Supplementary Information

Uracil-Cu(I) Catalyst: Allylation of Cyclopropanols with Morita-Baylis-Hillman Alcohols under Water-tolerant Conditions

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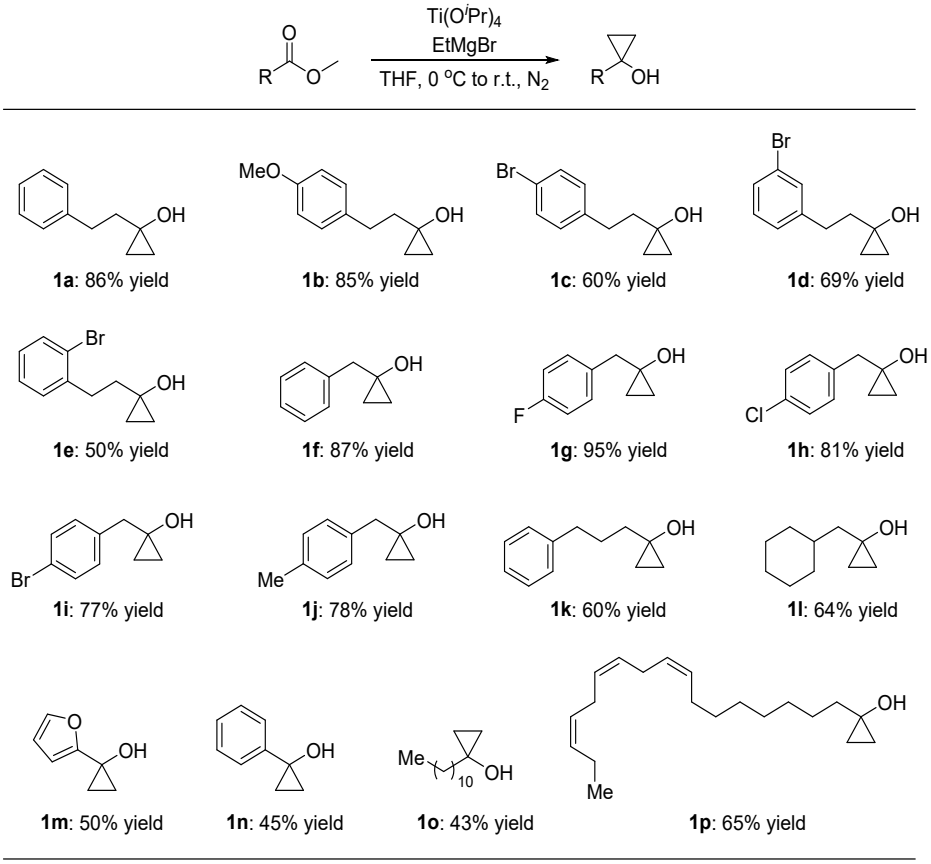
1. General Information

Unless otherwise noted, all commercially available compounds were used as received. All solvents were purified according to standard procedures. NMR spectra were recorded on a JEOL ECS-400S. The ^{1}H NMR and spectra was recorded at 400 MHz, ^{13}C NMR was recorded at 101 MHz, ^{19}F NMR and spectra were recorded at 376 MHz. The ^{1}H and ^{13}C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (*J*) are in Hertz (Hz). IR spectra were recorded on a Thermo Scientific Nicolet iS-5 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource (analyzer type: TOF). Melting points were measured on a RY-I apparatus and are reported uncorrected. The starting materials Morita-Baylis-Hillman alcohols[1-3] and cyclopropanols[4-5] were readily prepared according to the related literatures. $Cu(MeCN)_4PF_6$, Uracil, and 40% aqueous solution of dimethylamine were purchased from *Energy Chemical* (Shanghai).

2. General procedure to the preparation of cyclopropanols

Scheme S1. Preparation of cyclopropanols **1a-1p**



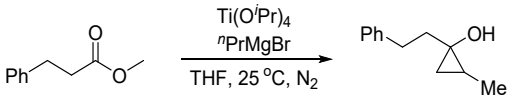
Procedure A:
Following the literature procedure[4]. Under the protection of nitrogen, EtMgBr (22 mmol, 1 M in THF, 2.2 equiv.) was slowly added to a solution of the ester (10 mmol, 1.0 equiv.) and $Ti(O^iPr)_4$ (2 mmol, 0.2 equiv.) in 40 mL of anhydrous THF at 0 °C over 40 minutes. The mixture was warmed to room temperature and allowed to stir overnight. Then saturated solution of NH_4Cl (aq.) was slowly added to quench the reaction. After the precipitate was removed by filtration, the filtrate was extracted by EtOAc and the combined organic phase was dried over anhydrous Na_2SO_4. The crude products were purified by column chromatography to afford the pure cyclopropanols.

Procedure B:
Following the literature procedure[5]. Under the protection of nitrogen, EtMgBr (28 mmol, 1 M in THF, 2.8 equiv.) was slowly added to a solution of the ester (10 mmol, 1.0 equiv.) and $Ti(O^iPr)_4$ (14 mmol, 1.4 equiv.) in 40 mL of anhydrous THF at 0 °C over 40 minutes. The mixture was warmed to room temperature and allowed to stir overnight. Then saturated solution of NH_4Cl (aq.) was slowly added to quench the reaction. After the precipitate was removed by filtration, the filtrate was extracted by EtOAc and the combined organic phase was dried over anhydrous Na_2SO_4. The crude products were purified by column chromatography to afford the pure cyclopropanols.

Cyclopropanols **1a**[4], **1b**, **1c**, **1d**[6], **1e**, **1f**[5], **1g**[7], **1h**[8], **1i**[9], **1l**[4], **1n**[5] were synthesized according to the previously reported procedure (procedure A), and analytical data were identical to those.

Cyclopropanols **1j**[10], **1k**[10], **1m**[10], **1o**[5], **1p** were synthesized according to the previously reported procedure (procedure B), and analytical data were identical to those.

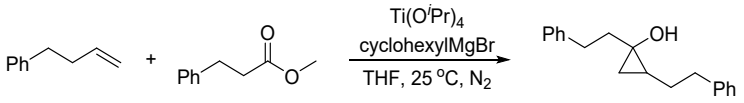
Preparation of **1q**:



1q: 80% yield

Following the literature procedure[11]. Under the protection of nitrogen, ^{n}PrMgBr (20 mmol, 1 M in THF, 4.0 equiv.) was slowly added to a solution of the ester (5 mmol, 1.0 equiv.) and $Ti(O^iPr)_4$ (5 mmol, 1.0 equiv.) in 20 mL of anhydrous THF at 25 °C over 30 minutes. The mixture was stirrde for 30 minutes at 25 °C. Then saturated solution of NH_4Cl (aq.) was slowly added to quench the reaction. After the precipitate was removed by filtration, the filtrate was extracted by EtOAc and the combined organic phase was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography to afford the pure cyclopropanol.

Preparation of **1r**:

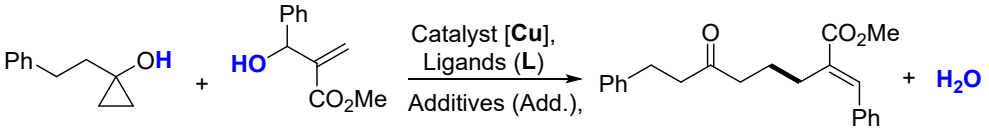


1r: 40% yield

$Ti(O^iPr)_4$ (5 mmol, 1.0 equiv.) was added to a flask at room temperature under the protection of nitrogen. Anhydrous THF (20 mL) was added to the flask, followed by the alkene (5 mmol, 1.0 equiv.) and the ester (7.5 mmol, 1.5 equiv.). Then cyclohexylMgBr (20 mmol, 1 M in THF, 4.0 equiv.) was slowly added over the period of 1 h at 25 °C. The mixture was stirred over night at 25 °C. Then saturated solution of NH_4Cl (aq.) was slowly added to quench the reaction. After the precipitate was removed by filtration, the filtrate was extracted by EtOAc and the combined organic phase was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography to afford the pure cyclopropanol.

3. Optimized the Reaction Conditions

Table 1. Optimization of the reaction conditions.[a]



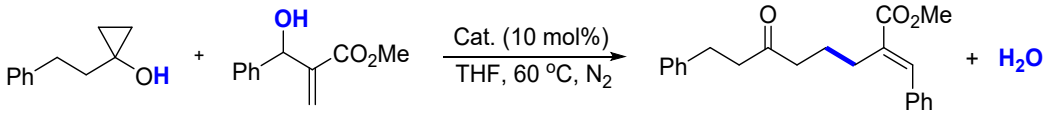
1a **2a** **3a**

Entry	[**Cu**] (10 mol%)	[**L**]	Add.	**3a**(%)[b]
1[c]	CuBr	--	--	< 5
2[c]	$Cu(OAc)_2$	--	--	n.r.
3[c]	$Cu(MeCN)_4BF_4$	--	--	5
4[c]	$Cu(MeCN)_4PF_6$	--	--	25
5	$Cu(MeCN)_4PF_6$	--	--	41
6	$Cu(MeCN)_4PF_6$	1,10-phen.	--	25
7	$Cu(MeCN)_4PF_6$	4,4'-bipyridine	--	32
8	$Cu(MeCN)_4PF_6$	uracil	--	65
9	$Cu(MeCN)_4PF_6$	uracil	H_2O (4 equiv.)	72
10[d]	$Cu(MeCN)_4PF_6$	uracil	H_2O (4 equiv.)	80
11[d]	$Cu(MeCN)_4PF_6$	**uracil**	**H_2O (4 equiv.), Me_2NH (7 mol%)**	**82 (80)**
12[d]	$Cu(MeCN)_4PF_6$	thymine	H_2O (4 equiv.), Me_2NH (7 mol%)	70
13[d]	$Cu(MeCN)_4PF_6$	cytosine	H_2O (4 equiv.), Me_2NH (7 mol%)	< 5
14[d,e]	$Cu(MeCN)_4PF_6$	uracil	H_2O (4 equiv.), Me_2NH (7 mol%)	46
15[d,f]	$Cu(MeCN)_4PF_6$	uracil	H_2O (4 equiv.), Me_2NH (7 mol%)	45

[a] Experimental conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Cu (Catalyst) (0.02 mmol), **L** (Ligands) (0.04 mmol) and Add. (Additives) was mixed in DMF (2.0 mL) under 60 °C (metal bath). [b] Determined by ^1H NMR of the crude product with mesitylene as internal standard. In parentheses were isolated yields. [c] **1a** (0.2 mmol), **2a** (0.24 mmol), Cu (Catalyst) (0.02 mmol) was mixed in THF (2.0 mL). [d] **1a** (0.4 mmol) and **2a** (0.2 mmol). [e] At 40 °C (metal bath). [f] $Cu(CH_3CN)_4PF_6$ (0.01 mmol) and uracil (0.02 mmol) was used. In all the tested case, the ratio of E/Z is over 99/1.

For the details, conncerning various parameters in all the tested case, see Tables S1-S8

Table S1: The effect of catalyst on this reaction. [a]

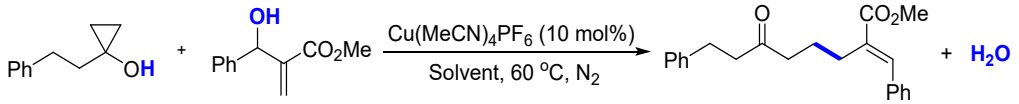


1a **2a** **3a**

Entry	Cat.	Time (h)	Yield [b] (%)
1	CuSN	34	NR
2	CuTc	24	trace
3	CuI	72	trace
4	CuBr	72	trace
5	CuCl	72	trace
6	$Cu(MeCN)_4PF_6$	14	25
7	$Cu(MeCN)_4BF_4$	22	5
8	Copper trifluoromethanethiol	34	NR
9	Bromo(1,10-Phenanthroline)(triphenylphosphine)copper	34	NR
10	Copper(I) trifluoromethanesulfonate benzene complex	34	6
11	$Cu(OAc)_2$	24	NR

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.2 equiv.) in THF (2.0 mL) at 60 °C under N_2 atmosphere. [b] The yield of **3a** was determined by ^1H NMR of the crude product with mesitylene as internal standard.

Table S2: The effect of solvent on this reaction. [a]

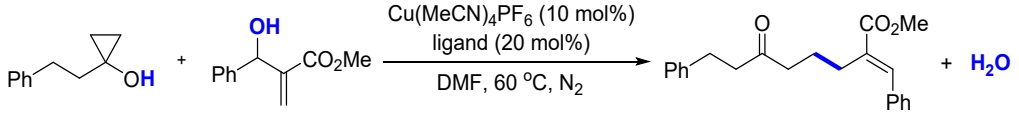


1a **2a** **3a**

Entry	Solvent	Time (h)	Yield [b] (%)
1	DMSO	14	17
2	DME	14	18
3	Acetone	14	trace
4	DMF	14	27
5	DMF	17	41[c]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.2 equiv.), $Cu(MeCN)_4PF_6$ (10 mol%) in solvent (2.0 mL), at 60 °C under N_2 atmosphere. [b] The yield of **3a** was determined by ^1H NMR of the crude product with mesitylene as internal standard. [c] **1a** (1.5 equiv.), **2a** (0.2 mmol).

Table S3: The effect of ligand on this reaction. [a]

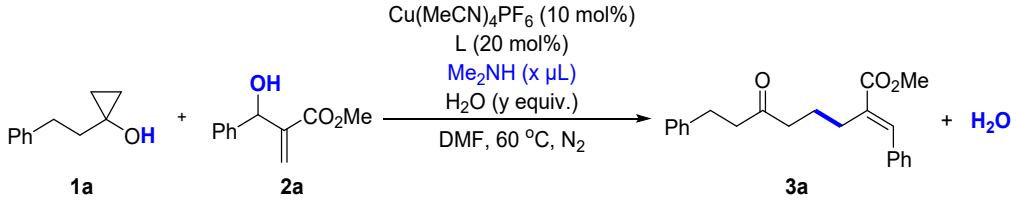


1a **2a** **3a**

Entry	Ligand	Time (h)	Yield [b] (%)
1	1,10-Phenanthroline	24	25
2	4,4'-Bipyridine	24	32
3	5-Fluorouracil	30	60
4	Uracil	28	65

[a] Reaction conditions: **1a** (1.5 equiv.), **2a** (0.2 mmol), $Cu(MeCN)_4PF_6$ (10 mol%) in DMF (2.0 mL), at 60 °C under N_2 atmosphere. [b] The yield of **3a** was determined by ^1H NMR of the crude product with mesitylene as internal standard.

Table S4: The effect of dimethylamine aqueous solution and water on this reaction. [a]

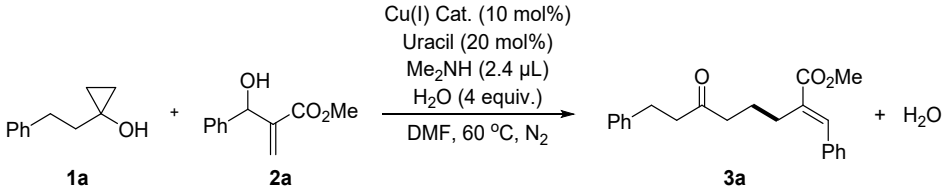


1a **2a** **3a**

Entry	Me_2NH [d] (x μL)	L	H_2O (y equiv.)	Time (h)	Yield [b] (%)
1[e]	0	Uracil	4	24	72
2	0	Uracil	4	24	80
3	**2.4**	Uracil	**4**	**24**	**82 (80)** [c]
4	2.4	Uracil	6	24	76
5	2.6	Uracil	4	24	77
6	2.6	Uracil	6	24	82
7	2.4	thymine	4	24	70
8	2.4	cytosine	4	24	< 5

[a] Reaction conditions: **1a** (2 equiv.), **2a** (0.2 mmol), $Cu(MeCN)_4PF_6$ (10 mol%) and Uracil (20 mol%) in DMF (2.0 mL), at 60 °C under N_2 atmosphere. [b] The yield of **3a** was determined by ^1H NMR of the crude product with mesitylene as internal standard. [c] Isolated yields. [d] Me_2NH in aq. (40 wt.% in H_2O). [e] **1a** (1.2 equiv.), **2a** (0.2 mmol).

Table S5: Screening other copper sources in combination with uracil.

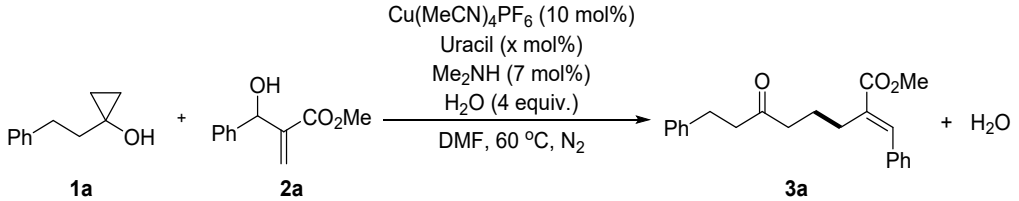


1a **2a** **3a**

Entry	Cu(I) Cat.	Time (h)	Yield [b] (%)
1	CuBr	24	35
2	CuI	24	trace

[a] Reaction conditions: **1a** (2 equiv.), **2a** (0.2 mmol), Uracil (20 mol%), Me_2NH (7 mol%) and H_2O (4 equiv.) in DMF (2.0 mL), at 60 °C under N_2 atmosphere. Me_2NH in aq. (40 wt.% in H_2O). [b] The yield of **3a** was determined by ^1H NMR of the crude product with mesitylene as internal standard.

Table S6: The influence of the ratio of $Cu(MeCN)_4PF_6$/Uracil on the yield of 3a.

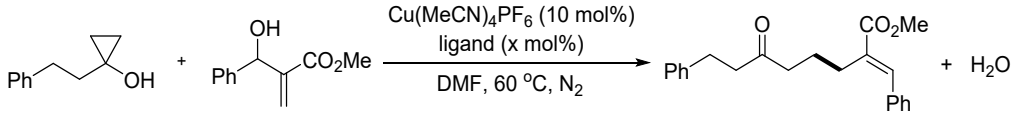


1a **2a** **3a**

Entry	Uracil (x mol%)	Time (h)	Yield [b] (%)
1	3	24	50
2	5	24	57
3	10	24	65
4	**20**	**24**	**82**
5	30	24	74
6	40	24	73

[a] Reaction conditions: **1a** (2 equiv.), **2a** (0.2 mmol), $Cu(MeCN)_4PF_6$ (10 mol%), Me_2NH (7 mol%) and H_2O (4 equiv.) in DMF (2.0 mL), at 60 °C under N_2 atmosphere. Me_2NH in aq. (40 wt.% in H_2O). [b] The yield of **3a** was determined by ^1H NMR of the crude product with mesitylene as internal standard.

Table S7: Screening other ligands.

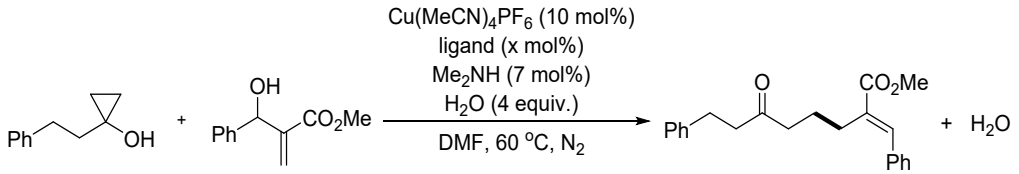


1a **2a** **3a**

Entry	Ligand (x mol%)	Time (h)	Yield [b] (%)
1	1,10-phenanthroline (3)	24	38
2	1,10-phenanthroline (5)	24	43
3	1,10-phenanthroline (10)	24	33
4	1,10-phenanthroline (20)	24	25
5	1,10-phenanthroline (30)	24	trace
6	2,2'-Bipyridine (3)	24	32
7	2,2'-Bipyridine (5)	24	42
8	2,2'-Bipyridine (10)	24	42
9	2,2'-Bipyridine (20)	24	27
10	2,2'-Bipyridine (30)	24	19

[a] Reaction conditions: **1a** (1.5 equiv.), **2a** (0.2 mmol), $Cu(MeCN)_4PF_6$ (10 mol%) in DMF (2.0 mL), at 60 °C under N_2 atmosphere. [b] The yield of **3a** was determined by ^1H NMR of the crude product with mesitylene as internal standard.

Table S8: Replace of Uracil with other ligands under the optimized conditions.



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

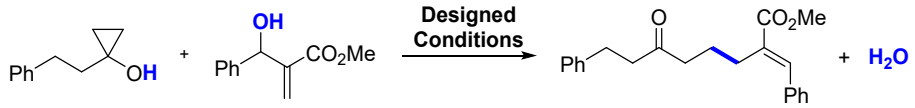
Entry	Ligand (x mol%)	Time (h)	Yield [b] (%)
1	1,10-phenanthroline (5)	24	48
2	2,2'-Bipyridine (5)	24	46

[a] Reaction conditions: **1a** (2 equiv.), **2a** (0.2 mmol) and $Cu(MeCN)_4PF_6$ (10 mol%), Me_2NH (7 mol%) and H_2O (4 equiv.) in DMF (2.0 mL), at 60 °C under N_2 atmosphere. Me_2NH in aq. (40 wt.% in H_2O). [b] The yield of **3a** was determined by ^1H NMR of the crude product with mesitylene as internal standard.

Sensitivity Assessment

The sets of experiments[12] that employed **1a** and **2a** were performed to evaluate the reaction-condition based sensitivity of this conversion, which will be valuable in increasing the insight of this new synthetic method and reproducibility. Various parameters, including concentration, temperature, oxygen level, water level and scale were chosen with positive and negative direction relative to the standard reaction conditions. Each experiment only deliberately changed one parameter, while keeping others at standard levels.

Table S9: Set of Experiments. [a]



1a 2a 3a

Parameter	Variation		Description	Yield [b] (%)	Deviation[c]
Concentration (c)	High c	Sol. -1 mL	1 mL DMF	78	-5%
	Low c	Sol. +1 mL	3 mL DMF	70	-15%
Temperature (*T*)	Hight *T*	*T* +10 °C	70 °C	78	-5%
	Low *T*	*T* -10 °C	50 °C	64	-22%
O_2 level	High O_2	air	10 mL air instead of N_2	65	-21%
Me_2NH [d] level	High Me_2NH	+ Me_2NH	3 μL Me_2NH	68	-17%
	Low Me_2NH	- Me_2NH	1.8 μL Me_2NH	62	-24%
H_2O level	High H_2O	+H_2O V_{H2O}= 4.8%V_{sol}.	0.1 mL in 2mL DMF	65	-21%
	Low H_2O	-H_2O	Without H_2O	72	-12%
Scale	Large scale	n*25 mmol	5 mmol of **2a**	73 (70) [e]	-11%

[a] Reaction conditions: $Cu(MeCN)_4PF_6$ (10 mol%), Uracil (20 mol%), 40% aqueous solution of dimethylamine (2.4 μL) and H_2O (4 equiv.) were stirred in DMF (2.0 mL) at 10 °C for 1 h under N_2 atmosphere, then **1a** (0.4 mmol) and **2a** (0.2 mmol) were added and heated to 60 °C for 24 h. [b] The yield of **3a** was determined by ^1H NMR of the crude product with mesitylene as internal standard. [c] Deviation from the ^1H NMR yield of standard reaction. [d] Me_2NH in aq. (40 wt.% in H_2O). [e] Isolated yields.

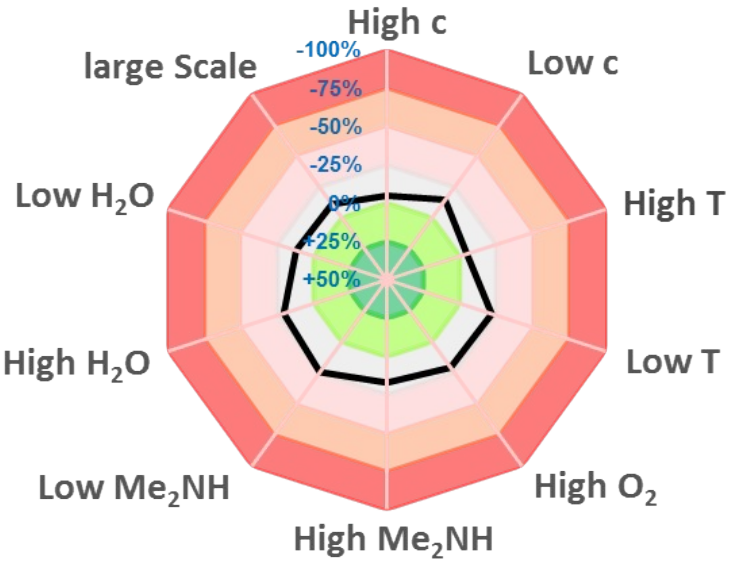
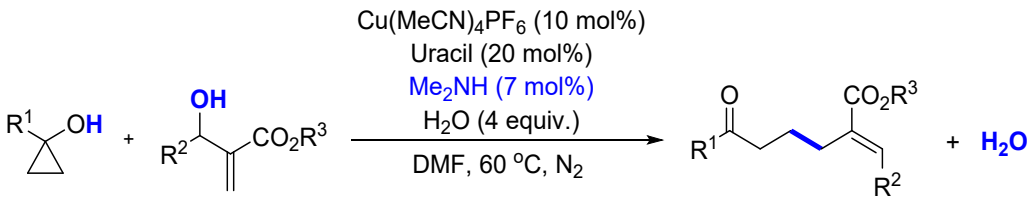


Figure S1. Sensitivity Assessment

4. General Procedure for Preparation of 3a-3az:

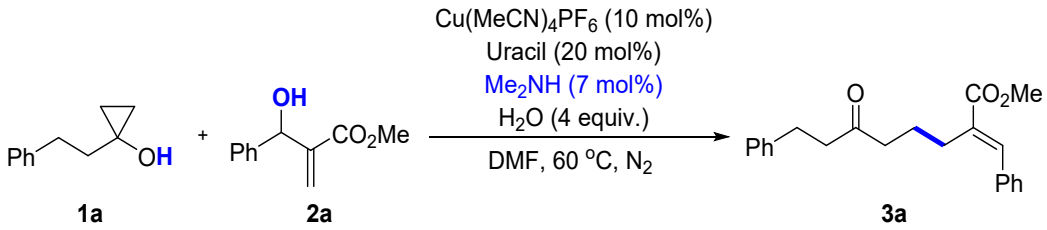


1 2 3

$Cu(MeCN)_4PF_6$ (0.02 mmol, 10 mol%), Uracil (0.04 mmol, 20 mol%), Me_2NH (2.4 μL Me_2NH in aq. (40 wt.% in H_2O), 0.014 mmol, 7 mol%) and H_2O (0.8 mmol, 4 equiv.) was stirred in DMF (2.0 mL) at 10 °C for 1 h under N_2 atmosphere in a dried schlenk tube, then cyclopropanol **1** (0.4 mmol, 2 equiv.) and allyl alcohols **2** (0.2 mmol, 1 equiv.) were added subsequently under N_2 atmosphere. The reaction mixture was heated at 60 °C (metal bath) for 24 h, allowed to cool to room temperature. Dilute the solvent with

ethyl acetate and wash the mixture with water. After the organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography or PTLC to afford the corresponding products (for the details, see each compound).

5. Procedure for Gram Scale (5 mmol) Reactions of 3a:

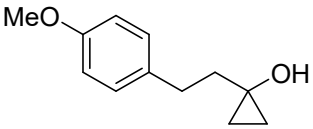


1a **2a** **3a**

$Cu(MeCN)_4PF_6$ (0.5 mmol, 10 mol%), Uracil (1 mmol, 20 mol%), Me_2NH (60 μL Me_2NH in aq. (40 wt.% in H_2O), 0.35 mmol, 7 mol%) and H_2O (20 mmol, 4 equiv.) was stirred in DMF (50 mL) at 10 °C for 1 h under N_2 atmosphere in a dried schlenk tube (100 mL), then cyclopropanol **1a** (10 mmol, 2 equiv.) and allyl alcohols **2a** (5 mmol, 1 equiv.) were added subsequently under N_2 atmosphere. The reaction mixture was heated at 60 °C (metal bath) for 24 h, allowed to cool to room temperature. Dilute the solvent with ethyl acetate and wash the mixture with water. After the organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether (bp: 60-90 °C)/ethyl acetate = 30/1) to afford the corresponding products **3a** (1.1823g, 70% yield).

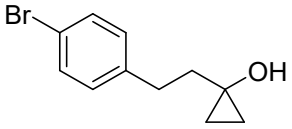
6. Analytical Data for All New Compounds

1-(4-methoxyphenethyl)cyclopropan-1-ol (1b)



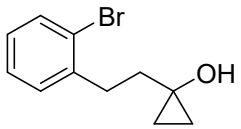
Following the procedure A, **1b** was purified by column chromatography (petroleum ether (bp: 60-90 °C)/ethyl acetate = 10/1) as white solid (3.28 g for 20 mmol scale, 85% yield). Mp: 45.7-47.1 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.86 – 6.80 (m, 2H), 3.78 (s, 3H), 2.83 – 2.74 (m, 2H), 2.04 (s, 1H), 1.87 – 1.79 (m, 2H), 0.77 – 0.72 (m, 2H), 0.47 – 0.42 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.9, 134.4, 129.4, 114.0, 55.8, 55.4, 40.7, 31.7, 13.7. IR (KBr): 3322, 3231, 3004, 2922, 2854, 2837, 1513, 1454, 1247, 1035, 813 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{12}H_{16}O_2K$ 231.0787; Found 231.0783.

1-(4-bromophenethyl)cyclopropan-1-ol (1c)



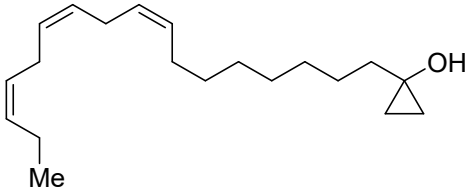
Following the procedure A, **1c** was purified by column chromatography (petroleum ether (bp: 60-90 °C)/ethyl acetate = 10/1) as white solid (2.91 g for 20 mmol scale, 60% yield). Mp: 89.7-91.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 2.85 – 2.78 (m, 2H), 1.87 (s, 1H), 1.86 – 1.80 (m, 2H), 0.79 – 0.73 (m, 2H), 0.48 – 0.41 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.3, 131.5, 130.3, 119.6, 55.7, 40.4, 32.0, 13.9. IR (KBr): 3211, 3004, 2916, 1486, 1260, 1009, 837, 750, 518 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{11}H_{14}BrO$ 241.0228; Found 241.0220

1-(2-bromophenethyl)cyclopropan-1-ol (1e)



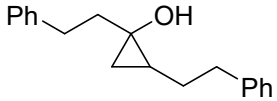
Following the procedure A, **1e** was purified by column chromatography (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 10/1) as white solid (2.48 g for 20 mmol scale, 50% yield). Mp: 50.0-51.7 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.06 (ddd, *J* = 7.9, 6.9, 2.2 Hz, 1H), 3.03 – 2.96 (m, 2H), 1.94 (s, 1H), 1.89 – 1.82 (m, 2H), 0.79 – 0.74 (m, 2H), 0.49 – 0.44 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.5, 132.9, 130.6, 127.7, 127.6, 124.5, 55.6, 38.9, 33.0, 13.7. IR (KBr): 3319, 3233, 3001, 2954, 2861, 1567, 1437, 1240, 1027, 744, 658 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{11}H_{14}BrO$ 241.0228; Found 241.0225.

1-((8Z,11Z,14Z)-heptadeca-8,11,14-trien-1-yl)cyclopropan-1-ol (1p)



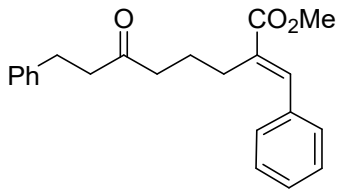
Following the procedure A, **1p** was purified by column chromatography (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 10/1) as colorless oil (0.95 g for 5 mmol scale, 65% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.45 – 5.26 (m, 6H), 2.88 – 2.74 (m, 4H), 2.14 – 2.01 (m, 5H), 1.59 – 1.22 (m, 12H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.75 – 0.70 (m, 2H), 0.47 – 0.39 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.1, 130.5, 128.4, 127.8, 127.2, 56.0, 38.4, 29.8, 29.7, 29.4, 27.4, 26.0, 25.8, 25.7, 20.7, 14.4, 13.6. IR (KBr): 3330, 3010, 2963, 2929, 2855, 1653, 1462, 1275, 1008, 913, 748 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{20}H_{35}O$ 291.2688; Found 291.2684.

1,2-diphenethylcyclopropan-1-ol (1r)



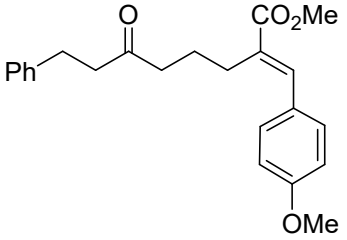
1r was purified by column chromatography (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 20/1) as light yellow oil (0.54 g for 5 mmol scale, 40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.24 (m, 4H), 7.23 – 7.14 (m, 6H), 2.93 – 2.78 (m, 2H), 2.76 – 2.62 (m, 2H), 1.95 – 1.84 (m, 1H), 1.82 – 1.69 (m, 3H), 1.45 – 1.34 (m, 1H), 1.07 (ddt, J = 10.1, 8.3, 6.3 Hz, 1H), 0.87 (ddd, J = 10.1, 5.4, 1.3 Hz, 1H), 0.11 (dd, J = 6.5, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.4, 142.3, 128.6, 128.5, 128.4, 126.0, 125.9, 59.1, 36.5, 36.0, 32.6, 31.7, 25.9, 19.8. IR (KBr): 3415, 3026, 2924, 2854, 1638, 1619, 1454, 698, 617 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{19}H_{23}O$ 267.1749; Found 267.1759.

methyl (E)-2-benzylidene-6-oxo-8-phenyloctanoate (3a)



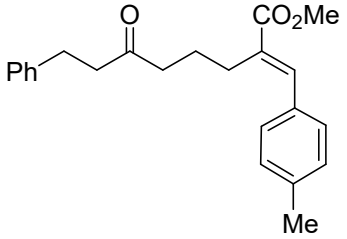
Following the general procedure, **3a** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as white solid (54 mg, 80% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 43.3-44.2 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.43 – 7.26 (m, 6H), 7.25 (d, *J* = 1.3 Hz, 1H), 7.21 – 7.14 (m, 3H), 3.81 (s, 3H), 2.86 (t, *J* = 7.7 Hz, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 2.55 – 2.47 (m, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 1.88 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.7, 168.9, 141.2, 139.9, 135.6, 132.6, 129.4, 128.7, 128.6, 128.4, 126.2, 52.2, 44.4, 42.7, 29.9, 26.9, 23.2. IR (KBr): 3026, 2923, 1711, 1275, 1136, 750, 699 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{25}O_3$ 337.1804; Found 337.1800.

methyl (E)-2-(4-methoxybenzylidene)-6-oxo-8-phenyloctanoate (3b)



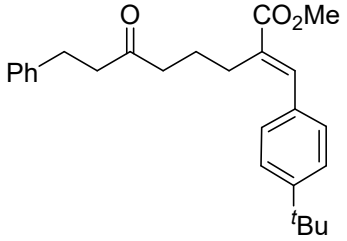
Following the general procedure, **3b** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (70 mg, 96% yield, E/Z = 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 8.3 Hz, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.58 – 2.50 (m, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 1.87 – 1.78 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.8, 169.1, 160.0, 141.2, 139.5, 131.3, 130.3, 128.6, 128.4, 128.0, 126.2, 114.2, 55.4, 52.1, 44.4, 42.7, 29.9, 26.9, 23.1. IR (KBr): 2950, 1710, 1511, 1275, 1176, 1030, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_4$ 367.1909; Found 367.1911.

methyl (E)-2-(4-methylbenzylidene)-6-oxo-8-phenyloctanoate (3c)



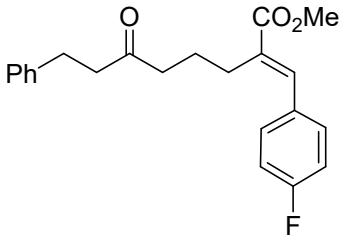
Following the general procedure, **3c** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (55 mg, 78% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.32 – 7.24 (m, 4H), 7.23 – 7.14 (m, 5H), 3.80 (s, 3H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.55 – 2.48 (m, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.87–1.77 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.8, 169.0, 141.2, 139.9, 138.8, 132.7, 131.6, 129.5, 129.4, 128.6, 128.4, 126.2, 52.1, 44.4, 42.7, 29.9, 27.0, 23.2, 21.4. IR (KBr): 3026, 2948, 1709, 1510, 1251, 750, 699 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_3$ 351.1960; Found 351.1955.

methyl (E)-2-(4-(tert-butyl)benzylidene)-6-oxo-8-phenyloctanoate (3d)



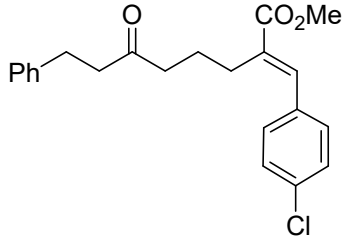
Following the general procedure, **3d** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (59 mg, 75% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.45 – 7.40 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.20 – 7.14 (m, 3H), 3.79 (s, 3H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.57 – 2.50 (m, 2H), 2.45 (t, *J* = 7.3 Hz, 2H), 1.89 – 1.78 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.8, 169.0, 152.0, 141.2, 139.7, 132.6, 131.6, 129.4, 128.6, 128.4, 126.2, 125.7, 52.1, 44.4, 42.8, 34.8, 31.3, 29.9, 27.0, 23.2. IR (KBr): 3027, 2954, 1712, 1496, 1248, 1191, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{26}H_{33}O_3$ 393.2430; Found 393.2434.

methyl (E)-2-(4-fluorobenzylidene)-6-oxo-8-phenyloctanoate (3e)



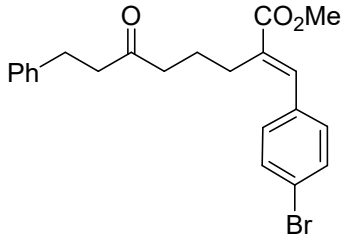
Following the general procedure, **3e** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (61 mg, 86% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.42 – 7.35 (m, 2H), 7.30 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 7.13 – 7.06 (m, 2H), 3.80 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.51 – 2.45 (m, 2H), 2.44 (t, *J* = 7.1 Hz, 2H), 1.85 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.7, 168.7, 162.8 (d, *J* = 249.4 Hz), 141.2, 138.6, 132.3, 131.6 (d, *J* = 3.4 Hz), 131.4 (d, *J* = 8.2 Hz), 128.6, 128.4, 126.2, 115.8 (d, *J* = 21.6 Hz) 52.2, 44.4, 42.6, 29.9, 26.9, 23.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.10. IR (KBr): 2917, 1712, 1600, 1508, 1275, 1159, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{22}H_{23}FO_3K$ 393.1268; Found 393.1265.

methyl (E)-2-(4-chlorobenzylidene)-6-oxo-8-phenyloctanoate (3f)



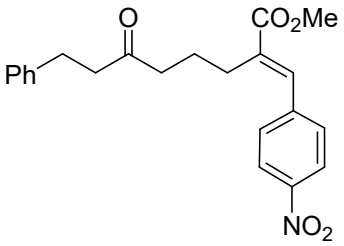
Following the general procedure, **3f** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (55 mg, 75% yield, E/Z = 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (s, 1H), 7.36 (q, *J* = 8.6 Hz, 4H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.22 – 7.13 (m, 3H), 3.81 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.45 (ddd, *J* = 14.1, 9.8, 6.5 Hz, 4H), 1.85 – 1.74 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.6, 168.6, 141.1, 138.4, 134.6, 134.0, 133.1, 130.7, 129.0, 128.6, 128.4, 126.2, 52.2, 44.4, 42.6, 29.9, 27.0, 23.0. IR (KBr): 3027, 2949, 1712, 1631, 1490, 1250, 1012, 750, 699 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}ClO_3$ 371.1414; Found 371.1408.

methyl (E)-2-(4-bromobenzylidene)-6-oxo-8-phenyloctanoate (3g)



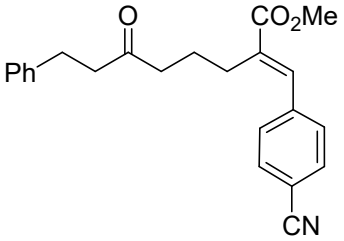
Following the general procedure, **3g** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as white solid (67 mg, 80% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 47.3-48.9 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.22 – 7.14 (m, 3H), 3.80 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.45 (ddd, *J* = 14.1, 9.7, 6.5 Hz, 4H), 1.84 – 1.73 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.6, 168.6, 141.1, 138.5, 134.4, 133.2, 131.9, 131.0, 128.6, 128.4, 126.2, 122.9, 52.3, 44.4, 42.6, 29.9, 27.0, 23.0. IR (KBr): 2926, 1714, 1633, 1508, 1276, 1199, 764, 699, 502 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}BrO_3$ 415.0909; Found 415.0907.

methyl (E)-2-(4-nitrobenzylidene)-6-oxo-8-phenyloctanoate (3h)



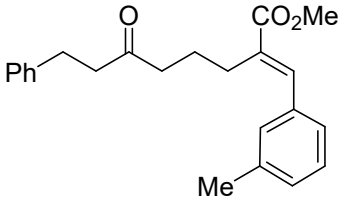
Following the general procedure, **3h** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (53 mg, 70% yield, E/Z = 98/2 as determined by ^{1}H NMR). Mp: 52.1-54.3 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.24 (m, 2H), 7.68 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 3.83 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.50 – 2.41 (m, 4H), 1.86 – 1.75 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 168.0, 147.4, 142.1, 141.0, 137.0, 135.9, 130.1, 128.6, 128.4, 126.2, 123.9, 52.4, 44.4, 42.5, 29.8, 27.2, 22.9. IR (KBr): 2950, 1713, 1596, 1519, 1345, 1260, 1204, 859, 764, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}NO_5$ 382.1654; Found 382.1657.

methyl (E)-2-(4-cyanobenzylidene)-6-oxo-8-phenyloctanoate (3i)



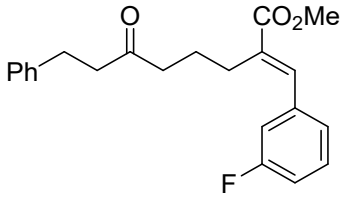
Following the general procedure, **3i** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (43 mg, 60% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.64 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.21 – 7.14 (m, 3H), 3.82 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.49 – 2.39 (m, 4H), 1.85 – 1.74 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 168.0, 141.0, 140.1, 137.4, 135.4, 132.4, 129.9, 128.6, 128.3, 126.2, 118.6, 112.0, 52.4, 44.4, 42.5, 29.8, 27.1, 22.9. IR (KBr): 3005, 2228, 1713, 1604, 1497, 1275, 1260, 832, 765, 701 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{24}NO_3$ 362.1756; Found 362.1758.

methyl (E)-2-(3-methylbenzylidene)-6-oxo-8-phenyloctanoate (3j)



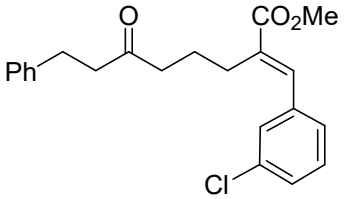
Following the general procedure, **3j** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (65 mg, 93% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.31 – 7.23 (m, 3H), 7.22 – 7.11 (m, 6H), 3.80 (s, 3H), 2.86 (t, *J* = 7.7 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.54 – 2.48 (m, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.86 – 1.77 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.6, 168.8, 141.2, 140.0, 138.3, 135.5, 132.3, 130.1, 129.4, 128.5, 128.4, 126.3, 126.1, 52.1, 44.3, 42.6, 29.8, 26.9, 23.2, 21.5. IR (KBr): 3026, 2949, 1713, 1627, 1496, 1275, 1192, 792, 764, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_3$ 351.1960; Found 351.1955.

methyl (E)-2-(3-fluorobenzylidene)-6-oxo-8-phenyloctanoate (3k)



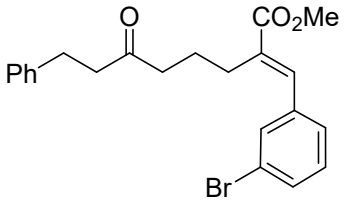
Following the general procedure, **3k** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (57 mg, 81% yield, E/Z = 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.37 (td, *J* = 8.0, 6.0 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.21 – 7.14 (m, 4H), 7.11 – 7.00 (m, 2H), 3.81 (s, 3H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.51 – 2.46 (m, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.85 – 1.75 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 168.4, 162.7 (d, *J* = 246.4 Hz), 141.1, 138.3 (d, *J* = 2.2 Hz), 137.6 (d, *J* = 7.7 Hz), 133.7, 130.1 (d, *J* = 8.4 Hz), 128.5, 128.3, 126.1, 125.0 (d, *J* = 3.0 Hz), 115.9 (d, *J* = 22.0 Hz), 115.4 (d, *J* = 21.2 Hz). 52.2, 44.3, 42.5, 29.8, 26.8, 23.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.47. IR (KBr): 2950, 1713, 1610, 1276, 1261, 1233, 764, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}FO_3$ 355.1709; Found 355.1703.

methyl (E)-2-(3-chlorobenzylidene)-6-oxo-8-phenyloctanoate (3l)



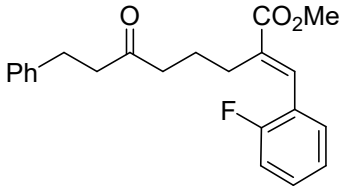
Following the general procedure, **3l** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as yellow oil (68 mg, 91% yield, E/Z = 98/2 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.36 – 7.29 (m, 3H), 7.29 – 7.23 (m, 3H), 7.20 – 7.14 (m, 3H), 3.80 (s, 3H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.50 – 2.44 (m, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.75 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 168.4, 141.1, 138.1, 137.4, 134.6, 133.9, 130.0, 129.2, 128.6, 128.4, 127.3, 126.2, 52.2, 44.3, 42.5, 29.8, 26.9, 23.1. IR (KBr): 3027, 2949, 1714, 1633, 1593, 1496, 1252, 1083, 885, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}ClO_3$ 371.1414; Found 371.1408.

methyl (E)-2-(3-bromobenzylidene)-6-oxo-8-phenyloctanoate (3m)



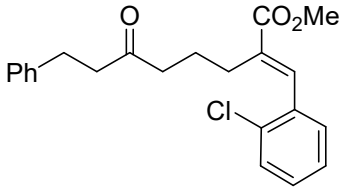
Following the general procedure, **3m** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (71 mg, 85% yield, E/Z = 98/2 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 7.50 – 7.43 (m, 2H), 7.34 – 7.23 (m, 4H), 7.17 (td, *J* = 7.5, 6.8, 1.4 Hz, 3H), 3.80 (s, 3H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.49 – 2.44 (m, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.83 – 1.74 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.5, 168.4, 141.1, 138.0, 137.7, 134.0, 132.1, 131.5, 130.2, 128.6, 128.4, 127.7, 126.2, 122.7, 52.3, 44.4, 42.5, 29.8, 26.9, 23.1. IR (KBr): 3026, 2949, 1713, 1603, 1496, 1260, 1199, 786, 750, 700, 684 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}BrO_3$ 415.0909; Found 415.0914.

methyl (E)-2-(2-fluorobenzylidene)-6-oxo-8-phenyloctanoate (3n)



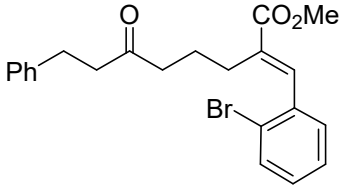
Following the general procedure, **3n** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (57 mg, 80% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.39 – 7.24 (m, 4H), 7.21 – 7.13 (m, 4H), 7.08 (ddd, *J* = 9.6, 8.2, 1.1 Hz, 1H), 3.81 (s, 3H), 2.85 (t, *J* = 7.7 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.46 – 2.41 (m, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 1.83 – 1.74 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.6, 168.2, 160.4 (d, *J* = 249.2 Hz), 141.2, 134.8, 132.5 (d, *J* = 3.8 Hz), 130.4 (d, *J* = 8.4 Hz), 130.2 (d, *J* = 2.8 Hz), 128.6, 128.4, 126.2, 124.2 (d, *J* = 3.7 Hz), 123.6 (d, *J* = 13.9 Hz), 115.8 (d, *J* = 21.9 Hz). 52.2, 44.3, 42.6, 29.8, 27.3, 23.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.16. IR (KBr): 3027, 2950, 1713, 1608, 1485, 1275, 1257, 1197, 799, 751, 700 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{22}H_{23}FO_3K$ 393.1268; Found 393.1263.

methyl (E)-2-(2-chlorobenzylidene)-6-oxo-8-phenyloctanoate (3o)



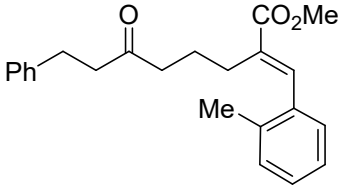
Following the general procedure, **3o** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (66 mg, 89% yield, E/Z = 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.40 (dd, *J* = 6.7, 1.7 Hz, 1H), 7.32 – 7.23 (m, 5H), 7.20 – 7.12 (m, 3H), 3.82 (s, 3H), 2.82 (t, *J* = 7.7 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.41 – 2.35 (m, 2H), 2.33 (t, *J* = 7.3 Hz, 2H), 1.80 – 1.70 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.5, 168.1, 141.1, 137.2, 134.4, 134.3, 133.9, 130.2, 129.7, 128.5, 128.4, 126.8, 126.1, 52.2, 44.2, 42.2, 29.8, 26.9, 23.0. IR (KBr): 3027, 2949, 1714, 1603, 1435, 1250, 1204, 1086, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}ClO_3$ 371.1414; Found 371.1410.

methyl (E)-2-(2-bromobenzylidene)-6-oxo-8-phenyloctanoate (3p)



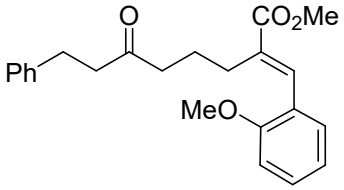
Following the general procedure, **3p** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (75 mg, 90% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (s, 1H), 7.60 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.34 (td, *J* = 7.4, 0.9 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.21 – 7.12 (m, 4H), 3.83 (s, 3H), 2.81 (t, *J* = 7.7 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.40 – 2.31 (m, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.78 – 1.70 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.6, 168.1, 141.2, 139.4, 136.3, 134.0, 132.8, 130.3, 129.8, 128.6, 128.4, 127.5, 126.2, 124.0, 52.3, 44.2, 42.3, 29.8, 26.8, 22.9. IR (KBr): 3026, 2949, 1714, 1603, 1496, 1259, 1205, 750, 700, 661 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}BrO_3$ 415.0909; Found 415.0906.

methyl (E)-2-(2-methylbenzylidene)-6-oxo-8-phenyloctanoate (3q)



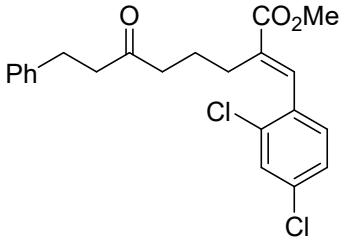
Following the general procedure, **3q** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (66 mg, 94% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.29 – 7.23 (m, 2H), 7.22 – 7.18 (m, 3H), 7.18 – 7.11 (m, 4H), 3.81 (s, 3H), 2.82 (t, *J* = 7.7 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.37 – 2.33 (m, 2H), 2.31 (t, *J* = 7.7 Hz, 2H), 2.26 (s, 3H), 1.77 – 1.68 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.6, 168.5, 141.2, 139.5, 136.6, 135.1, 133.2, 130.2, 128.6, 128.4, 126.2, 125.8, 52.1, 44.2, 42.6, 29.8, 26.9, 23.4, 20.1. IR (KBr): 3025, 2949, 1714, 1603, 1252, 1137, 749, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_3$ 351.1960; Found 351.1966.

methyl (E)-2-(2-methoxybenzylidene)-6-oxo-8-phenyloctanoate (3r)



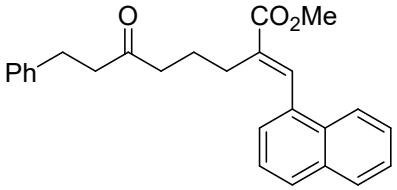
Following the general procedure, **3r** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as yellow solid (72 mg, 98% yield, E/Z = 98/2 as determined by ^{1}H NMR). Mp: 55.5-57.4 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.34 – 7.23 (m, 4H), 7.20 – 7.12 (m, 3H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.84 (t, *J* = 7.7 Hz, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.47 – 2.40 (m, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 1.84 – 1.74 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.8, 168.7, 157.5, 141.2, 136.0, 132.4, 130.1, 129.7, 128.6, 128.4, 126.1, 124.7, 120.5, 110.6, 55.6, 52.0, 44.2, 42.6, 29.8, 27.1, 23.3. IR (KBr): 3026, 2948, 1711, 1597, 1487, 1248, 1192, 1049, 1027, 751, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_4$ 367.1909; Found 367.1906.

methyl (E)-2-(2,4-dichlorobenzylidene)-6-oxo-8-phenyloctanoate (3s)



Following the general procedure, **3s** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (66 mg, 81% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 54.5-59.0 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.43 (d, *J* = 1.2 Hz, 1H), 7.31 – 7.24 (m, 4H), 7.21 – 7.13 (m, 3H), 3.82 (s, 3H), 2.84 (t, *J* = 7.7 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.41 – 2.29 (m, 4H), 1.79 – 1.70 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 167.9, 141.1, 135.8, 134.8, 134.7, 132.8, 131.0, 129.5, 128.6, 128.4, 127.3, 126.2, 52.3, 44.3, 42.3, 29.8, 27.0, 22.8. IR (KBr): 3027, 2950, 1714, 1584, 1469, 1261, 1202, 1100, 817, 750, 699 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{23}Cl_2O_3$ 405.1024; Found 405.1021.

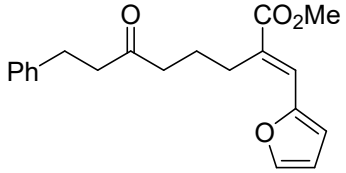
methyl (E)-2-(naphthalen-1-ylmethylene)-6-oxo-8-phenyloctanoate (3t)



Following the general procedure, **3t** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (54 mg, 70% yield, E/Z = 98/2 as determined by ^{1}H NMR). Mp: 54.0-56.8 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.92 – 7.79 (m, 3H), 7.54 – 7.45 (m, 3H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 2H), 3.87 (s, 3H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.44 (t, *J* = 7.8 Hz, 2H), 2.41 – 2.36 (m, 2H), 2.23 (t, *J* = 7.4 Hz, 2H), 1.77-1.68 (m, 2H).

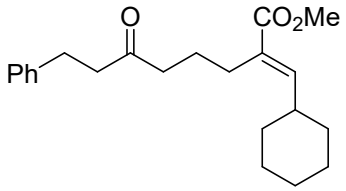
^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.6, 168.4, 141.1, 138.8, 134.7, 133.5, 133.0, 131.5, 128.8, 128.7, 128.5, 128.4, 126.5, 126.3, 126.2, 126.1, 125.4, 124.7, 52.2, 44.0, 42.4, 29.7, 27.1, 23.2. IR (KBr): 3027, 2949, 1713, 1633, 1507, 1253, 1193, 783, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{26}H_{27}O_3$ 387.1960; Found 387.1963.

methyl (E)-2-(furan-2-ylmethylene)-6-oxo-8-phenyloctanoate (3u)



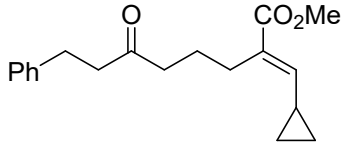
Following the general procedure, **3u** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as yellow oil (49 mg, 75% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 1.6 Hz, 1H), 7.42 (s, 1H), 7.30 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 6.69 (d, *J* = 3.4 Hz, 1H), 6.49 (dd, *J* = 3.4, 1.8 Hz, 1H), 3.78 (s, 3H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.75 – 2.68 (m, 4H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.85 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.1, 168.8, 151.4, 144.4, 141.3, 128.6, 128.4, 126.3, 126.2, 115.7, 112.3, 52.2, 44.4, 42.6, 29.8, 27.1, 22.9. IR (KBr): 2949, 1707, 1631, 1454, 1434, 1260, 1209, 1085, 1019, 928, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{20}H_{23}O_4$ 327.1596; Found 327.1591.

methyl (E)-2-(cyclohexylmethylene)-6-oxo-8-phenyloctanoate (3v)



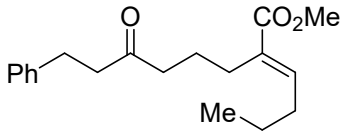
Following the general procedure, $Cu(MeCN)_4PF_6$ (15 mol%), Uracil (30 mol%) was selected, **3v** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (62 mg, 91% yield, E/Z = 98/2 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 6.59 (d, *J* = 10.2 Hz, 1H), 3.71 (s, 3H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.36 – 2.23 (m, 3H), 1.77 – 1.56 (m, 7H), 1.37 – 1.09 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.9, 168.7, 148.7, 141.2, 129.5, 128.6, 128.4, 126.2, 51.8, 44.3, 42.6, 37.8, 32.4, 29.9, 26.3, 25.9, 25.6, 23.8. IR (KBr): 2926, 2850, 1712, 1644, 1449, 1260, 1191, 750, 699 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{31}O_3$ 343.2273; Found 343.2267.

methyl (E)-2-(cyclopropylmethylene)-6-oxo-8-phenyloctanoate (3w)



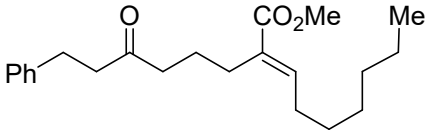
Following the general procedure, **3w** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (46 mg, 77% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 6.14 (d, *J* = 11.7 Hz, 1H), 3.70 (s, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.46-2.36 (m, 4H), 1.79-1.70 (m, 2H), 1.66 – 1.56 (m, 1H), 0.94 (td, *J* = 6.4, 4.4 Hz, 2H), 0.59 (td, *J* = 6.4, 4.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.0, 168.2, 149.0, 141.2, 128.9, 128.6, 128.4, 126.2, 51.7, 44.4, 42.3, 29.8, 26.1, 23.3, 11.6, 8.7. IR (KBr): 3006, 2949, 1709, 1638, 1496, 1454, 1261, 1191, 809, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{19}H_{25}O_3$ 301.1804; Found 301.1799.

methyl (E)-2-butylidene-6-oxo-8-phenyloctanoate (3x)



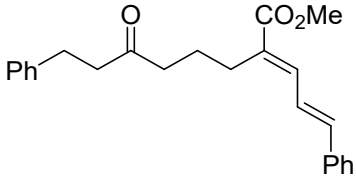
Following the general procedure, $Cu(MeCN)_4PF_6$ (15 mol%), Uracil (30 mol%) was selected, **3x** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (54 mg, 89% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 6.78 (t, *J* = 7.5 Hz, 1H), 3.72 (s, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 2.30 – 2.25 (m, 2H), 2.15 (q, *J* = 7.4 Hz, 2H), 1.72 – 1.62 (m, 2H), 1.47 (td, *J* = 14.4, 7.2 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.9, 168.4, 143.7, 141.2, 131.6, 128.6, 128.4, 126.2, 51.8, 44.3, 42.5, 30.6, 29.8, 26.1, 23.3, 22.2, 14.0. IR (KBr): 3027, 2957, 2873, 1713, 1644, 1454, 1435, 1373, 1276, 1193, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{19}H_{27}O_3$ 303.1960; Found 303.1964.

methyl (E)-2-(4-oxo-6-phenylhexyl)non-2-enoate (3y)



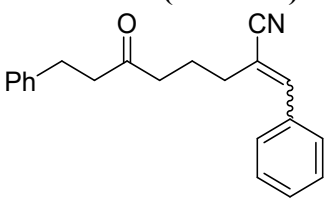
Following the general procedure, $Cu(MeCN)_4PF_6$ (15 mol%), Uracil (30 mol%) was selected, **3y** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (60 mg, 87% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 3H), 6.78 (t, *J* = 7.6 Hz, 1H), 3.72 (s, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 2.30 – 2.24 (m, 2H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.72 – 1.62 (m, 2H), 1.47 – 1.37 (m, 2H), 1.36 – 1.23 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.9, 168.4, 144.1, 141.2, 131.4, 128.6, 128.4, 126.2, 51.8, 44.3, 42.6, 31.8, 29.9, 29.2, 28.9, 28.7, 26.1, 23.3, 22.7, 14.2. IR (KBr): 3027, 2928, 2857, 1714, 1644, 1496, 1454, 1435, 1261, 1194, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{33}O_3$ 345.2430; Found 345.2426.

methyl (E)-6-oxo-8-phenyl-2-((E)-3-phenylallylidene)octanoate (3z)



Following the general procedure, **3z** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (50 mg, 70% yield, E/Z = 95/5 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 2H), 7.42 – 7.29 (m, 4H), 7.26 – 7.21 (m, 2H), 7.19 – 7.06 (m, 4H), 6.88 (d, *J* = 15.4 Hz, 1H), 3.77 (s, 3H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.54 – 2.48 (m, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 1.82 – 1.72 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.9, 168.5, 141.2, 140.0, 139.7, 136.5, 131.0, 129.0 128.6, 128.4, 127.3, 126.2, 123.7, 52.0, 44.5, 41.9, 29.8, 26.3, 23.4. IR (KBr): 3481, 3026, 2948, 1706, 1621, 1495, 1435, 1233, 1191, 750, 694 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{24}H_{27}O_3$ 363.1960; Found 363.1965.

