Supporting Information

Direct Synthesis of Dialkyl Ketones from Deoxygenative Cross-Coupling of Carboxylic Acids and Alcohols

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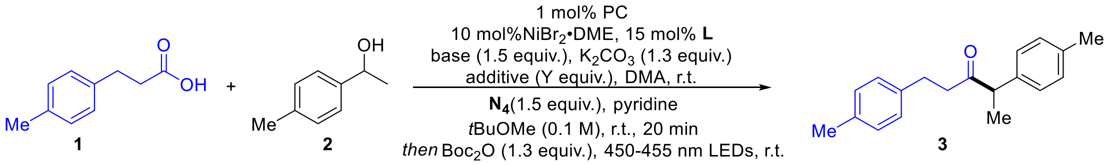
I. General Information

Dry DMAc and 1,4-dioxane were 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 alcohols from suppliers were used directly without further purification. NMR spectra were recorded on a Bruker-500 instrument. ^{1}H NMR chemical shifts were referenced to the tetramethylsilane (0 ppm); ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Mass spectra (HRMS) were obtained using Waters G2-XS Q-TOF LC/MS (ESI) mass spectrometer. Melting points were determined using a hot stage apparatus. All manipulations were conducted under Schlenk tubes.

II. Optimization of Reaction Conditions

Screening of various bases, photocatalysts (PC) and ligands (L)

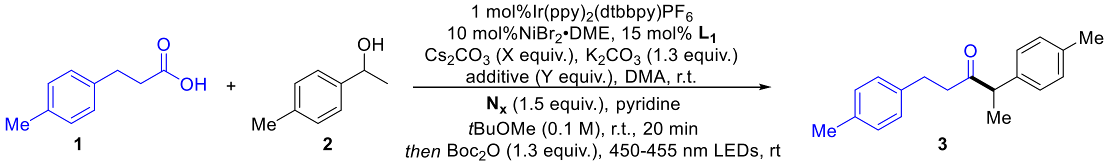


Entry	Base	PC	[L]	Yield (%)[a]
1	NaOAc	$Ir(ppy)_2(dtbbpy)PF_6$	dtbbpy	60
2	quinuclidine	$Ir(ppy)_2(dtbbpy)PF_6$	dtbbpy	trace
3	2,6-lutidine	$Ir(ppy)_2(dtbbpy)PF_6$	dtbbpy	34
4	Cs_2CO_3	$Ir(ppy)_2(dtbbpy)PF_6$	dtbbpy	42
5	DBU	$Ir(ppy)_2(dtbbpy)PF_6$	dtbbpy	5
6	Na_2CO_3	$Ir(ppy)_2(dtbbpy)PF_6$	dtbbpy	trace
7	Cs_2CO_3	$Ir(ppy)_2(dtbbpy)PF_6$	dtbbpy	48
8	NaOAc	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	dtbbpy	50

9	NaOAc	Ir[dF(Me)ppy]$_2$(dtbbpy)PF$_6$	dtbbpy	38
10	NaOAc	4CzIPN	dtbbpy	62
11	NaOAc	4CzIPN	bpy	37
12	NaOAc	4CzIPN	dtbbpy	39

[a] Yields were determined by ^{1}H NMR spectroscopy with mesitylene as an internal standard.

Screening of various NHCs and additives

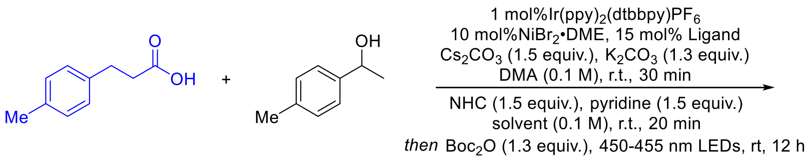


Entry	X	Additive/Y	Yield (%)[a]
1	2	/	31
2	1.5	/	48
3	1.0	/	42
4	0.5	/	trace
5	0	/	trace
6	1.0	/	trace
7	1.0	H$_2$O/5	52
8	1.5	H$_2$O/10	54
9	1.5	H$_2$O/0	26
10	1.5	H$_2$O/5	53
11	1.5	H$_2$O/15	36
12[b]	1.5	H$_2$O/5	46
13[c]	1.5	H$_2$O/5	25
14	1.5	H$_2$O/5	16
15	1.5	H$_2$O/NH$_4$Cl/5/1	16

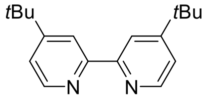
[a] Yields were determined by ^{1}H NMR spectroscopy with mesitylene as an internal standard. [b] Boc$_2$O/K$_2$CO$_3$ 1.5 eq; [c] Boc$_2$O/K$_2$CO$_3$ 1.7 equiv.

Note: The experiments showed good tolerance when water was added to the system, indicating its potential practicality.

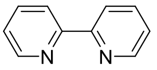
Screening of different kinds of NHCs and Ligands



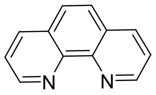
Entry	Solvent	Ligand	Yield (%)[a]
1	*t*BuOMe	L_1	60
2	*t*BuOMe	L_2	37
3	*t*BuOMe	L_3	32
4	*t*BuOMe	L_4	30
5	*t*BuOMe	L_5	trace
6	PhCF$_3$	L_1	54
7	1,4-Dioxane	L_1	72
8	THF	L_1	13
9	MeCN	L_1	<10%
10[b]	1,4-Dioxane	L_1	75
11[b,c]	1,4-Dioxane	L_1	78



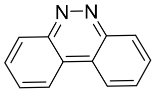
L$_1$



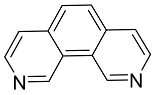
L$_2$



L$_3$



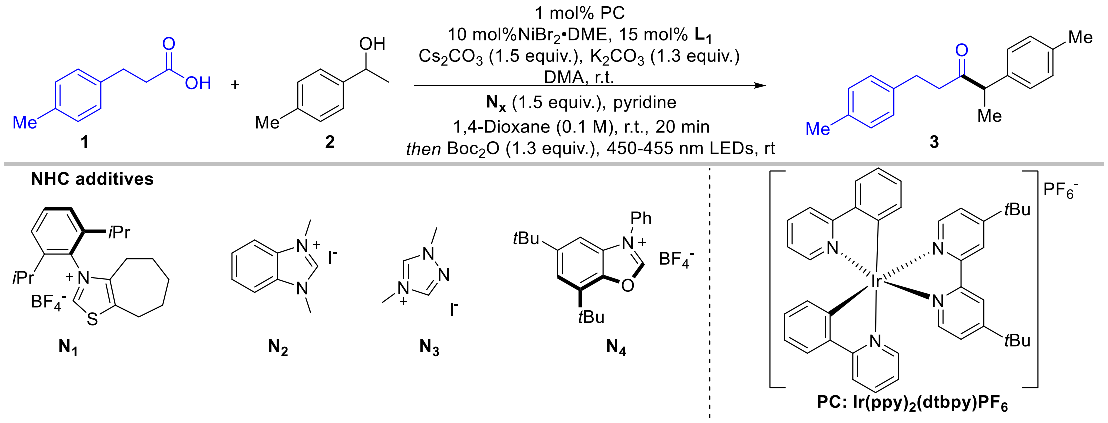
L$_4$



L$_5$

[a] Yields were determined by ^{1}H NMR spectroscopy with mesitylene as an internal standard. [b] 20 h; [c] 5 mol% NiBr$_2$•DME, 7.5 mol% dtbbpy

Systematic screening of different kinds of NHCs

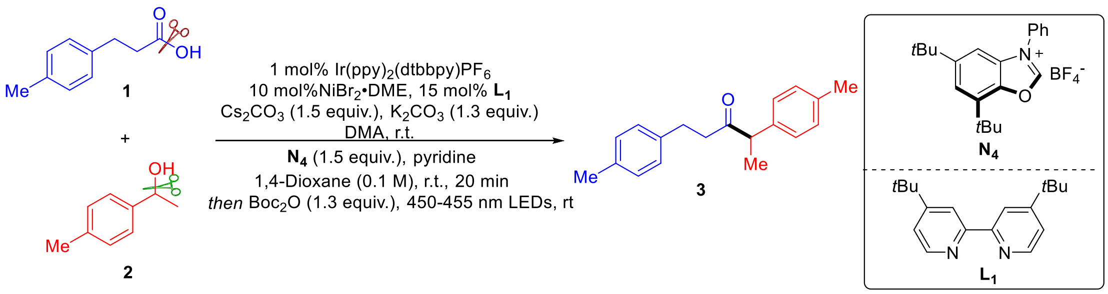


Entry	Nx	Yield (%)[a]
1	**N$_1$**	0
2	**N$_2$**	trace
3	**N$_3$**	0

4	$\mathbf{N_4}$	75

[a]Yields were determined by ^{1}H NMR spectroscopy with mesitylene as an internal standard.

III. General Procedure for Direct Ketone Synthesis from Carboxylic Acids and Alcohols via Metallaphotoredox Catalysis



General procedure A:

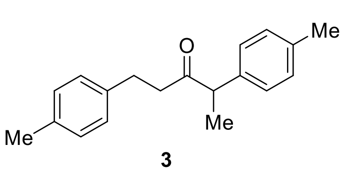
An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, $Ir(ppy)_2(dtbbpy)PF_6$ (0.003 mmol), dtbbpy (L_1) (0.0225 mmol), K_2CO_3 (0.39 mmol), Cs_2CO_3 (0.45 mmol) and $NiBr_2$•DME (0.015 mmol) were added sequentially under N_2 atmosphere. Then DMAc (3 mL) was added. The reaction mixture was stirred at room temperature for 30 min.

Another oven-dried 10 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, NHC (N_4) (0.45 mmol), 1,4-dioxane (3 mL) and alcohol **2** (0.42 mmol) were added. Then pyridine (0.42 mmol) was added dropwise via a microsyringe. The reaction mixture was stirred for 20 min at room temperature. The 1,4-dioxane suspension was transferred to a 5 ml syringe under N_2. Then a syringe filter and a new needle were installed on the syringe, and the 1,4-dioxane solution was injected through the syringe filter into the mentioned above flask containing the Ir/Ni catalysts followed by adding carboxylic acid **1** (0.3 mmol) and Boc_2O (0.39 mmol). The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDS at a distance of 5 cm for 24 h at room temperature. The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography on silica gel to afford the desired ketone.

General procedure B:

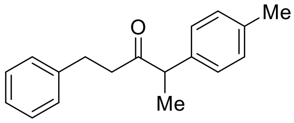
An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.004 mmol), dtbbpy (L_1) (0.03 mmol), K_2CO_3 (0.52 mmol), Cs_2CO_3 (0.60 mmol) and $NiBr_2$•DME (0.02 mmol) were added sequentially under N_2 atmosphere. Then DMAc (4 mL) was added. The reaction mixture was stirred at room temperature for 30 min.

Another oven-dried 10 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, NHC (N_4) (0.60 mmol), 1,4-dioxane (4 mL) and alcohol **2** (0.56 mmol) were added. Then pyridine (0.56 mmol) was added dropwise via a microsyringe. The reaction mixture was stirred for 20 min at room temperature. The 1,4-dioxane suspension was transferred to a 5 ml syringe under N_2. Then a syringe filter and a new needle were installed on the syringe, and the 1,4-dioxane solution was injected through the syringe filter into the mentioned above flask containing the Ir/Ni catalysts followed by adding carboxylic acid **1** (0.4 mmol) and Boc$_2$O (0.52 mmol). The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDS at a distance of 5 cm for 24 h at room temperature. The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography on silica gel to afford the desired ketone.



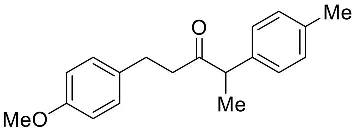
3

1,4-di-*p*-tolylpentan-3-one (**3**). Prepared according to the general procedure A employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.7mg, 0.003 mmol), dtbbpy (L_1) (6.4 mg, 0.0225 mmol), K_2CO_3 (53.8 mg, 0.39 mmol), Cs_2CO_3 (147.0 mg, 0.45 mmol), $NiBr_2$•DME (4.7 mg, 0.015 mmol), NHC (177.6 mg, 0.45 mmol), 1,4-dioxane (3 mL), 1-(4-Methylphenyl)ethanol (56.8 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 3-(4-methylphenyl)propionic acid (49.8 mg, 0.3 mmom) and Boc$_2$O (85.2 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 45/1) on silica gel to afford **3** (59.9 mg, 0.225 mmol, 75% yield) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 6.98 (m, 6H), 6.94 (d, *J* = 8.0 Hz, 2H), 3.65 (q, *J* = 6.8 Hz, 1H), 2.86 – 2.57 (m, 4H), 2.31 (s, 3H), 2.28 (s, 3H), 1.34 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.1, 137.9, 137.4, 136.7, 135.3, 129.5, 129.0, 128.1, 127.7, 52.7, 42.6, 29.5, 21.0, 20.9, 17.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{22}ONa$ $[M+Na]^+$: 289.1563; Found 289.1570.



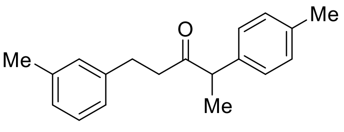
4

1-phenyl-4-(*p*-tolyl)pentan-3-one (**4**).[1] Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.9 mg, 0.004 mmol), dtbbpy (L_1) (8.5 mg, 0.03 mmol), K_2CO_3 (72.1 mg, 0.60 mmol), Cs_2CO_3 (196.1 mg, 0.60 mmol), $NiBr_2$•DME (6.4 mg, 0.02 mmol), NHC (236.0 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-Methylphenyl)ethanol (78.1 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-Phenylpropanoic acid (60.2 mg, 0.4 mmom) and Boc_2O (114.0 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **4** (60.5 mg, 0.24 mmol, 60% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (dd, *J* = 6.8, 6.4 Hz, 2H), 7.17 – 6.98 (m, 7H), 3.65 (q, *J* = 7.2 Hz, 1H), 2.91 – 2.71 (m, 2H), 2.69 – 2.57 (m, 2H), 2.30 (s, 3H), 1.35 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.0, 141.0, 137.4, 136.7, 129.5, 128.3, 128.2, 127.6, 125.9, 52.7, 42.4, 29.9, 21.0, 17.3.



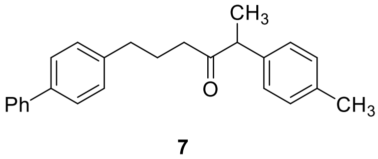
5

1-(4-methoxyphenyl)-4-(*p*-tolyl)pentan-3-one (**5**).[2] Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.9 mg, 0.004 mmol), dtbbpy (L_1) (8.5 mg, 0.03 mmol), K_2CO_3 (72.0 mg, 0.60 mmol), Cs_2CO_3 (194.7 mg, 0.60 mmol), $NiBr_2$•DME (6.6mg, 0.02 mmol), NHC (237.9 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.7 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-methoxyphenyl)propanoic acid (50.8 mg, 0.4 mmom) and Boc_2O (113.7 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **5** (60.5 mg, 0.18 mmol, 45% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 3.65 (q, *J* = 6.8 Hz, 1H), 2.84 – 2.55 (m, 4H), 2.31 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.2, 157.8, 137.4, 136.7, 133.1, 129.5, 129.1, 127.7, 113.7, 55.2, 52.7, 42.7, 29.1, 21.0, 17.3.



6

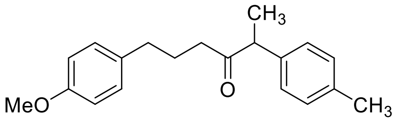
1-(m-tolyl)-4-(p-tolyl)pentan-3-one (**6**). Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.9 mg, 0.004 mmol), dtbbpy (L_1) (8.0 mg, 0.03 mmol), K_2CO_3 (71.9 mg, 0.60 mmol), Cs_2CO_3 (194.7 mg, 0.60 mmol), $NiBr_2$•DME (6.6mg, 0.02 mmol), NHC (236.7 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (77.7 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(3-methylphenyl)propionic acid (66.0 mg, 0.4 mmom) and Boc_2O (113.5 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **6** (66.0 mg, 0.248 mmol, 62% yield) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 7.07 (m, 3H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.88 – 6.82 (m, 2H), 3.66 (q, *J* = 6.8 Hz, 1H), 2.85 – 2.55 (m, 4H), 2.31 (s, 3H), 2.26 (s, 3H), 1.35 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.1, 141.0, 137.9, 137.4, 136.7, 129.5, 129.0, 128.2, 127.7, 126.6, 125.2, 52.7, 42.5, 29.8, 21.3, 21.0, 17.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{22}ONa$ $[M+Na]^+$: 289.1563; Found 289.1571.



7

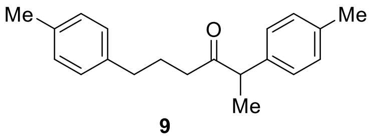
6-([1,1'-biphenyl]-4-yl)-2-(*p*-tolyl)hexan-3-one (**7**). Prepared according to the general procedure A employing $Ir(ppy)_2(dtbbpy)PF_6$ (2.7 mg, 0.003 mmol), dtbbpy (L_1) (6.2 mg, 0.0225 mmol), K_2CO_3 (53.3 mg, 0.39 mmol), Cs_2CO_3 (147.1 mg, 0.45 mmol), $NiBr_2$•DME (4.8 mg, 0.015 mmol), NHC (177.5 mg, 0.45 mmol), 1,4-dioxane (3 mL), 1-(4-methylphenyl)ethanol (57.4

mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 4-(4-biphenylyl)butyric acid (72.2 mg, 0.3 mmom) and Boc$_2$O (85.2 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 45/1) on silica gel to afford **7** (62.7 mg, 0.183 mmol, 61% yield) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.49 – 7.39 (m, 4H), 7.35 – 7.29 (m, 1H), 7.17-7.05 (m, 6H), 3.70 (q, *J* = 6.8 Hz, 1H), 2.61 – 2.35 (m, 4H), 2.33 (s, 3H), 1.90-1.79 (m, 2H), 1.36 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.8, 141.0, 140.8, 138.7, 137.6, 136.8, 129.6, 128.8, 128.7, 127.7, 127.0, 126.9, 52.6, 40.0, 34.5, 25.3, 21.0, 17.4; HRMS (ESI-TOF) Calcd for $C_{25}H_{26}ONa$ $[M+Na]^+$: 365.1876; Found 365.1885.



8

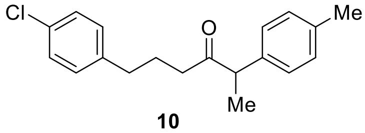
6-(4-methoxyphenyl)-2-(*p*-tolyl)hexan-3-one (**8**).[3] Prepared according to the general procedure A employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.8 mg, 0.003 mmol), dtbbpy (L$_1$) (6.2 mg, 0.0225 mmol), K$_2$CO$_3$ (54.5 mg, 0.39 mmol), Cs$_2$CO$_3$ (147.0 mg, 0.45 mmol), NiBr$_2$•DME (4.7 mg, 0.015 mmol), NHC (178.0 mg, 0.45 mmol), 1,4-dioxane (3 mL), 1-(4-methylphenyl)ethanol (57.2 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 4-(4-methoxyphenyl)butyric acid (58.3 mg, 0.3 mmol) and Boc$_2$O (85.2 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 45/1) on silica gel to afford **8** (53.3 mg, 0.18 mmol, 60% yield) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.68 (q, *J* = 7.2 Hz, 1H), 2.50 – 2.31 (m, 7H), 1.82-1.72 (m, 2H), 1.48 (s, 3H), 1.35 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.9, 136.7, 133.7, 129.8, 129.6, 129.3, 127.7, 125.5, 113.6, 55.2, 52.5, 40.0, 34.0, 31.6, 29.7, 25.5, 21.0.



9

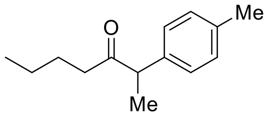
2,6-di-*p*-tolylhexan-3-one (**9**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.7 mg, 0.004 mmol), dtbbpy (L$_1$) (8.5 mg, 0.03 mmol), K$_2$CO$_3$ (72.0 mg, 0.60

mmol), Cs_2CO_3 (196.0 mg, 0.60 mmol), $NiBr_2$•DME (6.6 mg, 0.02 mmol), NHC (237.5 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.7 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 4-(*p*-Tolyl)butanoic acid (72.0 mg, 0.4 mmol) and Boc_2O (113.6 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **9** (140.2 mg, 0.20 mmol, 50% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.00 (m, 4H), 6.93 (d, *J* = 8.0 Hz, 2H), 3.67 (q, *J* = 7.0 Hz, 1H), 2.52 – 2.31 (m, 7H), 2.29 (s, 3H), 1.78 (p, *J* = 7.2 Hz, 2H), 1.35 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.8, 138.6, 137.6, 136.7, 135.1, 129.5, 128.9, 128.2, 127.7, 52.5, 40.1, 34.4, 25.4, 21.0, 20.9, 17.4; HRMS (ESI-TOF) Calcd for $C_{20}H_{24}ONa$ $[M+Na]^+$: 303.1719; Found 303.1727.



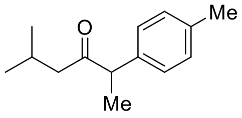
10

6-(4-chlorophenyl)-2-(*p*-tolyl)hexan-3-one (**10**). Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.7 mg, 0.004 mmol), dtbbpy (L_1) (8.4 mg, 0.03 mmol), K_2CO_3 (71.9 mg, 0.60 mmol), Cs_2CO_3 (196.0 mg, 0.60 mmol), $NiBr_2$•DME (6.5 mg, 0.02 mmol), NHC (237.0 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.7 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 4-(4-chlorophenyl)butyric acid (79.4 mg, 0.4 mmol) and Boc_2O (114.0 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **10** (66.0 mg, 0.22 mmol, 55% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 3.68 (q, *J* = 6.8 Hz, 1H), 2.53 – 2.25 (m, 7H), 1.83-1.72 (m, 2H), 1.36 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.6, 140.1, 137.5, 136.8, 129.7, 129.6, 128.3, 127.7, 52.6, 39.7, 34.1, 25.1, 21.0, 17.4; HRMS (ESI-TOF) Calcd for $C_{19}H_{21}ClONa$ $[M+Na]^+$: 323.1173; Found 323.1179.



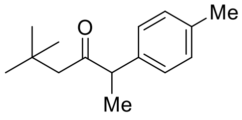
11

2-(*p*-tolyl)heptan-3-one (**11**).[4] Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.3 mg, 0.03 mmol), K$_2$CO$_3$ (71.8 mg, 0.60 mmol), Cs$_2$CO$_3$ (196.0 mg, 0.60 mmol), NiBr$_2$•DME (6.3 mg, 0.02 mmol), NHC (237.0 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.8 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), valeric acid (41.3 mg, 0.4 mmol) and Boc$_2$O (114.0 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 30/1) on silica gel to afford **11** (49.8 mg, 0.244 mmol, 61% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16-7.06 (m, 4H), 3.71 (q, *J* = 7.2 Hz, 1H), 2.39 – 2.27 (m, 5H), 1.53-1.40 (m, 2H), 1.36 (d, *J* = 7.2 Hz, 3H), 1.24 – 1.13 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.3, 137.7, 136.6, 129.5, 127.7, 52.5, 40.6, 25.9, 22.2, 21.0, 17.5, 13.8.



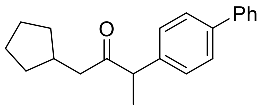
12

5-methyl-2-(*p*-tolyl)hexan-3-one (**12**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.3 mg, 0.03 mmol), K$_2$CO$_3$ (71.7 mg, 0.60 mmol), Cs$_2$CO$_3$ (196.0 mg, 0.60 mmol), NiBr$_2$•DME (6.5 mg, 0.02 mmol), NHC (236.7 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.8 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-methylbutanoic acid (41.0 mg, 0.4 mmol) and Boc$_2$O (113.9 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **12** (65.3 mg, 0.32 mmol, 80% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (q, *J* = 8.0 Hz, 4H), 3.68 (q, *J* = 6.8 Hz, 1H), 2.32 (s, 3H), 2.28 – 2.16 (m, 2H), 2.15 – 2.03 (m, 1H), 1.35 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.6, 137.5, 136.6, 129.5, 127.7, 52.8, 49.9, 24.3, 22.5, 22.2, 21.0, 17.4; HRMS (ESI-TOF) Calcd for $C_{14}H_{20}ONa$ $[M+Na]^+$: 227.1406; Found 227.1405.



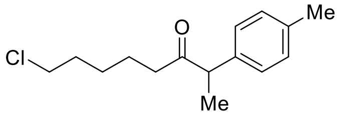
13

2-([1,1'-biphenyl]-4-yl)-5,5-dimethylhexan-3-one (**13**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.3 mg, 0.03 mmol), K_2CO_3 (71.7 mg, 0.60 mmol), Cs_2CO_3 (196.0 mg, 0.60 mmol), NiBr$_2$•DME (6.4 mg, 0.02 mmol), NHC (237.6 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.8 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3,3-dimethylbutyric acid (47.0 mg, 0.4 mmol) and Boc$_2$O (113.9 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **13** (78.6 mg, 0.36 mmol, 90% yield) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.53 (m, 4H), 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.76 (q, *J* = 6.8 Hz, 1H), 2.37 (d, *J* = 15.6 Hz, 1H), 2.22 (d, *J* = 15.6 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.3, 140.6, 139.9, 139.5, 128.7, 128.4, 127.5, 127.3, 127.0, 54.0, 53.4, 31.0, 29.6, 17.5; HRMS (ESI-TOF) Calcd for $C_{15}H_{22}ONa$ $[M+Na]^+$: 241.1563; Found 241.1559.



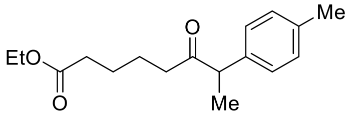
14

3-([1,1'-biphenyl]-4-yl)-1-cyclopentylbutan-2-one (**14**). Prepared according to the general procedure A employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.9 mg, 0.003 mmol), dtbbpy (L$_1$) (6.0 mg, 0.0225 mmol), K_2CO_3 (54.0 mg, 0.39 mmol), Cs_2CO_3 (147.1 mg, 0.45 mmol), NiBr$_2$•DME (4.8 mg, 0.015 mmol), NHC (177.2 mg, 0.45 mmol), 1,4-dioxane (3 mL), 1-(4-methylphenyl)ethanol (83.4 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 2-cyclopentylacetic acid (38.5 mg, 0.3 mmom) and Boc$_2$O (85.2 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 45/1) on silica gel to afford **14** (47.3 mg, 0.162 mmol, 54% yield) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.53 (m, 4H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.31 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.79 (q, *J* = 7.0 Hz, 1H), 2.48-2.34 (m, 2H), 2.29 – 2.14 (m, 1H), 1.86 – 1.66 (m, 2H), 1.56 – 1.45 (m, 4H), 1.41 (d, *J* = 7.2 Hz, 3H), 1.07 – 0.83 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.7, 140.6, 139.9, 139.7, 128.8, 128.3, 127.5, 127.3, 127.0, 52.7, 47.4, 35.5, 32.6, 32.3, 24.9, 24.8, 17.5; HRMS (ESI-TOF) Calcd for $C_{21}H_{24}ONa$ $[M+Na]^+$: 315.1719; Found 315.1721.



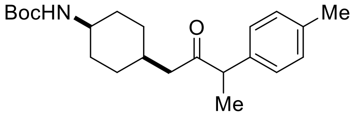
15

8-chloro-2-(*p*-tolyl)octan-3-one (**15**). Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.8 mg, 0.004 mmol), dtbbpy (L_1) (8.3 mg, 0.03 mmol), K_2CO_3 (72.0 mg, 0.60 mmol), Cs_2CO_3 (196.0 mg, 0.60 mmol), $NiBr_2$•DME (6.5 mg, 0.02 mmol), NHC (237.6 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.7 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 6-chlorohexanoic acid (60.5 mg, 0.4 mmol) and Boc_2O (114.0 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1 to 30/1) on silica gel to afford **15** (64.6 mg, 0.256 mmol, 64% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.05 (m, 4H), 3.70 (q, J = 6.8 Hz, 1H), 3.45 (t, J = 6.8 Hz, 2H), 2.45-2.27 (m, 5H), 1.72-1.61 (m, 2H), 1.56 – 1.45 (m, 2H), 1.36 (d, J = 6.8 Hz, 3H), 1.34 – 1.26 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.8, 137.6, 136.8, 129.6, 127.7, 52.6, 44.8, 40.5, 32.3, 26.2, 23.0, 21.0, 17.4; HRMS (ESI-TOF) Calcd for $C_{15}H_{21}ClONa$ $[M+Na]^+$: 275.1173; Found 275.1185.



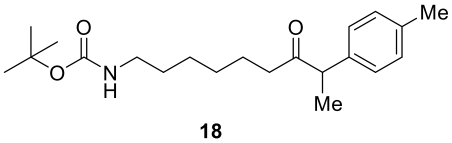
16

ethyl 6-oxo-7-(*p*-tolyl)octanoate (**16**). Prepared according to the general procedure A employing $Ir(ppy)_2(dtbbpy)PF_6$ (2.9 mg, 0.003 mmol), dtbbpy (L_1) (6.3 mg, 0.0225 mmol), K_2CO_3 (53.9 mg, 0.39 mmol), Cs_2CO_3 (147.0 mg, 0.45 mmol), $NiBr_2$•DME (4.8 mg, 0.015 mmol), NHC (177.4 mg, 0.45 mmol), 1,4-dioxane (3 mL), 1-(4-methylphenyl)ethanol (57.8 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 6-ethoxy-6-oxohexanoic acid (52.4 mg, 0.3 mmom) and Boc_2O (85.2 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 25/1) on silica gel to afford **16** (67.0 mg, 0.243 mmol, 81% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.04 (m, 4H), 4.09 (q, J = 7.1 Hz, 2H), 3.70 (q, J = 7.0 Hz, 1H), 2.41 – 2.28 (m, 5H), 2.24 – 2.15 (m, 2H), 1.58 – 1.44 (m, 4H), 1.36 (d, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.5, 173.3, 137.5, 136.7, 129.5, 127.6, 60.1, 52.5, 40.3, 33.9, 24.2, 23.2, 20.9, 17.3, 14.1; HRMS (ESI-TOF) Calcd for $C_{17}H_{24}O_3Na$ $[M+Na]^+$: 299.1618; Found 299.1627.



17

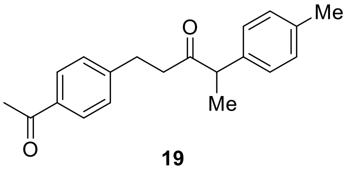
tert-butyl ((1s,4s)-4-(2-oxo-3-(*p*-tolyl)butyl)cyclohexyl)carbamate (**17**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.3 mg, 0.03 mmol), K_2CO_3 (72.0 mg, 0.60 mmol), Cs_2CO_3 (196.0 mg, 0.60 mmol), NiBr$_2$•DME (6.5 mg, 0.02 mmol), NHC (237.6 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 2-(*cis*-4-((*tert*-butoxycarbonyl)amino)cyclohexyl)acetic acid (102.8 mg, 0.4 mmol) and Boc$_2$O (114.0 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1 to 30/1) on silica gel to afford **17** (103.5 mg, 0.288 mmol, 72% yield) as a yellow oil. The *dr* could not be determined through ^{1}H NMR analysis. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 4.59 (s, 1H), 3.67 (q, J = 6.8 Hz, 2H), 2.33 (s, 3H), 2.29 – 2.24 (m, 2H), 1.99-1.83 (m, 1H), 1.61-1.38 (m, 17H), 1.35 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.0, 155.0, 137.3, 136.7, 129.5, 127.6, 78.9, 52.9, 46.5, 31.4, 29.5, 28.3, 27.6, 20.9, 17.2; HRMS (ESI-TOF) Calcd for $C_{22}H_{33}NO_3Na$ $[M+Na]^+$: 382.2353; Found 382.2359.



18

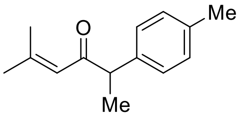
tert-butyl (7-oxo-8-(*p*-tolyl)nonyl)carbamate (**18**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.3 mg, 0.03 mmol), K_2CO_3 (72.0 mg, 0.60 mmol), Cs_2CO_3 (196.0 mg, 0.60 mmol), NiBr$_2$•DME (6.5 mg, 0.02 mmol), NHC (237.5 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 7-((*tert*-

butoxycarbonyl)amino) heptanoic acid (98.1 mg, 0.4 mmol) and Boc_2O (114.1 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 10/1) on silica gel to afford **18** (86.1 mg, 0.248 mmol, 62% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 3.64 (q, *J* = 6.8 Hz, 1H), 2.85 – 2.55 (m, 4H), 2.28 (s, 3H), 1.34 (d, *J* = 7.2 Hz, 3H).; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.3, 158.6, 138.0, 135.4, 132.5, 129.0, 128.8, 128.1, 114.2, 55.2, 52.2, 42.6, 29.5, 20.9, 17.3; HRMS (ESI-TOF) Calcd for $C_{21}H_{33}NO_3Na$ $[M+Na]^+$: 370.2353; Found 370.2360.



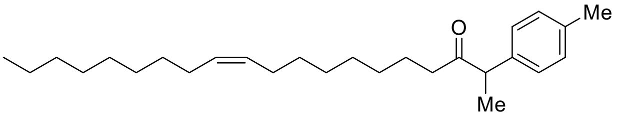
19

1-(4-acetylphenyl)-4-(*p*-tolyl)pentan-3-one (**19**). *tert*-butyl (7-oxo-8-(*p*-tolyl)nonyl)carbamate (**18**). Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.7 mg, 0.004 mmol), dtbbpy (L_1) (8.3 mg, 0.03 mmol), K_2CO_3 (71.5 mg, 0.60 mmol), Cs_2CO_3 (196.0 mg, 0.60 mmol), $NiBr_2$•DME (6.5 mg, 0.02 mmol), NHC (236.9 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-acetylphenyl)propanoic acid (77.0 mg, 0.4 mmol) and Boc_2O (113.5 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 15/1) on silica gel to afford **19** (68.2 mg, 0.232 mmol, 58% yield) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.67 (q, *J* = 6.8 Hz, 1H), 2.93 – 2.78 (m, 2H), 2.77 – 2.60 (m, 2H), 2.55 (s, 3H), 2.31 (s, 3H), 1.35 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.3, 197.6, 146.8, 137.1, 136.8, 135.0, 129.5, 128.42, 128.40, 127.6, 52.7, 41.6, 29.7, 26.4, 20.9, 17.2; HRMS (ESI-TOF) Calcd for $C_{20}H_{22}O_2Na$ $[M+Na]^+$: 317.1512; Found 317.1519.



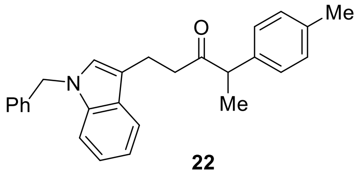
20

5-methyl-2-(*p*-tolyl)hex-4-en-3-one (**20**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.2 mg, 0.03 mmol), K$_2$CO$_3$ (71.5 mg, 0.60 mmol), Cs$_2$CO$_3$ (195.9 mg, 0.60 mmol), NiBr$_2$•DME (6.5 mg, 0.02 mmol), NHC (237.3 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.7 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-methylbut-2-enoic acid (40.0 mg, 0.4 mmol) and Boc$_2$O (113.4 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **20** (66.3 mg, 0.328 mmol, 82% yield) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.07 (m, 4H), 5.99 (s, 1H), 3.70 (q, J = 6.8 Hz, 1H), 2.32 (s, 3H), 2.14 (s, 3H), 1.79 (s, 3H), 1.37 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.5, 156.0, 138.2, 136.4, 129.5, 127.8, 123.0, 53.1, 27.7, 21.0, 20.8, 17.6; HRMS (ESI-TOF) Calcd for $C_{14}H_{18}O$ Na [M+Na]$^+$: 225.1250; Found 225.1254.



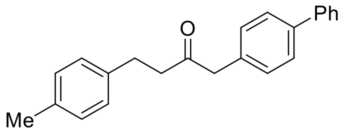
21

(*Z*)-2-(*p*-tolyl)icos-11-en-3-one (**21**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.9 mg, 0.004 mmol), dtbbpy (L$_1$) (8.3 mg, 0.03 mmol), K$_2$CO$_3$ (71.7 mg, 0.60 mmol), Cs$_2$CO$_3$ (195.8 mg, 0.60 mmol), NiBr$_2$•DME (6.5 mg, 0.02 mmol), NHC (238.0 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.6 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), (9Z)-9-Octadecenoicacid (113.1 mg, 0.4 mmol) and Boc$_2$O (113.8 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 40/1) on silica gel to afford **21** (115.0 mg, 0.299 mmol, 75% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.39 – 5.26 (m, 2H), 3.70 (q, J = 7.0 Hz, 1H), 2.41 – 2.24 (m, 5H), 2.08 – 1.88 (m, 4H), 1.55-1.41 (m, 2H), 1.40 – 1.06 (m, 23H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.0, 137.7, 136.6, 129.8, 129.7, 129.5, 127.6, 52.5, 40.8, 31.8, 29.7, 29.6, 29.5, 29.3, 29.2, 29.0, 28.9, 27.14, 27.10, 23.8, 22.6, 20.9, 17.4, 14.1; HRMS (ESI-TOF) Calcd for $C_{27}H_{44}ONa$ $[M+Na]^+$: 407.3284; Found 407.3293.



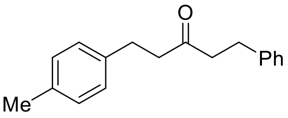
22

1-(1-benzyl-1*H*-indol-3-yl)-4-(*p*-tolyl)pentan-3-one (**22**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.4 mg, 0.03 mmol), K_2CO_3 (71.8 mg, 0.60 mmol), Cs_2CO_3 (195.0 mg, 0.60 mmol), NiBr$_2$•DME (6.5 mg, 0.02 mmol), NHC (238.1 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-methylphenyl)ethanol (76.6 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), corresponding carboxylic acid (111.5 mg, 0.4 mmol) and Boc$_2$O (113.7 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 30/1 to 20/1) on silica gel to afford **22** (57.0 mg, 0.150 mmol, 37% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, J = 7.6 Hz, 1H), 7.29 – 7.16 (m, 4H), 7.12 (t, J = 7.6 Hz, 1H), 7.09 – 6.97 (m, 7H), 6.73 (s, 1H), 5.18 (s, 2H), 3.65 (q, J = 6.8 Hz, 1H), 3.05 – 2.84 (m, 2H), 2.83-2.65 (m, 2H), 2.29 (s, 3H), 1.33 (d, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.7, 137.6, 137.5, 136.7, 136.5, 129.5, 128.6, 127.8, 127.7, 127.4, 126.6, 125.5, 121.6, 118.9, 118.8, 114.4, 109.6, 52.7, 49.7, 41.4, 21.0, 19.5, 17.3; HRMS (ESI-TOF) Calcd for $C_{27}H_{27}NONa$ $[M+Na]^+$: 404.1985; Found 404.1993.



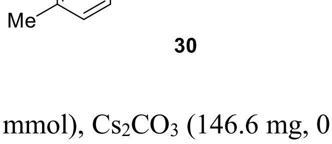
28

1-([1,1'-biphenyl]-4-yl)-4-(*p*-tolyl)butan-2-one (**28**). Prepared according to the general procedure A employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.6 mg, 0.003 mmol), dtbbpy (L$_1$) (6.1 mg, 0.0225 mmol), K_2CO_3 (53.4 mg, 0.39 mmol), Cs_2CO_3 (146.6 mg, 0.45 mmol), NiBr$_2$•DME (4.7 mg, 0.015 mmol), NHC (177.5 mg, 0.45 mmol), 1,4-dioxane (3 mL), 4-biphenylmethanol (78.5 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 3-(4-methylphenyl)propionic acid (49.3 mg, 0.3 mmom) and Boc$_2$O (85.2 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 45/1) on silica gel to afford **28** (61.9 mg, 0.197 mmol, 62% yield) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 3H), 7.26 – 7.19 (m, 2H), 7.10-6.98 (m, 4H), 3.69 (s, 2H), 2.90 – 2.73 (m, 4H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.5, 140.8, 140.0, 137.8, 135.6, 133.1, 129.8, 129.2, 128.8, 128.2, 127.5, 127.3, 127.1, 50.0, 43.8, 29.4, 21.0; HRMS (ESI-TOF) Calcd for $C_{23}H_{22}ONa$ [M+Na]$^+$: 337.1563; Found 337.1572.



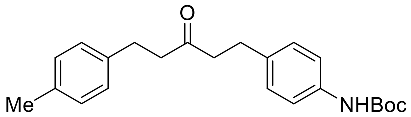
29

1-phenyl-5-(*p*-tolyl)pentan-3-one (**29**). Prepared according to the general procedure A employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.8 mg, 0.003 mmol), dtbbpy (L$_1$) (6.1 mg, 0.0225 mmol), K_2CO_3 (53.4 mg, 0.39 mmol), Cs_2CO_3 (146.6 mg, 0.45 mmol), NiBr$_2$•DME (4.7 mg, 0.015 mmol), NHC (177.5 mg, 0.45 mmol), 1,4-dioxane (3 mL), Phenethyl alcohol (51.1 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 3-(4-methylphenyl)propionic acid (50.0 mg, 0.3 mmom) and Boc$_2$O (85.1 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 45/1) on silica gel to afford **29** (37.8 mg, 0.20 mmol, 50% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 6.4 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.10-7.01 (m, 4H), 2.92-2.80 (m, 4H), 2.74-2.64 (m, 4H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.2, 141.0, 137.9, 135.6, 129.1, 128.5, 128.3, 128.1, 126.1, 44.6, 44.5, 29.7, 29.3, 21.0; HRMS (ESI-TOF) Calcd for $C_{18}H_{20}ONa$ [M+Na]$^+$: 275.1406; Found 275.1415.

