

Supporting Information

Copper-Catalyzed Carbonylative Hiyama-Coupling of Alkyl Bromides and Aryl Trimethoxysilanes Toward Arylalkyl Ketones

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1. General Information

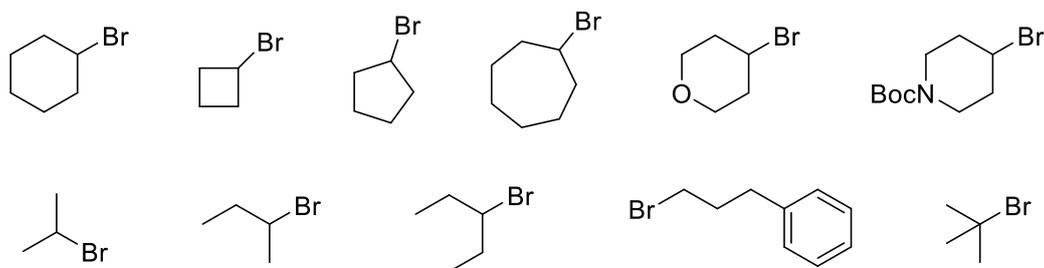
Reagents, solvents, and analytical methods:

Unless otherwise noted, all reactions were carried out under carbon monoxide or nitrogen atmosphere. The reagents were ordered from Adamas-beta®, Energy Chemical, Sigma-Aldrich, Bidepharm and used without 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 (^1H , 400 MHz; $^{13}\text{C}\{^1\text{H}\}$, 101 MHz, ^{19}F 376MHz), Bruker AVANCE III HD 700 MHz NMR spectrometers (^1H , 700 MHz; $^{13}\text{C}\{^1\text{H}\}$, 176 MHz). ^1H 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) whereas $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are reported relative to TMS via the carbon signals of the deuterated solvent. Data for ^1H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, 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).

NOTE: Carbon monoxide should only be handled in a well-ventilated fume hood. The laboratory should be well-equipped with a CO detector and alarm system.

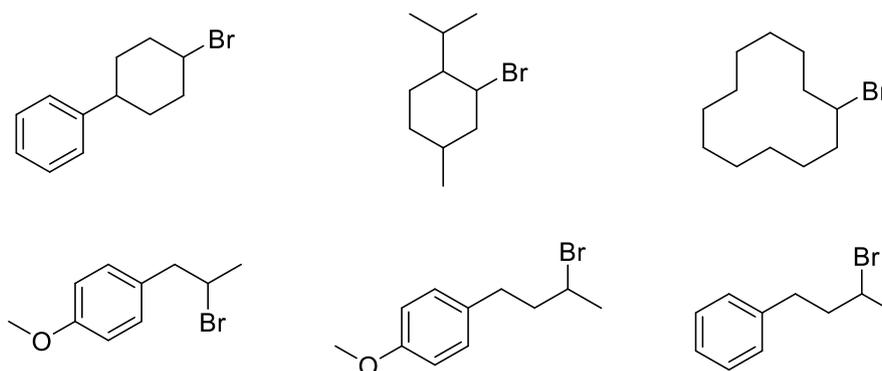
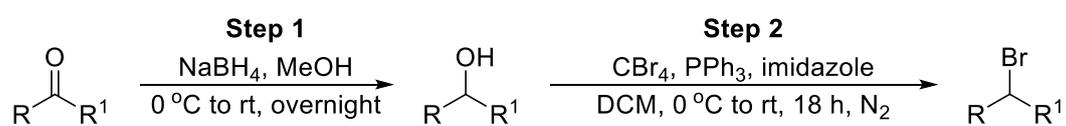
2. Procedures for the Preparation of the Starting Materials

a) Preparation of Alkyl Halides



The above-mentioned alkyl bromides were purchased directly and not purified again, directly used in the reaction

General Procedure A

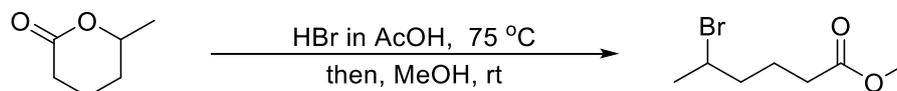


Step 1: Following the reported procedures,^[1] to an oven-dried round-bottom flask equipped with a stir bar was added the ketone (10 mmol) in anhydrous MeOH (20 mL), and the solution was placed in an ice bath for about 10 min. Then, NaBH₄ (1.14 g, 30 mmol, 3.0 equiv.) was slowly added to the mixture. The reaction mixture was warmed up to room temperature and stirred overnight. The above solution was quenched with saturated NaHCO₃ and extracted with dichloromethane (DCM, 3 x 20 mL). The combined organics were dried with MgSO₄, filtered, and

concentrated under reduced pressure. The residue was directly used for the next step without further purification.

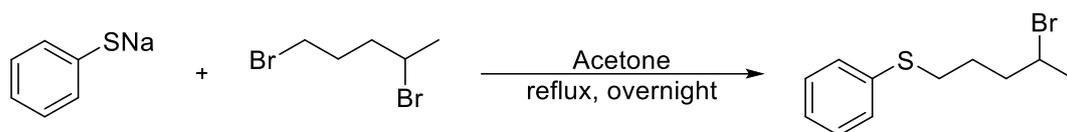
Step 2: Following the reported procedures,^[2] minor modifications have been made based on the above literature. An oven-dried flask equipped with a stir bar was charged with PPh₃ (3.15 g, 12 mmol, 1.2 equiv.) and imidazole (817 mg, 12 mmol, 1.2 equiv.) under a nitrogen atmosphere. Anhydrous DCM (30 mL) was added, and the flask was then cooled in an ice bath for about 10 min. Bromine (0.66 mL, 12 mmol, 1.2 equiv.) was added dropwise, and the mixture was stirred for 30 minutes. A solution of the corresponding alcohol in dichloromethane (10 mmol in 20 mL DCM) was added dropwise to the above solution at 0 °C. The reaction mixture was further stirred at the same temperature for 30 minutes. After 1 h, the reaction mixture was warmed to room temperature and stirred for an additional 18 h. The solution was concentrated under reduced pressure and purified by column chromatography.

Methyl 5-bromohexanoate



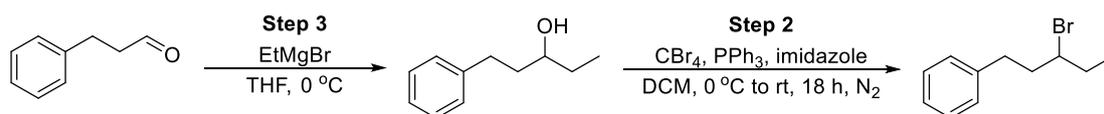
Following the reported procedures^[3], an oven-dried flask equipped with a stir bar was charged with a solution of 33% HBr in AcOH (3.5 mL) under a nitrogen atmosphere. δ -Hexalactone (1.14 g, 10 mmol) was added and fitted with a reflux condenser. The reaction solution was heated to 75 °C for 4 h, and then the mixture was cooled to room temperature. MeOH (9.2 mL) was added and the mixture was stirred at room temperature overnight. Next, the reaction solution was quenched with saturated NaHCO₃ and extracted with EtOAc (3 x 15 mL). The combined organics were dried with MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 200:1) to obtain the product as colorless liquid.

(4-bromopentyl)(phenyl)sulfane



Following the reported procedures^[4], To an oven-dried flask equipped with a stir bar were charged with sodium thiophenoxide (1.72 g, 13 mmol, 1.3 equiv) and 1,4-dibromopentane (2.29, 10 mmol). Acetone (30 mL) was added to the flask, and the reaction mixture was heated to reflux overnight. After filtering off the precipitate, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether : ethyl acetate = 200:1) to obtain the product as colour-less liquid.

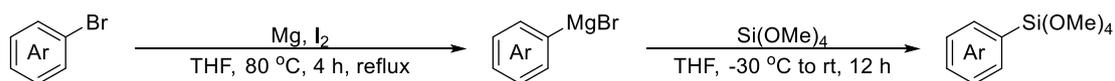
(3-bromopentyl)benzene



Step 3: Following the reported procedures,^[5] the above crude aldehyde (1.0 equiv) and dry THF (0.50 M) were added to a flame-dried flask under N₂. The reaction mixture was cooled to 0 °C, and a Grignard solution in THF (1.2 equiv) was added dropwise. The reaction was monitored by TLC. Upon completion, the reaction mixture was quenched slowly with NH₄Cl (sat. aq.) and then extracted with EtOAc (×3). Organic layers were combined, washed with brine, dried over Na₂SO₄, filtered, and concentrated under a vacuum to afford the crude alcohol, which was used for the next step without further purification.

The corresponding alcohols were then brominated according to **step 2** of **General Procedure A**.

b) Preparation of trimethoxy(aryl)silanes



Following the reported procedures,^[6] to a flame dried 3-neck round bottom flask equipped with a stir bar was added Si(OMe)₄ (13.7 g, 90 mmol, 3.0 equiv) and THF (20 mL) at -30 °C. Then, a solution of aryl Grignard reagent in THF [prepared from 30 mmol (1.0 equiv) of the corresponding aryl bromide and magnesium turnings [1.1 g, 45 mmol, (1.5 equiv)]] by heating at

80°C for 4 h.] was dropwise added to the solution. The resulting mixture was warmed to room temperature and stirred overnight. Finally, the reaction solution was diluted with H₂O (10 mL) and extracted with ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by distillation.

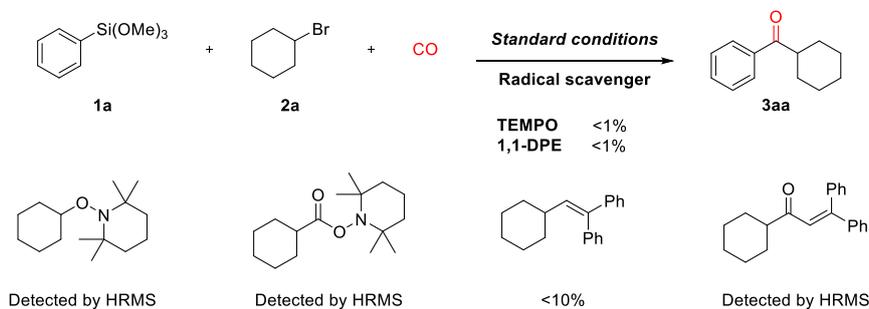
3. General Procedure

3.1 General procedure I for the Cu-catalyzed Carbonylative Hiyama cross-couplings.

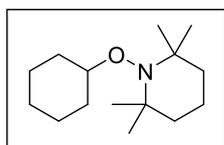


In a glovebox, to an oven-dried screw capped vial equipped with a stir bar were added aryl trimethoxysilane **1** (0.40 mmol), NaOMe (44.9 mg, 0.30 mmol), CuBr(Me₂S) (2.05 mg, 0.01 mmol), Si(OMe)₃·HCl (3.45 mg, 0.01 mmol) and alkyl bromides (0.20 mmol) in Toluene (0.50 mL). The vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N₂ atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 10 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 100 °C for 20 h. The reaction mixture was cooled to room temperature and diluted with EtOAc. After completion, the reaction mixture was directly purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding product.

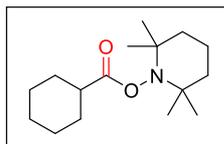
3.2 Typical Procedures for the Radical Trapping Experiments.



In a glovebox, to an oven-dried screw capped vial equipped with a stir bar were added phenyl trimethoxysilane **1a** (79.2 mg, 0.40 mmol), NaOMe (44.9 mg, 0.30 mmol), CuBr(Me₂S) (2.05 mg, 0.01 mmol), SIMes·HCl (3.45 mg, 0.01 mmol) and cyclohexyl bromide **2a** (32.4 mg, 0.20 mmol) in Toluene (0.50 mL). Then, radical scavenger TEMPO (93.5 mg, 0.60 mmol) were added to the solution. The vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N₂ atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 10 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 100 °C for 20 h. The reaction mixture was cooled to room temperature. Dilute the mixture and use HRMS for detection.



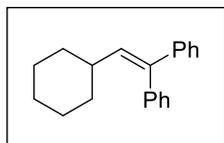
HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₅H₃₀NO 240.2322; found: 240.2331.



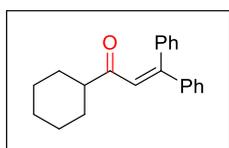
HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₆H₃₀NO₂ 268.2271; found: 268.2280.

The same reactions were repeated in the presence of 1,1-diphenylethene (108 mg, 0.6 mmol)

under otherwise identical conditions. The reaction mixture was cooled to room temperature. Dilute the mixture and use HRMS for detection.



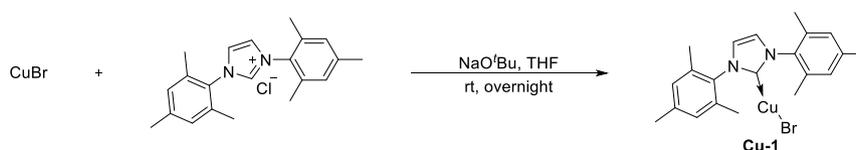
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{24}Na$ 287.1770; found: 287.1782.



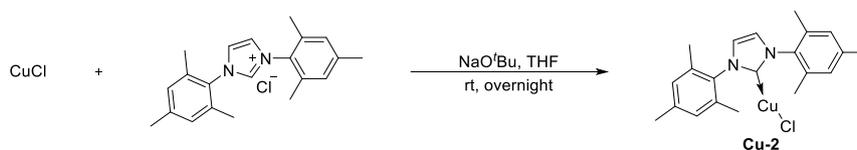
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{23}O$ 291.1743; found: 291.1750.

3.2 Catalytic Reaction with Copper Complexes Cu-1 and Cu-2

a) Preparation of Copper Complexes Cu-1 and Cu-2 ^[7]

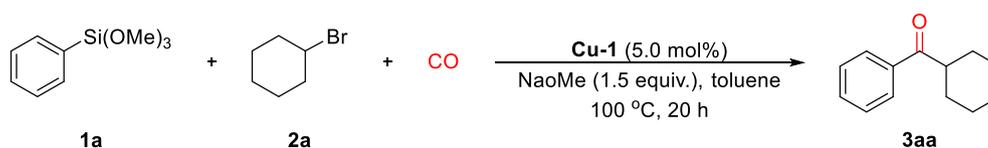


In an oven-dried vial, copper(I) bromide (0.519 g, 3.63 mmol), SIMes·HCl (0.86 g, 2.52 mmol) and sodium tert-butoxide (0.243 g, 2.52 mmol) were loaded inside a glovebox and stirred in dry THF (18 mL) overnight at room temperature outside of the glovebox. After filtration of the reaction mixture through a plug of Celite, the filtrate was mixed with hexane to form a precipitate. A second filtration afforded Copper Complexes **Cu-1** as an off-white solid.



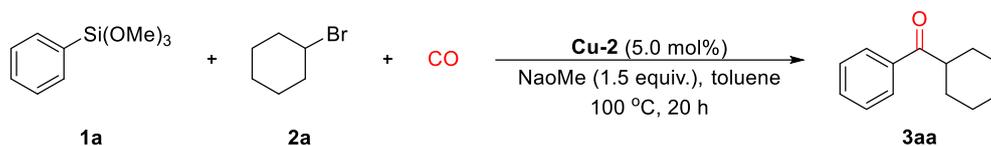
In an oven-dried vial, copper(I) chloride (0.359 g, 3.63 mmol), SIMes·HCl (0.86 g, 2.52 mmol) and sodium tert-butoxide (0.243 g, 2.52 mmol) were loaded inside a glovebox and stirred in dry THF (18 mL) overnight at room temperature outside of the glovebox. After filtration of the reaction mixture through a plug of Celite, the filtrate was mixed with hexane to form a precipitate. A second filtration afforded Copper Complexes **Cu-2** as an off-white solid.

a) Procedure of the catalytic Reaction with Copper Complexes **Cu-1**



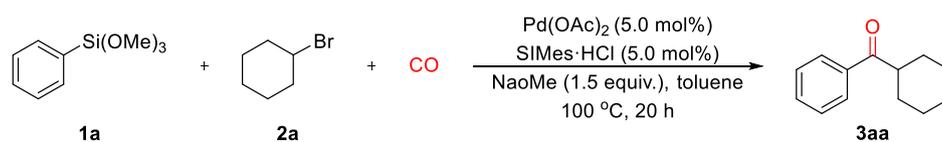
In a glovebox, to an oven-dried screw capped vial equipped with a stir bar were added phenyl trimethoxysilane **1a** (79.2 mg, 0.40 mmol), NaOMe (44.9 mg, 0.30 mmol), **Cu-1** (4.5 mg, 0.01 mmol) and cyclohexyl bromide **2a** (32.4 mg, 0.20 mmol) in Toluene (0.50 mL). The vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N₂ atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 10 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 100 °C for 20 h. The reaction mixture was cooled to room temperature and diluted with EtOAc. The yields were determined by GC analyses against n-dodecane as a calibrated internal standard.

c) Procedure of the catalytic Reaction with Copper Complexes Cu-2



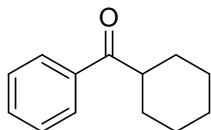
In a glovebox, to an oven-dried screw capped vial equipped with a stir bar were added phenyl trimethoxysilane **1a** (79.2 mg, 0.40 mmol), NaOMe (44.9 mg, 0.30 mmol), **Cu-2** (4.0 mg, 0.01 mmol) and cyclohexyl bromide **2a** (32.4 mg, 0.20 mmol) in Toluene (0.50 mL). The vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N₂ atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 10 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 100 °C for 20 h. The reaction mixture was cooled to room temperature and diluted with EtOAc. The yields were determined by GC analyses against n-dodecane as a calibrated internal standard.

3.2 Catalytic Reaction with Pd(OAc)₂



In a glovebox, to an oven-dried screw capped vial equipped with a stir bar were added phenyl trimethoxysilane **1a** (79.2 mg, 0.40 mmol), NaOMe (44.9 mg, 0.30 mmol), Pd(OAc)₂ (2.2 mg, 0.01 mmol), SiMes·HCl (3.45 mg, 0.01 mmol) and cyclohexyl bromide **2a** (32.4 mg, 0.20 mmol) in Toluene (0.50 mL). The vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N₂ atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 10 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 100 °C for 20 h. The reaction mixture was cooled to room temperature and diluted with EtOAc. The yields were determined by GC analyses against n-dodecane as a calibrated internal standard.

4. Characterization of Products

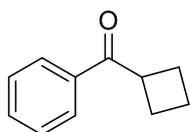


cyclohexyl(phenyl)methanone (3aa)^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (30.8 mg, 82% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.94 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.58 – 7.50 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.32 – 3.20 (m, 1H), 1.94 – 1.79 (m, 4H), 1.79 – 1.68 (m, 1H), 1.57 – 1.19 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 203.9, 136.3, 132.7, 128.6, 128.2, 45.6, 29.4, 25.9, 25.8.

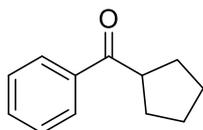


cyclobutyl(phenyl)methanone (3ab)^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (18.1 mg, 56% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.01 (p, *J* = 8.5 Hz, 1H), 2.49 – 2.36 (m, 2H), 2.35 – 2.24 (m, 2H), 2.16 – 2.03 (m, 1H), 1.97 – 1.86 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 201.0, 135.6, 132.8, 128.5, 128.3, 42.2, 25.1, 18.2.



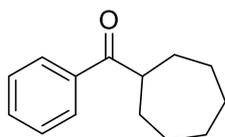
cyclopentyl(phenyl)methanone (3ac)^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title

compound as a Colorless oil (29.0 mg, 83% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.72 (p, *J* = 7.8 Hz, 1H), 2.01 – 1.85 (m, 4H), 1.81 – 1.58 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 202.8, 136.9, 132.7, 128.5, 128.4, 46.3, 30.0, 26.3.

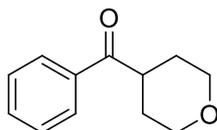


cycloheptyl(phenyl)methanone (3ad)^[9]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (35.1 mg, 87% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.44 (tt, *J* = 9.2, 3.9 Hz, 1H), 1.99 – 1.88 (m, 2H), 1.86 – 1.74 (m, 2H), 1.74 – 1.49 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 204.2, 136.4, 132.6, 128.5, 128.3, 46.6, 30.8, 28.3, 26.8.

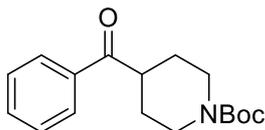


phenyl(tetrahydro-2H-pyran-4-yl)methanone (3ae)^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 5/1) to afford the title compound as a Colorless oil (29.8 mg, 78% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.10 – 4.01 (m, 2H), 3.61 – 3.45 (m, 3H), 1.95 – 1.81 (m, 2H), 1.84 – 1.73 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 201.8, 135.8, 133.0, 128.7, 128.2, 67.3, 42.6, 29.0

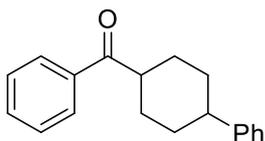


tert-butyl 4-benzoylpiperidine-1-carboxylate (3af) ^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 5/1) to afford the title compound as a Colorless oil (34.6 mg, 60% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.25 – 4.08 (m, 2H), 3.46 – 3.34 (m, 1H), 2.90 (t, *J* = 12.5 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.77 – 1.65 (m, 2H), 1.46 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 202.1, 154.7, 135.8, 133.1, 128.7, 128.2, 79.6, 43.5, 28.4.

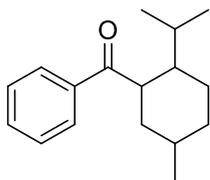


phenyl(4-phenylcyclohexyl)methanone (3ag) ^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (38.5 mg, 73% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.16 (m, 3H), 3.42 – 3.30 (m, 1H), 2.66 – 2.53 (m, 1H), 2.12 – 1.99 (m, 4H), 1.78 – 1.56 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 203.6, 146.9, 136.3, 132.8, 128.6, 128.4, 128.2, 126.8, 126.1, 45.2, 43.8, 33.5, 29.6.



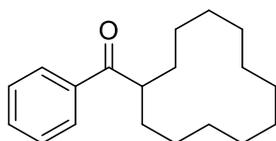
(2-isopropyl-5-methylcyclohexyl)(phenyl)methanone (3ah) ^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude

product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (32.0 mg, 66% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 (d, $J = 7.7$ Hz, 2H), 7.56 (t, $J = 6.7$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 3.39 (td, $J = 11.4, 3.4$ Hz, 1H), 1.90 – 1.73 (m, 4H), 1.67 – 1.59 (m, 1H), 1.53 – 1.41 (m, 1H), 1.21 – 0.95 (m, 3H), 0.88 (t, $J = 6.5$ Hz, 6H), 0.71 (d, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 204.6, 137.3, 132.8, 128.6, 128.1, 48.1, 44.0, 39.9, 34.6, 32.7, 28.7, 24.2, 22.3, 21.5, 16.5.

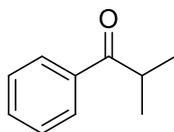


cyclododecyl(phenyl)methanone (3ai) ^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (40.3 mg, 74% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 (d, $J = 7.4$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 3.59 – 3.51 (m, 1H), 1.81 – 1.70 (m, 2H), 1.66 – 1.58 (m, 2H), 1.49 – 1.28 (m, 18H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 204.2, 137.1, 132.7, 128.6, 128.2, 42.1, 26.5, 23.9, 23.6, 23.4, 22.6.

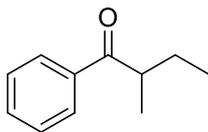


2-methyl-1-phenylpropan-1-one (3aj) ^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (16.7 mg, 56% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.8$ Hz, 2H), 7.55 (t, $J = 7.1$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 3.56 (p, $J = 6.8$ Hz, 1H), 1.22 (d, $J = 6.8$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 204.5, 136.2, 132.8, 128.6, 128.3, 35.3, 19.1.

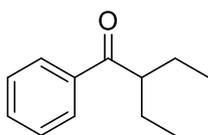


2-methyl-1-phenylbutan-1-one (3ak) ^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (23.9 mg, 74% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 3.40 (h, *J* = 6.7 Hz, 1H), 1.84 (dp, *J* = 14.3, 7.3 Hz, 1H), 1.50 (dp, *J* = 14.3, 7.3 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 204.5, 136.8, 132.8, 128.6, 128.2, 42.1, 26.6, 16.7, 11.8.

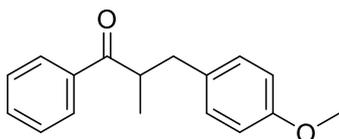


2-ethyl-1-phenylbutan-1-one (3al) ^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (25.1 mg, 71% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 6.9 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 3.30 (tt, *J* = 7.5, 5.5 Hz, 1H), 1.79 (dt, *J* = 13.5, 7.4 Hz, 2H), 1.64 – 1.49 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 204.5, 137.8, 132.7, 128.6, 128.1, 49.1, 24.8, 11.9.



