

Supporting Information

A Visible-Light-Promoted Site-Specific and Diverse Functionalization of the C(sp³)–C(sp³) Bond Adjacent to Arene

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Content

| | |
|--|-----|
| 1. Reagents | S2 |
| 2. Instruments | S2 |
| 3. Synthesis of substrates | S3 |
| 4. Reaction optimization for deconstructive oxygenation and nitrogenation of cyclic alkanes by C(sp ³)-C(sp ³) cleavage | S15 |
| 5. Reaction optimization for deconstructive oxygenation and nitrogenation of acyclic alkanes by C(sp ³)-C(sp ³) cleavage | S20 |
| 6. Deconstructive oxygenation and nitrogenation of cyclic alkanes by inert C(sp ³)-C(sp ³) cleavage | S22 |
| 7. Deconstructive oxygenation and nitrogenation of acyclic alkanes by inert C(sp ³)-C(sp ³) cleavage | S37 |
| 8. Deconstructive oxygenation and peroxidation of cyclic alkanes by inert C(sp ³)-C(sp ³) cleavage | S44 |
| 9. Deconstructive oxygenation and chlorination of cyclic alkanes by inert C(sp ³)-C(sp ³) cleavage | S47 |
| 10. Gram-scale deconstructive nitrogenation of cyclopentylbenzene via selective C(sp ³)-C(sp ³) bond cleavage | S50 |
| 11. Mechanistic studies..... | S51 |
| 12. X-ray crystallographic data for compound 34..... | S61 |
| 13. References | S61 |
| 14. ¹ H-NMR and ¹³ C-NMR spectra | S65 |

1. Reagents

All commercial materials were used as received unless otherwise noted. Superdry solvents (DCE (99.5%), TCE (99.5%), CH₃CN (99.0%), EtOAc (99.5%), MeOAc (99.5%), *t*BuOAc (99.5%), PhCl (99.5%), PhCH₃ (99.5%), PhNO₂ (99.5%), DCM, DMF, DMSO, acetone, EtOH, *t*BuOH, HFIP) and deuterated solvents were purchased from J&K Chemical. Azidoiodane BIN₃ **1**¹⁻³ and chloroiodane BICl **1'**⁴ was synthesized according to reported procedures and used as freshly prepared. Starting materials for this study were purchased from TCI or were synthesized according to reported procedures. Starting materials were synthesized according to reported procedures. LiCl (≥99%, Aladdin), Bu₄NBr (99%, Energy Chemical), and Ru(bpy)₃Cl₂ (98%, Ru > 15.75%, Energy Chemical) were used in the deconstructive nitrogenation, chloridation and peroxidation reactions of alkanes.

TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching ($\lambda_{\text{max}} = 254 \text{ nm}$). Flash chromatography was performed using silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China.

2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 500 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br = broad singlet, m = multiplet. High resolution ESI mass experiments were operated on a Waters LCT Premier instrument. All reactions were carried out in a 4 mL glass vial (Thermo SCIENTIFIC National B7999-2, made from superior quality 33 expansion borosilicate clear glass), sealed with a PTEF cap on bench top if necessary.

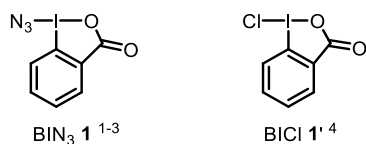
Lights: PHILIPS TORNADO 24W CFL and Cnlight blue LED lights 24 W were used

for photo-promoted reactions.

Note: All azidation reactions and subsequent workup were performed behind a blast shield with the sash positioned as low as possible. Once isolated, organic azides were stored in a freezer and away from sources of heat, light, pressure and shock. While we did not encounter any issues during their synthesis, proper precautions were taken.

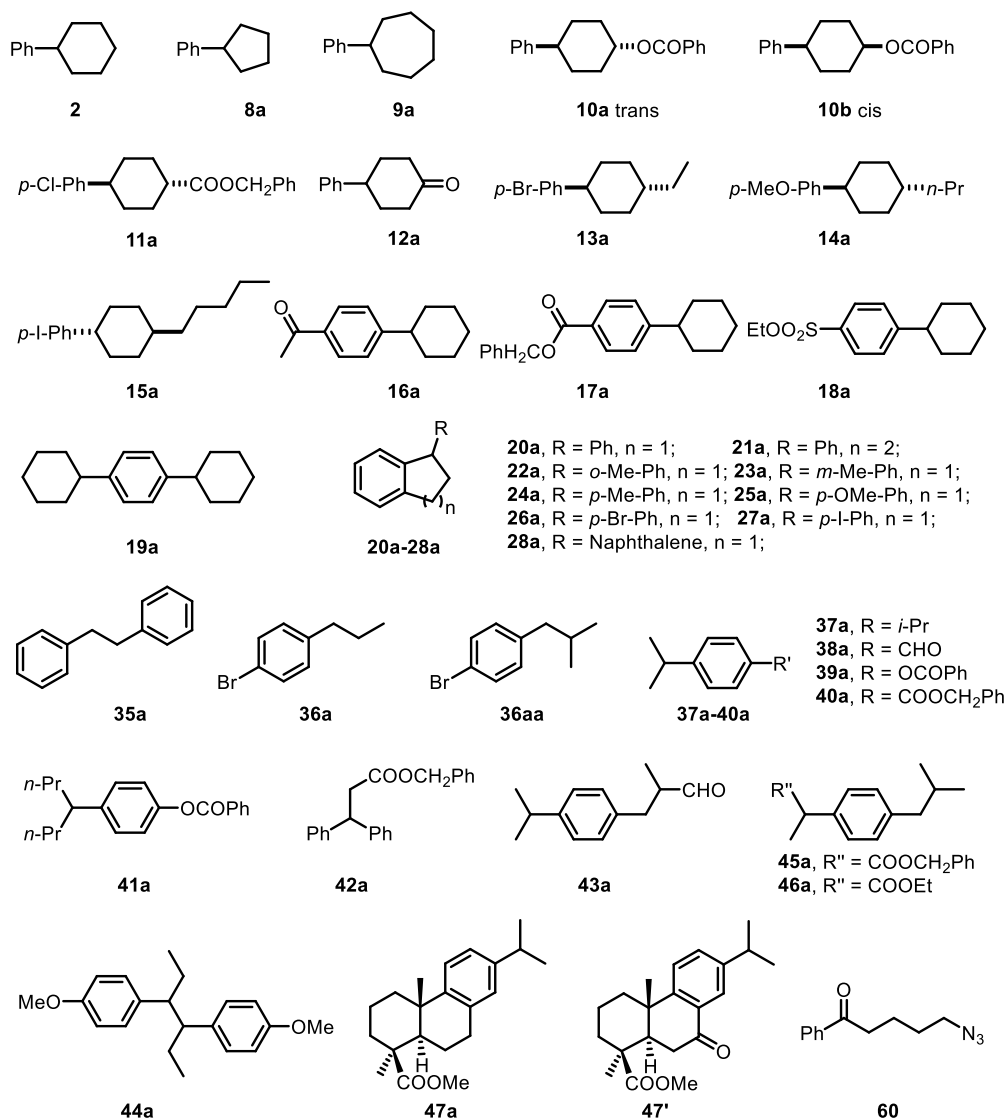
3. Synthesis of substrates

Hypervalent iodines reagents:



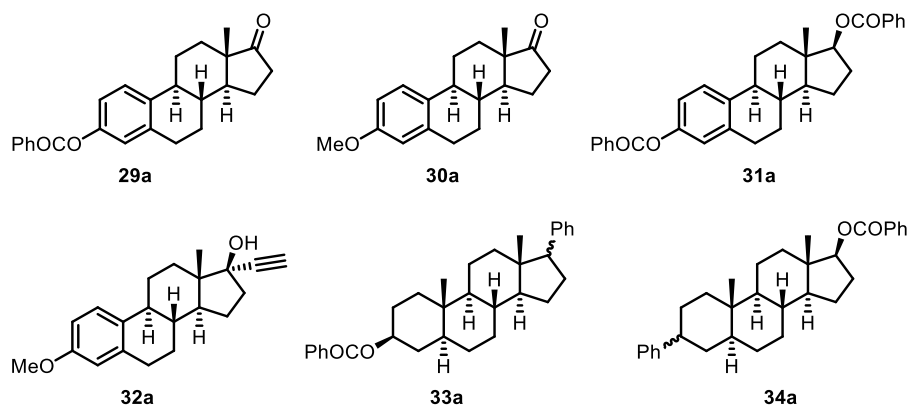
Scheme S1. List of hypervalent iodines reagents used in this study

Alkanes:



Scheme S2. Alkanes substrates used in this study

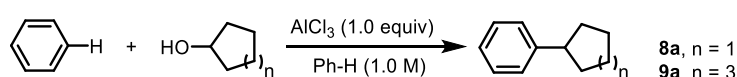
Steroids derivatives:



Scheme S3. Steroids derivatives substrates used in this study

Azidoiodane BIN₃ **1**¹⁻³ and chloroiodane BICI **1'**⁴ was synthesized according to reported procedures and used as freshly prepared. Alkanes for this study were purchased from TCI or were synthesized according to reported procedures. Compounds **11a**, **17a**, **18a**, **29a**, **30a**, **32a**, **33a** and **34a** were new compounds.

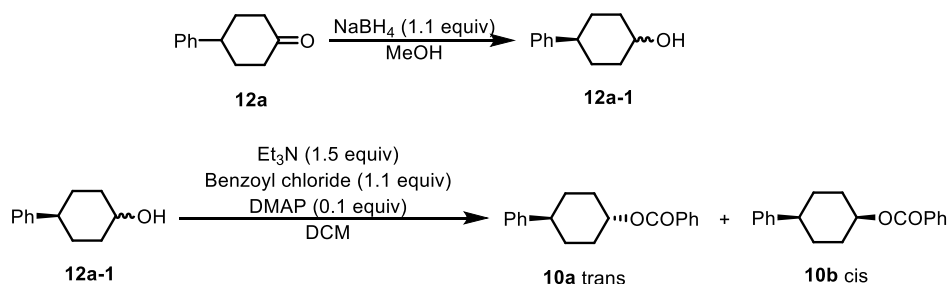
3.1 Synthesis of compound **8a** and **9a**



Scheme S4. General synthesis of compounds **8a** and **9a**

To a suspension of AlCl₃ (11.6 mmol, 1.0 equiv) in benzene (10.0 mL) at 25 °C was slowly added cyclopentanol or cycloheptanol (11.6 mmol, 1.0 equiv). The reaction mixture was stirred at 25 °C for 72 hours. Subsequently, the organic layer was washed with sat. Na₂CO₃ solution, washed with brine, dried and concentrated to an oil that was purified by vacuum distillation to afford 1-cyclopentylbenzene (9.7 g, 57%) or 1-cycloheptylbenzene (10.0 g, 50%). The spectroscopic data were consistent with those previously reported in the literature^{5, 6}.

3.2 Synthesis of compound **10a** and **10b**

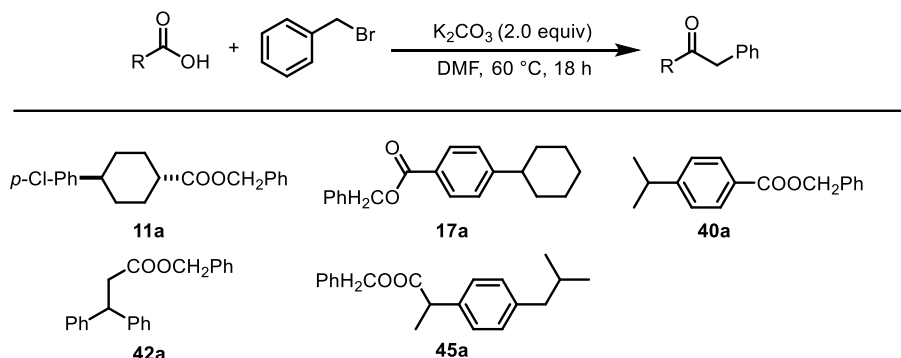


Scheme S5. Synthesis of **10a** and **10b**

To a solution of 4-phenylcyclohexanone (1.7 g, 10.0 mmol, 1.0 equiv) in THF (80.0 mL) was added NaBH₄ (416.1 mg, 11.0 mmol, 1.1 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 12 h before quenched with H₂O (2.0 mL) and 15% NaOH (aq) (0.5 mL). The resulting reaction mixture was filtered through a

pad of celite and the filtrate was concentrated in vacuo. The residue was dissolved in DCM (60.0 mL) then 4-dimethylaminepyridine (122.2 mg, 1.0 mmol, 0.1 equiv) and Et₃N (1.5 g, 15.0 mmol, 1.5 equiv) were added at room temperature. Benzoyl chloride (1.5 g, 11.0 mmol, 1.1 equiv) was slowly added to the above solution at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. H₂O (60.0 mL) was added and the mixture was extracted with DCM (3 x 20.0 mL). The combined organic layer was dried over Na₂SO₄, filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes/acetone 20:1 (v/v) to give compound **10a** and **10b** (trans:cis = 3.6:1) in 74% yield as a white solid. The spectroscopic data were consistent with those previously reported in the literature ⁷.

3.3 Synthesis of compound **11a**, **17a**, **40a**, **42a**, **45a**.



Scheme S6. Synthesis of **11a**, **17a**, **40a**, **42a**, **45a**

To a solution of acid (4.0 mmol, 1.0 equiv) in DMF (15.0 mL) was added potassium carbonate (1.1 g, 8.0 mmol, 2.0 equiv) followed by benzyl bromide (752.6 mg, 4.4 mmol, 1.1 equiv). The mixture was heated at 60 °C for 18 h, then cooled to rt. The mixture was diluted with water (30.0 mL) and extracted with ethyl acetate (2 x 30.0 mL). The organic layers were washed with water (3 x 30.0 mL), then with brine and dried over Na₂SO₄. The drying agent was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was purified by flash

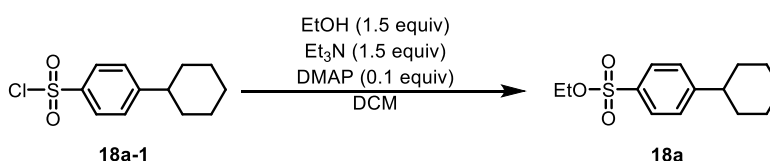
chromatography, eluting with hexanes/acetone 10:1 (v/v) to give product. The spectroscopic data of

40a⁸, **42a**⁹ and **45a**¹⁰ were consistent with those previously reported in the literature.

Compound **11a**: ¹H NMR (500 MHz, CDCl₃) δ 7.42 (dd, *J* = 4.4, 1.4 Hz, 4H), 7.37 (dd, *J* = 8.2, 3.8 Hz, 1H), 7.29 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 5.20 (d, *J* = 1.8 Hz, 2H), 2.57 – 2.49 (m, 1H), 2.49 – 2.40 (m, 1H), 2.24 – 2.14 (m, 2H), 2.00 – 1.96 (m, 2H), 1.72 – 1.61 (m, 2H), 1.51 – 1.46 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 175.44, 145.21, 136.22, 136.21, 131.61, 128.53, 128.43, 128.11, 128.08, 127.97, 66.01, 42.91, 42.84, 33.16, 29.17. HRMS Calcd for C₂₀H₂₂ClO₂ [M+H⁺]: 329.1303; Found: 329.1306.

Compound **17a**: ¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.39 (s, 2H), 2.65 – 2.52 (m, 1H), 1.89 (s, 4H), 1.82 – 1.76 (m, 1H), 1.50 – 1.38 (m, 4H), 1.32 – 1.28 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 166.53, 153.67, 136.34, 129.92, 128.63, 128.21, 128.16, 127.80, 126.95, 66.52, 44.77, 34.21, 26.82, 26.12. HRMS Calcd for C₁₇H₂₀N₂NaO₅ [M+H⁺]: 295.1693; Found: 295.1694.

3.4 Synthesis of compound 18a.



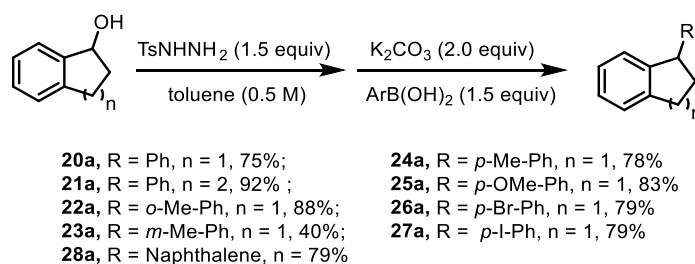
Scheme S7. Synthesis of **18a**

To a solution of ethanol (138.2 mg, 3.0 mmol, 1.5 equiv) in DCM (25.0 mL) was added 4-dimethylaminopyridine (24.4 mg, 0.2 mmol, 0.1 equiv) and Et₃N (303.6 mg, 3.0 mmol, 1.5 equiv). The solution was cooled down to 0 °C and 4-Cyclohexyl-Benzenesulfonyl Chloride (517.6 mg, 2.0 mmol, 1.0 equiv) was added dropwise. The resulting solution was stirred at room temperature during 3 h. H₂O

(30.0 mL) was added and the mixture was extracted with DCM (3 x 20.0 mL). The combined organic layer was dried over Na₂SO₄, filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography using 3% EtOAc in petroleum ether to afford **18a** (451 mg, 84% yield) as a colorless oil.

Compound **18a**: ¹H NMR (500 MHz, CDCl₃) δ 7.83 – 7.73 (m, 2H), 7.39 – 7.29 (m, 2H), 4.13 – 4.00 (m, 2H), 2.56 (s, 1H), 1.82 (s, 4H), 1.75 – 1.65 (m, 1H), 1.45 – 1.32 (m, 4H), 1.28 – 1.17 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 154.42, 133.42, 127.87, 127.68, 66.81, 44.55, 34.00, 26.58, 25.88, 14.69. HRMS Calcd for C₁₄H₂₁O₃S [M+H⁺]: 269.1206; Found: 269.1209.

3.5 Synthesis of compound 20a, 21a, 22a, 23a, 24a, 25a, 26a, 27a and 28a

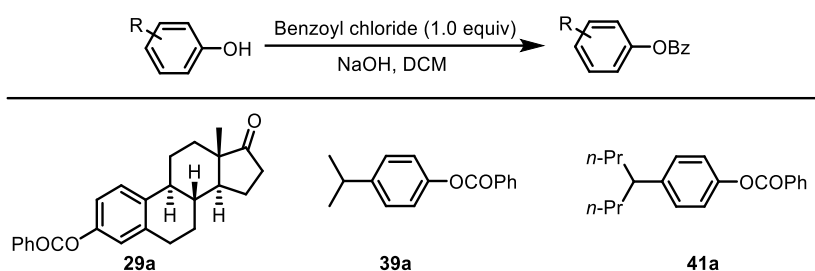


Scheme S8. Synthesis of compound **20a-27a**

General procedure for one-pot two-step reductive coupling of benzocyclohexanone, tosylhydrazide, and arylboronic acid. A solution of benzocyclohexanone **1** (5.0 mmol, 1.0 equiv) and tosylhydrazide (7.5 mmol, 1.5 equiv) in 50 mL of toluene was stirred at 80 °C for 2 h in a reaction tube. Potassium carbonate (10.0 mmol, 2.0 equiv) and the appropriate arylboronic acid (7.5 mmol, 1.5 equiv) were added to the reaction mixture. The system was refluxed at 110 °C for 5 h with stirring. When the reaction was complete, the crude mixture was allowed to cool to room temperature. Dichloromethane and a saturated solution of NaHCO₃ were added and the layers were separated. The aqueous phase was extracted three times using dichloromethane. The combined organic layers were dried over Na₂SO₄ and then filtered. The solvent was

removed under reduced pressure. The products were purified by chromatography on silica gel. The spectroscopic data were consistent with those previously reported in the literature ¹¹.

3.6 Synthesis of compound 29a, 39a, 41a.



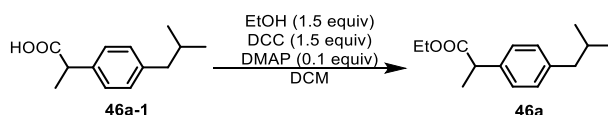
Scheme S9. Synthesis of **29a**, **39a**, **41a**

In a typical procedure, substituted phenol (15.0 mmol, 1.0 equiv) was dissolved in 20.0 mL of 10% aqueous sodium hydroxide (2.0 g, 50.0 mmol NaOH) solution in a 100.0 mL flask. Solutions of tetra-*n*-butylammonium chloride (416.9 mg, 1.5 mmol, 0.1 equiv) in 5.0 mL of dichloromethane and Benzoyl chloride (2.1 g, 15.0 mmol, 1.0 equiv) in 15.0 mL of dichloromethane were prepared. After cooling all solutions at 0 °C, they were mixed at once. The reaction mixture was kept under vigorous magnetic stirring (400 rpm) at 0 °C for 5 min and then poured over 50.0 mL of icy water. The organic layer was separated and the aqueous layer was extracted twice with 40.0 mL of diethyl ether. The combined organic extracts were washed with saturated NaCl solution. The combined organic layer was dried over Na₂SO₄, filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography to afford as a colorless oil. The spectroscopic data were consistent with those previously reported in the literature ¹².

Compound **29a**: ¹H NMR (500 MHz, CDCl₃) δ 8.28 – 8.12 (m, 2H), 7.67 – 7.60 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.04 – 6.89 (m, 2H), 3.00 – 2.89 (m, 2H), 2.57 – 2.48 (m, 1H), 2.47 – 2.39 (m, 1H), 2.36 – 2.28 (m, 1H), 2.19 – 2.11 (m, 1H), 2.10 – 1.95 (m, 3H), 1.65 – 1.47 (m, 6H), 0.93 (s, 3H). ¹³C NMR (126

MHz, CDCl₃) δ 220.81, 165.49, 148.91, 138.14, 137.51, 133.60, 130.21, 129.72, 128.62, 126.54, 121.78, 118.95, 50.51, 48.03, 44.25, 38.10, 35.94, 31.65, 29.51, 26.44, 25.86, 21.68, 13.93. **HRMS** Calcd for C₂₅H₂₇O₃ [M+H⁺]: 375.1955; Found: 375.1957.

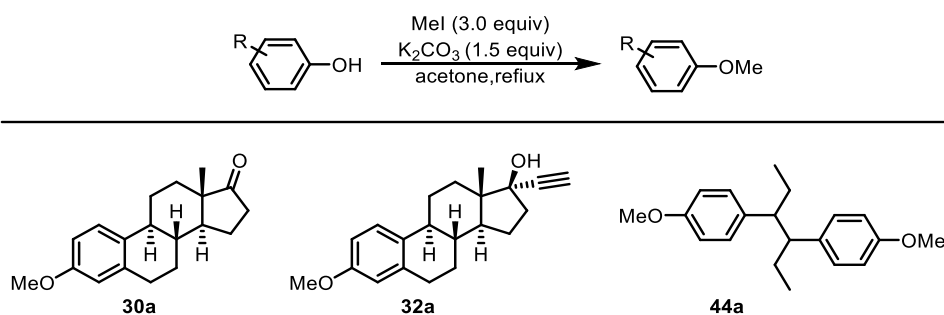
3.7 Synthesis of compound 46a.



Scheme S10. Synthesis of **46a**

To a solution of ethanol (690.0 mg, 15.0 mmol, 1.5 equiv) in DCM (25.0 mL) was added 4-Dimethylaminopyridine (12.2 mg, 0.1 mmol, 0.1 equiv). Add ibuprofen (2.1 g, 10.0 mmol, 1.0 equiv) and DCC (3.1 g, 15.0 mmol, 1.5 equiv) in turn to the mixture. The resulting solution was stirred at room temperature during 3 h. The combined organic layer was filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography using 5% EtOAc in petroleum ether to afford **46a** (1.9 g, 80.2% yield) as a colorless oil. The spectroscopic data were consistent with those previously reported in the literature¹⁰.

3.8 Synthesis of compound 30a, 32a, 44a.



Scheme S11. Synthesis of **30a**, **32a**, **44a**

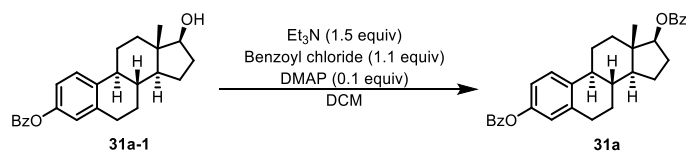
100 mL round-bottom flask was charged with phenol (10 mmol, 1.0 equiv), K₂CO₃ (2.1 g, 15.0 mmol, 1.5 equiv) and 20 mL anhydrous acetone. Then a solution of MeI (4.3 g, 30.0 mmol, 3.0 equiv) in 10.0 mL of anhydrous acetone was added dropwise to the mixture at room temperature. After being stirred for 30 min at room temperature,

the reaction mixture was refluxed overnight. The reaction was cooled to room temperature and filtered. The filtrate was concentrated to afford the crude product, which was purified by flash chromatography to give the desired products. The spectroscopic data of **44a** were consistent with those previously reported in the literature¹³.

Compound **30a**: ¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.65 (d, *J* = 2.2 Hz, 1H), 3.78 (s, 3H), 2.95 – 2.85 (m, 2H), 2.55 – 2.47 (m, 1H), 2.44 – 2.36 (m, 1H), 2.30 – 2.22 (m, 1H), 2.19 – 2.10 (m, 1H), 2.09 – 1.98 (m, 2H), 1.98 – 1.92 (m, 1H), 1.65 – 1.46 (m, 6H), 0.91 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 220.96, 157.66, 137.80, 132.08, 126.40, 113.95, 111.63, 55.27, 50.47, 48.08, 44.04, 38.45, 35.95, 31.67, 29.75, 26.63, 26.01, 21.67, 13.93. HRMS Calcd for C₁₉H₂₅O₂ [M+H⁺]: 285.1849; Found: 285.1851.

Compound **32a**: ¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 8.6 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 3.79 (s, 3H), 2.86 (d, *J* = 4.6 Hz, 2H), 2.62 (s, 1H), 2.36 (dd, *J* = 6.9, 2.6 Hz, 2H), 2.28 – 2.20 (m, 1H), 2.07 – 2.00 (m, 1H), 1.97 – 1.91 (m, 2H), 1.90 (d, *J* = 2.9 Hz, 1H), 1.81 – 1.69 (m, 3H), 1.51 – 1.36 (m, 4H), 0.90 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 157.50, 138.02, 132.62, 126.44, 113.89, 111.58, 87.68, 79.94, 74.15, 55.28, 49.54, 47.22, 43.61, 39.52, 39.05, 32.84, 29.92, 27.36, 26.50, 22.91, 12.81. HRMS Calcd for C₂₁H₂₇O₂ [M+H⁺]: 311.2006; Found: 311.2005.

3.9 Synthesis of compound 31a

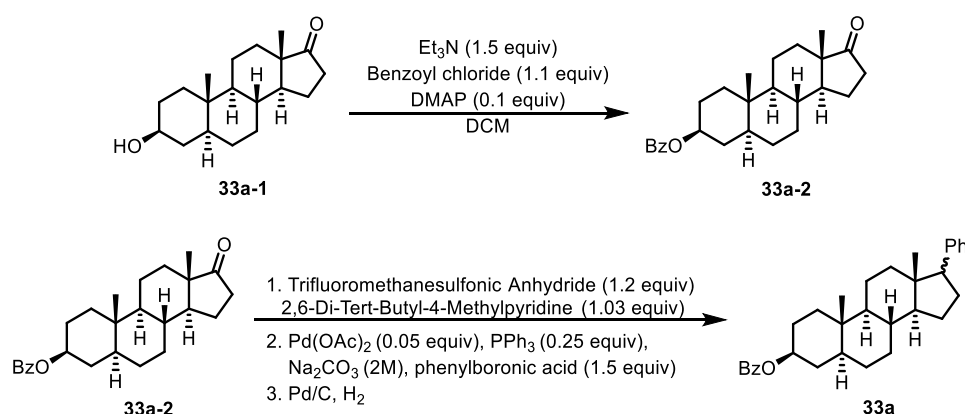


Scheme S12. Synthesis of **31a**

To a solution of Estradiol Benzoate (941.2 mg, 2.5 mmol, 1.0 equiv) in DCM (20.0 mL) was added 4-Dimethylaminopyridine (30.5 mg, 0.25 mmol, 0.1 equiv) and Et₃N

(379.5 mg, 3.75 mmol, 1.5 equiv). The solution was cooled down to 0 °C and Benzoyl chloride (386.7 mg, 2.75 mmol, 1.1 equiv) was added dropwise. The resulting solution was stirred at room temperature during 3 h. H₂O (30.0 mL) was added and the mixture was extracted with DCM (3 x 20.0 mL). The combined organic layer was dried over Na₂SO₄, filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography using 3% EtOAc in petroleum ether to afford (**31a**) (451 mg, 84% yield) as a white solid. The spectroscopic data were consistent with those previously reported in the literature ¹⁴.

3.10 Synthesis of compound **33a** and **34a** ¹⁵



Scheme S13. Synthesis of **33a**

To a solution of Epiandrosterone (1.2 g, 4.0 mmol, 1.0 equiv) in DCM (30.0 mL) was added 4-Dimethylaminopyridine (48.8 mg, 0.4 mmol, 0.1 equiv) and Et₃N (607.2 mg, 6.0 mmol, 1.5 equiv). The solution was cooled down to 0 °C and benzoyl chloride (618.6 mg, 4.4 mmol, 1.1 equiv) was added dropwise. The resulting solution was stirred at room temperature during 3 h. H₂O (30.0 mL) was added and the mixture was extracted with DCM (3 x 20.0 mL). The combined organic layer was dried over Na₂SO₄, filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography using 5% EtOAc in petroleum ether to afford (**33a-2**) (1.3 g, 81% yield) as a white solid.

In a flame dried 50 mL round bottom flask equipped with a stir bar was added

Benzoyl epiandrosterone (1.1 g, 3.0 mmol, 1.0 equiv), 2,6-Di-Tert-Butyl-4-Methylpyridine (636.6 mg, 3.1 mmol, 1.03 equiv) and DCM (15.0 mL). Trifluoromethanesulfonic anhydride (1.0 g, 3.6 mmol, 1.2 equiv) was added dropwise into the reaction mixture while stirring. The reaction was stirred for 6 h. Saturated NaHCO₃ (10.0 mL) was then added to quench the reaction and the aqueous layer was extracted with DCM (3 x 10.0 mL). The combined organic layer was washed with saturated NaHCO₃ (5.0 mL) and brine (5.0 mL), dried over Na₂SO₄ and concentrated in vacuo. Purification by flash chromatography on silica (50.0 mL) eluting with 2% EtOAc in petroleum ether to afford the product (**33a-3**) (1.5 g, 95.7%) as a white solid.

To a solution of **33a-3** (1.5 g, 2.9 mmol, 1.0 equiv), Pd(OAc)₂ (33.7 mg, 0.15 mmol, 0.05 equiv), and triphenylphosphine (188.8 mg, 0.72 mmol, 0.25 equiv) in DME (15.0 mL) was added phenylboronic acid (524.3 mg, 4.3 mmol, 1.5 equiv) in 2 mol/L Na₂CO₃ (2.0 mL) and EtOH (0.4 mL) at room temperature under N₂. The mixture was heated under reflux for 4 h. The reaction mixture was filtered and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na₂SO₄, and evaporated. The residue was purified by flash chromatography using 5% EtOAc in petroleum ether to afford (**33a-4**) (1.0 g, 79.8%) as a white solid.

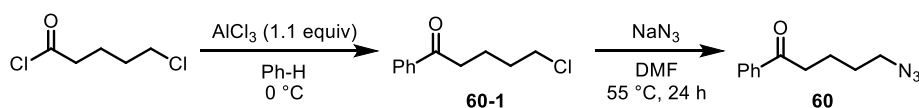
To a stirred solution of **33a-4** (1.0 g, 2.3 mmol, 1.0 equiv) in THF (10.0 mL) was added Pd-C (10% w/w, 100 mg) at room temperature. The resulting mixture was stirred under H₂ (1 atm) for 10 h before it was filtered and washed with EtOAc (3 x 50.0 mL). The combined organic layers were concentrated in vacuo. The residue was purified by flash chromatography using 5% EtOAc in petroleum ether to afford (**33a**) (977 mg, 93%) as a white solid.

The method for synthesizing compound **34a** is the same as that for compound **33a**.

Compound **33a**: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.9$ Hz, 2H), 7.54 (t, $J = 7.3$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 2H), 7.25 – 7.17 (m, 3H), 5.04 – 4.91 (m, 1H), 2.69 (t, $J = 9.8$ Hz, 1H), 2.17 – 2.03 (m, 1H), 2.01 – 1.92 (m, 2H), 1.86 – 1.72 (m, 4H), 1.58 (d, $J = 7.6$ Hz, 5H), 1.37 – 1.21 (m, 7H), 1.17 – 1.08 (m, 1H), 1.05 – 0.94 (m, 1H), 0.88 (s, 3H), 0.80 – 0.76 (m, 1H), 0.48 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.27, 141.31, 132.79, 131.08, 129.65, 128.80, 128.37, 127.78, 126.05, 74.46, 57.21, 56.37, 54.66, 44.99, 44.45, 37.88, 36.99, 36.13, 35.81, 34.29, 32.23, 28.77, 27.73, 26.24, 24.63, 21.04, 12.93, 12.49. **HRMS** Calcd for $\text{C}_{32}\text{H}_{41}\text{O}_2$ $[\text{M}+\text{H}^+]$: 457.3101; Found: 457.3105.

Compound **34a**: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.9$ Hz, 2H), 7.56 (t, $J = 7.1$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.36 – 7.27 (m, 2H), 7.24 (t, $J = 8.4$ Hz, 2H), 7.18 (t, $J = 7.1$ Hz, 1H), 4.86 (t, $J = 8.5$ Hz, 1H), 2.63 – 2.48 (m, 1H), 2.37 – 2.22 (m, 1H), 1.89 – 1.78 (m, 2H), 1.77 – 1.59 (m, 7H), 1.55 – 1.45 (m, 3H), 1.38 – 1.27 (m, 6H), 1.20 – 1.05 (m, 3H), 0.95 (s, 3H), 0.91 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.70, 147.77, 132.85, 130.94, 129.65, 128.43, 128.41, 126.95, 125.94, 83.58, 54.73, 51.04, 47.18, 44.91, 43.24, 39.04, 37.27, 36.70, 36.01, 35.54, 31.84, 29.99, 28.87, 27.90, 23.83, 20.69, 12.65, 12.57. **HRMS** Calcd for $\text{C}_{32}\text{H}_{41}\text{O}_2$ $[\text{M}+\text{H}^+]$: 457.3101; Found: 457.3100.

3.11 Synthesis of compound 60



Scheme S14. Synthesis of compound **60**

To a solution of 5-chloroyl chloride (4.6 g, 30 mmol, 1.0 equiv) in benzene (15 mL) at 0 °C was added AlCl_3 (4.4 g, 33 mmol, 1.1 equiv) and the reaction mixture was stirred at 0 °C for 1 hour. The reaction mixture was then carefully quenched with water, partitioned between sat. aqueous NaHCO_3 and EtOAc and extracted with EtOAc. The

combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with hexane/acetone (v/v 100:1) as eluent to afford **61'** as a colorless solid (4.7g, 79%).

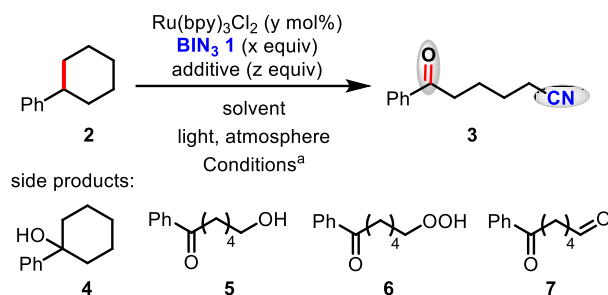
To a solution of compound **60-1** (4.7 g, 24 mmol, 1.0 equiv) in DMF (50 mL) was added NaN_3 (1.7 g, 26 mmol, 1.1 equiv) and the reaction mixture was stirred at 55 °C for 24 hours. The reaction mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with hexane/acetone (v/v 100:1) as eluent to afford compound **60** as a colorless liquid (3.9 g, 80%). The spectroscopic data were consistent with those previously reported in the literature ¹⁶.

4. Reaction optimization for deconstructive oxygenation and nitrogenation of cyclic alkanes by $\text{C}(\text{sp}^3)$ - $\text{C}(\text{sp}^3)$ cleavage

All screening reactions were carried out at a 0.2 mmol scale in a 4 mL glass vial (Thermo Scientific, National B7999-2) sealed with PTEF cap and stirred on bench top. A 24 W (4 x 6 W) blue led light or 24 W white Compact Fluorescent Lamp (24 W white CFL) was positioned 5 cm aside from the reaction vials if necessary. Stock solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (0.01 mmol in 5 mL of HFIP) was used if necessary.

Cyclohexylbenzene **2** (32.0 mg, 0.2 mmol, 1.0 equiv) and other specified reagents were first dispersed in specific solvent and stirred for 5 min at rt. Reagent **1** BIN_3 was then added and the resulting mixture was vigorously stirred at 30 °C with or without light irradiation for 12h or 24 h. After removal of the solvent *in vacuo*, the resulting residue was dissolved in 1 mL of CDCl_3 along with $\text{Cl}_2\text{CHCHCl}_2$ (20 μL) as an internal standard for ^1H -NMR analysis. The composition of reaction mixture was analyzed based on the methylene peaks at 3.03 (t, J = 7.0 Hz, 2H) and 2.39 (t, J = 7.1 Hz, 2H) for compound **3**, δ 3.67 (t, J = 6.5 Hz, 2H) and 2.99 (t, J = 7.3 Hz, 2H) for compound **5**, δ 4.47 (t, J = 6.6 Hz, 2H) and 3.00 (t, J = 7.2 Hz, 2H) for compound **6**, δ

3.01 (t, $J = 6.5$ Hz, 2H) and 2.51 (t, $J = 7.0$ Hz, 2H) for compound **7**, and the peak at δ 1.17-1.29 (m, 1H) for compound **4**.



| entry | reagent (equiv)/ atmosphere/ T (°C)/ Time (h) | Solvent (mL) | 3 (p%) | 4, 5, 6, 7 (side p%) |
|-------|---|-------------------------------|------------------|---|
| 1 | BIN_3 (2), $\text{Ru(bpy)}_3\text{Cl}_2$ (0.001), Air, white CFL (24 W), 30 °C, 24 h | HFIP (2) | 21 | 30 (7) <10 (4,5,6) |
| 2 | BIN_3 (2), $\text{Ru(bpy)}_3\text{Cl}_2$ (0.005), Air, white CFL (24 W), 30 °C, 24 h | HFIP (2) | 25 | 29 (7) <10 (4,5,6) |
| 3 | BIN_3 (2), $\text{Ru(bpy)}_3\text{Cl}_2$ (0.01), Air, white CFL (24 W), 30 °C, 24 h | HFIP (2) | 37 | 35 (7) <10 (4,5,6) |
| 4 | BIN_3 (2), $\text{Ru(bpy)}_3\text{Cl}_2$ (0.02), Air, white CFL (24 W), 30 °C, 24 h | HFIP (2) | 36 | 32 (7) <10 (4,5,6) |
| 5 | BIN_3 (2), $\text{Ru(bpy)}_3\text{Cl}_2$ (0.01), Air, white CFL (24 W), 30 °C, 24 h | CH_3CN (2) | 14 | 14 (7) <10 (4,5,6) |
| 6 | BIN_3 (2), $\text{Ru(bpy)}_3\text{Cl}_2$ (0.01), Air, white CFL (24 W), 30 °C, 24 h | Acetone (2) | 10 | <10 (4,5,6,7) |
| 7 | BIN_3 (2), $\text{Ru(bpy)}_3\text{Cl}_2$ (0.01), | DCM | 16 | 65 (4) ^b |

| | | | | |
|----|---|--------------------------|-----|---|
| | Air, white CFL (24 W), 30 °C, 24 h | (2) | | <10 (5,6,7) |
| 8 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | TCE (2) | 15 | 35 (4) <10 (5,6,7) |
| 9 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | DCE (2) | 16 | 55 (4) <10 (5,6,7) |
| 10 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | DMF (2) | <10 | <10 (4,5,6,7) |
| 11 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | DMSO (2) | 21 | <10 (4,5,6,7) |
| 12 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | PhCl (2) | 10 | <10 (4,5,6,7) |
| 13 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | PhNO ₂ (2) | 10 | <10 (4,5,6,7) |
| 14 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | PhCH ₃ (2) | <10 | <10 (4,5,6,7) |
| 15 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | <i>t</i> BuOH (2) | <10 | <10 (4,5,6,7) |
| 16 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | EtOH (2) | <10 | <10 (4,5,6,7) |

| | | | | |
|----|---|-----------------------|--------------------------|------------------------------------|
| 17 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | EtOAc (2) | 18 | 53 (6) ^b <10 (4,5,7) |
| 18 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | <i>t</i> BuOAc (2) | <10 | 43 (6) <10 (4,5,7) |
| 19 | BIN ₃ (2), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | MeOAc (2) | 30 | 30 (6) <10 (4,5,7) |
| 20 | BIN ₃ (1), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | HFIP (2) | 22 | 28 (7) <10 (4,5,6) |
| 21 | BIN ₃ (3), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | HFIP (2) | 52 | 39 (7) <10 (4,5,6) |
| 22 | BIN ₃ (4), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | HFIP (2) | 58 | 28 (7) <10 (4,5,6) |
| 23 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | HFIP (2) | 68 (63 ^b) | 15 (7) <10 (4,5,6) |
| 24 | BIN ₃ (6), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 24 h | HFIP (2) | 75 (68 ^b) | 15 (7) <10 (4,5,6) |
| 25 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), N ₂ , white CFL (24 W), 30 °C, 24 h | HFIP (2) | <10 | <10 (4,5,6,7) |
| 26 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), O ₂ (purged with O ₂), white | HFIP (2) | 66 | 15 (7) <10 (4,5,6) |

| | | | | |
|----|--|----------------|-------|------------------------|
| | CFL (24 W), 30 °C, 24 h | | | |
| 27 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 12 h | HFIP (2) | 51 | <10 (4,5,6,7) |
| 28 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), Air, blue leds (24 W), 30 °C, 12 h | HFIP (2) | 50 | <10 (4,5,6,7) |
| 29 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), Air, darkness, 30 °C, 12 h | HFIP (2) | <10 | <10 (4,5,6,7) |
| 30 | BIN ₃ (5), Air, white CFL (24 W), 30 °C, 12 h | HFIP (2) | 19 | <10 (4,5,6,7) |
| 31 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 12 h | HFIP (1) | 48 | <10 (4,5,6,7) |
| 32 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 12 h | HFIP (0.5) | 46 | <10 (4,5,6,7) |
| 33 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 12 h | HFIP (0.25) | 46 | <10 (4,5,6,7) |
| 34 | BIN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), Metal salts ^c (Cu, Fe, Co, Ce, Ru) (0.20), Air, white CFL (24 W), 30 °C, 12 h | HFIP (0.25) | 10-38 | <10 (4,5,6,7) |
| 35 | BIN ₃ (0.5), TMSN ₃ (5), Ru(bpy) ₃ Cl ₂ (0.01), Air, white CFL (24 W), 30 °C, 12 h | HFIP (2) | <10 | <10 (4,5,6,7) |

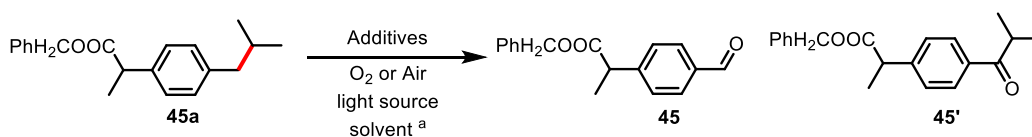
a) Yields are based on ¹H-NMR analysis of reaction mixture on a 0.2 mmol scale at a 0.1 M concentration using ACS grade solvents under Air atmosphere unless specified otherwise. Source of VL source: 24 W blue LEDs or 24 W white CFL. t = 12 h or 24 h. b) Isolated yield. c) Metal salts (Co(OAc)₂, Co(acac)₂, Fe(OAc)₂, FeCl₂·4H₂O, FeBr₂, CeCl₃·7H₂O, CeC₃O₉, RuCl₂, Cu(acac)₂, CuCl,

CuCl₂, Cu(OTf)₂, Cu(OAc)₂, CuI, CuBr, Cu₂O) were used.

Table S1. Reaction optimization for deconstructive oxygenation and nitrogenation of cyclic alkane by inert C(sp³)-C(sp³) cleavage

5. Reaction optimization for deconstructive oxygenation and nitrogenation of acyclic alkanes by C(sp³)-C(sp³) cleavage

BnO-Ibuprofen **45a** (59.2 mg, 0.2 mmol, 1.0 equiv) and other specified reagents were first dispersed in specific solvent and stirred for 5 min at rt. Reagent **1** BIN₃ was then added and the resulting mixture was vigorously stirred at 30 °C with or without light irradiation for 3 h. After removal of the solvent *in vacuo*, the resulting residue was dissolved in 1 mL of CDCl₃ along with Cl₂CHCHCl₂ (20 μL) as an internal standard for ¹H-NMR analysis. The composition of reaction mixture was analyzed based on the -CHO- peaks at δ 10.00 (s, 1H) for compound **45**, δ 3.60-3.46 (m, 1H) for compound **45'**.



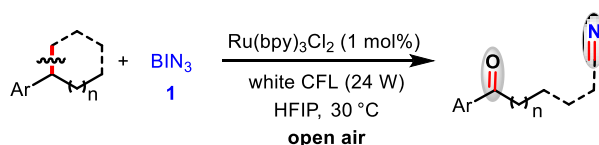
| entry | reagent (equiv)/ atmosphere/ T (°C)/ Time (h) | Solvent (mL) | 39 (p%) | 39' (side p%) |
|-------|--|-----------------|-------------------|----------------------------|
| 1 | BIN ₃ (1.0), Ru(bpy) ₃ Cl ₂ (0.01), O ₂ , blue leds (24 W), 30 °C, 3 h | HFIP (1) | 51 | 12 |
| 2 | BIN ₃ (1.0), Ru(bpy) ₃ Cl ₂ (0.01), air, blue leds (24 W), 30 °C, 3 h | HFIP (1) | 51 | 10 |
| 3 | BIN ₃ (1.0), Ru(bpy) ₃ Cl ₂ (0.01), TFA (1.0), air, blue leds (24 W), 30 °C, 3 h | HFIP (1) | 5 | 4 RSM (78) ^c |

| | | | | |
|----|--|----------|--------------------------|----------------------------|
| 4 | BIN ₃ (1.0), Acid Red 91 (0.01), air, blue leds (24 W), 30 °C, 3 h | HFIP (1) | 30 | 4 RSM (58) ^c |
| 5 | NCS (1.0), Ru(bpy) ₃ Cl ₂ (0.01), air, blue leds (24 W), 30 °C, 3 h | HFIP (1) | 3 | 6 RSM (63) ^c |
| 6 | NBS (1.0), Ru(bpy) ₃ Cl ₂ (0.01), air, blue leds (24 W), 30 °C, 3 h | HFIP (1) | 7 | 9 RSM (55) ^c |
| 7 | NIS (1.0), Ru(bpy) ₃ Cl ₂ (0.01), air, blue leds (24 W), 30 °C, 3 h | HFIP (1) | 4 | 2 RSM (93) ^c |
| 8 | BIN ₃ (1.0), Ru(bpy) ₃ Cl ₂ (0.01), air, white CFL (24 W), 30 °C, 3 h | HFIP (1) | 59 (51 ^b) | 7 RSM (29) ^c |
| 9 | BIN ₃ (0.5), Ru(bpy) ₃ Cl ₂ (0.01), air, white CFL (24 W), 30 °C, 3 h | HFIP (1) | 13 | 4 RSM (41) ^c |
| 10 | BIN ₃ (0.2), Ru(bpy) ₃ Cl ₂ (0.01), air, white CFL (24 W), 30 °C, 3 h | HFIP (1) | 6 | 2 RSM (83) ^c |
| 11 | BIN ₃ (0.1), Ru(bpy) ₃ Cl ₂ (0.01), air, white CFL (24 W), 30 °C, 3 h | HFIP (1) | 5 | 2 RSM (76) ^c |
| 12 | BIN ₃ (0.1), air, white CFL (24 W), 30 °C, 3 h | HFIP (1) | 8 | 4 RSM (68) ^c |

a) Yields are based on ¹H-NMR analysis of reaction mixture on a 0.2 mmol scale at a 0.2 M concentration using ACS grade solvents under Air atmosphere unless specified otherwise. Source of VL source: 24 W blue LEDs or 24 W white CFL. t = 3 h. b) Isolated yield. c) RSM is the short for of recovery starting material.

Table S2. Reaction optimization for deconstructive oxygenation and nitrogeneration of acyclic alkane by inert C(sp³)-C(sp³) cleavage

6. Deconstructive oxygenation and nitrogeneration of cyclic alkanes by inert C(sp³)-C(sp³) cleavage



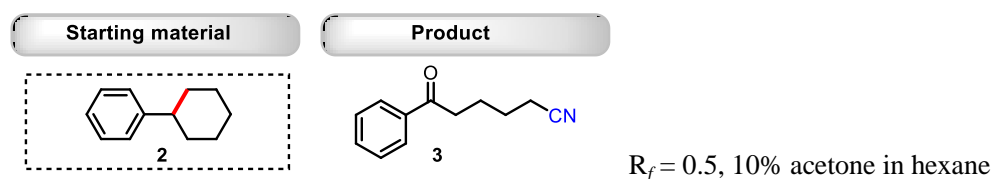
Scheme S15. Deconstructive oxygenation and nitrogeneration of cyclic alkanes by inert C(sp³)-C(sp³) cleavage

General conditions A: Stock solution of Ru(bpy)₃Cl₂ (0.02 mmol in 20 mL of HFIP) was used if necessary. Substrate cyclic alkanes (0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M Ru(bpy)₃Cl₂ solution in HFIP and stirred for 5 min at room temperature. BIN₃ **1** (289.0 mg, 1.0 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 24 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air during C(sp³)-C(sp³) bonds cleavage reactions.

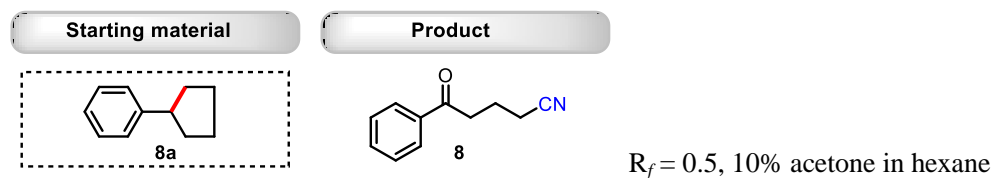
General conditions B: Stock solution of Ru(bpy)₃Cl₂ (0.02 mmol in 20 mL of HFIP) was used if necessary. Substrate cyclic alkanes (0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M Ru(bpy)₃Cl₂ solution in HFIP and stirred for 5 min at room temperature. BIN₃ **1** (289.0 mg, 1.0 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 12 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air during C(sp³)-C(sp³) bonds cleavage reactions.

General conditions C: Stock solution of Ru(bpy)₃Cl₂ (0.02 mmol in 20 mL of HFIP) was used if necessary. Substrate cyclic alkanes (0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M Ru(bpy)₃Cl₂ solution in HFIP and stirred for 5 min at room temperature. BIN₃ **1** (289.0 mg, 1.0 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 48 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air during C(sp³)-C(sp³) bonds cleavage reactions.

6.1 Deconstructive oxygenation and nitrogenation of simple cyclic alkanes by inert C(sp³)-C(sp³) cleavage

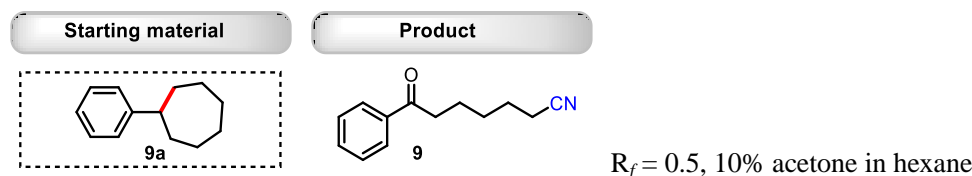


Compound **3** was isolated in 63% yield following the general conditions **A** (¹H NMR yield: 68%). ¹H NMR (500 MHz, CDCl₃) δ 7.98 – 7.90 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.03 (t, *J* = 7.0 Hz, 2H), 2.39 (t, *J* = 7.1 Hz, 2H), 1.97 – 1.83 (m, 2H), 1.82 – 1.69 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 199.13, 136.78, 133.27, 128.73, 128.03, 119.58, 37.43, 25.09, 23.17, 17.25 ¹⁷.

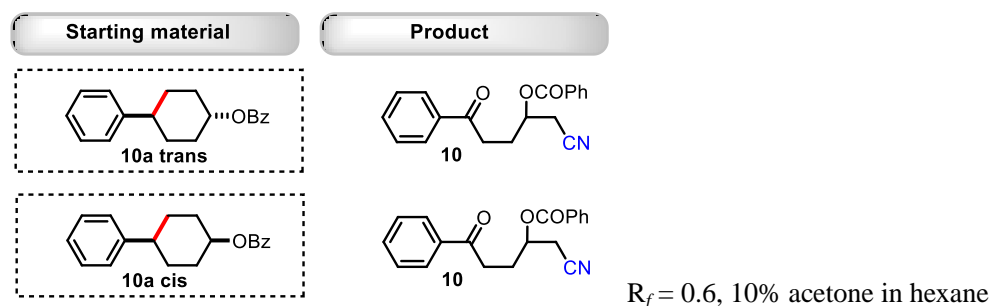


Compound **8** was isolated in 75% yield following the general conditions **A**. Compound **8** was isolated in 58% yield following the general conditions **B**. ¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 6.9 Hz, 1H), 7.49 (t, *J* = 7.1

Hz, 2H), 3.19 (t, $J = 6.8$ Hz, 2H), 2.53 (t, $J = 6.9$ Hz, 2H), 2.25 – 2.01 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.29, 136.58, 133.64, 128.89, 128.13, 119.52, 36.47, 19.88, 16.82 ¹⁸.



Compound **9** was isolated in 70% yield following the general conditions **A**. Compound **9** was isolated in 64% yield following the general conditions **B**. ^1H NMR (500 MHz, CDCl_3) δ 8.00 – 7.91 (m, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 3.00 (t, $J = 7.2$ Hz, 2H), 2.37 (t, $J = 7.1$ Hz, 2H), 1.83 – 1.75 (m, 2H), 1.75 – 1.68 (m, 2H), 1.59 – 1.51 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.86, 137.01, 133.23, 128.77, 128.12, 119.77, 38.18, 28.47, 25.47, 23.36, 17.19 ¹⁷.



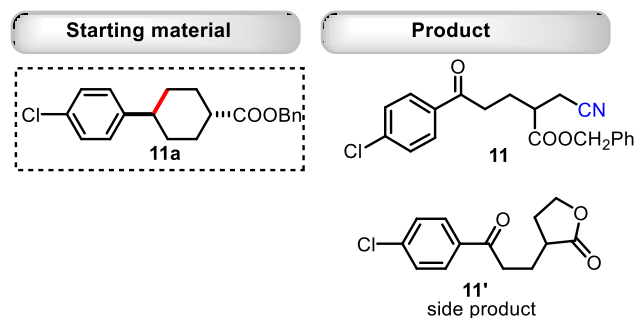
When **10a** is starting material, compound **10** was isolated in 72% yield following the general conditions **A**. Compound **10** was isolated in 66% yield following the general conditions **B**.

When **10b** is starting material, compound **10** cis was isolated in 76% yield following the general conditions **A**. Compound **10** cis was isolated in 71% yield following the general conditions **B**.

^1H NMR (500 MHz, CDCl_3) δ 8.07 – 8.01 (m, 2H), 7.95 – 7.89 (m, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.49 – 7.39 (m, 4H), 5.43 – 5.31 (m, 1H), 3.16 (t,

$J = 7.0$ Hz, 2H), 2.95 (dd, $J = 17.1, 5.4$ Hz, 1H), 2.83 (dd, $J = 17.1, 4.6$ Hz, 1H), 2.43 – 2.28 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.34, 165.89, 136.55, 133.74, 133.49, 129.94, 129.26, 128.80, 128.69, 128.12, 116.26, 68.84, 34.10, 28.00, 23.68.

HRMS Calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_3$ [$\text{M}+\text{H}^+$]: 308.1281; Found: 308.1285.



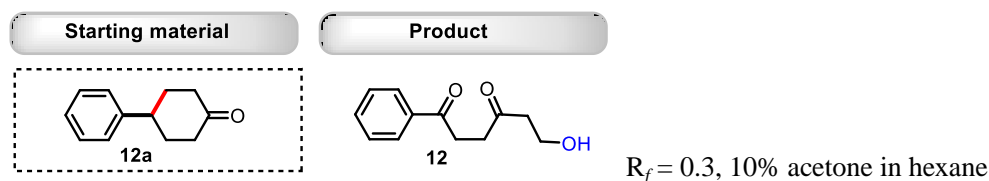
$R_f = 0.6$, 10% acetone in hexane (**11**)

$R_f = 0.8$, 10% acetone in hexane (**11'**)

Compound **11** was isolated in 54% yield and side product compound **11'** was isolated in 16% yield following the general conditions **A**. Compound **11** was isolated in 37% yield and compound **11'** was isolated in 16% yield following the general conditions **B**.

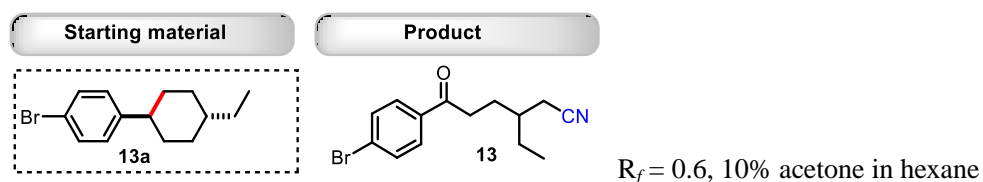
Compound **11**: ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, $J = 8.5$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.33 (m, 5H), 5.22 – 5.09 (m, 2H), 2.97 (t, $J = 7.1$ Hz, 2H), 2.95 – 2.89 (m, 1H), 2.73 (dd, $J = 16.9, 6.9$ Hz, 1H), 2.64 (dd, $J = 16.9, 6.8$ Hz, 1H), 2.20 – 2.11 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.10, 172.19, 139.95, 135.30, 134.92, 129.51, 129.12, 128.85, 128.79, 128.70, 117.55, 67.51, 40.90, 35.23, 25.75, 20.05. **HRMS** Calcd for $\text{C}_{20}\text{H}_{19}\text{ClNO}_3$ [$\text{M}+\text{H}^+$]: 356.1048; Found: 356.1045.

Compound **11'**: ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, $J = 8.5$ Hz, 2H), 7.44 (d, $J = 8.5$ Hz, 2H), 4.37 (td, $J = 8.8, 2.9$ Hz, 1H), 4.21 (td, $J = 9.3, 6.7$ Hz, 1H), 3.32 – 3.13 (m, 2H), 2.71 – 2.61 (m, 1H), 2.49 – 2.41 (m, 1H), 2.17 – 2.10 (m, 1H), 2.10 – 1.99 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.21, 179.14, 139.88, 135.18, 129.65, 129.15, 66.59, 38.38, 35.63, 29.32, 24.79. **HRMS** Calcd for $\text{C}_{13}\text{H}_{14}\text{ClO}_3$ [$\text{M}+\text{H}^+$]: 253.0626; Found: 253.0626.

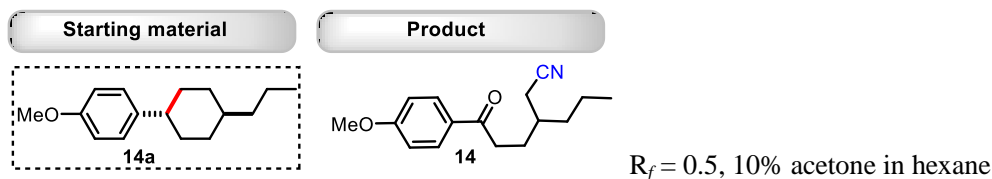


Stock solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (0.02 mmol in 20 mL of HFIP) was used if necessary. Substrate 4-phenylcyclohexanone (34.8mg, 0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M $\text{Ru}(\text{bpy})_3\text{Cl}_2$ solution in HFIP and stirred for 5 min at room temperature. BIN_3 **1** (289.0 mg, 1.0 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at O_2 (O_2 ball) and room temperature (30 °C) under the compact fluorescent light (24W) irradiation for 24 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired product compound **12** in the yield of 59%.

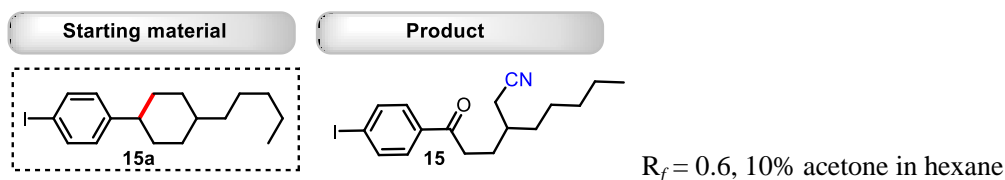
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.98 (d, $J = 8.2$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 3.91 (t, $J = 5.4$ Hz, 2H), 3.33 (t, $J = 6.1$ Hz, 2H), 2.88 (t, $J = 6.0$ Hz, 2H), 2.81 (t, $J = 5.4$ Hz, 2H), 2.47 (dr, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 210.31, 198.79, 136.55, 133.47, 128.76, 128.22, 58.35, 45.16, 36.86, 32.61. **HRMS** Calcd for $\text{C}_{12}\text{H}_{14}\text{NaO}_3$ [$\text{M}+\text{Na}^+$]: 229.0835; Found: 229.0833.



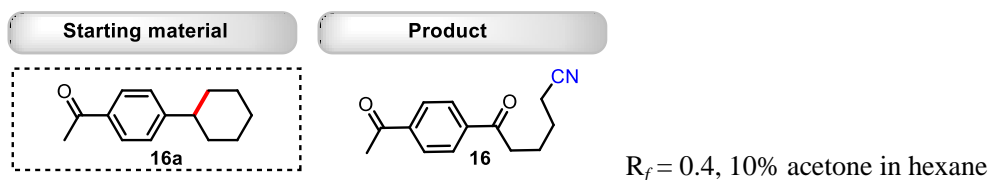
Compound **13** was isolated in 66% yield following the general conditions **A**. Compound **13** was isolated in 56% yield following the general conditions **B**. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.82 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 3.10 – 2.90 (m, 2H), 2.40 (d, $J = 5.7$ Hz, 2H), 1.96 – 1.88 (m, 1H), 1.84 – 1.80 (m, 1H), 1.80 – 1.72 (m, 1H), 1.59 – 1.52 (m, 1H), 1.51 – 1.44 (m, 1H), 0.95 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 198.31, 135.50, 132.15, 129.67, 128.56, 118.68, 36.24, 35.64, 27.64, 26.25, 21.52, 10.96. **HRMS** Calcd for $\text{C}_{14}\text{H}_{17}\text{BrNO}$ [$\text{M}+\text{H}^+$]: 294.0488; Found: 294.0486.



Compound **14** was isolated in 60% yield following the general conditions **A**. Compound **14** was isolated in 52% yield following the general conditions **B**. **¹H NMR** (500 MHz, CDCl₃) δ 8.01 – 7.87 (m, 2H), 7.01 – 6.86 (m, 2H), 3.87 (s, 3H), 3.05 – 2.87 (m, 2H), 2.39 (d, $J = 4.8$ Hz, 2H), 1.95 – 1.87 (m, 1H), 1.86 – 1.77 (m, 2H), 1.49 – 1.32 (m, 4H), 0.93 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 198.01, 163.72, 130.44, 129.92, 118.79, 113.96, 55.63, 35.81, 35.27, 34.57, 28.35, 21.90, 19.83, 14.18. **HRMS** Calcd for C₁₆H₂₂NO₂ [M+H⁺]: 260.1645; Found: 260.1643.

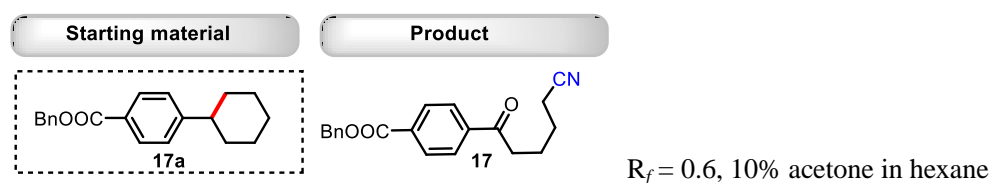


Compound **15** was isolated in 40% yield following the general conditions **A**. Compound **15** was isolated in 33% yield following the general conditions **B**. **¹H NMR** (500 MHz, CDCl₃) δ 7.84 (d, $J = 8.5$ Hz, 2H), 7.66 (d, $J = 8.5$ Hz, 2H), 3.07 – 2.90 (m, 2H), 2.39 (dd, $J = 5.3, 1.7$ Hz, 2H), 1.93 – 1.87 (m, 2H), 1.87 – 1.77 (m, 3H), 1.49 – 1.41 (m, 3H), 1.34 – 1.30 (m, 3H), 0.89 (t, $J = 6.9$ Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 198.66, 138.15, 136.03, 129.54, 118.69, 101.33, 35.57, 34.74, 33.55, 31.90, 28.03, 26.30, 22.66, 21.94, 14.14. **HRMS** Calcd for C₁₇H₂₃INO [M+H⁺]: 384.0819; Found: 384.0818.