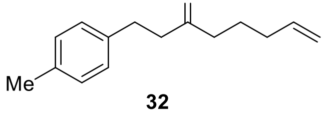


30

6-phenyl-1-(*p*-tolyl)hexan-3-one (**30**).[5] Prepared according to the general procedure A employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.8 mg, 0.003 mmol), dtbbpy (L$_1$) (6.1 mg, 0.0225 mmol), K_2CO_3 (53.4 mg, 0.39 mmol), Cs_2CO_3 (146.6 mg, 0.45 mmol), NiBr$_2$•DME (4.7 mg, 0.015 mmol), NHC (177.5 mg, 0.45 mmol), 1,4-dioxane (3 mL), 3-phenyl-1-propanol (56.9 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 3-(4-methylphenyl)propionic acid (50.0 mg, 0.3 mmom) and Boc$_2$O (85.3 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 45/1) on silica gel to afford **30** (43.95 mg, 0.165 mmol, 55% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.14 (dd, *J* = 7.2, 6.8 Hz, 2H), 7.11 – 7.02 (m, 4H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.71 – 2.64 (m, 2H), 2.62 – 2.55 (m, 2H), 2.41-2.34 (m, 2H), 2.30 (s, 3H), 1.95 – 1.83 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.0, 141.6, 138.0, 135.5, 129.1, 128.4, 128.3, 128.1, 125.9, 44.4, 42.1, 35.0, 29.3, 25.1, 21.0.

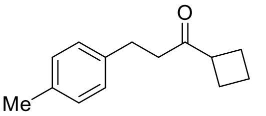

31

tert-butyl (4-(3-oxo-5-(*p*-tolyl)pentyl)phenyl)carbamate (**31**). Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.8 mg, 0.004 mmol), dtbbpy (L_1) (8.4 mg, 0.03 mmol), K_2CO_3 (71.8 mg, 0.60 mmol), Cs_2CO_3 (195.0 mg, 0.60 mmol), $NiBr_2$•DME (6.5 mg, 0.02 mmol), NHC (237.4 mg, 0.60 mmol), 1,4-dioxane (4 mL), *N*-Boc-2-(4-aminophenyl)ethanol (131.2 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-methylphenyl)propionic acid (66.0 mg, 0.4 mmol) and Boc_2O (113.6 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 10/1 to 5/1) on silica gel to afford **31** (58.8 mg, 0.160 mmol, 40% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.11-7.00 (m, 6H), 6.49 (s, 1H), 2.87-2.77 (m, 4H), 2.71-2.61 (m, 4H), 2.30 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.3, 152.8, 137.8, 136.4, 135.6, 135.5, 129.1, 128.7, 128.1, 118.7, 80.3, 44.6, 44.5, 29.2, 29.0, 28.3, 20.9; HRMS (ESI-TOF) Calcd for $C_{23}H_{29}NO_3ONa$ $[M+Na]^+$: 390.2040; Found 390.2046.


32

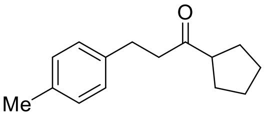
1-(*p*-tolyl)oct-7-en-3-one (**32**). Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.8 mg, 0.004 mmol), dtbbpy (L_1) (8.1 mg, 0.03 mmol), K_2CO_3 (69.7 mg, 0.60 mmol), Cs_2CO_3 (195.0 mg, 0.60 mmol), $NiBr_2$•DME (6.5 mg, 0.02 mmol), NHC (238.1 mg, 0.60 mmol), 1,4-dioxane (4 mL), 4-penten-1-ol (47.6 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-

methylphenyl)propionic acid (65.8 mg, 0.4 mmol) and Boc$_2$O (114.0 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA =50/1 to 40/1) on silica gel to afford **32** (38.9 mg, 0.180 mmol, 45% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 – 7.02 (m, 4H), 5.81 – 5.67 (m, 1H), 5.05 – 4.91 (m, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.38 (t, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 2.03 (q, *J* = 7.2 Hz, 2H), 1.71 – 1.62 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.1, 138.0, 137.9, 135.5, 129.1, 128.1, 115.2, 44.5, 42.1, 33.0, 29.3, 22.7, 20.9; HRMS (ESI-TOF) Calcd for C$_{15}$H$_{20}$ONa [M+Na]$^+$: 239.1406; Found 239.1406.



33

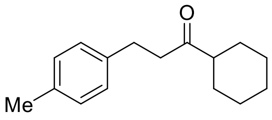
1-cyclobutyl-3-(*p*-tolyl)propan-1-one (**33**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.6 mg, 0.004 mmol), dtbbpy (L$_1$) (8.4 mg, 0.03 mmol), K$_2$CO$_3$ (71.8 mg, 0.60 mmol), Cs$_2$CO$_3$ (195.0 mg, 0.60 mmol), NiBr$_2$•DME (6.5 mg, 0.02 mmol), NHC (237.3 mg, 0.60 mmol), 1,4-dioxane (4 mL), cyclobutanol (39.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-methylphenyl)propionic acid (66.5 mg, 0.4 mmol) and Boc$_2$O (113.7 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 45/1) on silica gel to afford **33** (32.3 mg, 0.160 mmol, 40% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 – 7.03 (m, 4H), 3.22 (p, *J* = 8.0 Hz, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 2.25 – 2.04 (m, 4H), 2.01 – 1.88 (m, 1H), 1.84 – 1.73 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.1, 138.2, 135.5, 129.1, 128.1, 45.4, 41.7, 29.2, 24.2, 20.9, 17.7; HRMS (ESI-TOF) Calcd for C$_{14}$H$_{18}$ONa [M+Na]$^+$: 225.1250; Found 225.1253.



34

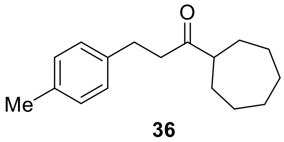
1-cyclopentyl-3-(*p*-tolyl)propan-1-one (**34**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.6 mg, 0.004 mmol), dtbbpy (L$_1$) (8.4 mg, 0.03 mmol), K$_2$CO$_3$ (71.8 mg, 0.60 mmol),

Cs_2CO_3 (195.0 mg, 0.60 mmol), $NiBr_2$•DME (6.5 mg, 0.02 mmol), NHC (237.3 mg, 0.60 mmol), 1,4-dioxane (4 mL), cyclopentanol (48.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-methylphenyl)propionic acid (65.1 mg, 0.4 mmol) and Boc_2O (113.5 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 60/1) on silica gel to afford **34** (44.1 mg, 0.204 mmol, 51% yield) as a colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 4H), 2.89 – 2.80 (m, 3H), 2.78 – 2.71 (m, 2H), 2.31 (s, 3H), 1.83 – 1.52 (m, 8H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.4, 138.3, 135.4, 129.1, 128.2, 51.5, 43.5, 29.4, 28.8, 25.9, 21.0; HRMS (ESI-TOF) Calcd for $C_{15}H_{20}OONa$ $[M+Na]^+$: 239.1406; Found 239.1409.



35

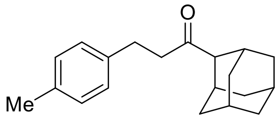
1-cyclohexyl-3-(*p*-tolyl)propan-1-one (**35**). Prepared according to the general procedure A employing $Ir(ppy)_2(dtbbpy)PF_6$ (2.8 mg, 0.003 mmol), dtbbpy (L_1) (6.1 mg, 0.0225 mmol), K_2CO_3 (53.4 mg, 0.39 mmol), Cs_2CO_3 (146.6 mg, 0.45 mmol), $NiBr_2$•DME (4.7 mg, 0.015 mmol), NHC (177.3 mg, 0.45 mmol), 1,4-dioxane (3 mL), cyclohexanol (42.2 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 3-(4-methylphenyl)propionic acid (49.5 mg, 0.3 mmom) and Boc_2O (85.1 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **35** (42.1 mg, 0.183 mmol, 61% yield) as a colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.10-7.03 (m, 4H), 2.87 – 2.79 (m, 2H), 2.77 – 2.63 (m, 2H), 2.36-2.24 (m, 4H), 1.89 – 1.72 (m, 4H), 1.67 – 1.62 (m, 1H), 1.38 – 1.16 (m, 5H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.2, 138.3, 135.4, 129.1, 128.1, 50.9, 42.3, 29.3, 28.4, 25.8, 25.6, 20.9; HRMS (ESI-TOF) Calcd for $C_{16}H_{22}ONa$ $[M+Na]^+$: 253.1563; Found 253.1570.



36

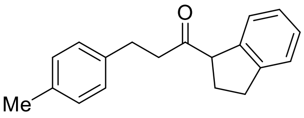
1-cycloheptyl-3-(*p*-tolyl)propan-1-one (**36**). Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), dtbbpy (L_1) (8.4 mg, 0.03 mmol), K_2CO_3 (71.8 mg, 0.60 mmol),

Cs_2CO_3 (195.0 mg, 0.60 mmol), $NiBr_2$•DME (6.5 mg, 0.02 mmol), NHC (237.3 mg, 0.60 mmol), 1,4-dioxane (4 mL), cycloheptanol (65.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-methylphenyl)propionic acid (65.5 mg, 0.4 mmol) and Boc_2O (113.3 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 60/1) on silica gel to afford **36** (48.8 mg, 0.20 mmol, 50% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (s, 4H), 2.87 – 2.80 (m, 2H), 2.76 – 2.69 (m, 2H), 2.53-2.43 (m, 1H), 2.31 (s, 3H), 1.84 – 1.65 (m, 5H), 1.57 – 1.37 (m, 7H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.5, 138.3, 135.4, 129.1, 128.1, 52.4, 42.5, 29.7, 29.4, 28.2, 26.6, 20.9; HRMS (ESI-TOF) Calcd for $C_{17}H_{24}ONa$ $[M+Na]^+$: 267.1719; Found 267.1724.



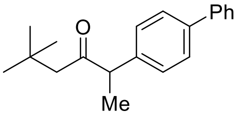
37

1-((1*R*,3*S*,5*r*,7*r*)-adamantan-2-yl)-3-(*p*-tolyl)propan-1-one (**37**). Prepared according to the general procedure B employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.7 mg, 0.004 mmol), dtbbpy (L_1) (8.4 mg, 0.03 mmol), K_2CO_3 (71.8 mg, 0.60 mmol), Cs_2CO_3 (195.0 mg, 0.60 mmol), $NiBr_2$•DME (6.3 mg, 0.02 mmol), NHC (237.4 mg, 0.60 mmol), 1,4-dioxane (4 mL), 2-Adamantanol (85.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-methylphenyl)propionic acid (65.7 mg, 0.4 mmol) and Boc_2O (113.3 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **37** (45.2 mg, 0.16 mmol, 40% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 1H), 2.86 (t, *J* = 7.6 Hz, 1H), 2.73 (t, *J* = 7.6 Hz, 1H), 2.46 (s, 0H), 2.35 (s, 1H), 2.31 (s, 1H), 1.94 – 1.67 (m, 3H), 1.60 (s, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.0, 138.4, 135.4, 129.1, 128.2, 57.2, 41.6, 38.4, 37.2, 33.3, 29.4, 29.1, 27.6, 27.5, 21.0; HRMS (ESI-TOF) Calcd for $C_{20}H_{26}ONa$ $[M+Na]^+$: 305.1876; Found 305.1880.



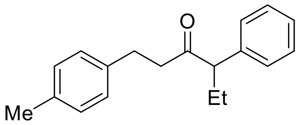
38

1-(2,3-dihydro-1*H*-inden-1-yl)-3-(*p*-tolyl)propan-1-one (**38**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.4 mg, 0.03 mmol), K$_2$CO$_3$ (71.8 mg, 0.60 mmol), Cs$_2$CO$_3$ (195.0 mg, 0.60 mmol), NiBr$_2$•DME (6.3 mg, 0.02 mmol), NHC (237.3 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-indanol (75.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-methylphenyl)propionic acid (65.7 mg, 0.4 mmol) and Boc$_2$O (113.5 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **38** (45.4 mg, 0.172 mmol, 43% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.11 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.07 (t, *J* = 7.2 Hz, 1H), 3.11-3.00 (m, 1H), 2.97 – 2.72 (m, 5H), 2.33 – 2.24 (m, 5H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.9, 144.6, 140.8, 138.0, 135.5, 129.1, 128.2, 127.5, 126.4, 124.9, 124.7, 58.3, 42.2, 31.9, 29.4, 28.5, 21.0; HRMS (ESI-TOF) Calcd for $C_{19}H_{20}ONa$ [M+Na]$^+$: 287.1406; Found 287.1415.



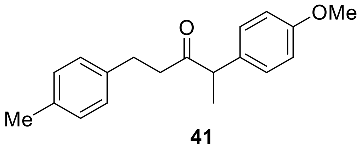
39

2-([1,1'-biphenyl]-4-yl)-5,5-dimethylhexan-3-one (**39**). Prepared according to the general procedure A employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.8 mg, 0.003 mmol), dtbbpy (L$_1$) (6.1 mg, 0.0225 mmol), K$_2$CO$_3$ (53.4 mg, 0.39 mmol), Cs$_2$CO$_3$ (146.6 mg, 0.45 mmol), NiBr$_2$•DME (4.7 mg, 0.015 mmol), NHC (177.8 mg, 0.45 mmol), 1,4-dioxane (3 mL), 1-(4-biphenylyl) ethanol (83.3 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), *t*ert-butyl acetic acid (35.1 mg, 0.3 mmom) and Boc$_2$O (85.1 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **39** (39.5 mg, 0.141 mmol, 47% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.53 (m, 4H), 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.76 (q, *J* = 6.8 Hz, 1H), 2.37 (d, *J* = 15.6 Hz, 1H), 2.22 (d, *J* = 15.6 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.3, 140.6, 139.9, 139.5, 128.7, 128.4, 127.5, 127.3, 127.0, 54.0, 53.4, 31.0, 29.6, 17.5; HRMS (ESI-TOF) Calcd for $C_{20}H_{24}ONa$ [M+Na]$^+$: 303.1719; Found 303.1724.



40

4-phenyl-1-(*p*-tolyl)hexan-3-one (**40**). Prepared according to the general procedure B employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.4 mg, 0.03 mmol), K_2CO_3 (71.8 mg, 0.60 mmol), Cs_2CO_3 (195.0 mg, 0.60 mmol), NiBr$_2$•DME (6.3 mg, 0.02 mmol), NHC (236.9 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-Phenyl-1-propanol (76.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-methylphenyl)propionic acid (65.8 mg, 0.4 mmol) and Boc$_2$O (113.5 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **40** (67.2 mg, 0.24 mmol, 60% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32-7.20 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 2H), 3.47 (t, *J* = 7.4 Hz, 1H), 2.86 – 2.56 (m, 4H), 2.28 (s, 3H), 2.11-1.97 (m, 1H), 1.77-1.62 (m, 1H), 0.79 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.7, 138.7, 137.8, 135.3, 129.0, 128.7, 128.2, 128.0, 127.1, 60.9, 43.5, 29.3, 25.0, 20.9, 12.0; HRMS (ESI-TOF) Calcd for $C_{20}H_{24}ONa$ [M+Na]$^+$: 303.1719; Found 303.1714.

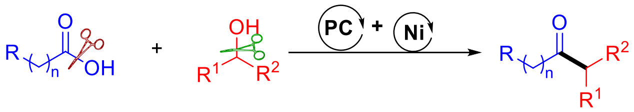


41

4-(4-methoxyphenyl)-1-(*p*-tolyl)pentan-3-one (**41**). Prepared according to the general procedure A employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.8 mg, 0.003 mmol), dtbbpy (L$_1$) (6.1 mg, 0.0225 mmol), K_2CO_3 (53.4 mg, 0.39 mmol), Cs_2CO_3 (146.6 mg, 0.45 mmol), NiBr$_2$•DME (4.7 mg, 0.015 mmol), NHC (177.9 mg, 0.45 mmol), 1,4-dioxane (3 mL), 1-(4-methoxyphenyl)ethanol (63.9 mg, 0.42 mmol), pyridine (33.3 mg, 0.42 mmol), 3-(4-methylphenyl)propionic acid (49.5 mg, 0.3 mmom) and Boc$_2$O (85.1 mg, 0.39 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1) on silica gel to afford **41** (52.5 mg, 0.186 mmol, 62%

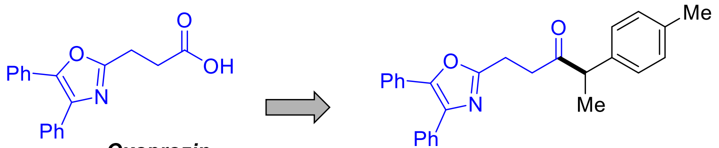
yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 3H), 3.64 (q, *J* = 7.0 Hz, 1H), 2.85 – 2.55 (m, 4H), 2.28 (s, 3H), 1.34 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.3, 158.6, 138.0, 135.4, 132.5, 129.0, 128.8, 128.1, 114.2, 55.2, 52.2, 42.6, 29.5, 20.9, 17.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{22}O_2Na$ [M+Na]$^+$: 305.1512; Found 305.1522.

IV. Late-stage Functionalization of Complex Molecules



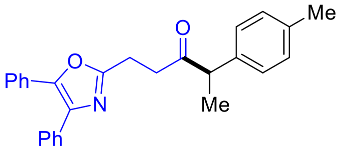
An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.004 mmol), dtbbpy (L_1) (0.03 mmol), K_2CO_3 (0.52 mmol), Cs_2CO_3 (0.60 mmol) and NiBr$_2$•DME (0.02 mmol) were added sequentially under N_2. Then DMAc (4 mL) was added. The reaction mixture was stirred at room temperature for 30 min.

Another oven-dried 10 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, NHC (N_4) (0.60 mmol), 1,4-dioxane (4 mL) and alcohol (o.56 mmol) were added. Then pyridine (0.56 mmol) was added dropwise via a microsyringe. The reaction mixture was stirred for 20 min at room temperature. The 1,4-dioxane suspension was transferred to a 5 ml syringe under N_2. Then a syringe filter and a new needle were installed on the syringe, and the 1,4-dioxane solution was injected through the syringe filter into the mentioned above flask containing the Ir/Ni catalysts followed by adding carboxylic acid (0.4 mmol) and Boc$_2$O (0.52 mmol). The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDS at a distance of 5 cm for 24 h at rt. The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography on silica gel to afford the Late-stage functionalized ketone.



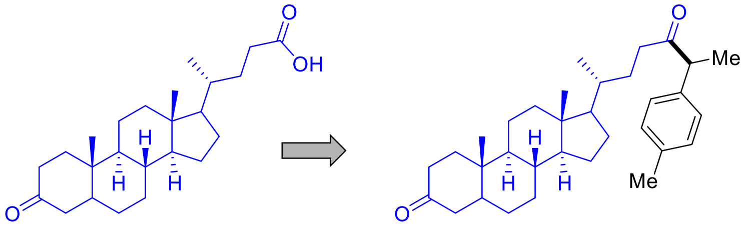
Oxaprozin

44, 55%



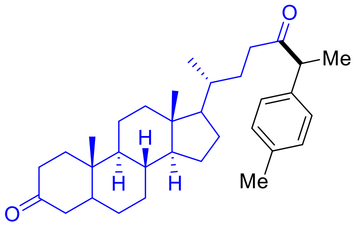
44

1-(4,5-diphenyloxazol-2-yl)-4-(*p*-tolyl)pentan-3-one (**44**). Prepared according to the general procedure employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.4 mg, 0.03 mmol), K$_2$CO$_3$ (71.8 mg, 0.60 mmol), Cs$_2$CO$_3$ (195.0 mg, 0.60 mmol), NiBr$_2$•DME (6.3 mg, 0.02 mmol), NHC (236.9 mg, 0.60 mmol), 1,4-dioxane (4 mL), alcohol (76.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), Oxaprozin (117.0 mg, 0.4 mmol) and Boc$_2$O (113.5 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 15/1) on silica gel to afford **44** (86.9 mg, 0.22 mmol, 55% yield) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.37-7.26 (m, 6H), 7.11 (s, 4H), 3.81 (q, *J* = 6.8 Hz, 1H), 3.15 – 2.88 (m, 4H), 2.29 (s, 3H), 1.41 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.7, 162.3, 145.1, 137.2, 136.8, 134.9, 132.4, 129.6, 128.9, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 126.3, 52.5, 37.4, 22.3, 21.0, 17.4; HRMS (ESI-TOF) Calcd for $C_{27}H_{26}NO_2$ [M+H]$^+$: 396.1958; Found 396.1967.



Lithocholic acid analogue

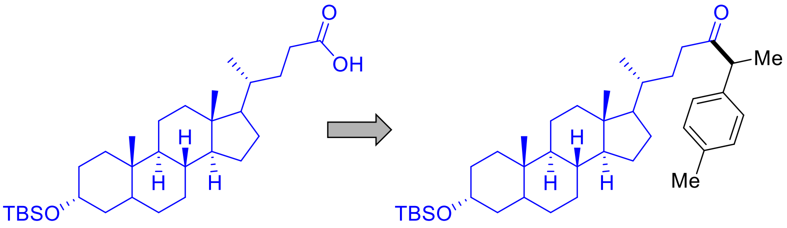
45, 60%， 1/1 *dr*



45

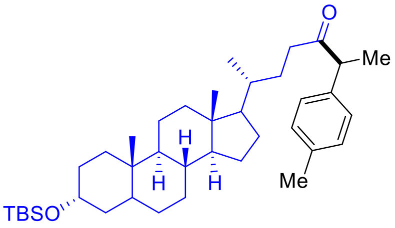
(8R,9S,10S,13R,14S)-10,13-dimethyl-17-((2R,6S)-5-oxo-6-(p-tolyl)heptan-2-yl)hexadecahydro-3H-cyclopenta[a]phenanthren-3-one (**45**). Prepared according to the general procedure employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.8 mg, 0.004 mmol), dtbbpy (L$_1$) (8.4 mg, 0.03 mmol), K$_2$CO$_3$ (71.8 mg, 0.60 mmol), Cs$_2$CO$_3$

(195.0 mg, 0.60 mmol), $NiBr_2$•DME (6.3 mg, 0.02 mmol), NHC (236.9 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-Methylphenyl)ethanol (76.5 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), Lithocholic acid analogue (149.9 mg, 0.4 mmol) and Boc_2O (113.5 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 50/1 to 20/1) on silica gel to afford **45** (114.3 mg, 0.24 mmol, 60% yield, 1/1 *dr*) as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.13 (q, *J* = 8.0 Hz, 4H), 3.79 – 3.68 (m, 1H), 2.69 (t, *J* = 14.0 Hz, 1H), 2.45 – 2.22 (m, 6H), 2.21 – 1.76 (m, 7H), 1.51 – 1.11 (m, 17H), 1.09 – 0.98 (s, 6H), 0.80 (d, *J* = 6.4 Hz, 1.5H), 0.74 (d, *J* = 6.4 Hz, 1.5H), 0.63 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.2, 211.6, 211.4, 137.7, 137.6, 136.6, 136.0, 129.4, 127.7, 127.6, 124.6, 56.30, 56.26, 56.0, 55.9, 52.6, 52.4, 44.2, 42.6, 42.3, 40.6, 39.9, 37.9, 37.7, 37.1, 36.9, 35.4, 35.2, 35.1, 34.8, 30.2, 29.9, 28.0, 27.9, 26.5, 25.7, 24.0, 22.6, 21.1, 20.9, 18.3, 18.1, 17.44, 17.42, 11.95, 11.93; HRMS (ESI-TOF) Calcd for $C_{33}H_{48}O_2Na$ $[M+Na]^+$: 499.3547; Found 499.3554.



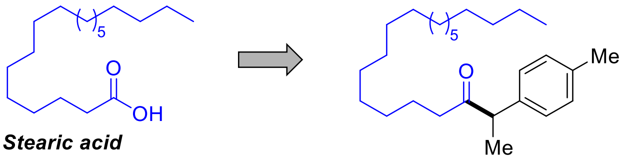
Lithocholic acid analogue

46，62%, 1/1 *dr*



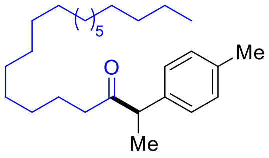
46

(6*R*)-6-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*)-3-((*tert*-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-2-(*p*-tolyl)heptan-3-one (**46**). Prepared according to the general procedure employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.8 mg, 0.004 mmol), dtbbpy (L_1) (8.4 mg, 0.03 mmol), K_2CO_3 (71.8 mg, 0.60 mmol), Cs_2CO_3 (195.0 mg, 0.60 mmol), $NiBr_2$•DME (6.3 mg, 0.02 mmol), NHC (236.5 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-Methylphenyl)ethanol (76.1 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), corresponding Lithocholic acid analogue (196.4 mg, 0.4 mmol) and Boc_2O (113.6 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 15/1) on silica gel to afford **46** (146.9 mg, 0.248 mmol, 62% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.10 (m, 4H), 3.79-3.71 (m, 1H), 3.65 – 3.55 (m, 1H), 2.41 – 2.22 (m, 5H), 1.94 – 1.65 (m, 6H), 1.61 – 1.52 (m, 2H), 1.47 – 1.32 (m, 11H), 1.26 – 0.96 (m, 10H), 0.94 – 0.89 (m, 12H), 0.80 (d, *J* = 6.4 Hz, 1.5H), 0.74 (d, *J* = 6.4 Hz, 1.5H), 0.60 (d, *J* = 6.4 Hz, 3H), 0.09 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.7, 211.6, 137.70, 137.67, 136.6, 129.5, 127.72, 127.70, 72.8, 56.33, 56.29, 55.9, 55.8, 52.7, 52.4, 42.60, 42.59, 42.2, 40.1, 40.0, 37.9, 37.7, 36.9, 35.8, 35.5, 35.2, 35.1, 34.5, 31.0, 30.02, 29.99, 29.7, 28.1, 28.0, 27.2, 26.3, 25.9, 24.15, 24.13, 23.3, 21.02, 21.00, 20.7, 18.35, 18.30, 18.2, 17.49, 17.47, 11.94, 11.92, -4.6; HRMS (ESI-TOF) Calcd for $C_{39}H_{64}O_2SiNa$ $[M+Na]^+$: 615.4568; Found 615.4576.



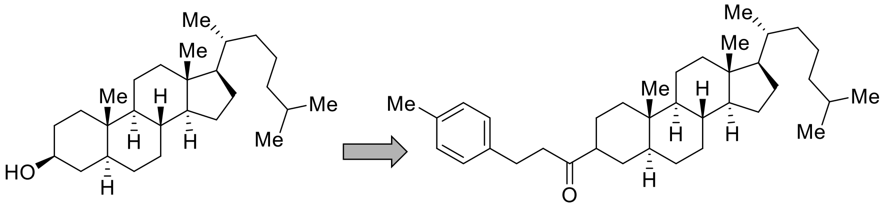
Stearic acid

47, 75%

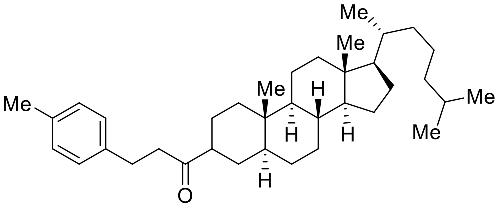


47

2-(*p*-tolyl)icosan-3-one (**47**). Prepared according to the general procedure employing Ir(ppy)$_2$(dtbbpy)PF_6 (3.9 mg, 0.004 mmol), dtbbpy (L_1) (8.4 mg, 0.03 mmol), K_2CO_3 (71.8 mg, 0.60 mmol), Cs_2CO_3 (196.0 mg, 0.60 mmol), $NiBr_2$•DME (6.3 mg, 0.02 mmol), NHC (237.5 mg, 0.60 mmol), 1,4-dioxane (4 mL), 1-(4-Methylphenyl)ethanol (76.3 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), stearic acid (113.6 mg, 0.4 mmol) and Boc_2O (113.6 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 40/1) on silica gel to afford **47** (115.9 mg, 0.30 mmol, 75% yield) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.70 (q, *J* = 6.8 Hz, 1H), 2.37 – 2.27 (m, 5H), 1.54 – 1.40 (m, 2H), 1.36 (d, *J* = 7.2 Hz, 3H), 1.33-1.06 (m, 28H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.2, 137.7, 136.6, 129.5, 127.7, 52.5, 40.9, 31.9, 29.7, 29.65, 29.64, 29.62, 29.56, 29.4, 29.35, 29.30, 29.0, 23.8, 22.7, 21.0, 17.4, 14.1; HRMS (ESI-TOF) Calcd for $C_{27}H_{46}ONa$ $[M+Na]^+$: 409.3441; Found 409.3450.

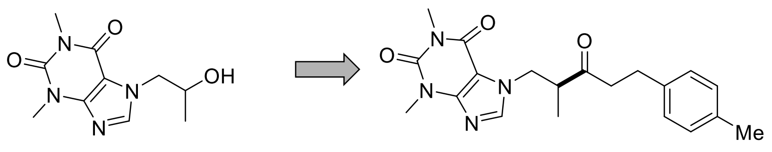


48, 34%

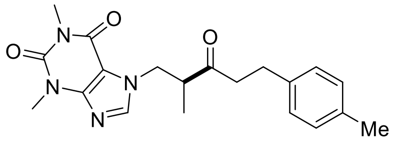


48

1-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)-3-(*p*-tolyl)propan-1-one (**48**). Prepared according to the general procedure employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.9 mg, 0.004 mmol), dtbbpy (L$_1$) (8.4 mg, 0.03 mmol), K_2CO_3 (71.8 mg, 0.60 mmol), Cs_2CO_3 (195.5 mg, 0.60 mmol), NiBr$_2$•DME (6.3 mg, 0.02 mmol), NHC (237.4 mg, 0.60 mmol), 1,4-dioxane (4 mL), dihydrocholesterol (217.8 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-methylphenyl)propionic acid (66.0 mg, 0.4 mmol) and Boc$_2$O (113.6 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 40/1) on silica gel to afford **48** (70.5 mg, 0.136 mmol, 34% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (s, 4H), 2.89 – 2.78 (m, 2H), 2.78 – 2.66 (m, 2H), 2.53 – 2.44 (m, 1H), 2.30 (s, 3H), 2.00 – 1.89 (m, 2H), 1.85-1.73 (m, 2H), 1.69 – 1.60 (m, 3H), 1.58 – 1.42 (m, 7H), 1.38 -1.28 (m, 6H), 1.17 – 1.07 (m, 7H), 1.04-0.95 (m, 4H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 6H), 0.77 (d, *J* = 9.6 Hz, 3H), 0.63 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.8, 138.4, 135.4, 129.1, 128.2, 56.4, 56.3, 56.2, 54.4, 54.1, 51.4, 46.9, 46.1, 42.54, 42.51, 42.3, 41.8, 39.9, 39.5, 36.1, 35.84, 35.79, 35.76, 35.4, 35.3, 34.9, 31.7, 29.6, 29.0, 28.8, 28.2, 28.0, 24.1, 23.8, 22.8, 22.5, 22.1, 20.9, 20.7, 18.65, 18.63, 12.2, 12.0, 11.6; HRMS (ESI-TOF) Calcd for $C_{37}H_{58}ONa$ $[M+Na]^+$: 541.4380; Found 541.4391.



Proxyphylline **49**, 21%



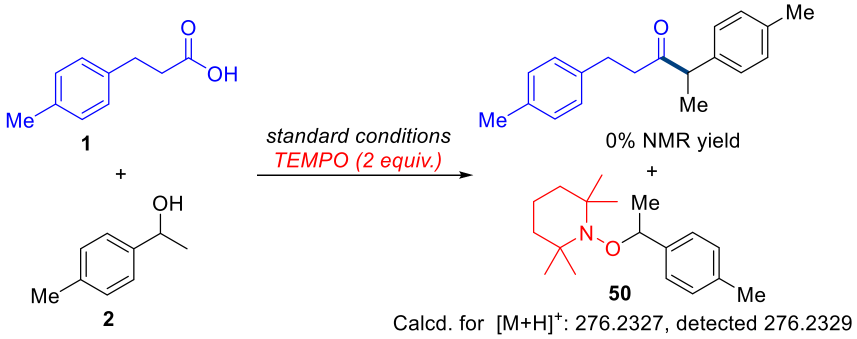
49

1,3-dimethyl-7-(2-methyl-3-oxo-5-(*p*-tolyl)pentyl)-3,7-dihydro-1*H*-purine-2,6-dione (**49**). Prepared according to the general procedure employing Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.9 mg, 0.004 mmol), dtbbpy (L$_1$) (8.4 mg, 0.03 mmol), K_2CO_3 (71.8 mg, 0.60 mmol), Cs_2CO_3 (195.5 mg, 0.60 mmol), NiBr$_2$•DME (6.3 mg, 0.02 mmol), NHC (237.4 mg, 0.60 mmol), 1,4-dioxane (4 mL), Proxyphylline (135.0 mg, 0.56 mmol), pyridine (44.3 mg, 0.56 mmol), 3-(4-Methylphenyl)propionic acid (65.6 mg, 0.4 mmol) and Boc$_2$O (113.6 mg, 0.52 mmol). After 20 h, The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 40/1) on silica gel to afford **49** (30.9 mg, 0.084 mmol, 21% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (s, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 4.47 (dd, *J* = 13.6, 8.8 Hz, 1H), 4.16 (dd, *J* = 13.2, 4.8 Hz, 1H), 3.58 (s, 3H), 3.40 (s, 3H), 3.33 – 3.18 (m, 1H), 2.86 – 2.72 (m, 3H), 2.68 – 2.51 (m, 1H), 2.27 (s, 3H), 1.14 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.1, 155.1, 151.5, 148.9, 142.5, 137.2, 135.6, 129.0, 127.9, 106.5, 48.0, 46.8, 43.1, 29.8, 29.1, 27.9, 20.9, 14.6; HRMS (ESI-TOF) Calcd for $C_{20}H_{24}N_4O_3Na$ $[M+Na]^+$: 391.1741; Found 391.1749.

V. Mechanistic Studies

(a) Benzylic radical trapping experiments

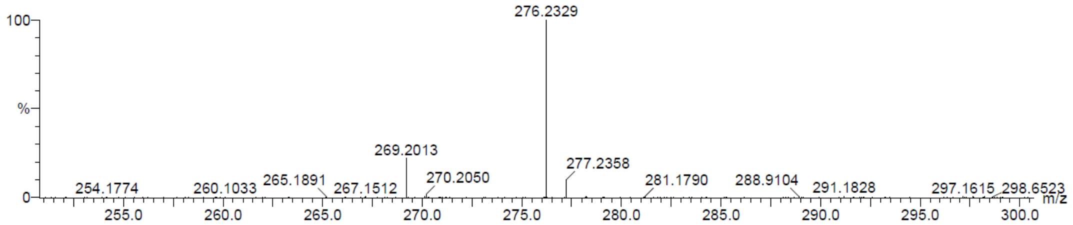


An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.8 mg, 0.003 mmol), dtbbpy (L_1) (6.3 mg, 0.0225 mmol), K_2CO_3 (53.6 mg, 0.39 mmol), Cs_2CO_3 (147.0 mg, 0.45 mmol) and $NiBr_2$•DME (4.9 mg, 0.015 mmol) were added sequentially under N_2. Then DMAc (3 mL) was added. The reaction mixture was stirred at room temperature for 30 min.

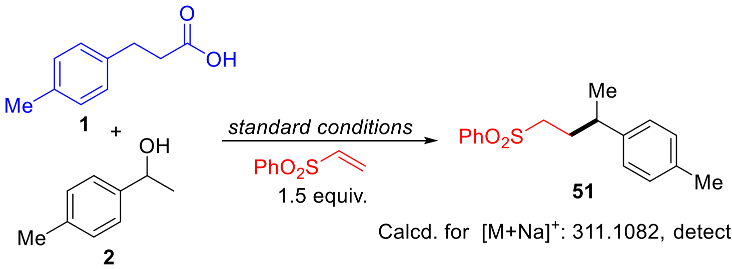
Another oven-dried 10 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, NHC (N_4) (177.4 mg, 0.45 mmol), 1,4-dioxane (3 mL) and alcohol **2** (58.0 mg, 0.42 mmol) were added. Then pyridine (34 μL, 0.42 mmol) was added dropwise via a microsyringe. The reaction mixture was stirred for 20 min at room temperature. The 1,4-dioxane suspension was transferred to a 5 ml syringe under N_2. Then a syringe filter and a new needle were installed on the syringe, and the 1,4-dioxane solution was injected through the syringe filter into the mentioned above flask containing the Ir/Ni catalysts followed by adding carboxylic acid **1** (50.0 mg, 0.3 mmol), Boc$_2$O (85.2 mg, 0.39 mmol) and TEMPO (94.1 mg, 0.6 mmol). The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDS at a distance of 5 cm for 24 h at rt. The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The reaction mixture was then diluted with EtOAc and filtered through a short pad of silica using EtOAc. The filtrate was concentrated in *vacuo*. The crude mixture was monitored by ^{1}H NMR (0% NMR yield) with mesitylene as an internal standard. However, the benzylic radical-trapping adduct **50** was observed by HRMS and the detailed information is illustrated as follows:

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
329 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 18-18 H: 30-30 N: 0-100 O: 0-100 Na: 0-1
15
240127-1-39 23 (0.119) 1: TOF MS ES+ 3.73e+004



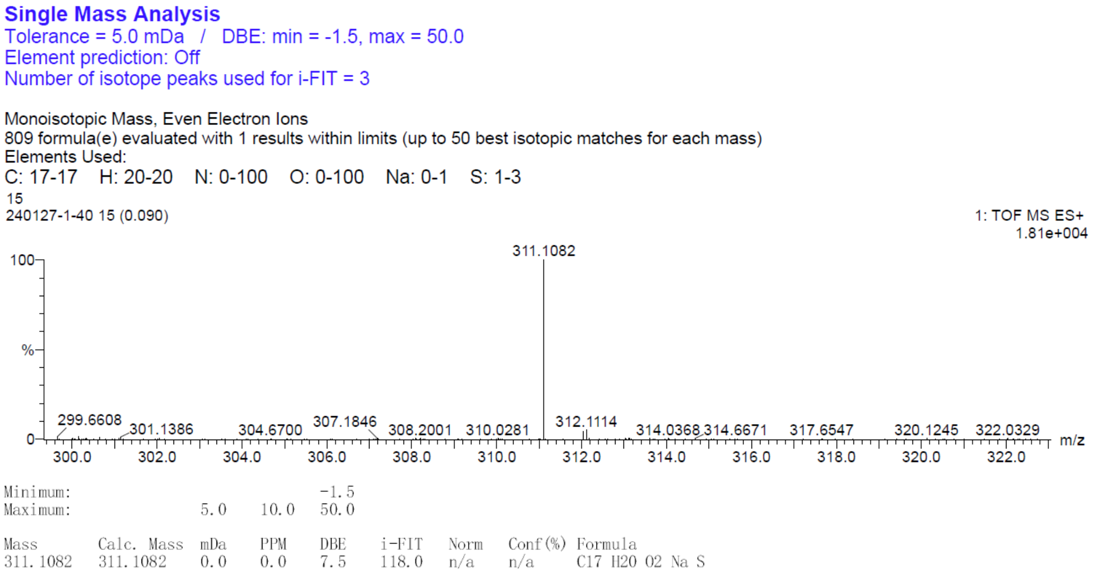
```
Minimum:                                  -1.5
Maximum:                    5.0    10.0   50.0

Mass      Calc. Mass   mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula
276.2329  276.2327     0.2    0.7    4.5    63.0    n/a    n/a      C18 H30 N O
```



Calcd. for [M+Na]$^+$: 311.1082, detected: 311.1082

An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, Ir(ppy)$_2$(dtbbpy)PF$_6$ (3.9 mg, 0.004 mmol), dtbbpy (L$_1$) (8.2 mg, 0.03 mmol), K_2CO_3 (72.2 mg, 0.52 mmol), Cs_2CO_3 (193.3 mg, 0.60 mmol) and NiBr$_2$•DME (6.2 mg, 0.02 mmol) were added sequentially under N_2. Then DMAc (4 mL) was added. The reaction mixture was stirred at room temperature for 30 min.