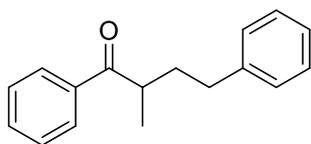
3-(4-methoxyphenyl)-2-methyl-1-phenylpropan-1-one (3am) ^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**, using 10 mol% CuBr·(Me₂S) and 10 mol% SiMe₃·HCl. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 30/1) to afford the title compound as a Colorless oil (39.4 mg,

78% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 6.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 3.77 (s, 3H), 3.71 (p, *J* = 6.9 Hz, 3H), 3.12 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.65 (dd, *J* = 13.8, 7.7 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 203.8, 158.0, 136.5, 132.8, 131.9, 123.0, 128.6, 128.2, 113.7, 55.1, 42.9, 38.5, 17.3.

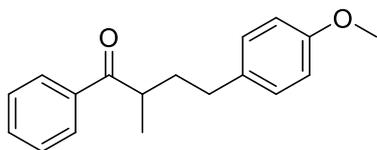


2-methyl-1,4-diphenylbutan-1-one (3an)^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (37.3 mg, 78% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.1 Hz, 2H), 7.23 – 7.11 (m, 3H), 3.47 (h, *J* = 6.8 Hz, 1H), 2.71 – 2.57 (m, 2H), 2.24 – 2.11 (m, 1H), 1.81 – 1.68 (m, 1H), 1.23 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 204.1, 141.7, 136.5, 132.8, 128.6, 128.5, 128.4, 128.2, 125.9, 39.7, 35.1, 33.4, 17.3.

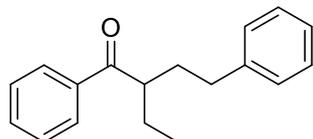


4-(4-methoxyphenyl)-2-methyl-1-phenylbutan-1-one (3ao)^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 30/1) to afford the title compound as a Colorless oil (45.2 mg, 84% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 6.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 3.79 (s, 3H), 3.46 (h, *J* = 6.8 Hz, 1H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.21 – 2.08 (m, 1H), 1.78 – 1.65 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 204.1, 157.8, 136.5, 133.8, 132.8, 129.3, 128.6, 128.2, 113.8, 55.2, 39.6, 35.4, 32.5, 17.2.

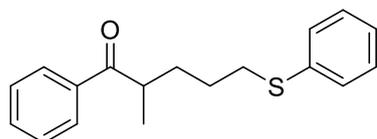


2-ethyl-1,4-diphenylbutan-1-one (3ap)^[9]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (38.0 mg, 75% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.25 (t, J = 7.8 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 7.5 Hz, 2H), 3.44 – 3.31 (m, 1H), 2.69 – 2.48 (m, 2H), 2.21 – 2.07 (m, 1H), 1.89 – 1.74 (m, 2H), 1.68 – 1.53 (m, 1H), 0.88 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 204.1, 141.9, 137.5, 132.8, 128.6, 128.4, 128.3, 128.2, 125.9, 46.7, 33.6, 33.3, 25.4, 11.8.

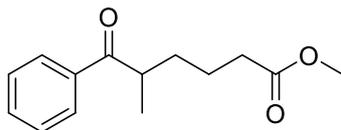


2-methyl-1-phenyl-5-(phenylthio)pentan-1-one (3aq)^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 5/1) to afford the title compound as a Colorless oil (29.7 mg, 52% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.32 – 7.21 (m, 4H), 7.20 – 7.11 (m, 1H), 3.47 (h, J = 6.7 Hz, 1H), 2.98 – 2.83 (m, 2H), 2.02 – 1.89 (m, 1H), 1.70 – 1.57 (m, 3H), 1.19 (d, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 203.9, 136.4, 136.5, 132.9, 129.1, 128.8, 128.6, 128.2, 125.8, 40.2, 33.6, 32.5, 26.9, 17.4.

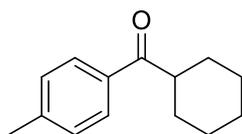


methyl 5-methyl-6-oxo-6-phenylhexanoate (3ar)^[8]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 20/1) to afford the title compound as a Colorless oil (27.2 mg, 58% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.64 (s, 3H), 3.48 (h, *J* = 6.8 Hz, 1H), 2.36 – 2.27 (m, 2H), 1.91 – 1.77 (m, 1H), 1.73 – 1.59 (m, 2H), 1.54 – 1.39 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 203.9, 173.8, 136.5, 132.9, 128.6, 128.2, 51.5, 40.4, 34.0, 32.9, 22.8, 17.4.

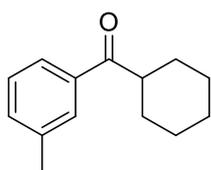


cyclohexyl(*p*-tolyl)methanone (3ba)^[10]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (33.2 mg, 82% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.24 (tt, *J* = 11.5, 3.3 Hz, 1H), 2.40 (s, 3H), 1.93 – 1.78 (m, 4H), 1.78 – 1.68 (m, 1H), 1.57 – 1.25 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 203.5, 143.4, 133.8, 129.2, 128.4, 45.5, 29.4, 26.0, 25.9, 21.6.



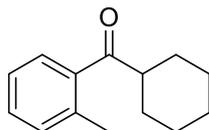
cyclohexyl(*m*-tolyl)methanone (3ca)^[10]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title

compound as a Colorless oil (31.3 mg, 77% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.70 (m, 2H), 7.38 – 7.30 (m, 2H), 3.25 (tt, *J* = 11.5, 3.3 Hz, 1H), 2.41 (s, 3H), 1.92 – 1.80 (m, 4H), 1.78 – 1.70 (m, 1H), 1.55 – 1.27 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 204.1, 138.3, 136.4, 133.4, 128.7, 128.4, 125.4, 45.6, 29.4, 26.0, 25.8, 21.4.

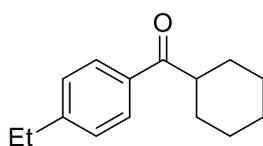


cyclohexyl(*o*-tolyl)methanone (3da)^[10]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (18.1 mg, 45% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.19 (m, 2H), 3.03 (tt, *J* = 11.4, 3.4 Hz, 1H), 2.41 (s, 3H), 1.91 – 1.76 (m, 4H), 1.74 – 1.65 (m, 1H), 1.51 – 1.25 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 208.8, 138.9, 137.2, 131.5, 130.4, 127.2, 125.4, 49.0, 28.8, 25.9, 25.8, 20.6.

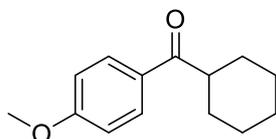


cyclohexyl(4-ethylphenyl)methanone (3ea)

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (32.8 mg, 76% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.25 (tt, *J* = 11.6, 3.3 Hz, 1H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.95 – 1.79 (m, 4H), 1.79 – 1.69 (m, 1H), 1.57 – 1.27 (m, 5H), 1.26 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 203.5, 149.6, 134.0, 128.5, 128.1, 45.5, 29.5, 28.9, 26.0, 25.9, 15.2.

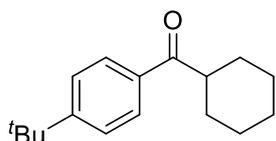


cyclohexyl(4-methoxyphenyl)methanone (3fa) ^[10]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 20/1) to afford the title compound as a Colorless oil (35.6 mg, 82% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H), 3.21 (tt, J = 11.5, 3.2 Hz, 1H), 1.90 – 1.79 (m, 4H), 1.76 – 1.70 (m, 1H), 1.55 – 1.25 (m, 5H).

^{13}C NMR (101 MHz, CDCl_3) δ 202.4, 163.2, 130.4, 129.2, 113.7, 55.4, 45.3, 29.5, 26.0, 25.9.

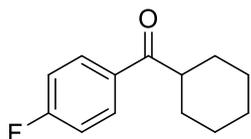


(4-(tert-butyl)phenyl)(cyclohexyl)methanone (3ga) ^[10]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 20/1) to afford the title compound as a Colorless oil (34.1 mg, 70% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 3.25 (tt, J = 11.6, 3.4 Hz, 1H), 1.93 – 1.80 (m, 4H), 1.78 – 1.70 (m, 1H), 1.57 – 1.34 (m, 4H), 1.34 (s, 9H), 1.31 – 1.25 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 203.5, 156.4, 133.7, 128.2, 125.5, 45.5, 35.04, 31.1, 29.5, 26.0, 25.9.



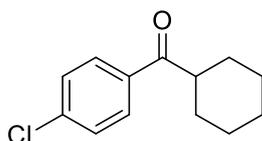
cyclohexyl(4-fluorophenyl)methanone (3ha)^[10]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**, using 10 mol% CuBr·(Me₂S) and 10 mol% SIMes·HCl. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (22.3 mg, 54% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.93 (m, 2H), 7.16 – 7.09 (m, 2H), 3.21 (tt, *J* = 11.4, 3.2 Hz, 1H), 1.92 – 1.81 (m, 4H), 1.80 – 1.69 (m, 1H), 1.53 – 1.29 (m, 5H).

¹³C NMR (176 MHz, CDCl₃) δ 202.2, 165.5 (d, *J* = 254.2 Hz), 132.7 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 9.1 Hz), 115.6 (d, *J* = 21.7 Hz), 45.6, 29.4, 25.9, 25.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -106.01.

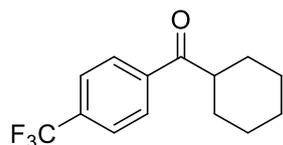


(4-chlorophenyl)(cyclohexyl)methanone (3ia)^[10]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (29.1 mg, 66% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 3.20 (tt, *J* = 11.3, 3.2 Hz, 1H), 1.90 – 1.80 (m, 4H), 1.78 – 1.70 (m, 1H), 1.54 – 1.27 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 202.6, 139.1, 134.6, 129.7, 128.9, 45.6, 29.3, 25.9, 25.8.



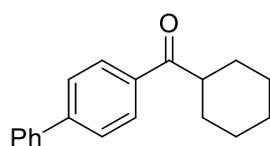
cyclohexyl(4-(trifluoromethyl)phenyl)methanone (3ja)^[11]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (26.6 mg, 52% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 3.25 (tt, *J* = 11.4, 3.3 Hz, 1H), 1.95 – 1.80 (m, 4H), 1.79 – 1.70 (m, 1H), 1.55 – 1.27 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 202.8, 139.1, 134.0 (q, *J* = 32.8 Hz), 128.6, 125.6 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.7 Hz), 45.9, 29.2, 25.8, 25.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.09.

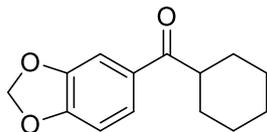


[1,1'-biphenyl]-4-yl(cyclohexyl)methanone (3ka)^[10]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (27.1 mg, 51% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.99 (m, 2H), 7.71 – 7.66 (m, 2H), 7.65 – 7.59 (m, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H), 3.30 (tt, *J* = 11.4, 3.3 Hz, 1H), 1.97 – 1.82 (m, 4H), 1.80 – 1.72 (m, 1H), 1.53 – 1.27 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 203.5, 145.4, 134.0, 135.0, 128.9, 128.9, 128.1, 127.2, 45.7, 29.5, 26.0, 25.9.

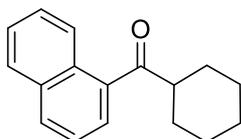


benzo[d][1,3]dioxol-5-yl(cyclohexyl)methanone (3la) ^[10]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**, using 10 mol% CuBr·(Me₂S) and 10 mol% SIMes·HCl. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 30/1) to afford the title compound as a Colorless oil (24.5 mg, 53% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.43 (s, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.03 (s, 2H), 3.16 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.90 – 1.79 (m, 4H), 1.78 – 1.68 (m, 1H), 1.56 – 1.25 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 201.9, 151.4, 148.2, 131.1, 124.2, 108.2, 107.8, 101.7, 45.5, 29.6, 25.9, 25.9.



cyclohexyl(naphthalen-1-yl)methanone (3ma) ^[12]

This reaction was conducted on a 0.2 mmol scale with the **General procedure I**. The crude product was purified by silica gel chromatography (PE/EA = 1/0 to 50/1) to afford the title compound as a Colorless oil (30.4 mg, 64% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 7.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.1 Hz, 1H), 7.61 – 7.45 (m, 3H), 3.21 (tt, *J* = 11.4, 3.4 Hz, 1H), 1.99 – 1.89 (m, 2H), 1.89 – 1.78 (m, 2H), 1.75 – 1.66 (m, 1H), 1.62 – 1.51 (m, 3H), 1.43 – 1.26 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 208.6, 137.2, 133.9, 131.4, 130.4, 128.3, 127.4, 126.3, 125.6, 124.4, 49.7, 28.9, 25.9, 25.8.

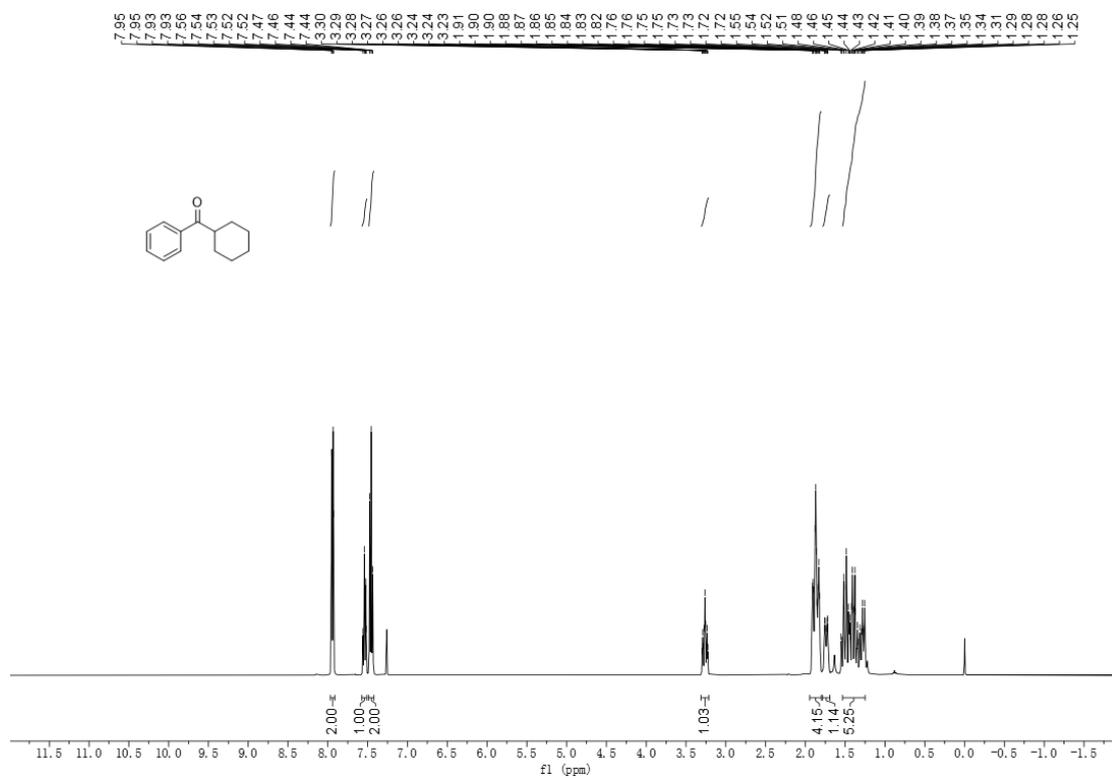
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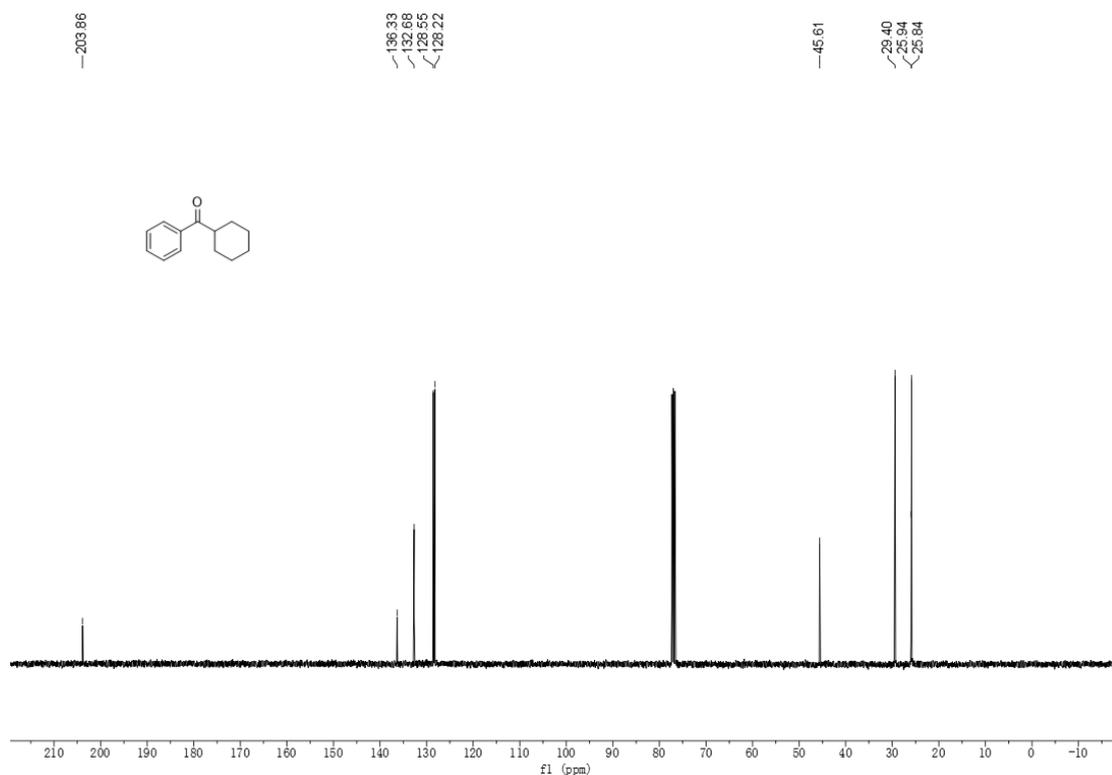
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6. Copy of ^1H , ^{13}C and ^{19}F NMR Spectra of Products

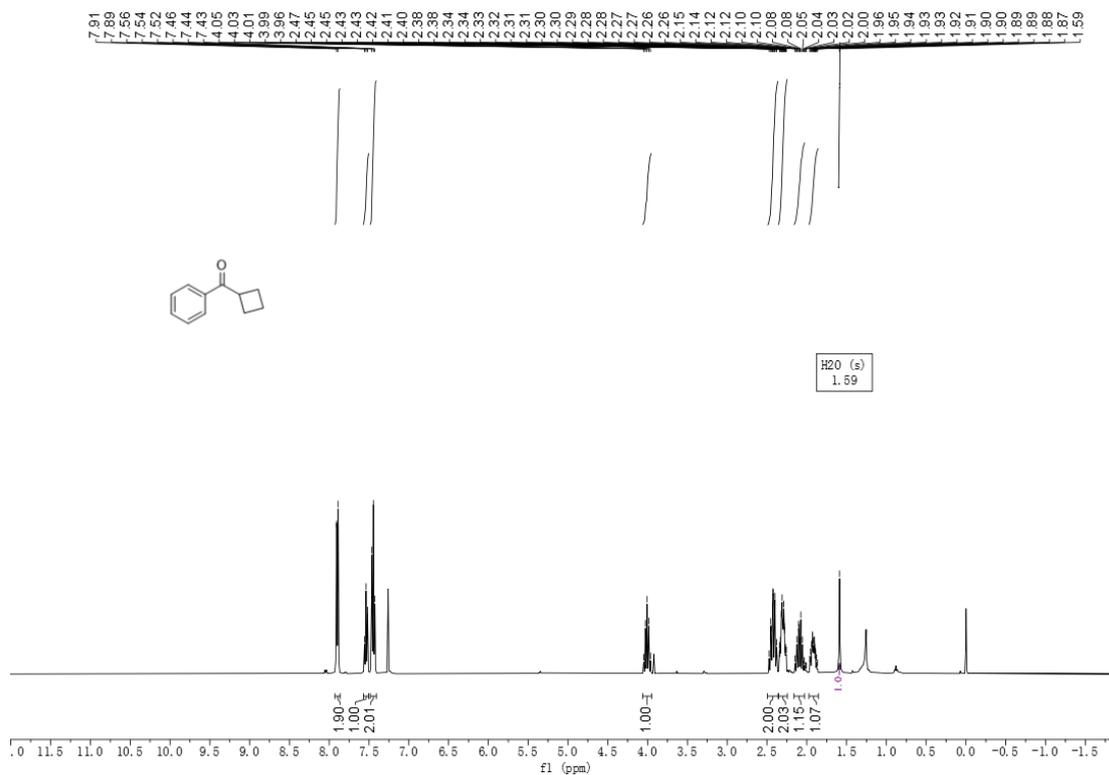
^1H NMR (400 MHz, CDCl_3) (3aa)



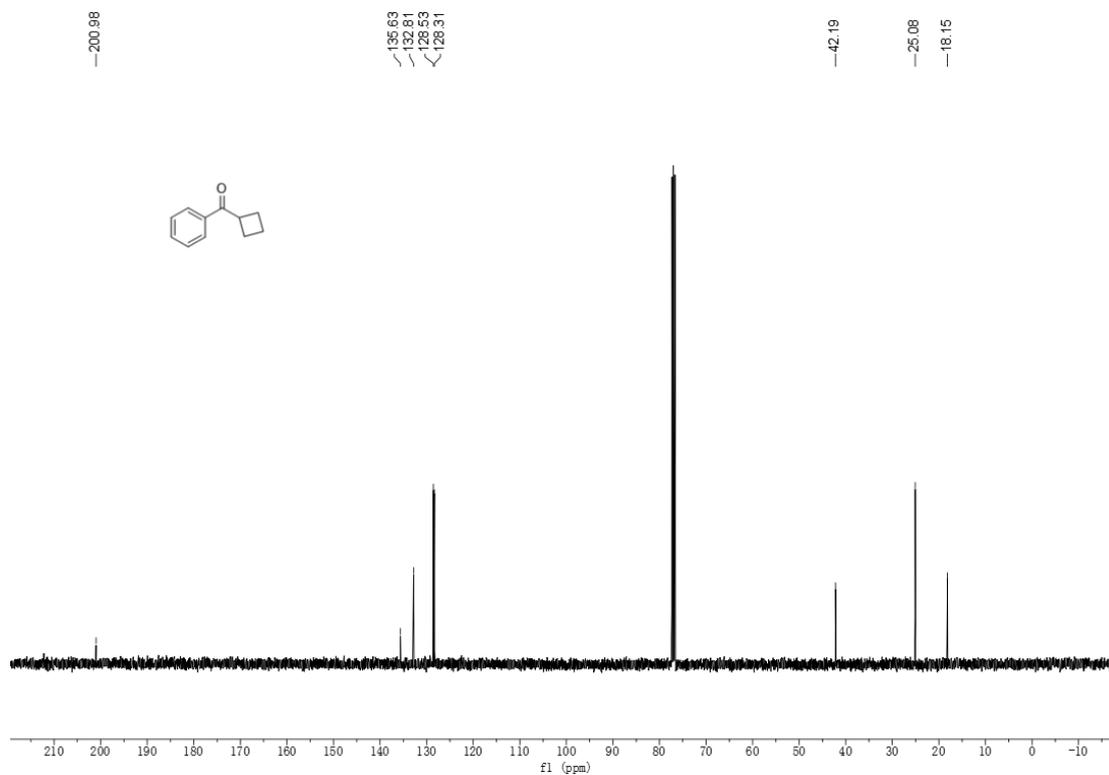
^{13}C NMR (101 MHz, CDCl_3) (3aa)



