Supporting Information

Direct Allylic C(sp³)-H Acylation of Alkenes via Metallaphotoredox Catalysis Using Carboxylic Acids

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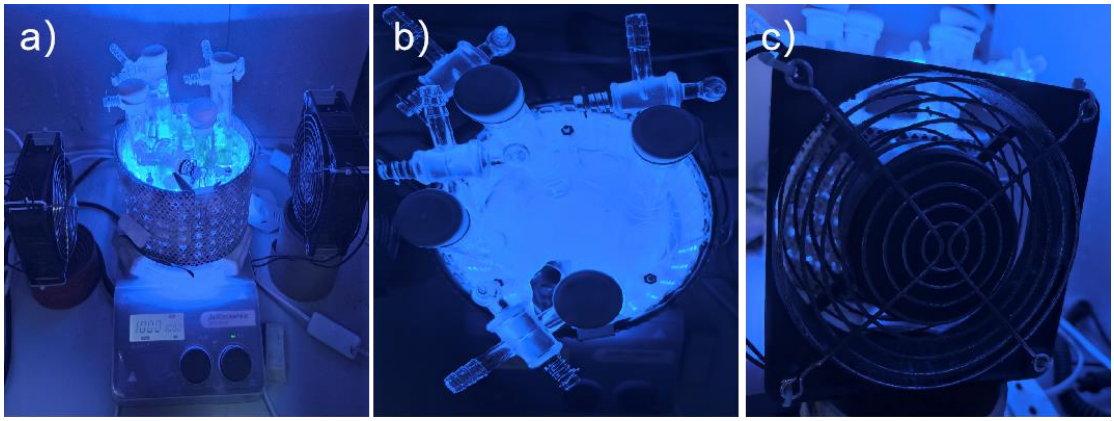
Table of Contents

I. General Information

Dry *i*PrOAc was purchased from suppliers and used directly. Unless stated otherwise, reactions were performed in flame-dried glassware. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates and visualization on TLC was achieved by UV light (254 and 365 nm) or by phosphomolybdic acid. Flash column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all the corresponding carboxylic acids and alkenes from suppliers were used directly without further purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AV500 or Bruker AV300 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm). Mesitylene was used as an internal standard to calculate NMR yields. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. HRMS were obtained using Waters G2-XS Q-TOF LC/MS (ESI) mass spectrometer. All manipulations were conducted under Schlenk tubes and stirred (1000 rpm) at a distance of 2 cm from the irradiating plate. Blue LEDs (30 W) purchased from JIADENG (LS) was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature maintain a temperature of 25 °C − 30 °C.



Set-up for the photoredox reactions

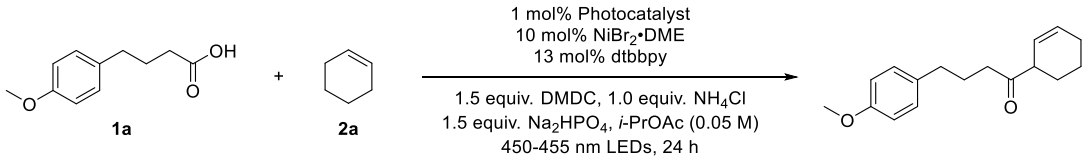
a) front view

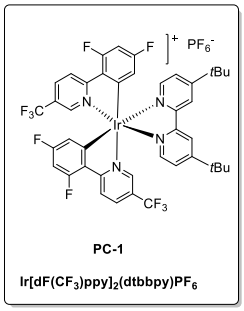
b) top view

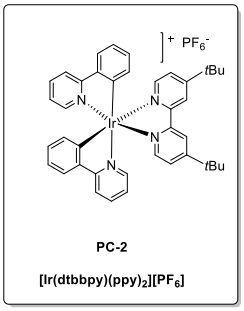
c) lateral view

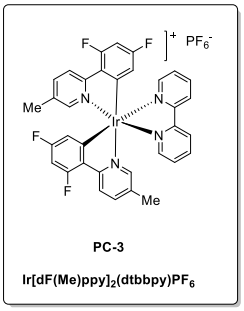
II. Optimization of the Reaction Conditions

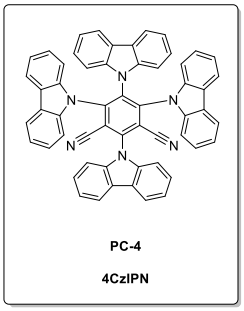
Table S1. The Effect of Photocatalyst[a]

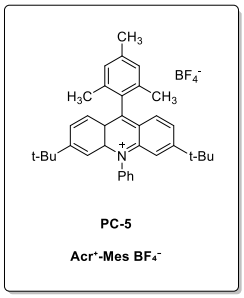


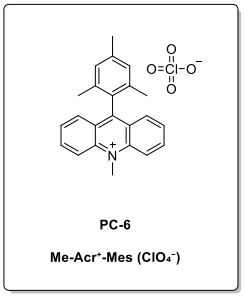


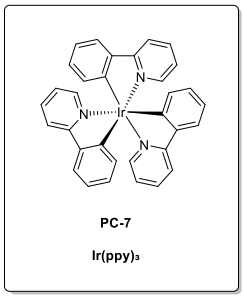


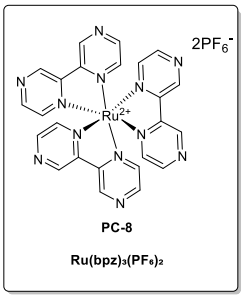








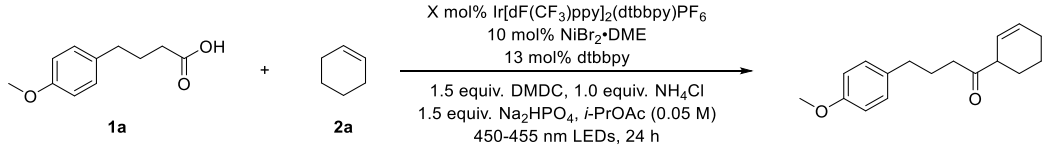




Entry	Photocatalyst	Yield(%)[b]
1	**PC-1**	42
2	**PC-2**	＜10
3	**PC-3**	22
4	**PC-4**	trace
5	**PC-5**	trace
6	**PC-6**	n.d.
7	**PC-7**	n.d.
8	**PC-8**	n.d.

[a] General conditions, unless otherwise noted: **1a** (0.3 mmol), **2a** (0.6 mmol), $NiBr_2$·DME (0.03 mmol), dtbbpy (0.039 mmol), photocatalyst (0.003 mmol), Na_2HPO_4 (0.45 mmol), NH_4Cl (0.3 mmol), DMDC (0.45mmol) and *i*PrOAc (6.0 mL) under N_2 atmosphere. [b] Determined by ^1H NMR spectroscopy with mesitylene as an internal standard. n.d., not detected.

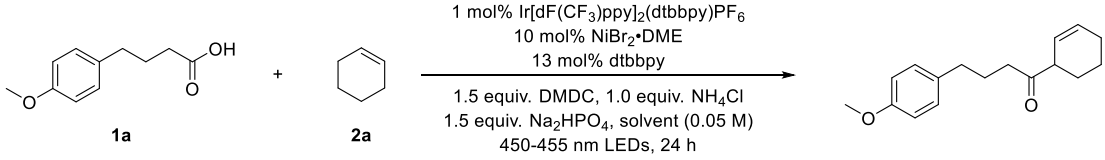
Table S2. The Effect of the amount of photocatalysts[a]



Entry	X	Yield (%)[b]
1	0	n.d.
2	1	42
3	2.5	25
4	5	5

[a] General conditions, unless otherwise noted: **1a** (0.3 mmol), **2a** (0.6 mmol), $NiBr_2$·DME (0.03 mmol), dtbbpy (0.039 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.003 mmol), Na_2HPO_4 (0.45 mmol), NH_4Cl (0.3 mmol), DMDC (0.45 mmol) and *i*PrOAc (6.0 mL) under N_2 atmosphere. [B] Determined by ^1H NMR spectroscopy with mesitylene as an internal standard. n.d., not detected.

Table S3. The Effect of different solvents[a]

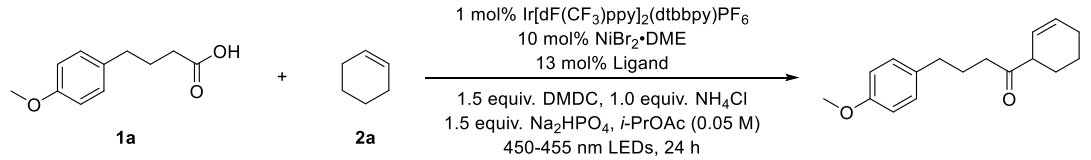


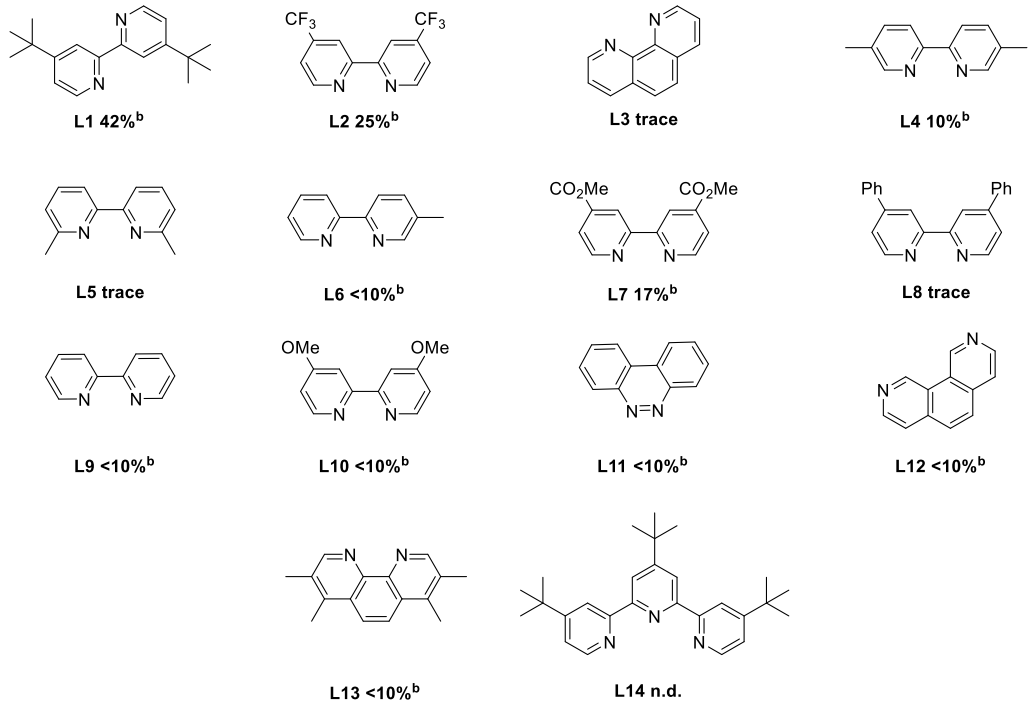
Entry	Solvent	Yield (%)[b]
1	EA	30
2	THF	17
3	MeCN	17
4	DMSO	0
5	*t*-BuOMe	11
6	PhCl	<10
7	$PhCF_3$	24
8	DCM	14
9	DCE	<10
10	*i*PrOAc	42
11	Dioxane	32
12	benzene	32
13	DMAc	<10
14	DMF	<10
15	Acetone	24
16	*i*PrOH	<10
17	DME	n.d.
18[c]	*i*PrOAc	36
19[d]	*i*PrOAc	15

[a] General conditions, unless otherwise noted: **1a** (0.3 mmol), **2a** (0.6 mmol), $NiBr_2$·DME (0.03

mmol), dtbbpy (0.039 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), Na_2HPO_4 (0.45 mmol), NH_4Cl (0.3 mmol), DMDC (0.45 mmol) and solvent (6.0 mL) under N_2 atmosphere. [b] Determined by ^1H NMR spectroscopy with mesitylene as an internal standard. [c] 0.1 M. [d] 0.03 M. n.d., not detected.

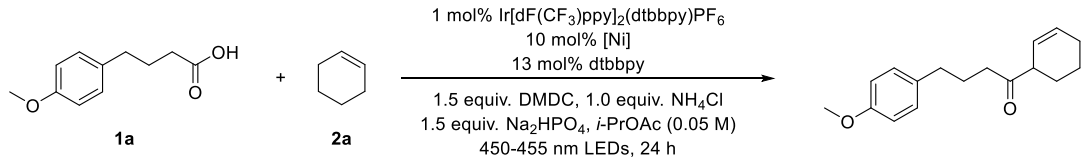
Table S4. The Effect of Ligand[a]





[a] General conditions, unless otherwise noted: **1a** (0.3 mmol), **2a** (0.6 mmol), $NiBr_2$·DME (0.03 mmol), ligand (0.039 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.003 mmol), Na_2HPO_4 (0.45 mmol), NH_4Cl (0.3 mmol), DMDC (0.45 mmol) and *i*PrOAc (6.0 mL) under N_2 atmosphere. [b] Determined by ^1H NMR spectroscopy with mesitylene as an internal standard. n.d., not detected.

Table S5. The Effect of Ni-catalyst[a]

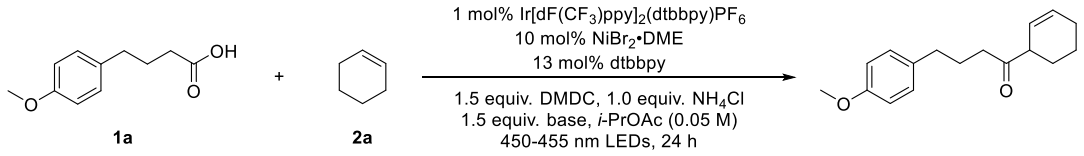


Entry	[Ni]	Yield(%)[b]
1	$NiCl_2(PPh_3)_2$	n.d.

2	$Ni(acac)_2$	n.d.
3	$Ni(dppe)Cl_2$	n.d.
4	$NiBr_2(PPh_3)_2$	27
5	$NiCl_2$	n.d.
6	$NiBr_2$•DME	42
7	$NiCl_2$•DME	n.d.
8	$NiBr_2$	22

[a] General conditions, unless otherwise noted: **1a** (0.3 mmol), **2a** (0.6 mmol), [Ni] (0.03 mmol), dtbbpy (0.039 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.003 mmol), Na_2HPO_4 (0.45 mmol), NH_4Cl (0.3 mmol), DMDC (0.45 mmol) and *i*PrOAc (6.0 mL) under N_2 atmosphere. [b] Determined by ^1H NMR spectroscopy with mesitylene as an internal standard. n.d., not detected.

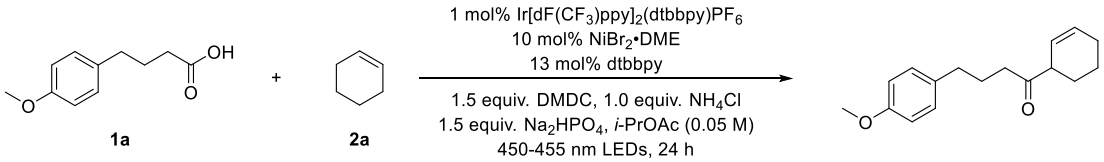
Table S6. The Effect of base[a]



Entry	Base	Yield (%)[b]
1	Na_2HPO_4	42
2	K_2CO_3	trace
3	Cs_2CO_3	0
4	K_2HPO_4	37
5	DBU	n.d.
6	TMG	0
7	2,6-lutidine	30
8	pyridine	18
9	K_3PO_4	0
10	$NaHCO_3$	40
11	KO*t*Bu	trace
12	$KHCO_3$	24
13	NaOAc	n.d.
14	Et_3N	n.d.

[a] General conditions, unless otherwise noted: **1a** (0.3 mmol), **2a** (0.6 mmol), $NiBr_2$·DME (0.03 mmol), dtbbpy (0.039 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.003 mmol), base (0.45 mmol), NH_4Cl (0.3 mmol), DMDC (0.45 mmol) and *i*PrOAc (6.0 mL) under N_2 atmosphere. [b] Determined by ^1H NMR spectroscopy with mesitylene as an internal standard. n.d., not detected.

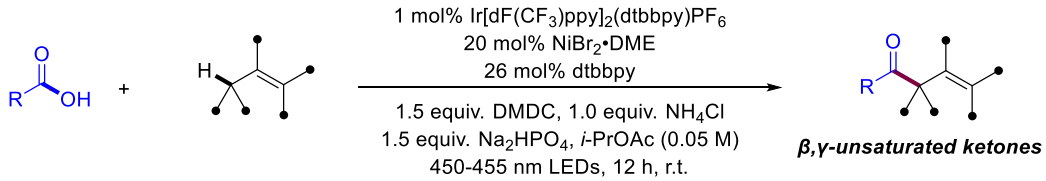
Table S7. Control Experiments[a]



Entry	Variation from "standard conditions"	Yield(%)[b]
1	2.0 equiv Na_2HPO_4	35
2	2.5 equiv Na_2HPO_4	36
3	10% $NiBr_2$·DME, 13% dtbbpy	42
4	20% $NiBr_2$·DME, 26% dtbbpy	62
5	12 h instead of 24 h	55
6	**1a**/**2a**=1/2	62[c]
7	**1a**/**2a**=1/3	56
8	**1a**/**2a**=1/4	54
9	2.0 equiv. DMDC	31
10	Boc_2O instead of DMDC	n.d.
11	no NH_4Cl	53
12	no DMDC	n.d.
13	no light	n.d.
14	no Ni and ligand	n.d.
15	no photocatalyst	n.d.

[a] General conditions, unless otherwise noted: **1a** (0.3 mmol), **2a** (0.6 mmol), $NiBr_2$·DME (0.03 mmol), dtbbpy (0.039 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.003 mmol), Na_2HPO_4 (0.45 mmol), NH_4Cl (0.3 mmol), DMDC (0.45 mmol) and *i*PrOAc (6.0 mL) under N_2 atmosphere. [b] Determined by ^1H NMR spectroscopy with mesitylene as an internal standard. [c] Isolated yield. n.d., not detected.

III. General Procedure for Direct Allylic C(sp^3)-H Acylation of Alkenes

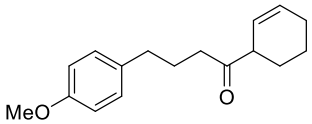


General procedure A:

An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (0.003 mmol), dtbbpy (**L1**) (0.078 mmol), Na_2HPO_4 (0.45 mmol), NH_4Cl (0.3 mmol), $NiBr_2$·DME (0.06 mmol), carboxylic acid (0.3 mmol), DMDC (0.45 mmol) and *i*PrOAc (3 mL) were added sequentially under N_2 atmosphere. The reaction

mixture was stirred at room temperature for 30 min. Then alkene (0.6 mmol) and *i*PrOAc (3 mL) was injected through the syringe into the mentioned above flask. The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDs at a distance of 2 cm for 12 h at room temperature. After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography on silica gel to afford the desired ketone.

(Cyclohex-2-en-1-yl)-4-(4-methoxyphenyl)butan-1-one (3)



3

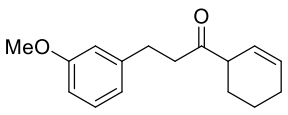
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2 \cdot DME$ (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **3** (48.1 mg, 0.186 mmol, 62% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.89 – 5.82 (m, 1H), 5.73 – 5.66 (m, 1H), 3.79 (s, 3H), 3.13 – 3.03 (m, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.05 – 1.97 (m, 2H), 1.91 – 1.84 (m, 2H), 1.82 – 1.66 (m, 3H), 1.61 – 1.51 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.8, 157.8, 133.7, 130.0, 129.3, 124.1, 113.7, 55.2, 48.9, 39.7, 34.2, 25.4, 24.8, 24.7, 20.8.

HRMS (ESI) for $C_{17}H_{23}O_2^+$ [$(M+H)^+$]: calculated 259.1693, found 259.1683.

1-(Cyclohex-2-en-1-yl)-3-(3-methoxyphenyl)propan-1-one (4)



4

Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3

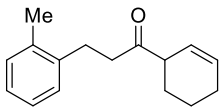
mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(3-methoxyphenyl)propionic acid (54.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **4** (43.9 mg, 0.18 mmol, 60% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 1H), 6.78 – 6.72 (m, 3H), 5.89 – 5.83 (m, 1H), 5.74 – 5.68 (m, 1H), 3.79 (s, 3H), 3.11 – 3.05 (m, 1H), 2.90 – 2.85 (m, 2H), 2.81 – 2.76 (m, 2H), 2.05 – 1.94 (m, 2H), 1.85 – 1.66 (m, 3H), 1.58 – 1.49 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 159.8, 143.1, 130.4, 129.6, 124.1, 120.9, 114.3, 111.5, 55.3, 49.2, 42.3, 30.0, 24.9, 24.8, 20.9.

HRMS (ESI) calcd for $C_{16}H_{21}O_2^+$ [$(M+H)^+$]: calculated 245.1536, found 245.1534.

1-(Cyclohex-2-en-1-yl)-3-(o-tolyl)propan-1-one (5)



5

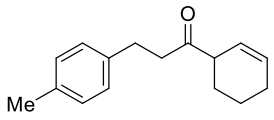
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol,1%), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(2-methylphenyl)propanoic acid (49.2mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **5** (39.7 mg, 0.174 mmol, 58% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 4H), 5.99 – 5.81 (m, 1H), 5.78 – 5.68 (m, 1H), 3.16 – 3.04 (m, 1H), 2.92 – 2.85 (m, 2H), 2.79 – 2.71 (m, 2H), 2.31 (s, 3H), 2.05 – 1.98 (m, 2H), 1.85 – 1.68 (m, 3H), 1.61 – 1.51 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 139.5, 136.1, 130.4, 130.4, 128.8, 126.4, 126.2, 124.1, 49.2, 41.0, 27.3, 24.9, 24.8, 20.9, 19.4.

HRMS (ESI) calcd for $C_{16}H_{21}O^+$ [$(M+H)^+$]: calculated 229.1587, found 229.1581.

1-(Cyclohex-2-en-1-yl)-3-(p-tolyl)propan-1-one (6)



6

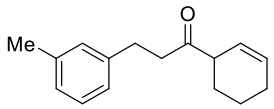
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(4-methylphenyl)propionic acid (49.2mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **6** (43.8 mg, 0.192 mmol, 64% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 – 7.06 (m, 4H), 6.02 – 5.77 (m, 1H), 5.76 – 5.66 (m, 1H), 3.11 – 3.03 (m, 1H), 2.89 – 2.83 (m, 2H), 2.81 – 2.70 (m, 2H), 2.31 (s, 3H), 2.04 – 1.97 (m, 2H), 1.83 – 1.68 (m, 3H), 1.60 – 1.49 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 138.3, 135.6, 130.2, 129.2, 128.4, 128.3, 124.1, 49.2, 42.6, 29.6, 24.9, 24.8, 21.1, 20.9.

HRMS (ESI) calcd for $C_{16}H_{20}ONa^+$ [$(M+Na)^+$]: calculated 251.1406, found 251.1388.

1-(Cyclohex-2-en-1-yl)-3-(m-tolyl)propan-1-one (7)



7

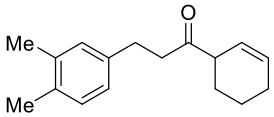
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(3-methylphenyl)propanoic acid (49.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **7** (36.3 mg, 0.159 mmol, 53% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 1H), 7.03 – 6.96 (m, 3H), 5.90 – 5.83 (m, 1H), 5.74– 5.69 (m, 1H), 3.12 – 3.04 (m, 1H), 2.89 – 2.83 (m, 2H), 2.81 – 2.75 (m, 2H), 2.32 (s, 3H), 2.05 – 1.97 (m, 2H), 1.82 – 1.66 (m, 3H), 1.59 – 1.50 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 141.4, 138.2, 130.3, 129.3, 128.5, 126.9, 125.4, 124.2, 49.2, 42.47, 29.9, 24.9, 24.8, 21.5, 20.9.

HRMS (ESI) calcd for $C_{16}H_{21}O^+$ [$(M+H)^+$]: calculated 229.1587, found 229.1582.

1-(Cyclohex-2-en-1-yl)-3-(3,4-dimethylphenyl)propan-1-one (8)



8

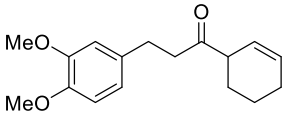
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(3,4-dimethylphenyl)propanoic acid (53.4 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **8** (43.5 mg, 0.18 mmol, 60% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, J = 7.6 Hz, 1H), 6.97 – 6.89 (m, 2H), 5.92 – 5.81 (m, 1H), 5.74 – 5.69 (m, 1H), 3.1 – 3.05 (m, 1H), 2.85 – 2.73 (m, 4H), 2.23 (s, 3H), 2.22 (s, 3H), 2.04 – 1.97 (m, 2H), 1.85 – 1.58 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 138.8, 136.7, 134.3, 130.3, 129.9, 129.8, 125.8, 124.2, 49.2, 42.7, 29.6, 24.9, 24.9, 20.9, 19.8, 19.4.

HRMS (ESI) calcd for $C_{17}H_{22}ONa^+$ [$(M+Na)^+$]: calculated 265.1563, found 265.1557.

1-(Cyclohex-2-en-1-yl)-3-(3,4-dimethoxyphenyl)propan-1-one (9)



9

Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.1

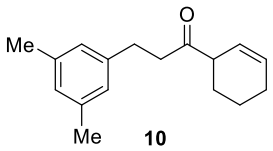
mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3,4-dimethoxyhydrocinnamic acid (63.1 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **9** (50.1 mg, 0.183 mmol, 61% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.7 Hz, 1H), 6.71 (dd, *J* = 5.5, 2.0 Hz, 2H), 6.06 – 5.79 (m, 1H), 5.76 – 5.64 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.11 – 3.03 (m, 1H), 2.87 – 2.81 (m, 2H), 2.81 – 2.70 (m, 2H), 2.05 – 1.95 (m, 2H), 1.80 – 1.68 (m, 3H), 1.59 – 1.48 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 148.9, 147.4, 134.1, 130.3, 124.1, 120.3, 111.9, 111.5, 56.1, 55.9, 49.2, 42.6, 29.6, 24.8, 24.8, 20.9.

HRMS (ESI) calcd for $C_{17}H_{22}O_3Na^+$ [$(M+Na)^+$]: calculated 297.1461, found 297.1451.

1-(Cyclohex-2-en-1-yl)-3-(3,5-dimethylphenyl)propan-1-one (10)



10

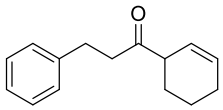
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.1 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(3,5-dimethylphenyl)propanoic acid (53.4 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **10** (40.7 mg, 0.168 mmol, 56% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (d, *J* = 9.4 Hz, 3H), 5.99 – 5.80 (m, 1H), 5.75 – 5.69 (m, 1H), 3.12 – 3.04 (m, 1H), 2.85 – 2.73 (m, 4H), 2.28 (s, 6H), 2.04 – 1.97 (m, 2H), 1.83 – 1.67 (m, 3H), 1.60 – 1.54 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 141.4, 138.1, 130.3, 127.8, 126.3, 124.2, 49.2, 44.8, 42.6, 29.9, 24.9, 24.9, 21.4, 20.9.

HRMS (ESI) calcd for $C_{17}H_{23}O^+$ [$(M+H)^+$]: calculated 243.1743, found 243.1739.

1-(Cyclohex-2-en-1-yl)-3-phenylpropan-1-one (11)



11

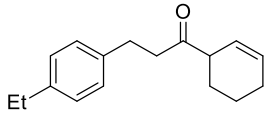
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.1 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-phenylpropionic acid (45.1 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **11** (34.6 mg, 0.162 mmol, 54% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 –7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 5.94 – 5.80 (m, 1H), 5.77 – 5.63 (m, 1H), 3.13 – 3.03 (m, 1H), 2.94 – 2.86 (m, 2H), 2.85 – 2.71 (m, 2H), 2.06 – 1.95 (m, 2H), 1.83 – 1.66 (m, 3H), 1.57 – 1.49 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 141.5, 130.4, 128.6, 128.5, 126.2, 124.1, 49.2, 42.4, 29.9, 24.9, 24.8, 20.9.

HRMS (ESI) calcd for $C_{15}H_{19}O^+$ [$(M+H)^+$]: calculated 215.1430, found 215.1426.

1-(Cyclohex-2-en-1-yl)-3-(4-ethylphenyl)propan-1-one (12)



12

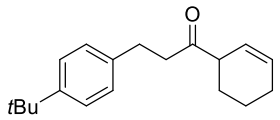
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.1 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(4-ethylphenyl)propanoic acid (53.4 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **12** (42.8 mg, 0.177 mmol, 59% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 4H), 5.99 – 5.80 (m, 1H), 5.78 – 5.61 (m, 1H), 3.16 – 3.02 (m, 1H), 2.91 – 2.74 (m, 4H), 2.61 (q, *J* = 7.8 Hz, 2H), 2.07 – 1.93 (m, 2H), 1.82 – 1.67 (m, 3H), 1.57 – 1.46 (m, 1H), 1.22 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 142.1, 138.6, 130.3, 128.4, 128.1, 124.2, 49.2, 42.5, 29.6, 28.6, 24.9, 24.8, 21.0, 15.8.

HRMS (ESI) calcd for $C_{17}H_{23}O^+$ [$(M+H)^+$]: calculated 243.1743, found 243.1726.

2-(4-(Tert-butyl)phenyl)-1-(cyclohex-2-en-1-yl)propan-1-one(13)



13

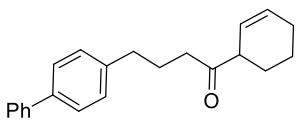
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(4-*tert*-butyl-phenyl)-propionic acid (61.8 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **13** (54.3 mg, 0.20 mmol, 67% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.93 – 5.80 (m, 1H), 5.78 – 5.64 (m, 1H), 3.15 – 3.04 (m, 1H), 2.91 – 2.72 (m, 4H), 2.05 – 1.97 (m, 2H), 1.84 – 1.66 (m, 3H), 1.58 – 1.51 (m, 1H), 1.30 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 149.0, 138.3, 130.3, 128.1, 125.5, 124.2, 49.2, 42.4, 34.5, 31.5, 29.4, 24.9, 24.9, 20.9.

HRMS (ESI) calcd for $C_{19}H_{26}O^+$ [$(M+H)^+$]: calculated 271.2056, found 271.2051.

4-([1,1'-Biphenyl]-4-yl)-1-(cyclohex-2-en-1-yl)butan-1-one(14)



14

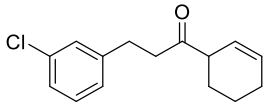
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-biphenylyl)butyric acid (72.1 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **14** (63.8 mg, 0.21 mmol, 70% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 5.94 – 5.80 (m, 1H), 5.74 – 5.68 (m, 1H), 3.12 – 3.06 (m, 1H), 2.66 (t, J = 7.8 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.08 – 1.89 (m, 4H), 1.85 – 1.68 (m, 3H), 1.61 (d, *J* = 6.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.9, 141.2, 140.9, 139.0, 130.3, 129.0, 128.9, 127.3, 127.2, 127.1, 124.3, 49.1, 39.9, 34.9, 25.3, 25.0, 24.9, 21.0.

HRMS (ESI) calcd for $C_{24}H_{24}ONa^+$ [$(M+Na)^+$]: calculated 327.1719, found 327.1713.

3-(3-Chlorophenyl)-1-(cyclohex-2-en-1-yl)propan-1-one (15)



15

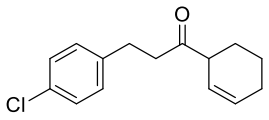
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(3-chlorophenyl)propanoic acid (55.3 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **15** (52.1 mg, 0.21 mmol, 70% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 – 7.16 (m, 3H), 7.09 – 7.05 (m, 1H), 5.93 – 5.81 (m, 1H), 5.77 – 5.64 (m, 1H), 3.10 – 3.04 (m, 1H), 2.90 – 2.83 (m, 2H), 2.83 – 2.70 (m, 2H), 2.04 – 1.97 (m, 2H), 1.83 – 1.68 (m, 3H), 1.59 – 1.51 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.7, 143.5, 134.3, 130.5, 129.9, 128.6, 126.8, 126.4, 124.0, 49.2, 42.0, 29.6, 24.9, 24.8, 20.9.

HRMS (ESI) calcd for $C_{15}H_{18}ClO^+$ [$(M+H)^+$]: calculated 249.1041, found 249.1037.

4-(4-Chlorophenyl)-1-(cyclohex-2-en-1-yl)butan-1-one (16)



16

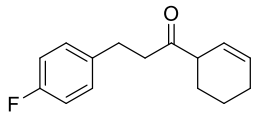
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol),Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.4 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-chloro-benzenepropanoic acid (55.3 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **16** (52.1 mg, 0.21 mmol, 55% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 5.96 – 5.80 (m, 1H), 5.74 – 5.65 (m, 1H), 3.12 – 3.01 (m, 1H), 2.92 – 2.84 (m, 2H), 2.79 – 2.74 (m, 2H), 2.00 (d, J = 3.2 Hz, 2H), 1.79 – 1.66 (m, 3H), 1.59 – 1.50 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.8, 139.9, 132.0, 130.5, 129.9, 128.7, 124.0, 49.2, 42.1, 29.2, 24.9, 24.8, 20.9.

HRMS (ESI) calcd for $C_{15}H_{18}ClO^+$ [$(M+H)^+$]: calculated 249.1041, found 249.1031.

1-(Cyclohex-2-en-1-yl)-3-(4-fluorophenyl)propan-1-one (17)



17

Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol),Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-fluoro-benzenepropanoic acid (50.4 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of

silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **17** (49.4 mg, 0.21 mmol, 71% yield) as a colorless liquid.

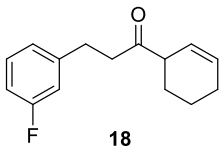
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 2H), 7.01 – 6.94 (m, 2H), 5.90 – 5.83 (m, 1H), 5.72 – 5.66 (m, 1H), 3.11 – 3.02 (m, 1H), 2.90-2.85 (m, 2H), 2.80 – 2.74 (m, 2H), 2.03 – 1.97 (m, 2H), 1.81 – 1.65 (m, 3H), 1.58 – 1.50 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.9, 161.5(d, J = 243.2 Hz), 137.1 (d, J = 3.2 Hz), 130.4, 129.9 (d, J = 7.8 Hz), 124.0, 115.3 (d, J = 21.0 Hz), 49.2, 42.4, 29.1, 24.9, 24.8, 20.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -117.38.

HRMS (ESI) calcd for $C_{15}H_{18}FO^+$ [$(M+H)^+$]: calculated 233.1336, found 233.1354

1-(Cyclohex-2-en-1-yl)-3-(3-fluorophenyl)propan-1-one (18)



18

Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), *M*-fluorophenylpropionic acid (50.4 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **18** (44.6 mg, 0.192 mmol, 64% yield) as a colorless liquid.

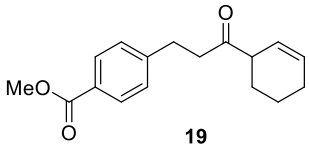
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 1H), 6.99 – 6.83 (m, 3H), 5.90 – 5.83 (m, 1H), 5.73 – 5.68 (m, 1H), 3.11 – 3.04 (m, 1H), 2.94 – 2.86 (m, 2H), 2.82 – 2.76 (m, 2H), 2.04 – 1.97 (m, 2H), 1.84 – 1.65 (m, 3H), 1.63 – 1.57 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.7, 163.0 (d, J = 245.4 Hz), 144.0, 130.5, 130.0 (d, J = 8.4 Hz), 124.2 (d, J = 2.8 Hz), 124.0, 115.4 (d, J = 21.0 Hz), 113.1 (d, J = 21.1 Hz), 49.2, 41.9, 29.6, 24.9, 24.8, 20.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -113.6.

HRMS (ESI) calcd for $C_{15}H_{17}FNaO^+$ [$(M+Na)^+$]: calculated 255.1156, found 255.1148.

Methyl 4-(3-(cyclohex-2-en-1-yl)-3-oxopropyl)benzoate (19)



19

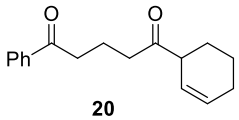
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (160.4 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(4-(methoxycarbonyl)phenyl)propanoic acid (62.4 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **19** (54.1 mg, 0.189 mmol, 63% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 5.99 – 5.78 (m, 1H), 5.77 – 5.59 (m, 1H), 3.90 (s, 3H), 3.11 – 3.03 (m, 1H), 2.99 – 2.91 (m, 2H), 2.87 – 2.74 (m, 2H), 2.05 – 1.95 (m, 2H), 1.82 – 1.66 (m, 3H), 1.59 – 1.49 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 167.2, 147.0, 130.5, 130.0, 129.9, 128.6, 128.2, 123.9, 52.2, 49.2, 41.8, 29.9, 24.9, 24.8, 20.9.

HRMS (ESI) calcd for $C_{17}H_{21}O_3^+$ [$(M+H)^+$]: calculated 273.1458, found 273.1449.

1-(Cyclohex-2-en-1-yl)-6-phenylhexane-1,6-dione (20)



20

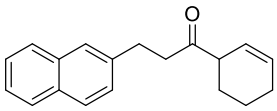
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.1 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 5-oxo-5-phenylpentanoic acid (57.6 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **20** (46.1 mg, 0.18 mmol, 60% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 5.98 – 5.81 (m, 1H), 5.75 – 5.71 (m, 1H), 3.16 – 3.06 (m, 1H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.07 – 1.97 (m, 4H), 1.86 – 1.69 (m, 3H), 1.61 – 1.53 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.8, 200.1, 137.0, 133.2, 130.3, 128.7, 128.2, 124.2, 49.1, 39.6, 37.7, 25.0, 24.9, 21.0, 18.5.

HRMS (ESI) calcd for $C_{17}H_{20}O_2Na^+$ [$(M+Na)^+$]: calculated 293.1512, found 293.1519.

1-(Cyclohex-2-en-1-yl)-3-(naphthalen-2-yl)propan-1-one(21)



21

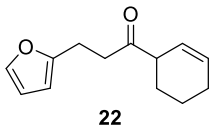
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(2-naphthyl)propanoic acid (60.3 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **21** (49.1 mg, 0.186 mmol, 62% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.44 (m, 2H), 7.43 – 7.30 (m, 2H), 5.97 – 5.79 (m, 1H), 5.76 – 5.60 (m, 1H), 3.44 – 3.30 (t, *J* = 6.6 Hz, 2H), 3.12 – 3.06 (m, 1H), 2.92 (t, *J* = 8.1 Hz, 2H), 2.08 – 1.91 (m, 2H), 1.84 – 1.65 (m, 3H), 1.56 – 1.49 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 137.5, 134.0, 131.8, 130.4, 129.0, 127.1, 126.24, 126.17, 125.75, 125.70, 124.1, 123.6, 49.3, 41.7, 27.1, 24.92, 24.86, 20.9.

HRMS (ESI) calcd for $C_{19}H_{20}ONa^+$ [$(M+Na)^+$]: calculated 287.1406, found 287.1403.

1-(Cyclohex-2-en-1-yl)-3-(furan-2-yl)propan-1-one (22)



22

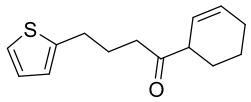
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-(2-furyl)propanoic acid (42.0 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **22** (37.9 mg, 0.186 mmol, 62% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 1.2 Hz, 0.6 Hz, 1H), 6.27 – 6.25 (m, 1H), 6.01 – 5.97 (m, 1H), 5.95 – 5.85 (m, 1H), 5.80 – 5.70 (m, 1H), 3.17 – 3.09 (m, 1H), 2.94 – 2.89 (m, 2H), 2.89 – 2.75 (m, 2H), 2.05 (d, *J* = 8.7 Hz, 2H), 1.88 – 1.69 (m, 3H), 1.59 – 1.51 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 154.9, 141.2, 130.4, 124.0, 110.3, 105.3, 49.1, 38.9, 24.90, 24.86, 22.4, 20.9.

HRMS (ESI) calcd for $C_{13}H_{16}O_2Na^+$ [$(M+Na)^+$]: calculated 241.1199, found 241.1196.

1-(Cyclohex-2-en-1-yl)-4-(thiophen-2-yl)butan-1-one (23)



23

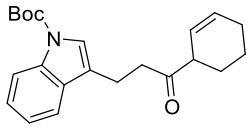
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5mg, 0.06 mmol), 4-(2-thienyl)butyric acid (51.0 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **23** (34.2 mg, 0.201 mmol, 67% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 5.1 Hz, 1.2 Hz, 1H), 6.93 – 6.90 (m, 1H), 6.79 – 6.77 (m, 1H), 5.90 – 5.83 (m, 1H), 5.74 – 5.68 (m, 1H), 3.12 – 3.06 (m, 1H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.05 – 1.93 (m, 4H), 1.82 – 1.69 (m, 3H), 1.62 – 1.54 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.6, 144.6, 130.3, 126.9, 124.6, 124.2, 123.3, 49.1, 39.5, 29.3, 25.7, 25.0, 24.9, 21.0.

HRMS (ESI) calcd for $C_{14}H_{18}OSNa^+$ [$(M+Na)^+$]: calculated 234.1078, found 234.1081.

***Tert*-butyl 3-(3-(cyclohex-2-en-1-yl)-3-oxopropyl)-1H-indole-1-carboxylate (24)**



24

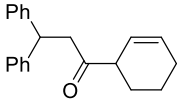
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-{1-[(*tert*-butoxy)carbonyl]-1*H*-indol-3-yl}propanoic acid (86.7 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **24** (70.9 mg, 0.201 mmol, 67% yield) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 5.99 – 5.81 (m, 1H), 5.78 – 5.69 (m, 1H), 3.15 – 3.08 (m, 1H), 3.00 – 2.95 (m, 2H), 2.92 – 2.83 (m, 2H), 2.04 – 1.98 (m, 2H), 1.84 – 1.70 (m, 3H), 1.66 (s, 9H), 1.60 – 1.54 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 149.9, 135.7, 130.5, 130.4, 124.5, 124.1, 122.6, 122.5, 120.13, 119.0, 115.4, 83.6, 49.2, 40.2, 28.4, 24.91, 24.89, 20.9, 19.1.

HRMS (ESI) calcd for $C_{22}H_{27}NO_3Na^+$ [$(M+Na)^+$]: calculated 376.1883, found 376.1875.

1-(Cyclohex-2-en-1-yl)-3,3-diphenylpropan-1-one (25)



25

Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3,3-diphenylpropionic acid (67.8 mg, 0.3 mmol),

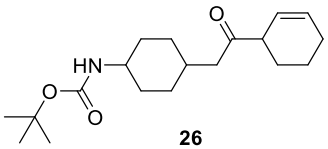
DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **25** (34.8 mg, 0.12 mmol, 40% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.16 (m, 10H), 5.95 – 5.76 (m, 1H), 5.71 – 5.56 (m, 1H), 4.65 (t, *J* = 7.5 Hz, 1H), 3.32 – 3.14 (m, 2H), 3.05 – 2.95 (m, 1H), 2.02 – 1.92 (m, 2H), 1.76 – 1.59 (m, 3H), 1.55 – 1.46 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 144.2, 130.4, 128.7, 128.0, 127.9, 126.5, 123.9, 49.5, 46.9, 45.9, 24.9, 24.6, 20.9.

HRMS (ESI) calcd for $C_{21}H_{22}ONa^+$ [$(M+Na)^+$]: calculated 313.1563, found 313.1558.

***Tert*-butyl (4-(2-(cyclohex-2-en-1-yl)-2-oxoethyl)cyclohexyl)carbamate (26)**



26

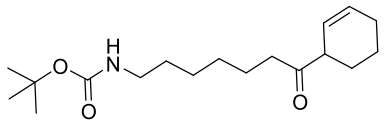
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(boc-amino)cyclohexane acetic acid (77.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **26** (38.5 mg, 0.12 mmol, 40% yield, *dr* 7.3/1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99 – 5.80 (m, 1H), 5.75 – 5.54 (m, 1H), 4.60 (s, 1H), 3.71 (s, 1H), 3.17 – 2.94 (m, 1H), 2.60 (d, *J* = 6.9 Hz, 0.24H), 2.40 (d, *J* = 6.9 Hz, 1.76H), 2.04 – 1.99 (m, 2H), 1.82 – 1.72 (m, 2H), 1.71 – 1.49 (m, 9H), 1.44 (s, 9H), 1.25 – 1.15 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.4, 130.4, 124.1, 60.6, 58.6, 49.6, 29.8, 28.6, 24.9, 24.9, 21.2, 21.0, 18.6, 14.3.

HRMS (ESI) calcd for $C_{19}H_{31}NO_3Na^+$ [$(M+Na)^+$]: calculated 344.2196, found 344.2192.

***Tert*-butyl (7-(cyclohex-2-en-1-yl)-7-oxoheptyl)carbamate (27)**



27

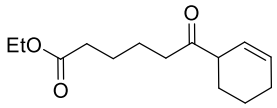
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), Boc-7-aminoheptanoic acid (73.6 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **27** (32.4 mg, 0.105 mmol, 35% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 – 5.82 (m, 1H), 5.74 – 5.67 (m, 1H), 4.53 (s, 1H), 3.11 – 3.04 (m, 3H), 2.45 (t, *J* = 7.3 Hz, 2H), 2.03 – 1.96 (m, 2H), 1.92 – 1.63 (m, 4H), 1.63 – 1.47 (m, 4H), 1.42 (s, 9H), 1.32 – 1.25 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.2, 156.1, 130.1, 124.3, 79.1, 49.0, 40.6, 40.5, 30.0, 29.0, 28.5, 26.7, 24.9, 24.9, 23.7, 20.9.

HRMS (ESI) calcd for $C_{18}H_{31}NO_3Na^+$ [$(M+Na)^+$]: calculated 332.2196, found 332.2191.

Ethyl 6-(cyclohex-2-en-1-yl)-6-oxohexanoate (28)



28

Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), Monoethyl adipate (53 μL, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue

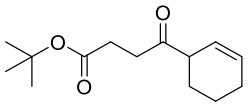
was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **28** (30.7 mg, 0.129 mmol, 43% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 – 5.84 (m, 1H), 5.75 – 5.69 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.14 – 3.05 (m, 1H), 2.52 – 2.47 (m, 2H), 2.33 – 2.28 (m, 2H), 2.08 – 1.93 (m, 2H), 1.87 – 1.67 (m, 3H), 1.66 – 1.58 (m, 5H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.7, 173.6, 130.3, 124.2, 60.4, 49.1, 40.2, 34.3, 24.9, 24.9, 24.7, 23.4, 21.0, 14.4.

HRMS (ESI) calcd for $C_{14}H_{23}O_3^+$ [$(M+H)^+$]: calculated 239.1642, found 245.1649.

***Tert*-butyl 4-(cyclohex-2-en-1-yl)-4-oxobutanoate (29)**



29

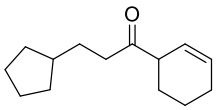
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-tert-butoxy-4-oxobutanoic acid (52 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **29** (42.8 mg, 0.18 mmol, 60% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 – 5.81 (m, 1H), 5.79 – 5.73 (m, 1H), 3.18 – 3.10 (m, 1H), 2.80 – 2.69 (m, 2H), 2.53 – 2.46 (m, 2H), 2.05 – 1.97 (m, 2H), 1.88 – 1.69 (m, 3H), 1.60 – 1.52 (m, 1H), 1.43 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.3, 172.2, 130.3, 124.2, 80.7, 48.9, 35.4, 29.4, 28.2, 25.0, 24.9, 21.0.

HRMS (ESI) calcd for $C_{14}H_{22}O_3Na^+$ [$(M+Na)^+$]: calculated 261.1461, found 261.1458.

1-(Cyclohex-2-en-1-yl)-2-cyclopentylethan-1-one (30)



30

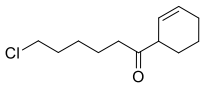
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.8 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 3-cyclopentylpropionic acid (43 μL, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE) on silica gel to afford **30** (37.1 mg, 0.18 mmol, 60% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 – 5.83 (m, 1H), 5.75 – 5.70 (m, 1H), 3.15 – 3.05 (m, 1H), 2.50 (d, *J* = 7.6 Hz, 2H), 2.30 – 2.17 (m, 2H), 2.00 (d, *J* = 6.6 Hz, 2H), 1.87 – 1.74 (m, 6H), 1.65 – 1.57 (m, 5H), 1.08 – 1.03 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.2, 130.1, 124.4, 49.5, 49.2, 47.0, 35.7, 35.6, 32.8, 25.1, 25.0, 21.0.

HRMS (ESI) calcd for $C_{14}H_{23}O^+$ [$(M+H)^+$]: calculated 207.1743, found 207.1750.

6-Chloro-1-(cyclohex-2-en-1-yl)hexan-1-one (31)



31

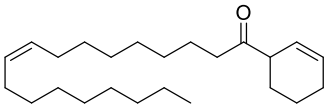
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 6-chlorohexanoic acid (45.1 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE) on silica gel to afford **31** (39.1 mg, 0.183 mmol, 61% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 – 5.84 (m, 1H), 5.75 – 5.70 (m, 1H), 3.53 (t, *J* = 6.9 Hz, 2H), 3.13 – 3.06 (m, 1H), 2.50 (t, *J* = 7.5 Hz, 2H), 2.05 – 1.98 (m, 2H), 1.85 – 1.71 (m, 5H), 1.58 – 1.55 (m, 3H), 1.47 – 1.39 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.9, 130.3, 124.2, 49.1, 45.0, 40.4, 32.6, 26.7, 25.0, 24.9, 23.1, 21.0.

