Supporting Information

Carbonate-Assisted Selectively Deoxygenative Cross-Coupling Reaction between Aryl and Aliphatic Aldehydes: A Straightforward Route to Access α-Alkylated Aryl Ketones

Yu Sun,[†] Yi Wang,[†] Zhijun Zuo*

Key Laboratory of Synthetic and Natural Functional Molecule of the Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an 710127, China.

E-mail: zuozj@nwu.edu.cn

[†]These authors contributed this work equally

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A. General information:

All reactions were carried out under nitrogen atmosphere and involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware using standard Schlenk techniques. All reagents were used as received unless otherwise noted. DMSO, DMF, DCM, CCl_4 and MeCN were dried over CaH_2. Benzene, Toluene, cyclohexane, 1,4-dioxane and THF were dried over sodium.

Thin layer chromatography (TLC) was performed with 0.25 m coated commercial silica gel plates (TLC Silica Gel 60 F254) and visualized by fluorescence quenching under UV light (254 nm and 365 nm). Flash chromatography was performed with silica gel (300-400 mesh).

Proton nuclear magnetic resonance (^{1}H NMR) data were acquired on Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; dd, quartet; t, triplet; q, quartet; m, multiple; dd, double doublet. Coupling constants J is quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on Bruker Ascend 400 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for $CDCl_3$-*d* and the center line of a septet at 44.0 ppm for DMSO-d_6. Fluorine nuclear magnetic resonance (^{19}F NMR) data were acquired at 376 MHz on a JEOL ECZ 400 spectrometer.

Mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer.

UV-vis spectra were determined on a Hitachi U-1700 spectrometer.

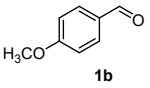
EPR spectra in continuous wave (CW) mode were collected on Bruker ELEXSYS II E 500.

B. Preparation of substrates:

Substrates Preparation:

aryl aldehyde:


1a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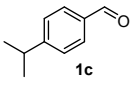
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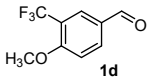
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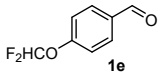
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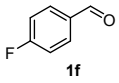
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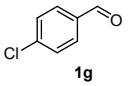
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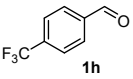
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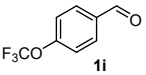
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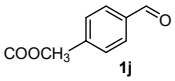
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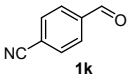
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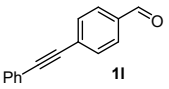
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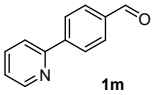
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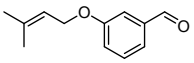
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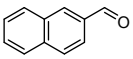
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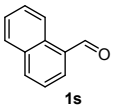
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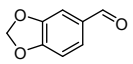
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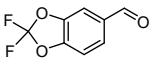
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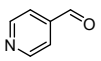
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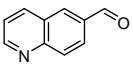
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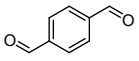
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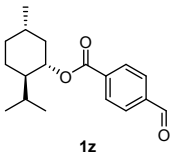
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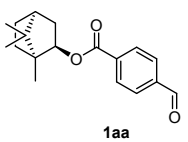
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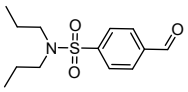
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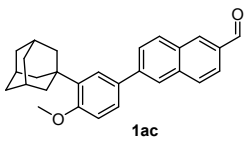
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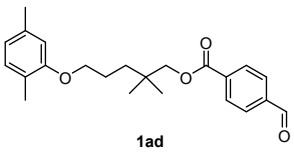
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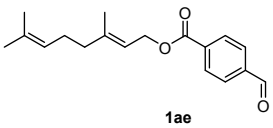
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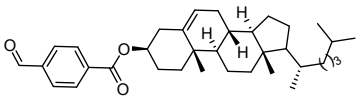
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alkyl aldehyde:


2a

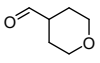

2b


2c


2d


2e


2f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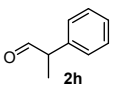

2h

2i

2j

2k

2l

2m

2n

2o

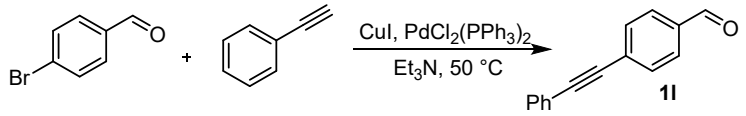
2p

2q

2r

2s

Procedure for preparation of aryl aldehyde 1l:

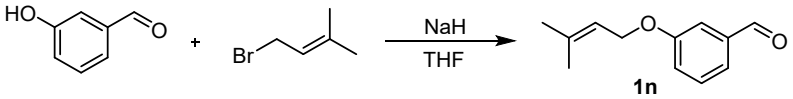


According to the reported literature.[1] In a 50 mL oven-dried round-bottom flask with a stir bar, was added 4-bromobenzaldehyde (5.0 mmol, 1.0 equiv.), $PdCl_2(PPh_3)_2$ (0.25 mmol, 0.05 equiv.) and CuI (0.5 mmol, 0.1 equiv.) in triethylamine (20.0 mL). The phenylacetylene (6.0 mmol, 1.2 equiv.) was then added dropwise to the reaction mixture. The media was stirred overnight at 50 °C. After completion of the reaction, the reaction mixture was solved with ethyl acetate. The filtrate was washed with saturated aqueous NH_4Cl solution until pH of the aqueous phase was neutral. The combined organic phases were washed with brine and dried over Na_2SO_4. After filtration and evaporation to dryness, the crude material was purified by flash chromatography on silica gel to give the titled product **1l**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.38 – 7.35 (m, 3H).

The spectroscopic data correspond to the reported values.[1]

Procedure for preparation of aryl aldehyde 1n:

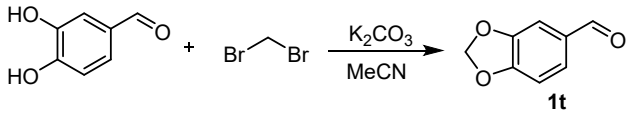


According to the reported literature.[2] In a 50 mL oven-dried round-bottom flask with a stir bar, was added 3'-hydroxyacetophenone (5.0 mmol, 1.0 equiv.) and THF (10.0 mL). The solution was slowly added NaH (7.5 mmol, 1.5 equiv.) open to air at 0 °C. The reaction mixture was allowed naturally to come to room temperature while stirring for 30 minutes. Then 3,3-dimethylallyl bromide (6.0 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was monitored by TLC for completion. On completion, the reaction was quenched with saturated aqueous NH_4Cl, and the aqueous phase extracted with DCM. The combined organic layers were washed with saturated aqueous NaCl and dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The crude material was purified by flash chromatography on silica gel to give the titled product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.47 – 7.36 (m, 3H), 7.23 – 7.13 (m, 1H), 5.53 – 5.44 (m, 1H), 4.56 (d, *J* = 6.9 Hz, 2H), 1.80 (s, 3H), 1.75 (s, 3H).

The spectroscopic data correspond to the reported values.[2]

Procedure for preparation of aryl aldehyde 1t:[3]

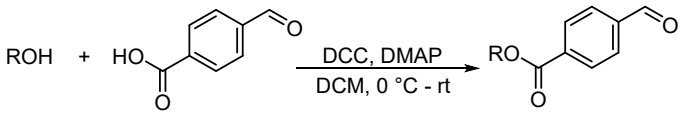


According to the reported literature.[3] In a 50 mL oven-dried round-bottom flask with a stir bar, was added 3,4-dihyroxybenzaldehyde (5.0 mmol, 1.0 equiv.) in dry MeCN. The solution was added potassium carbonate K_2CO_3 (15.0 mmol, 3.0 equiv.) and dibromomethane (6.0 mmol, 1.2 equiv.). The reaction mixture was then stirred at 90 °C for 24 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with water, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated, and the residue purified by column chromatography on silica gel to give the titled product **1t**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.44 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.36 (s, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.10 (s, 2H).

The spectroscopic data correspond to the reported values.[3]

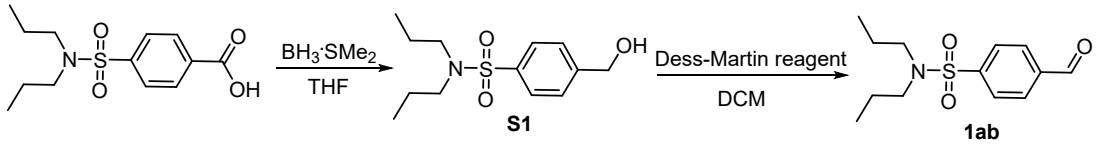
Procedure for preparation of aryl aldehyde 1z-1aa, 1ad-1af:



According to the reported literature.[4] To a stirred solution of 4-formylbenzoic acid (5.0 mmol, 1.0 equiv.), DMAP (0.75 mmol, 0.15 equiv.) and alcohol/phenol (6.0 mmol, 1.2 equiv.) in CH_2Cl_2 (50.0 mL), After DCC (7.5 mmol, 1.5 equiv.) in CH_2Cl_2 (10.0 mL) was added at 0 °C and stirred for 12 h at room temperature. The reaction mixture was then passed through as short pad of celite. The solvent was evaporated and the residue purified by column chromatography on silica gel to give the titled product.

All the spectroscopic datas correspond to the reported values.[4]

Procedure for preparation of aryl aldehyde 1ab:[5]



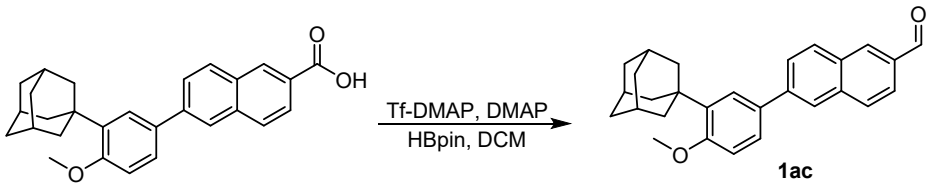
According to the reported literature.[5] Probenecid (5.0 mmol, 1.0 equiv.) was dissolved in THF and $BH_3{\cdot}Me_2S$ (10.0 mmol, 2.0 equiv.) was added dropwise at 0 °C in argon atmosphere. The mixture was stirred at room temperature for 24 h and then quenched with MeOH slowly at 0 °C, washed with saturated NH_4Cl and extracted with EtOAc, dried with Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The residue purified by column chromatography on silica gel to afford corresponding alcohol **S1** in 90% yield.

A 100 mL Schlenk flask was charged with a magnetic agitator, The alcohol above (3.0 mmol, 1.0 equiv.). Then 30.0 mL dry CH_2Cl_2 was added to the mixture. The system was allowed to cool to 0 °C with an ice-water bath, and Dess-Martin reagent (6.0 mmol, 2.0 equiv.) was added in one portion. This reaction was stirred for 12 h after the mixture was slowly warmed to room temperature. After the reaction was finished, 50.0 mL saturated $NaHCO_3$ was added to the mixture and extracted with DCM. The organic phase was collected, dried over Na_2SO_4, and concentrated *in vacuo*. The residue purified by column chromatography on silica gel to give the titled product **1ab**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 3.10-3.06 (m, 4H), 1.58 – 1.45 (m, 4H), 0.83 (t, *J* = 7.4 Hz, 6H).

The spectroscopic data correspond to the reported values.[5]

Procedure for preparation of aryl aldehyde 1ac:[6]



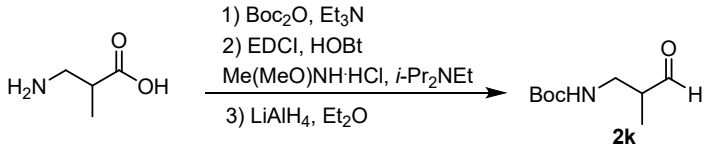
According to the reported literature.[6] To a 50 mL Schlenk tube equipped with a magnetic stirring bar, 6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoic acid (3.0 mmol, 1.0 equiv.), DMAP (4.8 mmol, 1.6 equiv.) and DCM (15.0 mL) were added under a dry nitrogen atmosphere. Then the Tf-DMAP (5.1 mmol, 1.7 equiv.) and HBpin (4.5 mmol, 1.5 equiv.) were added to the reaction mixture.

After the reaction was stirred for 10 min, the crude mixture was quenched by H_2O and extracted by DCM. The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford the desired aldehydes **1ac**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.37 (s, 1H), 8.07 (dd, *J* = 5.0, 3.3 Hz, 2H), 8.00 (s, 2H), 7.87 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.63 (d, *J* = 2.4 Hz, 1H), 7.58 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 2.21 (s, 6H), 2.13 (s, 3H), 1.83 (s, 6H).

The spectroscopic data correspond to the reported values.[6]

Procedure for preparation of aryl aldehyde 2k:[7]



According to the reported literature.[7] In a 50 mL oven-dried round-bottom flask with a stir bar, was added Et_3N (5.5 mmol, 1.1 equiv.), Boc_2O (5.5 mmol, 1.1 equiv.), and DL-3-aminoisobutyric acid (5.0 mmol, 1.0 equiv.) were combined in THF (5.0 mL) and allowed to stir at room temperature for 24 h. The white mixture slowly dissolved into a clear solution. The reaction was diluted with 1 N HCl until acidic (pH <2) and extracted with EtOAc, dried over $MgSO_4$, and concentrated to a white solid. The crude acid was used directly without purification.

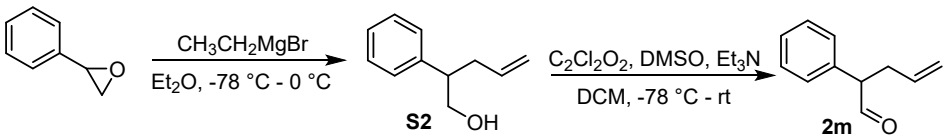
The crude acid (5.0 mmol, 1.0 equiv.), EDCI (5.5 mmol, 1.1 equiv.), and HOBt (5.5 mmol, 1.1 equiv.) were combined in CH_2Cl_2 (10.0 mL) and stirred 15 min before cooling to 0 °C and adding a previously made solution of Me(MeO)NH•HCl (7.5 mmol, 1.5 equiv.) and *i*-Pr_2NEt (7.5 mmol, 1.5 equiv.) in CH_2Cl_2 (5.0 mL). The combined solution was allowed to warm to room temperature and stir for 18 h before quenching with 1 N HCl (pH <2). The mixture was diluted with EtOAc and subsequently washed with 1 N HCl, saturated $NaHCO_3$, H_2O, and brine before drying over $MgSO_4$. Concentration gave a colorless oil. The crude acid was used directly without purification.

$LiAlH_4$ (3.15 mmol, 1.05 equiv.) was added in one portion to the crude amide (3.0 mmol, 1.0 equiv.) dissolved in Et_2O (20.0 mL) at -10 °C. After 2 h the reaction was quenched with MeOH (1.0 mL) and 1 M Rochelles salt (5.0 mL) at 0 °C. The reaction was allowed to stir at room temperature for 1 h before extracting with Et_2O, drying over $MgSO_4$, and concentrating. The residue purified by column chromatography on silica gel to give the titled product **2k** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 4.95 (s, 1H), 3.40 – 3.23 (m, 2H), 2.69 – 2.56 (m, 1H), 1.42 (s, 9H), 1.14 (d, *J* = 7.4 Hz, 3H).

The spectroscopic data correspond to the reported values.[7]

Procedure for preparation of aryl aldehyde 2m:[8]



According to the reported literature.[8] Under an N_2 atmosphere, a flame-dried flask equipped with a stir bar was charged with styrene oxide (5.0 mmol, 1.0 equiv.) and Et_2O (25.0 mL). The solution was cooled to -78 °C, and a 1.0 M allylmagnesium bromide solution in Et_2O (6.5 mmol, 1.3 equiv.) was slowly added via syringe over 10 min. The reaction mixture was warmed to 0 °C and stirred for 2 h. The reaction was quenched with saturated NH_4Cl (aq). The organic phase was washed with water, dried over $MgSO_4$, and

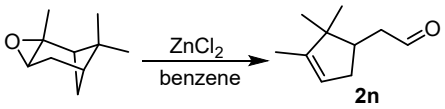
filtered. The filtrate was concentrated to dryness under reduced pressure, and the crude material was purified by column chromatography on silica gel to give the titled product **S2** as a colorless oil.

To a stirred solution of the corresponding alcohol **S2** (3.0 mmol, 1.0 equiv.) in DCM (2.5 mL/mmol) at 0 ºC and under inert atmosphere DMP (3.3 mmol, 1.1 equiv.) was added in one portion. The reaction mixture was allowed to warm up to room temperature and stirred until reaction completion (followed by TLC). Then, the reaction was quenched with saturated $Na_2S_2O_3$ and saturated $NaHCO_3$. The mixture was extracted with DCM and the organic layers were collected, washed with H_2O and brine, dried over $MgSO_4$ and evaporated under reduced pressure. The resulting crude was purified by flash column chromatography on silica gel to give the titled product **2m** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 1.7 Hz, 1H), 7.43 – 7.27 (m, 3H), 7.23 – 7.16 (m, 2H), 5.78 – 5.65 (m, 1H), 5.11 – 4.96 (m, 2H), 3.71 – 3.50 (m, 1 H), 2.85 – 2.49 (m, 2H).

The spectroscopic data correspond to the reported values.[8]

Procedure for preparation of aryl aldehyde 2n:[9]



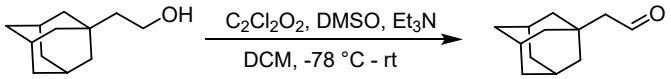
2n

According to the reported literature.[9] Freshly dried $ZnCl_2$ (10.0 mol%) was added to a solution of α-Pinene oxide (5.0 mmol, 1.0 equiv.) in 5.0 mL of dry benzene. The reaction mixture was stirred for 2 h at room temperature. Then CH_3COOH (0.3 mL) and H_2O (0.3 mL) were added. The organic phase was dried over Na_2SO_4, the drying agent was filtered off and the solvent was removed. The resulting crude was purified by flash column chromatography on silica gel to give the titled product **2n** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 5.24 (s, 1H), 2.55 – 2.47 (m, 1H), 2.43 – 2.36 (m, 2H), 2.32 – 2.24 (m, 1H), 1.93 – 1.87 (m, 1H), 1.62 (s, 3H), 1.01 (s, 3H), 0.80 (s, 3H)

The spectroscopic data correspond to the reported values.[9]

Procedure for preparation of aryl aldehyde 2p:[10]



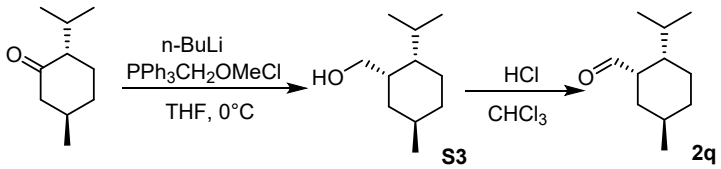
2p

According to the reported literature.[10] A 100 mL flask was charged with oxalyl chloride (6.0 mmol, 1.2 equiv.) and dry DCM (20.0 mL) under argon. After the mixture was cooled to -78 °C, a solution of tricyclo[3.3.1.13,7]decaneethanol (5.0 mmol, 1.0 equiv.) and dimethyl sulfoxide (11.0 mmol, 2.2 equiv.) in dry DCM (5.0 mL) was added in 1 h by syringe pump . The reaction was stirred at -78 °C for 15 min. Triethylamine (25.0 mmol, 5.0 equiv.) was added, and the reaction was warmed to room temperature and stirred for 2 h. The reaction was quenched with water and extracted with DCM. The combined organic layer was washed with 1 M HCl, water, $NaHCO_3$, and brine, dried over anhydrous Na_2SO_4, and resulting crude was purified by flash column chromatography on silica gel to give the titled product **2p** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 2.11 (d, *J* = 3.3 Hz, 2H), 2.01 – 1.94 (m, 3H), 1.76 – 1.61 (m, 12H).

The spectroscopic data correspond to the reported values.[10]

Procedure for preparation of aryl aldehyde 2q:[11]

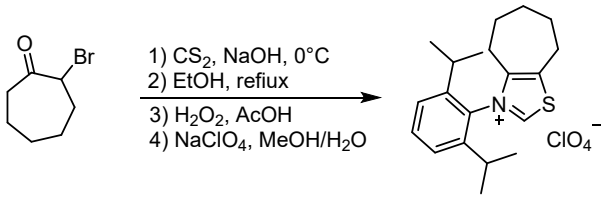


According to the reported literature.[11] To a suspension of (methoxymethyl)triphenylphosphonium chloride (5.0 mmol, 1.0 equiv.) in 20.0 mL of dry THF, cooled to 0 °C, was added a 2 M solution of *n*-BuLi (7.5 mmol, 1.5 equiv.) in hexanes via syringe over 10 min. The red solution was stirred 30 min at 0 °C and (-)-menthone (5.0 mmol, 1.0 equiv.) was added over 5 min., dried over anhydrous magnesium sulfate and concentrated partially under reduced pressure. The residue was filtered to remove the solid triphenyl phosphine oxide **S3** and the filtrate was concentrated under reduced pressure. The enol ether obtained was then dissolved in 20.0 mL of chloroform and 3.0 mL of 12 N HCl was added. The solution was stirred 4 h at room temperature and the chloroform was evaporated. Diethyl ether and water were added and the aqueous phase was extracted with diethyl ether and the combined organic layers were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography on silica gel to give the titled product **2q**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, 1H, *J* = 4.3 Hz), 2.24 – 2.15 (m, 1H), 1.82 – 1.63 (m, 4H), 1.54 – 1.48 (m, 1H), 1.47 – 1.26 (m, 2H), 1.17 – 0.88 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 6H), 0.80 (d, *J* = 7.5 Hz, 3H).

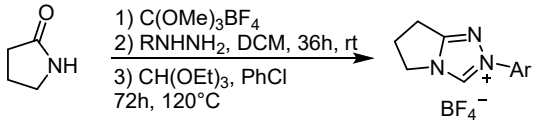
The spectroscopic data correspond to the reported values.[11]

Preparation of NHC catalyst



According to the reported literature.[12] A solution of the 2,6-diisopropylaniline (10.0 mmol) in DMSO (0.50 mL/mmol) was treated with 20 N aq. NaOH solution (1.0 equiv.). At 0 °C CS_2 (1.0 equiv.) was added dropwise and stirred for 1 h at room temperature. The ketone (1.0 equiv.) was added 0 °C and the mixture was stirred for 1-3 h at room temperature. H_2O (1 mL/mmol) was added, the mixture was stirred for 10 - 20 min at 0 °C and the supernatant solution was decanted three times. The resulting slurry was suspended in EtOH (1 mL/mmol), concd. HCl (0.05 mL/mmol) was added and the mixture was heated to reflux for 1 h. After cooling to room temperature, the resulting precipitate was collected by suction filtration and was washed with cold EtOH (3 × 20 mL). The crystallization afforded the 3-(2,6-diisopropylphenyl)- 3,4,5,6,7,8-hexahydro-2H-cyclohepta[d]thiazole-2-thione as a white solid. 3-(2,6-diisopropylphenyl)- 3,4,5,6,7,8-hexahydro-2H-cyclohepta[d]thiazole-2-thione and H_2O_2 (3.3 equiv., 30%) in glacial acetic acid were reacted. After 1 h the volatiles were removed, the residue was dissolved in MeOH and a solution of sodium perchlorate monohydrate (4.12 equiv.) in MeOH/H_2O = 2:1 was added at room temperature. After stirring for 10 min, the volume of the solvent was reduced to the half. The solid was collected by suction filtration and was washed with H_2O. The following recrystallisation with MeOH afforded the **NHC 1** as a colorless solid (2.8 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 3.28 – 3.13 (m, 2H), 2.68 – 2.51 (m, 2H), 2.13 – 2.04 (m, 2H), 2.01 – 1.89 (m, 4H), 1.75 – 1.61 (m, 2H), 1.20 (dd, *J* = 6.8, 4.4 Hz, 12H). Spectroscopic data are in accordance with those described in literature.[12]

NHC catalysts **1** were obtained from suppliers.

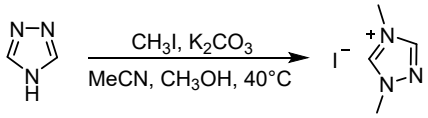


According to the reported literature,[13] to a stirred solution of pyrrolidin-2-one (0.463 mL, 6.00 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (25.0 mL) was added trimethyloxonium tetrafluoroborate (905 g, 6.12 mmol, 1.02 equiv.) and the mixture stirred at room temperature for 18 hours. Then, the corresponding hydrazine (1.02 equiv.) was added to the reaction mixture and the resulting orange solution was stirred for additional 18 h at room temperature. The mixture was then concentrated *in vacuo* and EtOAc (50.0 mL) was added. The solid was collected by filtration, washed with EtOAc and then dried under vacuum to give the hydrazone as an of white solid. To the hydrazone was added chlorobenzene (10.0 mL) and triethylorthoformate (2.49 mL, 15.0 mmol) and the reaction mixture was heated at 120 °C for 72 h. The mixture was concentrated *in vacuo* and EtOAc (30.0 mL) was added. Then the solid was collected by filtration, washed with EtOAc and dried under vacuum to obtain NHC catalyst **2-4**.

2-Mesityl-6,7-dihydro-5Hpyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate (**NHC 2**) as a an off-white solid. (910 mg, 48% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 6.96 (s, 2H), 4.73 – 4.49 (m, 2H), 3.21 (t, *J* = 7.7 Hz, 2H), 2.85 (p, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.04 (s, 6H). Spectroscopic data are in accordance with those described in literature.[13]

2-Phenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate (**NHC 3**) as an off-white solid. (730 mg, 44% yield). ^{1}H NMR (400 MHz, DMSO) δ 10.69 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.47 – 7.40 (m, 1H), 4.42 (t, *J* = 7.4 Hz, 2H), 3.22 (t, *J* = 7.7 Hz, 2H), 2.76 (p, *J* = 7.6 Hz, 2H). Spectroscopic data are in accordance with those described in literature.[13]

2-(Perfluorophenyl)-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate (**NHC 4**) as an orange solid (850 mg, 51% yield). ^{1}H NMR (400 MHz, DMSO) δ 10.62 (s, 1H), 4.40 (t, *J* = 6.0 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H), 3.20 – 2.72 (m, 2H). Spectroscopic data are in accordance with those described in literature.[13]

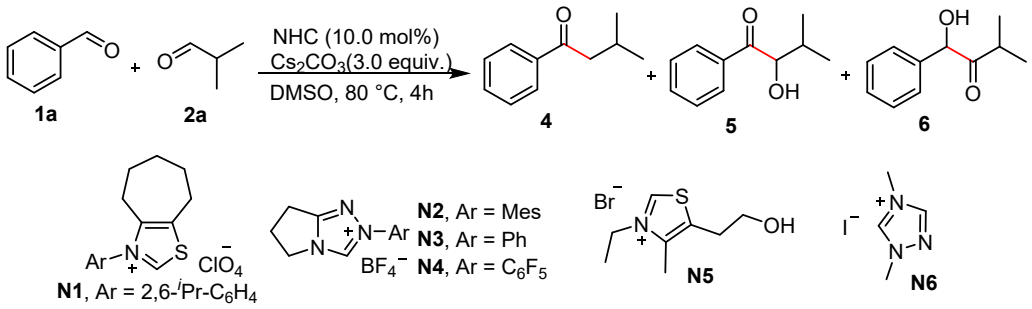


According to the reported literature.[14] A mixture of 1,2,4-triazole (1.0 g, 14.5 mmol, 1.0 equiv.), iodomethane (6.2 g, 43.5 mmol, 3.0 equiv.), and potassium carbonate (3.0 g, 21.7 mmol, 1.5 equiv.) in acetonitrile (8.0 mL) and methanol (2.0 mL) was heated at 40 °C for 3 days. The white mixture was filtered with a Buckner funnel, and the white solid was washed with CH_2Cl_2. The filtrate was concentrated to give 2,4-dimethyl-1,2,4-triazolium iodide **NHC 6** as a brown solid (3.28 g, 100%).

^{1}H NMR (400 MHz, DMSO) δ 9.95 (s, 1H), 9.08 (s, 1H), 4.02 (s, 3H), 3.84 (s, 3H). Spectroscopic data are in accordance with those described in literature.[14]

C. Optimization of reaction conditions:

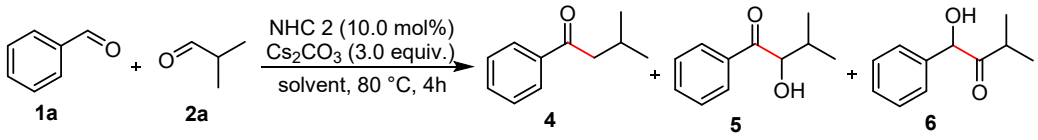
Screening of NHC



Entry	NHC	Yield (%) for **4/5/6**[a]
1	NHC 1	trace/trace/trace
2	NHC 2	89/trace/trace
3	NHC 3	trace/trace/trace
4	NHC 4	trace/trace/trace
5	NHC 5	trace/trace/trace
6	NHC 6	trace/trace/trace

[a] Yield was determined by ^{1}H NMR of the crude mixture of the reaction using dibromomethane as internal standard.

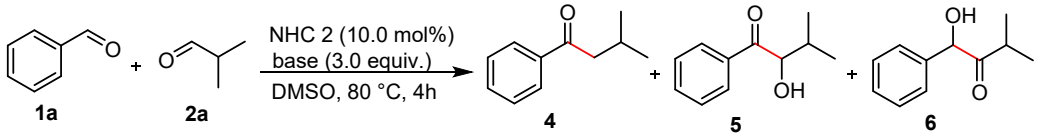
Screening of solvent



Entry	Solvent	Yield (%) for **4/5/6**[a]
1	DMSO	89/trace/trace
2	DMF	47/20/20
3	DCM	25/46/21
4	MeCN	29/22/14
5	THF	37/30/22
6	Toluene	26/45/23
7	Cyclohexane	19/51/25
8	CCl_4	trace/trace/trace
9	Benzene	trace/trace/trace

[a] Yield was determined by ^{1}H NMR of the crude mixture of the reaction using dibromomethane as internal standard.

Screening of base

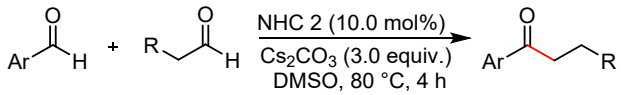


Entry	Base	Yield (%) for **4/5/6**[a]
1	Cs_2CO_3	89/trace/trace
2	Cs_2CO_3 (99.995%)	86/trace/trace
3	K_2CO_3	31/35/30
4	Na_2CO_3	20/43/34
5	Rb_2CO_3	43/32/21
6	$NaHCO_3$	trace/55/42
7	KOH	trace/trace/trace
8	K_3PO_4	trace/48/33
9	Na_3PO_4	trace/51/47
10	KOAc	trace/55/40
11	DBU	trace/51/44
12	Et_3N	trace/trace/trace

[a] Yield was determined by ^{1}H NMR of the crude mixture of the reaction using dibromomethane as internal standard.

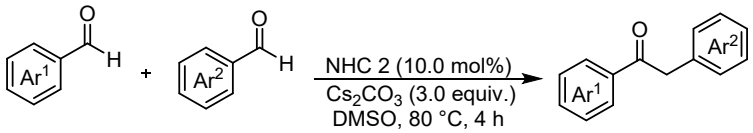
D. Catalytic results:

General procedure A:



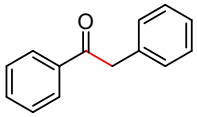
To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, were added NHC 2 (6.9 mg, 10.0 mol%) and Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After aryl aldehyde (0.2 mmol, 1.0 equiv.), alkyl aldehyde (0.6 mmol, 3.0 equiv.) and anhydrous DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography to afford the desired product.

General procedure B:



To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, were added NHC 2 (6.9 mg, 10.0 mol%) and Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After aryl aldehyde 1 (0.2 mmol, 1.0 equiv.), aryl aldehyde 2 (0.3 mmol, 1.5 equiv.) and anhydrous DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room

temperature and filtered, then quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography to afford the desired product.



1,2-diphenylethan-1-one (3)

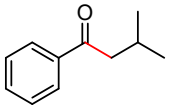
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

White solid (8.2 mg, 21% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.61 – 7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 3H), 4.32 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 136.6, 134.5, 133.2, 129.5, 128.8, 128.7, 128.6, 126.9, 45.5.

The spectroscopic data correspond to the reported values.[15]



3-methyl-1-phenylbutan-1-one (4)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

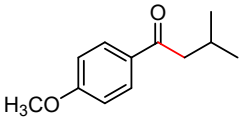
Yellow oil (28.9 mg, 89% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.85 (m, 2H), 7.58 – 7.52 (m, 1H), 7.50 – 7.41 (m, 2H), 2.84 (d, J = 6.9 Hz, 2H), 2.37 – 2.23 (m, 1H), 1.00 (d, J = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 137.5, 132.8, 128.5, 128.1, 47.5, 25.2, 22.8.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{11}H_{15}O$ 163.1117; found: 163.1119.

The spectroscopic data correspond to the reported values.[16]



1-(4-methoxyphenyl)-3-methylbutan-1-one (7)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

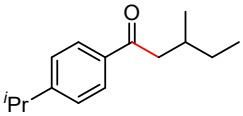
Colorless oil (19.2 mg, 50% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.80 (d, J = 6.9 Hz, 2H), 2.37 – 2.23 (m, 1H), 1.01 (d, J = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 163.3, 130.6, 130.4, 113.7, 55.4, 47.2, 25.4, 22.8.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{12}H_{16}O_2Na$ 215.1043; found: 215.1038.

The spectroscopic data correspond to the reported values.[17]



1-(4-isopropylphenyl)-3-methylpentan-1-one (8)

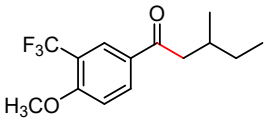
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (36.7 mg, 84% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.06 – 2.90 (m, 2H), 2.74 (dd, *J* = 15.6, 8.0 Hz, 1H), 2.17 – 2.03 (m, *J* = 6.7 Hz, 1H), 1.51 – 1.38 (m, 1H), 1.37 – 1.21 (m, 7H), 1.00 – 0.88 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 154.3, 135.4, 128.4, 126.6, 45.5, 34.2, 31.5, 29.8, 23.7, 19.6, 11.5.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{15}H_{23}O$ 219.1743; found: 219.1744.



1-(4-methoxy-3-(trifluoromethyl)phenyl)-3-methylpentan-1-one (9)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

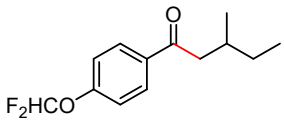
Yellow oil (42.2 mg, 77% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 3.98 (s, 3H), 2.91 (dd, *J* = 15.7, 5.7 Hz, 1H), 2.70 (dd, *J* = 15.7, 8.0 Hz, 1H), 2.15 – 1.99 (m, 1H), 1.49 – 1.38 (m, 1H), 1.33 – 1.26 (m, 1H), 1.00 – 0.88 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 160.4, 133.4, 129.3, 127.3 (q, *J* = 21.0 Hz), 124.1 (q, *J* = 270.0 Hz), 111.1, 55.9, 44.8, 31.1, 29.3, 19.1, 11.1.

^{19}FNMR (376 MHz, $CDCl_3$) δ -63.35.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{14}H_{18}F_3O_2$ 275.1253; found: 275.1250.



1-(4-(difluoromethoxy)phenyl)-3-methylpentan-1-one (10)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

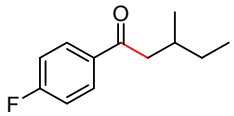
Yellow oil (36.3 mg, 75% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.58 (t, *J* = 73.1 Hz, 1H), 2.92 (dd, *J* = 15.7, 5.7 Hz, 1H), 2.71 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.13 – 1.97 (m, 1H), 1.49 – 1.34 (m, 1H), 1.32 – 1.26 (m, 1H), 1.00 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 154.1, 133.9, 129.9, 118.3, 114.9 (t, *J* = 261.2 Hz), 45.1, 31.0, 29.3, 19.1, 11.1.

^{19}FNMR (376 MHz, $CDCl_3$) δ -82.14 (d, *J* = 73.0 Hz).

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{13}H_{16}F_2O_2Na$ 265.1011; found: 265.1011.



1-(4-fluorophenyl)-3-methylpentan-1-one (11)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (34.2 mg, 88% yield)

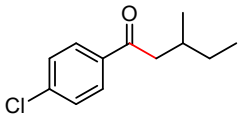
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 2H), 7.19 – 7.09 (m, 2H), 2.94 (dd, *J* = 15.7, 5.7 Hz, 1H), 2.74 (dd, *J* = 15.7, 8.0 Hz, 1H), 2.18 – 2.03 (m, 1H), 1.52 – 1.38 (m, 1H), 1.32 – 1.22 (m, 1H), 1.04 – 0.83 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 130.8, 130.7, 115.7, 115.5, 45.5, 31.4, 29.7, 19.5, 11.4.

^{19}FNMR (376 MHz, $CDCl_3$) δ -106.16.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{12}H_{16}FO$ 195.1179; found: 195.1175.

The spectroscopic data correspond to the reported values.[18]



1-(4-chlorophenyl)-3-methylpentan-1-one (12)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

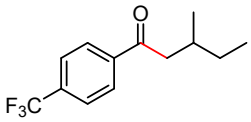
Yellow oil (37.8 mg, 90% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 2.94 (dd, *J* = 15.8, 5.7 Hz, 1H), 2.73 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.17 – 2.01 (m, 1H), 1.49 – 1.39 (m, 1H), 1.36 – 1.27 (m, 1H), 1.02 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 139.3, 135.7, 129.6, 128.9, 45.6, 31.4, 29.7, 19.5, 11.4.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{12}H_{15}ClONa$ 233.0704; found: 233.0701.

The spectroscopic data correspond to the reported values.[18]



3-methyl-1-(4-(trifluoromethyl)phenyl)pentan-1-one (13)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (39.5 mg, 81% yield)

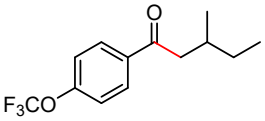
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 2.96 (dd, *J* = 16.0, 5.7 Hz, 1H), 2.76 (dd, *J* = 15.9, 7.9 Hz, 1H), 2.16 – 1.98 (m, 1H), 1.51 – 1.35 (m, 1H), 1.32 – 1.26 (m, 1H), 1.01 – 0.83 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 140.1, 134.0 (q, *J* = 128.0 Hz), 129.2, 128.4 (q, *J* = 15.0 Hz), 125.7 (q, *J* = 3.0 Hz), 45.9, 31.3, 29.7, 19.5, 11.4.

^{19}FNMR (376 MHz, $CDCl_3$) δ -63.51.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{13}H_{15}OF_3Na$ 267.0967; found: 267.0967.

The spectroscopic data correspond to the reported values.[17]



3-methyl-1-(4-(trifluoromethoxy)phenyl)pentan-1-one (14)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

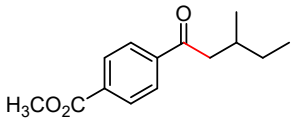
Yellow oil (43.2 mg, 83% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 2.69 (dd, *J* = 15.9, 5.6 Hz, 1H), 2.48 (dd, *J* = 15.9, 8.0 Hz, 1H), 1.92 – 1.75 (m, 1H), 1.25 – 1.11 (m, 1H), 1.08 – 0.97 (m, 1H), 0.77 – 0.61 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 152.4, 135.7, 130.1, 120.4 (q, *J* = 136.0 Hz), 45.6, 31.4, 29.7, 19.5, 11.4.

^{19}FNMR (376 MHz, $CDCl_3$) δ -57.99.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{13}H_{15}F_3O_2Na$ 283.0916; found: 283.0913.



methyl 4-(3-methylpentanoyl)benzoate (15)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

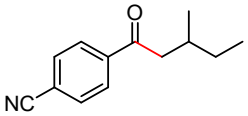
Yellow oil (34.7 mg, 74% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 3H), 3.00 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.80 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.18 – 2.05 (m, 1H), 1.53 – 1.37 (m, 1H), 1.37 – 1.26 (m, 1H), 1.01 – 0.89 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 166.3, 140.7, 133.7, 129.8, 128.0, 52.4, 46.0, 31.3, 29.7, 19.5, 11.4.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{14}H_{18}O_3Na$ 257.1148; found: 257.1142.

The spectroscopic data correspond to the reported values.[17]



4-(3-methylpentanoyl)benzonitrile (16)

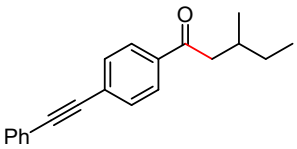
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow oil (32.2 mg, 80% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 2.90 (dd, *J* = 16.1, 5.6 Hz, 1H), 2.69 (dd, *J* = 16.1, 8.0 Hz, 1H), 2.09 – 1.93 (m, 1H), 1.43 – 1.29 (m, 1H), 1.25 – 1.20 (m, 1H), 1.01 – 0.68 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 140.3, 132.5, 128.5, 118.0, 116.1, 45.8, 31.2, 29.6, 19.5, 11.4.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{13}H_{16}ON$ 202.1226; found: 202.1235.



3-methyl-1-(4-(phenylethynyl)phenyl)pentan-1-one (17)

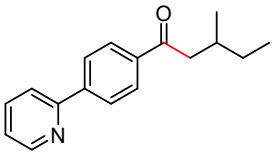
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (43.1 mg, 78% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.18 – 7.13 (m, 3H), 2.74 (dd, *J* = 15.8, 5.7 Hz, 1H), 2.54 (dd, *J* = 15.8, 8.0 Hz, 1H), 1.96 – 1.80 (m, 1H), 1.25 – 1.18 (m, 1H), 1.10 – 1.05 (m, 1H), 0.79 – 0.67 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 136.1, 131.4, 131.3, 128.4, 128.1, 127.7, 127.5, 122.3, 92.1, 88.3, 45.2, 31.0, 29.3, 19.1, 11.0.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{20}H_{20}ONa$ 299.1406; found: 299.1397.



3-methyl-1-(4-(pyridin-2-yl)phenyl)pentan-1-one (18)

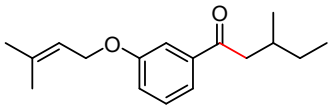
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (39.5 mg, 78% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 – 8.73 (m, 1H), 8.10 (q, *J* = 8.5 Hz, 4H), 7.90 – 7.79 (m, 2H), 7.38 – 7.30 (m, 1H), 3.01 (dd, *J* = 15.7, 5.7 Hz, 1H), 2.80 (dd, *J* = 15.7, 8.0 Hz, 1H), 2.21 – 2.05 (m, 1H), 1.56 – 1.39 (m, 1H), 1.37 – 1.25 (m, 1H), 1.03 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 155.9, 149.5, 142.7, 137.7, 137.5, 128.7, 127.2, 123.0, 121.3, 45.8, 31.5, 29.7, 19.6, 11.5.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{17}H_{20}NO$ 254.1539; found: 254.1538.



3-methyl-1-(3-((3-methylbut-2-en-1-yl)oxy)phenyl)pentan-1-one (19)

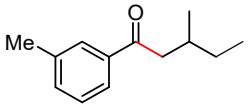
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (29.7 mg, 57% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.16 – 7.09 (m, 1H), 5.57 – 5.47 (m, 1H), 4.58 (d, *J* = 6.8 Hz, 2H), 2.95 (dd, *J* = 15.7, 5.7 Hz, 1H), 2.74 (dd, *J* = 15.7, 8.0 Hz, 1H), 2.17 – 2.02 (m, 1H), 1.80 (d, *J* = 17.1 Hz, 6H), 1.52 – 1.37 (m, 1H), 1.33 – 1.25 (m, 1H), 0.99 – 0.91 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 159.1, 138.8, 138.7, 129.5, 120.7, 119.9, 119.3, 113.2, 64.9, 45.7, 31.5, 29.7, 25.9, 19.5, 18.3, 11.4.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{17}H_{24}O_2Na$ 283.1669; found: 283.1669.



3-methyl-1-(m-tolyl)pentan-1-one (20)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

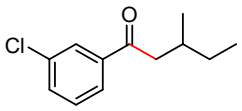
Yellow oil (32.7 mg, 86% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.40 – 7.30 (m, 2H), 2.94 (dd, *J* = 15.7, 5.7 Hz, 1H), 2.73 (dd, *J* = 15.7, 8.0 Hz, 1H), 2.41 (s, 3H), 2.16 – 2.01 (m, 1H), 1.48 – 1.35 (m, 1H), 1.34 – 1.21 (m, 1H), 1.06 – 0.81 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 138.3, 137.5, 133.6, 128.6, 128.4, 125.4, 45.7, 31.4, 29.7, 21.4, 19.6, 11.5.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{13}H_{18}ONa$ 213.1250; found: 213.1251.

The spectroscopic data correspond to the reported values.[18]



1-(3-chlorophenyl)-3-methylpentan-1-one (21)

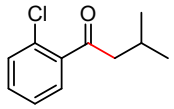
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (34.5 mg, 82% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.88 – 7.81 (m, 1H), 7.58 – 7.51 (m, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 2.95 (dd, *J* = 16.0, 5.7 Hz, 1H), 2.75 (dd, *J* = 15.9, 7.9 Hz, 1H), 2.18 – 2.02 (m, 1H), 1.51 – 1.41 (m, 1H), 1.37 – 1.27 (m, 1H), 1.04 – 0.88 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 139.0, 134.9, 132.8, 129.9, 128.2, 126.2, 45.7, 31.3, 29.7, 19.5, 11.4.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{12}H_{15}OClNa$ 233.0704; found: 233.0704.



1-(2-chlorophenyl)-3-methylpentan-1-one (22)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

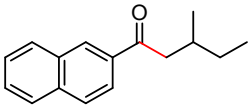
Yellow oil (18.4 mg, 47% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 3H), 7.34 – 7.28 (m, 1H), 2.82 (d, *J* = 7.0 Hz, 2H), 2.34 – 2.15 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 131.5, 130.6, 128.8, 127.0, 52.0, 25.1, 22.7.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{11}H_{13}ClONa$ 219.0547; found: 219.0545.

The spectroscopic data correspond to the reported values.[19]



3-methyl-1-(naphthalen-2-yl)pentan-1-one (23)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

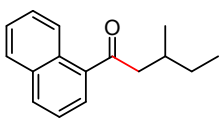
Yellow oil (34.8 mg, 77% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (dd, *J* = 8.6, 6.6 Hz, 2H), 7.66 – 7.53 (m, 2H), 3.11 (dd, *J* = 15.7, 5.7 Hz, 1H), 2.91 (dd, *J* = 15.6, 8.0 Hz, 1H), 2.25 – 2.11 (m, *J* = 6.6, 6.1 Hz, 1H), 1.58 – 1.44 (m, 1H), 1.43 – 1.29 (m, 1H), 1.07 – 0.94 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 135.5, 134.9, 132.6, 129.7, 129.6, 128.4, 128.3, 127.8, 126.7, 124.0, 45.7, 31.6, 29.8, 19.6, 11.5.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{16}H_{18}ONa$ 249.1249; found: 249.1247.

The spectroscopic data correspond to the reported values.[20]



3-methyl-1-(naphthalen-1-yl)pentan-1-one (24)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate

= 20:1)

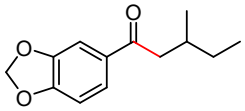
Yellow oil (31.2 mg, 69% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.50 (m, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.63 – 7.50 (m, 3H), 3.09 (dd, *J* = 15.6, 5.7 Hz, 1H), 2.86 (dd, *J* = 15.6, 8.1 Hz, 1H), 2.24 – 2.07 (m, 1H), 1.53 – 1.42 (m, 1H), 1.36 – 1.30 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 136.9, 134.0, 132.3, 130.1, 128.4, 127.8, 127.2, 126.4, 125.7, 124.4, 49.4, 31.9, 29.7, 19.6, 11.4.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{16}H_{19}O$ 227.1430; found: 227.1422.

The spectroscopic data correspond to the reported values.[18]



1-(benzo[d][1,3]dioxol-5-yl)-3-methylpentan-1-one (25)

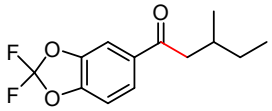
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (21.1 mg, 48% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 1H), 7.46 (s, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.06 (s, 2H), 2.89 (dd, *J* = 15.4, 5.7 Hz, 1H), 2.68 (dd, *J* = 15.4, 8.0 Hz, 1H), 2.15 – 2.00 (m, 1H), 1.51 – 1.36 (m, 1H), 1.36 – 1.21 (m, 1H), 0.99 – 0.85 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 151.5, 148.2, 132.5, 124.3, 108.0, 107.8, 101.8, 45.4, 31.7, 29.7, 19.5, 11.4.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{13}H_{16}O_3Na$ 243.0992; found: 243.0993.



1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)-3-methylpentan-1-one (26)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

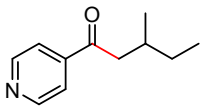
Yellow oil (38.4 mg, 75% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 1H), 7.67 (s, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 2.89 (dd, *J* = 15.8, 5.7 Hz, 1H), 2.69 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.14 – 1.99 (m, 1H), 1.45 – 1.35 (m, 1H), 1.32 – 1.25 (m, 1H), 0.96 – 0.85 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 146.9, 144.2, 134.0, 131.7, 125.2, 109.3, 109.1, 45.5, 31.5, 29.7 (q, *J* = 4.6 Hz), 19.5, 11.4.

^{19}FNMR (376 MHz, $CDCl_3$) δ -50.15.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{13}H_{15}F_2O_3$ 257.0984; found: 257.0983.



3-methyl-1-(pyridin-4-yl)pentan-1-one (27)

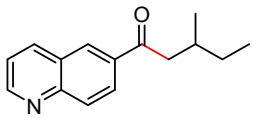
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow oil (27.6 mg, 78% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 5.9 Hz, 2H), 7.74 (d, *J* = 6.0 Hz, 2H), 2.97 (dd, *J* = 16.2, 5.6 Hz, 1H), 2.77 (dd, *J* = 16.2, 7.9 Hz, 1H), 2.18 – 2.04 (m, 1H), 1.52 – 1.38 (m, 1H), 1.39 – 1.17 (m, 1H), 1.01 – 0.90 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 150.8, 143.3, 121.2, 45.8, 31.1, 29.6, 19.5, 11.4.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{11}H_{15}NONa$ 200.1046; found: 200.1041.



3-methyl-1-(quinolin-6-yl)pentan-1-one (28)

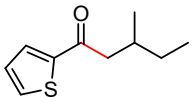
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 5:1)

Yellow oil (36.8 mg, 81% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 2.4 Hz, 1H), 8.41 (s, 1H), 8.29 – 8.19 (m, 2H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.05 (dd, *J* = 15.9, 5.7 Hz, 1H), 2.85 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.20 – 2.04 (m, 1H), 1.53 – 1.36 (m, 1H), 1.34 – 1.23 (m, 1H), 1.00 – 0.88 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 152.6, 150.1, 137.7, 135.3, 130.1, 129.5, 127.9, 127.6, 122.0, 45.9, 31.5, 29.8, 19.7, 11.6.

HRMS (ESI) m/z: [M+H^+] Calcd for $C_{15}H_{18}ON$ 228.1383; found: 228.1383.



3-methyl-1-(thiophen-2-yl)pentan-1-one (29)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

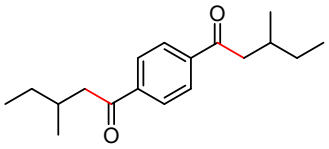
Yellow oil (16.0 mg, 44% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 3.7 Hz, 1H), 7.64 (d, *J* = 5.0 Hz, 1H), 7.16 – 7.13 (m, 1H), 2.90 (dd, *J* = 15.0, 5.8 Hz, 1H), 2.70 (dd, *J* = 15.0, 8.1 Hz, 1H), 2.20 – 2.02 (m, 1H), 1.53 – 1.38 (m, 1H), 1.35 – 1.28 (m, 1H), 1.05 – 0.89 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 145.1, 133.4, 131.7, 128.0, 46.5, 32.0, 29.7, 19.5, 11.4.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{10}H_{14}OSNa$ 205.0658; found: 205.0659.

The spectroscopic data correspond to the reported values.[18]



1,1'-(1,4-phenylene)bis(3-methylpentan-1-one) (30)

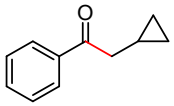
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (42.8 mg, 78% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 4H), 3.00 (dd, *J* = 15.9, 5.7 Hz, 2H), 2.79 (dd, *J* = 15.9, 8.0 Hz, 2H), 2.17 – 2.03 (m, 2H), 1.53 – 1.38 (m, 2H), 1.37 – 1.28 (m, 2H), 1.03 – 0.84 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 140.4, 128.3, 46.0, 31.4, 29.7, 19.5, 11.4.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{18}H_{26}O_2Na$ 297.1825; found: 297.1818.



2-cyclopropyl-1-phenylethan-1-one (31)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

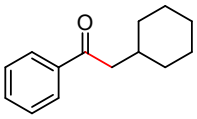
Yellow oil (17.3 mg, 54% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.61 – 7.53 (m, 1H), 7.52 – 7.44 (m, 2H), 2.91 (d, *J* = 6.8 Hz, 2H), 0.91 – 0.85 (m, 1H), 0.67 – 0.58 (m, 2H), 0.26 – 0.18 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 136.9, 133.0, 128.6, 128.2, 43.8, 29.7, 6.7, 4.6.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{11}H_{12}ONa$ 183.0780; found: 183.0780.

The spectroscopic data correspond to the reported values.[21]



2-cyclohexyl-1-phenylethan-1-one (32)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

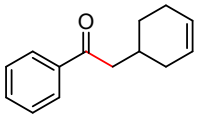
Yellow oil (31.9 mg, 79% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.82 (m, 2H), 7.53 – 7.44 (m, 1H), 7.45 – 7.32 (m, 2H), 2.76 (d, *J* = 6.9 Hz, 2H), 2.01 – 1.85 (m, 1H), 1.74 – 1.60 (m, 4H), 1.26 – 1.15 (m, 4H), 1.02 – 0.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 137.5, 132.9, 128.5, 128.2, 46.2, 34.6, 33.5, 26.3, 26.2.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{14}H_{18}ONa$ 225.1250; found: 225.1250.

The spectroscopic data correspond to the reported values.[22]



2-(cyclohex-3-en-1-yl)-1-phenylethan-1-one (33)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

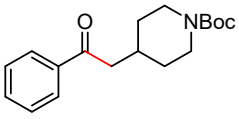
Yellow oil (33.6 mg, 84% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.62 – 7.53 (m, 1H), 7.52 – 7.39 (m, 2H), 5.73 – 5.64 (m, 2H), 2.94 (d, *J* = 6.8 Hz, 2H), 2.37 – 2.23 (m, 1H), 2.19 – 2.04 (m, 3H), 1.87 – 1.76 (m, 2H), 1.45 – 1.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 137.3, 132.9, 128.6, 128.1, 126.9, 126.0, 45.1, 31.6, 30.1, 28.8, 24.8.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{14}H_{16}ONa$ 223.1093; found: 223.1092.

The spectroscopic data correspond to the reported values.[23]



tert-butyl 4-(2-oxo-2-phenylethyl)piperidine-1-carboxylate (34)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

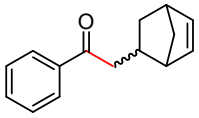
Yellow oil (46.7 mg, 77% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.60 – 7.55 (m, 1H), 7.51 – 7.44 (m, 2H), 4.19 – 4.02 (m, 2H), 2.90 (d, *J* = 6.7 Hz, 2H), 2.81 – 2.70 (m, 2H), 2.21 – 2.12 (m, 1H), 1.80 – 1.69 (m, 2H), 1.46 (s, 9H), 1.31 – 1.13 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 154.9, 137.2, 133.1, 128.8, 128.1, 79.3, 45.0, 43.5, 32.4, 32.2, 28.5.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{18}H_{25}O_3NNa$ 326.1727; found: 326.1729.

The spectroscopic data correspond to the reported values.[22]



2-(bicyclo[2.2.1]hept-5-en-2-yl)-1-phenylethan-1-one (35)

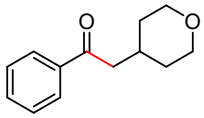
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1) as inseparable diastereomer.

Yellow oil (30.5 mg, 72% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.92 (m, 2H), 7.62 – 7.52 (m, 1H), 7.52 – 7.40 (m, 2H), 6.19 (dd, *J* = 27.9, 3.1 Hz, 1H), 6.04 (dd, *J* = 29.5, 2.9 Hz, 1H), 3.18 – 3.02 (m, 1H), 2.92 – 2.75 (m, 2H), 2.75 – 2.61 (m, 1H), 2.09 – 1.99 (m, 1H), 1.50 – 1.41 (m, 2H), 1.30 – 1.19 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 200.1, 137.9, 137.2, 136.6, 136.5, 132.9, 132.9, 132.4, 128.6, 128.5, 128.1, 128.0, 49.7, 46.5, 45.7, 45.3, 43.8, 42.6, 42.2, 34.3, 34.2, 33.0, 32.5.

HRMS (ESI) m/z: [M+H^+] Calcd for $C_{15}H_{17}O$ 213.1274; found: 213.1274.



1-phenyl-2-(tetrahydro-2H-pyran-4-yl)ethan-1-one (36)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

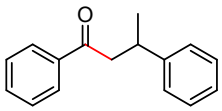
Yellow oil (26.1 mg, 64% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.61 – 7.52 (m, 1H), 7.52 – 7.40 (m, 2H), 3.95 (d, *J* = 8.4 Hz, 2H), 3.44 (t, *J* = 10.9 Hz, 2H), 2.90 (d, *J* = 6.7 Hz, 2H), 2.35 – 2.17 (m, 1H), 1.74 – 1.63 (m, 2H), 1.46 – 1.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 137.3, 133.2, 128.7, 128.2, 68.0, 45.5, 33.1, 31.4.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{13}H_{16}O_2Na$ 227.1043; found: 227.1041.