Another oven-dried 10 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, NHC (N$_4$) (237.0 mg, 0.60 mmol), 1,4-dioxane (4 mL) and alcohol **2** (76.5 mg, 0.56 mmol) were added. Then pyridine (0.56 mmol) was added dropwise via a microsyringe. The reaction mixture was stirred for 20 min at room temperature. The 1,4-dioxane suspension was transferred to a 5 ml syringe under N_2. Then a syringe filter and a new needle were installed on the syringe, and the 1,4-dioxane solution was injected through the syringe filter into the mentioned above flask containing the Ir/Ni catalysts followed by adding carboxylic acid **1** (0.4 mmol), Boc$_2$O (0.52 mmol) and phenylvinyl sulfone (101.1 mg, 0.60 mmol). The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDS at a distance of 5 cm for 24 h at rt with a fan. The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* and monitored by HRMS, which suggested the generation of adduct **51**. The detailed information was illustrated as follows:

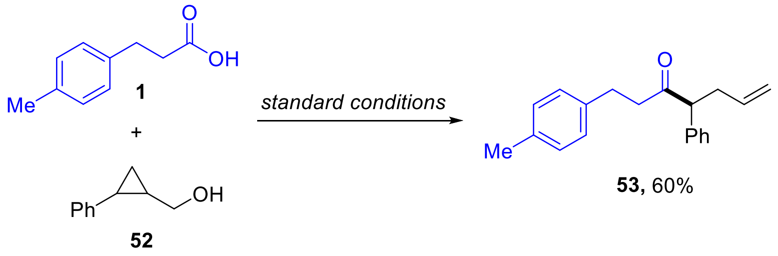


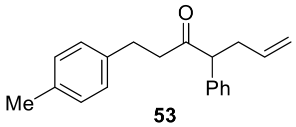
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
809 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 17-17 H: 20-20 N: 0-100 O: 0-100 Na: 0-1 S: 1-3
15
240127-1-40 15 (0.090)

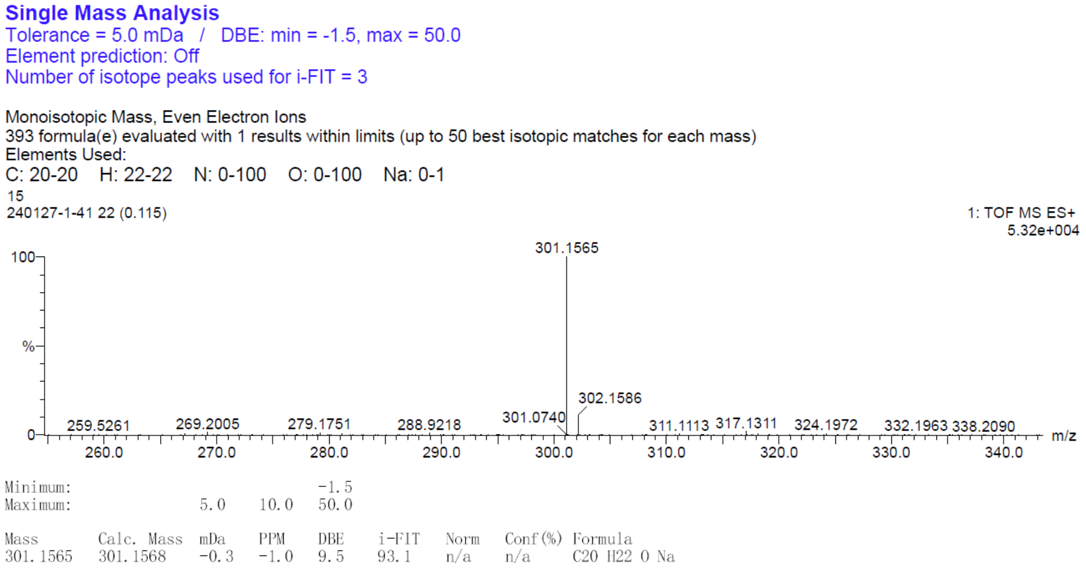
```
Minimum:                              -1.5
Maximum:                  5.0   10.0   50.0

Mass      Calc. Mass  mDa   PPM   DBE   i-FIT   Norm   Conf(%)  Formula
311.1082  311.1082    0.0   0.0   7.5   118.0   n/a    n/a      C17 H20 O2 Na S
```

(b) Radical-Clock experiment




53

4-phenyl-1-(*p*-tolyl)hept-6-en-3-one (**53**). Prepared according to the general procedure employing $Ir(ppy)_2(dtbbpy)PF_6$ (3.7 mg, 0.004 mmol), K_2CO_3 (71.0 mg, 0.52 mmol), Cs_2CO_3 (196.0 mg, 0.60 mmol), K_2HPO_4 (210.0 mg, 1.2 mmol), MeCN (19 mL) and H_2O (1 mL). After 24 h, the reaction mixture was cooled to rt and filtered through a short pad of silica using EA. The filtrate was concentrated in *vacuo* before it was purified by flash chromatography (PE/EA = 15/1) on silica gel to afford **53** (66.7 mg, 0.24 mmol, 60% yield) as a yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.21 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 2H), 5.71 – 5.55 (m, 1H), 4.98 (d, *J* = 16.8 Hz, 1H), 4.93 (d, *J* = 10.0 Hz, 1H), 3.65 (t, *J* = 7.6 Hz, 1H), 2.88 – 2.76 (m, 2H), 2.75 – 2.60 (m, 3H), 2.48 – 2.37 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.8, 138.2, 137.8, 135.7, 135.4, 129.0, 128.9, 128.3, 128.1, 127.2, 116.6, 58.9, 43.5, 36.2, 29.3, 20.9; HRMS (ESI-TOF) Calcd for $C_{20}H_{22}ONa$ $[M+Na]^+$: 301.1563; Found 301.1565.

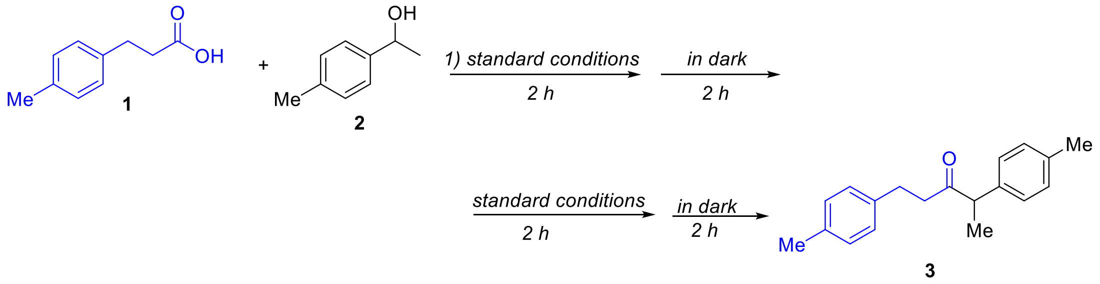


Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
393 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 20-20 H: 22-22 N: 0-100 O: 0-100 Na: 0-1

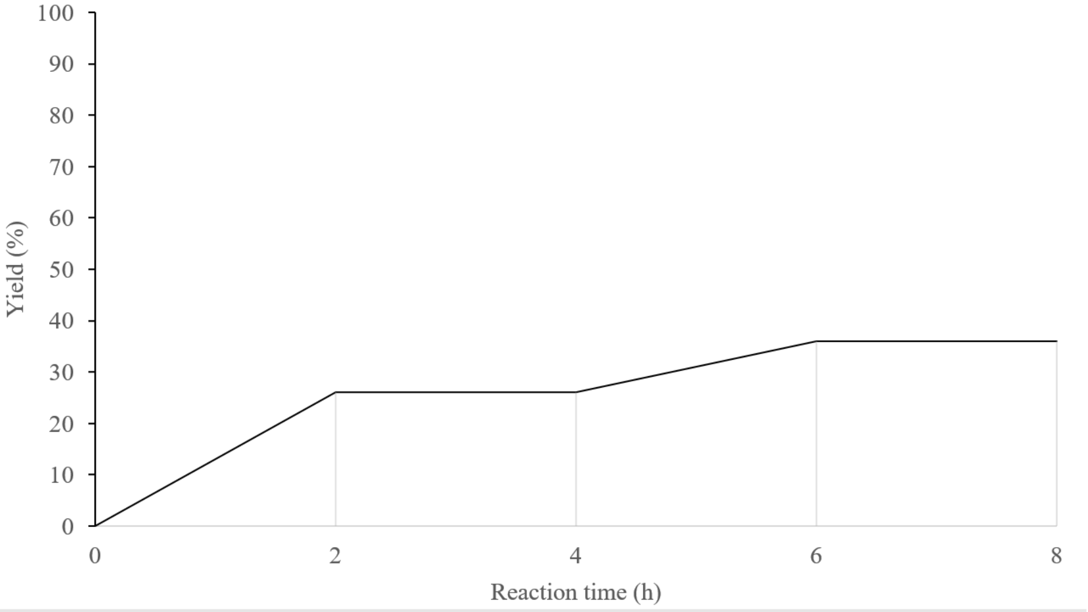
```
Minimum:                              -1.5
Maximum:                  5.0   10.0  50.0

Mass      Calc. Mass  mDa   PPM   DBE   i-FIT  Norm  Conf(%)  Formula
301.1565  301.1568    -0.3  -1.0  9.5   93.1   n/a   n/a      C20 H22 O Na
```

(c) The light-on-off experiment



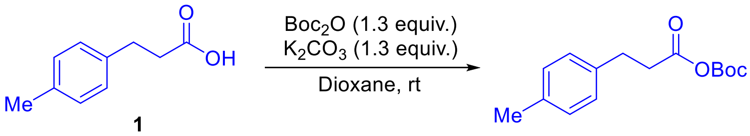
Four oven-dried 25 mL flasks was evacuated and back-filled with N_2 for three times. After cooling at room temperature, Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.004 mmol), dtbbpy (L$_1$) (0.03 mmol), K_2CO_3 (0.52 mmol), Cs_2CO_3 (0.60 mmol) and NiBr$_2$•DME (0.02 mmol) were added sequentially under N_2. Then DMAc (4 mL) was added. The reaction mixture was stirred at room temperature for 30 min.

Another oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, NHC (N$_4$) (2.40 mmol), 1,4-dioxane (16 mL) and alcohol **2** (2.24 mmol) were added. Then pyridine (2.24 mmol) was added dropwise via a microsyringe. The reaction mixture was stirred for 20 min at room temperature. The 1,4-dioxane suspension was transferred to a 20 ml syringe under N_2. Then a syringe filter and a new needle were installed on the syringe, and the 1,4-dioxane solution was injected through the syringe filter into the mentioned above four flasks containing the Ir/Ni catalysts followed by adding carboxylic acid **1** (0.4 mmol) and Boc_2O (0.52 mmol) equally. The resulting crude mixtures were then allowed to stir at room temperature and irradiated by 450-455 nm LEDS at a distance of 5 cm for 2 h, 2 h with LEDs + 2 hours without light, 2 h with LEDs + 2 hours without light + 2 h with LEDs and 2 h with LEDs + 2 hours without light + 2 h with LEDs + 2 h without light, respectively. The reaction yields were determined by ^1H NMR analysis with mesitylene as an internal standard.



The light-on-off experiment

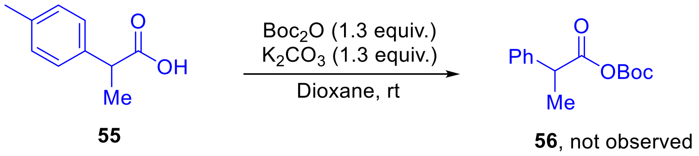
(d)Carboxylic acids activation



1

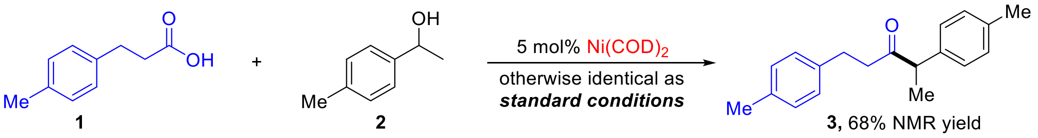
54, 11% yield

An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, carboxylic acid **1** (49.5 mg, 0.3 mmol), K_2CO_3 (54.0 mg, 0.39 mmol) and 1,4-dioxane (3 mL) were added sequentially under N_2. The reaction mixture was stirred at room temperature for 3h. The reaction mixture was then diluted with EtOAc and filtered through a short pad of silica using EtOAc. The filtrate was concentrated in *vacuo*. The crude mixture was monitored by ^1H NMR (11% NMR yield) with mesitylene as an internal standard.



An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, carboxylic acid **55** (49.6 mg, 0.3 mmol), K_2CO_3 (53.7 mg, 0.39 mmol) and 1,4-dioxane (3 mL) were added sequentially under N_2. The reaction mixture was stirred at room temperature for 3h. The reaction mixture was then diluted with EtOAc and filtered through a short pad of silica using EtOAc. The filtrate was concentrated in *vacuo*. The crude mixture was monitored by ^1H NMR (0% NMR yield) with mesitylene as an internal standard.

(e) Demonstration of the presence of Ni(0) species



An oven-dried 25 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, $Ir(ppy)_2(dtbbpy)PF_6$ (0.003 mmol), dtbbpy (L_1) (0.0225 mmol), K_2CO_3 (0.39 mmol), Cs_2CO_3 (0.45 mmol) and $Ni(COD)_2$ (6.5 mg, 0.015 mmol) were added sequentially under N_2 atmosphere. Then DMAc (3 mL) was added. The reaction mixture was stirred at room temperature for 30 min.

Another oven-dried 10 mL flask was evacuated and back-filled with N_2 for three times. After cooling at room temperature, NHC (N_4) (0.45 mmol), 1,4-dioxane (3 mL) and alcohol **2** (0.42 mmol) were added. Then pyridine (0.42 mmol) was added dropwise via a microsyringe. The reaction mixture was stirred for 20 min at room temperature. The 1,4-dioxane suspension was transferred to a 5 ml syringe under N_2. Then a syringe filter and a new needle were installed on the syringe, and the 1,4-dioxane solution was injected through the syringe filter into the mentioned above flask containing the Ir/Ni catalysts followed by adding carboxylic acid **1** (0.3 mmol) and Boc_2O (0.39 mmol). The resulting crude mixture was then allowed to stir at room temperature and irradiated by 450-455 nm LEDS at a distance of 5 cm for 24 h at room temperature. The reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (15 mL) for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* and monitored through ^1H NMR analysis with mesitylene as an internal standard (68% NMR yield).

VI. References

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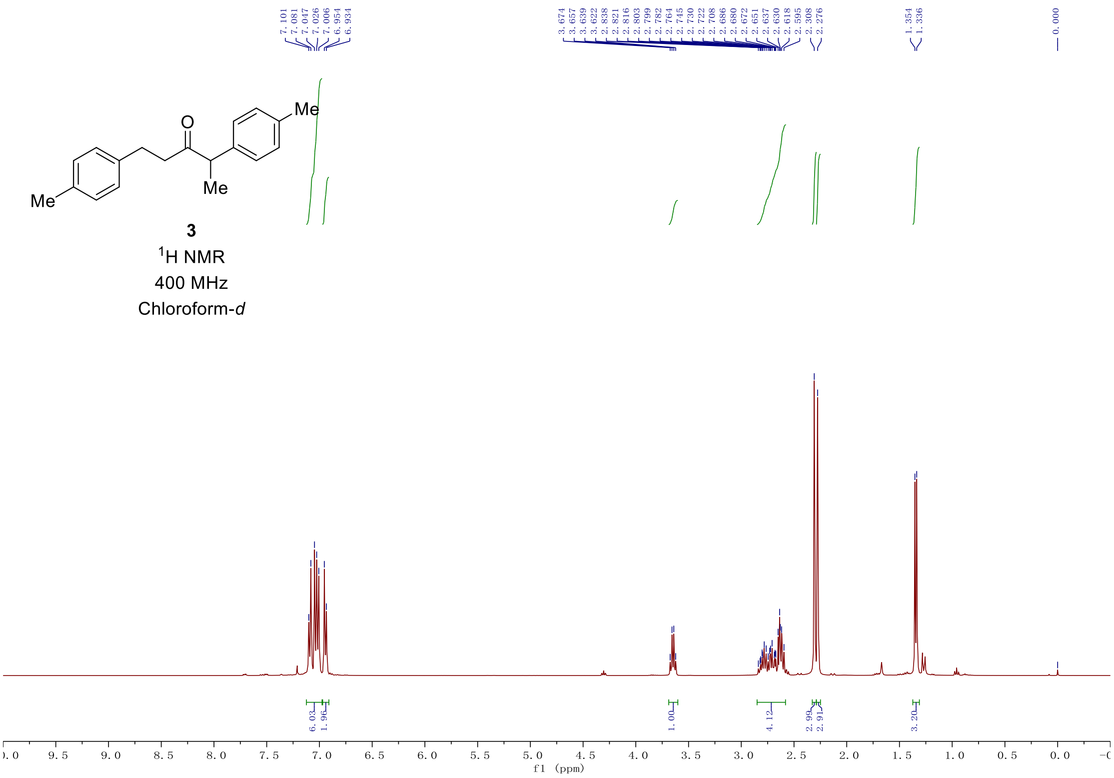
[2] A. H. Cherney, N. T. Kadunce, S. E. Reisman. *J. Am. Chem. Soc*. **2013**, *135*, 7442−7445.

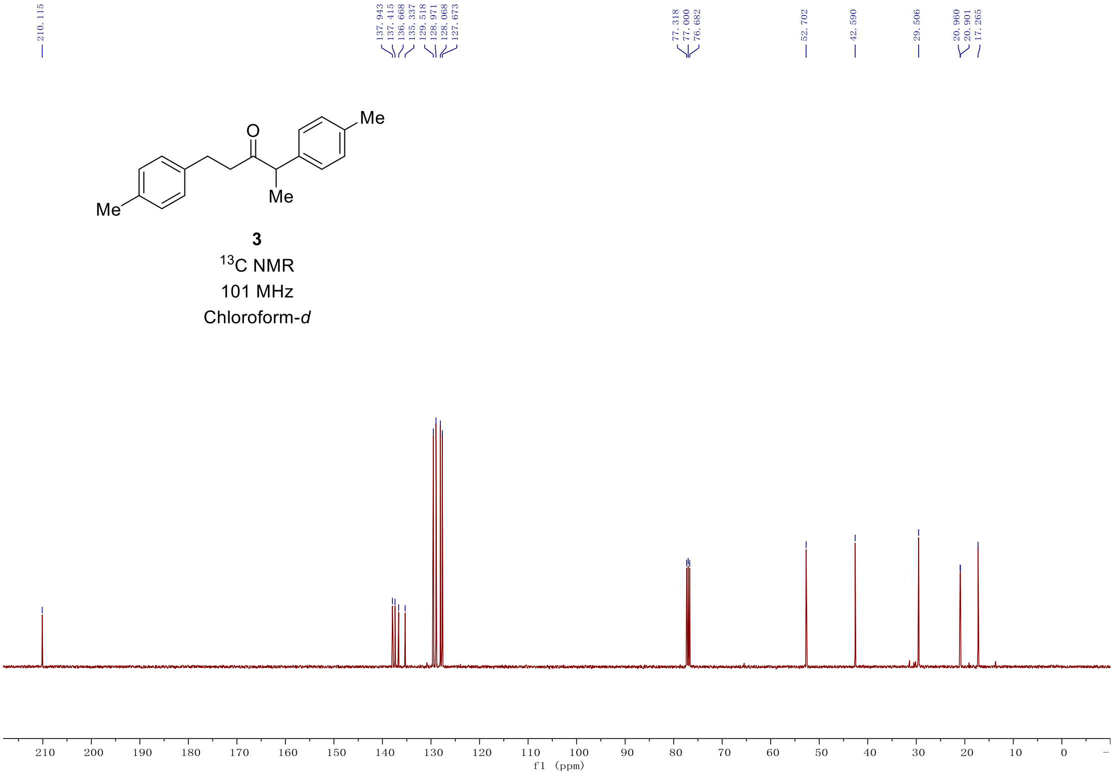
[3] A. Whyte, T. P. Yoon. *Angew. Chem. Int. Ed*. **2022**, *61*, e202213739.

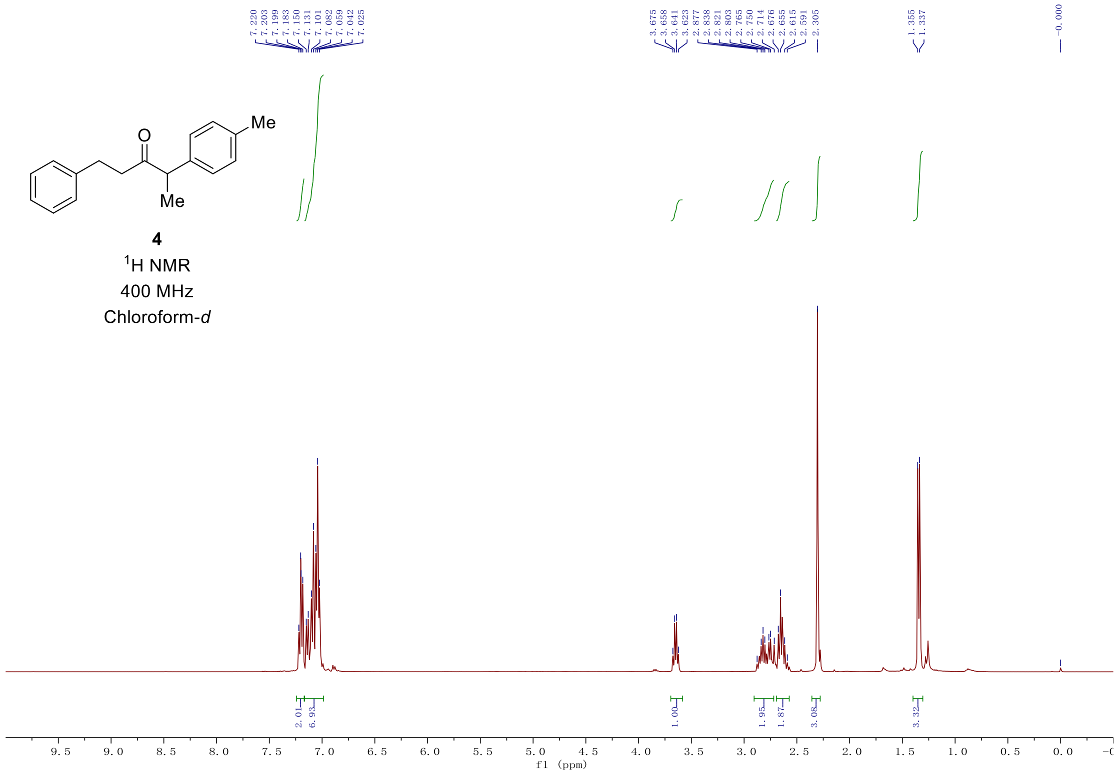
[4] B. Roh, A. O. Farah, B. Kim, T. Feoktistova, F. Moeller, K. D. Kim, P. H.-Y. Cheong, H. G. Lee. *J. Am. Chem. Soc*. **2023**, *145*, 7075−7083.

[5] T. Yuan, X. Ye, P. Zhao, S. Teng, Y. Yi, J. Wang, C. Shan, L. Wojtas, J. Jean, H. Chen, X. Shi, *Chem.* **2020**, *6*, 1420–1431.

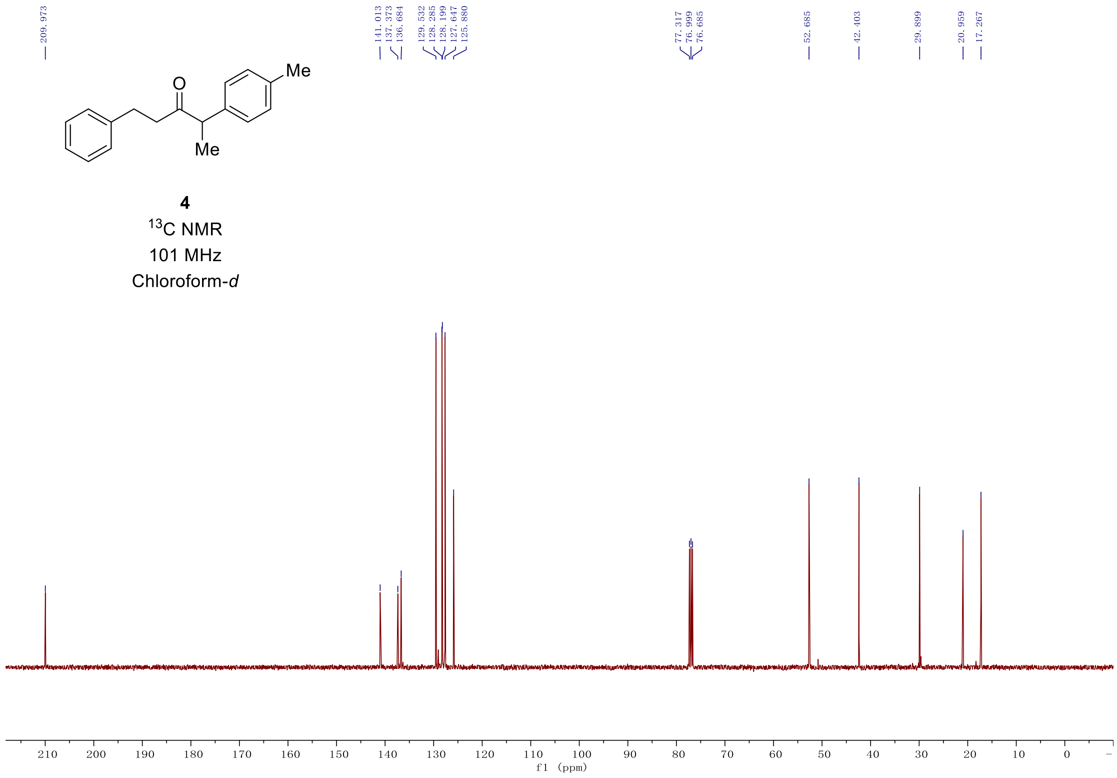
VII. NMR Spectra



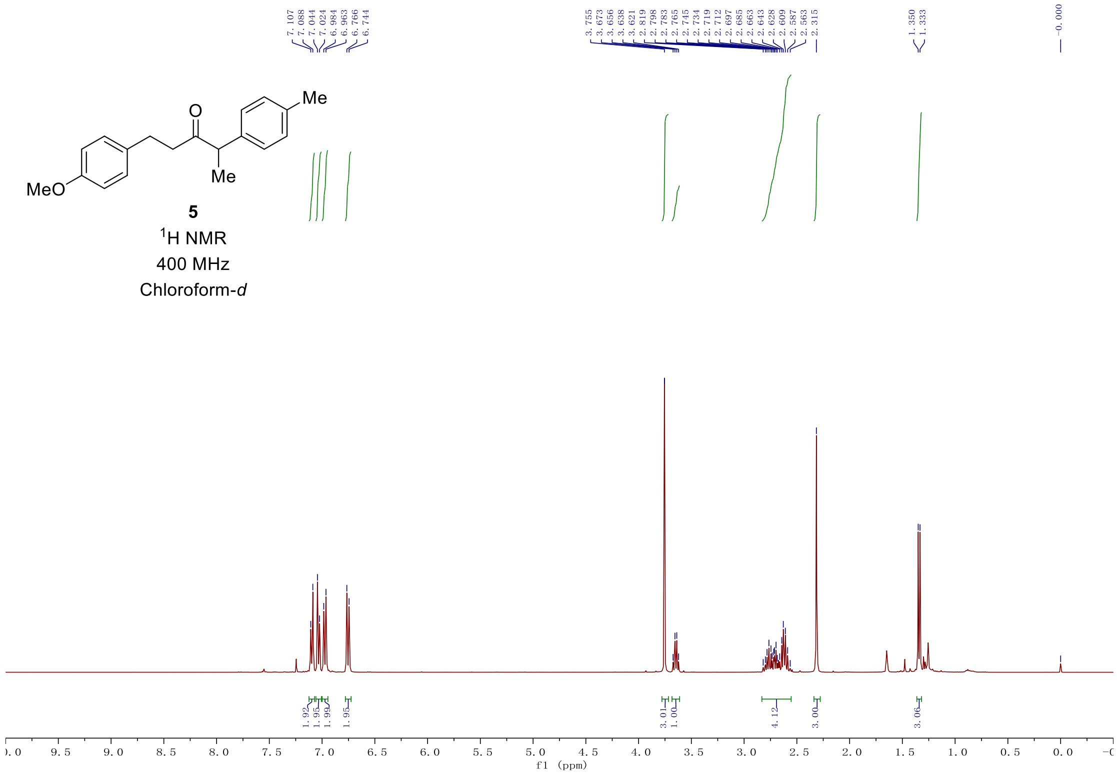




4
^{1}H NMR
400 MHz
Chloroform-*d*



4
^{13}C NMR
101 MHz
Chloroform-*d*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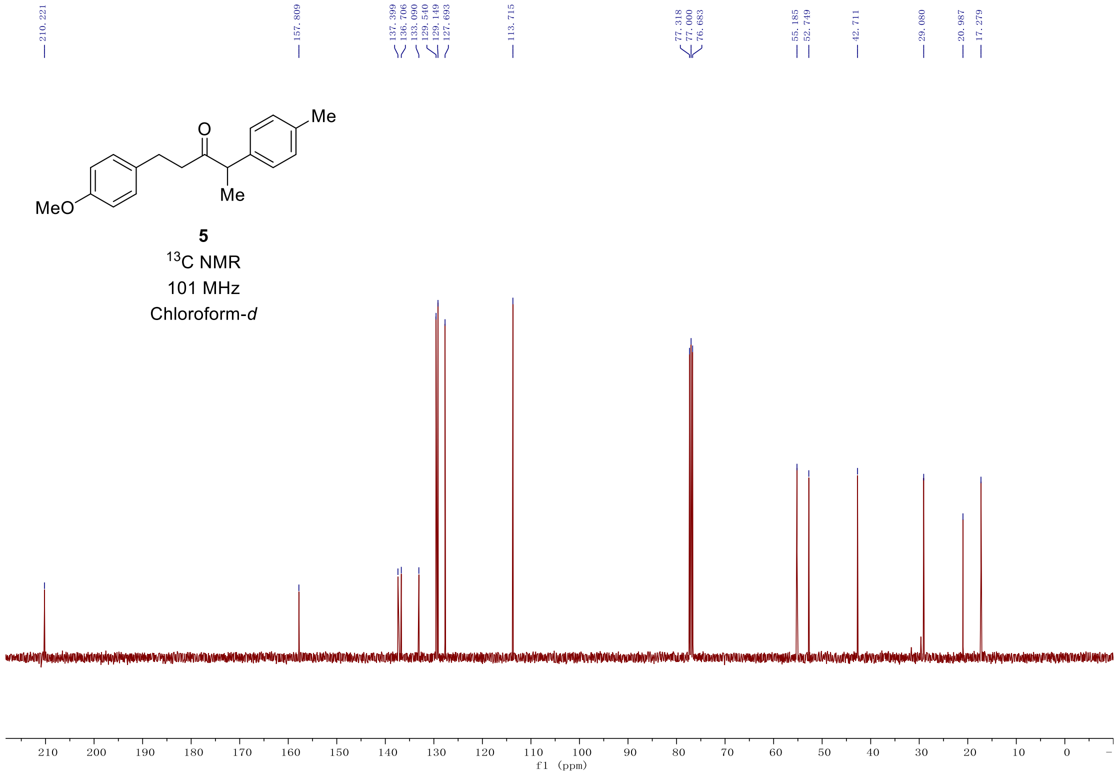
7.088
7.044
7.024
6.984
6.963
6.766
6.744
3.755
3.673
3.656
3.638
3.621
2.819
2.798
2.783
2.765
2.745
2.734
2.719
2.712
2.697
2.685
2.663
2.643
2.628
2.609
2.587
2.563
2.315
1.350
1.333
-0.000
Me
O
MeO
Me
5
^{1}H NMR
400 MHz
Chloroform-*d*
1.92
1.95
1.99
1.95
3.01
1.00
4.12
3.00
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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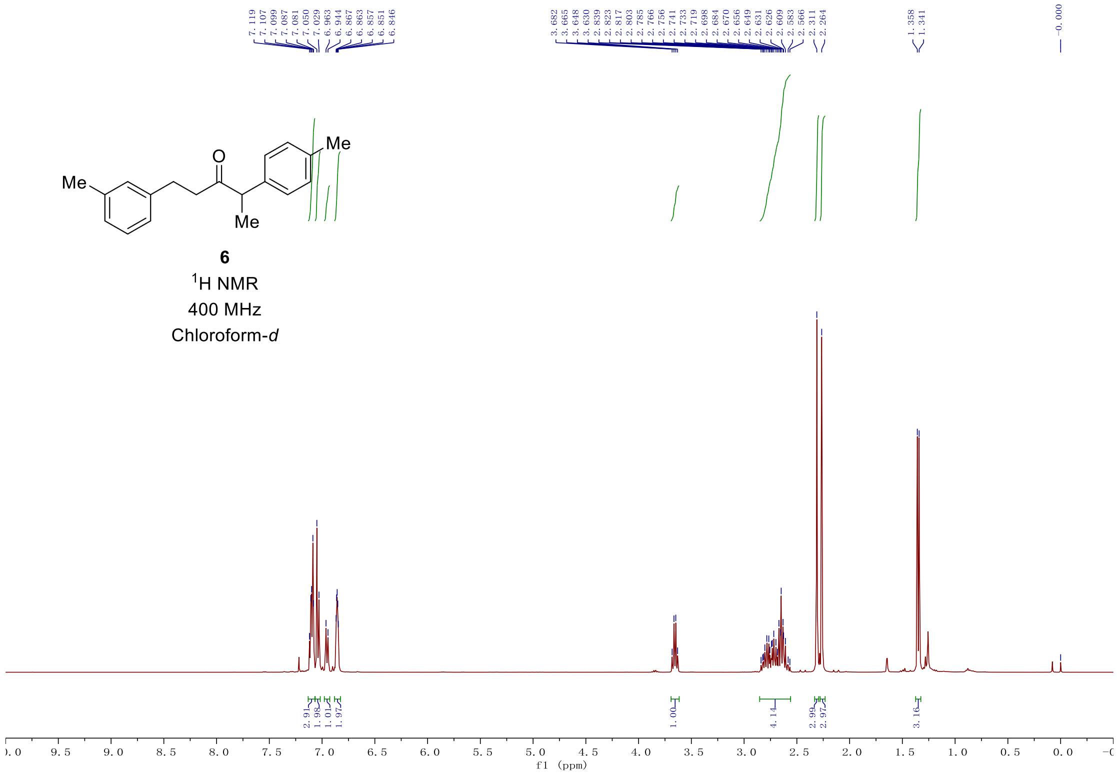
157.809
137.399
136.706
133.090
129.540
129.149
127.693
113.715
77.318
77.000
76.683
55.185
52.749
42.711
29.080
20.987
17.279
Me
O
MeO
Me
5
^{13}C NMR
101 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.107
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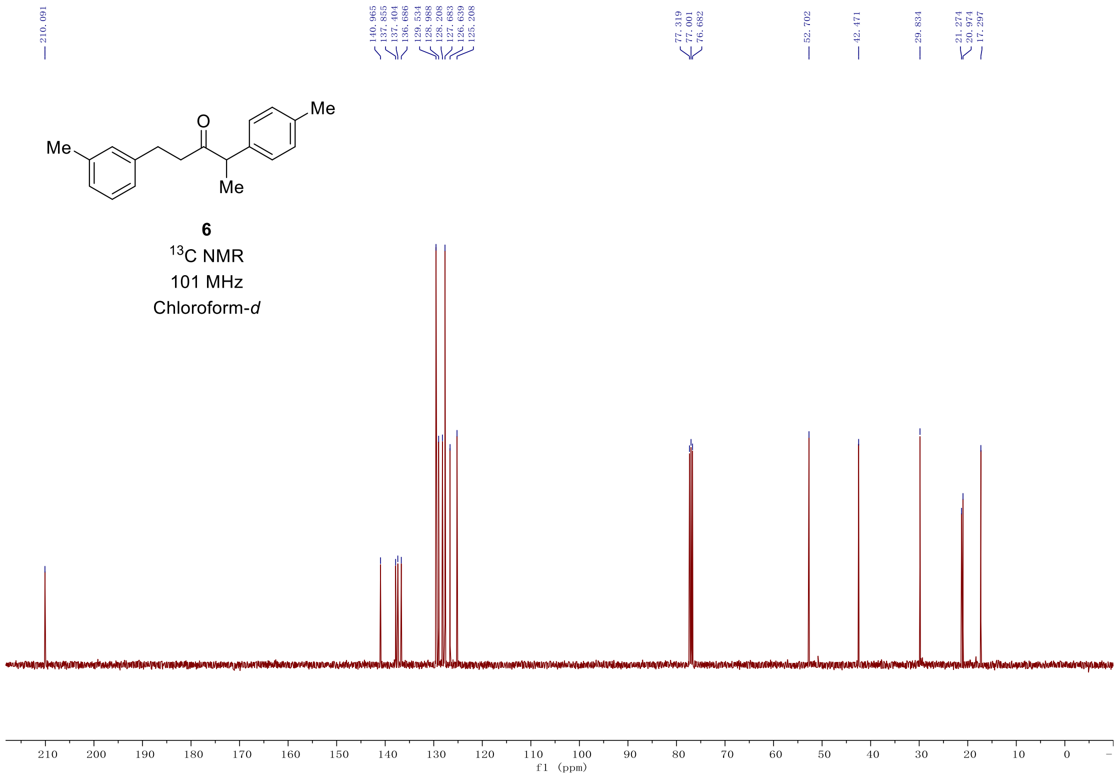
6.863
6.857
6.851
6.846
3.682
3.665
3.648
3.630
2.839
2.823
2.817
2.803
2.785
2.766
2.756
2.741
2.733
2.719
2.698
2.684
2.670
2.656
2.649
2.631
2.626
2.609
2.583
2.566
2.311
2.264
1.358
1.341
-0.000
Me
O
Me
Me
6
^{1}H NMR
400 MHz
Chloroform-*d*
2.91
1.98
1.01
1.97
1.00
4.14
2.99
2.97
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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140.965
137.855
137.404
136.686
129.534
128.988
128.208
127.683
126.639
125.208
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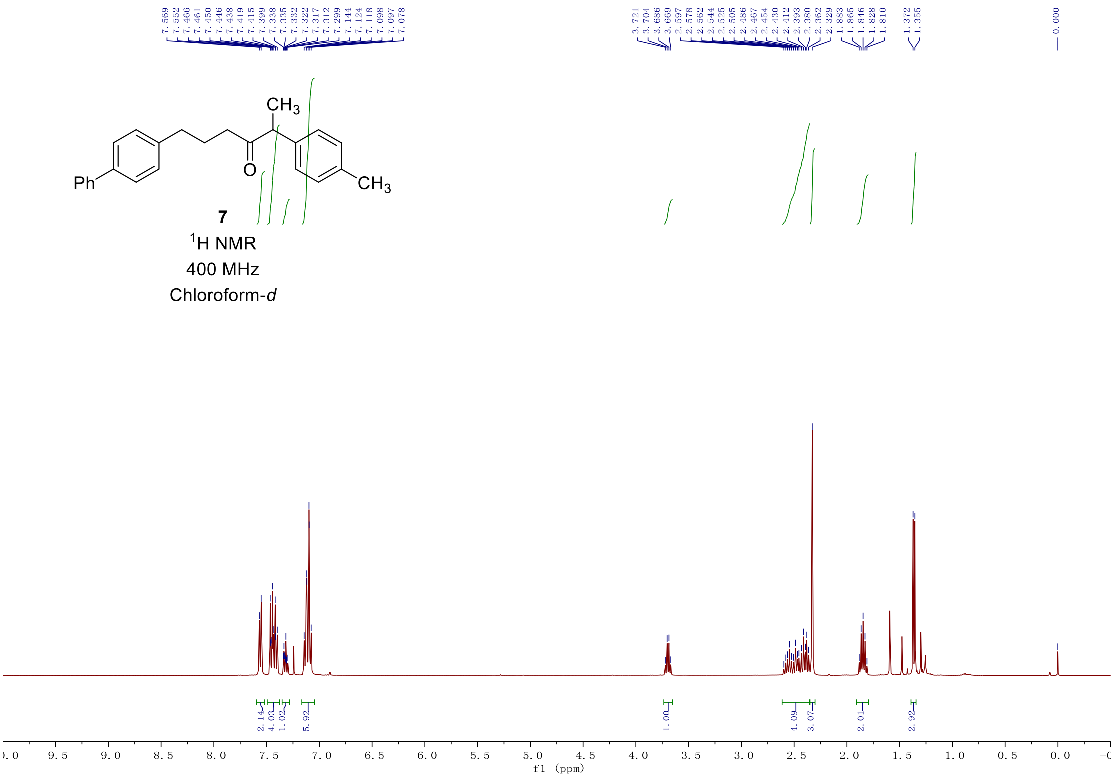
77.001
76.682
52.702
42.471
29.834
21.274
20.974
17.297
Me
O
Me
Me
6
^{13}C NMR
101 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

