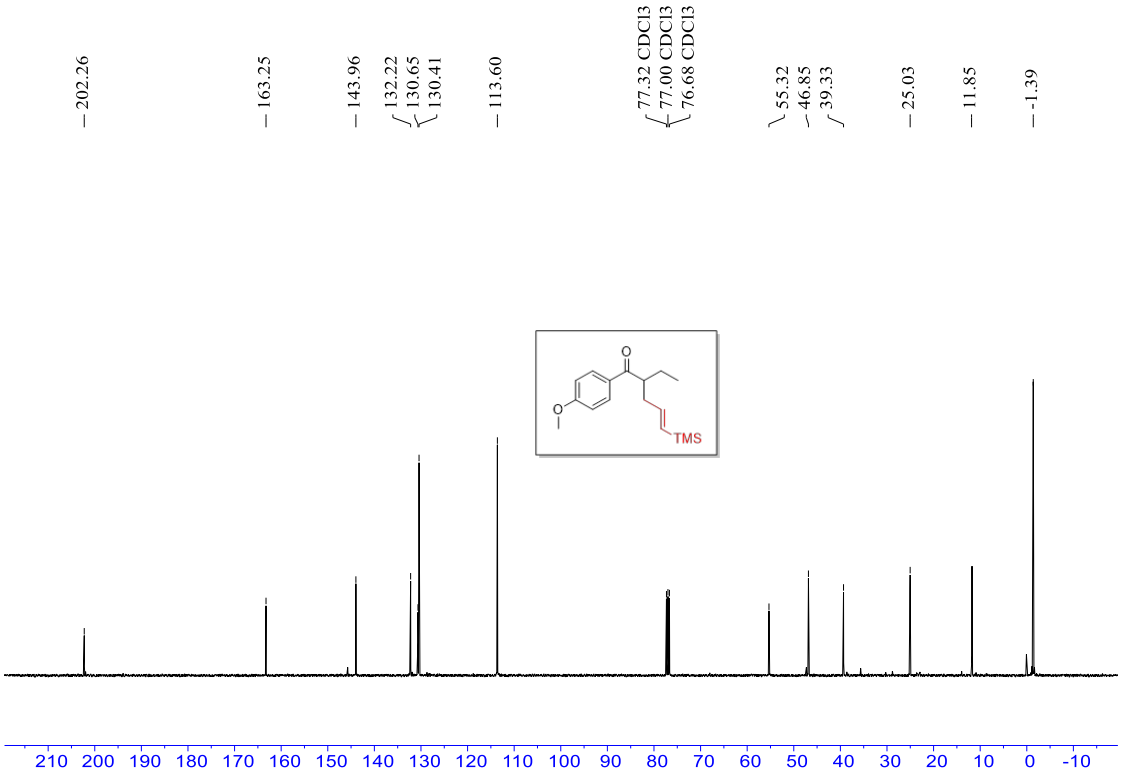
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **2v**



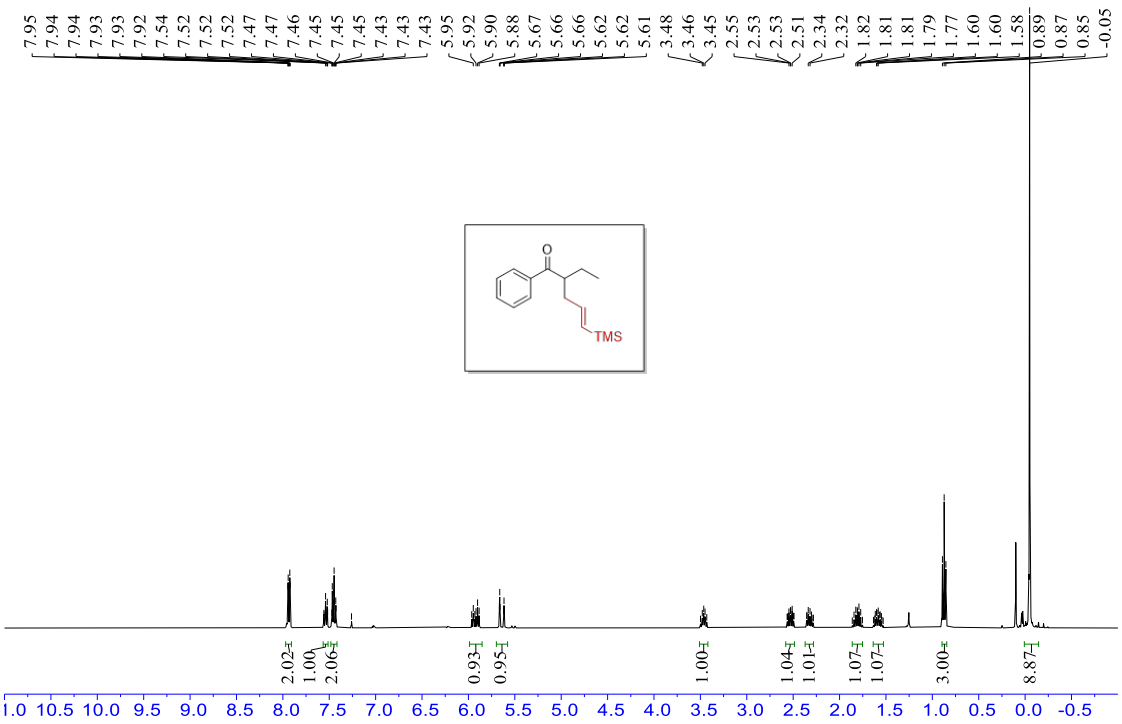
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **2v**



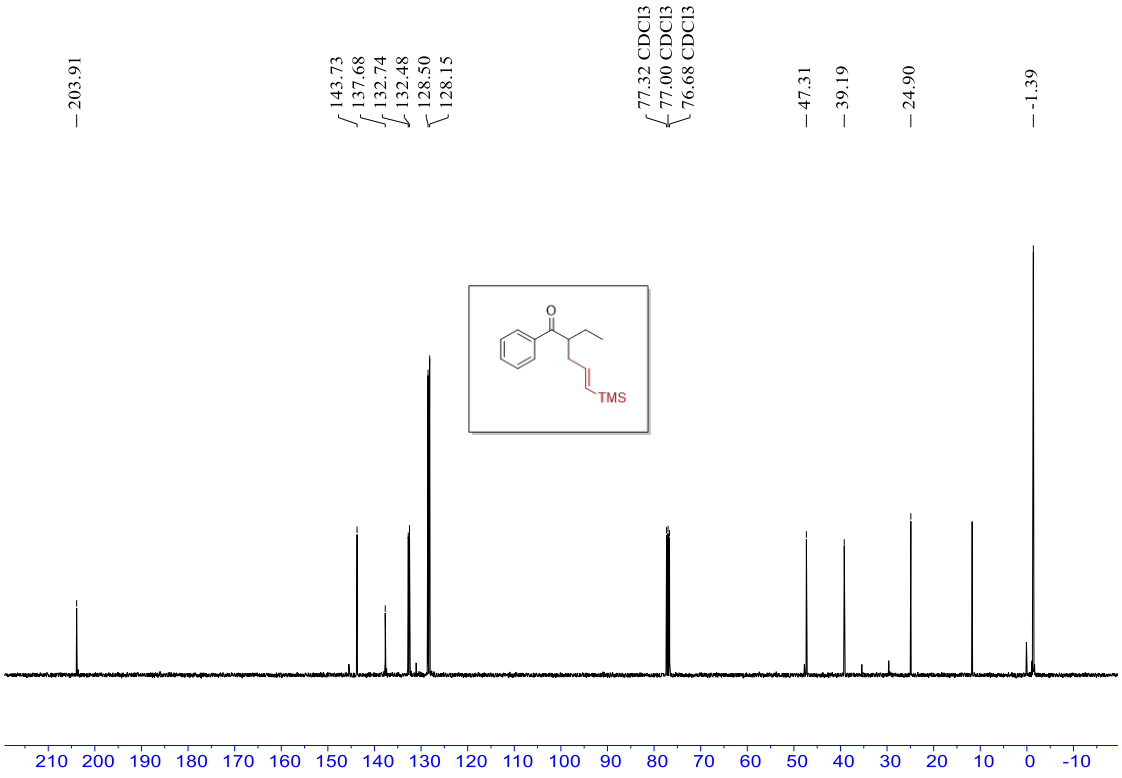
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3a**



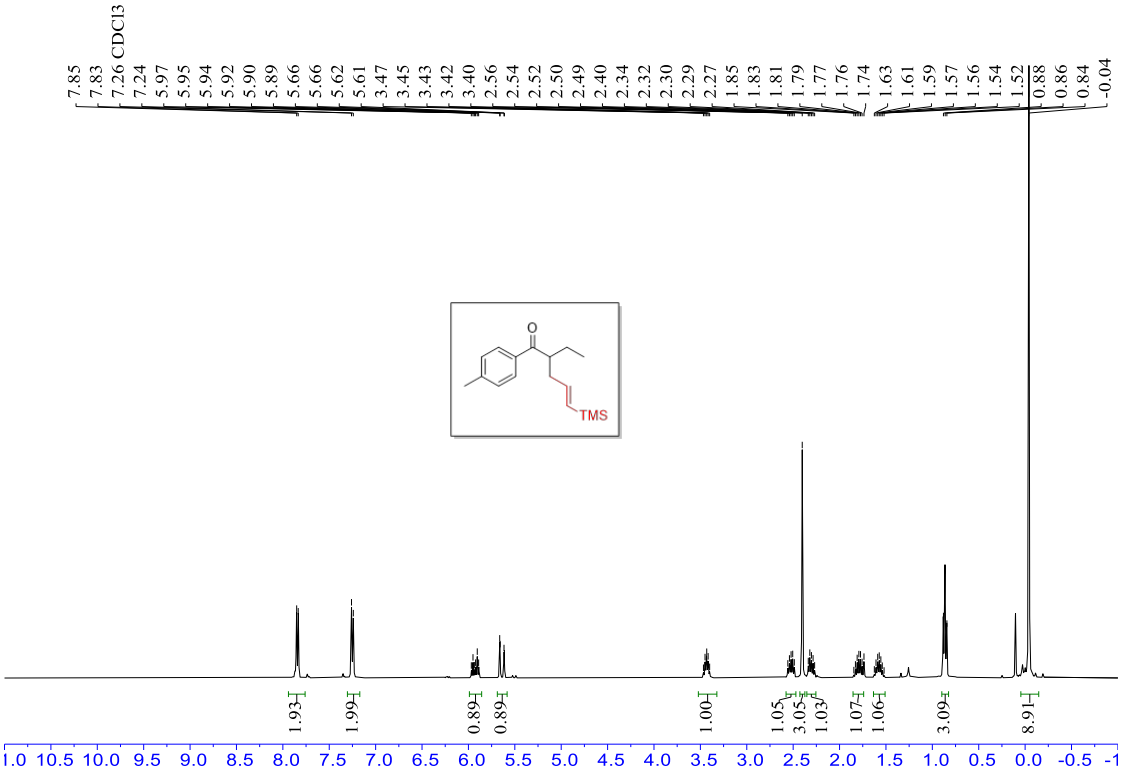
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3a**



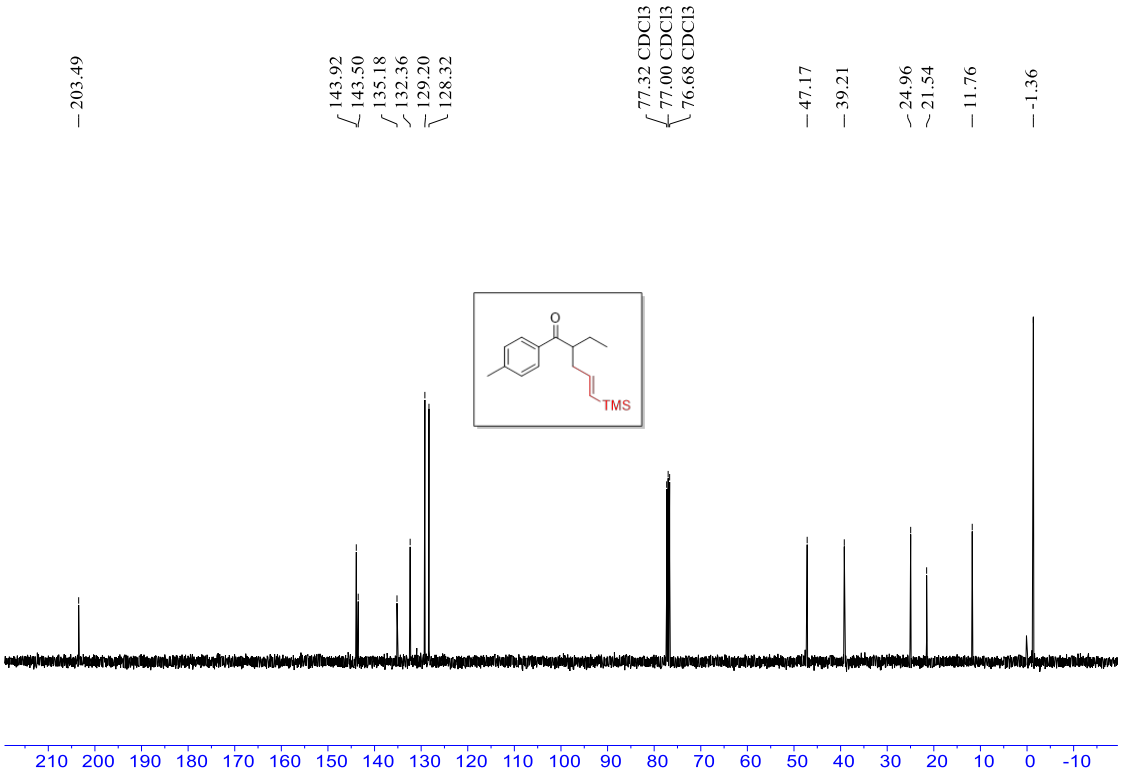
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3b**



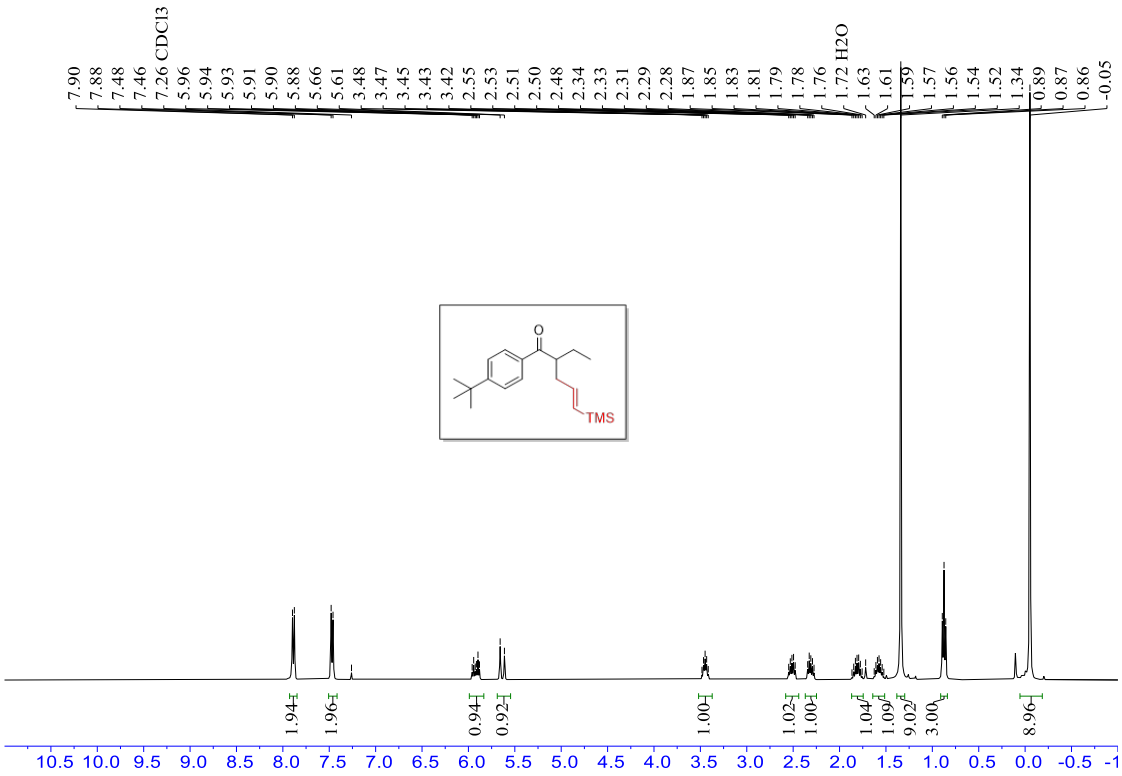
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3b**



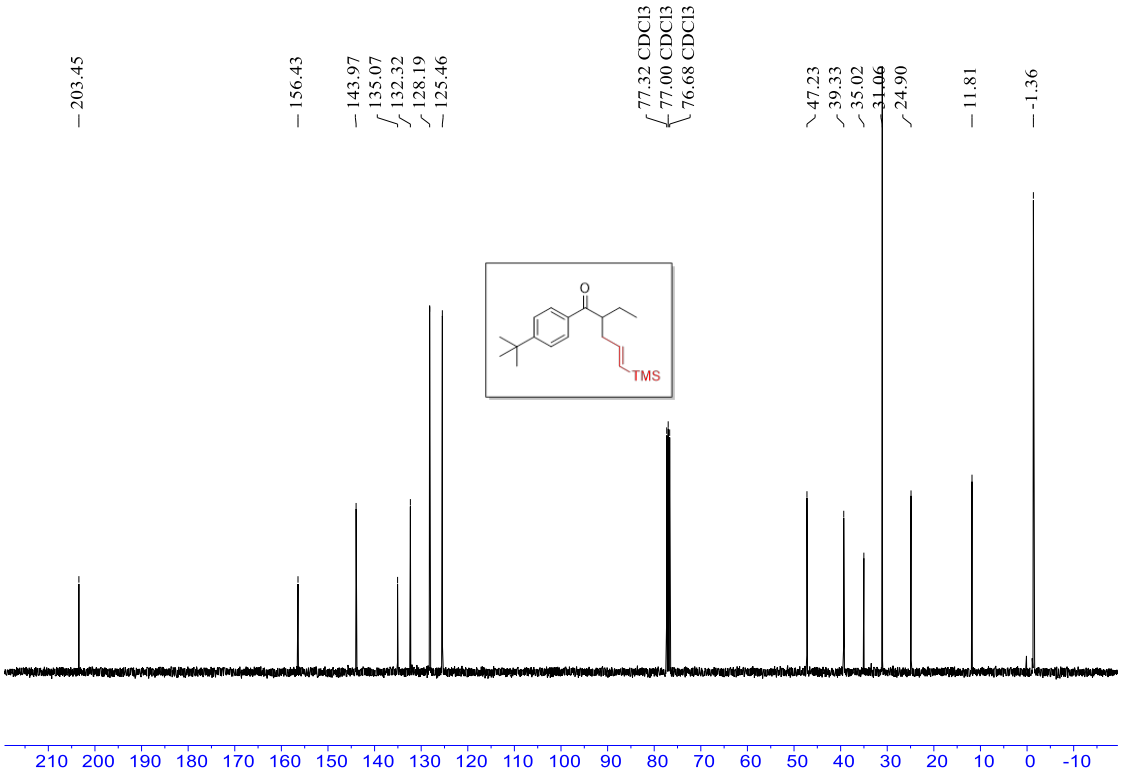
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3c**



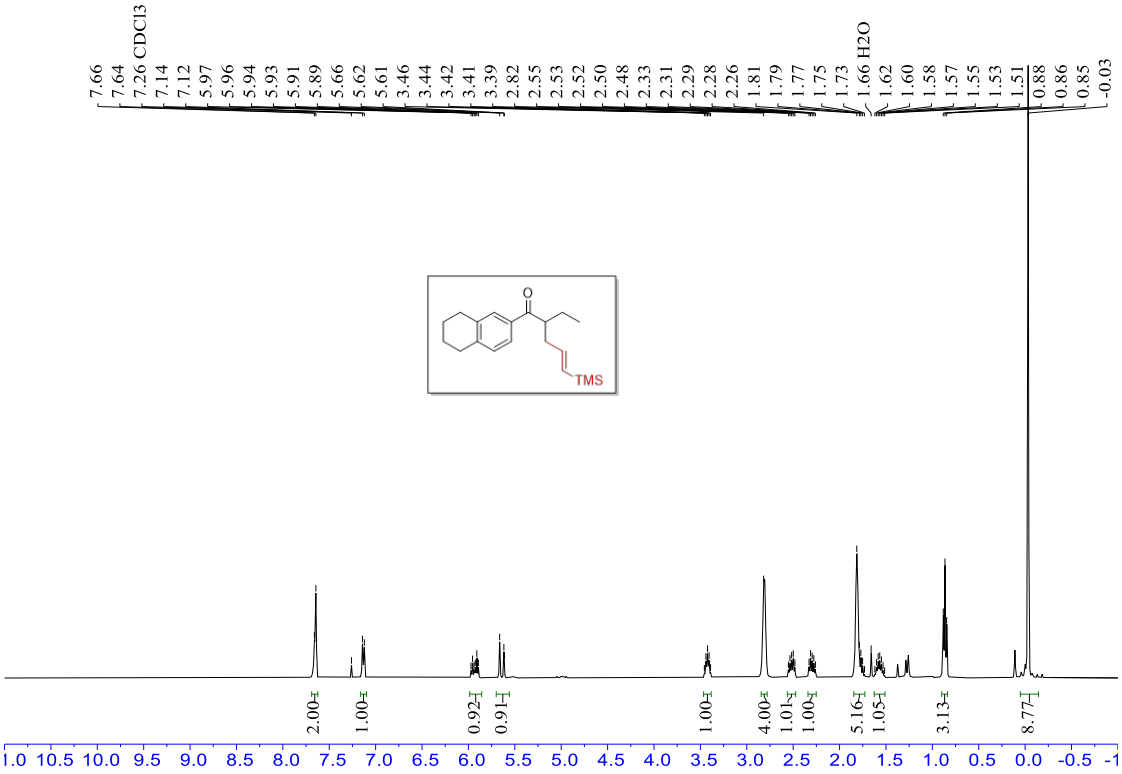
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3c**



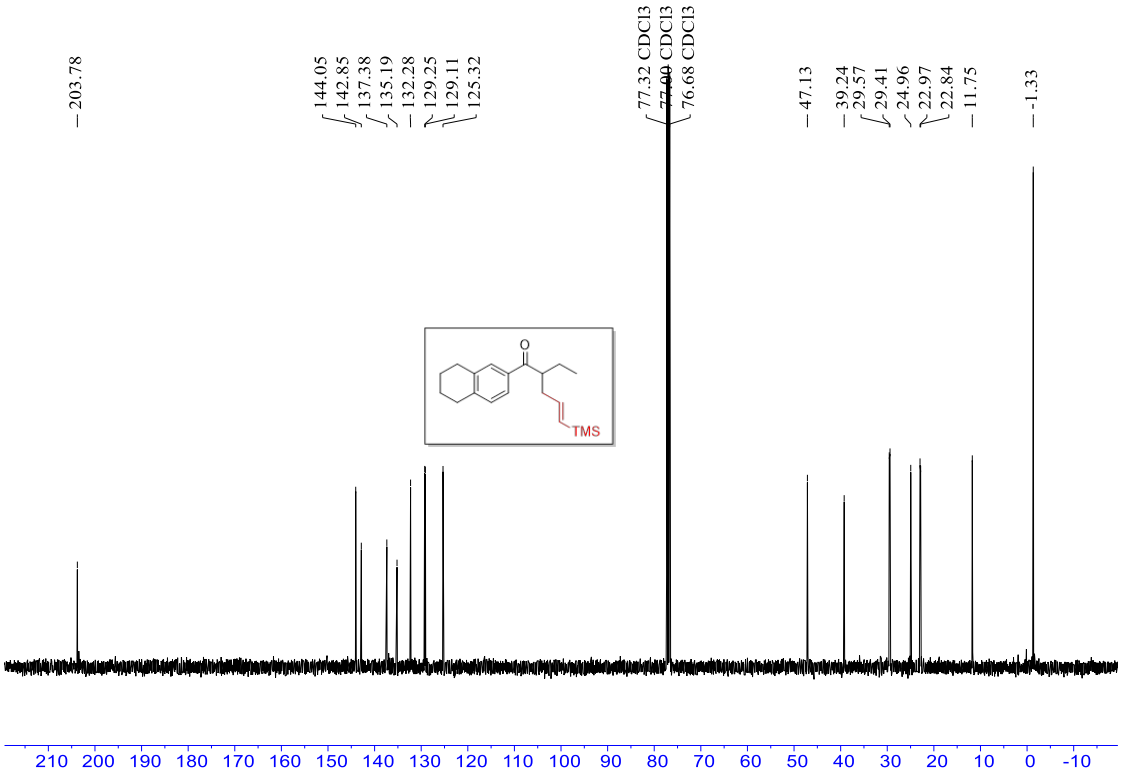
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3d**



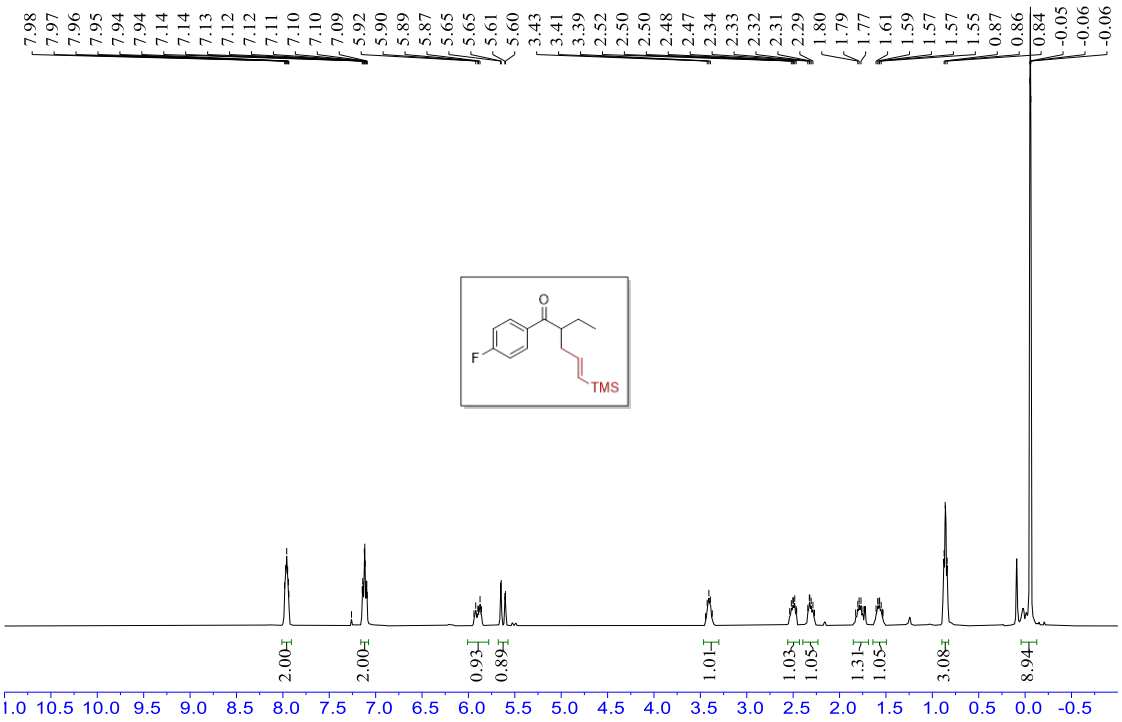
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3d**



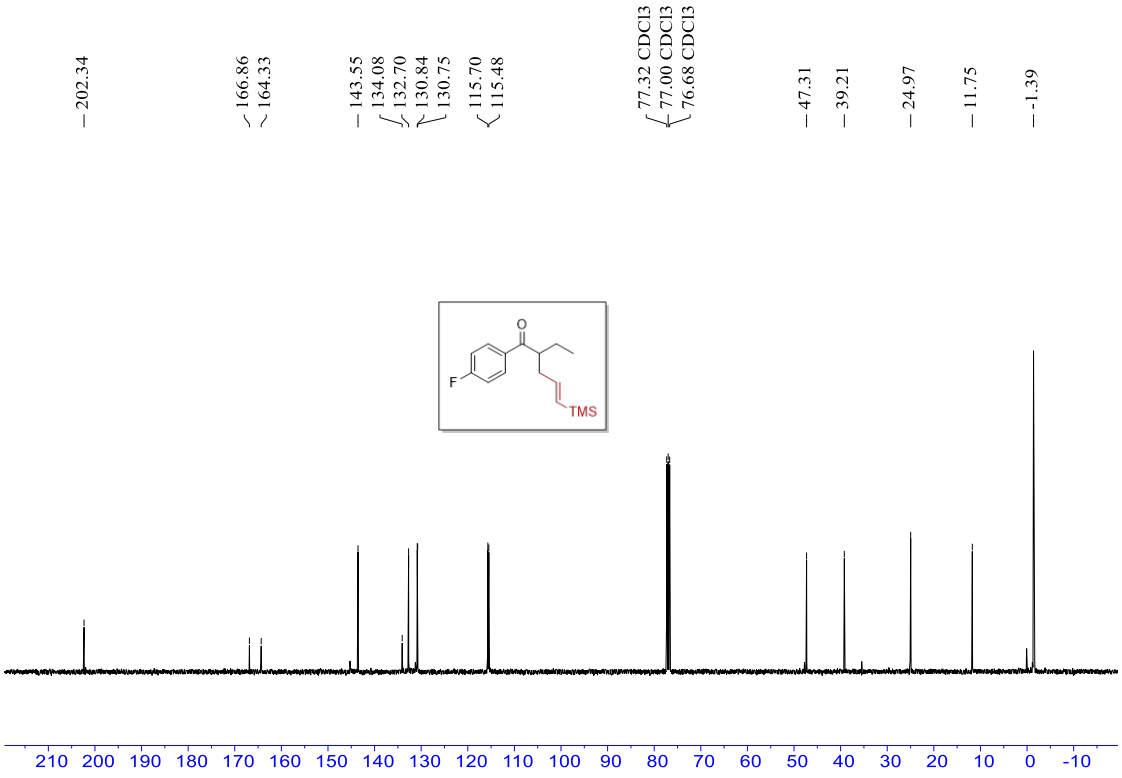
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3e**



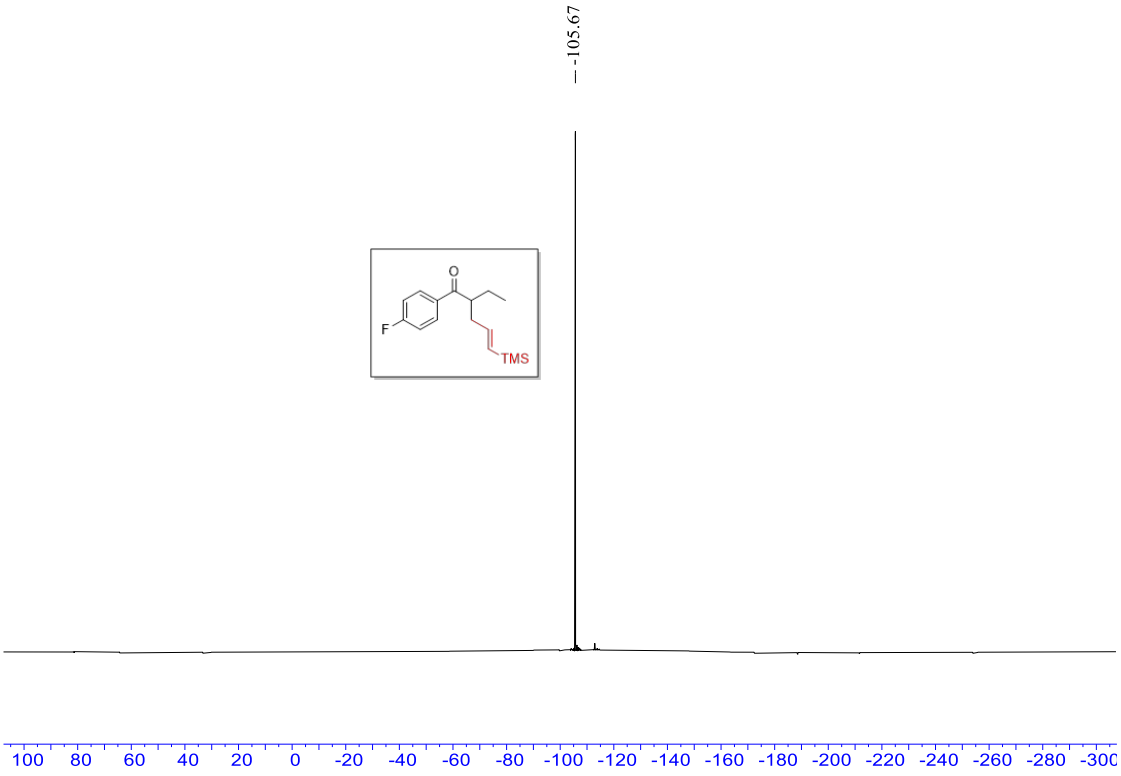
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3e**



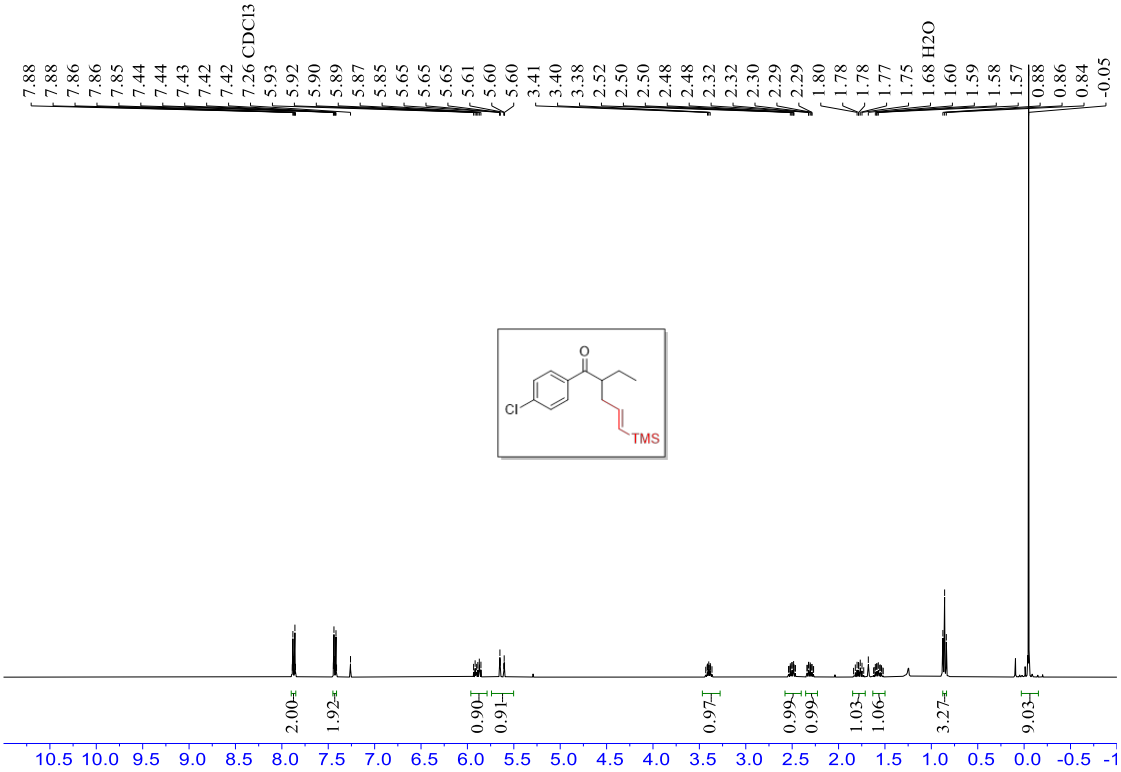
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3f**



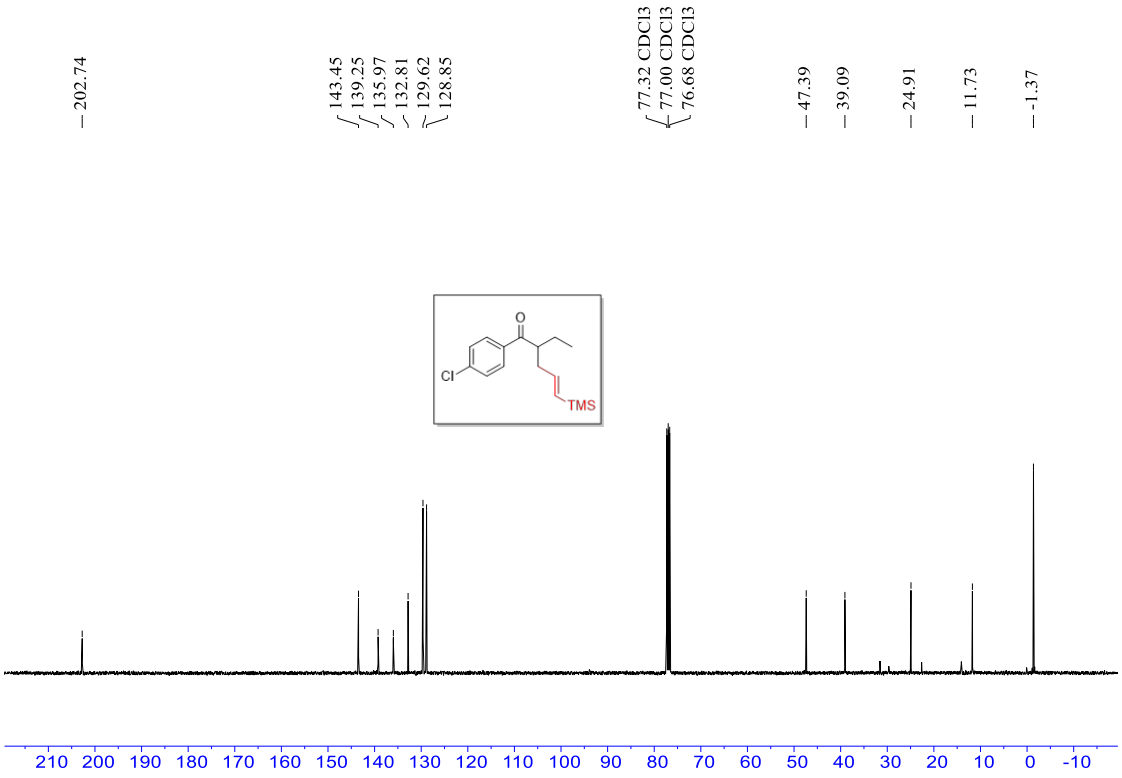
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3f**



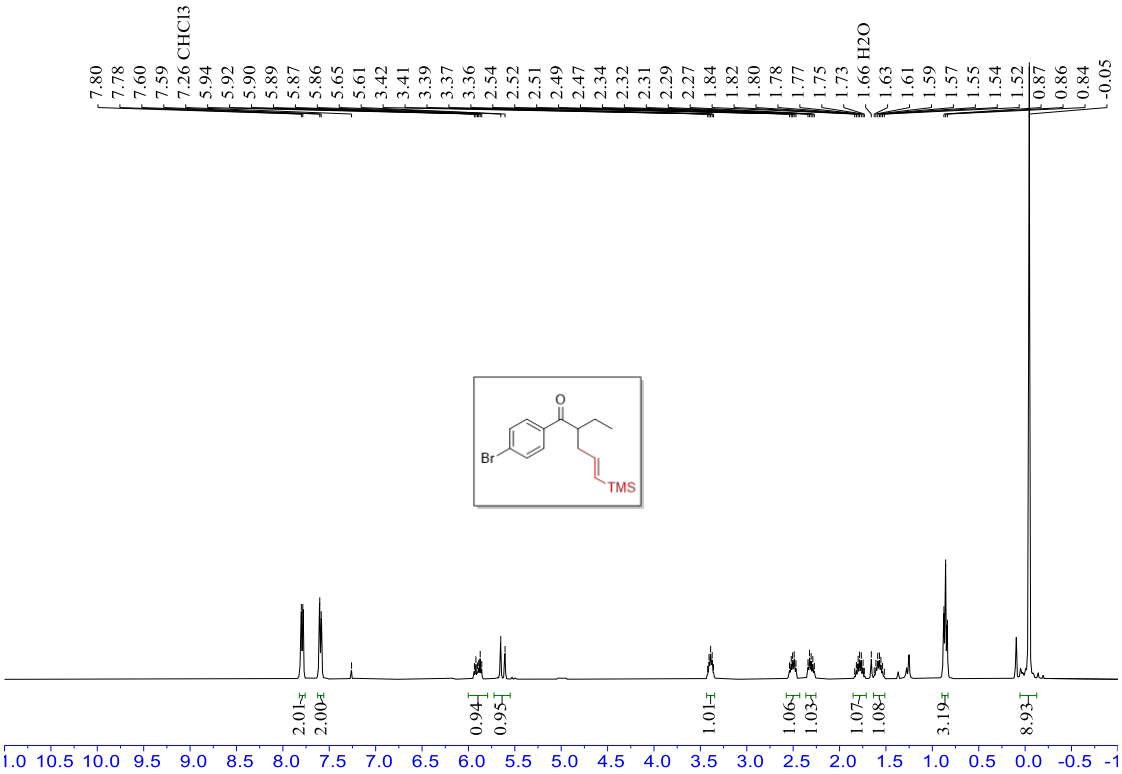
^{19}F NMR (376MHz, $CDCl_3$) spectrum for **3f**



