Supporting Information For

Nickel-catalyzed *γ*-alkylation of cyclopropyl ketones with unactivated primary alkyl chlorides：balancing reactivity and selectivity *via* halide exchange

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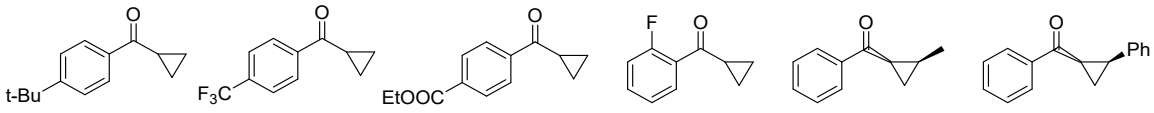
1. General Information

All reactions were carried out under an atmosphere of dry nitrogen. Zn powder was activated by reported procedure [1]. All Ni-salts were purchased from Energy Chemical, Aladdin, Leyan, Bide pharm, and were used as received. All ligands were purchased from Energy Chemical, Aikon, D&B, Laajoo, and were used as received. All solvents were purchased from Energy Chemical and used as received. Other commercial reagents were purchased from Leyan, Bide pharm, Maya Reagent, TCI, J&K, HEOWNS, MERYER, Aladdin, 9dingchem and Energy Chemical, and were used as received.

Reactions were monitored through thin layer chromatography [Nuo Tai SHF254 precoated silica gel plate (0.2-0.3 mm thickness)]. Flash chromatography was performed with LIANG CHEN GUI YUAN flash silica gel (200-300 mesh).

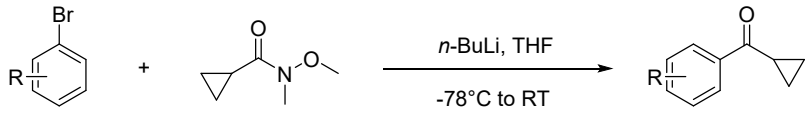
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker Advance 500M NMR spectrometer at ambient temperature in $CDCl_3$ at 500, 125 and 470 MHz, respectively. The chemical shifts are reported in ppm and are referenced to the residual solvent peak for $CDCl_3$ (δ = 7.26 ppm, ^{1}H NMR; δ = 77.16 ppm, ^{13}C NMR). Coupling constants (*J*) are reported in Hertz. Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), etc. GC analyses were performed on a Shimadzu GC-2014C instrument. GC/MS analyses were performed on an Agilent 7000D instrument. High-resolution mass spectral (HRMS) were obtained on a Waters XEVO G2-XS QTOF mass spectrometer with ESI resource.

2. General Procedure for the Synthesis of Aryl Alkyl Ketones



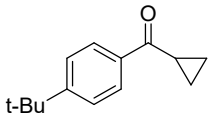
1b **1e** **1f** **1g** (±)-*trans*-**1j** (±)-*trans*-**1k**

Procedure for Preparation of the Cyclopropyl Ketones 1b, 1e and 1g.



According to a ***reported procedure A*** [2], *n*-BuLi (4.2 mL of a 2.5 M solution in n-hexane, 10.5 mmol, 1.05 equiv) is added dropwise to a solution of the corresponding aryl bromide (10 mmol, 1.0 equiv) in anhydrous THF (20 mL) at –78 °C. The mixture is stirred at this temperature for additional 30 min, and a solution of N-methoxy-N methylcyclopropanecarboxamide (1.4 g, 10.5 mmol, 1.05 equiv) is added. The mixture is allowed to warm to room temperature and stirred at this temperature for additional 2 h. The reaction mixture is quenched by the addition of water (10 mL) and saturated aqueous NH_4Cl solution (10 mL). The organic phase is separated, and the aqueous layer is extracted with EtOAc (3 × 20 mL). The combined organic phases are dried over $MgSO_4$ and concentrated under reduced pressure. The residue is purified by flash column chromatography on silica gel using cyclohexane/EtOAc mixtures as eluent to afford the corresponding ketone in analytically pure form.

(4-(tert-butyl)phenyl)(cyclopropyl)methanone (**1b**)



1b

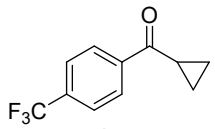
The title compound **1b** was isolated as a white solid (1.66 g, 8.2 mmol, 82% yield)through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 2.67 (tt, *J* = 7.8, 4.5 Hz, 1H), 1.35 (s, 9H), 1.22 (dt, *J* = 6.8, 3.4 Hz, 2H), 1.01 (dq, *J* = 7.2, 3.6 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.2, 156.4, 135.4, 128.0, 125.5, 35.1, 31.1,

17.0, 11.4.

cyclopropyl(4-(trifluoromethyl)phenyl)methanone (**1e**)



1e

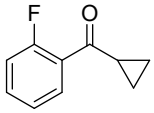
The title compound **1e** was isolated as a clear oil (1.84 g, 8.6 mmol, 86% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 2.67 (tt, J = 7.8, 4.5 Hz, 1H), 1.33 – 1.26 (m, 3H), 1.11 (dq, J = 7.4, 3.7 Hz, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.8, 140.7 (q, *J* = 0.8 Hz), 134.1 (q, *J* = 32.6 Hz), 128.3, 125.6 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 273.07 Hz), 17.6, 12.2.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -63.06.

cyclopropyl(2-fluorophenyl)methanone (**1g**)



1g

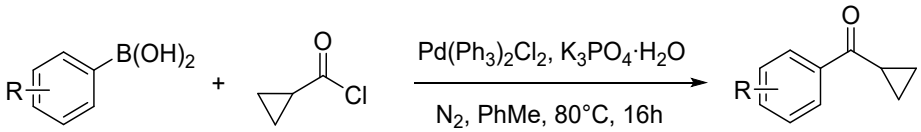
The title compound **1g** was isolated as a clear oil (1.15 g, 7.0 mmol, 70% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (td, *J* = 7.6, 1.9 Hz, 1H), 7.50 (dddd, *J* = 8.3, 7.1, 5.2, 1.9 Hz, 1H), 7.22 (td, *J* = 7.6, 1.1 Hz, 1H), 7.18 – 7.11 (m, 1H), 2.66 (dddd, *J* = 12.3, 7.6, 4.5, 2.7 Hz, 1H), 1.28 (quin, *J* = 3.9 Hz, 2H), 1.07 (dq, *J* = 7.3, 3.6 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 198.6 (d, *J* = 3.8 Hz), 160.7 (d, *J* = 254.3 Hz), 132.9 (d, *J* = 8.9 Hz), 129.3 (d, *J* = 2.7 Hz), 126.2 (d, *J* = 12.9 Hz), 123.3 (d, *J* = 3.6 Hz), 115.6 (d, *J* = 23.5 Hz), 20.4 (d, *J* = 8.8 Hz), 11.4.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -111.51.

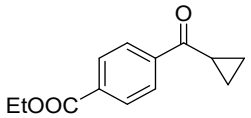
Procedure for Preparation of the Cyclopropyl Ketones 1f.



According to a ***reported procedure B*** [3], a mixture of phenylboronic acid (20 mmol, 1.0 equiv), dichlorobis(triphenylphosphine)palladium (0.4 mmol, 2 mol%), potassium

phosphate tribasic monohydrate (30 mmol, 1.5 equiv), acid chlorides (24 mmol, 1.2 equiv) and toluene (100 mL) were heated at 80 °C for 16 hours. The reaction mixture was cool to room temperature and filtered through a short pad of celite. The solvent was removed under reduced pressure. Then the residue was purified by silica gel flash column chromatography (PE/EA = 10:1) to afford cyclopropylketone.

ethyl 4-(cyclopropanecarbonyl)benzoate (**1f**)



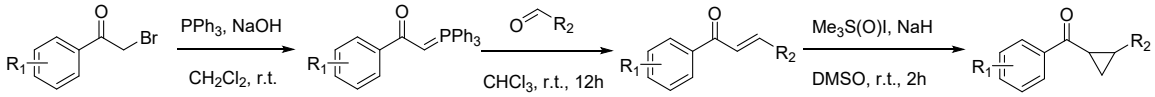
1f

The title compound **1f** was isolated as a clear oil (3.06 g, 14 mmol, 70% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.5 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.68 (tt, *J* = 8.0, 4.5 Hz, 1H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.28 (p, *J* = 3.9 Hz, 2H), 1.10 (dq, *J* = 7.3, 3.6 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.3, 165.9, 141.2, 133.9, 129.7, 127.9, 61.4, 17.6, 14.3, 12.2.

Procedure for Preparation of the Cyclopropyl Ketones 1j and **1k.**



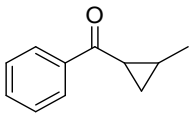
S1 **S2** **S3** **1**

According to a ***reported procedure C*** [4], to a solution of *α*-bromoacetophenone **S1** (20 mmol, 1 equiv) in CH_2Cl_2 (40 mL) was added triphenylphosphine (5.2 g, 20 mmol, 1 equiv) slowly at room temperature. The solution was allowed to stir for 4 h, and the resulting mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2: H_2O (50 mL, 40:60), and NaOH (1.6 g, 40 mmol, 2 equiv) was added. Then the mixture was stirred at room temperature for 1 h before being extracted with CH_2Cl_2 (3×70 mL). The combine organic extracts were washed with brine (3×100 mL), dried, filtered and concentrated under vacuum to give the crude **S2**, which was used without further purification. To a solution of aldehydes (20 mmol, 1 equiv) in $CHCl_3$ (40 mL) at room temperature was added the crude **S2**, and the solution was allowed to stir for 12 h. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate= 20:1) to provide the desired

products **S3**.

A flame-dried round bottom flask was charged with solid NaH (60% in mineral oil, 1.2 equiv), trimethylsulfoxonium iodide (1.2 equiv), and a magnetic stir bar. The flask was placed under N_2 atmosphere, and DMSO (0.35 M) was added dropwise with stirring. After the hydrogen evolution ceased, the reaction mixture was stirred for an additional 15 min, during which the solution became clear. A solution of the α, β-unsaturated ketone **S3** (1 equiv) in DMSO (0.5 M) was added by syringe. The reaction was allowed to stir at room temperature. After 2 h, the reaction was quenched with water, and the mixture was extracted 3× with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate= 20:1) to provide the desired products **1**.

(±)-*trans-(2-methylcyclopropyl)(phenyl)methanone* (**1j)**



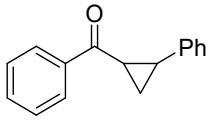
1j

The title compound **1j** was isolated as a clear oil (0.63 g, 3.95 mmol, 79% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 2.39 (dt, *J* = 8.2, 4.2 Hz, 1H), 1.60 (dqt, *J* = 12.2, 6.0, 2.8 Hz, 1H), 1.49 (dt, *J* = 8.5, 4.0 Hz, 1H), 1.22 (d, *J* = 6.0 Hz, 3H), 0.89 (ddd, *J* = 7.7, 6.4, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.2, 138.2, 132.6, 128.5, 128.0, 26.4, 21.3, 20.1, 18.3.

(±)-*trans-(2- phenylcyclopropyl)(phenyl)methanone* (**1k)**



1k

The title compound **1k** was isolated as a clear oil (0.83 g, 3.75 mmol, 75% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

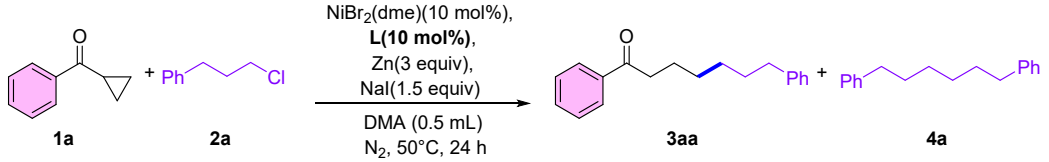
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.95 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48

– 7.43 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.20 – 7.15 (m, 2H), 2.93 – 2.87 (m, 1H), 2.73 – 2.67 (m, 1H), 1.92 (dt, *J* = 9.3, 4.7 Hz, 1H), 1.55 (ddd, *J* = 7.9, 6.6, 4.2 Hz, 1H).

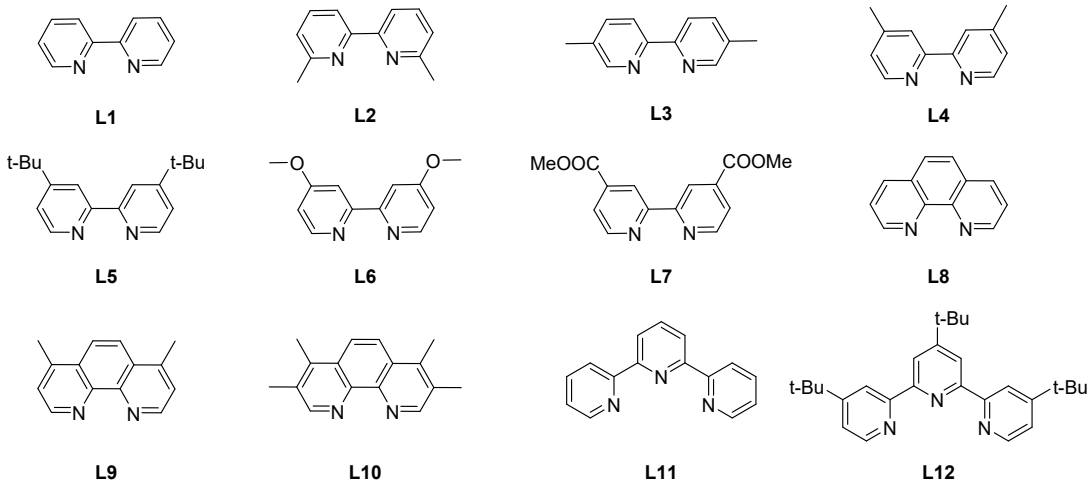
^{13}C NMR (125 MHz, Chloroform-*d*) δ 198.6, 140.5, 137.8, 132.9, 128.6, 128.1, 126.6, 126.3, 30.0, 29.3, 19.2.

3. Optimization of the Reaction Conditions

Table S1. Optimization of the Ligands



1a 2a 3aa 4a

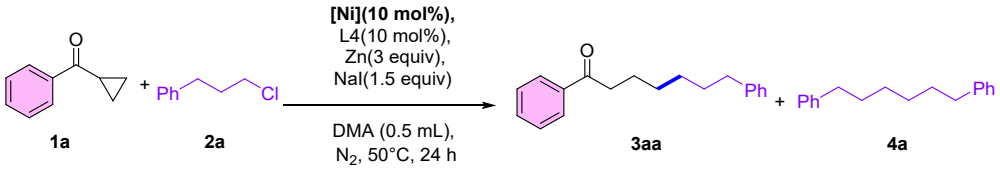


L1 L2 L3 L4 L5 L6 L7 L8 L9 L10 L11 L12

Entry	Ligand	3aa[a]	4a[a]	1a[b]
1	L1	45%	13%	44%
2	L2	N.D.	N.D.	80%
3	L3	64%	6%	23%
4	**L4**	**78%**	**7%**	**N.D.**
5	L5	74%	5%	6%
6	L6	64%	28%	31%
7	L7	21%	18%	62%
8	L8	40%	29%	35%
9	L9	23%	19%	64%
10	L10	61%	15%	N.D.
11	L11	N.D.	36%	84%
12	L12	N.D.	38%	77%

Reaction conditions：**1a** (0.2 mmol), **2a** (0.4 mmol), $NiBr_2$(dme) (10 mol%), ligand (10 mol%), NaI (1.5 equiv), and Zn (3.0 equiv) in DMA (0.5 mL) at 50 °C for 24 h. [a] Yields were detected by GC yields vs hexadecane internal standard. [b] Yields of the recovered **1a** after the reaction. N.D. = not detected.

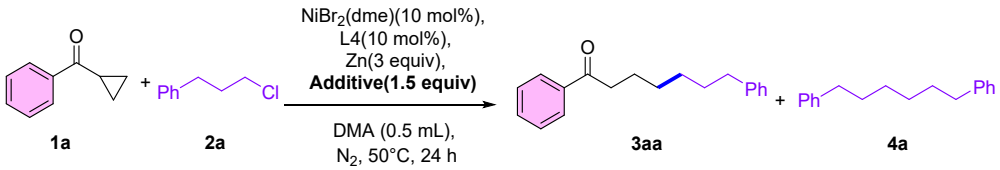
Table S2. Optimization of the Catalysts



Entry	Catalyst	3aa[a]	4a[a]	1a[b]
1	**$NiBr_2$(dme)**	**78%**	**7%**	**N.D.**
2	$NiCl_2$(dme)	67%	8%	13%
3	NiI_2	12%	41%	77%
4	$NiBr_2$	20%	13%	62%
5	$NiCl_2$	61%	11%	N.D.
6	$NiBr_2$·diglyme	67%	13%	24%
7	$NiClO_4·6H_2O$	Trace	13%	73%
8	$Ni(COD)_2$	28%	5%	8%

Reaction conditions：**1a** (0.2 mmol), **2a** (0.4 mmol), [Ni] (10 mol%), L4 (10 mol%), NaI (1.5 equiv), and Zn (3.0 equiv) in DMA (0.5 mL) at 50 °C for 24 h. [a] Yields were detected by GC yields vs hexadecane internal standard. [b] Yields of the recovered **1a** after the reaction. N.D. = not detected.

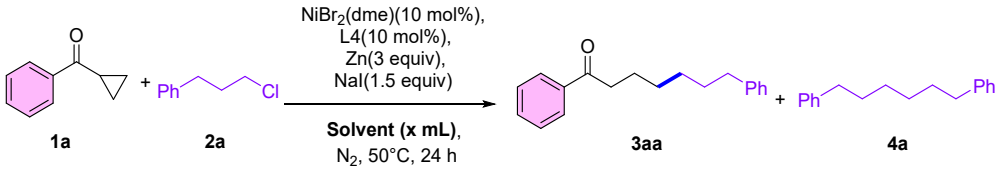
Table S3. Optimization of the Additives



Entry	Additive	3aa[a]	4a[a]	1a[b]
1	**NaI**	**78%**	**7%**	**N.D.**
2	KI	54%	3%	N.D.
3	LiI	61%	12%	15%
4	NH_4I	N.D.	N.D.	N.D.
5	TBAI	61%	9%	20%
6	LiBr	27%	45%	35%
7	NaBr	37%	15%	38%
8	KBr	10%	N.D.	57%
9	TBAB	30%	45%	38%

Reaction conditions：**1a** (0.2 mmol), **2a** (0.4 mmol), $NiBr_2$(dme) (10 mol%), L4 (10 mol%), additive (1.5 equiv), and Zn (3.0 equiv) in DMA (0.5 mL) at 50 °C for 24 h. [a] Yields were detected by GC yields vs hexadecane internal standard. [b] Yields of the recovered **1a** after the reaction. N.D. = not detected.

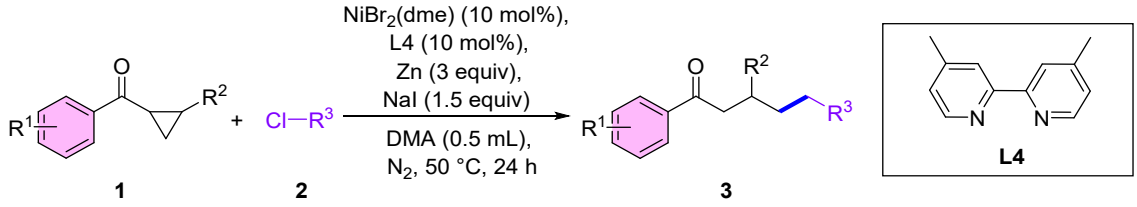
Table S4. Optimization of the Solvents



Entry	Solvent	3aa[a]	4a[a]	1a[b]
1	**DMA (0.5mL)**	**78%**	**7%**	**N.D.**
2	DMA (1.0mL)	16%	31%	70%
3	DMF (0.5mL)	56%	2%	N.D.
4	NMP (0.5mL)	38%	6%	6%
5	THF (0.5mL)	Trace	N.D.	48%
6	CH_3CN (0.5mL)	N.D.	N.D.	46%

Reaction conditions：**1a** (0.2 mmol), **2a** (0.4 mmol), $NiBr_2$(dme) (10 mol%), L4 (10 mol%), NaI (1.5 equiv), and Zn (3.0 equiv) in solvent (x mL) at 50 °C for 24 h. [a] Yields were detected by GC yields vs hexadecane internal standard. [b] Yields of the recovered **1a** after the reaction. N.D. = not detected.