HRMS (ESI) calcd for $C_{12}H_{19}ClO_2Na^+$ [$(M+Na)^+$]: calculated 237.1017, found 237.1011.

(Z)-1-(cyclohex-2-en-1-yl)octadec-9-en-1-one (32)



32

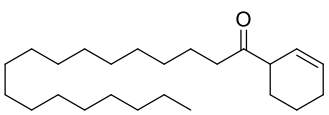
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), Oleic acid (95 μL, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE) on silica gel to afford **32** (41.5 mg, 0.12 mmol, 40% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 – 5.81 (m, 1H), 5.77 – 5.69 (m, 1H), 5.39 – 5.33 (m, 2H), 3.15 –3.05 (m, 1H), 2.46 (t, *J* = 7.4 Hz, 2H), 2.02 – 1.93 (m, 6H), 1.84 – 1.69 (m, 3H), 1.63 – 1.55 (m, 3H), 1.31 – 1.25 (m, 20H), 0.87 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.3, 130.6, 130.4, 130.1, 124.4, 49.1, 40.7, 32.7, 32.7, 32.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 27.4, 25.0, 24.0, 22.8, 21.0, 14.2.

HRMS (ESI) calcd for $C_{24}H_{42}ONa^+$ [$(M+Na)^+$]: calculated 369.3128, found 369.3119.

1-(Cyclohex-2-en-1-yl)octadecan-1-one (33)



33

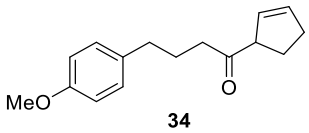
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), Stearic acid (85.3 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE) on silica gel to afford **33** (59.5 mg, 0.171 mmol, 57% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 – 5.83 (m, 1H), 5.77 – 5.69 (m, 1H), 3.15 – 3.05 (m, 1H), 2.46 (t, *J* = 7.4 Hz, 2H), 2.05 – 1.98 (m, 2H), 1.84 – 1.69 (m, 3H), 1.64 – 1.55 (m, 3H), 1.25 (m, 28H), 0.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.4, 130.1, 124.4, 49.1, 40.8, 32.1, 29.85, 29.82, 29.81, 29.76, 29.64, 29.60, 29.51, 29.50, 24.96, 24.95, 24.0, 22.8, 21.0, 14.3.

HRMS (ESI) calcd for $C_{24}H_{45}O^+$ [$(M+H)^+$]: calculated 349.3465, found 349.3457.

1-(Cyclopent-2-en-1-yl)-4-(4-methoxyphenyl)butan-1-one (34)



34

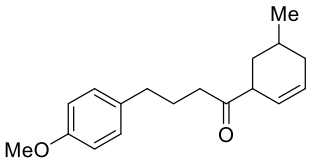
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclopentene (40.9 mg, 53.0 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **34** (49.8 mg, 0.204 mmol, 68% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.00 – 5.84 (m, 1H), 5.75 – 5.63 (m, 1H), 3.79 (s, 3H), 3.61 – 3.54 (m, 1H), 2.59 – 2.53 (m, 2H), 2.49 – 2.31 (m, 4H), 2.10 – 2.00 (m, 2H), 1.93 – 1.83 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.6, 158.0, 134.4, 133.9, 129.5, 128.6, 113.9, 77.4, 58.9, 55.4, 40.1, 34.3, 32.4, 25.6, 25.5.

HRMS (ESI) calcd for $C_{16}H_{21}O_2^+$ [$(M+H)^+$]: calculated 245.1536, found 245.1531.

4-(4-Methoxyphenyl)-1-(6-methylcyclohex-2-en-1-yl)butan-1-one (35)



35

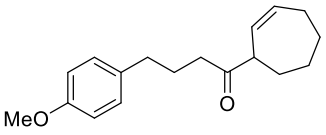
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, 4-methyl-1-cyclohexene (57.7 mg, 73 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **35** (50.6 mg, 0.186 mmol, 62% yield) as a colorless liquid. The obtained product is a mixture of regio-isomers and diastereoisomers (1.1/2.2/3.0/1.0).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11– 7.06 (m, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.87 – 5.79 (m, 0.86H), 5.77 – 5.60 (m, 0.67H), 5.51 – 5.44 (m, 0.47H), 3.79 (s, 3H), 3.24 – 3.16 (m, 0.16H), 3.11 – 3.02 (m, 0.32H), 2.82 – 2.75 (m, 0.45H), 2.70 – 2.64 (m, 0.07H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.52 – 2.38 (m, 2H), 2.12 – 2.04 (m, 1H), 2.02 – 1.93 (m, 1H), 1.92 – 1.83 (m, 2H), 1.75 – 1.66 (m, 1H), 1.38 – 1.21 (m, 1.67H), 1.08 – 1.04 (m, 0.33H), 1.00 – 0.91 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 212.5, 211.5, 158.0, 133.9, 130.1, 129.9, 129.50, 129.48, 123.6, 123.5, 113.9, 57.9, 55.4, 50.9, 48.2, 40.3, 40.2, 34.39, 34.37, 33.4, 31.8, 29.8, 29.1, 25.7, 25.6, 25.5, 24.5, 21.6, 20.4.

HRMS (ESI) calcd for $C_{18}H_{25}O_2^+$ [$(M+H)^+$]: calculated 273.1849, found 273.1844.

1-(Cyclohept-2-en-1-yl)-4-(4-methoxyphenyl)butan-1-one (36)



36

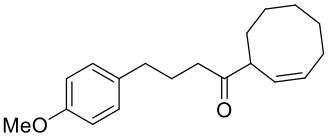
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cycloheptene (57.7 mg, 70.0 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **36** (35.1 mg, 0.129 mmol, 43% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.97 – 5.86 (m, 1H), 5.83 – 5.73 (m, 1H), 3.79 (s, 3H), 3.33 – 3.20 (m, 1H), 2.56 (d, *J* = 7.2 Hz, 2H), 2.52 – 2.42 (m, 2H), 2.23 – 2.07 (m, 2H), 2.04 – 1.96 (m, 1H), 1.94 – 1.83 (m, 2H), 1.83 – 1.74 (m, 1H), 1.72 – 1.60 (m, 2H), 1.55 – 1.33 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.1, 158.0, 133.9, 133.8, 130.0, 129.5, 113.9, 55.4, 53.4, 40.2, 34.4, 30.5, 29.6, 28.7, 26.6, 25.7.

HRMS (ESI) calcd for $C_{18}H_{25}O_2^+$ [$(M+H)^+$]: calculated 273.1849, found 273.1839.

(Z)-1-(cyclooct-2-en-1-yl)-4-(4-methoxyphenyl)butan-1-one (37)



37

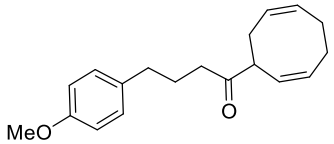
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclooctene (66.1 mg, 78 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **37** (46.3 mg, 0.162 mmol, 54% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.85 – 5.72 (m, 1H), 5.60 – 5.50 (m, 1H), 3.79 (s, 3H), 3.54 – 3.41 (m, 1H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 2.24 – 2.05 (m, 2H), 1.93 – 1.81 (m, 2H), 1.73 – 1.63 (m, 2H), 1.59 – 1.49 (m, 2H), 1.46 – 1.24 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.7, 158.0, 133.9, 131.9, 129.5, 127.8, 113.9, 55.4, 49.9, 41.0, 34.4, 32.1, 29.4, 26.8, 26.6, 25.6, 25.4.

HRMS (ESI) calcd for $C_{19}H_{26}NaO_2^+$ [$(M+Na)^+$]: calculated 309.1825, found 309.1819.

1-((2Z,6Z)-cycloocta-2,6-dien-1-yl)-4-(4-methoxyphenyl)butan-1-one (38)



38

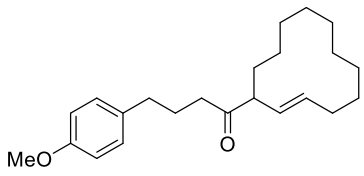
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, 1,5-cyclooctadiene (64.9 mg, 74 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **38** (42.6 mg, 0.15 mmol, 50% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.76 – 5.65 (m, 1H), 5.61 – 5.38 (m, 3H), 3.79 (s, 3H), 3.71 – 3.59 (m, 1H), 2.75 – 2.61 (m, 1H), 2.60 – 2.46 (m, 5H), 2.46 – 2.37 (m, 1H), 2.37 – 2.20 (m, 3H), 1.94 – 1.82 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.9, 158.0, 133.8, 131.4, 129.47, 129.46, 127.0, 126.4, 113.9, 55.4, 52.7, 40.8, 34.3, 29.9, 28.0, 27.6, 25.6.

HRMS (ESI) calcd for $C_{19}H_{24}O_2Na^+$ [$(M+Na)^+$]: calculated 307.1669, found 307.1661.

(Z)-1-(cyclododec-2-en-1-yl)-4-(4-methoxyphenyl)butan-1-one (39)



39

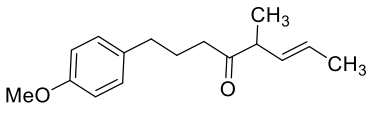
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol, 1.5 equiv), a teflon stir bar, 1-cyclododecene (99.8 mg, 115 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **39** (41.0 mg, 0.12 mmol, 40% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.59 – 5.47 (m, 1H), 5.35 – 5.26 (m, 1H), 3.78 (s, 3H), 3.06 – 2.98 (m, 1H), 2.55 – 2.50 (m, 2H), 2.47 – 2.39 (m, 2H), 2.26 – 2.16 (m, 1H), 1.92 – 1.79 (m, 3H), 1.51 – 1.43 (m, 3H), 1.36 – 1.19 (m, 13H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.0, 157.9, 135.2, 133.9, 129.4, 128.7, 113.8, 56.9, 55.3, 48.9, 40.4, 34.3, 32.5, 28.6, 26.3, 25.9, 25.5, 25.0, 24.8, 24.7, 24.6, 24.3.

HRMS (ESI) calcd for $C_{23}H_{35}O_2^+$ [$(M+H)^+$]: calculated 343.2632, found 343.2625.

(*E*)-1-(4-methoxyphenyl)-5-methyloct-6-en-4-one (40)



40

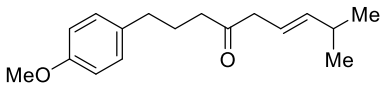
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, trans-2-pentene (42.1 mg, 65 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **40** (44.3 mg, 0.18 mmol, 60% yield, *E/Z* 6.1/1) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.61 – 5.51 (m, 1H), 5.41 – 5.33 (m, 0.86H), 5.29 – 5.21 (m, 0.14H), 3.78 (s, 3H), 3.16 – 3.04 (m, 1H), 2.60 – 2.45 (m, 3H), 2.44 – 2.35 (m, 1H), 1.86 – 1.81 (m, 2H), 1.71 – 1.63 (m, 3H), 1.15 – 1.08 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 212.1, 211.8, 157.9, 133.9, 130.4, 130.0, 129.4, 127.8, 126.5, 113.8, 55.3, 50.4, 45.3, 39.8, 34.3, 25.5, 18.1, 16.3, 13.2.

HRMS (ESI) calcd for $C_{16}H_{23}O_2^+$ [$(M+H)^+$]: calculated 247.1693, found 274.1682

(*E*)-1-(4-methoxyphenyl)-8-methylnon-6-en-4-one (41)



41

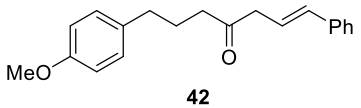
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (L1) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, trans-4-methyl-2-pentene (50.5 mg, 74 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **41** (39.0 mg, 0.15 mmol, 50% yield, *E/Z* 7.7/1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.54 – 5.42 (m, 1.75H), 5.41 – 5.36 (m, 0.32H), 3.79 (s, 3H), 3.13 (d, *J* = 5.7 Hz, 0.23H), 3.05 (d, *J* = 5.4 Hz, 1.77H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.33 – 2.22 (m, 1H), 1.92 – 1.79 (m, 2H), 0.98 (s, 2.66H), 0.96 (s, 2.66H), 0.95 (s, 0.34H), 0.93 (s, 0.34H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 158.0, 142.3, 133.9, 129.5, 119.1, 113.9, 55.4, 47.0, 41.3, 34.3, 31.2, 25.5, 22.5.

HRMS (ESI) calcd for $C_{17}H_{25}O_2^+$ [$(M+H)^+$]: calculated 261.1849, found 261.1844.

(*E*)-7-(4-methoxyphenyl)-1-phenylhept-1-en-4-one (42)



42

Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3

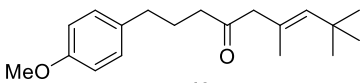
mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, trans-β-methylstyrene (70.9 mg, 78 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **42** (47.6 mg, 0.162 mmol, 54% yield, *E/Z* 6.1/1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.25 – 7.19 (m, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.34 – 6.21 (m, 1H), 3.78 (s, 3H), 3.39 (dd, *J* = 7.2, 1.5 Hz, 0.28H), 3.28 (dd, *J* = 6.9, 0.9 Hz, 1.72H), 2.57 (t, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.94 – 1.84 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.7, 158.0, 137.1, 133.8, 133.7, 129.5, 128.7, 127.7, 126.4, 122.2, 114.0, 55.4, 47.2, 41.6, 34.2, 29.9, 25.5.

HRMS (ESI) calcd for $C_{20}H_{23}O_2^+$ [$(M+H)^+$]: calculated 295.1693, found 295.1683.

(*E*)-1-(4-methoxyphenyl)-6,8,8-trimethylnon-6-en-4-one (43)



43

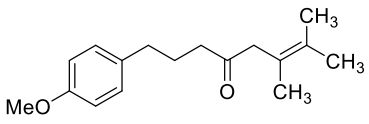
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol, 26%), Na_2HPO_4 (63.9 mg, 0.45 mmol, 1.5 equiv), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, 2,2,4-trimethyl-3-pentene (67.3 mg, 94 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a shortpad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **43** (56.2 mg, 0.195 mmol, 65% yield, *E/Z* 13.3/1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.40 (s, 0.07H), 5.27 (q, *J* = 1.2 Hz, 0.93H), 3.78 (s, 3H), 3.26 (s, 0.14H), 2.94 (s, 1.86H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.90 – 1.80 (m, 2H), 1.70 (d, *J* = 1.5 Hz, 2.79H), 1.65 (d, *J* = 1.5 Hz, 0.21H), 1.10 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.0, 158.0, 140.4, 133.9, 129.4, 128.1, 113.9, 56.3, 55.3, 40.5, 34.3, 32.5, 31.4, 30.9, 25.6, 17.7.

HRMS (ESI) calcd for $C_{19}H_{28}O_2Na^+$ [$(M+Na)^+$]: calculated 311.1982, found 311.1975.

1-(4-Methoxyphenyl)-6,7-dimethyloct-6-en-4-one (44)



44

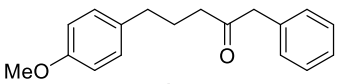
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.1 mg, 0.3 mmol), $NiBr_2$·DME (18.5mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, 2,3-dimethyl-2-butene (50.5 mg, 71 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **44** (47.6 mg, 0.183 mmol, 61% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.78 (s, 3H), 3.10 (s, 2H), 2.54 (t, J = 7.5 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H), 1.91 – 1.80 (m, 2H), 1.70 (s, 3H), 1.64 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 158.0, 133.9, 129.5, 128.6, 121.4, 113.9, 55.4, 49.3, 41.0, 34.3, 25.7, 20.9, 20.8, 19.4.

HRMS (ESI) calcd for $C_{17}H_{25}O_2^+$ [$(M+H)^+$]: calculated 261.1849, found 261.1845.

5-(4-Methoxyphenyl)-1-phenylpentan-2-one (45)



45

Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, toluene (55.3 mg, 63 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica

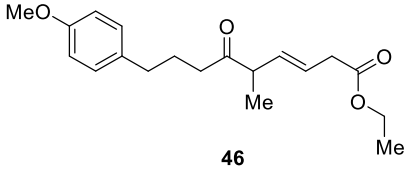
gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **45** (45.8 mg, 0.171 mmol, 57% yield) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.0 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 3.65 (s, 2H), 2.50 (t, *J* = 7.5 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.87 – 1.82 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.3, 158.0, 133.8, 133.0, 129.6, 129.5, 128.9, 127.1, 113.9, 55.4, 50.3, 41.2, 34.2, 25.5.

HRMS (ESI) calcd for $C_{18}H_{21}O_2^+$ [$(M+H)^+$]: calculated 269.1536, found 269.1545.

Ethyl (*E*)-3-(4-(4-methoxyphenyl)butanoyl)hept-4-enoate (46)



46

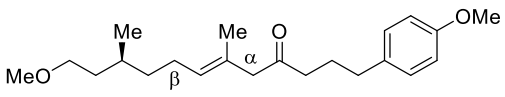
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, ethyl 3-hexenoate (85.3 mg, 95 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **46** (60.1 mg, 0.189 mmol, 63% yield, *E/Z* 4.6/1) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.72 – 5.57 (m, 1H), 5.32 – 5.17 (m, 1H), 4.17 – 4.02 (m, 2H), 3.96 – 3.84 (m, 0.17H), 3.78 (s, 3H), 3.59 – 3.44 (m, 0.83H), 2.85 (dd, *J* = 16.5, 9.0 Hz, 1H), 2.65 – 2.42 (m, 4H), 2.39 – 2.28 (m, 1H), 1.86 (p, *J* = 7.5 Hz, 2H), 1.73 (dd, *J* = 6.9, 1.8 Hz, 0.49H), 1.67 (dd, *J* = 6.3, 1.5 Hz, 2.51H), 1.26 – 1.18 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.0, 172.3, 158.0, 134.0, 130.3, 129.5, 127.4, 113.9, 60.7, 55.4, 51.9, 40.6, 35.8, 34.3, 25.4, 18.2, 14.3.

HRMS (ESI) calcd for $C_{20}H_{29}O_4^+$ [$(M+H)^+$]: calculated 333.2060, found 333.2051.

(*E*)-12-methoxy-1-(4-methoxyphenyl)-6,10-dimethyldodec-6-en-4-one (47)



47

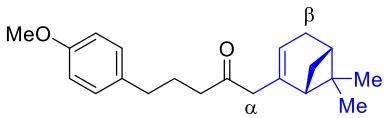
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, 8-methoxy-2,6-dimethyloct-2-ene (102.1 mg, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **47** (57.1 mg, 0.165 mmol, 55% yield, α/β 4/1, E/Z 1.7/1, dr 1/1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 – 7.03 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.33 (t, *J* = 7.1 Hz, 0.30H), 5.27 – 5.16 (m, 0.50H), 4.95 – 4.83 (m, 0.20H), 3.78 (s, 3H), 3.44 – 3.35 (m, 2H), 3.34 – 3.28 (m, 3H), 3.08 (s, 0.58 H), 3.01 (s, 1.02H), 2.59 – 2.49 (m, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 2.09 – 1.91 (m, 2H), 1.90 – 1.78 (m, 2H), 1.73 – 1.64 (m, 2H), 1.59 – 1.49 (m, 2H), 1.44 – 1.31 (m, 2H), 1.30 – 1.06 (m, 2H), 0.93 – 0.80 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 208.8, 158.0, 133.9, 133.8, 130.2, 129.5, 129.3, 128.9, 113.94, 113.92, 113.89, 71.24, 71.20, 58.7, 55.4, 54.2, 46.7, 41.2, 40.9, 37.0, 36.7, 34.3, 29.75, 29.73, 26.0, 25.7, 25.6, 24.3, 19.6, 16.5.

HRMS (ESI) calcd for $C_{22}H_{34}O_3Na^+$ [$(M+Na)^+$]: calculated 369.2400, found 369.2395.

1-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-5-(4-methoxyphenyl)pentan-2-one (48)



48

Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, α-pinene (81.7 mg, 95 μL, 0.6 mmol)

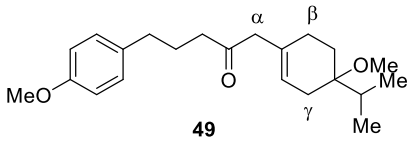
and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **48** (54.3 mg, 0.174 mmol, 58% yield, α/β 9.5/1, α: *dr* 4.9/1, *β*: 3.9/1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.38 – 5.29 (m, 1H), 3.79 (s, 3H), 3.15 – 3.11 (m, 0.18H), 3.11 – 2.93 (m, 1.72H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.50 – 2.34 (m, 3H), 2.33 – 2.19 (m, 2H), 2.16 – 2.04 (m, 1H), 2.03 – 1.96 (m, 1H), 1.89 – 1.81 (m, 2H), 1.71 (t, *J* = 1.8 Hz, 0.54H), 1.32 (s, 0.44H), 1.25 (s, 2.14H), 1.17 (s, 0.43H), 1.16 (s, 0.11H), 1.14 (s, 0.43H), 1.13 (m, 0.11H), 0.85 (s, 0.44H), 0.81 (s, 2.14H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.2, 158.0, 141.9, 133.9, 129.5, 121.3, 113.9, 55.4, 51.7, 46.0, 41.3, 40.6, 38.1, 34.3, 31.9, 31.7, 26.3, 25.5, 21.1.

HRMS (ESI) calcd for $C_{21}H_{28}O_2Na^+$ [$(M+Na)^+$]: calculated 335.1982, found 335.1974.

1-(6-Isopropyl-6-methoxy-3-methylcyclohex-2-en-1-yl)-4-(4-methoxyphenyl)butan-1-one (49)



49

Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, 4-isopropyl-4-methoxy-1-methylcyclohex-1-ene (100.8 mg, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **49** (61.9 mg, 0.18 mmol, 60% yield, a mixture of regioisomers and diastereoisomers, 5.6/1.3/1) as a colorless liquid.

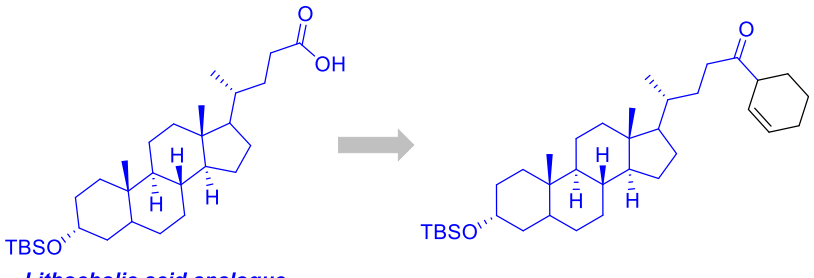
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.82 (m, d, *J* = 8.7 Hz, 2H), 5.46 – 5.37 (m, 1H), 3.78 (s, 3H), 3.13 (s, 2.11H), 3.09 (s, 0.51H), 3.01 (s, 1.38H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.44 (t, *J* = 7.5 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 1H), 2.21 – 1.91 (m, 4H), 1.88 – 1.70 (m, 4H), 1.63 (d, *J* = 5.7 Hz, 1H), 0.95 – 0.82 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.9, 158.0, 133.9, 131.7, 129.5, 123.4, 113.9, 76.3, 55.4, 52.1, 48.2, 40.9, 34.3, 31.5, 30.1, 26.8, 25.9, 25.6, 17.7, 16.6.

HRMS (ESI) calcd for $C_{22}H_{32}O_3Na^+$ [$(M+Na)^+$]: calculated 367.2244, found 367.2235.

IV. Late-stage functionalization of bioactive molecules

(4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*)-3-((*tert*-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[α]phenanthren-17-yl)-1-(cyclohex-2-en-1-yl)pentan-1-one (51)



Lithocholic acid analogue 50

51, 45%

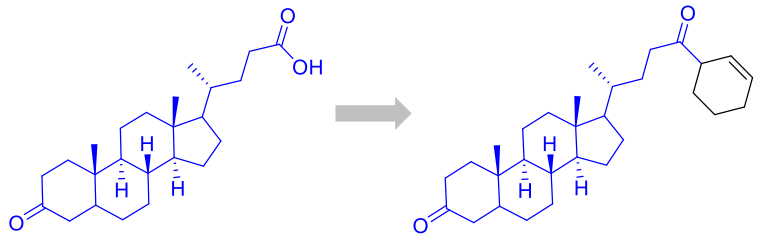
Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), lithocholic acid analogue (166.3 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **51** (74.8 mg, 0.135 mmol, 45% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 – 5.83 (m, 1H), 5.77 – 5.71 (m, 1H), 3.60 – 3.54 (m, 1H), 3.15 – 3.08 (m, 1H), 2.49 – 2.37 (m, 2H), 2.02 – 1.98 (m, 2H), 1.86 – 1.70 (m, 10H), 1.62 – 1.55 (m, 3H), 1.42 – 1.23 (m, 16H), 1.13 – 0.99 (m, 7H), 0.89 (s, 9H), 0.62 (s, 3H), 0.05 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.8, 130.1, 124.5, 72.9, 60.6, 58.6, 56.6, 56.2, 56.1, 49.1, 42.9, 42.5, 40.4, 40.3, 37.1, 36.0, 35.7, 35.5, 34.7, 31.2, 28.4, 27.5, 26.6, 26.1, 24.9, 24.4, 23.5, 20.9, 18.6, 18.5, 14.4, 12.2, -4.4.

HRMS (ESI) calcd for $C_{36}H_{62}O_2SiNa^+$ [$(M+Na)^+$]: calculated 577.4411, found 577.4404.

(8*R*,9*S*,10*S*,13*R*,14*S*)-17-((2*R*)-5-(cyclohex-2-en-1-yl)-5-oxopentan-2-yl)-10,13 Dimethylhexadecahydro-3*H*-cyclopenta[α]phenanthren-3-one (53)



Lithocholic acid analogue
52

53, 40%

Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.8 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), lithocholic acid analogue (112.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **53** (52.6 mg, 0.12 mmol, 40% yield) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 – 5.83 (m, 1H), 5.78 – 5.67 (m, 1H), 3.14 – 3.08 (m, 1H), 2.69 (t, *J* = 13.5 Hz, 1H), 2.52 – 2.46 (m, 1H), 2.42 – 2.31 (m, 2H), 2.16 – 2.13 (m, 1H), 2.02 – 1.99 (m, 4H), 1.87 – 1.73 (m, 7H), 1.59 – 1.55 (m, 1H), 1.49 – 1.41 (m, 5H), 1.39 – 1.33 (m, 3H), 1.30 – 1.19 (m, 5H), 1.10 – 1.06 (m, 3H), 1.00 (s, 3H), 0.92 – 0.89 (m, 4H), 0.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.7, 212.7, 130.1, 124.4, 56.6, 56.2, 49.1, 44.4, 42.9, 42.5, 40.8, 40.2, 37.6, 37.3, 37.1, 35.6, 35.5, 35.0, 29.9, 28.3, 26.7, 25.9, 25.0, 24.94, 24.91, 24.3, 22.8, 21.3, 21.00, 20.98, 18.6, 12.2.

HRMS (ESI) calcd for $C_{30}H_{46}O_2Na^+$ [$(M+Na)^+$]: calculated 461.3390, found 461.3380.

1-(Cyclohex-2-en-1-yl)-3-(4,5-diphenyloxazol-2-yl)propan-1-one (55)

Oxaprozin
54

55, 60%

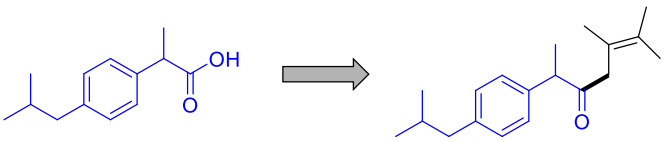
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5mg, 0.06 mmol), Oxaprozin (87.9 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/2) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 5/1) on silica gel to afford **55** (64.3 mg, 0.18 mmol, 60% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.59 – 7.53 (m, 2H), 7.41 – 7.29 (m, 6H), 5.95 – 5.86 (m, 1H), 5.85 – 5.75 (m, 1H), 3.26 – 3.18 (m, 1H), 3.17 – 3.04 (m, 4H), 2.08 – 1.98 (m, 2H), 1.94 – 1.81 (m, 2H), 1.78 – 1.69 (m, 1H), 1.63 – 1.52 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 162.6, 145.5, 135.2, 132.7, 130.6, 129.2, 128.8, 128.7, 128.5, 128.2, 128.0, 126.6, 124.0, 49.1, 37.2, 24.95, 24.93, 22.4, 20.9.

HRMS (ESI) calcd for $C_{24}H_{24}NO_2^+$ [(M+H)$^+$]: calculated 358.1802, found 358.1796.

2-(4-Isobutylphenyl)-5,6-dimethylhept-5-en-3-one (57)



56 **57**

Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.1 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), ibuprofen (61.8 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, 2,3-dimethyl-2-butene (50.5 mg, 71 μL, 0.6 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **57** (50.6 mg, 0.186 mmol, 62% yield) as a colorless liquid.

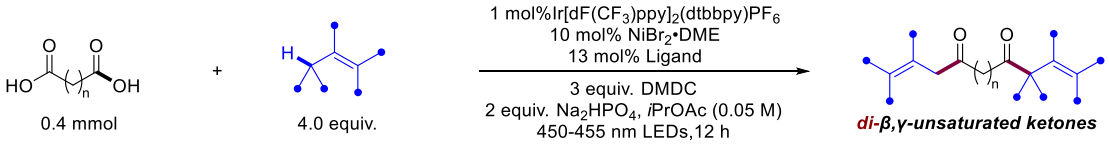
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 – 7.06 (m, 4H), 3.77 (q, J = 7.0 Hz, 1H), 3.13 (d, J = 16.0 Hz, 1H), 3.04 (d, J = 16.0 Hz, 1H), 2.44 (d, J = 7.0 Hz, 2H), 1.89 – 1.78 (m, 1H), 1.65 (s, 3H), 1.52 (s, 3H), 1.47 (s, 3H), 1.35 (d, J = 7.0 Hz, 3H), 0.88 (d, J = 7.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 140.7, 138.1, 129.7, 128.6, 127.8, 121.4, 51.7, 47.4, 45.2, 30.3, 22.5, 20.7, 19.2, 18.0.

HRMS (ESI) calcd for $C_{19}H_{29}O^+$ [$(M+H)^+$]: calculated 273.2213, found 273.2217.

V. Synthetic applications and large-scale synthesis

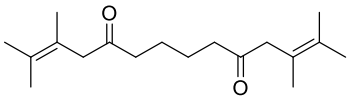
Sequential allylation of dicarboxylic acids



General procedure B:

An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (0.003 mmol), dtbbpy (**L1**) (0.039 mmol), Na_2HPO_4 (0.6 mmol), $NiBr_2$·DME (0.03 mmol), Adipic acid (0.3 mmol), DMDC (0.9 mmol) and *i*PrOAc (4 mL) were added sequentially under N_2 atmosphere. The reaction mixture was stirred at room temperature for 30 min. Then corresponding alkene (1.2 mmol) and the *i*PrOAc (2 mL) was injected through the syringe into the mentioned above flask containing the Ir/Ni catalysts. The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDs at a distance of 2 cm for 12 h at room temperature. After 12 h, the reaction mixture was then passed through a short pad of silica gel, using EtOAc/hexanes (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography on silica gel, before it was purified by flash chromatography on silica gel to afford the desired *di*β,γ-unsaturated ketone.

2,3,12,13-Tetramethyltetradeca-2,12-diene-5,10-dione (58)



58

Prepared according to the general procedure B employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (10.4 mg, 0.039 mmol), Na_2HPO_4 (85.1 mg, 0.6 mmol), $NiBr_2$·DME (9.2 mg, 0.03 mmol), Adipic acid (43.8 mg, 0.3 mmol), DMDC (134.1 mg, 97 μL, 0.9 mmol), a teflon stir bar, 2,3-dimethyl-2-butene (101 mg, 143 μL, 1.2 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the

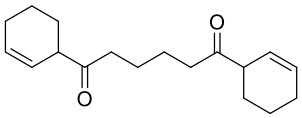
eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **58** (55.9 mg, 0.201 mmol, 67% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.11 (s, 4H), 2.43 – 2.35 (m, 4H), 1.70 (s, 6H), 1.67 (s, 6H), 1.65 (s, 6H), 1.55 – 1.49 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 128.7, 121.4, 49.3, 41.6, 23.5, 20.9, 20.8, 19.4.

HRMS (ESI) calcd for $C_{18}H_{31}O_2^+$ [$(M+H)^+$]: calculated 279.2319, found 279.2312.

1,6-Di(cyclohex-2-en-1-yl)hexane-1,6-dione (59)



59

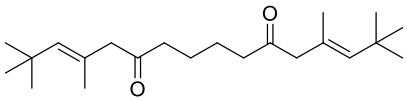
Prepared according to the general procedure B employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (10.4 mg, 0.039 mmol), Na_2HPO_4 (85.1 mg, 0.6 mmol), $NiBr_2$·DME (9.2 mg, 0.03 mmol), Adipic acid (43.8 mg, 0.3 mmol), DMDC (134.1 mg, 97 μL, 0.9 mmol), a teflon stir bar, cyclohexene (98.6 mg, 122 μL, 1.2 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a shortpad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **59** (49.3 mg, 0.18 mmol, 60% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 – 5.81 (m, 2H), 5.75 – 5.67 (m, 2H), 3.15 – 3.02 (m, 2H), 2.54 – 2.42 (m, 4H), 2.05 – 1.94 (m, 4H), 1.84 – 1.65 (m, 6H), 1.62 – 1.50 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.9, 130.2, 124.2, 49.1, 40.5, 24.93, 24.91, 23.5, 21.0.

HRMS (ESI) calcd for $C_{18}H_{27}O_2^+$ [$(M+H)^+$]: calculated 275.2006, found 275.2014.

(3*E*,13*E*)-2,2,4,13,15,15-hexamethylhexadeca-3,13-diene-6,11-dione (60)



60

Prepared according to the general procedure B employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (10.4 mg, 0.039 mmol), Na_2HPO_4 (85.1 mg, 0.6 mmol), $NiBr_2$·DME (9.2 mg, 0.03 mmol), Adipic acid (43.8 mg, 0.3 mmol), DMDC (134.1 mg, 97 μL, 0.90 mmol), a teflon stir bar, 2,2,4-trimethyl-3-pentene (134.7 mg, 187.0 μL, 1.2 mmol) and *i*PrOAc (6 mL). After 12 h,

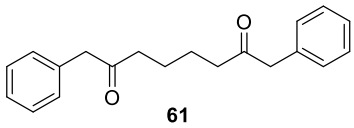
the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **60** (70.2 mg, 0.21 mmol, 70% yield, *E/Z* 14.4/1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.38 (s, 0.13H), 5.27 (s, 1.87H), 3.24 (s, 0.26H), 2.94 (s, 3.74H), 2.47 – 2.34 (m, 4H), 1.69 (s, 2.81H), 1.68 (s, 2.80H), 1.63 (s, 0.19H), 1.62 (s, 0.19H), 1.55 – 1.44 (m, 4H), 1.09 (s, 16.83H), 1.05 (s, 1.17H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 208.6, 140.4, 139.1, 128.1, 127.1, 56.3, 47.0, 42.1, 41.1, 32.5, 31.4, 30.9, 26.3, 23.4, 17.6.

HRMS (ESI) calcd for $C_{22}H_{39}O_2^+$ [$(M+H)^+$]: calculated 335.2945, found 335.2950.

1,8-Diphenyloctane-2,7-dione (61)



61

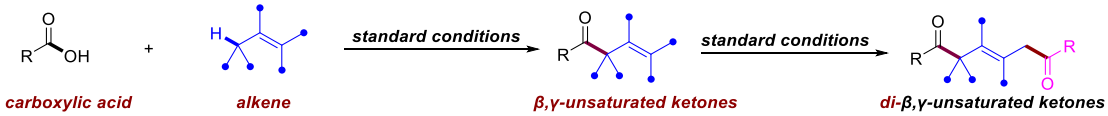
Prepared according to the general procedure B employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (10.4 mg, 0.039 mmol), Na_2HPO_4 (85.1 mg, 0.6 mmol), $NiBr_2$·DME (9.2 mg, 0.03 mmol), adipic acid (43.8 mg, 0.3 mmol), DMDC (134.1 mg, 97 µL, 0.90 mmol), a teflon stir bar, toluene (110.6 mg, 127 µL, 1.2 mmol) and *i*PrOAc (6 mL). After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/PE (1/2) as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 5/1) on silica gel to afford **61** (44.1 mg, 0.15 mmol, 50% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 6H), 7.23 – 7.15 (m, 4H), 3.66 (s, 4H), 2.47 – 2.36 (m, 4H), 1.54 – 1.44 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.1, 134.4, 129.5, 128.8, 127.1, 50.3, 41.7, 23.1.

HRMS (ESI) calcd for $C_{20}H_{22}O_2Na^+$ [$(M+Na)^+$]: calculated 317.1512, found 317.1503.

Sequential acylation of alkenes



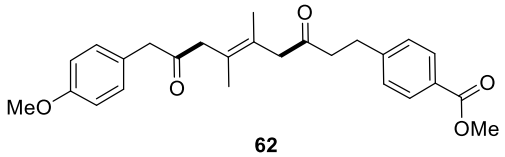
General procedure C:

An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (0.004 mmol), dtbbpy (**L1**) (0.052 mmol), Na_2HPO_4(0.8 mmol), $NiBr_2$·DME (0.04 mmol), carboxylic acid (0.4 mmol), DMDC (0.6 mmol) and *i*PrOAc (4 mL) were added sequentially under N_2 atmosphere. The reaction mixture was stirred at room temperature for 30 min. Then 2,3-dimethyl-2-butene (0.8 mmol) and the *i*PrOAc (4 mL) was injected through the syringe into the mentioned above flask containing the Ir/Ni catalysts.

The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDs at a distance of 2 cm for 18 h at room temperature. After 18 h, the reaction mixture was then passed through a short pad of silica gel, with EtOAc as the eluent (~25 mL)，before it was purified by flash chromatography on silica gel to afford the desired ketone.

Adding the obtained ketone (2.0 equiv.) and carboxylic acid (1.0 equiv.) to the above reaction steps. The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDs at a distance of 2 cm for 18 h at room temperature. After 18 h, the reaction mixture was then passed through a short pad of silica gel with(EtOAc) as the eluent (~25 mL)，before it was purified by flash chromatography on silica gel to afford the desired ketone.

Methyl (E)-4-(9-(4-methoxyphenyl)-5,6-dimethyl-3,8-dioxonon-5-en-1-yl)benzoate (62)



62

Prepared according to the general procedure C employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (4.8 mg, 0.004 mmol), dtbbpy (**L1**) (13.9 mg, 0.052 mmol), Na_2HPO_4 (113.5 mg, 0.8 mmol), $NiBr_2$·DME(12.3 mg, 0.04 mmol), 4-methoxyphenylacetic acid (66.5 mg, 0.4 mmol), DMDC (80.5 mg, 64 μL, 0.60 mmol), a teflon stir bar, 2,3-dimethyl-2-butene (67.3 mg, 95 μL, 0.8 mmol) and *i*PrOAc (8 mL). After 18 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc as the eluent (~25 mL), before it was purified by flash chromatography on silica gel to afford the corresponding ketone. Adding the obtained ketone (185.8 mg, 2.0 equiv.) and 3-[4-(methoxycarbonyl)phenyl]propanoic acid (83.3 mg, 1.0 equiv.) to the above reaction steps. The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDs at a distance of 2 cm for 18 h at room temperature. After 18 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc as the eluent (~25 mL). The resulting mixture

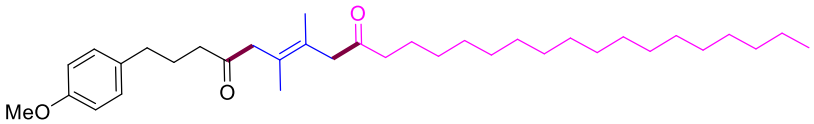
was concentrated, and the residue was purified by flash chromatography (PE/EA = 3/1) on silica gel to afford **62** (84.4 mg, 0.2 mmol, 50% yield, E/Z 7.7/1) as a yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 3.79 (s, 3H), 3.77 (s, 0.23H), 3.63 (s, 1.77H), 3.21 (s, 2H), 3.16 (s, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 1.58 (s, 3H), 1.53 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 207.6, 206.5, 167.2, 158.8, 146.8, 130.5, 129.9, 128.6, 128.2, 126.5, 126.3, 126.2, 114.3, 55.4, 52.1, 49.5, 48.7, 48.0, 42.8, 29.8, 19.9, 19.8.

HRMS (ESI) for $C_{27}H_{31}O_5^+$ [$(M+H)^+$]: calculated 423.2166, found 423.2174.

(*E*)-1-(4-methoxyphenyl)-6,7-dimethylhexacos-6-ene-4,9-dione (63)



63

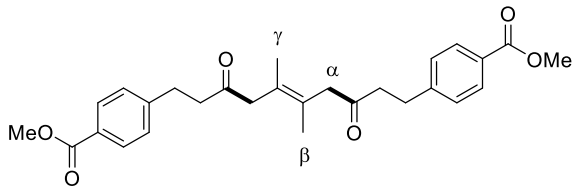
Prepared according to the general procedure D employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.004 mmol), dtbbpy (**L1**) (13.9 mg, 0.052 mmol), Na_2HPO_4 (113.5 mg, 0.8 mmol), $NiBr_2$·DME(12.3 mg, 0.04 mmol), 4-(4-methoxyphenyl)butyric acid (77.7 mg, 0.4 mmol), DMDC (80.5 mg, 64 μL, 0.60 mmol), a teflon stir bar, 2,3-dimethyl-2-butene (67.3 mg, 95 μL, 0.8 mmol) and *i*PrOAc (8 mL). After 18 h, the reaction mixture was then passed through a short pad of silica gel with EtOAc as the eluent (~25 mL) before it was purified by flash chromatography on silica gel to afford the corresponding ketone. Adding the obtained ketone (208.3 mg, 2.0 equiv.) and stearic acid (113.8 mg, 1.0 equiv) to the above reaction steps. The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDs at a distance of 2 cm for 18 h at room temperature. After 18 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 3/1) on silica gel to afford **63** (105.2 mg, 0.2 mmol, 50% yield, E/Z 5.3/1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.65 (d, *J* = 8.1 Hz, 0.64H), 3.13 (d, *J* = 21.0 Hz, 3.36H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.45 – 2.28 (m, 4H), 1.95 – 1.77 (m, 2H), 1.75 – 1.60 (m, 6H), 1.58 – 1.44 (m, 2H), 1.38 – 1.09 (m, 28H), 0.87 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 209.2, 209.0, 208.8, 158.0, 133.9, 132.9, 129.5, 126.3, 126.1, 119.7, 114.5, 113.93, 113.91, 55.4, 49.2, 49.1, 47.3, 47.2, 42.6, 41.6, 41.4, 32.1, 29.83, 29.79, 29.76, 29.63, 29.58, 29.56, 29.5, 29.4, 25.64, 25.60, 24.0, 23.9, 22.8, 21.2, 20.0, 19.9, 14.3.

HRMS (ESI) calcd for $C_{35}H_{59}O_3^+$ [$(M+H)^+$]: calculated 527.4459, found 527.4449.

Dimethyl 4,4'-(5,6-dimethyl-3,8-dioxodec-5-ene-1,10-diyl) (*E*)-dibenzoate (64)



64

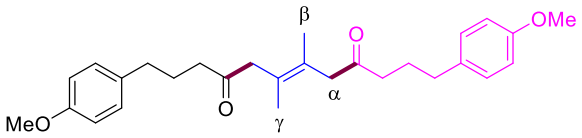
Prepared according to the general procedure D employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.004 mmol, 0.010 equiv), dtbbpy (**L1**) (13.9 mg, 0.052 mmol), Na_2HPO_4 (113.5 mg, 0.8 mmol, 2.0 equiv), $NiBr_2$·DME (12.3 mg, 0.04 mmol), 3-[4-(methoxycarbonyl)phenyl]propanoic acid (83.2 mg, 0.4 mmol), DMDC (80.5 mg, 64 μL, 0.60 mmol, 1.5 equiv), a teflon stir bar, 2,3-dimethyl-2-butene (67.3 mg, 95 μL, 0.8 mmol) and *i*PrOAc (8 mL). After 18 h, the reaction mixture was then passed through a short pad of silica gel, with(EtOAc) as the eluent (~25 mL)，before it was purified by flash chromatography on silica gel to afford the desired ketone. Add the obtained ketone (219.5 mg, 2.0 equiv.) and 3-[4-(methoxycarbonyl)phenyl]propanoic acid (83.2 mg, 1.0 equiv.) to the above reaction steps. The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDs at a distance of 2 cm for 18 h at room temperature. After 18 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 3/1) on silica gel to afford **64** (185.7 mg, 0.208 mmol, 52% yield, α/β/γ = 2.1/1.9/1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 4H), 7.26 – 7.16 (d, *J* = 8.4 Hz, 4H), 3.89 – 3.83 (m, 6H), 3.14 (s, 0.80H), 3.11 (s, 1.52H)，3.04 (s, 1.68H), 2.95 – 2.82 (m, 4H), 2.79 – 2.65 (m, 4H), 1.65 (s, 2.52H), 1.63 (s, 2.28H), 1.55 (s, 1.20H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 207.3, 207.2, 167.04, 167.03, 146.7, 146.6, 133.6, 129.9, 128.6, 128.5, 128.23, 128.21, 126.25, 126.23, 119.1, 52.0, 49.29, 49.26, 47.3, 43.2, 43.0, 42.8, 29.72, 29.68, 21.1, 20.0, 19.8.

HRMS (ESI) calcd for $C_{28}H_{32}O_6Na^+$ [$(M+Na)^+$]: calculated 487.2091, found 487.2085.

(*E*)-1,12-bis(4-methoxyphenyl)-6,7-dimethyldodec-6-ene-4,9-dione (65)



65 (major)

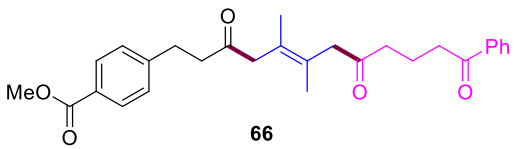
Prepared according to the general procedure D employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (4.8 mg, 0.004 mmol,0.010 equiv), dtbbpy (**L1**) (13.9 mg, 0.052 mmol), Na_2HPO_4 (113.5 mg, 0.8 mmol, 2.0 equiv), $NiBr_2$·DME(12.3 mg, 0.04 mmol), 4-(4-methoxyphenyl)butyric acid (77.7 mg, 0.4 mmol), DMDC (80.5 mg, 64 μL, 0.60 mmol, 1.5 equiv), a teflon stir bar, 2,3-dimethyl-2-butene (67.3 mg, 95 μL, 0.8 mmol) and *i*PrOAc (8 mL). After 18 h, the reaction mixture was then passed through a short pad of silica gel, with(EtOAc) as the eluent (~25 mL)，before it was purified by flash chromatography on silica gel to afford the desired ketone. Add the obtained ketone (208.3 mg, 2.0 equiv.) and 4-(4-methoxyphenyl)butyric acid (77.7 mg, 1.0 equiv.) to the above reaction steps. The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDs at a distance of 2 cm for 18 h at room temperature. After 18 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 3/1) on silica gel to afford **65** (174.5 mg, 0.256 mmol, 64% yield) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.6 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 4H), 3.78 (s, 6H), 3.62 (s, 0.44H), 3.16 (s, 3.56H), 2.55 (s, 4H), 2.42 (s, 4H), 1.89 – 1.84 (m, 4H), 1.63 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.8, 158.0, 133.8, 129.5, 126.2, 113.9, 55.4, 49.2, 41.3, 34.3, 25.6, 19.9.

HRMS (ESI) calcd for $C_{28}H_{36}O_4Na^+$ [$(M+Na)^+$]: calculated 459.2506, found 459.2499.

Methyl (*E*)-4-(5,6-dimethyl-3,8,12-trioxo-12-phenyldodec-5-en-1-yl)benzoate (66)



66

Prepared according to the general procedure D employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (4.8 mg, 0.004 mmol), dtbbpy (**L1**) (13.9 mg, 0.052 mmol), Na_2HPO_4 (113.5 mg, 0.8 mmol),

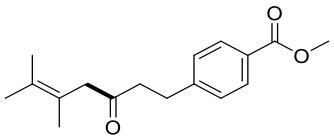
$NiBr_2$·DME(12.3 mg, 0.04 mmol), 3-[4-(methoxycarbonyl)phenyl]propanoic acid (83.2 mg, 0.4 mmol), DMDC (80.5 mg, 64 μL, 0.60 mmol), a teflon stir bar, 2,3-dimethyl-2-butene (67.3 mg, 95 μL, 0.8 mmol) and *i*PrOAc (8 mL). After 18 h, the reaction mixture was then passed through a short pad of silica gel, with(EtOAc) as the eluent (~25 mL)， before it was purified by flash chromatography on silica gel to afford the desired ketone. Add the obtained ketone (219.5 mg, 2.0 equiv.) and 4-benzoylbutanoic acid (76.9 mg, 1.0 equiv.) to the above reaction steps. The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDs at a distance of 2 cm for 18 h at room temperature. After 18 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc as the eluent (~25 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography (PE/EA = 3/1) on silica gel to afford **66** (71.7 mg, 0.16 mmol, 40% yield) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.87 (m, 4H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 3H), 3.89 (s, 3H), 3.17 (d, *J* = 9.7 Hz, 2H), 3.01 (t, *J* = 7.0 Hz, 2H), 2.92 (d, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.03 – 1.96 (m, 2H), 1.70 – 1.59 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.4, 207.5 199.9, 167.2, 146.8, 137.0, 133.2, 129.9, 128.8, 128.6, 128.3, 128.2, 126.5, 126.1, 52.1, 49.4, 49.2, 42.9, 41.1, 37.6, 29.8, 20.0, 19.9, 18.4.