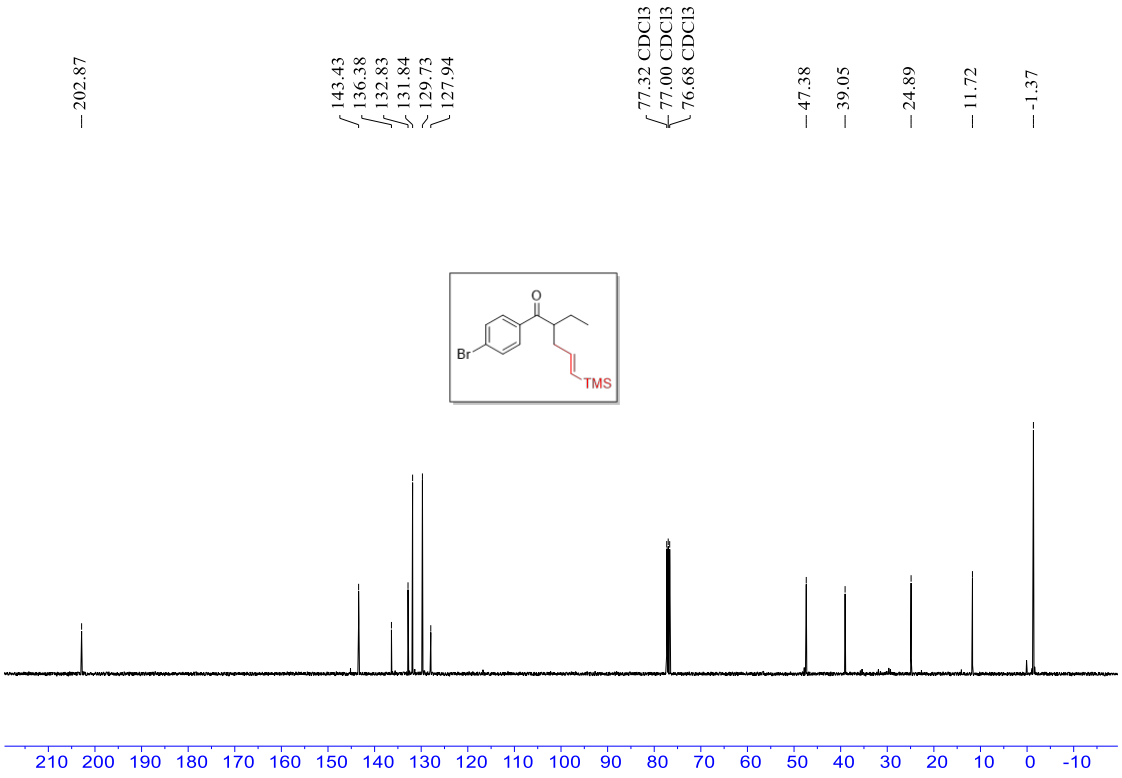
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3g**



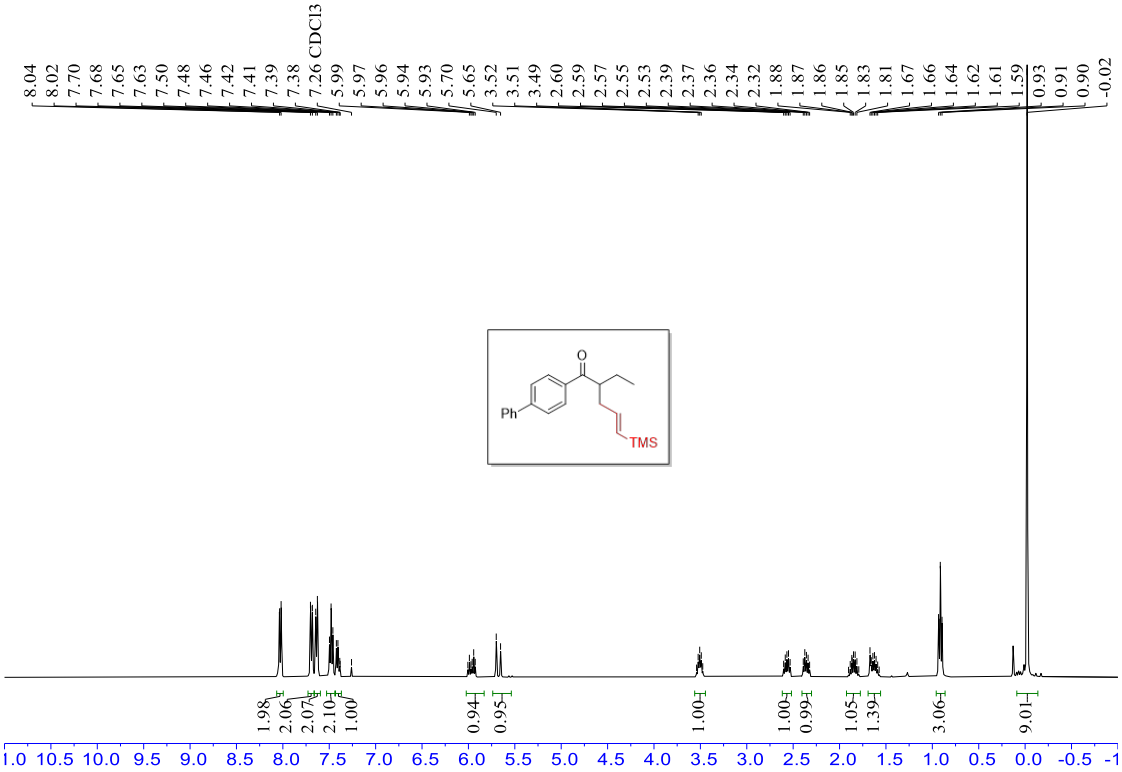
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3g**



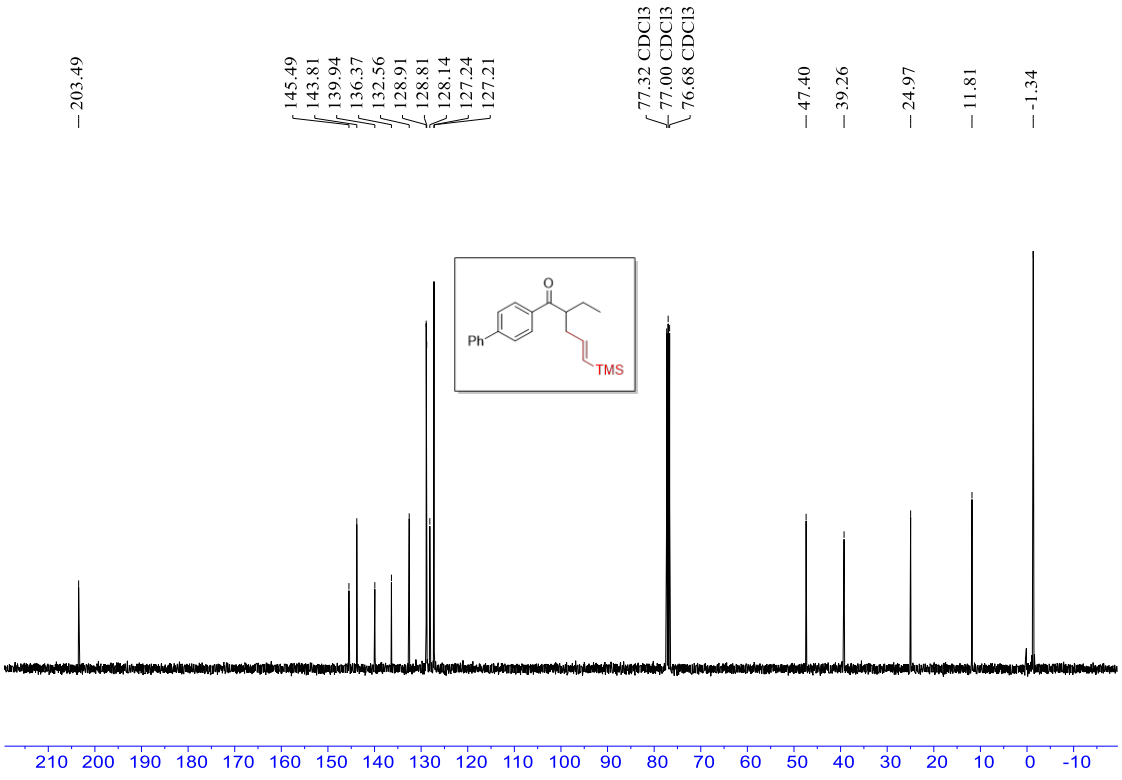
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3h**



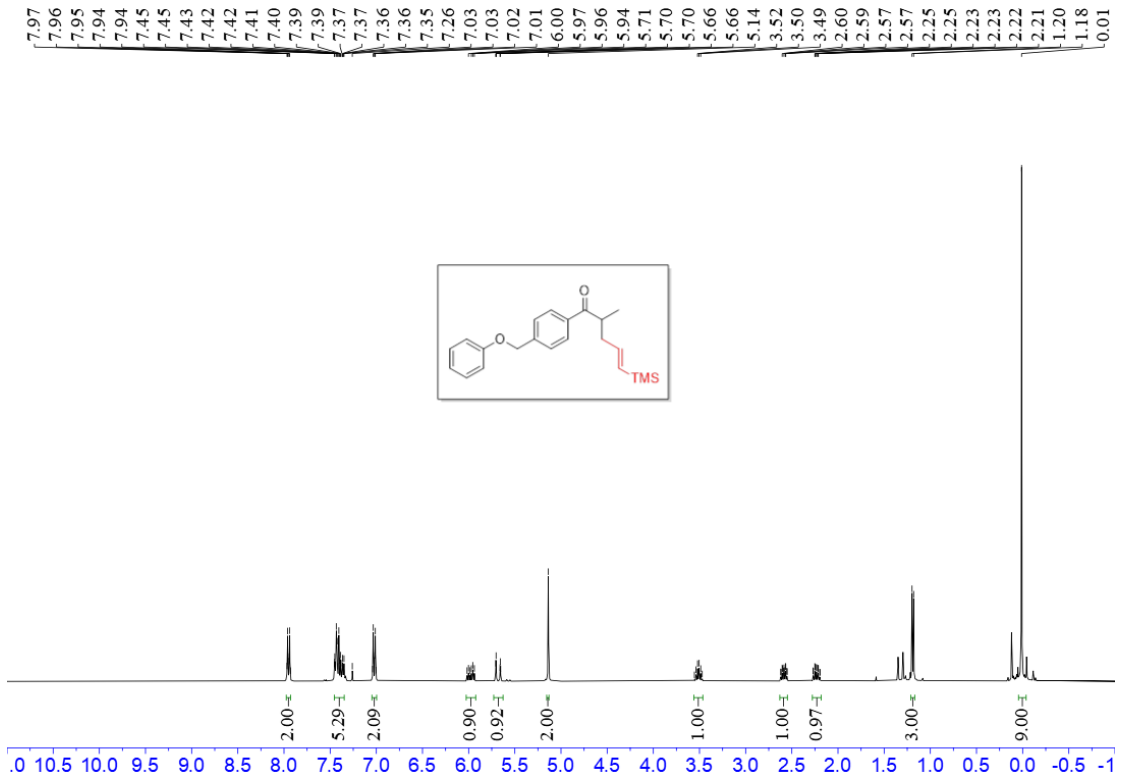
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3h**



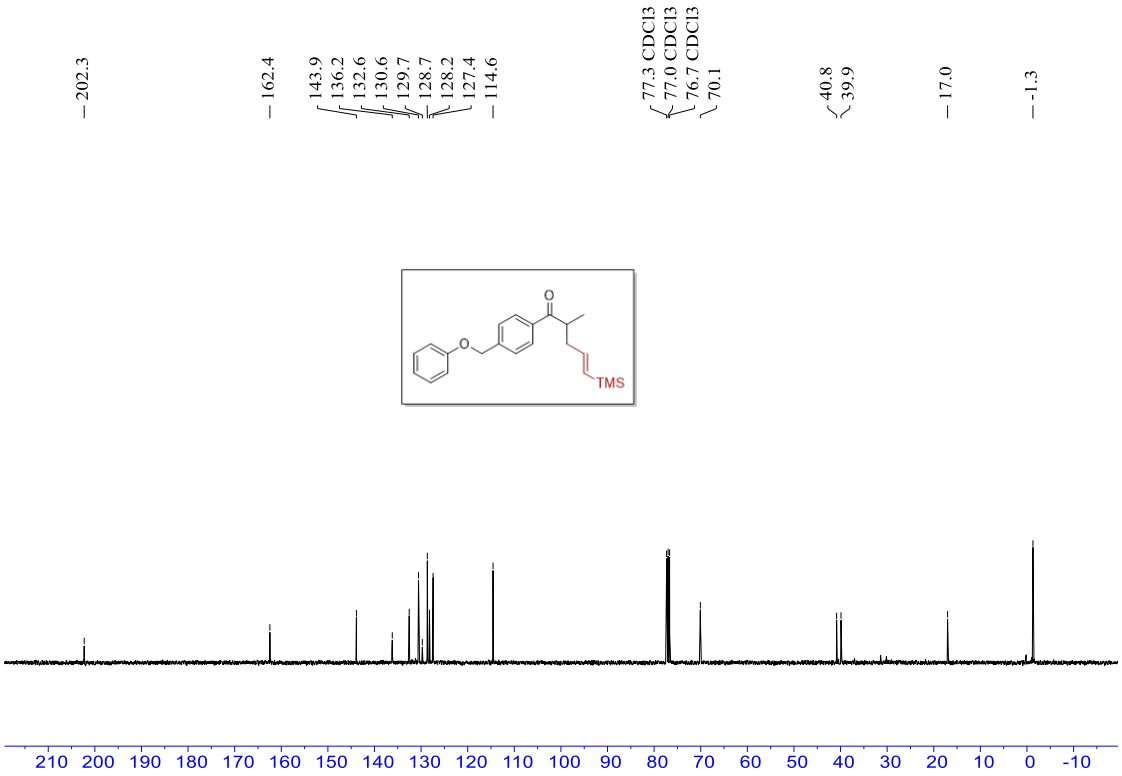
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3i**



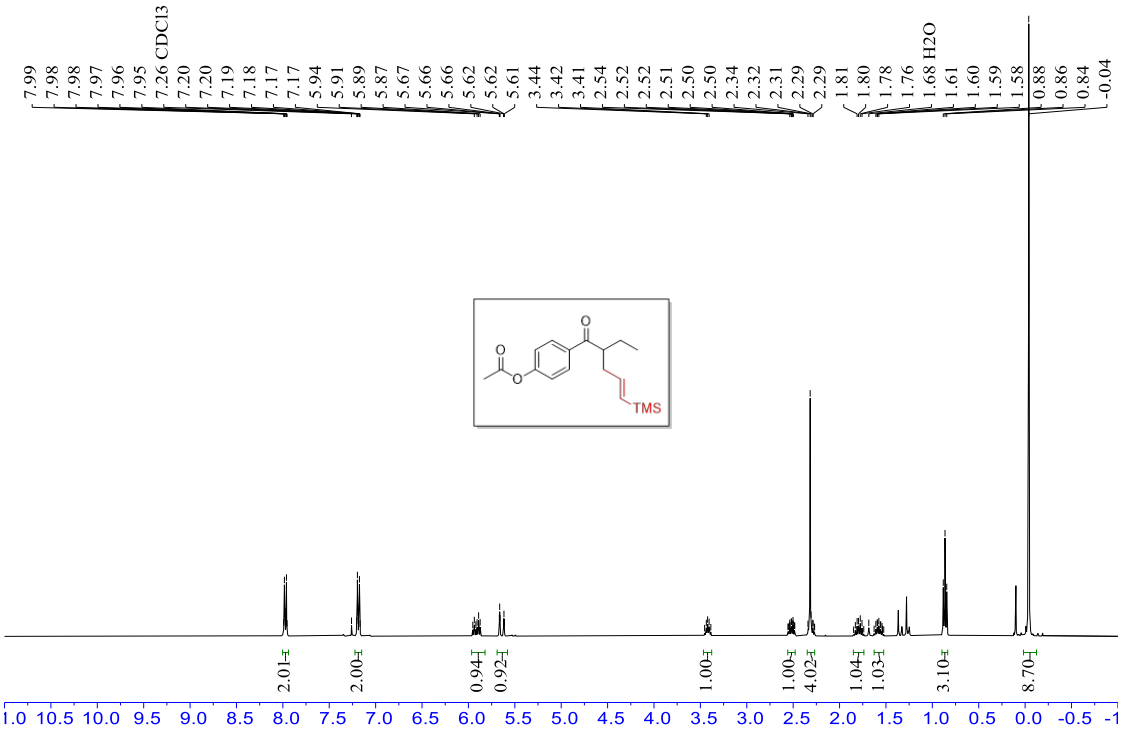
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3i**



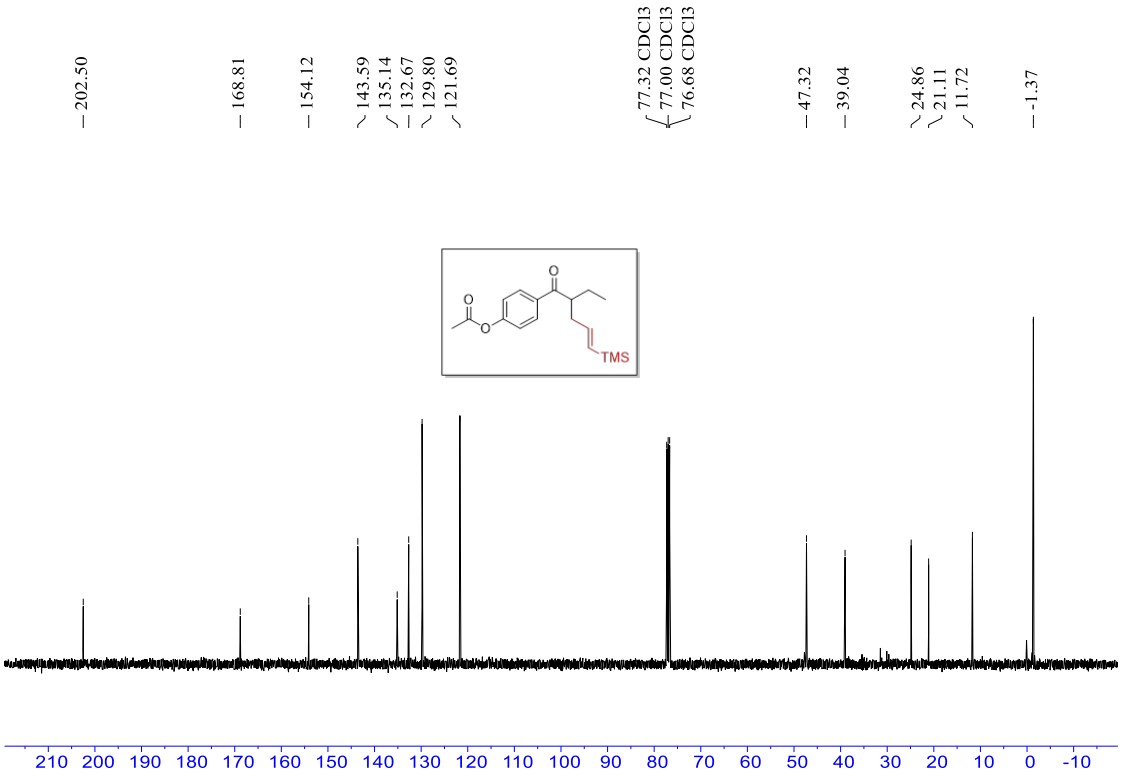
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3j**



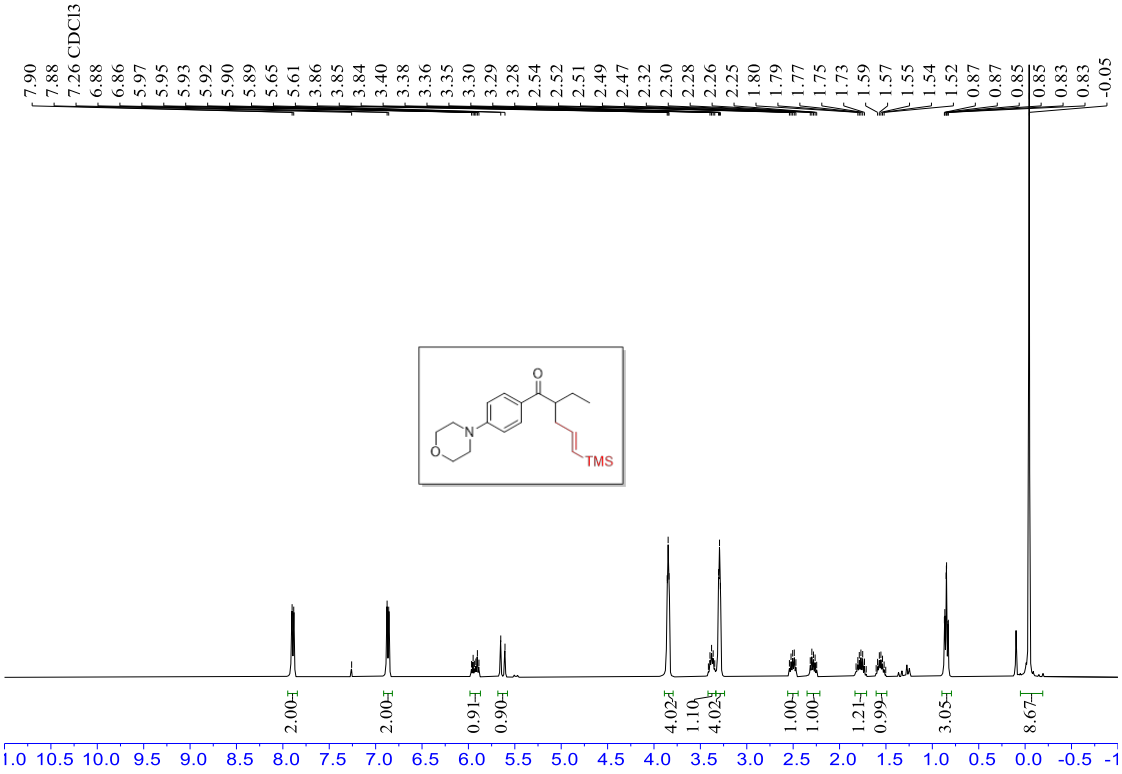
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3j**



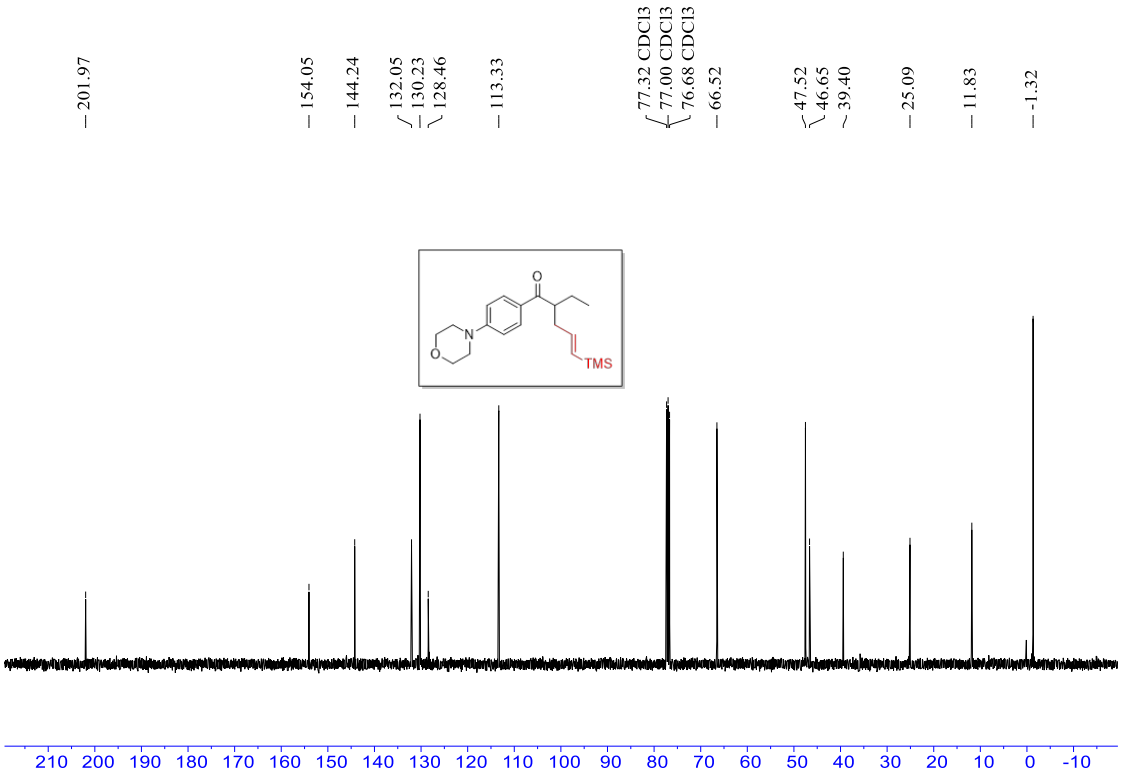
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3k**



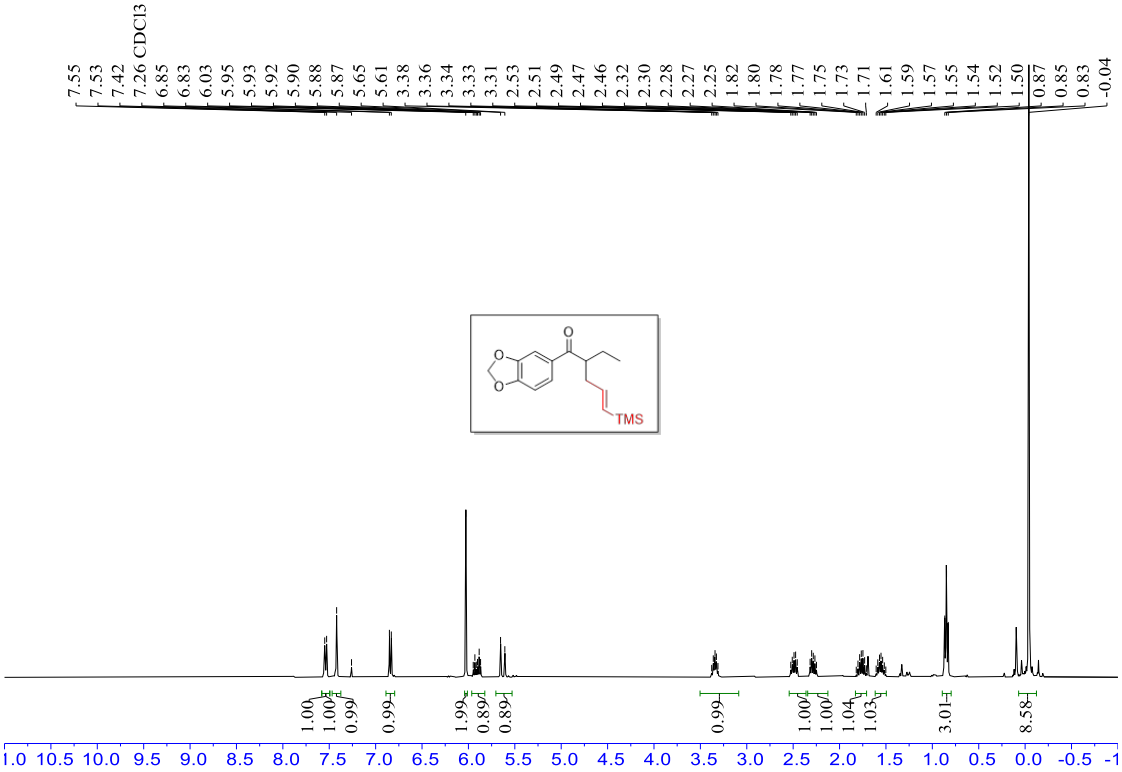
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3k**



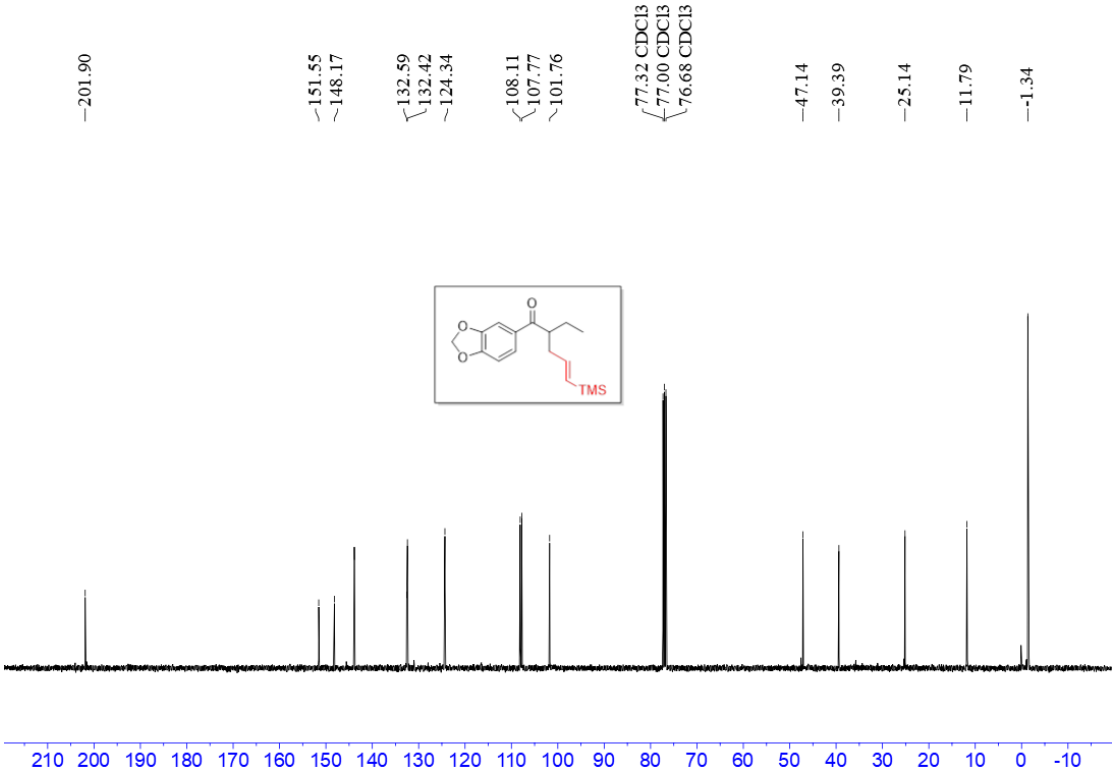
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3l**



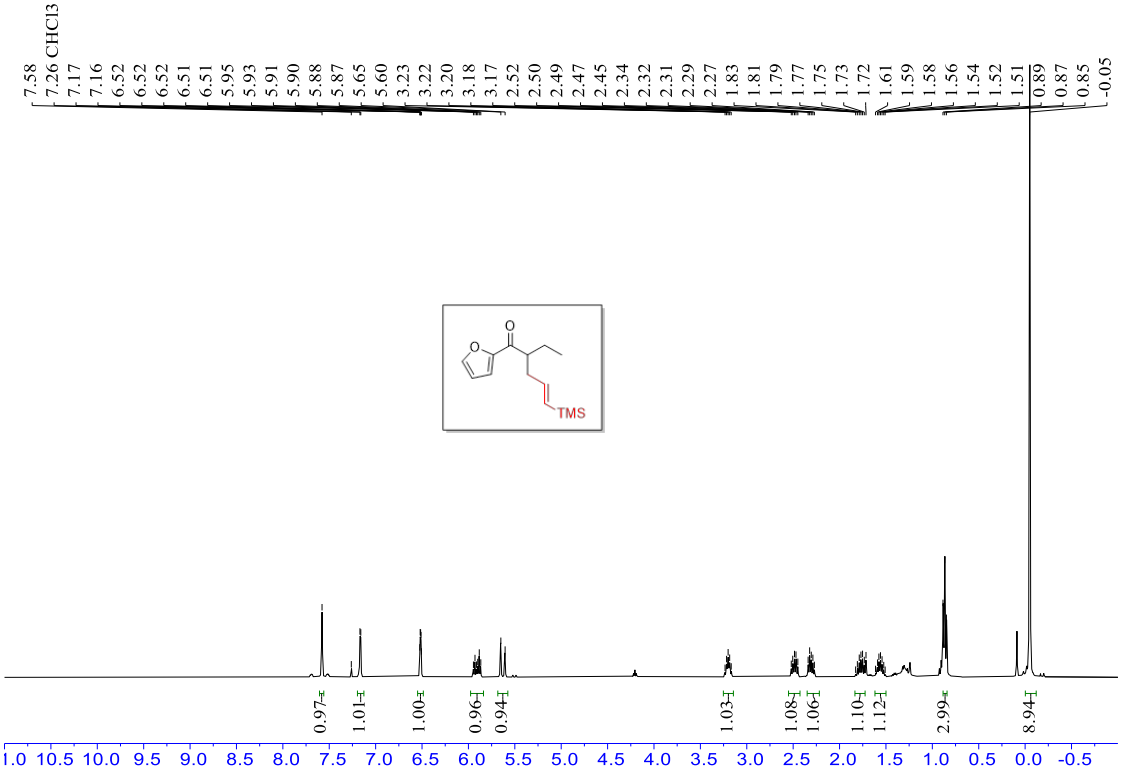
^{13}C NMR (101MHz, $CDCl_3$) spectrum for **3l**



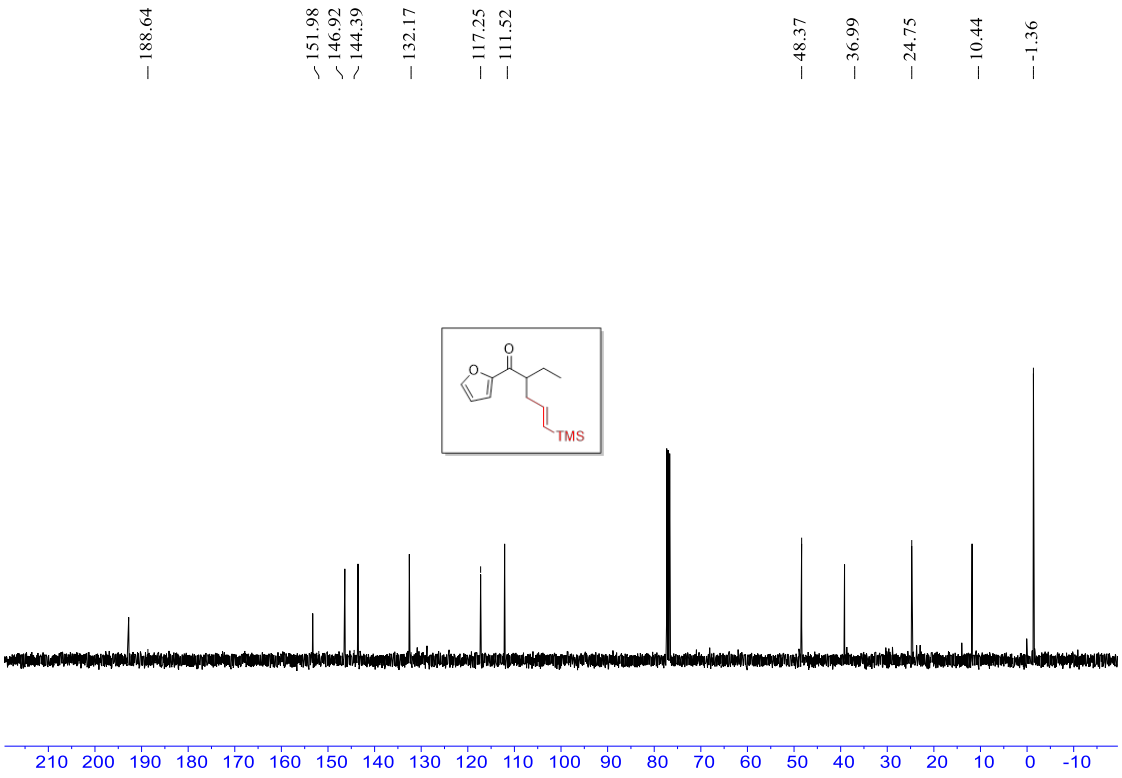
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3m**



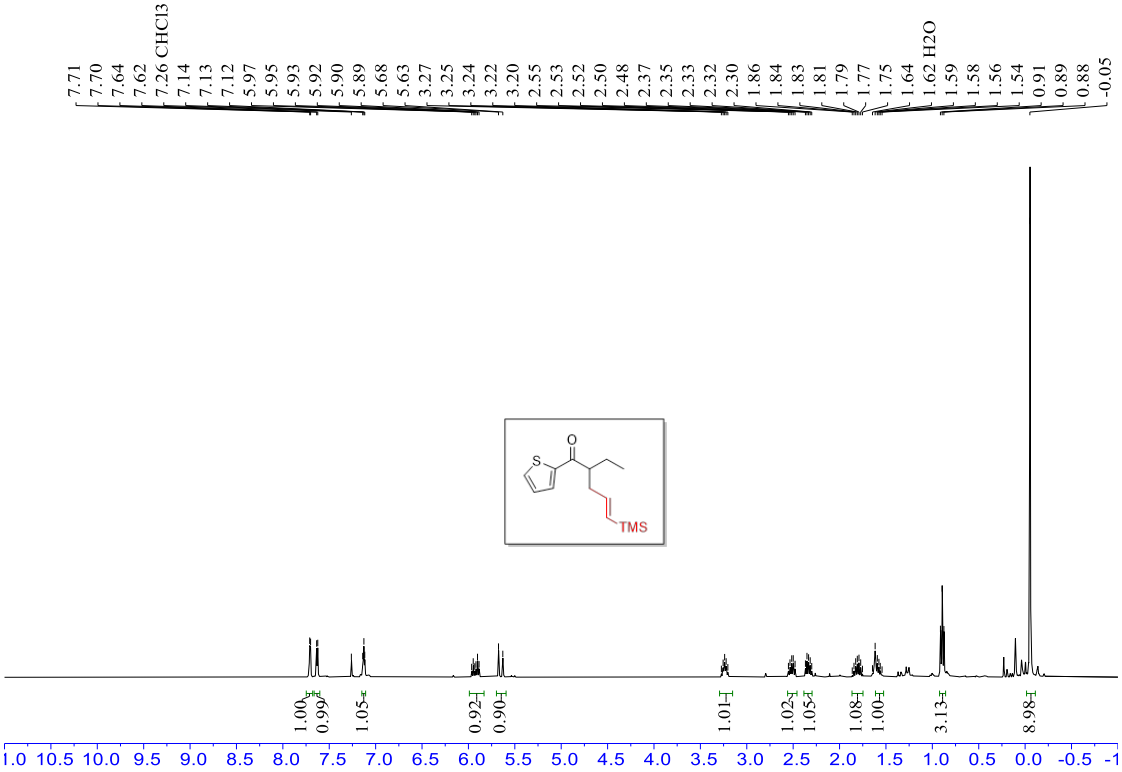
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3m**



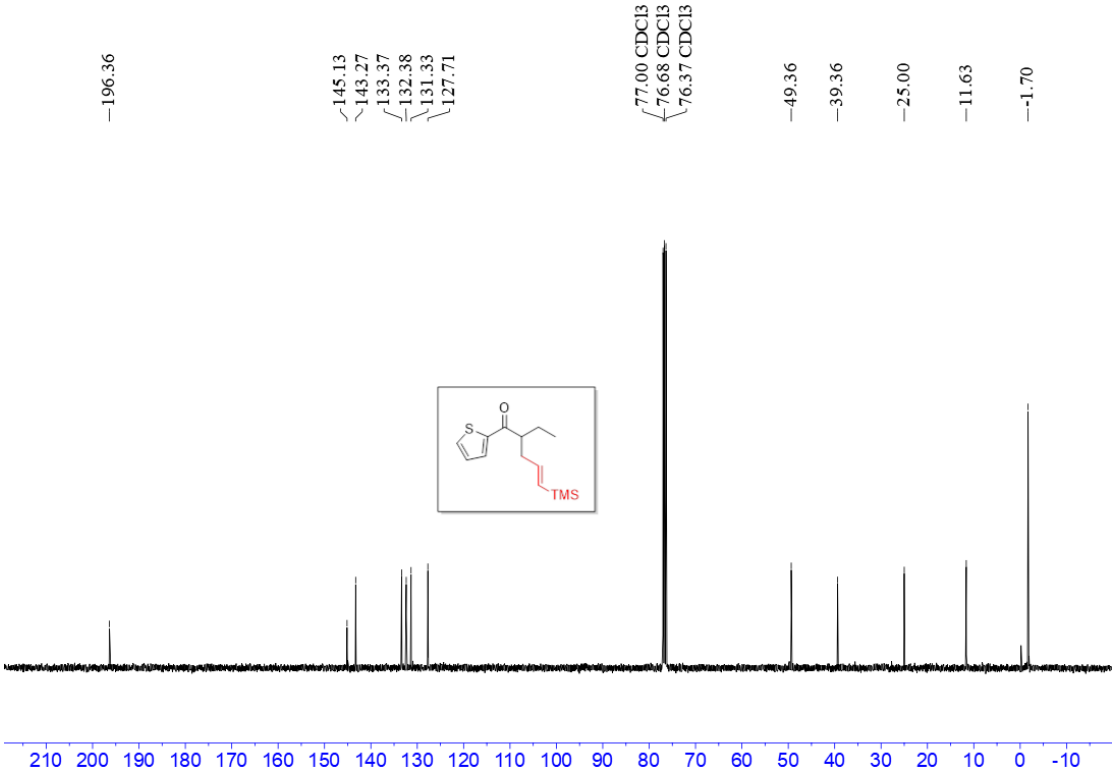
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3n**



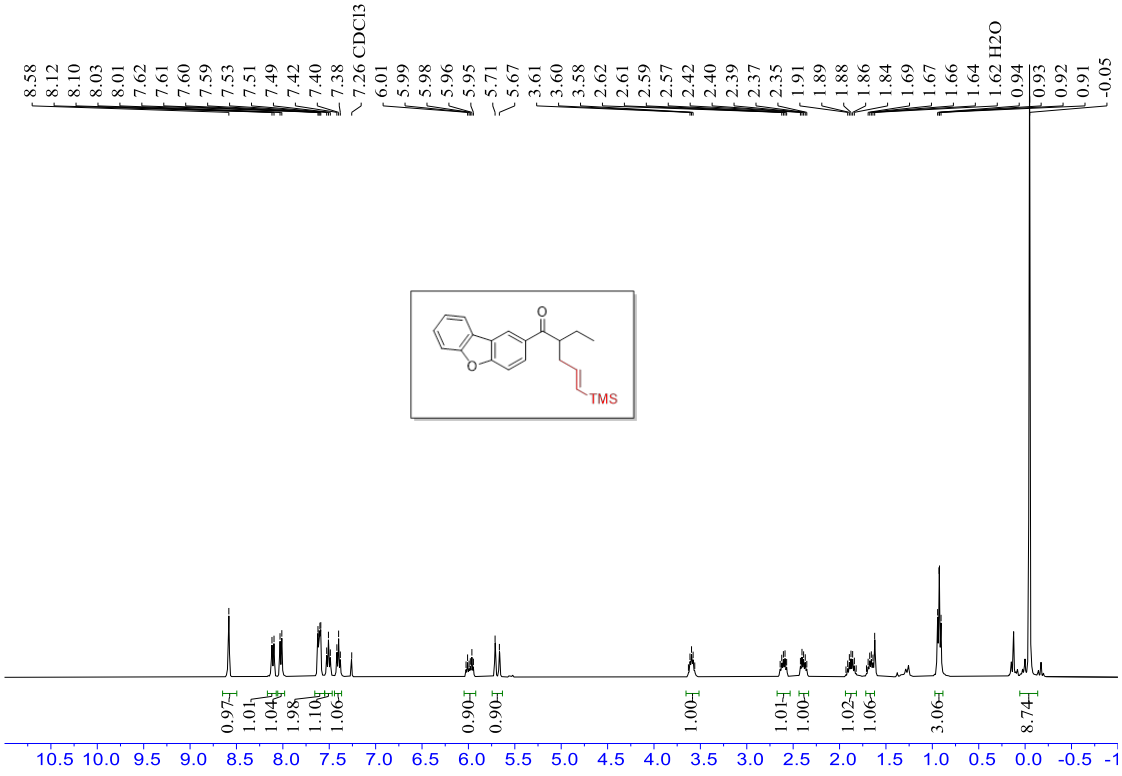
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3n**