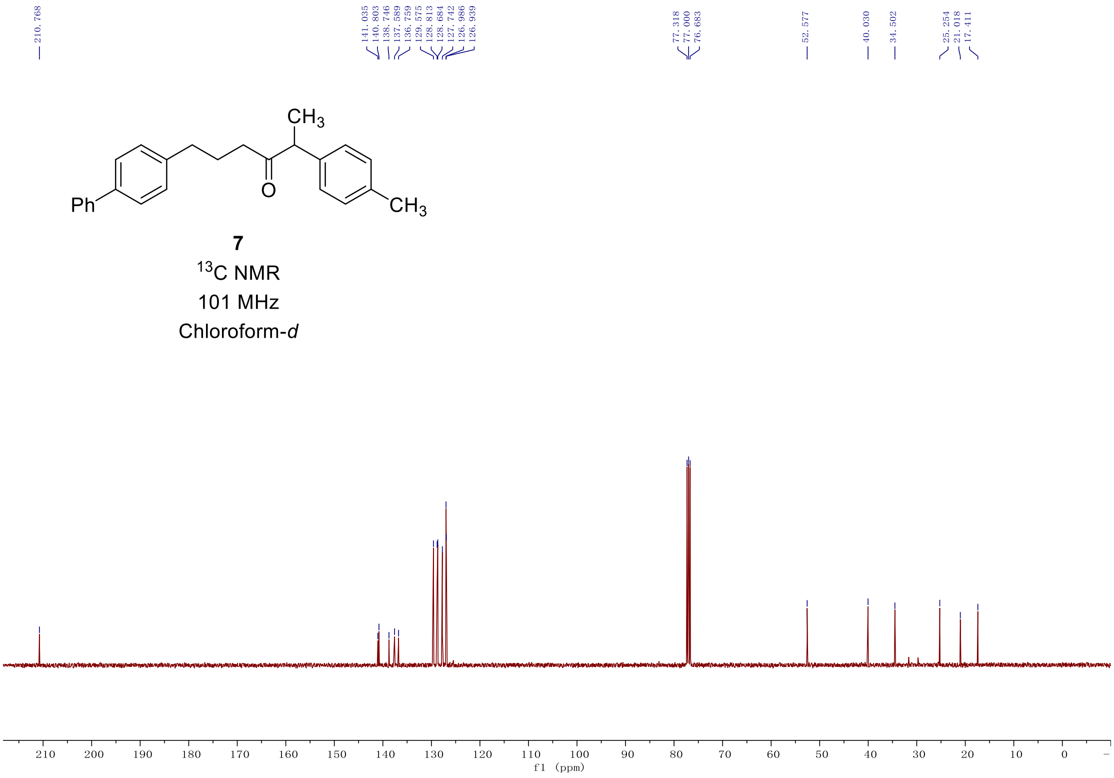


7

^{1}H NMR

400 MHz

Chloroform-*d*

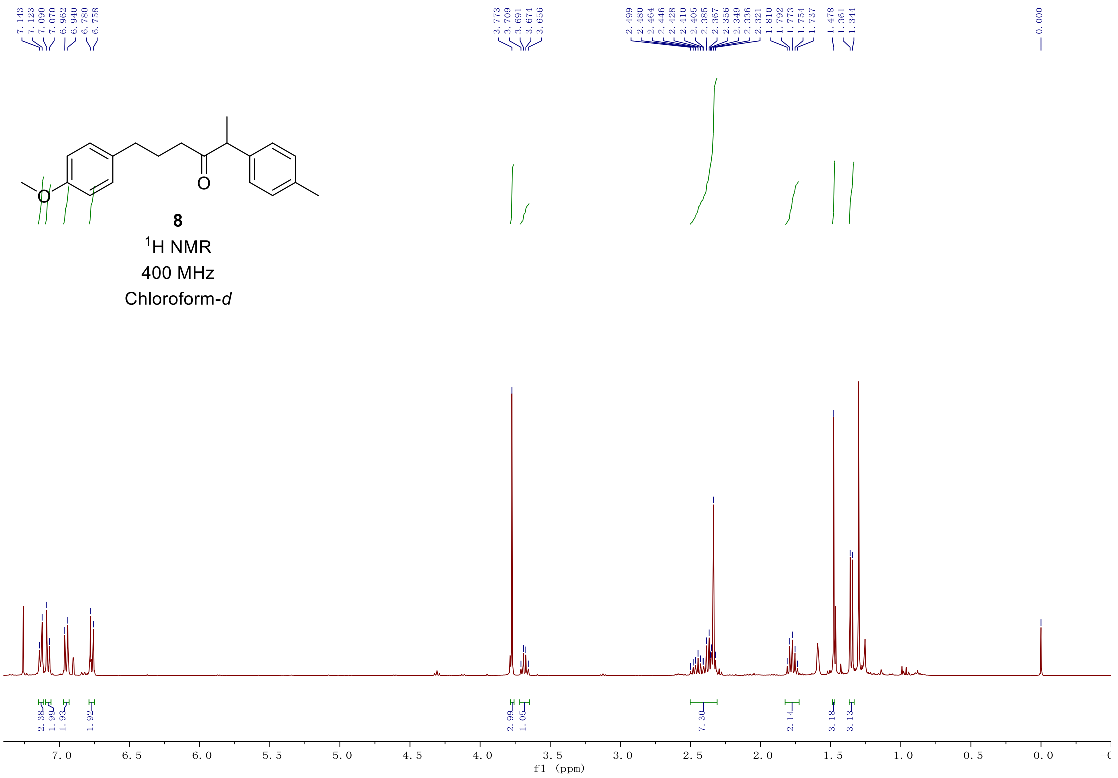


7

^{13}C NMR

101 MHz

Chloroform-*d*

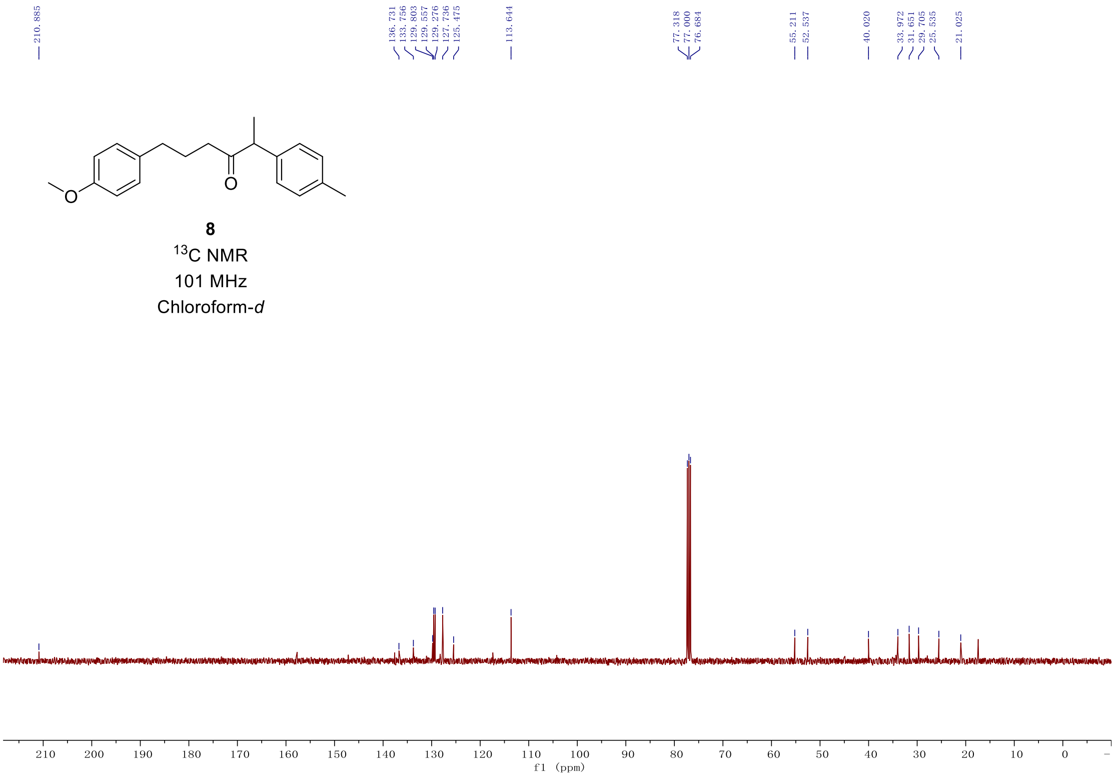


8

^{1}H NMR

400 MHz

Chloroform-*d*

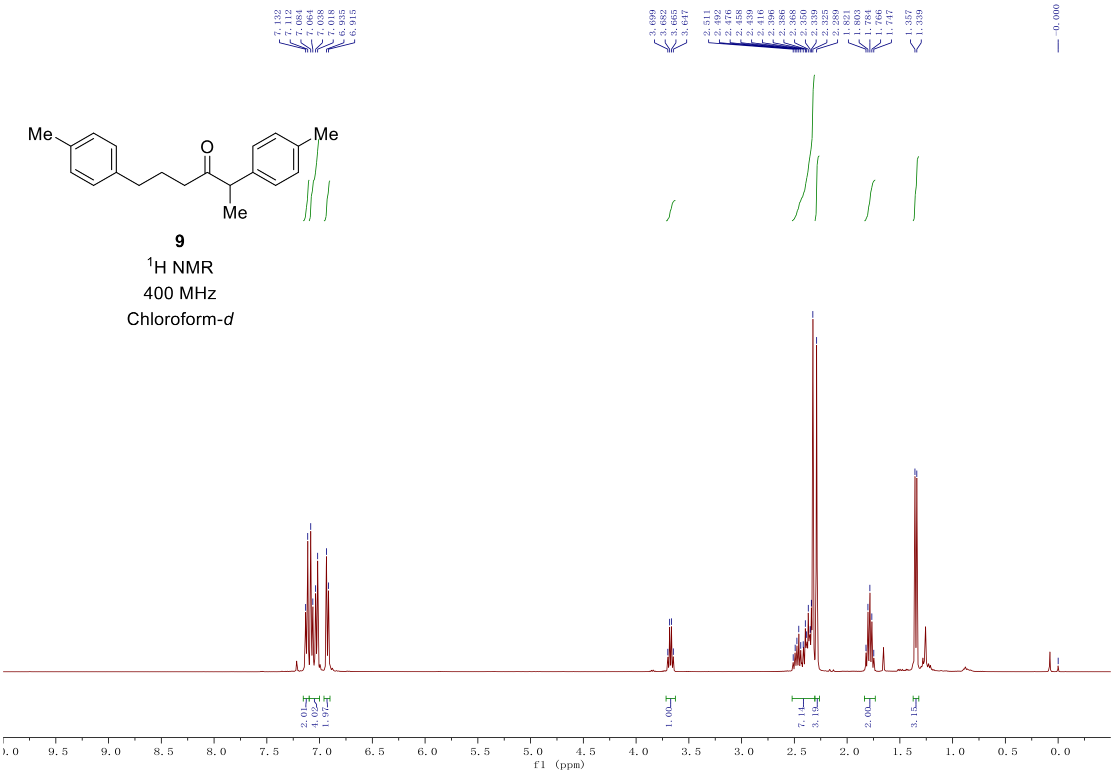


8

^{13}C NMR

101 MHz

Chloroform-*d*

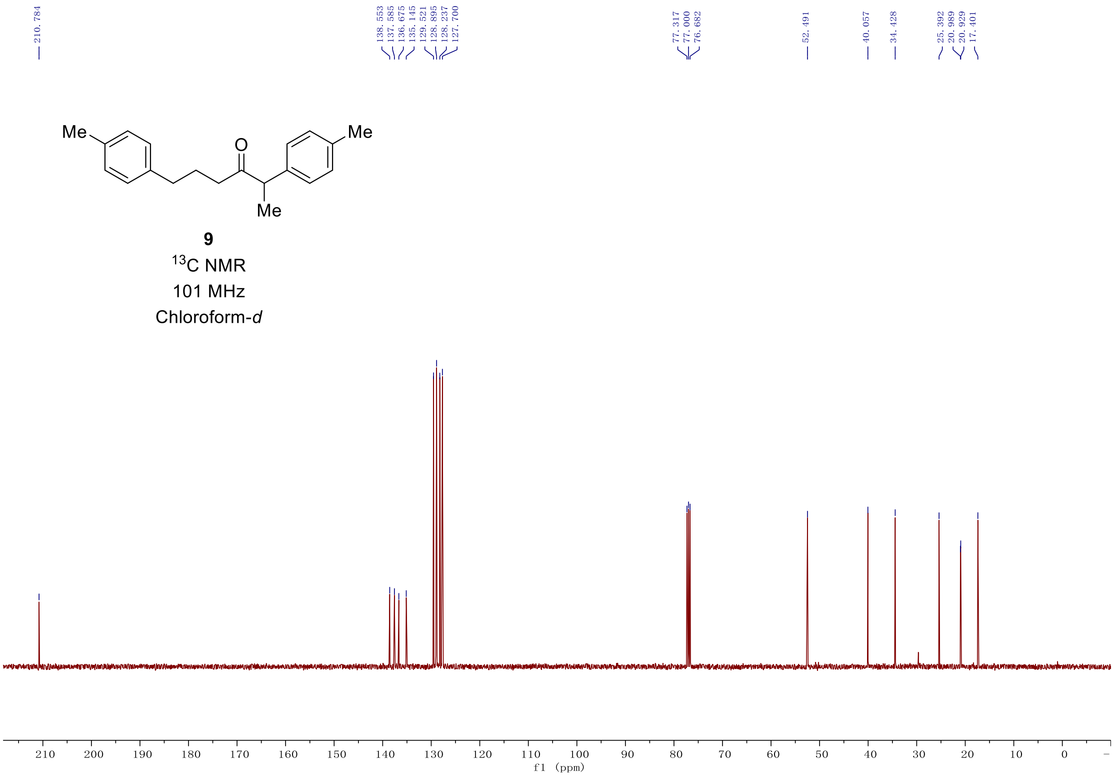


9

^{1}H NMR

400 MHz

Chloroform-*d*

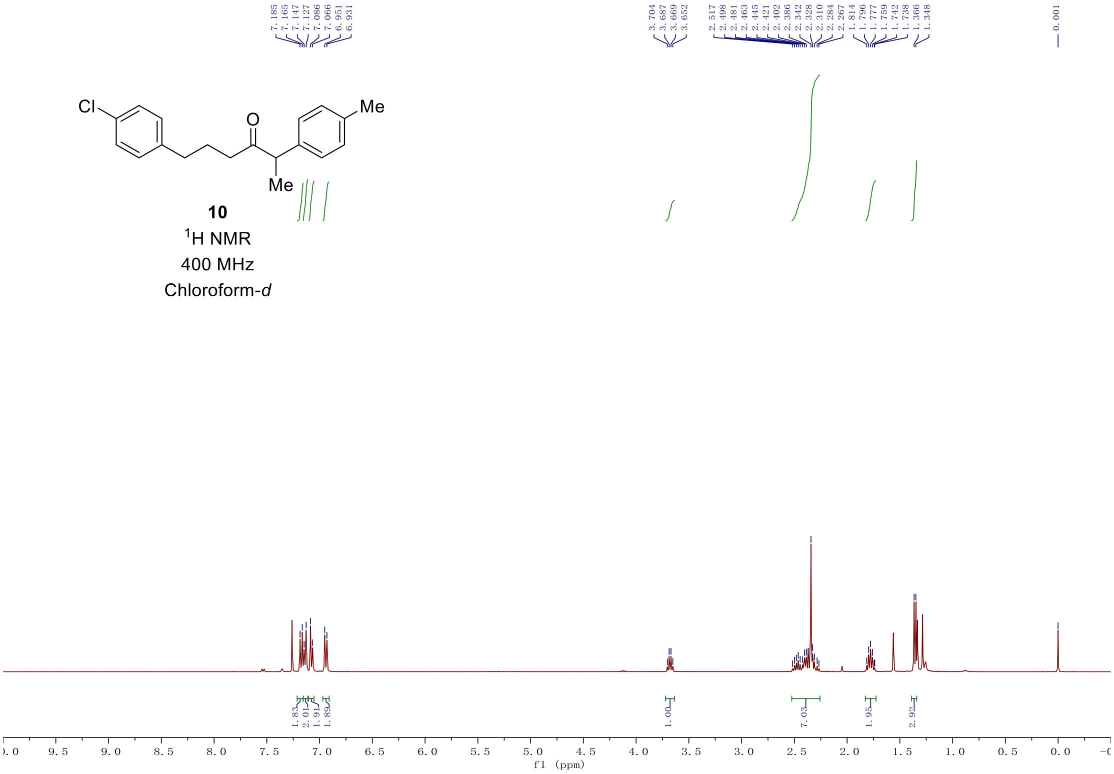


9

^{13}C NMR

101 MHz

Chloroform-*d*

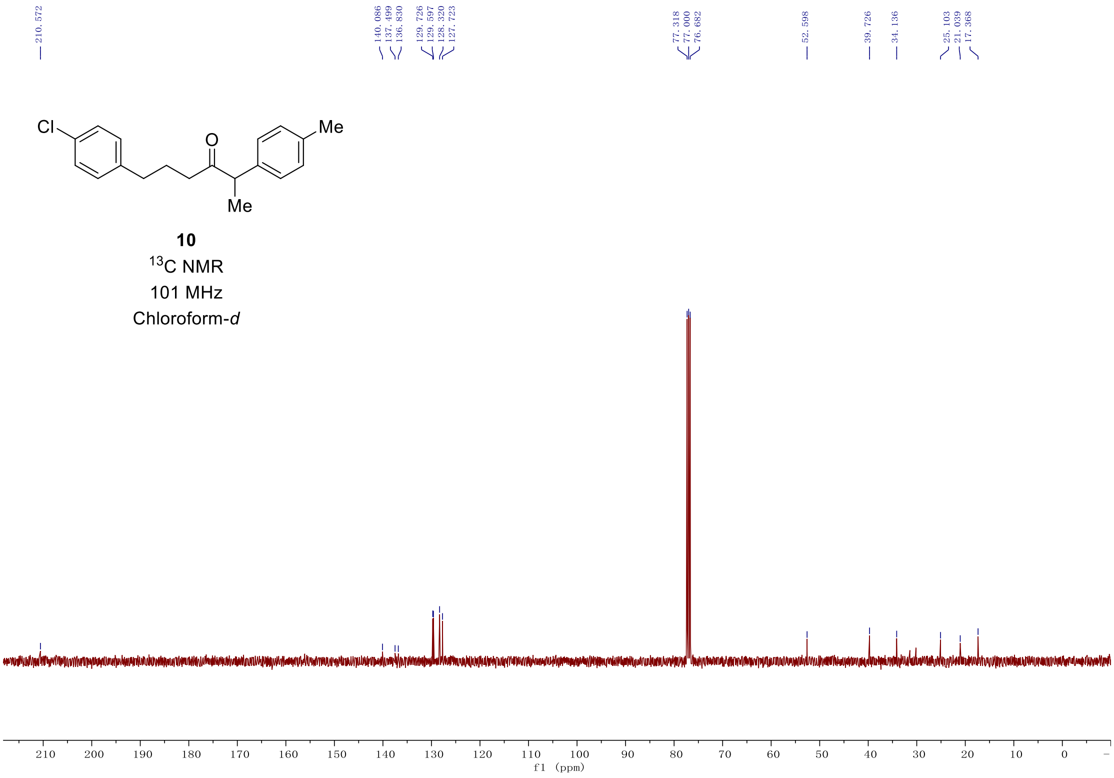


10

^{1}H NMR

400 MHz

Chloroform-*d*

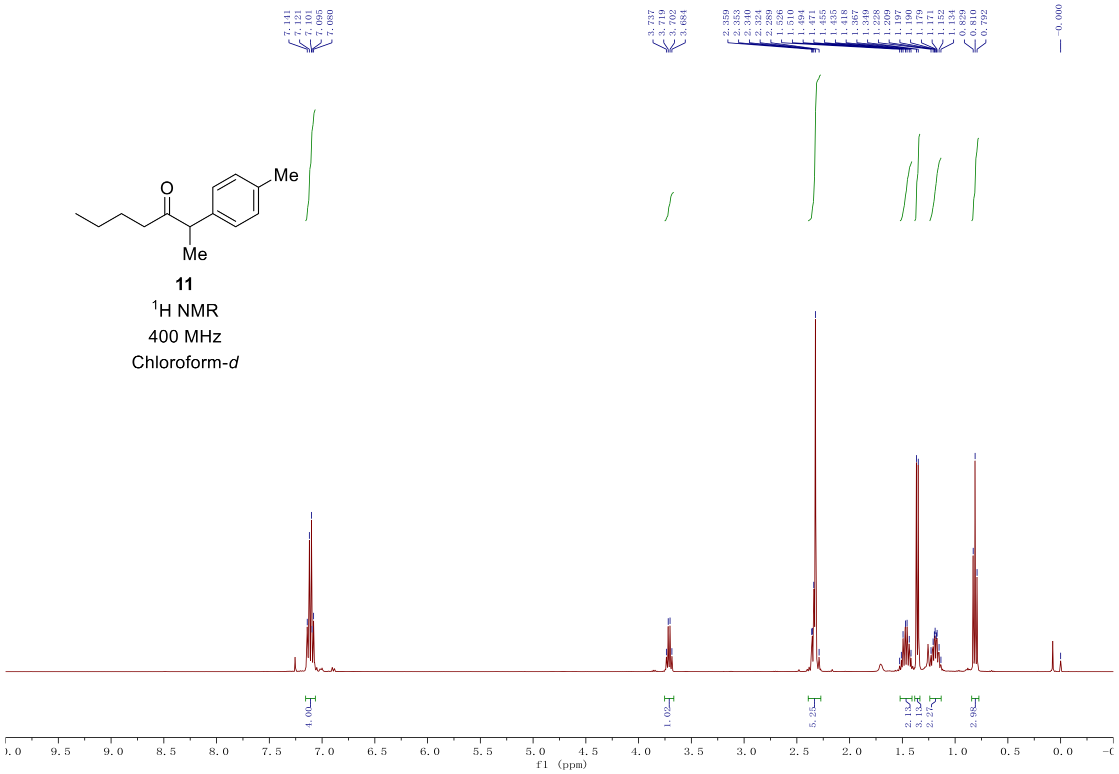


10

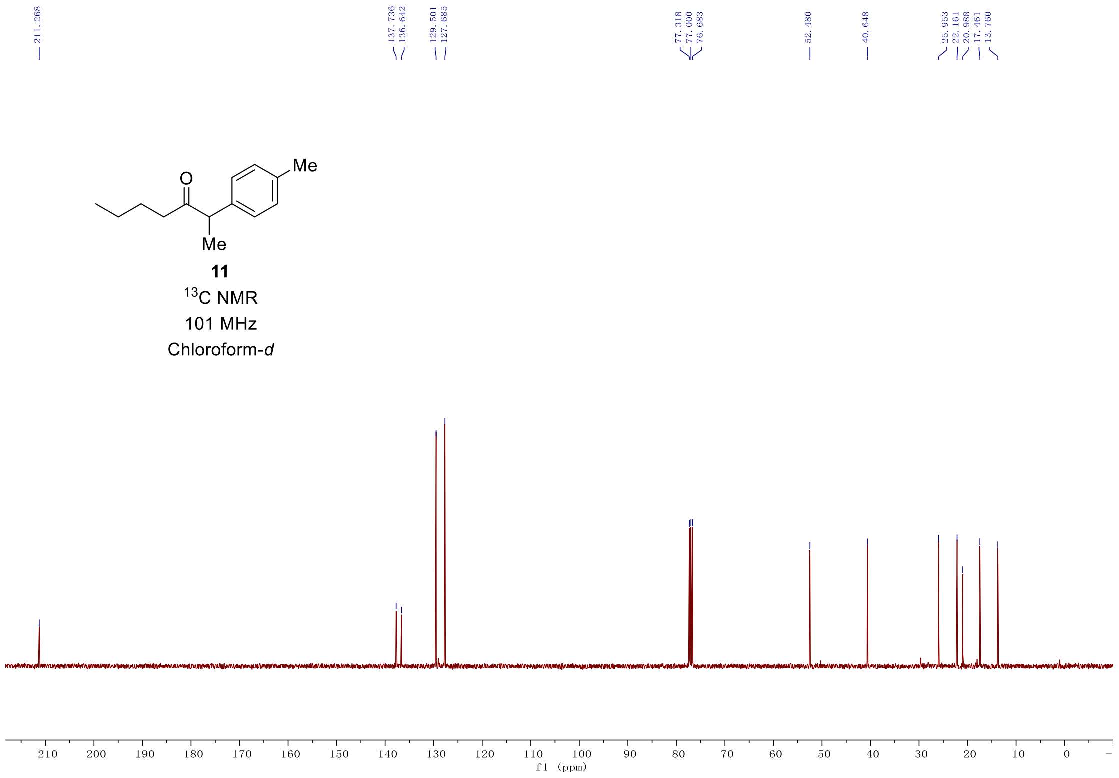
^{13}C NMR

101 MHz

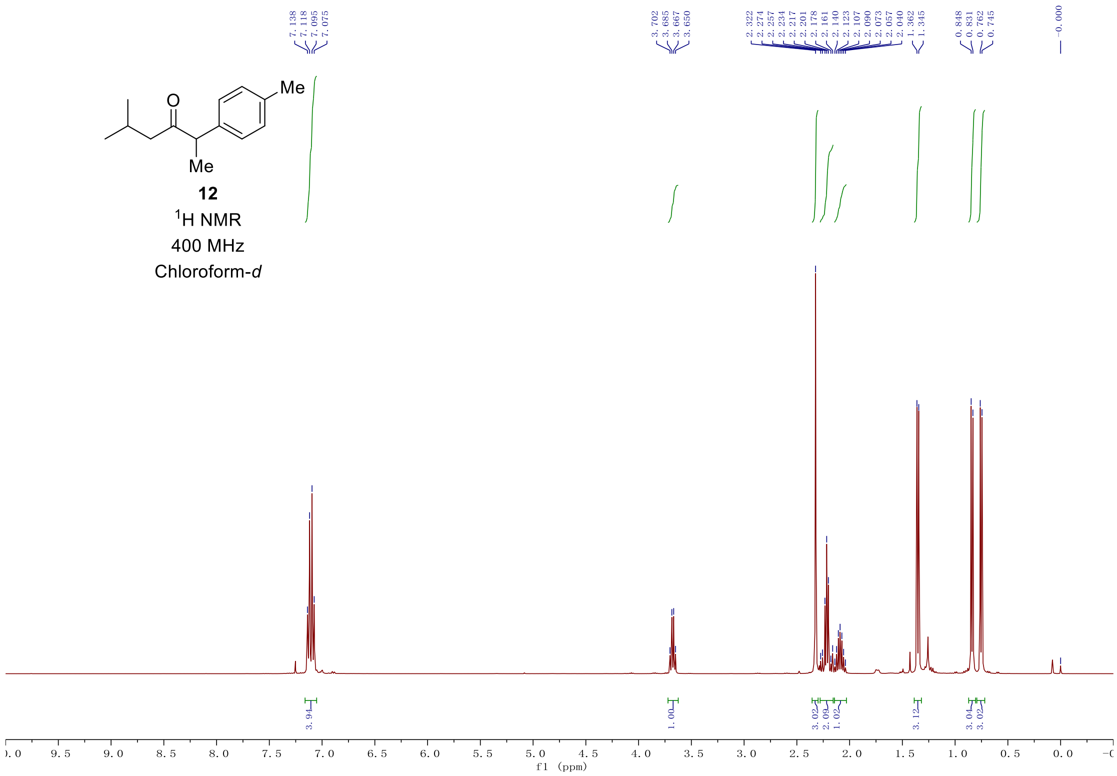
Chloroform-*d*



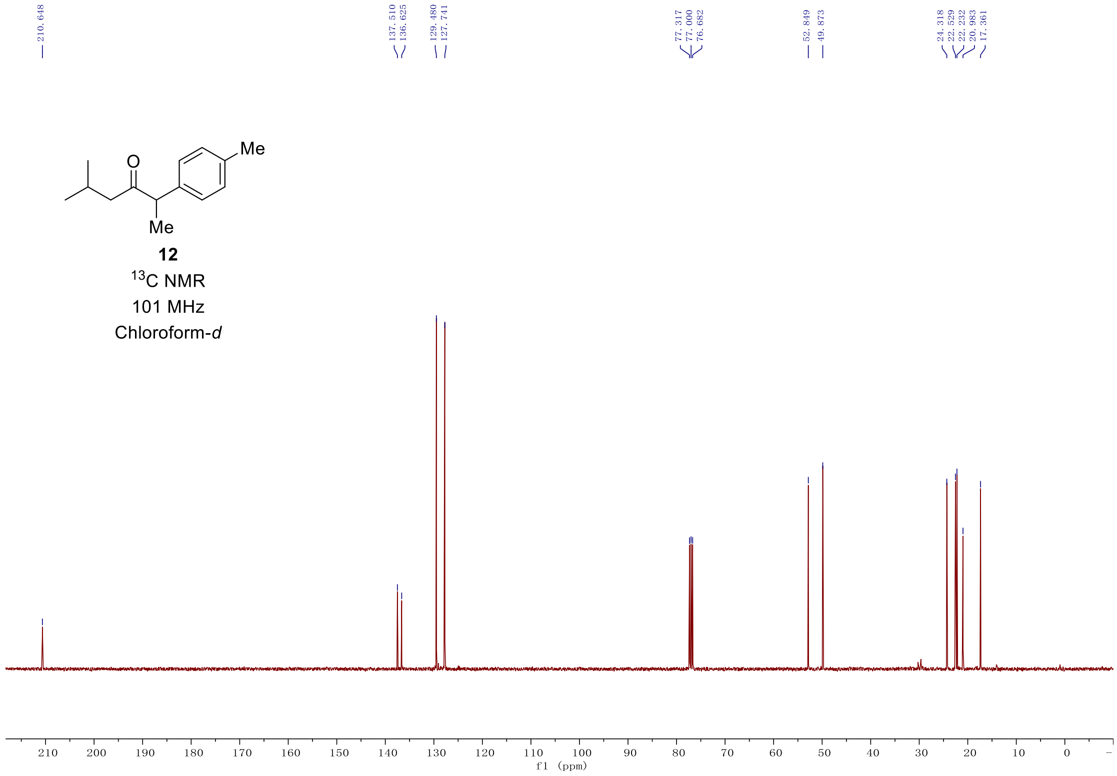
11
^{1}H NMR
400 MHz
Chloroform-*d*



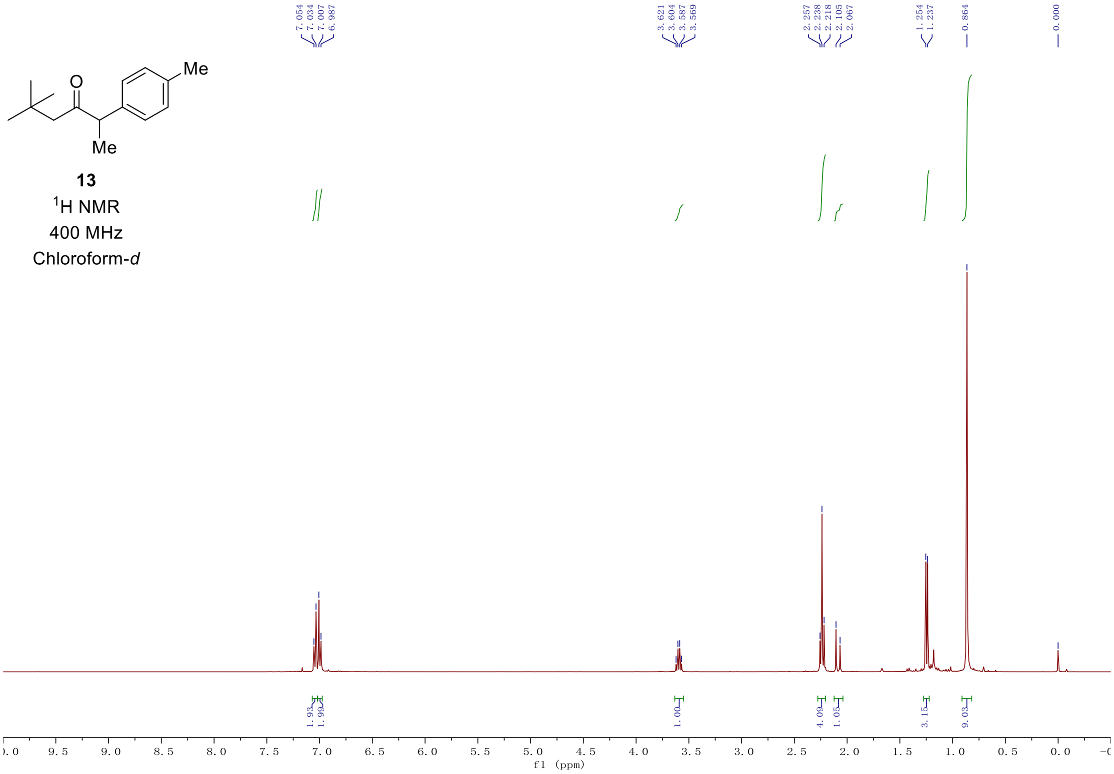
11
^{13}C NMR
101 MHz
Chloroform-*d*



12
^{1}H NMR
400 MHz
Chloroform-*d*



12
^{13}C NMR
101 MHz
Chloroform-*d*

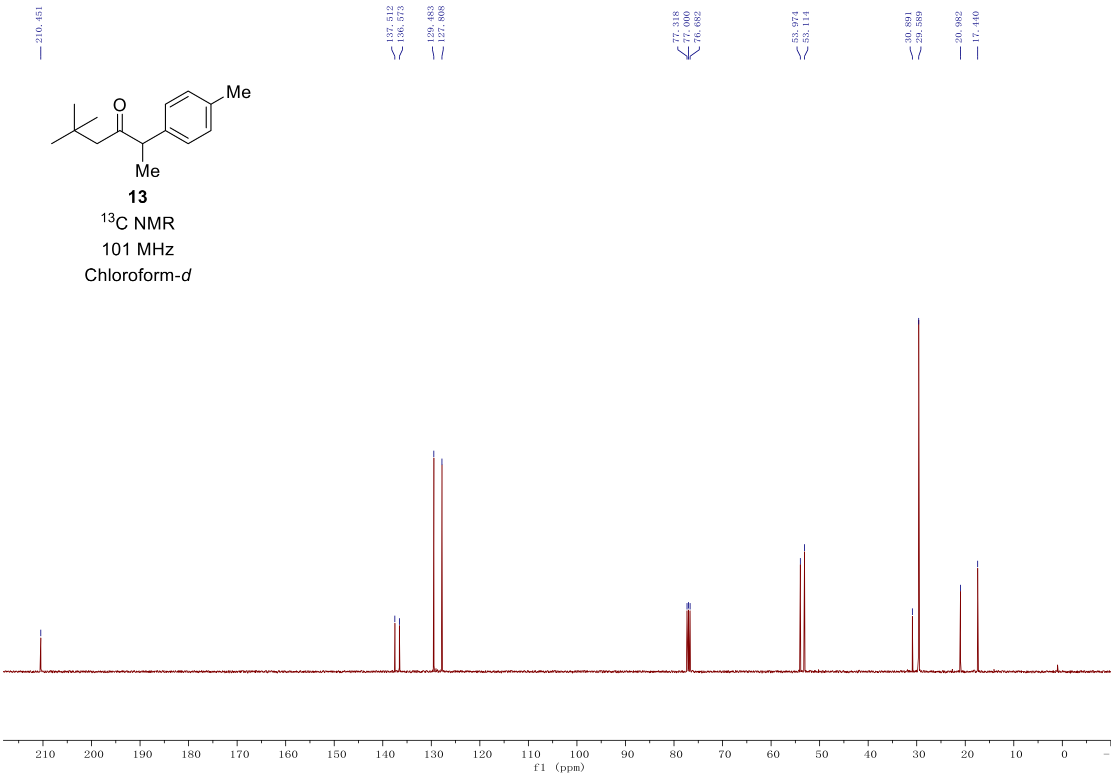


13

^{1}H NMR

400 MHz

Chloroform-*d*

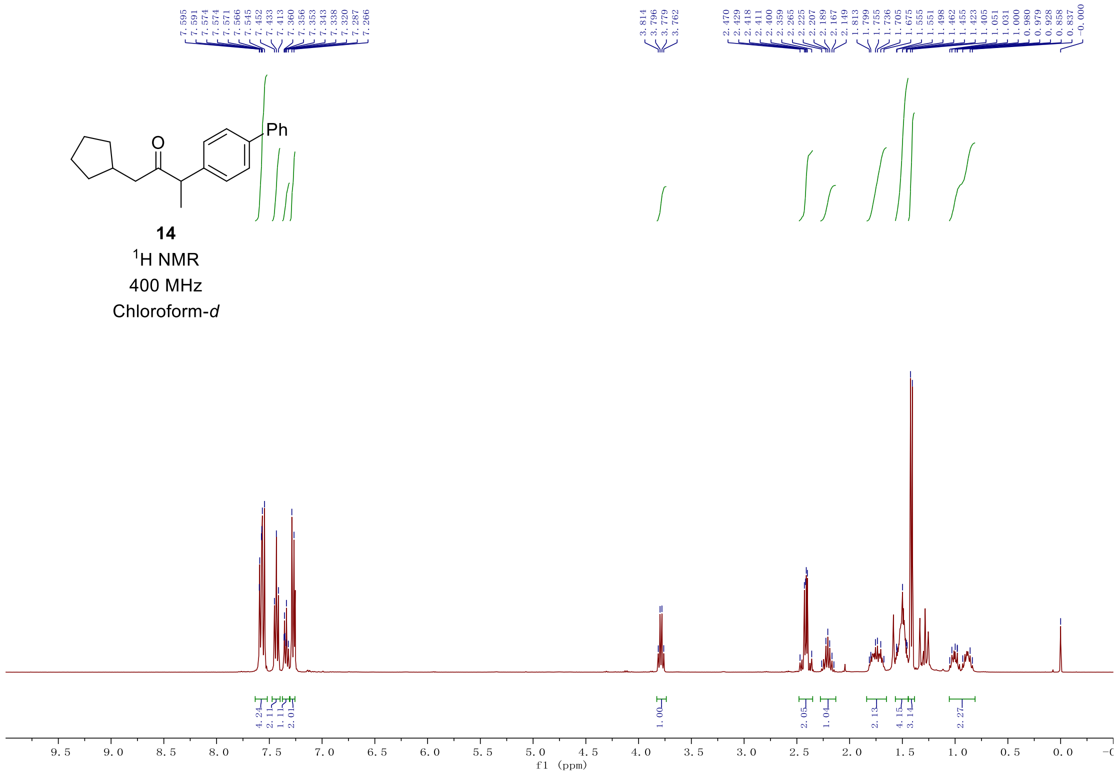


13

^{13}C NMR

101 MHz

Chloroform-*d*

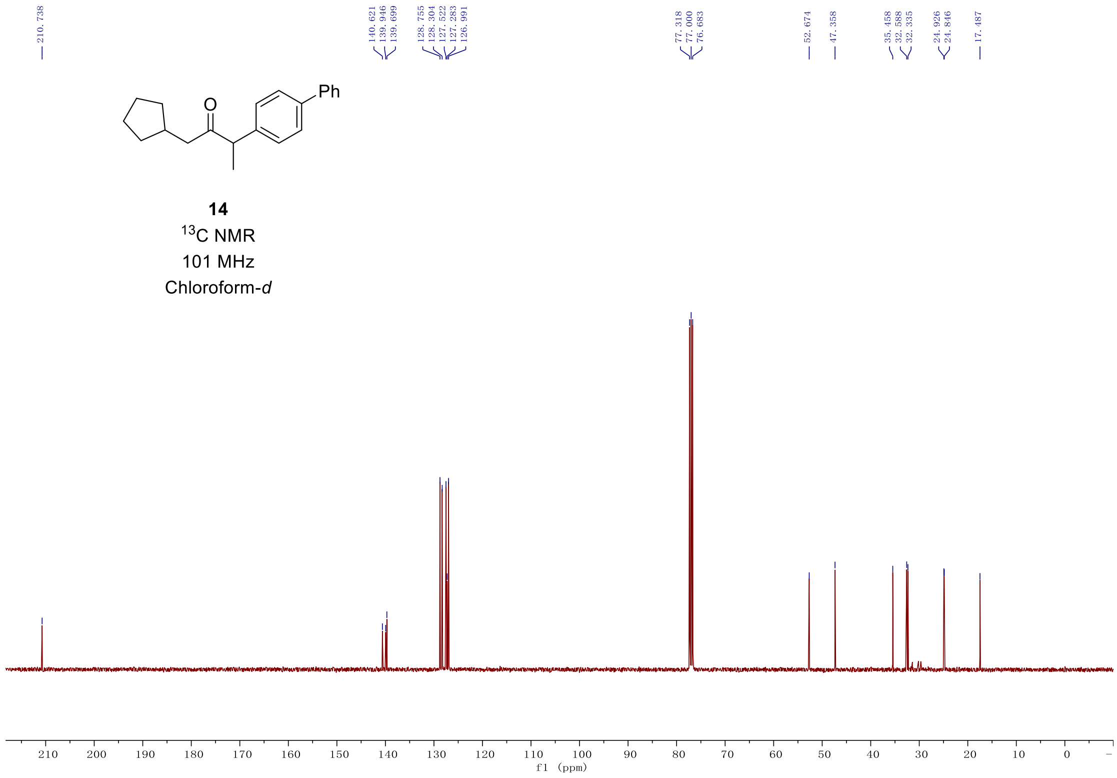


14

^{1}H NMR

400 MHz

Chloroform-*d*

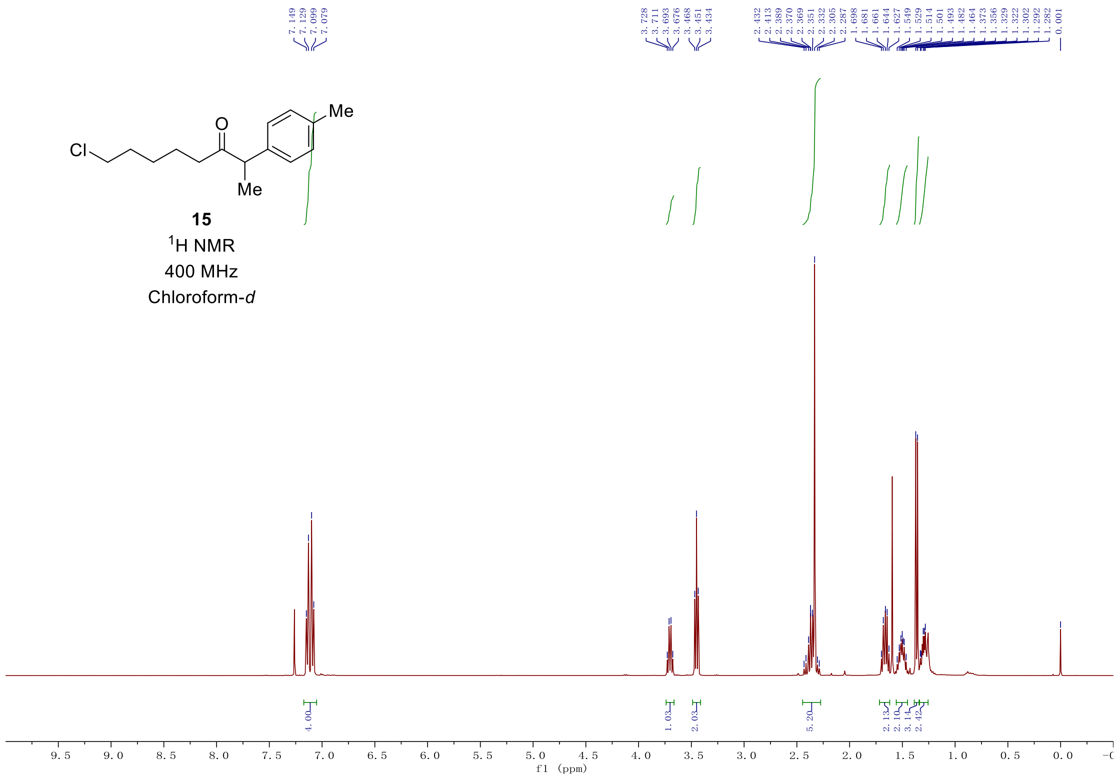


14

^{13}C NMR

101 MHz

Chloroform-*d*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7.079
3.728
3.711
3.693
3.676
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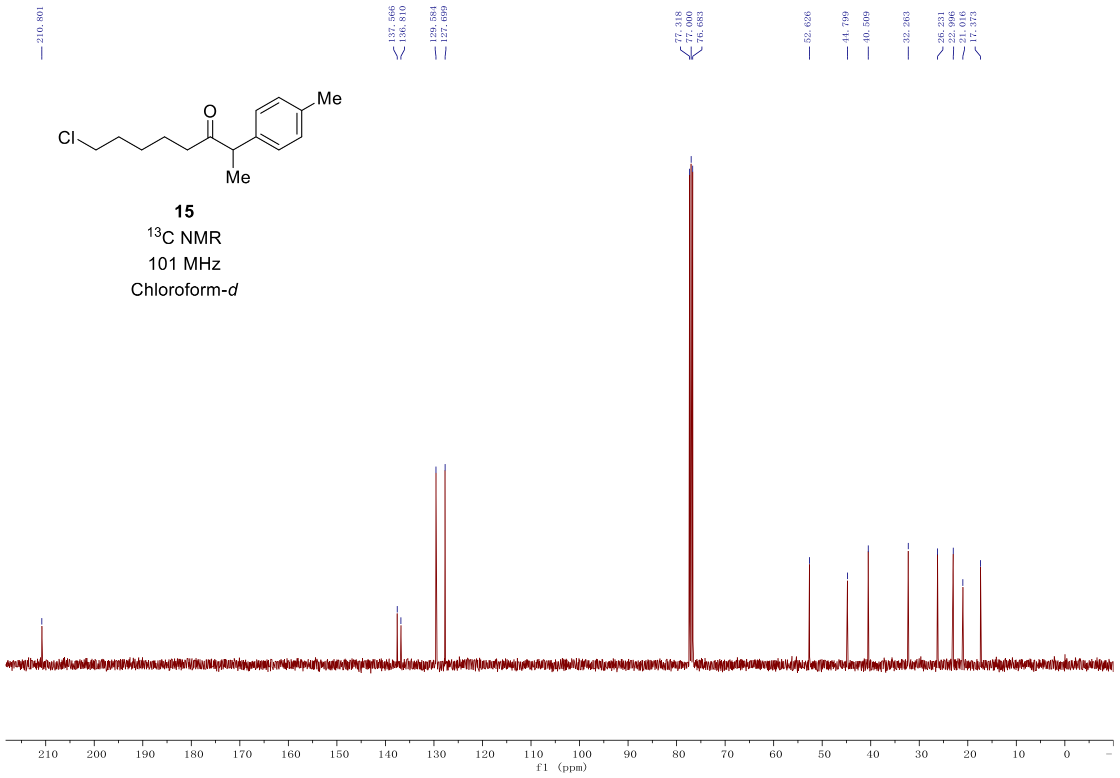
3.451
3.434
2.432
2.413
2.389
2.370
2.369
2.351
2.332
2.305
2.287
1.698
1.681
1.661
1.644
1.627
1.549
1.529
1.514
1.501
1.493
1.482
1.464
1.373
1.356
1.329
1.322
1.302
1.292
1.282
0.001
Cl
O
Me
Me
15
1H NMR
400 MHz
Chloroform-d
4.00
1.03
2.03
5.20
2.13
2.10
3.14
2.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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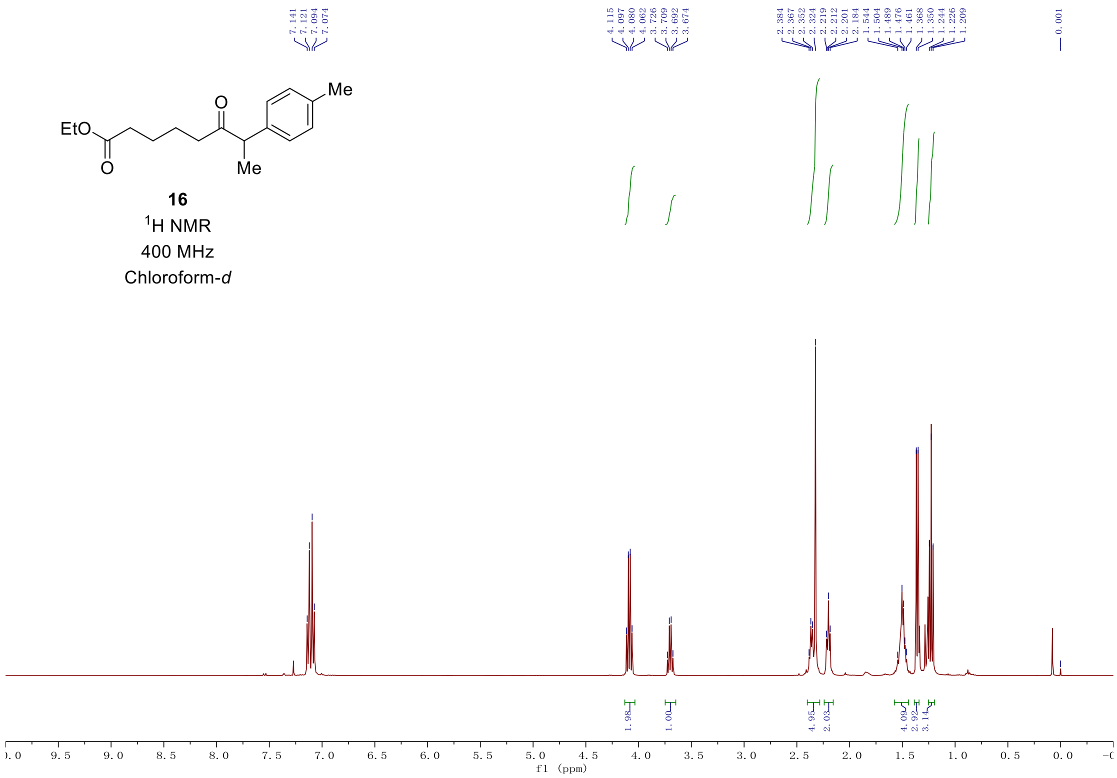
129.584
127.699
77.318
77.000
76.683
52.626
44.799
40.509
32.263
26.231
22.996
21.016
17.373
Cl
O
Me
Me
15
13C NMR
101 MHz
Chloroform-d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

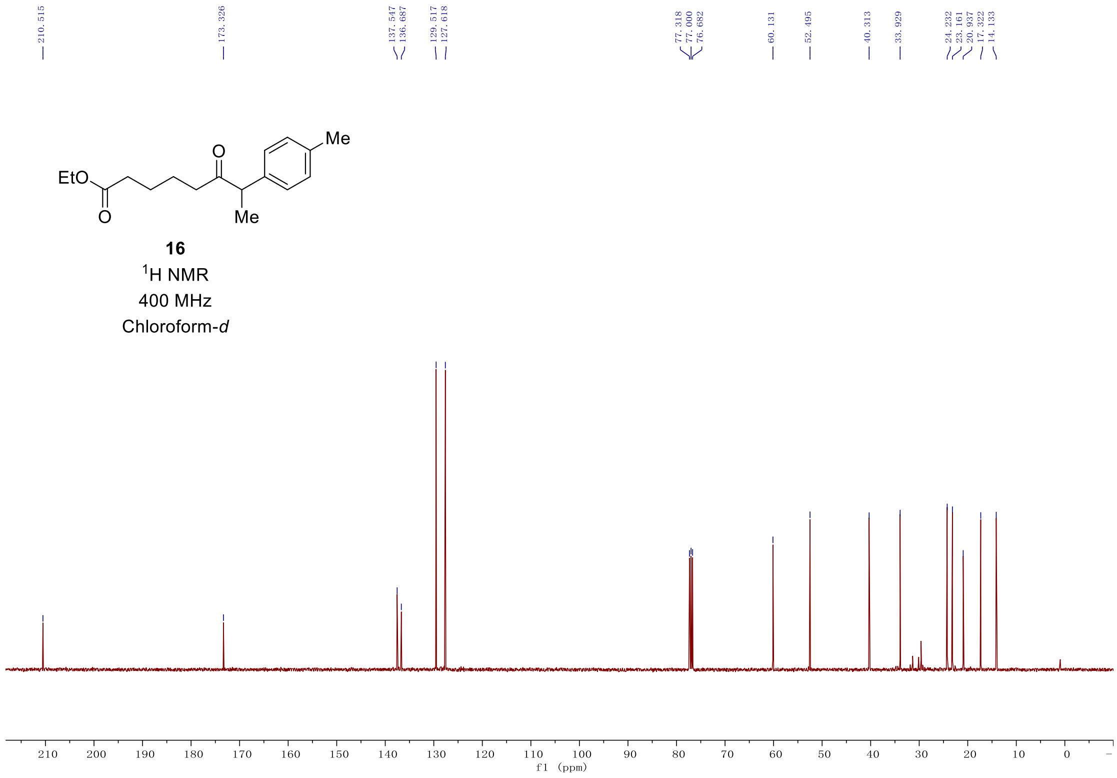


16

^{1}H NMR

400 MHz

Chloroform-*d*

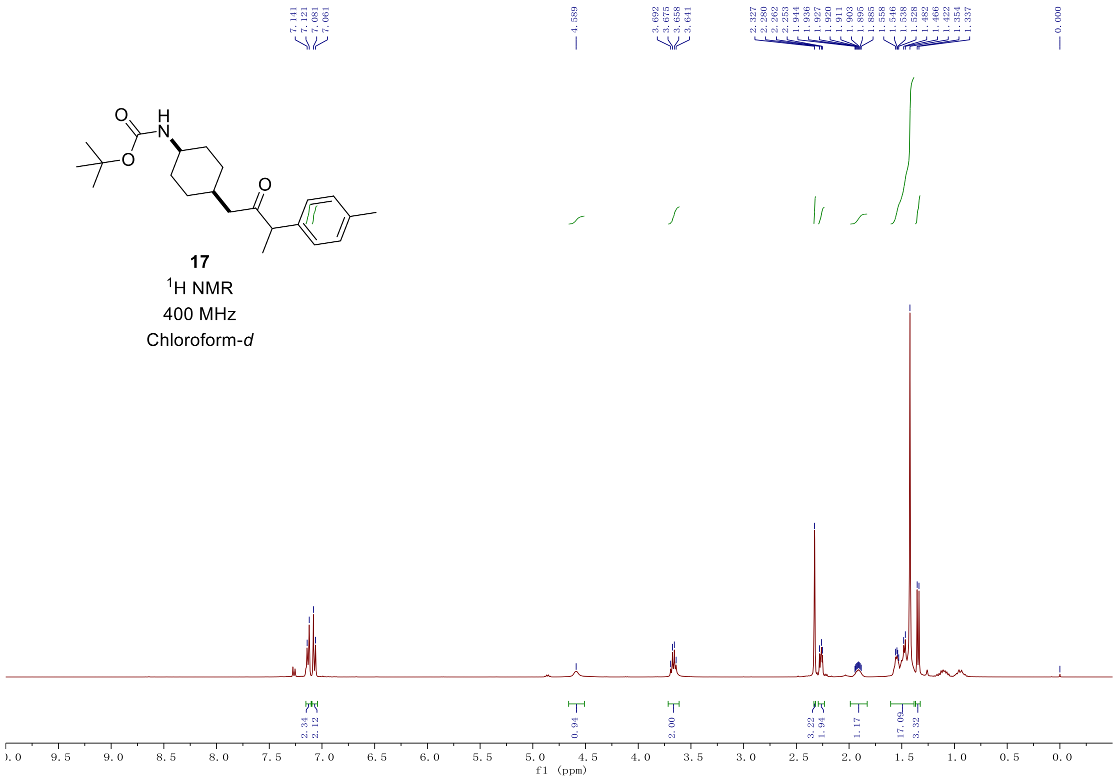


16

^{1}H NMR

400 MHz

Chloroform-*d*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7.061
4.589
3.692
3.675
3.658
3.641
2.327
2.280
2.262
2.253
1.944
1.936
1.927
1.920
1.911
1.903
1.895
1.885
1.558
1.546
1.538
1.528
1.482
1.466
1.422
1.354
1.337
0.000
17
^{1}H NMR
400 MHz
Chloroform-*d*
2.34
2.12
0.94
2.00
3.22
1.94
1.17
17.09
3.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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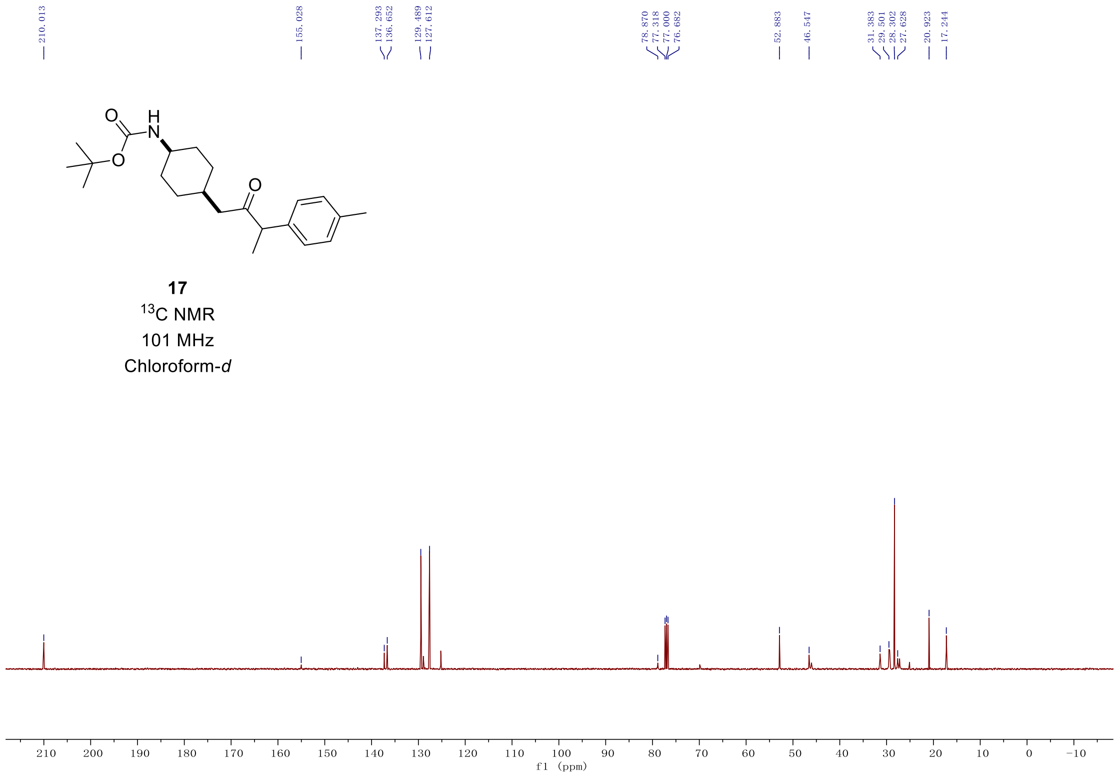
1.0
0.5
0.0
f1 (ppm)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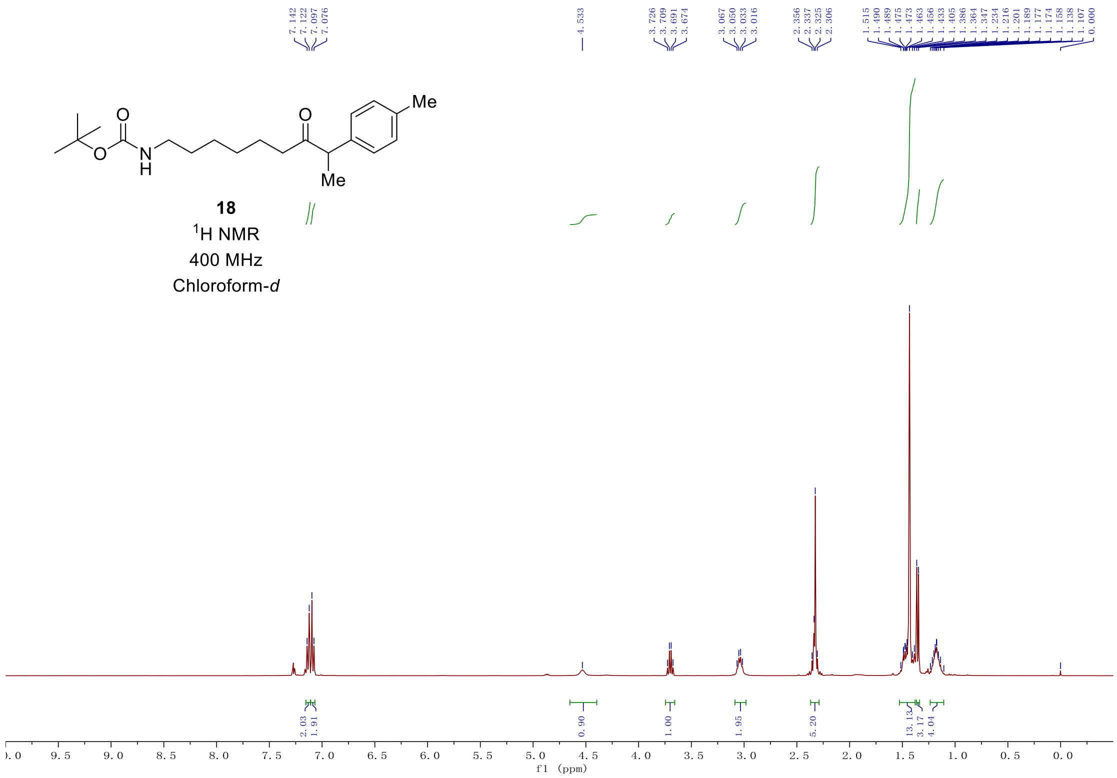
78.870
77.318
77.000
76.682
52.883
46.547
31.383
29.501
28.302
27.628
20.923
17.244
17
^{13}C NMR
101 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