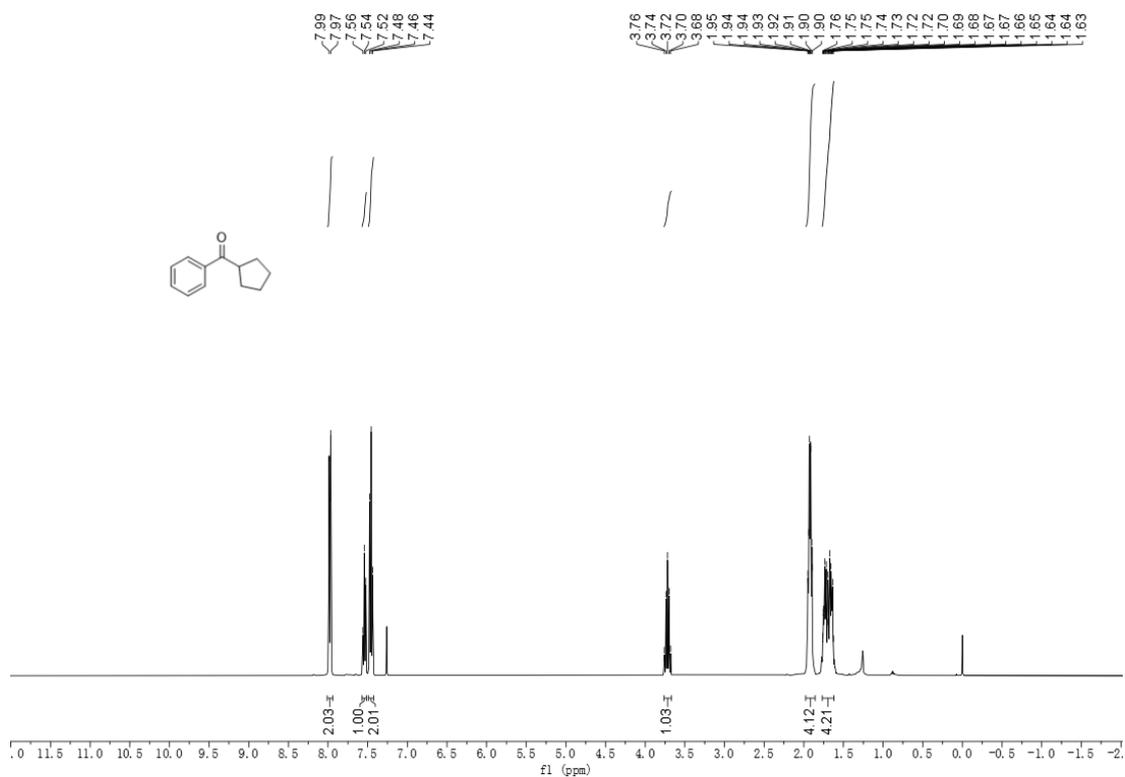
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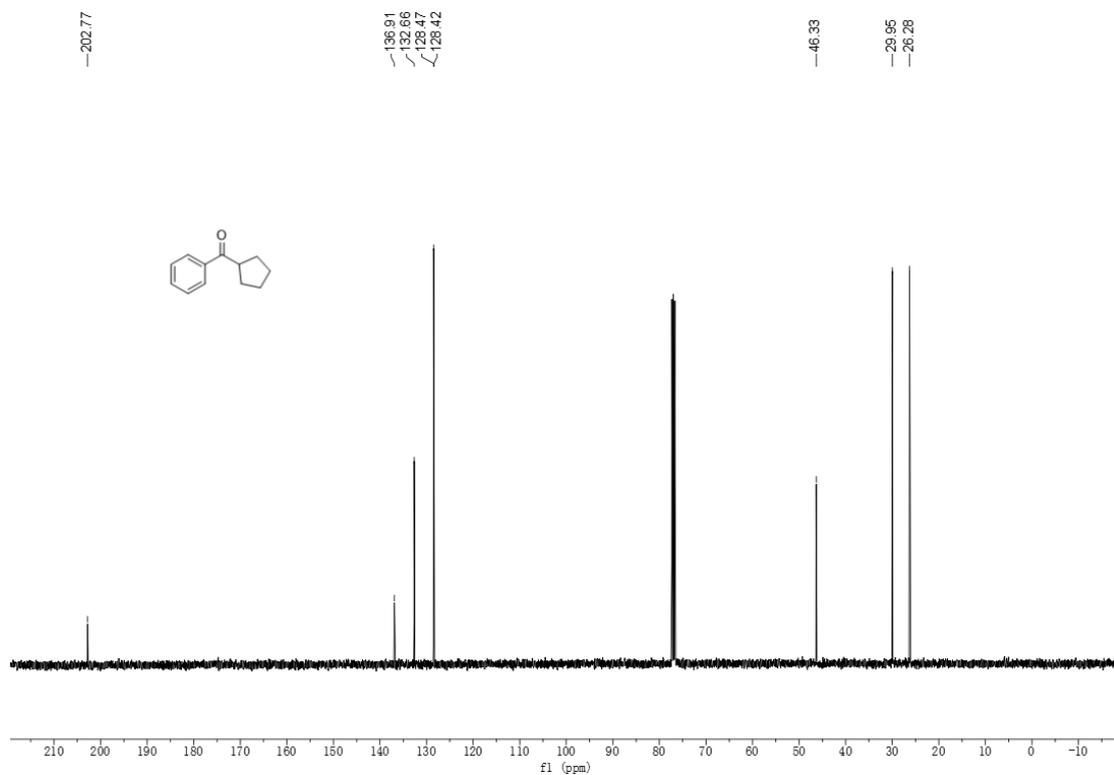
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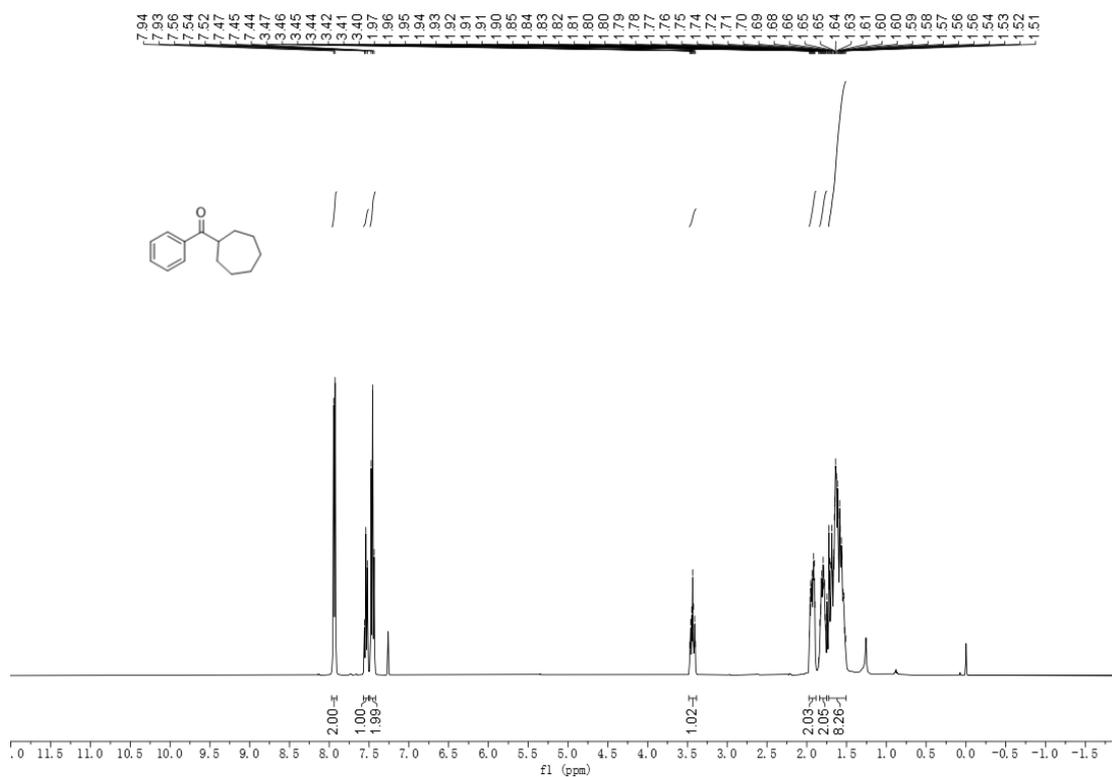
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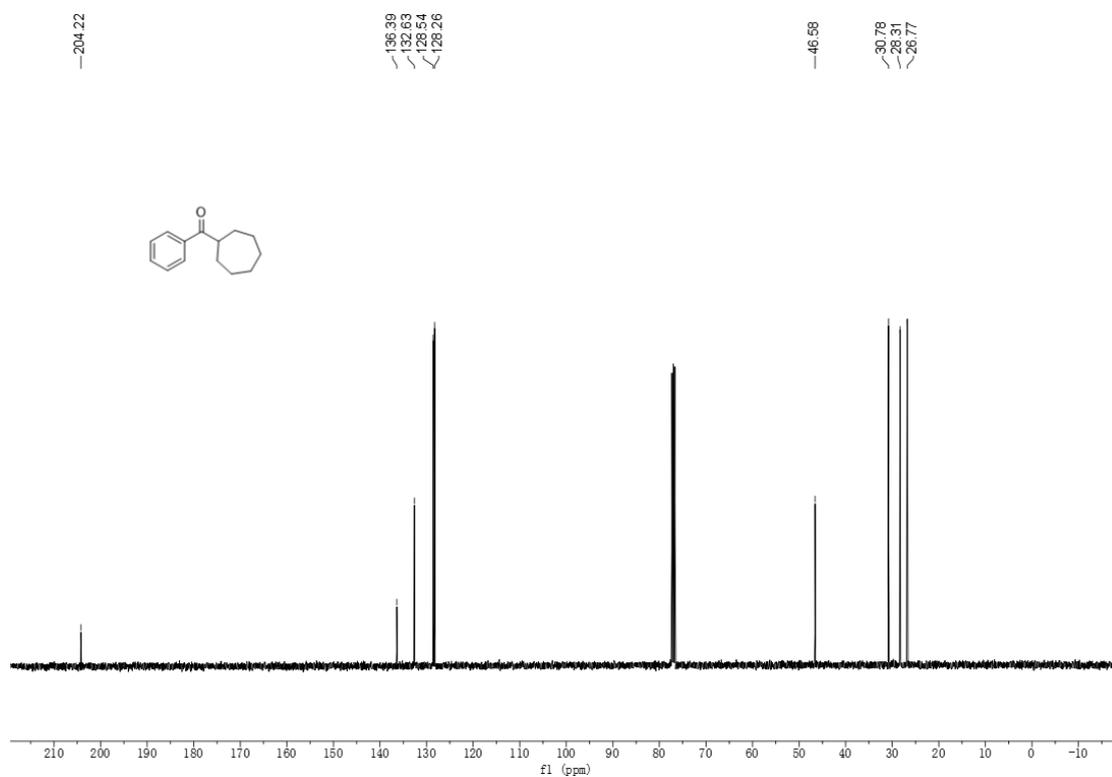
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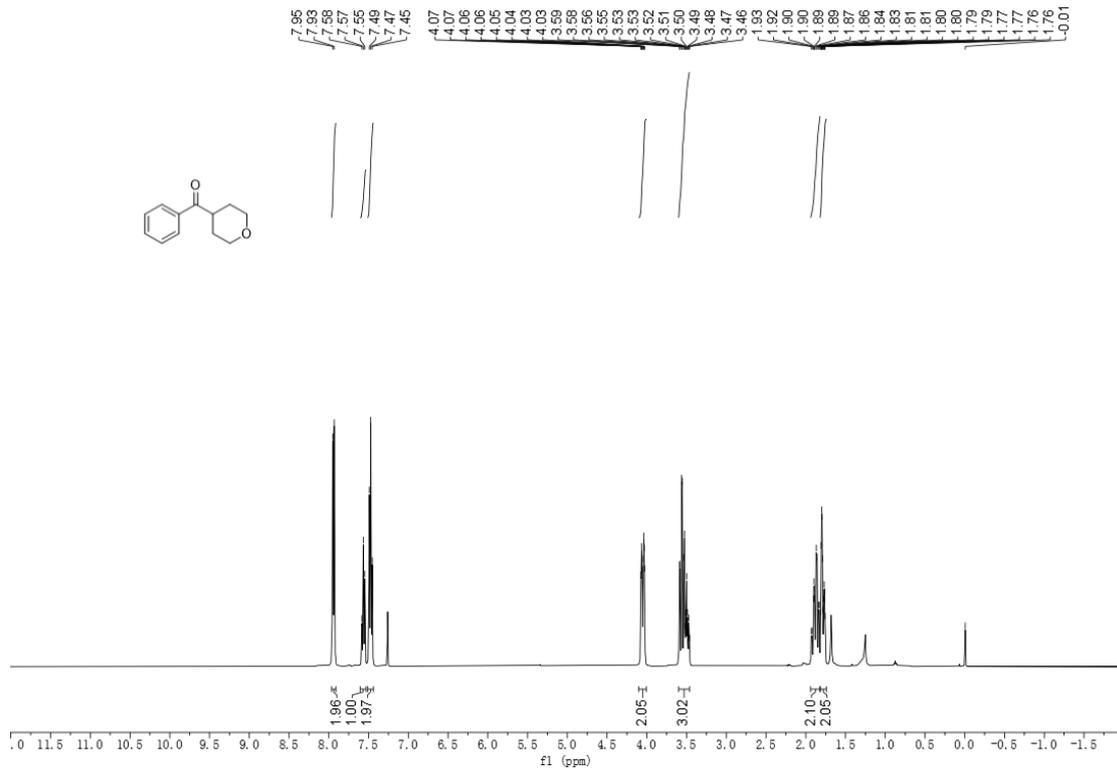
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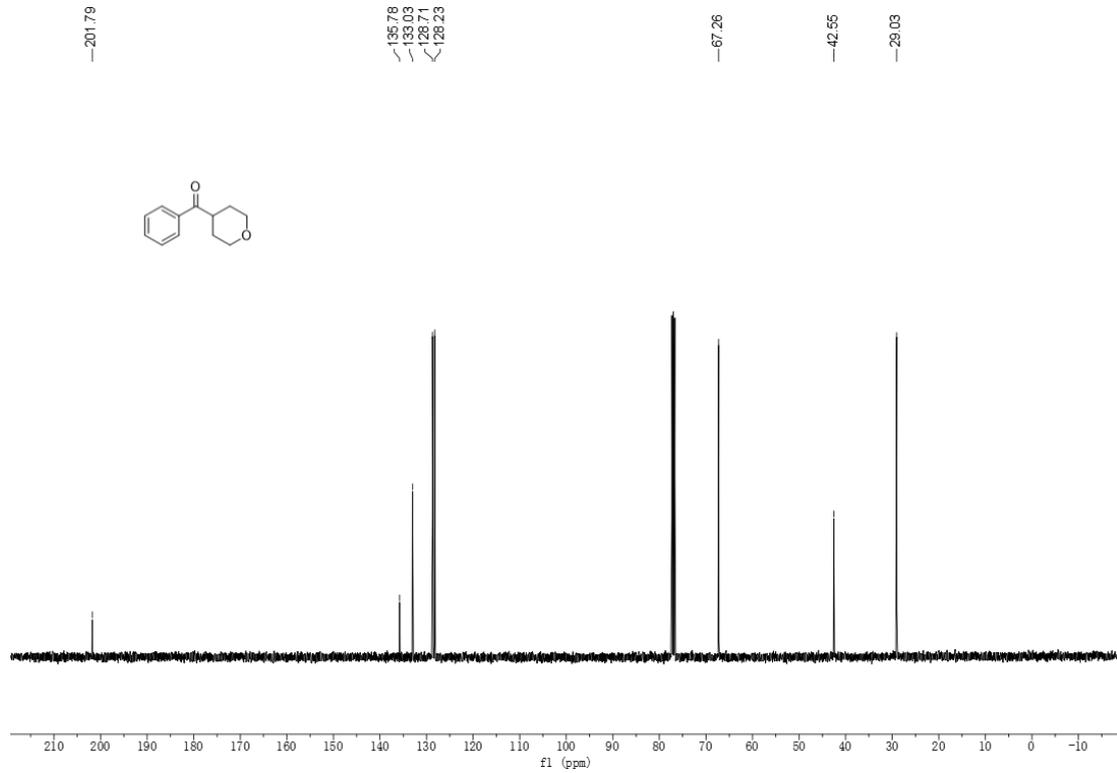
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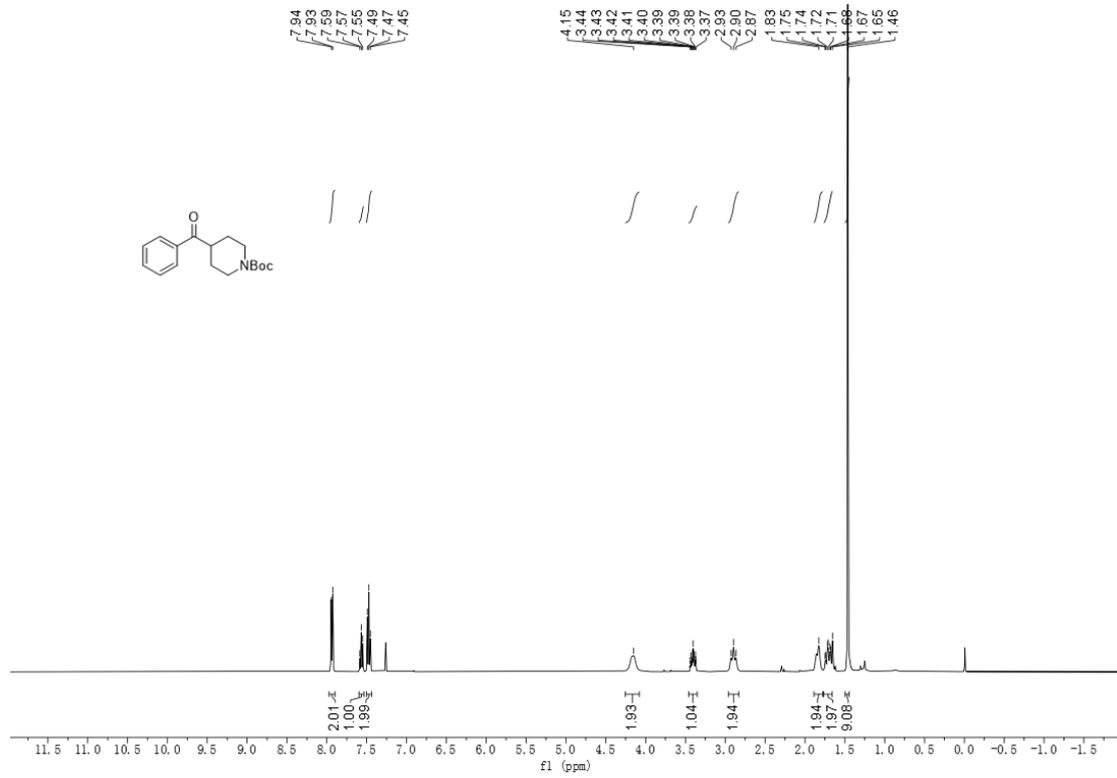
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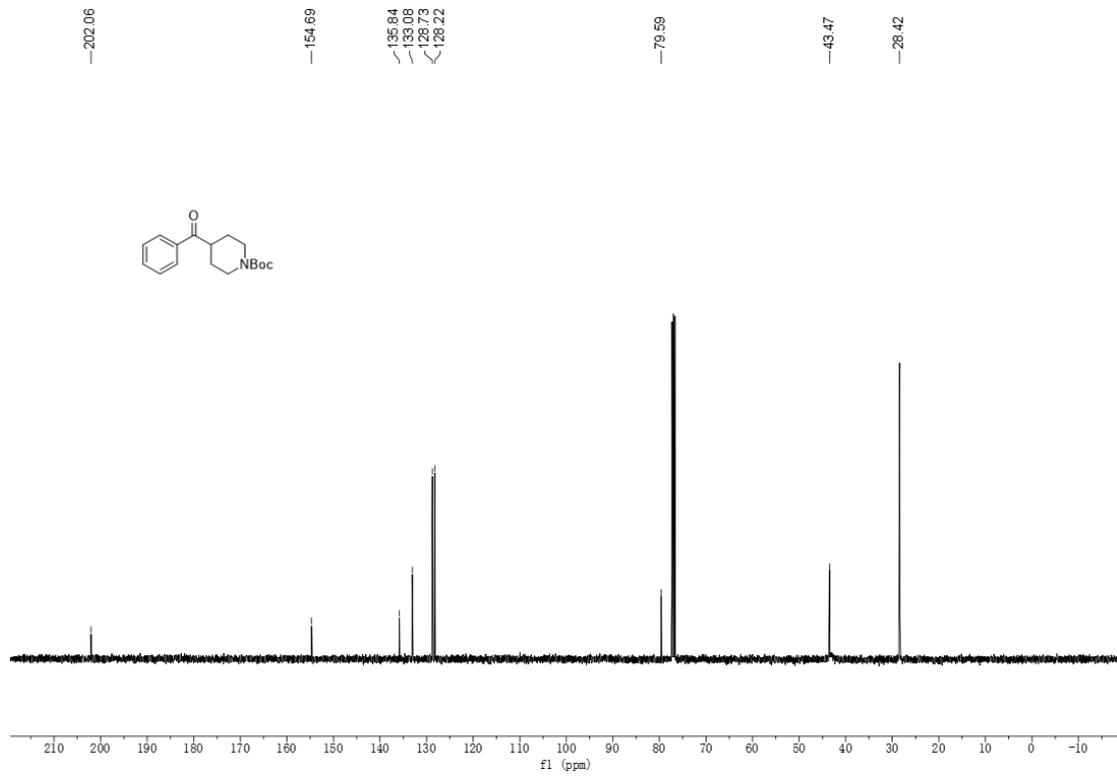
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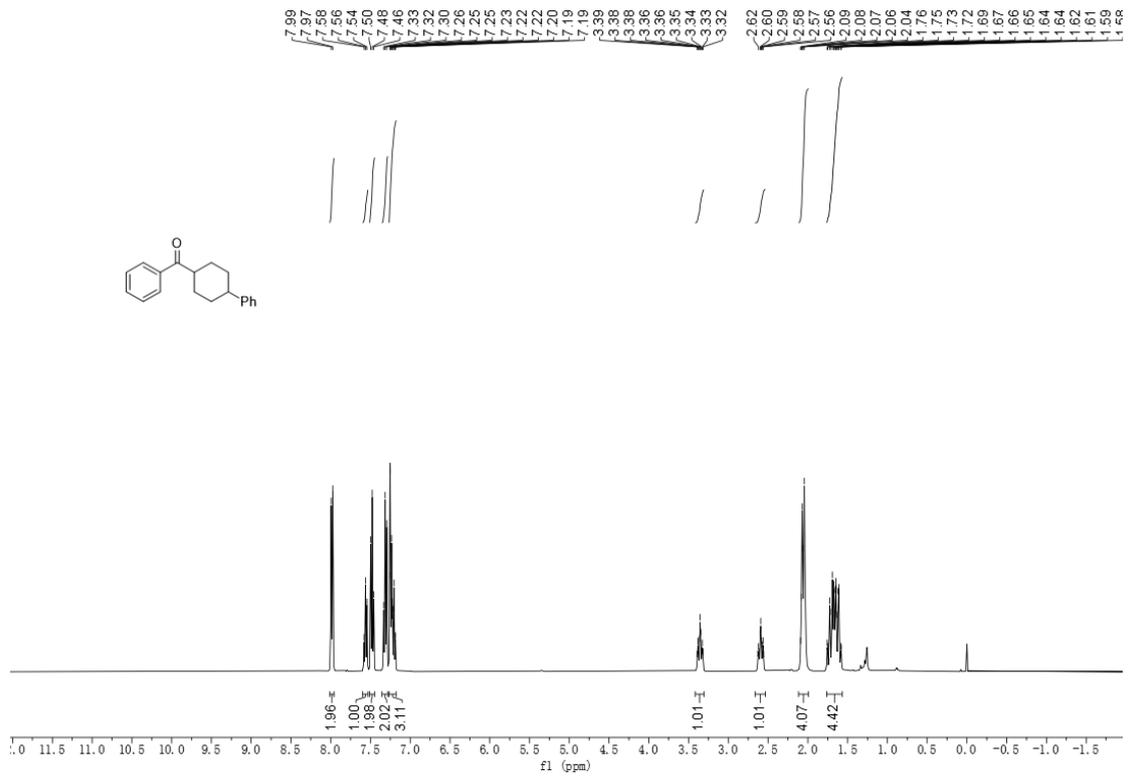
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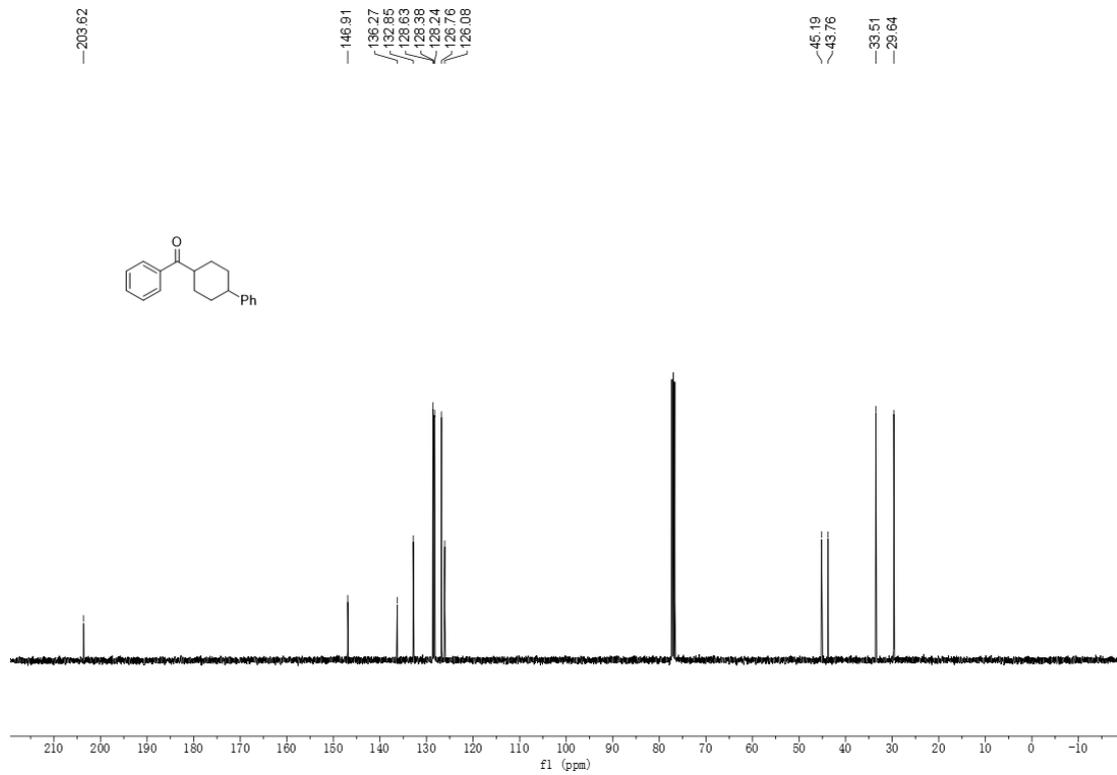