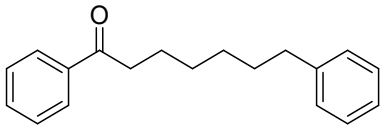
4. Nickel-Catalyzed Ring Opening of Cyclopropyl Ketones with Alkyl Chlorides



To a Schlenk tube (10 mL) equipped with a stir bar was added $NiBr_2$(dme) (6.2 mg, 0.02 mmol, 10 mol%), Ligand **L4** (3.7 mg, 0.02 mmol, 10 mol%) under an argon atmosphere inside a glove box at 25 °C. Next, 0.5 mL of dry DMA was added via syringe. The catalyst/ligand solution was stirred for 1 hour at 25 °C inside the glove box. Subsequently, removed from the glove box, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this solution, NaI (45.0 mg, 0.3 mmol, 1.5 equiv), Zn powder (39.2 mg, 0.6 mmol, 3 equiv), cyclopropyl(phenyl)methanone (**1**) (0.2 mmol, 1.0 equiv) and alkyl chloride (**2**) (0.4 mmol, 2.0 equiv) was added successively under nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 24 hours. The resulting black solution was cooled to room temperature, passed through a plug of silica gel (200-300 mesh) and the silica gel was rinsed with 5 mL of ethyl acetate to afford a yellow solution. The solvent and volatile materials were removed by rotary evaporator. The crude residue was purified by flash column chromatography on silica gel to furnish the corresponding product **3** in 72% yield (38.3 mg).

5. Analytical Data of Substrates and Products

1,7-diphenylheptan-1-one (3aa)



3aa

The title compound **3aa** was isolated as a clear oil (38.3 mg, 72%); R_f = 0.45 (petroleum ether:ethyl acetate = 20:1).

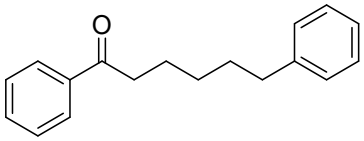
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.17 (d, *J* = 7.3 Hz, 3H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.74 (quin, *J* = 7.0 Hz, 2H), 1.67 – 1.59 (m, 3H), 1.45 – 1.34

(m, 4H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.6, 142.7, 137.1, 132.9, 128.6, 128.4, 128.3, 128.1, 125.6, 38.6, 35.9, 31.3, 29.2, 29.1, 24.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{22}O$: 267.1749, found: 267.1751.

1,6-diphenylhexan-1-one (3ab) [5]



3ab

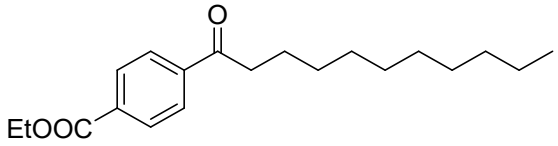
The title compound **3ab** was isolated as a clear oil (31.8 mg, 63%); R_f = 0.55 (petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 – 7.92 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.14 (m, 3H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H), 1.78 (quin, *J* = 7.5 Hz, 2H), 1.68 (quin, *J* = 7.7 Hz, 2H), 1.43 (quin, *J* = 7.7 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.4, 142.6, 137.1, 132.9, 128.6, 128.4, 128.3, 128.1, 125.7, 38.5, 35.8, 31.3, 29.0, 24.2.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{20}O$: 275.1412, found: 275.1415.

ethyl 4-undecanoylbenzoate (3fc)



3fc

The title compound **3ac** was isolated as a white solid (43.3 mg, 68%); R_f = 0.45 (petroleum ether:ethyl acetate = 20:1).

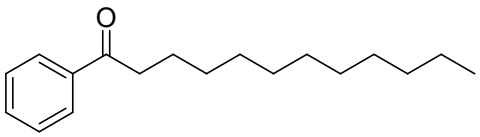
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 1.74 (quin, *J* = 7.4 Hz, 2H), 1.45 – 1.20 (m, 17H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.1, 165.8, 140.2, 134.0, 129.8, 127.9, 61.4, 39.0, 31.9, 29.58, 29.50, 29.47, 29.3, 24.2, 22.7, 14.3, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{30}O_3$: 319.2273, found: 319.2273.

Melting point: 49.2 - 49.7 °C.

1-phenyldodecan-1-one (3ad)[5]



3ad

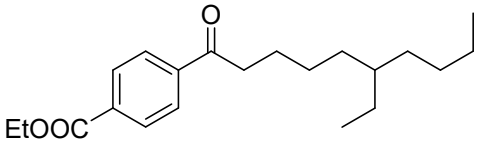
The title compound **3ad** was isolated as a white solid (37.5 mg, 72%); R_f = 0.55 (petroleum ether:ethyl acetate = 60:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.73 (quin, *J* = 7.4 Hz, 2H), 1.43 – 1.20 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.6, 137.1, 132.9, 128.5, 128.1, 38.7, 31.9, 29.63, 29.62, 29.52, 29.49, 29.4, 29.3, 24.4, 22.7, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{28}O$: 261.2218, found: 261.2223.

ethyl 4-(6-ethyldecanoyl)benzoate (3fe)



3fe

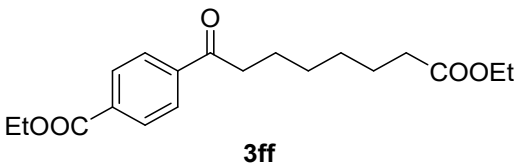
The title compound **3ae** was isolated as a clear oil (17.9 mg, 27%); R_f = 0.5 (petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.5 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H), 1.73 (quin, *J* = 7.4 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.38 – 1.19 (m, 14H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.1, 165.8, 140.2, 134.1, 129.8, 127.9, 61.4, 39.1, 38.7, 33.0, 32.8, 29.0, 26.5, 25.8, 24.7, 23.1, 14.3, 14.2, 10.9.

HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{21}H_{32}O_3$: 371.1988, found: 371.1994.

ethyl 4-(8-ethoxy-8-oxooctanoyl)benzoate (3ff)



3ff

The title compound **3af** was isolated as a white solid (47.5 mg, 71%); R_f = 0.5 (petroleum

ether:ethyl acetate = 6:1).

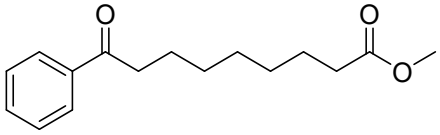
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.99 (t, *J* = 7.3 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.75 (quin, *J* = 7.3 Hz, 2H), 1.65 (quin, *J* = 7.5 Hz, 2H), 1.46 – 1.34 (m, 7H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.8, 173.7, 165.8, 140.2, 134.1, 129.8, 127.9, 61.4, 60.2, 38.8, 34.3, 28.93, 28.90, 24.8, 23.9, 14.27, 14.25.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{26}O_5$: 335.1858, found: 335.1867.

Melting point: 56.5 – 57.0 °C.

methyl 9-oxo-9-phenylnonanoate (3ag)



3ag

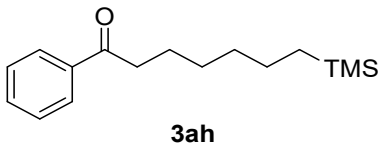
The title compound **3ag** was isolated as a clear oil (17.8 mg, 34%); R_f = 0.5 (petroleum ether:ethyl acetate = 10:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.66 (s, 3H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.73 (quin, *J* = 7.4 Hz, 2H), 1.63 (quin, *J* = 7.4 Hz, 2H), 1.43 – 1.31 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.5, 174.3, 137.1, 132.9, 128.6, 128.1, 51.5, 38.5, 34.1, 29.2, 29.1, 29.0, 24.9, 24.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{22}O_3$: 263.1647, found: 263.1651.

1-phenyl-7-(trimethylsilyl)heptan-1-one (3ah)



3ah

The title compound **3ah** was isolated as a clear oil (33.6 mg, 64%); R_f = 0.55 (petroleum ether:ethyl acetate = 40:1).

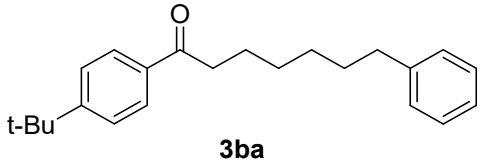
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.73 (quin, *J* = 7.2 Hz, 2H), 1.43 – 1.34 (m, 4H), 0.52 – 0.44 (m, 2H), -0.03 (s, 9H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 202.1, 138.6, 134.3, 130.0, 129.5, 40.1, 34.9,

30.6, 25.8, 25.2, 18.1, -0.2.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{26}OSi$: 285.1651, found: 285.1656.

1-(4-(tert-butyl)phenyl)-7-phenylheptan-1-one (3ba)



3ba

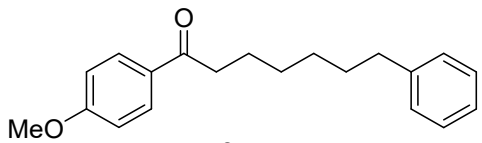
The title compound **3ba** was isolated as a yellow oil (23.8 mg, 37%); R_f = 0.45 (petroleum ether:ethyl acetate = 30:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.60 (t, *J* = 7.4 Hz, 2H), 1.73 (quin, *J* = 7.4 Hz, 2H), 1.63 (quin, *J* = 7.4 Hz, 2H), 1.43 – 1.36 (m, 4H), 1.34 (s, 9H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.3, 156.6, 142.8, 134.5, 128.4, 128.3, 128.1, 125.6, 125.5, 38.5, 35.9, 35.1, 31.3, 31.1, 29.3, 29.1, 24.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{30}O$: 323.2375, found: 323.2379.

1-(4-methoxyphenyl)-7-phenylheptan-1-one (3ca)



3ca

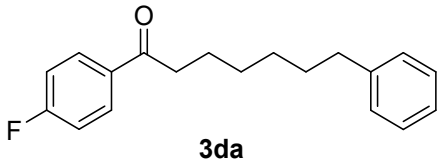
The title compound **3ca** was isolated as a clear oil (19.5 mg, 33%); R_f = 0.45 (petroleum ether:ethyl acetate = 10:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.19 – 7.14 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.60 (t, 2H), 1.72 (quin, *J* = 7.4 Hz, 2H), 1.63 (quin, *J* = 7.5 Hz, 2H), 1.45 – 1.34 (m, 4H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.2, 163.3, 142.8, 130.3, 130.2, 128.4, 128.3, 125.6, 113.7, 55.5, 38.3, 35.9, 31.4, 29.3, 29.2, 24.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}O_2$: 297.1854, found: 297.1851.

1-(4-fluorophenyl)-7-phenylheptan-1-one (3da) [6]



3da

The title compound **3da** was isolated as a yellow oil (48.3 mg, 85%); R_f = 0.55 (petroleum ether:ethyl acetate = 20:1).

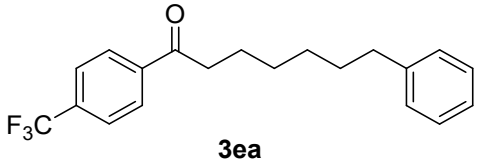
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.20 – 7.08 (m, 5H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 1.73 (quin, *J* = 7.3 Hz, 2H), 1.63 (quin, *J* = 7.5 Hz, 2H), 1.45 – 1.34 (m, 4H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 198.9, 165.7 (d, *J* = 254.7 Hz), 142.7, 133.5 (d, *J* = 3.3 Hz), 130.7 (d, *J* = 9.4 Hz), 128.4, 128.3, 125.6, 115.6 (d, *J* = 21.8 Hz), 38.5, 35.9, 31.3, 29.2, 29.1, 24.3.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -105.73.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}FO$: 285.1654, found: 285.1654.

7-phenyl-1-(4-(trifluoromethyl)phenyl)heptan-1-one (3ea)



3ea

The title compound **3ea** was isolated as a white solid (54.8 mg, 82%); R_f = 0.55 (petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.19 – 7.14 (m, 3H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 1.75 (quin, *J* = 7.3 Hz, 2H), 1.64 (quin, *J* = 7.5 Hz, 2H), 1.46 – 1.35 (m, 4H).

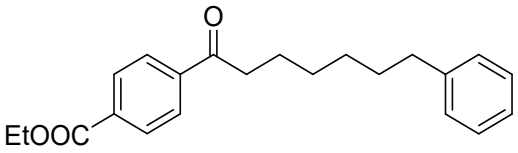
^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.4, 142.7, 139.7, 134.2 (p, *J* = 32.6 Hz), 128.40, 128.36, 128.3, 125.66 (p, *J* = 3.7 Hz), 125.64, 123.6 (p, *J* = 273.3 Hz), 38.9, 35.9, 31.3, 29.10, 29.05, 24.0.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -63.08.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}F_3O$: 335.1622, found: 335.1623.

Melting point: 39.8 – 40.3 °C.

Ethyl 4-(7-phenylheptanoyl)benzoate (3fa)



3fa

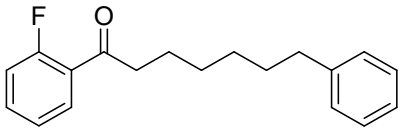
The title compound **3fa** was isolated as a clear oil (49.4 mg, 73%); R_f = 0.45 (petroleum ether:ethyl acetate = 15:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.20 – 7.14 (m, 3H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.74 (quin, *J* = 7.3 Hz, 2H), 1.64 (quin, *J* = 7.5 Hz, 2H), 1.46 – 1.36 (m, 7H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.0, 165.8, 142.7, 140.2, 134.1, 129.8, 128.4, 128.3, 127.9, 125.6, 61.4, 38.9, 35.9, 31.3, 29.12, 29.06, 24.1, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{26}O_3$: 339.1960, found: 339.1959.

1-(2-fluorophenyl)-7-phenylheptan-1-one (3ga)



3ga

The title compound **3ga** was isolated as a clear oil (33.0 mg, 58%); R_f = 0.45 (petroleum ether:ethyl acetate = 15:1).

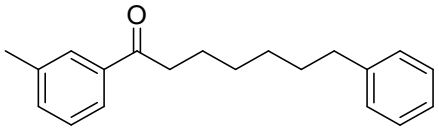
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (td, *J* = 7.6, 2.0 Hz, 1H), 7.49 (dddd, *J* = 8.3, 7.1, 5.2, 1.9 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 3H), 7.12 (ddd, *J* = 11.2, 8.4, 0.8 Hz, 1H), 2.96 (td, *J* = 7.3, 3.0 Hz, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 1.71 (quin, *J* = 7.2 Hz, 2H), 1.63 (quin, *J* = 7.6 Hz, 2H), 1.44 – 1.34 (m, 4H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.0 (d, J = 4.1 Hz), 161.8 (d, J = 254.6 Hz), 142.8, 134.3 (d, *J* = 8.8 Hz), 130.6 (d, *J* = 2.8 Hz), 128.4, 128.2, 126.0 (d, *J* = 13.4 Hz),125.6, 124.4 (d, *J* = 3.4 Hz), 116.6 (d, *J* = 24.0 Hz), 43.6 (d, *J* = 6.9 Hz), 35.9, 31.3, 29.1, 23.94, 23.93.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -109.71.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}FO$: 285.1654, found: 285.1657.

7-phenyl-1-(m-tolyl)heptan-1-one (3ha)



3ha

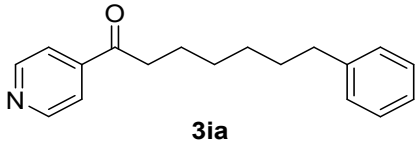
The title compound **3ha** was isolated as a yellow oil (34.2 mg, 61%); R_f = 0.6 (petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 – 7.70 (m, 2H), 7.38 – 7.31 (m, 2H), 7.27 (t, *J* = 7.6 Hz, 3H), 7.20 – 7.13 (m, 3H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 2.41 (s, 3H), 1.73 (quin, *J* = 7.4 Hz, 2H), 1.63 (quin, *J* = 7.5 Hz, 2H), 1.45 – 1.35 (m, 4H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.8, 142.8, 138.3, 137.2, 133.6, 128.6, 128.43, 128.41, 128.3, 125.6, 125.3, 38.6, 35.9, 31.3, 29.2, 29.1, 24.3, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}O$: 281.1905, found: 281.1910.

7-phenyl-1-(pyridin-4-yl)heptan-1-one (3ia)



3ia

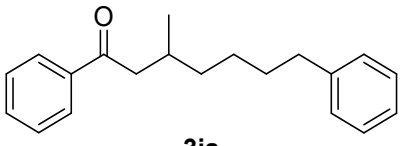
The title compound **3ia** was isolated as a brown oil (35.8 mg, 67%); R_f = 0.5 (petroleum ether:ethyl acetate = 2:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.82 – 8.77 (m, 2H), 7.73 – 7.68 (m, 2H), 7.30 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 2.95 (t, *J* = 7.3 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.74 (quin, *J* = 7.3 Hz, 3H), 1.64 (quin, *J* = 7.5 Hz, 2H), 1.45 – 1.35 (m, 4H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.8, 151.0, 142.8, 142.6, 128.4, 128.3, 125.7, 121.1, 38.8, 35.9, 31.2, 29.03, 29.00, 23.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{21}NO$: 290.1521, found: 290.1518.

(S)-3-methyl-1,7-diphenylheptan-1-one (3ja) [7]



3ja

The title compound **3ja** was isolated as a clear oil (34.7 mg, 62%); R_f = 0.45 (petroleum ether:ethyl acetate = 30:1).

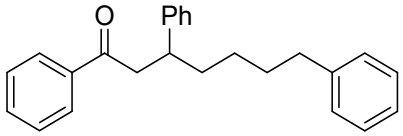
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H),

7.45 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.19 – 7.14 (m, 3H), 2.93 (dd, *J* = 15.8, 5.7 Hz, 1H), 2.75 (dd, *J* = 15.8, 7.9 Hz, 1H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.20 – 2.12 (m, 1H), 1.65 – 1.57 (m, 2H), 1.46 – 1.38 (m, 2H), 1.32 – 1.21 (m, 2H), 0.95 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.4, 142.7, 137.5, 132.9, 128.6, 128.4, 128.3, 128.1, 125.6, 46.0, 36.9, 35.9, 31.6, 29.8, 26.7, 20.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}O$: 281.1905, found: 281.1909.

(S)-1,3,7-triphenylheptan-1-one (3ka) [7]



3ka

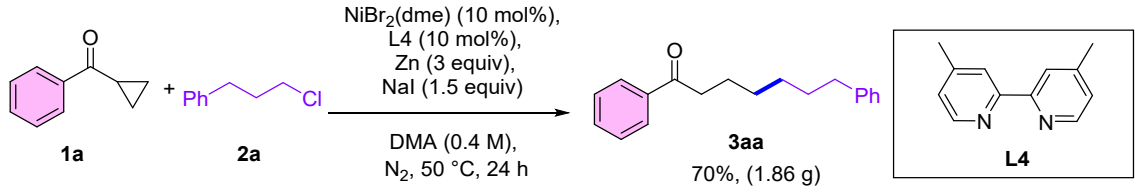
The title compound **3ka** was isolated as a clear oil (21.2 mg, 31%); R_f = 0.55 (petroleum ether:ethyl acetate = 20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.07 (m, 11H), 3.39 – 3.16 (m, 3H), 2.60 – 2.43 (m, 2H), 1.81 – 1.64 (m, 2H), 1.61 – 1.52 (m, 2H), 1.27 – 1.15 (m, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.1, 144.9, 142.7, 137.2, 132.9, 128.5, 128.5, 128.3, 128.2, 128.1, 127.6, 126.3, 125.6, 45.9, 41.2, 36.1, 35.7, 31.4, 27.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{26}O$: 343.2062, found: 343.2069.