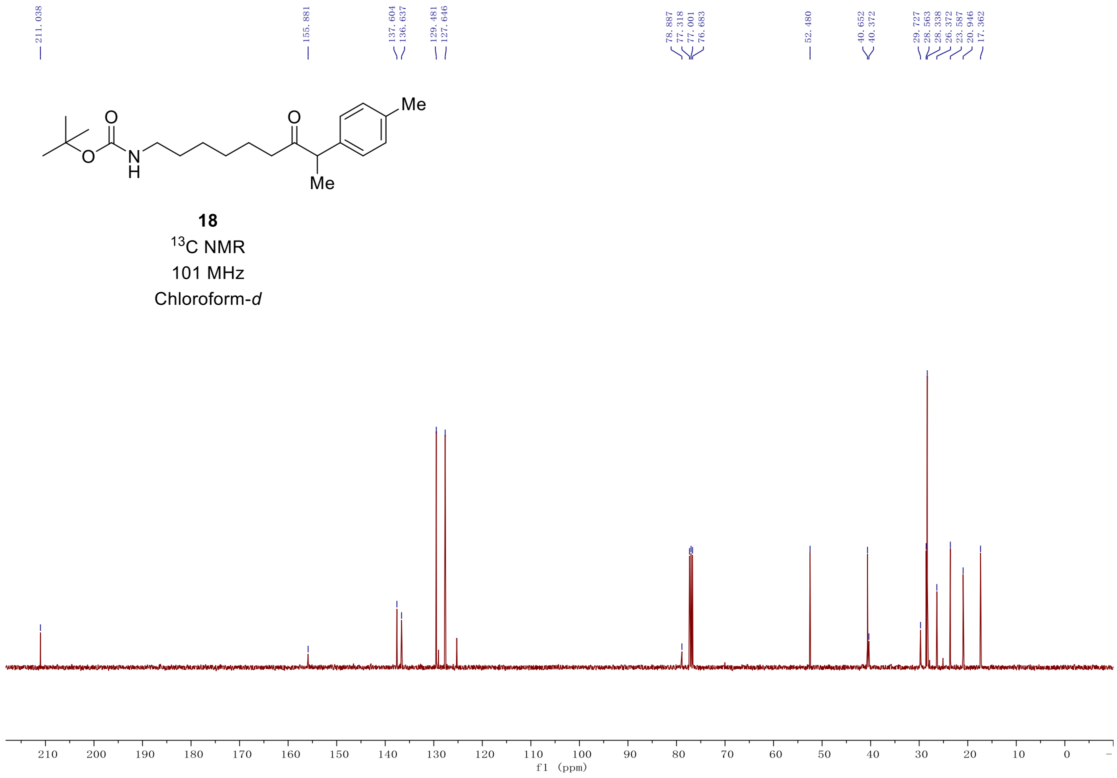


18

^{1}H NMR

400 MHz

Chloroform-*d*

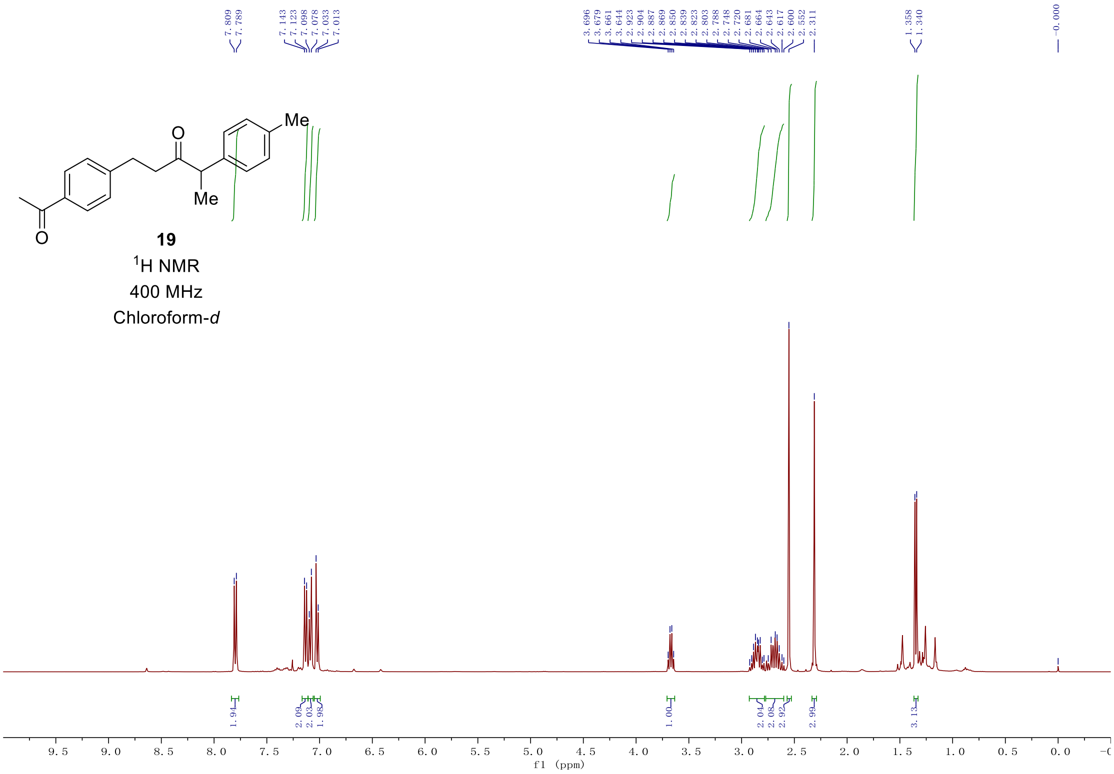


18

^{13}C NMR

101 MHz

Chloroform-*d*

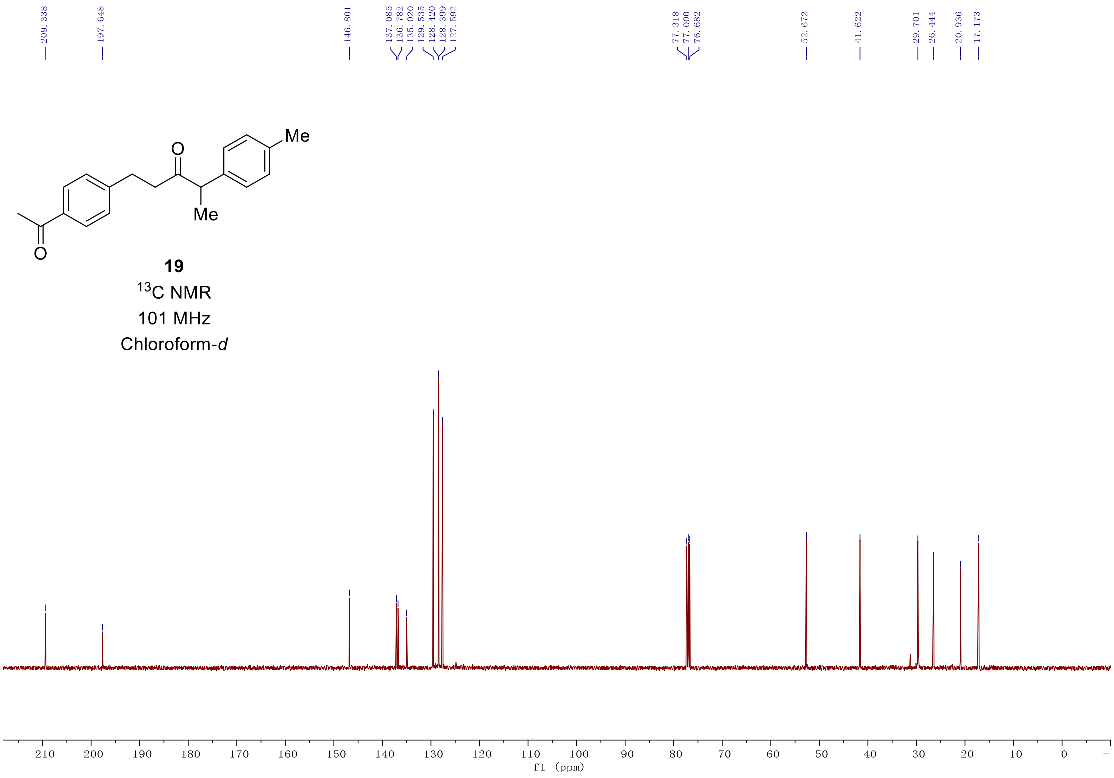


19

^{1}H NMR

400 MHz

Chloroform-*d*

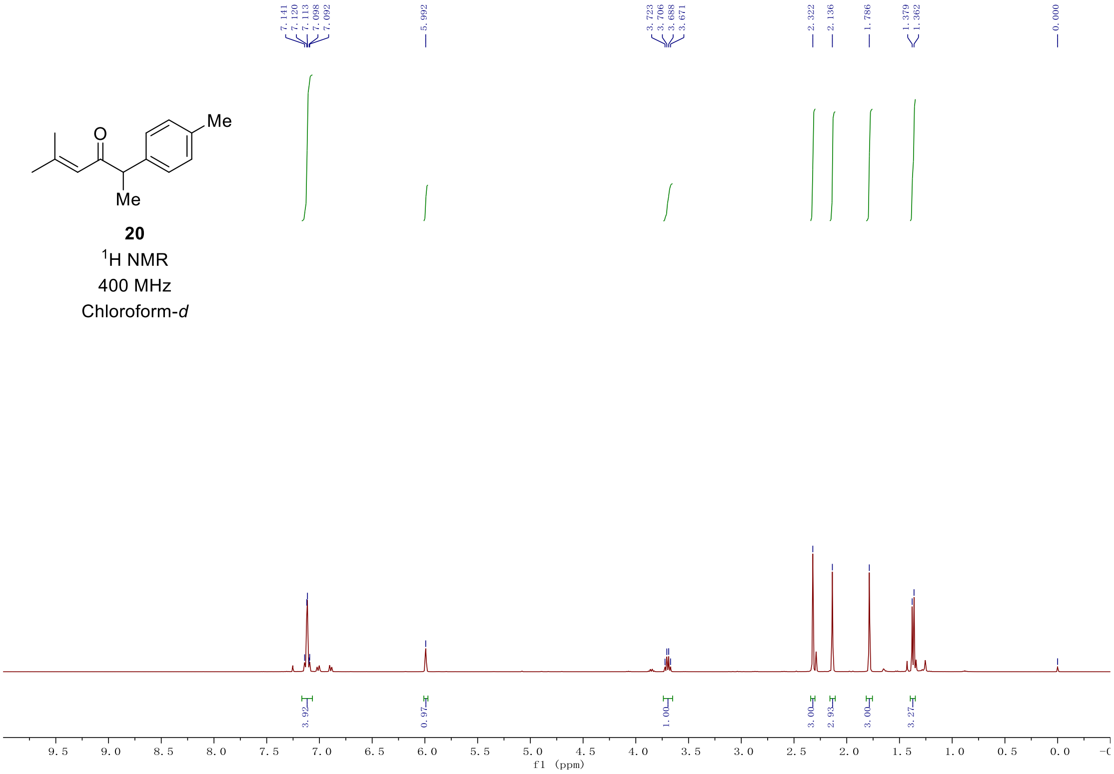


19

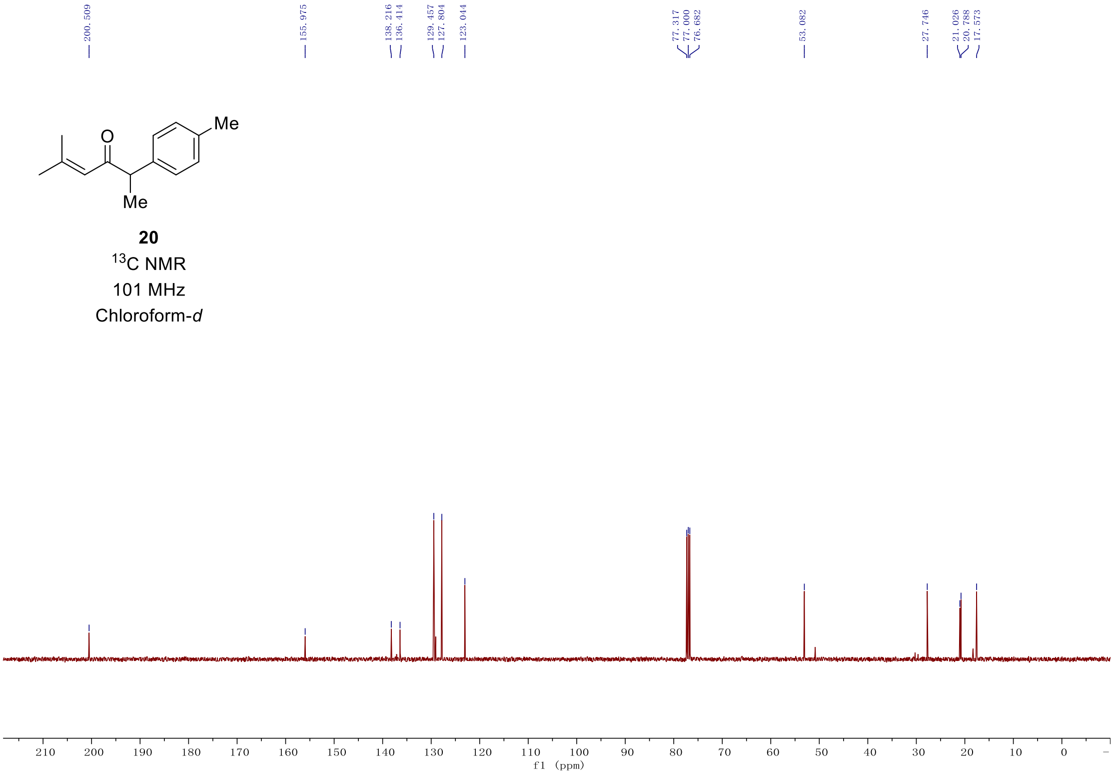
^{13}C NMR

101 MHz

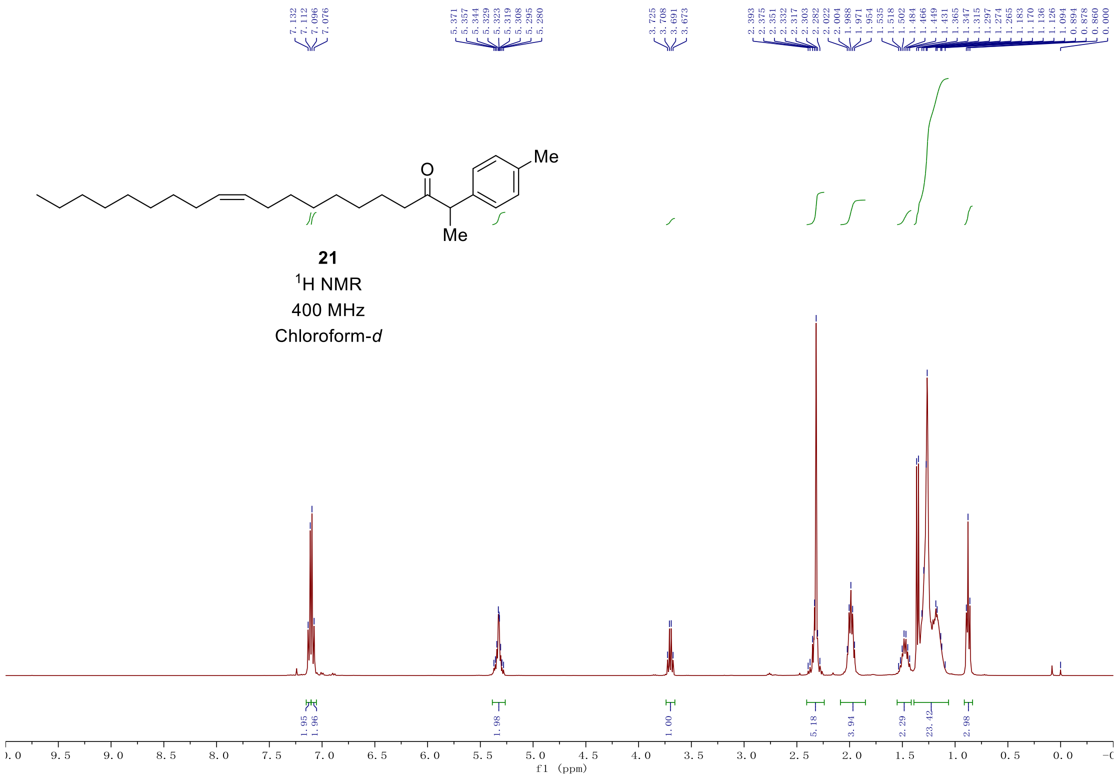
Chloroform-*d*



20
^{1}H NMR
400 MHz
Chloroform-*d*



20
^{13}C NMR
101 MHz
Chloroform-*d*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5.371
5.357
5.344
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3.725
3.708
3.691
3.673
2.393
2.375
2.351
2.332
2.317
2.303
2.282
2.022
2.004
1.988
1.971
1.954
1.535
1.518
1.502
1.484
1.466
1.449
1.431
1.365
1.347
1.315
1.297
1.274
1.265
1.183
1.170
1.136
1.126
1.094
0.894
0.878
0.860
0.000
O
Me
Me
21
^{1}H NMR
400 MHz
Chloroform-*d*
1.95
1.96
1.98
1.00
5.18
3.94
2.29
23.42
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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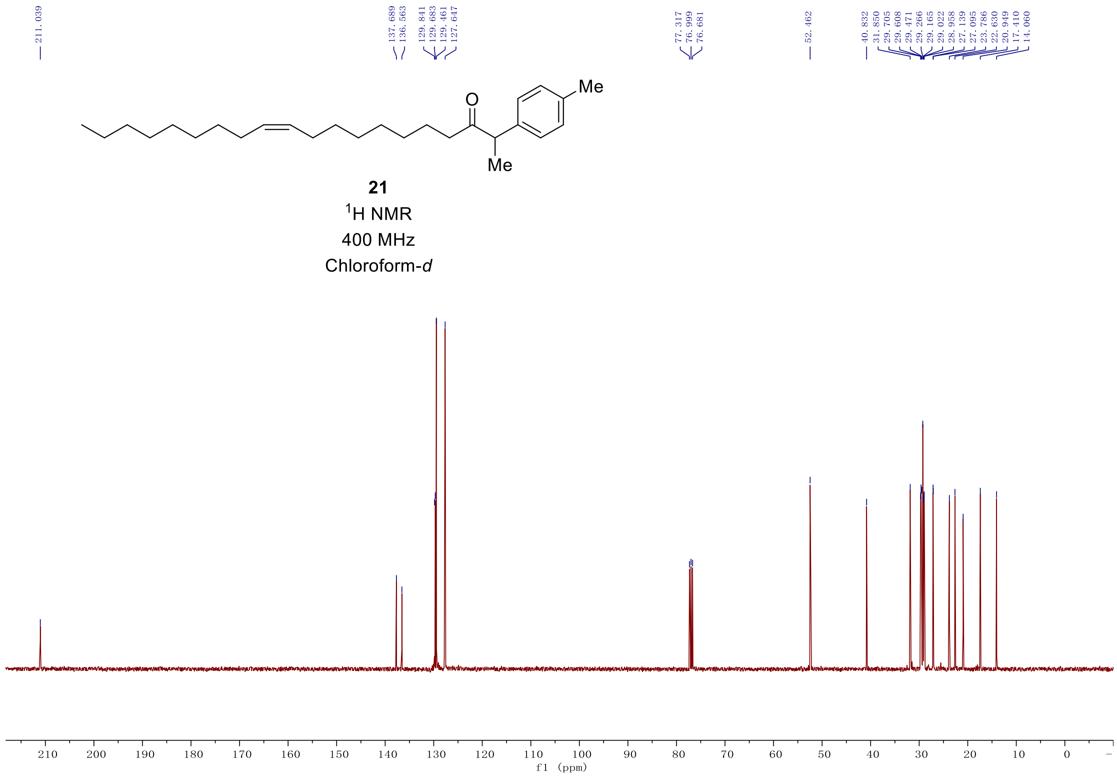
1.0
0.5
0.0
f1 (ppm)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76.681
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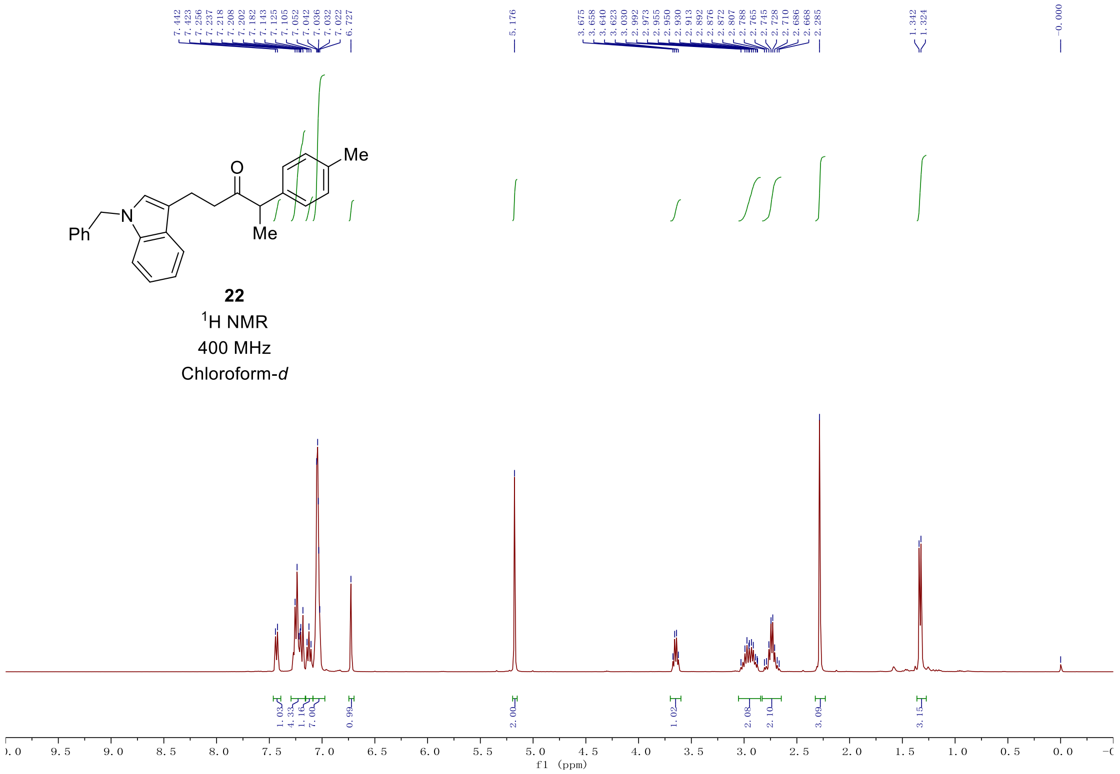
31.850
29.765
29.608
29.471
29.266
29.165
29.022
28.958
27.139
27.095
23.786
22.630
20.949
17.410
14.060
O
Me
Me
21
^{1}H NMR
400 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.125
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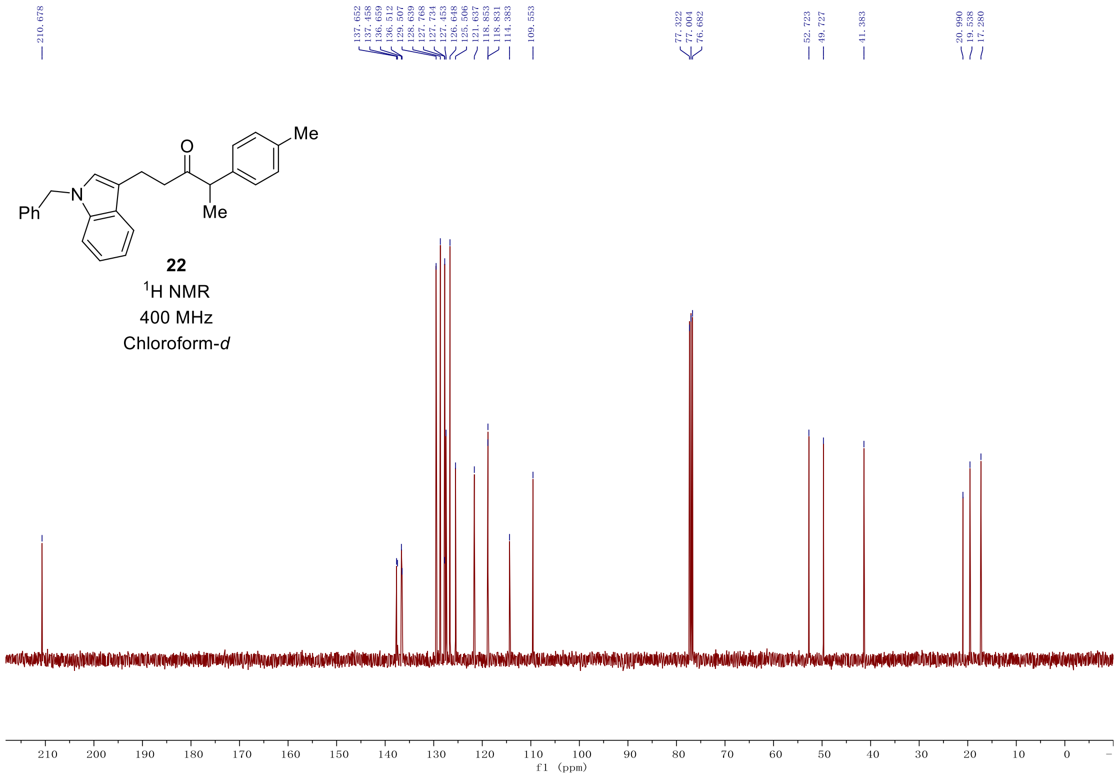
7.052
7.042
7.036
7.032
7.022
6.727
5.176
3.675
3.658
3.640
3.623
3.030
2.992
2.973
2.955
2.950
2.930
2.913
2.892
2.876
2.872
2.807
2.788
2.765
2.745
2.728
2.710
2.686
2.668
2.285
1.342
1.324
-0.000
Me
O
N
Ph
Me
22
^{1}H NMR
400 MHz
Chloroform-*d*
1.03
4.33
1.16
7.00
0.99
2.00
1.02
2.08
2.10
3.09
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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136.512
129.507
128.639
127.768
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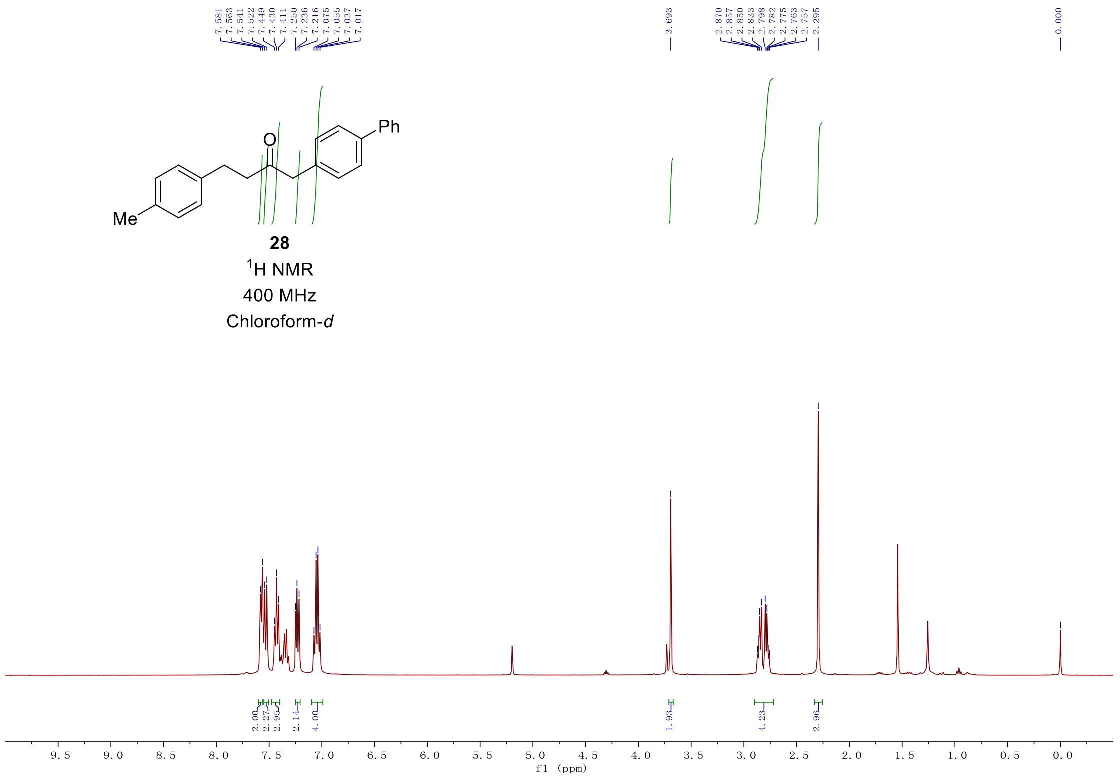
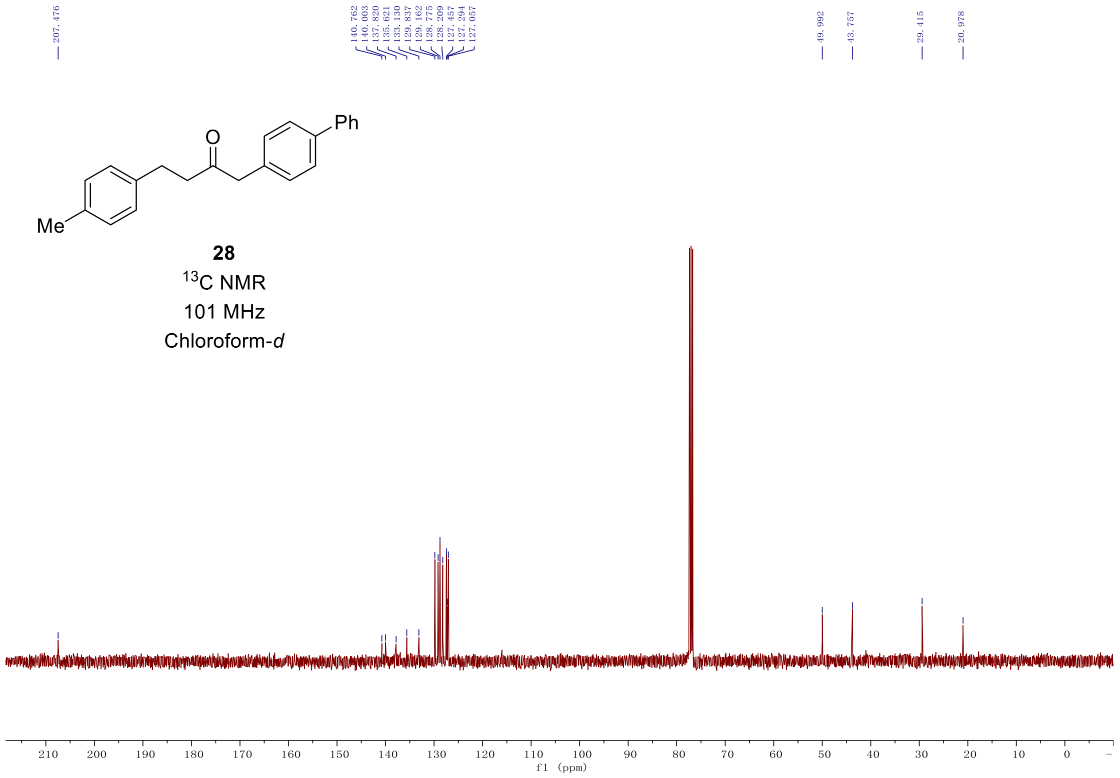
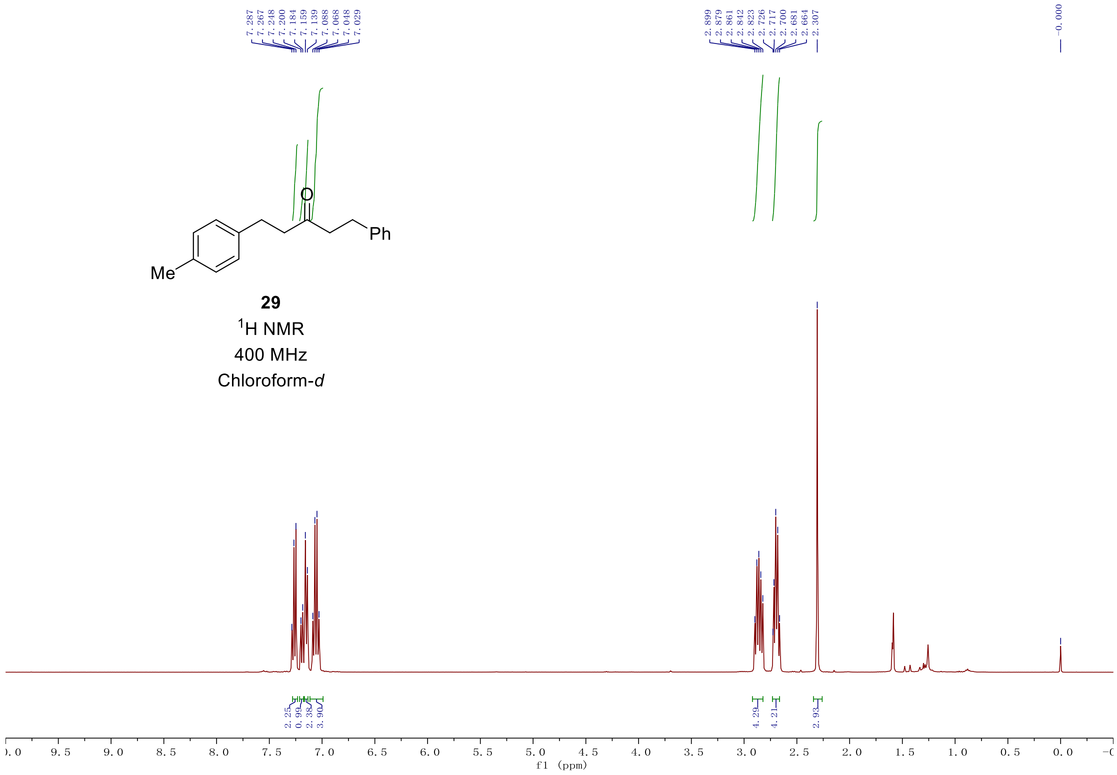
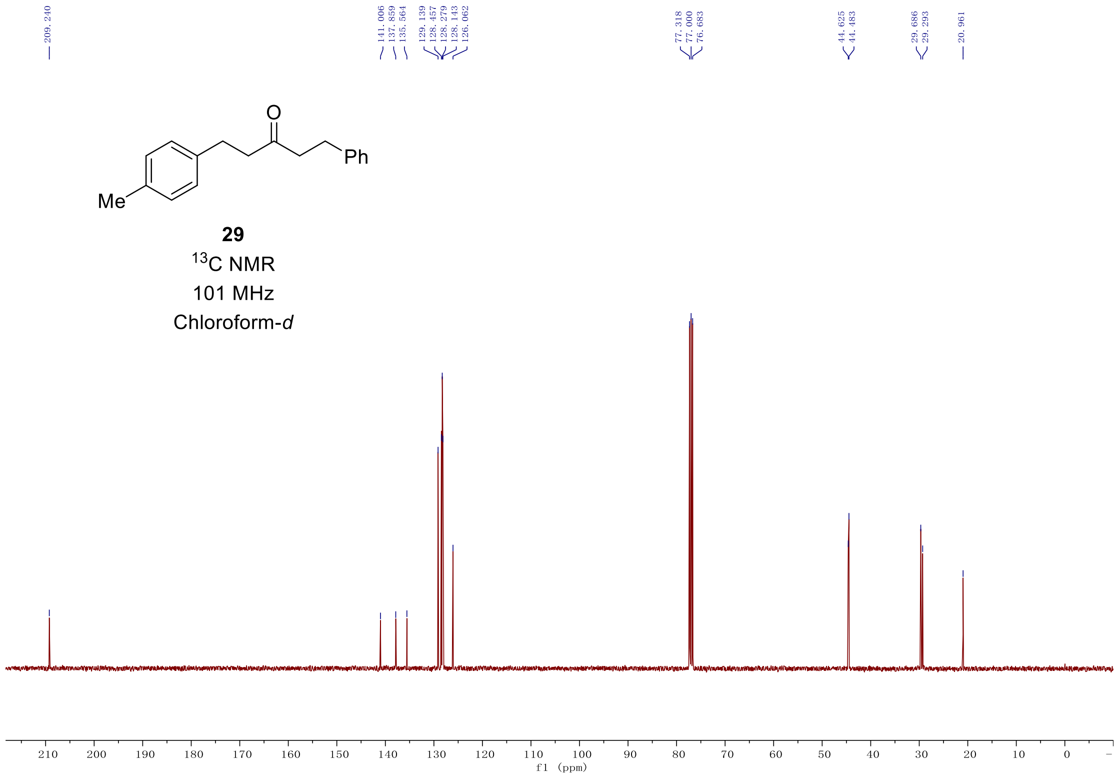
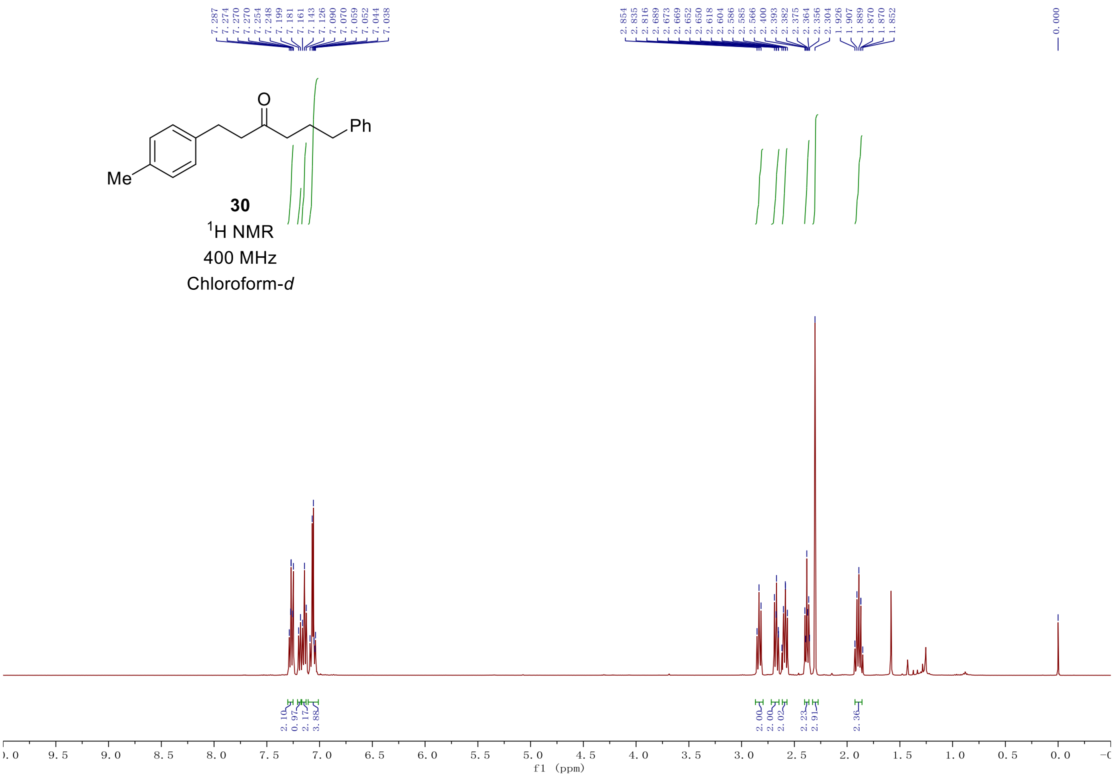
126.648
125.506
121.637
118.853
118.831
114.383
109.553
77.322
77.004
76.682
52.723
49.727
41.383
20.990
19.538
17.280
Me
O
N
Ph
Me
22
^{1}H NMR
400 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.581