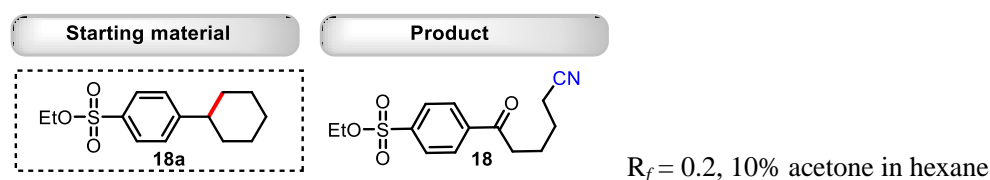


Compound **16** was isolated in 67% yield following the general conditions **A**. Compound **16** was isolated in 59% yield following the general conditions **B**. **¹H NMR**

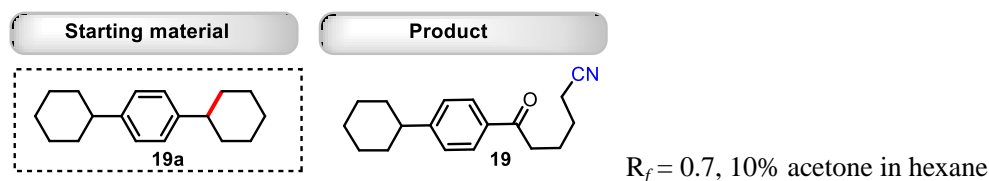
(500 MHz, CDCl₃) δ 8.13 – 8.00 (m, 5H), 3.07 (t, J = 6.9 Hz, 2H), 2.64 (s, 3H), 2.41 (t, J = 7.1 Hz, 2H), 1.95 – 1.88 (m, 2H), 1.80 – 1.73 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 198.64, 197.59, 140.38, 139.91, 128.70, 128.31, 119.53, 37.92, 27.01, 25.06, 23.05, 17.33. **HRMS** Calcd for C₁₄H₁₆NO₂ [M+H⁺]: 230.1176; Found: 230.1174.



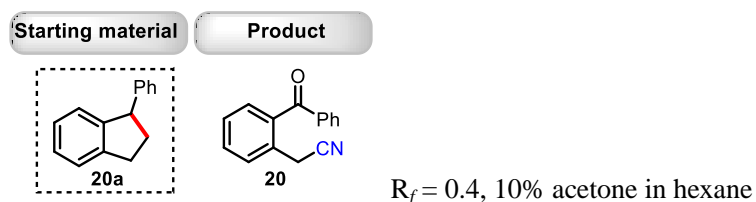
Compound **17** was isolated in 49% yield following the general conditions **A**. Compound **17** was isolated in 39% yield following the general conditions **B**. **¹H NMR** (500 MHz, CDCl₃) δ 8.16 (d, J = 7.7 Hz, 2H), 7.99 (d, J = 7.6 Hz, 2H), 7.44 (dt, J = 8.1, 3.9 Hz, 2H), 7.42 – 7.35 (m, 3H), 5.39 (s, 2H), 3.06 (t, J = 6.9 Hz, 2H), 2.41 (t, J = 7.1 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.81 – 1.73 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 198.63, 165.63, 140.05, 135.74, 134.13, 130.16, 128.80, 128.59, 128.43, 128.02, 119.53, 67.33, 37.89, 25.08, 23.05, 17.35. **HRMS** Calcd for C₂₀H₁₉NNaO₃ [M+Na⁺]: 344.1257; Found: 344.1254.



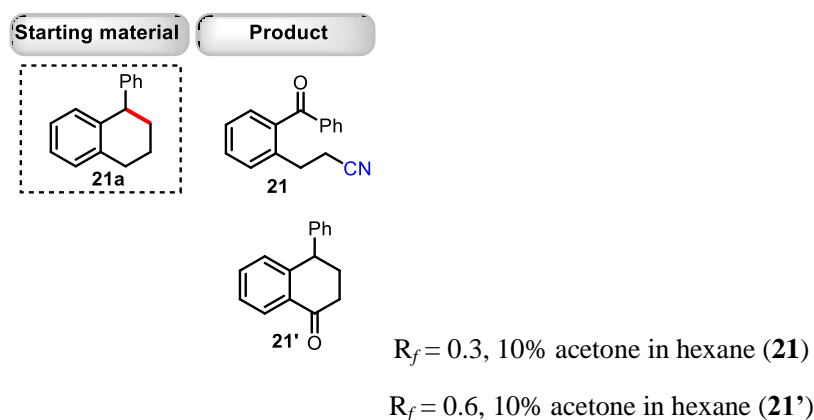
Compound **18** was isolated in 58% yield following the general conditions **A**. Compound **18** was isolated in 52% yield following the general conditions **B**. **¹H NMR** (500 MHz, CDCl₃) δ 8.10 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.08 (t, J = 6.9 Hz, 2H), 2.43 (t, J = 7.0 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.82 – 1.75 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 197.79, 140.59, 140.49, 128.80, 128.38, 119.48, 67.75, 38.02, 25.03, 22.95, 17.38, 14.93. **HRMS** Calcd for C₁₄H₁₈NO₄S [M+H⁺]: 296.0951; Found: 296.0949.



Compound **18** was isolated in 57% yield following the general conditions **A**. Compound **18** was isolated in 40% yield following the general conditions **B**. **¹H NMR** (500 MHz, CDCl₃) δ 7.88 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 3.01 (t, $J = 6.9$ Hz, 2H), 2.63 – 2.50 (m, 1H), 2.40 (t, $J = 7.1$ Hz, 2H), 1.94 – 1.83 (m, 7H), 1.79 – 1.73 (m, 3H), 1.45 – 1.37 (m, 4H). **¹³C NMR** (126 MHz, CDCl₃) δ 198.93, 154.07, 134.70, 128.35, 127.28, 119.66, 44.82, 37.37, 34.23, 26.85, 26.15, 25.19, 23.36, 17.34. **HRMS** Calcd for C₁₈H₂₄NO [M+H⁺]: 270.1852; Found: 270.1849.



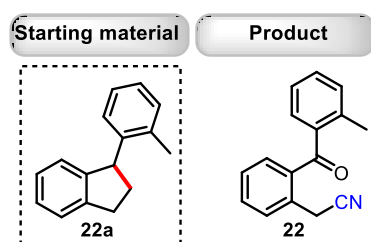
Compound **20** was isolated in 65% yield following the general conditions **A**. **¹H NMR** (500 MHz, CDCl₃) δ 7.79 (d, $J = 8.0$ Hz, 2H), 7.68 – 7.56 (m, 3H), 7.52 – 7.46 (m, 3H), 7.42 (t, $J = 7.5$ Hz, 1H), 4.00 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 197.25, 137.39, 136.92, 133.65, 131.89, 130.82, 130.44, 130.37, 130.06, 128.73, 127.67, 117.90, 22.04. **HRMS** Calcd for C₁₅H₁₂NO [M+H⁺]: 222.0913; Found: 222.0913.



Compound **21** was isolated in 62% yield and side product **21'** was isolated in 21% yield following the general conditions **A**.

Compound **21**: ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.40 – 7.34 (m, 2H), 3.03 (t, J = 7.2 Hz, 2H), 2.76 (t, J = 7.3 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.11, 138.03, 137.98, 137.69, 133.57, 131.31, 131.16, 130.47, 130.07, 128.67, 126.78, 119.36, 29.80, 19.70. HRMS Calcd for $\text{C}_{16}\text{H}_{14}\text{NO}$ [$\text{M}+\text{H}^+$]: 236.1070; Found: 236.1067.

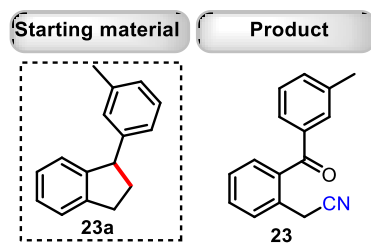
Compound **21'**: ^1H NMR (500 MHz, CDCl_3) δ 8.12 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.12 (d, J = 7.5 Hz, 2H), 6.99 (d, J = 7.7 Hz, 1H), 4.31 (dd, J = 7.9, 4.6 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.67 – 2.60 (m, 1H), 2.52 – 2.44 (m, 1H), 2.35 – 2.27 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.28, 146.42, 143.83, 133.77, 132.96, 129.70, 128.79, 128.75, 127.25, 127.20, 126.94, 45.47, 36.89, 32.00. HRMS Calcd for $\text{C}_{16}\text{H}_{15}\text{O}$ [$\text{M}+\text{H}^+$]: 223.1117; Found: 223.1117.



R_f = 0.3, 10% acetone in hexane

Compound **22** was isolated in 28% yield following the general conditions A. ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, J = 7.7 Hz, 1H), 7.57 (t, J = 7.3 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.24 (t, J = 7.5 Hz, 1H), 4.17 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.73, 138.41, 138.17, 137.11, 132.63, 132.44, 131.61, 131.47, 131.09, 130.35, 130.00, 128.07, 125.63, 118.02, 22.62, 20.58.

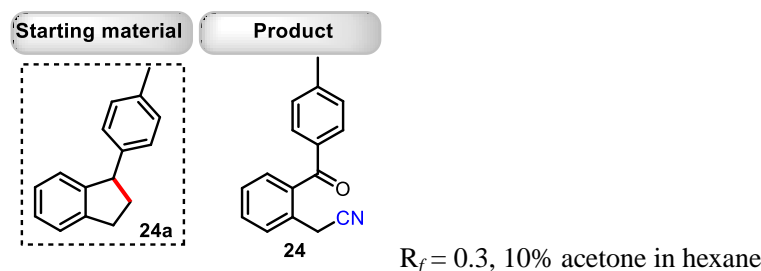
HRMS Calcd for $\text{C}_{16}\text{H}_{14}\text{NO}$ [$\text{M}+\text{H}^+$]: 236.1070; Found: 236.1067.



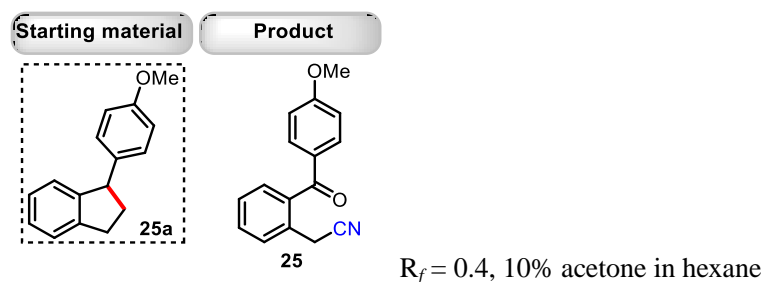
R_f = 0.3, 10% acetone in hexane

Compound **23** was isolated in 62% yield following the general conditions A. ^1H

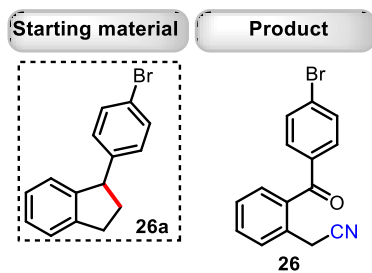
NMR (500 MHz, CDCl_3) δ 7.67 – 7.60 (m, 2H), 7.59 – 7.53 (m, 2H), 7.48 – 7.39 (m, 3H), 7.36 (t, J = 7.6 Hz, 1H), 3.98 (s, 2H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 197.37, 138.61, 137.37, 137.11, 134.41, 131.72, 130.70, 130.68, 130.21, 129.93, 128.52, 127.74, 127.60, 117.86, 21.95, 21.40. **HRMS** Calcd for $\text{C}_{16}\text{H}_{14}\text{NO}$ [$\text{M}+\text{H}^+$]: 236.1070; Found: 236.1070.



Compound **24** was isolated in 51% yield following the general conditions **A**. **^1H NMR** (500 MHz, CDCl_3) δ 7.70 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 7.7 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 6.4 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 3.96 (s, 2H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 196.87, 144.74, 137.35, 134.74, 131.58, 130.61, 130.46, 130.06, 129.91, 129.44, 127.60, 117.89, 21.93, 21.86. **HRMS** Calcd for $\text{C}_{16}\text{H}_{14}\text{NO}$ [$\text{M}+\text{H}^+$]: 236.1070; Found: 236.1070.

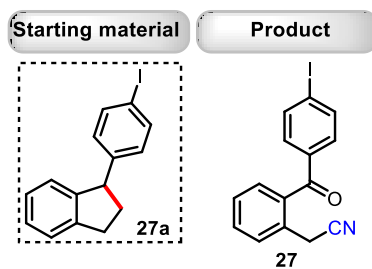


Compound **25** was isolated in 50% yield following the general conditions **A**. **^1H NMR** (500 MHz, CDCl_3) δ 7.79 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 – 7.40 (m, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.94 (s, 2H), 3.89 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 195.77, 164.22, 137.73, 132.92, 131.33, 130.04, 130.03, 129.86, 129.79, 127.61, 117.91, 114.05, 55.73, 21.85. **HRMS** Calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_2$ [$\text{M}+\text{H}^+$]: 252.1019; Found: 252.1018.



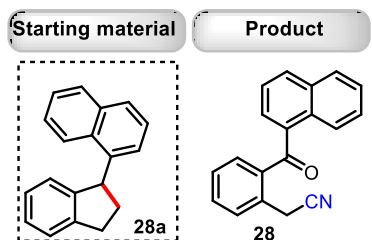
$R_f = 0.3$, 10% acetone in hexane

Compound **26** was isolated in 47% yield following the general conditions A. **^1H NMR** (500 MHz, CDCl_3) δ 7.68 – 7.56 (m, 6H), 7.46 – 7.39 (m, 2H), 3.99 (s, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 196.09, 136.37, 136.12, 132.15, 132.06, 131.84, 130.69, 130.56, 130.30, 128.95, 127.76, 117.77, 22.03. **HRMS** Calcd for $\text{C}_{15}\text{H}_{11}\text{BrNO}$ $[\text{M}+\text{H}^+]$: 300.0019; Found: 300.0020.



$R_f = 0.3$, 10% acetone in hexane

Compound **27** was isolated in 57% yield following the general conditions A. **^1H NMR** (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.62 – 7.56 (m, 1H), 7.50 (d, $J = 8.5$ Hz, 2H), 7.45 – 7.39 (m, 2H), 3.99 (s, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 196.42, 138.07, 136.69, 136.33, 132.17, 131.69, 130.73, 130.58, 130.30, 127.76, 117.78, 101.80, 22.06. **HRMS** Calcd for $\text{C}_{15}\text{H}_{11}\text{INO}$ $[\text{M}+\text{H}^+]$: 347.9880; Found: 347.9880.

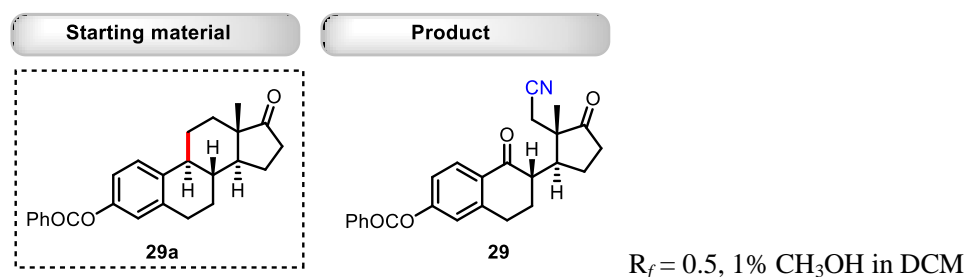


$R_f = 0.4$, 10% acetone in hexane

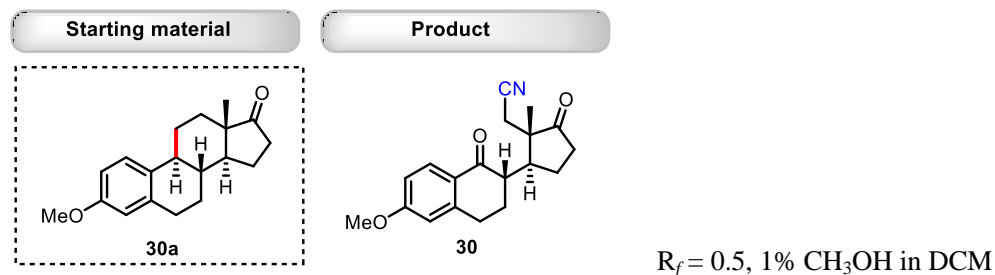
Compound **28** was isolated in 52% yield following the general conditions A. **^1H NMR** (500 MHz, CDCl_3) δ 8.20 (s, 1H), 7.99 – 7.94 (m, 2H), 7.91 (t, $J = 7.6$ Hz, 2H),

7.71 (d, $J = 7.8$ Hz, 1H), 7.67 – 7.59 (m, 2H), 7.56 (dd, $J = 14.5, 7.4$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 1H), 4.03 (s, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 197.18, 137.28, 135.90, 134.70, 132.98, 132.40, 131.84, 130.77, 130.38, 130.09, 129.81, 129.09, 128.84, 128.01, 127.74, 127.18, 125.30, 117.89, 22.06. **HRMS** Calcd for $\text{C}_{19}\text{H}_{14}\text{NO}$ [$\text{M}+\text{H}^+$]: 272.1070; Found: 272.1067.

6.2 Deconstructive oxygenation and nitrogenation of steroids by inert $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ cleavage

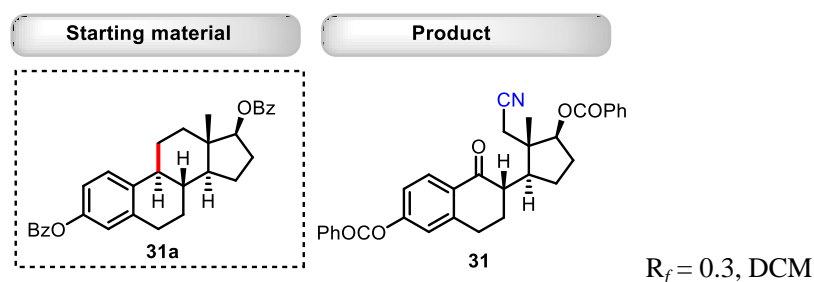


Compound **29** was isolated in 58% yield following the general conditions **C**. **^1H NMR** (500 MHz, CDCl_3) δ 8.23 – 8.16 (m, 2H), 8.11 (d, $J = 8.4$ Hz, 1H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.53 (t, $J = 7.8$ Hz, 2H), 7.23 – 7.12 (m, 2H), 3.20 – 3.03 (m, 2H), 2.92 – 2.84 (m, 1H), 2.83 – 2.75 (m, 1H), 2.67 (q, $J = 16.7$ Hz, 2H), 2.52 (dd, $J = 18.8, 8.5$ Hz, 1H), 2.39 – 2.27 (m, 2H), 2.27 – 2.10 (m, 2H), 1.78 – 1.66 (m, 1H), 1.11 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 218.42, 198.93, 164.74, 155.21, 145.21, 134.07, 130.41, 130.16, 129.93, 129.24, 128.84, 121.72, 120.88, 117.56, 49.93, 47.56, 41.84, 35.90, 27.79, 26.53, 25.21, 23.54, 17.46. **HRMS** Calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_4$ [$\text{M}+\text{H}^+$]: 402.1700; Found: 402.1695.

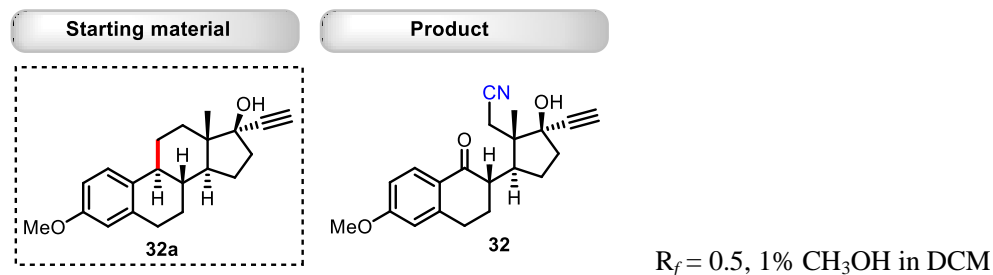


Compound **30** was isolated in 52% yield following the general conditions **C**. **^1H NMR** (500 MHz, CDCl_3) δ 7.98 (d, $J = 8.7$ Hz, 1H), 6.84 (d, $J = 8.7$ Hz, 1H), 6.69 (s,

1H), 3.84 (s, 3H), 3.13 – 3.04 (m, 1H), 3.01 – 2.91 (m, 1H), 2.83 – 2.75 (m, 1H), 2.75 – 2.68 (m, 1H), 2.66 – 2.57 (m, 2H), 2.49 (dd, $J = 18.0, 8.4$ Hz, 1H), 2.30 – 2.18 (m, 3H), 2.14 – 2.08 (m, 1H), 1.72 – 1.65 (m, 1H), 1.11 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 218.67, 198.93, 164.03, 145.73, 130.25, 125.74, 117.53, 113.72, 112.67, 55.58, 50.00, 47.20, 41.67, 35.80, 27.48, 26.49, 24.84, 23.67, 17.36. **HRMS** Calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_3$ [$\text{M}+\text{H}^+$]: 312.1594; Found: 312.1590.

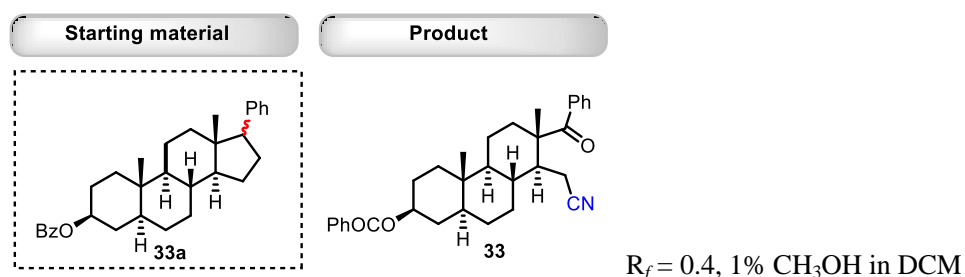


Compound **31** was isolated in 56% yield following the general conditions **C**. ^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, $J = 7.4$ Hz, 2H), 8.11 (d, $J = 8.5$ Hz, 1H), 8.04 (d, $J = 7.4$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.8$ Hz, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.21 – 7.11 (m, 2H), 5.19 – 5.12 (m, 1H), 3.20 – 3.09 (m, 1H), 3.09 – 2.99 (m, 1H), 2.80 – 2.72 (m, 1H), 2.62 – 2.54 (m, 1H), 2.51 (q, $J = 17.0$ Hz, 2H), 2.41 – 2.28 (m, 2H), 2.14 – 2.06 (m, 1H), 2.02 – 1.93 (m, 1H), 1.80 – 1.67 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.77, 166.08, 164.74, 155.08, 145.28, 134.04, 133.30, 130.40, 130.27, 130.15, 129.89, 129.77, 129.23, 128.82, 128.60, 121.71, 120.80, 117.62, 80.35, 47.35, 45.07, 41.33, 27.26, 26.95, 26.83, 26.78, 25.15, 14.72. **HRMS** Calcd for $\text{C}_{32}\text{H}_{29}\text{NO}_5$ [$\text{M}+\text{H}^+$]: 508.2118; Found: 508.2114.

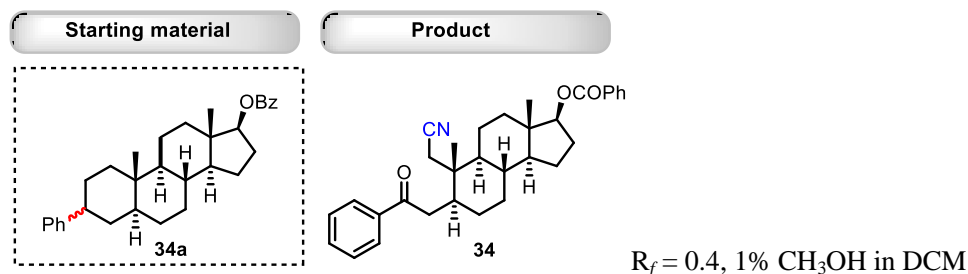


Compound **32** was isolated in 53% yield following the general conditions **C**. ^1H NMR (500 MHz, CDCl_3) δ 7.02 (d, $J = 8.7$ Hz, 1H), 6.78 (dd, $J = 8.7, 3.0$ Hz, 1H),

6.71 (d, $J = 2.9$ Hz, 1H), 3.80 (s, 3H), 2.96 – 2.86 (m, 1H), 2.80 (d, $J = 16.8$ Hz, 1H), 2.63 – 2.53 (m, 4H), 2.28 – 2.20 (m, 1H), 2.14 – 2.05 (m, 1H), 1.95 – 1.82 (m, 3H), 1.44 – 1.32 (m, 1H), 0.90 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 174.72, 157.40, 144.65, 131.08, 119.70, 119.26, 115.25, 112.85, 84.25, 79.06, 75.74, 55.75, 48.88, 45.74, 42.38, 37.79, 33.17, 28.73, 27.94, 24.85, 15.43. **HRMS** Calcd for $\text{C}_{21}\text{H}_{23}\text{NNaO}_3$ [$\text{M}+\text{Na}^+$]: 360.1570; Found: 360.1572.



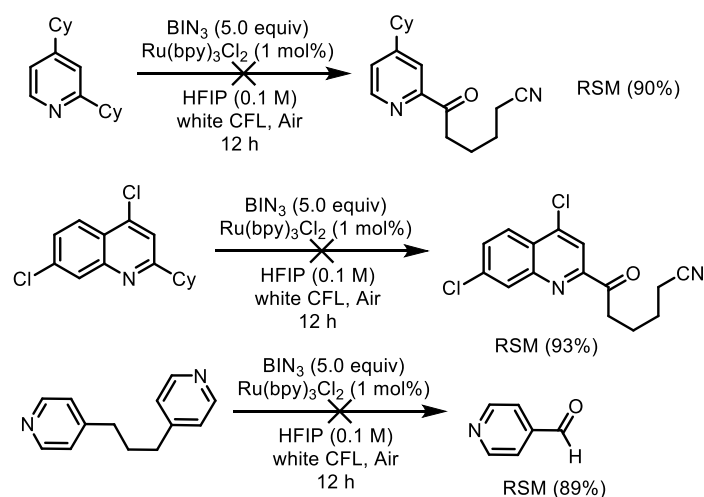
Compound **33** was isolated in 48% yield following the general conditions **C**. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, $J = 7.9$ Hz, 2H), 7.95 (d, $J = 7.9$ Hz, 2H), 7.59 – 7.52 (m, 2H), 7.43 (t, $J = 7.0$ Hz, 4H), 5.02 – 4.89 (m, 1H), 2.79 – 2.72 (m, 1H), 2.65 – 2.62 (m, 1H), 2.16 – 2.11 (m, 1H), 2.06 – 1.96 (m, 2H), 1.86 – 1.77 (m, 3H), 1.74 – 1.63 (m, 5H), 1.58 – 1.11 (m, 9H), 1.00 (s, 1H), 0.90 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.24, 165.34, 133.01, 132.89, 131.48, 130.92, 129.66, 129.49, 128.54, 128.41, 119.36, 85.38, 74.03, 52.75, 47.89, 44.14, 37.46, 36.76, 36.72, 35.74, 33.85, 31.49, 28.26, 27.52, 22.27, 18.90, 15.50, 12.27. **HRMS** Calcd for $\text{C}_{32}\text{H}_{38}\text{NO}_3$ [$\text{M}+\text{H}^+$]: 484.2846; Found: 484.2847.



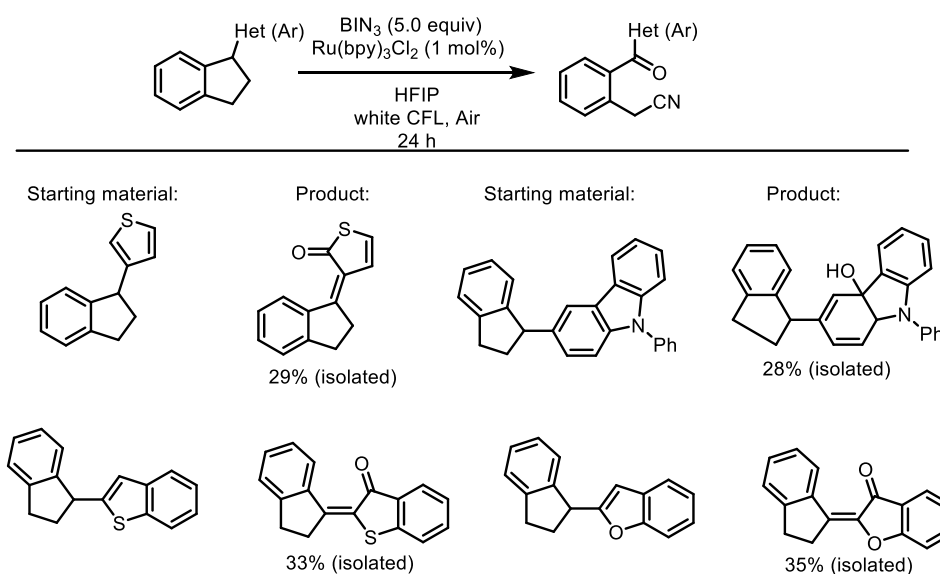
Compound **34** was isolated in 56% yield following the general conditions **C**. ^1H NMR (500 MHz, CDCl_3) δ 8.03 (d, $J = 7.7$ Hz, 2H), 7.97 (d, $J = 7.7$ Hz, 2H), 7.58 – 7.53 (m, 2H), 7.50 – 7.46 (m, 2H), 7.43 (s, 2H), 4.83 (t, $J = 8.4$ Hz, 1H), 3.04 (dd, $J =$

15.4, 2.9 Hz, 1H), 2.68 (dd, $J = 15.4, 10.1$ Hz, 1H), 2.46 (q, $J = 17.5$ Hz, 2H), 2.37 – 2.26 (m, 2H), 1.89 – 1.84 (m, 1H), 1.73 – 1.55 (m, 7H), 1.44 – 1.29 (m, 6H), 0.96 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.40, 166.49, 136.99, 133.31, 132.87, 130.77, 129.60, 128.79, 128.41, 128.31, 117.63, 83.11, 50.49, 49.41, 42.77, 40.66, 40.20, 39.39, 36.76, 35.22, 30.66, 27.89, 27.85, 26.55, 23.67, 21.52, 14.68, 12.35. HRMS Calcd for $\text{C}_{32}\text{H}_{38}\text{NO}_3$ $[\text{M}+\text{H}^+]$: 484.2846; Found: 484.2844.

6.3 Deconstructive oxygenation and nitrogenation of alkyl substituted heteroarenes by inert $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ cleavage



Scheme S16. Selective cleavage of inert $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ bond for pyridine or quinoline substituted alkanes

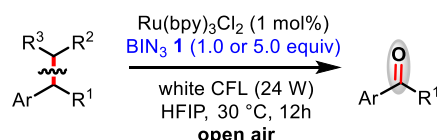


Scheme S17. Selective cleavage of inert $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ bond for electron-rich heteroaryl substituted alkanes

As shown in Scheme S16 and Scheme S17, this reaction system is not applicable to alkyl substituted heteroarenes such as alkyl pyridine, alkyl furan and alkyl thiophene.

7. Deconstructive oxygenation and nitrogenation of acyclic alkanes by inert

C(sp³)-C(sp³) cleavage

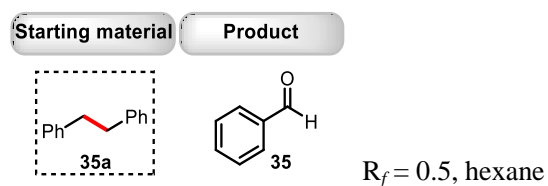


Scheme S18. Deconstructive oxygenation and nitrogenation of acyclic alkanes by inert C(sp³)-C(sp³) cleavage

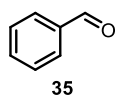
General conditions B: Stock solution of Ru(bpy)₃Cl₂ (0.02 mmol in 20 mL of HFIP) was used if necessary. Substrate cyclic alkanes (0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M Ru(bpy)₃Cl₂ solution in HFIP and stirred for 5 min at room temperature. BIN₃ **1** (289.0 mg, 1.0 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 12 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air during C(sp³)-C(sp³) bonds cleavage reactions.

General conditions D: Stock solution of Ru(bpy)₃Cl₂ (0.02 mmol in 20 mL of HFIP) was used if necessary. Substrate cyclic alkanes (0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M Ru(bpy)₃Cl₂ solution in HFIP and stirred for 5 min at room temperature. BIN₃ **1** (57.8 mg, 0.2 mmol, 1.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 12 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air

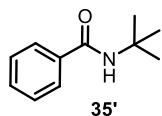
during C(sp³)-C(sp³) bonds cleavage reactions.



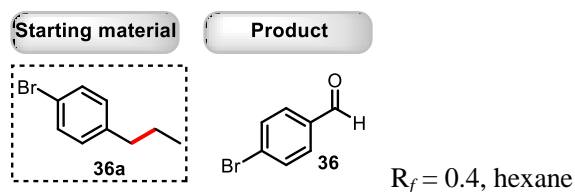
Compound **35** was isolated in 35% yield following the general conditions **B** (¹H NMR yield: 75%). After C(sp³)-C(sp³) bonds cleavage reaction, the conversion of the product of C-C cleavage reaction (benzonitrile) to *N-tert*-butyl amides in 28% yield via the Ritter reaction was carried out employing *tert*-butyl acetate and acetic acid¹⁹.



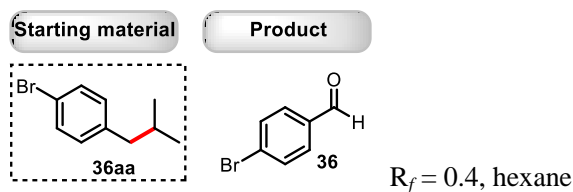
¹H NMR (500 MHz, CDCl₃) δ 10.01 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.58 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 2H)²⁰.



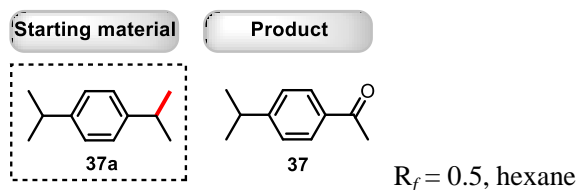
¹H NMR (500 MHz, CDCl₃) δ 7.75 – 7.65 (m, 2H), 7.48 – 7.42 (m, 1H), 7.42 – 7.35 (m, 2H), 4.77 (s, 1H), 1.46 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 167.08, 135.99, 131.15, 128.54, 126.79, 51.70, 28.96¹⁹.



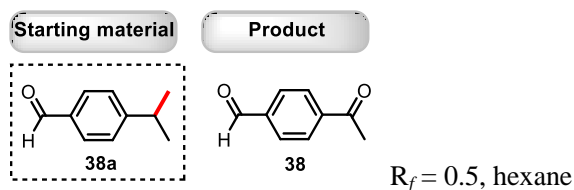
Compound **36** was isolated in 30% yield following the general conditions **D** (¹H NMR yield: 70%). ¹H NMR (500 MHz, CDCl₃) δ 9.98 (s, 1H), 7.75 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.72 – 7.65 (m, 2H)²¹.



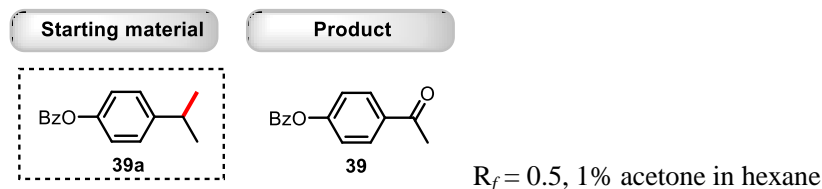
Compound **36** was isolated in 25% yield following the general conditions **D** (^1H NMR yield: 68%). ^1H NMR (500 MHz, CDCl_3) δ 9.98 (s, 1H), 7.75 (dd, $J = 8.2, 1.4$ Hz, 2H), 7.72 – 7.65 (m, 2H)²¹.



Compound **37** was isolated in 31% yield following the general conditions **D** (^1H NMR yield: 68%). ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 7.3$ Hz, 2H), 7.31 (d, $J = 7.5$ Hz, 2H), 3.00 – 2.93 (m, 1H), 2.58 (s, 3H), 1.27 (d, $J = 6.9$ Hz, 6H)²².

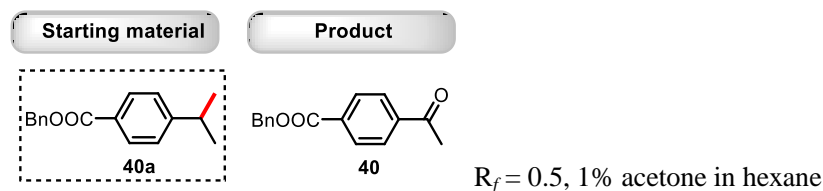


Compound **38** was isolated in 20% yield following the general conditions **D** (Recovery starting material is 55%). ^1H NMR (500 MHz, CDCl_3) δ 10.11 (s, 1H), 8.10 (d, $J = 7.4$ Hz, 2H), 7.98 (d, $J = 7.4$ Hz, 2H), 2.66 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.53, 191.73, 141.37, 139.20, 129.97, 128.97, 27.12²³.

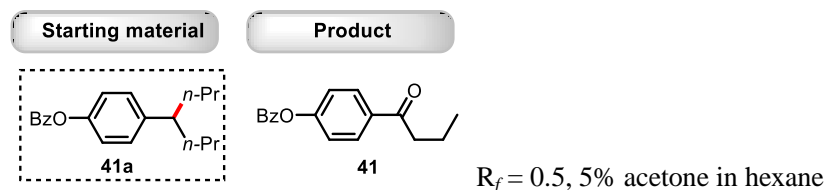


Compound **39** was isolated in 76% yield following the general conditions **B**. ^1H NMR (500 MHz, CDCl_3) δ 8.21 (d, $J = 7.9$ Hz, 2H), 8.05 (d, $J = 8.5$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 2.62 (s, 3H). ^{13}C NMR

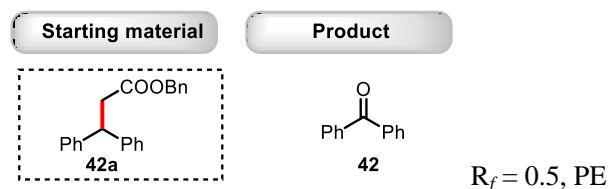
(126 MHz, CDCl₃) δ 197.02, 164.74, 154.81, 134.91, 134.04, 130.36, 130.13, 129.16, 128.80, 122.05, 26.74 ²⁴.



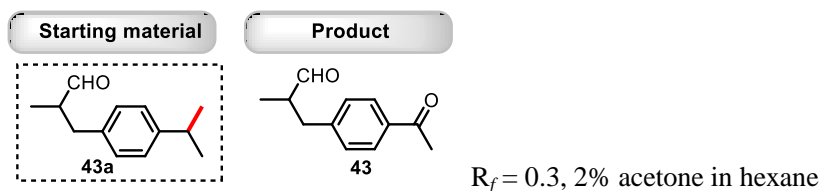
Compound **40** was isolated in 69% yield following the general conditions **B**. ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, $J = 8.2$ Hz, 2H), 8.00 (d, $J = 8.2$ Hz, 2H), 7.46 (d, $J = 7.1$ Hz, 2H), 7.43 – 7.33 (m, 3H), 5.39 (s, 2H), 2.64 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.66, 165.71, 140.45, 135.79, 134.04, 130.10, 128.81, 128.59, 128.44, 128.35, 67.32, 27.03 ²⁵.



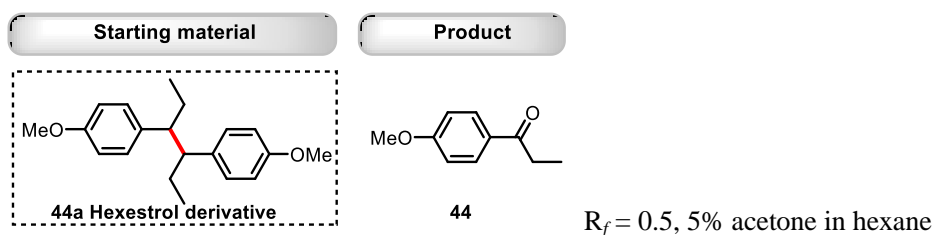
Compound **41** was isolated in 71% yield following the general conditions **B**. ¹H NMR (500 MHz, CDCl₃) δ 8.21 (dd, $J = 8.2, 1.1$ Hz, 2H), 8.05 (d, $J = 8.7$ Hz, 2H), 7.69 – 7.62 (m, 1H), 7.53 (t, $J = 7.8$ Hz, 2H), 7.33 (d, $J = 8.6$ Hz, 2H), 2.96 (t, $J = 7.3$ Hz, 2H), 1.85 – 1.72 (m, 2H), 1.02 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 199.30, 164.78, 154.63, 134.89, 134.03, 130.37, 129.85, 129.21, 128.80, 122.01, 40.65, 17.90, 14.01. HRMS Calcd for C₁₇H₁₇O₃ [M+H⁺]: 269.1172; Found: 269.1172.



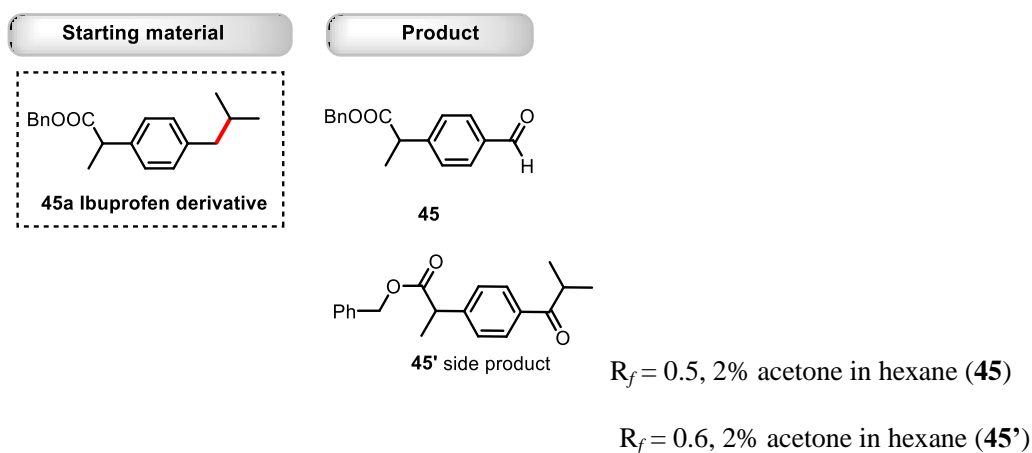
Compound **42** was isolated in 53% yield following the general conditions **B**. ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, $J = 7.8$ Hz, 4H), 7.59 (t, $J = 7.0$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 196.90, 137.73, 132.55, 130.19, 128.41 ²⁶.



Compound **43** was isolated in 52% yield following the general conditions **D**. ^1H NMR (500 MHz, CDCl_3) δ 9.72 (s, 1H), 7.89 (d, $J = 6.9$ Hz, 2H), 7.27 (d, $J = 6.9$ Hz, 2H), 3.15 (dd, $J = 12.9, 5.2$ Hz, 1H), 2.75 – 2.62 (m, 2H), 2.59 (s, 3H), 1.10 (d, $J = 5.7$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 203.75, 197.88, 144.82, 135.70, 129.39, 128.79, 47.87, 36.60, 26.72, 13.41. HRMS Calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}^+]$: 191.1067; Found: 191.1066.

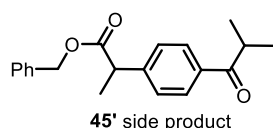


Compound **44** was isolated in 34% yield following the general conditions **B**. ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 3.85 (s, 3H), 2.94 (q, $J = 7.2$ Hz, 2H), 1.20 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.59, 163.41, 130.32, 130.15, 113.78, 55.55, 31.52, 8.56²⁷.

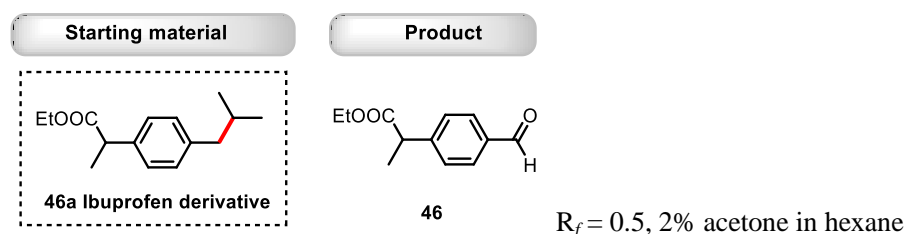


Compound **45** was isolated in 51% yield following the general conditions **D** (^1H NMR

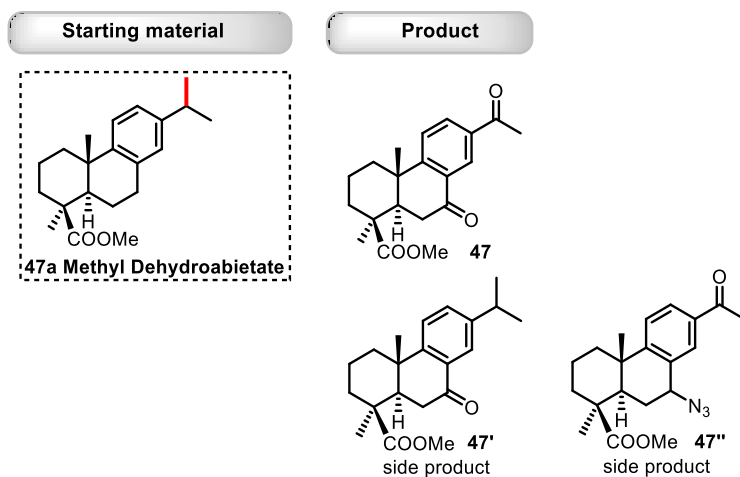
yield: 59%). **¹H NMR** (500 MHz, CDCl₃) δ 10.00 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.25 – 7.22 (m, 2H), 5.12 (q, *J* = 12.4 Hz, 2H), 3.86 (q, *J* = 7.1 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 191.93, 173.51, 147.33, 135.79, 135.59, 130.21, 128.66, 128.46, 128.40, 128.12, 66.93, 45.89, 18.46²⁸.



Side product compound **45'** was isolated in 20% yield following the general conditions **D**. **¹H NMR** (500 MHz, CDCl₃) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 5.11 (q, *J* = 12.4 Hz, 2H), 3.84 (q, *J* = 7.1 Hz, 1H), 3.60 – 3.46 (m, 1H), 1.54 (d, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 204.13, 173.76, 145.46, 135.89, 135.29, 128.86, 128.65, 128.35, 128.09, 128.00, 66.84, 45.69, 35.51, 19.29, 18.45. **HRMS** Calcd for C₂₀H₂₃O₃ [M+H⁺]: 311.1642; Found: 311.1643.

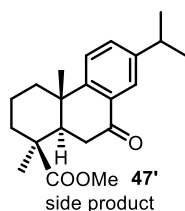


Compound **46** was isolated in 59% yield following the general conditions **D**. **¹H NMR** (500 MHz, CDCl₃) δ 9.99 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 4.20 – 4.06 (m, 2H), 3.79 (q, *J* = 7.2 Hz, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **HRMS** Calcd for C₁₂H₁₅O₃ [M+H⁺]: 207.1016; Found: 207.1017²⁹.



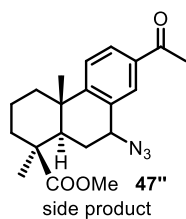
$R_f = 0.3$ (**47**); $R_f = 0.7$ (**47'**); $R_f = 0.5$ (**47''**), 10% acetone in hexane.

Compound **47** was isolated in 30% yield following the general conditions **B**. **^1H NMR** (500 MHz, CDCl_3) δ 8.54 (d, $J = 1.6$ Hz, 1H), 8.14 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.49 (d, $J = 8.3$ Hz, 1H), 3.67 (s, 3H), 2.80 – 2.69 (m, 2H), 2.62 (s, 3H), 2.45 – 2.36 (m, 2H), 1.84 – 1.72 (m, 5H), 1.36 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 197.53, 197.34, 177.72, 159.99, 135.54, 133.11, 131.02, 128.20, 124.39, 52.44, 46.85, 43.56, 38.20, 37.84, 37.06, 36.62, 26.77, 23.59, 18.21, 16.57. **HRMS** Calcd for $\text{C}_{20}\text{H}_{25}\text{O}_4$ $[\text{M}+\text{H}^+]$: 329.1747; Found: 329.1745.



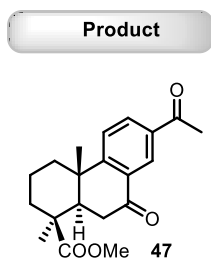
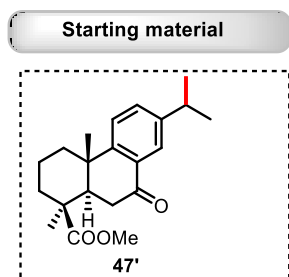
$R_f = 0.7$, 10% acetone in hexane

Side product compound **47'** was isolated in 16% yield following the general conditions **B**. **^1H NMR** (500 MHz, CDCl_3) δ 7.87 (d, $J = 1.8$ Hz, 1H), 7.40 (dd, $J = 8.1, 2.0$ Hz, 1H), 7.29 (d, $J = 8.2$ Hz, 1H), 3.66 (d, $J = 9.1$ Hz, 3H), 2.99 – 2.86 (m, 1H), 2.76 – 2.66 (m, 2H), 2.41 – 2.27 (m, 2H), 1.83 – 1.79 (m, 2H), 1.74 – 1.70 (m, 1H), 1.68 – 1.60 (m, 2H), 1.34 (s, 3H), 1.28 – 1.22 (m, 9H). **^{13}C NMR** (126 MHz, CDCl_3) δ 198.66, 177.94, 153.14, 147.10, 132.71, 130.88, 125.20, 123.61, 52.31, 46.87, 43.97, 38.01, 37.48, 37.30, 36.72, 33.75, 23.95, 23.89, 23.84, 18.34, 16.54. **HRMS** Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_3$ $[\text{M}+\text{H}^+]$: 329.2111; Found: 329.2107.



$R_f = 0.5$, 10% acetone in hexane

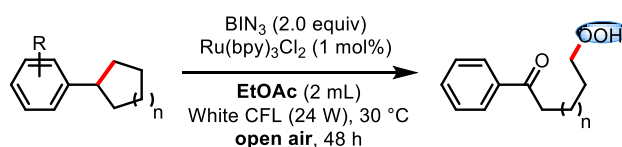
Side product compound **47''** was isolated in 20% yield following the general conditions **B**. **¹H NMR** (500 MHz, CDCl₃) δ 7.87 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.82 (d, $J = 1.6$ Hz, 1H), 7.41 (d, $J = 8.3$ Hz, 1H), 3.74 (s, 3H), 2.58 (d, $J = 4.3$ Hz, 3H), 2.52 (dd, $J = 12.8, 1.5$ Hz, 1H), 2.34 (d, $J = 13.4$ Hz, 1H), 2.18 – 2.09 (m, 1H), 1.88 – 1.70 (m, 7H), 1.29 (s, 3H), 1.19 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 197.45, 178.22, 154.97, 135.35, 132.15, 130.59, 128.66, 125.36, 59.64, 52.39, 47.42, 40.24, 38.28, 37.42, 36.15, 28.00, 26.67, 24.60, 18.57, 16.74. **HRMS** Calcd for C₂₀H₂₅N₃NaO₃ [M+Na⁺]: 378.1788; Found: 378.1785.



$R_f = 0.3$, 10% acetone in hexane

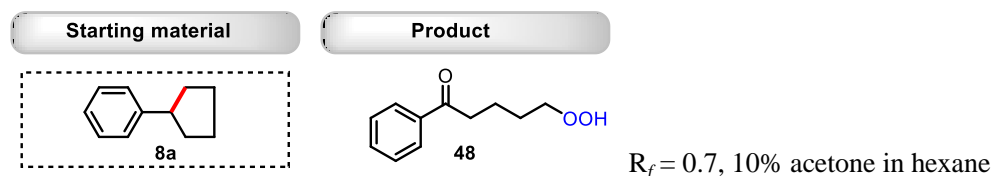
Compound **47** was isolated in 78% yield following the general conditions **B**. **¹H NMR** (500 MHz, CDCl₃) δ 8.54 (d, $J = 1.6$ Hz, 1H), 8.14 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.49 (d, $J = 8.3$ Hz, 1H), 3.67 (s, 3H), 2.80 – 2.69 (m, 2H), 2.62 (s, 3H), 2.45 – 2.36 (m, 2H), 1.84 – 1.72 (m, 5H), 1.36 (s, 3H), 1.28 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 197.53, 197.34, 177.72, 159.99, 135.54, 133.11, 131.02, 128.20, 124.39, 52.44, 46.85, 43.56, 38.20, 37.84, 37.06, 36.62, 26.77, 23.59, 18.21, 16.57. **HRMS** Calcd for C₂₀H₂₅O₄ [M+H⁺]: 329.1747; Found: 329.1745.

8. Deconstructive oxygenation and peroxidation of cyclic alkanes by inert C(sp³)-C(sp³) cleavage

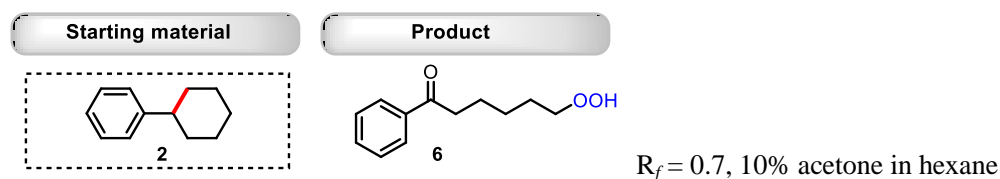


Scheme S19. Deconstructive oxygenation and peroxidation of cyclic alkanes by inert $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ cleavage

General conditions E: Stock solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (0.02 mmol in 20 mL of EtOAc) was used if necessary. Substrate cyclic alkanes (0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M $\text{Ru}(\text{bpy})_3\text{Cl}_2$ solution in EtOAc and stirred for 5 min at room temperature. BIN_3 **1** (115.6 mg, 0.4 mmol, 2.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature (30°C) under the compact fluorescent light (24 W) irradiation for 48 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air during $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ bonds cleavage reactions.

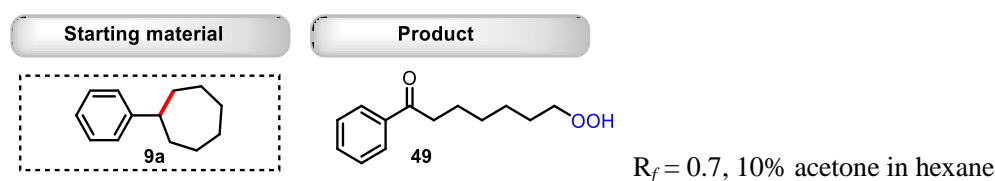


Compound **48** was isolated in 58% yield and deconstructive nitrogenation product **8** was isolated in 25% yield following the general conditions **E**. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.0$ Hz, 2H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 4.50 (t, $J = 6.0$ Hz, 2H), 3.04 (t, $J = 6.6$ Hz, 2H), 1.93 – 1.75 (m, 4H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 199.38, 136.90, 133.33, 128.81, 128.12, 73.20, 37.76, 26.53, 20.39. **HRMS** Calcd for $\text{C}_{11}\text{H}_{14}\text{NaO}_3$ [$\text{M}+\text{Na}^+$]: 217.0835; Found: 217.0829.

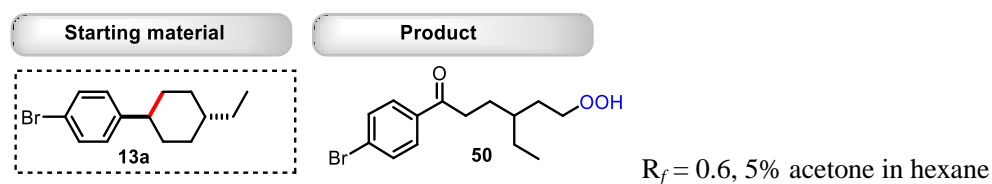


Compound **6** was isolated in 53% yield and deconstructive nitrogenation product **3**

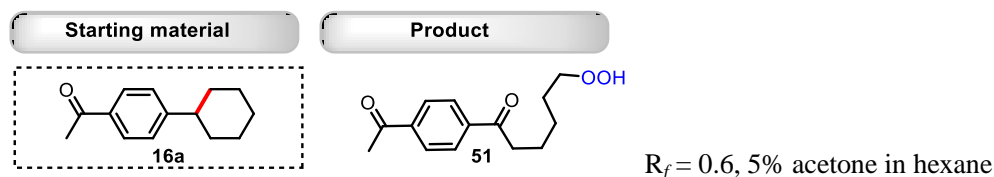
was isolated in 18% yield following the general conditions **E**. **¹H NMR** (500 MHz, CDCl₃) δ 7.98 – 7.93 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 4.47 (t, *J* = 6.6 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.71 (m, 4H), 1.54 – 1.44 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 199.96, 137.04, 133.23, 128.77, 128.15, 73.24, 38.27, 26.89, 25.56, 23.75. **HRMS** Calcd for C₁₂H₁₆NaO₃ [M+Na⁺]: 231.0992; Found: 231.0992.



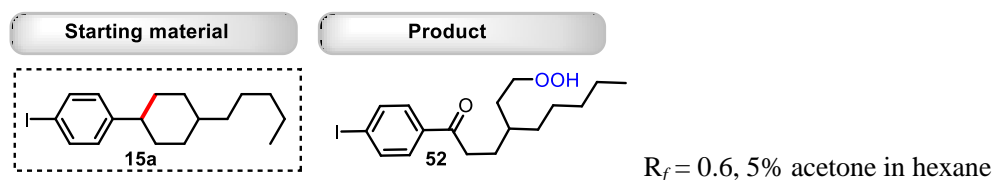
Compound **49** was isolated in 60% yield and deconstructive nitrogenation product **9** was isolated in 27% yield following the general conditions **E**. **¹H NMR** (500 MHz, CDCl₃) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.45 (t, *J* = 6.6 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 1.82 – 1.67 (m, 4H), 1.52 – 1.38 (m, 4H). **¹³C NMR** (126 MHz, CDCl₃) δ 200.25, 137.17, 133.13, 128.74, 128.16, 73.41, 38.43, 28.95, 26.80, 25.73, 24.09. **HRMS** Calcd for C₁₃H₁₉O₃ [M+H⁺]: 223.1329; Found: 223.1325.



Compound **50** was isolated in 54% yield and deconstructive nitrogenation product **13** was isolated in 28% yield following the general conditions **E**. **¹H NMR** (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 4.51 (t, *J* = 6.8 Hz, 2H), 2.98 – 2.87 (m, 2H), 1.78 – 1.65 (m, 4H), 1.55 – 1.49 (m, 1H), 1.45 – 1.34 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 199.02, 135.77, 132.11, 129.68, 128.39, 71.75, 35.78, 35.71, 30.19, 27.27, 25.83, 10.65. **HRMS** Calcd for C₁₄H₂₀BrO₃ [M+H⁺]: 315.0590; Found: 315.0595.

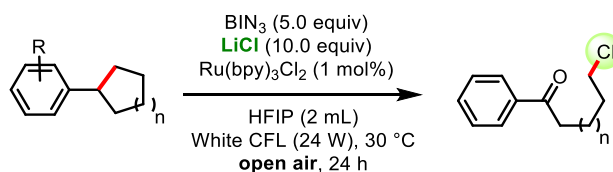


Compound **51** was isolated in 56% yield and deconstructive nitrogenation product **16** was isolated in 23% yield following the general conditions **E**. **^1H NMR** (500 MHz, CDCl_3) δ 8.03 (m, 4H), 4.47 (t, $J = 6.6$ Hz, 2H), 3.02 (t, $J = 7.2$ Hz, 2H), 2.64 (s, 3H), 1.83 – 1.77 (m, 4H), 1.55 – 1.47 (m, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 199.30, 197.54, 140.19, 128.69, 128.34, 125.01, 73.14, 38.68, 26.92, 25.53, 23.60, 22.13. **HRMS** Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_4$ [$\text{M}+\text{H}^+$]: 251.1278; Found: 251.1277.



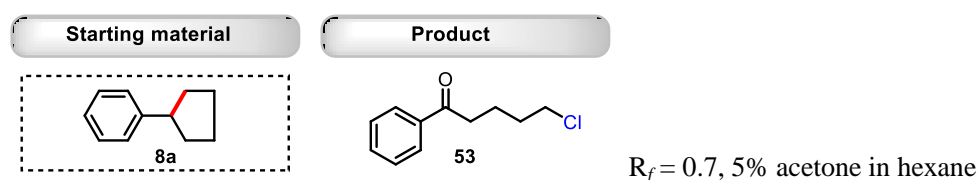
Compound **51** was isolated in 51% yield and deconstructive nitrogenation product **15** was isolated in 26% yield following the general conditions **E**. **^1H NMR** (500 MHz, CDCl_3) δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 4.51 (t, $J = 7.0$ Hz, 2H), 2.98 – 2.88 (m, 2H), 1.77 – 1.69 (m, 4H), 1.35 – 1.24 (m, 9H), 0.89 (t, $J = 7.0$ Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 199.36, 138.13, 136.31, 129.57, 101.12, 71.76, 35.71, 34.41, 33.48, 32.23, 30.64, 27.78, 26.17, 22.75, 14.19. **HRMS** Calcd for $\text{C}_{17}\text{H}_{26}\text{IO}_3$ [$\text{M}+\text{H}^+$]: 405.0921; Found: 405.0922.

9. Deconstructive oxygenation and chlorination of cyclic alkanes by inert $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ cleavage

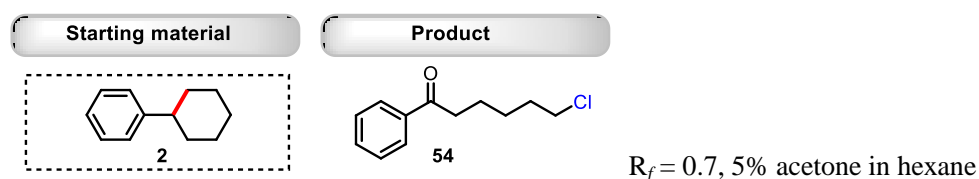


Scheme S20. Deconstructive oxygenation and chlorination of cyclic alkanes by inert $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ cleavage

General conditions F: Stock solution of Ru(bpy)₃Cl₂ (0.02 mmol in 20 mL of HFIP) was used if necessary. Substrate cyclic alkanes (0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M Ru(bpy)₃Cl₂ solution in HFIP and stirred for 5 min at room temperature. BIN₃ **1** (115.6 mg, 0.4 mmol, 2.0 equiv) and LiCl (84 mg, 2.0 mmol, 10.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 24 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air during C(sp³)-C(sp³) bonds cleavage reactions.

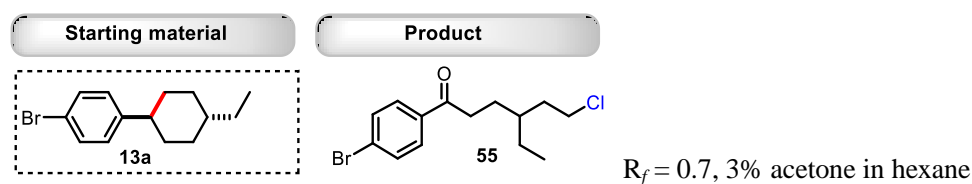


Compound **53** was isolated in 59% yield and deconstructive nitrogenation product **8** was isolated in 18% yield following the general conditions **F**. **¹H NMR** (500 MHz, CDCl₃) δ 7.96 (d, $J = 7.2$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 3.59 (t, $J = 6.2$ Hz, 2H), 3.02 (t, $J = 6.8$ Hz, 2H), 1.96 – 1.82 (m, 4H). **¹³C NMR** (126 MHz, CDCl₃) δ 199.77, 137.01, 133.23, 128.77, 128.16, 44.86, 37.71, 32.20, 21.66. **HRMS** Calcd for C₁₁H₁₄ClO [M+H⁺]: 197.0728; Found: 197.0725.

