Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photoredox-Catalyzed Carbonylative Acylation of Styrenes with Hantzsch Esters

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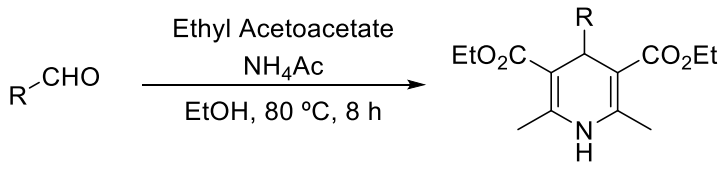
1. General Information

Unless otherwise noted, all reactions were carried out under carbon monoxide or nitrogen atmosphere. All reagents were from commercial sources (Sigma-Aldrich, Bidepharm, EnergyChemical) and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C), dichloromethane and ethyl acetate as eluent. All NMR spectra were recorded at ambient temperature using Bruker Avance III 400 MHz NMR (^{1}H, 400 MHz; ^{13}C{^{1}H}, 101 MHz, ^{19}F 376 MHz), Bruker AVANCE III HD 700 MHz NMR spectrometers (^{1}H, 700 MHz; ^{13}C{^{1}H}, 176 MHz). ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm; d6-DMSO: 2.50 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS via the carbon signals of the deuterated solvent ($CDCl_3$: 77.0 ppm; d6-DMSO: 39.5 ppm. Data for 1H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd (doublet of doublets), dt (doublet of triplets), qd (quartet of doublets), quint = quintet, m = multiplet, br = broad), coupling constant (Hz), and integration. All ^{13}C NMR spectra were broad-band 1H decoupled. All reactions were monitored by GC-FID or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI-TOF) or Agilent 6540 Accurate-MS spectrometer (Q-TOF). Because of the high toxicity of carbon monoxide, all the reactions should be performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.

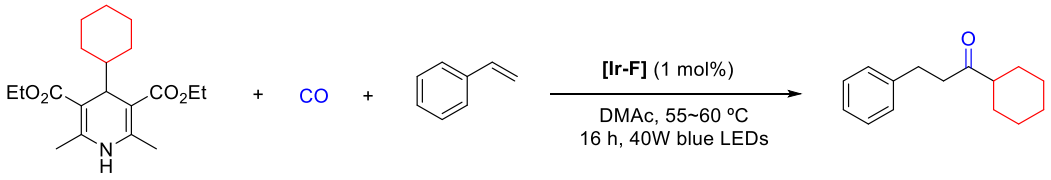
2. Preparation of Hantzsch Ester[1]



To an oven-dried flask was charged with aldehyde (5 mmol, 1.0 equiv), Ethyl Acetoacetate (10 mmol, 2.0 equiv), Ammonium acetate (5 mmol, 1.0 equiv) and. Then EtOH (15 mL) were added to the flask. The mixture was stirred under blue light irradiation for 8 hours at 80 ℃. After completion of reaction as monitored by TLC

analysis, the solvent was evaporated, vacuum the crude product, half an hour later add petroleum ether ultrasound, to give the corresponding Hantzsch ester.

3. Optimization of the Reaction Conditions



1a 2a

[Ir-F] = $IrdF(CF_3)ppy_2(dtbpy)PF_6$

Table S1 **Optimization of solvent**

Entry	Solvent	Yield (%)
1	MeCN	49
2	DCM	48
3	THF	51
4	MeOH	37
5	$PhCF_3$	48
6	1,4-dioxane	42
7	DMF	57
8	DMAc	61

Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), [**Ir-F**] (2 mol%), CO (60 bar), solvent (1 mL), 24 h. The yields were determined by GC using dodecane as the internal standard.

Table S2 **Optimization of solvent volume**

Entry	Solvent	Yield (%)
1	1 mL	61
2	2 mL	66

Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), [**Ir-F**] (2 mol%), CO (60 bar), DMAc, 24 h. The yields were determined by GC using dodecane as the internal standard.

Table S3 **Optimization of photosensitizer's amount**

Entry	Pc	Yield (%)
1	1 mol%	74
2	2 mol%	61
3	3 mol%	66

Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), [**Ir-F**] (2 mol%), CO (60 bar), DMAc (2 mL), 24 h. The yields were determined by GC using dodecane as the internal standard.

Table S4 **Optimization of time**

entry	time	Yield (%)
1	24 h	74
2	16 h	73

Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), [**Ir-F**] (1 mol%), CO (60 bar), DMAc (2 mL). The yields were determined by GC using dodecane as the internal standard.

Table S5 **Optimization of photosensitizer**

Entry	Pc	Yield (%)
1	4CzIPN	45
2	$MesAcr^{+}ClO^{-}_{4}$	<10
3	Eosin Y	trace
4	Fluorescein	trace
5	Phenol red	trace
6	Rhodamine B	trace
7	**[Ir-F]**	74

Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), CO (60 bar), DMAc (2 mL). Pc (1 mol%), 16 h.The yields were determined by GC using dodecane as the internal standard.

Table S6 **Optimization of pressure**

Entry	Pressure (bar)	Yield (%)
1	10	36
2	30	66
3	60	74

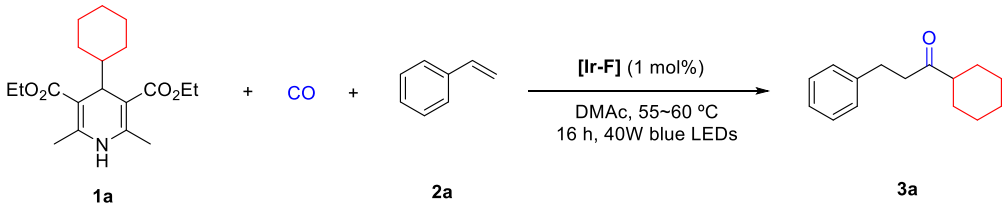
Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), [**Ir-F**] (1 mol%), DMAc (2 mL), 16 h. The yields were determined by GC using dodecane as the internal standard.

Table S7 **Optimization of equivalent ratio**

Entry	**1** : **2**	Yield (%)
1	1.0 : 1.5	56
2	1.0 : 2.0	66
3	2.0 : 1.0	58
4	1.5 : 1.0	74

Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), [**Ir-F**] (1 mol%), CO (60 bar), DMAc (2 mL), 16 h. The yields were determined by GC using dodecane as the internal standard.

4. General Experimental Procedure and Characterization Data

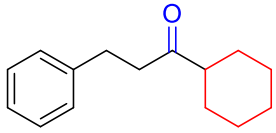


1a **2a** **3a**

[Ir-F] = IrdF(CF_3)ppy$_2$(dtbpy)PF_6

A 4 mL screw-cap vial was charged with **1a** Hantzsch easter (51 mg, 1.5equiv), [**Ir-F**] (1.1 mg, 1 mol%.) and an oven-dried stirring bar. After replacing nitrogen in the bottle three times, DMAc (2 mL) was added, then add **2a** styrene (11 μL, 1.0 equiv) with a microinjector. the vial was moved to an alloy plate and put into a autoclave which are euphotic under argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 60 atm of CO. The autoclave was placed on a environment equipped with a magnetic stirrer and two Kesill light (390nm, 40W). The reaction mixture was stirred for 16 h. After the reaction was complete, the autoclave was cooled to room temperature and the pressure was released carefully. The reaction mixture was extracted with DCM (15 mL×3), dried with anhydrous sodium sulfate. The solvent was removed in vacuum, purified by column chromatog-

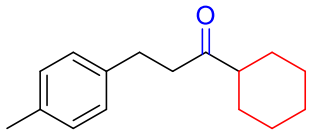
raphyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3a**, the product was colored with phosphomolybdate.



cyclohexyl-3-phenylpropan-1-one[2] (3a): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3a** as a colorless oil liquid. (15.1 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.19 (t, *J* = 6.5 Hz, 3H), 2.93 – 2.85 (m, 2H), 2.80 – 2.71 (m, 2H), 2.31 (tt, *J* = 11.2, 3.3 Hz, 1H), 1.85 – 1.72 (m, 4H), 1.67 – 1.64 (m, 1H), 1.36 – 1.14 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.3, 141.4, 128.5, 128.4, 126.0, 51.0, 42.3, 29.7, 28.4, 25.9, 25.7.

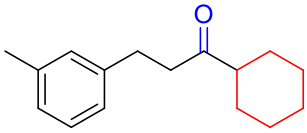


1-cyclohexyl-3-(p-tolyl)propan-1-one (3b): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3b** as a yellow oil liquid. (11.2 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.04 (m, 4H), 2.88 – 2.80 (m, 2H), 2.78 – 2.70 (m, 2H), 2.36 – 2.26 (m, 4H), 1.86 – 1.73 (m, 4H), 1.70 – 1.62 (m, 1H), 1.38 – 1.17 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.3, 138.3, 135.5, 129.1, 128.2, 51.0, 42.4, 29.3, 28.4, 25.9, 25.7, 21.0.

HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{16}H_{22}O$ 231.1743, found: 231.1748.

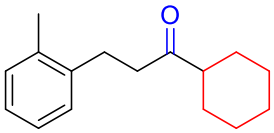


1-cyclohexyl-3-(m-tolyl)propan-1-one (3c): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3c** as a colorless oil liquid. (11.0 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 1H), 6.99 (t, *J* = 8.7 Hz, 3H), 2.85 – 2.81 (m, 2H), 2.34 – 2.30 (m, 2H), 2.36 – 2.29 (m, 4H), 1.86 – 1.73 (m, 4H), 1.70 – 1.63 (m, 1H), 1.33 – 1.21 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.3, 141.4, 138.0, 129.2, 128.4, 126.8, 125.3, 51.0, 42.4, 29.7, 28.4, 25.9, 25.7, 21.4.

HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{16}H_{22}O$ 231.1743, found: 231.1741.

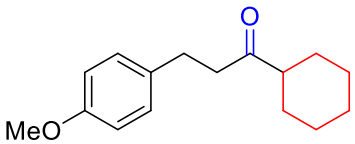


1-cyclohexyl-3-(o-tolyl)propan-1-one (3d): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3d** as a colorless oil liquid. (10.2 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.04 (m, 4H), 2.89 – 2.83 (m, 2H), 2.70 (dd, *J* = 10.3, 5.2 Hz, 2H), 2.30 (s, 4H), 1.87 – 1.71 (m, 4H), 1.69 – 1.62 (m, 1H), 1.37 – 1.20 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.3, 139.5, 135.9, 130.3, 128.6, 126.2, 126.1, 51.0, 40.9, 28.5, 27.1, 25.9, 25.7, 19.3.

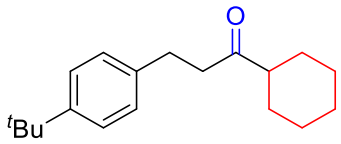
HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{16}H_{22}O$ 231.1743, found: 231.1748.



1-cyclohexyl-3-(4-methoxyphenyl)propan-1-one[2] (3e): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica

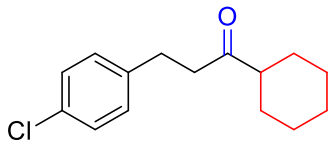
gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3e** as a colorless oil liquid. (8.6 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.85 – 2.78 (m, 2H), 2.71 (dd, *J* = 11.1, 4.3 Hz, 2H), 2.30 – 2.27 (m, 1H), 1.81 – 1.75 m, 4H), 1.65 (d, *J* = 10.0 Hz, 1H), 1.36 – 1.17 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.3, 157.9, 133.5, 129.3, 113.9, 55.3, 51.0, 42.5, 28.9, 28.4, 25.9, 25.7.



3-(4-(tert-butyl)phenyl)-1-cyclohexylpropan-1-one (3f): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3f** as a colorless oil liquid. (12.3 mg, 45%).

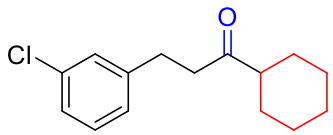
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 2.82 – 2.73 (m, 2H), 2.66 (dd, *J* = 11.2, 4.4 Hz, 2H), 2.26 – 2.20 (m, 1H), 1.79 – 1.65 (m, 4H), 1.62 – 1.54 (m, 1H), 1.32 – 1.11 (m, 14H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.3, 148.9, 138.3, 128.0, 125.4, 50.98, 42.2, 34.3, 31.4, 29.2, 28.5, 25.8, 25.6.
HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{19}H_{28}O$ 273.2213, found: 273.2217.



3-(4-chlorophenyl)-1-cyclohexylpropan-1-one[2] (3g): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3g** as a colorless oil liquid. (8.7 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 2.85 (t, *J* = 7.3 Hz, 2H), 2.75 – 2.71 (m, 2H), 2.32 – 2.26 (m, 1H), 1.80 – 1.75 (m, 4H), 1.69 – 1.62 (m, 1H), 1.31 – 1.21 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8, 139.9, 131.7, 129.7, 128.5, 50.9, 42.0, 28.9, 28.4, 25.8, 25.6.

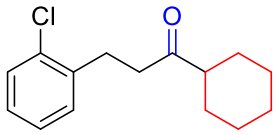


3-(3-chlorophenyl)-1-cyclohexylpropan-1-one (3h): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3h** as a colorless oil liquid. (10.1 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.06 (m, 3H), 6.98 (d, *J* = 7.1 Hz, 1H), 2.78 (t, J = 7.4 Hz, 2H), 2.67 (dd, *J* = 9.5, 5.0 Hz, 2H), 2.26 – 2.22 (m, 1H), 1.78 – 1.64 (m, 4H), 1.62 – 1.56 (m, 1H), 1.29 – 1.09 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 143.5, 134.1, 129.6, 128.4, 126.6, 126.2, 50.9, 41.8, 29.3, 28.4, 25.8, 25.6.

HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{15}H_{19}ClO$ 251.1197, found: 251.1201.

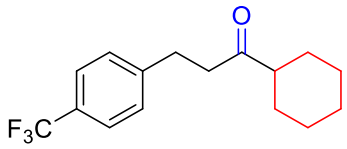


3-(2-chlorophenyl)-1-cyclohexylpropan-1-one (3i): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3i** as a light yellow oil liquid. (17.0 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.22 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.19 – 7.10 (m, 2H), 3.03 – 2.92 (m, 2H), 2.82 – 2.71 (m, 2H), 2.31 (tt, *J* = 11.2, 3.3 Hz, 1H), 1.87 – 1.71 (m, 4H), 1.69 – 1.62 (m, 1H), 1.36 – 1.15 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.9, 138.9, 133.8, 130.7, 129.5, 127.6, 126.9, 50.9, 40.1, 28.4, 27.9, 25.8, 25.6.

HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{15}H_{19}ClO$ 251.1197, found: 251.1201.

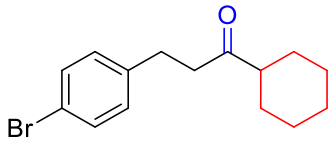


1-cyclohexyl-3-(4-(trifluoromethyl)phenyl)propan-1-one[2] (3j): The reaction solution was extracted by DCM for three times, then purified by column chromatography-on silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3j** as a light yellow oil solid. (22.9 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.17 (m, 2H), 2.86 (t, J = 7.4 Hz, 2H), 2.70 (dd, *J* = 9.5, 5.3 Hz, 2H), 2.26 – 2.22 (m, 1H), 1.77 – 1.63 (m, 4H), 1.62 – 1.52 (m, 1H), 1.29 – 1.07 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 145.6, 128.7, 128.5, 128.2, 125.3, 125.3, 125.3, 50.9, 41.6, 29.3, 28.4, 25.8, 25.6.