7.563
7.541
7.522
7.449
7.430
7.411
7.250
7.236
7.216
7.075
7.055
7.037
7.017
3.693
2.870
2.857
2.850
2.833
2.798
2.782
2.775
2.763
2.757
2.295
0.000
Ph
O
Me
28
^{1}H NMR
400 MHz
Chloroform-*d*
2.00
2.27
2.95
2.14
4.00
1.93
4.23
2.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.476
140.762
140.003
137.820
135.621
133.130
129.837
129.162
128.775
128.209
127.457
127.294
127.057
49.992
43.757
29.415
20.978
Ph
O
Me
28
^{13}C NMR
101 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.287
7.267
7.248
7.200
7.184
7.159
7.139
7.088
7.068
7.048
7.029
2.899
2.879
2.861
2.842
2.823
2.726
2.717
2.700
2.681
2.664
2.307
-0.000
O
Ph
Me
29
^{1}H NMR
400 MHz
Chloroform-*d*
2.25
0.94
2.38
3.90
4.29
4.21
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


209.240
141.006
137.859
135.564
129.139
128.457
128.279
128.143
126.062
77.318
77.000
76.683
44.625
44.483
29.686
29.293
20.961
O
Ph
Me
29
^{13}C NMR
101 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

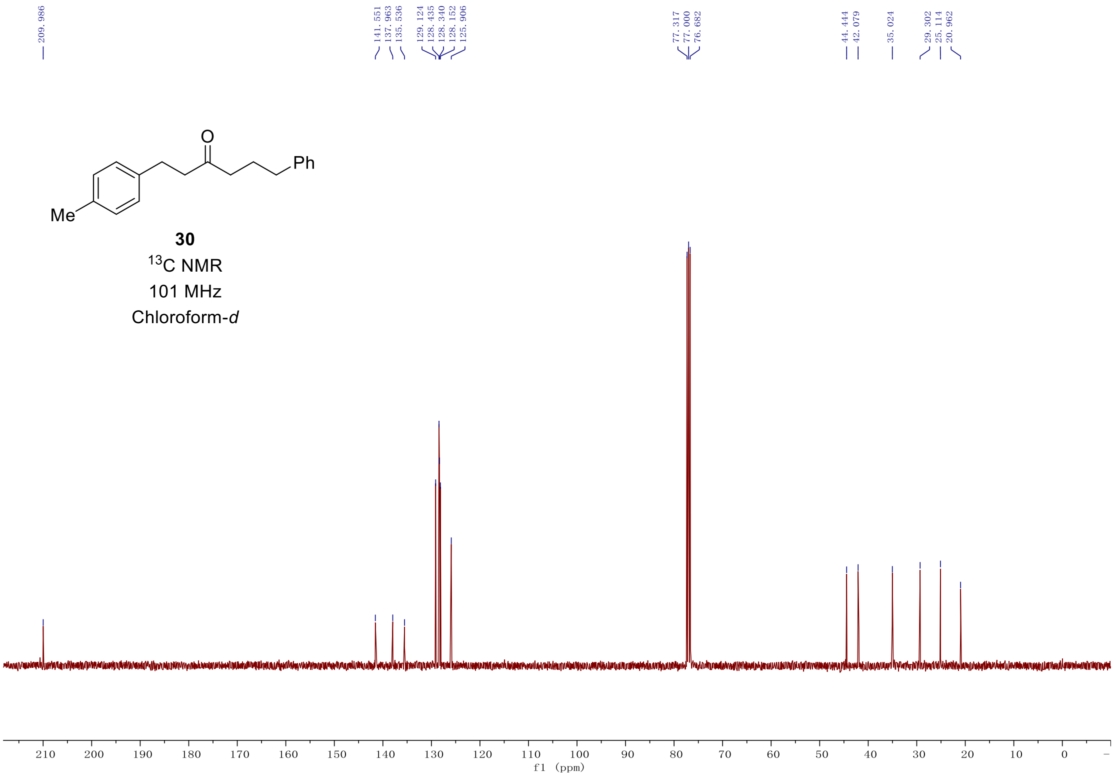


30

^{1}H NMR

400 MHz

Chloroform-*d*

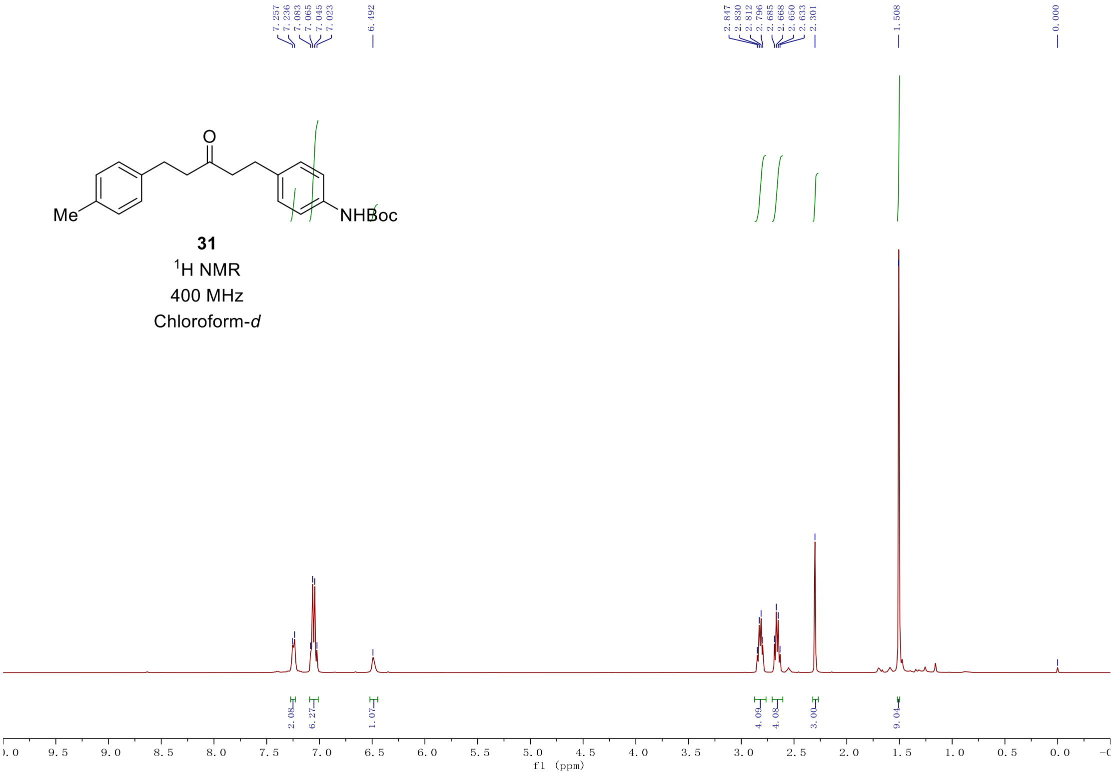


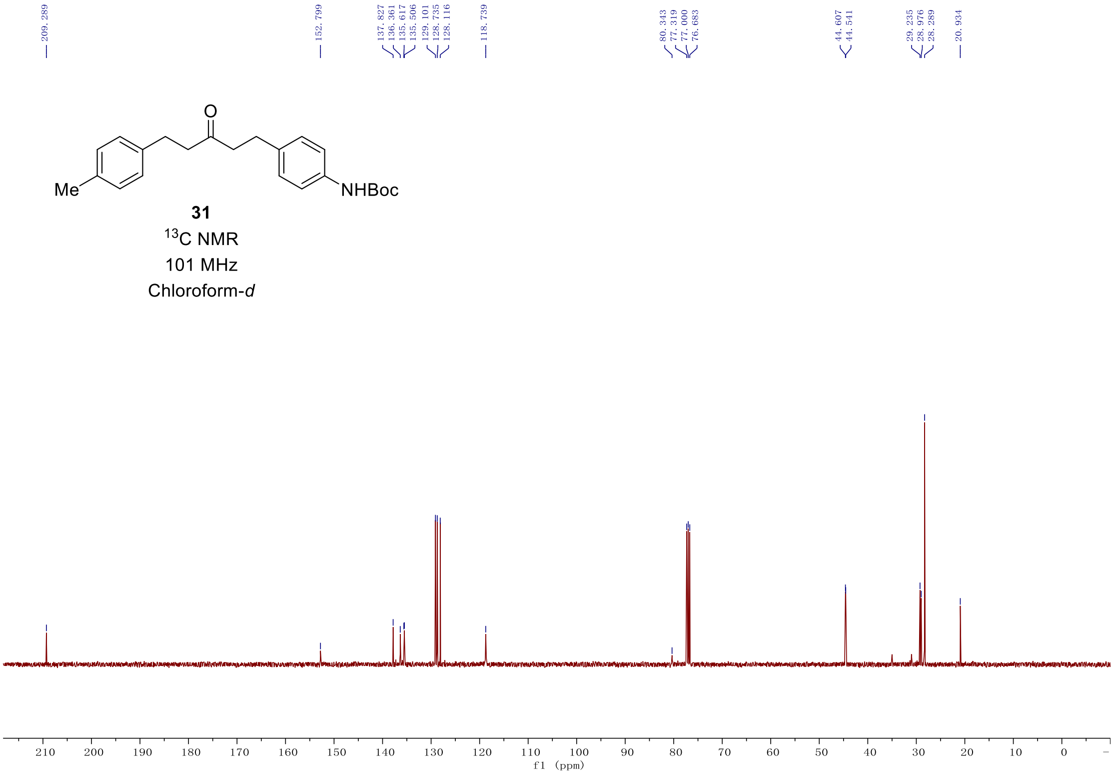
30

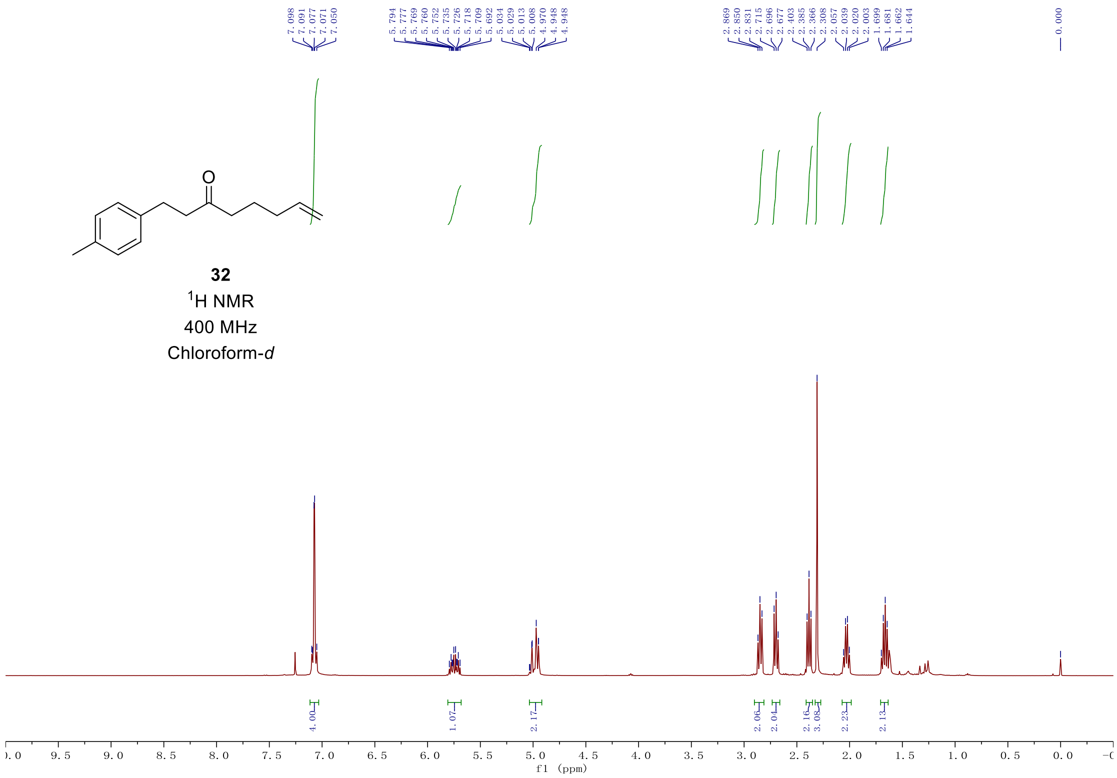
^{13}C NMR

101 MHz

Chloroform-*d*


7.257
7.236
7.083
7.065
7.045
7.023
6.492
2.847
2.830
2.812
2.796
2.685
2.668
2.650
2.633
2.301
1.508
0.000
O
Me
NHBoc
31
^{1}H NMR
400 MHz
Chloroform-*d*
2.08
6.27
1.07
4.09
4.08
3.00
9.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


209.289
152.799
137.827
136.361
135.617
135.506
129.101
128.735
128.116
118.739
80.343
77.319
77.000
76.683
44.607
44.541
29.235
28.976
28.289
20.934
O
Me
NHBoc
31
^{13}C NMR
101 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

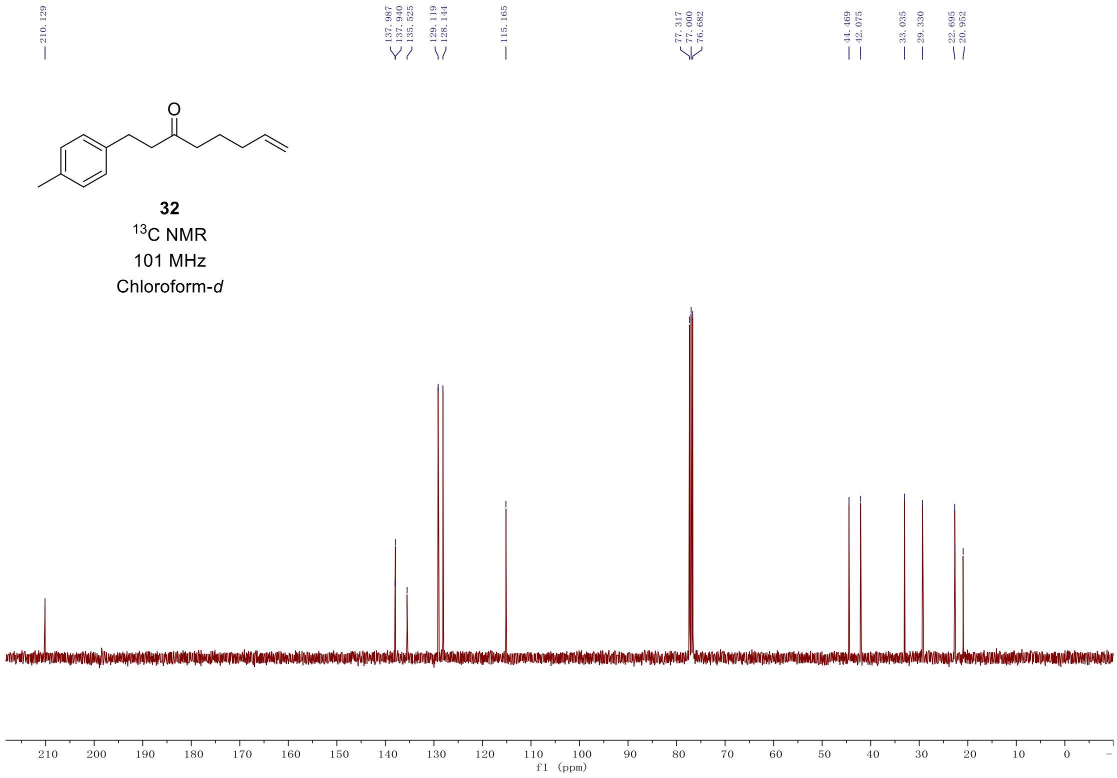


32

^{1}H NMR

400 MHz

Chloroform-*d*

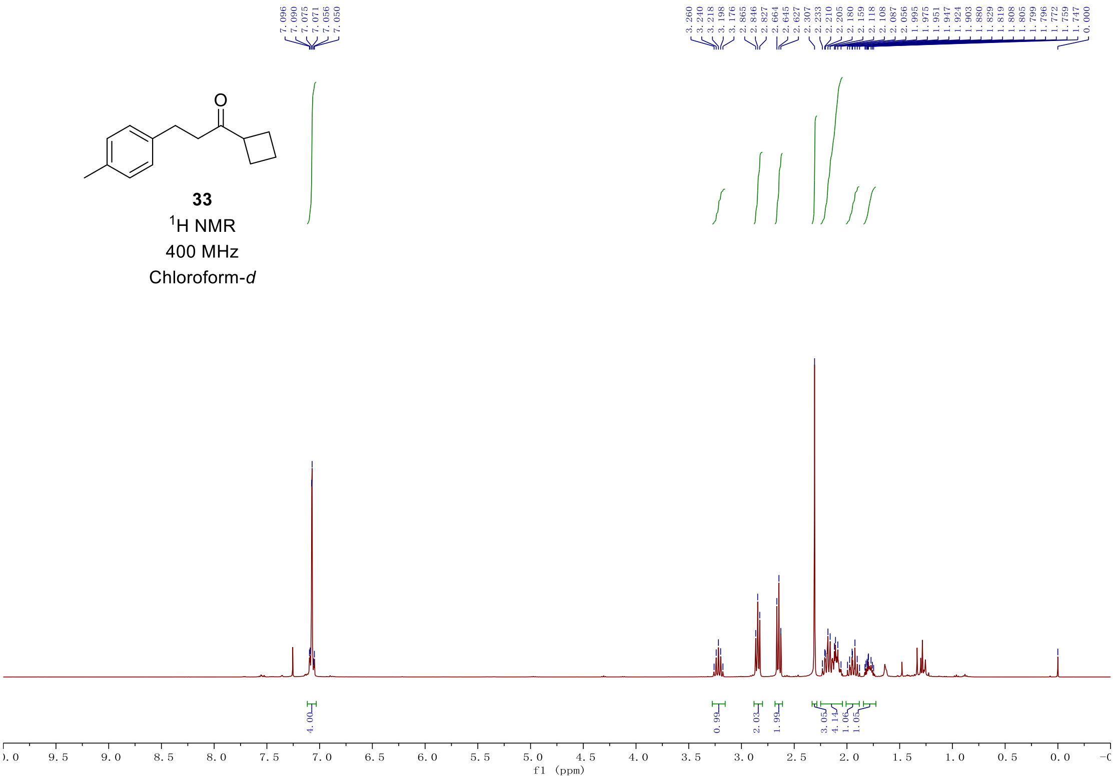


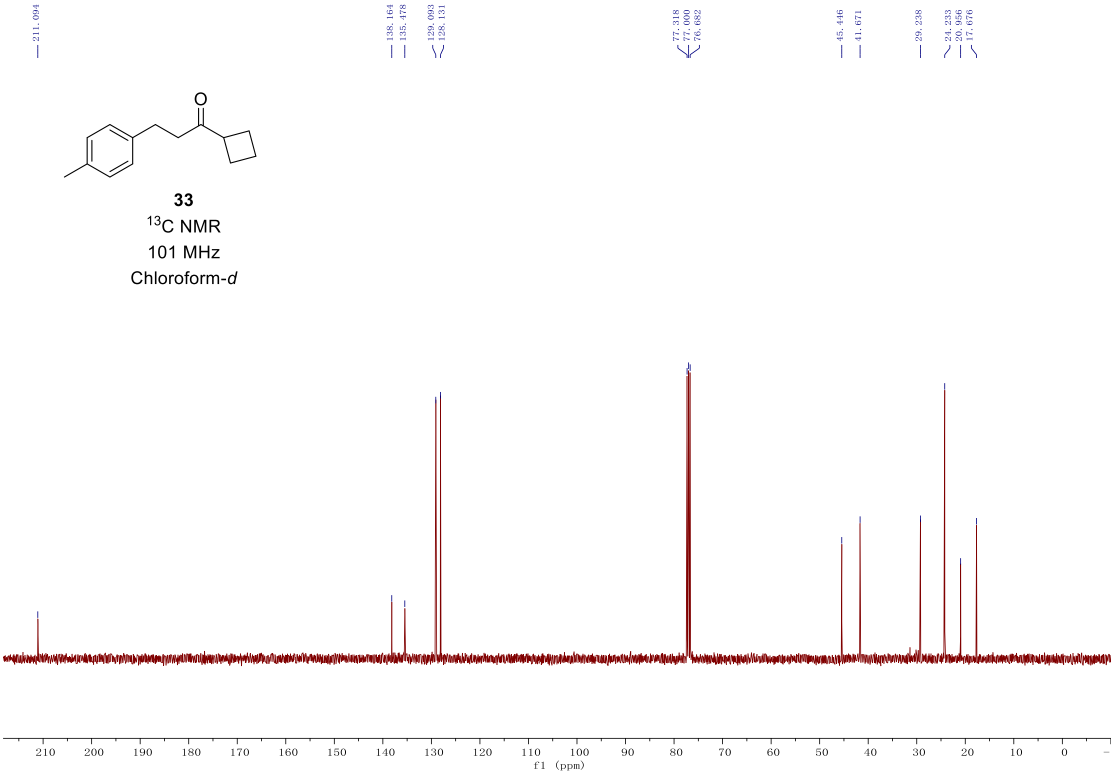
32

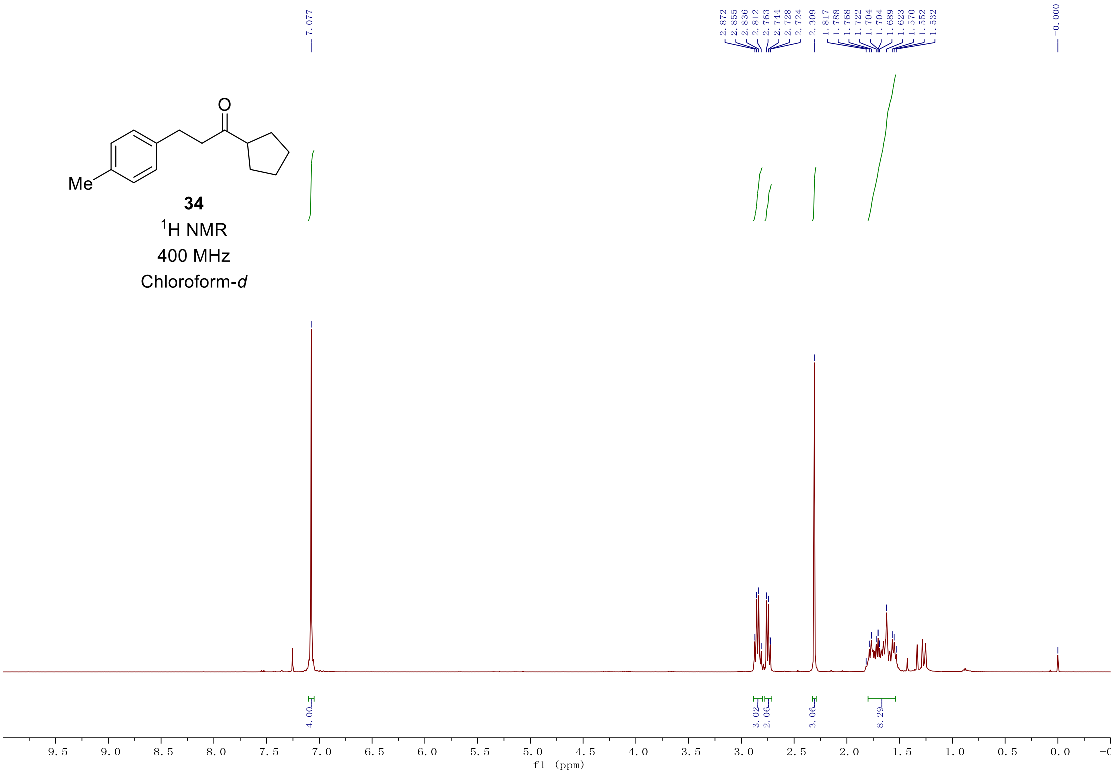
^{13}C NMR

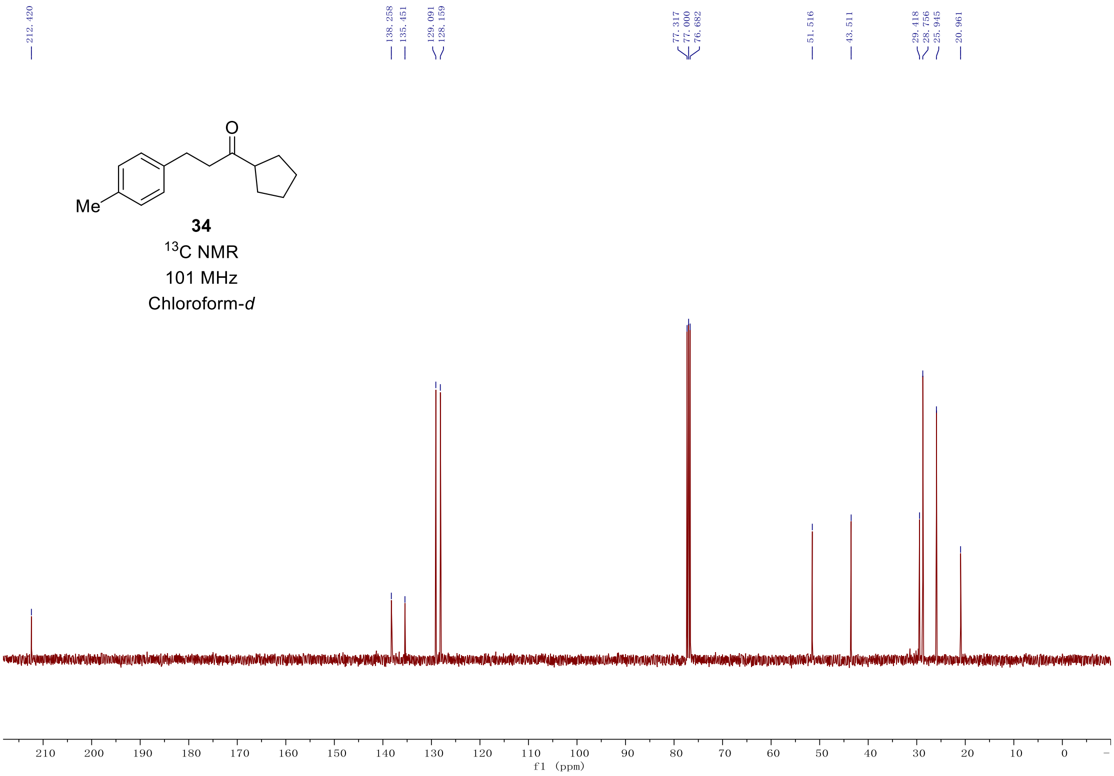
101 MHz

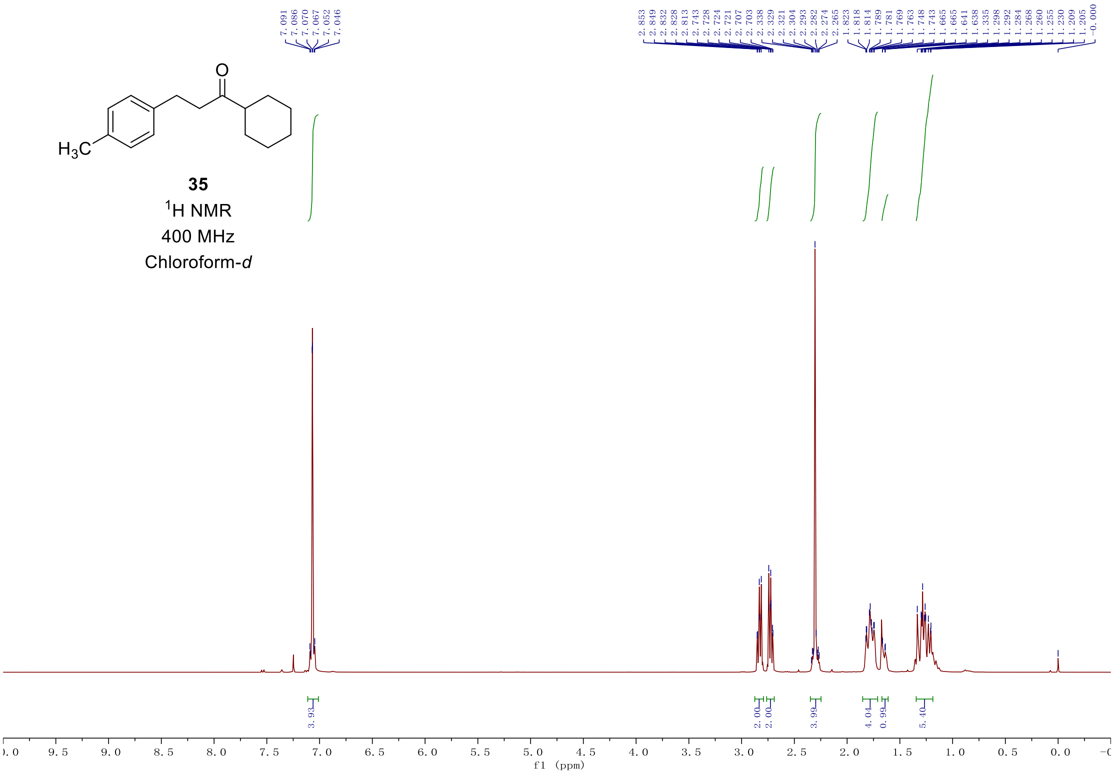
Chloroform-*d*


7.096
7.090
7.075
7.071
7.056
7.050
3.260
3.240
3.218
3.198
3.176
2.865
2.846
2.827
2.664
2.645
2.627
2.307
2.233
2.210
2.205
2.180
2.159
2.118
2.108
2.087
2.056
1.995
1.975
1.951
1.947
1.924
1.903
1.880
1.829
1.819
1.808
1.805
1.799
1.796
1.772
1.759
1.747
0.000
O
33
^{1}H NMR
400 MHz
Chloroform-*d*
4.00
0.99
2.03
1.99
3.05
4.14
1.06
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


