

Supporting Information for

**Palladium-Catalyzed Coupling of Amides and Cyclopropanols
for the Synthesis of γ -Diketones**

Lili Fang, Shuqi Jia, Shuaixin Fan, and Jin Zhu*

School of Chemistry and Chemical Engineering, State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210023, China.

*Corresponding Author. E-mail: jinz@nju.edu.cn.

Content

General Information	3
Optimization of the Reaction Conditions.....	3
Optimization of the Reaction Conditions for <i>N</i> -acyl phthalimides.....	3
Optimization of the Reaction Conditions for <i>N</i> -glutarimide benzamides.....	5
Optimization of the Reaction Conditions for certain <i>N</i> -glutarimide amides	6
Typical Procedure for the Synthesis of γ -Diketones	8
Characterization data of <i>N</i> -glutarimide amide	9
Characterization data of cyclopropanols	9
Characterization data of γ -diketones	10
Mechanistic Studies	21
Coupling of cyclopropanol and amide in the presence of BHT	21
Radical clock experiment.....	22
NMR spectrum evidence for the release of glutarimide.	22
Competition experiment.....	24
Control experiments	24
Proposed mechanism.....	26
Exploration for the cross-coupling reaction of acid chloride with cyclopropanol.....	26
Kinetic competition experiment	28
Reactivity order chemistry set.....	29
Reduction of γ -diketones to alkane	29
Reference.....	31
NMR spectra	32

General Information

All reactions were performed in a nitrogen-filled dry box unless otherwise stated. All solvents were obtained from commercial suppliers and were used as received. Toluene (PhMe) were purchased as HPLC-grade from Guoyao. Other commercially available reagents were used without further purification. Reaction temperature was reported corresponding to the oil bath temperature. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed using 40-63 μm silica gel (Si 60, Merck). ^1H and ^{13}C NMR spectra were recorded on Bruker 500 or 400 (stated especially) MHz NMR spectrometer in the solvents indicated. Chemical shifts (δ) are given in ppm relative to TMS. HRMS were obtained on a Thermo Fisher Scientific LTQ FT Ultra.

Tertiary cyclopropanols were prepared by Kulinkovich reaction or Simmons-Smith sequence according to the reported procedure.¹ The substrates of amide were prepared according to the reported literature procedures.² All the characteristic data are consistent with the data reported before.³⁻¹⁰

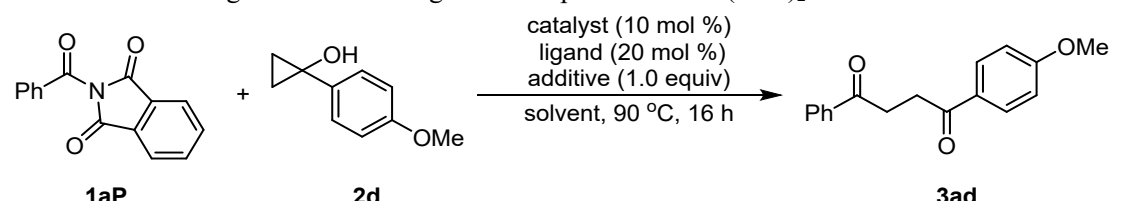
The amount of ligand PCy_3 is critical for the yield of γ -diketones, excessive ligand will reduce yields of γ -diketones. Otherwise, addition of 1.0 equiv amount of $\text{B}(\text{OH})_3$ can promote the yield of γ -diketones derived from the reaction of **1a** and **2d**, but it seems ineffective for the other reactions sometime.

Additive distortion parameters ($\Sigma\tau + \chi_{\text{N}}$) refer to the literature reported before.¹¹

Optimization of the Reaction Conditions

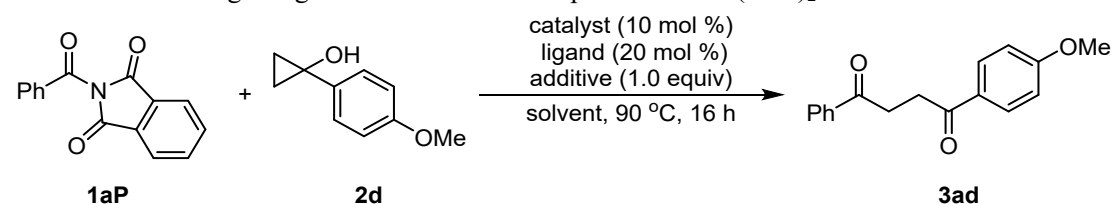
Optimization of the Reaction Conditions for *N*-acyl phthalimides

Table S1. Screening of solvent and ligand in the presence of $\text{Pd}(\text{OAc})_2$

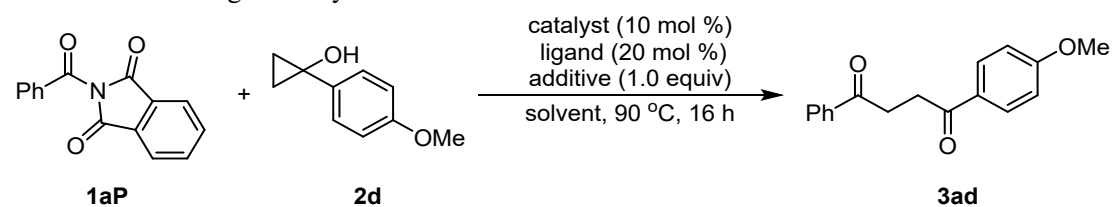


The reaction scheme shows the reaction of **1aP** (N-acyl phthalimide) and **2d** (cyclopropanol) to form **3ad** (γ -diketone). The reaction conditions are: catalyst (10 mol %), ligand (20 mol %), additive (1.0 equiv), solvent, 90 °C, 16 h.

Entry	catalyst	ligand	additive (1.0 equiv.)	solvent	Yield ^[a]
1	$\text{Pd}(\text{OAc})_2$	PCy_3	K_2CO_3	1,4-Dioxane	Trace
2	$\text{Pd}(\text{OAc})_2$	PCy_3	K_2CO_3	MeCN	Trace
3	$\text{Pd}(\text{OAc})_2$	PCy_3	K_2CO_3	MeOH	ND
4	$\text{Pd}(\text{OAc})_2$	PCy_3	K_2CO_3	THF	25%
5	$\text{Pd}(\text{OAc})_2$	PCy_3	K_2CO_3	PhMe	30%
6	$\text{Pd}(\text{OAc})_2$	PPh_3 (10 mol %)	K_2CO_3	PhMe	ND
7	$\text{Pd}(\text{OAc})_2$	Dppf (10 mol %)	K_2CO_3	PhMe	ND
8	$\text{Pd}(\text{OAc})_2$	IPr	K_2CO_3	PhMe	Trace
9	$\text{Pd}(\text{OAc})_2$	PCy_3	Et_3N	PhMe	28%

Table S2. Screening of ligand and additive in the presence of Pd(OAc)₂

Entry	catalyst	ligand	additive	solvent	Yield ^[b]
1	Pd(OAc) ₂	PCy ₃	Et ₃ N	PhMe	29%
2	Pd(OAc) ₂	P ^t Bu ₃	Et ₃ N	PhMe	ND
3	Pd(OAc) ₂	Dppm	Et ₃ N	PhMe	17%
4	Pd(OAc) ₂	Dcype	Et ₃ N	PhMe	Trace
5	Pd(OAc) ₂	X-phos	Et ₃ N	PhMe	messy
6	Pd(OAc) ₂	Davephos	Et ₃ N	PhMe	ND
7	Pd(OAc) ₂	2,2'-Bipyridine	Et ₃ N	PhMe	ND
8	Pd(OAc) ₂	PCy ₃	---	PhMe	20%
9	Pd(OAc) ₂	PCy ₃	KOAc	PhMe	23%
10	Pd(OAc) ₂	PCy ₃	K ₃ PO ₄	PhMe	<20%
11	Pd(OAc) ₂	PCy ₃	KO ^t Bu	PhMe	ND
12	Pd(OAc) ₂	PCy ₃	DABCO	PhMe	40%
13	Pd(OAc) ₂	PCy ₃	HOAc	PhMe	<20%
14	Pd(OAc) ₂	PCy ₃	B(OH) ₃	PhMe	ND
15	Pd(OAc) ₂	PCy ₃	PhCOOH	PhMe	ND

Table S3. Screening of catalyst

Entry	catalyst	ligand	additive	solvent	yield ^[a]
1	Pd(OAc) ₂	PCy ₃	Et ₃ N	PhMe	29%
2	Pd(OPiv) ₂	PCy ₃	Et ₃ N	PhMe	40%
3	Pd(CF ₃ COO) ₂	PCy ₃	Et ₃ N	PhMe	ND
4	Pd(acac) ₂	PCy ₃	DABCO	PhMe	37%
5	Pd ₂ (dba) ₃ (5 mol %)	PCy ₃	Et ₃ N	PhMe	17%
6	[Pd(allyl)Cl] ₂ (5 mol %)	PCy ₃	Et ₃ N	PhMe	ND
7	Pd(PPh ₃)Cl ₂ (5 mol %)	PCy ₃	Et ₃ N	PhMe	ND
8	Pd(PPh ₃) ₄ (5 mol %)	PCy ₃	Et ₃ N	PhMe	ND
9	NiI ₂	2,2'-Bipyridine	Zn (2.0 equiv)	DMF	ND
10	NiI ₂	2,2'-Bipyridine	Zn (2.0 equiv)	PhMe	ND
11	NiBr ₂ (dme)	1,10-Phenanthroline	Zn (2.0 equiv)	MeOH	ND
12	Ni(cod) ₂	IPr	---	PhMe	<30%
13	Ru ₃ (CO) ₁₂	Dppp	---	PhMe	ND
14	Ru ₃ (CO) ₁₂	PCy ₃	---	PhMe	ND

15	Pd(OPiv) ₂	PCy ₃	DABCO	PhMe	41%
16	Pd(OPiv) ₂	PCy ₃	Et ₃ N	PhMe	62% ^[d]

Optimization of the Reaction Conditions for *N*-glutarimide benzamides

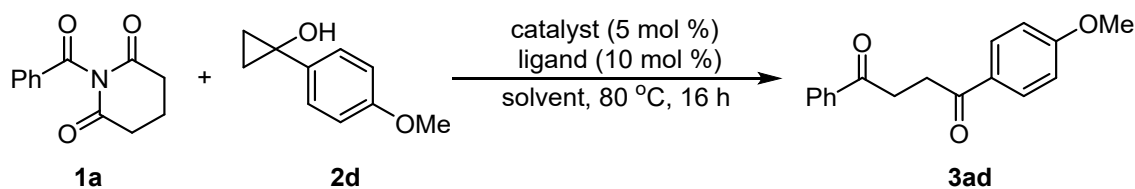


Table S4. Screening of solvent

Entry	catalyst	ligand	solvent	Yield ^[a]
1	Pd(OAc) ₂	PCy ₃	PhMe	56%
2	Pd(OAc) ₂	PCy ₃	1,4-dioxane	52%
3	Pd(OAc) ₂	PCy ₃	THF	55%
4	Pd(OAc) ₂	PCy ₃	MeCN	Trace
5	Pd(OAc) ₂	PCy ₃	DMF	ND
6	Pd(OAc) ₂	PCy ₃	DMSO	ND

Table S5. Screening of catalyst

Entry	catalyst	ligand	solvent	yield ^{[a][b]}
1	Pd(OAc) ₂	PCy ₃	PhMe	56%
2	Pd(OPiv) ₂	PCy ₃	PhMe	58%
3	Pd(PPh ₃) ₄	PCy ₃	PhMe	43%
4	Pd(acac) ₂	PCy ₃	PhMe	60%
5	Pd ₂ (dba) ₃	PCy ₃	PhMe	60%
6	PdCl ₂	PCy ₃	PhMe	ND
7	Pd(acac) ₂	PCy ₃	PhMe	68% ^[c]

Table S6. Screening of ligand

Entry	catalyst	ligand	solvent	yield ^{[a][d]}
1	Pd(acac) ₂	PPh ₃	PhMe	16%
2	Pd(acac) ₂	P ^t Bu ₃	PhMe	ND
3	Pd(acac) ₂	X-phos	PhMe	12%
4	Pd(acac) ₂	Dcype	PhMe	Trace
5	Pd(acac) ₂	Xantphos	PhMe	18%
6	Pd(acac) ₂	Dppf	PhMe	10%
7	Pd(acac) ₂	Dppm	PhMe	ND

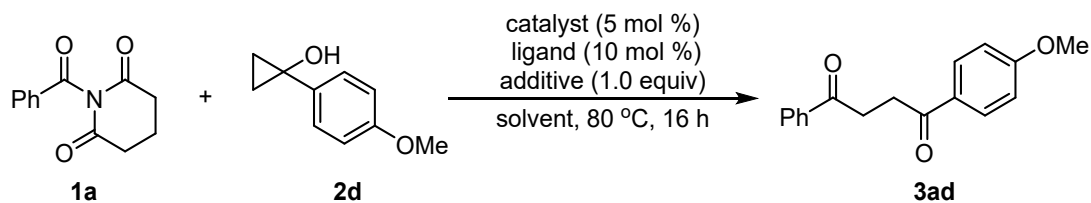
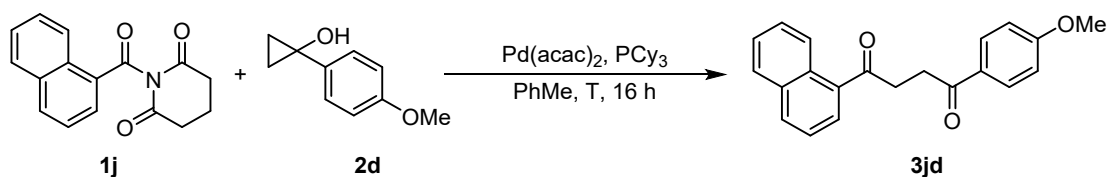


Table S7. Screening of Screening for additive

Entry	catalyst	ligand	additive (1.0 equiv)	solvent	Yield ^{[b]/[d]}
1	Pd(acac) ₂	PCy ₃	B(OMe) ₃	PhMe	55%
2	Pd(acac) ₂	PCy ₃	PhCOOH	PhMe	61%
3	Pd(acac) ₂	PCy ₃	HOAc	PhMe	67%
4	Pd(acac) ₂	PCy ₃	Zn(OTf) ₂	PhMe	ND
5	Pd(acac) ₂	PCy ₃	CuCl	PhMe	ND
6	Pd(acac) ₂	PCy ₃	H ₃ PO ₄	PhMe	Trace
7	Pd(acac) ₂	PCy ₃	K ₂ CO ₃	PhMe	17%
8	Pd(acac) ₂	PCy ₃	NaO ^t Bu	PhMe	ND
9	Pd(acac) ₂	PCy ₃	Et ₃ N	PhMe	33%

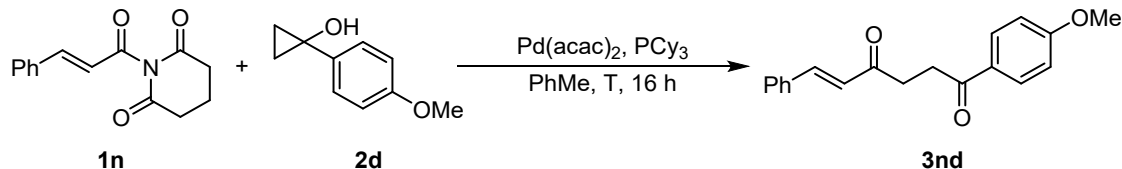
Optimization of the Reaction Conditions for certain *N*-glutarimide amides

Table S8. Optimization of the Reaction Conditions for the coupling of **1j** and **2d**

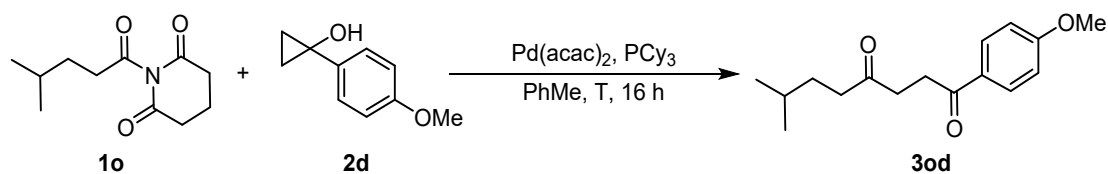


Entry	Pd(acac) ₂	PCy ₃	T	Yield ^[b]
1	5 mol %	10 mol %	80 °C	48%
2	10 mol %	20 mol %	80 °C	62%
3	5 mol %	10 mol %	100 °C	56%
4	10 mol %	20 mol %	100 °C	57%

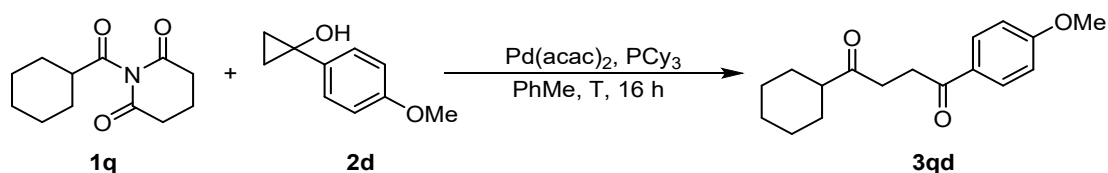
Table S9. Optimization of the Reaction Conditions for the coupling of **1n** and **2d**



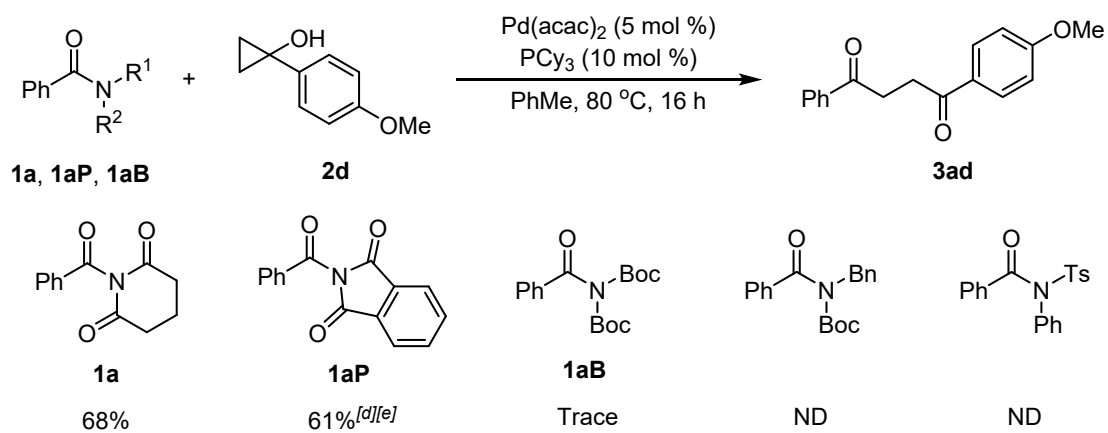
Entry	Pd(acac) ₂	PCy ₃	T	Yield ^[b]
1	5 mol %	10 mol %	80 °C	30%
2	5 mol %	10 mol %	100 °C	40%
3	10 mol %	20 mol %	100 °C	35%

Table S10. Optimization of the Reaction Conditions for the coupling of **1o** and **2d**

Entry	Pd(acac) ₂	PCy ₃	T	Yield ^[a]
1	10 mol %	20 mol %	100 °C	56%

Table S11. Optimization of the Reaction Conditions for the coupling of **1q** and **2d**

Entry	Pd(acac) ₂	PCy ₃	T	Yield ^[a]
1	5 mol %	10 mol %	80 °C	<30%
2	10 mol %	20 mol %	80 °C	53%
3	5 mol %	10 mol %	100 °C	39%
4	10 mol %	20 mol %	100 °C	66%

Scheme S1. *N*-substitutes evaluation of benzamides^{[a][c]}

All reactions were performed on 0.2 mmol scale benzamide with 1.0 equiv of the cyclopropanol under N₂ unless stated in 2 mL toluene;

^[a]isolated yields;

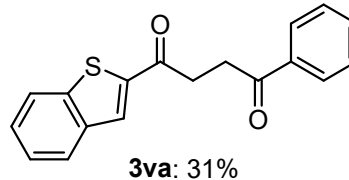
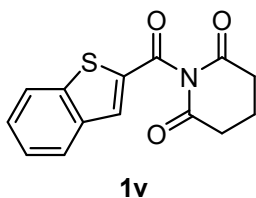
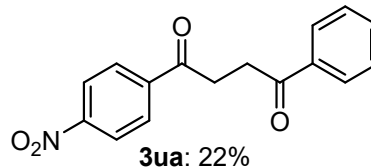
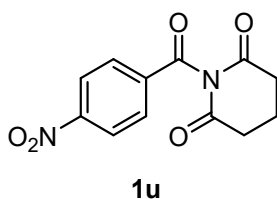
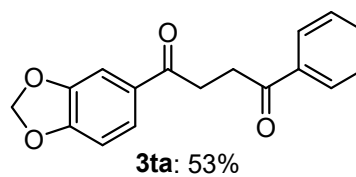
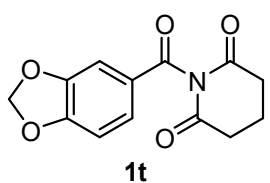
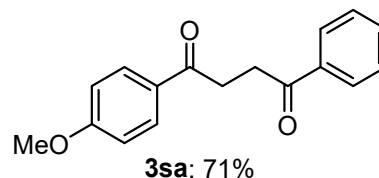
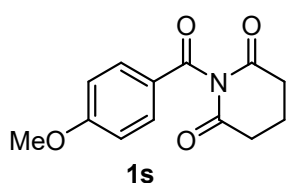
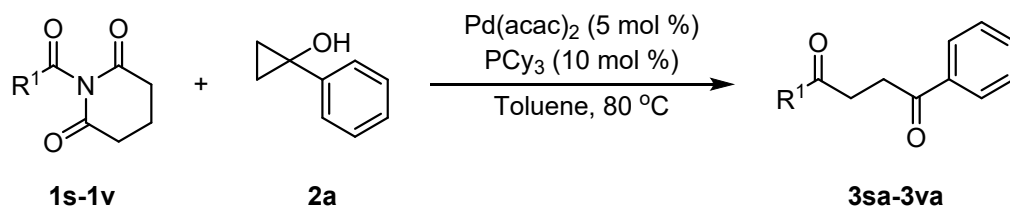
^[b]yields determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard.

^[c]1.25 equiv cyclopropanol was used;

^[d]1.5 equiv cyclopropanol was used;

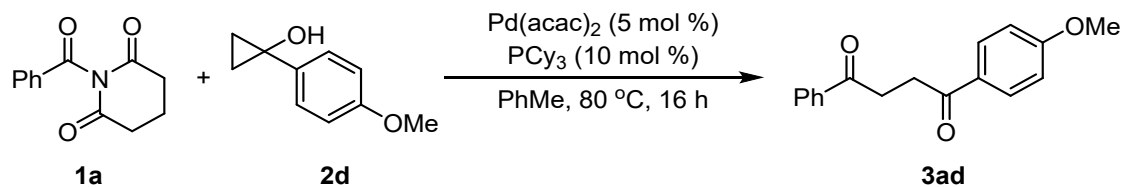
^[e]Pd(OPiv)₂ (10 mol %), PCy₃ (20 mol %), Et₃N (1.0 equiv) at 90 °C.

Scheme S2. Substrate scope of *N*-glutarimide amide with **2a** as coupling partner



All reactions were performed on 0.2 mmol scale benzamide with 1.25 equiv of the cyclopropanol under N_2 unless stated in 2 mL toluene;

Typical Procedure for the Synthesis of γ -Diketones

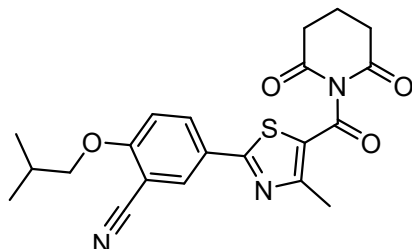


General procedure: A 10 mL oven-dried reaction vessel equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv, 43.4 mg), **2d** (0.25 mmol, 1.25 equiv, 41 mg), Pd(acac)_2 (0.01 mol, 0.05 equiv, 3.1 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy_3 (10 mol %, 0.02 mmol, 5.6 mg) then was added and removed from glove. The reaction

mixture was resolved in PhMe (2 mL) and allowed to stir at 80 °C for 16 h. The reaction was cooled to room temperature then mixture was filtered on celite and concentrated to yield the crude product, which was further purified by flash chromatography (Petroleum ether/EtOAc = 5:1 or Petroleum ether/ Dichloromethane = 1:2) to give the desired product **3ad**.

Characterization data of *N*-glutarimide amide

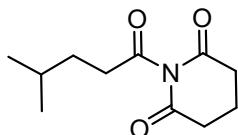
5-(5-(2,6-Dioxopiperidine-1-carbonyl)thiazol-2-yl)-2-isobutoxybenzonitrile (**1m**)



This compound was prepared according to the general procedure. Purification by column chromatography on silica gel (Petroleum ether/ Ethyl acetate = 1/1, v/v) afforded **3qd** as a yellow solid (29 mg). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 2.0 Hz, 1H), 8.11 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.81 (s, 3H), 2.76 (t, *J* = 6.5 Hz, 4H), 2.20 (hept, *J* = 6.5 Hz, 1H), 2.13 (p, *J* = 6.5 Hz, 2H), 1.09 (d, *J* = 7.0 Hz, 6H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 171.39, 169.15, 164.90, 163.01, 162.65, 132.84, 132.45, 126.26, 125.26, 115.13, 112.70, 103.11, 75.77, 32.38, 28.12, 19.01, 18.21, 17.29.

HRMS (ESI) *m/z* calcd. for C₂₁H₂₁N₃O₄S [M-H]⁻ 410.1180, found 410.1176.

1-(4-Methylpentanoyl)piperidine-2,6-dione (**1o**)

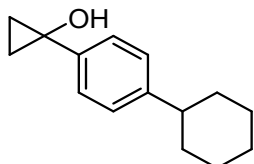


White solid. ¹H NMR (500 MHz, Chloroform-*d*) δ 2.73 – 2.59 (m, 6H), 2.01 (h, *J* = 6.4 Hz, 2H), 1.60 (qd, *J* = 7.4, 6.4, 2.3 Hz, 3H), 0.90 (t, *J* = 5.8 Hz, 6H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 178.36, 171.56, 171.52, 39.09, 39.07, 32.24, 32.22, 32.03, 27.22, 22.20, 17.29.

HRMS (FI) *m/z* calcd. for C₁₁H₁₇NO₃ [M]⁺ 211.1203, found 211.1197.

Characterization data of cyclopropanols

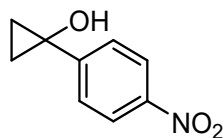
1-(4-cyclohexylphenyl)cyclopropan-1-ol (**2c**)



White solid. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.26 – 7.23 (m, 2H), 7.20 – 7.17 (m, 2H), 2.52 – 2.45 (m, 1H), 2.01 (br, 1H), 1.91 – 1.81 (m, 4H), 1.78 – 1.71 (m, 1H), 1.47 – 1.33 (m, 4H), 1.31 – 1.25 (m, 1H), 1.24 – 1.22 (m, 2H), 1.04 – 1.00 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 146.47, 141.51, 126.83, 124.60, 56.70, 44.17, 34.49, 26.91, 26.16, 17.45.

HRMS (FI) *m/z* calcd. for C₁₅H₂₀O [M]⁺ 216.1509, found 216.1511.

1-(4-Nitrophenyl)cyclopropan-1-ol (2i)

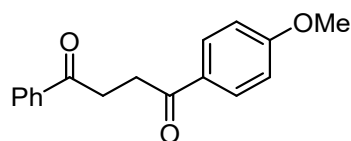


Yellow solid. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.17 – 8.13 (m, 2H), 7.40 – 7.36 (m, 2H), 2.69 (br, 1H), 1.47 – 1.42 (m, 2H), 1.20 – 1.15 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.87, 146.16, 124.26, 123.55, 56.12, 20.28.

HRMS (FI) m/z calcd. for $\text{C}_9\text{H}_{10}\text{O}_3\text{N}$ $[\text{M}]^+$ 180.0654, found 180.0655.

Characterization data of γ -diketones

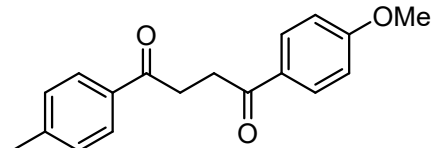
1-(4-Methoxyphenyl)-4-phenylbutane-1,4-dione (3ad/3sa)



White solid (36.7 mg, 68%). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 4H), 7.60 – 7.55 (m, 1H), 7.50 – 7.45 (m, 2H), 6.98 – 6.93 (m, 2H), 3.87 (s, 3H), 3.47 – 3.39 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.85, 197.15, 163.50, 136.81, 133.07, 130.35, 129.86, 128.55, 128.10, 113.70, 55.45, 32.65, 32.21.

The spectroscopic data matched literature values.¹²

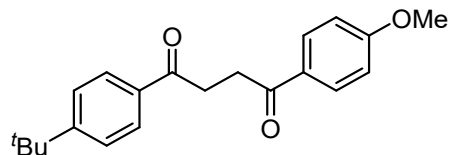
1-(4-Methoxyphenyl)-4-(*p*-tolyl)butane-1,4-dione (3bd)



White solid (31.2 mg, 62%). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.99 (m, 2H), 7.95 – 7.91 (m, 2H), 7.29 – 7.24 (m, 2H), 6.96 – 6.92 (m, 2H), 3.86 (s, 3H), 3.44 – 3.36 (m, 4H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.45, 197.25, 163.45, 143.80, 134.30, 130.32, 129.87, 129.22, 129.20, 128.18, 113.66, 55.41, 32.51, 32.21, 21.59.

The spectroscopic data matched literature values.¹³

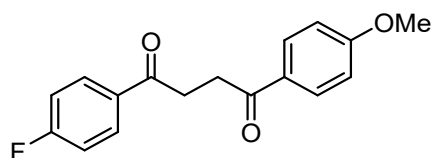
1-(4-(*tert*-Butyl)phenyl)-4-(4-methoxyphenyl)butane-1,4-dione (3cd)



White solid (35.7 mg, 68%). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.99 (m, 2H), 7.99 – 7.95 (m, 2H), 7.48 (dt, J = 8.0, 2.0 Hz, 2H), 6.96 – 6.92 (m, 2H), 3.86 (s, 3H), 3.44 – 3.38 (m, 4H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.47, 197.21, 163.43, 156.72, 134.21, 130.30, 129.86, 128.02, 125.45, 113.65, 55.39, 35.04, 32.50, 32.23, 31.03.

HRMS (FI) m/z calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_3$ $[\text{M}]^+$ 324.1720, found 324.1712.

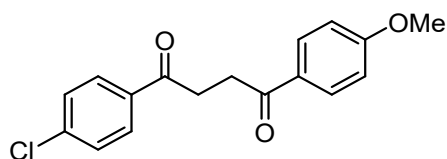
1-(4-Fluorophenyl)-4-(4-methoxyphenyl)butane-1,4-dione (3dd)



White solid (44.4 mg, 78%). $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.07 – 8.02 (m, 2H), 8.02 – 7.97 (m, 2H), 7.15 – 7.10 (m, 2H), 6.95 – 6.91 (m, 2H), 3.85 (s, 3H), 3.40–3.37 (m, 4H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 197.22, 196.99, 166.70, 164.67, 163.50, 133.24, 133.21, 130.71, 130.64, 130.30, 129.73, 115.67, 115.49, 113.68, 55.40, 32.45, 32.14. $^{19}\text{F NMR}$ (471 MHz, Chloroform-*d*) δ -105.36.

The spectroscopic data matched literature values.¹⁴

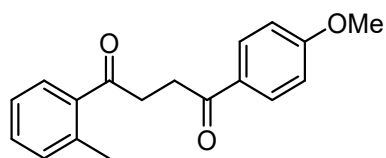
1-(4-Chlorophenyl)-4-(4-methoxyphenyl)butane-1,4-dione (3ed)



White solid (28.8 mg, 53%). $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.04 – 7.95 (m, 4H), 7.48 – 7.43 (m, 2H), 6.98 – 6.93 (m, 2H), 3.88 (s, 3H), 3.44 – 3.37 (m, 4H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 197.69, 196.97, 163.58, 139.51, 135.16, 130.37, 129.76, 129.54, 128.89, 113.74, 55.47, 32.58, 32.19.

The spectroscopic data matched literature values.¹⁴

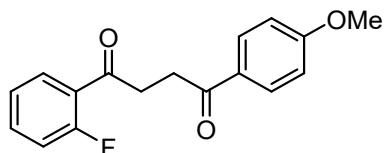
1-(4-Methoxyphenyl)-4-(*o*-tolyl)butane-1,4-dione (3fd)



White solid (33.5 mg, 59%). $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.02 – 7.98 (m, 2H), 7.80 (dd, J = 8.0, 1.5 Hz, 1H), 7.37 (td, J = 7.5, 1.5 Hz, 1H), 7.30 – 7.22 (m, 2H), 6.95 – 6.92 (m, 2H), 3.86 (s, 3H), 3.41 – 3.37 (m, 2H), 3.34 – 3.30 (m, 2H), 2.50 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 202.81, 197.05, 163.44, 137.95, 137.88, 131.79, 131.18, 130.28, 129.82, 128.53, 125.63, 113.65, 55.40, 35.34, 32.43, 21.19.

The spectroscopic data matched literature values.¹⁵

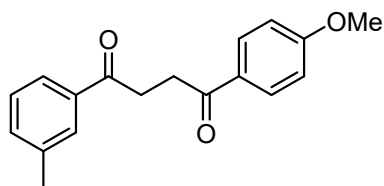
1-(2-Fluorophenyl)-4-(4-methoxyphenyl)butane-1,4-dione (3gd)



White solid (20.1 mg, 35%). $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.03 – 7.98 (m, 2H), 7.89 (td, J = 7.5, 2.0 Hz, 1H), 7.54–7.49 (m, 1H), 7.22 (td, J = 7.5, 1.0 Hz, 1H), 7.15 (ddd, J = 11.0, 8.0, 1.0 Hz, 1H), 6.96 – 6.92 (m, 2H), 3.87 (s, 3H), 3.45–3.37 (m, 4H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 197.16, 197.12, 196.94, 163.46, 163.06, 161.04, 134.51, 134.43, 130.65, 130.63, 130.32, 129.85, 124.37, 124.35, 116.74, 116.55, 113.67, 55.43, 37.47, 37.40, 32.19, 32.17. $^{19}\text{F NMR}$ (471 MHz, Chloroform-*d*) δ -109.01.

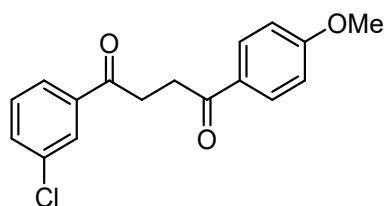
HRMS (FI) m/z calcd. for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{F}$ $[\text{M}]^+$ 286.1000, found 286.0985.

1-(4-Methoxyphenyl)-4-(*m*-tolyl)butane-1,4-dione (3hd)



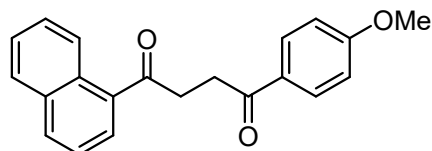
White solid (40.5 mg, 72%). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.99 (m, 2H), 7.85 – 7.80 (m, 2H), 7.39 – 7.32 (m, 2H), 6.96 – 6.91 (m, 2H), 3.86 (s, 3H), 3.44 – 3.37 (m, 4H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.00, 197.17, 163.44, 138.25, 136.79, 133.77, 130.30, 129.83, 128.58, 128.38, 125.25, 113.64, 55.39, 32.65, 32.20, 21.28. The spectroscopic data matched literature values.¹⁶

1-(3-Chlorophenyl)-4-(4-methoxyphenyl)butane-1,4-dione (3id)



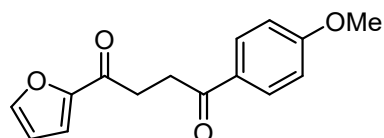
White solid (25.3 mg, 42%). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.98 (m, 3H), 7.91 (dt, J = 8.0, 1.5 Hz, 1H), 7.54 (ddd, J = 8.0, 2.5, 1.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 6.97 – 6.92 (m, 2H), 3.87 (s, 3H), 3.44 – 3.37 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.62, 196.83, 163.56, 134.89, 132.97, 130.34, 129.90, 129.71, 128.23, 126.19, 113.72, 55.45, 32.69, 32.16. The spectroscopic data matched literature values.¹⁴

1-(4-Methoxyphenyl)-4-(naphthalen-1-yl)butane-1,4-dione (3jd)



White solid (39.2 mg, 62%). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.61 (dd, J = 8.5, 1.0 Hz, 1H), 8.07 – 8.02 (m, 3H), 7.99 (dt, J = 8.5, 1.0 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.60 – 7.56 (m, 1H), 7.55 – 7.50 (m, 2H), 6.98 – 6.94 (m, 2H), 3.87 (s, 3H), 3.49 (s, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 203.03, 197.05, 163.48, 136.02, 133.87, 132.45, 130.33, 130.07, 129.83, 128.29, 127.76, 127.55, 126.32, 125.81, 124.39, 113.69, 55.42, 36.02, 32.63. The spectroscopic data matched literature values.¹⁷

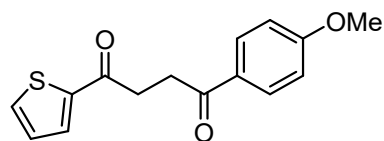
1-(Furan-2-yl)-4-(4-methoxyphenyl)butane-1,4-dione (3kd)



White solid (34.5 mg, 67%). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.96 (m, 2H), 7.58 (dd, J = 1.5, 0.5 Hz, 1H), 7.24 (dd, J = 3.5, 1.0 Hz, 1H), 6.94 – 6.90 (m, 2H), 6.53 (dd, J = 3.5, 2.0 Hz, 1H), 3.85 (s, 3H), 3.40 – 3.36 (m, 2H), 3.29 – 3.25 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.78, 187.98, 163.48, 152.50, 146.27, 130.29, 129.67, 117.04, 113.66, 112.13, 55.40, 32.26, 31.86.

The spectroscopic data matched literature values.¹⁴

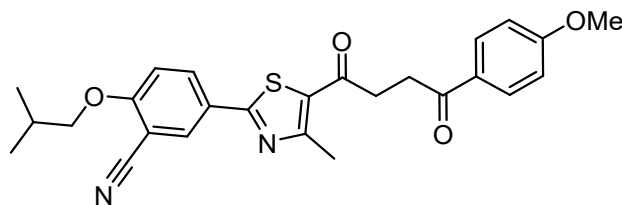
1-(4-Methoxyphenyl)-4-(thiophen-2-yl)butane-1,4-dione (3ld)



White solid (39 mg, 71%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.97 (m, 2H), 7.82 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.63 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.14 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.96 – 6.91 (m, 2H), 3.86 (s, 3H), 3.42 – 3.35 (m, 4H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 196.90, 191.78, 163.52, 143.91, 133.45, 131.98, 130.37, 130.33, 129.71, 128.07, 113.69, 55.43, 33.23, 32.22.

The spectroscopic data matched literature values.¹⁸

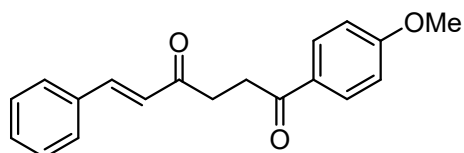
2-Isobutoxy-5-(5-(4-(4-methoxyphenyl)-4-oxobutanoyl)-4-methylthiazol-2-yl)benzonitrile (3md)



Light yellow solid (27 mg, 29%) ¹H NMR (500 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 2.5 Hz, 1H), 8.11 (dd, *J* = 9.0, 2.5 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.97 – 6.93 (m, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 3.87 (s, 3H), 3.43 – 3.39 (m, 2H), 3.30 – 3.26 (m, 2H), 2.78 (s, 3H), 1.09 (d, *J* = 6.5 Hz, 6H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 196.61, 191.52, 166.53, 163.62, 162.56, 159.79, 132.66, 132.17, 130.64, 130.36, 129.58, 125.85, 115.34, 113.75, 112.62, 103.00, 55.46, 36.82, 32.31, 28.13, 19.02, 18.49.

HRMS (ESI) *m/z* calculated for C₂₆H₂₆N₂O₄S [M+H]⁺ 463.1687, found 463.1686.

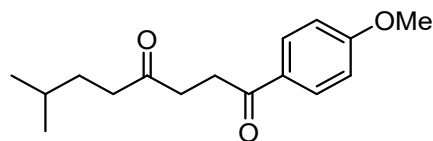
(*E*)-1-(4-Methoxyphenyl)-6-phenylhex-5-ene-1,4-dione (3nd)



White solid. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.98 (m, 2H), 7.64 (d, *J* = 16.5 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.42 – 7.38 (m, 3H), 6.97 – 6.92 (m, 2H), 6.82 (d, *J* = 16.5 Hz, 1H), 3.87 (s, 3H), 3.35 (t, *J* = 6.5 Hz, 2H), 3.14 (t, *J* = 6.5 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.84, 197.16, 163.51, 142.75, 134.51, 130.42, 130.35, 129.82, 128.91, 128.29, 126.19, 113.70, 55.45, 34.51, 32.23.

The spectroscopic data matched literature values.¹⁷

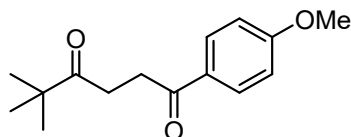
1-(4-Methoxyphenyl)-7-methyloctane-1,4-dione (3od)



Light green solid (29.1 mg, 56%). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.97 – 7.93 (m, 2H), 6.94 – 6.89 (m, 2H), 3.85 (s, 3H), 3.24 – 3.20 (m, 2H), 2.83 (t, *J* = 6.5 Hz, 2H), 2.54 – 2.49 (m, 2H), 1.59

– 1.47 (m, 3H), 0.89 (d, $J = 6.5$ Hz, 6H). ^{13}C NMR (126 MHz, Chloroform- d) δ 210.05, 197.15, 163.44, 130.25, 129.76, 113.64, 55.40, 41.03, 36.20, 32.62, 31.98, 27.69, 22.31. The spectroscopic data matched literature values.¹⁹

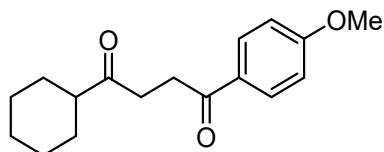
1-(4-Methoxyphenyl)-5,5-dimethylhexane-1,4-dione (3pd)



Colorless liquid (3mg, 6%). ^1H NMR (500 MHz, Chloroform- d) δ 8.02 – 7.98 (m, 2H), 6.98 – 6.93 (m, 2H), 3.89 (s, 3H), 3.23 (t, $J = 6.5$ Hz, 2H), 2.97 (t, $J = 6.5$ Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (126 MHz, Chloroform- d) δ 214.81, 197.44, 163.43, 130.28, 129.95, 113.66, 55.44, 44.07, 32.03, 30.82, 26.63.

The spectroscopic data matched literature values.²⁰

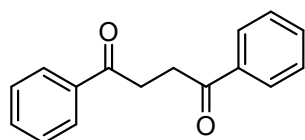
1-Cyclohexyl-4-(4-methoxyphenyl)butane-1,4-dione (3qd)



White solid (35.9 mg, 66%). ^1H NMR (500 MHz, Chloroform- d) δ 7.98 – 7.94 (m, 2H), 6.94 – 6.90 (m, 2H), 3.86 (s, 3H), 3.24 – 3.19 (m, 2H), 2.87 (m, 2H), 2.46 (tt, $J = 11.5, 3.5$ Hz, 1H), 1.95 – 1.88 (m, 2H), 1.79 (dt, $J = 12.5, 3.5$ Hz, 2H), 1.70 – 1.64 (m, 1H), 1.43 – 1.15 (m, 6H). ^{13}C NMR (126 MHz, Chloroform- d) δ 212.80, 197.28, 163.44, 130.27, 129.85, 113.65, 55.43, 50.92, 34.30, 31.94, 28.56, 25.87, 25.67.

HRMS (FI) m/z calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_3$ $[\text{M}]^+$ 274.1564, found 274.1560.

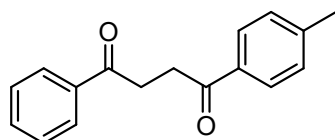
1,4-Diphenylbutane-1,4-dione (3aa)



Colorless liquid (37.5 mg, 79%). ^1H NMR (500 MHz, Chloroform- d) δ 8.06 – 8.02 (m, 4H), 7.60 – 7.55 (m, 2H), 7.50 – 7.45 (m, 4H), 3.46 (s, 4H). ^{13}C NMR (126 MHz, Chloroform- d) δ 198.62, 136.72, 133.10, 128.55, 128.07, 32.54.