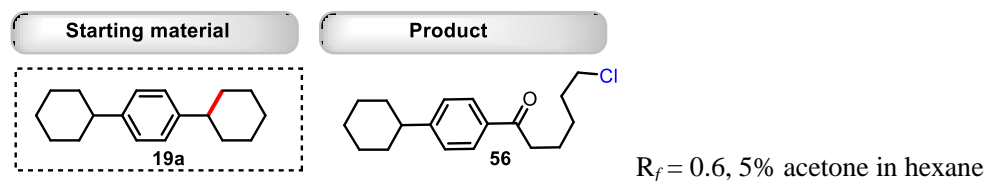


Compound **54** was isolated in 54% yield and deconstructive nitrogenation product **3** was isolated in 20% yield following the general conditions **F**. **¹H NMR** (500 MHz, CDCl₃) δ 7.96 (d, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.7$ Hz, 2H), 3.56 (t, $J = 6.7$ Hz, 2H), 3.00 (t, $J = 7.3$ Hz, 2H), 1.88 – 1.73 (m, 4H), 1.56 – 1.50 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 200.19, 137.12, 133.15, 128.74, 128.16, 45.01, 38.46, 32.62, 26.76, 23.61. **HRMS** Calcd for C₁₂H₁₆ClO [M+H⁺]: 211.0884; Found:

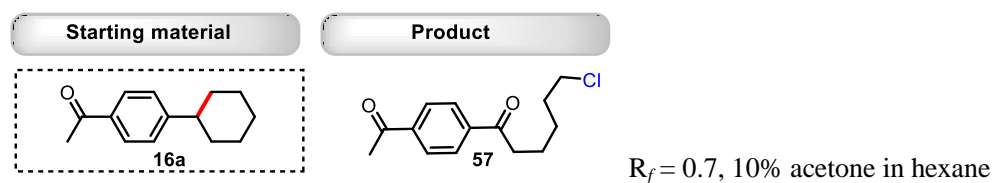
211.0880.



Compound **55** was isolated in 57% yield and deconstructive nitrogenation product **13** was isolated in 33% yield following the general conditions **F**. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.82 (d, $J = 8.6$ Hz, 2H), 7.61 (d, $J = 8.6$ Hz, 2H), 3.58 (t, $J = 7.1$ Hz, 2H), 2.98 – 2.86 (m, 2H), 1.83 – 1.68 (m, 5H), 1.62 – 1.59 (m, 1H), 1.41 – 1.35 (m, 2H), 0.90 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 199.29, 135.80, 132.07, 129.70, 128.30, 43.22, 36.39, 36.32, 35.92, 27.03, 25.52, 10.63. **HRMS** Calcd for $\text{C}_{14}\text{H}_{19}\text{BrClO}$ [$\text{M}+\text{H}^+$]: 317.0302; Found: 317.0299.

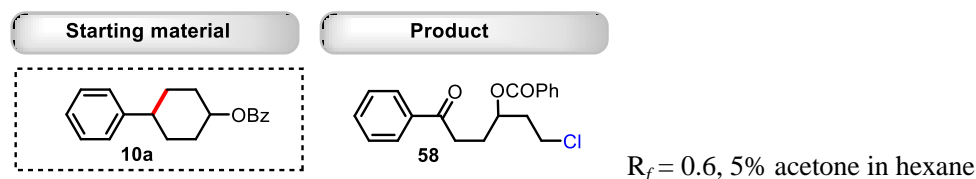


Compound **56** was isolated in 57% yield and deconstructive nitrogenation product **19** was isolated in 14% yield following the general conditions **F**. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.97 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 3.56 (t, $J = 6.6$ Hz, 2H), 2.99 (t, $J = 7.3$ Hz, 2H), 2.05 – 1.97 (m, 2H), 1.89 – 1.63 (m, 12H), 1.56 – 1.49 (m, 2H), 1.36 – 1.29 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 199.61, 149.70, 136.24, 128.60, 125.93, 66.63, 45.01, 38.50, 35.96, 32.62, 26.76, 25.24, 23.59, 22.42. **HRMS** Calcd for $\text{C}_{18}\text{H}_{24}\text{ClO}$ [$\text{M}-\text{H}^+$]: 291.1521; Found: 291.1518.



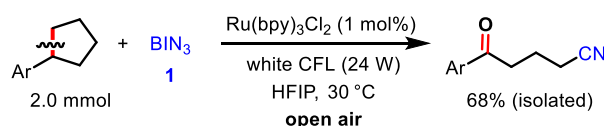
Compound **57** was isolated in 72% yield and deconstructive nitrogenation product **16**

was isolated in 16% yield following the general conditions **F**. **¹H NMR** (500 MHz, CDCl₃) δ 8.02 (m, 4H), 3.55 (t, *J* = 6.6 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.64 (s, 3H), 1.88 – 1.75 (m, 4H), 1.58 – 1.51 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 199.52, 197.56, 140.26, 140.25, 128.64, 128.32, 44.91, 38.84, 32.55, 26.99, 26.66, 23.42. **HRMS** Calcd for C₁₄H₁₈ClO₂ [M+H⁺]: 253.0990; Found: 253.0986.



Compound **58** was isolated in 65% yield and deconstructive nitrogenation product **10** was isolated in 19% yield following the general conditions **F**. **¹H NMR** (500 MHz, CDCl₃) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.40 (m, 4H), 5.49 – 5.37 (m, 1H), 3.67 – 3.58 (m, 2H), 3.15 – 3.05 (m, 2H), 2.34 – 2.17 (m, 4H). **¹³C NMR** (126 MHz, CDCl₃) δ 199.04, 166.29, 136.84, 133.31, 133.28, 130.10, 129.80, 128.74, 128.59, 128.16, 71.91, 40.81, 37.87, 34.55, 28.85. **HRMS** Calcd for C₁₉H₁₉ClNaO₃ [M+Na⁺]: 353.0915; Found: 353.0912.

10. Gram-scale deconstructive nitrogenation of cyclopentylbenzene via selective C(sp³)-C(sp³) bond cleavage



Scheme S21. Gram-scale deconstructive nitrogenation of cyclopentylbenzene via selective C(sp³)-C(sp³) bond cleavage

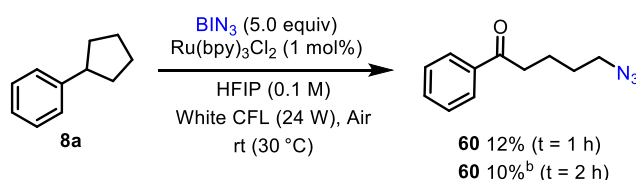
Substrate cyclopentylbenzene (292.0 mg, 2.0 mmol, 1.0 equiv) and Ru(bpy)₃Cl₂ (12.8 mg, 0.02 mmol, 1.0 mol%) were first dispersed in 20.0 mL HFIP and stirred for 5 min

S50

at rt. BIN₃ **1** (2.89 g, 10.0 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature under the compact fluorescent light (24 W) irradiation for 24 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography (eluted with hexane/acetone (v/v 15:1)) to give the desired product **8** in the isolated yield of 68%. It is worth noting that the reaction mixture always opened to air during C(sp³)-C(sp³) bonds cleavage reactions.

11. Mechanistic studies

11.1 The reaction of trapping intermediate **60**

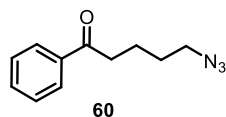


Scheme S22. The reaction of trapping intermediate **60**

Stock solution of Ru(bpy)₃Cl₂ (0.02 mmol in 20 mL of HFIP) was used if necessary. Substrate cyclopentylbenzene (29.2 mg, 0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M Ru(bpy)₃Cl₂ solution in HFIP and stirred for 5 min at rt. BIN₃ **1** (289.0 mg, 1.0 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature under the compact fluorescent light (24 W) irradiation for 1 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography (eluted with hexane/acetone (v/v 15:1)) to give the intermediate **60** in the isolated yield of 12%.

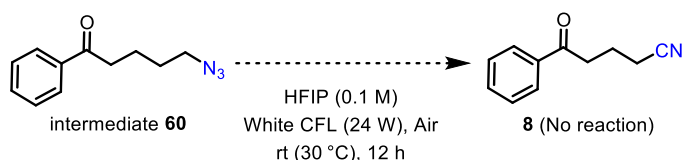
Substrate cyclopentylbenzene (29.2 mg, 0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M Ru(bpy)₃Cl₂ solution in HFIP and stirred for 5 min at rt. BIN₃ **1** (289.0 mg, 1.0 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature under the compact fluorescent light (24 W)

irradiation for 2 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography (eluted with hexane/acetone (v/v 15:1)) to give the intermediate **60** in the isolated yield of 10%.



^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.3$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 3.33 (t, $J = 6.7$ Hz, 2H), 3.02 (t, $J = 7.1$ Hz, 2H), 1.92 – 1.77 (m, 2H), 1.76 – 1.62 (m, 2H) ¹⁶.

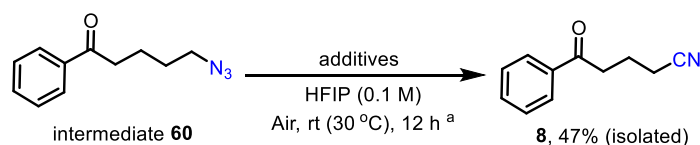
11.2 The reaction of intermediate **60** without BIN_3



Scheme S23. The reaction of intermediate **60** without BIN_3

Substrate cyclopentylbenzene (29.2 mg, 0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL HFIP and stirred for 5 min at rt. The reaction mixture vigorously stirred at air and room temperature under the compact fluorescent light (24W) irradiation for 12 h. Product compound **8** is not observed.

11.3 The reaction of intermediate **60** with BIN_3



| Entry | Reagent (equiv), light sources, | 8 % | RSM% |
|-------|--|------------|------|
| 1 | BIN_3 (5), $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (0.01), white CFL (24 W) | 47 | 45 |
| 2 | BIN_3 (5), white CFL (24 W) | 40 | 42 |
| 3 | BIN_3 (5), in darkness | 0 | 93 |
| 4 | $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (0.01), white CFL (24 W) | 0 | 95 |

| | | | |
|---|---|---|----|
| 5 | No additives, white CFL (24 W) | 0 | 95 |
| 6 | BIN ₃ (5), white CFL (24 W), TEMPO (5) | 0 | 90 |

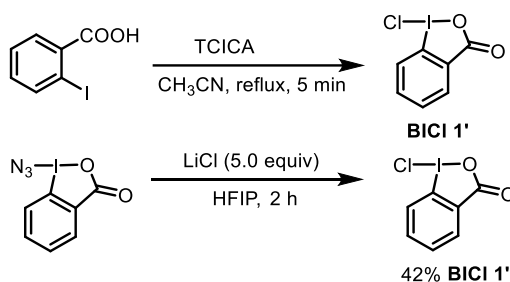
[a] Yields are based on isolated yield of reaction mixture on a 0.2 mmol scale at a 0.1 M concentration unless specified otherwise using ACS grade solvents under an air atmosphere (open reactions). Source of light: 24 W white Compact Fluorescent Lamp (white CFL). RSM is short for recovery of starting material.

Table S3. Control experiments of conversion of the azide into a nitrile

The reaction of intermediate **60 with BIN₃:** Stock solution of Ru(bpy)₃Cl₂ (0.02 mmol in 20 mL of HFIP) was used if necessary. Intermediate **60** (40.6 mg, 0.2 mmol, 1.0 equiv) were first dispersed in 2.0 mL of 0.001 M Ru(bpy)₃Cl₂ solution in HFIP and stirred for 5 min at rt. BIN₃ **1** (289.0 mg, 1.0 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at air and room temperature under the compact fluorescent light (24W) irradiation for 12 h. The solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography (eluted with hexane/acetone (v/v 15:1)) to give the compound **8** in the isolated yield of 47%.

A series of control experiments were performed to reveal the mechanism of conversion of the azide into a nitrile. As shown in Table S3, deconstructive azidation of cyclopentylbenzene product could easily form compound **8** in the yield of 47% (entry 1). The desired product was observed without Ru(bpy)₃Cl₂, indicating Ru(bpy)₃Cl₂ was not necessary, but only promoted the conversion (entry 1 vs entry 2). BIN₃ and visible light irradiation would play a significant role in this conversion (entry 2 vs entry 4 vs entry 5 and entry 2 vs entry 3). Furthermore, the reaction was suppressed by adding radical scavengers BHT (2,6-bis(1,1-dimethylethyl)-4-methylphenol). This reaction indicated that the conversion might be proceeding through a radical intermediate. Plausible mechanism for the conversion of intermediate **60** to nitrile was proposed (Scheme S29 and Scheme S30).

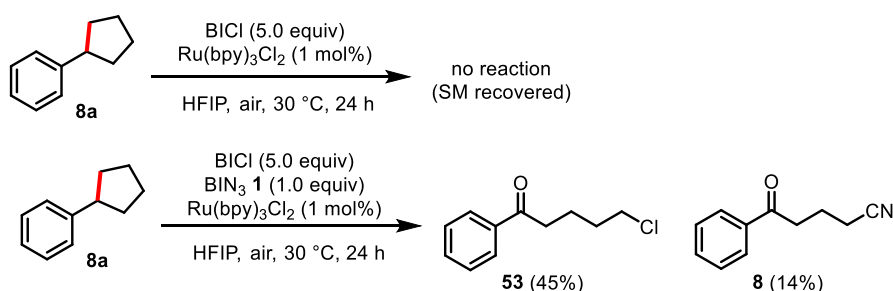
11.4 Deconstructive chlorination of **8a** with chloriodane BICI 1'



Scheme S24. Deconstructive chlorination of **8a** with chloriodane **BICI 1'**

Chloriodane **BICI 1'** is a stable white solid and can be easily synthesized from ortho-iodobenzoic acid in one step following Togni's procedure (Scheme S24)⁴.

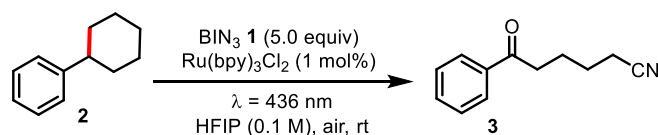
Proof of in situ formation of BICI 1': We observed that chloriodane **BICI 1'** could also be readily formed by mixing **BIN₃ 1** with LiCl at rt (Scheme S24): To a solution of azidoiodane **1** (28.9 mg, 0.1 mmol, 1.0 equiv) in HFIP (0.1 mL) was added LiCl (21 mg, 0.5 mmol, 5.0 equiv) at rt. The reaction mixture was stirred at rt for 2 h in the absence of visible light irradiation. The solvent was removed under reduced pressure. The ¹H NMR analysis of the resulting sample showed that 42% yield of chloriodane **BICI 1'** was formed in HFIP (Scheme S24).



Scheme S25. Control reactions of **8a** with chloriodane **BICI 1'** and **BIN₃ 1**

Control experiments of 8a with azidoiodane 1 and chloriodane 1': experiments were performed under the conditions at a 0.2 mmol scale (Scheme S25). Reactions were analyzed by ¹H-NMR 45% yield of the deconstructive chlorination product **53** and 14% yield of the deconstructive nitrogenation product were isolated under the conditions of using 1 equiv of **BIN₃ 1**.

11.5 Measurement of quantum yield (Φ) for deconstructive nitrogenation of cyclohexylbenzene.



Scheme S26. Measurement of quantum yield (Φ) for deconstructive nitrogenation of cyclohexylbenzene

General information: All the experiments were carried out based on deconstructive nitrogenation of cyclohexylbenzene following Yoon's procedure²⁹. Solutions used were prepared in the dark and reactions were conducted in a 1 cm square quartz cuvette. A Hitachi F-4600 fluorescence spectrophotometer with a 150 W Xe lamp was used as the light source for the quantum yield measurements. A 24 W compact fluorescent light bulb was used for "light/dark" at a distance of 5 cm away from the reaction flask. UV-vis data were measured on a Hitachi U-3900 spectrophotometer.

The quantum yield can be calculated using eq 1:

$$\Phi = \frac{\text{mols of product formed}}{\text{einsteins of light absorbed}} = \frac{\text{mols of starting material} \cdot \text{yield}}{\text{flux} \cdot t \cdot f} \quad (1)$$

Where flux is the photon flux of the spectrophotometer, t is the reaction time and f is the light absorbance of catalyst.

A) Absorbance of catalyst:

The absorbance of Ru(bpy)₃Cl₂ in HFIP was measured at the reaction concentration of 1.0×10^{-3} M. The absorbance at 436 nm for a 1.0×10^{-3} M solution is >3 (**Figure S1**) indicating the fraction of light absorbed is >0.999.

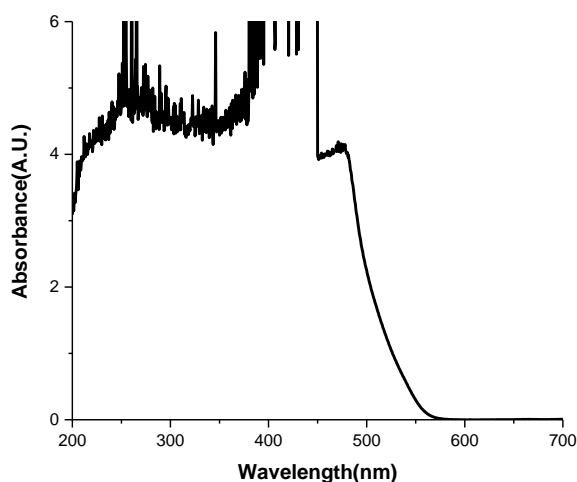
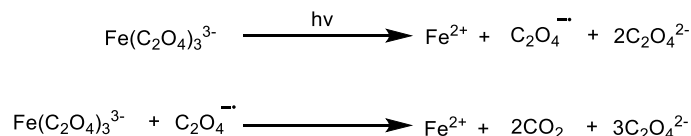


Figure S1. Absorbance of a 1.0×10^{-3} M solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in HFIP.

B) Determination of the light intensity at 436 nm:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4 . A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4 . Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at $\lambda = 436$ nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the resulting solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Under light excitation the potassium ferrioxalate decomposes according to the following equations:



Scheme S27. The reaction of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$

The quantity of ferrous ions formed during an irradiation period is monitored by conversion to the colored tris-phenanthroline complex. The original ferric ions are not appreciably complexed by phenanthroline and the complex does not absorb at 510 nm. The mols of ferrous ions formed in the irradiated volume are given by eq 2.

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \quad (2)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity of phenanthroline complex at 510 nm ($11,100 \text{ L mol}^{-1} \text{ cm}^{-1}$)³⁰. The difference in absorbance at 510 nm between the irradiated and non-irradiated solutions was measured to be 0.328 (average of three experiments). The conversion was calculated using eq 2:

$$\text{mol Fe}^{2+} = \frac{0.00235 \text{ L} \cdot 0.328}{1.000 \text{ cm} \cdot 11,100 \text{ L mol}^{-1} \text{ cm}^{-1}} = 6.94 \times 10^{-8} \text{ mol}$$

The photon flux can be calculated using eq 3.

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} \quad (3)$$

Where mol Fe^{2+} is the mols of Fe^{2+} formed during irradiation ($6.94 \times 10^{-8} \text{ mol}$), Φ_{Fe} is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at $\lambda = 436 \text{ nm}$), t is the time (90.0 s), and f_{Fe} is the fraction of light absorbed of the ferrioxalate solution at $\lambda = 436 \text{ nm}$.

The fraction of light absorbed (f_{Fe}) by this solution was calculated using eq 4, where A is the measured absorbance at 436 nm.

$$f_{Fe} = 1 - 10^{-A} \quad (4)$$

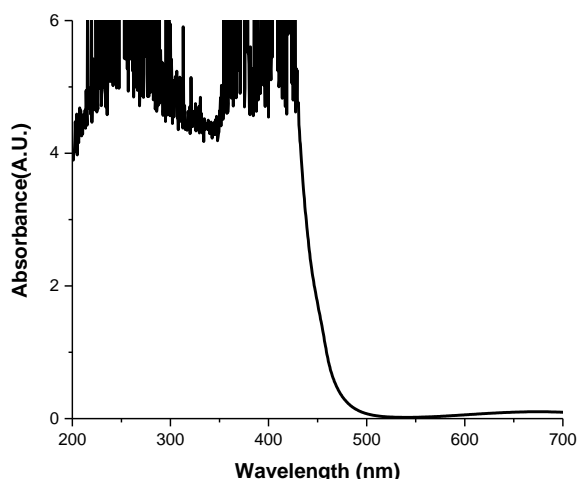


Figure S2. Absorbance of the ferrioxalate actinometer solution

The absorbance of the above ferrioxalate solution at 436 nm was measured to be 3.389 (average of three experiments). The light absorbed (f_{Fe}) was calculated using eq 4:

$$f = 1 - 10^{-3.389} = 0.99959$$

The photon flux was calculated using eq 3:

$$\text{photon flux} = \frac{6.94 \times 10^{-8} \text{ mol}}{1.01 \cdot 90.0 \text{ s} \cdot 0.99959} = 7.63 \times 10^{-10} \text{ einstein s}^{-1}$$

C) Determination of quantum yield:

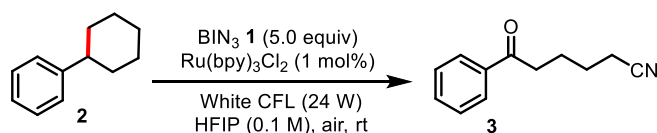
A clear vial was charged with **2** (1.0 mmol, 1.0 equiv), azidoiodinane **1** (5.0 mmol, 5.0 equiv), Ru(bpy)₃Cl₂ (0.01 mmol, 1 mol%), and HFIP (0.1 M). The resulting mixture open air. The reaction mixture was irradiated ($\lambda = 436 \text{ nm}$, slit width= 10.0 nm) for 32400 s (9 h). After irradiation, the solvent of the reaction mixture was removed under

reduced pressure. The yield of **3** was determined by ^1H NMR based on a $\text{Cl}_2\text{CHCHCl}_2$ standard to be 46%. The quantum yield was calculated using eq 1:

$$\Phi = \frac{1.0 \times 10^{-3} \text{ mol} \cdot 46\%}{7.63 \times 10^{-10} \text{ einstein s}^{-1} \cdot 32400 \text{ s} \cdot 1.00} \approx 19$$

The quantum yield was calculated to be Φ (46%) = 19, indicating that 19 equivalents of product are formed for every photon absorbed by the photocatalyst.

11.6 Light/dark experiment of deconstructive nitrogenation of cyclohexylbenzene



Scheme S28. Light/dark experiment of deconstructive nitrogenation of cyclohexylbenzene

Six vials were equipped with a stir bar and charged with **2** (0.2 mmol, 1.0 equiv) and 2.0 mL of the 0.001 M $\text{Ru}(\text{bpy})_3\text{Cl}_2$ solvent HFIP. Azidoiodinane **1** (1.0 mmol, 5.0 equiv) was then added and the reaction was stirred under air atmosphere. The reactions were alternatively irradiated with a 24 W white CFL bulb and kept in the dark in 3 h intervals. After each interval, one vial was taken out, the solvent was removed under reduced pressure, and the yield was determined by ^1H NMR based on a $\text{Cl}_2\text{CHCHCl}_2$ as an internal standard.

| Vial | Time (h)/conditions | | | | | | Yield (%) ^a |
|------|---------------------|----------|--------|-----------|----------|------------|------------------------|
| 1 | 0-3/hv | | | | | | 28 |
| 2 | 0-3/hv | 3-6/dark | | | | | 28 |
| 3 | 0-3/hv | 3-6/dark | 6-9/hv | | | | 37 |
| 4 | 0-3/hv | 3-6/dark | 6-9/hv | 9-12/dark | | | 37 |
| 5 | 0-3/hv | 3-6/dark | 6-9/hv | 9-12/dark | 12-15/hv | | 43 |
| 6 | 0-3/hv | 3-6/dark | 6-9/hv | 9-12/dark | 12-15/hv | 15-18/dark | 43 |

a) NMR yield, average of three experiments.

Table S4. Yields of Light/Dark experiment

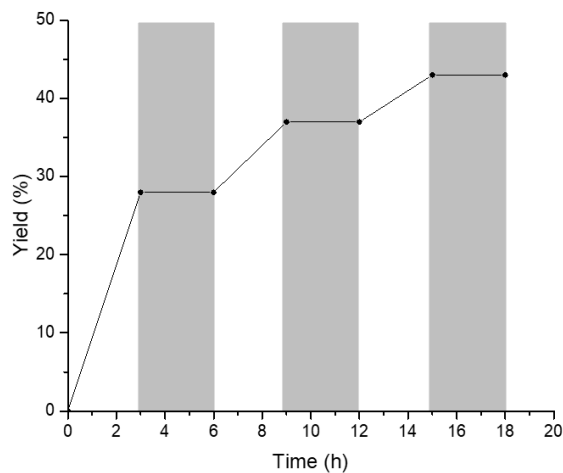
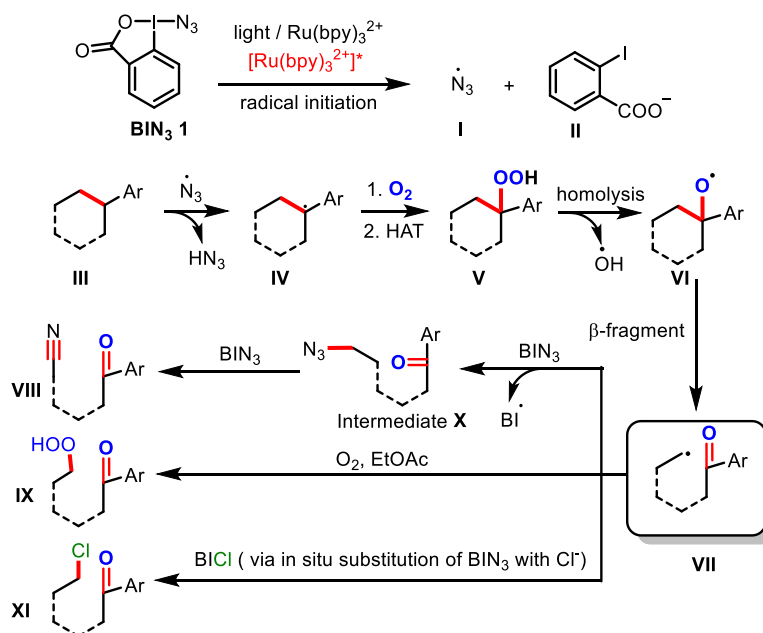
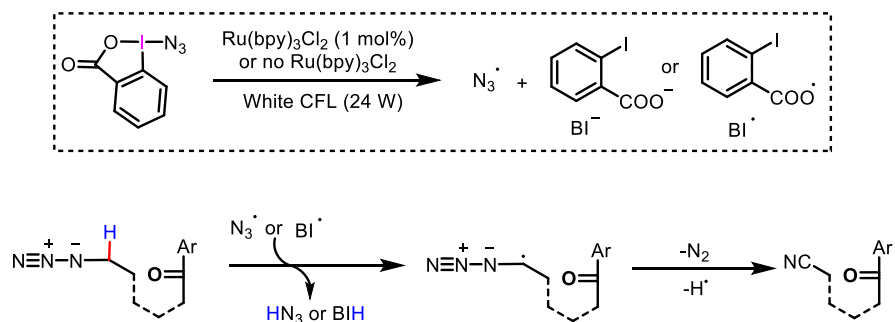


Figure S3. Light/dark experiment of deconstructive nitrogeneration of cyclohexylbenzene

11.7 Plausible mechanism for deconstructive nitrogeneration, peroxidation and chlorination of alkanes by selective C(sp³)-C(sp³) bond cleavage

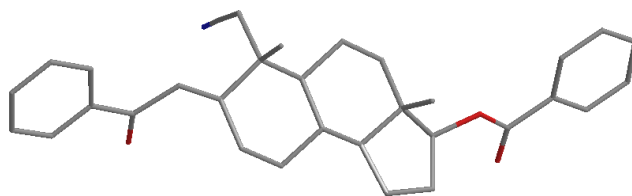


Scheme S29. Plausible mechanism for deconstructive functionalization of alkanes



Scheme S30. Plausible mechanism for the conversion of intermediate **60** to deconstructive nitrogenation

12. X-ray crystallographic data for compound **34**



Scheme S31. X-ray structure of compound **34**

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **34** in a mixture of acetone and hexane at room temperature. The X-ray data of compound **34** is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 1977526.

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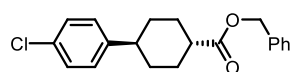
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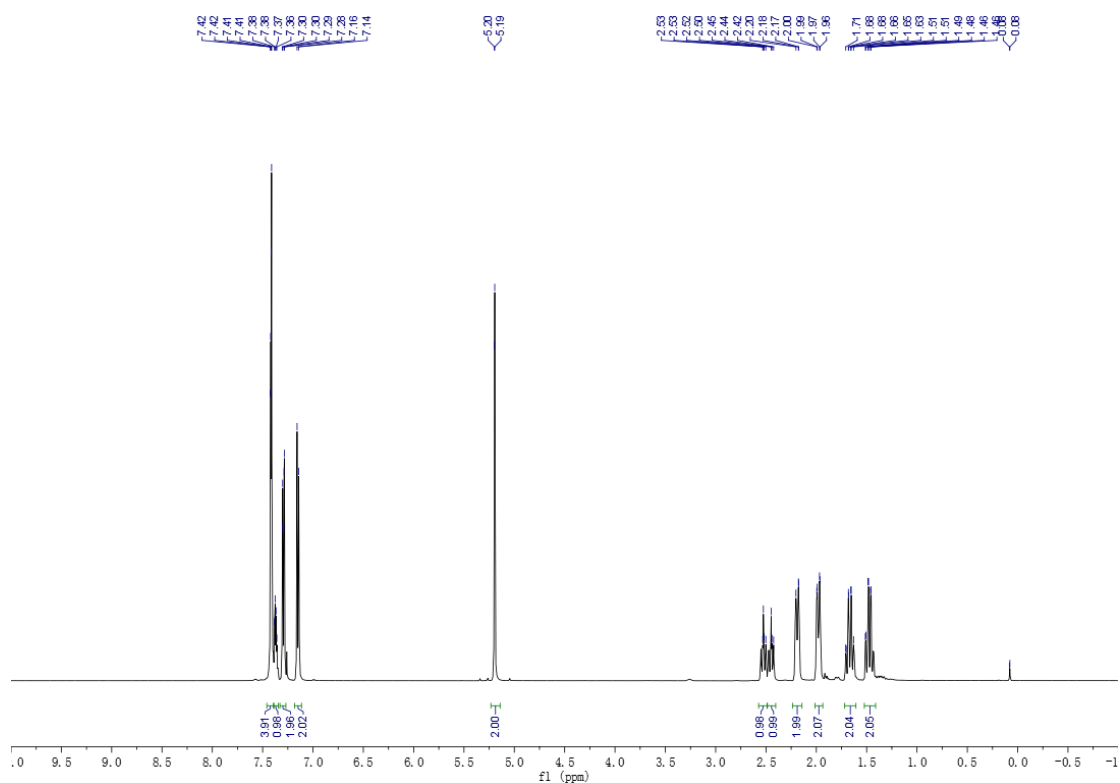
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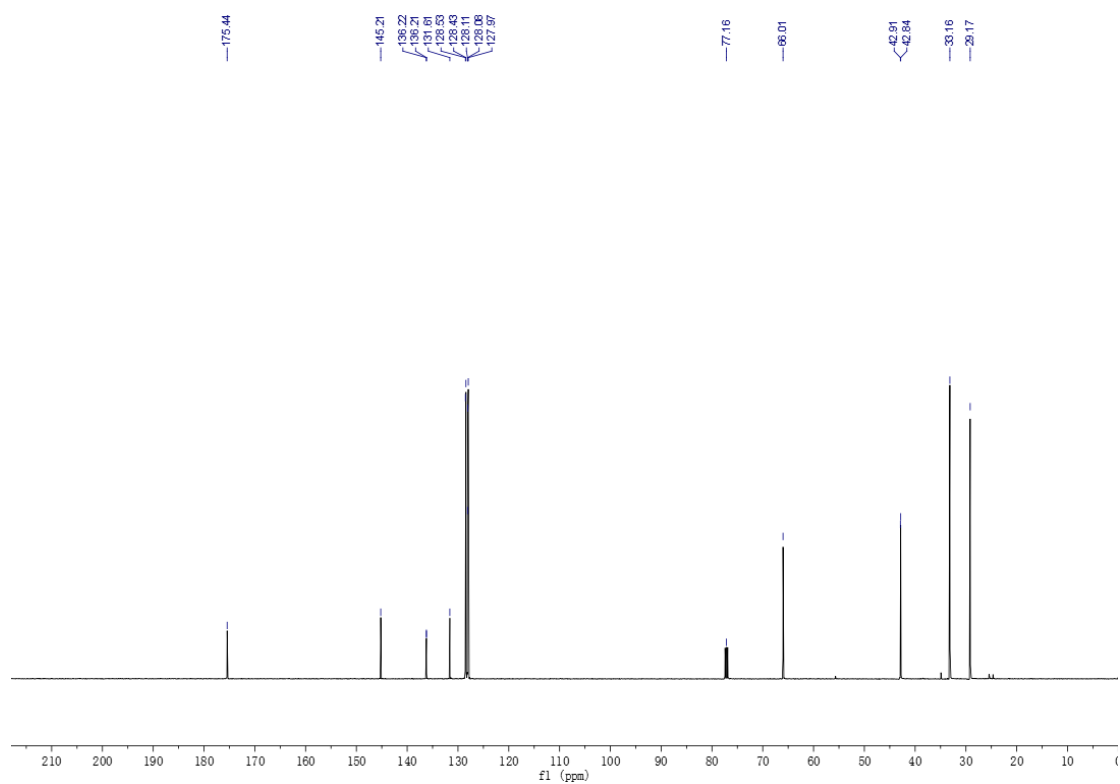
14. ^1H -NMR and ^{13}C -NMR spectra



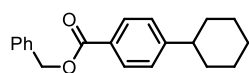
11a



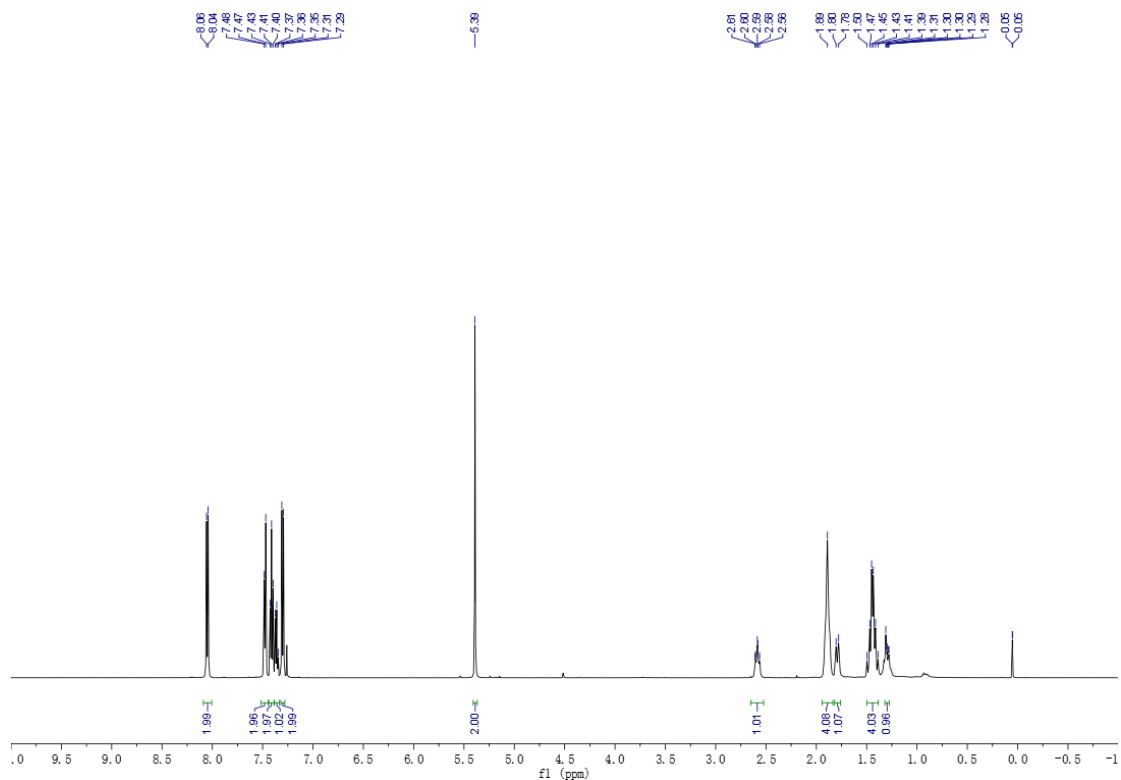
^1H NMR of compound **11a**



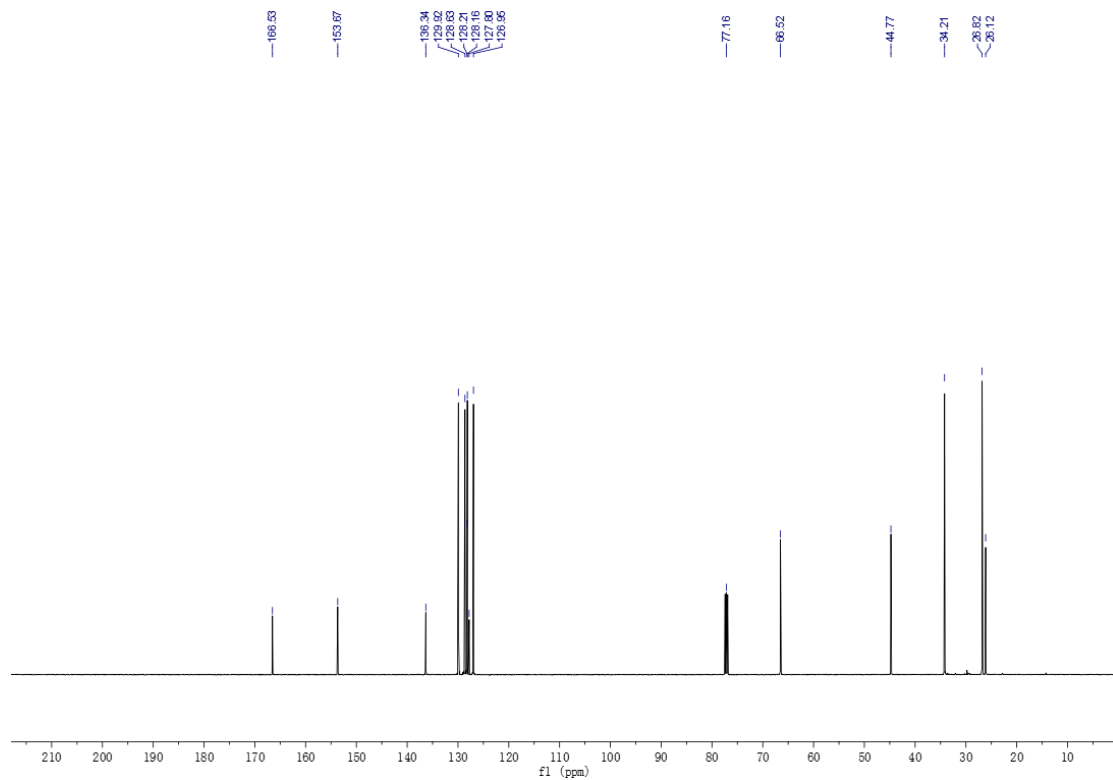
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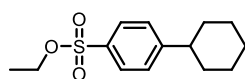
17a



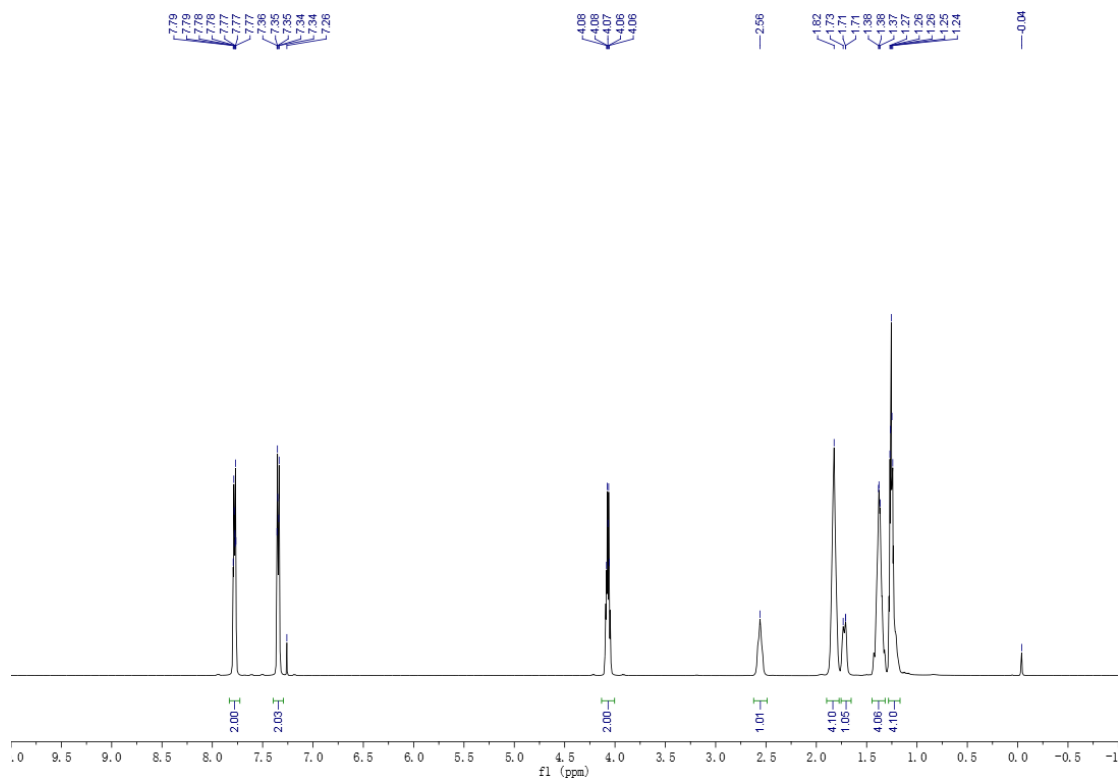
¹H NMR of compound **17a**



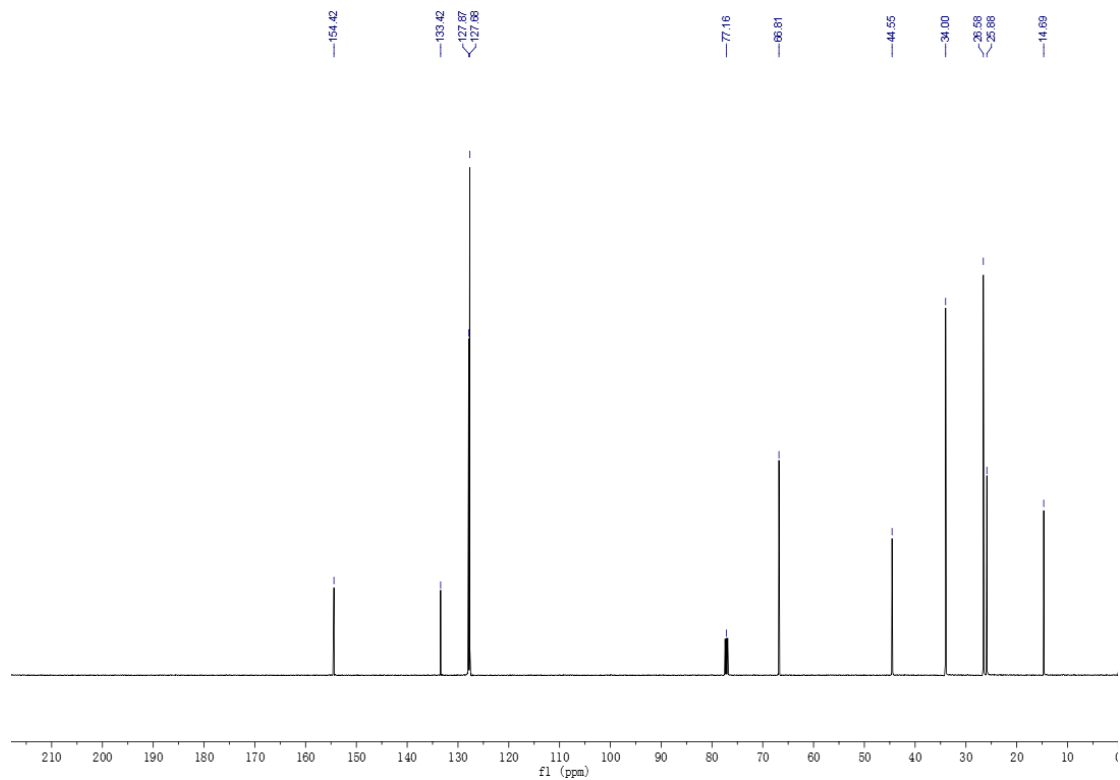
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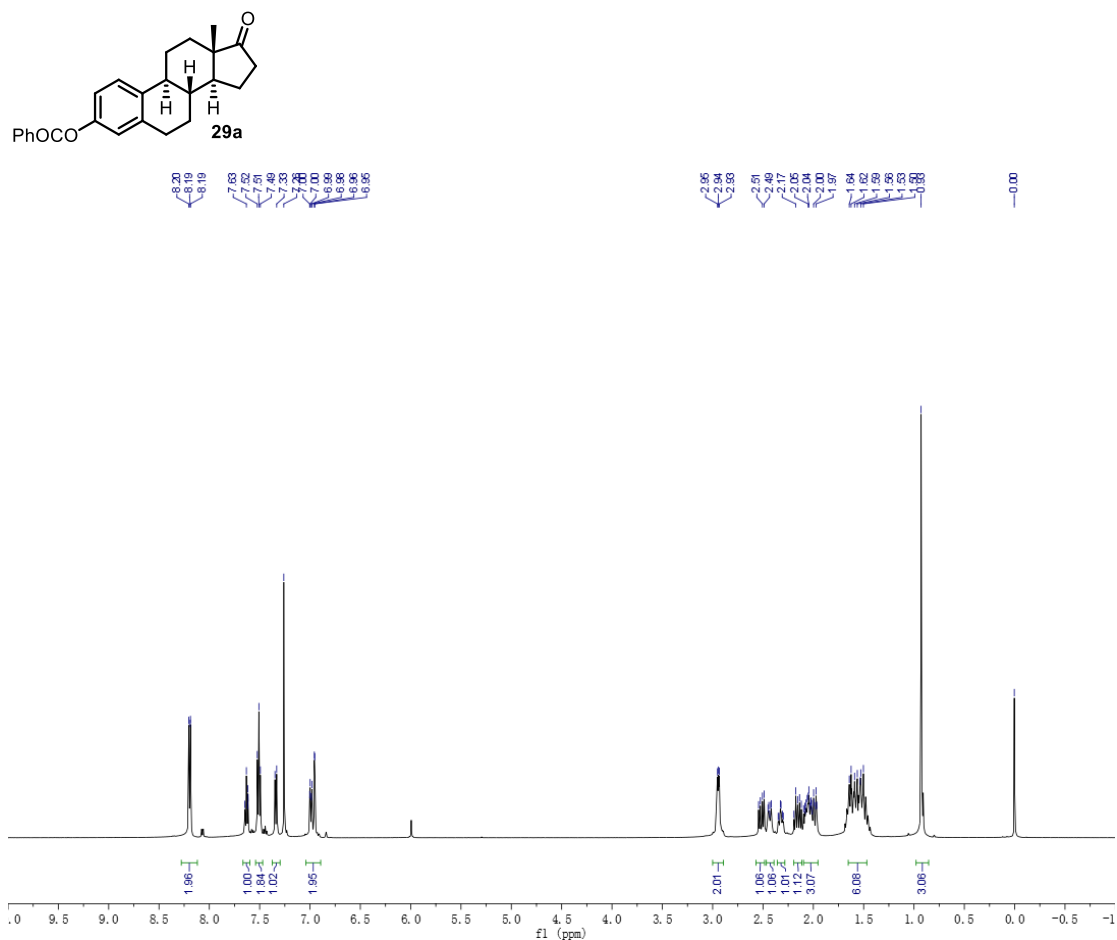
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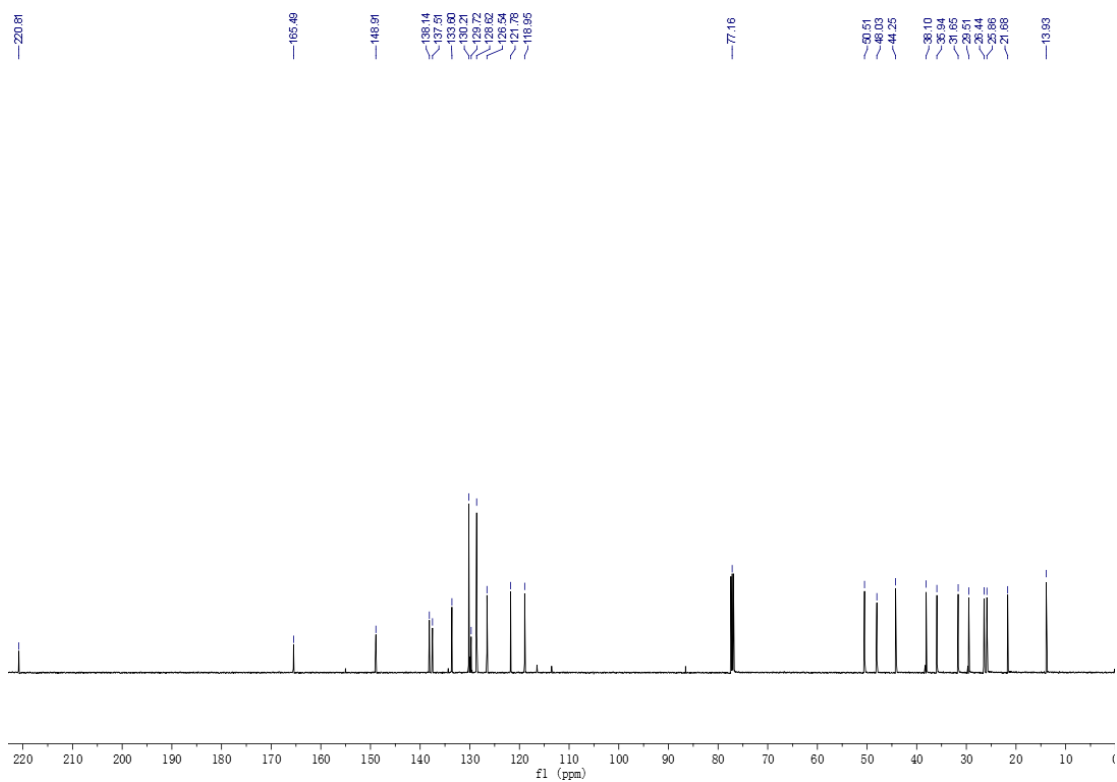
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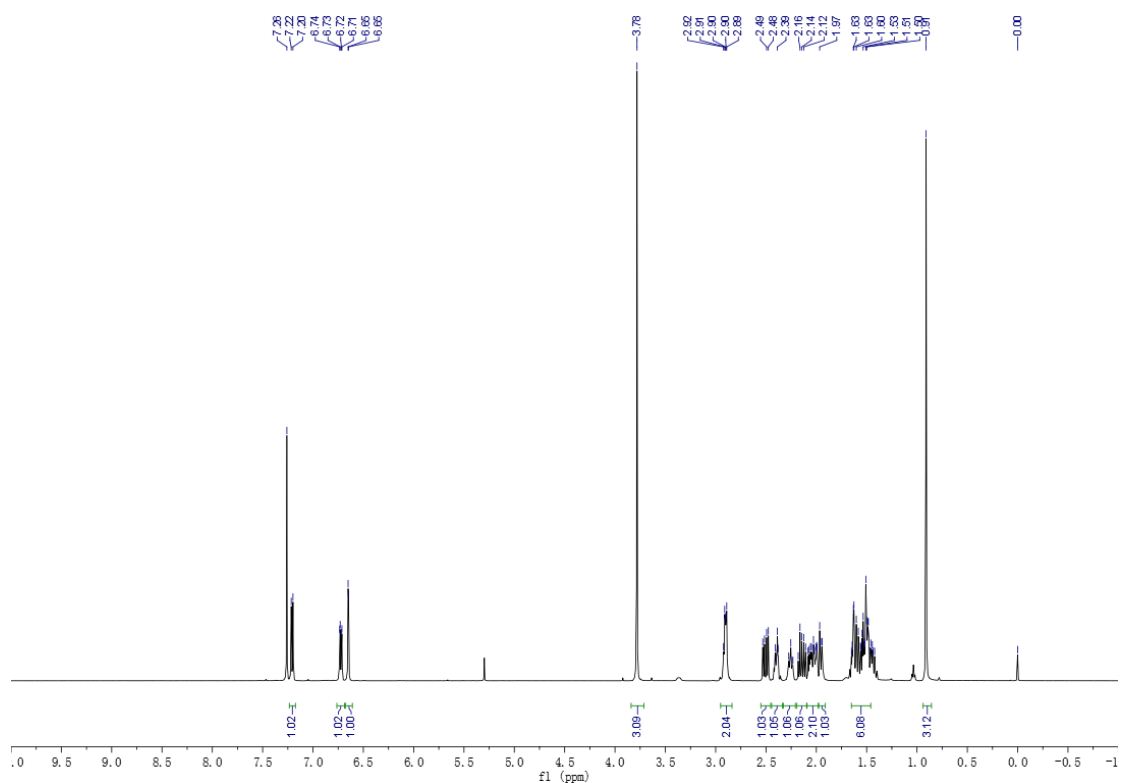
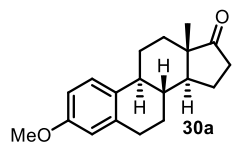
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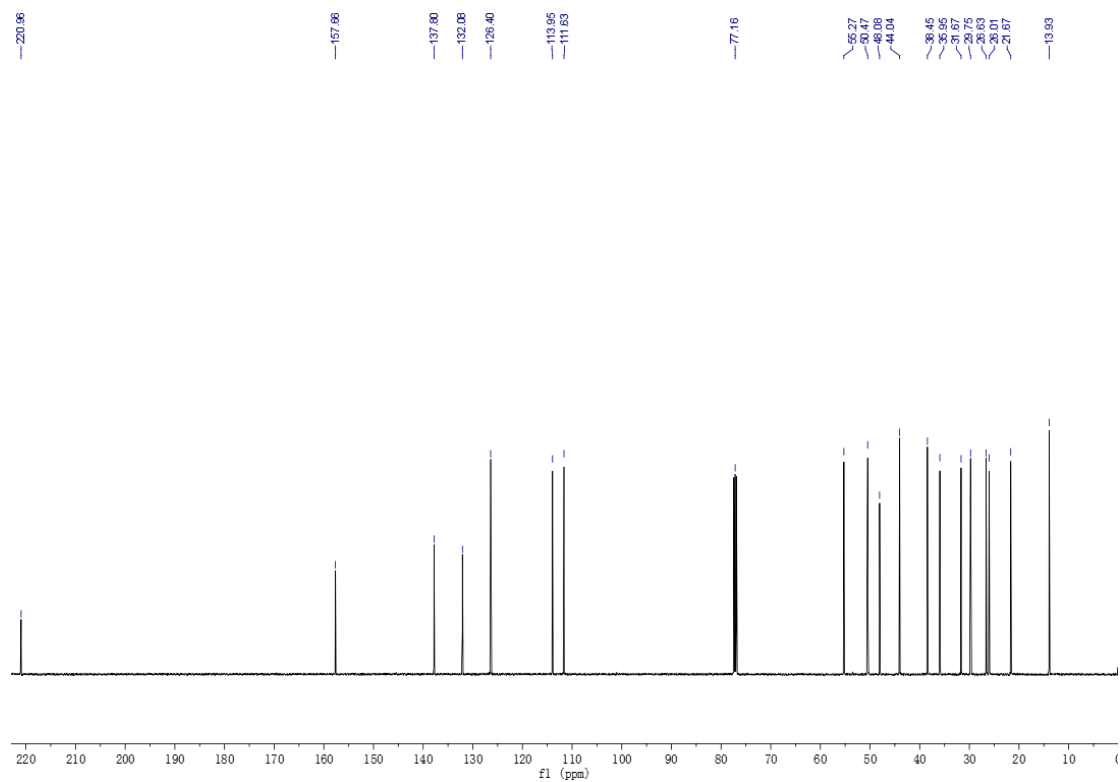
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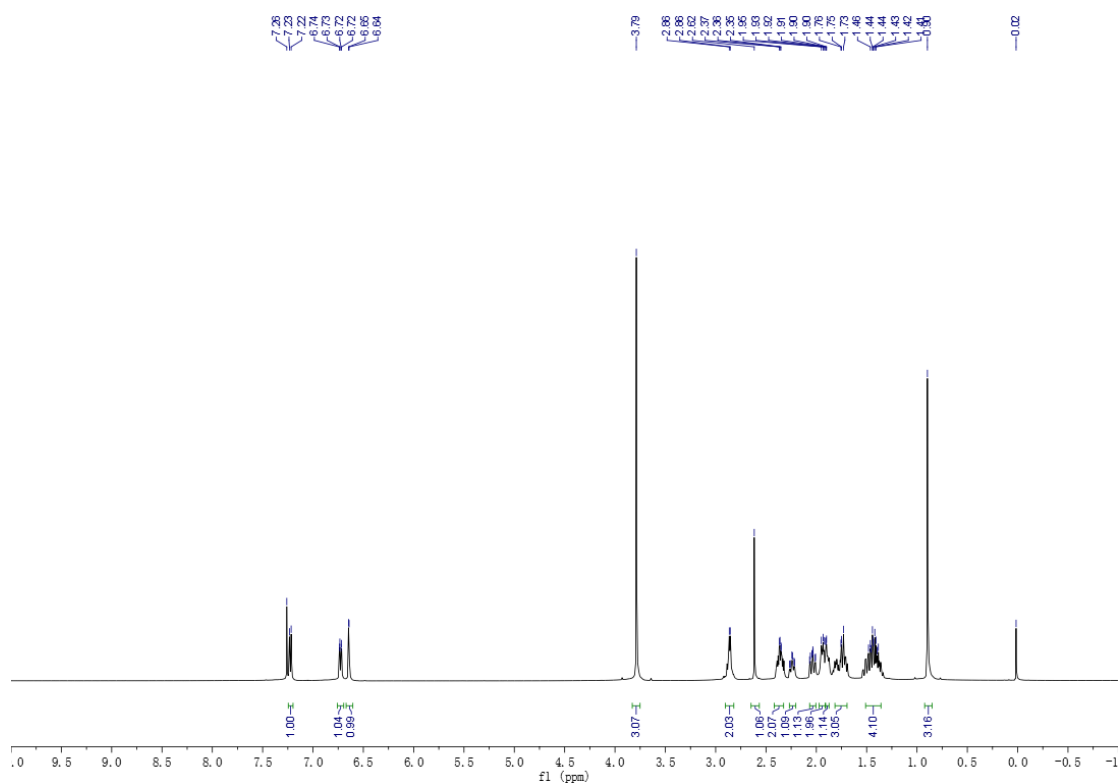
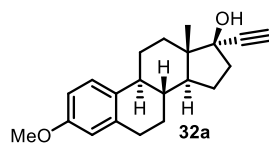
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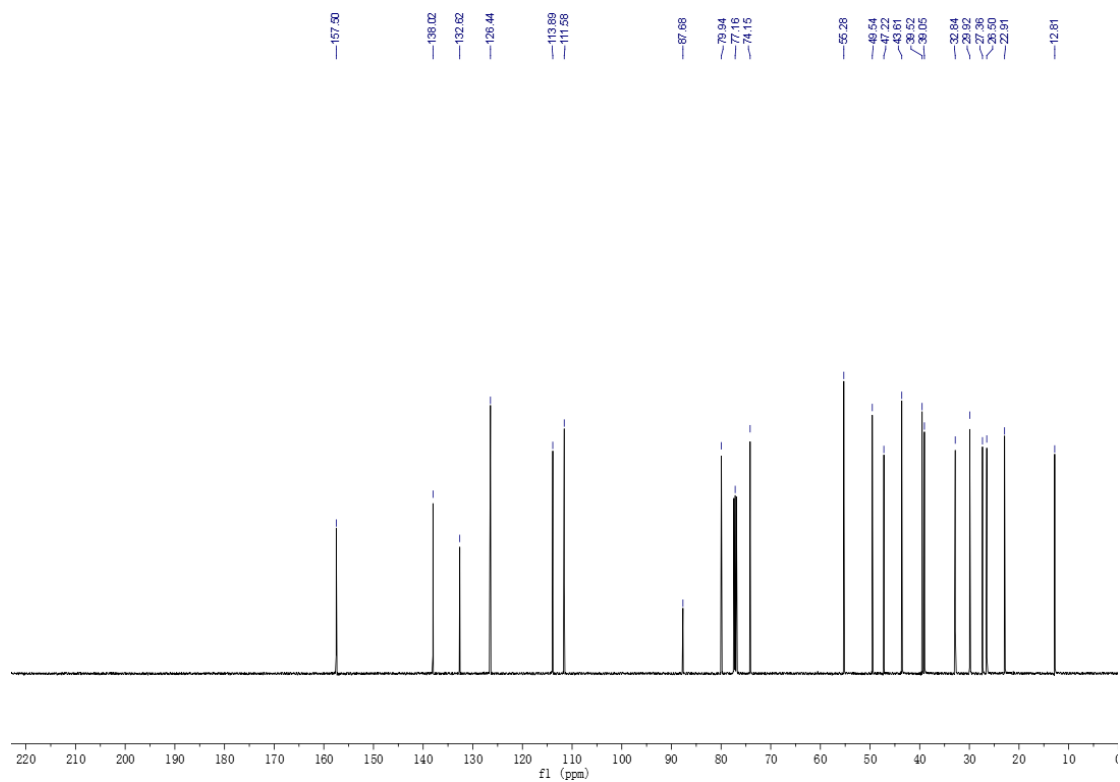
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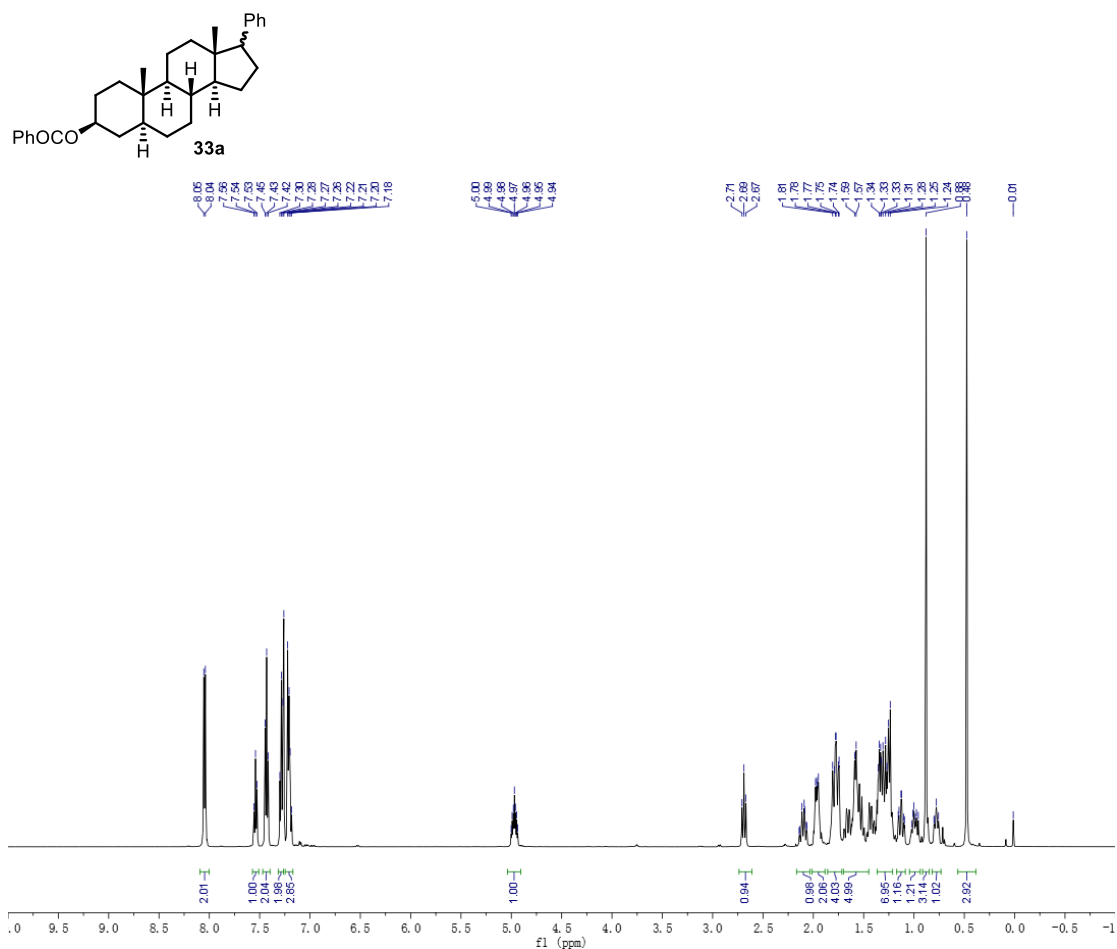
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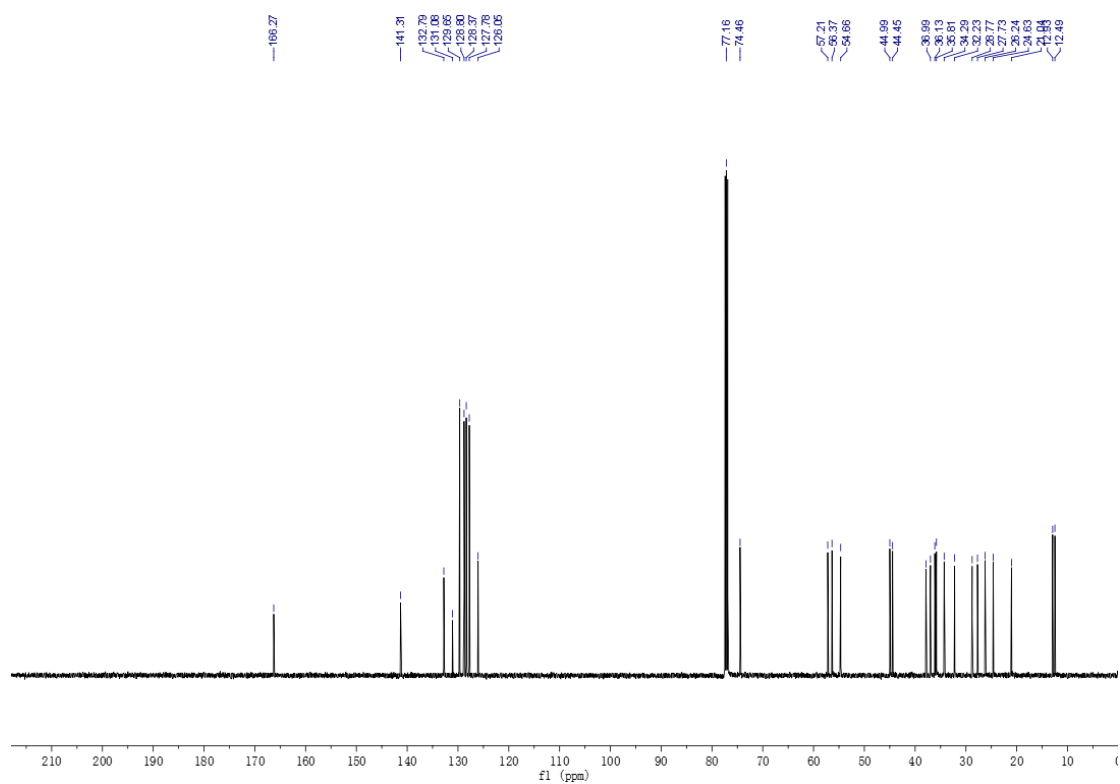
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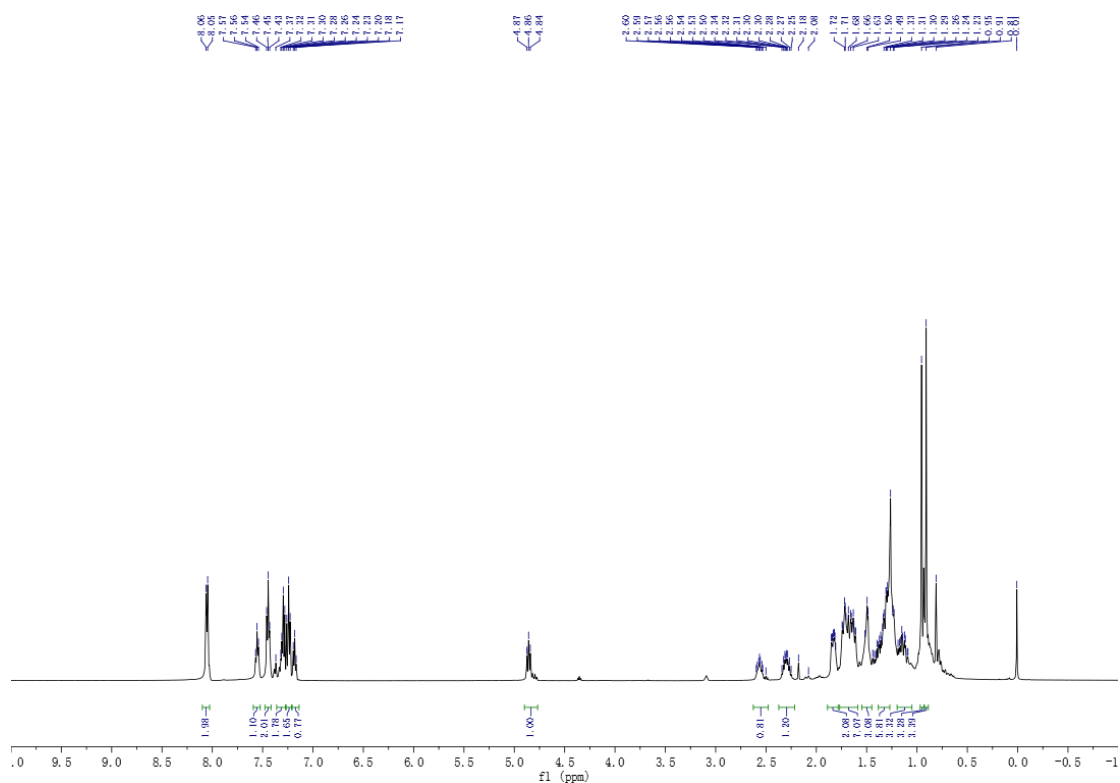
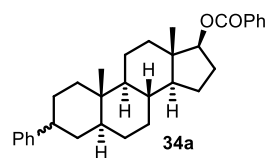
¹³C NMR of compound **32a**