The spectroscopic data correspond to the reported values.[24]



1,3-diphenylbutan-1-one(37)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

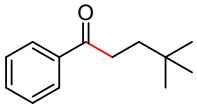
Yellow oil (25.1 mg, 56% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.51 – 7.45 (m, 1H), 7.41 – 7.35 (m, 2H), 7.25 – 7.19 (m, 4H), 7.16 – 7.10 (m, 1H), 3.50 – 3.37 (m, 1H), 3.23 (dd, *J* = 16.5, 5.7 Hz, 1H), 3.12 (dd, *J* = 16.5, 8.3 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 146.6, 137.2, 133.0, 128.6, 128.5, 128.1, 126.9, 126.3, 47.0, 35.6, 21.9.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{16}H_{16}ONa$ 247.1093; found: 247.1093.

The spectroscopic data correspond to the reported values.[25]



4,4-dimethyl-1-phenylpentan-1-one (38)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

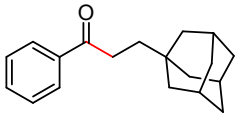
Yellow oil (28.1 mg, 74% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.59 – 7.50 (m, 1H), 7.48 – 7.34 (m, 2H), 2.97 – 2.89 (m, 2H), 1.69 – 1.59 (m, 2H), 0.95 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 137.1, 132.9, 128.6, 128.1, 38.1, 34.3, 30.2, 29.2.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{13}H_{19}O$ 191.1430; found: 191.1430.

The spectroscopic data correspond to the reported values.[26]



3-((1r,3s)-adamantan-1-yl)-1-phenylpropan-1-one (39)

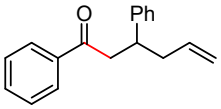
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (37.5 mg, 70% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.59 – 7.50 (m, 1H), 7.50 – 7.41 (m, 2H), 2.96 – 2.87 (m, 2H), 2.01 – 1.93 (m, 3H), 1.74 – 1.59 (m, 7H), 1.55 – 1.45 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 137.1, 132.9, 128.6, 128.1, 42.3, 38.5, 37.1, 32.3, 32.1, 28.7.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{19}H_{25}O$ 269.1899; found: 269.1899.



1,3-diphenylhex-5-en-1-one (40)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

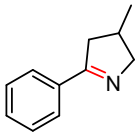
Yellow oil (34.0 mg, 68% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.49 – 7.43 (m, 1H), 7.38 – 7.33 (m, 2H), 7.24 – 7.15 (m, 4H), 7.14 – 7.08 (m, 1H), 5.69 – 5.54 (m, 1H), 4.96 – 4.86 (m, 2H), 3.41 (p, J = 7.1 Hz, 1H), 3.25 – 3.19 (m, 2H), 2.43 – 2.35 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 144.4, 137.2, 136.3, 133.0, 128.5, 128.4, 128.0, 127.6, 126.4, 116.8, 44.6, 40.8, 40.7.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{18}H_{18}ONa$ 273.1250; found: 273.1250.

The spectroscopic data correspond to the reported values.[27]



3-methyl-5-phenyl-3,4-dihydro-2H-pyrrole (41a)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

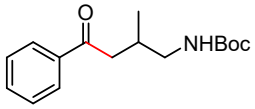
Yellow oil (8.9 mg, 28% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.49 – 7.35 (m, 3H), 4.36 – 4.06 (m, 1H), 3.73 – 3.61 (m, 1H), 3.22 – 3.10 (m, 1H), 2.71 – 2.47 (m, 2H), 1.13 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 134.7, 130.3, 128.4, 127.6, 68.9, 43.2, 31.4, 20.4.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{11}H_{13}NNa$ 182.0940; found: 182.0942.

The spectroscopic data correspond to the reported values.[28]



tert-butyl (2-methyl-4-oxo-4-phenylbutyl)carbamate (41b)

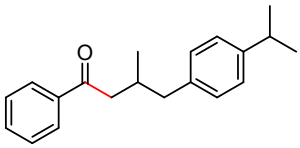
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (20.0 mg, 36% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.70 (s, 1H), 3.14 (t, *J* = 6.6 Hz, 2H), 3.05 (dd, *J* = 16.4, 5.9 Hz, 1H), 2.82 (dd, *J* = 16.4, 7.4 Hz, 1H), 2.44 – 2.35 (m, 1H), 1.43 (s, 9H), 1.02 (dd, *J* = 6.8, 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 156.2, 137.1, 133.1, 128.6, 128.1, 79.2, 46.4, 43.2, 30.6, 28.4, 18.1.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{16}H_{23}NO_3Na$ 300.1570; found: 300.1570.



4-(4-isopropylphenyl)-3-methyl-1-phenylbutan-1-one (42)

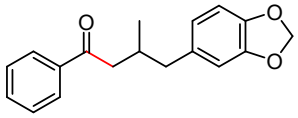
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

White solid (46.5 mg, 83% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.81 (m, 2H), 7.60 – 7.53 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.21 – 7.10 (m, 4H), 3.02 (dd, *J* = 15.9, 5.1 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.77 (dd, *J* = 15.9, 8.1 Hz, 1H), 2.71 – 2.56 (m, 2H), 2.54 – 2.45 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 6H), 1.02 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 146.6, 137.8, 137.3, 132.9, 129.2, 128.5, 128.1, 126.3, 45.0, 43.0, 33.7, 31.9, 24.1, 20.1.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{20}H_{25}O$ 281.1899; found: 281.1899.



4-(benzo[d][1,3]dioxol-5-yl)-3-methyl-1-phenylbutan-1-one (43)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

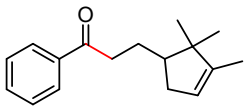
Yellow oil (43.4 mg, 77% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.84 (m, 2H), 7.61 – 7.52 (m, 1H), 7.52 – 7.42 (m, 2H), 6.78 – 6.70 (m, 2H), 6.70 – 6.58 (m, 1H), 5.95 (s, 2H), 2.98 (dd, *J* = 16.1, 5.2 Hz, 1H), 2.77 (dd, *J* = 16.1, 7.8 Hz, 1H), 2.62 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.54 – 2.41 (m, 2H), 0.99 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 147.5, 145.8, 137.3, 134.3, 132.9, 128.6, 128.1, 122.1, 109.6, 108.0, 100.8, 44.9, 43.1, 31.9, 19.9.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{18}H_{18}O_3Na$ 305.1148; found: 305.1148.

The spectroscopic data correspond to the reported values.[25]



1-phenyl-3-(2,2,3-trimethylcyclopent-3-en-1-yl)propan-1-one (44)

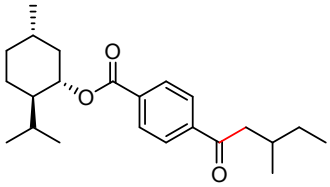
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (30.5 mg, 63% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 2H), 7.60 – 7.50 (m, 1H), 7.49 – 7.43 (m, 2H), 5.27 – 5.21 (m, 1H), 3.04 (ddd, *J* = 16.6, 10.2, 5.2 Hz, 1H), 2.93 (ddd, *J* = 16.5, 9.7, 5.9 Hz, 1H), 2.39 – 2.26 (m, 1H), 1.99 – 1.74 (m, 3H), 1.71 – 1.63 (m, 1H), 1.63 – 1.59 (m, 3H), 1.01 (s, 3H), 0.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 148.9, 137.1, 132.9, 128.6, 128.1, 121.4, 50.1, 47.0, 37.9, 35.5, 25.8, 24.8, 19.7, 12.7.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{17}H_{22}ONa$ 265.1563; found: 265.1563.



(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(3-methylpentanoyl)benzoate (45)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

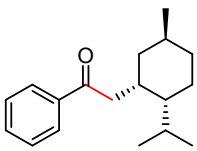
Yellow oil (38.7 mg, 54% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 5.01 – 4.90 (m, 1H), 2.98 (dd, *J* = 16.0, 5.7 Hz, 1H), 2.76 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.18 – 2.04 (m, 2H), 1.99 – 1.90 (m, 1H), 1.74 (d, *J* = 12.8 Hz, 2H), 1.65 – 1.52 (m, 2H), 1.49 – 1.37 (m, 1H), 1.35 – 1.27 (m, 2H), 1.17 – 1.08 (m, 2H), 0.99 – 0.85 (m, 12H), 0.79 (dd, *J* = 6.9, 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 165.3, 140.5, 134.4, 129.8, 128.0, 75.4, 47.3, 46.0, 40.9, 34.3, 31.5, 29.7, 26.6, 23.7, 22.0, 20.8, 19.5, 16.5, 11.4.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{23}H_{35}O_3$ 359.2581; found: 359.2575.

$[\alpha]^{27}_D$ = -11.8 (c 1.0 $CHCl_3$)



2-((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)-1-phenylethan-1-one (46)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

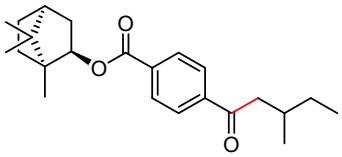
Yellow oil (26.3 mg, 51% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52 – 7.41 (m, 2H), 3.19 (dd, *J* = 15.6, 3.8 Hz, 1H), 2.62 (dd, *J* = 15.7, 9.3 Hz, 1H), 2.07 – 1.89 (m, 2H), 1.79 – 1.63 (m, 4H), 1.41 – 1.29 (m, 2H), 1.15 – 0.99 (m, 2H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.82 (dd, *J* = 10.0, 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 137.7, 132.8, 128.6, 128.1, 47.6, 43.0, 42.3, 36.3, 35.2, 32.5, 27.2, 24.3, 22.6, 21.7, 15.4.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{18}H_{26}ONa$ 281.1876; found: 281.1875.

$[\alpha]^{27}_D$ = -44.8 (c 1.0 $CHCl_3$)



(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(3-methylpentanoyl)benzoate (47)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

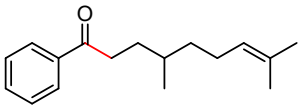
Yellow oil (42.7 mg, 60% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 5.77 – 5.71 (m, 1H), 3.75 – 3.61 (m, 1H), 2.66 (dd, *J* = 15.8, 5.7 Hz, 1H), 2.45 (dd, *J* = 15.8, 8.0 Hz, 1H), 1.85 – 1.69 (m, 3H), 1.54 – 1.31 (m, 4H), 1.20 – 1.05 (m, 4H), 0.99 – 0.87 (m, 7H), 0.75 – 0.50 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 165.7, 139.4, 138.7, 128.3, 127.2, 49.0, 45.9, 33.2, 31.4, 29.7, 25.5, 24.9, 19.5, 11.5.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{23}H_{32}O_3Na$ 379.2244; found: 379.2251.

$[\alpha]^{27}_D$ = 37.0 (c 1.0 $CHCl_3$)



4,8-dimethyl-1-phenylnon-7-en-1-one (48)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

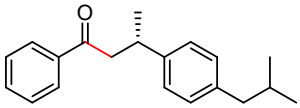
Yellow oil (19.5 mg, 40% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.62 – 7.54 (m, 1H), 7.52 – 7.46 (m, 2H), 5.18 – 5.08 (m, 1H), 3.05 – 2.92 (m, 2H), 2.09 – 1.94 (m, 4H), 1.86 – 1.76 (m, 1H), 1.70 (s, 3H), 1.63 (s, 3H), 1.26 – 1.21 (m, 2H), 0.97 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 137.1, 132.9, 131.3, 128.6, 128.1, 124.7, 36.9, 36.3, 32.3, 31.3, 25.7, 25.5, 19.4, 17.7.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{17}H_{24}ONa$ 267.1719; found: 267.1718.

The spectroscopic data correspond to the reported values.[29]



(S)-3-(4-isobutylphenyl)-1-phenylbutan-1-one (49)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (30.8 mg, 55% yield)

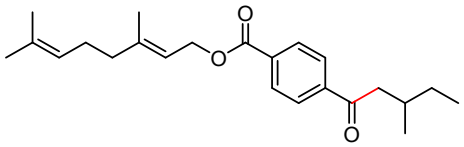
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 2H), 7.34 – 7.25 (m, 1H), 7.22 – 7.17 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 2H), 3.30 – 3.17 (m, 1H), 3.05 (dd, *J* = 16.3, 5.5 Hz, 1H), 2.92 (dd, *J* = 16.3, 8.4 Hz, 1H), 2.19 (d, *J* = 7.2 Hz, 2H), 1.67 – 1.52 (m, 1H), 1.09 (d, *J* = 6.9 Hz, 3H), 0.65 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 143.8, 139.6, 137.3, 133.0, 129.3, 128.6, 128.1, 126.5, 47.2, 45.0, 35.3, 30.2, 22.4, 21.9.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{20}H_{24}ONa$ 303.1719; found: 303.1715.

$[\alpha]^{27}_D$ = 7.8 (c 1.0 $CHCl_3$)

The spectroscopic data correspond to the reported values.[30]



(*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-(3-methylpentanoyl)benzoate (50)

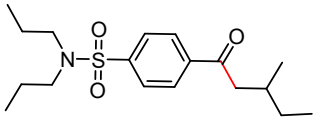
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (51.3 mg, 72% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H), 5.59 – 5.37 (m, 1H), 5.14 – 5.04 (m, 1H), 4.86 (d, *J* = 7.1 Hz, 2H), 2.97 (dd, *J* = 15.9, 5.6 Hz, 1H), 2.77 (dd, *J* = 15.9, 8.0 Hz, 1H), 2.18 – 2.00 (m, 5H), 1.77 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.48 – 1.38 (m, 1H), 1.32 – 1.24 (m, 1H), 0.99 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 166.0, 143.0, 140.6, 134.1, 132.0, 129.9, 128.1, 123.8, 118.1, 62.4, 46.0, 39.6, 31.4, 29.8, 26.4, 25.8, 19.6, 17.8, 16.7, 11.5.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{23}H_{32}O_3Na$ 379.2244; found: 379.2242.



4-(3-methylpentanoyl)-N,N-dipropylbenzenesulfonamide (51)

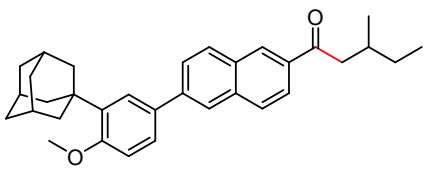
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (47.5 mg, 70% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H), 3.18 – 3.07 (m, 4H), 2.99 (dd, *J* = 16.1, 5.6 Hz, 1H), 2.79 (dd, *J* = 16.1, 7.9 Hz, 1H), 2.17 – 2.04 (m, 1H), 1.57 (h, *J* = 7.5 Hz, 4H), 1.49 – 1.38 (m, 1H), 1.36 – 1.28 (m, 1H), 1.01 – 0.92 (m, 6H), 0.89 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 143.9, 140.1, 128.6, 127.3, 50.0, 45.9, 31.2, 29.7, 22.0, 19.5, 11.4, 11.2.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{18}H_{29}NSO_3Na$ 362.1760; found: 362.1760.



1-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-3-methylpentan-1-one (52)

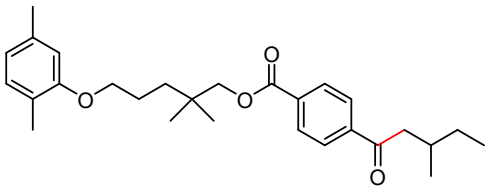
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (70.9 mg, 76% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.10 – 8.01 (m, 3H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.84 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.64 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H), 3.12 (dd, *J* = 15.6, 5.8 Hz, 1H), 2.92 (dd, *J* = 15.6, 8.0 Hz, 1H), 2.27 – 2.14 (m, 7H), 2.20 – 2.12 (m, 3H), 1.87 – 1.78 (m, 6H), 1.60 – 1.43 (m, 1H), 1.43 – 1.26 (m, 1H), 1.11 – 0.95 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 159.0, 141.5, 139.0, 136.0, 134.5, 132.5, 131.3, 129.9, 129.5, 128.5, 126.5, 126.0, 125.7, 124.7, 124.4, 112.2, 55.2, 45.7, 40.6, 37.2, 37.2, 31.7, 29.8, 29.1, 19.7, 11.5.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{33}H_{38}O_2Na$ 489.2764; found: 489.2760.



5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl 4-(3-methylpentanoyl)benzoate (53)

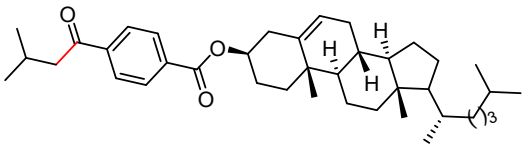
Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (64.9 mg, 74% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 6.54 (s, 1H), 4.04 (s, 2H), 3.87 (t, *J* = 6.2 Hz, 2H), 2.91 (dd, *J* = 15.8, 5.7 Hz, 1H), 2.70 (dd, *J* = 15.9, 7.9 Hz, 1H), 2.22 (s, 3H), 2.07 (s, 3H), 2.05 – 1.97 (m, 1H), 1.82 – 1.70 (m, 2H), 1.54 – 1.46 (m, 2H), 1.39 – 1.31 (m, 1H), 1.25 – 1.19 (m, 1H), 0.99 (s, 6H), 0.94 – 0.80 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 165.8, 157.0, 140.6, 136.5, 133.9, 130.3, 129.8, 128.1, 123.5, 120.7, 111.9, 73.1, 68.2, 46.0, 35.6, 34.0, 31.4, 29.7, 24.4, 24.2, 21.4, 19.5, 15.8, 11.5.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{28}H_{38}O_4Na$ 461.2662; found: 461.2667.



(3R,8R,9R,10S,13S,14R)-10,13-dimethyl-17-((S)-4-methylpentan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl4-(3-methylbutanoyl)benzoate (54)

Following General procedure A. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

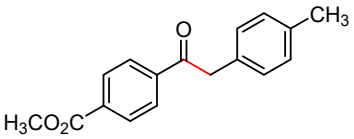
Yellow oil (89.6 mg, 78% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 5.45 – 5.39 (m, 1H), 4.96 – 4.78 (m, 1H), 2.86 (d, *J* = 6.9 Hz, 2H), 2.47 (d, *J* = 7.7 Hz, 2H), 2.36 – 2.23 (m, 1H), 2.07 – 1.88 (m, 4H), 1.86 – 1.71 (m, 2H), 1.64 – 1.40 (m, 8H), 1.38 – 1.29 (m, 3H), 1.27 – 1.08 (m, 9H), 1.07 (s, 3H), 1.00 (d, *J* = 6.6 Hz, 6H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 165.2, 140.4, 139.5, 134.4, 129.8, 127.9, 123.0, 75.2, 56.7, 56.1, 50.0, 47.8, 42.3, 39.7, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 32.0, 31.9, 28.3, 28.0, 27.9, 25.1, 24.3, 23.8, 22.9, 22.7, 22.6, 21.1, 19.4, 18.7, 11.9.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{39}H_{58}O_3Na$ 597.4278; found: 597.4268.

$[\alpha]^{27}_{D}$ = -35.0 (c 1.0 $CHCl_3$)



methyl 4-(2-(p-tolyl)acetyl)benzoate (61)

Following General procedure B. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

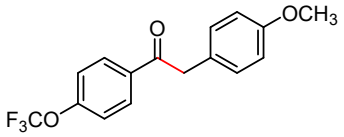
White solid (34.9 mg, 65% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.13 (s, 4H), 4.26 (s, 2H), 3.93 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 166.3, 139.9, 136.8, 133.9, 130.9, 129.9, 129.6, 129.4, 128.6, 52.6, 45.6, 21.2.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{17}H_{16}O_3Na$ 291.0992; found: 291.0991.

The spectroscopic data correspond to the reported values.[31]



2-(4-methoxyphenyl)-1-(4-(trifluoromethoxy)phenyl)ethan-1-one (62)

Following General procedure B. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

White solid (33.5 mg, 54% yield)

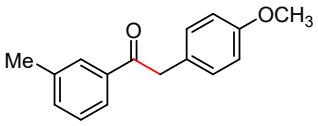
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.14 (s, 2H), 3.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 158.7, 152.7, 134.8, 130.7, 130.5, 126.1, 120.5 (q, *J* = 140.4 Hz), 114.3, 55.3, 44.8.

^{19}FNMR (376 MHz, $CDCl_3$) δ -57.46.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{16}H_{13}F_3O_3Na$ 333.0709; found: 333.0709.

The spectroscopic data correspond to the reported values.[32]



2-(4-methoxyphenyl)-1-(m-tolyl)ethan-1-one (63)

Following General procedure B. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

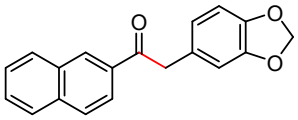
Yellow oil (60.0 mg, 50% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H), 7.33 – 7.22 (m, 2H), 7.15 – 7.06 (m, 2H), 6.83 – 6.75 (m, 2H), 4.14 (s, 2H), 3.71 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 158.5, 138.4, 136.7, 133.9, 130.5, 129.1, 128.5, 126.6, 125.9, 114.1, 55.3, 44.6, 21.4.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{16}H_{16}O_2Na$ 263.1043; found: 263.1043.

The spectroscopic data correspond to the reported values.[15]



2-(benzo[d][1,3]dioxol-5-yl)-1-(naphthalen-2-yl)ethan-1-one (64)

Following General procedure B. Purified by flash silica column chromatography (hexane/ethyl acetate = 20:1)

Yellow oil (36.6 mg, 63% yield)

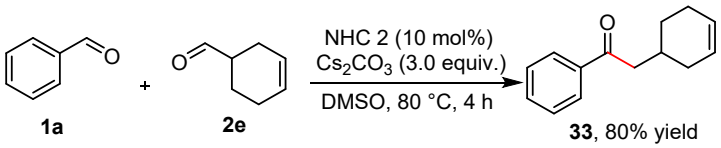
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (t, *J* = 7.9 Hz, 2H), 7.66 – 7.55 (m, 2H), 6.87 – 6.75 (m, 3H), 5.95 (s, 2H), 4.35 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 147.9, 146.6, 135.6, 133.9, 132.5, 130.3, 129.6, 128.2, 127.8, 126.8, 124.3, 122.6, 109.9, 108.5, 101.0, 45.2.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{19}H_{14}O_3Na$ 313.0835; found: 313.0835.

The spectroscopic data correspond to the reported values.[33]

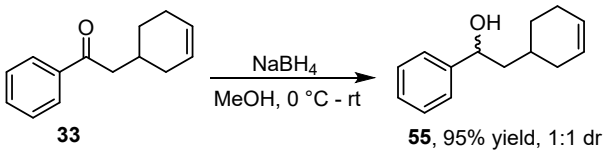
E. Procedure for large-scale synthesis:



To an oven-dried 25 mL round-bottomed flask equipped with a stir bar, were added **NHC 2** (102.0 mg, 10.0 mol%) and Cs_2CO_3 (2.9 g, 9.0 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After aryl aldehyde **1a** (3.0 mmol, 1.0 equiv.), alkyl aldehyde **2e** (9.0 mmol, 3.0 equiv.) and anhydrous DMSO (15.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered then was quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography to afford the desired product **33** (480.3 mg, 80% yield).

F. Derivatization reactions:

a. Selective reduction of 33



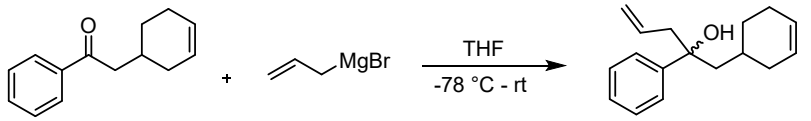
To an oven-dried 10 mL vial equipped with a magnetic stir bar was charged with **33** (0.2 mmol, 1.0 equiv.) and MeOH (1.0 mL). The reaction mixture was cooled to 0 °C using an ice-bath. Then $NaBH_4$ (0.26 mmol, 1.3 equiv.) was added and the resulting mixture was allowed to react at room temperature for 6 h until it was complete by TLC. After completion of the reaction, the solvent was evaporated under vacuum. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 20:1) to afford the desired product **55** as yellow oil as inseparable diastereomer (38.4 mg, 95% yield and 1:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 5H), 5.75 – 5.62 (m, 2H), 4.86 – 4.78 (m, 1H), 2.26 – 2.14 (m, 1H), 2.12 – 2.01 (m, 2H), 1.98 – 1.90 (m, 1H), 1.84 – 1.63 (m, 4H), 1.38 – 1.26 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 145.1, 128.6, 128.5, 127.6, 127.5, 127.1, 127.0, 126.4, 126.2, 125.9, 125.8, 72.4, 72.3, 46.2, 46.0, 32.3, 31.5, 30.2, 29.4, 28.5, 25.1, 24.9.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{14}H_{18}ONa$ 225.1250; found: 225.1244.

b. Nucleophilic addition of 33



33 **56**, 77% yield, 1:1 dr

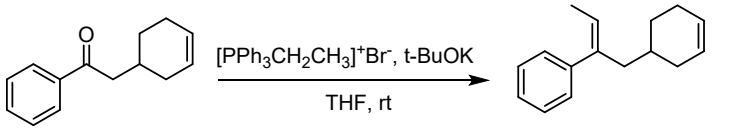
To an oven-dried 10 mL vial equipped with a magnetic stir bar was charged with **33** (0.2 mmol, 1.0 equiv.) and dry THF (2.0 mL). The reaction mixture was cooled to -78 °C under nitrogen atmosphere. And was added vinyl magnesium bromide (0.6 mmol, 3.0 equiv., 1.0 M in THF) dropwise via a syringe. The resulting mixture was stirred at the same temperature for 3 h until it was complete by TLC, then quenched by slow addition of MeOH (1.0 mL). The mixture was warmed to room temperature and diluted with Et_2O (5.0 mL) and water (3.0 mL). The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 20:1) to afford the desired product **56** as yellow oil as inseparable diastereomer (37.3 mg, 77% yield and 1:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 5.58 – 5.41 (m, 3H), 5.19 – 5.06 (m, 2H), 2.78 – 2.68 (m, 1H), 2.54 – 2.43 (m, 1H), 2.20 – 2.02 (m, 1H), 1.98 – 1.91 (m, 1H), 1.89 – 1.71 (m, 4H), 1.62 – 1.49 (m, 1H), 1.36 – 1.22 (m, 1H), 1.15 – 1.07 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 146.1, 133.4, 128.1, 126.9, 126.8, 126.7, 126.4, 125.3, 125.2, 120.0, 76.3, 76.2, 49.6, 49.5, 48.6, 48.5, 33.3, 33.2, 30.2, 30.1, 29.4, 29.3, 25.2, 25.0.

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{17}H_{22}ONa$ 265.1563; found: 265.1563.

c. Wittig reaction of 33



33 **57**, 86% yield, >19:1 *Z/E*

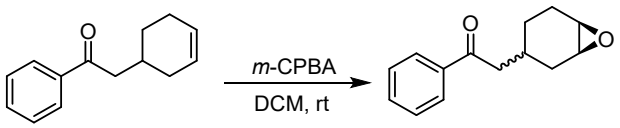
To an oven-dried 10 mL vial equipped with a magnetic stir bar, a solution of ethyltriphenylphosphonium bromide (0.24 mmol, 1.2 equiv.) in THF (1.0 mL) under nitrogen atmosphere. t-BuOK (0.24 mmol, 1.2 equiv.) was added at rt and stirring for 1 h. After **33** (0.2 mmol, 1.0 equiv.) was added dropwise and stirring for 1 h at 50 ℃ until it was complete by TLC, the precipitated solid materials were removed by filtration. The filtrate was poured into H_2O, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 20:1) to afford the desired product **57** as yellow oil (36.5 mg, 86% yield, >19:1 *Z/E*). The geometry of alkene was assigned by comparison with chemical shift of double bond with known compound.[34]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.20 – 7.11 (m, 1H), 7.10 – 7.05 (m, 2H), 5.56 – 5.50 (m, 2H), 5.46 (q, *J* = 6.9 Hz, 1H), 2.31 – 2.16 (m, 2H), 1.97 – 1.82 (m, 3H), 1.66 – 1.55 (m, 2H), 1.50 (dd, *J* = 6.9, 1.2 Hz, 3H), 1.44 – 1.33 (m, 1H), 1.16 – 1.05 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.0, 128.6, 128.0, 127.0, 126.6, 126.3, 122.5, 46.5, 31.6, 31.3, 28.5, 25.0, 14.7.

HRMS (EI) m/z: [M$^+$] Calcd for $C_{16}H_{20}$ 212.1637; found: 212.1634.

d. Cycloaddition of 33



33 **58**, 88% yield, >19:1 dr

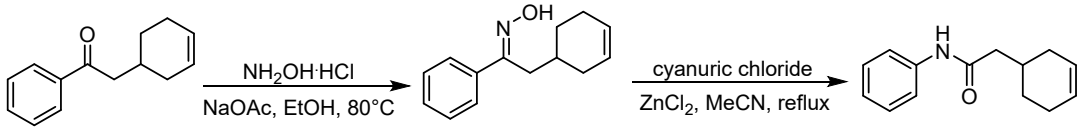
To an oven-dried 10 mL vial equipped with a magnetic stir bar was charged with **33** (0.2 mmol, 1.0 equiv.) and 3-chloroperoxybenzoic acid (0.4 mol, 2.0 equiv.) in dry DCM (4.0 mL) under nitrogen atmosphere. Then the resulting mixture was allowed to react at room temperature for 1 h until it was complete by TLC. After completion of the reaction, the solvent was evaporated under vacuum. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 30:1) to afford the desired product **58** as yellow oil (38.0 mg, 88% yield, >19:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.60 – 7.51 (m, 1H), 7.49 – 7.41 (m, 2H), 3.23 – 3.10 (m, 2H), 2.90 – 2.74 (m, 2H), 2.24 – 2.09 (m, 2H), 2.08 – 1.92 (m, 1H), 1.88 – 1.74 (m, 1H), 1.57 – 1.45 (m, 1H), 1.44 – 1.34 (m, 1H), 1.34 – 1.17 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 137.2, 133.1, 128.6, 128.0, 52.4, 51.7, 45.3, 30.6, 28.9, 25.0, 24.6.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{14}H_{16}O_2Na$ 239.1043; found: 239.1043.

e. Reaction with hydroxylamine and follow-up Beckmann rearrangment



33 **59**, 90% yield, >19:1 *Z/E* **60**, 85% yield

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, NaOAc (0.3 mmol, 1.5 equiv.) and $NH_2OH{\cdot}HCl$ (0.3 mmol, 1.5 equiv.) was added to a solution of **33** (0.2 mmol, 1.0 equiv.) in EtOH (1.5 mL) under nitrogen atmosphere. The resulting mixture was allowed to react at 80 ℃ for 12 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with brine, and the aqueous phase extracted with DCM. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 10:1) to afford the desired product **59** as white solid (38.7 mg, 90% yield, >19:1 *Z/E*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H), 7.49 – 7.32 (m, 3H), 5.67 – 5.55 (m, 2H), 2.93 – 2.79 (m, 2H), 2.12 – 1.89 (m, 4H), 1.87 – 1.69 (m, 2H), 1.46 – 1.30 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 136.1, 129.2, 128.6, 126.9, 126.5, 126.1, 32.4, 31.7, 31.6, 28.9, 25.1.

HRMS (ESI) m/z: [M+H^+] Calcd for $C_{14}H_{18}ON$ 216.1383; found: 216.1379.

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, **59** (0.2 mmol, 1.0 equiv.), cyanuric chloride (5 mol%) and $ZnCl_2$ (5 mol%) was added in MeCN (2.0 mL) under nitrogen atmosphere. The resulting mixture was allowed to react at 85 ℃ for 2 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with saturated aqueous sodium hydrogen carbonate, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 10:1) to afford the desired product **60** as white solid (38.7 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.34 (s, 1H), 7.23 (t, J = 7.9 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 5.66 – 5.52 (m, 2H), 2.30 – 2.20 (m, 2H), 2.17 – 2.07 (m, 2H), 2.05 – 1.96 (m, 2H), 1.81 – 1.64 (m, 2H), 1.32 – 1.23 (m, 1H).

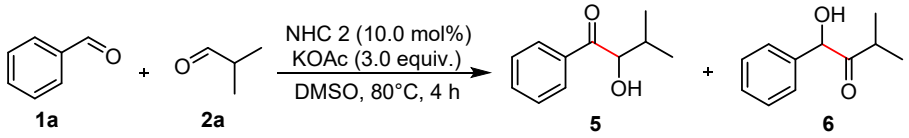
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 137.9, 129.0, 127.0, 125.7, 124.3, 119.9, 44.6, 31.3, 31.2, 28.5, 24.7.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{14}H_{17}NONa$ 238.1202; found: 238.1200.

G. Mechanistic studies:

a. Investigations of intermediate and role for NHC

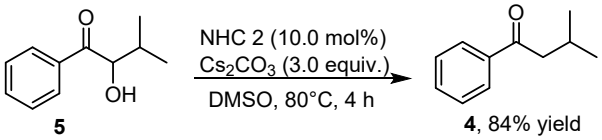
Preparation of intermediate 5 and 6



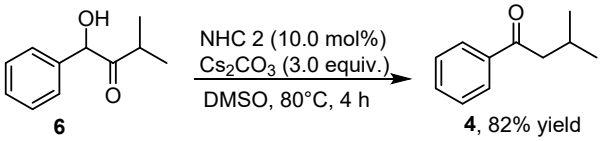
To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, were added NHC 2 (6.9 mg, 10.0 mol%) and KOAc (58.9 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After benzaldehyde (21.2 mg, 0.2 mmol, 1.0 equiv.), isobutyraldehyde (43.3 mg, 0.6 mmol, 3.0 equiv.) and anhydrous DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography to afford the desired intermediate **5** (19.6 mg, 55% yield) and intermediate **6** (14.2 mg, 40% yield).

intermediate **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.75 (m, 2H), 7.64 – 7.53 (m, 1H), 7.50 – 7.43 (m, 2H), 4.96 (d, J = 2.5 Hz, 1H), 3.62 (s, 1H), 2.19 – 2.04 (m, 1H), 1.15 (d, J = 6.9 Hz, 3H), 0.63 (d, J = 6.8 Hz, 3H). Spectroscopic data are in accordance with those described in literature.[35]

intermediate **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 3H), 7.35 – 7.30 (m, 2H), 5.24 (s, 1H), 2.80 – 2.65 (m, 1H), 1.16 (d, J = 7.0 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H). Spectroscopic data are in accordance with those described in literature.[36]

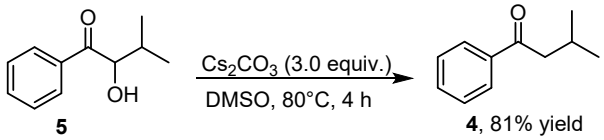


To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, were added NHC 2 (6.9 mg, 10.0 mol%) and Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After intermediate **5** (35.6 mg, 0.2 mmol, 1.0 equiv.) and anhydrous DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography to afford the desired product **4** (27.2mg, 84% yield).

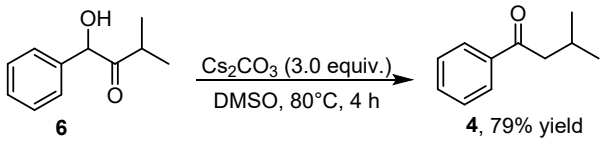


To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, were added NHC 2 (6.9 mg, 10.0 mol%) and Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After intermediate **6** (35.6 mg, 0.2 mmol, 1.0 equiv.) and anhydrous DMSO

(1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography to afford the desired product **4** (26.6 mg, 82% yield).



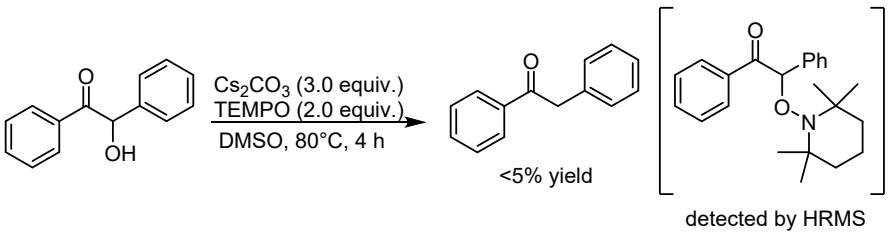
To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, was added Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After intermediate **5** (35.6 mg, 0.2 mmol, 1.0 equiv.) and anhydrous DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography to afford the desired product **4** (26.3 mg, 81% yield).



To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, was added Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After intermediate **6** (35.6 mg, 0.2 mmol, 1.0 equiv.) and anhydrous DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was purified by silica gel chromatography to afford the desired product **4** (25.6 mg, 79% yield).

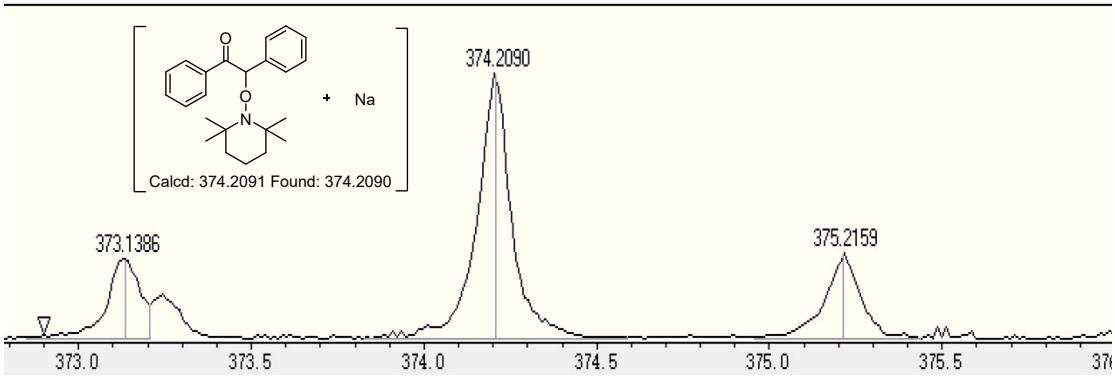
Conclusion: The above results indicated that the α-hydroxy ketones could be the intermediate of reaction and NHC catalyst might not be involved in the dehydroxylation process.

b. Radical probing experiments



To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, were added Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) (31.7 mg, 0.2 mmol, 2.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After 2-hydroxy-1,2-diphenylethan-1-one (42.4 mg, 0.2 mmol, 1.0 equiv.) and anhydrous DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then was quenched with brine, and

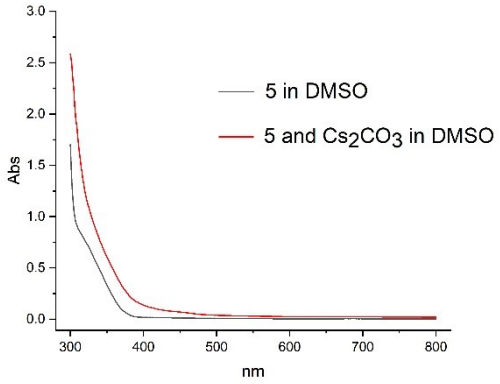
the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The mixture was detected by HRMS (see below).

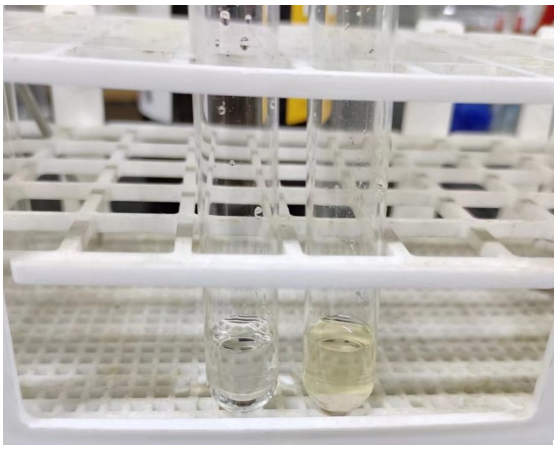


Conclusion: This study shows that the presence of the radical scavenger such as TEMPO are added to the reaction, only trace amount of desired product was observed, along with the TEMPO-adduct detected by HRMS, which suggesting that the reaction likely proceeded through a radical intermediate.

c. UV-vis spectroscopic measurement

UV-vis absorption studies were performed in Shimadzu (UV-1700) instrument using a 0.05M solution of 5 (0.015 mmol, 1.0 equiv.) in DMSO (0.3 mL) was treated with Cs_2CO_3 (3.0 equiv.), stirred at 80 ℃ for 5 min and the spectra were recorded from 300 to 800 nm.



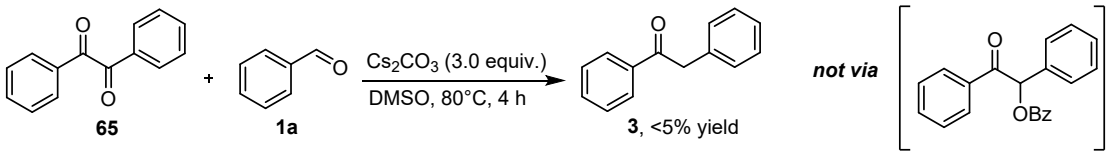


left: **5** in DMSO

Figure **S1**. **UV-vis spectroscopic data**

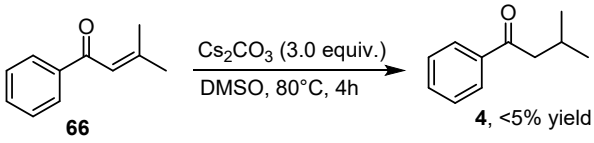
Conclusion: This study shows that the UV-vis spectroscopic measurements on various combination of **5** and Cs_2CO_3 in DMSO showed a red shift of absorption and the color change of this mixture was also observed, which indicating that an electron donor-acceptor (EDA) complex is proposed to form.

d. Investigations of dehydroxylation pathways



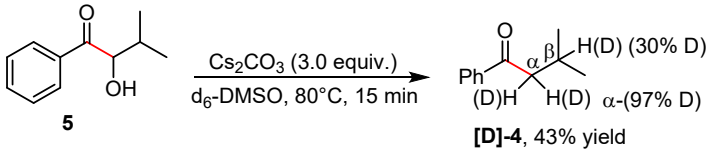
To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, was added Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After benzil **65** (42.0 mg, 0.2 mmol, 1.0 equiv.), benzaldehyde (21.2 mg, 0.2 mmol, 1.0 equiv.) and anhydrous DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then

quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was analyzed by ^1H NMR, and product **3** was not detected. **Conclusion:** This study shows that the product is not derived from activated hydroxy group.



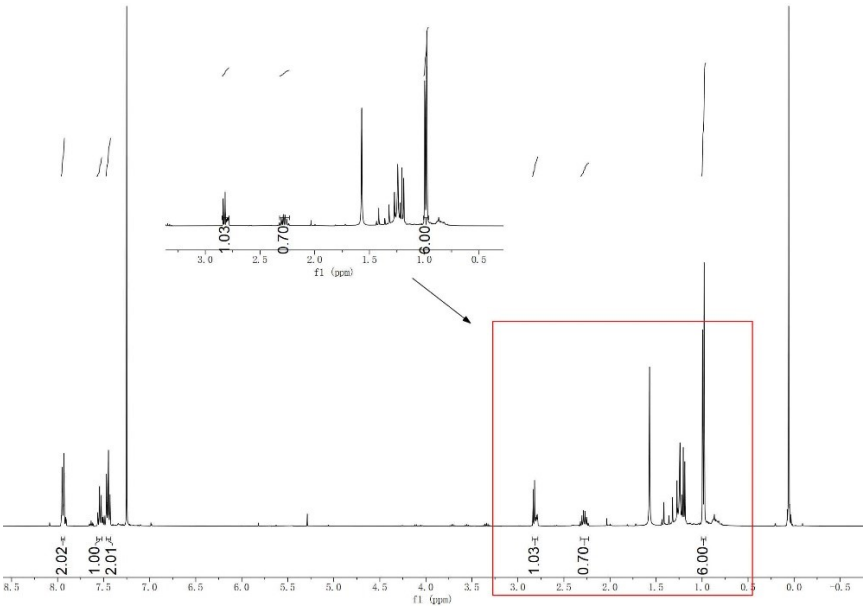
To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, was added Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After 3-methyl-1-phenylbut-2-en-1-one (32.0 mg, 0.2 mmol, 1.0 equiv.) and anhydrous DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 4 h. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was analyzed by ^1H NMR, and product **4** was not detected. **Conclusion:** This study shows that the product is not derived from unsaturated ketone.

e. Isotope labeling experiments



To an oven-dried 10 mL round-bottomed flask equipped with a stir bar, was added Cs_2CO_3 (192.0 mg, 0.6 mmol, 3.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After intermediate **5** (35.6 mg, 0.2 mmol, 1.0 equiv.) and anhydrous d_6-DMSO (1.0 mL) were added. The reaction mixture was warmed at 80 ℃ for 15 min. The reaction mixture was monitored by TLC. After completion, the mixture was cooled to room temperature and filtered, then quenched with brine, and the aqueous phase extracted with EA. Thereafter, the organic layer was dried over anhydrous $MgSO_4$, concentrated. The residue was analyzed by ^1H NMR, and was detected in the reaction except that 43% yield (α-H 97% D, β-H 30% D) of **[D]-4**.

Conclusion: This study shows that one proton of desired product was likely to derive from the solvent.



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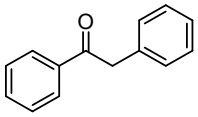

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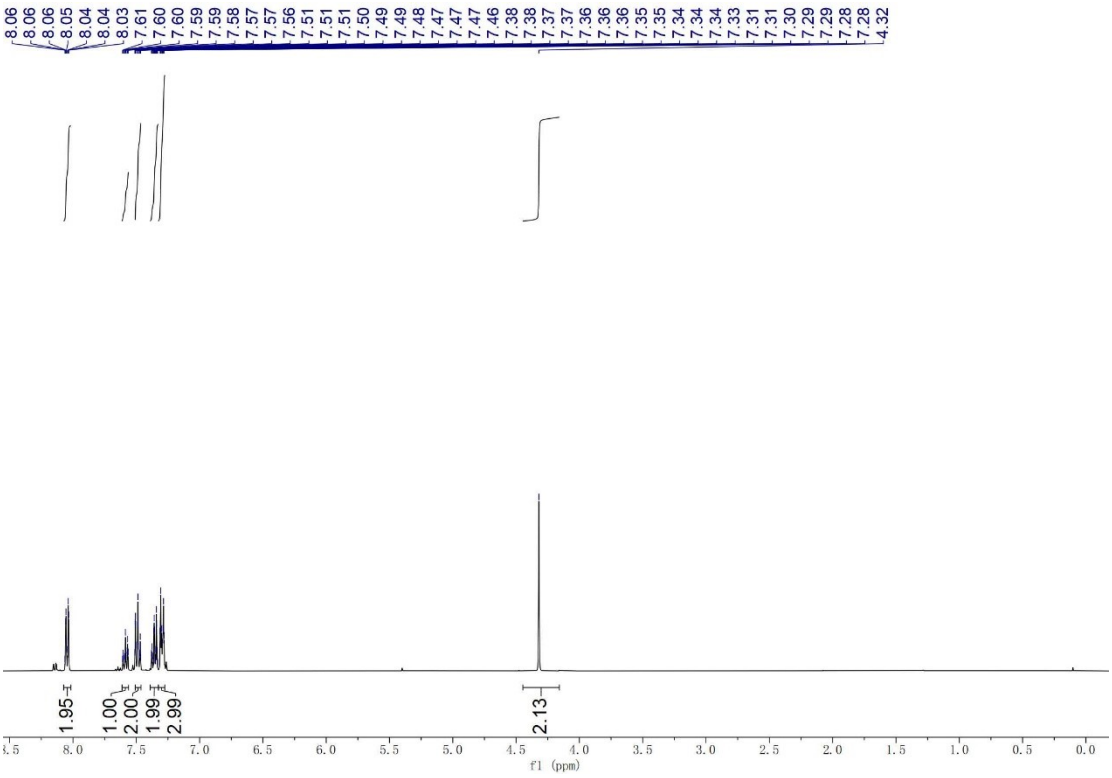

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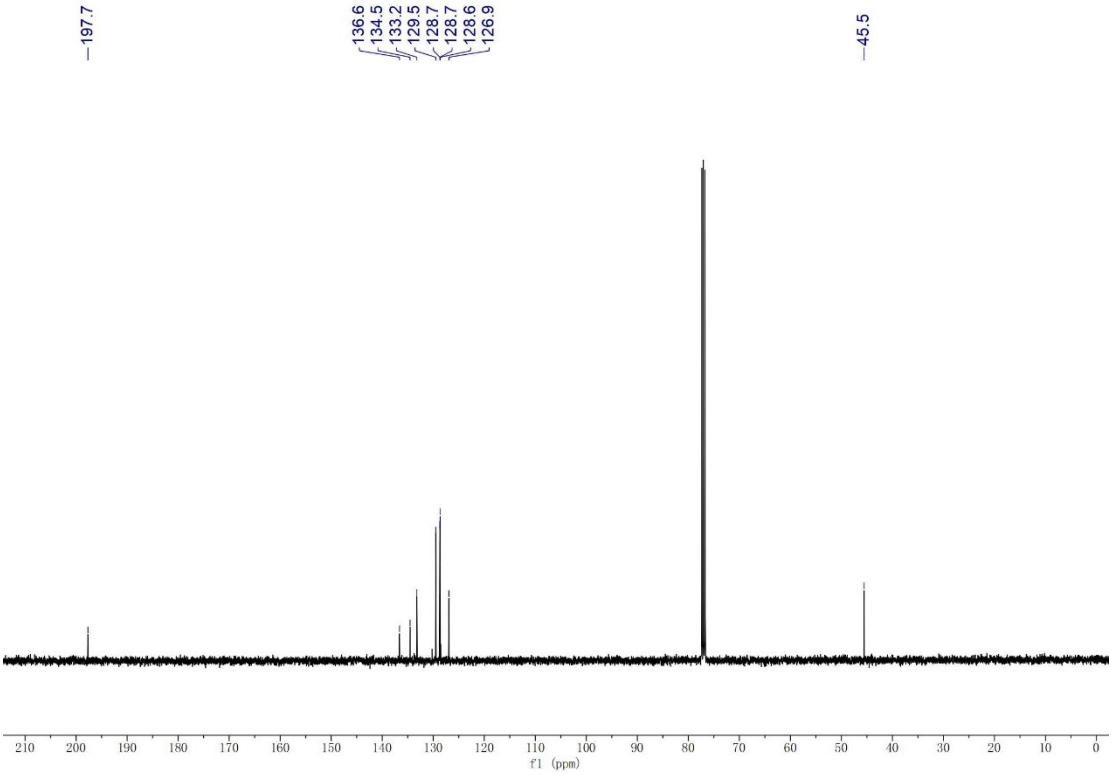

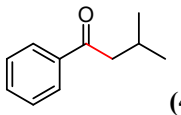

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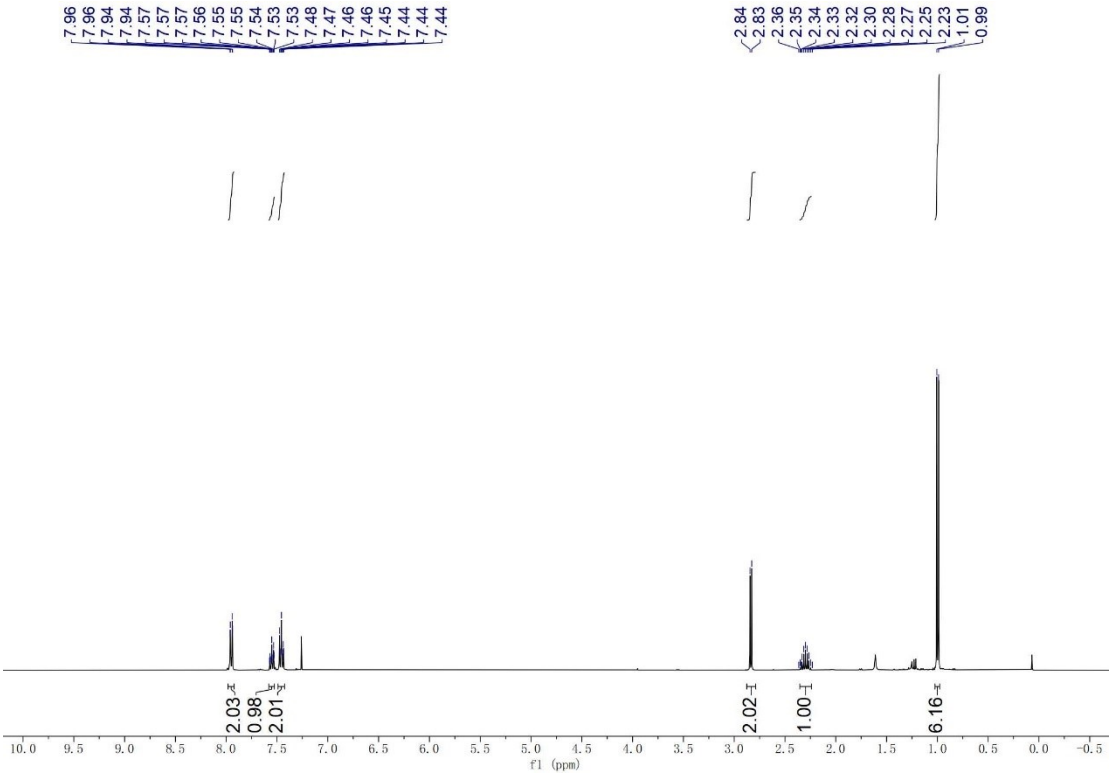

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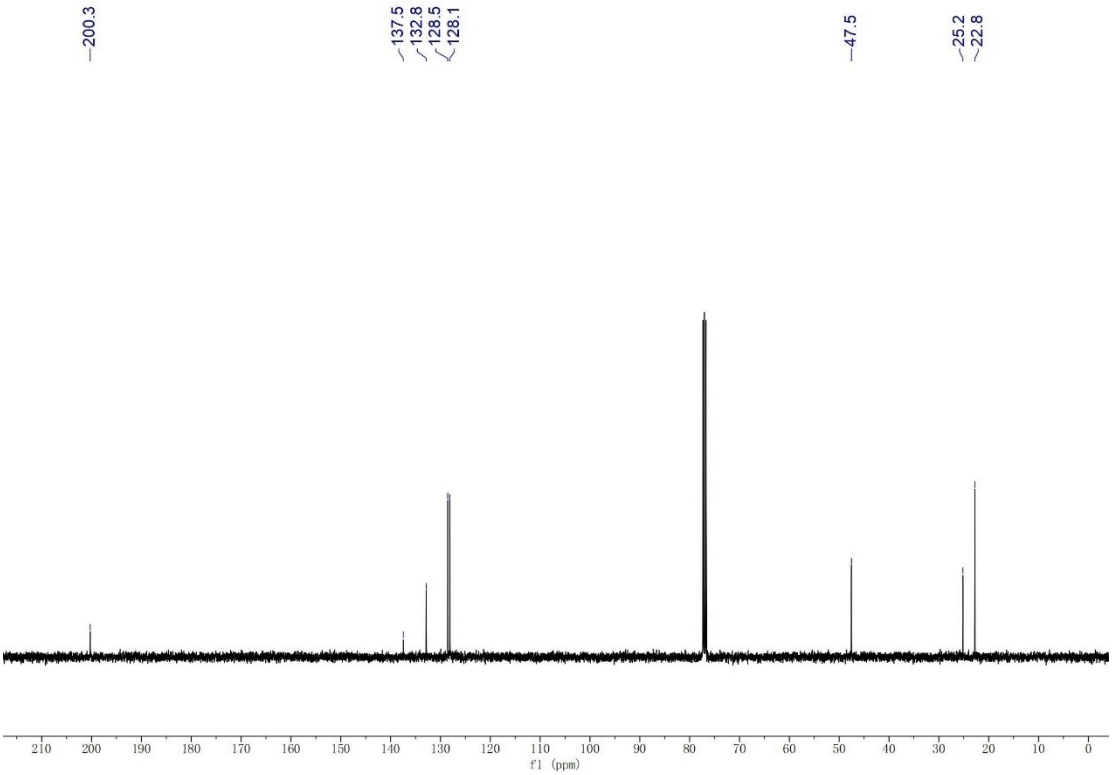

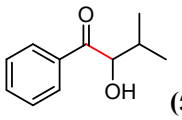

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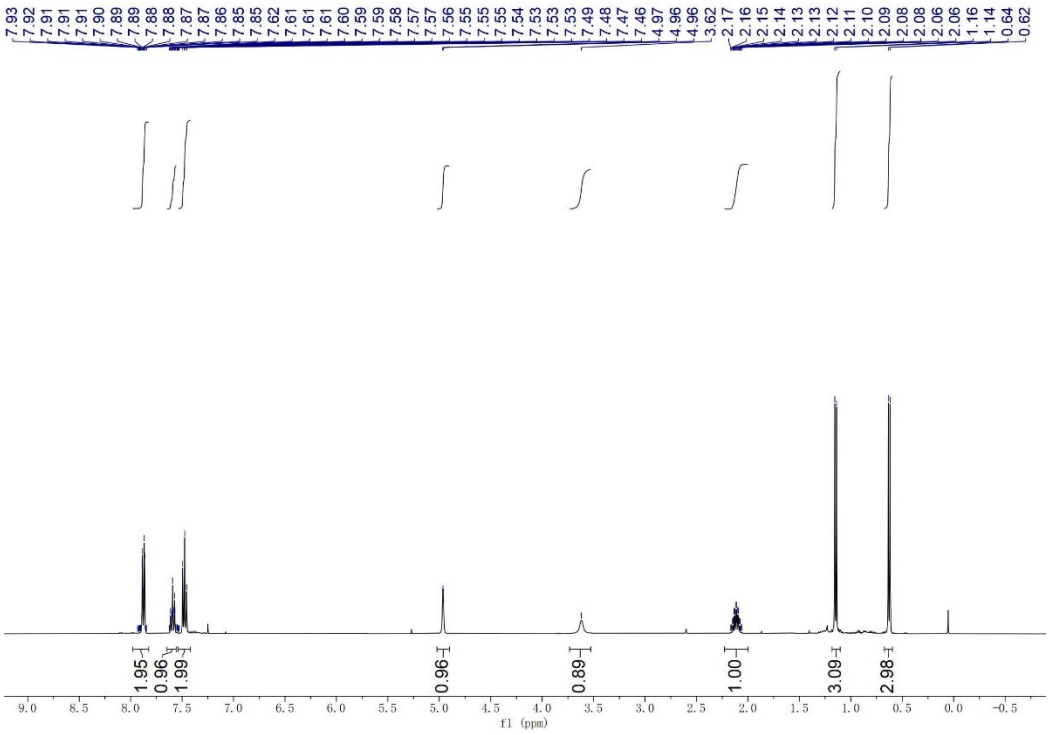