The spectroscopic data matched literature values.²¹

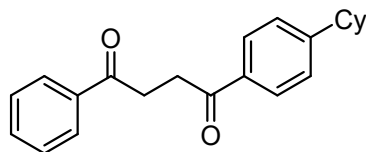
1-Phenyl-4-(*p*-tolyl)butane-1,4-dione (3ab)



White solid (31.2 mg, 62%). ^1H NMR (500 MHz, Chloroform- d) δ 8.06 – 8.02 (m, 2H), 7.96 – 7.92 (m, 2H), 7.59 – 7.55 (m, 1H), 7.50 – 7.45 (m, 2H), 7.29 – 7.25 (m, 2H), 3.46 – 3.42 (m, 4H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, Chloroform- d) δ 198.75, 198.26, 143.87, 136.77, 134.26, 133.07, 129.22, 128.54, 128.19, 128.08, 32.58, 32.44, 21.61.

The spectroscopic data matched literature values.¹²

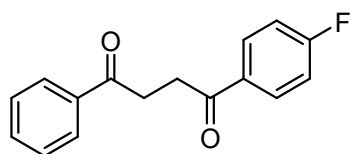
1-(4-Cyclohexylphenyl)-4-phenylbutane-1,4-dione (3ac)



White solid (43.3 mg, 68%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 8.02 (m, 2H), 7.99 – 7.95 (m, 2H), 7.59 – 7.54 (m, 1H), 7.50 – 7.44 (m, 2H), 7.33 – 7.29 (m, 2H), 3.48 – 3.41 (m, 4H), 2.57 (tt, *J* = 11.5, 3.5 Hz, 1H), 1.92 – 1.83 (m, 4H), 1.80 – 1.74 (m, 1H), 1.49 – 1.35 (m, 4H), 1.32 – 1.22 (m, 1H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.73, 198.28, 153.74, 136.76, 134.58, 133.04, 128.52, 128.29, 128.06, 127.02, 44.65, 34.06, 32.60, 32.43, 26.68, 25.99.

HRMS (FI) *m/z* calcd. for C₂₂H₂₄O₂ [M]⁺ 320.1771, found 320.1766.

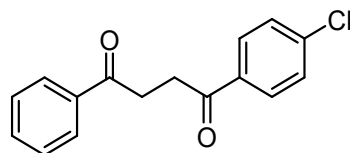
1-(4-Fluorophenyl)-4-phenylbutane-1,4-dione (3ae)



White solid (39.8 mg, 77%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 4H), 7.60 – 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 7.17 – 7.12 (m, 2H), 3.48 – 3.44 (m, 2H), 3.44 – 3.40 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.53, 197.05, 166.77, 164.74, 136.66, 133.19, 133.17, 130.75, 130.68, 128.58, 128.07, 115.73, 115.56, 32.53, 32.41. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -105.24.

The spectroscopic data matched literature values.²²

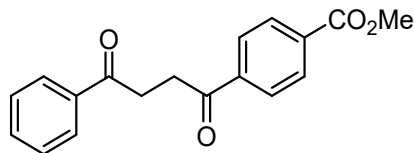
1-(4-Chlorophenyl)-4-phenylbutane-1,4-dione (3af)



White solid (28.8 mg, 53%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 2H), 7.99 – 7.95 (m, 2H), 7.60 – 7.55 (m, 1H), 7.50 – 7.42 (m, 4H), 3.48 – 3.44 (m, 2H), 3.43 – 3.39 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.43, 197.43, 139.51, 136.61, 135.06, 133.17, 129.50, 128.86, 128.57, 128.06, 32.50, 32.45.

The spectroscopic data matched literature values.¹⁸

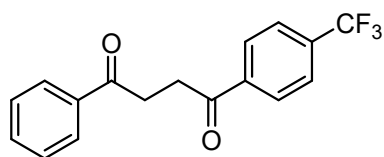
Methyl 4-(4-oxo-4-phenylbutanoyl)benzoate (3ag)



White solid (47.3 mg, 80%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.16 – 8.12 (m, 2H), 8.10 – 8.07 (m, 2H), 8.05 – 8.02 (m, 2H), 7.61 – 7.56 (m, 1H), 7.51 – 7.46 (m, 2H), 3.95 (s, 3H), 3.49 – 3.45 (m, 4H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.28, 198.13, 166.12, 139.90, 136.54, 133.80, 133.14, 129.74, 128.53, 128.01, 127.94, 32.80, 32.44.

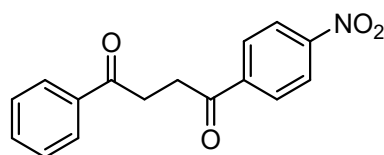
The spectroscopic data matched literature values.²³

1-Phenyl-4-(4-(trifluoromethyl)phenyl)butane-1,4-dione (3ah)



White solid (44.9 mg, 73%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.5 Hz, 2H), 8.05 – 8.02 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.47 (m, 2H), 3.52 – 3.44 (m, 4H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.30, 197.81, 139.46, 136.57, 133.30, 128.65, 128.45, 128.11, 125.74, 125.71, 125.68, 125.65, 32.79, 32.55. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -63.10. The spectroscopic data matched literature values.²⁴

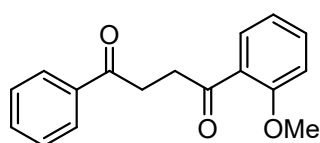
1-(4-Nitrophenyl)-4-phenylbutane-1,4-dione (3ai/3ua)



Yellow solid (42 mg, 74%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.34 – 8.30 (m, 2H), 8.20 – 8.16 (m, 2H), 8.04 – 8.00 (m, 2H), 7.61 – 7.56 (m, 1H), 7.51 – 7.46 (m, 2H), 3.53 – 3.49 (m, 2H), 3.48 – 3.44 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.09, 197.30, 150.30, 141.24, 136.39, 133.35, 129.11, 128.63, 128.06, 123.81, 32.96, 32.56.

The spectroscopic data matched literature values.²⁵

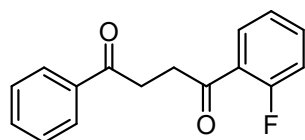
1-(2-Methoxyphenyl)-4-phenylbutane-1,4-dione (3aj)



White solid (27.4 mg, 51%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 2H), 7.77 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.50 – 7.44 (m, 3H), 7.04 – 6.96 (m, 2H), 3.94 – 3.90 (m, 3H), 3.50 – 3.44 (m, 2H), 3.44 – 3.38 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 200.57, 199.03, 158.78, 136.91, 133.55, 132.95, 130.47, 128.55, 128.50, 128.08, 127.81, 120.61, 111.53, 55.50, 37.91, 32.97.

The spectroscopic data matched literature values.¹⁶

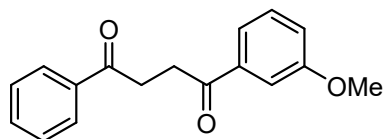
1-(2-Fluorophenyl)-4-phenylbutane-1,4-dione (3ak)



White solid (24.6 mg, 48%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 2H), 7.90 (td, *J* = 7.5, 2.0 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.54 – 7.49 (m, 1H), 7.49 – 7.44 (m, 2H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 7.15 (ddd, *J* = 11.0, 8.0, 1.0 Hz, 1H), 3.48 – 3.41 (m, 4H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.40, 196.89, 196.86, 163.07, 161.04, 136.70, 134.56, 134.49, 133.04, 130.63, 130.60, 128.51, 128.04, 125.44, 125.33, 124.37, 124.34, 116.73, 116.54, 37.36, 37.30, 32.51, 32.49. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -108.95.

HRMS (FI) *m/z* calcd. for C₁₆H₁₃O₂F [M]⁺ 256.0894, found 256.0876.

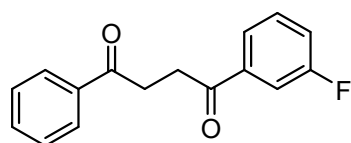
1-(3-Methoxyphenyl)-4-phenylbutane-1,4-dione (3al)



White solid (32 mg, 60%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 2H), 7.65 – 7.62 (m, 1H), 7.59 – 7.55 (m, 1H), 7.54 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.12 (ddd, *J* = 8.5, 3.0, 1.0 Hz, 1H), 3.85 (s, 3H), 3.45 (s, 4H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.59, 198.43, 159.76, 138.06, 136.71, 133.08, 129.54, 128.53, 128.05, 120.74, 119.64, 112.22, 55.38, 32.67, 32.54.

The spectroscopic data matched literature values.¹⁸

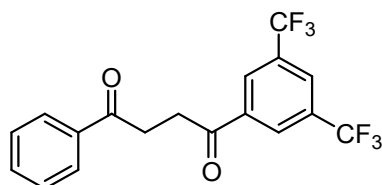
1-(3-Fluorophenyl)-4-phenylbutane-1,4-dione (3am)



White solid (37.2 mg, 73%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 2H), 7.83 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.71 (ddd, *J* = 9.5, 2.5, 1.5 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.51 – 7.43 (m, 3H), 7.30 – 7.25 (m, 1H), 3.49 – 3.45 (m, 2H), 3.44 – 3.40 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.38, 197.43, 197.41, 163.81, 161.84, 138.85, 138.80, 136.61, 133.19, 130.27, 130.21, 128.59, 128.07, 123.87, 123.85, 120.19, 120.02, 114.90, 114.73, 32.66, 32.49. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -111.89.

The spectroscopic data matched literature values.²⁶

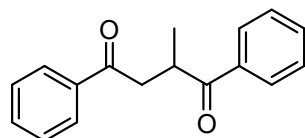
1-(3,5-Bis(trifluoromethyl)phenyl)-4-phenylbutane-1,4-dione (3an)



White solid (49.1 mg, 65%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.47 (t, *J* = 1.0 Hz, 2H), 8.08 (t, *J* = 1.5 Hz, 1H), 8.05 – 8.01 (m, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 3.56 – 3.51 (m, 2H), 3.49 – 3.45 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 197.99, 196.03, 138.26, 136.36, 133.41, 132.74, 132.47, 132.20, 131.93, 128.66, 128.49, 128.20, 128.17, 128.14, 128.09, 126.34, 126.31, 126.28, 126.25, 126.22, 126.16, 123.99, 121.82, 119.65, 32.63, 32.54. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -62.92.

The spectroscopic data matched literature values.²⁷

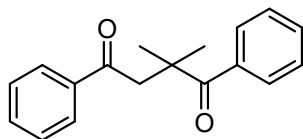
2-Methyl-1,4-diphenylbutane-1,4-dione (3ao)



White solid (22.1 mg, 44%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 8.04 (m, 2H), 8.01 – 7.97 (m, 2H), 7.60 – 7.54 (m, 2H), 7.52 – 7.43 (m, 4H), 4.23 – 4.14 (m, 1H), 3.73 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.12 (dd, *J* = 18.0, 5.0 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 203.38, 198.46, 136.64, 136.06, 133.16, 132.95, 128.64, 128.54, 128.49, 128.08, 42.32, 36.26, 17.94.

The spectroscopic data matched literature values.²²

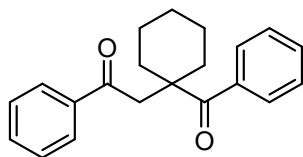
2,2-Dimethyl-1,4-diphenylbutane-1,4-dione (3ap)



White solid (37.5 mg, 70%). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.92 (m, 2H), 7.71 – 7.67 (m, 2H), 7.57 – 7.52 (m, 1H), 7.46 – 7.37 (m, 5H), 3.54 (s, 2H), 1.46 (s, 6H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 210.00, 197.67, 139.79, 136.85, 133.05, 130.14, 128.48, 127.96, 127.93, 127.90, 127.24, 50.41, 45.39, 26.82.

The spectroscopic data matched literature values.²⁸

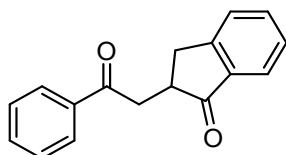
2-(1-Benzoylcyclohexyl)-1-phenylethan-1-one (3aq)



Colorless liquid (28.9 mg, 47%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 2H), 7.70 – 7.65 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 3H), 3.68 (s, 2H), 1.97 – 1.85 (m, 4H), 1.64 – 1.55 (m, 3H), 1.51 – 1.41 (m, 2H), 1.31 – 1.22 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 211.20, 198.04, 140.59, 137.10, 133.08, 129.69, 128.52, 127.97, 127.83, 127.22, 49.54, 43.93, 33.86, 25.61, 22.20.

HRMS (ESI) *m/z* calcd. for C₂₁H₂₂O₂ [M]⁺ 306.1614, found 306.1606.

2-(2-Oxo-2-phenylethyl)-2,3-dihydro-1*H*-inden-1-one (3ar)



This mixture compound was prepared according to the typical procedure. Purification by column chromatography on silica gel (Petroleum ether/ Ethyl acetate = 5/1, v/v) afforded **3ar** as a lightyellow liquid (37 mg, 74%). Then the mixture compound was purified by by column chromatography on silica gel (Petroleum ether / Ethyl acetate = 10/1, v/v then Petroleum ether / dichloromethane = 1/2).

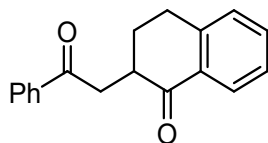
¹H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.97 (m, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.50 – 7.45 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 1H), 3.77 (dd, *J* = 17.5, 2.5 Hz, 1H), 3.56 (dd, *J* = 17.0, 7.5 Hz, 1H), 3.26 (dd, *J* = 17.5, 9.5 Hz, 1H), 3.23 – 3.17 (m, 1H), 2.85 (dd, *J* = 17.0, 4.0 Hz, 1H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 207.89, 197.95, 153.58, 136.51, 136.44, 134.80, 133.33, 128.66, 128.08, 127.41, 126.54, 123.89, 43.19, 40.02, 33.57.

The spectroscopic data matched literature values.²⁹

¹H NMR (500 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.00 – 7.96 (m, 2H), 7.64 – 7.59 (m, 1H), 7.53 – 7.48 (m, 3H), 7.39 – 7.34 (m, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 4.25 – 4.18 (m, 1H), 3.34 – 3.26 (m, 1H), 3.20 (dd, *J* = 16.5, 4.5 Hz, 1H), 2.94 – 2.90 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 199.79, 196.45, 141.68, 135.14, 133.91, 133.62, 131.98, 128.95, 128.85, 128.44, 127.21, 127.19, 42.65, 41.25, 32.63.

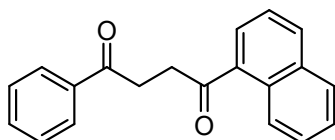
HRMS (ESI) m/z calcd. for $C_{17}H_{14}O_2$ $[M+H]^+$ 251.1067, found 251.1061.

2-(2-Oxo-2-phenylethyl)-3,4-dihydronaphthalen-1(2H)-one (3as)



White solid (32.6 mg, 62%). 1H NMR (500 MHz, Chloroform-*d*) δ 8.04 (dt, $J = 8.5, 1.5$ Hz, 3H), 7.60 – 7.55 (m, 1H), 7.50 – 7.45 (m, 3H), 7.33 – 7.29 (m, 1H), 7.26 (d, $J = 8.0$ Hz, 1H), 3.86 (dd, $J = 17.5, 5.0$ Hz, 1H), 3.36 – 3.29 (m, 1H), 3.23 – 3.14 (m, 1H), 3.02 – 2.95 (m, 2H), 2.33 – 2.27 (m, 1H), 1.99 (qd, $J = 13.0, 4.5$ Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.98, 198.51, 144.11, 136.99, 133.33, 133.06, 132.26, 128.74, 128.56, 128.11, 127.44, 126.57, 44.21, 38.99, 29.54, 29.37. The spectroscopic data matched literature values.³⁰

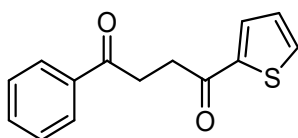
1-(Naphthalen-1-yl)-4-phenylbutane-1,4-dione (3at)



White Solid. (47.6 mg, 83%). 1H NMR (500 MHz, Chloroform-*d*) δ 8.63 (dd, $J = 8.5, 1.0$ Hz, 1H), 8.09 – 8.04 (m, 3H), 7.99 (dt, $J = 8.5, 1.0$ Hz, 1H), 7.88 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.61 – 7.56 (m, 2H), 7.56 – 7.51 (m, 2H), 7.51 – 7.47 (m, 2H), 3.56 – 3.48 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.77, 198.54, 136.70, 135.89, 133.85, 133.08, 132.49, 130.05, 128.53, 128.29, 128.05, 127.78, 127.55, 126.33, 125.78, 124.37, 35.87, 32.96.

The spectroscopic data matched literature values.¹⁸

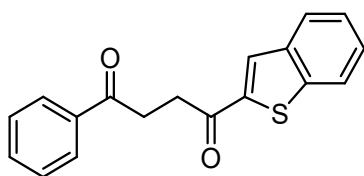
1-Phenyl-4-(thiophen-2-yl)butane-1,4-dione (3au)



Light yellow solid (15.8 mg, 32%). 1H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 2H), 7.84 (dd, $J = 4.0, 1.5$ Hz, 1H), 7.64 (dd, $J = 5.0, 1.0$ Hz, 1H), 7.59 – 7.55 (m, 1H), 7.50 – 7.45 (m, 2H), 7.15 (dd, $J = 5.0, 4.0$ Hz, 1H), 3.48 – 3.44 (m, 2H), 3.43 – 3.38 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.41, 191.58, 143.87, 136.63, 133.53, 133.18, 132.01, 128.58, 128.09, 33.15, 32.59.

The spectroscopic data matched literature values.¹⁸

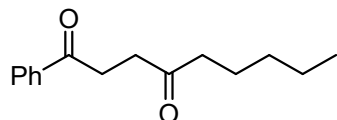
1-(Benzo[b]thiophen-2-yl)-4-phenylbutane-1,4-dione (3av/3va)



Yellow solid (35.4 mg, 60%). 1H NMR (500 MHz, Chloroform-*d*) δ 8.08 (d, $J = 0.5$ Hz, 1H), 8.05 – 8.01 (m, 2H), 7.89 (ddt, $J = 18.0, 8.0, 1.0$ Hz, 2H), 7.60 – 7.55 (m, 1H), 7.50 – 7.44 (m, 3H), 7.43 – 7.39

(m, 1H), 3.52 – 3.46 (m, 4H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.25, 193.12, 143.21, 142.41, 139.10, 136.55, 133.20, 129.20, 128.58, 128.07, 127.34, 125.93, 124.94, 122.92, 33.06, 32.62.
HRMS (FI) *m/z* calcd. for C₁₈H₁₄O₂S [M]⁺ 294.0709, found 294.0701.

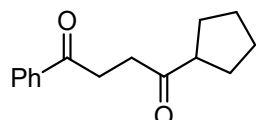
1-Phenylnonane-1,4-dione (3aw)



Colorless liquid (26 mg, 56%). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.95 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 – 7.42 (m, 2H), 3.27 (dd, *J* = 7.0, 5.5 Hz, 2H), 2.85 (t, *J* = 6.5 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.37 – 1.24 (m, 5H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 209.73, 198.63, 136.65, 133.06, 128.51, 127.99, 42.93, 36.13, 32.32, 31.37, 23.52, 22.41, 13.88.

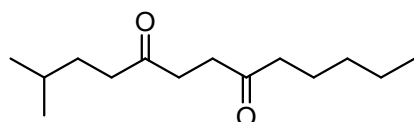
The spectroscopic data matched literature values.³¹

1-Cyclopentyl-4-phenylbutane-1,4-dione (3ax)



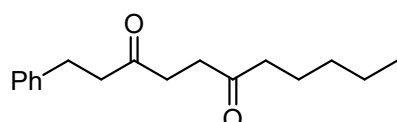
Colorless liquid (32.8 mg, 71%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.96 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 – 7.42 (m, 2H), 3.29 – 3.25 (m, 2H), 2.98 (p, *J* = 8.0 Hz, 1H), 2.91 (dd, *J* = 6.5, 5.5 Hz, 2H), 1.91 – 1.77 (m, 4H), 1.69 – 1.54 (m, 4H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 211.70, 198.74, 136.71, 133.01, 128.49, 127.99, 51.44, 35.28, 32.33, 28.90, 25.97.
HRMS (ESI) *m/z* calcd. for C₁₅H₁₈O₂ [M+H]⁺ 231.1380, found 231.1374.

2-Methyltridecane-5,8-dione (3ow)



Yellow liquid (19.9 mg, 44%). ¹H NMR (500 MHz, Chloroform-*d*) δ 2.68 – 2.64 (m, 4H), 2.46 – 2.40 (m, 4H), 1.60 – 1.49 (m, 3H), 1.48 – 1.43 (m, 2H), 1.32 – 1.22 (m, 4H), 0.89 – 0.85 (m, 9H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 209.87, 209.77, 42.80, 40.86, 35.97, 35.94, 32.59, 31.34, 27.66, 23.49, 22.40, 22.29, 13.86.
HRMS (ESI) *m/z* calcd. for C₁₄H₂₆O₂ [M+H]⁺ 227.2006, found 227.2002.

1-Phenylundecane-3,6-dione (3rw)

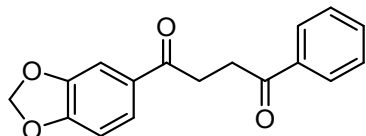


Yellow liquid. (24.1 mg, 44%) ¹H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.16 (m, 3H), 2.92 – 2.88 (m, 2H), 2.82 – 2.77 (m, 2H), 2.70 – 2.64 (m, 4H), 2.44 (t, *J* = 7.5 Hz, 2H), 1.58 (p, *J* = 7.5 Hz, 2H), 1.34 – 1.24 (m, 4H), 0.89 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (126 MHz,

Chloroform-*d*) δ 209.68, 208.53, 140.98, 128.43, 128.24, 126.03, 44.28, 42.76, 36.14, 35.97, 31.34, 29.69, 23.49, 22.40, 13.88.

HRMS (ESI) m/z calcd. for $C_{17}H_{24}O_2$ $[M+H]^+$ 261.1849, found 261.1842.

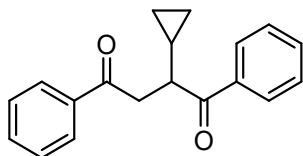
1-(Benzo[d][1,3]dioxol-5-yl)-4-phenylbutane-1,4-dione (3ta)



White solid (30.3 mg, 53%). 1H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 8.02 (m, 2H), 7.67 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.60 – 7.55 (m, 1H), 7.50 – 7.45 (m, 3H), 6.87 (d, $J = 8.0$ Hz, 1H), 6.05 (s, 2H), 3.46 – 3.42 (m, 2H), 3.40 – 3.36 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.74, 196.69, 151.77, 148.14, 136.76, 133.12, 131.64, 128.57, 128.10, 124.38, 107.93, 107.89, 101.80, 32.69, 32.31.

The spectroscopic data matched literature values.¹⁸

2-Clopropyl-1,4-diphenylbutane-1,4-dione (3ay)

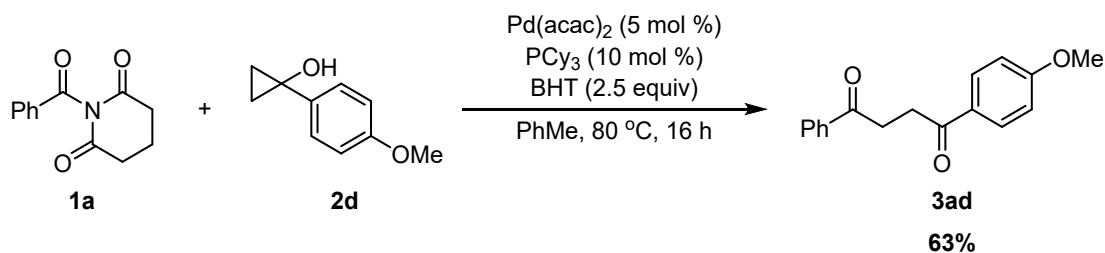


Colorless liquid (27.3 mg, 50%). 1H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 8.02 (m, 2H), 8.01 – 7.97 (m, 2H), 7.60 – 7.53 (m, 2H), 7.51 – 7.43 (m, 4H), 3.92 (dd, $J = 18.0, 9.5$ Hz, 1H), 3.46 (td, $J = 9.5, 3.5$ Hz, 1H), 3.32 (dd, $J = 18.0, 3.5$ Hz, 1H), 1.31 (d, $J = 25.5$ Hz, 1H), 0.98 – 0.90 (m, 1H), 0.56 – 0.54 (m, 1H), 0.49 – 0.42 (m, 1H), 0.32 – 0.21 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.80, 198.75, 137.70, 136.51, 133.18, 132.79, 128.61, 128.53, 128.12, 45.25, 41.96, 13.85, 4.68, 4.14.

HRMS (FI) m/z calcd. for $C_{19}H_{18}O_2$ $[M]^+$ 278.1301, found 278.1293.

Mechanistic Studies

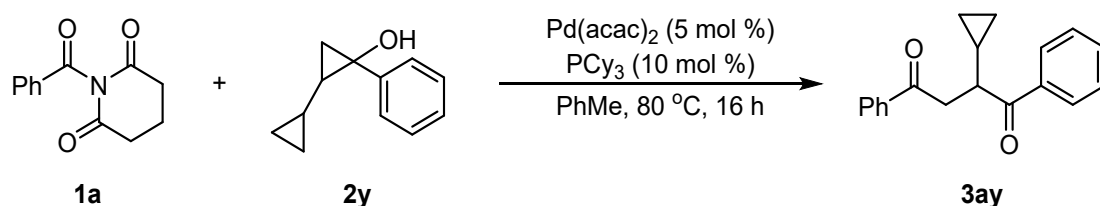
Coupling of cyclopropanol and amide in the presence of BHT



A 10 mL oven-dried reaction vessel equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv, 43.4 mg), **2d** (0.25 mmol, 1.25 equiv, 41mg), $Pd(acac)_2$ (0.01 mol, 0.05 equiv, 3.1 mg), and BHT (0.3 mmol, 2.5 equiv, 110.2 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy_3 (10 mol %, 0.02 mmol, 5.6 mg) then was added and removed from glove. The reaction mixture was resolved in PhMe (2 mL) and allowed to stir at 80 °C for 16 h. The reaction was cooled to room temperature then mixture was filtered on celite and concentrated to yield the crude product, which was further purified by flash chromatography (Petroleum ether / Ethyl acetate = 5/1) to give the desired product **3aa** in 63% of yield. No trapped

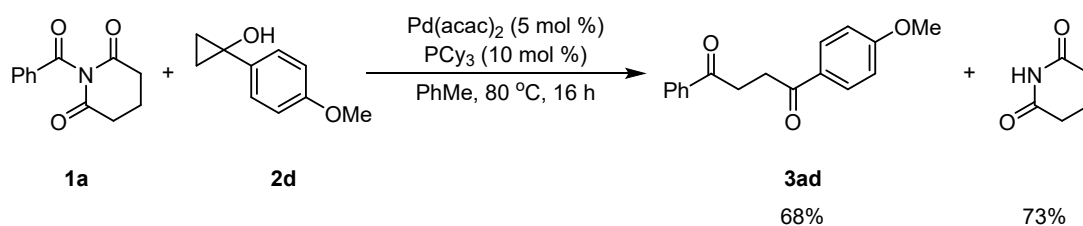
intermediate is detected.

Radical clock experiment



A 10 mL oven-dried reaction vessel equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv, 43.4 mg), **2aa** (1.25 equiv, 0.25 mmol, 41mg), Pd(acac)₂ (0.01 mol, 0.05 equiv, 3.1 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy₃ (10 mol %, 0.02 mmol, 5.6 mg) then was added and removed from glove. The reaction mixture was resolved in PhMe (2 mL) and allowed to stir at 80 °C for 16 h. The reaction was cooled to room temperature then mixture was filtered on celite and concentrated to yield the crude product, which was further purified by flash chromatography (Petroleum ether / ethyl acetate = 5/1) to give the desired product **3aaa** in 50% yields, no cyclopropyl-opening product was observed.

NMR spectrum evidence for the release of glutarimide.



A 10 mL oven-dried reaction vessel equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv, 43.4 mg), **2d** (0.25 mmol, 1.25 equiv, 41mg), Pd(acac)₂ (0.01 mol, 0.05 equiv, 3.1 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy₃ (10 mol %, 0.02 mmol, 5.6 mg) then was added and removed from glove. The reaction mixture was resolved in Toluene (2 mL) and allowed to stir at 80 °C for 16 h. After completion of reaction as monitored by TLC, solvent was removed under reduced pressure and the crude was subjected to perform an NMR test. From the NMR spectrum of the crude, we can clearly see the peak of glutarimide. Then the crude product was recovered, followed by glutarimides (0.2 mmol, 1.0 equiv, 22.6 mg) added, then was subjected to NMR test again. We can see the overlap of the peaks of glutarimide. Meanwhile, another same reaction mixture was filtered on celite and concentrated to yield crude product, which was further purified by flash chromatography (Petroleum ether / Ethyl acetate = 3/1 to Dichloromethane / Methanol = 10/1) to give the pure byproduct glutarimide in 73% (16.8 mg) yields. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (br, 1H), 2.62 – 2.56 (d, *J* = 2.0 Hz, 4H), 2.05 – 1.97 (m, 2H).

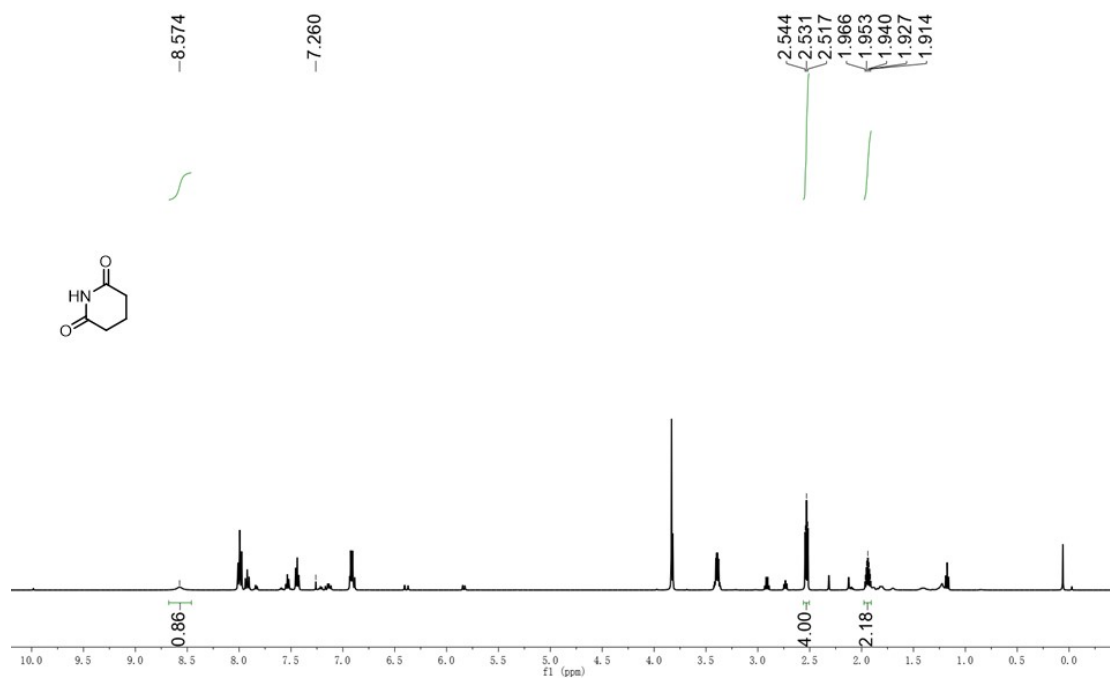


Figure S3. NMR spectrum of **3ad** crude product

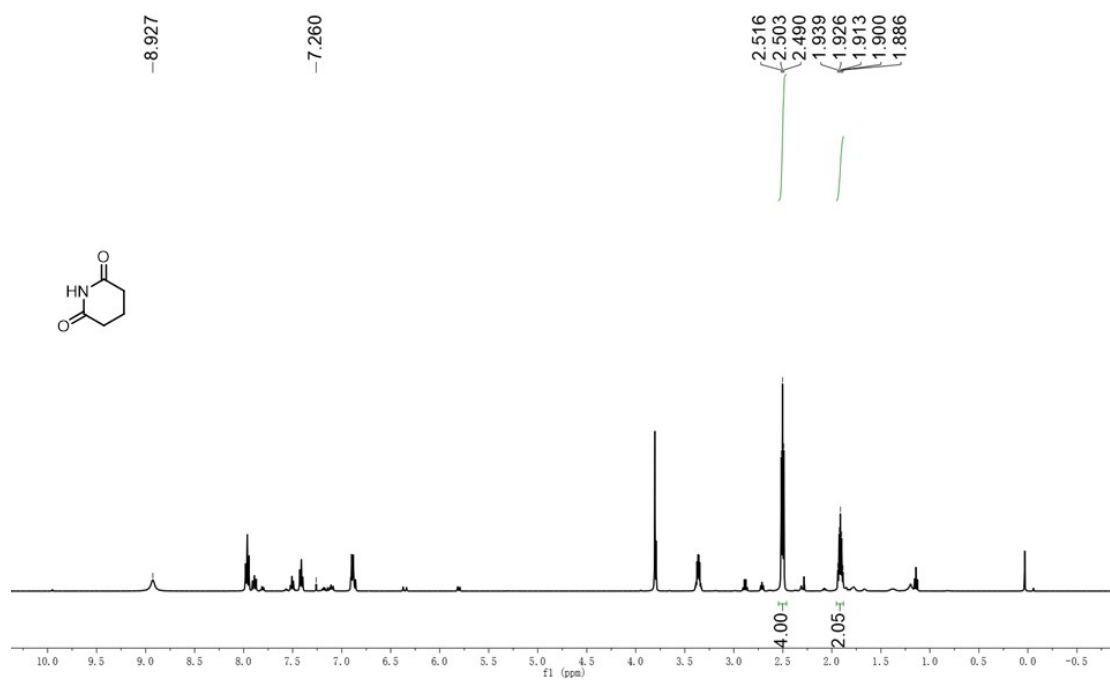
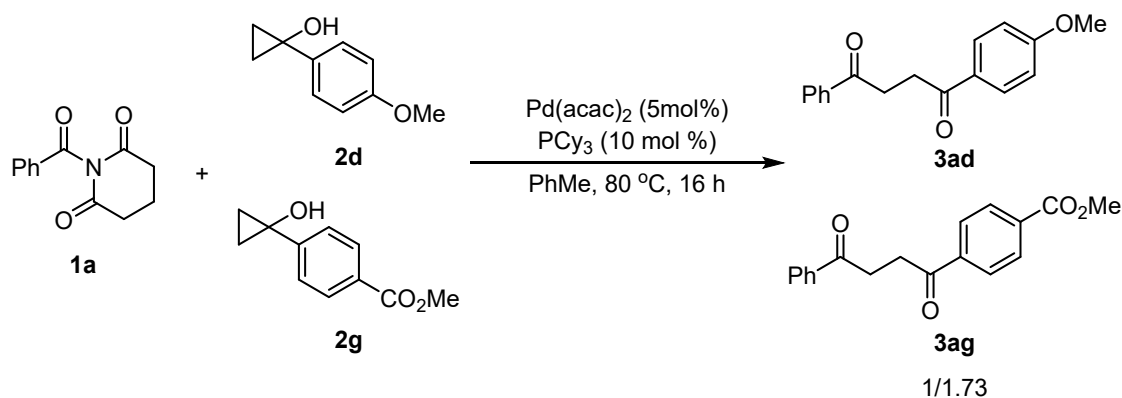


Figure S4. NMR spectrum of **3ad** crude product after 0.2 mmol glutarimide added

Competition experiment



A 10 mL oven-dried reaction vessel equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv, 43.4 mg), **2d** (0.2 mmol, 1.0 equiv, 32.8 mg), **2i** (0.2 mmol, 1.0 equiv, 38.4 mg) and $\text{Pd}(\text{acac})_2$ (0.01 mol, 0.05 equiv, 3.1 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy_3 (10 mol %, 0.02 mmol, 5.6 mg) then was added and removed from glove. The reaction mixture was resolved in Toluene (2 mL) and allowed to stir at $80\text{ }^\circ\text{C}$ for 16 h. After completion of reaction as monitored by TLC, solvent was removed under reduced pressure and the crude was subjected to perform an NMR test. NMR spectrum indicates ratio of **3ad** vs **3ai** is 1/1.73.

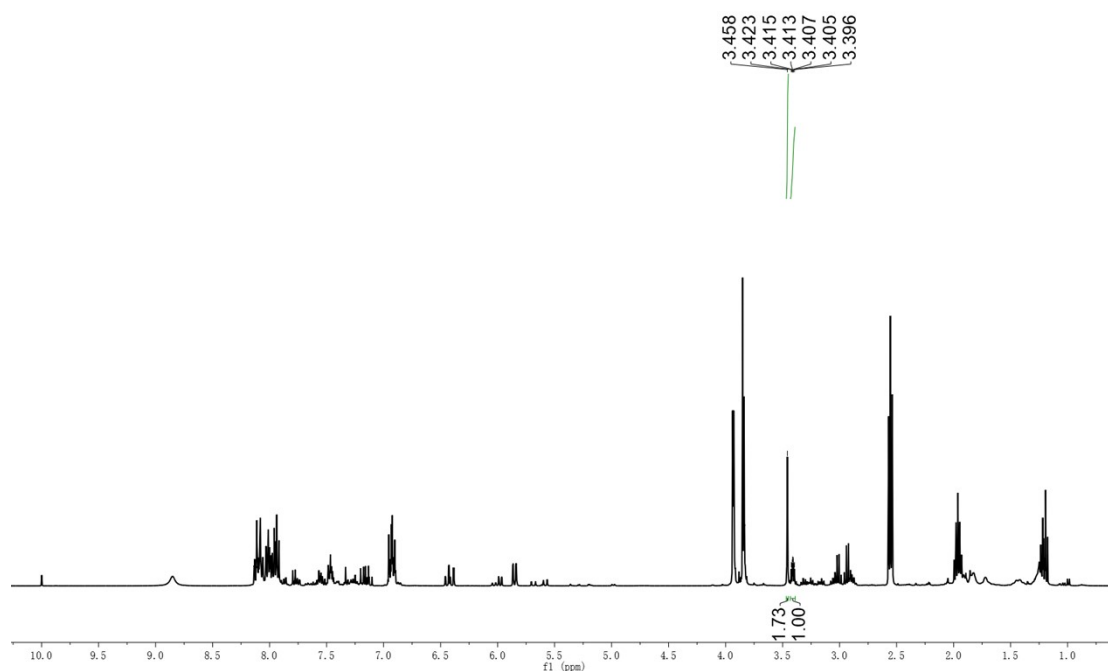
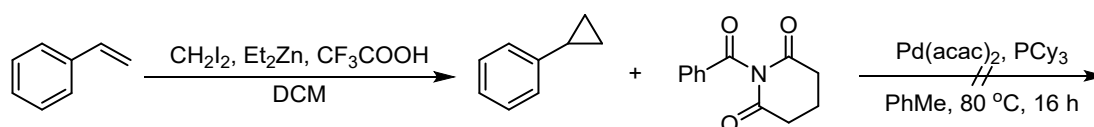
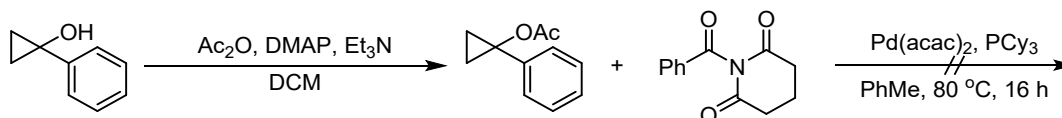


Figure S5. NMR spectrum of **3ad** and **3ai** crude product

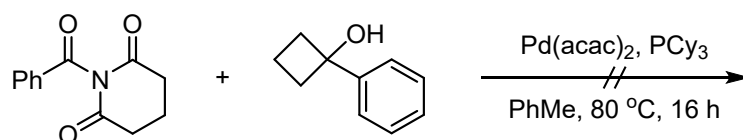
Control experiments



Phenylcyclopropane (**2aO**) was obtained as colorless liquid according to the literature reported before.³² To a 10 mL dry test tube with stir bar was added *N*-glutarimide benzamide **1a** (0.2 mmol, 1.0 equiv, 43.4 mg), Pd(acac)₂ (0.01 mmol, 5 mol %, 3.1 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy₃ (0.02 mmol, 10 mol %, 5.6 mg) then was added and removed from glove. Phenylcyclopropane (0.25 mmol, 1.25 equiv, 29.5 mg) dissolved in 2 mL Toluene was added and stand for 16 h at 80 °C, after completion of reaction, TLC indicated that no desired product was yielded.



1-Phenylcyclopropyl acetate (**2aA**) was prepared according to the literature before.³³ To a 10 mL dry test tube with stir bar was added *N*-glutarimide benzamide **1a** (0.2 mmol, 1.0 equiv, 43.4 mg), Pd(acac)₂ (5 mol %, 0.01 mmol, 3.1 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy₃ (0.02 mmol, 10 mol %, 5.6 mg) then was added and removed from glove. 1-phenylcyclopropyl acetate (0.25 mmol, 1.25 equiv, 44 mg) dissolved in 2 mL Toluene was added and stand for 16 h at 80 °C, after completion of reaction, TLC indicated that no desired product was yielded.



To a 10 mL dry test tube with stir bar was added *N*-glutarimide benzamide **1a** (0.2 mmol, 1.0 equiv, 43.4 mg), 1-phenylcyclobutan-1-ol (1.25 equiv, 37 mg) and Pd(acac)₂ (5 mol %, 0.01 mmol, 3.1 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy₃ (0.02 mmol, 10 mol %, 5.6 mg) then was added and removed from glove. The reaction mixture was dissolved in 2 mL Toluene and stand for 16 h at 80 °C, after cooling to room temperature, TLC indicated that no desired product was yielded.