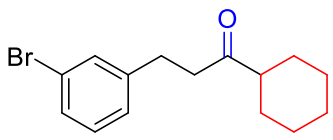
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4.



3-(4-bromophenyl)-1-cyclohexylpropan-1-one[2] (3k): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3k** as a colorless oil liquid. (12.1 mg, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 2.83 (t, J = 7.2 Hz, 2H), 2.72 (dd, *J* = 11.1, 4.2 Hz, 2H), 2.33 – 2.26 (m, 1H), 1.78 (dd, *J* = 13.2, 7.4 Hz, 4H), 1.70 – 1.63 (m, 1H), 1.37 – 1.16 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 140.4, 131.4, 130.1, 119.7, 50.9, 41.8, 29.0, 28.4, 25.8, 25.6.



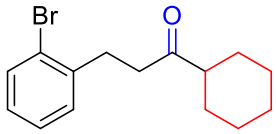
3-(3-bromophenyl)-1-cyclohexylpropan-1-one (3l): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel

using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3l** as a colorless oil liquid. (17.7 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.09 – 7.00 (m, 2H), 2.82 – 2.74 (m, 2H), 2.68 – 2.64 (m, 2H), 2.26 – 2.20 (m, 1H), 1.78 – 1.64 (m, 4H), 1.59 (d, *J* = 10.1 Hz, 1H), 1.30 – 1.12 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 143.8, 131.3, 130.0, 129.1, 127.1, 122.4, 50.9, 41.8, 29.2, 28.4, 25.8, 25.6.

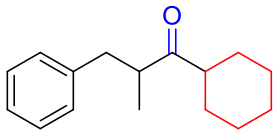
HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{15}H_{19}BrO$ 295.0692, found: 295.0697.



3-(2-bromophenyl)-1-cyclohexylpropan-1-one[3] (3m): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3m** as a colorless oil liquid. (19.1 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.08 – 7.03 (m, 1H), 3.03 – 2.94 (m, 2H), 2.81 – 2.71 (m, 2H), 2.34 – 2.28 (m, 1H), 1.87 – 1.70 (m, 4H), 1.71 – 1.64 (m, 1H), 1.37 – 1.16 (m, 5H).

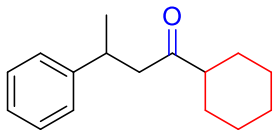
^{13}C NMR (100 MHz, $CDCl_3$) δ 212.8, 140.6, 132.8, 130.7, 127.8, 127.5, 124.2, 50.9, 40.3, 30.3, 28.4, 25.8, 25.6.



1-cyclohexyl-2-methyl-3-phenylpropan-1-one[4] (3n): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3n** as a yellow oil liquid. (9.3 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.3 Hz, 2H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.15 – 7.08 (m, 2H), 3.00 – 2.89 (m, 2H), 2.55 – 2.48 (m, 1H), 2.29 – 2.22 (m, 1H), 1.77 – 1.64 (m, 3H), 1.73 – 1.67 (m, 2H), 1.33 – 1.20 (m, 2H), 1.20 – 1.08 (m, 3H), 1.08 – 1.00 (m, 3H).

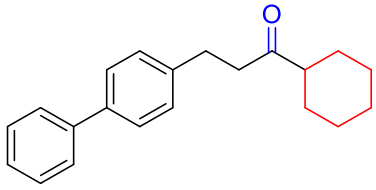
^{13}C NMR (100 MHz, $CDCl_3$) δ 217.1, 140.0, 129.0, 128.3, 126.1, 50.4, 46.5, 39.3, 28.2, 28.0, 25.8, 25.6, 17.0.



1-cyclohexyl-3-phenylbutan-1-one[5] (3o): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3o** as a colorless oil liquid. (7.9 mg, 34%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.16 (m, 3H), 3.41 – 3.28 (m, 1H), 2.77 – 2.63 (m, 2H), 2.30 – 2.17 (m, 1H), 1.86 – 1.67 (m, 4H), 1.65 – 1.63 (m, 1H), 1.32 – 1.15 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.0, 146.6, 128.4, 126.8, 126.2, 51.2, 49.1, 35.0, 28.3, 28.1, 25.8, 25.7, 25.6, 21.8.

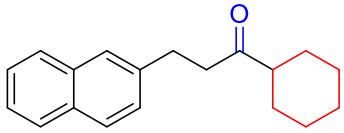


3-([1,1'-biphenyl]-4-yl)-1-cyclohexylpropan-1-one (3p): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3p** as a colorless oil liquid. (10.8 mg, 37%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 4.1 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.81 – 2.77 (m, 2H), 2.33 (tt, *J* = 11.2, 3.3 Hz, 1H), 1.87 – 1.72 (m, 4H), 1.70 – 1.61 (m, 1H), 1.39 – 1.18 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 141.0, 140.5, 139.0, 128.7, 128.7, 127.1, 127.1, 127.0, 51.0, 42.1, 29.3, 28.4, 25.8, 25.6.

HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{21}H_{24}O$ 293.19, found: 293.1908.

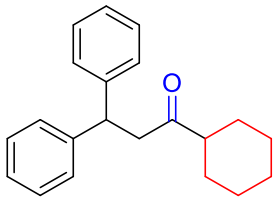


1-cyclohexyl-3-(naphthalen-2-yl)propan-1-one (3q): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3q** as a colorless oil liquid. (17.5 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 3H), 7.62 (s, 1H), 7.47 – 7.41 (m, 2H), 7.33 (dd, *J* = 8.4, 1.4 Hz, 1H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.85 (dd, *J* = 9.9, 5.3 Hz, 2H), 2.34 (tt, *J* = 11.2, 3.3 Hz, 1H), 1.89 – 1.72 (m, 4H), 1.70 – 1.63 (m, 1H), 1.41 – 1.18 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 138.9, 133.6, 132.0, 128.0, 127.6, 127.4, 127.1, 126.4, 126.0, 125.2, 51.0, 42.2, 29.8, 28.4, 25.8, 25.6.

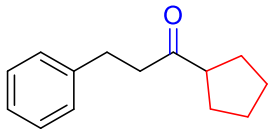
HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{19}H_{22}O$ 267.1743, found: 267.1748.



1-cyclohexyl-3,3-diphenylpropan-1-one[2] (3r): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3r** as a light yellow solid. (21.0 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.25 – 7.18 (m, 6H), 7.18 – 7.13 (m, 2H), 4.62 (t, *J* = 7.4 Hz, 1H), 3.18 (d, *J* = 7.4 Hz, 2H), 2.30 – 2.17 (m, 1H), 1.70 (d, *J* = 7.7 Hz, 4H), 1.65 – 1.59 (m, 1H), 1.27 – 1.12 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8, 144.2, 128.5, 127.8, 126.3, 51.3, 46.8, 45.6, 28.1, 25.8, 25.6.



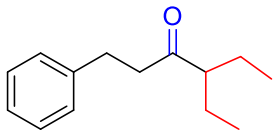
1-cyclopentyl-3-phenylpropan-1-one (3s): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using pe-

troleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3s** as a light yellow oil liquid. (9.2 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.20 – 7.18 (m, 3H), 2.93 – 2.87 (m, 1H), 2.87 – 2.81 (m, 1H), 2.80 – 2.74 (m, 1H), 1.85 – 1.48 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 141.4, 128.4, 128.3, 126.0, 51.5, 43.4, 29.9, 28.8, 26.0.

HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{14}H_{18}O$ 203.143, found: 203.1429.

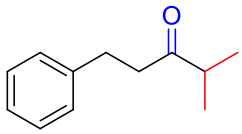


4-ethyl-1-phenylhexan-3-one (3t): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3t** as a light yellow oil liquid. (14.1 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 3H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.78 – 2.69 (m, 2H), 2.35 – 2.28 (m, 1H), 1.66 – 1.54 (m, 2H), 1.51 – 1.38 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.8, 141.4, 128.4, 128.4, 126.0, 55.6, 44.0, 29.5, 24.2, 11.8.

HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{14}H_{20}O$ 205.1587, found: 205.1582.

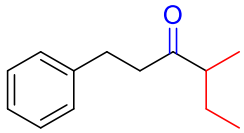


4-methyl-1-phenylpentan-3-one (3u): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3u** as a light yellow solid. (9.5 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.19 (t, *J* = 6.2 Hz, 3H), 2.93 – 2.86 (m, 2H), 2.77 (dd, *J* = 9.7, 5.1 Hz, 2H), 2.60 – 2.53(m, 1H), 1.08 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.8, 141.3, 128.4, 128.3, 126.0, 42.0, 41.0, 29.8, 18.1.

HRMS(ESI-TOF) m/z: calcd for [M+]H+ $C_{12}H_{16}O$ 177.1274, found: 177.1276.



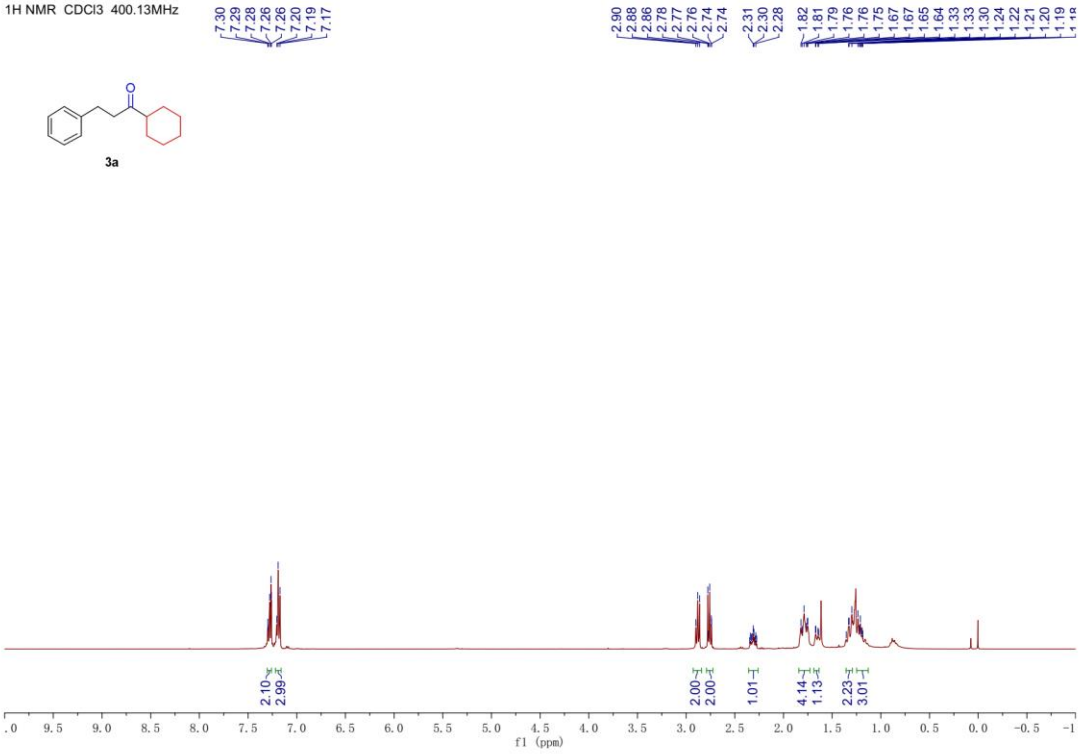
4-methyl-1-phenylhexan-3-one[6] (3v): The reaction solution was extracted by DCM for three times, then purified by column chromatographyon silica gel using petroleum ether and ethyl acetate (80:1-50:1) to afford the corresponding product **3v** as a colorless oil liquid. (10.3 mg, 54%).

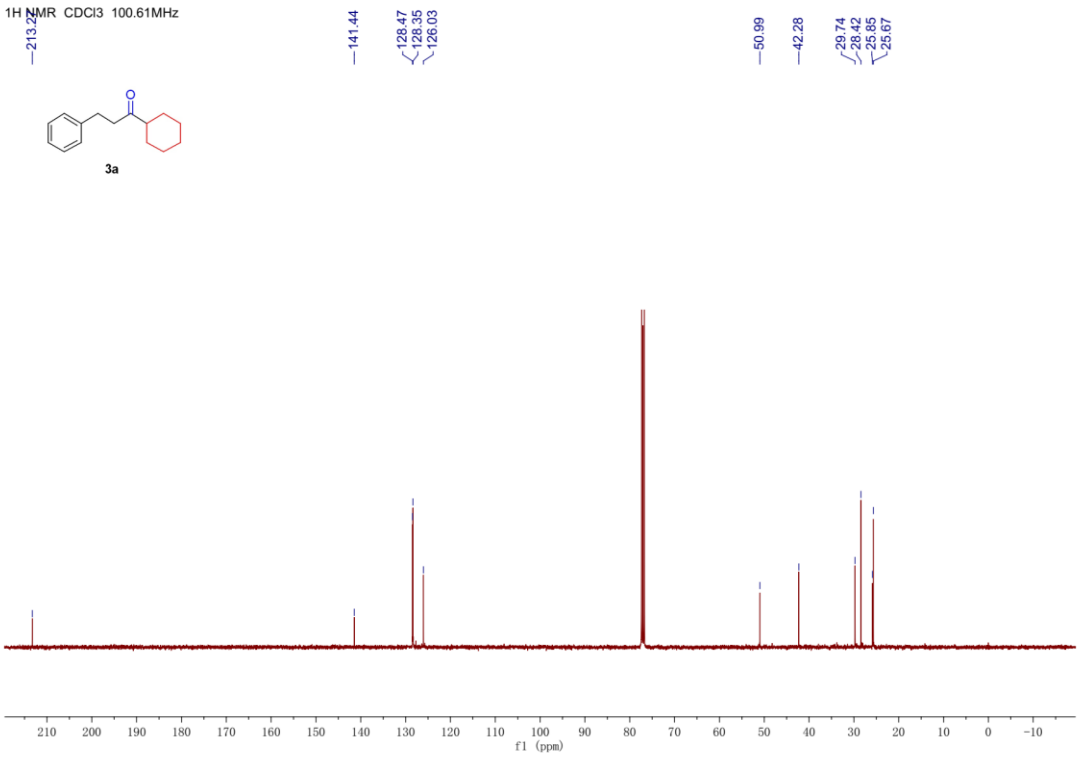
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 2H), 7.22 – 7.15 (m, 3H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.79 – 2.72 (m, 2H), 2.43 (dd, *J* = 13.7, 6.9 Hz, 1H), 1.69 – 1.60 (m, 1H), 1.40 – 1.33 (m, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.8, 141.3, 128.4, 128.3, 126.0, 48.0, 42.8, 29.7, 25.8, 15.7, 11.6.