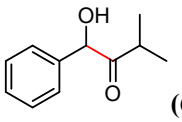

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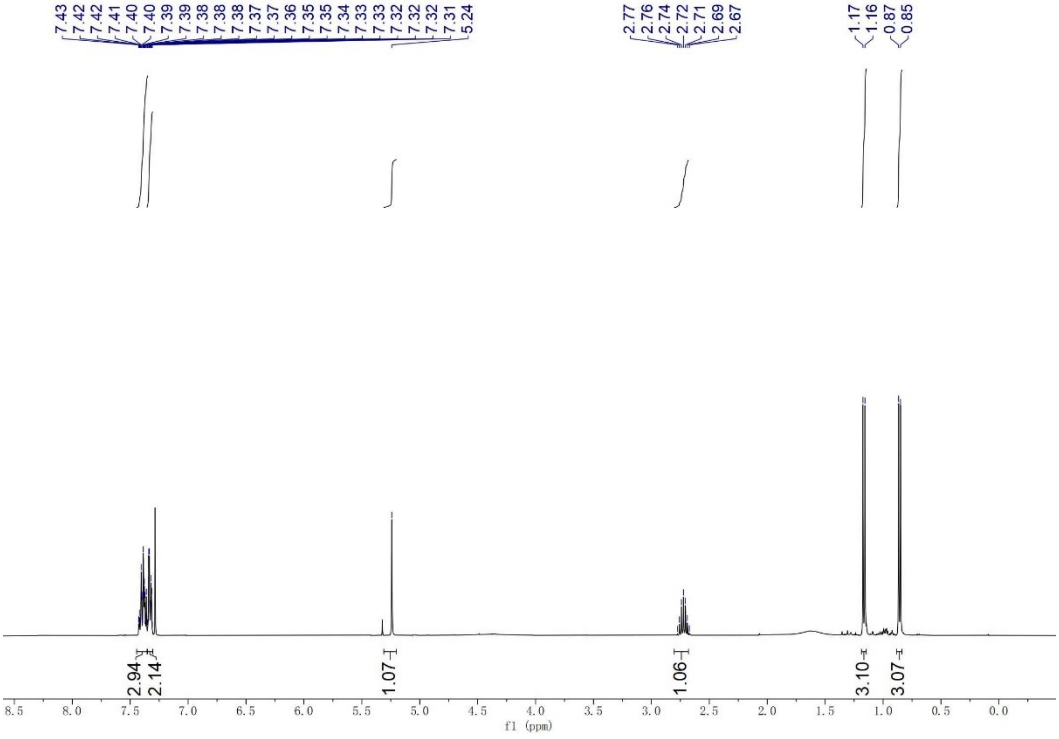

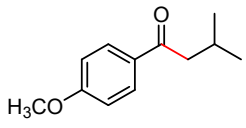

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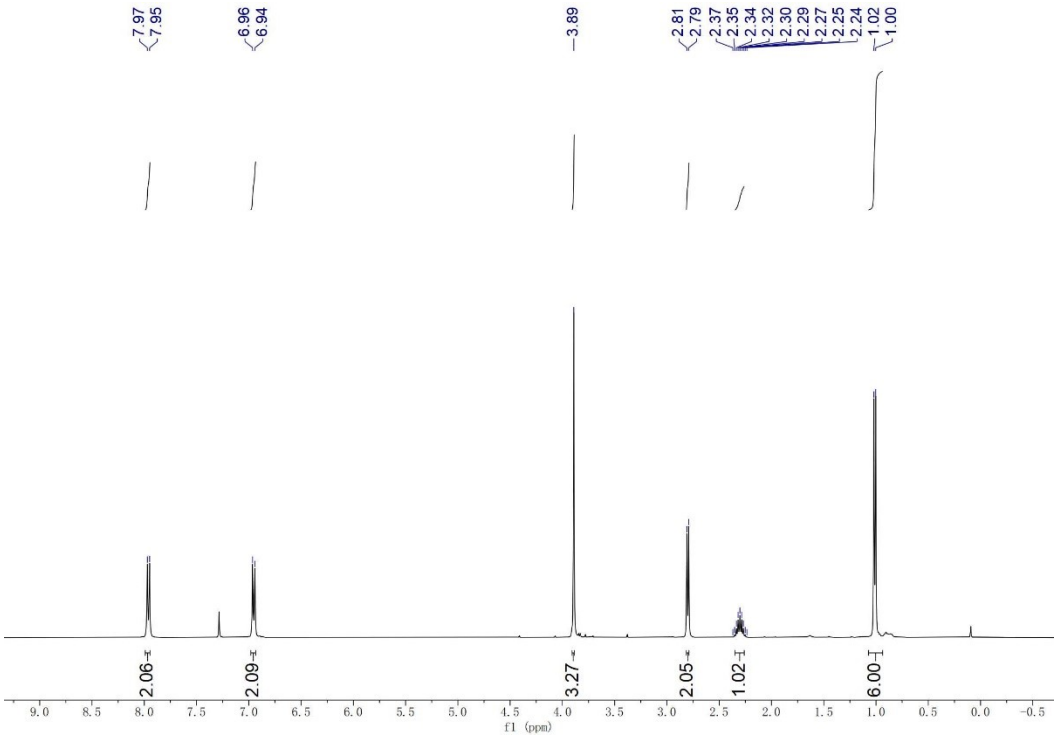

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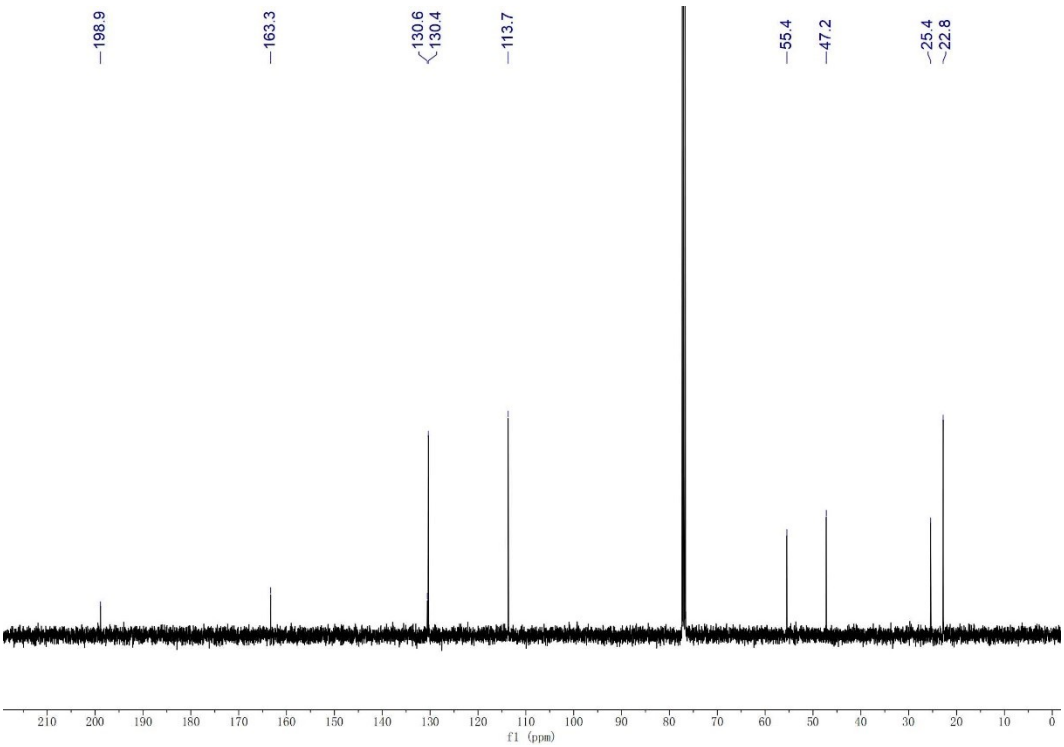

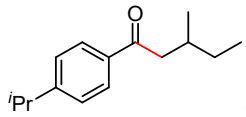

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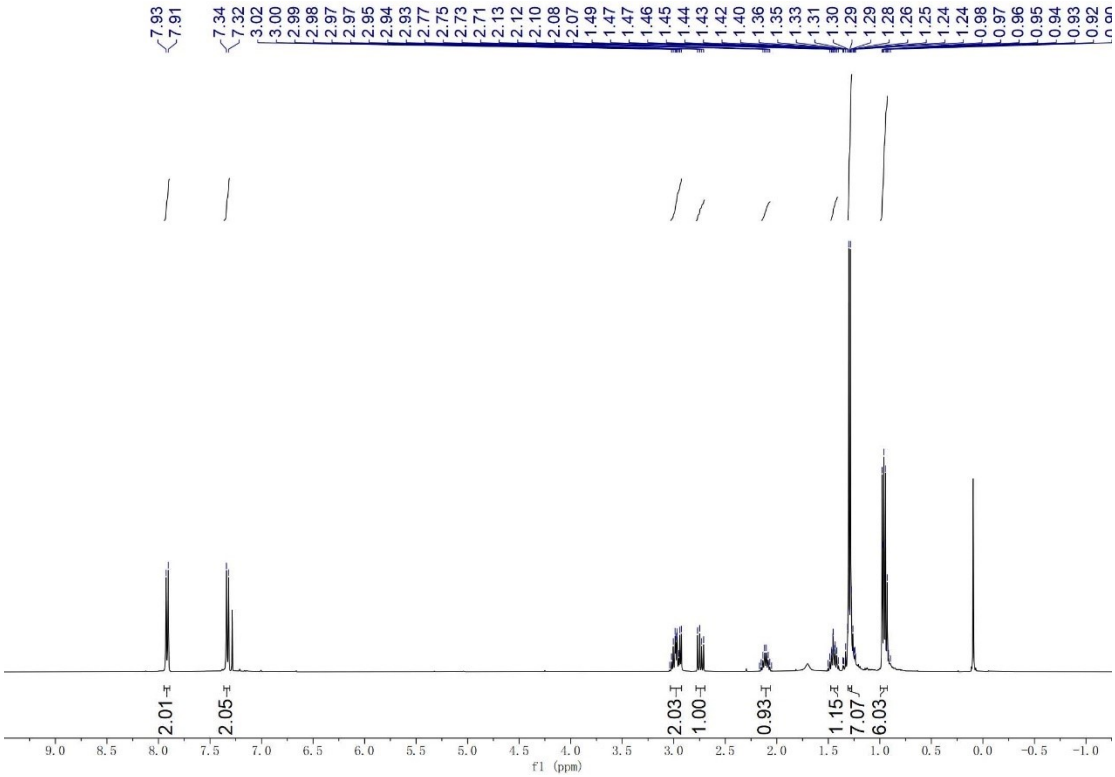

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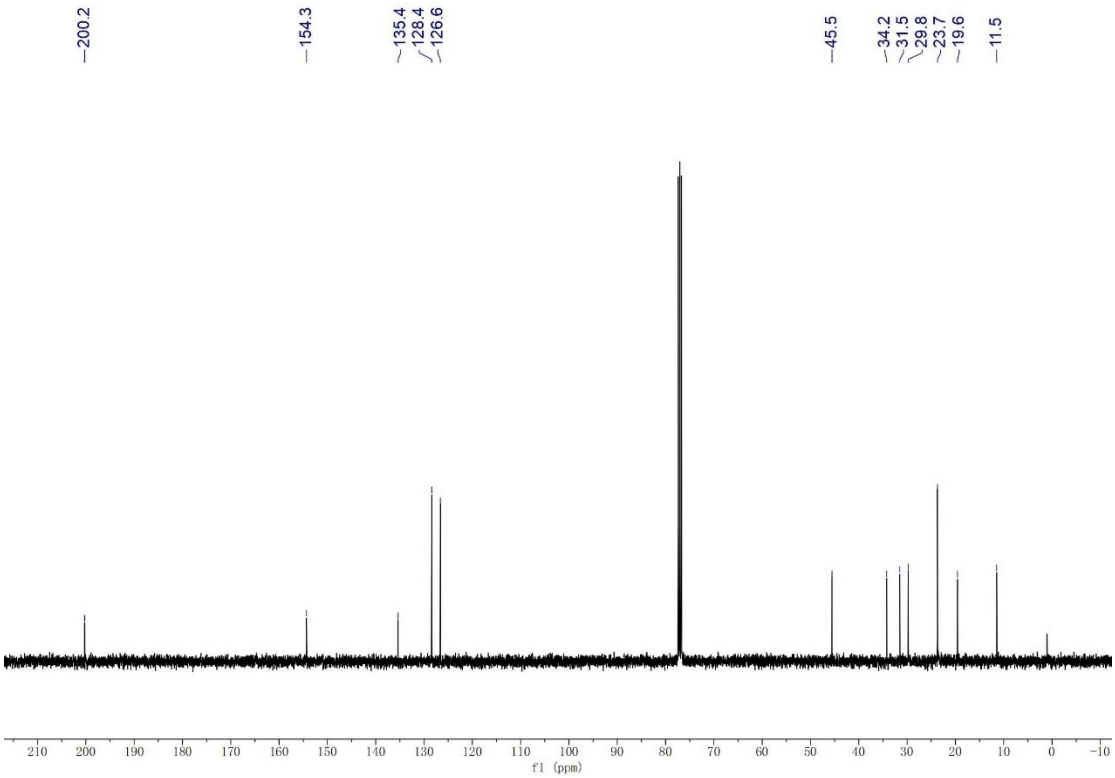

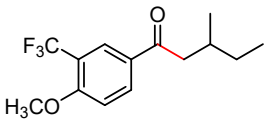

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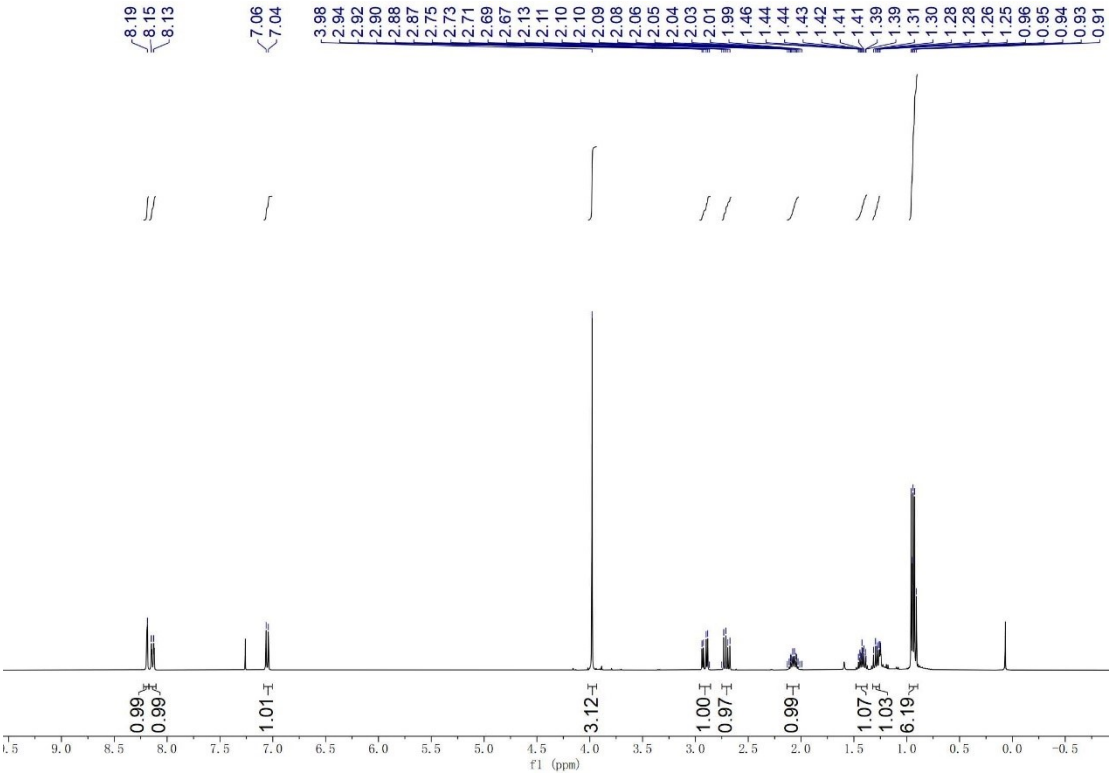

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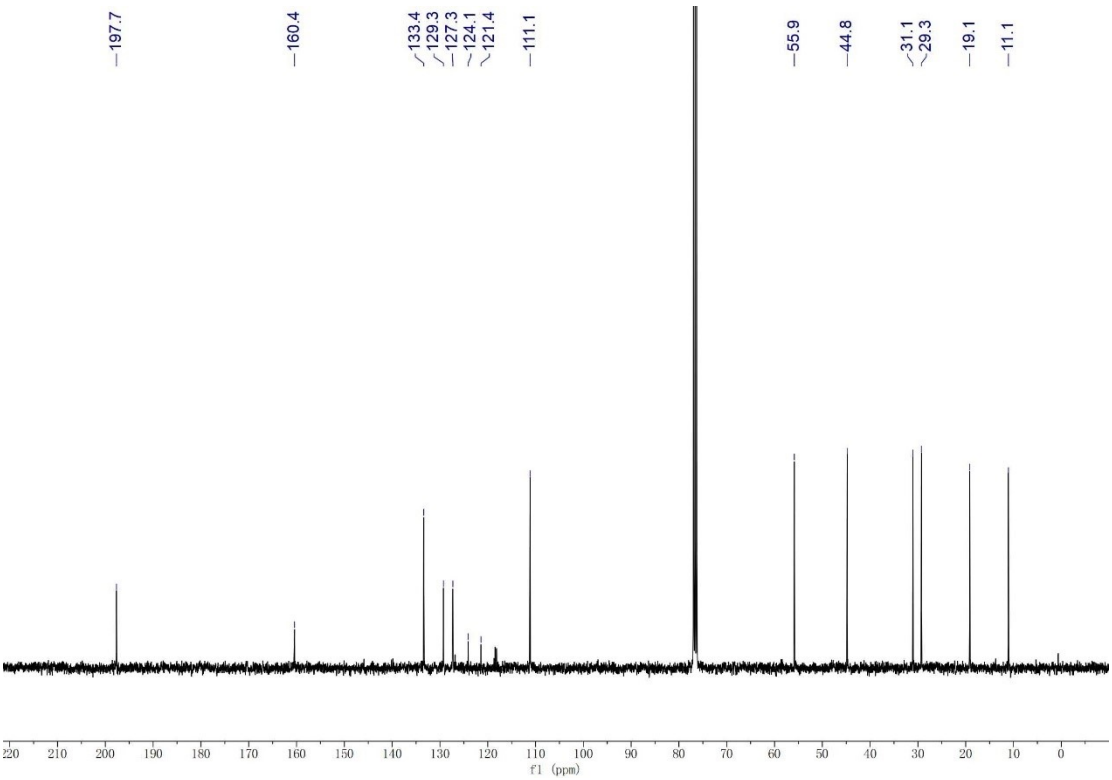

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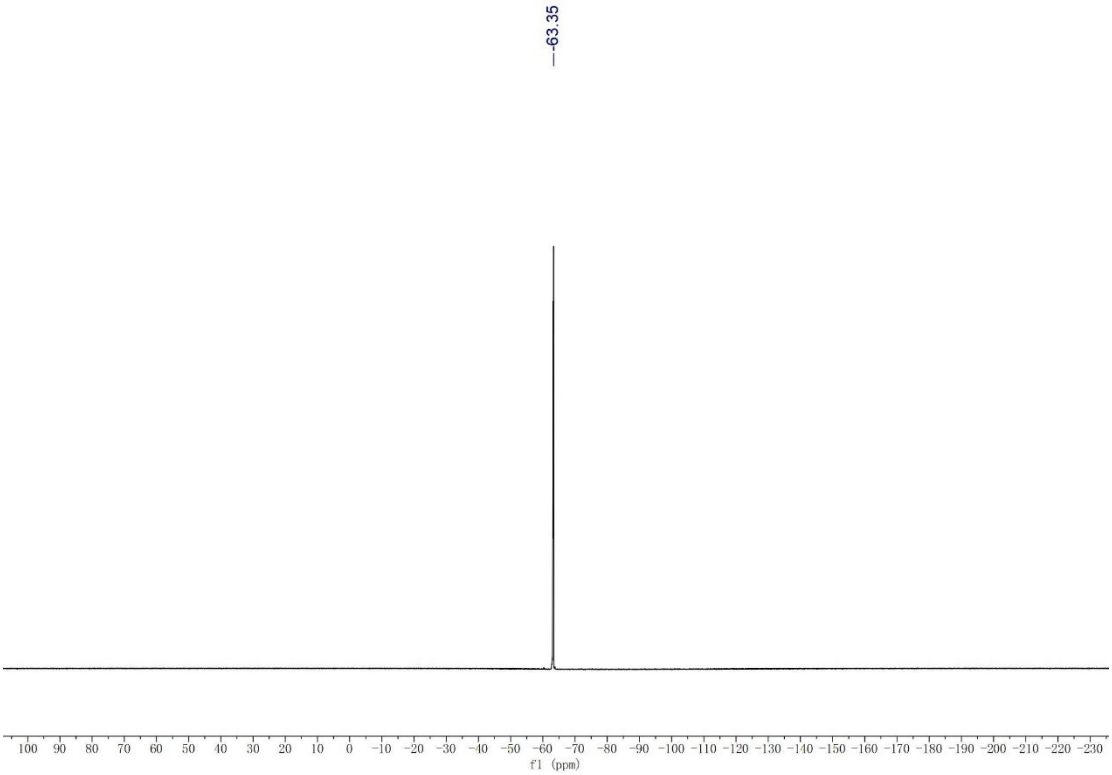

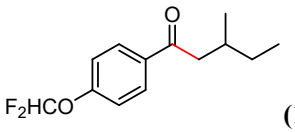

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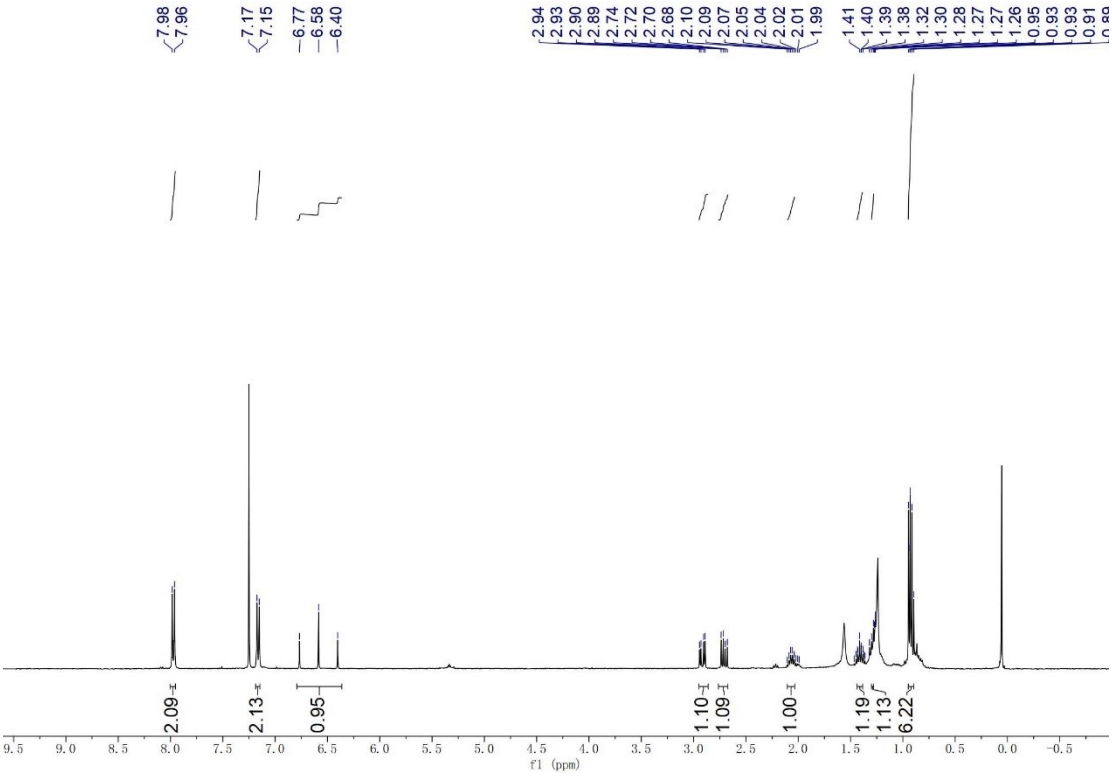

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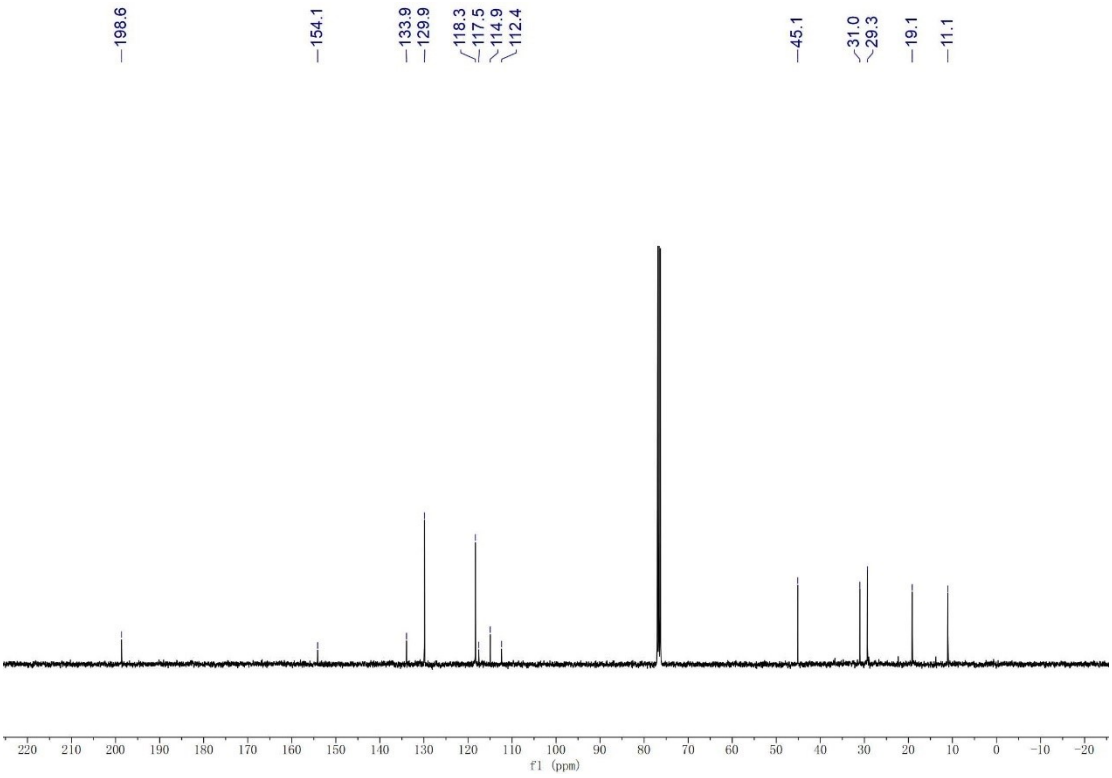

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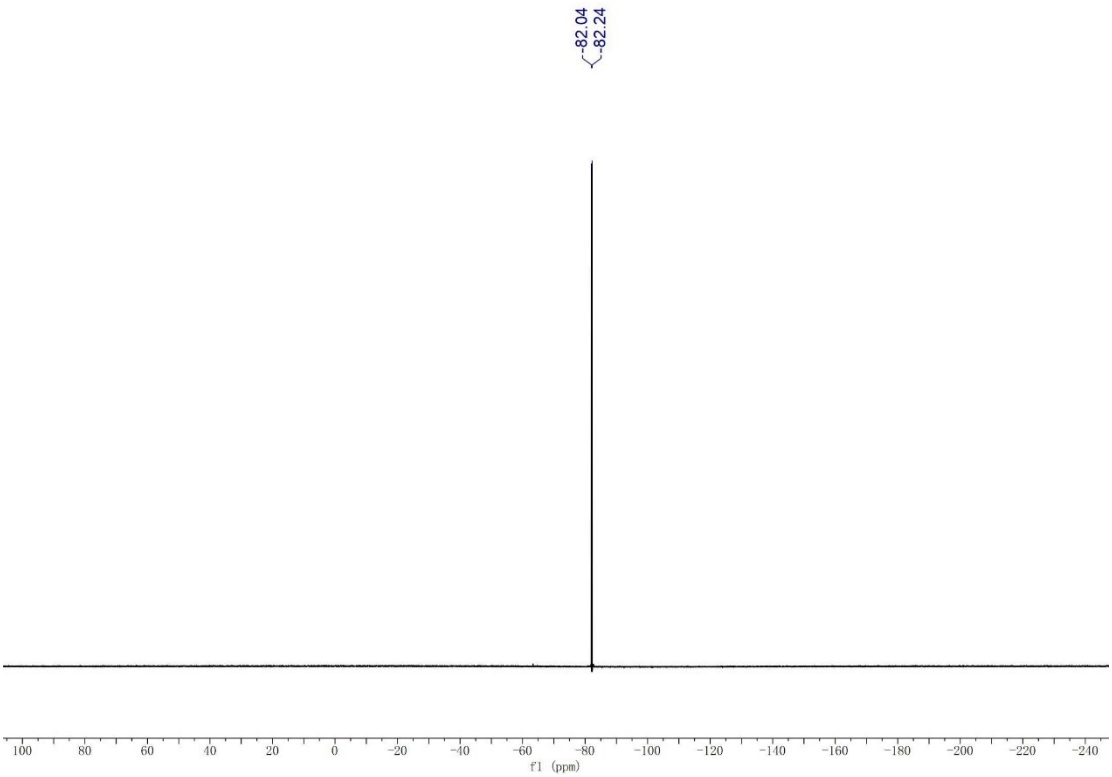

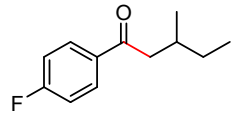

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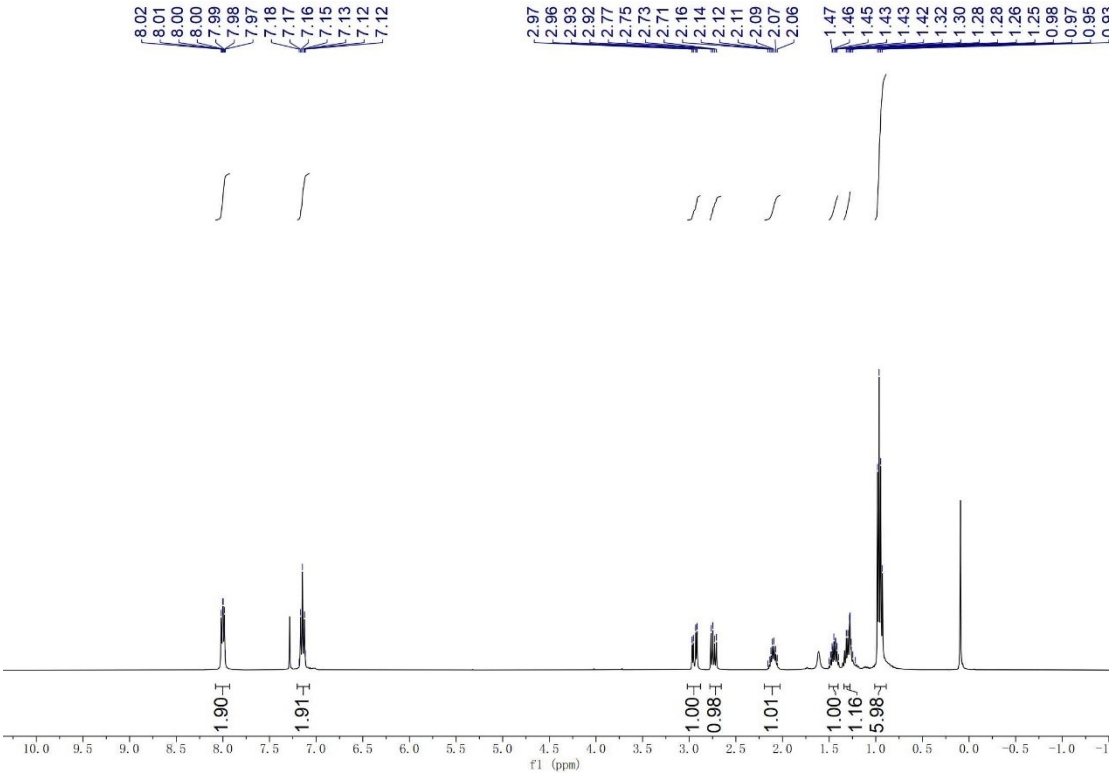
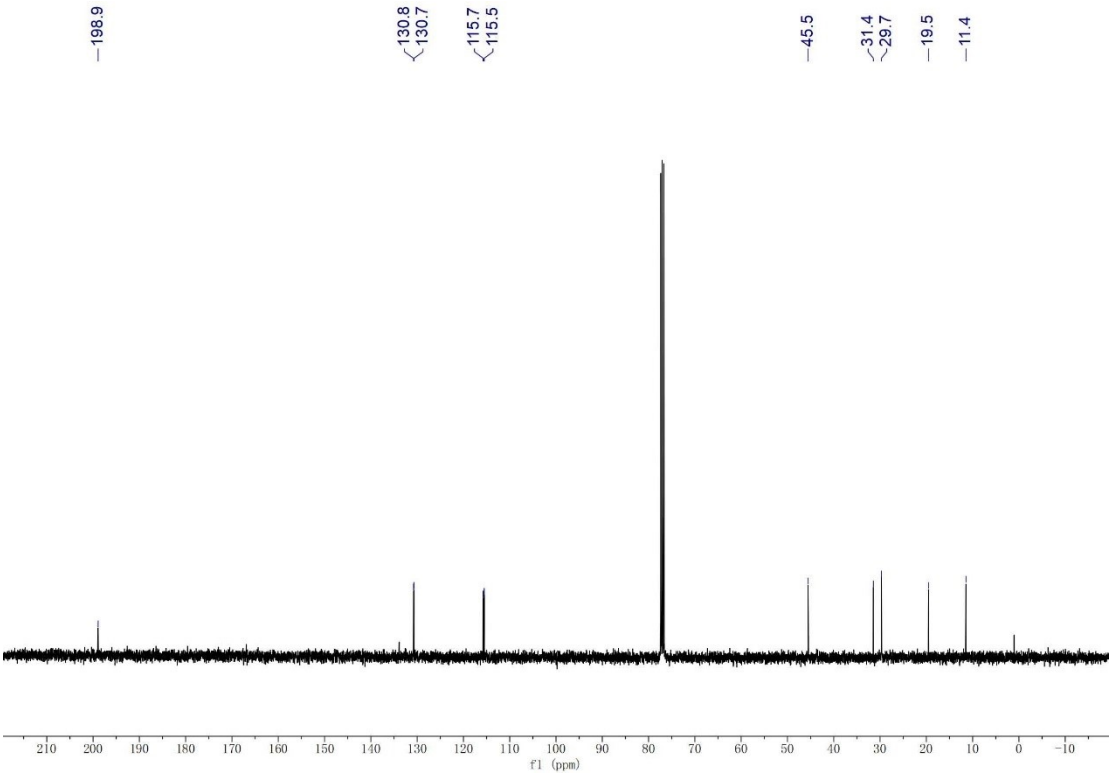


100 MHz in $CDCl_3$



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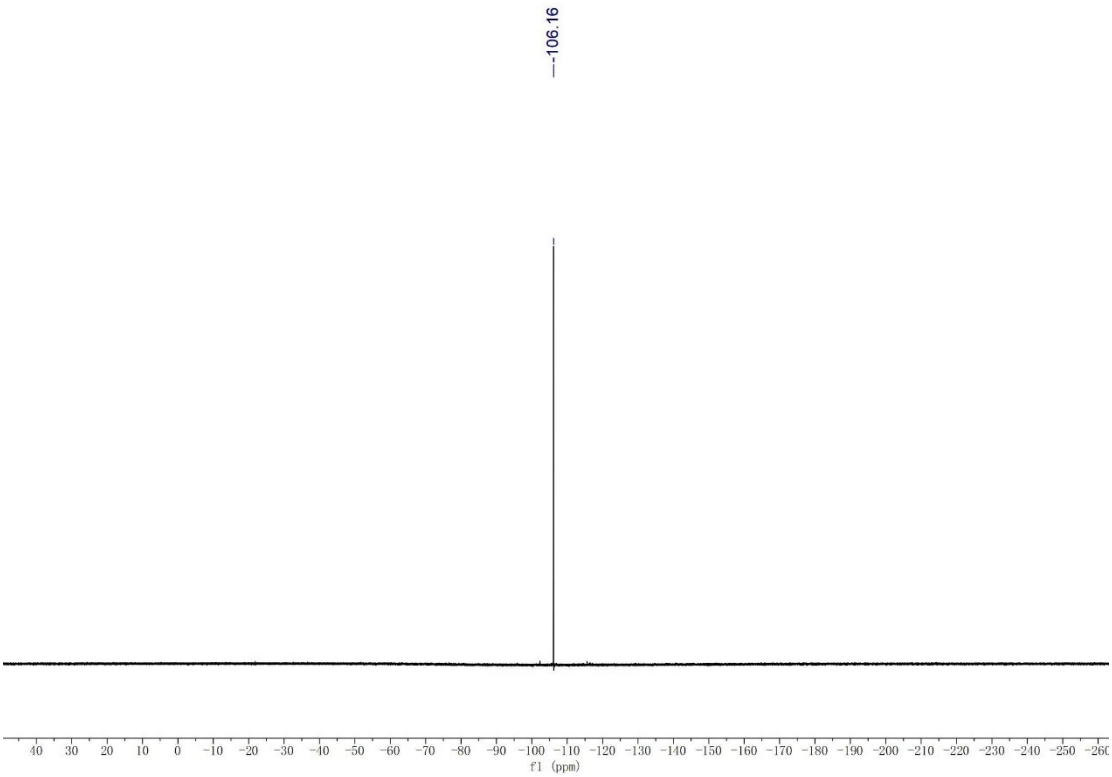

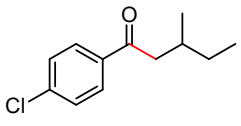

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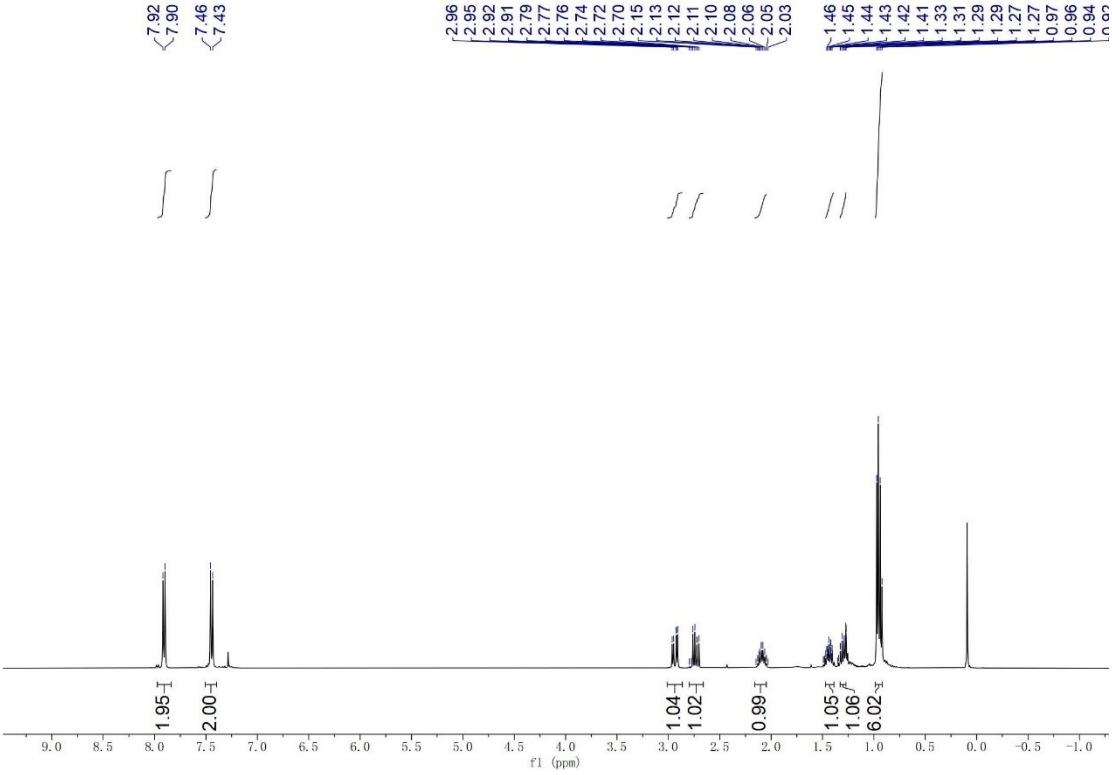

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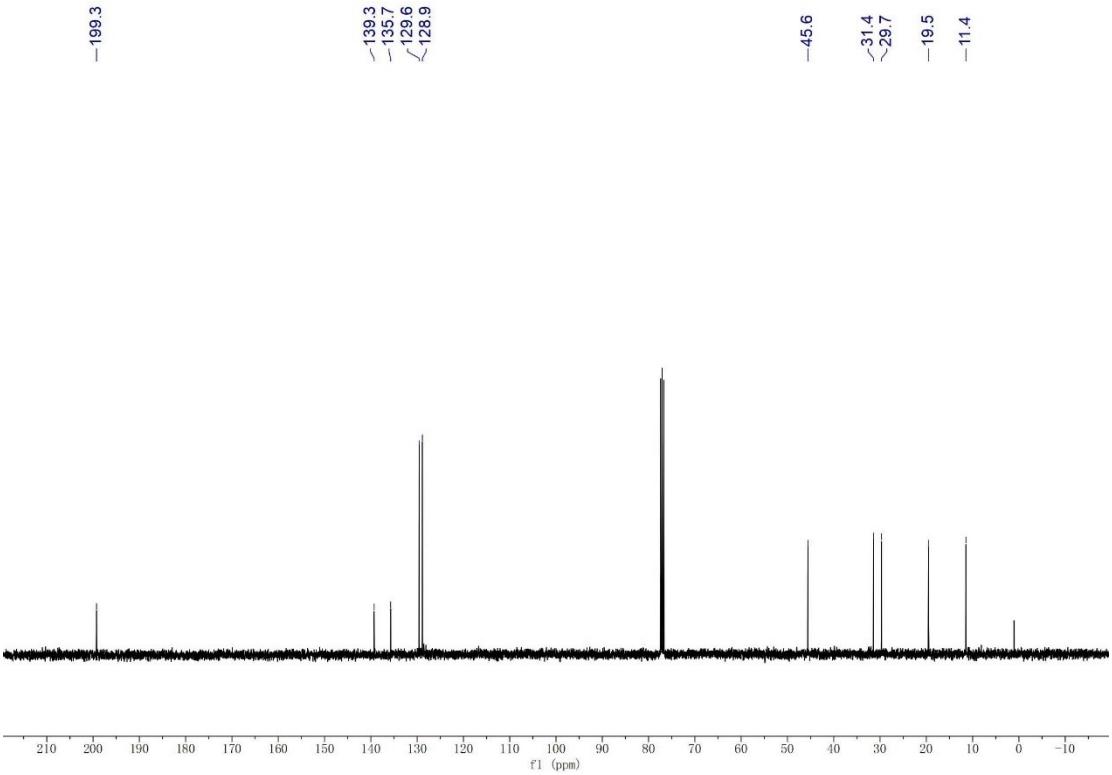
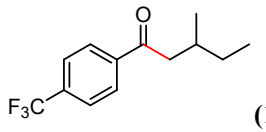
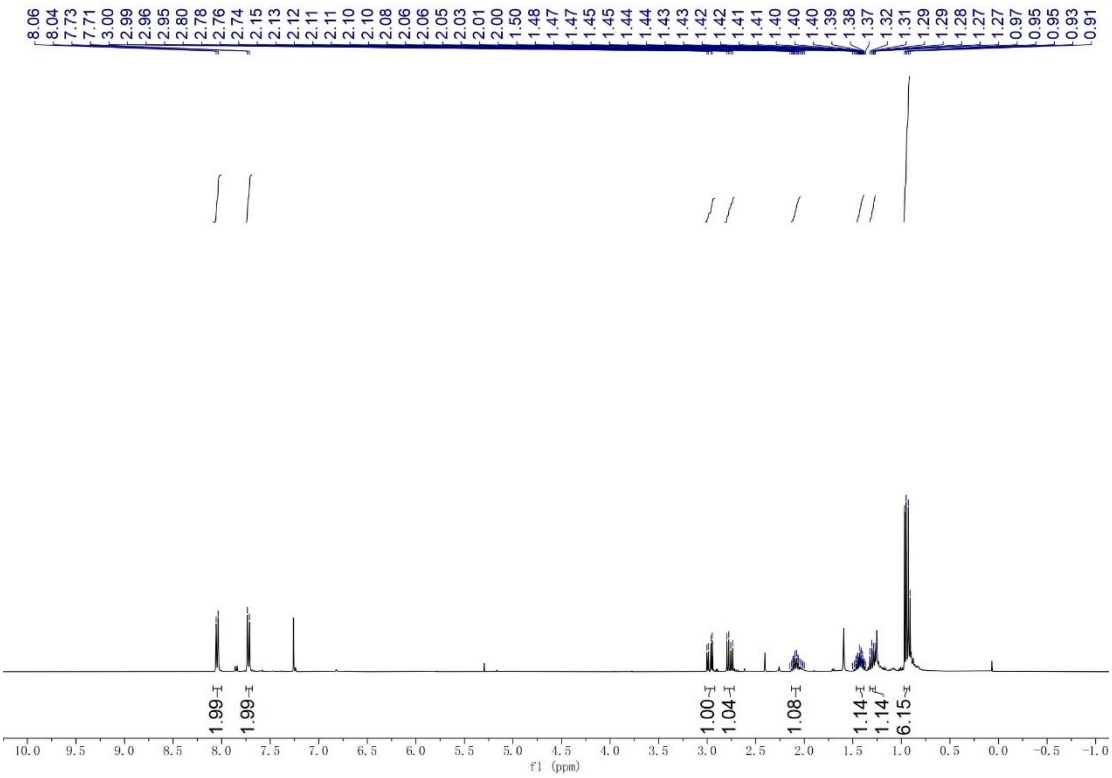


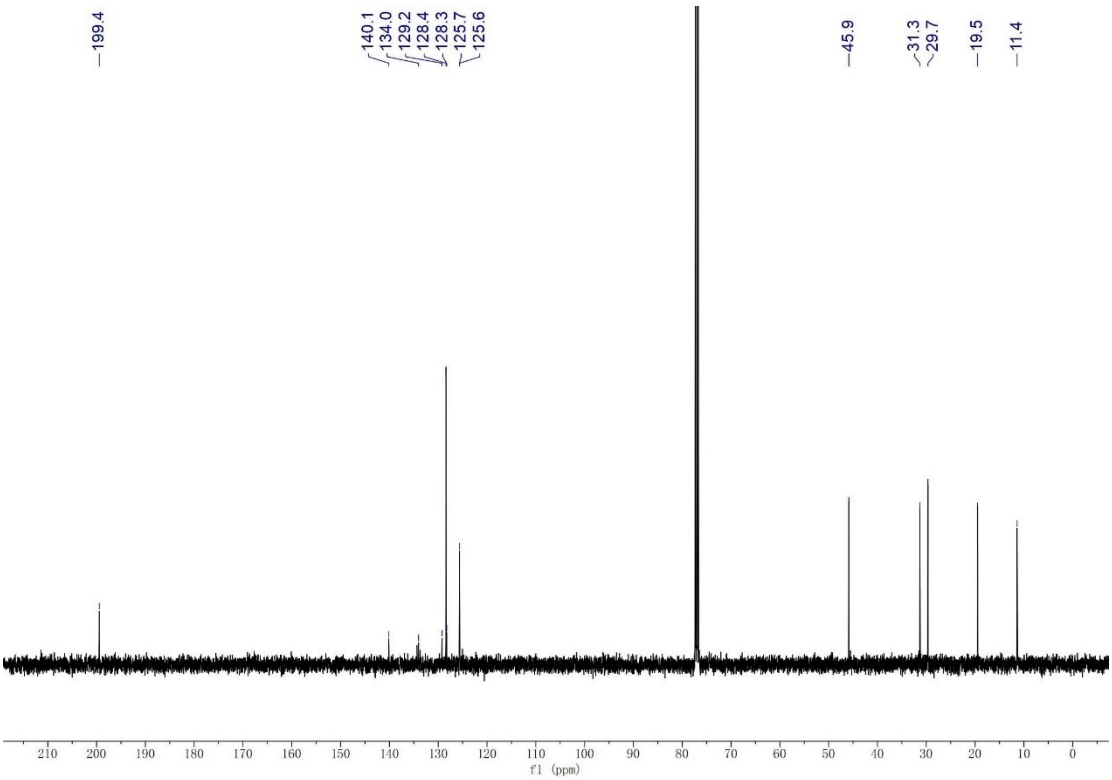


(13)

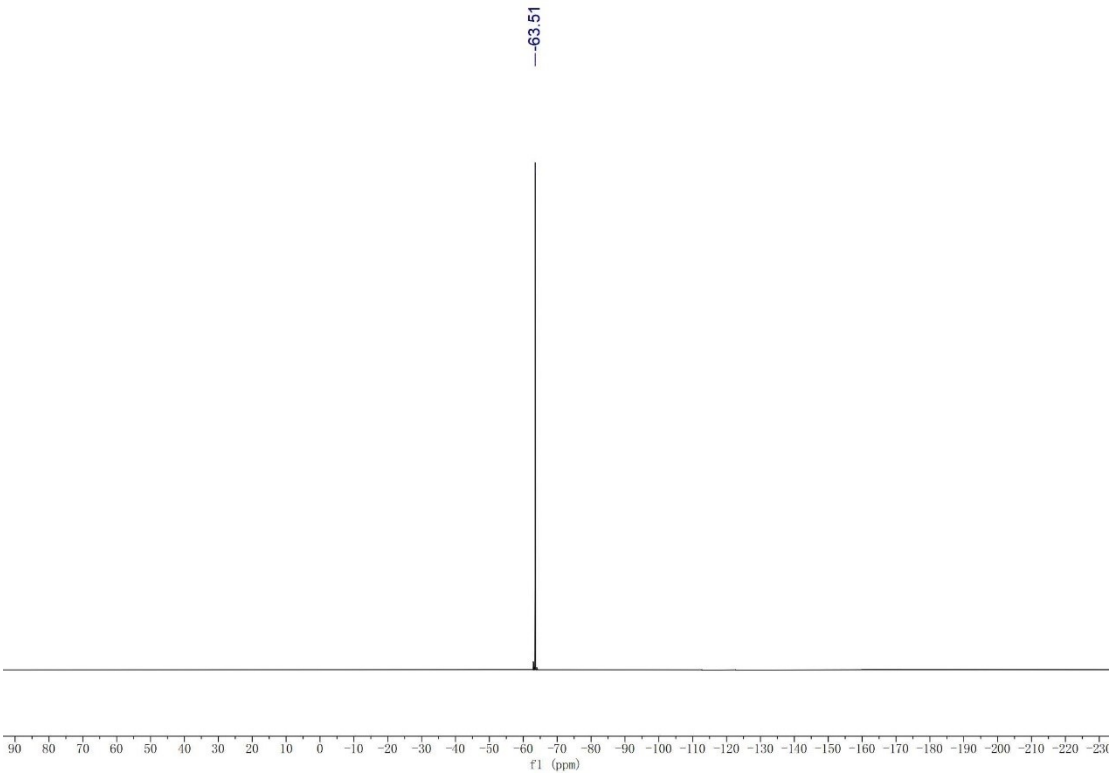
400 MHz in $CDCl_3$

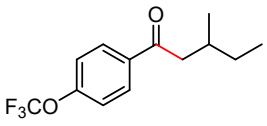


100 MHz in $CDCl_3$



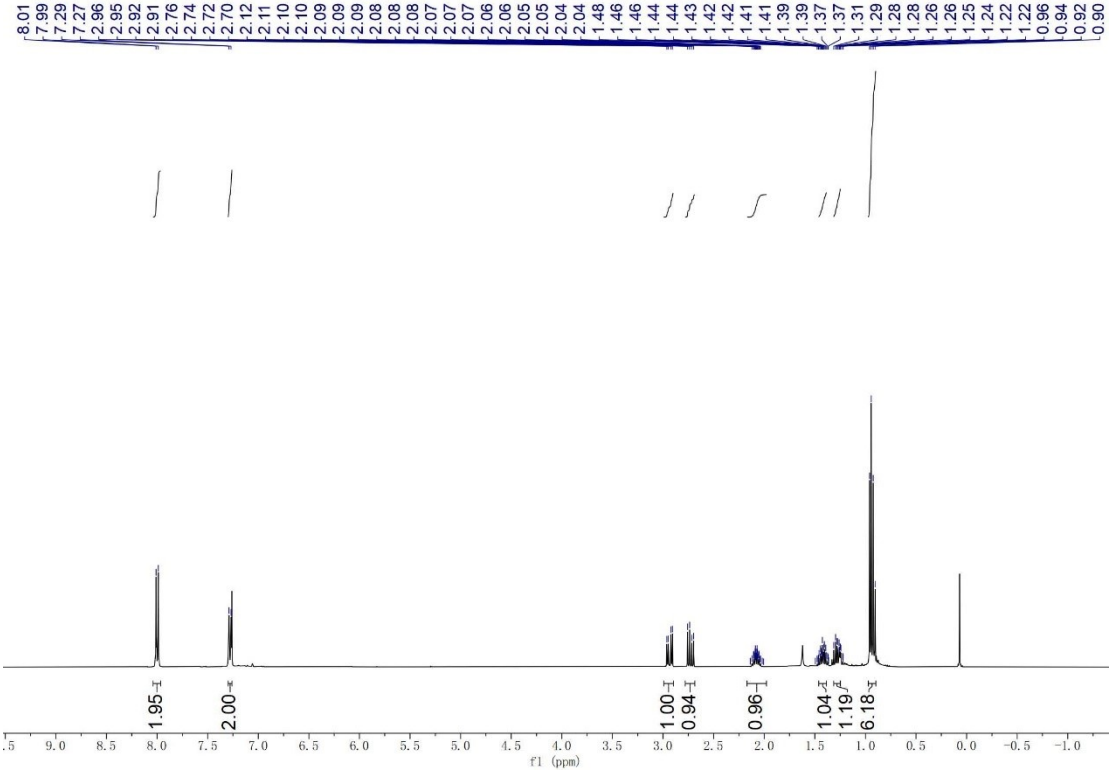
376 MHz in $CDCl_3$



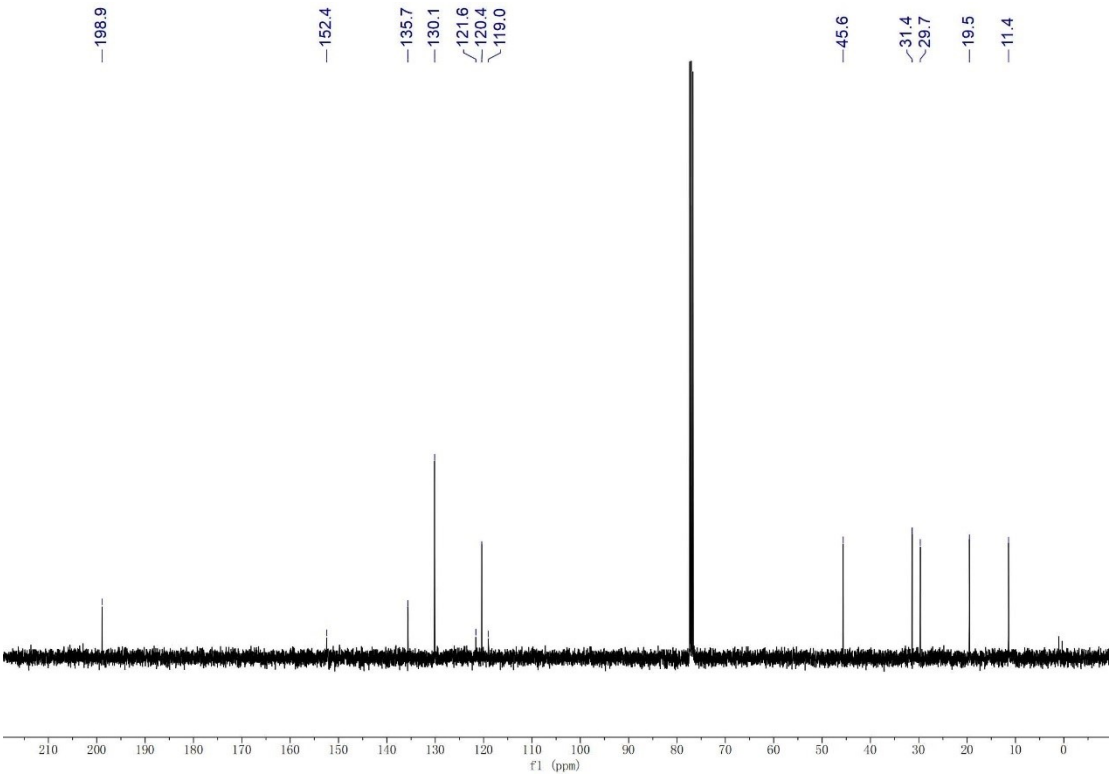


(14)