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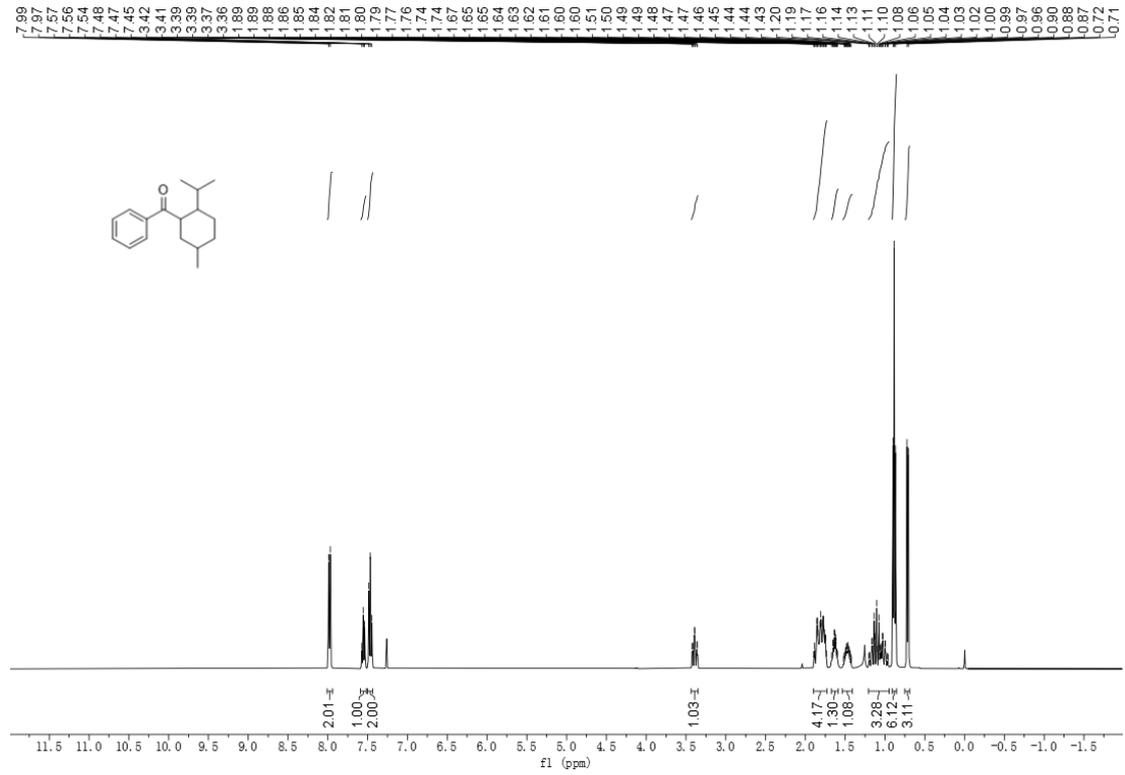
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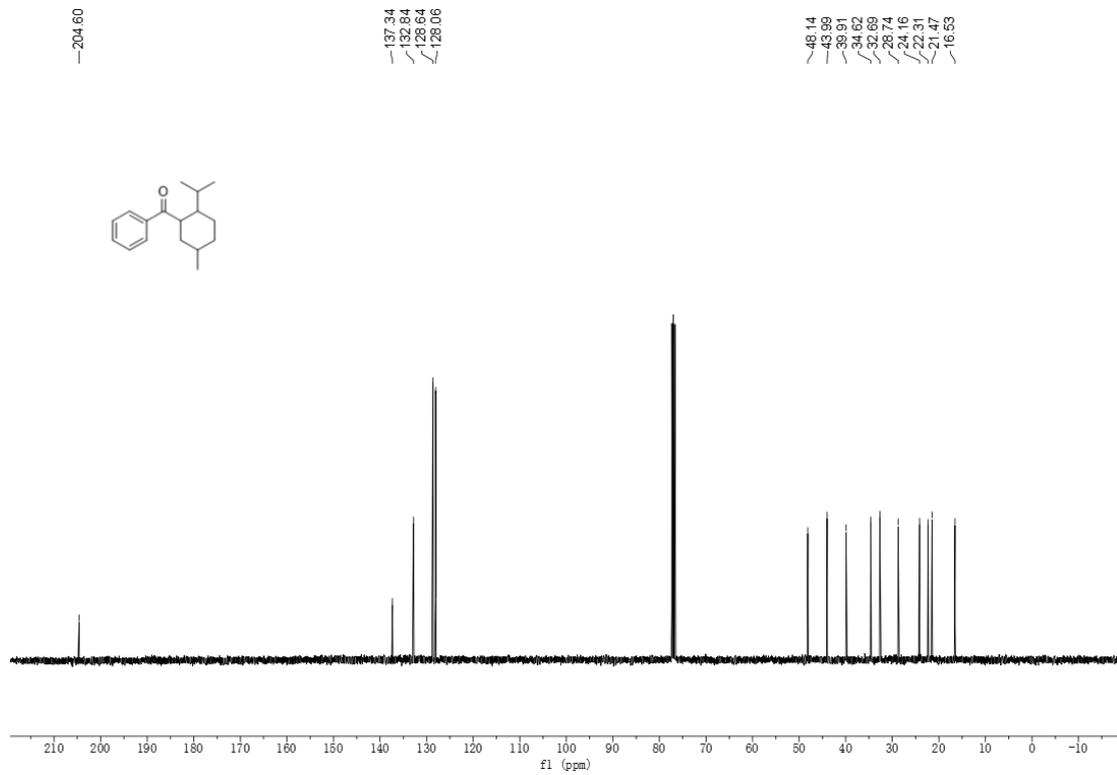
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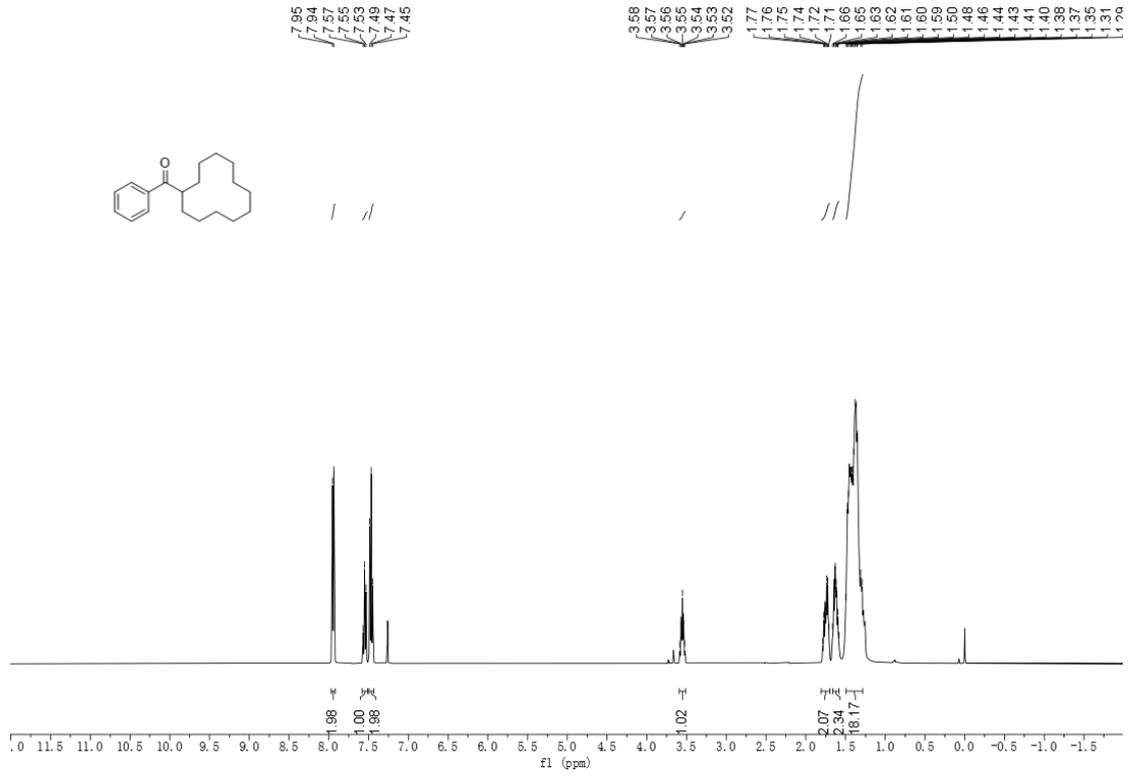
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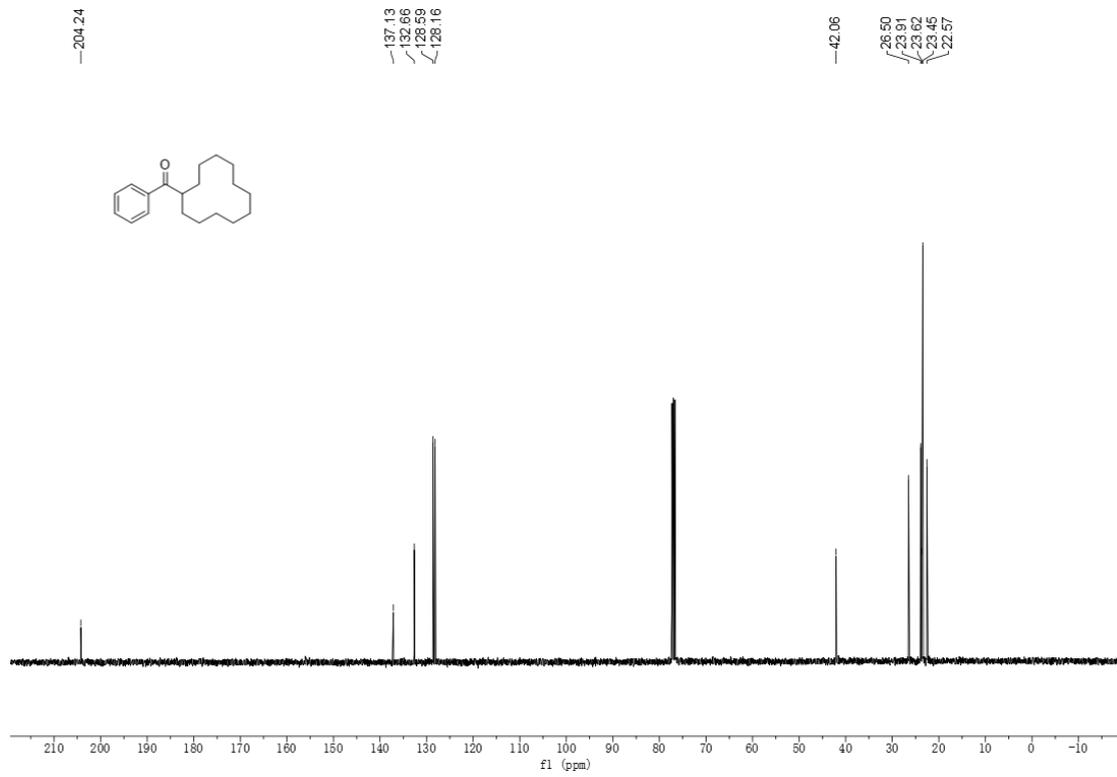
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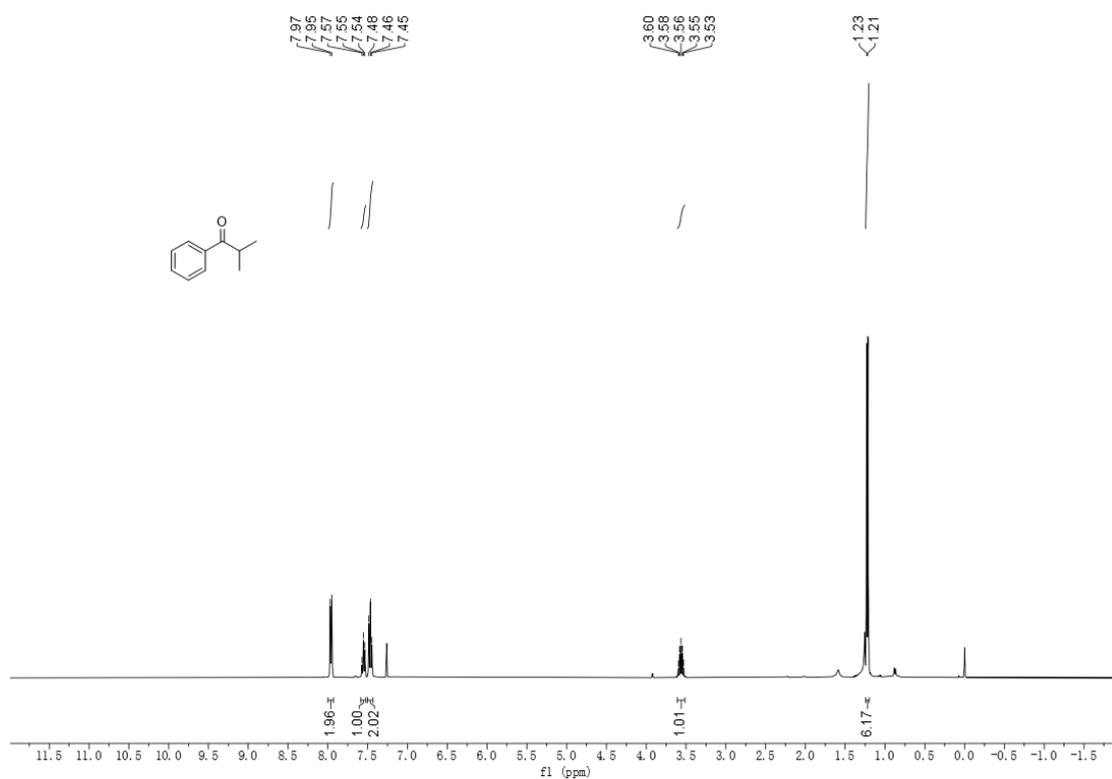
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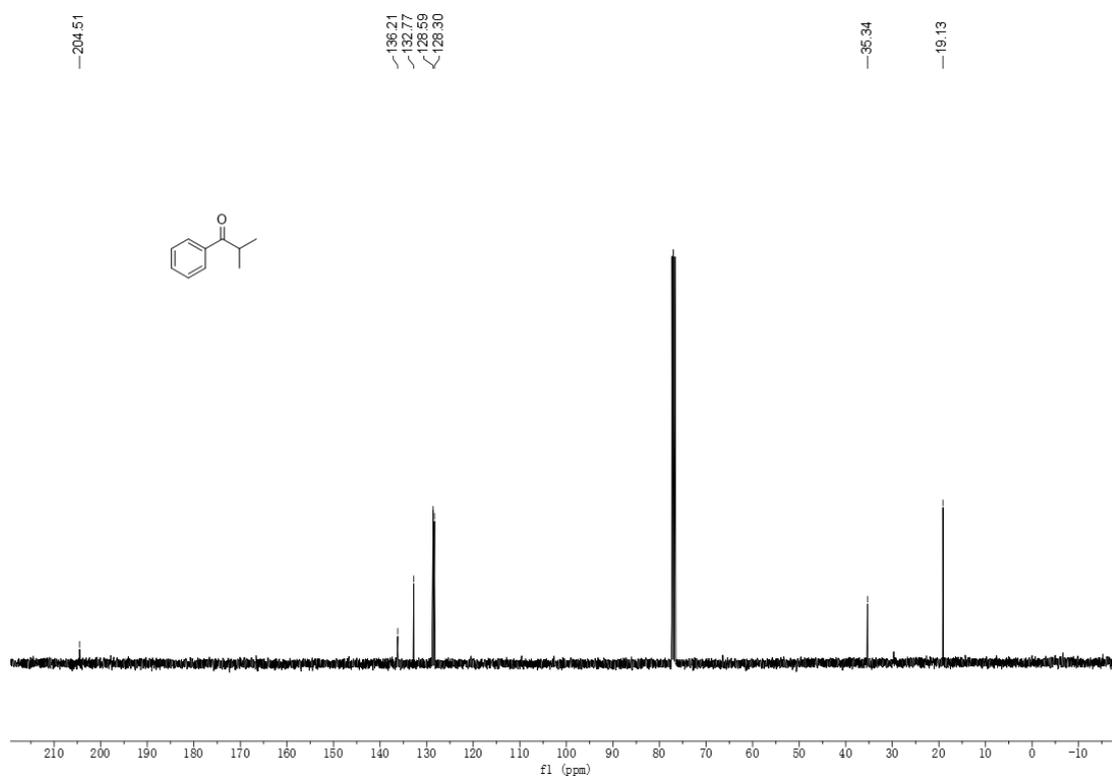
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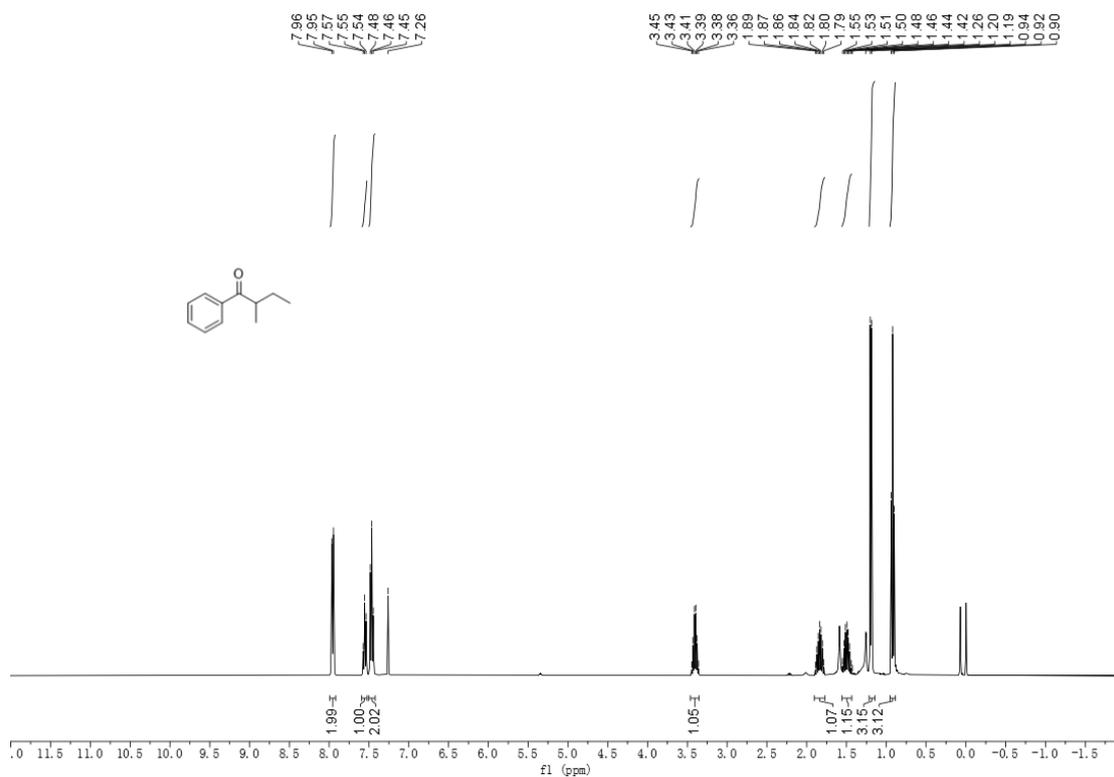
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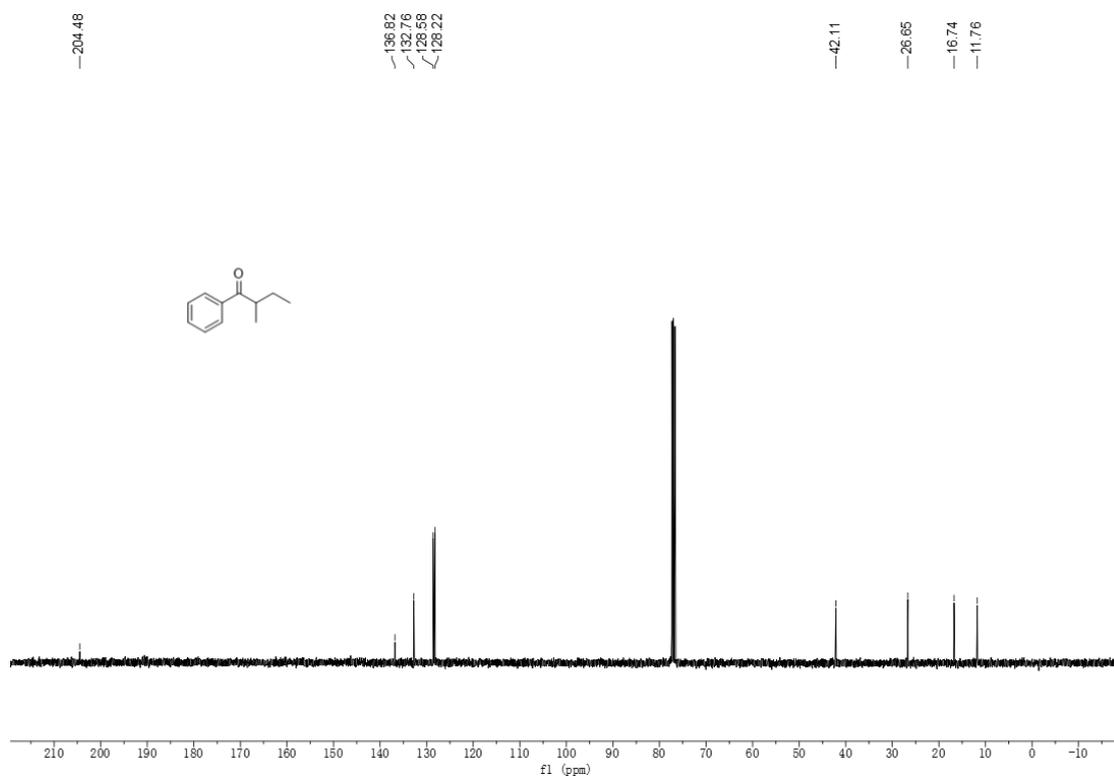
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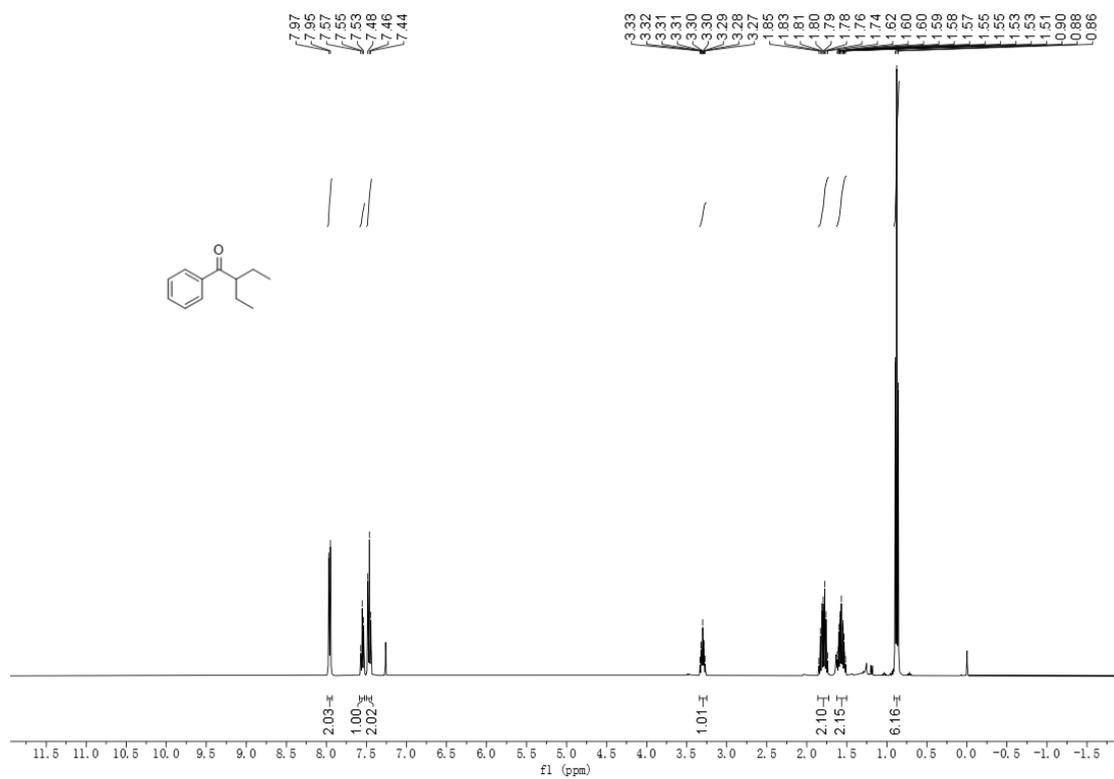
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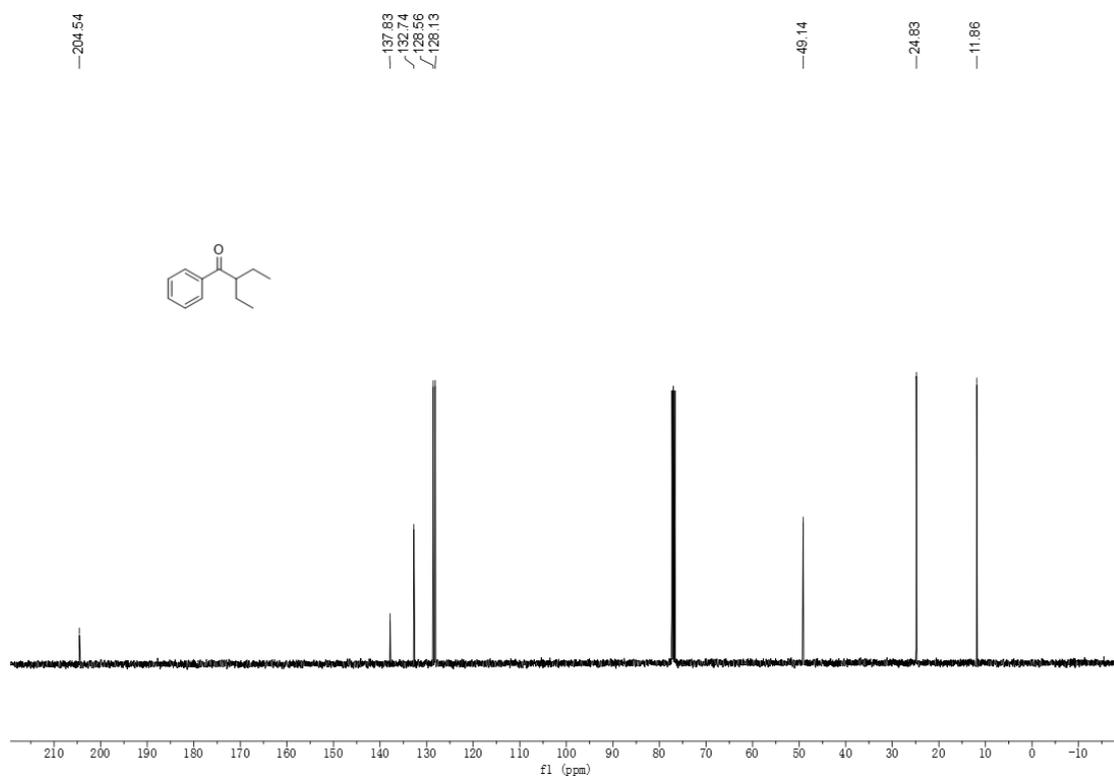