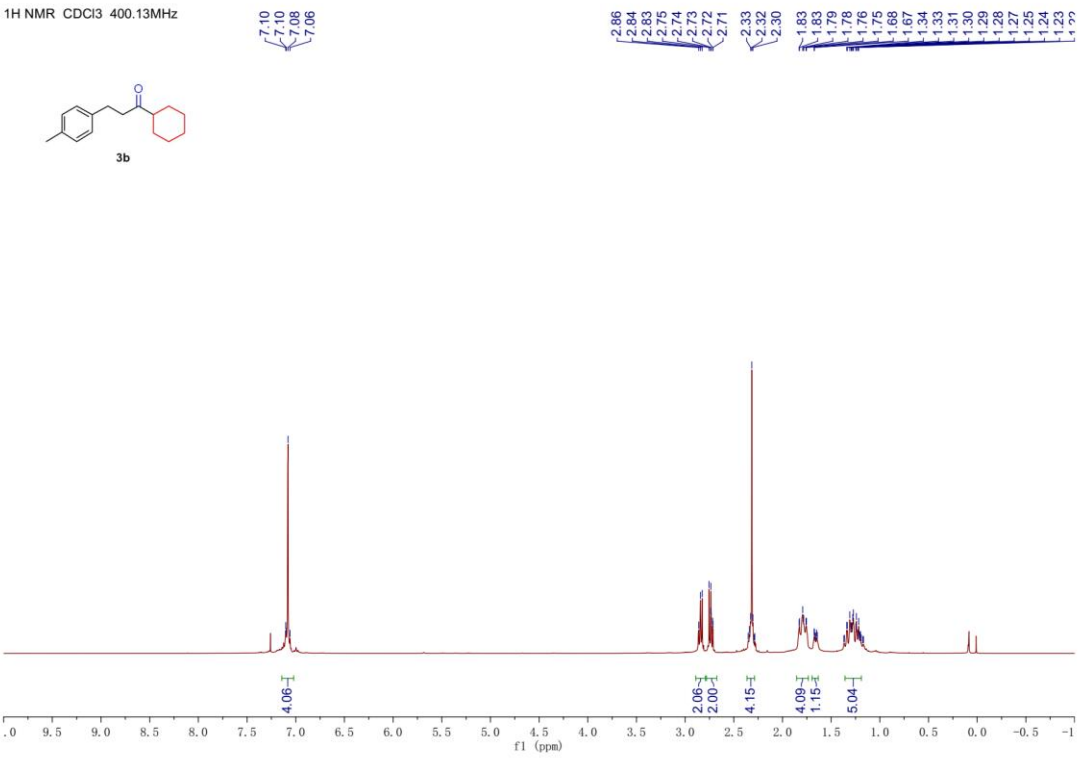
5. References

[1] B. Chen, C.-S. Kuai, J.-X. Xu, X.-F. Wu, *Adv. Synth. Catal.* **2021**, *364*, 487-492.
[2] J. A. Forni, V. H. Gandhi, A. Polyzos, *ACS Catal.* **2022**, *12*, 10018-10027.
[3] J. Garca-Fortanet, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2008**, *47*, 8108-8111.
[4] J. Barluenga, E. Aguilar, B. Olano, S. Fustero, *J. Org. Chem.* **1988**, *53*, 1741-1744.
[5] M. Kunitski, N. Eicke, P. Huber et al. *Nature Communications* **2019**, *10*,1.
[6] Elis Erbing, A. Vázquez-Romero, A. B. Gómez et al. *Chem. Eur. J.* **2016**, *22*, 15659-15663.