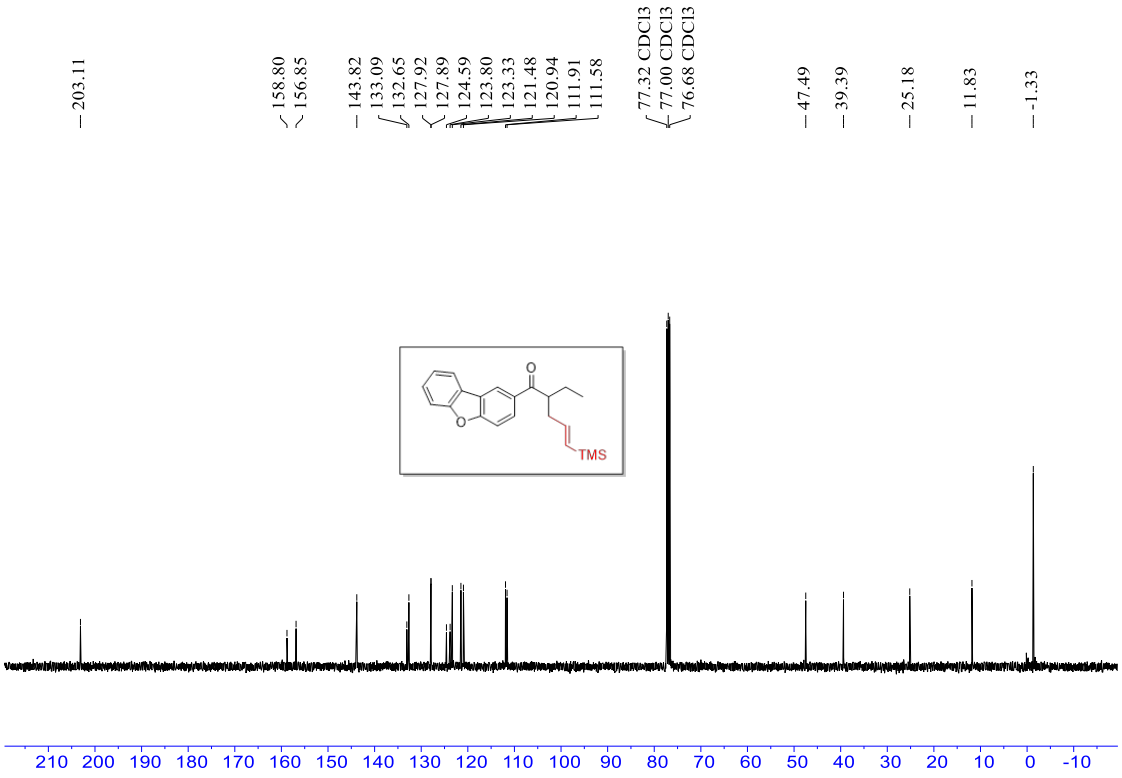
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3o**



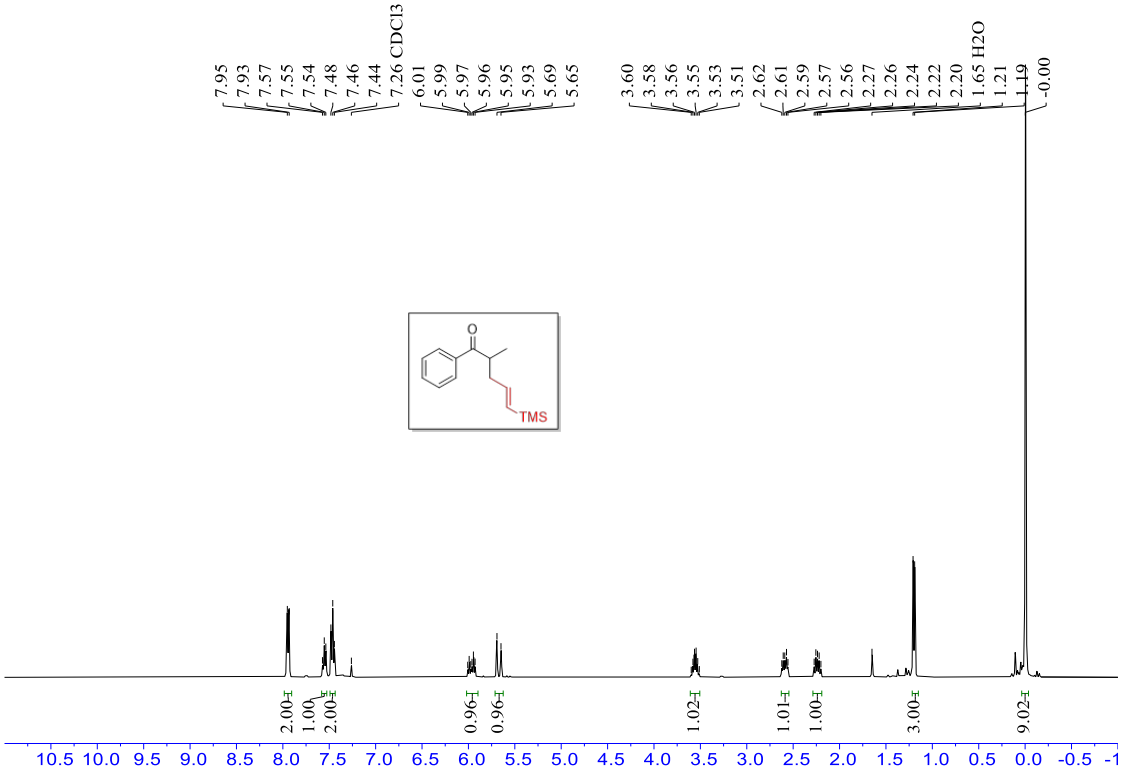
^{13}C NMR ($CDCl_3$) spectrum for **3o**



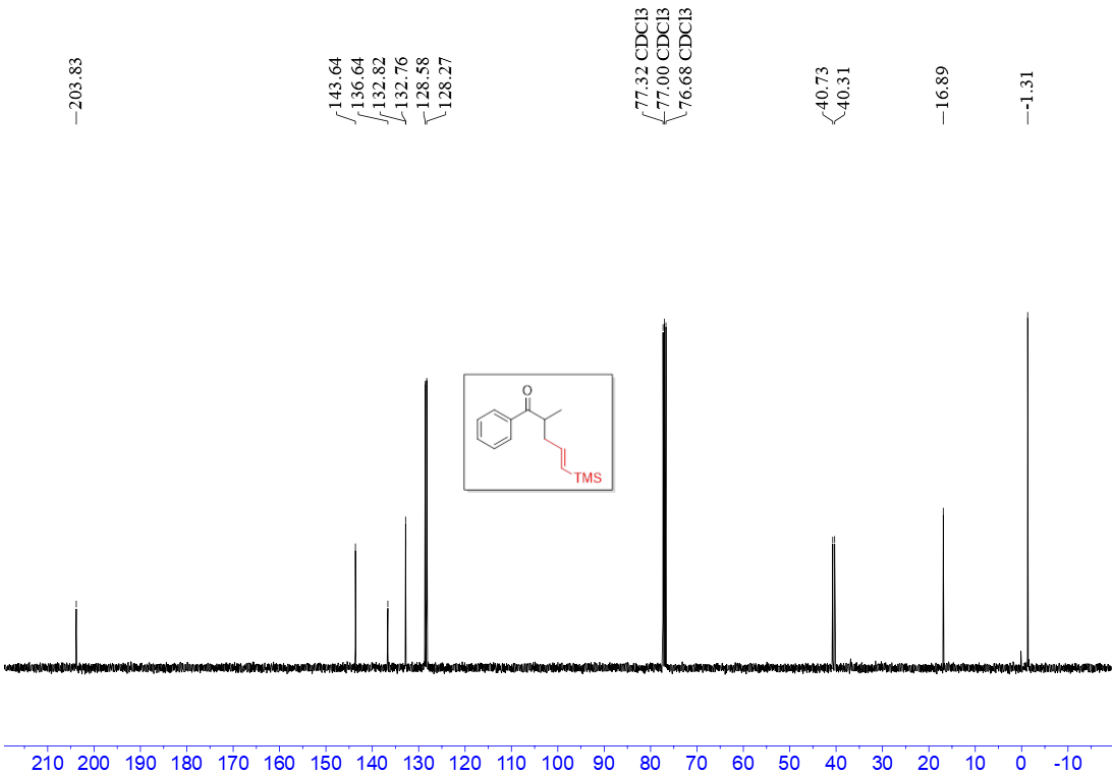
^{1}H NMR ($CDCl_3$) spectrum for **3p**



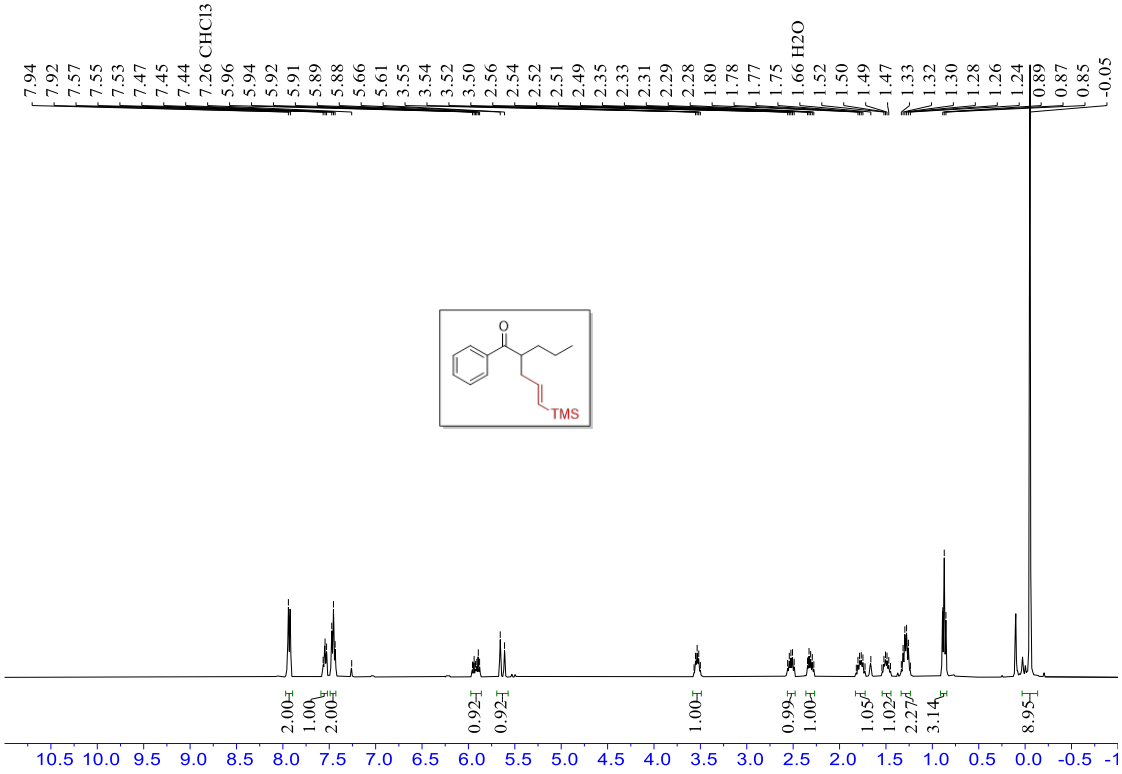
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3p**



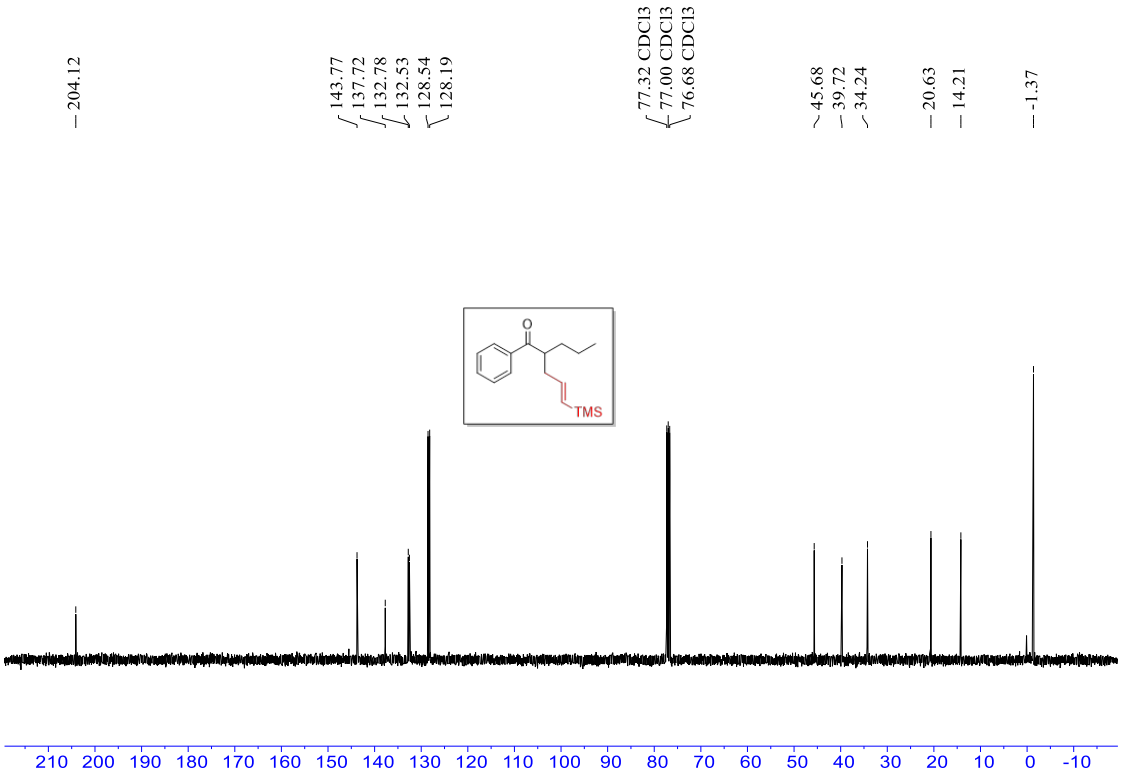
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3q**



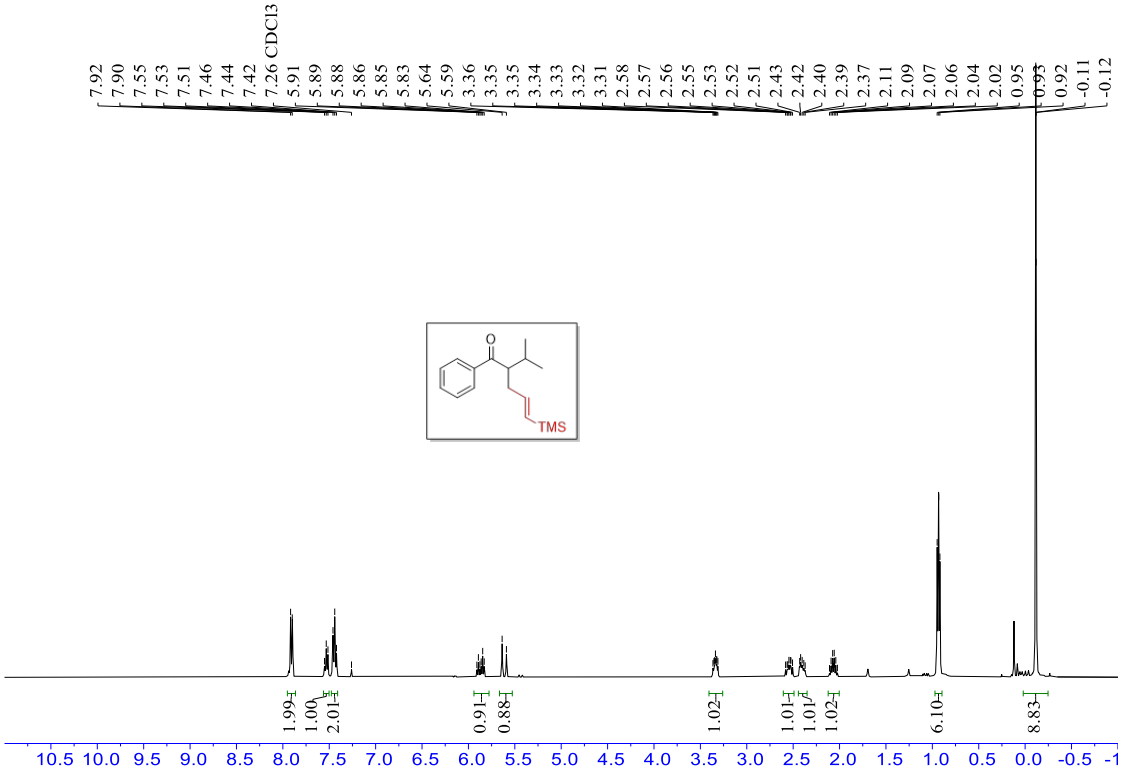
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3q**



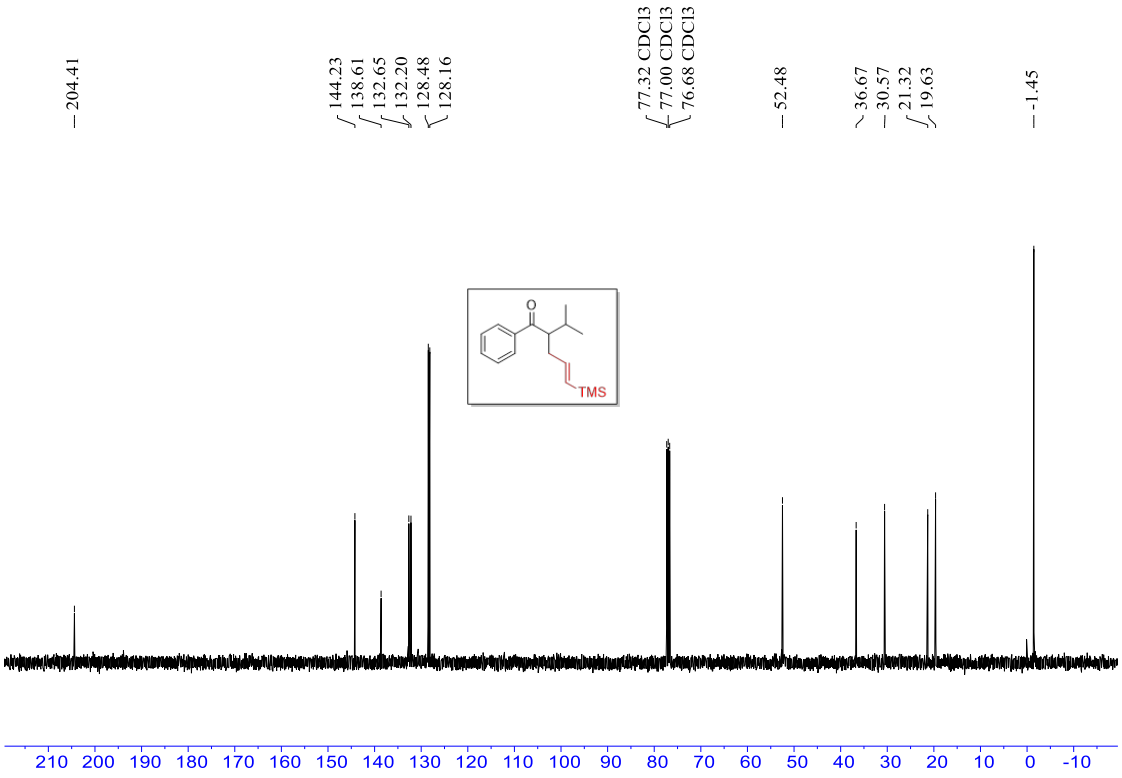
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3r**



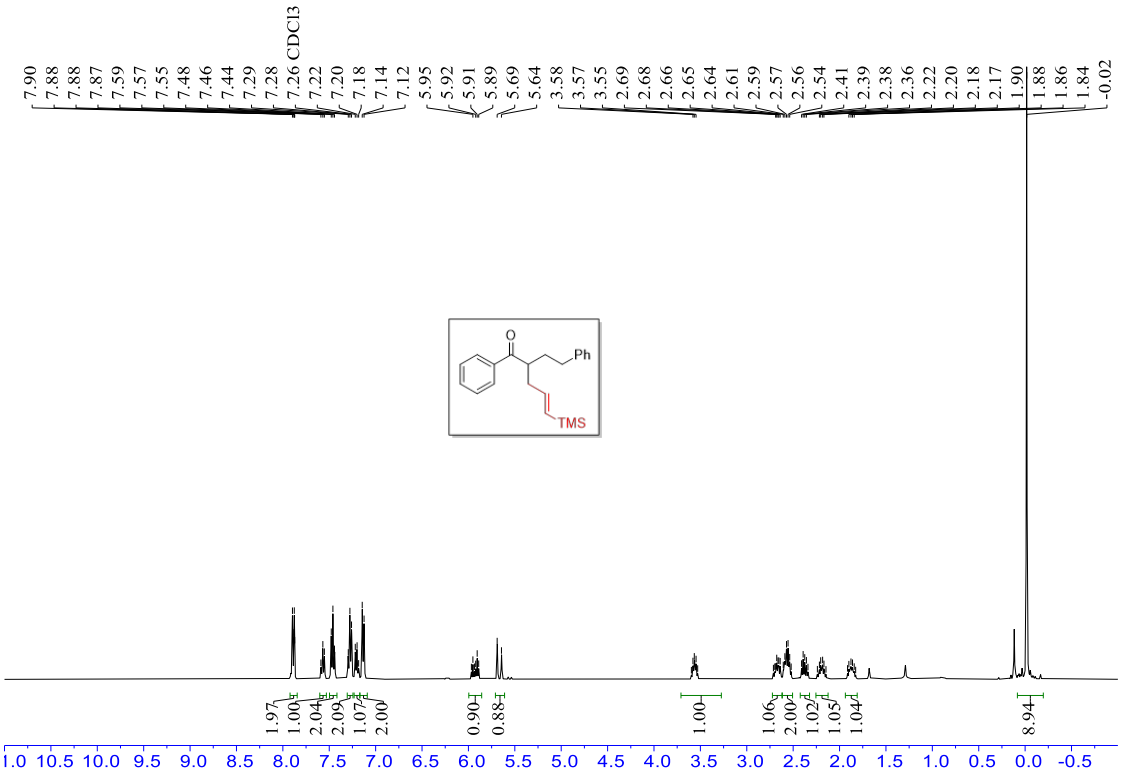
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3r**



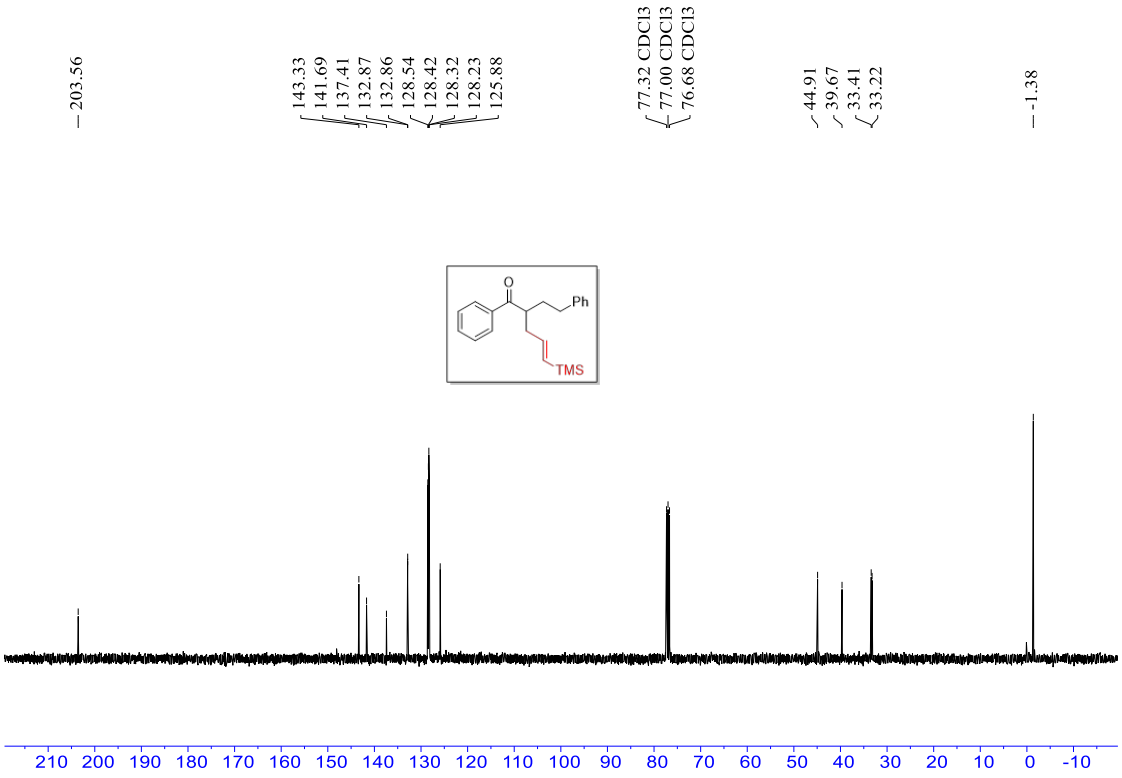
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3s**



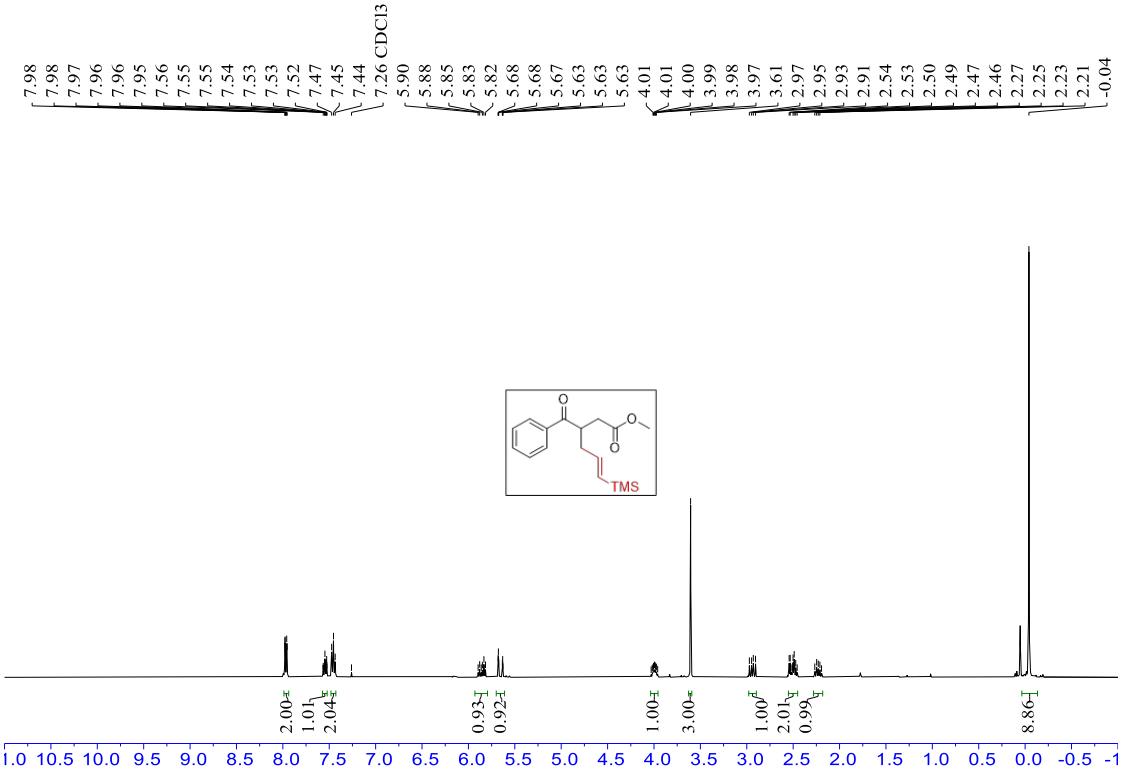
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3s**



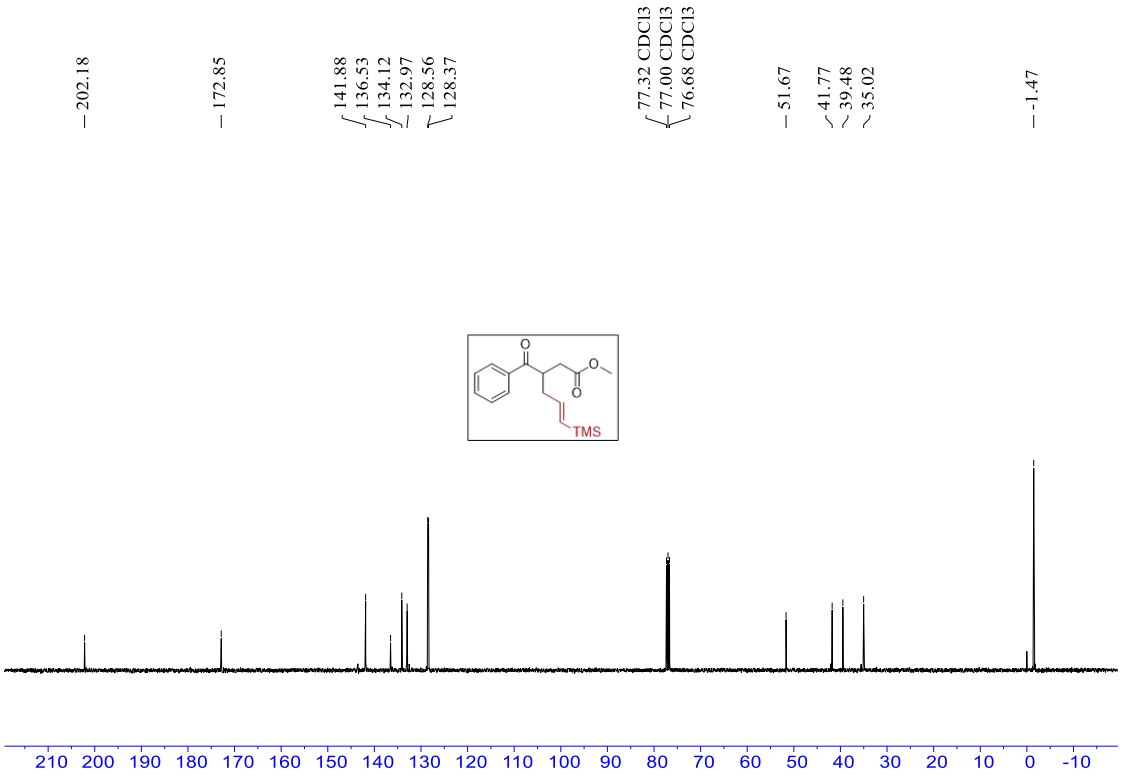
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3t**



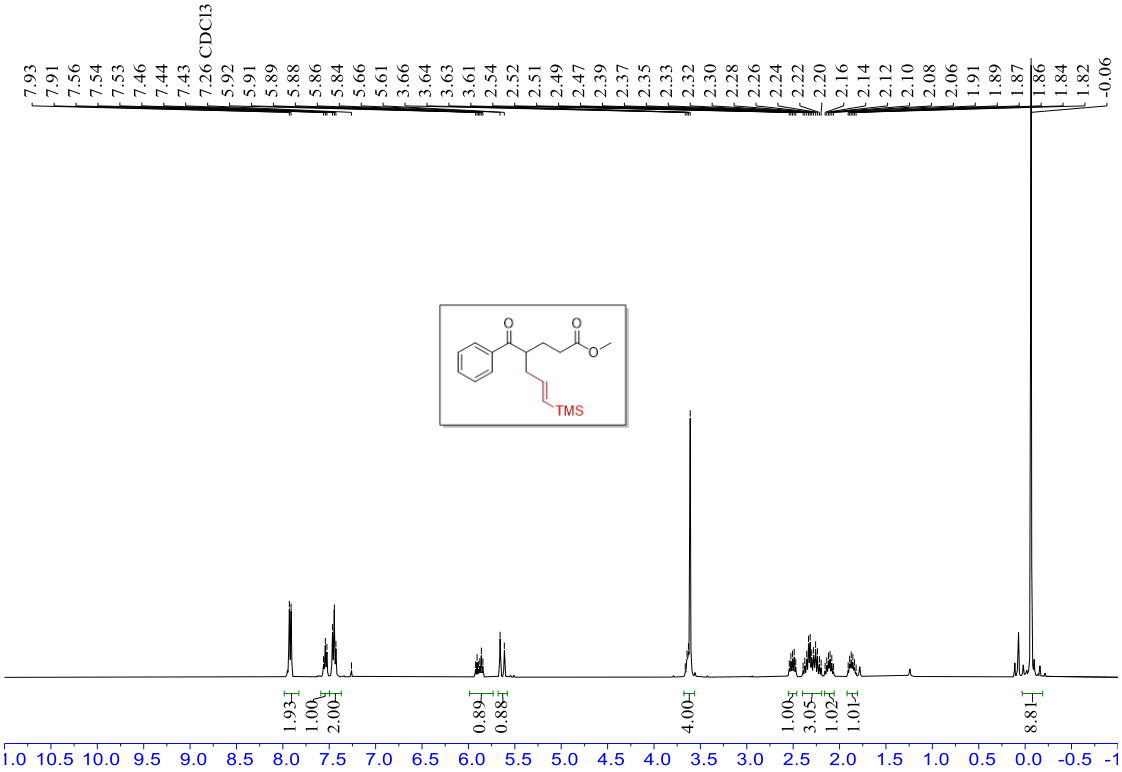
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3t**



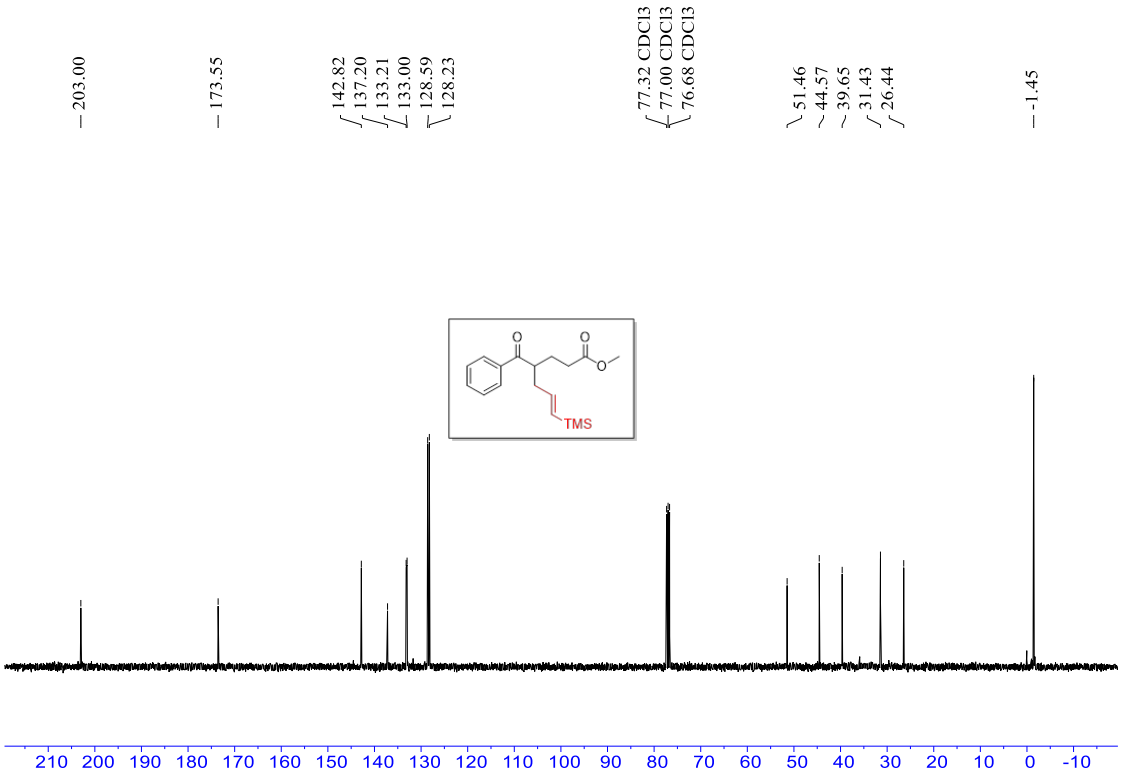
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3u**



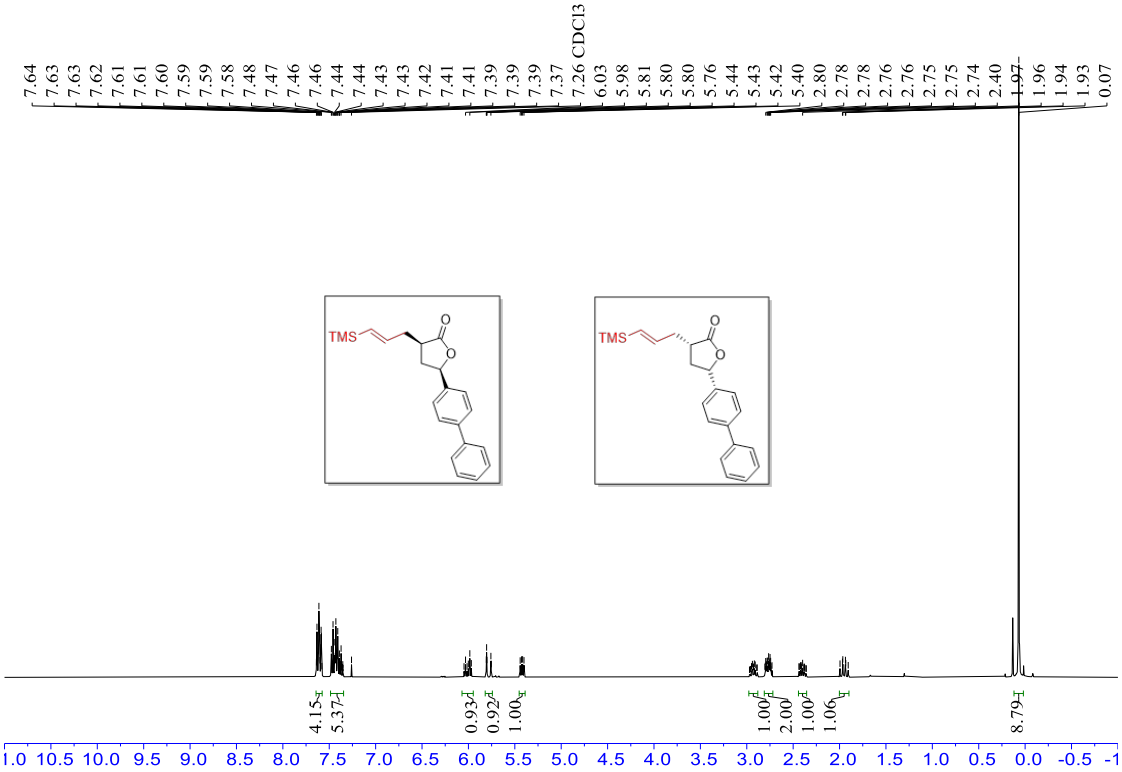
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3u**



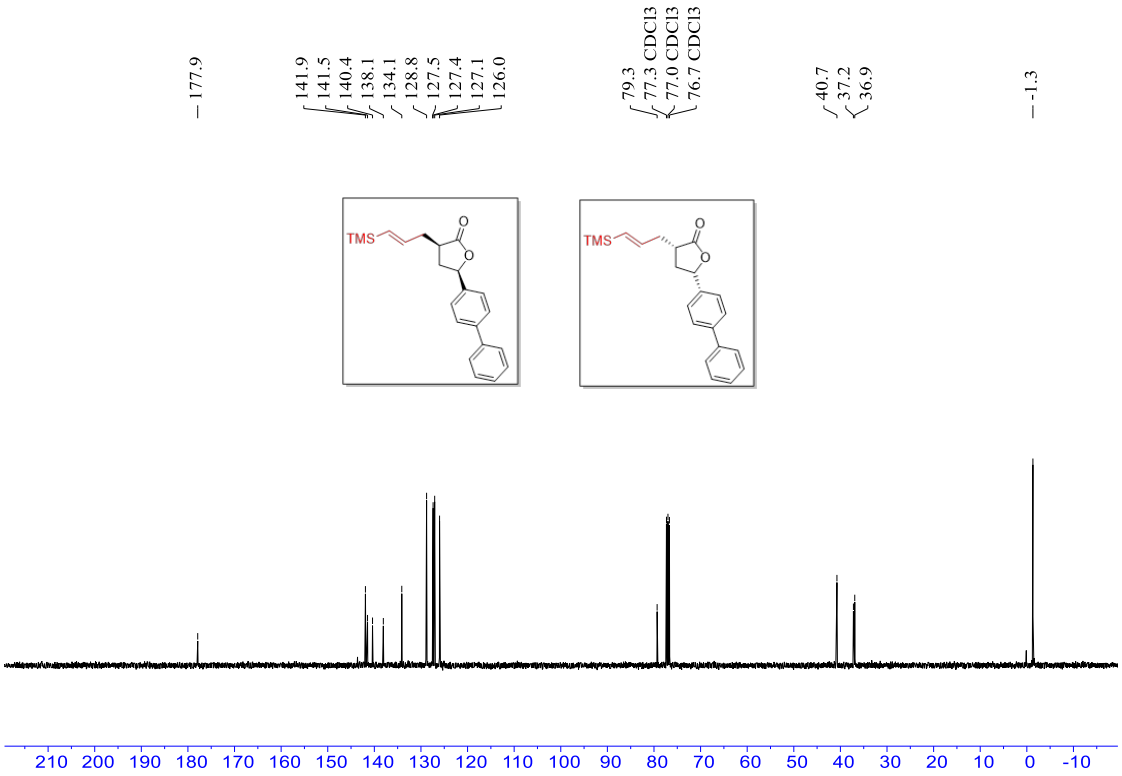
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **3v**