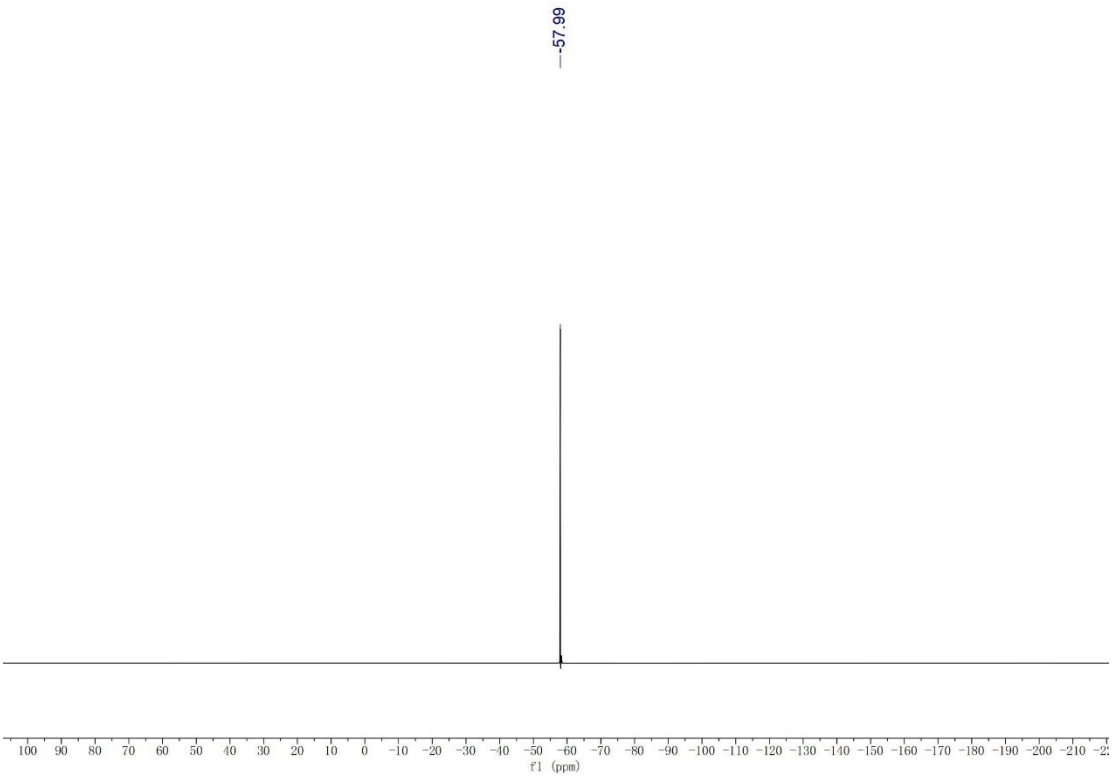
400 MHz in $CDCl_3$

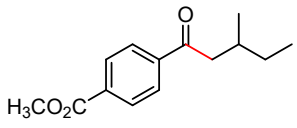


100 MHz in $CDCl_3$



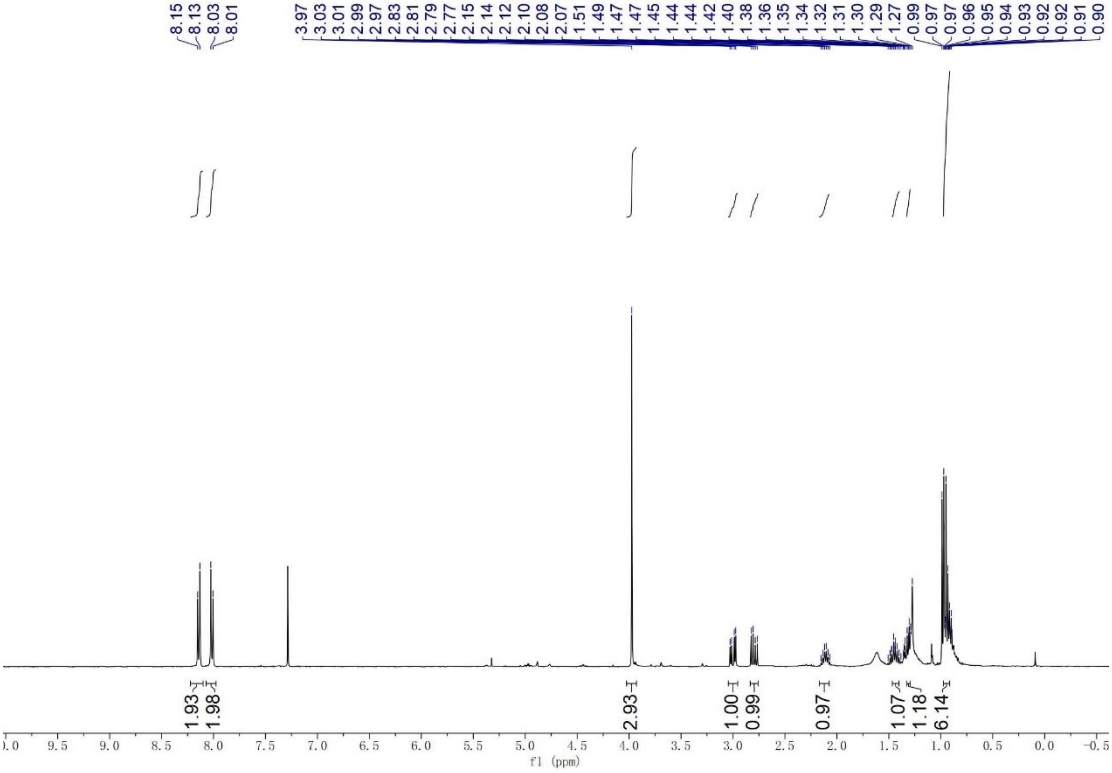
376 MHz in $CDCl_3$



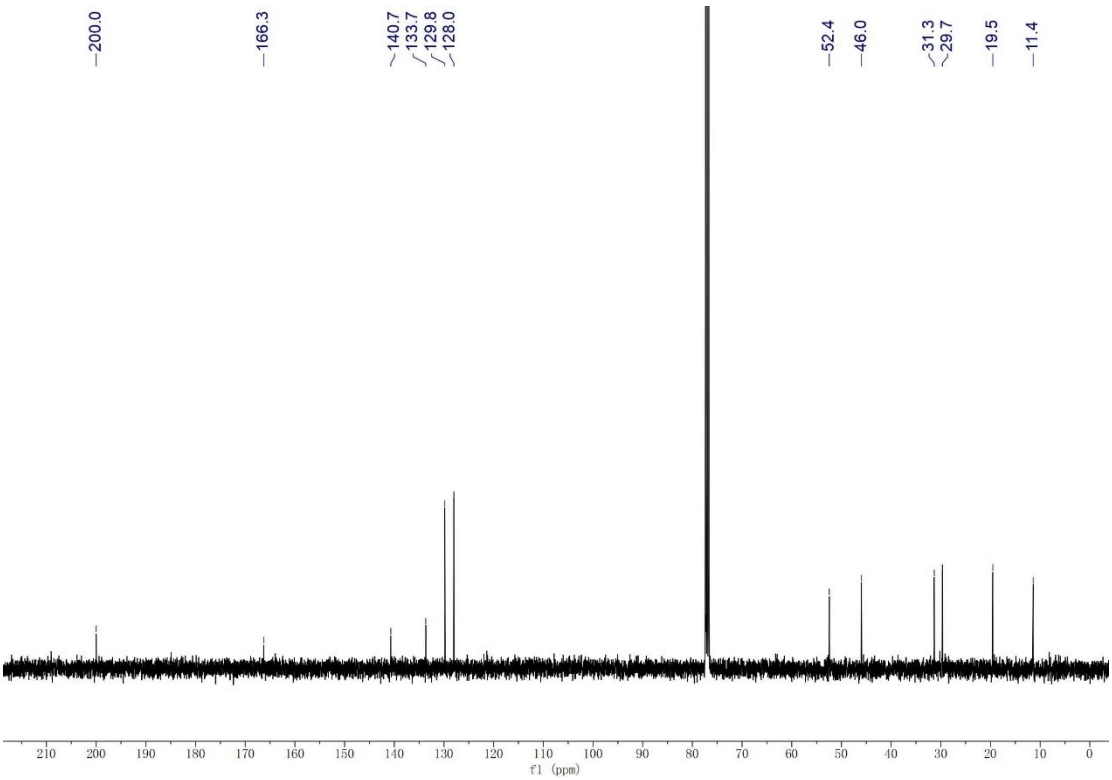


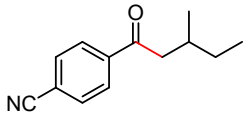
(15)

400 MHz in $CDCl_3$



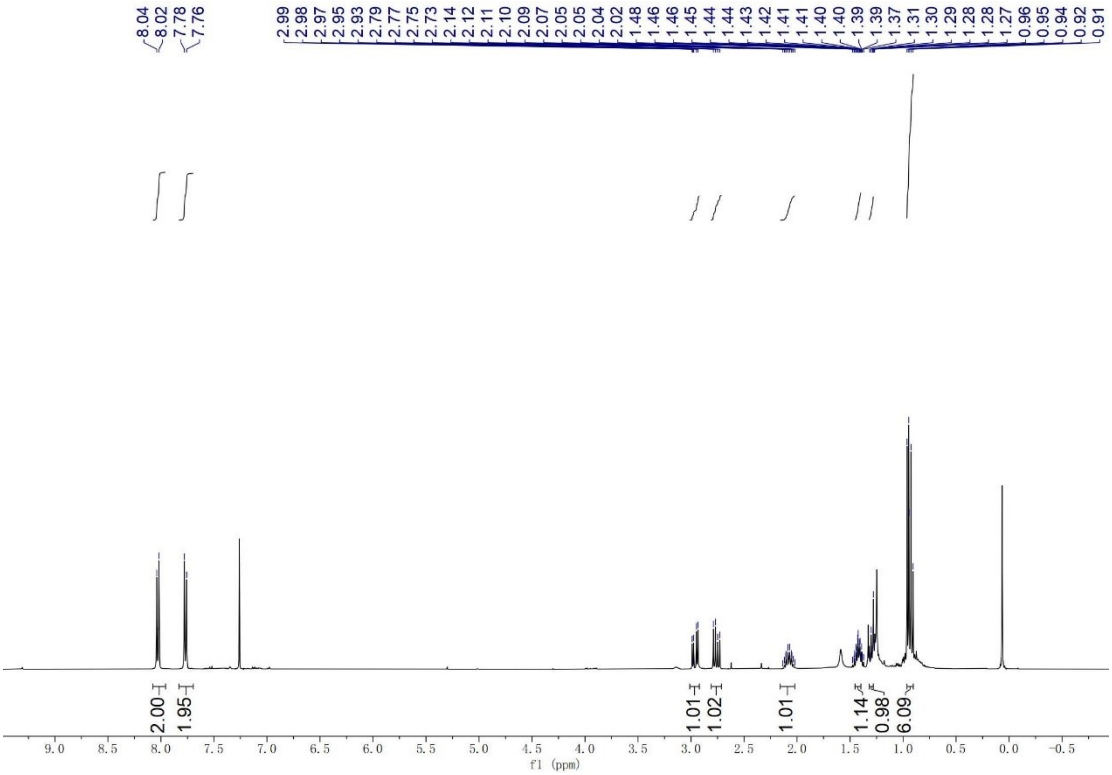
100 MHz in $CDCl_3$



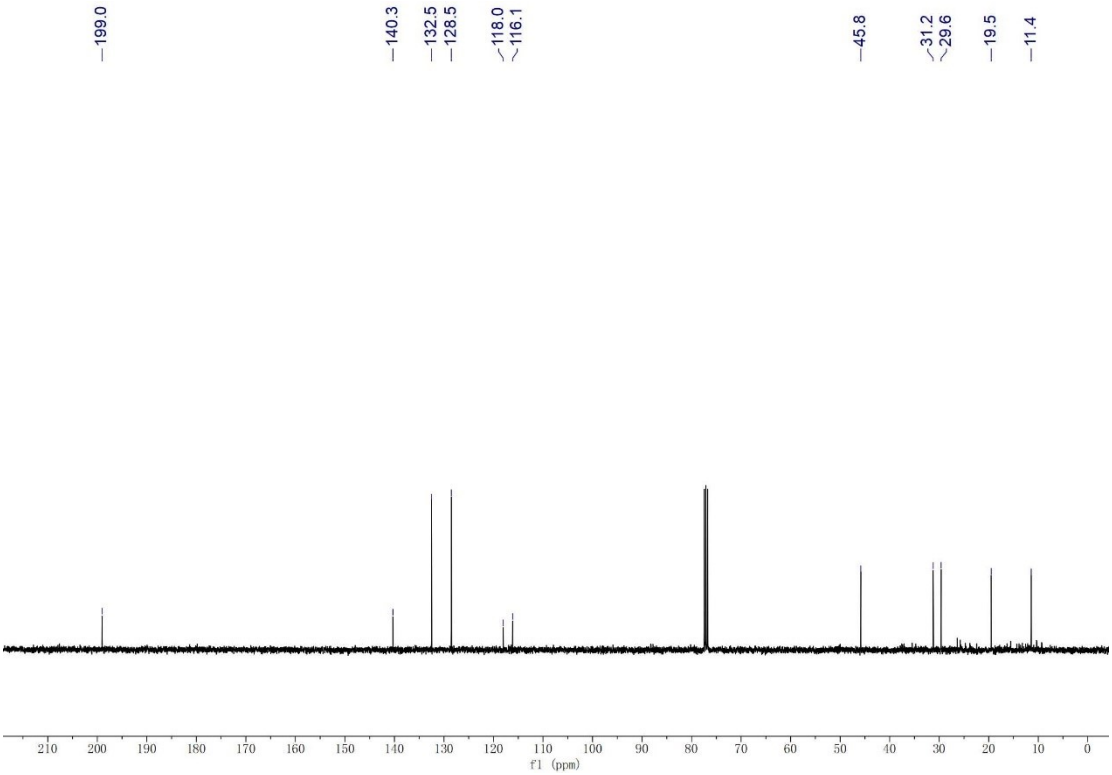


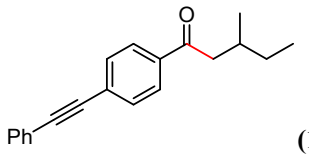
(16)

400 MHz in $CDCl_3$



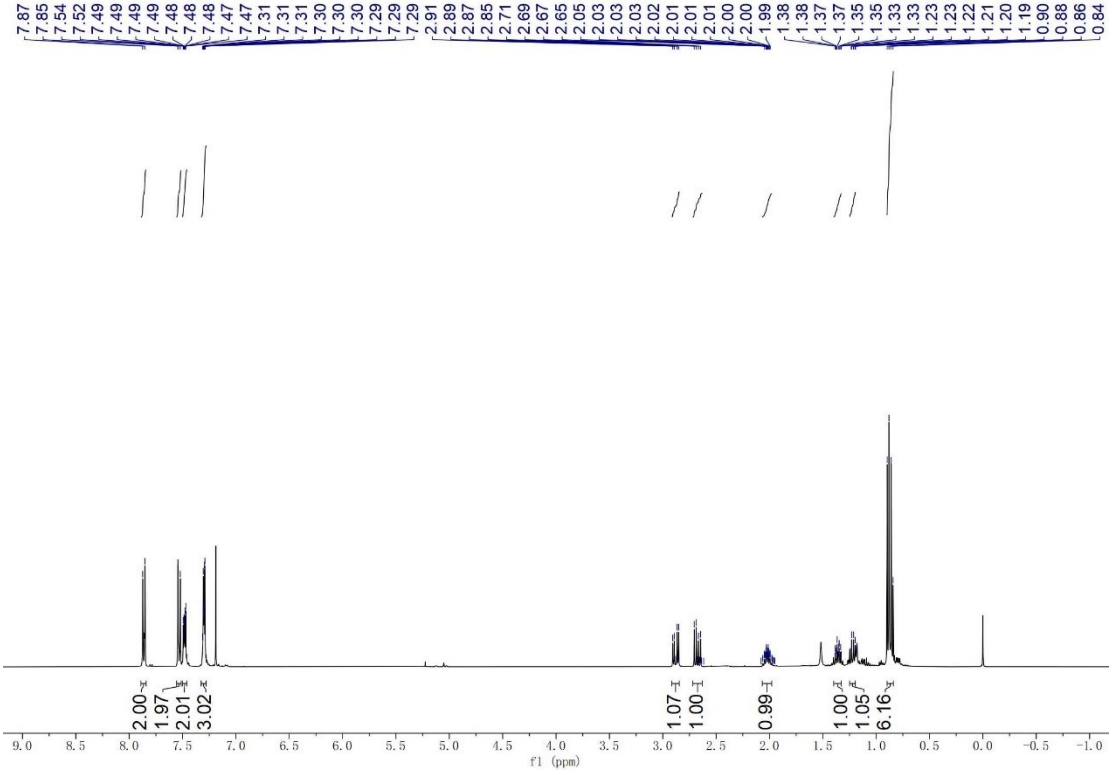
100 MHz in $CDCl_3$



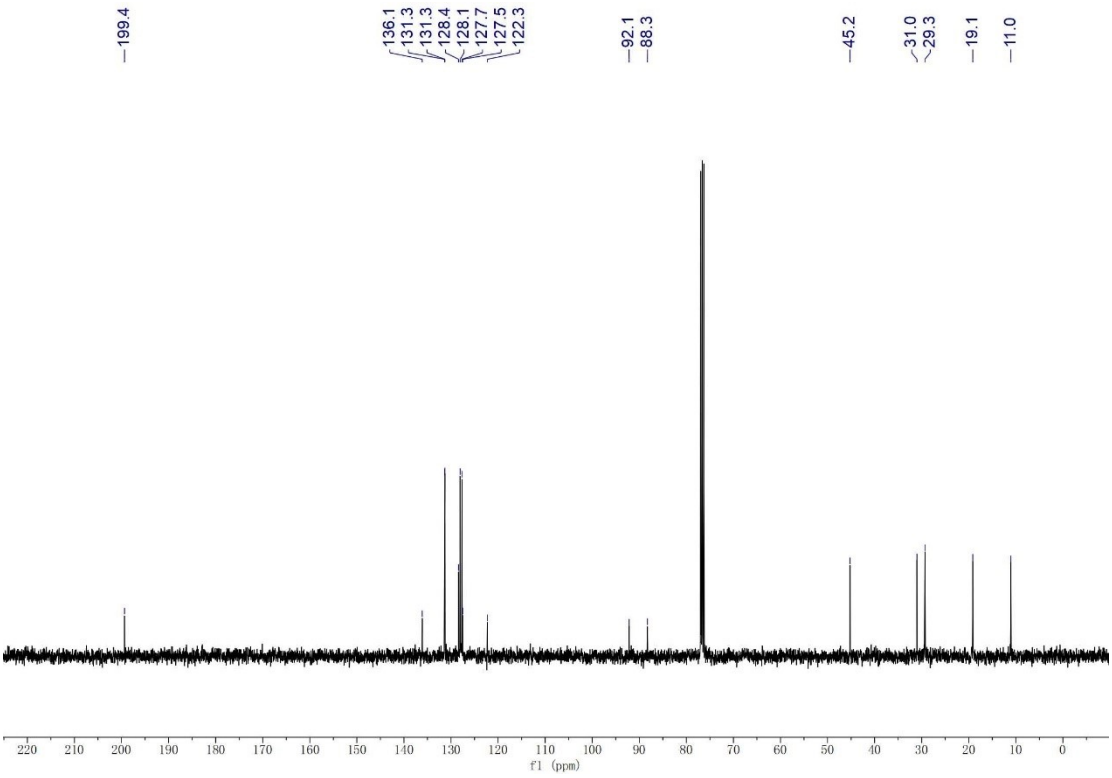


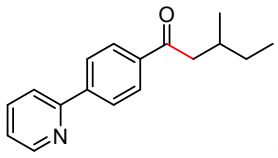
(17)

400 MHz in $CDCl_3$



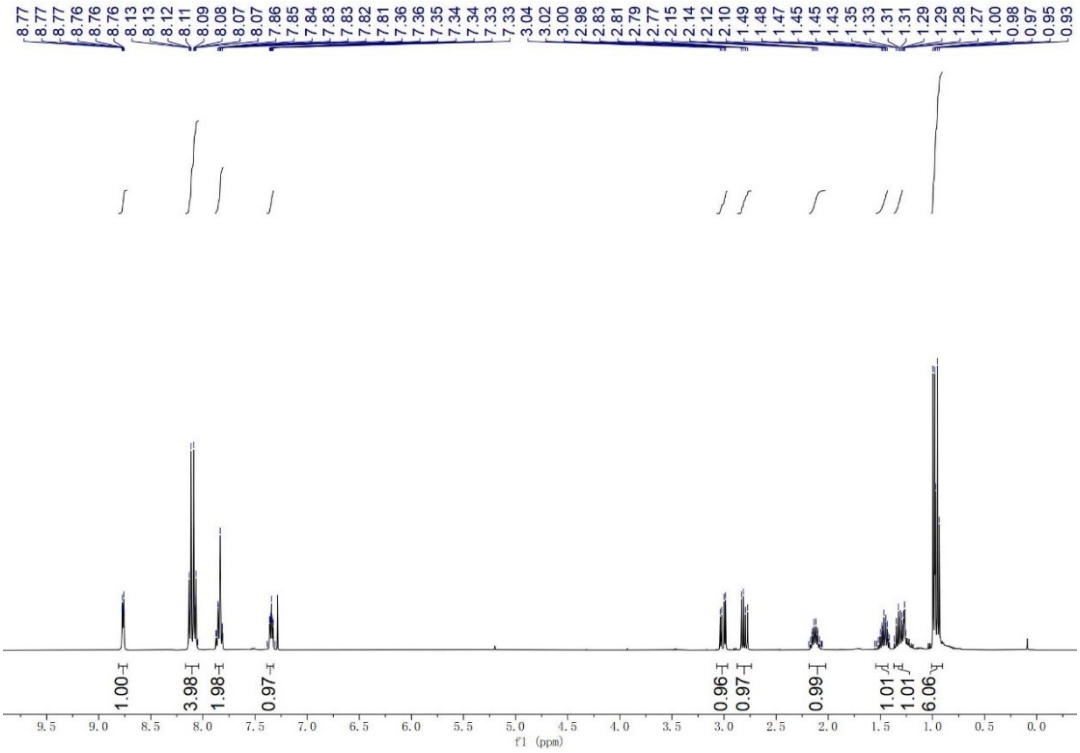
100 MHz in $CDCl_3$



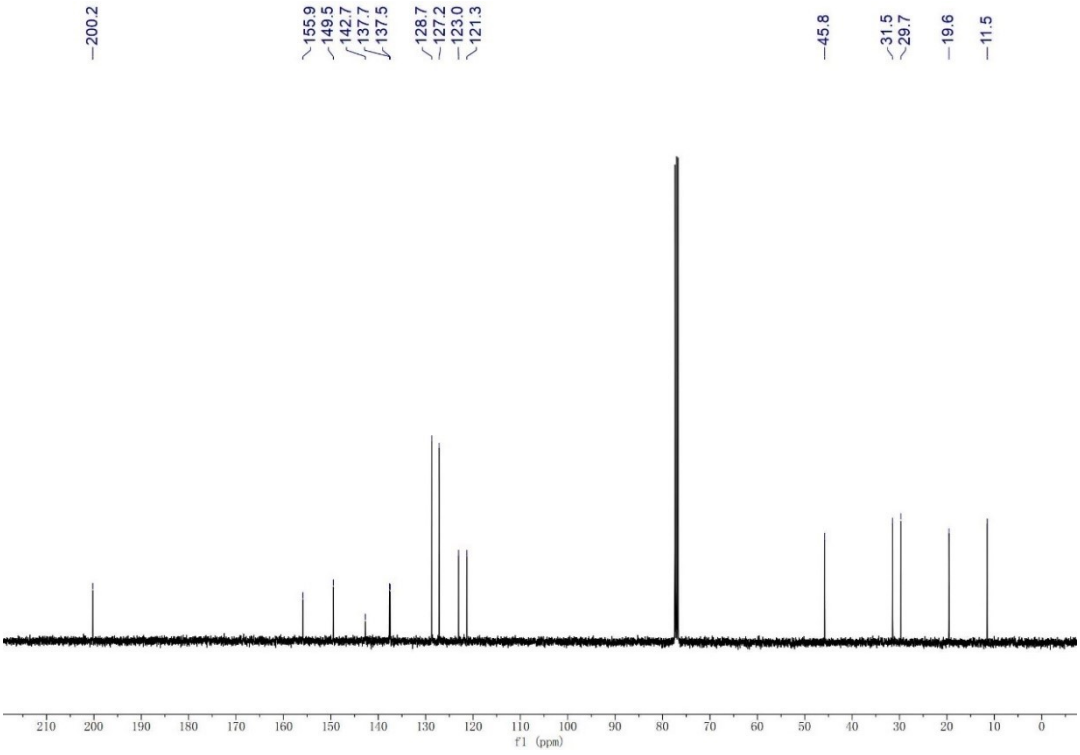


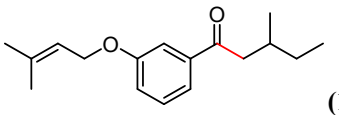
(18)

400 MHz in $CDCl_3$



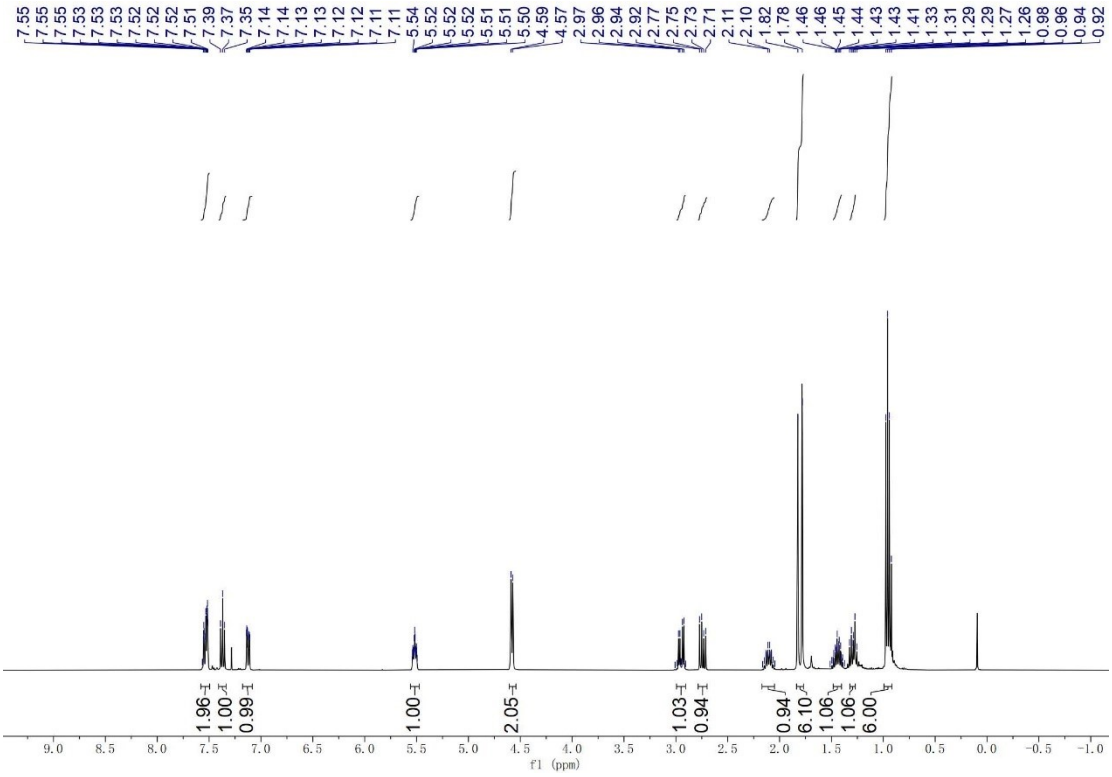
100 MHz in $CDCl_3$



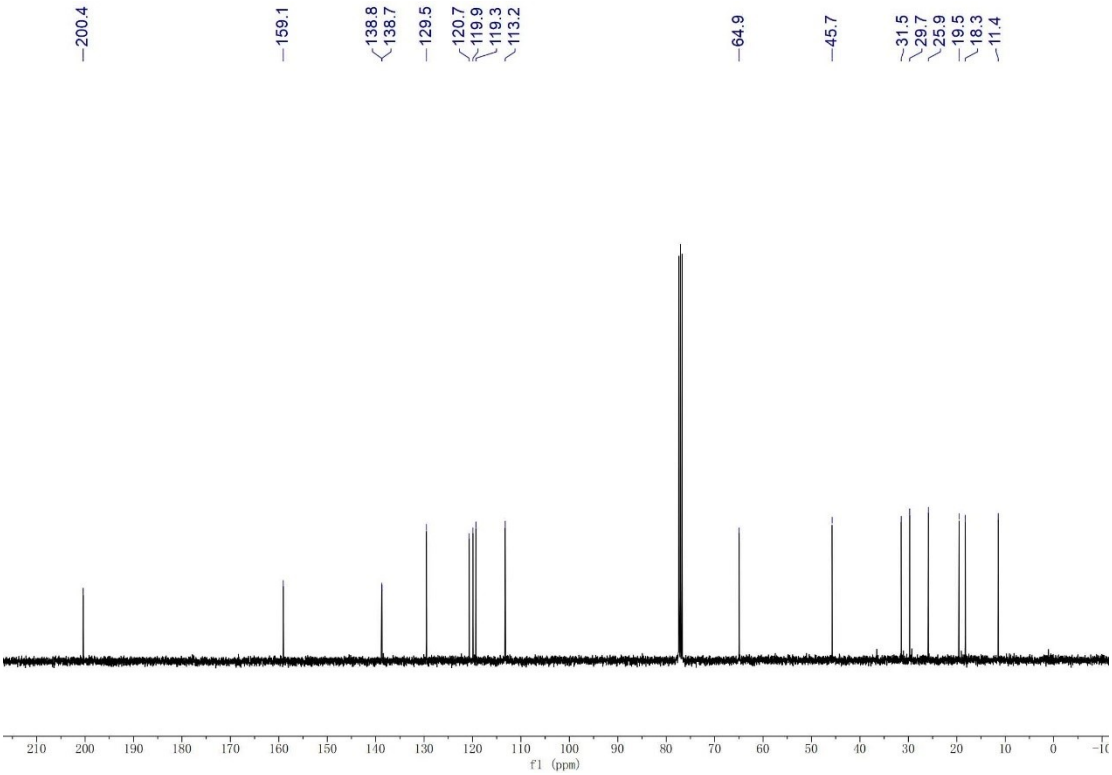


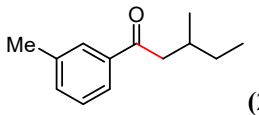
(19)

400 MHz in $CDCl_3$



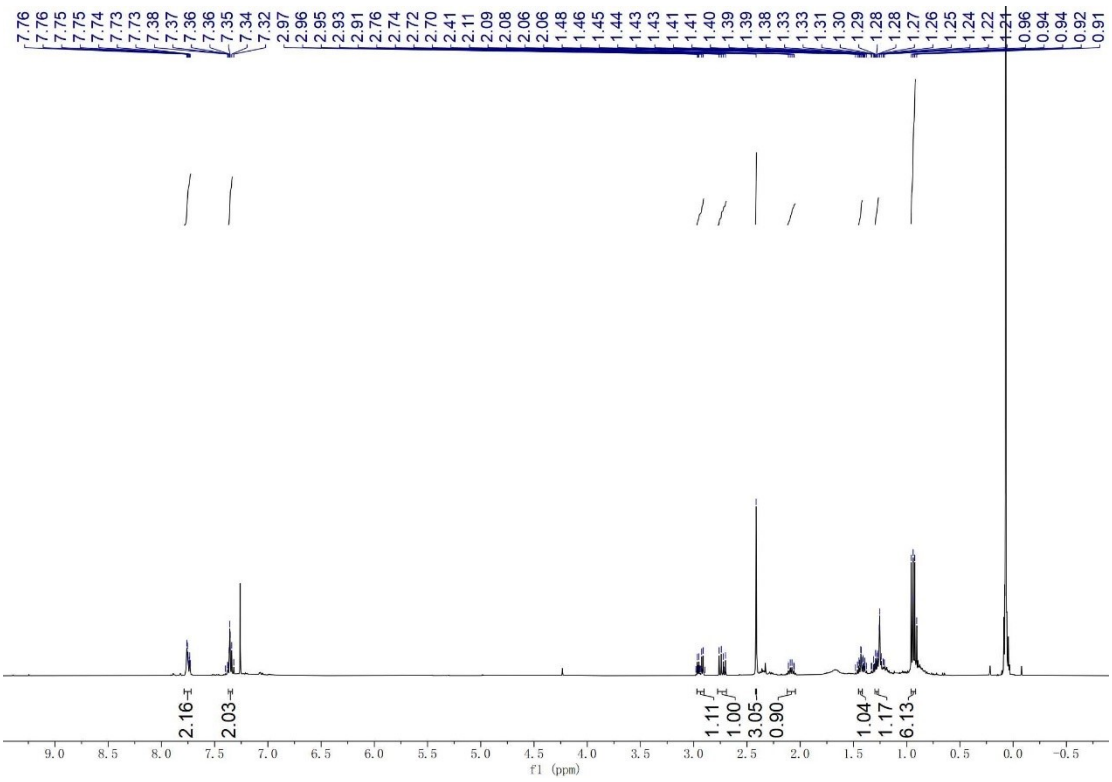
100 MHz in $CDCl_3$



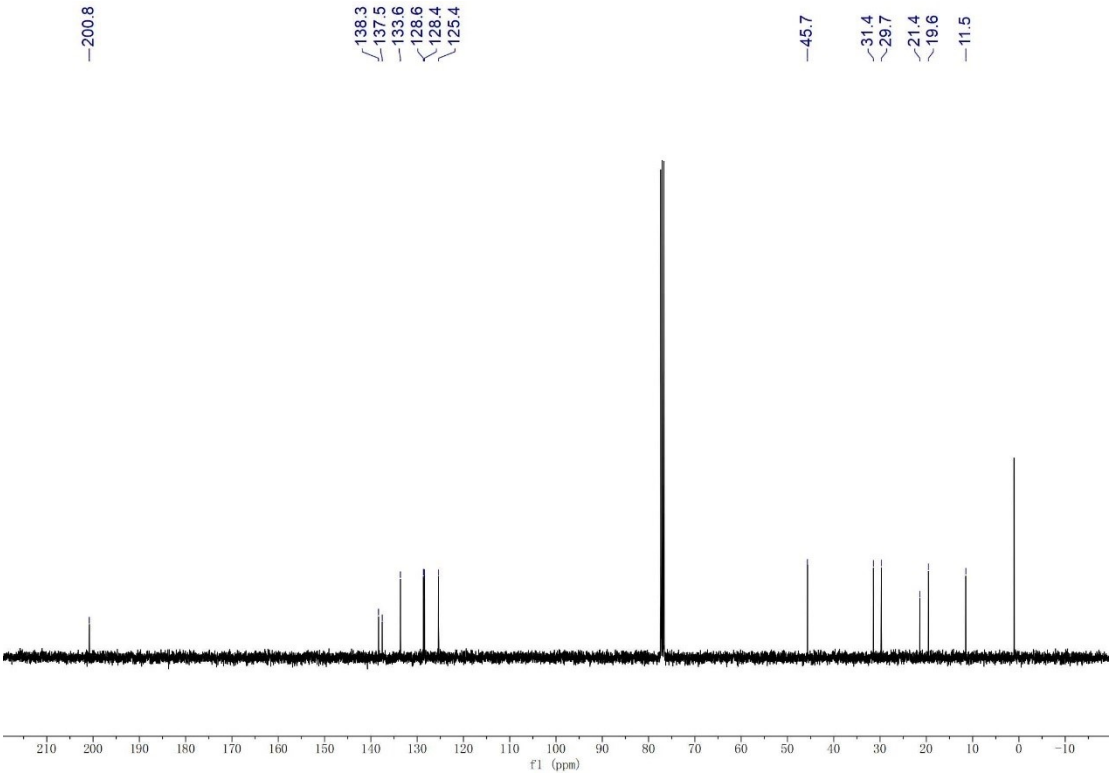


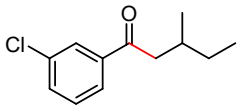
(20)

400 MHz in $CDCl_3$



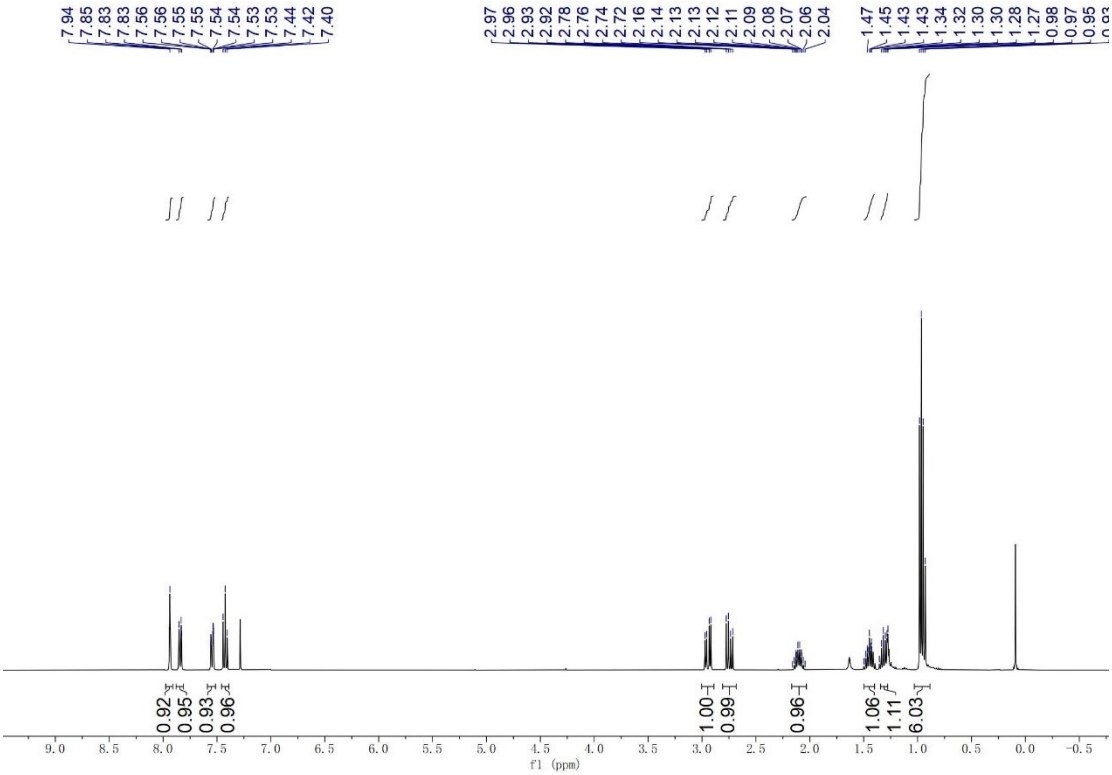
100 MHz in $CDCl_3$



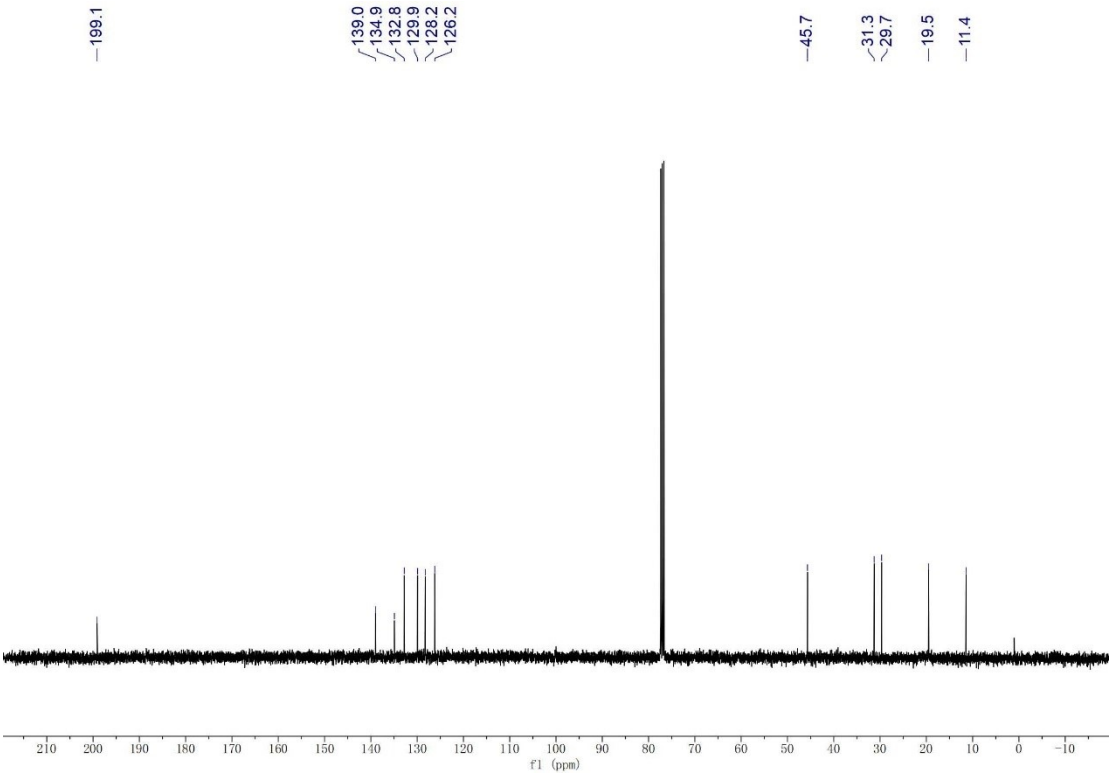


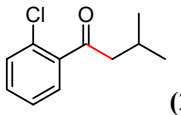
(21)

400 MHz in $CDCl_3$



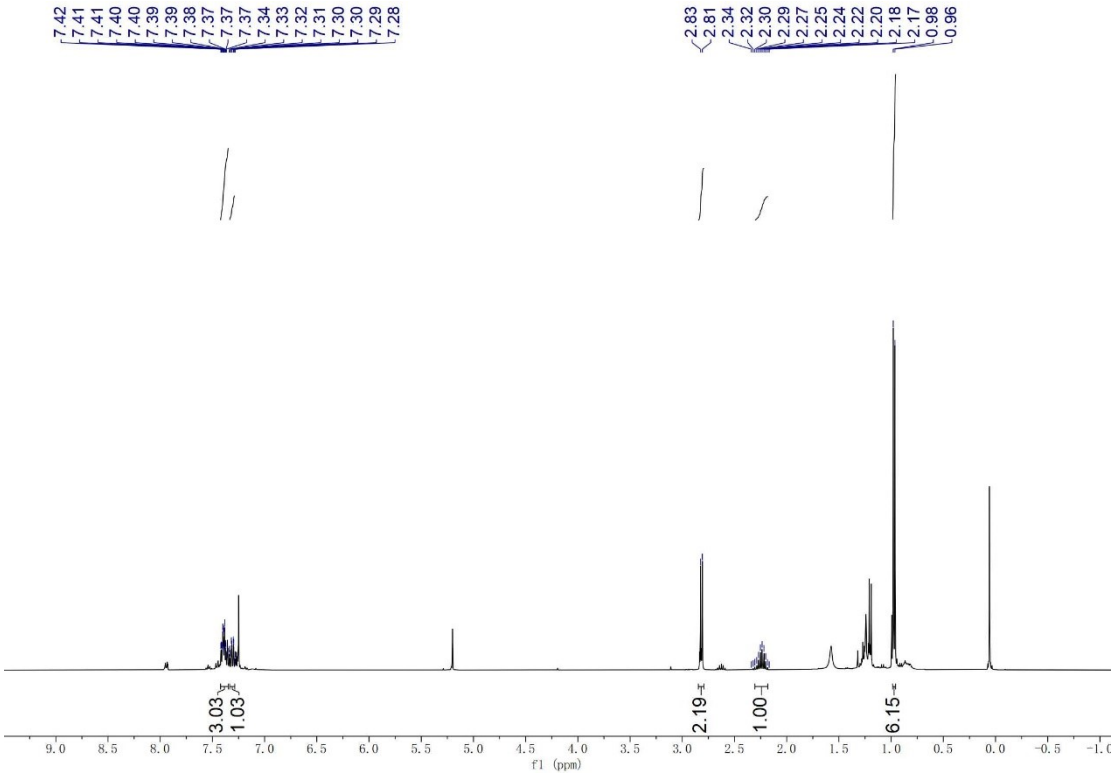
100 MHz in $CDCl_3$



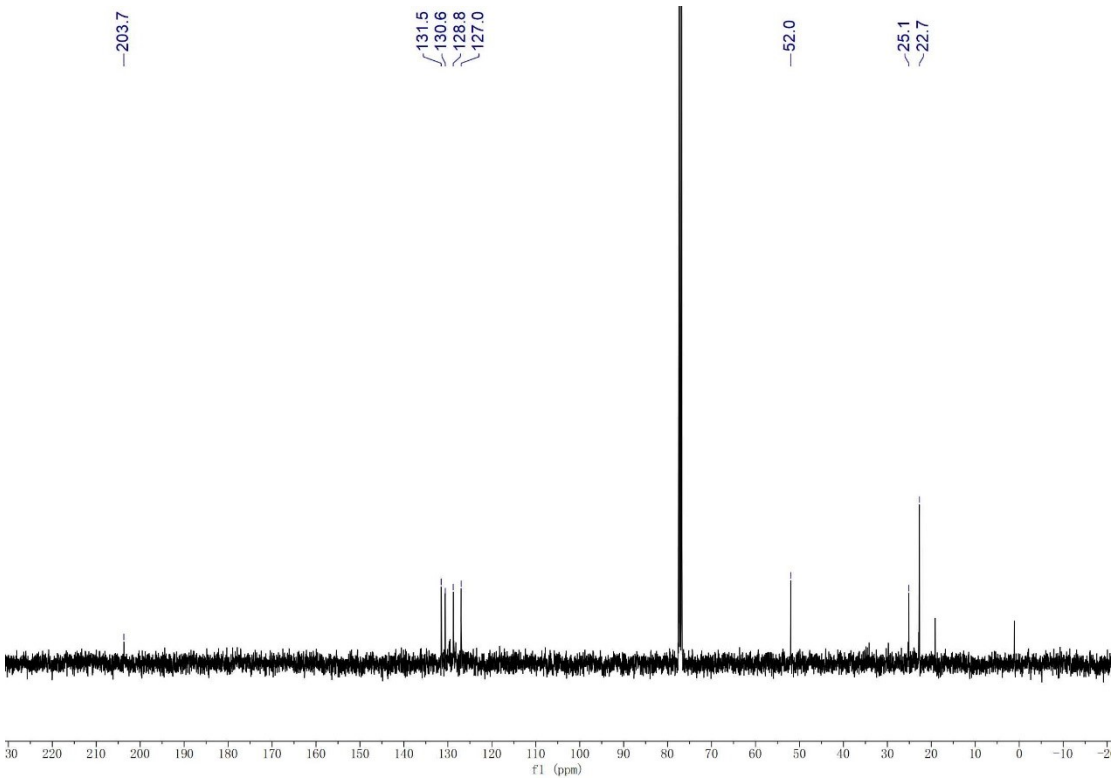


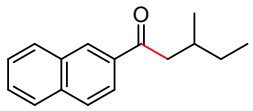
(22)

400 MHz in $CDCl_3$



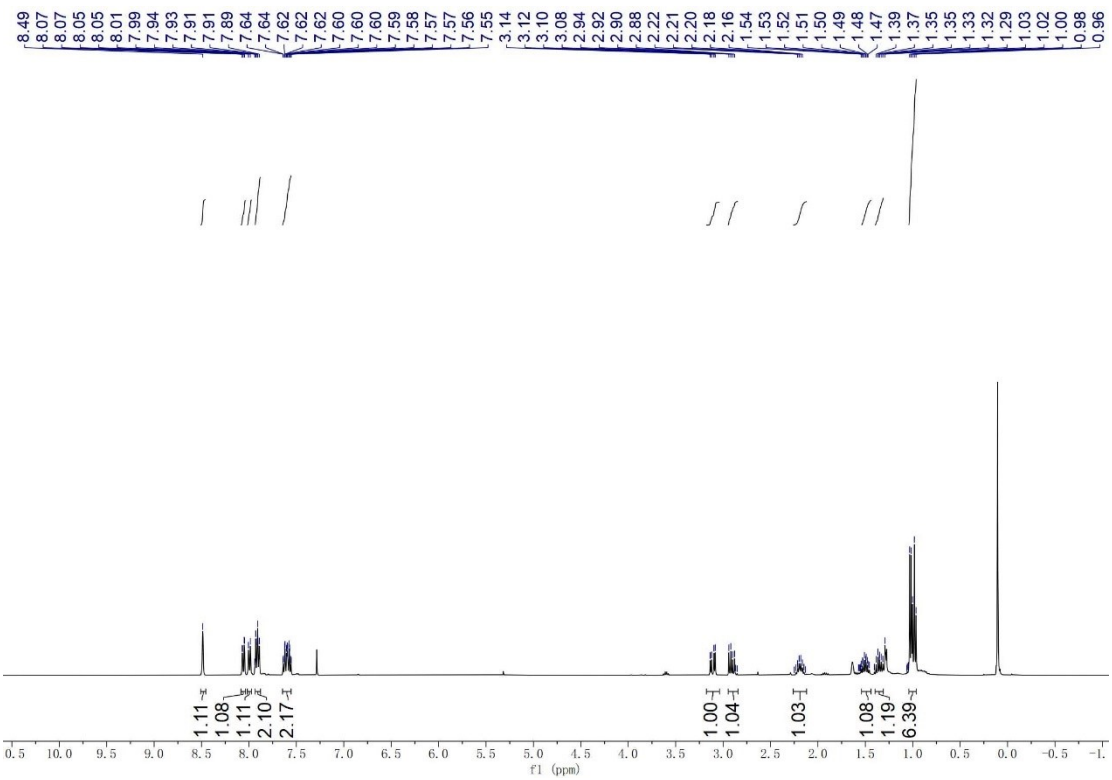
100 MHz in $CDCl_3$



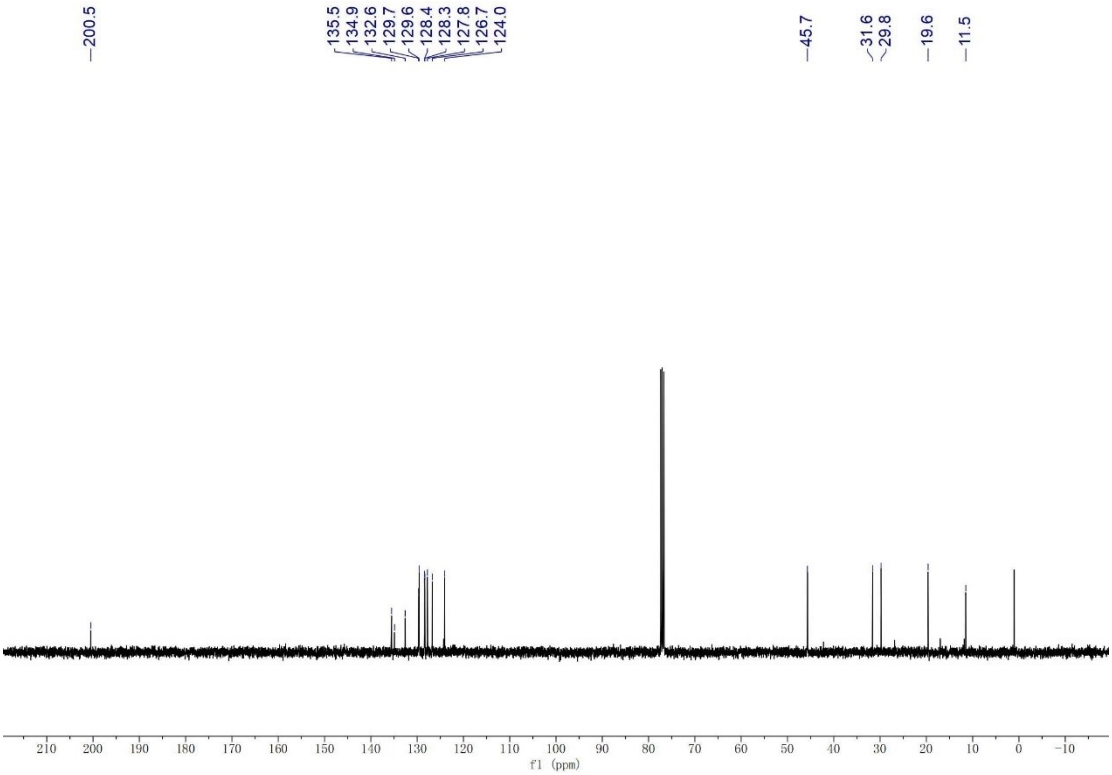


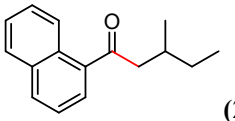
(23)

400 MHz in $CDCl_3$



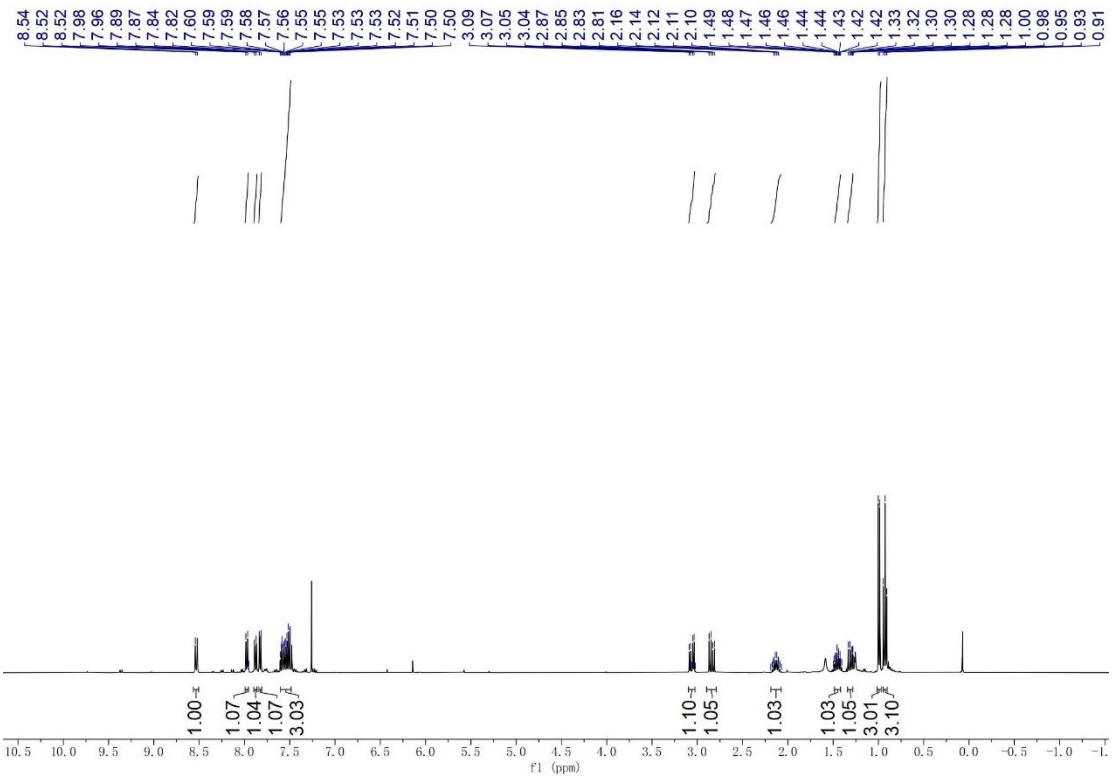
100 MHz in $CDCl_3$



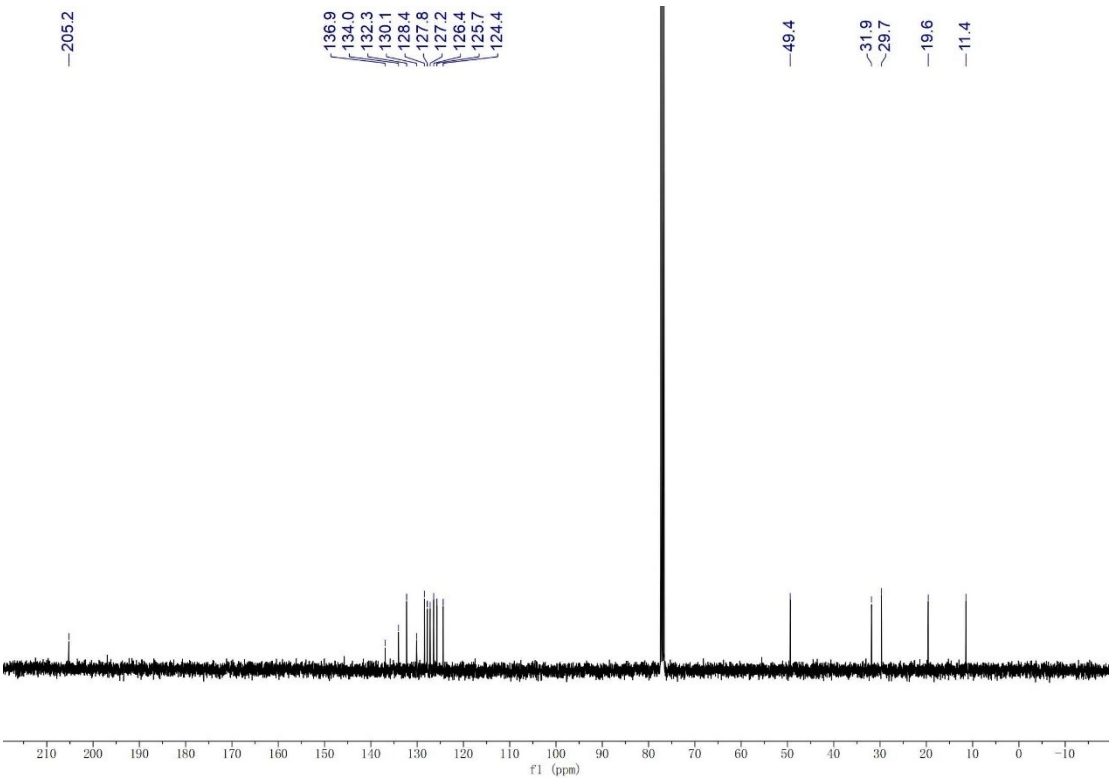


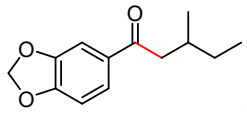
(24)