HRMS (ESI) calcd for $C_{28}H_{33}O_5^+$ [$(M+H)^+$]: calculated 449.2323, found 449.2338.

Methyl 4-(5,6-dimethyl-3-oxohept-5-en-1-yl)benzoate (67)



67

An oven-dried 250 mL flask was evaculated and back-filled with N_2 for three times. After cooling at room temperature added Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (44.8 mg, 0.04 mmol), dtbbpy (**L1**) (137.5 mg, 0.52 mmol), Na_2HPO_4 (851.8 mg, 6.0 mmol), $NiBr_2$·DME (123.4 mg, 0.4 mmol), 3-[4-(methoxycarbonyl)phenyl]propanoic acid (832.8 mg, 4.0 mmol), DMDC (804.5 mg, 640 μL, 6 mmol), *i*PrOAc (0.05 M, 80 mL) and 2,3-dimethyl-2-butene (673.3 mg, 0.95 mL, 8.0 mmol). The reaction mixture was irradiated with 30 W blue LED lamps (30 W , at approximately 2 cm away

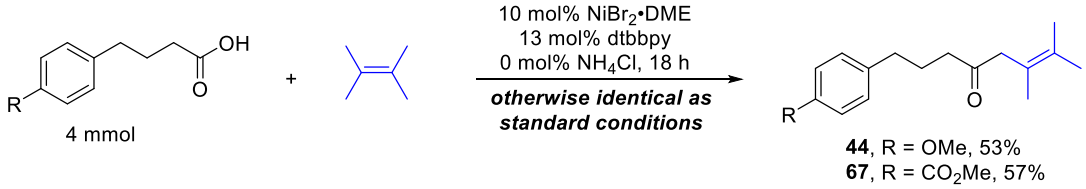
from the light source， Light wavelength 450nm-455nm) with cooling from a fan for 18 h. After 12 h, the reaction mixture was then passed through a short pad of silica gel, with (1:5 EtOAc/hexanes) as the eluent (~150 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography on silica gel, the residue was isolated by flash chromatography (PE/EA = 10:1) on silica gel to afford **67** (625.1 mg, 0.186 mmol, 62% yield) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.88 (s, 3H), 3.10 (s, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 1.67 (s, 3H), 1.62 (s, 3H), 1.59 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.1, 167.0, 146.8, 129.8, 128.9, 128.4, 128.1, 120.9, 52.0, 49.4, 42.6, 29.7, 20.8, 20.6, 19.2.

HRMS (ESI) calcd for $C_{17}H_{23}O_3^+$ [$(M+H)^+$]: calculated 275.1642, found 275.1649.

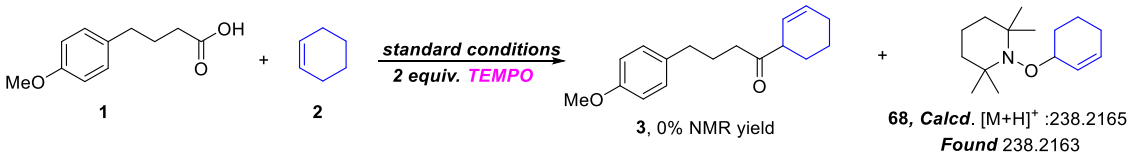
Scale-up synthesis



An oven-dried 250 mL flask was evaculated and back-filled with N_2 for three times. After cooling at room temperature added Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (44.8 mg, 0.04 mmol), dtbbpy (**L1**) (137.5 mg, 0.52 mmol), Na_2HPO_4 (851.8 mg, 6.0 mmol), $NiBr_2$·DME (123.4 mg, 0.4 mmol), 4-(4-methoxyphenyl)butyricacid (776.9 mg, 4.0 mmol) or 4-(4-(methoxycarbonyl)phenyl)butanoic acid (888.9 mg, 4.0 mmol), DMDC (804.5 mg, 640 μL, 6 mmol), *i*PrOAc (0.05 M, 80 mL) and 2,3-dimethyl-2-butene (673.3 mg, 0.95 mL, 8.0 mmol). The reaction mixture was irradiated with 30 W blue LED lamps (30 W , at approximately 2 cm away from the light source, Light wavelength 450nm-455nm) with cooling from a fan for 18 h. After 12 h, the reaction mixture was then passed through a short pad of silica gel, with(1:5 EtOAc/hexanes) as the eluent (~150 mL). The resulting mixture was concentrated, and the residue was purified by flash chromatography on silica gel, the residue was isolated by flash chromatography (PE/EA = 10:1) on silica gel to afford the product as a colorless oil (**44,** 551.0 mg, 53% yield and **67,** 625.1 mg, 57% yield).

VI. Mechanistic studies

Radical trap experiment



Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol),Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), cyclohexene (49.3 mg, 61 μL, 0.6 mmol), 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO, 93.7 mg, 0.6 mmol) and *i*PrOAc (6 mL) were added via a syringe. After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/hexanes (1/5) as the eluent (~25 mL). The resulting mixture was concentrated and the TEMPO-trapped adduct **68** was detected by HRMS and no cross-coupled product was observed.

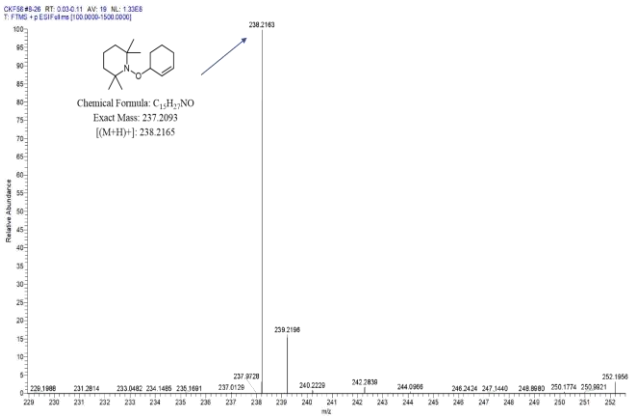
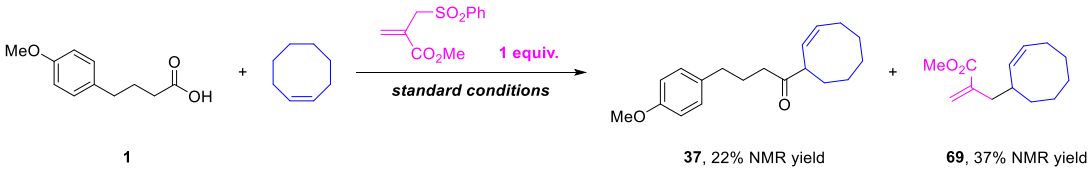
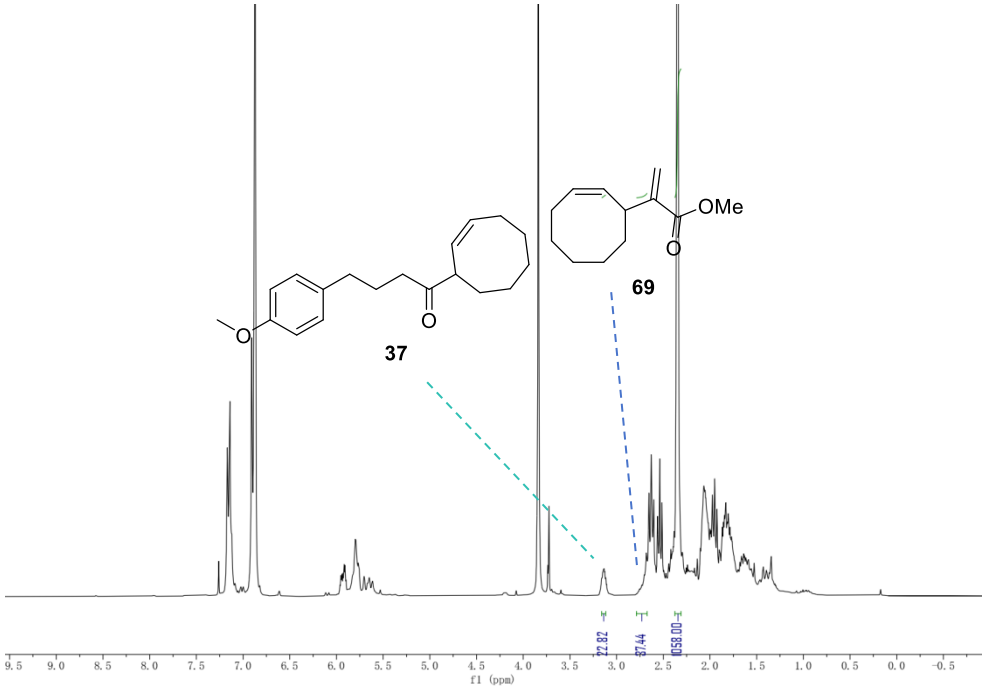


Figure S1. HRMS spectra of **68**

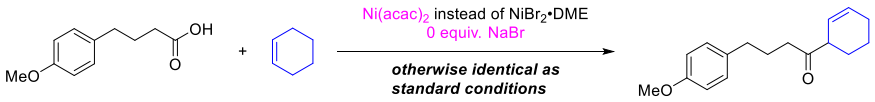


Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.2 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), cyclooctene (66.1 mg, 78 μL, 0.6 mmol), methyl 2-((phenylsulfonyl)methyl)acrylate (72.2 mg, 0.3 mmol) and *i*PrOAc (6 mL) were added via a syringe. After 12 h, the reaction mixture was then passed through a short pad of silica gel, with (1/5 EtOAc/hexanes) as the eluent (~25 mL). The resulting mixture was concentrated, and then mesitylene (42 μL, 0.30 mmol) was added as an internal standard. The methyl 2-

((phenylsulfonyl)methyl)acrylate-trapped adduct **69** was detected in 37% NMR yield and cross coupling product was observed in 22% NMR yield.

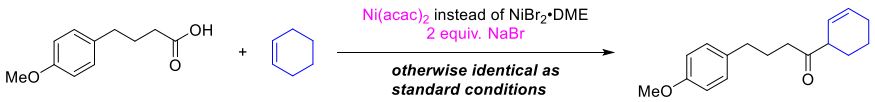


The evaluation of the role of halogen anion



1 **2** **3**, 0% NMR yield

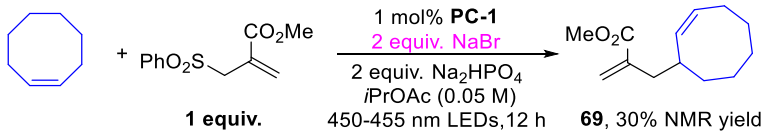
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), Ni(acac)$_2$ (16.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), cyclohexene (49.3 mg, 61 μL, 0.6 mmol), *i*PrOAc (6 mL) was added via a syringe. After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/hexanes (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and then mesitylene (42 μL, 0.30 mmol) was added as an internal standard. The **3** was no detected by NMR and no cross-coupled product was observed.



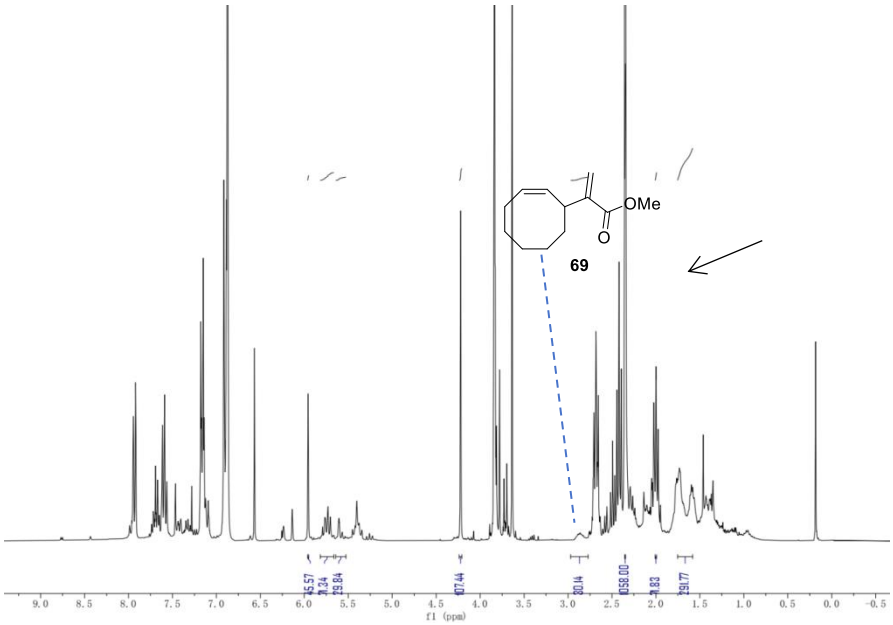
1 **2** **3**, 35% NMR yield

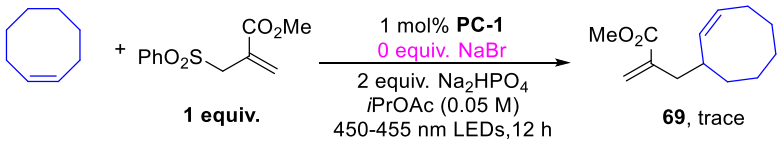
Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg,

0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16.3 mg, 0.3 mmol), $Ni(acac)_2$ (16.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), NaBr (61.7mg, 0.6mmol), cyclohexene (49.3 mg, 61 μL, 0.6 mmol), *i*PrOAc (6 mL) was added via a syringe. After 12 h, the reaction mixture was then passed through a short pad of silica gel, with(1:5 EtOAc/hexanes) as the eluent (~25 mL). The resulting mixture was concentrated, and then mesitylene (42 μL, 0.30 mmol) was added as an internal standard. The NMR yield of **3** was found to be 35%.



Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NaBr (61.7mg, 0.6mmol), methyl 2-((*p* henylsulfonyl)methyl)acrylate (72 mg, 0.3 mmol), cyclooctene (66.1 mg, 78 μL, 0.6 mmol) and *i*PrOAc (6 mL) was added via a syringe. After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/hexanes (1/5) as the eluent (~25 m L). The resulting mixture was concentrated, and then mesitylene (42 μL, 0.30 mmol) was added as an internal standard. The NMR yield of **69** products was 30% in the presence o f NaBr.





Prepared according to the general procedure A employing Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.6 mg, 0.003 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), no NaBr, methyl 2-((phenylsulfonyl)methyl)acrylate (72 mg, 0.3 mmol), cyclooctene (66.1 mg, 78 μL, 0.6 mmol) and *i*PrOAc 6 mL) was added via a syringe. After 12 h, the reaction mixture was then passed through a short pad of silica gel using EtOAc/hexanes (1/5) as the eluent (~25 mL). The resulting mixture was concentrated, and then Mesitylene (42 μL, 0.30 mmol) was added as an internal standard. No product was detected through ^{1}H NMR analysis.

Fluorescence quenching (Stern-Volmer) studies[1]

Emission intensities were recorded using F-7000 FL spectrophotometer. All Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 solutions were excited at 400 nm and the emission intensity was collected at 456 ~ 600 nm. In a typical experiment, to a 1.0 x 10^{-5} M solution of Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 in *i*PrOAc was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. the emission of the sample was collected.

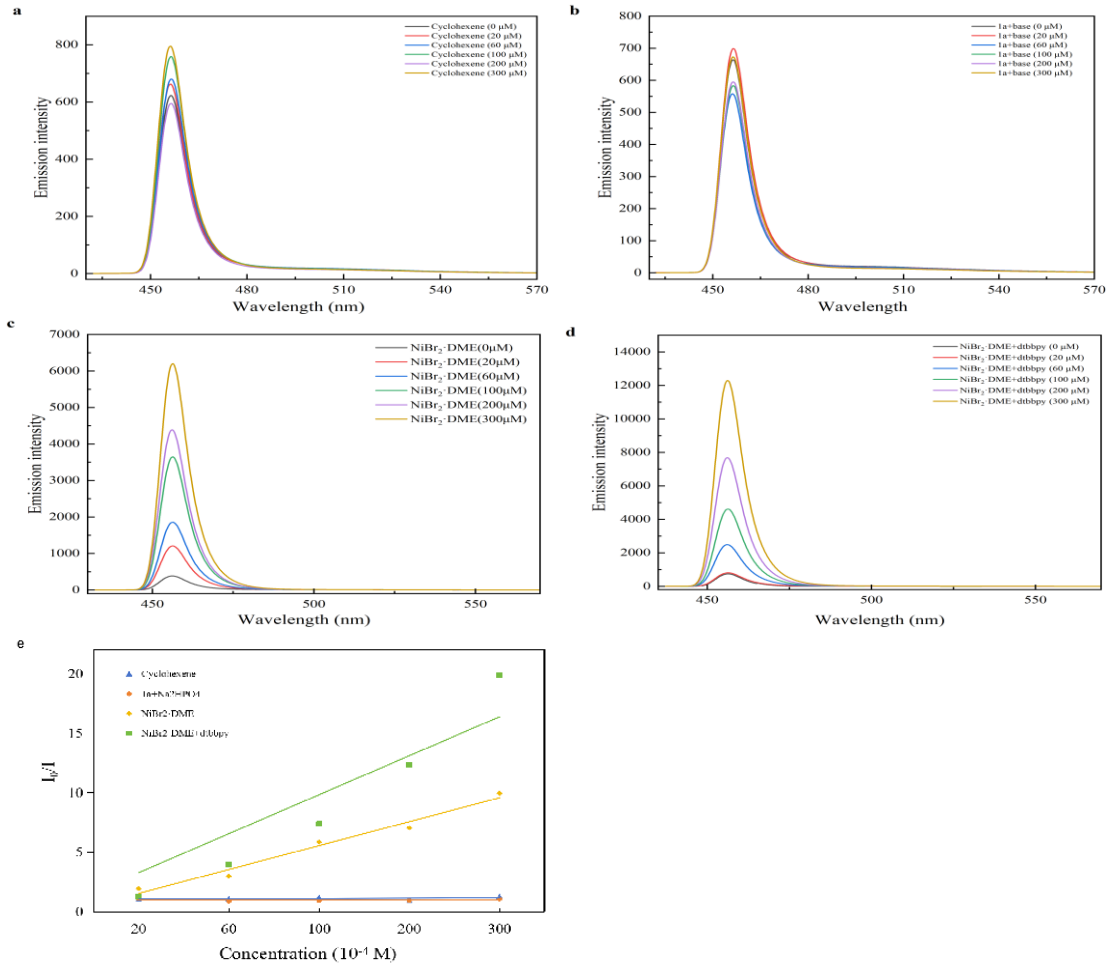
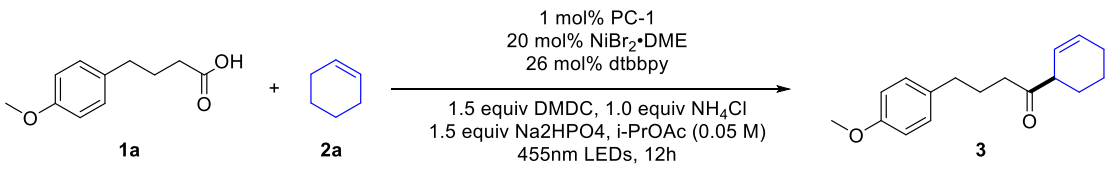


Figure S2. (a) Stern–Volmer quenching with cyclohexene. (b) Stern–Volmer quenching with 1a and Na_2HPO_4. (c) Stern–Volmer quenching with $NiBr_2$·DME. (d) Stern–Volmer quenching with $NiBr_2$·DME + dtbbpy. (e) Stern–Volmer analysis.

Light on-off experiment[2]



Prepared according to the general procedure A employing $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.003 mmol), dtbbpy (**L1**) (20.9 mg, 0.078 mmol), Na_2HPO_4 (63.9 mg, 0.45 mmol), NH_4Cl (16 mg, 0.3 mmol), $NiBr_2$·DME (18.5 mg, 0.06 mmol), 4-(4-methoxyphenyl)butyric acid (58.2 mg, 0.3 mmol), DMDC (60.3 mg, 48 μL, 0.45 mmol), a teflon stir bar, cyclohexene (49.3 mg, 61 μL, 0.6 mmol) and *i*PrOAc (6 mL).The resulting crude mixtures were then allowed to stir at room temperature and irradiated by 450-455 nm LEDS at a distance of 2 cm for a sequential light on/off

experiment was conducted. Initial irradiation for 2 hours yielded 11%. Subsequent reaction in the dark for 2 hours exhibited no increase in yield, maintaining 11%. Upon re-illumination for 2 hours, the yield increased to 16%. A following 2-hour dark period again showed no significant change, with the yield remaining at 17%. This pattern continued: illumination (2 h) raised the yield to 24%, followed by dark conditions (2 h) with no increase (24%); illumination (2 h) to 33%, dark (2 h) stable at 33%; illumination (2 h) to 43%, dark (2 h) stable at 43%; and finally, illumination (2 h) to 56%, followed by dark reaction (2 h) yielding no further increase (56%).The reaction yields were determined by ^{1}H NMR analysis with mesitylene as an internal standard.

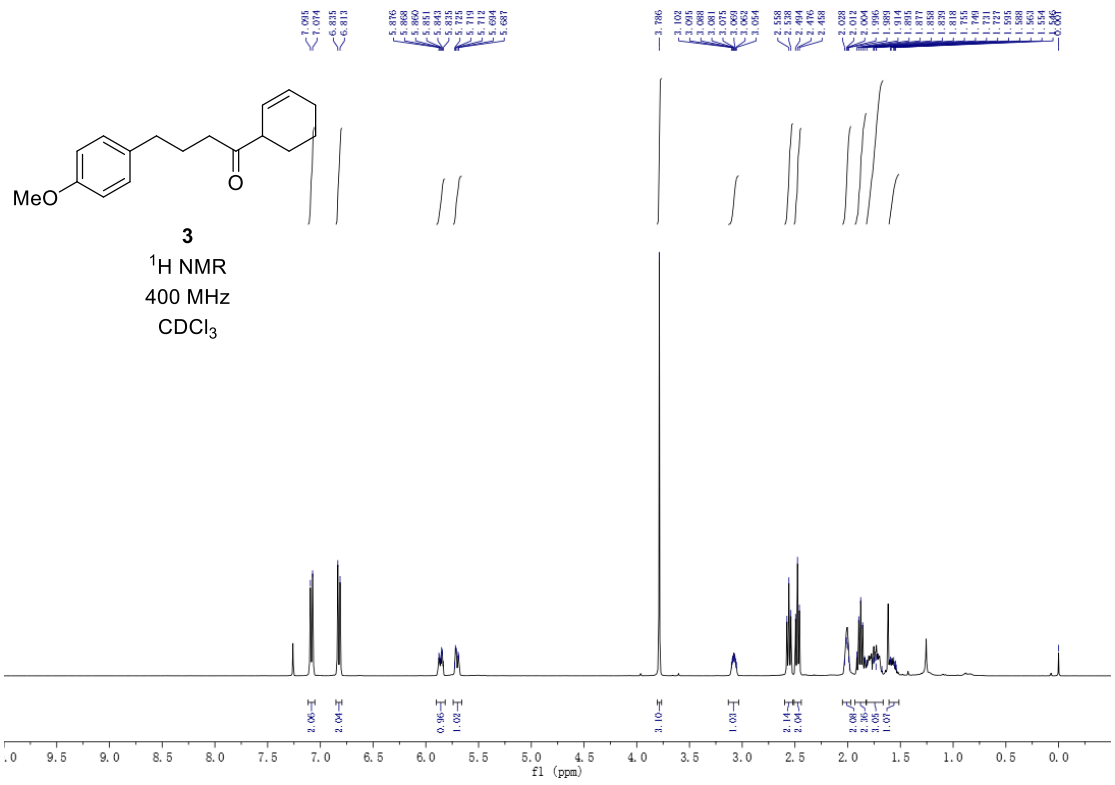
entry	light on and off conditions	yield (%)
1	on 2 hours	11%
2	off 2 hours	11%
3	on 2 hours	16%
4	off 2 hours	17%
5	on 2 hours	24%
6	off 2 hours	24%
7	on 2 hours	33%
8	off 2 hours	33%
9	on 2 hours	43%
10	off 2 hours	43%
11	on 2 hours	56%
12	off 2 hours	56%

Table S8. Light on-off experiment

VII. Supplementary References

1. X. Xi, Y. Luo, W. Li, M. Xu, H. Zhao, Y. Chen, S. Zheng, X. Qi and W. Yuan, *Angew. Chem. Int. Ed*, 2022, **61**, e202114731.
2. X. Wang, R. Yang, B. Zhu, Y. Liu, H. Song, J. Dong and Q. Wang, *NAT COMMUN*, 2023, **14**, 2951.

VIII. NMR spectra

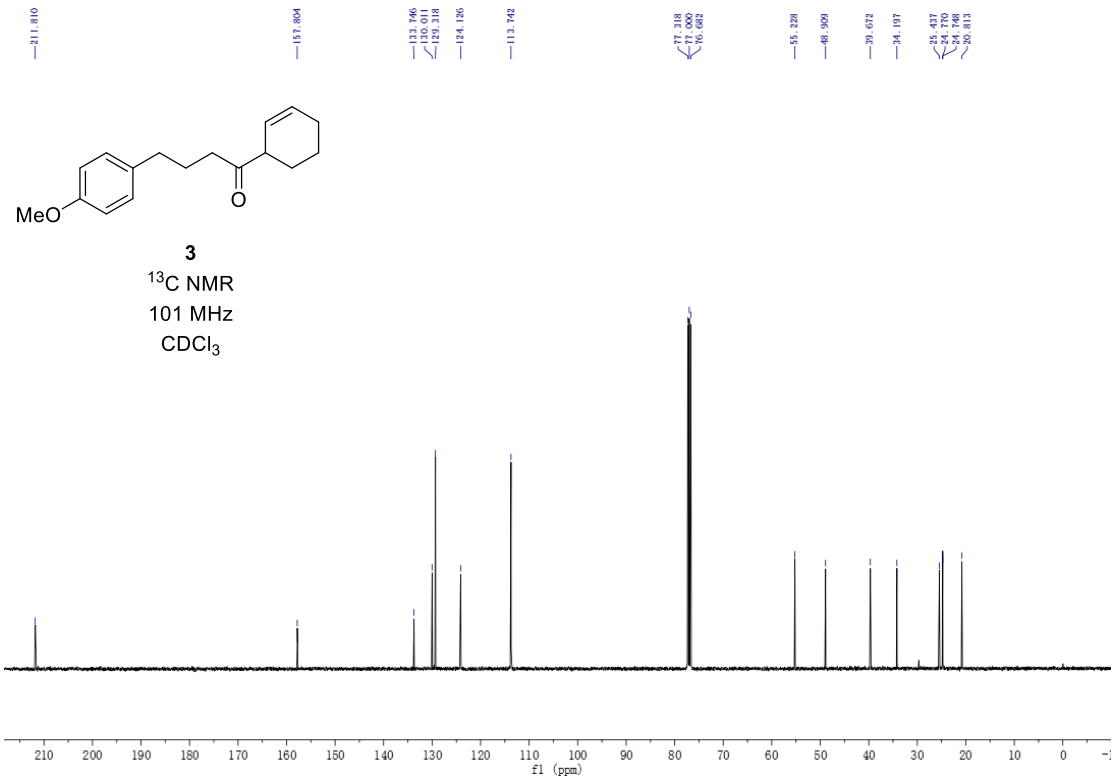


3

^{1}H NMR

400 MHz

$CDCl_3$

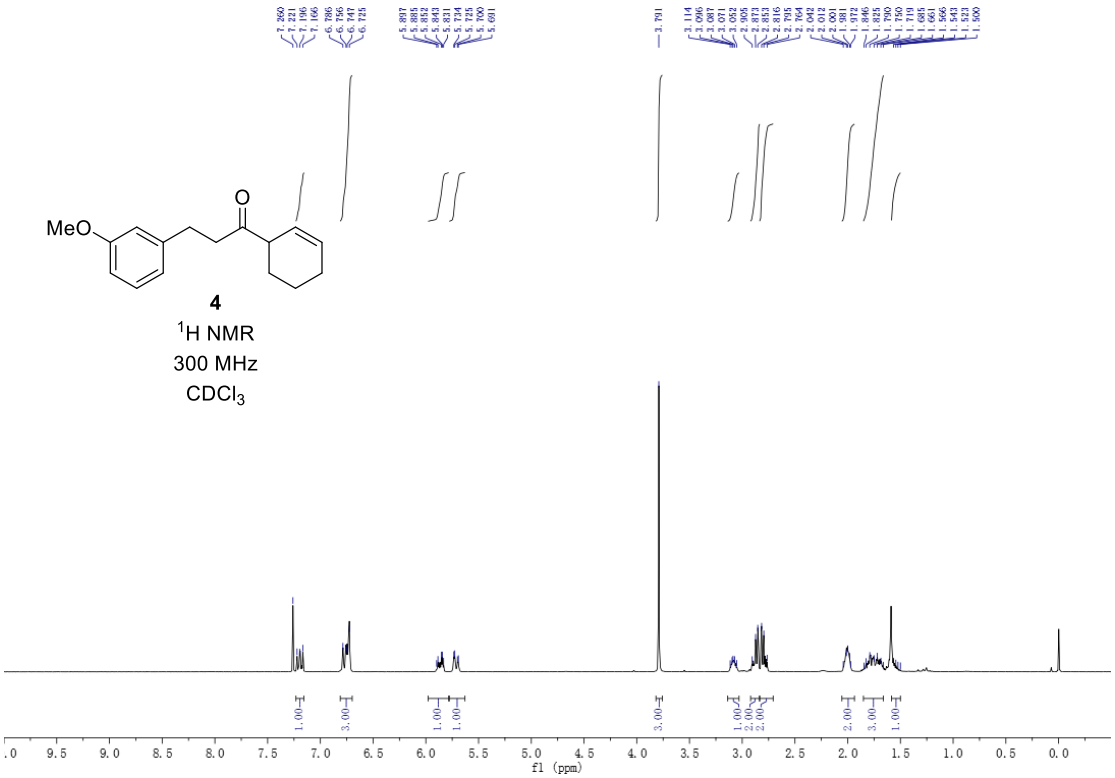


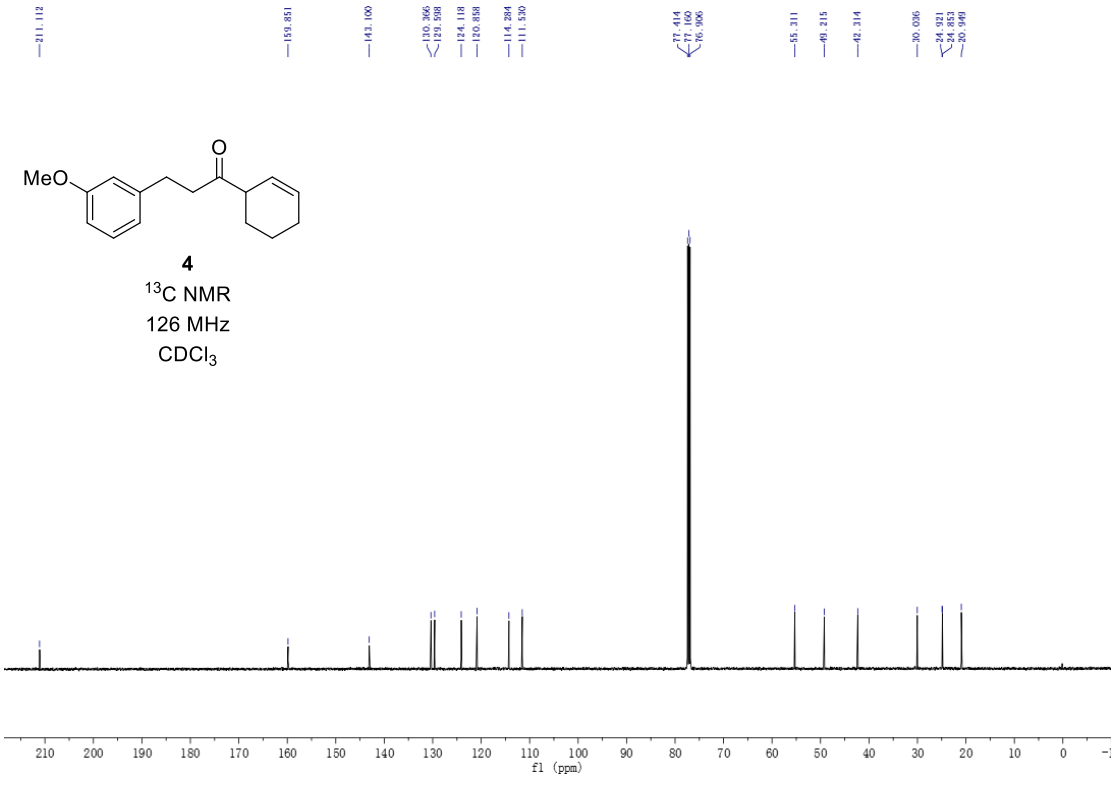
3

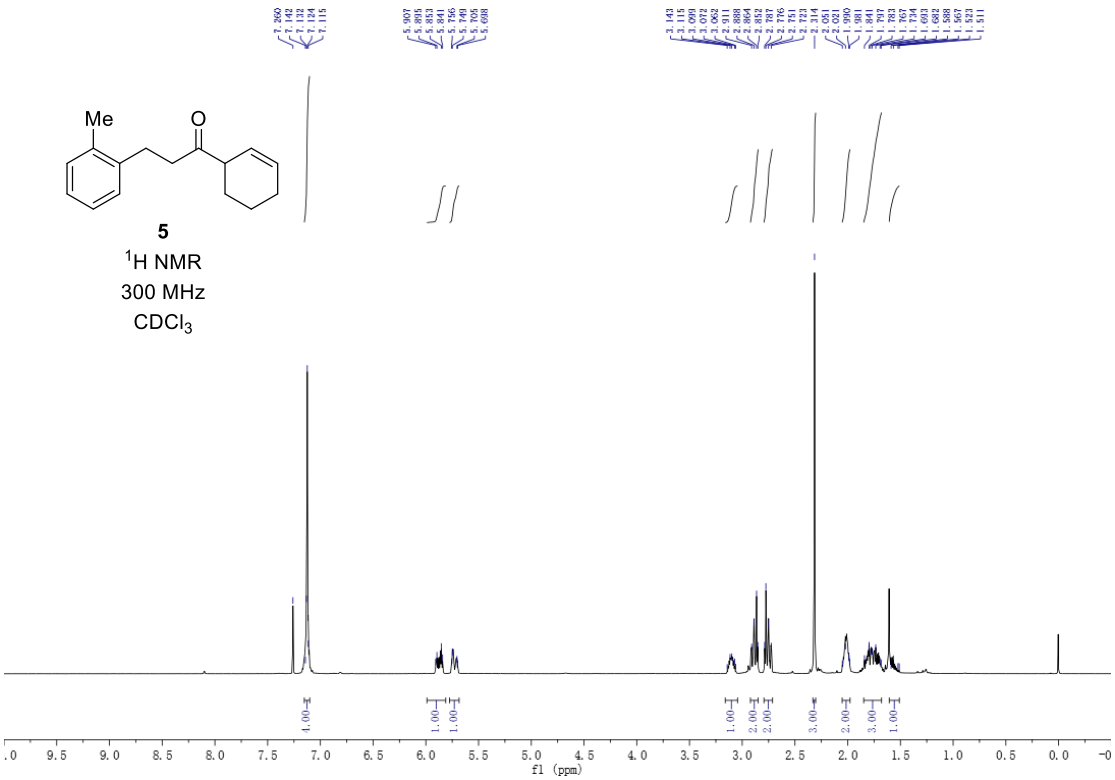
^{13}C NMR

101 MHz

$CDCl_3$


MeO
O
4
1H NMR
300 MHz
CDCl3
f1 (ppm)


MeO
O
4
13C NMR
126 MHz
CDCl3
f1 (ppm)

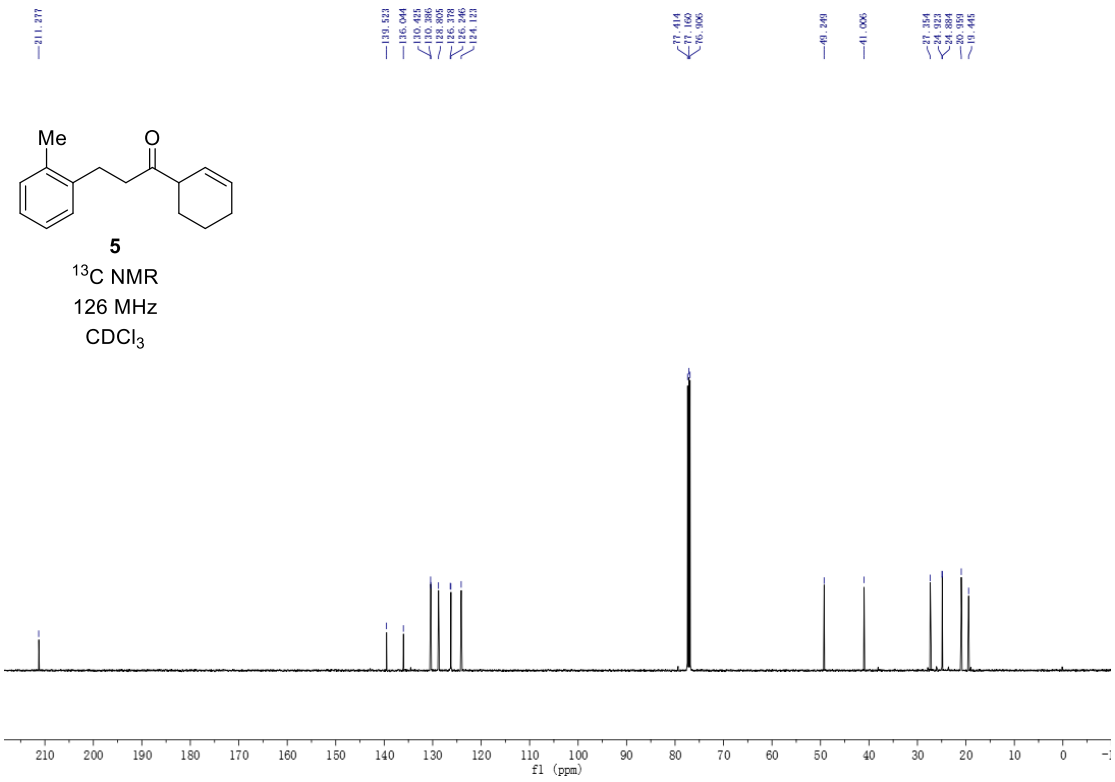


5

^{1}H NMR

300 MHz

$CDCl_3$

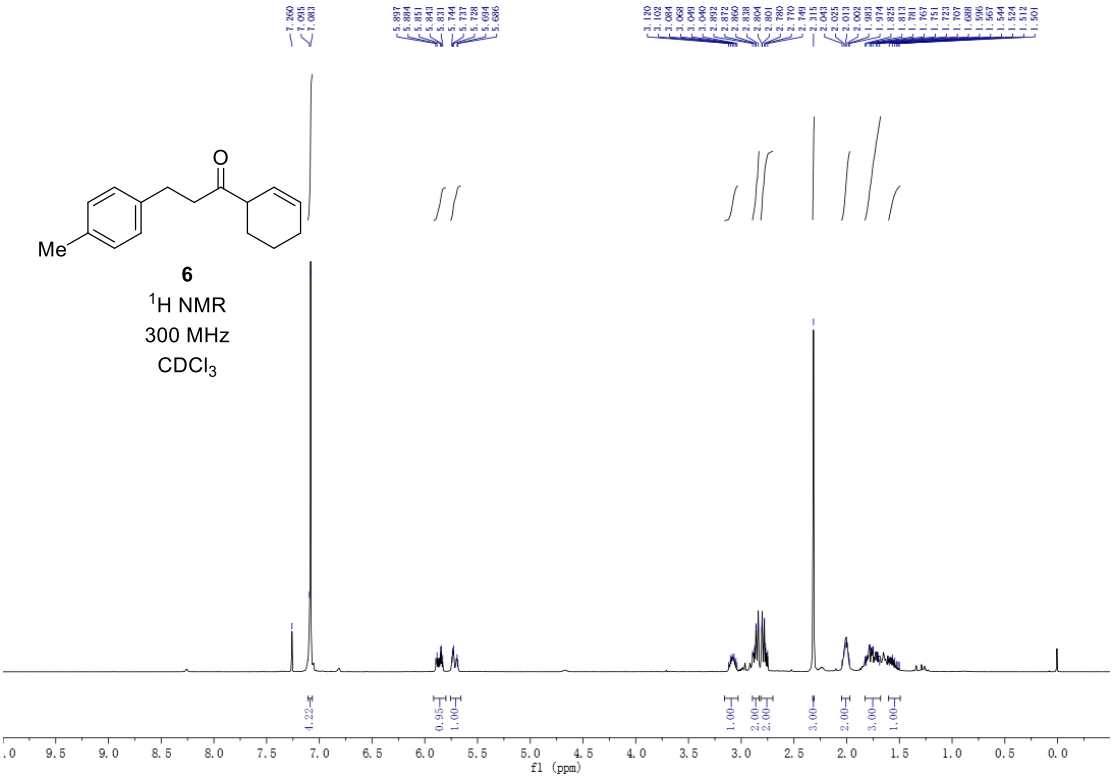


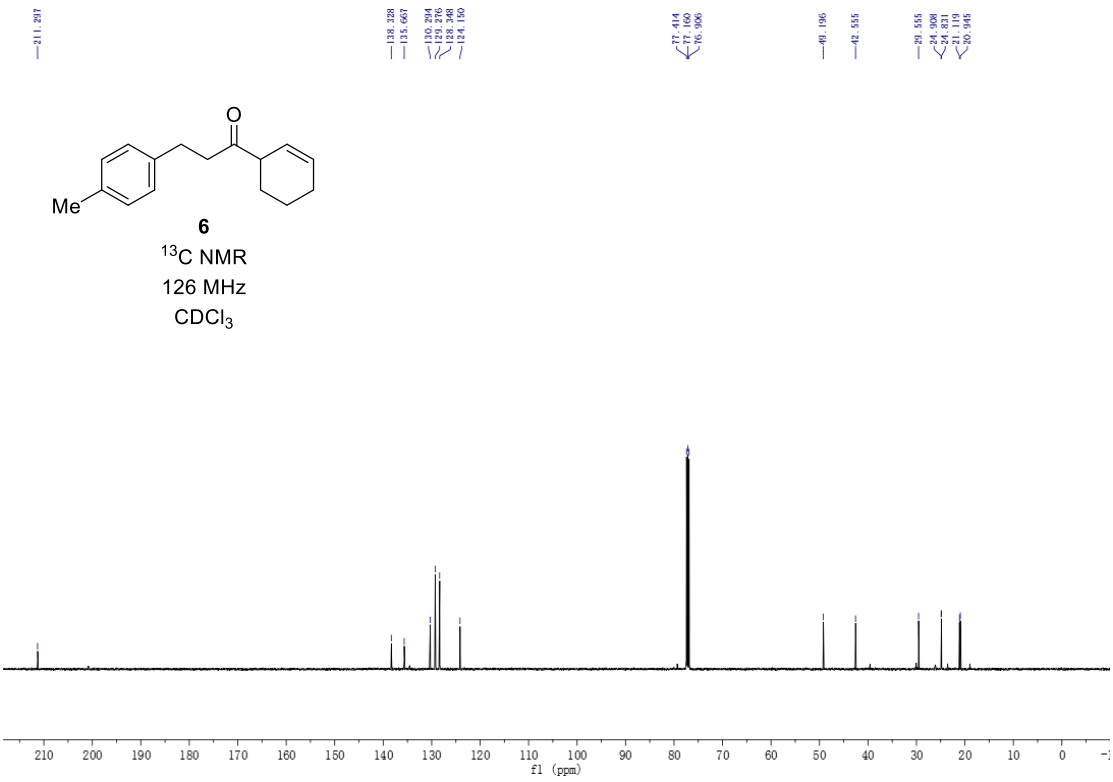
5

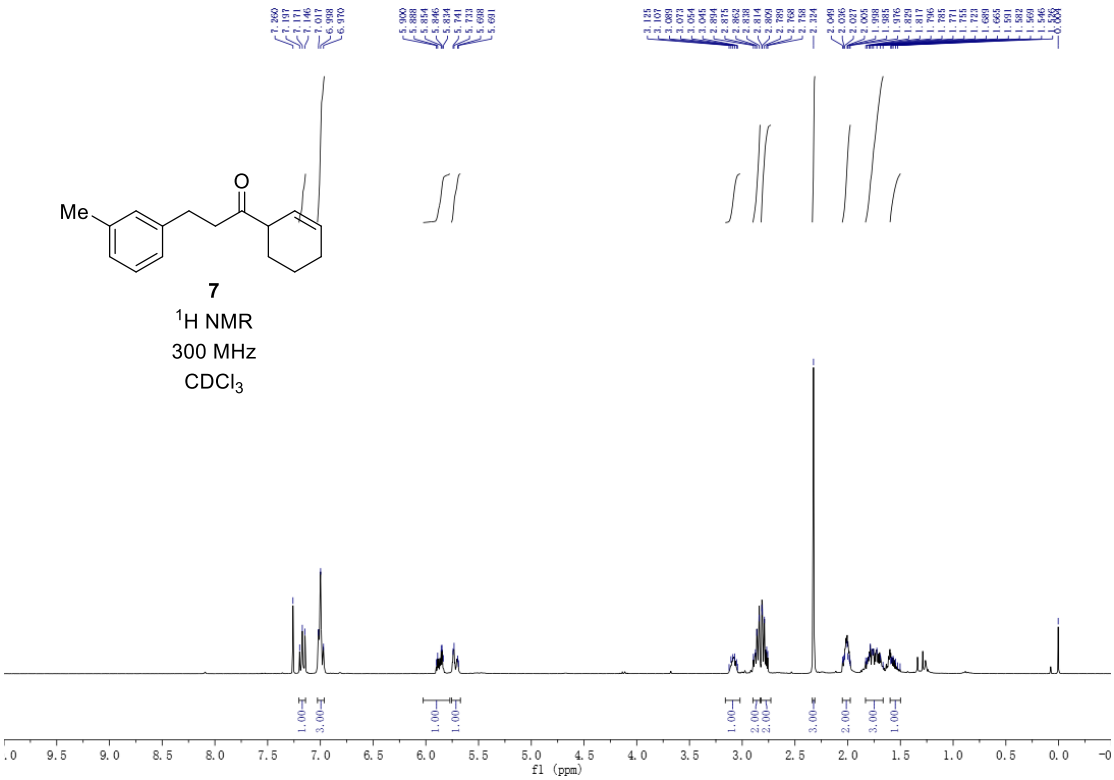
^{13}C NMR

126 MHz

$CDCl_3$


O
Me
6
1H NMR
300 MHz
CDCl3
f1 (ppm)


O
Me
6
13C NMR
126 MHz
CDCl3
f1 (ppm)