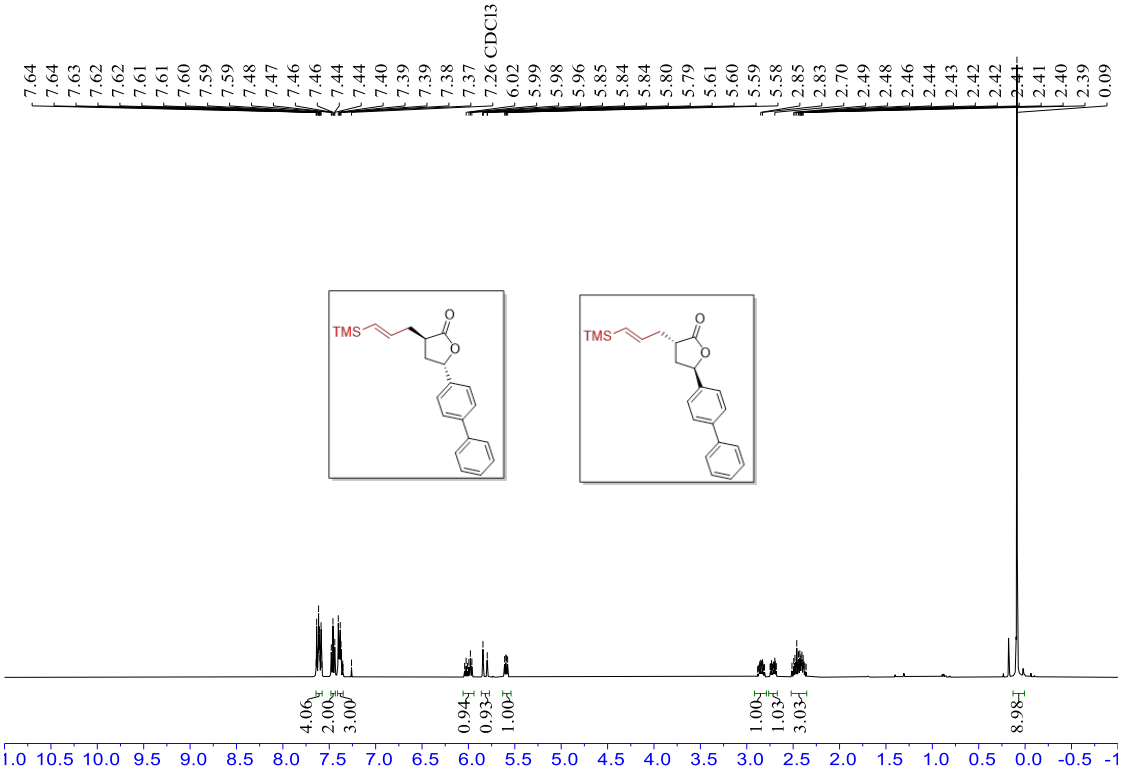
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **3v**



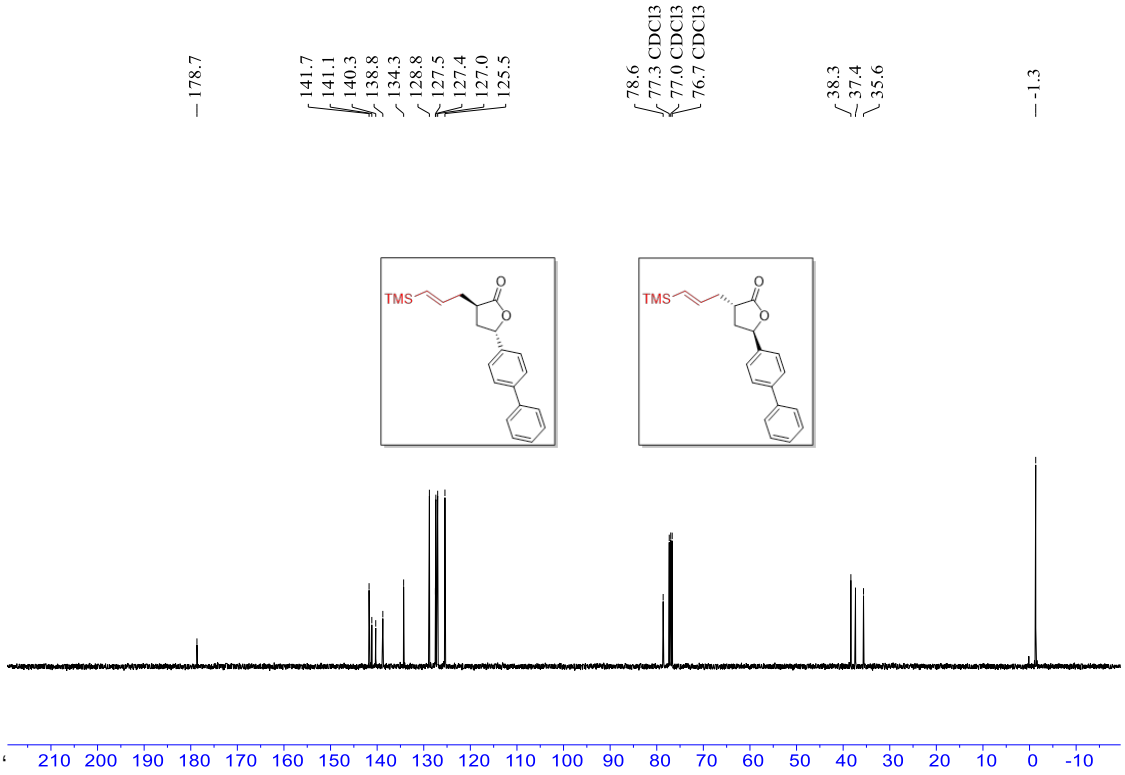
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5a**



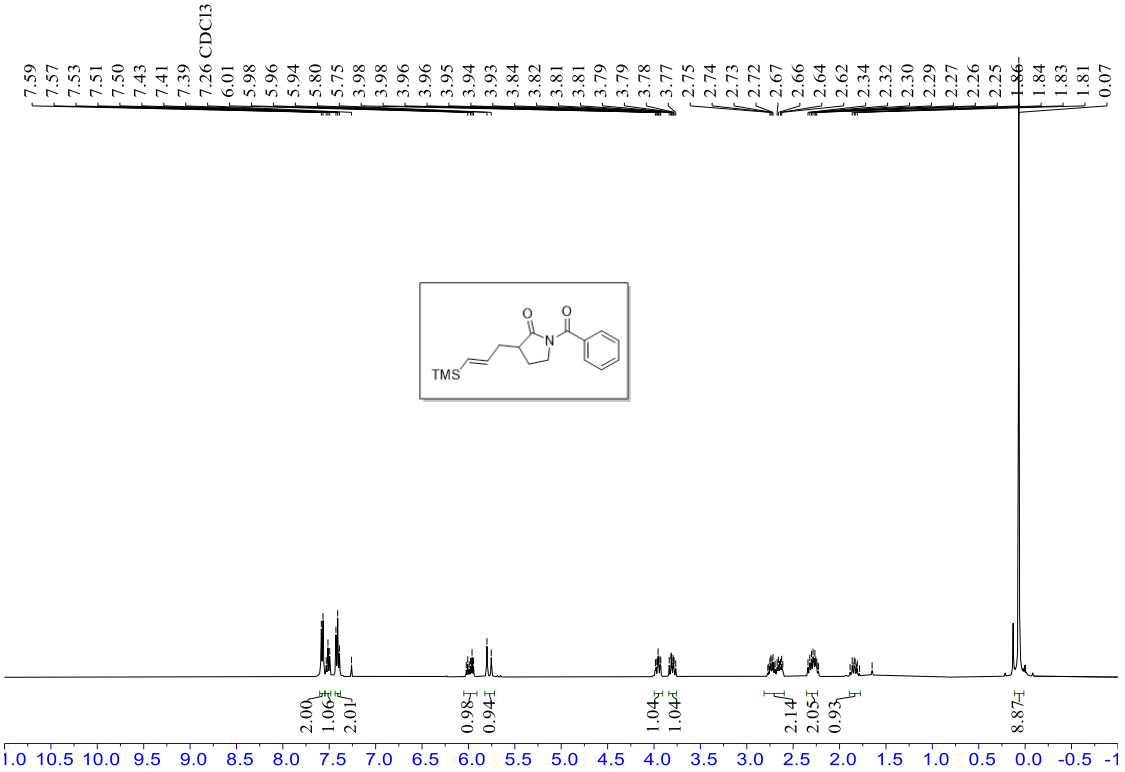
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **5a**



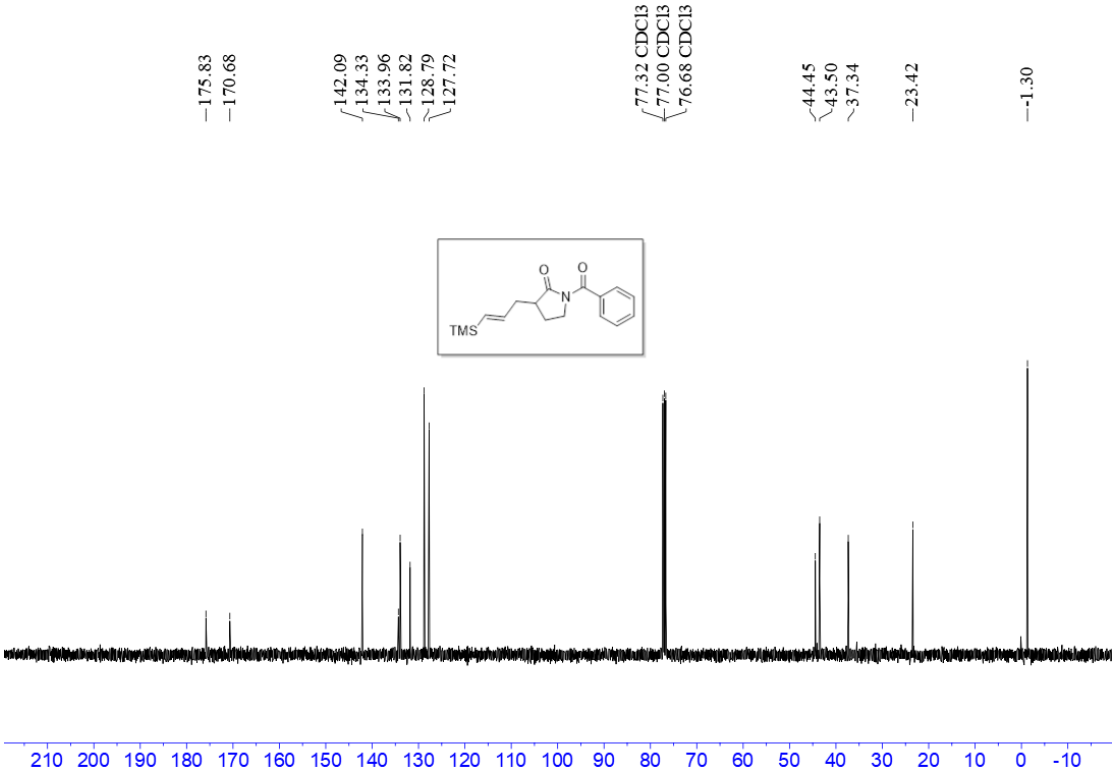
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **5a'**



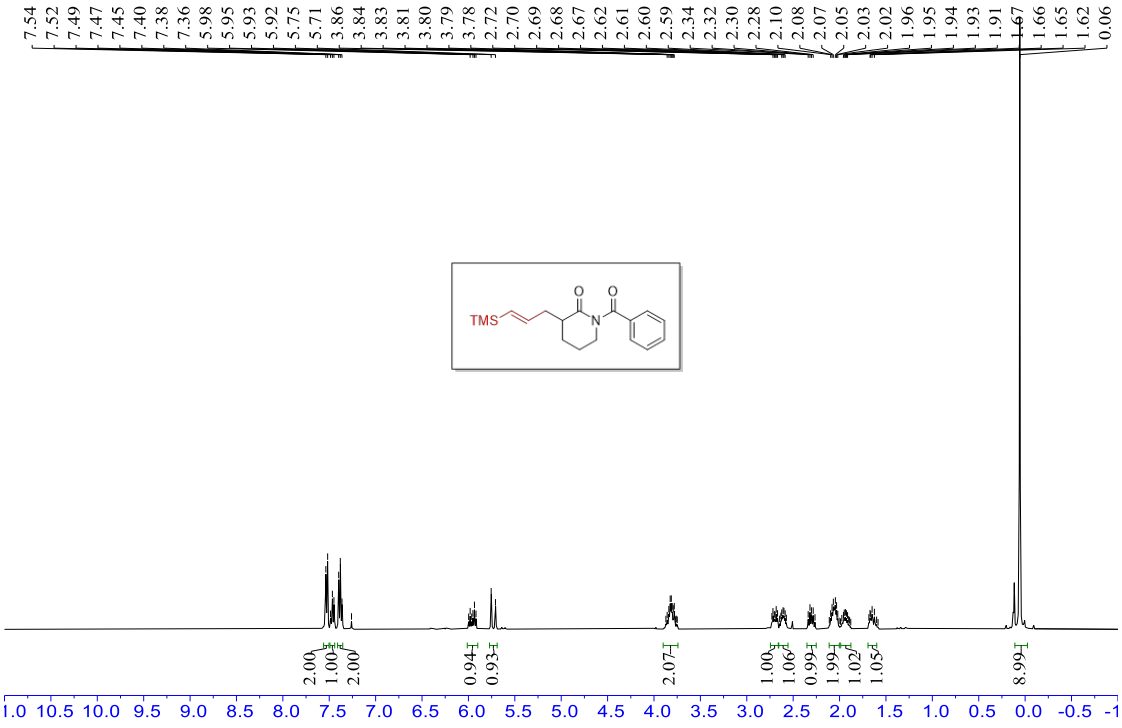
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **5a'**



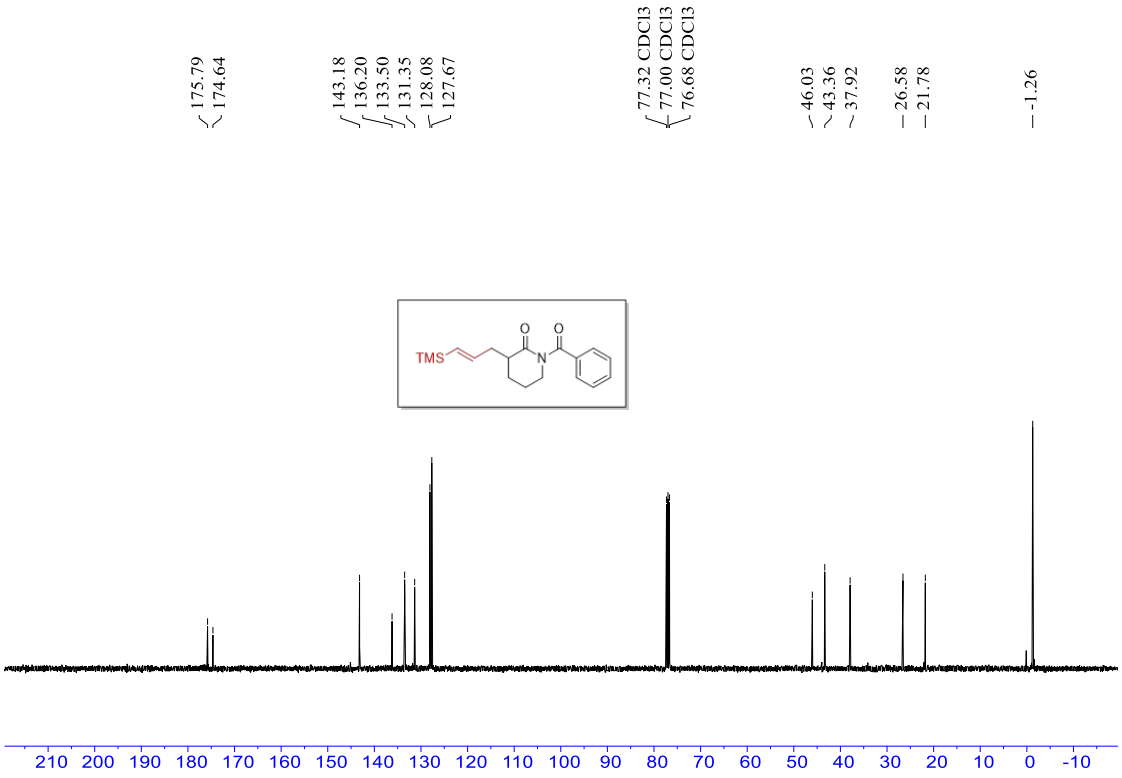
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **7a**



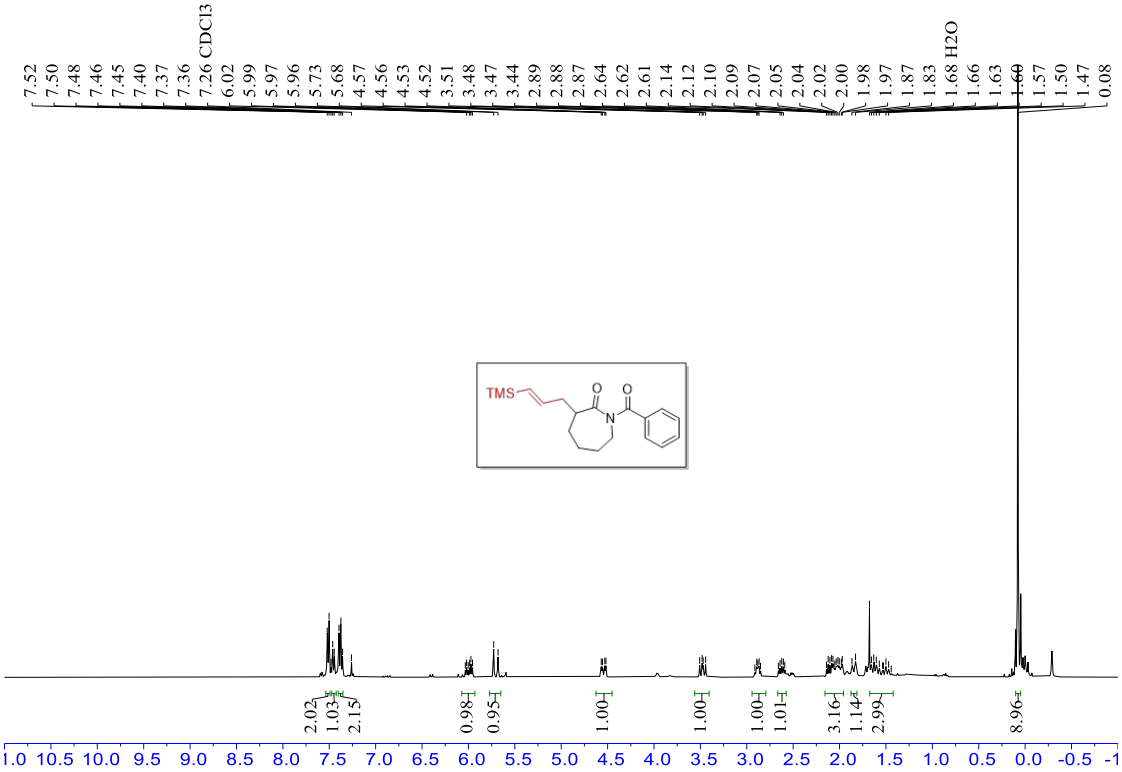
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for**7a**



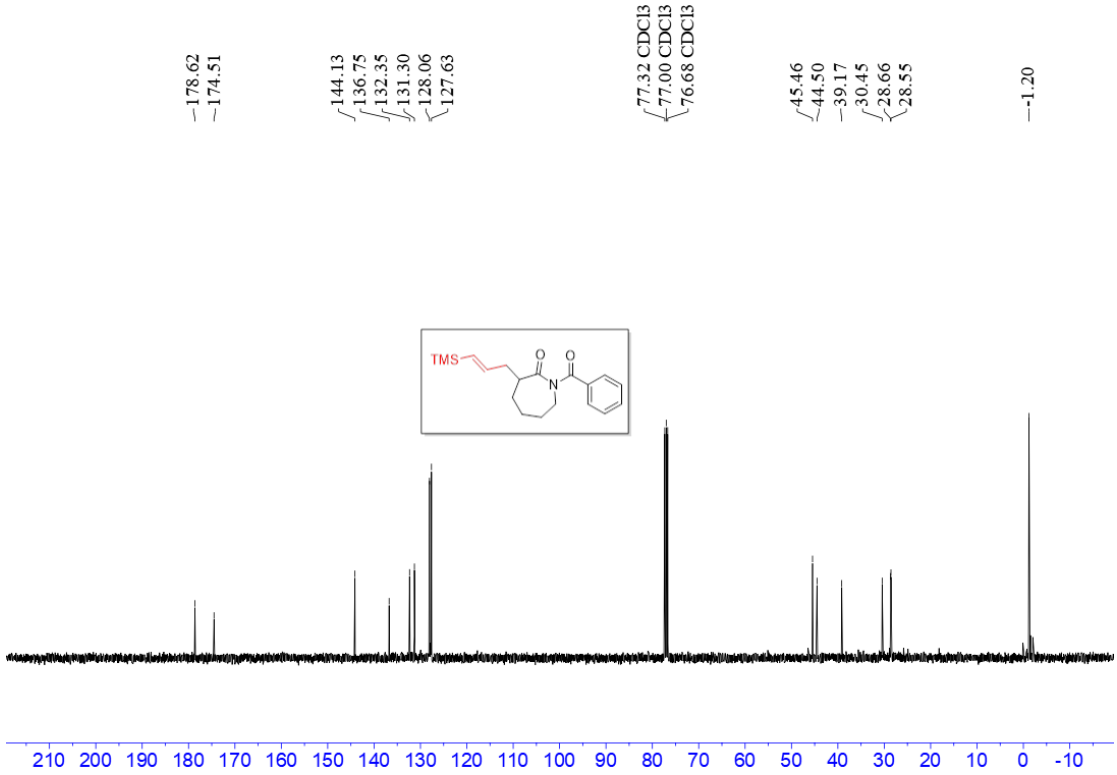
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **7b**



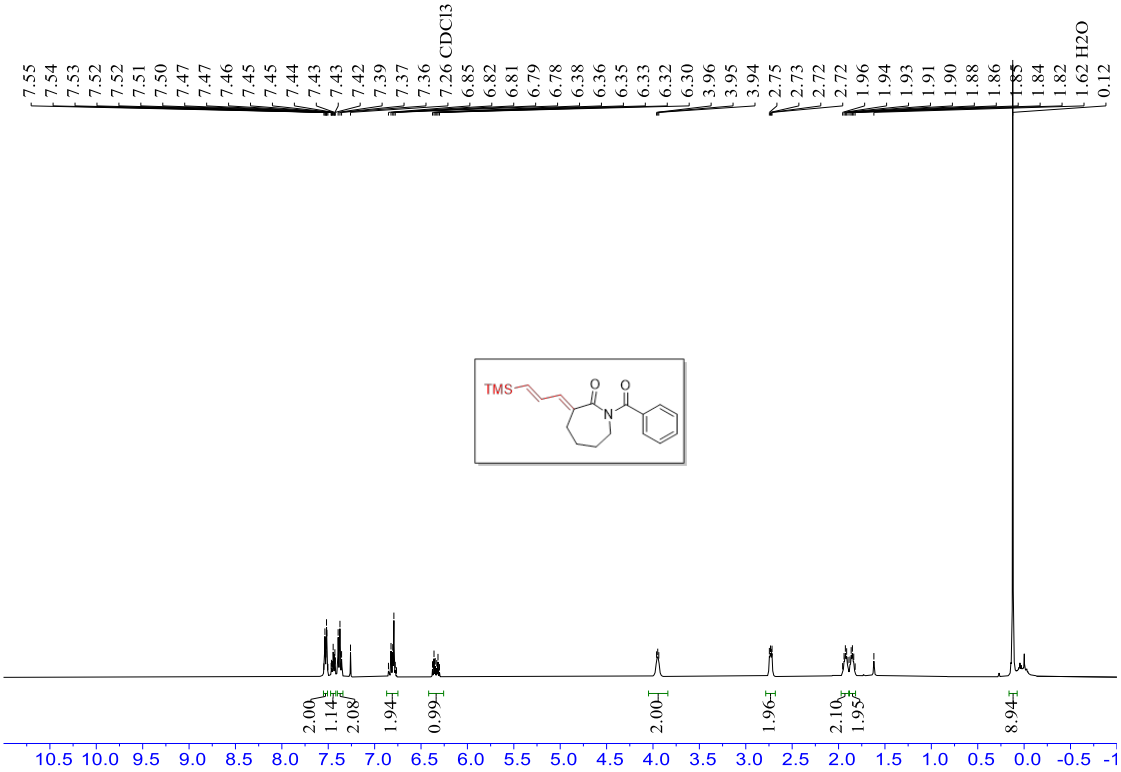
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **7b**



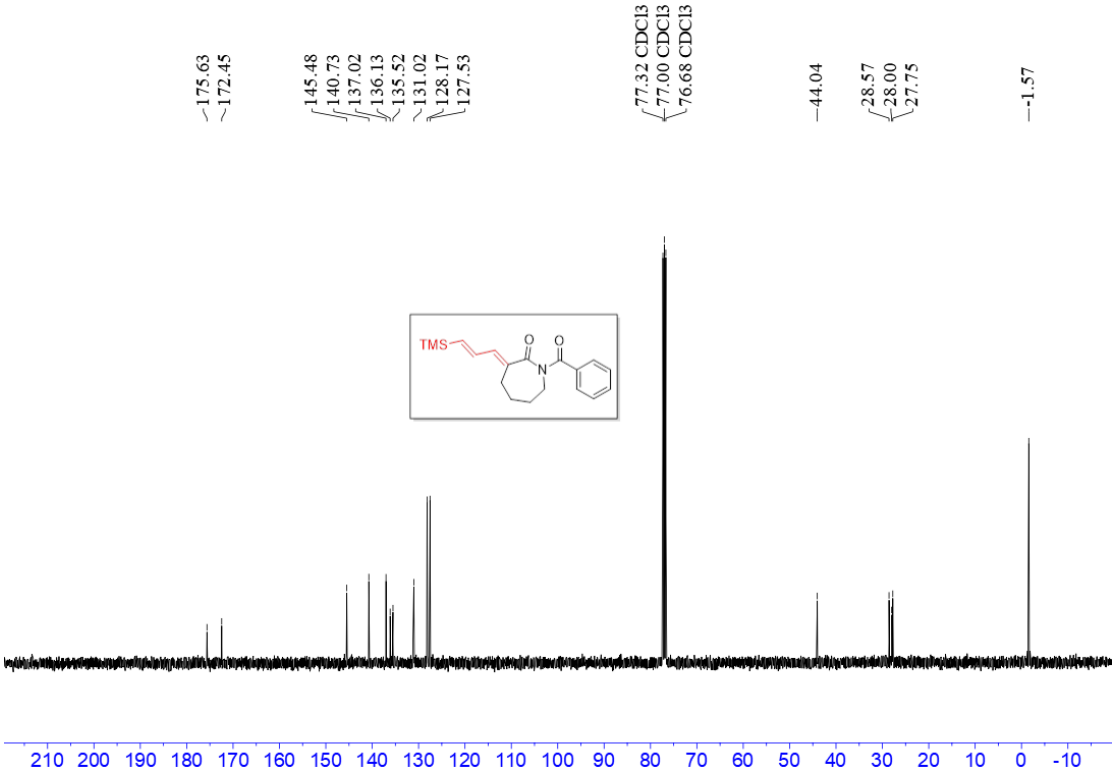
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **7c**



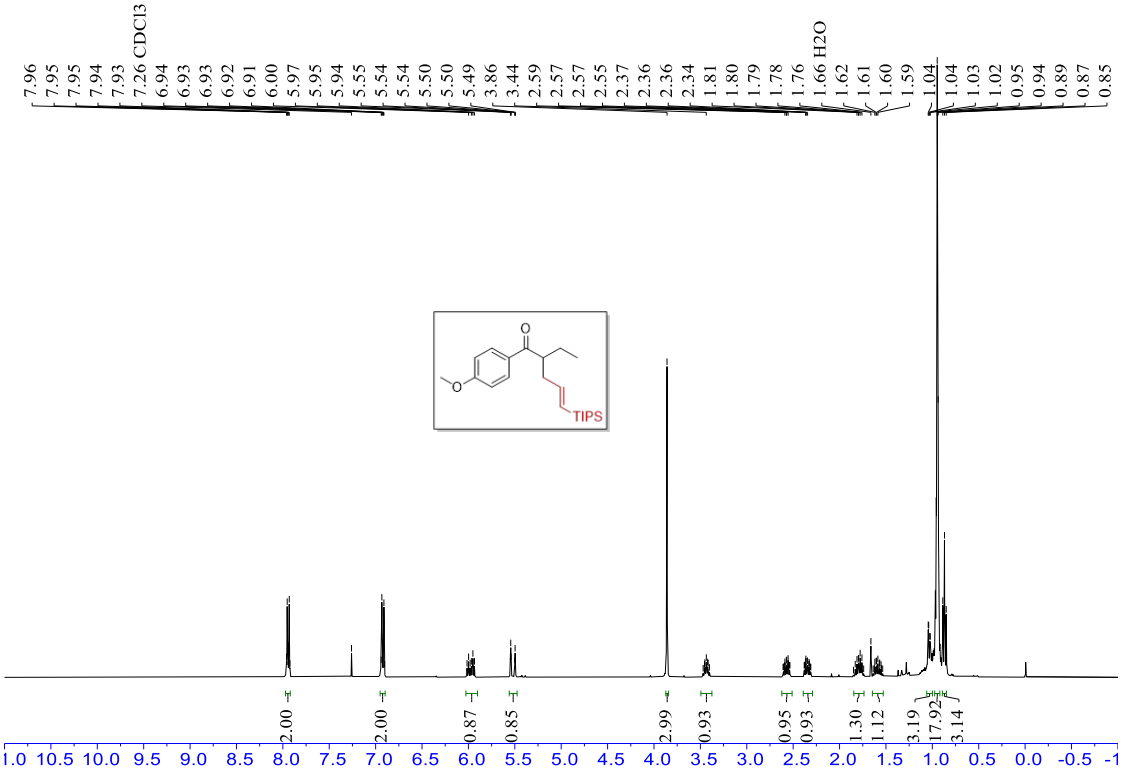
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **7c**



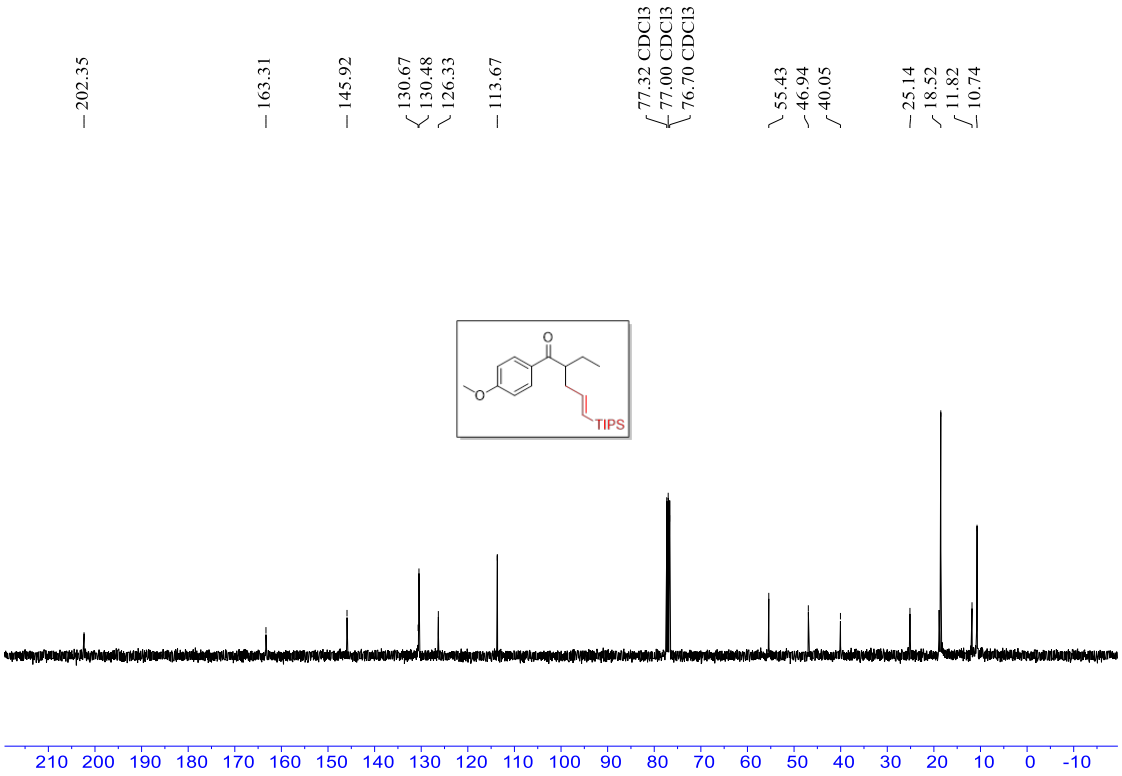
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **7c'**



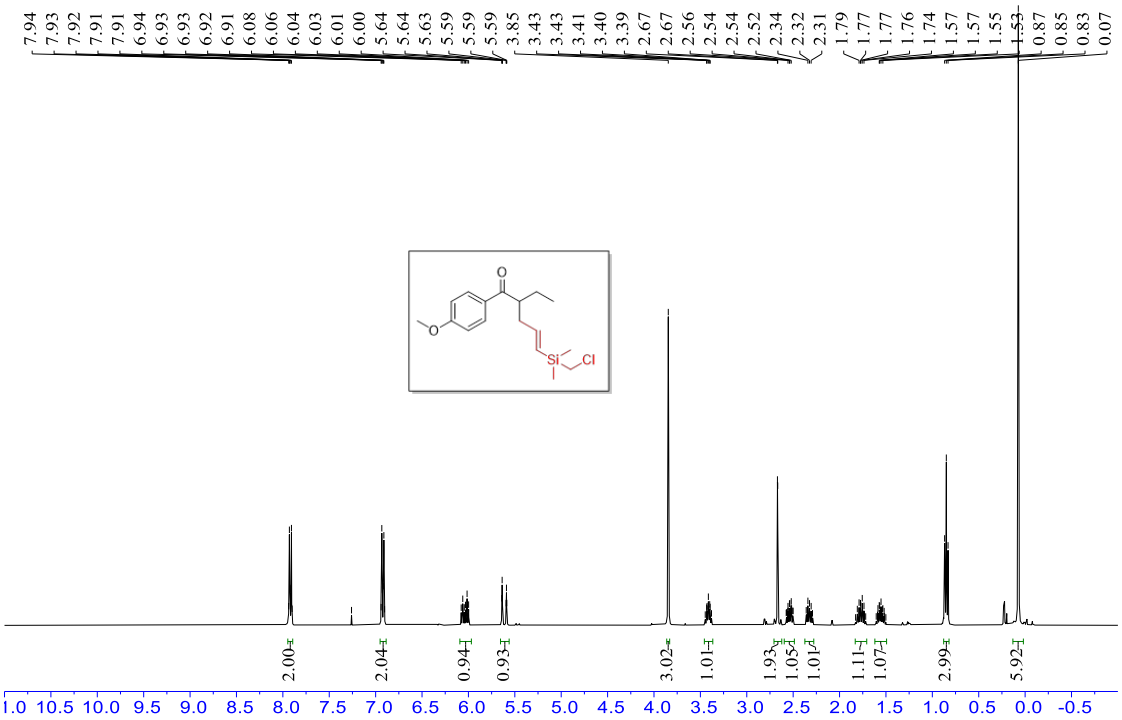
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **7c'**



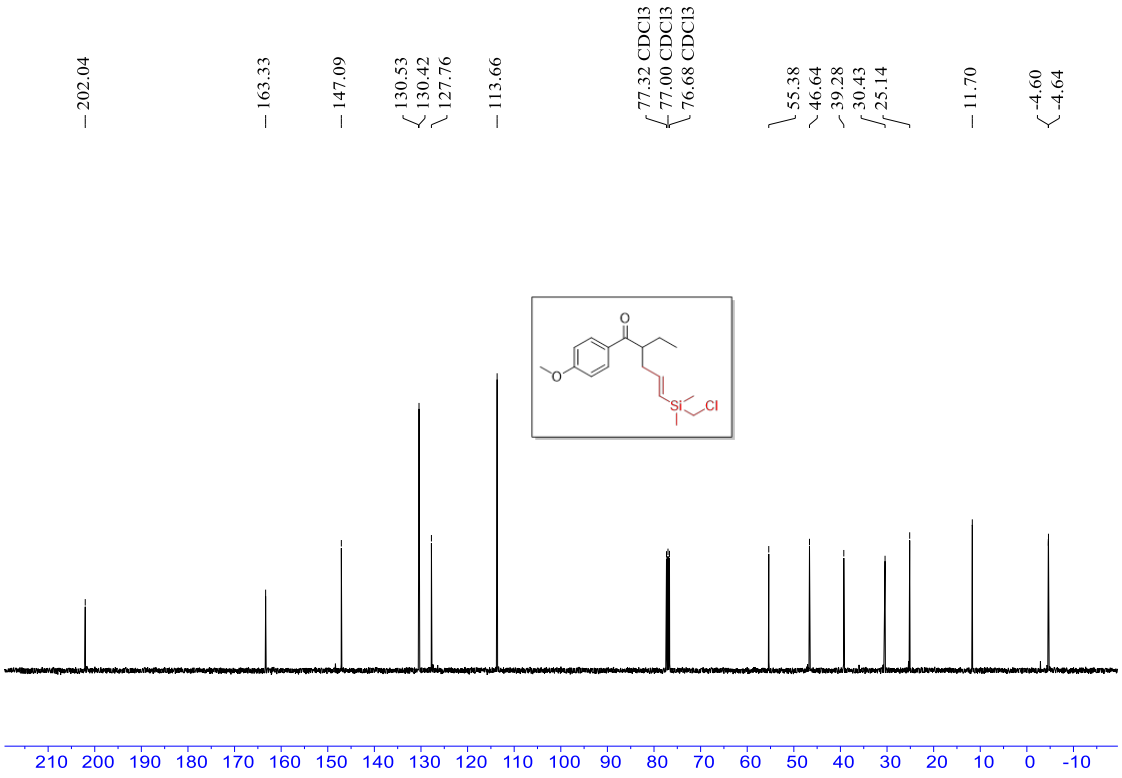
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8a**



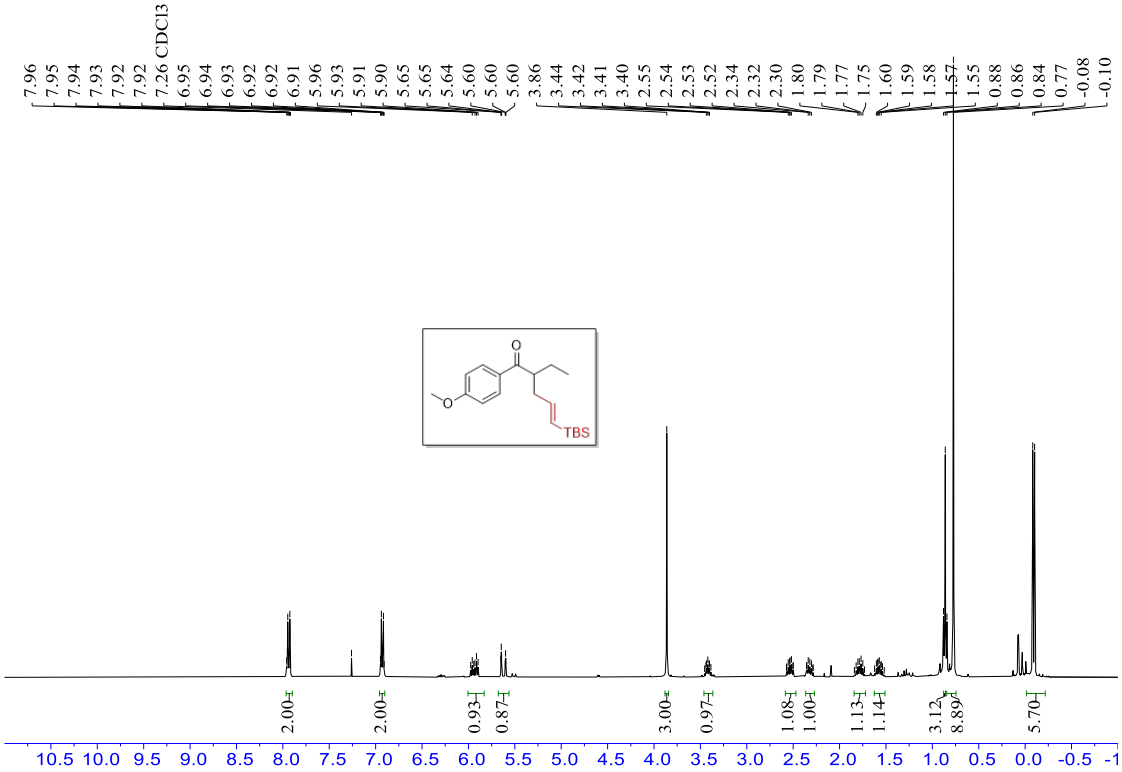
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8a**



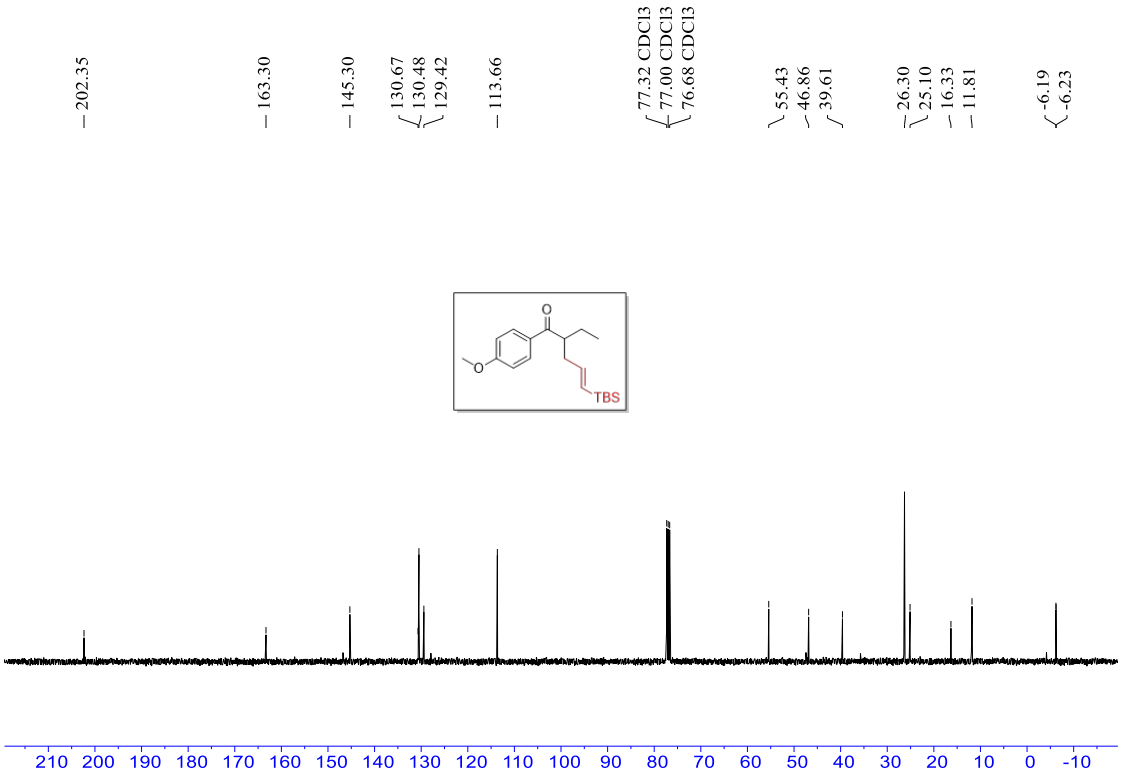
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8b**