211.094
138.164
135.478
129.093
128.131
77.318
77.000
76.682
45.446
41.671
29.238
24.233
20.956
17.676
O
33
^{13}C NMR
101 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


34
^{1}H NMR
400 MHz
Chloroform-*d*


34
^{13}C NMR
101 MHz
Chloroform-*d*

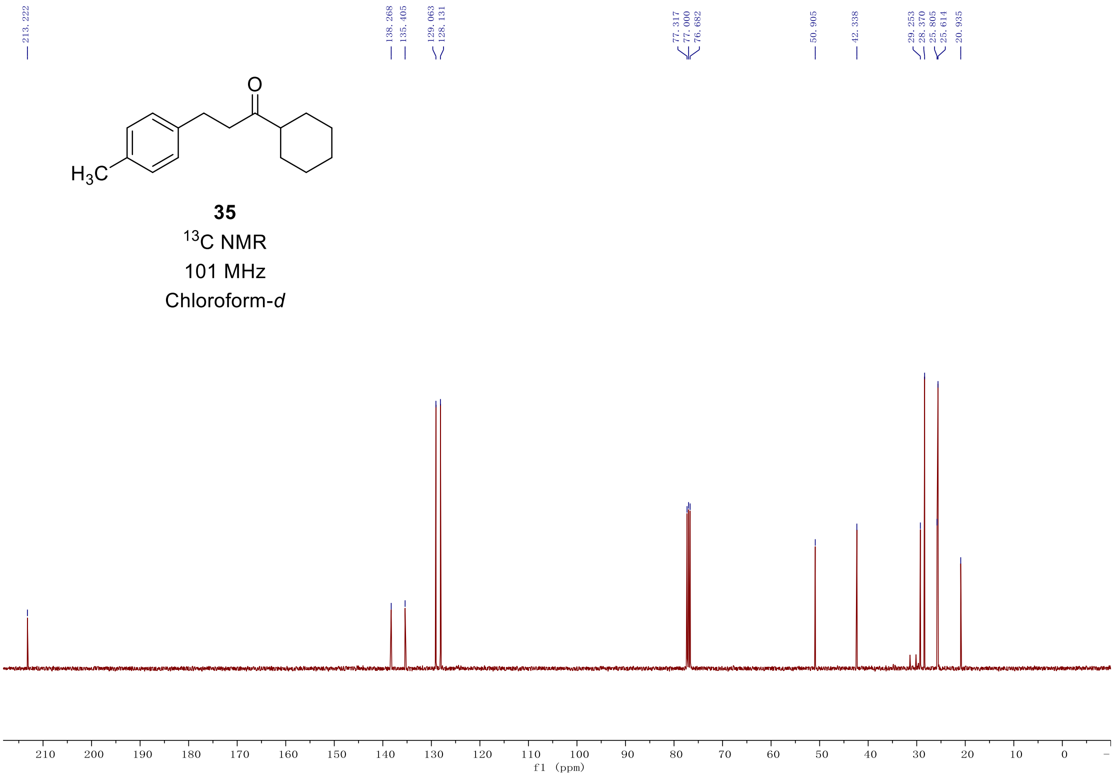


35

^{1}H NMR

400 MHz

Chloroform-*d*

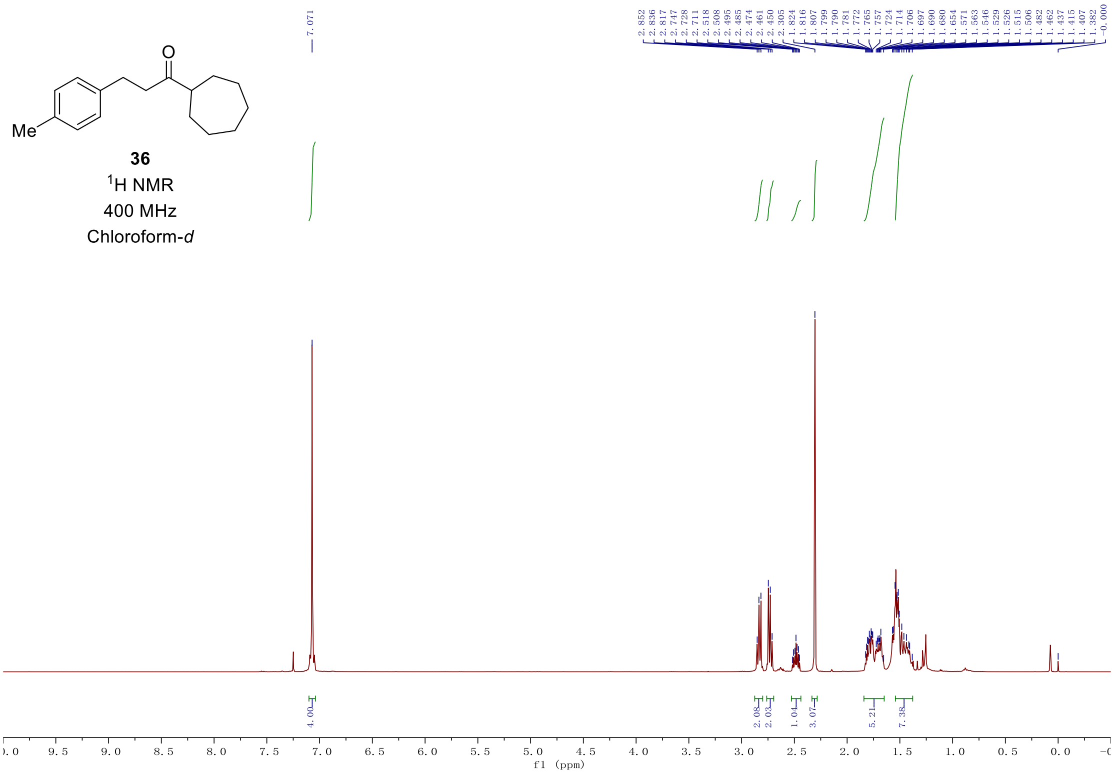


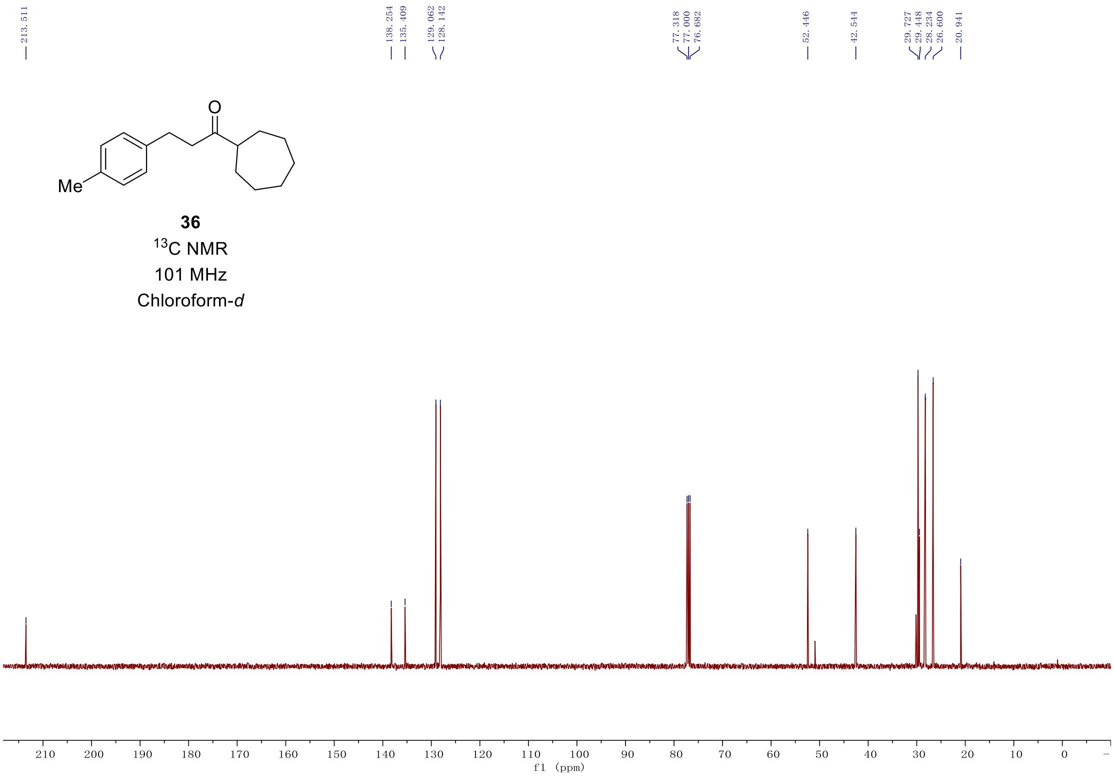
35

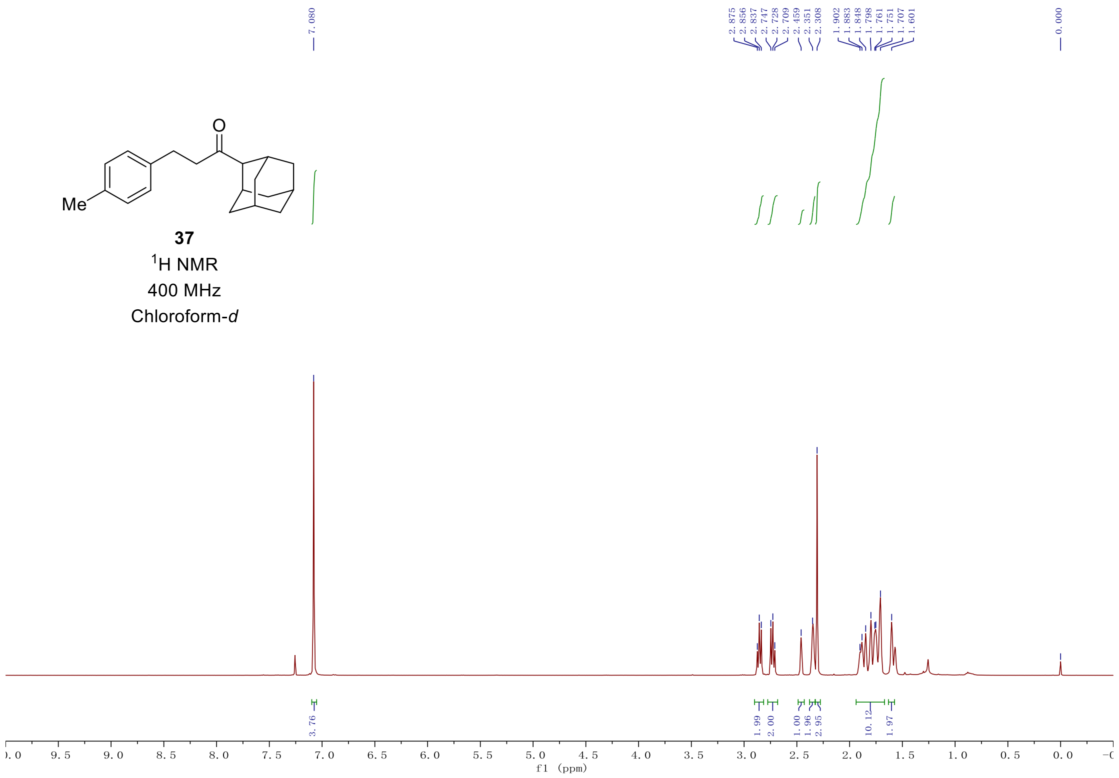
^{13}C NMR

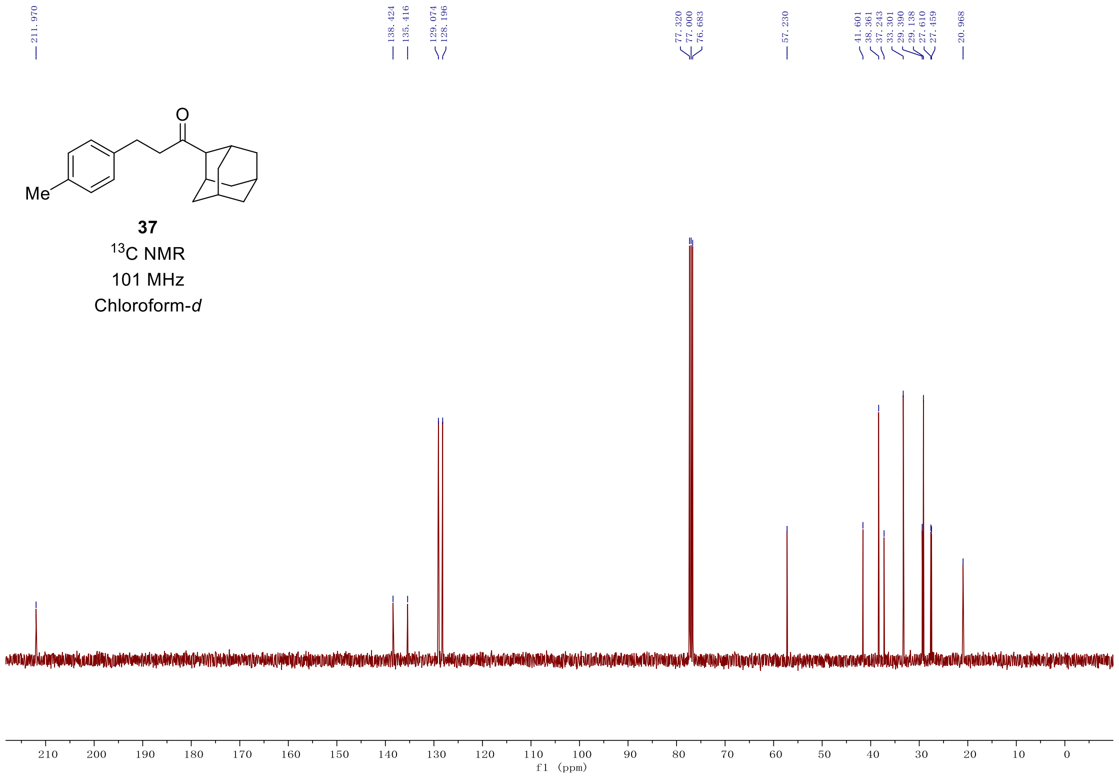
101 MHz

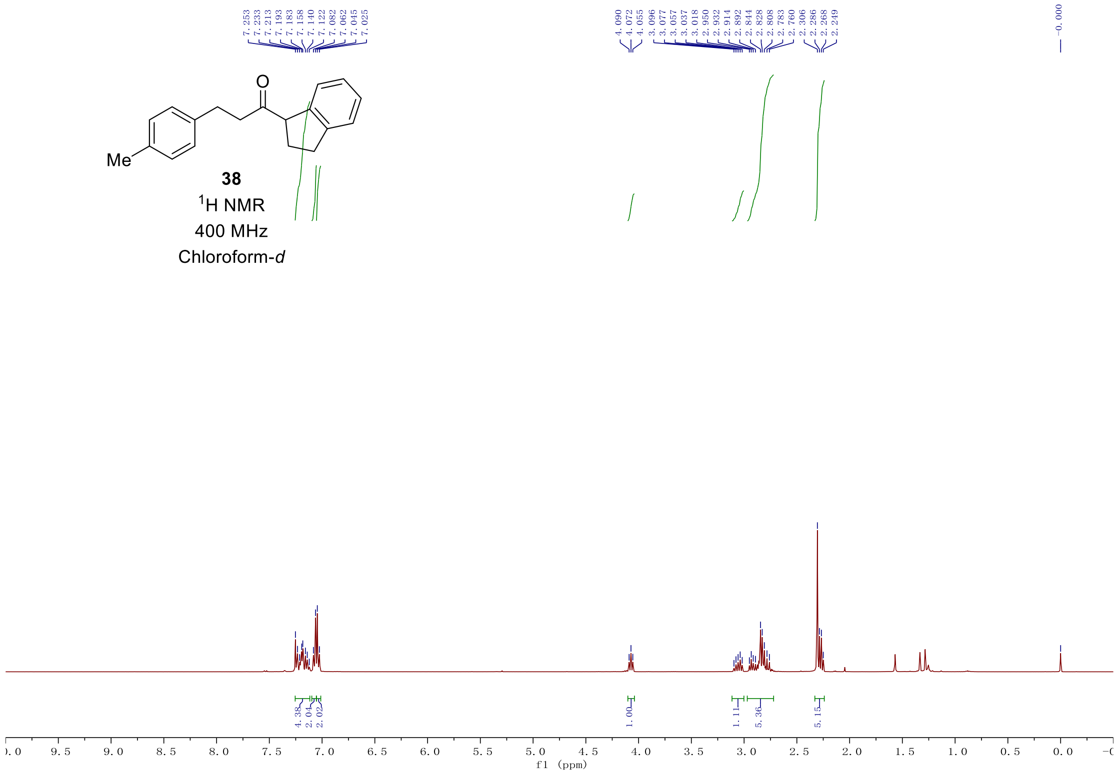
Chloroform-*d*


O
Me
36
^{1}H NMR
400 MHz
Chloroform-*d*
7.071
2.852
2.836
2.817
2.747
2.728
2.711
2.518
2.508
2.495
2.485
2.474
2.461
2.450
2.305
1.824
1.816
1.807
1.799
1.790
1.781
1.772
1.765
1.757
1.724
1.714
1.706
1.697
1.690
1.680
1.654
1.571
1.563
1.546
1.529
1.526
1.515
1.506
1.482
1.462
1.437
1.415
1.407
1.382
-0.000
4.00
2.08
2.03
1.04
3.07
5.21
7.38
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


213.511
138.254
135.409
129.062
128.142
77.318
77.000
76.682
52.446
42.544
29.727
29.448
28.234
26.060
20.941
O
Me
36
^{13}C NMR
101 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.080
2.875
2.856
2.837
2.747
2.728
2.709
2.459
2.351
2.308
1.902
1.883
1.848
1.798
1.761
1.751
1.707
1.601
0.000
O
Me
37
^{1}H NMR
400 MHz
Chloroform-*d*
3.76
1.99
2.00
1.00
1.96
2.95
10.12
1.97
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


211.970
138.424
135.416
129.074
128.196
77.320
77.000
76.683
57.230
41.601
38.361
37.243
33.301
29.390
29.138
27.610
27.459
20.968
O
Me
37
^{13}C NMR
101 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

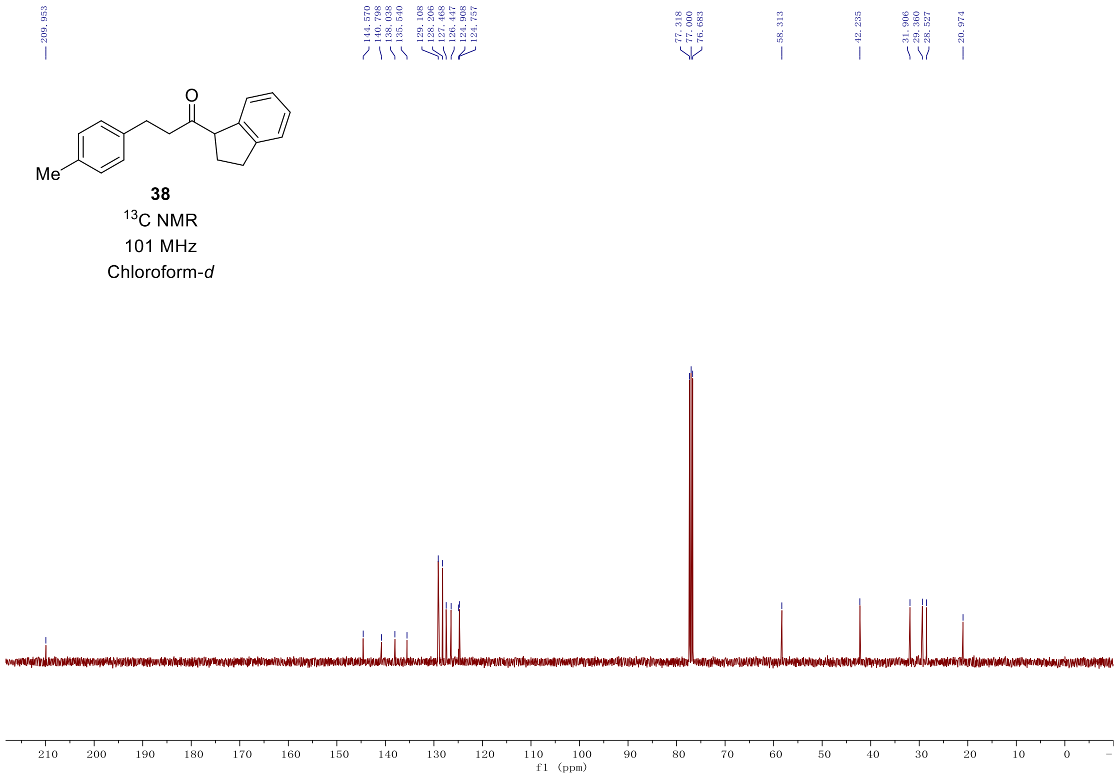


38

^{1}H NMR

400 MHz

Chloroform-*d*

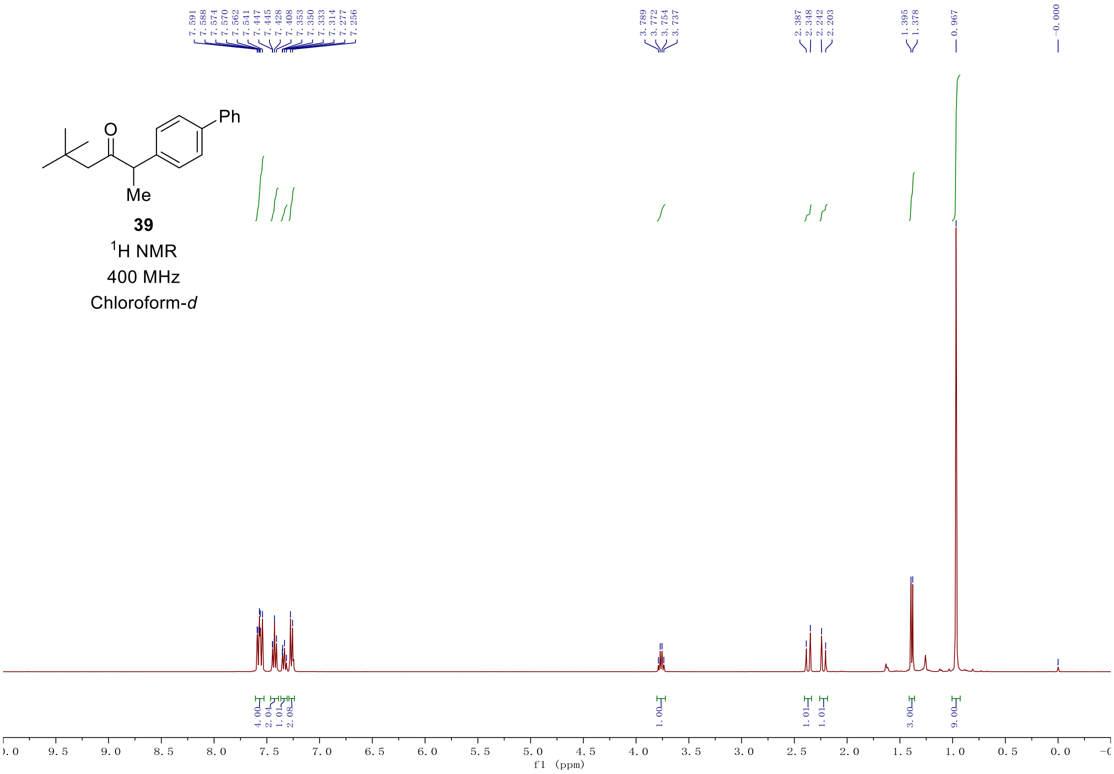


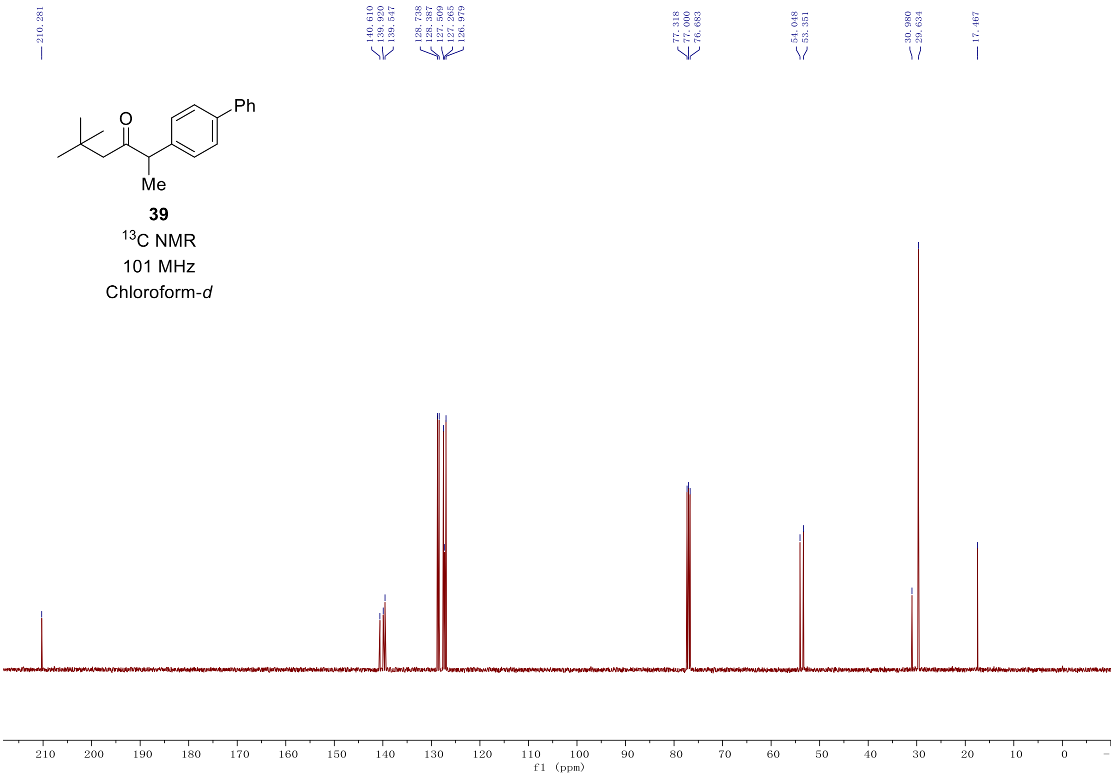
38

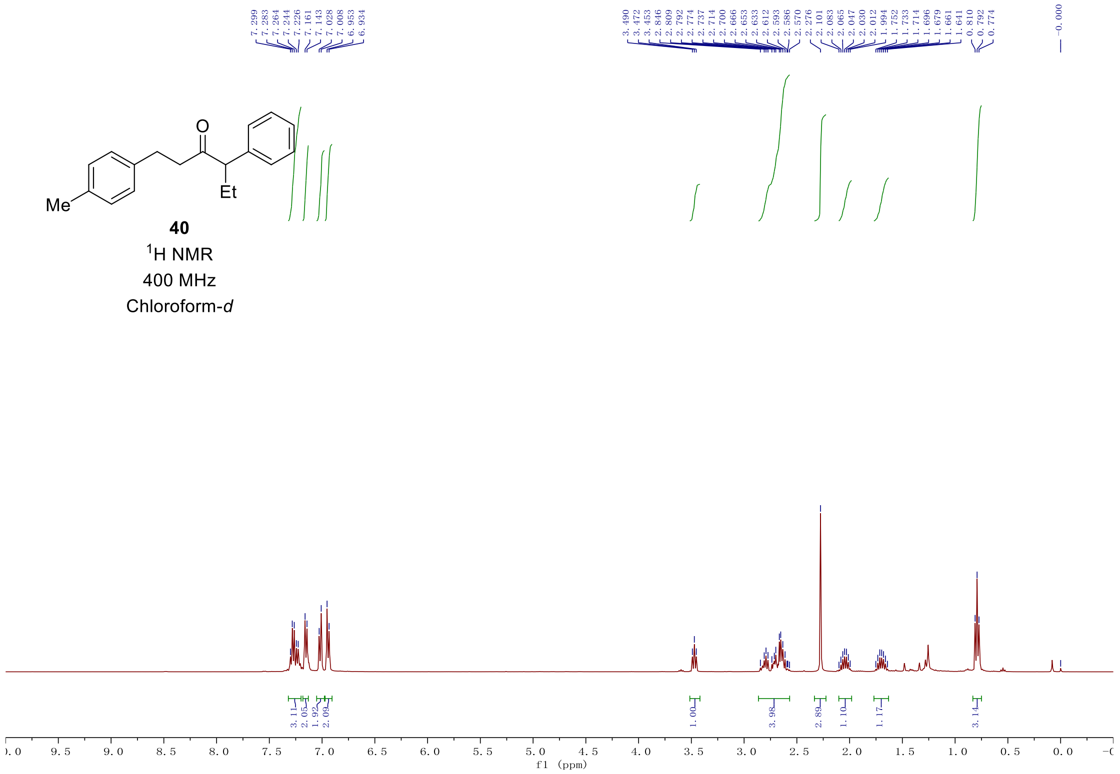
^{13}C NMR

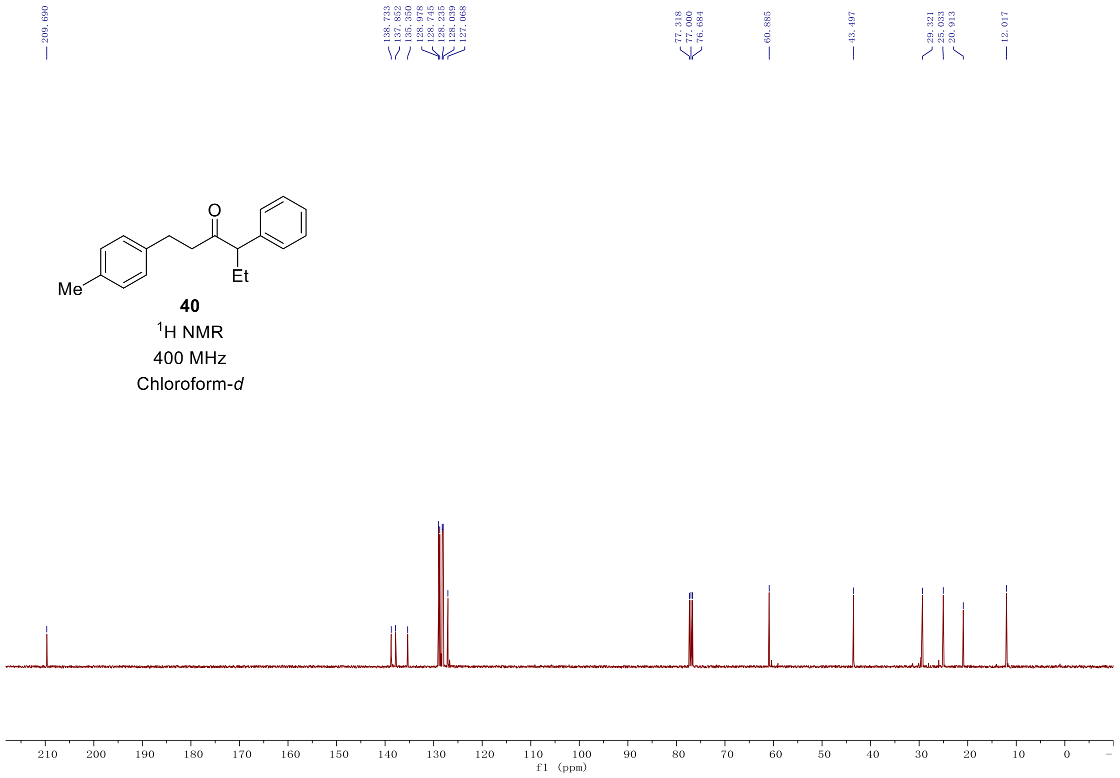
101 MHz

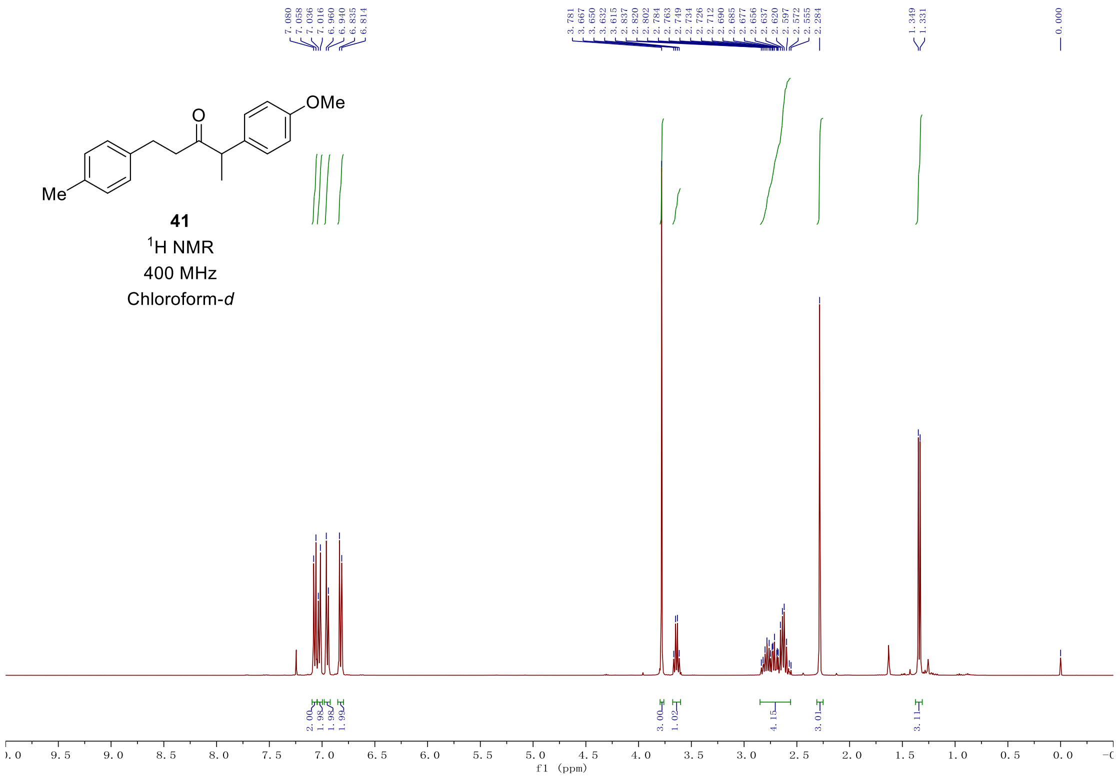
Chloroform-*d*


7.591
7.588
7.574
7.570
7.562
7.541
7.447
7.445
7.428
7.408
7.353
7.350
7.333
7.314
7.277
7.256
3.789
3.772
3.754
3.737
2.387
2.348
2.242
2.203
1.395
1.378
0.967
-0.000
Ph
O
Me
39
1H NMR
400 MHz
Chloroform-d
4.00
2.04
1.01
2.08
1.00
1.01
1.01
3.00
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


210.281
140.610
139.920
139.547
128.738
128.387
127.509
127.265
126.979
77.318
77.000
76.683
54.048
53.351
30.980
29.634
17.467
Ph
O
Me
39
13C NMR
101 MHz
Chloroform-d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.299
7.283
7.264
7.244
7.226
7.161
7.143
7.028
7.008
6.953
6.934
3.490
3.472
3.453
2.846
2.809
2.792
2.774
2.737
2.714
2.700
2.666
2.653
2.633
2.612
2.593
2.586
2.570
2.276
2.101
2.083
2.065
2.047
2.030
2.012
1.994
1.752
1.733
1.714
1.696
1.679
1.661
1.641
0.810
0.792
0.774
-0.000
O
Et
Me
40
^{1}H NMR
400 MHz
Chloroform-*d*
3.11
2.05
1.92
2.09
1.00
3.98
2.89
1.10
1.17
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


209.690
138.733
137.852
135.350
128.978
128.745
128.235
128.039
127.068
77.318
77.000
76.684
60.885
43.497
29.321
25.033
20.913
12.017
O
Et
Me
40
^{1}H NMR
400 MHz
Chloroform-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