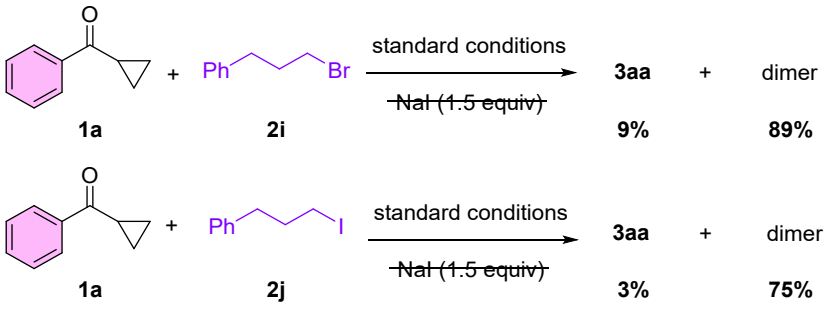
6. Scale-up to 10.0 mmol for the Synthesis of 3aa.



To a Schlenk tube (100 mL) equipped with a stir bar was added $NiBr_2$(dme) (309 mg, 1.0 mmol, 10 mol %), Ligand **L4** (184 mg, 1.0 mmol, 10 mol %) under an argon atmosphere inside a glove box at 25 °C. Next, 25 mL of dry DMA was added via syringe. The catalyst/ligand solution was stirred for 1 hour at 25 °C inside the glove box. Subsequently, removed from the glove box, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this solution, NaI (2.25 g, 15.0 mmol, 1.5 equiv), Zn powder (1.96 g, 30.0 mmol, 3 equiv), cyclopropyl(phenyl)methanone (**1a**) (10.0 mmol, 1.0 equiv) and alkyl chloride (**2a**) (20.0 mmol, 2.0 equiv) was added successively under nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 24 hours. The resulting black solution was cooled to room temperature, passed through a plug of silica gel (200–300 mesh) and the silica gel was rinsed with 75 mL of ethyl acetate to afford a yellow solution. The solvent and volatile materials were removed by rotary evaporator. The crude residue was purified by flash column chromatography on silica gel to provide the corresponding product **3aa** in 70% yield (1.86 g).

7. Control Experiments.

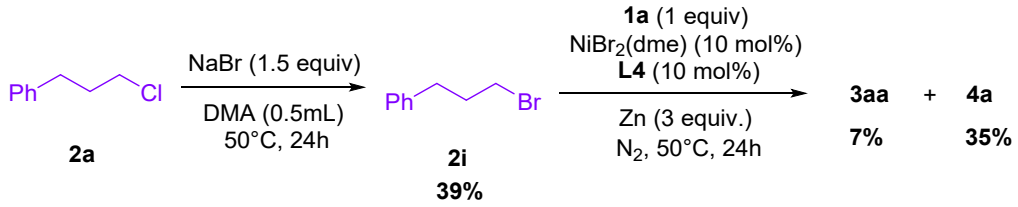
A)



A dry test tube equipped with a stirring bar was charged with $NiBr_2$(dme) (6.2 mg, 0.02 mmol 10 mol %), **L4** (3.7 mg, 0.02 mmol, 10 mol %) under an argon atmosphere inside a glove box at 25 °C. Next, 0.5 mL of dry DMA was added via syringe. The catalyst/ligand solution was stirred for 1 hour at 25 °C inside the glove box. Subsequently, removed from

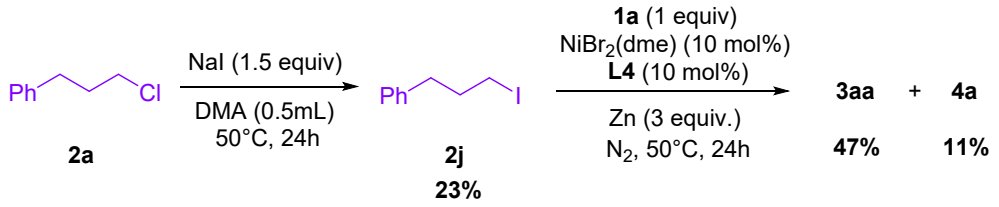
the glove box, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this solution, NaI (45.0 mg, 0.3 mmol, 1.5 equiv), Zn powder (39.2 mg, 0.6 mmol, 3 equiv), cyclopropyl(phenyl)methanone (**1a**) (0.2 mmol, 1.0 equiv) and alkyl bromide (**2i**) or alkyl iodide (**2j**) (0.4 mmol, 2.0 equiv) was added successively under nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 24 hours. The reaction was subjected to GC, GC/MS and NMR analysis.

B)



A dry test tube equipped with a stirring bar was charged with NaBr (31.0 mg, 0.3 mmol, 1.5 equiv), the Schlenk tube was evacuated and filled with nitrogen (three cycles), 0.5 mL of dry DMA and alkyl chloride (**2a**) (0.2 mmol, 1.0 equiv) was then added via syringe, respctively. The reaction mixture was stirred at 50 °C for 24 hours. To this solution, $NiBr_2$(dme) (6.2 mg, 0.02 mmol 10 mol %), **L4** (3.7 mg, 0.02 mmol, 10 mol %), Zn powder (39.2 mg, 0.6 mmol, 3 equiv) and cyclopropyl(phenyl)methanone (**1a**) (0.2 mmol, 1.0 equiv) was added successively inside the glove box. Subsequently, removed from the glove box, the reaction mixture was stirred at 50 °C for 24 hours again. The reaction was subjected to GC, GC/MS and NMR analysis.

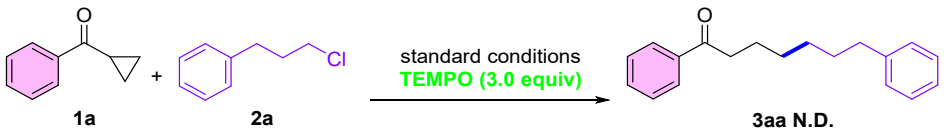
C)



A dry test tube equipped with a stirring bar was charged with NaI (45.0 mg, 0.3 mmol, 1.5 equiv), the Schlenk tube was evacuated and filled with nitrogen (three cycles), 0.5 mL of dry DMA and alkyl chloride (**2a**) (0.2 mmol, 1.0 equiv) was then added via syringe, respctively. The reaction mixture was stirred at 50 °C for 24 hours. To this solution, $NiBr_2$(dme) (6.2 mg, 0.02 mmol 10 mol %), **L4** (3.7 mg, 0.02 mmol, 10 mol %), Zn powder (39.2 mg, 0.6 mmol, 3 equiv) and cyclopropyl(phenyl)methanone (**1a**) (0.2 mmol,

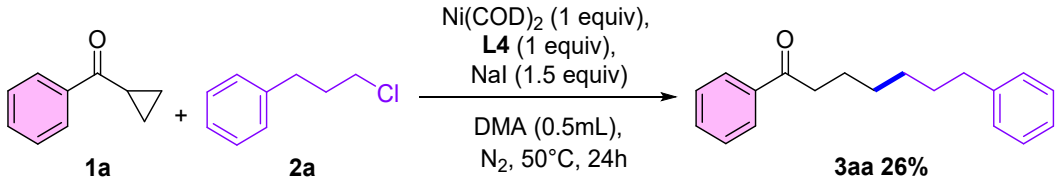
1.0 equiv) was added successively inside the glove box. Subsequently, removed from the glove box, the reaction mixture was stirred at 50 °C for 24 hours again. The reaction was subjected to GC, GC/MS and NMR analysis.

D)



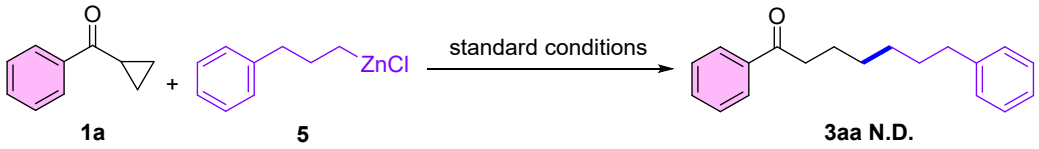
A dry test tube equipped with a stirring bar was charged with $NiBr_2$(dme) (6.2 mg, 0.02 mmol 10 mol %), **L4** (3.7 mg, 0.02 mmol, 10 mol %) under an argon atmosphere inside a glove box at 25 °C. Next, 0.5 mL of dry DMA was added via syringe. The catalyst/ligand solution was stirred for 1 hour at 25 °C inside the glove box. Subsequently, removed from the glove box, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this solution, NaI (45.0 mg, 0.3 mmol, 1.5 equiv), Zn powder (39.2 mg, 0.6 mmol, 3 equiv), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv), cyclopropyl(phenyl)methanone (**1a**) (0.2 mmol, 1.0 equiv) and alkyl chloride (**2a**) (0.4 mmol, 2.0 equiv) was added successively under nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 24 hours. The reaction was subjected to GC, GC/MS and NMR analysis.

E)



A dry test tube equipped with a stirring bar was charged with $NiBr_2$(dme) (55.0 mg, 0.2 mmol 1.0 equiv), **L4** (36.8 mg, 0.2 mmol, 1.0 equiv) under an argon atmosphere inside a glove box at 25 °C. Next, 0.5 mL of dry DMA was added via syringe. The catalyst/ligand solution was stirred for 1 hour at 25 °C inside the glove box. Subsequently, removed from the glove box, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this solution, NaI (45.0 mg, 0.3 mmol, 1.5 equiv), cyclopropyl(phenyl)methanone (**1a**) (0.2 mmol, 1.0 equiv) and alkyl chloride (**2a**) (0.4 mmol, 2.0 equiv) was added successively under nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 24 hours. The reaction was subjected to GC, GC/MS and NMR analysis.

F)



1a **5** **3aa N.D.**

A dry test tube equipped with a stirring bar was charged with $NiBr_2$(dme) (3.1 mg, 0.01 mmol 10 mol %), **L4** (1.8 mg, 0.01 mmol, 10 mol %) under an argon atmosphere inside a glove box at 25 °C. Next, 0.5 mL of dry DMA was added *via* syringe. The catalyst/ligand solution was stirred for 1 hour at 25 °C inside the glove box. Subsequently, removed from the glove box, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this solution, NaI (22.5 mg, 0.15 mmol, 1.5 equiv), cyclopropyl(phenyl)methanone (**1a**) (0.1 mmol, 1.0 equiv) and organozinc reagent (**5**)[8] (0.8 mL of a 0.25 M solution in THF, 0.2 mmol, 2.0 equiv) was added successively under nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 24 hours. The reaction was subjected to GC, GC/MS and NMR analysis.

8. References

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[4] a) Chen, Y.-Z.; Wang, N.; Hou, Z.-R.; Zhou, X.-L.; Li, X.; Gao, F.; Jiang, T. *Org. Biomol. Chem.* **2022**, *20*, 5412. b) Yuan, B.; Ding, D.; Wang, C. *ACS Catal.* **2022**, *12*, 4261.

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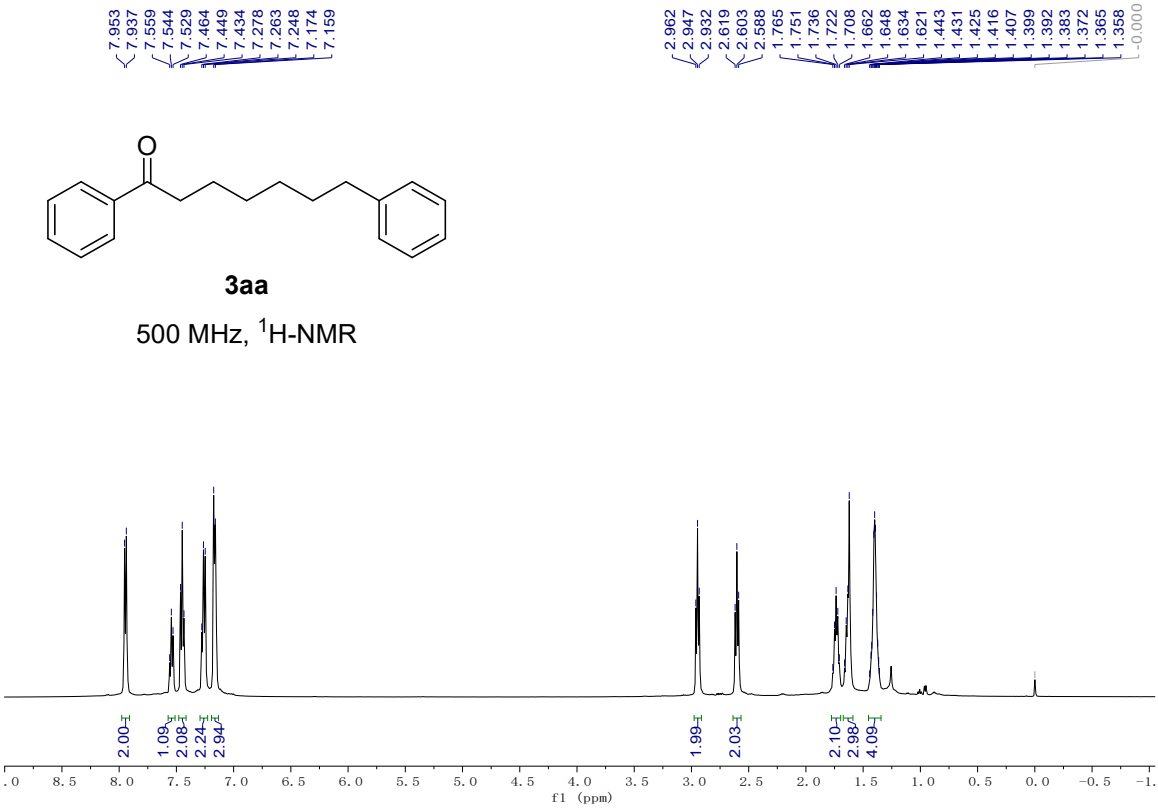
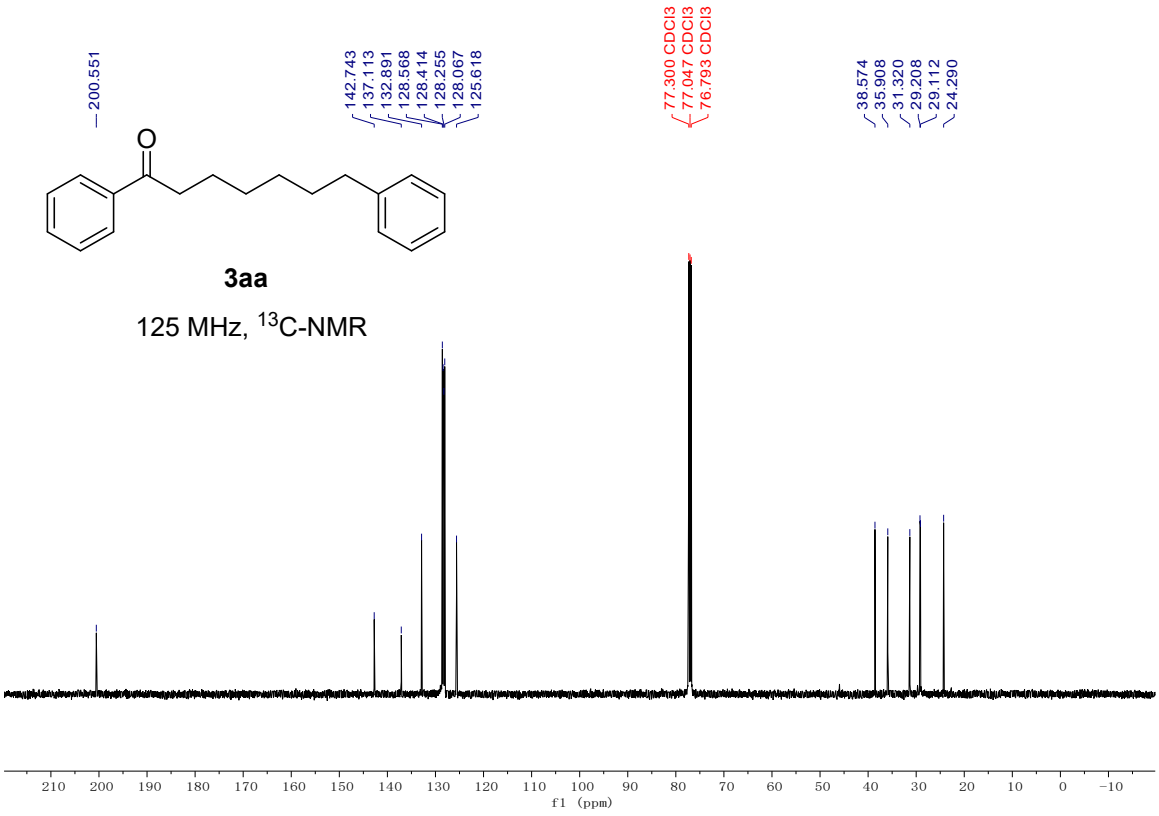
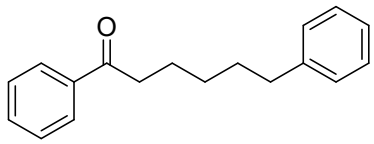
[7] Brethomé, A. V.; Paton, R. S.; Fletcher, S. P. *ACS Catal.* **2019**, *9*, 7179.

[8] S. Graßl and P. Knochel, *Org. Lett.*, **2020**, *22*, 1947.