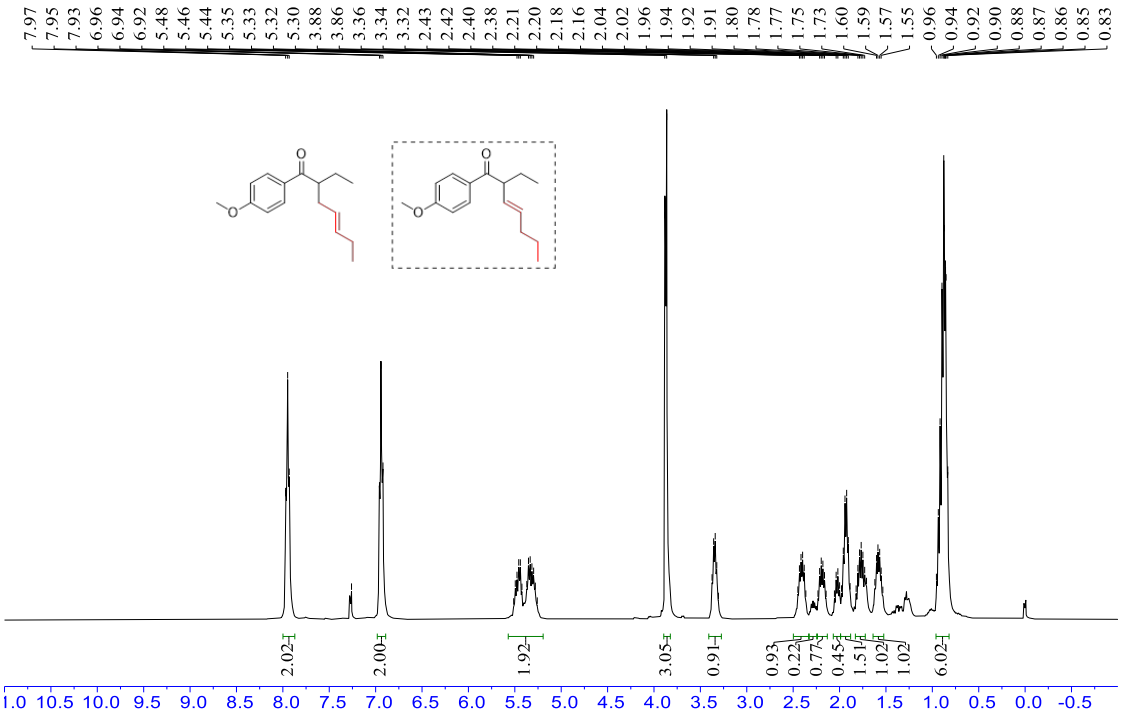
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8b**



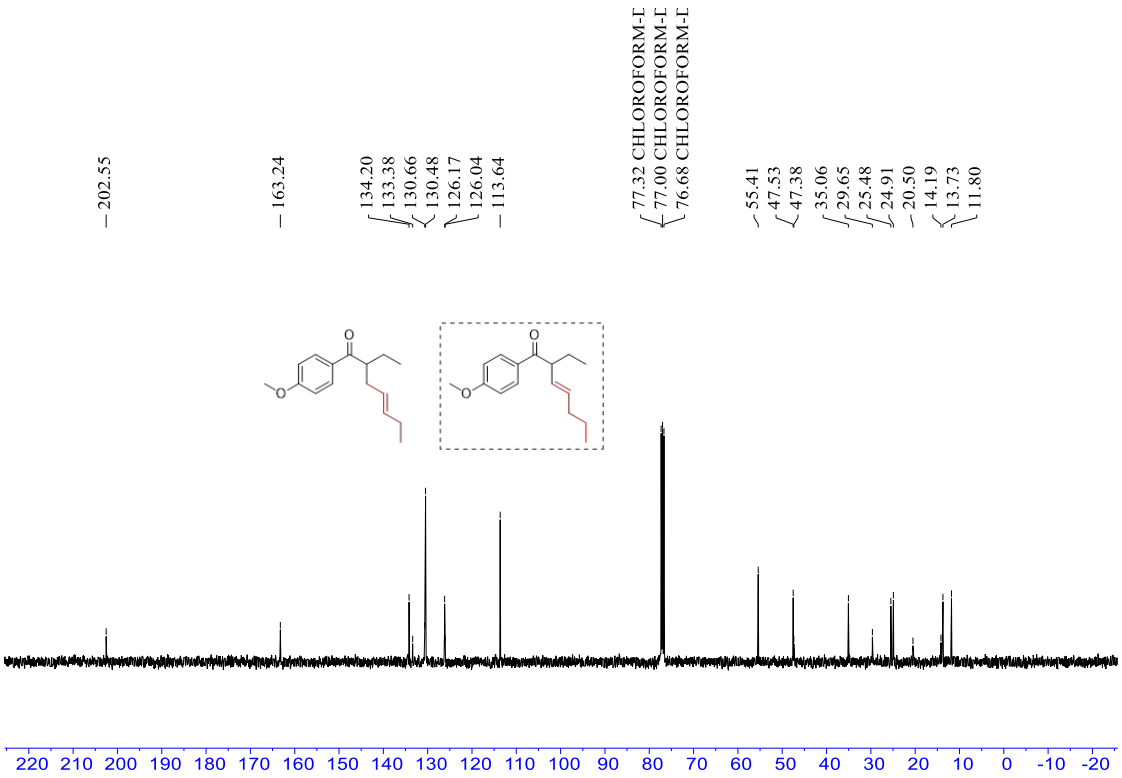
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8c**



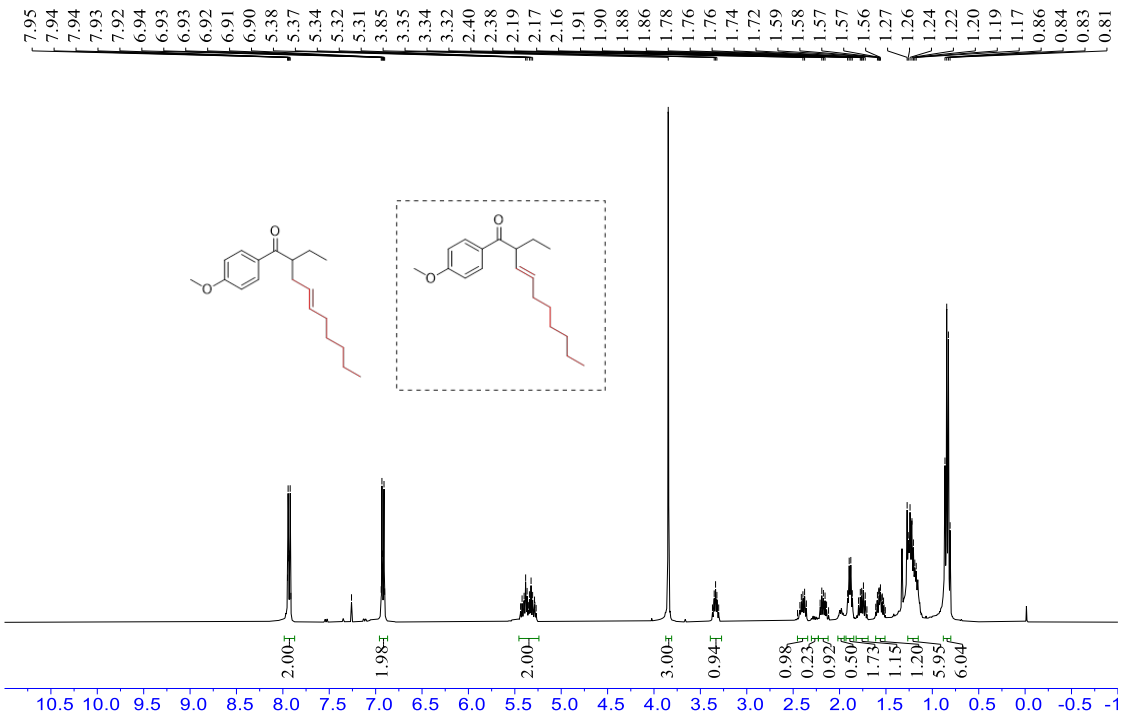
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8c**



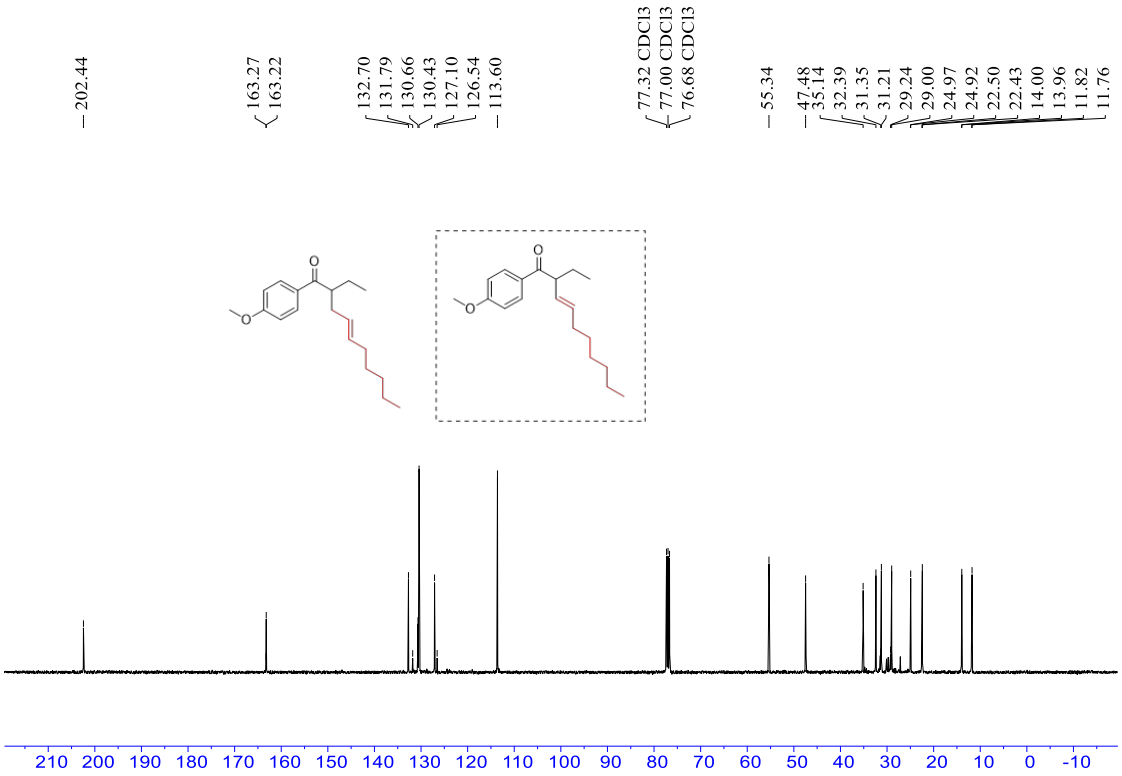
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8d and 8d'**



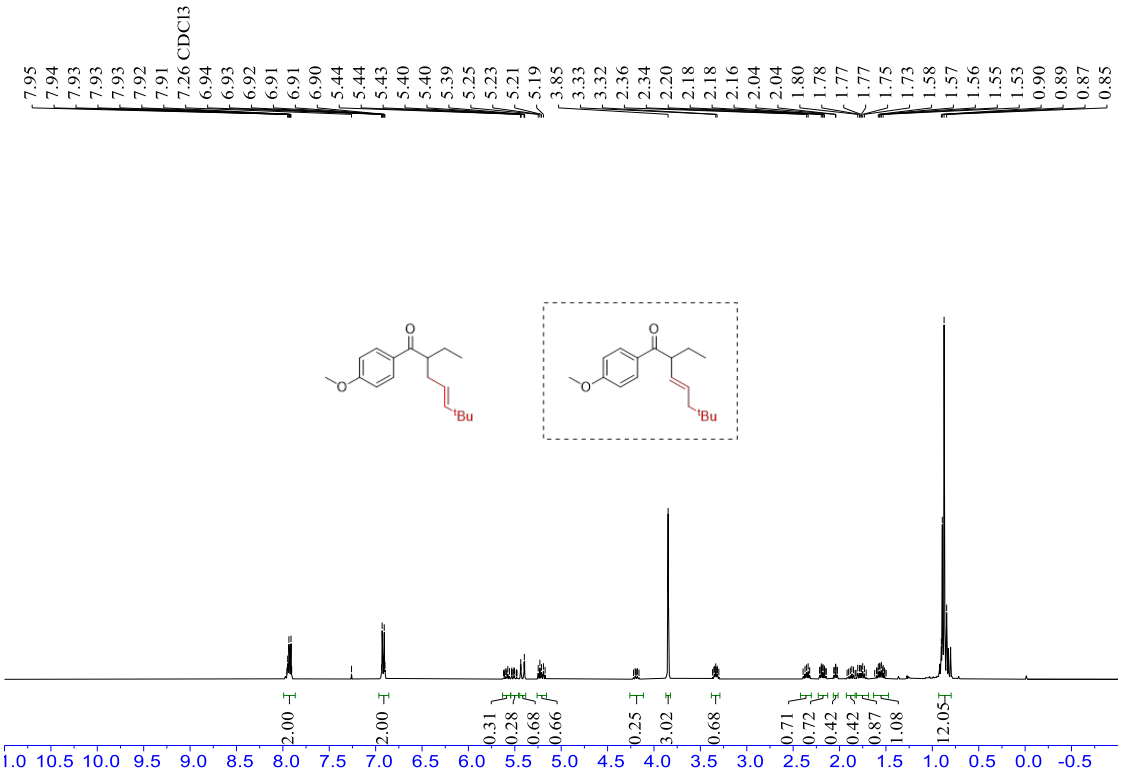
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8d and 8d'**



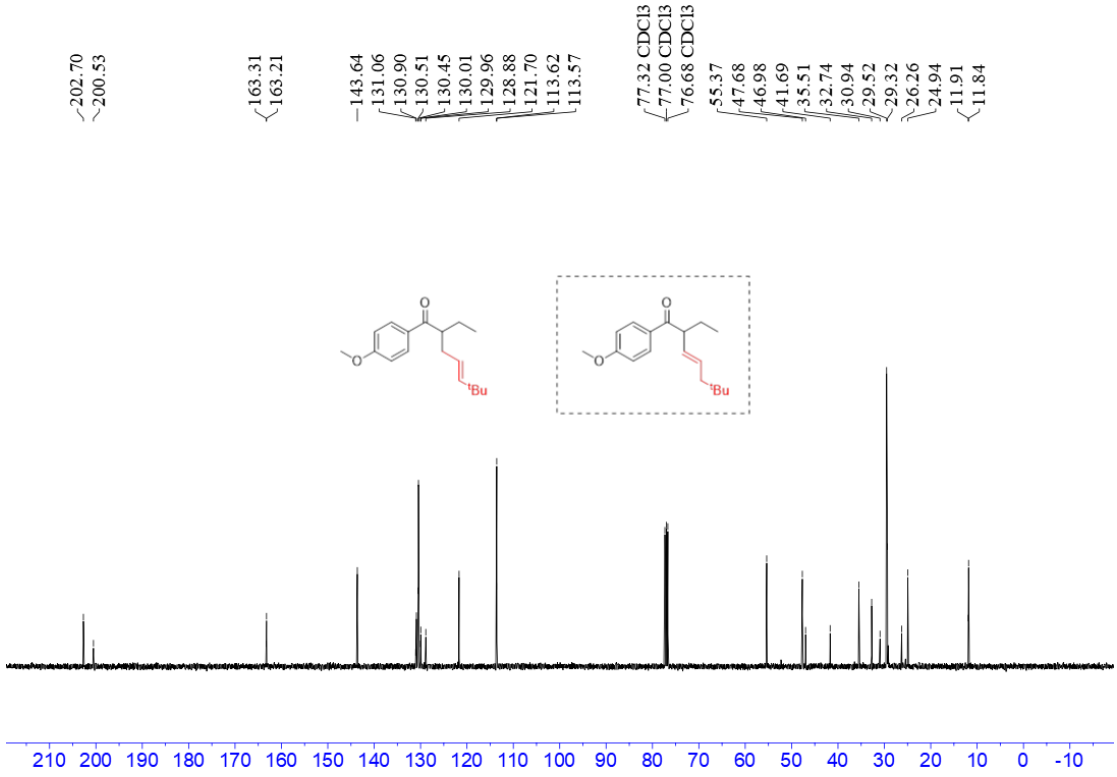
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8e and 8e'**



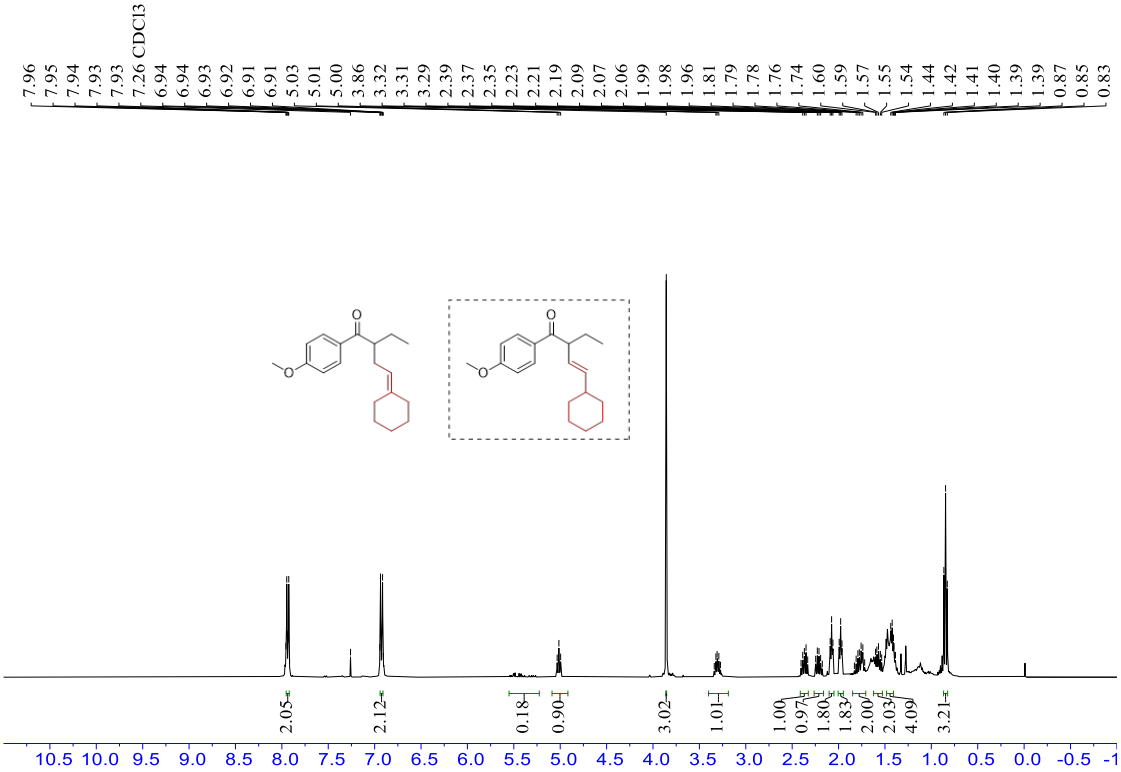
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8e and 8e'**



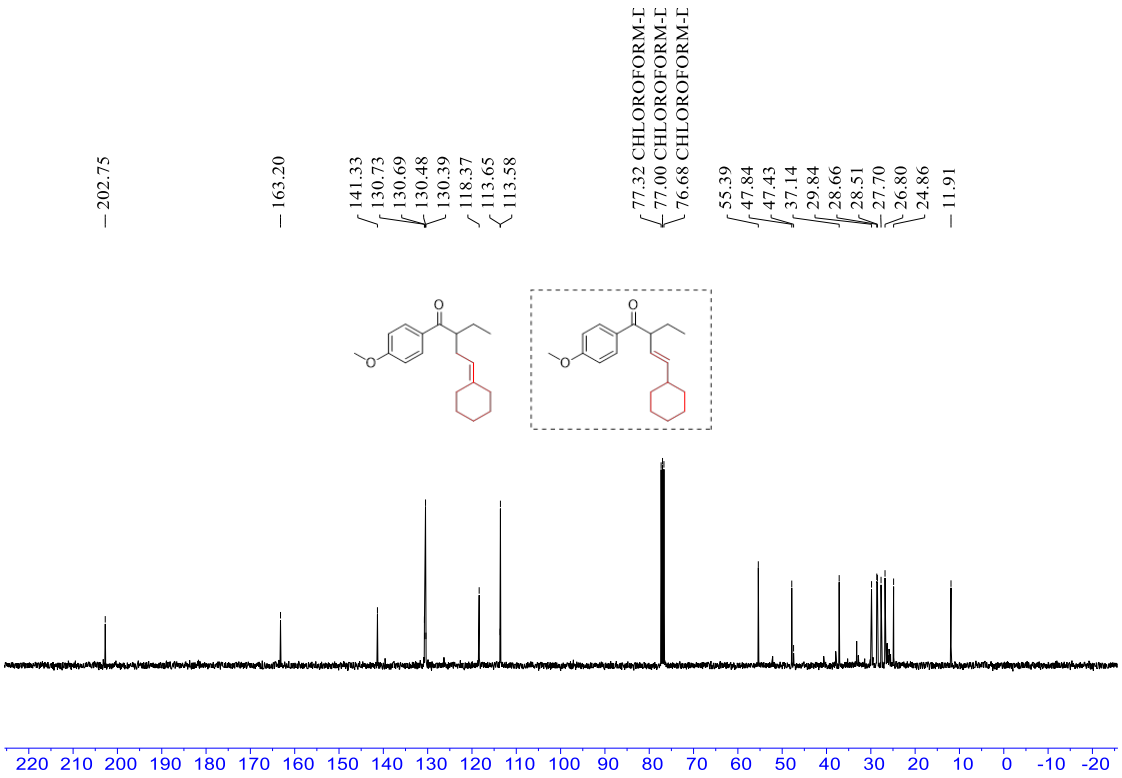
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8f and 8f'**



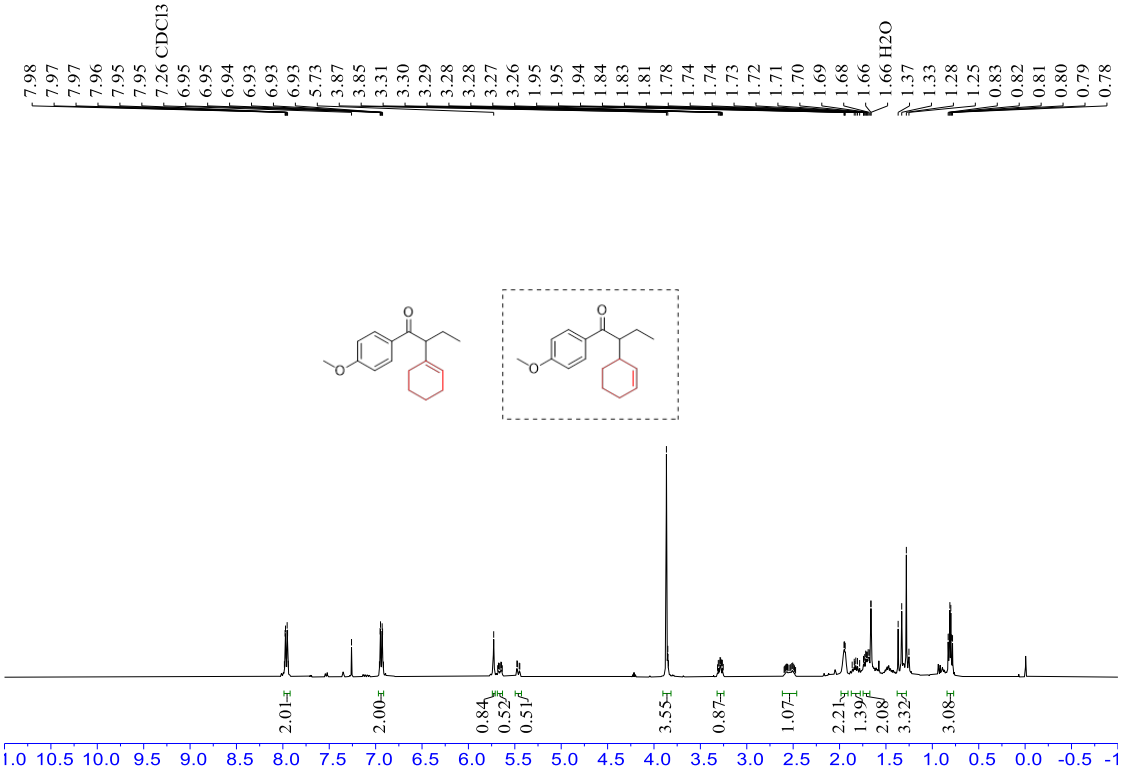
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8f and 8f'**



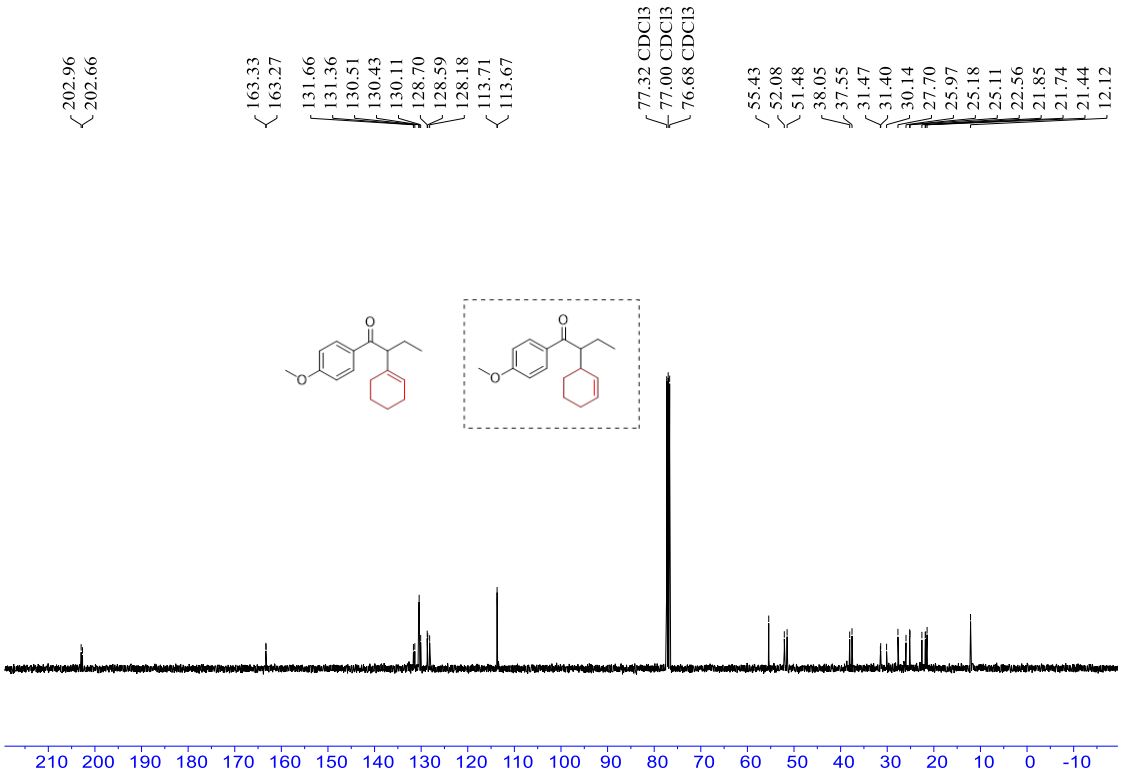
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8g and 8g'**



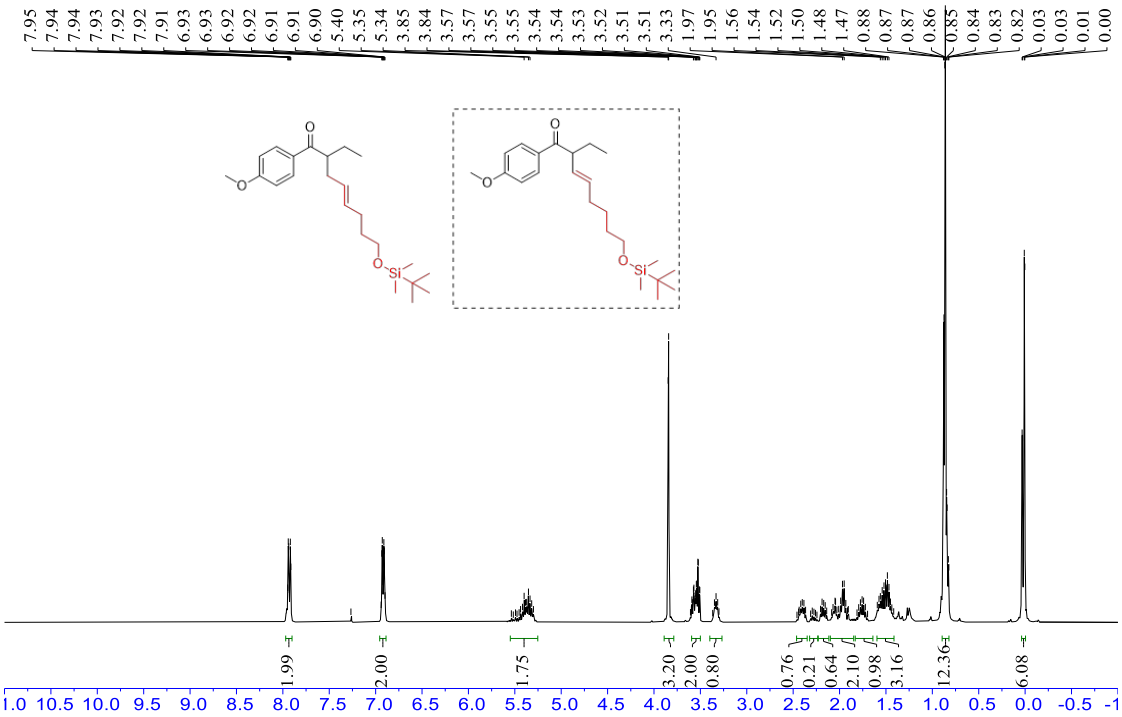
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8g and 8g'**



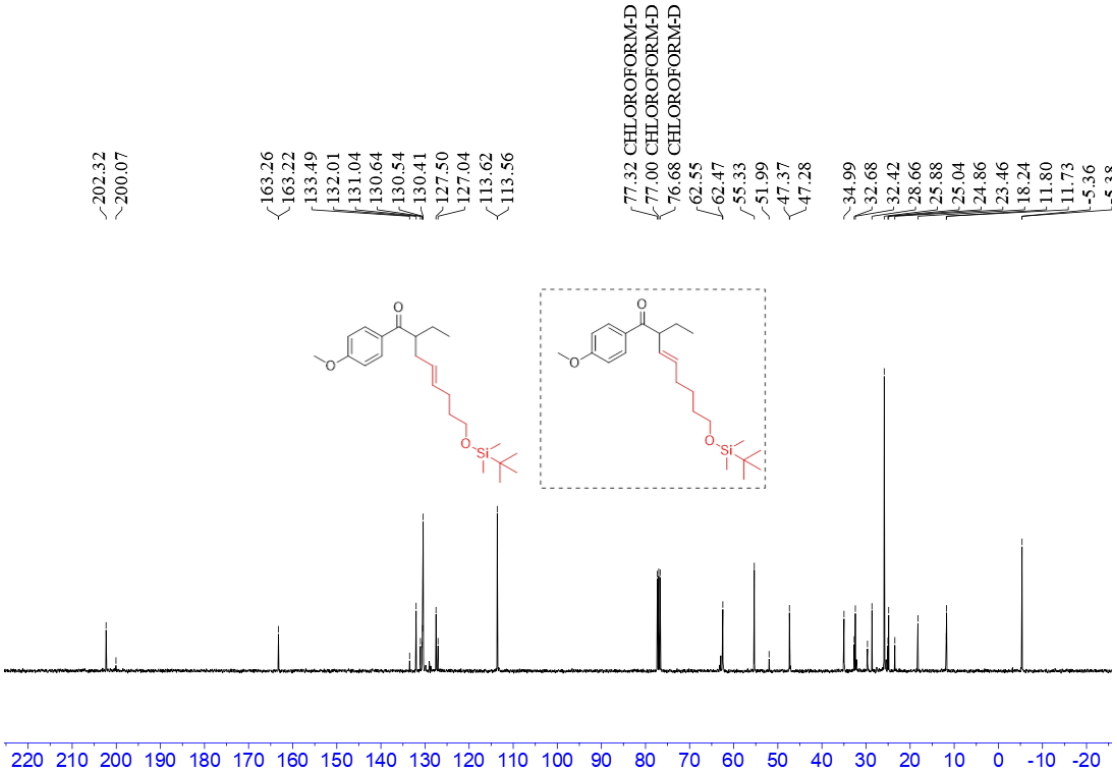
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8h and 8h'**



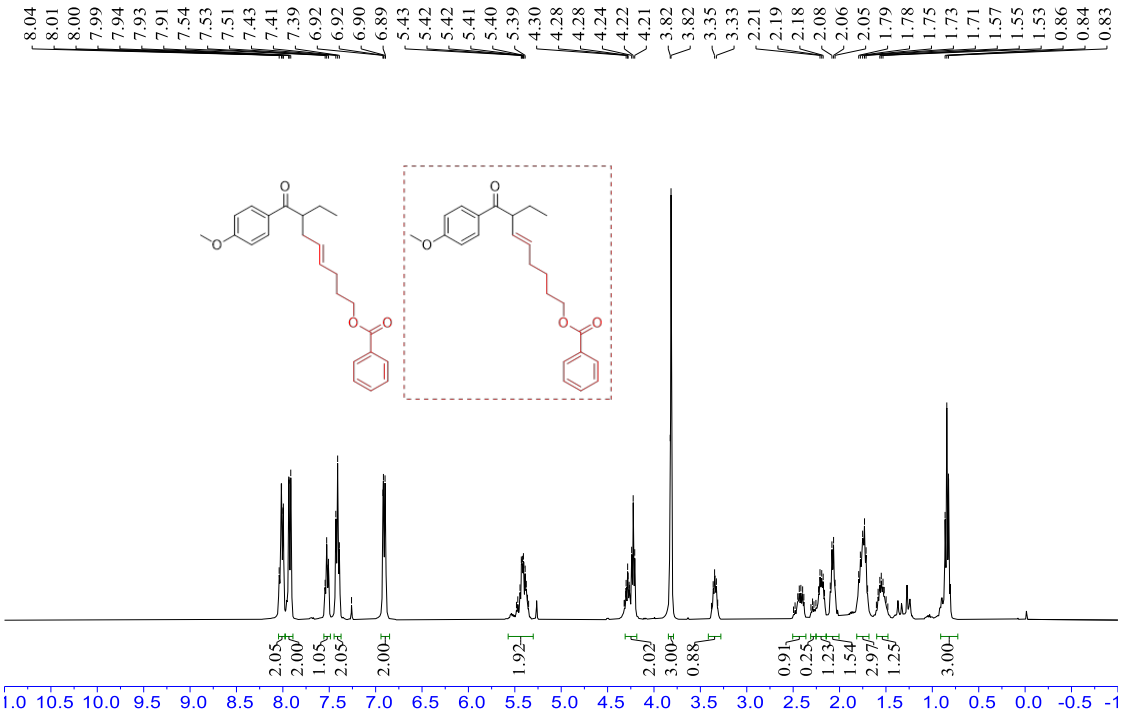
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8h and 8h'**



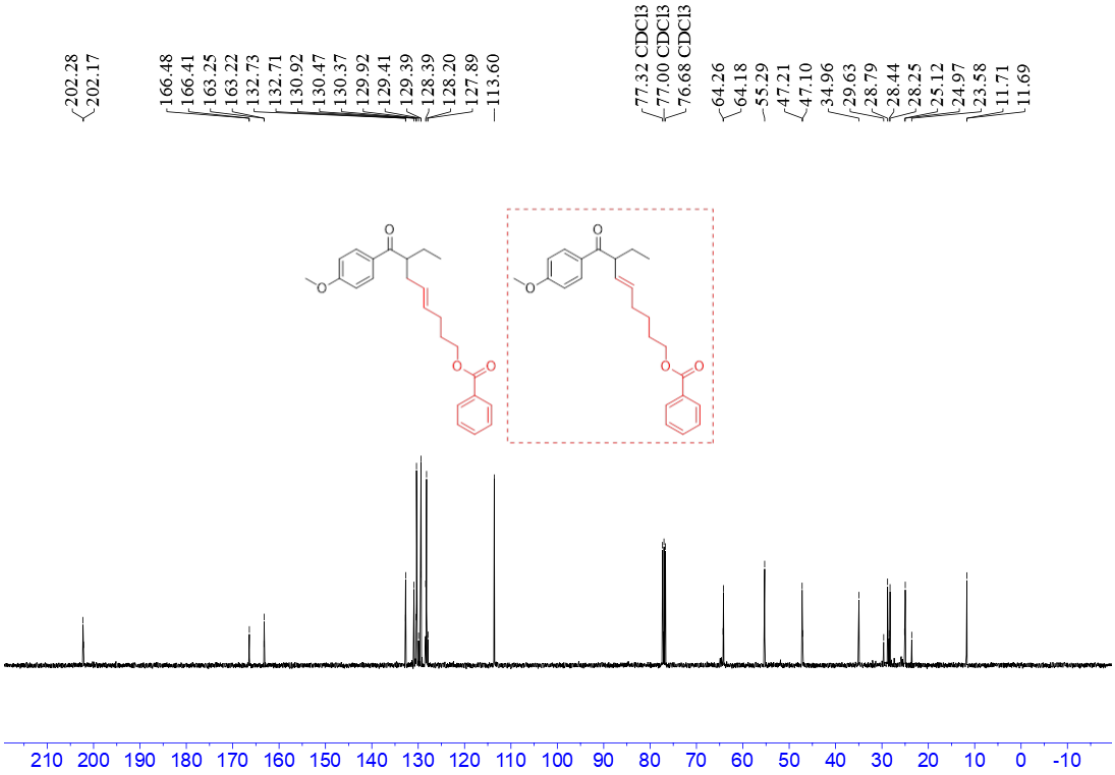
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8i and 8i'**



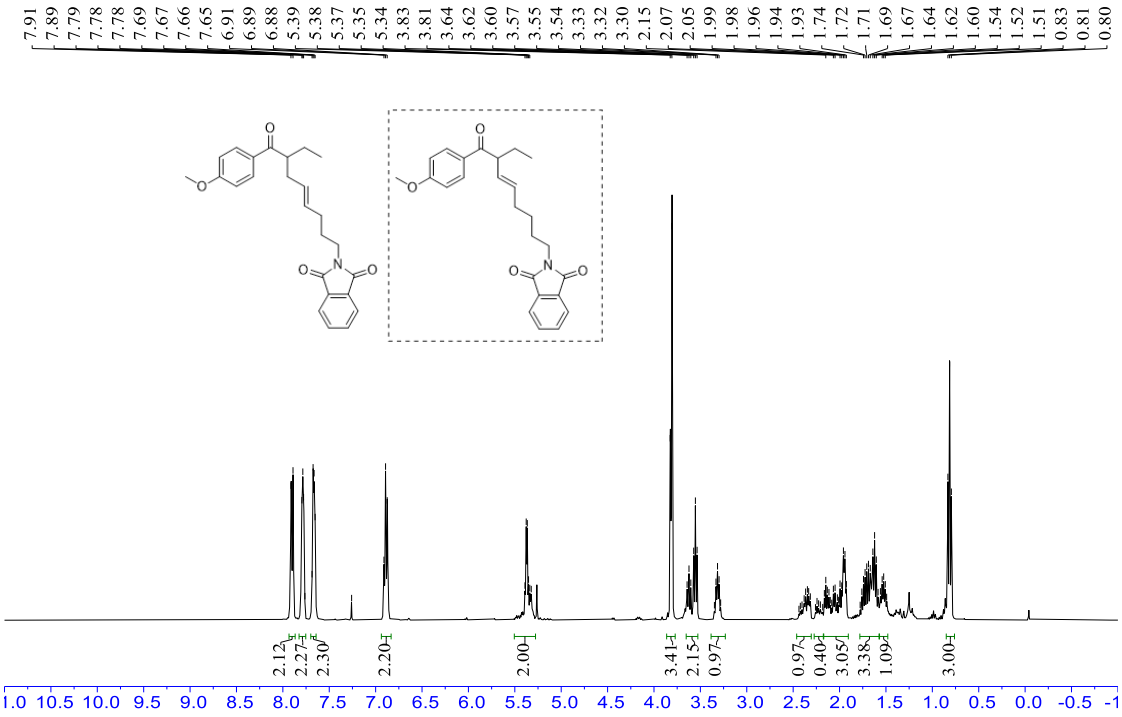
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8i and 8i'**