6. Copies of ^{1}H ,^{13}C and ^{19}F NMR Spectra.



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2.71
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2.30
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1.83
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1.27
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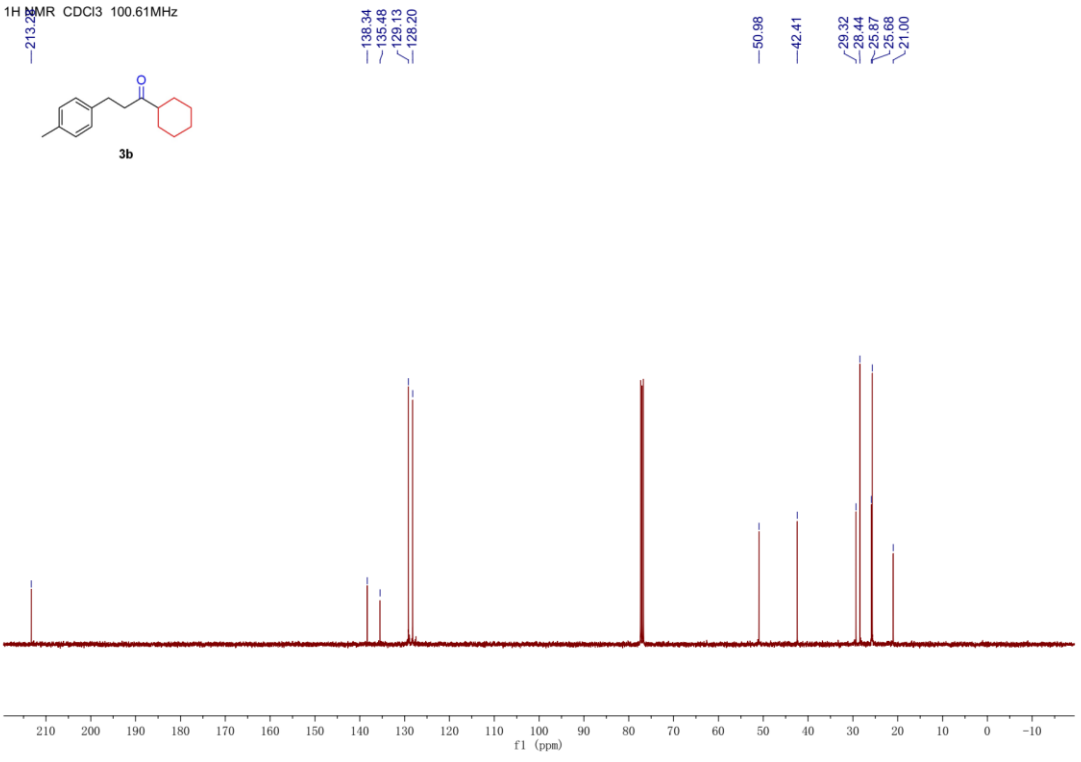
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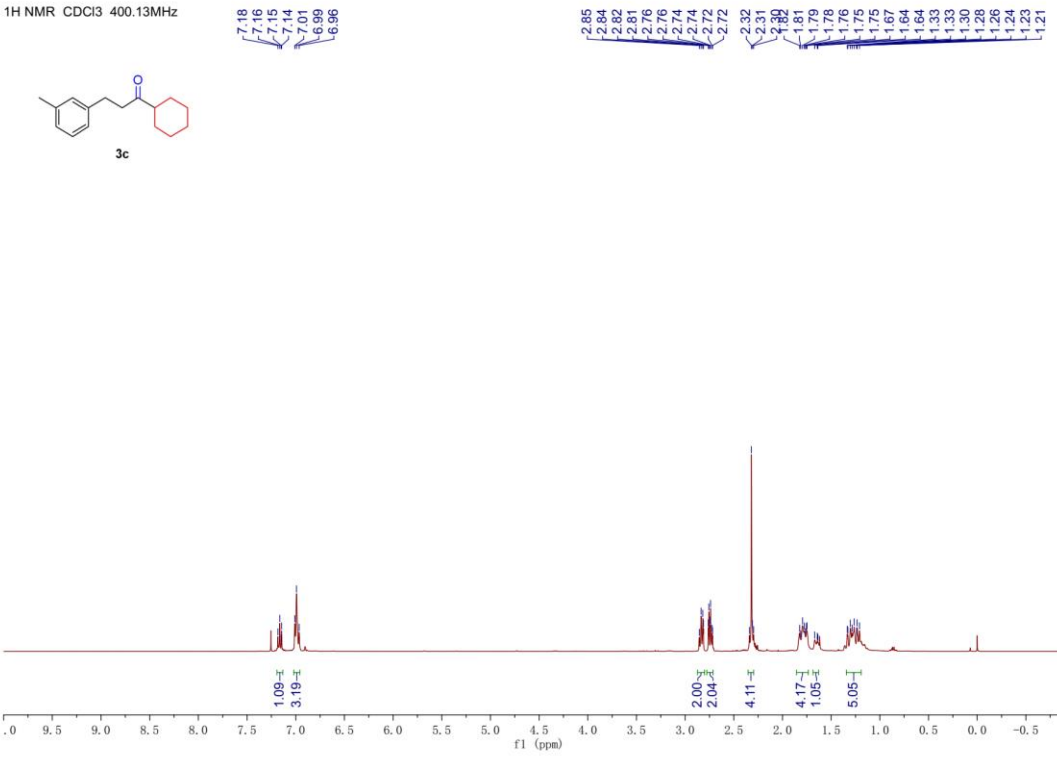
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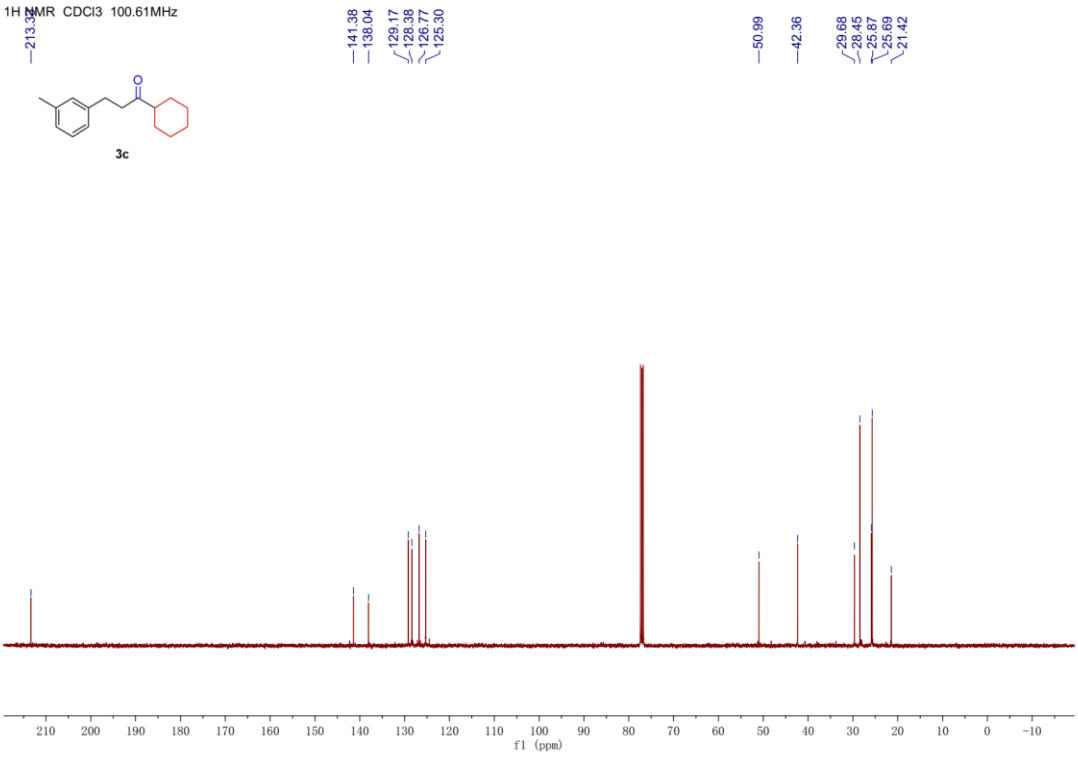
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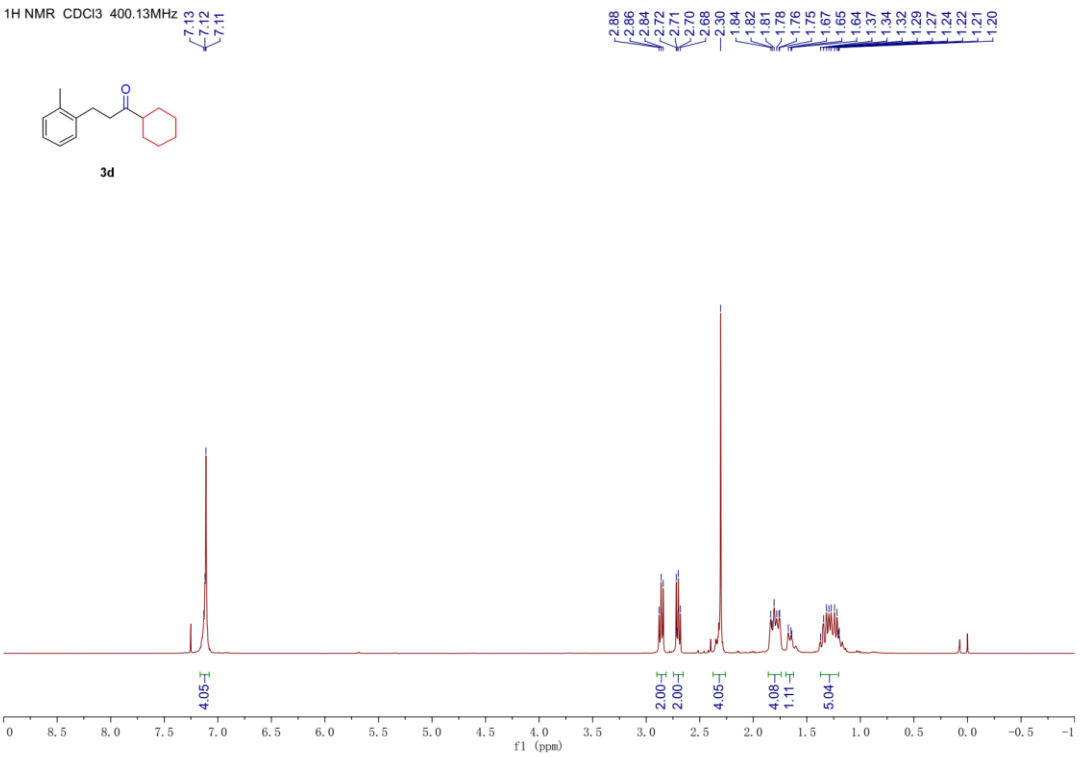
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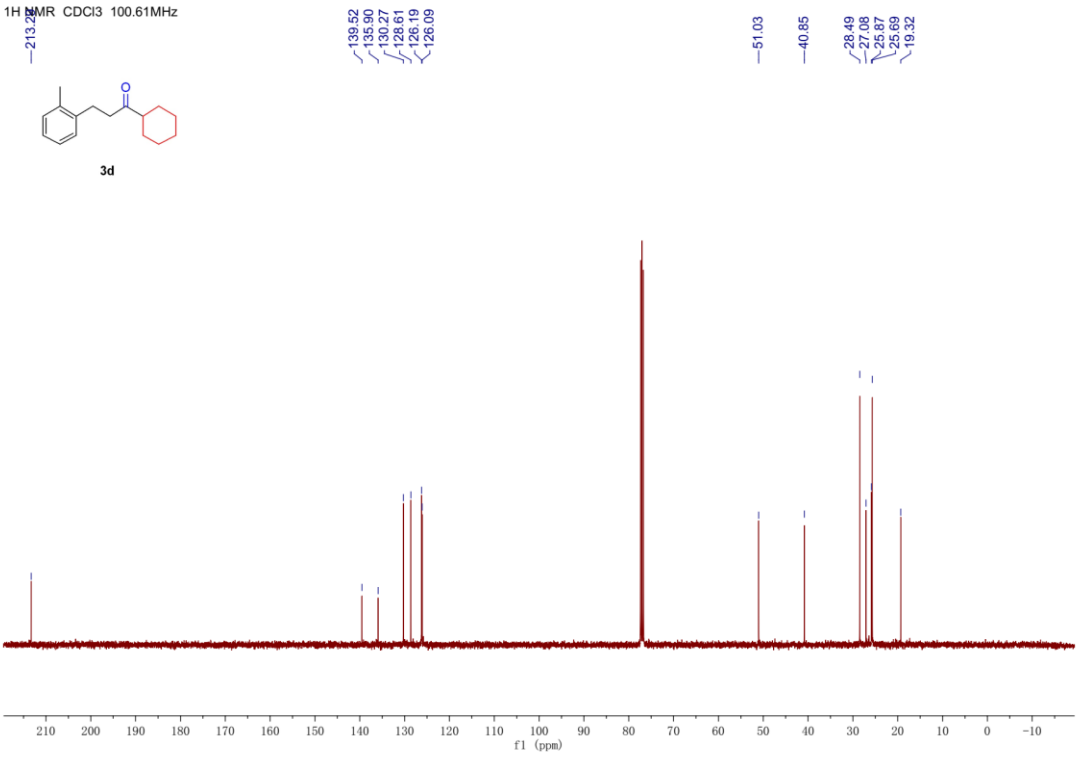
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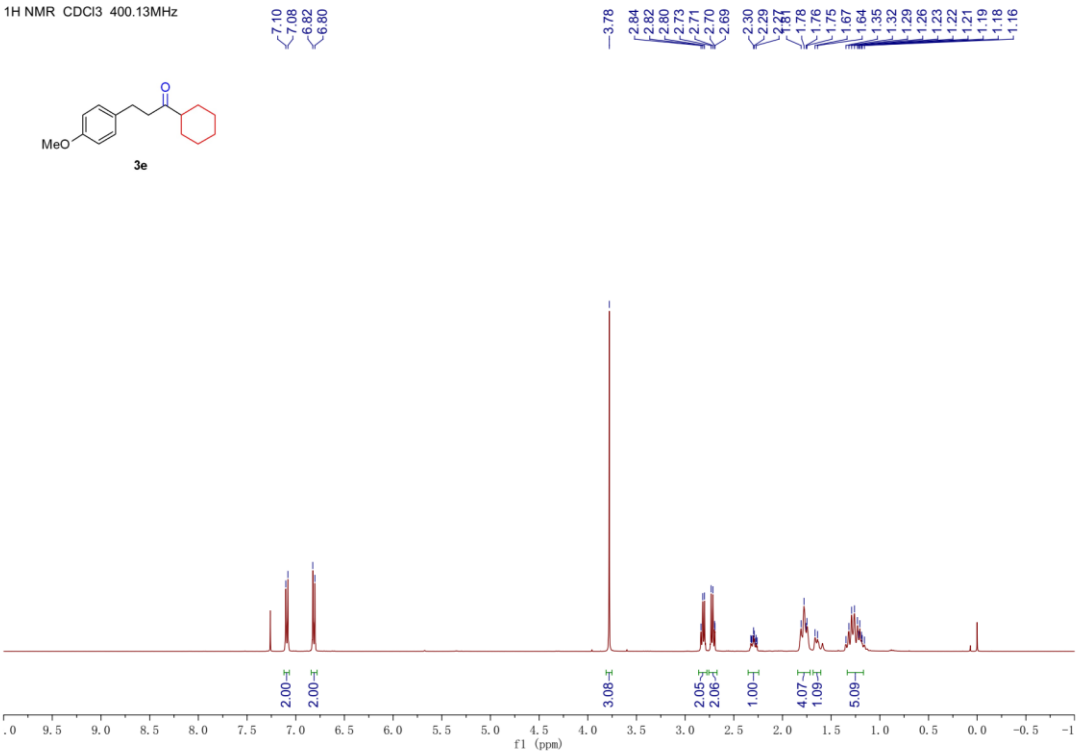
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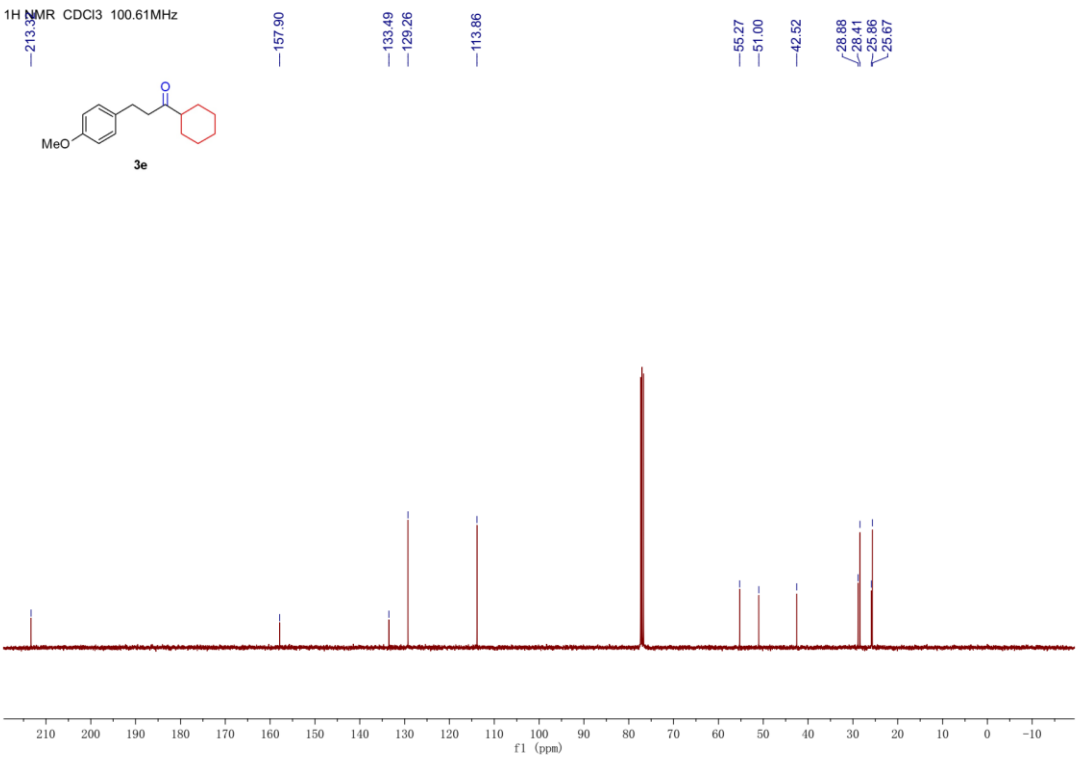
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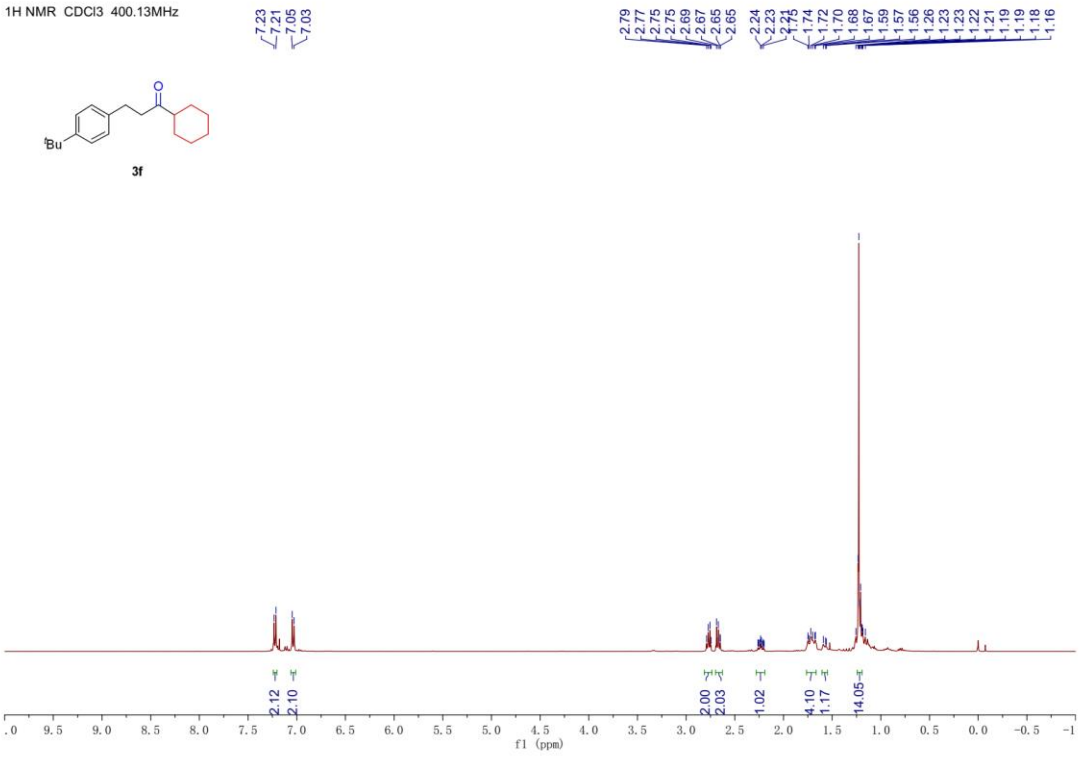
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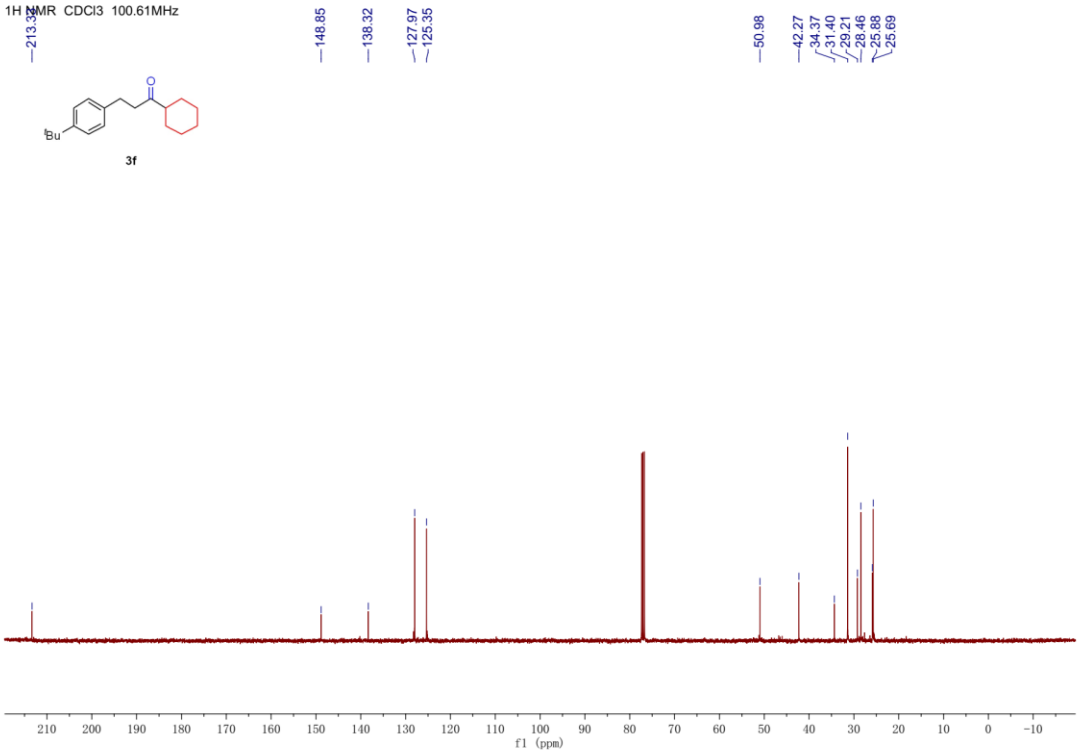
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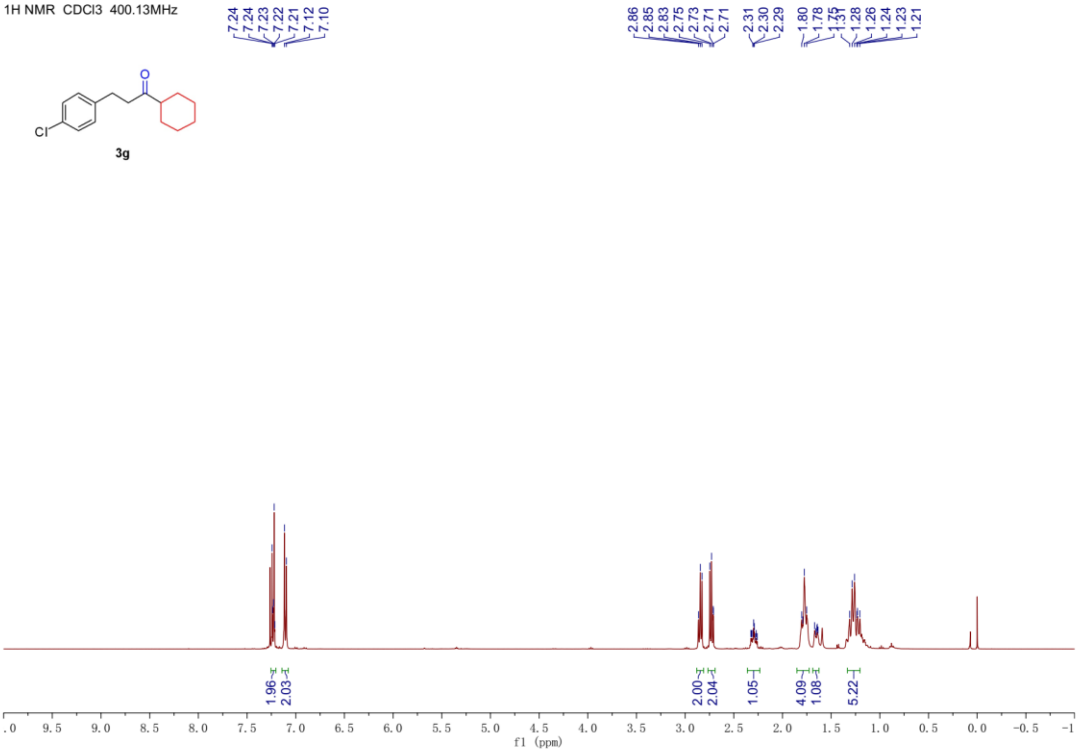
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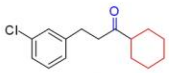
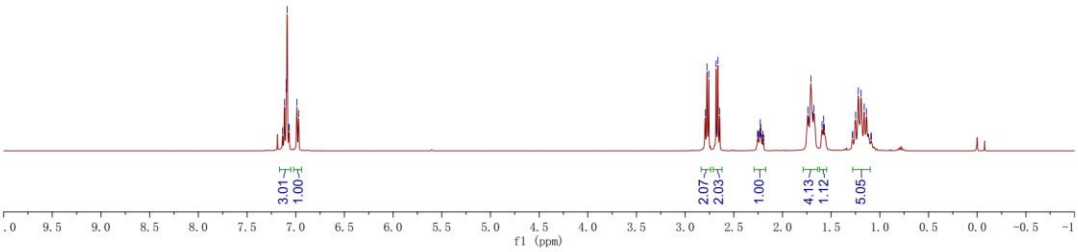
2.73
2.71
2.71
2.31
2.30
2.29
1.80
1.78
1.75
1.31
1.28
1.26
1.24
1.23
1.21
Cl
O
3g
1.96
2.03
2.00
2.04
1.05
4.09
1.08
5.22
f1 (ppm)
1H NMR CDCl3 100.61MHz
212.86
139.91
131.73
129.76
128.52
50.98
42.00
28.99
28.40
25.82
25.64
Cl
O
3g
f1 (ppm)