400 MHz in $CDCl_3$



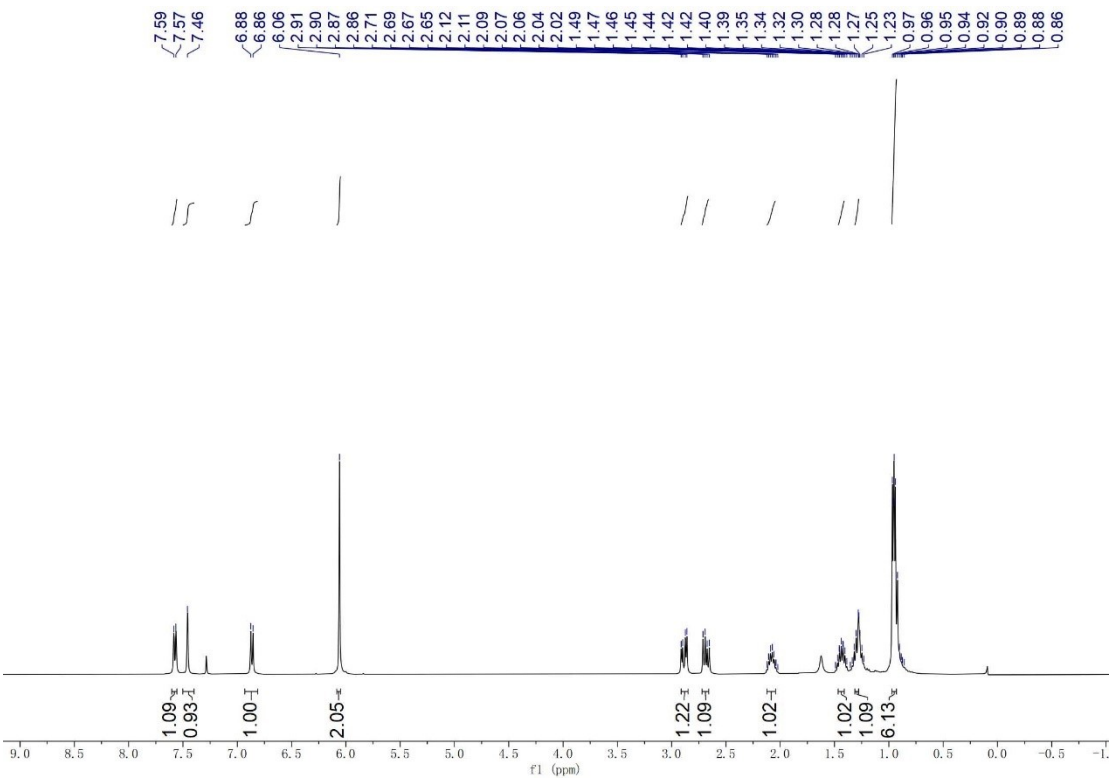
100 MHz in $CDCl_3$



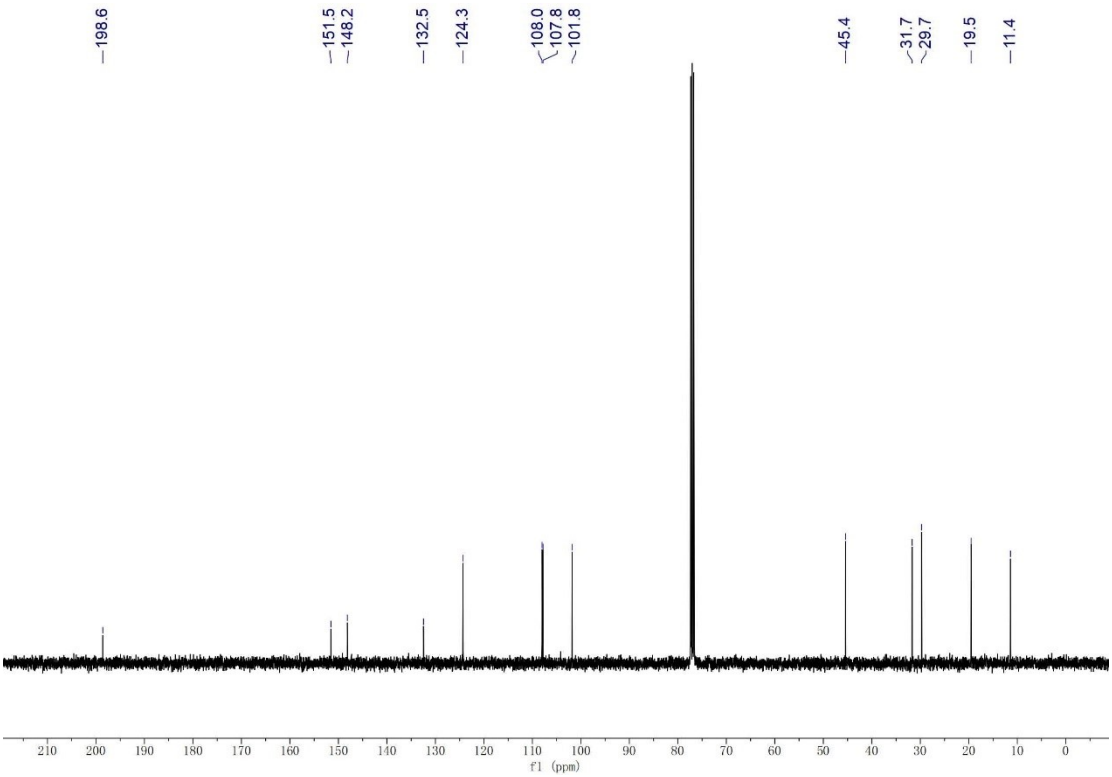


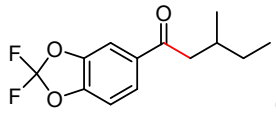
(25)

400 MHz in $CDCl_3$



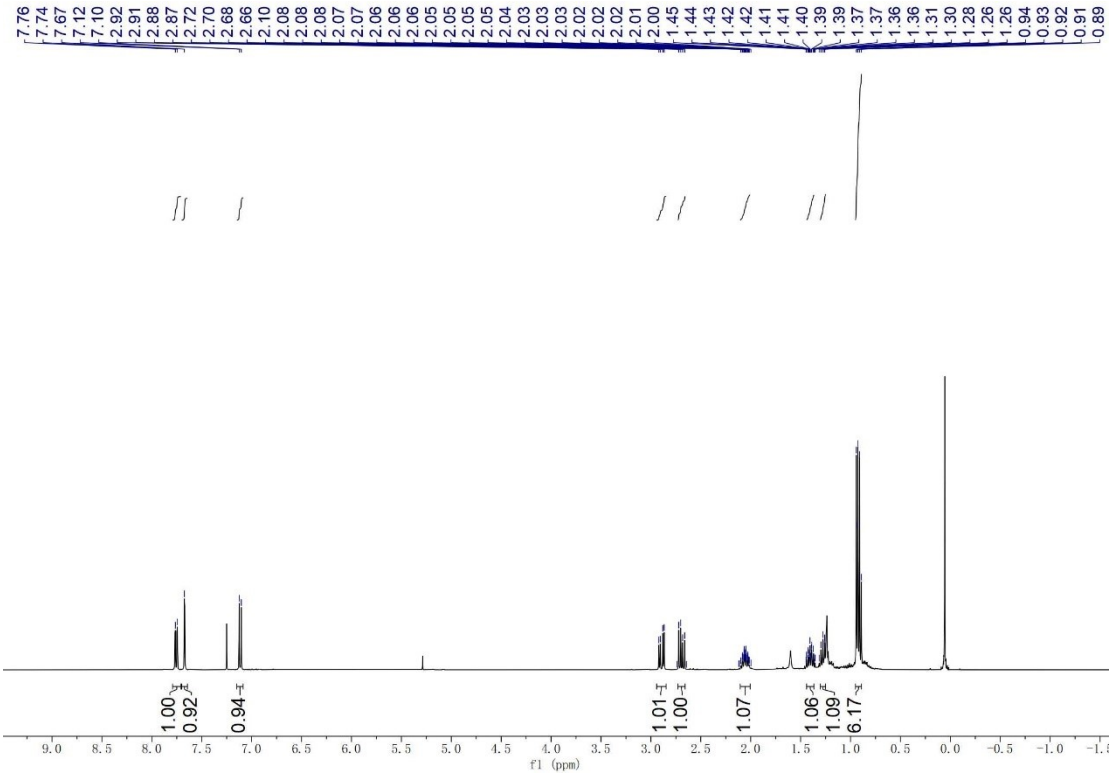
100 MHz in $CDCl_3$



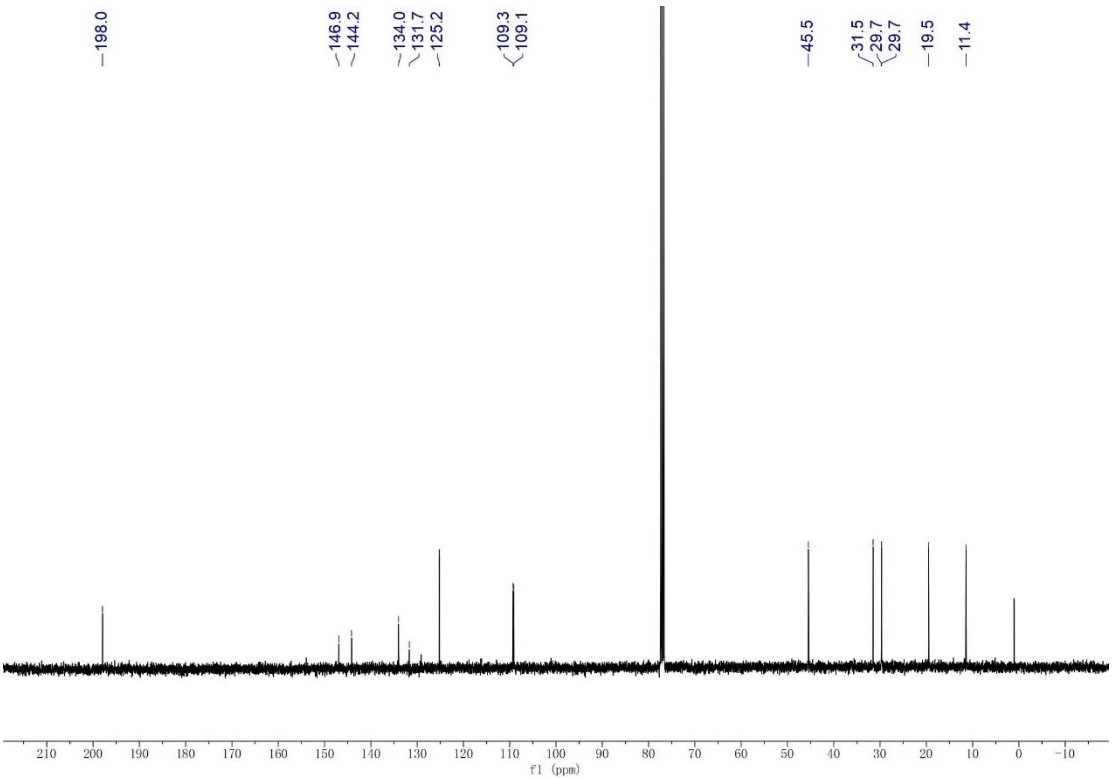


(26)

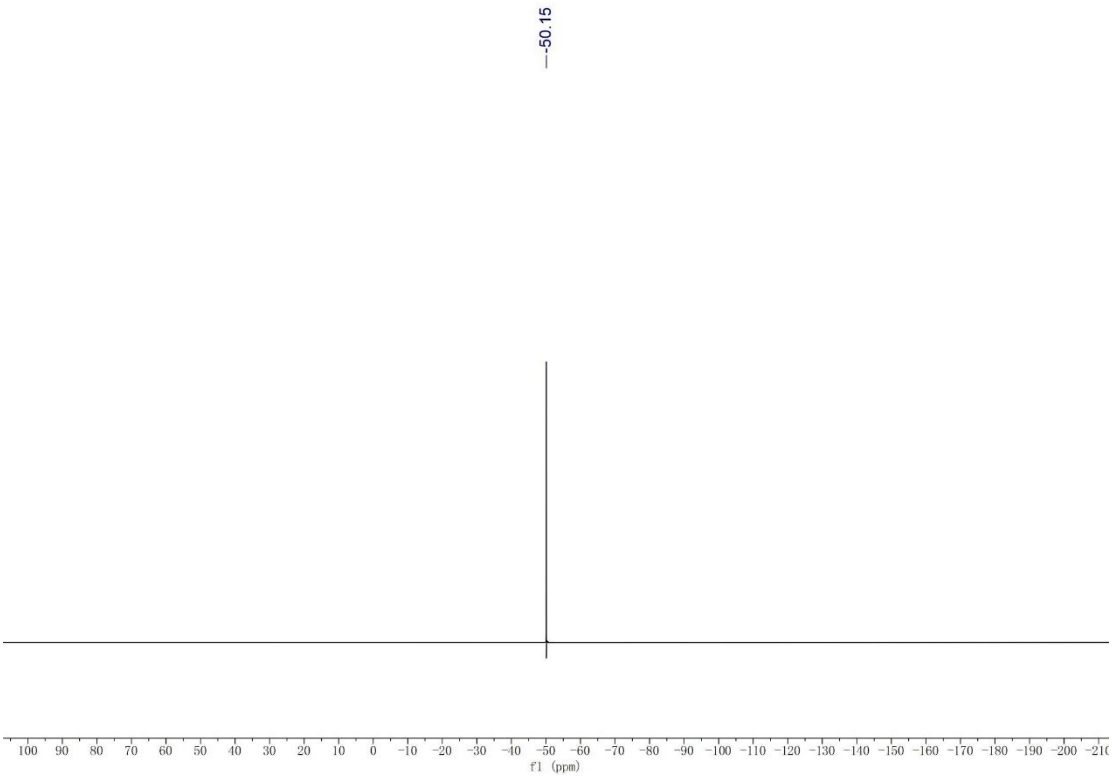
400 MHz in $CDCl_3$

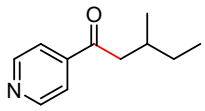


100 MHz in $CDCl_3$



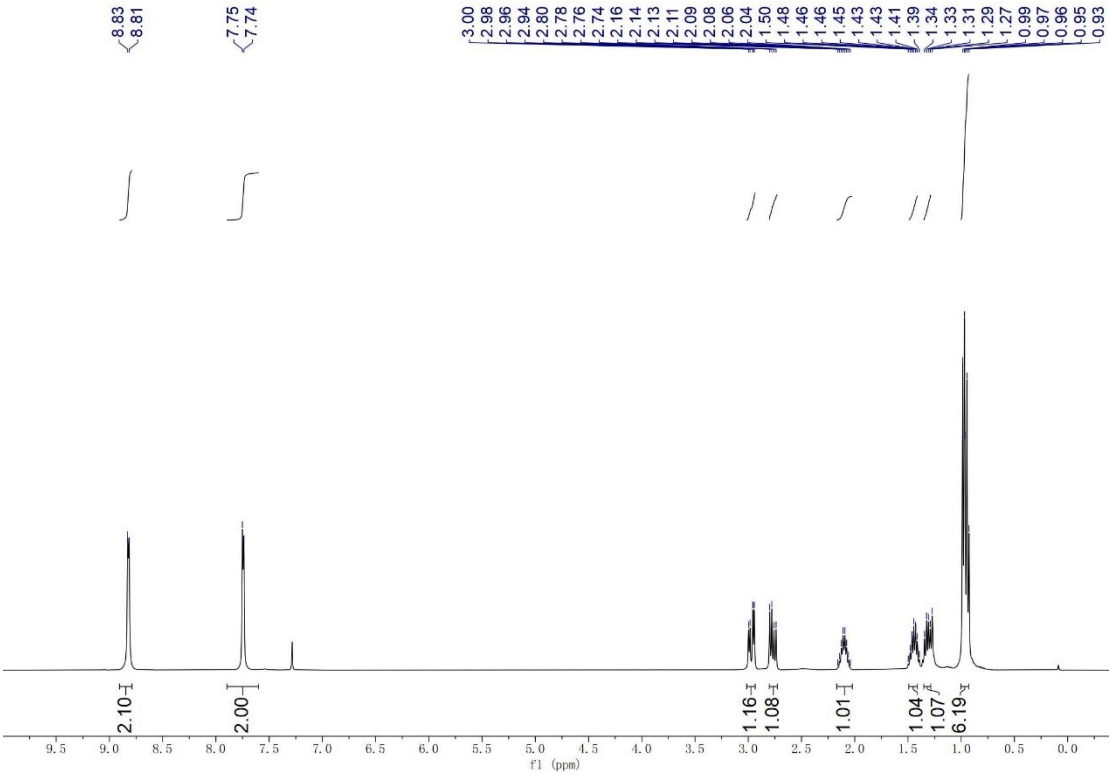
376 MHz in $CDCl_3$



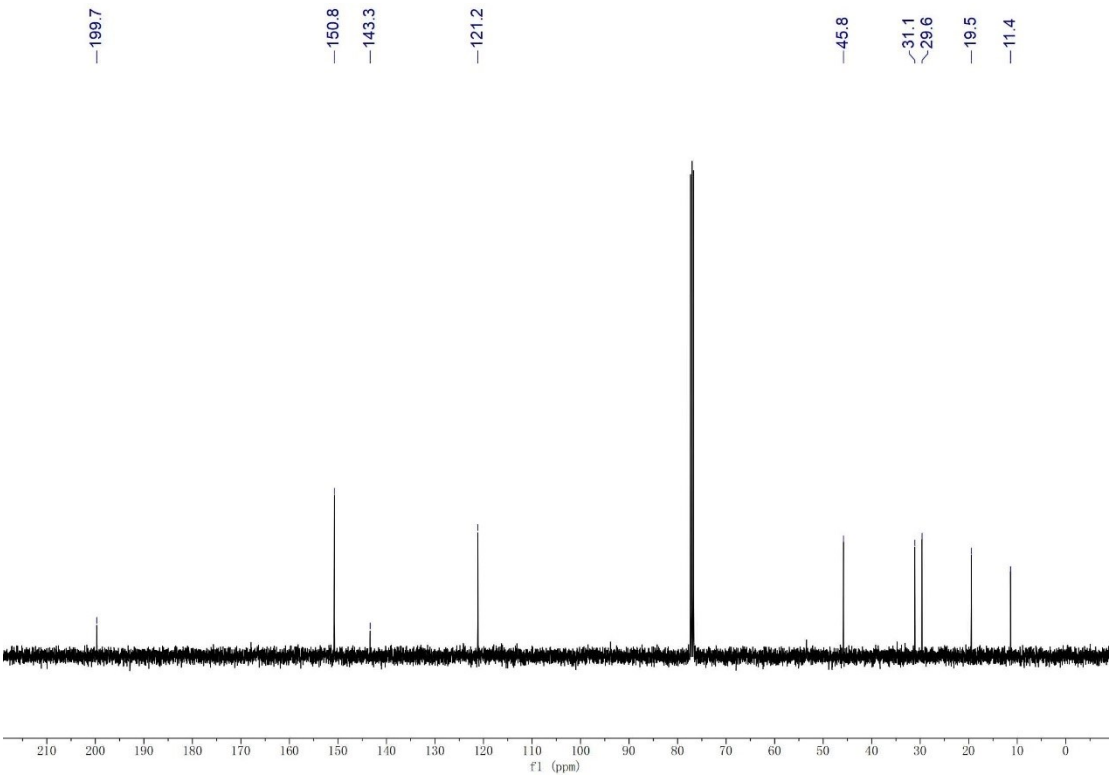


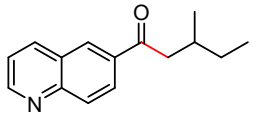
(27)

400 MHz in $CDCl_3$



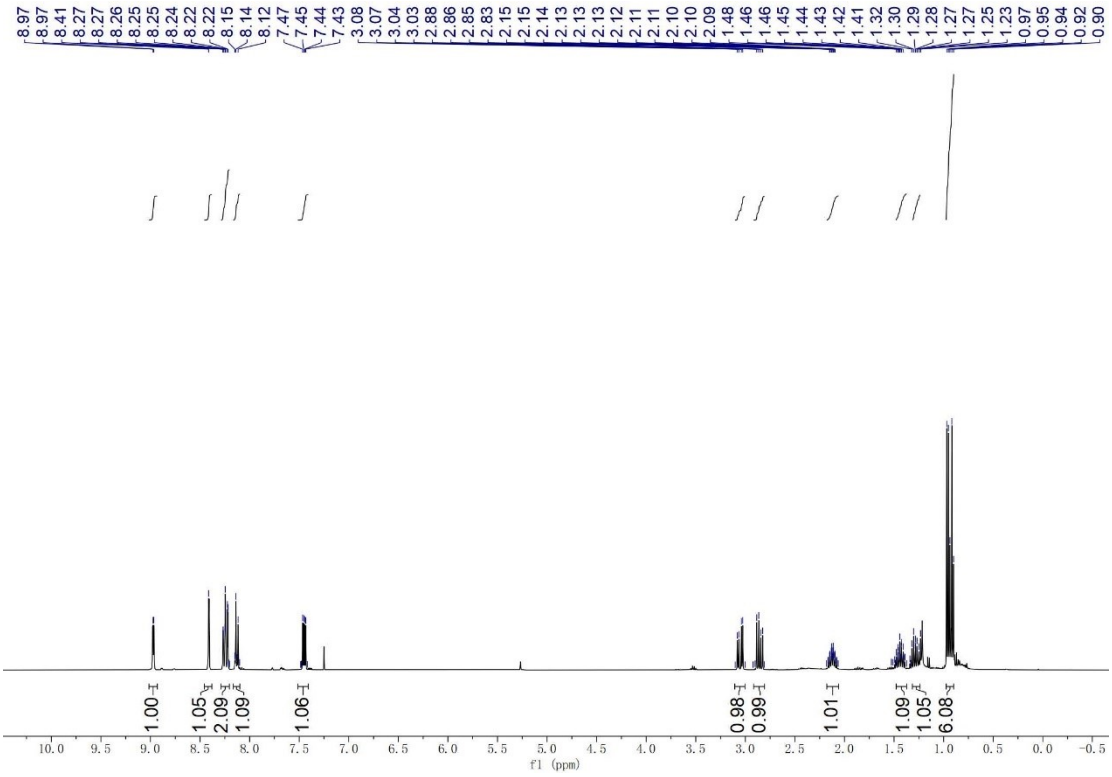
100 MHz in $CDCl_3$



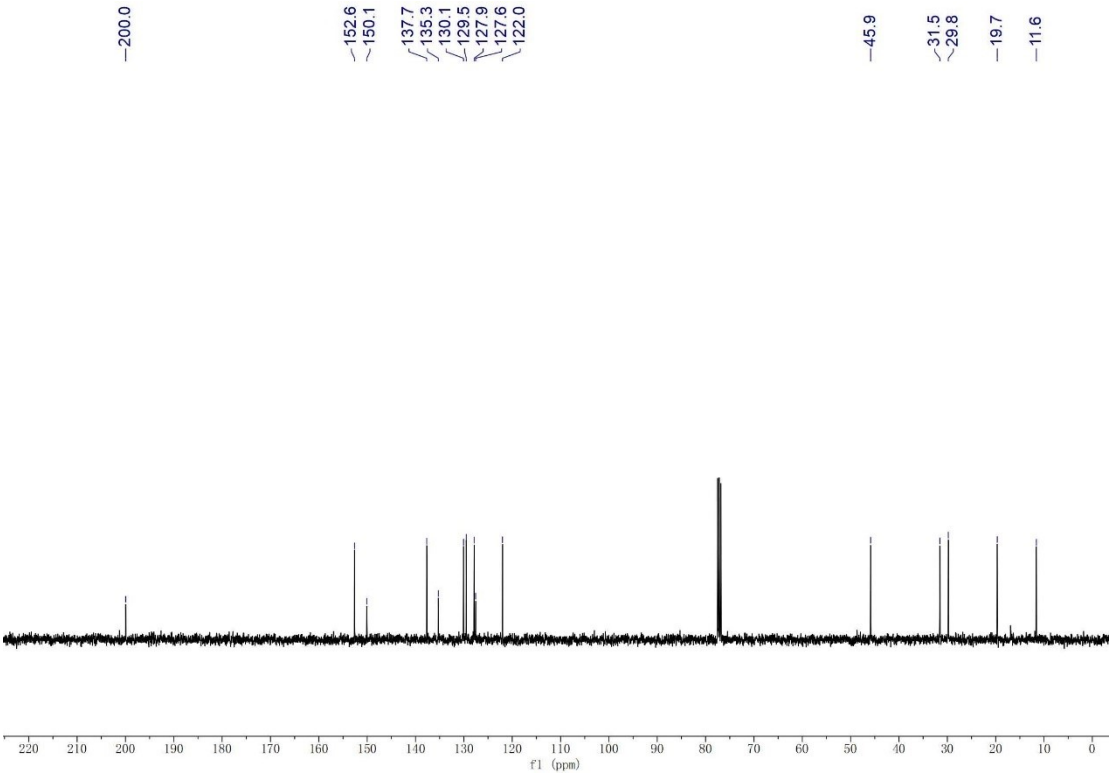


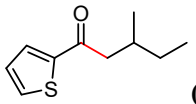
(28)

400 MHz in $CDCl_3$



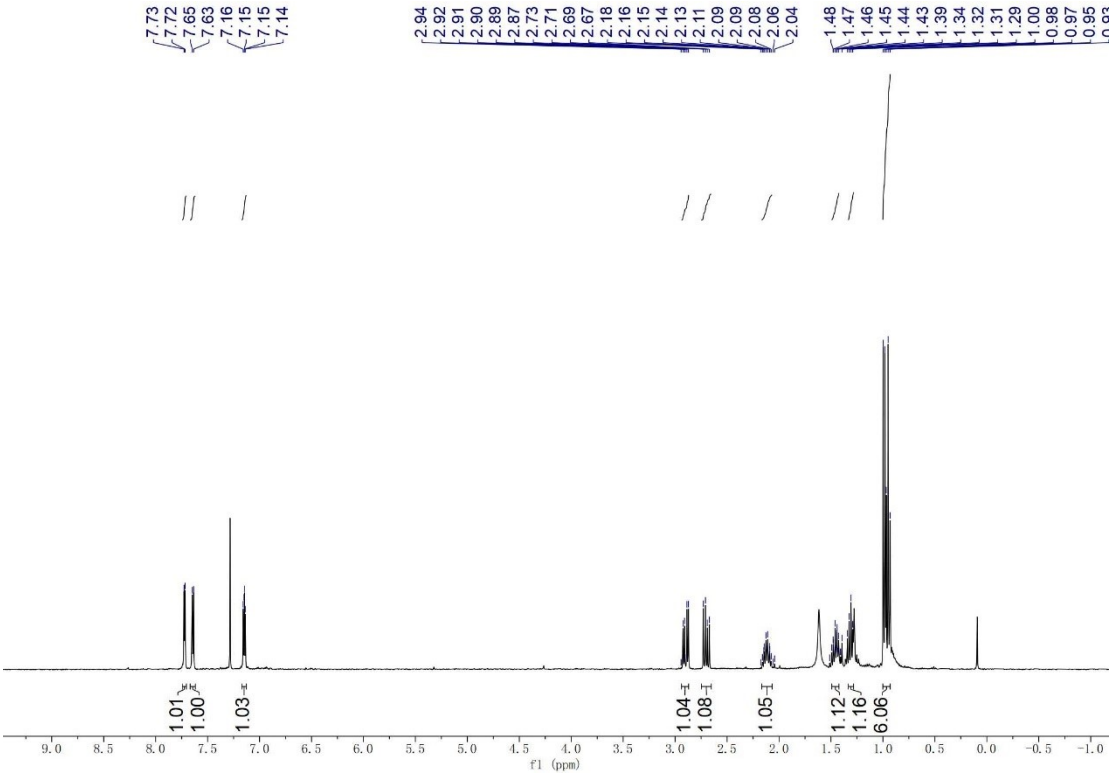
100 MHz in $CDCl_3$



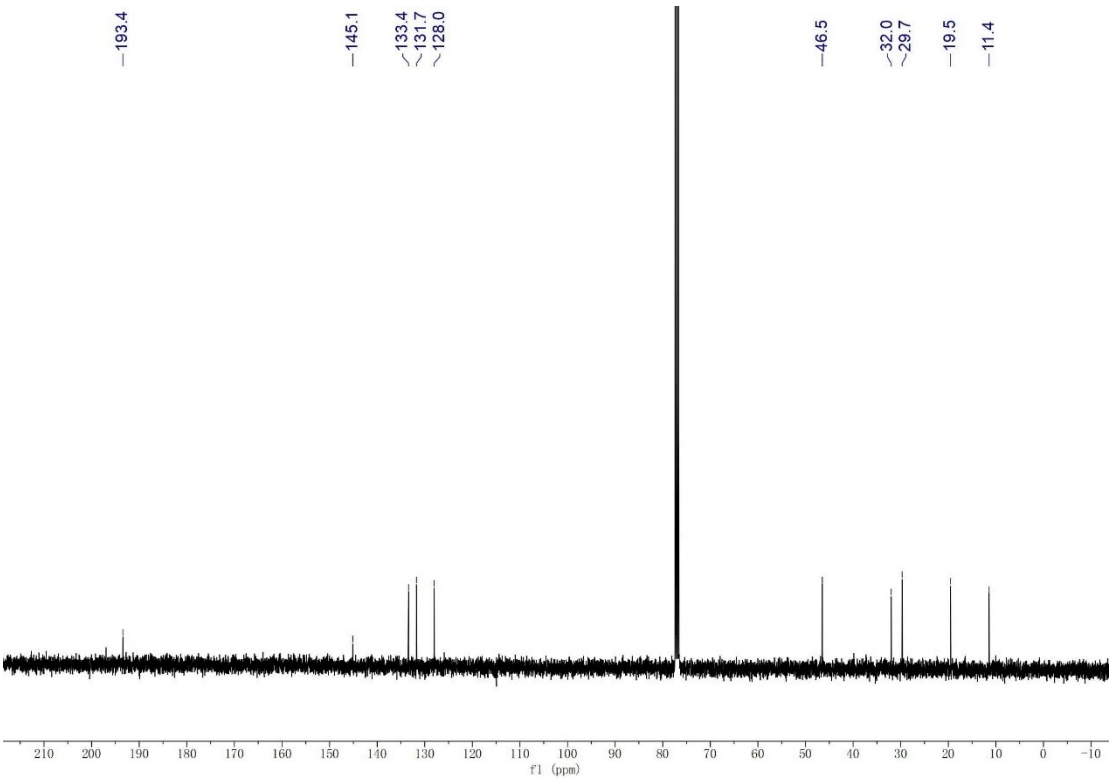


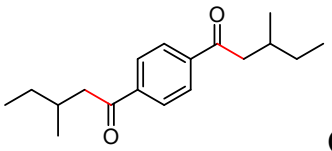
(29)

400 MHz in $CDCl_3$



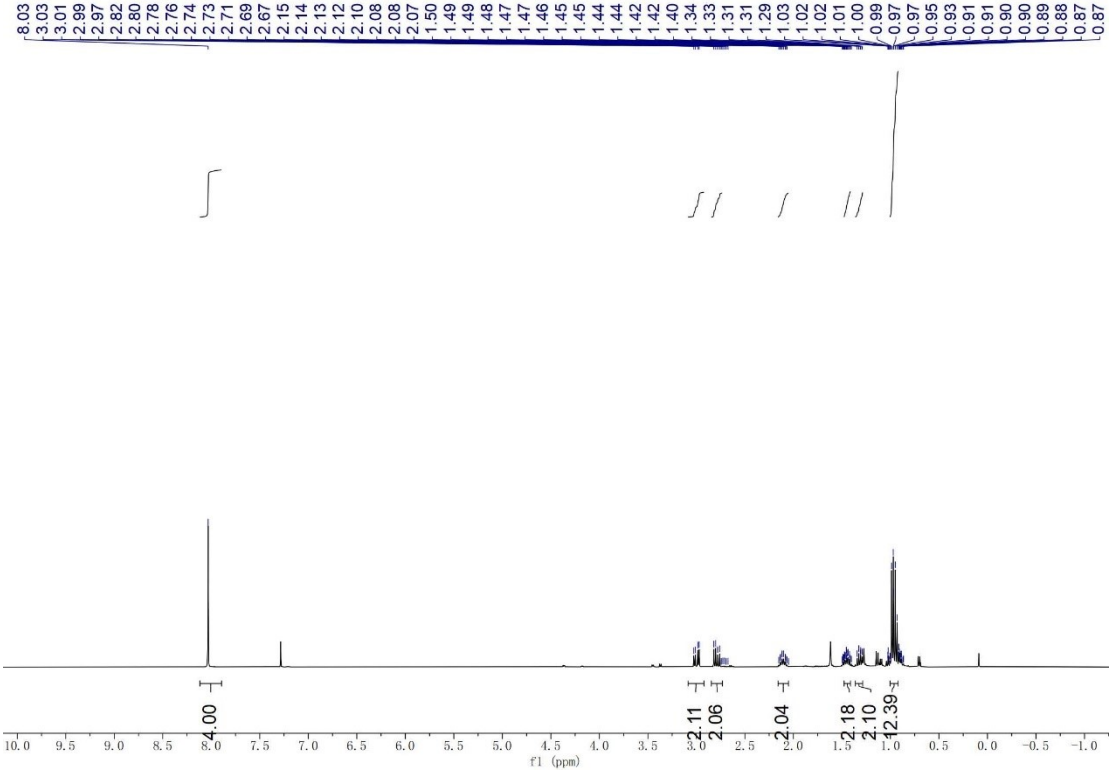
100 MHz in $CDCl_3$



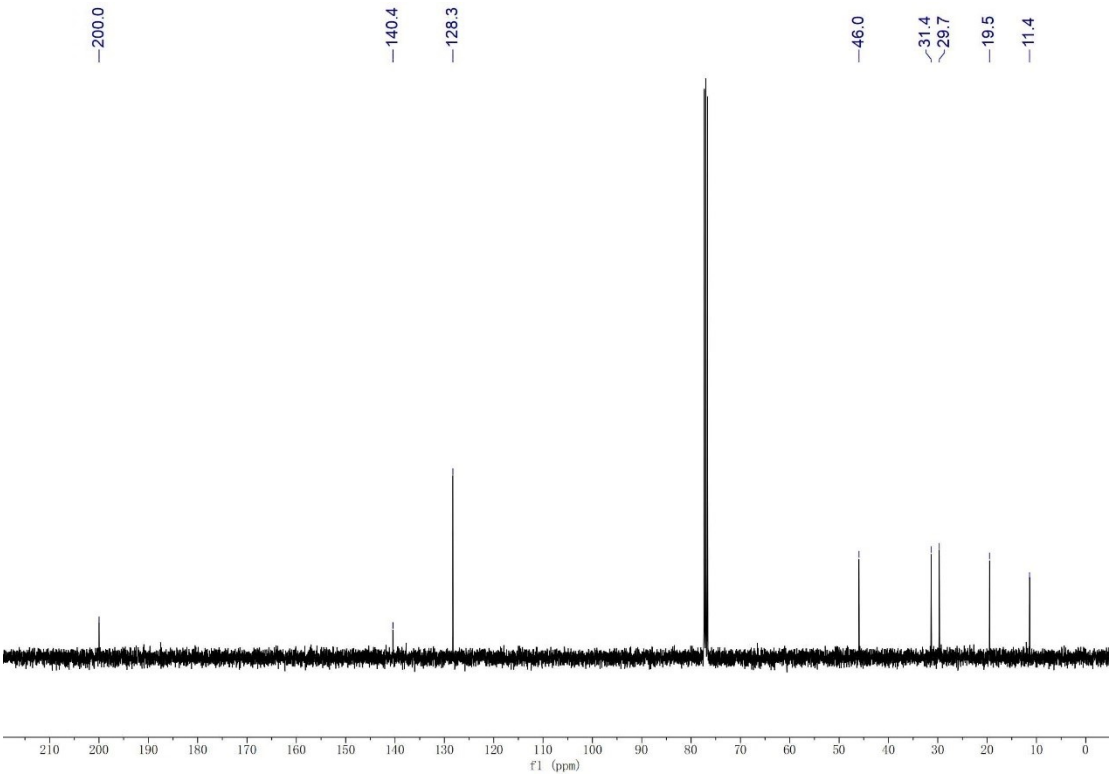


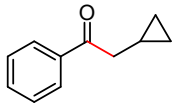
(30)

400 MHz in $CDCl_3$



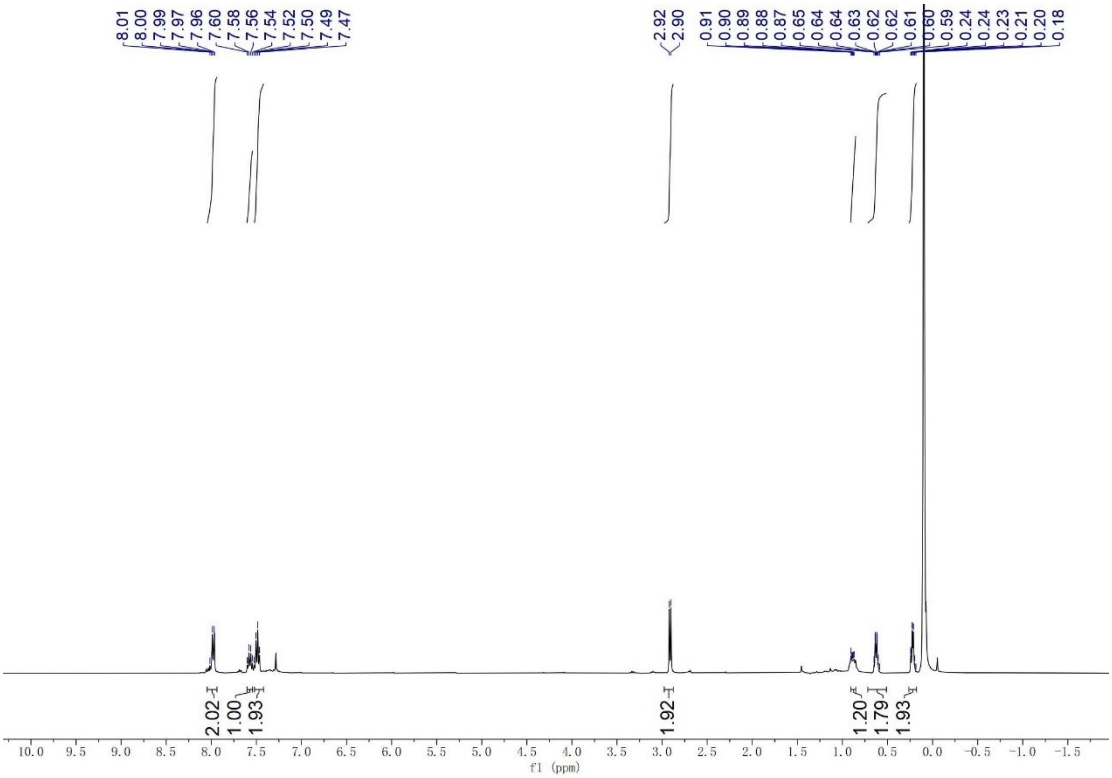
100 MHz in $CDCl_3$



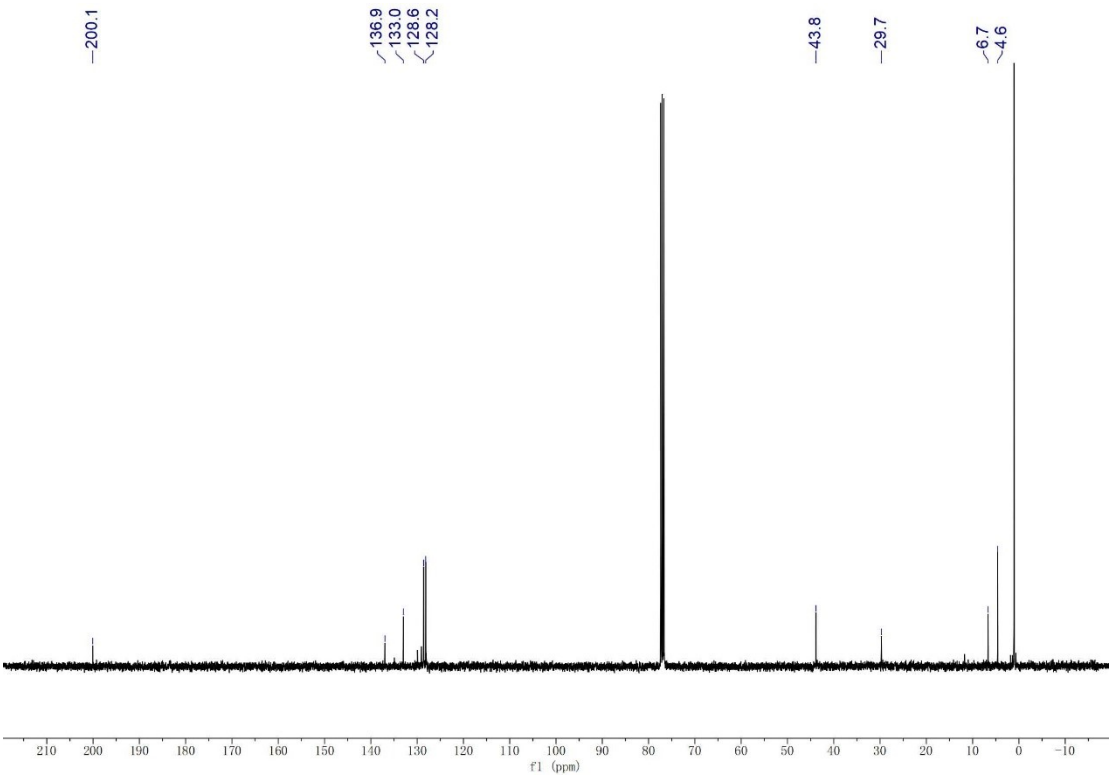


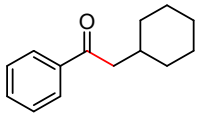
(31)

400 MHz in $CDCl_3$



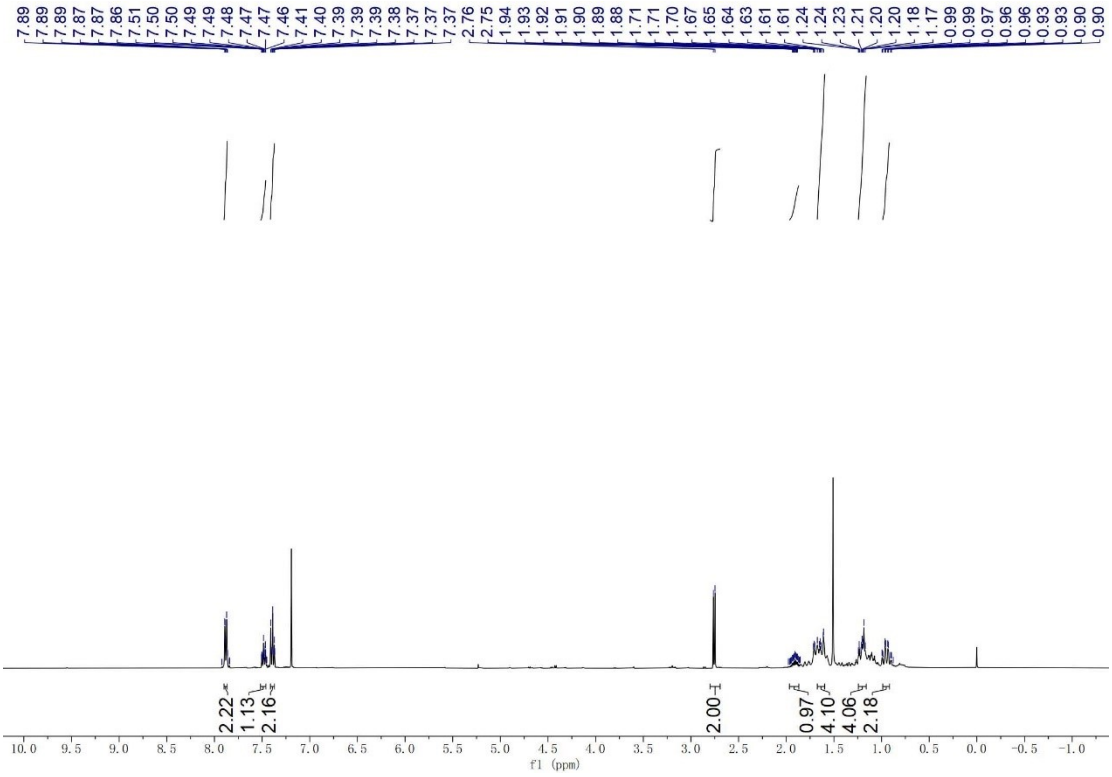
100 MHz in $CDCl_3$



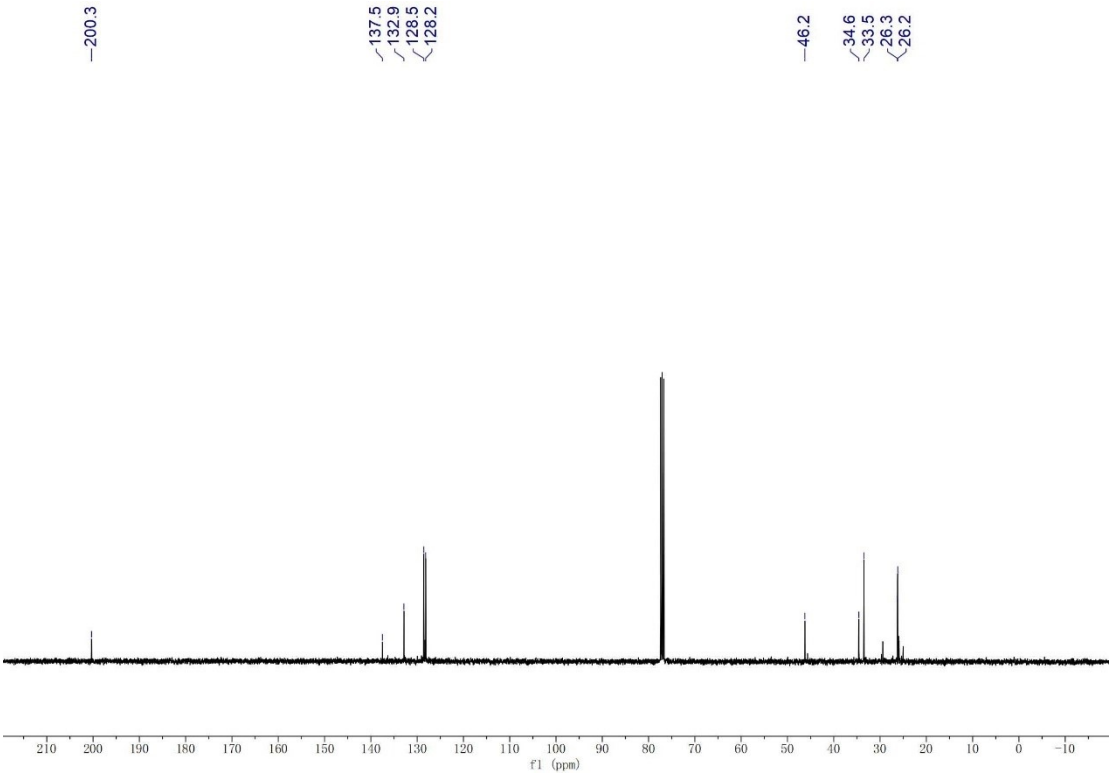


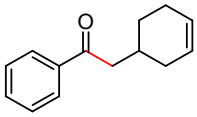
(32)

400 MHz in $CDCl_3$



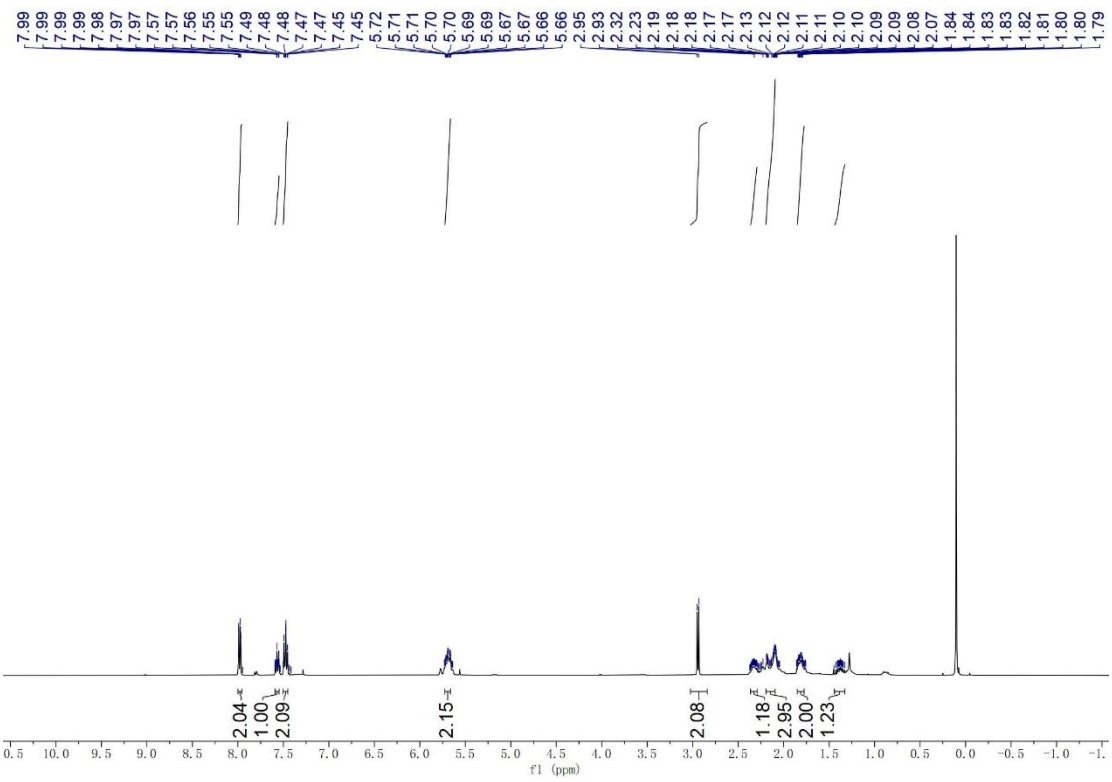
100 MHz in $CDCl_3$



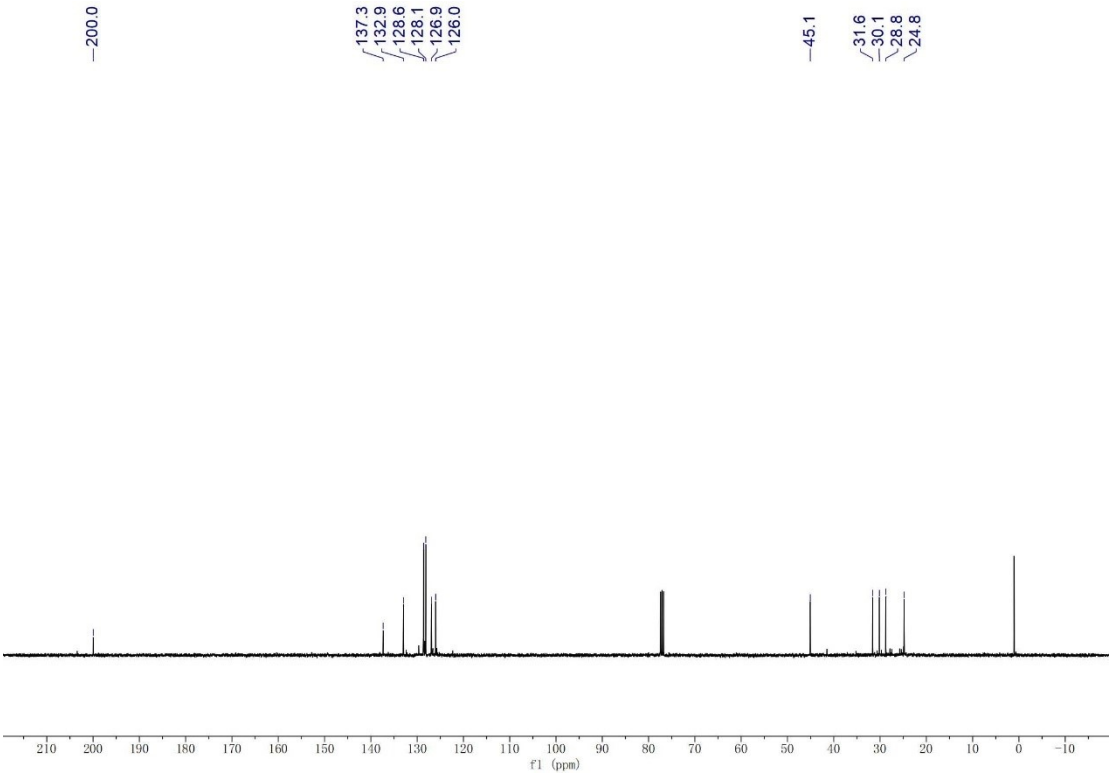


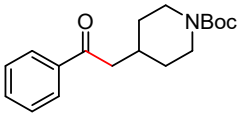
(33)

400 MHz in $CDCl_3$



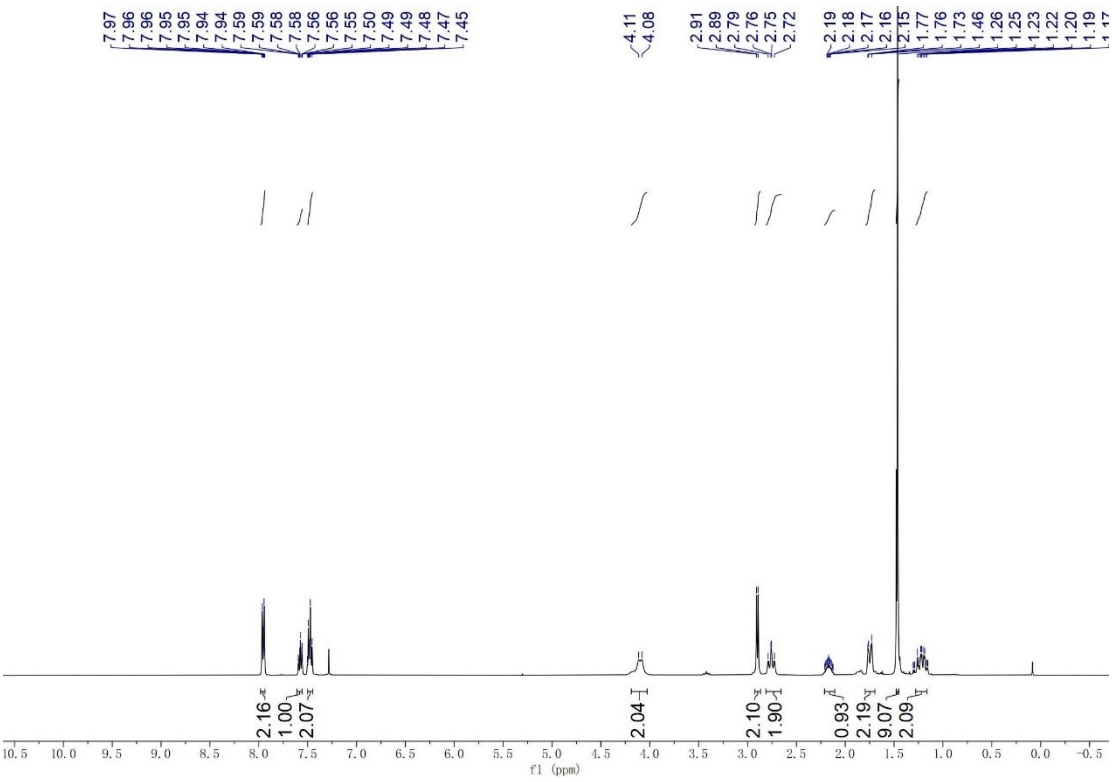
100 MHz in $CDCl_3$



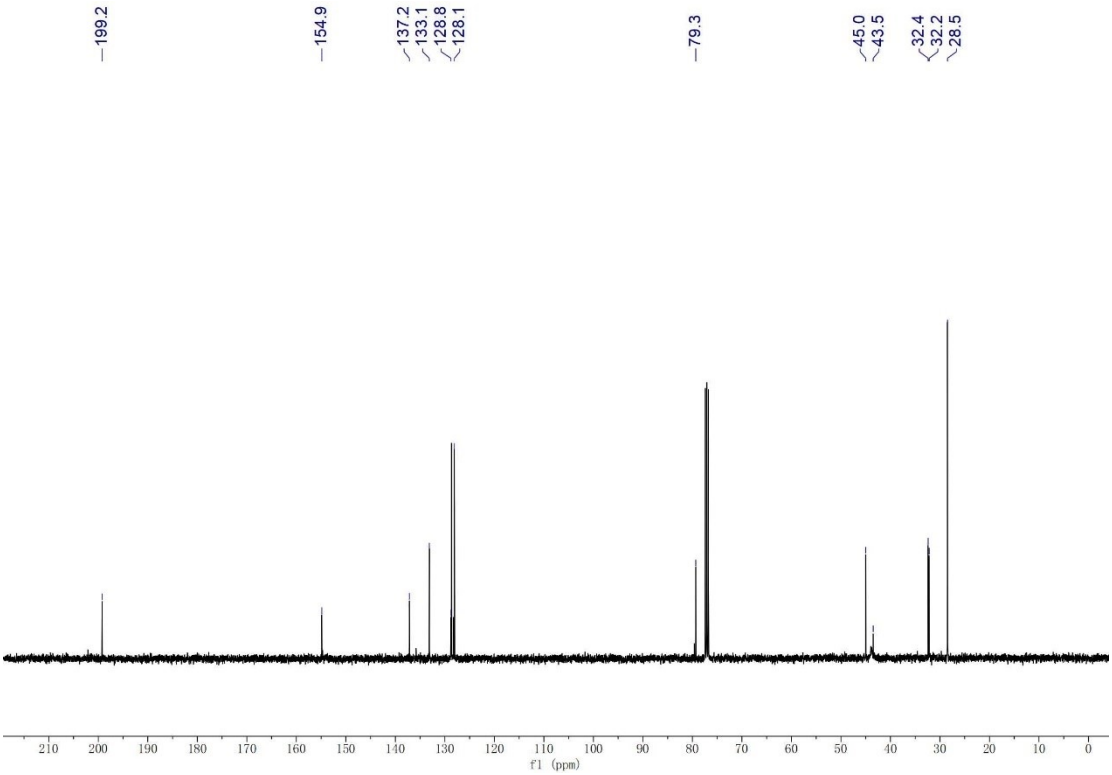


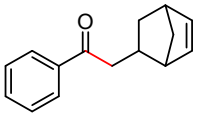
(34)