Proposed mechanism

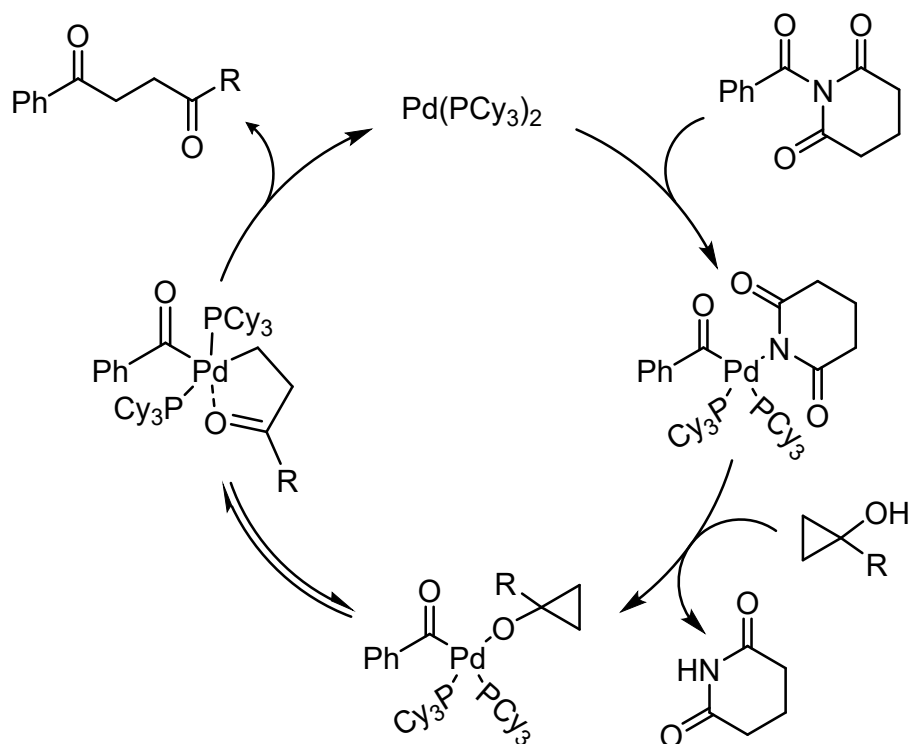
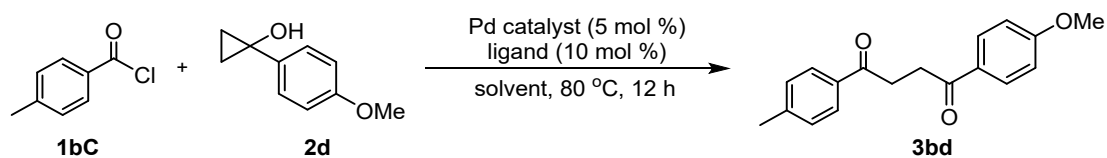


Figure S6. Proposed mechanistic cycle

Exploration for the cross-coupling reaction of acid chloride with cyclopropanol

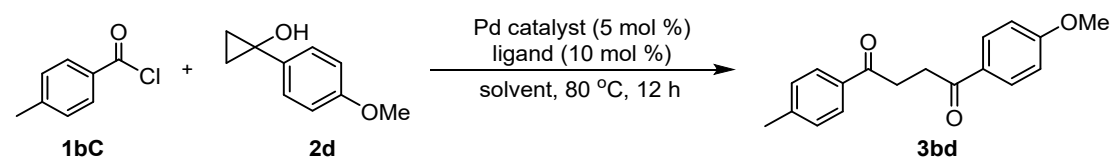
Table S12. Screening for the catalyst and solvent



Entry	catalyst	ligand	solvent	yield ^[b]
1	Pd(P ^t Bu ₃) ₂	DPE-Phos	PhMe	15%
2	Pd ₂ (dba) ₃	DPE-Phos	PhMe	9%
3	Pd(OAc) ₂	DPE-Phos	PhMe	10%
4	Pd(acac) ₂	DPE-Phos	PhMe	ND
5	Pd(PPh ₃) ₄	DPE-Phos	PhMe	10%
6	Pd(acac) ₂	PCy ₃	PhMe	ND
7	Pd(P ^t Bu ₃) ₂	DPE-Phos	MeCN	12%

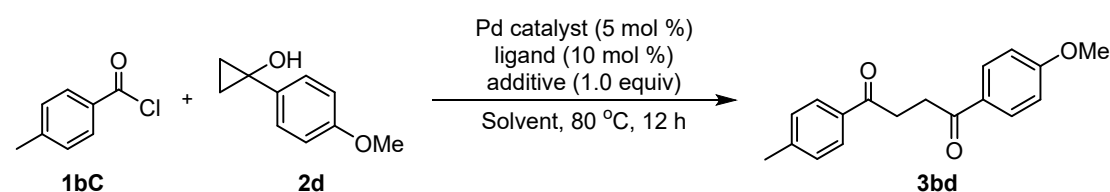
8	Pd(P ^t Bu ₃) ₂	DPE-Phos	THF	7%
9	Pd(P ^t Bu ₃) ₂	DPE-Phos	MeOH	ND

Table S13. Screening for the catalyst and solvent



Entry	catalyst	ligand	solvent	yield ^[b]
1	Pd(P ^t Bu ₃) ₂	X-Phos	PhMe	14%
2	Pd(P ^t Bu ₃) ₂	Dppbz	PhMe	ND
3	Pd(P ^t Bu ₃) ₂	BINAP	PhMe	10%
4	Pd(P ^t Bu ₃) ₂	Dppm	PhMe	15%
5	Pd(P ^t Bu ₃) ₂	Dppe	PhMe	13%
6	Pd(P ^t Bu ₃) ₂	Dppf	PhMe	19%
7	Pd(P ^t Bu ₃) ₂	PPh ₃	PhMe	12%
8	Pd(P ^t Bu ₃) ₂	PCy ₃	PhMe	6%

Table S14. Screening for the additive

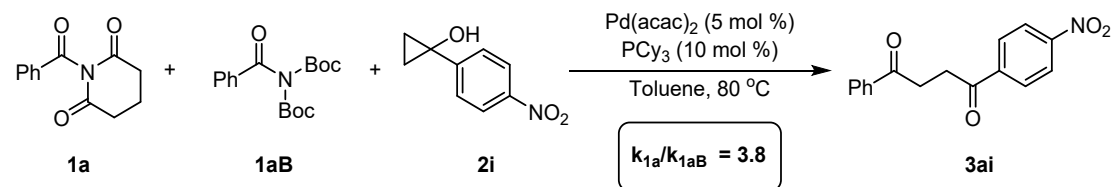


Entry	catalyst	ligand	additive	solvent	T	yield ^[b]
1	Pd(PPh ₃) ₄	---	---	THF	RT	ND
2	Pd(P ^t Bu ₃) ₂	---	---	PhMe	80 °C	ND
3	Pd(P ^t Bu ₃) ₂	PPh ₃	Et ₃ N	PhMe	80 °C	30%
4	Pd(P ^t Bu ₃) ₂	PPh ₃	K ₂ CO ₃	PhMe	80 °C	35%
5	Pd(P ^t Bu ₃) ₂	PPh ₃	KO ^t Bu	PhMe	80 °C	ND
6	Pd(P ^t Bu ₃) ₂	Dppf	Et ₃ N	PhMe	80 °C	40%
7	Pd(P ^t Bu ₃) ₂	Dppf	K ₂ CO ₃	PhMe	80 °C	36%

8	Pd(P ^t Bu ₃) ₂	Dppf	KO ^t Bu	PhMe	80 °C	ND
---	--	------	--------------------	------	-------	----

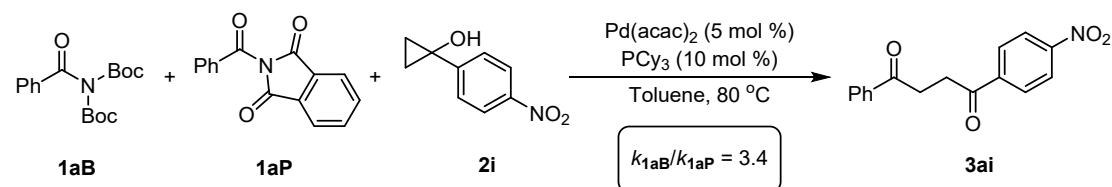
Unless otherwise noted, all reactions were performed on 0.2 mmol acid chloride with 1.0 equiv of the cyclopropanol under nitrogen for 12 h.

Kinetic competition experiment



A 10 mL oven-dried reaction vessel equipped with a magnetic stir bar was charged with **1a** (0.1 mmol, 1.0 equiv, 21.7 mg), **1aB** (0.1 mmol, 1.0 equiv, 32.1 mg), **2i** (0.3 mmol, 3.0 equiv, 53.7 mg), and Pd(acac)₂ (0.005 mol, 0.05 equiv, 1.6 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy₃ (10 mol %, 0.01 mmol, 2.8 mg) then was added and removed from glove. The reaction mixture was resolved in toluene (1 mL) and allowed to stir at 80 °C for 1 h. The mixture was allowed to room temperature after 1 h, and filtered through celite, then concentrated under vacuum. The crude substrate-product mixture was purified by flash chromatography (Petroleum ether / Ethyl acetate = 5/1 then Petroleum ether/ Dichloromethane = 1:2) to give the substrates mixture (**1a** and **1aB**).

Time	Concentration of 1a	Concentration of 1aB
0 h	0.1 mol/L	0.1 mol/L
1 h	0.06525 mol/L	0.08925 mol/L



A 10 mL oven-dried reaction vessel equipped with a magnetic stir bar was charged with **1aP** (0.1 mmol, 1.0 equiv, 25.1 mg), **1aB** (0.1 mmol, 1.0 equiv, 32.1 mg), **2i** (0.3 mmol, 3.0 equiv, 53.7 mg), and Pd(acac)₂ (0.005 mol, 0.05 equiv, 1.6 mg). The vessel was capped with a rubber septum and then transferred to the glove. PCy₃ (10 mol %, 0.01 mmol, 2.8 mg) then was added and removed from glove. The reaction mixture was resolved in toluene (1 mL) and allowed to stir at 80 °C for 1 h. The mixture was allowed to room temperature after 1 h, and filtered through celite, then concentrated under vacuum. The crude substrate-product mixture was purified by flash chromatography (Petroleum ether / Ethyl acetate = 5/1 then Petroleum ether/ Dichloromethane = 1:2) to give the substrates mixture (**1aB** and **1aP**).

Time	Concentration of 1aB	Concentration of 1aP
0 h	0.1 mol/L	0.1 mol/L
1 h	0.087 mol/L	0.096 mol/L

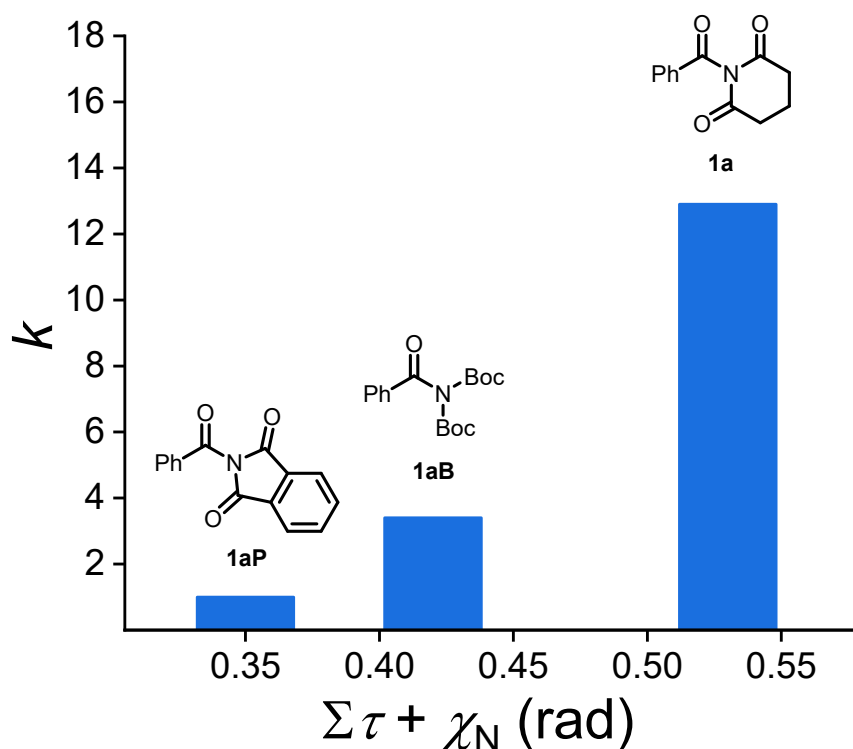


Figure S7. Relative reactivity versus the additive parameter of the three amides

Reactivity order chemistry set

{(1a, R, P, k_{1a} -12.9, EC),

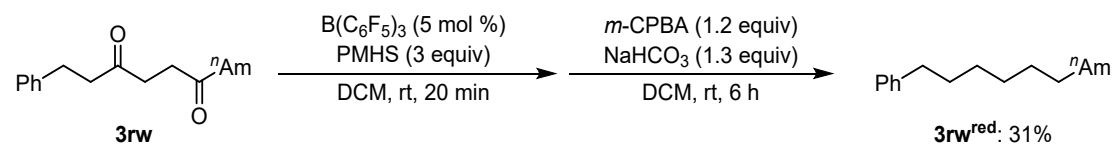
(1aB, R, P, k_{1aB} -3.4, EC),

(1aP, R, P, k_{1aP} -1, EC)},

where R = 2i, P = 3ai,

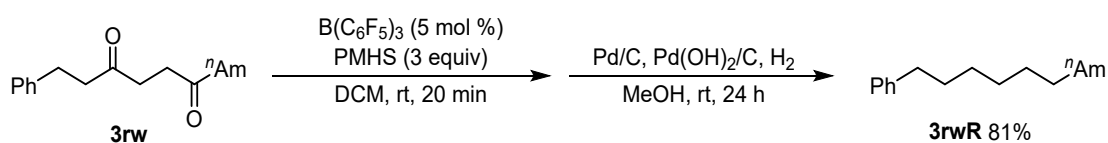
EC = Pd(acac)₂ (5 mol %)/PCy₃ (10 mol %)/Toluene/80 °C/1 h

Reduction of γ -diketones to alkane

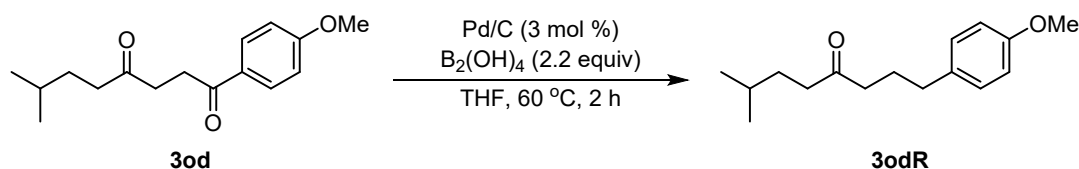


According to the literature reported,³⁴ to a solution of 1, 4 - diketones compound **3rw** (0.2 mmol, 1.0 equiv, 52 mg) in dry CH₂Cl₂ (2 mL) and tris (pentafluoro phenyl) borane (5 mol %, 0.01 mmol, 5.1 mg) was slowly added polymethylhydrosiloxane (0.6 mmol, 3 equiv, 134 mg, 133 μ L) at room temperature. After 20 min, a vigorous effervescence (like foam) was observed. At this point, the reaction mixture was dissolved in hexane and filtered through a silica gel pad using hexane. Evaporation of the solvents afforded the product in crude form (alkane and alkene product presumably). To eliminate alkene product and acquire pure alkane product, we converted alkene product to epoxides according to the literature.³⁵ To a 10 mL dried test tube was added alkene -

alkane crude product (1.0 equiv, 0.2 mmol), NaHCO₃ (1.3 equiv, 0.26 mmol, 21.8 mg) and CH₂Cl₂ (1 mL) under N₂ atmosphere. The test tube was then added *m*-CPBA (1.2 equiv, 0.24 mmol, 41.4 mg) dissolved in CH₂Cl₂ (1 mL) dropwise at 0 °C. The reaction was then stirred for an additional 1 h and then allowed to warm to room temperature. After completion of the reaction (TLC monitoring), the reaction mixture is quenched with aqueous Na₂S₂O₄, and the aqueous phase is extracted with CH₂Cl₂. The combined organic layers are washed successively with a saturated solution of NaHCO₃ and brine and dried over Na₂SO₄. The filtrate was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: n-hexane) afforded the corresponding alkane product (**3rwR**) with 31% yields (14.3 mg) as colorless liquid. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.21 – 7.15 (m, 3H), 2.61 (t, *J* = 8.0 Hz, 2H), 1.66 – 1.59 (m, 2H), 1.36 – 1.25 (m, 16H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 142.96, 128.38, 128.19, 125.51, 35.99, 31.92, 31.53, 29.67, 29.63, 29.60, 29.52, 29.35, 22.69, 14.12. The spectroscopic data of product (**3rwR**) matched literature values.³⁶



Crude alkane and alkene product was obtained according to the procedure in 0.2 mmol scale, the crude product was mixed with MeOH (2 mL), Pd(OH)₂/C (15 mg), and Pd/C (15 mg) and the suspension was kept under H₂ atmosphere for 24 h at room temperature. Filtration through a Celite pad followed by evaporation and chromatography on silica gel (eluent: n-hexane) afforded the products (**3rwR**) with 81% yields (37.8 mg) as colorless liquid. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 2.62 (t, *J* = 8.0 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.36 – 1.26 (m, 16H), 0.90 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 142.95, 128.38, 128.19, 125.51, 36.00, 31.92, 31.53, 29.67, 29.64, 29.60, 29.53, 29.35, 22.69, 14.12.



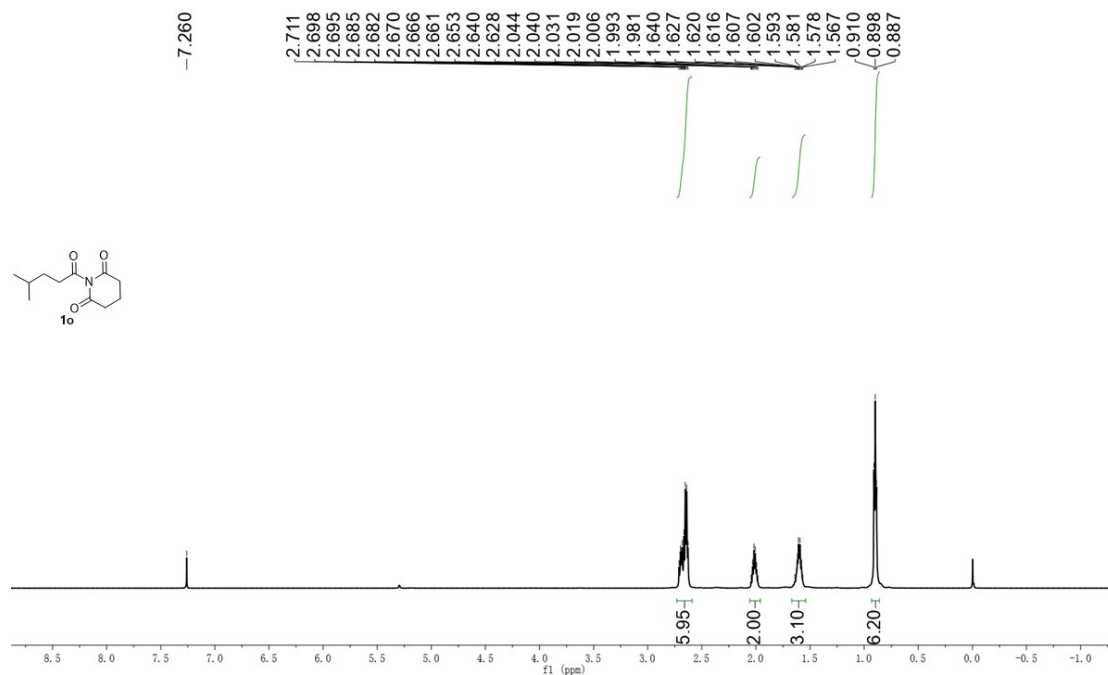
According to the literature reported³⁷, Reactions were carried out on 0.2 mmol scale. A 10 mL reaction vessel equipped with a magnetic stir bar was charged with 12 mg of 5 weight % of Pd/C (3 mol%), 39.4 mg of tetrahydroxydiboron (2.2 equiv), and 52 mg of the diketones **3od** (0.2 mmol) in 2 mL THF, then the reaction mixture was stirred at 60 °C for 2 h. The crude mixture was passed through Celite plug rinsing the reaction vial with DCM; the eluent was removed by rotary evaporation, followed by flash column chromatography (Petroleum ether / Ethyl acetate = 10/1) to afford the product (**3odR**) with 67% yields (33.1 mg) as colorless liquid. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.10 – 7.06 (m, 2H), 6.84 – 6.80 (m, 2H), 3.78 (s, 3H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.38 (dt, *J* = 19.5, 7.5 Hz, 4H), 1.87 (p, *J* = 7.5 Hz, 2H), 1.56 – 1.47 (m, 1H), 1.47 – 1.41 (m, 2H), 0.87 (d, *J* = 6.5 Hz, 6H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 211.32, 157.79, 133.66, 129.29, 113.72, 55.19, 41.79, 40.84, 34.16, 32.58, 27.66, 25.46, 22.29. HRMS (ESI) *m/z* calcd. for C₁₉H₁₈O₂ [M+H]⁺ 249.1849, found 249.1842.

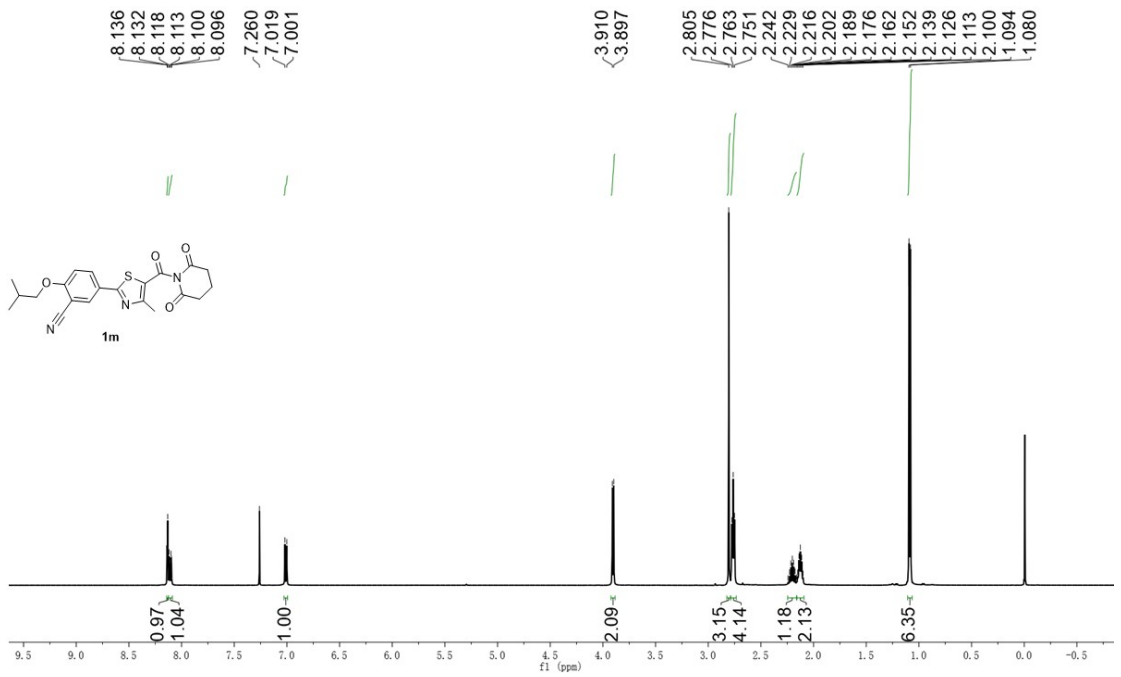
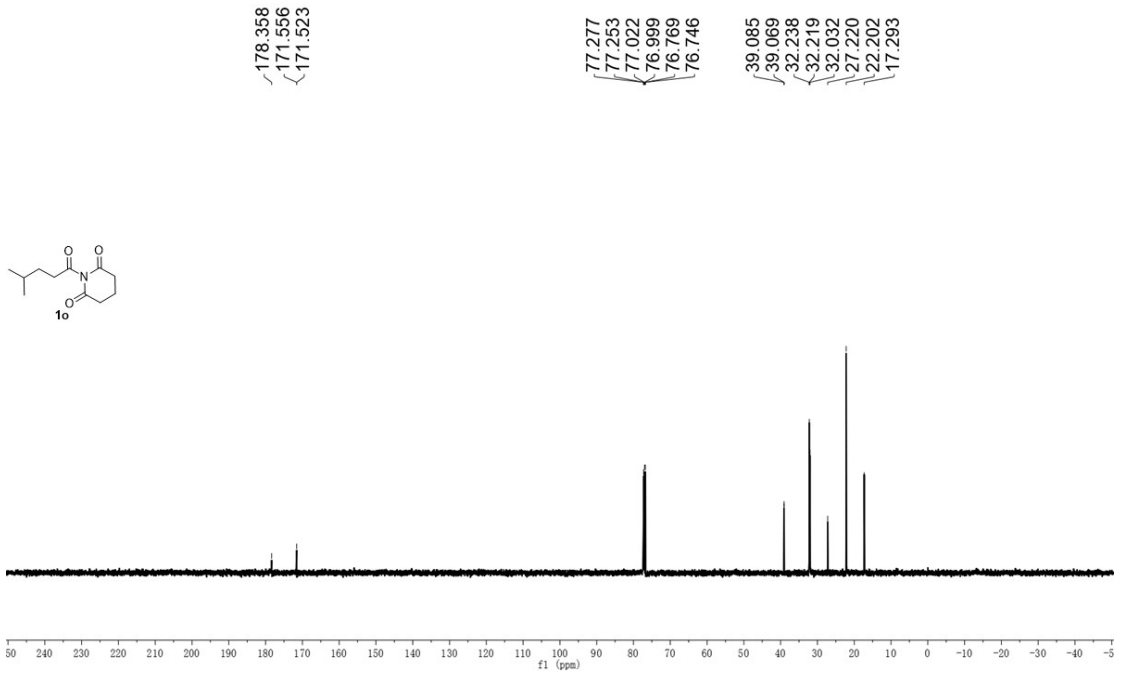
Reference

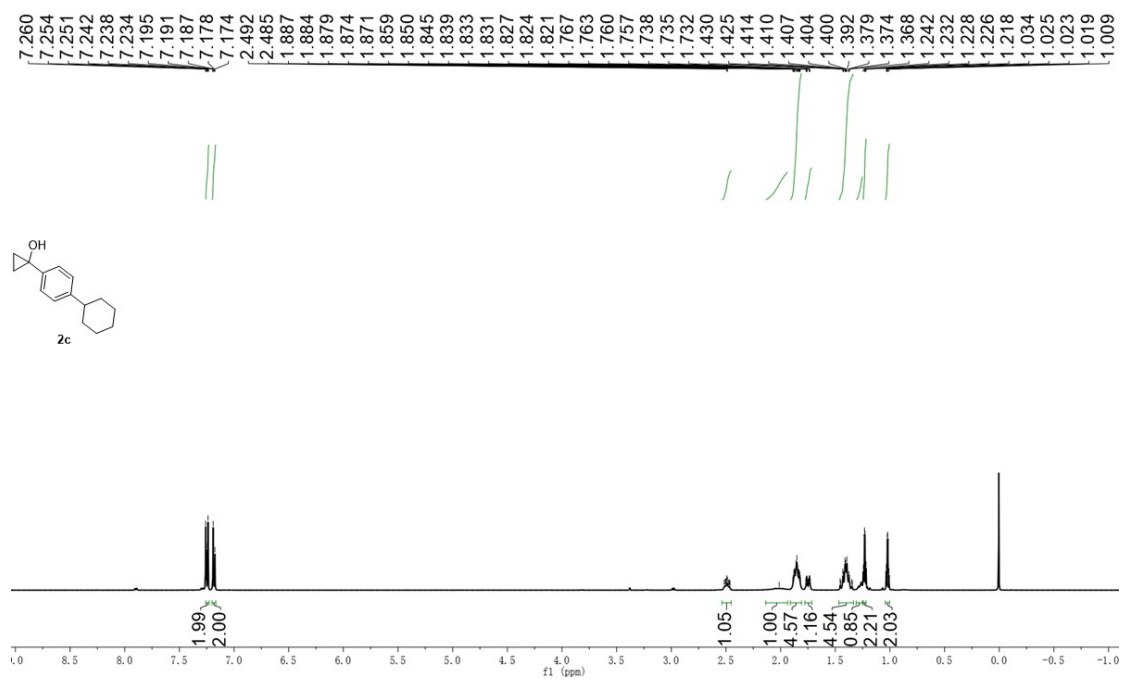
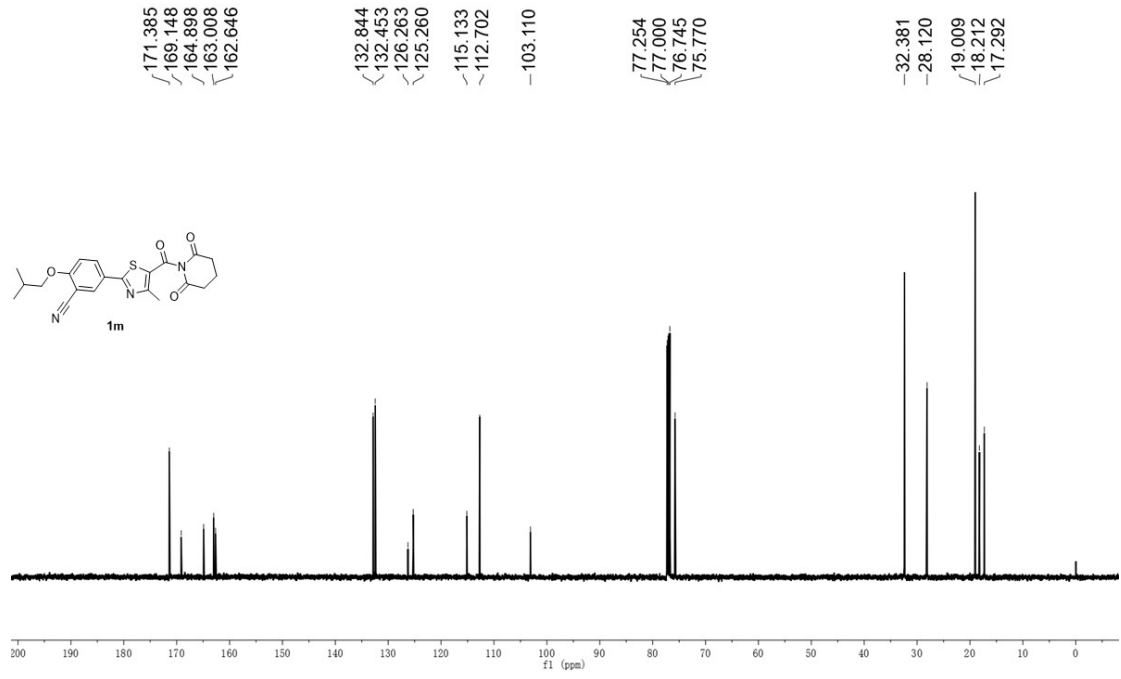
1. L. R. Mills, C. Zhou, E. Fung and S. A. L. Rousseaux, *Org. Lett.*, 2019, **21**, 8805-8809.
2. C. Dorval, O. Stetsiuk, S. Gaillard, E. Dubois, C. Gosmini and G. Danoun, *Org. Lett.*, 2022, **24**, 2778-2782.
3. J. Yang, Q. Sun and N. Yoshikai, *ACS Catal.*, 2019, **9**, 1973-1978.
4. K. Nomura and S. Matsubara, *Asian J. Chem.*, 2010, **5**, 147-152.
5. M. Ji, Z. Wu and C. Zhu, *Chem. Comm.*, 2019, **55**, 2368-2371.
6. R. M. Rivera, Y. Jang, C. M. Poteat and V. N. G. Lindsay, *Org. Lett.*, 2020, **22**, 6510-6515.
7. J. Liu, E. Xu, J.-Y. Jiang, Z. Huang, L.-Y. Zheng and Z.-Q. Liu, *Chem. Comm.*, 2020, **56**, 2202-2205.
8. W. Srimontree, A. Chatupheeraphat, H.-H. Liao and M. Rueping, *Organic Letters*, 2017, **19**, 3091-3094.
9. F.-S. Bie, X.-J. Liu, H. Cao, Y.-J. Shi, T.-L. Zhou, M. Szostak and C.-W. Liu, *Org. Lett.*, 2021, **23**, 8098-8103.
10. L. Fang, S. Fan, W. Wu, T. Li and J. Zhu, *Chem. Commu.*, 2021, **57**, 7386-7389.
11. P. Gao, M. M. Rahman, A. Zamalloa, J. Feliciano and M. Szostak, *J. Org. Chem.*, 2022, DOI: 10.1021/acs.joc.2c01094.
12. Y. Dong, R. Li, J. Zhou and Z. Sun, *Org. Lett.*, 2021, **23**, 6387-6390.
13. H. Yin, D. U. Nielsen, M. K. Johansen, A. T. Lindhardt and T. Skrydstrup, *ACS Catal.*, 2016, **6**, 2982-2987.
14. L. Xu, X. Liu, G. R. Alvey, A. Shatskiy, J.-Q. Liu, M. D. Kärkäs and X.-S. Wang, *Org. Lett.*, 2022, **24**, 4513-4518.
15. T. Fujimura, S. Aoki and E. Nakamura, *J. Org. Chem.*, 1991, **56**, 2809-2821.
16. C. C. Derek, R. S. Joseph, C. Rajiv, C. Rebecca, W. E. John, Y. F. Kristi, L. H. Boyd, H. Yun, J. Steve, D. J. Lee, J. Guixian, A. L. Peter, S. M. Michael, S. M. Eric, J. M. William, O. D. Mary-Margaret, M. O. Andrea, J. R. Albert, S. Kristine, W. JunJun, W. Eric and B. Jonathan, *Bioorganic Med. Chem. Lett.*, 2008, **18**, 1063-1066.
17. V. Selvamurugan and I. S. Aidhen, *Tetrahedron*, 2001, **57**, 6065-6069.
18. L.-H. Wang and J. Zhao, *Eur. J. Org. Chem.*, 2018, **2018**, 4345-4348.
19. L. Debien, B. Quiclet-Sire and S. Z. Zard, *Org. Lett.*, 2011, **13**, 5676-5679.
20. R. Ilhyong, I. Masanobu, S. Noboru, Y. Shin-ya, Y. Go-hei and K. Mitsuo, *Tetrahedron Lett.*, 2002, **43**, 1257-1259.
21. D. Yu, W.-P. To, G. S. M. Tong, L.-L. Wu, K.-T. Chan, L. Du, D. L. Phillips, Y. Liu and C.-M. Che, *Chem. Sci.*, 2020, **11**, 6370-6382.
22. Q. Liu, R.-G. Wang, H.-J. Song, Y.-X. Liu and Q.-M. Wang, *Adv. Synth. Catal.*, 2020, **362**, 4391-4396.
23. C. Che, Z.-S. Qian, M.-C. Wu, Y. Zhao and G.-G. Zhu, *J. Org. Chem.*, 2018, **83**, 5665-5673.
24. I. Y. Ajibola, L. Ai and B. Li, *ChemistrySelect*, 2021, **6**, 9559-9564.
25. M. Egbertson and S. J. Danishefsky, *J. Org. Chem.*, 1989, **54**, 11-12.
26. Y.-X. Zhang, X.-T. Li, L.-M. Xu, X.-M. Xie, Y. Lu and Z.-G. Zhang, *Org. Lett.*, 2022, **24**, 7512-7516.
27. S. Kortet, A. Claraz and P. M. Pihko, *Org. Lett.*, 2020, **22**, 3010-3013.
28. T. Amaya, Y. Maegawa, T. Masuda, Y. Osafune and T. Hirao, *J. Am. Chem. Soc.*, 2015, **137**, 10072-10075.

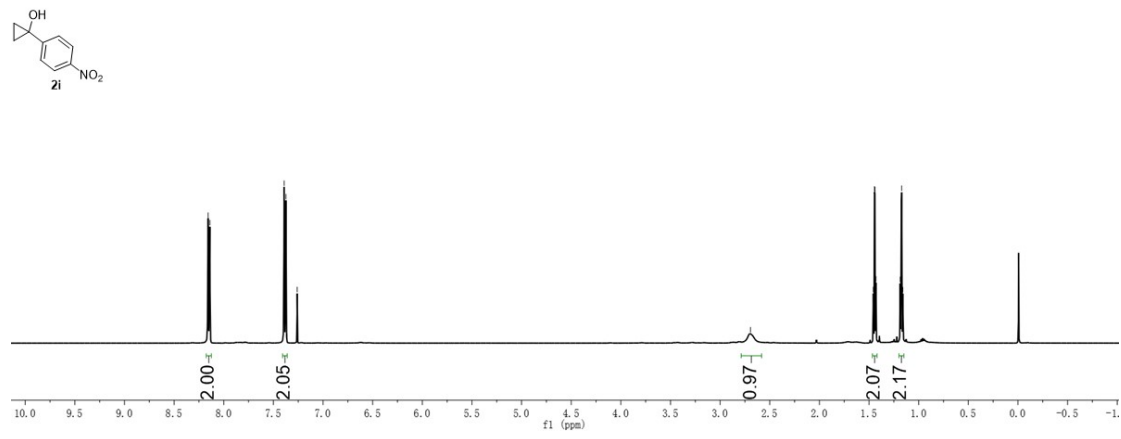
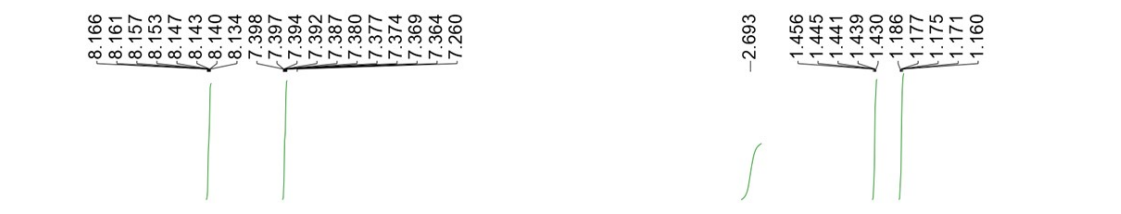
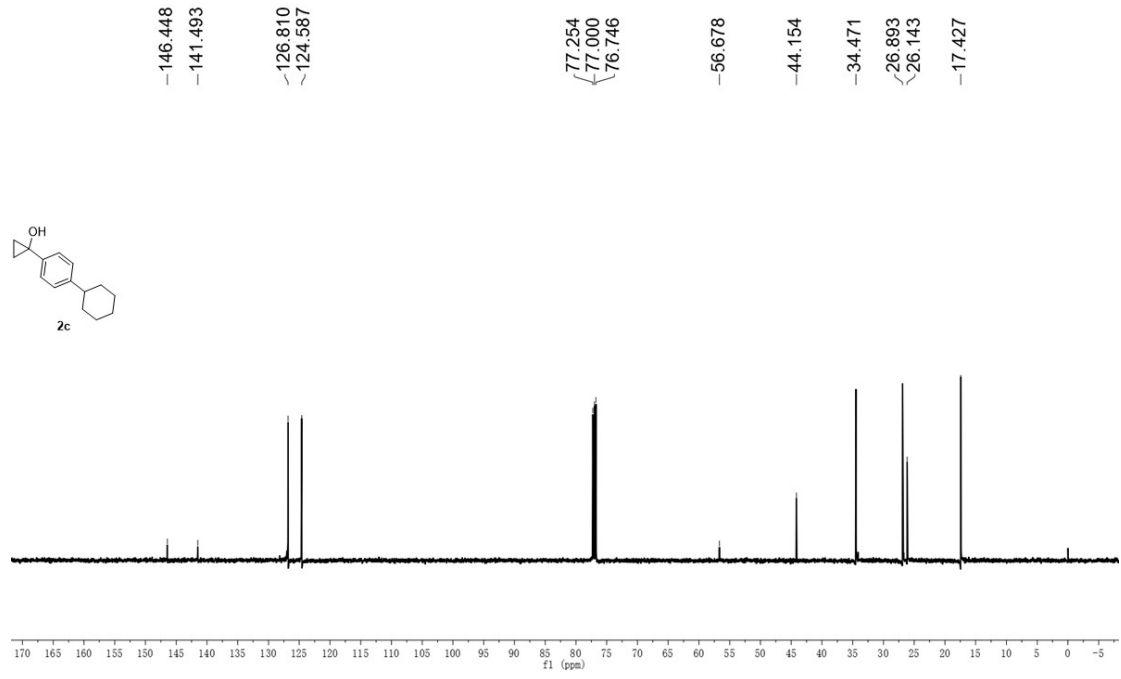
29. F. Behler, F. Habecker, W. Saak, T. Klüner and J. Christoffers, *Eur. J. Org. Chem.*, 2011, **2011**, 4231-4240.
30. Y. Luo, Q. Wei, L.-K. Yang, Y.-Q. Zhou, W.-D. Cao, Z.-S. Su, X.-H. Liu and X.-M. Feng, *ACS Catal.*, 2022, **12**, 12984-12992.
31. K. Tanaka, T. Shoji and M. Hirano, *Eur. J. Org. Chem.*, 2007, **2007**, 2687-2699.
32. J. C. Lorenz, J. Long, Z.-Q. Yang, S. Xue, Y.-N. Xie and Y.-A. Shi, *J. Org. Chem.*, 2004, **69**, 327-334.
33. T. Avullala, P. Asgari, Y. Hua, A. Bokka, S. G. Ridlen, K. Yum, H. V. R. Dias and J. Jeon, *ACS Catal.*, 2019, **9**, 402-408.
34. S. Chandrasekhar, C. R. Reddy and B. N. Babu, *J. Org. Chem.*, 2002, **67**, 9080-9082.
35. W. Liu, T. Leischner, W. Li, K. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2020, **59**, 11321-11324.
36. F. Zhou, J. Zhu, Y. Zhang and S. Zhu, *Angew. Chem. Int. Ed.*, 2018, **57**, 4058-4062.
37. W. C. Spaller, J. Q. Lu and B. J. Stokes, *Adv. Synth. Catal.*, 2022, **364**, 2571-2575.