9. NMR Spectra

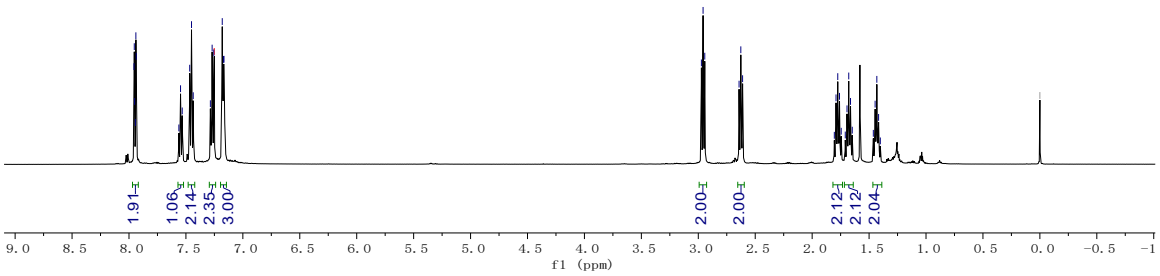


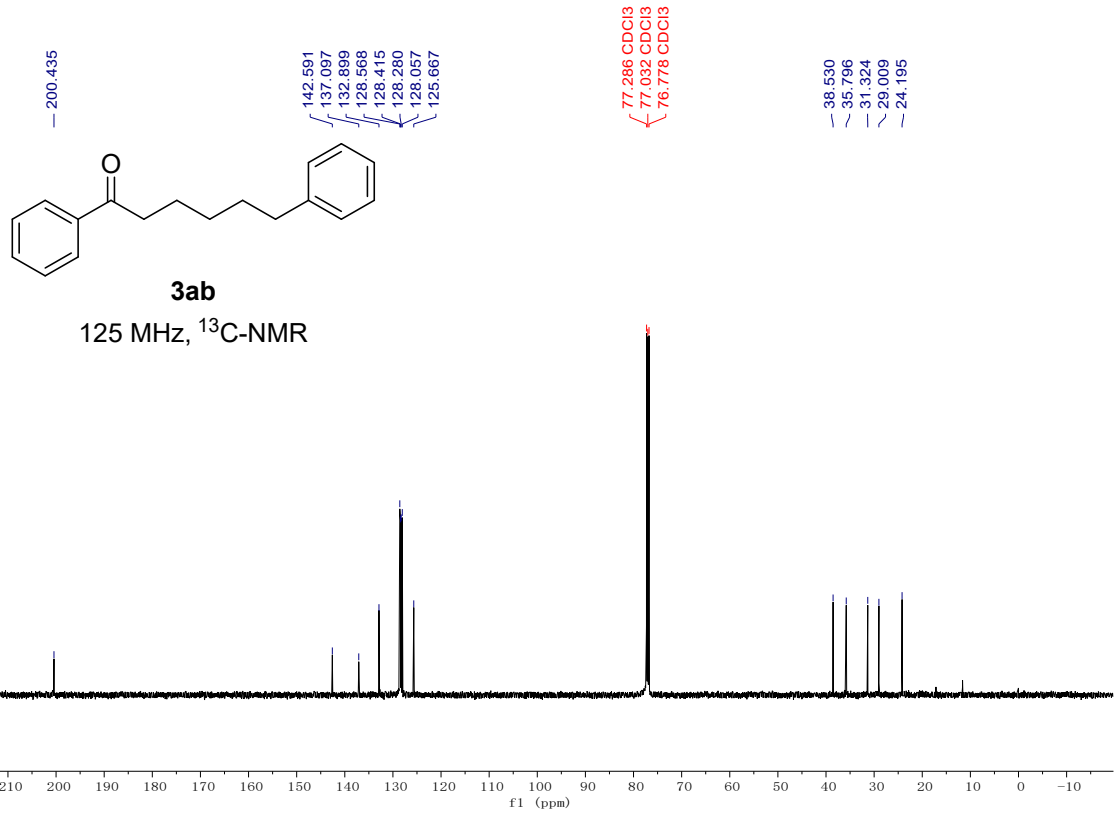




3ab

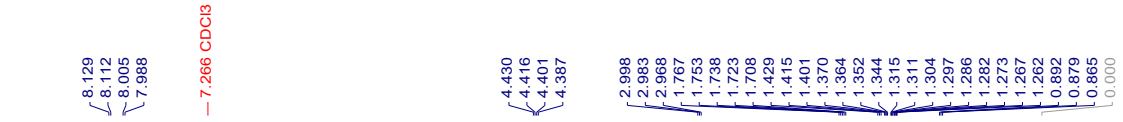
500 MHz, ^{1}H-NMR

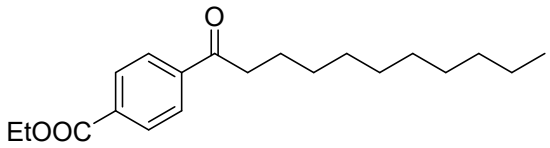




3ab

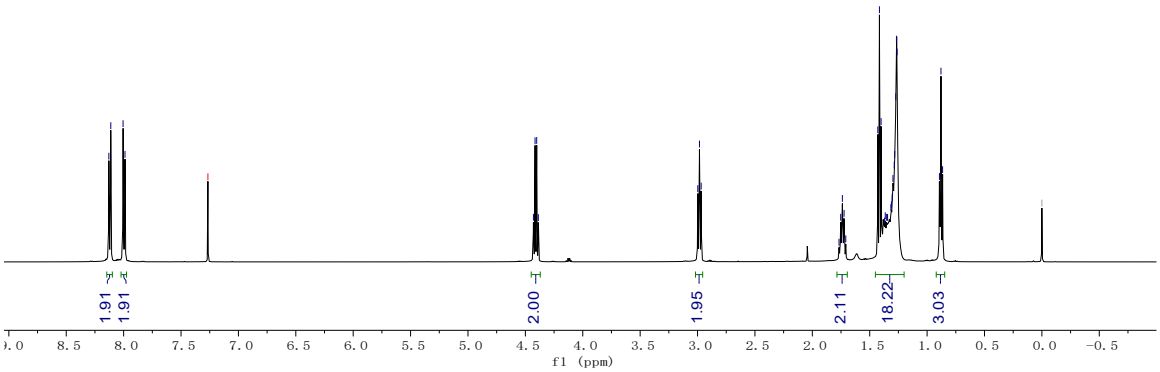
125 MHz, ^{13}C-NMR

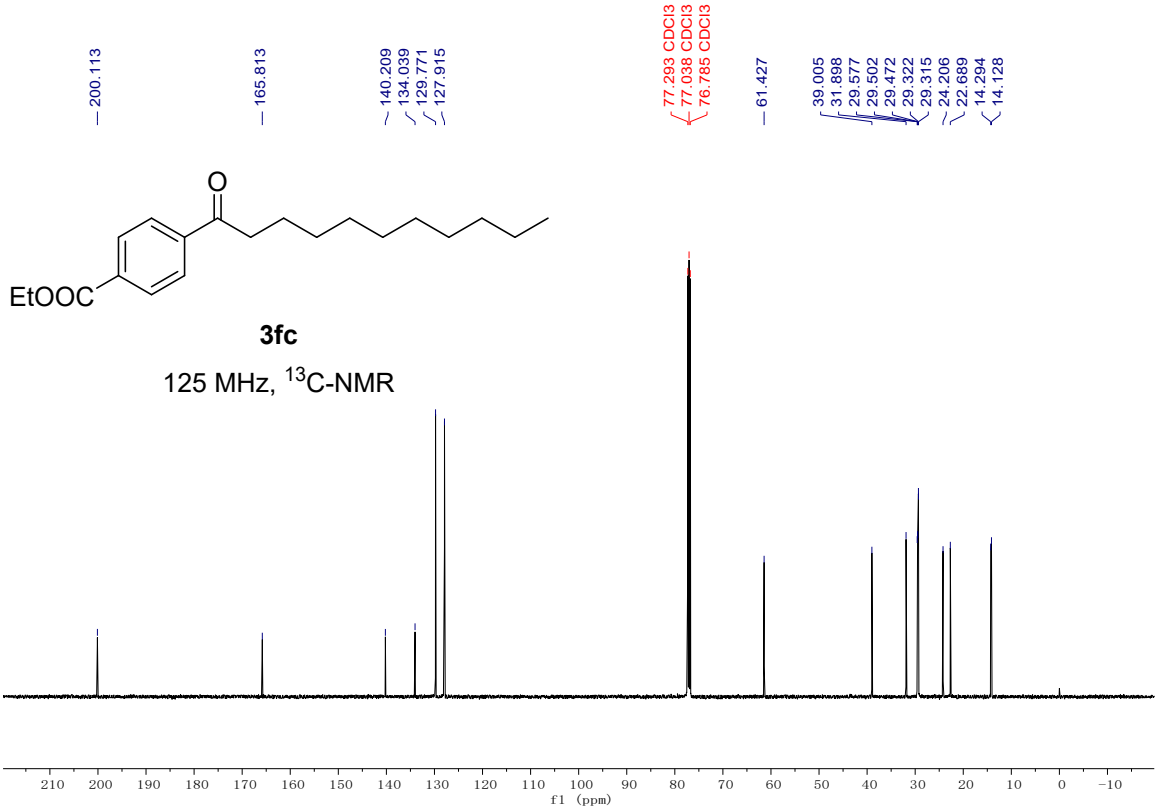




3fc

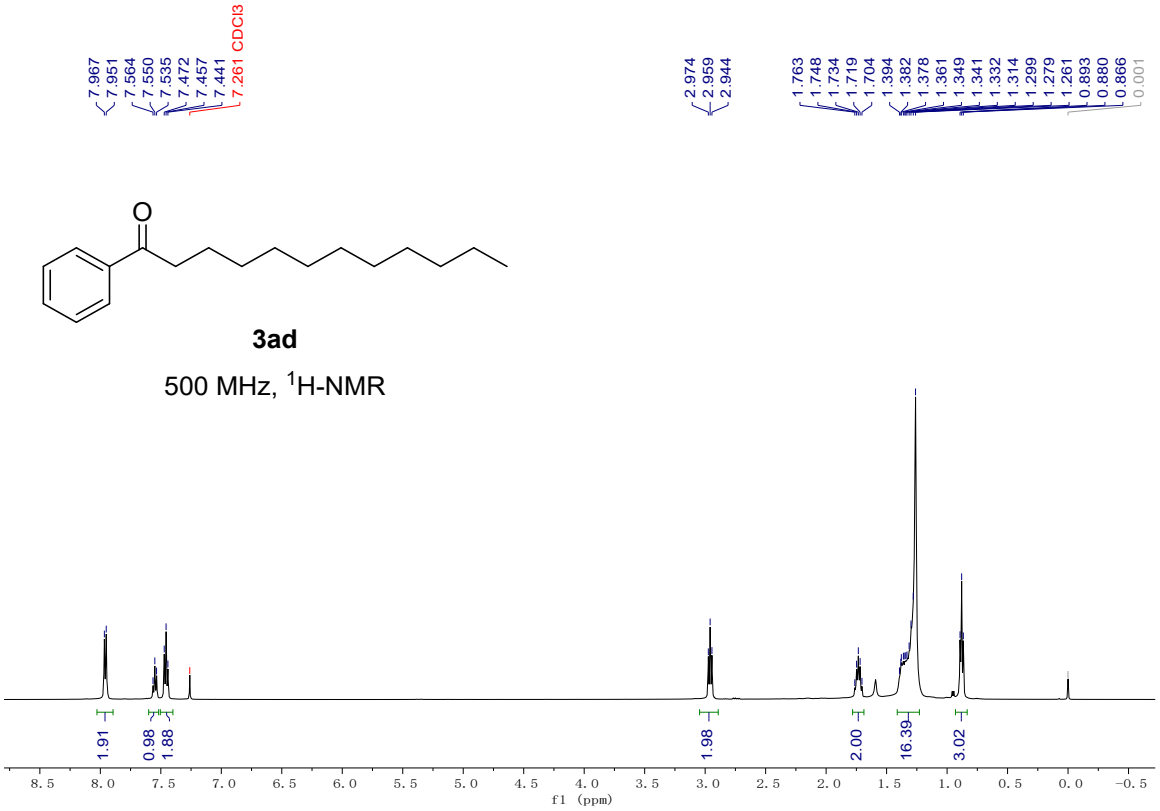
500 MHz, ^{1}H-NMR

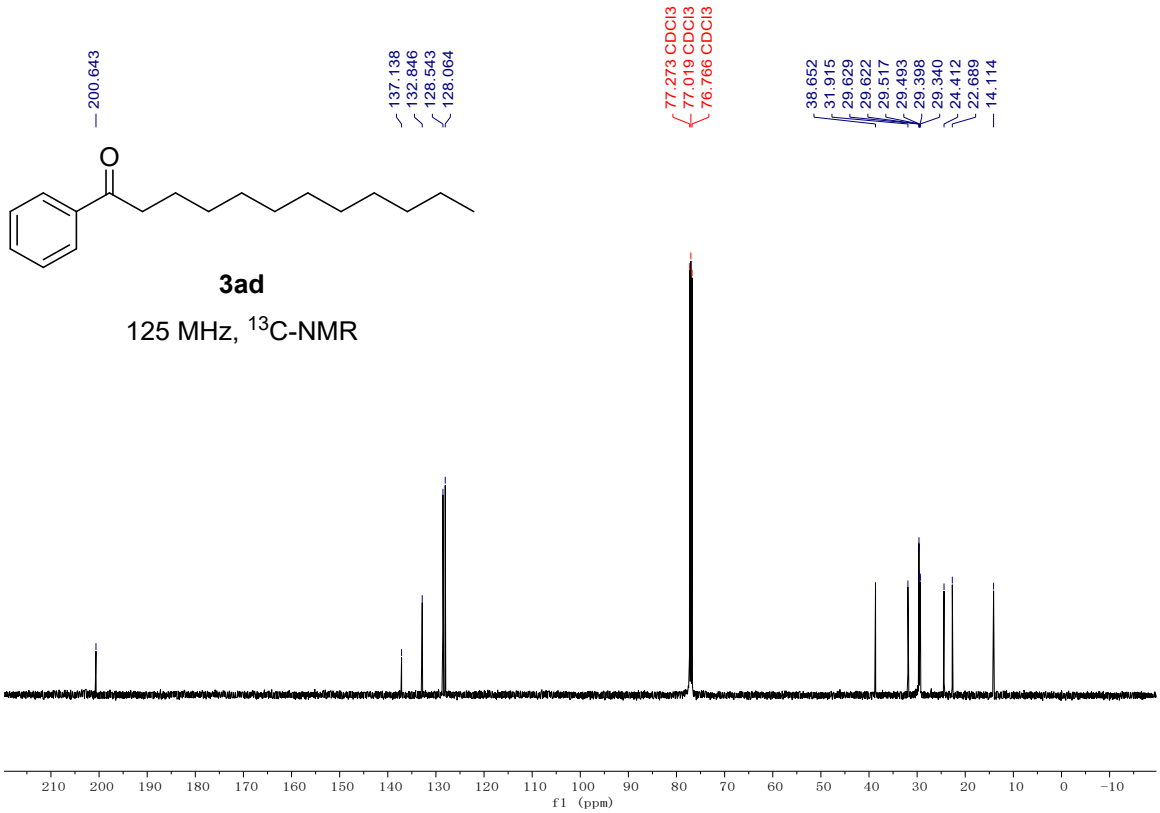


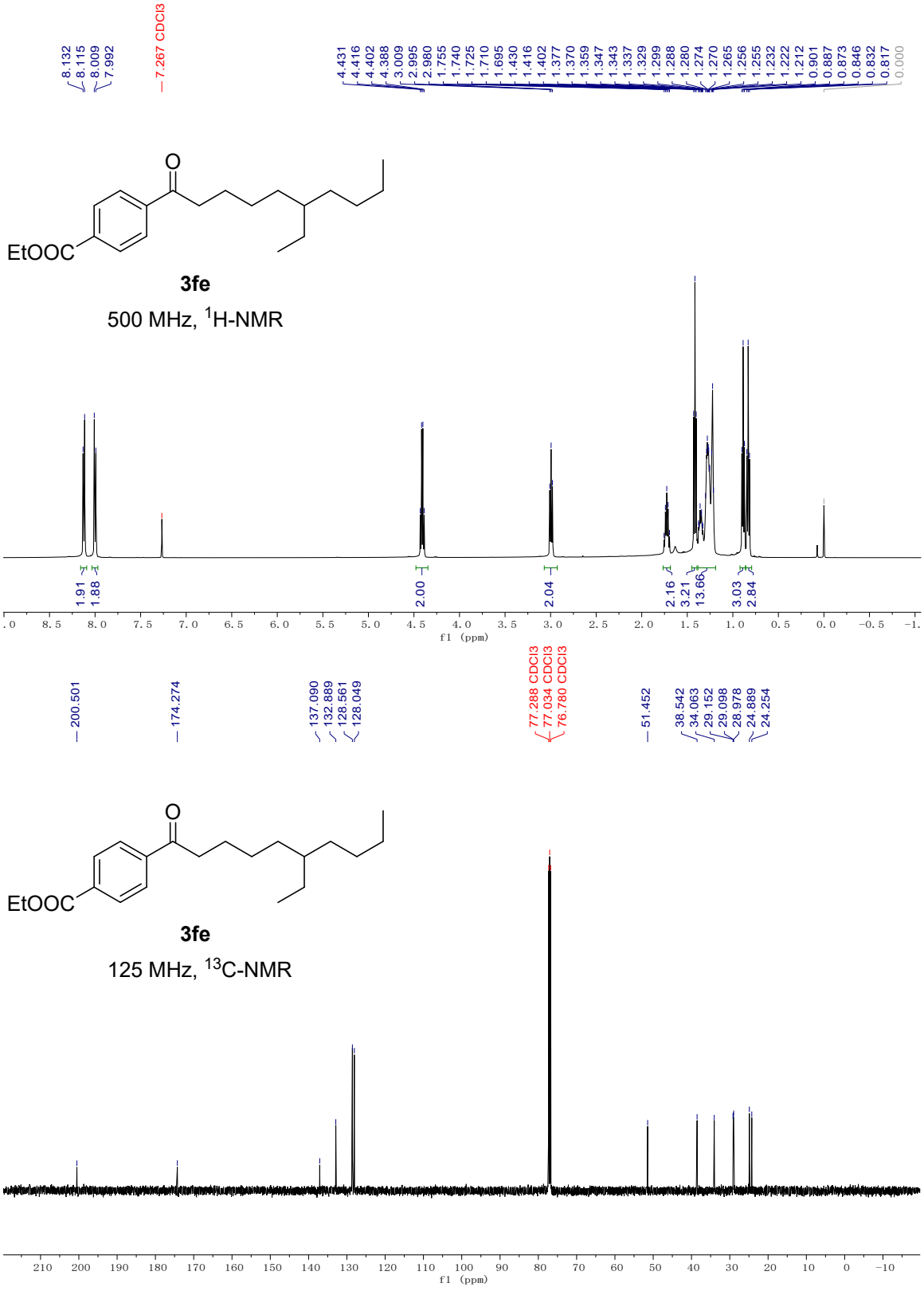


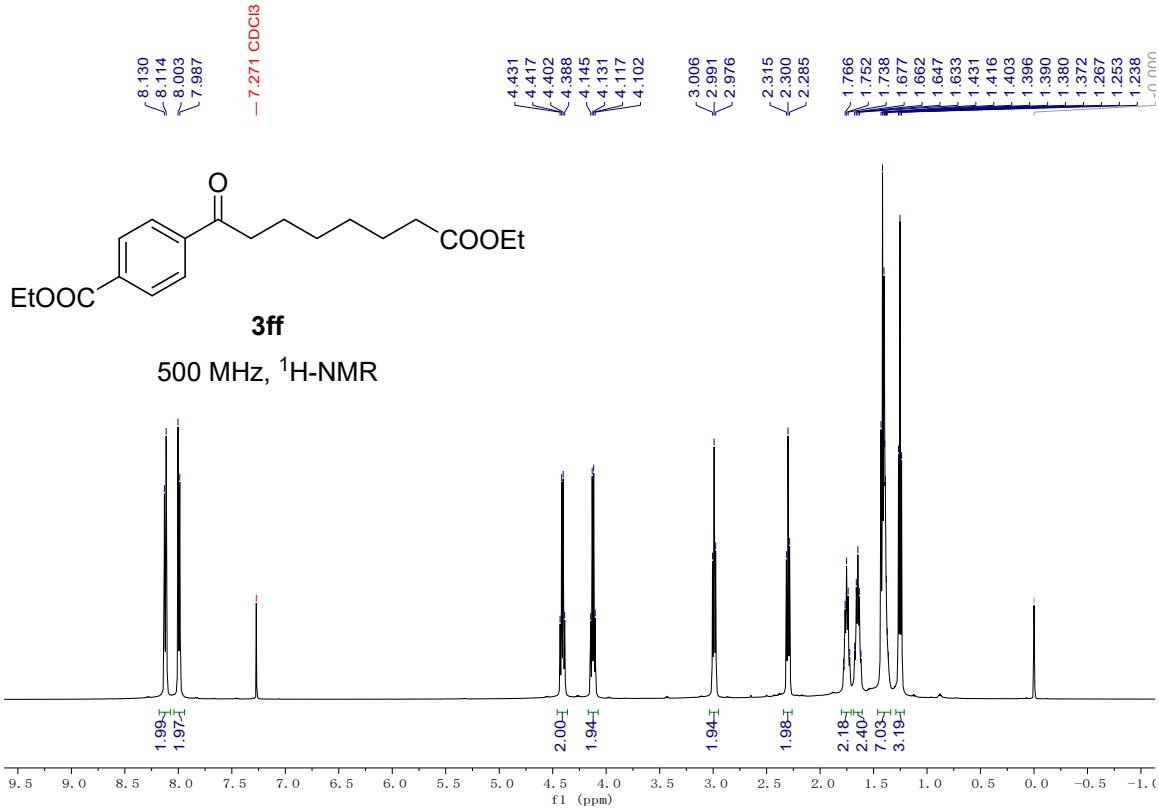
3fc

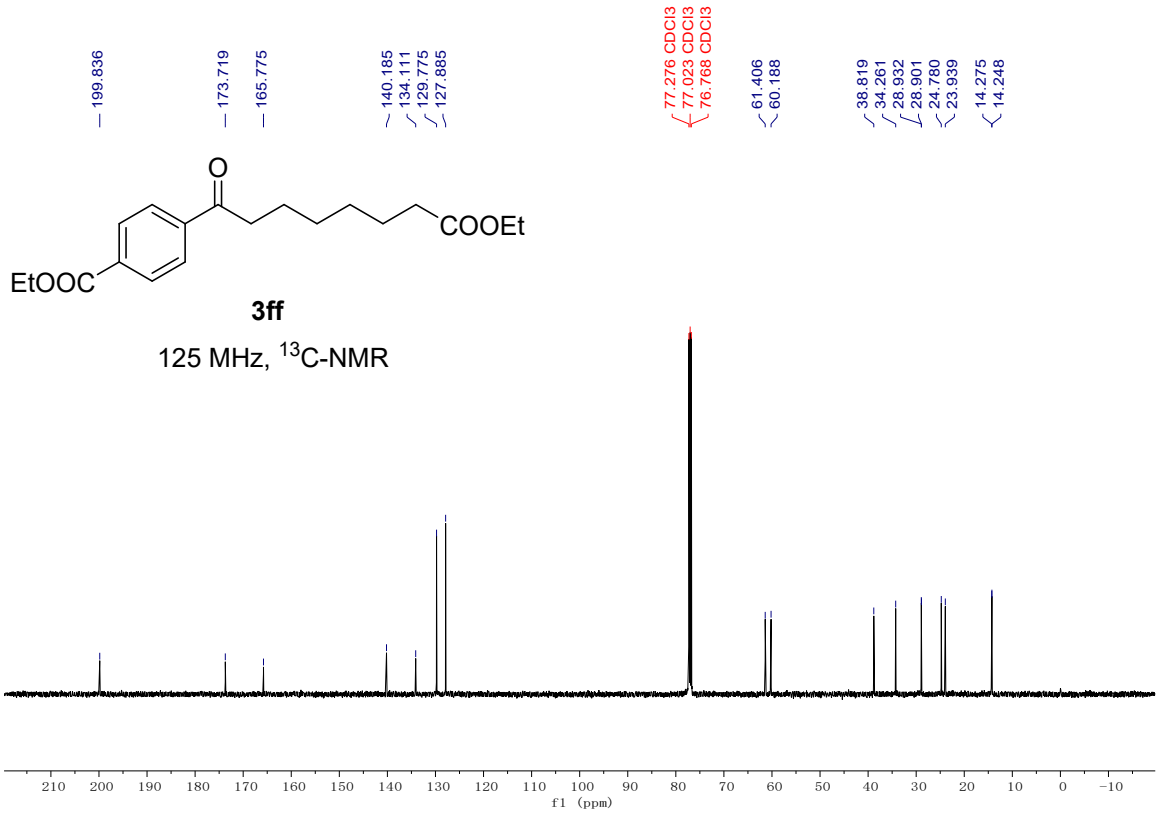
125 MHz, ^{13}C-NMR

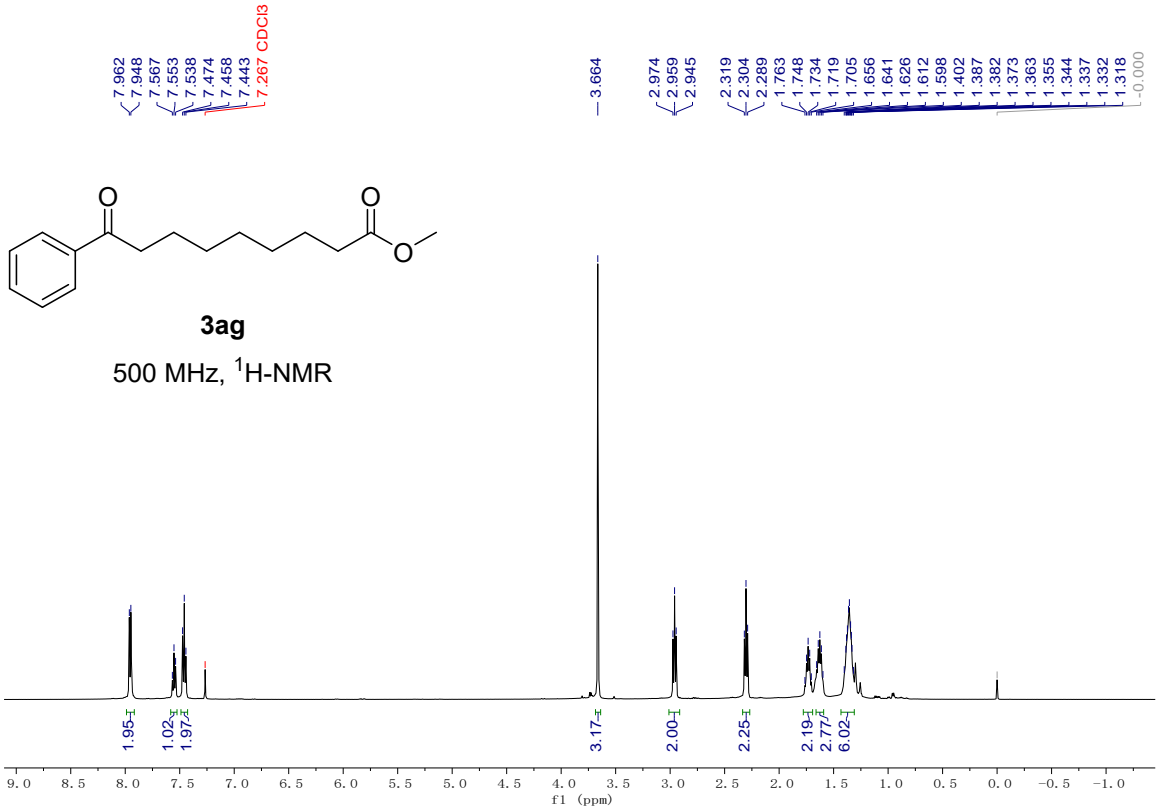

7.967
7.951
7.564
7.550
7.535
7.472
7.457
7.441
7.261 CDCl3
2.974
2.959
2.944
1.763
1.748
1.734
1.719
1.704
1.394
1.382
1.378
1.361
1.349
1.341
1.332
1.314
1.299
1.279
1.261
0.893
0.880
0.866
0.001
O
3ad
500 MHz, 1H-NMR
1.91
0.98
1.88
1.98
2.00
16.39
3.02
f1 (ppm)


200.643
137.138
132.846
128.543
128.064
77.273 CDCl3
77.019 CDCl3
76.766 CDCl3
38.652
31.915
29.629
29.622
29.517
29.493
29.398
29.340
24.412
22.689
14.114
O
3ad
125 MHz, 13C-NMR
f1 (ppm)


8.132
8.115