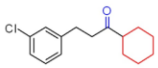
1H NMR CDCl3 400.13MHz



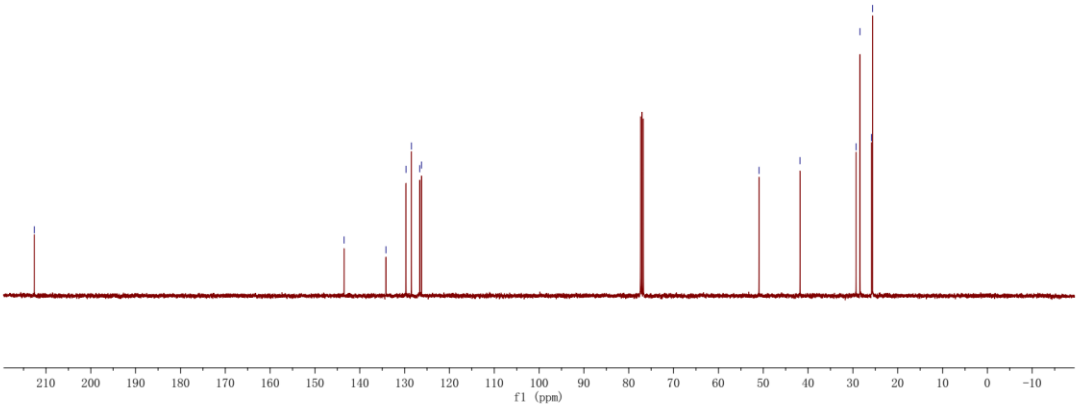
3h



1H NMR CDCl3 100.61MHz

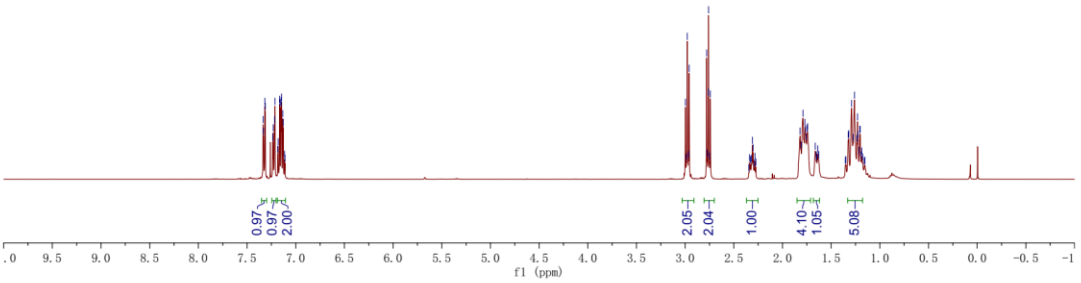


3h



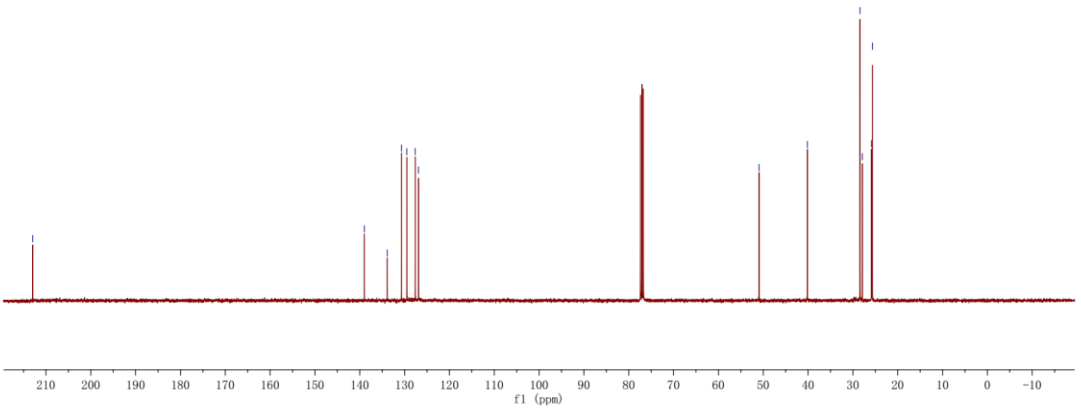

1H NMR CDCl3 400.13MHz

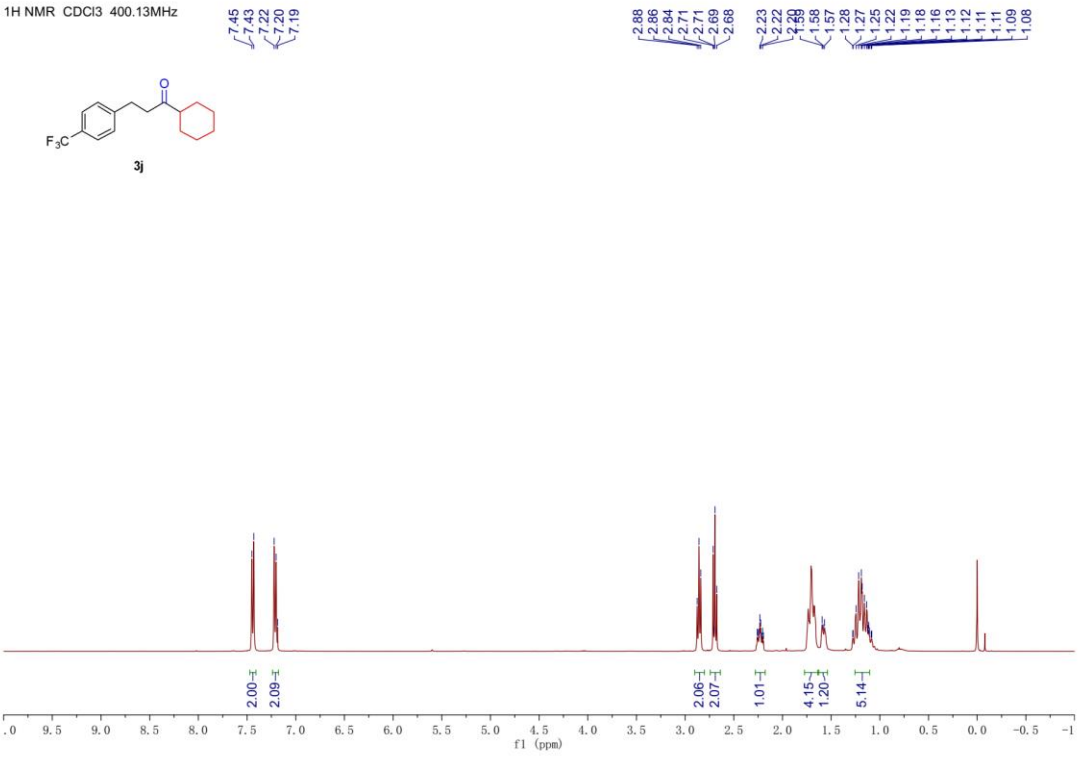
3i

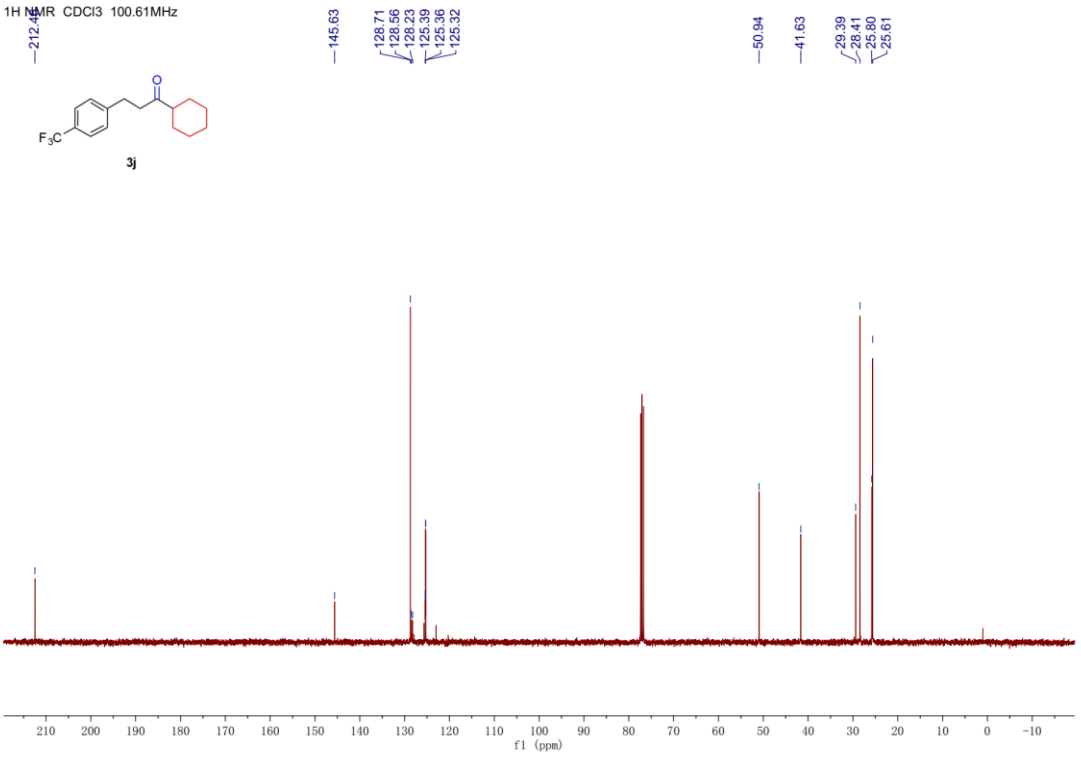

0.97
0.97
2.00
2.05
2.04
1.00
4.10
1.05
5.08
f1 (ppm)


1H NMR CDCl3 100.61MHz
212.98
138.97
133.85
130.72
129.50
127.62
126.91
50.95
40.16
28.41
27.90
25.85
25.67

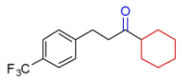
3i


f1 (ppm)


1H NMR CDCl3 400.13MHz
7.45
7.43
7.22
7.20
7.19
2.88
2.86
2.84
2.71
2.71
2.69
2.68
2.23
2.22
2.20
1.59
1.58
1.57
1.28
1.27
1.25
1.22
1.19
1.18
1.16
1.13
1.12
1.11
1.11
1.09
1.08
F3C
O
3j
2.00
2.09
2.06
2.07
1.01
4.15
1.20
5.14
f1 (ppm)

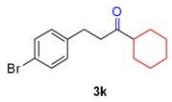

1H NMR CDCl3 100.61MHz
212.46
145.63
128.71
128.56
128.23
125.39
125.36
125.32
50.94
41.63
29.39
28.41
25.80
25.61
F3C
O
3j
f1 (ppm)