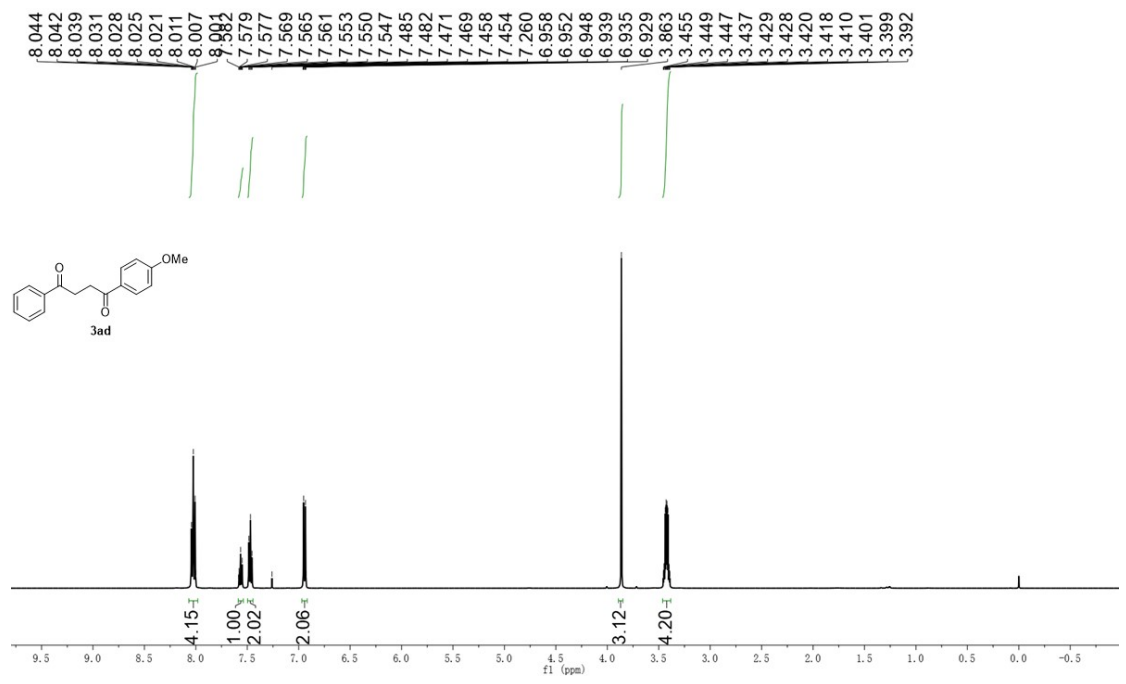
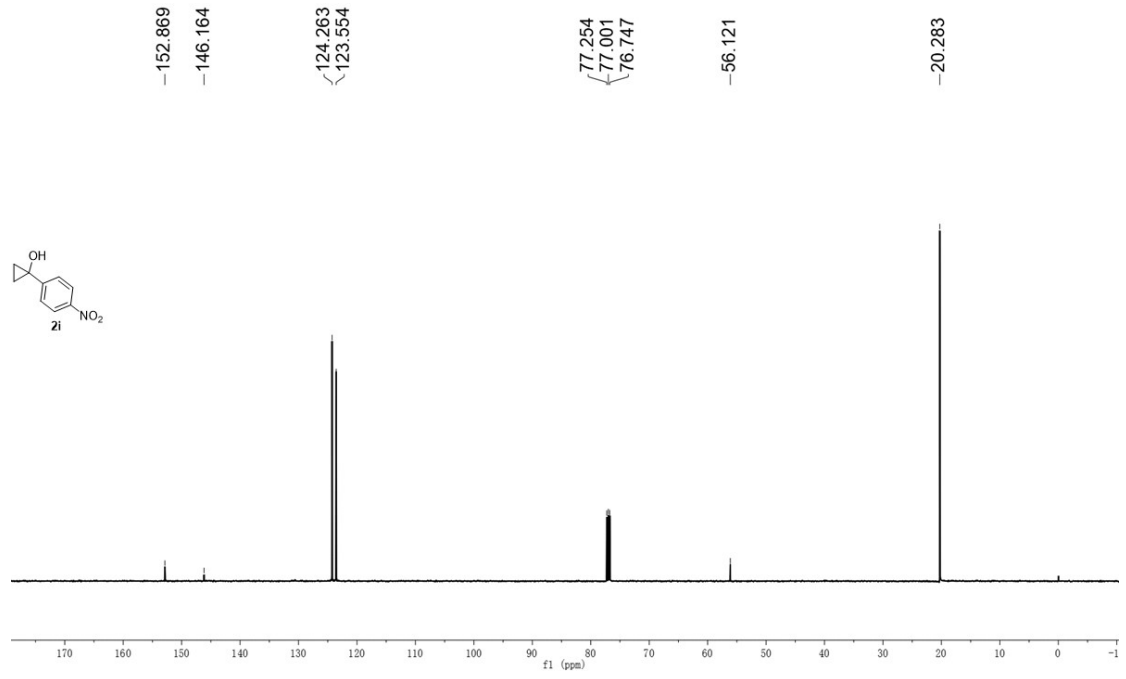
NMR spectra

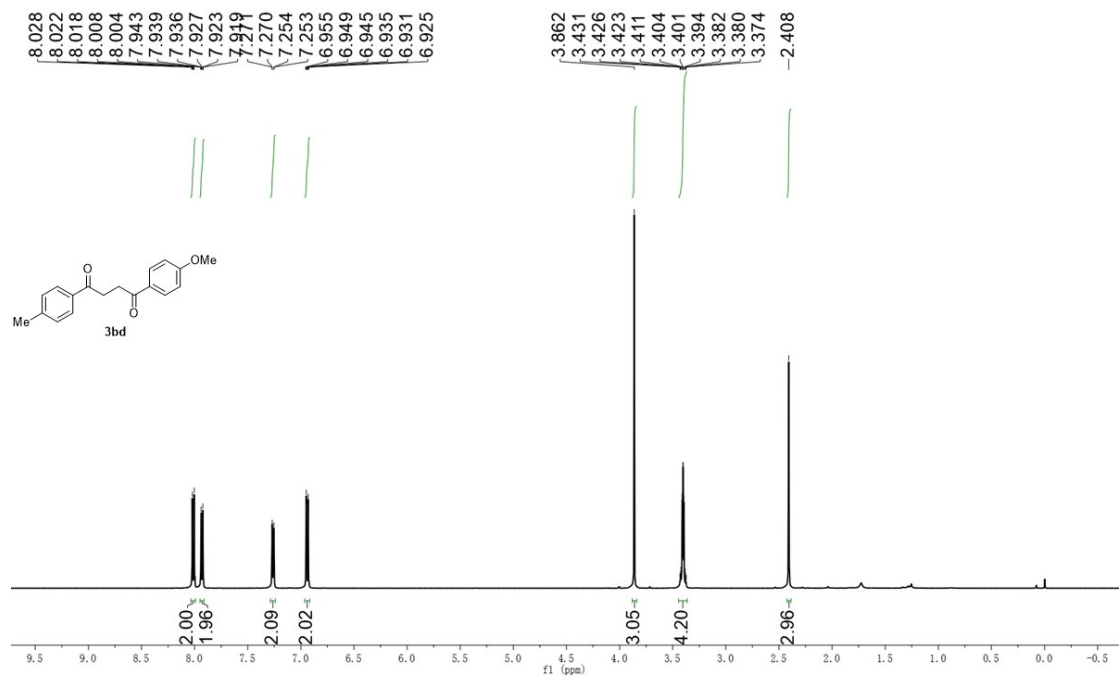
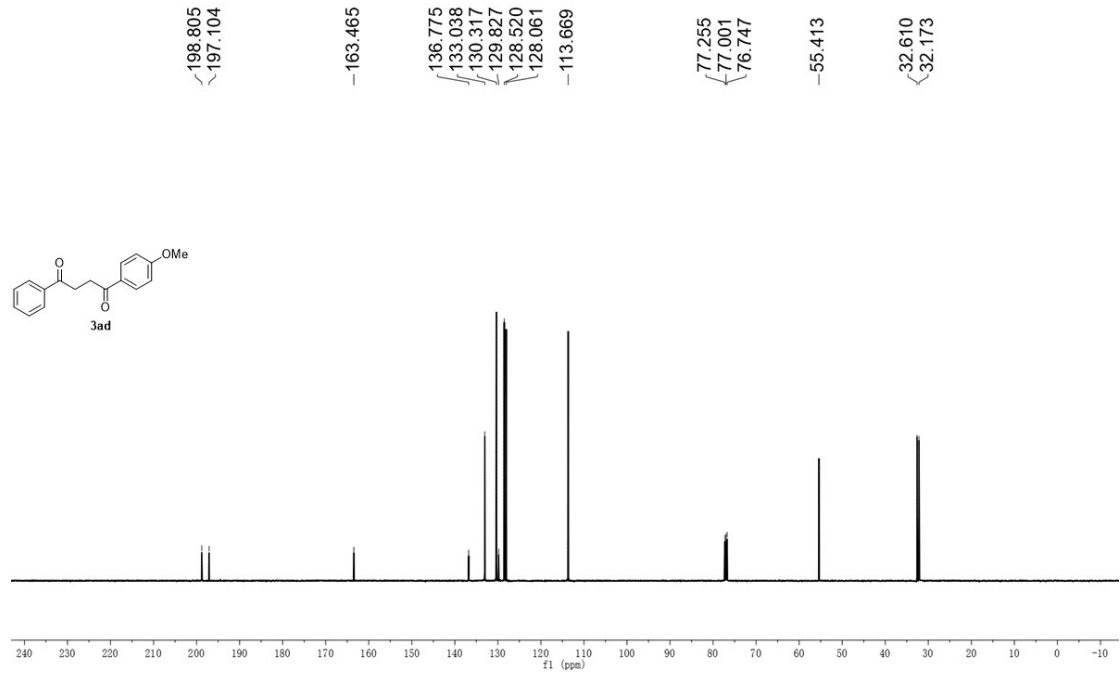


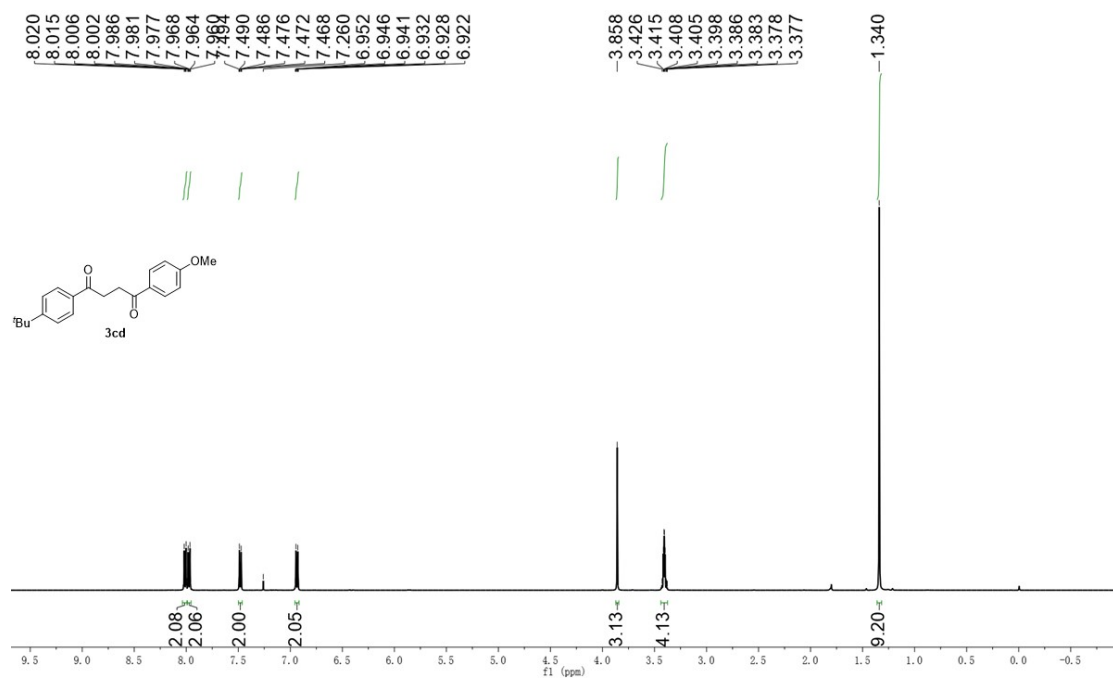
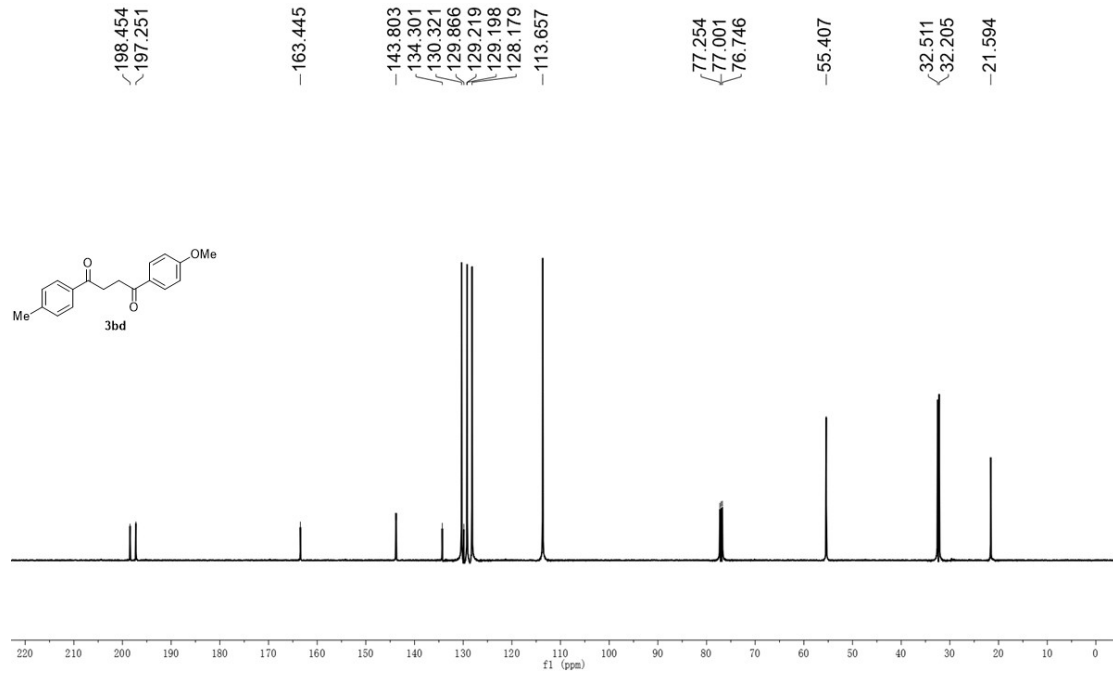


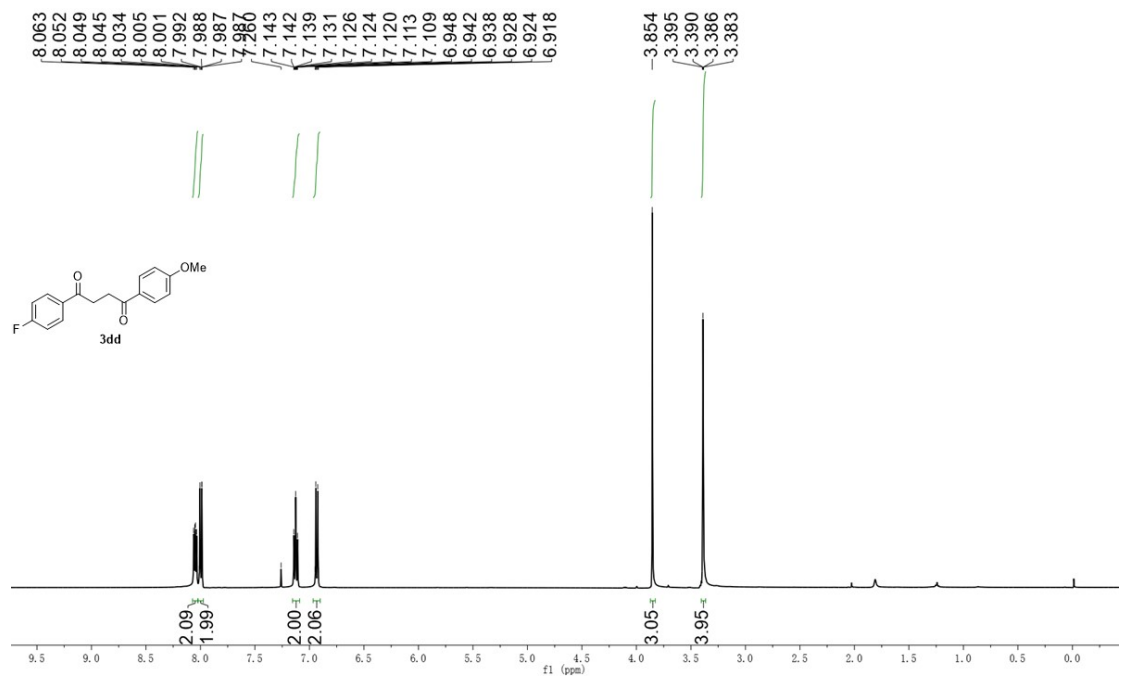
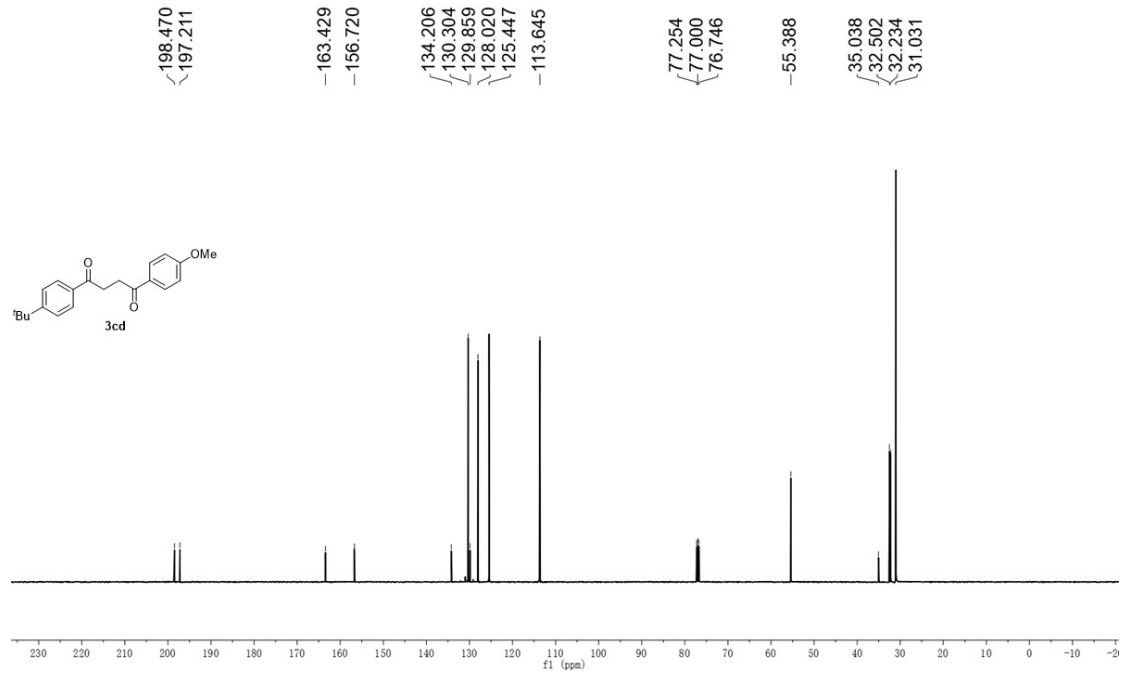


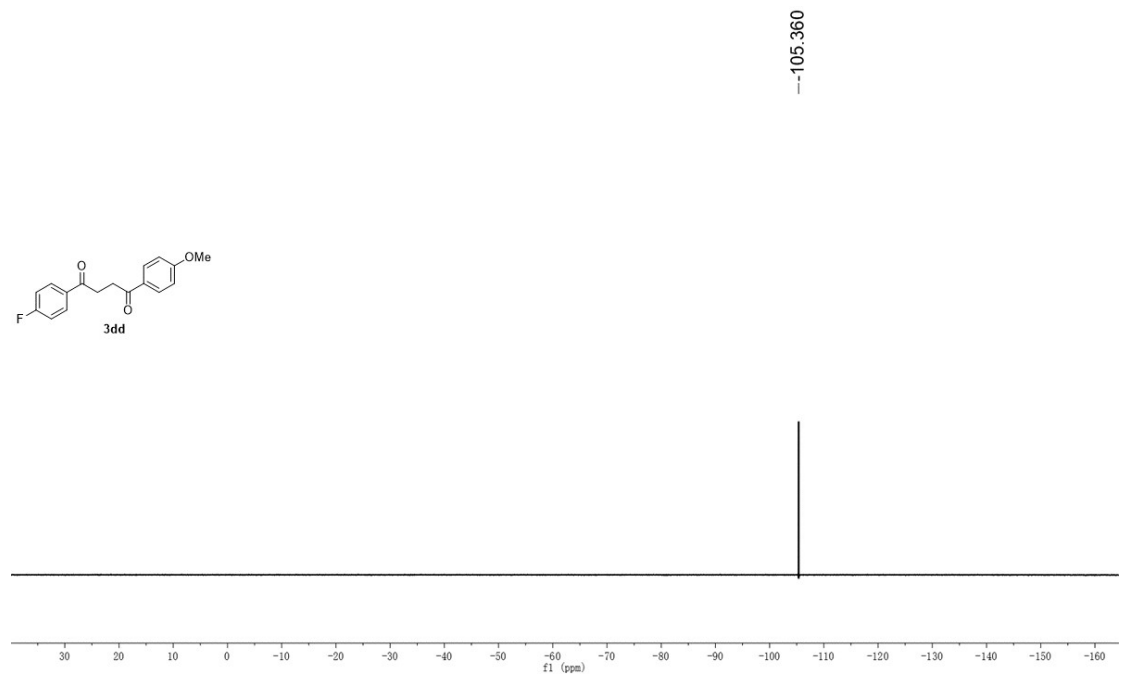
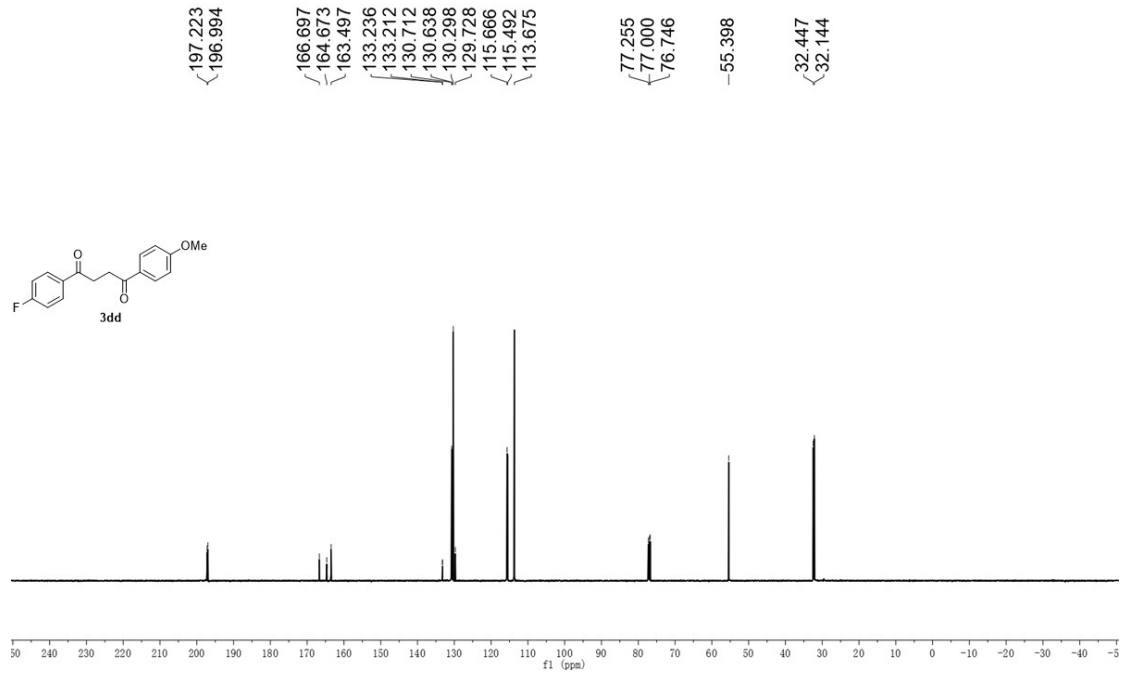


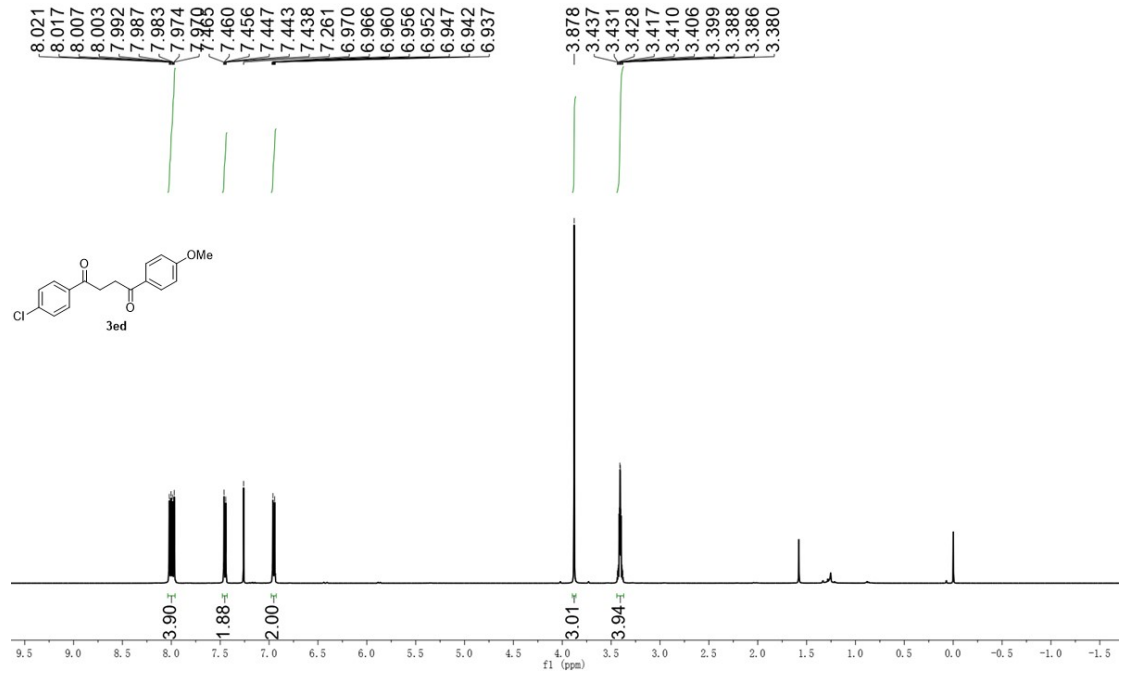




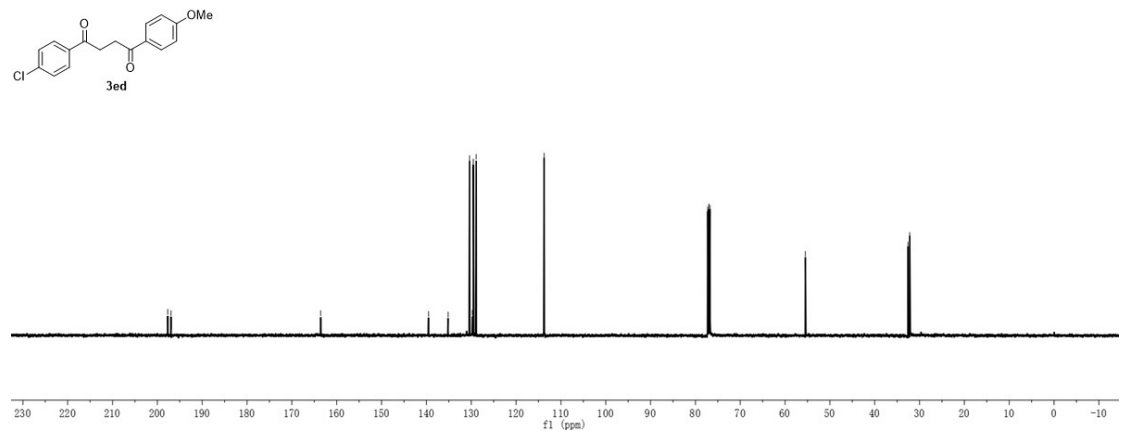


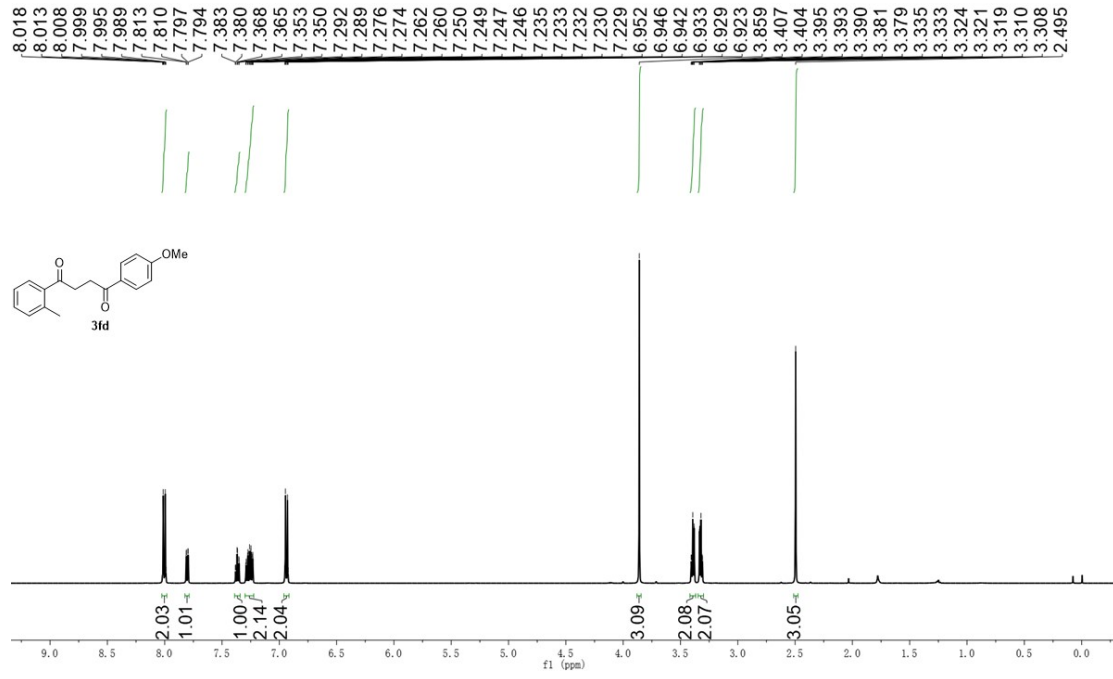




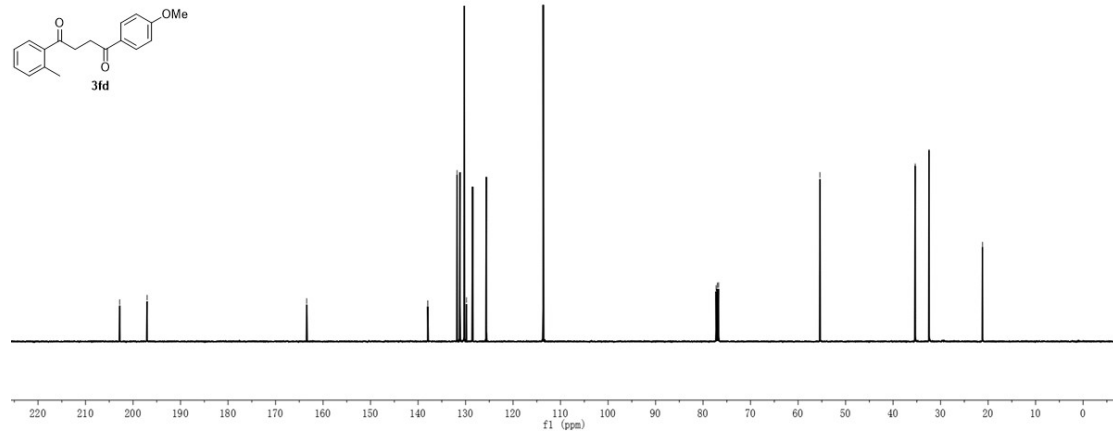


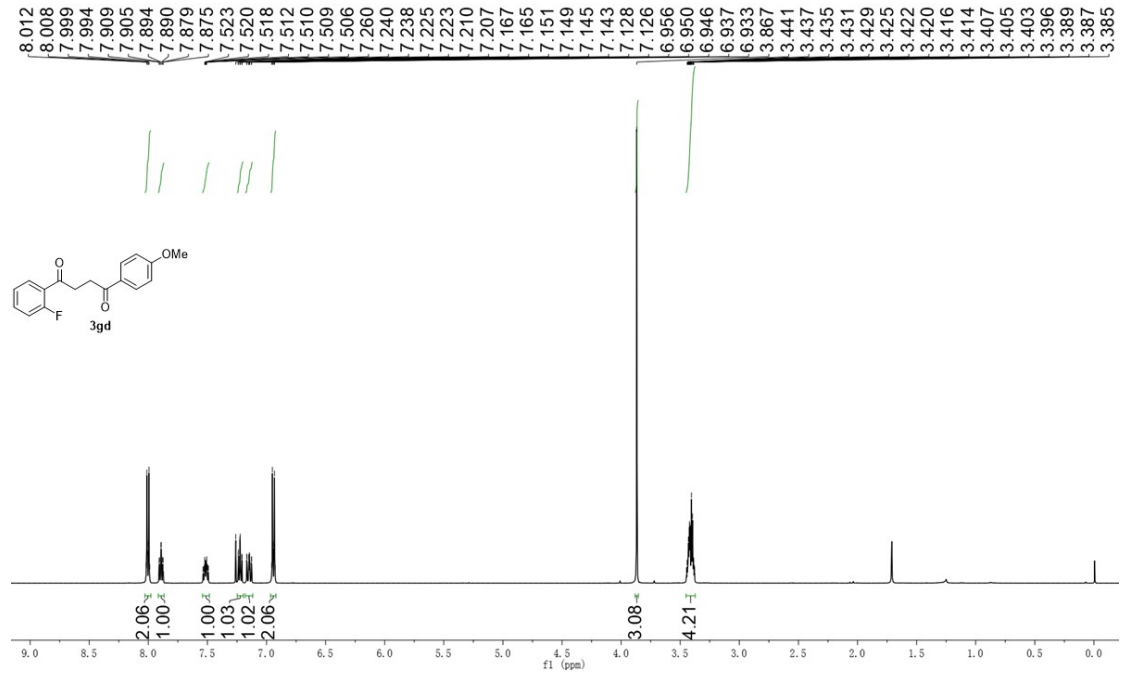
- 197.690
- 196.970
- 163.577
- 139.515
- 135.159
- 130.365
- 129.759
- 129.538
- 128.886
- 113.739
- 77.254
- 77.001
- 76.747
- 55.468
- 32.576
- 32.190



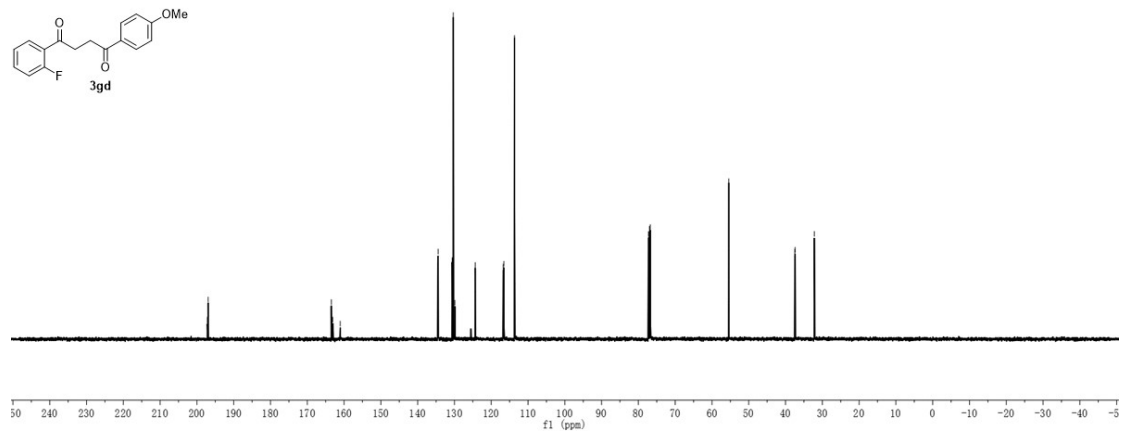


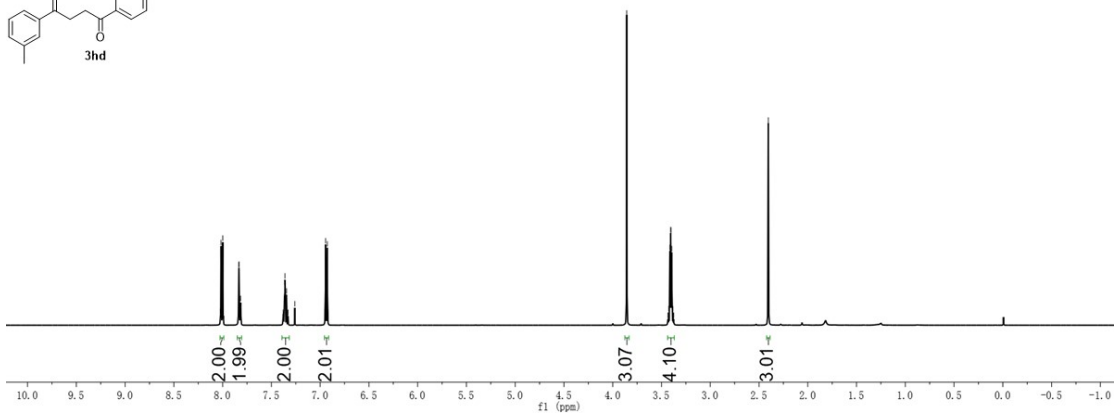
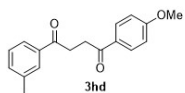
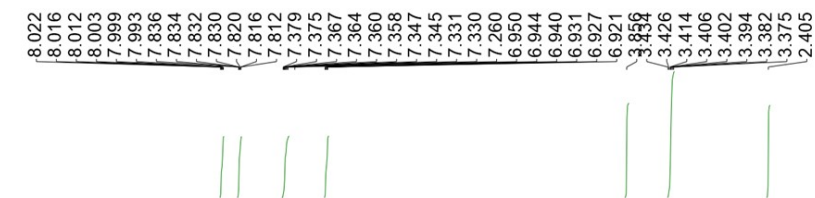
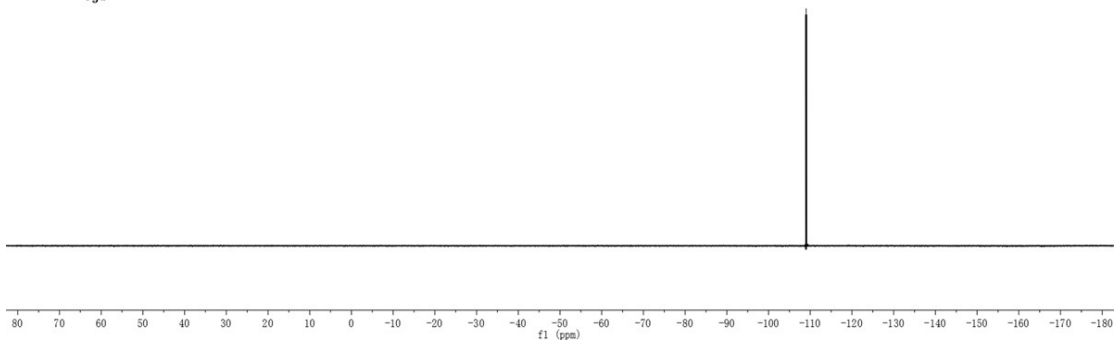
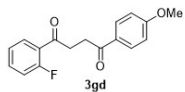
- 202.806
- 197.047
- 163.444
- 137.954
- 137.876
- 131.786
- 131.182
- 130.280
- 129.819
- 128.530
- 125.629
- 113.653
- 77.254
- 77.000
- 76.745
- 55.399
- 35.345
- 32.434
- 21.189

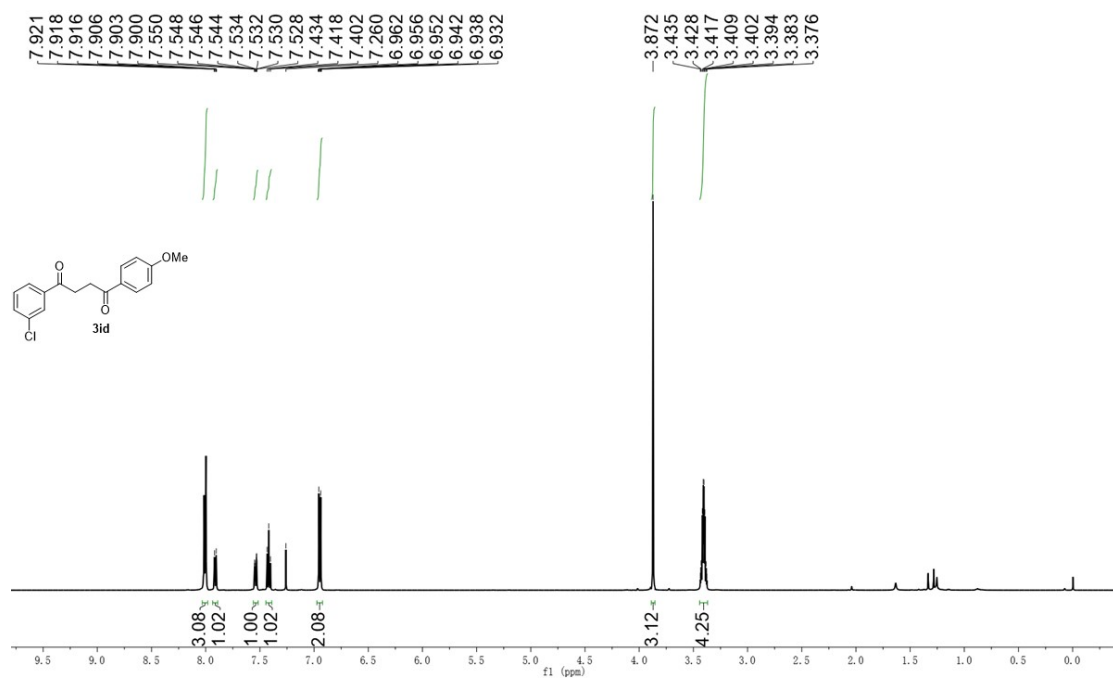
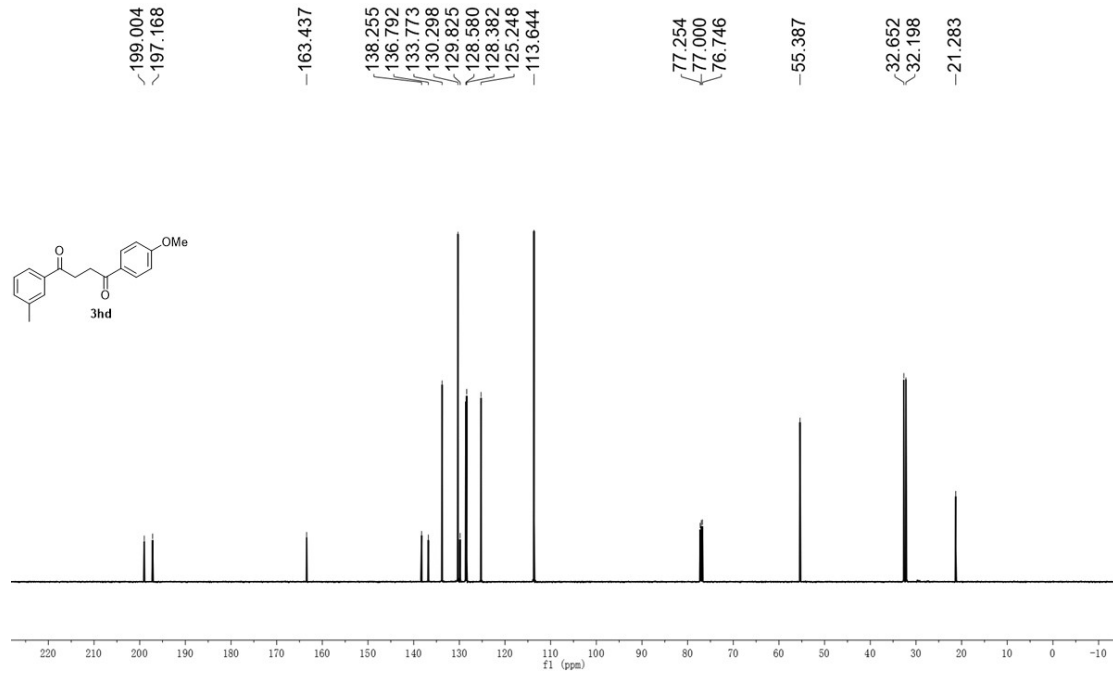


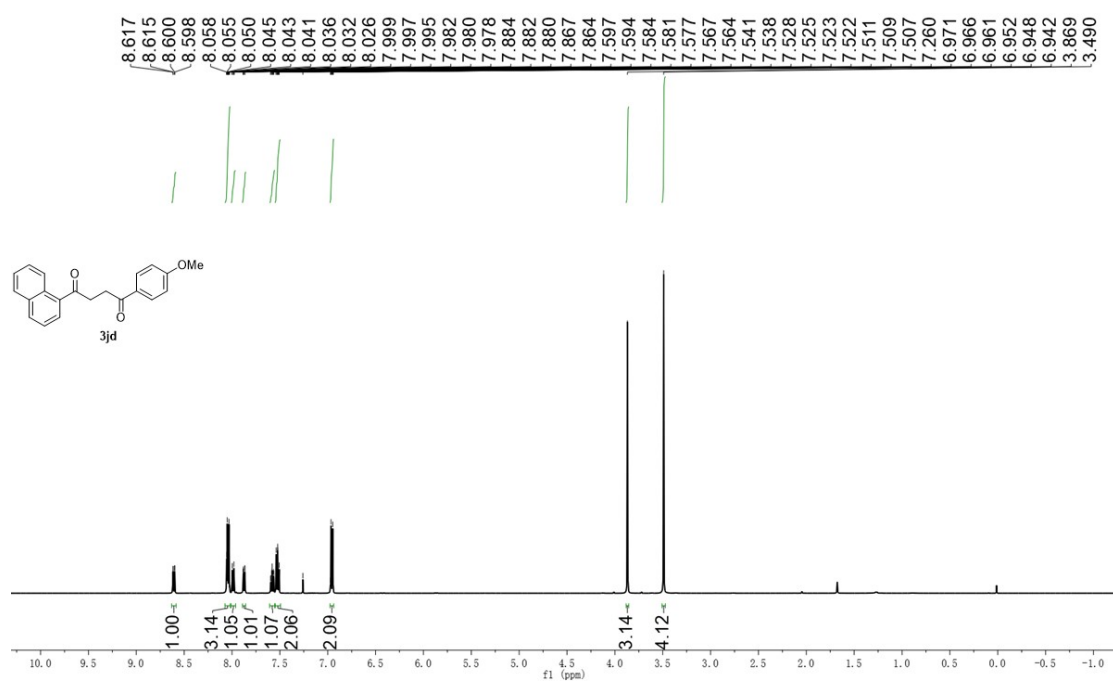
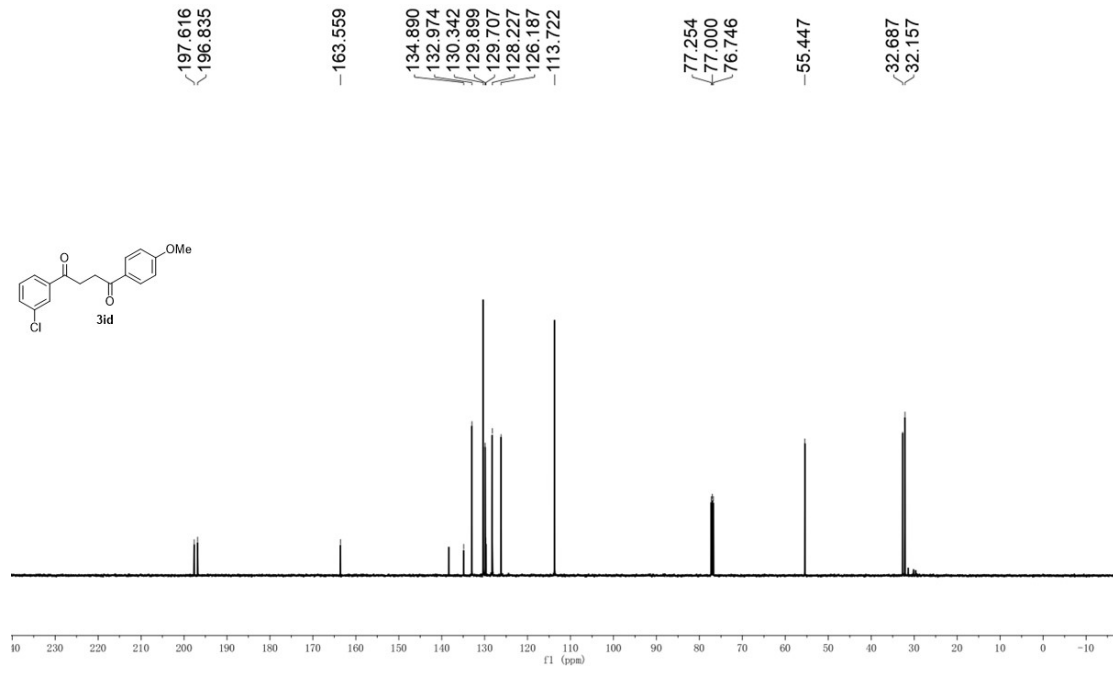


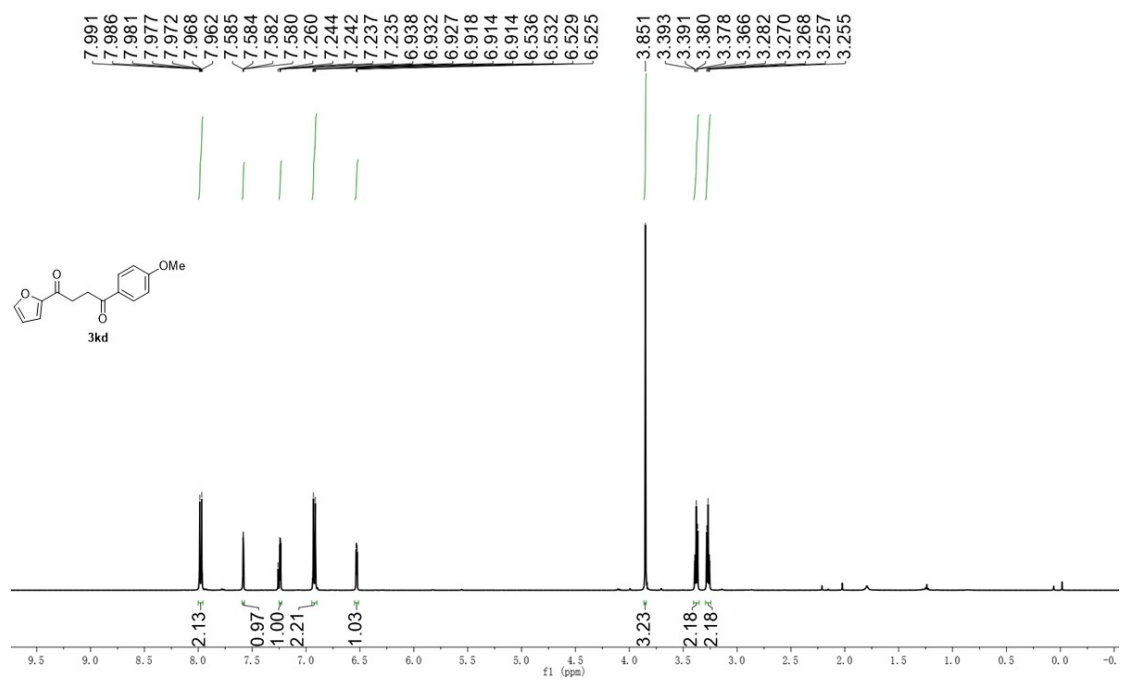
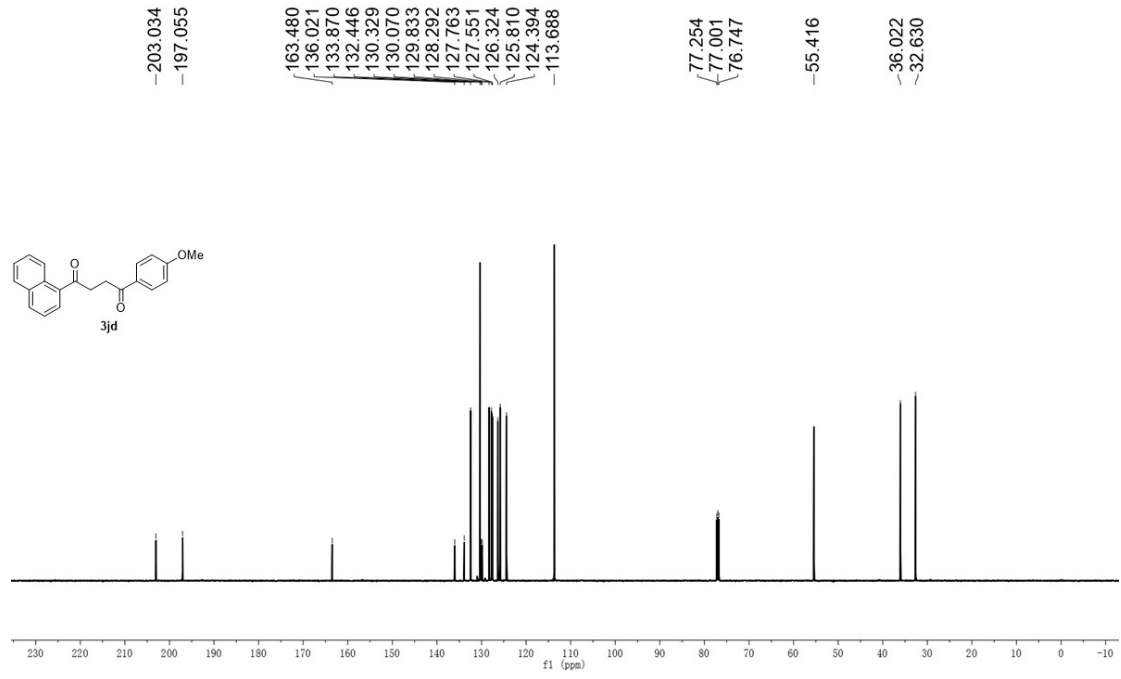
- Chemical shifts (ppm): 197.158, 197.125, 196.943, 163.459, 163.061, 161.037, 134.507, 134.435, 130.652, 130.630, 130.322, 129.847, 124.374, 124.347, 116.737, 116.549, 113.672, 77.255, 77.000, 76.746, -55.428, 37.468, 37.404, 32.192, 32.174.