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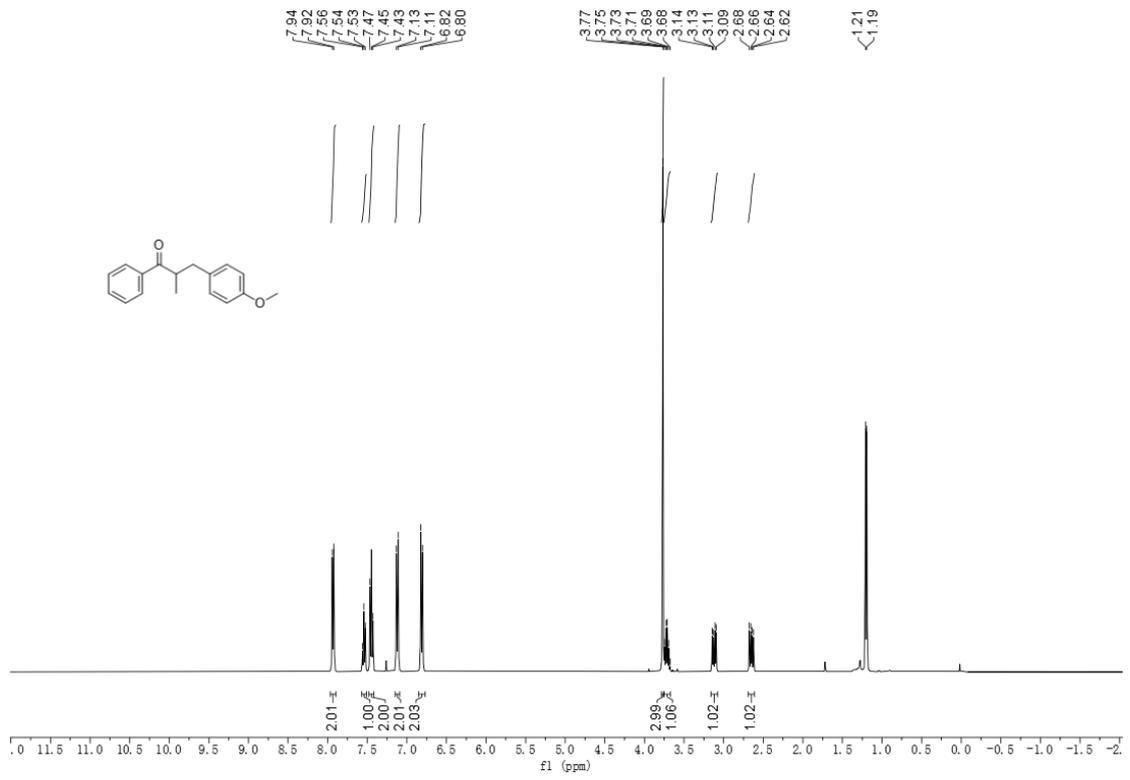
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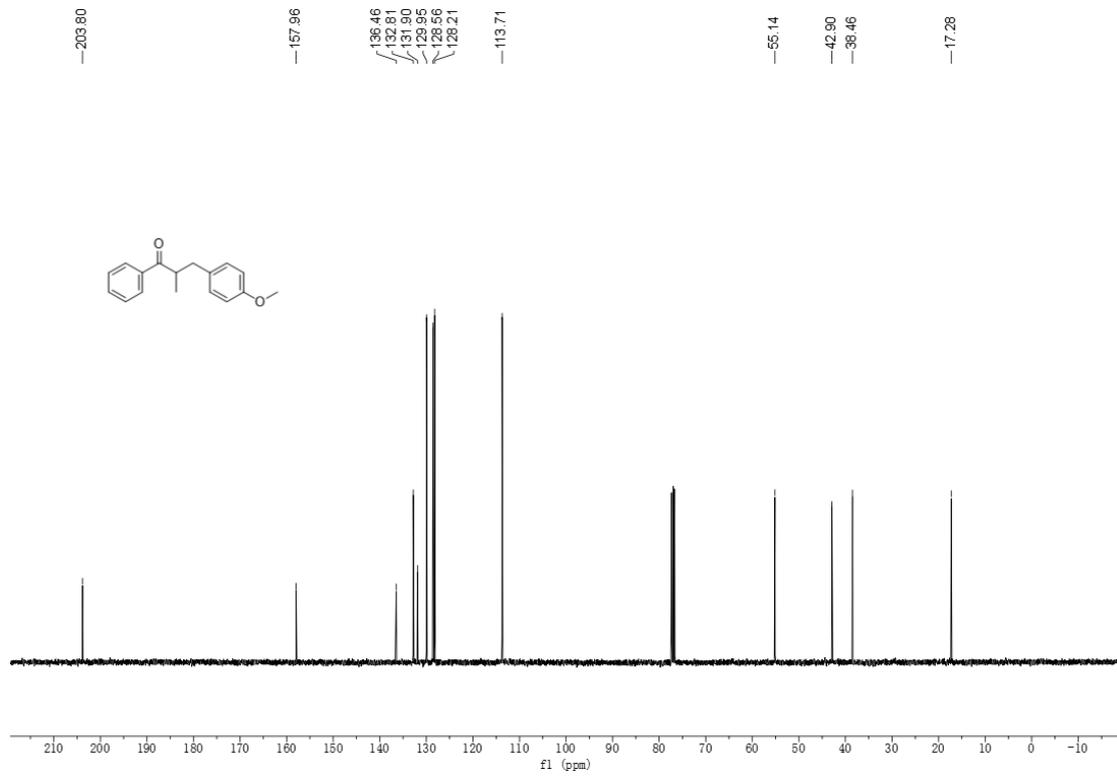
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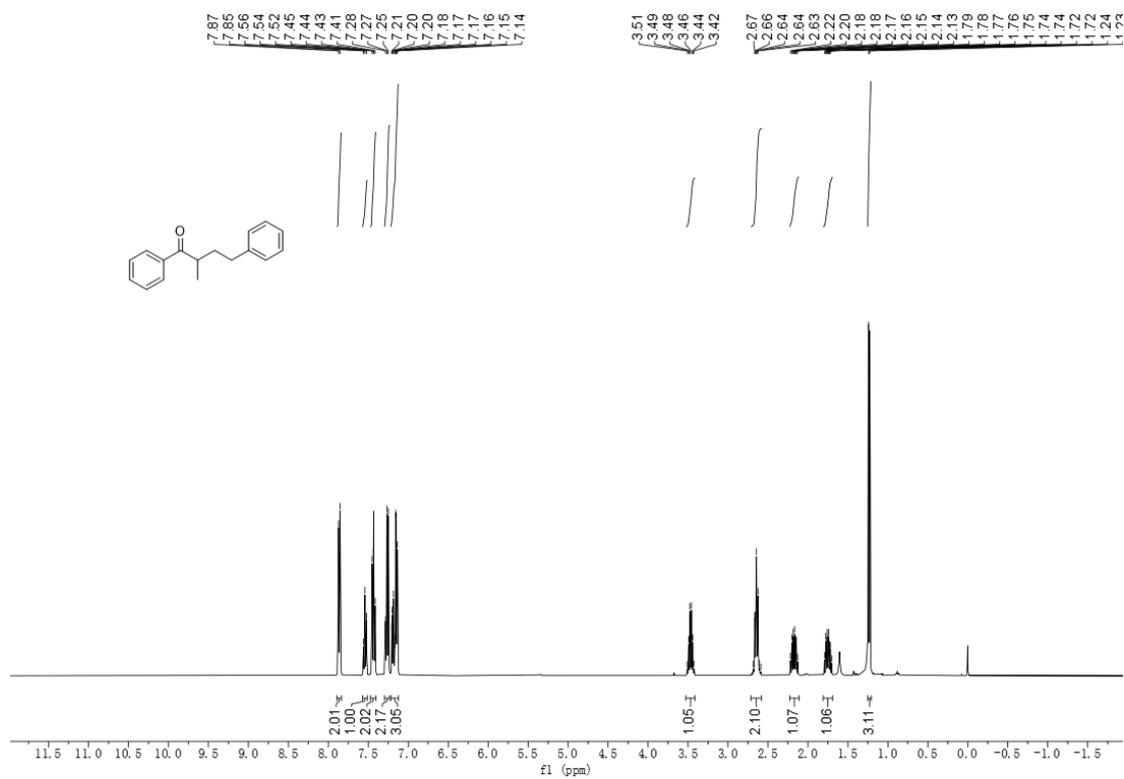
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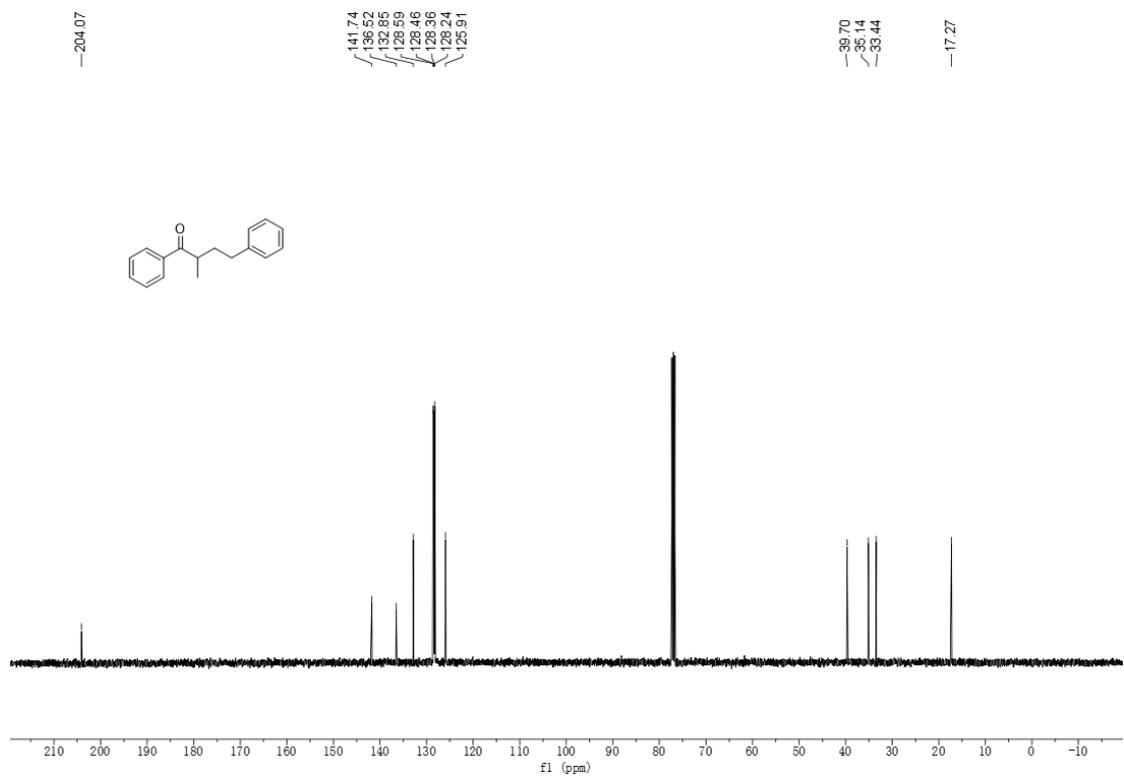
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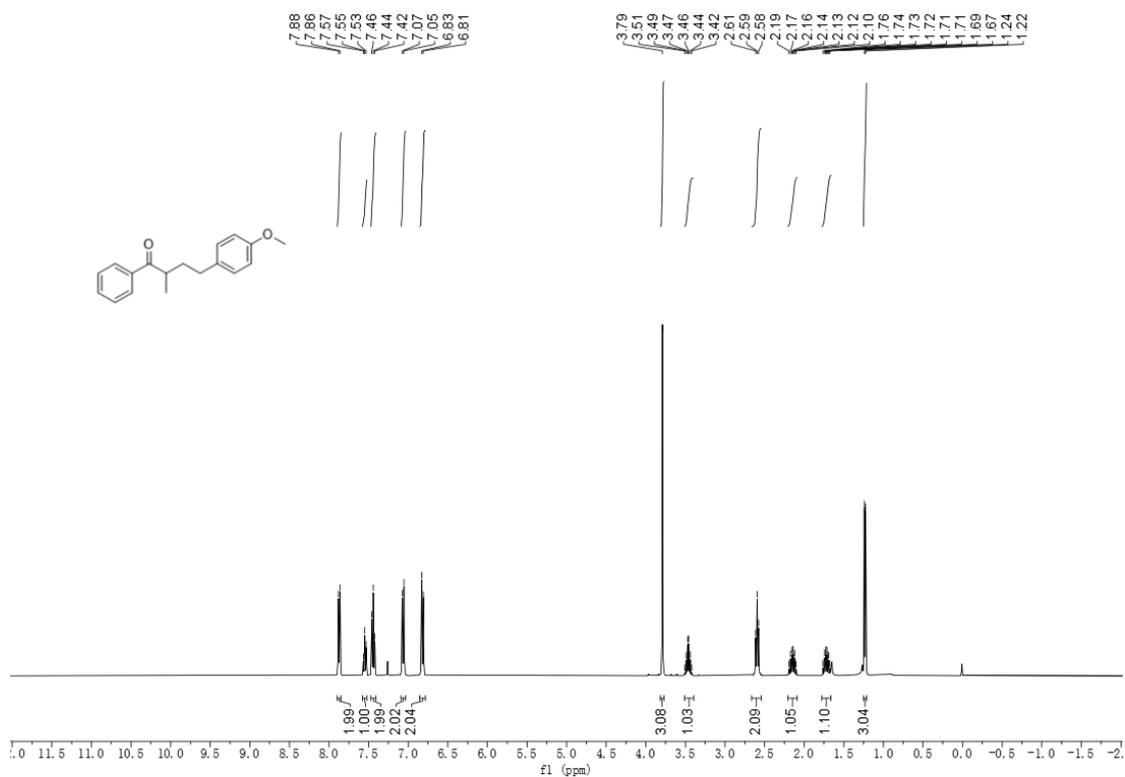
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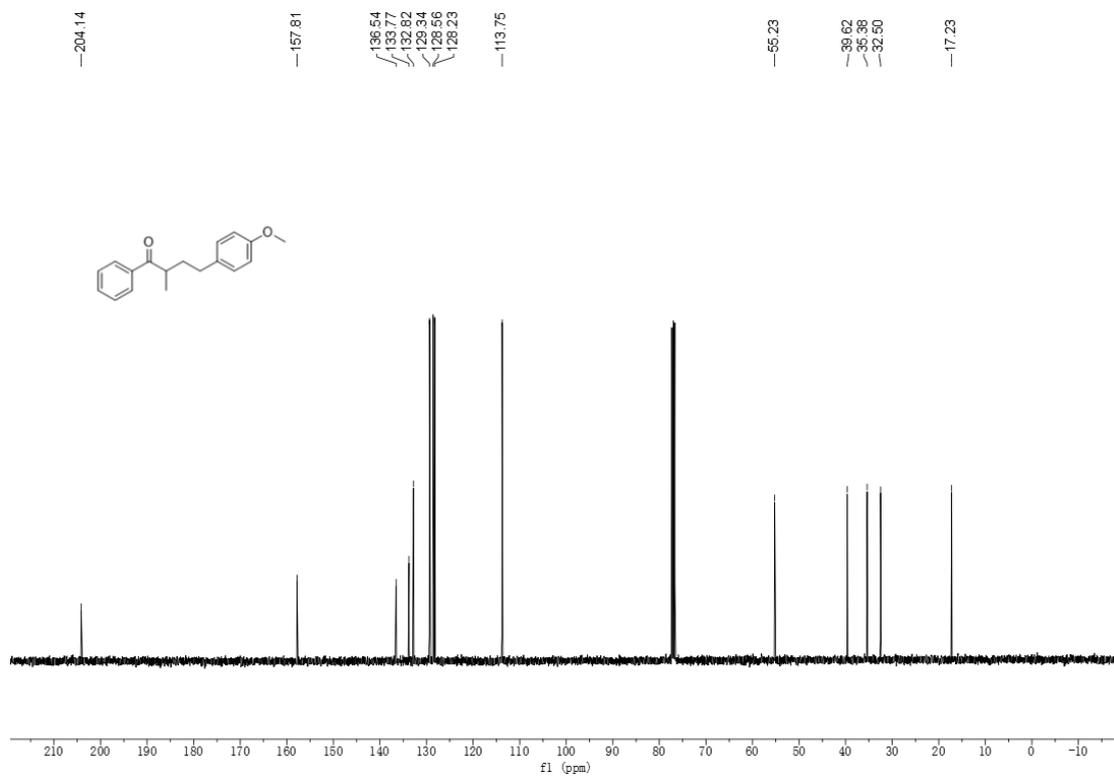
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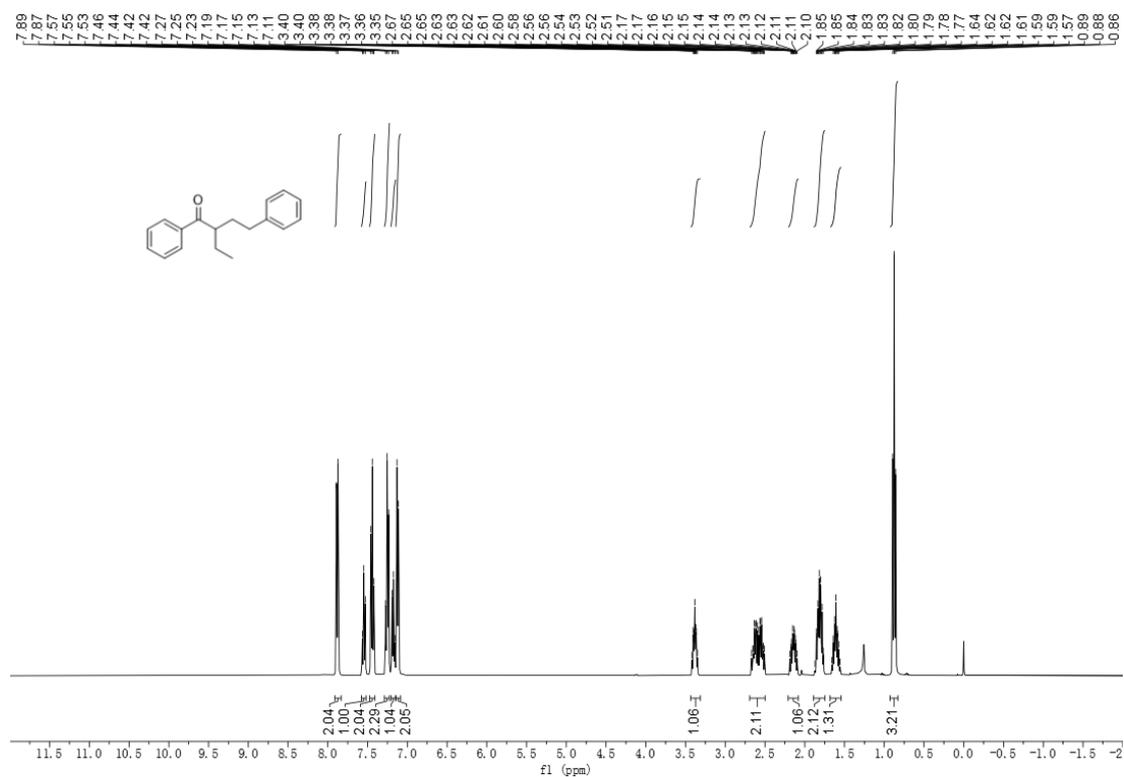
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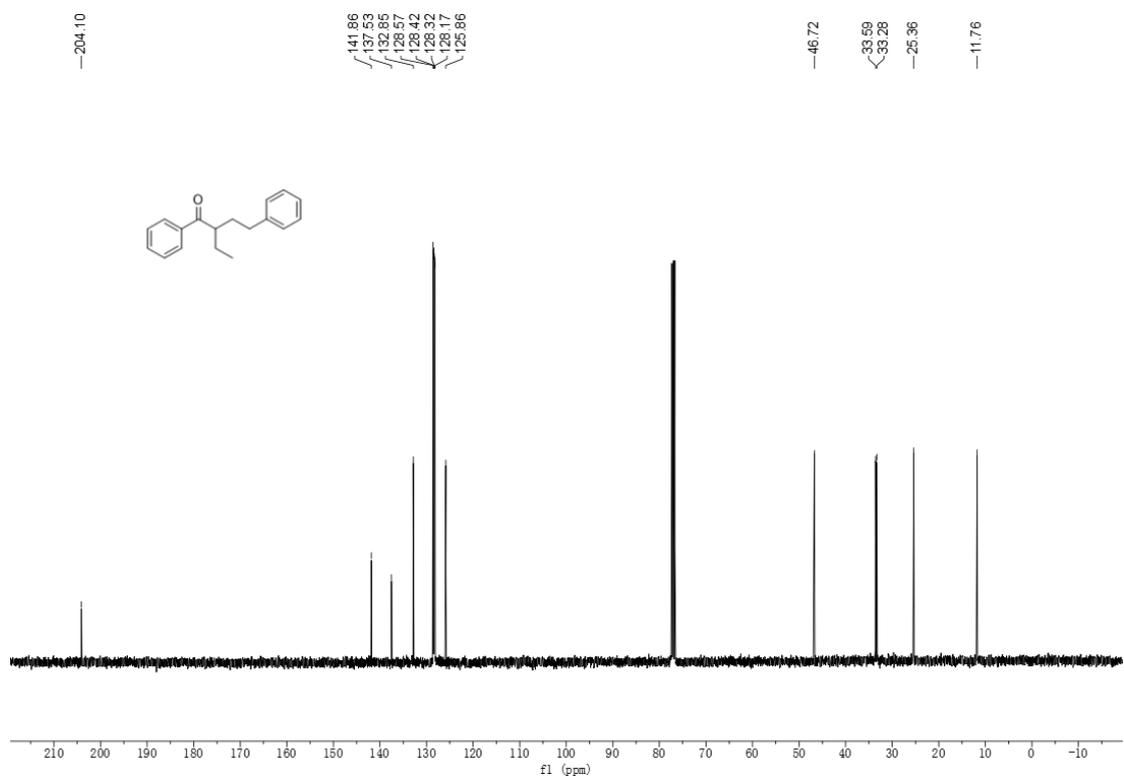
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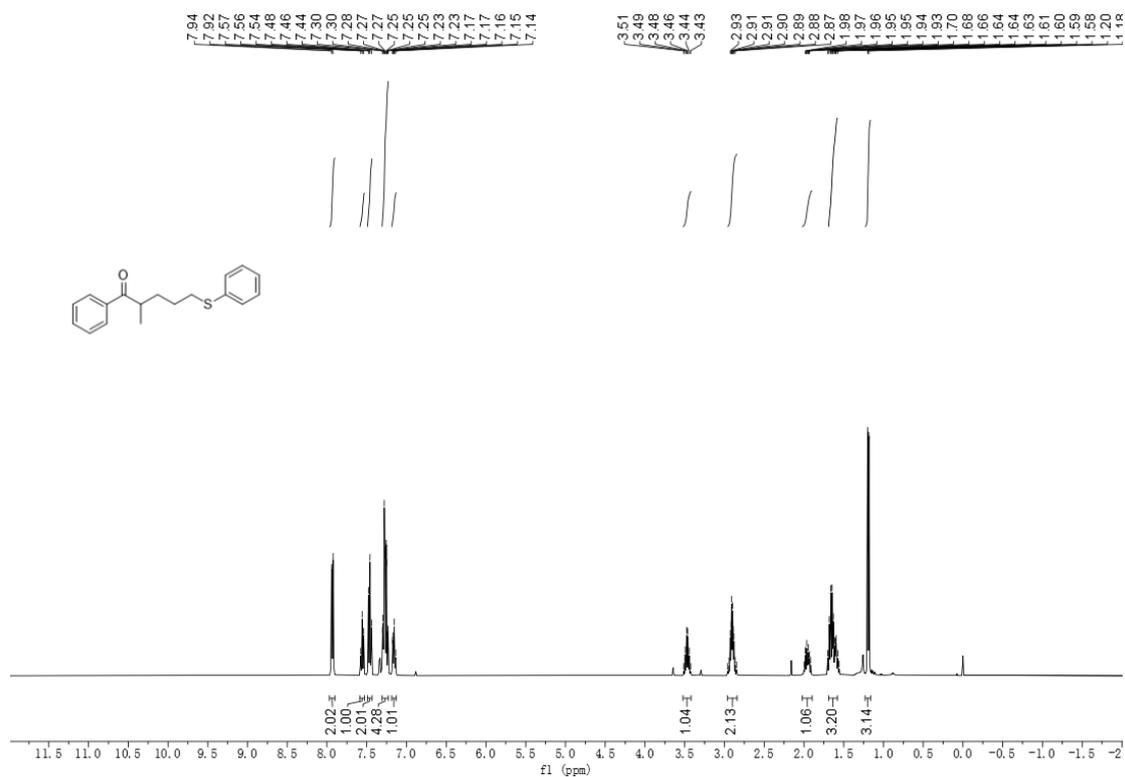
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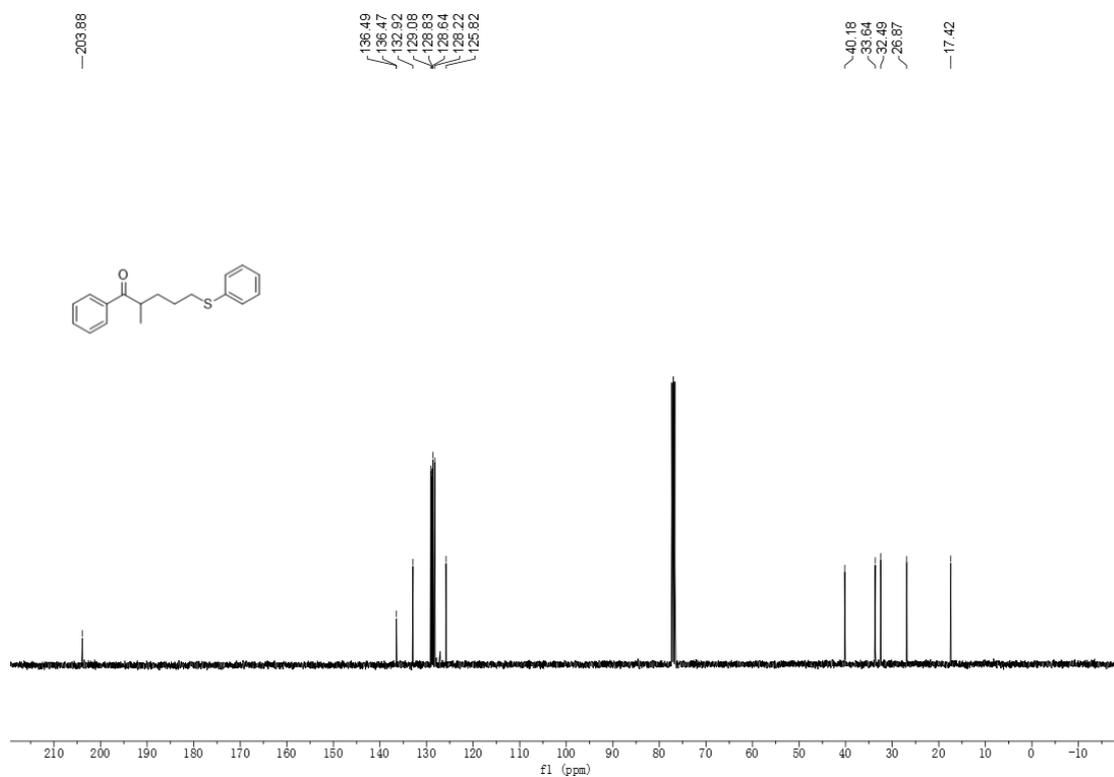