8.009
7.992
7.267 CDCl3
4.431
4.416
4.402
4.388
3.009
2.995
2.980
1.755
1.740
1.725
1.710
1.695
1.430
1.416
1.402
1.377
1.370
1.359
1.347
1.343
1.337
1.329
1.299
1.288
1.280
1.274
1.270
1.265
1.256
1.255
1.232
1.222
1.212
0.901
0.887
0.873
0.846
0.832
0.817
0.000
O
EtOOC
3fe
500 MHz, 1H-NMR
1.91
1.88
2.00
2.04
2.16
3.21
13.66
3.03
2.84
f1 (ppm)
200.501
174.274
137.090
132.889
128.561
128.049
77.288 CDCl3
77.034 CDCl3
76.780 CDCl3
51.452
38.542
34.063
29.152
29.098
28.978
24.889
24.254
O
EtOOC
3fe
125 MHz, 13C-NMR
f1 (ppm)

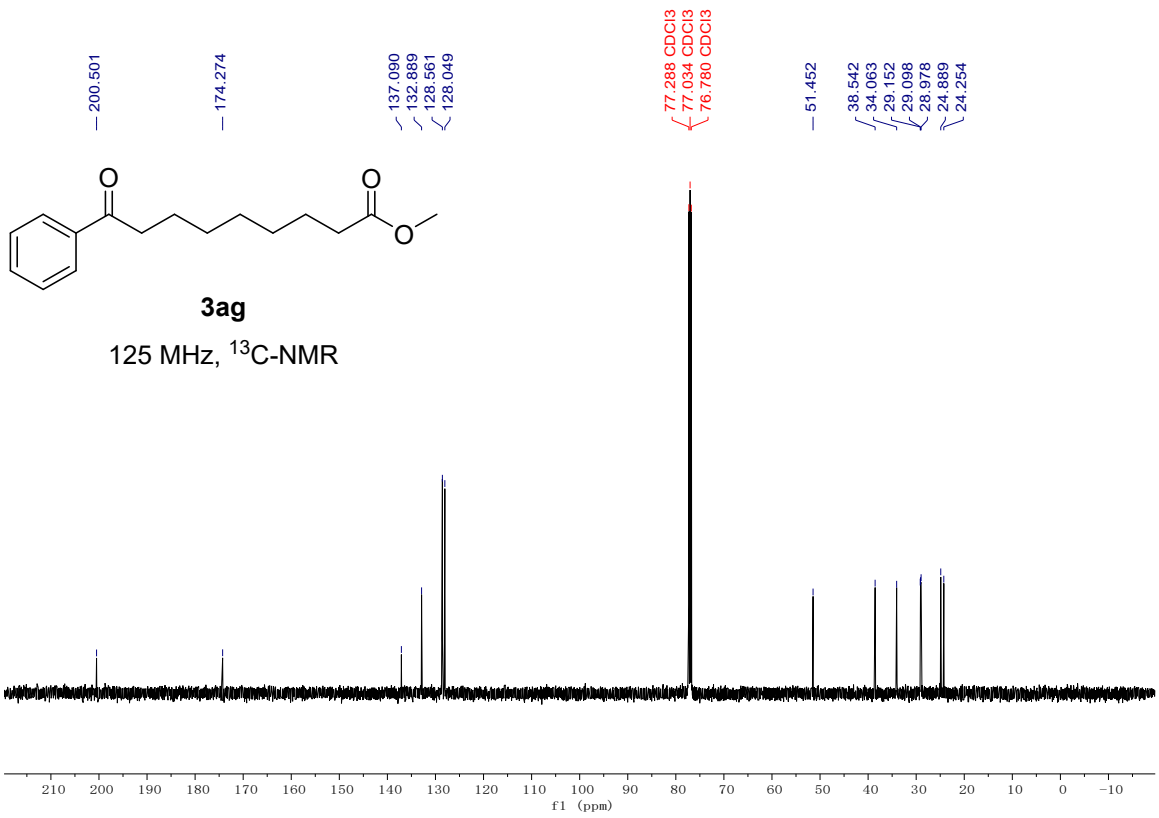

8.130
8.114
8.003
7.987
7.271 CDCl3
4.431
4.417
4.402
4.388
4.145
4.131
4.117
4.102
3.006
2.991
2.976
2.315
2.300
2.285
1.766
1.752
1.738
1.677
1.662
1.647
1.633
1.431
1.416
1.403
1.396
1.390
1.380
1.372
1.267
1.253
1.238
O
COOEt
EtOOC
3ff
500 MHz, 1H-NMR
1.99
1.97
2.00
1.94
1.94
1.98
2.18
2.40
7.03
3.19
f1 (ppm)


199.836
173.719
165.775
140.185
134.111
129.775
127.885
77.276 CDCl3
77.023 CDCl3
76.768 CDCl3
61.406
60.188
38.819
34.261
28.932
28.901
24.780
23.939
14.275
14.248
O
COOEt
EtOOC
3ff
125 MHz, 13C-NMR
f1 (ppm)