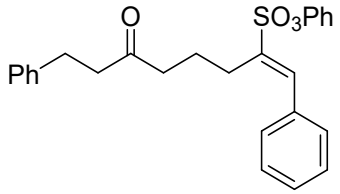
(E/Z)-2-benzylidene-6-oxo-8-phenyloctanenitrile (3aa/3aa')



Following the general procedure, **3aa** were isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) (24 mg, 40% yield). The E/Z of **3aa** is 80/20 (determined by crude ^{1}H NMR). *E*-isomer of

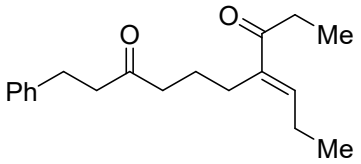
3aa was light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.67 (m, 2H), 7.44 – 7.37 (m, 3H), 7.31 – 7.23 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 3H), 6.89 (s, 1H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 1.97 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.2, 144.1, 141.0, 133.6, 130.2, 128.9, 128.7, 128.6, 128.4, 126.3, 118.8, 110.5, 44.4, 41.3, 35.4, 29.8, 22.2. IR (KBr): 3027, 2926, 2208, 1713, 1603, 1495, 1452, 1275, 1204, 1094, 913, 750, 693 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{21}H_{22}NO$ 304.1701; Found 304.1694. *Z*-isomer of **3aa (3aa')** was light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 3H), 7.34 – 7.27 (m, 3H), 7.25 (d, *J* = 2.5 Hz, 2H), 7.21 – 7.13 (m, 3H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.49 – 2.42 (m, 4H), 1.98 – 1.88 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.0, 145.0, 141.0, 133.9, 129.6, 129.3, 128.9, 128.6, 128.4, 126.3, 120.4, 115.0, 44.4, 41.6, 29.9, 28.7, 22.1. IR (KBr): 2922, 2209, 1712, 1603, 1494, 1453, 1275, 1261, 1091, 927, 750, 697 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{21}H_{21}NOK$ 342.1260; Found 342.1257.

phenyl (E)-6-oxo-1,8-diphenyloct-1-ene-2-sulfonate (3ab)



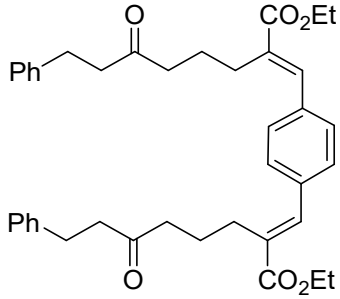
Following the general procedure, **3ab** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (66 mg, 76% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.33 (m, 8H), 7.30 – 7.24 (m, 3H), 7.24 – 7.14 (m, 5H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.79 – 2.73 (m, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.51 (t, *J* = 6.8 Hz, 2H), 2.12 – 2.02 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.3, 149.7, 142.0, 141.0, 136.1, 132.7, 130.1, 129.9, 129.6, 129.1, 128.6, 128.4, 127.2, 126.2, 122.4, 44.3, 42.2, 29.9, 27.2, 22.3. IR (KBr): 3027, 2935, 1713, 1627, 1487, 1261, 1145, 856, 750, 691 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{26}H_{27}O_4S$ 435.1630; Found 435.1627.

(E)-1-phenyl-7-propylidenedecane-3,8-dione (3ac)



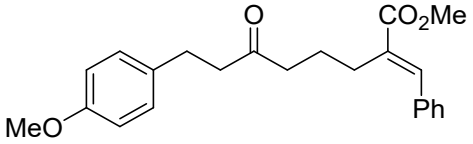
Following the general procedure, **3ac** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as colorless oil (25 mg, 43% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 6.59 (t, *J* = 7.3 Hz, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.8 Hz, 2H), 2.66 (q, *J* = 7.3 Hz, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 2.30 – 2.21 (m, 4H), 1.62 – 1.51 (m, 2H), 1.10 – 1.05 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.1, 202.4, 144.8, 141.2, 140.4, 128.6, 128.4, 126.2, 44.3, 42.8, 30.4, 29.8, 25.0, 23.4, 22.3, 13.6, 9.0. IR (KBr): 2973, 1712, 1666, 1454, 1275, 1261, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{19}H_{27}O_2$ 287.2011; Found 287.2014.

diethyl 2,2'-(1,4-phenylenebis(methanylylidene))(2E,2'E)-bis(6-oxo-8-phenyloctanoate) (3ad)



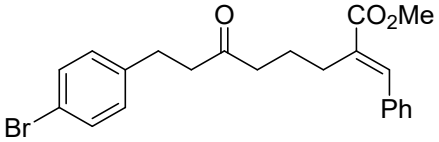
Following the general procedure, $Cu(MeCN)_4PF_6$ (20 mol%), Uracil (40 mol%), Me_2NH (14 mol%), H_2O (8 equiv.) and DMF (4 mL) was selected, **1** (4 equiv.), **2a** (0.2 mmol, 1 equiv.) was used, **3ad** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as white solid (69 mg, 55% yield, E/Z = 98/2 as determined by ^{1}H NMR). Mp: 68.0-69.1 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 2H), 7.44 (s, 4H), 7.25 (t, *J* = 7.3 Hz, 4H), 7.20 – 7.12 (m, 6H), 4.27 (q, *J* = 7.1 Hz, 4H), 2.86 (t, *J* = 7.6 Hz, 4H), 2.69 (t, *J* = 7.6 Hz, 4H), 2.58 – 2.50 (m, 4H), 2.45 (t, *J* = 7.2 Hz, 4H), 1.89 – 1.79 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.6, 168.2, 141.1, 138.6, 135.8, 133.4, 129.7, 128.6, 128.4, 126.2, 61.0, 44.4, 42.6, 29.8, 27.0, 23.2, 14.4. IR (KBr): 2921, 2850, 1706, 1260, 1180, 798, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{40}H_{47}O_6$ 623.3373; Found 623.3370.

methyl (E)-2-benzylidene-8-(4-methoxyphenyl)-6-oxooctanoate (3ae)



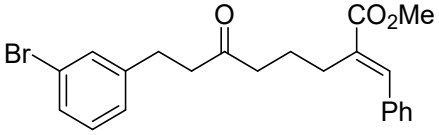
Following the general procedure, **3ae** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (60 mg, 81% yield, E/Z = 98/2 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.43 – 7.30 (m, 5H), 7.10 – 7.05 (m, 2H), 6.83 – 6.78 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.55 – 2.46 (m, 2H), 2.41 (t, *J* = 7.3 Hz, 2H), 1.86 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.9, 168.8, 158.0, 139.8, 135.6, 133.2, 132.5, 129.4, 129.3, 128.7, 128.6, 114.0, 55.3, 52.2, 44.6, 42.7, 29.0, 26.9, 23.2. IR (KBr): 2995, 2950, 2836, 1712, 1612, 1584, 1247, 1202, 1081, 827, 750, 702 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_4$ 367.1909; Found 367.1912.

methyl (E)-2-benzylidene-8-(4-bromophenyl)-6-oxooctanoate (3af)



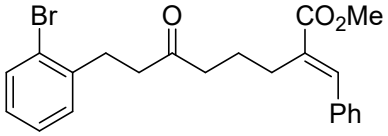
Following the general procedure, **3af** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (53 mg, 64% yield, E/Z = 98/2 as determined by ^{1}H NMR). Mp: 51.0-53.0 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.42 – 7.30 (m, 7H), 7.05 – 7.01 (m, 2H), 3.81 (s, 3H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.54 – 2.47 (m, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.86 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.3, 168.8, 140.2, 139.9, 135.6, 132.5, 131.6, 130.3, 129.4, 128.7, 128.6, 119.9, 52.2, 44.0, 42.7, 29.2, 26.9, 23.2. IR (KBr): 2948, 1712, 1632, 1488, 1260, 1201, 814, 750, 702, 518 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}BrO_3$ 415.0909; Found 415.0905.

methyl (E)-2-benzylidene-8-(3-bromophenyl)-6-oxooctanoate (3ag)



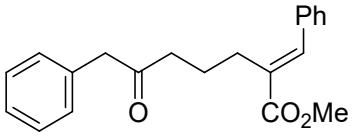
Following the general procedure, **3ag** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (54 mg, 65% yield, E/Z = 98/2 as determined by ^{1}H NMR). Mp: 50.2-51.6 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.43 – 7.29 (m, 7H), 7.15 – 7.06 (m, 2H), 3.81 (s, 3H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.55 – 2.48 (m, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.87 – 1.77 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.1, 168.8, 143.6, 139.9, 135.6, 132.5, 131.5, 130.1, 129.4, 129.3, 128.7, 128.6, 127.2, 122.6, 52.2, 43.9, 42.6, 29.4, 26.9, 23.2. IR (KBr): 3481, 2948, 1711, 1632, 1475, 1260, 1073, 750, 693 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}BrO_3$ 415.0909; Found 415.0905.

methyl (E)-2-benzylidene-8-(2-bromophenyl)-6-oxooctanoate (3ah)



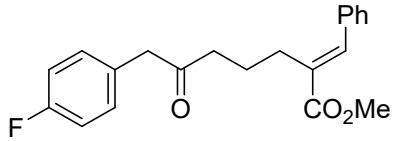
Following the general procedure, **3ah** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (66 mg, 80% yield, E/Z = 98/2 as determined by ^{1}H NMR). Mp: 44.0-45.3 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.30 (m, 5H), 7.23 – 7.17 (m, 2H), 7.05 (ddd, *J* = 8.8, 5.8, 3.3 Hz, 1H), 3.81 (s, 3H), 2.97 (t, *J* = 7.7 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.56 – 2.48 (m, 2H), 2.44 (t, *J* = 7.3 Hz, 2H), 1.89 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 168.8, 140.4, 139.9, 135.5, 132.9, 132.4, 130.7, 129.3, 128.7, 128.6, 128.0, 127.7, 124.4, 52.2, 42.5, 30.4, 26.9, 23.2. IR (KBr): 2948, 1712, 1630, 1471, 1259, 1080, 750, 702, 658 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{24}BrO_3$ 415.0909; Found 415.0907.

methyl (E)-2-benzylidene-6-oxo-7-phenylheptanoate (3ai)



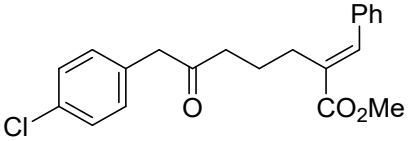
Following the general procedure, **3ai** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (48 mg, 75% yield, E/Z = 98/2 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (s, 1H), 7.43 – 7.26 (m, 8H), 7.17 (d, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.64 (s, 2H), 2.48 (q, *J* = 6.7, 6.2 Hz, 4H), 1.85 – 1.75 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.1, 168.8, 139.8, 135.6, 134.3, 132.5, 129.5, 129.4, 128.8, 128.7, 128.6, 127.1, 52.2, 50.2, 41.7, 26.8, 23.2. IR (KBr): 3027, 2949, 1710, 1631, 1495, 1257, 1219, 834, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{21}H_{23}O_3$ 323.1647; Found 323.1652.

methyl (E)-2-benzylidene-7-(4-fluorophenyl)-6-oxoheptanoate (3aj)



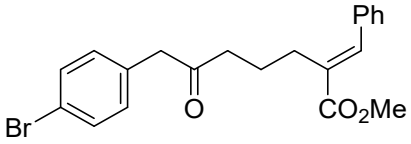
Following the general procedure, **3aj** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (56 mg, 83% yield, E/Z = 98/2 as determined by ^{1}H NMR). Mp: 40.5-43.1 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.42 – 7.30 (m, 5H), 7.15 – 7.08 (m, 2H), 7.03 – 6.96 (m, 2H), 3.80 (s, 3H), 3.60 (s, 2H), 2.48 (td, *J* = 7.5, 3.6 Hz, 4H), 1.85 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.8, 168.8, 162.0 (d, *J* = 245.3 Hz), 139.9, 135.6, 132.4, 131.0 (d, *J* = 8.0 Hz), 130.0 (d, *J* = 3.3 Hz), 129.3, 128.7, 128.6, 115.6 (d, *J* = 21.4 Hz), 52.1, 49.1, 41.8, 26.8, 23.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.83. IR (KBr): 2950, 1711, 1602, 1509, 1257, 1221, 1158, 827, 750, 701 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{21}H_{22}FO_3$ 341.1553; Found 341.1551.

methyl (E)-2-benzylidene-7-(4-chlorophenyl)-6-oxoheptanoate (3ak)



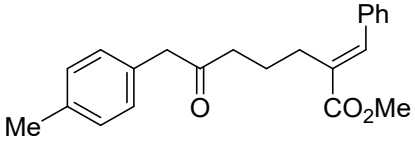
Following the general procedure, **3ak** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (60 mg, 84% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 59.3-60.8 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.43 – 7.25 (m, 7H), 7.09 (d, *J* = 8.1 Hz, 2H), 3.80 (s, 3H), 3.61 (s, 2H), 2.52 – 2.45 (m, 4H), 1.86 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.5, 168.8, 139.9, 135.5, 133.0, 132.7, 132.4, 130.9, 129.3, 128.9, 128.7, 128.6, 52.2, 49.2, 41.9, 26.8, 23.2. IR (KBr): 2949, 1711, 1632, 1492, 1253, 1089, 766, 750, 701 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{21}H_{22}ClO_3$ 357.1257; Found 357.1253.

methyl (E)-2-benzylidene-7-(4-bromophenyl)-6-oxoheptanoate (3al)



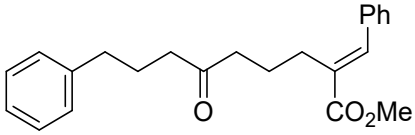
Following the general procedure, **3al** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as white solid (67 mg, 83% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 69.5-71.3 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.46 – 7.30 (m, 7H), 7.03 (d, *J* = 8.3 Hz, 2H), 3.80 (s, 3H), 3.58 (s, 2H), 2.52 – 2.44 (m, 4H), 1.85 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.4, 168.8, 139.9, 135.5, 133.2, 132.3, 131.8, 131.3, 129.3, 128.7, 128.6, 121.1, 52.2, 49.3, 41.9, 26.8, 23.1. IR (KBr): 2948, 1711, 1631, 1488, 1259, 1202, 1071, 750, 702, 487 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{21}H_{22}BrO_3$ 401.0752; Found 401.0749.

methyl (E)-2-benzylidene-6-oxo-7-(p-tolyl)heptanoate (3am)



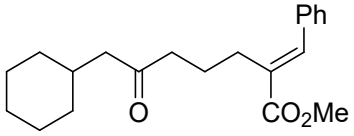
Following the general procedure, **3am** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (61 mg, 91% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 46.6-48.2 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (s, 1H), 7.44 – 7.28 (m, 5H), 7.15 – 7.02 (m, 4H), 3.79 (s, 3H), 3.59 (s, 2H), 2.47 (t, *J* = 7.5 Hz, 4H), 2.32 (s, 3H), 1.84 – 1.74 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.3, 168.8, 139.8, 136.7, 135.6, 132.5, 131.3, 129.5, 129.4, 128.7, 128.6, 52.1, 49.8, 41.6, 26.9, 23.2, 21.2. IR (KBr): 2949, 1712, 1630, 1514, 1259, 1219, 1078, 809, 750, 702 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{25}O_3$ 337.1804; Found 337.1799.

methyl (E)-2-benzylidene-6-oxo-9-phenylnonanoate (3an)



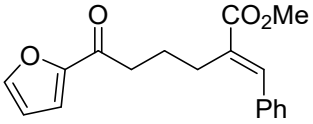
Following the general procedure, **3an** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow solid (52 mg, 75% yield, E/Z = 99/1 as determined by ^{1}H NMR). Mp: 39.3-41.2 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.42 – 7.24 (m, 7H), 7.21 – 7.12 (m, 3H), 3.80 (s, 3H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.54 – 2.48 (m, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.85 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.4, 168.8, 141.7, 139.8, 135.6, 132.6, 129.3, 128.7, 128.5, 128.4, 126.0, 52.1, 42.5, 42.0, 35.2, 26.9, 25.3, 23.2. IR (KBr): 3027, 2928, 2857, 1714, 1644, 1454, 1261, 1194, 1082, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_3$ 351.1960; Found 351.1964.

methyl (E)-2-benzylidene-7-cyclohexyl-6-oxoheptanoate (3ao)



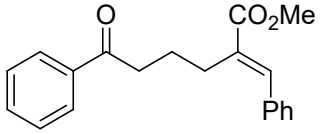
Following the general procedure, **3ao** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (48 mg, 74% yield, E/Z = 98/2 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.45 – 7.29 (m, 5H), 3.81 (s, 3H), 2.55 – 2.48 (m, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.22 (d, *J* = 6.9 Hz, 2H), 1.87 – 1.74 (m, 3H), 1.71 – 1.58 (m, 5H), 1.34 – 1.19 (m, 2H), 1.19 – 1.05 (m, 1H), 0.97 – 0.82 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.6, 168.8, 139.8, 135.6, 132.6, 129.4, 128.7, 128.6, 52.1, 50.6, 43.2, 34.0, 33.3, 27.0, 26.3, 26.2, 23.3. IR (KBr): 2924, 2851, 1712, 1630, 1447, 1259, 1201, 1103, 750, 702 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{21}H_{29}O_3$ 329.2117; Found 329.2114.

methyl (E)-2-benzylidene-6-(furan-2-yl)-6-oxohexanoate (3ap)



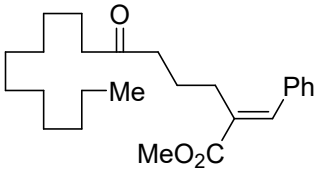
Following the general procedure, **3ap** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (45 mg, 75% yield, E/Z = 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.57 (d, *J* = 1.2 Hz, 1H), 7.42 – 7.29 (m, 5H), 7.15 (d, *J* = 3.5 Hz, 1H), 6.52 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.81 (s, 3H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.65 – 2.58 (m, 2H), 2.03 – 1.94 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.1, 168.8, 152.8, 146.3, 140.0, 135.6, 132.5, 129.4, 128.7, 128.6, 117.0, 112.3, 52.2, 38.3, 27.1, 23.6. IR (KBr): 2950, 1709, 1678, 1631, 1568, 1469, 1247, 1156, 1013, 883, 764, 702 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{18}H_{19}O_4$ 299.1283; Found 299.1274.

methyl (E)-2-benzylidene-6-oxo-6-phenylhexanoate (3aq)



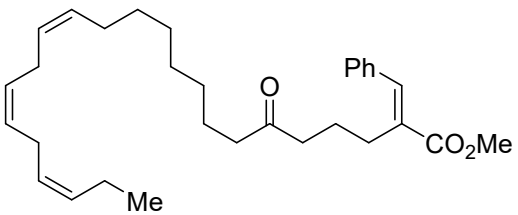
3aq was a known compound[13]. Following the general procedure, **3aq** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as white solid (48 mg, 78% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 69.9-72.1 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.90 (m, 2H), 7.72 (s, 1H), 7.58 – 7.52 (m, 1H), 7.49 – 7.28 (m, 7H), 3.80 (s, 3H), 3.02 (t, *J* = 7.1 Hz, 2H), 2.68 – 2.59 (m, 2H), 2.06 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.9, 168.9, 139.9, 137.0, 135.6, 133.0, 132.6, 129.3, 128.6, 128.1, 52.2, 38.4, 27.0, 23.7. IR (KBr): 3058, 3025, 2949, 1710, 1597, 1448, 1262, 1096, 836, 750, 691, 573 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{20}H_{21}O_3$ 309.1491; Found 309.1483.

methyl (E)-2-benzylidene-6-oxoheptadecanoate (3ar)



Following the general procedure, **3ar** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as as light yellow solid (60 mg, 77% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 39.3-40.1 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.44 – 7.30 (m, 5H), 3.81 (s, 3H), 2.56 – 2.49 (m, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.87 – 1.76 (m, 2H), 1.58 – 1.48 (m, 2H), 1.33 – 1.20 (m, 16H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.0, 168.8, 139.8, 135.6, 132.6, 129.3, 128.6, 52.1, 42.9, 42.4, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 27.0, 23.9, 23.3, 22.8, 14.2. IR (KBr): 2925, 2853, 1714, 1631, 1494, 1447, 1259, 1219, 1073, 750, 702 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{25}H_{39}O_3$ 387.2899; Found 387.2895.

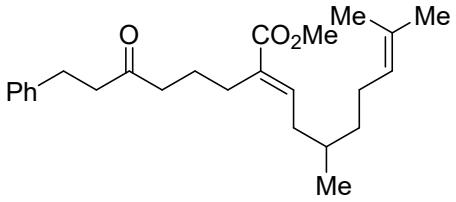
methyl (14Z,17Z,20Z)-2-((E)-benzylidene)-6-oxotricosa-14,17,20-trienoate (3as)



Following the general procedure, $Cu(MeCN)_4PF_6$ (20 mol%), Uracil (40 mol%) was selected, **3as** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (39 mg, 42% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.44 – 7.30 (m, 5H), 5.44 – 5.27 (m, 6H), 3.82 (s, 3H), 2.84 – 2.74 (m, 4H), 2.56 – 2.48 (m, 2H), 2.44 (t, *J* = 7.3

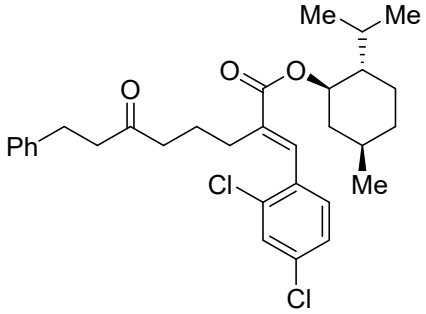
Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.13 – 1.99 (m, 4H), 1.87 – 1.77 (m, 2H), 1.58 – 1.48 (m, 2H), 1.40 – 1.18 (m, 8H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.0, 168.9, 139.8, 135.6, 132.6, 132.1, 130.4, 129.4, 128.7, 128.6, 128.4, 127.8, 127.2, 52.2, 42.9, 42.5, 29.7, 29.4, 29.3, 29.2, 27.3, 27.0, 25.7, 25.6, 23.9, 23.3, 20.7, 14.4. IR (KBr): 3010, 2929, 2854, 1714, 1494, 1434, 1260, 1201, 1072, 750, 702 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{31}H_{45}O_3$ 465.3369; Found 465.3365.

methyl (E)-5,9-dimethyl-2-(4-oxo-6-phenylhexyl)deca-2,8-dienoate (3at)



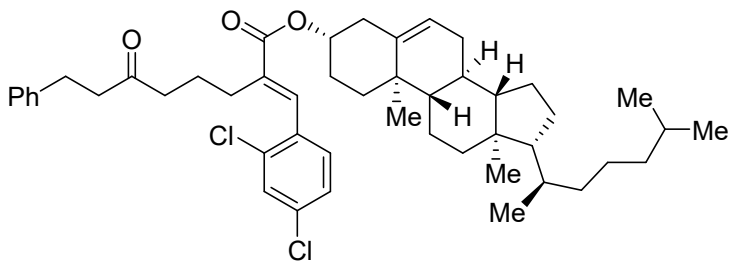
Following the general procedure, $Cu(MeCN)_4PF_6$ (15 mol%), Uracil (30 mol%) was selected, **3at** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (23 mg, 30% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.16 (m, 3H), 6.80 (t, *J* = 7.5 Hz, 1H), 5.08 (tt, *J* = 7.1, 1.3 Hz, 1H), 3.72 (s, 3H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.30 – 2.24 (m, 2H), 2.17 (ddd, *J* = 14.9, 7.1, 5.9 Hz, 1H), 2.08 – 1.90 (m, 3H), 1.71 – 1.57 (m, 9H), 1.42 – 1.30 (m, 1H), 1.29 – 1.13 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) 209.9, 168.4, 142.9, 141.2, 132.1, 131.6, 128.6, 128.4, 126.2, 124.6, 51.8, 44.4, 42.6, 37.0, 36.0, 32.8, 29.9, 26.2, 25.9, 25.8, 23.3, 19.8, 17.8. IR (KBr): 2925, 1714, 1645, 1455, 1275, 1194, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{25}H_{36}O_3K$ 423.2302; Found 423.2308.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl-2-((E)-2,4-dichlorobenzylidene)-6-oxo-8-phenyloctanoate (3au)



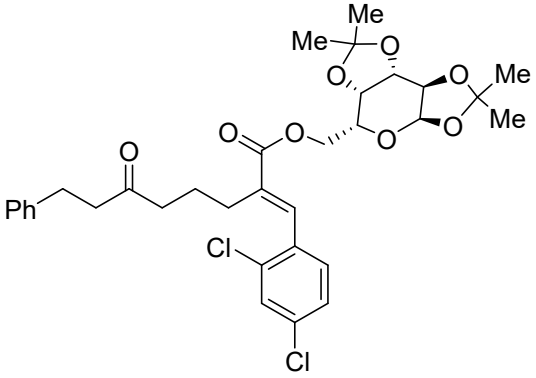
Following the general procedure, **3au** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (86 mg, 81% yield, E/Z = 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.43 (s, 1H), 7.34 – 7.23 (m, 4H), 7.21 – 7.13 (m, 3H), 4.82 (td, *J* = 10.9, 4.3 Hz, 1H), 2.84 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.40 – 2.30 (m, 4H), 2.09 (ddt, *J* = 11.8, 6.7, 2.6 Hz, 1H), 1.92 (heptd, *J* = 6.8, 2.5 Hz, 1H), 1.79 – 1.67 (m, 4H), 1.59 – 1.44 (m, 2H), 1.17 – 1.00 (m, 2H), 0.92 (dd, *J* = 6.9, 5.1 Hz, 7H), 0.80 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 167.0, 141.1, 135.6, 135.2, 134.8, 133.0, 131.0, 129.6, 128.6, 128.4, 127.2, 126.2, 75.2, 47.3, 44.3, 42.4, 41.0, 34.4, 31.6, 29.9, 27.1, 26.7, 23.8, 23.0, 22.2, 20.9, 16.7. IR (KBr): 3027, 2955, 2929, 1708, 1584, 1468, 1261, 1181, 1100, 821, 750, 699 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{31}H_{39}Cl_2O_3$ 529.2276; Found 529.2278.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-((E)-2,4-dichlorobenzylidene)-6-oxo-8-phenyloctanoate (3av)



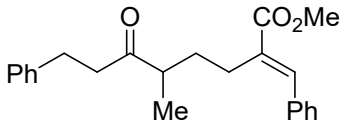
Following the general procedure, **3av** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (99 mg, 65% yield, E/Z = 98/2 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.43 (d, *J* = 1.2 Hz, 1H), 7.30 – 7.23 (m, 4H), 7.20 – 7.12 (m, 3H), 5.41 (d, *J* = 3.9 Hz, 1H), 4.80 – 4.68 (m, 1H), 2.84 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.41 (d, *J* = 6.9 Hz, 2H), 2.38 – 2.30 (m, 4H), 2.05 – 1.96 (m, 2H), 1.95 – 1.87 (m, 2H), 1.86 – 1.80 (m, 1H), 1.79 – 1.72 (m, 2H), 1.71 – 1.62 (m, 2H), 1.61 – 1.54 (m, 2H), 1.54 – 1.50 (m, 2H), 1.49 – 1.42 (m, 2H), 1.40 – 1.33 (m, 2H), 1.33 – 1.23 (m, 2H), 1.23 – 1.16 (m, 2H), 1.15 – 1.08 (m, 4H), 1.07 – 1.02 (m, 4H), 1.02 – 0.95 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 1.8 Hz, 3H), 0.86 (d, *J* = 1.8 Hz, 3H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 166.8, 141.1, 139.7, 135.5, 135.4, 134.8, 133.0, 131.0, 129.6, 128.6, 128.4, 127.2, 126.2, 122.9, 74.9, 56.8, 56.2, 50.1, 44.3, 42.4, 39.8, 39.6, 38.3, 37.1, 36.8, 36.3, 35.9, 32.1, 32.0, 29.9, 28.4, 28.1, 28.0, 27.1, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.8, 12.0. IR (KBr): 3446, 2934, 2867, 1712, 1584, 1468, 1275, 1101, 750, 699 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{48}H_{64}Cl_2O_3K$ 797.3870; Found 797.3863.

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 2-((E)-2,4-dichlorobenzylidene)-6-oxo-8-phenyloctanoate (3aw)



Following the general procedure, **3aw** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (122 mg, 97% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.42 (t, *J* = 1.2 Hz, 1H), 7.31 – 7.23 (m, 4H), 7.20 – 7.12 (m, 3H), 5.52 (d, *J* = 4.9 Hz, 1H), 4.64 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.42 (dd, *J* = 11.6, 4.2 Hz, 1H), 4.37 – 4.31 (m, 2H), 4.28 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.12 (ddd, *J* = 7.9, 4.3, 1.9 Hz, 1H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.39 – 2.32 (m, 4H), 1.82 – 1.72 (m, 2H), 1.50 (s, 3H), 1.47 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 167.3, 141.1, 136.0, 134.8, 132.8, 131.0, 129.5, 128.5, 128.3, 127.2, 126.1, 109.8, 108.8, 96.3, 71.2, 70.8, 70.6, 66.3, 64.2, 44.2, 42.3, 29.8, 27.0, 26.1, 26.0, 25.1, 24.5, 22.8. IR (KBr): 2988, 2934, 1714, 1584, 1470, 1259, 1212, 1070, 897, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{33}H_{39}Cl_2O_8$ 633.2022; Found 633.2025.

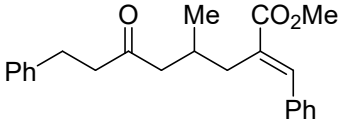
methyl (E)-2-benzylidene-5-methyl-6-oxo-8-phenyloctanoate (3az)



Following the general procedure, **3az** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (40 mg, 57% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.43 – 7.31 (m, 5H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.9 Hz, 3H), 3.80

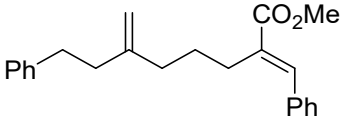
(s, 3H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.81 – 2.72 (m, 1H), 2.71 – 2.62 (m, 1H), 2.54 (q, *J* = 6.7 Hz, 1H), 2.49 – 2.42 (m, 2H), 1.96 – 1.83 (m, 1H), 1.63 – 1.50 (m, 1H), 1.05 (d, *J* = 5.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.3, 168.7, 141.4, 139.8, 135.5, 132.5, 129.3, 128.7, 128.6, 128.4, 126.2, 52.2, 46.6, 42.8, 32.0, 29.8, 25.4, 16.4. IR (KBr): 3027, 2929, 1710, 1454, 1249, 1200, 1134, 1059, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_3$ 351.1960; Found 351.1956.

methyl (E)-2-benzylidene-4-methyl-6-oxo-8-phenyloctanoate (3az')



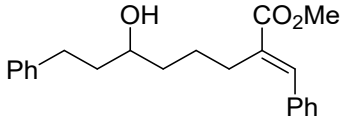
Following the general procedure, **3az'** was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 5/1) as light yellow oil (29 mg, 41% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.40 – 7.25 (m, 6H), 7.24 – 7.12 (m, 4H), 3.80 (s, 3H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.55 – 2.45 (m, 2H), 2.36 – 2.25 (m, 2H), 2.18 – 2.07 (m, 1H), 0.80 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.7, 169.1, 141.2, 140.6, 135.8, 131.9, 129.3, 128.7, 128.6, 128.5, 128.4, 126.2, 52.2, 50.0, 44.7, 33.8, 29.8, 29.3, 20.0. IR (KBr): 3027, 2926, 2853, 1711, 1619, 1455, 1261, 1200, 1124, 1076, 749, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_3$ 351.1960; Found 351.1967.

methyl (E)-2-benzylidene-6-methylene-8-phenyloctanoate (4)



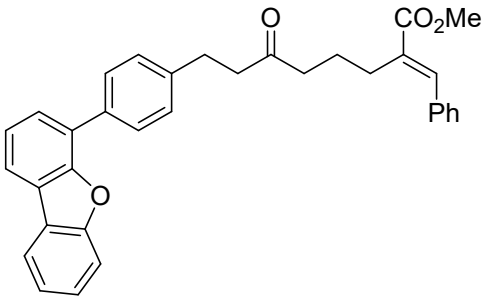
4 was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 10/1) as light yellow oil (45 mg for 0.2 mmol scale, 80% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (s, 1H), 7.41 – 7.24 (m, 7H), 7.22 – 7.15 (m, 3H), 4.77 (s, 1H), 4.76 (s, 1H), 3.81 (s, 3H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.56 – 2.48 (m, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 2.12 (t, *J* = 7.5 Hz, 2H), 1.76 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 148.7, 142.3, 139.3, 135.8, 133.4, 129.3, 128.6, 128.5, 128.44, 128.42, 125.9, 109.7, 52.2, 37.9, 36.3, 34.4, 27.4, 27.3. IR (KBr): 3062, 3026, 2947, 1713, 1644, 1495, 1434, 1250, 1094, 892, 750, 699 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{27}O_2$ 335.2011; Found 335.2003.

methyl (E)-2-benzylidene-6-hydroxy-8-phenyloctanoate (5)



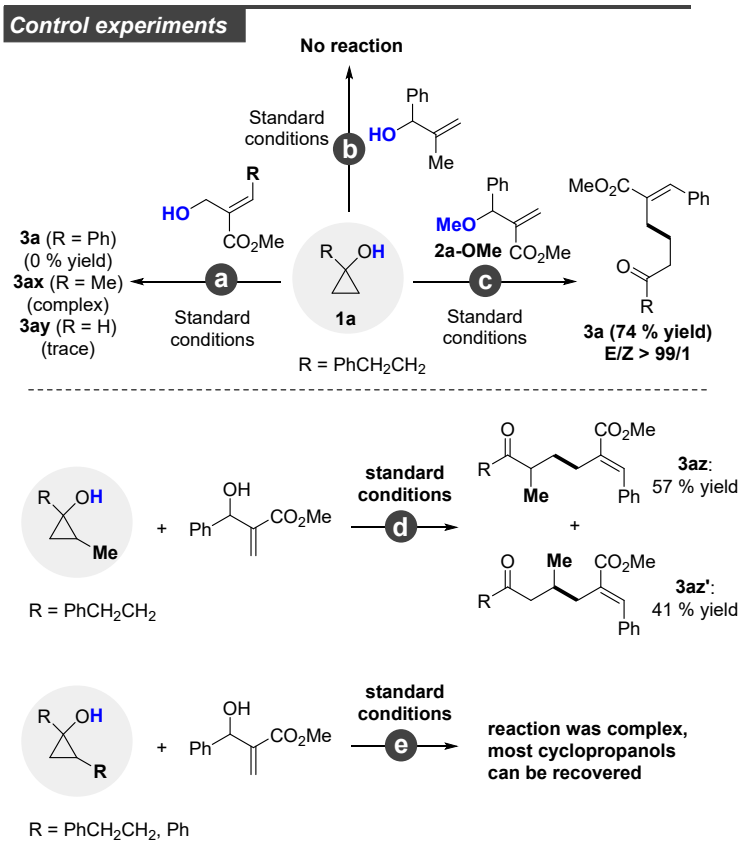
5 was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 10/1) as light yellow oil (164 mg for 0.5 mmol scale, 97% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.39 – 7.22 (m, 7H), 7.21 – 7.13 (m, 3H), 3.78 (s, 3H), 3.69 – 3.56 (m, 1H), 2.78 (ddd, *J* = 13.7, 9.1, 6.4 Hz, 1H), 2.64 (ddd, *J* = 13.7, 9.2, 7.1 Hz, 1H), 2.59 – 2.45 (m, 2H), 2.16 (s, 1H), 1.80 – 1.56 (m, 4H), 1.56 – 1.46 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 142.2, 139.3, 135.6, 133.1, 129.2, 128.5, 128.43, 128.38, 125.8, 70.6, 52.1, 39.2, 37.2, 32.1, 27.2, 25.3. IR (KBr): 3462, 3060, 3025, 2947, 2863, 1711, 1629, 1447, 1250, 1114, 1063, 750, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{27}O_3$ 339.1960; Found 339.1954.

methyl (E)-2-benzylidene-8-(4-(dibenzo[b,d]furan-4-yl)phenyl)-6-oxooctanoate (6)



6 was isolated by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 10/1) as light yellow solid (33 mg for 0.1 mmol scale, 67% yield, E/Z = 96/4 as determined by ^{1}H NMR). Mp: 73.0-75.1 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 6.7 Hz, 2H), 7.71 (s, 1H), 7.58 (t, *J* = 7.3 Hz, 2H), 7.50 – 7.29 (m, 10H), 3.81 (s, 3H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.58 – 2.50 (m, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.91 – 1.79 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.7, 168.8, 156.2, 153.4, 140.9, 139.9, 135.6, 134.3, 132.5, 129.4, 129.0, 128.8, 128.7, 128.6, 127.3, 126.8, 125.7, 125.0, 124.3, 123.3, 122.9, 120.8, 119.6, 111.9, 52.2, 44.3, 42.7, 29.6, 26.9, 23.2. IR (KBr): 3026, 2948, 1712, 1629, 1450, 1259, 1189, 912, 842, 751, 702 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{34}H_{31}O_4$ 503.2222; Found 503.2227.

7. Control Experiments under the standard conditions



Reaction a: $Cu(MeCN)_4PF_6$ (0.02 mmol, 10 mol%), Uracil (0.04 mmol, 20 mol%), Me_2NH (2.4 μL Me_2NH in aq. (40 wt.% in H_2O), 0.014 mmol, 7 mol%) and H_2O (0.8 mmol, 4 equiv.) was stirred in DMF (2.0 mL) at 10 ºC for 1 h under N_2 atmosphere in a dried schlenk tube, then allylic alcohol (0.2 mmol, 1 equiv.) and cyclopropanol **1a** (0.4 mmol, 2 equiv.) were added subsequently under N_2 atmosphere. The reaction mixture was heated at 60 ºC (metal bath) for 24 h, allowed to cool to room temperature. Dilute the solvent with ethyl acetate and wash the mixture with water. After the organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure.

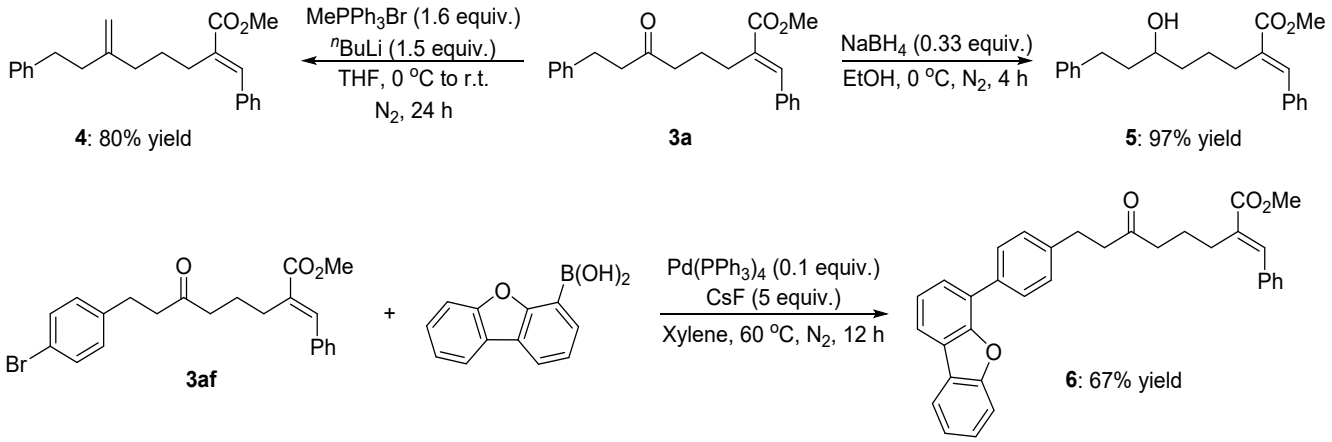
Reaction b: $Cu(MeCN)_4PF_6$ (0.02 mmol, 10 mol%), Uracil (0.04 mmol, 20 mol%), Me_2NH (2.4 μL Me_2NH in aq. (40 wt.% in H_2O), 0.014 mmol, 7 mol%) and H_2O (0.8 mmol, 4 equiv.) was stirred in DMF (2.0 mL) at 10 ºC for 1 h under N_2 atmosphere in a dried schlenk tube, then 2-methyl-1-phenylprop-2-en-1-ol (0.2 mmol, 1 equiv.) and cyclopropanol **1a** (0.4 mmol, 2 equiv.) were added subsequently under N_2 atmosphere. The reaction mixture was heated at 60 ºC (metal bath) for 24 h, allowed to cool to room temperature. Dilute the solvent with ethyl acetate and wash the mixture with water. After the organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure. No desired producted was detected and the strating material 2-methyl-1-phenylprop-2-en-1-ol was recovered over 94% yield.

Reaction c: $Cu(MeCN)_4PF_6$ (0.02 mmol, 10 mol%), Uracil (0.04 mmol, 20 mol%), Me_2NH (2.4 μL Me_2NH in aq. (40 wt.% in H_2O), 0.014 mmol, 7 mol%) and H_2O (0.8 mmol, 4 equiv.) was stirred in DMF (2.0 mL) at 10 ºC for 1 h under N_2 atmosphere in a dried schlenk tube, then **2a-OMe** (0.2 mmol, 1 equiv.) and cyclopropanol **1a** (0.4 mmol, 2 equiv.) were added subsequently under N_2 atmosphere. The reaction mixture was heated at 60 ºC (metal bath) for 24 h, allowed to cool to room temperature. Dilute the solvent with ethyl acetate and wash the mixture with water. After the organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 10/1) to afford the desired producted **3a** in 74% yield.

Reaction d: $Cu(MeCN)_4PF_6$ (0.02 mmol, 10 mol%), Uracil (0.04 mmol, 20 mol%), Me_2NH (2.4 μL Me_2NH in aq. (40 wt.% in H_2O), 0.014 mmol, 7 mol%) and H_2O (0.8 mmol, 4 equiv.) was stirred in DMF (2.0 mL) at 10 ºC for 1 h under N_2 atmosphere in a dried schlenk tube, then allyl alcohol **2a** (0.2 mmol, 1 equiv.) and cyclopropanol **1q** (0.4 mmol, 2 equiv.) were added subsequently under N_2 atmosphere. The reaction mixture was heated at 60 ºC (metal bath) for 24 h, allowed to cool to room temperature. Dilute the solvent with ethyl acetate and wash the mixture with water. After the organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 10/1) to afford the desired producted **3az** (57% yield) and **3az'** (41% yield).

Reaction e: $Cu(MeCN)_4PF_6$ (0.02 mmol, 10 mol%), Uracil (0.04 mmol, 20 mol%), Me_2NH (2.4 μL Me_2NH in aq. (40 wt.% in H_2O), 0.014 mmol, 7 mol%) and H_2O (0.8 mmol, 4 equiv.) was stirred in DMF (2.0 mL) at 10 ºC for 1 h under N_2 atmosphere in a dried schlenk tube, then allyl alcohol **2a** (0.2 mmol, 1 equiv.) and cyclopropanol **1r** (0.4 mmol, 2 equiv.) were added subsequently under N_2 atmosphere. The reaction mixture was heated at 60 ºC (metal bath) for 24 h, allowed to cool to room temperature. Dilute the solvent with ethyl acetate and wash the mixture with water. After the organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by PTLC (petroleum ether (bp: 60-90 ºC)/ethyl acetate = 10/1). The reaction was complex and only a trace amount of desired product was detected.

8. Preliminary Protocol Applications



Preparation of **4**:
Following the literature procedure[14]. To a solution of the methyl triphenyl phosphonium bromide (0.32 mmol, 1.6 equiv.) in THF was added ^{n}BuLi (0.3 mmol, 1.6 M in hexanes,1.5 equiv.) at 0 °C under N_2 atmosphere and the resulting mixture was stirred for 30 minutes at 0 °C. Then the **3a** (0.2 mmol, 1.0 equiv.) was added slowly at 0 °C. After 30 minutes, The mixture was warmed to room temperature and allowed to stir overnight. Then saturated solution of NH_4Cl (aq.) was slowly added to quench the reaction. The aqueous solution was extracted with diethyl ether three times. The combined organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by PTLC to afford the corresponding product **4** (45 mg, 80% yield).

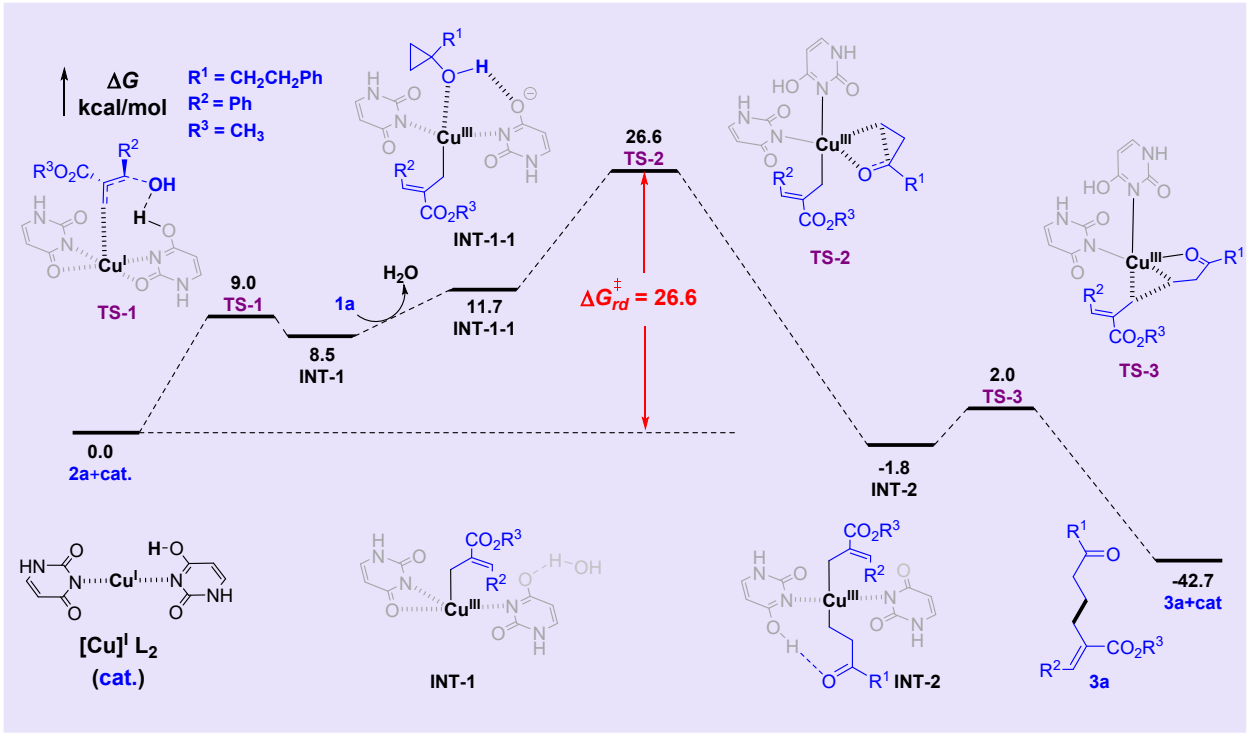
Preparation of **5**:
Following the literature procedure[15]. Sodium borohydride (0.17 mmol, 0.33 equiv.) was added in dry ethanol (6.5 mL) under N_2 atmosphere, and the mixture was cooled to 0 °C. After stirring for 5 min a solution of dry methanol (3.5 mL) containing **3a** (0.5 mmol, 1 equiv) was added dropwise. After stirring for 4 h at 0 °C, the reaction was quenched with saturated solution of NH_4Cl (aq.), and methanol was removed under reduced pressure. Then, water was added and extracted twice with ethyl acetate. The organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by PTLC to afford the corresponding product **5** (164 mg, 97% yield).

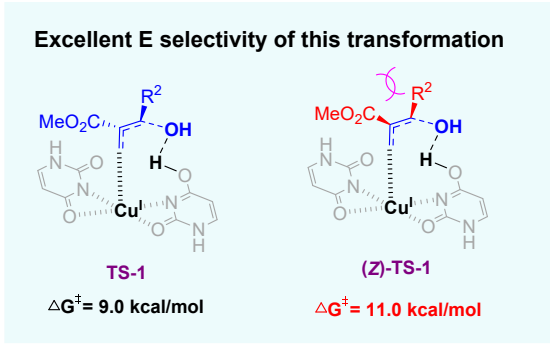
Preparation of **6**:
Following the literature procedure[16]. **3af** (0.1 mmol, 1 equiv.), dibenzo[b,d]furan-4-yl boronic acid (0.4 mmol, 4.0 equiv.), $Pd(PPh_3)_4$ (0.01 mmol, 0.1 equiv.), and CsF (0.5 mmol, 5.0 equiv.) was added in xylene (1.0 mL) under N_2 atmosphere. The reaction was stirred at 60 °C (metal bath) for 12 h. The solvent was removed under reduced pressure. The residue was purified by PTLC to afford the corresponding product **6** (33 mg, 67% yield).

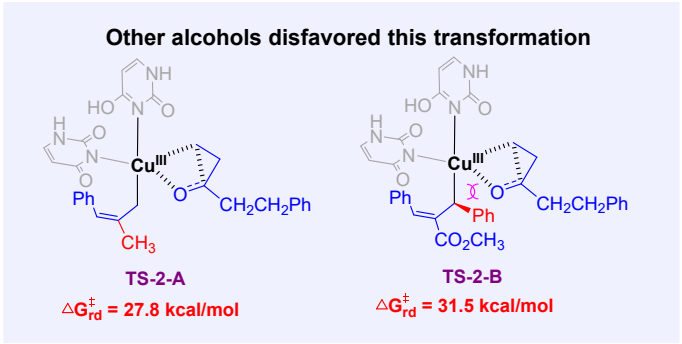
9. DFT calculations

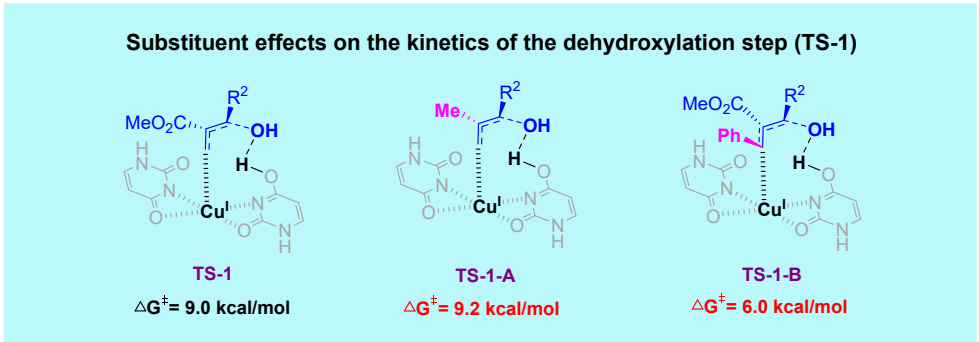
All calculations were finished using the Gaussian 09 computational program.[17] Geometrical optimizations were performed by the B3LYP density functional method[18] with the def2svp basis set[19] for all elements. The default self-consistent reaction field polarizable continuum model[20] was used to consider the implicit solvation effects of N,N-dimethylformamide. All of the resultant stationary point geometries were characterized by vibrational analyses, from which zero point energies and Gibbs free-energies were obtained, in addition to confirming whether all of the structures resided at minima or first-order saddle points on the potential energy surfaces. To further refine the electronic energies obtained, single point calculations by the B3LYP+D3(BJ) method[21] and the def2tzvpp basis set[22] have been carried out in N,N-dimethylformamide.

Table S10. Optimized Cartesian coordinates of the stationary points.









Name	Cartesian Coordinates			
cat	Cu	0.023438000	-0.023370000	0.016494000
	C	4.003245000	-0.859970000	-0.908154000
	C	2.540447000	-0.862311000	-0.889198000
	C	2.598577000	0.838245000	0.853858000
	C	4.673140000	-0.032738000	-0.068962000
	H	4.525036000	-1.523933000	-1.596212000
	H	4.496284000	1.409451000	1.414214000
	H	5.762912000	0.024271000	-0.025317000

	O	2.051285000	1.603808000	1.646124000
	N	1.925676000	0.002123000	0.005953000
	O	1.856978000	-1.587058000	-1.622485000
	N	3.995320000	0.790837000	0.785172000
	C	-3.960097000	-1.021265000	0.797683000
	C	-2.500729000	-1.004448000	0.772885000
	C	-2.645930000	0.882464000	-0.667983000
	C	-4.659268000	-0.098323000	0.098109000
	H	-4.463891000	-1.786022000	1.387271000
	H	-4.509534000	1.555987000	-1.171769000
	H	-5.747951000	-0.048284000	0.069085000
	O	-2.127748000	1.842456000	-1.404863000
	N	-1.908623000	0.016349000	-0.011324000
	O	-1.780322000	-1.791981000	1.369188000
	N	-3.996279000	0.857670000	-0.639349000
	H	-1.153092000	1.789710000	-1.371916000
2a	C	-1.132276000	0.973281000	0.042684000
	C	-1.506124000	1.893186000	0.943871000
	H	-2.397515000	1.756224000	1.557633000
	H	-0.922425000	2.807848000	1.070684000
	C	-1.930735000	-0.269130000	-0.190972000
	O	-1.739847000	-1.026093000	-1.122540000
	O	-2.890653000	-0.465099000	0.722293000
	C	-3.725883000	-1.613897000	0.546932000
	H	-3.127618000	-2.536670000	0.569340000
	H	-4.436884000	-1.603225000	1.381204000
	H	-4.263901000	-1.562032000	-0.411258000
	C	0.109065000	1.136520000	-0.837847000
	C	1.260878000	0.266067000	-0.342334000
	C	1.513078000	-0.989076000	-0.913693000
	C	2.083354000	0.714362000	0.703426000
	C	2.565323000	-1.784835000	-0.446788000
	H	0.876217000	-1.347292000	-1.725214000
	C	3.137535000	-0.077363000	1.166697000
	H	1.900637000	1.695391000	1.146642000
	C	3.381104000	-1.331561000	0.594262000
	H	2.750708000	-2.760526000	-0.903692000
	H	3.773120000	0.286464000	1.978460000
	H	4.205622000	-1.950831000	0.956976000
	H	-0.163245000	0.788204000	-1.849554000
	O	0.558567000	2.478356000	-0.866447000
	H	-0.151177000	3.023817000	-1.235098000
TS-1	Cu	0.427467000	1.114184000	0.066533000
	C	4.444717000	2.091645000	-0.241549000
	C	2.994417000	2.034646000	-0.396048000
	C	2.945568000	0.151273000	1.136548000
	C	5.055842000	1.197940000	0.573557000
	H	5.006436000	2.851044000	-0.783738000
	H	4.782515000	-0.414058000	1.858056000
	H	6.134217000	1.176724000	0.741800000
	O	2.359518000	-0.740886000	1.771103000
	N	2.326060000	1.049318000	0.329060000

	O	2.348271000	2.799702000	-1.117965000
	N	4.327070000	0.252698000	1.242657000
	C	-3.430948000	2.130604000	1.355475000
	C	-2.099944000	1.547736000	1.285990000
	C	-2.007450000	2.091563000	-1.074053000
	C	-3.977409000	2.649178000	0.226977000
	H	-3.961671000	2.132652000	2.306163000
	H	-3.704657000	2.994954000	-1.801827000
	H	-4.971393000	3.099346000	0.193602000
	O	-1.442391000	2.072746000	-2.166877000
	N	-1.444727000	1.595098000	0.073551000
	O	-1.545469000	1.022500000	2.273285000
	N	-3.290782000	2.622043000	-0.952801000
	C	0.389676000	-1.764478000	-0.800750000
	C	0.365104000	-0.580489000	-1.516091000
	H	1.261905000	-0.282282000	-2.060329000
	H	-0.549426000	-0.046966000	-1.767460000
	C	1.669359000	-2.544432000	-0.669688000
	O	1.762436000	-3.589158000	-0.059884000
	O	2.687452000	-1.984511000	-1.329490000
	C	3.942403000	-2.675144000	-1.288656000
	H	3.839851000	-3.686558000	-1.707382000
	H	4.635483000	-2.080000000	-1.893860000
	H	4.305454000	-2.749013000	-0.253544000
	C	-0.685033000	-2.292712000	-0.026111000
	O	-0.272300000	-1.325732000	1.939507000
	H	-0.736798000	-0.453765000	2.054744000
	H	0.693286000	-1.101082000	1.905394000
	C	-2.113742000	-2.071895000	-0.139166000
	C	-2.741483000	-1.470890000	-1.254922000
	C	-2.929684000	-2.558947000	0.912600000
	C	-4.128750000	-1.343528000	-1.301565000
	C	-4.311111000	-2.411176000	0.870583000
	C	-4.914723000	-1.800138000	-0.237449000
	H	-2.155353000	-1.150290000	-2.114676000
	H	-2.452794000	-3.026425000	1.775976000
	H	-4.600168000	-0.892713000	-2.177381000
	H	-4.924496000	-2.777250000	1.696716000
	H	-6.001444000	-1.693391000	-0.277090000
	H	-0.401849000	-3.168191000	0.556578000
INT-1	Cu	-0.075933000	-0.911685000	0.171299000
	C	-4.159626000	-1.708741000	-0.111150000
	C	-2.720887000	-1.620924000	-0.339574000
	C	-2.566358000	-0.047430000	1.507785000
	C	-4.715567000	-0.978390000	0.885773000
	H	-4.755939000	-2.363578000	-0.744864000
	H	-4.354954000	0.377195000	2.420413000
	H	-5.782130000	-0.991317000	1.117843000
	O	-1.936812000	0.705650000	2.267038000
	N	-2.004694000	-0.776175000	0.506365000
	O	-2.128044000	-2.247379000	-1.223226000
	N	-3.942169000	-0.166120000	1.668341000

	C	2.531834000	-3.828547000	0.748376000
	C	1.523853000	-2.795471000	0.682005000
	C	2.582866000	-1.820613000	-1.252893000
	C	3.507167000	-3.810669000	-0.200201000
	H	2.492067000	-4.589778000	1.525675000
	H	4.266434000	-2.836605000	-1.864713000
	H	4.309435000	-4.549804000	-0.244363000
	O	2.675639000	-0.966745000	-2.135418000
	N	1.604556000	-1.853273000	-0.306976000
	O	0.544924000	-2.680886000	1.466421000
	N	3.530395000	-2.846515000	-1.164392000
	C	-0.504018000	1.730120000	-0.909313000
	C	-0.131309000	0.450982000	-1.420158000
	H	-0.884650000	-0.090226000	-1.994678000
	H	0.901295000	0.248782000	-1.711271000
	C	-1.948132000	2.162764000	-1.023019000
	O	-2.407392000	3.161263000	-0.508910000
	O	-2.670226000	1.347882000	-1.798921000
	C	-4.039533000	1.708391000	-2.019552000
	H	-4.101724000	2.682658000	-2.525827000
	H	-4.461575000	0.920802000	-2.653674000
	H	-4.583689000	1.764336000	-1.066162000
	C	0.308948000	2.682903000	-0.310135000
	O	0.665946000	0.199507000	2.043433000
	H	0.750906000	-0.635636000	2.530704000
	H	-0.257082000	0.500157000	2.248865000
	C	1.715739000	2.773796000	-0.003177000
	C	2.709340000	1.816224000	-0.330226000
	C	2.125185000	3.951549000	0.678744000
	C	4.039864000	2.038658000	0.011159000
	C	3.455670000	4.163441000	1.025116000
	C	4.419524000	3.204778000	0.690899000
	H	2.464400000	0.901413000	-0.864338000
	H	1.373201000	4.701768000	0.934783000
	H	4.793057000	1.293841000	-0.255894000
	H	3.744865000	5.075261000	1.552179000
	H	5.467221000	3.365738000	0.956720000
	H	-0.255333000	3.567160000	0.001475000
INT-1-1	Cu	0.571415000	0.727963000	-0.042856000
	C	1.501405000	3.602109000	-0.276266000
	C	-0.048085000	3.221754000	1.519027000
	C	1.174977000	5.297632000	1.438948000
	H	-0.245442000	4.848184000	2.984511000
	H	1.468061000	6.291651000	1.782727000
	O	-0.930420000	2.491850000	2.054782000
	N	0.614804000	2.797909000	0.399169000
	O	2.055372000	3.297082000	-1.326300000
	C	4.611679000	0.789869000	0.775025000
	C	3.163519000	0.679258000	0.919462000
	C	2.984060000	0.454202000	-1.513099000
	C	5.157954000	0.729563000	-0.465281000
	H	5.221644000	0.923038000	1.667320000

	H	4.785646000	0.523064000	-2.497910000
	H	6.231366000	0.807879000	-0.648760000
	O	2.320469000	0.308734000	-2.535005000
	N	2.451900000	0.501619000	-0.254089000
	O	2.567191000	0.730484000	2.002465000
	N	4.373375000	0.560369000	-1.570976000
	C	1.239662000	-2.221788000	-0.962391000
	C	0.295856000	-1.365032000	-0.309146000
	H	-0.592582000	-1.137857000	-0.898437000
	H	0.113224000	-1.514293000	0.757405000
	C	1.197535000	-2.323489000	-2.467590000
	O	2.010685000	-2.929906000	-3.133160000
	O	0.130646000	-1.713514000	-2.993637000
	C	0.050965000	-1.675150000	-4.420813000
	H	0.038237000	-2.691899000	-4.839299000
	H	-0.882622000	-1.153035000	-4.660379000
	H	0.910751000	-1.125124000	-4.830102000
	C	2.151095000	-3.067471000	-0.362198000
	H	2.670696000	-3.711765000	-1.078282000
	C	2.503031000	-3.327425000	1.019319000
	C	3.213960000	-4.529659000	1.272154000
	C	2.203493000	-2.488366000	2.120959000
	C	3.570226000	-4.900215000	2.565475000
	H	3.471808000	-5.178579000	0.431583000
	C	2.574274000	-2.858580000	3.411913000
	H	1.736380000	-1.516849000	1.975690000
	C	3.246608000	-4.065685000	3.642460000
	H	4.106598000	-5.836291000	2.736643000
	H	2.347710000	-2.191373000	4.246707000
	H	3.530681000	-4.348331000	4.659130000
	C	-2.461514000	0.902443000	-0.469403000
	C	-2.547895000	2.214224000	-1.202935000
	C	-2.149208000	0.950607000	-1.939597000
	H	-1.760126000	2.945261000	-1.007282000
	H	-3.533817000	2.643699000	-1.398157000
	H	-2.857005000	0.503996000	-2.642873000
	H	-1.102249000	0.847909000	-2.240479000
	O	-1.360621000	0.716146000	0.407542000
	H	-1.311641000	1.455539000	1.160532000
	C	-3.683298000	0.186070000	0.091718000
	H	-3.871736000	0.591369000	1.101539000
	H	-3.410905000	-0.874006000	0.232473000
	C	0.264096000	4.521509000	2.079718000
	N	1.767526000	4.852965000	0.298166000
	H	2.431241000	5.436405000	-0.202076000
	C	-4.980750000	0.271717000	-0.729982000
	H	-5.264718000	1.327216000	-0.867146000
	H	-4.813372000	-0.149914000	-1.734025000
	C	-6.126933000	-0.466057000	-0.069384000
	C	-6.354881000	-1.827436000	-0.331870000
	C	-6.969104000	0.184014000	0.848401000
	C	-7.391442000	-2.519495000	0.302838000