1H NMR CDCl3 376.50MHz

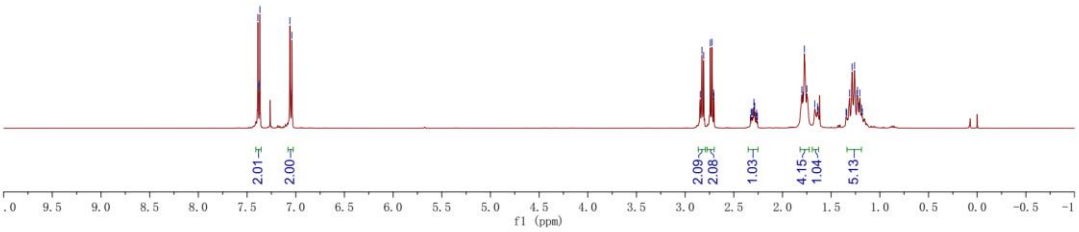


3j

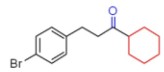
1H NMR CDCl3 400.13MHz



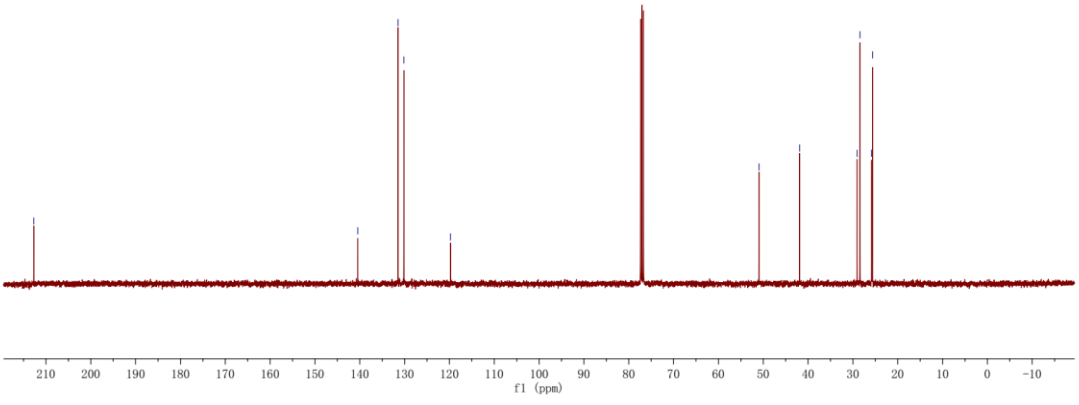
3k



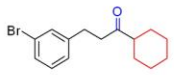
1H NMR CDCl3 100.61MHz



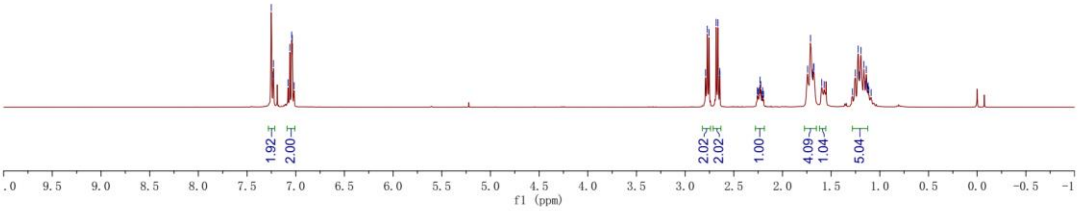
3k



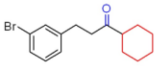
1H NMR CDCl3 400.13MHz



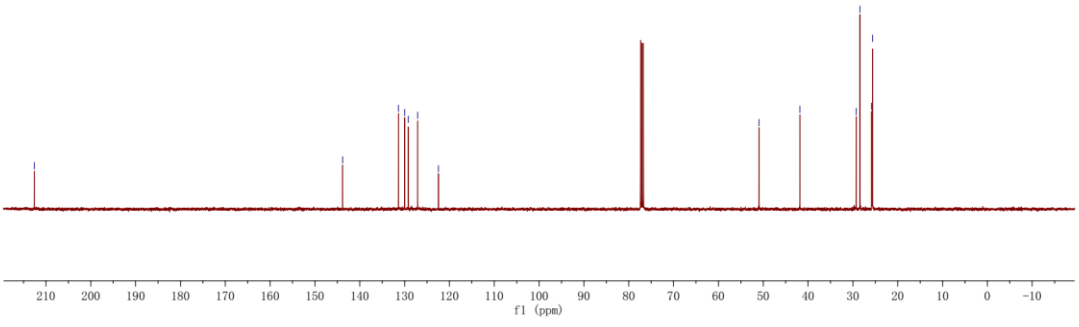
3l

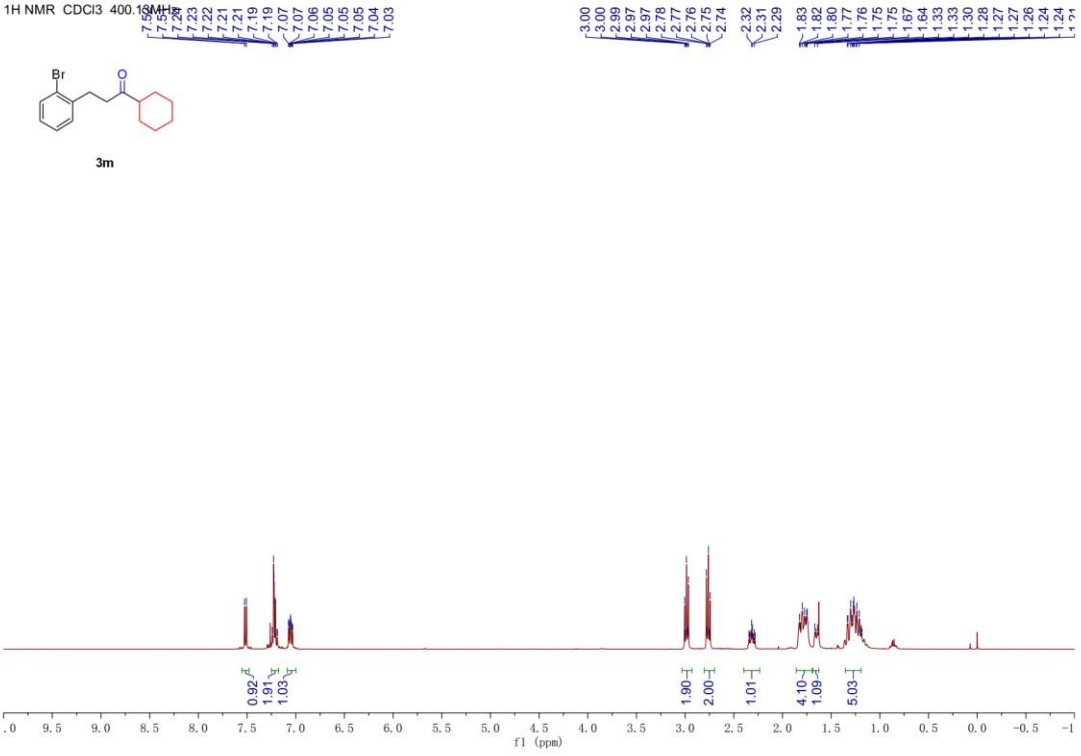


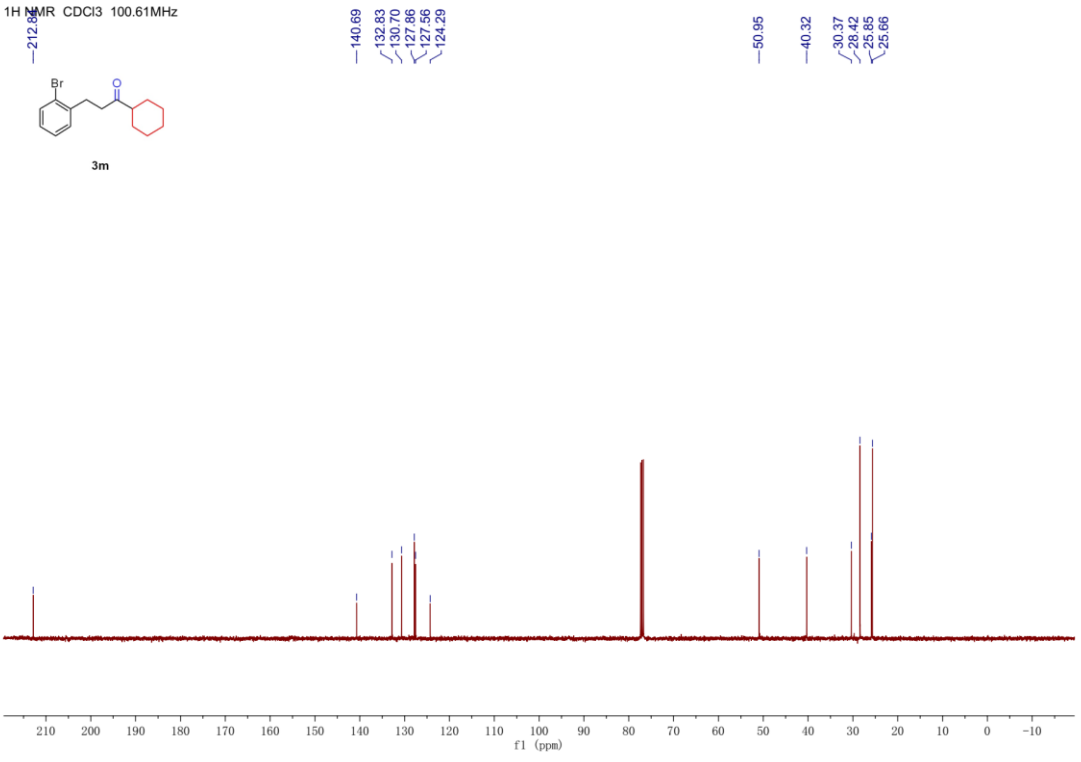
1H NMR CDCl3 100.61MHz

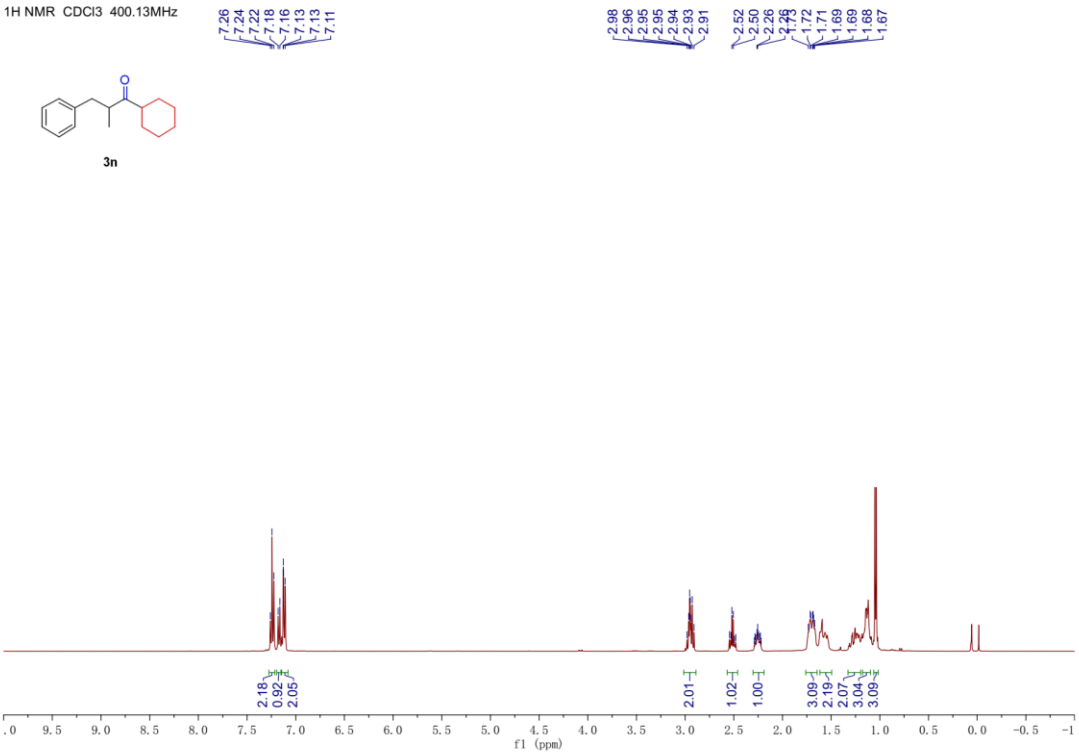


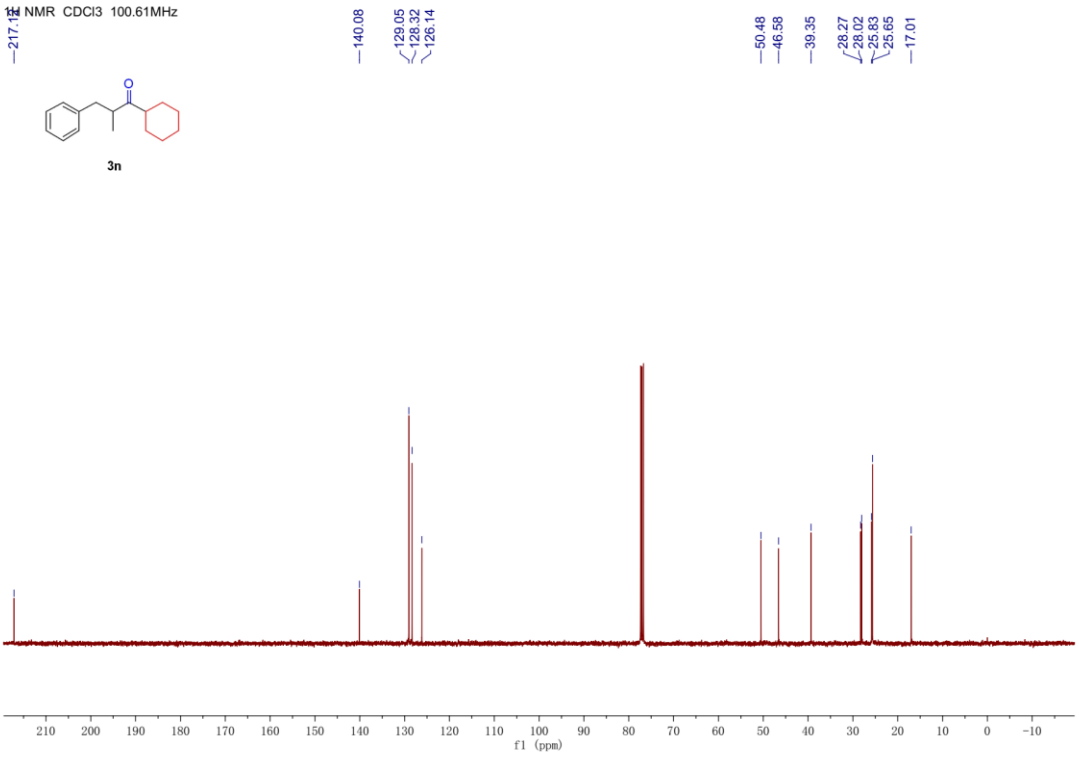
3l



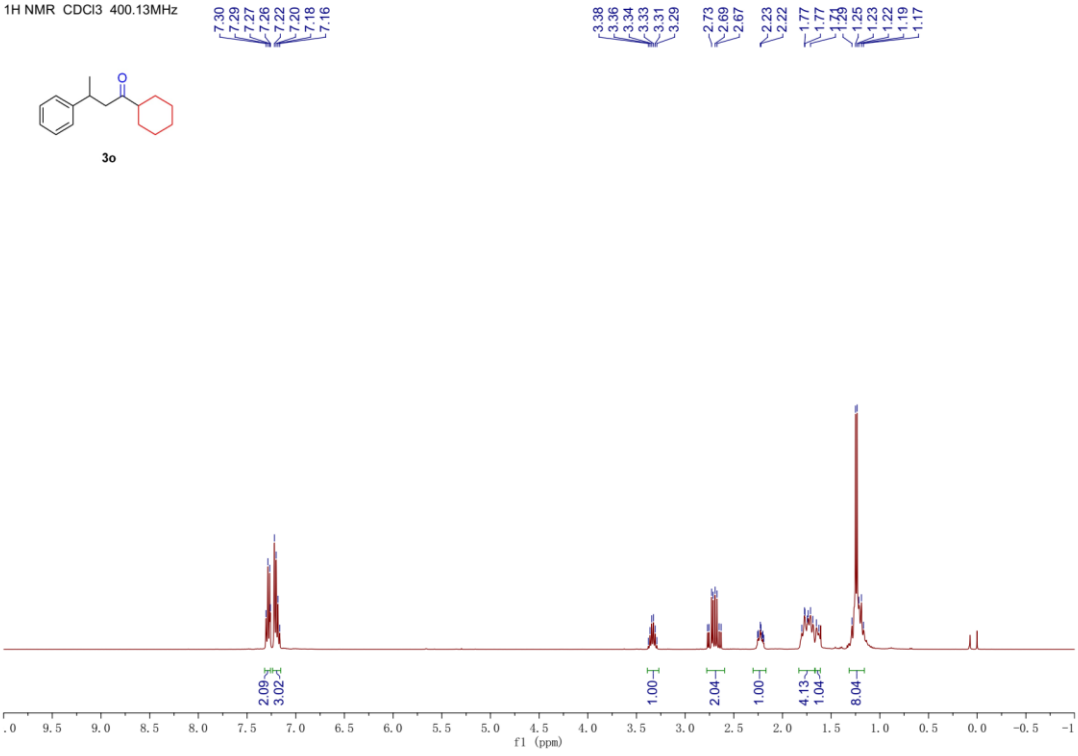

1H NMR CDCl3 400.13MHz
Br
O
3m
0.92
1.91
1.03
1.90
2.00
1.01
4.10
1.09
5.03
f1 (ppm)


1H NMR CDCl3 100.61MHz
212.84
140.69
132.83
130.70
127.86
127.56
124.29
50.95
40.32
30.37
28.42
25.85
25.66
Br
O
3m
f1 (ppm)


1H NMR CDCl3 400.13MHz
7.26
7.24
7.22
7.18
7.16
7.13
7.13
7.11
2.98
2.96
2.95
2.95
2.94
2.93
2.91
2.52
2.50
2.26
1.72
1.71
1.69
1.69
1.68
1.67
3n
2.18
0.92
2.05
2.01
1.02
1.00
3.09
2.19
2.07
3.04
3.09
f1 (ppm)