400 MHz in $CDCl_3$



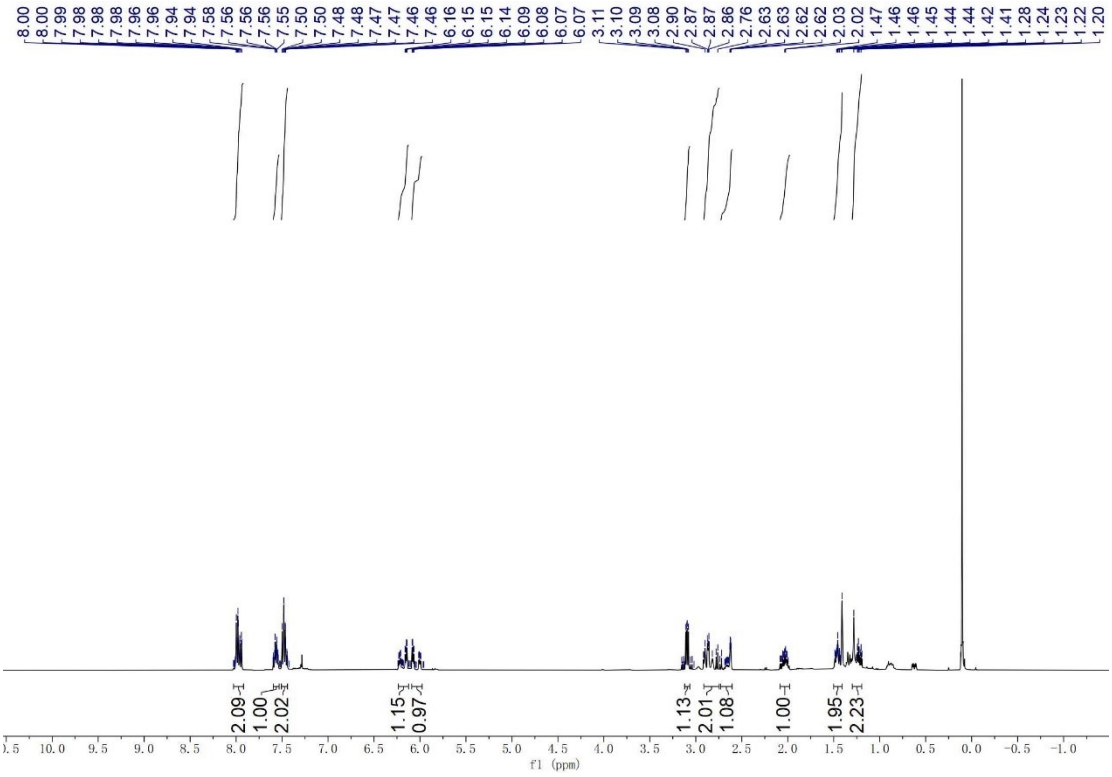
100 MHz in $CDCl_3$



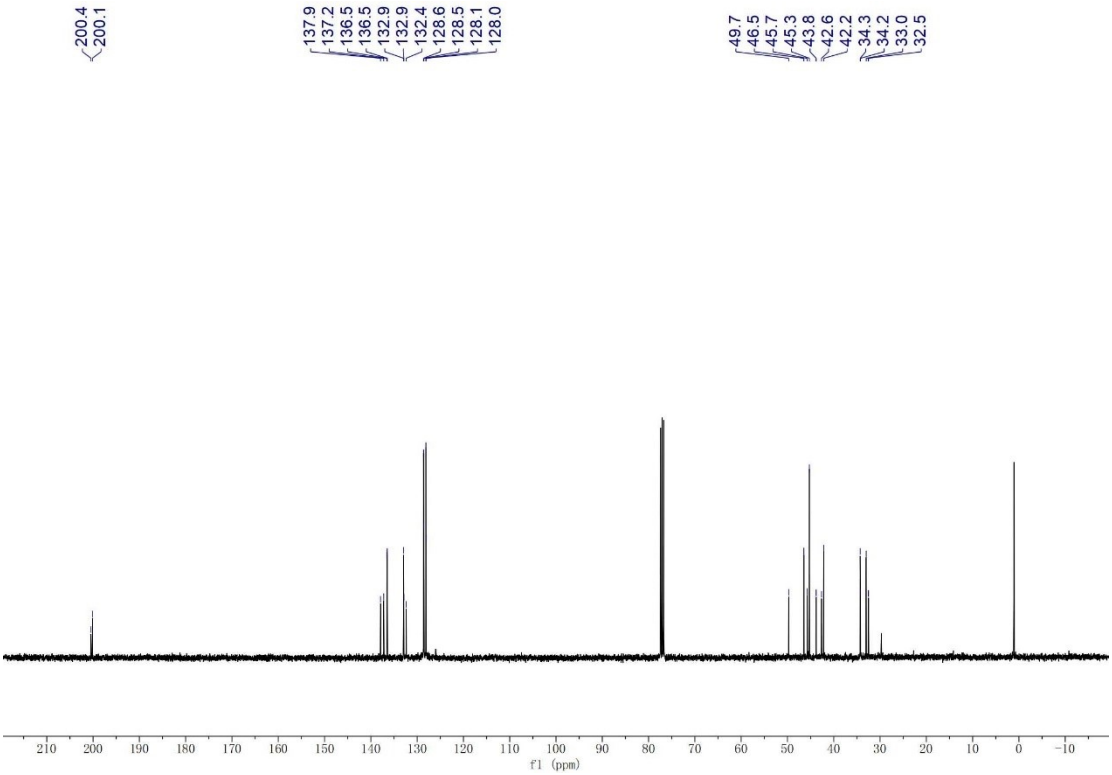


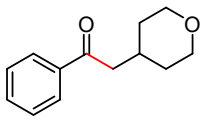
(35)

400 MHz in $CDCl_3$



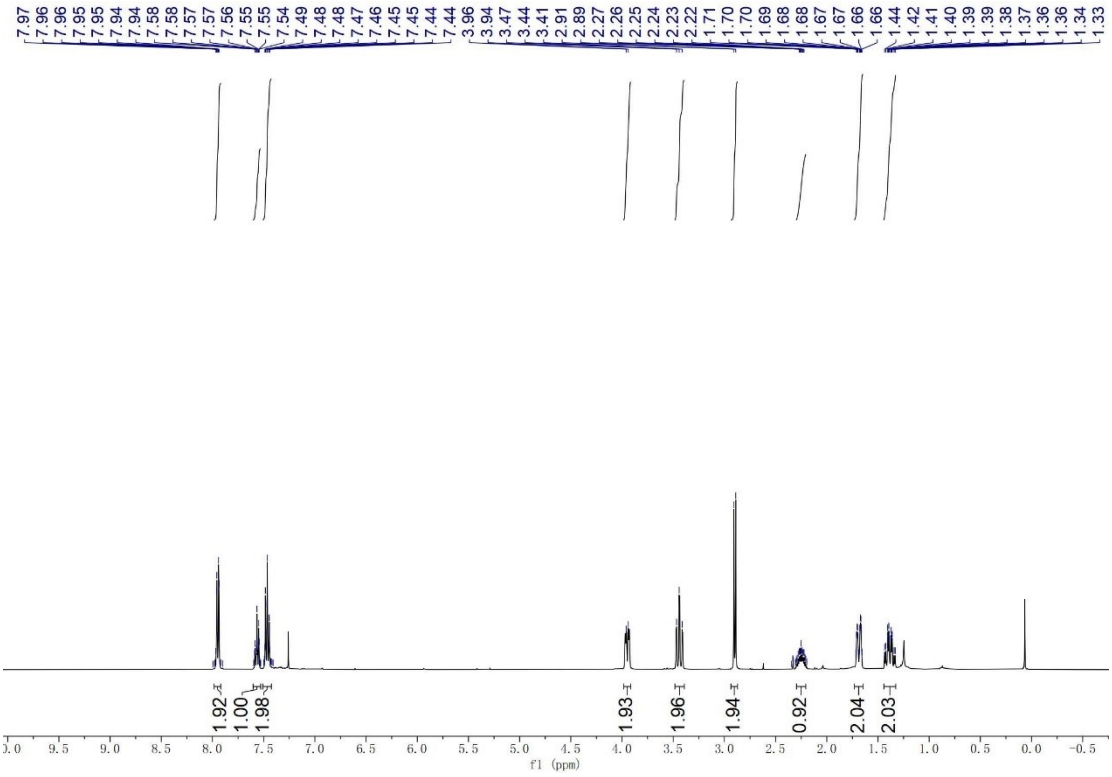
100 MHz in $CDCl_3$



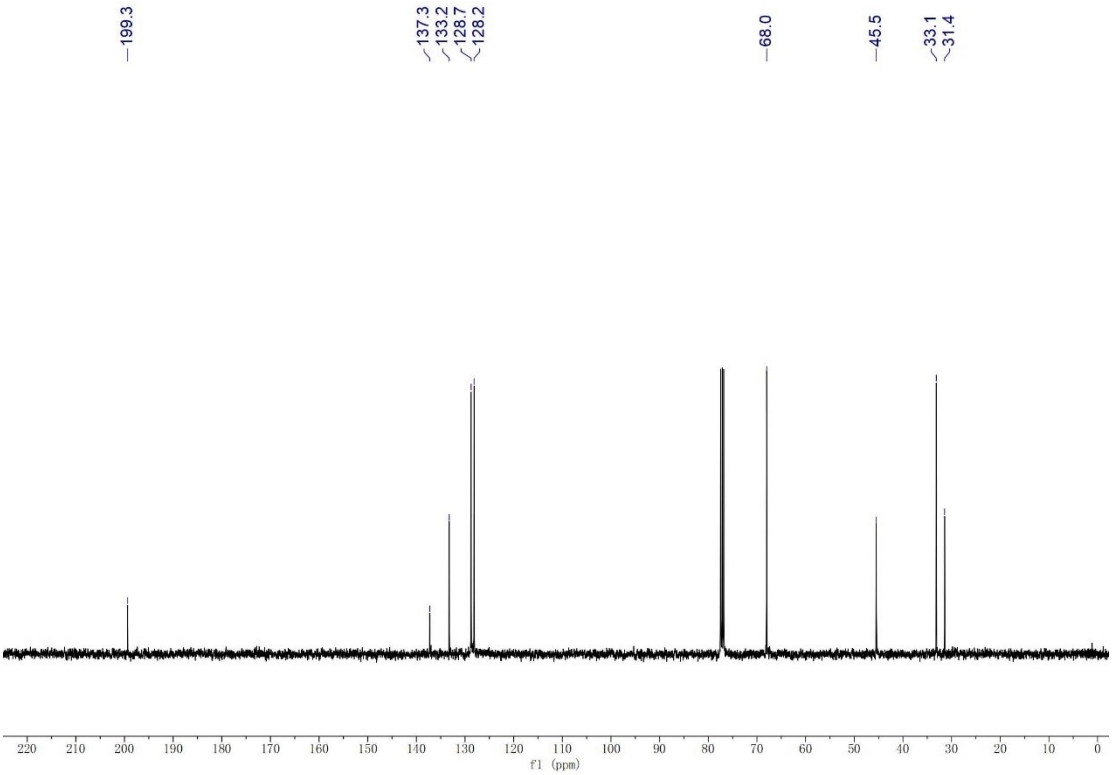


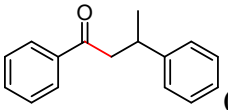
(36)

400 MHz in $CDCl_3$



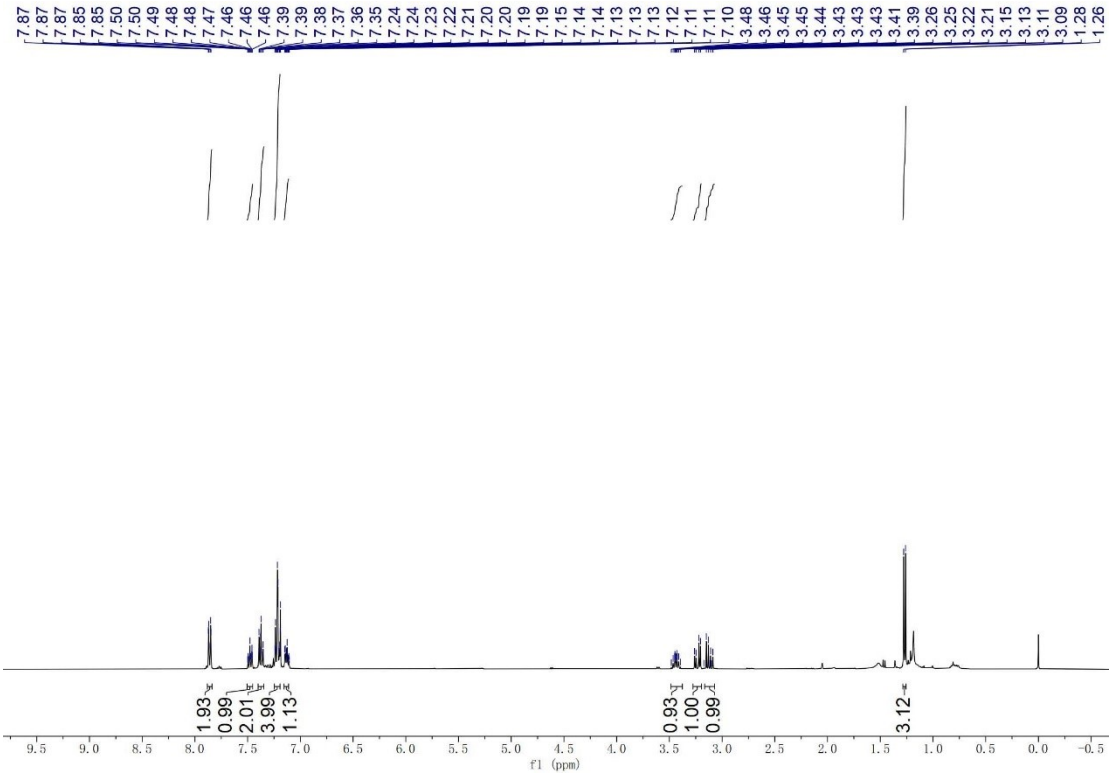
100 MHz in $CDCl_3$



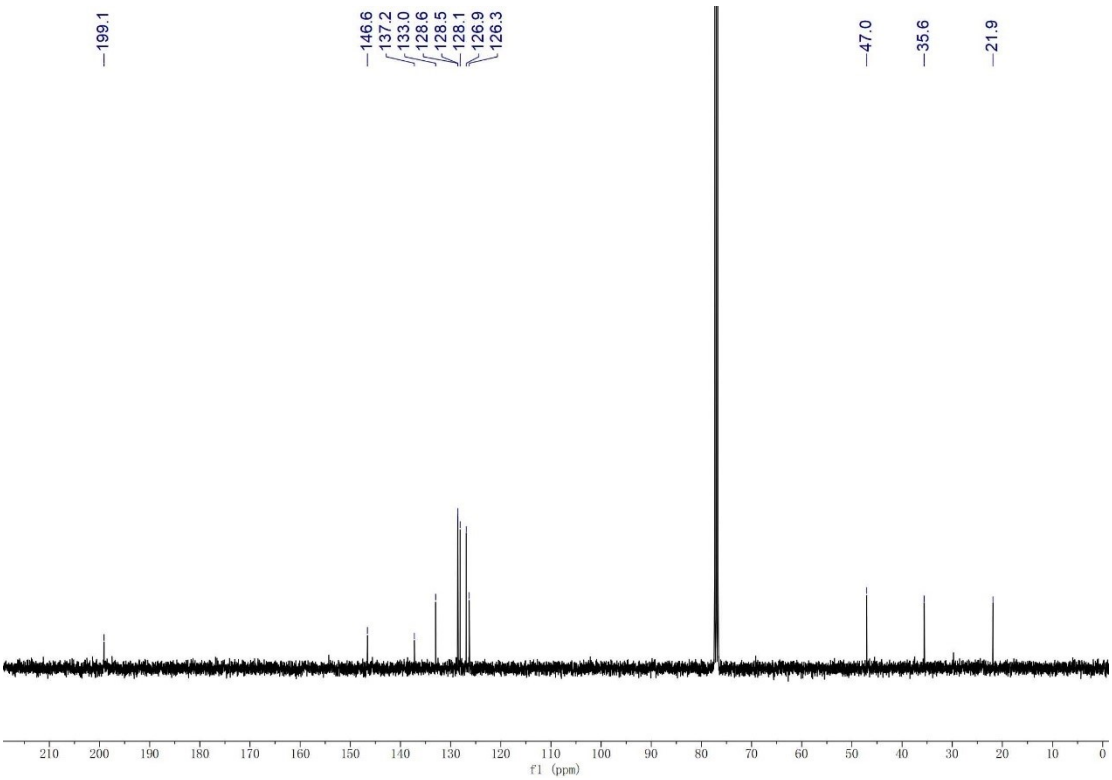


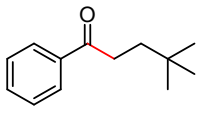
(37)

400 MHz in $CDCl_3$



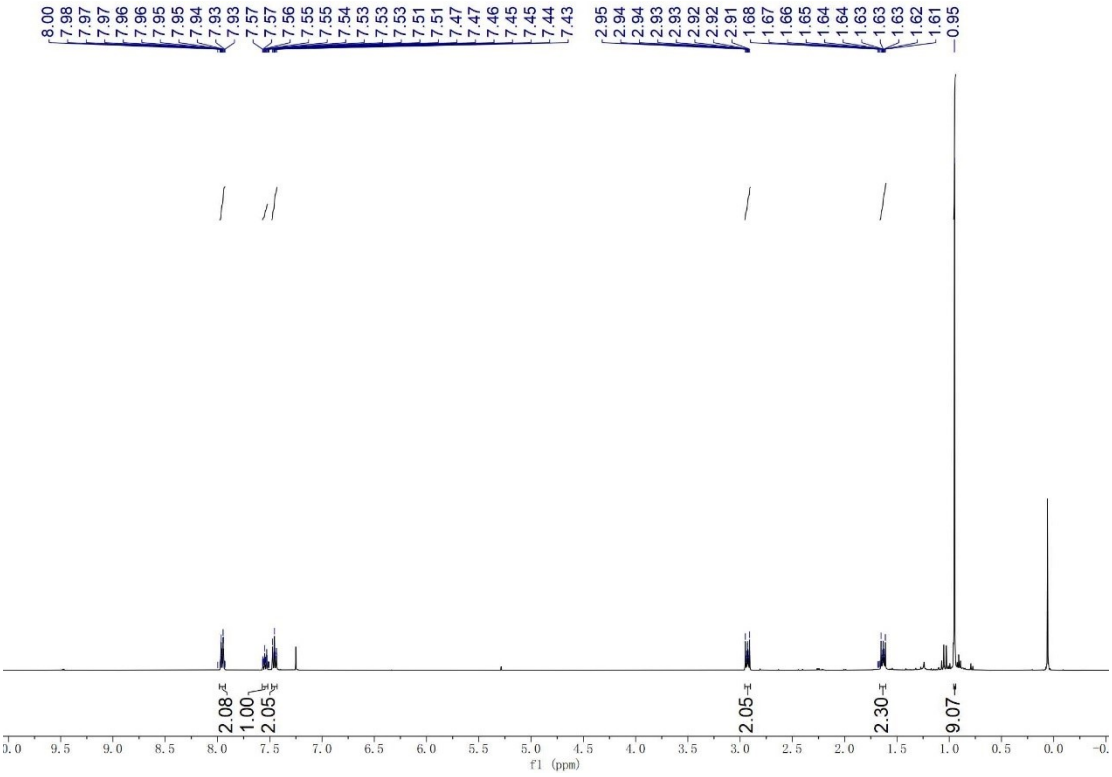
100 MHz in $CDCl_3$



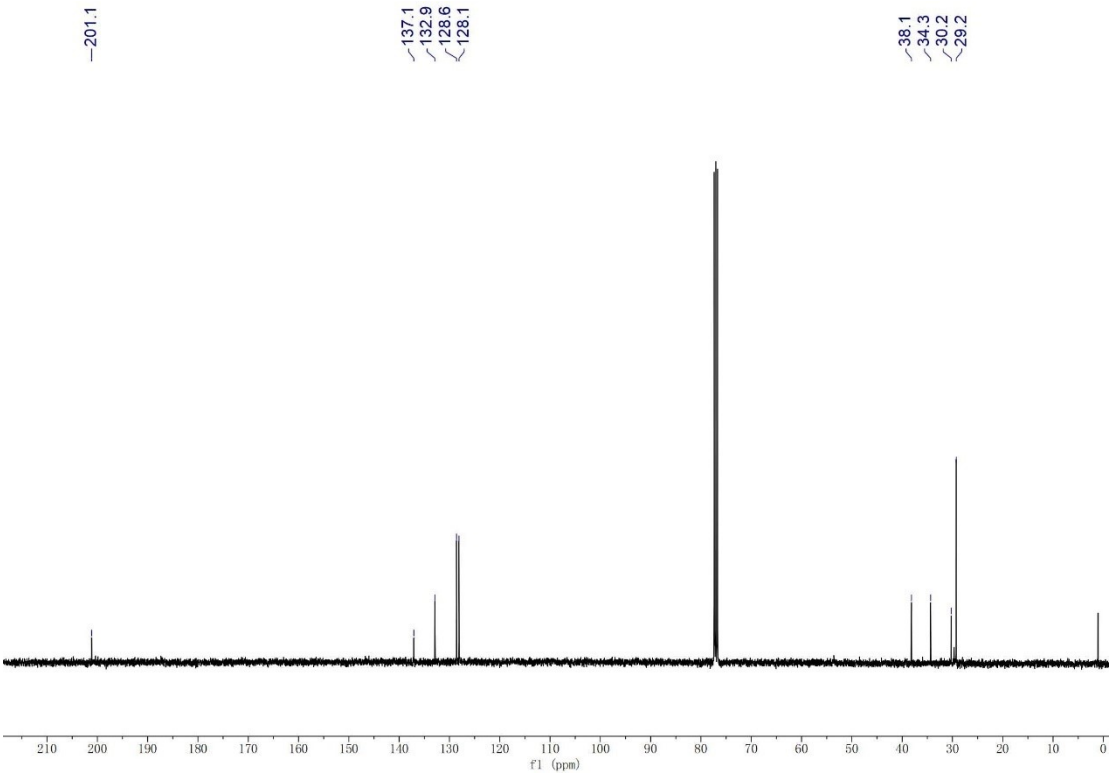


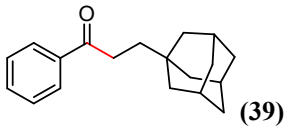
(38)

400 MHz in $CDCl_3$



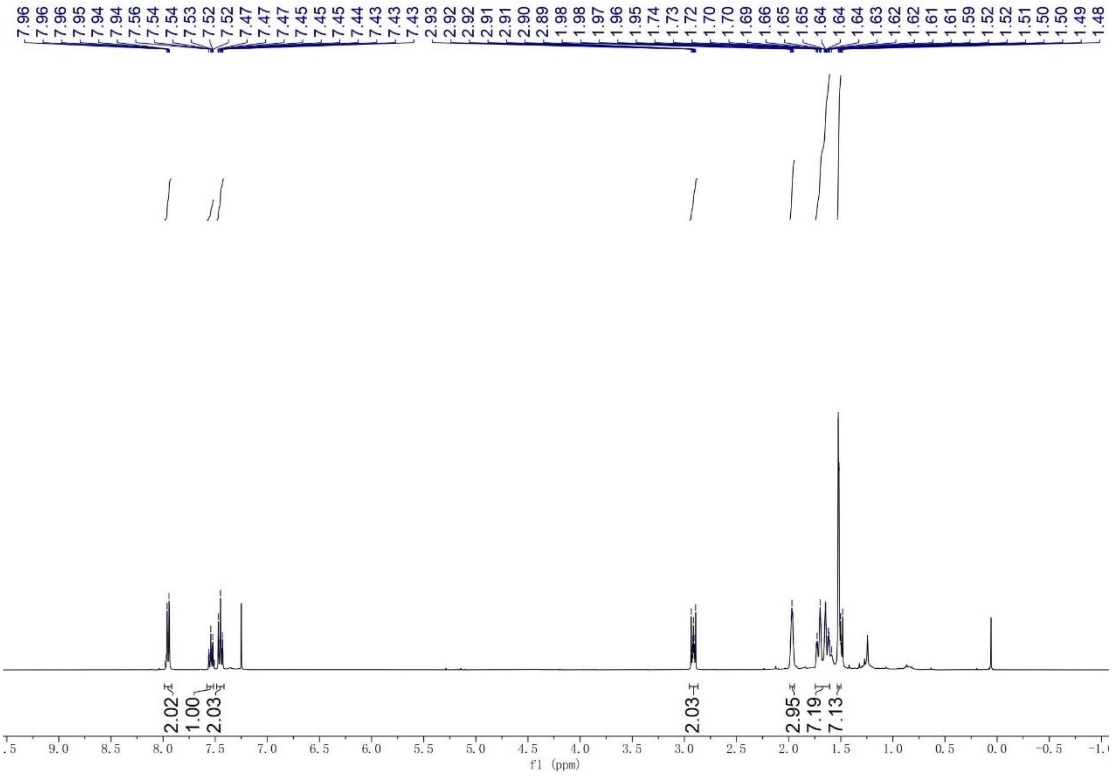
100 MHz in $CDCl_3$



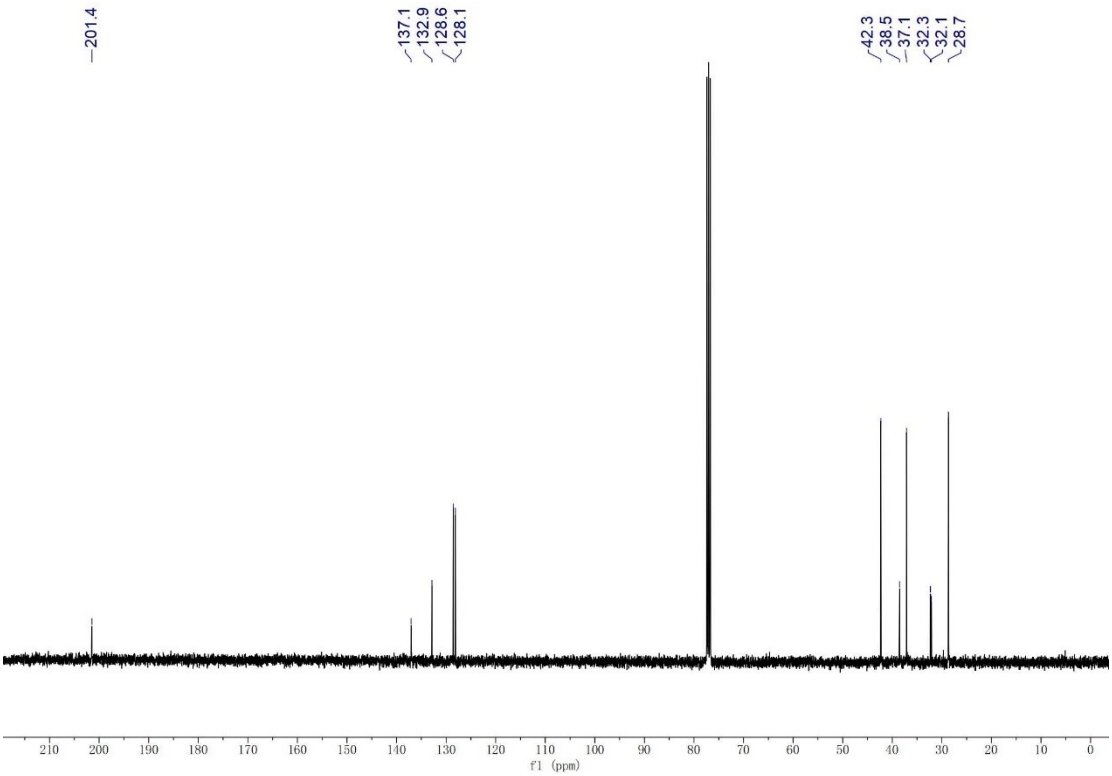


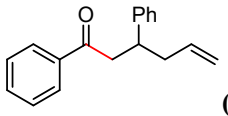
(39)

400 MHz in $CDCl_3$



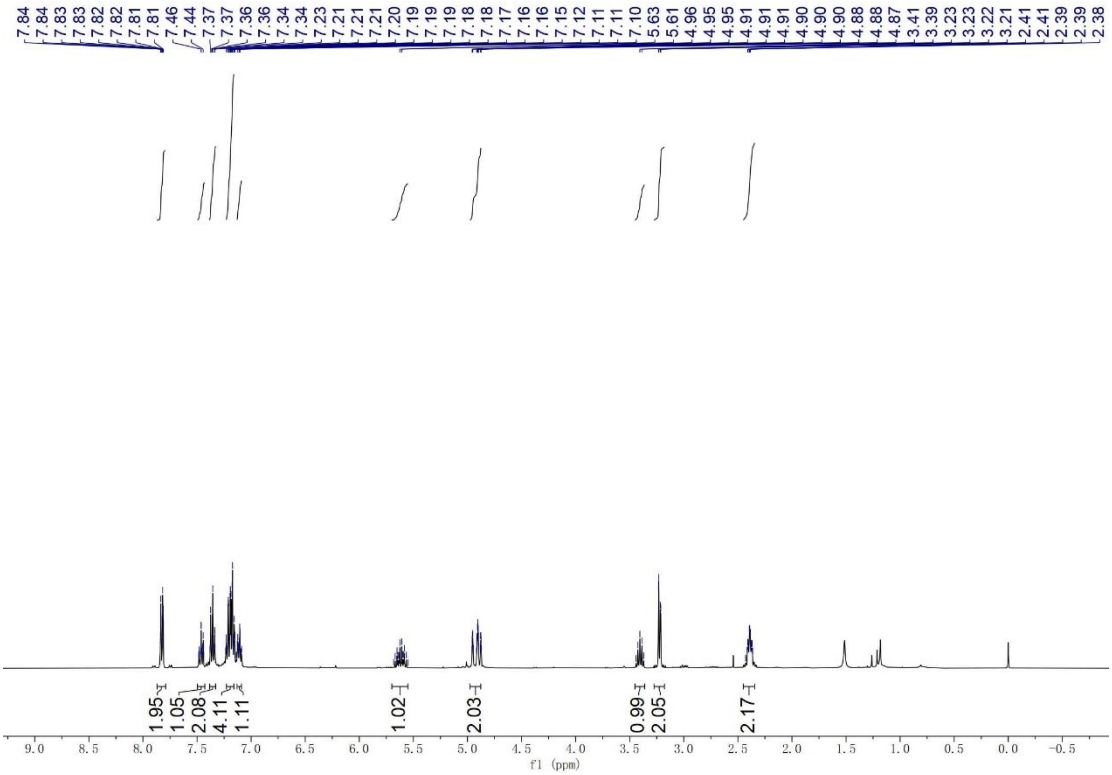
100 MHz in $CDCl_3$



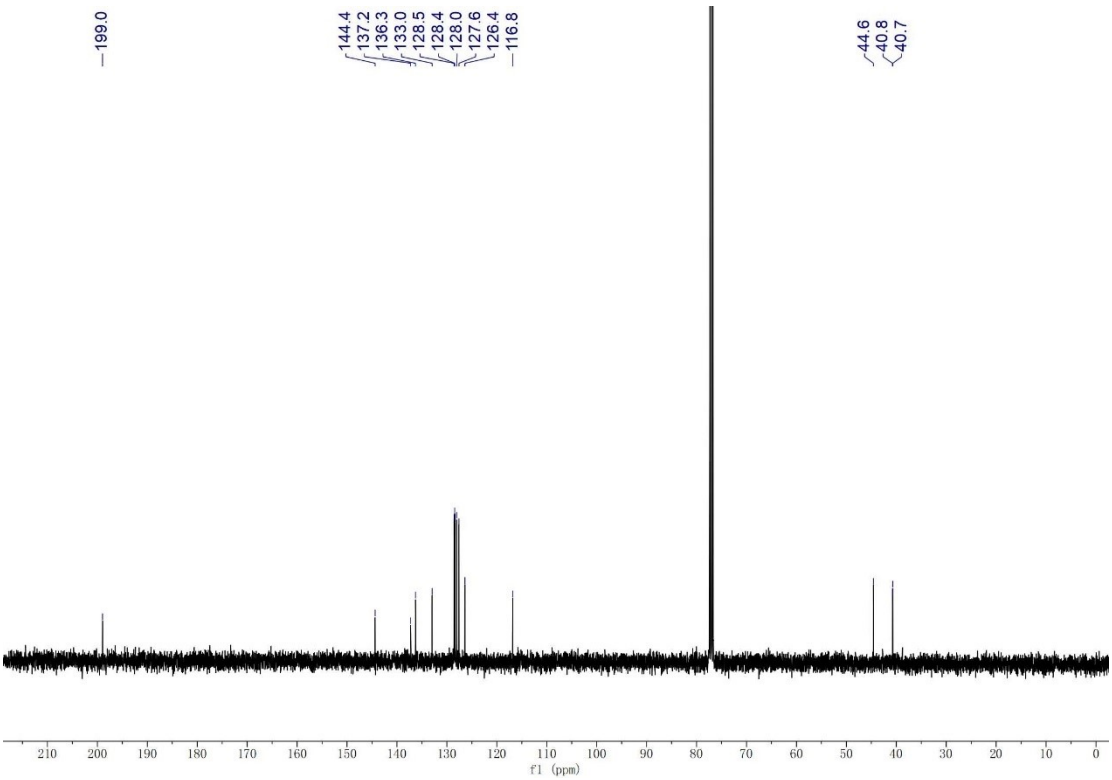


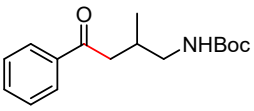
(40)

400 MHz in $CDCl_3$



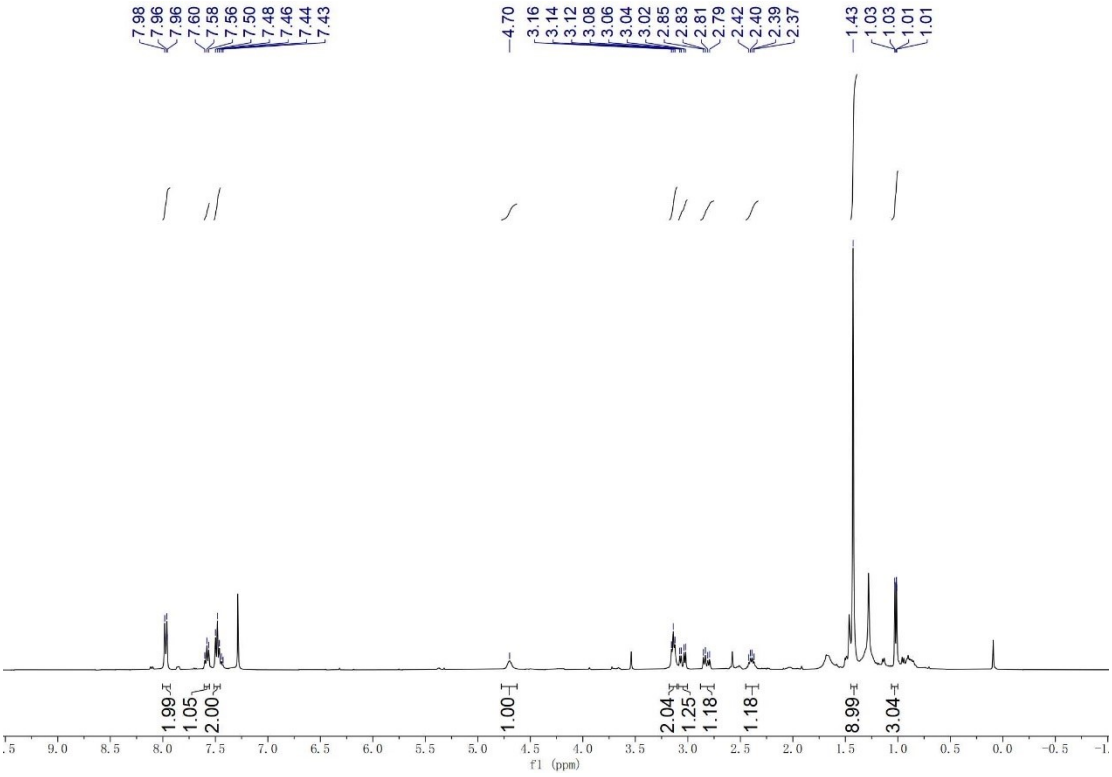
100 MHz in $CDCl_3$



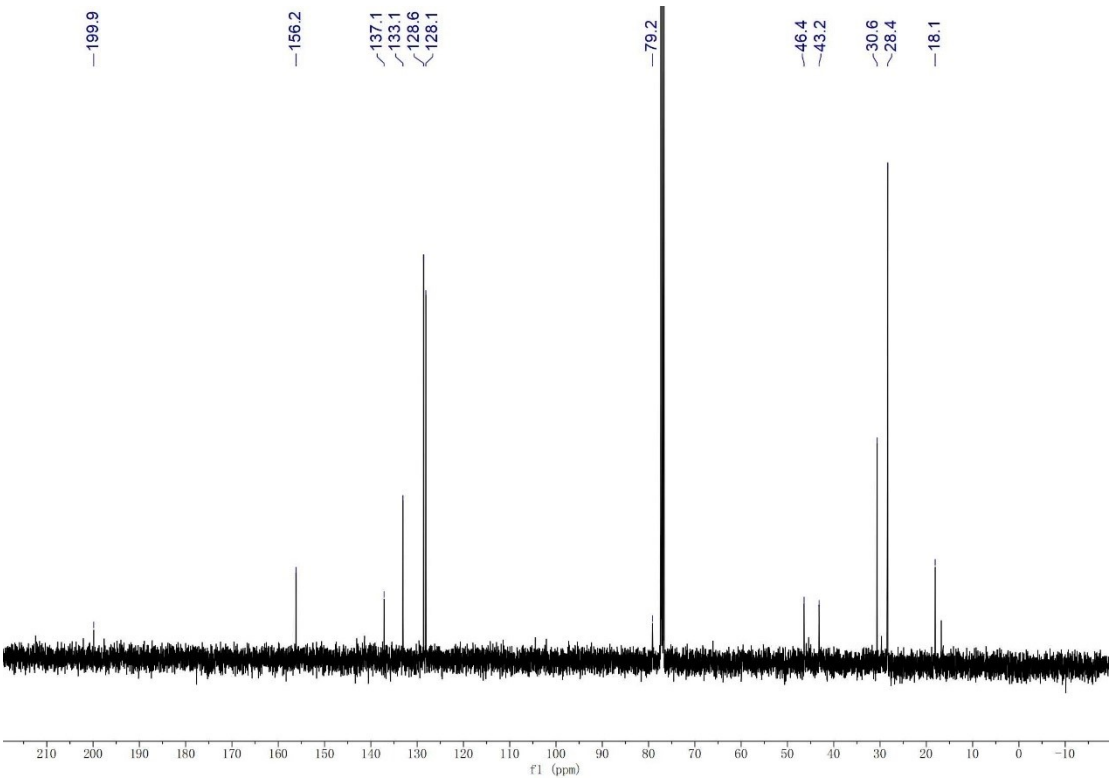


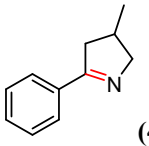
(41a)

400 MHz in $CDCl_3$



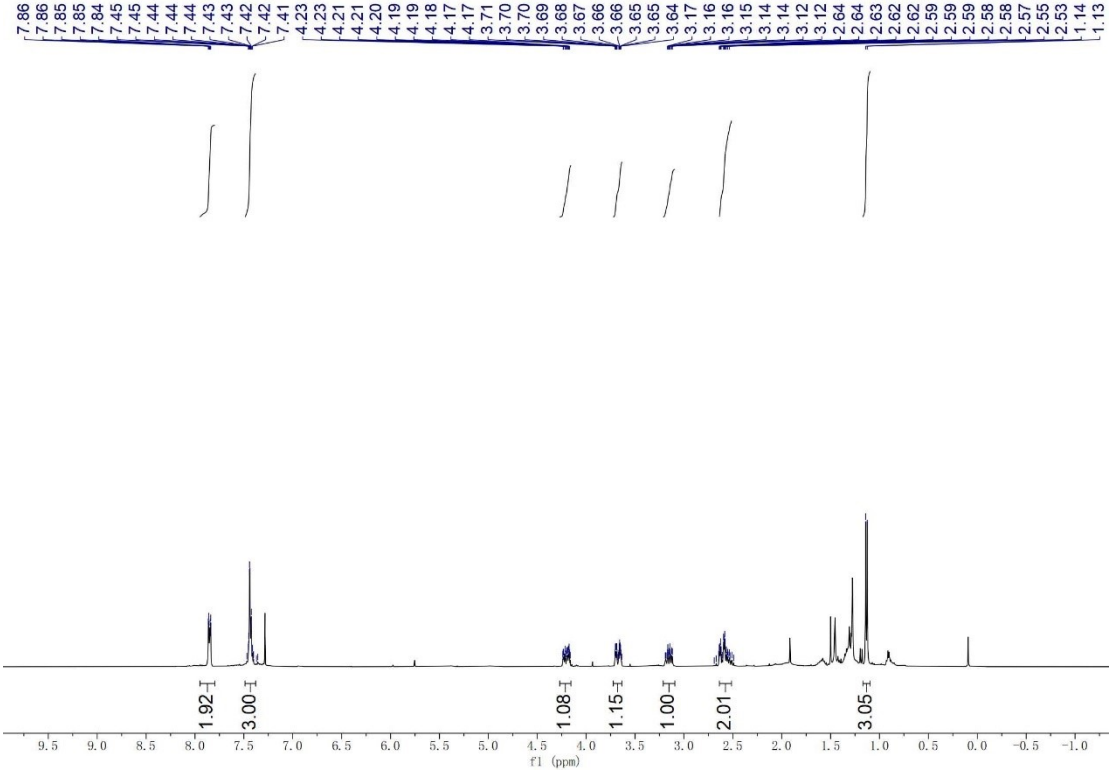
100 MHz in $CDCl_3$



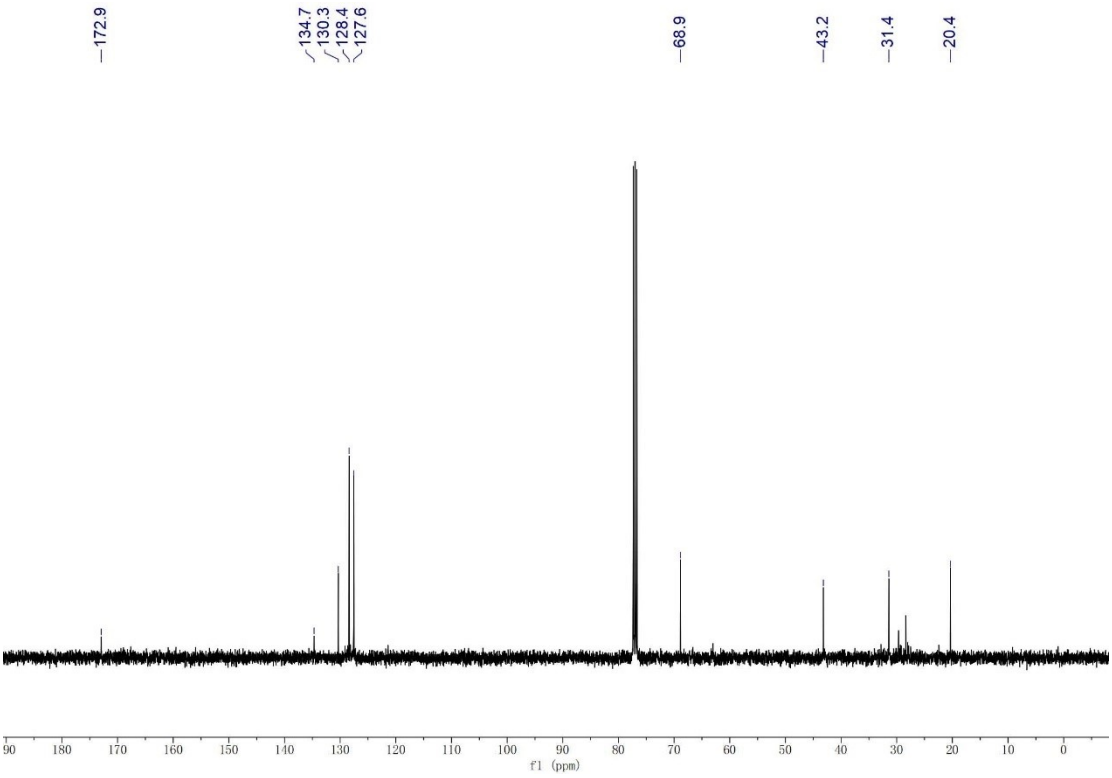


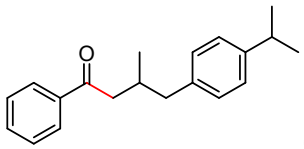
(41b)

400 MHz in $CDCl_3$



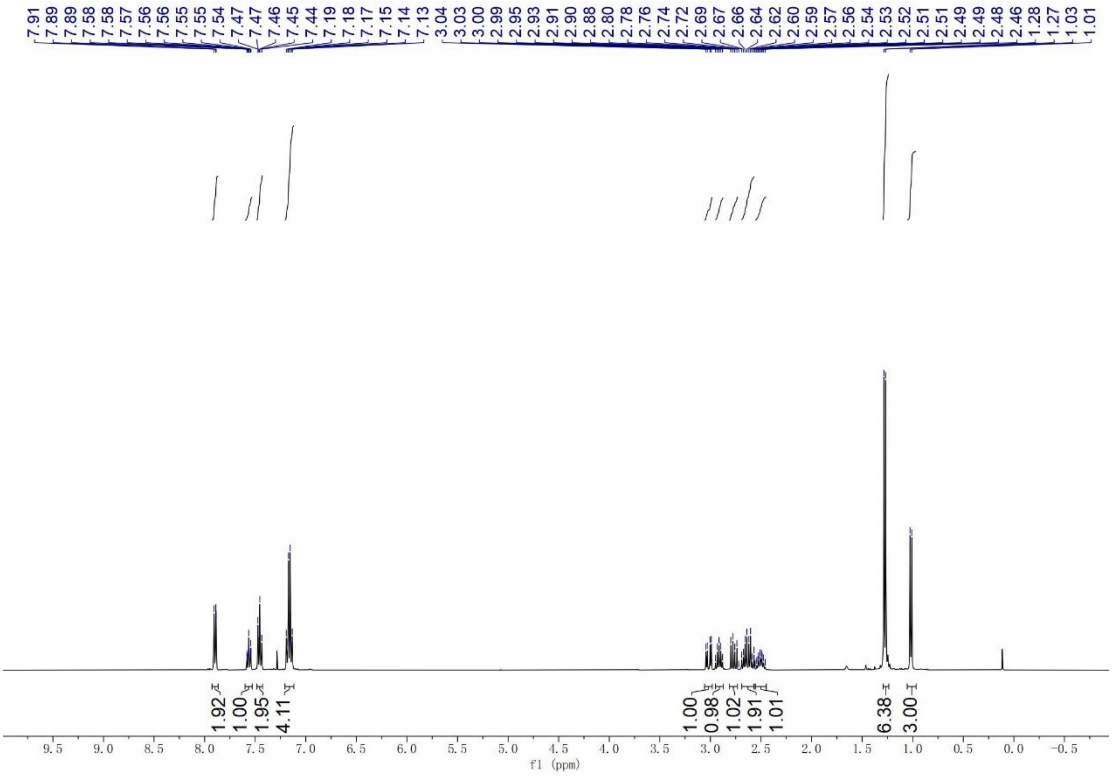
100 MHz in $CDCl_3$



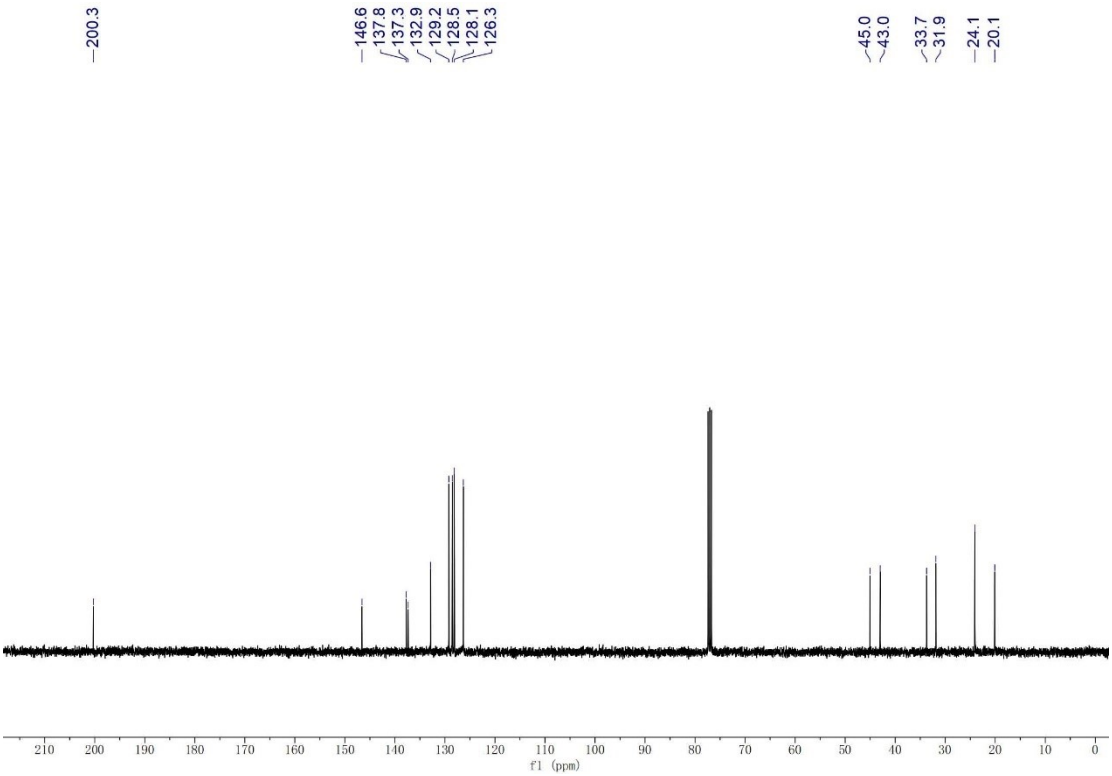


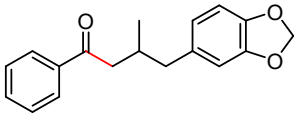
(42)

400 MHz in $CDCl_3$



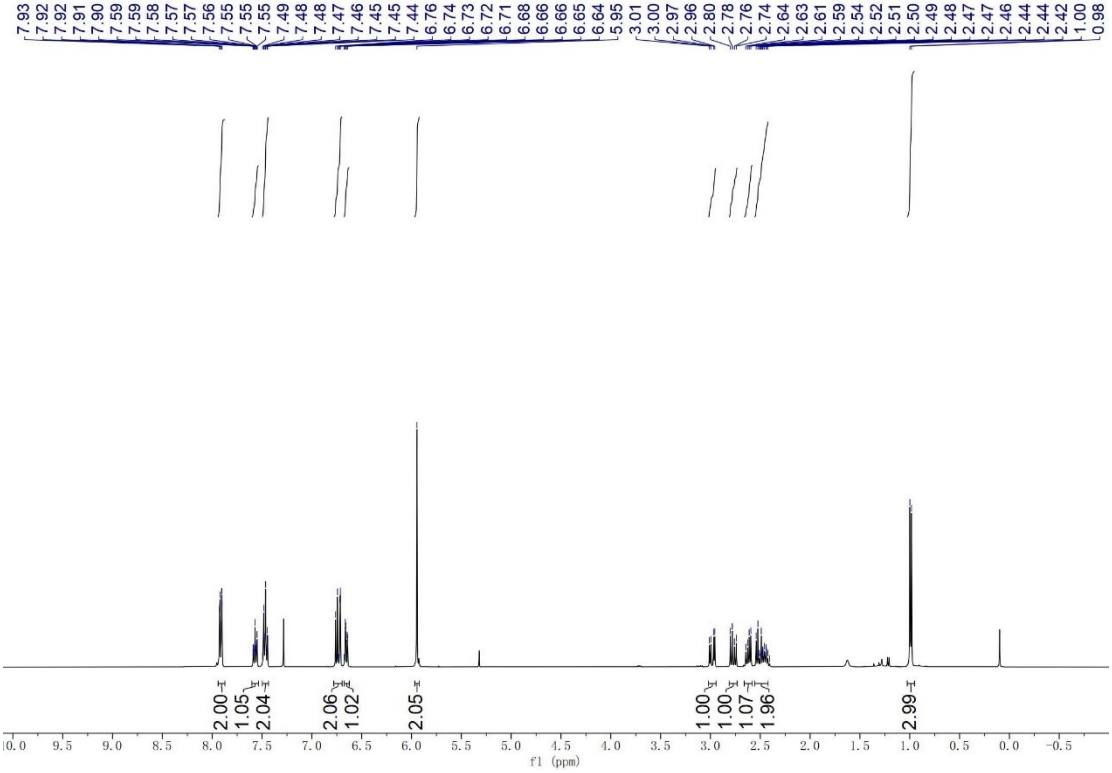
100 MHz in $CDCl_3$



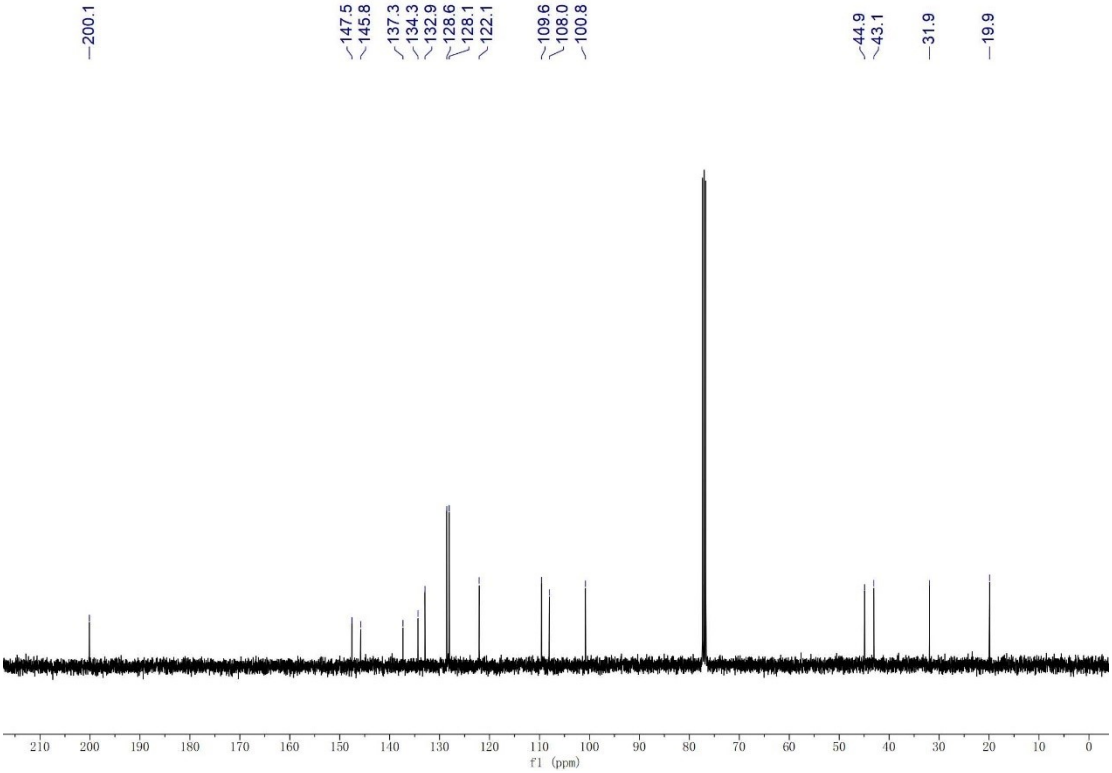


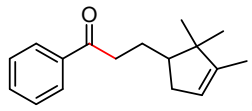
(43)