	C	-8.006937000	-0.503704000	1.485703000
	C	-8.221469000	-1.859582000	1.215498000
	H	-5.713926000	-2.351169000	-1.047504000
	H	-6.811871000	1.245332000	1.063120000
	H	-7.553609000	-3.577673000	0.080706000
	H	-8.652842000	0.022753000	2.193527000
	H	-9.033702000	-2.398128000	1.710535000
1a	C	2.630599000	0.008253000	0.307428000
	C	3.294942000	0.704763000	-0.854427000
	C	3.291431000	-0.811155000	-0.759642000
	H	4.234557000	1.219914000	-0.635789000
	H	2.680098000	1.179077000	-1.624553000
	H	2.672044000	-1.376805000	-1.460680000
	H	4.227564000	-1.300310000	-0.476702000
	O	3.340122000	0.009698000	1.523191000
	H	3.193935000	0.868157000	1.947661000
	C	1.123332000	0.020953000	0.526105000
	H	0.875033000	0.929795000	1.105446000
	H	0.878370000	-0.833247000	1.181430000
	C	0.229482000	-0.025563000	-0.724529000
	H	0.456416000	-0.933148000	-1.306842000
	H	0.455166000	0.836544000	-1.372445000
	C	-1.245707000	-0.014155000	-0.382292000
	C	-1.946844000	1.196644000	-0.252455000
	C	-1.942460000	-1.212450000	-0.151386000
	C	-3.300998000	1.211654000	0.097490000
	C	-3.296530000	-1.202840000	0.198953000
	C	-3.981329000	0.010618000	0.325696000
	H	-1.424917000	2.141305000	-0.432893000
	H	-1.417258000	-2.167113000	-0.252073000
	H	-3.827677000	2.165446000	0.188861000
	H	-3.819662000	-2.147531000	0.370340000
	H	-5.040152000	0.020006000	0.597071000
TS-2	Cu	-0.756349000	-0.612253000	-0.073985000
	C	-3.510921000	-2.100775000	1.151033000
	C	-3.287495000	-2.507727000	-1.147949000
	C	-5.451000000	-2.702027000	-0.178923000
	H	-5.093741000	-3.083071000	-2.267885000
	H	-6.525835000	-2.891364000	-0.167202000
	O	-2.525656000	-2.596028000	-2.210029000
	N	-2.751215000	-2.156424000	0.013578000
	O	-3.057806000	-1.855955000	2.266506000
	C	-2.966502000	2.346905000	-2.185927000
	C	-2.662032000	1.303124000	-1.205794000
	C	-0.289422000	1.611164000	-1.705710000
	C	-1.954195000	2.967865000	-2.837641000
	H	-4.008869000	2.613480000	-2.355525000
	H	0.107388000	3.105104000	-3.060500000
	H	-2.110057000	3.764592000	-3.567753000
	O	0.897290000	1.353338000	-1.514408000
	N	-1.320396000	0.961669000	-1.083158000
	O	-3.527717000	0.752769000	-0.520270000

	N	-0.654496000	2.622111000	-2.595276000
	C	0.335813000	1.002266000	2.032333000
	C	-0.937542000	0.414861000	1.692466000
	H	-1.258917000	-0.460818000	2.263796000
	H	-1.761936000	1.069192000	1.422532000
	C	1.332337000	0.164259000	2.795197000
	O	2.531934000	0.353766000	2.820160000
	O	0.738172000	-0.804041000	3.505641000
	C	1.576172000	-1.605751000	4.347365000
	H	2.102023000	-0.974512000	5.078070000
	H	0.907835000	-2.307190000	4.859420000
	H	2.319697000	-2.155439000	3.752061000
	C	0.796443000	2.272166000	1.751540000
	H	1.847860000	2.419340000	2.015743000
	C	0.173837000	3.461077000	1.195028000
	C	1.046290000	4.497203000	0.776141000
	C	-1.218678000	3.690224000	1.086834000
	C	0.556795000	5.685836000	0.240536000
	H	2.125074000	4.349646000	0.869862000
	C	-1.706008000	4.888219000	0.568262000
	H	-1.930742000	2.947865000	1.442177000
	C	-0.824511000	5.886319000	0.133580000
	H	1.251996000	6.463016000	-0.085516000
	H	-2.784876000	5.047662000	0.505861000
	H	-1.214158000	6.821519000	-0.275894000
	C	0.743780000	-2.305609000	-0.862512000
	C	0.339613000	-2.526901000	0.772039000
	C	0.540853000	-3.633751000	-0.247325000
	H	-0.672116000	-2.474803000	1.180908000
	H	1.142650000	-2.343850000	1.483045000
	H	1.414927000	-4.274750000	-0.102231000
	H	-0.367267000	-4.164356000	-0.545961000
	O	-0.214187000	-1.752275000	-1.623688000
	H	-1.556393000	-2.338224000	-1.973746000
	C	2.140504000	-1.757032000	-1.145922000
	H	2.072247000	-0.659183000	-1.123404000
	H	2.338897000	-2.024672000	-2.199822000
	C	-4.683269000	-2.802557000	-1.299959000
	N	-4.881214000	-2.359339000	1.004033000
	H	-5.442399000	-2.302820000	1.849449000
	C	3.314523000	-2.238368000	-0.277618000
	H	3.110374000	-2.021147000	0.781953000
	H	3.431791000	-3.330251000	-0.368472000
	C	4.615962000	-1.564066000	-0.660044000
	C	5.003699000	-0.361266000	-0.044786000
	C	5.447460000	-2.102595000	-1.655989000
	C	6.187688000	0.284858000	-0.415016000
	C	6.632210000	-1.459019000	-2.028847000
	C	7.006289000	-0.261425000	-1.409765000
	H	4.371044000	0.066365000	0.739077000
	H	5.165546000	-3.041280000	-2.142646000
	H	6.474365000	1.217396000	0.078683000

	H	7.267421000	-1.896900000	-2.803614000
	H	7.933152000	0.241209000	-1.698182000
INT-2	Cu	-1.012574000	-0.770554000	0.813793000
	C	-2.555137000	-3.265623000	1.074989000
	C	-1.915783000	-2.938234000	-1.179754000
	C	-3.688621000	-4.454473000	-0.716960000
	H	-2.984261000	-4.077822000	-2.718298000
	H	-4.469358000	-5.177011000	-0.960206000
	O	-1.127901000	-2.393527000	-2.072064000
	N	-1.790951000	-2.629104000	0.109590000
	O	-2.427316000	-3.086730000	2.274913000
	C	-4.731115000	0.687886000	-0.701711000
	C	-3.680927000	0.155672000	0.165706000
	C	-2.040293000	0.680595000	-1.540087000
	C	-4.387777000	1.196732000	-1.910702000
	H	-5.763880000	0.674649000	-0.355524000
	H	-2.822189000	1.587986000	-3.216880000
	H	-5.110037000	1.621070000	-2.611480000
	O	-0.889341000	0.697605000	-1.976425000
	N	-2.391207000	0.167960000	-0.327856000
	O	-3.906344000	-0.296381000	1.298709000
	N	-3.083372000	1.204939000	-2.314491000
	C	0.325883000	1.810320000	1.362122000
	C	-0.626306000	0.861244000	1.954961000
	H	-0.322169000	0.487854000	2.934812000
	H	-1.671819000	1.169960000	1.947562000
	C	1.789138000	1.658096000	1.686963000
	O	2.708526000	2.025488000	0.981760000
	O	1.986934000	1.114556000	2.899644000
	C	3.337725000	1.024060000	3.366641000
	H	3.798111000	2.021807000	3.408552000
	H	3.282171000	0.588901000	4.371147000
	H	3.940150000	0.381456000	2.708583000
	C	0.072984000	2.877666000	0.545132000
	H	0.974927000	3.353475000	0.147986000
	C	-1.159283000	3.542268000	0.119769000
	C	-1.086237000	4.361347000	-1.030982000
	C	-2.388562000	3.494589000	0.813138000
	C	-2.196090000	5.069109000	-1.490845000
	H	-0.138364000	4.431926000	-1.571001000
	C	-3.493170000	4.218980000	0.363840000
	H	-2.478287000	2.918651000	1.733715000
	C	-3.407525000	5.001652000	-0.793423000
	H	-2.113137000	5.685511000	-2.389544000
	H	-4.429317000	4.175193000	0.925801000
	H	-4.276787000	5.564464000	-1.142680000
	C	1.893710000	-1.859194000	-0.285813000
	C	0.464947000	-1.665649000	1.811207000
	C	1.270133000	-2.589123000	0.888846000
	H	-0.141719000	-2.244062000	2.520638000
	H	1.120194000	-0.978048000	2.350829000
	H	2.068307000	-3.070420000	1.481845000

	H	0.629319000	-3.385559000	0.483902000
	O	1.219521000	-1.520061000	-1.251682000
	H	-0.345329000	-1.910889000	-1.670763000
	C	3.367420000	-1.545608000	-0.223264000
	H	3.584525000	-1.138851000	0.779701000
	H	3.895217000	-2.518366000	-0.243576000
	C	-2.897929000	-3.861405000	-1.655810000
	N	-3.512852000	-4.167835000	0.595147000
	H	-4.085328000	-4.621081000	1.302838000
	C	3.877226000	-0.611317000	-1.326457000
	H	3.290286000	0.319236000	-1.289180000
	H	3.679546000	-1.073928000	-2.305496000
	C	5.350509000	-0.293530000	-1.184756000
	C	5.776065000	0.761795000	-0.358303000
	C	6.324879000	-1.058561000	-1.846668000
	C	7.137211000	1.041357000	-0.198519000
	C	7.687062000	-0.780969000	-1.688442000
	C	8.098223000	0.270499000	-0.862517000
	H	5.026551000	1.366792000	0.160151000
	H	6.012591000	-1.879922000	-2.498747000
	H	7.449146000	1.868390000	0.445250000
	H	8.429543000	-1.386348000	-2.215434000
	H	9.161933000	0.490630000	-0.739865000
TS-3	Cu	1.449059000	-0.303065000	-0.335230000
	C	3.876797000	-1.935112000	-0.714232000
	C	2.061111000	-3.428629000	-0.674453000
	C	4.245317000	-4.310235000	-0.371473000
	H	2.491322000	-5.561392000	-0.357331000
	H	4.992465000	-5.088159000	-0.205282000
	O	0.767926000	-3.656409000	-0.764249000
	N	2.526115000	-2.196008000	-0.790514000
	O	4.357485000	-0.815294000	-0.821353000
	C	1.038338000	-1.638119000	3.762123000
	C	1.604119000	-1.278139000	2.459454000
	C	-0.551121000	-0.404674000	1.802466000
	C	-0.262397000	-1.357935000	4.017842000
	H	1.679746000	-2.113252000	4.503622000
	H	-2.005997000	-0.526138000	3.255714000
	H	-0.754390000	-1.585160000	4.966049000
	O	-1.319382000	0.145240000	1.002539000
	N	0.749022000	-0.702796000	1.533008000
	O	2.797370000	-1.468472000	2.186619000
	N	-1.036148000	-0.755579000	3.066798000
	C	1.388276000	2.861762000	-0.919944000
	C	2.130576000	1.596350000	-0.784096000
	H	2.976942000	1.500156000	-1.463120000
	H	2.453923000	1.393019000	0.246614000
	C	1.418191000	3.576371000	-2.247927000
	O	0.717040000	4.519657000	-2.552890000
	O	2.349575000	3.079419000	-3.080681000
	C	2.483959000	3.717177000	-4.355330000
	H	2.748165000	4.777334000	-4.230382000

	H	3.286444000	3.184514000	-4.878647000
	H	1.545628000	3.648253000	-4.924836000
	C	0.646993000	3.511517000	0.026885000
	H	0.116824000	4.386424000	-0.362425000
	C	0.424124000	3.289712000	1.456883000
	C	-0.738628000	3.864392000	2.021605000
	C	1.312439000	2.618706000	2.324947000
	C	-1.025381000	3.737506000	3.379838000
	H	-1.426510000	4.413740000	1.373342000
	C	1.035819000	2.511002000	3.688422000
	H	2.248543000	2.208305000	1.948888000
	C	-0.137491000	3.056820000	4.220815000
	H	-1.937700000	4.180640000	3.786731000
	H	1.744775000	1.996350000	4.341314000
	H	-0.351653000	2.964113000	5.288459000
	C	-1.420917000	-0.639362000	-1.658887000
	C	0.904831000	0.306703000	-2.191229000
	C	-0.585856000	0.548886000	-2.096304000
	H	1.161445000	-0.725128000	-2.474555000
	H	1.389292000	0.981463000	-2.895319000
	H	-0.827266000	1.389374000	-1.422915000
	H	-0.983824000	0.862742000	-3.082151000
	O	-0.932682000	-1.739068000	-1.438852000
	H	0.256299000	-2.837081000	-0.992693000
	C	-2.914823000	-0.420449000	-1.589195000
	H	-3.090599000	0.535098000	-1.071125000
	H	-3.269991000	-0.267490000	-2.625552000
	C	2.907569000	-4.560762000	-0.452043000
	N	4.707513000	-3.043018000	-0.508486000
	H	5.703852000	-2.850084000	-0.450163000
	C	-3.684770000	-1.561038000	-0.913291000
	H	-3.525960000	-2.491043000	-1.479836000
	H	-3.248887000	-1.716840000	0.085491000
	C	-5.164826000	-1.273055000	-0.789201000
	C	-6.087146000	-1.783271000	-1.717233000
	C	-5.648161000	-0.459400000	0.250746000
	C	-7.451738000	-1.491750000	-1.611423000
	C	-7.010375000	-0.164806000	0.360204000
	C	-7.918330000	-0.680543000	-0.572050000
	H	-5.731774000	-2.422015000	-2.531365000
	H	-4.944097000	-0.055860000	0.984962000
	H	-8.152999000	-1.902750000	-2.342717000
	H	-7.365717000	0.466812000	1.178918000
	H	-8.984152000	-0.453584000	-0.486240000
3a	C	3.356327000	0.943965000	-0.238464000
	C	1.995360000	0.671708000	-0.834844000
	H	1.808928000	1.414019000	-1.626551000
	H	2.001869000	-0.313147000	-1.325665000
	C	3.758012000	2.370423000	-0.005500000
	O	4.811534000	2.739839000	0.475611000
	O	2.805454000	3.236794000	-0.395294000
	C	3.085482000	4.627314000	-0.216449000

	H	3.974775000	4.922790000	-0.792762000
	H	2.202568000	5.166123000	-0.580105000
	H	3.259728000	4.856292000	0.845366000
	C	4.298029000	0.024817000	0.094323000
	H	5.243732000	0.450551000	0.445429000
	C	4.293623000	-1.441552000	0.017127000
	C	5.545091000	-2.090786000	-0.083323000
	C	3.136251000	-2.249263000	0.069318000
	C	5.636739000	-3.479769000	-0.172581000
	H	6.456163000	-1.486677000	-0.100636000
	C	3.229930000	-3.640410000	-0.007881000
	H	2.155806000	-1.795459000	0.207421000
	C	4.476680000	-4.261793000	-0.138812000
	H	6.616924000	-3.954930000	-0.261129000
	H	2.320595000	-4.244454000	0.043425000
	H	4.544603000	-5.350765000	-0.200631000
	C	-1.700601000	0.606429000	0.484914000
	C	0.837012000	0.740565000	0.177210000
	C	-0.522085000	0.478803000	-0.466830000
	H	0.825872000	1.730667000	0.656973000
	H	1.002709000	0.013796000	0.990443000
	H	-0.704411000	1.190936000	-1.294219000
	H	-0.560746000	-0.518622000	-0.940207000
	O	-1.576709000	1.068152000	1.603490000
	C	-3.044855000	0.126265000	-0.039021000
	H	-3.186540000	0.519423000	-1.060886000
	H	-2.969129000	-0.969918000	-0.164443000
	C	-4.232478000	0.483319000	0.863967000
	H	-4.041426000	0.081590000	1.870880000
	H	-4.280127000	1.578875000	0.971170000
	C	-5.551369000	-0.039761000	0.338043000
	C	-6.017811000	-1.314824000	0.700716000
	C	-6.329115000	0.724227000	-0.548760000
	C	-7.222404000	-1.812661000	0.193254000
	C	-7.534368000	0.230812000	-1.058928000
	C	-7.985514000	-1.041068000	-0.689771000
	H	-5.431147000	-1.923715000	1.395262000
	H	-5.987890000	1.722605000	-0.838957000
	H	-7.568451000	-2.805793000	0.492255000
	H	-8.125503000	0.844173000	-1.744333000
	H	-8.928750000	-1.427208000	-1.084809000
	29	-1.602296000	0.070298000	0.142994000
	6	-1.430486000	4.259176000	0.130460000
	6	-1.615520000	2.873793000	-0.296378000
	6	-0.531276000	2.151233000	1.757660000
	6	-0.826212000	4.512583000	1.317278000
(*Z*)-TS-1	1	-1.788994000	5.061834000	-0.512478000
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	8	-0.106512000	1.270272000	2.518951000
	7	-1.153265000	1.889679000	0.574825000
	8	-2.146434000	2.554154000	-1.364494000

	7	-0.383016000	3.487015000	2.106615000
	6	-2.542233000	-4.088439000	0.126803000
	6	-1.785028000	-2.857759000	0.307778000
	6	-3.711576000	-1.598937000	-0.459966000
	6	-3.817661000	-4.016924000	-0.329296000
	1	-2.068817000	-5.039429000	0.365345000
	1	-5.342365000	-2.751776000	-0.948215000
	1	-4.448010000	-4.893817000	-0.489019000
	8	-4.269572000	-0.535531000	-0.717891000
	7	-2.414561000	-1.673200000	-0.010022000
	8	-0.609857000	-2.866525000	0.726453000
	7	-4.385161000	-2.808873000	-0.614361000
	6	1.182120000	0.037154000	-1.054349000
	6	-0.086829000	-0.153569000	-1.585135000
	1	-0.601764000	0.667241000	-2.089674000
	1	-0.460610000	-1.165248000	-1.744845000
	6	1.719431000	1.436000000	-0.969416000
	8	2.419551000	1.852319000	-0.071442000
	8	1.309171000	2.185795000	-1.995807000
	6	1.722896000	3.559510000	-2.009381000
	1	2.820027000	3.629209000	-2.012948000
	1	1.309619000	3.988857000	-2.928838000
	1	1.327728000	4.088915000	-1.131050000
	6	1.849403000	-1.096530000	-0.515997000
	1	1.221077000	-1.988976000	-0.520887000
	6	3.239209000	-1.383461000	-0.250161000
	6	3.526094000	-2.707673000	0.174216000
	6	4.320807000	-0.485571000	-0.427024000
	6	4.831264000	-3.115627000	0.423232000
	1	2.699419000	-3.407941000	0.313921000
	6	5.626463000	-0.903560000	-0.187938000
	1	4.142428000	0.537899000	-0.745988000
	6	5.886543000	-2.212393000	0.240784000
	1	5.031970000	-4.136582000	0.754784000
	1	6.452142000	-0.203774000	-0.334155000
	1	6.915055000	-2.529248000	0.430383000
	8	1.124069000	-1.052662000	1.719989000
	1	0.384649000	-1.666128000	1.496242000
	1	0.692230000	-0.203184000	1.974206000
TS-2-A	29	-0.159512000	0.705645000	-0.169067000
	6	-2.392683000	3.026798000	-1.223771000
	6	-1.616734000	3.528220000	0.932184000
	6	-3.713181000	4.426956000	0.257866000
	1	-2.862326000	4.835231000	2.193166000
	1	-4.634287000	5.002018000	0.368414000
	8	-0.688086000	3.422888000	1.849822000
	7	-1.464219000	2.900108000	-0.226036000
	8	-2.271251000	2.528116000	-2.339504000
	6	-2.775332000	-1.253393000	2.566241000
	6	-2.327042000	-0.341430000	1.511125000
	6	-0.171763000	-1.493932000	1.521193000
	6	-1.937479000	-2.216111000	3.020352000

	1	-3.787669000	-1.144237000	2.953117000
	1	-0.051868000	-3.071793000	2.833658000
	1	-2.212422000	-2.934423000	3.795213000
	8	0.967048000	-1.658372000	1.083490000
	7	-1.013163000	-0.506182000	1.091748000
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	7	-0.675667000	-2.340381000	2.508016000
	6	-0.413087000	-1.579068000	-1.986512000
	6	-1.047044000	-0.306910000	-1.720812000
	1	-0.854672000	0.505391000	-2.429271000
	1	-2.068017000	-0.300877000	-1.342226000
	6	-0.971586000	-2.799724000	-1.691213000
	1	-0.320147000	-3.666278000	-1.853413000
	6	-2.294516000	-3.160042000	-1.177922000
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	6	-3.483518000	-2.445644000	-1.452466000
	6	-3.628624000	-4.767873000	0.100420000
	1	-1.502937000	-4.934193000	-0.215415000
	6	-4.711054000	-2.875325000	-0.946322000
	1	-3.456287000	-1.573036000	-2.105513000
	6	-4.789835000	-4.029958000	-0.159334000
	1	-3.681186000	-5.680339000	0.699660000
	1	-5.616891000	-2.310517000	-1.180564000
	1	-5.753471000	-4.362874000	0.234088000
	6	1.945839000	1.812174000	0.106013000
	6	1.333710000	1.932316000	-1.483174000
	6	2.073987000	3.023990000	-0.727711000
	1	0.308696000	2.213245000	-1.737745000
	1	1.874265000	1.375839000	-2.249768000
	1	3.066548000	3.291353000	-1.100775000
	1	1.458224000	3.876556000	-0.428800000
	8	1.024006000	1.734901000	1.078127000
	1	0.066234000	2.802993000	1.517591000
	6	3.126979000	0.869506000	0.323884000
	1	2.716145000	-0.120179000	0.574858000
	1	3.606728000	1.245521000	1.245869000
	6	-2.764914000	4.334952000	1.231731000
	7	-3.532422000	3.790085000	-0.926926000
	1	-4.224937000	3.871325000	-1.666433000
	6	4.196199000	0.741029000	-0.773455000
	1	3.752767000	0.298928000	-1.679847000
	1	4.576942000	1.735720000	-1.054316000
	6	5.362443000	-0.117849000	-0.327645000
	6	5.325683000	-1.515483000	-0.467779000
	6	6.494624000	0.460442000	0.270382000
	6	6.387113000	-2.311446000	-0.025162000
	6	7.558662000	-0.331381000	0.714679000
	6	7.508364000	-1.721753000	0.568755000
	1	4.455236000	-1.986654000	-0.933631000
	1	6.545013000	1.547382000	0.385606000
	1	6.339414000	-3.396853000	-0.147558000
	1	8.431734000	0.140324000	1.173611000

	1	8.339771000	-2.342262000	0.913051000
	6	0.975023000	-1.552611000	-2.589250000
	1	1.014718000	-0.882219000	-3.463226000
	1	1.706101000	-1.178458000	-1.854762000
	1	1.299556000	-2.552736000	-2.908815000
TS-2-B	29	-0.893430000	-0.508478000	-0.209752000
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	6	-3.732966000	-2.779092000	-0.012387000
	6	-5.882415000	-2.447447000	0.946637000
	1	-5.560702000	-3.812755000	-0.686685000
	1	-6.956743000	-2.598848000	1.065555000
	8	-2.978883000	-3.386170000	-0.898575000
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	8	-3.462782000	-0.441279000	2.552191000
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	6	-2.686592000	0.354604000	-2.333090000
	6	-0.298337000	0.538494000	-2.769758000
	6	-1.889774000	1.122714000	-4.504041000
	1	-3.967193000	0.939519000	-4.028821000
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	1	-2.001397000	1.473731000	-5.531817000
	8	0.884288000	0.422728000	-2.427918000
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	8	-3.590652000	0.033610000	-1.560105000
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	6	0.978643000	1.230869000	2.630831000
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	6	1.462161000	1.911416000	0.258607000
	1	1.085514000	1.859659000	-0.763642000
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	6	3.578462000	2.295985000	-0.904101000
	6	3.496535000	2.914958000	1.439201000
	6	4.901583000	2.731349000	-0.978713000
	1	3.083283000	1.886672000	-1.788197000
	6	4.813506000	3.362872000	1.357196000
	1	2.962474000	3.015113000	2.382894000
	6	5.525339000	3.265703000	0.153787000
	1	5.444433000	2.662672000	-1.924533000
	1	5.290532000	3.797556000	2.239073000
	1	6.558835000	3.616633000	0.098572000
	6	0.292989000	-2.543657000	0.083811000
	6	-0.096414000	-1.747563000	1.582893000
	6	-0.045419000	-3.243986000	1.337217000
	1	-1.092732000	-1.395528000	1.864921000

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	6	1.737953000	-2.417867000	-0.391461000
	1	1.795919000	-1.544087000	-1.059656000
	1	1.885403000	-3.304540000	-1.035171000
	6	-5.132558000	-3.095105000	0.010477000
	7	-5.296659000	-1.560438000	1.791815000
	1	-5.849822000	-1.073702000	2.491741000
	6	2.865139000	-2.365915000	0.653813000
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	1	2.751725000	-3.192414000	1.373625000
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	6	4.807355000	-3.720868000	-0.265582000
	6	6.212939000	-1.409349000	-0.945280000
	6	6.060158000	-3.820013000	-0.878907000
	6	6.768513000	-2.662818000	-1.221724000
	1	4.535633000	-0.329977000	-0.119123000
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	1	6.758008000	-0.497937000	-1.205274000
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	1	7.749275000	-2.738357000	-1.698469000
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	6	-3.490420000	4.337892000	-0.651789000
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	1	-4.169727000	5.108354000	-1.025142000
TS-1-A	29	-1.487472000	0.184210000	0.037789000
	6	-1.579492000	4.348922000	-0.442233000
	6	-1.713885000	2.913847000	-0.683882000
	6	-0.383826000	2.501517000	1.300922000
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	6	-1.469743000	-2.696799000	0.567134000
	6	-3.514106000	-1.691279000	-0.254112000
	6	-3.431843000	-4.072973000	0.199139000

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	1	-5.072729000	-3.010022000	-0.497537000
	1	-4.000233000	-5.005067000	0.190835000
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	6	0.048274000	-0.196935000	-1.763650000
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	1	-0.233522000	-1.249858000	-1.725249000
	6	2.074771000	-0.777270000	-0.657332000
	1	1.602150000	-1.760381000	-0.623867000
	6	3.503310000	-0.815389000	-0.401850000
	6	4.086968000	-2.098888000	-0.266270000
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	6	5.453632000	-2.248326000	-0.047011000
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	1	6.339010000	1.048313000	0.058772000
	1	7.339817000	-1.226886000	0.243279000
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	1	2.657476000	1.691059000	-2.111995000
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TS-1-B	29	1.233362000	0.884467000	-0.779969000
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	1	1.407639000	-4.030840000	2.937432000
	1	4.001275000	-0.576221000	3.049591000
	1	3.652770000	-3.028926000	3.339902000

Table S11. Electronic energies (***E*** in au), Gibbs free energies (***G*** in au) and imaginary frequencies (***IF*** in cm^{-1})calculated at the B3LYP/def2svp level, and single-point electronic energies (***E^sp^*** in au)calculated at the B3LYP+D3(BJ)/def2tzvpp level. Energies are reported in au.

Name	*E*	*G*	*IF*	E^{sp}
cat	-2468.841361	-2468.724153	-	-2470.082135
2a	-651.5827739	-651.415119	-	-652.3687757
TS-1	-3120.417913	-3120.10861	-100.7 *i*	-3122.461222
INT-1	-3120.42324	-3120.114538	-	-3122.461088
H_2O	-76.36474959	-76.361253	-	-76.47377023
1a	-502.4350368	-502.250378	-	-503.0397798

INT-1-1	-3546.47768	-3545.986511	-	-3549.023279
TS-2	-3546.44856	-3545.956176	-99.1 *i*	-3549.000849
INT-2	-3546.49374	-3545.998663	-	-3549.048908
TS-3	-3546.487416	-3545.997631	-198.9 *i*	-3549.037433
3a	-1077.712068	-1077.362323	-	-1079.003778
(*Z*)-TS-1	-3120.415003	-3120.106633	-53.8 *i*	-3122.45687
TS-1-A	-2931.99805	-2931.700401	-133.4 *i*	-2933.812646
TS-1-B	-3351.31086	-3350.929102	-21.8 *i*	-3353.632523
TS-2-A	-3358.024337	-3357.544049	-116.4 *i*	-3360.350399
TS-2-B	-3777.329615	-3776.763728	-137.4 *i*	-3780.159773