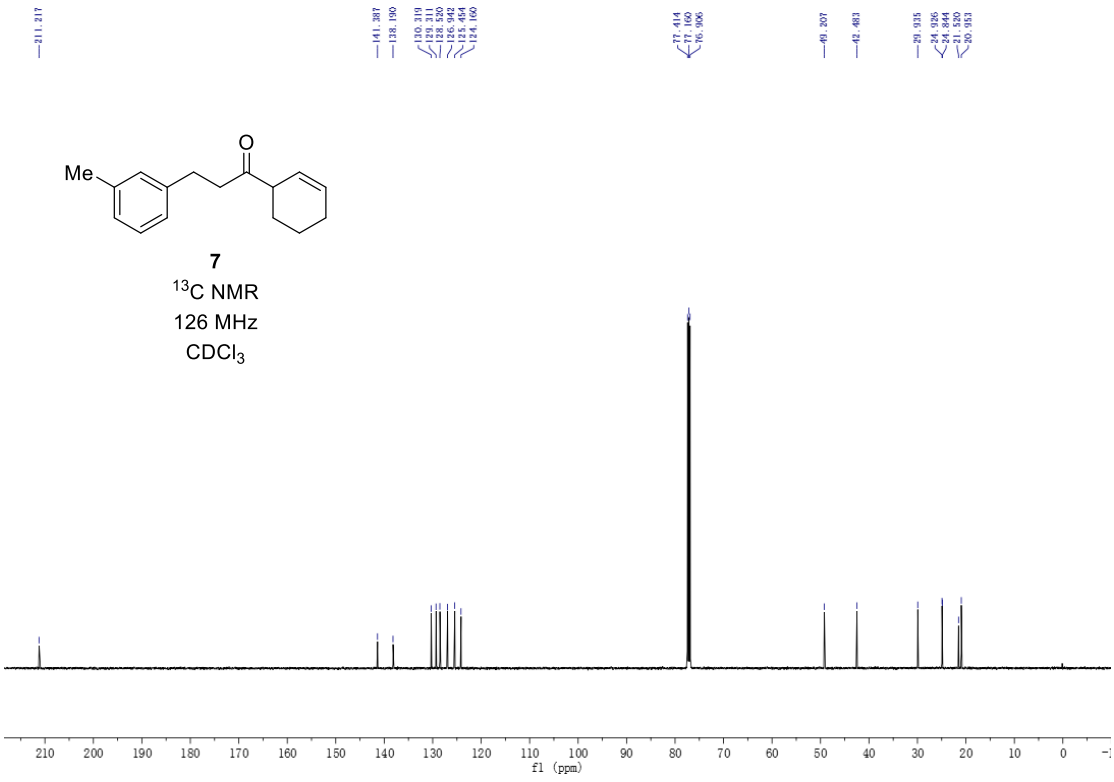


7

^{1}H NMR

300 MHz

$CDCl_3$

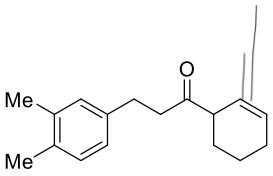


7

^{13}C NMR

126 MHz

$CDCl_3$

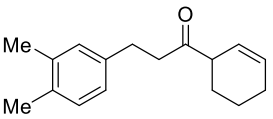


8

^{1}H NMR

300 MHz

$CDCl_3$

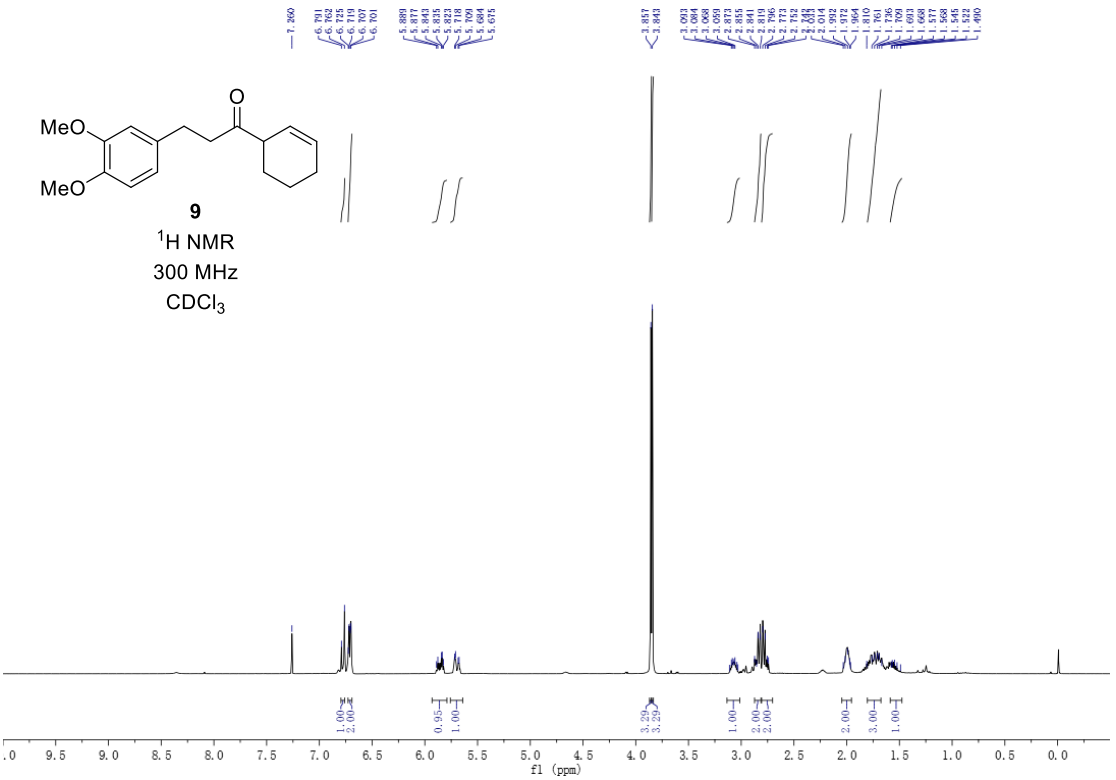


8

^{13}C NMR

126 MHz

$CDCl_3$

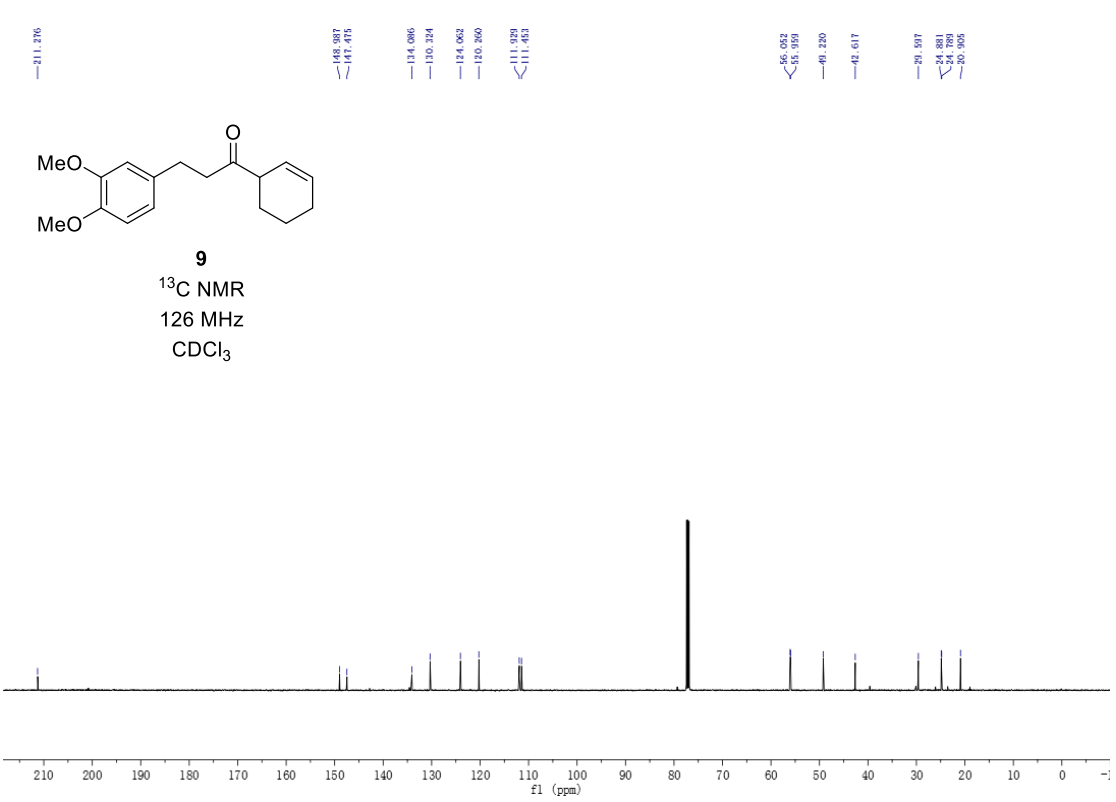


9

^{1}H NMR

300 MHz

$CDCl_3$

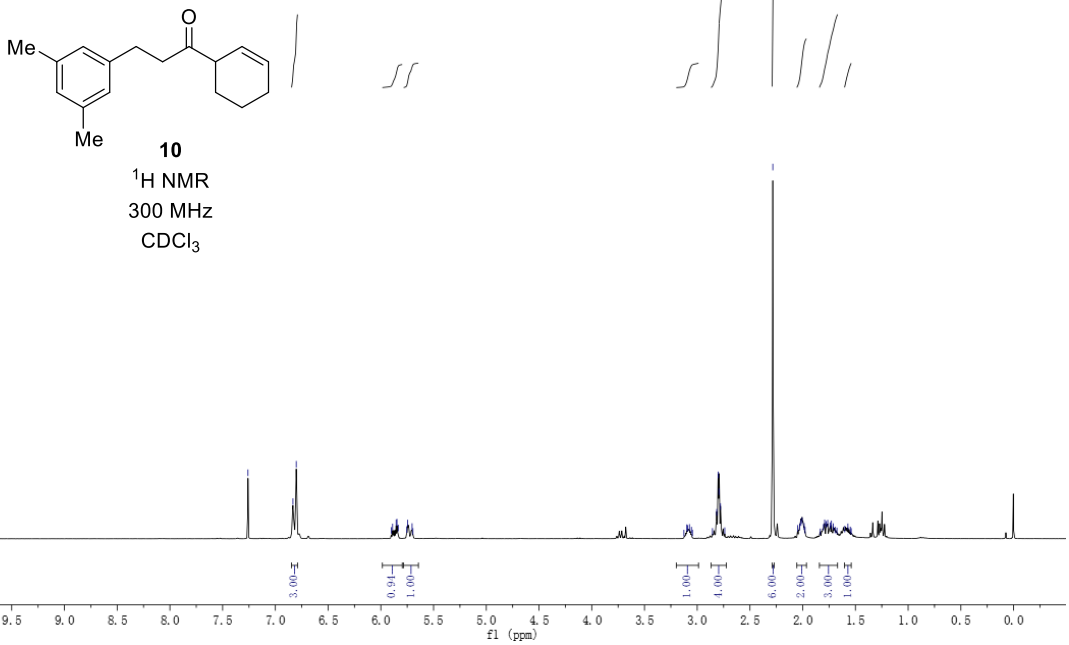


9

^{13}C NMR

126 MHz

$CDCl_3$

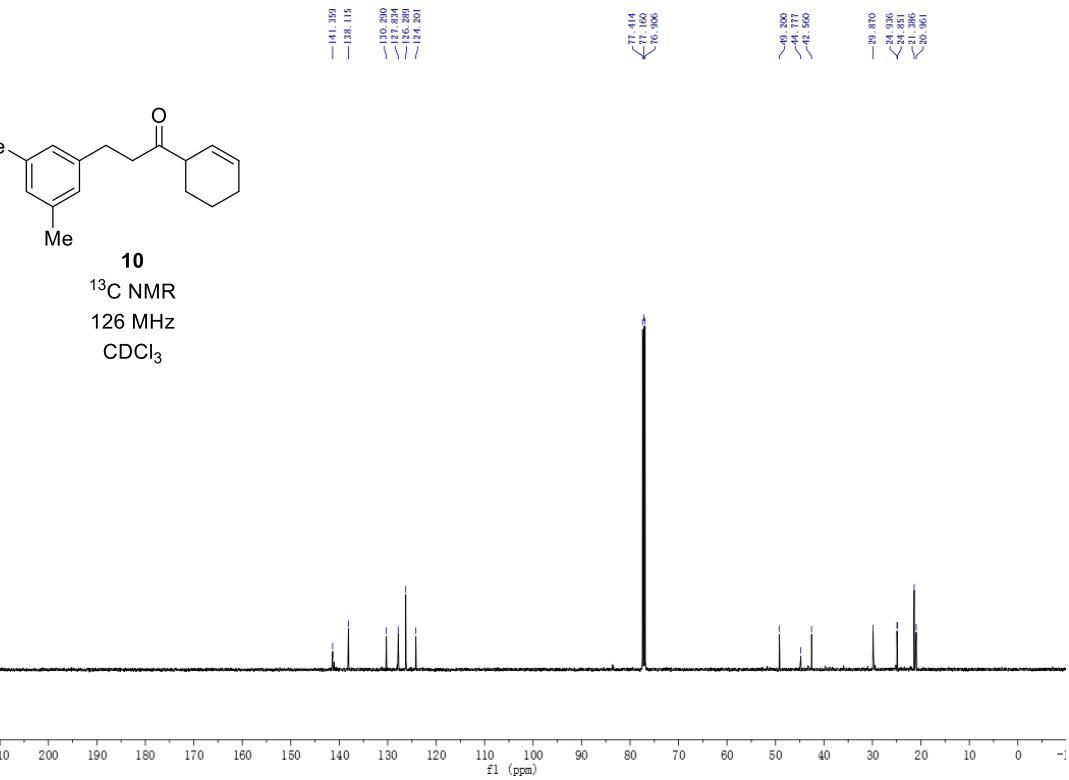


10

^{1}H NMR

300 MHz

$CDCl_3$

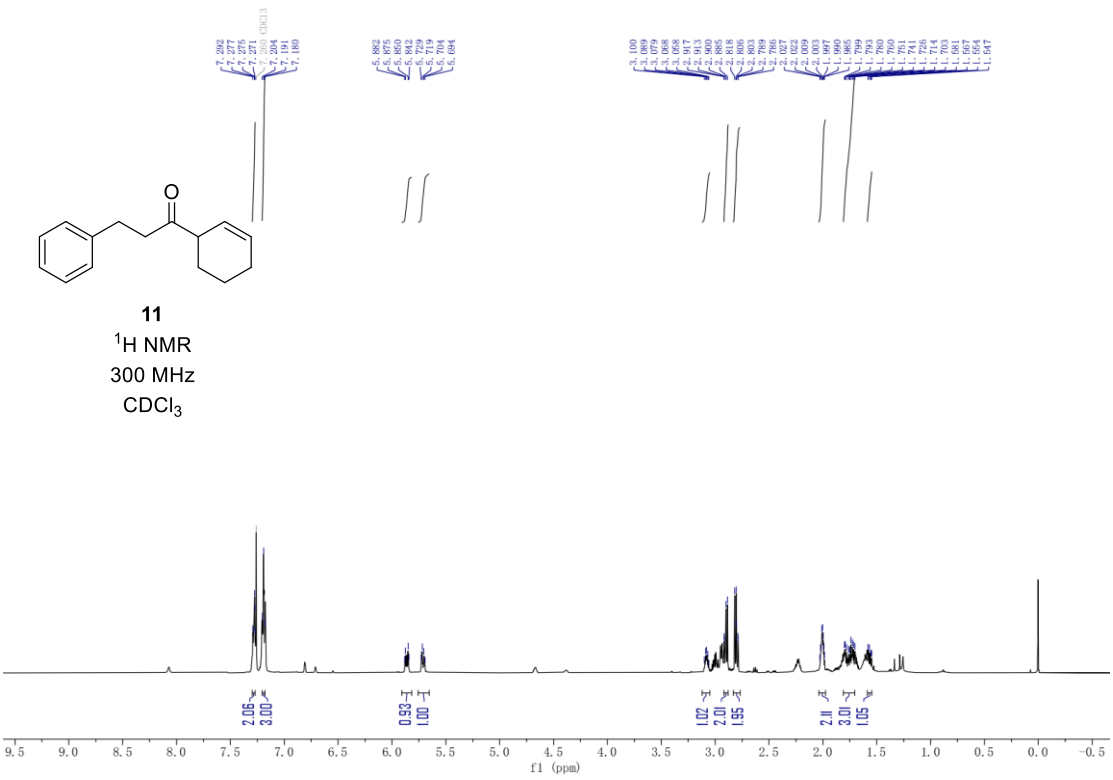


10

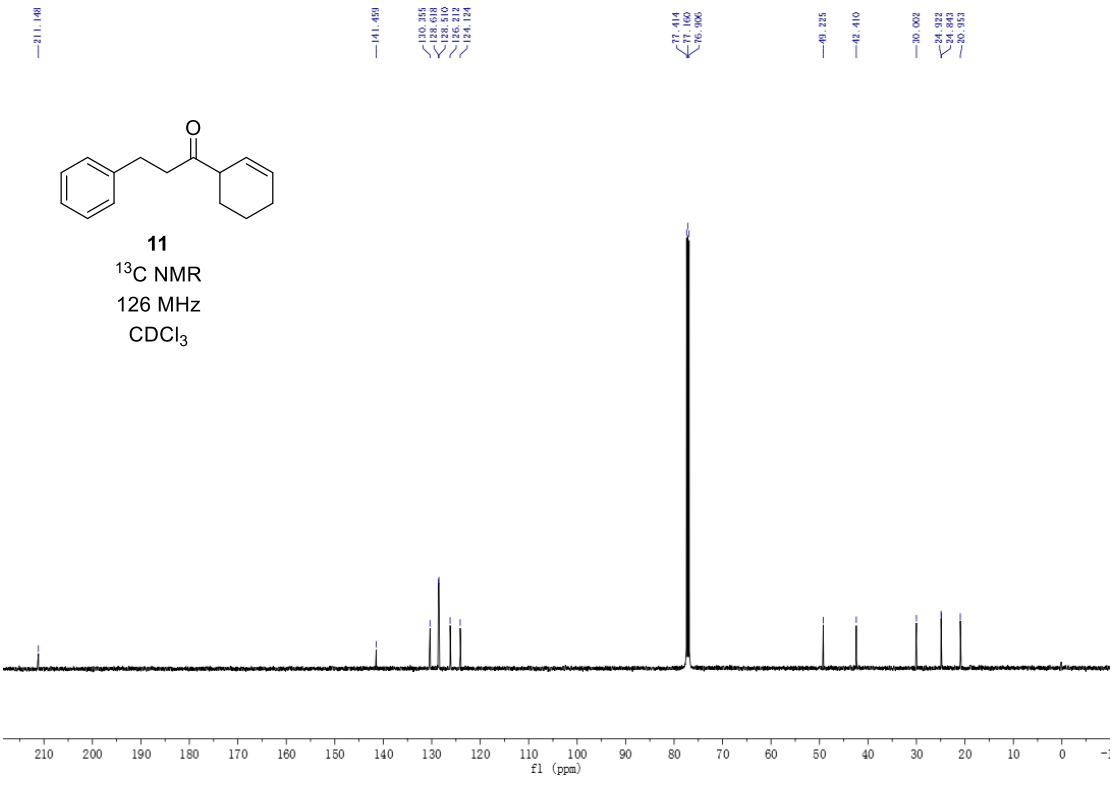
^{13}C NMR

126 MHz

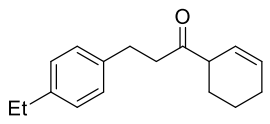
$CDCl_3$



11
^{1}H NMR
300 MHz
$CDCl_3$



11
^{13}C NMR
126 MHz
$CDCl_3$



12

^{1}H NMR

300 MHz

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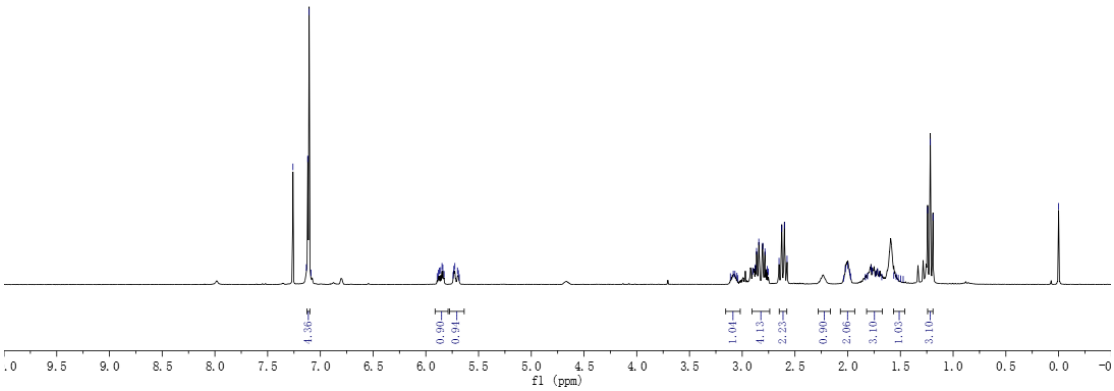
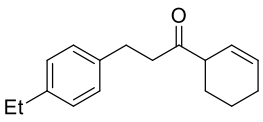


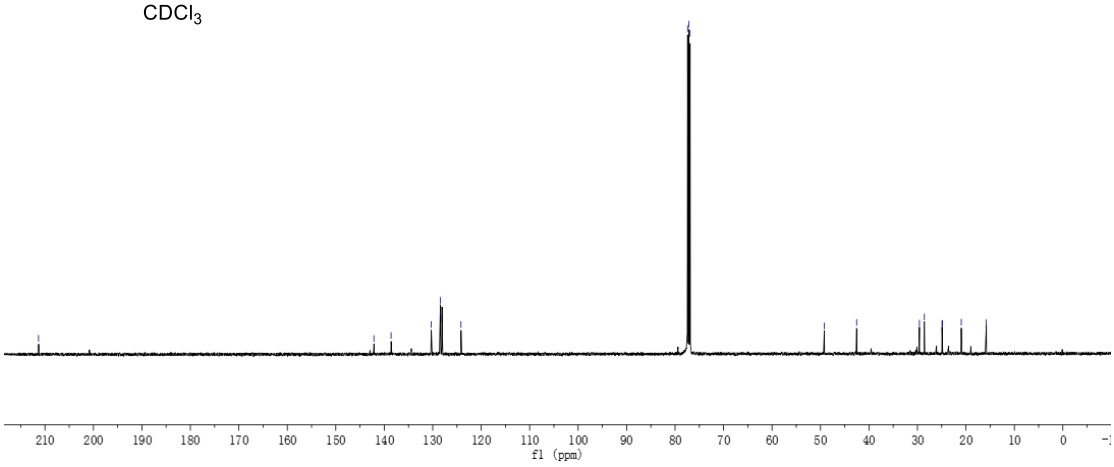


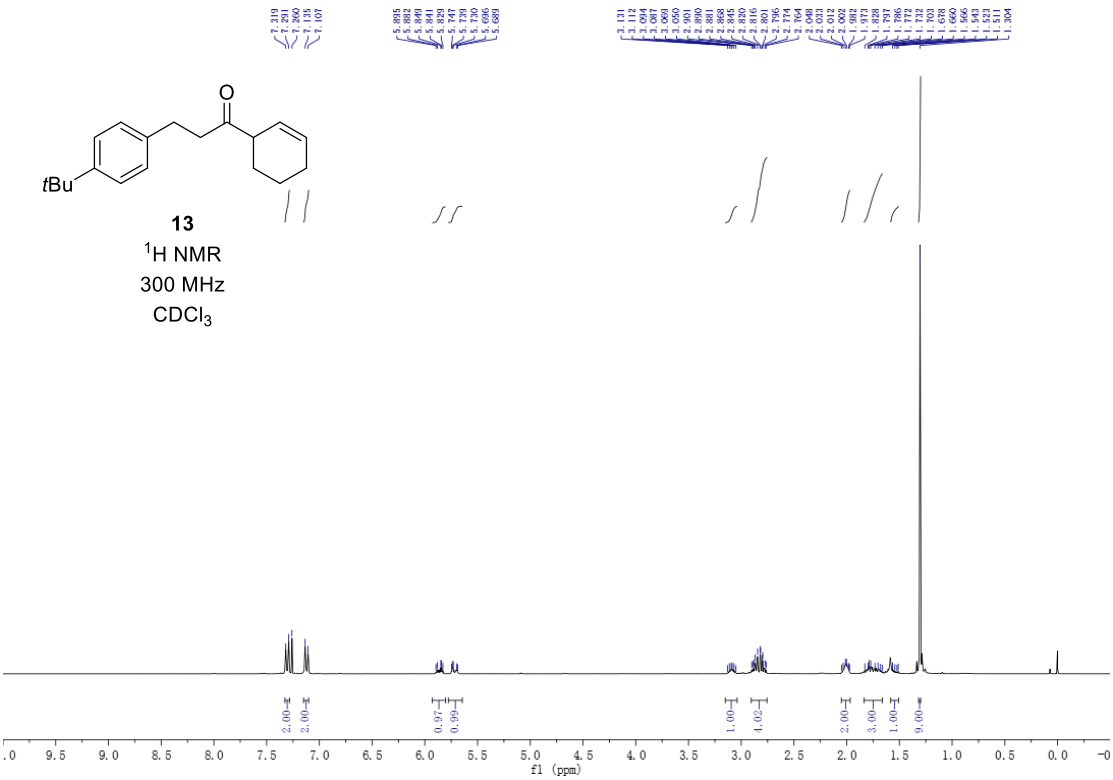
12

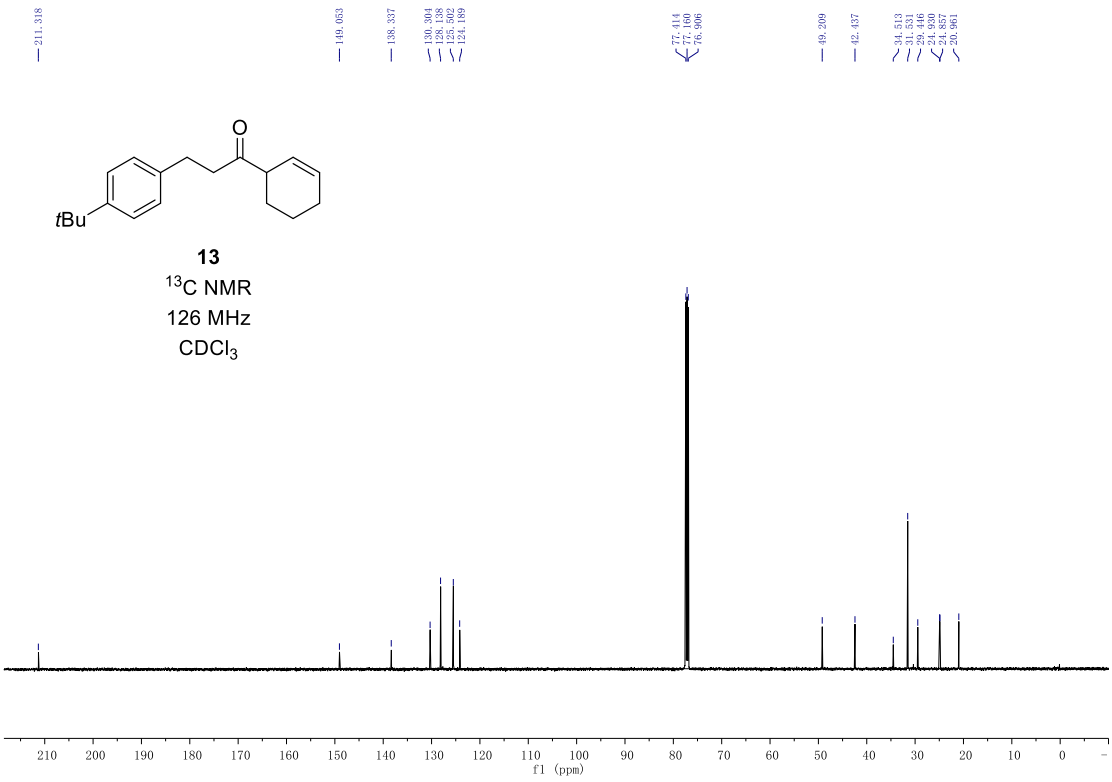
^{13}C NMR

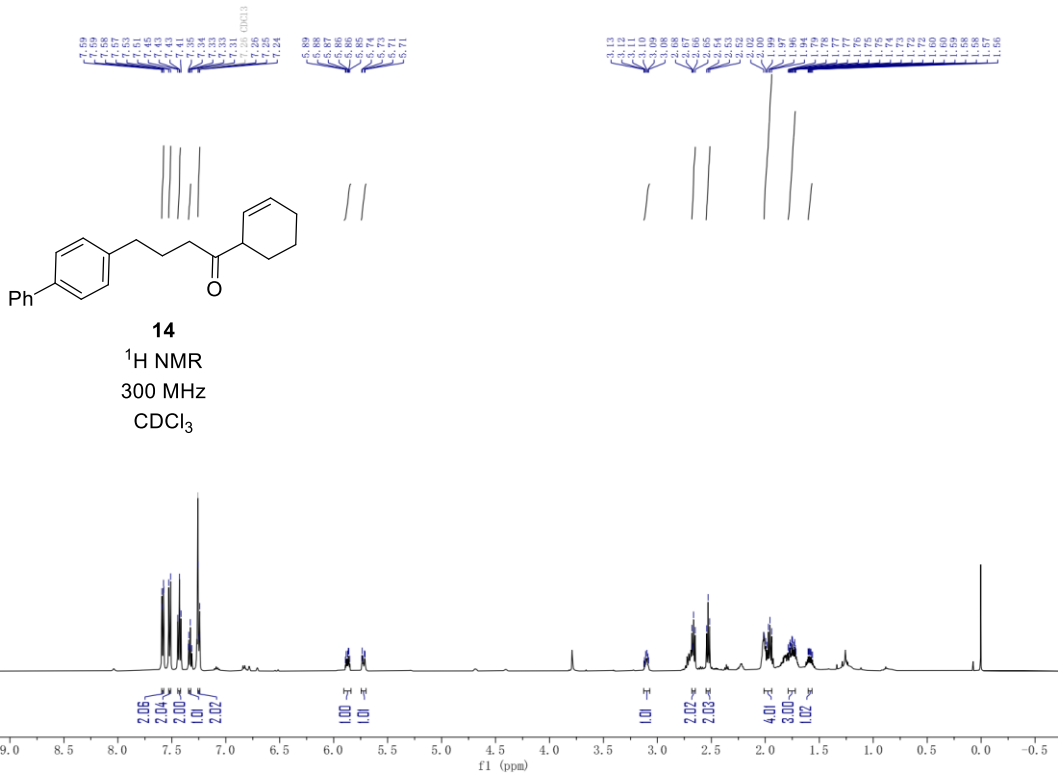
126 MHz

$CDCl_3$




tBu
O
13
1H NMR
300 MHz
CDCl3
f1 (ppm)


tBu
O
13
13C NMR
126 MHz
CDCl3
f1 (ppm)



14

^{1}H NMR

300 MHz

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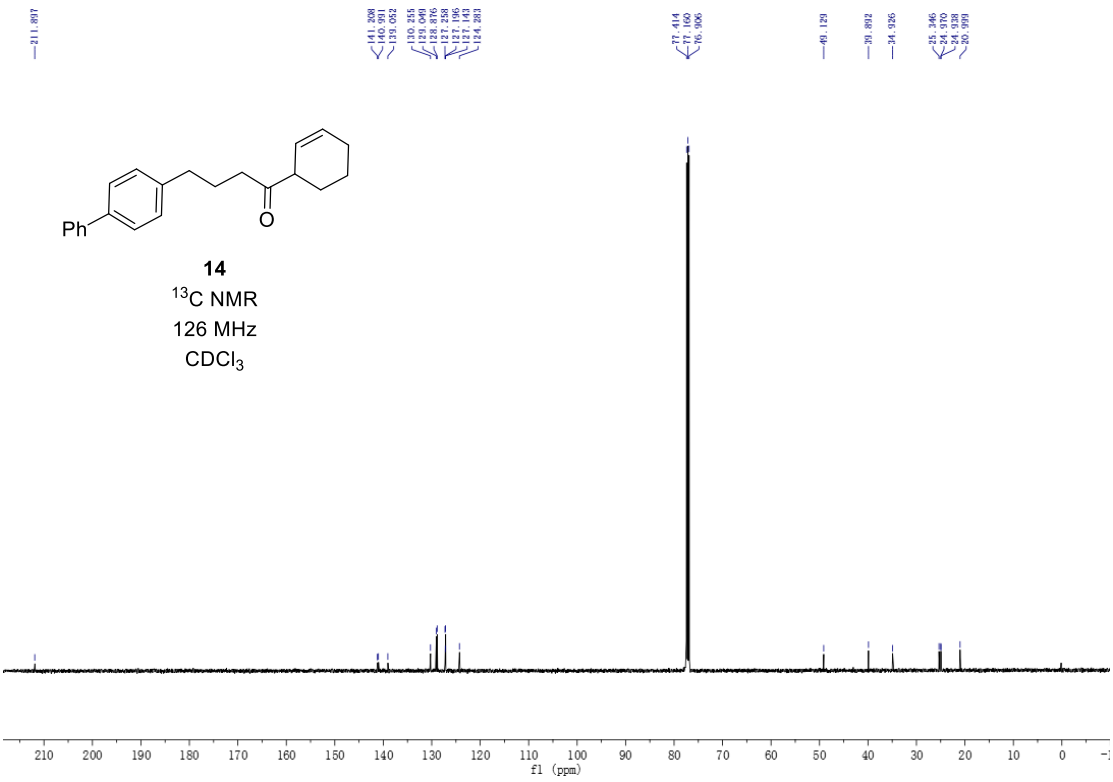

14

^{13}C NMR

126 MHz

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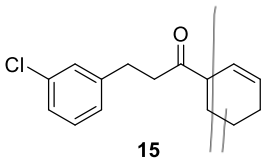

15

^{1}H NMR

300 MHz

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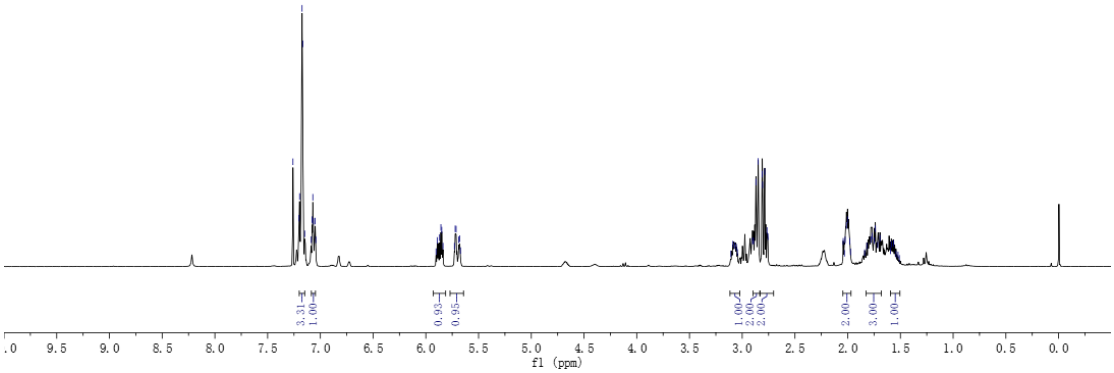

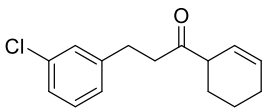

15

^{13}C NMR

126 MHz

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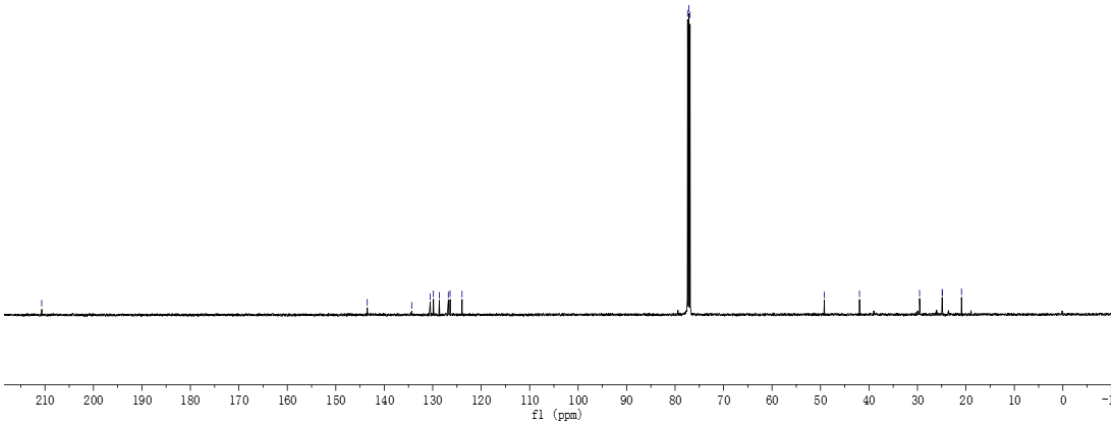
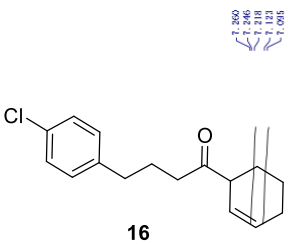


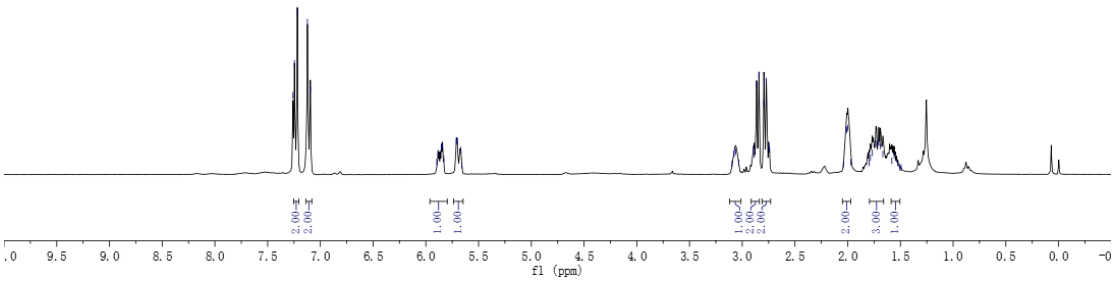


16

^{1}H NMR

300 MHz

$CDCl_3$

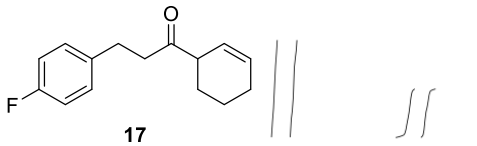


16

^{13}C NMR

126 MHz

$CDCl_3$

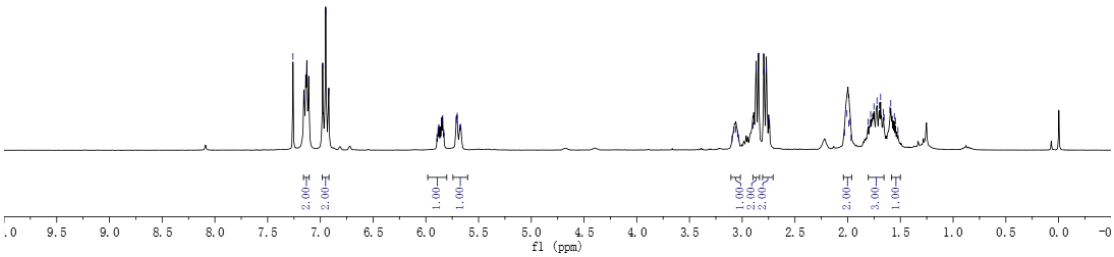


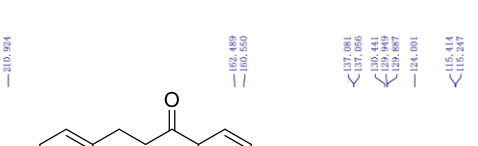
17

^{1}H NMR

300 MHz

$CDCl_3$



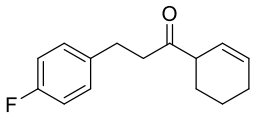


17

^{13}C NMR

126 MHz

$CDCl_3$

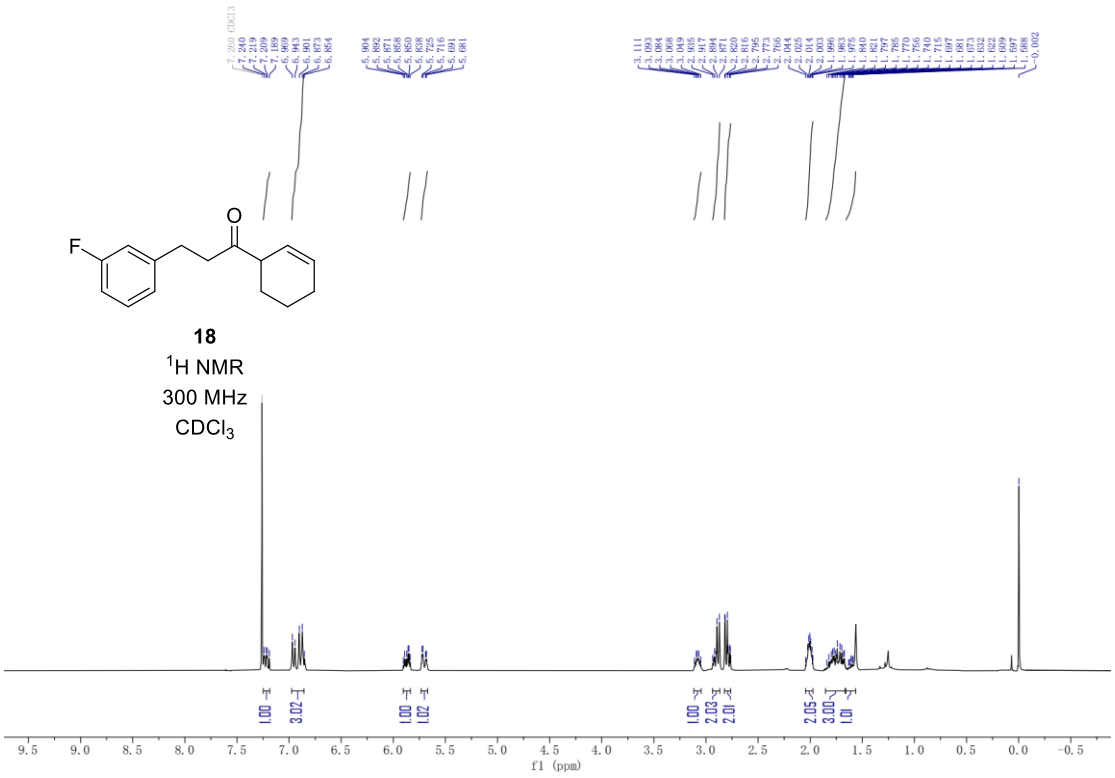


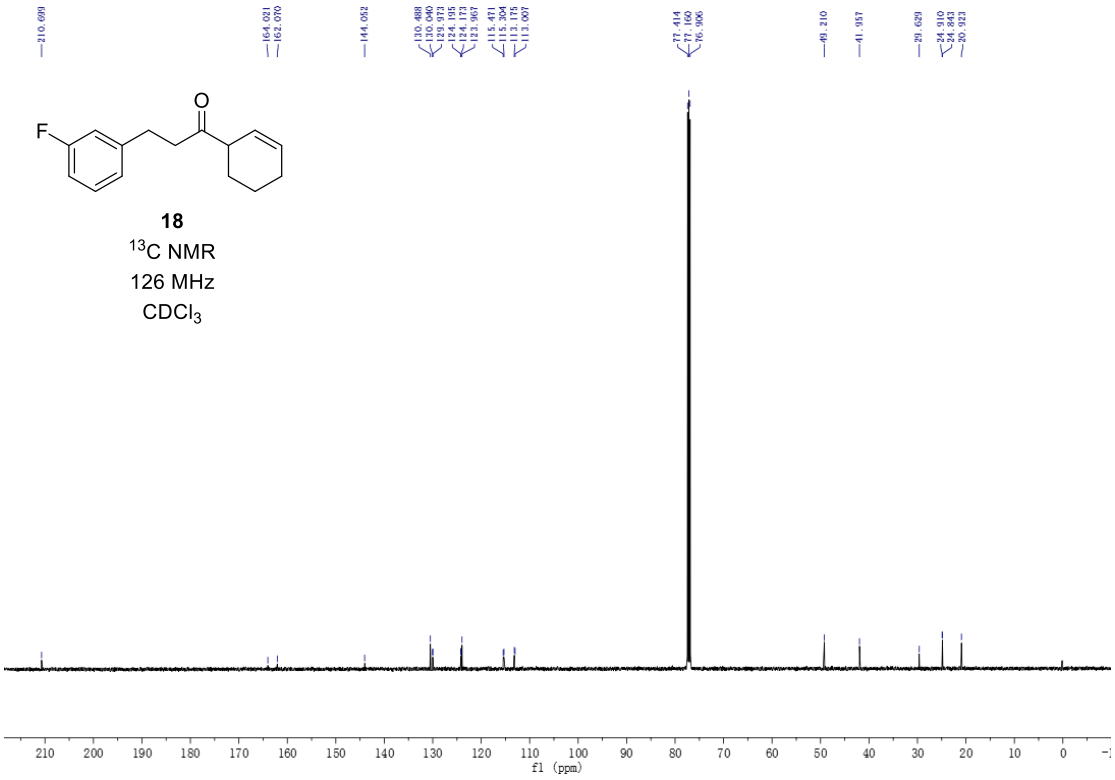
17

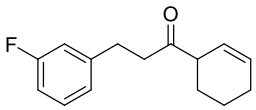
^{19}F NMR

471 MHz

$CDCl_3$


F
O
18
1H NMR
300 MHz
CDCl3
f1 (ppm)


F
O
18
13C NMR
126 MHz
CDCl3
f1 (ppm)

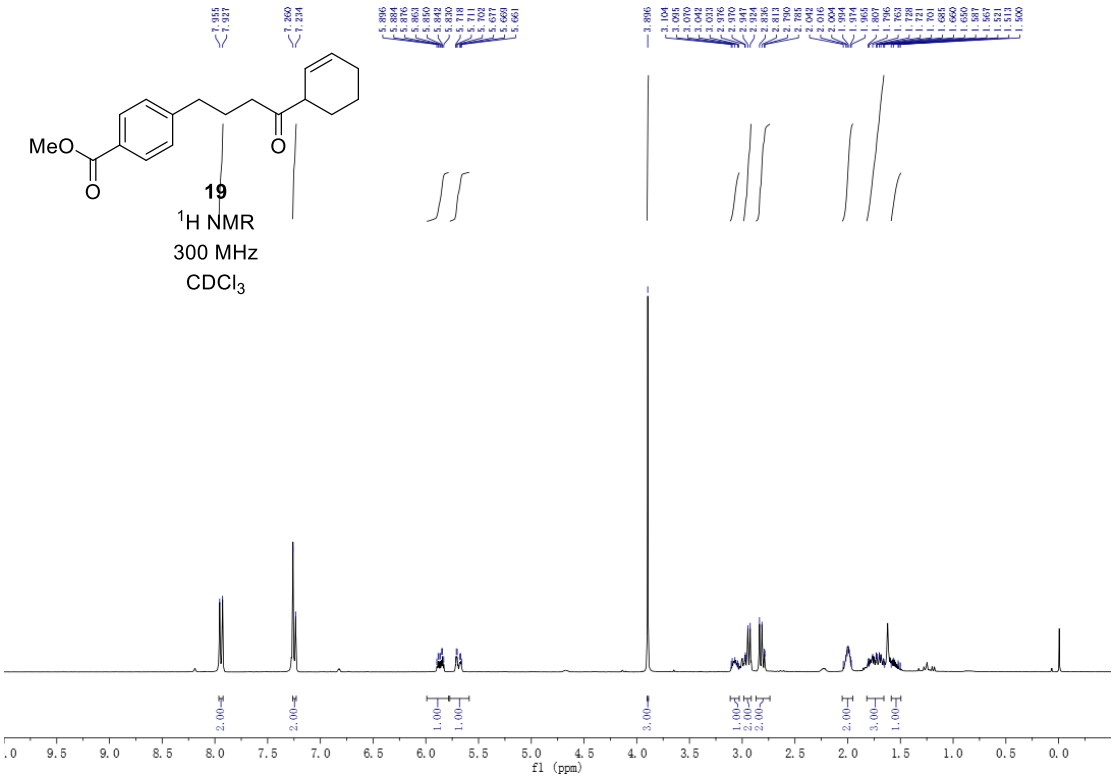


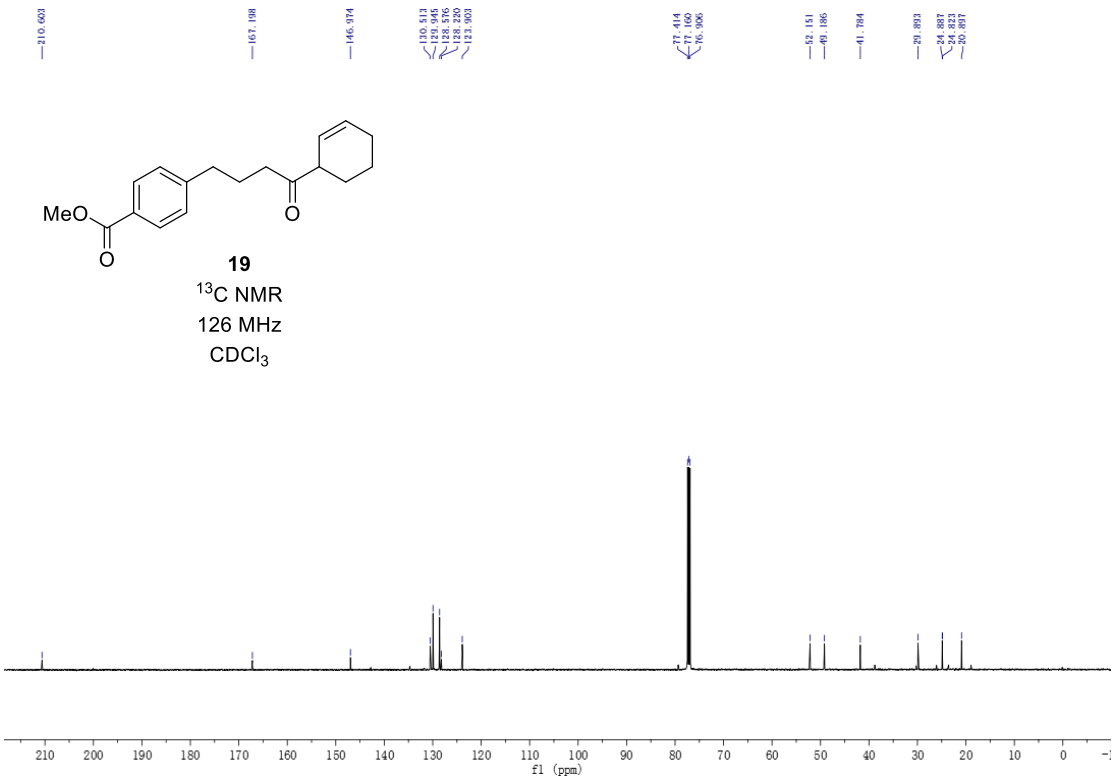
18

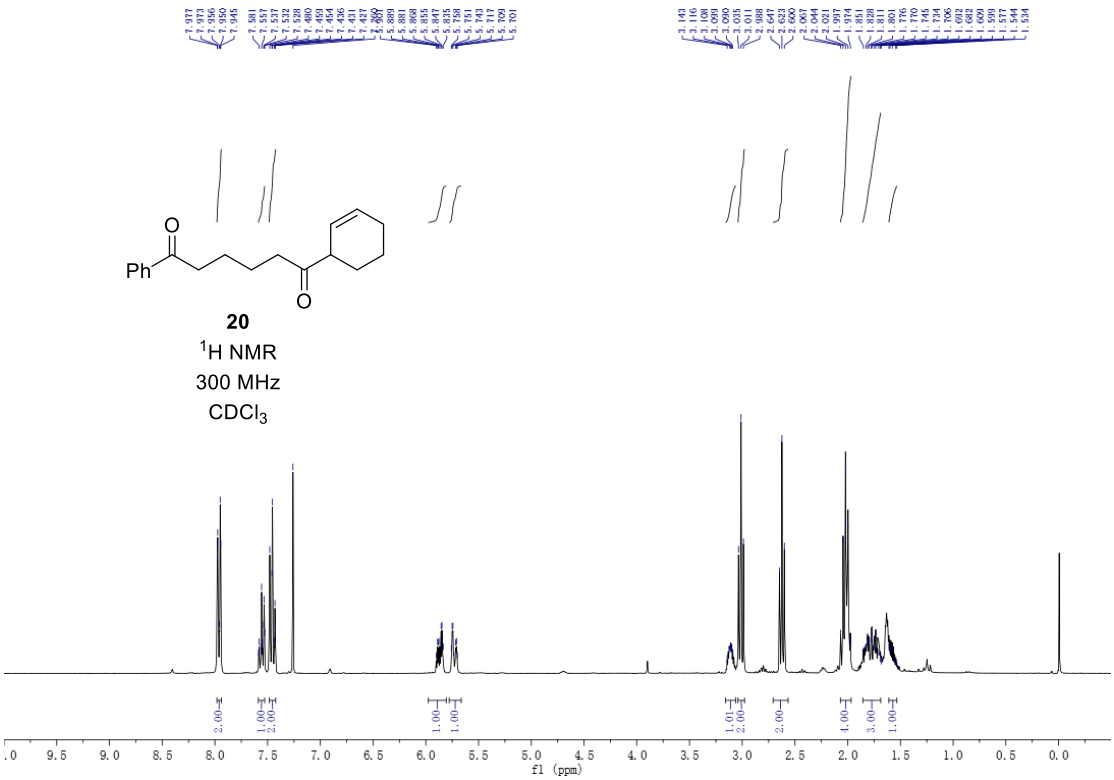
^{19}F NMR

471 MHz

$CDCl_3$


MeO
O
O
19
1H NMR
300 MHz
CDCl3
f1 (ppm)