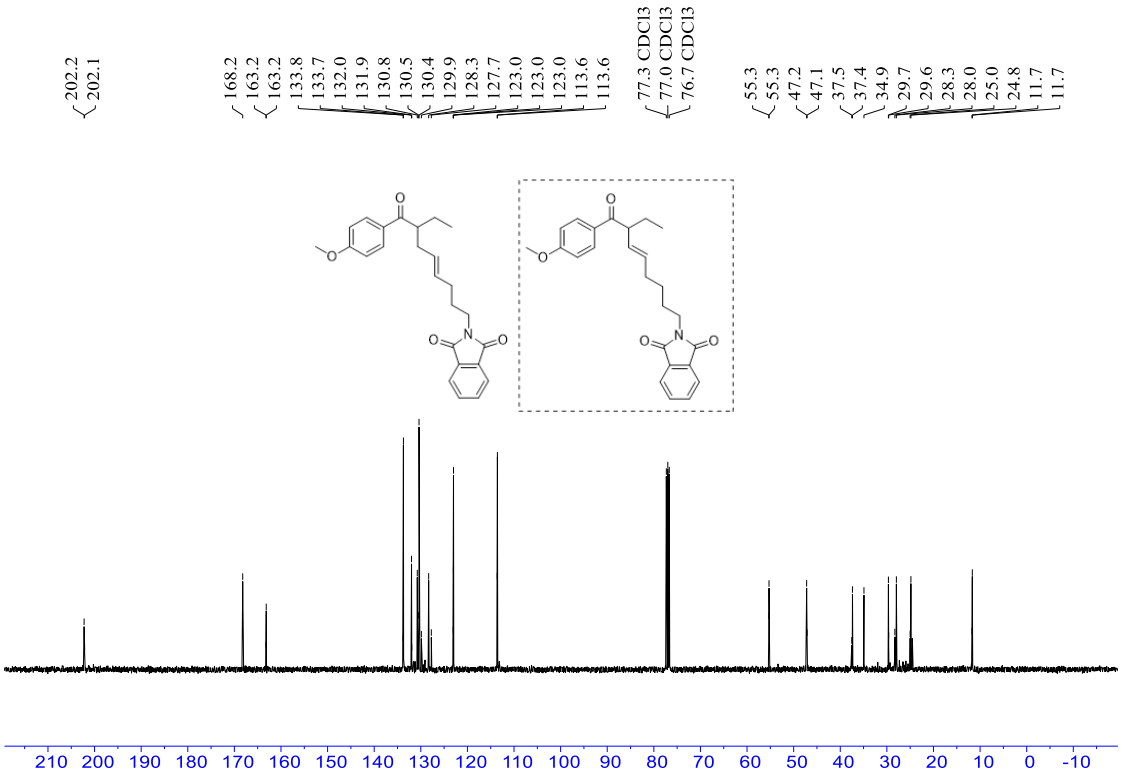
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8j and 8j'**



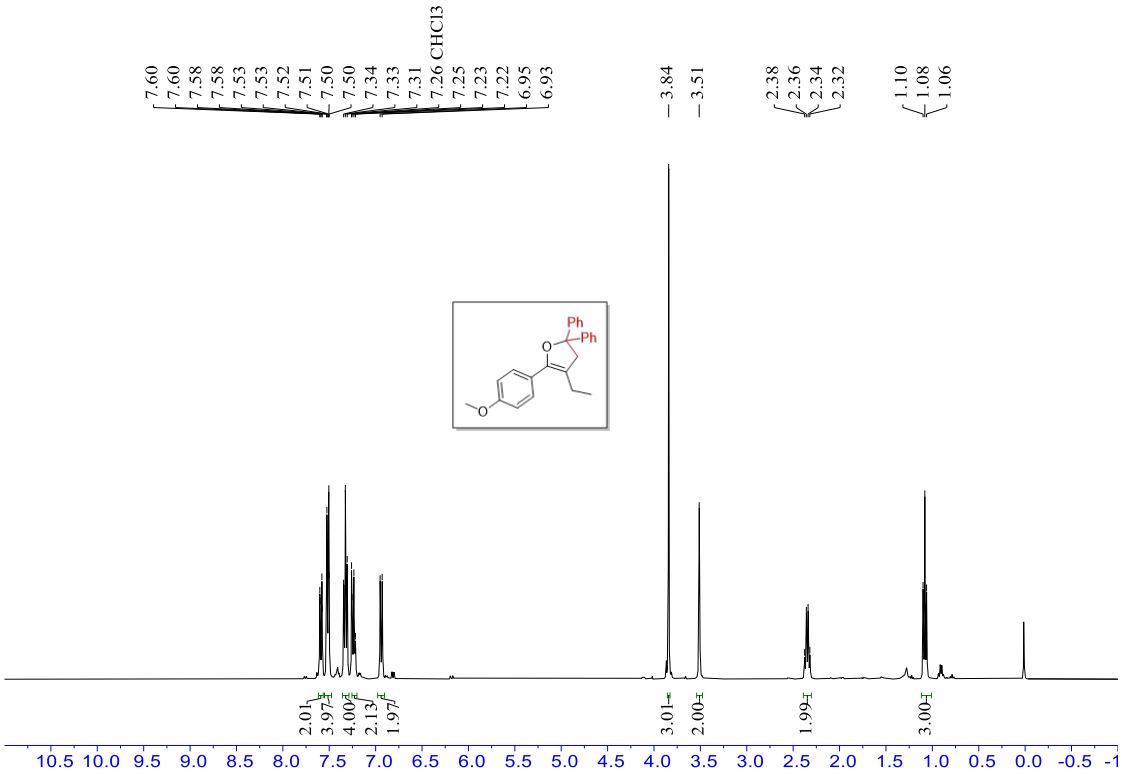
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8j and 8j'**



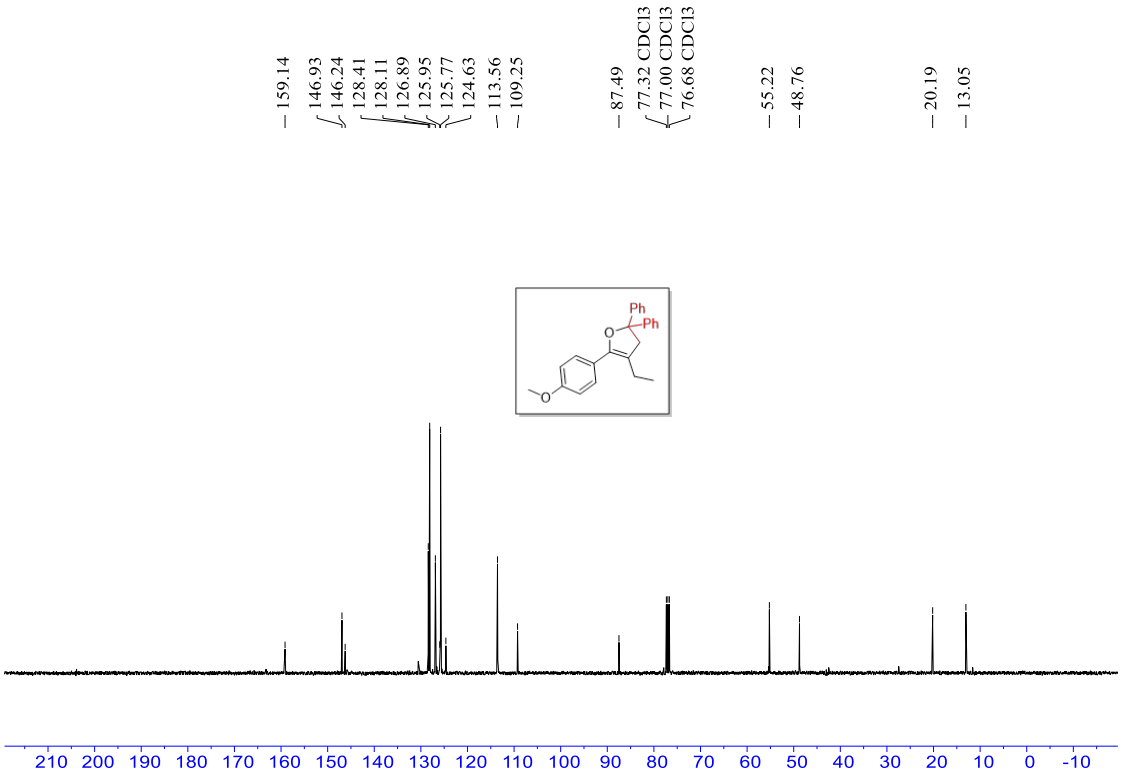
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **8k and 8k'**



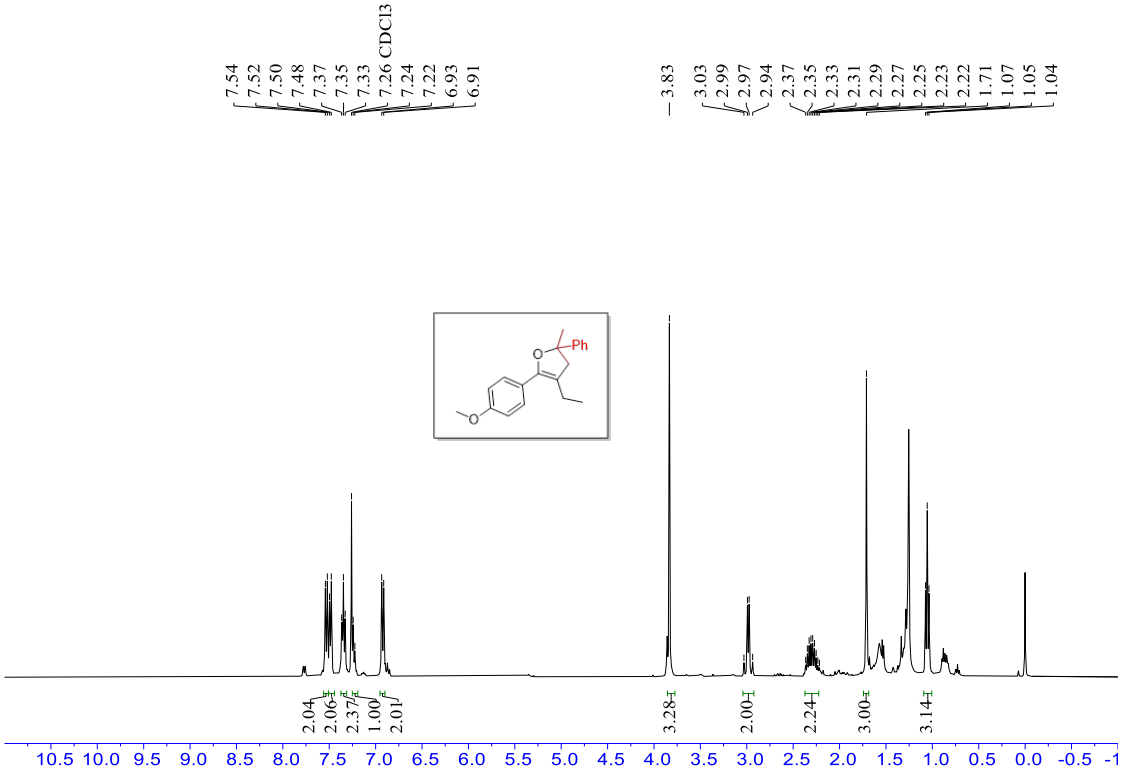
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **8k and 8k'**



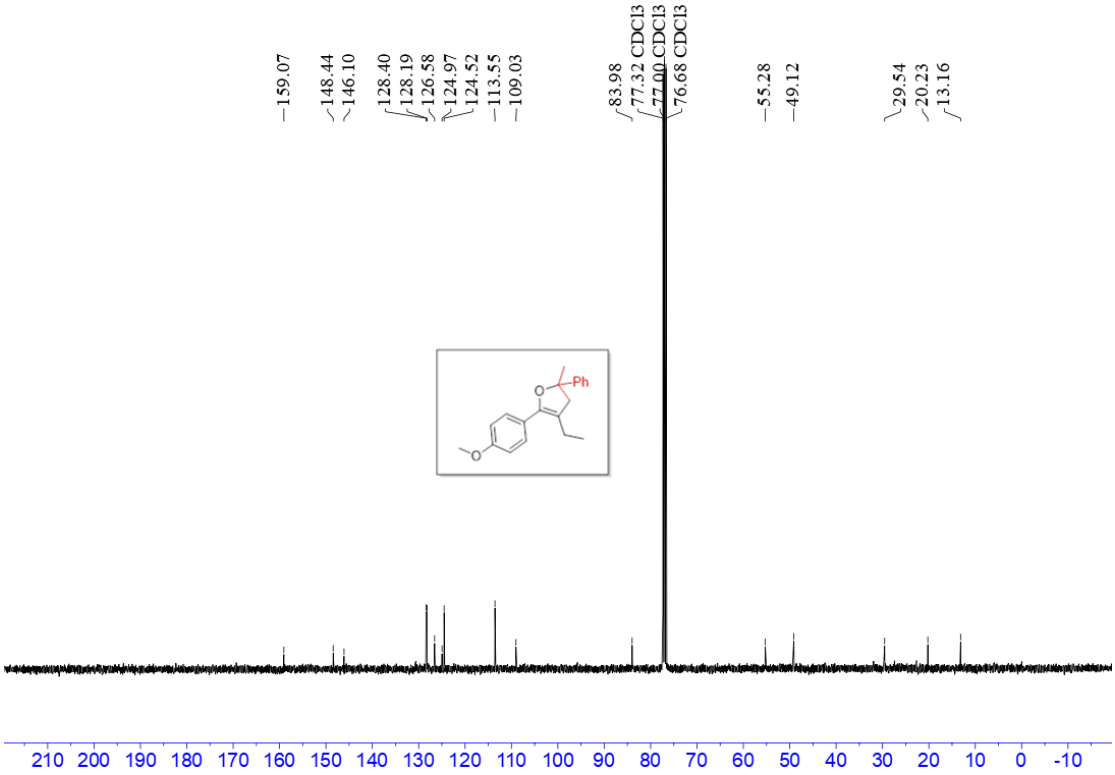
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9a**



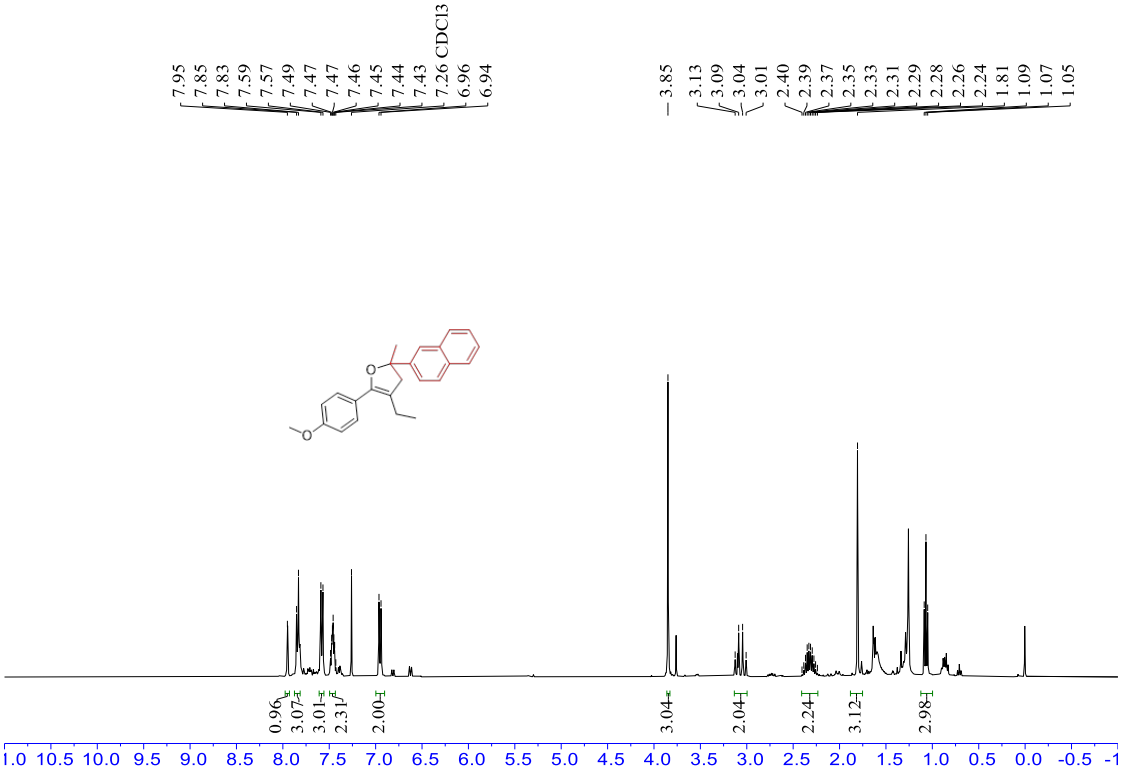
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9a**



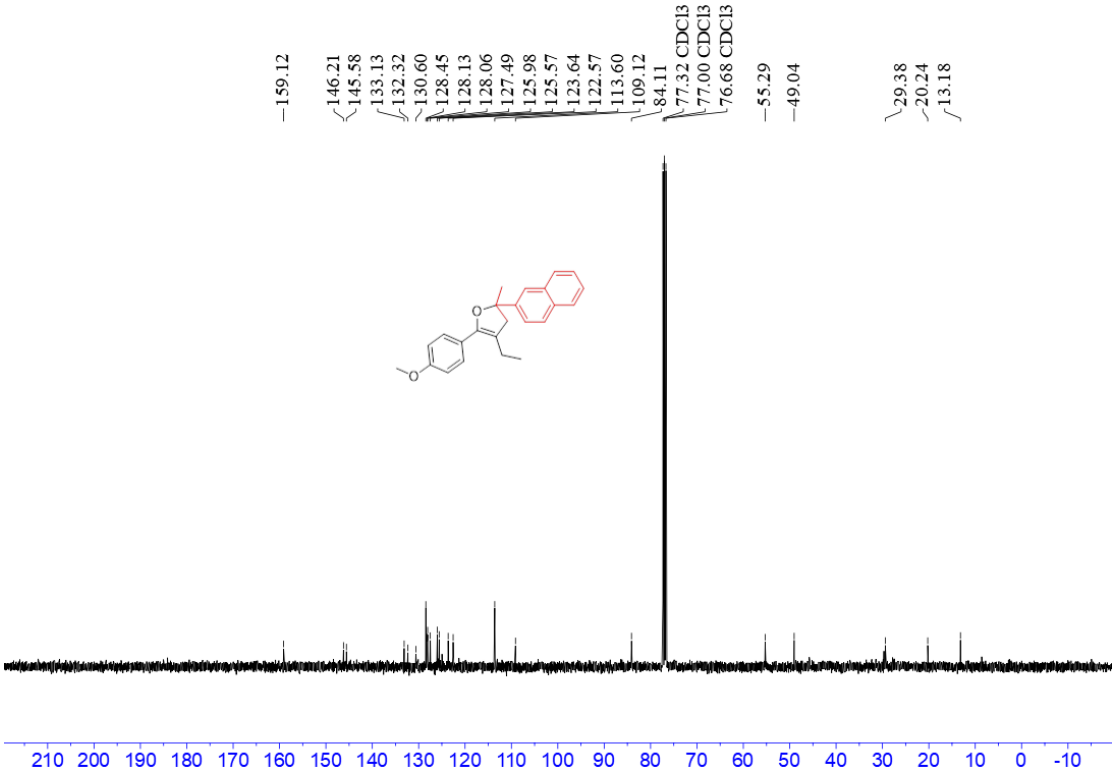
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9b**



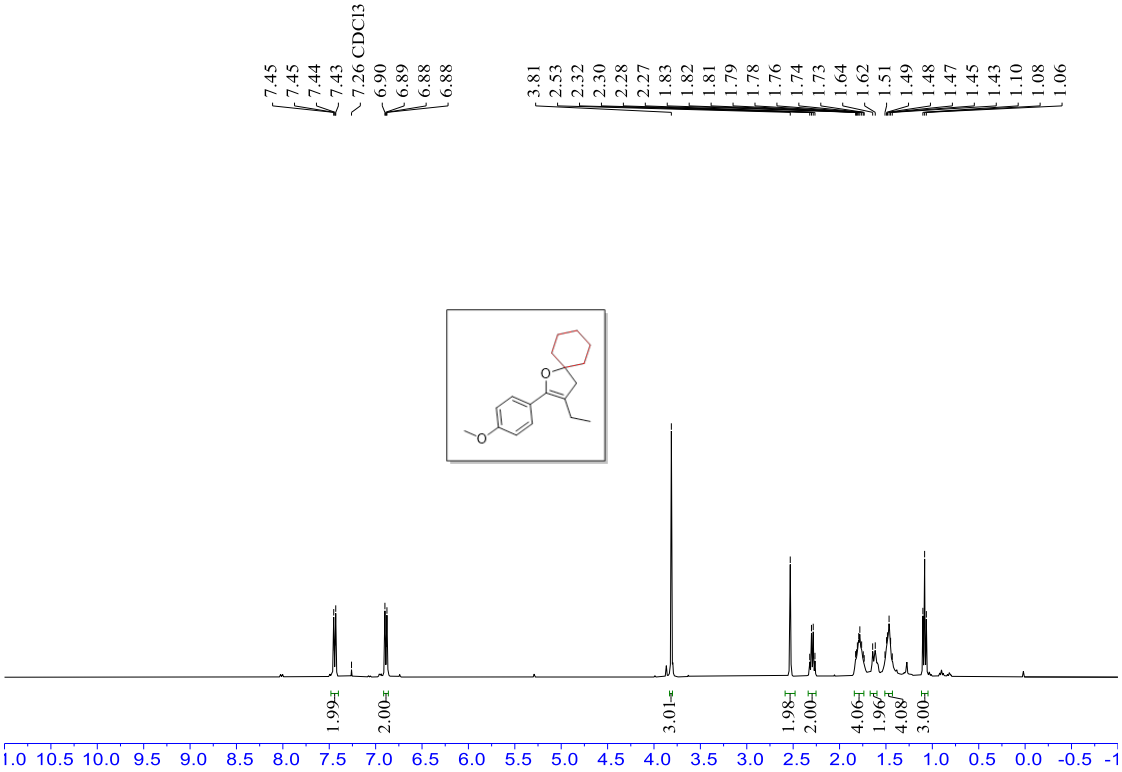
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9b**



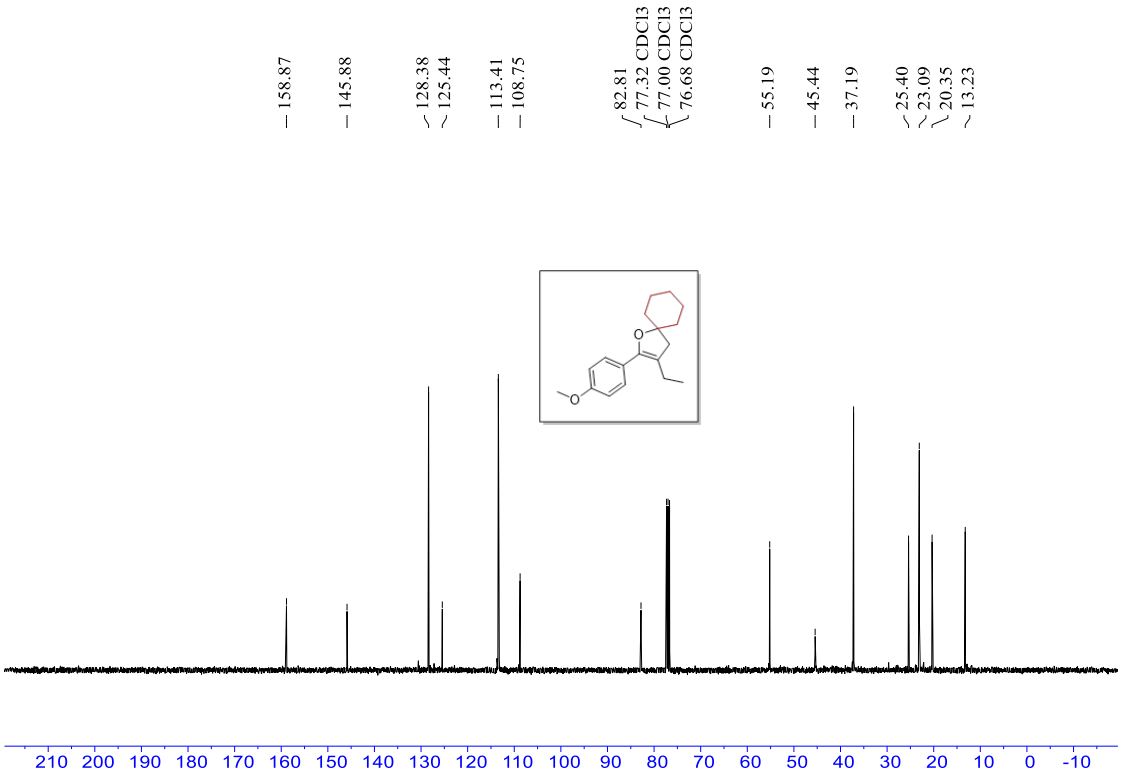
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9c**



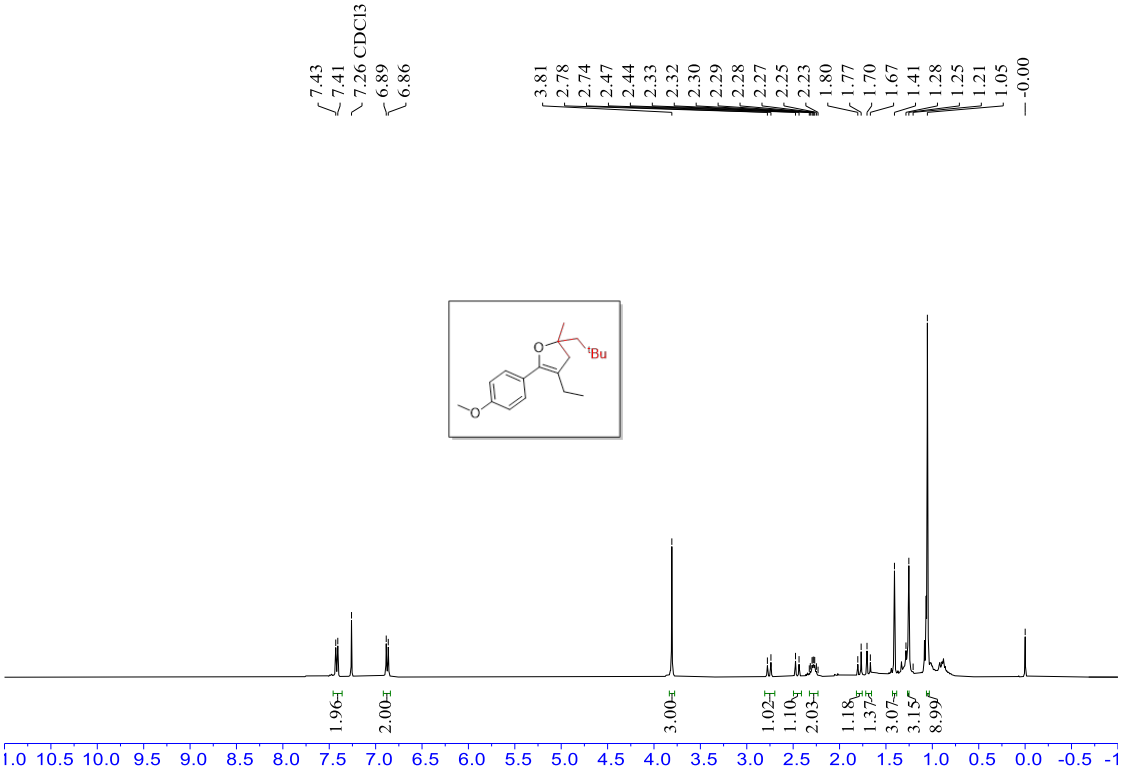
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9c**



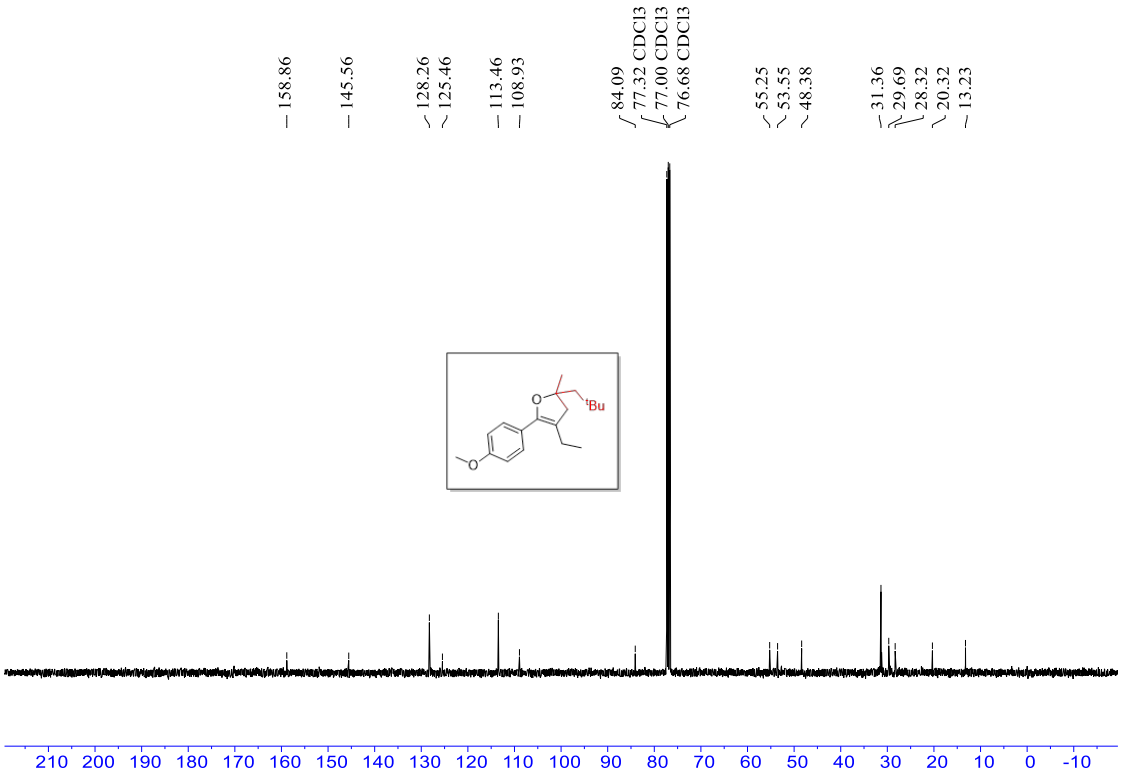
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9d**



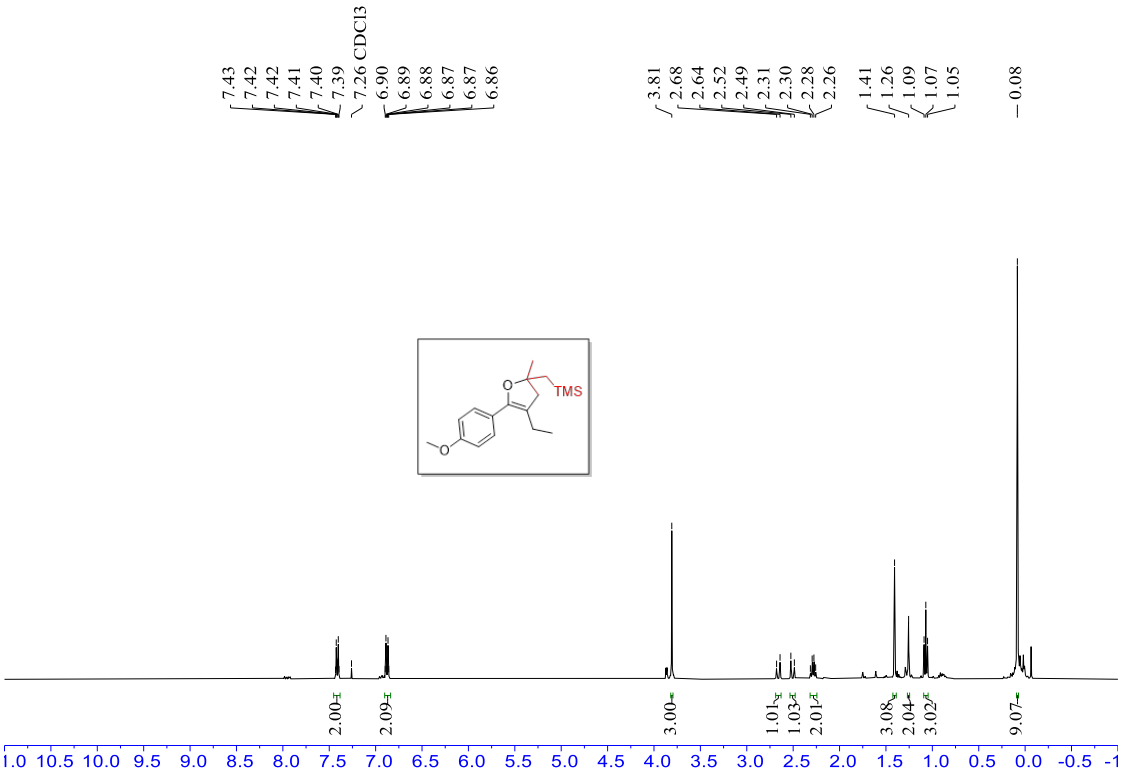
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9d**



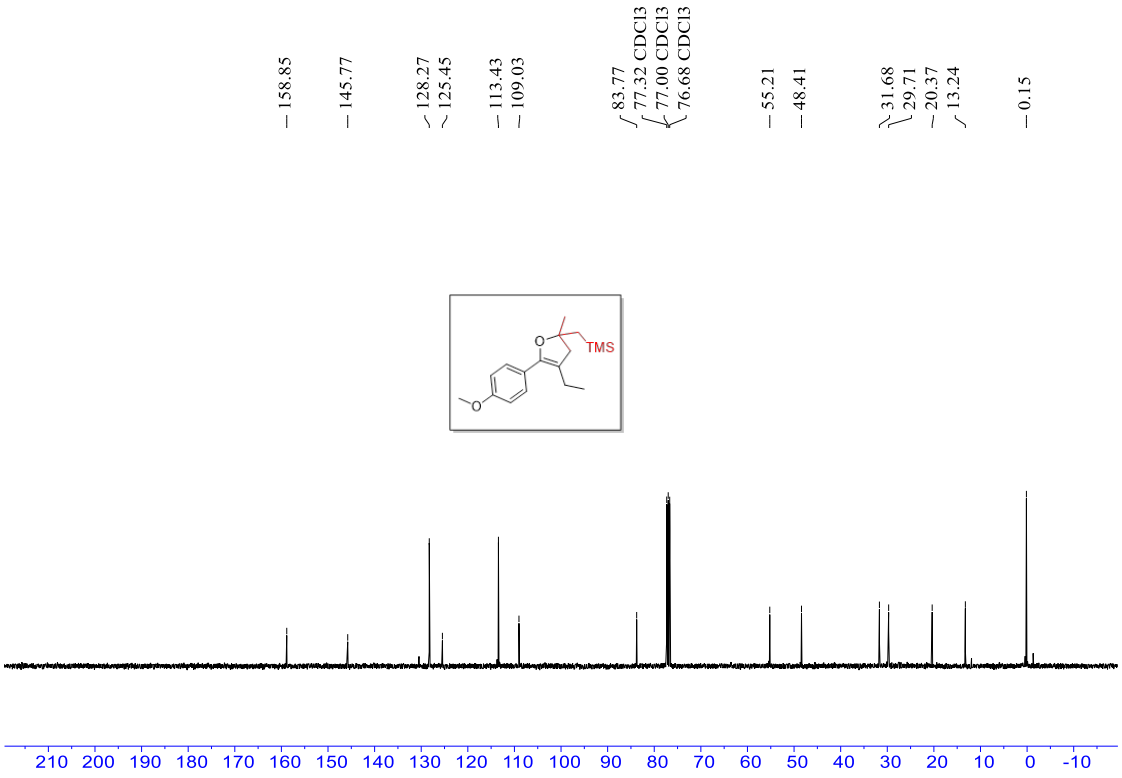
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9e**



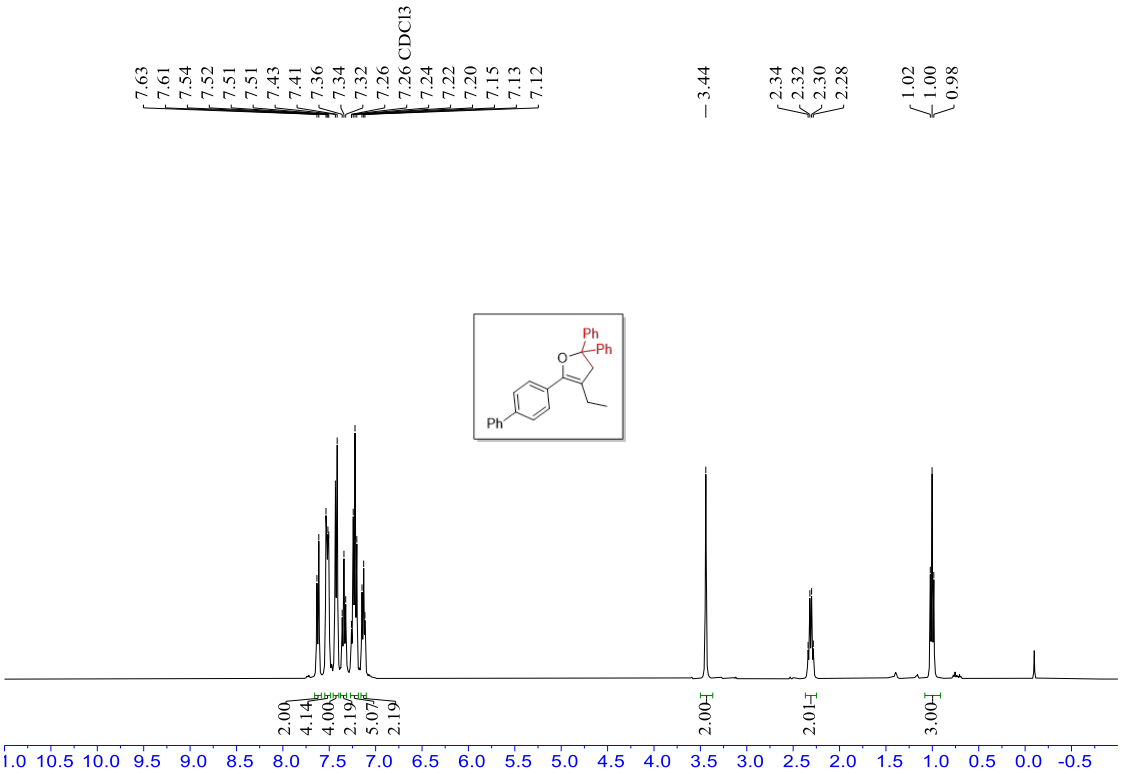
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9e**



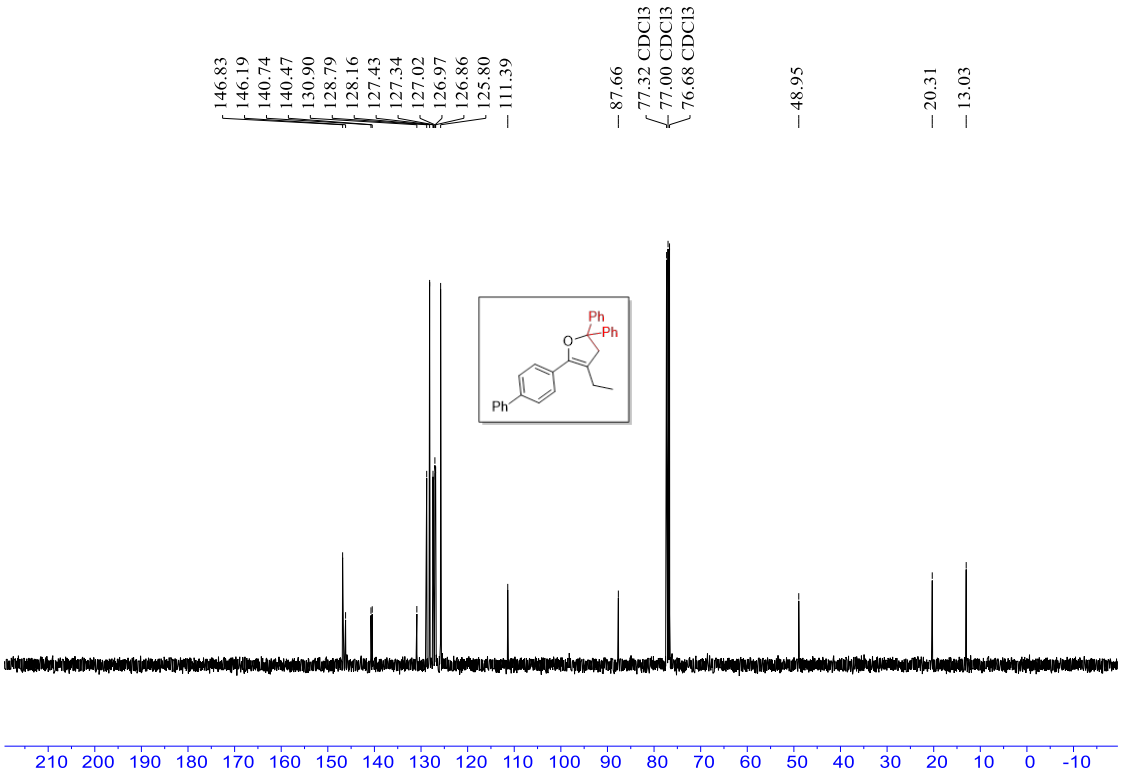
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9f**



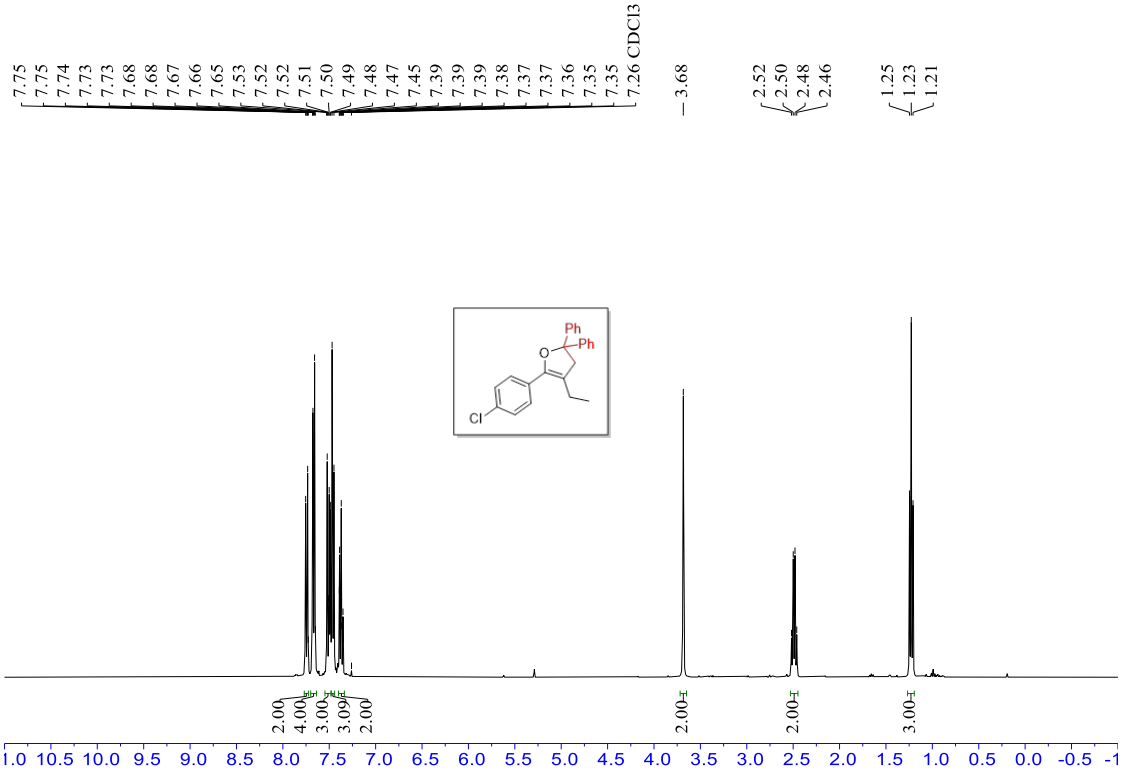
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9f**