10. NMR Spectra for New Compound

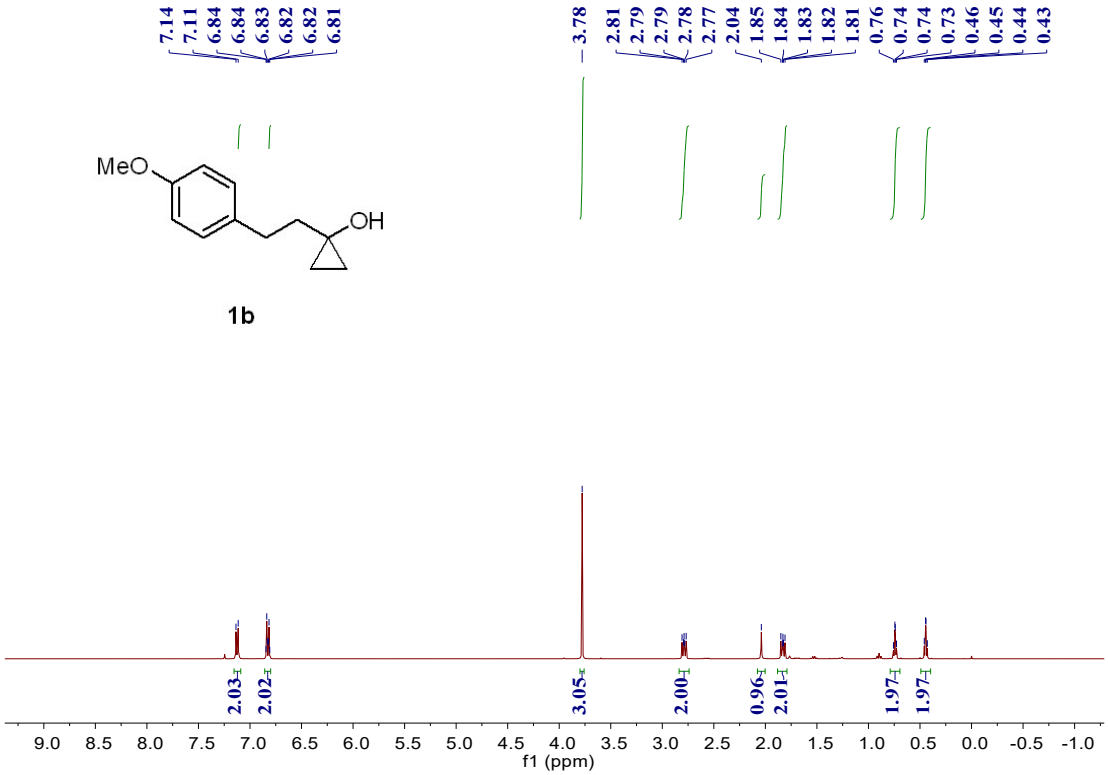


Figure S2 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **1b**

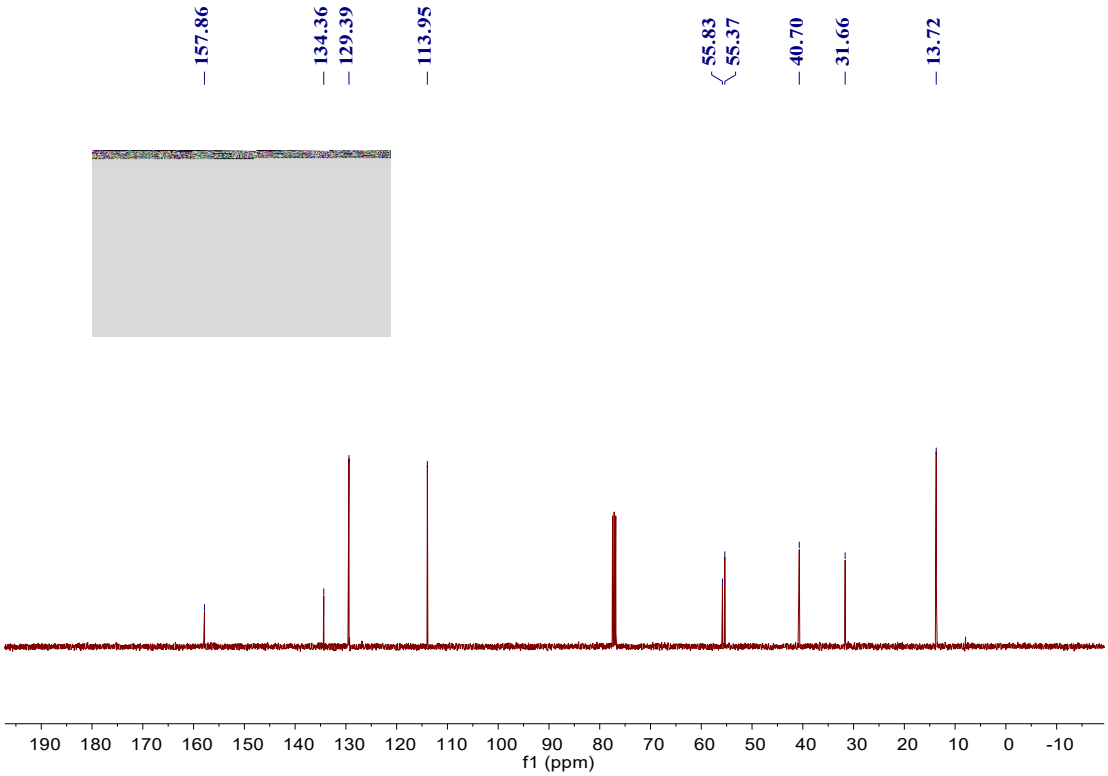


Figure S3 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **1b**

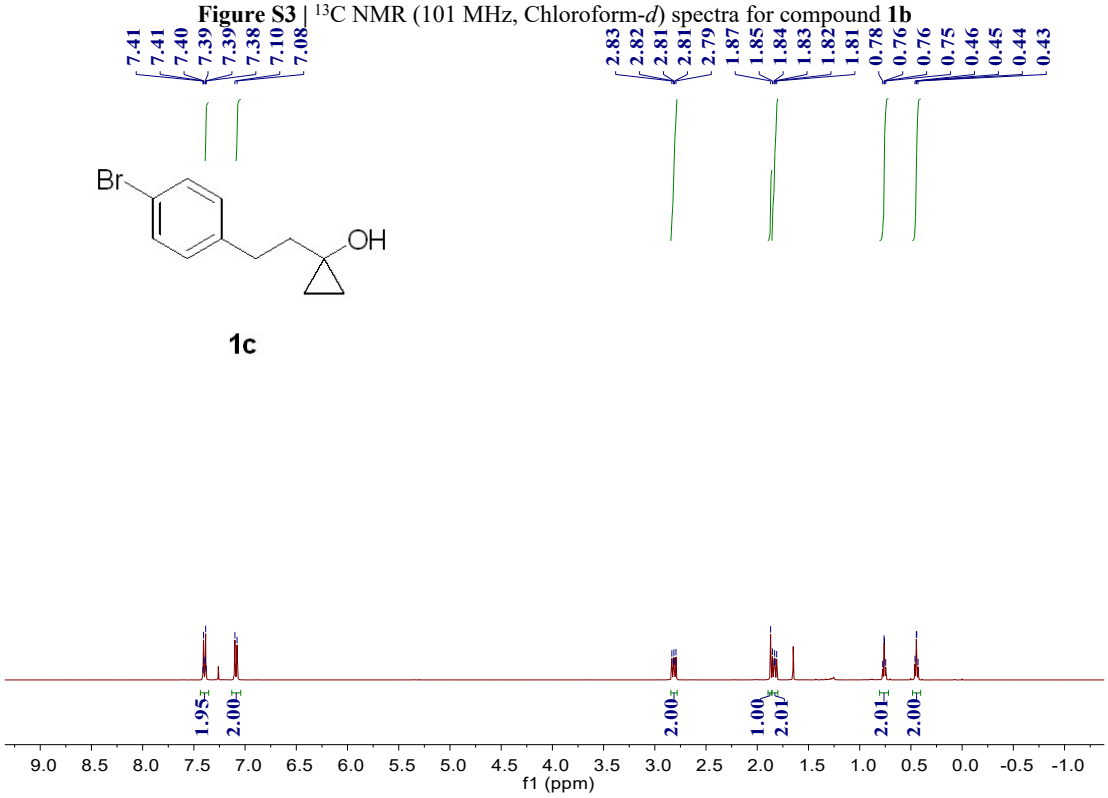


Figure S4 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **1c**

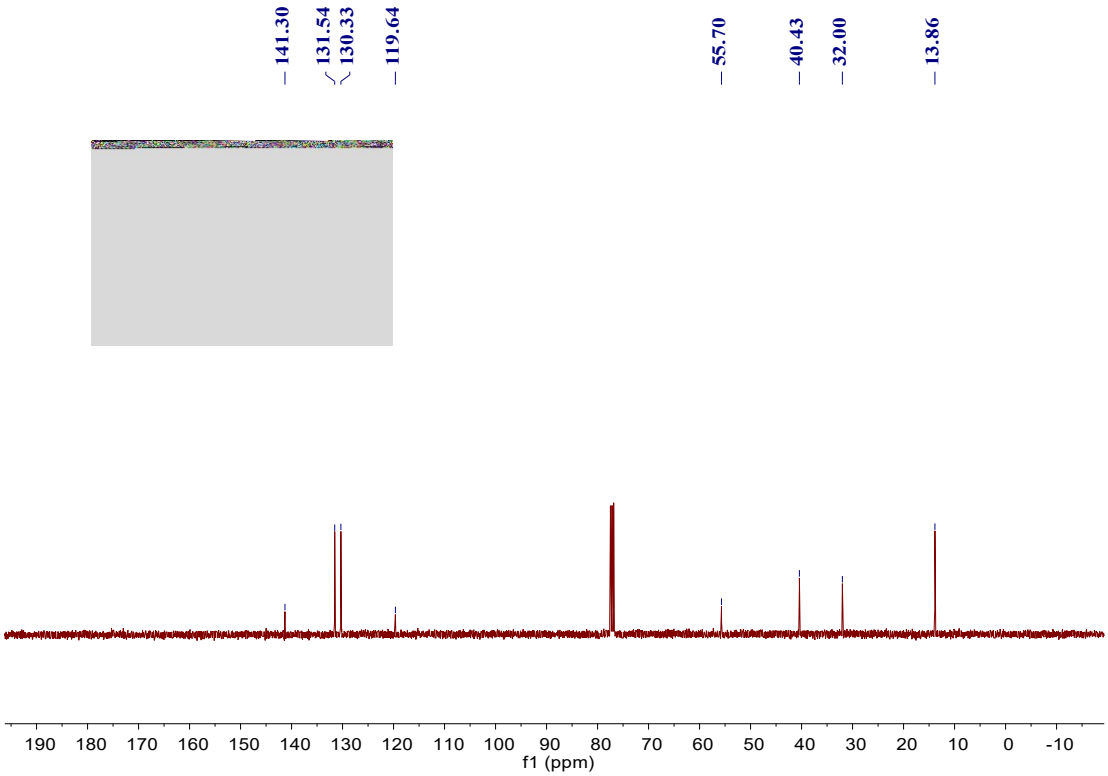


Figure S5 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **1c**

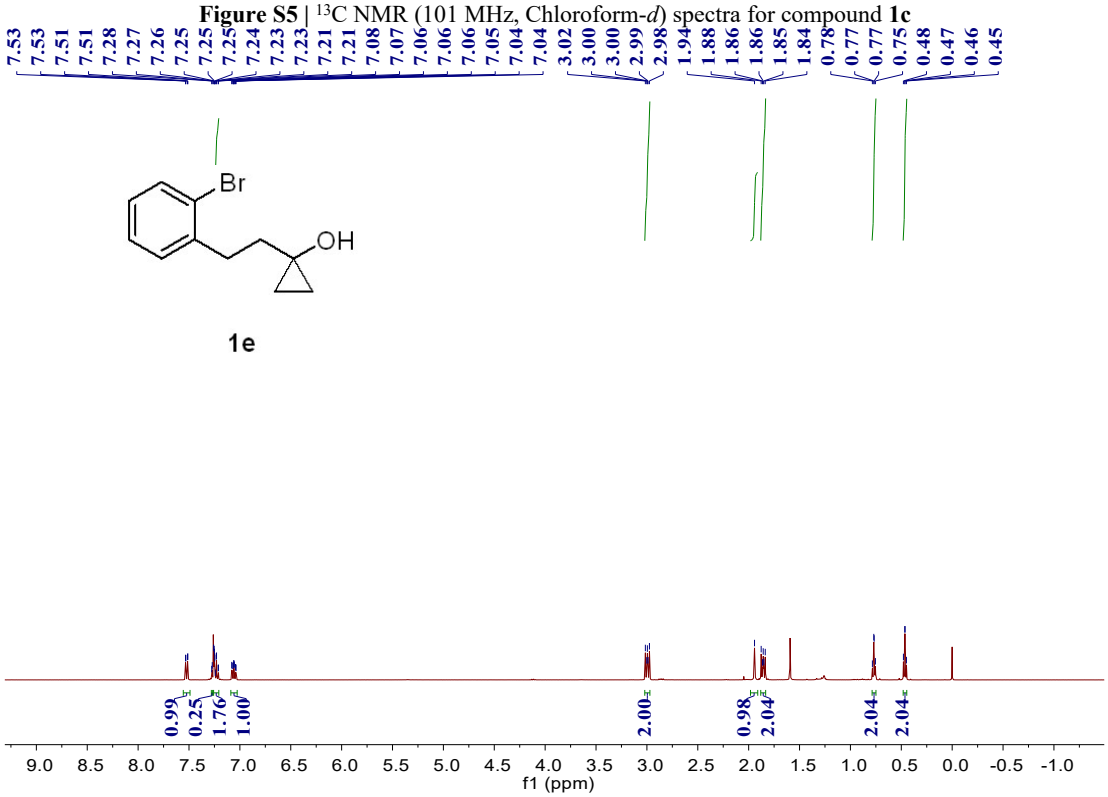


Figure S6 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **1e**

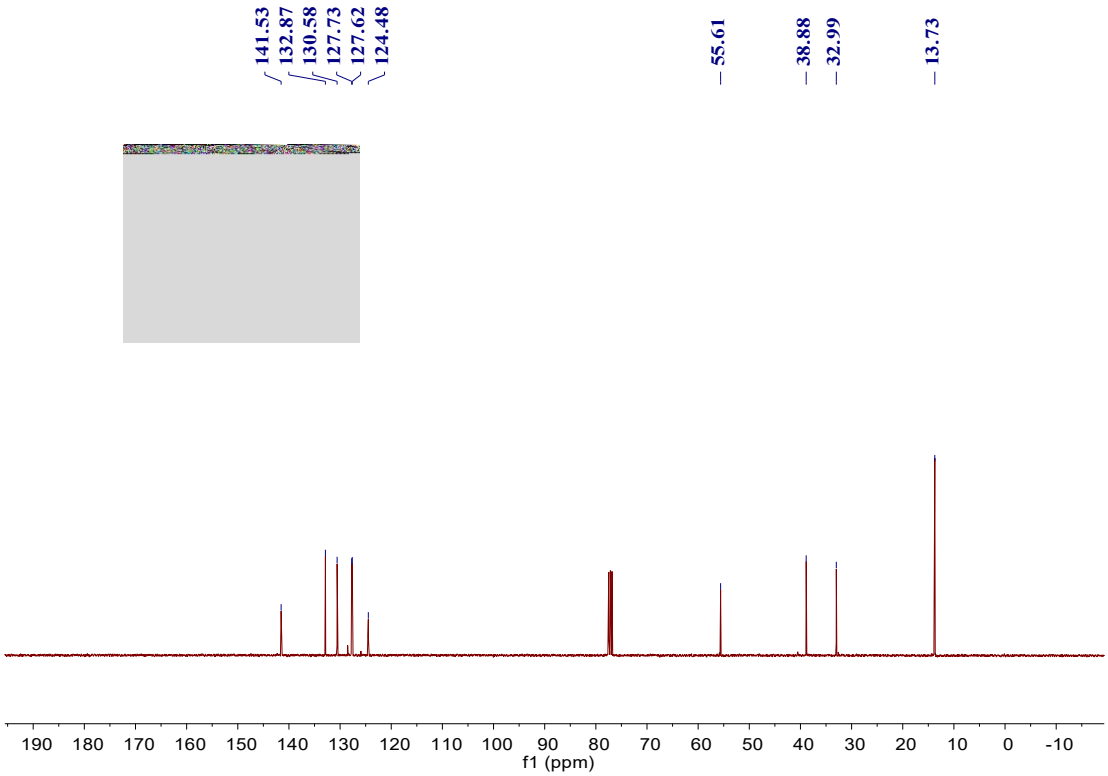


Figure S7 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **1e**

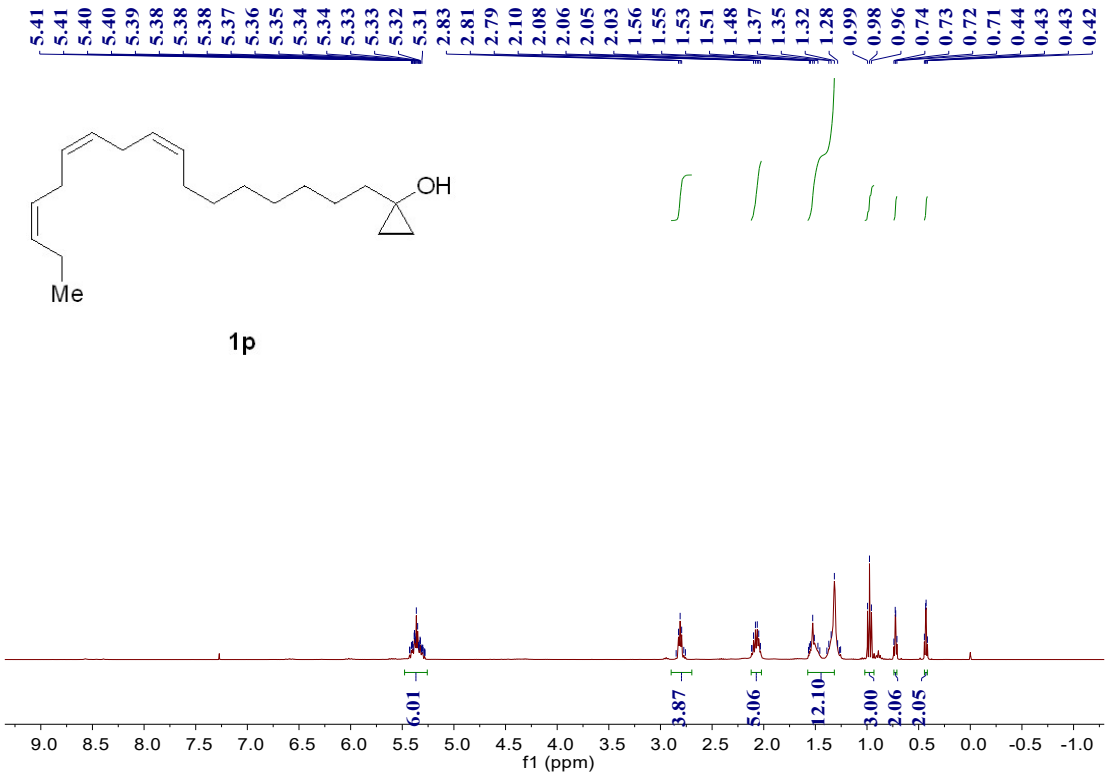


Figure S8 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **1p**

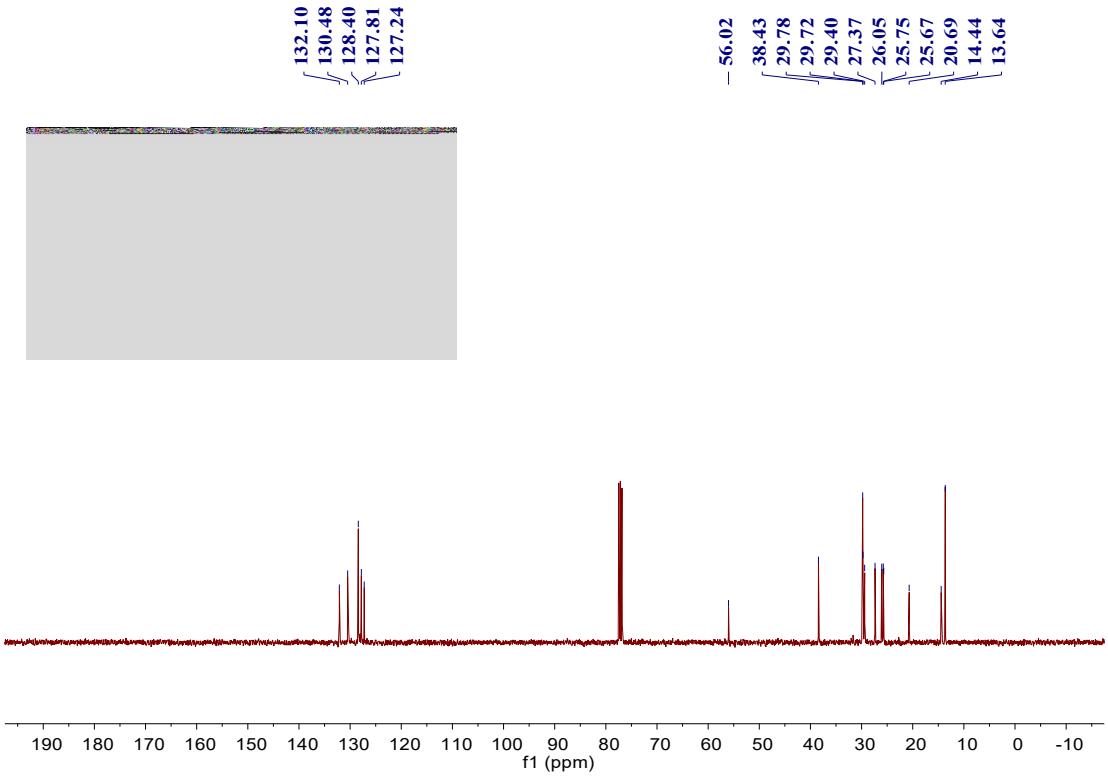


Figure S9 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **1p**

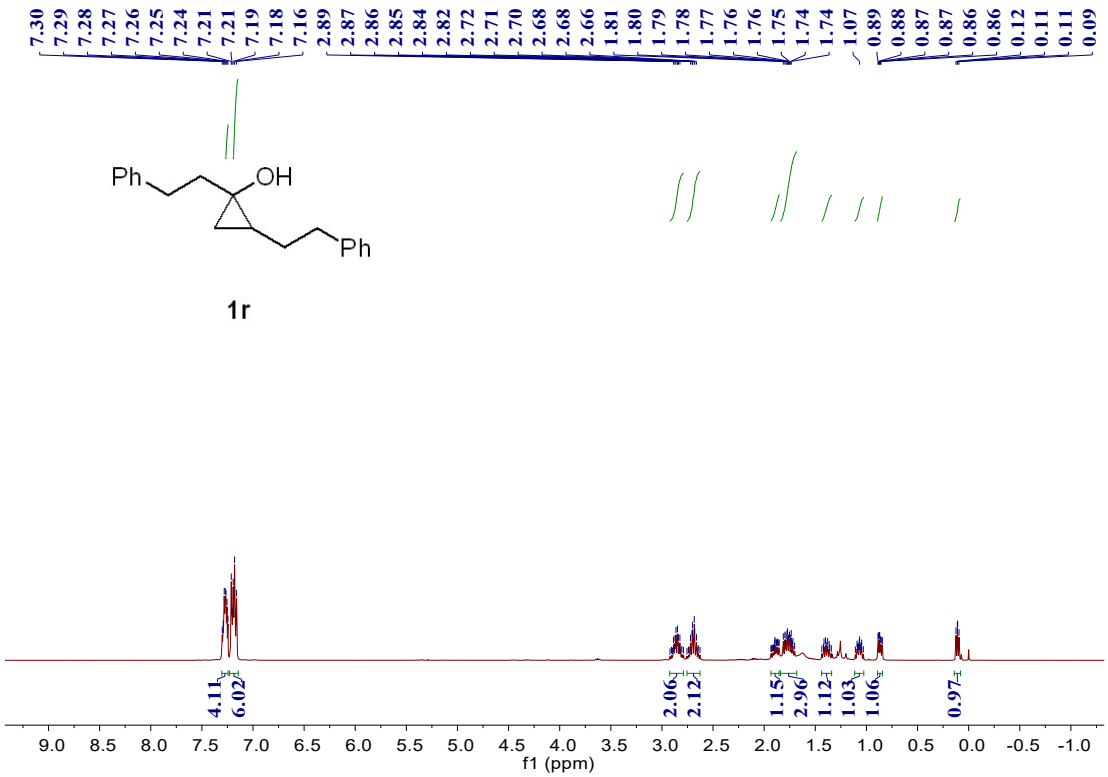


Figure S10 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **1r**

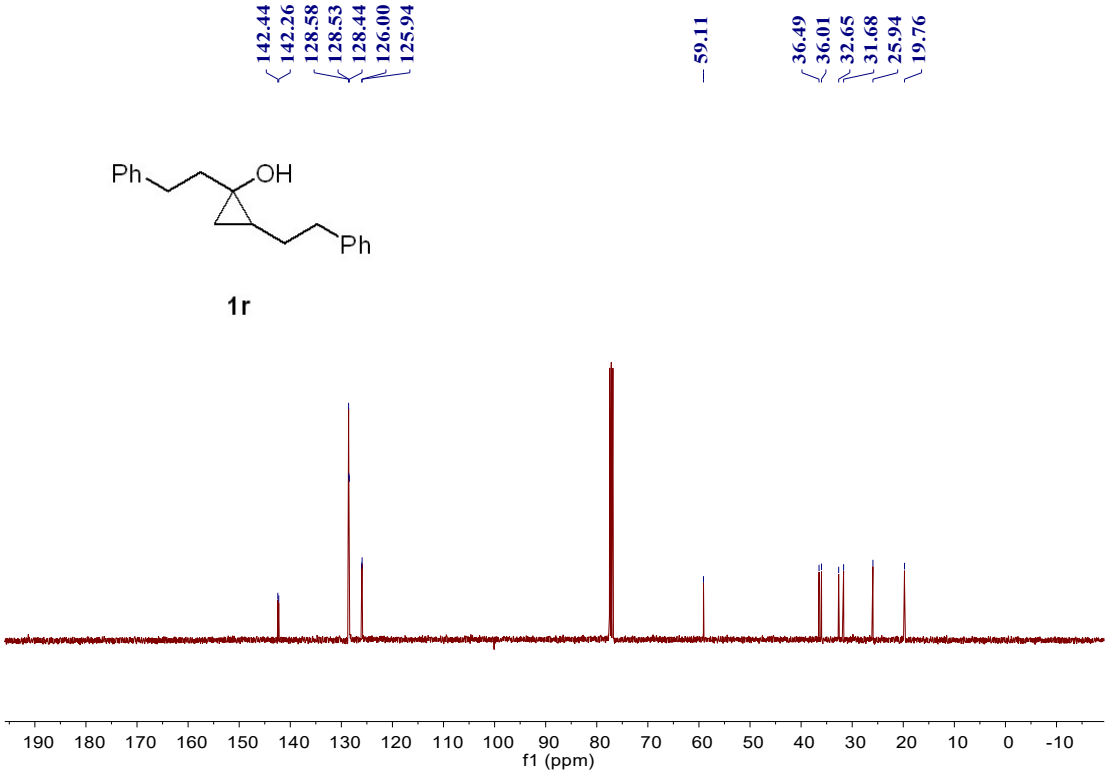


Figure S11 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **1r**

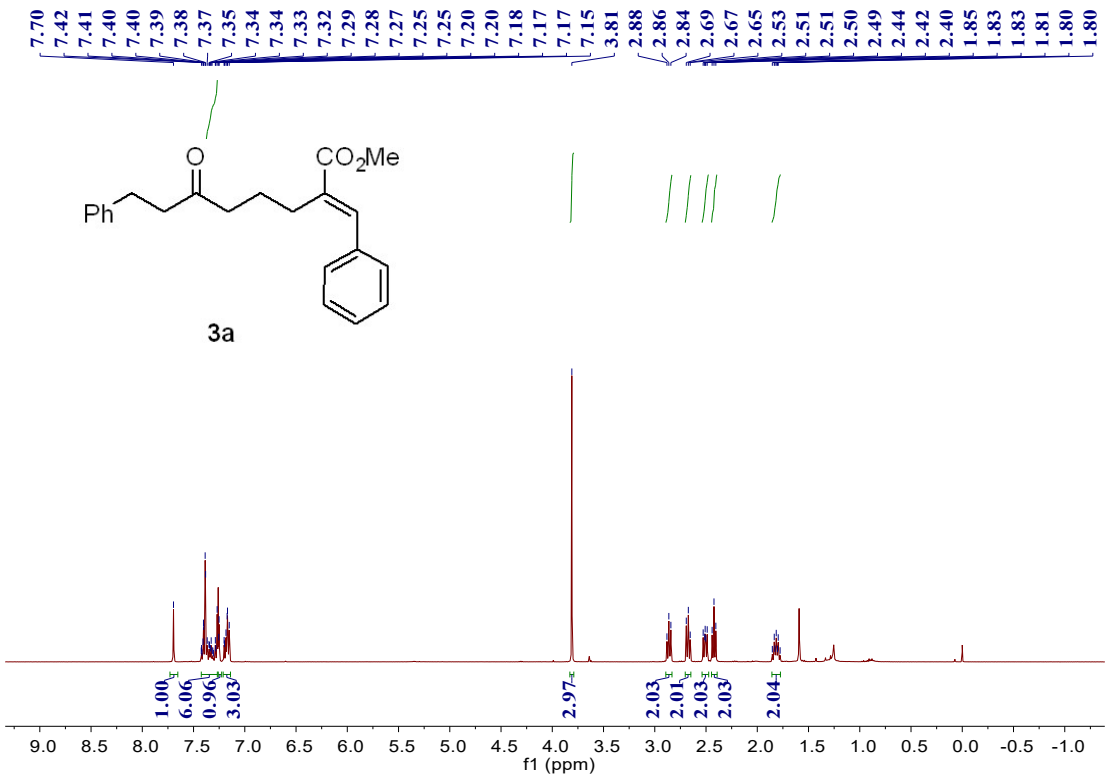


Figure S12 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3a**

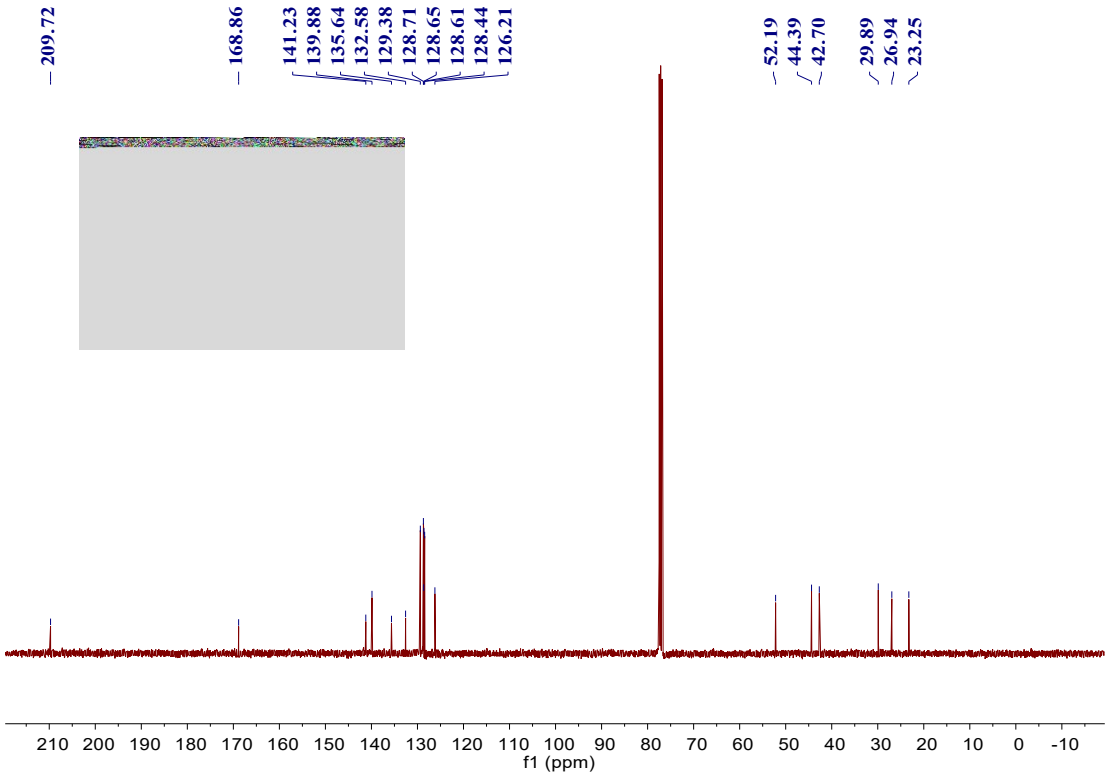


Figure S13 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3a**

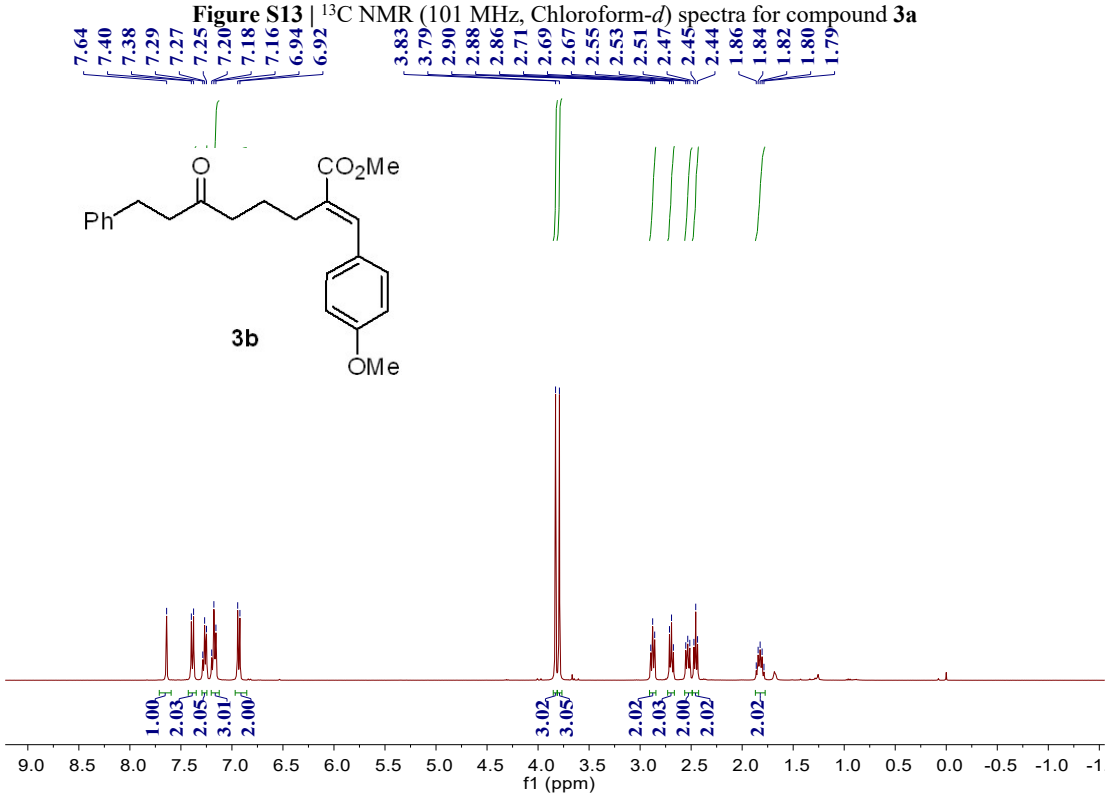


Figure S14 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3b**

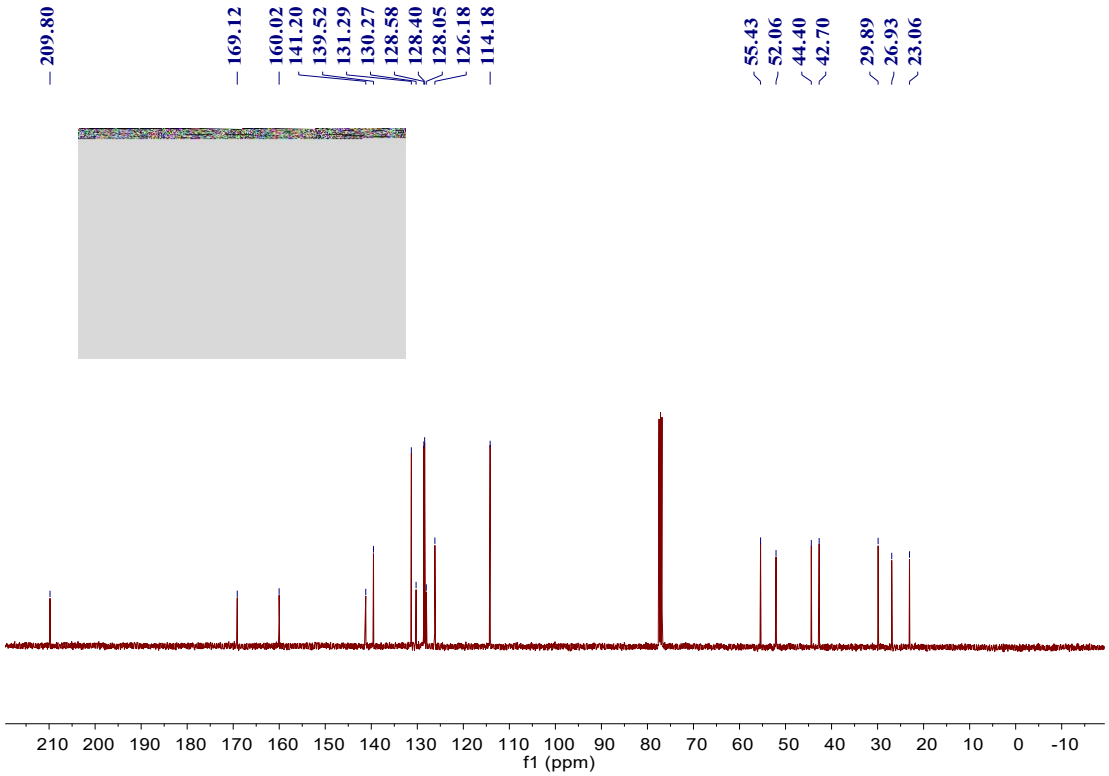


Figure S15 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3b**

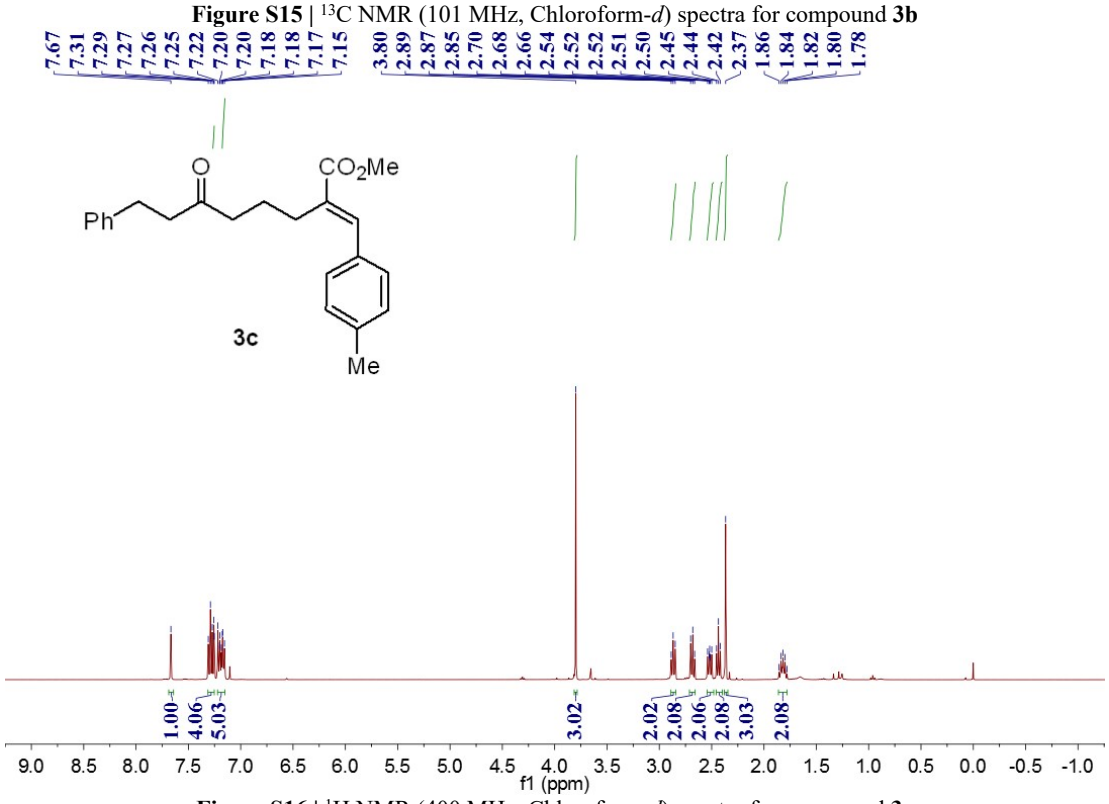


Figure S16 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3c**

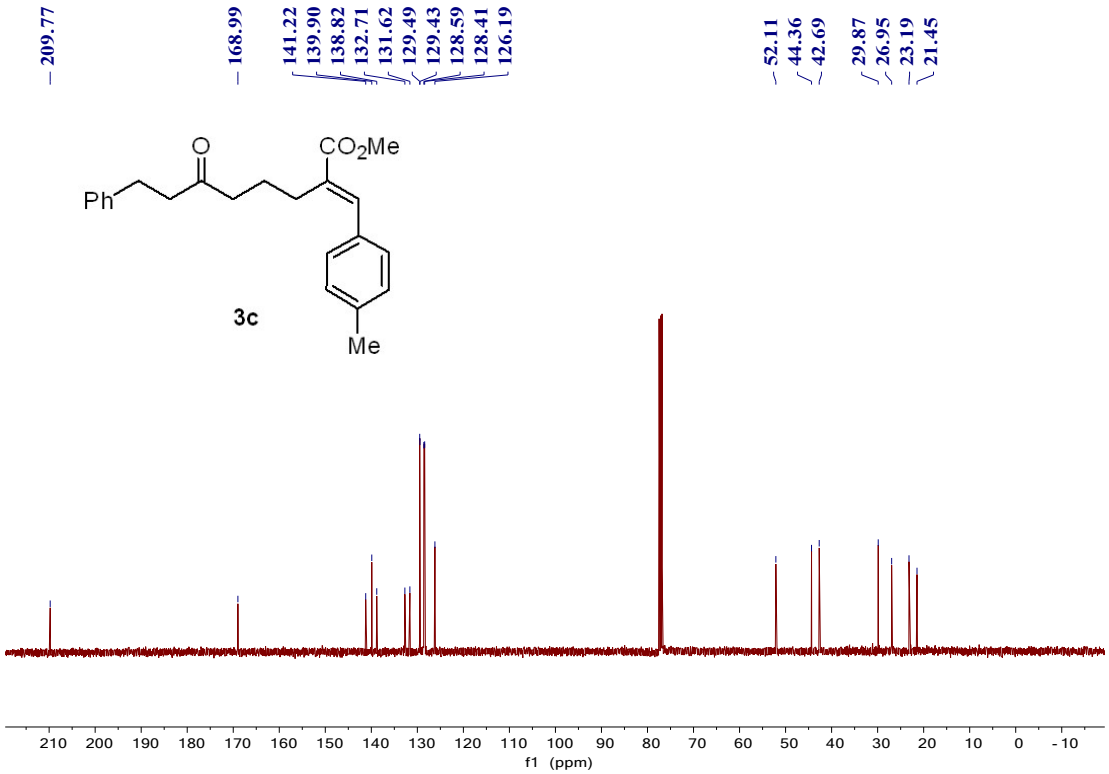


Figure S17 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3c**

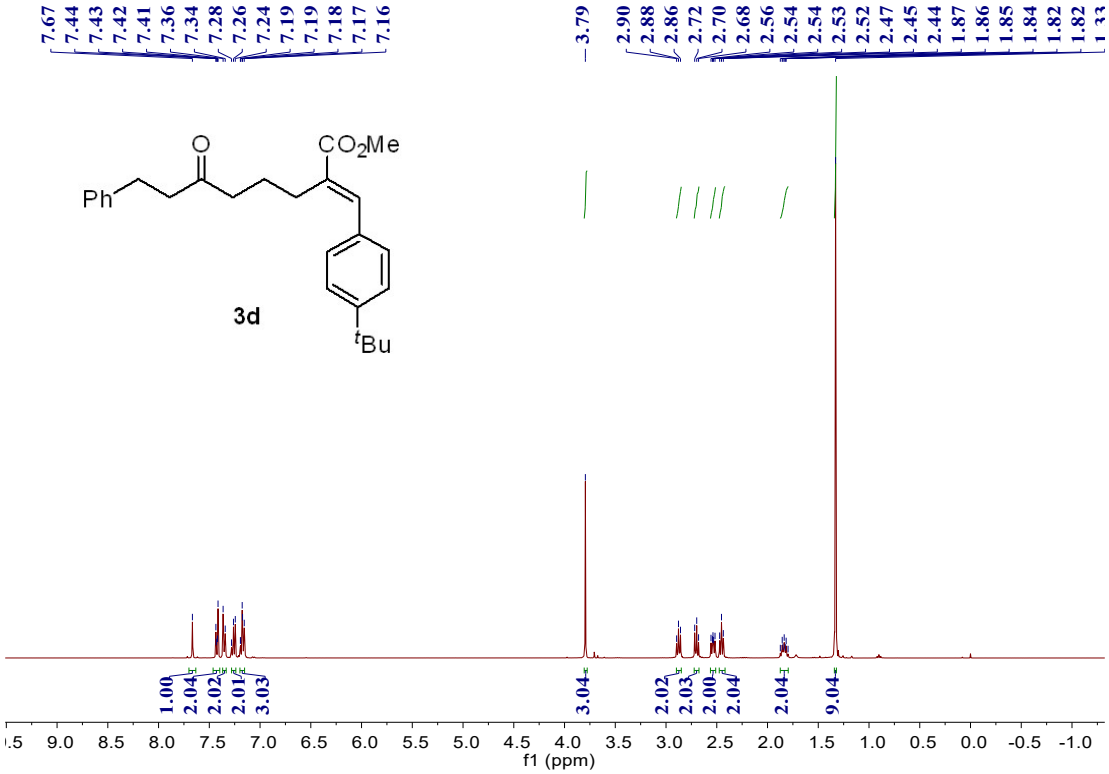


Figure S18 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3d**

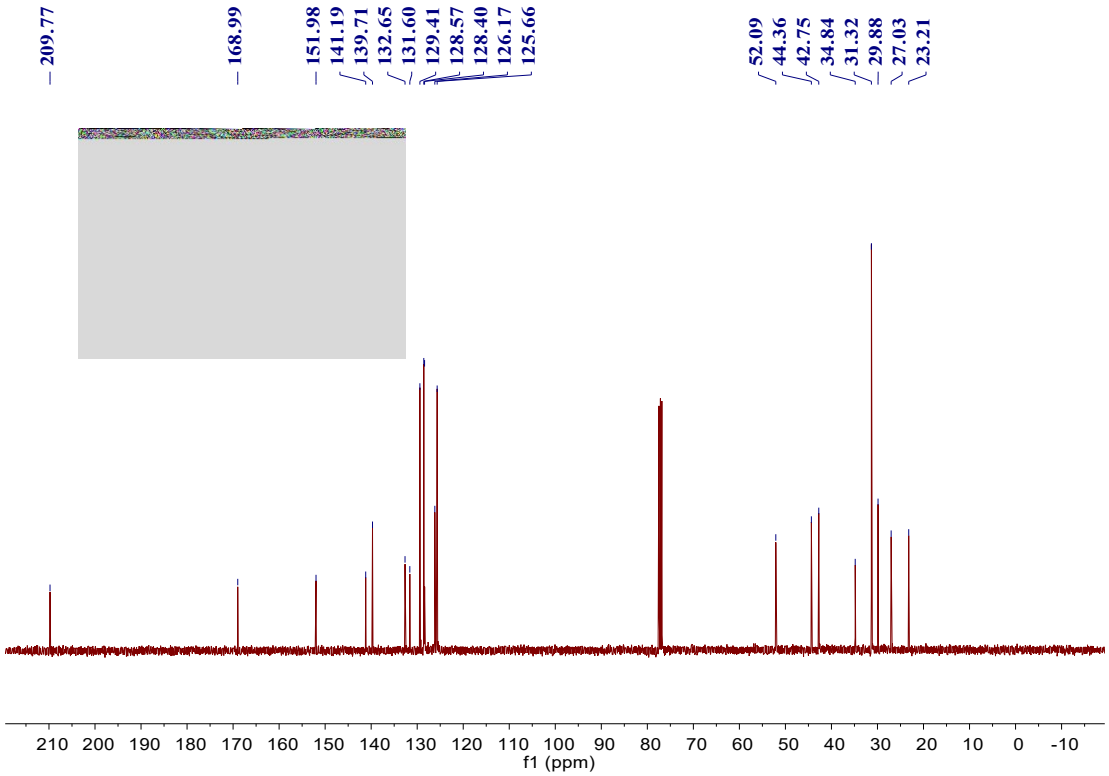


Figure S19 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3d**

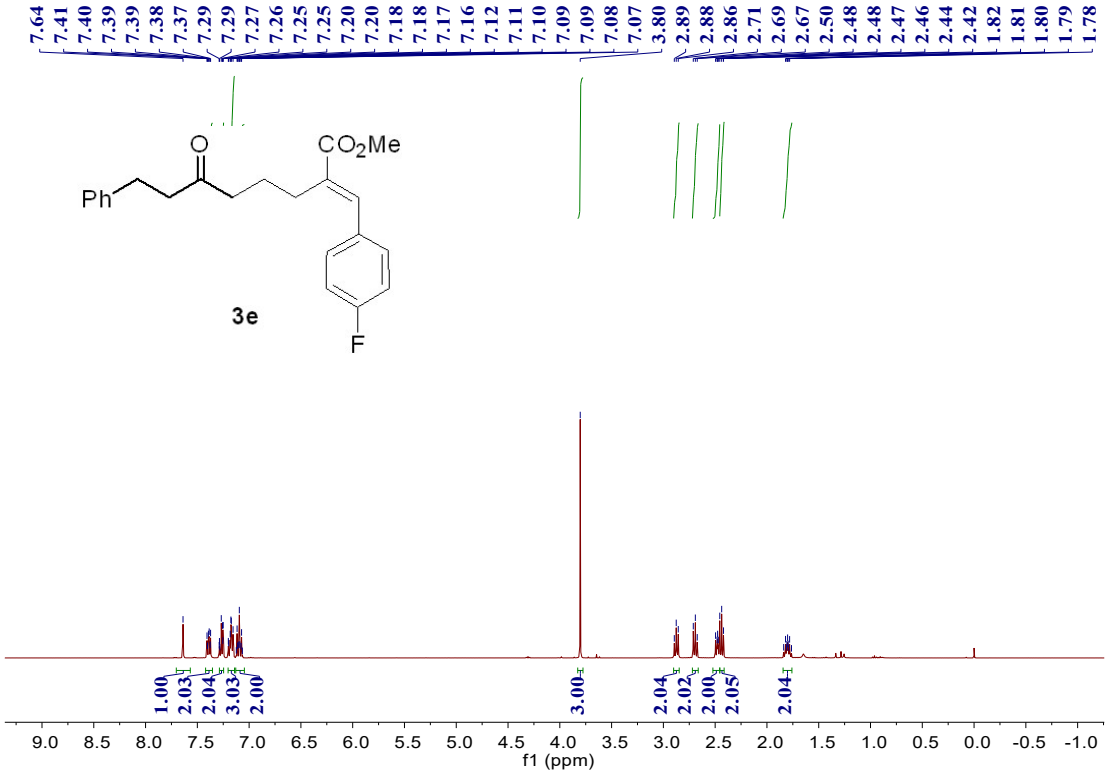


Figure S20 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3e**

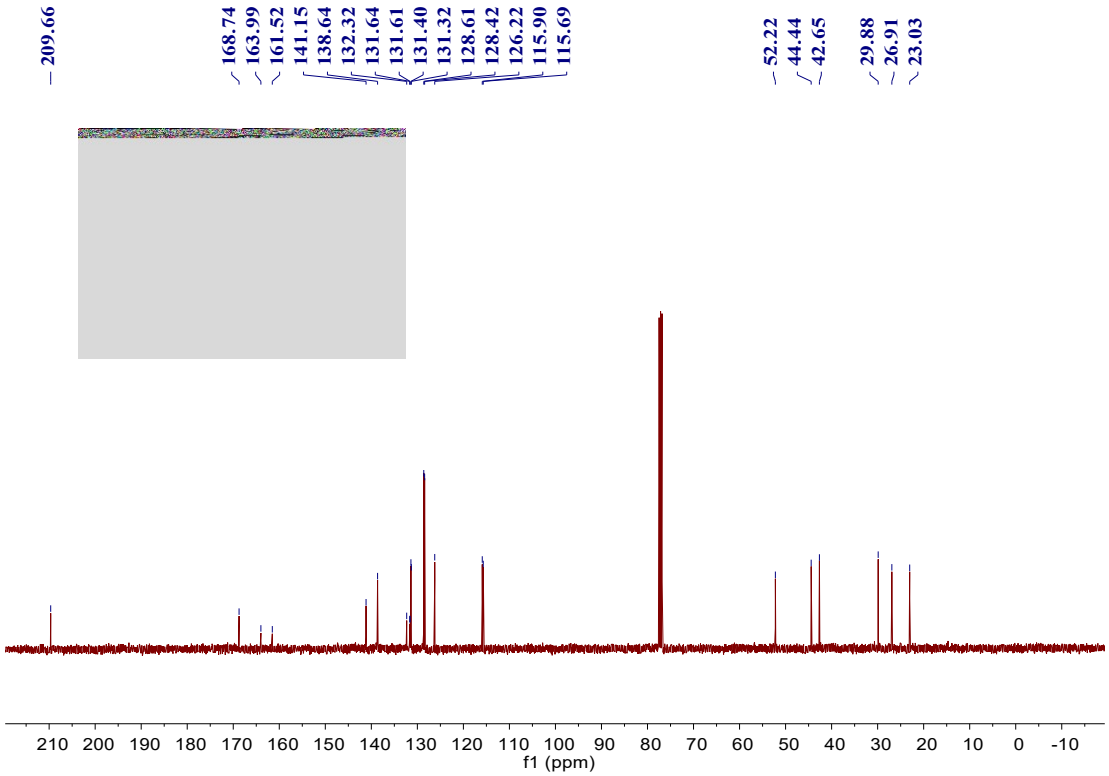


Figure S21 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3e**

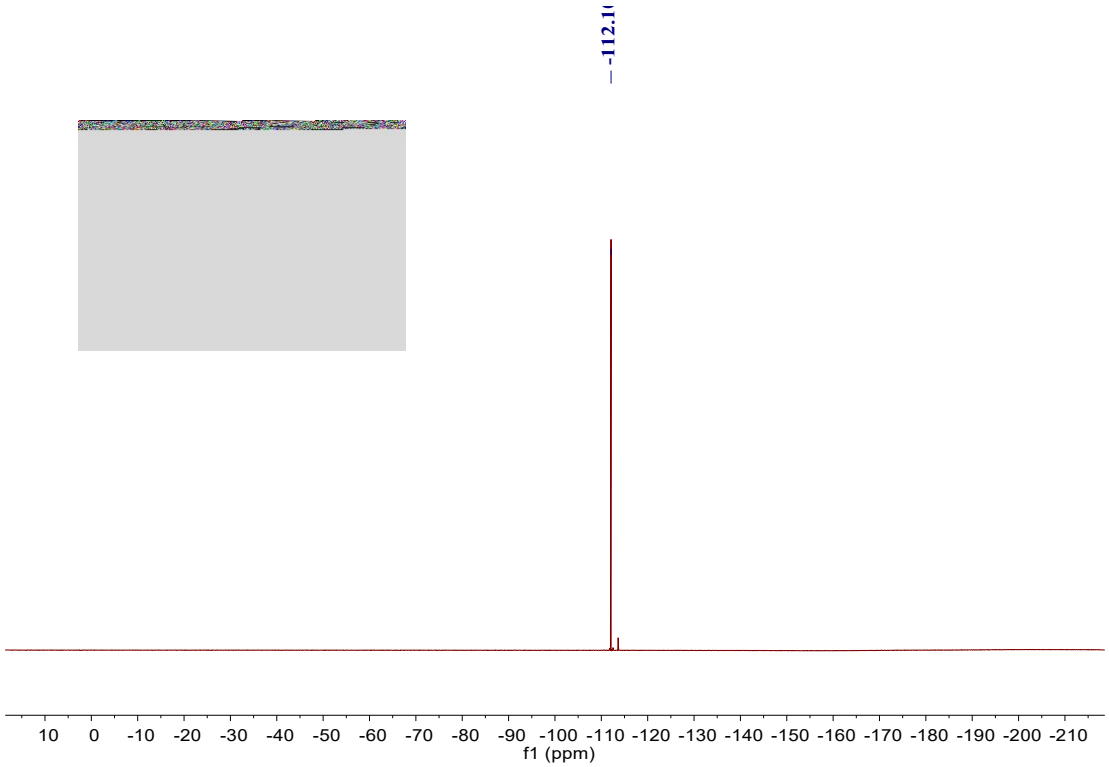


Figure S22 | ^{19}F NMR (376 MHz, Chloroform-*d*) spectra for compound **3e**

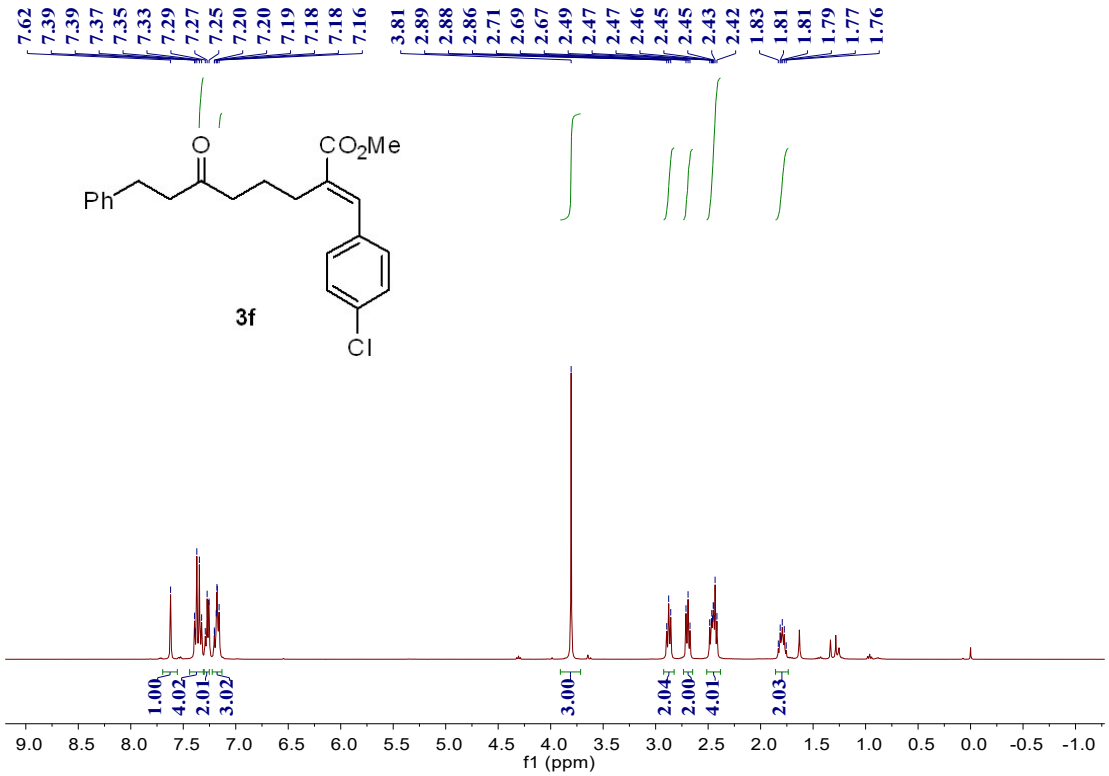


Figure S23 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3f**

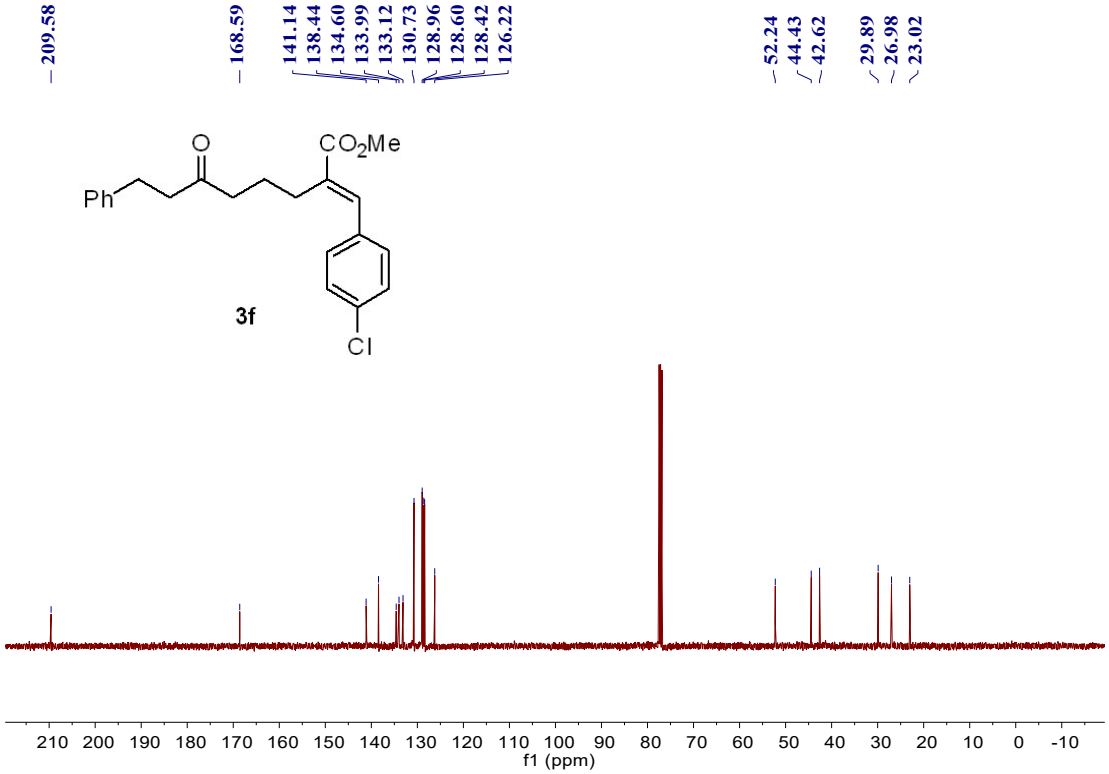


Figure S24 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3f**

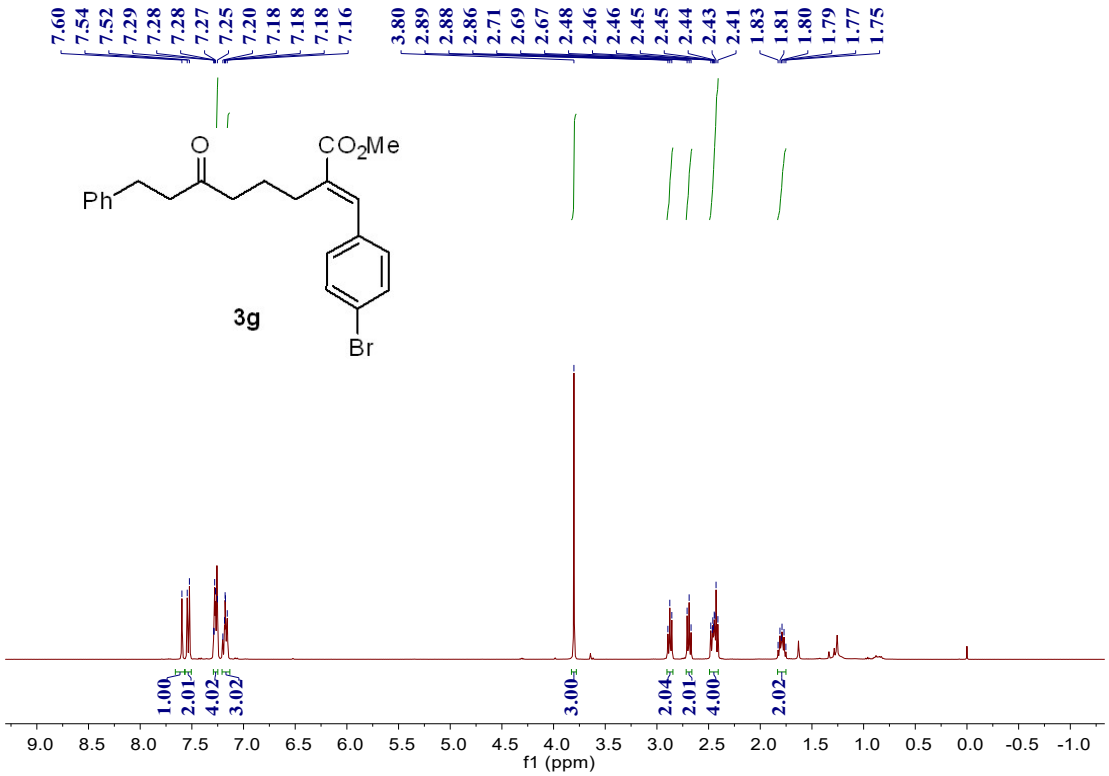


Figure S25 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3g**

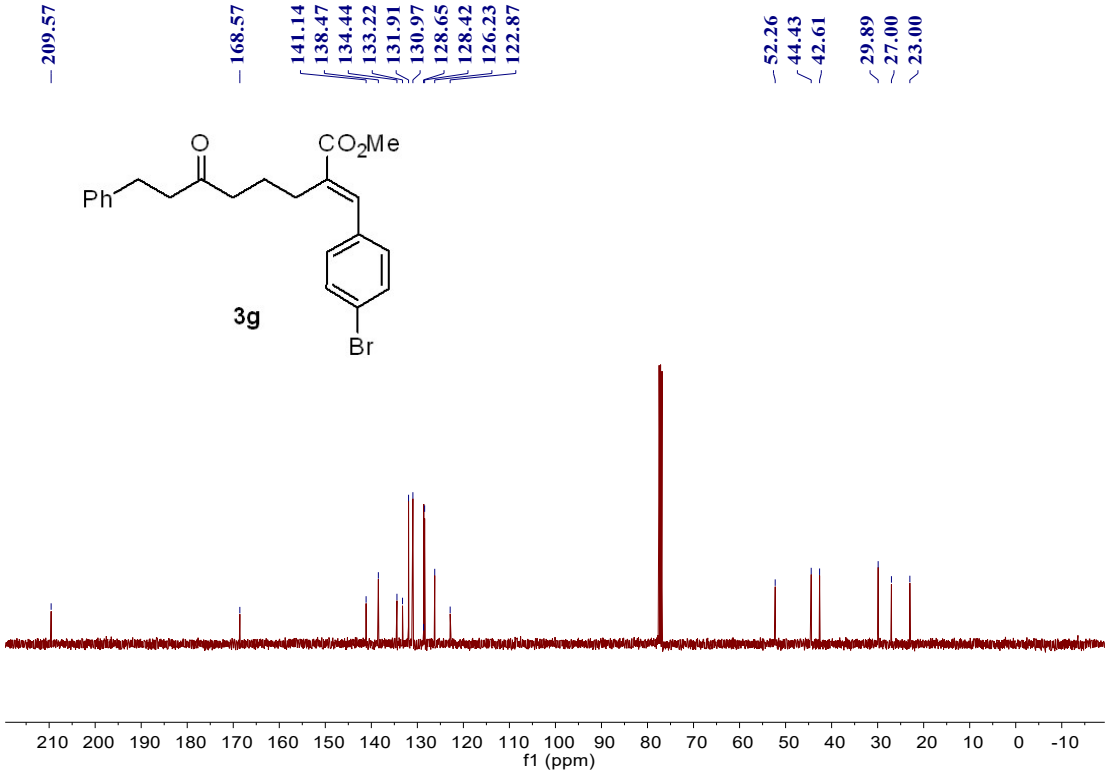


Figure S26 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3g**

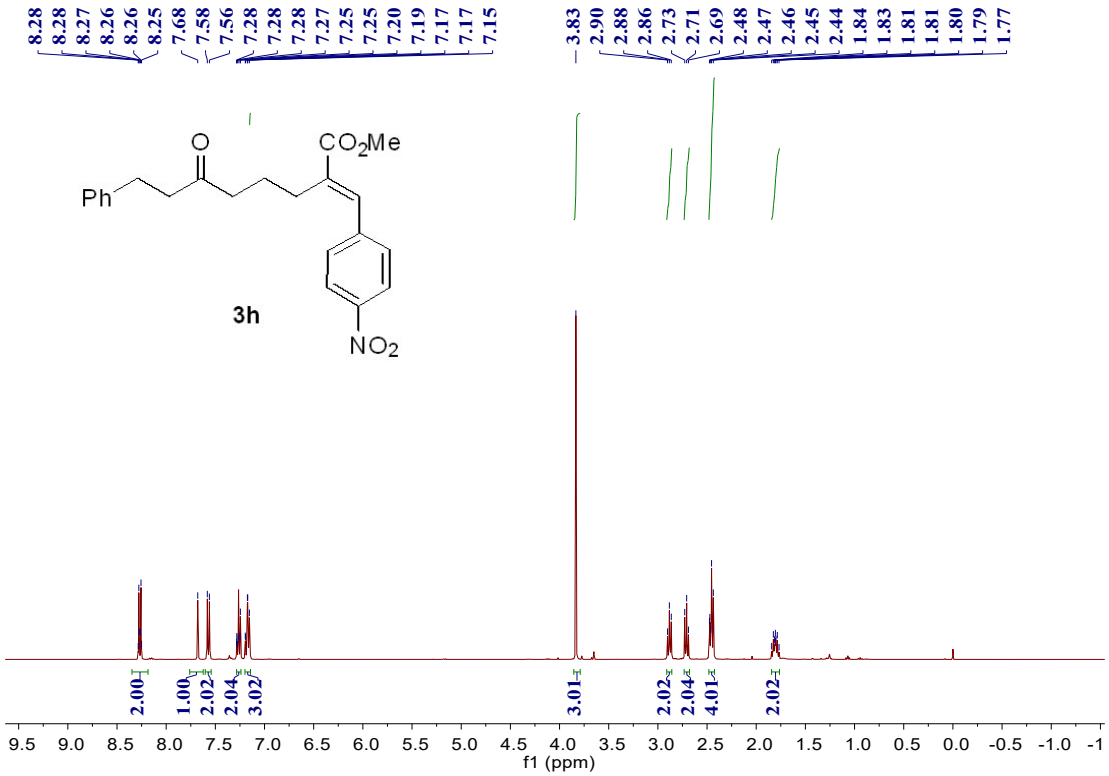


Figure S27 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3h**

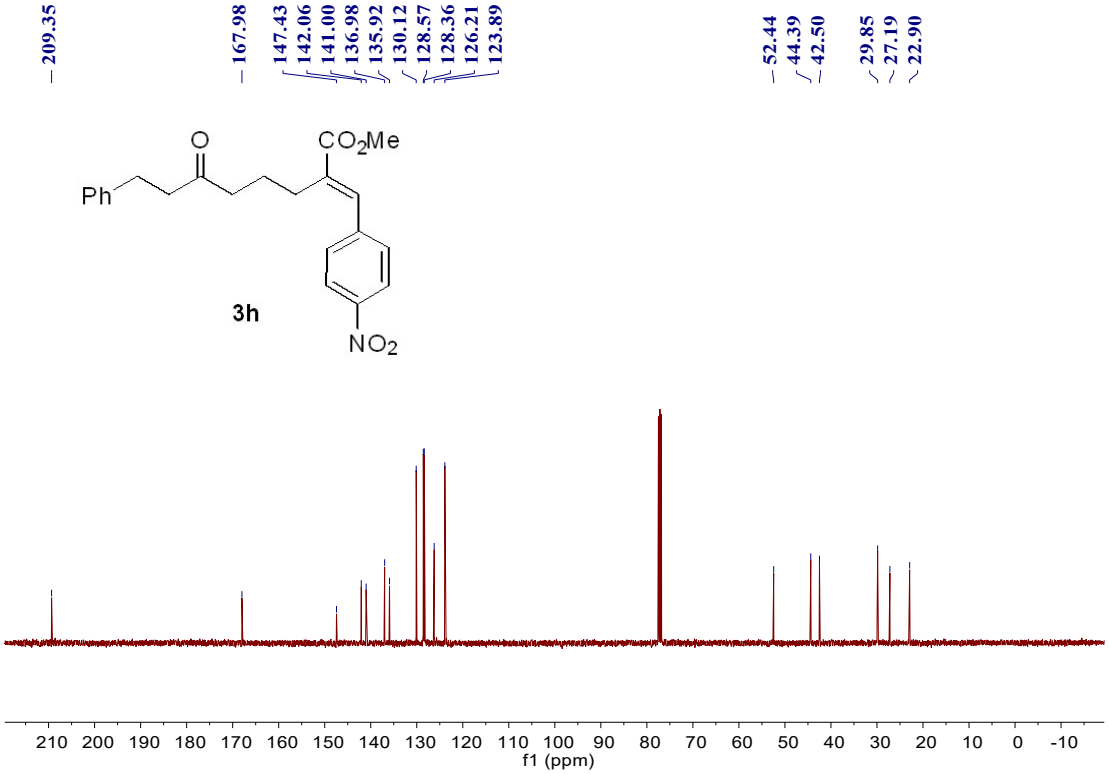


Figure S28 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3h**

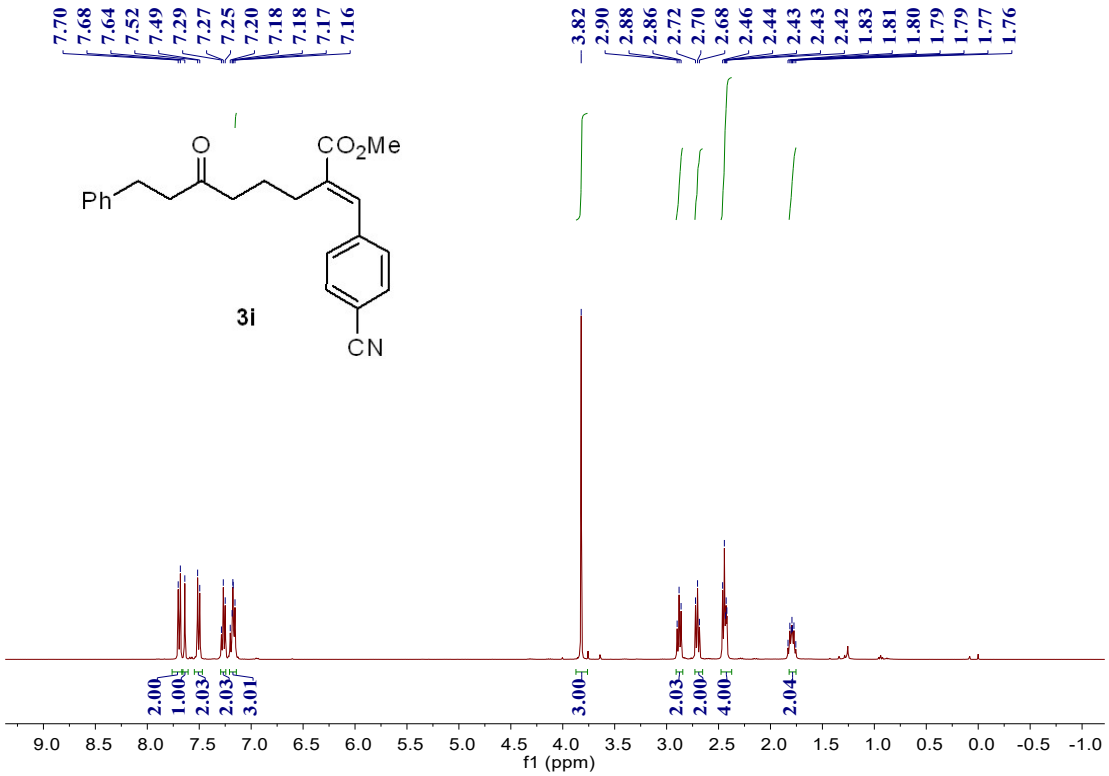