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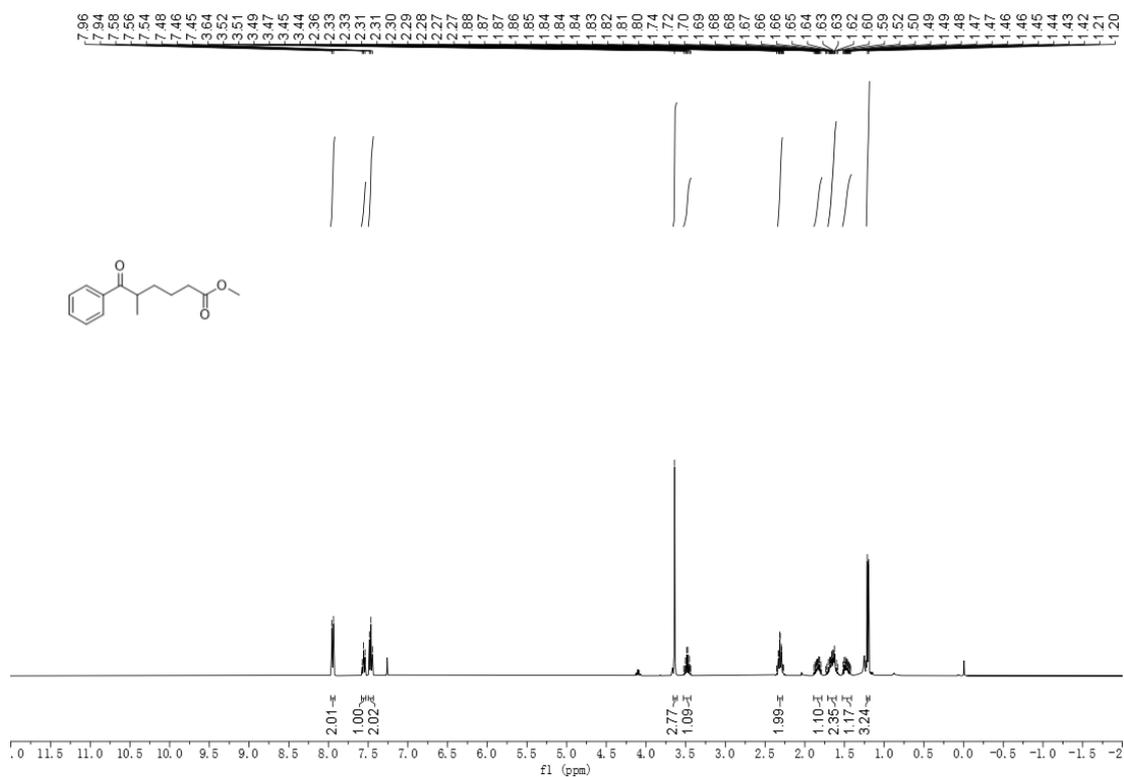
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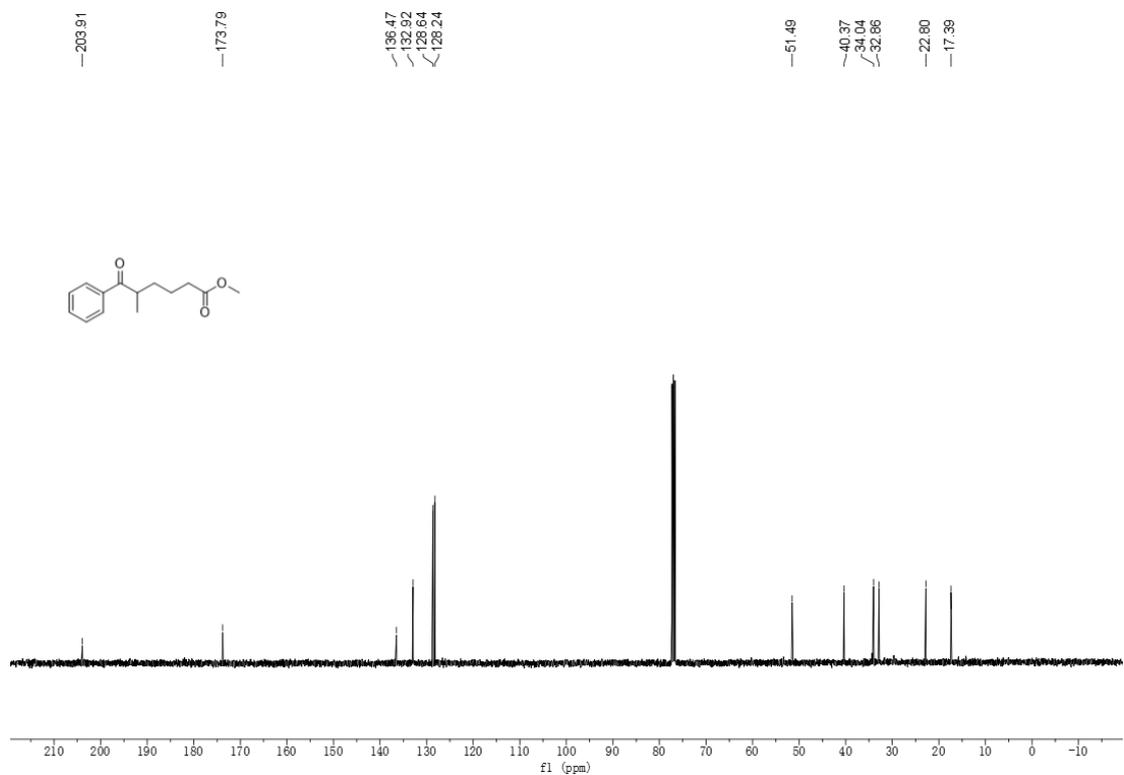
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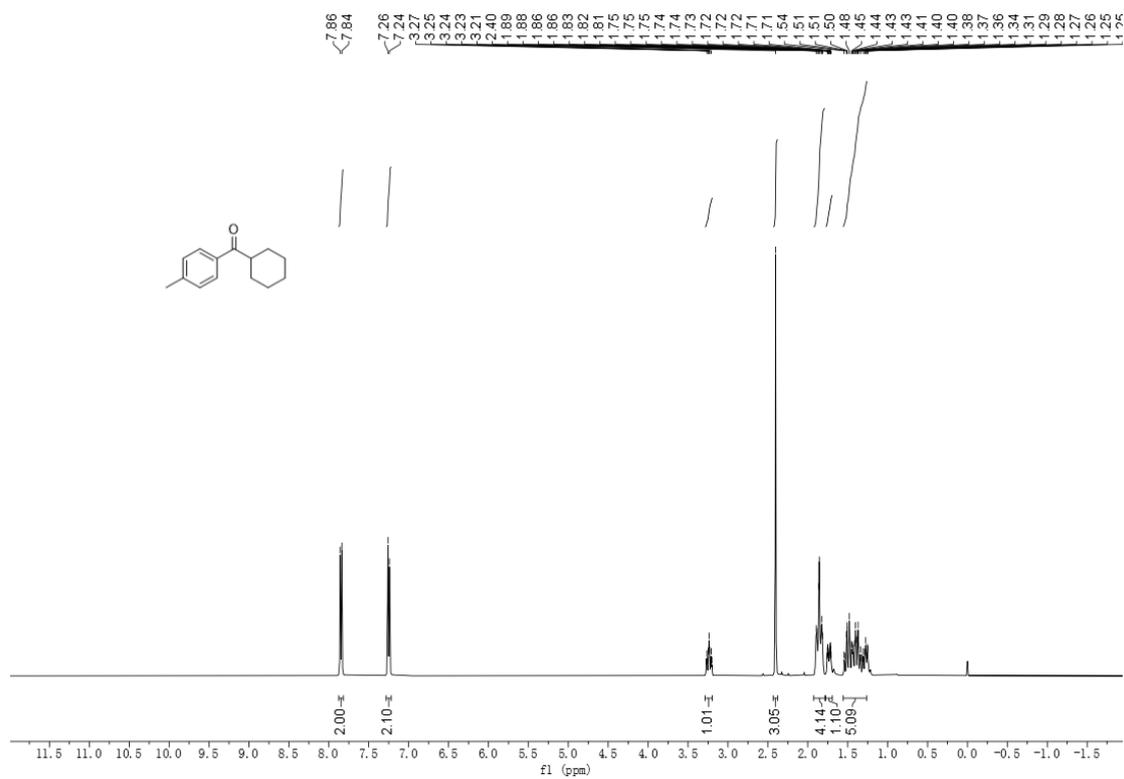
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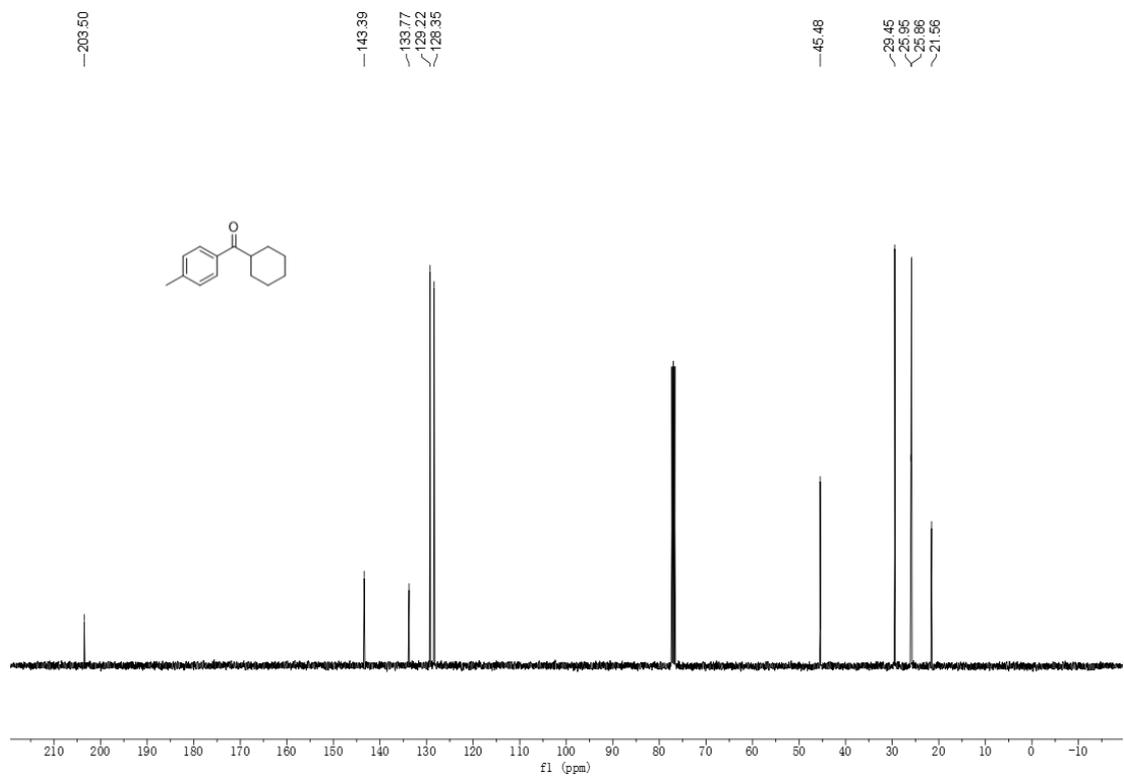
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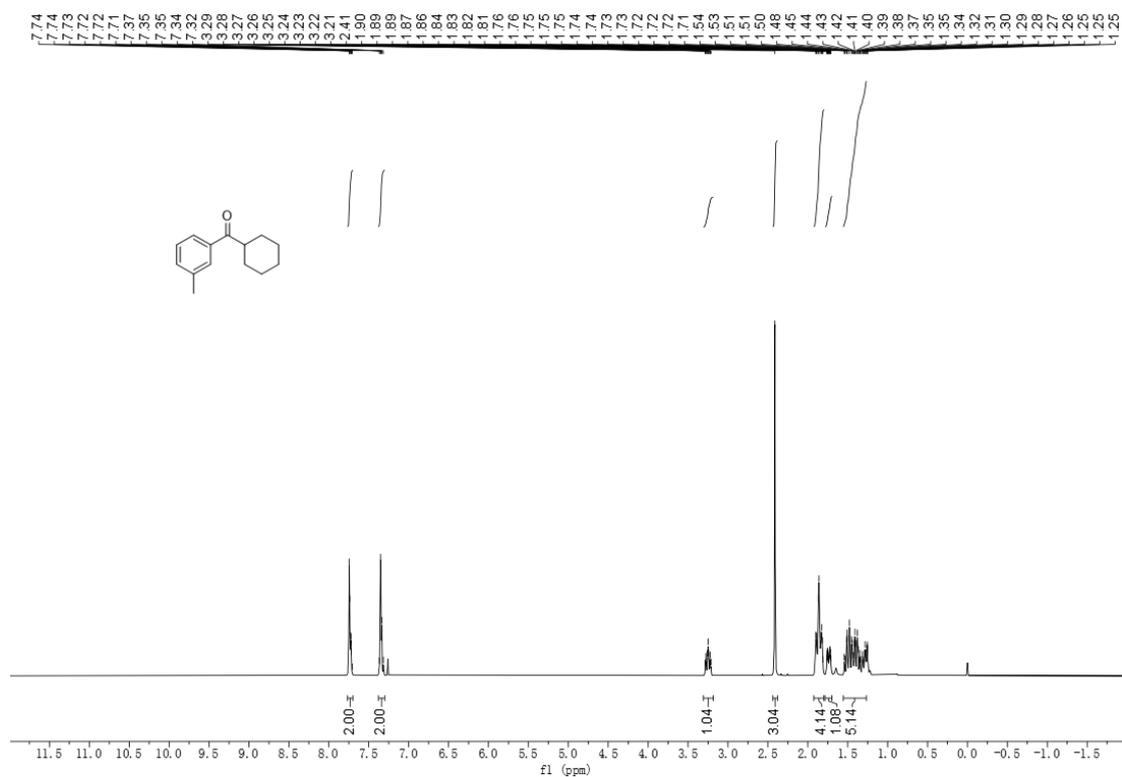
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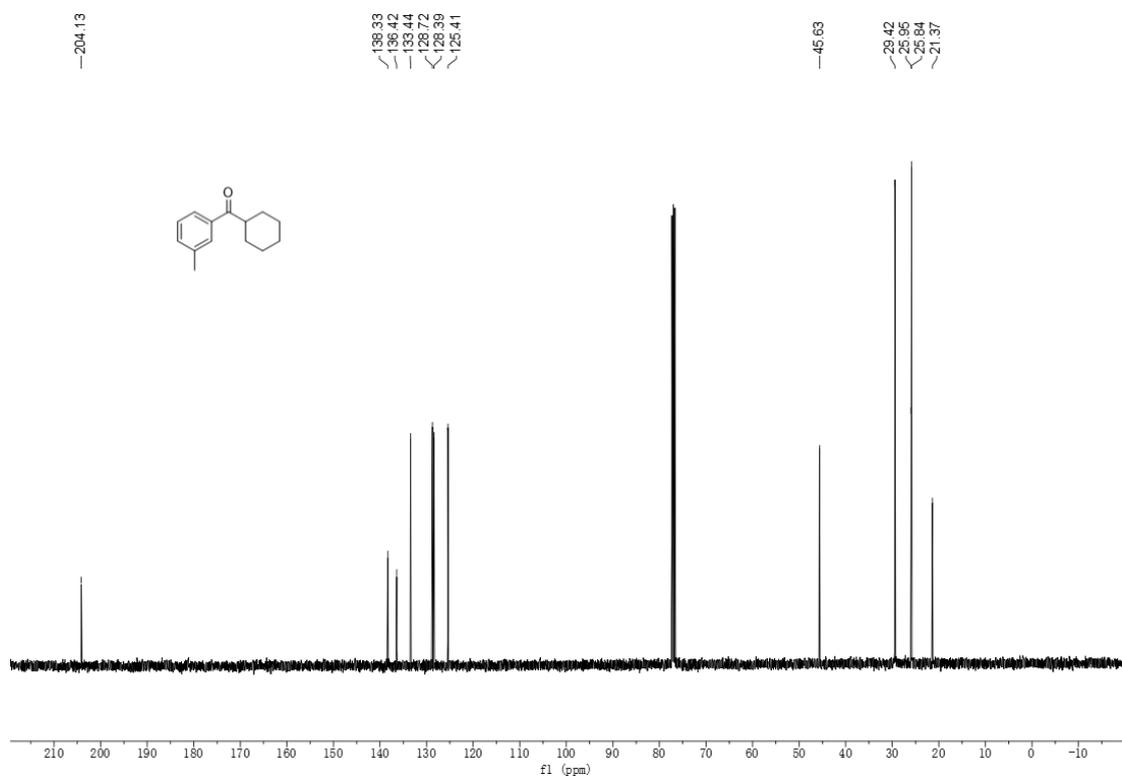
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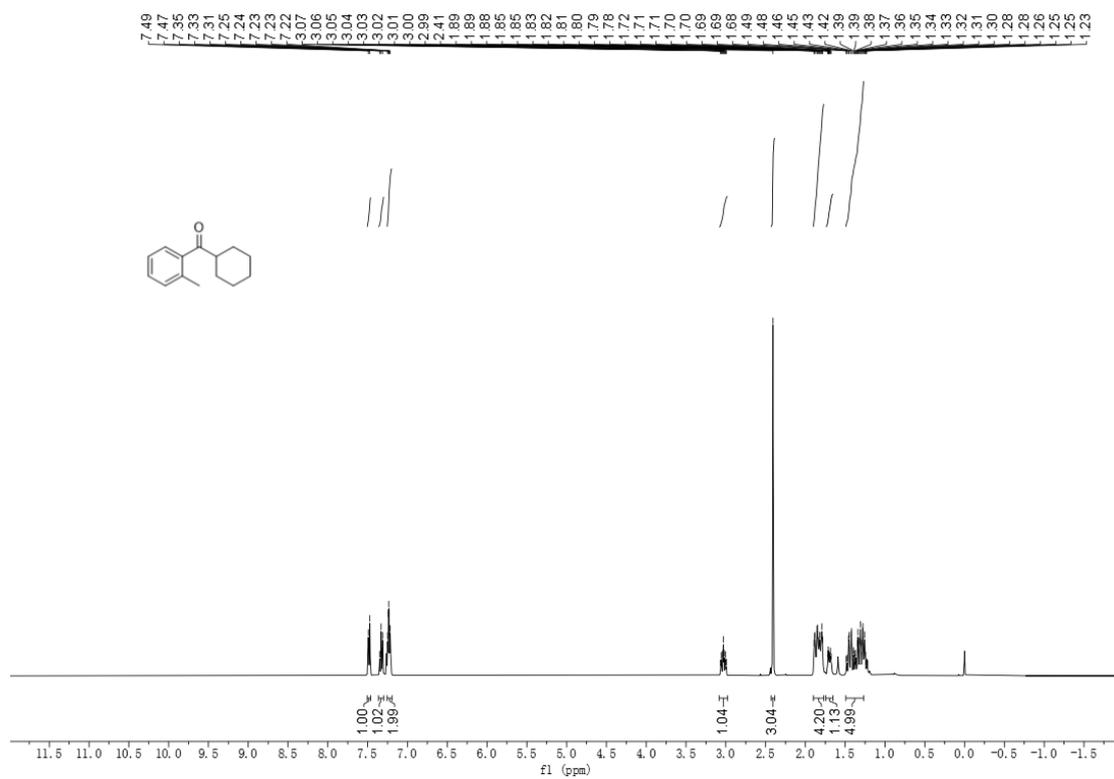
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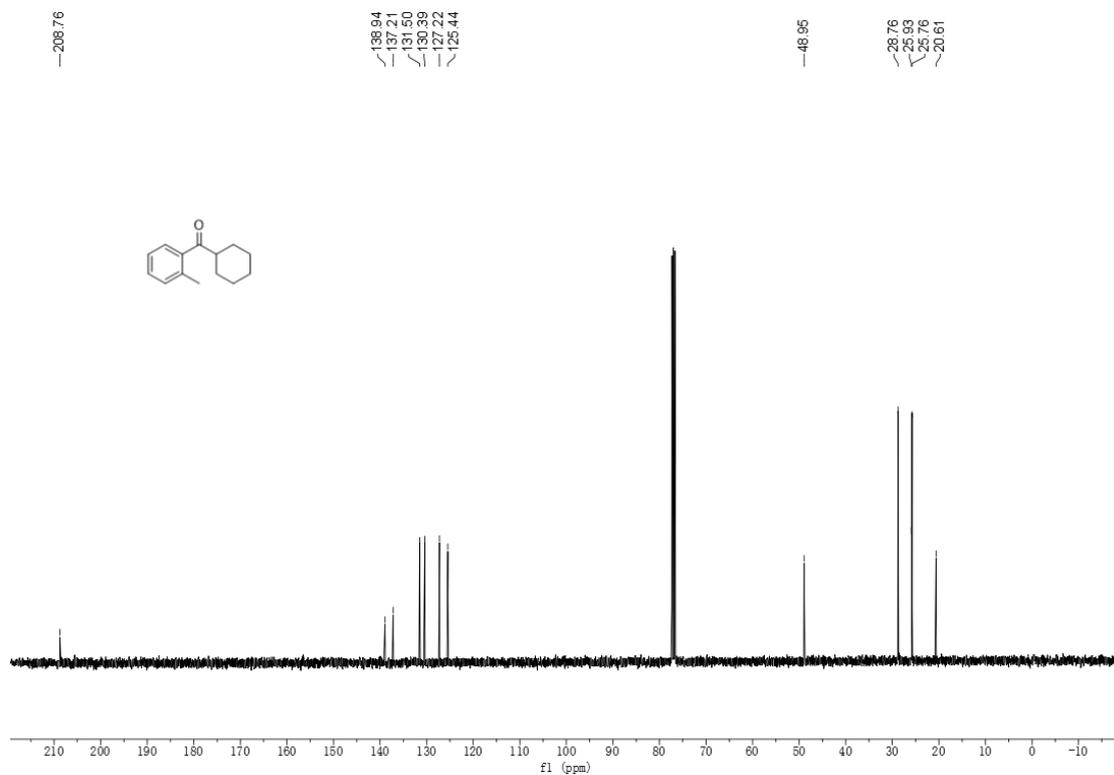
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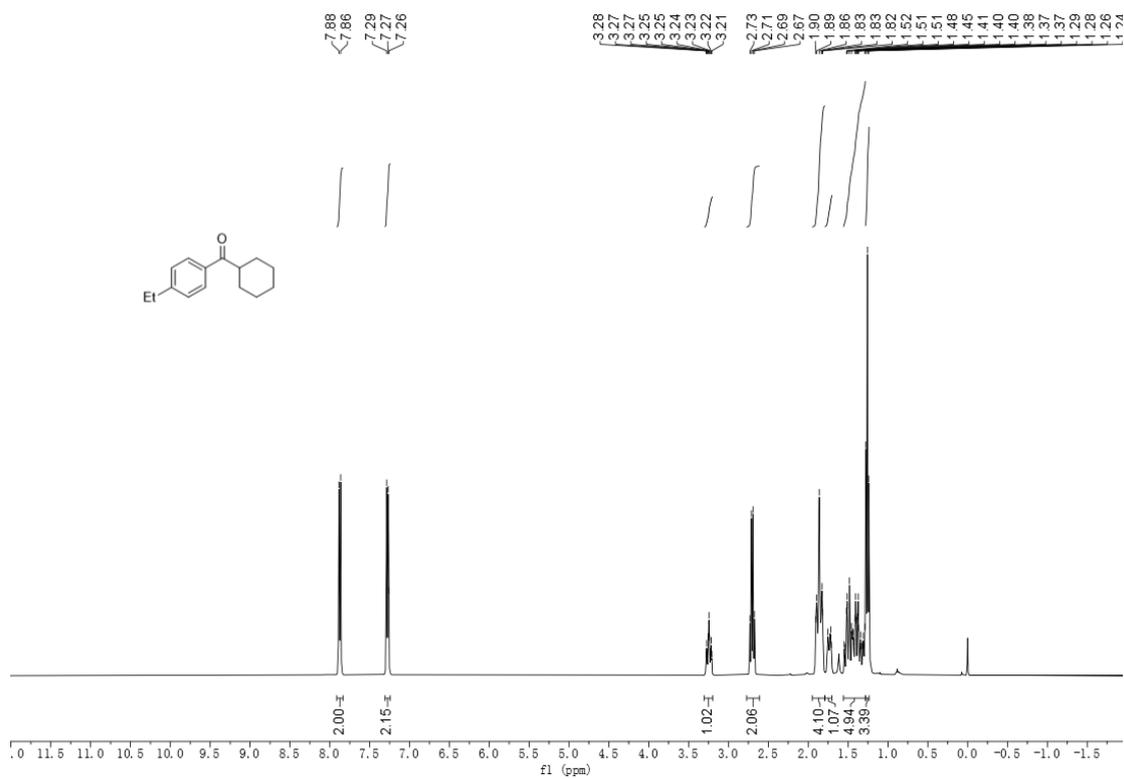
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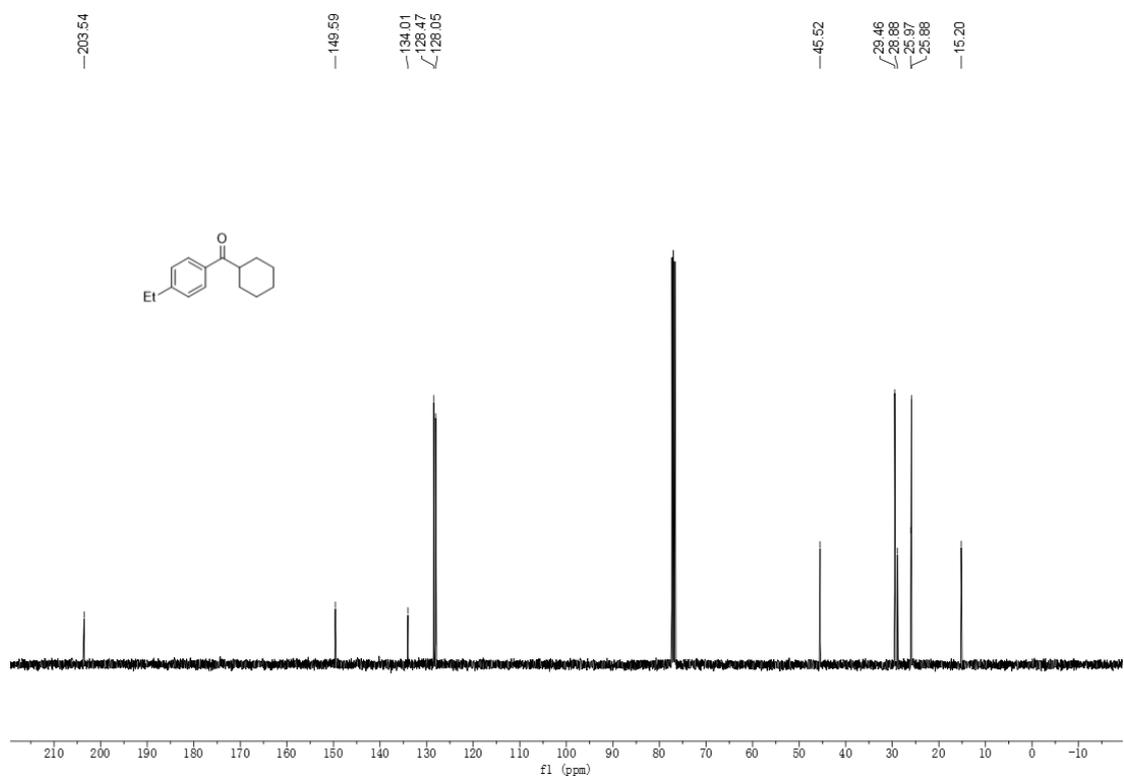