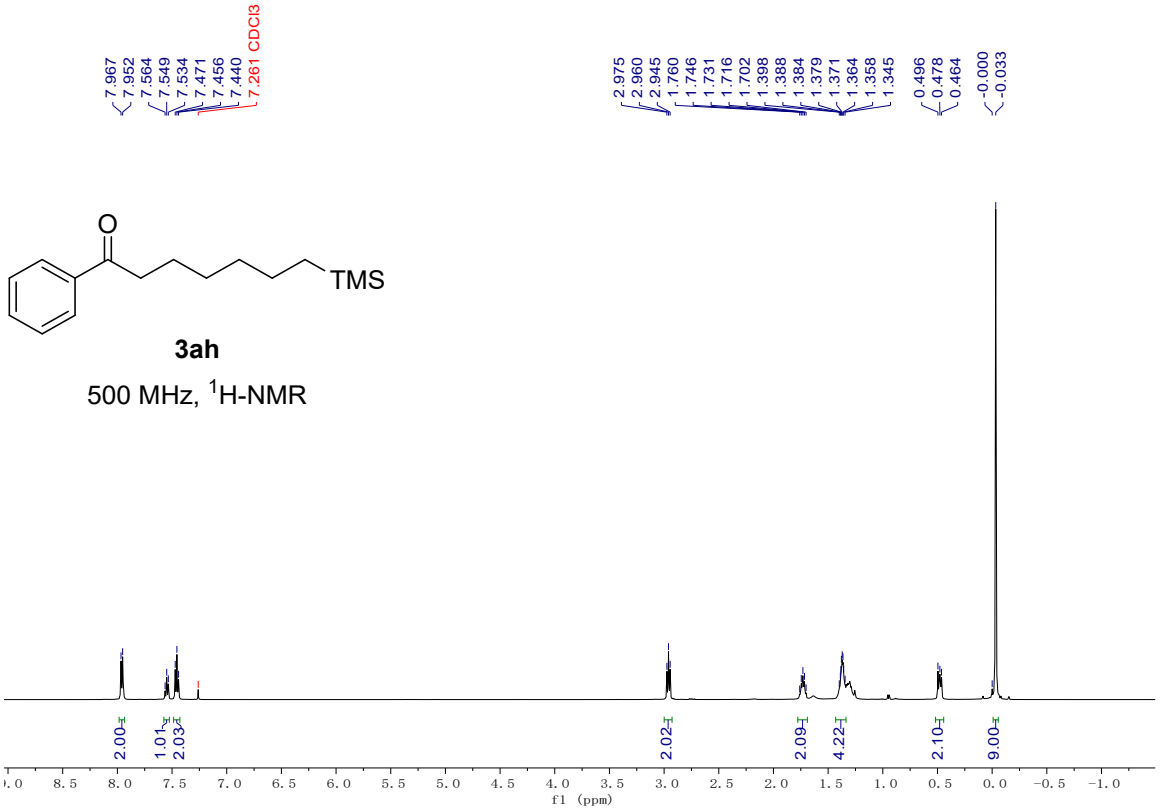
3ag

500 MHz, ^{1}H-NMR



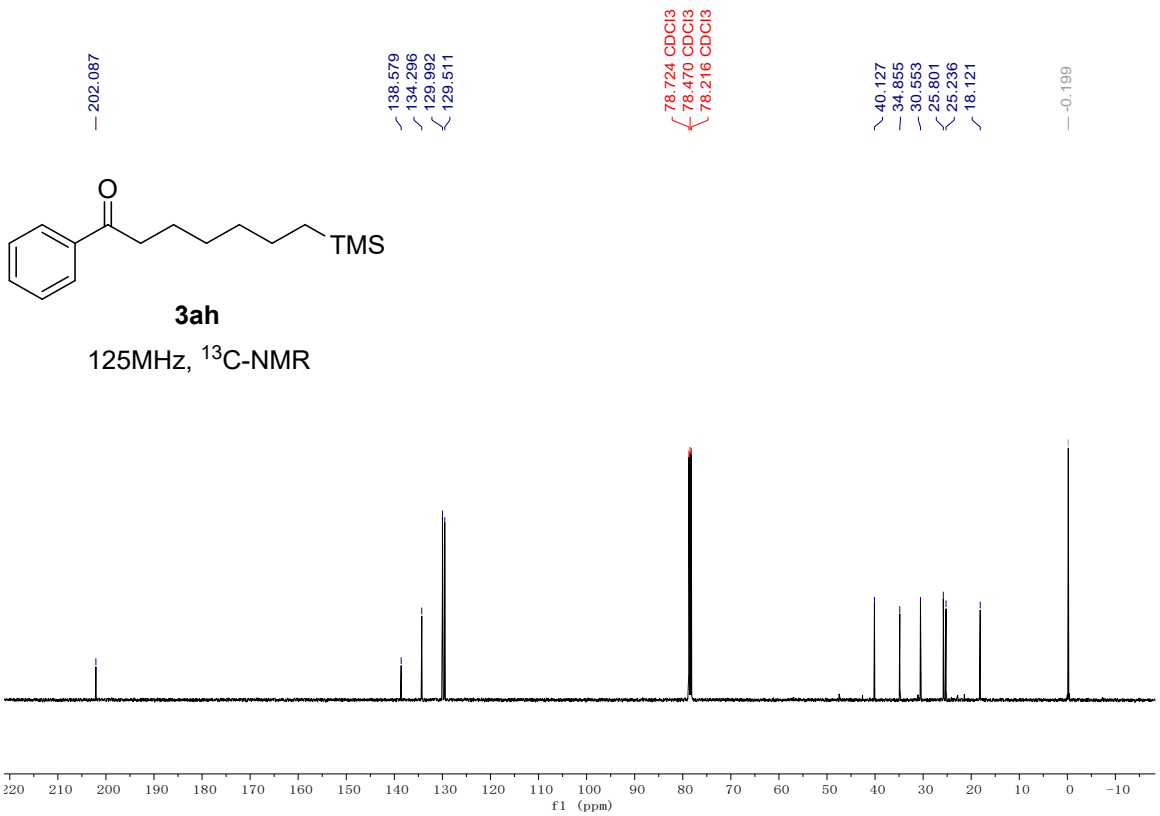
3ag

125 MHz, ^{13}C-NMR



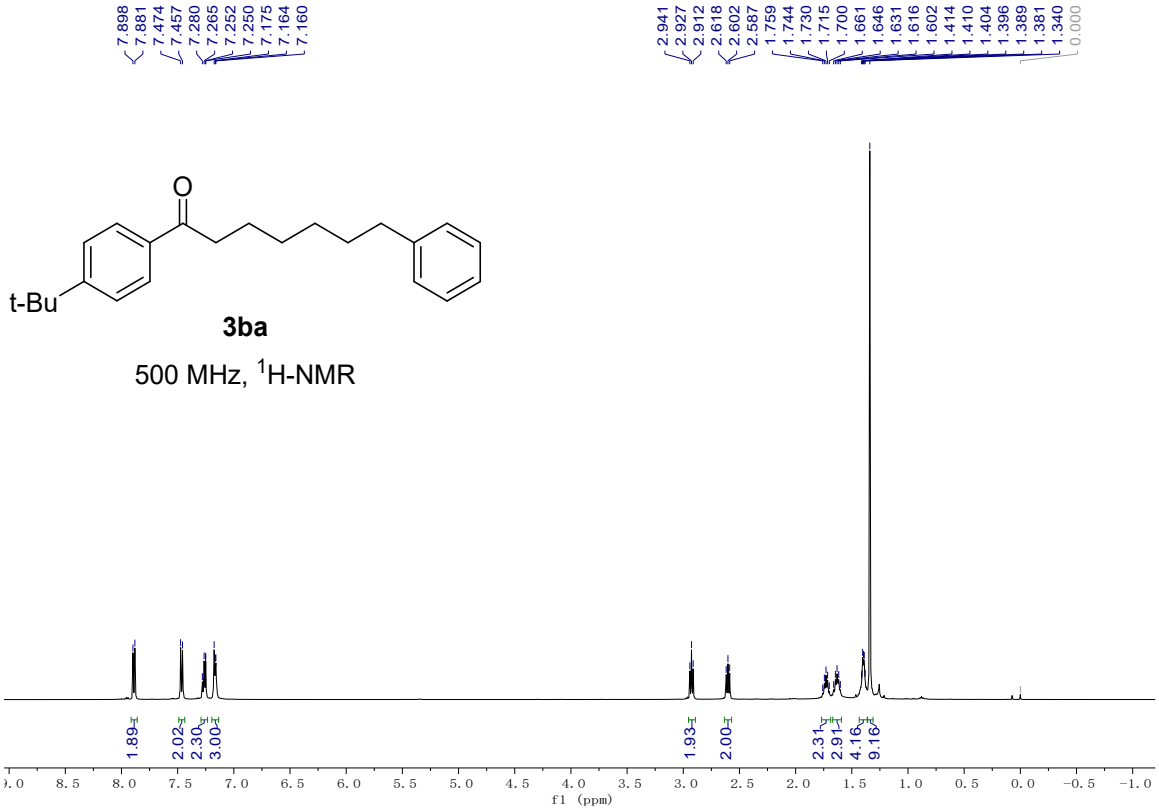
3ah

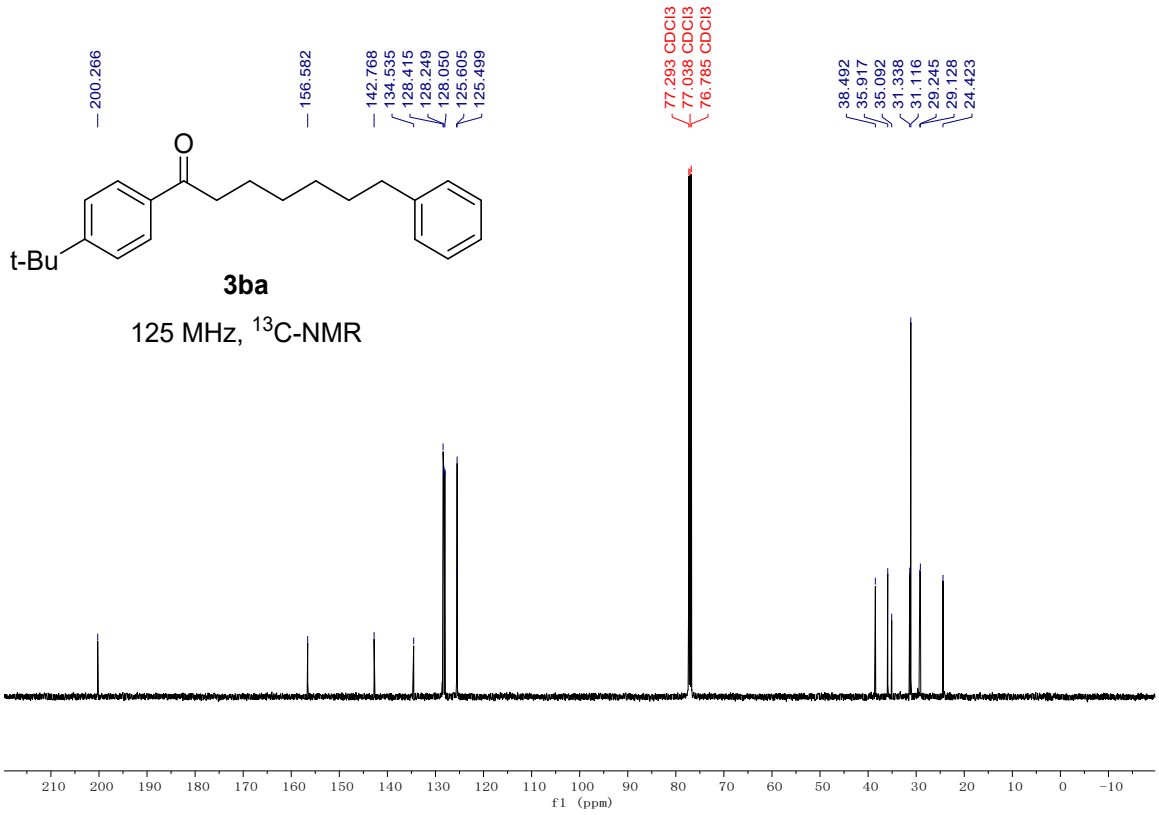
500 MHz, ^{1}H-NMR

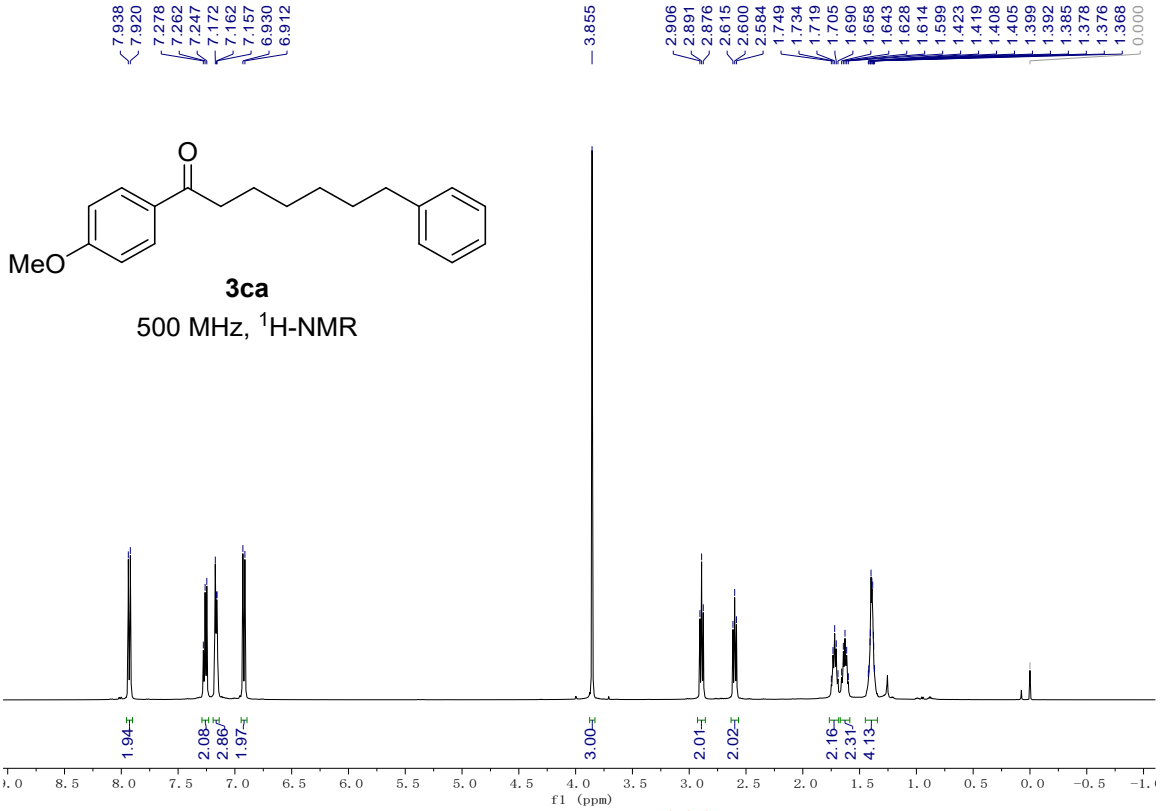


3ah

125MHz, ^{13}C-NMR

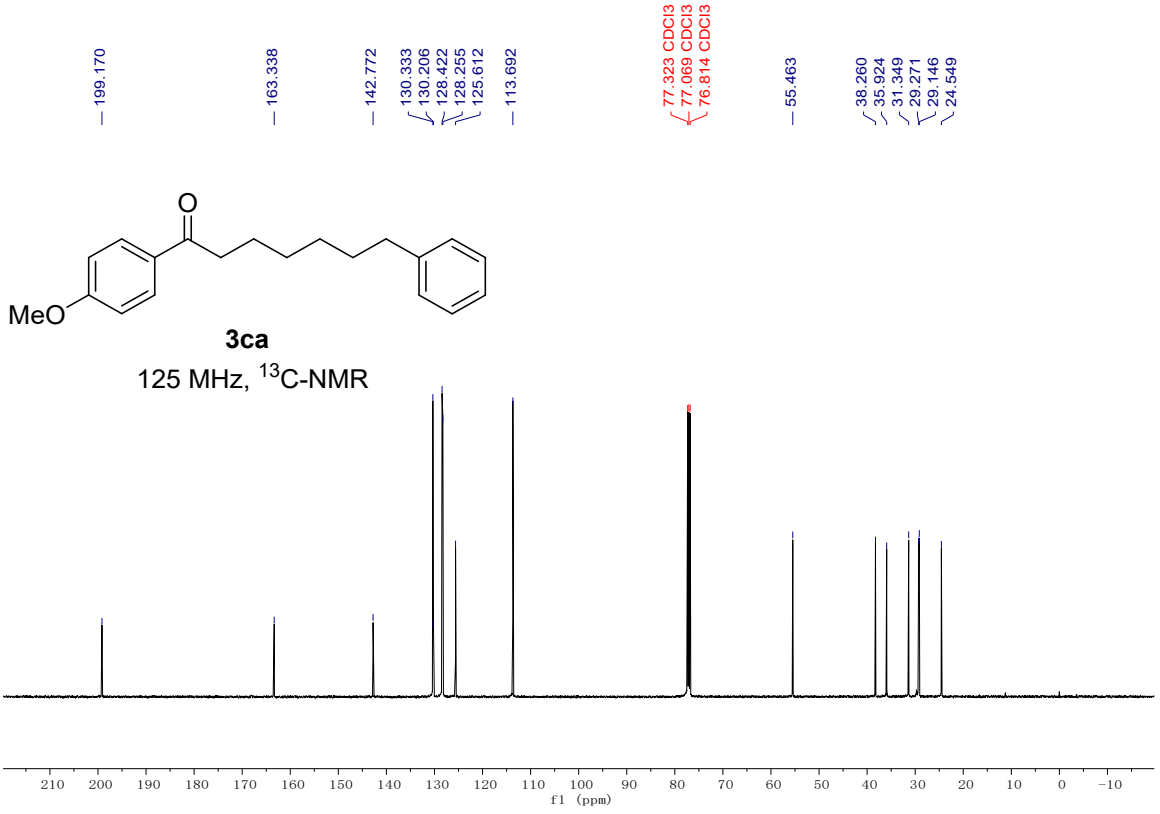

7.898
7.881
7.474
7.457
7.280
7.265
7.252
7.250
7.175
7.164
7.160
2.941
2.927
2.912
2.618
2.602
2.587
1.759
1.744
1.730
1.715
1.700
1.661
1.646
1.631
1.616
1.602
1.414
1.410
1.404
1.396
1.389
1.381
1.340
0.000
O
t-Bu
3ba
500 MHz, 1H-NMR
1.89
2.02
2.30
3.00
1.93
2.00
2.31
2.91
4.16
9.16
f1 (ppm)


200.266
156.582
142.768
134.535
128.415
128.249
128.050
125.605
125.499
77.293 CDCl3
77.038 CDCl3
76.785 CDCl3
38.492
35.917
35.092
31.338
31.116
29.245
29.128
24.423
O
t-Bu
3ba
125 MHz, 13C-NMR
f1 (ppm)



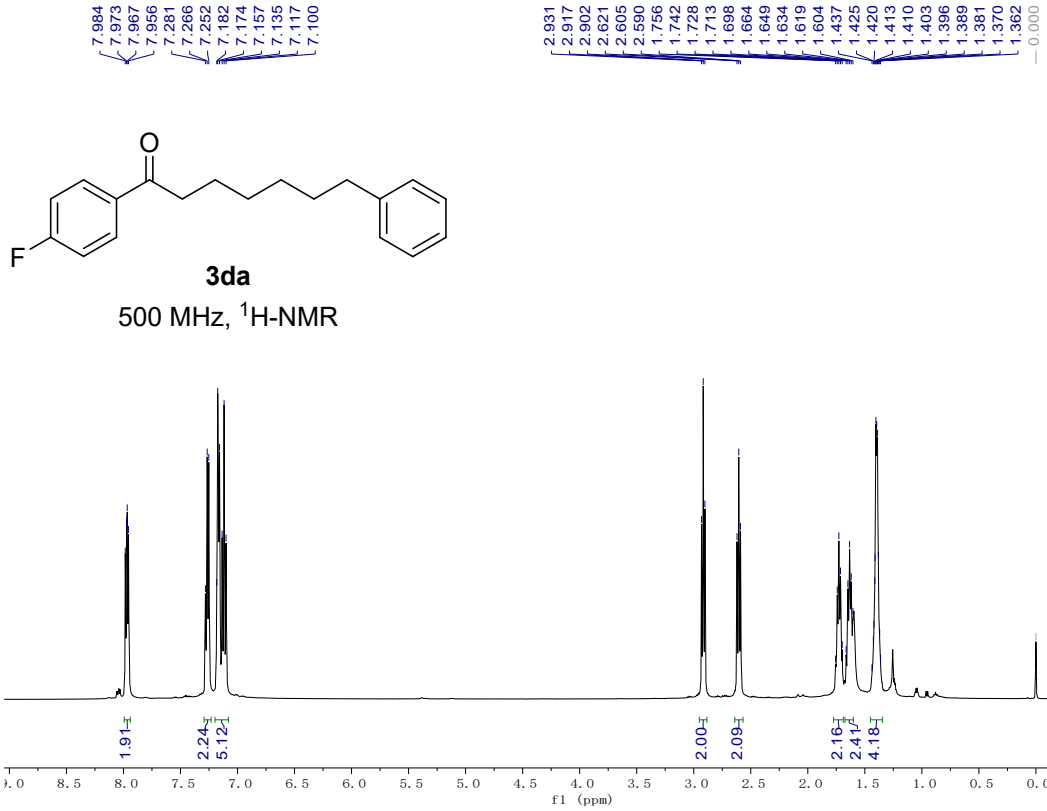
3ca

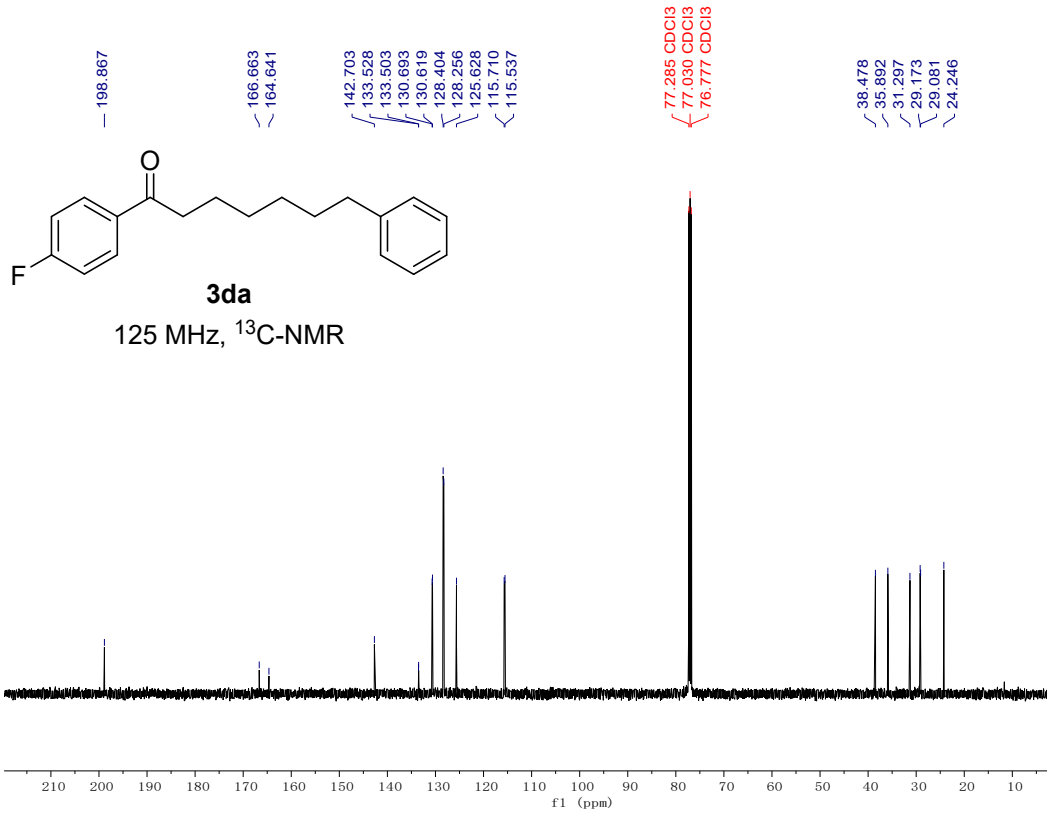
500 MHz, ^{1}H-NMR

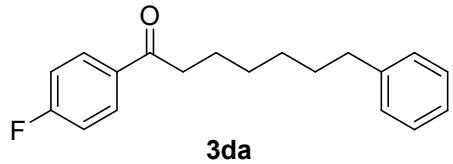


3ca

125 MHz, ^{13}C-NMR

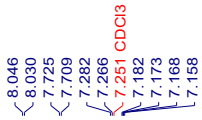

7.984
7.973
7.967
7.956
7.281
7.266
7.252
7.182
7.174
7.157
7.135
7.117
7.100
2.931
2.917
2.902
2.621
2.605
2.590
1.756
1.742
1.728
1.713
1.698
1.664
1.649
1.634
1.619
1.604
1.437
1.425
1.420
1.413
1.410
1.403
1.396
1.389
1.381
1.370
1.362
0.000
O
F
3da
500 MHz, 1H-NMR
1.91
2.24
5.12
2.00
2.09
2.16
2.41
4.18
f1 (ppm)

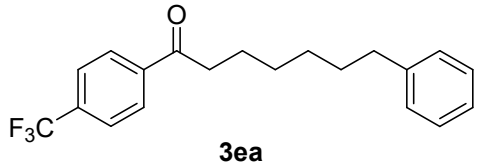

198.867
166.663
164.641
142.703
133.528
133.503
130.693
130.619
128.404
128.256
125.628
115.710
115.537
77.285 CDCl3
77.030 CDCl3
76.777 CDCl3
38.478
35.892
31.297
29.173
29.081
24.246
O
F
3da
125 MHz, 13C-NMR
f1 (ppm)