Figure S29 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3i**

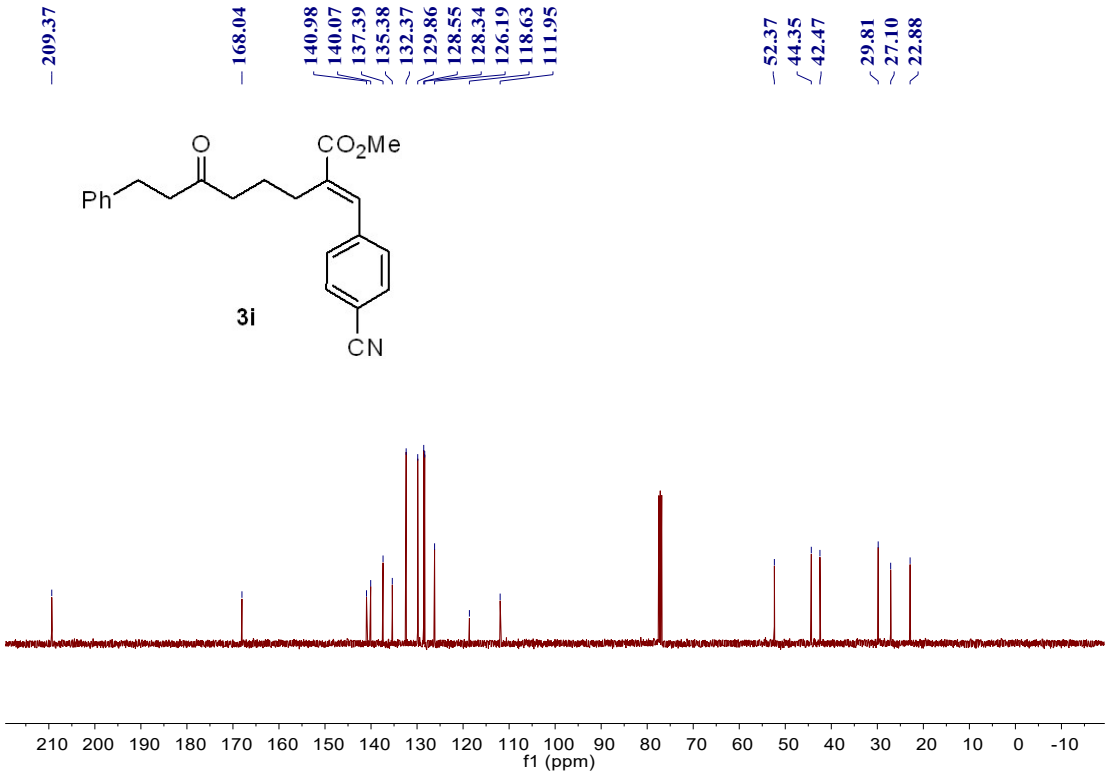


Figure S30 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3i**

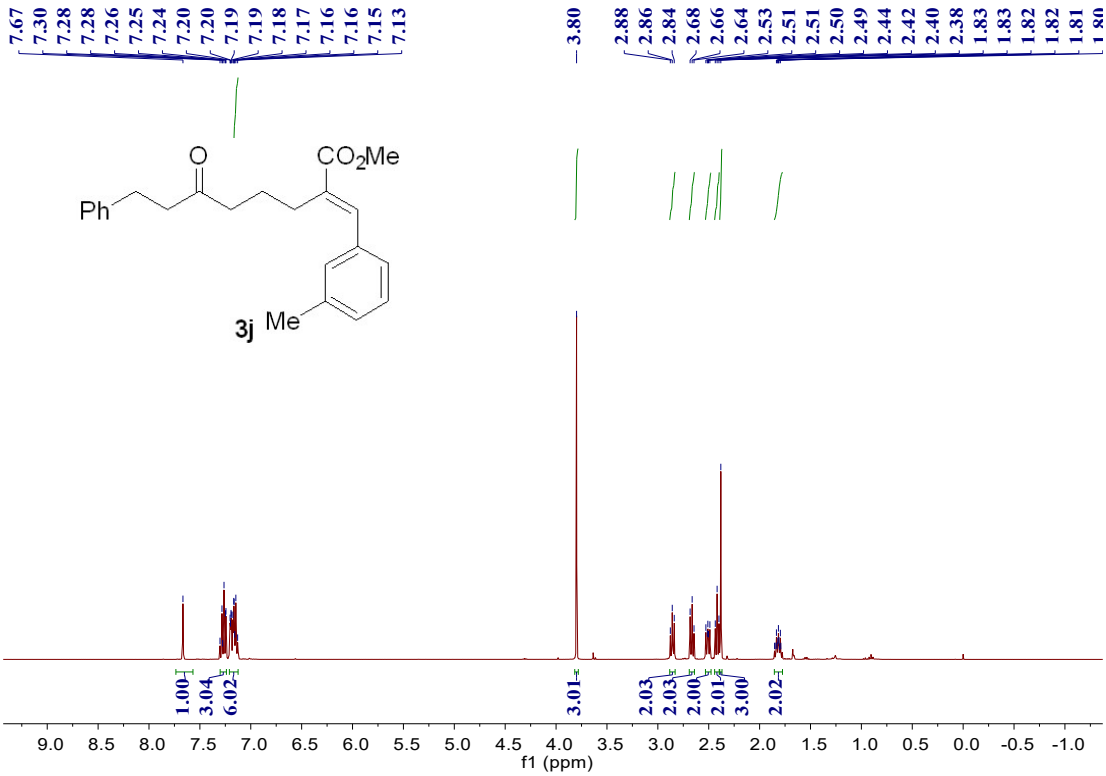


Figure S31 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3j**

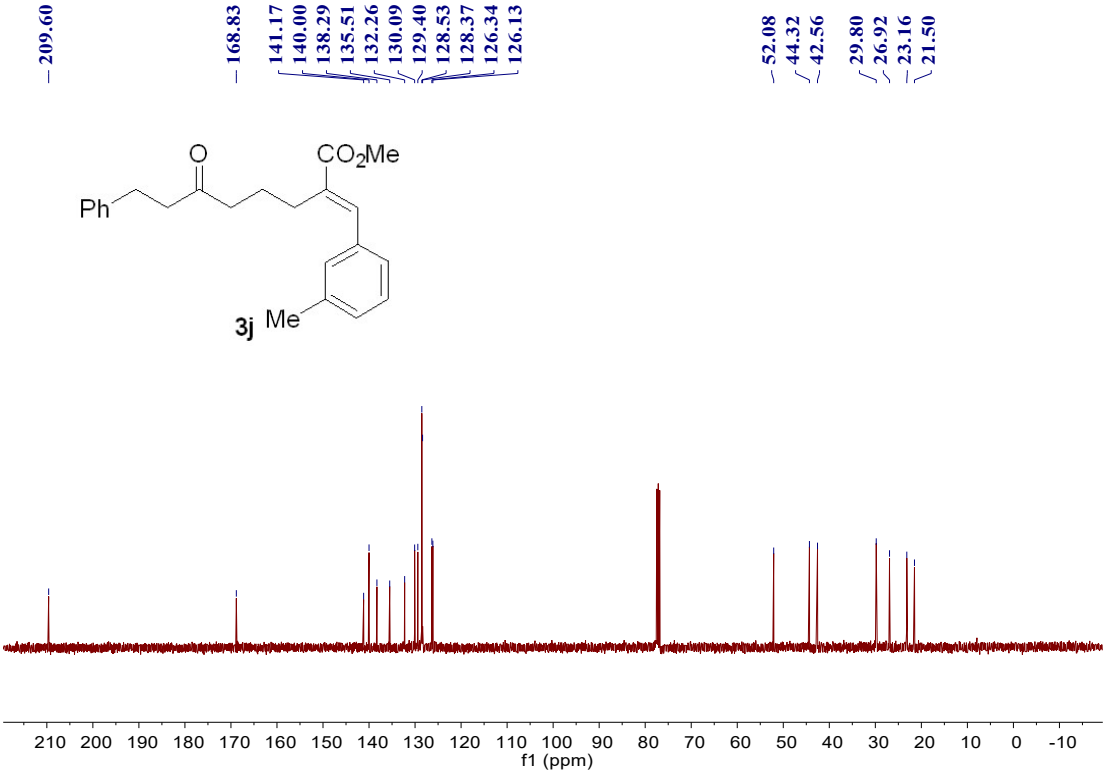


Figure S32 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3j**

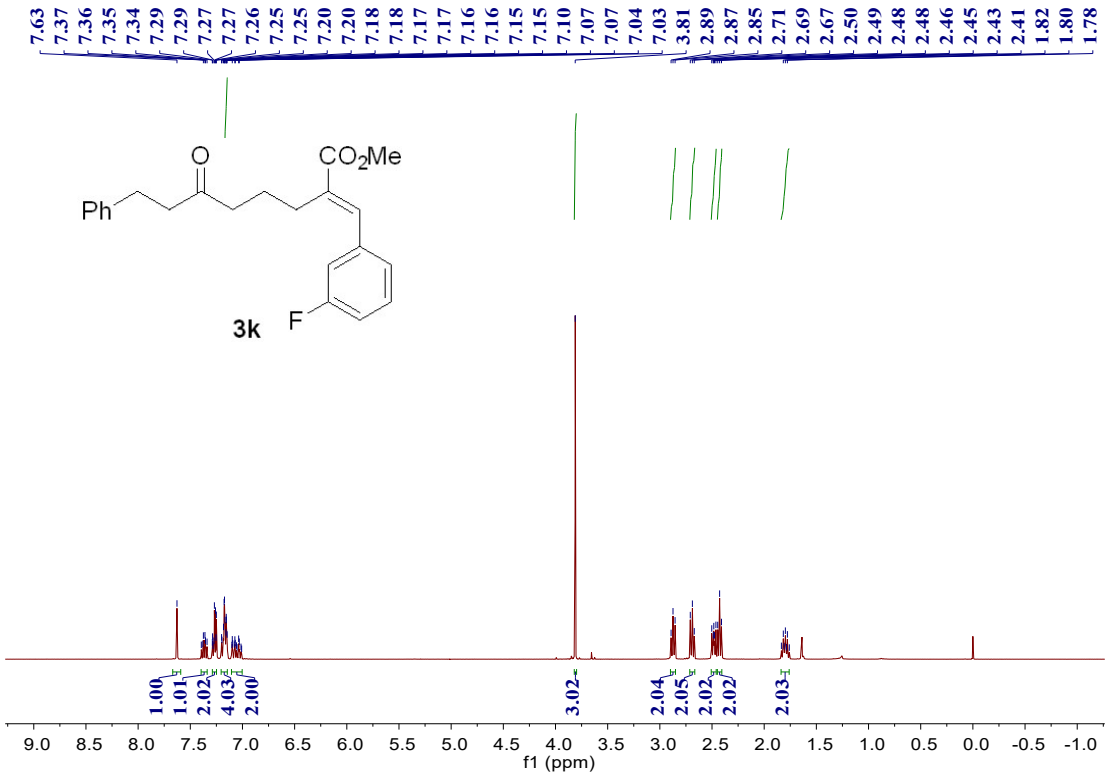


Figure S33 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3k**

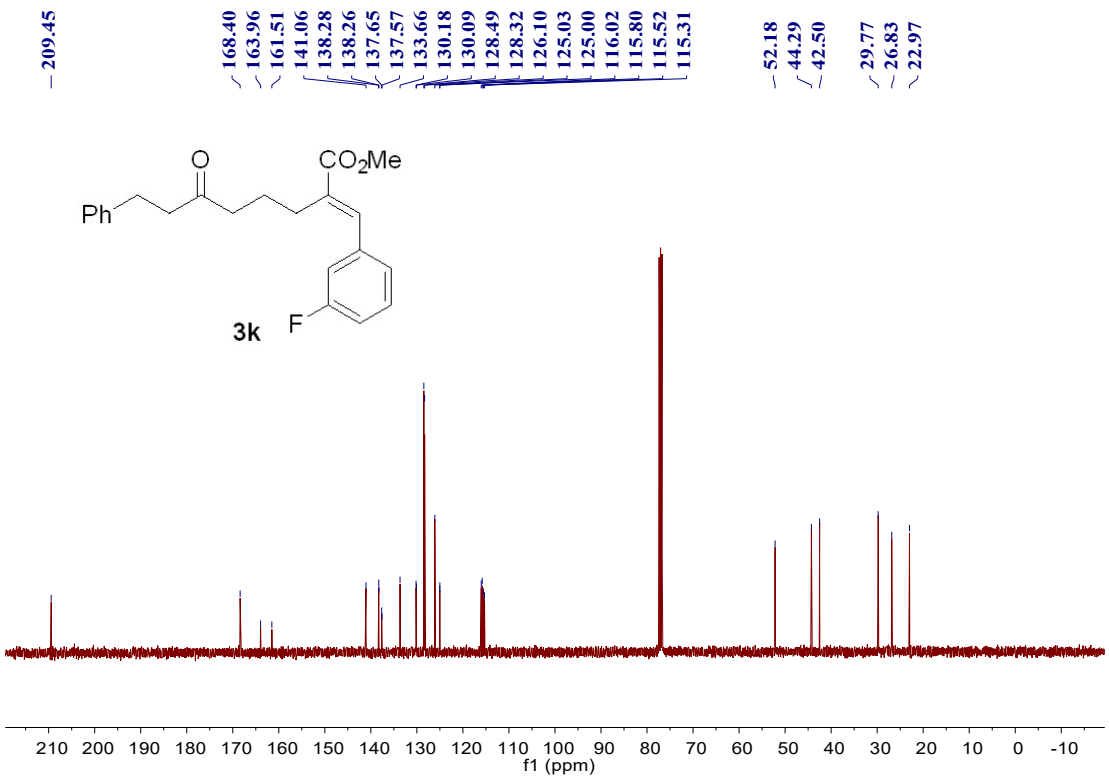


Figure S34 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3k**

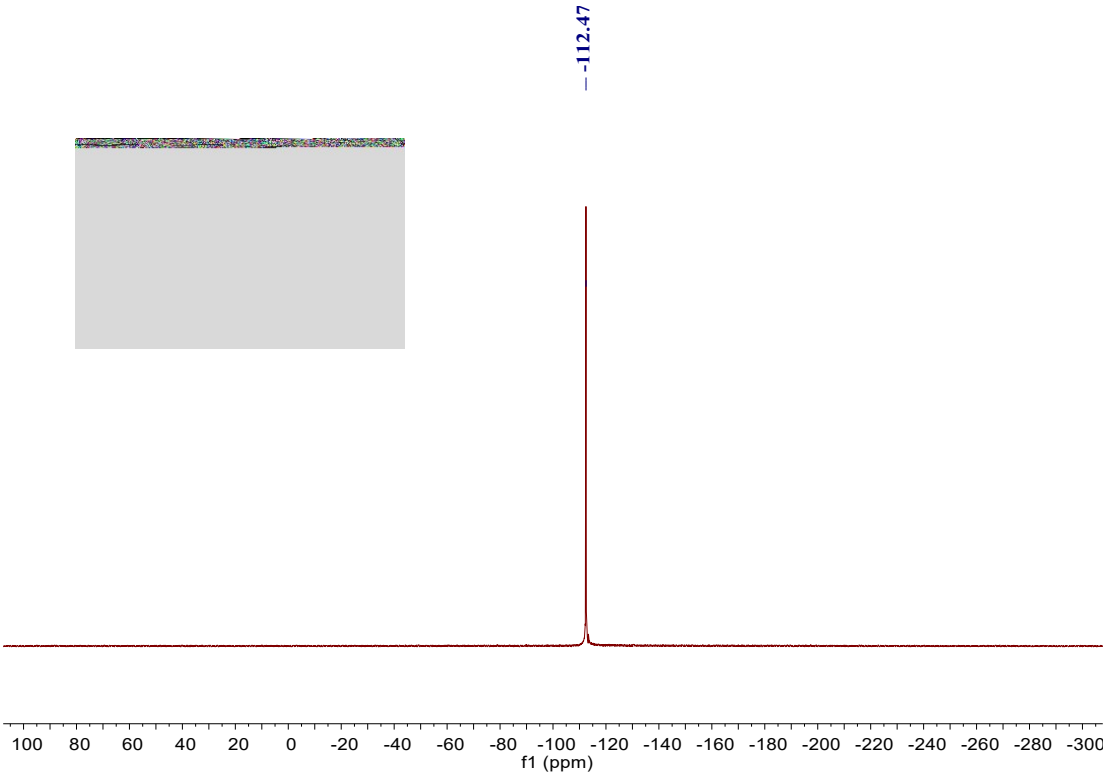


Figure S35 | ^{19}F NMR (376 MHz, Chloroform-*d*) spectra for compound **3k**

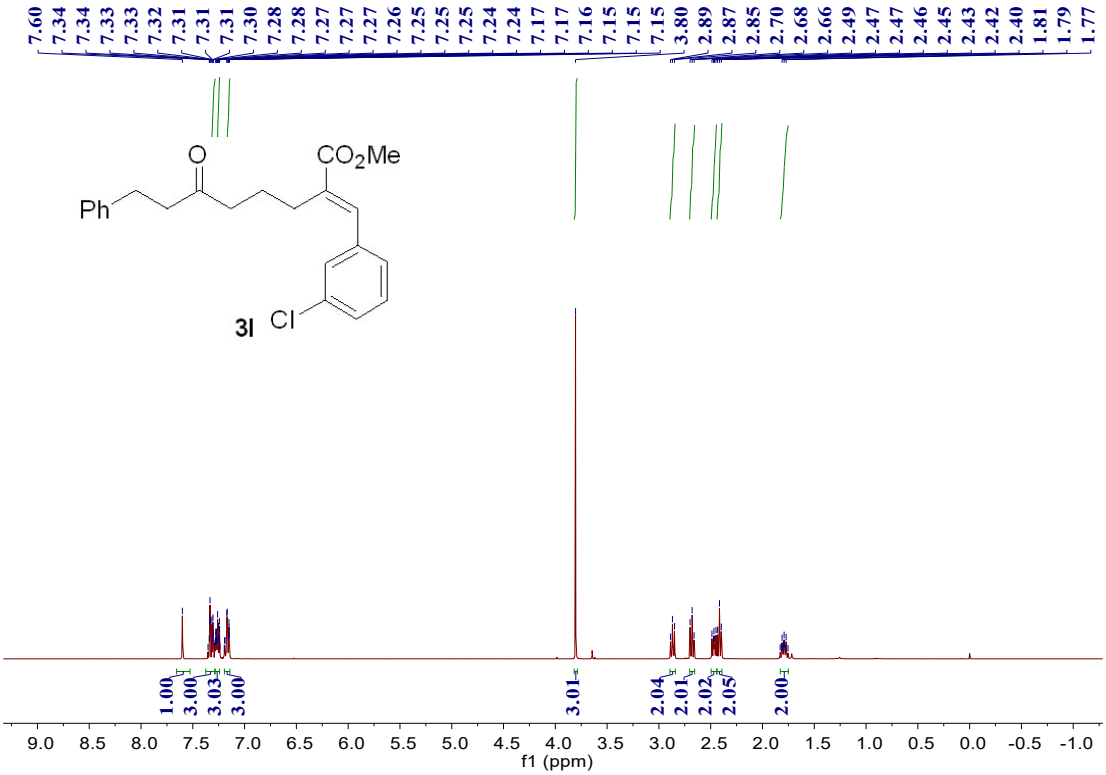


Figure S36 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3l**

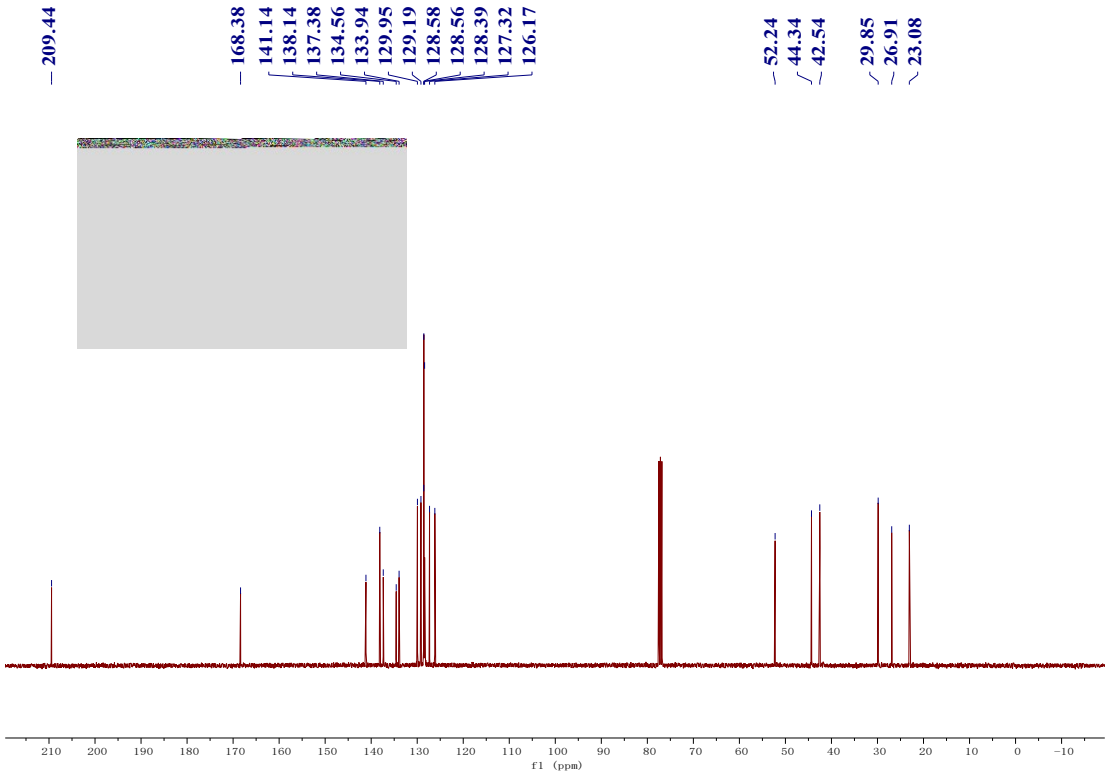


Figure S37 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3l**

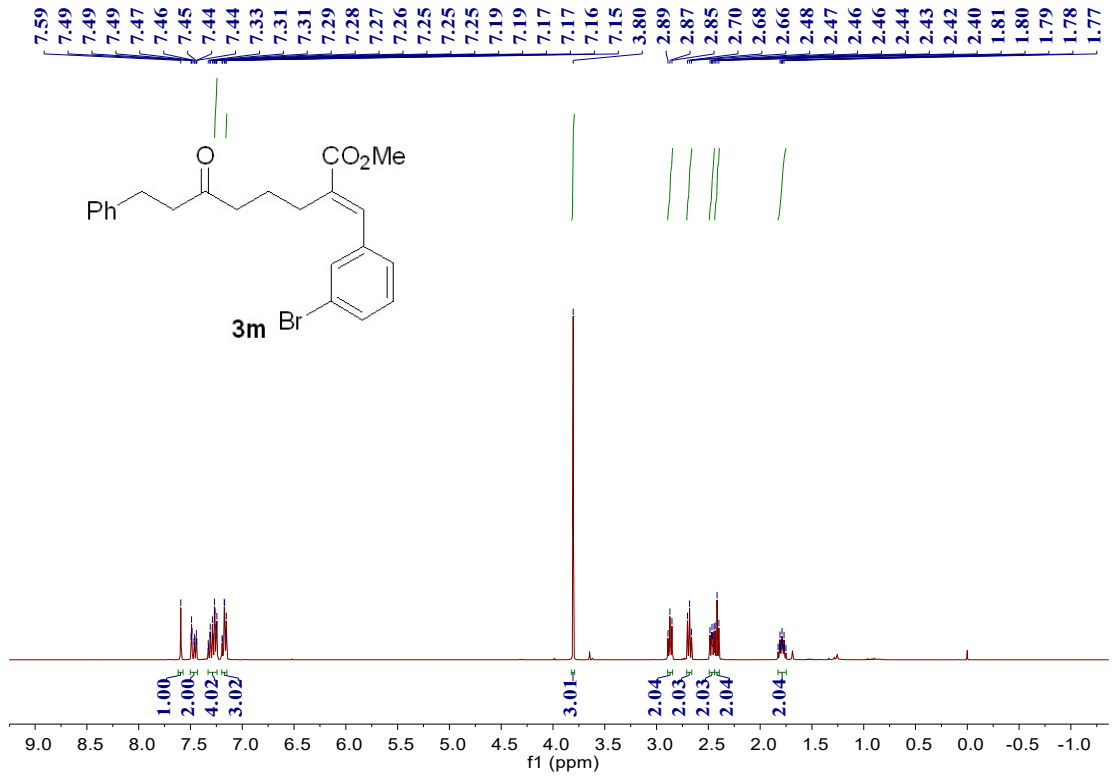


Figure S38 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3m**

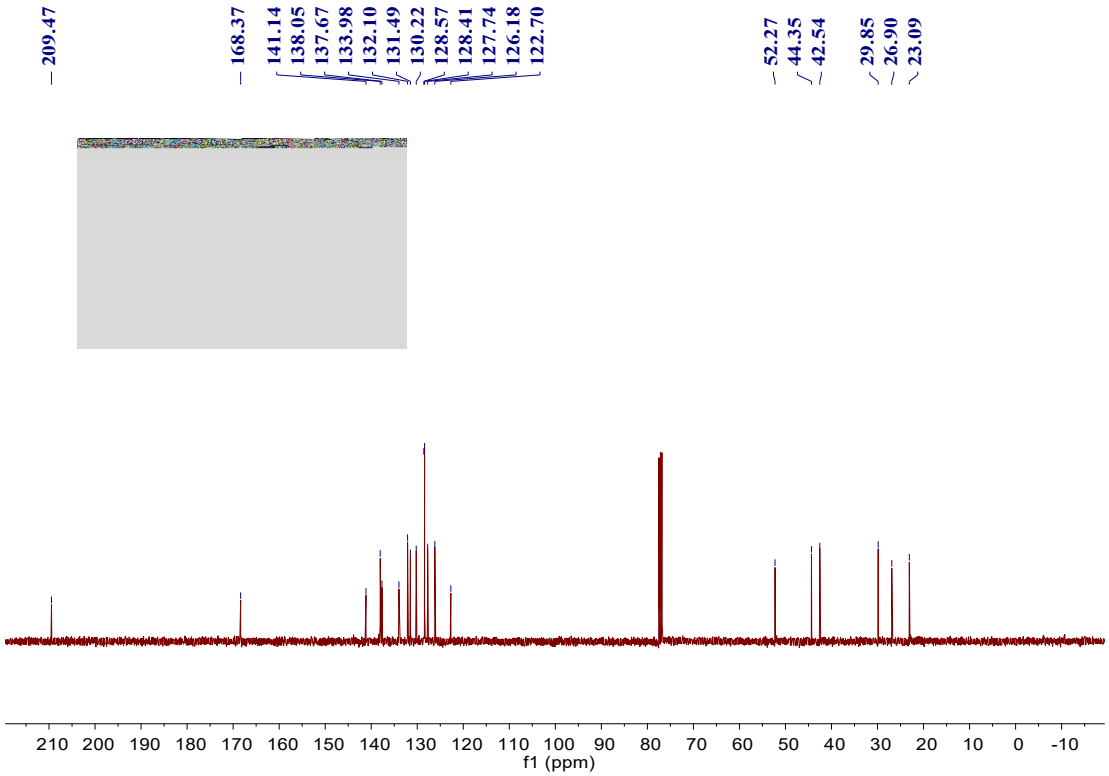


Figure S39 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3m**

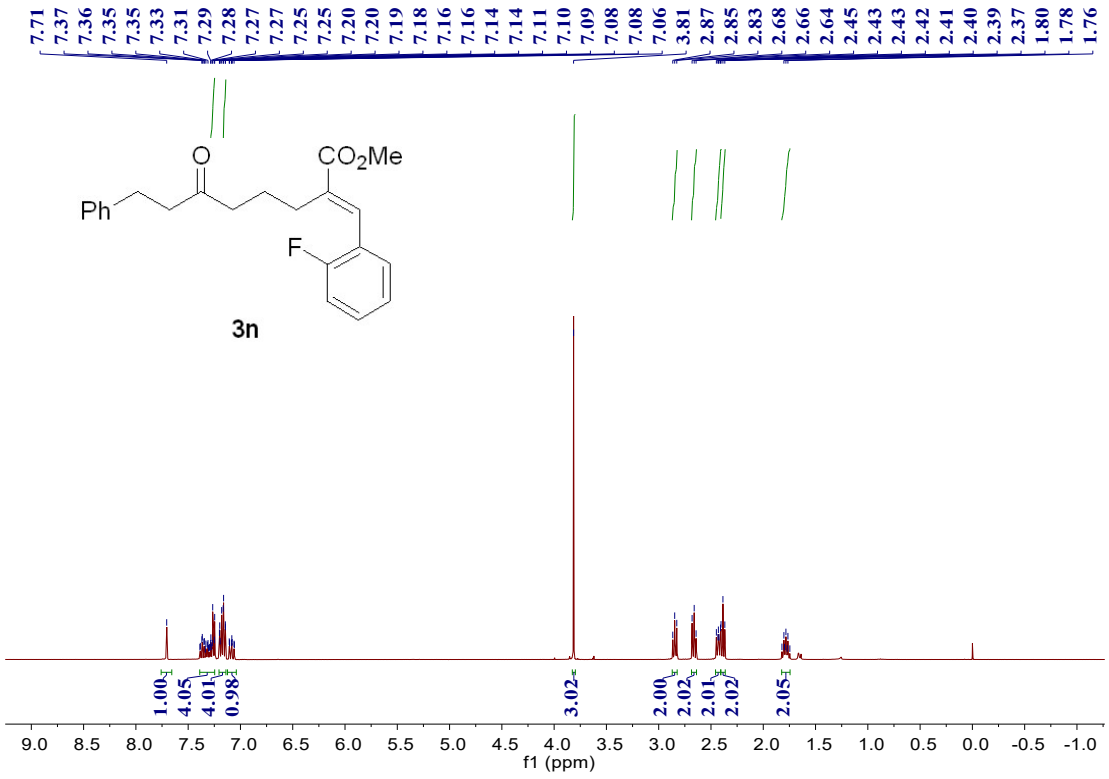


Figure S40 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3n**

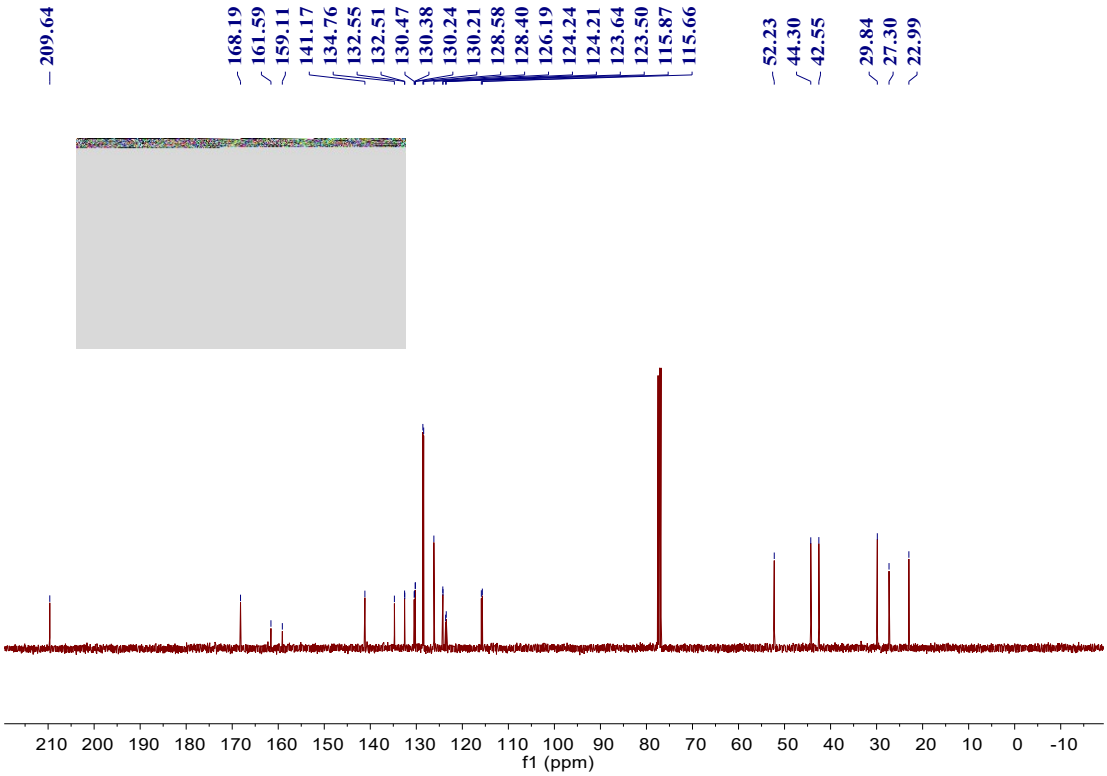


Figure S41 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3n**

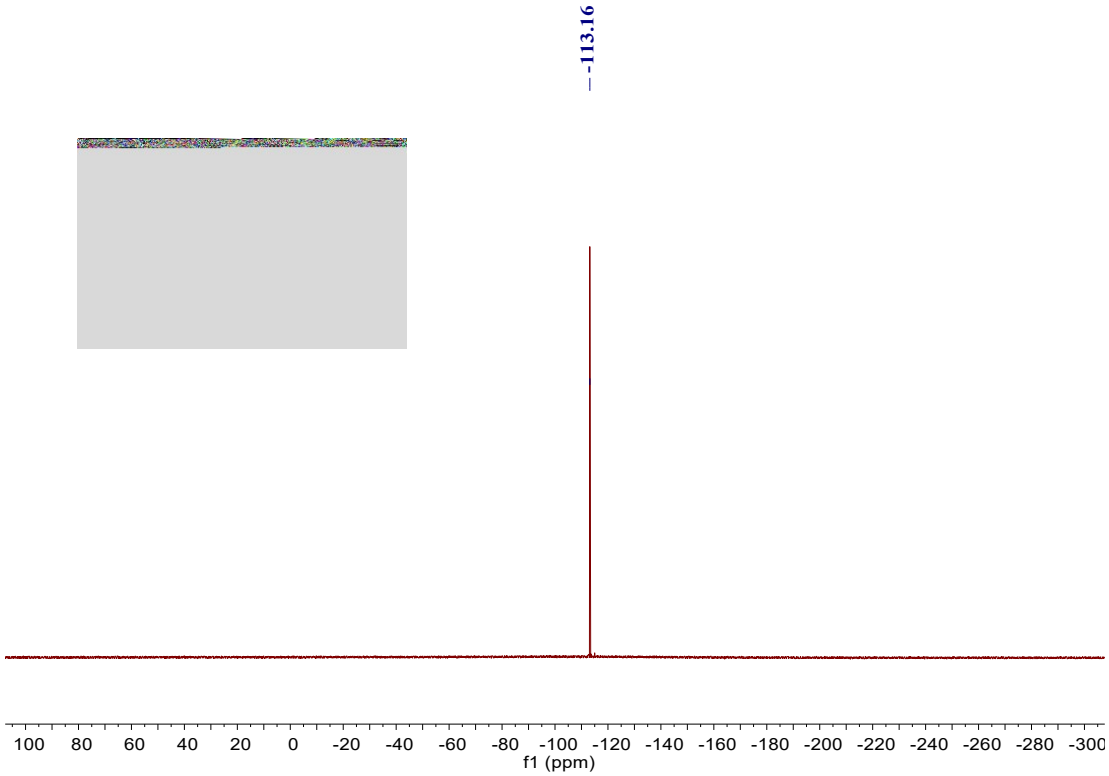


Figure S42 | ^{19}F NMR (376 MHz, Chloroform-*d*) spectra for compound **3n**

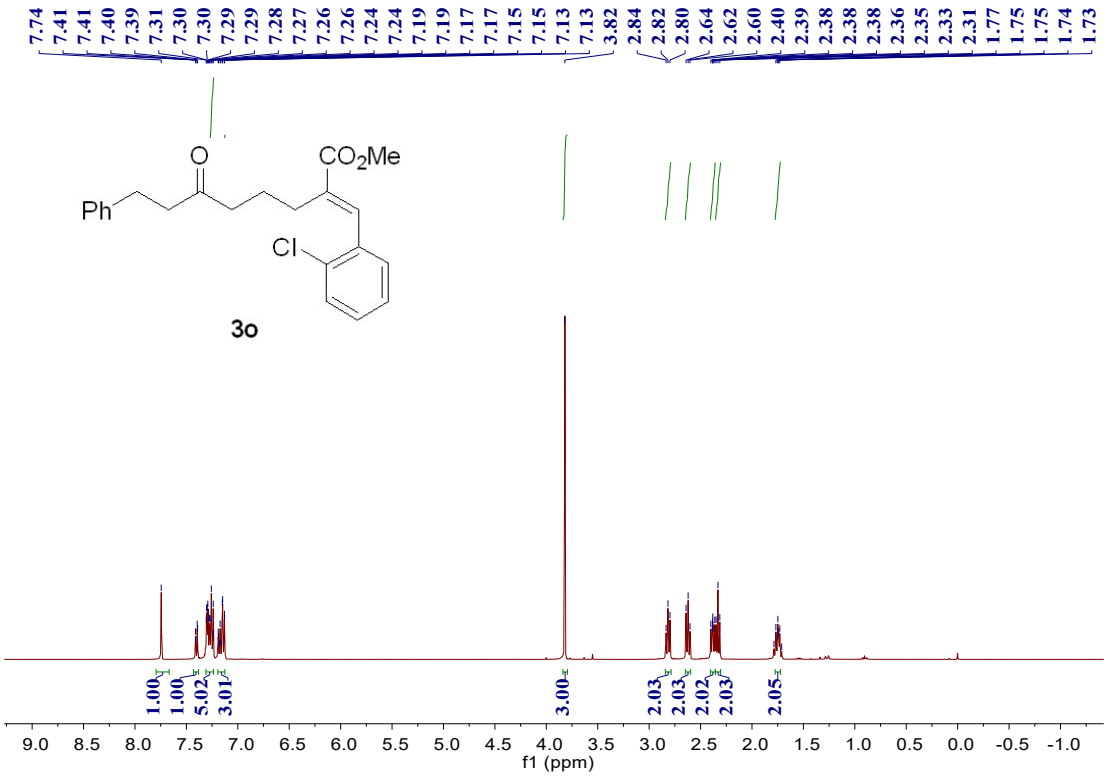


Figure S43 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3o**

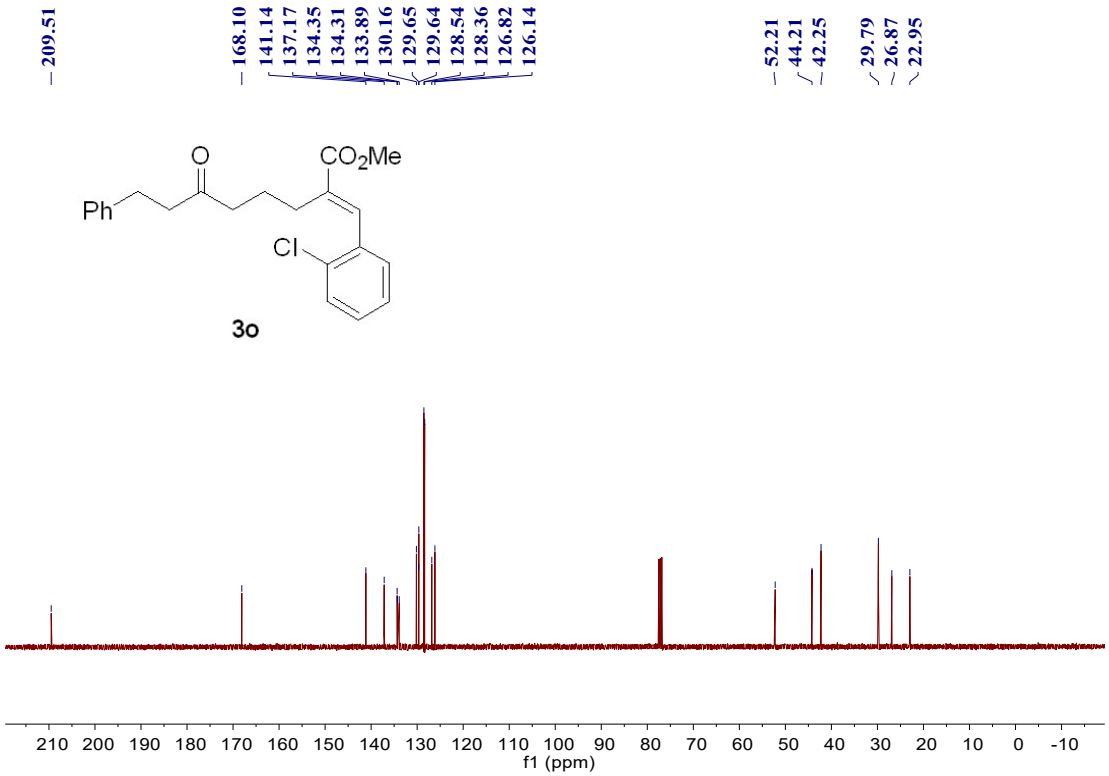


Figure S44 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3o**

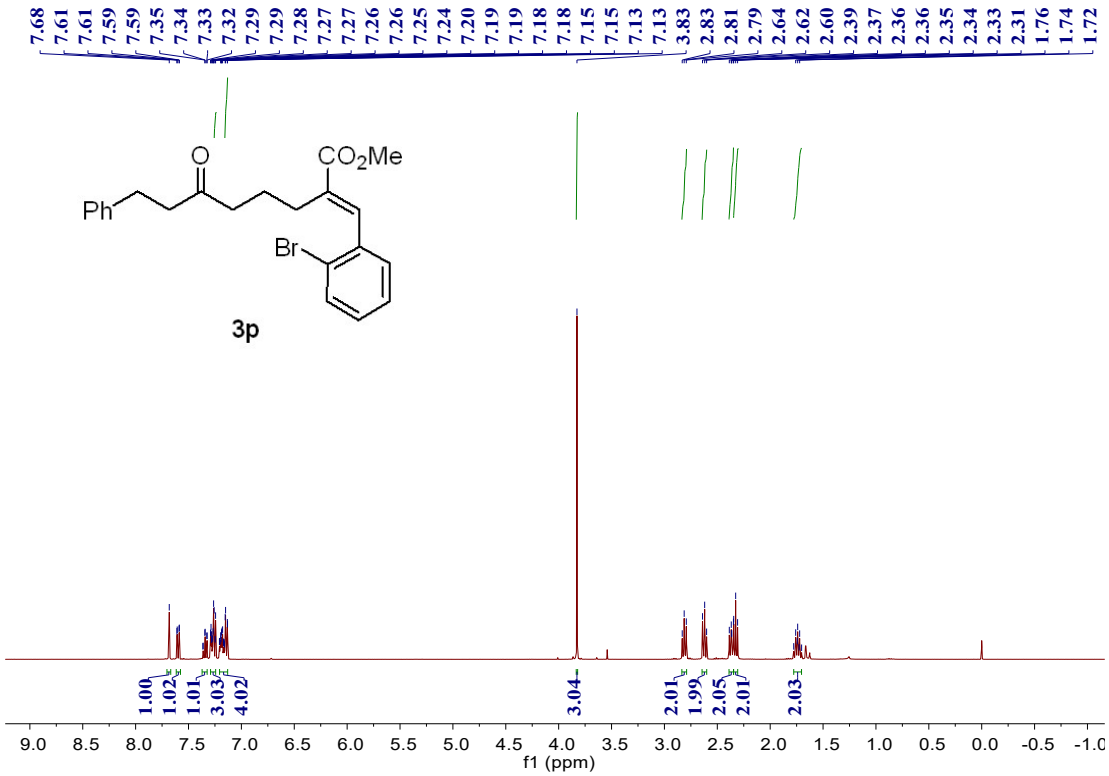


Figure S45 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3p**

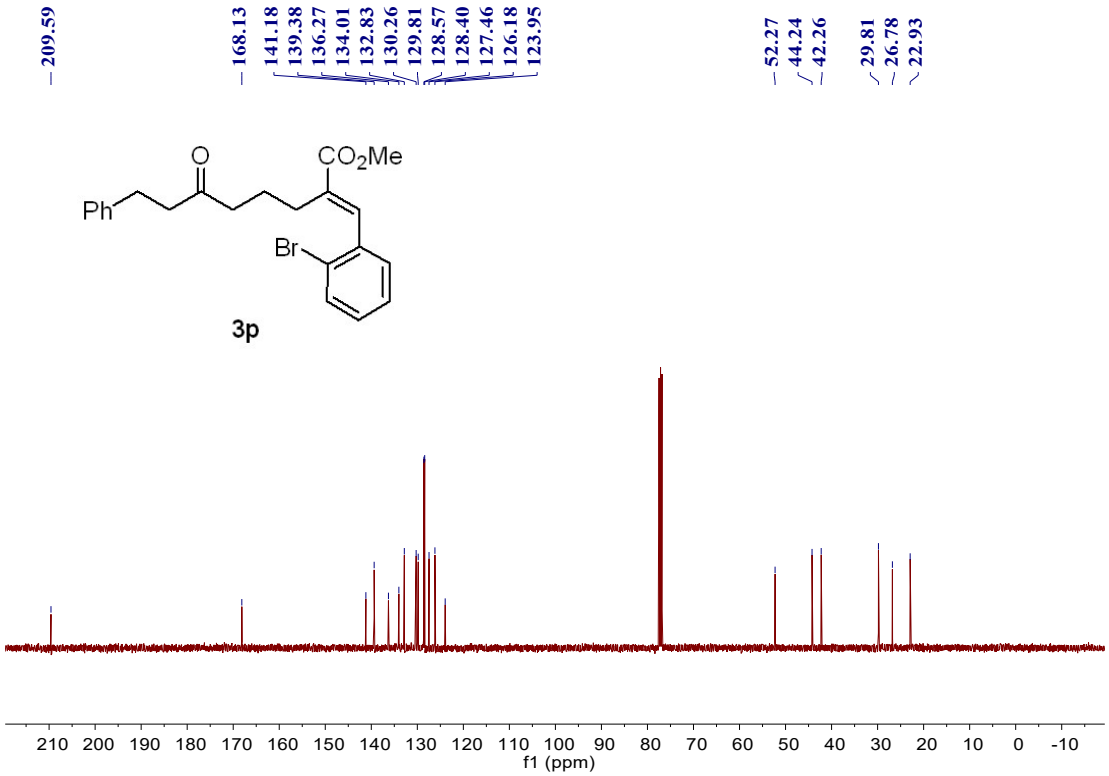


Figure S46 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3p**

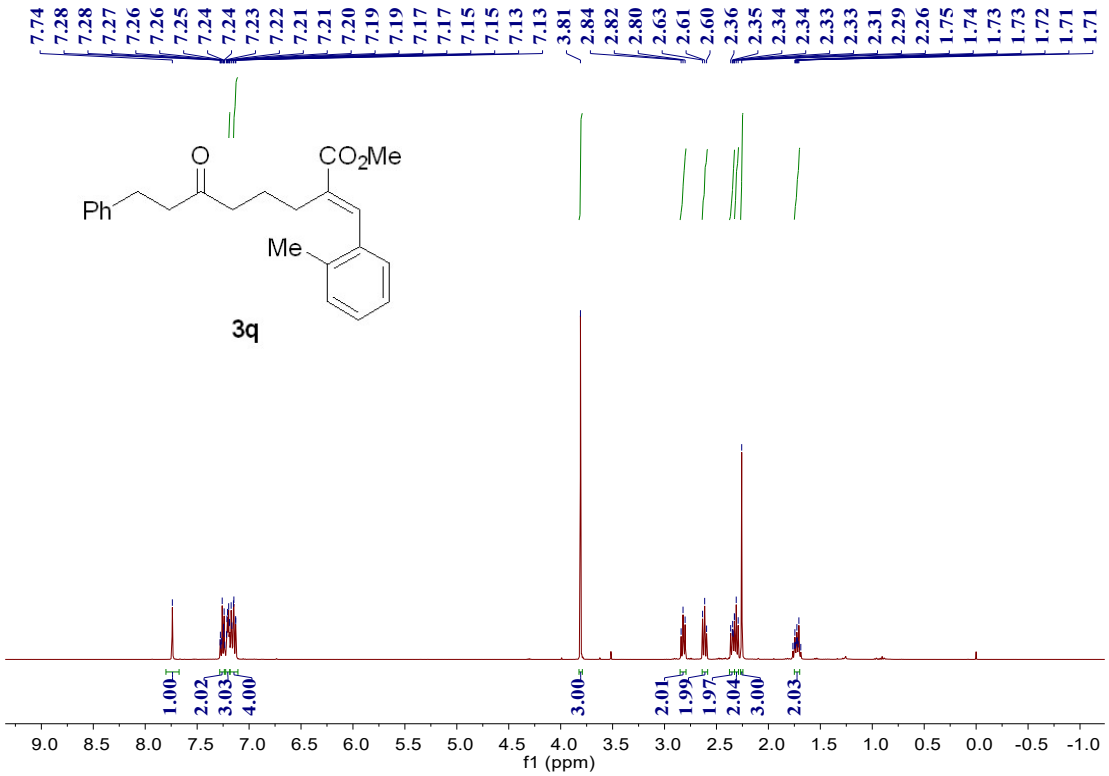


Figure S47 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3q**

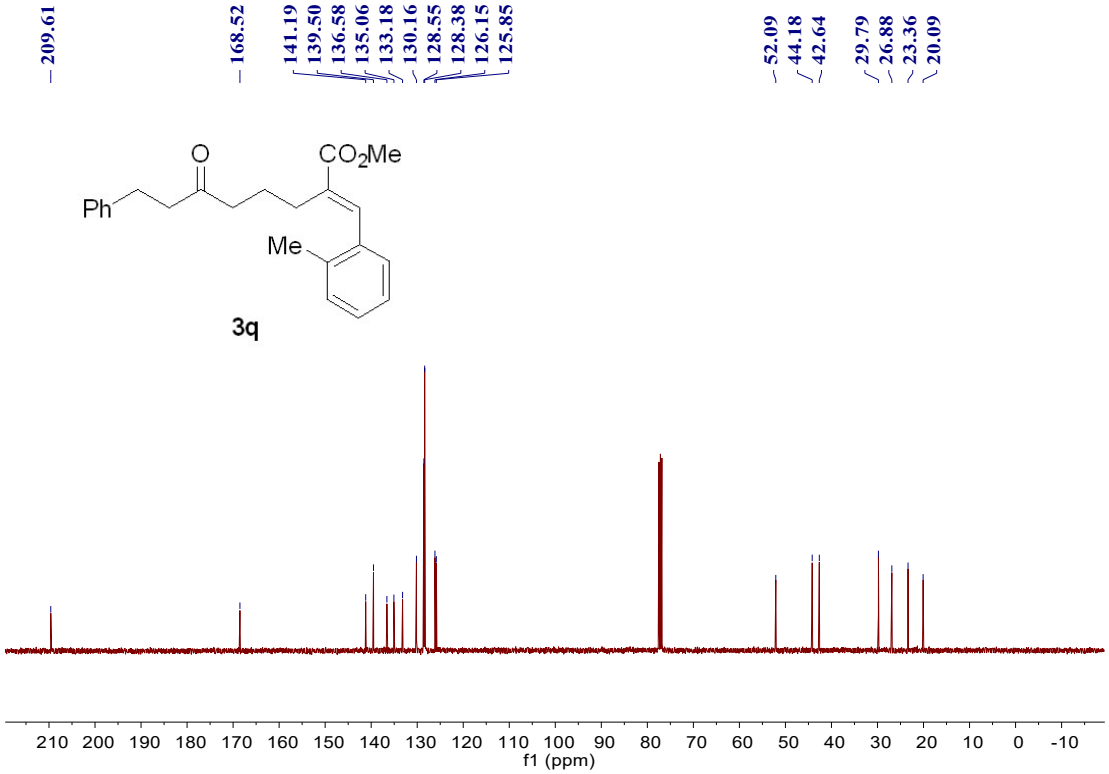


Figure S48 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3q**

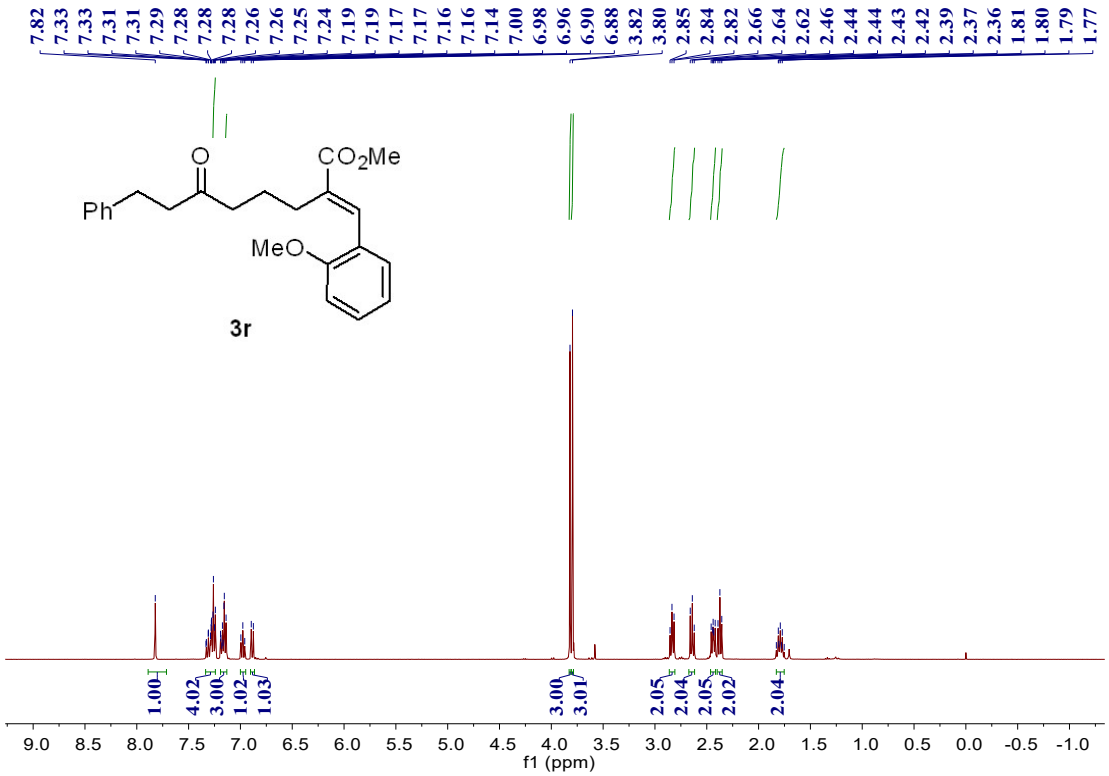


Figure S49 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3r**

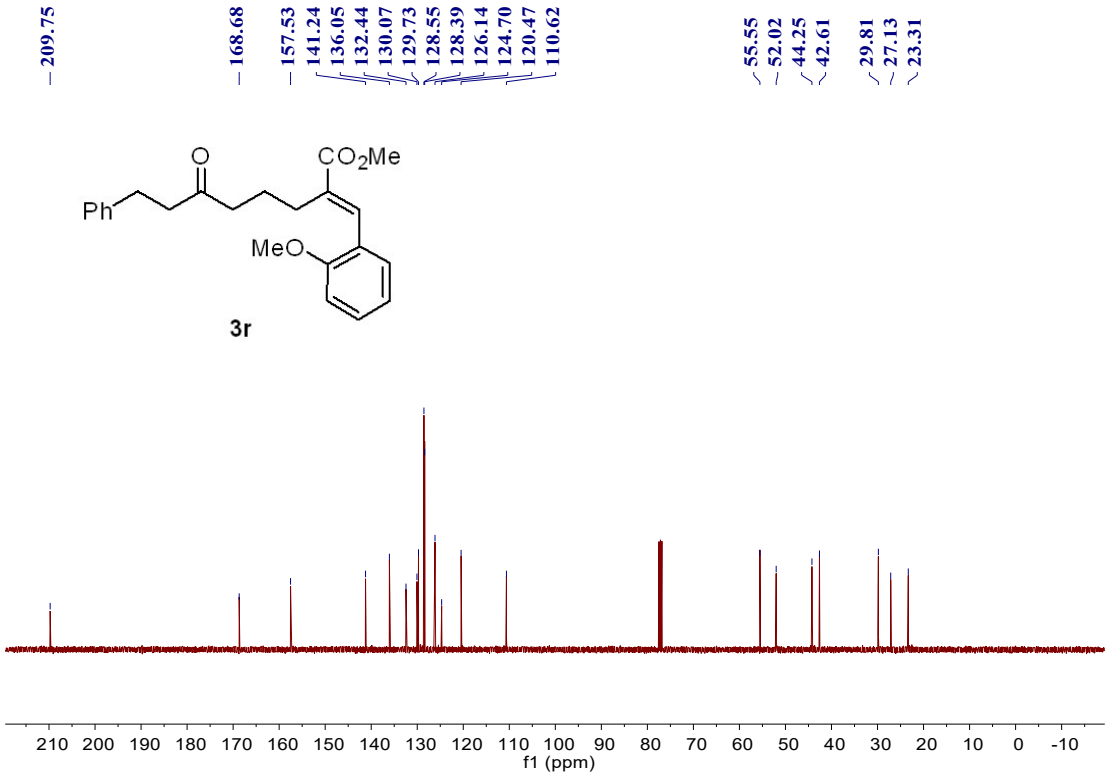


Figure S50 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3r**

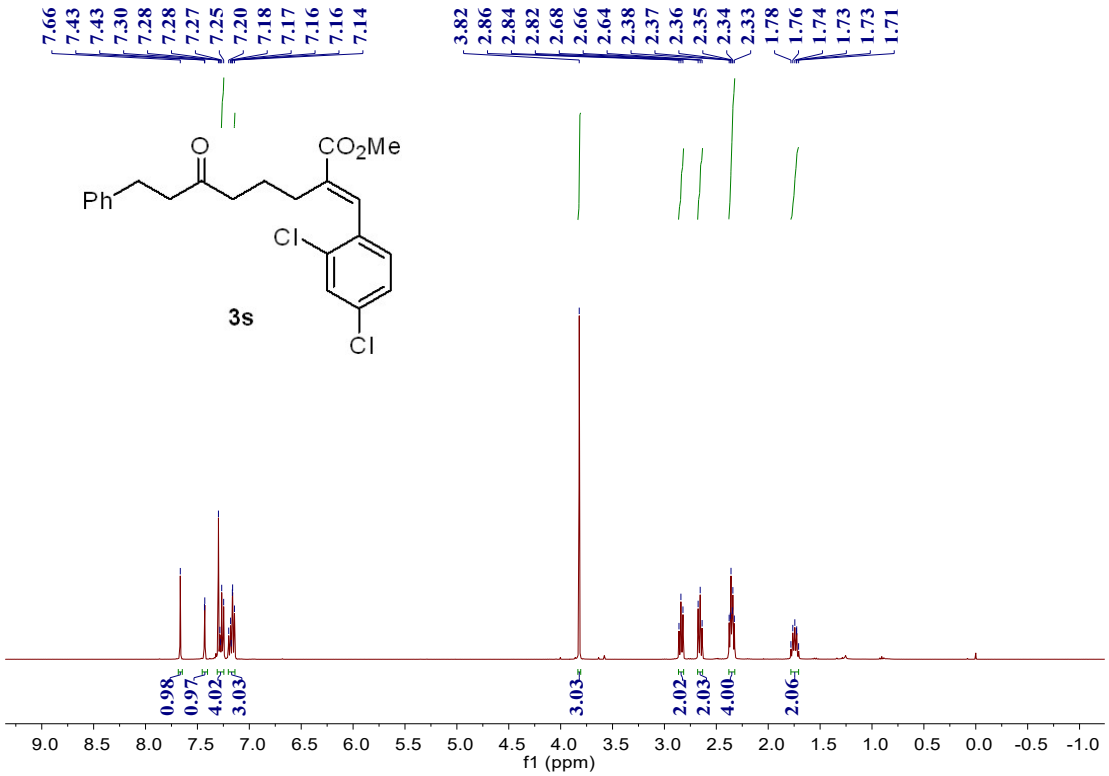


Figure S51 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3s**

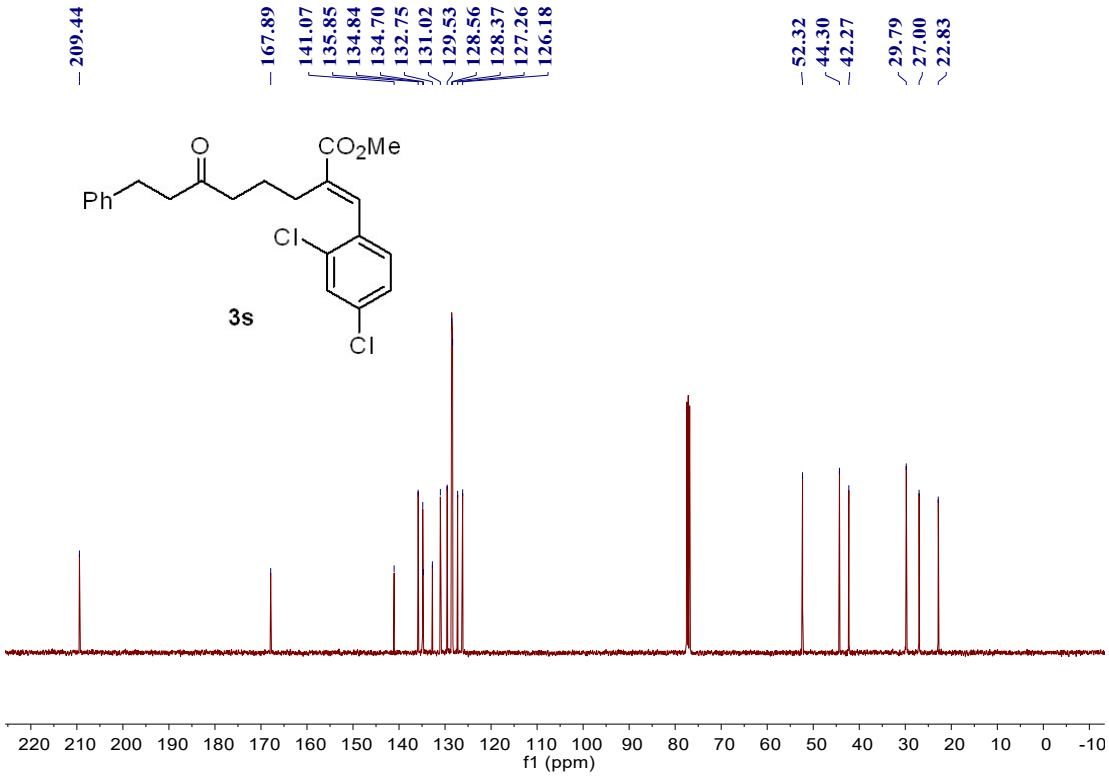


Figure S52 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3s**

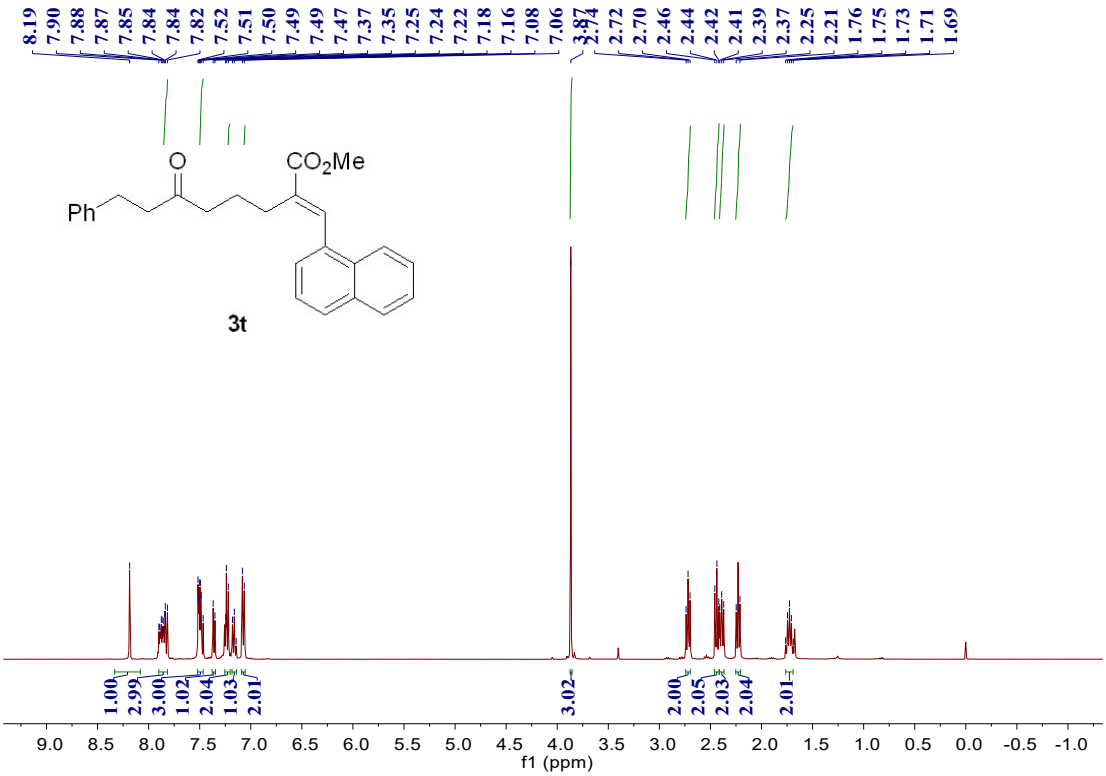


Figure S53 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3t**

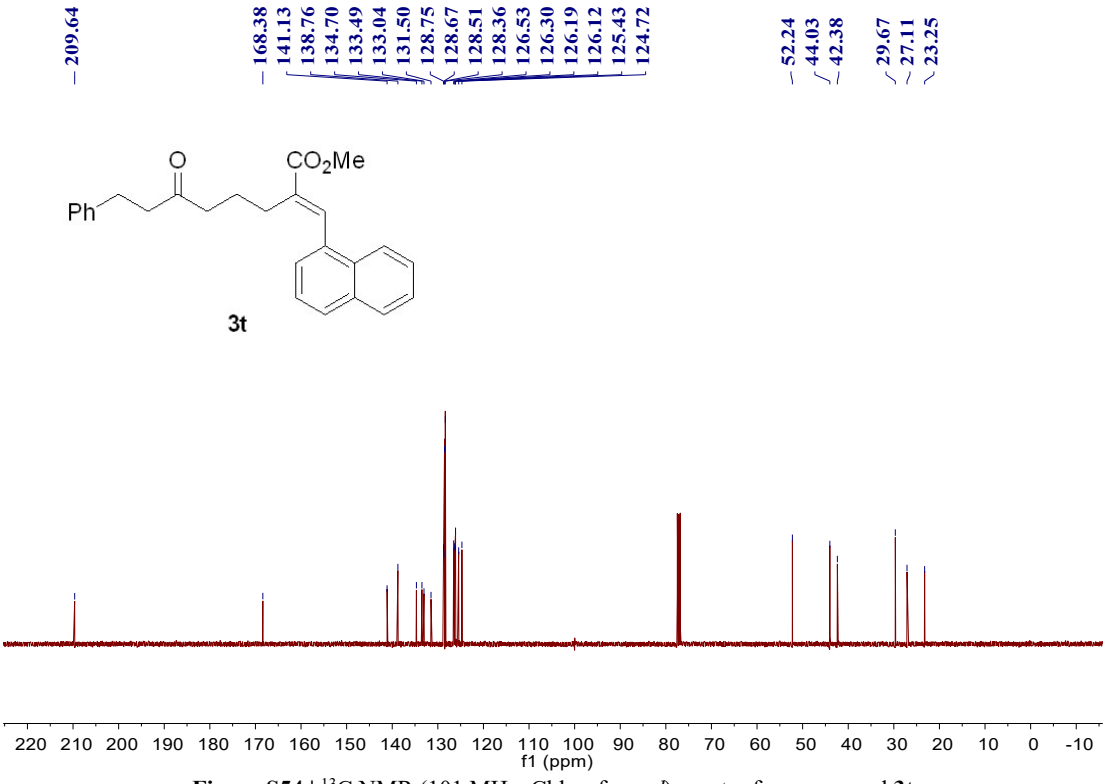


Figure S54 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3t**

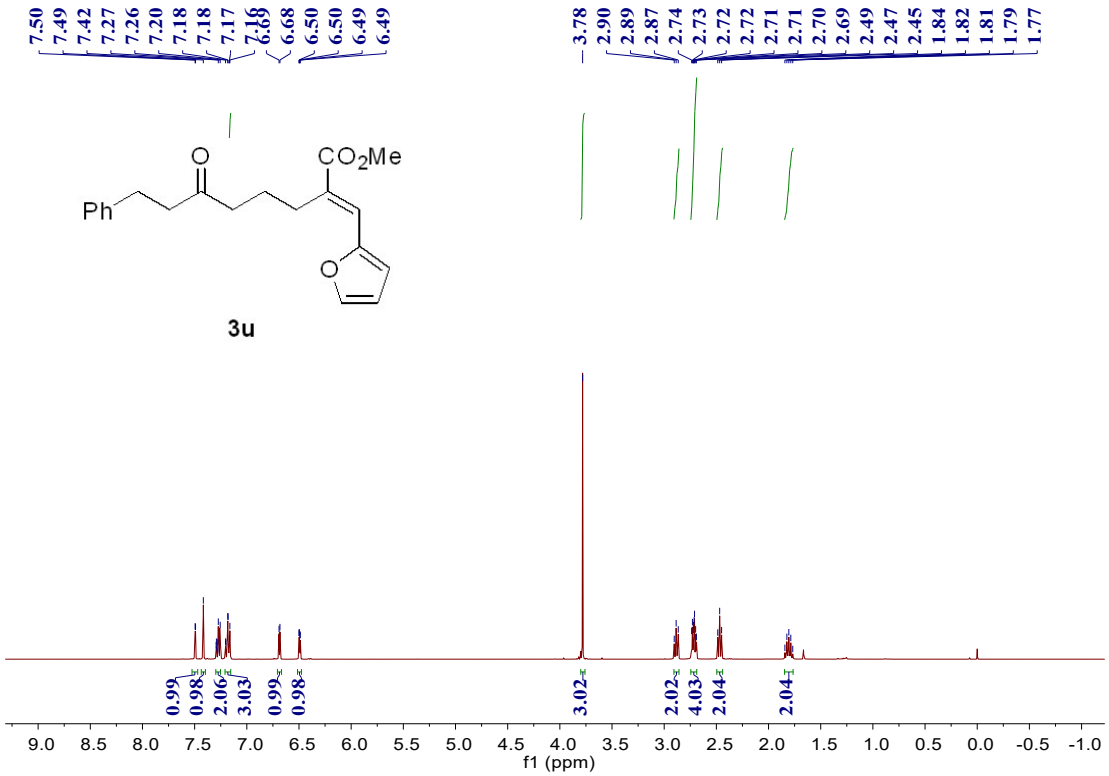


Figure S55 | [1]H NMR (400 MHz, Chloroform-*d*) spectra for compound **3u**

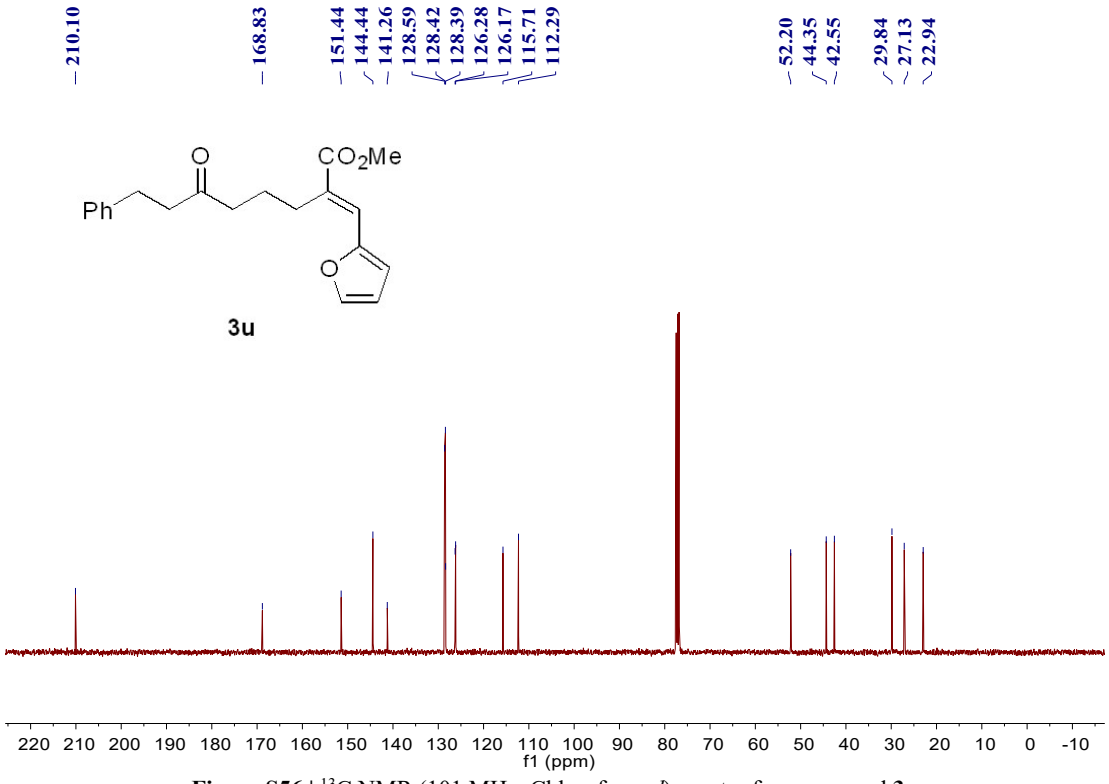


Figure S56 | [13]C NMR (101 MHz, Chloroform-*d*) spectra for compound **3u**

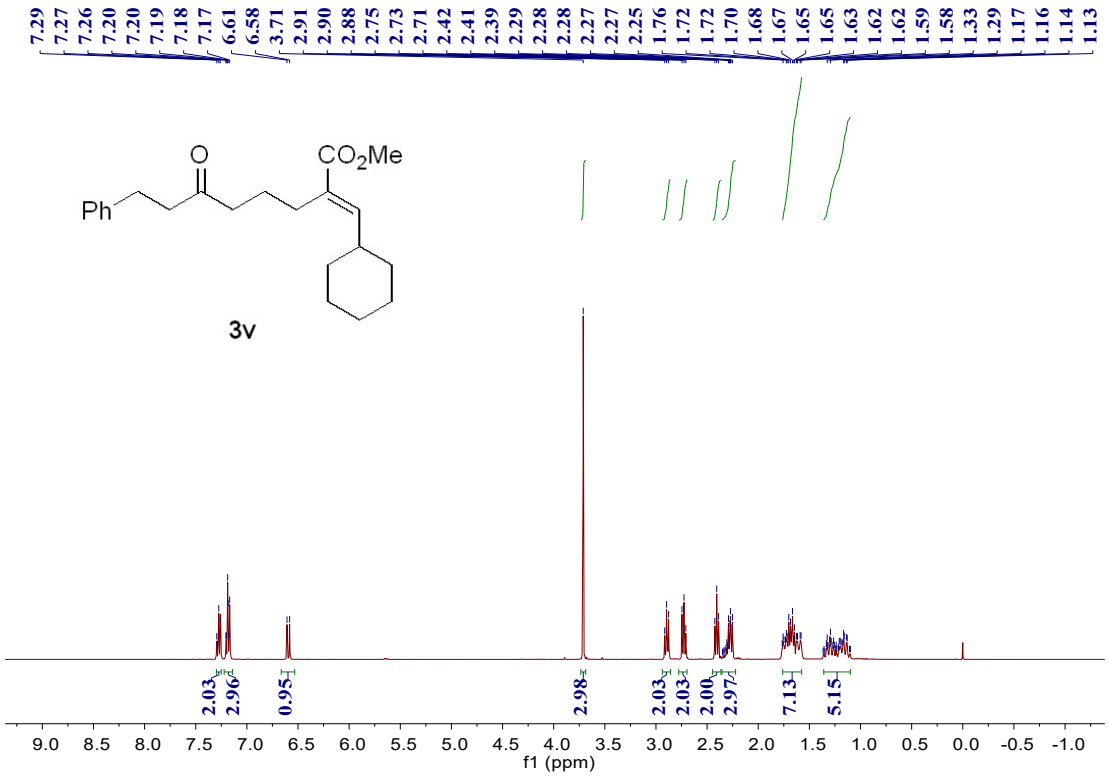