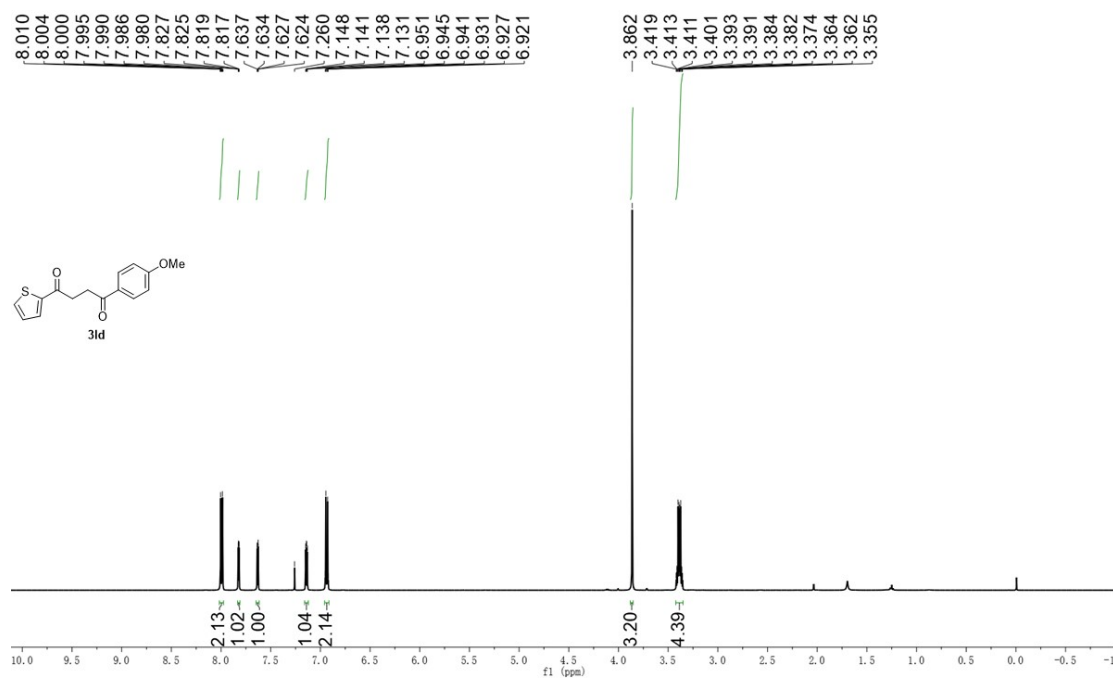
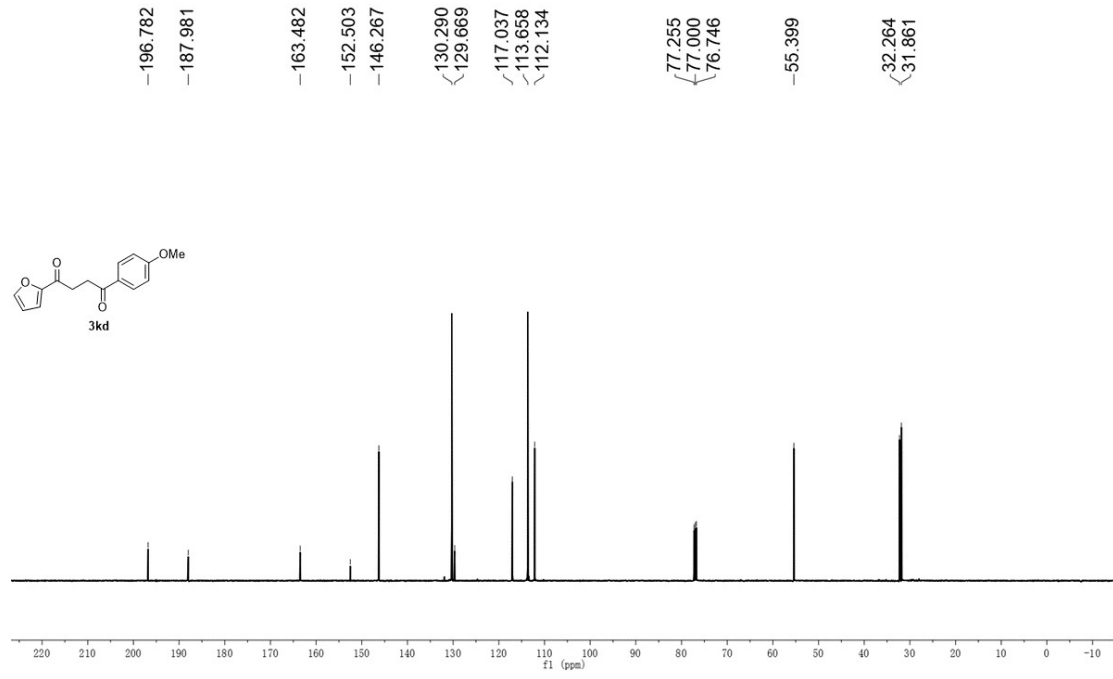


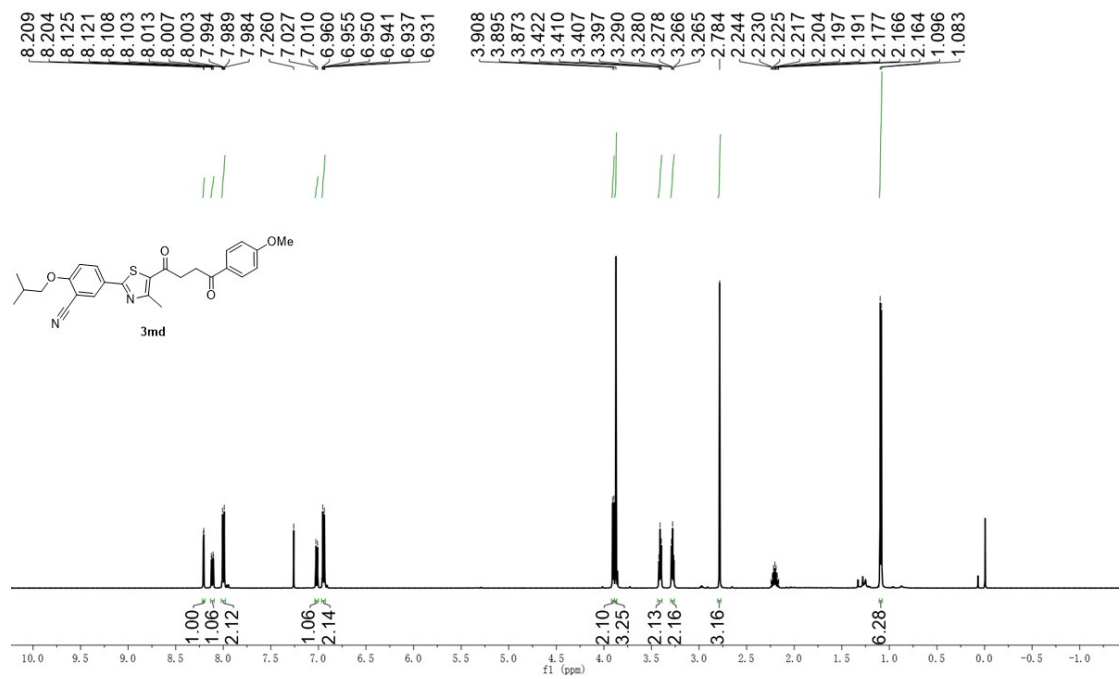
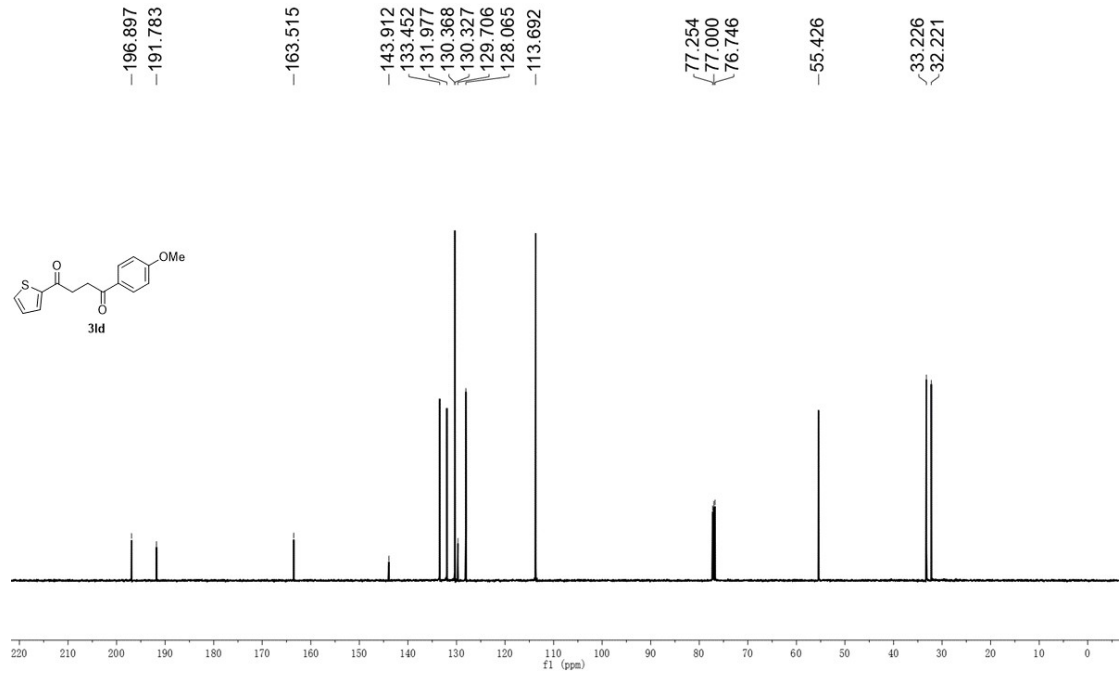


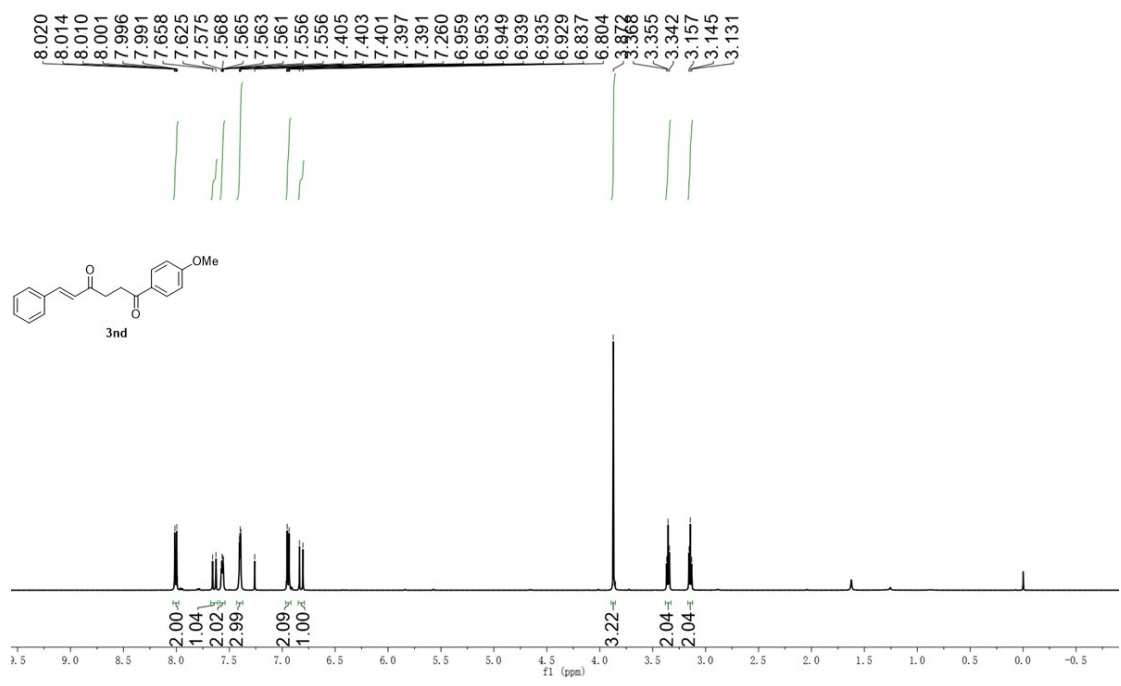
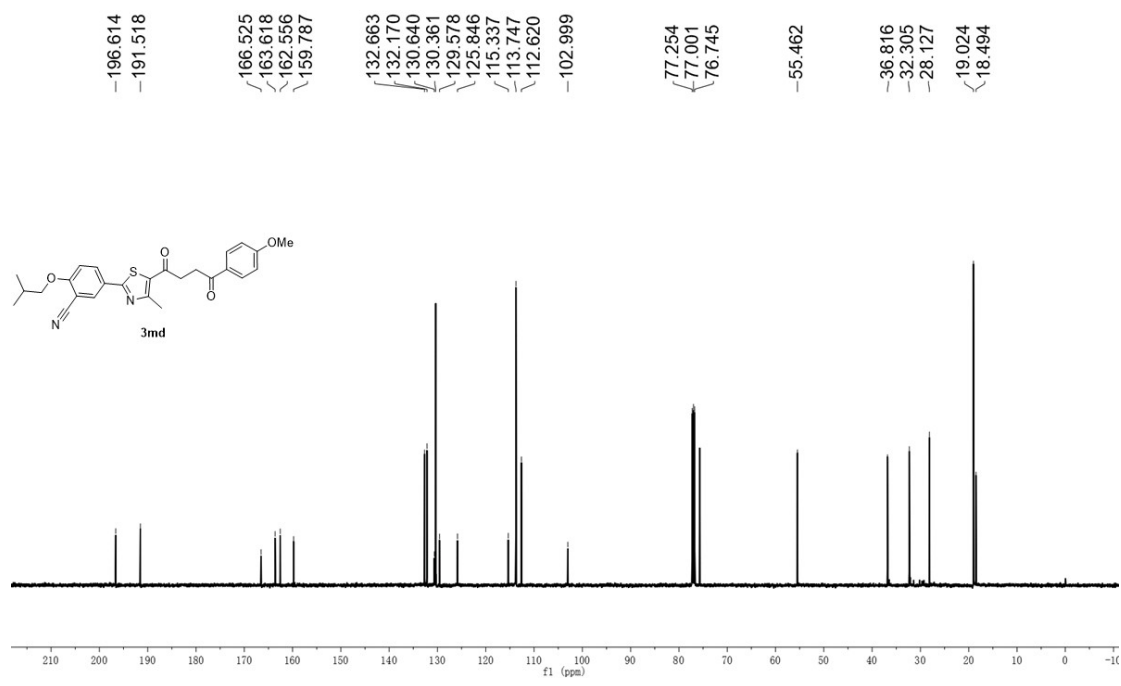


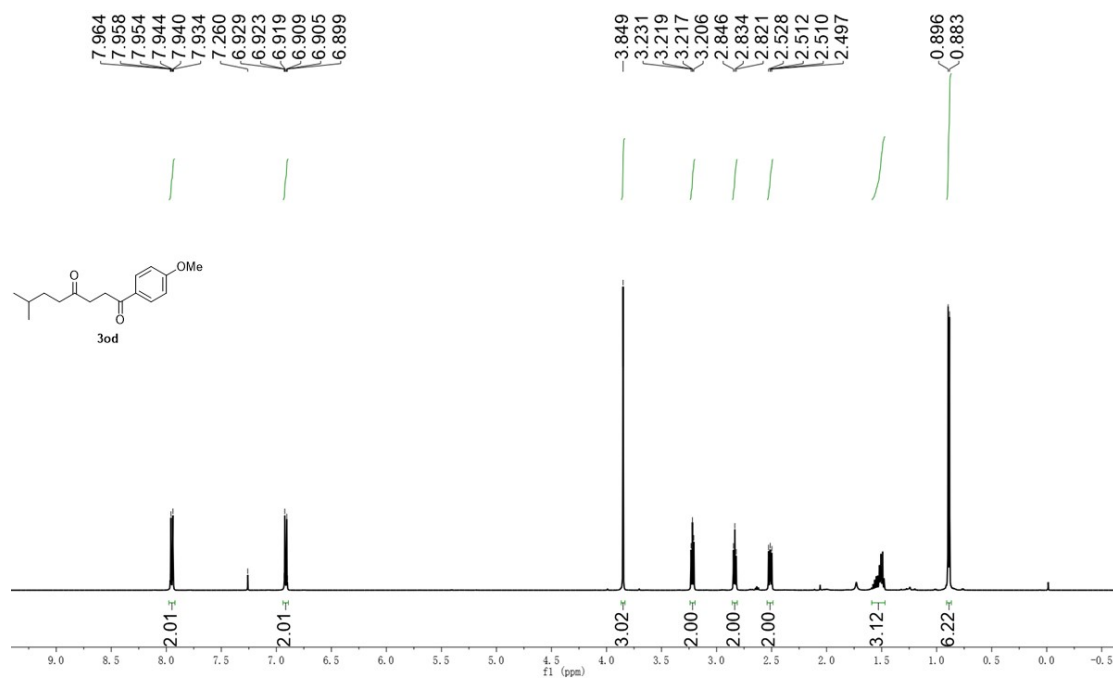
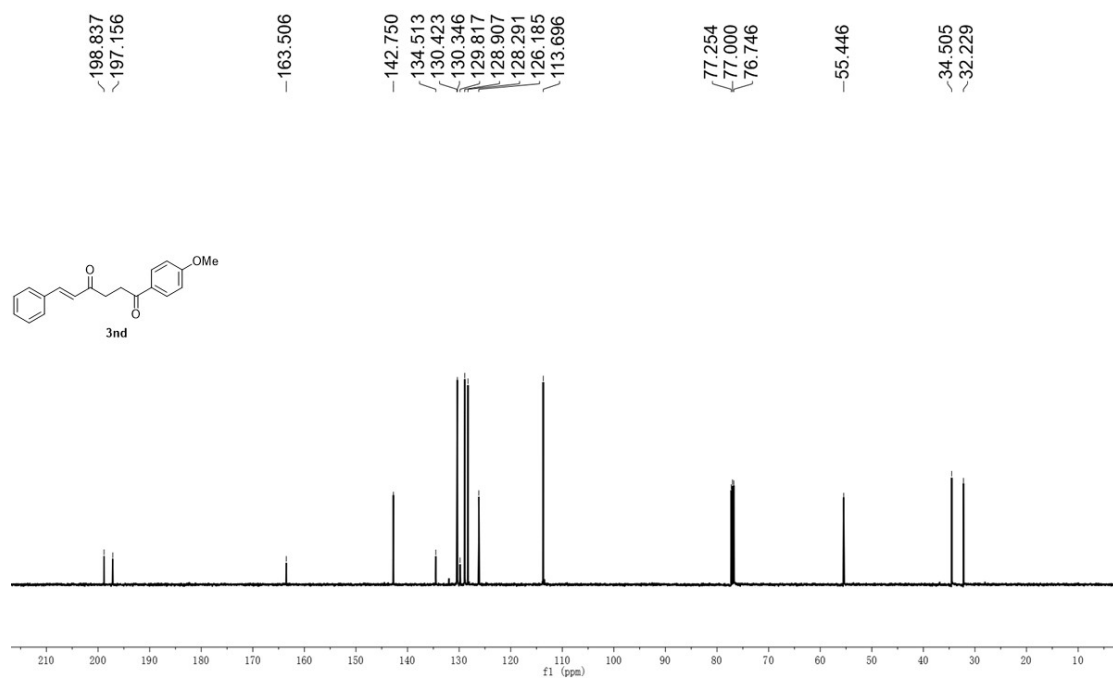


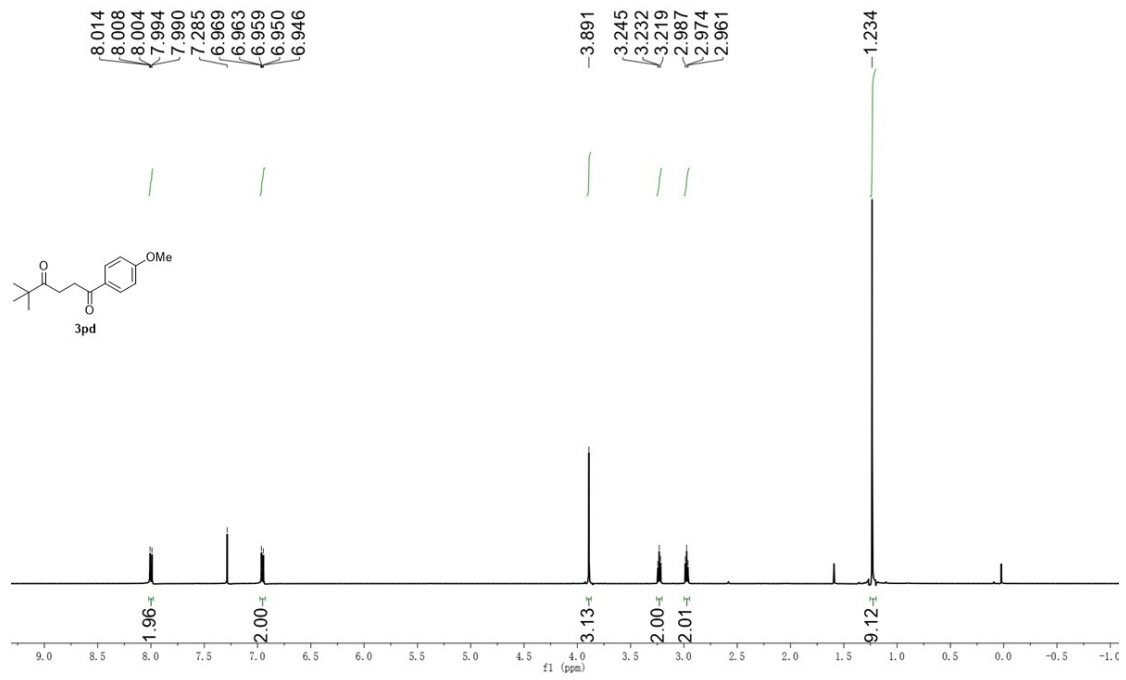
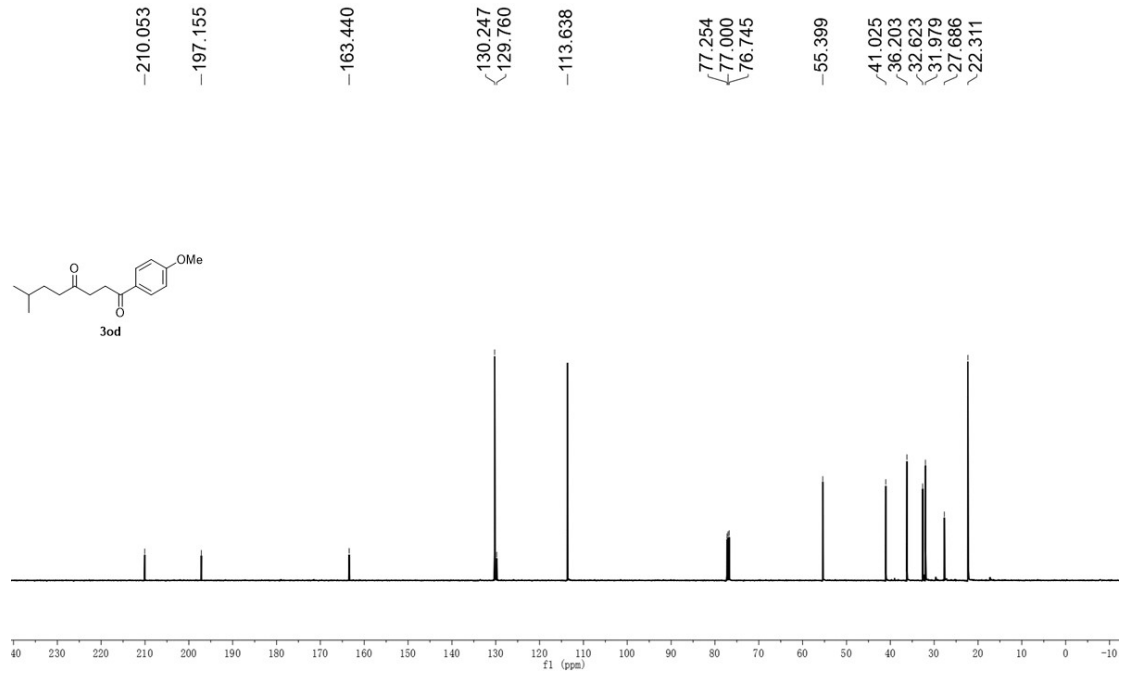


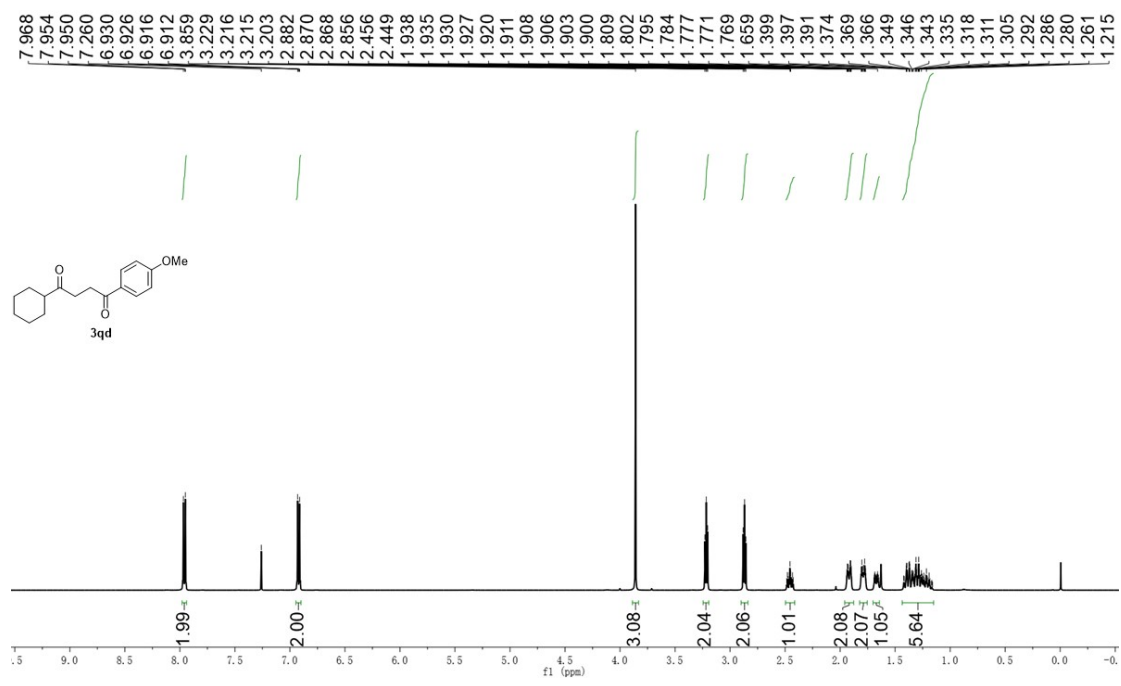
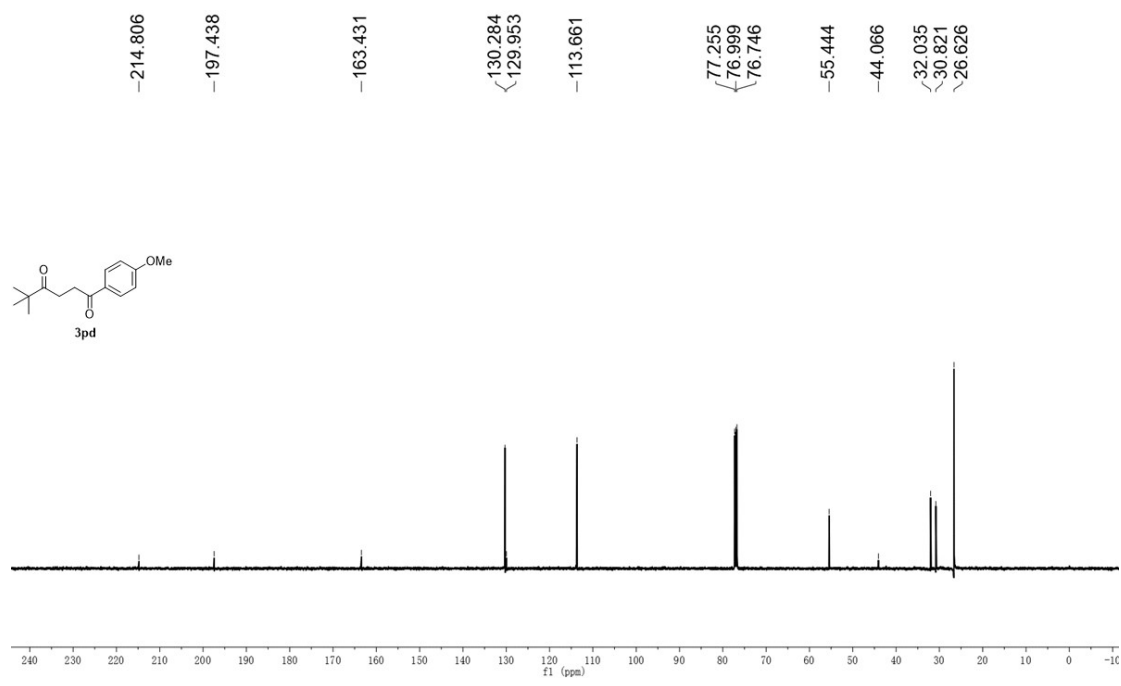


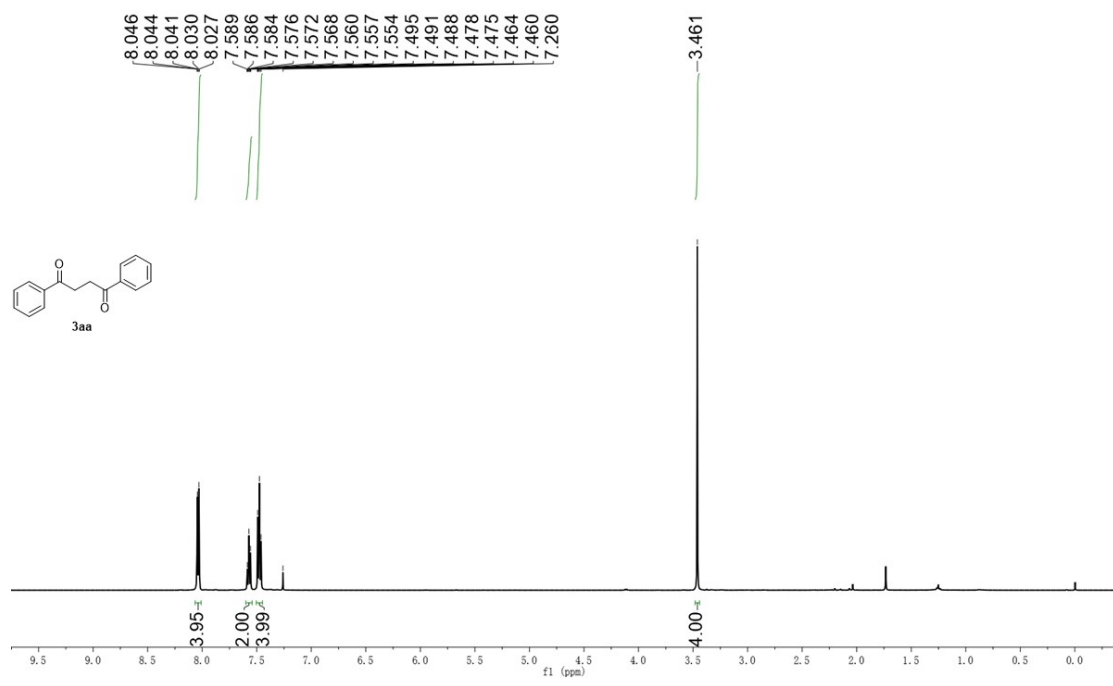
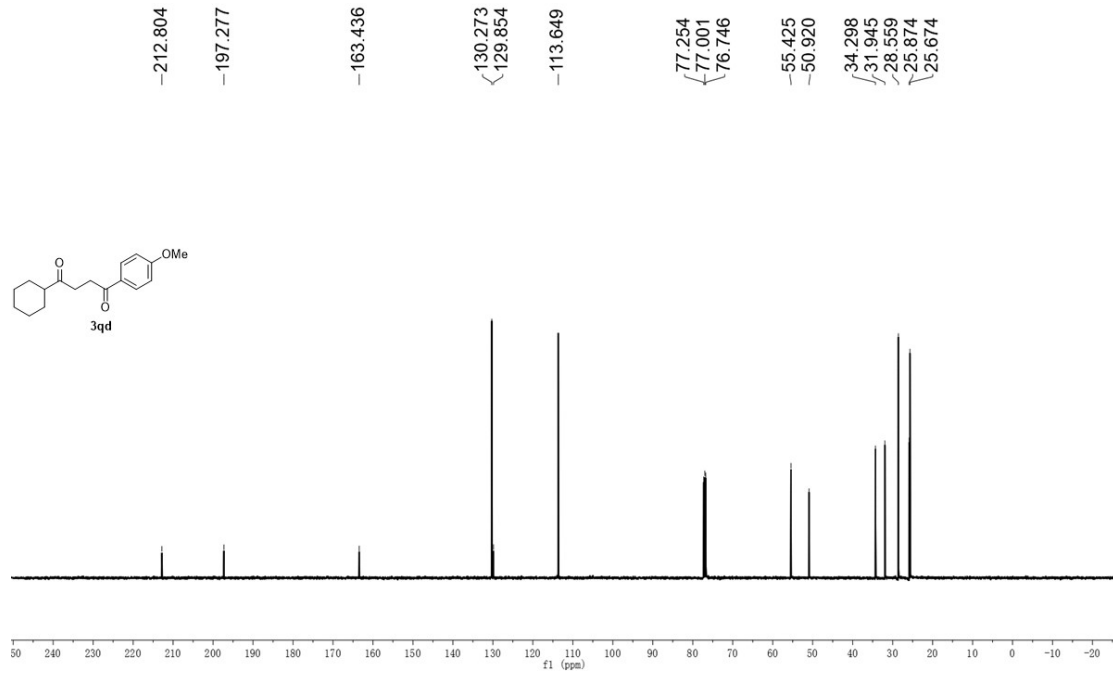


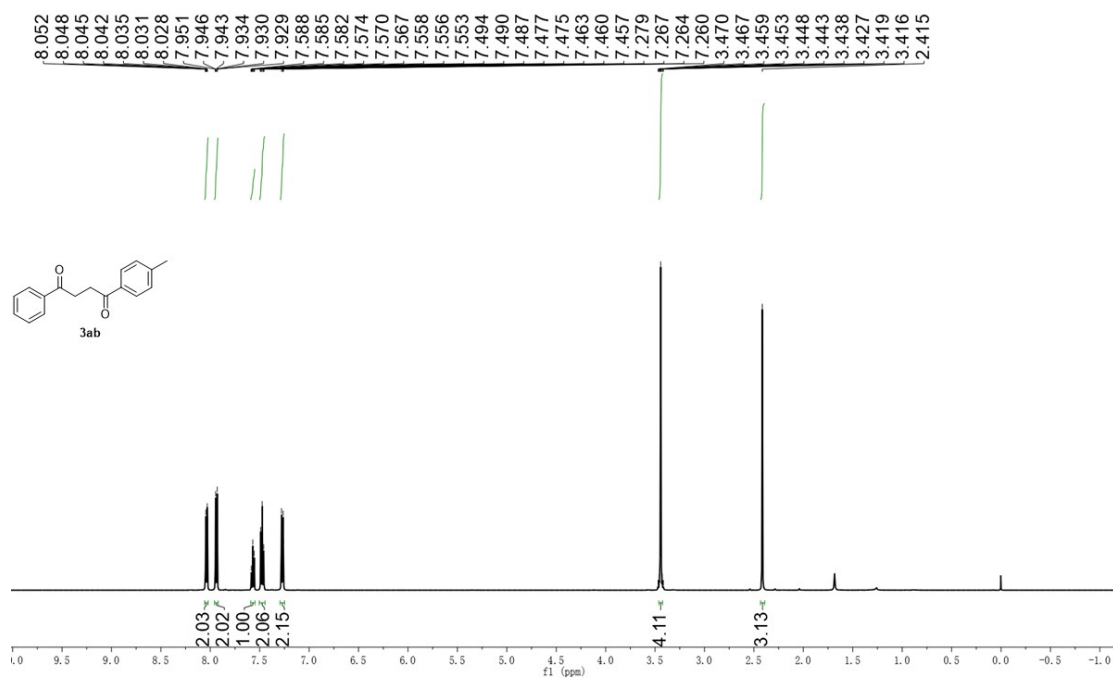
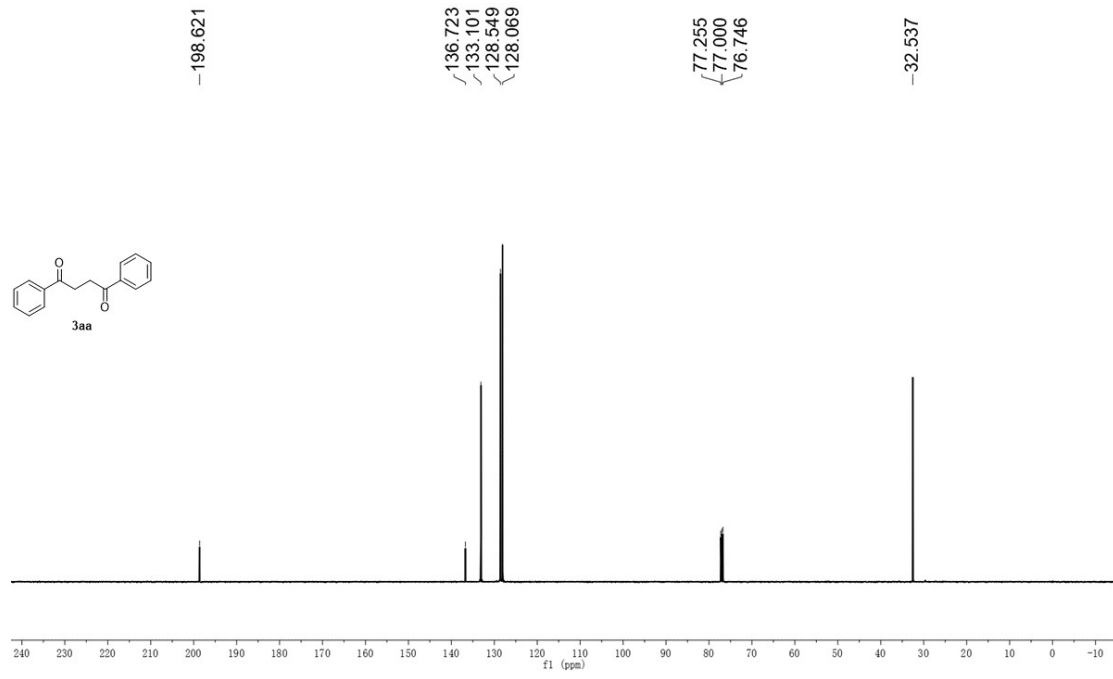