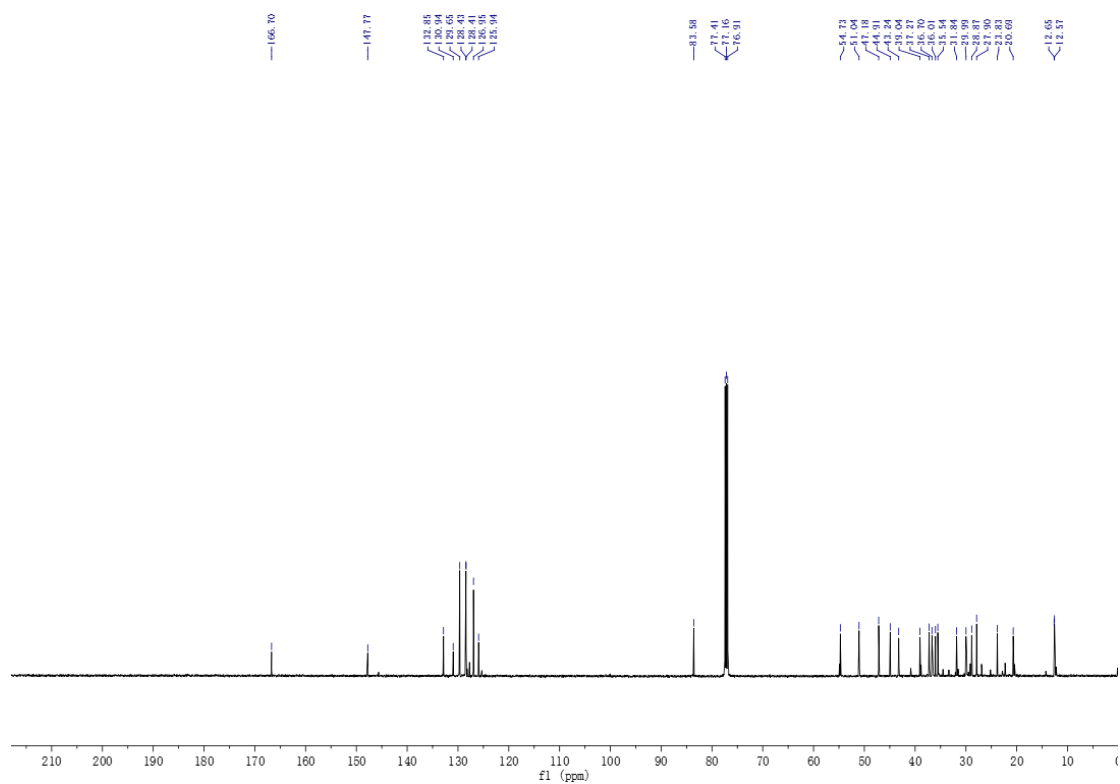
^1H NMR of compound **33a**



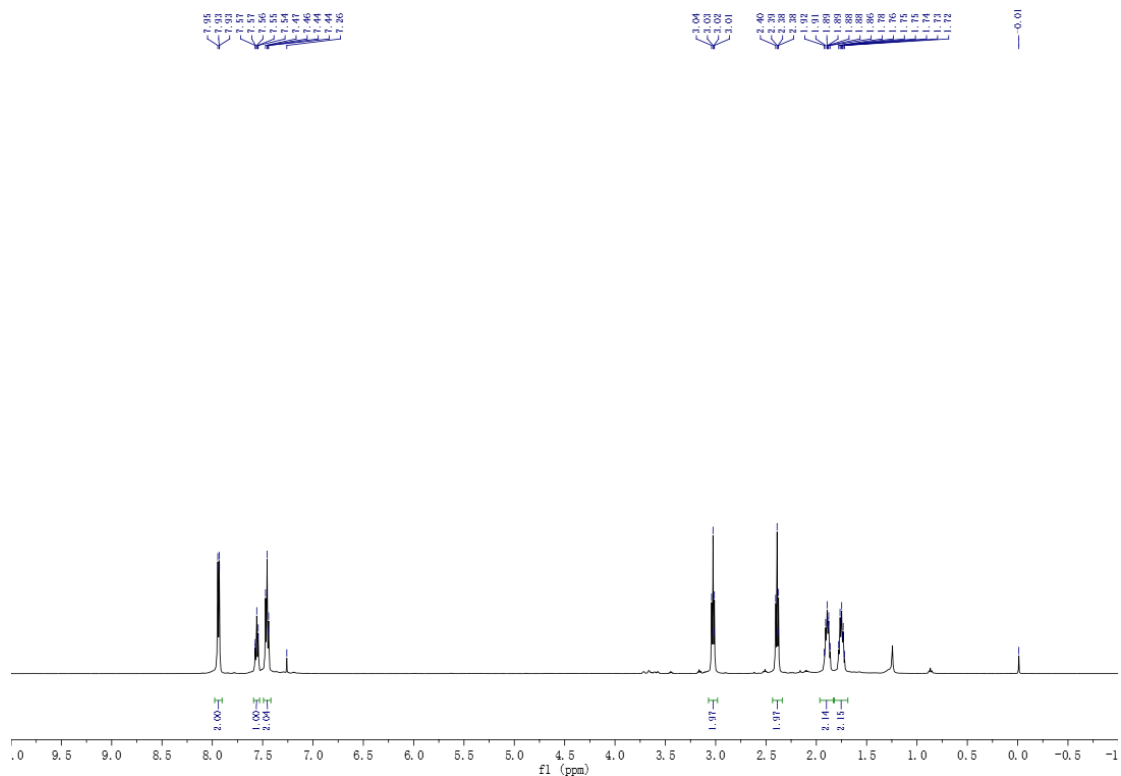
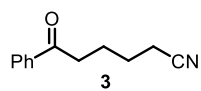
^{13}C NMR of compound **33a**



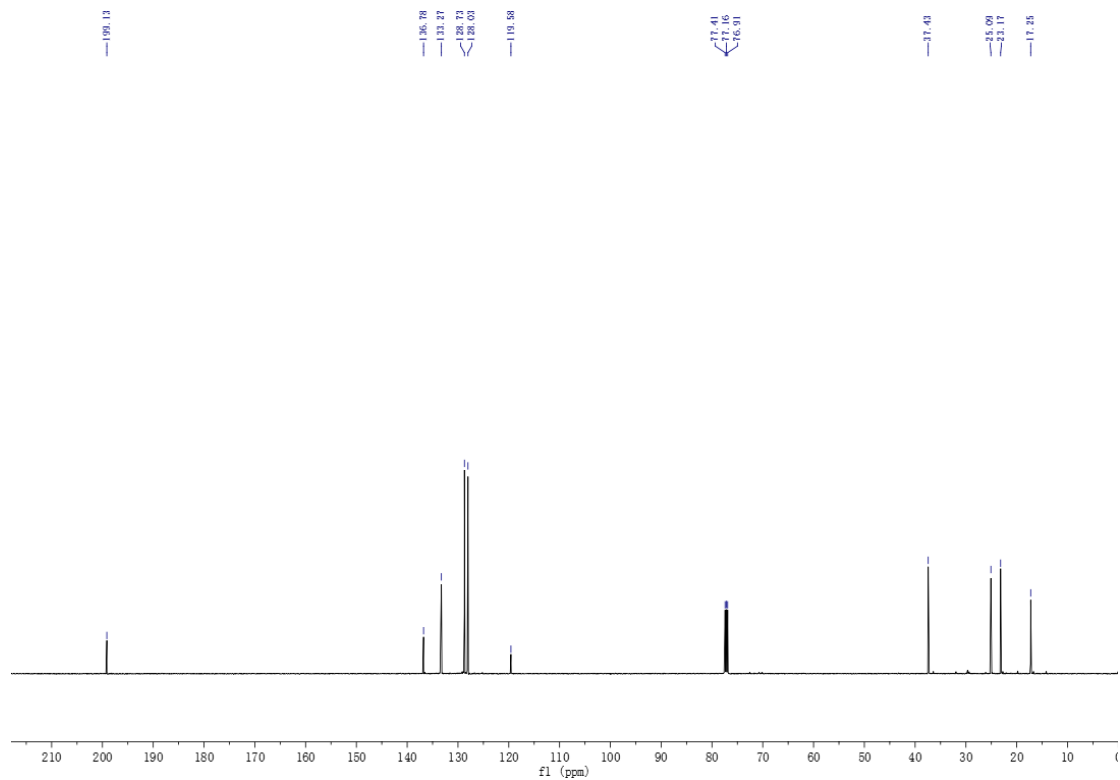
¹H NMR of compound **34a**



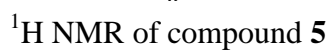
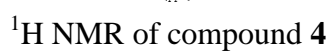
¹³C NMR of compound **34a**

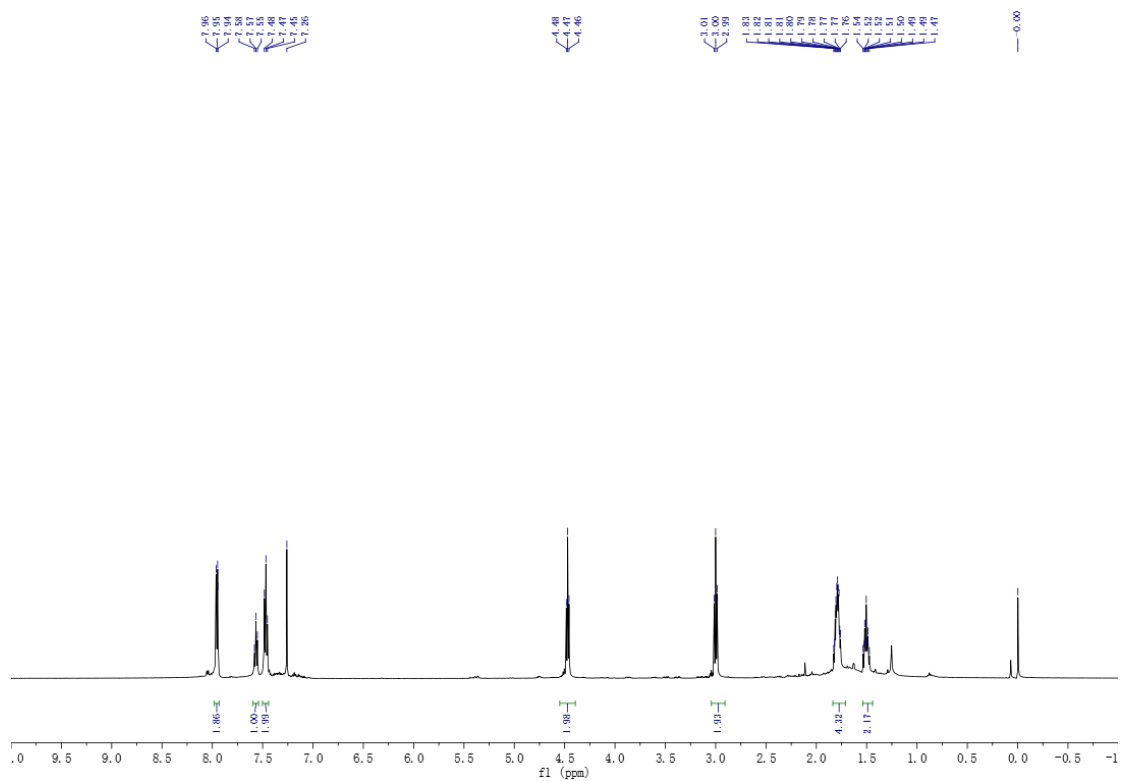
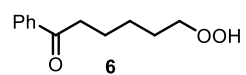


¹H NMR of compound **3**

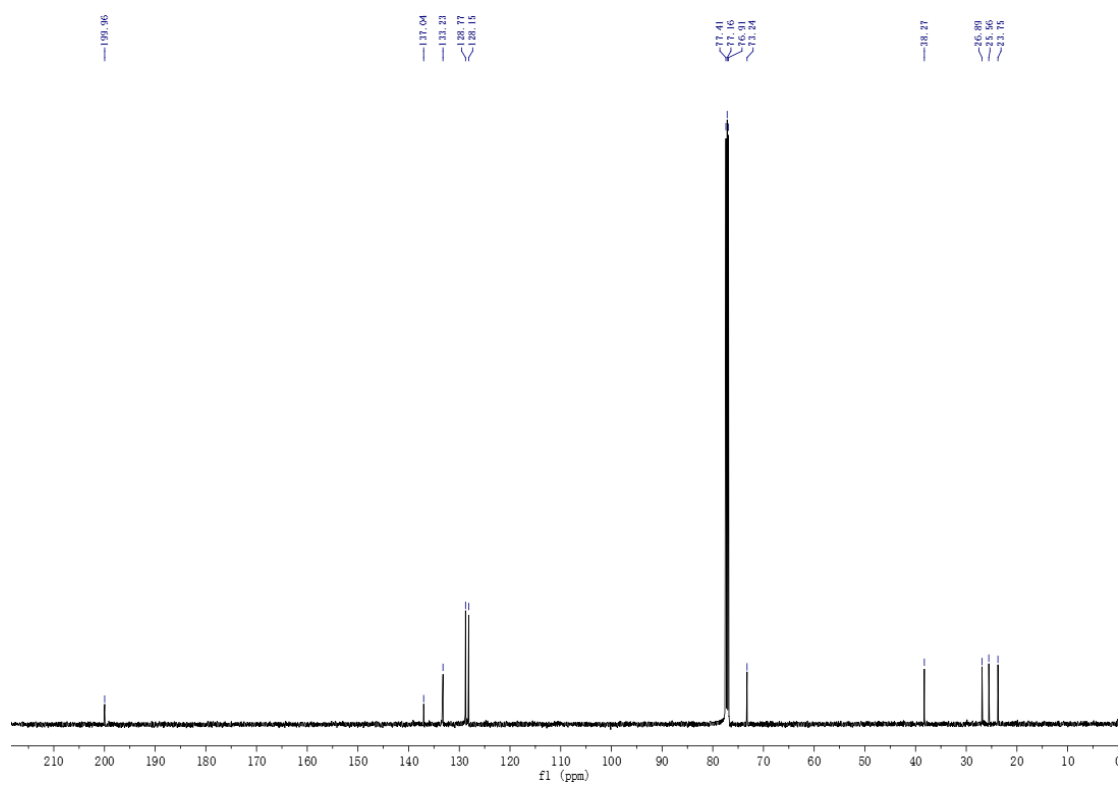


¹³C NMR of compound **3**

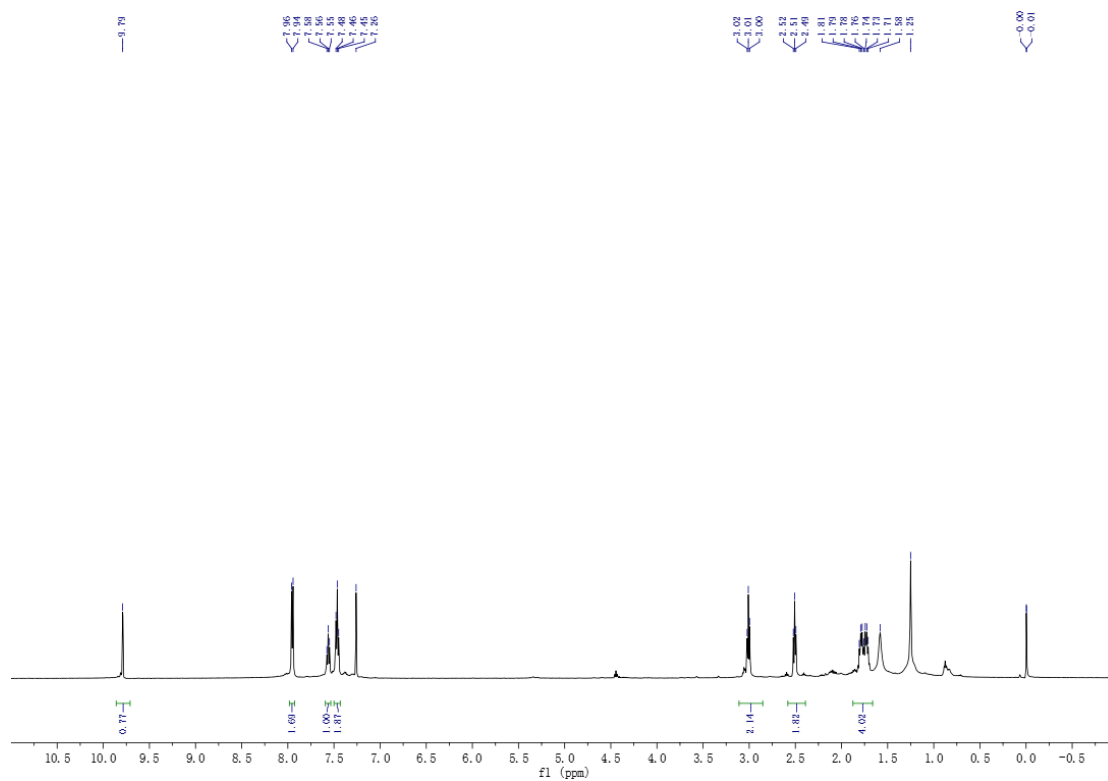
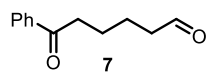




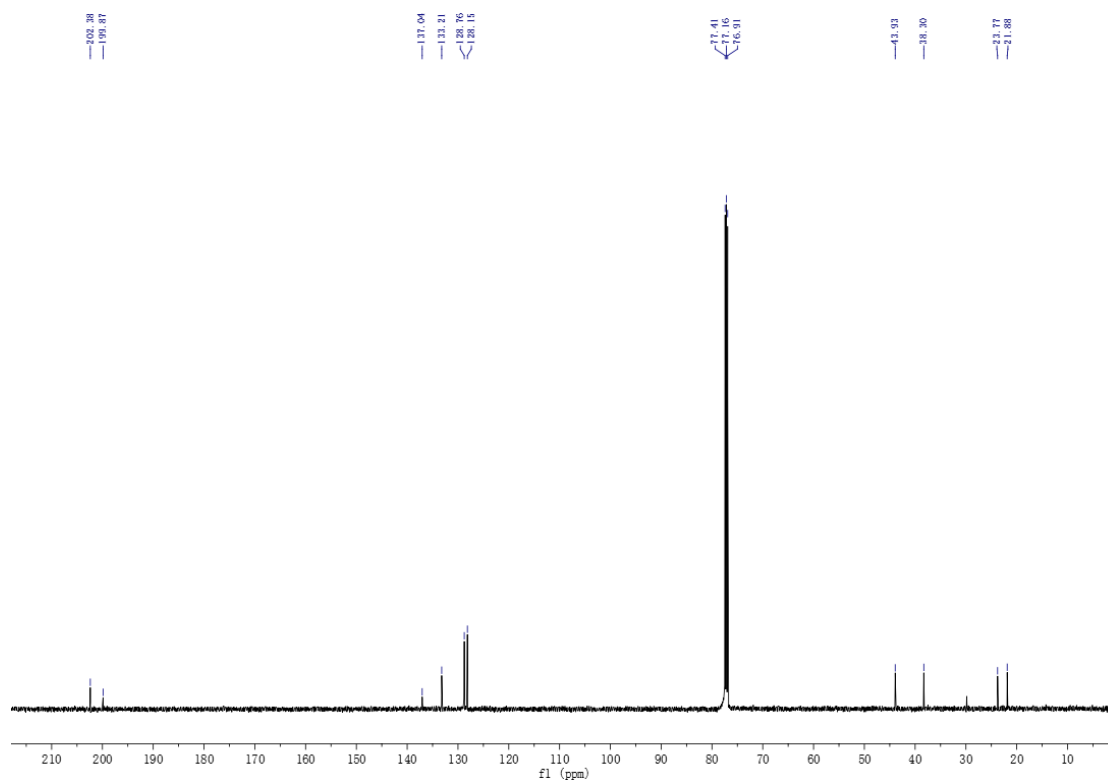
¹H NMR of compound **6**



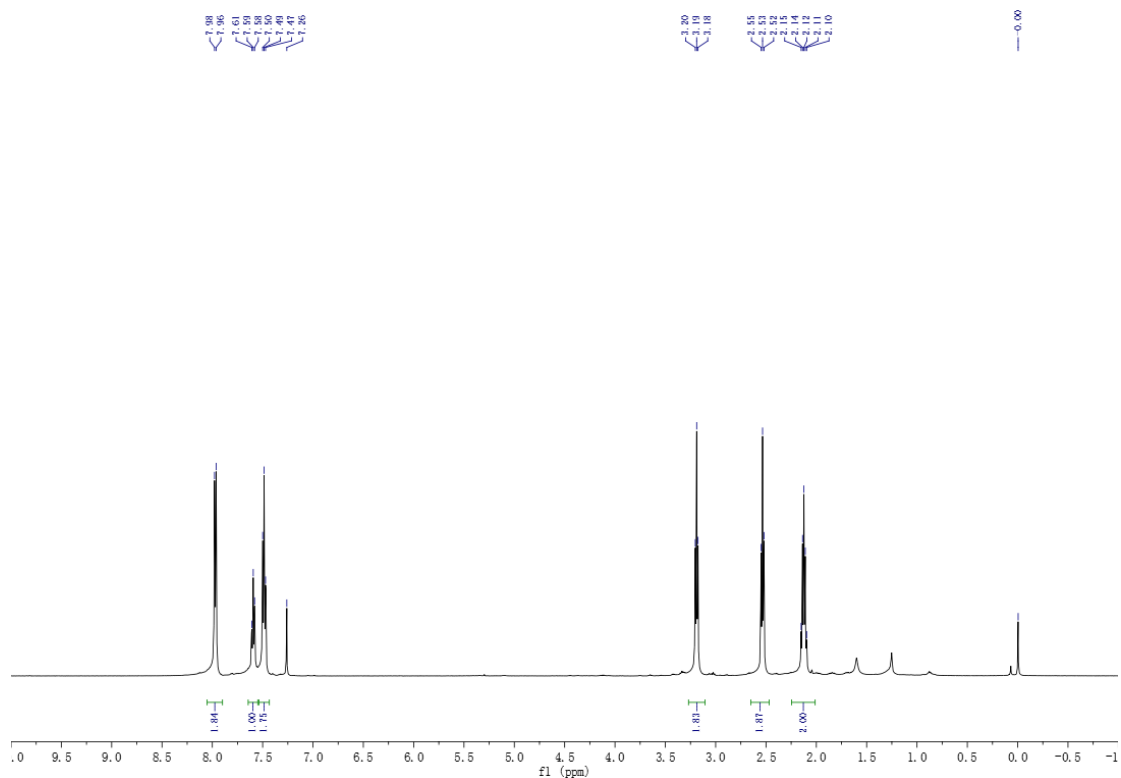
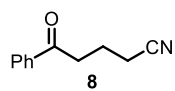
¹³C NMR of compound **6**



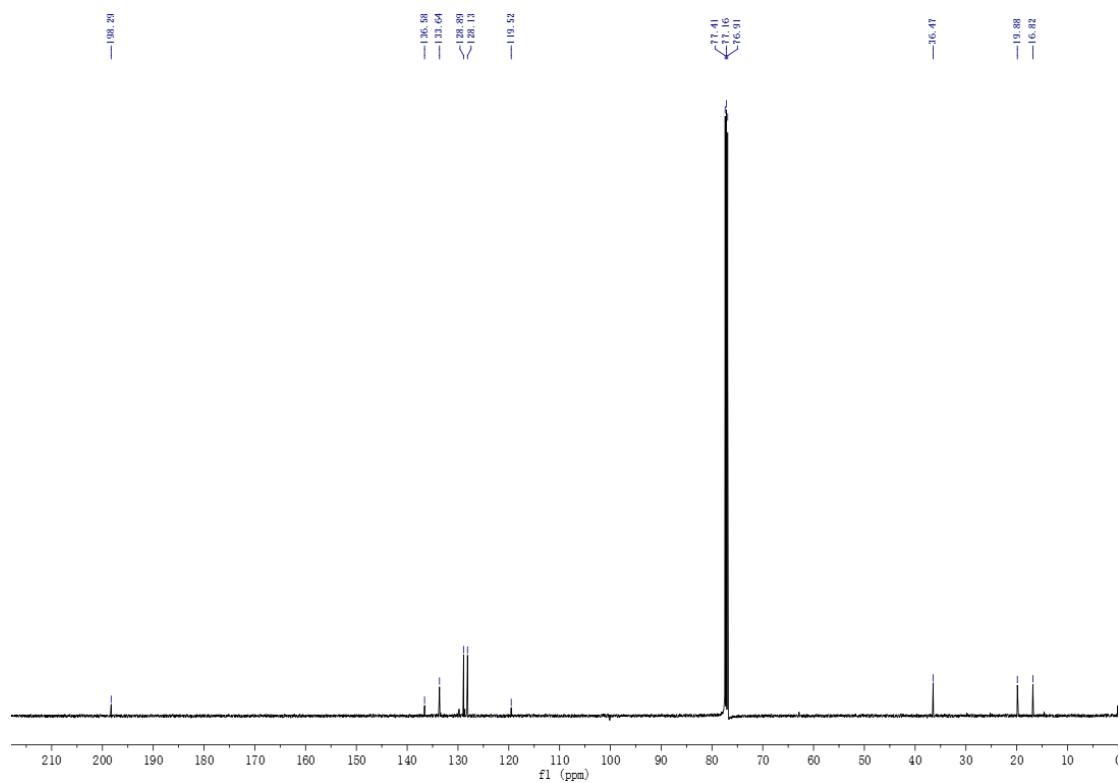
¹H NMR of compound 7



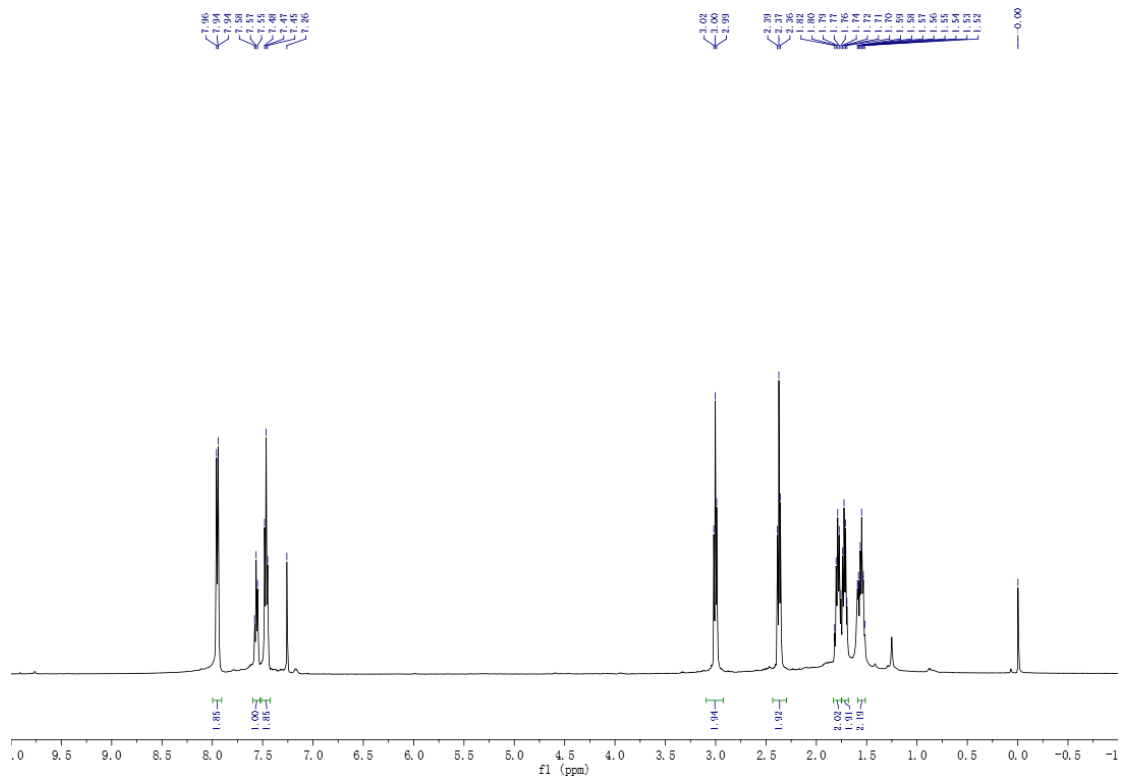
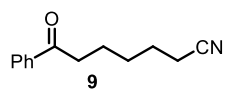
¹³C NMR of compound 7



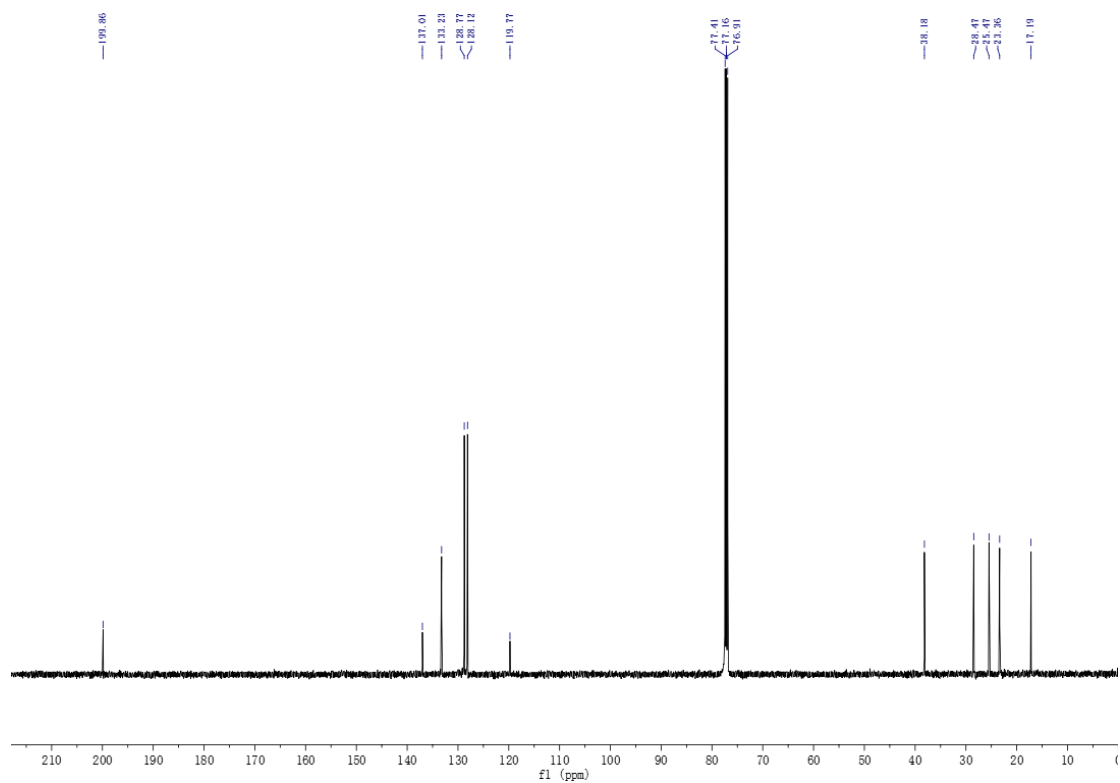
¹H NMR of compound **8**



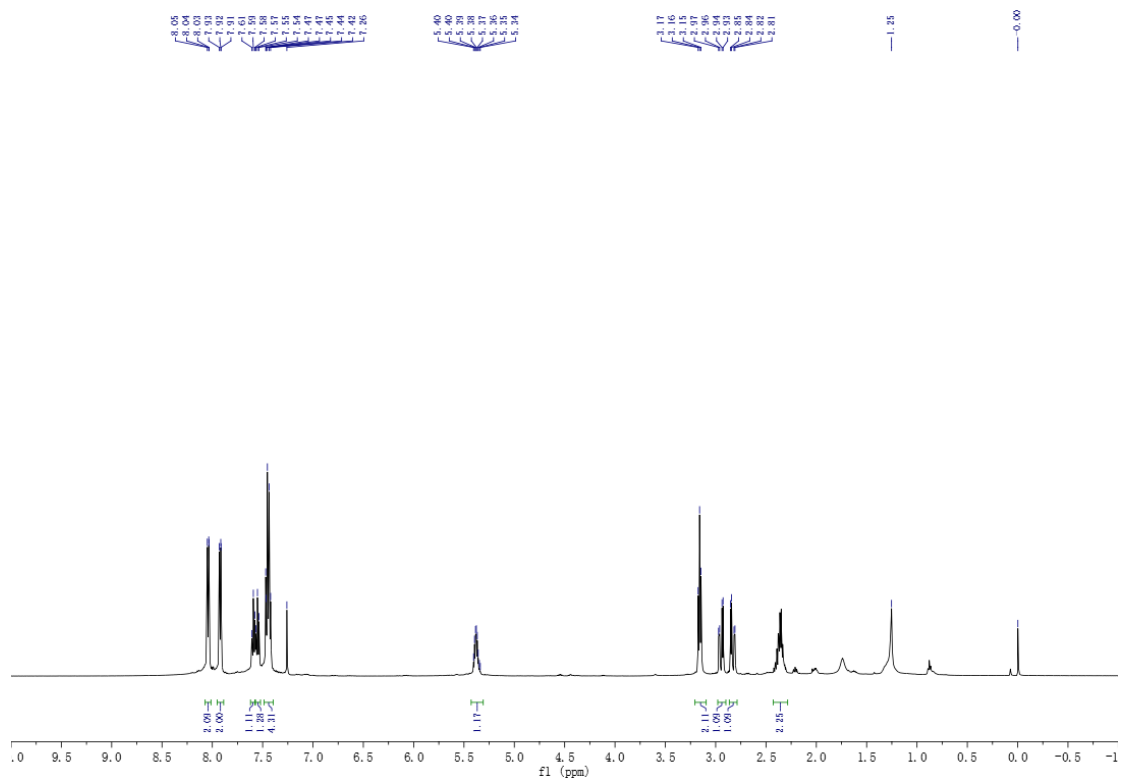
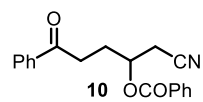
¹³C NMR of compound **8**



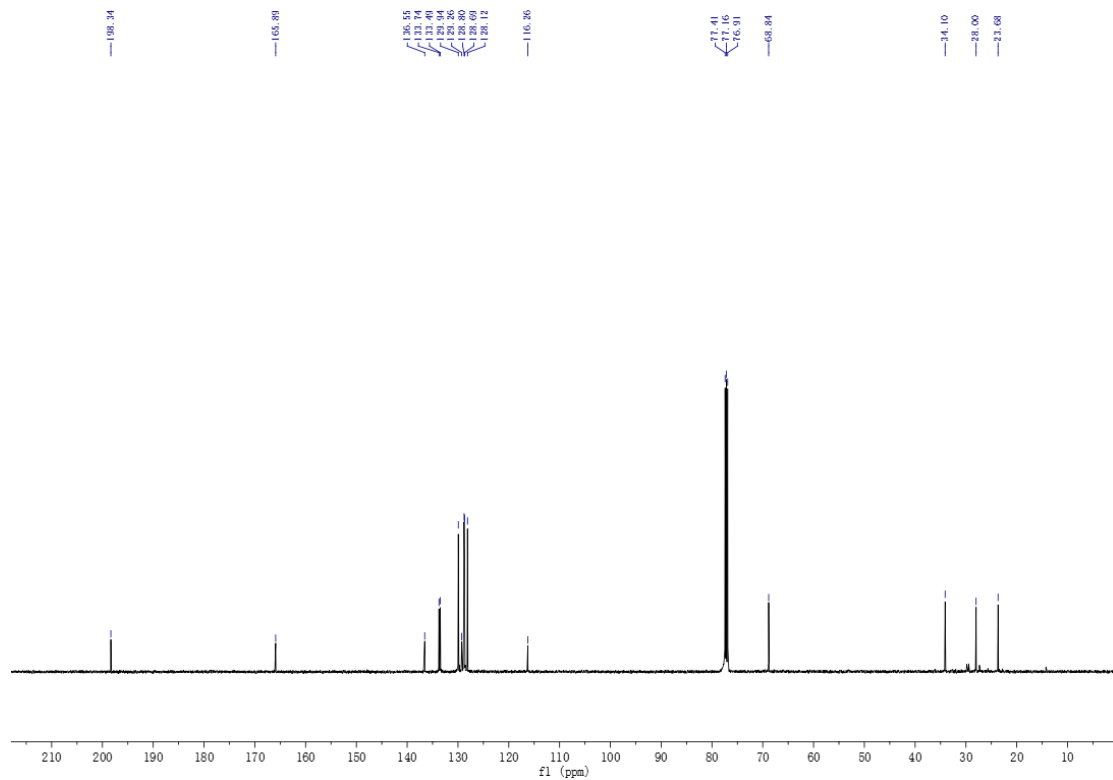
¹H NMR of compound 9



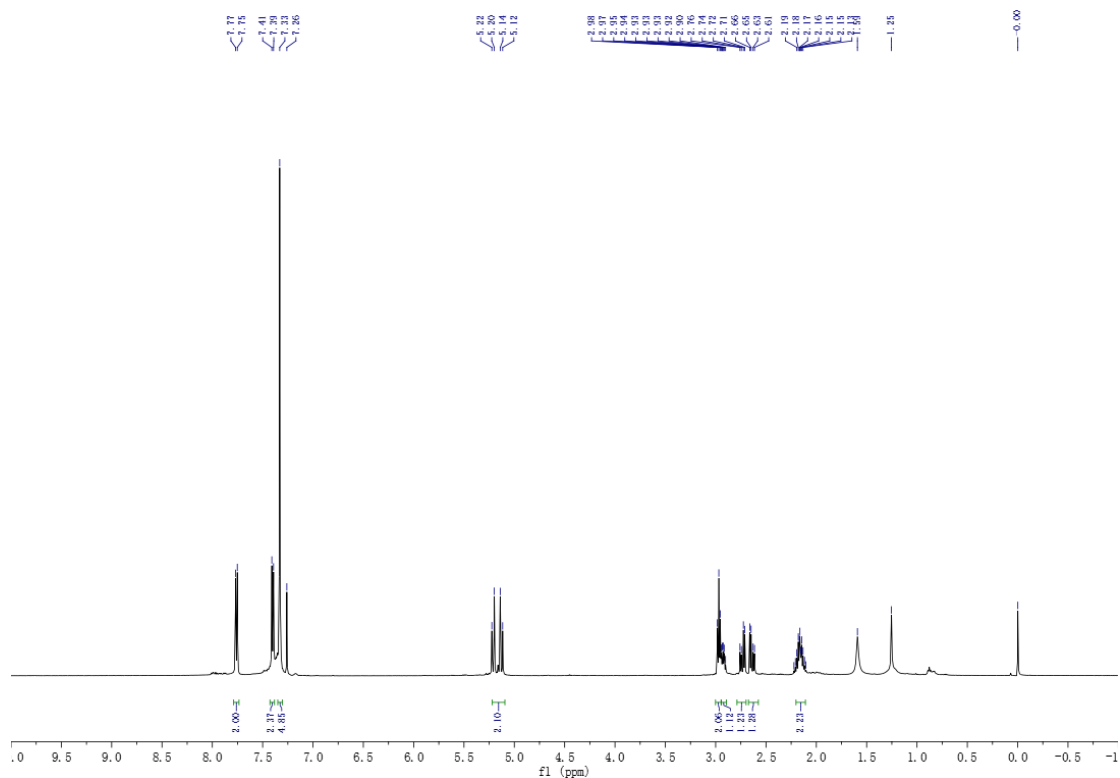
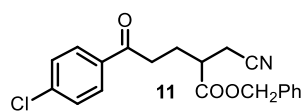
¹³C NMR of compound 9



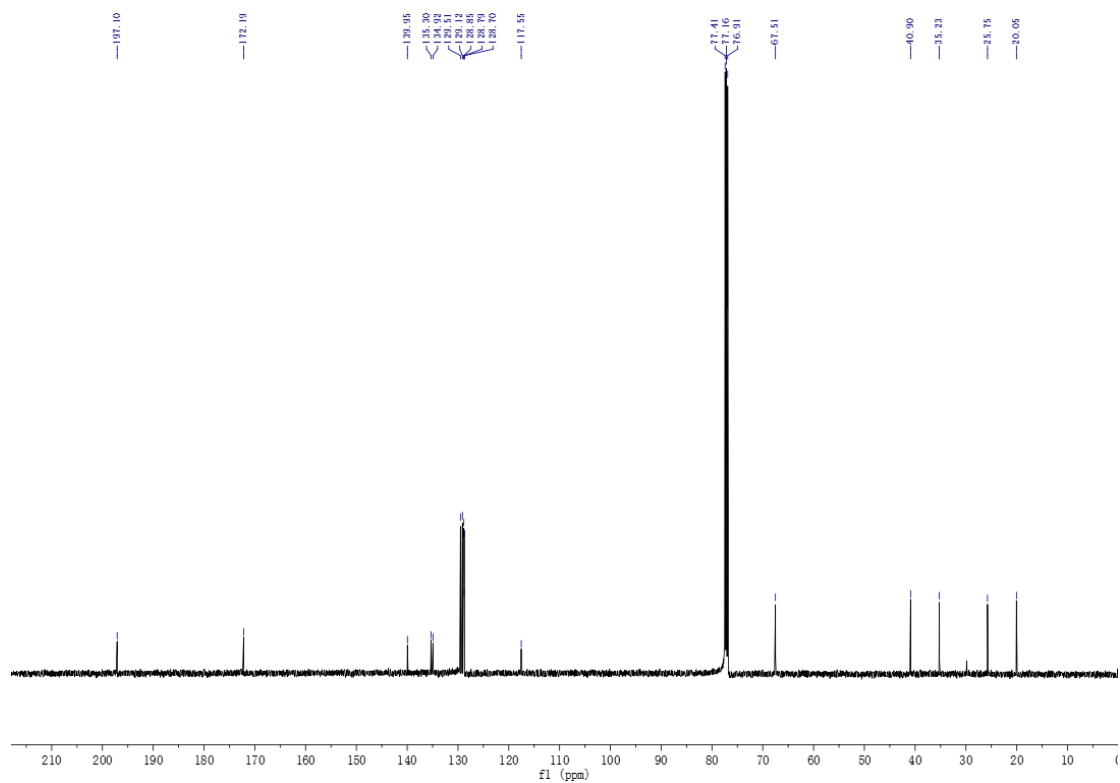
¹H NMR of compound **10**



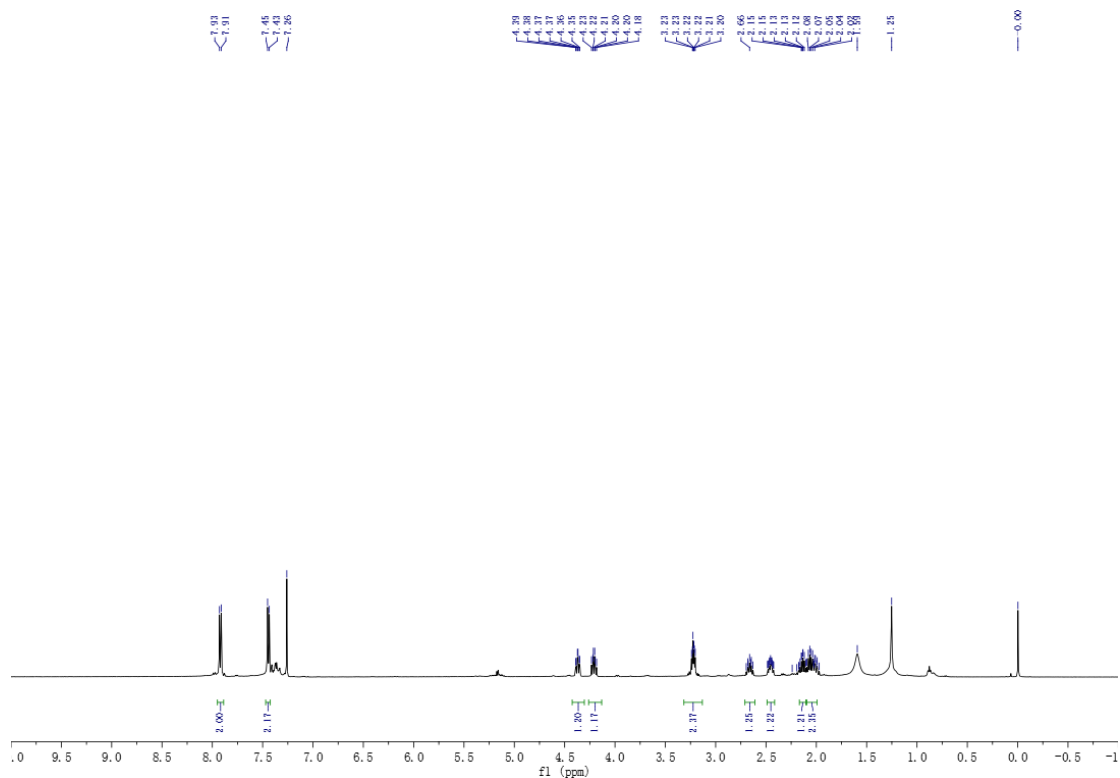
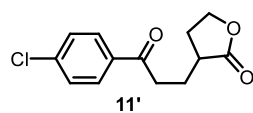
¹³C NMR of compound **10**



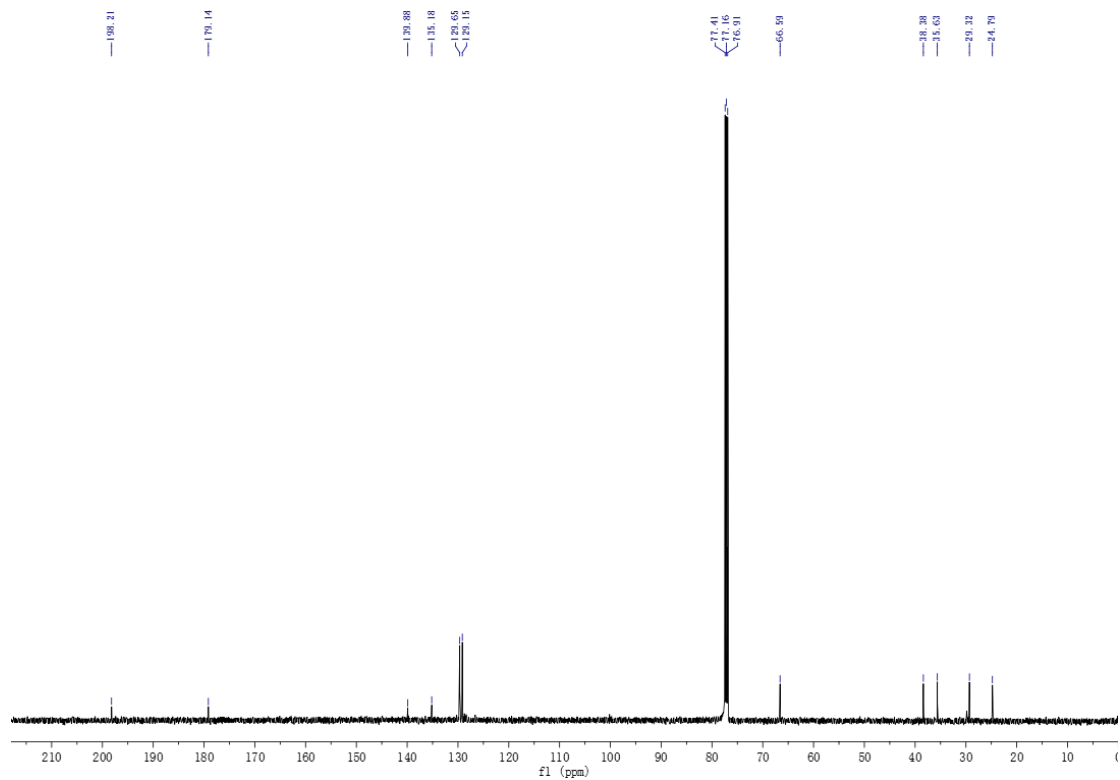
¹H NMR of compound **11**



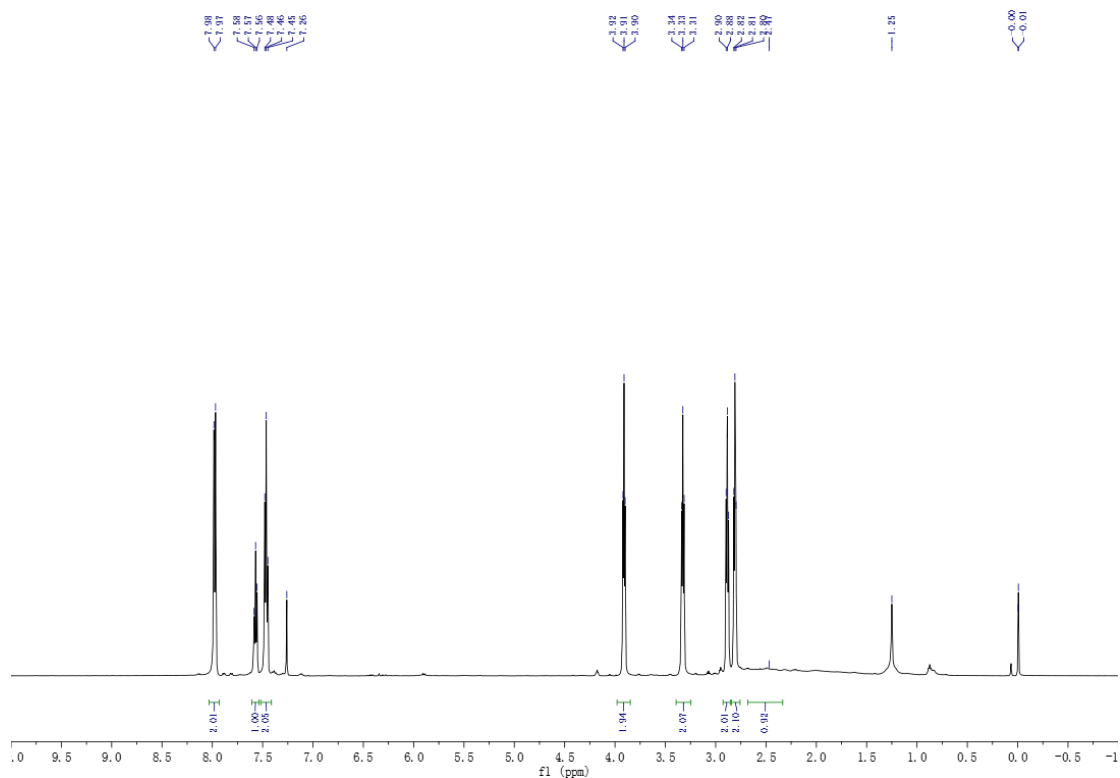
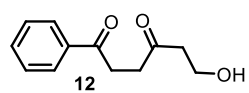
¹³C NMR of compound **11**



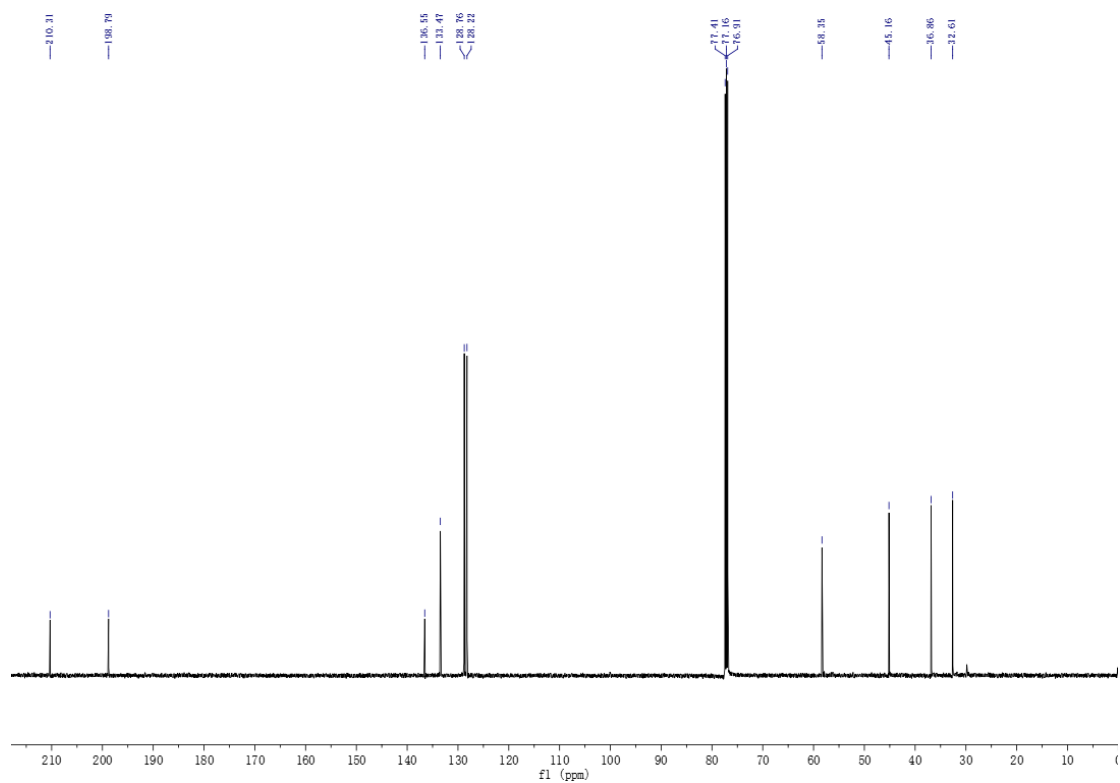
¹H NMR of compound **11'**



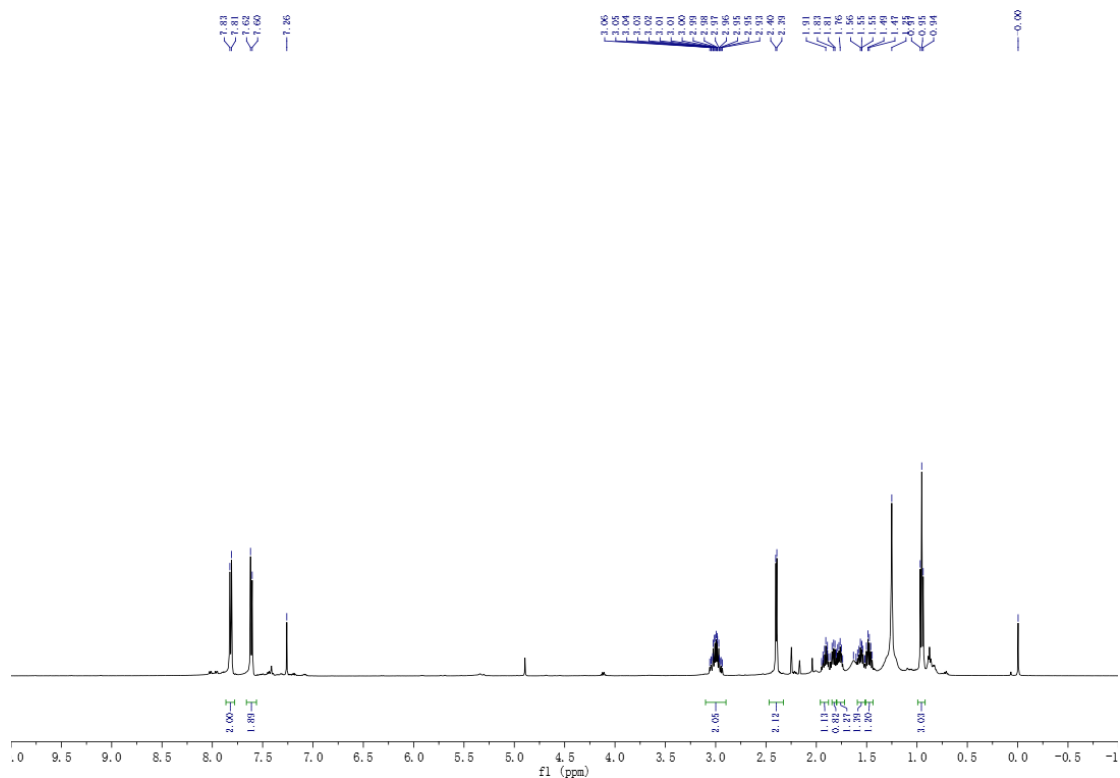
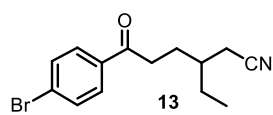
¹³C NMR of compound **11'**



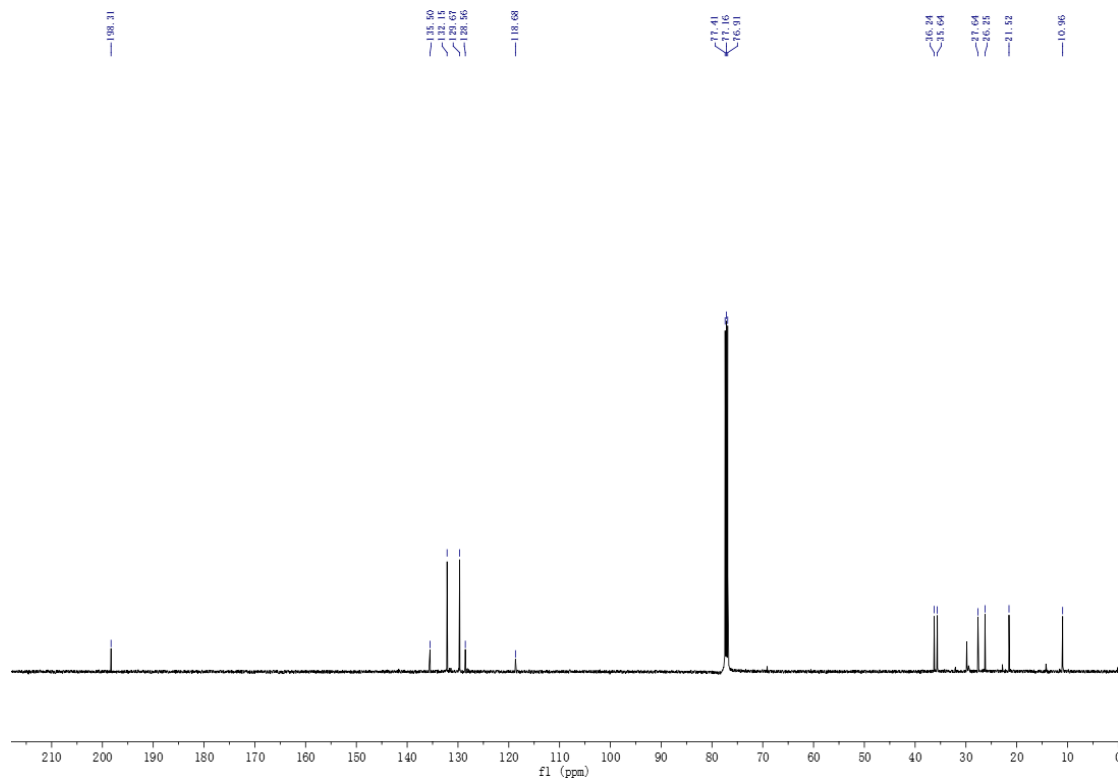
¹H NMR of compound **12**



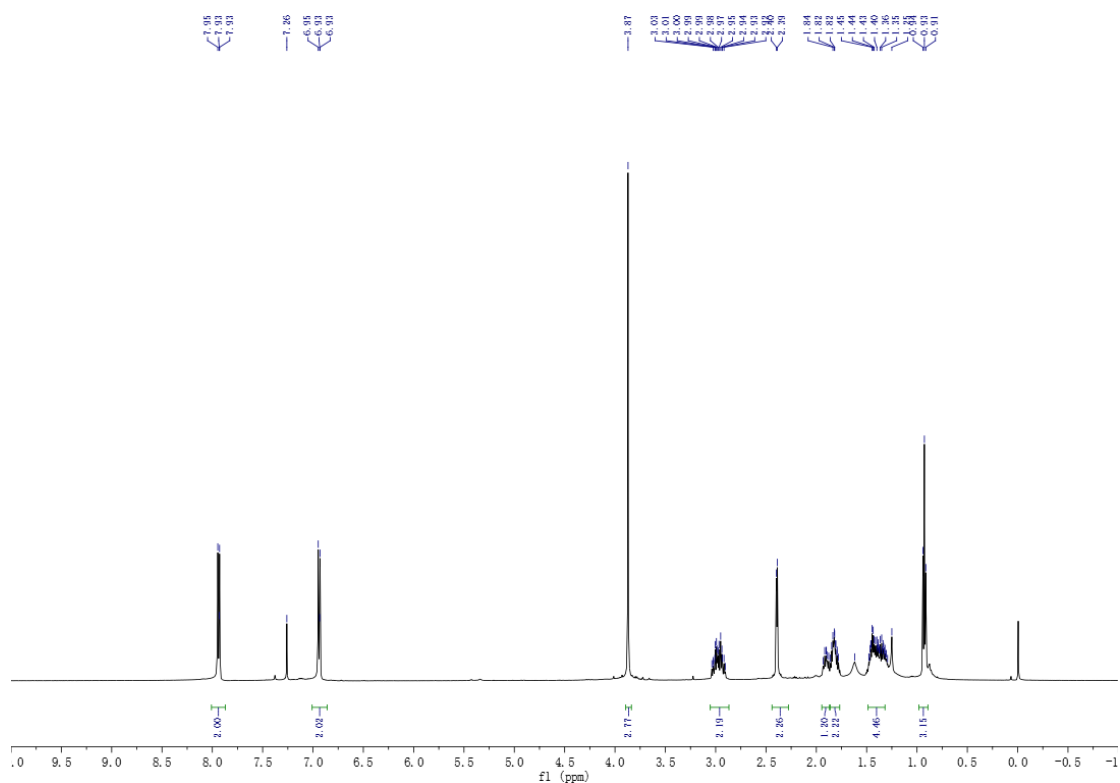
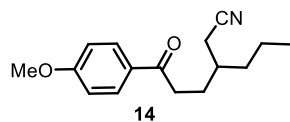
¹³C NMR of compound **12**