Figure S57 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3v**

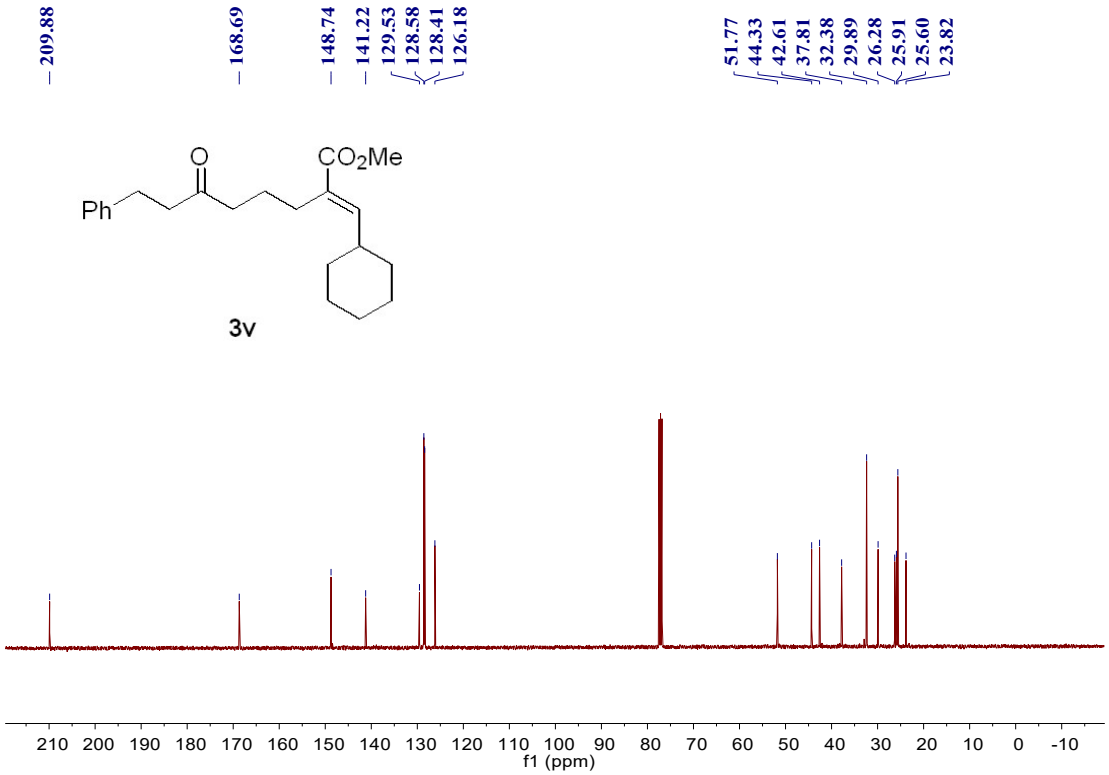


Figure S58 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3v**

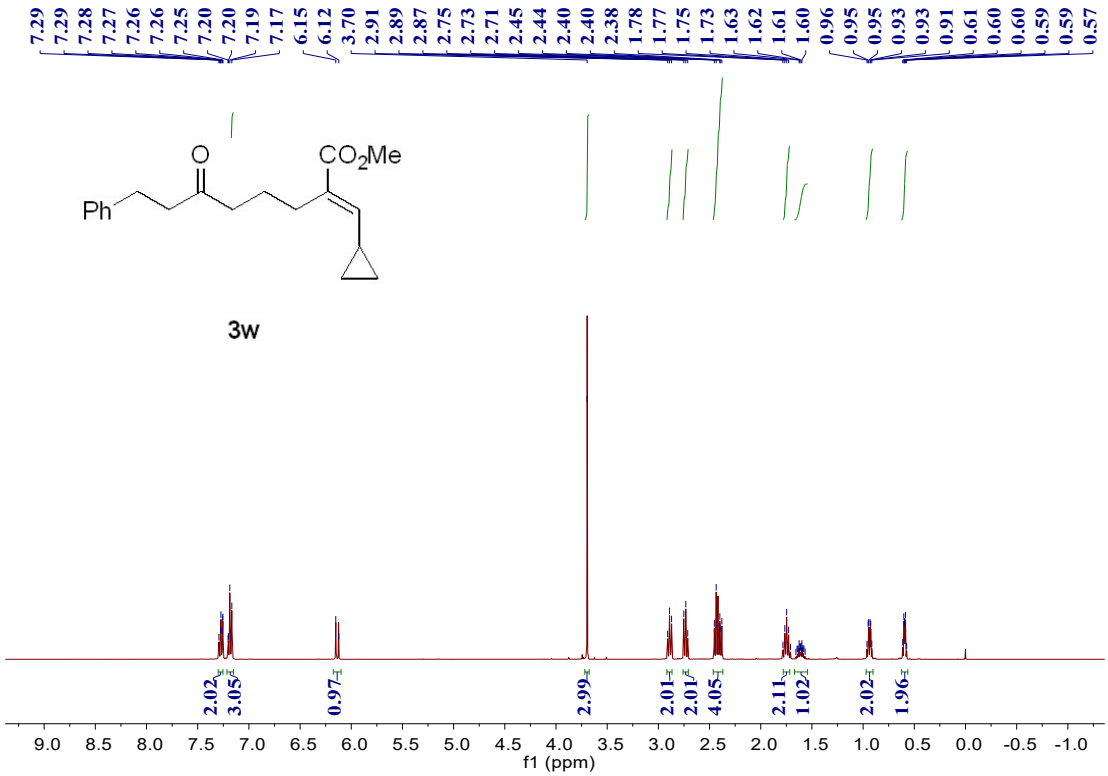


Figure S59 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3w**

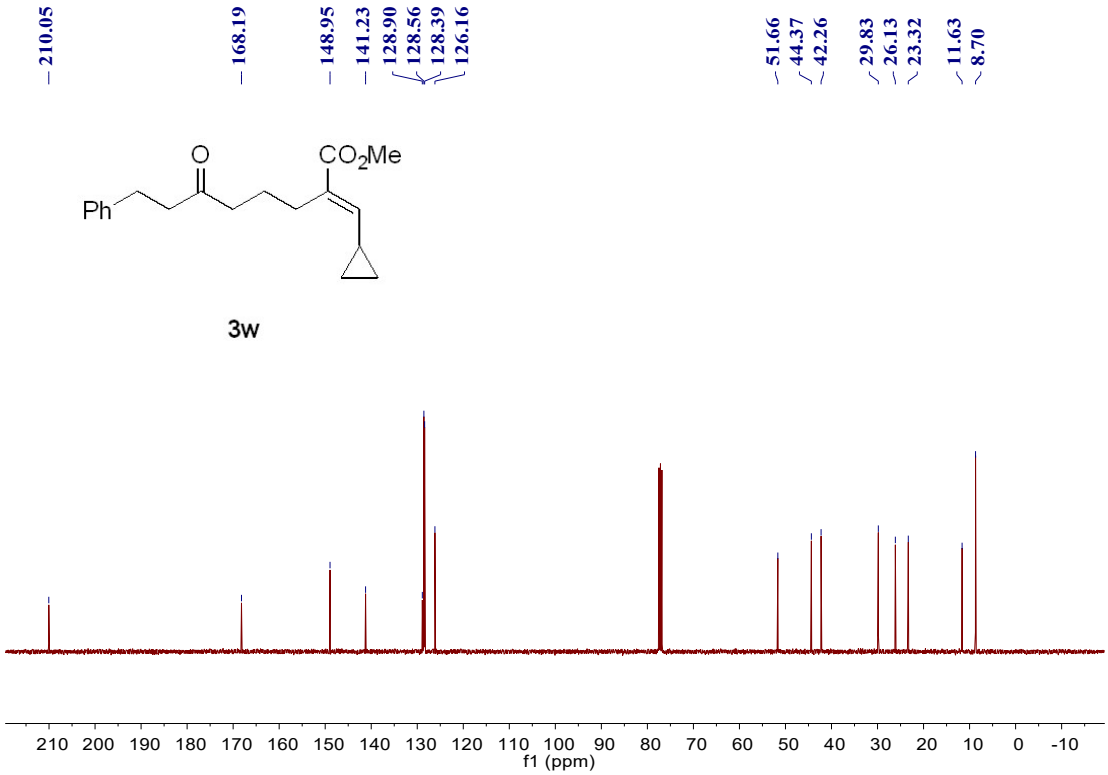


Figure S60 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3w**

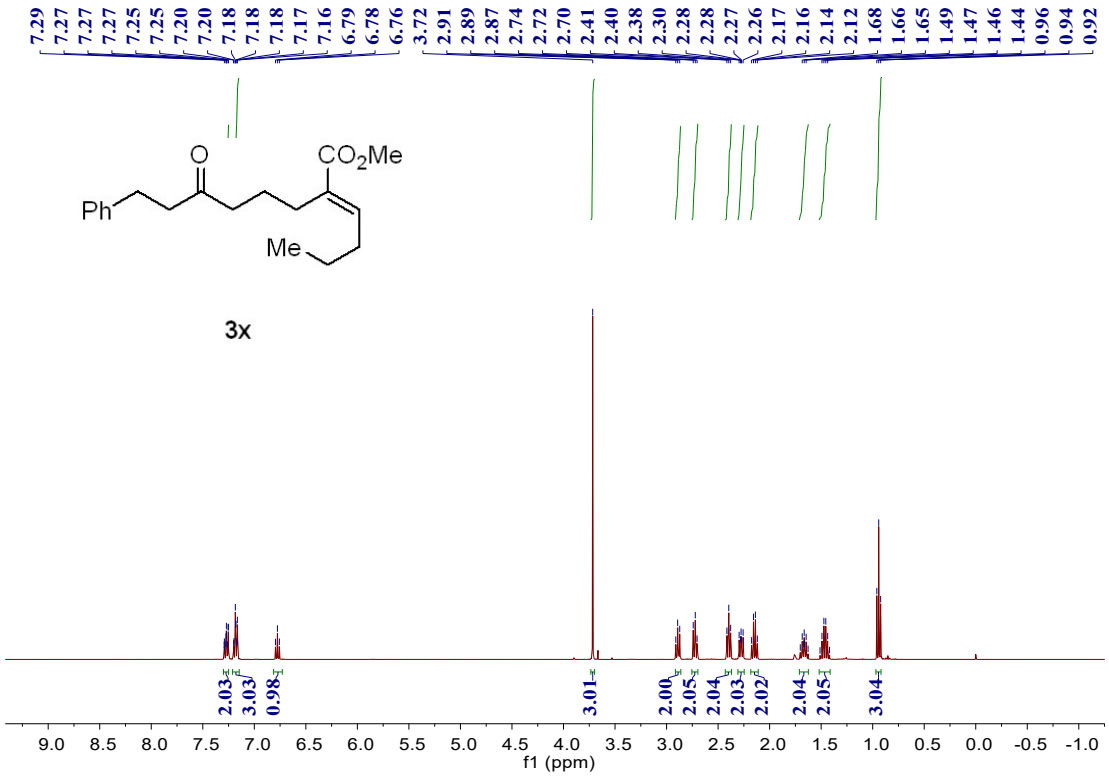


Figure S61 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3x**

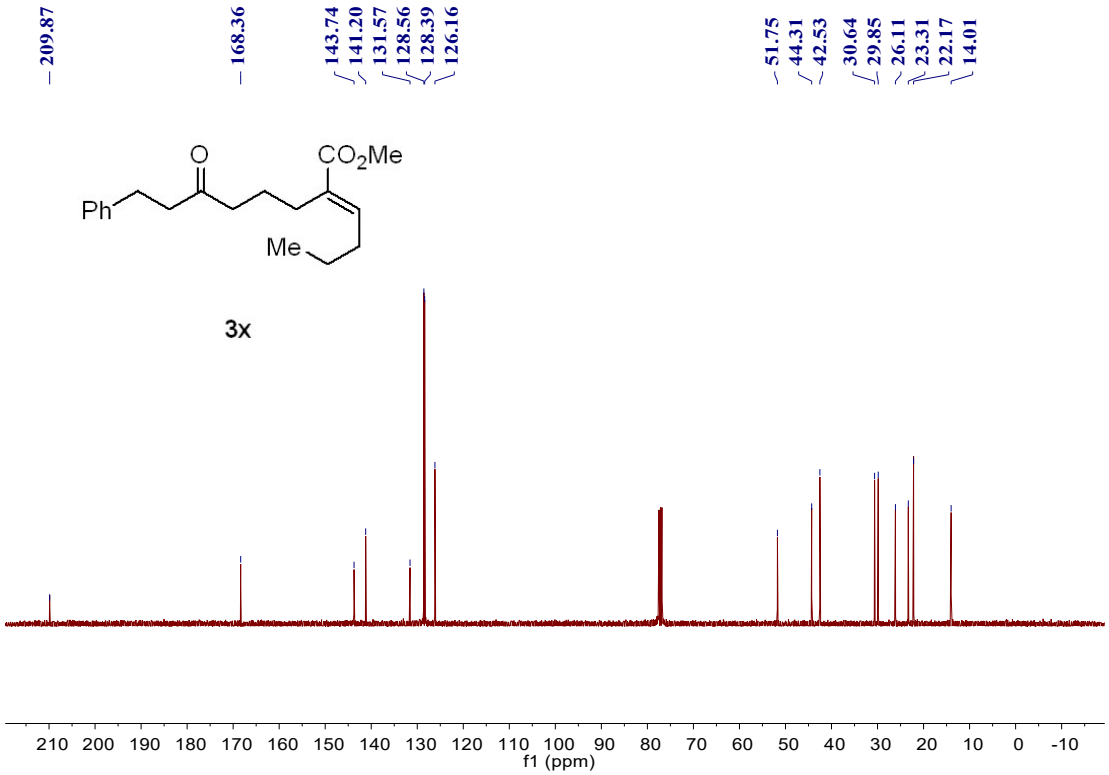


Figure S62 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3x**

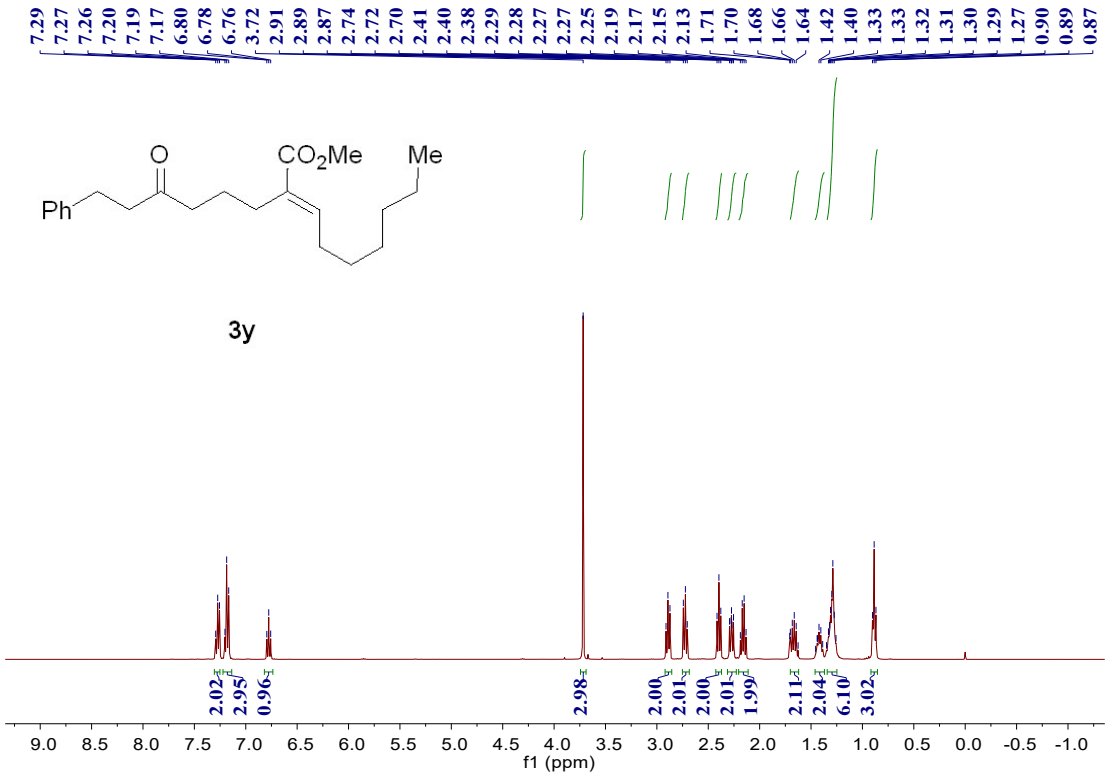


Figure S63 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3y**

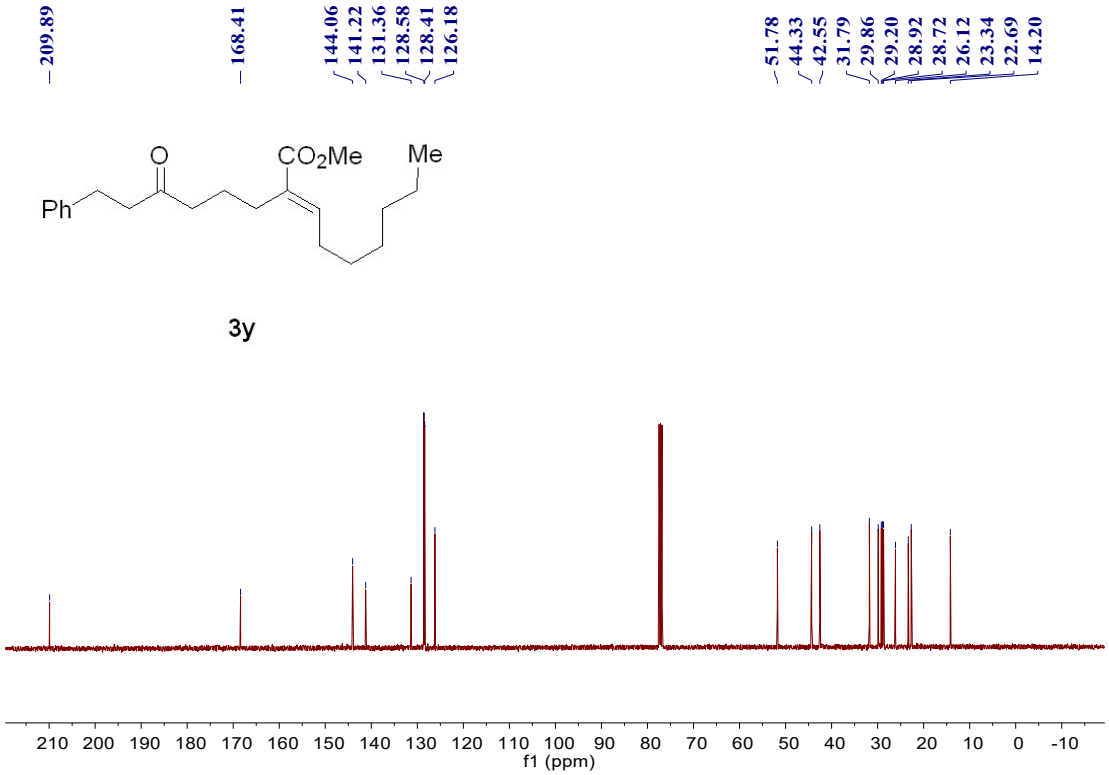


Figure S64 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3y**

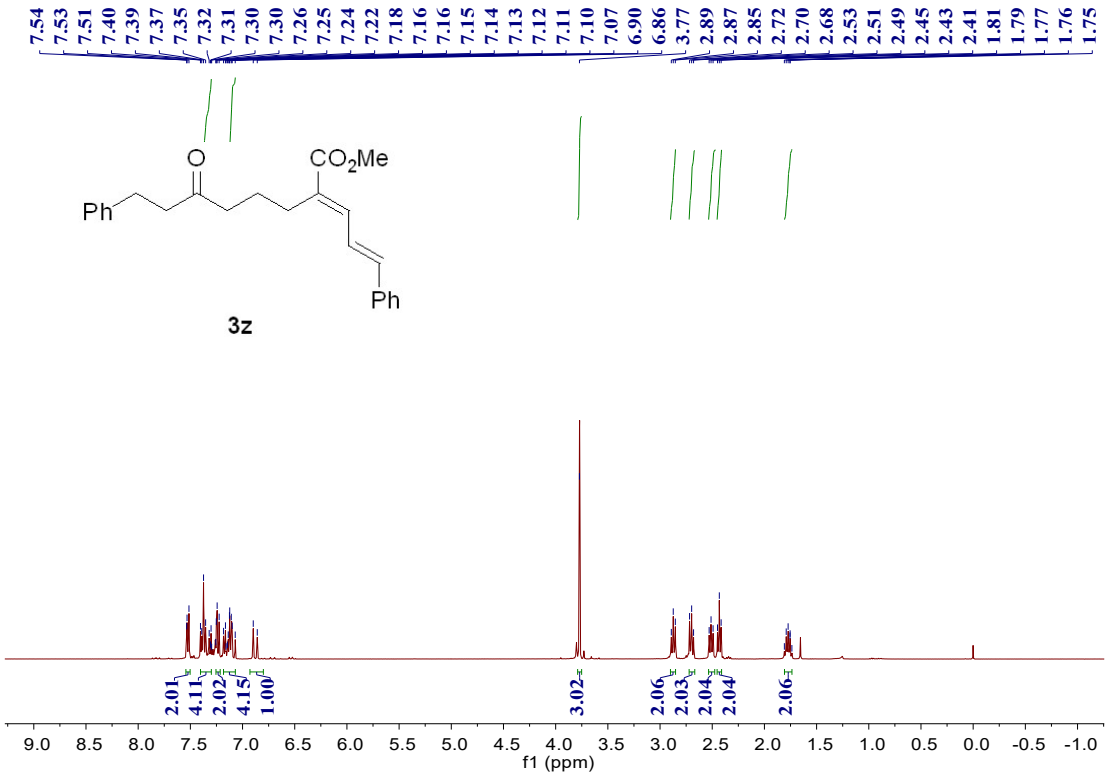


Figure S65 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3z**

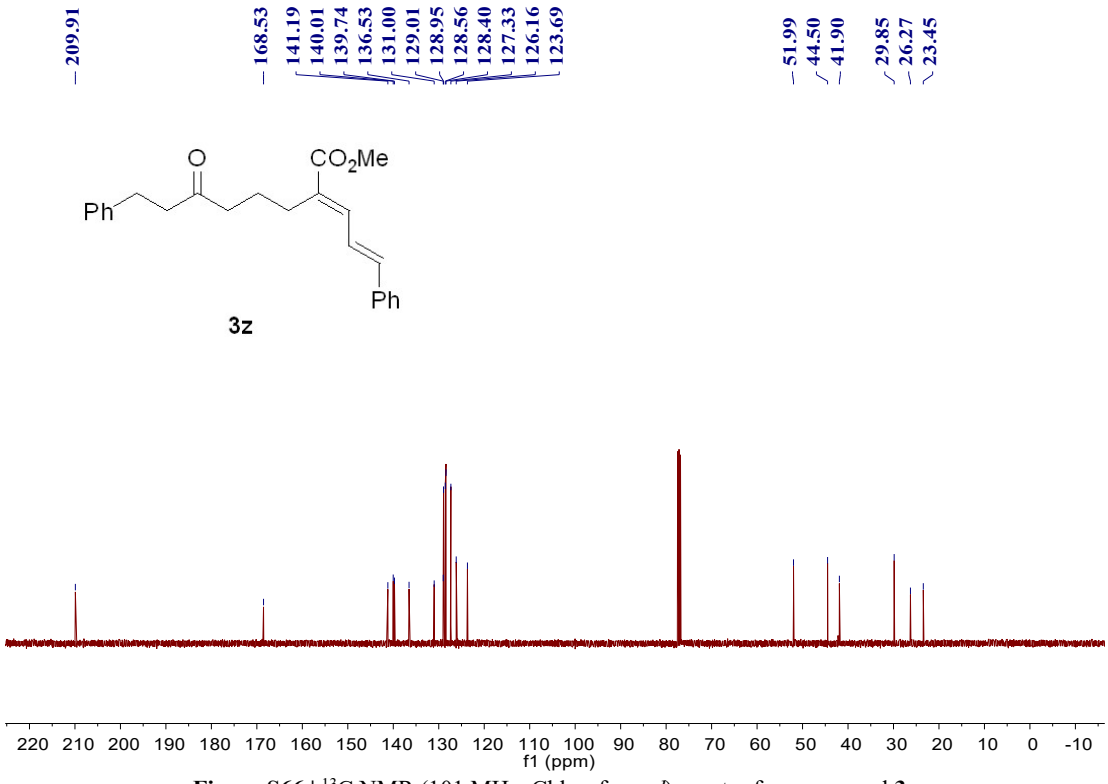


Figure S66 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3z**

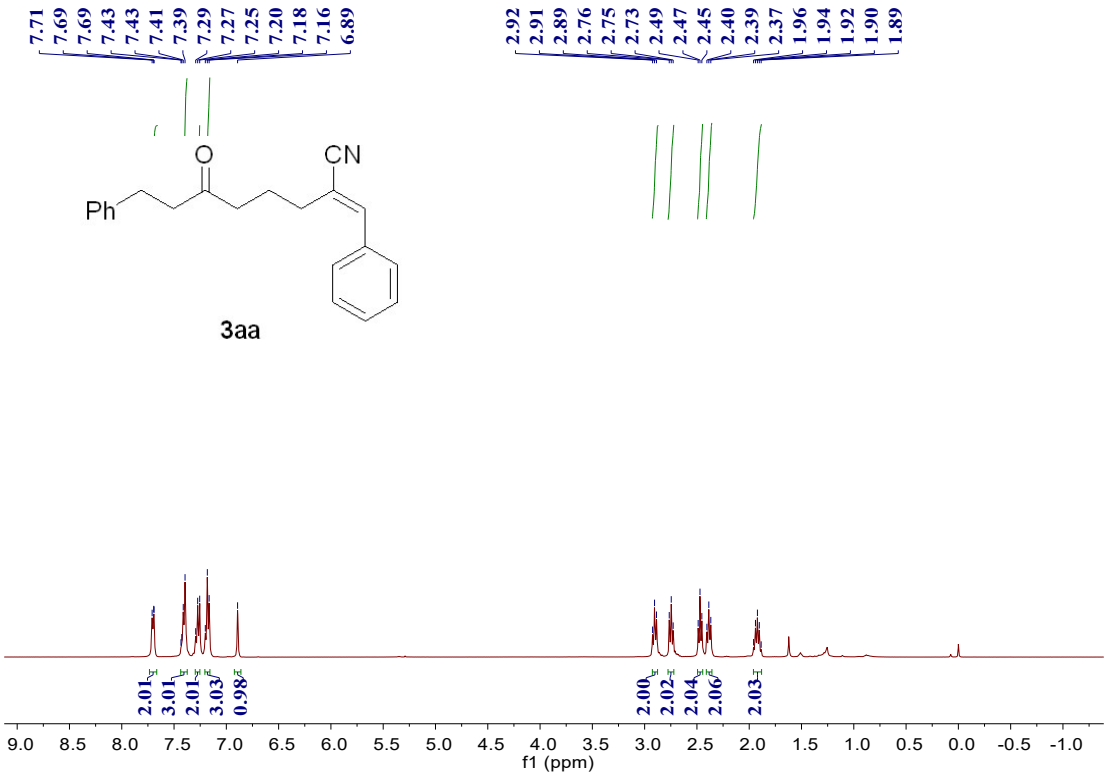


Figure S67 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3aa**

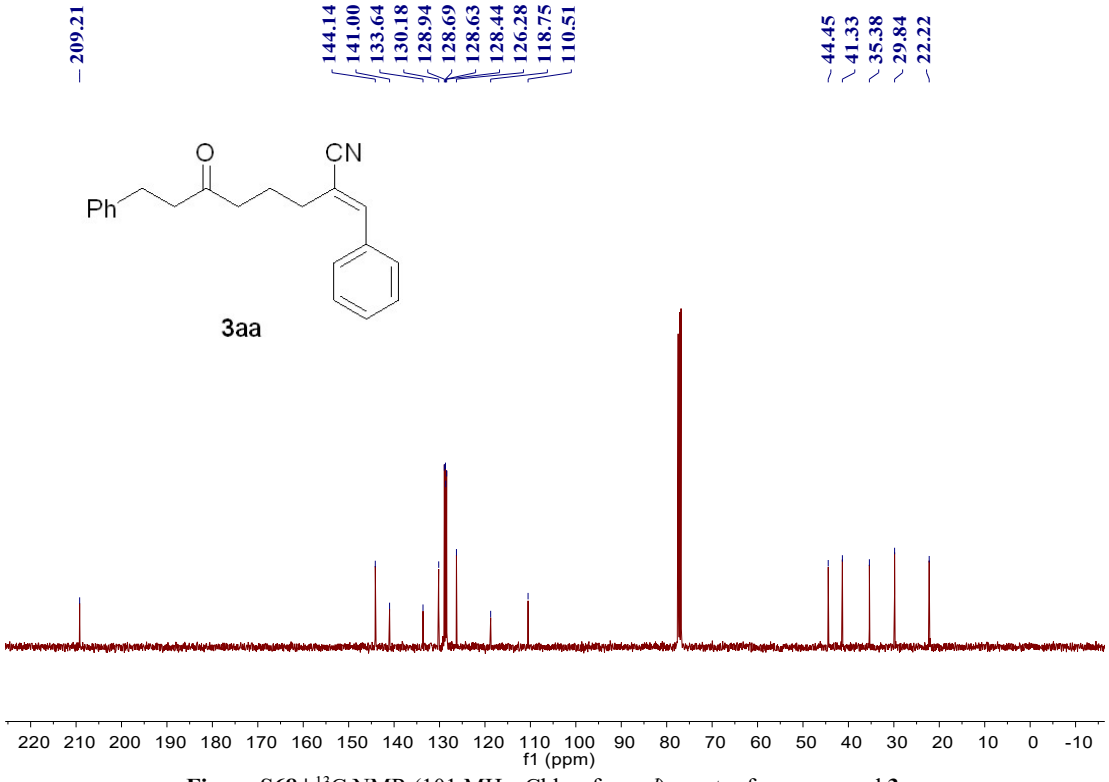


Figure S68 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3aa**

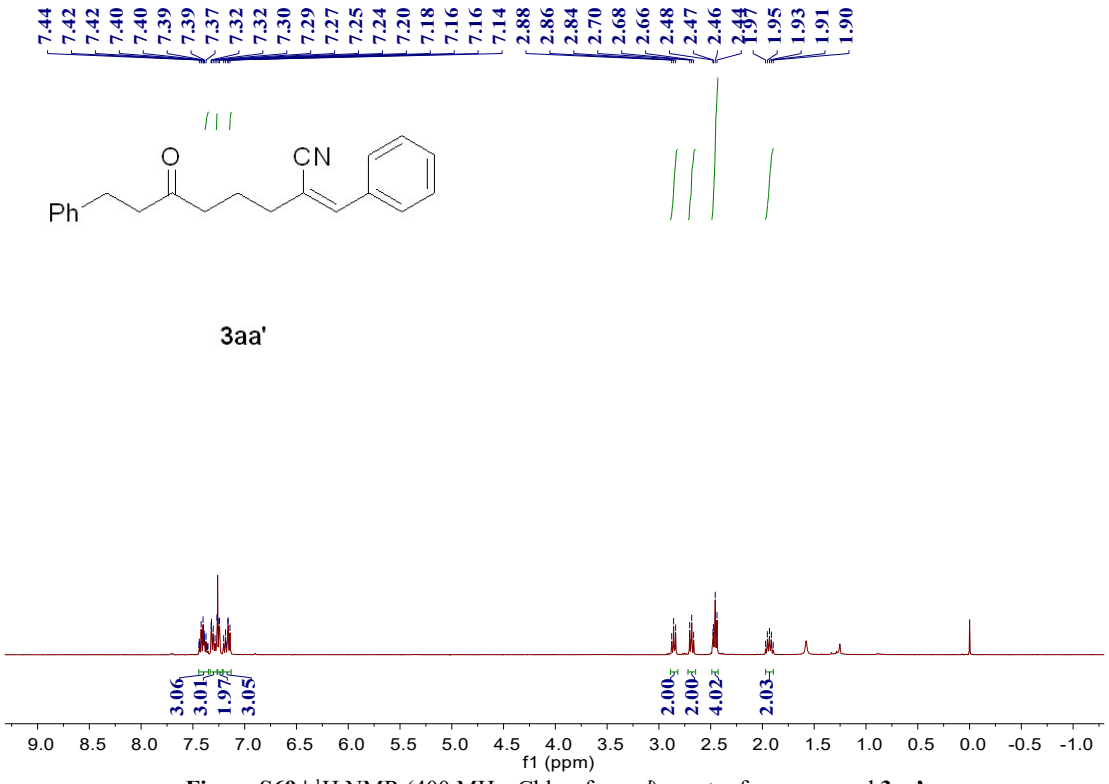


Figure S69 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3aa'**

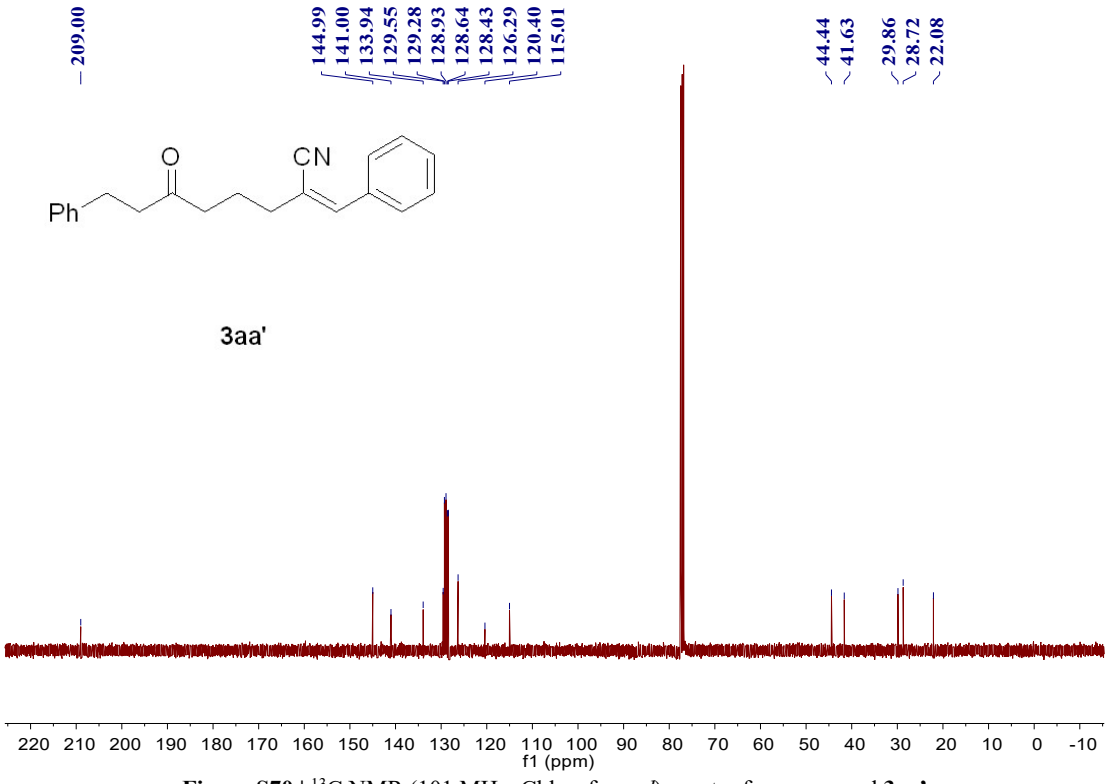


Figure S70 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3aa'**

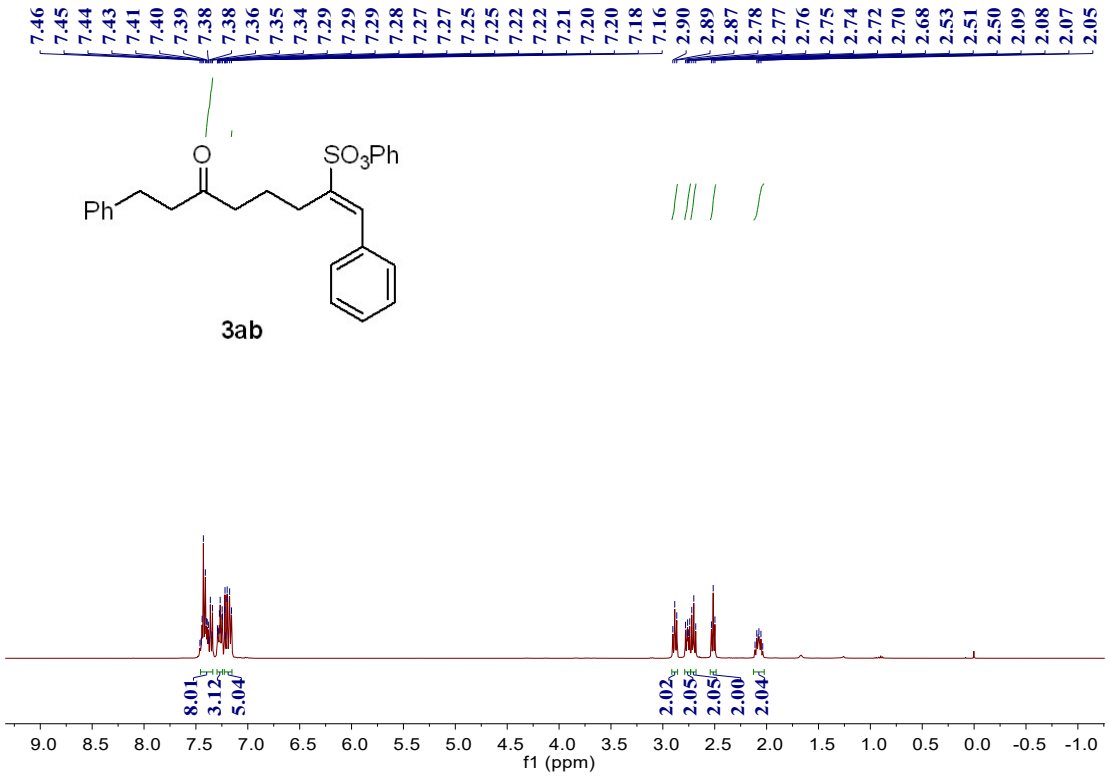


Figure S71 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ab**

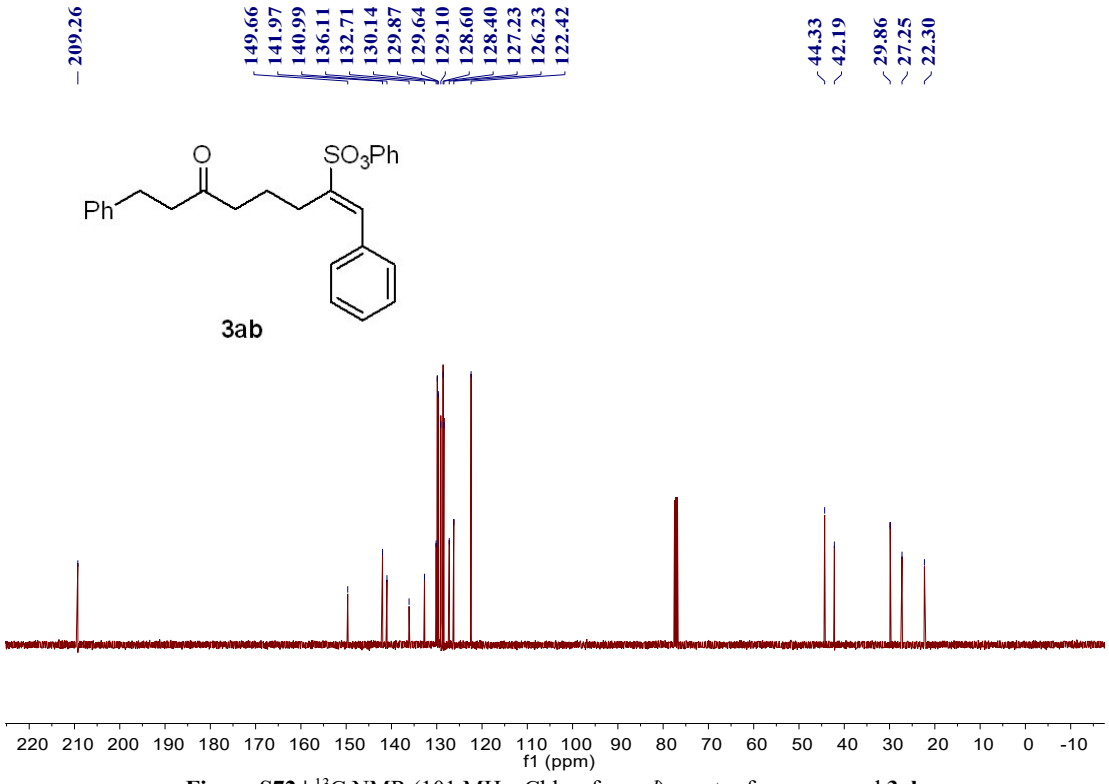


Figure S72 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ab**

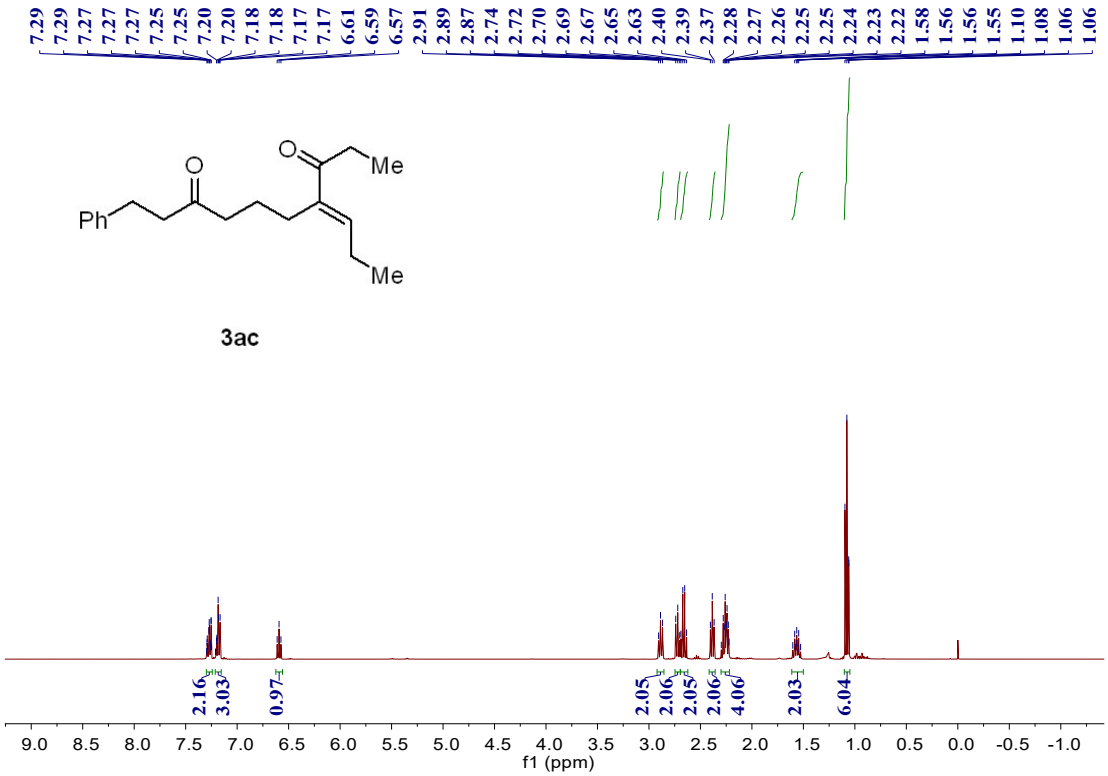


Figure S73 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ac**

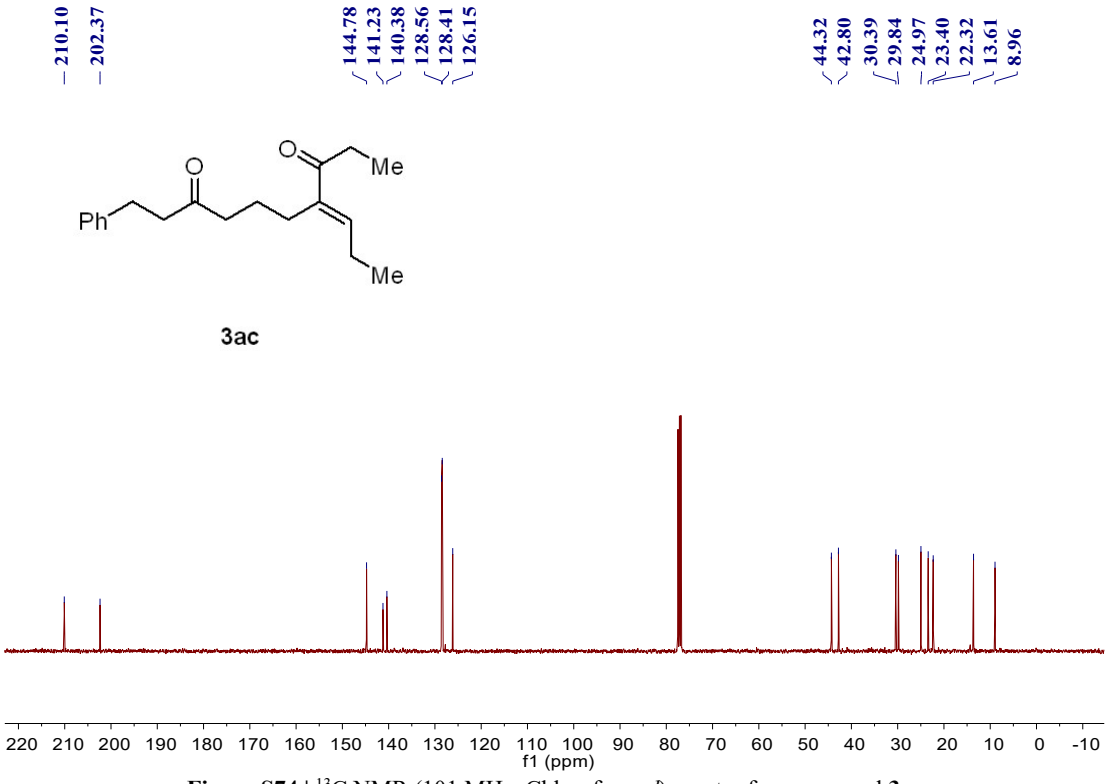


Figure S74 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ac**

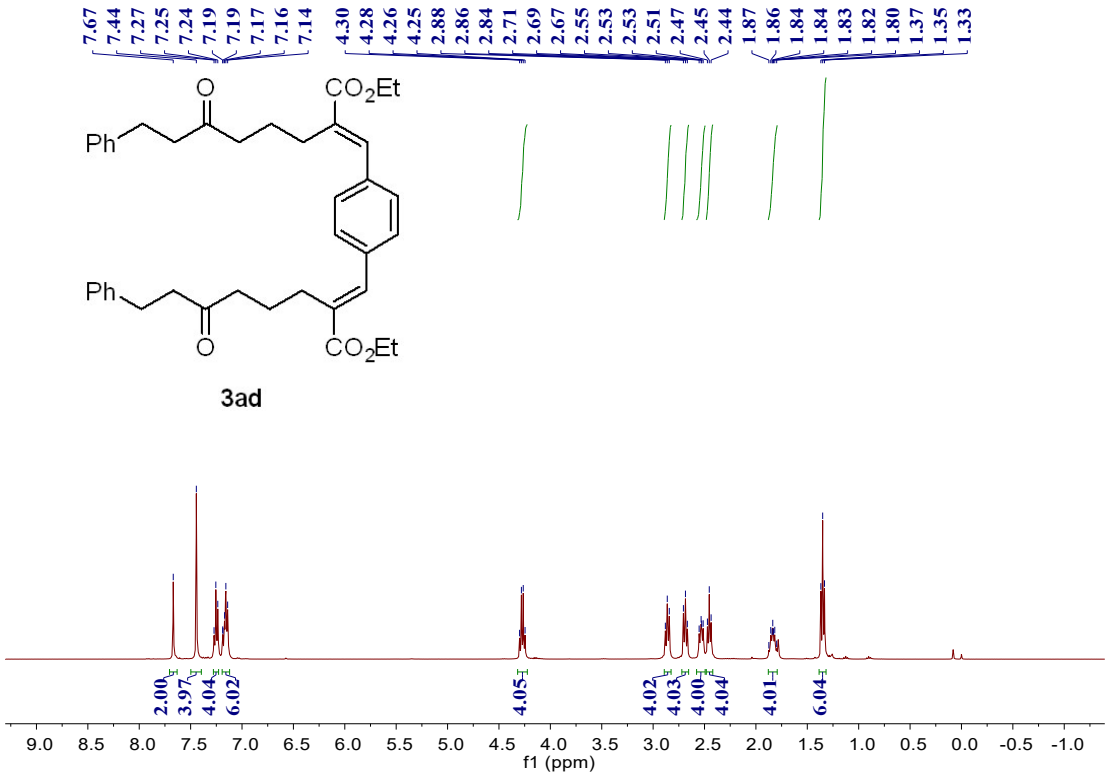


Figure S75 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ad**

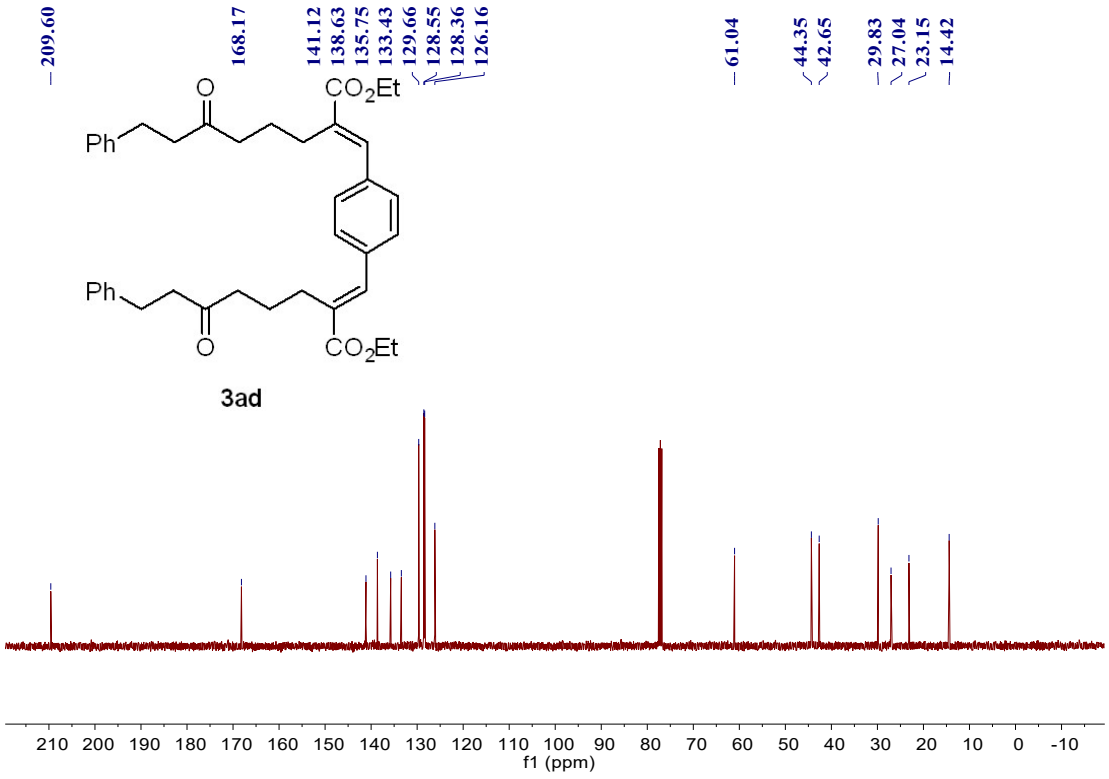


Figure S76 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ad**

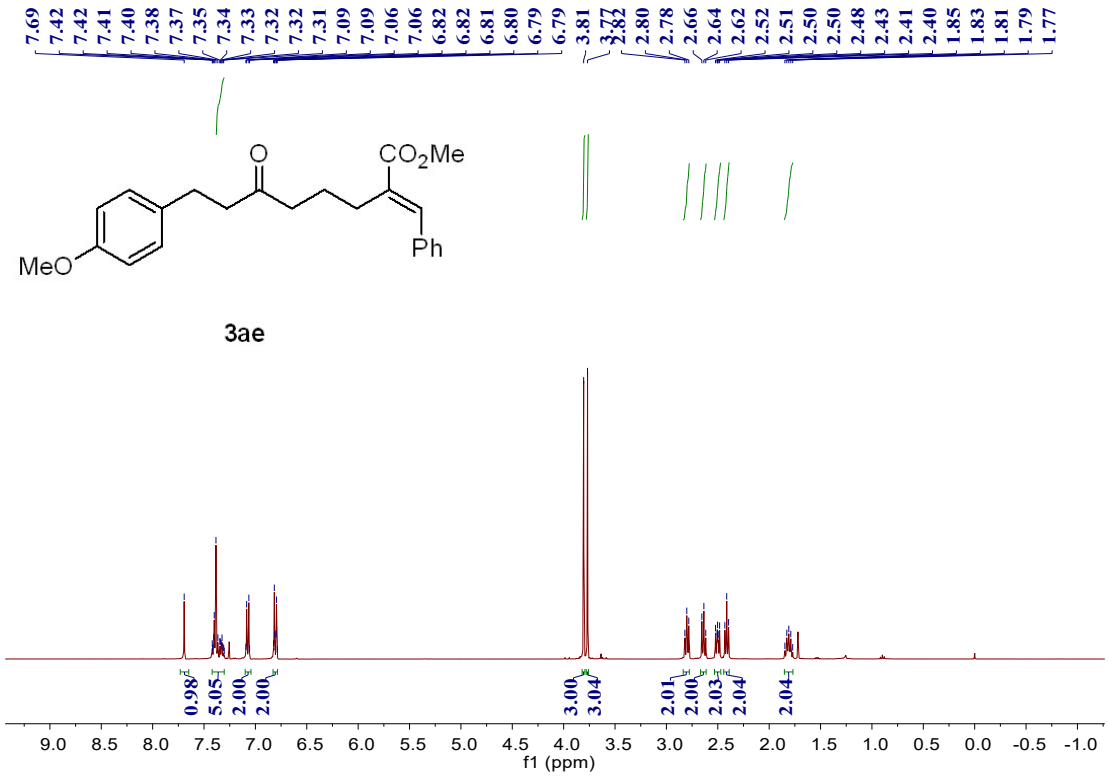


Figure S77 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ae**

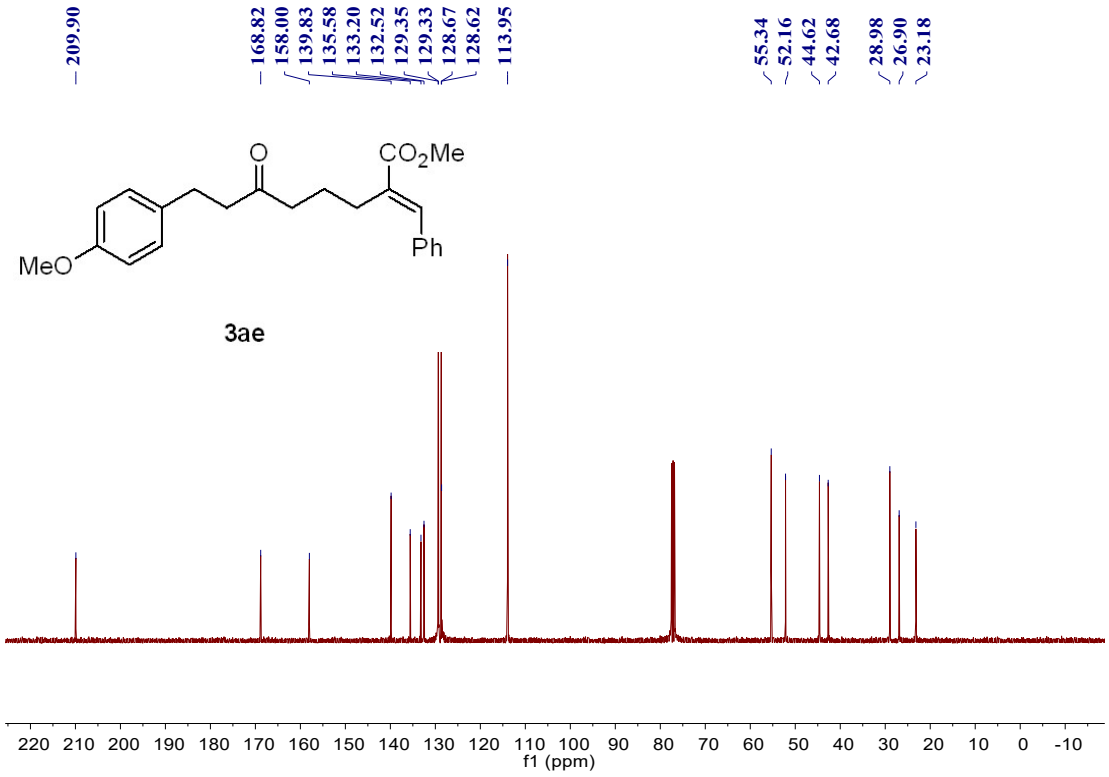


Figure S78 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ae**

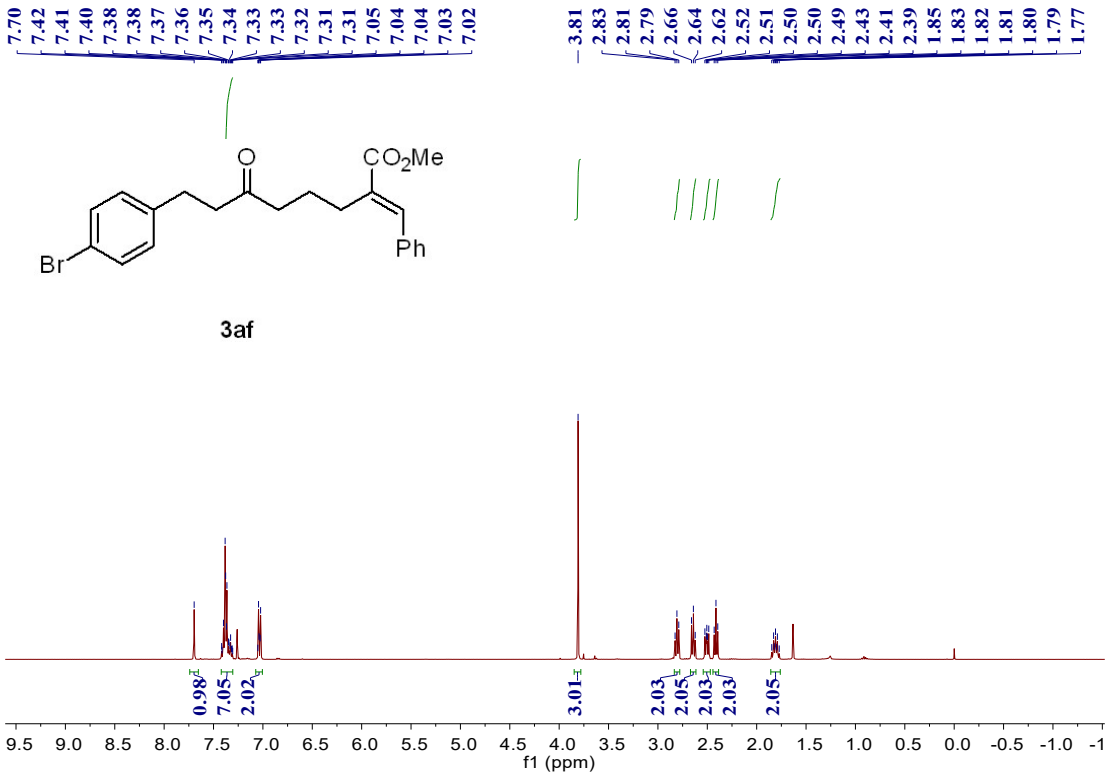


Figure S79 | [1]H NMR (400 MHz, Chloroform-*d*) spectra for compound **3af**

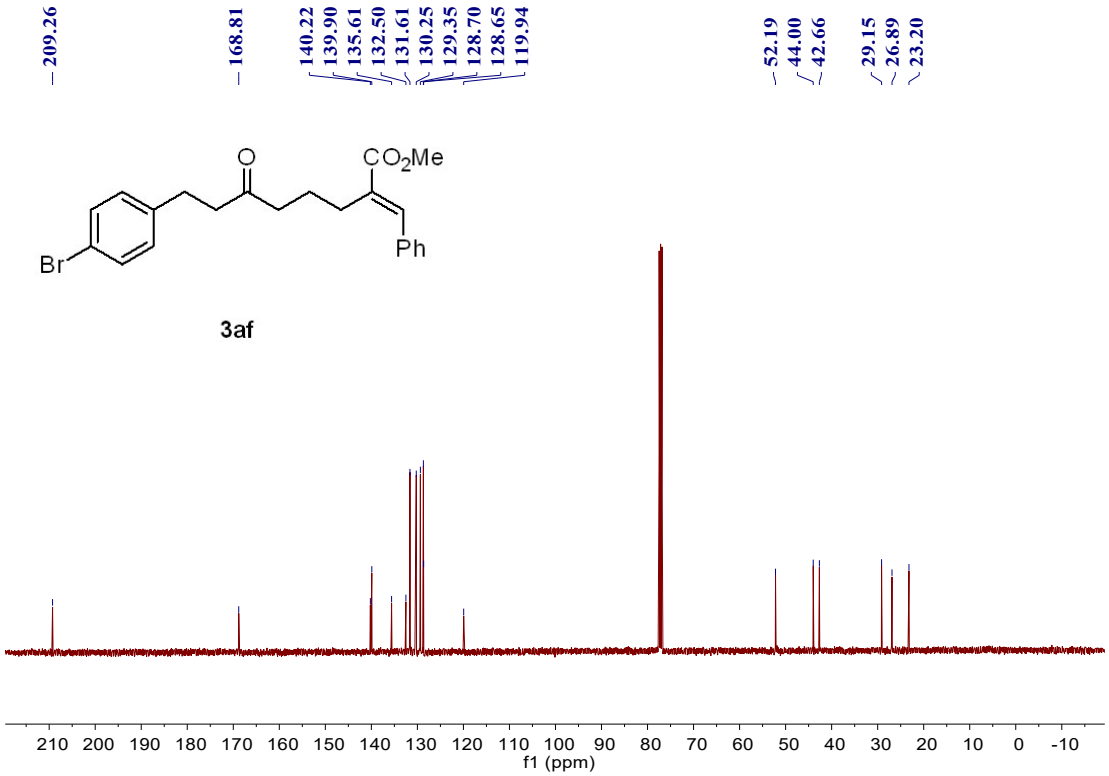


Figure S80 | [13]C NMR (101 MHz, Chloroform-*d*) spectra for compound **3af**

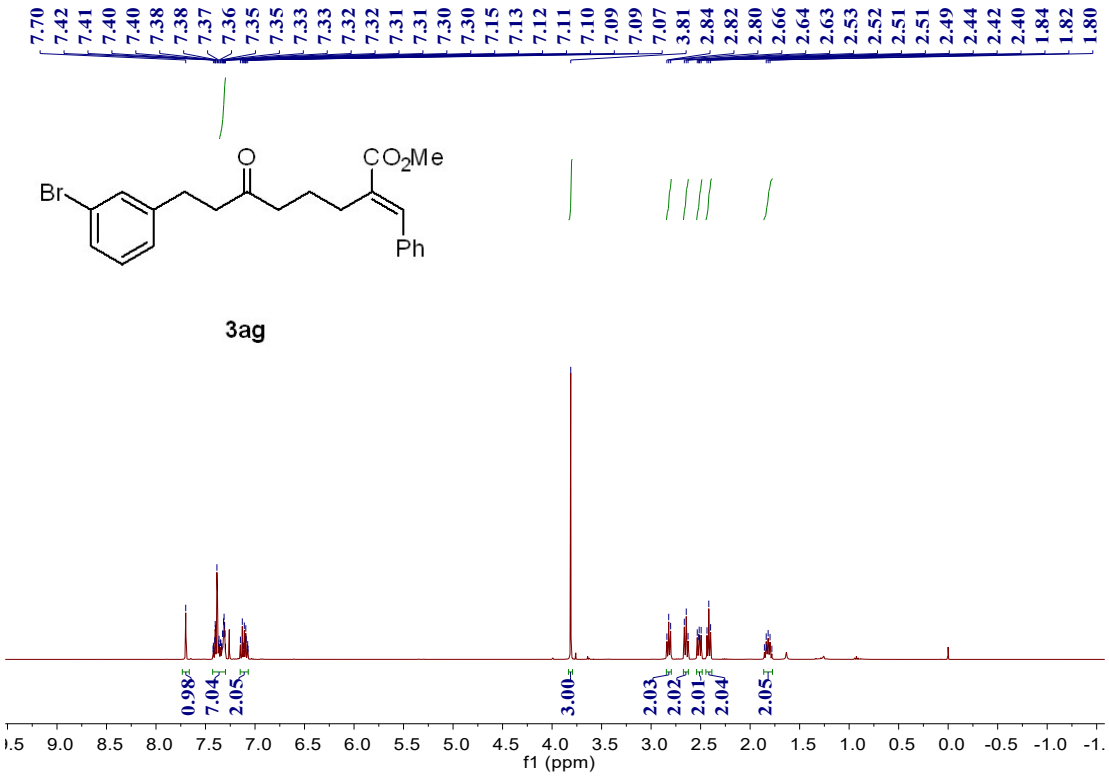


Figure S81 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ag**

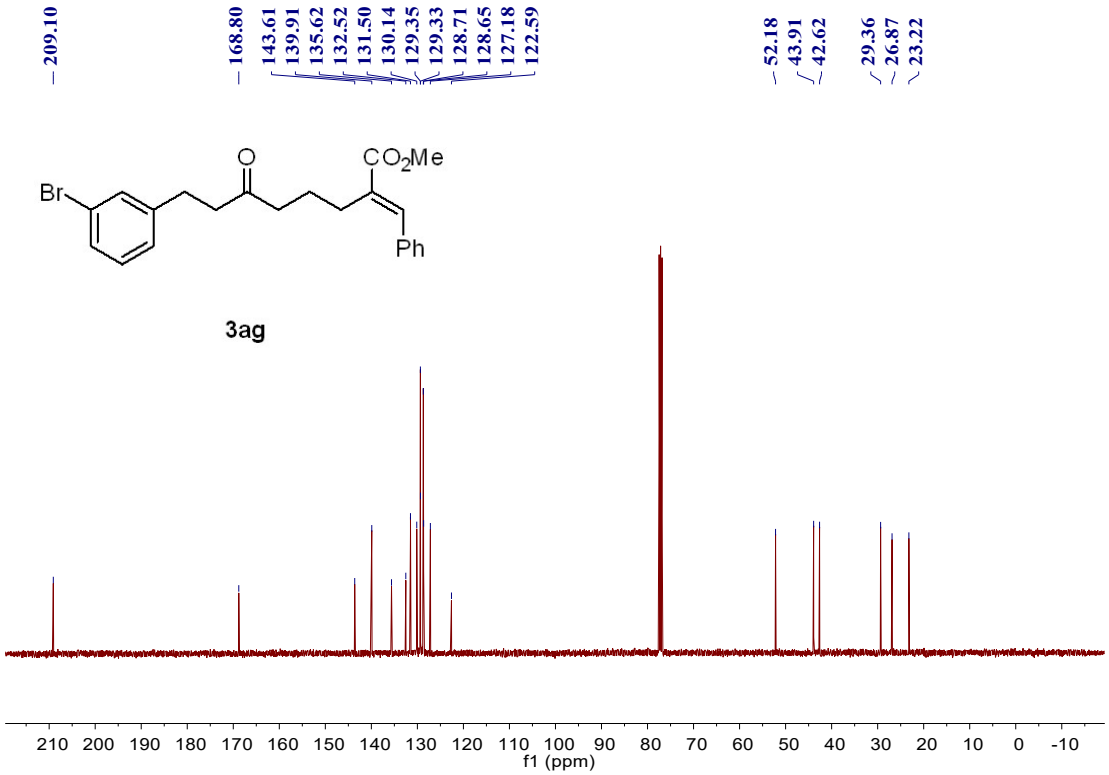


Figure S82 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ag**

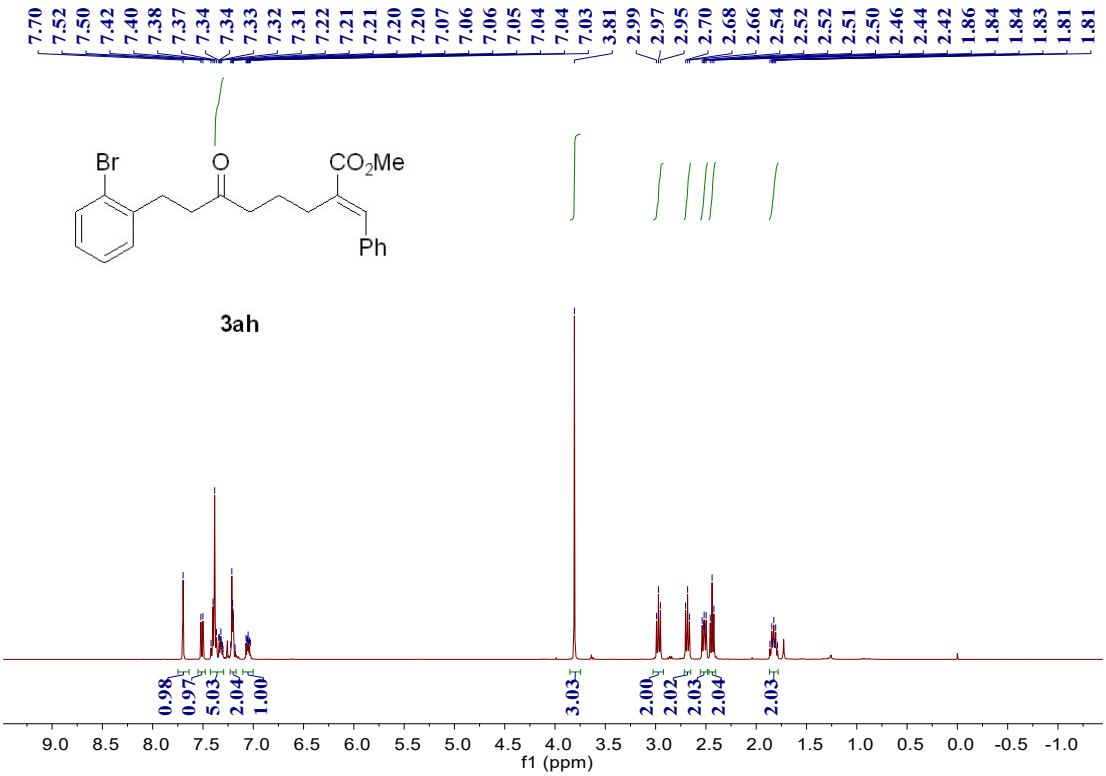


Figure S83 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ah**

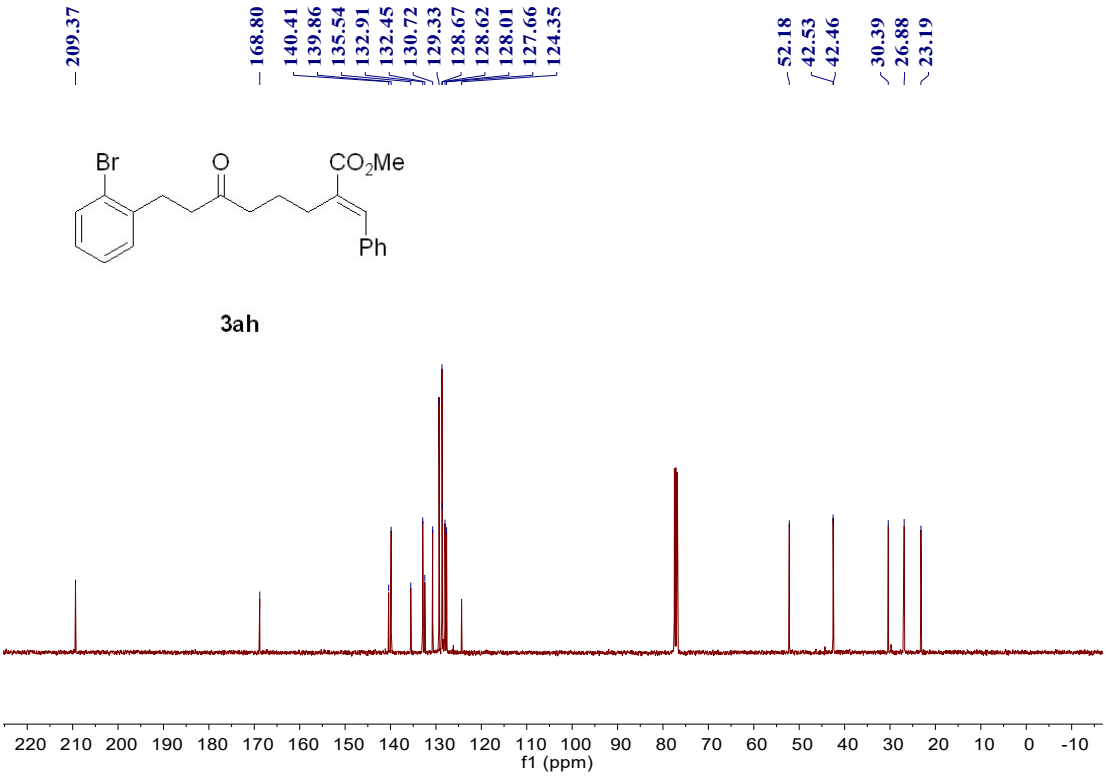


Figure S84 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ah**

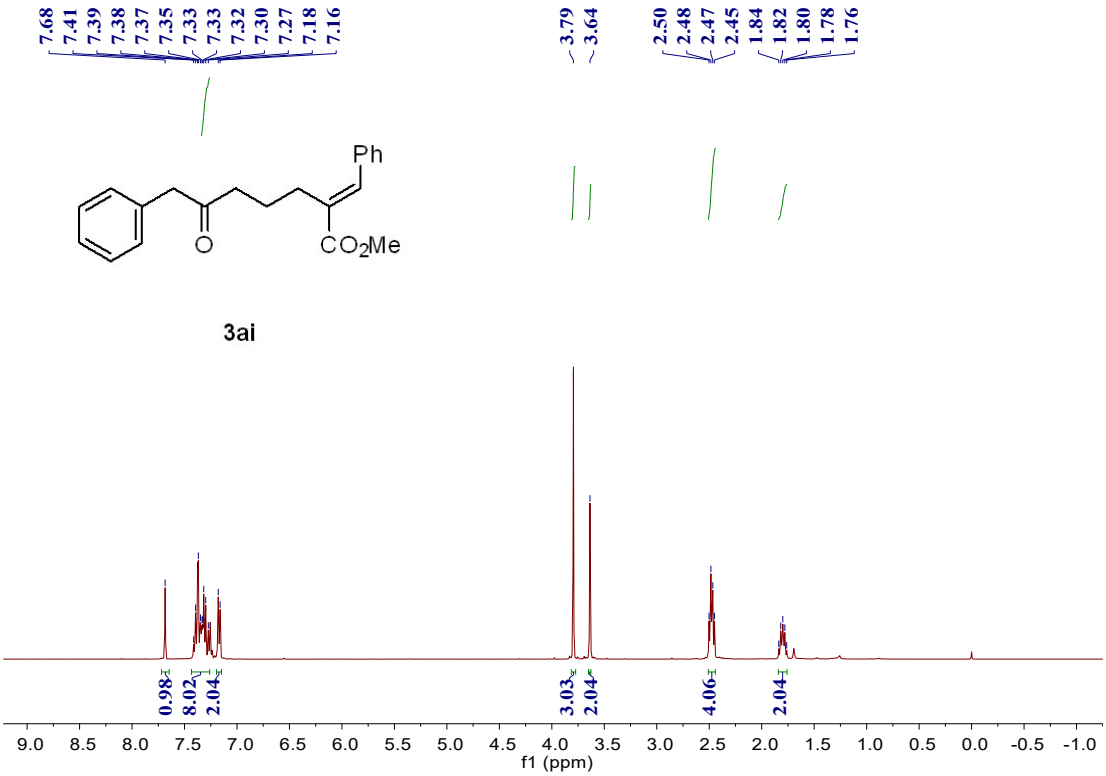