400 MHz in $CDCl_3$



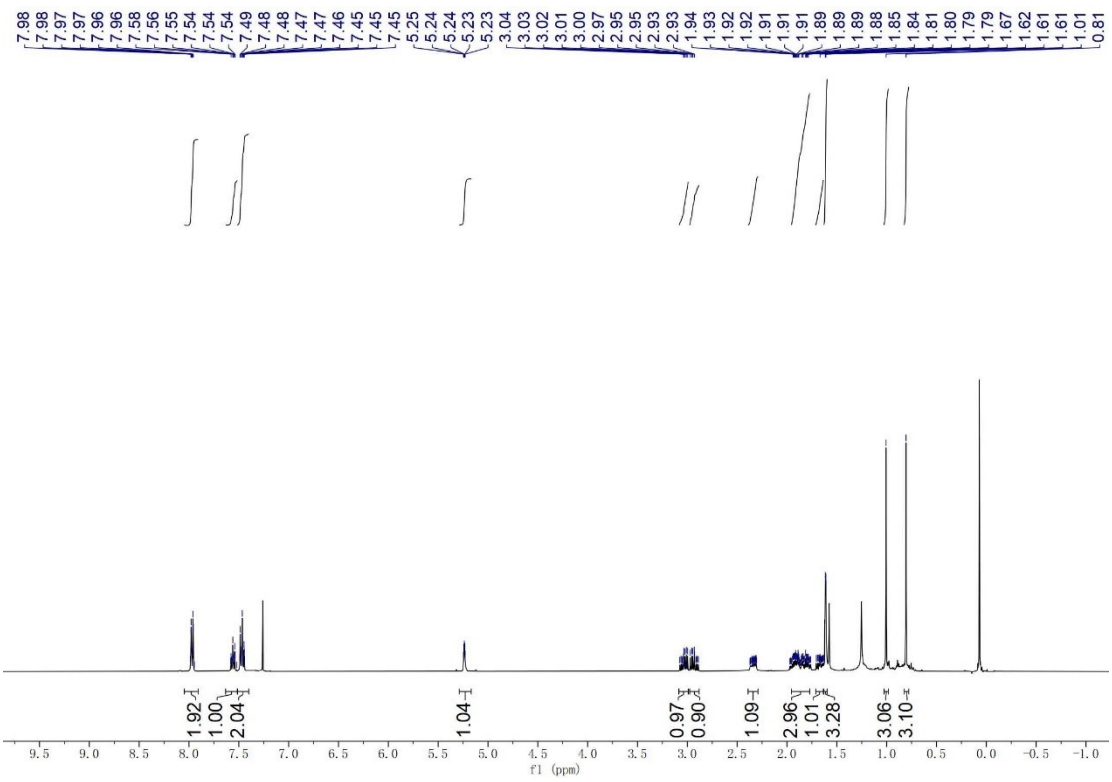
100 MHz in $CDCl_3$



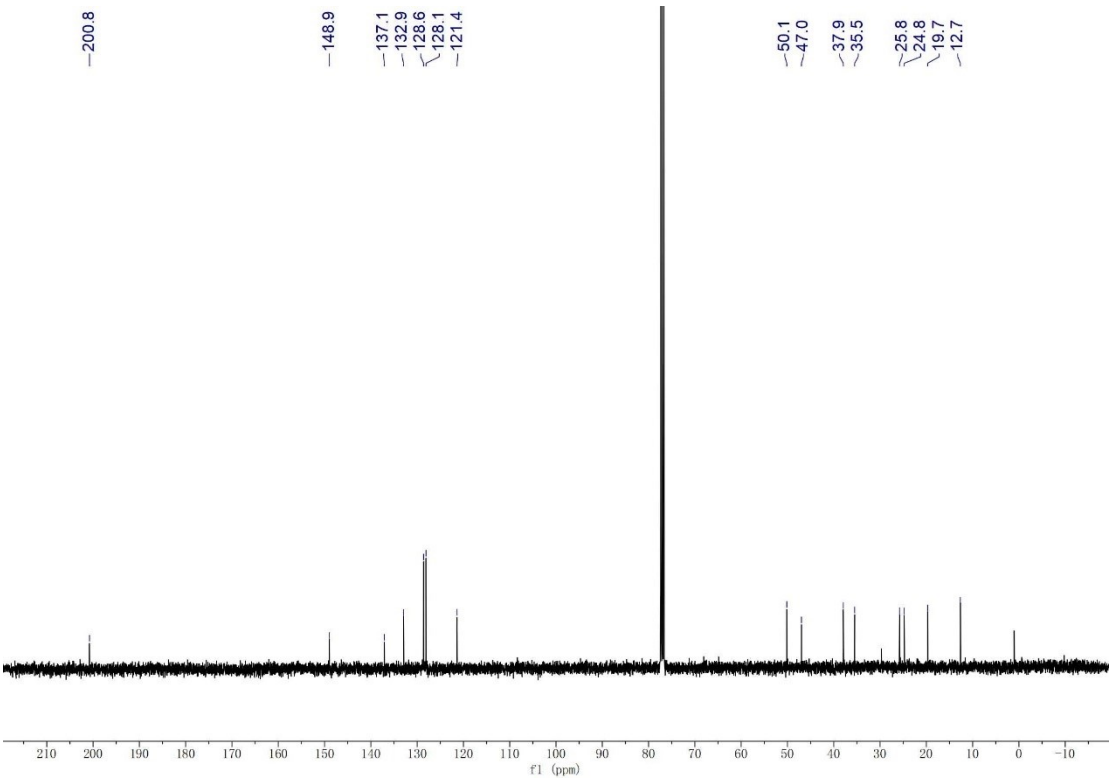


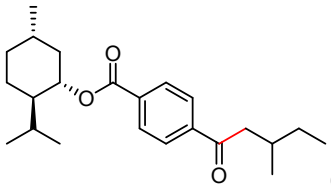
(44)

400 MHz in $CDCl_3$



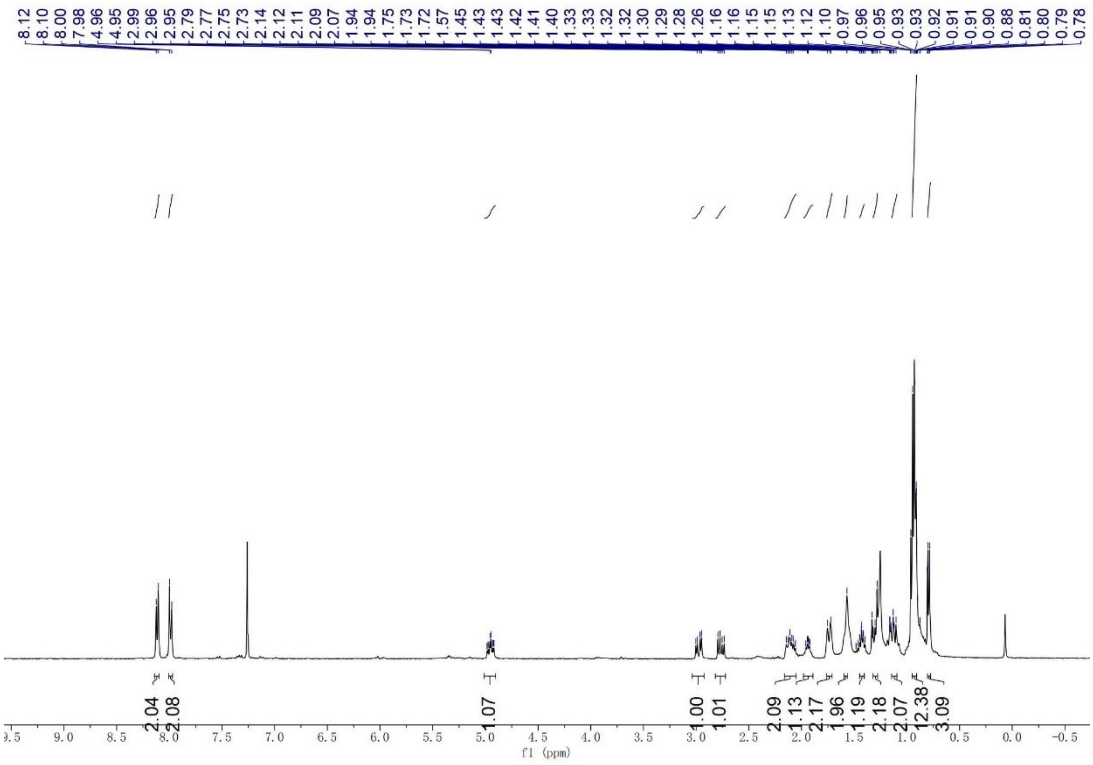
100 MHz in $CDCl_3$



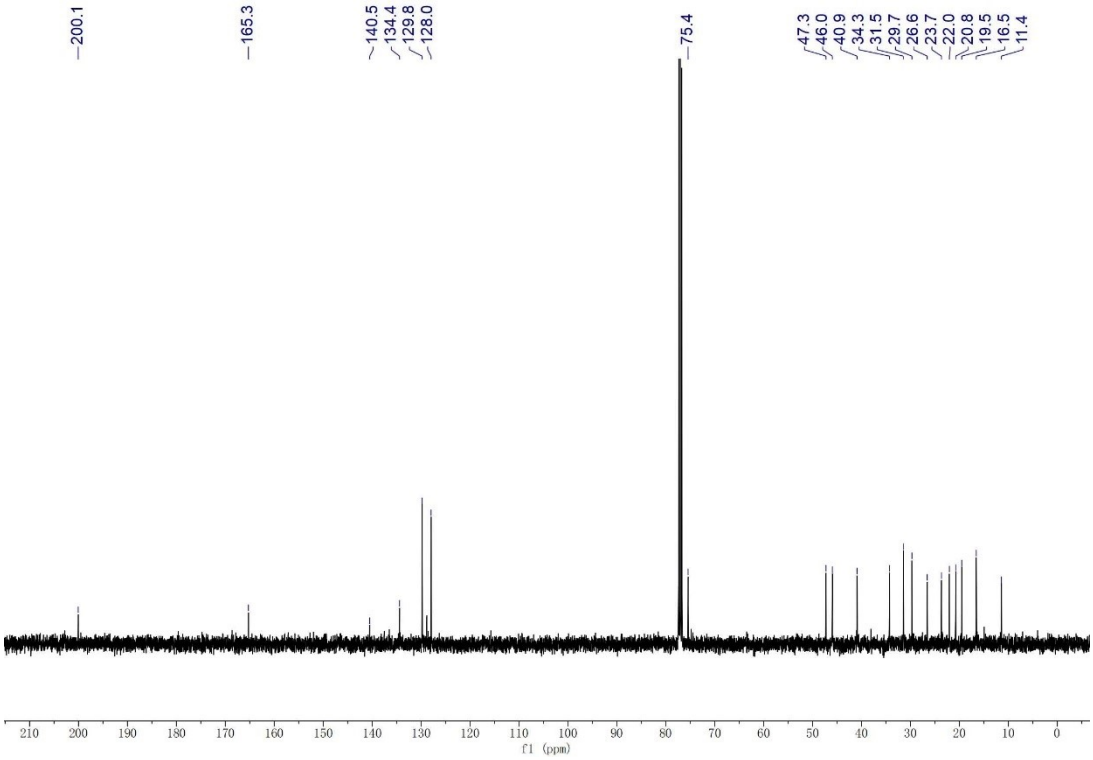


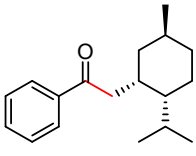
(45)

400 MHz in $CDCl_3$



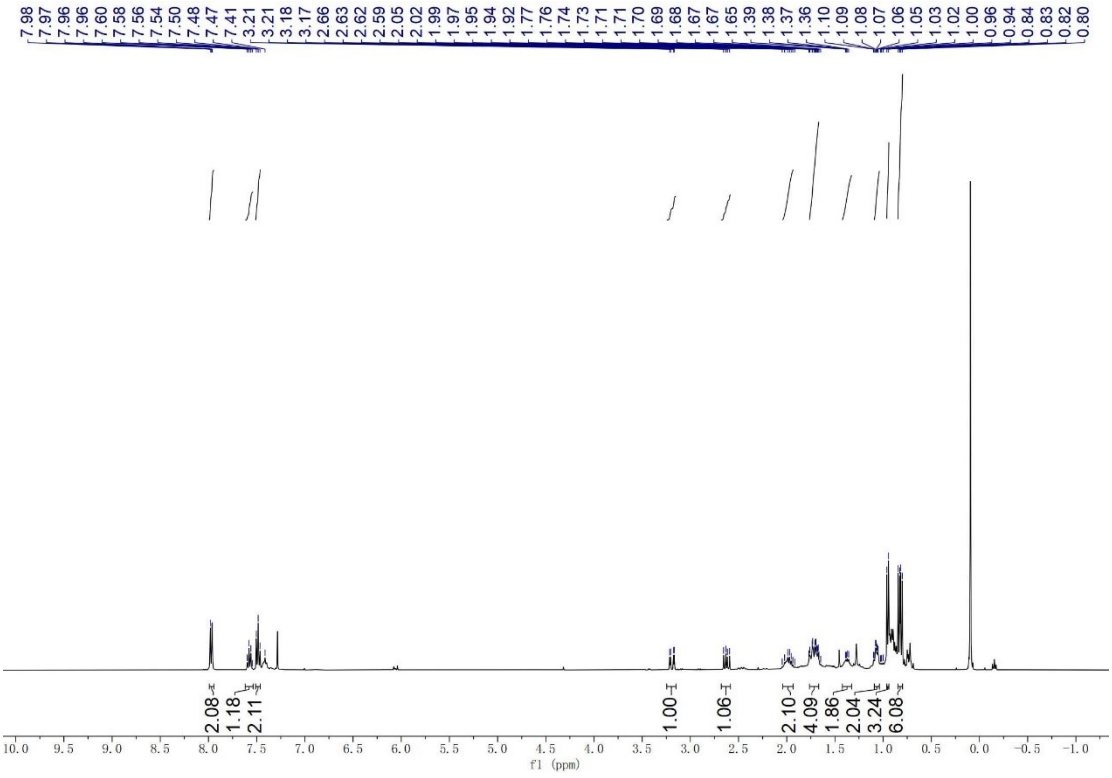
100 MHz in $CDCl_3$



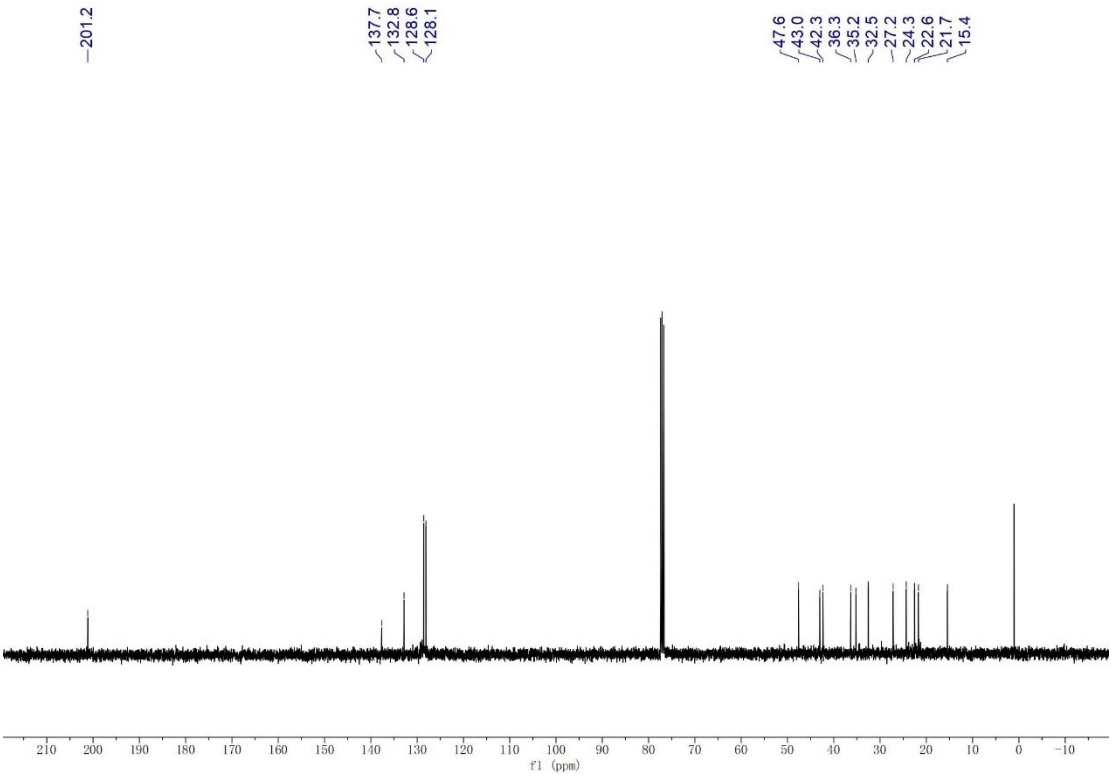


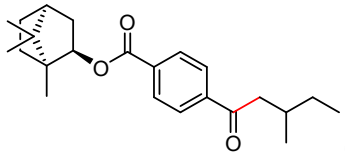
(46)

400 MHz in $CDCl_3$



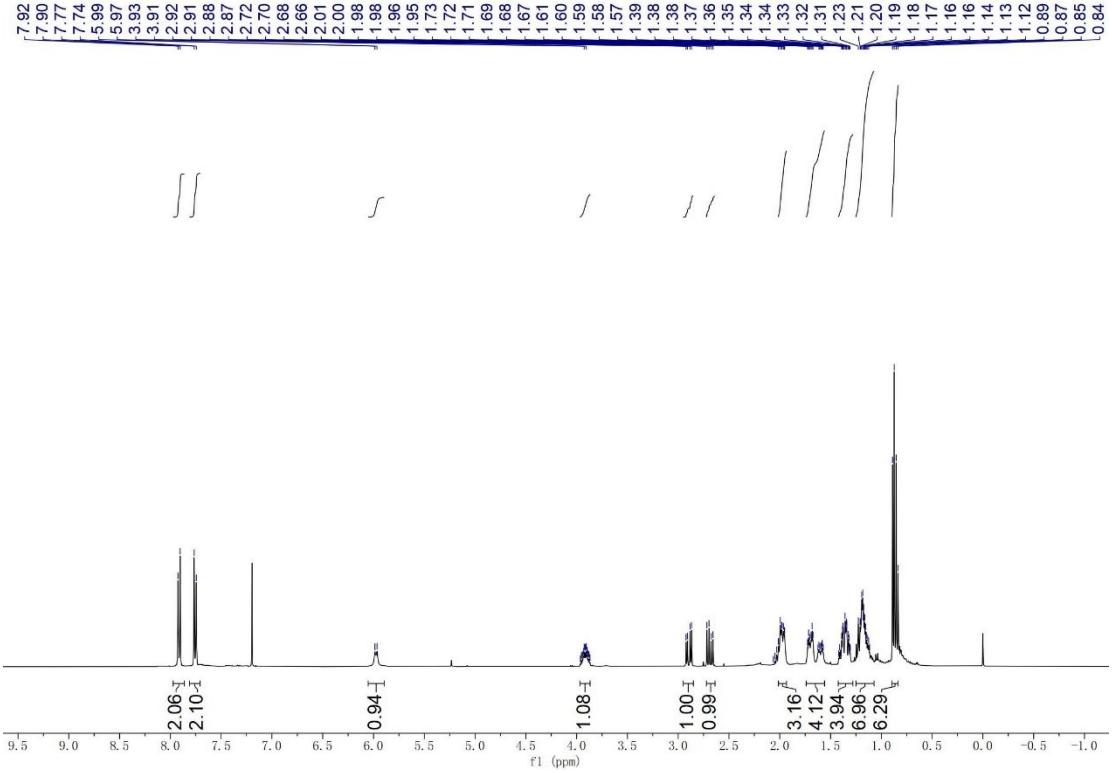
100 MHz in $CDCl_3$



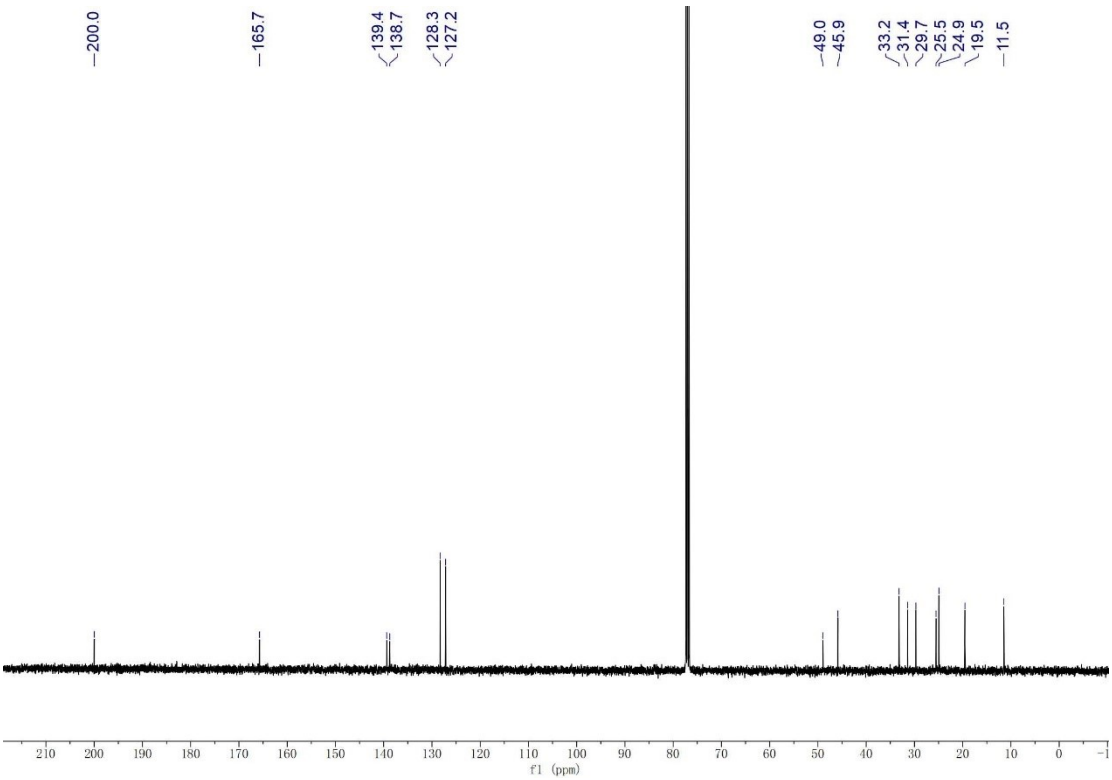


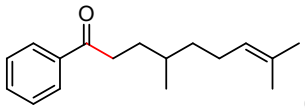
(47)

400 MHz in $CDCl_3$



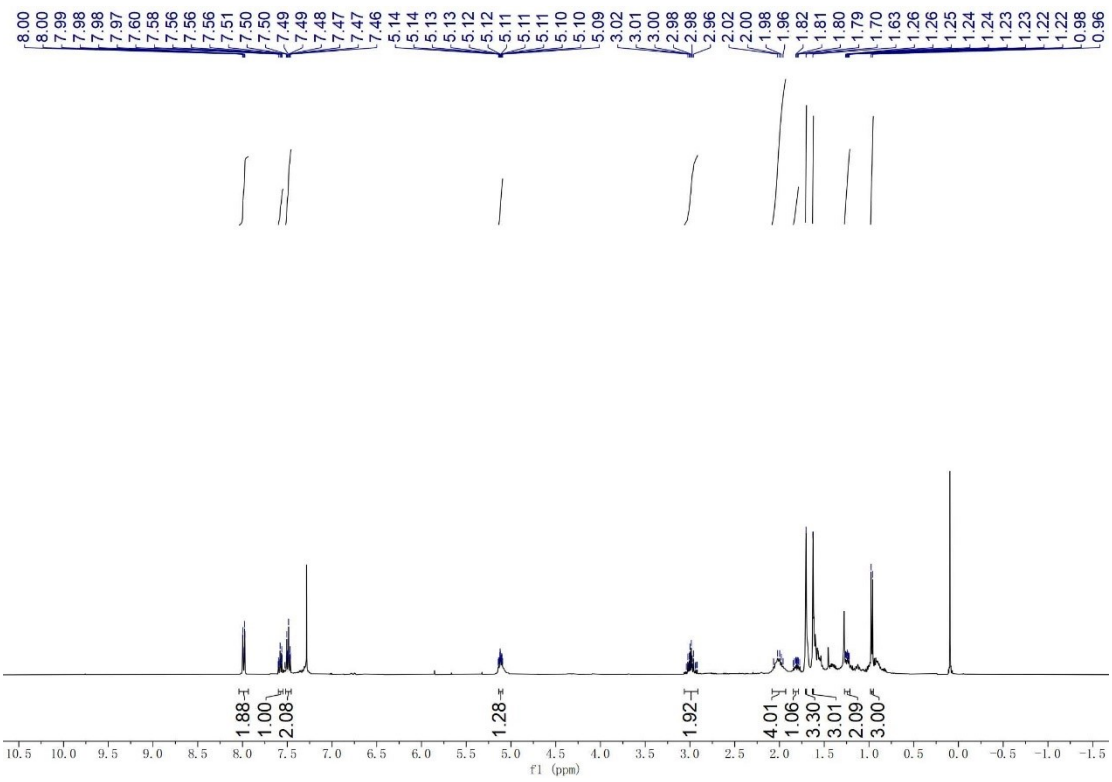
100 MHz in $CDCl_3$



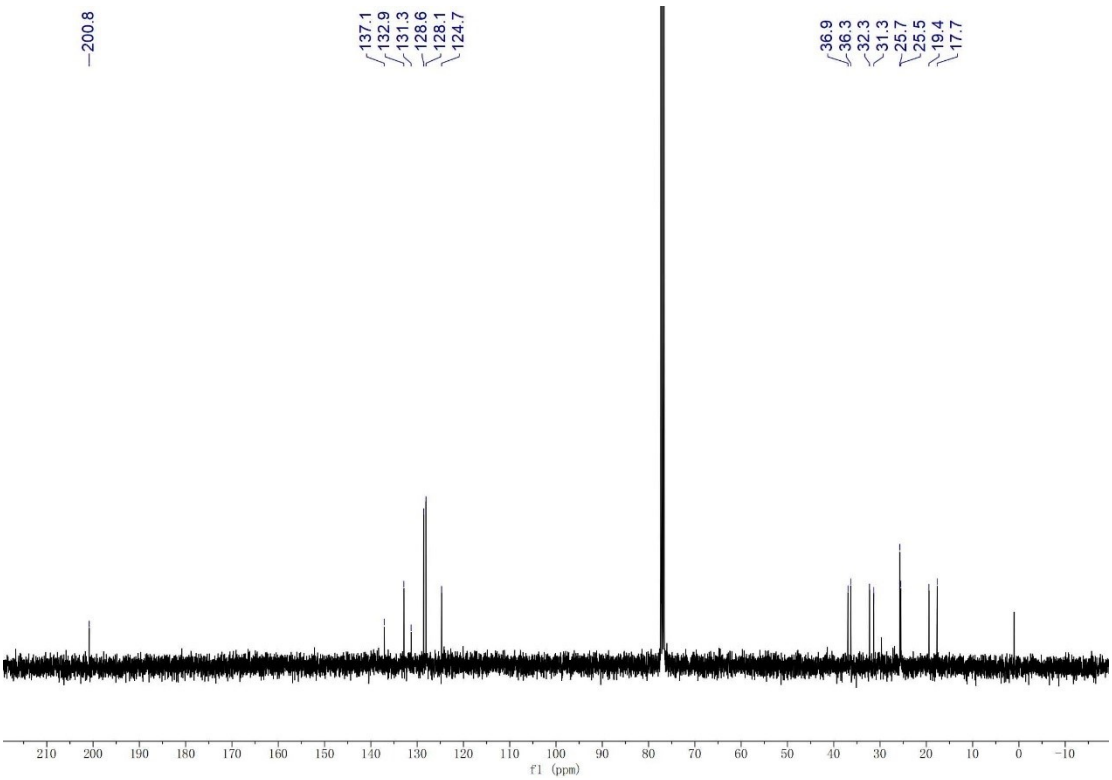


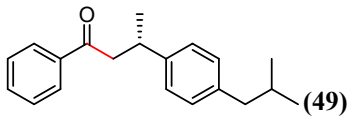
(48)

400 MHz in $CDCl_3$



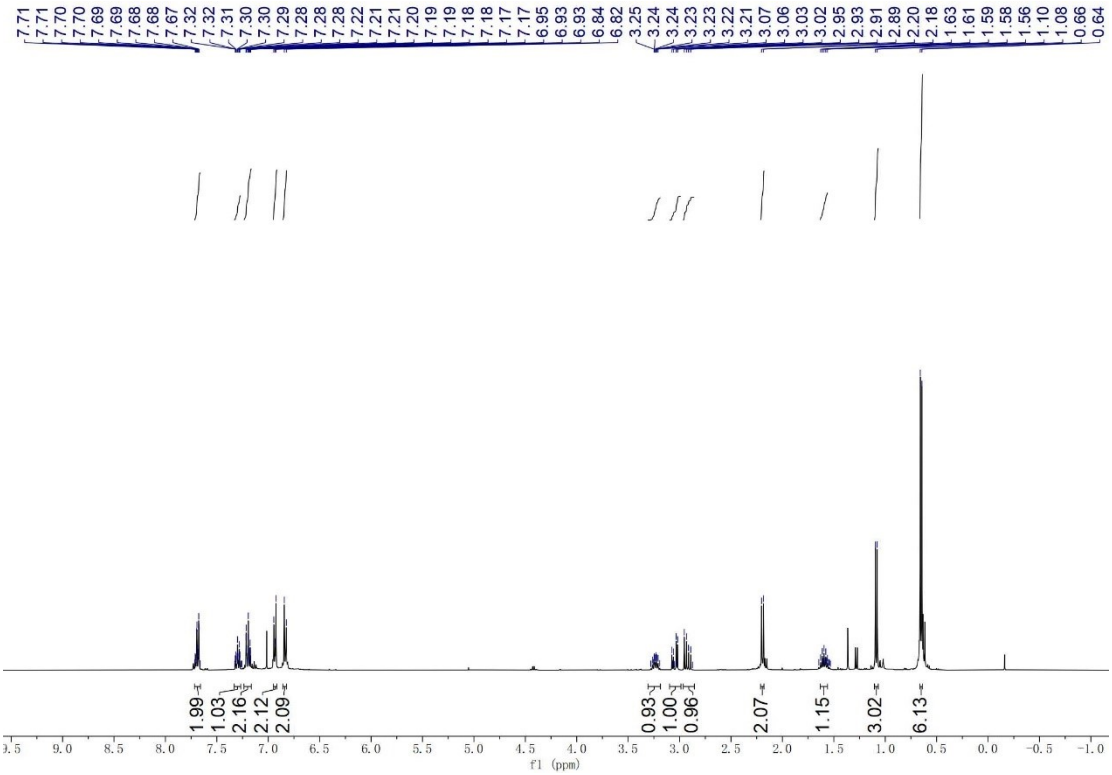
100 MHz in $CDCl_3$



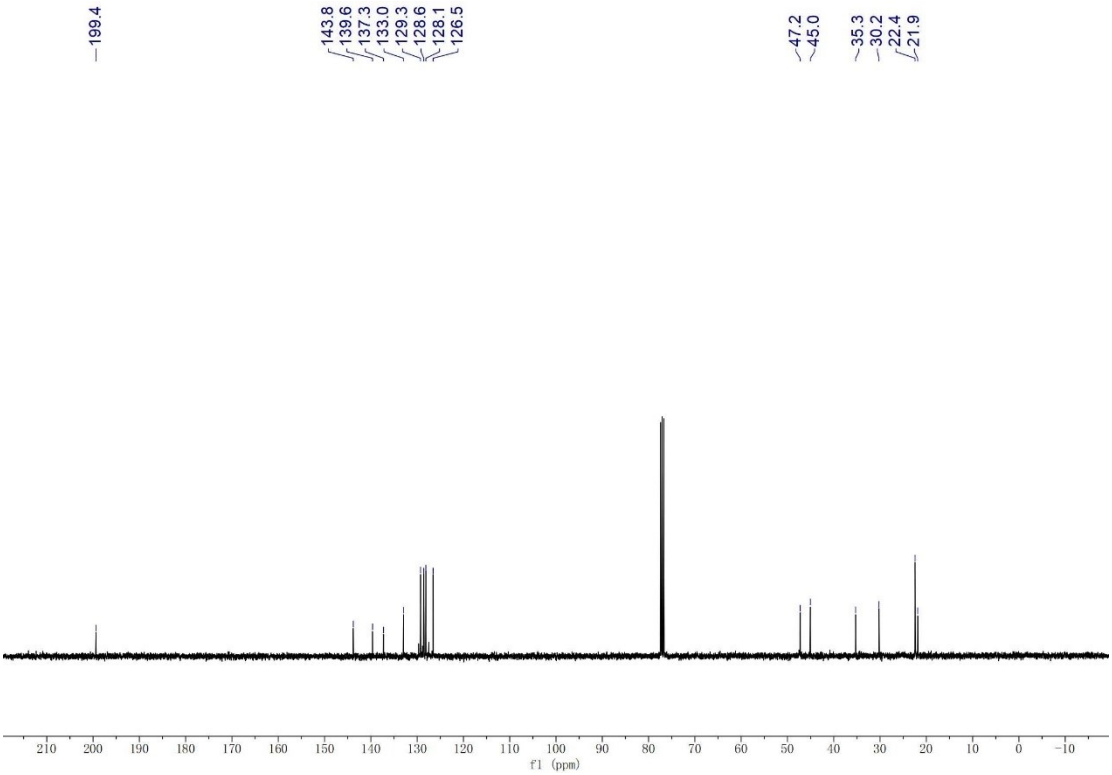


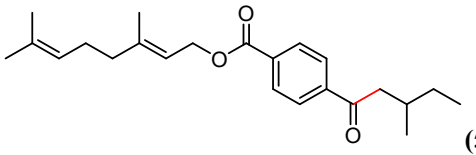
(49)

400 MHz in $CDCl_3$



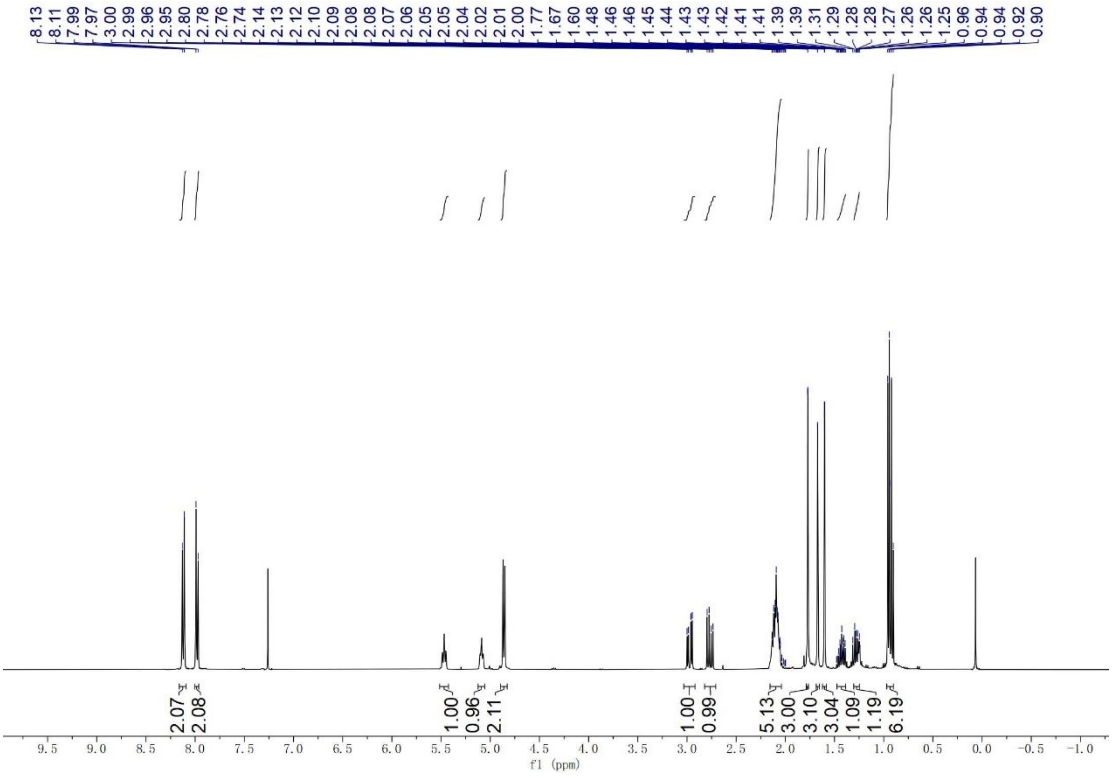
100 MHz in $CDCl_3$



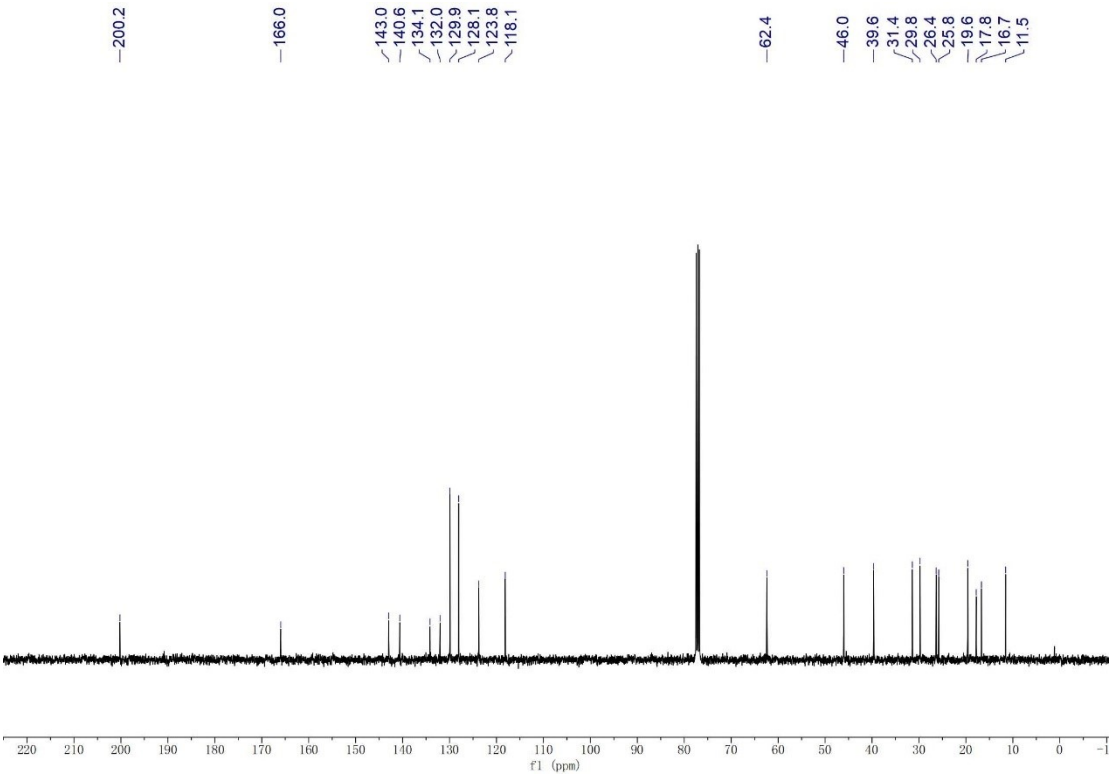


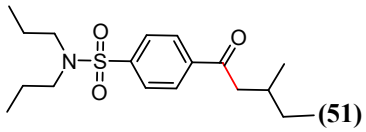
(50)

400 MHz in $CDCl_3$



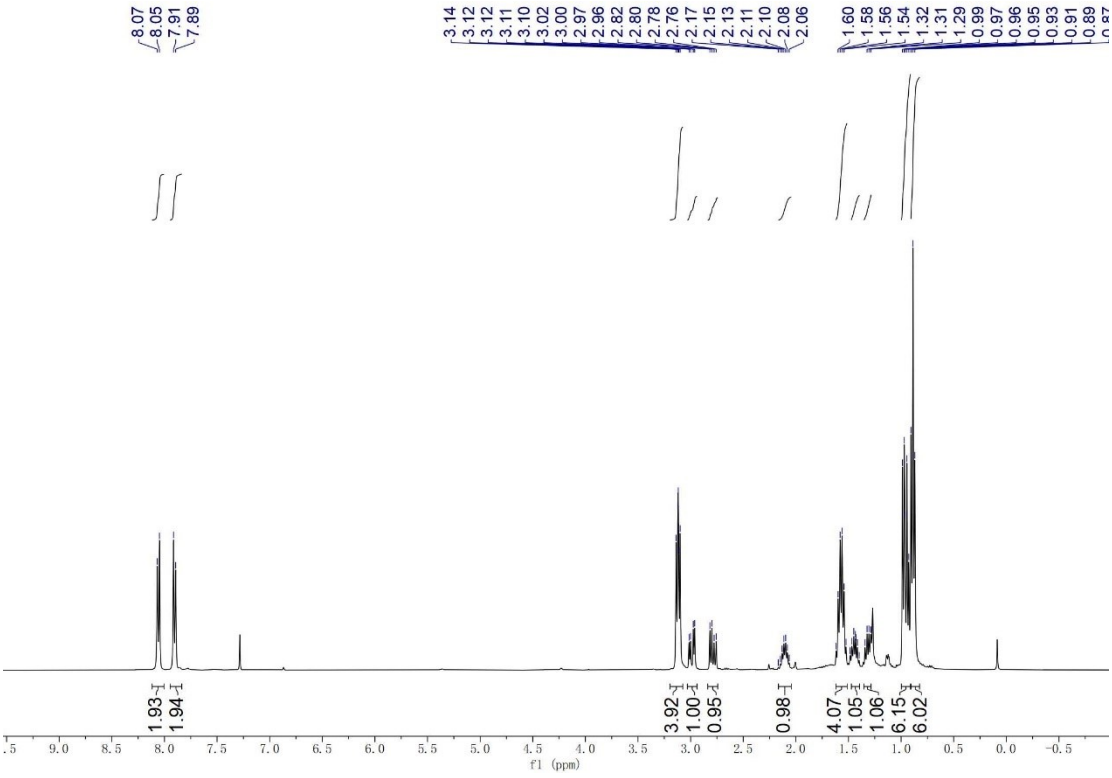
100 MHz in $CDCl_3$



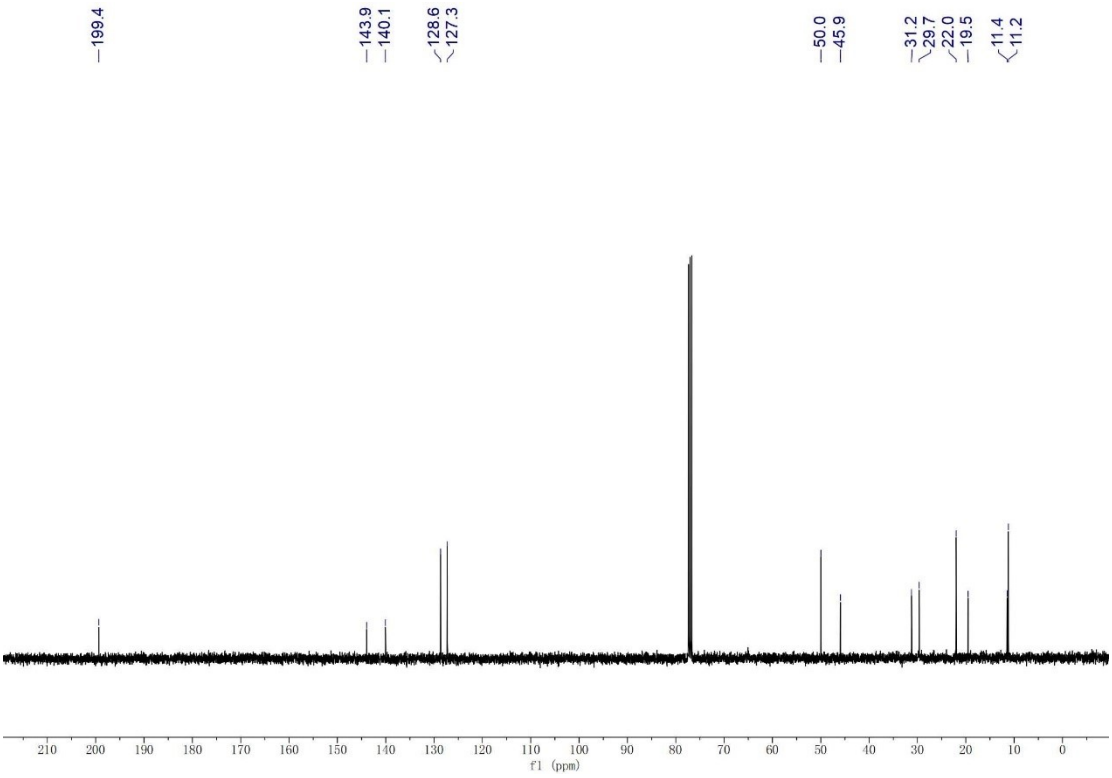


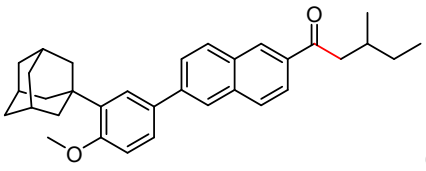
(51)

400 MHz in $CDCl_3$



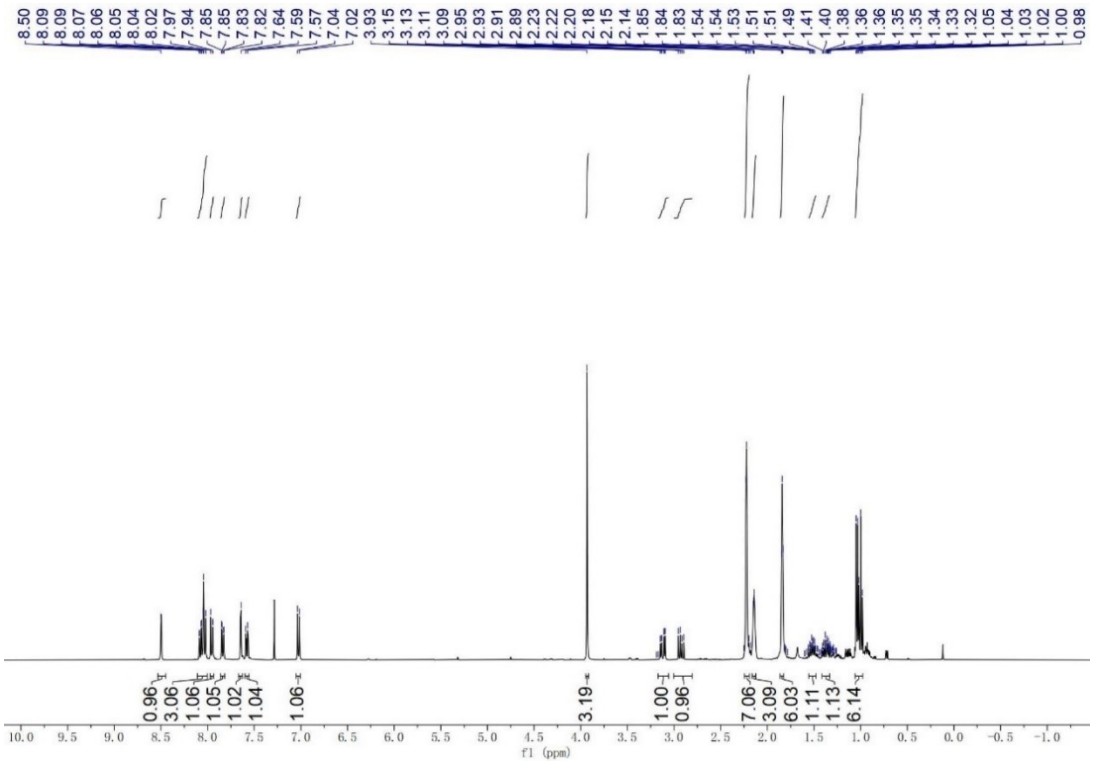
100 MHz in $CDCl_3$



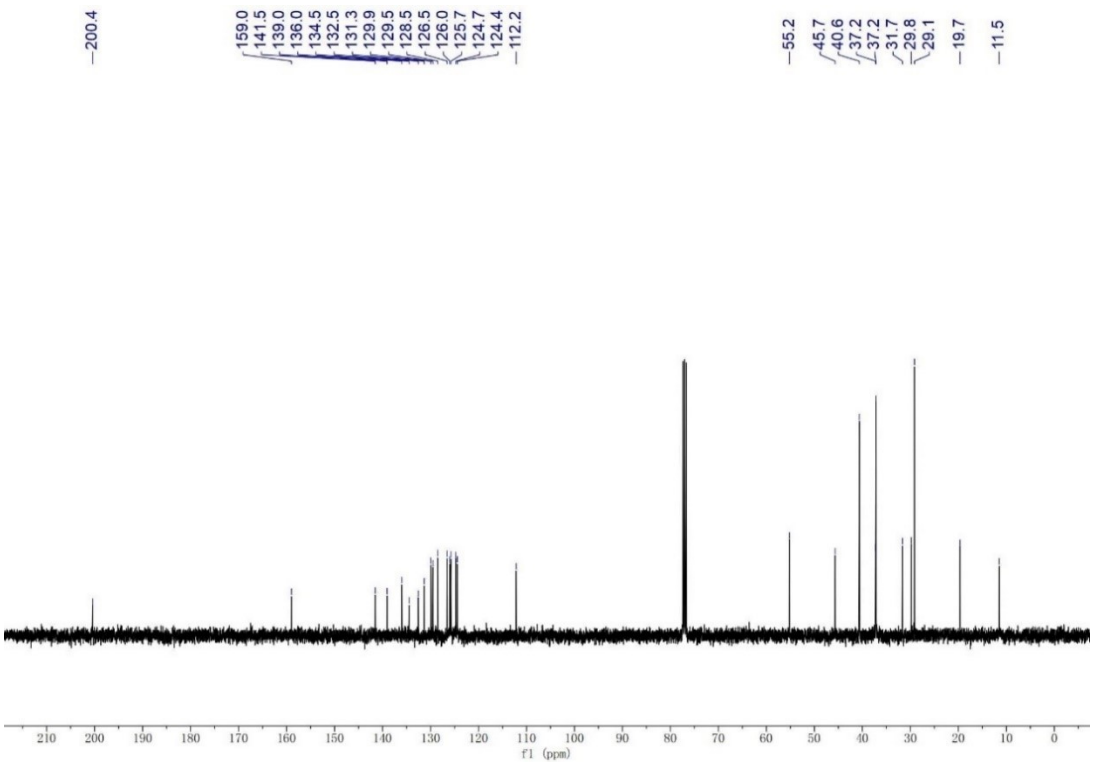


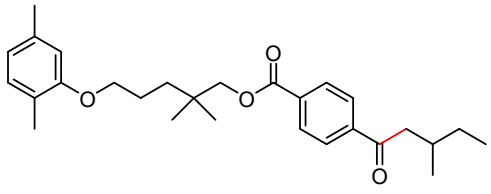
(52)

400 MHz in $CDCl_3$



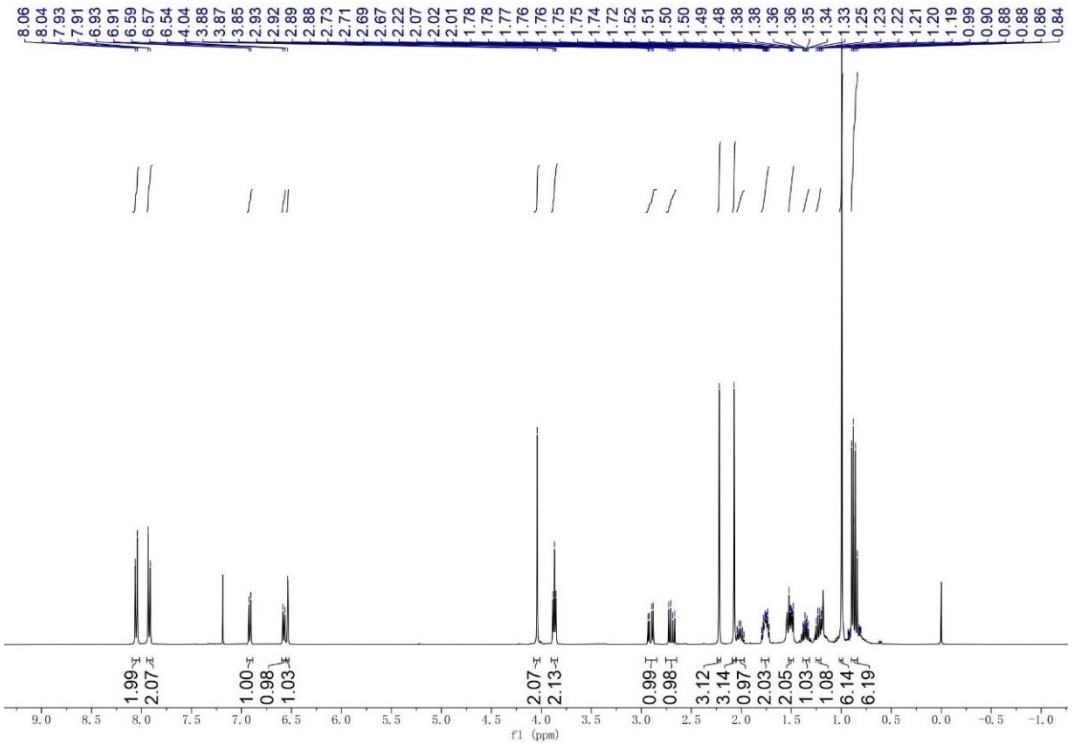
100 MHz in $CDCl_3$



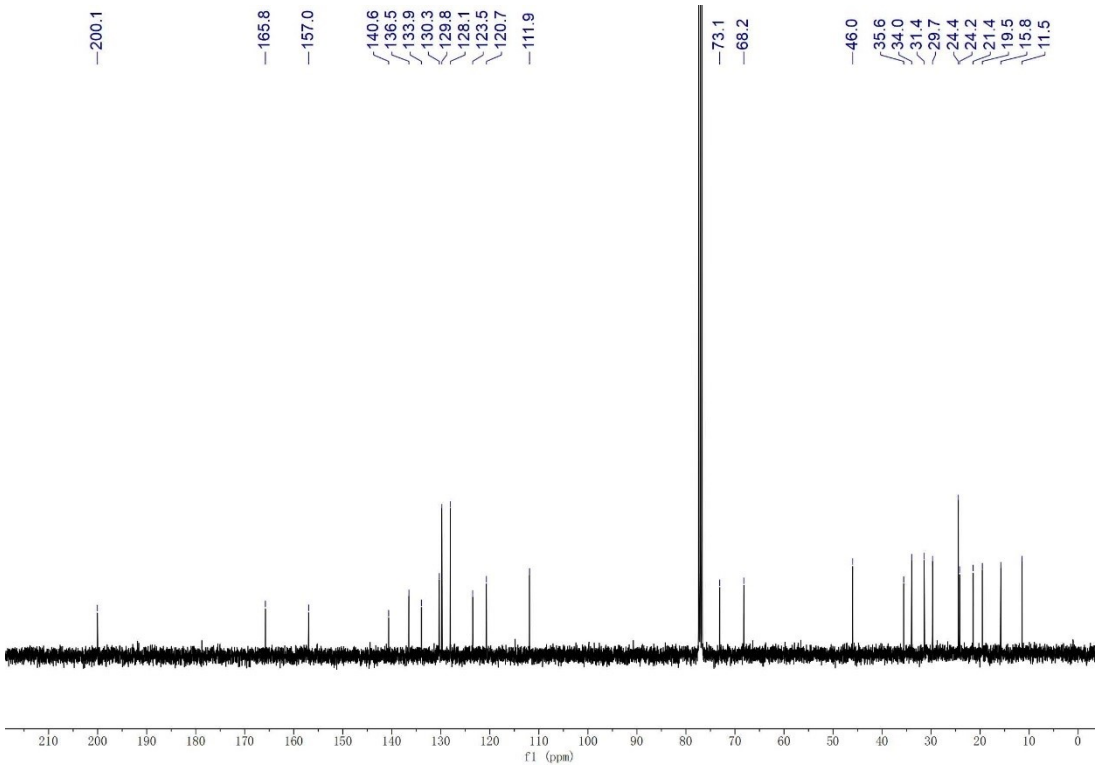


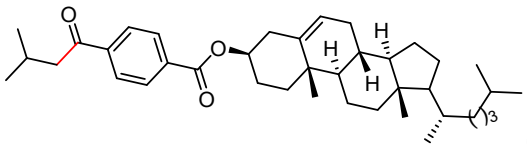
(53)

400 MHz in $CDCl_3$



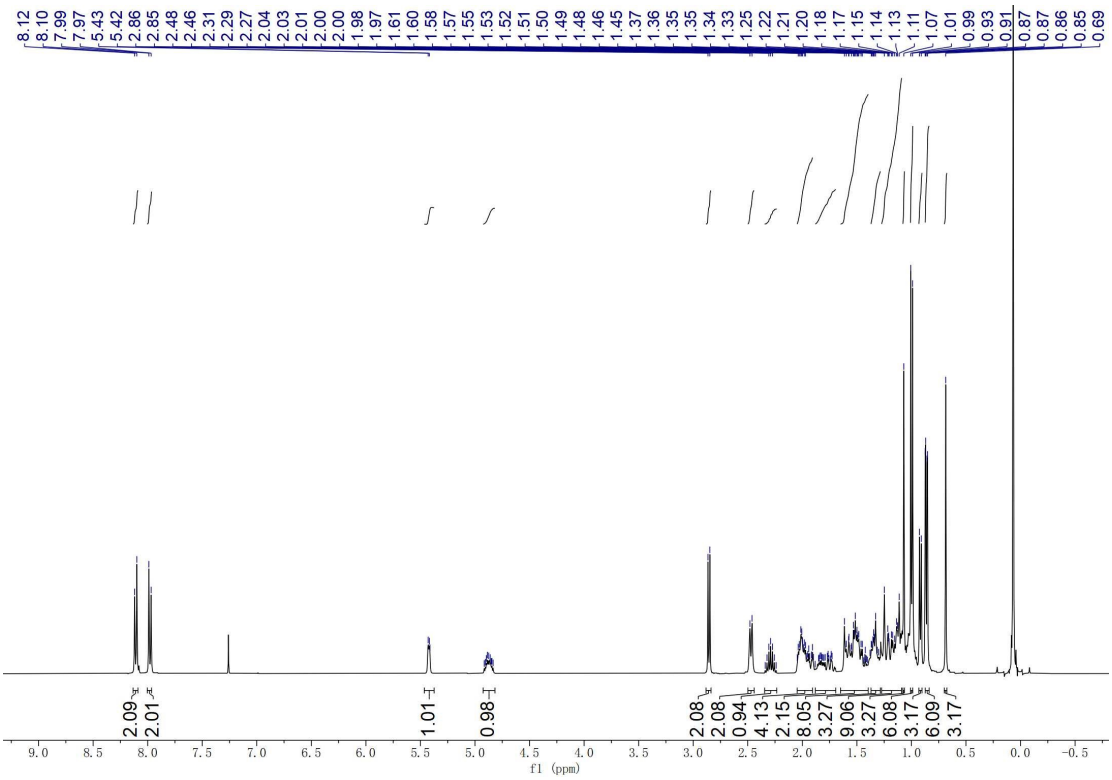
100 MHz in $CDCl_3$



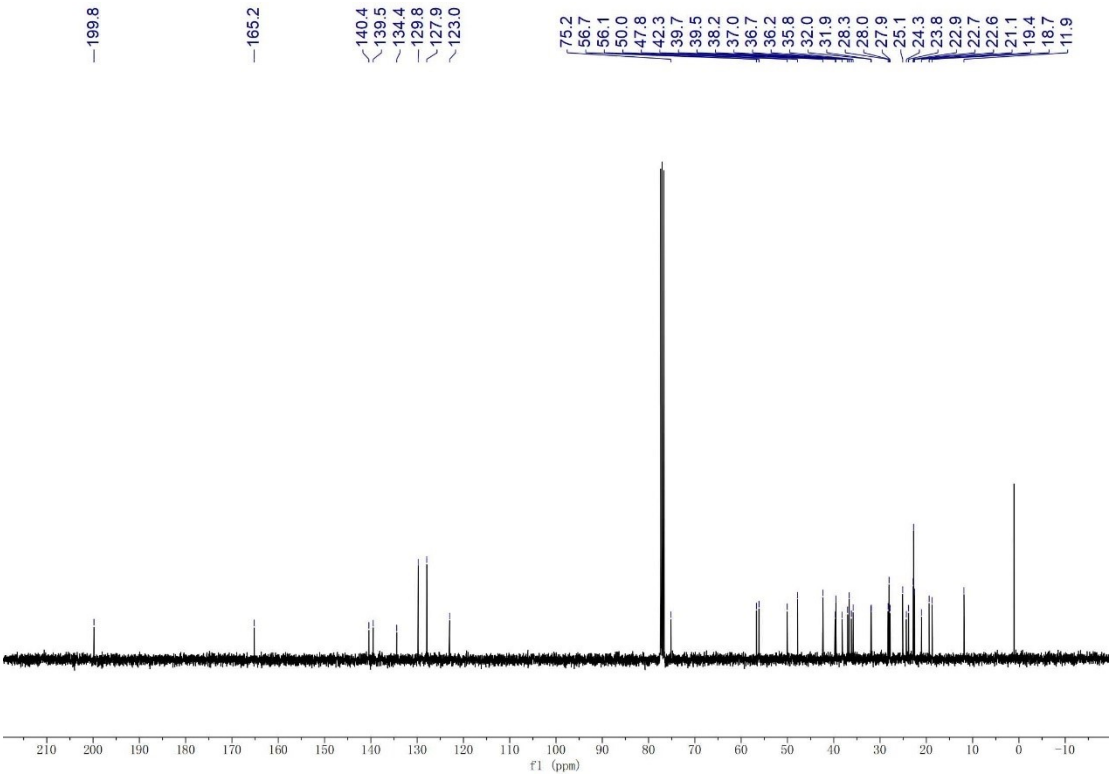


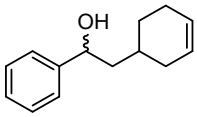
(54)