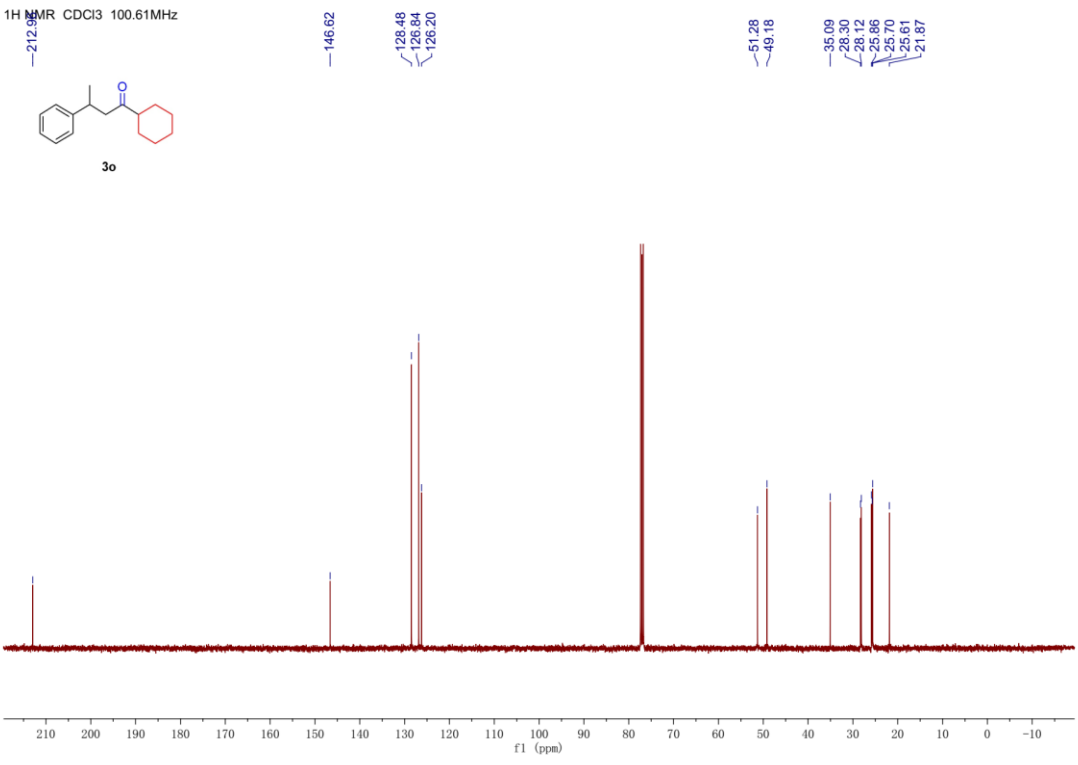

217.12
140.08
129.05
128.32
126.14
50.48
46.58
39.35
28.27
28.02
25.83
25.65
17.01
3n
f1 (ppm)

1H NMR CDCl3 400.13MHz

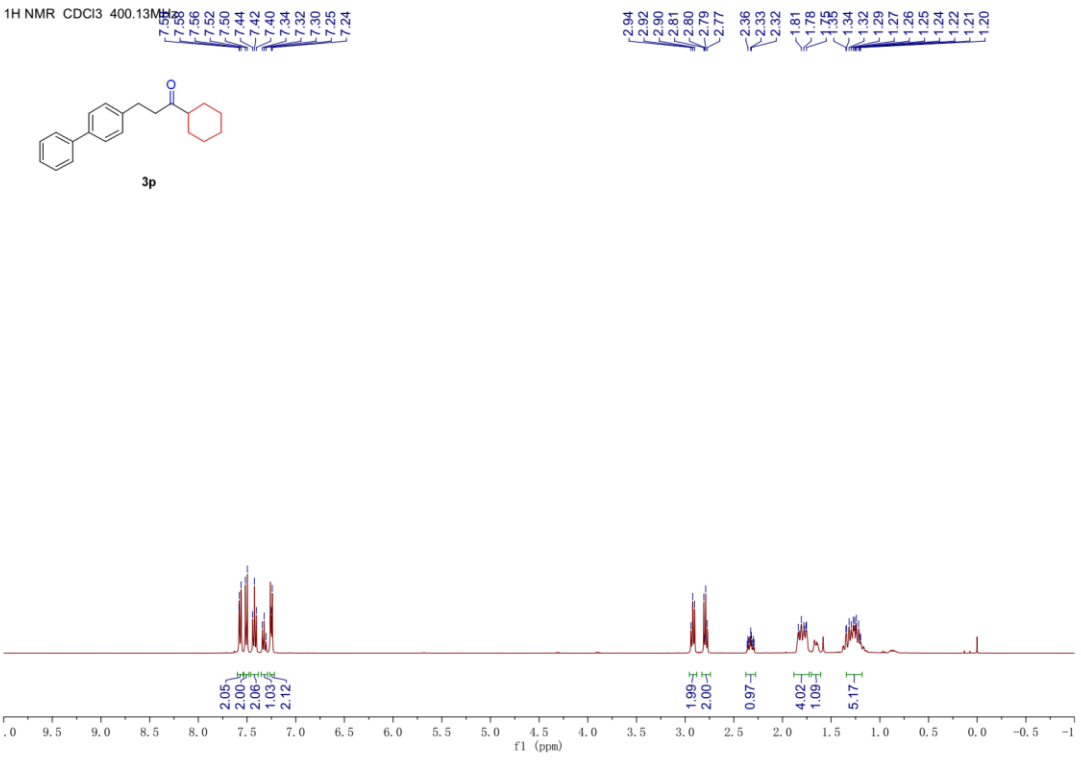


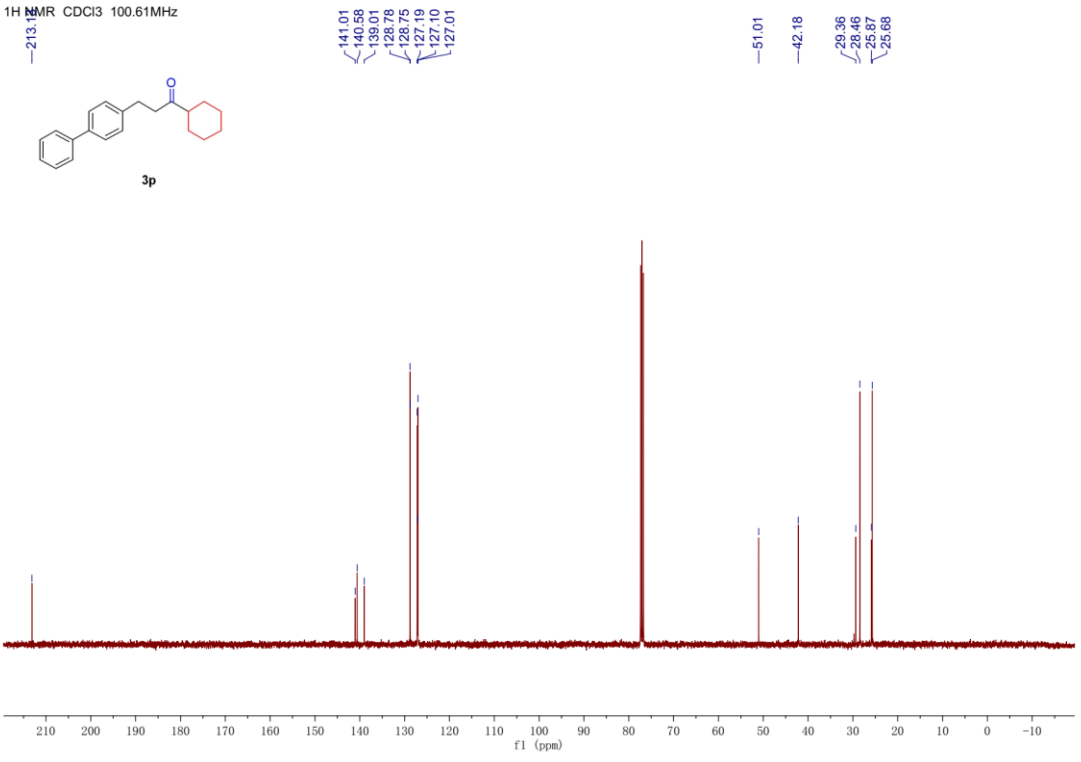
3o

1H NMR CDCl3 100.61MHz



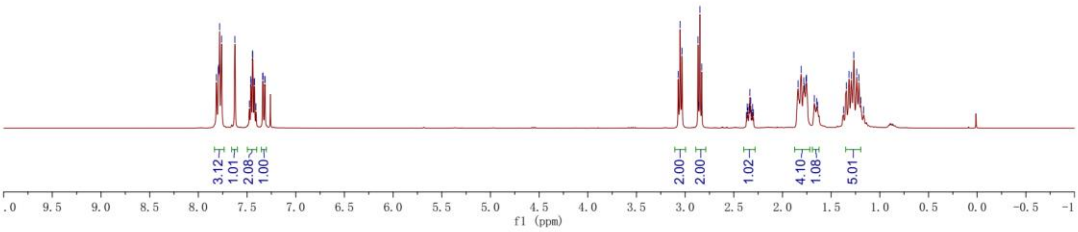
3o

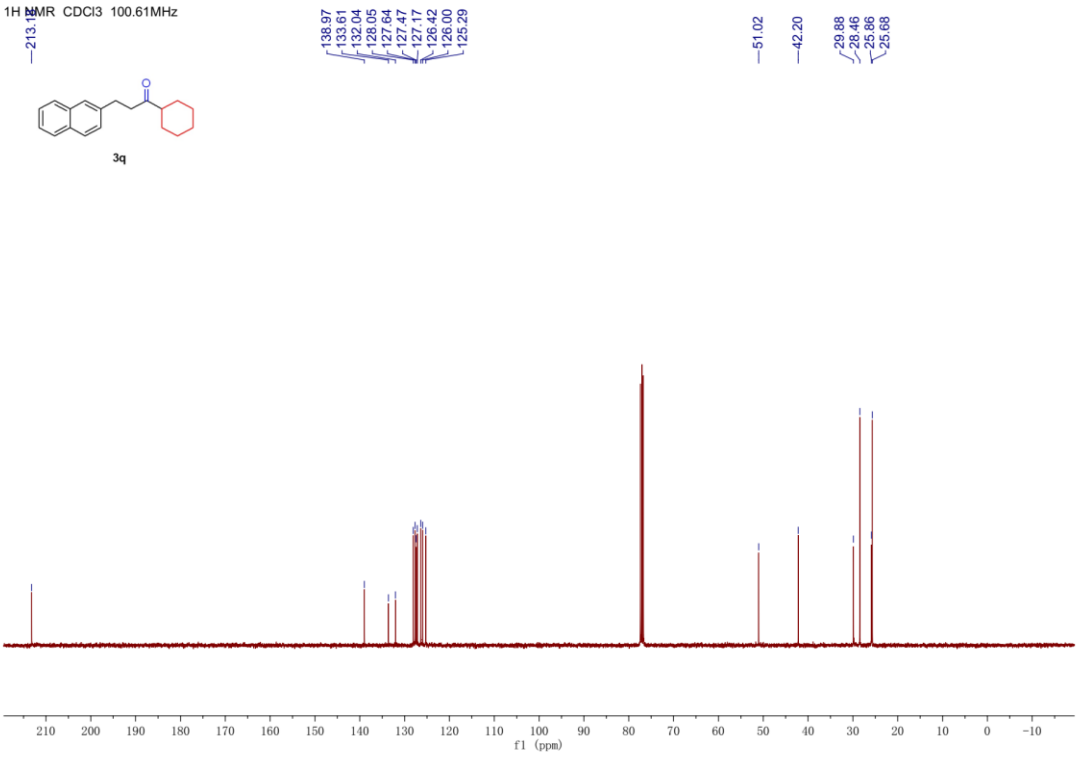

1H NMR CDCl3 400.13MHz
7.59
7.58
7.56
7.52
7.50
7.44
7.42
7.40
7.34
7.32
7.30
7.25
7.24
2.94
2.92
2.90
2.81
2.80
2.79
2.77
2.36
2.33
2.32
1.81
1.78
1.35
1.34
1.32
1.29
1.27
1.26
1.25
1.24
1.22
1.21
1.20
3p
2.05
2.00
2.06
1.03
2.12
1.99
2.00
0.97
4.02
1.09
5.17
f1 (ppm)


1H NMR CDCl3 100.61MHz
213.18
141.01
140.58
139.01
128.78
128.75
127.19
127.10
127.01
51.01
42.18
29.36
28.46
25.87
25.68
3p
f1 (ppm)

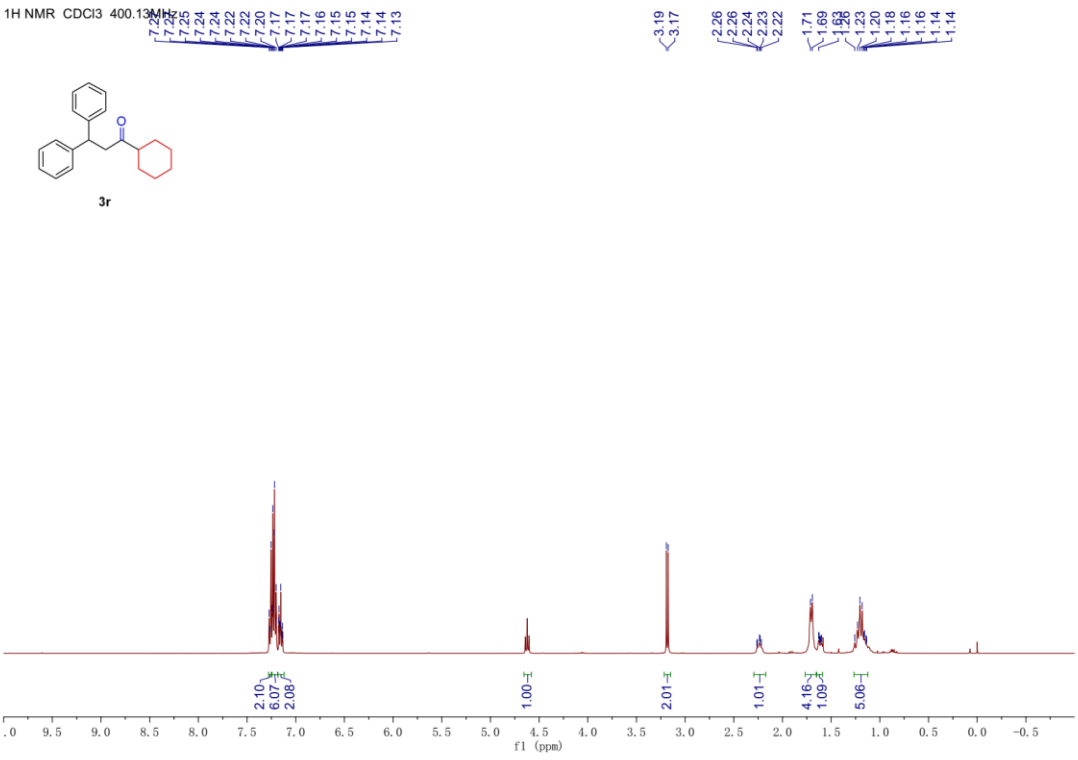

1H NMR CDCl3 400.13MHz
7.81
7.80
7.79
7.78
7.77
7.62
7.47
7.46
7.46
7.44
7.44
7.43
7.42
7.41
7.34
7.34
7.32
7.31
3.07
3.05
3.03
2.87
2.86
2.85
2.83
2.36
2.34
2.33
1.84
1.81
1.78
1.77
1.76
1.75
1.67
1.65
1.64
1.37
1.35
1.32
1.29
1.27
1.24
1.22
1.20
1.17