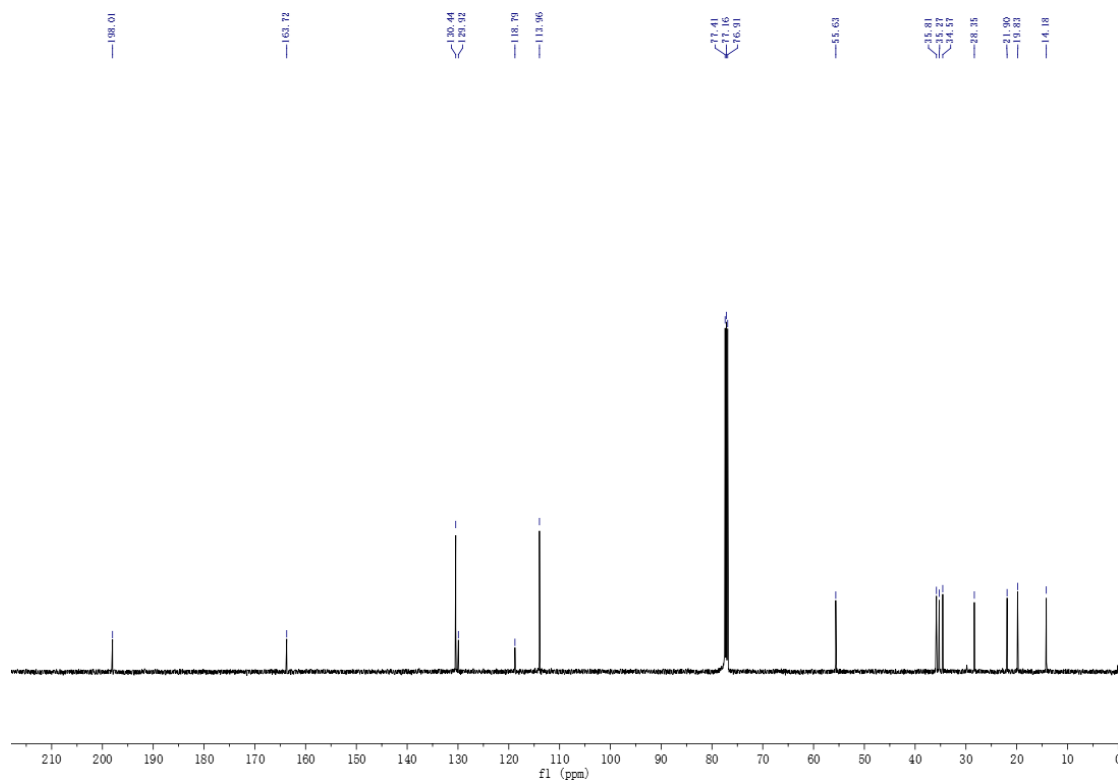
¹H NMR of compound **13**



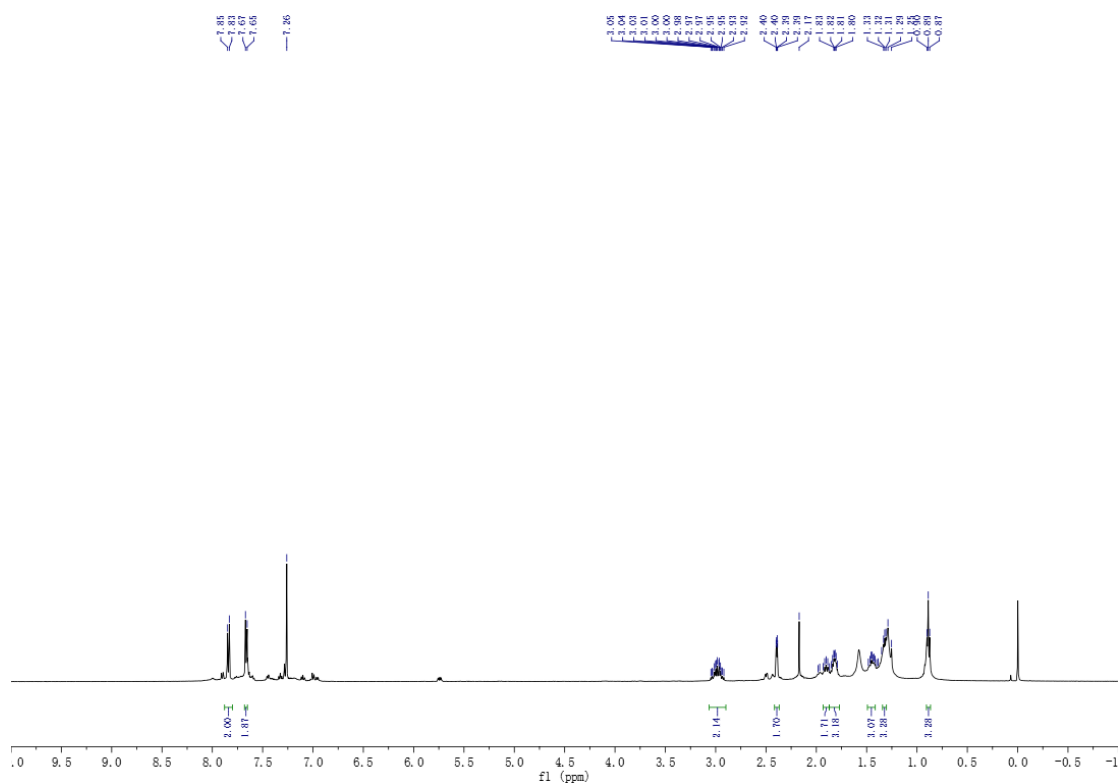
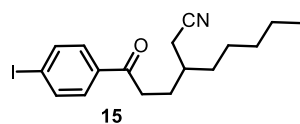
¹³C NMR of compound **13**



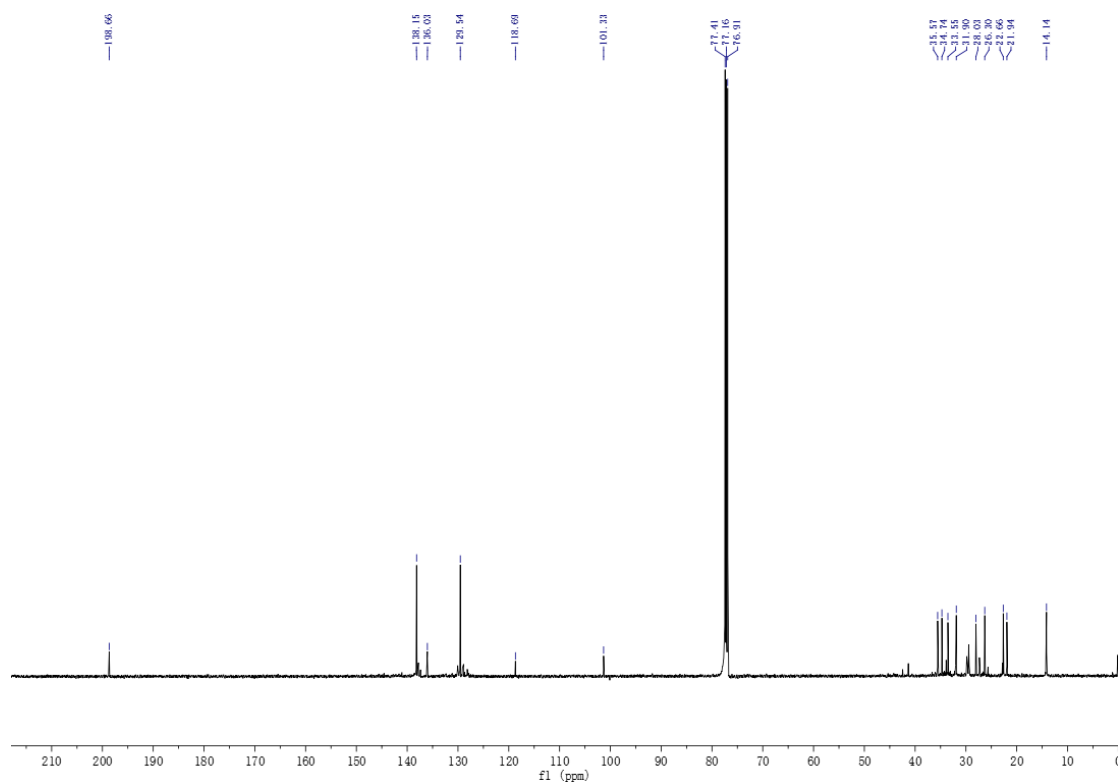
¹H NMR of compound **14**



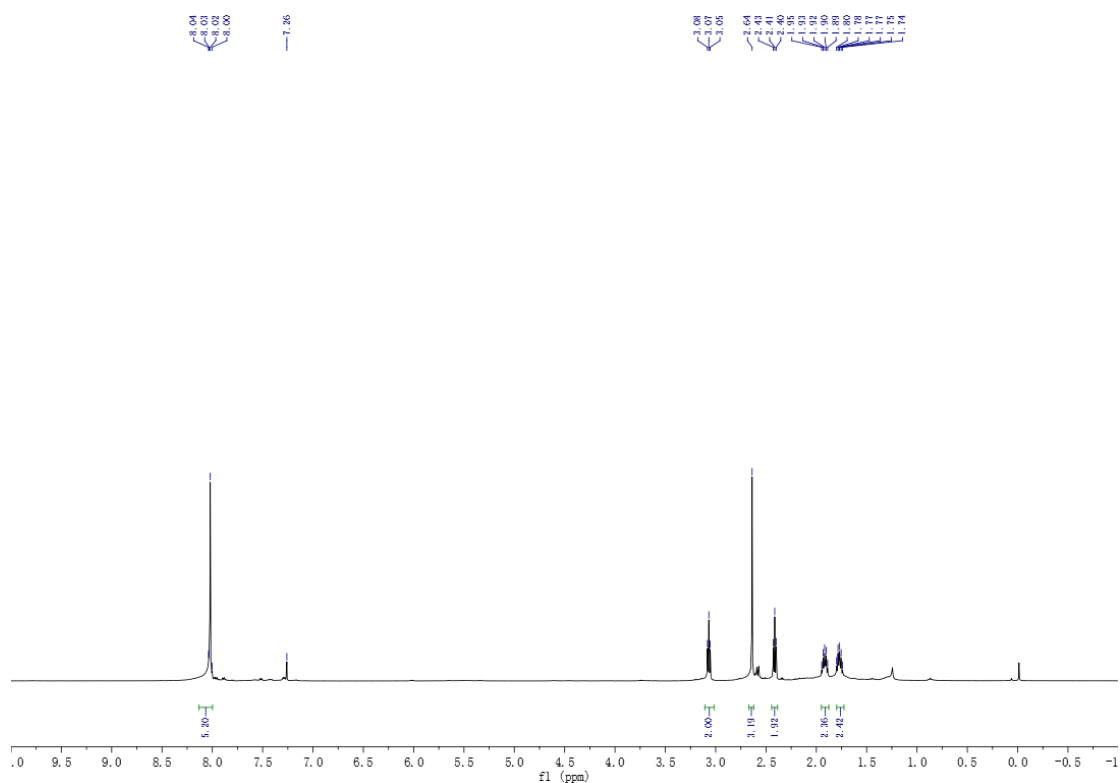
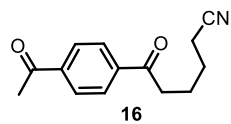
¹³C NMR of compound **14**



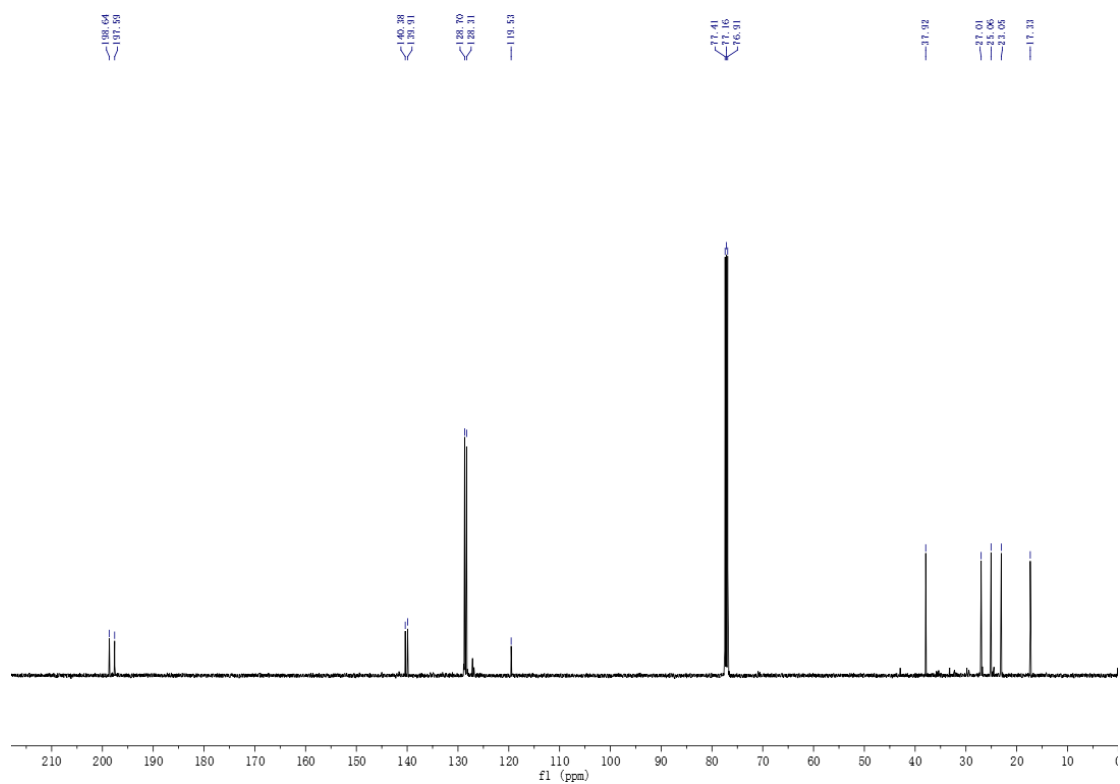
¹H NMR of compound **15**



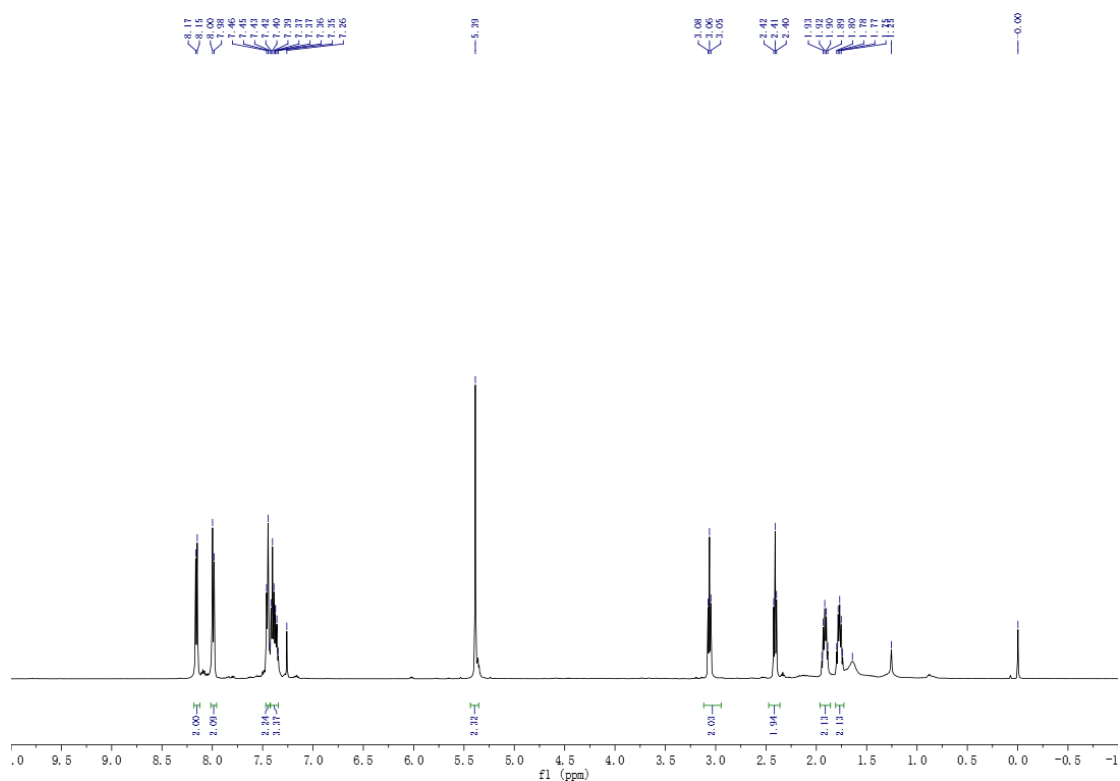
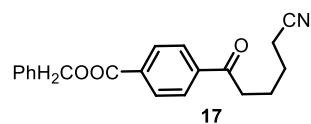
¹³C NMR of compound **15**



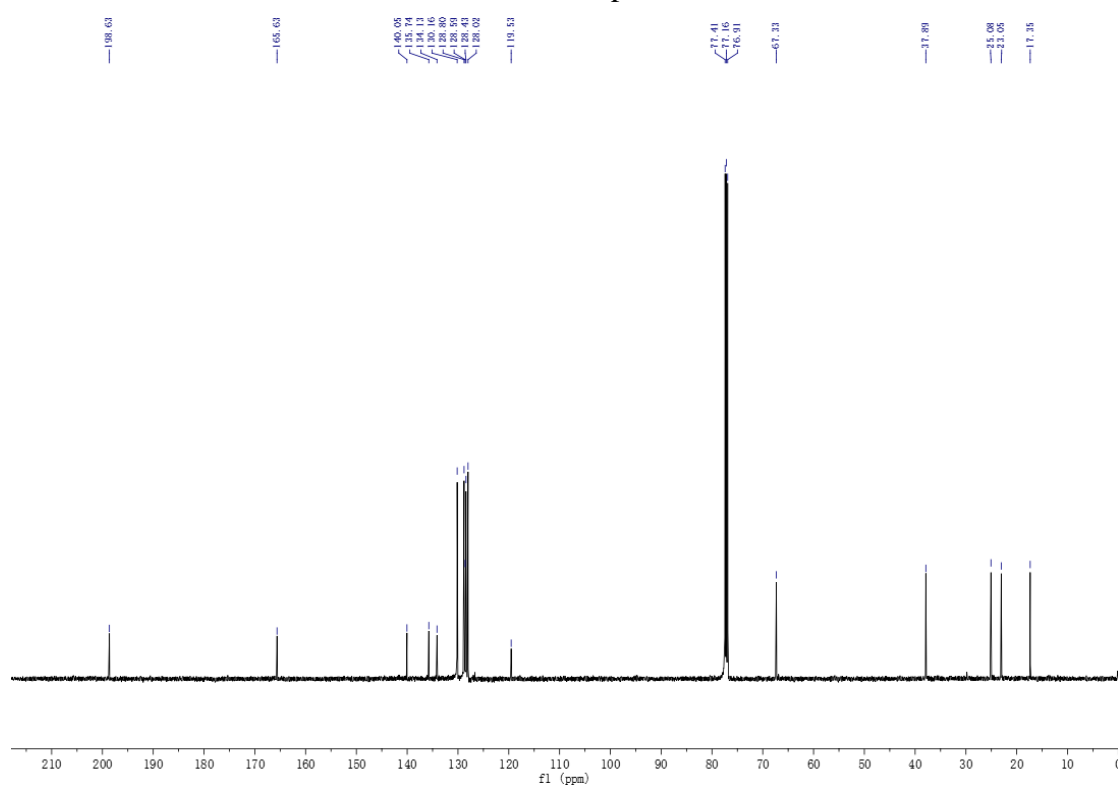
¹H NMR of compound **16**



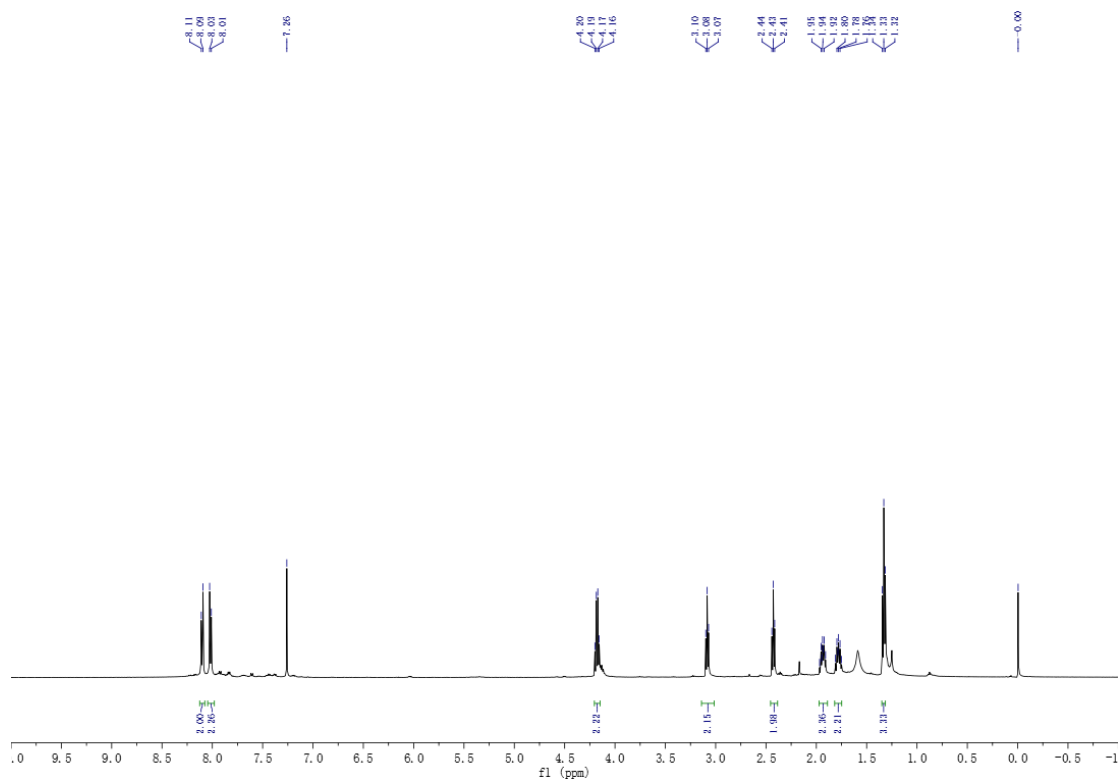
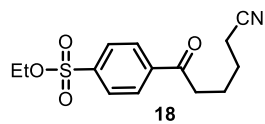
¹³C NMR of compound **16**



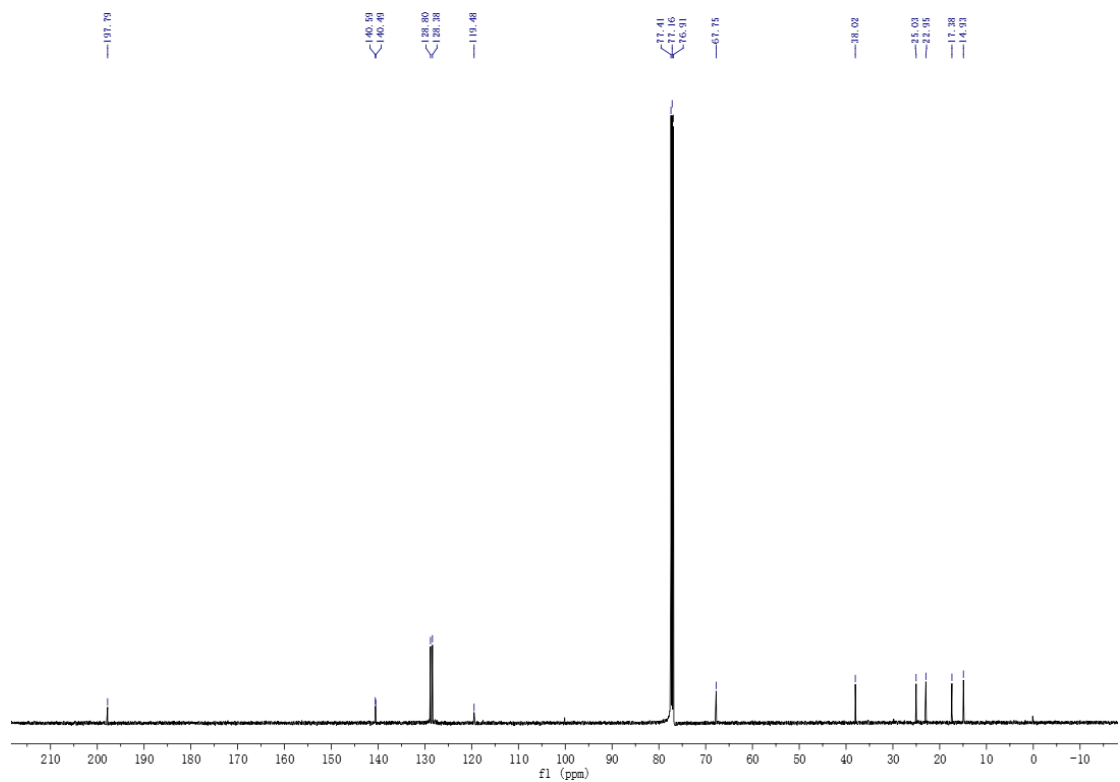
¹H NMR of compound **17**



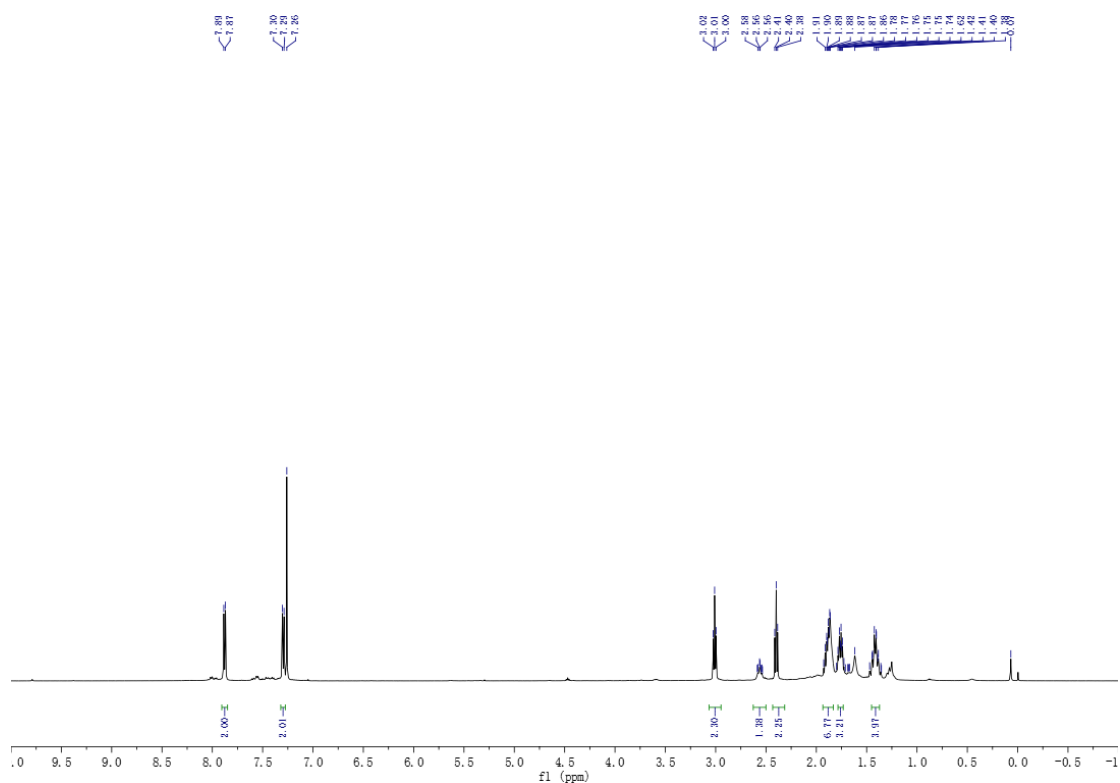
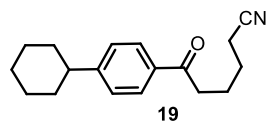
¹³C NMR of compound **17**



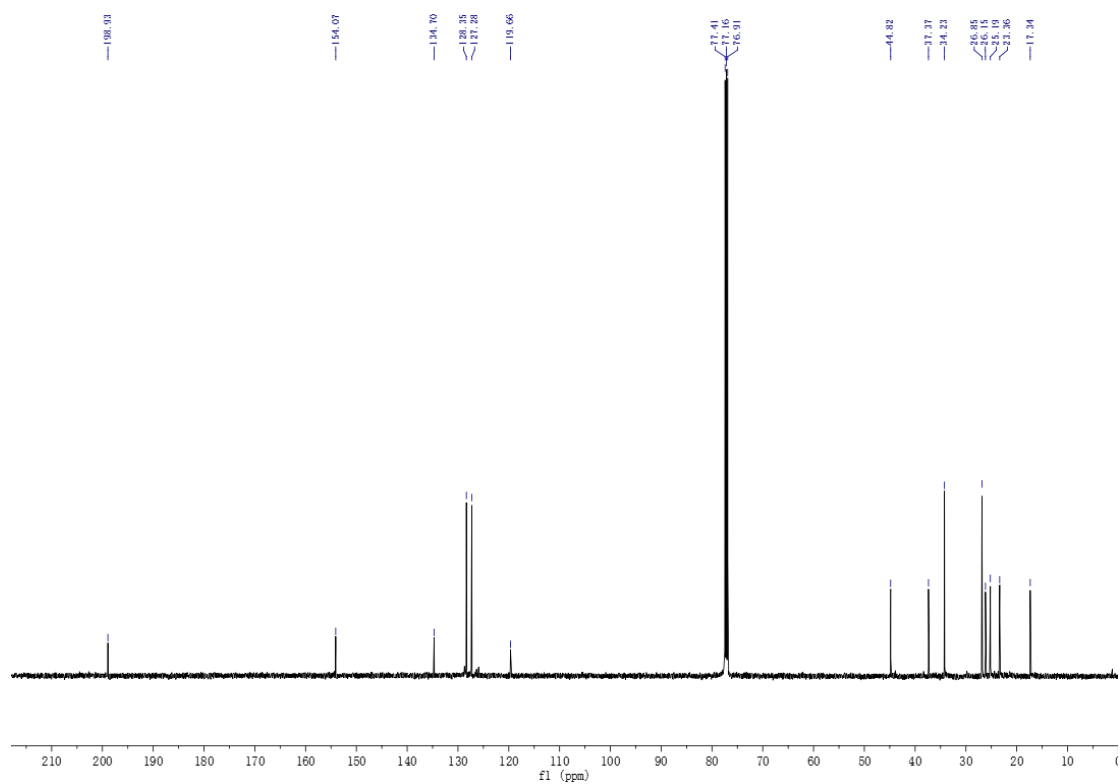
¹H NMR of compound **18**



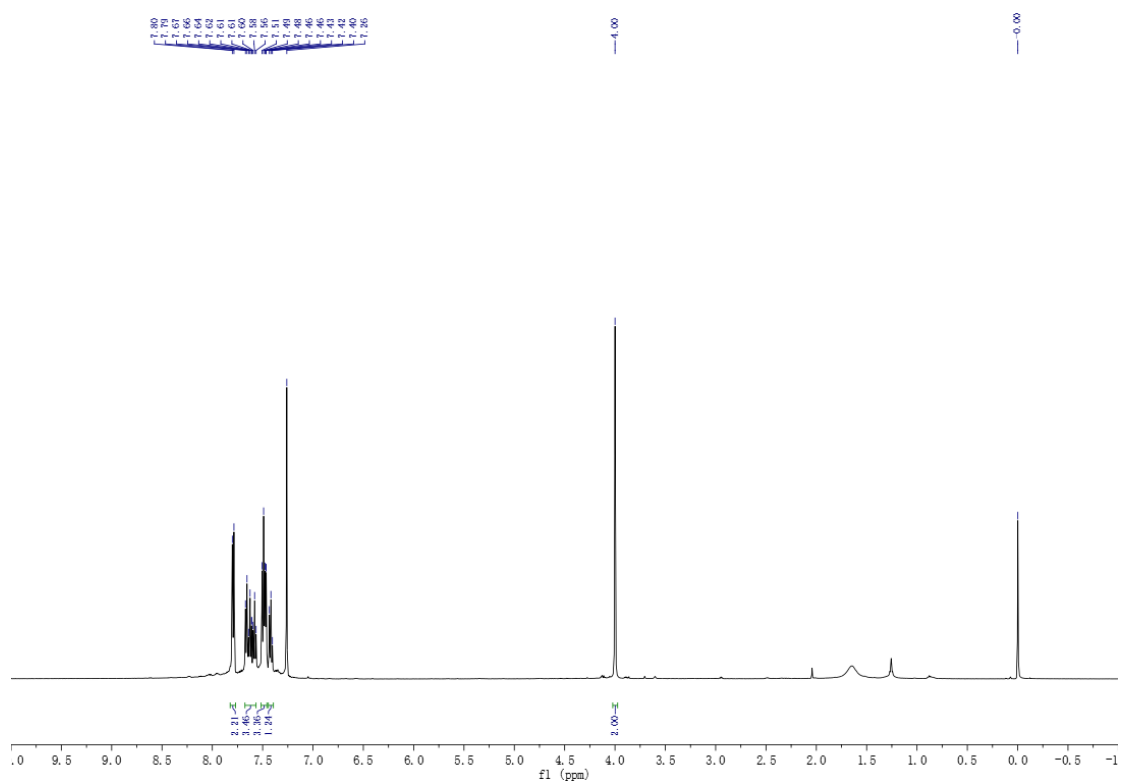
¹³C NMR of compound **18**



¹H NMR of compound **19**

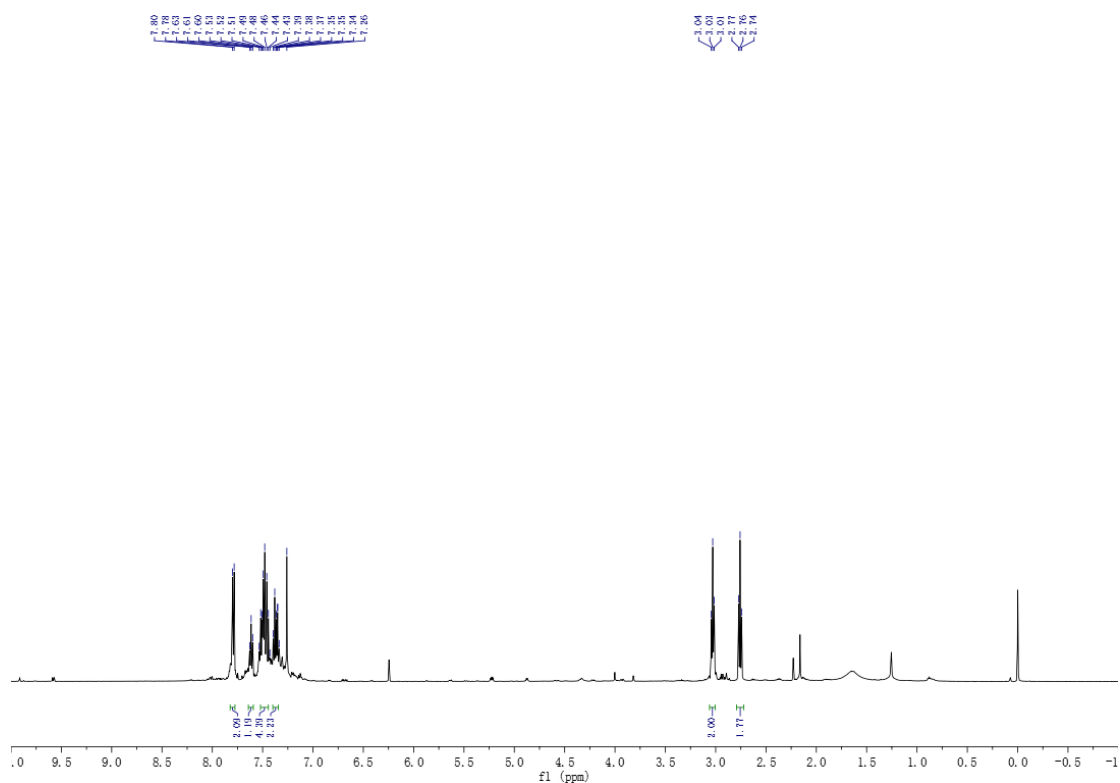
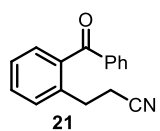


¹³C NMR of compound **19**

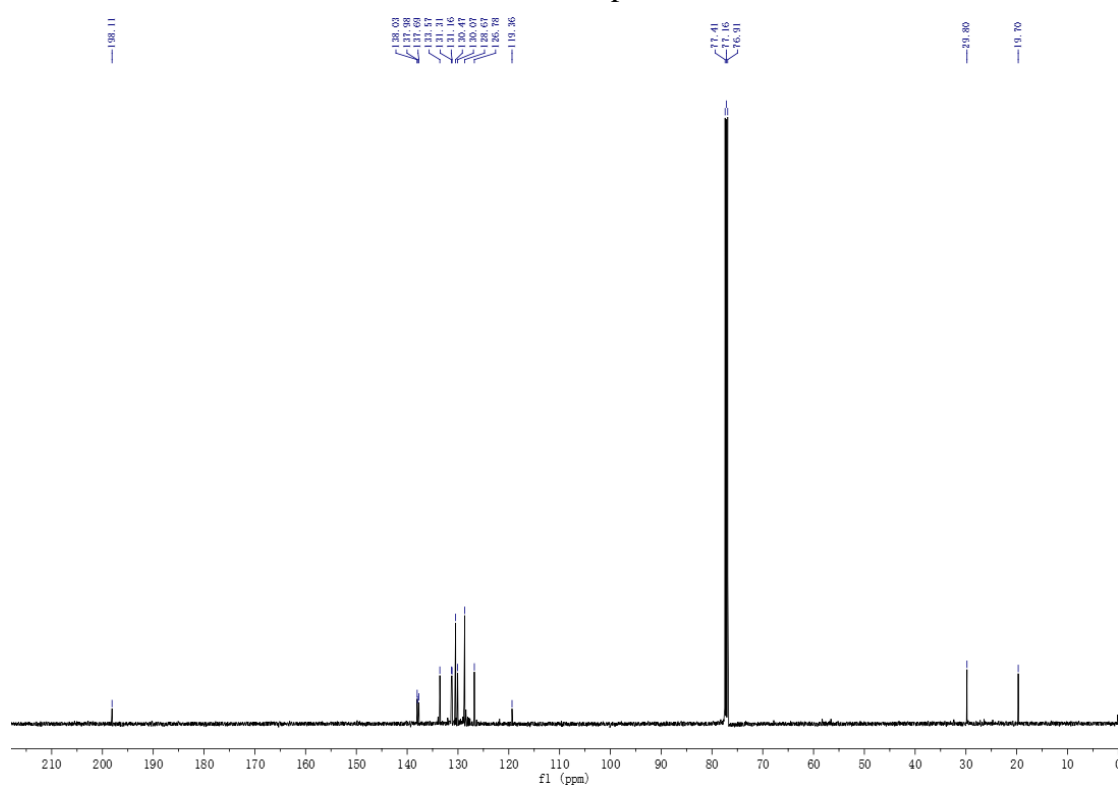


13C NMR spectrum of compound 10. The x-axis is labeled 'f1 (ppm)' and ranges from 210 to 10. The spectrum shows several peaks: a small peak at 197.25 ppm, a cluster of peaks between 127 and 137 ppm, a peak at 117.90 ppm, a very large solvent peak at 77.16 ppm (with labels 77.41, 77.16, 76.91), and a peak at 22.04 ppm.

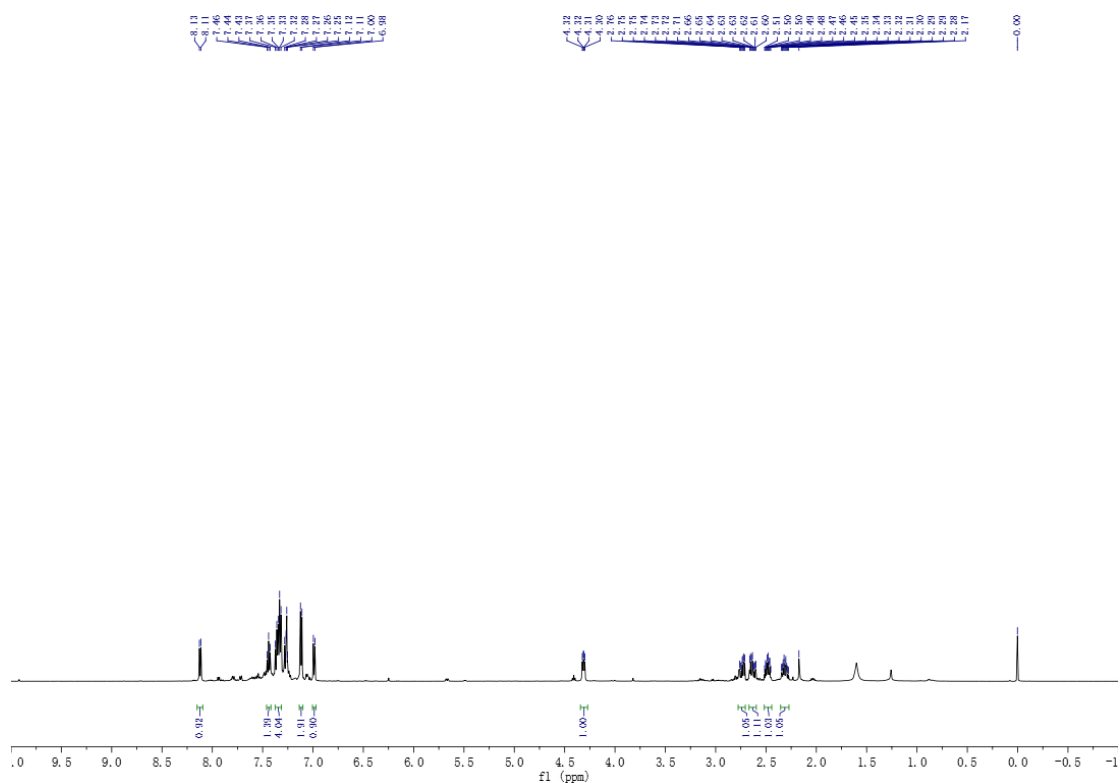
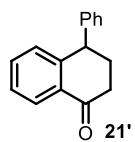
S90



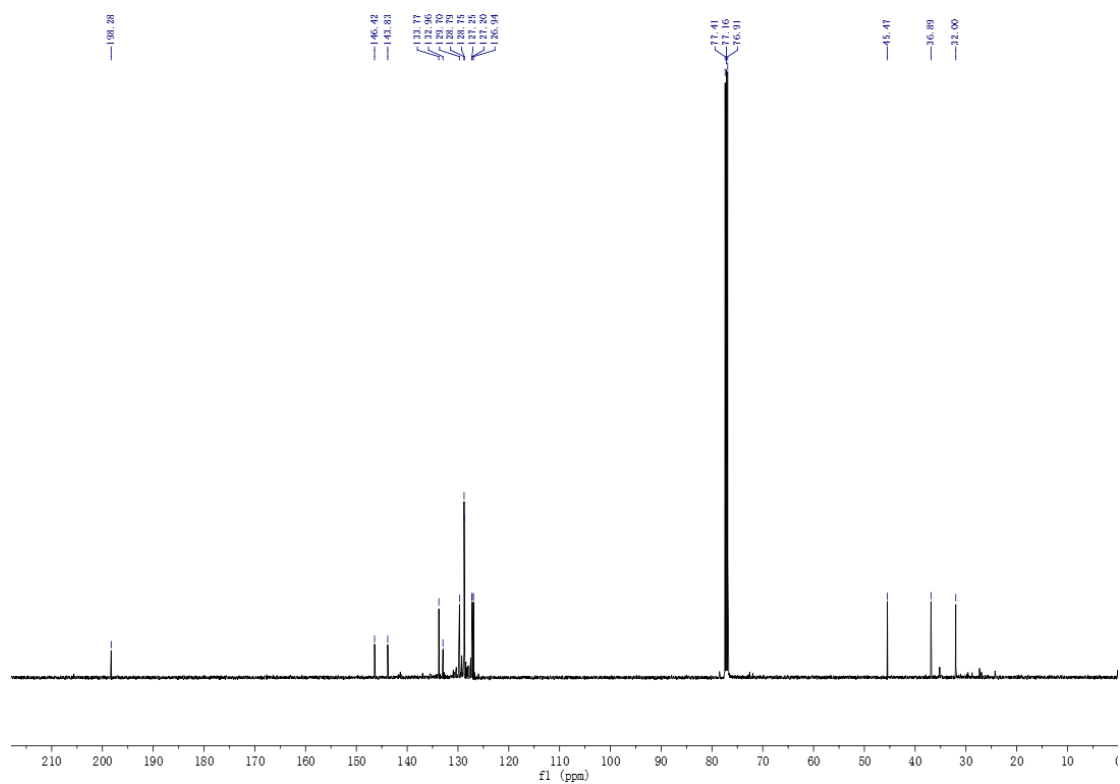
¹H NMR of compound **21**



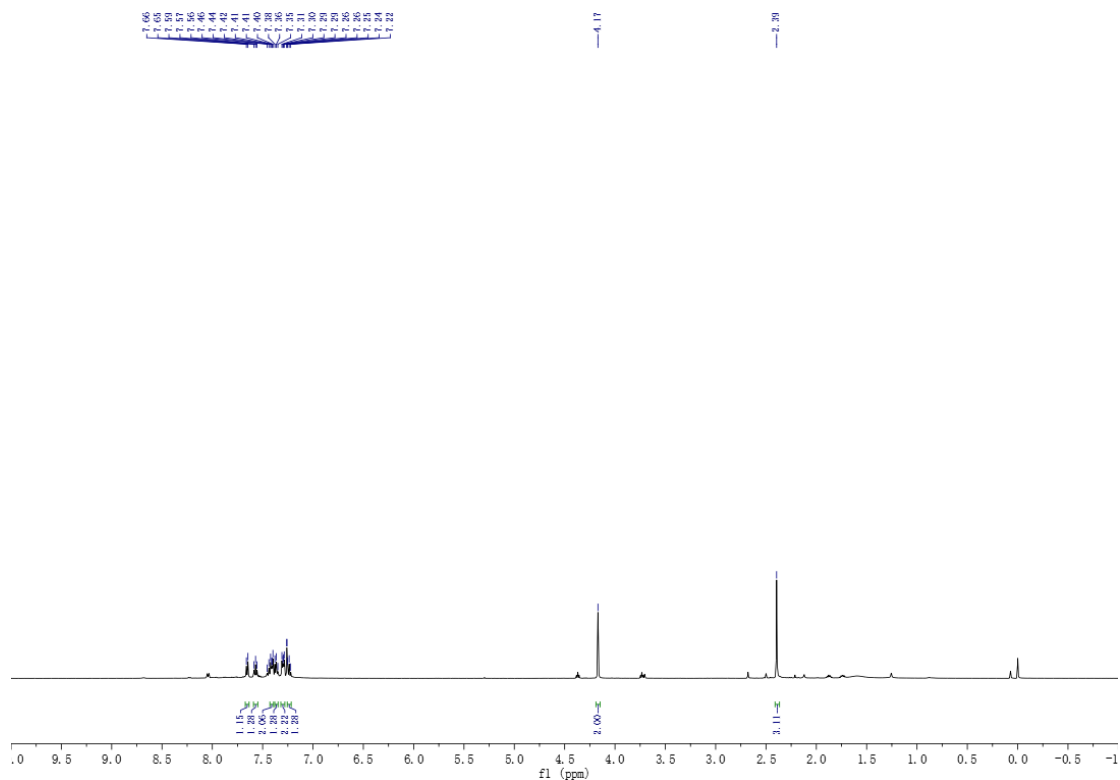
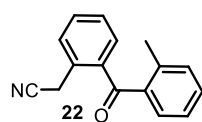
¹³C NMR of compound **21**



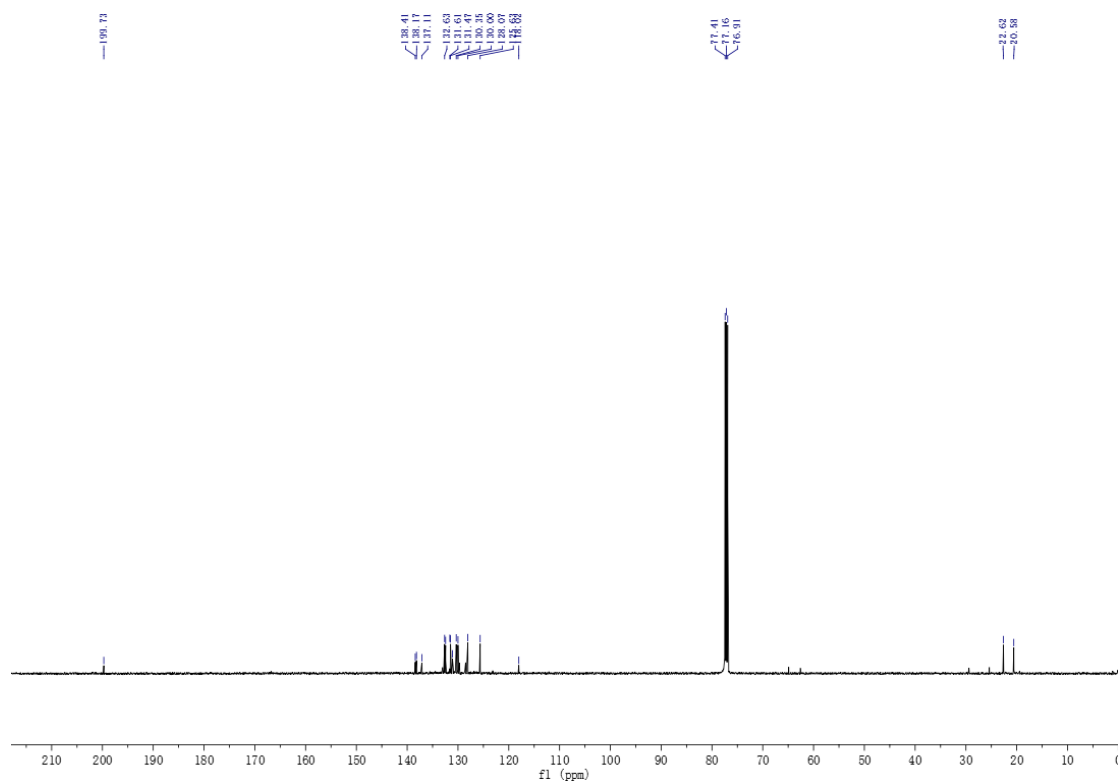
¹H NMR of compound **21'**



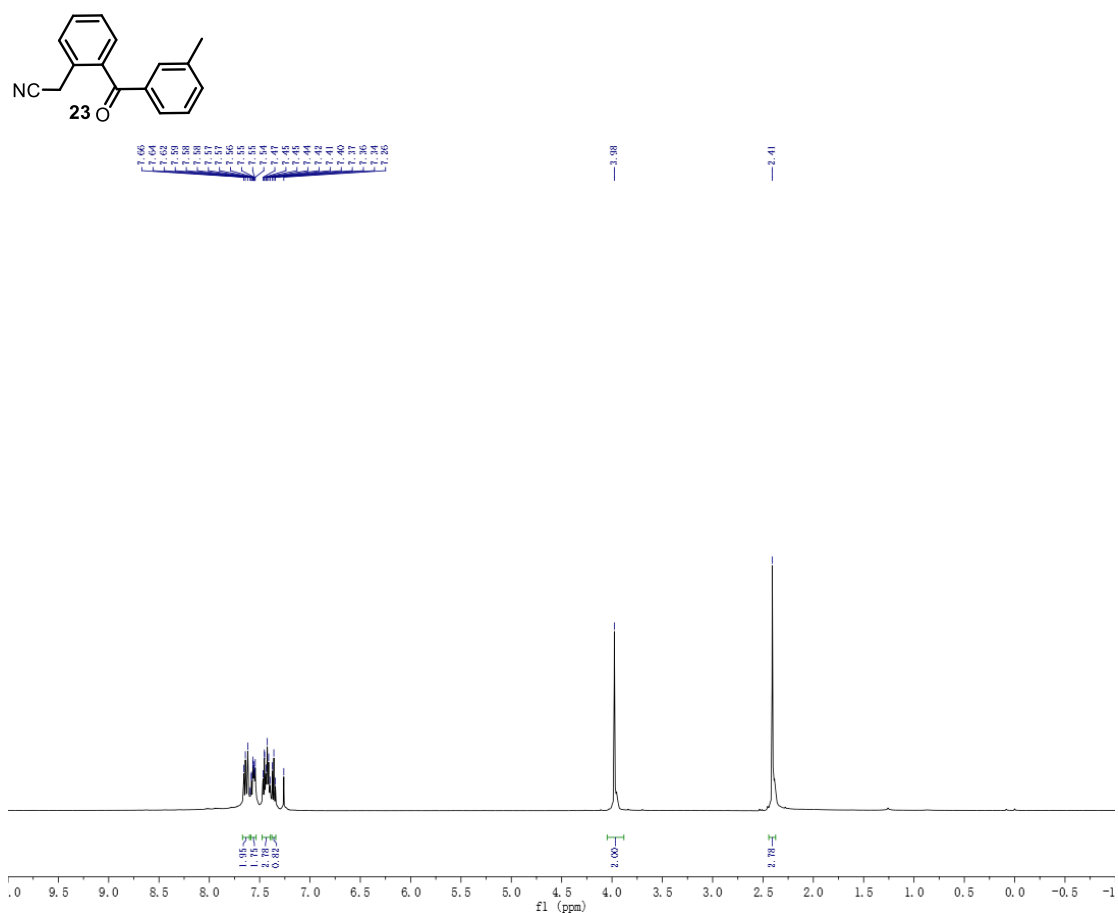
¹³C NMR of compound **21'**



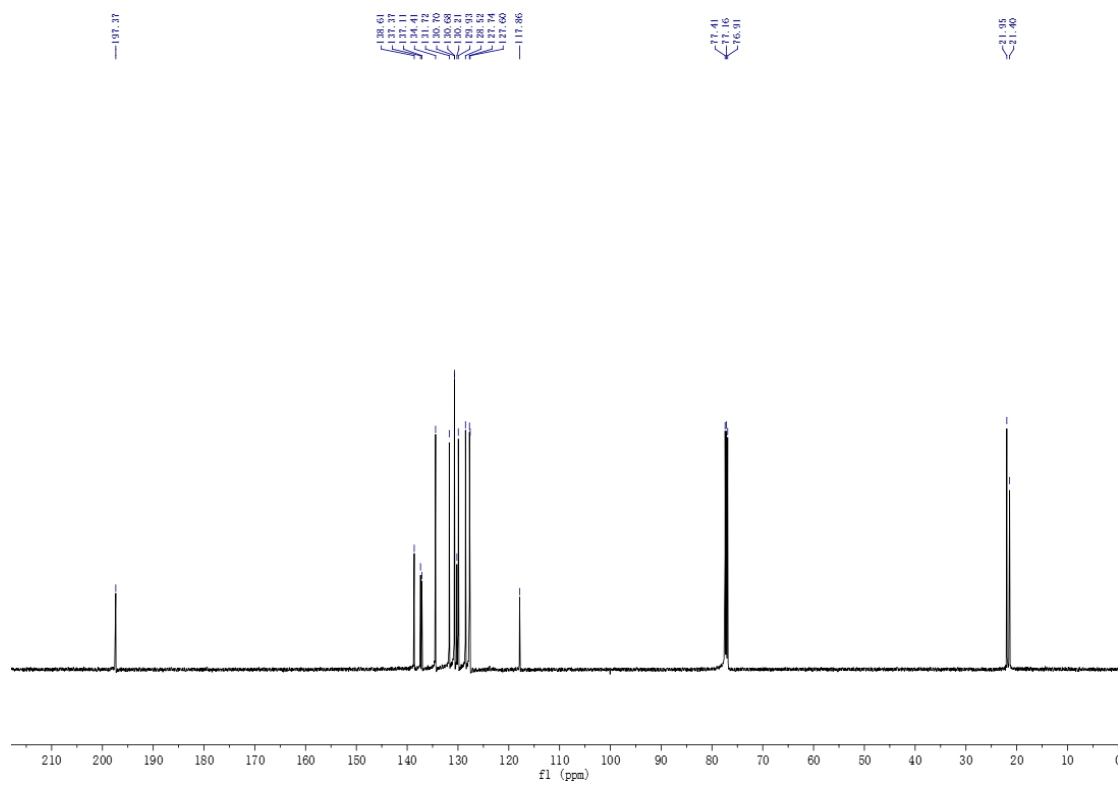
¹H NMR of compound **22**



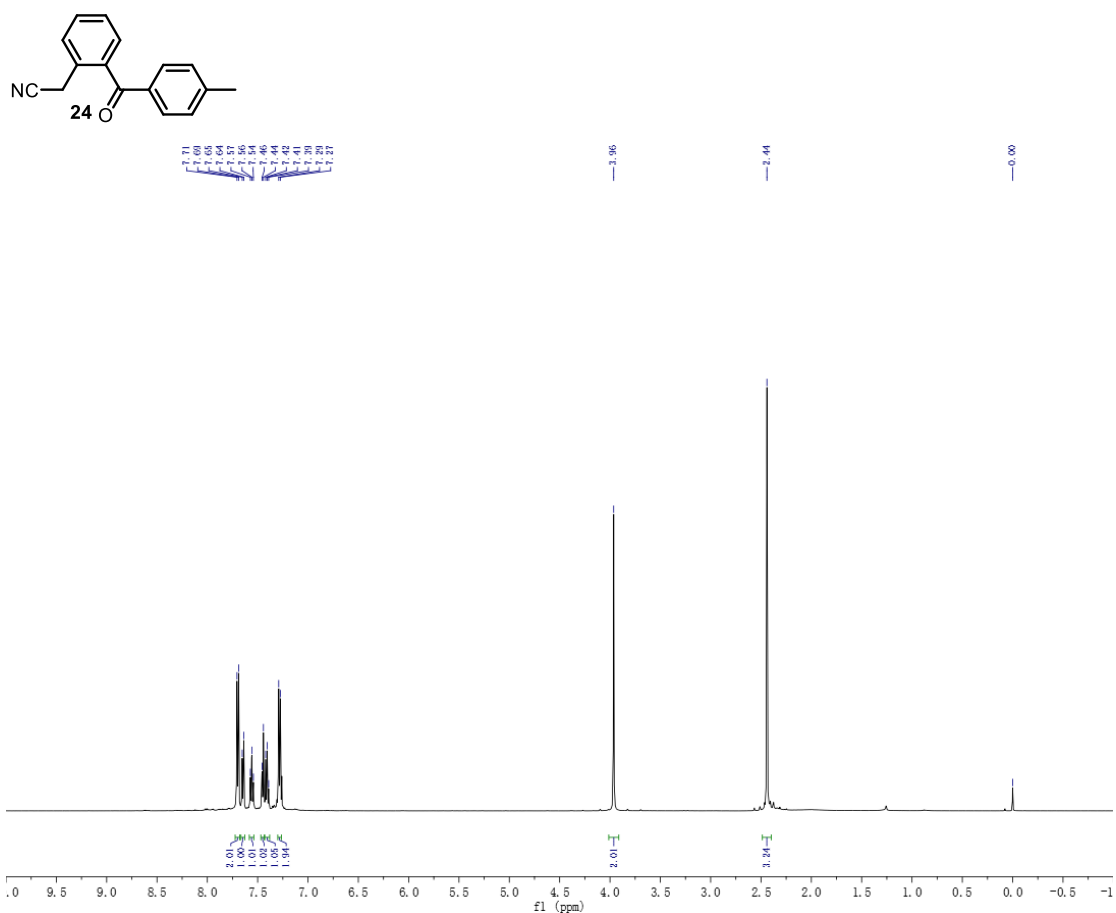
¹³C NMR of compound **22**



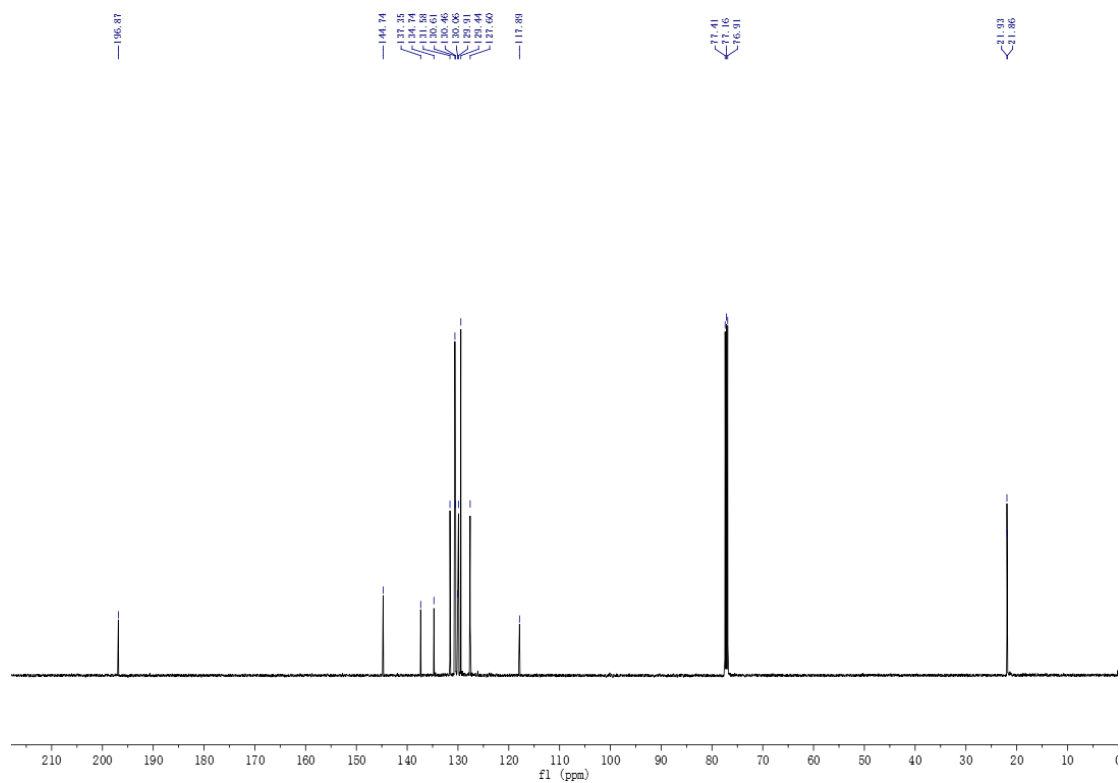
¹H NMR of compound **23**



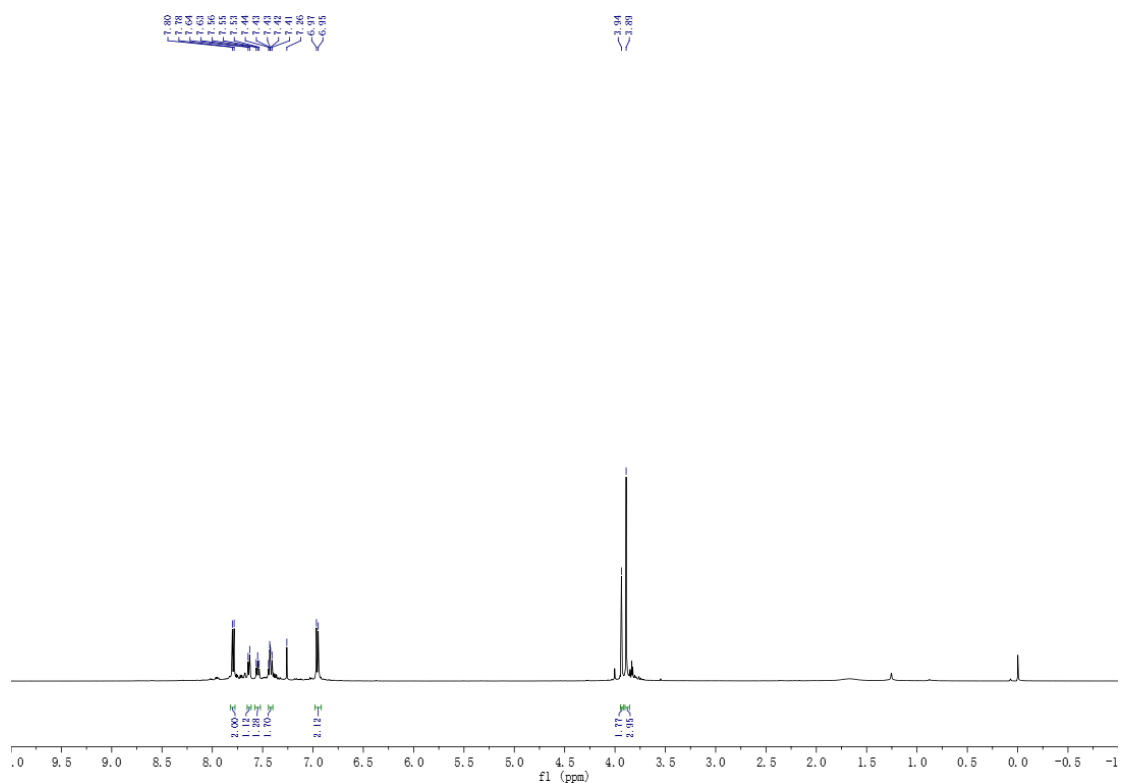
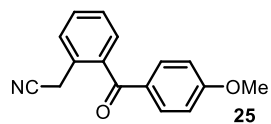
¹³C NMR of compound **23**