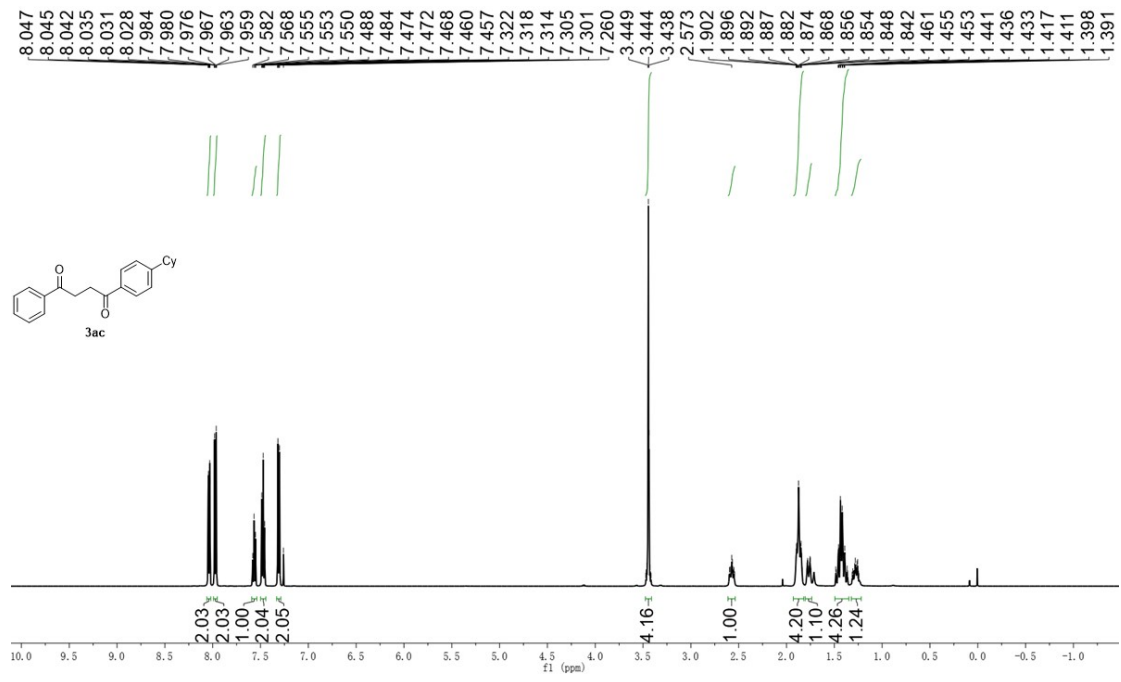
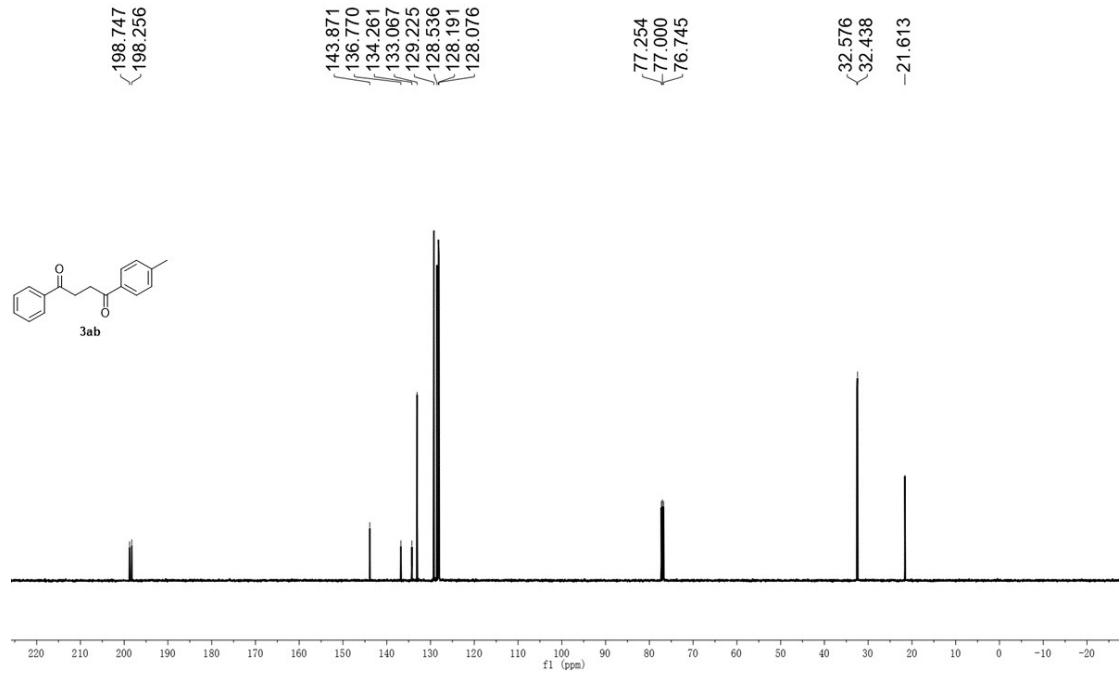


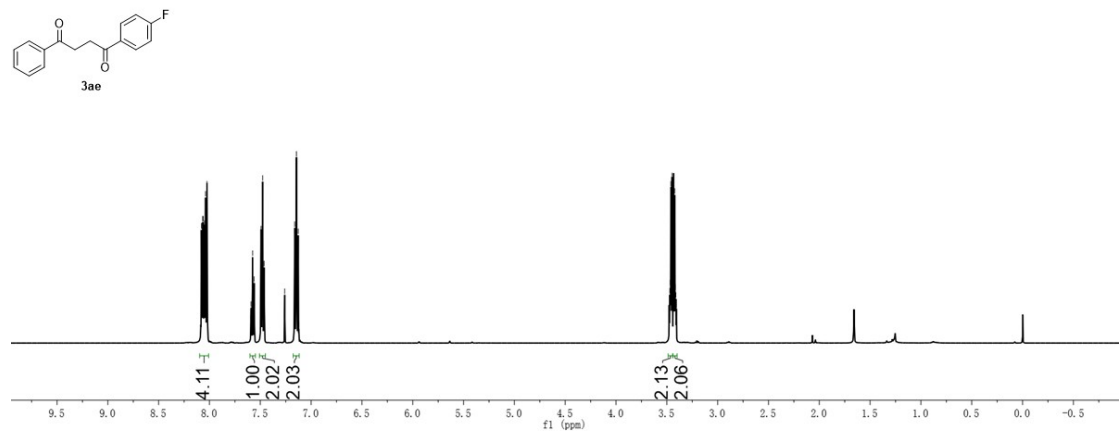
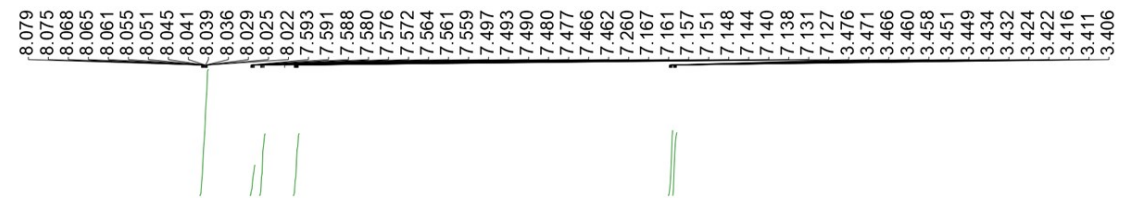
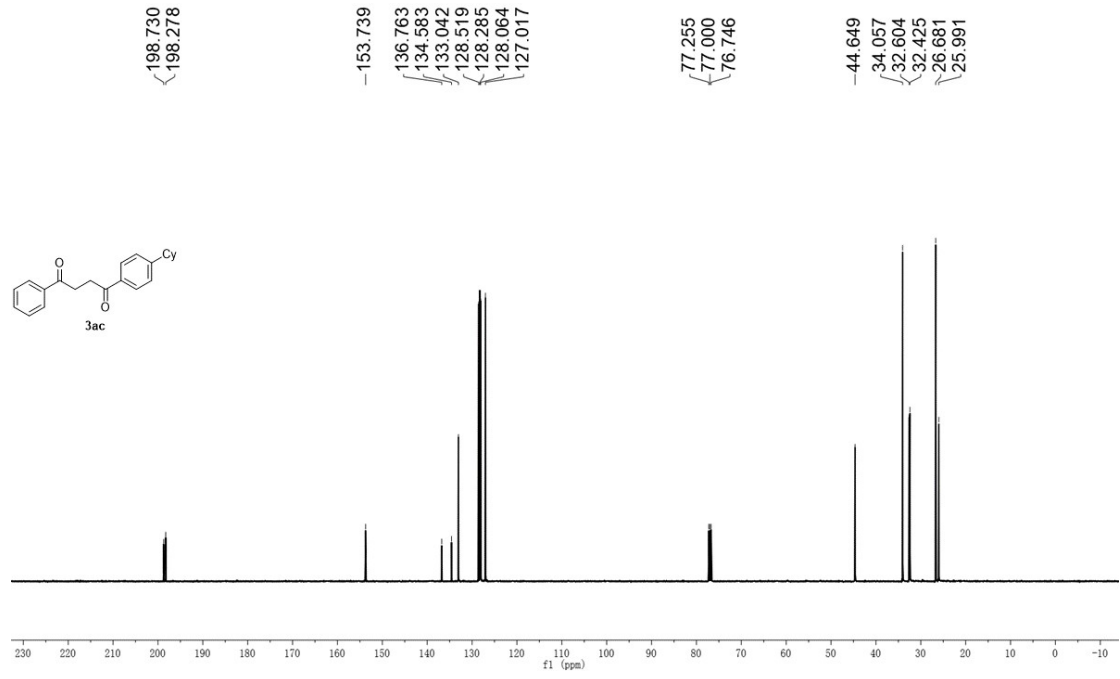


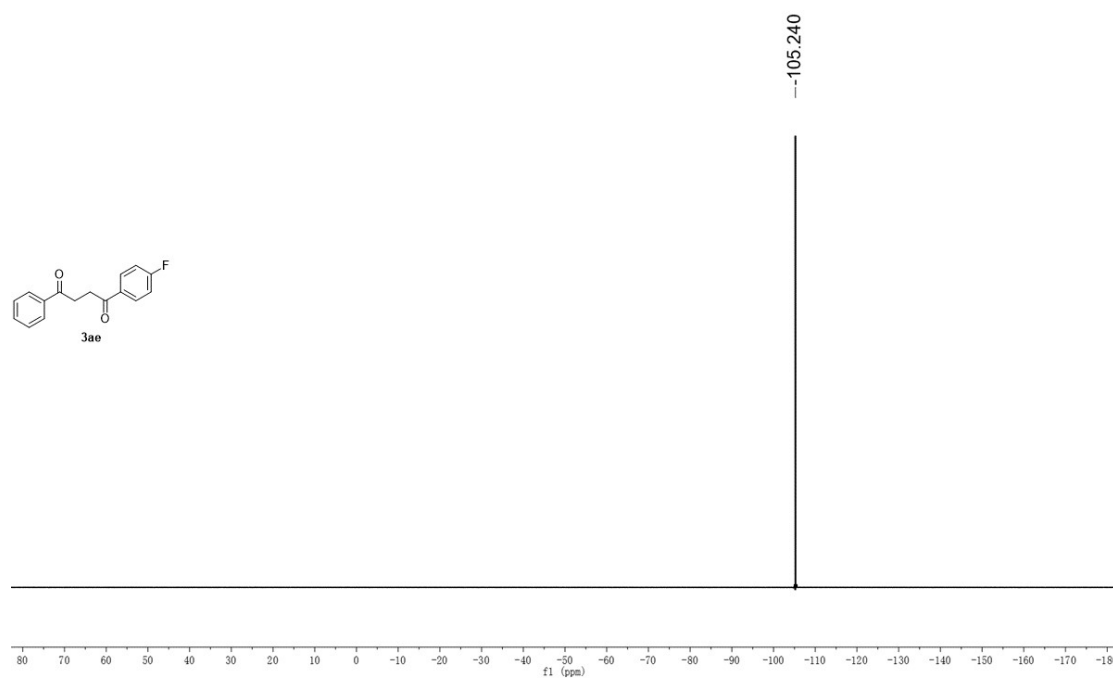
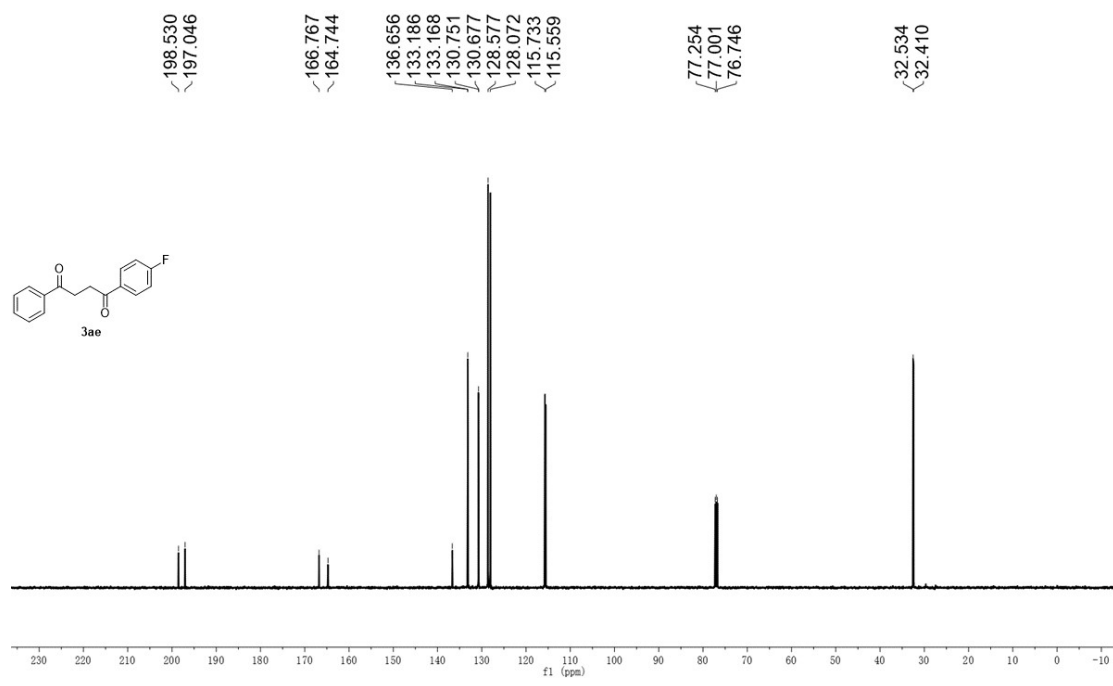


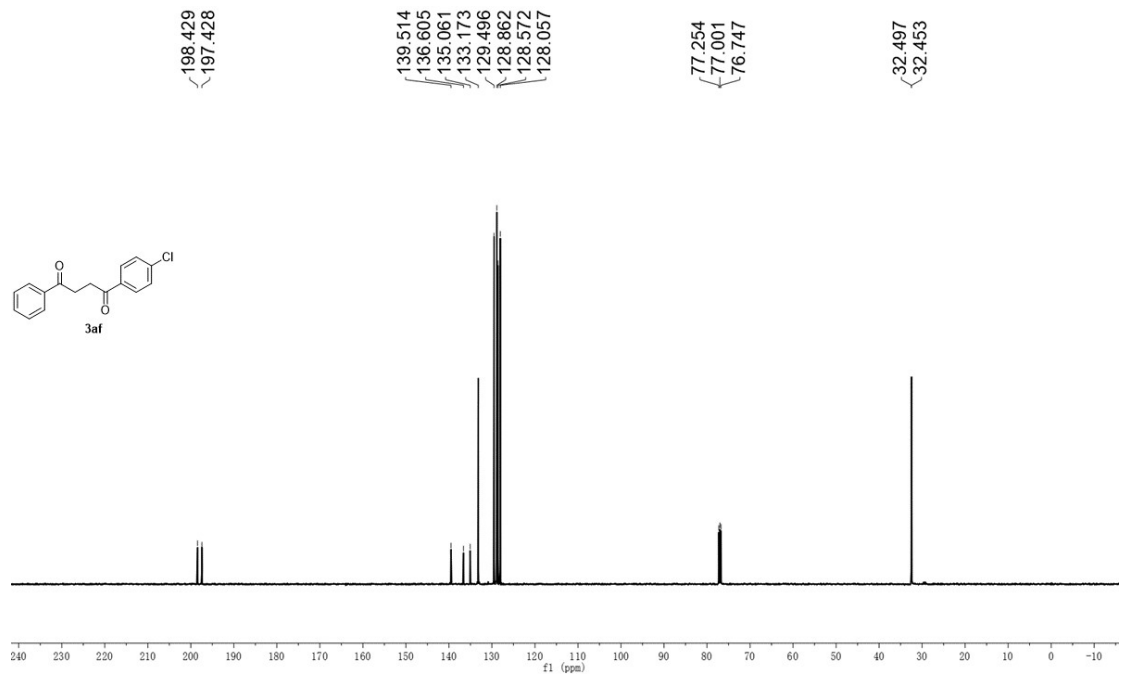
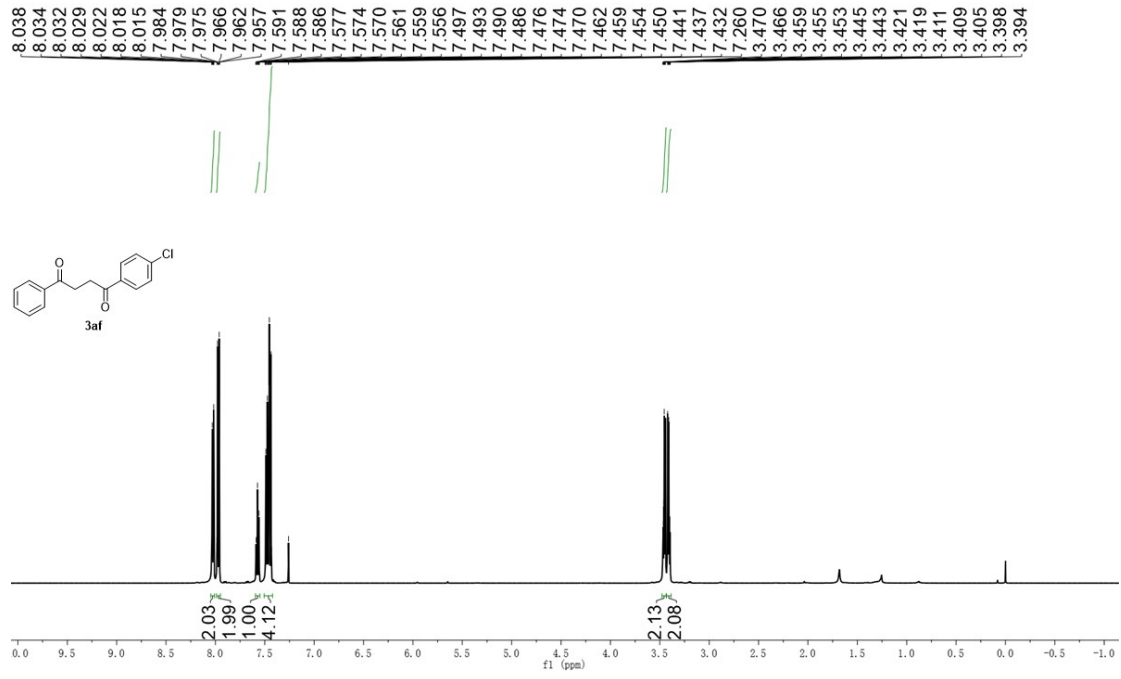


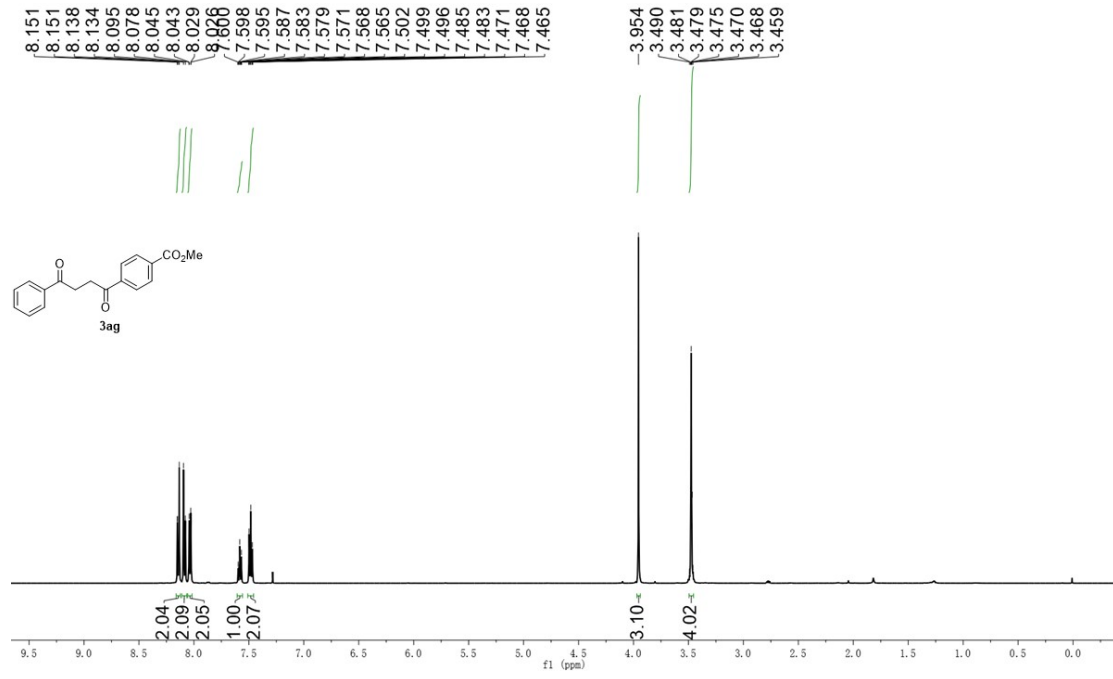




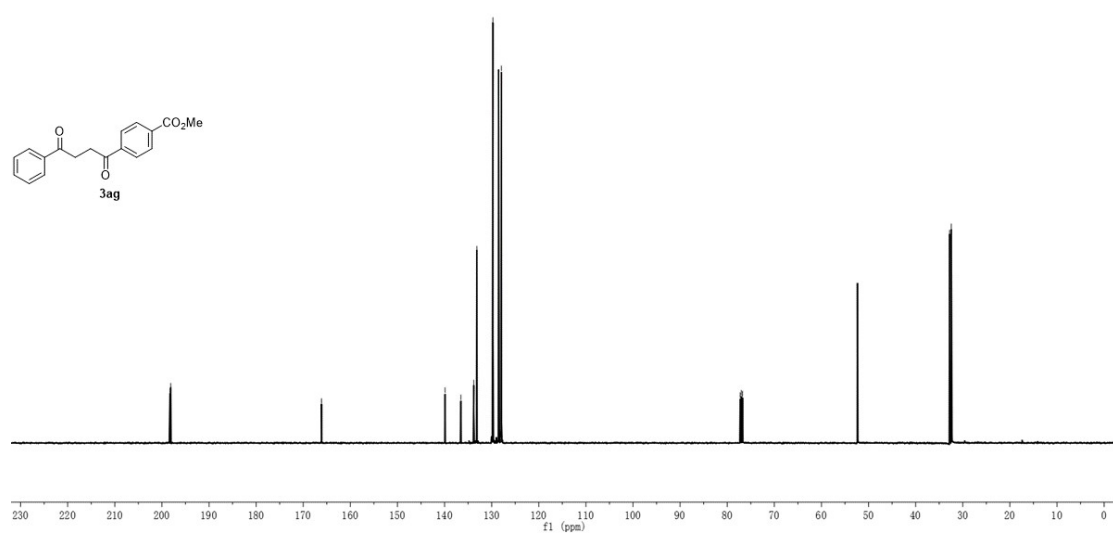


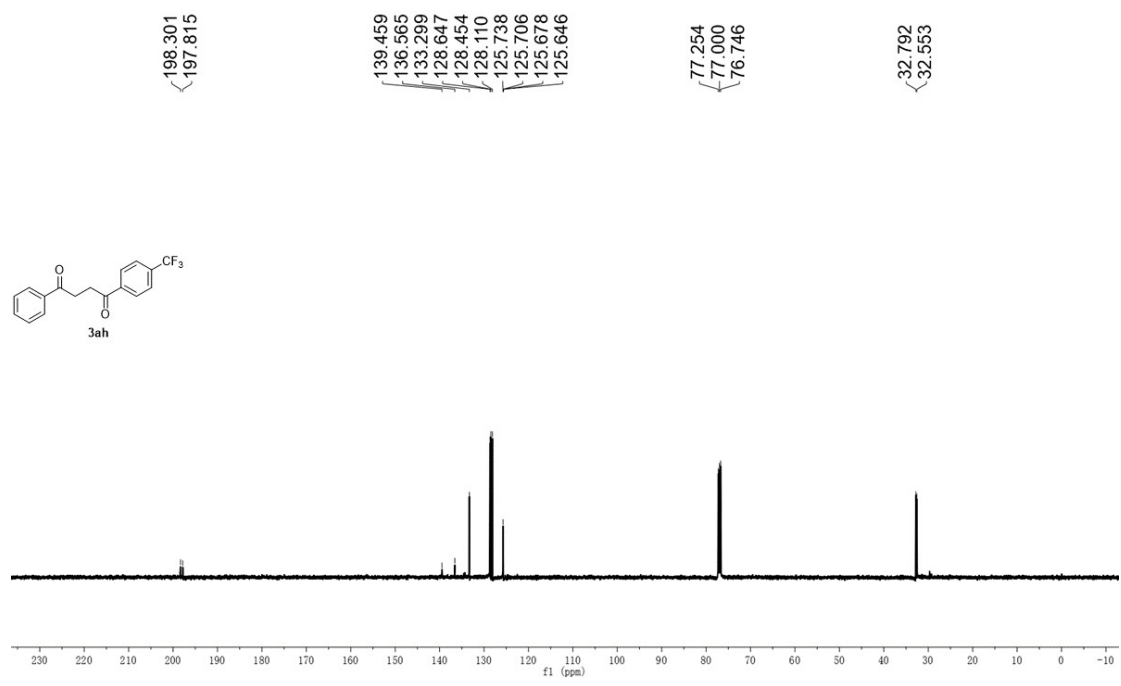
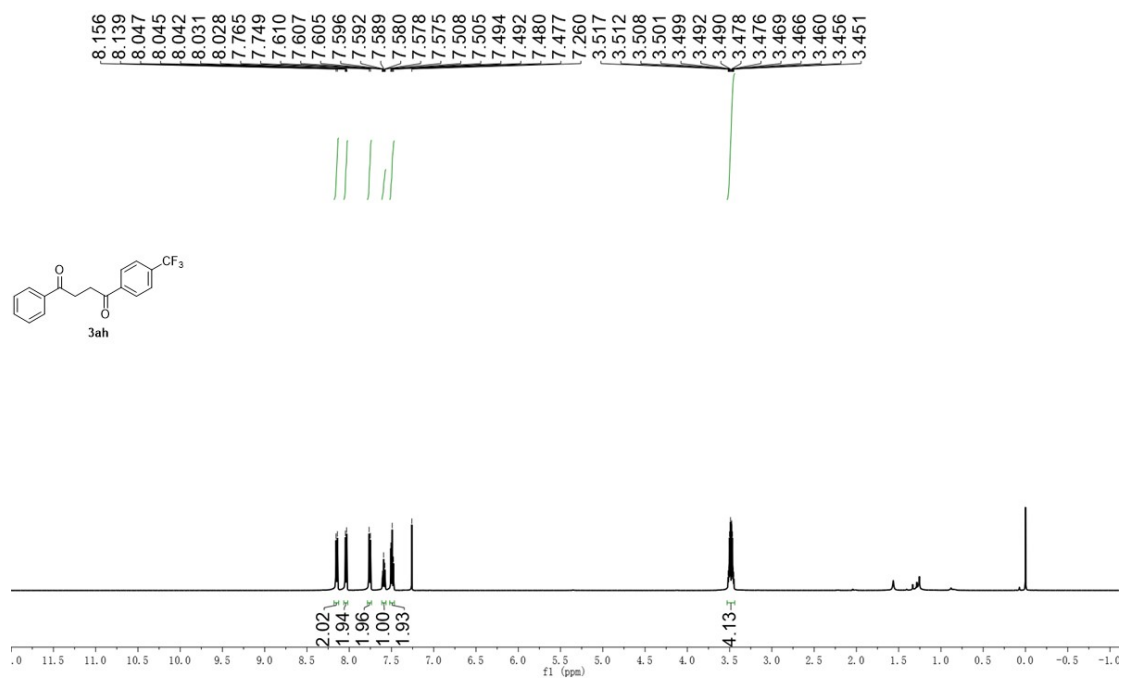


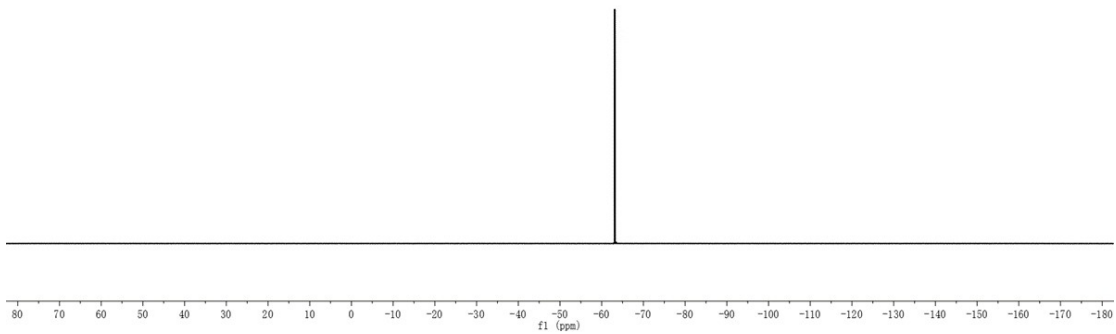
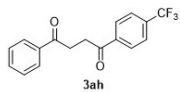




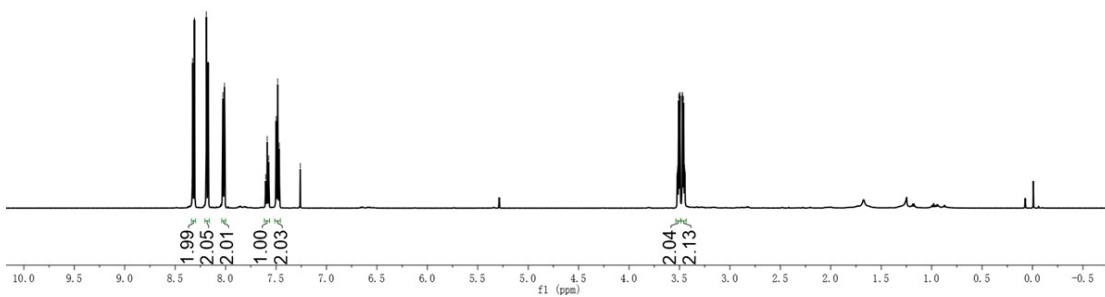
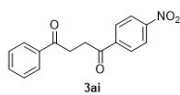
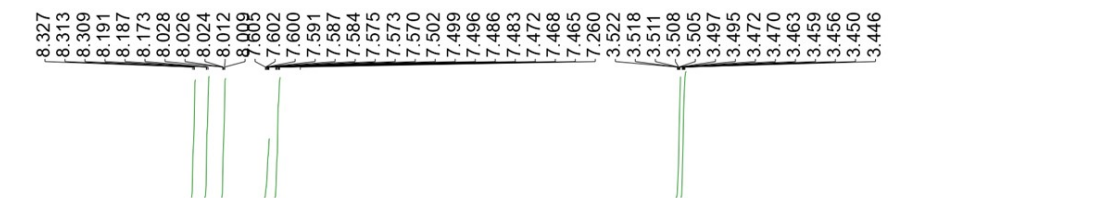
- 198.283
- 198.127
- 166.123
- 139.897
- 136.540
- 133.798
- 133.144
- 129.740
- 128.532
- 128.013
- 127.935
- 77.254
- 77.000
- 76.746
- 32.797
- 32.438

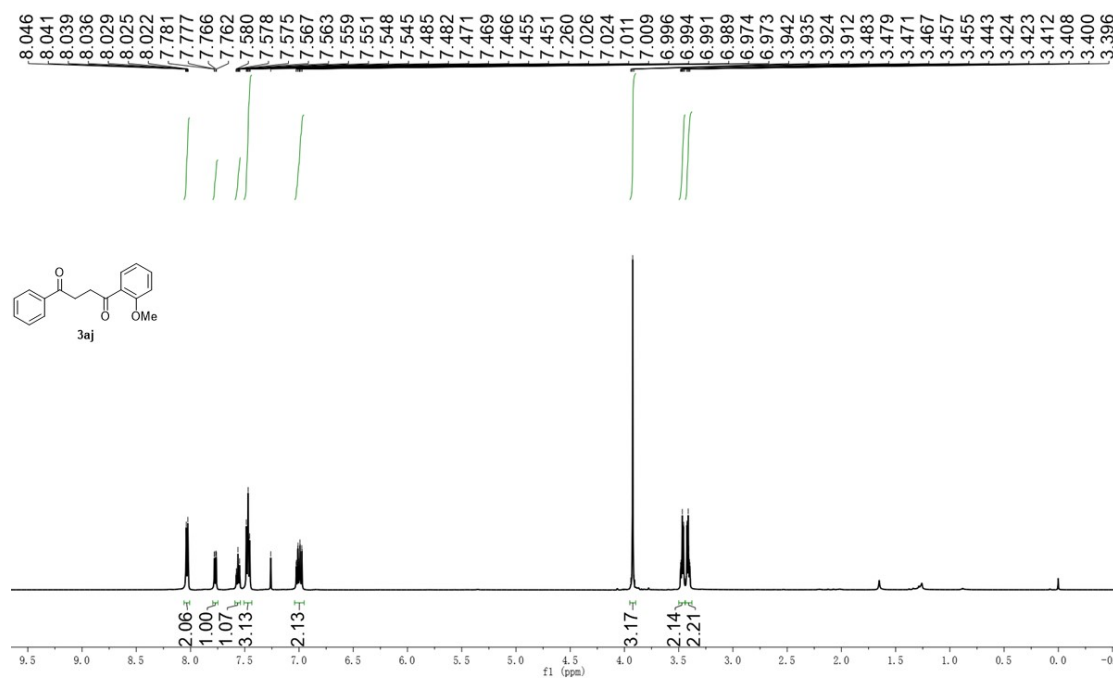
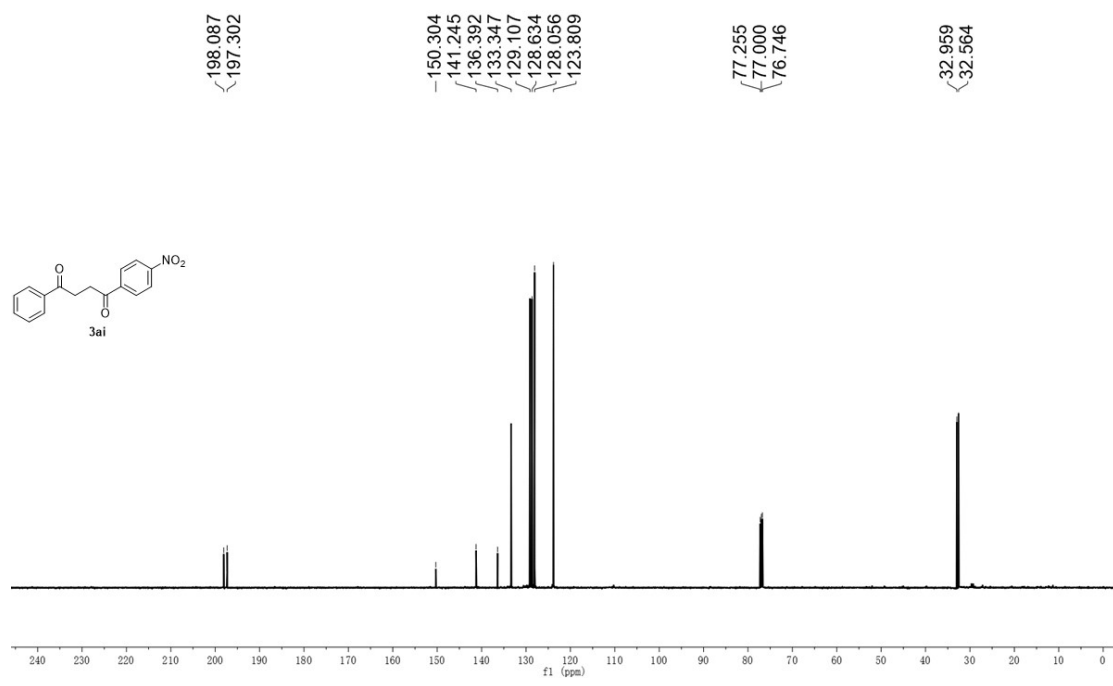


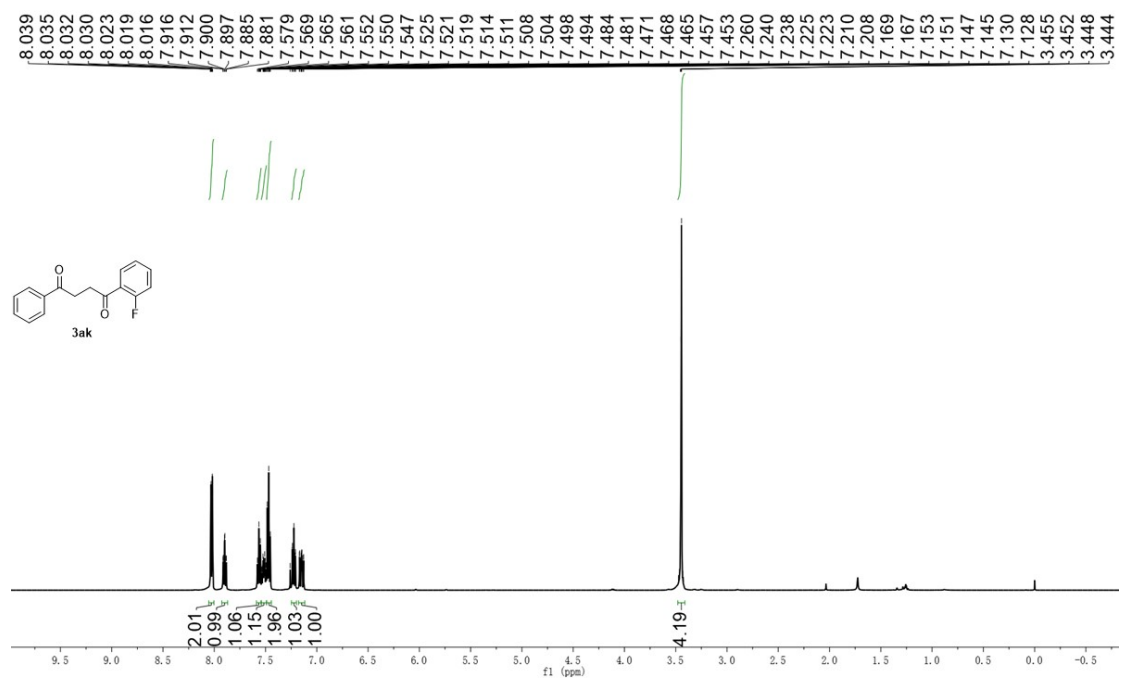
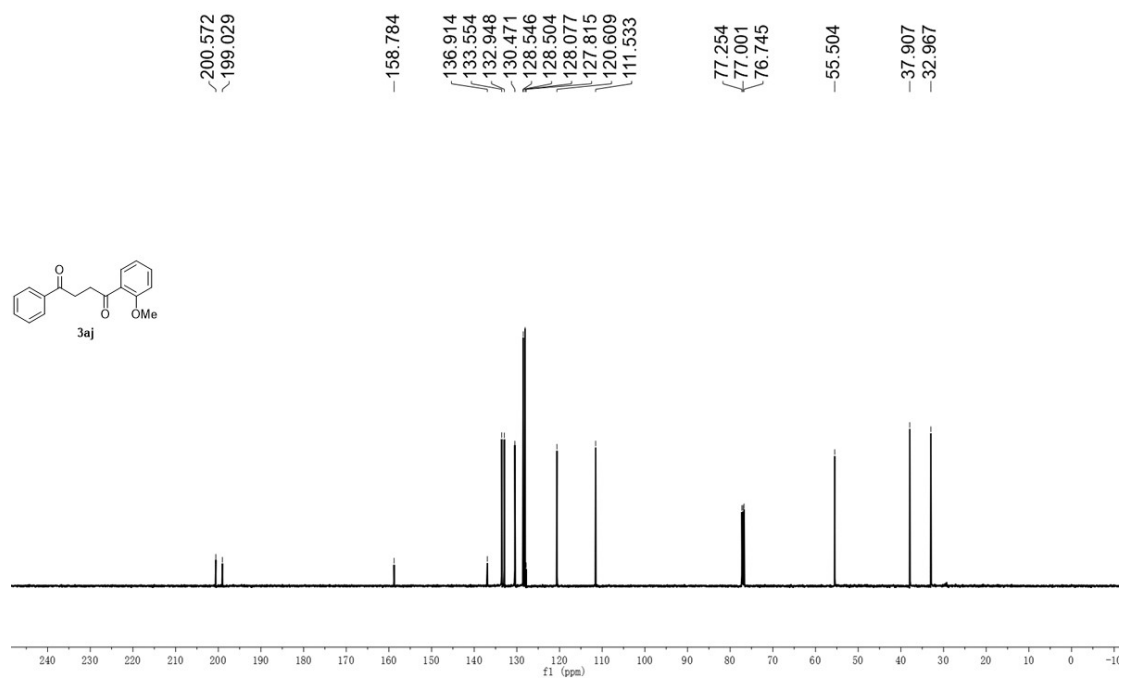


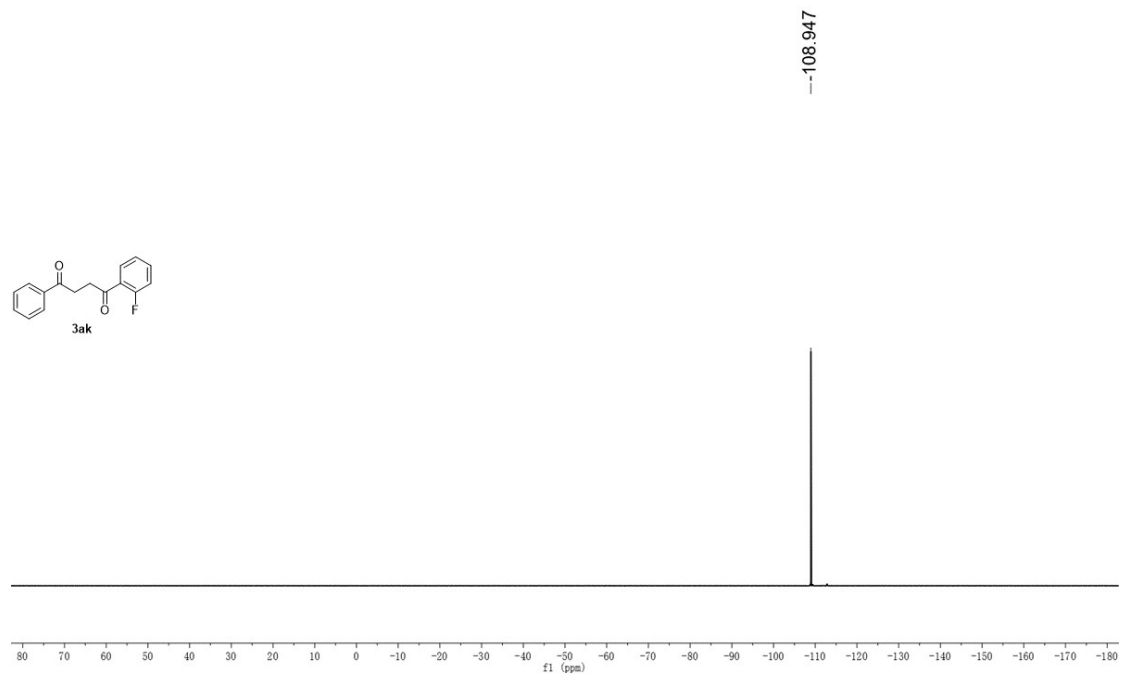
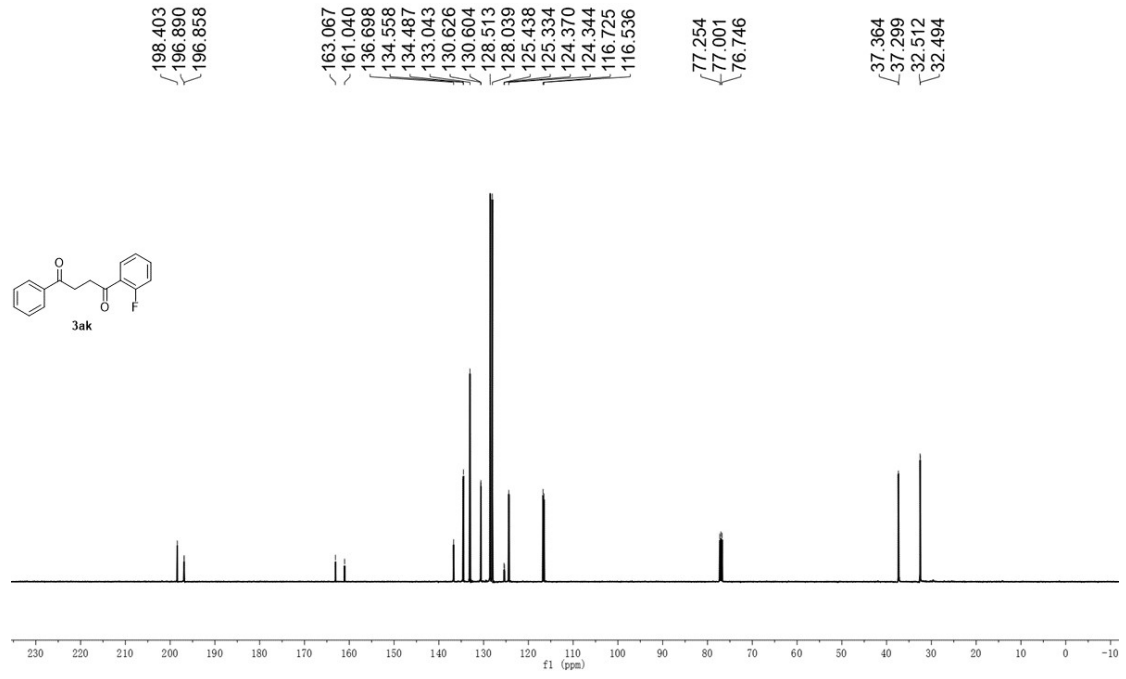