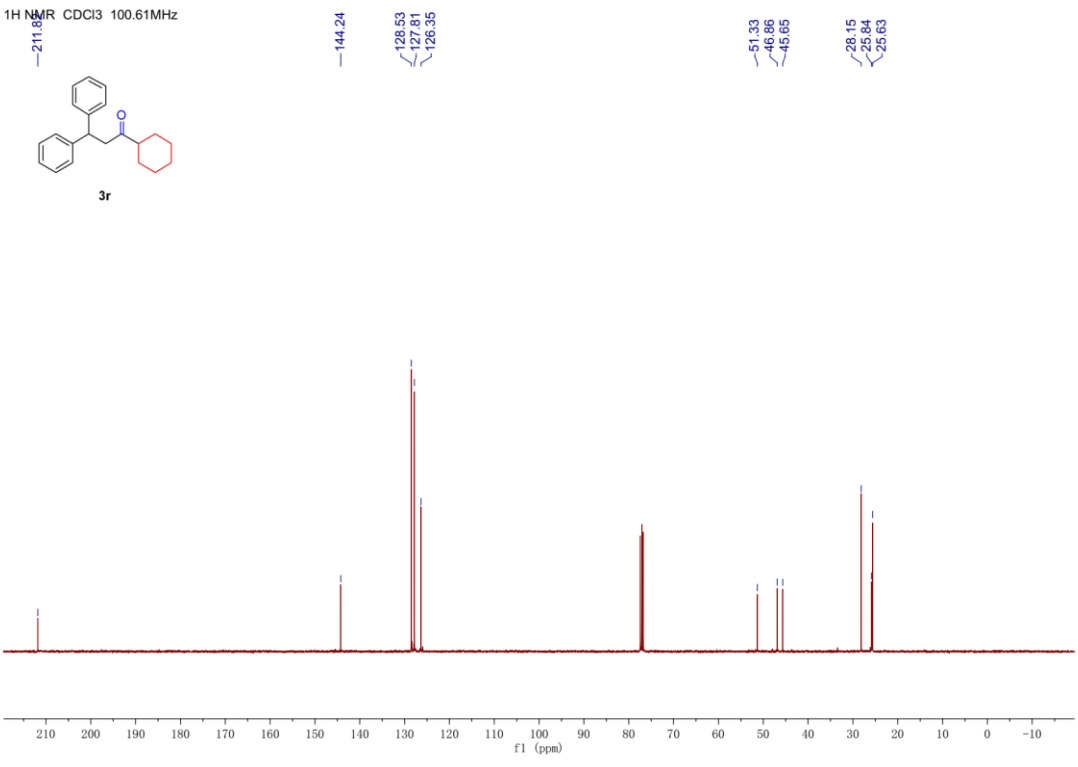
3q


3.12
1.01
2.08
1.00
2.00
2.00
1.02
4.10
1.08
5.01
f1 (ppm)


1H NMR CDCl3 100.61MHz
213.18
138.97
133.61
132.04
128.05
127.64
127.47
127.17
126.42
126.00
125.29
51.02
42.20
29.88
28.46
25.86
25.68
f1 (ppm)

3q


1H NMR CDCl3 400.13MHz
7.25
7.24
7.24
7.24
7.22
7.22
7.20
7.17
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.13
3.19
3.17
2.26
2.26
2.24
2.23
2.22
1.71
1.69
1.68
1.23
1.20
1.18
1.16
1.16
1.14
1.14
3r
2.10
6.07
2.08
1.00
2.01
1.01
4.16
1.09
5.06
f1 (ppm)


1H NMR CDCl3 100.61MHz
211.85
144.24
128.53
127.81
126.35
51.33
46.86
45.65
28.15
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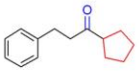
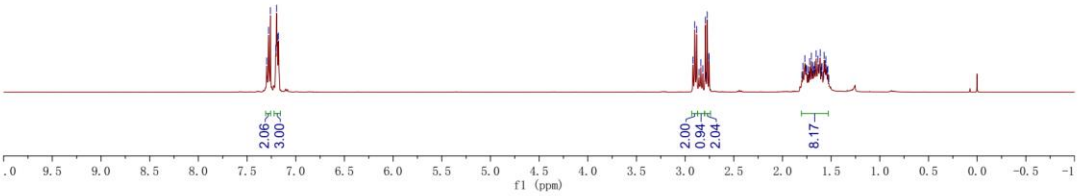
25.63
3r
f1 (ppm)

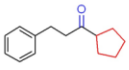
1H NMR CDCl3 400.13MHz



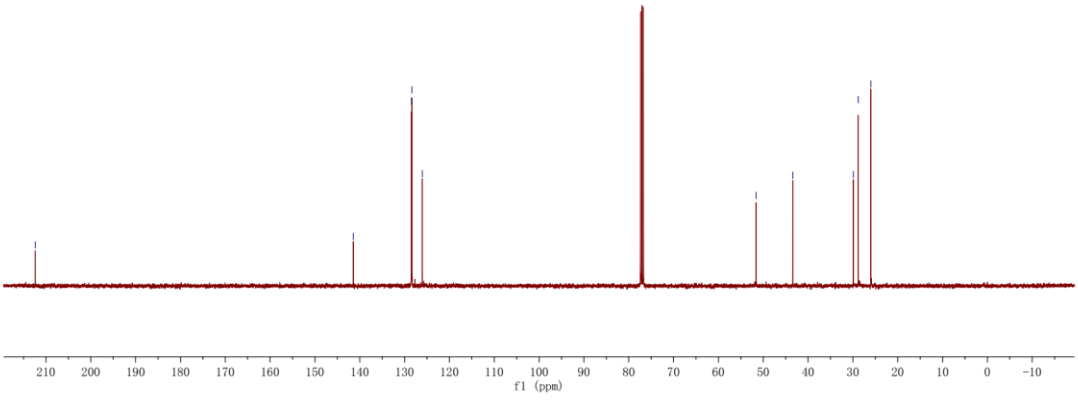
3s

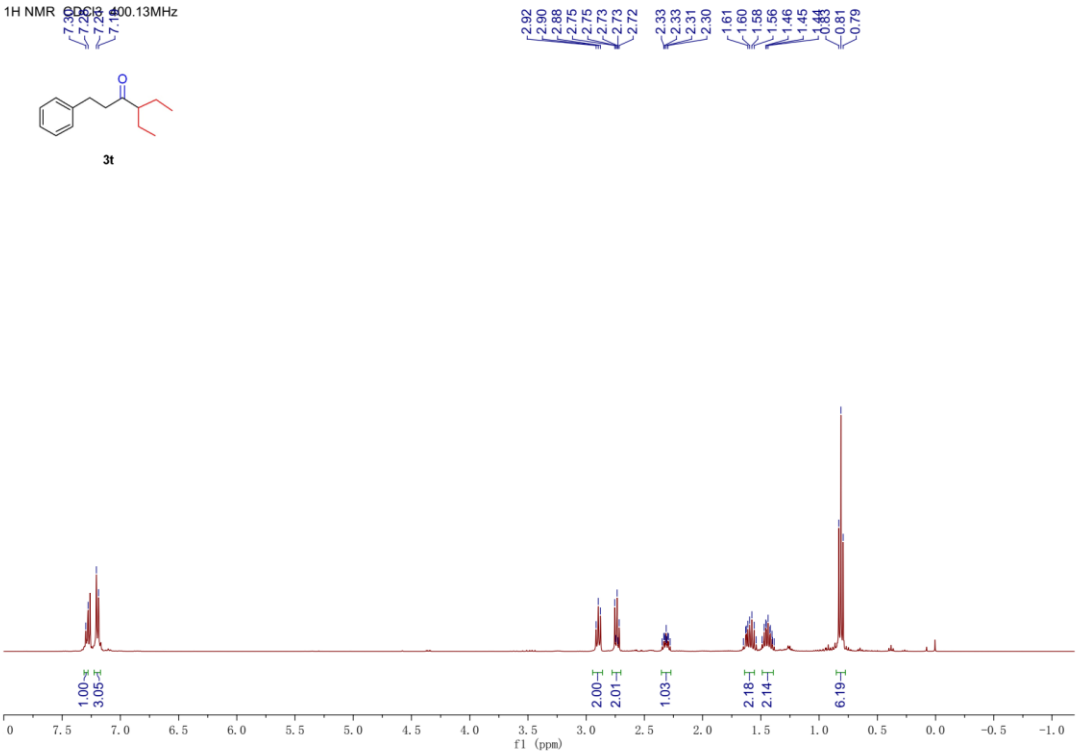


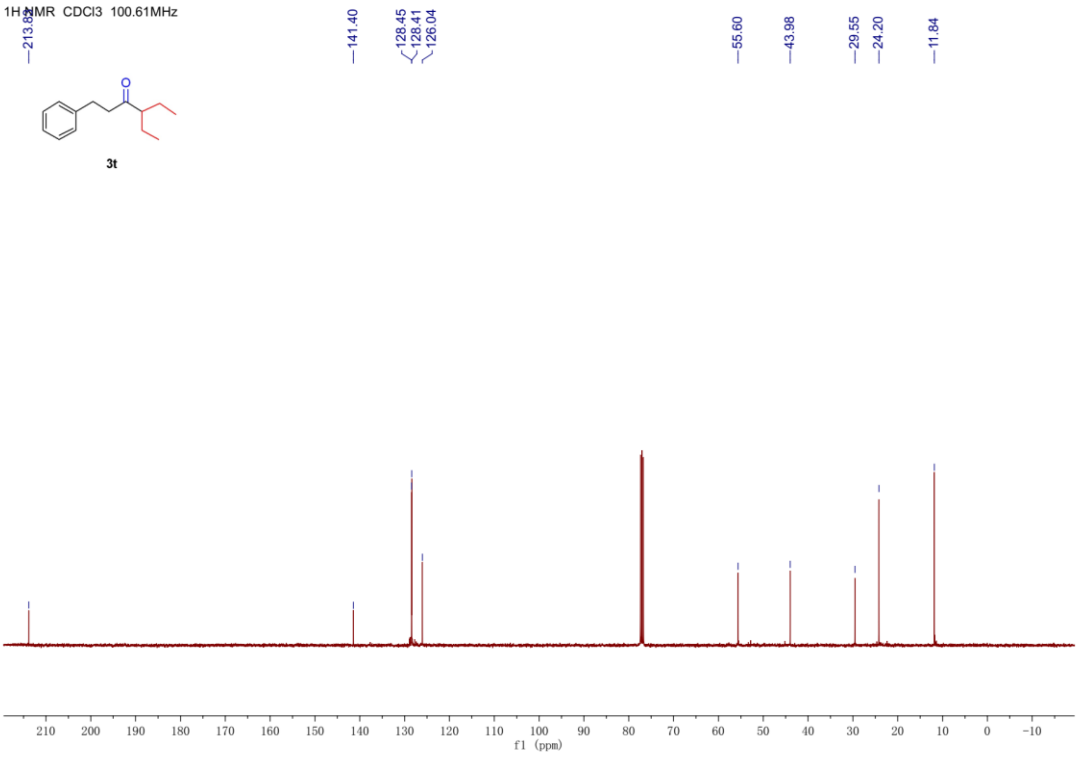
1H NMR CDCl3 100.61MHz



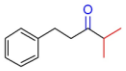
3s



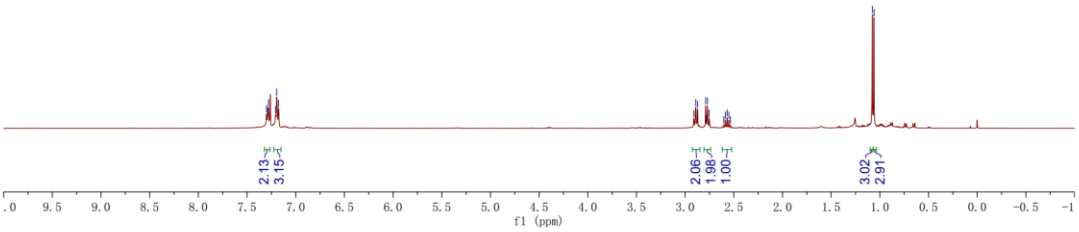

1H NMR CDCl3 400.13MHz
7.30
7.28
7.26
7.25
7.19
2.92
2.90
2.88
2.75
2.75
2.73
2.73
2.72
2.33
2.33
2.31
2.30
1.61
1.60
1.58
1.56
1.46
1.45
1.44
0.83
0.81
0.79
3t
1.00
3.05
2.00
2.01
1.03
2.18
2.14
6.19
f1 (ppm)


1H NMR CDCl3 100.61MHz
213.82
141.40
128.45
128.41
126.04
55.60
43.98
29.55
24.20
11.84
3t
f1 (ppm)

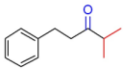
1H NMR CDCl3 400.13MHz



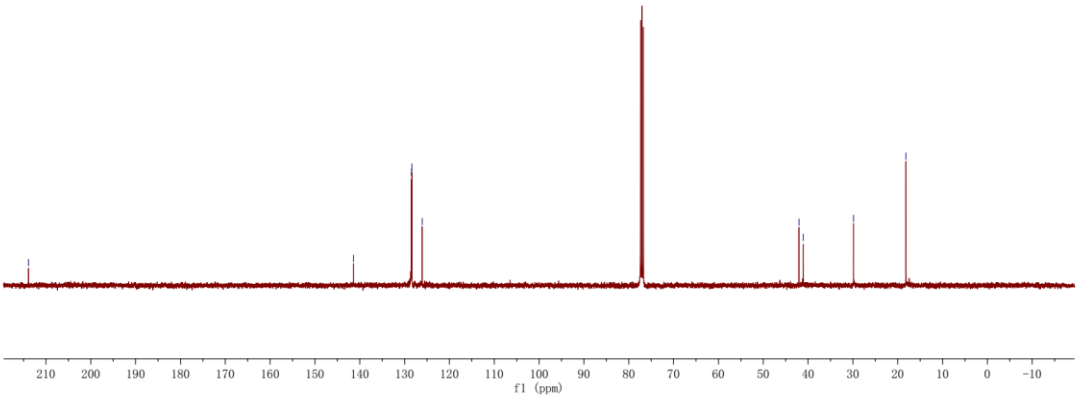
3u



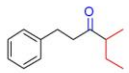
1H NMR CDCl3 100.61MHz



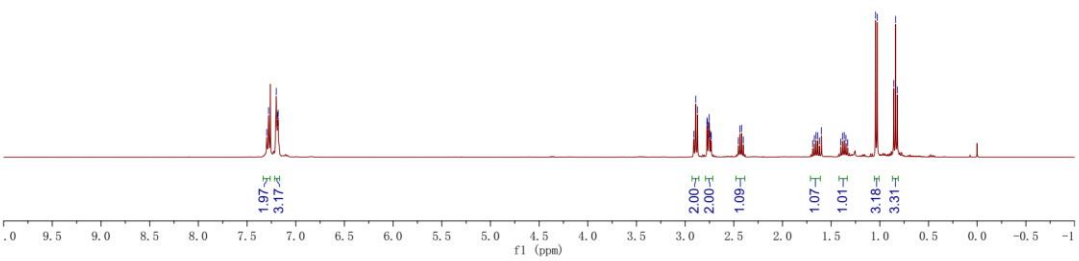
3u



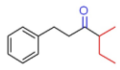
1H NMR CDCl3 400.13MHz



3v



1H NMR CDCl3 100.61MHz



3v