MeO
O
O
19
13C NMR
126 MHz
CDCl3
f1 (ppm)

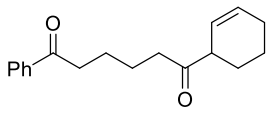


20

^{1}H NMR

300 MHz

$CDCl_3$

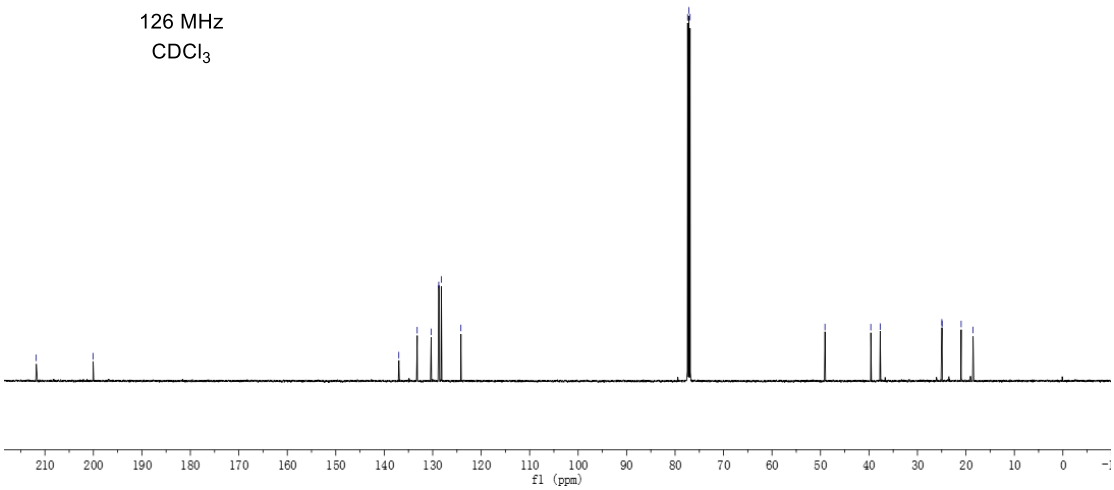


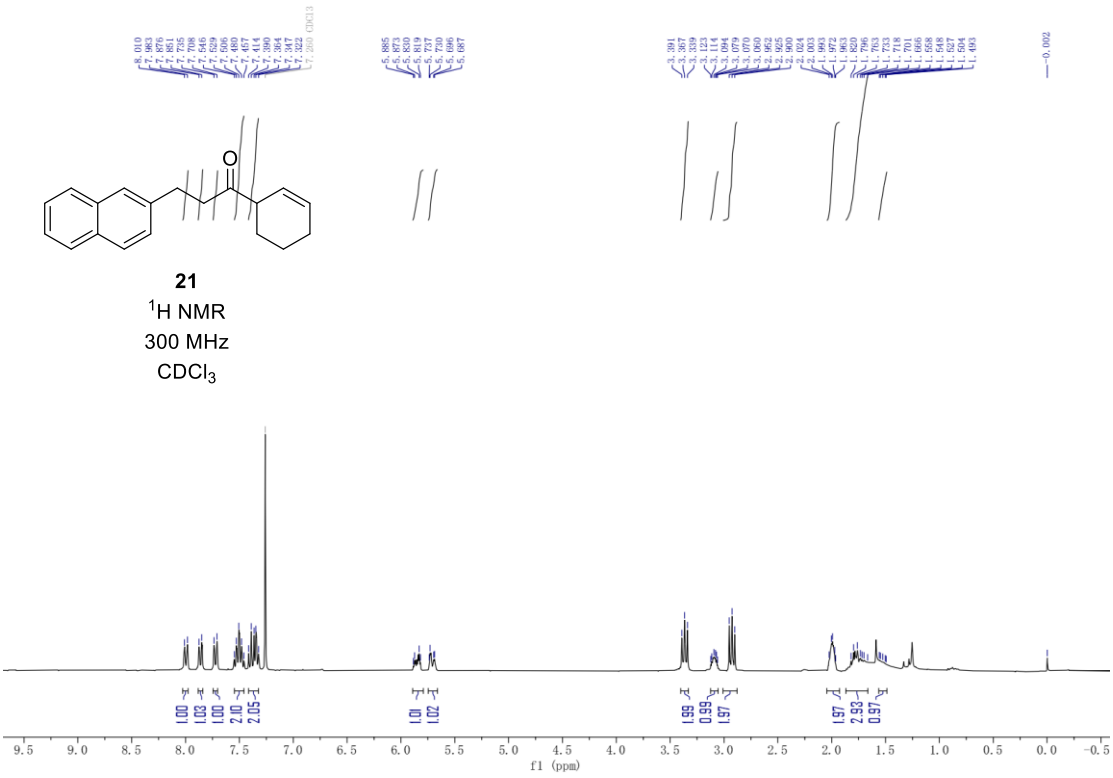
20

^{13}C NMR

126 MHz

$CDCl_3$



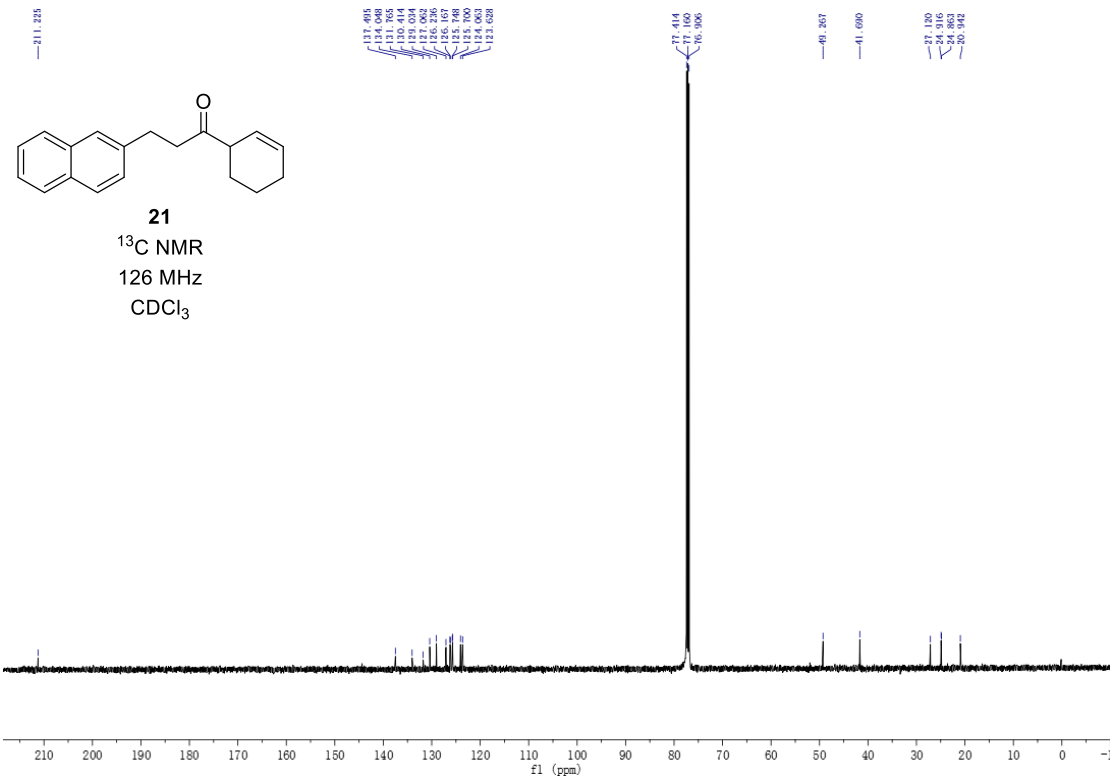


21

^{1}H NMR

300 MHz

$CDCl_3$

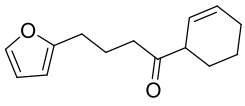


21

^{13}C NMR

126 MHz

$CDCl_3$

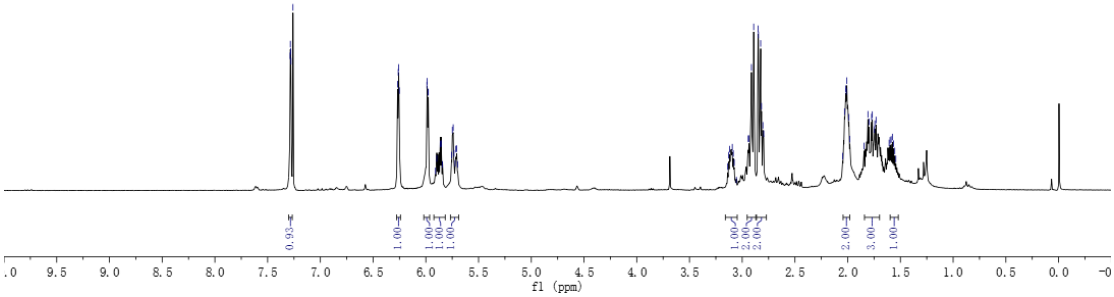


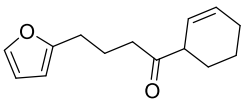
22

^{1}H NMR

300 MHz

$CDCl_3$



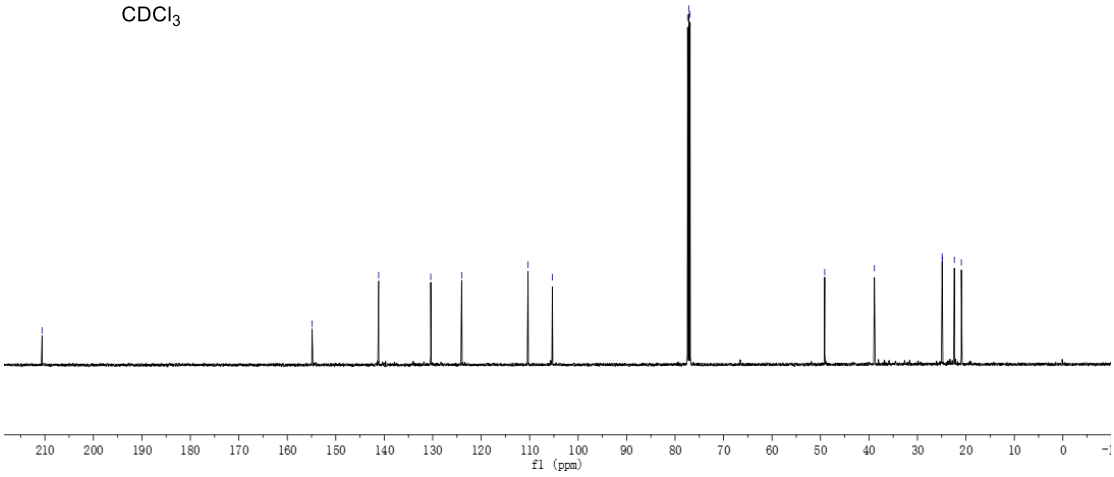


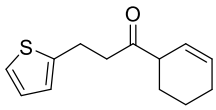
22

^{13}C NMR

126 MHz

$CDCl_3$



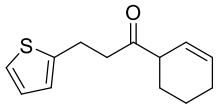


23

^{1}H NMR

300 MHz

$CDCl_3$

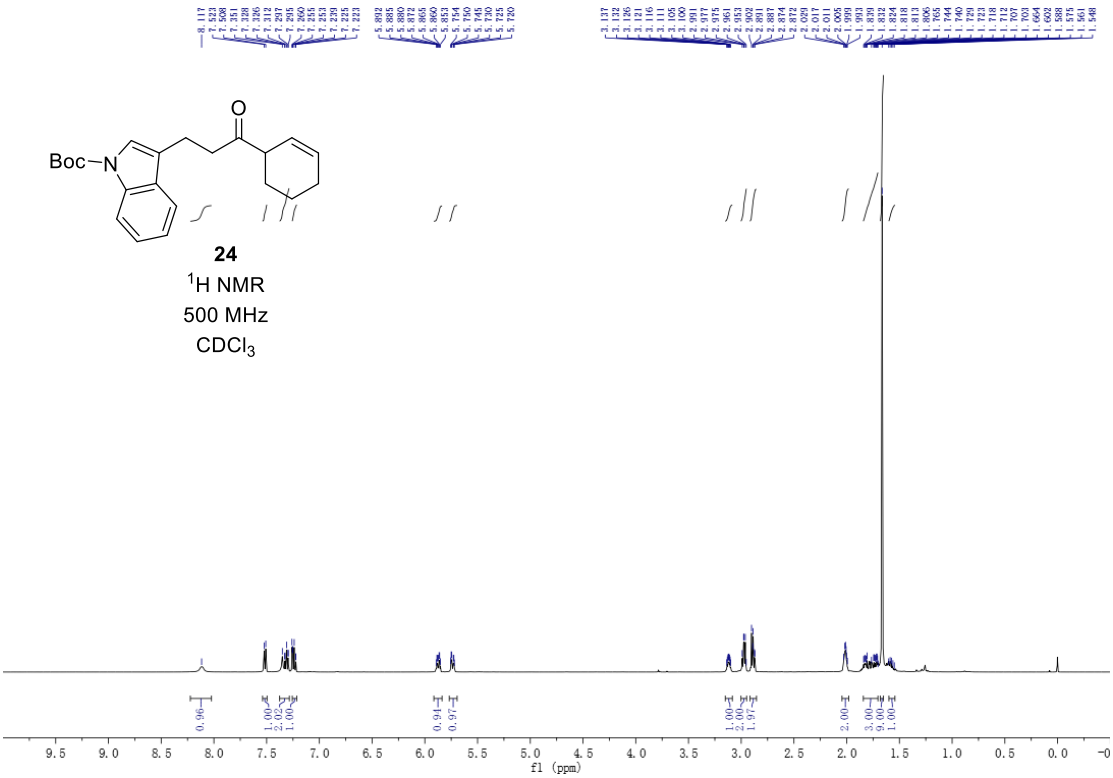


23

^{13}C NMR

126 MHz

$CDCl_3$

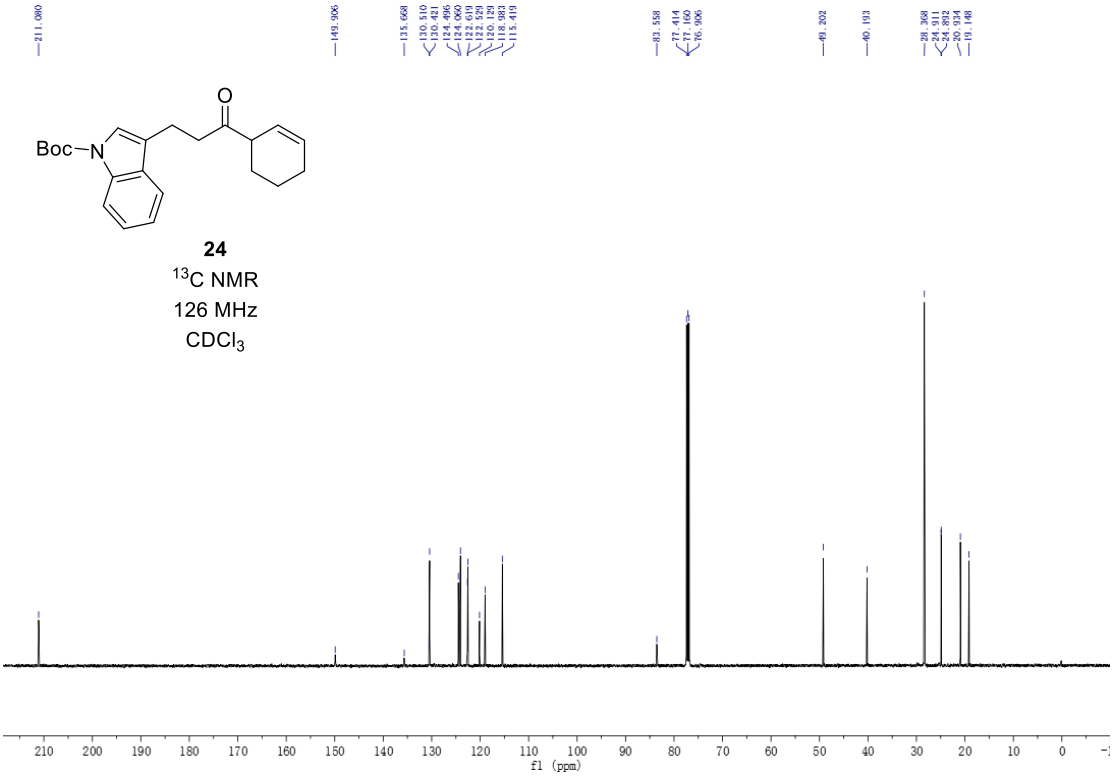


24

^{1}H NMR

500 MHz

$CDCl_3$

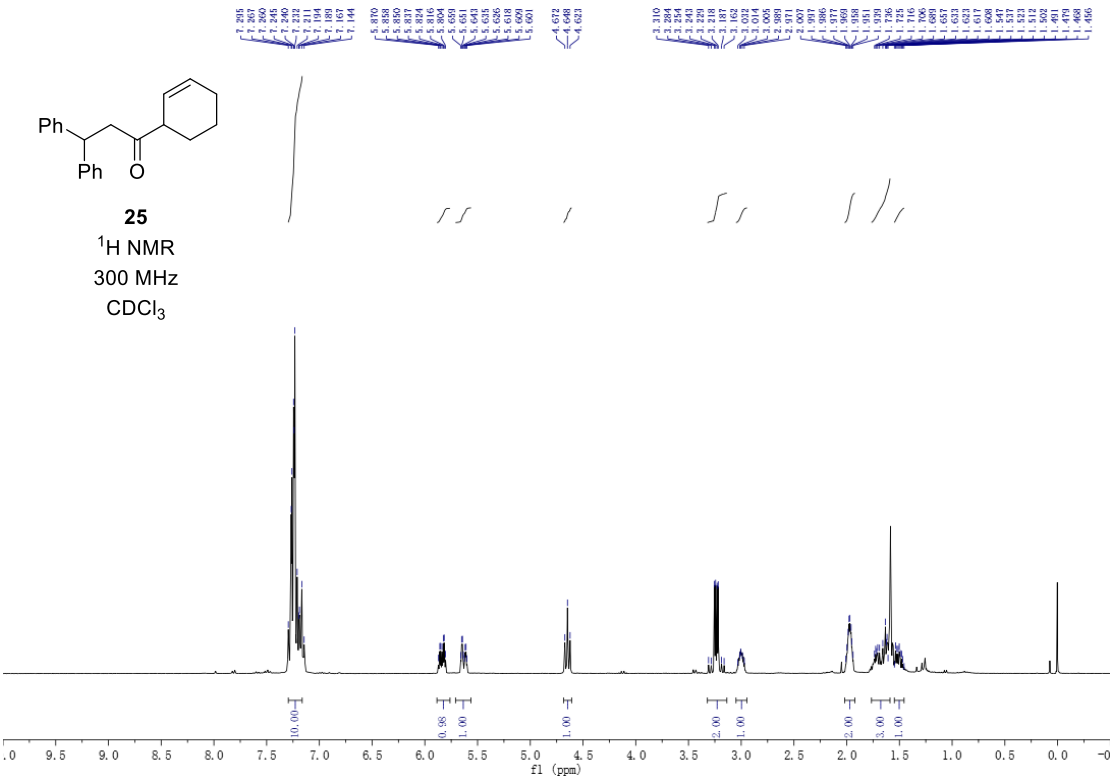


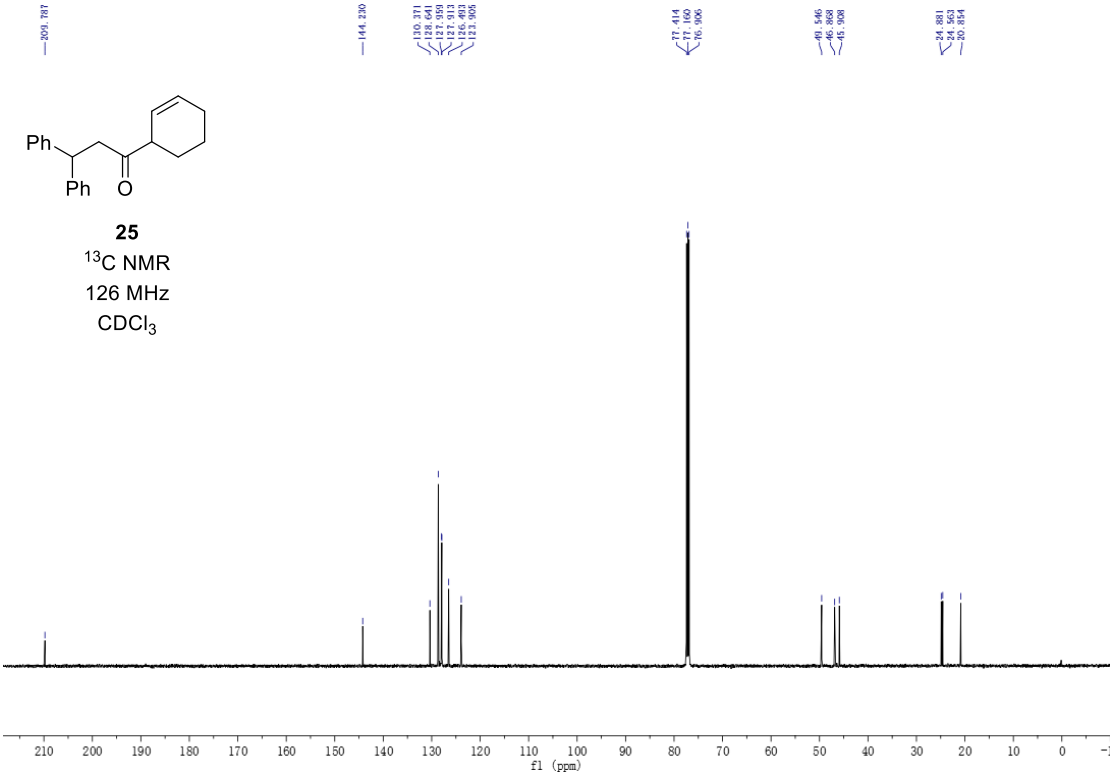
24

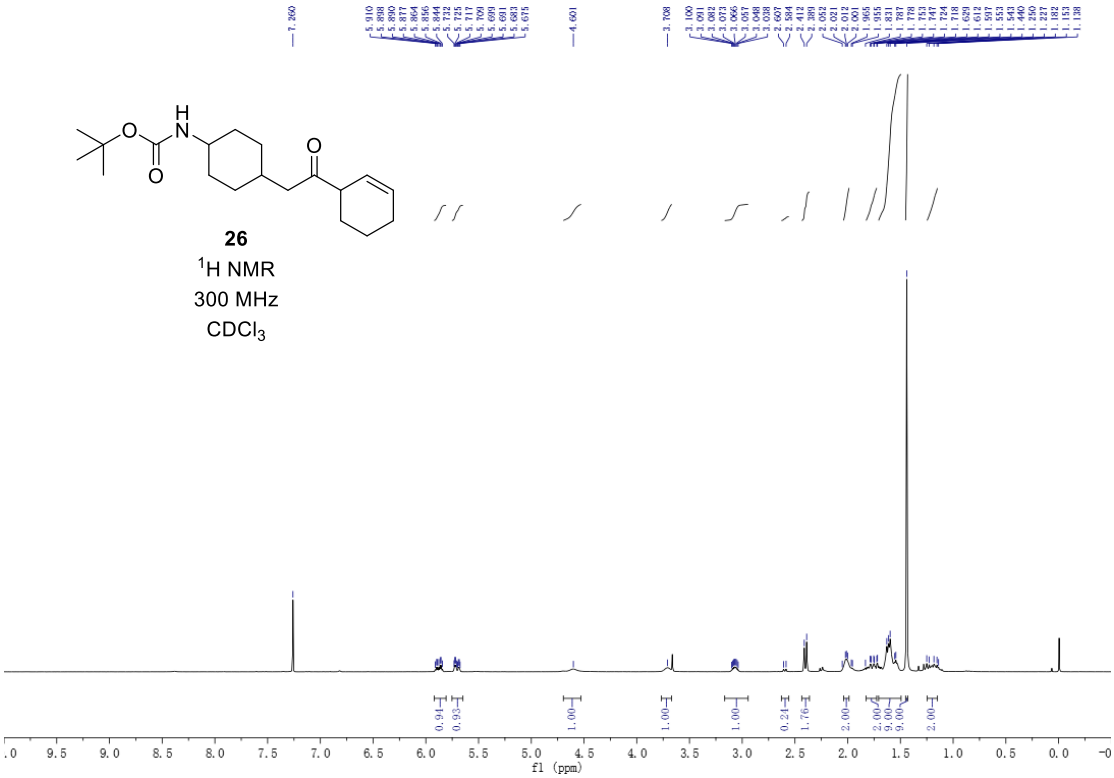
^{13}C NMR

126 MHz

$CDCl_3$


Ph
Ph
O
25
1H NMR
300 MHz
CDCl3
f1 (ppm)


Ph
Ph
O
25
13C NMR
126 MHz
CDCl3
f1 (ppm)

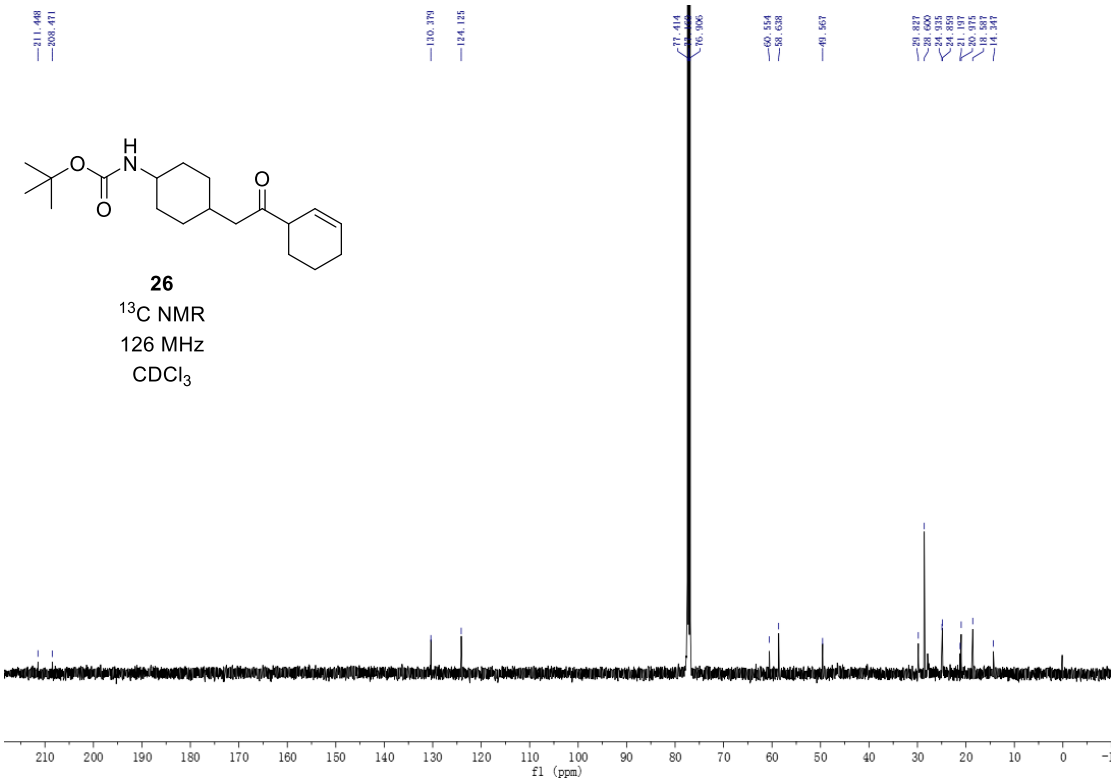


26

^{1}H NMR

300 MHz

$CDCl_3$

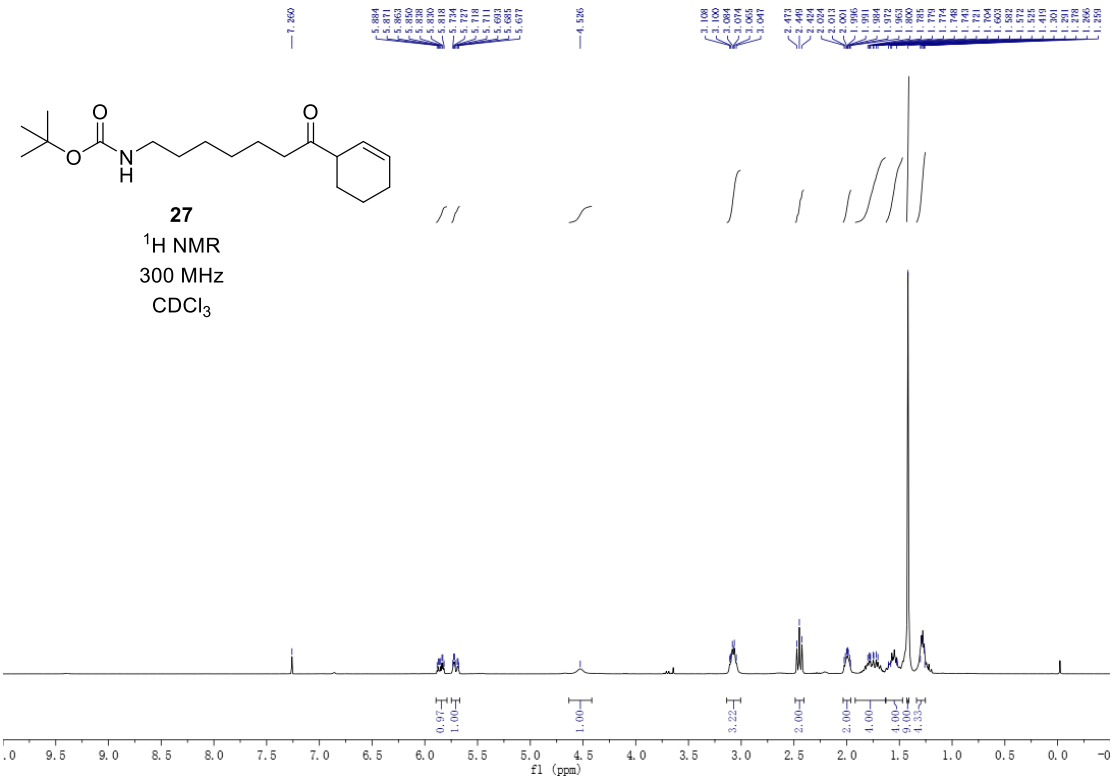


26

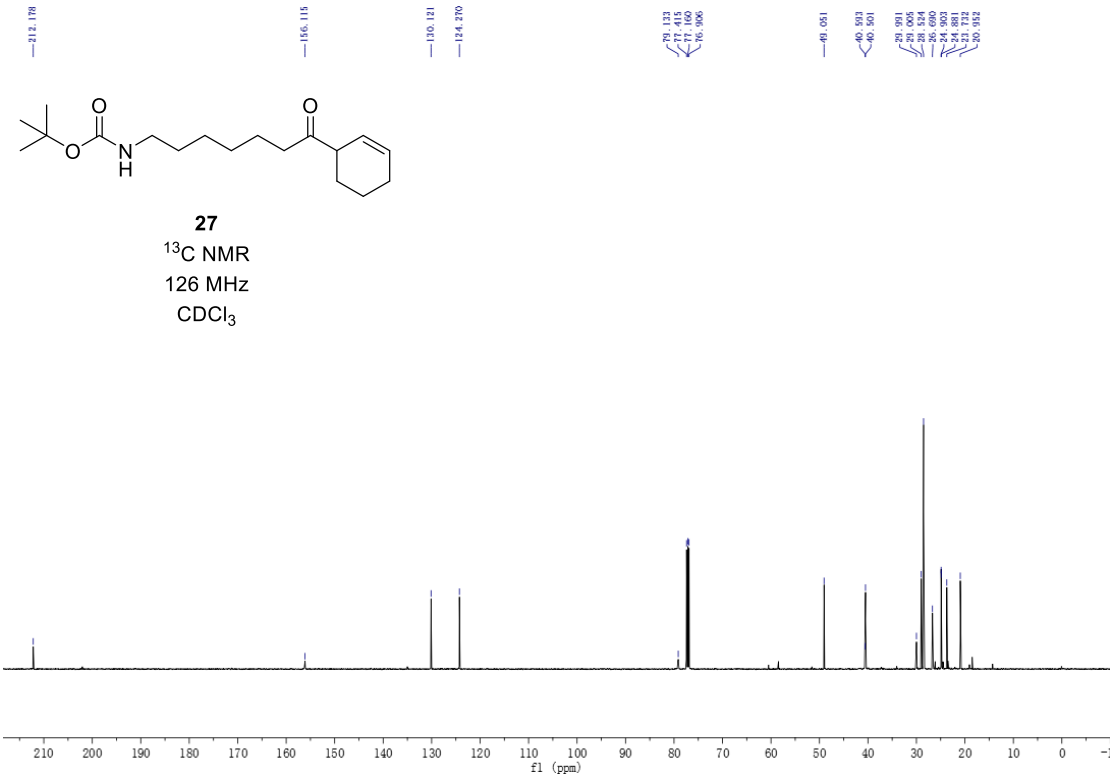
^{13}C NMR

126 MHz

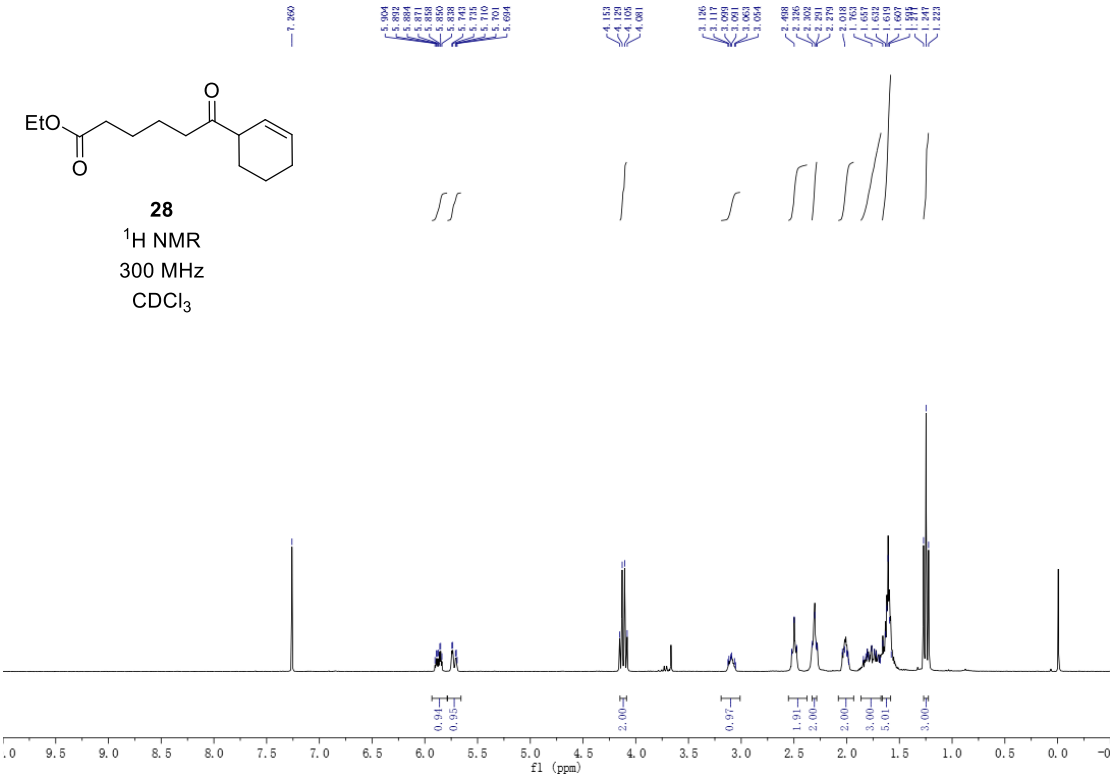
$CDCl_3$



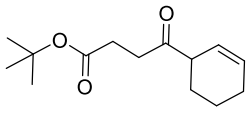
27
^{1}H NMR
300 MHz
$CDCl_3$



27
^{13}C NMR
126 MHz
$CDCl_3$


EtO
O
O
28
1H NMR
300 MHz
CDCl3
f1 (ppm)


EtO
O
O
28
13C NMR
126 MHz
CDCl3
f1 (ppm)