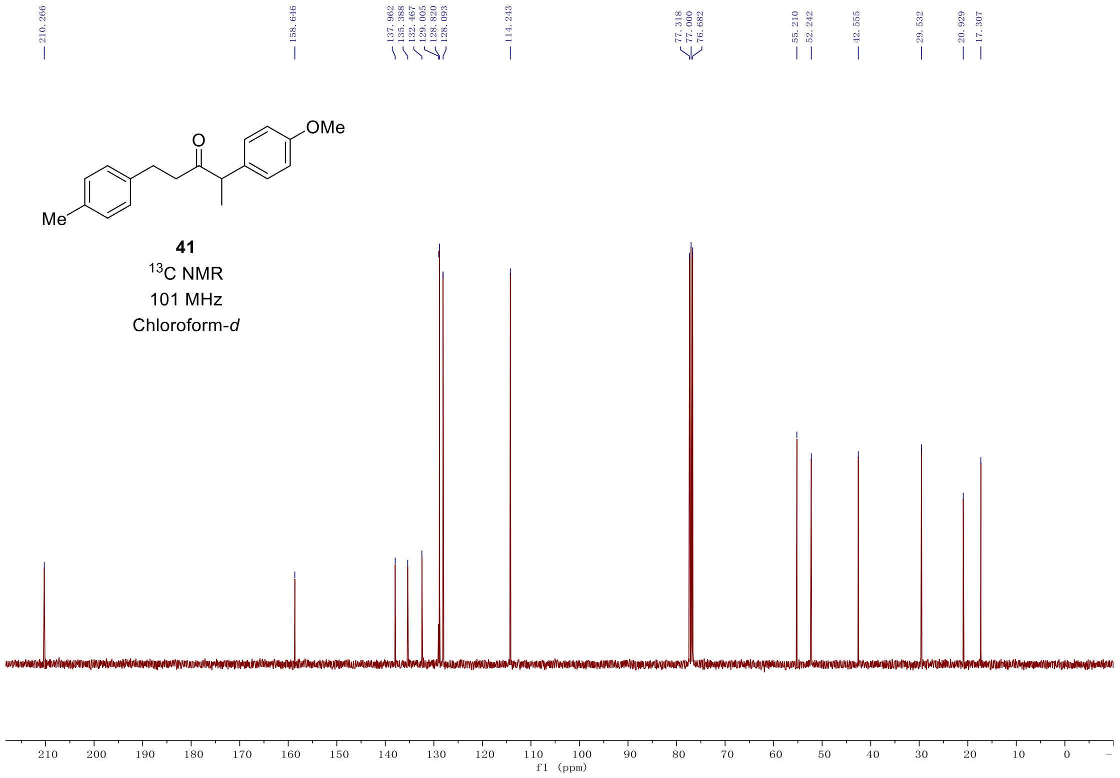


41

^{1}H NMR

400 MHz

Chloroform-*d*

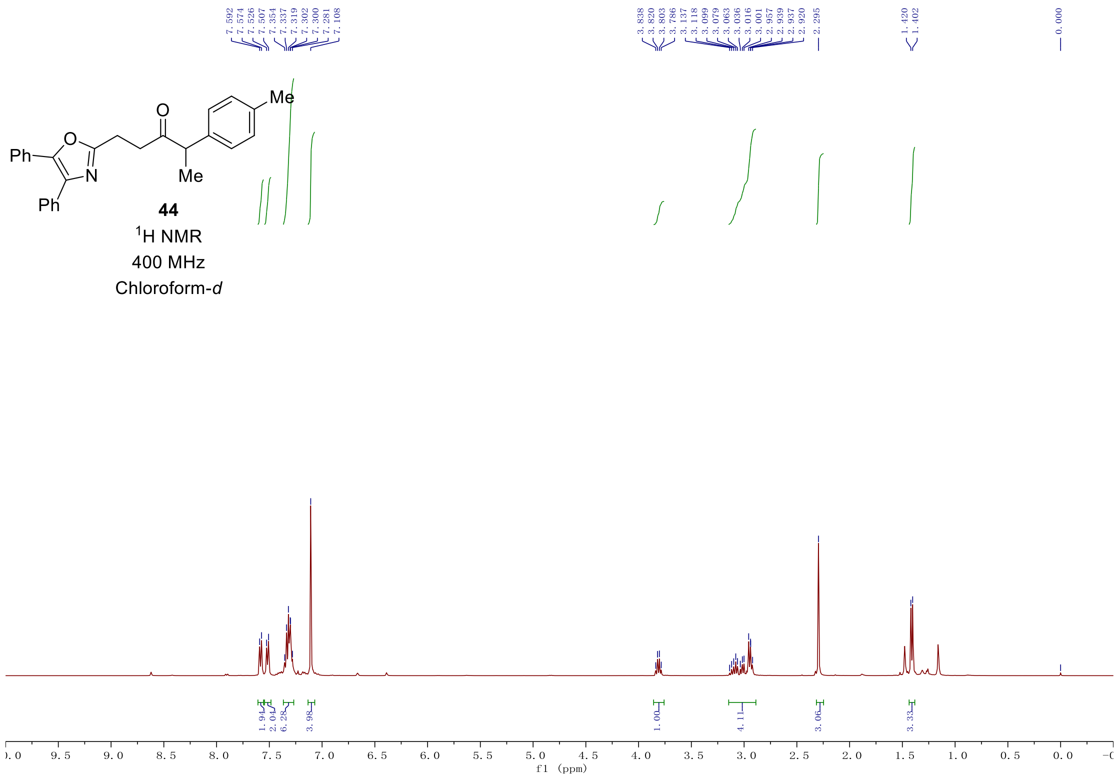


41

^{13}C NMR

101 MHz

Chloroform-*d*

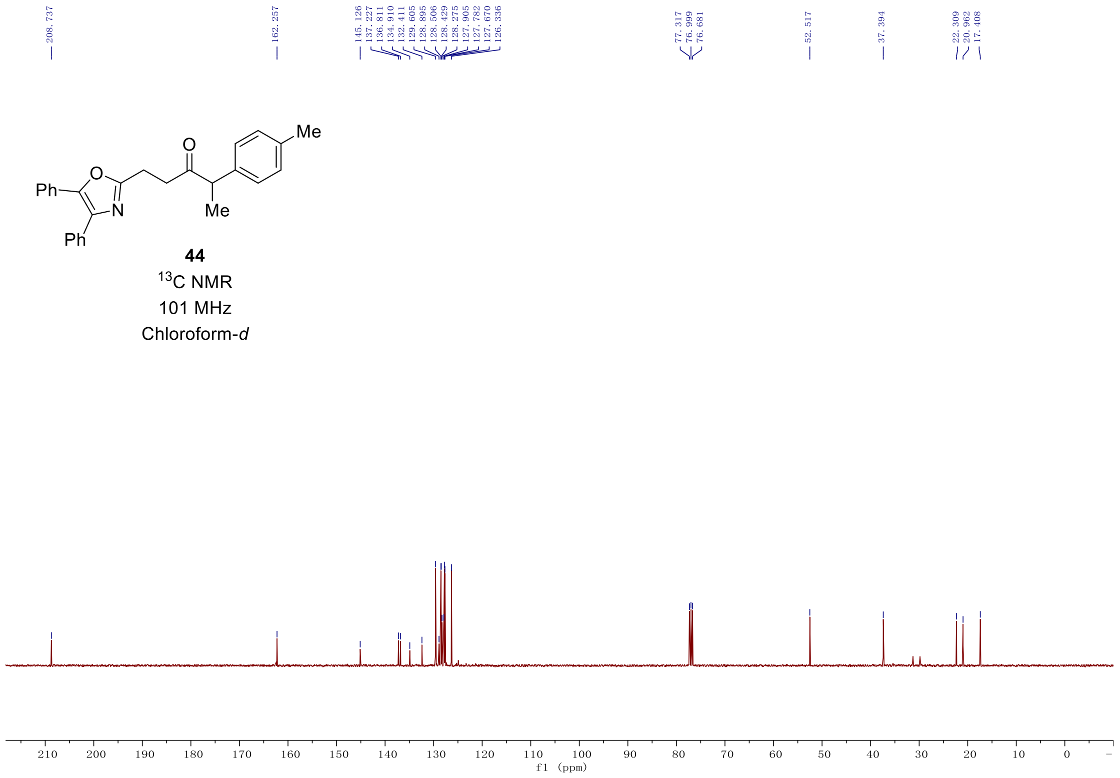


44

^{1}H NMR

400 MHz

Chloroform-*d*

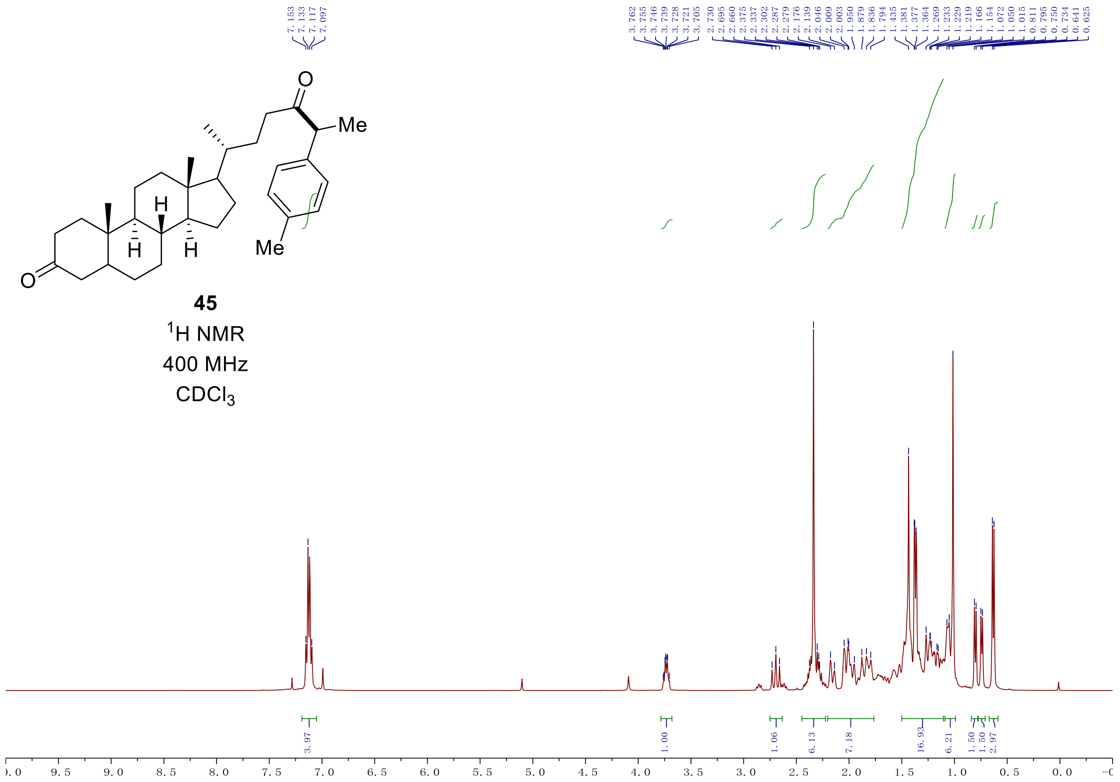


44

^{13}C NMR

101 MHz

Chloroform-*d*

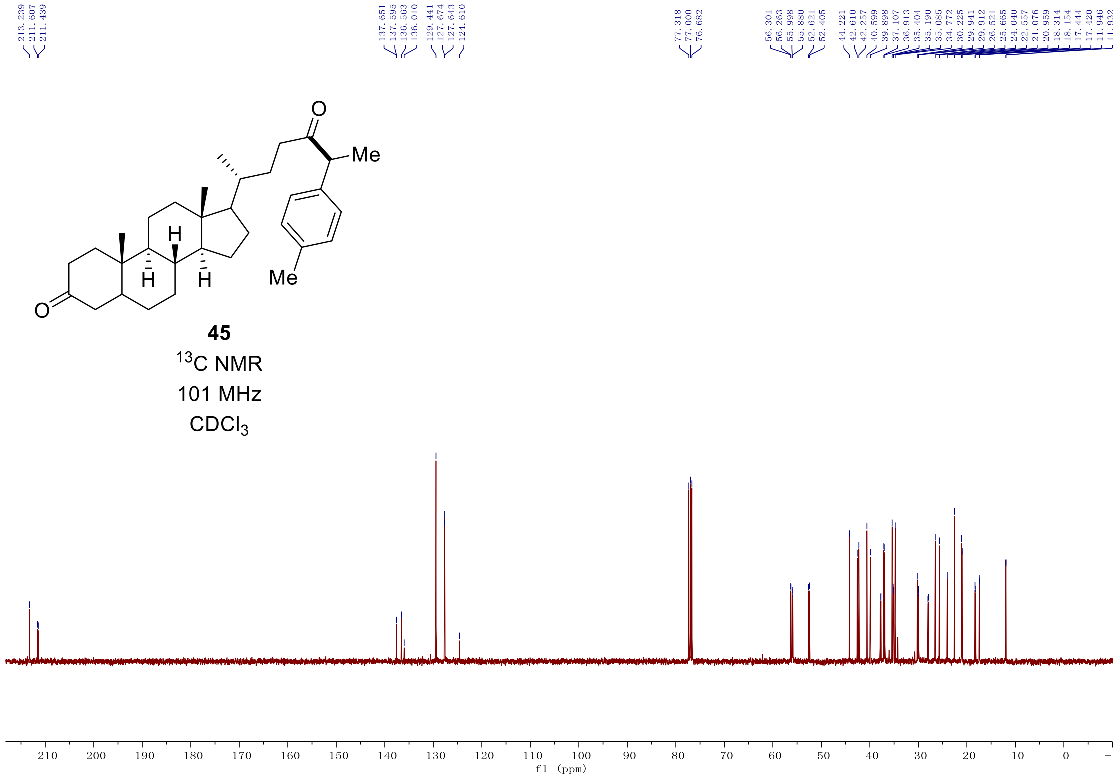


45

^{1}H NMR

400 MHz

$CDCl_3$

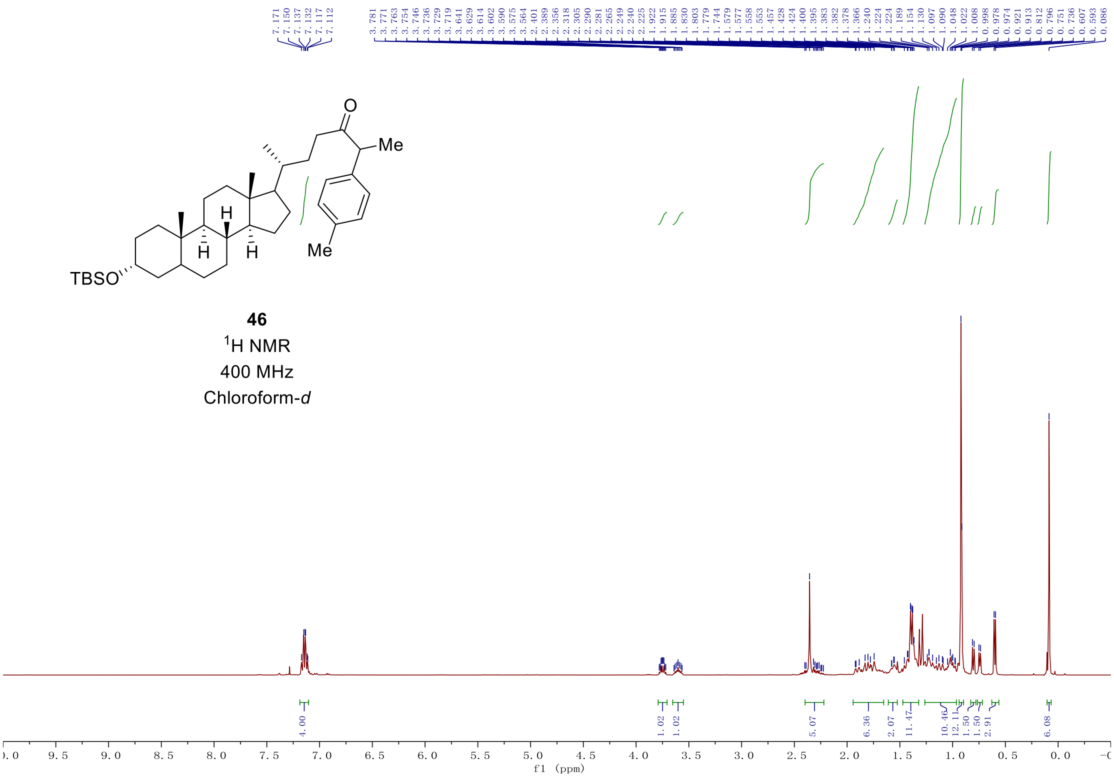


45

^{13}C NMR

101 MHz

$CDCl_3$

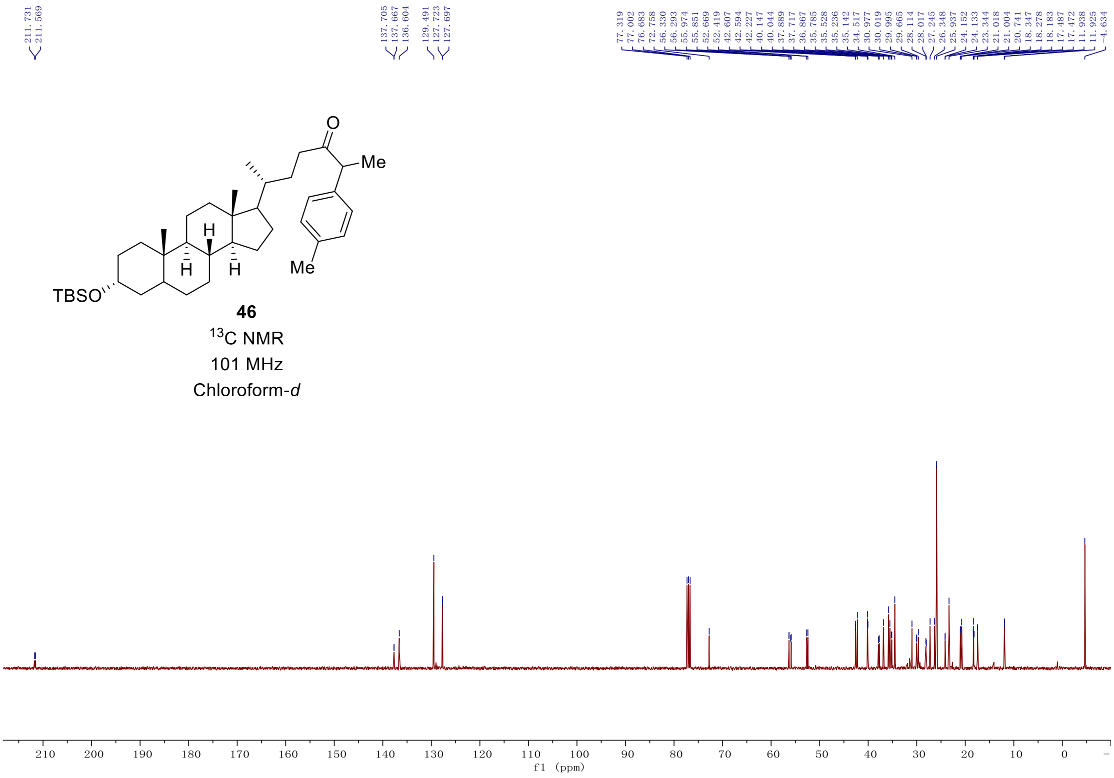


46

^{1}H NMR

400 MHz

Chloroform-*d*

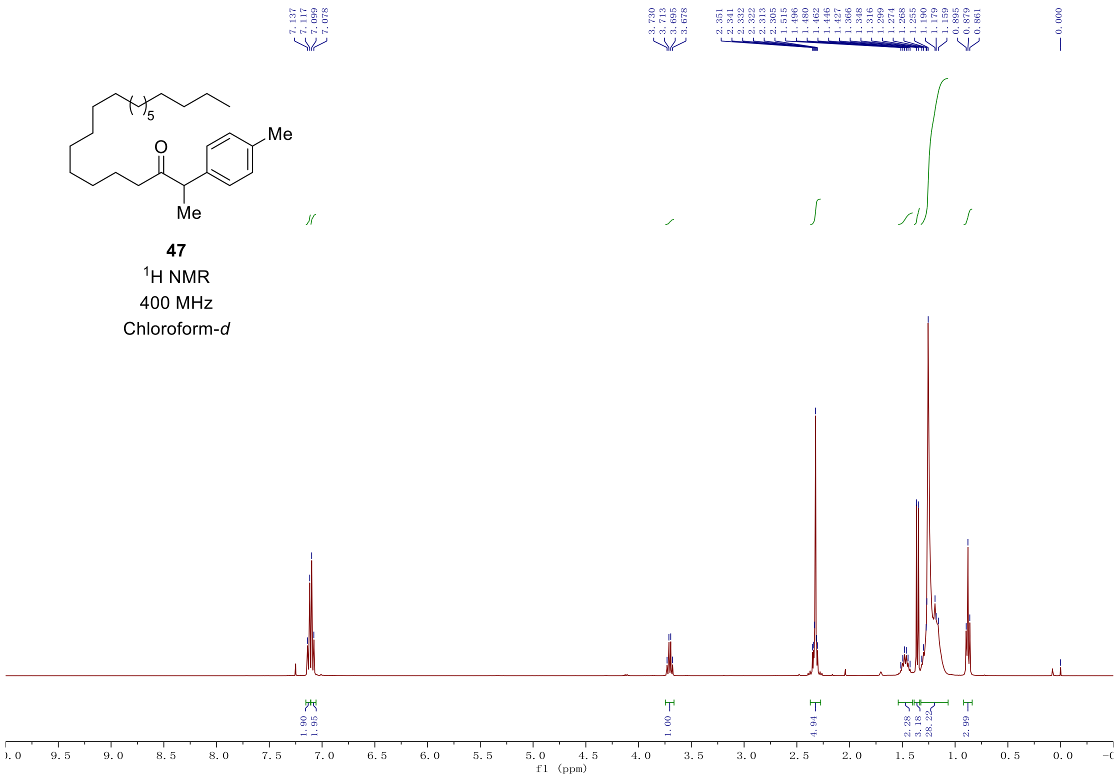


46

^{13}C NMR

101 MHz

Chloroform-*d*

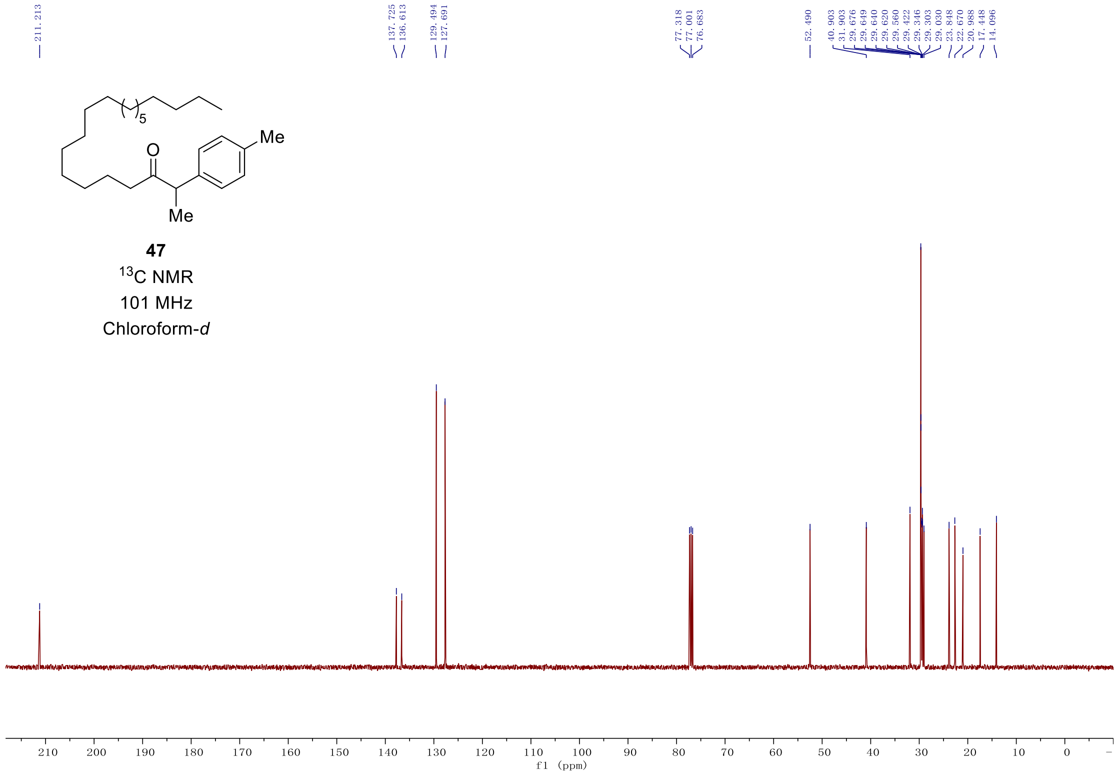


47

^{1}H NMR

400 MHz

Chloroform-*d*

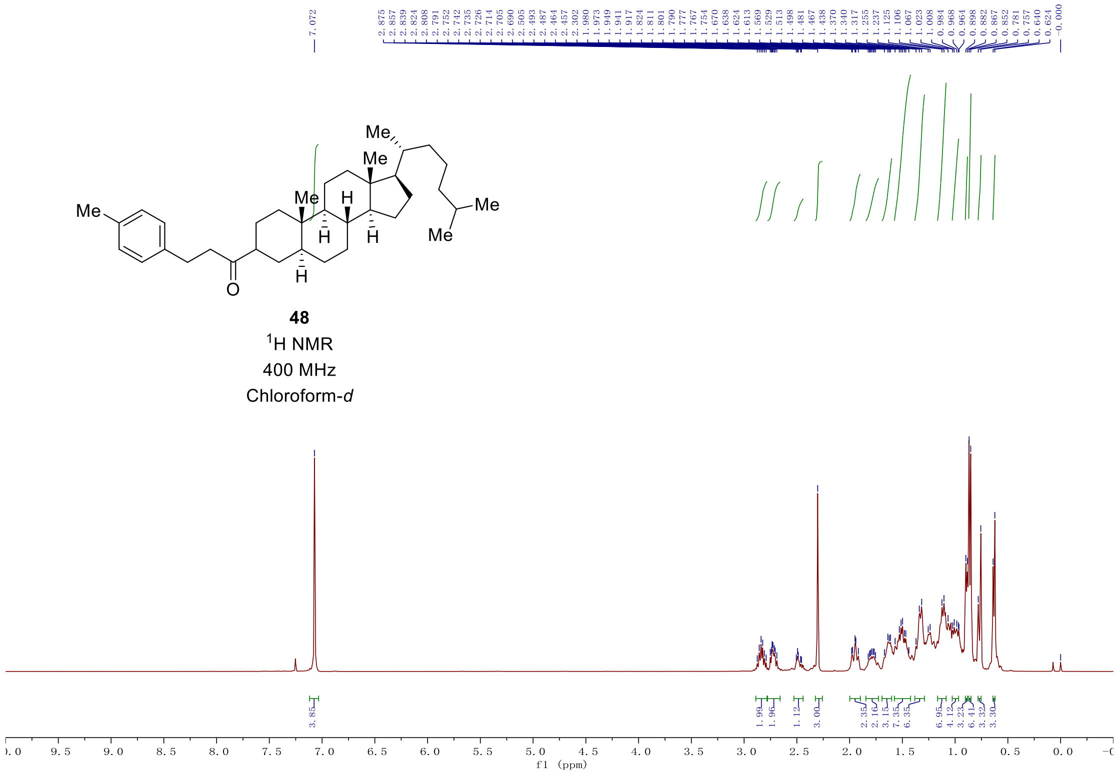


47

^{13}C NMR

101 MHz

Chloroform-*d*

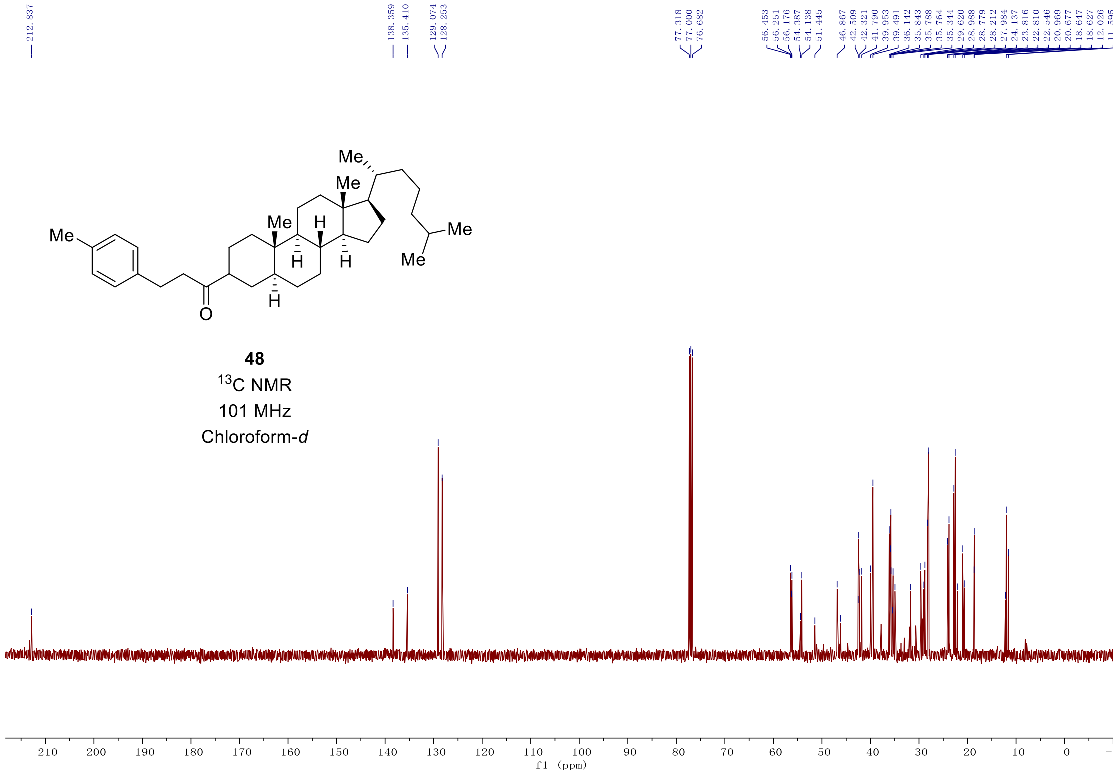


48

^{1}H NMR

400 MHz

Chloroform-*d*

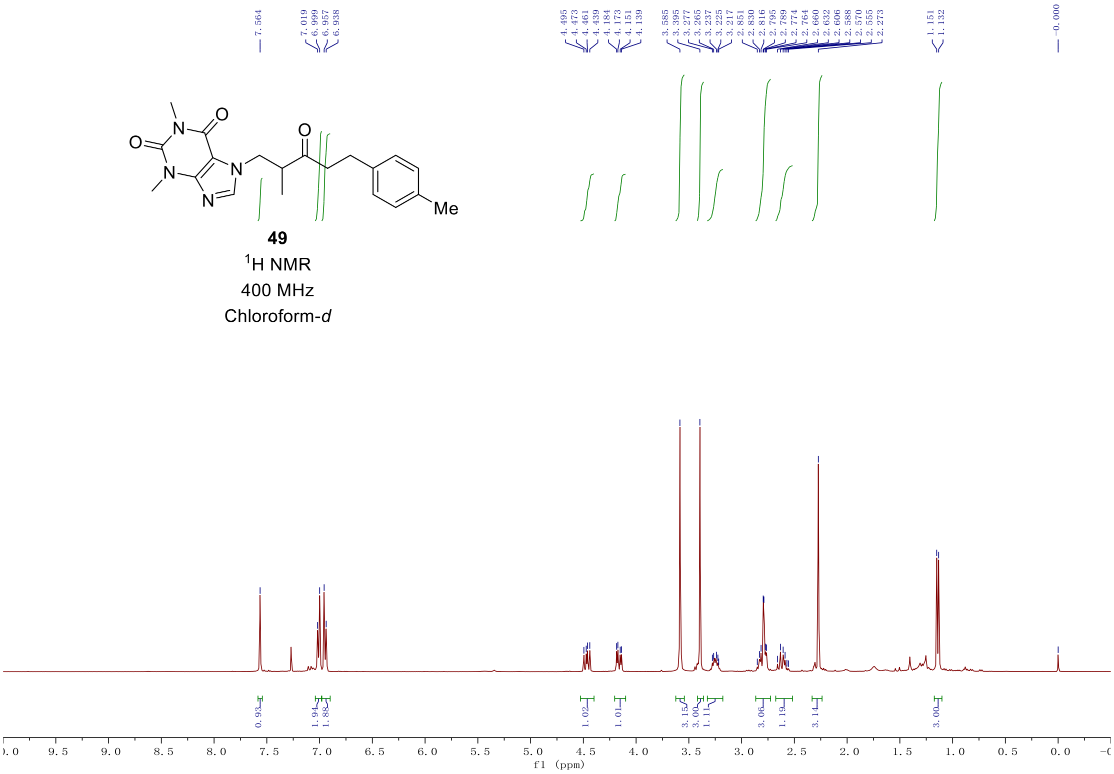


48

^{13}C NMR

101 MHz

Chloroform-*d*

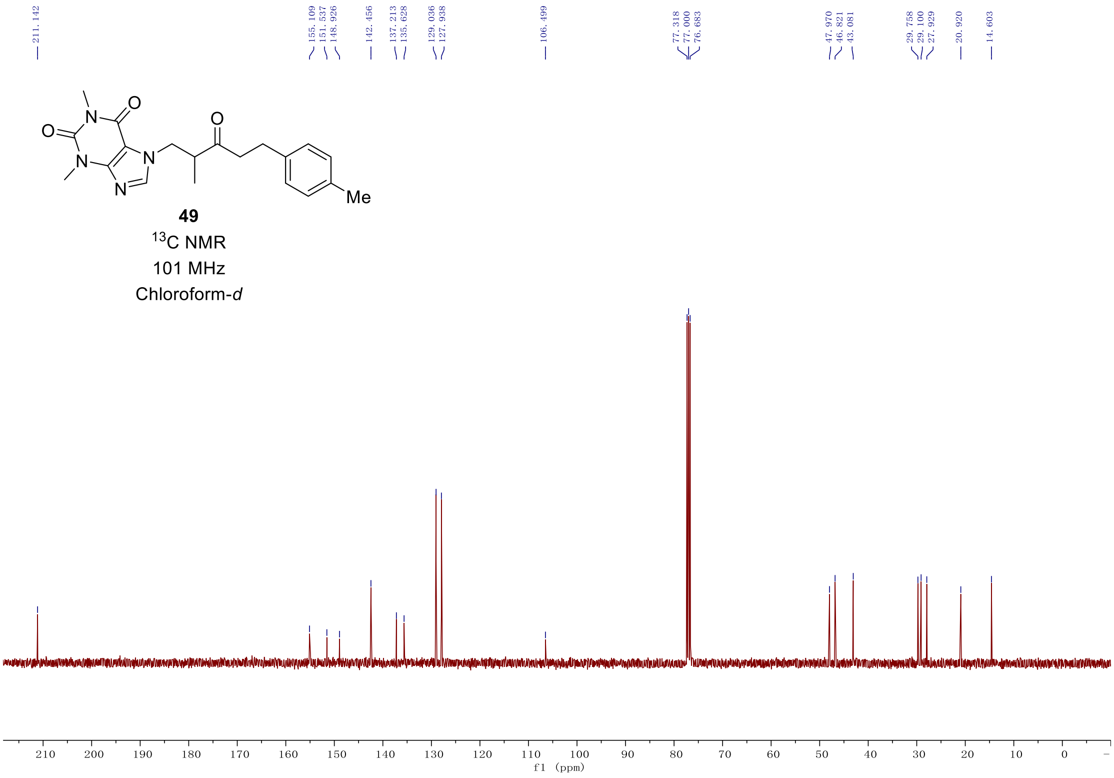


49

^{1}H NMR

400 MHz

Chloroform-*d*

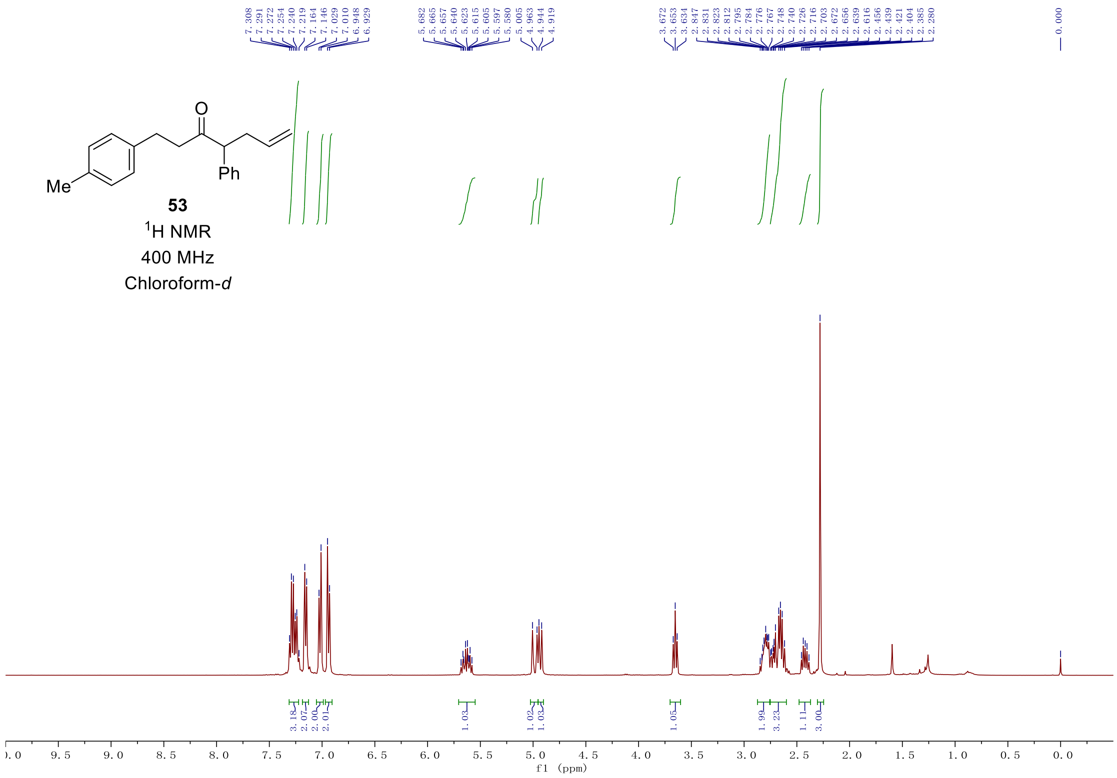


49

^{13}C NMR

101 MHz

Chloroform-*d*

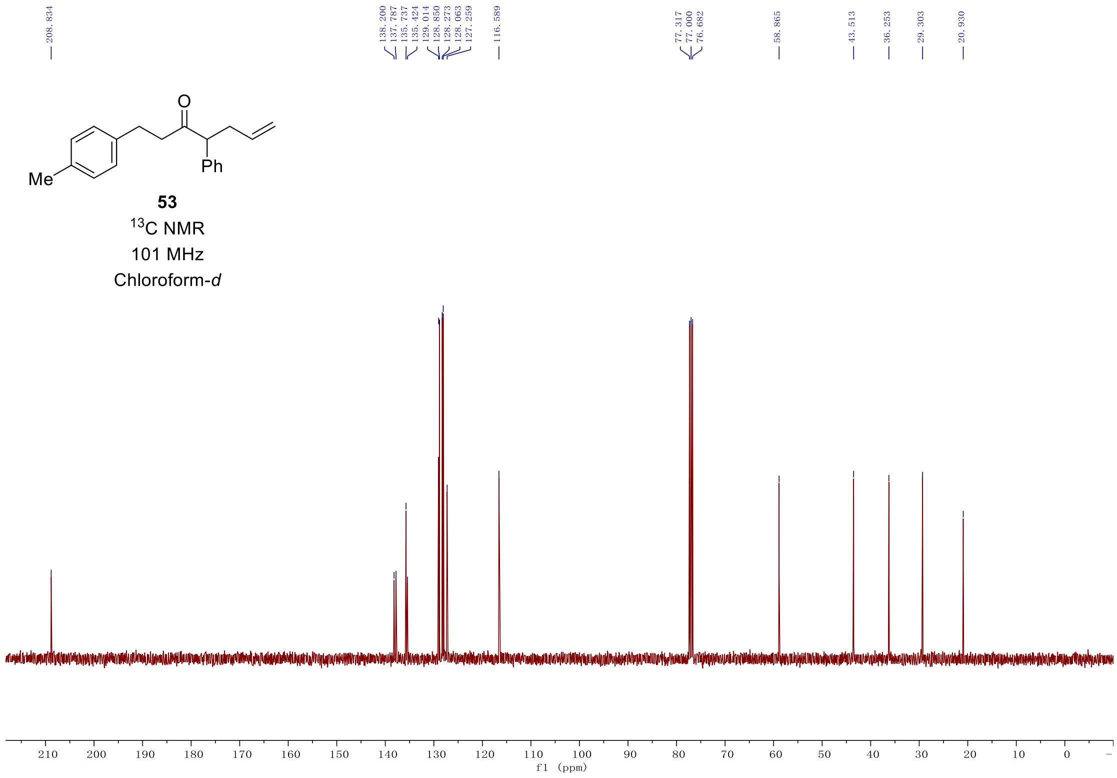


53

^{1}H NMR

400 MHz

Chloroform-*d*



53

^{13}C NMR

101 MHz

Chloroform-*d*