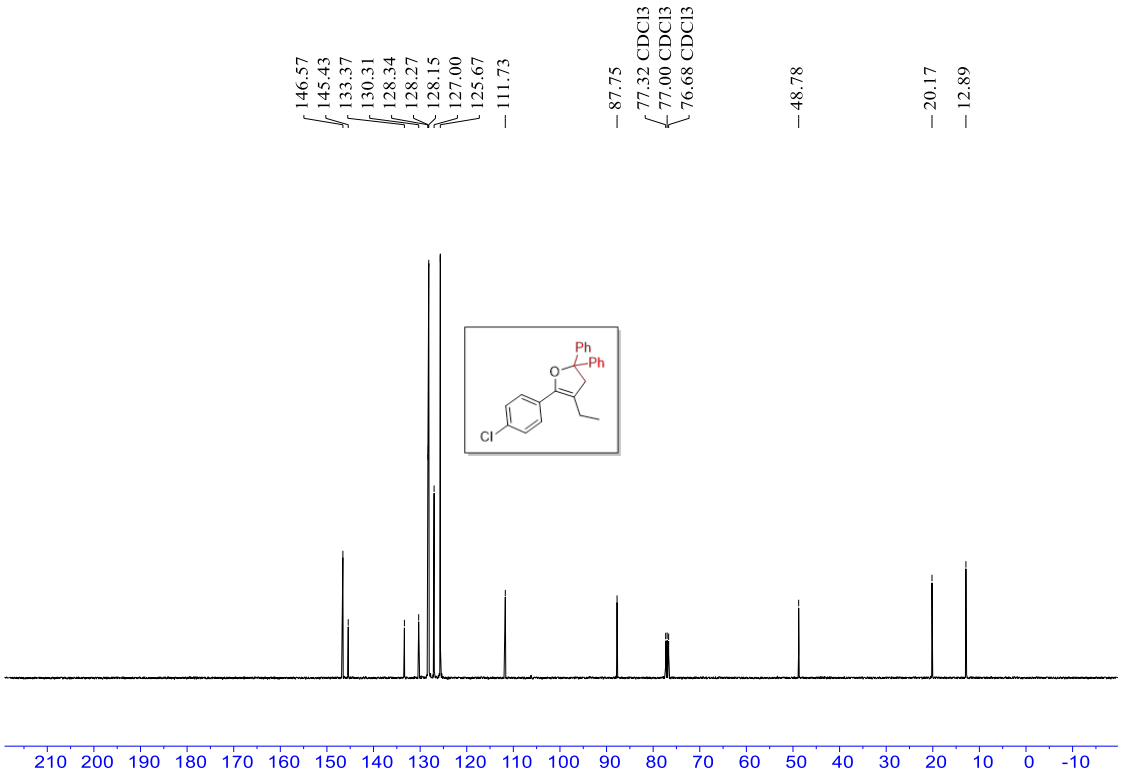
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9g**



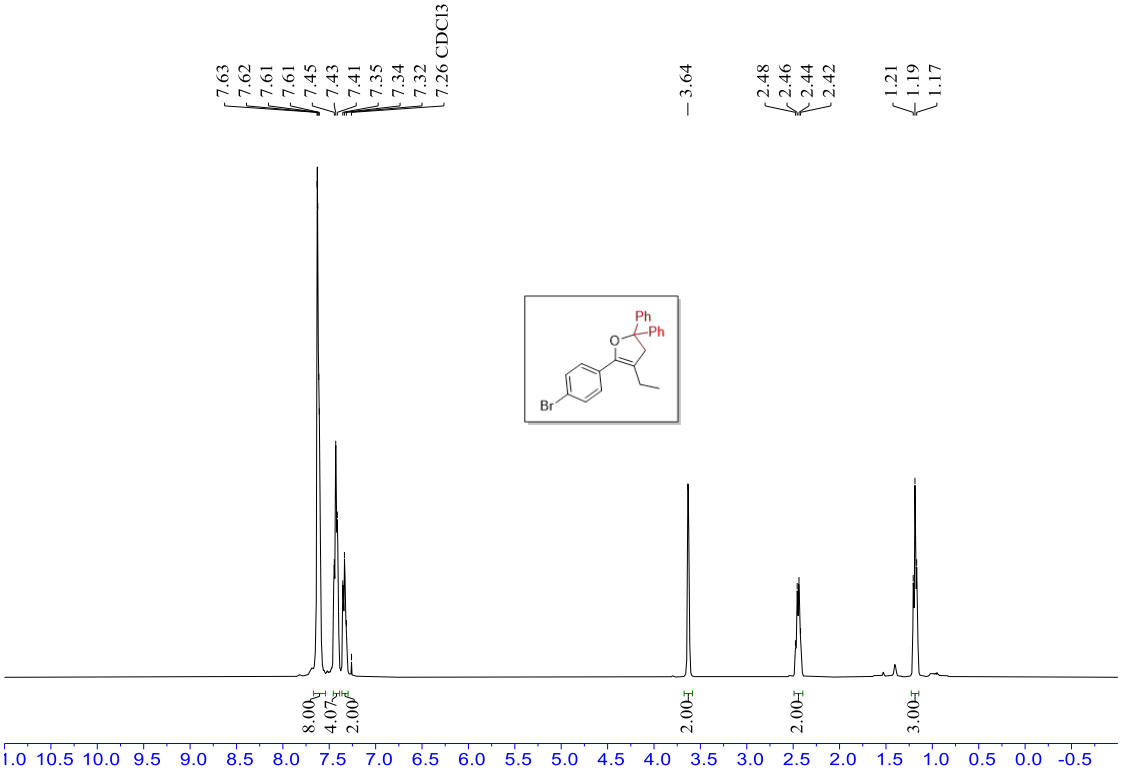
^{13}C NMR ($CDCl_3$) spectrum for **9g**



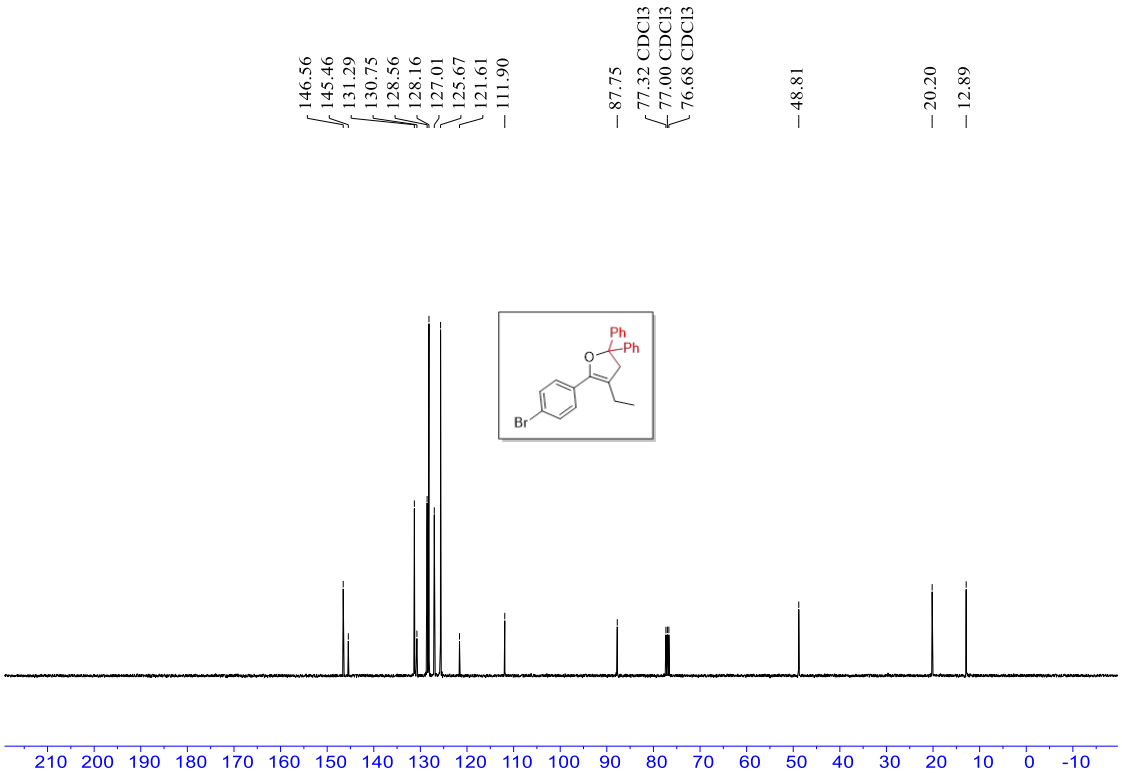
^{1}H NMR ($CDCl_3$) spectrum for **9h**



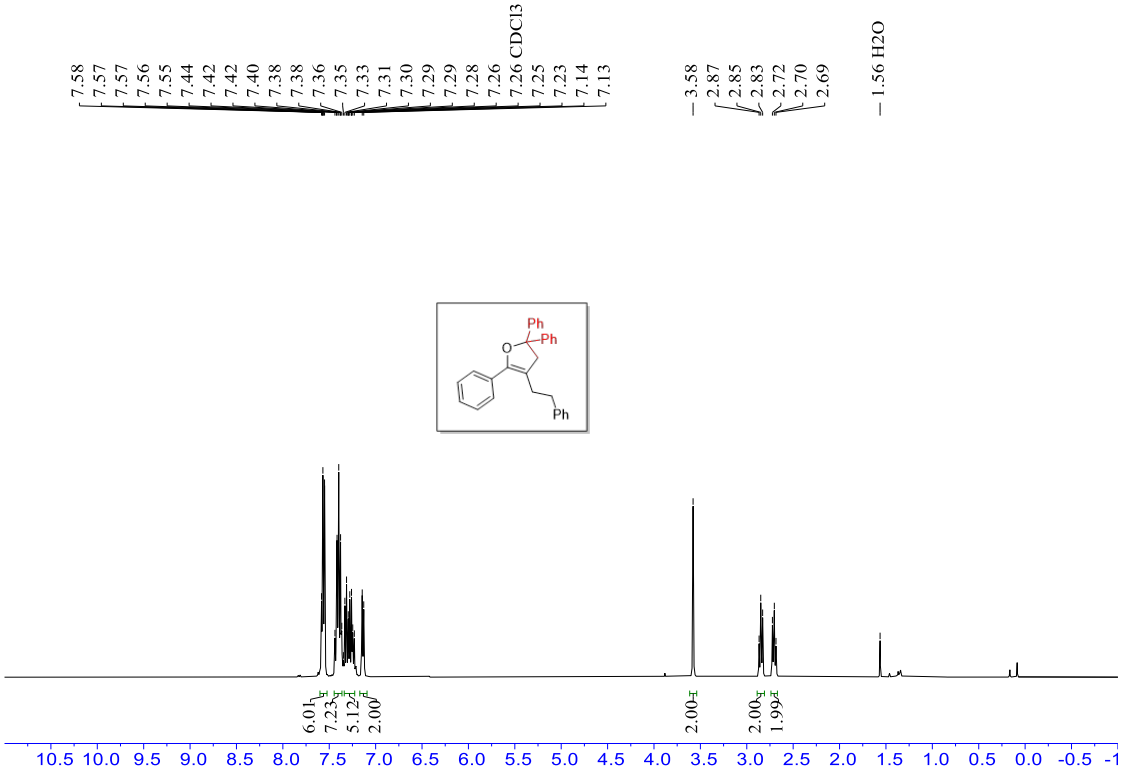
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9h**



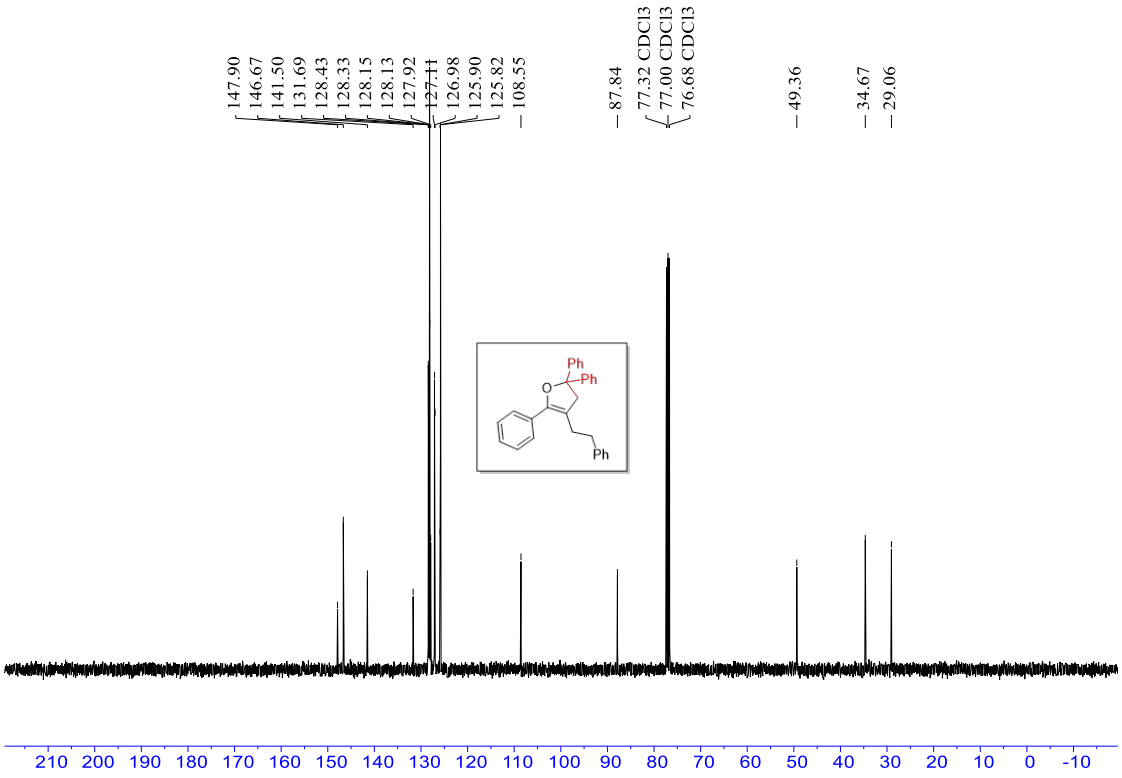
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9i**



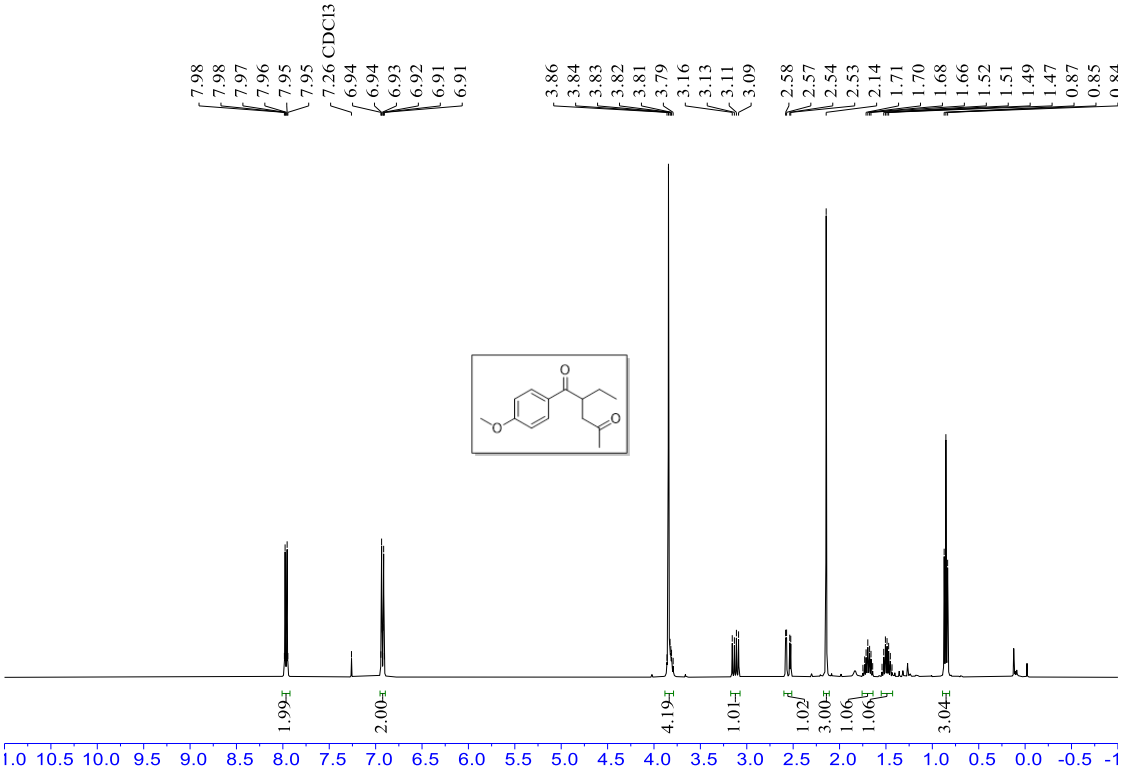
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9i**



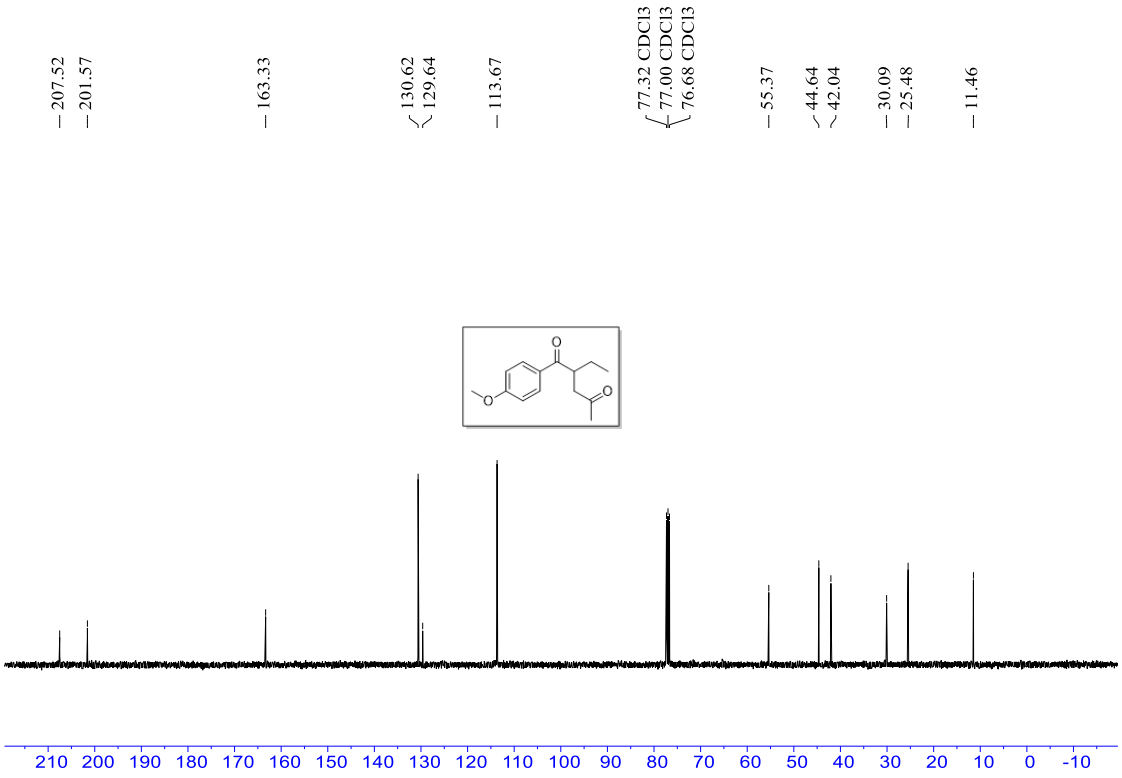
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9j**



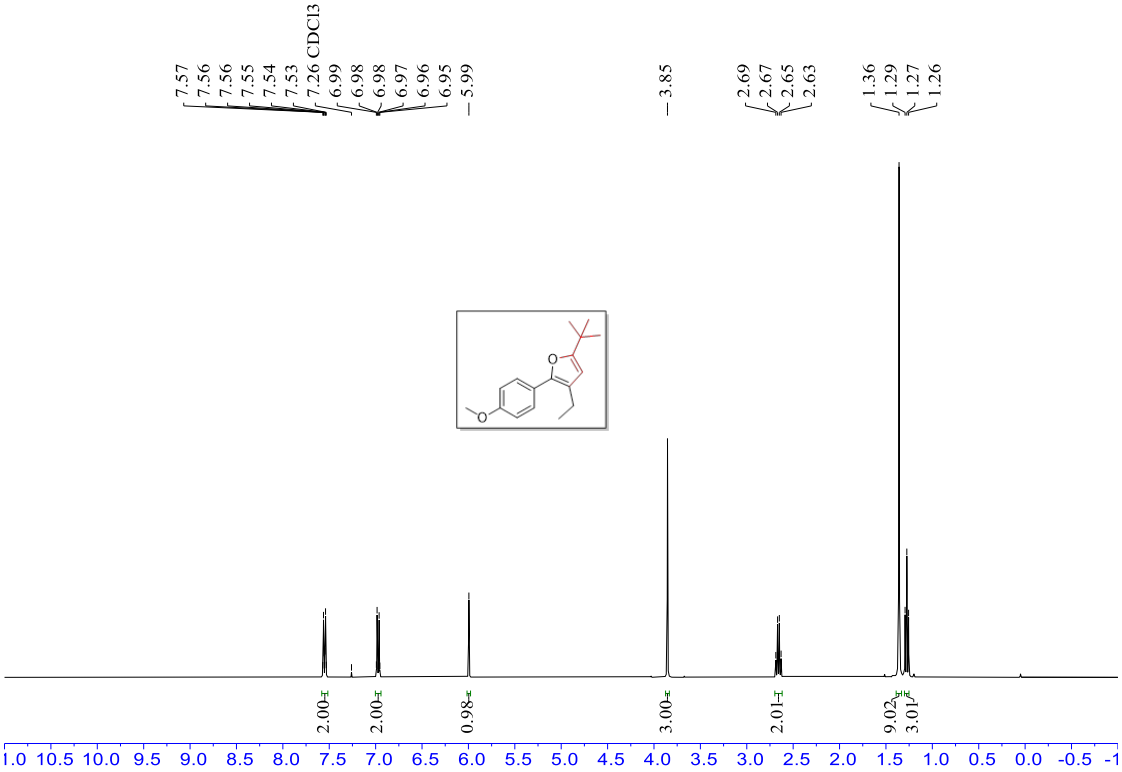
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9j**



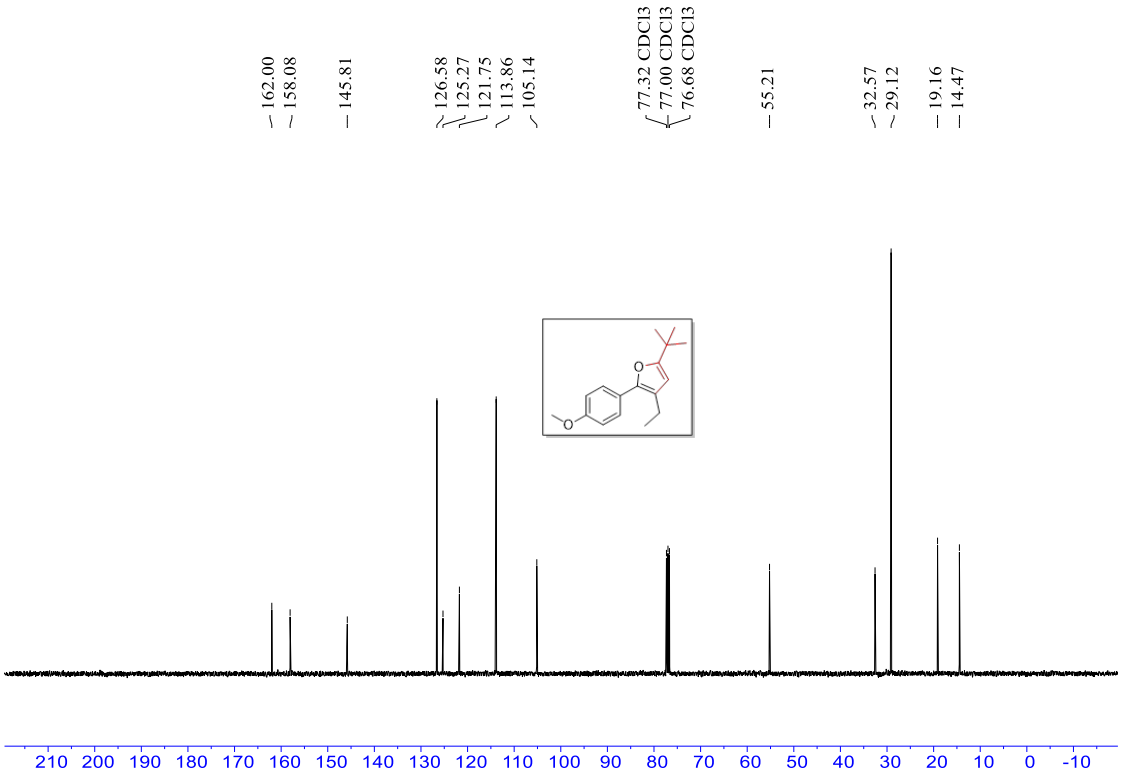
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9k**



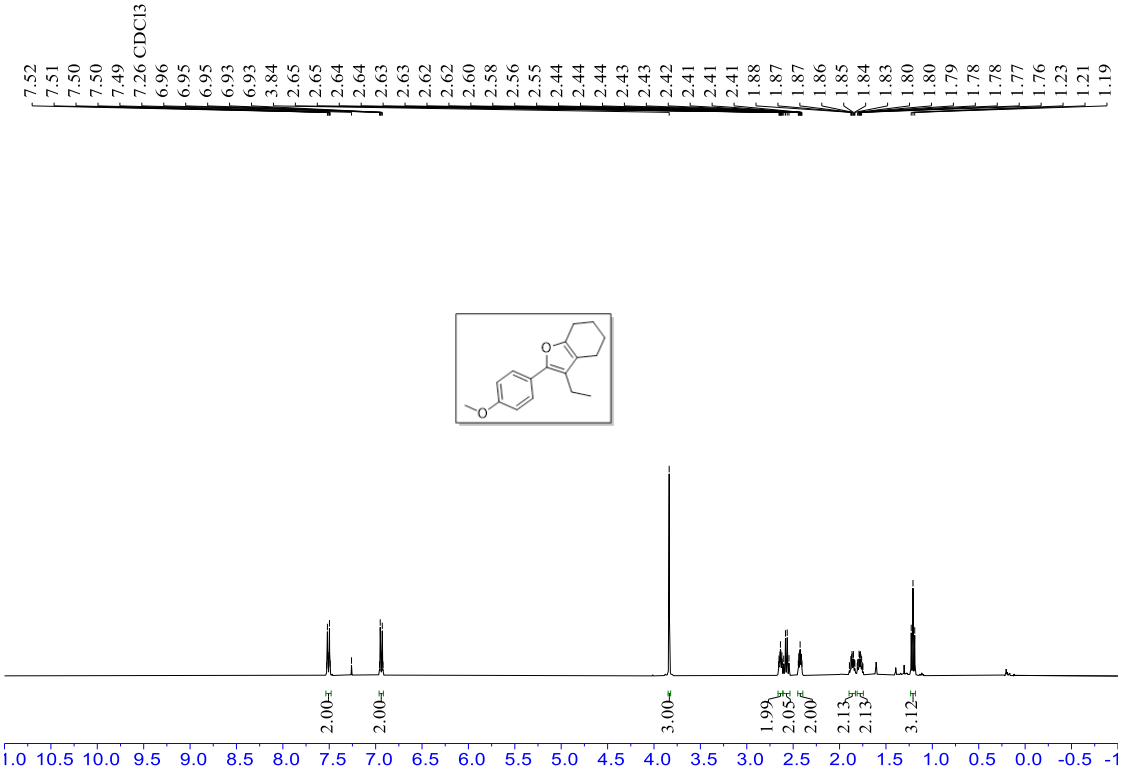
^{13}C NMR ($CDCl_3$) spectrum for **9k**



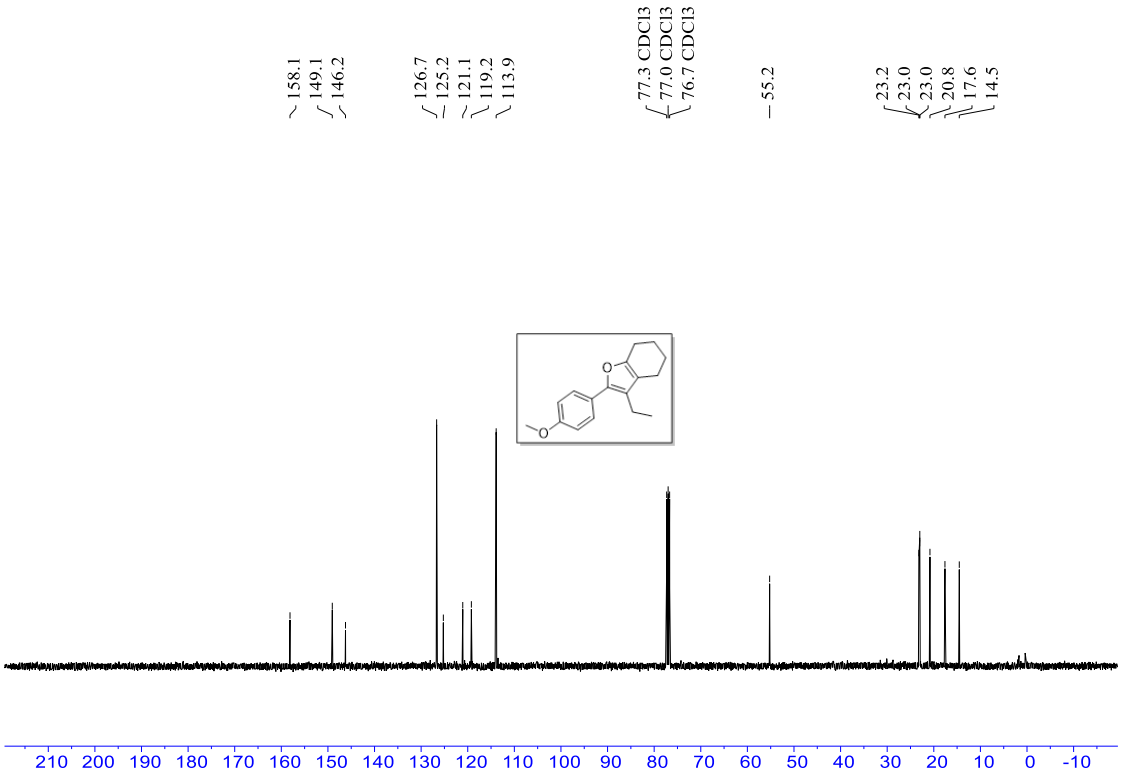
^{1}H NMR ($CDCl_3$) spectrum for **9l**



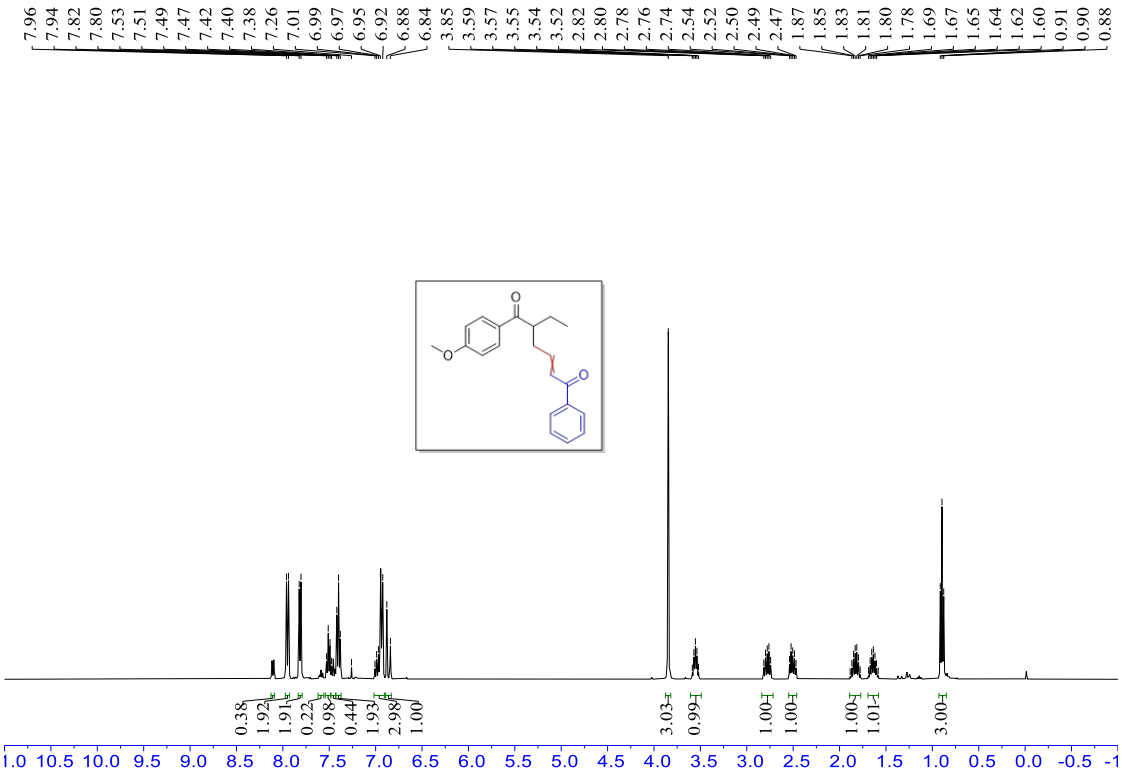
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9l**



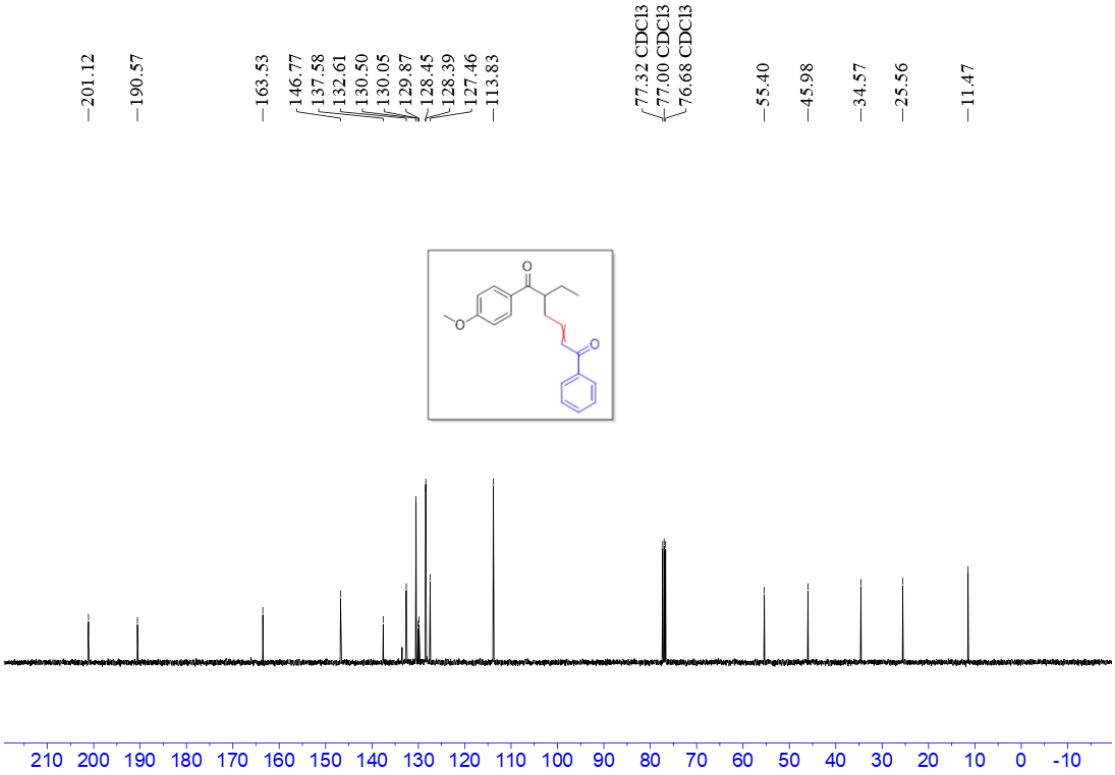
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **9m**



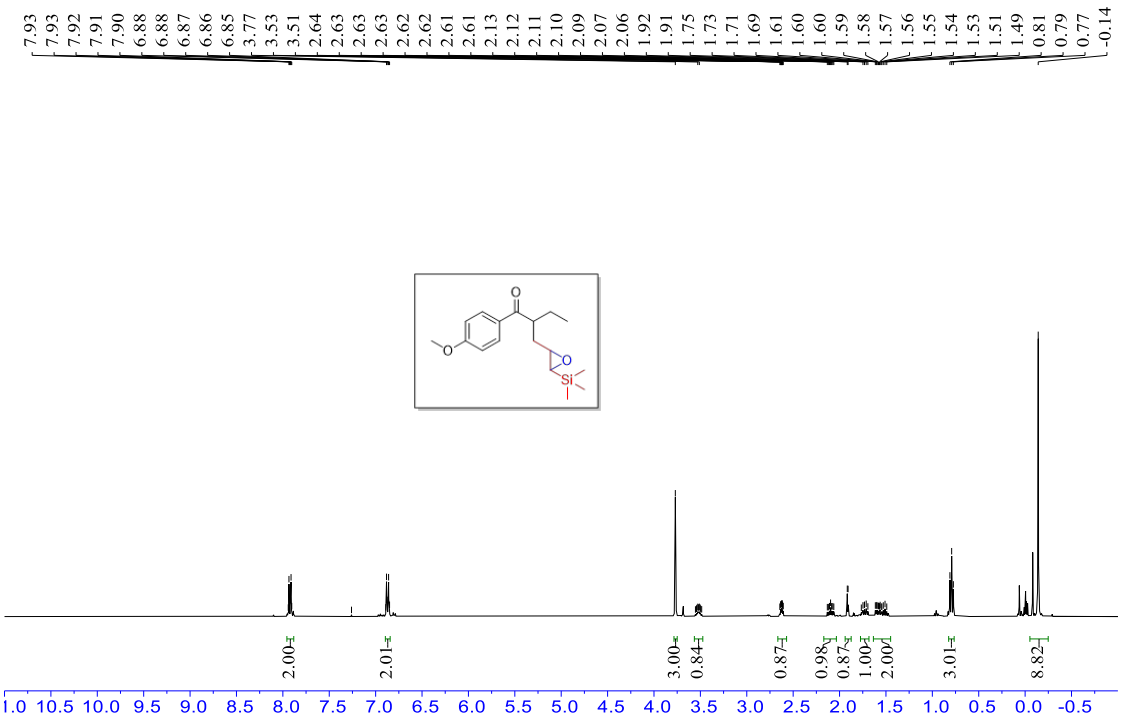
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **9m**



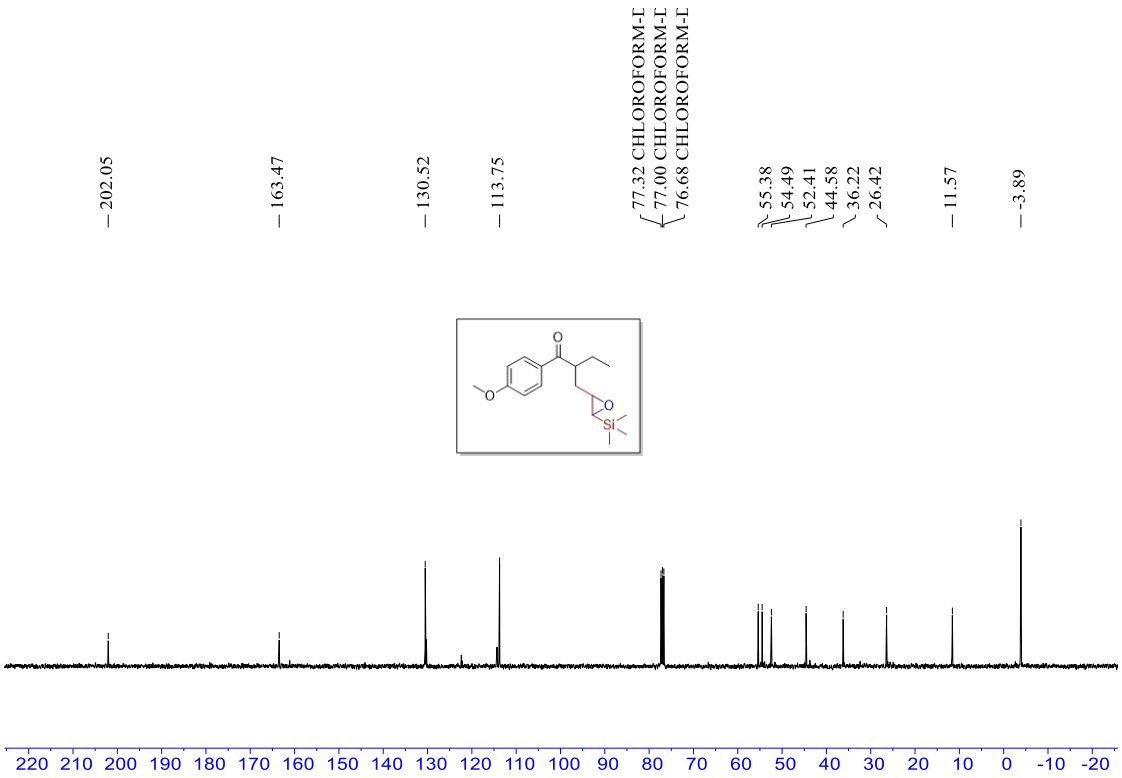
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **10**