3da

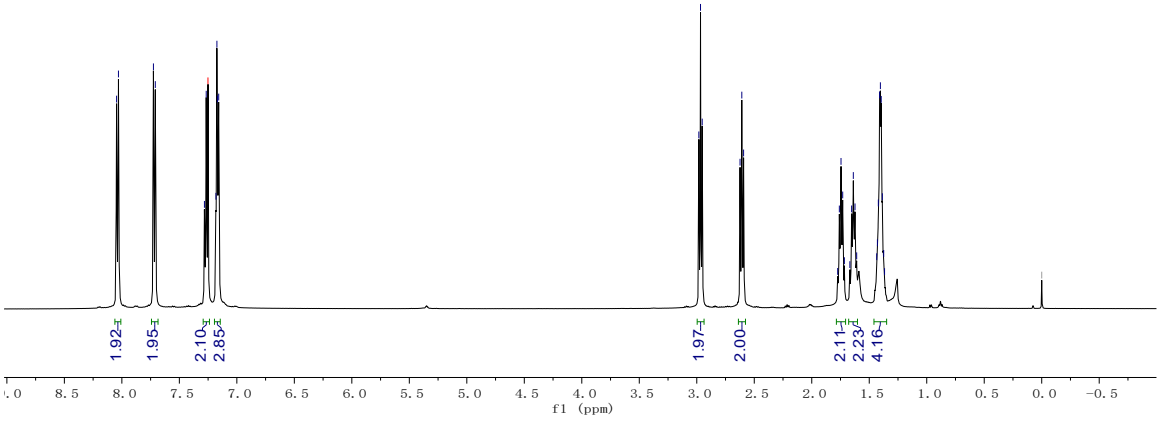
470 MHz, ^{19}F-NMR

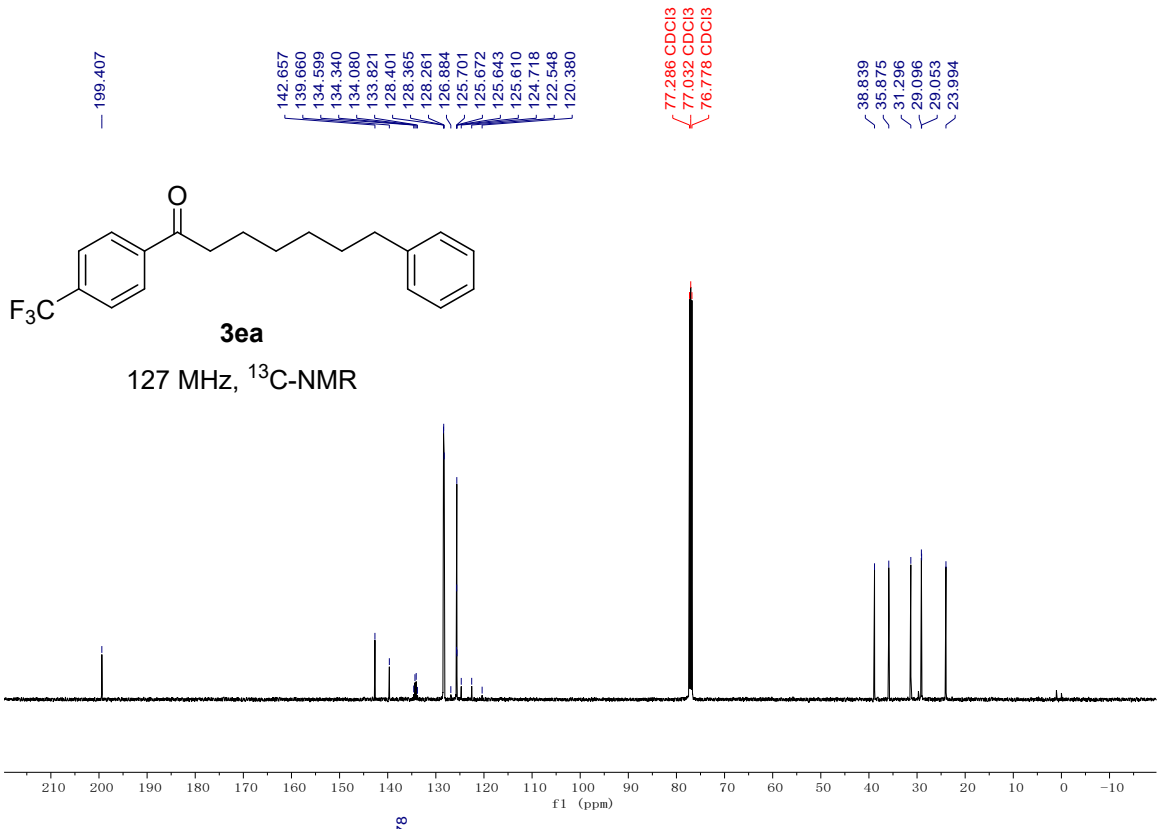


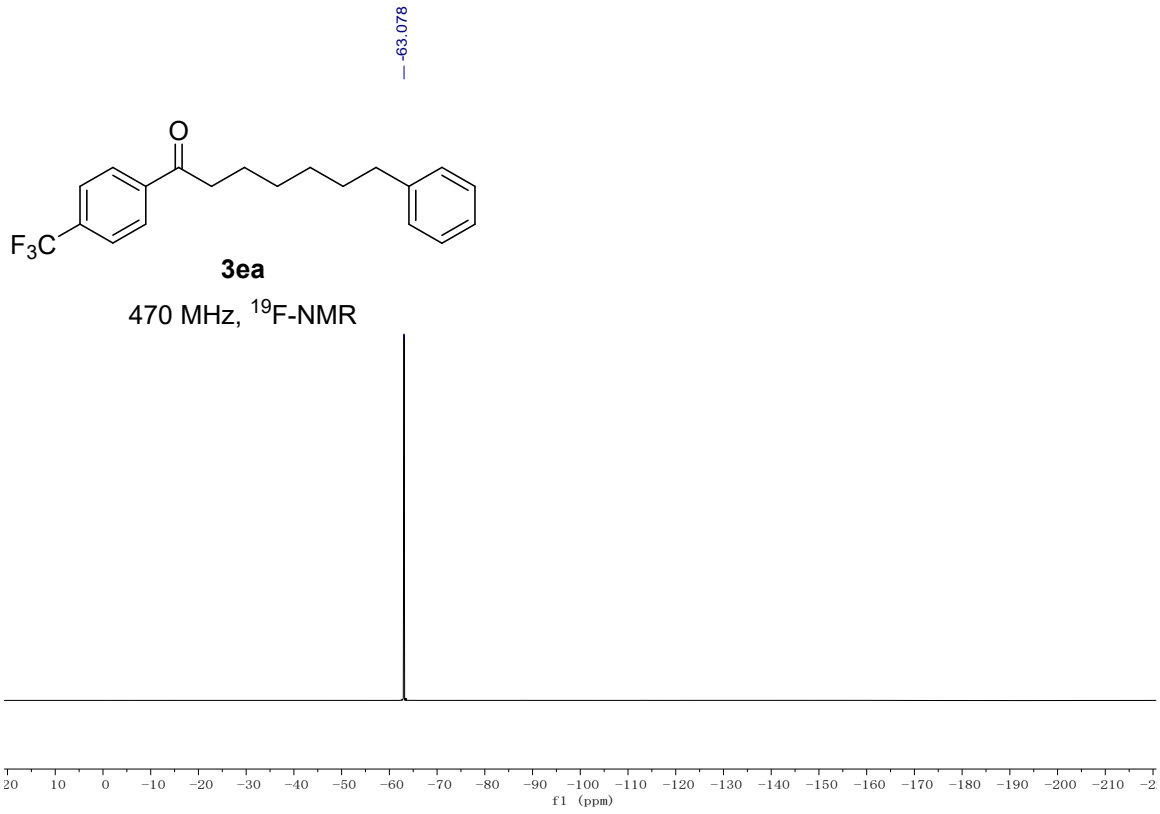


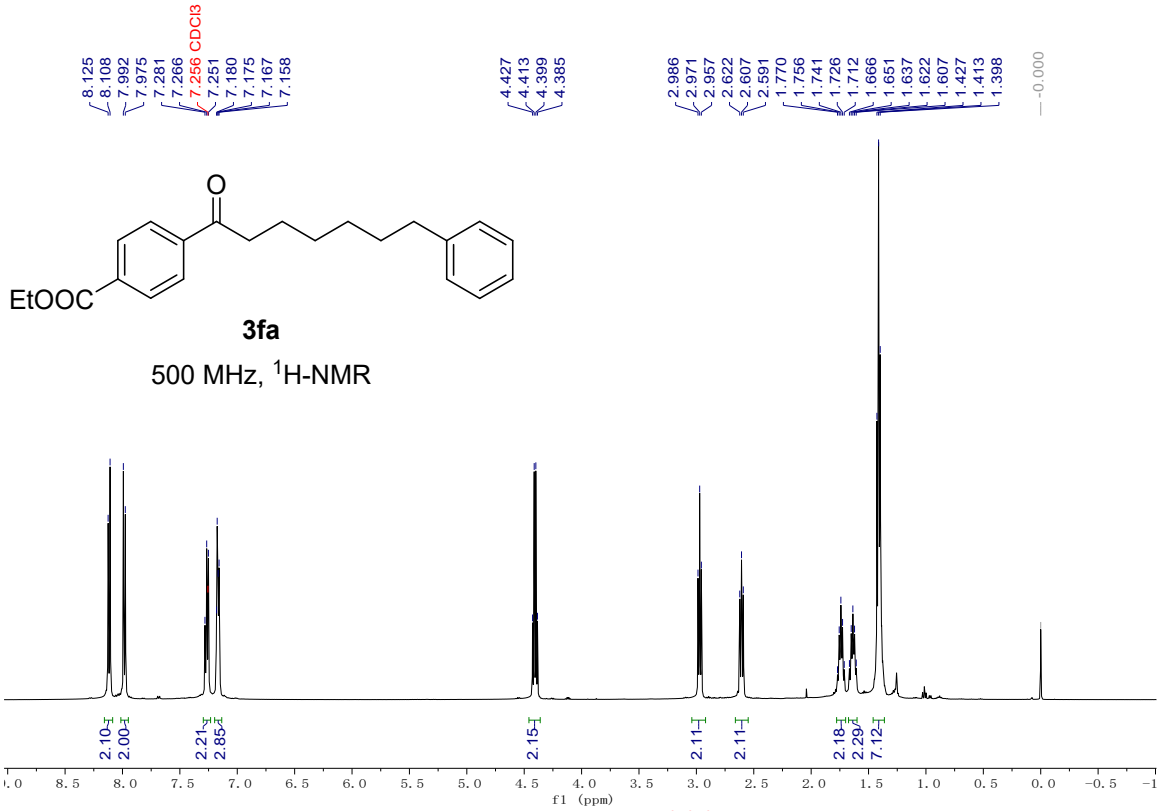
3ea

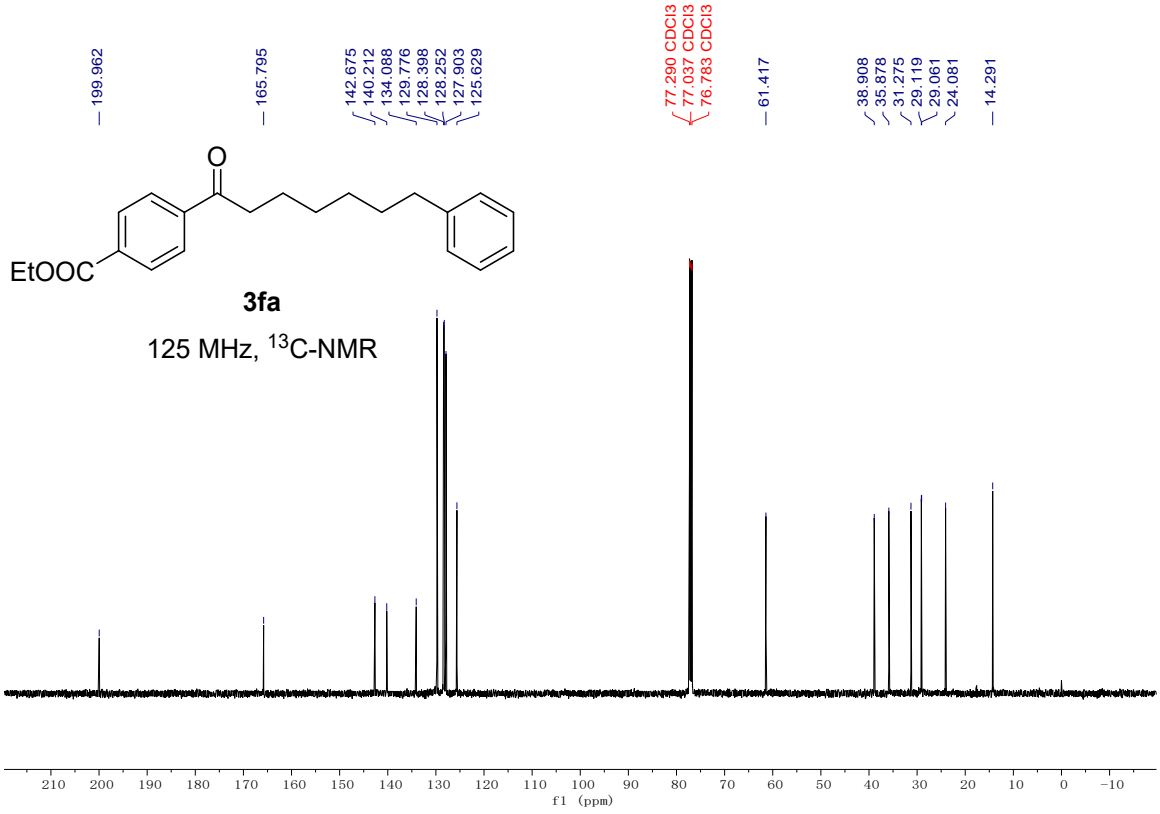
500 MHz, ^{1}H-NMR

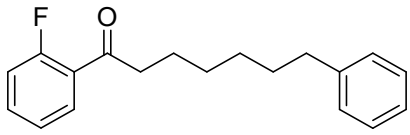



199.407
142.657
139.660
134.599
134.340
134.080
133.821
128.401
128.365
128.261
126.884
125.701
125.672
125.643
125.610
124.718
122.548
120.380
77.286 CDCl3
77.032 CDCl3
76.778 CDCl3
38.839
35.875
31.296
29.096
29.053
23.994
O
F3C
3ea
127 MHz, 13C-NMR
f1 (ppm)


-63.078
O
F3C
3ea
470 MHz, 19F-NMR
f1 (ppm)

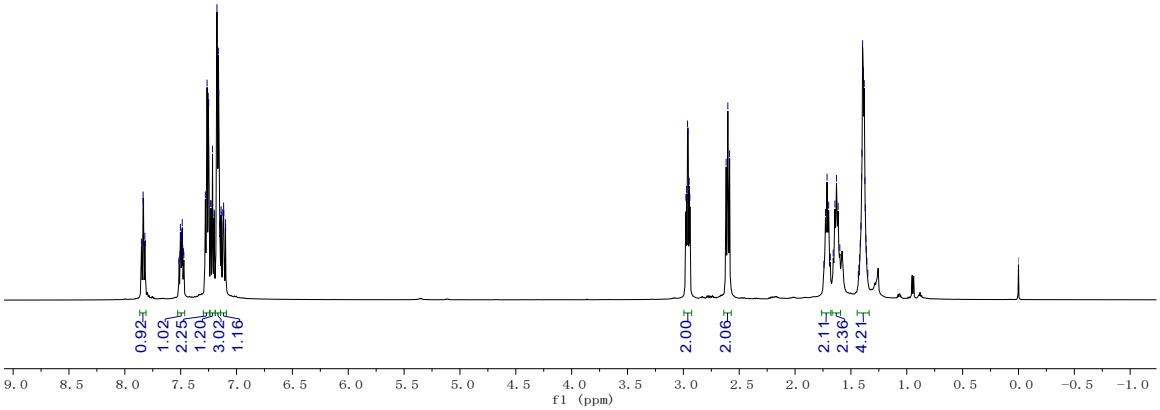

8.125
8.108
7.992
7.975
7.281
7.266
7.256 CDCl3
7.251
7.180
7.175
7.167
7.158
4.427
4.413
4.399
4.385
2.986
2.971
2.957
2.622
2.607
2.591
1.770
1.756
1.741
1.726
1.712
1.666
1.651
1.637
1.622
1.607
1.427
1.413
1.398
-0.000
O
EtOOC
3fa
500 MHz, 1H-NMR
2.10
2.00
2.21
2.85
2.15
2.11
2.11
2.18
2.29
7.12
f1 (ppm)

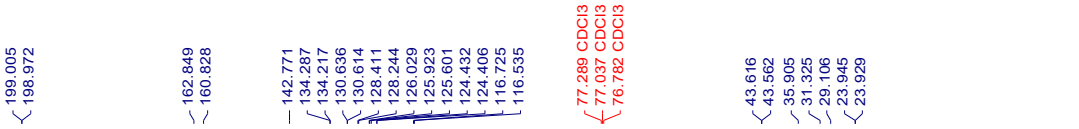

199.962
165.795
142.675
140.212
134.088
129.776
128.398
128.252
127.903
125.629
77.290 CDCl3
77.037 CDCl3
76.783 CDCl3
61.417
38.908
35.878
31.275
29.119
29.061
24.081
14.291
O
EtOOC
3fa
125 MHz, 13C-NMR
f1 (ppm)