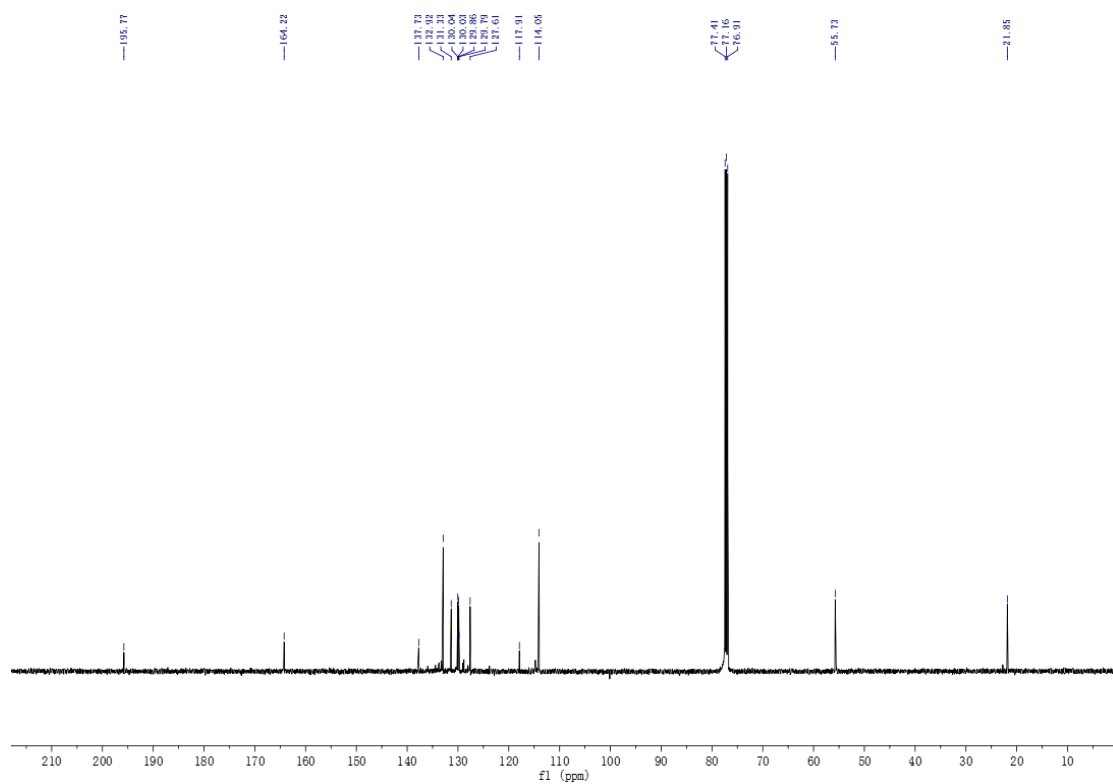
^1H NMR of compound **24**



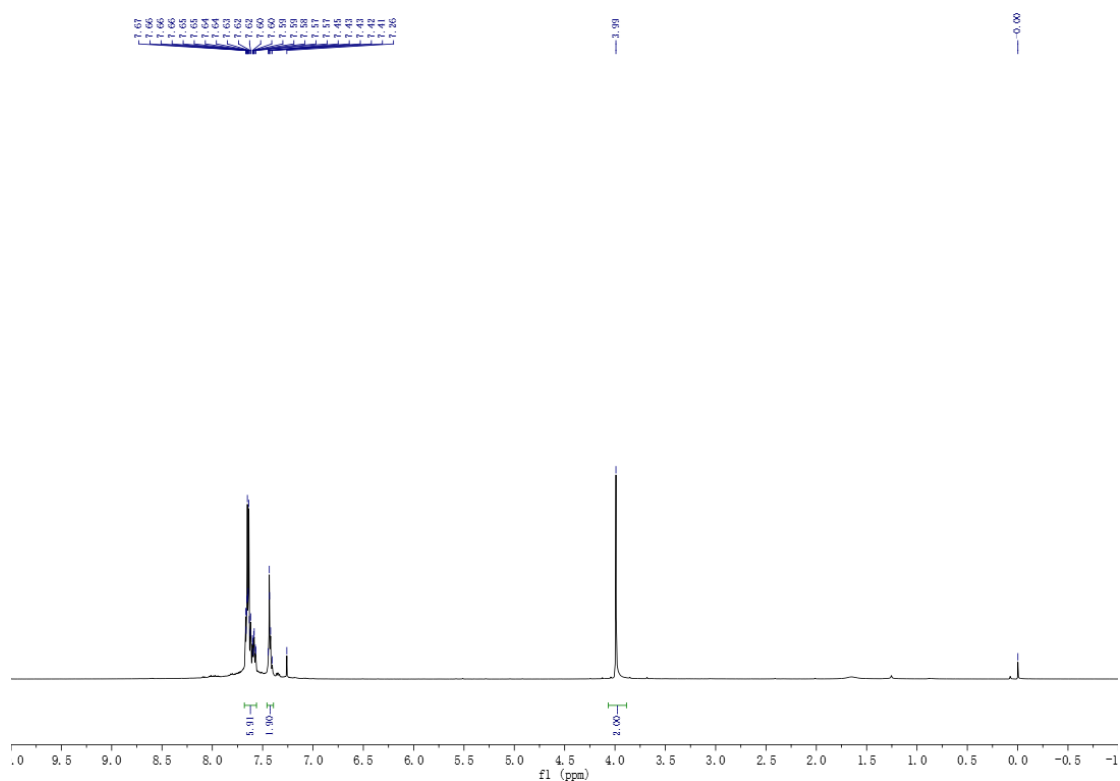
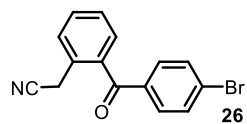
^{13}C NMR of compound **24**



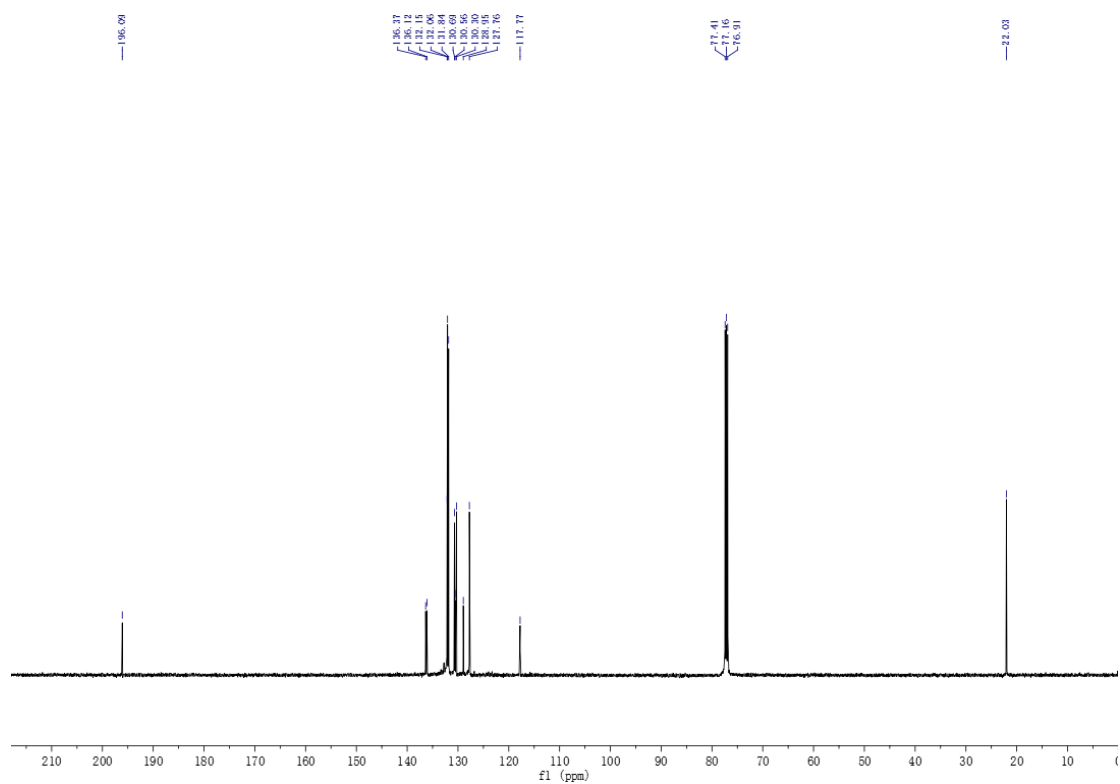
¹H NMR of compound **25**



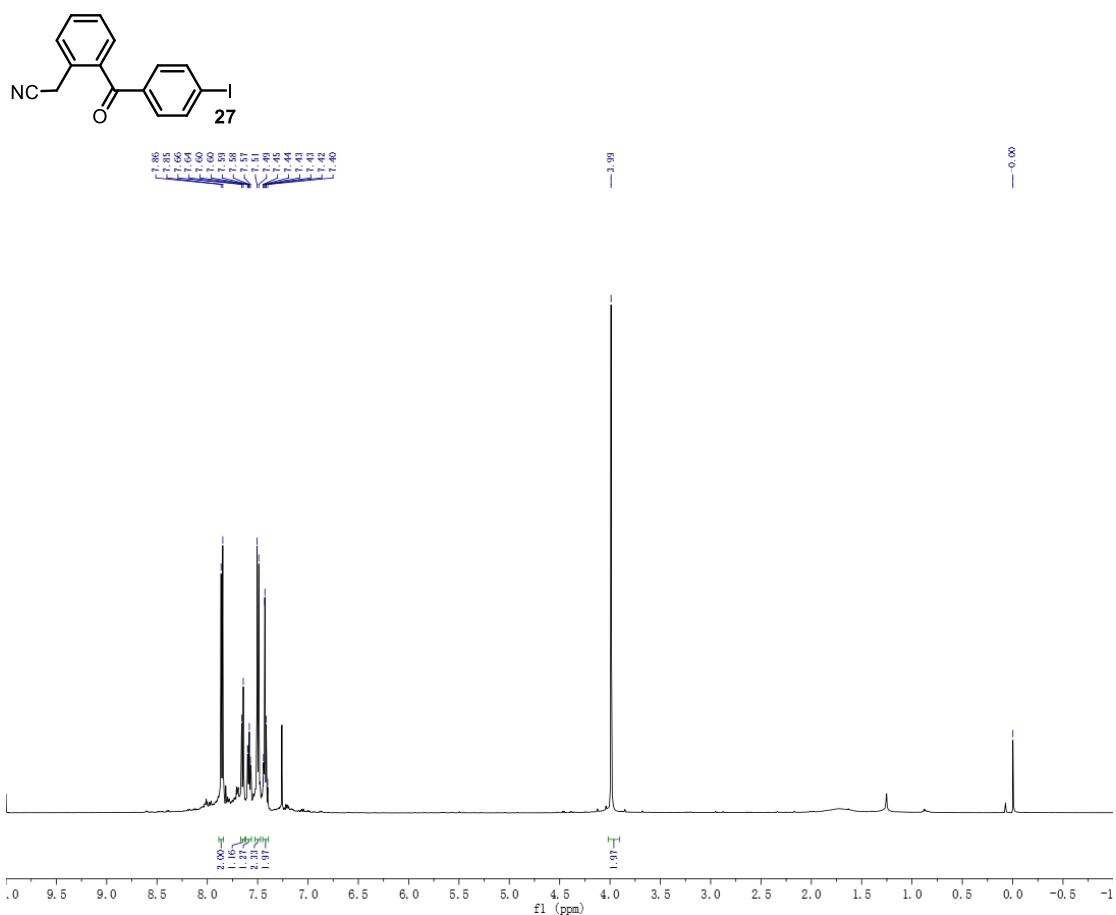
¹³C NMR of compound **25**



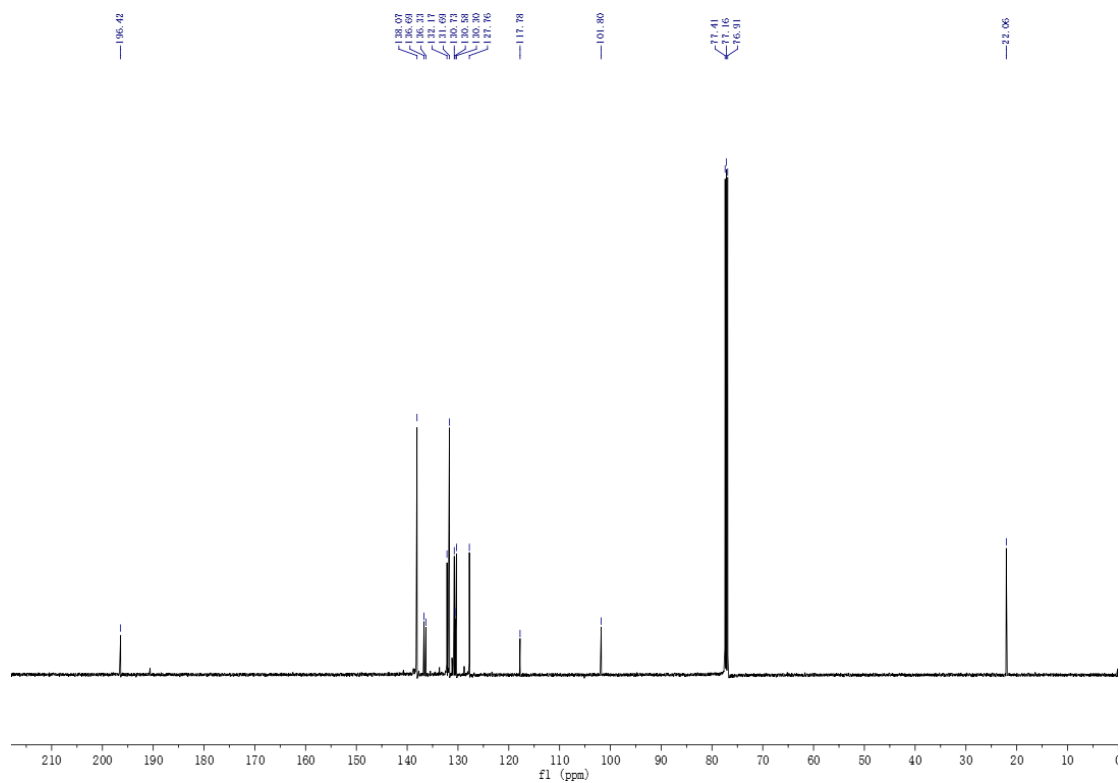
^1H NMR of compound **26**



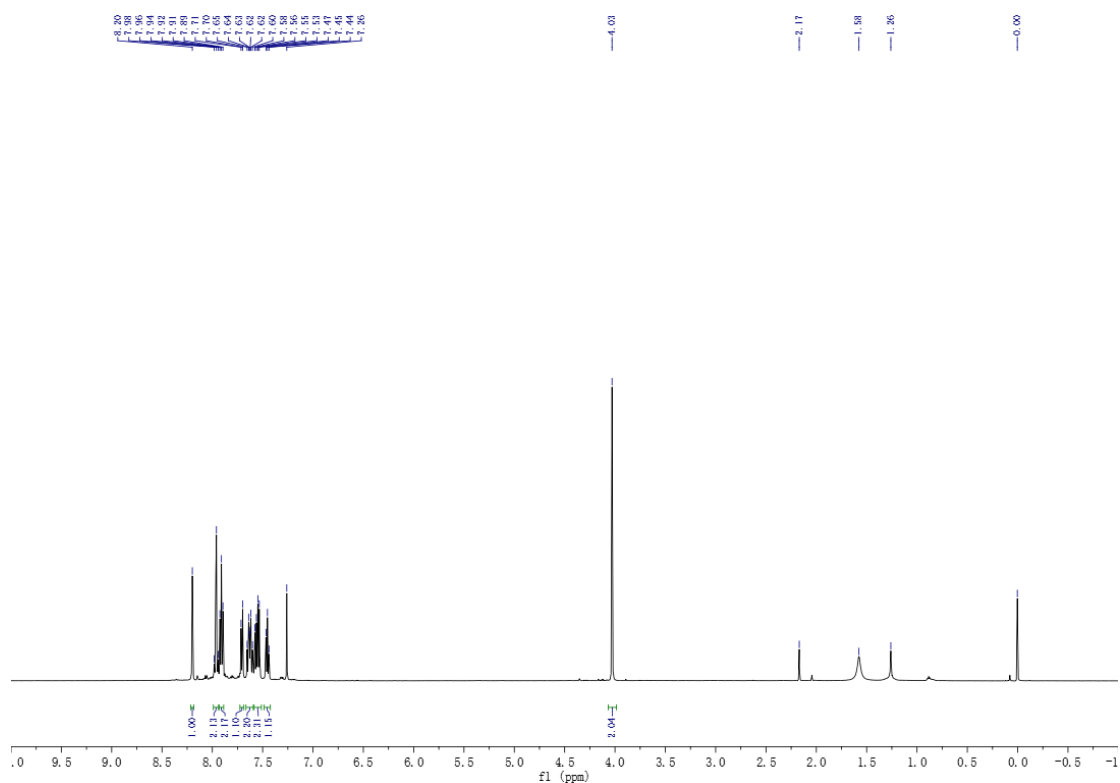
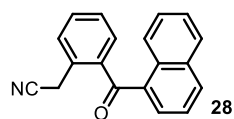
^{13}C NMR of compound **26**



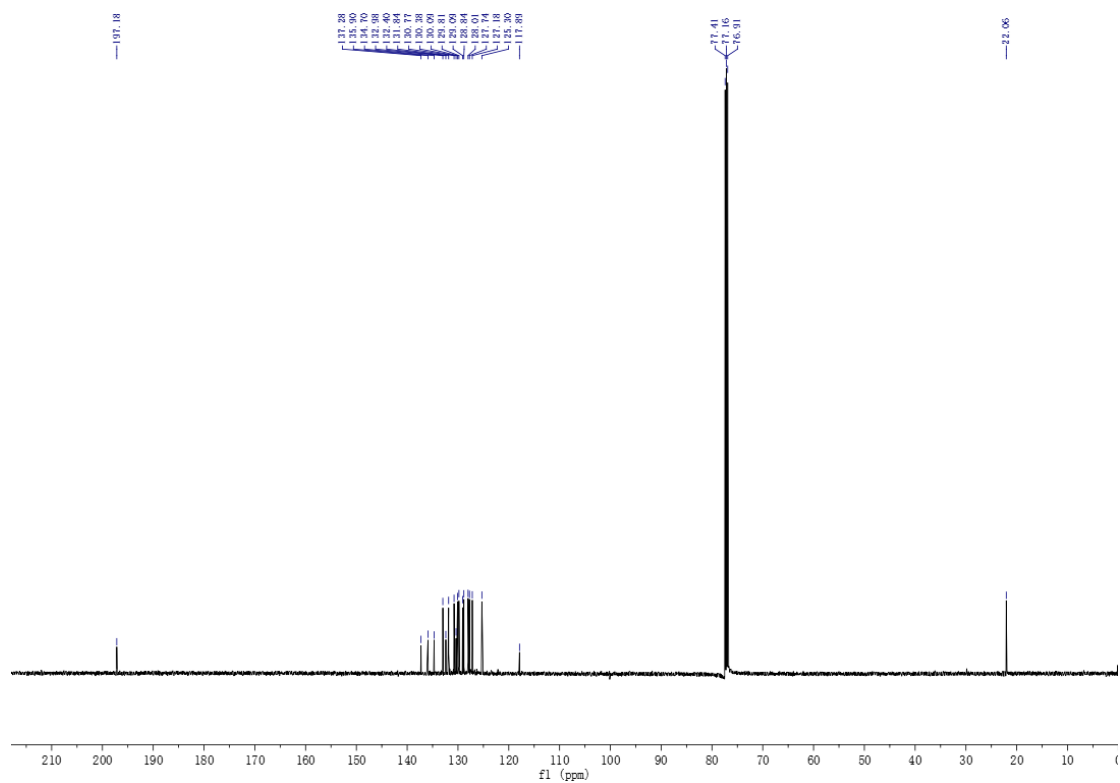
¹H NMR of compound **27**



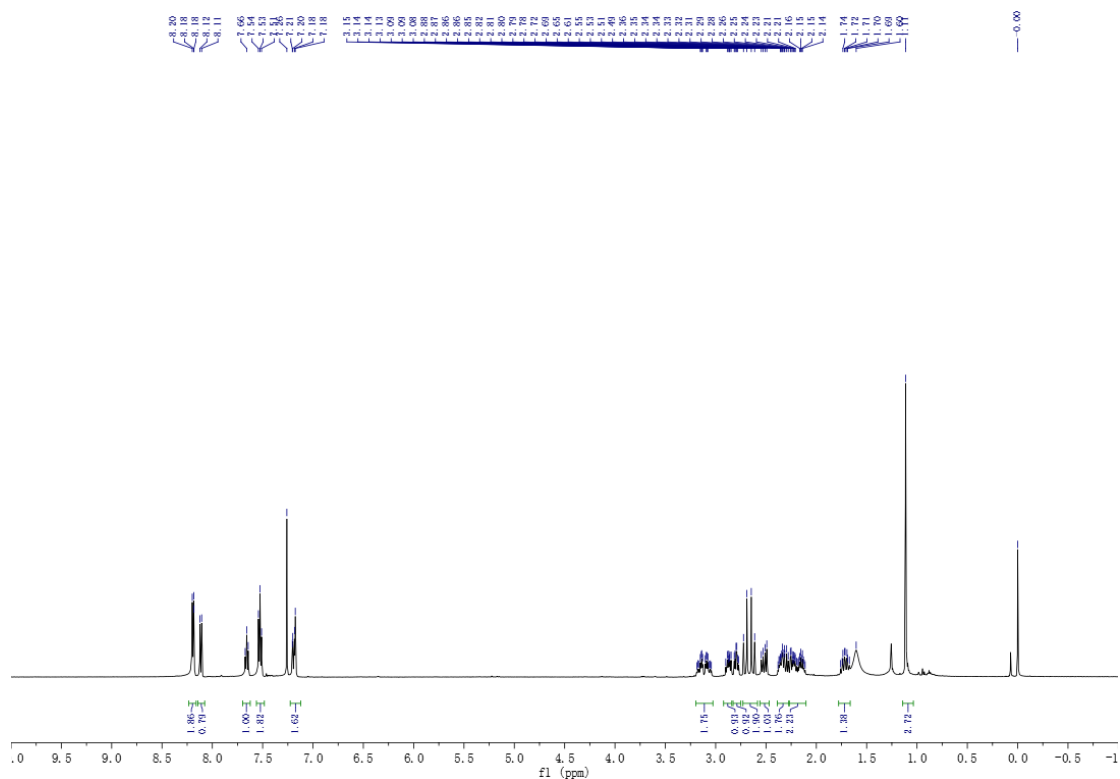
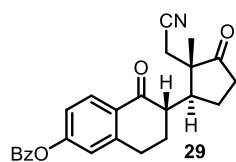
¹³C NMR of compound **27**

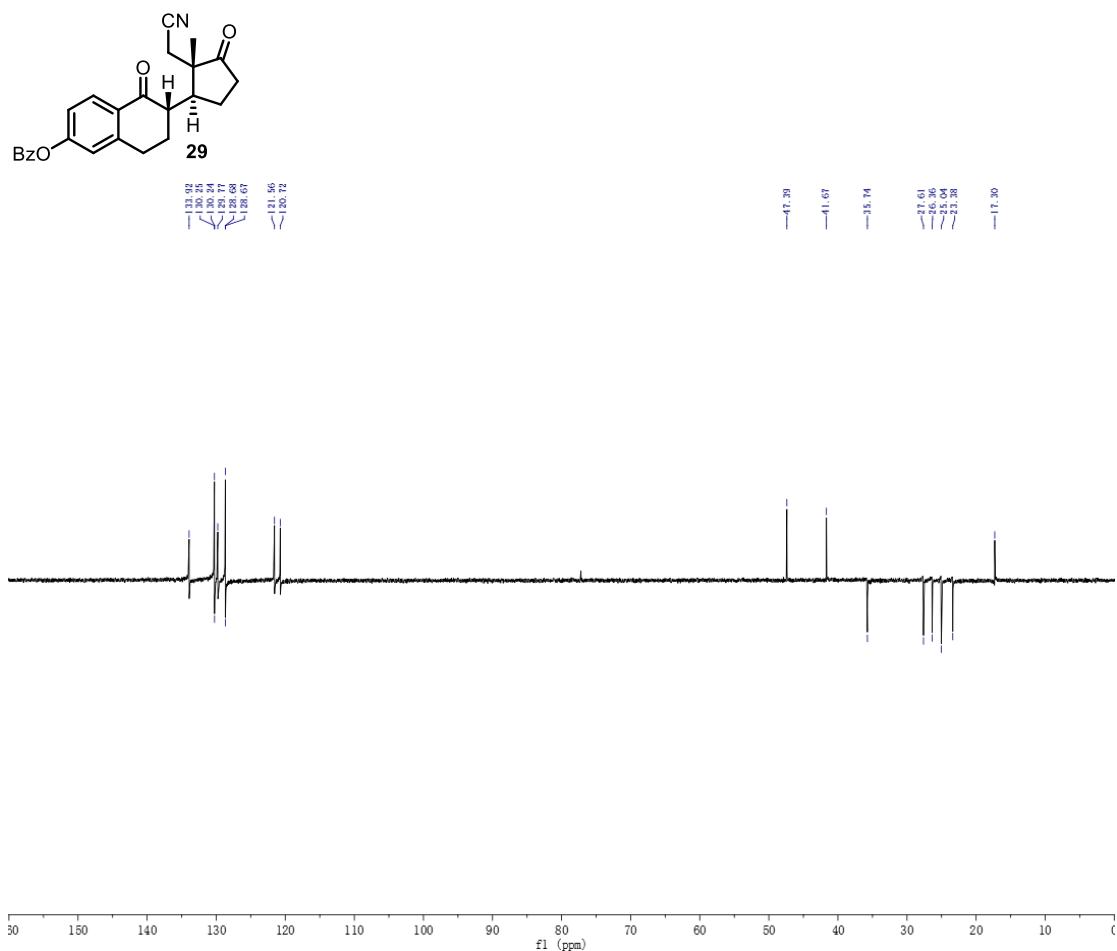


¹H NMR of compound **28**

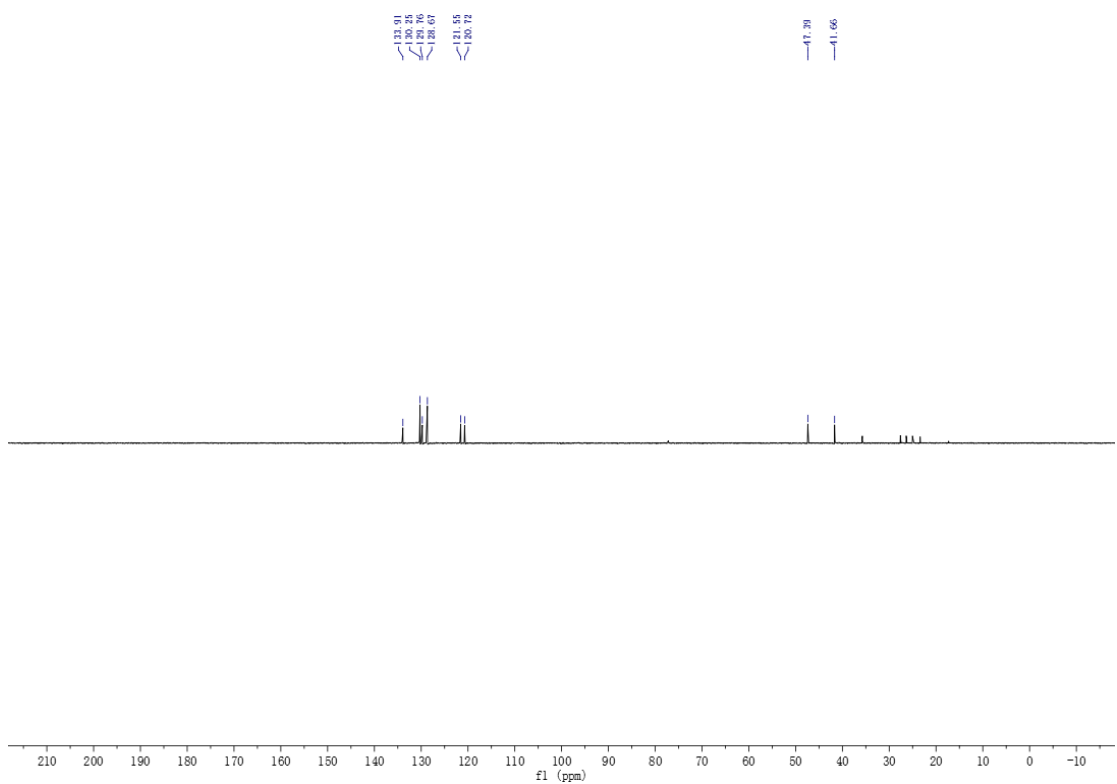


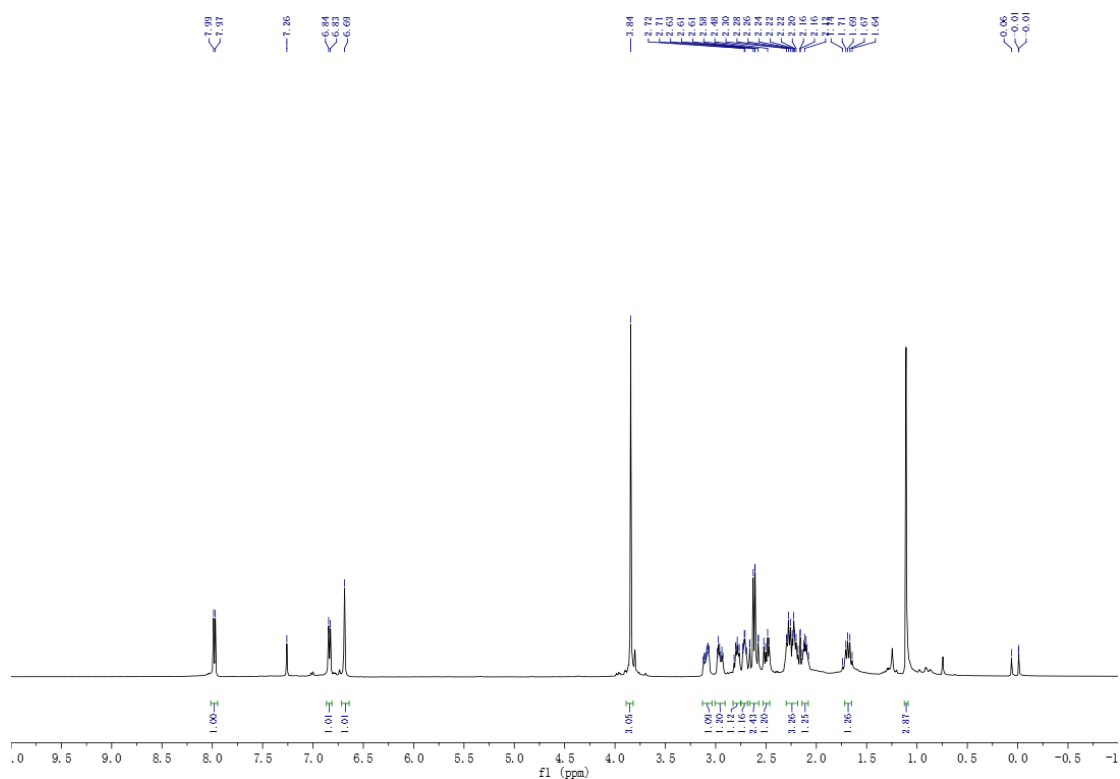
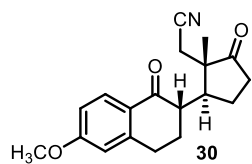
¹³C NMR of compound **28**



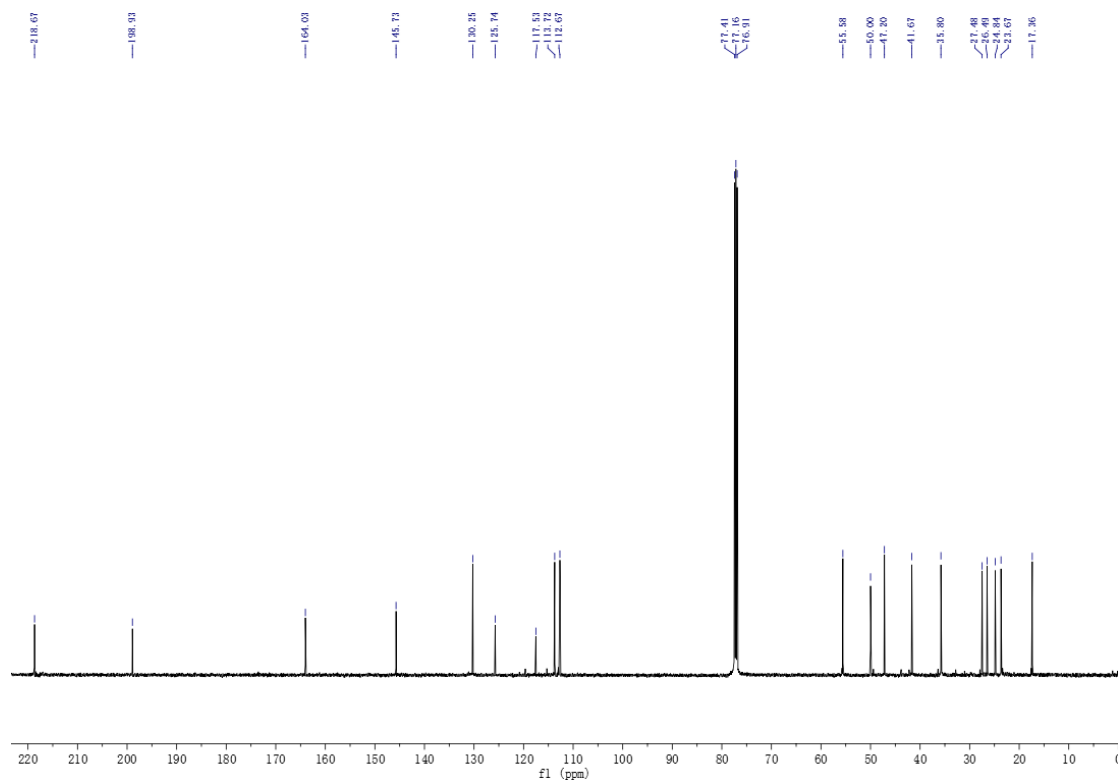


DEPT 135 of compound **29**

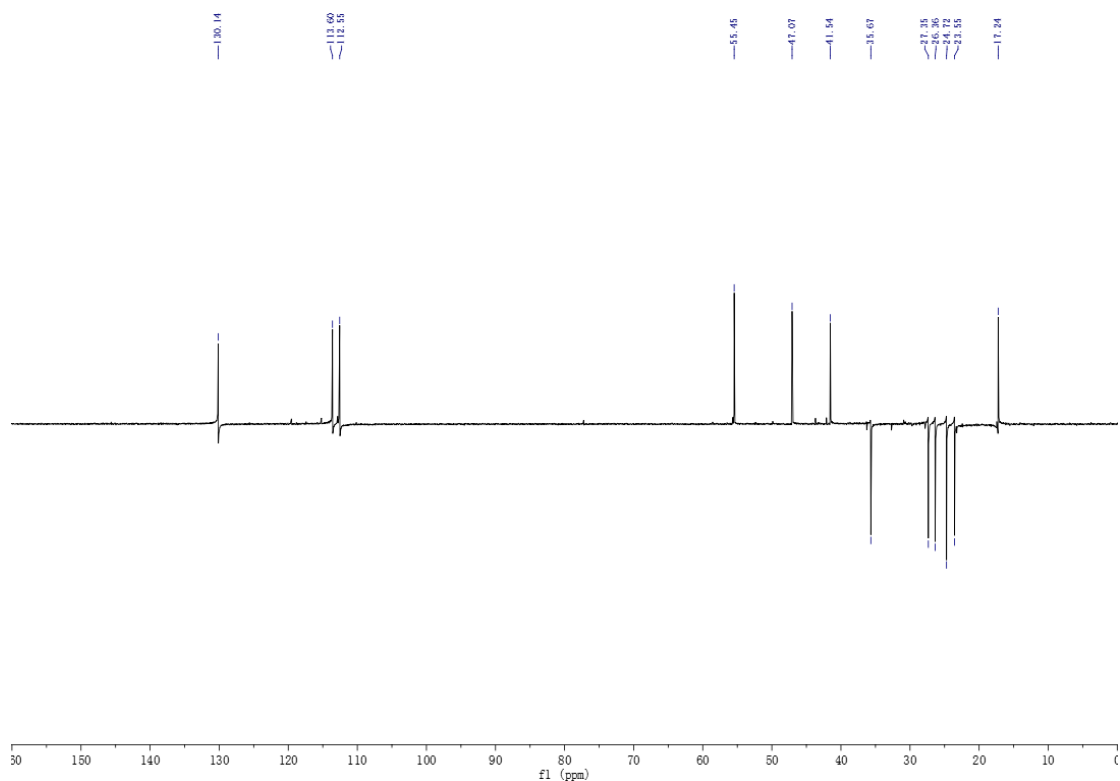
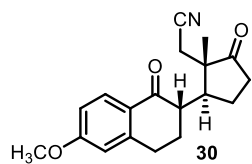




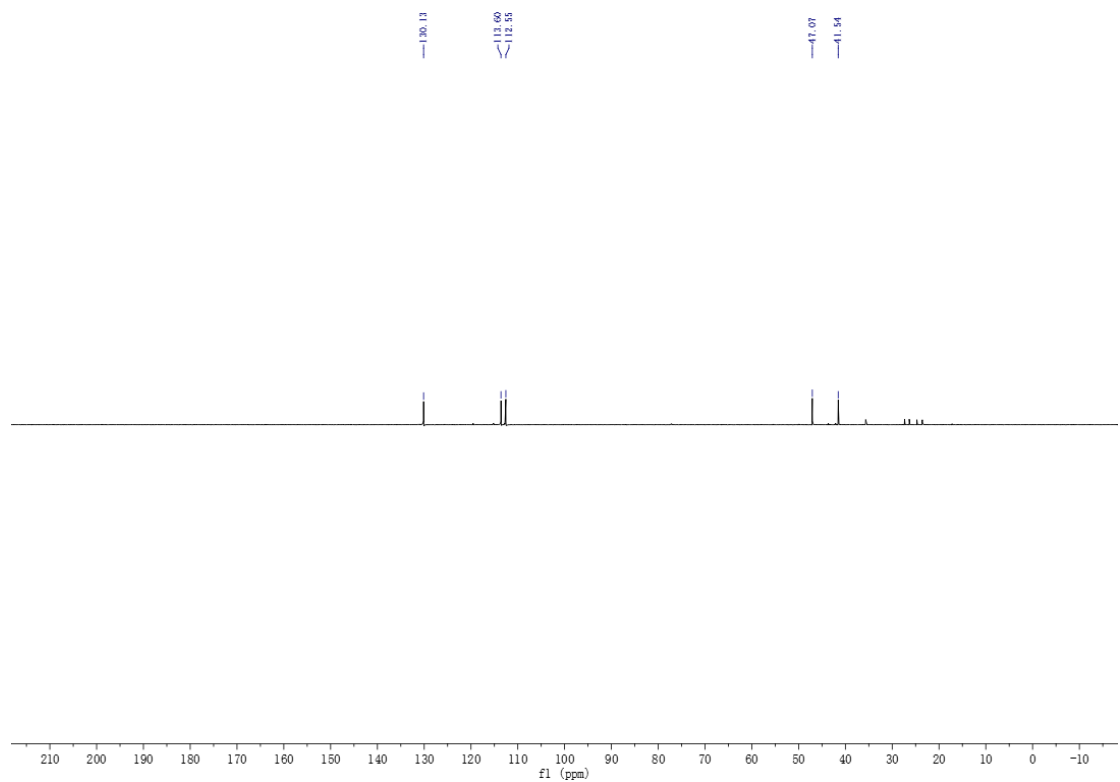
^1H NMR of compound **30**



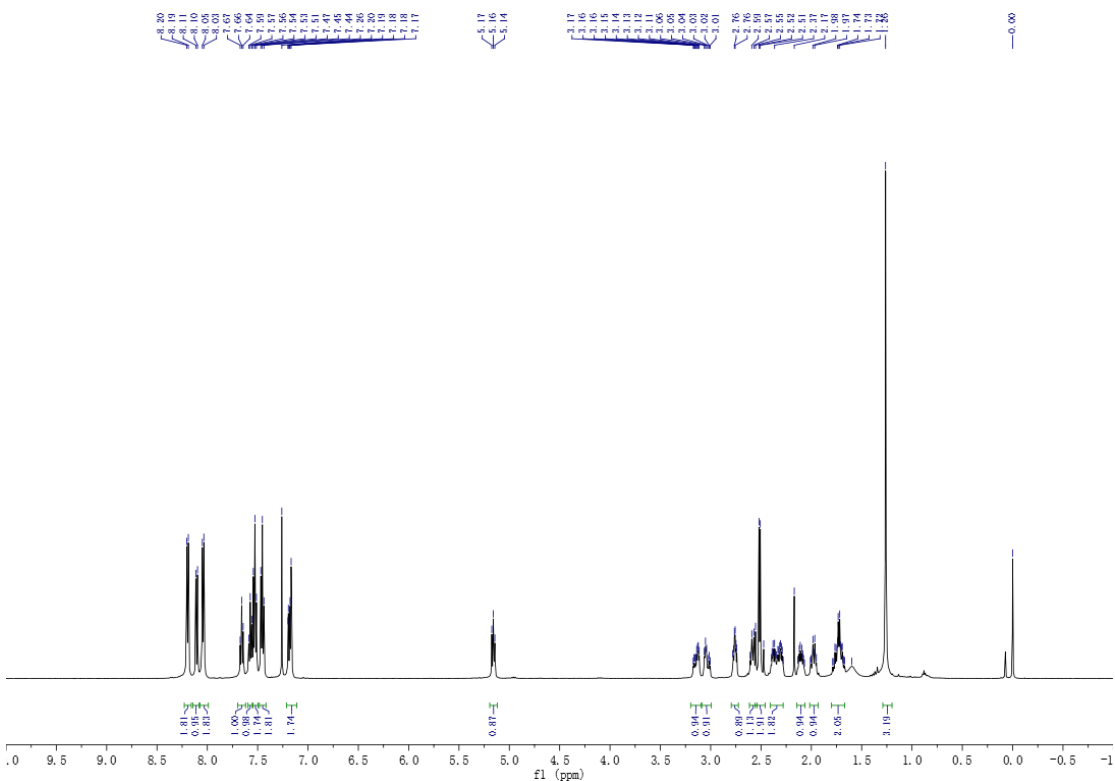
^{13}C NMR of compound **30**



DEPT 135 of compound **30**

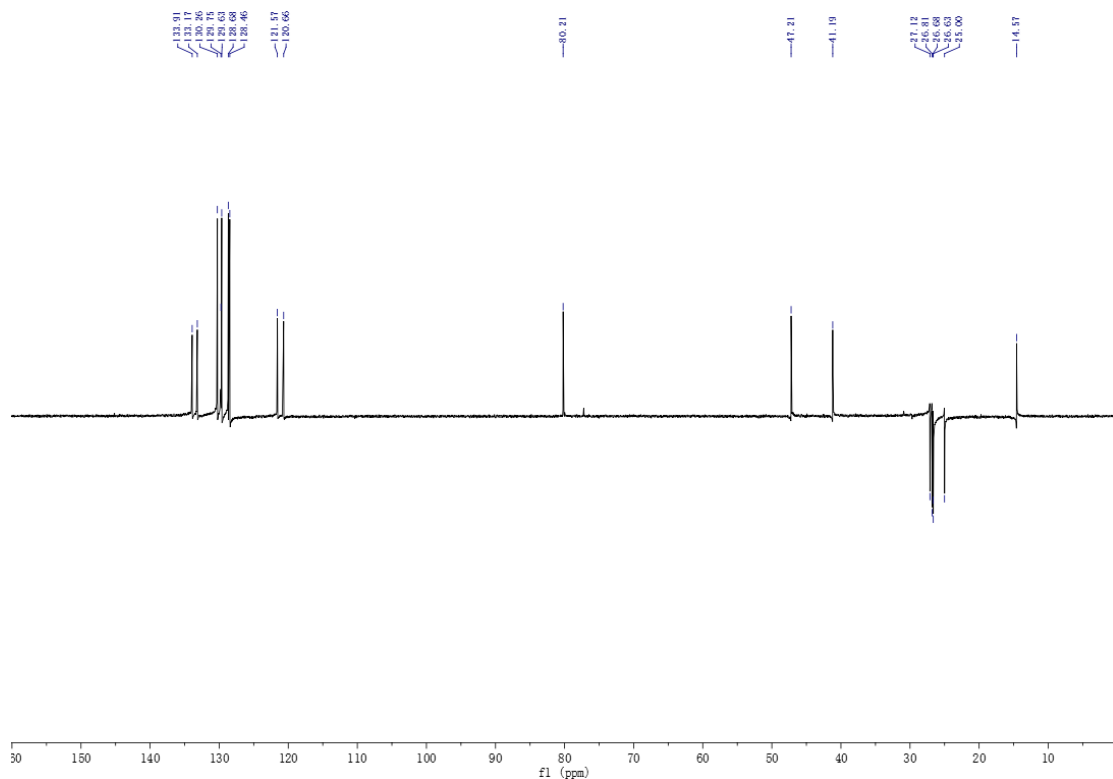
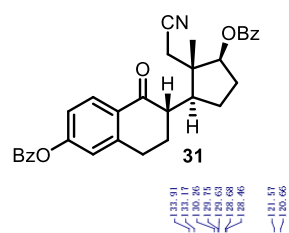


DEPT 90 of compound **30**

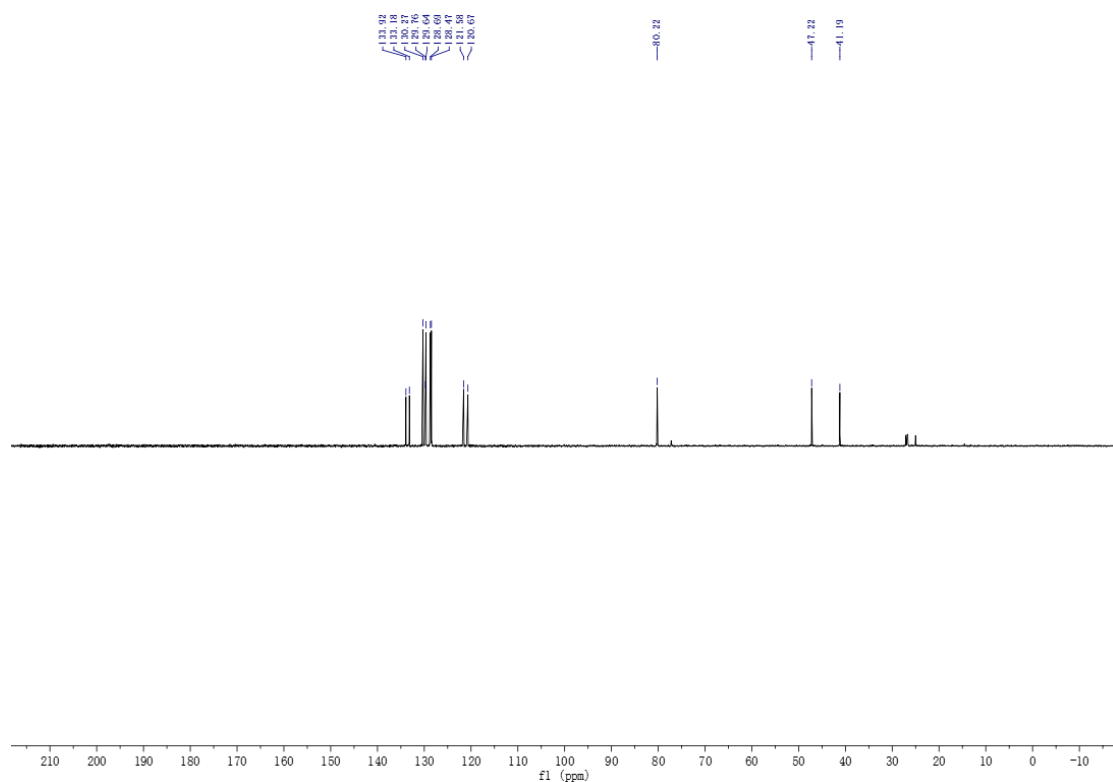


13C NMR spectrum (CDCl₃) of compound 10. The x-axis is labeled 'f1 (ppm)' and ranges from 0 to 210. The spectrum shows several peaks, with the most prominent one at approximately 77 ppm, which is the solvent peak (CDCl₃). Other significant peaks are labeled with their chemical shifts: 199.77, 166.08, 164.14, 155.08, 145.28, 137.54, 133.50, 130.40, 130.17, 128.89, 128.77, 128.61, 128.90, 117.62, 80.35, 77.41, 77.06, 76.81, 41.35, 45.07, 41.33, 27.85, 26.95, 26.83, 26.78, 24.19, and 14.72.

S104

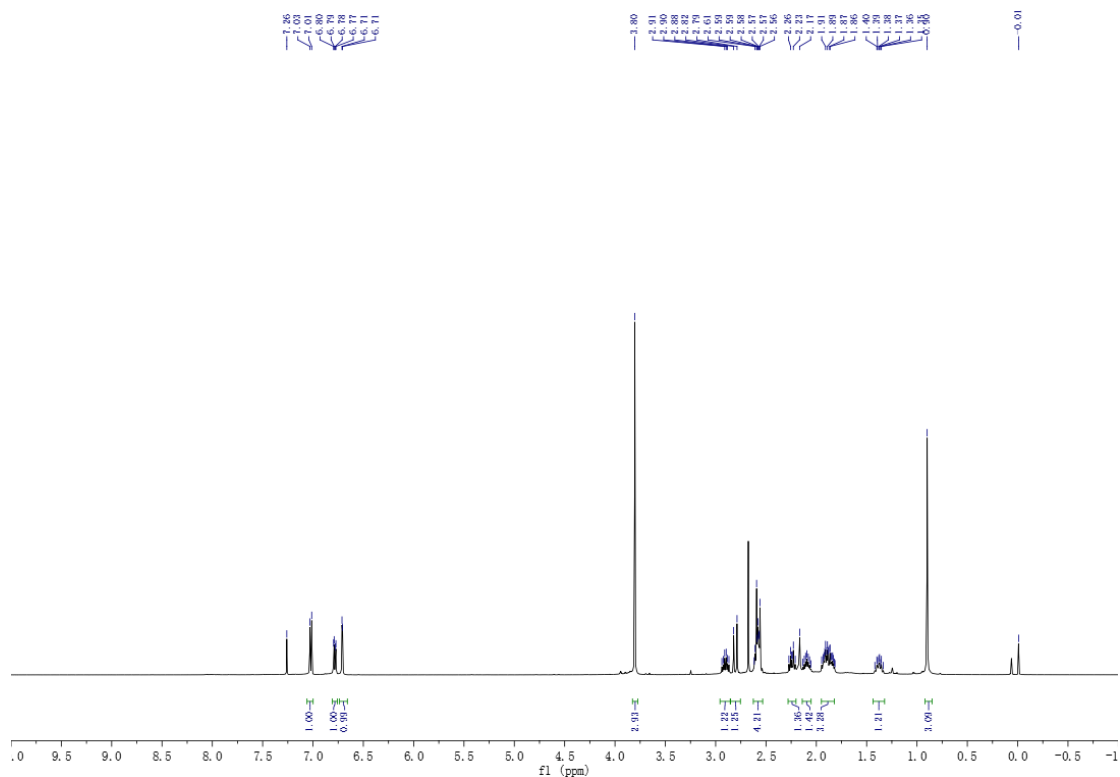
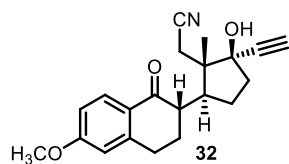


DEPT 135 of compound **31**

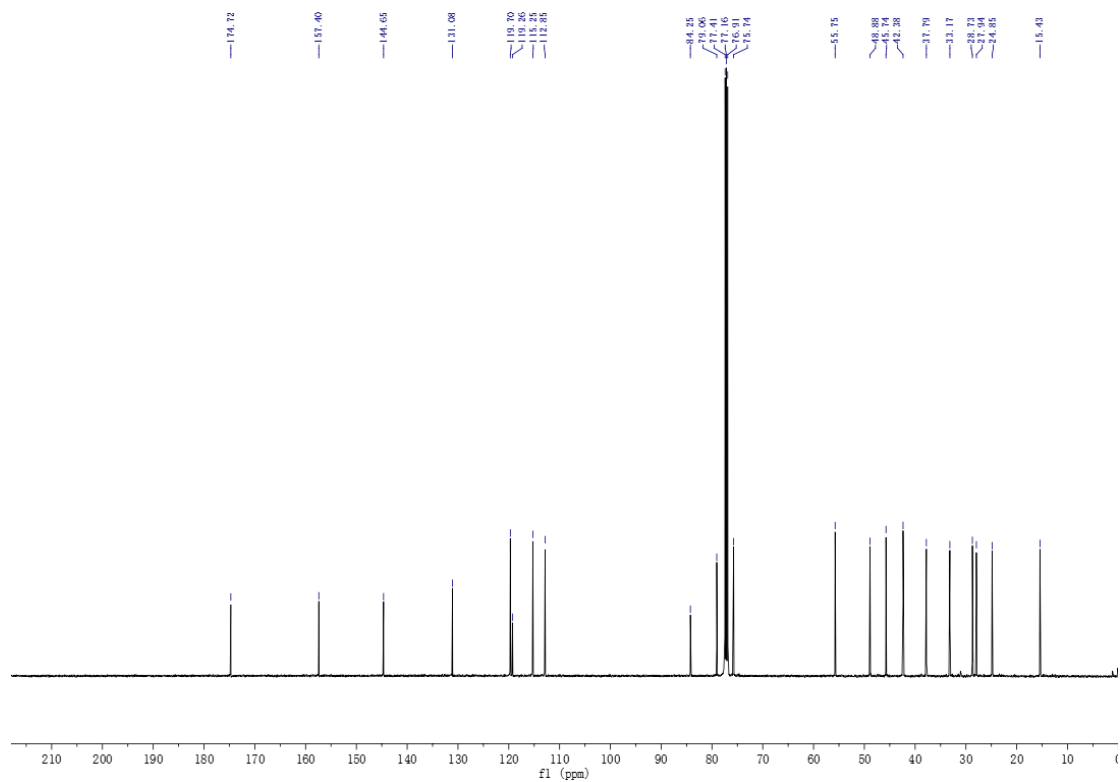


DEPT 90 of compound **31**

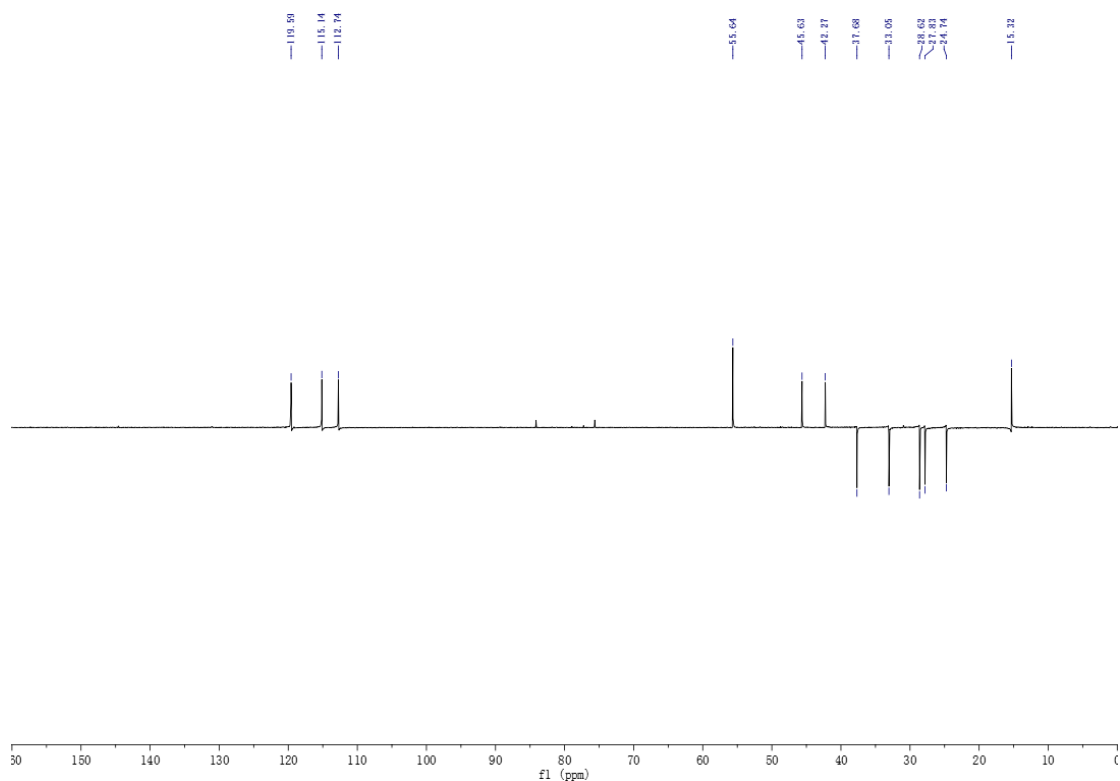
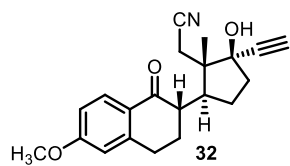
S105



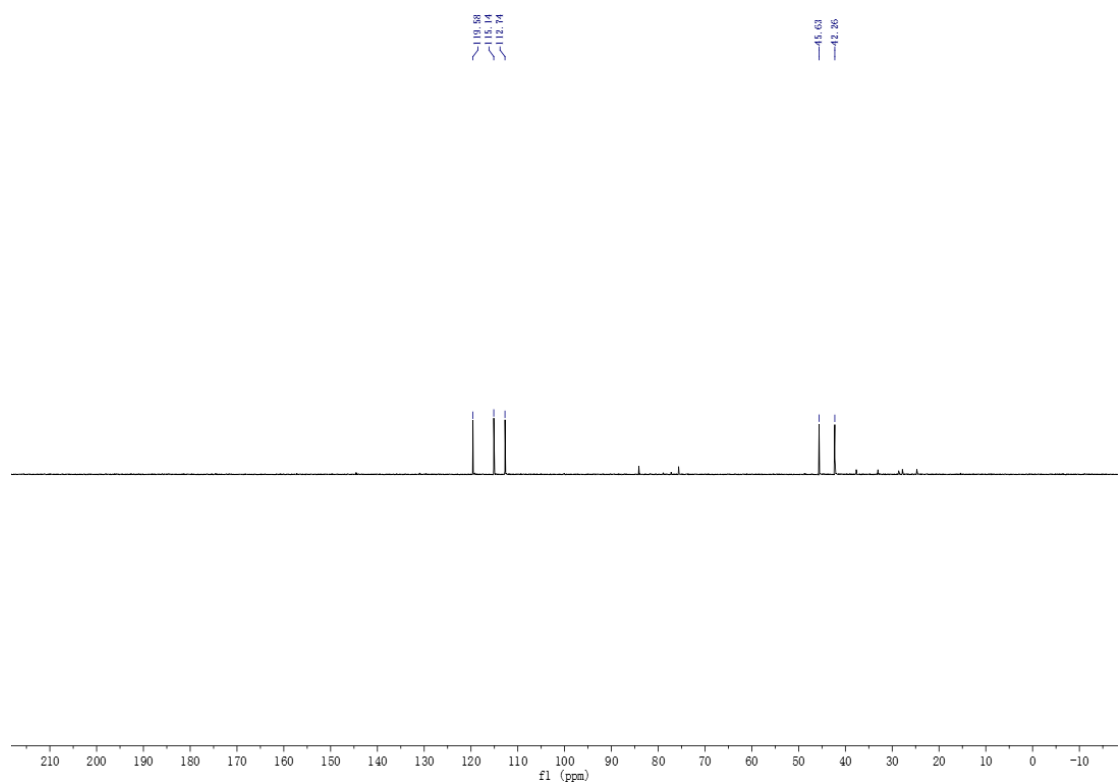
¹H NMR of compound **32**



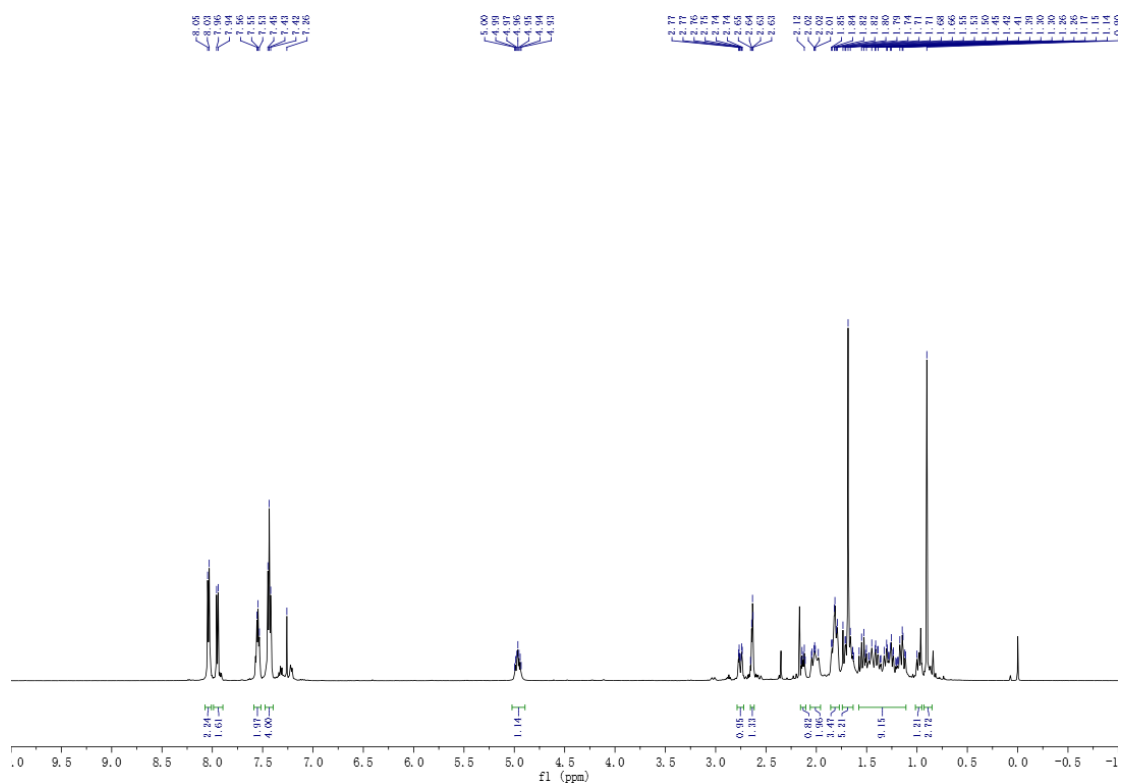
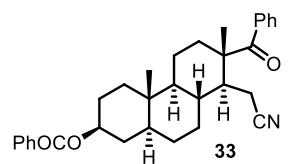
¹³C NMR of compound **32**