400 MHz in $CDCl_3$



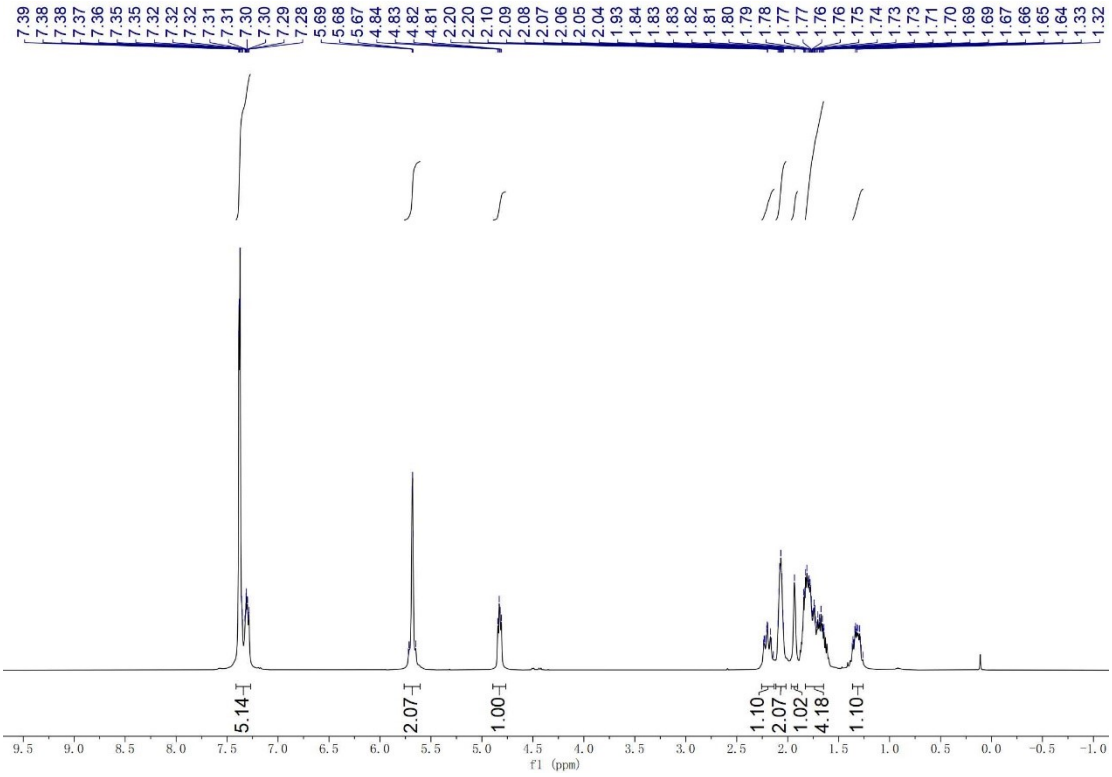
100 MHz in $CDCl_3$



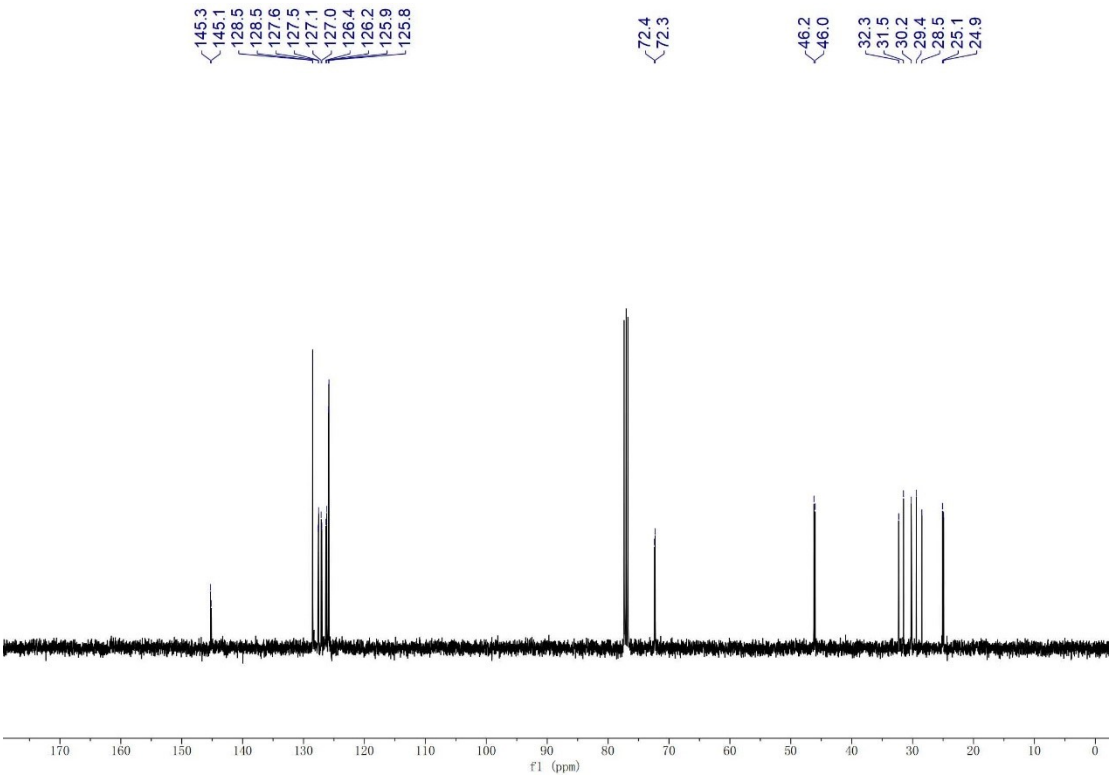


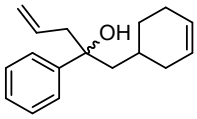
(55)

400 MHz in $CDCl_3$



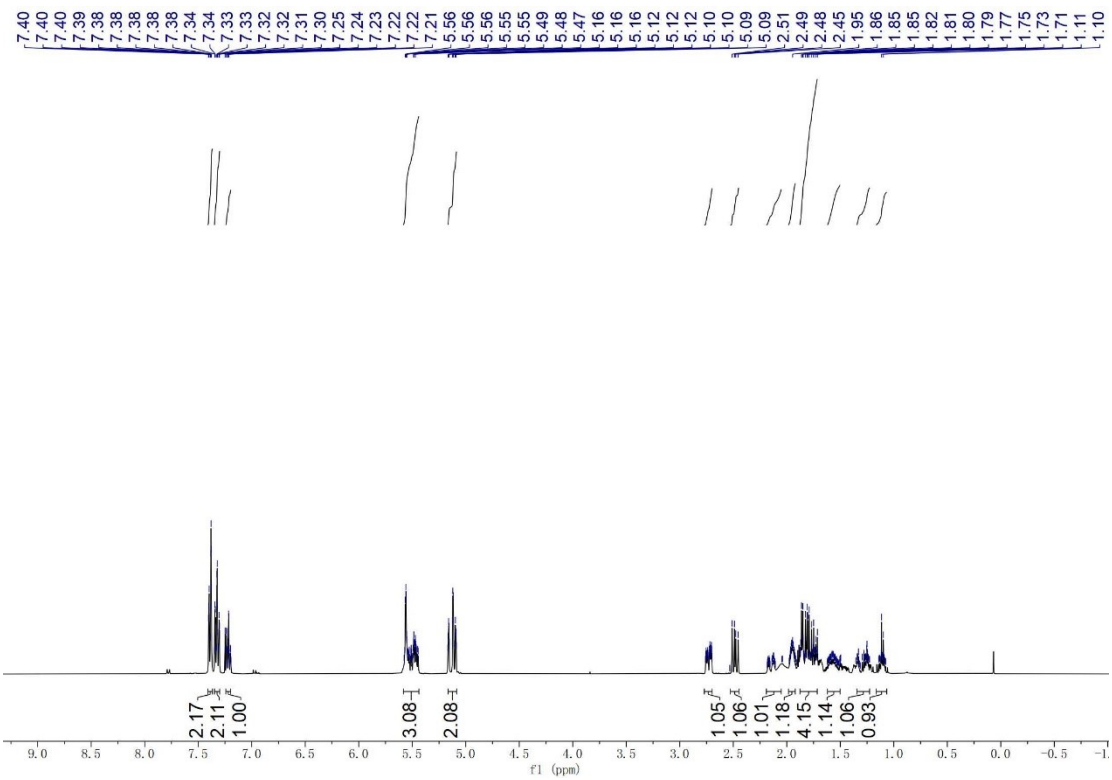
100 MHz in $CDCl_3$



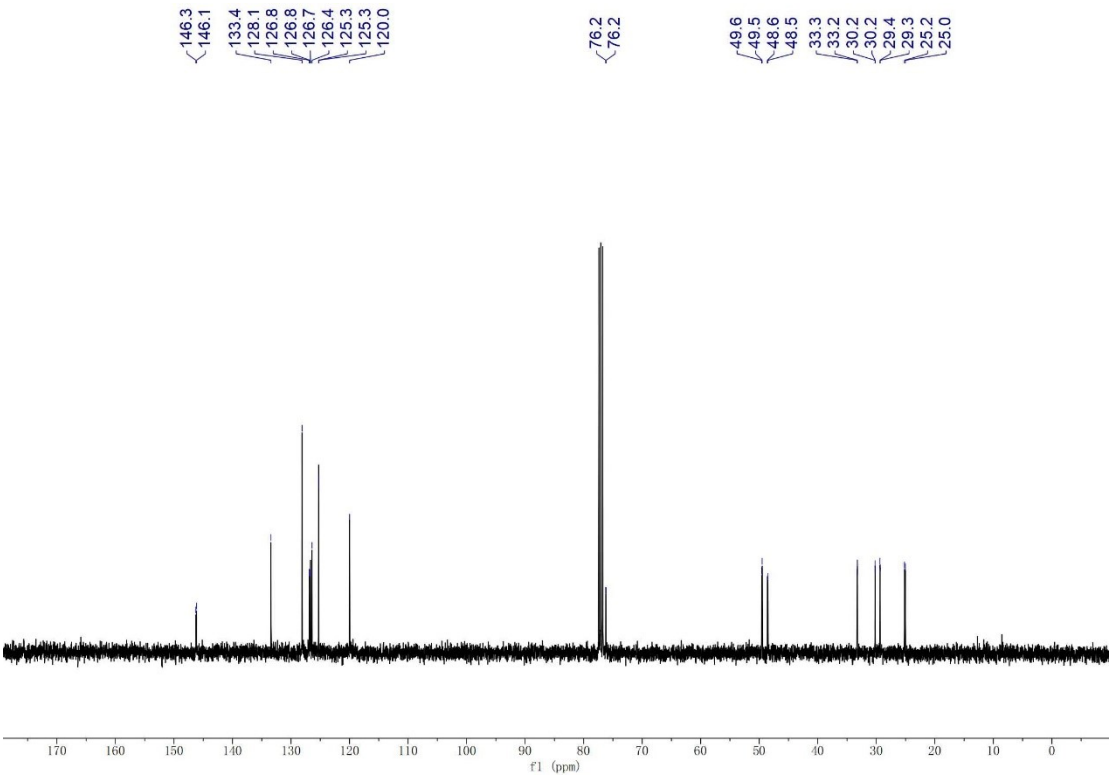


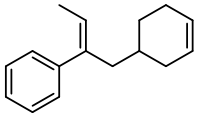
(56)

400 MHz in $CDCl_3$



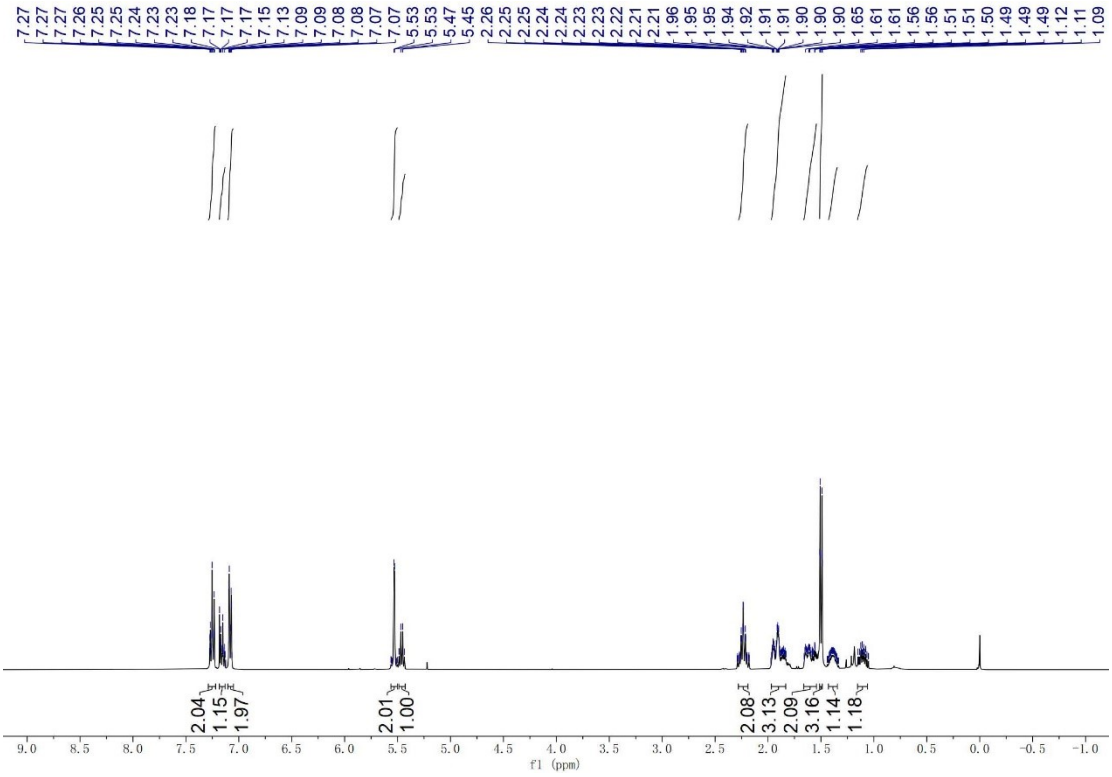
100 MHz in $CDCl_3$



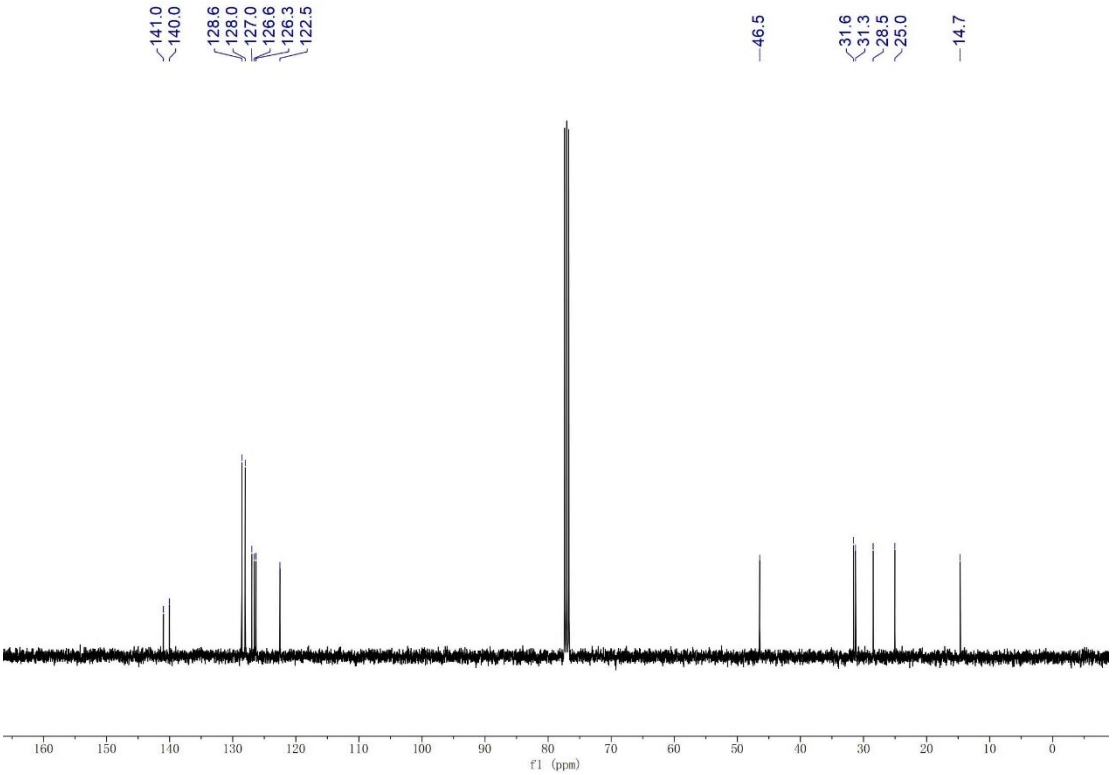


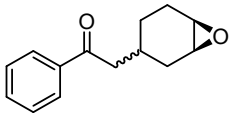
(57)

400 MHz in $CDCl_3$



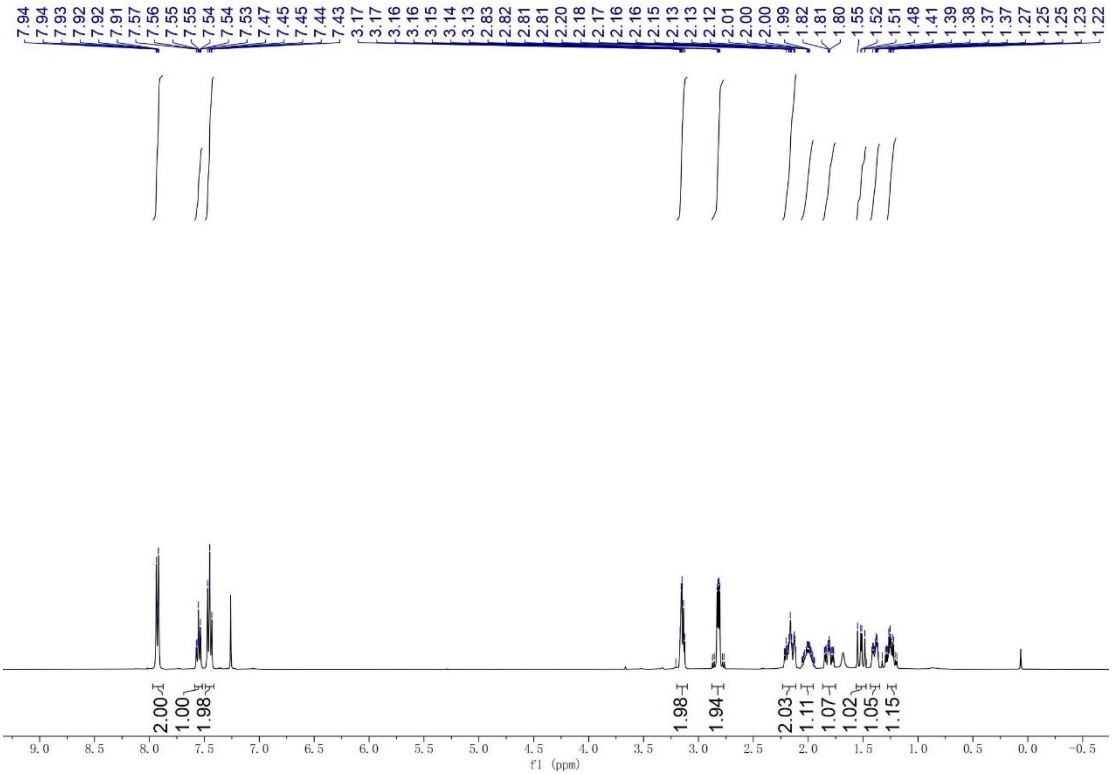
100 MHz in $CDCl_3$



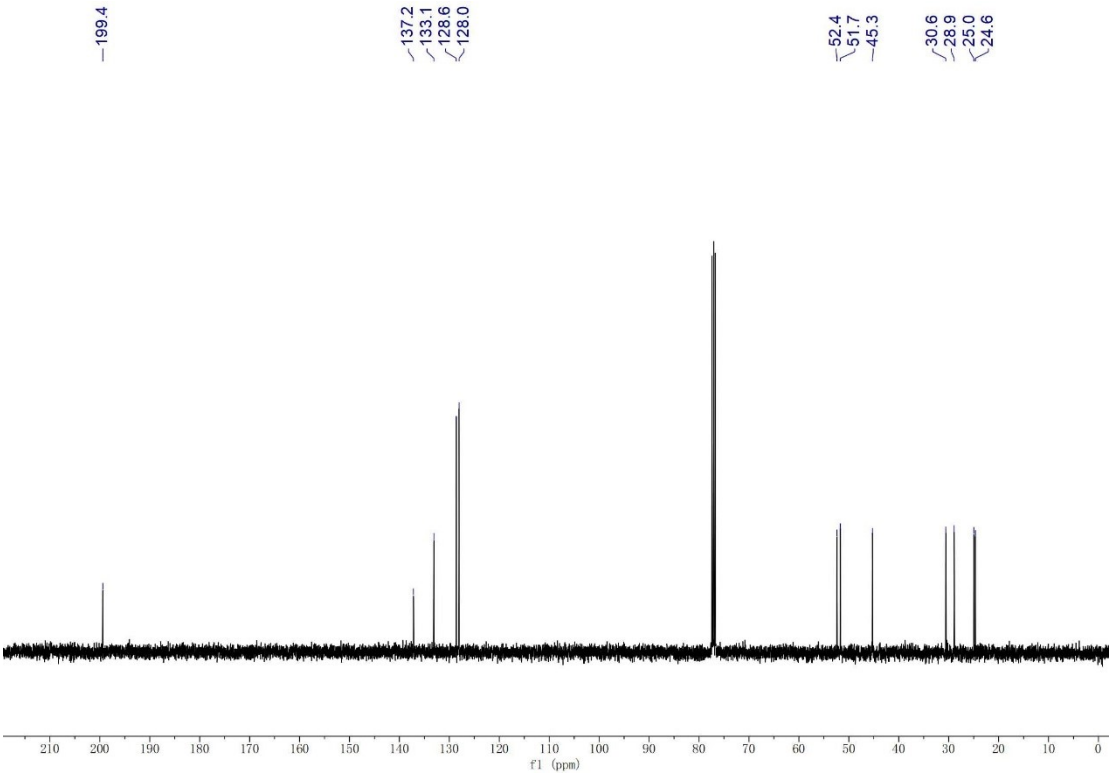


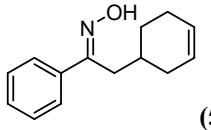
(58)

400 MHz in $CDCl_3$



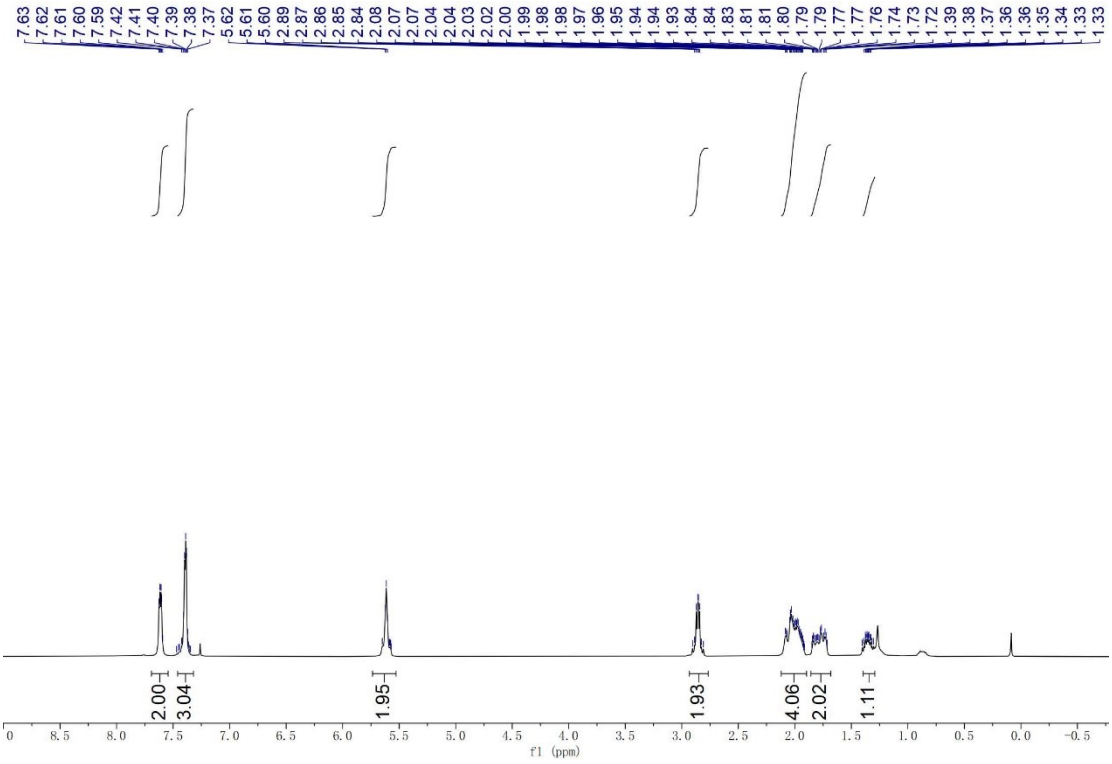
100 MHz in $CDCl_3$



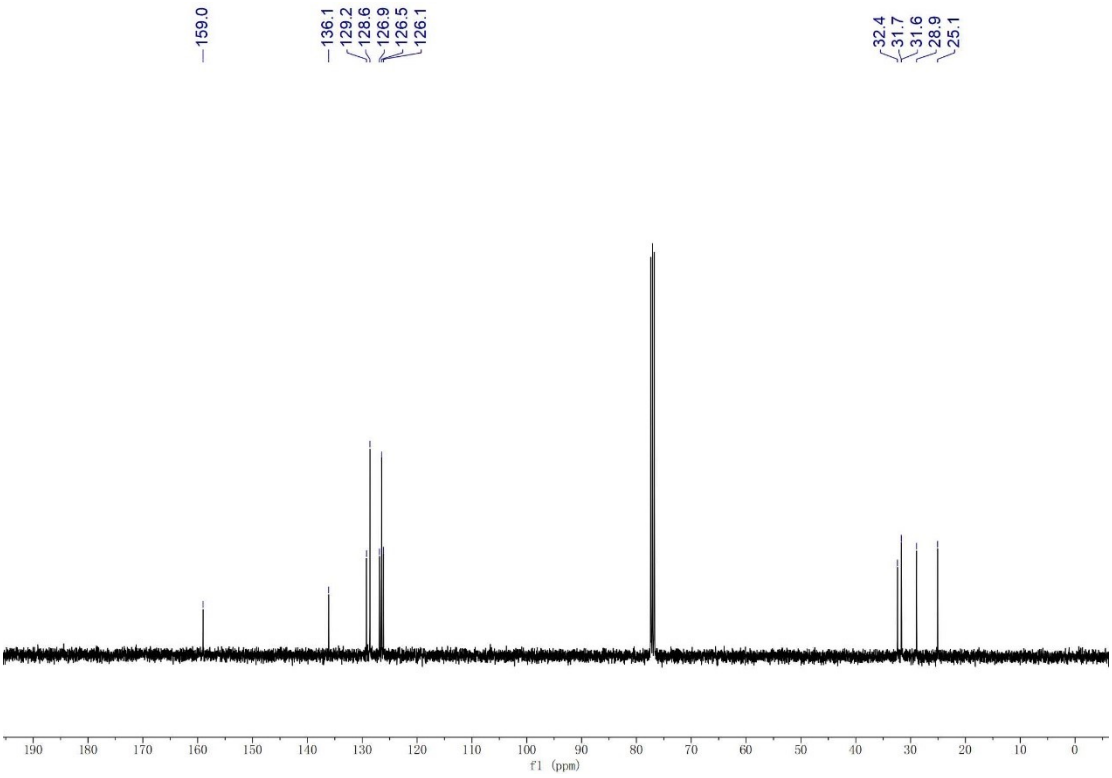


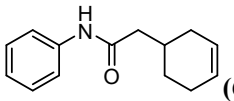
(59)

400 MHz in $CDCl_3$



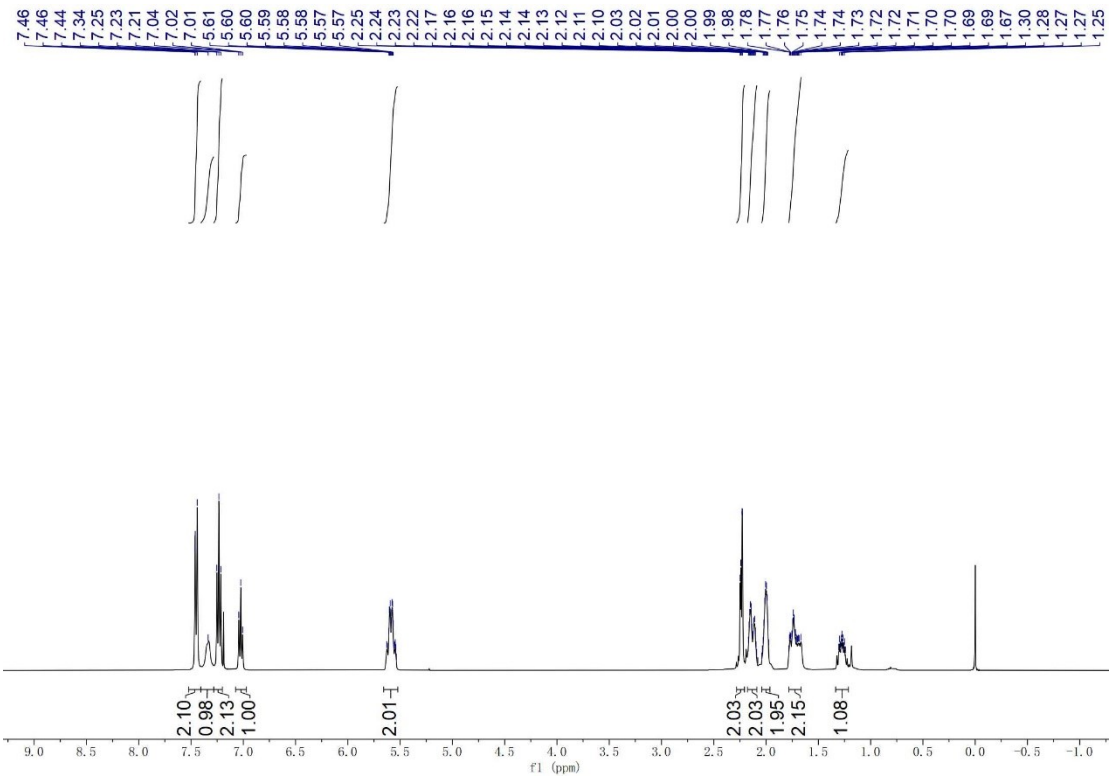
100 MHz in $CDCl_3$



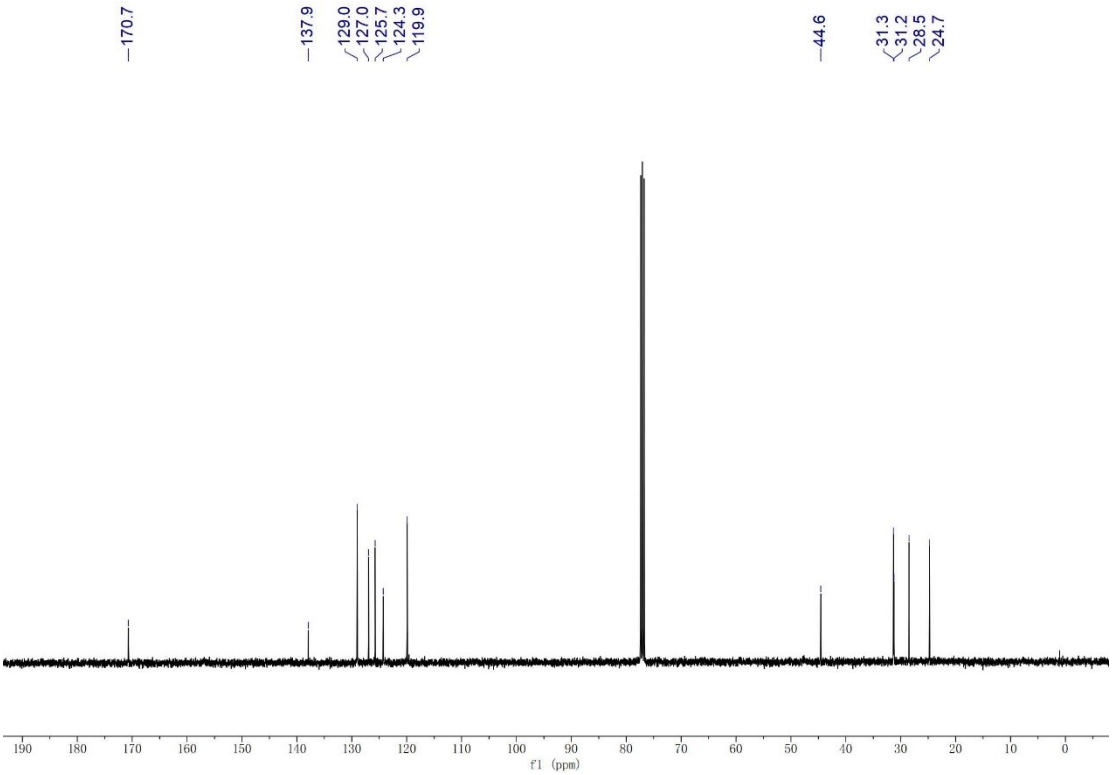


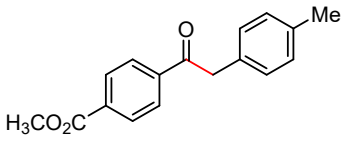
(60)

400 MHz in $CDCl_3$



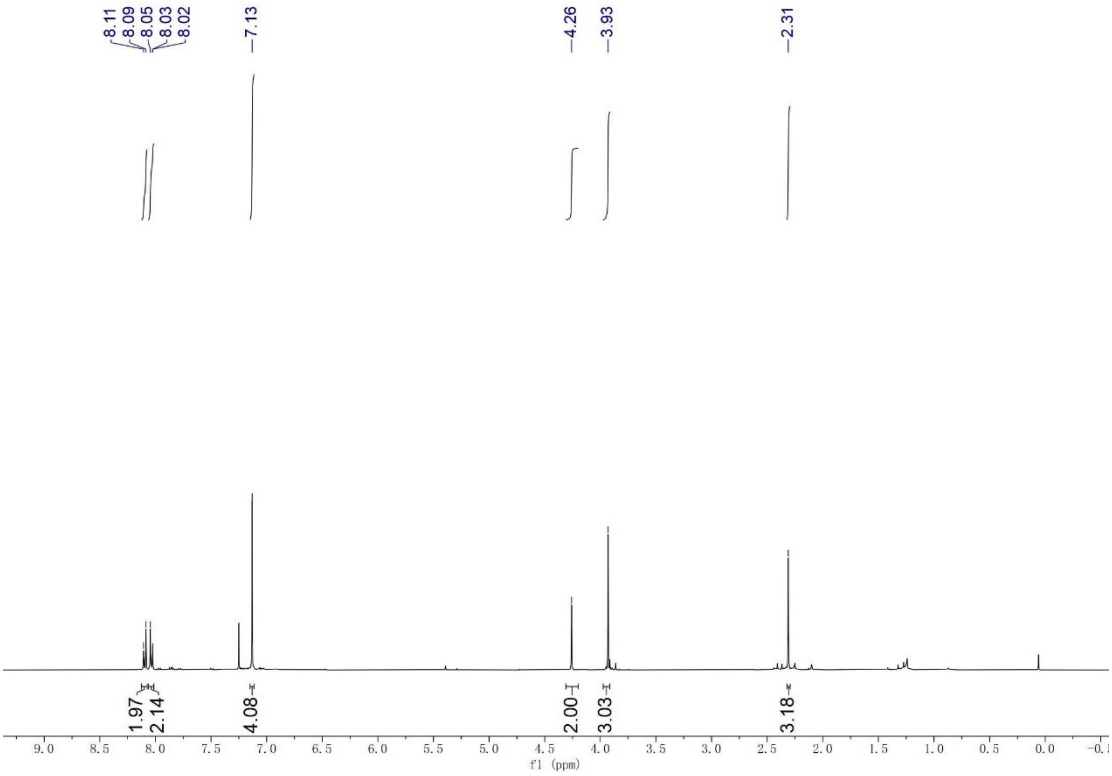
100 MHz in $CDCl_3$



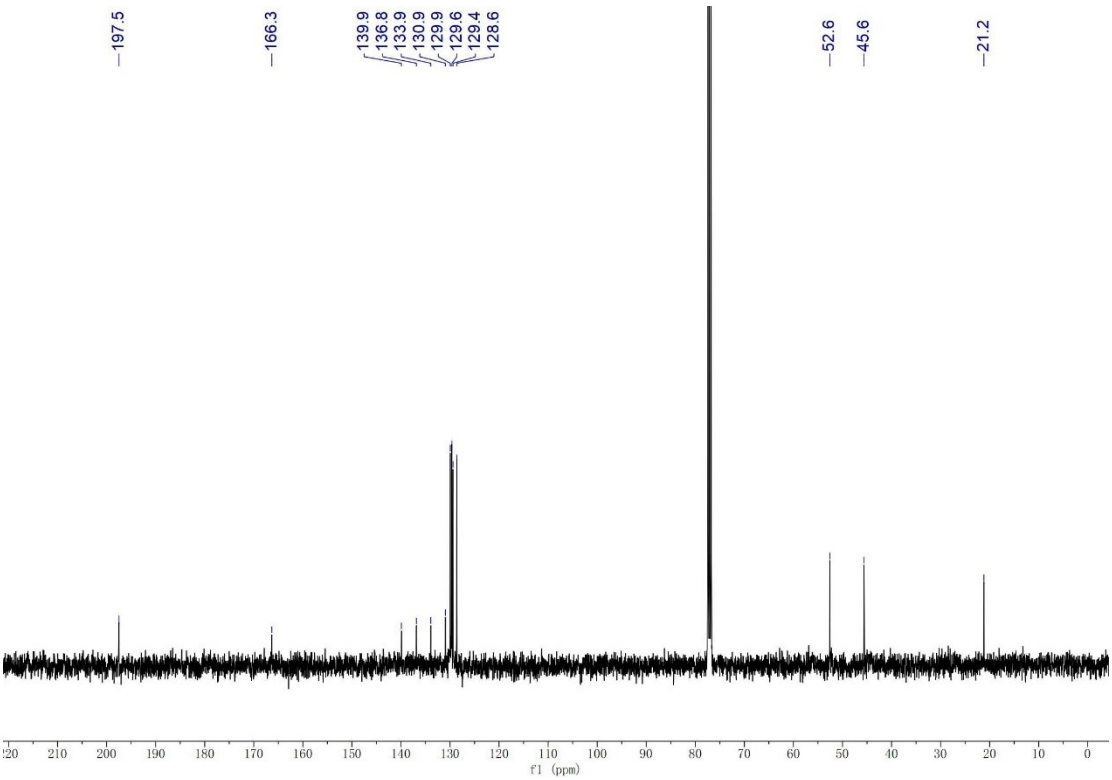


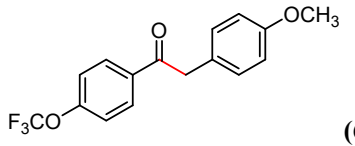
(61)

400 MHz in $CDCl_3$



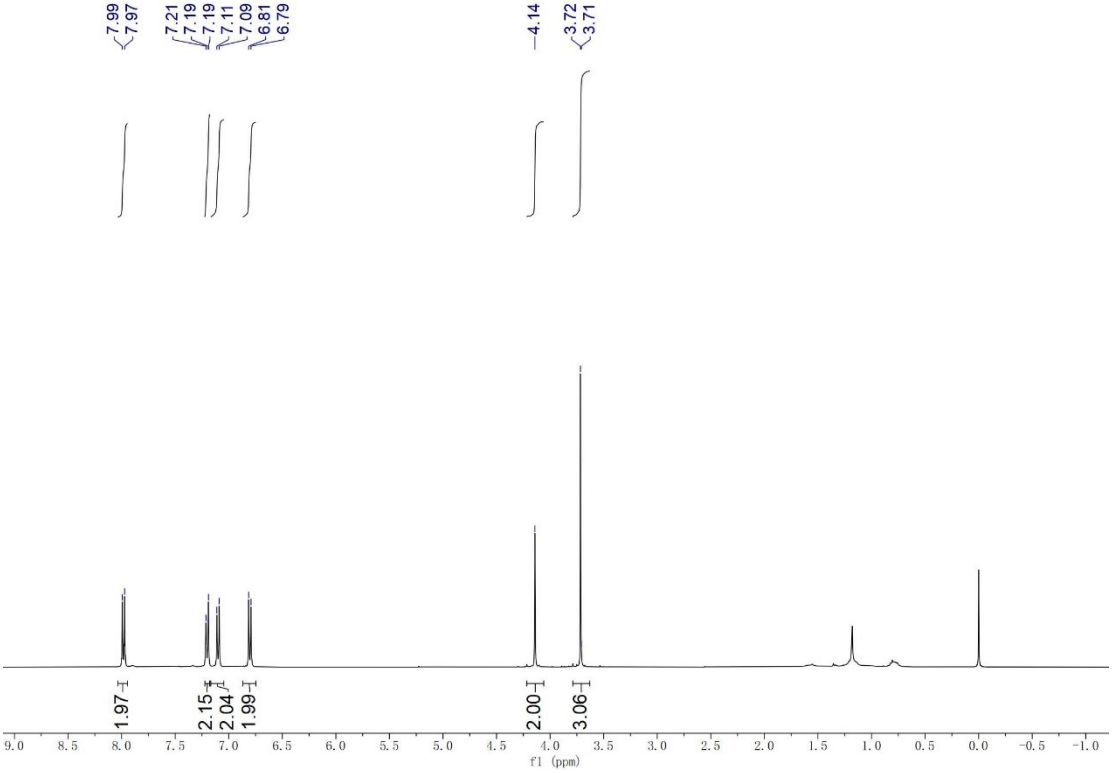
100 MHz in $CDCl_3$



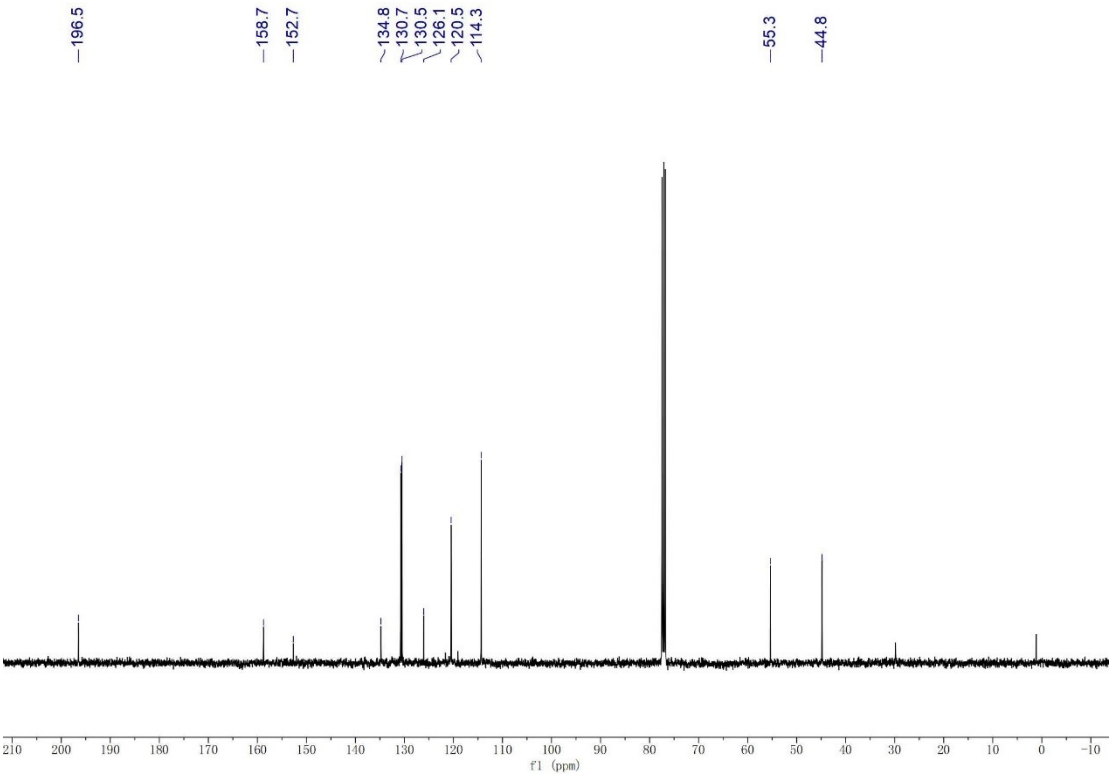


(62)

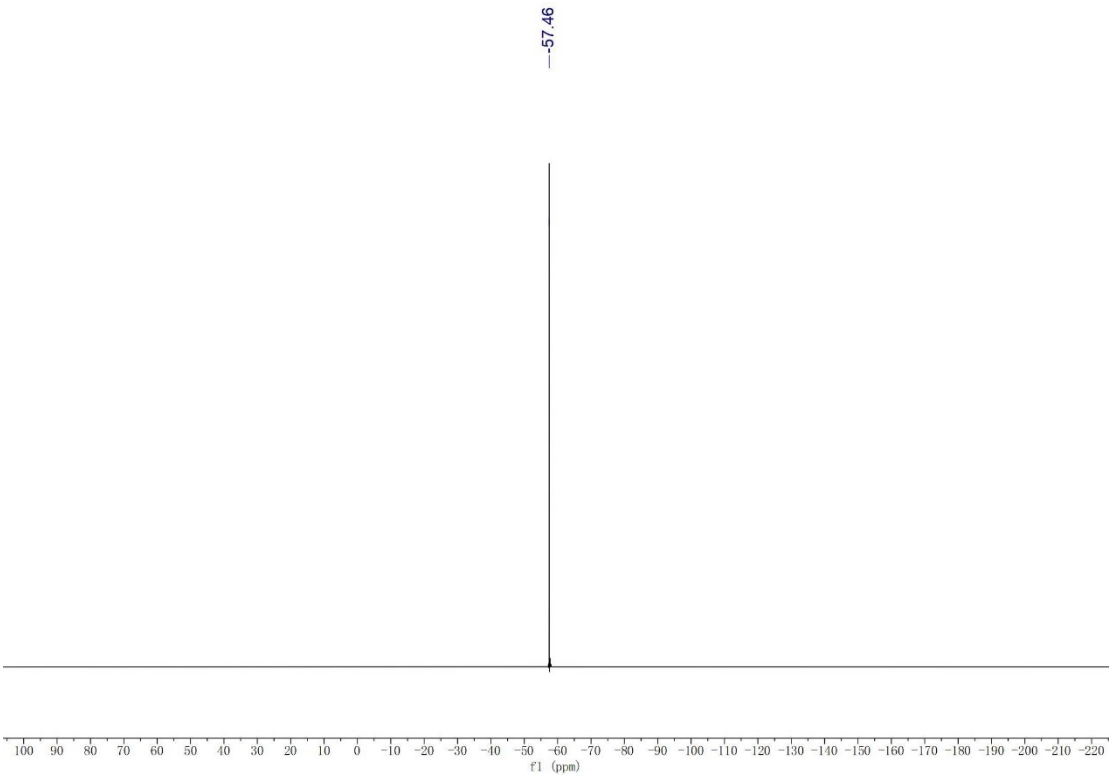
400 MHz in $CDCl_3$

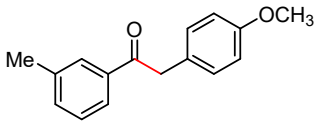


100 MHz in $CDCl_3$



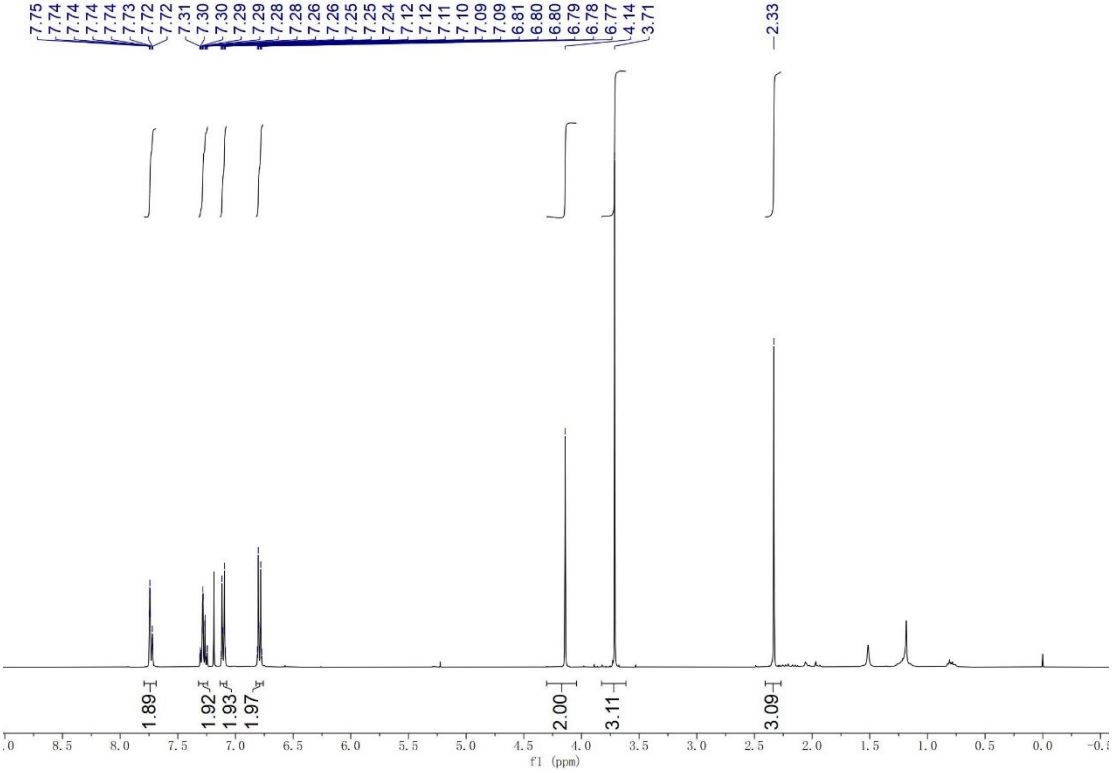
376 MHz in $CDCl_3$



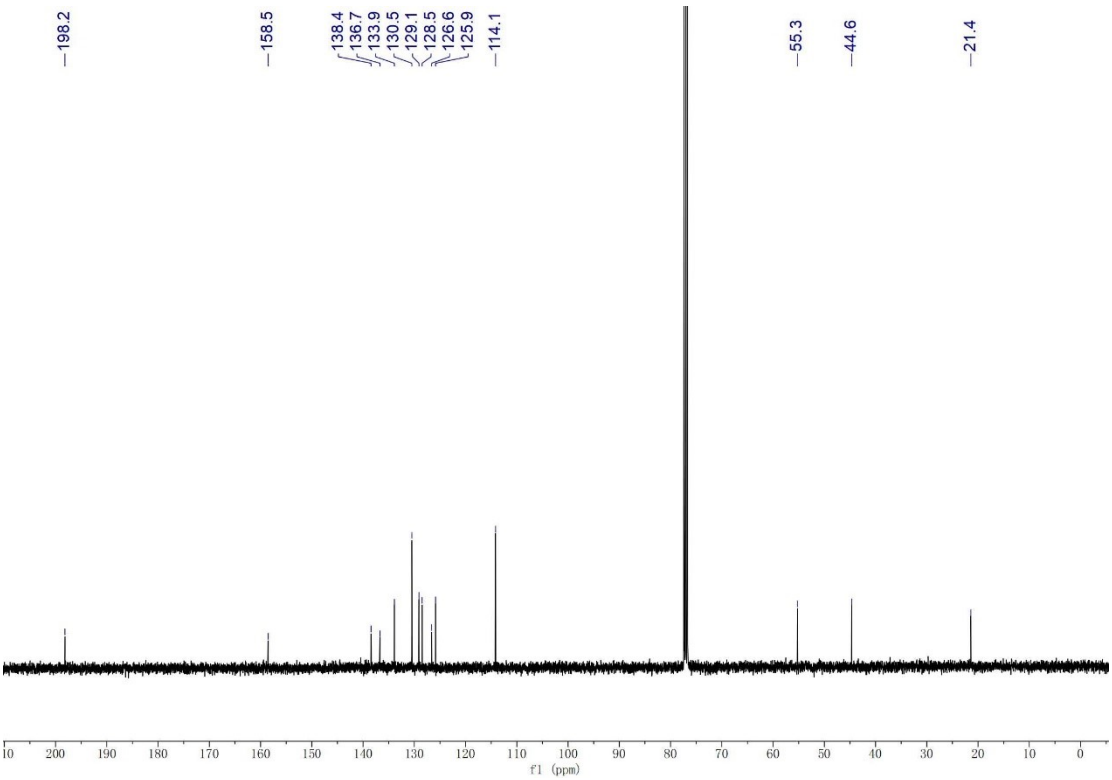


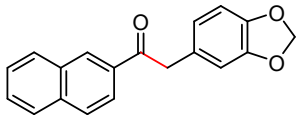
(63)

400 MHz in $CDCl_3$



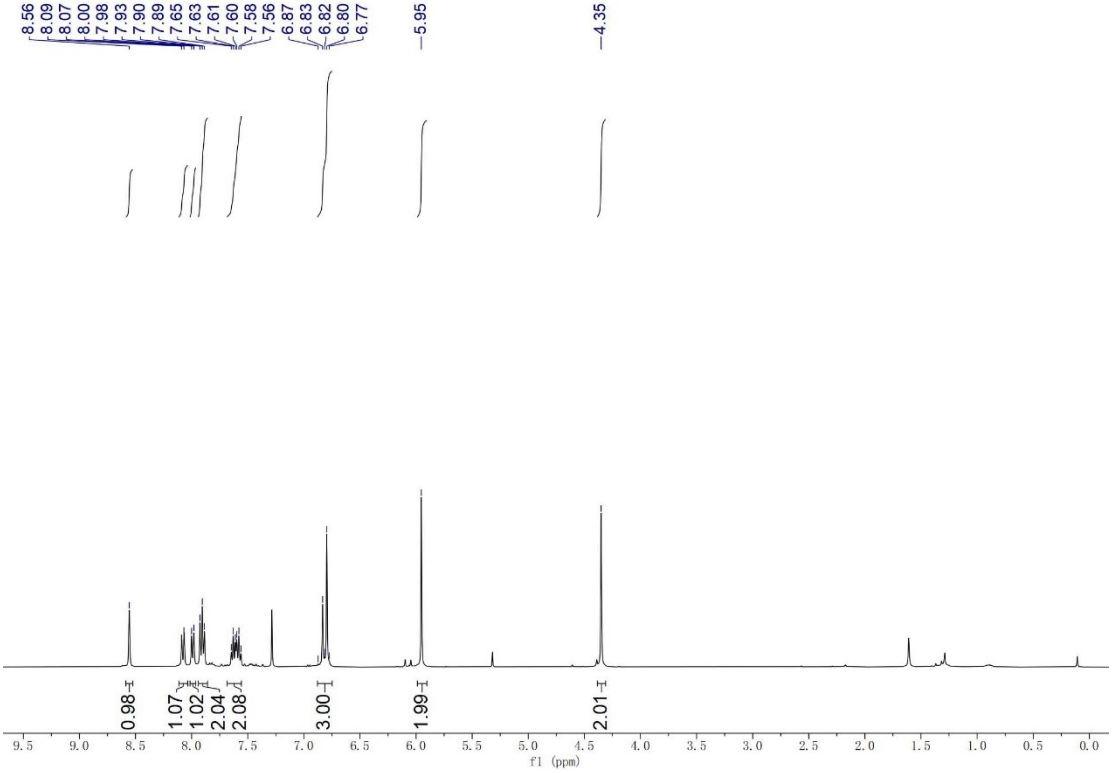
100 MHz in $CDCl_3$





(64)

400 MHz in $CDCl_3$



100 MHz in $CDCl_3$