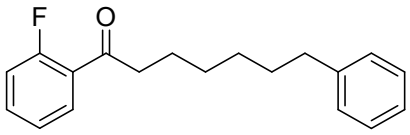


3ga

500 MHz, ^{1}H-NMR

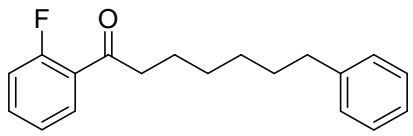






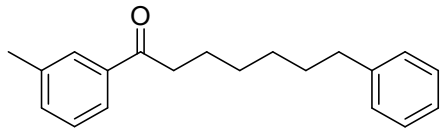
3ga

125 MHz, ^{13}C-NMR



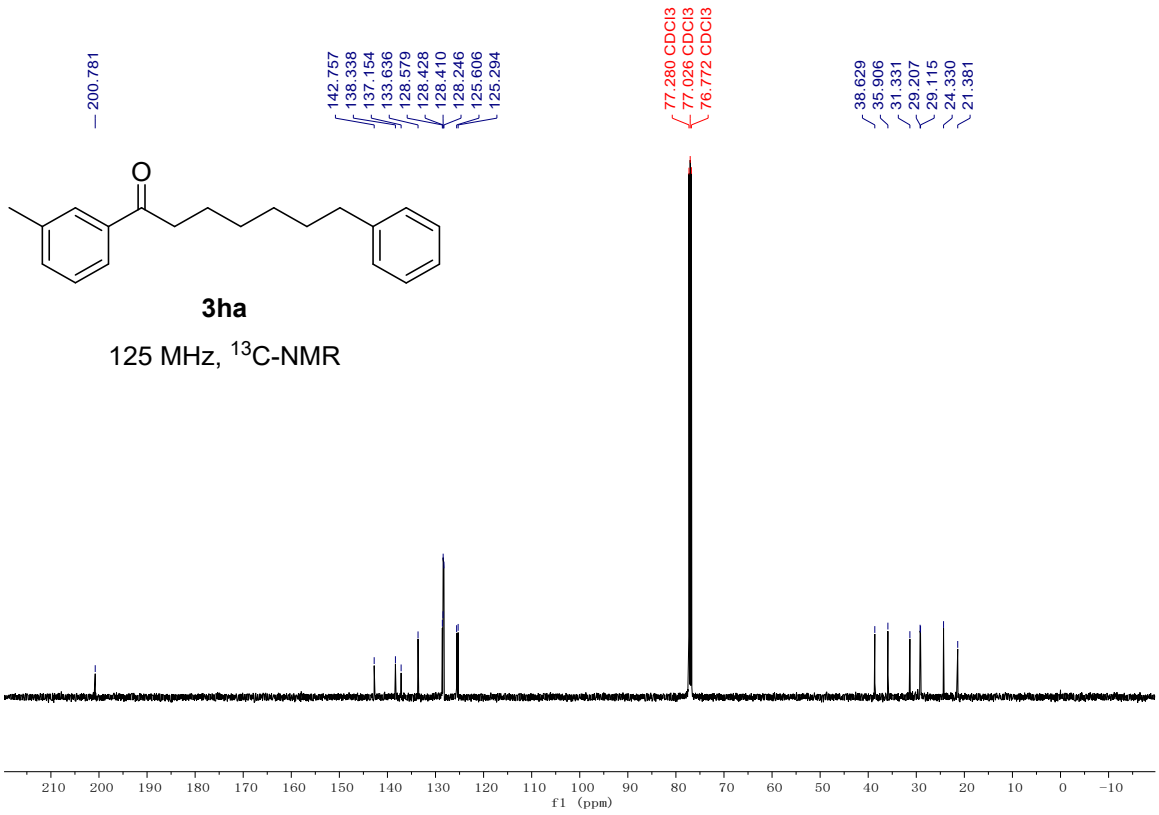
3ga

470 MHz, ^{19}F-NMR



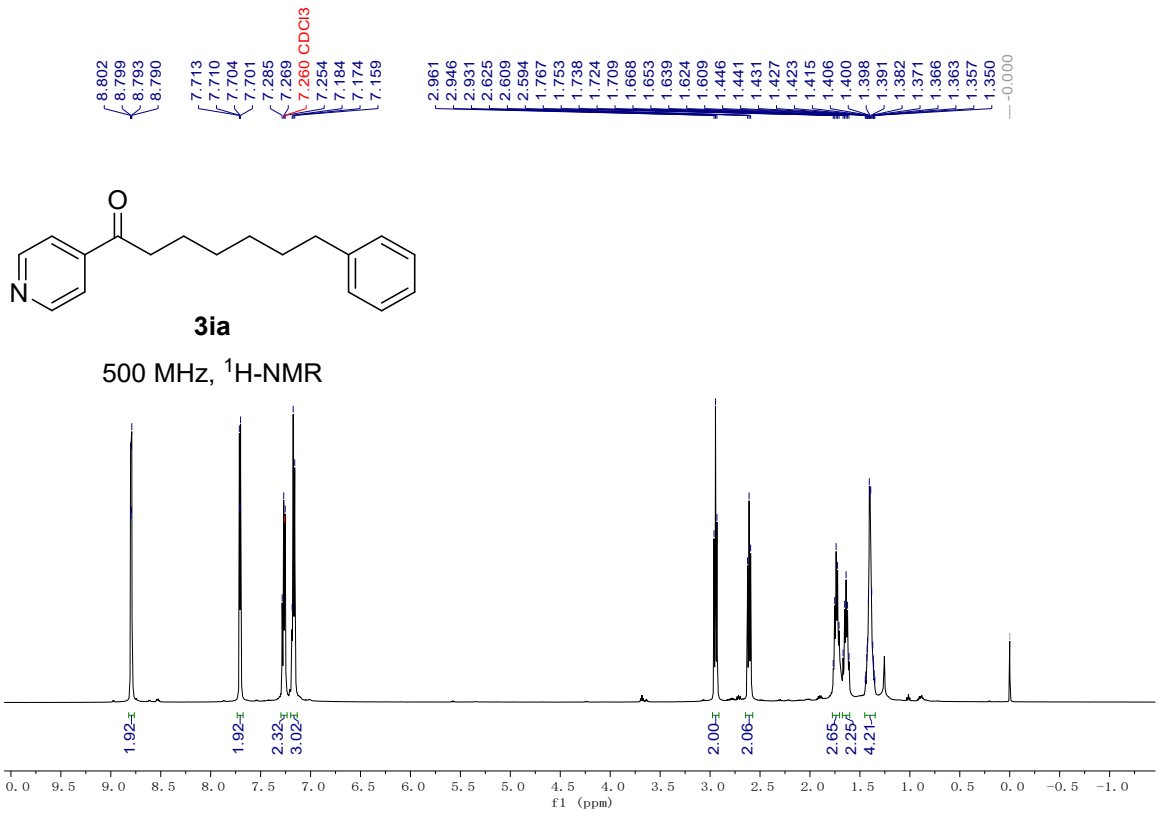
3ha

500 MHz, ^{1}H-NMR



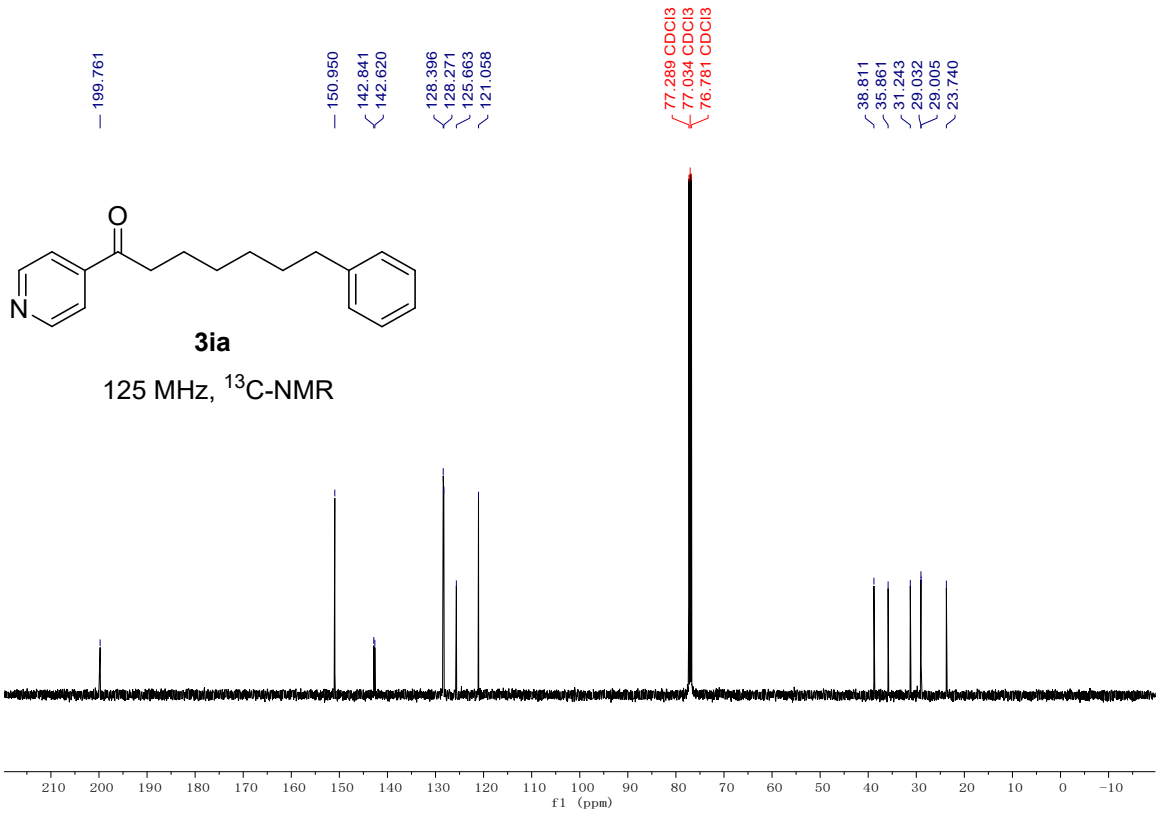
3ha

125 MHz, ^{13}C-NMR



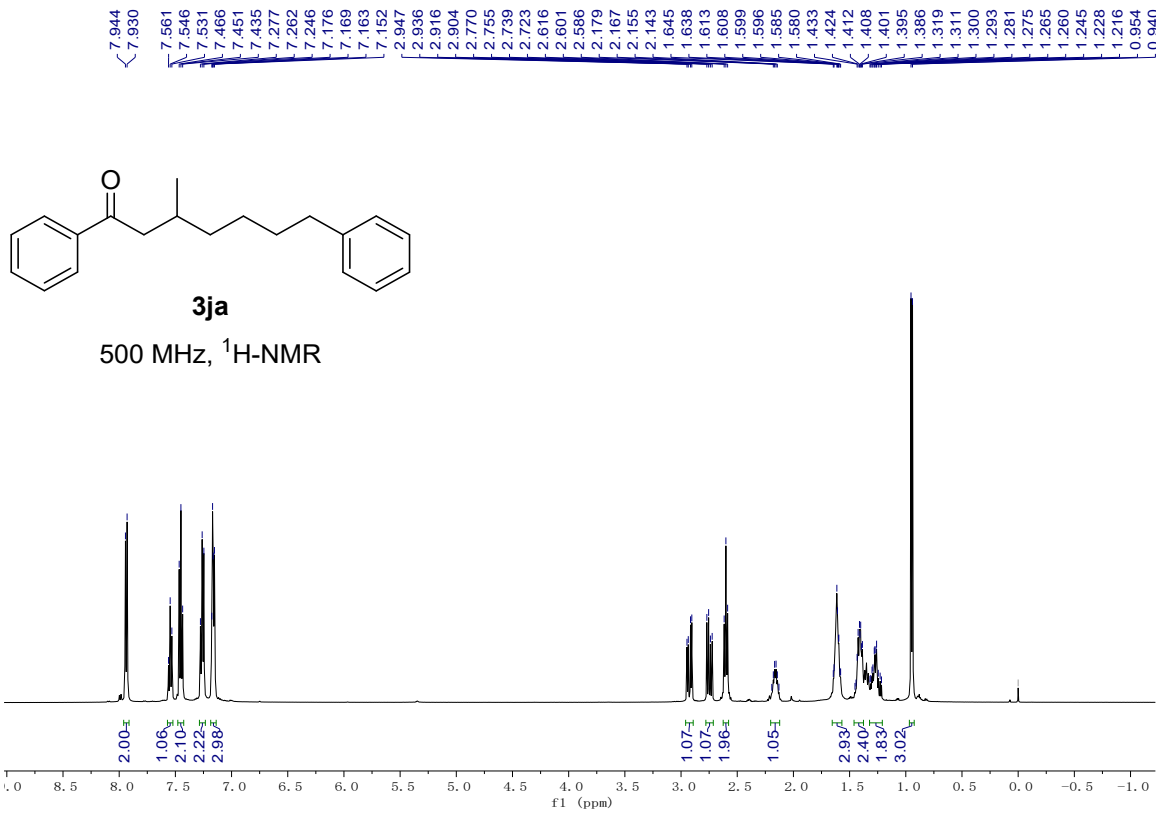
3ia

500 MHz, ^{1}H-NMR



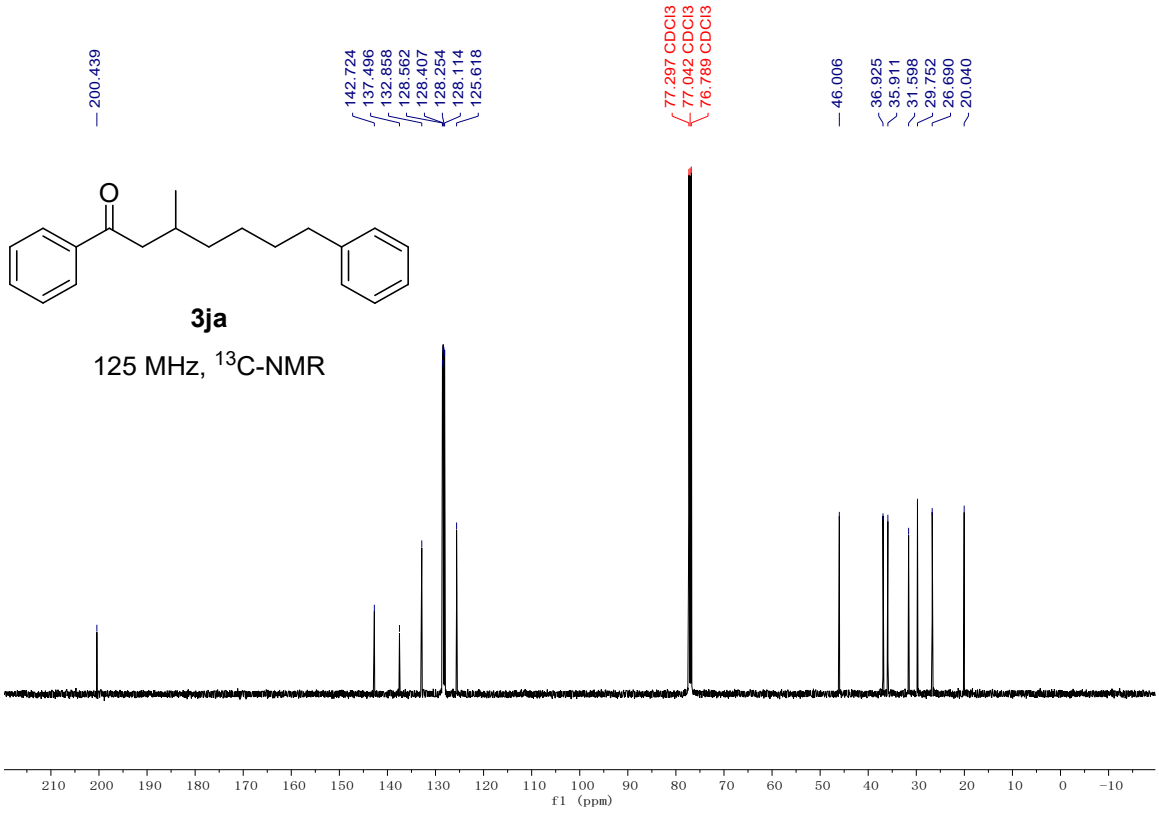
3ia

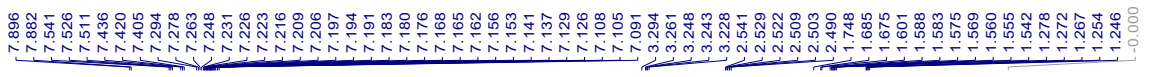
125 MHz, ^{13}C-NMR

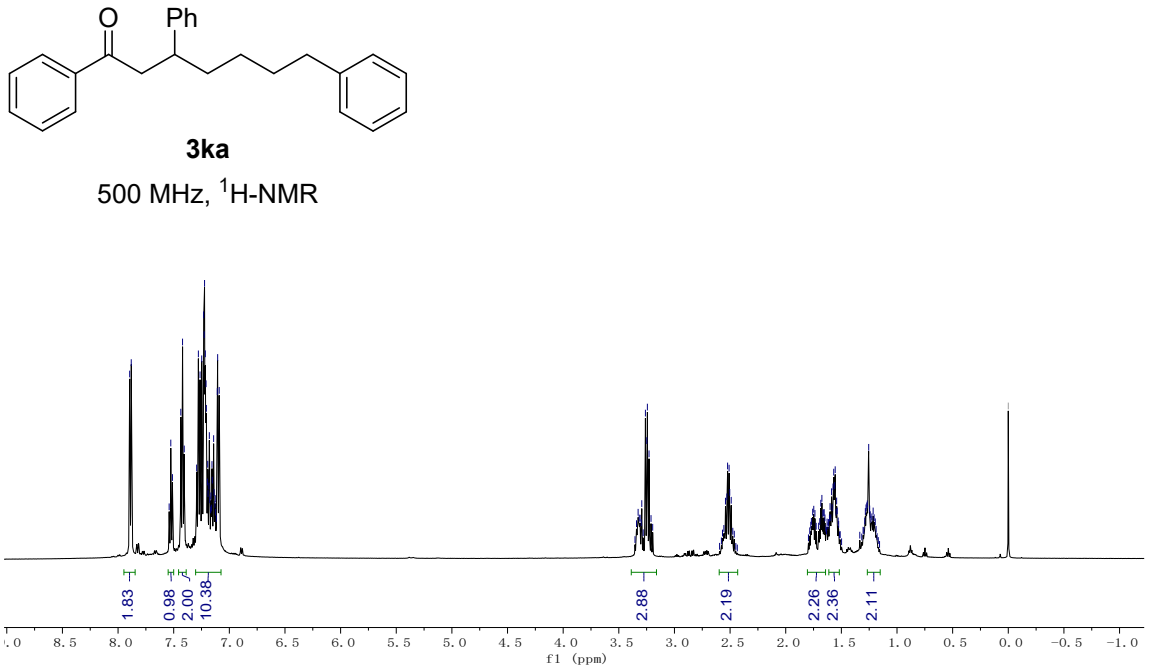


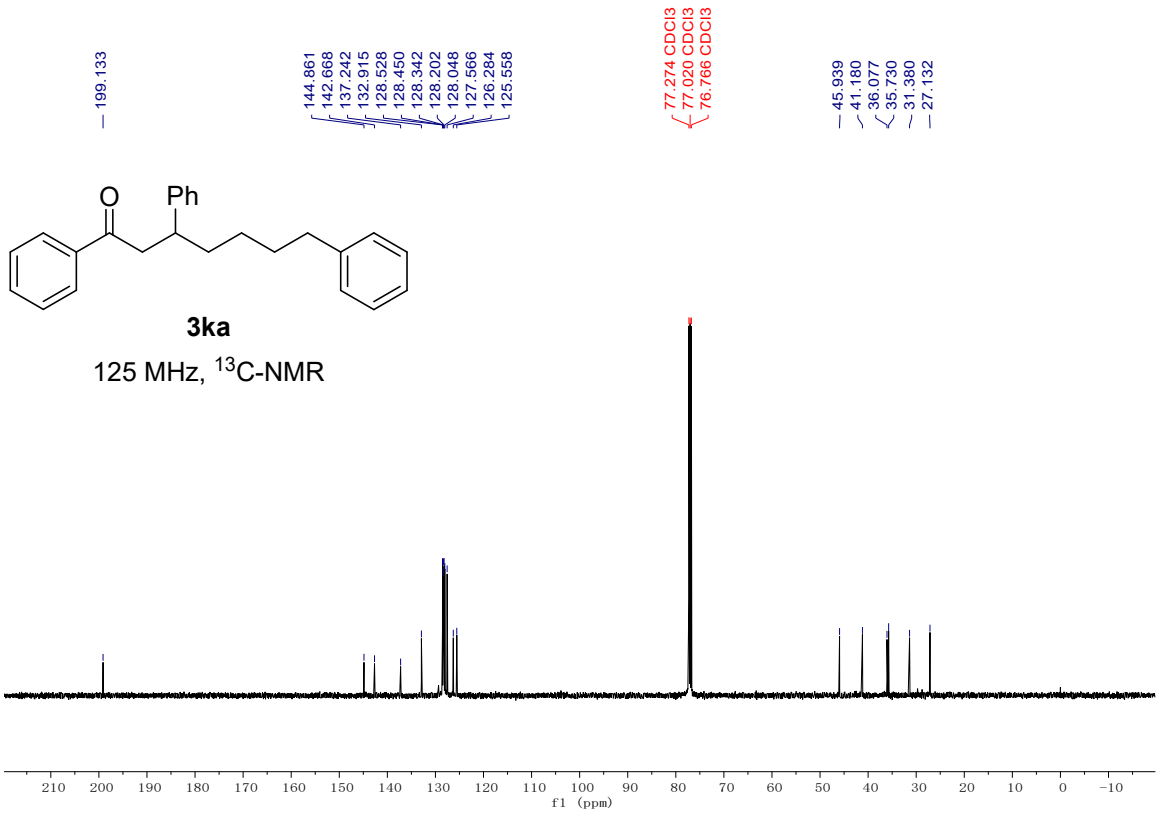
3ja

500 MHz, ^{1}H-NMR


200.439
142.724
137.496
132.858
128.562
128.407
128.254
128.114
125.618
77.297 CDCl3
77.042 CDCl3
76.789 CDCl3
46.006
36.925
35.911
31.598
29.752
26.690
20.040
O
3ja
125 MHz, 13C-NMR
f1 (ppm)


7.896
7.882
7.541
7.526
7.511
7.436
7.420
7.405
7.294
7.278
7.263
7.248
7.231
7.226
7.223
7.216
7.209
7.206
7.197
7.194
7.191
7.183
7.180
7.176
7.168
7.165
7.162
7.156
7.153
7.141
7.137
7.129
7.126
7.108
7.105
7.091
3.294
3.261
3.248
3.243
3.228
2.541
2.529
2.522
2.509
2.503
2.490
1.748
1.685
1.675
1.601
1.588
1.583
1.575
1.569
1.560
1.555
1.542
1.278
1.272
1.267
1.254
1.246
-0.000


O
Ph
3ka
500 MHz, 1H-NMR
1.83
0.98
2.00
10.38
2.88
2.19
2.26
2.36
2.11
f1 (ppm)


199.133
144.861
142.668
137.242
132.915
128.528
128.450
128.342
128.202
128.048
127.566
126.284
125.558
77.274 CDCl3
77.020 CDCl3
76.766 CDCl3
45.939
41.180
36.077
35.730
31.380
27.132
O
Ph
3ka
125 MHz, 13C-NMR
f1 (ppm)