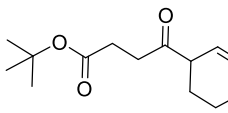


29

^{1}H NMR

300 MHz

$CDCl_3$

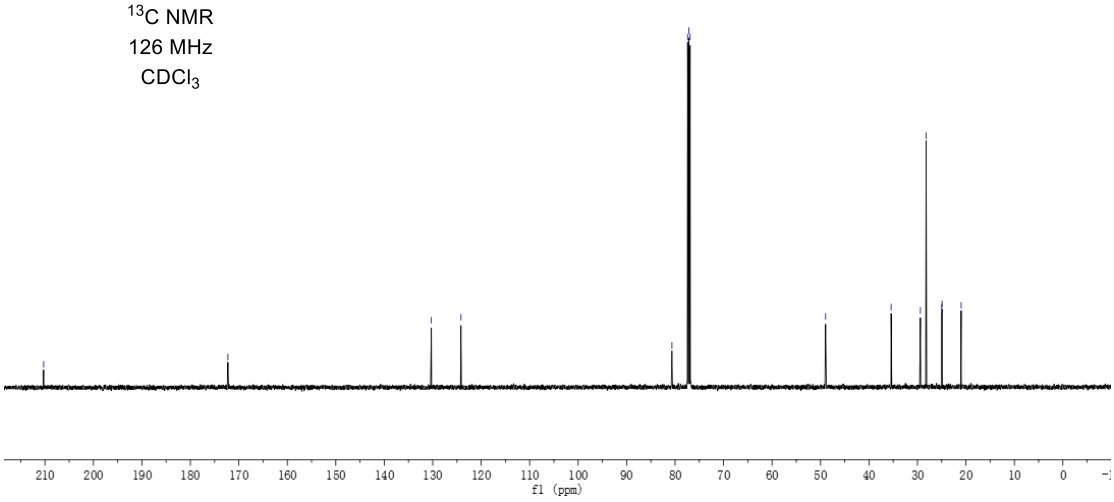


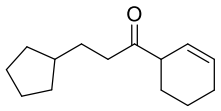
29

^{13}C NMR

126 MHz

$CDCl_3$



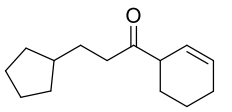


30

^{1}H NMR

300 MHz

$CDCl_3$

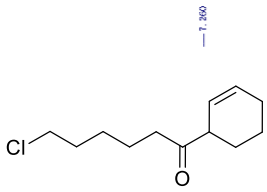


30

^{13}C NMR

126 MHz

$CDCl_3$

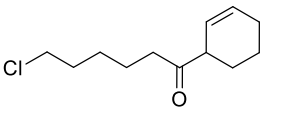


31

^{1}H NMR

300 MHz

$CDCl_3$

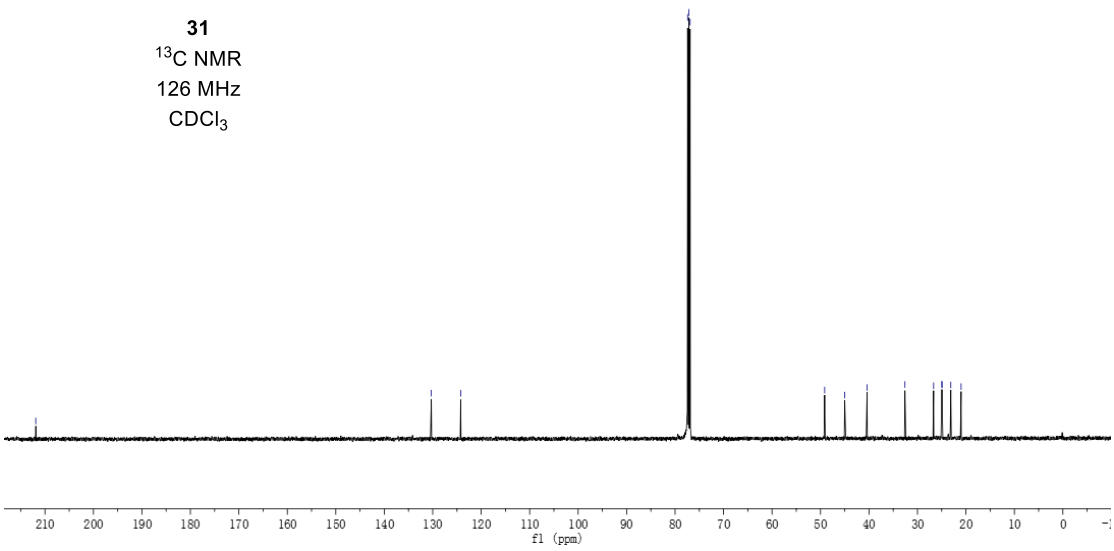


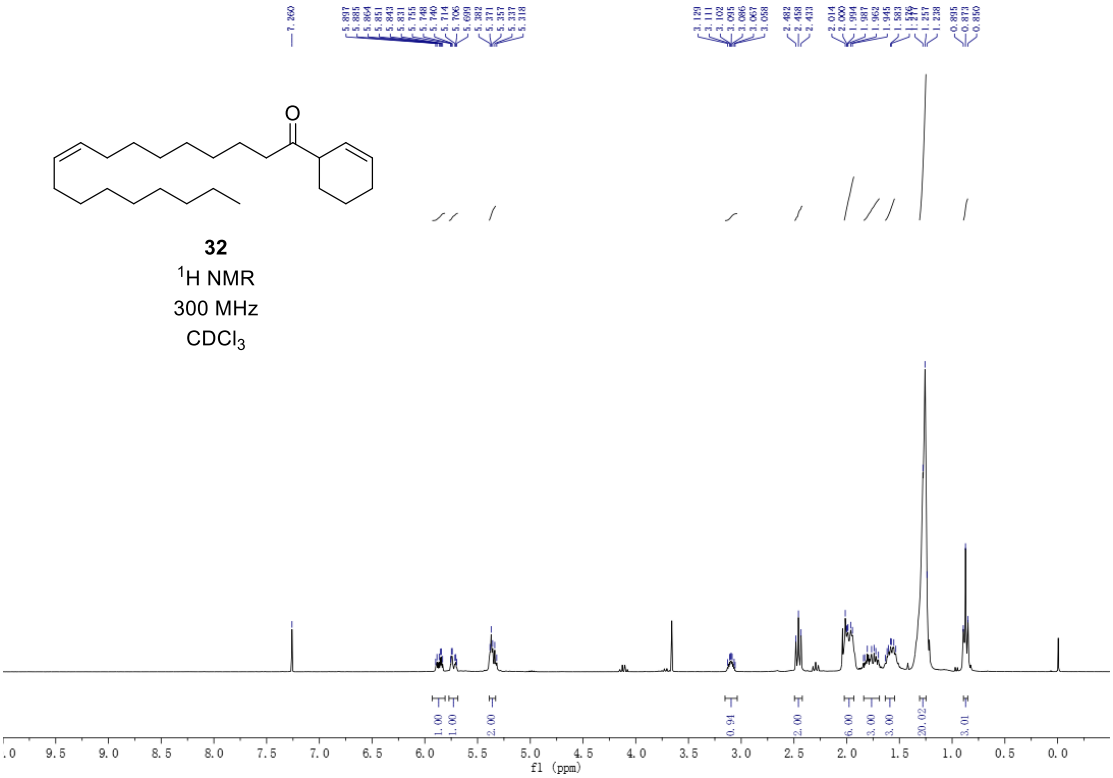
31

^{13}C NMR

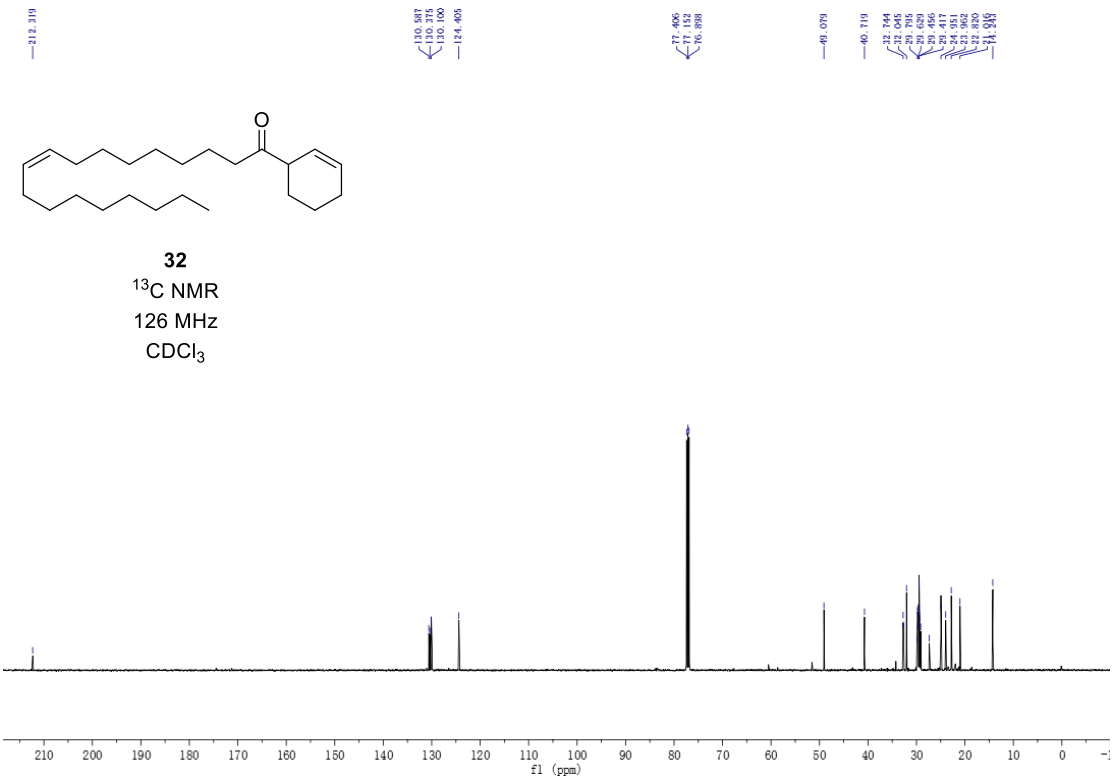
126 MHz

$CDCl_3$

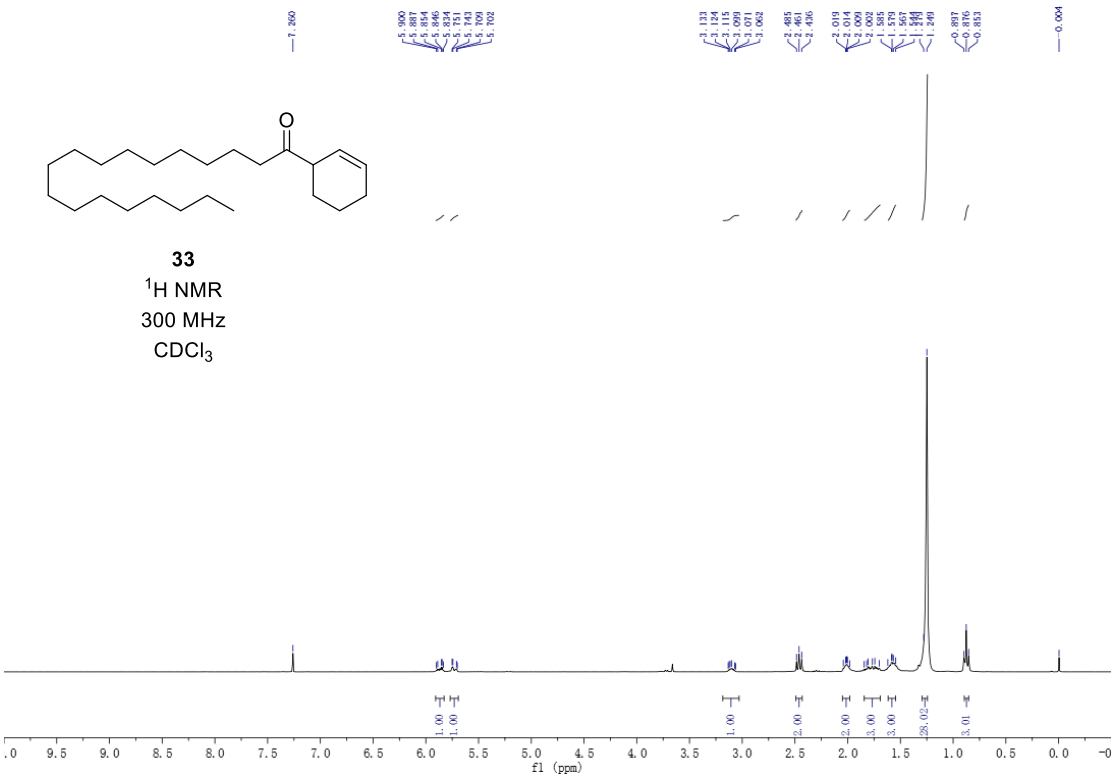




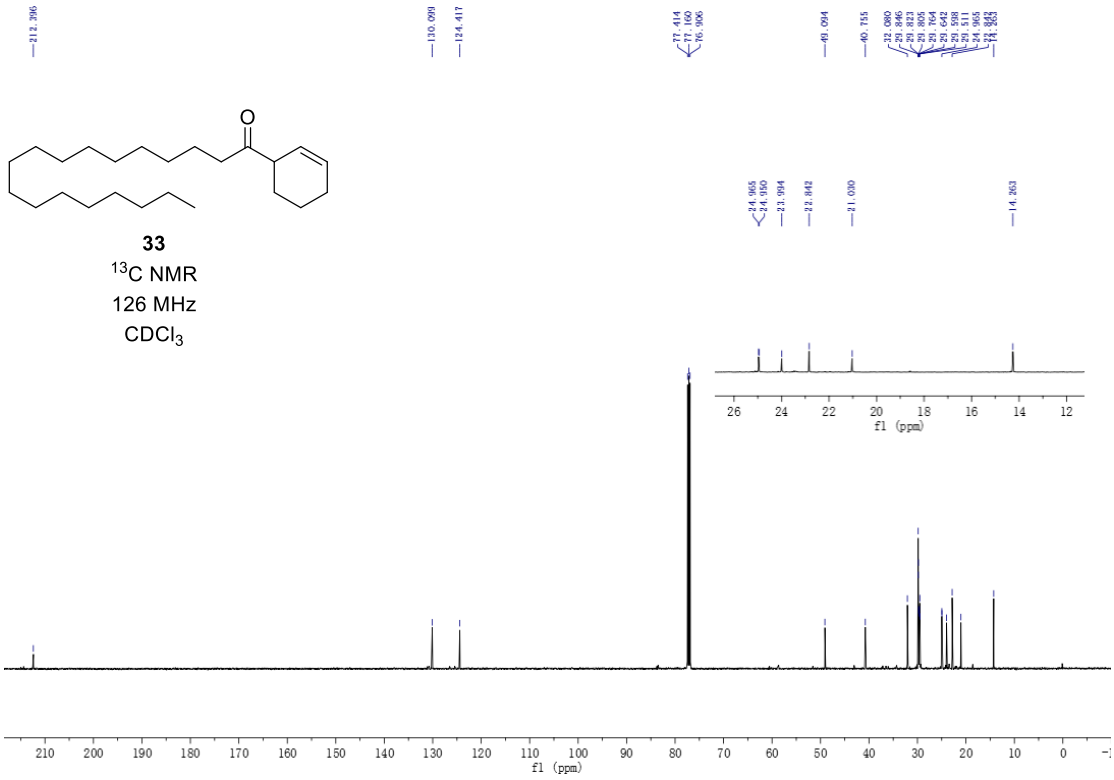
32
^{1}H NMR
300 MHz
$CDCl_3$



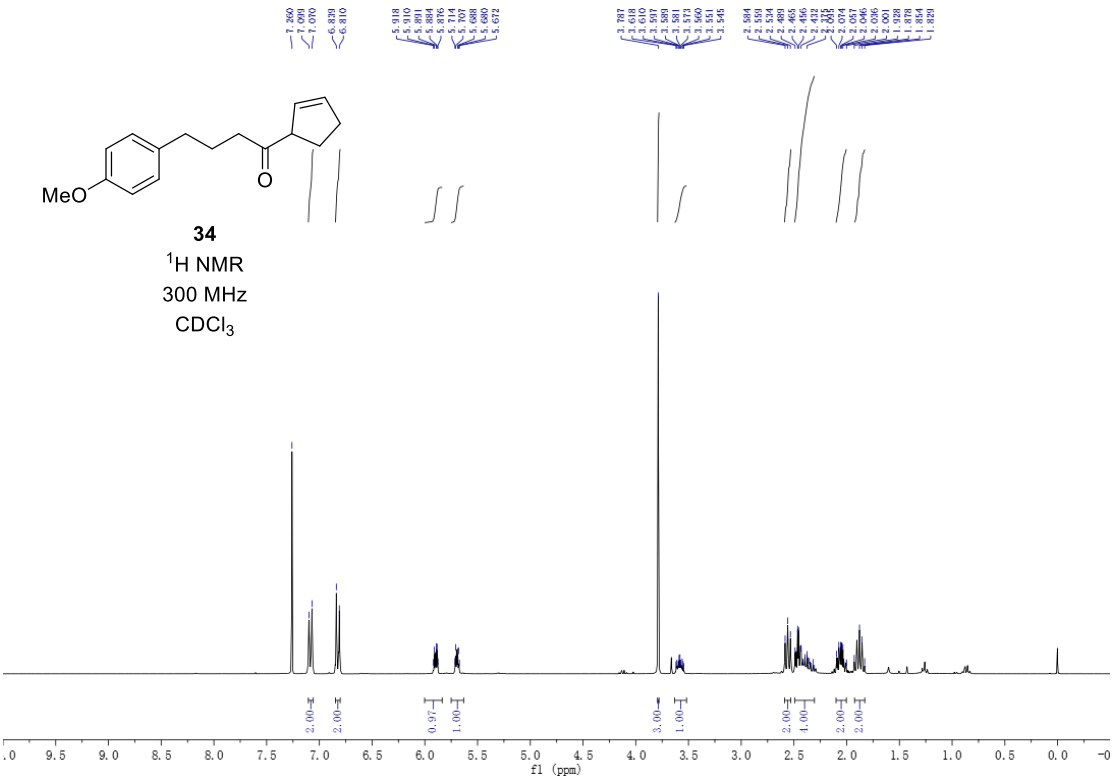
32
^{13}C NMR
126 MHz
$CDCl_3$



33
^{1}H NMR
300 MHz
$CDCl_3$



33
^{13}C NMR
126 MHz
$CDCl_3$

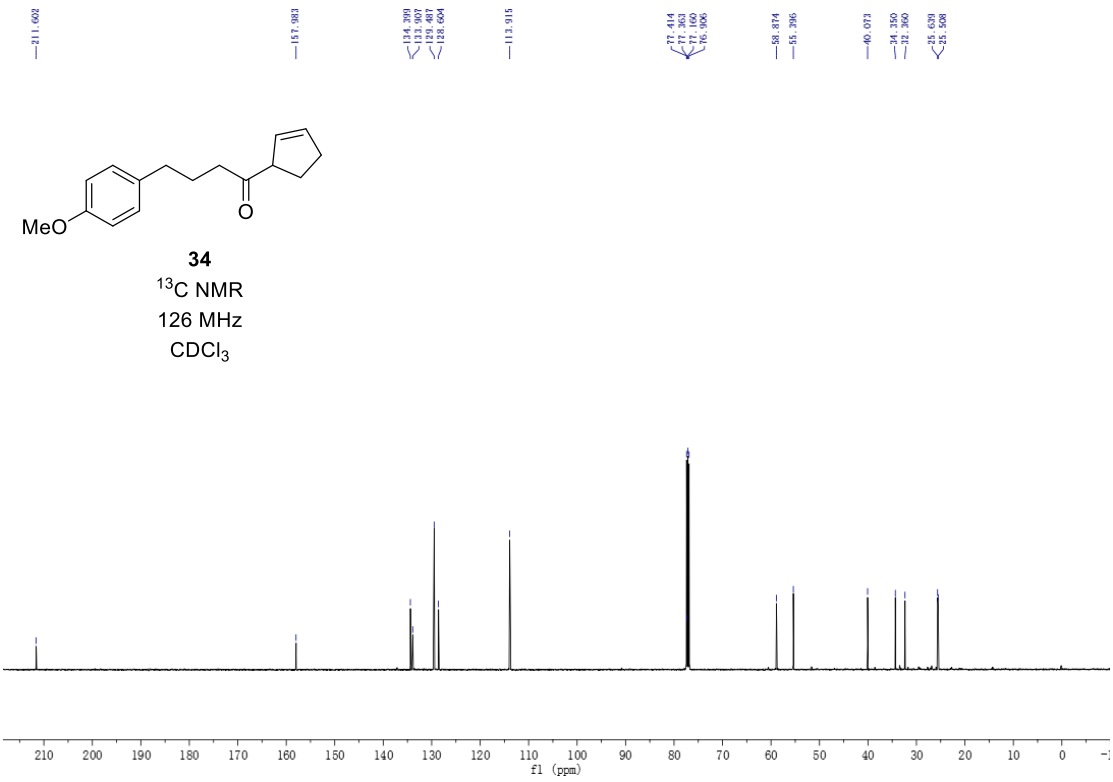


34

^{1}H NMR

300 MHz

$CDCl_3$

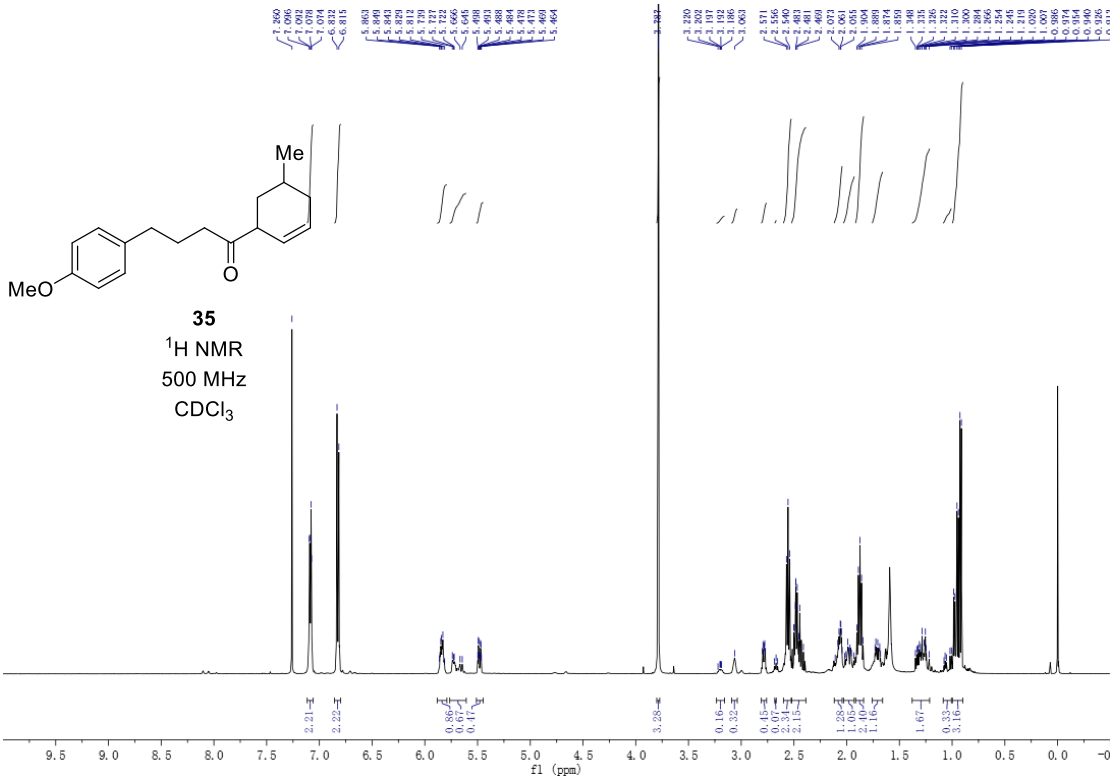


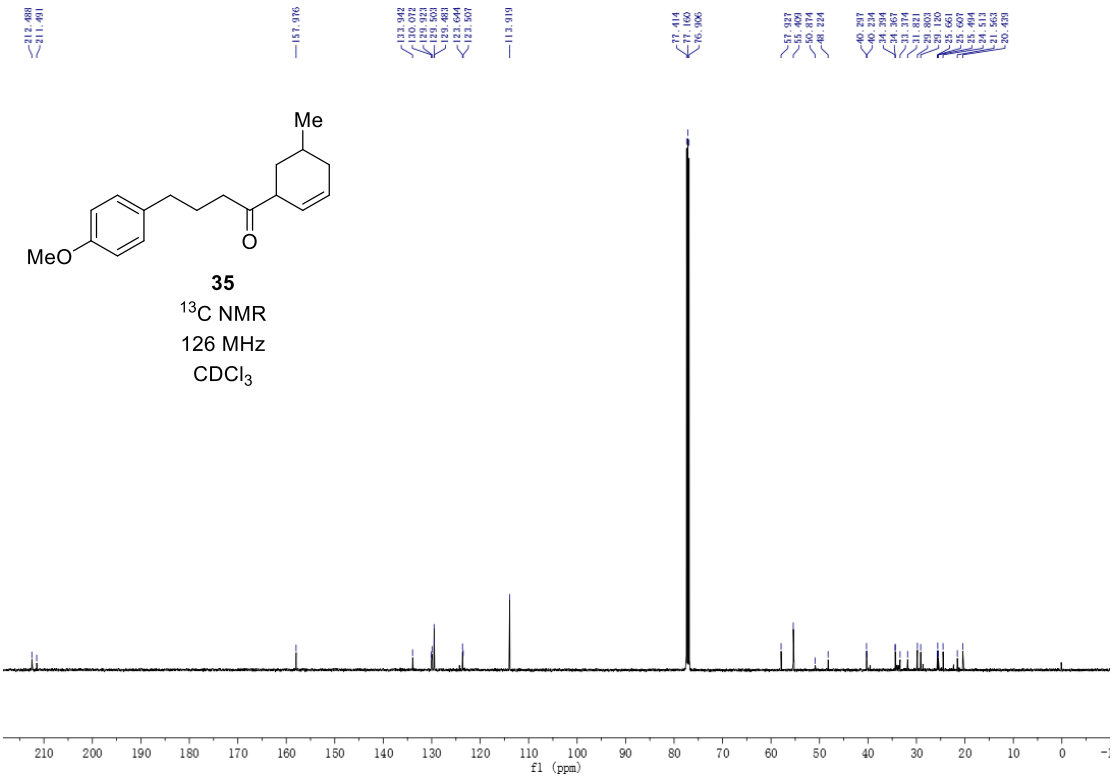
34

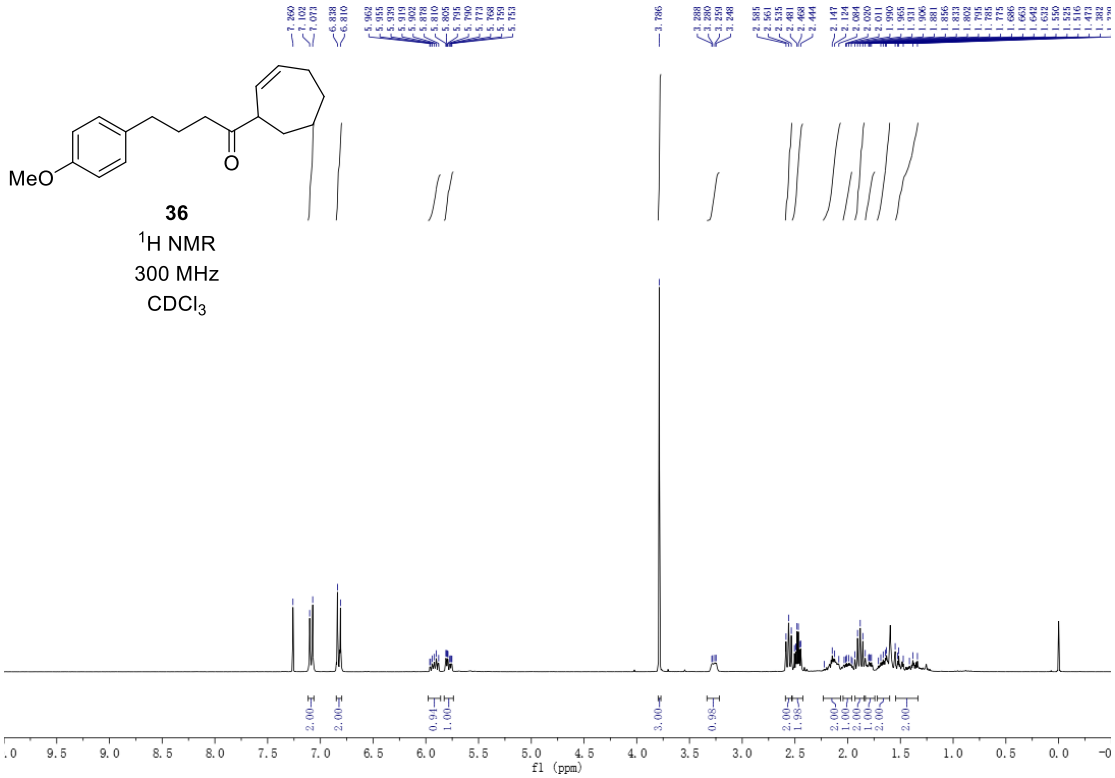
^{13}C NMR

126 MHz

$CDCl_3$


Me
MeO
O
35
1H NMR
500 MHz
CDCl3
f1 (ppm)


Me
MeO
O
35
13C NMR
126 MHz
CDCl3
f1 (ppm)

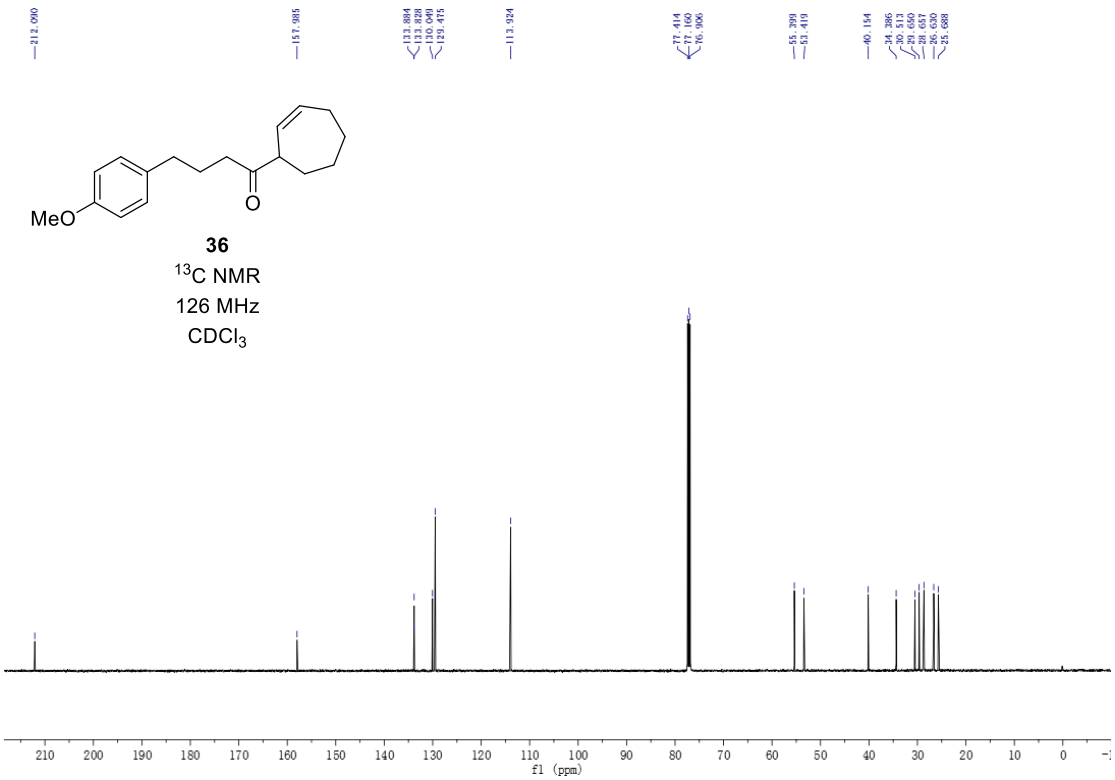


36

^{1}H NMR

300 MHz

$CDCl_3$

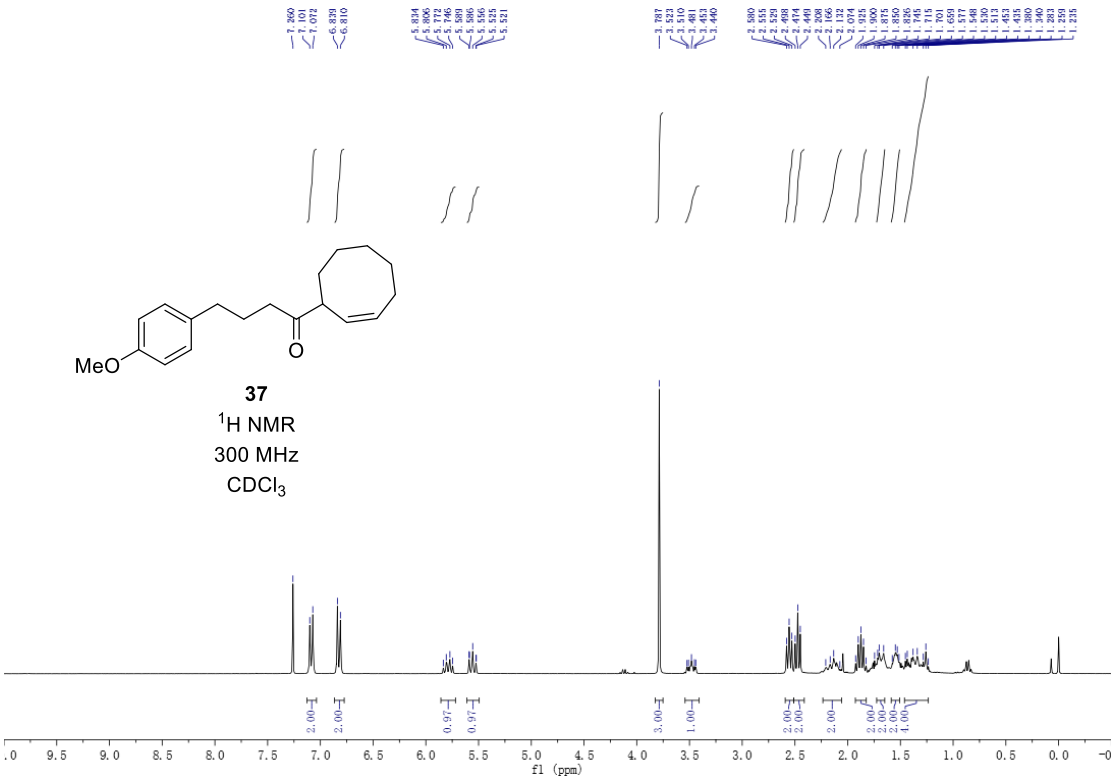


36

^{13}C NMR

126 MHz

$CDCl_3$

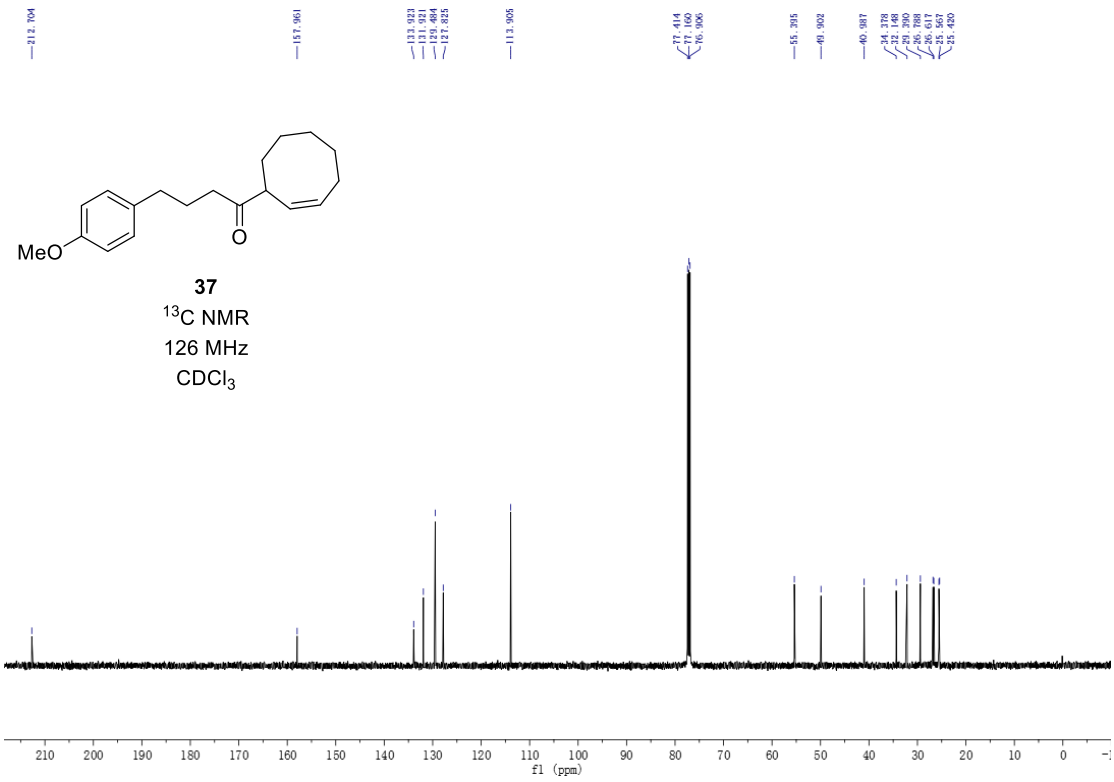


37

^{1}H NMR

300 MHz

$CDCl_3$

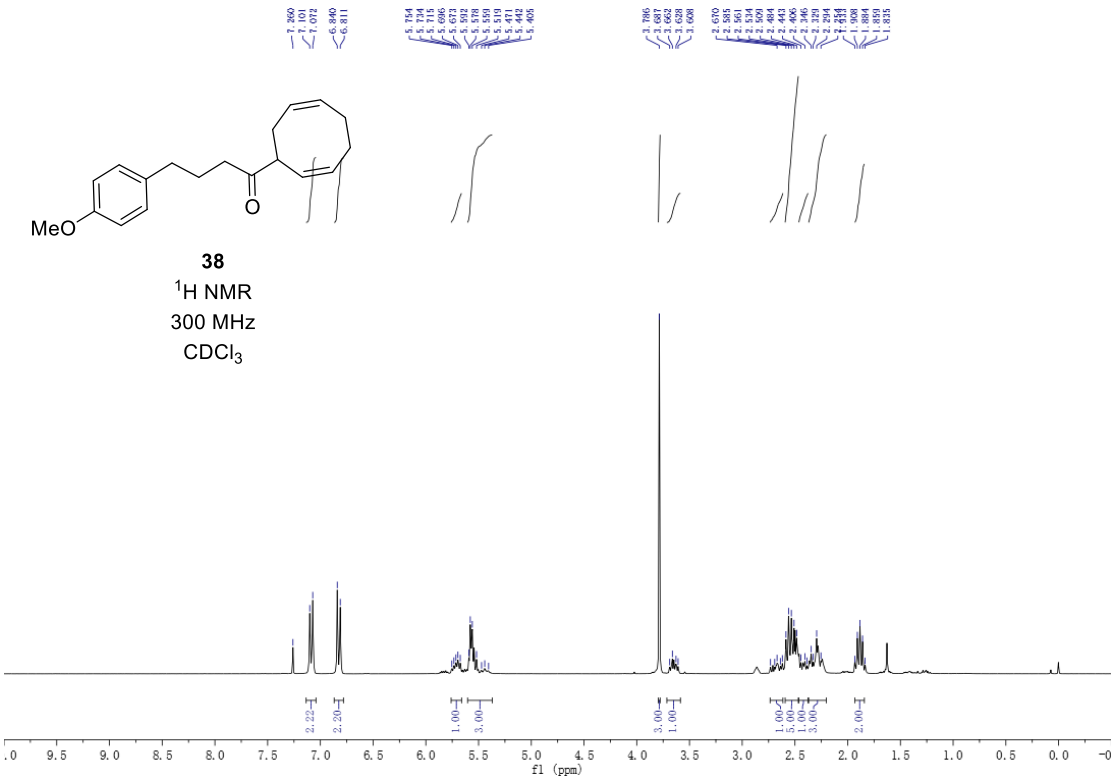


37

^{13}C NMR

126 MHz

$CDCl_3$

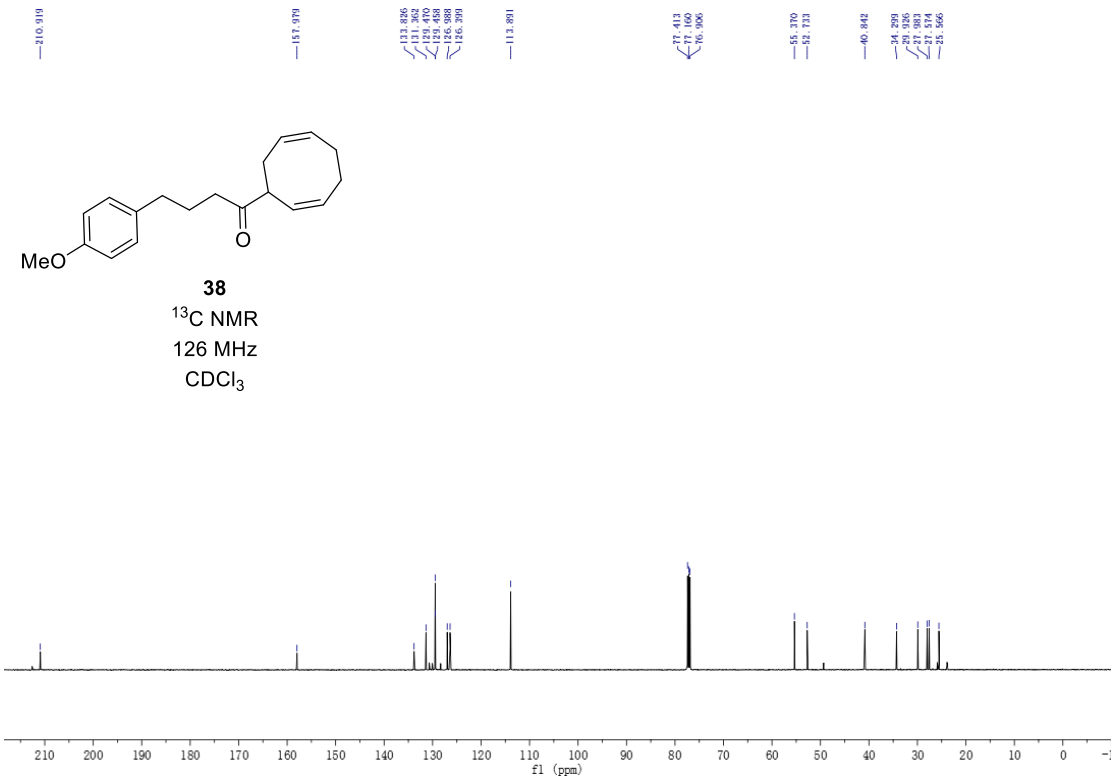


38

^{1}H NMR

300 MHz

$CDCl_3$

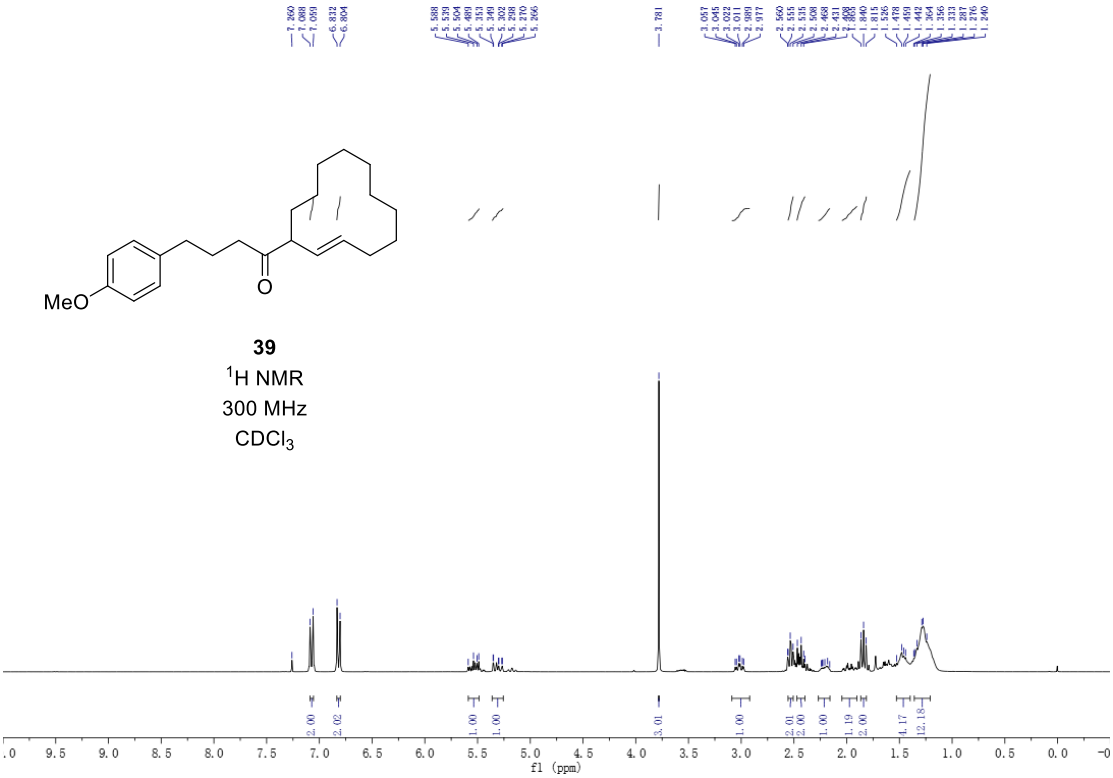


38

^{13}C NMR

126 MHz

$CDCl_3$

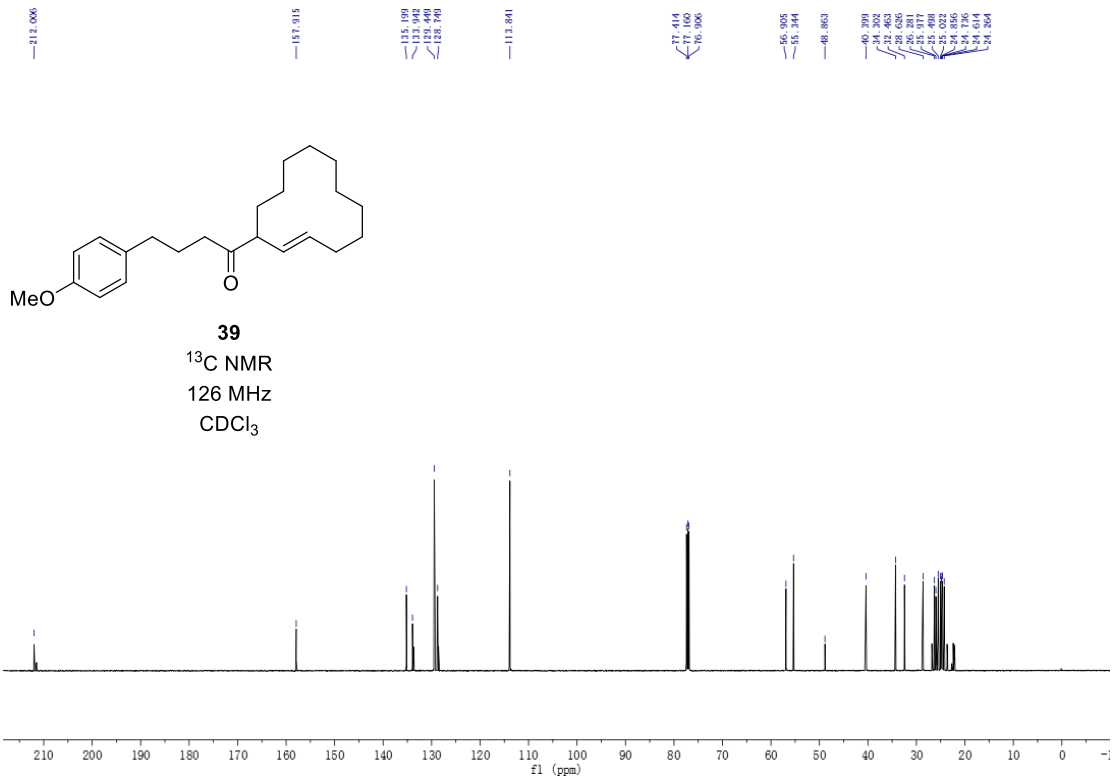


39

^{1}H NMR

300 MHz

$CDCl_3$

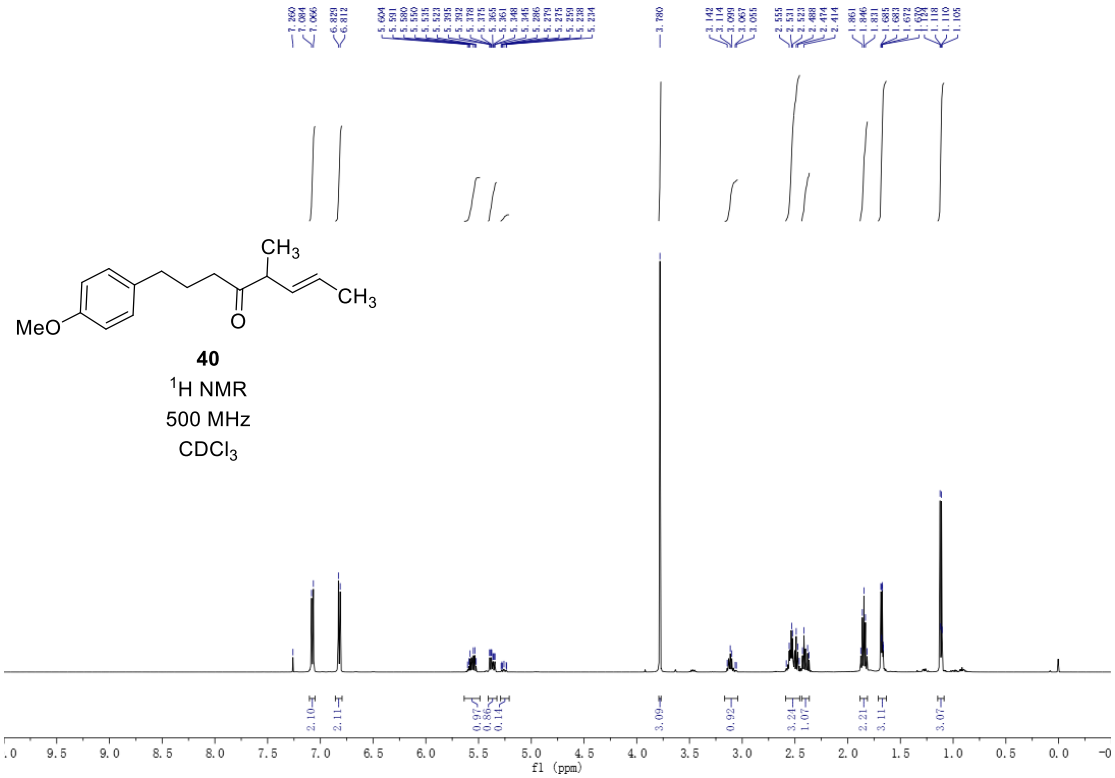


39

^{13}C NMR

126 MHz

$CDCl_3$

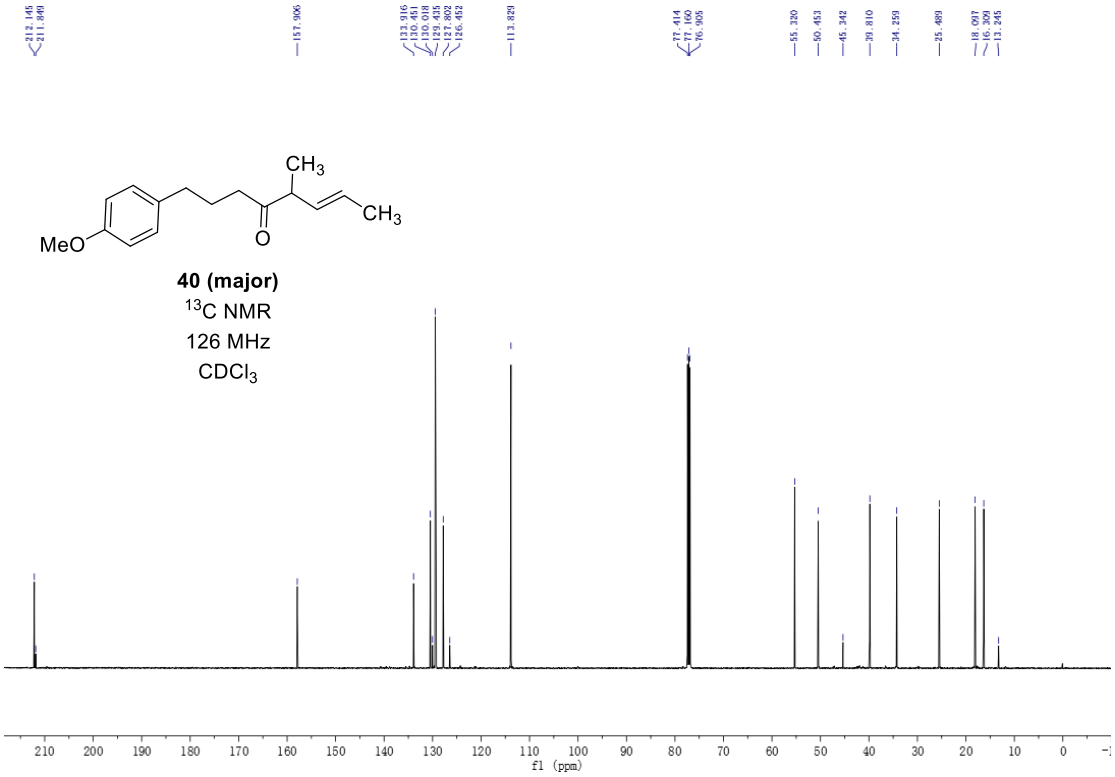


40

^{1}H NMR

500 MHz

$CDCl_3$

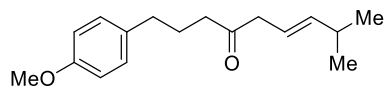


40 (major)