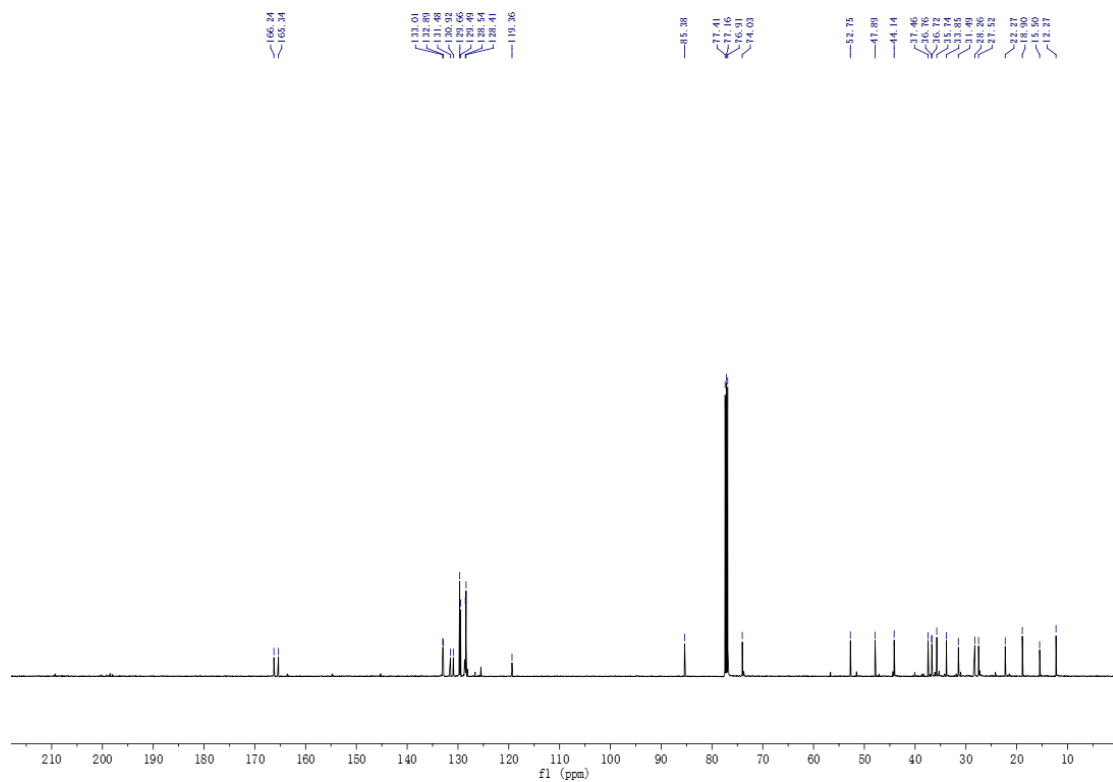
DEPT 135 of compound **32**



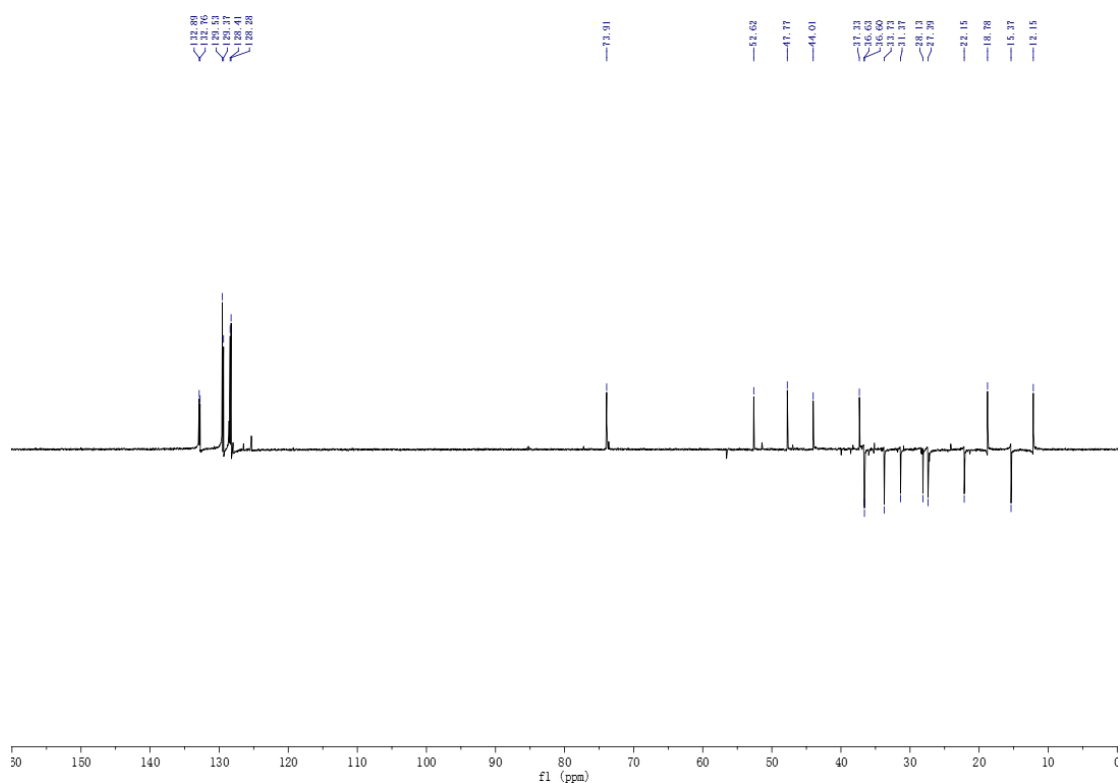
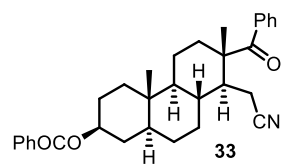
DEPT 90 of compound **32**



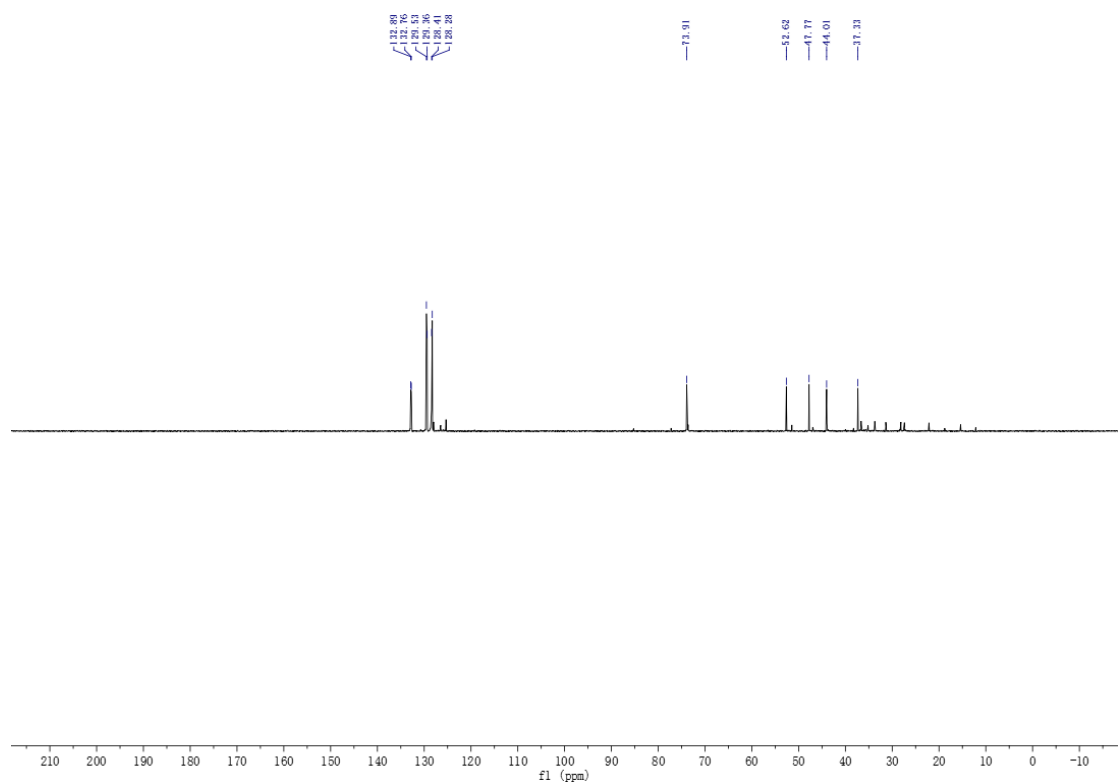
¹H NMR of compound **33**



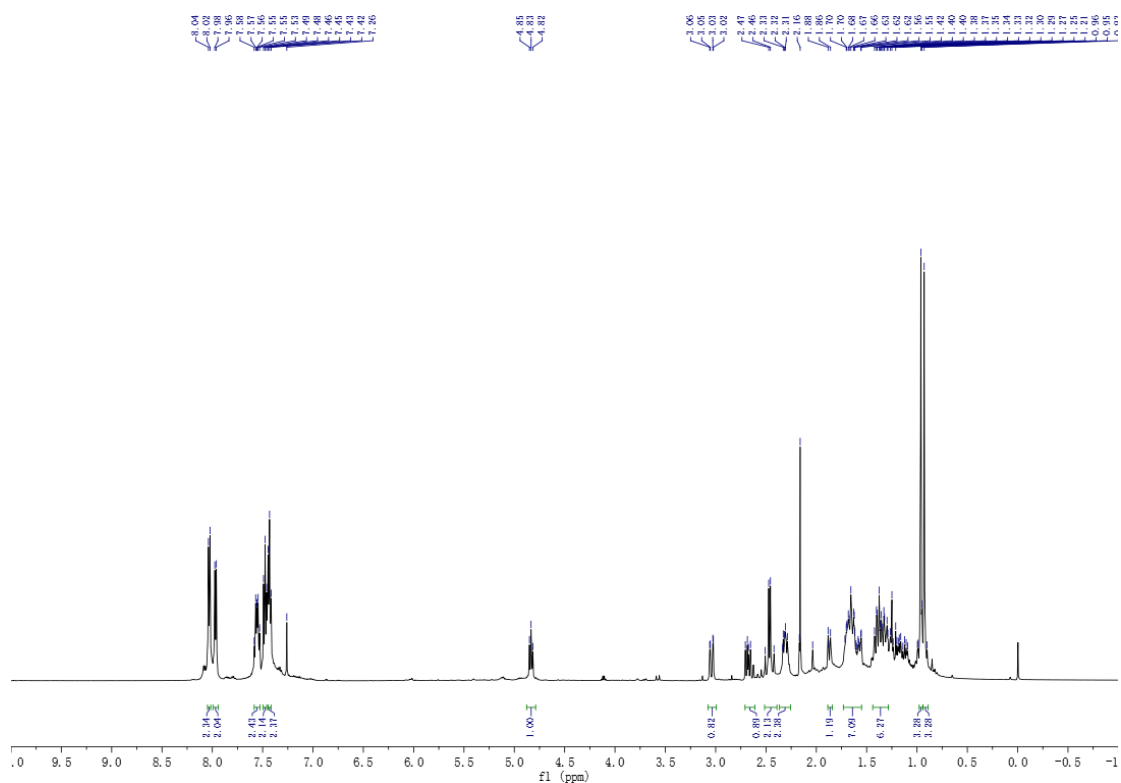
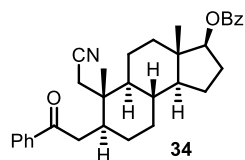
¹³C NMR of compound **33**



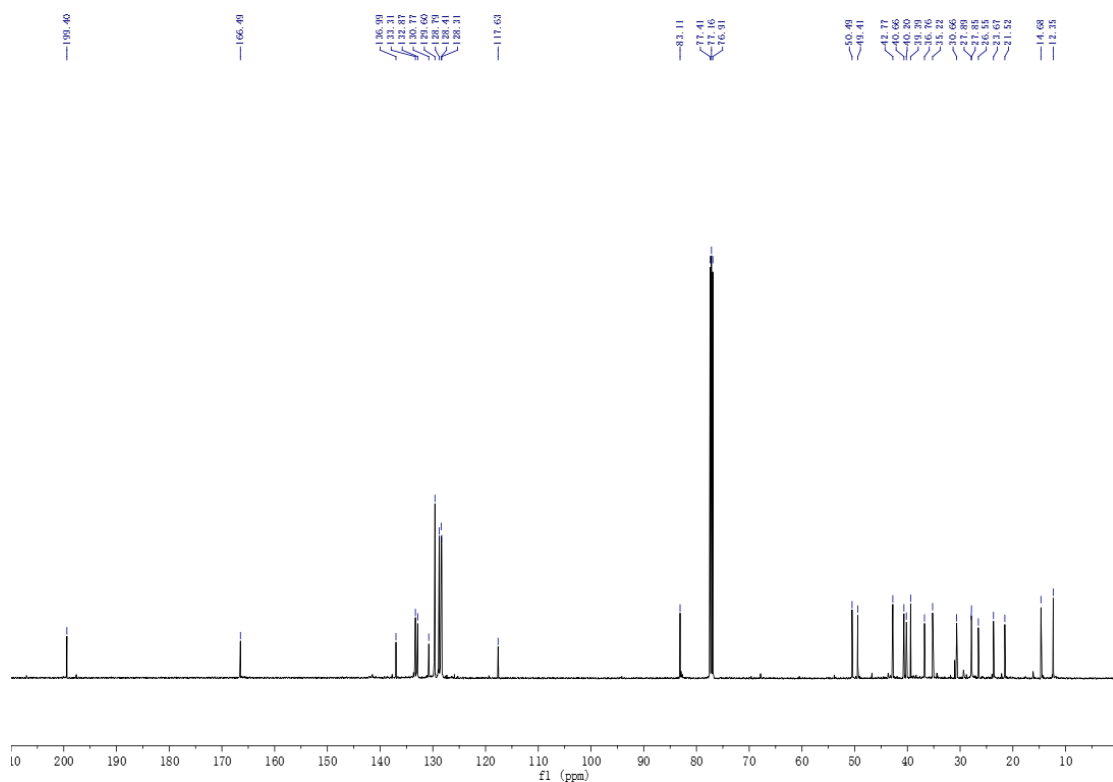
DEPT 135 of compound **33**



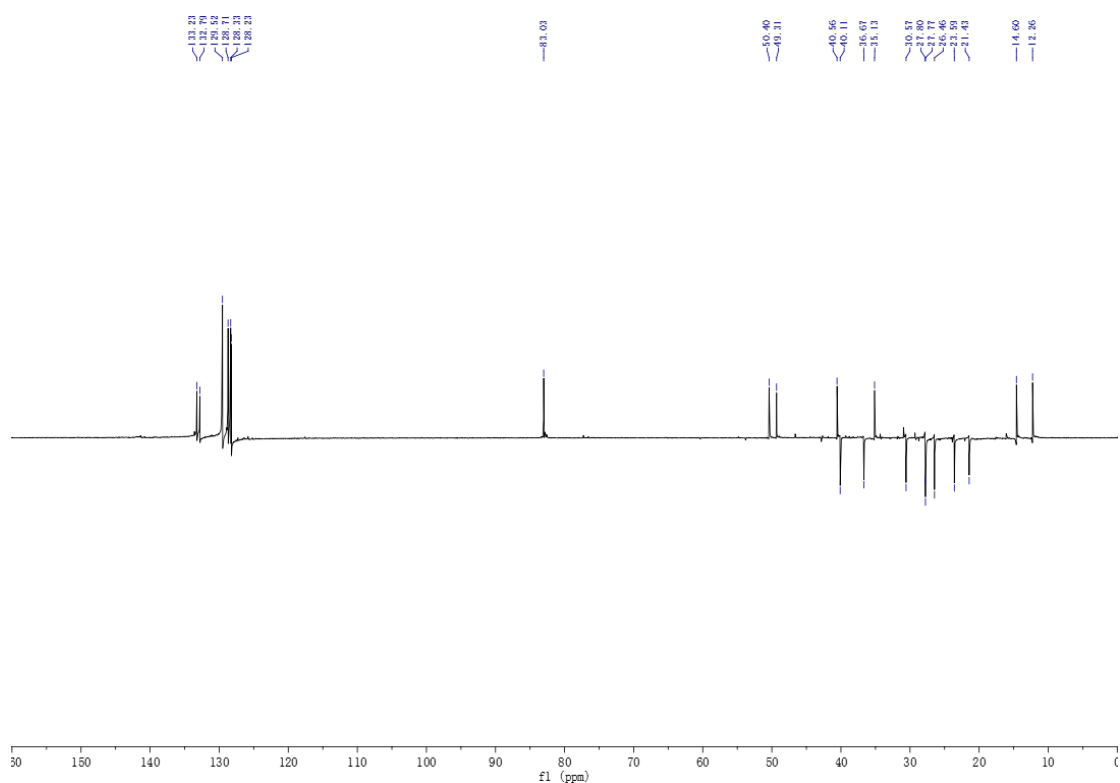
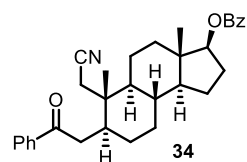
DEPT 90 of compound **33**



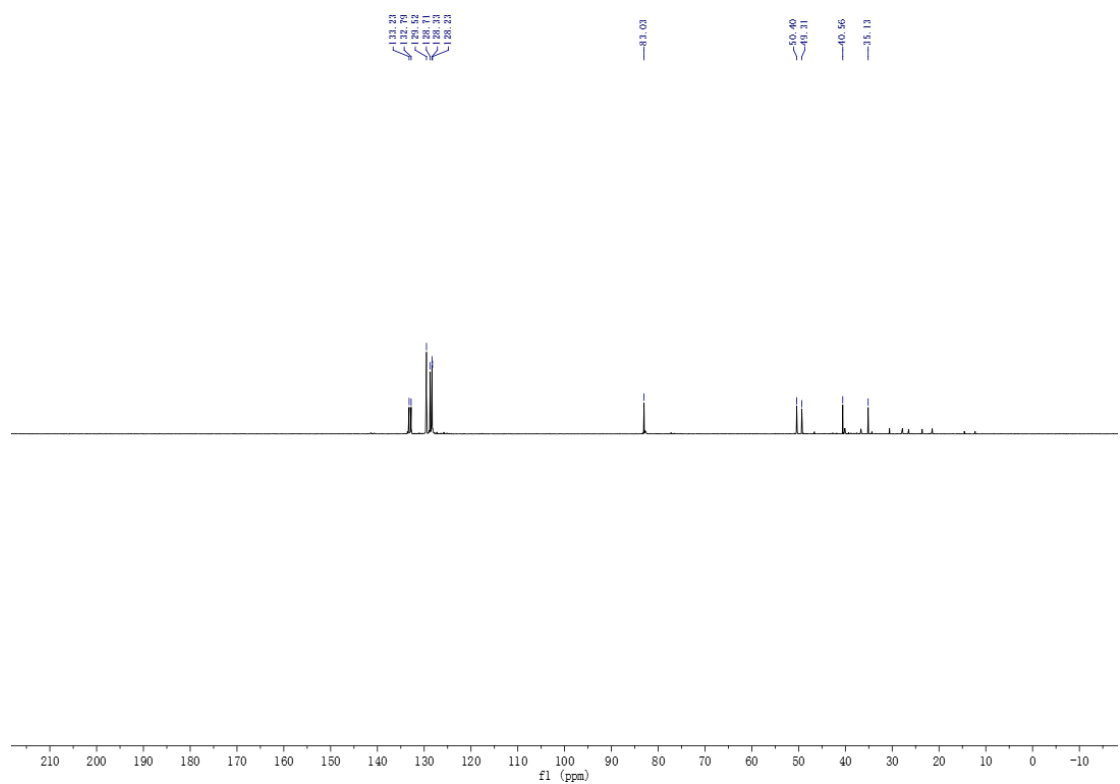
¹H NMR of compound **34**



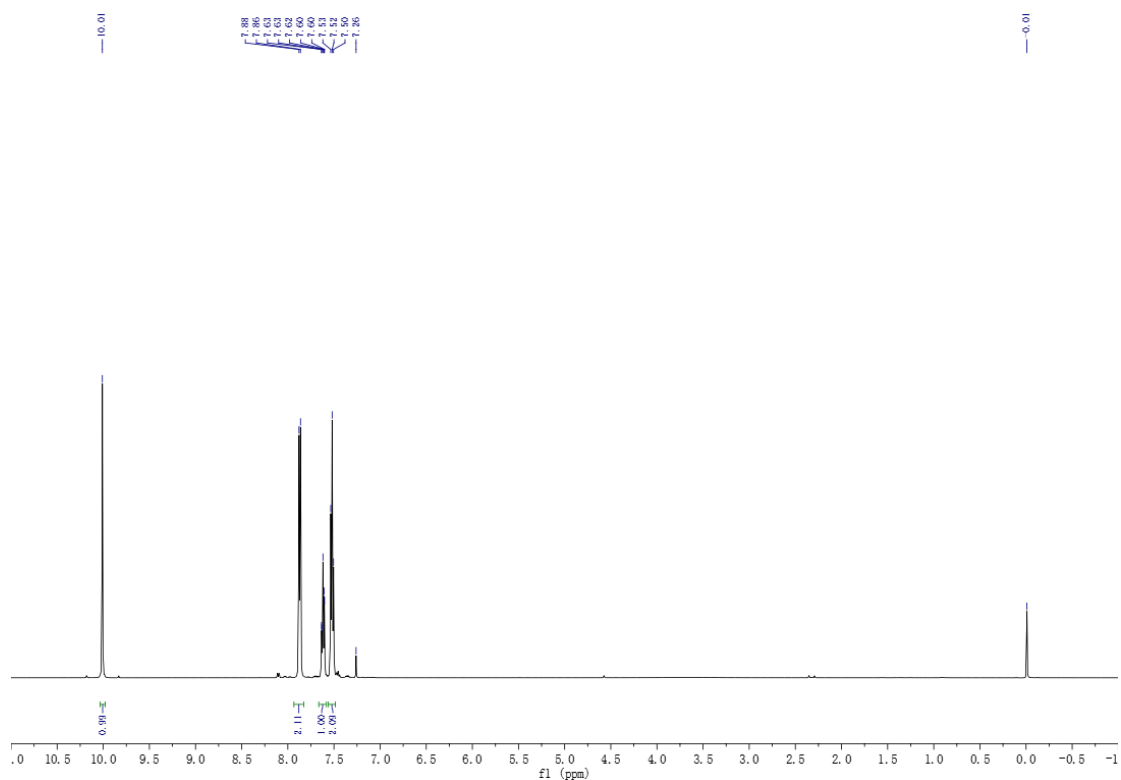
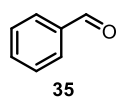
¹³C NMR of compound **34**



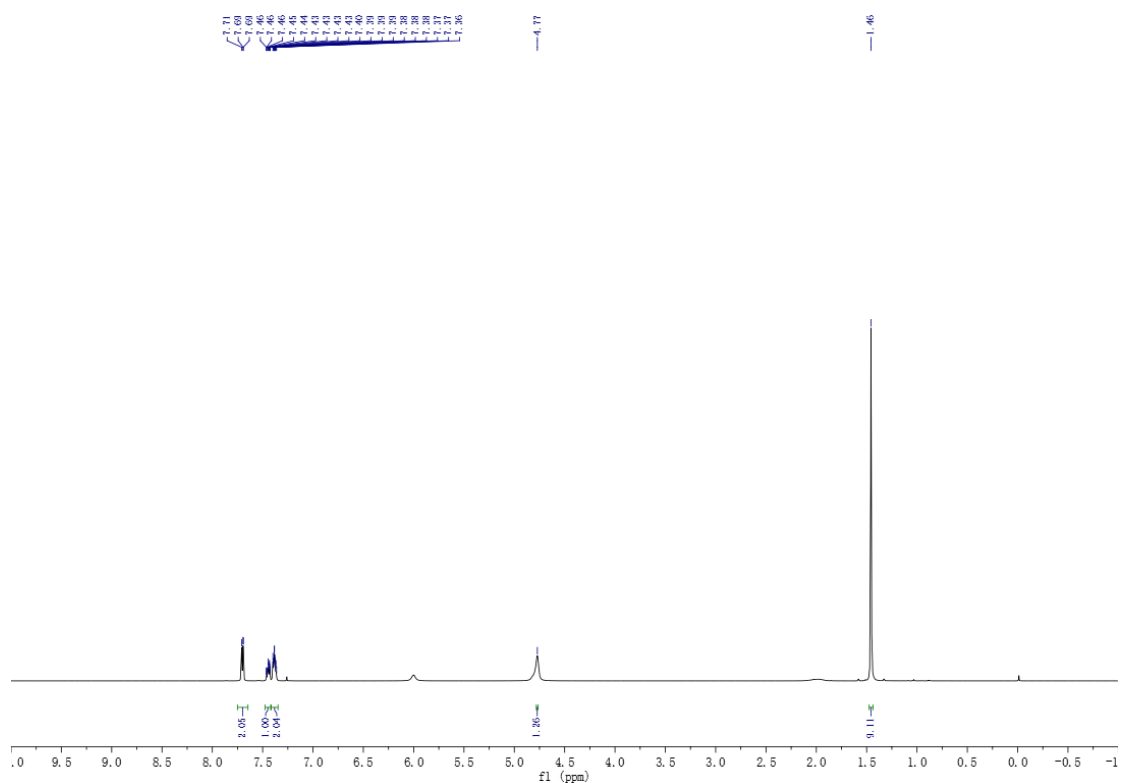
DEPT 135 of compound **34**



DEPT 90 of compound **34**

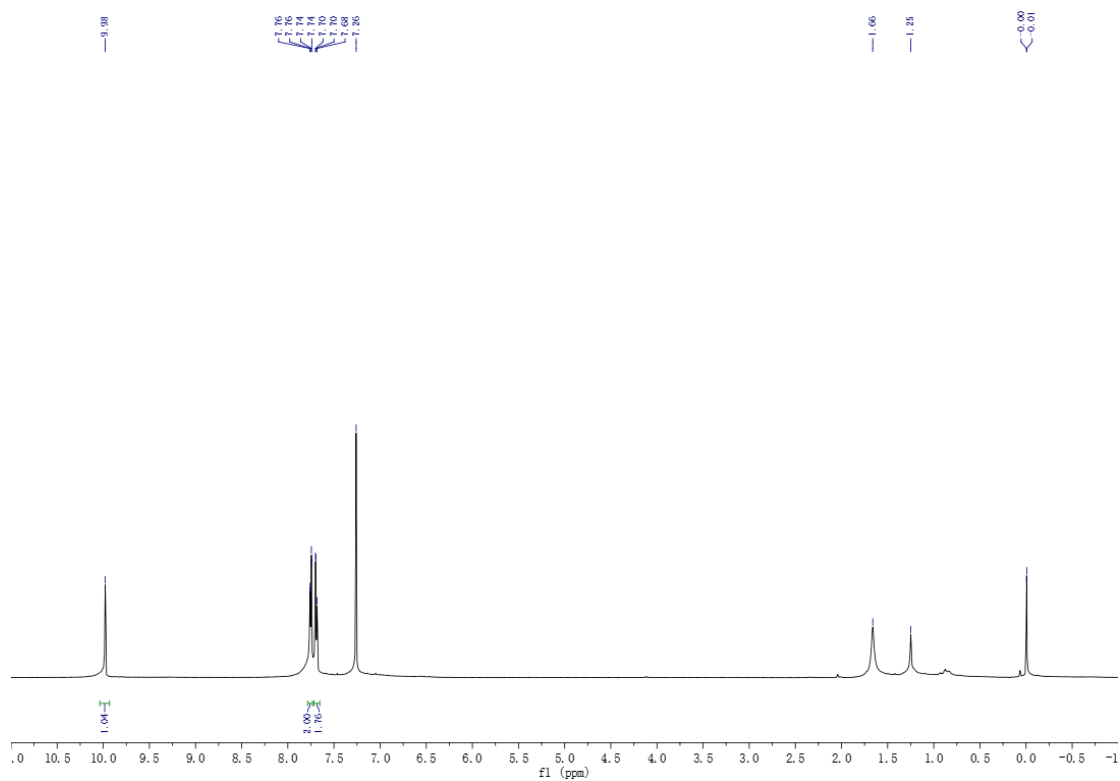
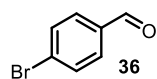


¹H NMR of compound **35**

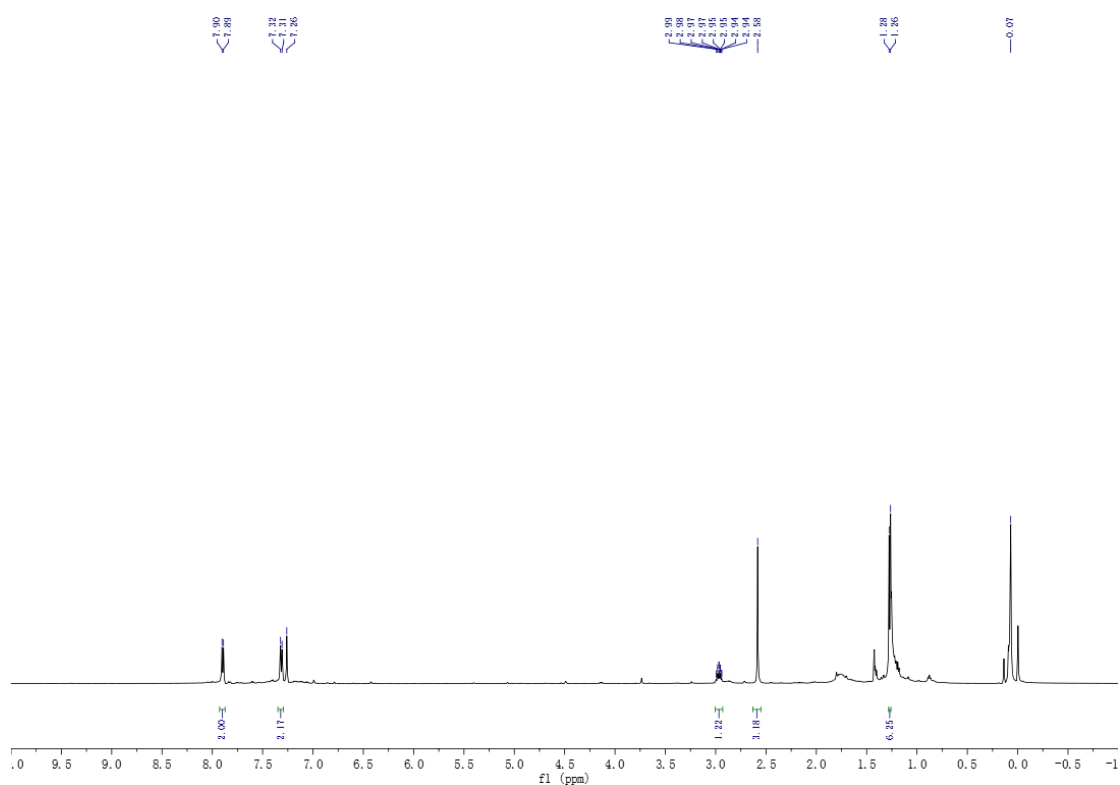
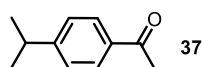


¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis is labeled 'f1 (ppm)' and ranges from 210 to 0. The spectrum shows several peaks with their corresponding chemical shifts labeled above them: 167.08, 135.99, 131.15, 129.54, 126.79, 77.41, 77.16, 76.91, 51.70, and 28.96. A solvent triplet is visible around 77 ppm.

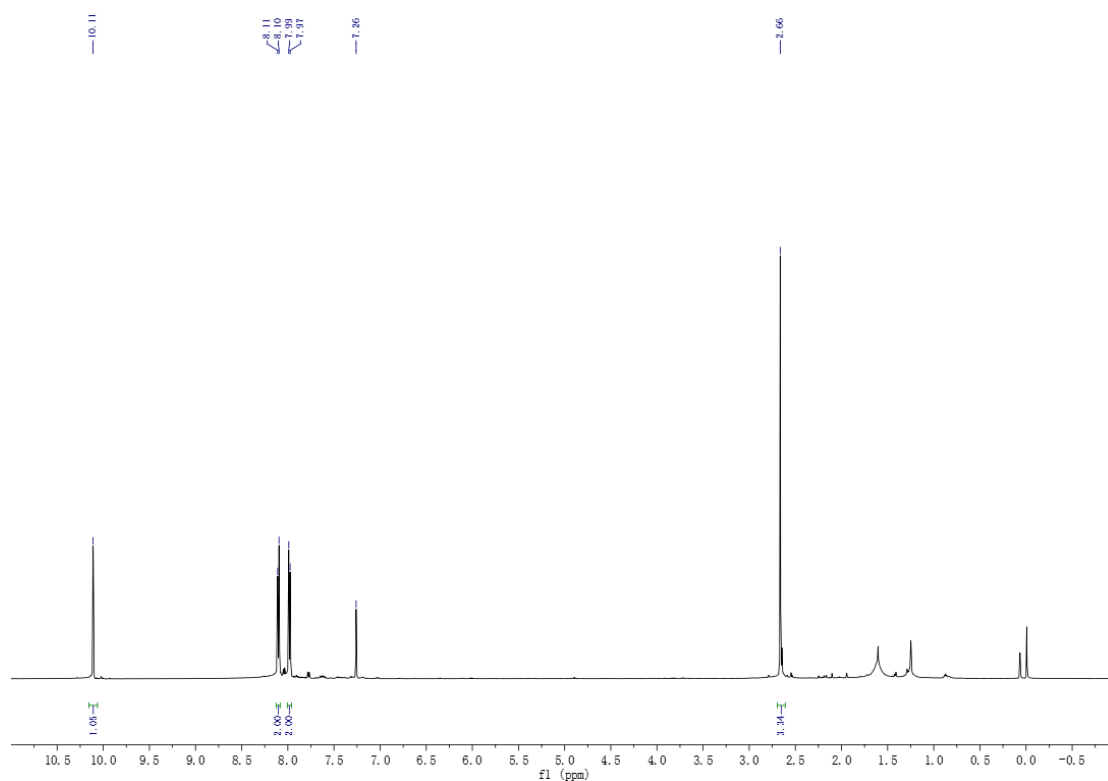
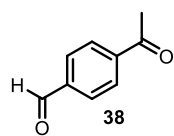
S113



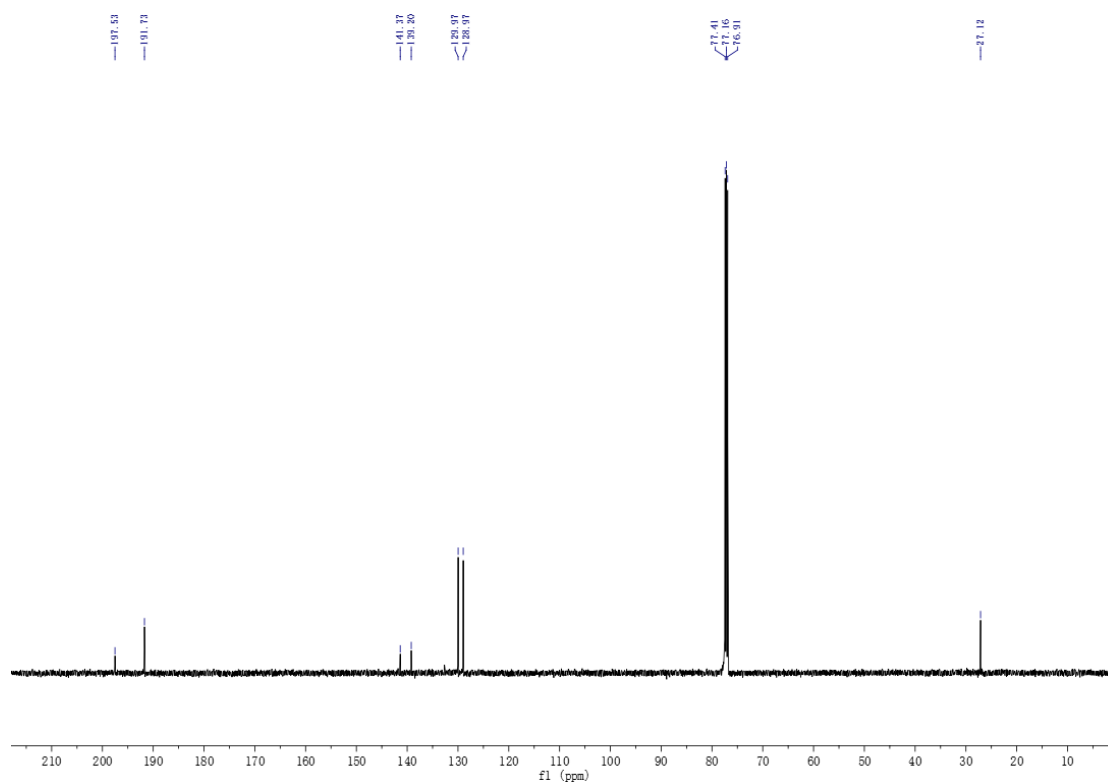
¹H NMR of compound **36**



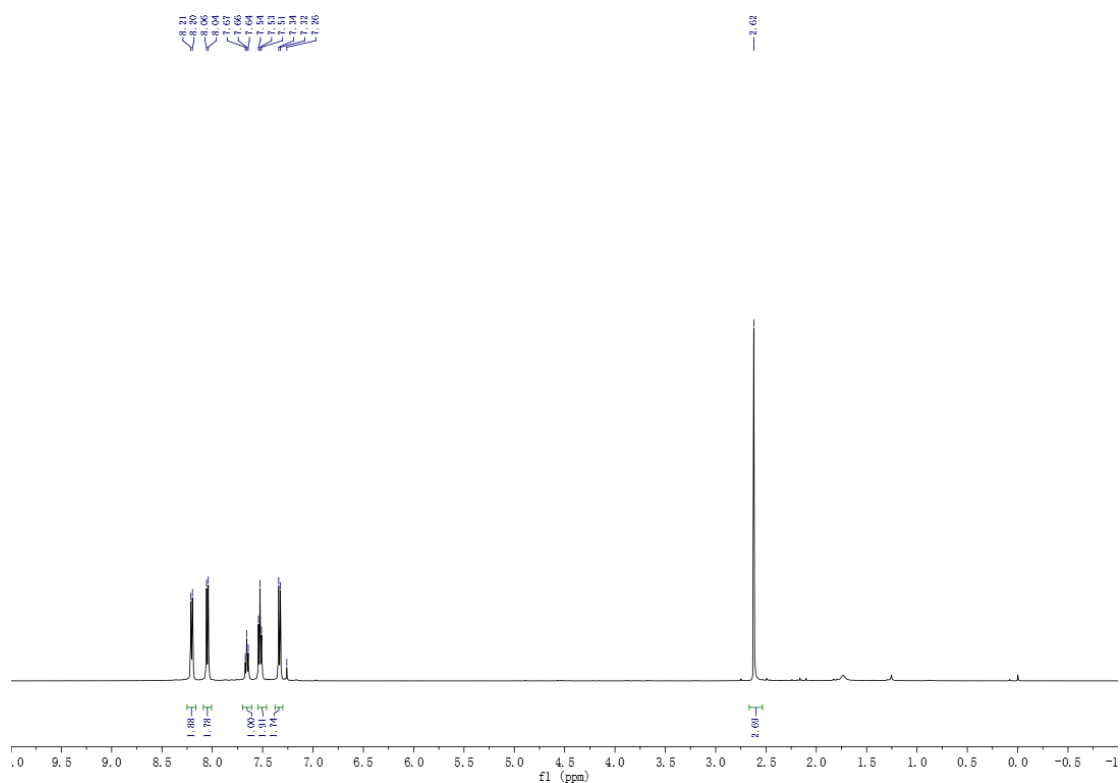
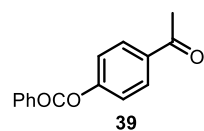
¹H NMR of compound **37**



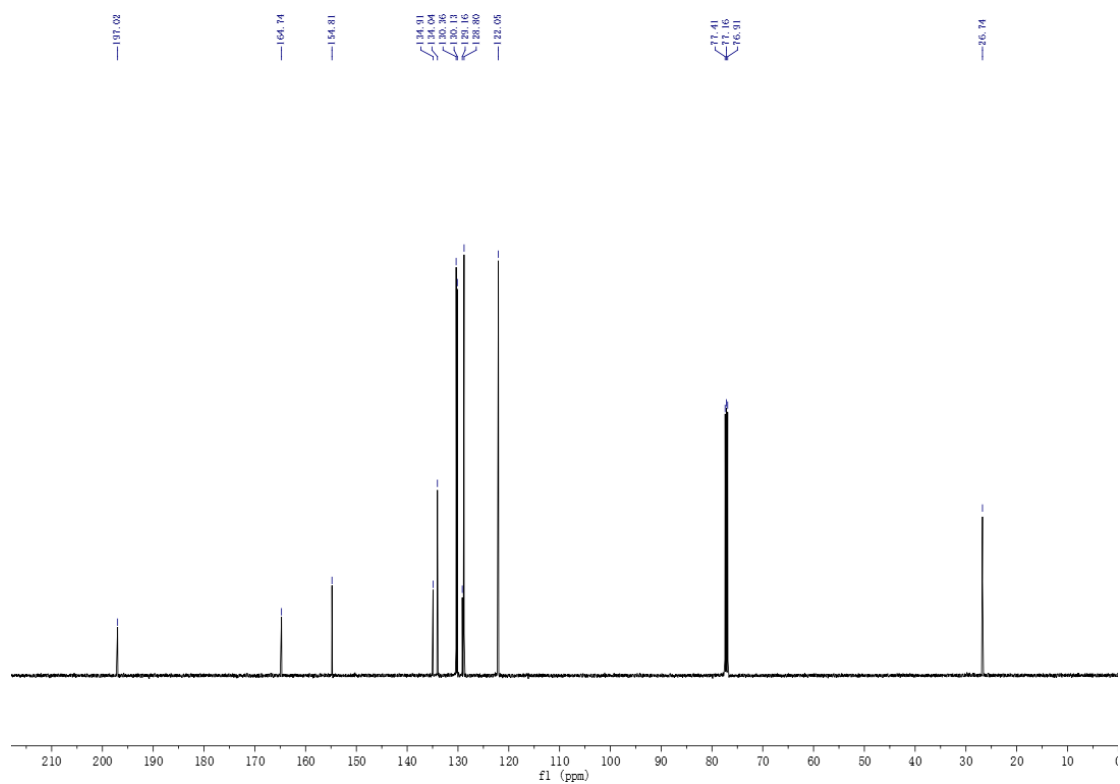
^1H NMR of compound **38**



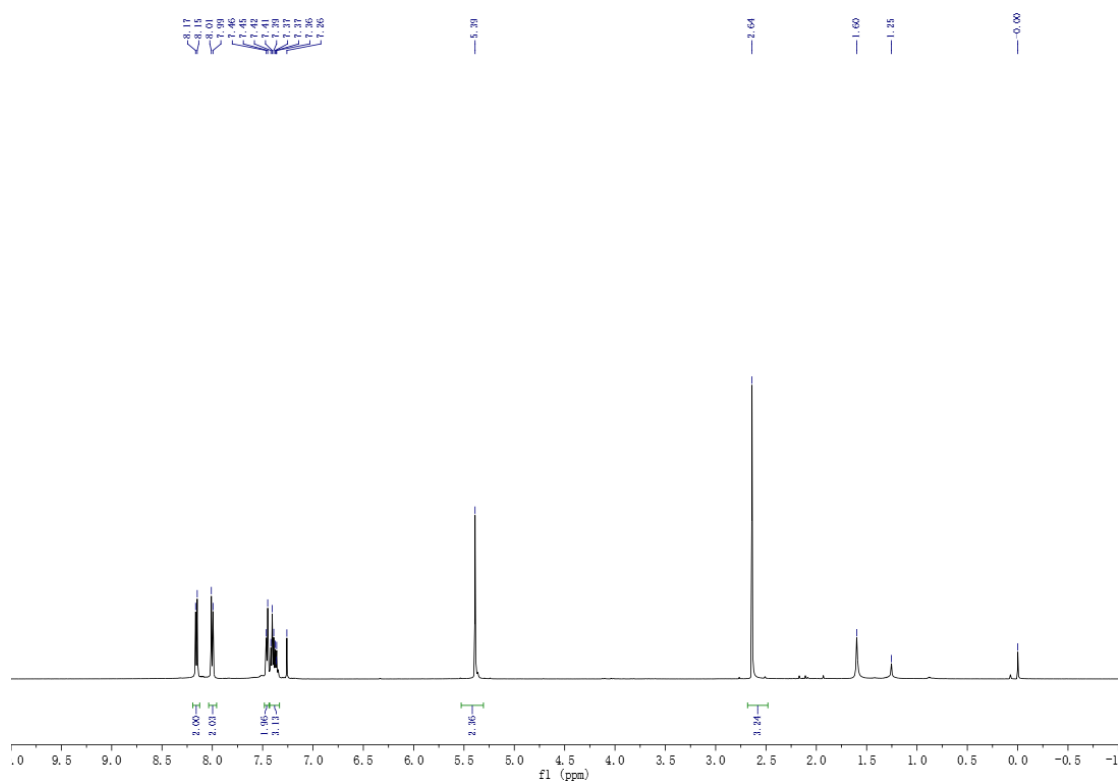
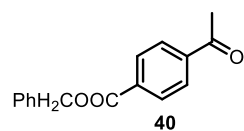
^{13}C NMR of compound **38**



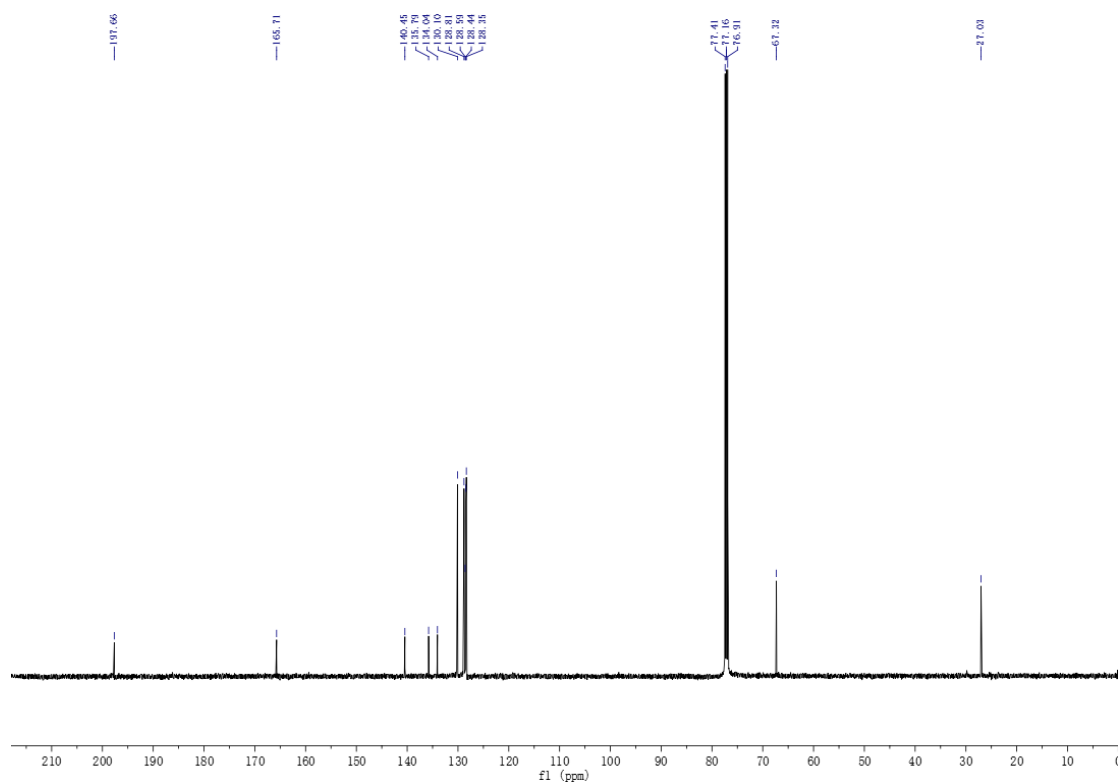
¹H NMR of compound **39**



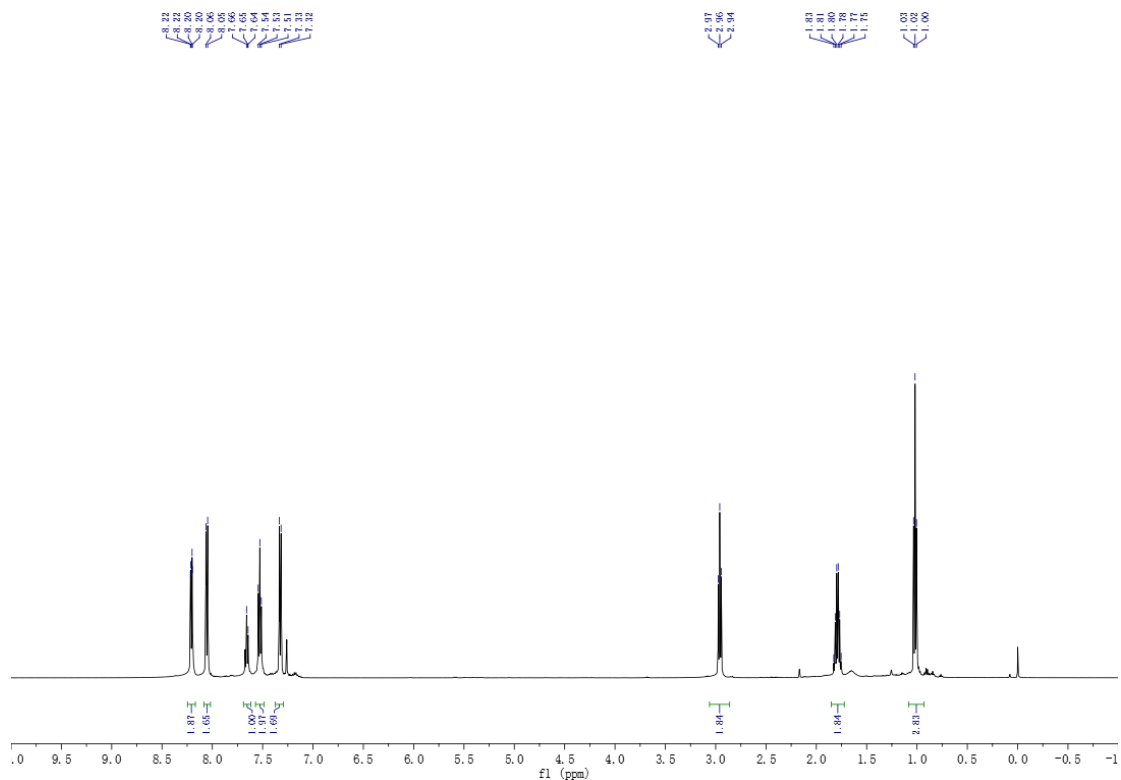
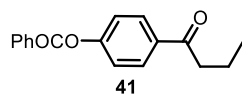
¹³C NMR of compound **39**



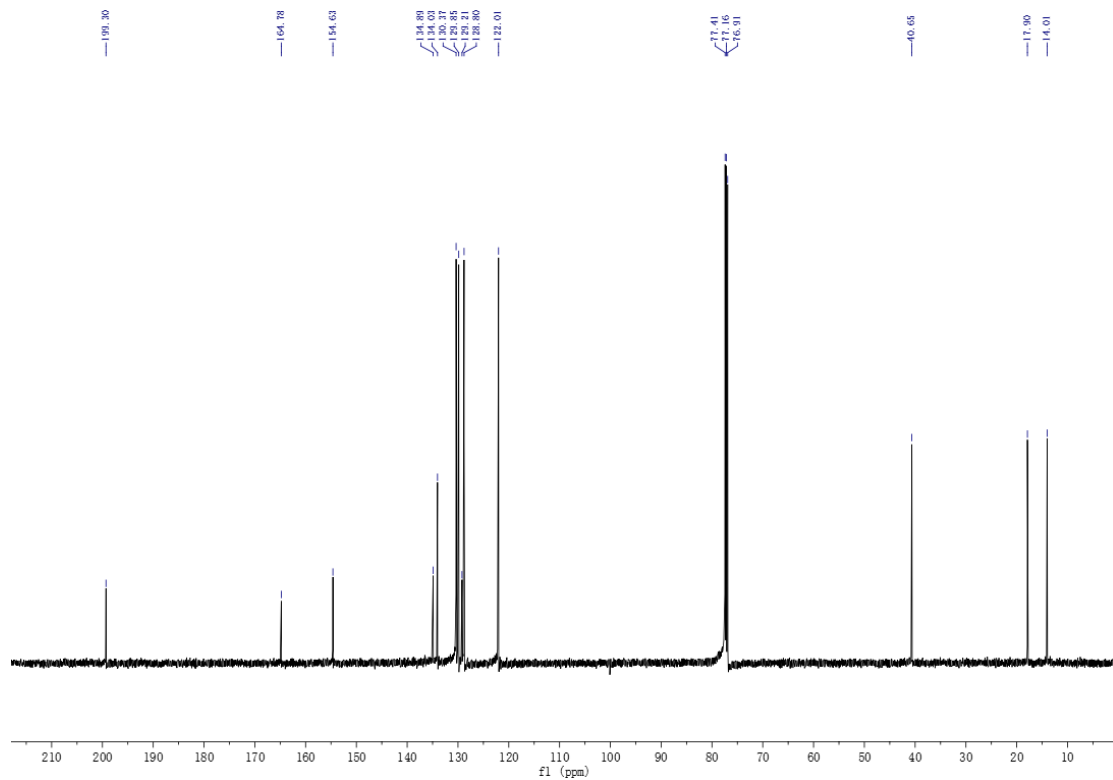
¹H NMR of compound **40**



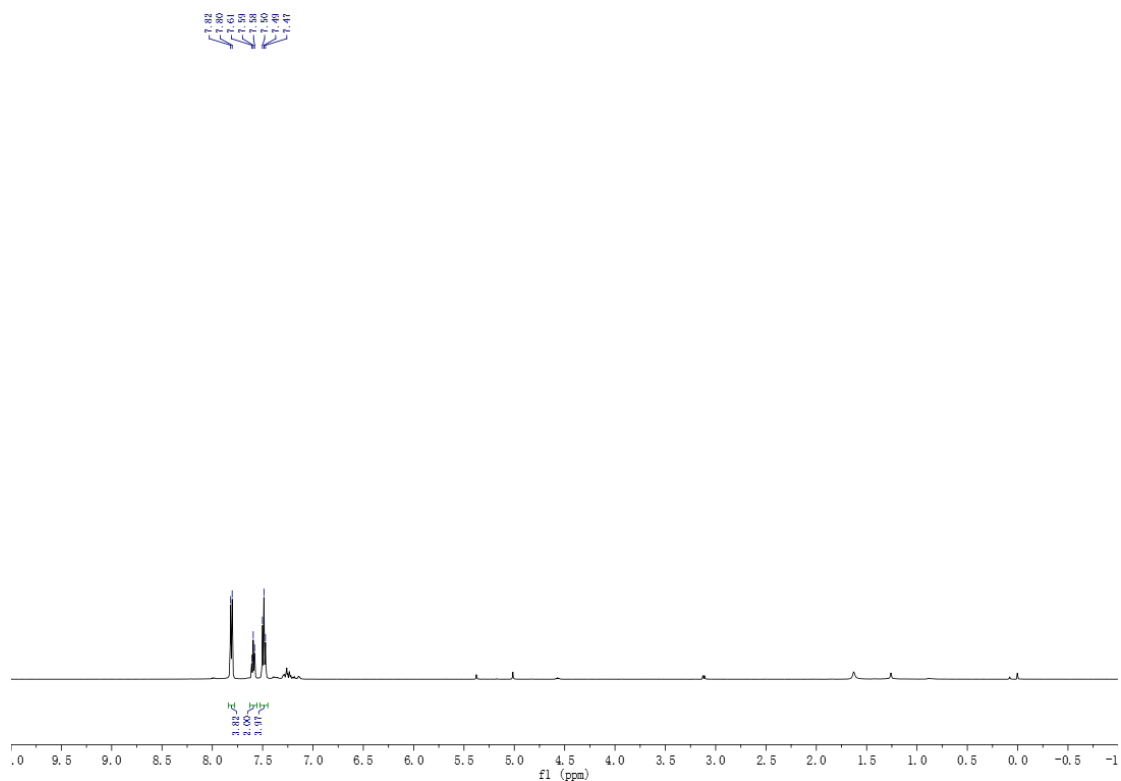
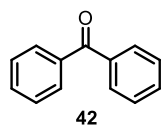
¹³C NMR of compound **40**



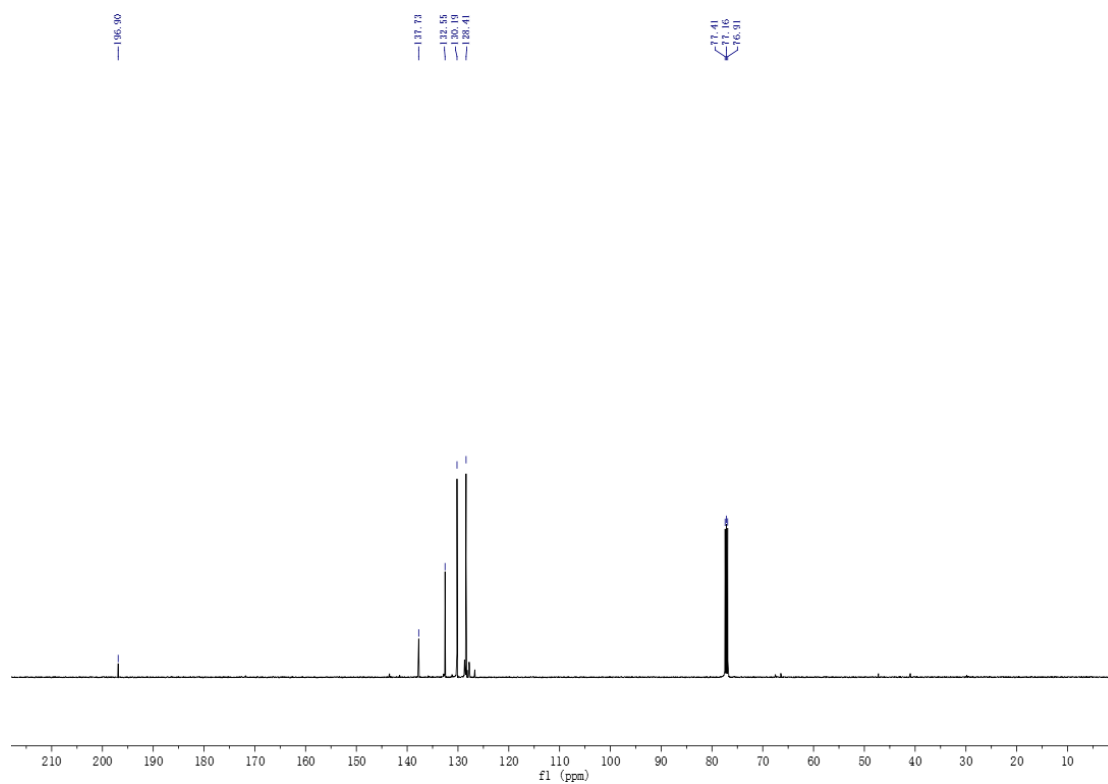
¹H NMR of compound **41**



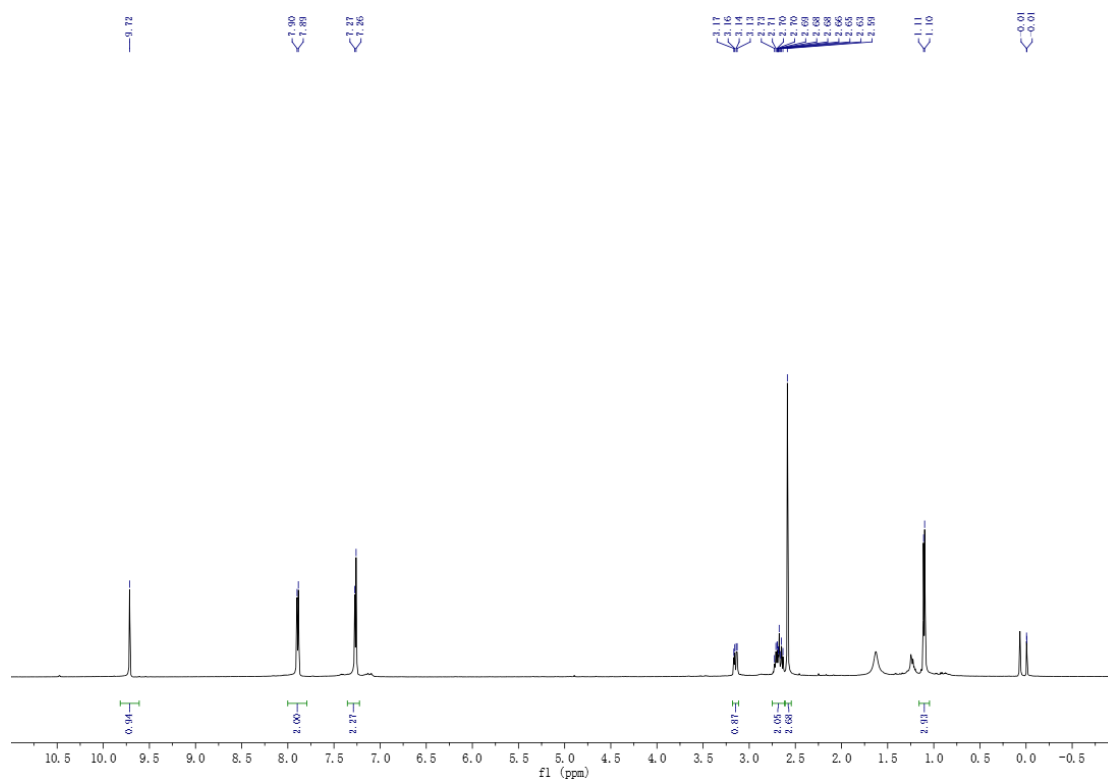
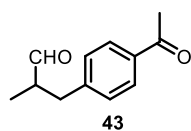
¹³C NMR of compound **41**