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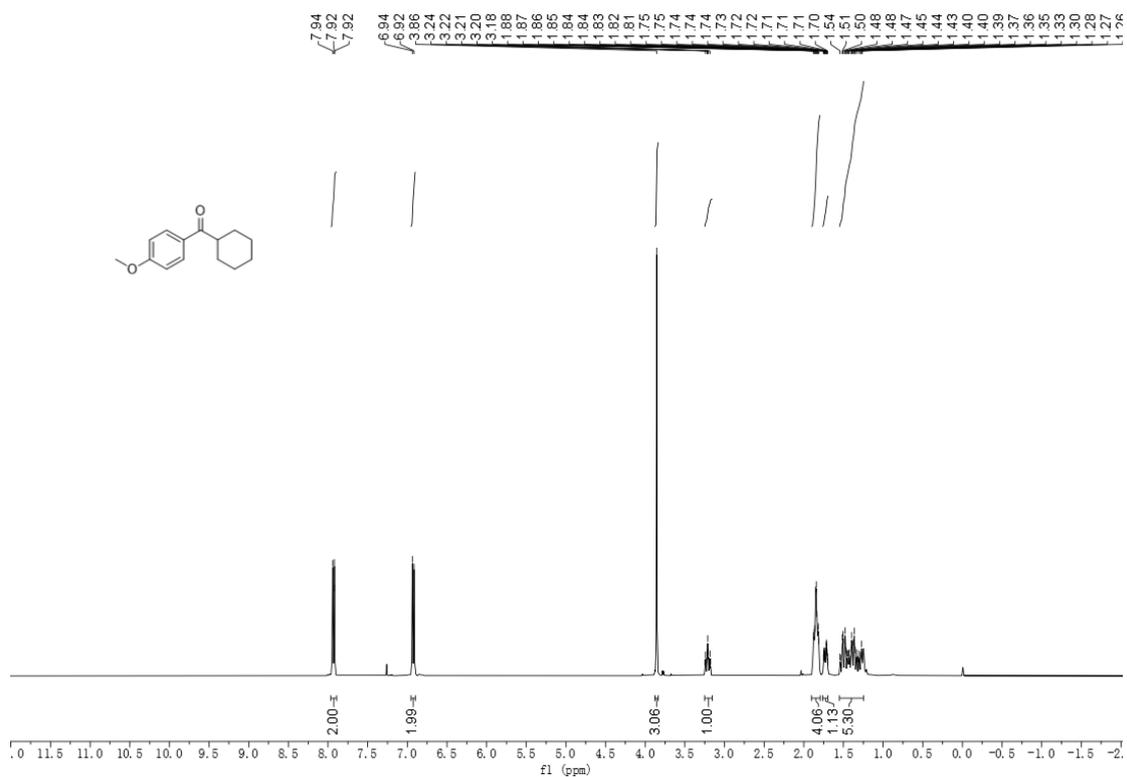
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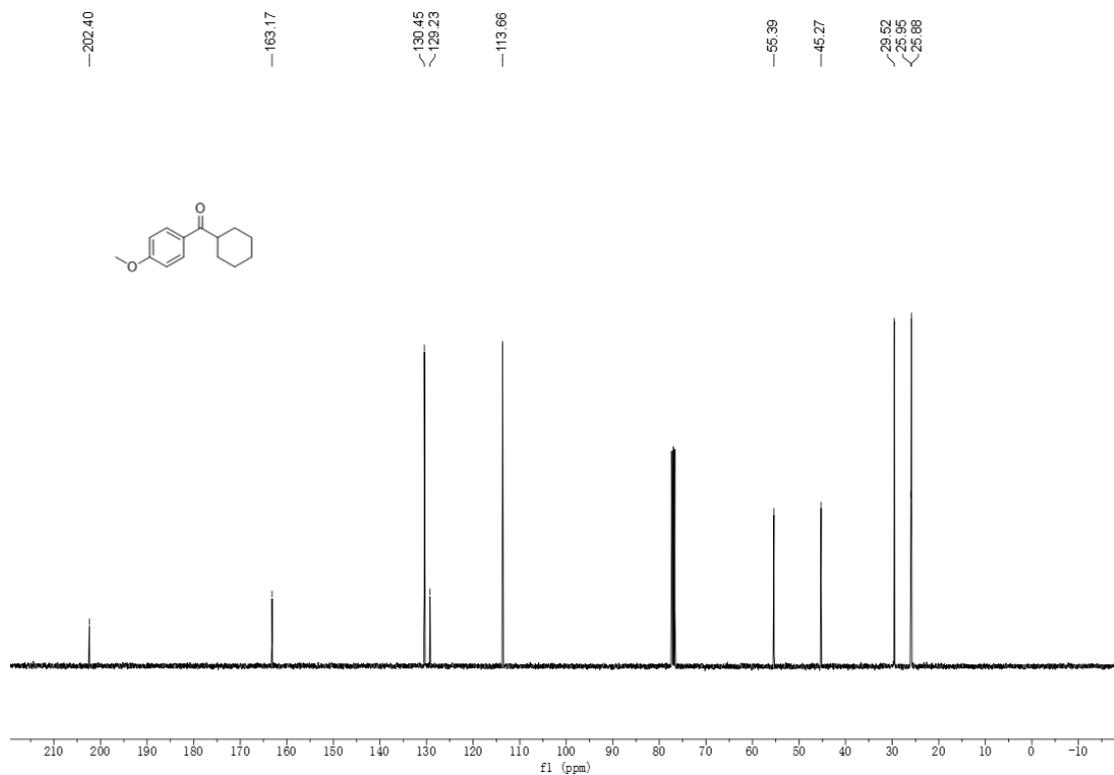
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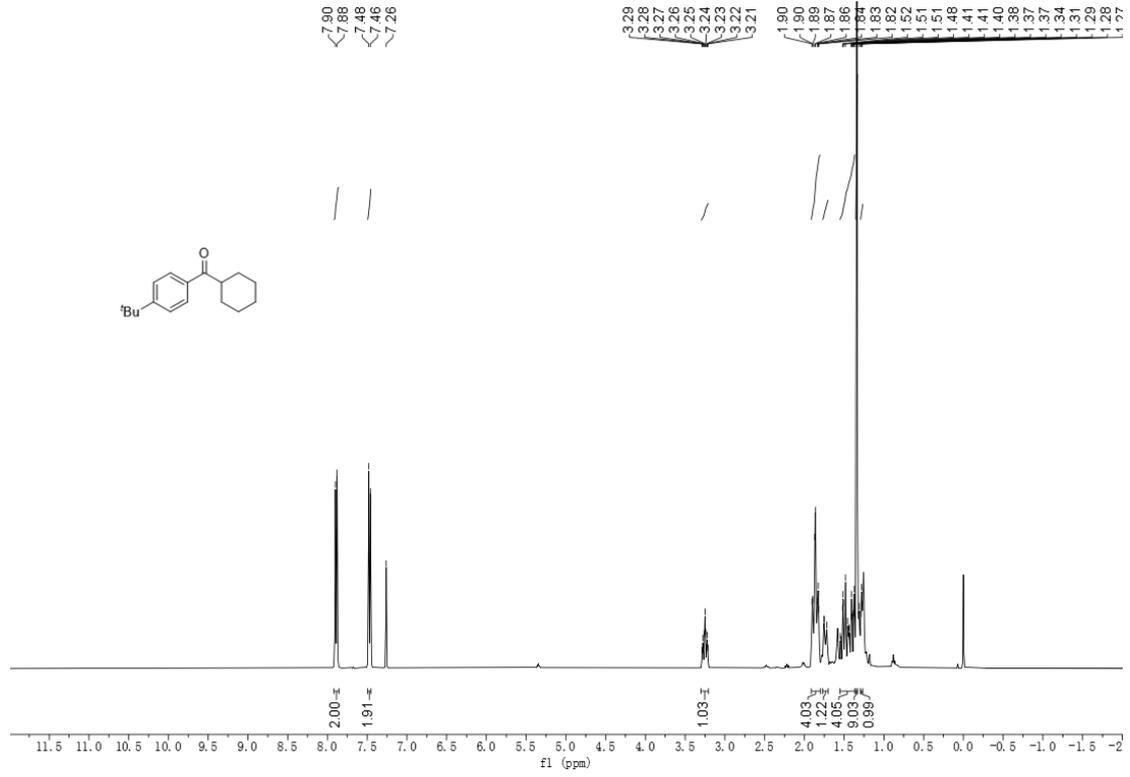
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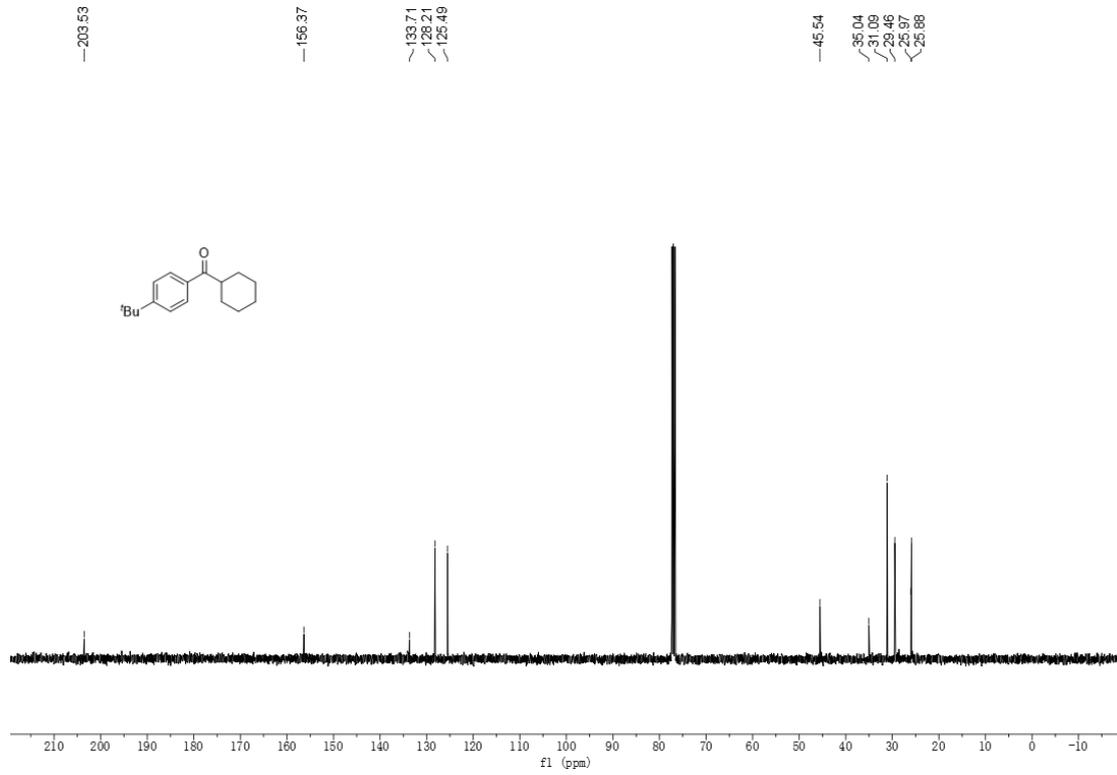
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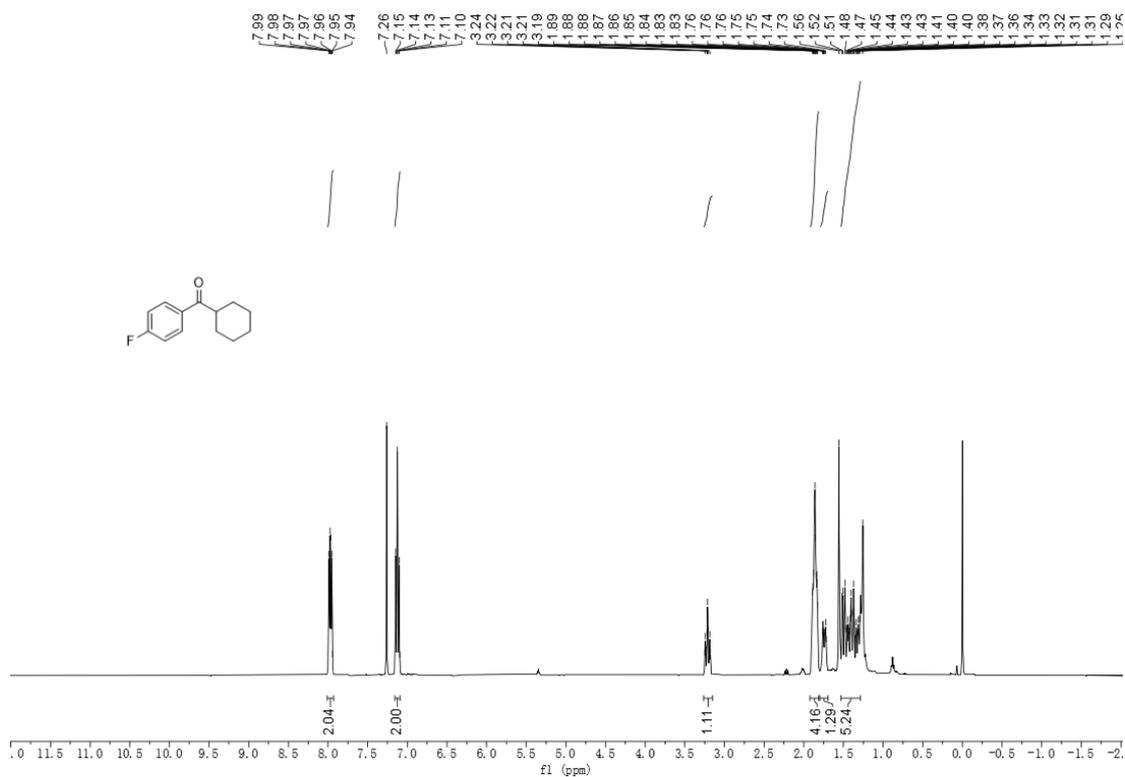
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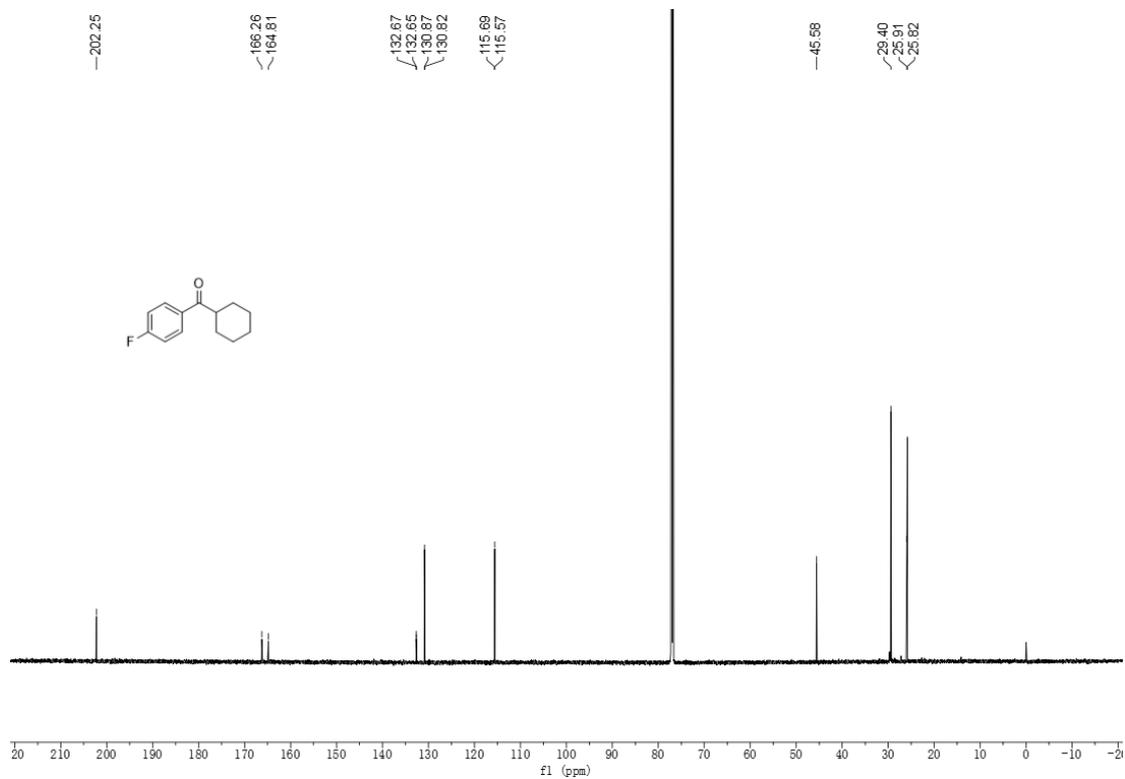
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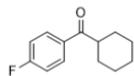
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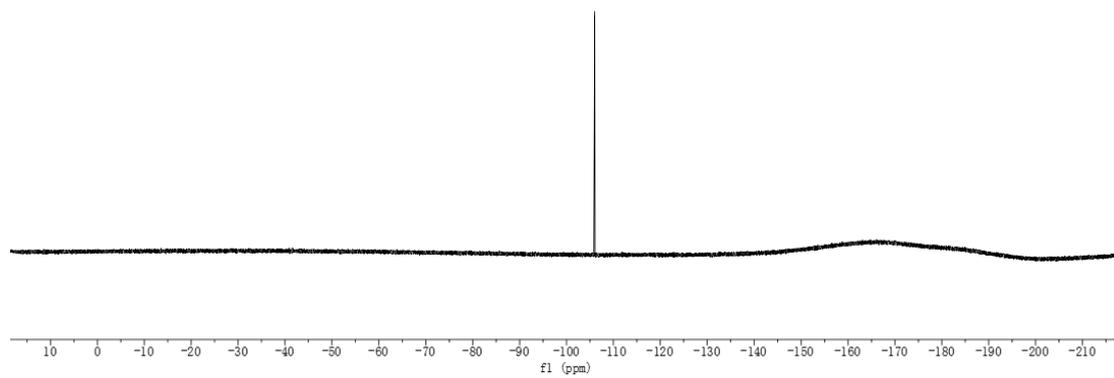
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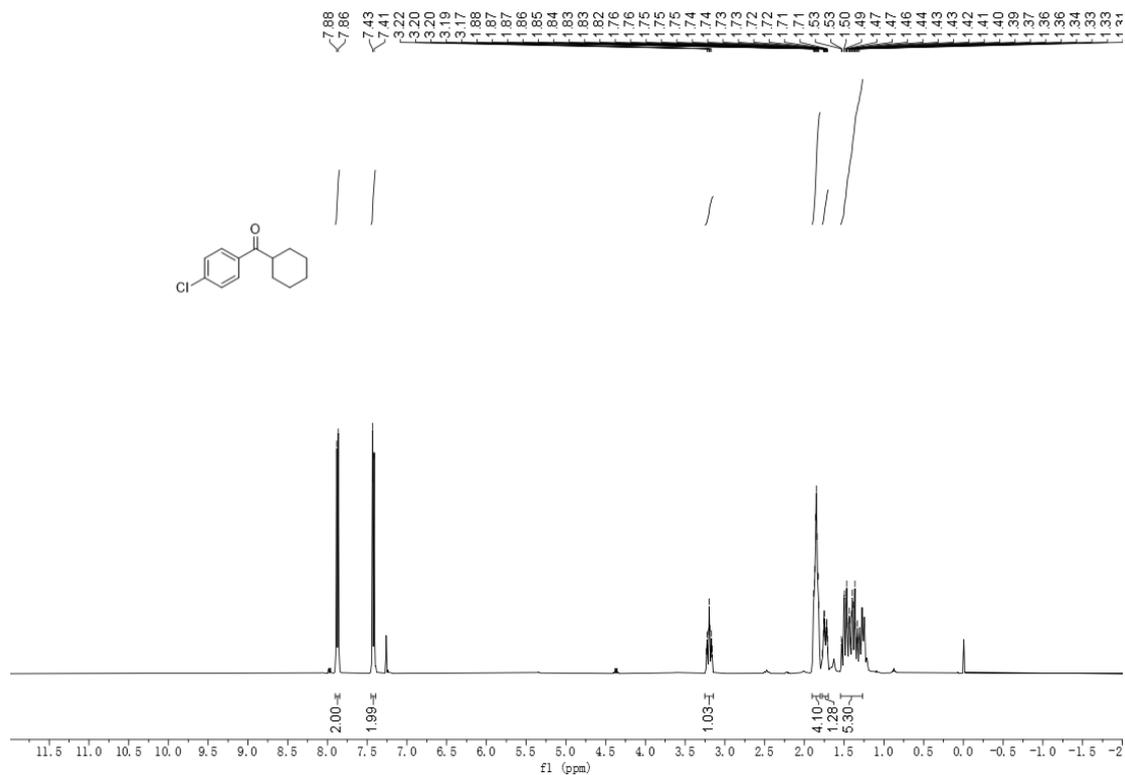
¹⁹F NMR (376 MHz, CDCl₃) (3ha)