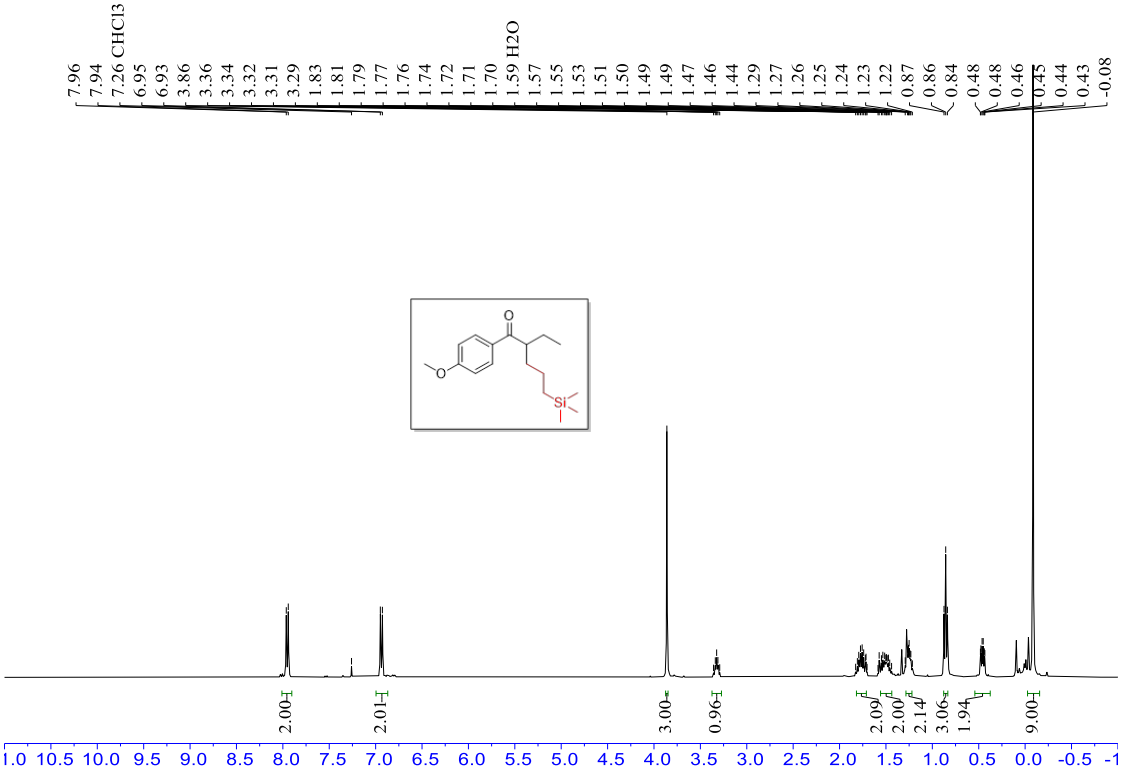
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **10**



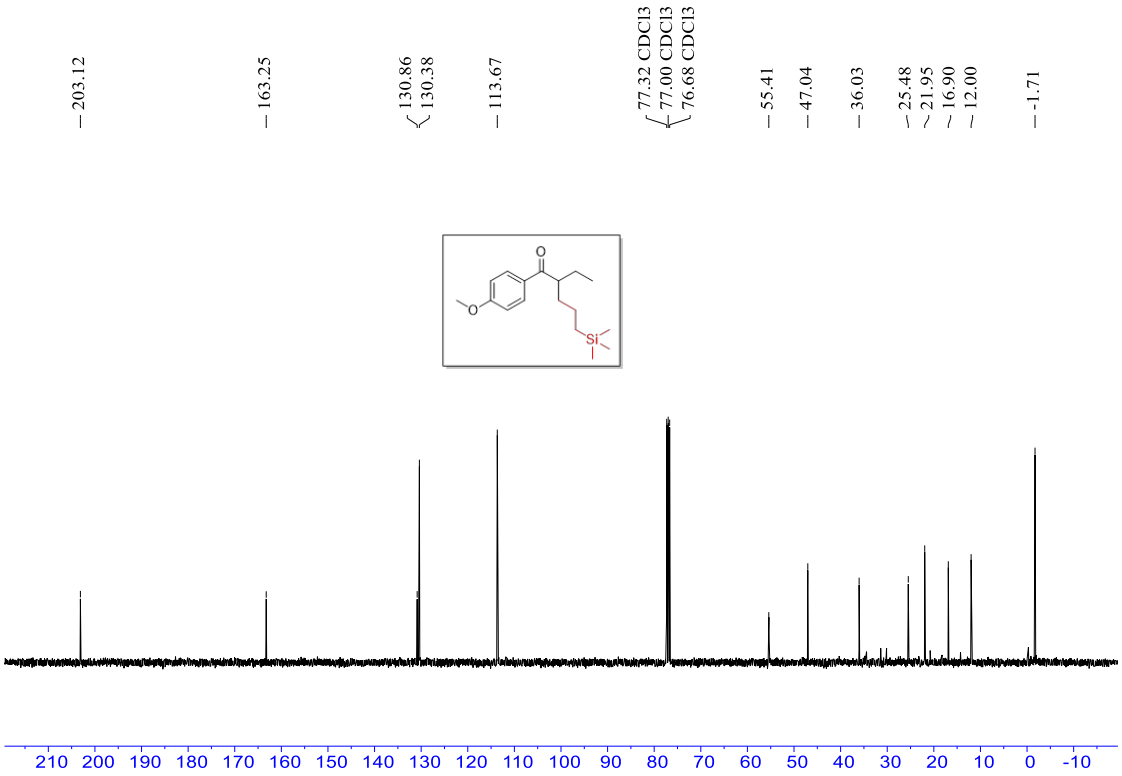
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **11**



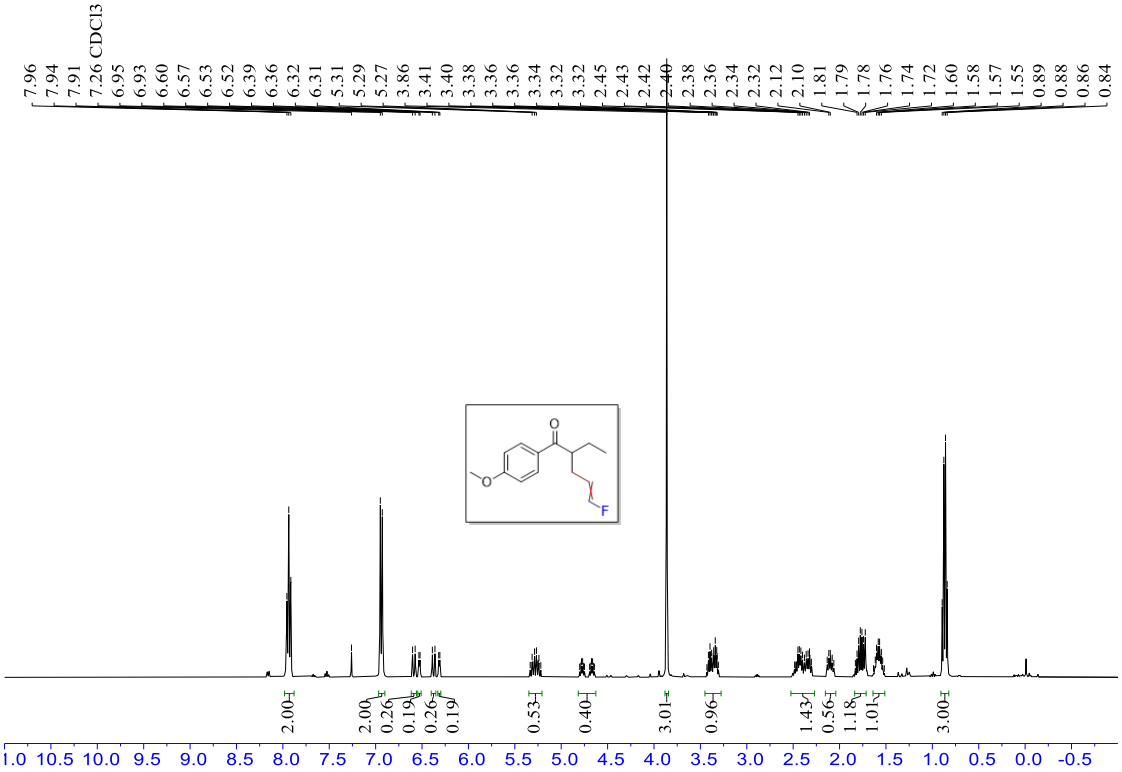
^{13}C NMR ($CDCl_3$) spectrum for **11**



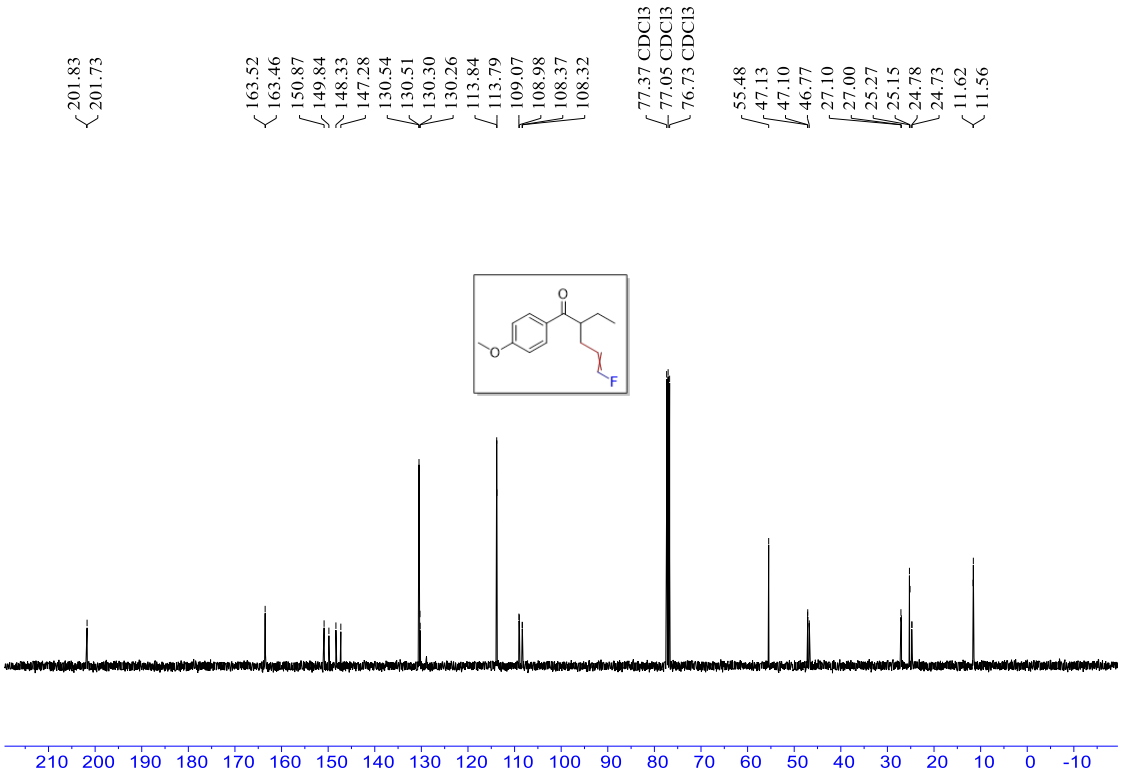
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **12**



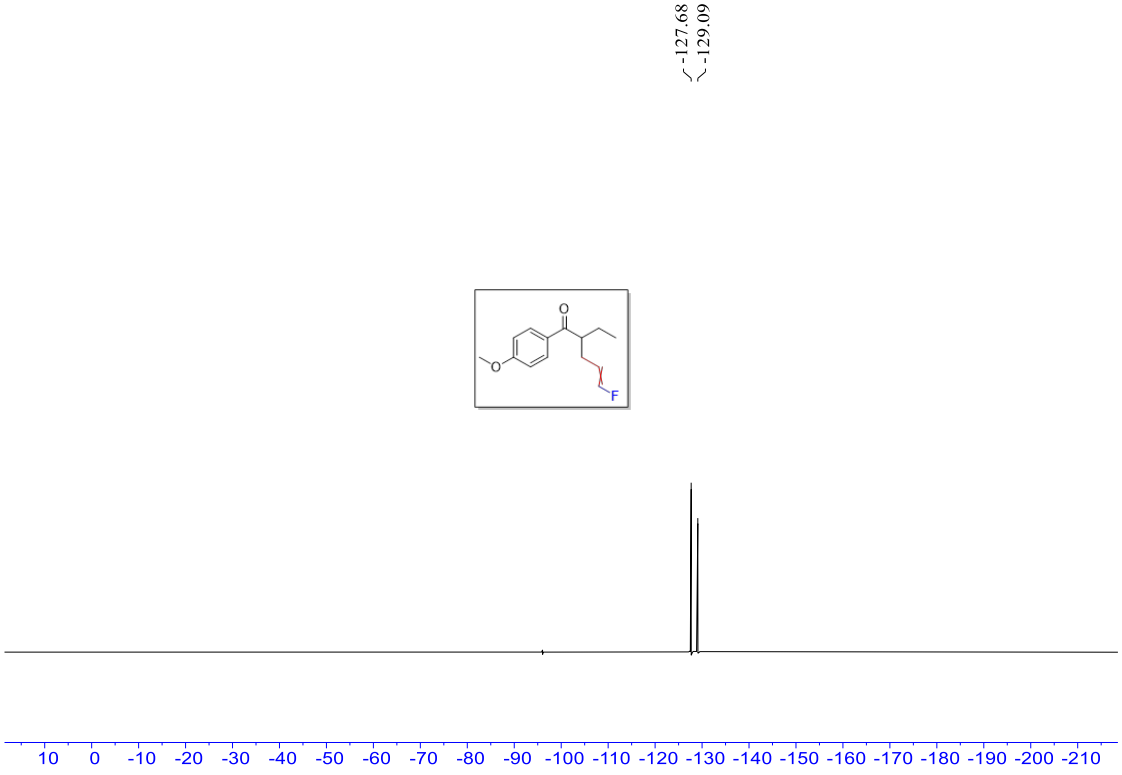
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **12**



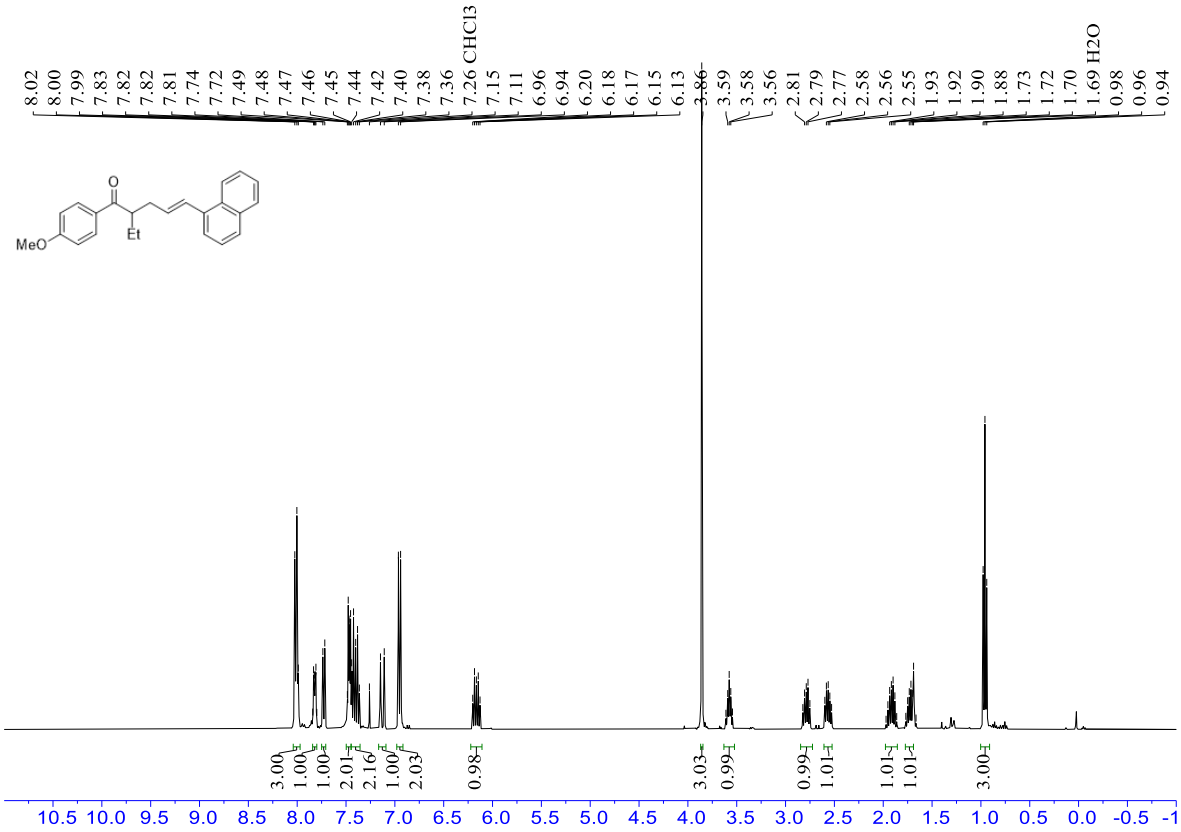
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **13**



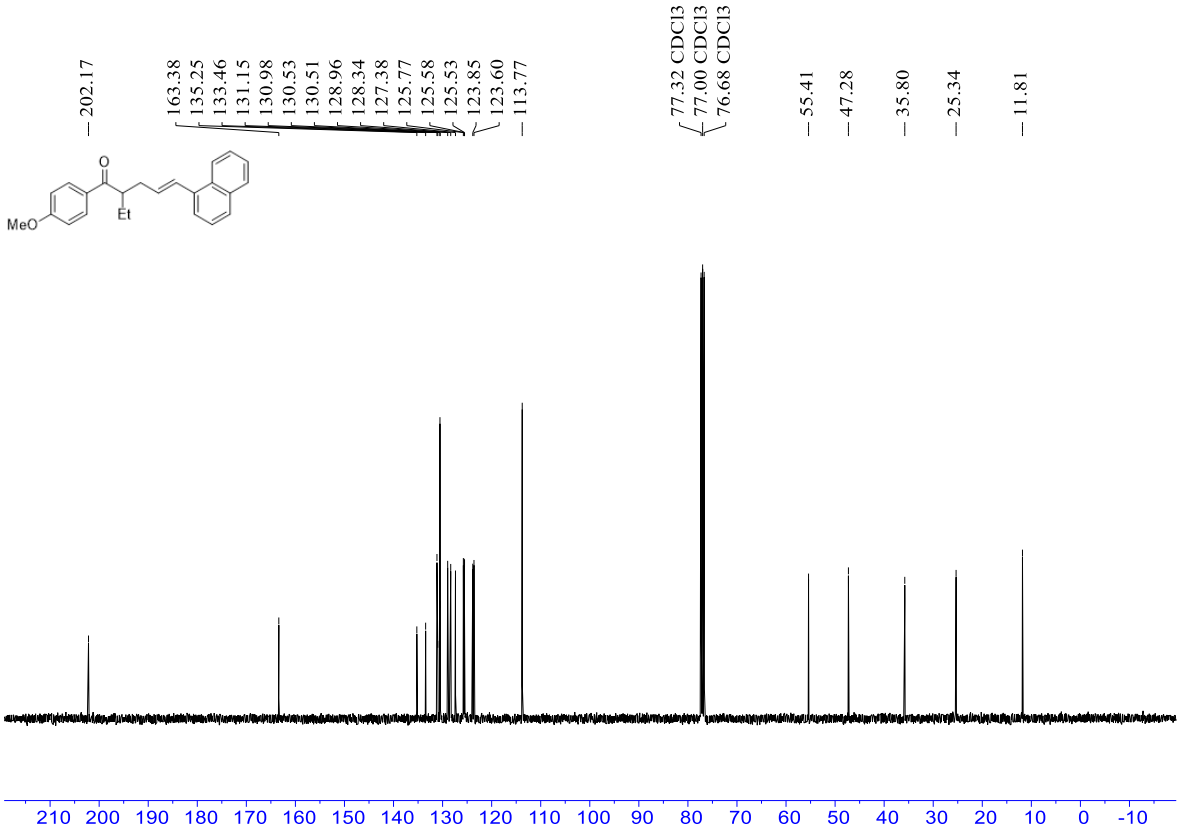
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **13**



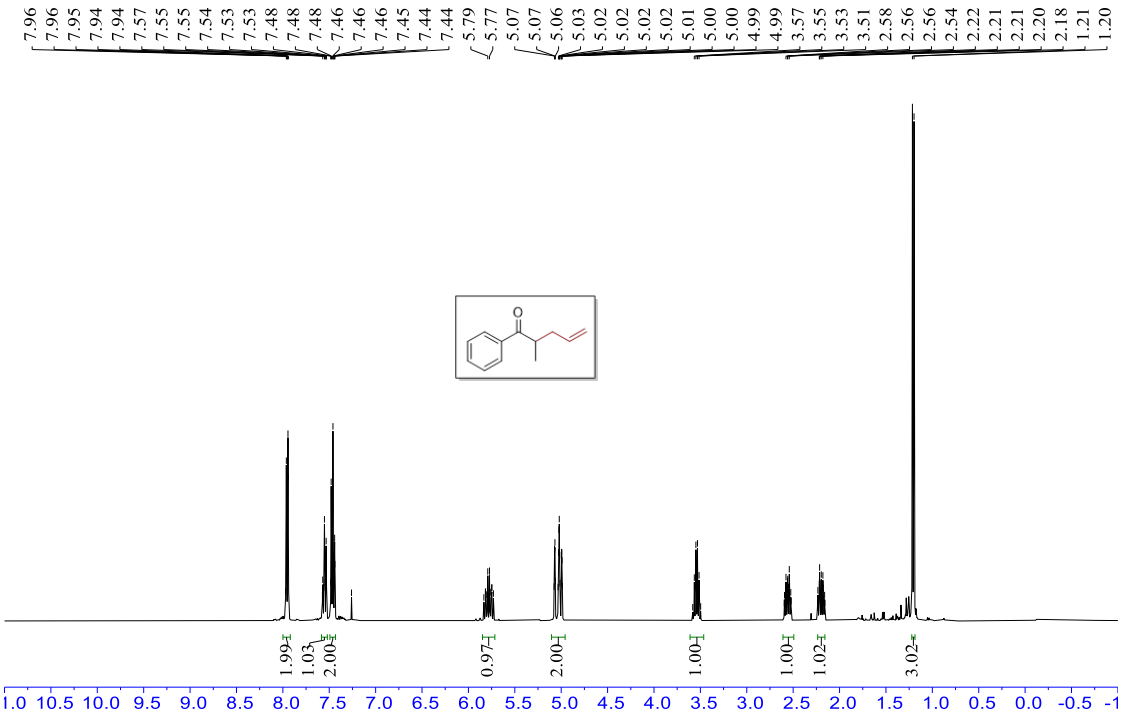
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **13**



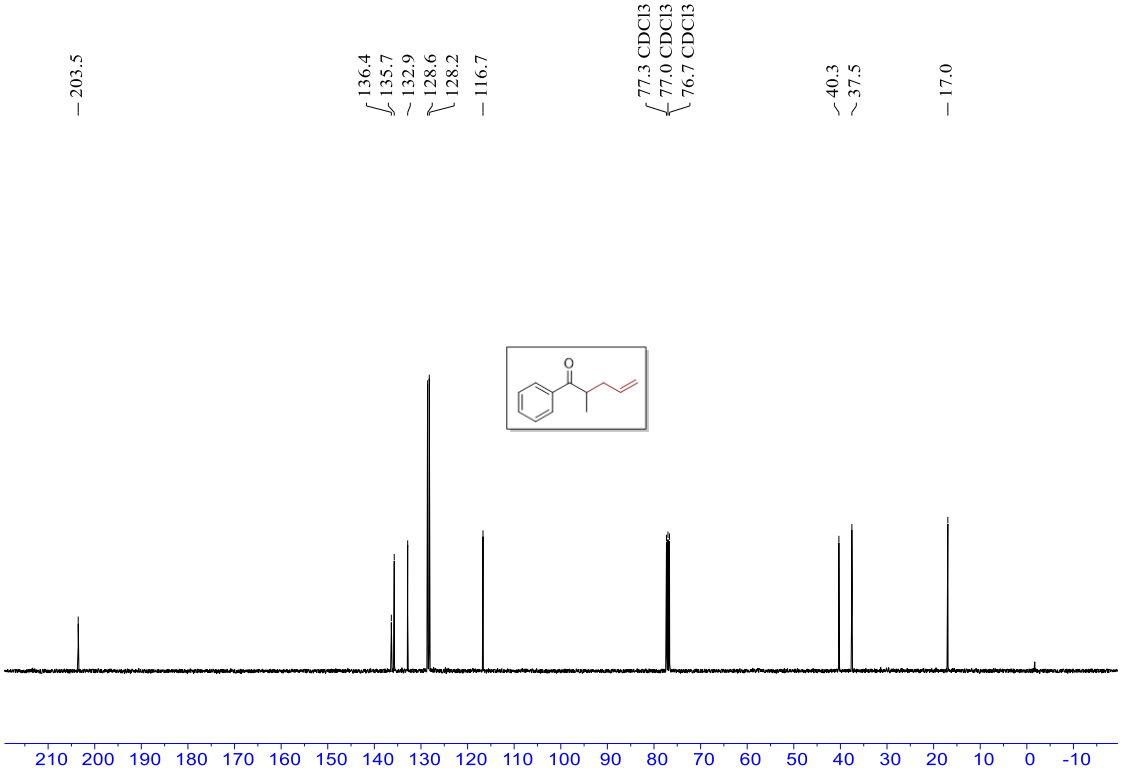
^{1}H NMR (376 MHz, $CDCl_3$) spectrum for **14**



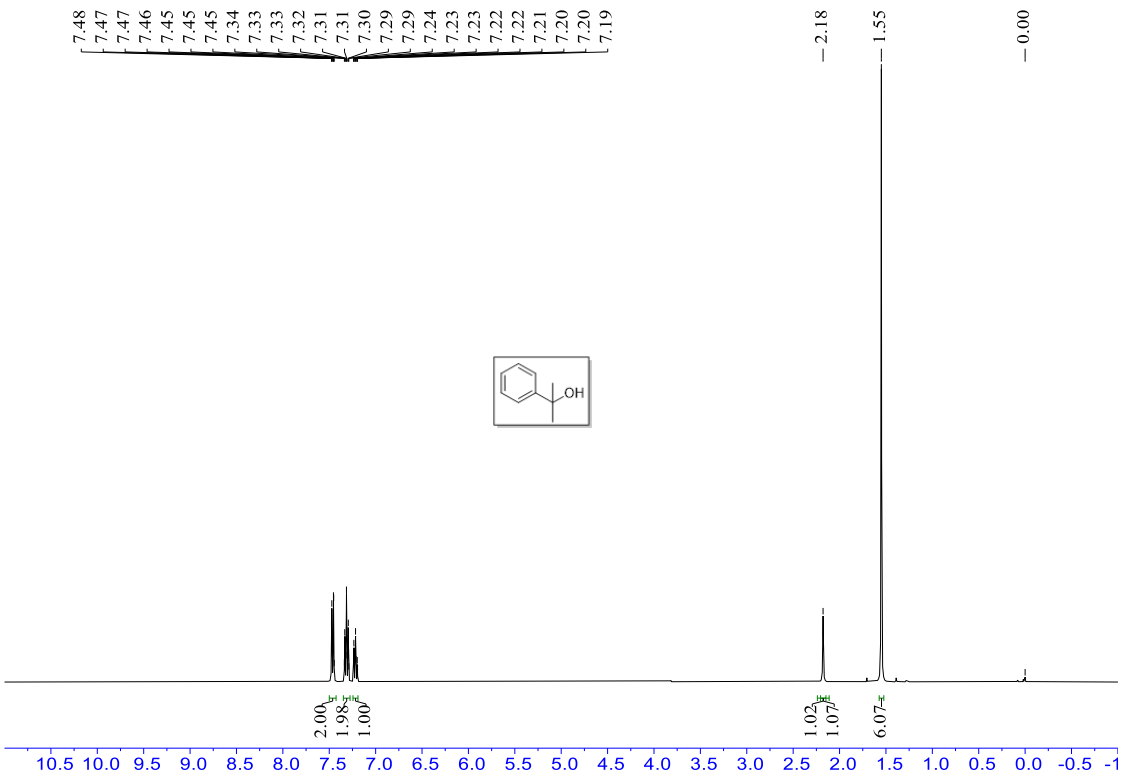
^{13}C NMR (376 MHz, $CDCl_3$) spectrum for **14**



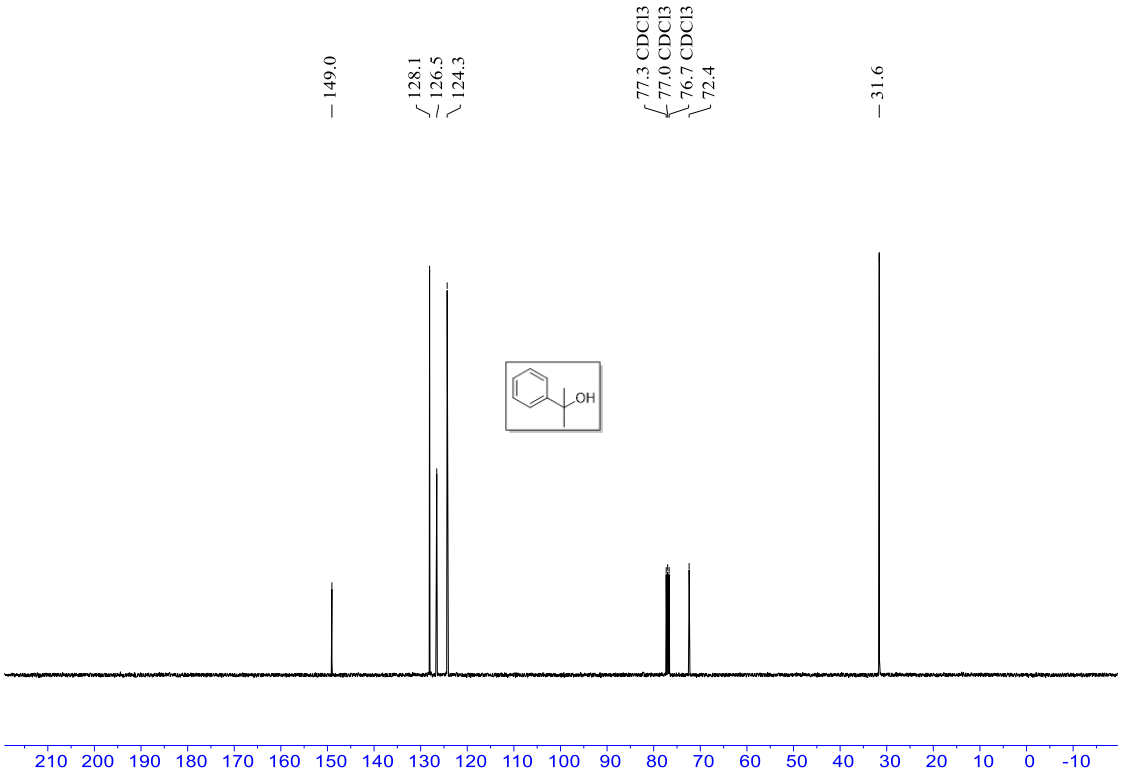
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **15**



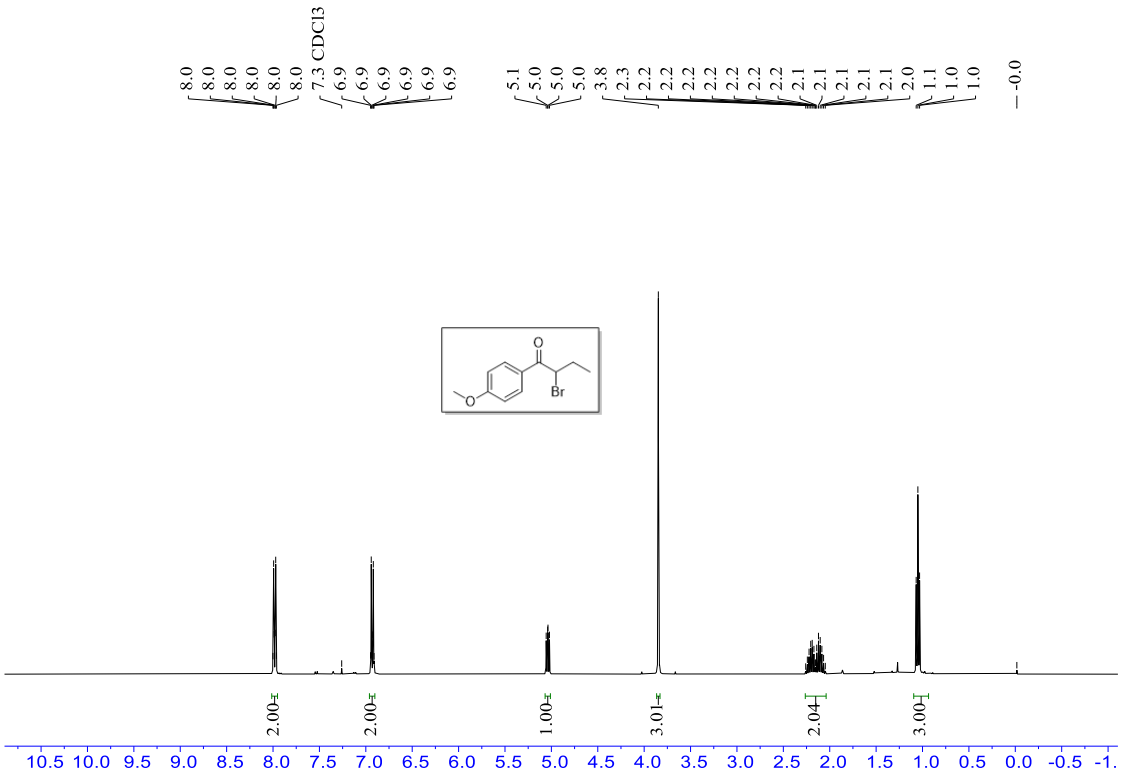
^{13} C NMR (101 MHz, $CDCl_3$) spectrum for **15**



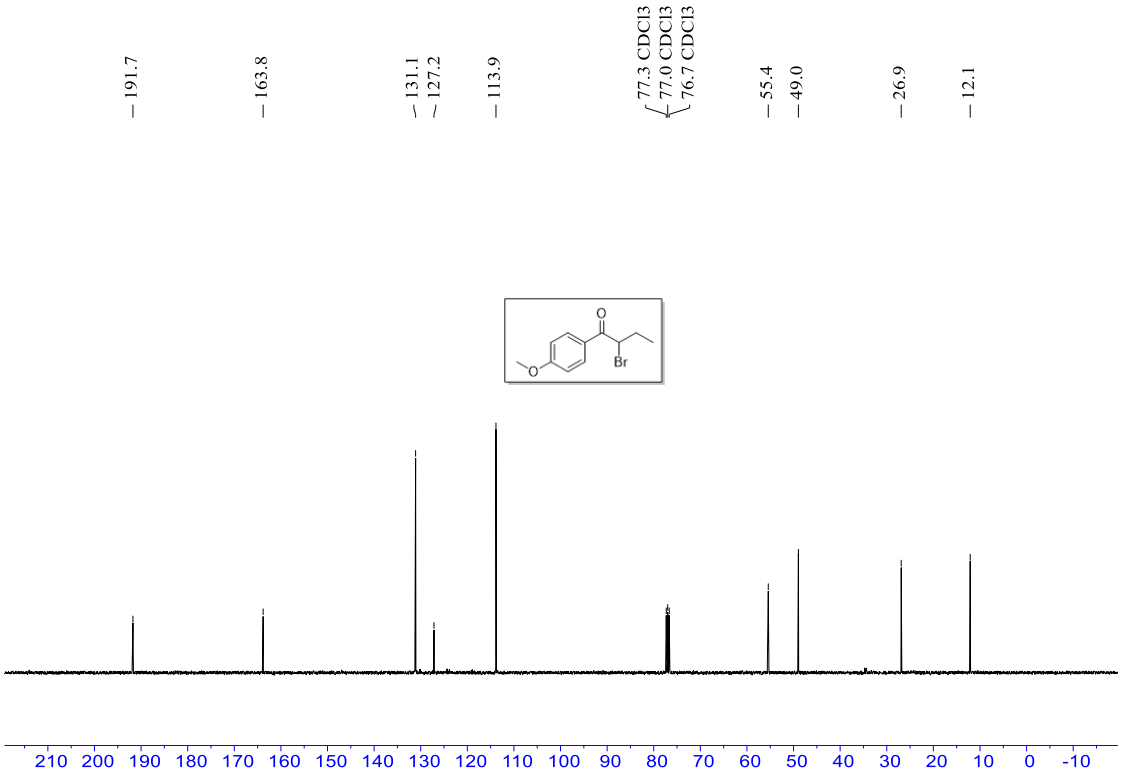
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **20**



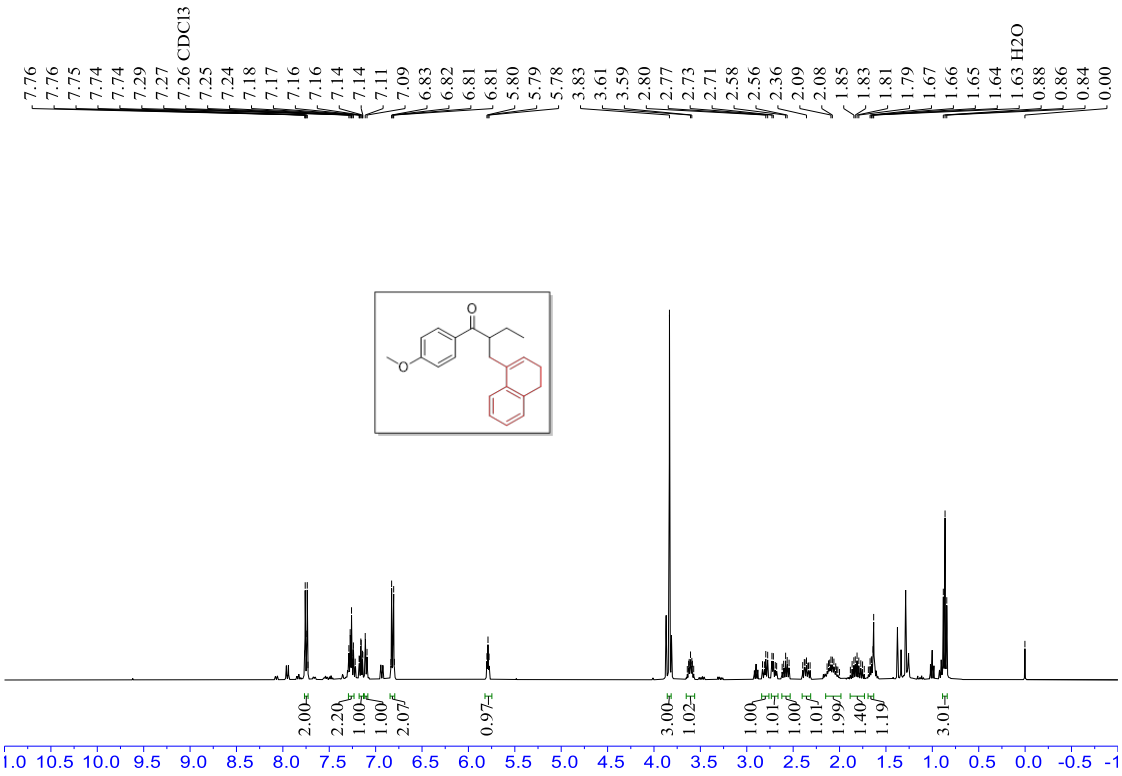
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **20**



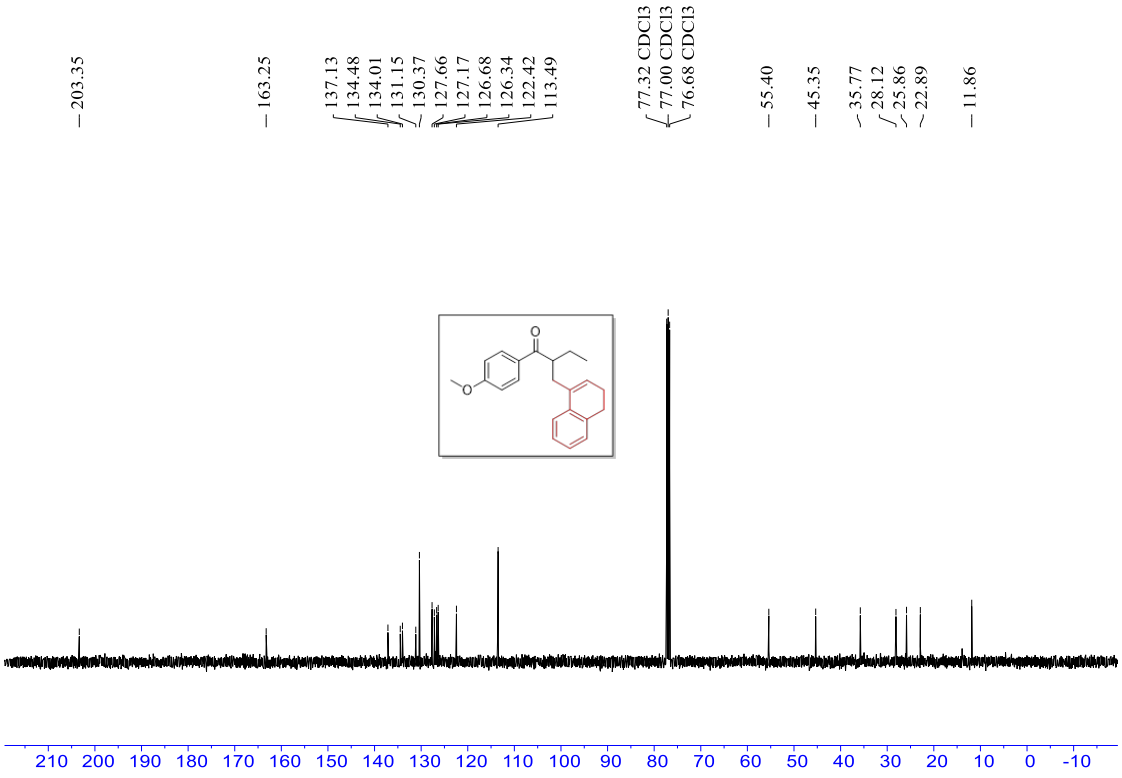
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **22**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **22**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for **23**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum for **23**