Figure S85 | [1]H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ai**

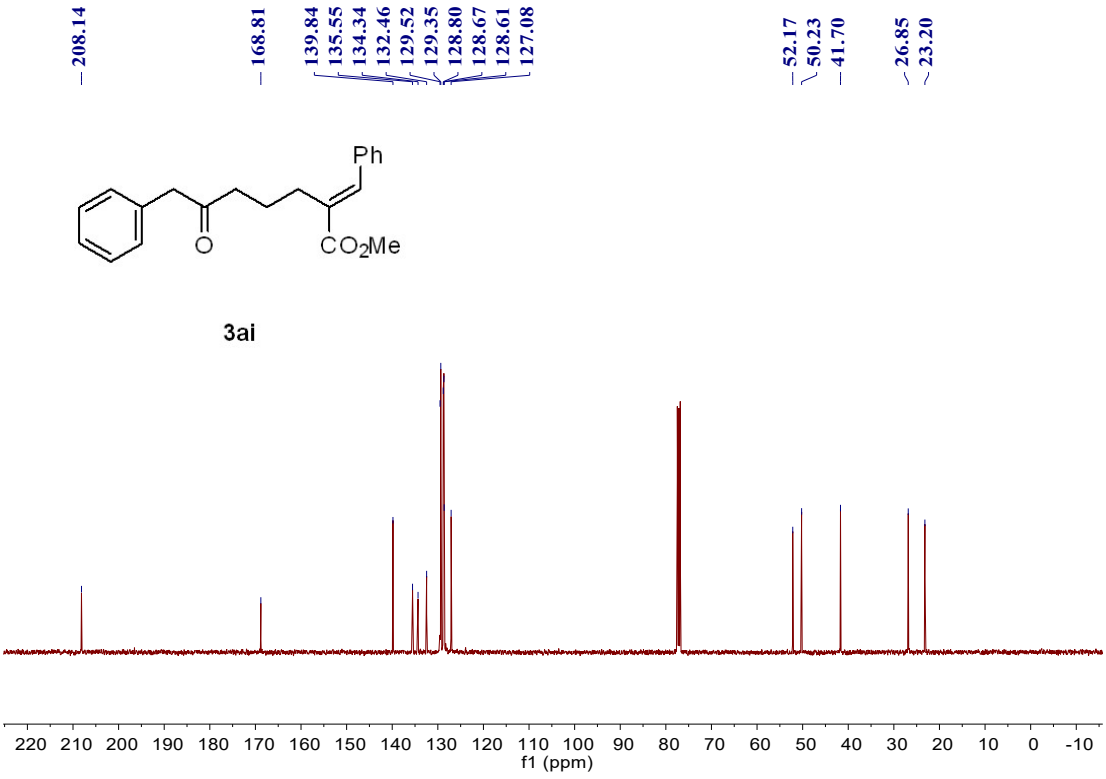


Figure S86 | [13]C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ai**

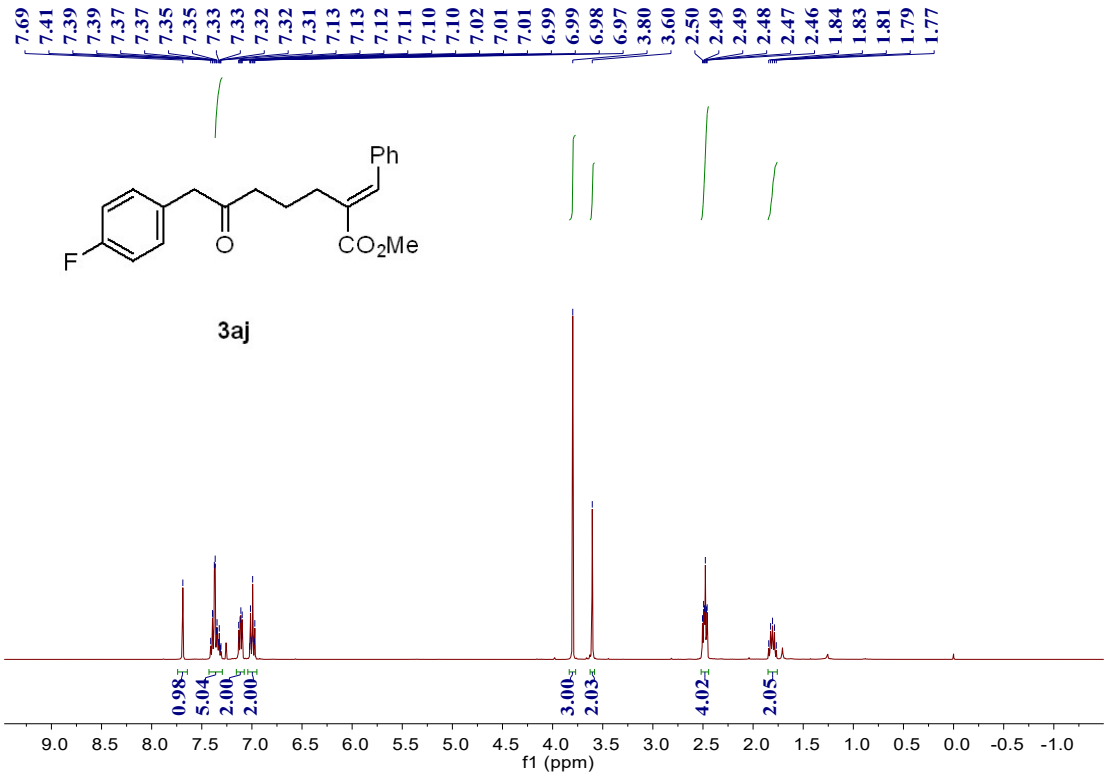


Figure S87 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3aj**

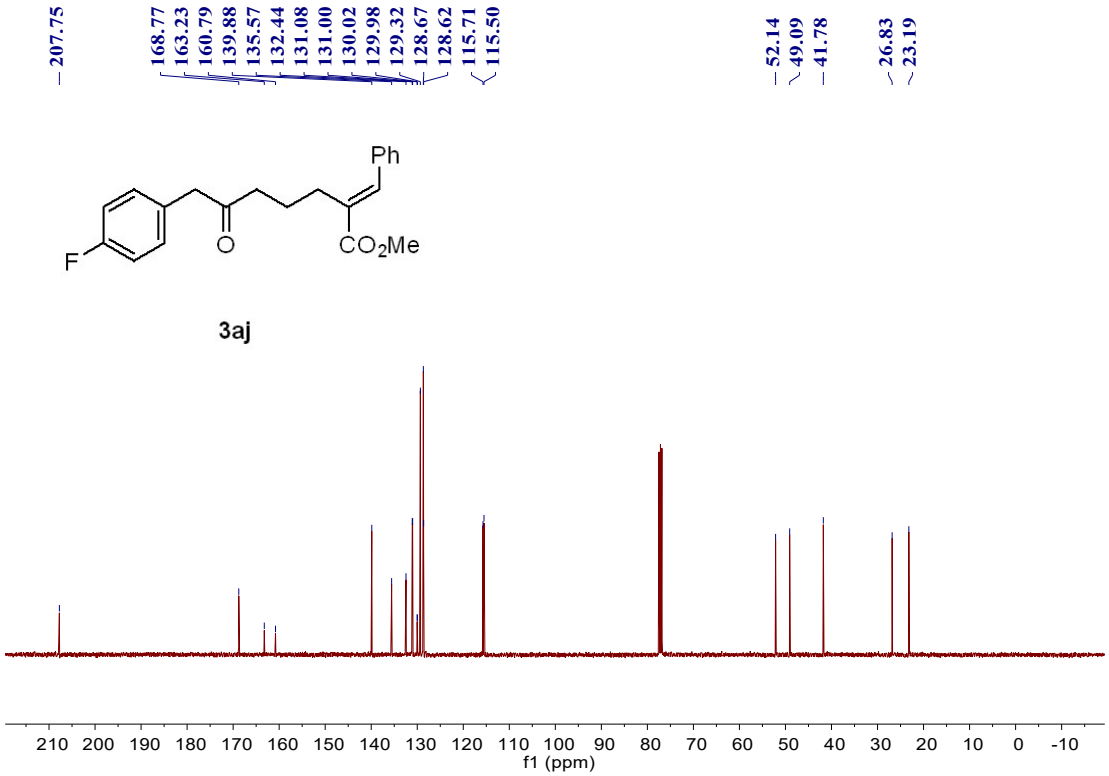


Figure S88 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3aj**

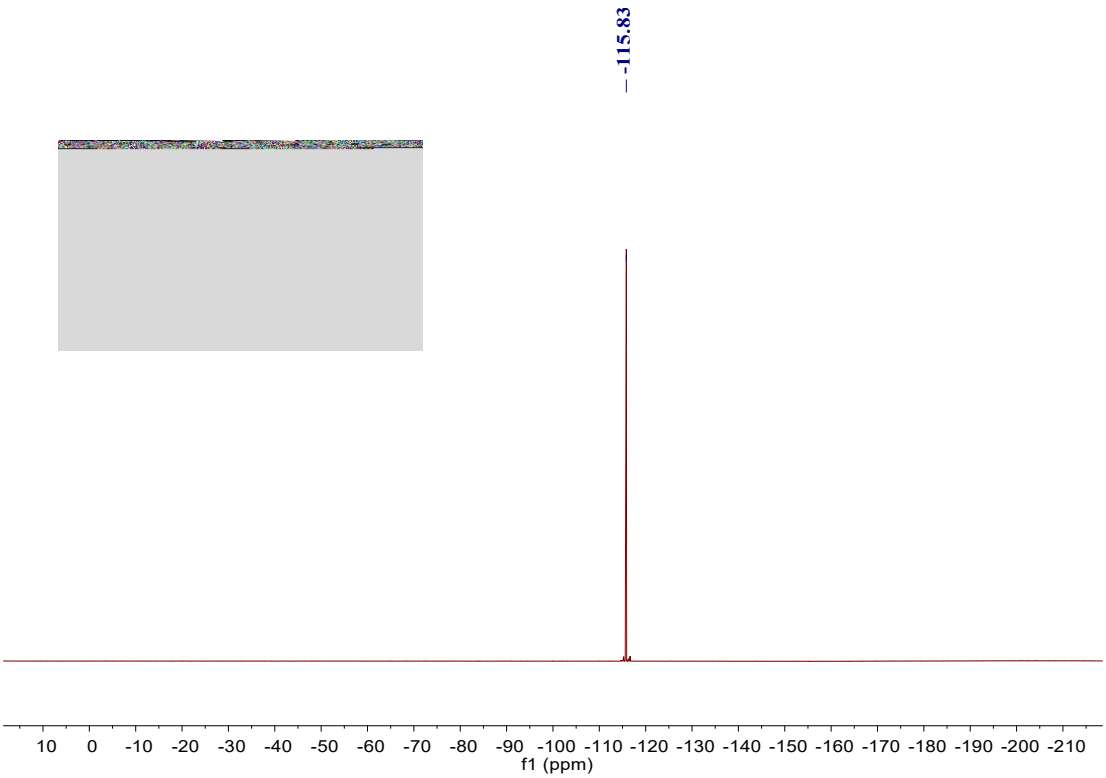


Figure S89 | ^{19}F NMR (376 MHz, Chloroform-*d*) spectra for compound **3aj**

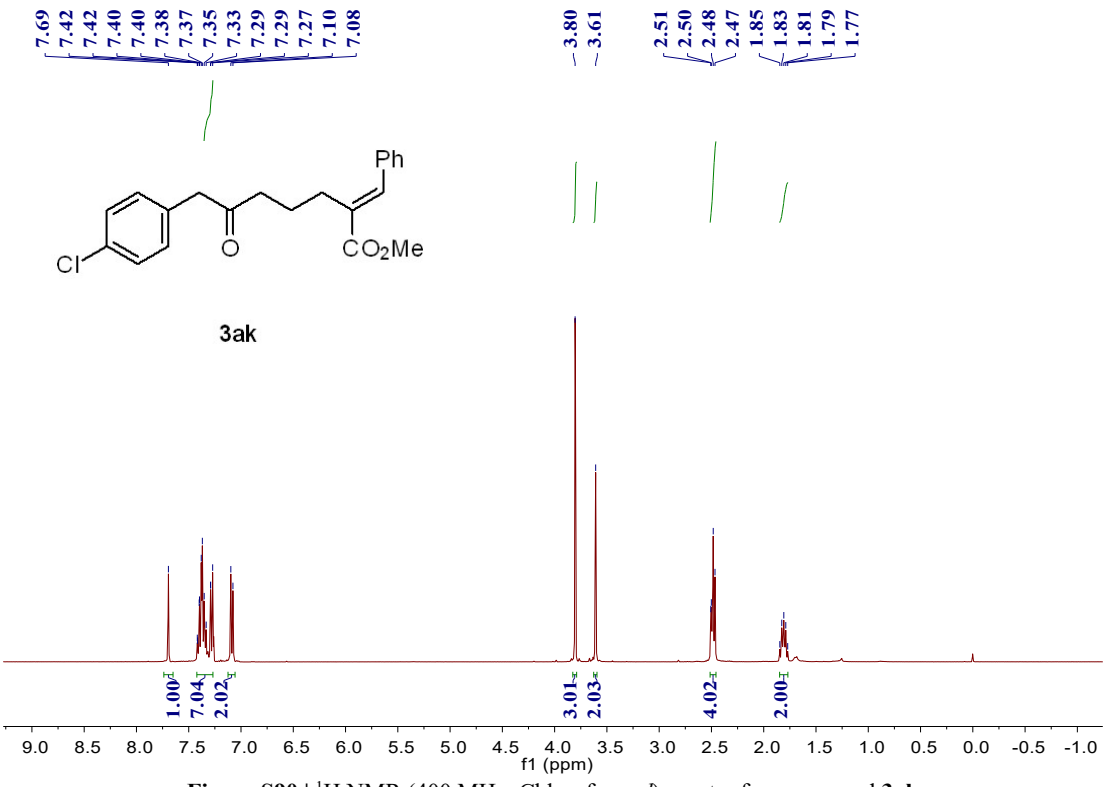


Figure S90 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ak**

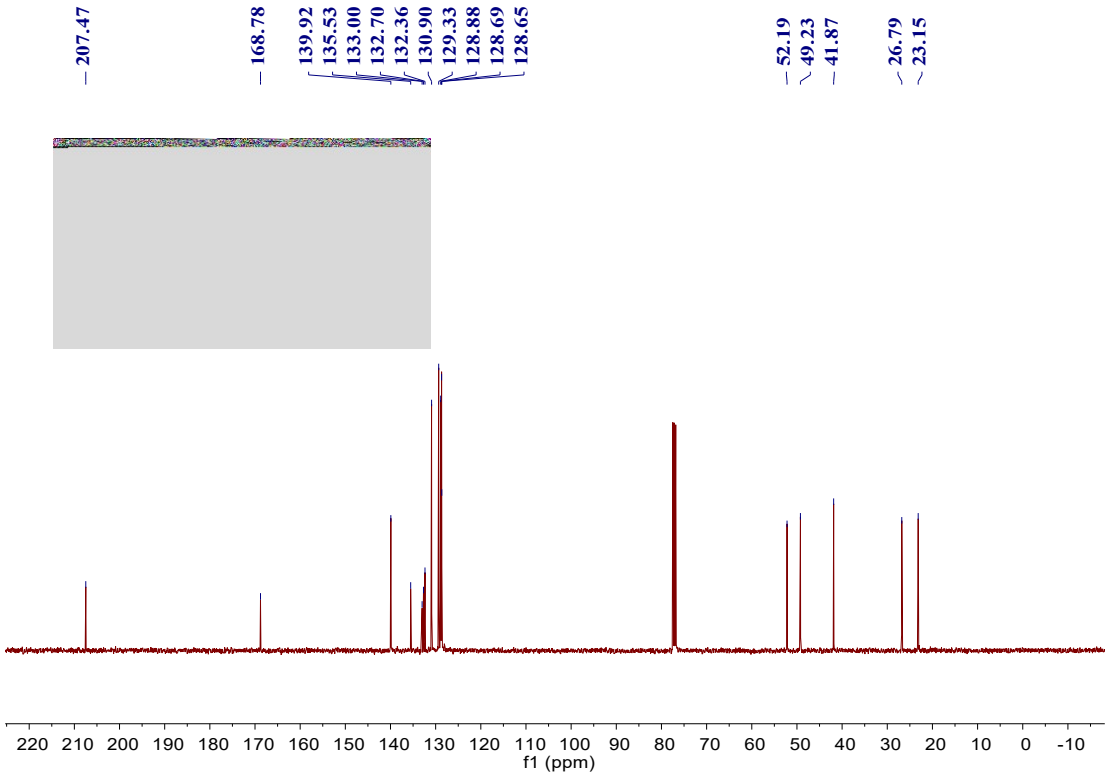


Figure S91 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ak**

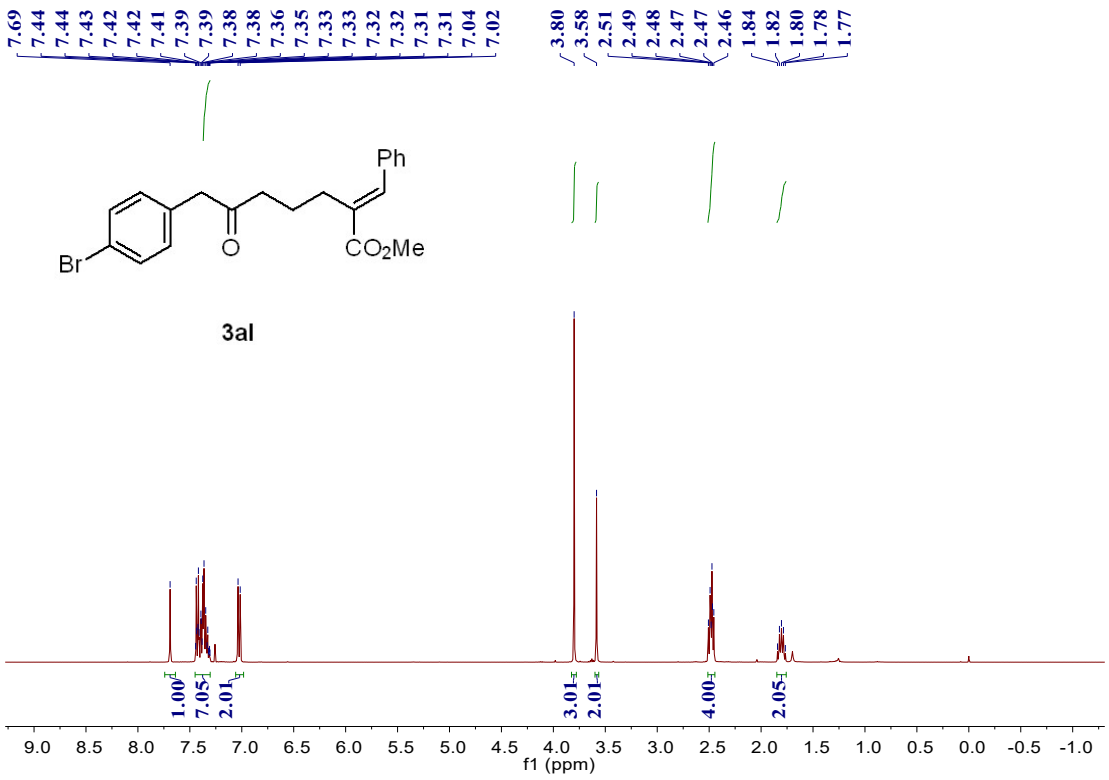


Figure S92 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3al**

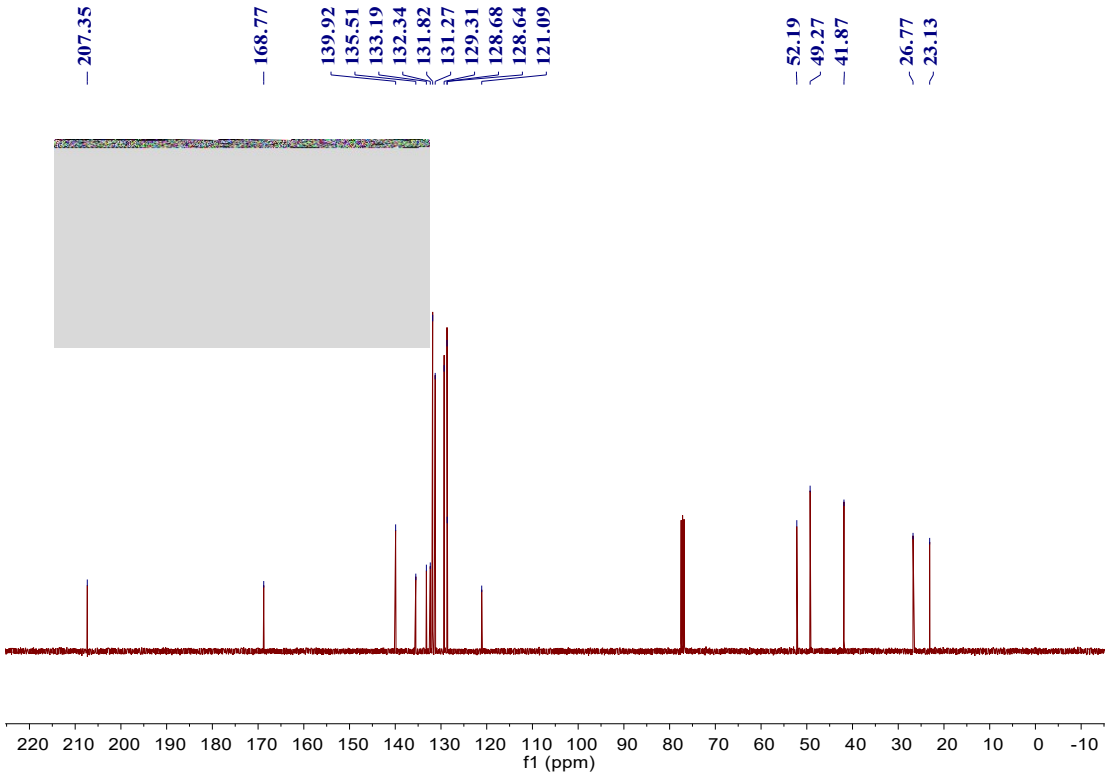


Figure S93 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3al**

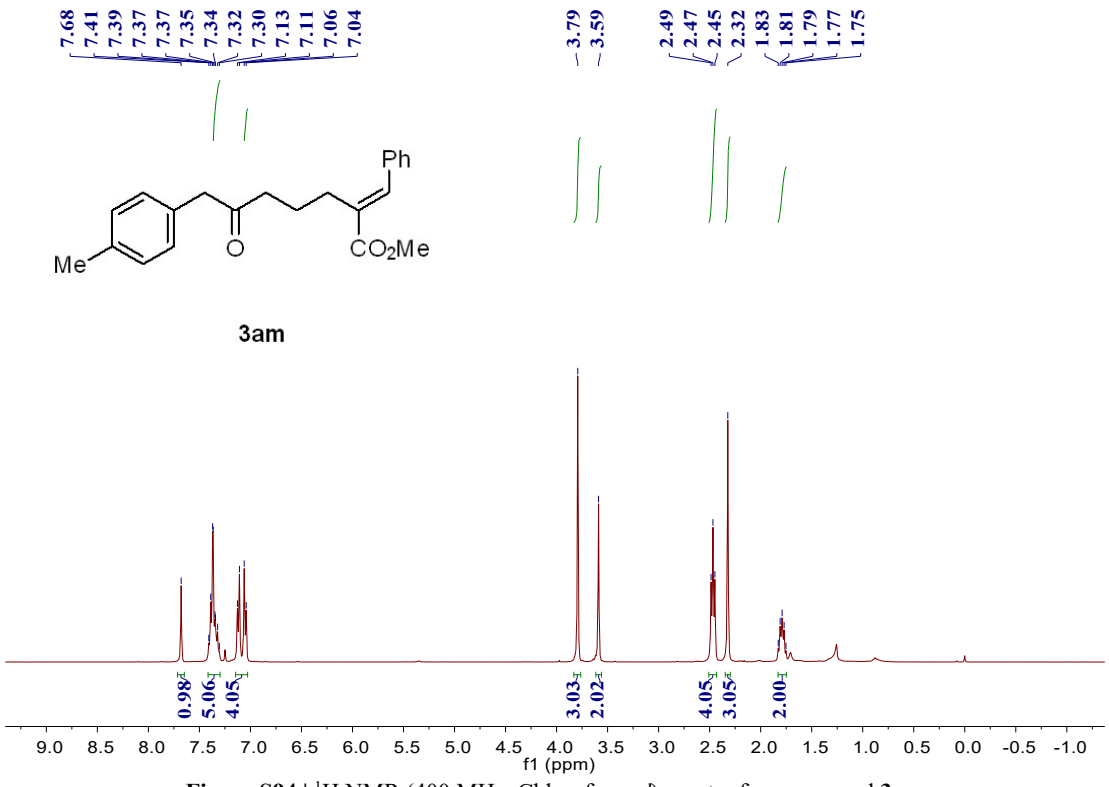


Figure S94 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3am**

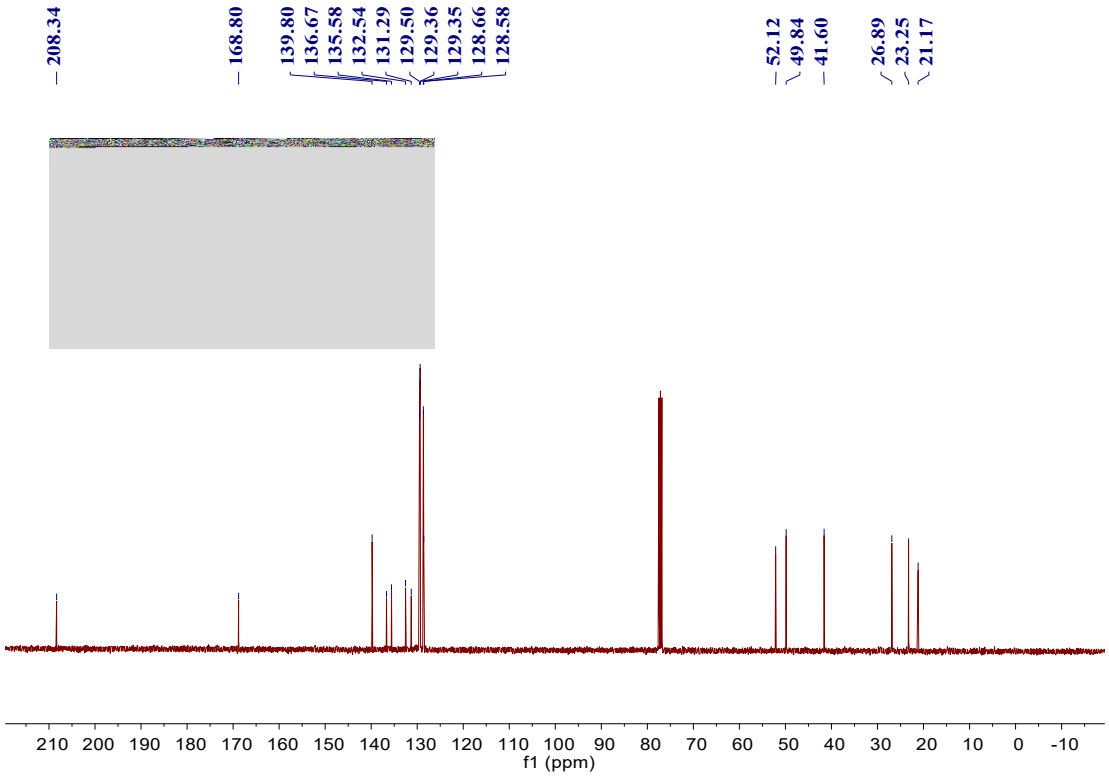


Figure S95 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3am**

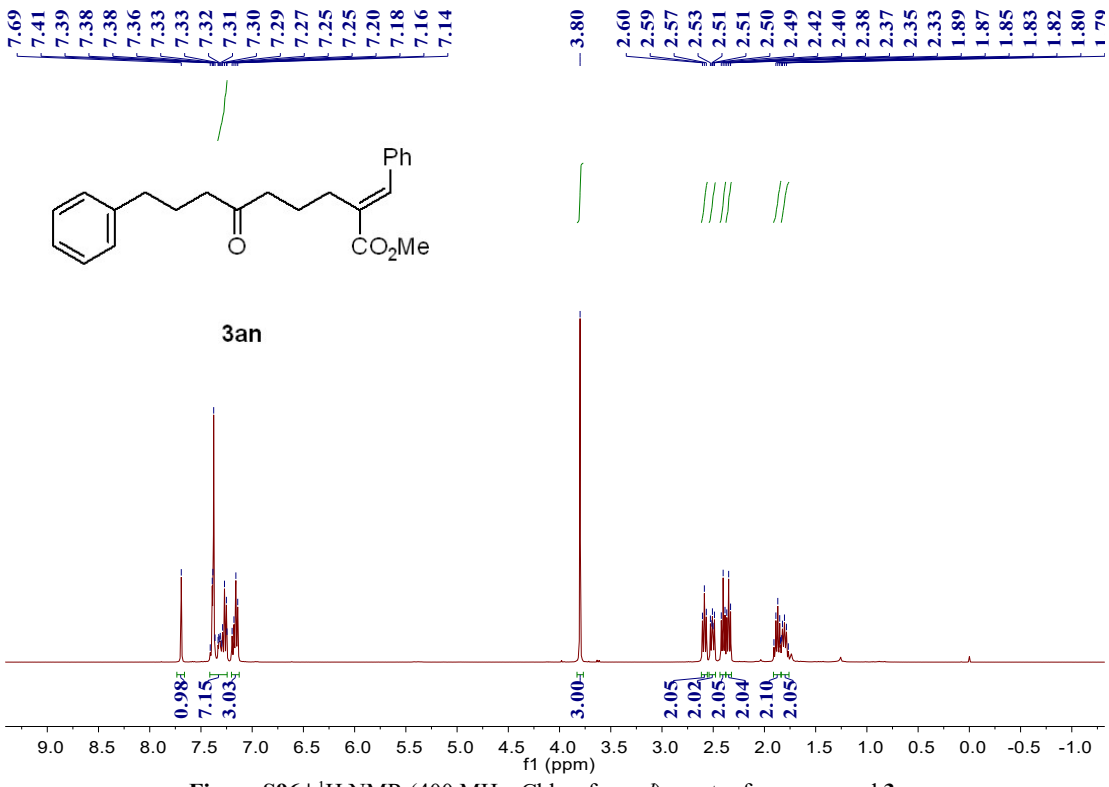


Figure S96 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3an**

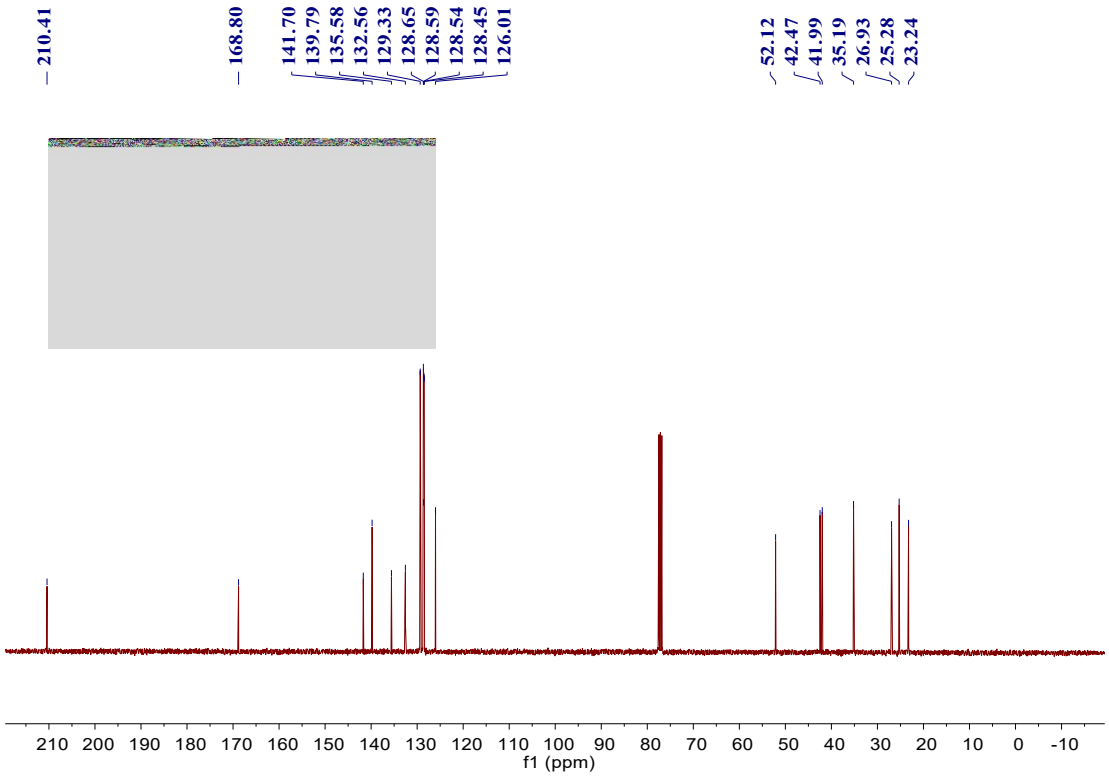


Figure S97 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3an**

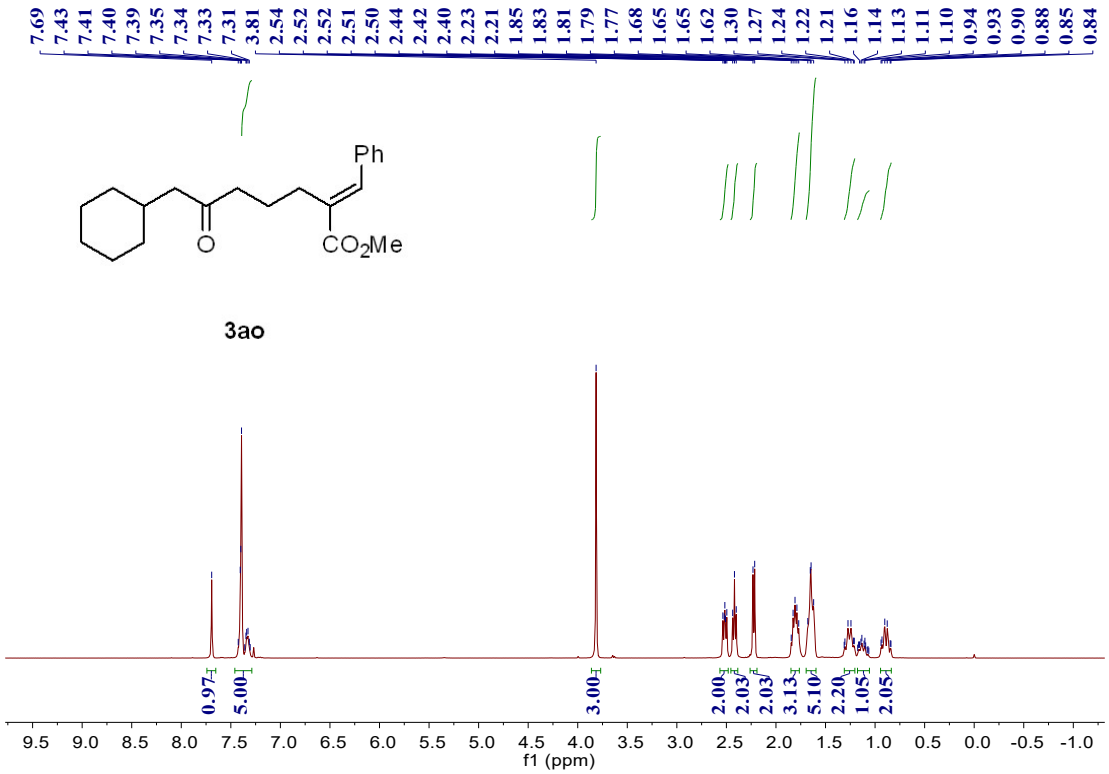


Figure S98 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ao**

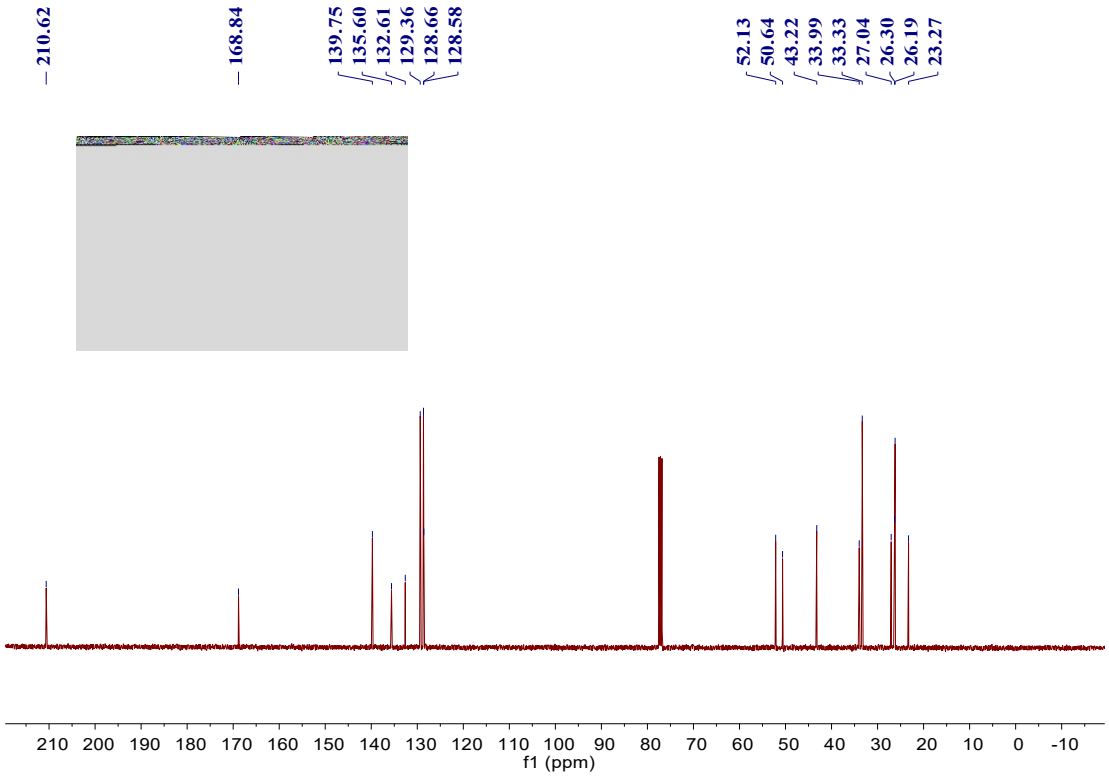


Figure S99 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ao**

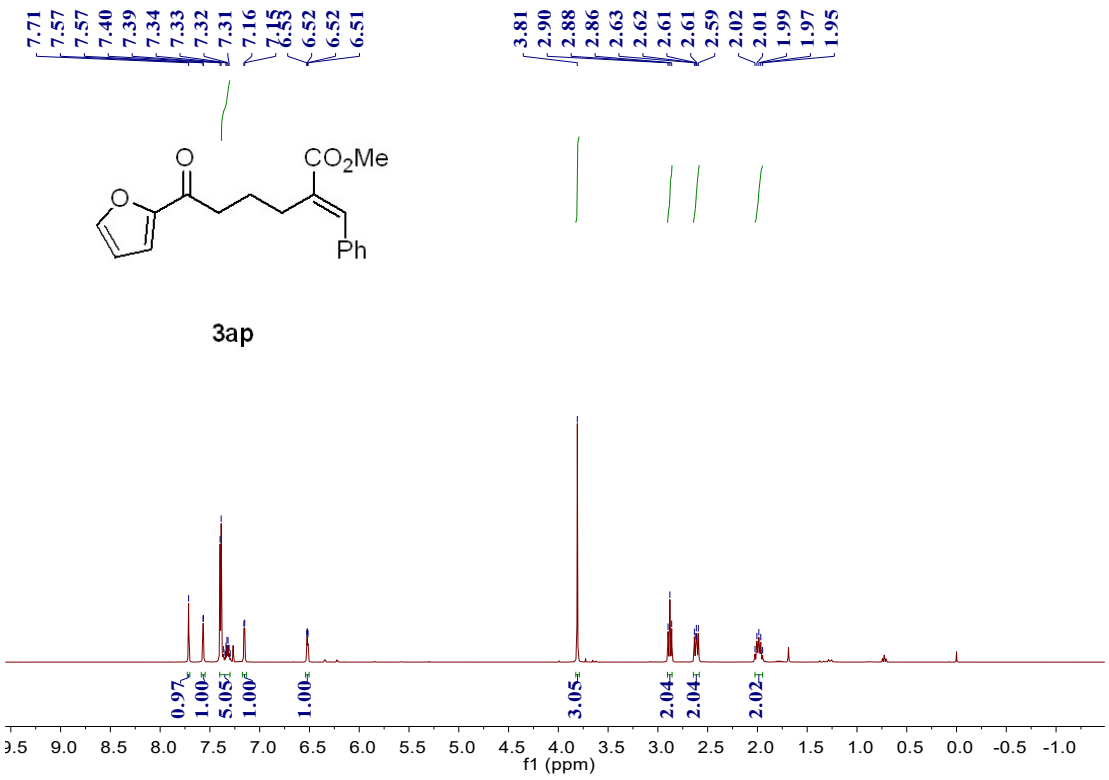


Figure S100 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ap**

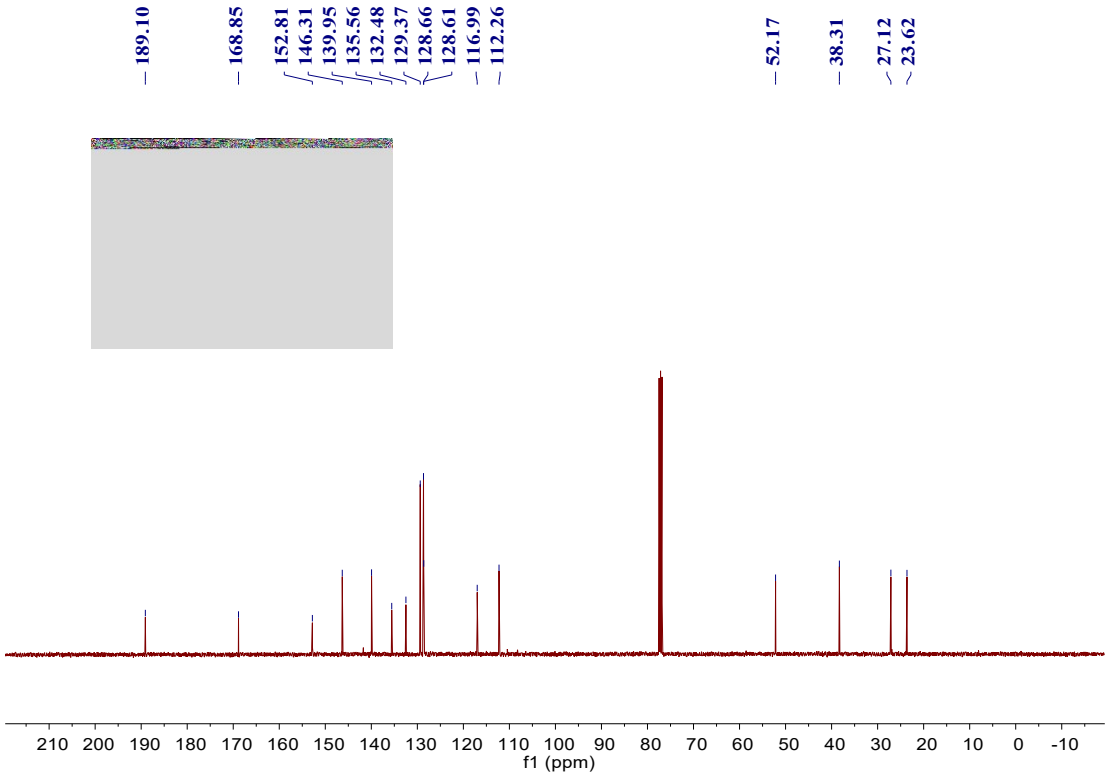


Figure S101 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ap**

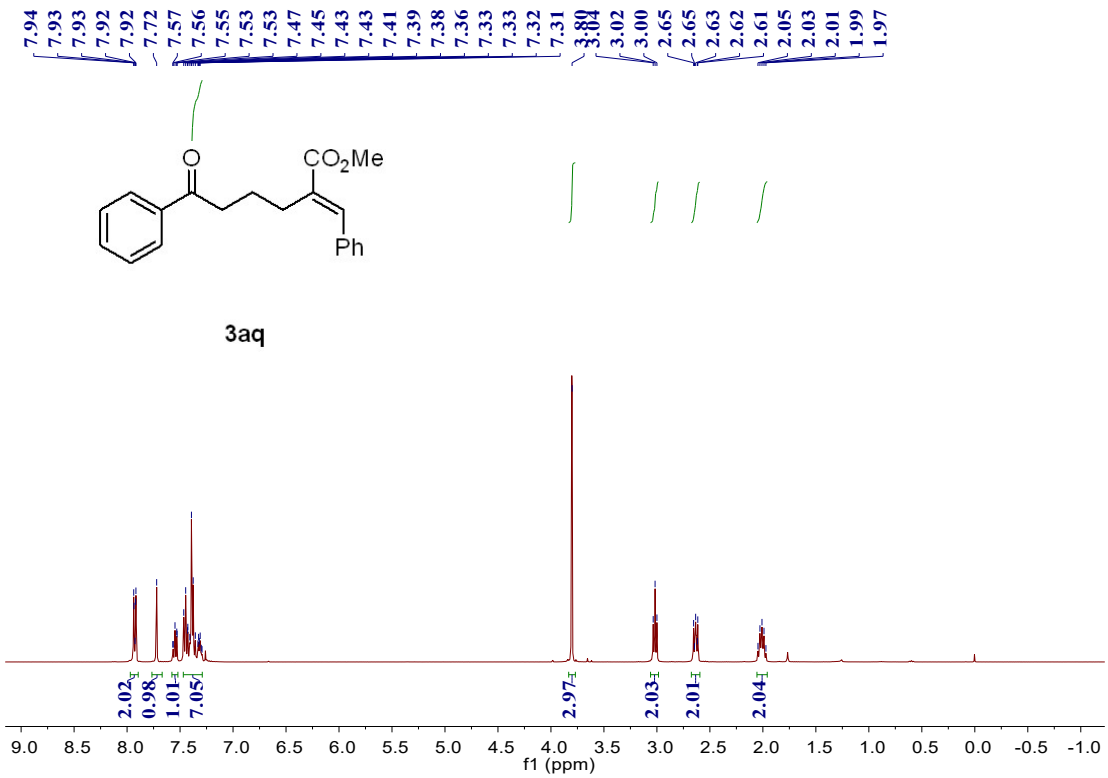


Figure S102 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3aq**

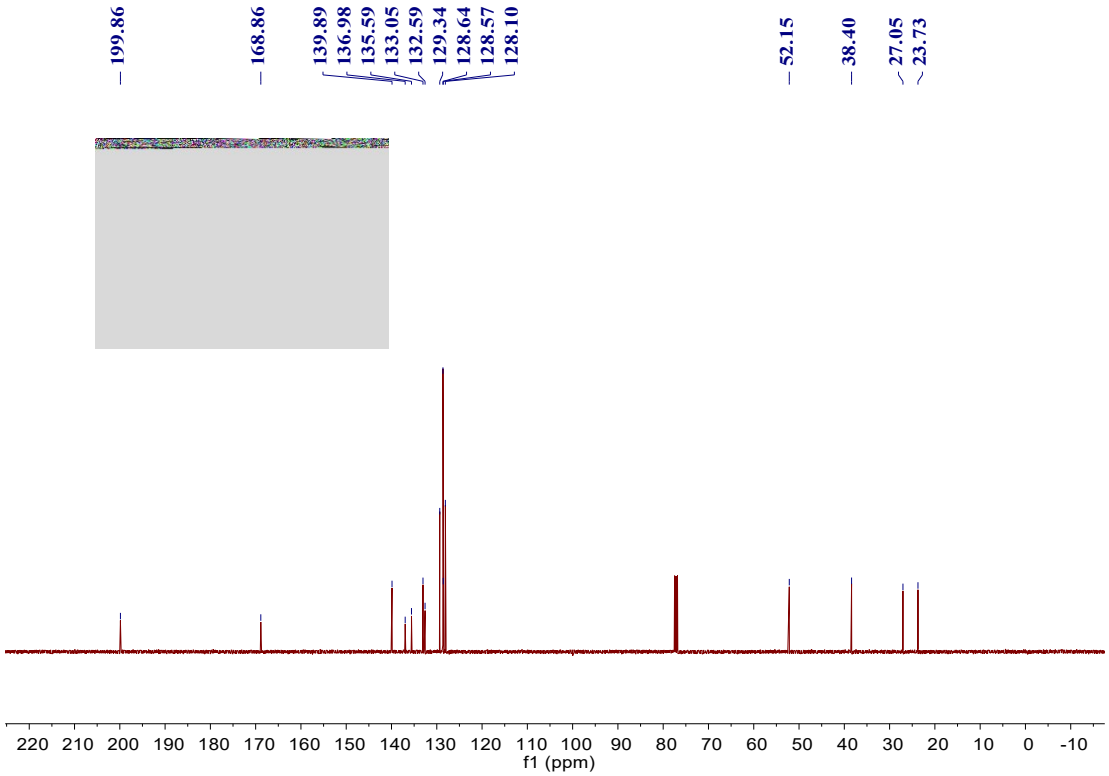


Figure S103 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3aq**

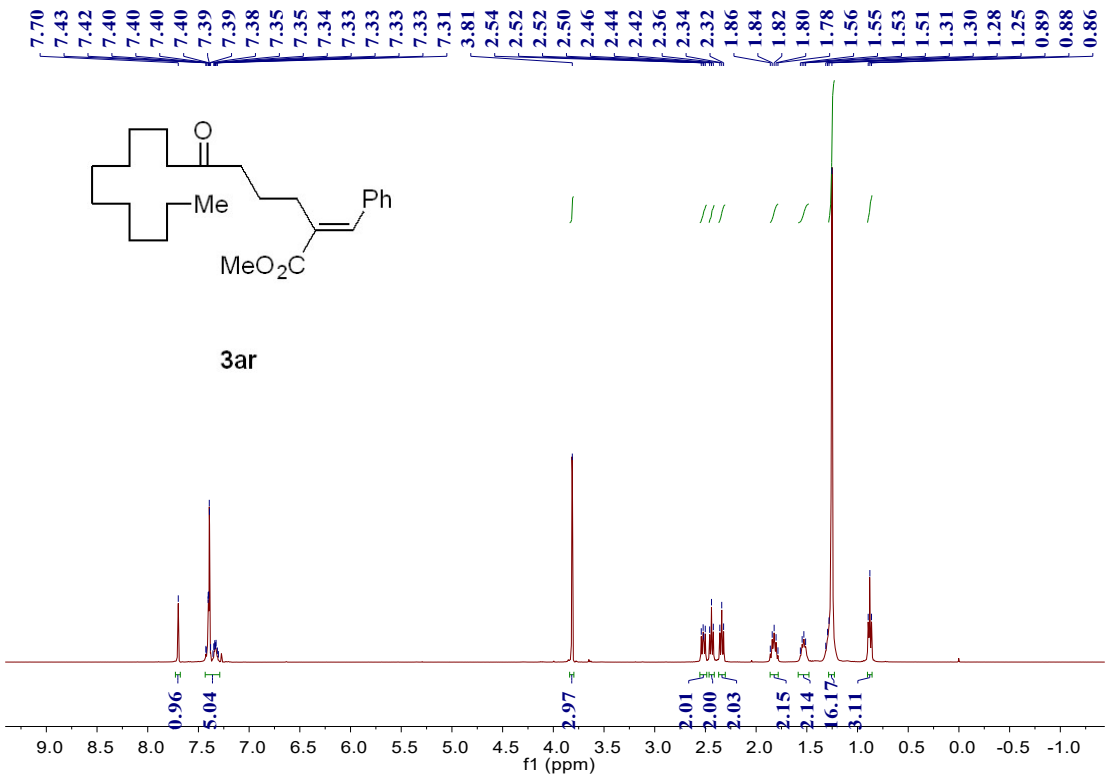


Figure S104 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3ar**

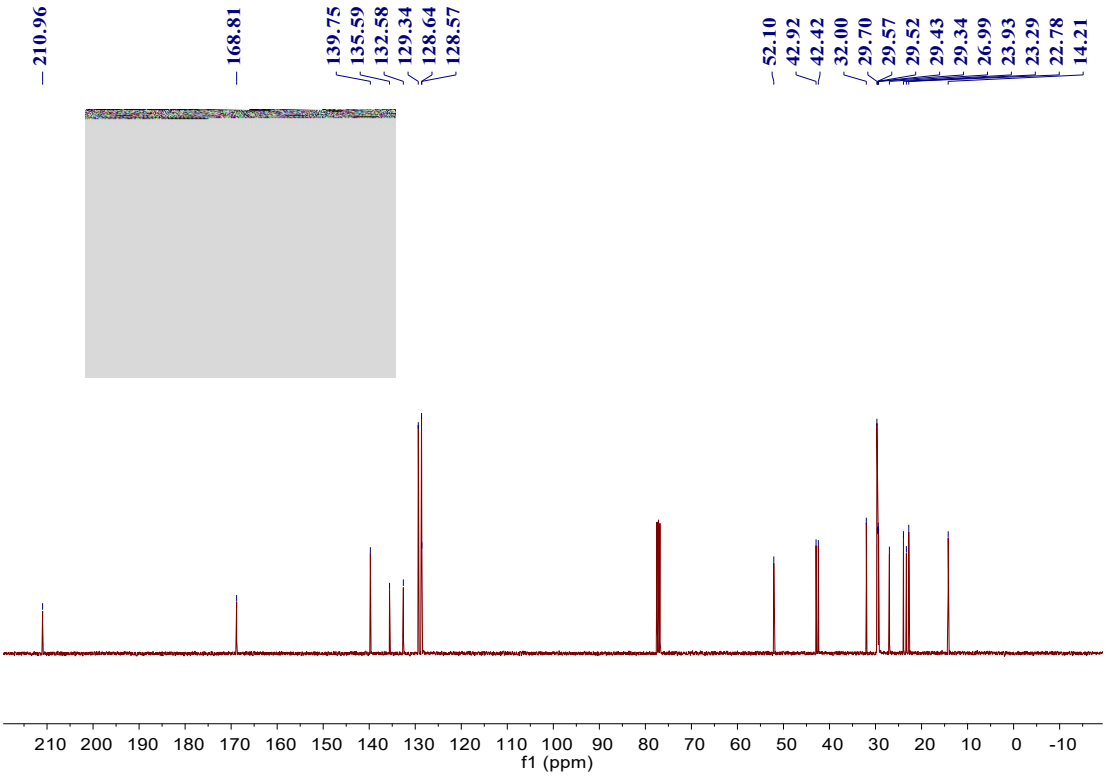


Figure S105 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ar**

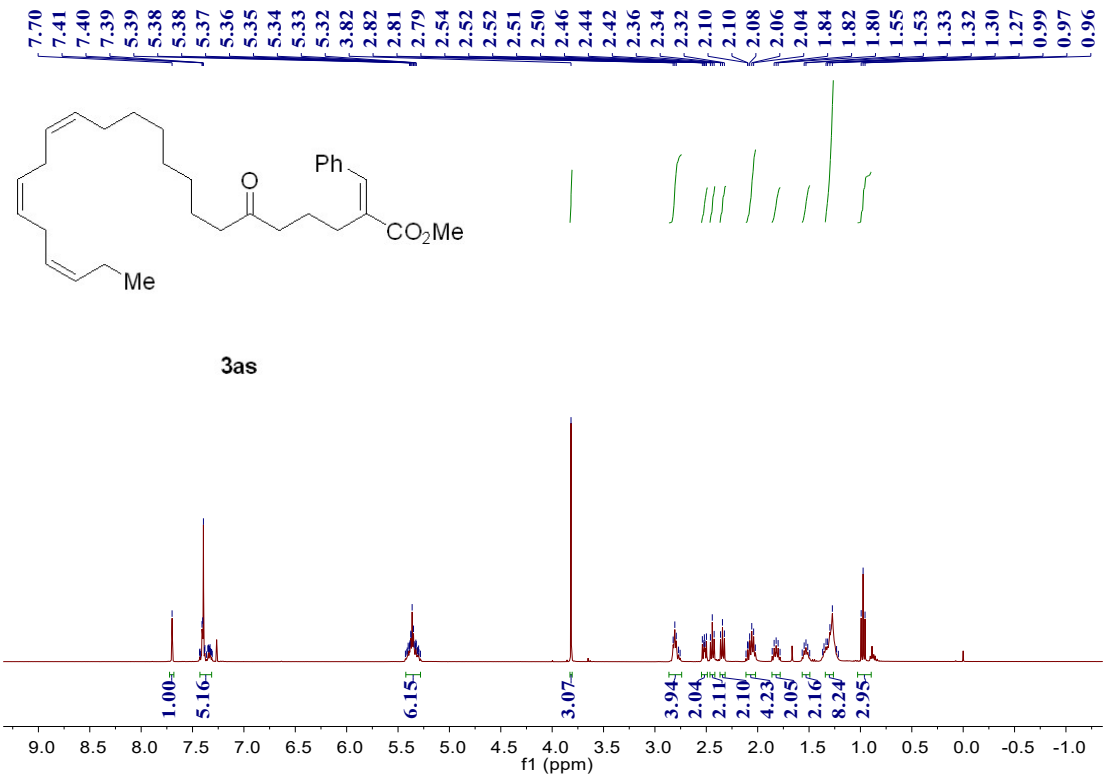


Figure S106 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3as**

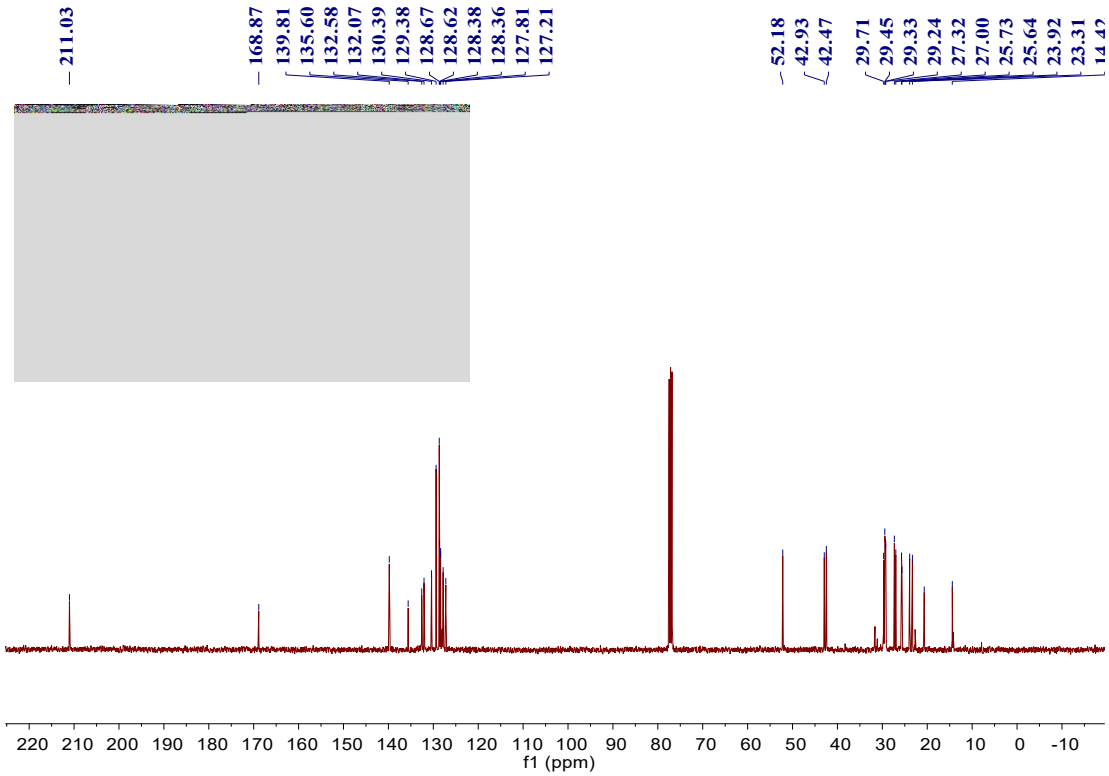


Figure S107 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3as**

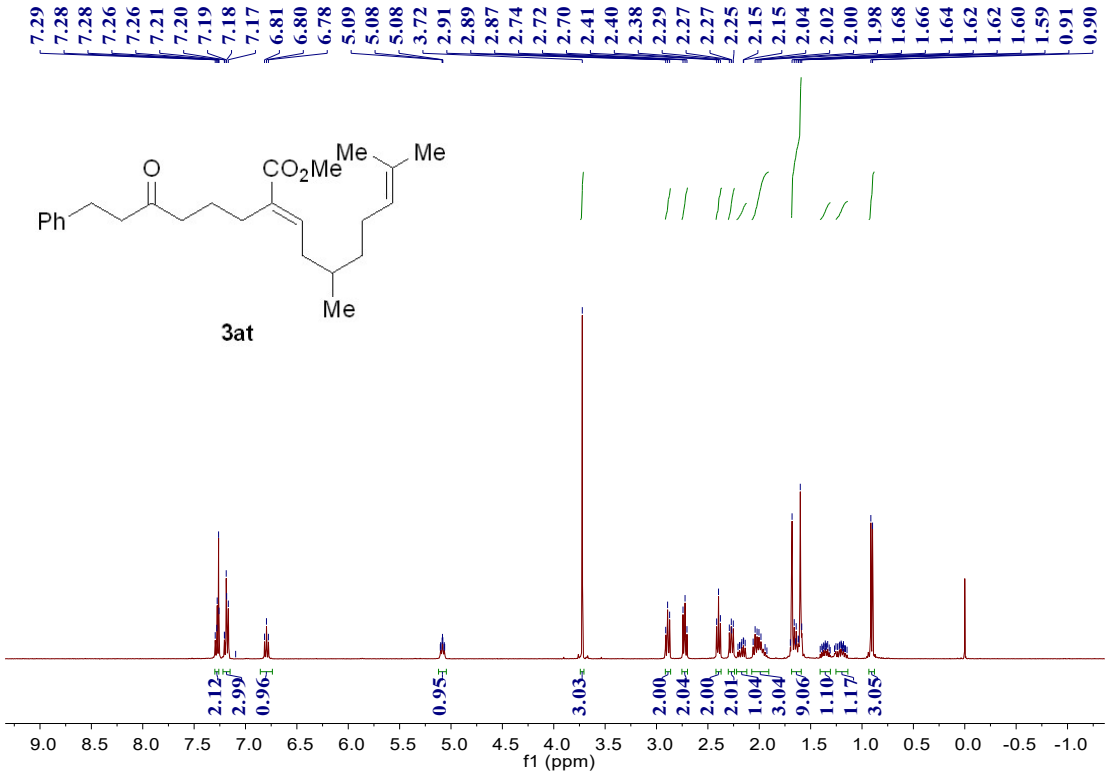


Figure S108 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3at**

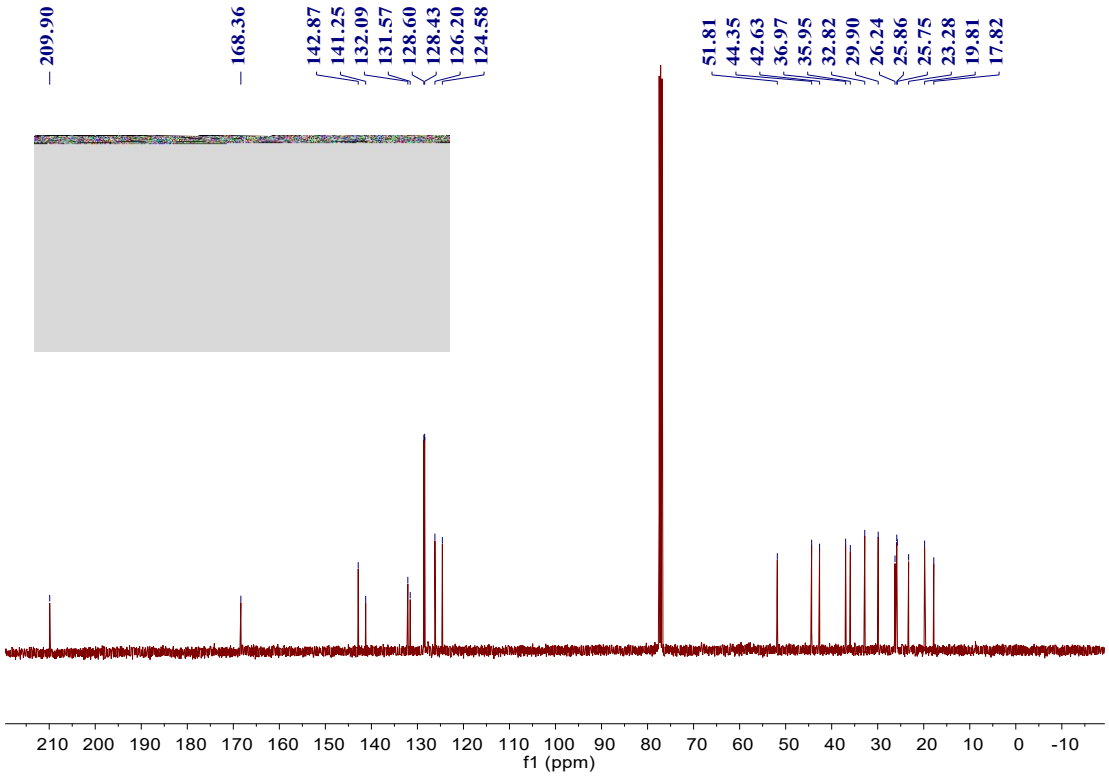


Figure S109 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3at**

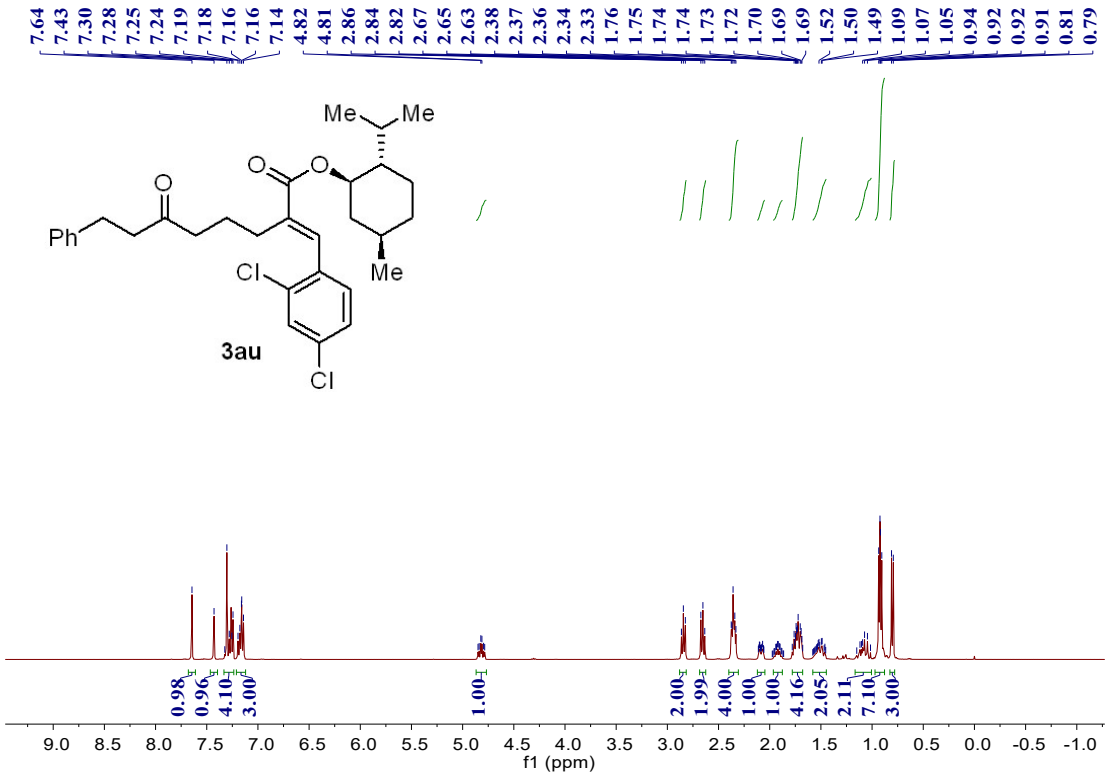


Figure S110 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3au**

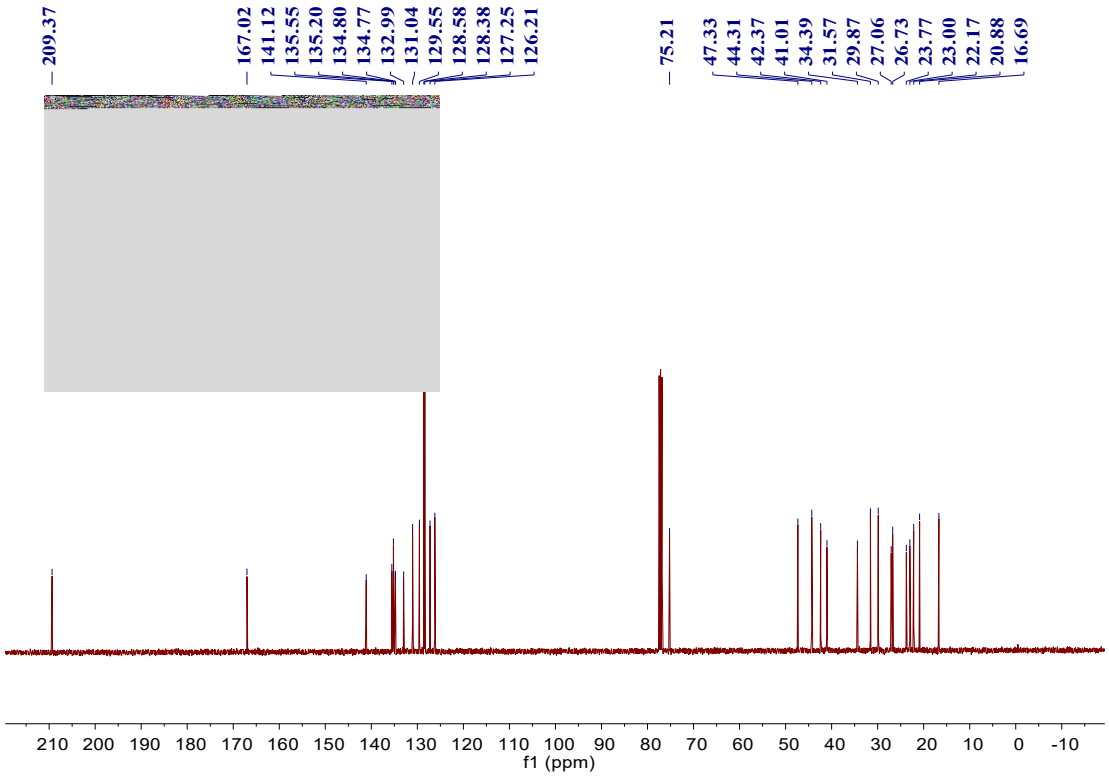


Figure S111 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3au**

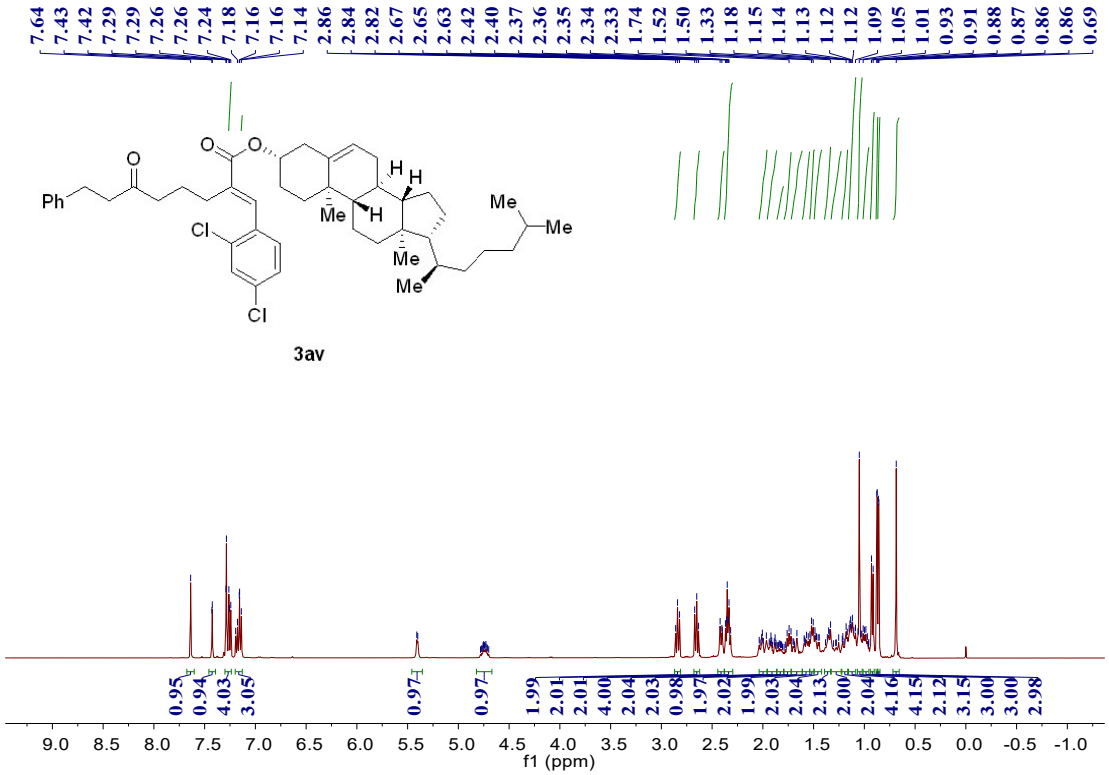


Figure S112 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3av**