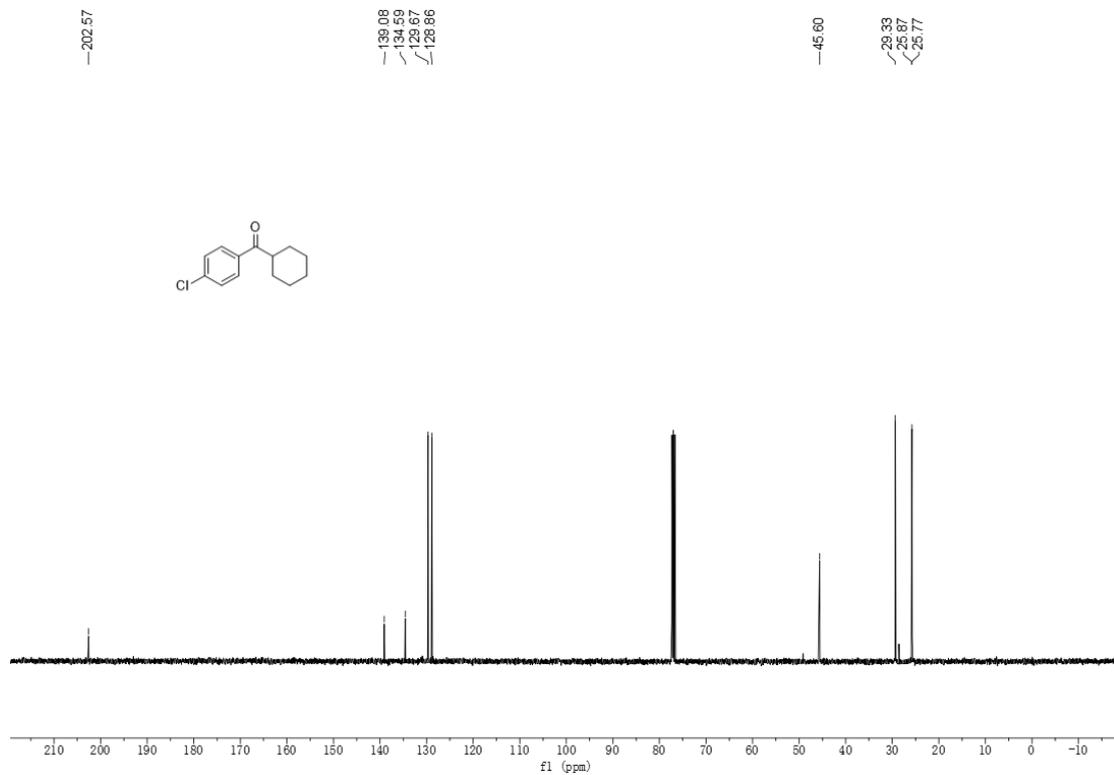
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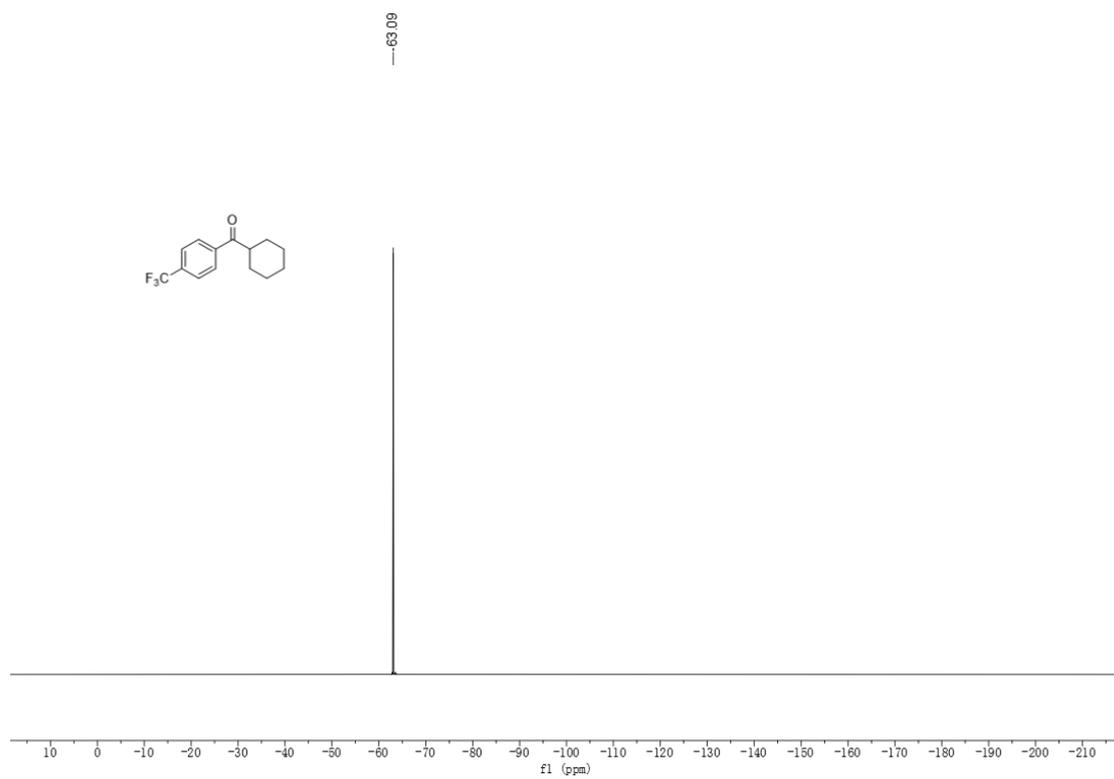
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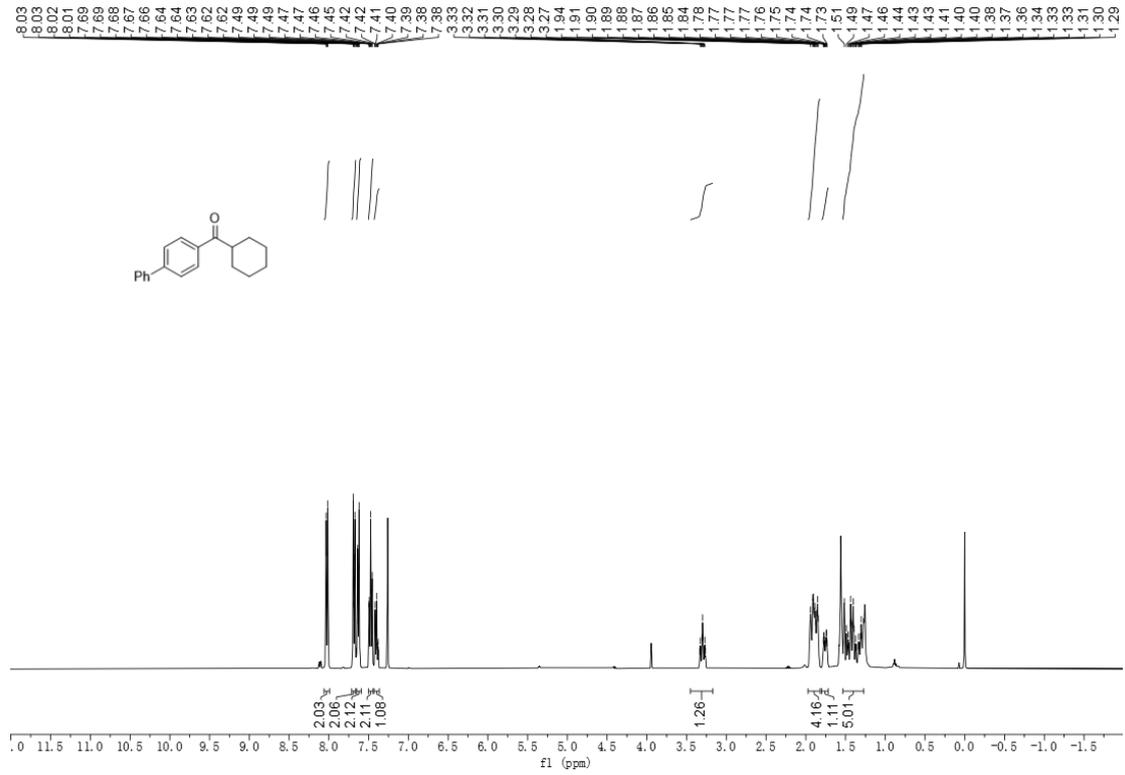
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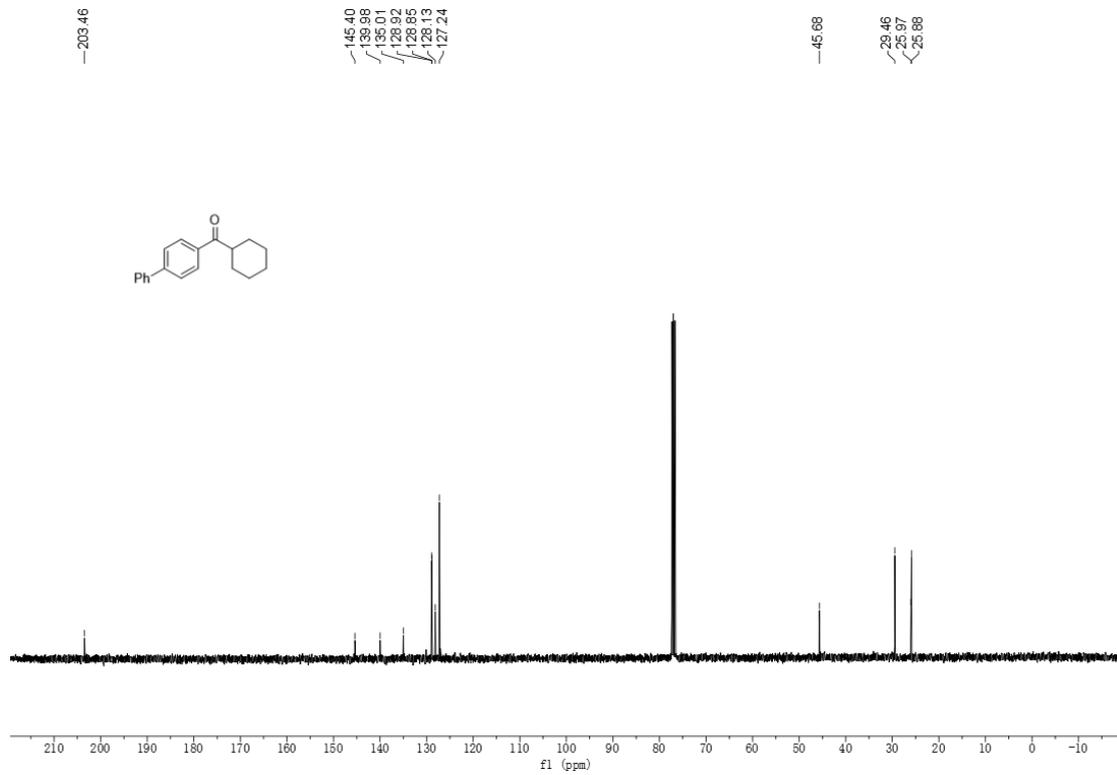
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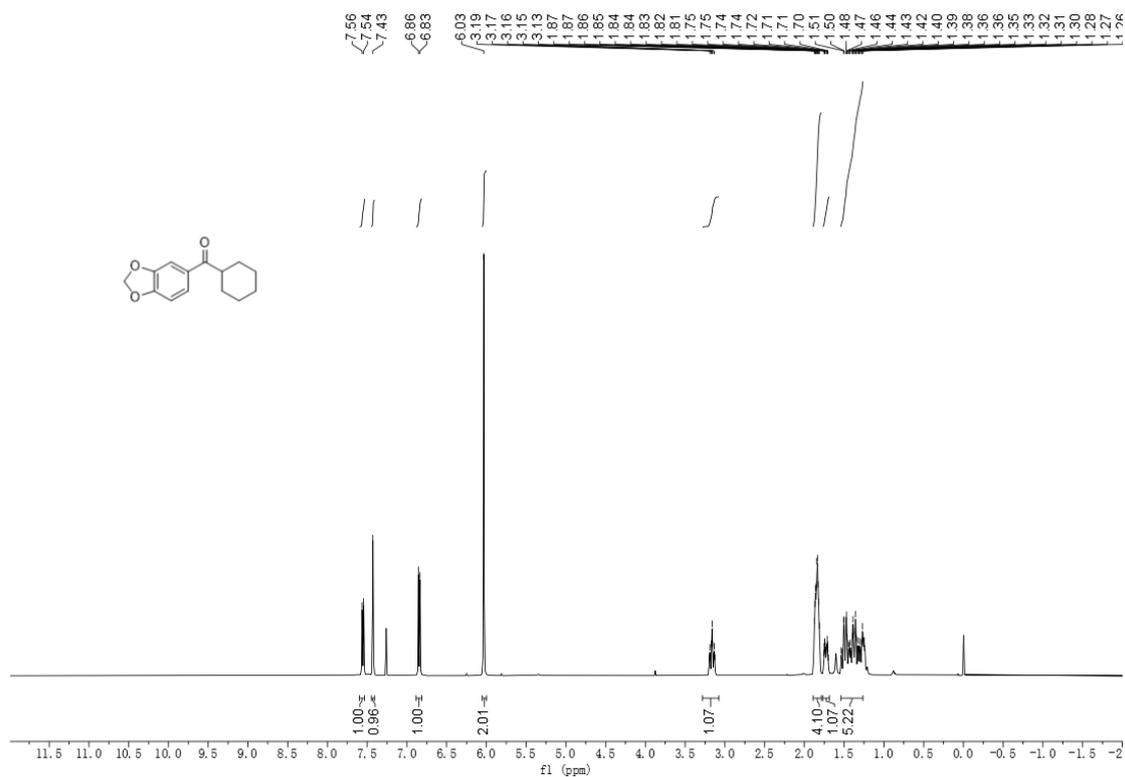
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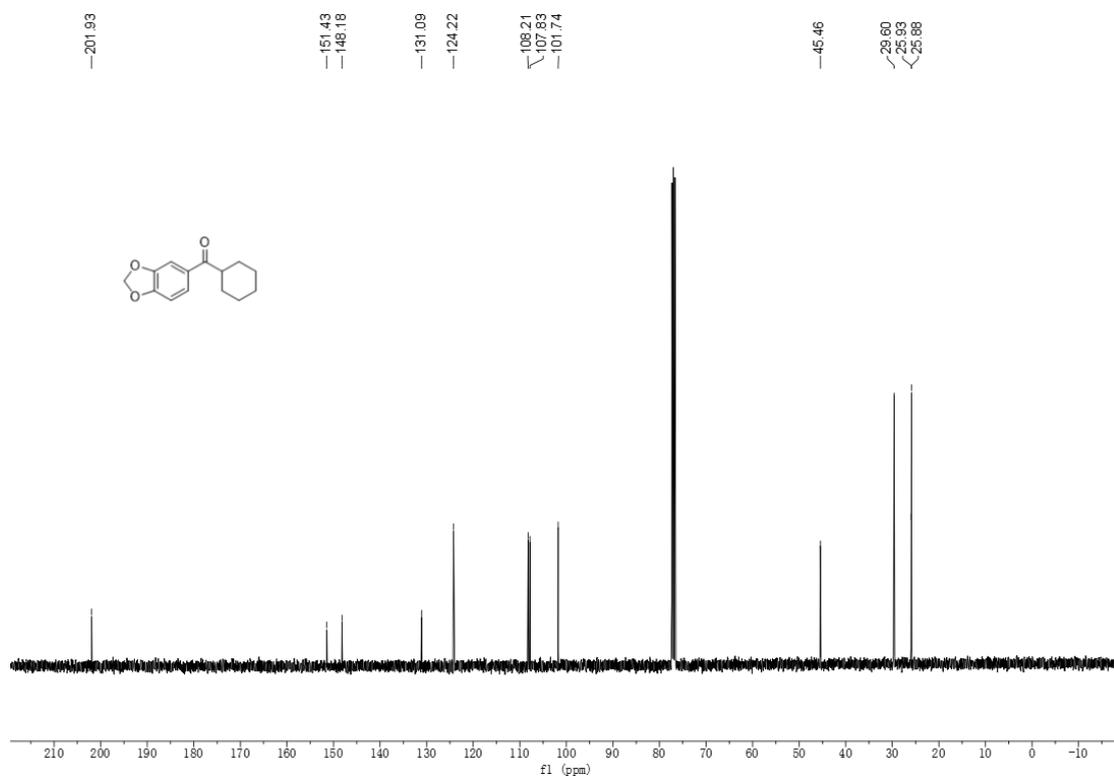
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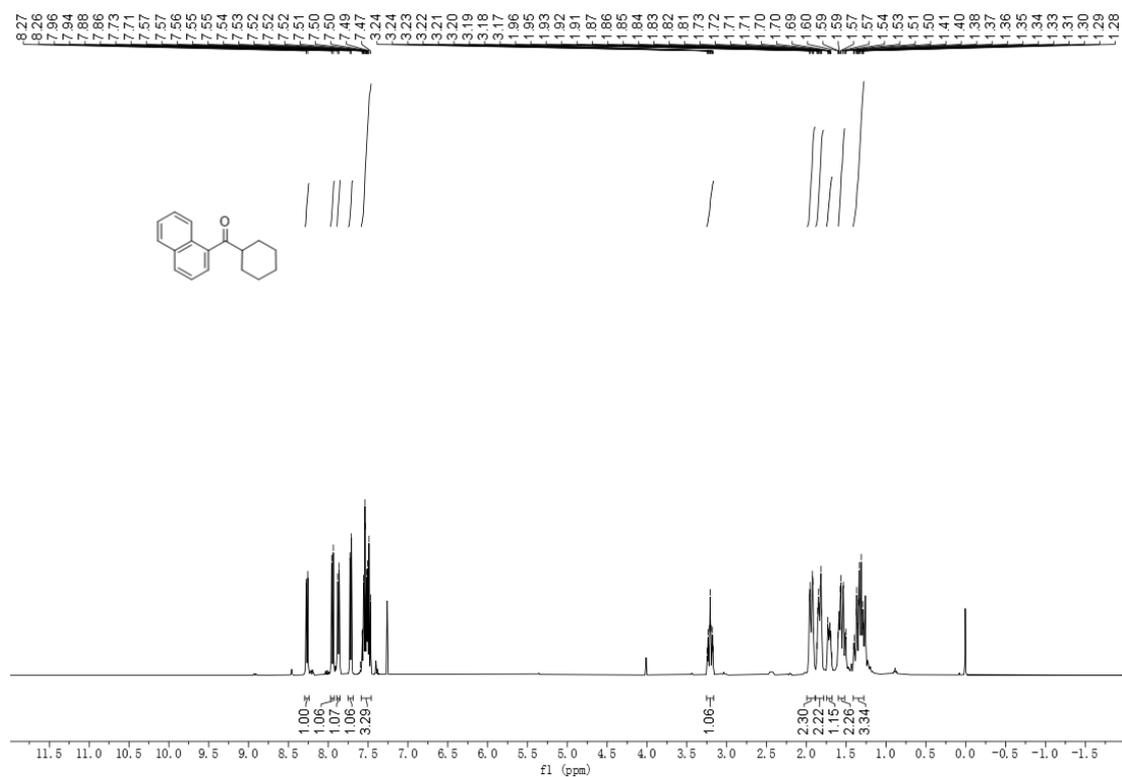
¹H NMR (400 MHz, CDCl₃) (3la)



¹³C NMR (101 MHz, CDCl₃) (3la)



¹H NMR (400 MHz, CDCl₃) (3ma)



¹³C NMR (101 MHz, CDCl₃) (3ma)