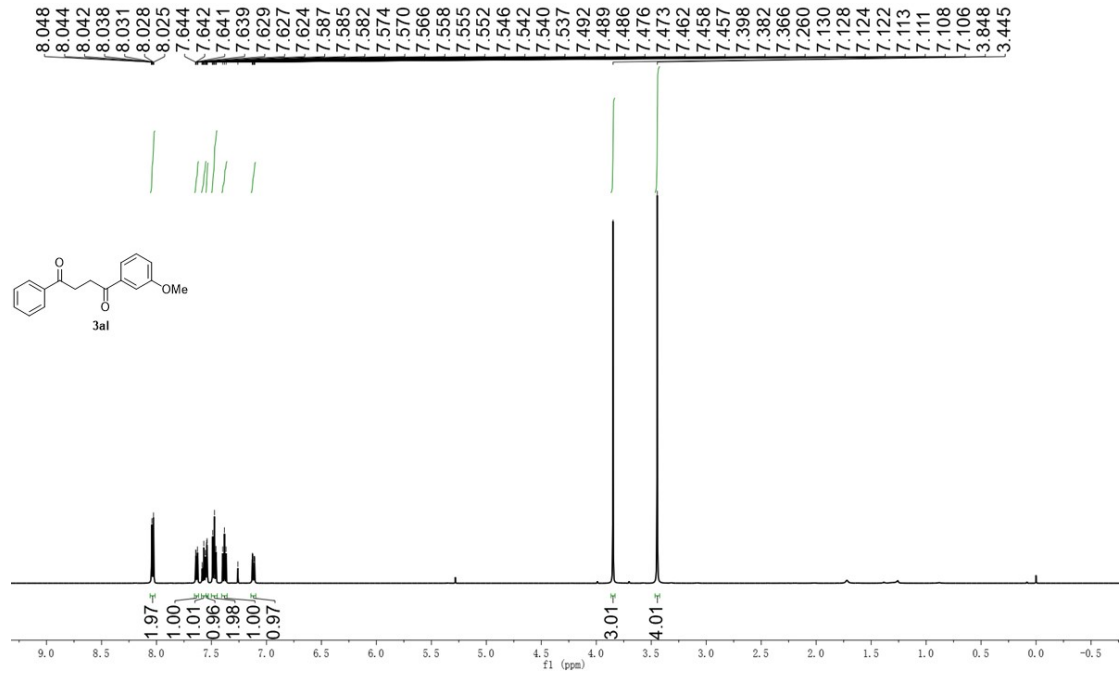
-63.105











198.593
198.427

159.760

138.064

136.714

133.083

129.540

128.534

128.055

120.739

119.643

112.215

77.254

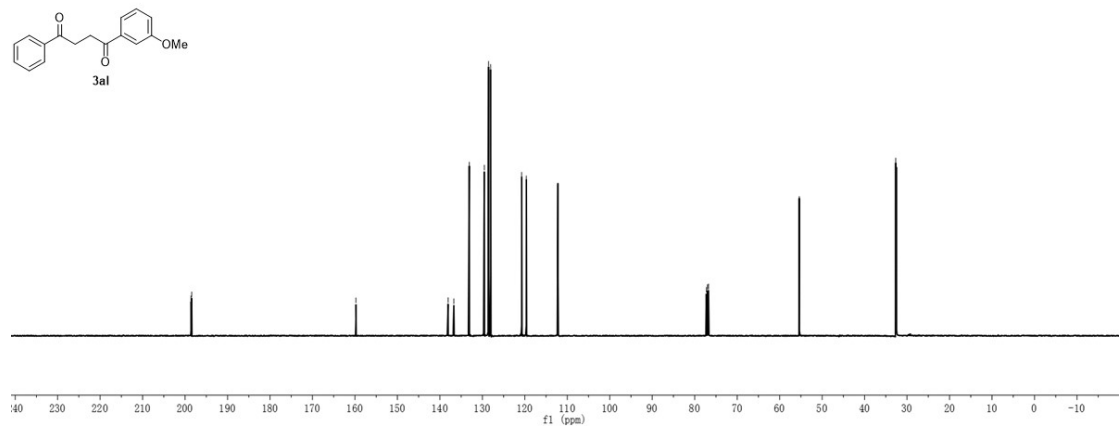
77.000

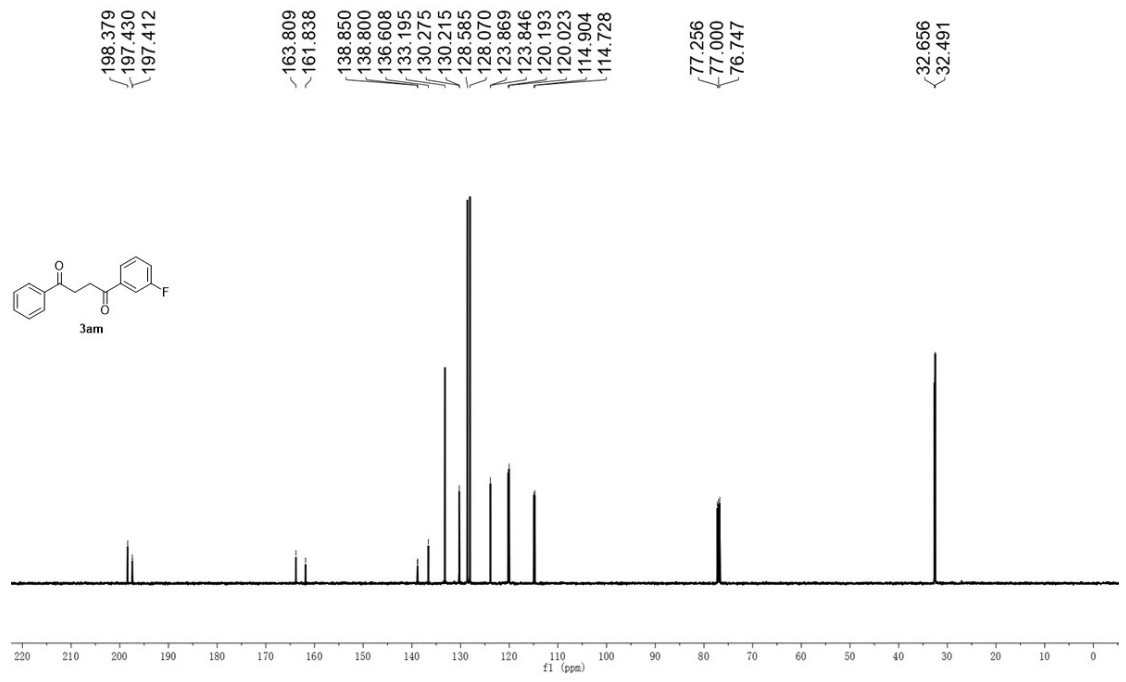
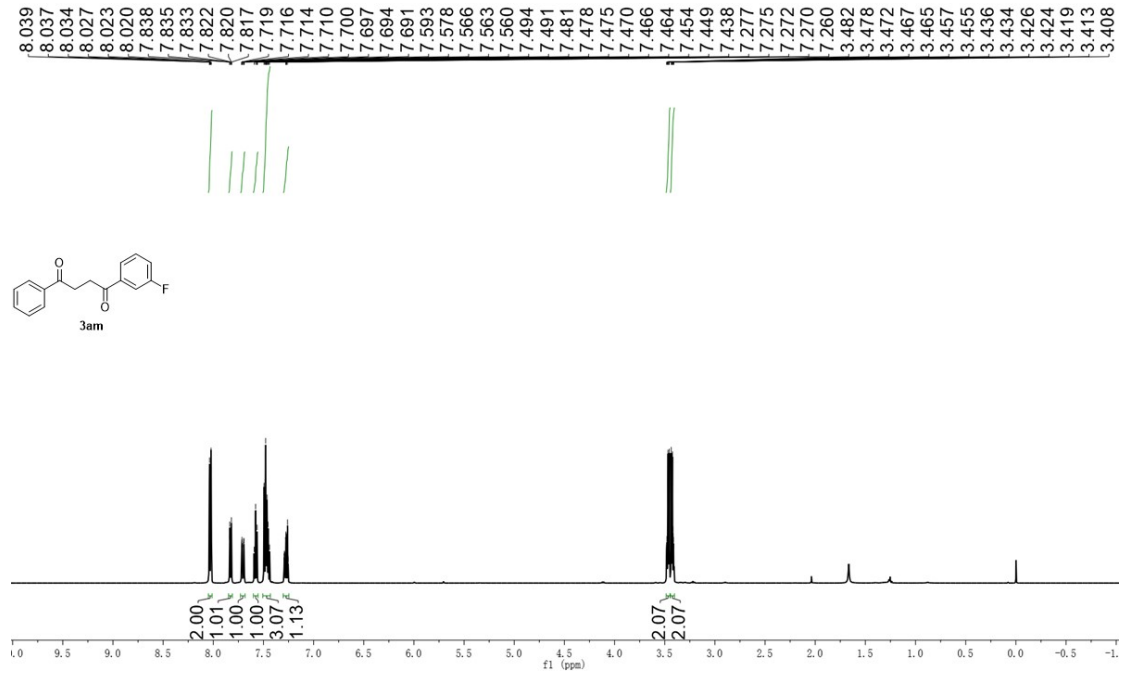
76.746

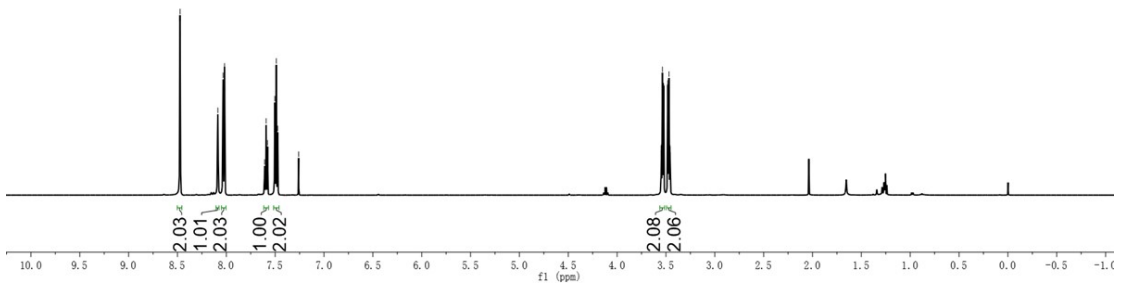
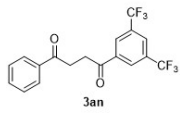
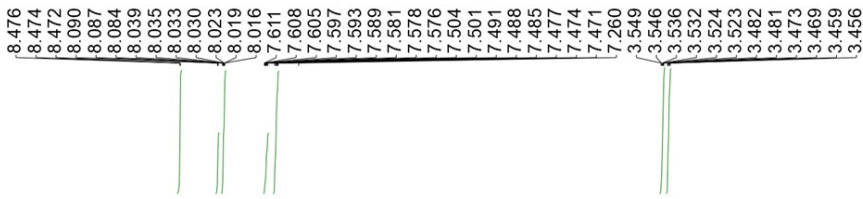
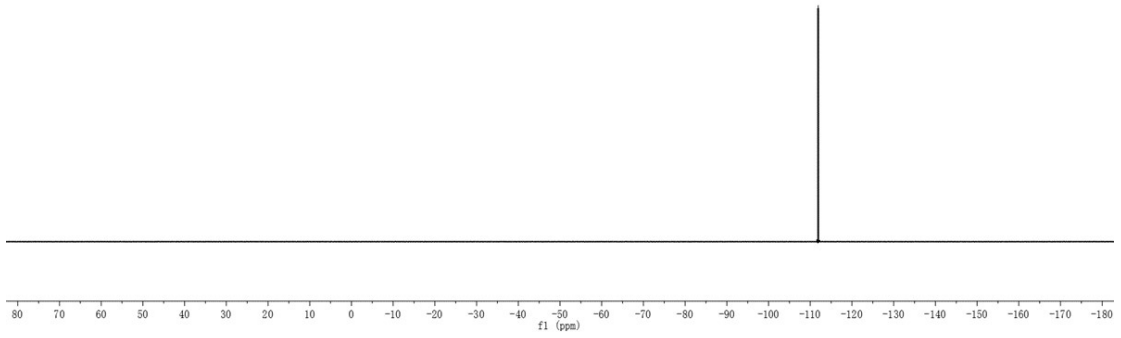
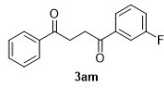
55.376

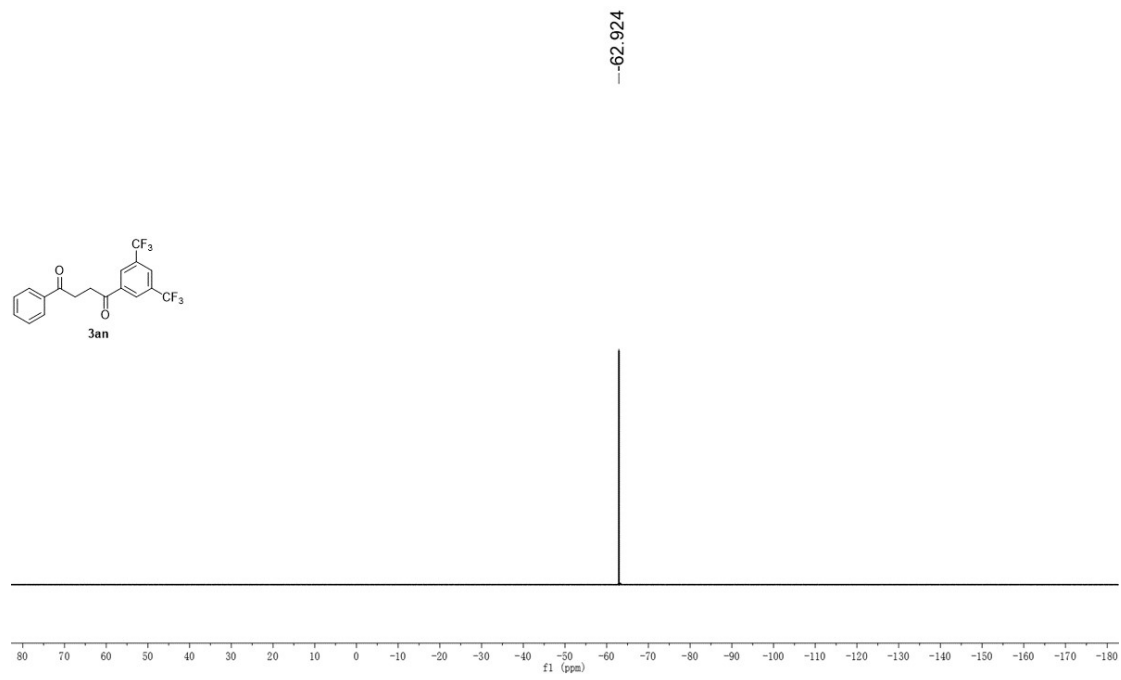
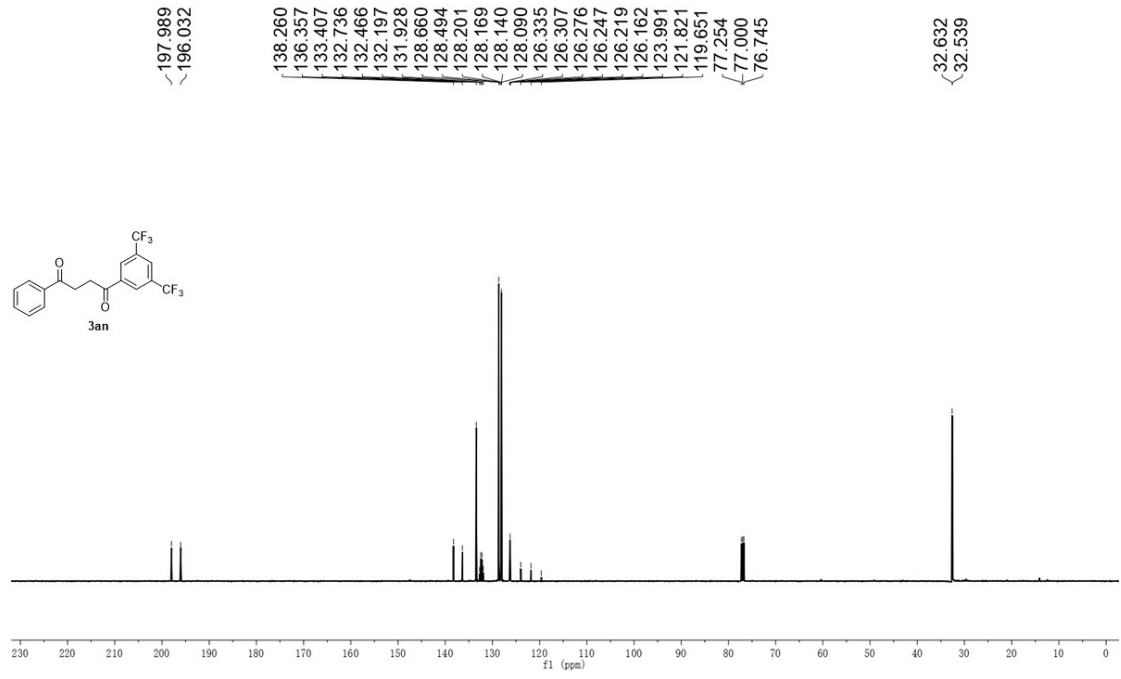
32.670

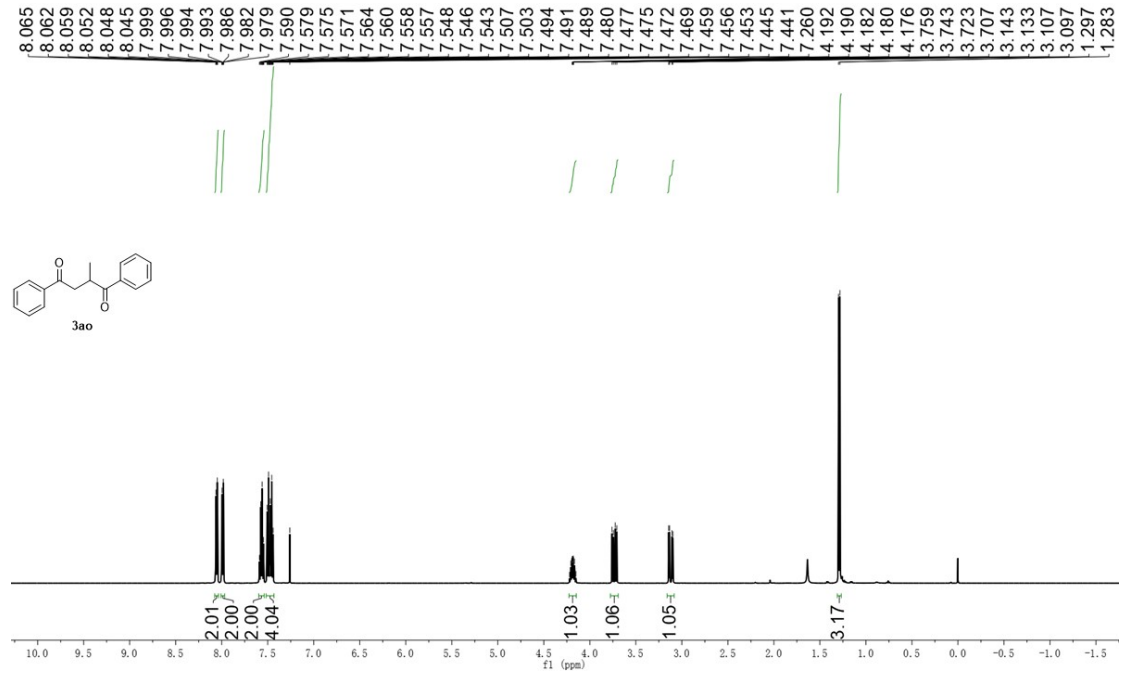
32.541











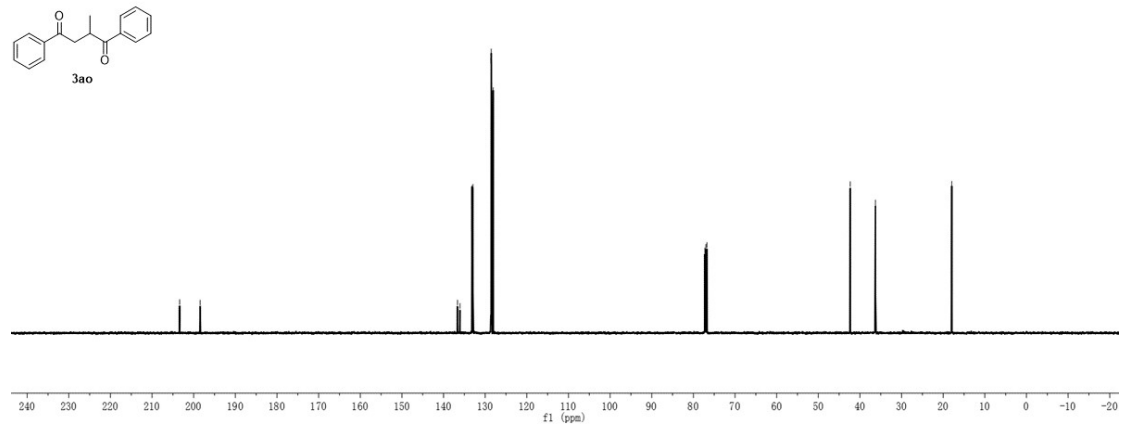
-203.377
-198.455

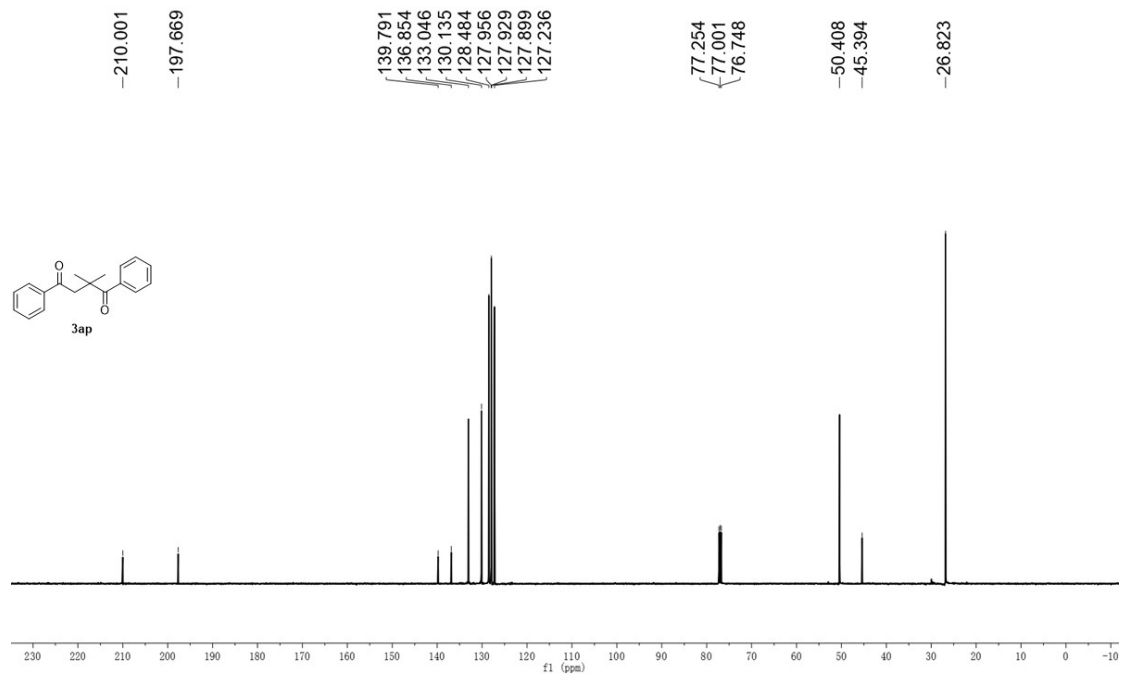
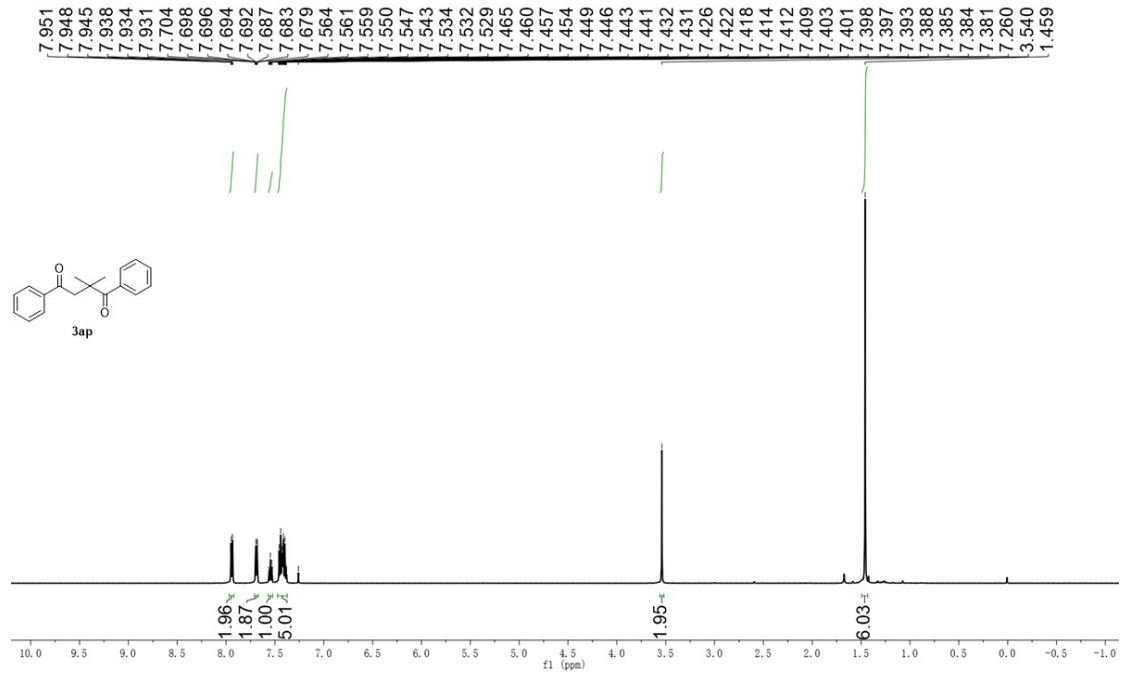
136.637
136.058
133.158
132.946
128.636
128.543
128.493
128.079

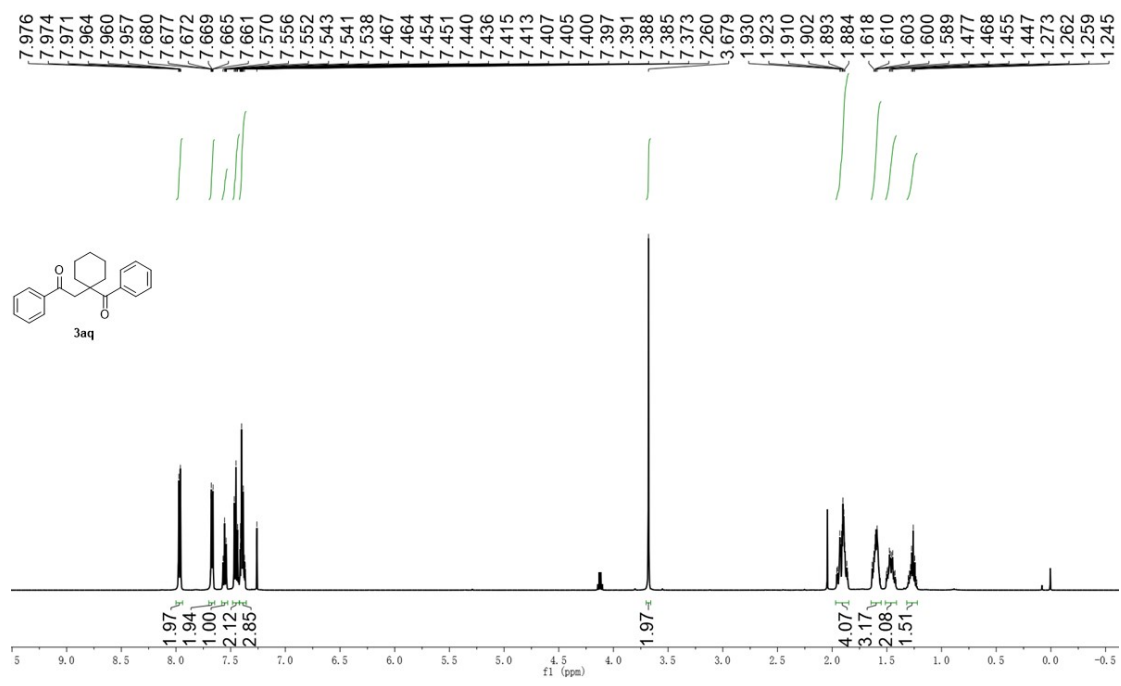
77.254
77.001
76.747

-42.322
-36.265

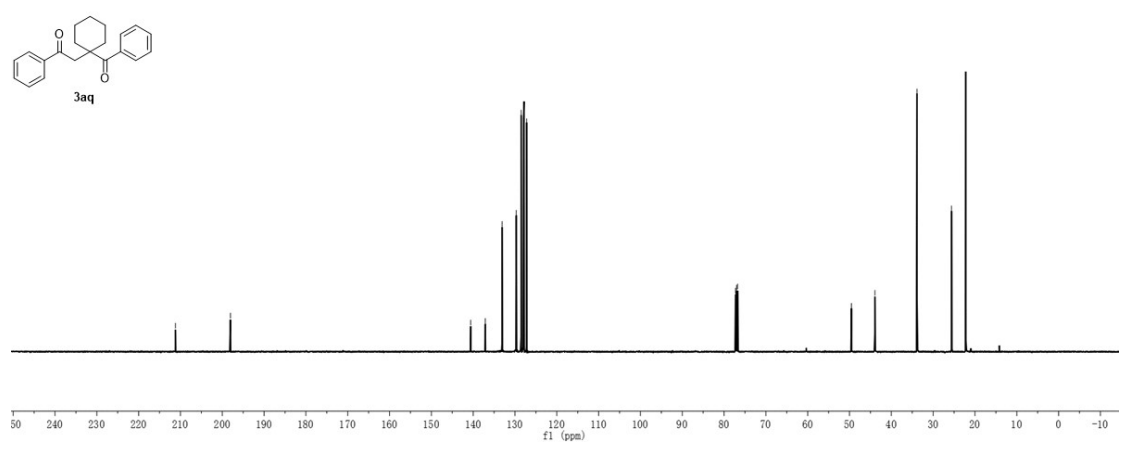
-17.938

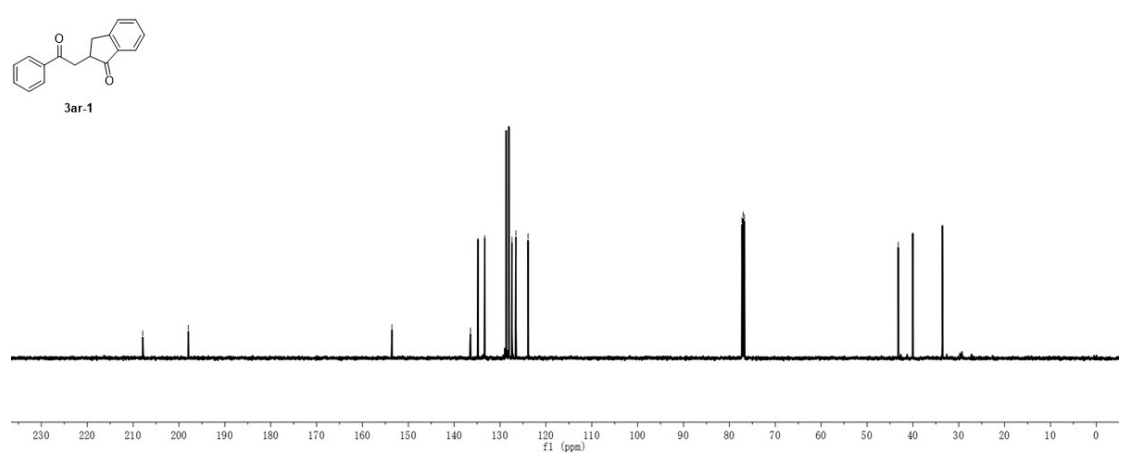
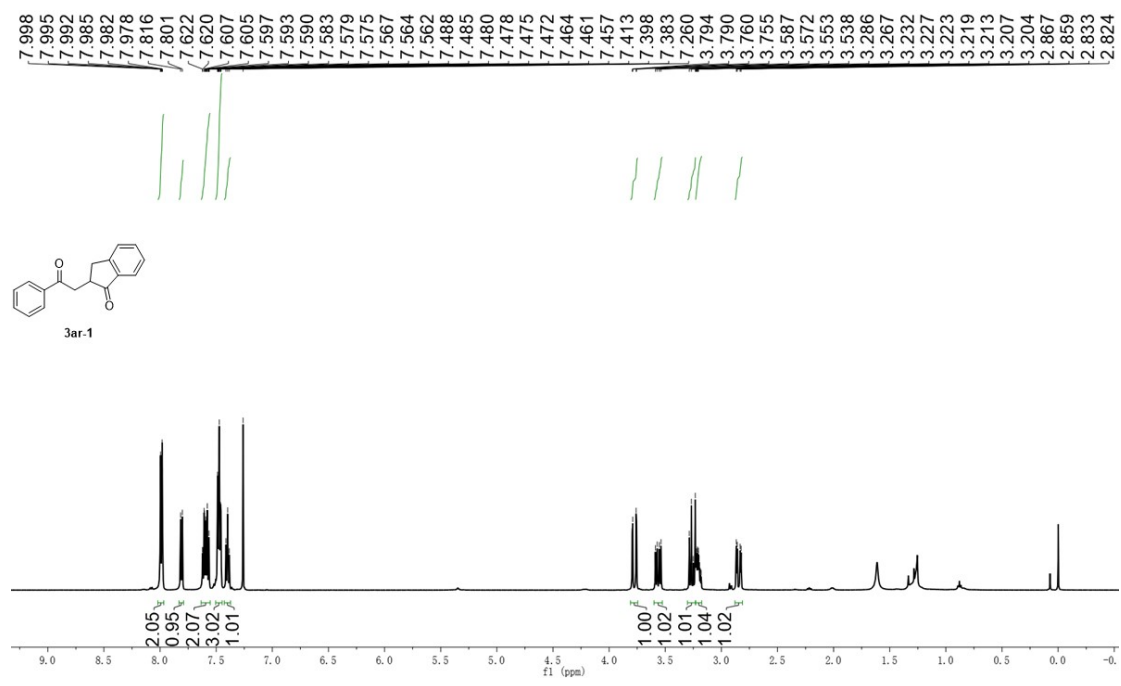


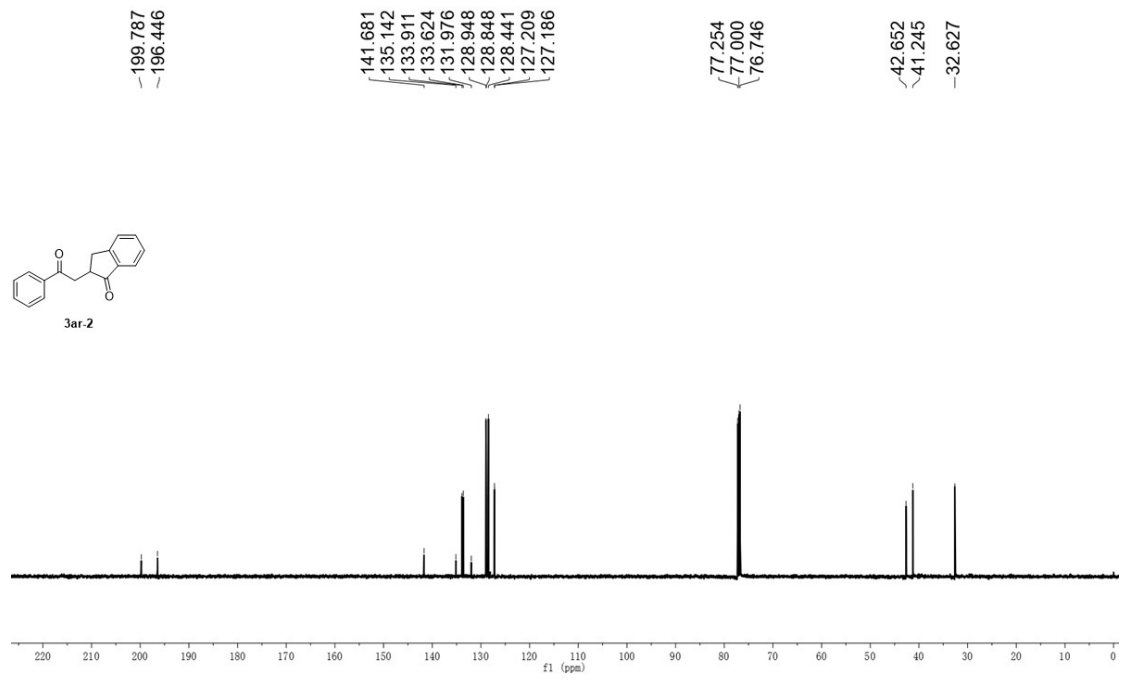
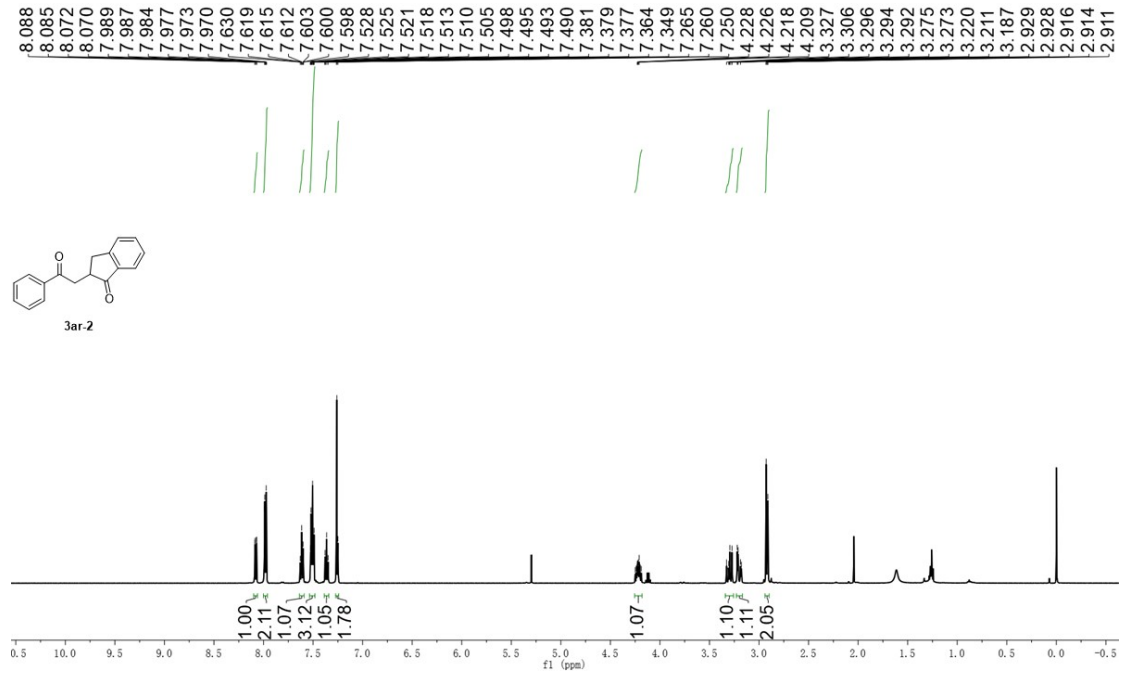


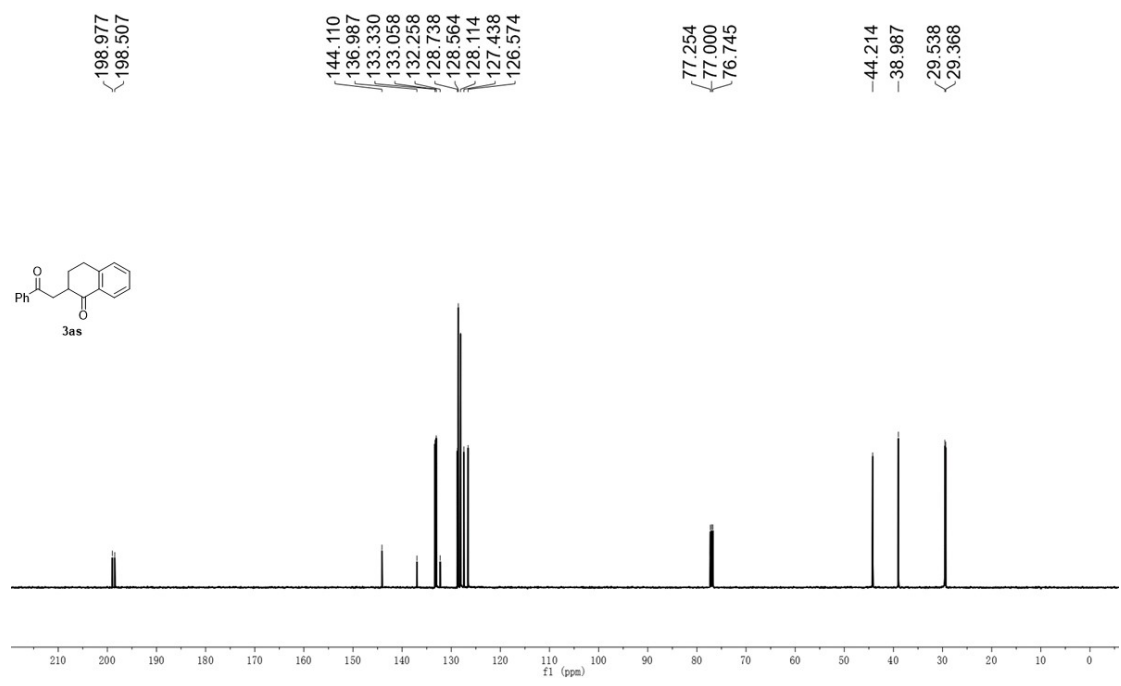
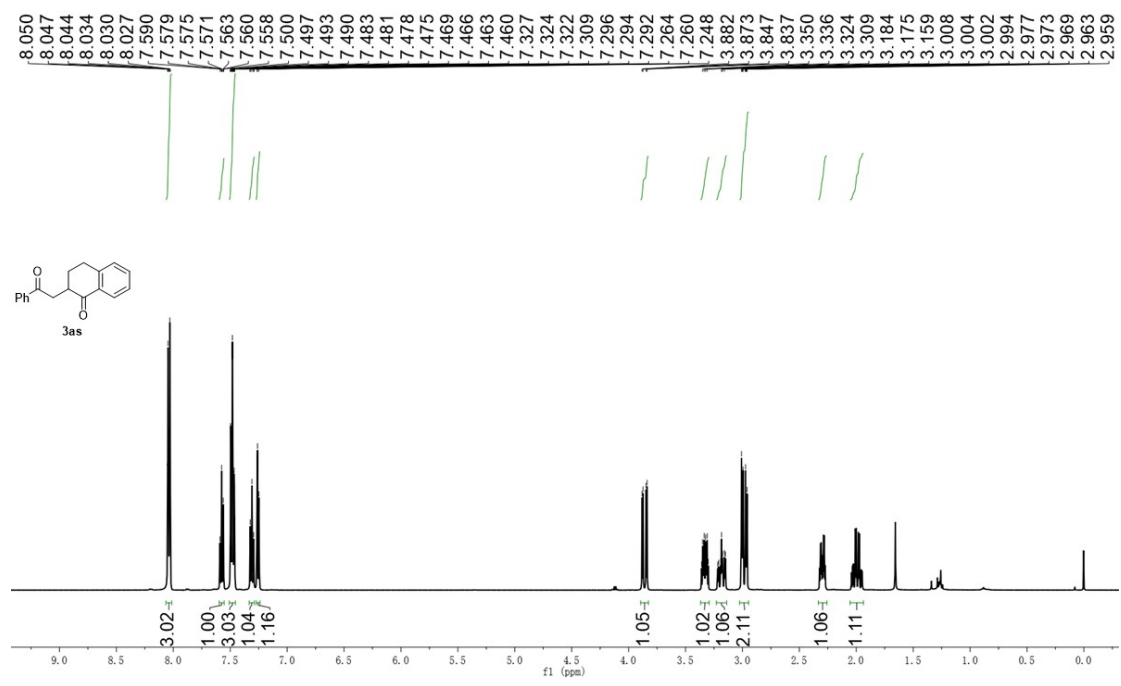