^{13}C NMR

126 MHz

$CDCl_3$

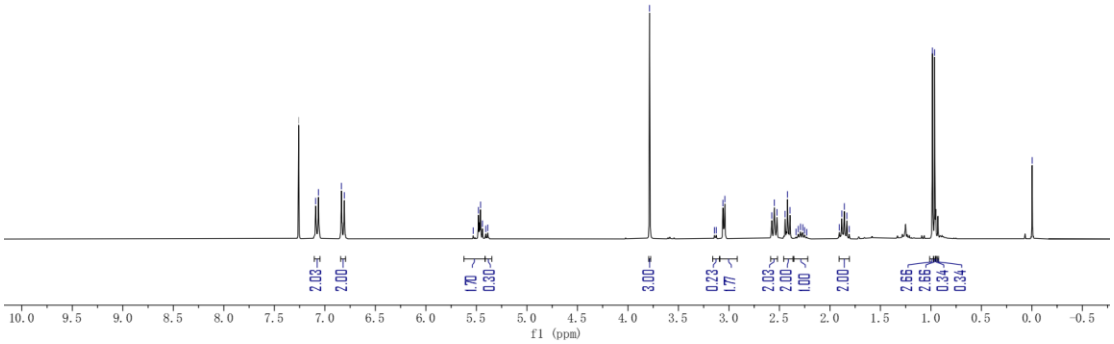


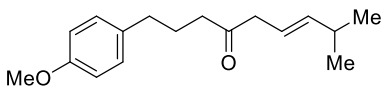
41

^{1}H NMR

300 MHz

$CDCl_3$



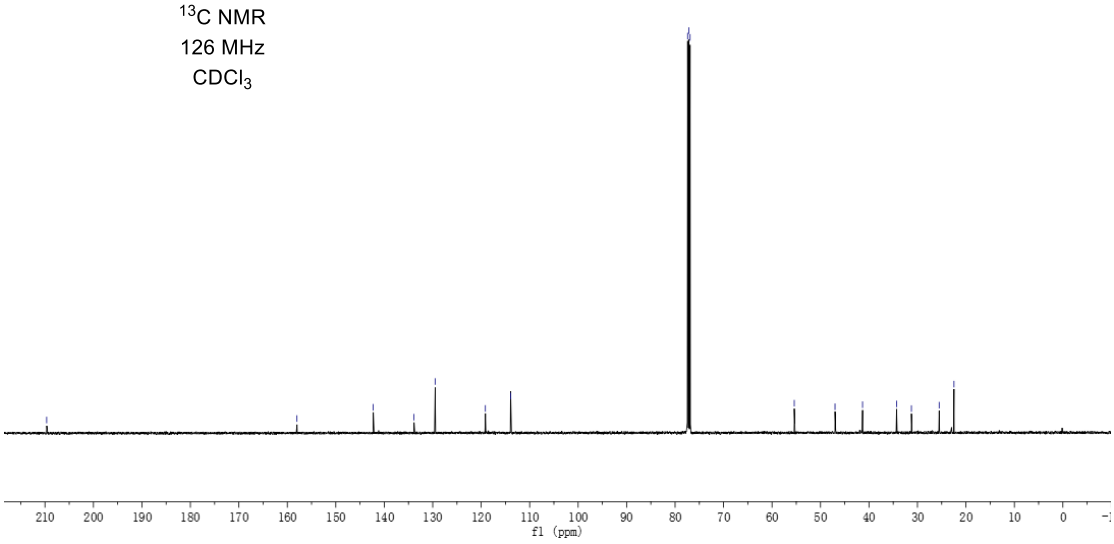


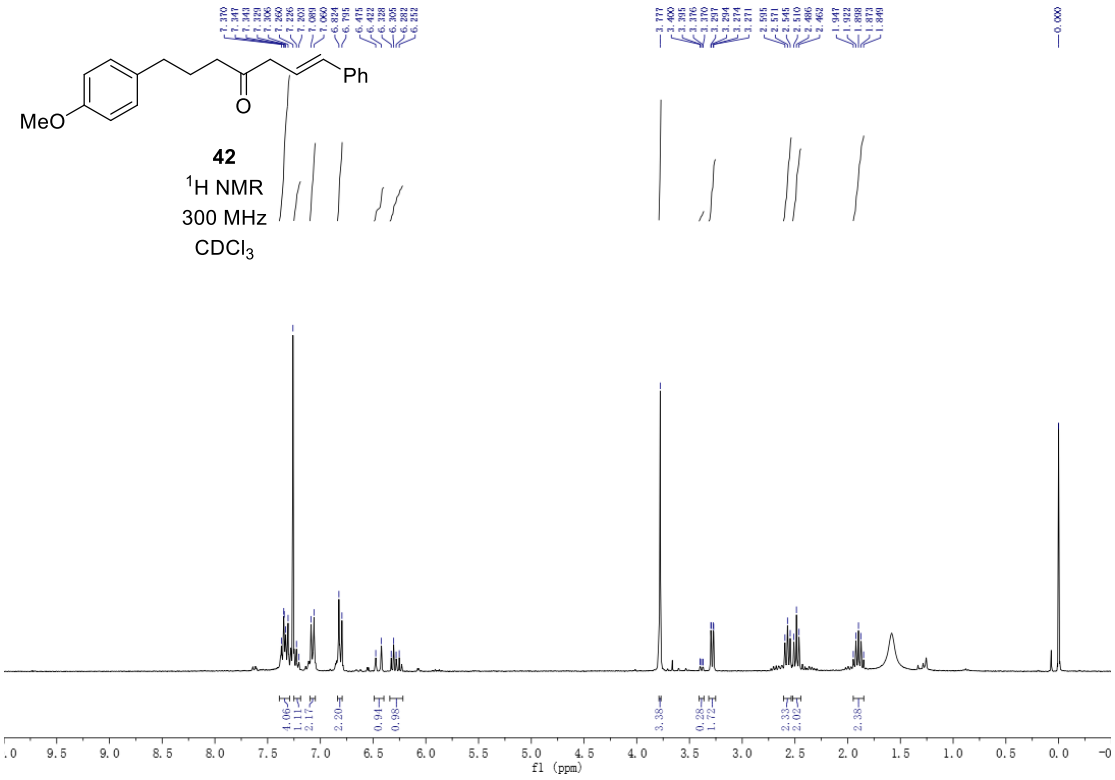
41

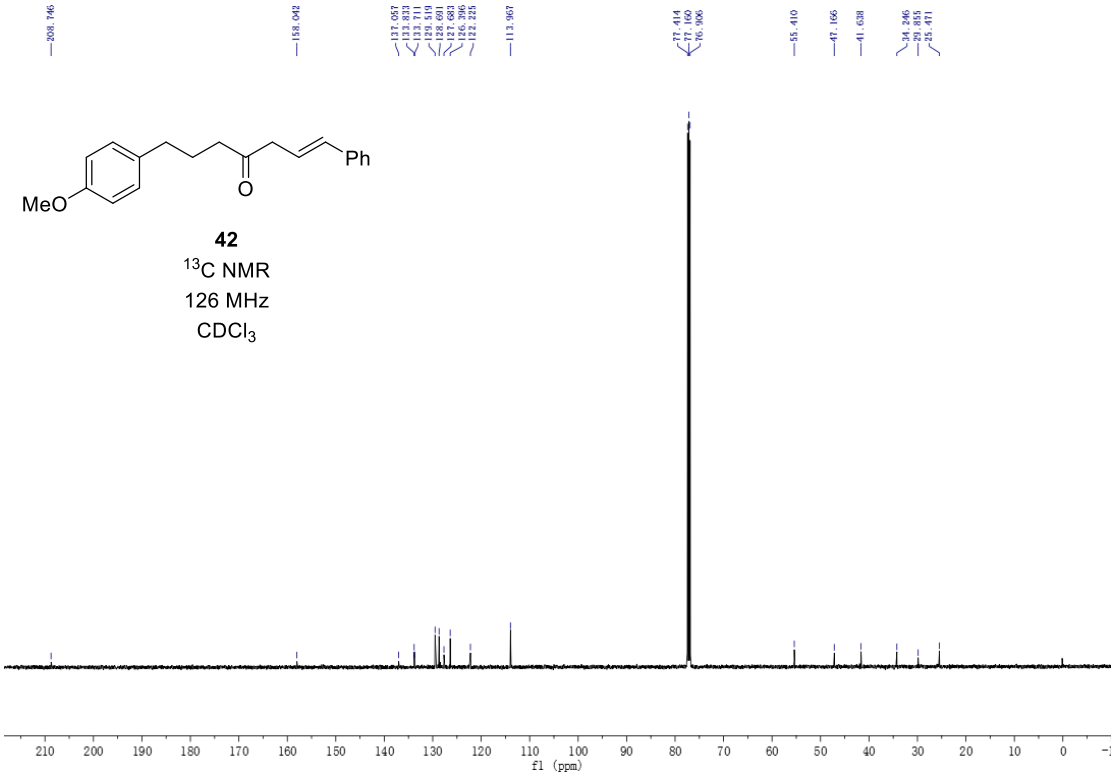
^{13}C NMR

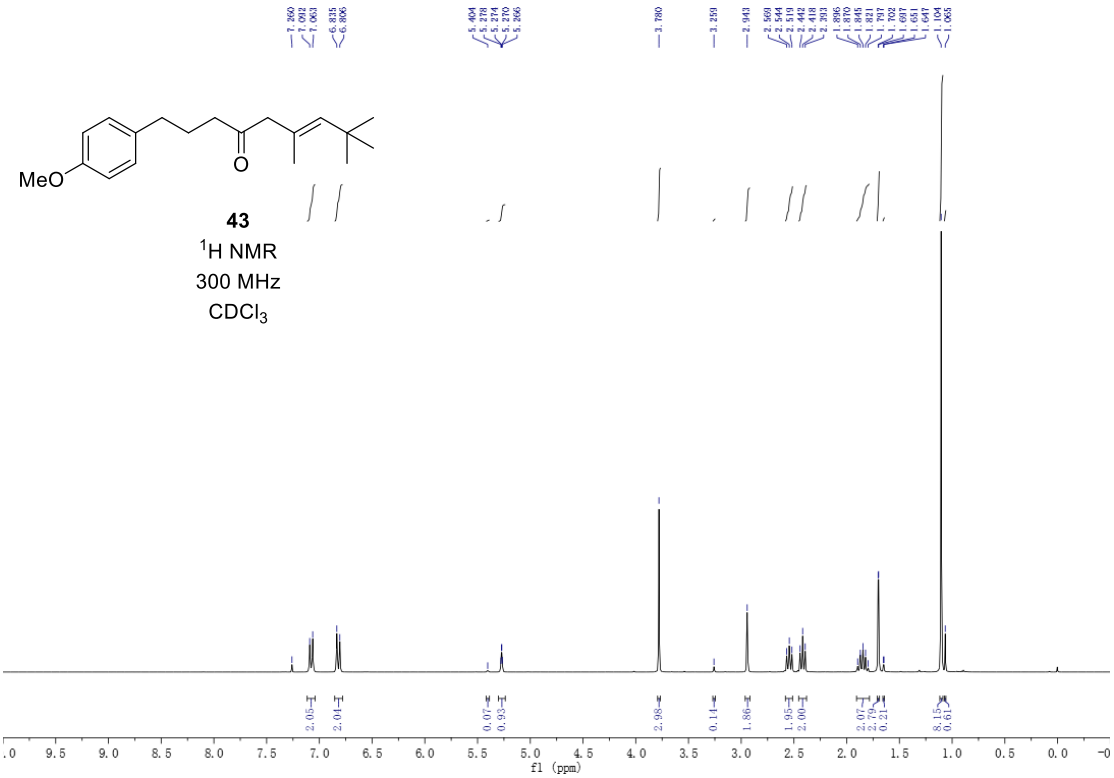
126 MHz

$CDCl_3$




MeO
Ph
O
42
1H NMR
300 MHz
CDCl3
f1 (ppm)


MeO
Ph
O
42
13C NMR
126 MHz
CDCl3
f1 (ppm)

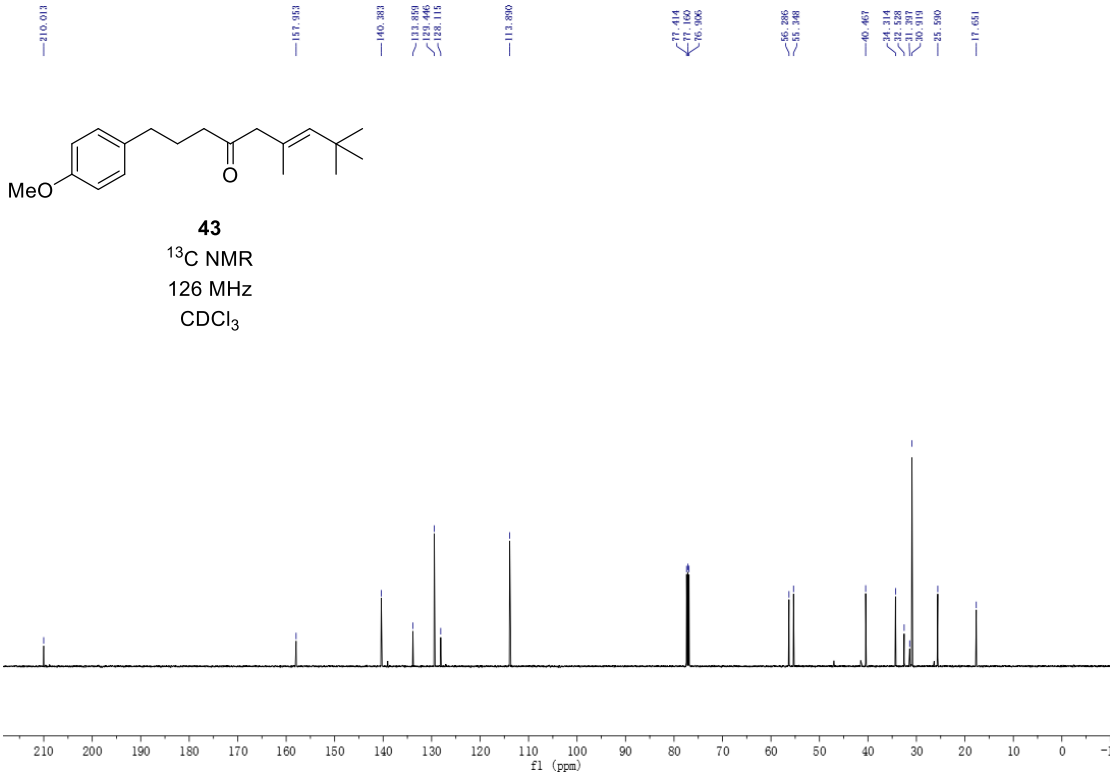


43

^{1}H NMR

300 MHz

$CDCl_3$

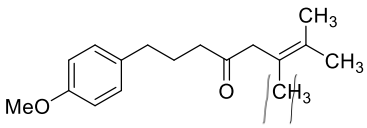


43

^{13}C NMR

126 MHz

$CDCl_3$

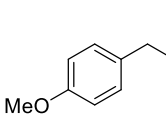


44

^{1}H NMR

300 MHz

$CDCl_3$

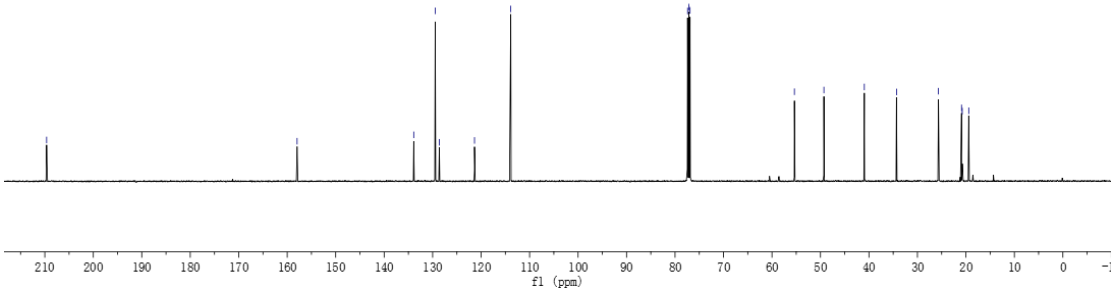


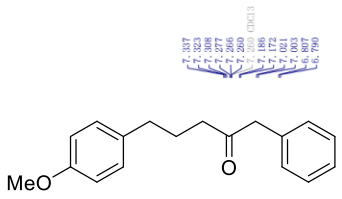
44

^{13}C NMR

126 MHz

$CDCl_3$



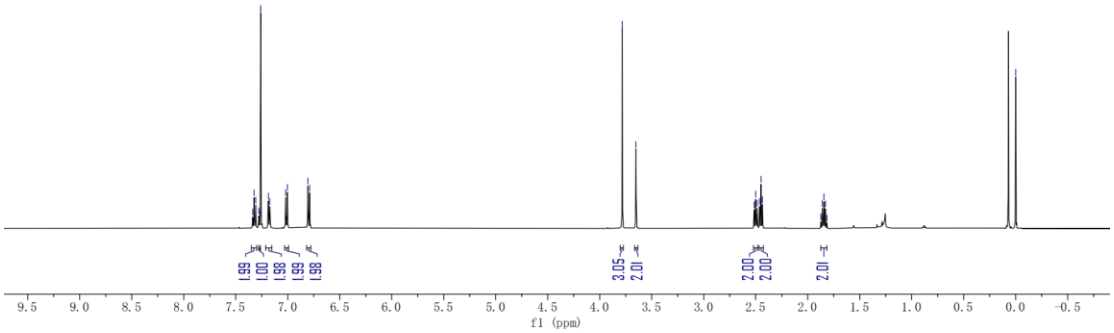


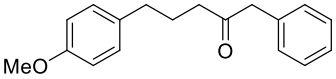
45

^{1}H NMR

500 MHz

$CDCl_3$



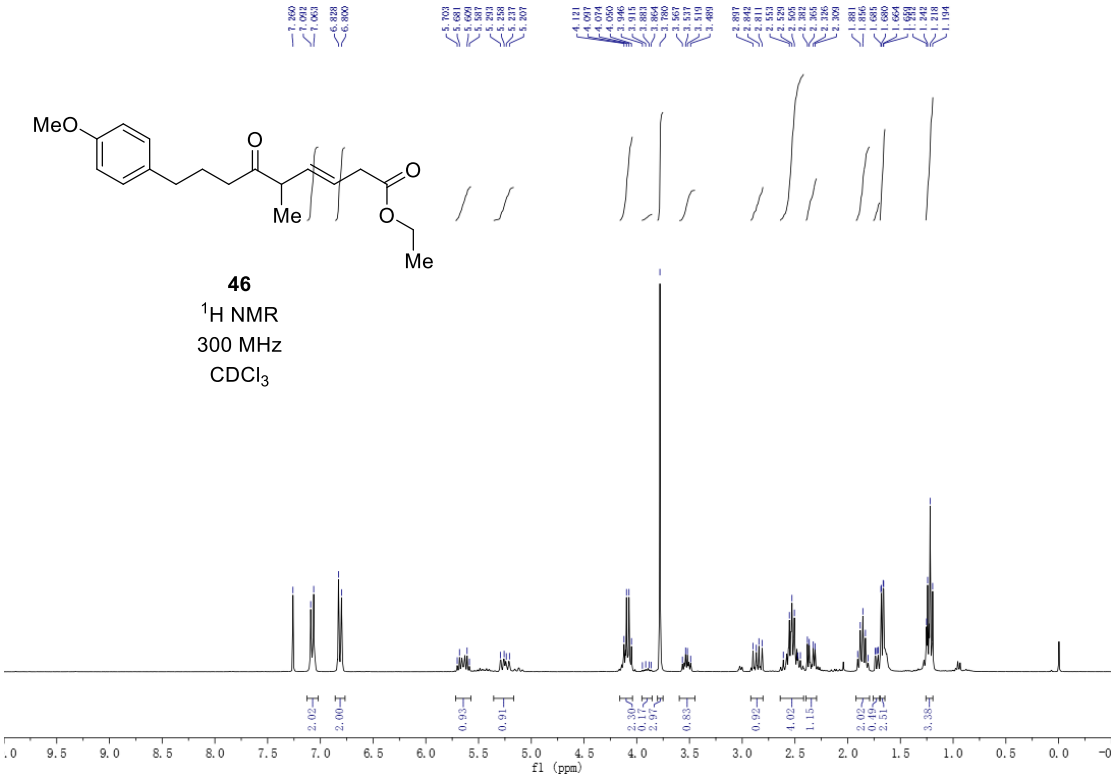


45

^{13}C NMR

126 MHz

$CDCl_3$

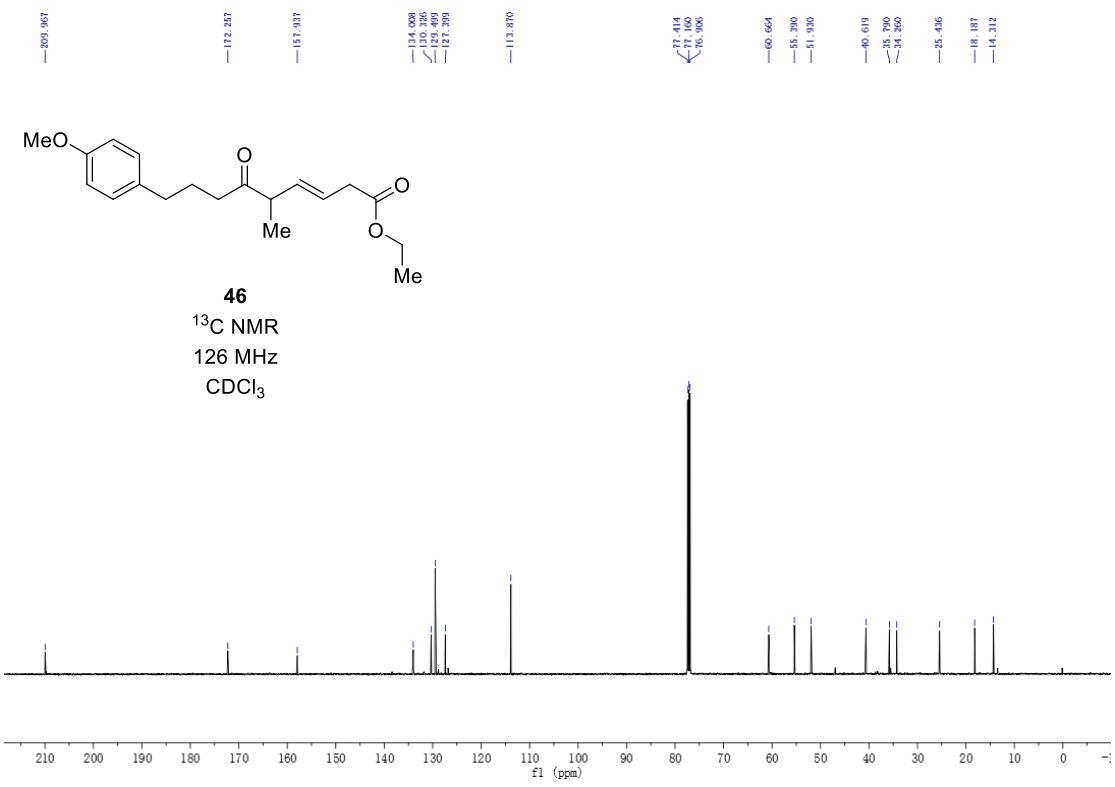


46

^{1}H NMR

300 MHz

$CDCl_3$

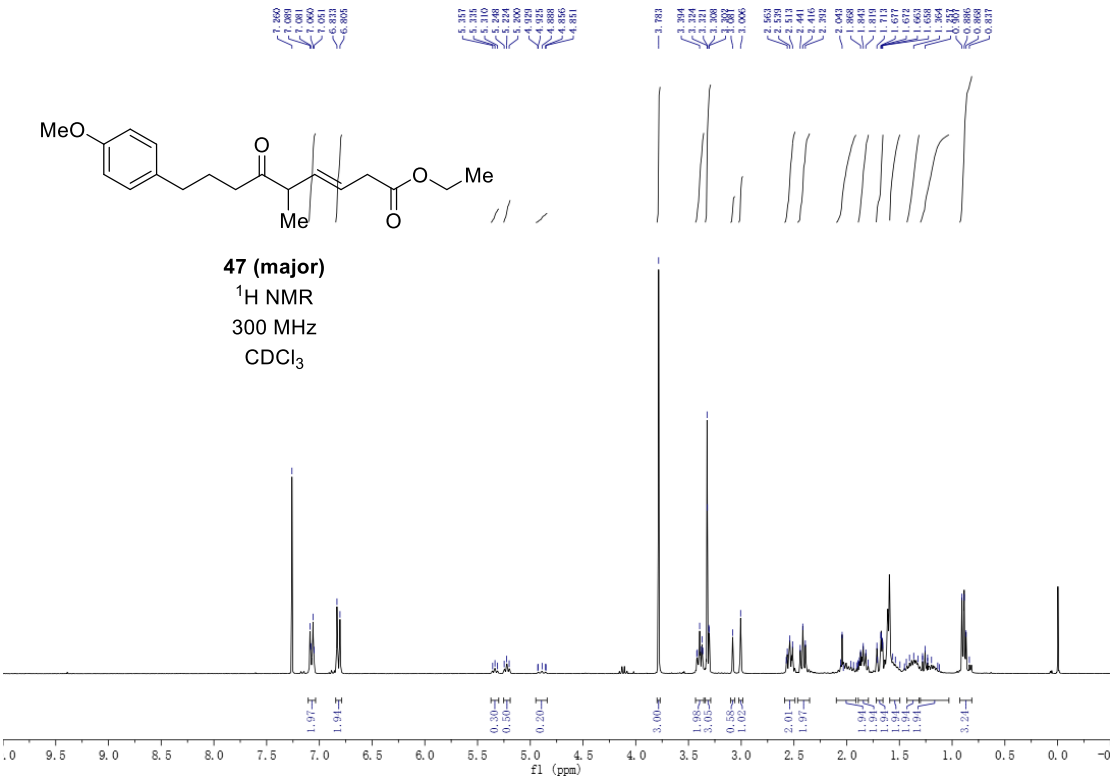


46

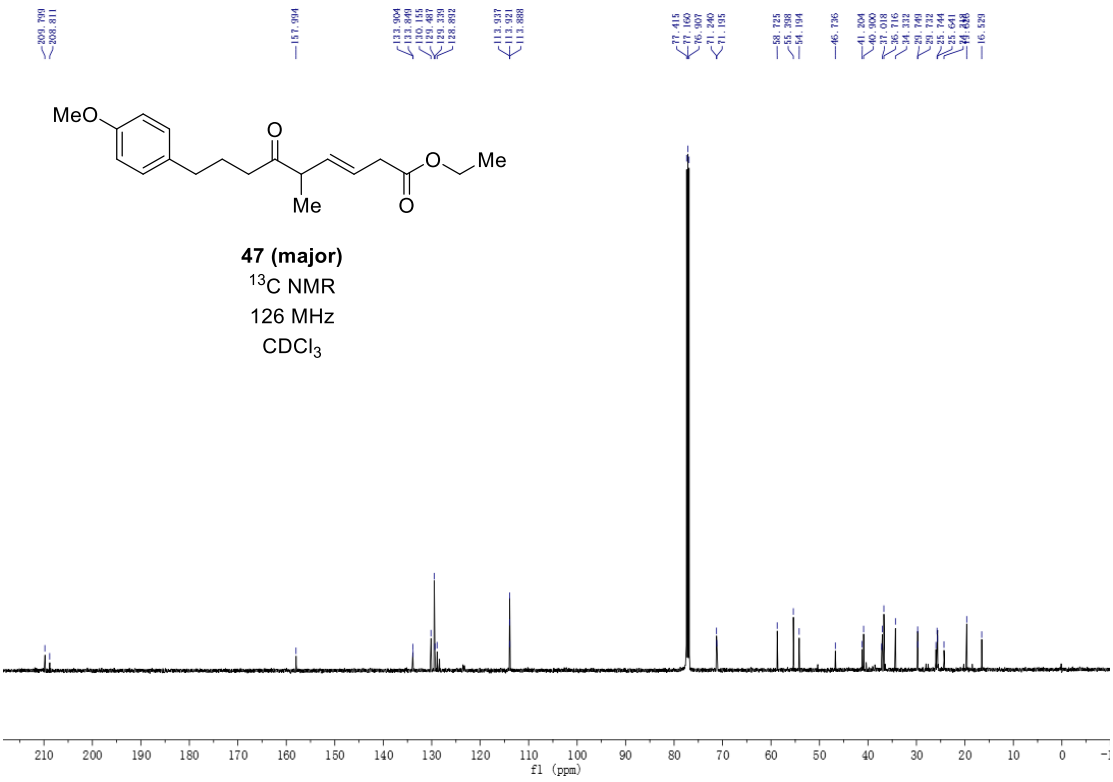
^{13}C NMR

126 MHz

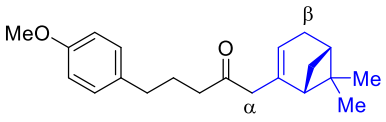
$CDCl_3$



47 (major)
^{1}H NMR
300 MHz
$CDCl_3$



47 (major)
^{13}C NMR
126 MHz
$CDCl_3$

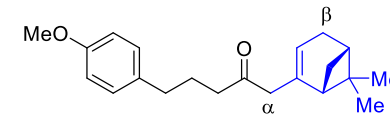


48 (major)

^{1}H NMR

300 MHz

$CDCl_3$

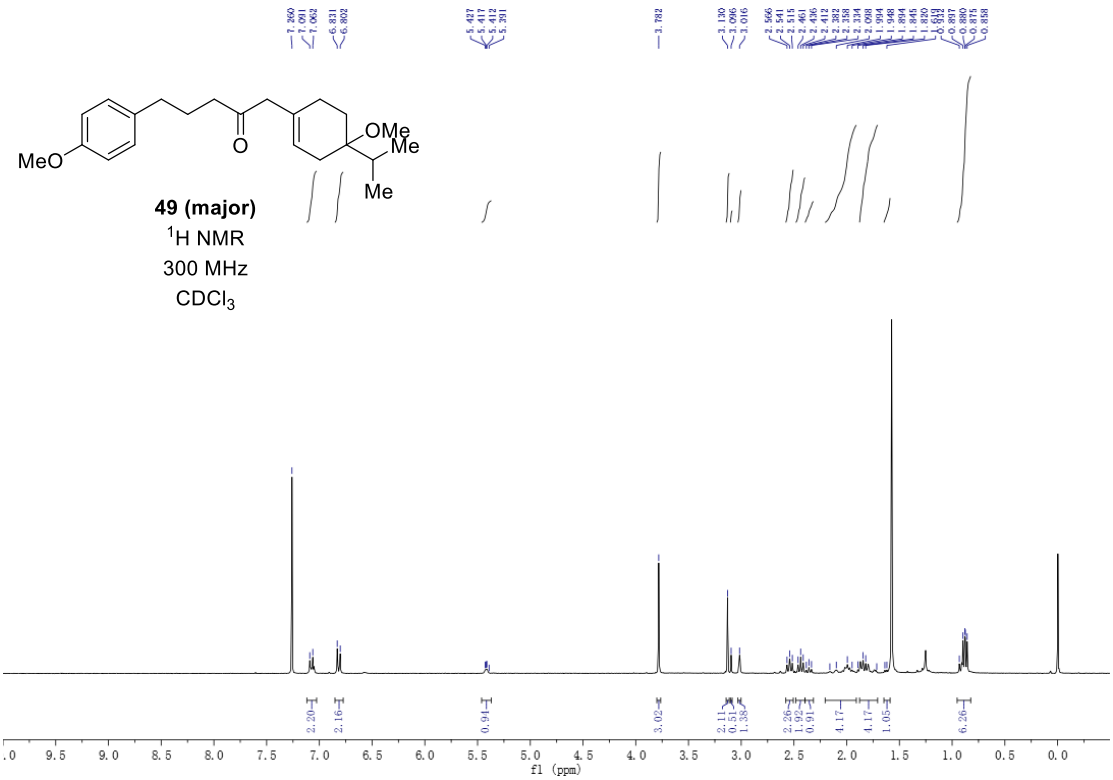


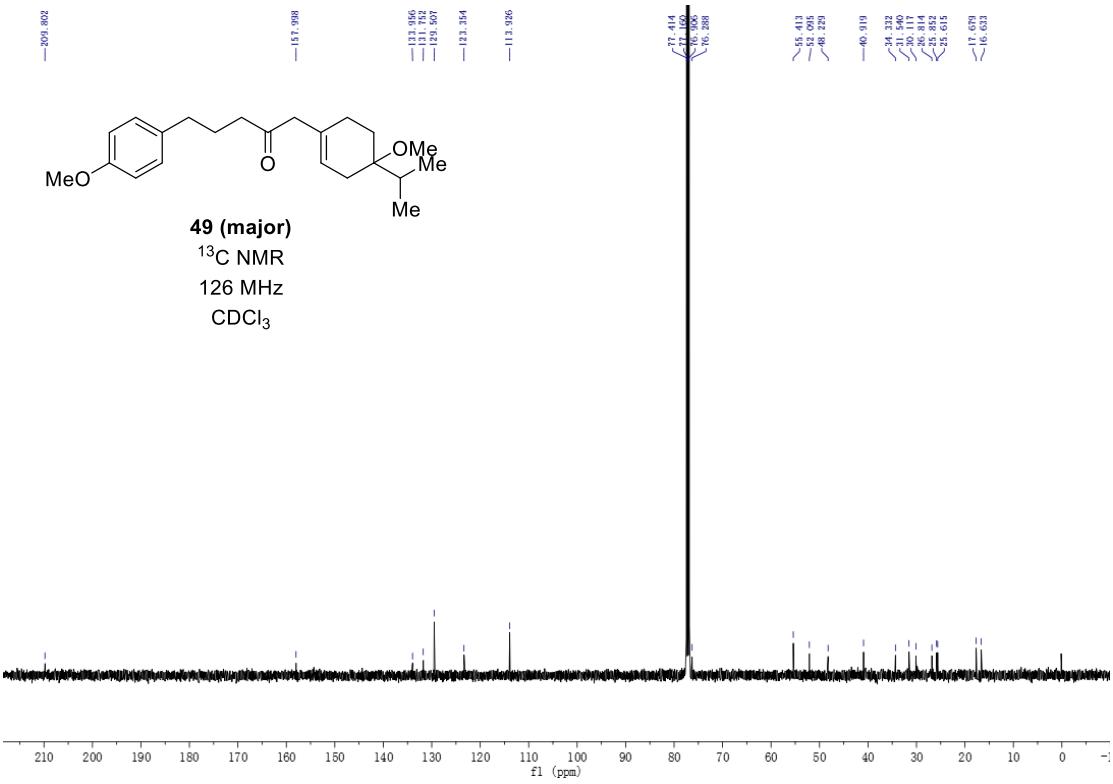
48 (major)

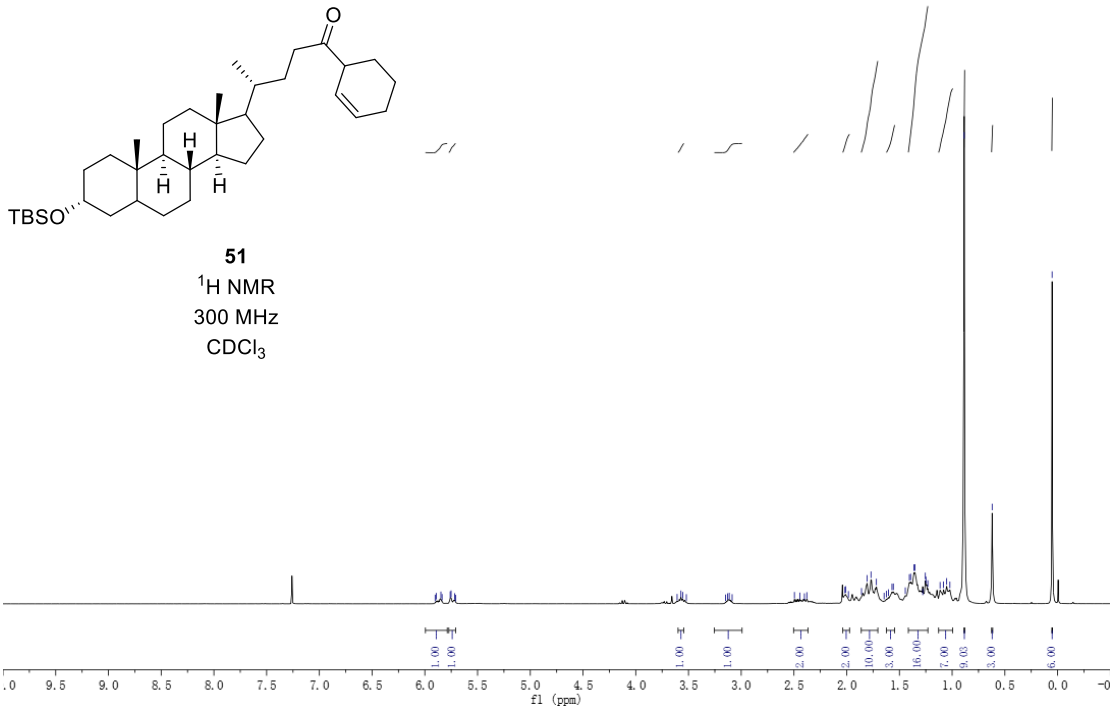
^{13}C NMR

126 MHz

$CDCl_3$


MeO
O
OMe
Me
Me
49 (major)
1H NMR
300 MHz
CDCl3
f1 (ppm)


MeO
O
OMe
Me
Me
49 (major)
13C NMR
126 MHz
CDCl3
f1 (ppm)

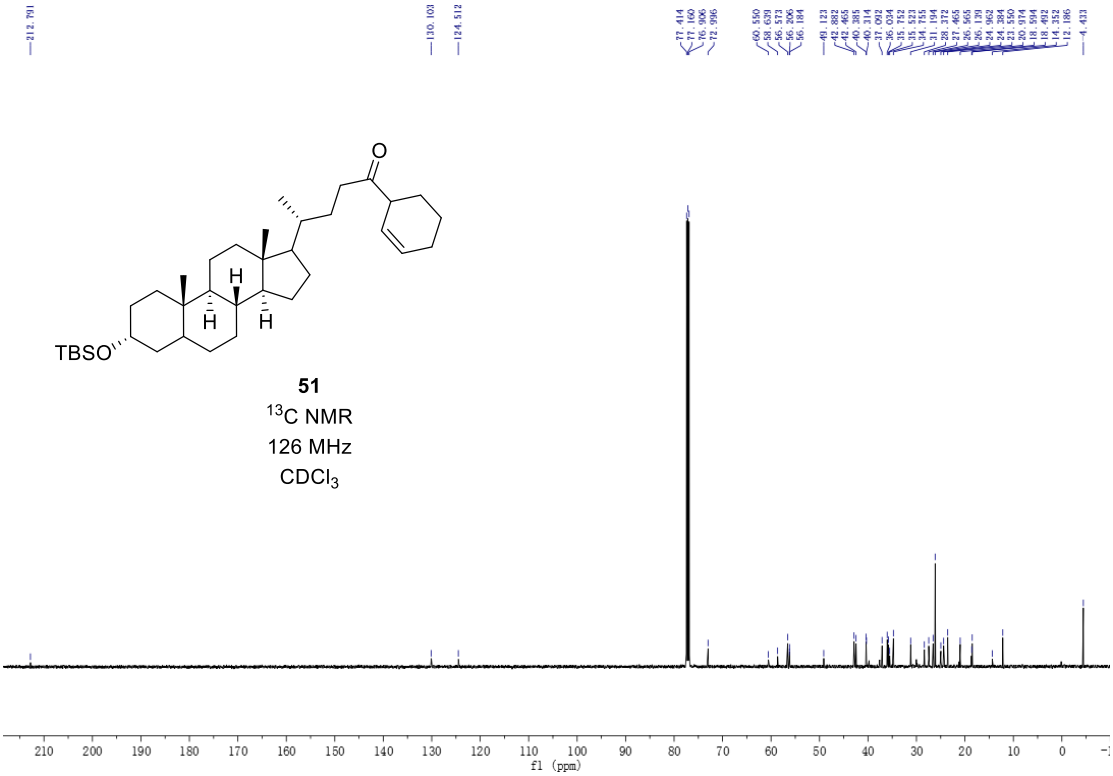


51

^{1}H NMR

300 MHz

$CDCl_3$

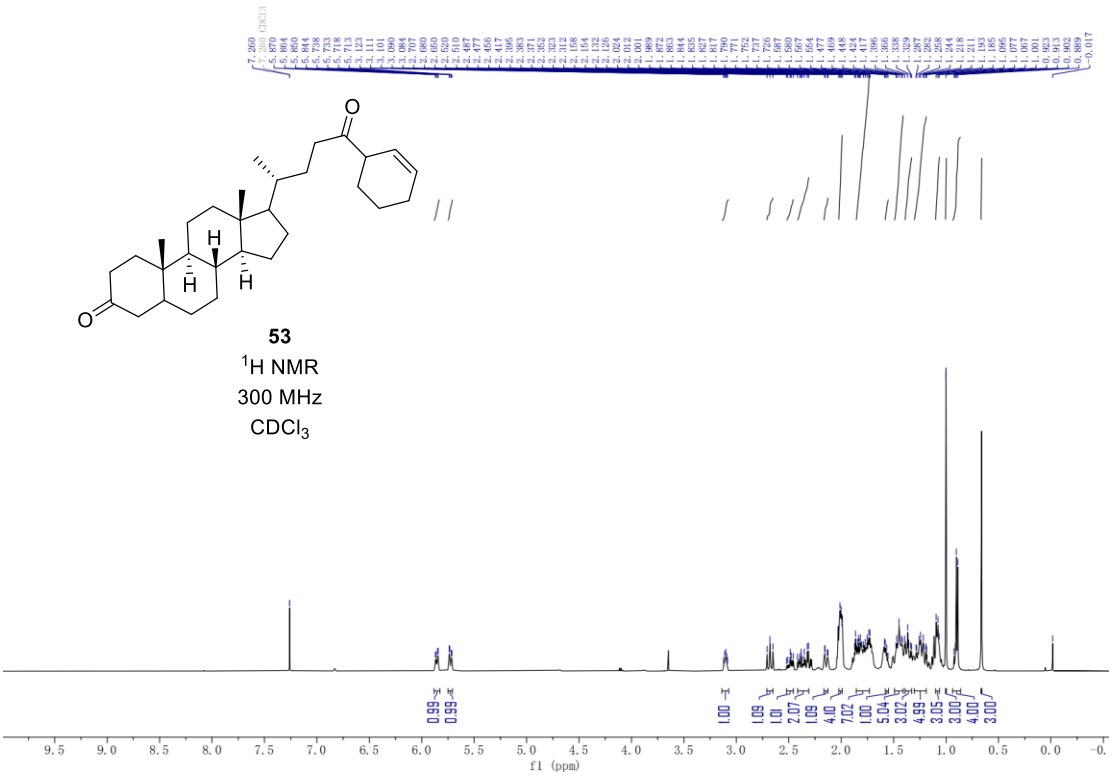


51

^{13}C NMR

126 MHz

$CDCl_3$

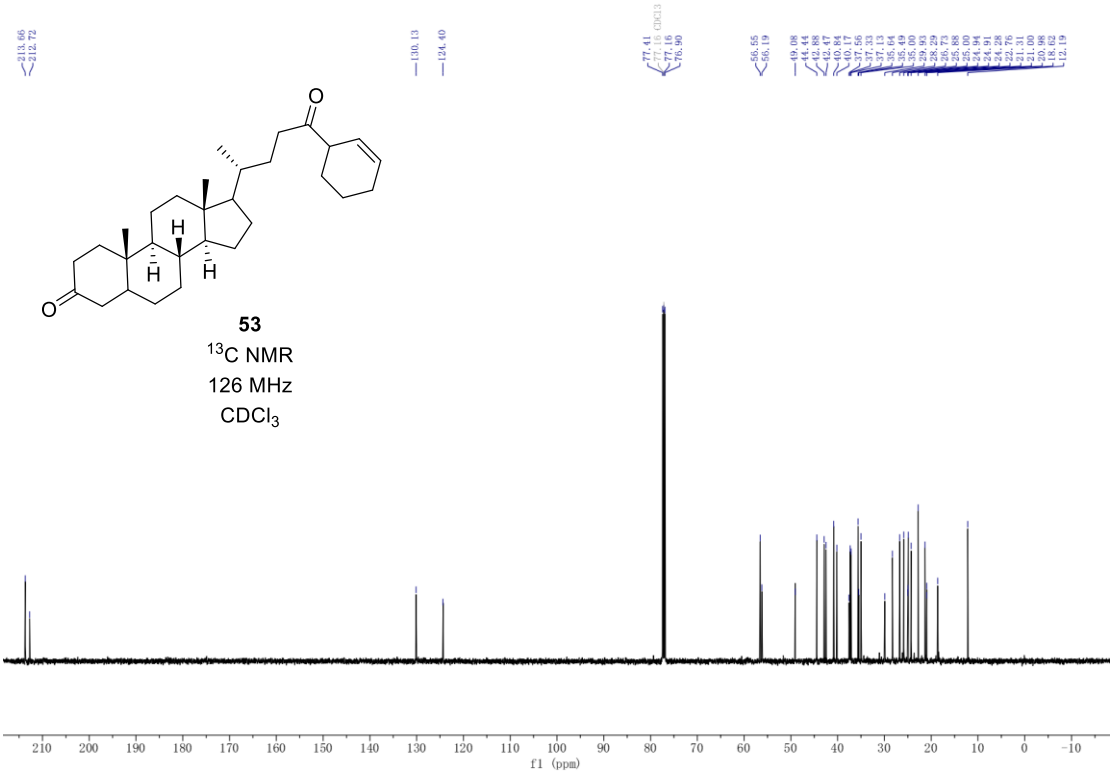


53

^{1}H NMR

300 MHz

$CDCl_3$

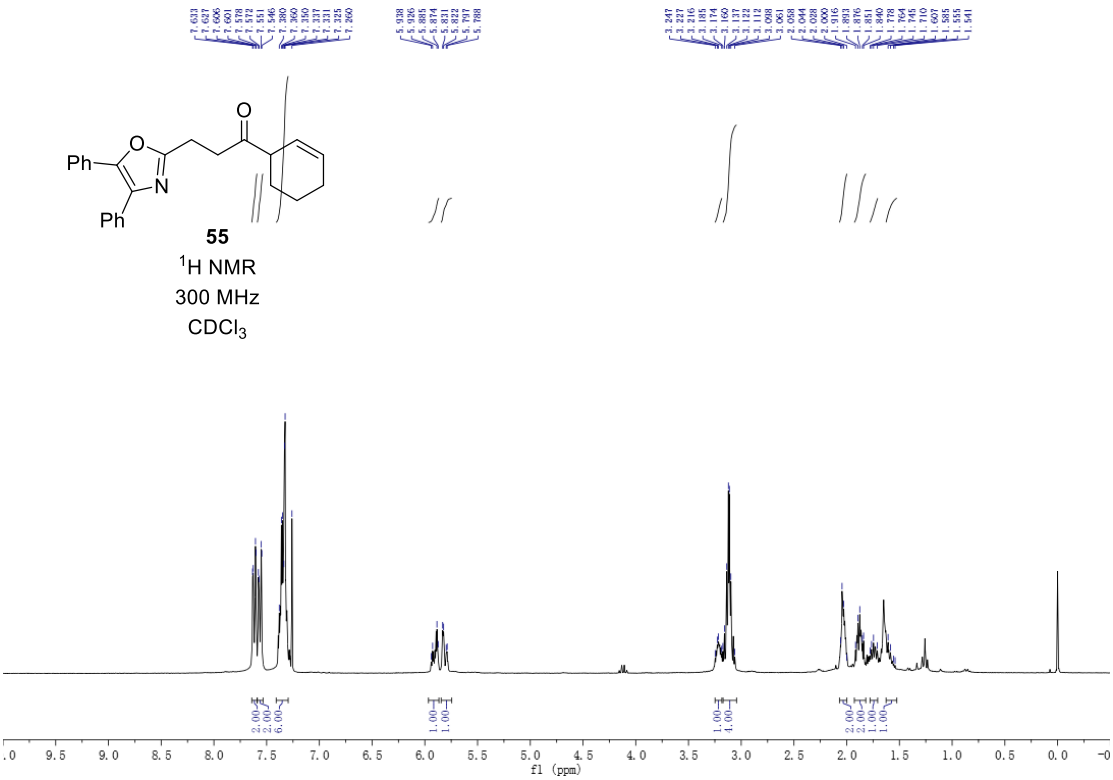


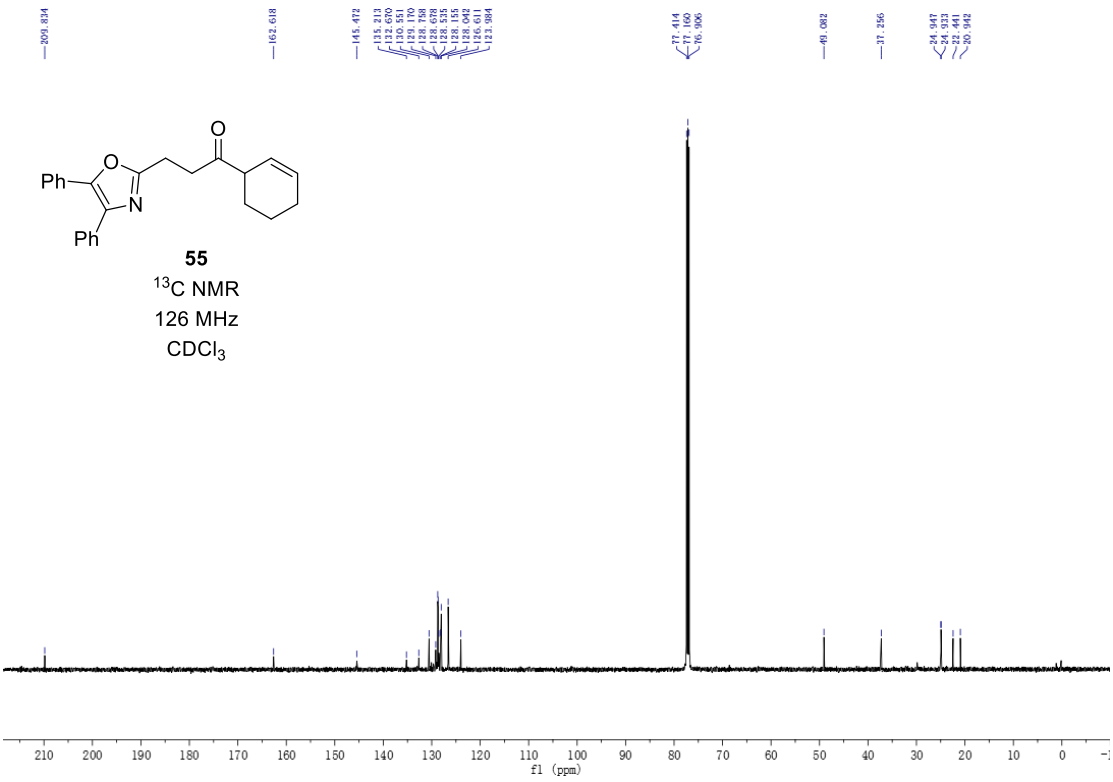
53

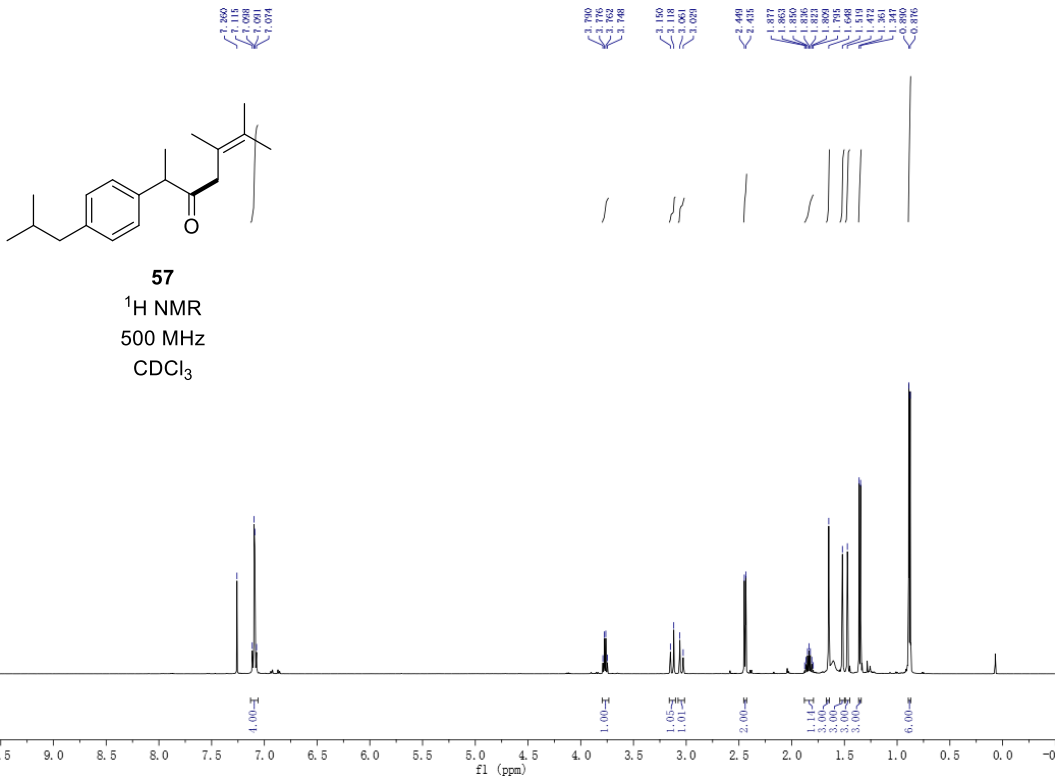
^{13}C NMR

126 MHz

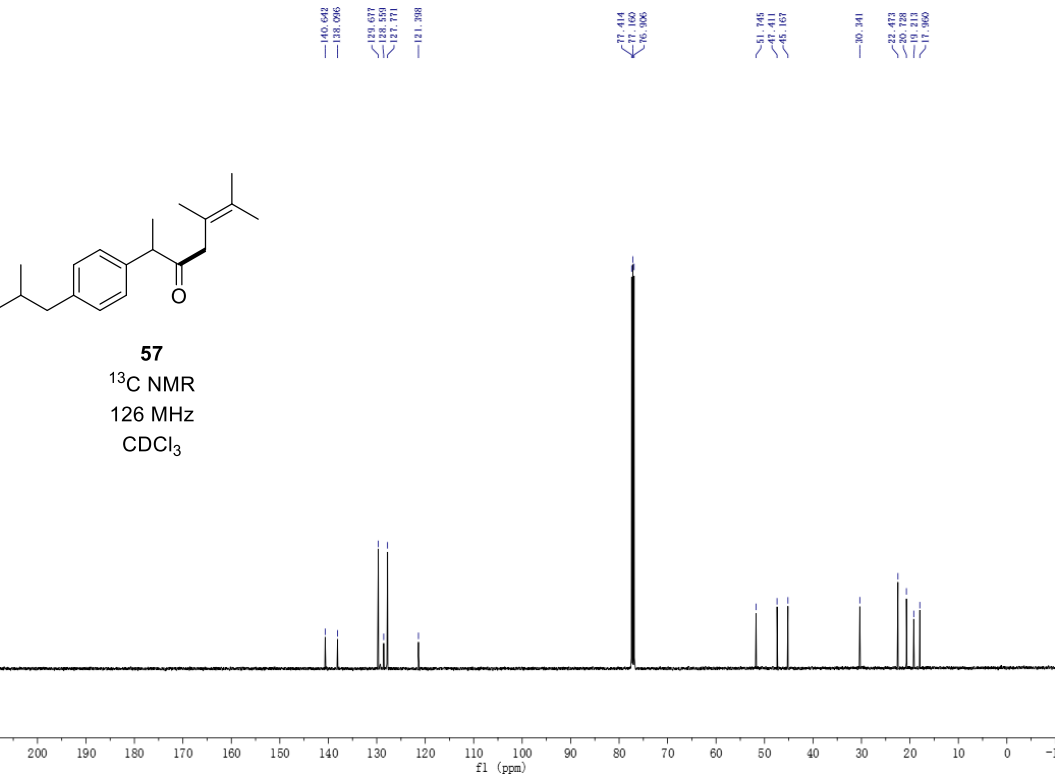
$CDCl_3$


Ph
O
N
Ph
O
55
1H NMR
300 MHz
CDCl3
f1 (ppm)