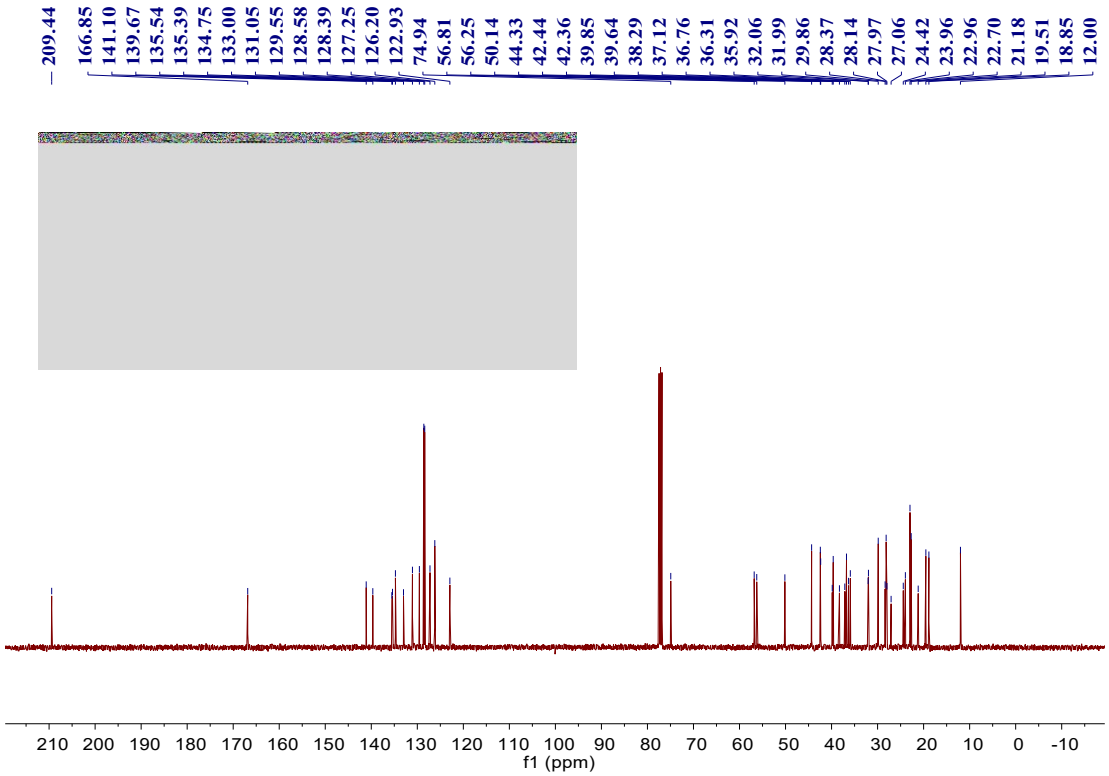


Figure S113 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3av**

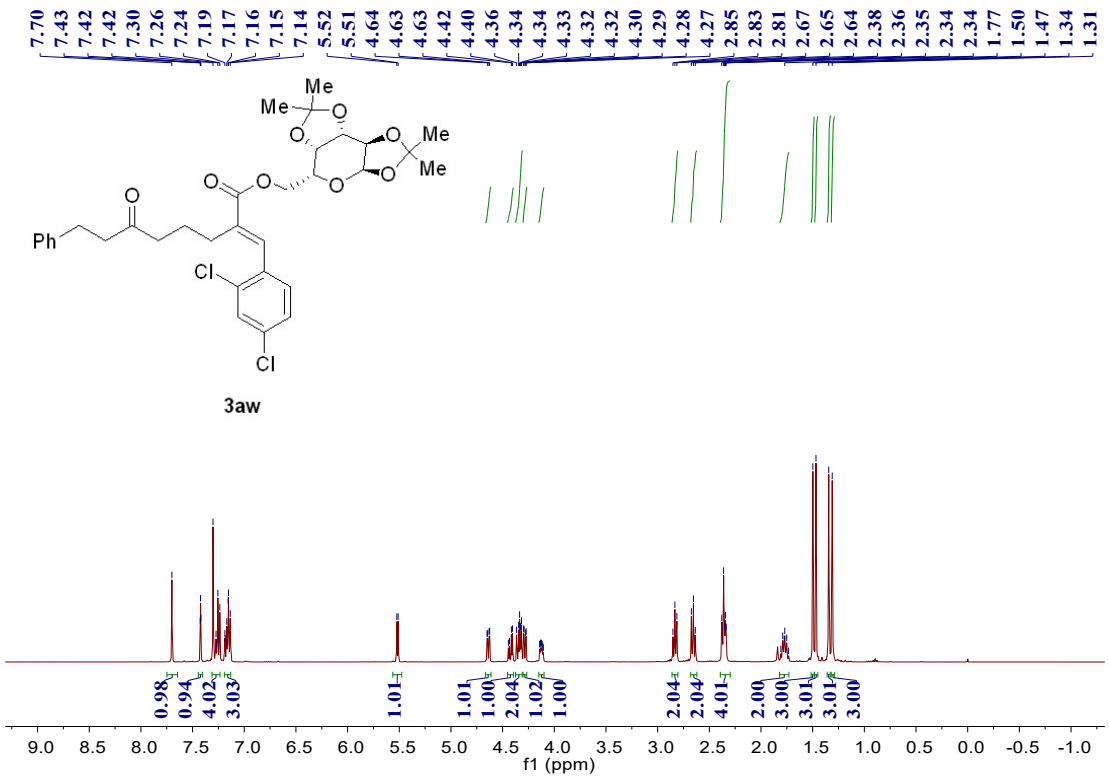


Figure S114 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3aw**

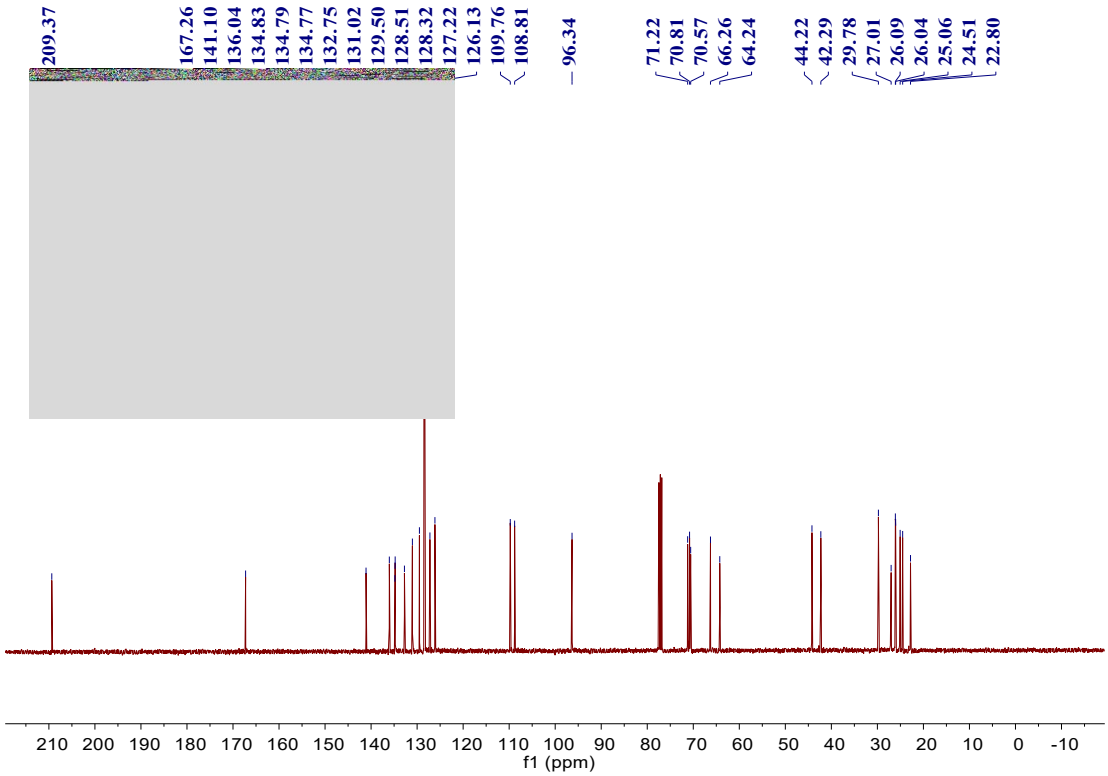


Figure S115 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3aw**

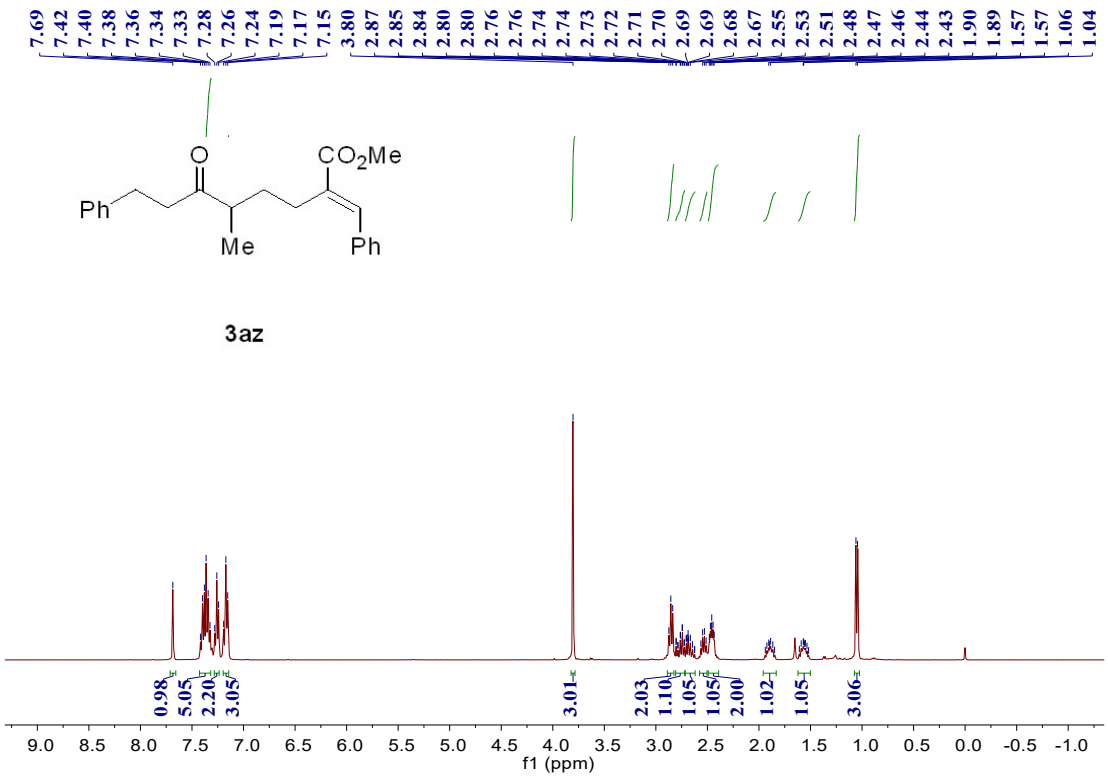


Figure S116 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3az**

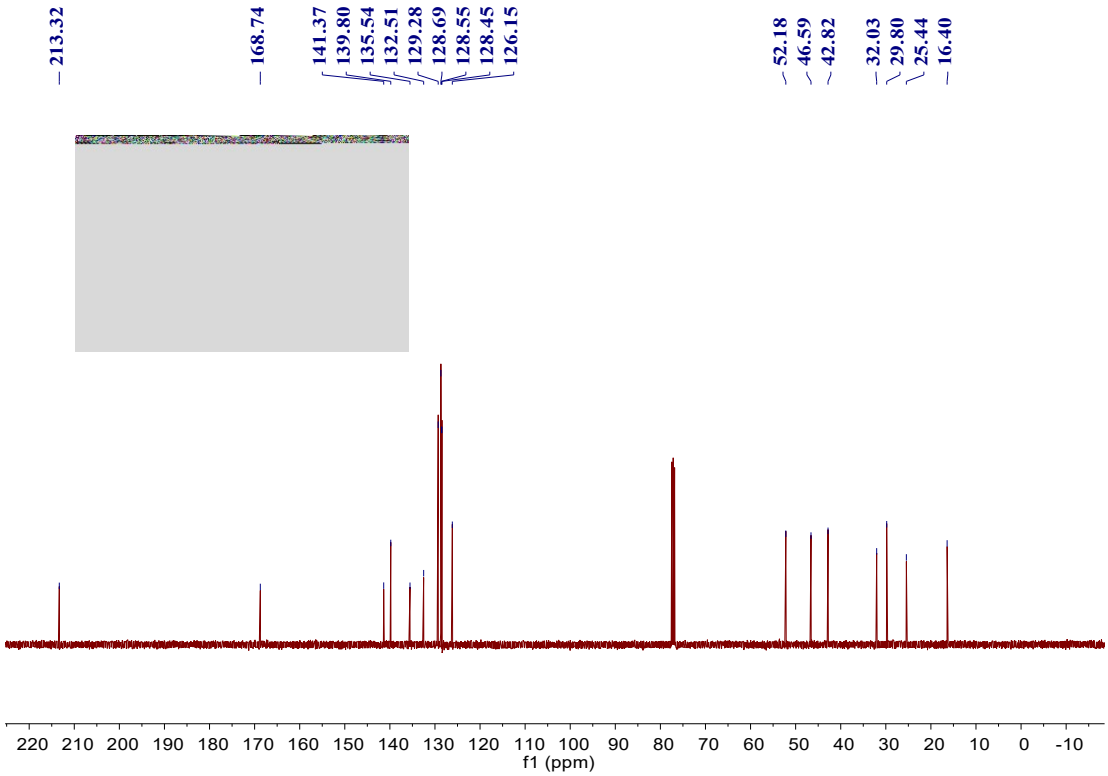


Figure S117 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3az**

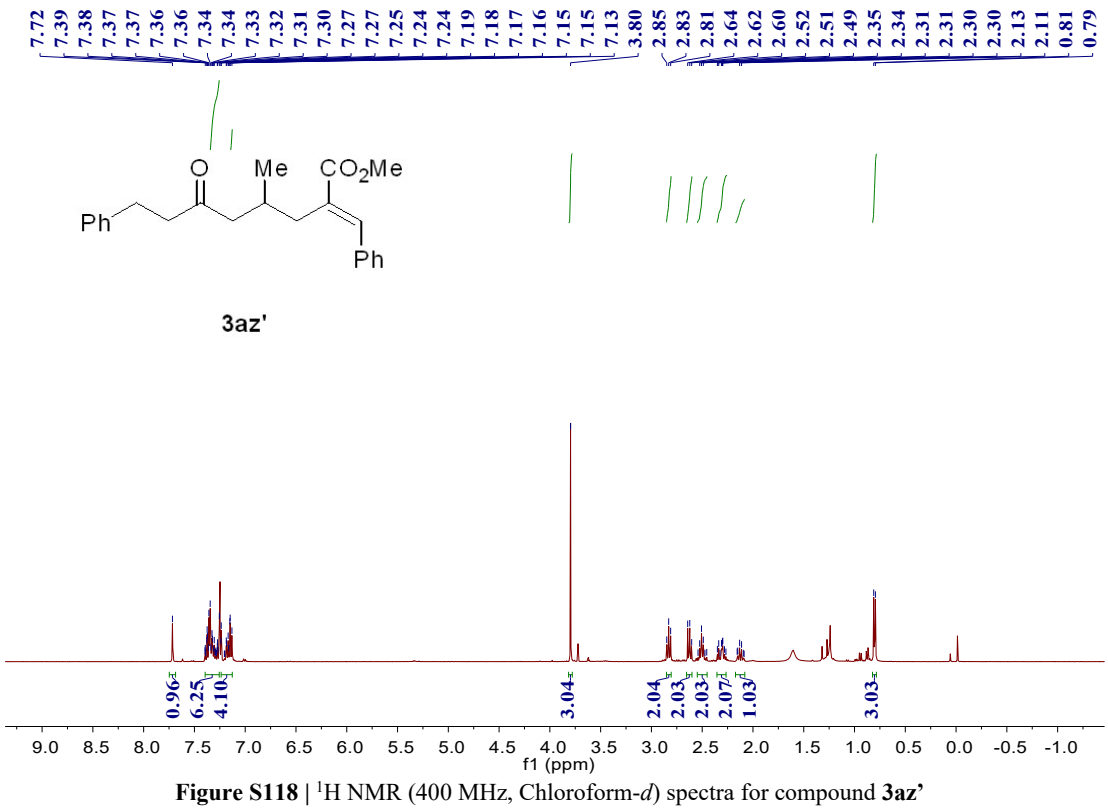


Figure S118 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **3az'**

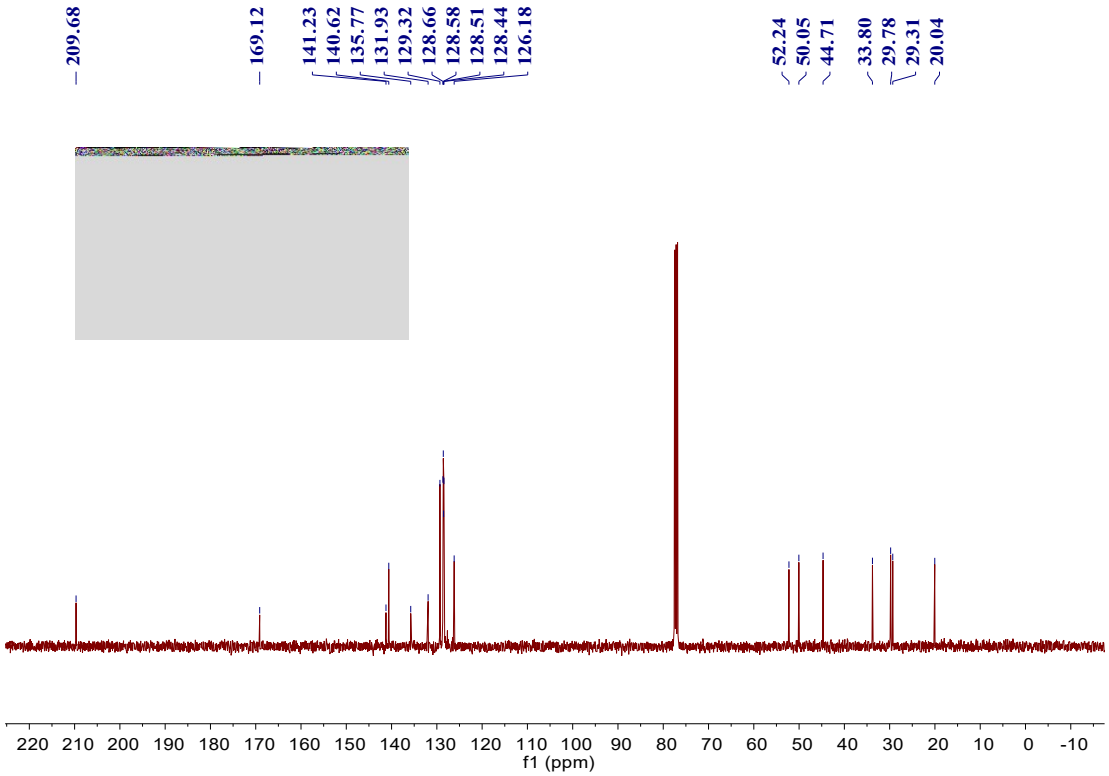


Figure S119 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3az'**

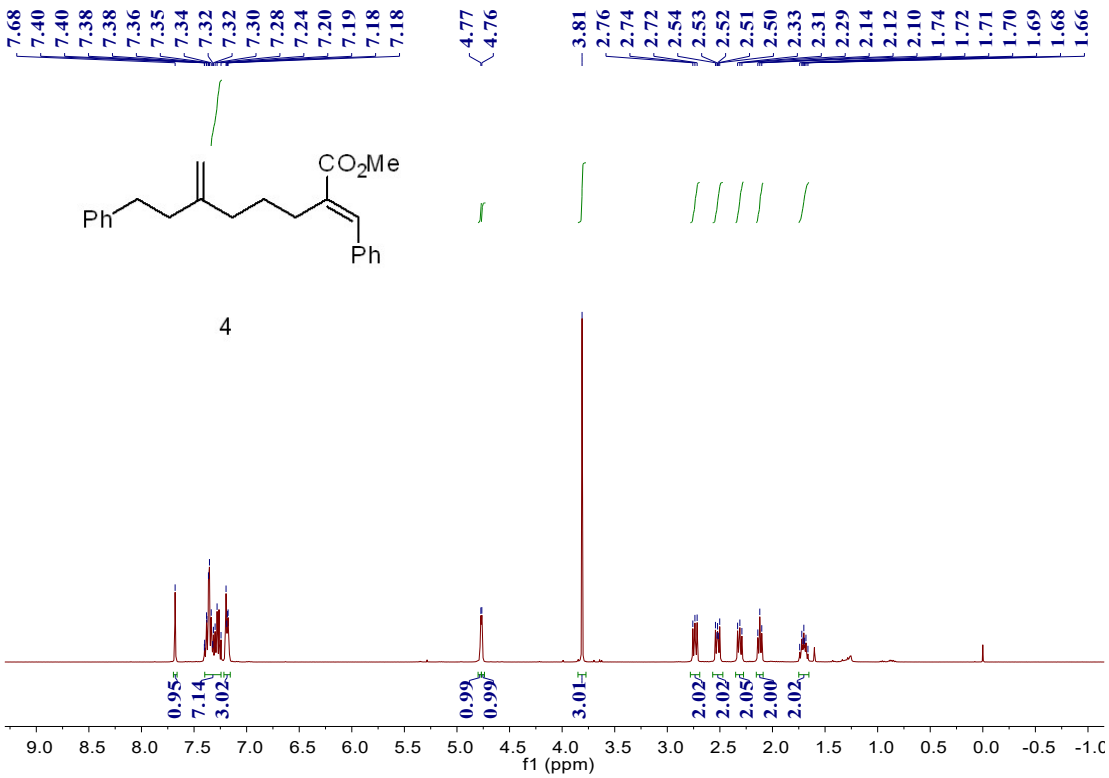


Figure S120 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **4**

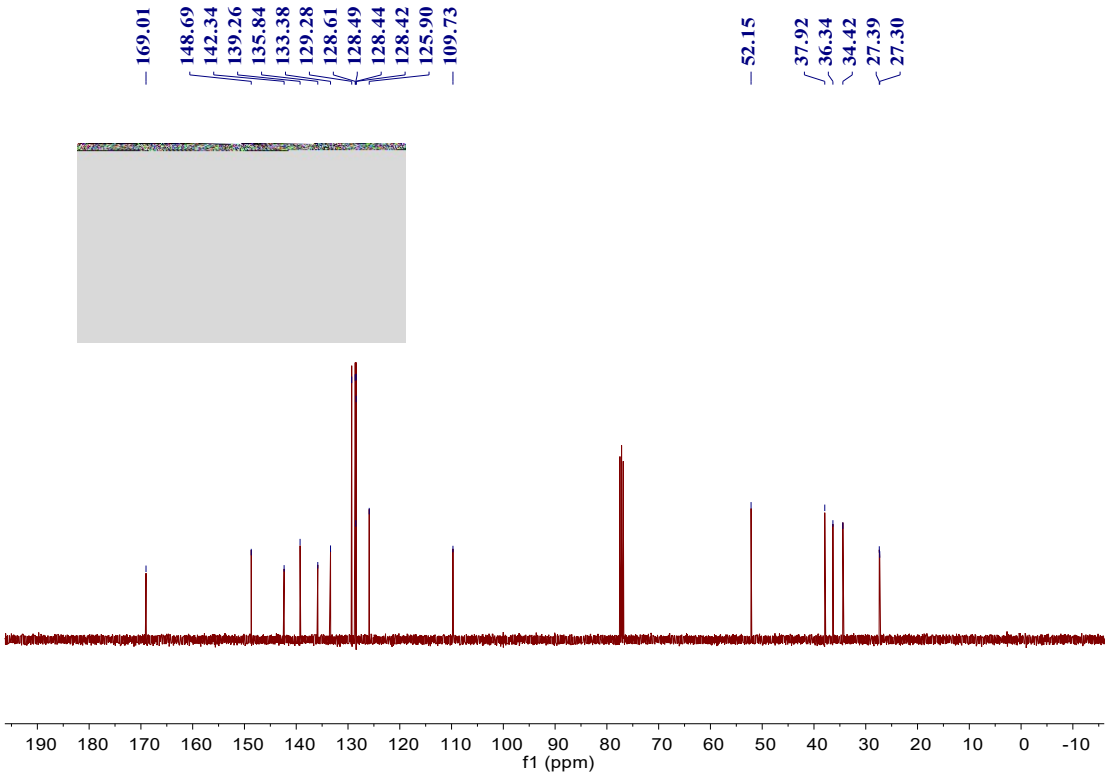


Figure S121 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **4**

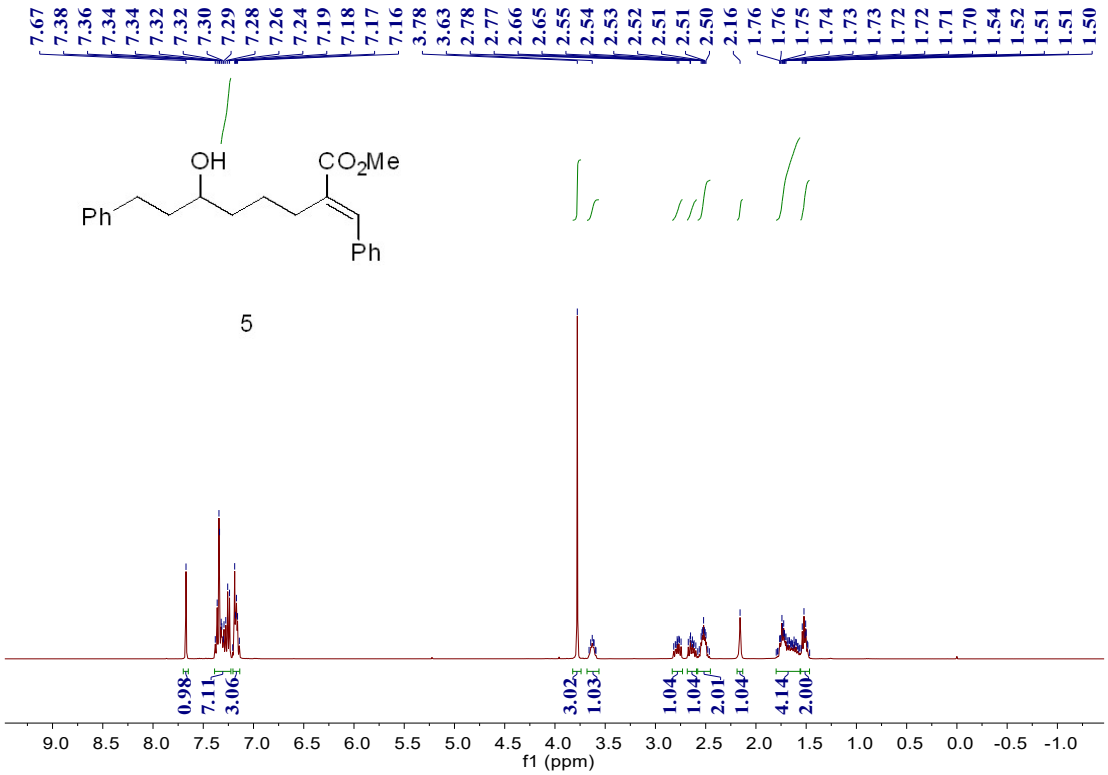


Figure S122 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **5**

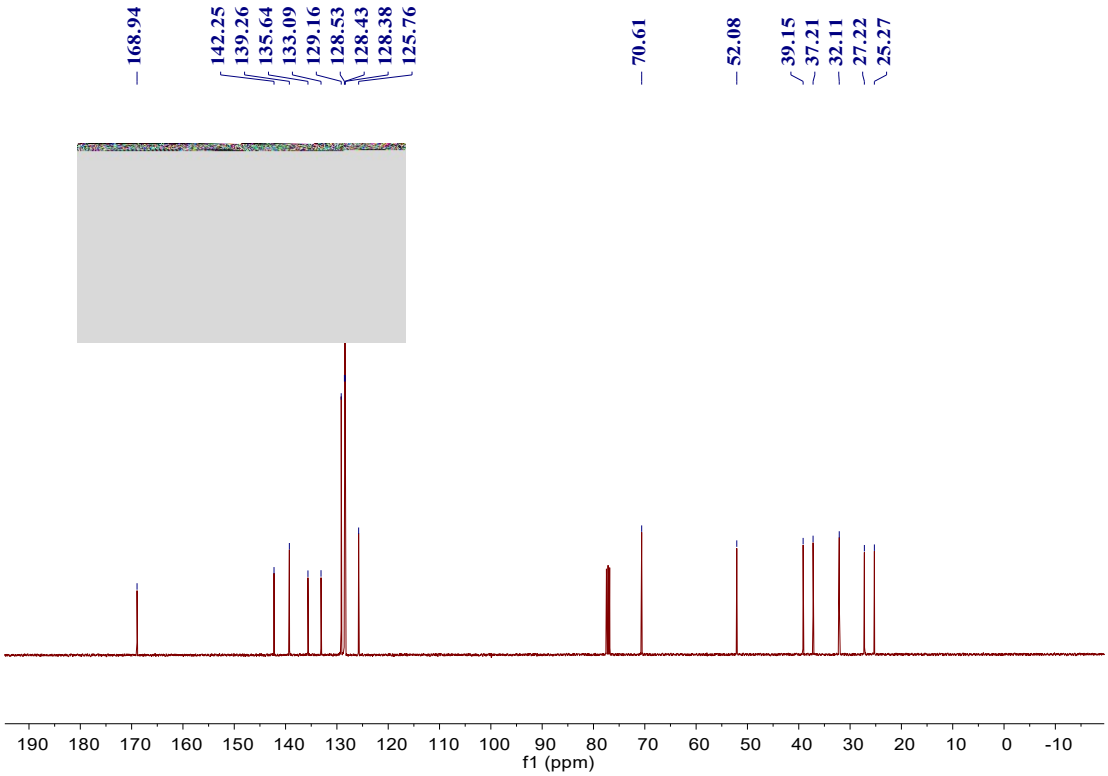


Figure S123 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **5**

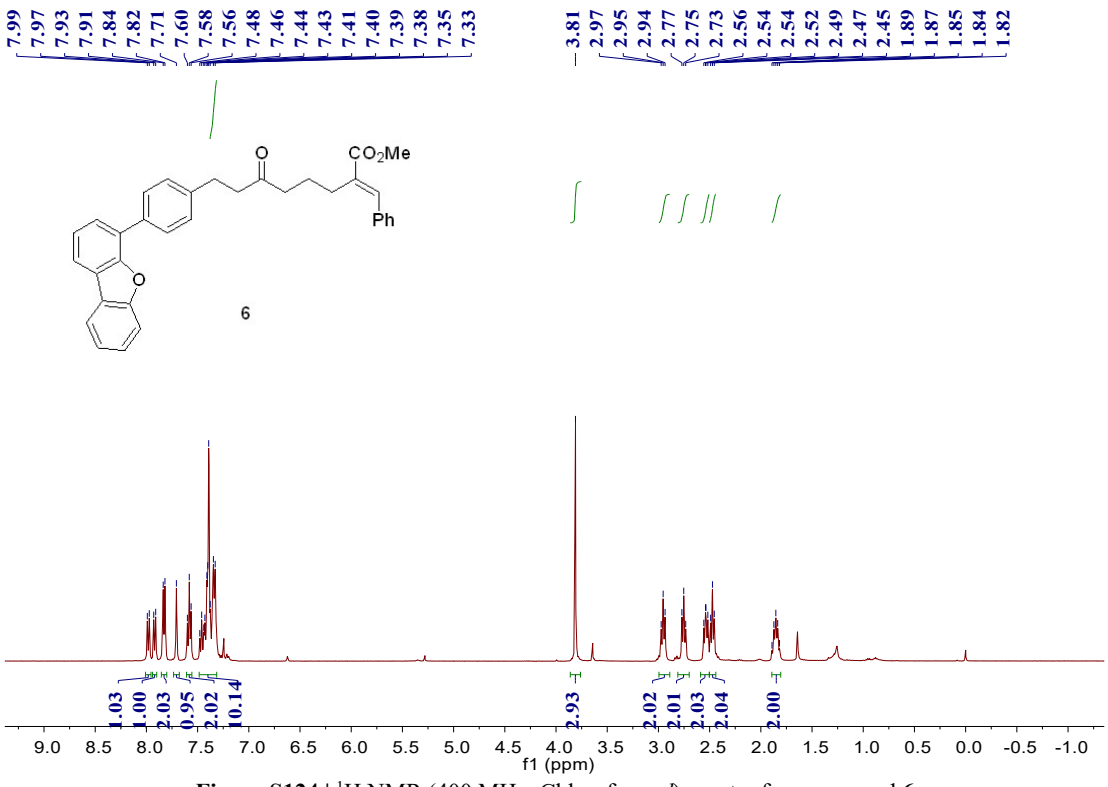


Figure S124 | ^{1}H NMR (400 MHz, Chloroform-*d*) spectra for compound **6**

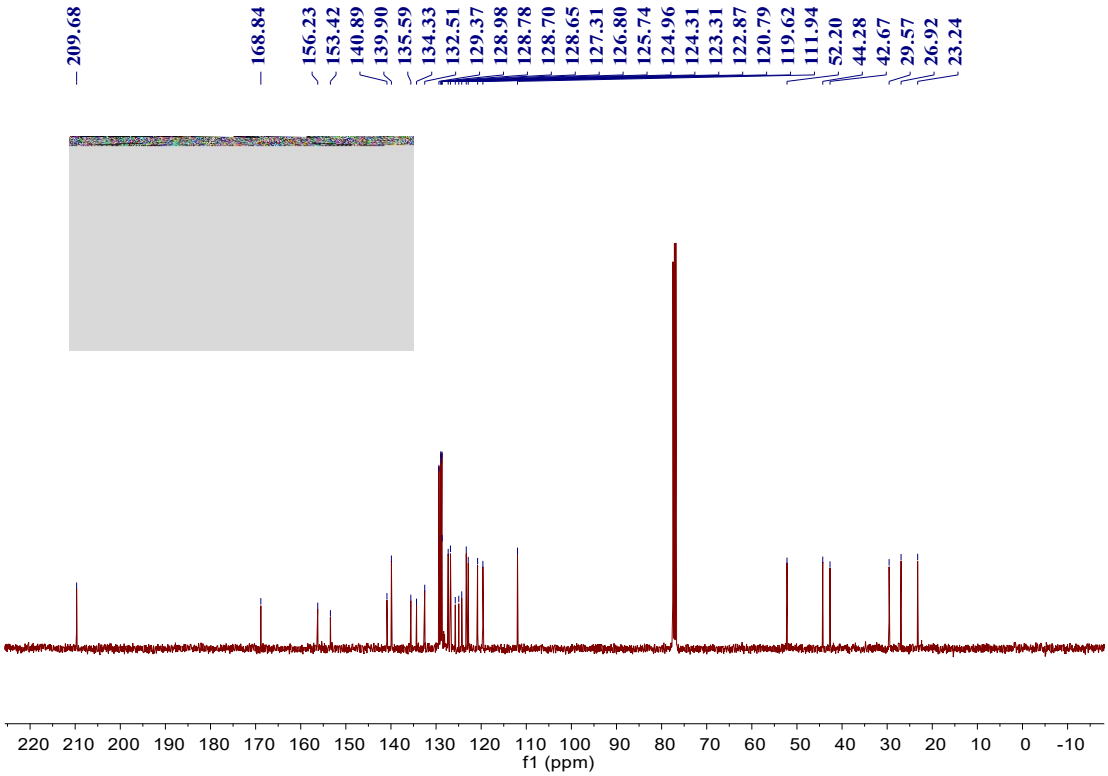


Figure S125 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **6**

11. X-ray Data Collection and Structure Determinations.

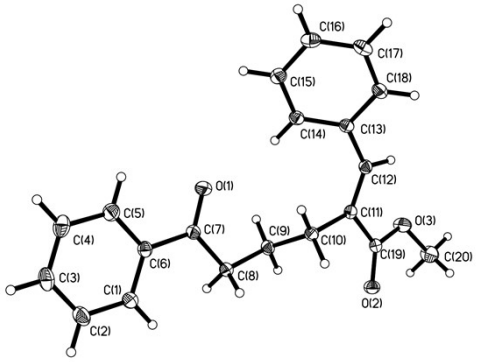
Single crystals of **3aq** were grown by slow diffusion of *n*-hexane into EtOAc solution. X-ray single-crystal diffraction data was collected on a Rigaku XtaLAB P200 diffractometer at 296(2) K with MoK α radiation (λ=0.71073 Å) in the ω scan mode. The program SAINT was used for integration of the diffraction profiles. All of the structures were solved using direct methods using the SHELXS program of the SHELXTL package and refined using full matrix least-squares methods with SHELXL (semi empirical absorption corrections were applied using the SADABS program). Other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on $F2$. The hydrogen atoms were generated theoretically onto the specific atoms and refined isotopically with fixed thermal factors. Detailed crystallographic data were summarized(**Table S12).**

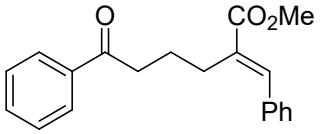
Table S12. Crystal Date and Structure Refinements for **3aq**.

	3aq
Chemical formula	$C_{20}H_{20}O_3$
Formula weight	308.36
Crystal system	monoclinic
Space group	C 2/c
a (Å)	33.9435(14)
b (Å)	5.7917(2)
c (Å)	17.1106(8)
V (Å^3)	3281.1(2)
α (°)	90
β (°)	102.733(2)
γ (°)	90
Z	2
F(000)	1312.0
GOF	1.020
D/g cm^{-3}	1.248
μ (mm^{-1})	0.083
T/K	193
ΛMoK\a (Å)	0.71073
R^a/R^b	0.0450(3407)/0.1099(4363)

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$

X-ray Crystal Structures (30% thermal ellipsoid probability levels) **3aq.**





CCDC-2202510 (**3aq**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/structures/Search?ccdc=2202510.

12. References

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