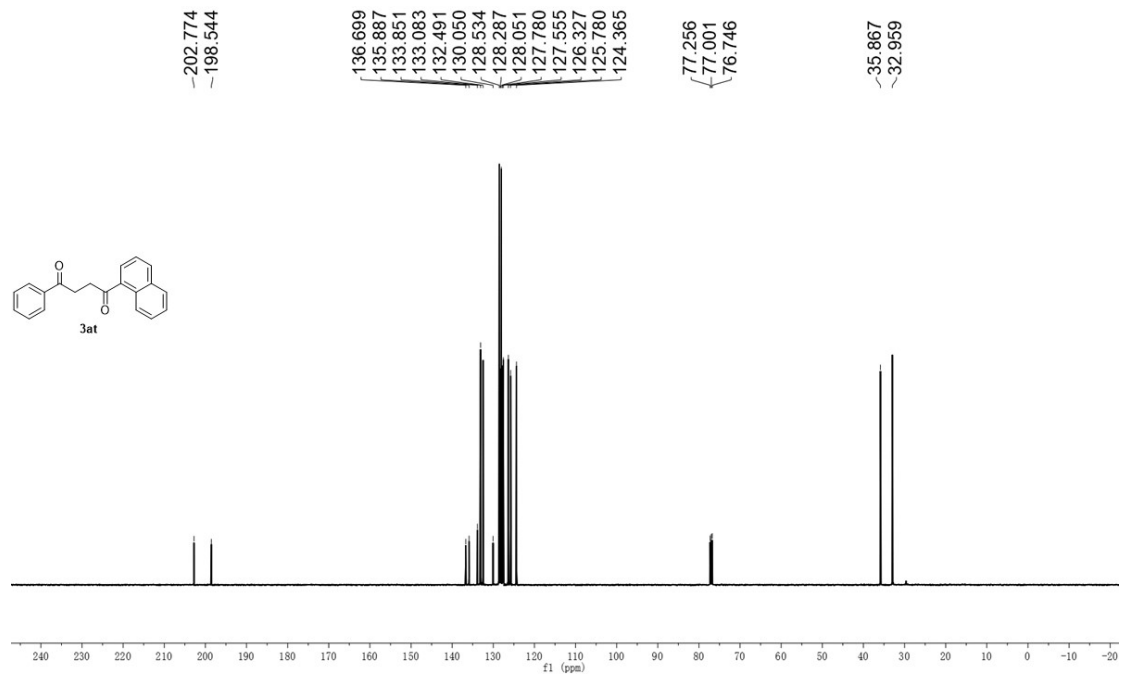
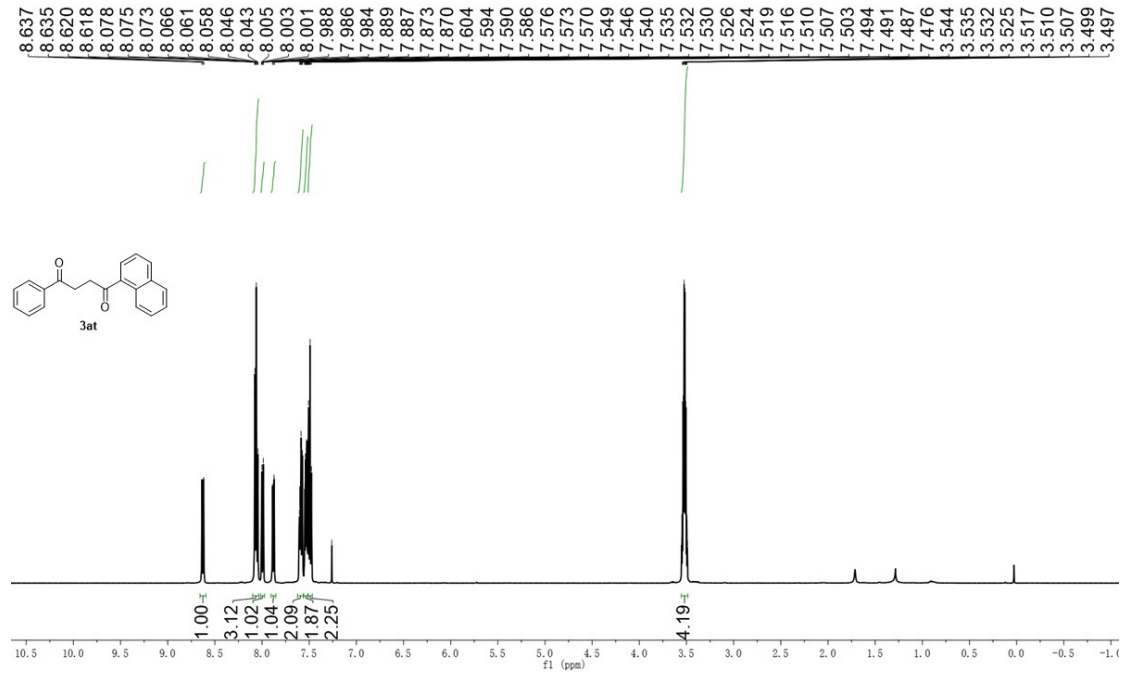
- 211.203
- 198.037
- 140.585
- 137.096
- 133.083
- 129.692
- 128.515
- 127.966
- 127.827
- 127.219
- 77.254
- 77.000
- 76.747
- 49.542
- 43.927
- 33.861
- 25.608
- 22.202



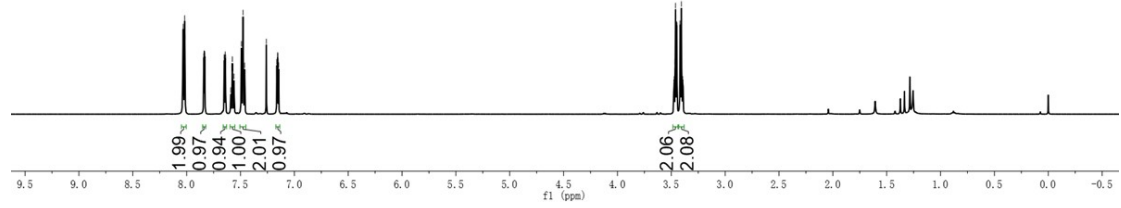
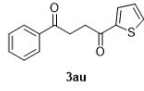




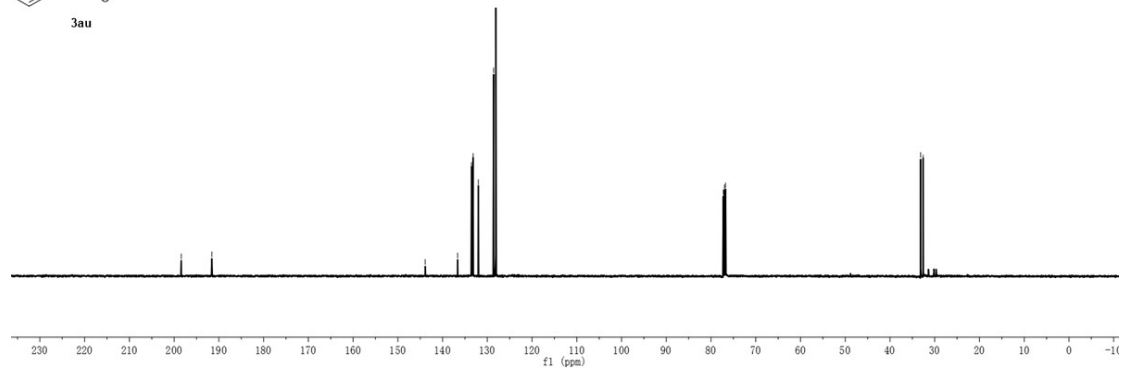
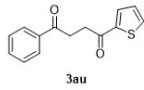


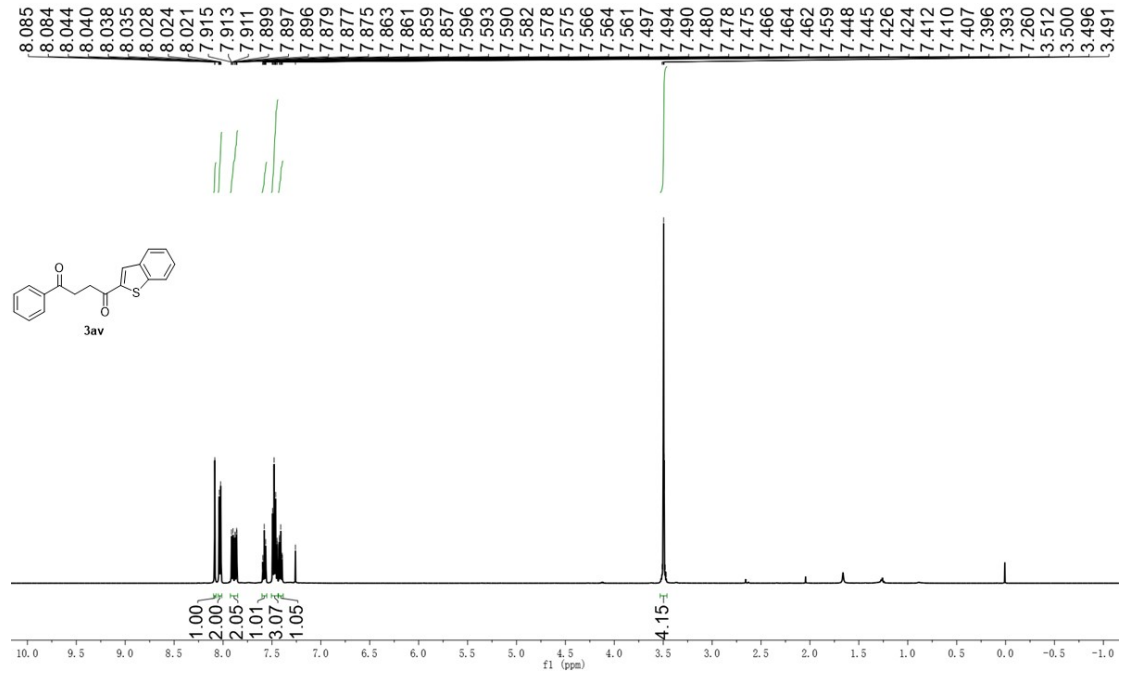


8.039
8.035
8.032
8.029
8.022
8.018
8.015
7.841
7.838
7.833
7.831
7.651
7.649
7.641
7.639
7.593
7.590
7.588
7.579
7.575
7.572
7.563
7.561
7.558
7.495
7.492
7.488
7.479
7.476
7.465
7.461
7.260
7.163
7.155
7.153
7.145
3.477
3.473
3.465
3.461
3.450
3.448
3.419
3.417
3.406
3.402
3.394
3.390



-198.413
-191.585
143.869
136.626
133.528
133.180
132.009
128.584
128.094
77.255
77.000
76.746
33.153
32.592



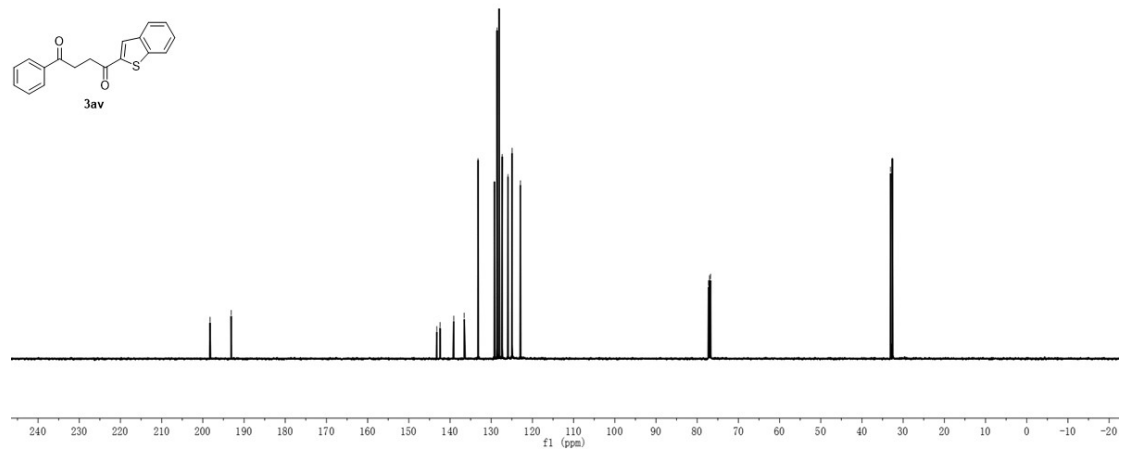


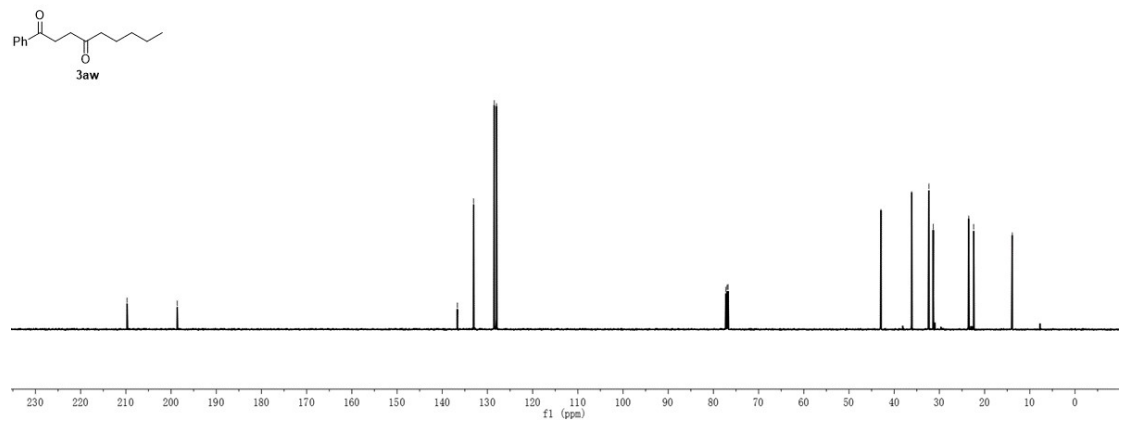
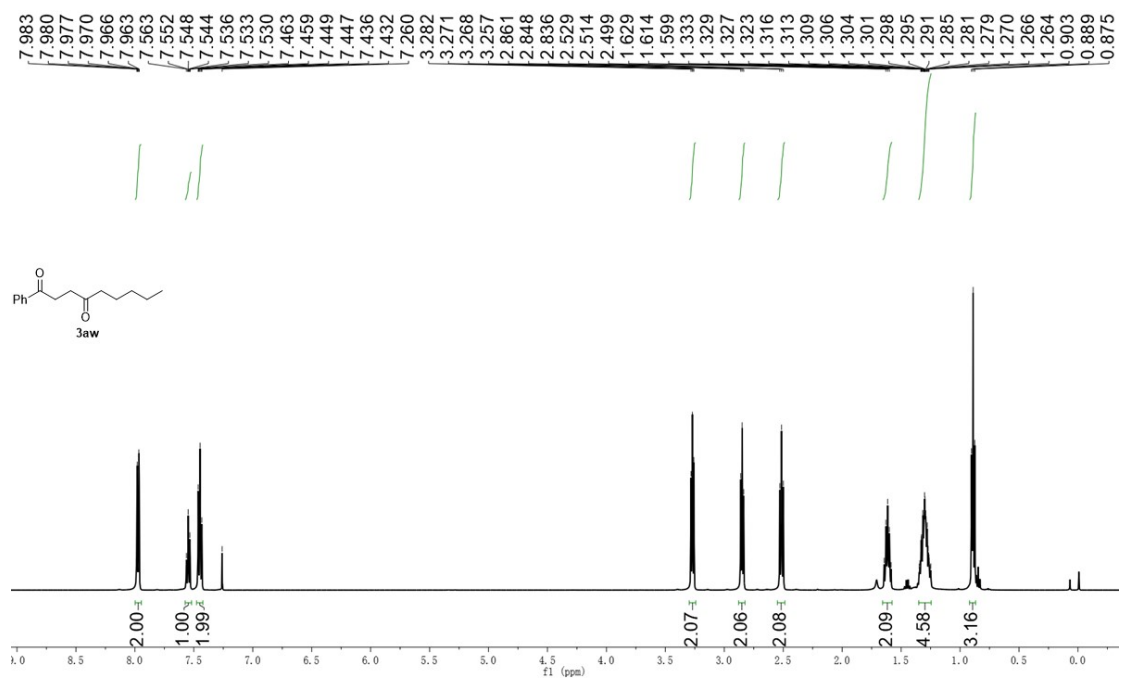
198.250
193.124

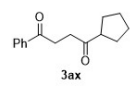
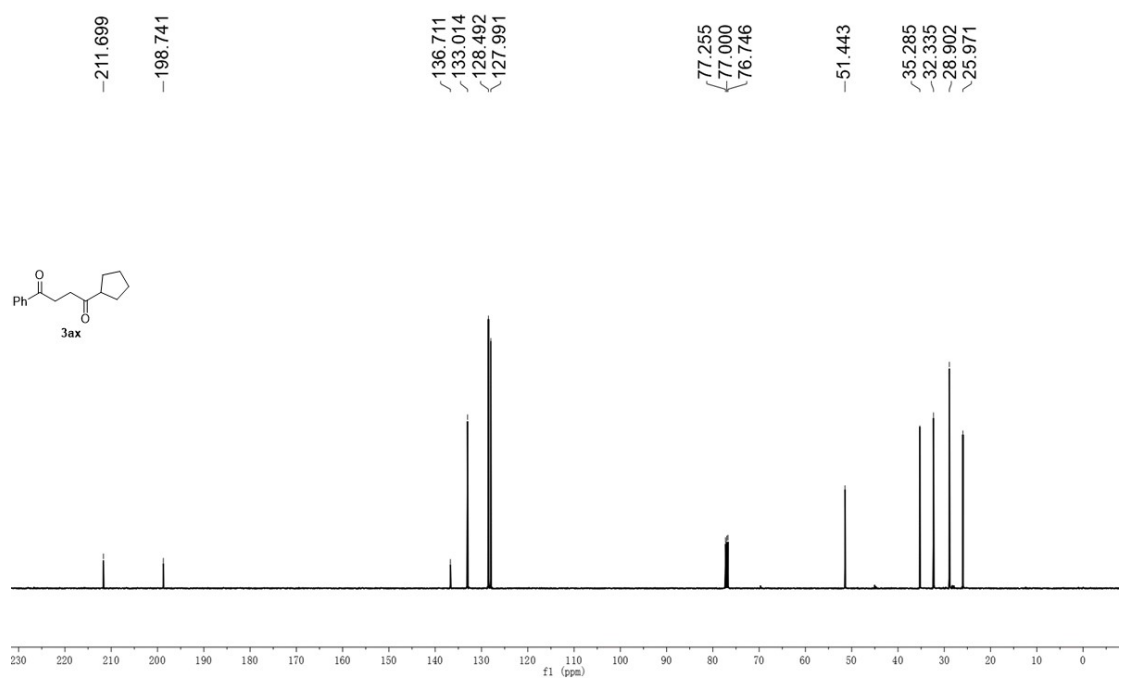
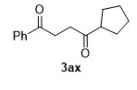
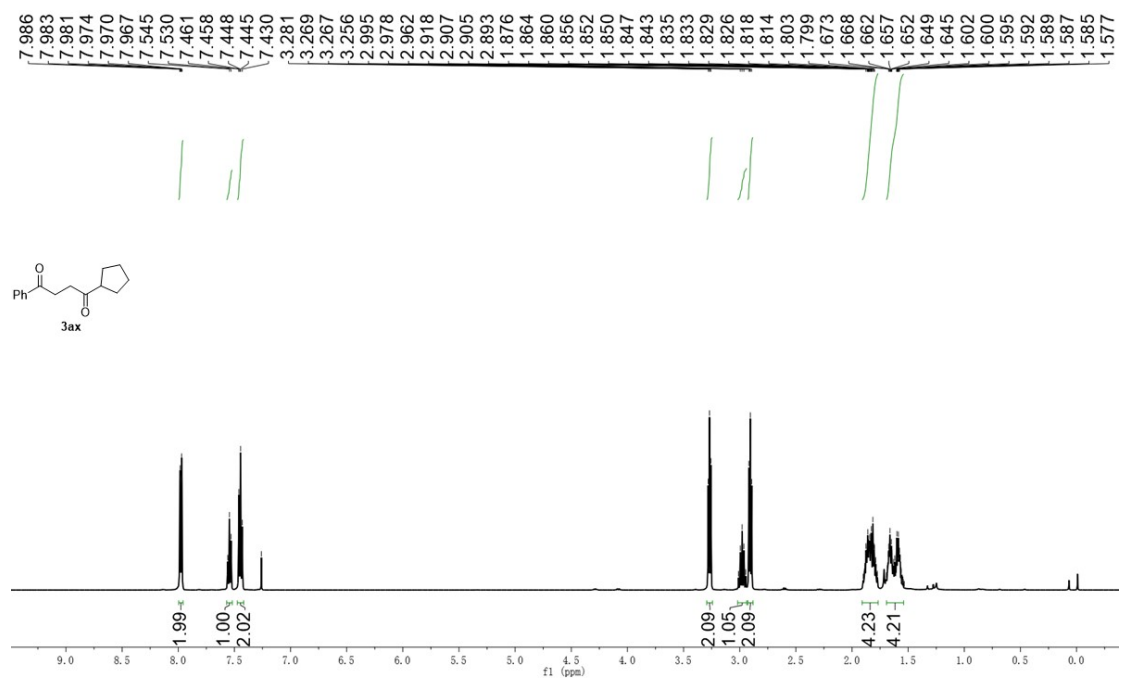
143.213
142.413
139.096
136.549
133.198
129.198
128.576
128.074
127.344
125.933
124.936
122.917

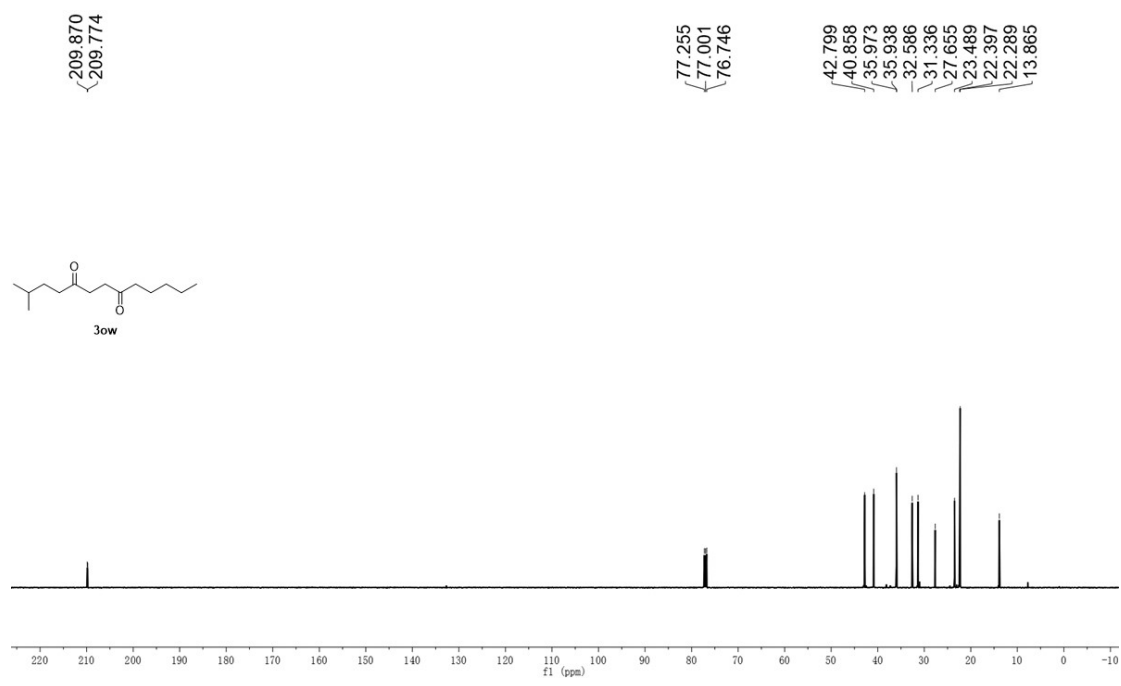
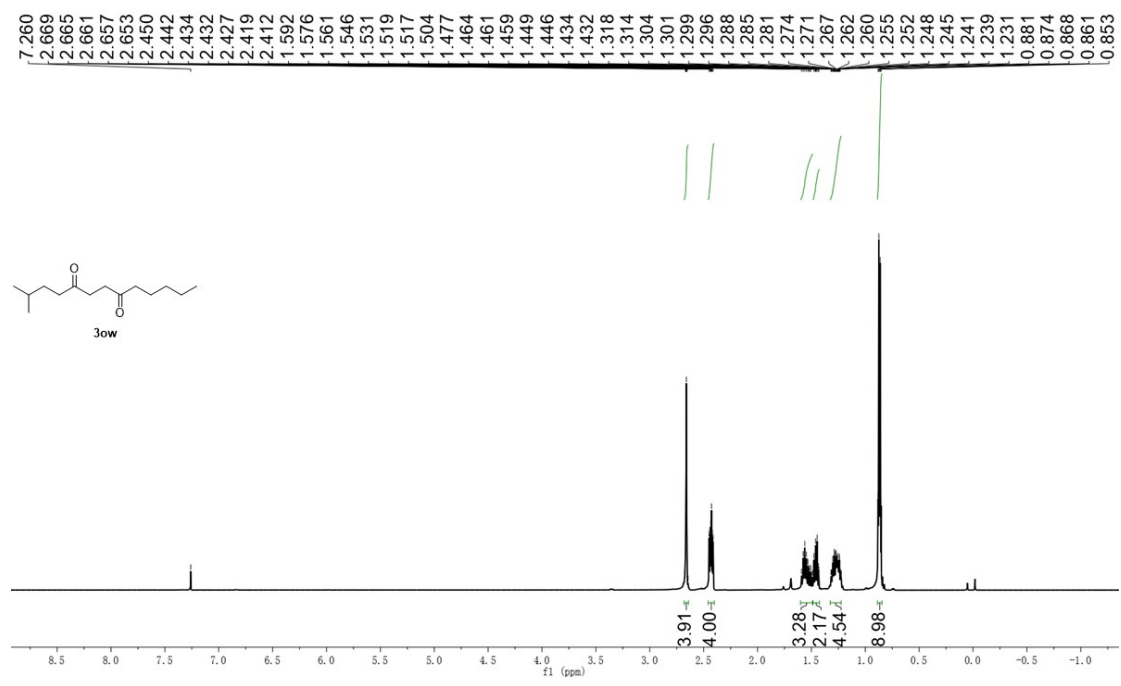
77.255
77.000
76.746

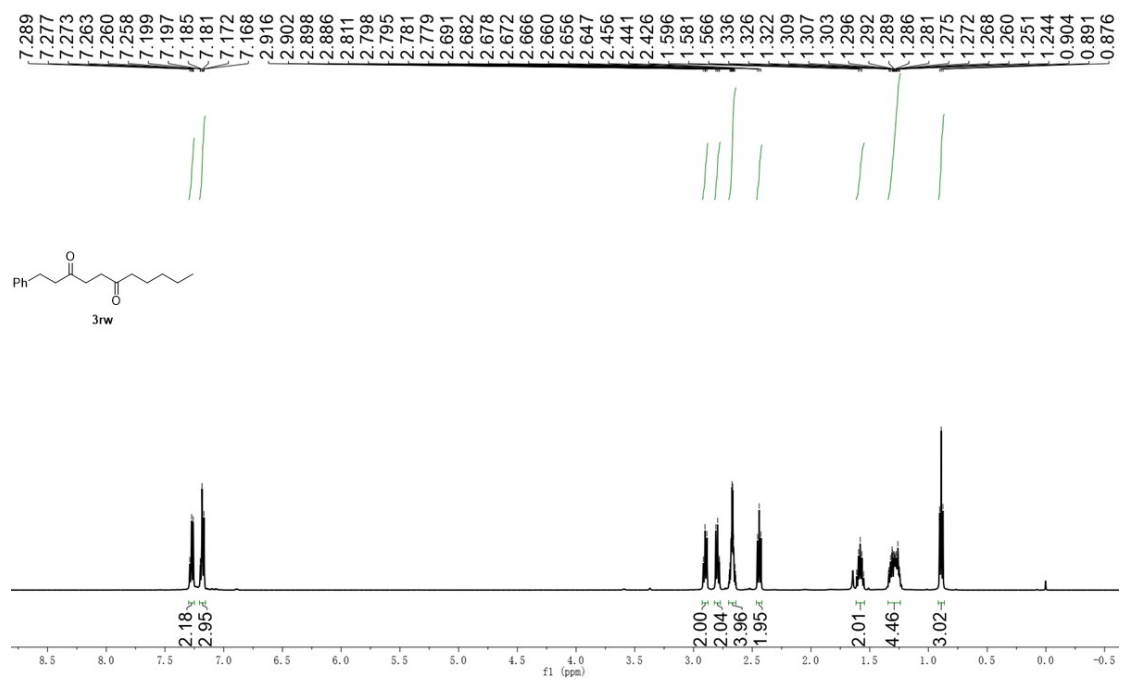
33.061
32.624









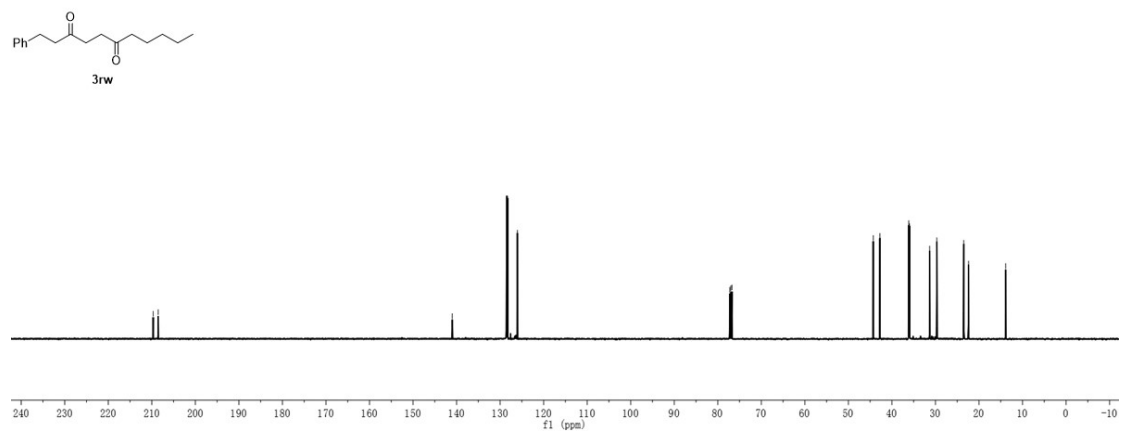


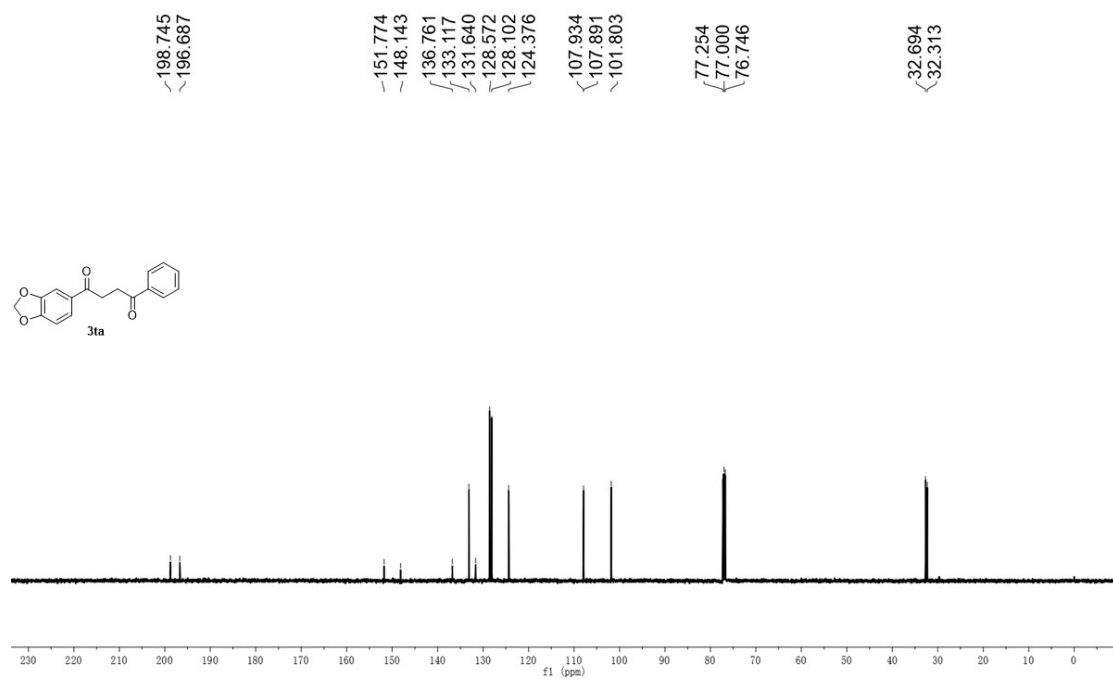
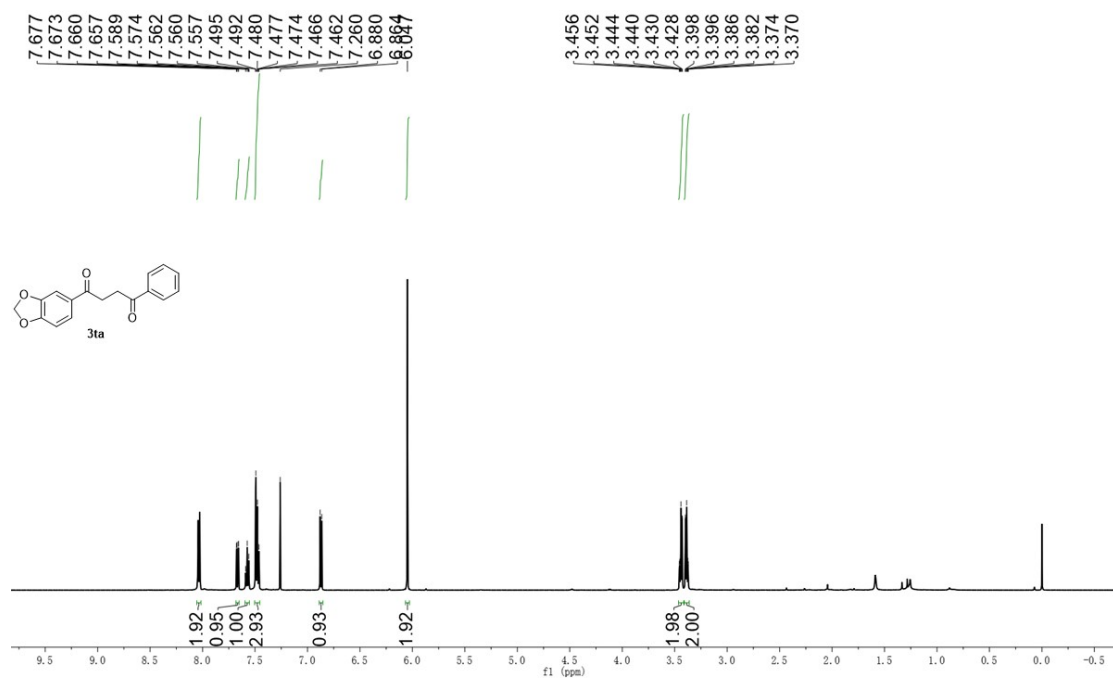
209.682
208.532

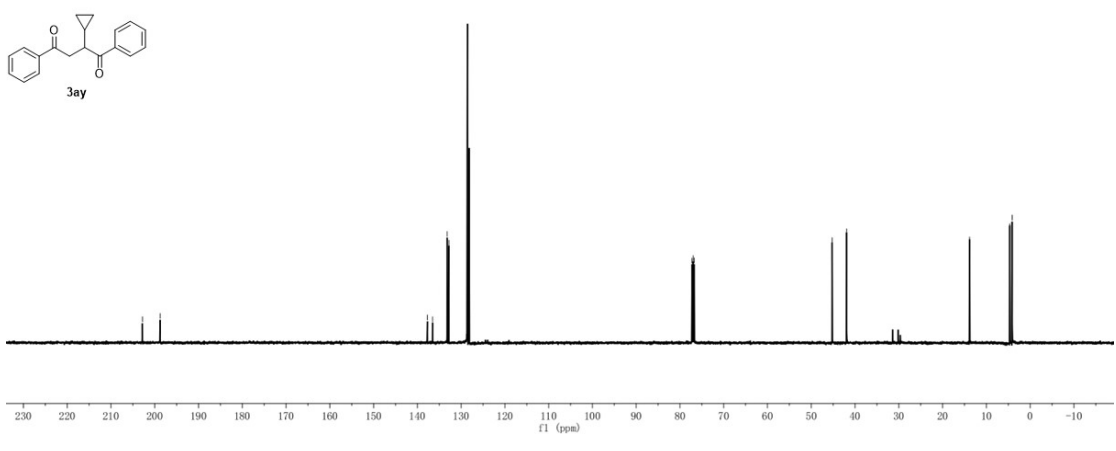
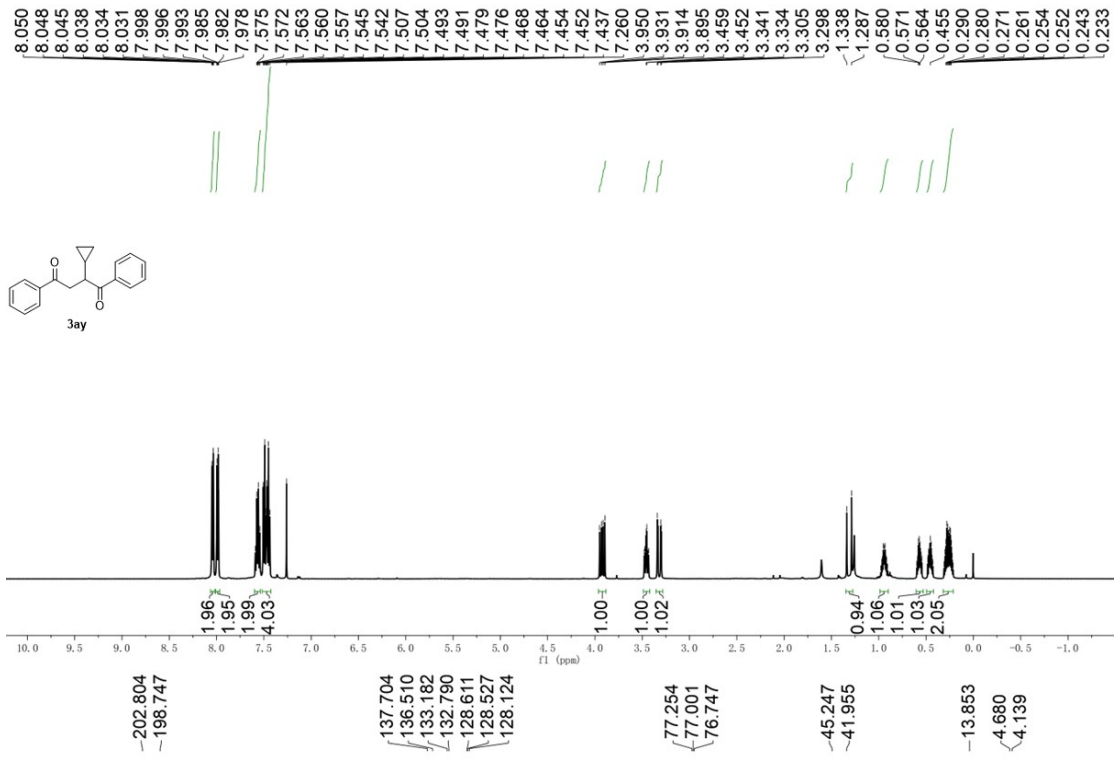
140.983
128.433
128.244
126.034

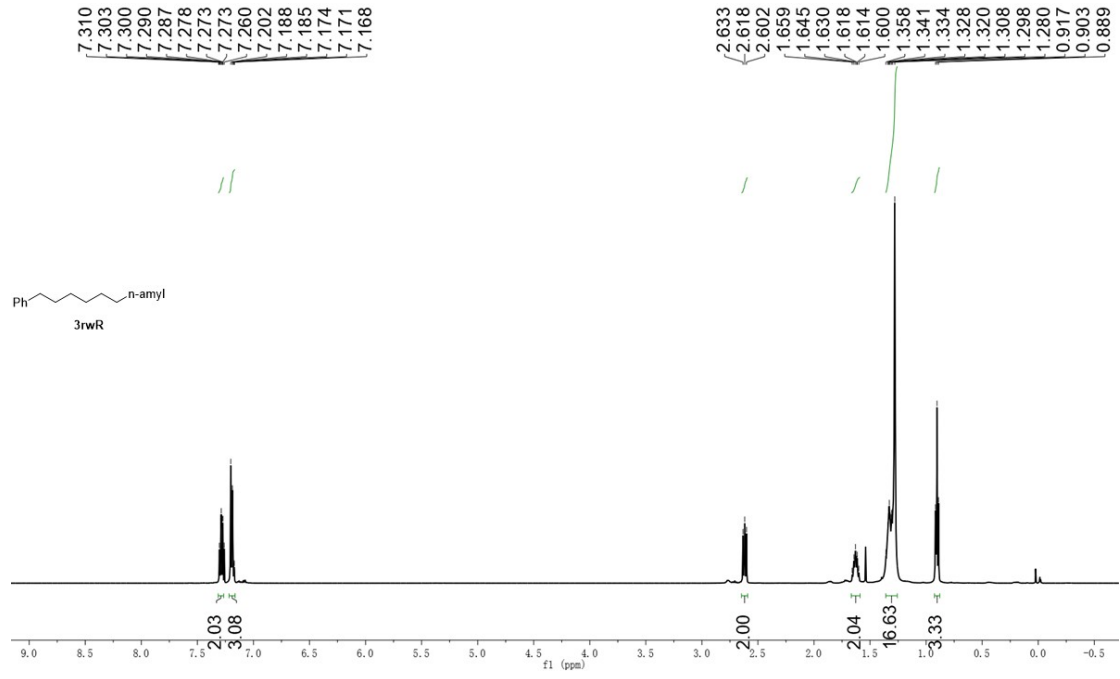
77.255
77.001
76.746

44.282
42.761
36.140
35.971
31.337
29.686
23.493
22.405
13.882









- 142.950
- 128.380, 128.189, 125.514
- 77.254, 77.001, 76.745
- 35.996, 31.921, 31.533, 29.673, 29.636, 29.599, 29.526, 29.350, 22.693
- 14.117