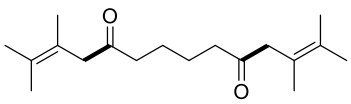

Ph
O
N
Ph
O
55
13C NMR
126 MHz
CDCl3
f1 (ppm)



57
^{1}H NMR
500 MHz
$CDCl_3$



57
^{13}C NMR
126 MHz
$CDCl_3$

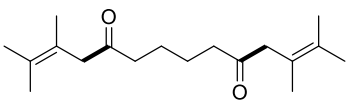


58

^{1}H NMR

300 MHz

$CDCl_3$

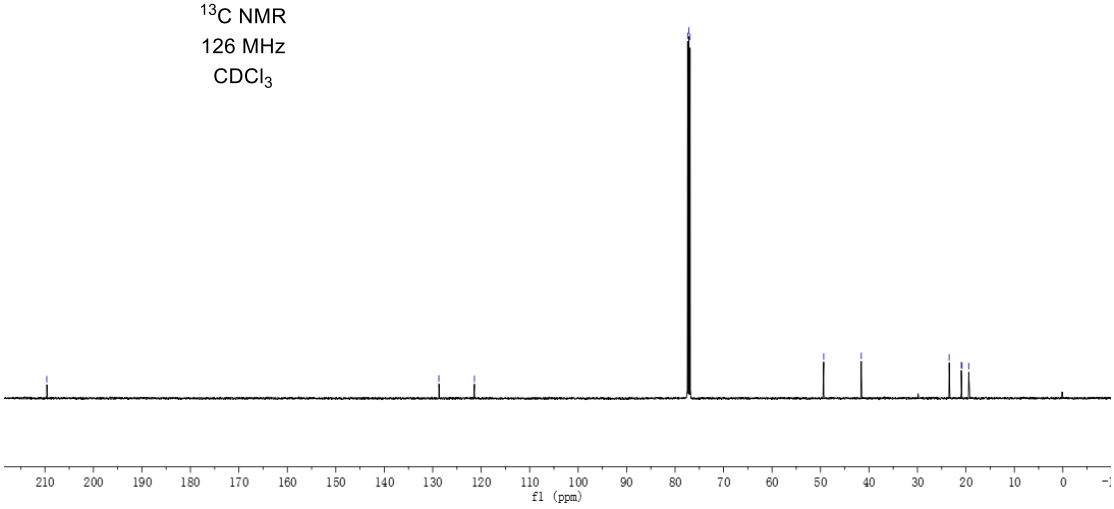


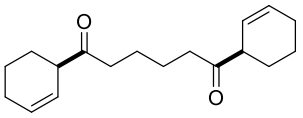
58

^{13}C NMR

126 MHz

$CDCl_3$



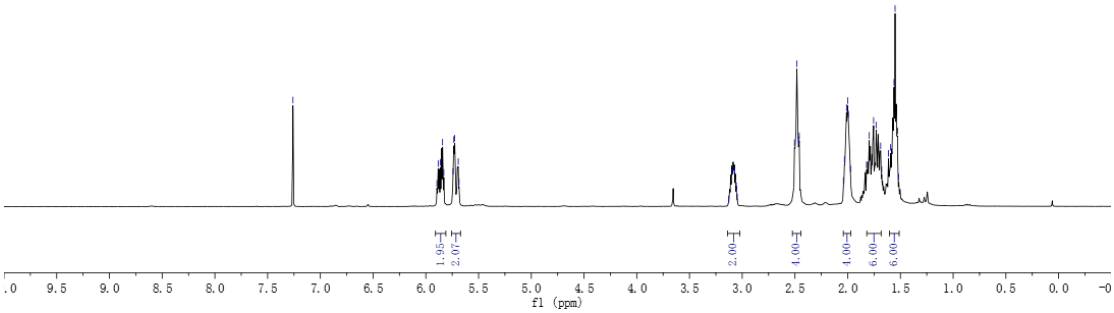


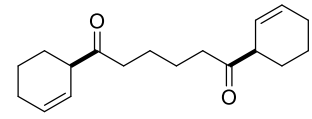
59

^{1}H NMR

300 MHz

$CDCl_3$



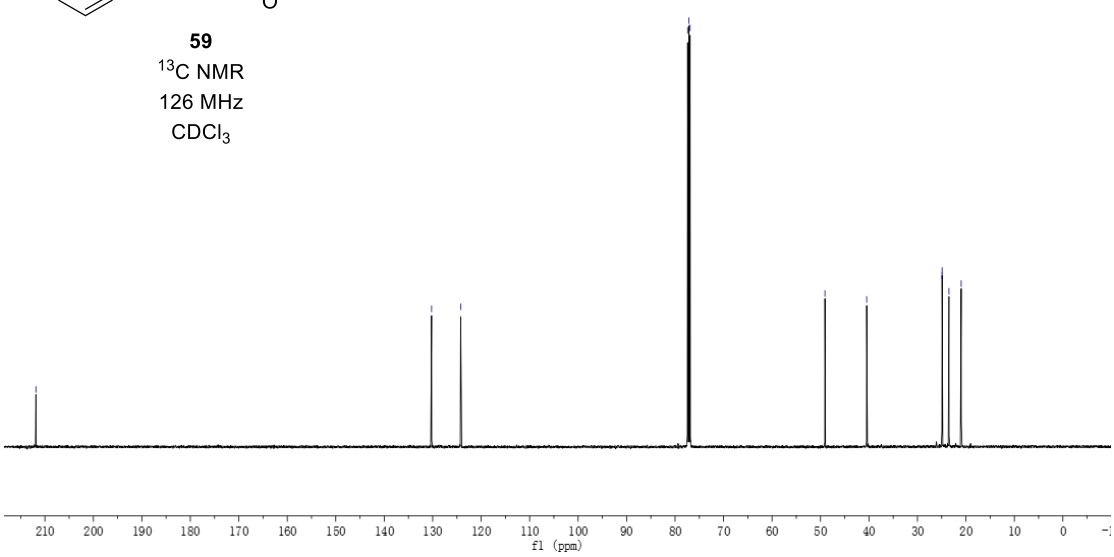


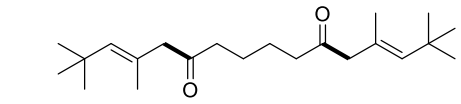
59

^{13}C NMR

126 MHz

$CDCl_3$



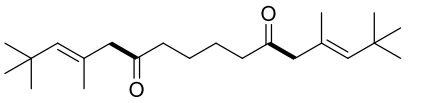


60

^{1}H NMR

300 MHz

$CDCl_3$

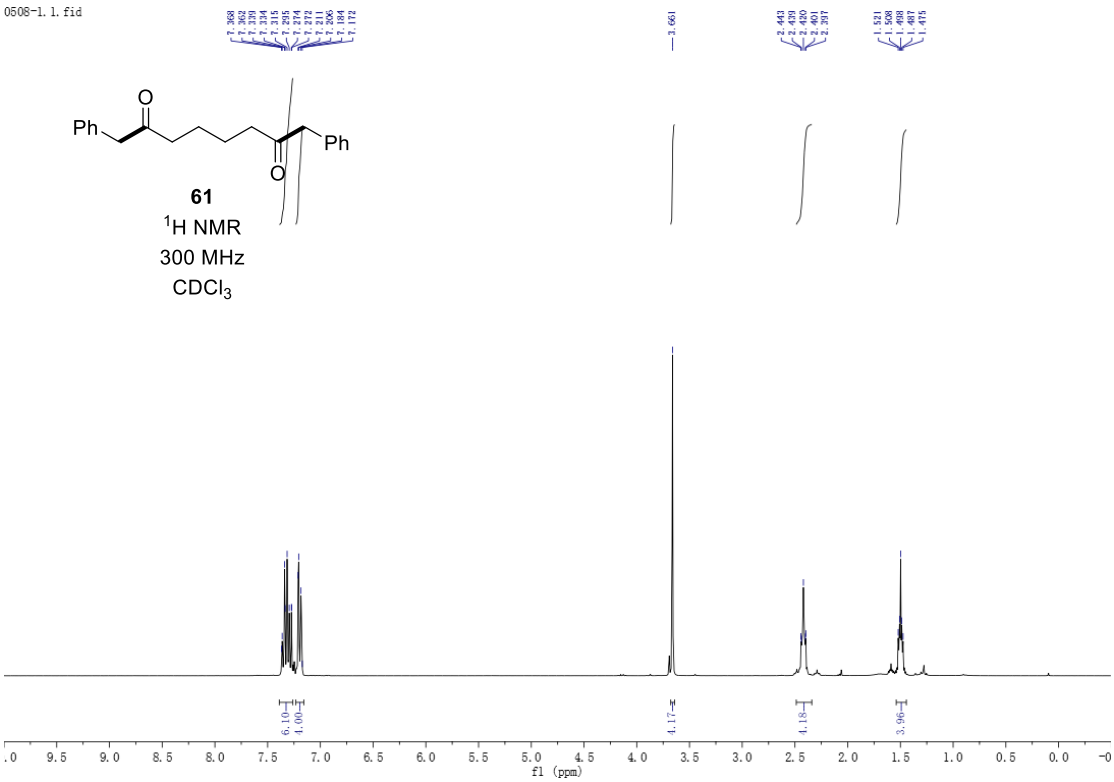


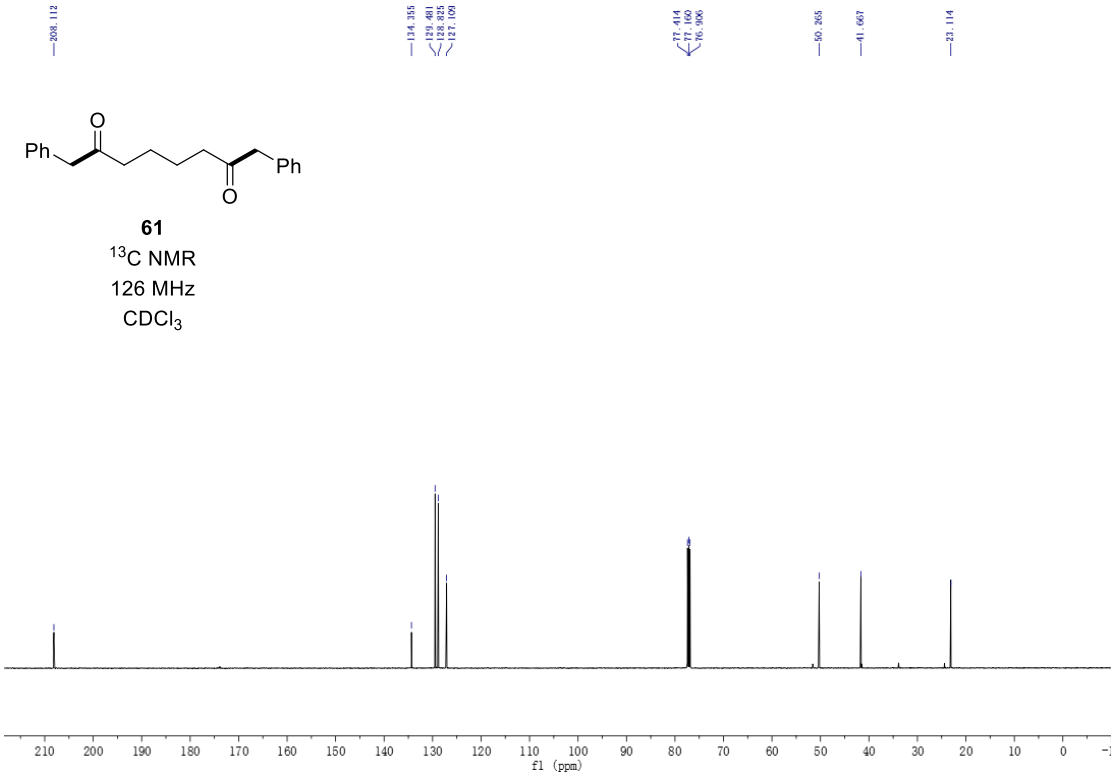
60

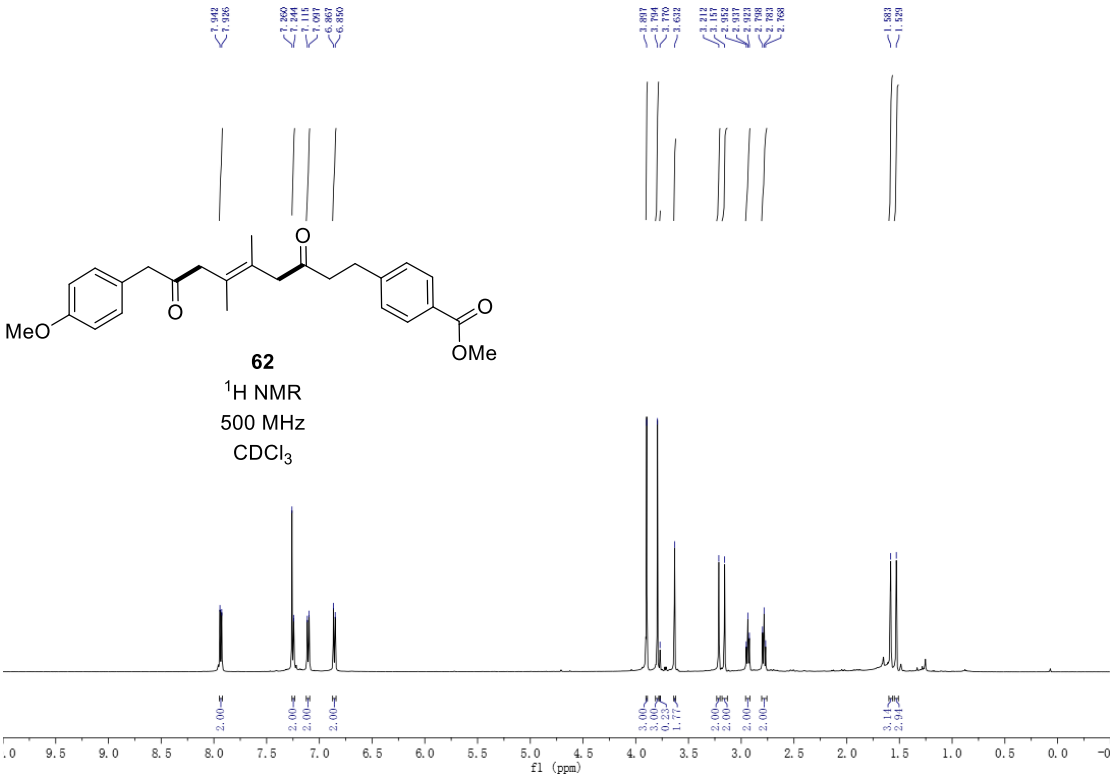
^{13}C NMR

126 MHz

$CDCl_3$


0508-1.1.fid
Ph
O
O
Ph
61
1H NMR
300 MHz
CDCl3
f1 (ppm)


Ph
O
O
Ph
61
13C NMR
126 MHz
CDCl3
f1 (ppm)

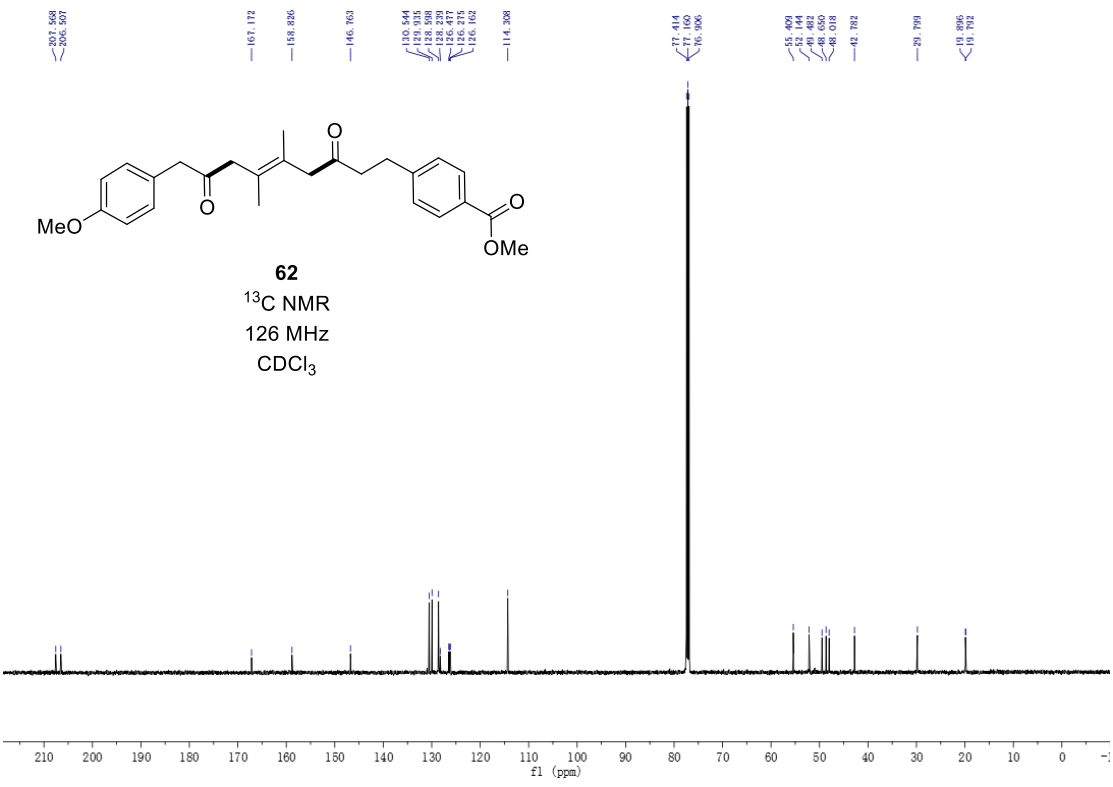


62

^{1}H NMR

500 MHz

$CDCl_3$

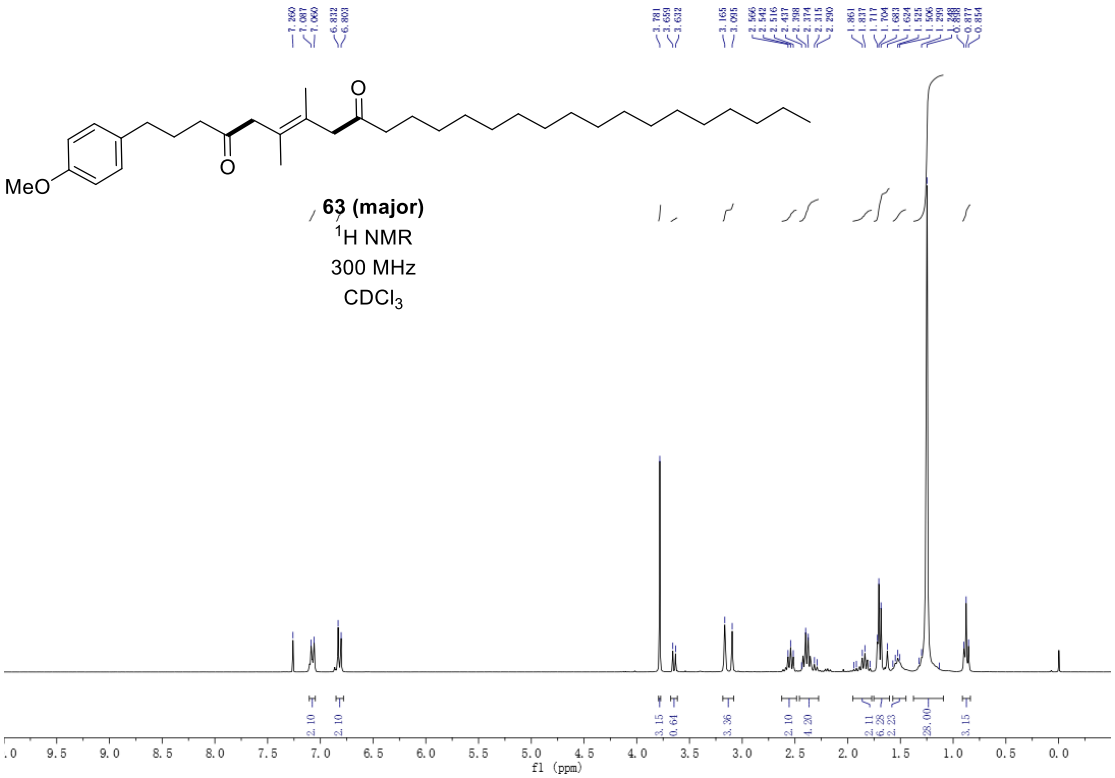


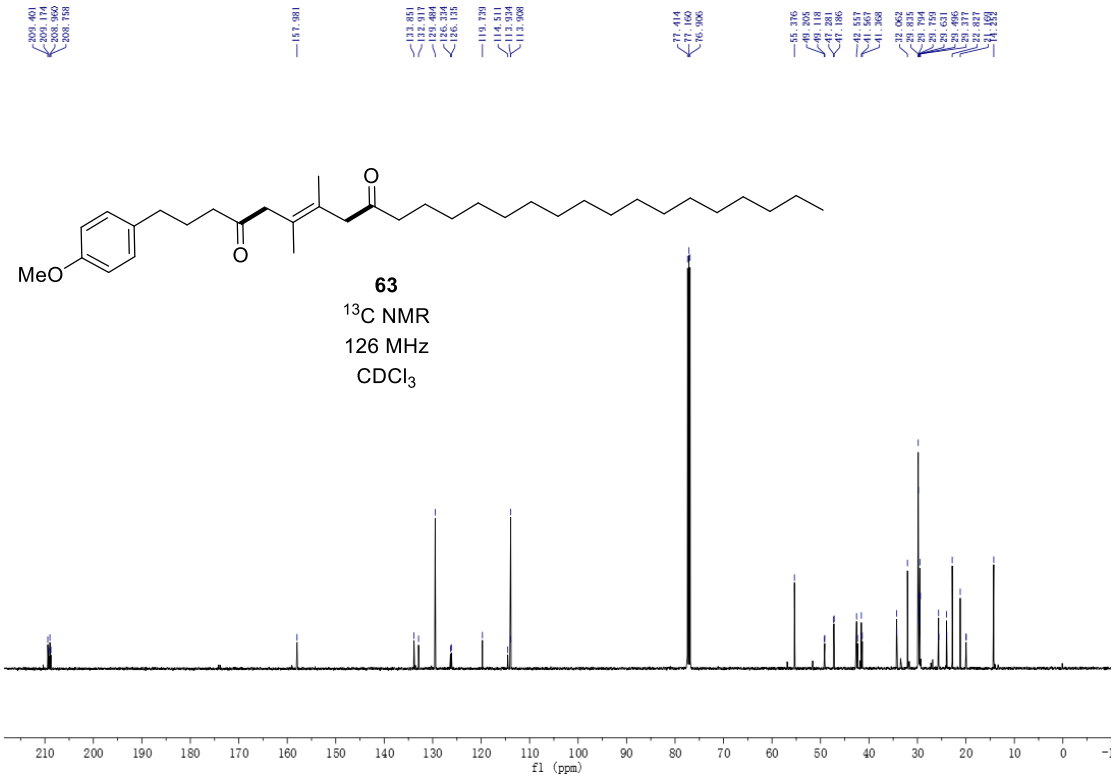
62

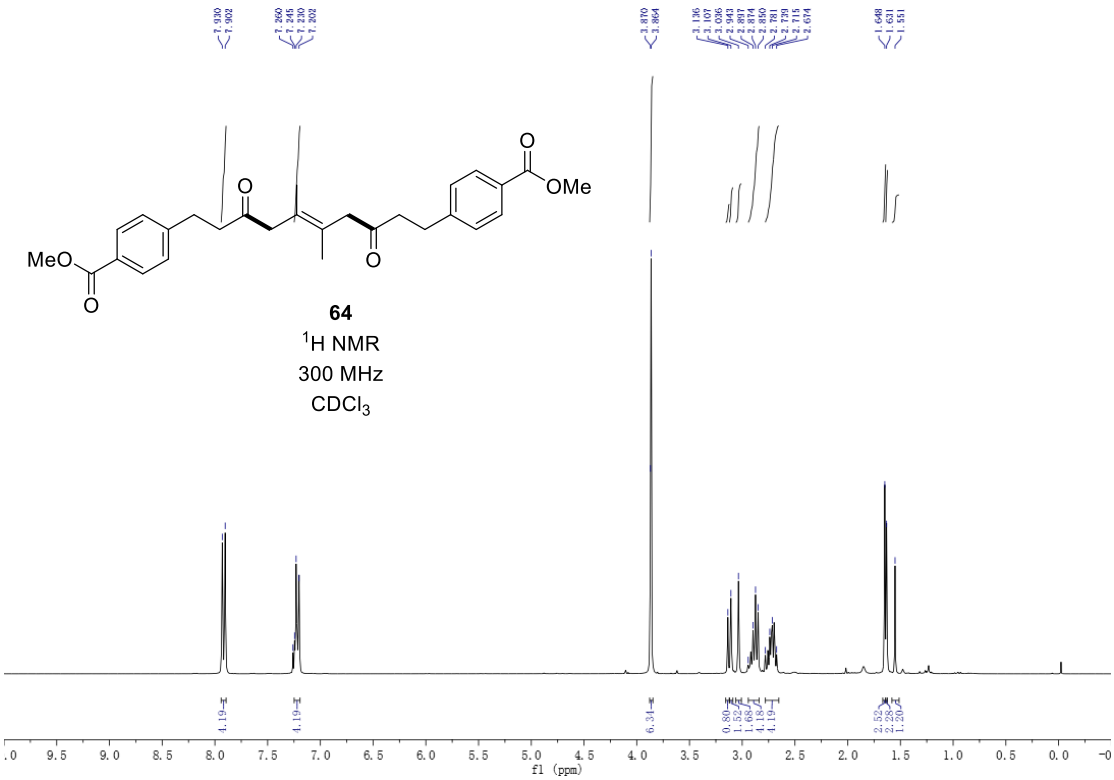
^{13}C NMR

126 MHz

$CDCl_3$


MeO
O
O
63 (major)
1H NMR
300 MHz
CDCl3
f1 (ppm)


MeO
O
O
63
13C NMR
126 MHz
CDCl3
f1 (ppm)

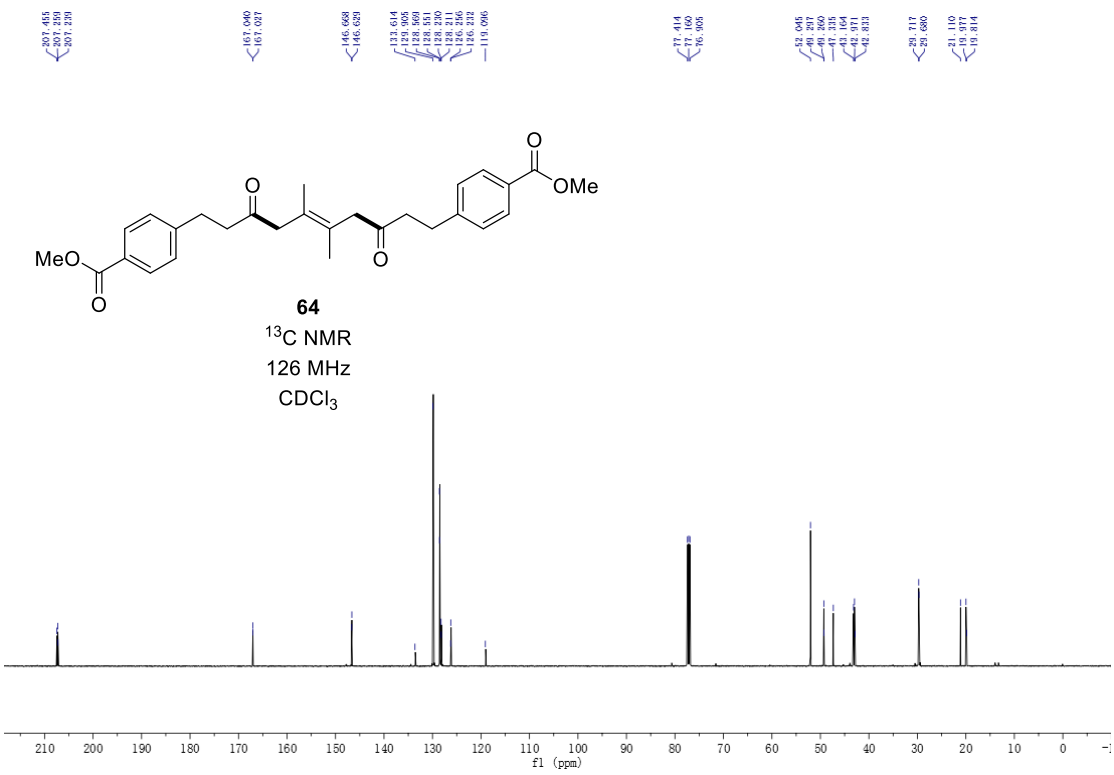


64

^{1}H NMR

300 MHz

$CDCl_3$

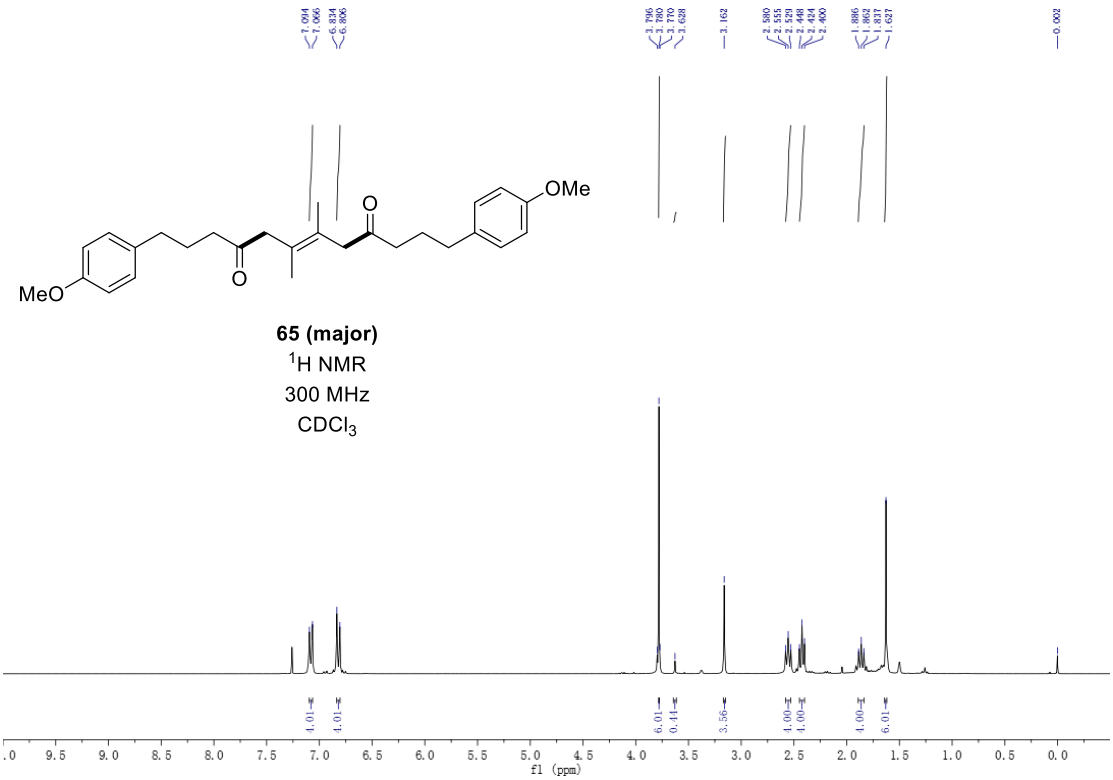


64

^{13}C NMR

126 MHz

$CDCl_3$

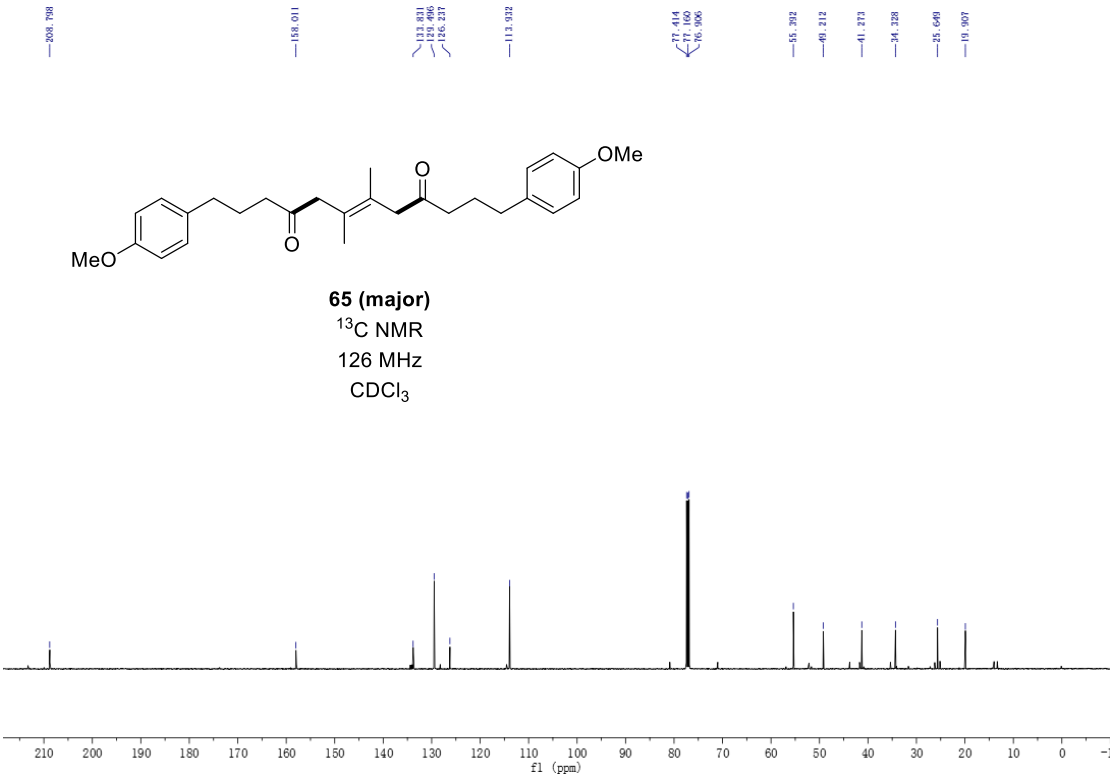


65 (major)

^{1}H NMR

300 MHz

$CDCl_3$

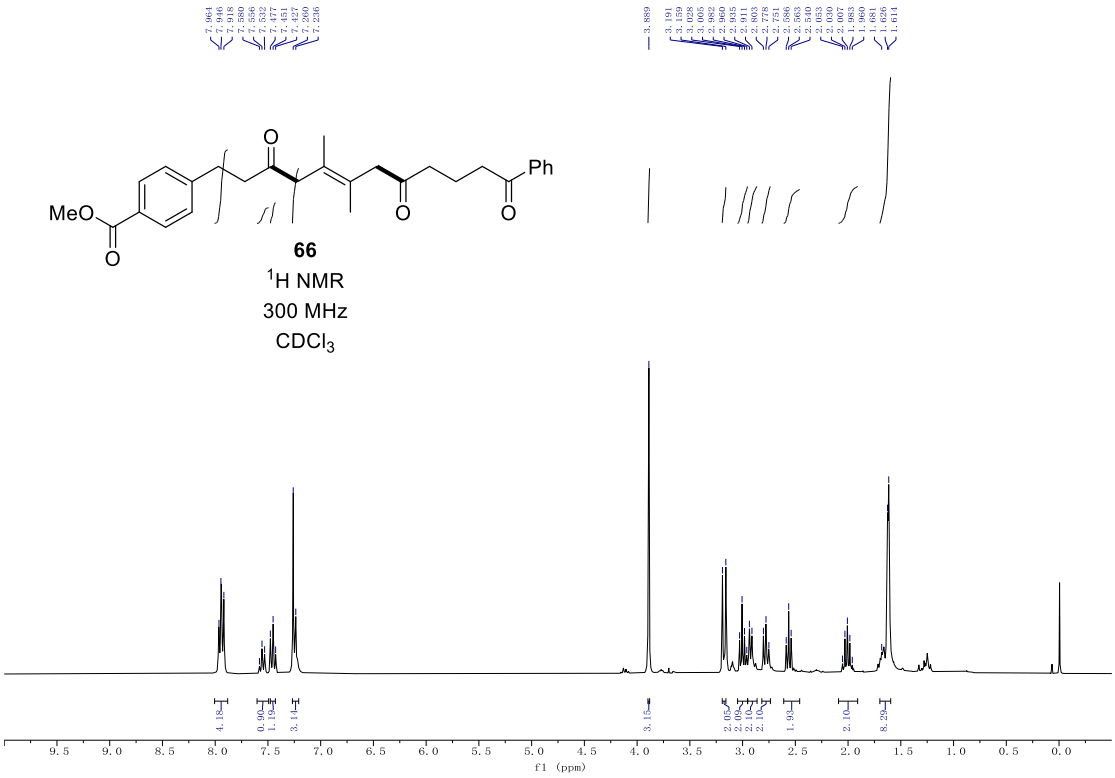


65 (major)

^{13}C NMR

126 MHz

$CDCl_3$

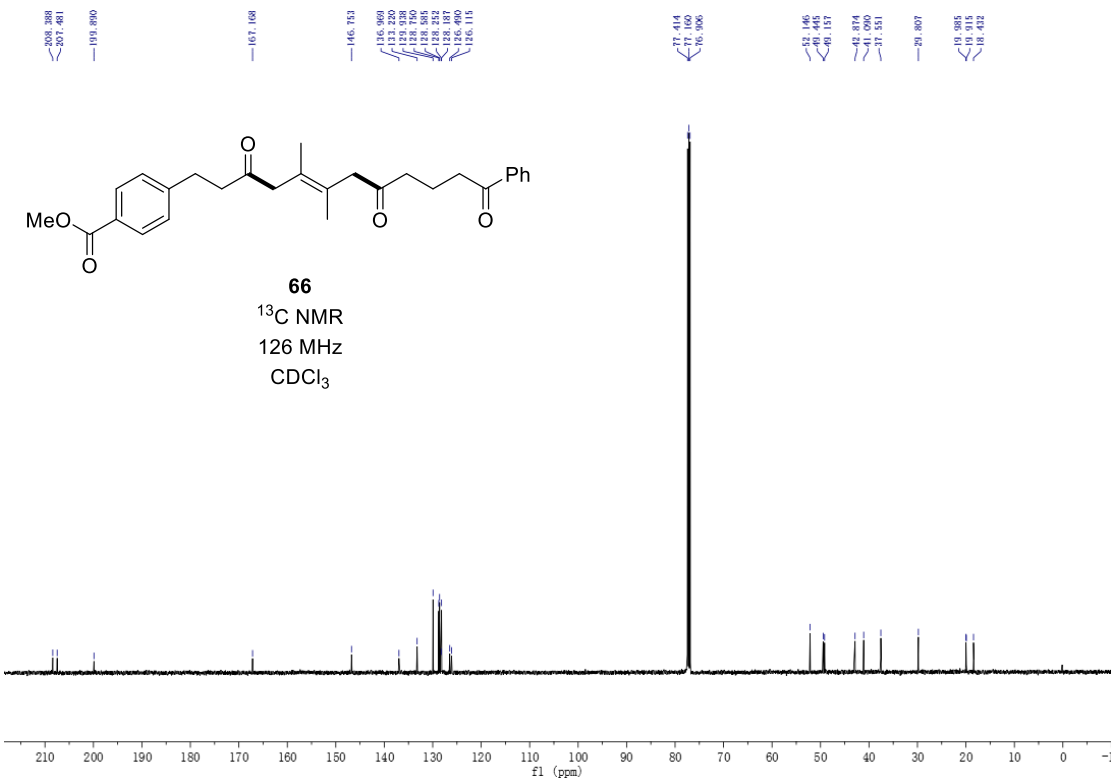


66

^{1}H NMR

300 MHz

$CDCl_3$

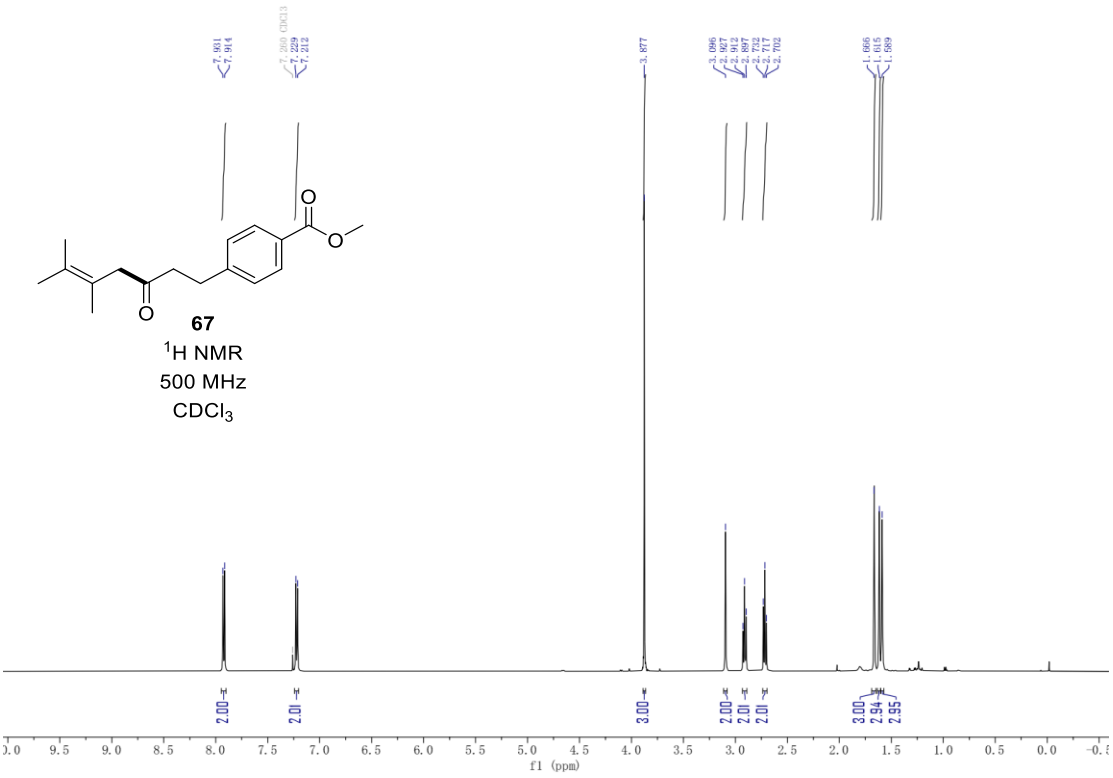


66

^{13}C NMR

126 MHz

$CDCl_3$

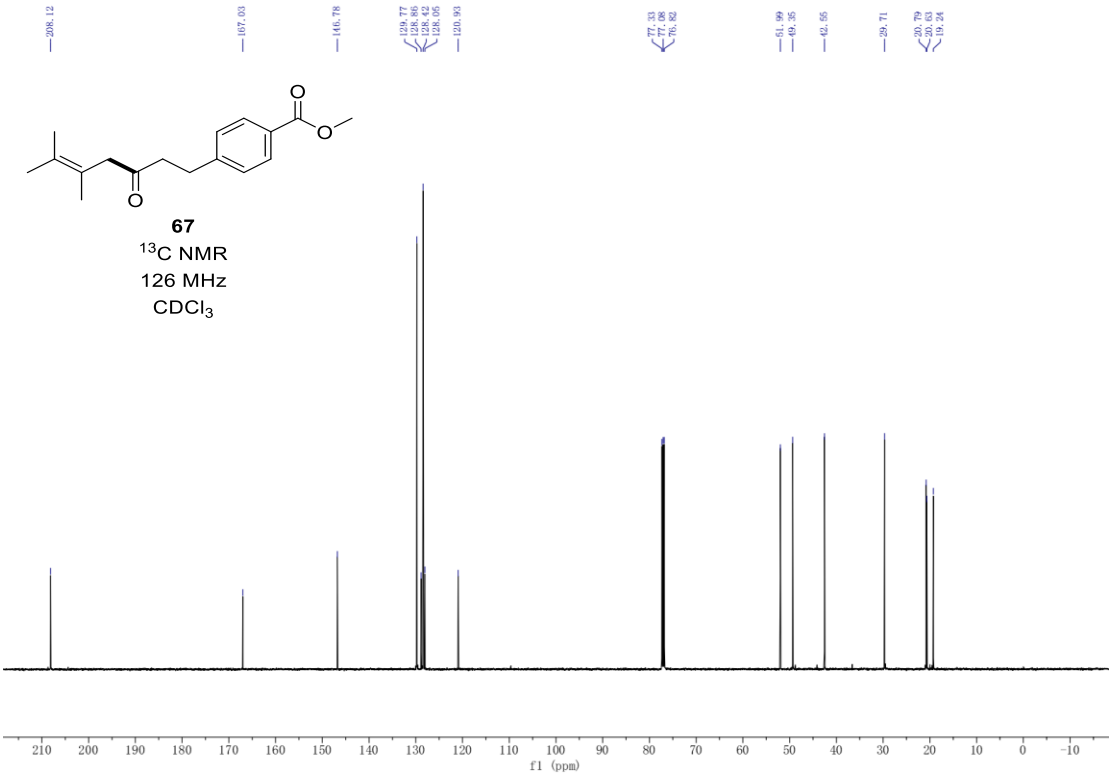


67

^{1}H NMR

500 MHz

$CDCl_3$



67

^{13}C NMR

126 MHz

$CDCl_3$