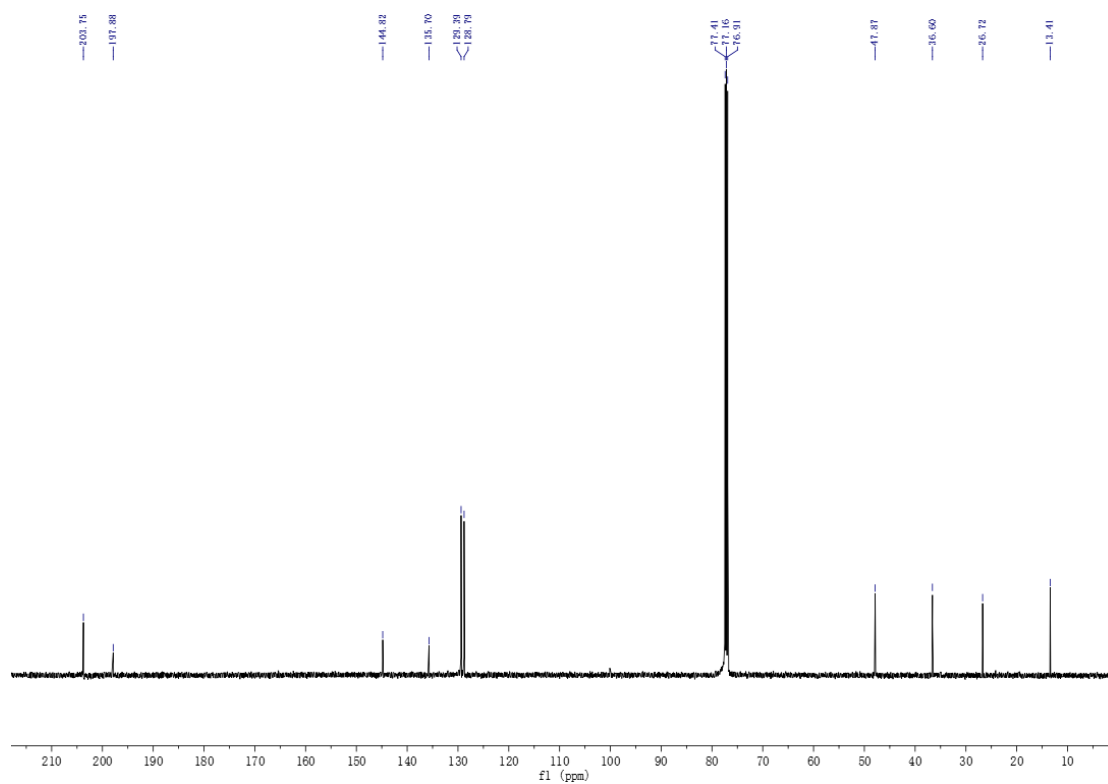
¹H NMR of compound **42**



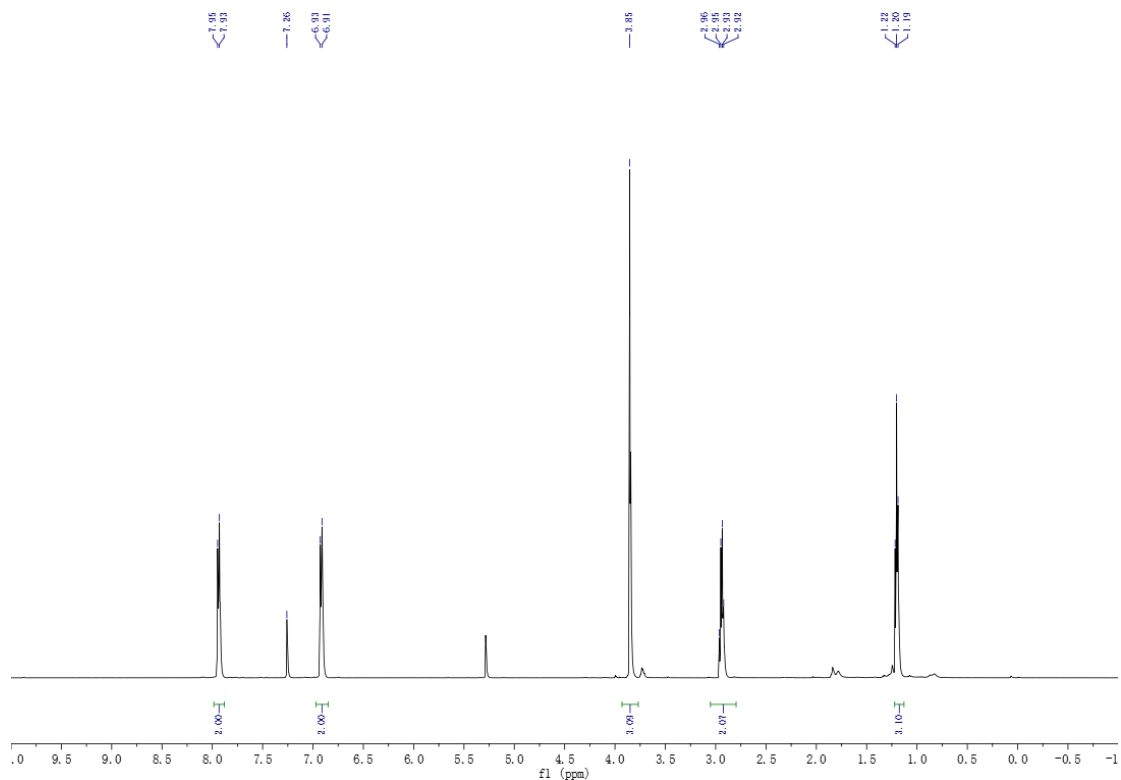
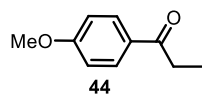
¹³C NMR of compound **42**



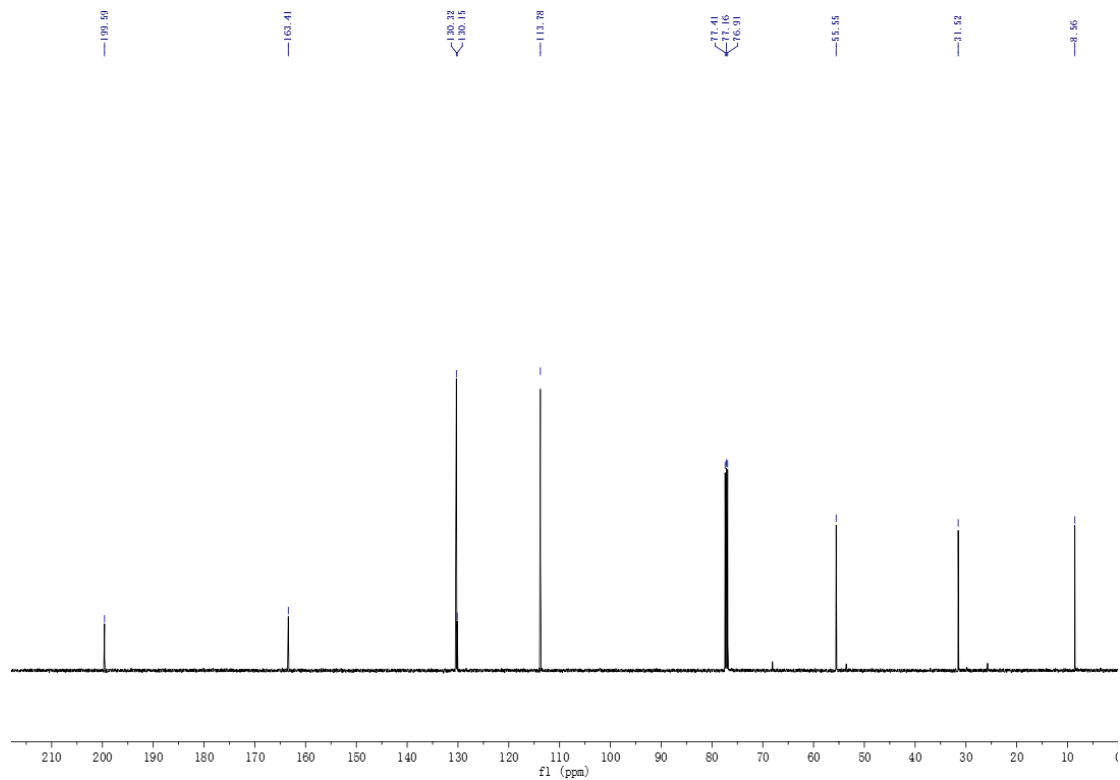
¹H NMR of compound **43**



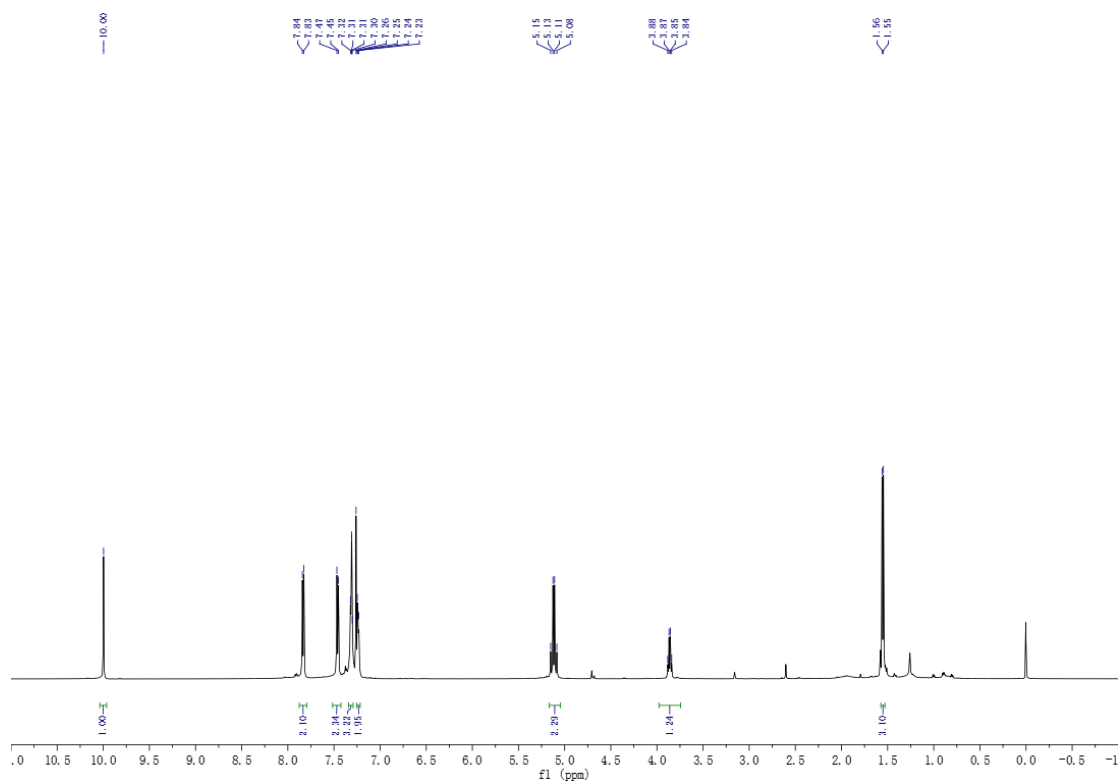
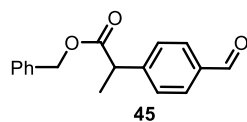
¹³C NMR of compound **43**



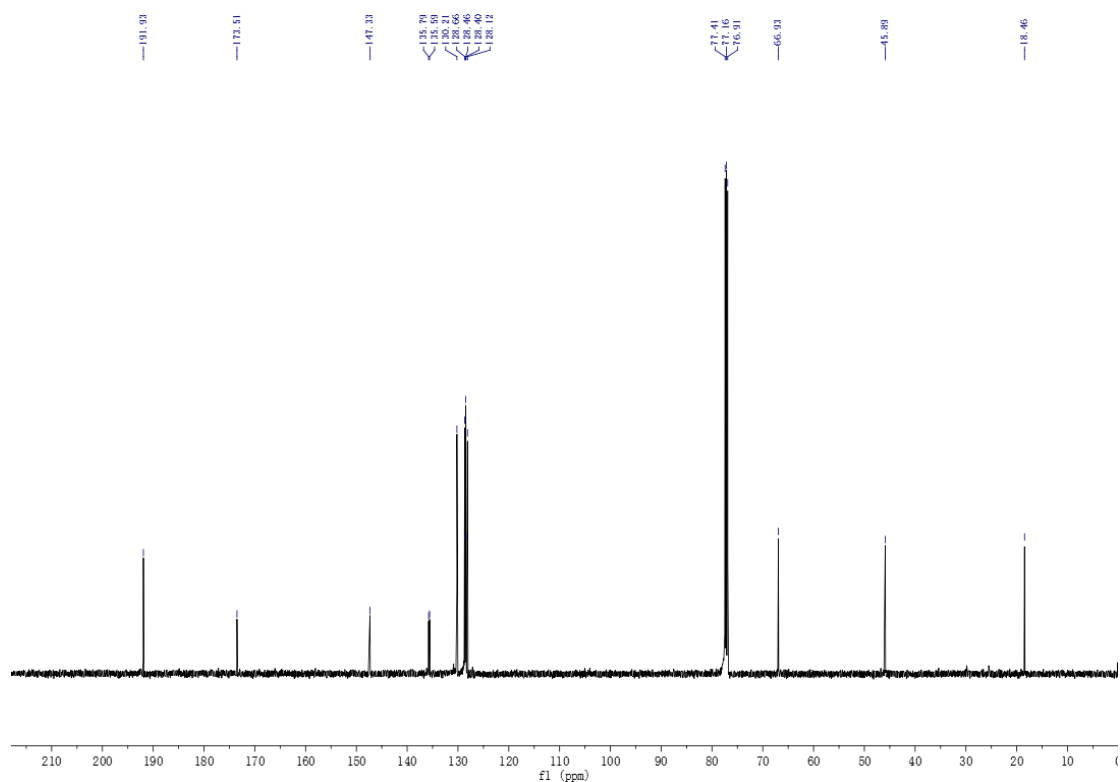
¹H NMR of compound **44**



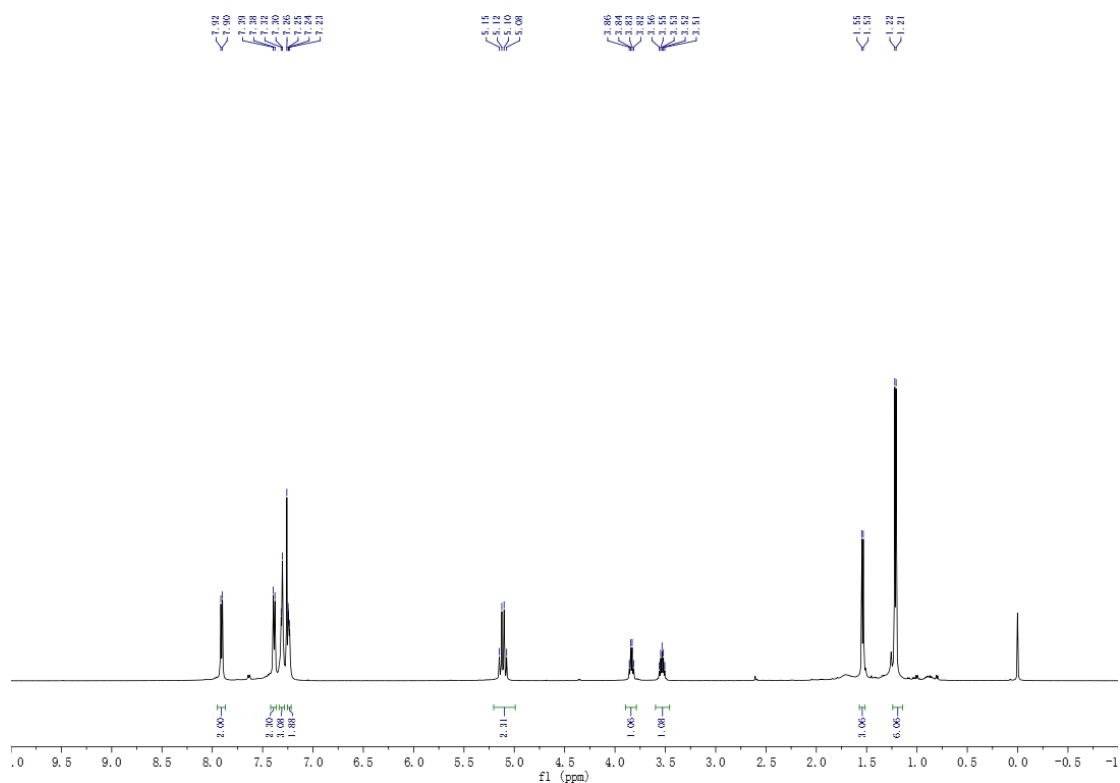
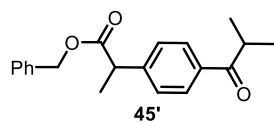
¹³C NMR of compound **44**



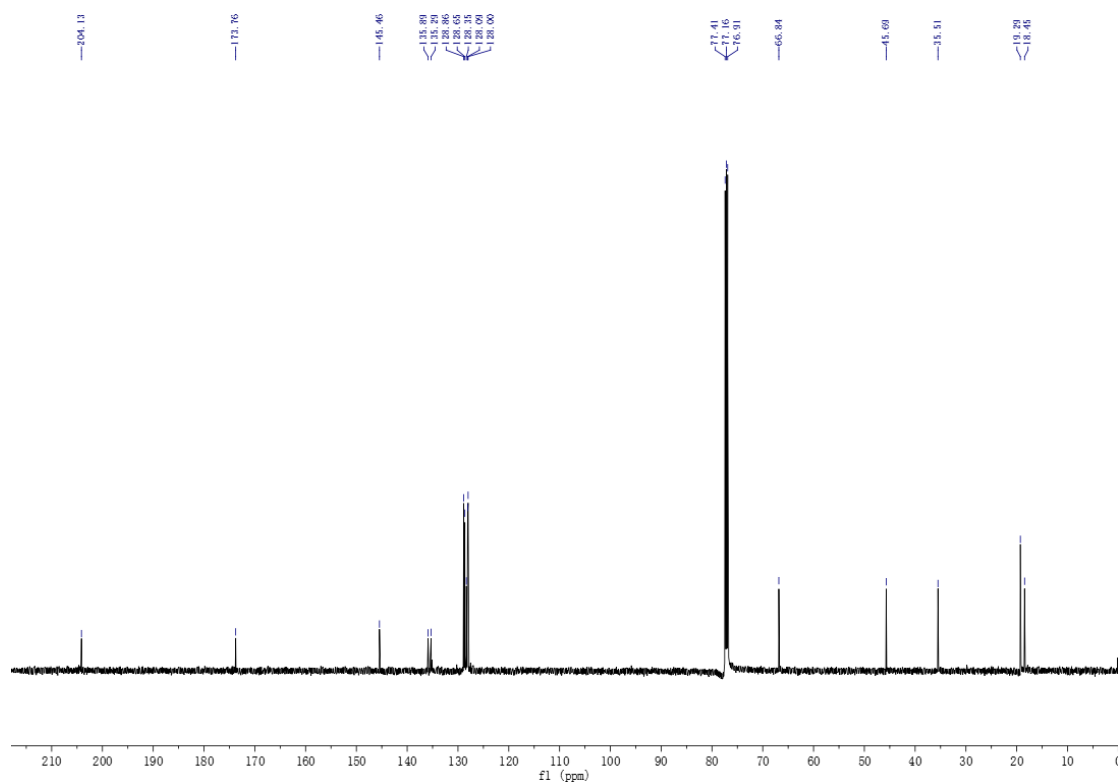
¹H NMR of compound **45**



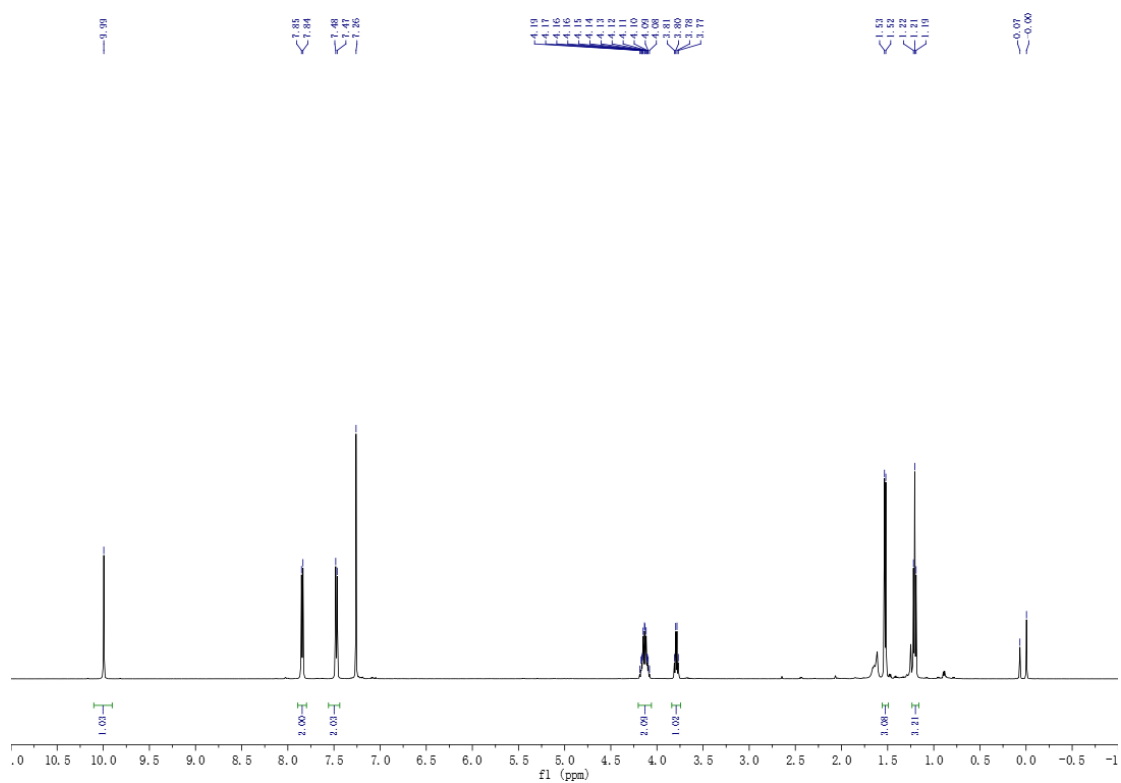
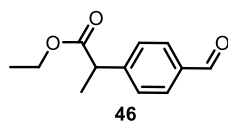
¹³C NMR of compound **45**



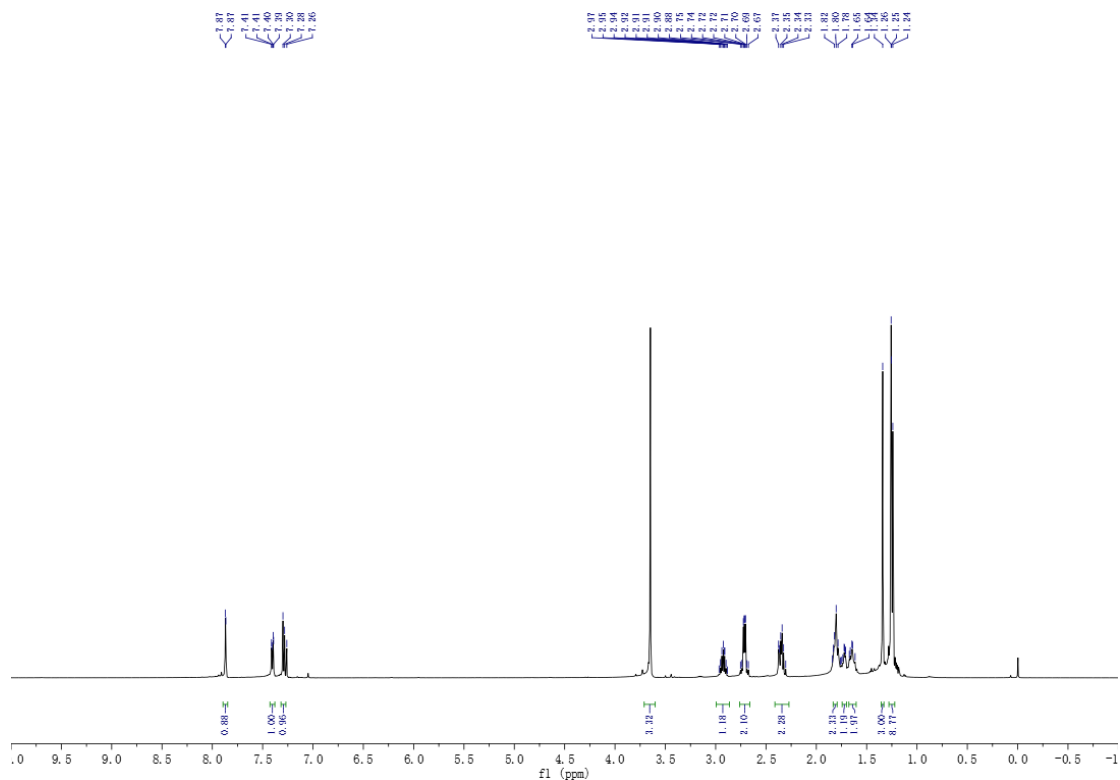
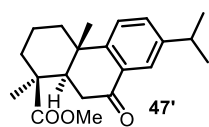
¹H NMR of compound **45'**



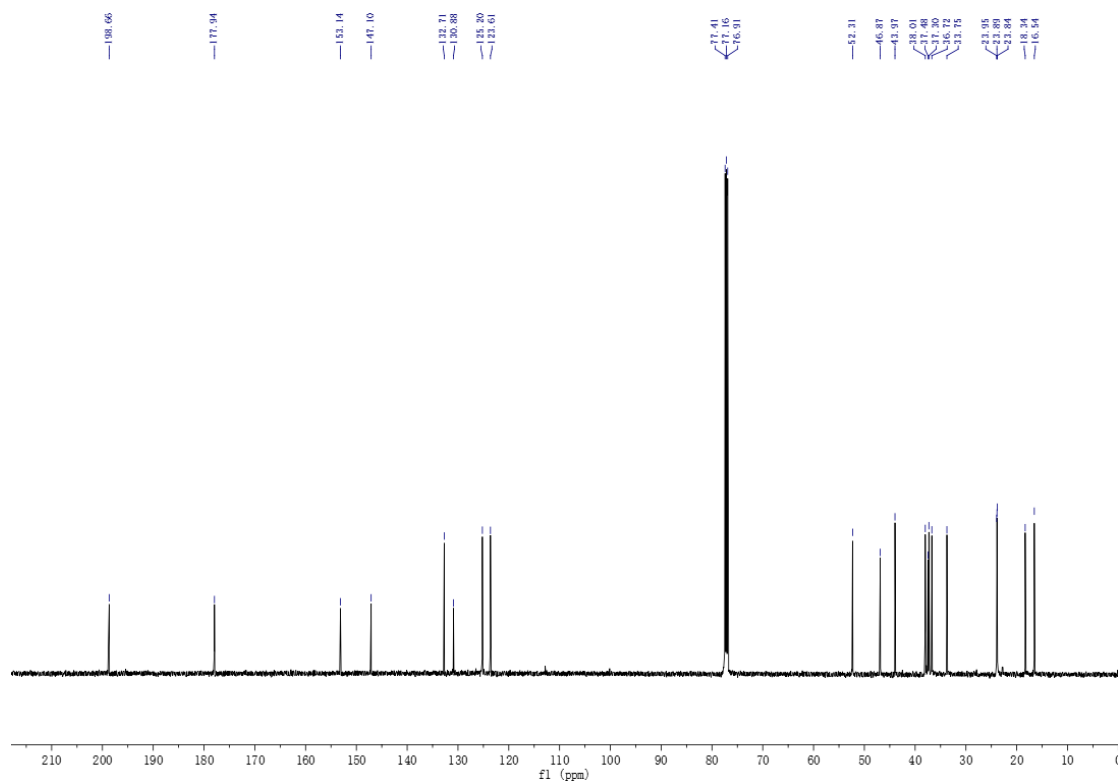
¹³C NMR of compound **45'**



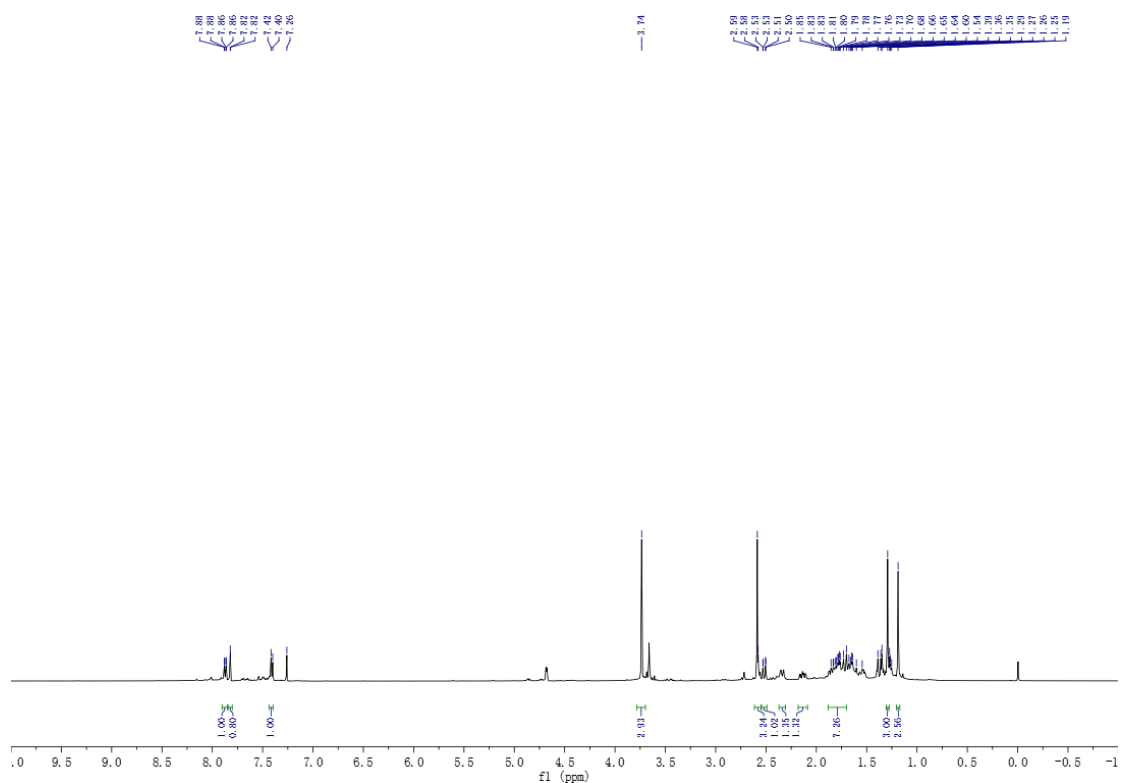
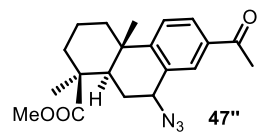
¹H NMR of compound **46**



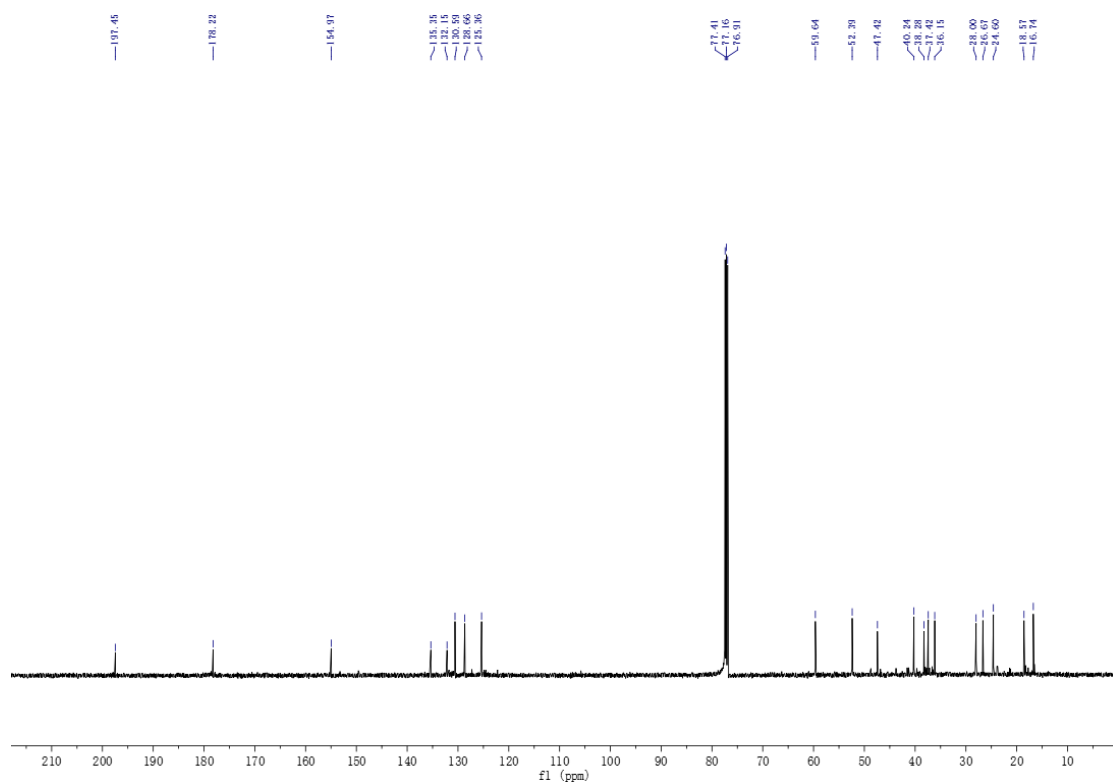
^1H NMR of compound 47'



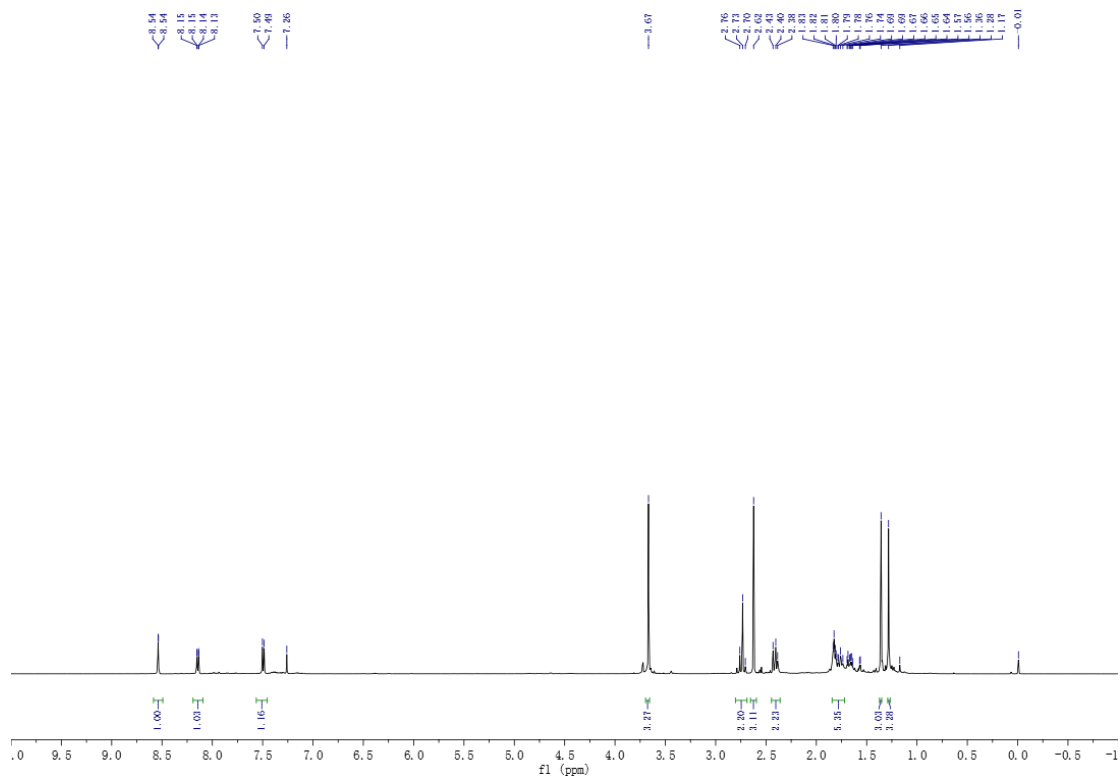
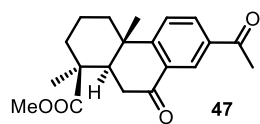
^{13}C NMR of compound 47'



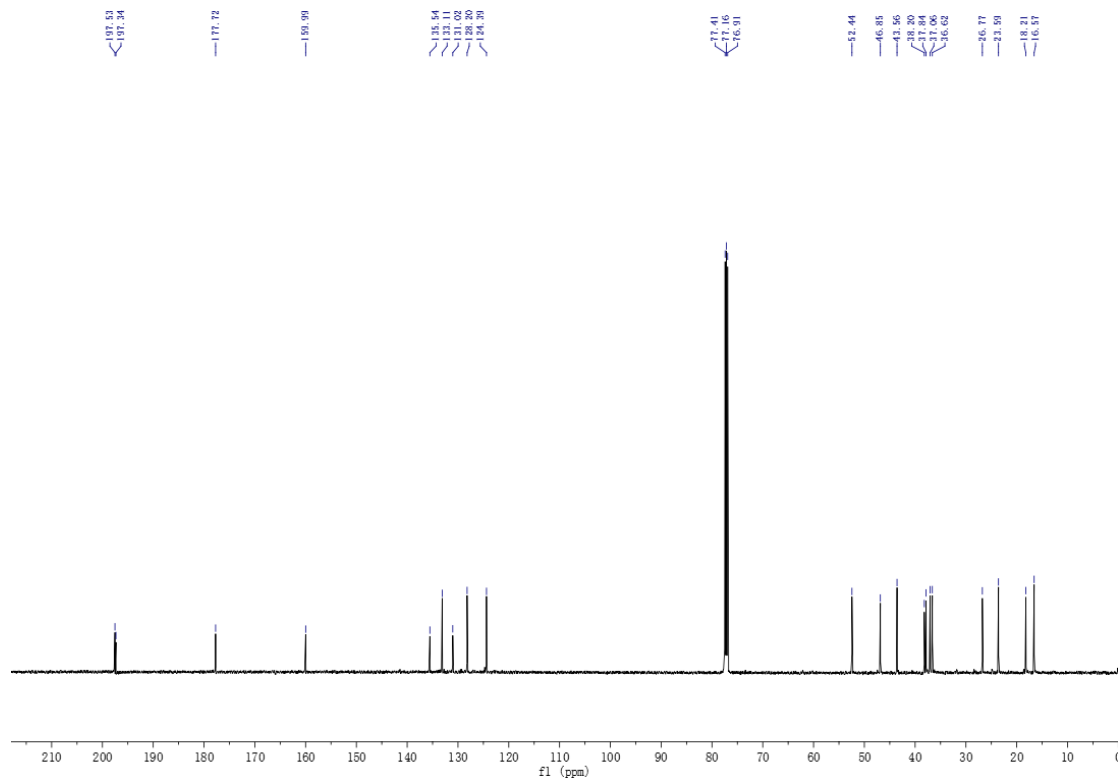
¹H NMR of compound **47''**



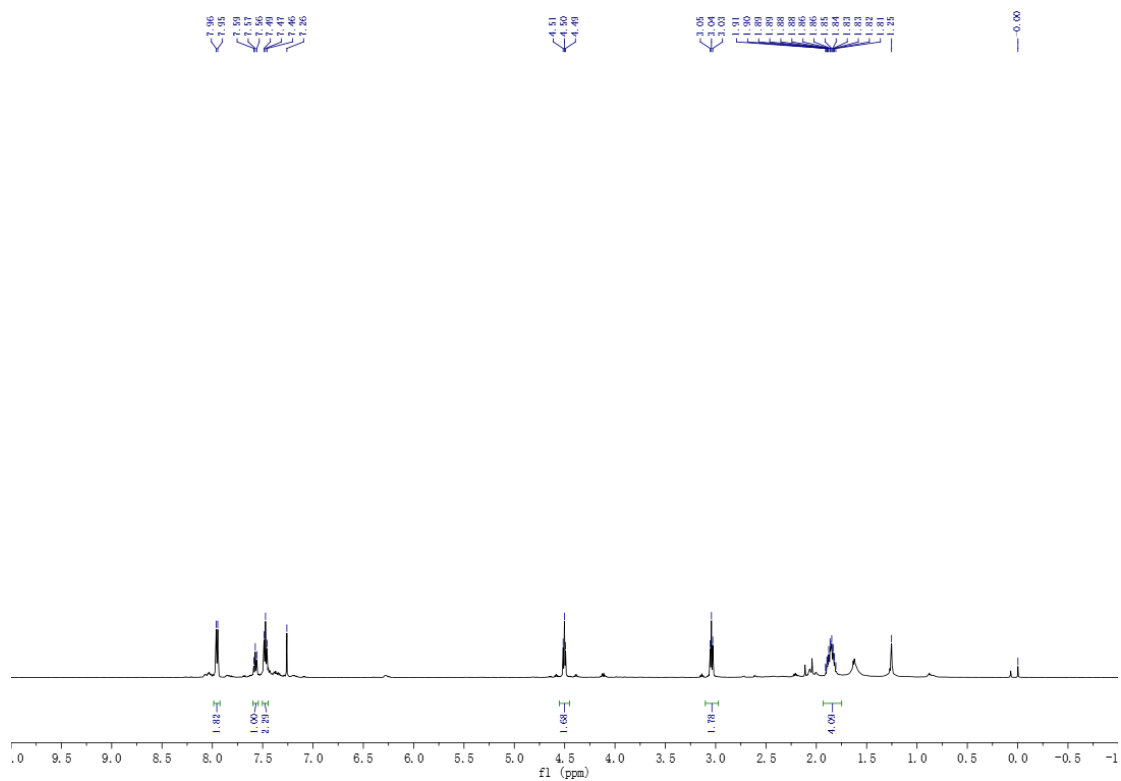
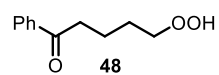
¹³C NMR of compound **47''**



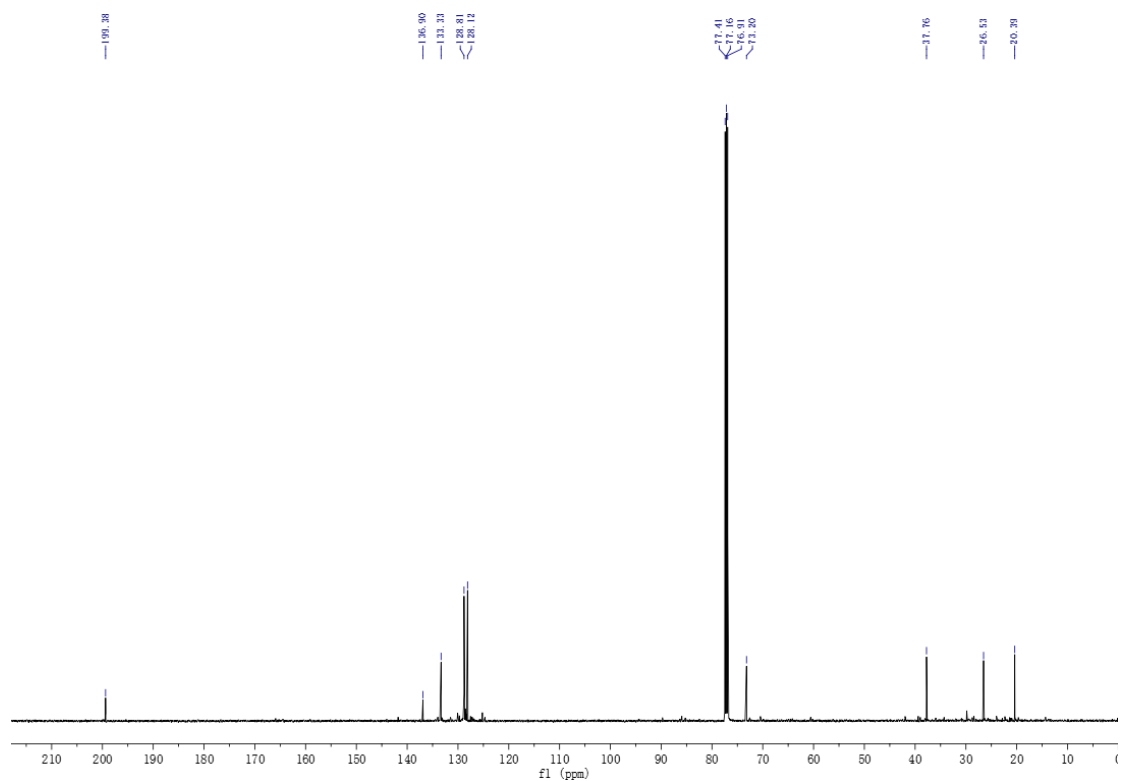
¹H NMR of compound **47**

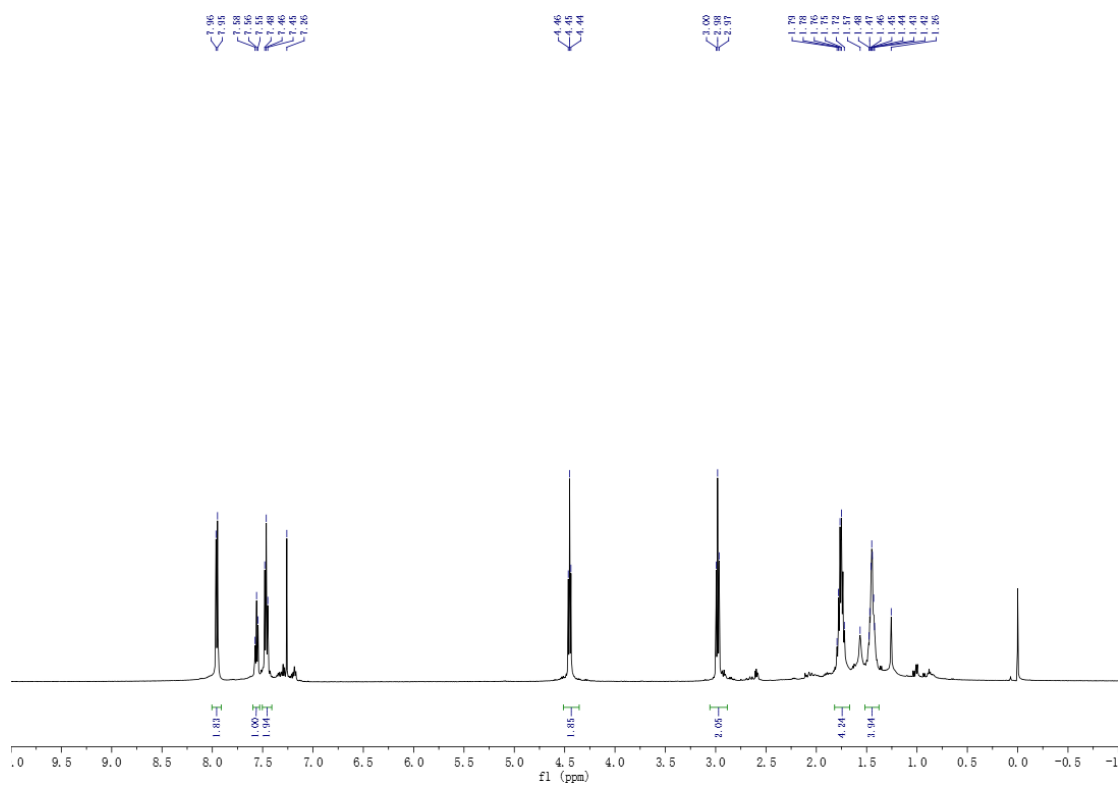
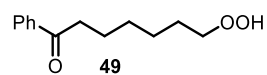


¹³C NMR of compound **47**

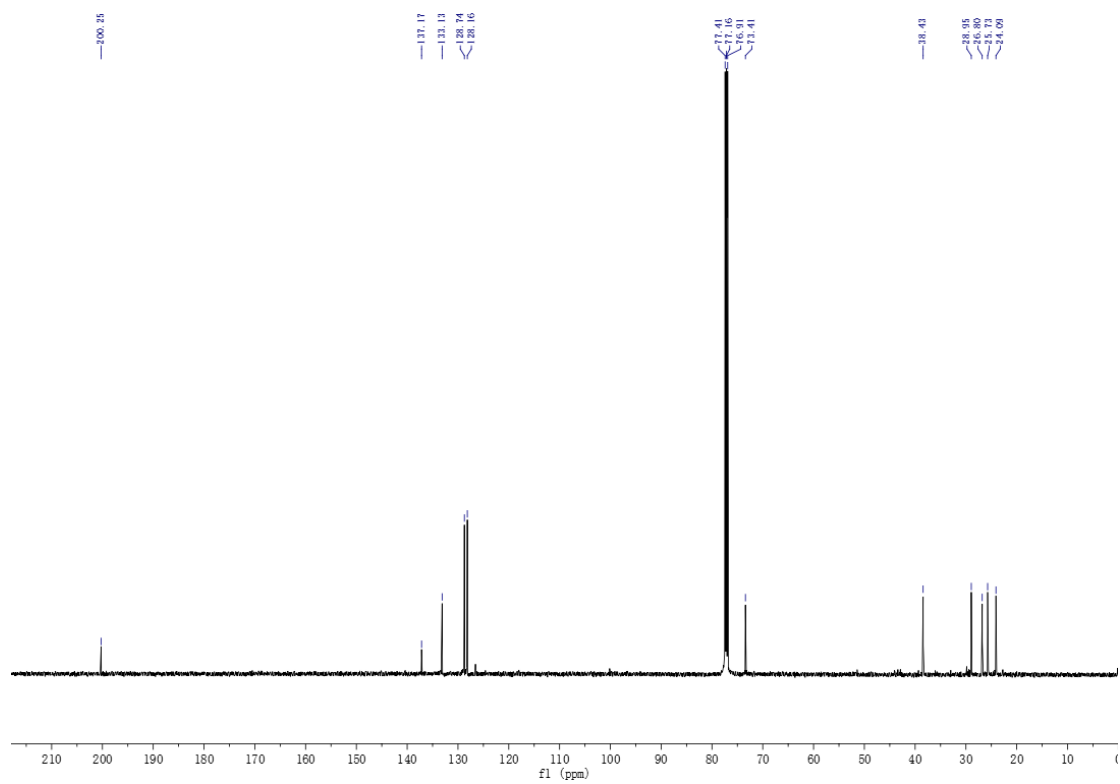


¹H NMR of compound **48**

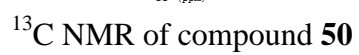
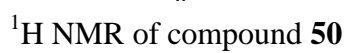


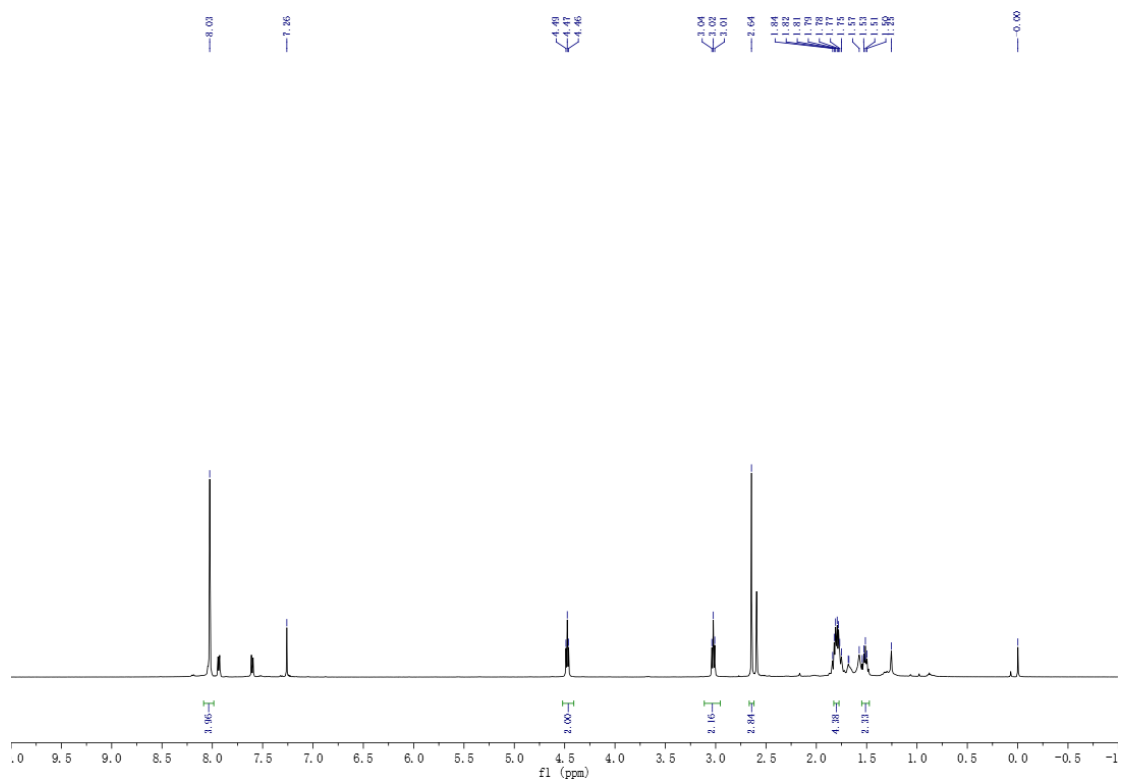
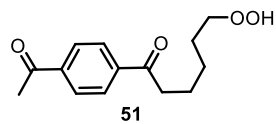


¹H NMR of compound **49**

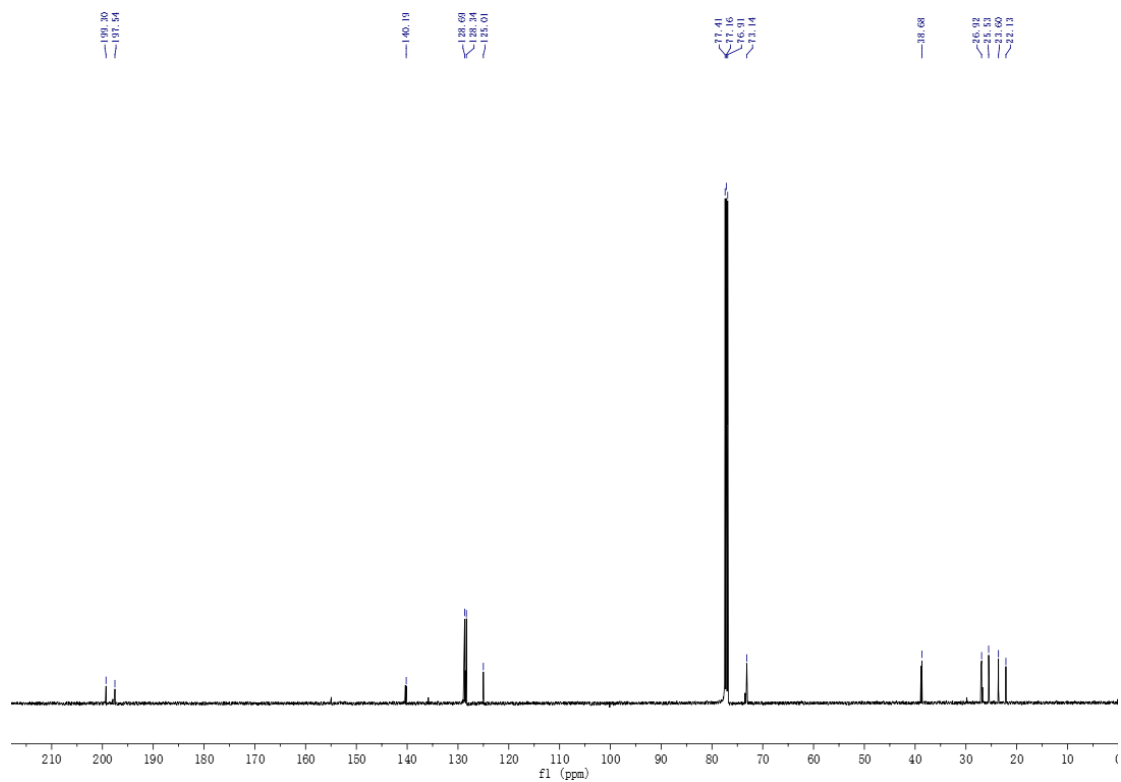


¹³C NMR of compound **49**

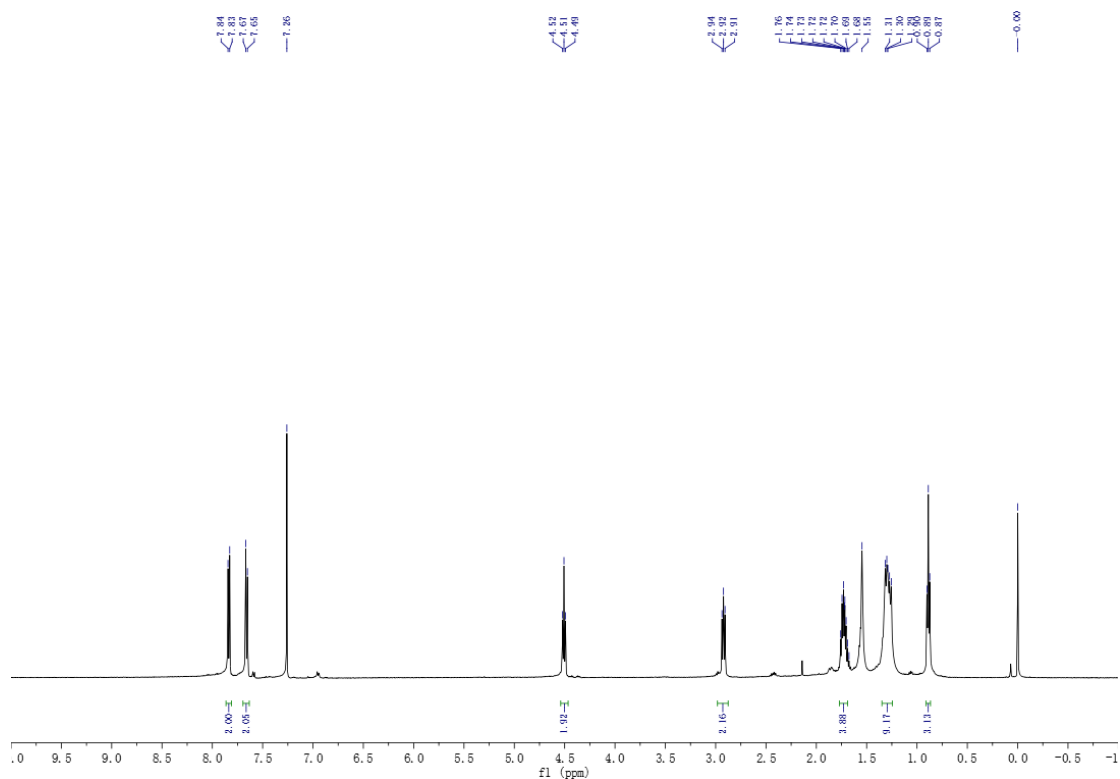
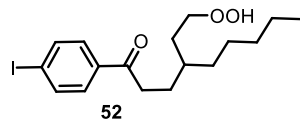




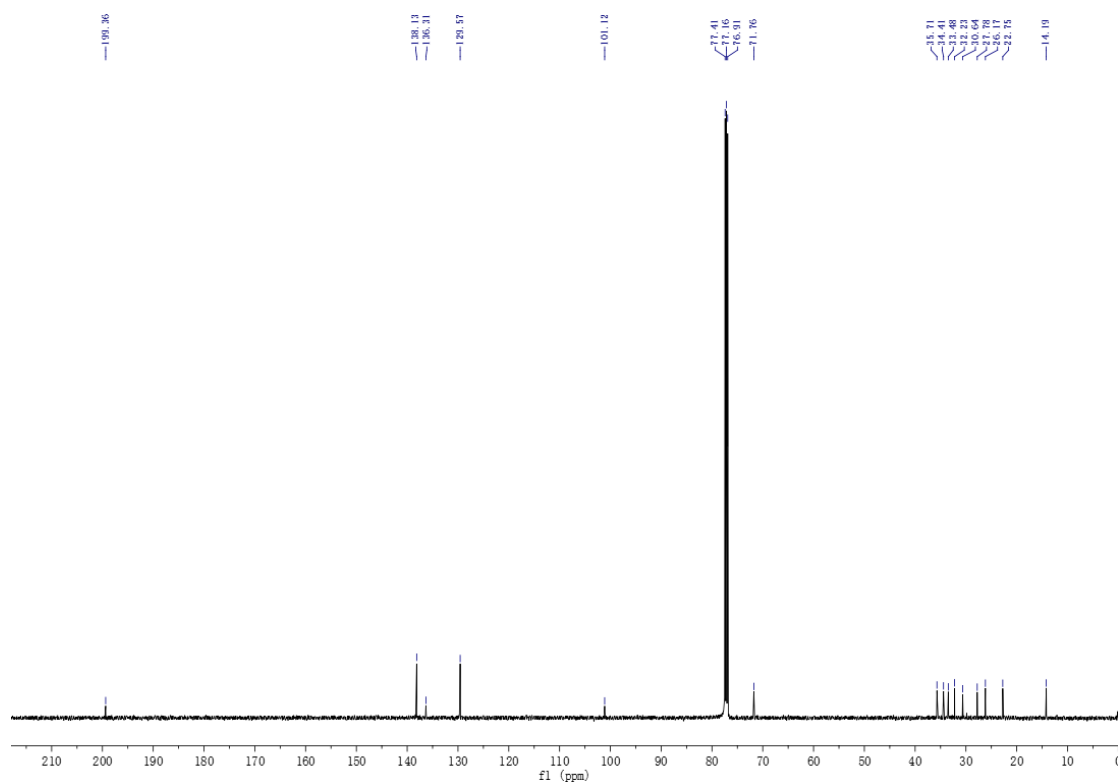
¹H NMR of compound **51**



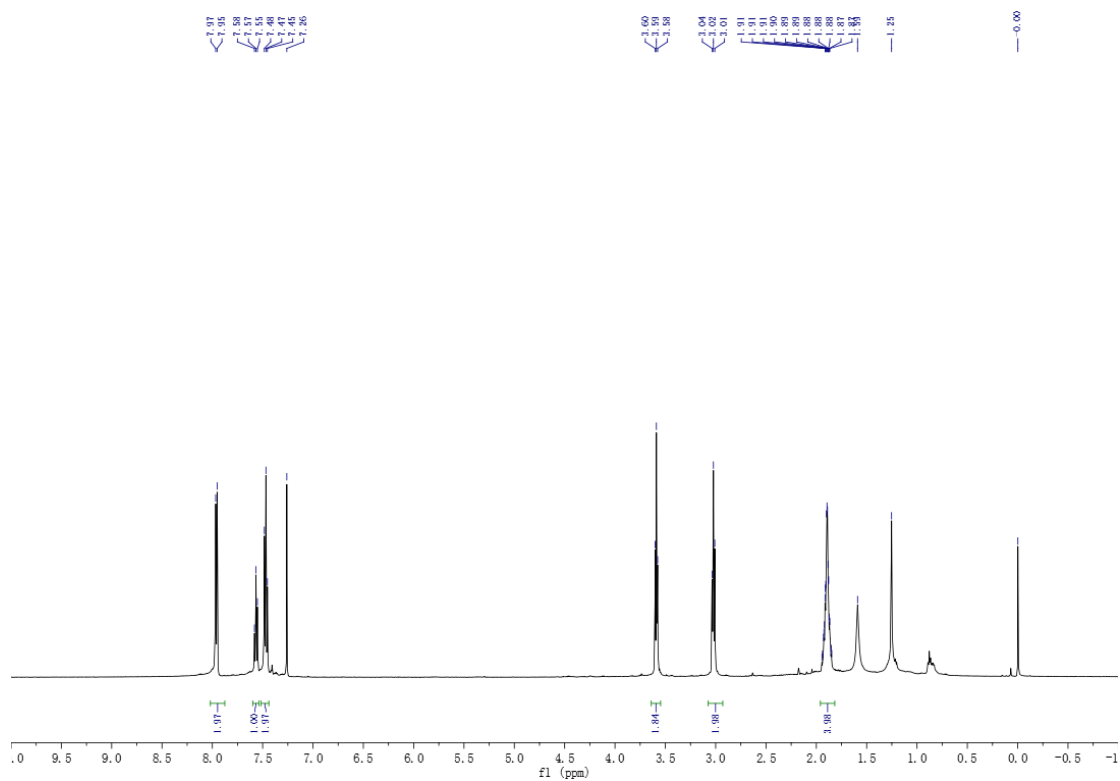
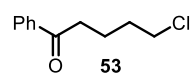
¹³C NMR of compound **51**



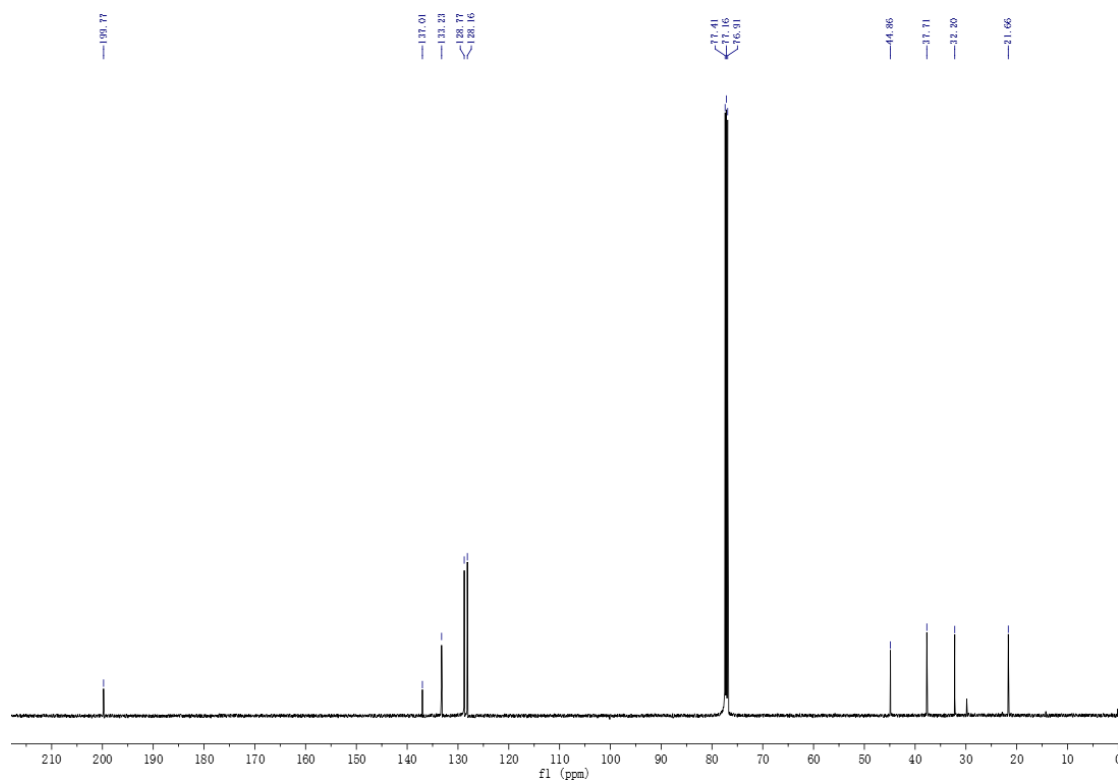
¹H NMR of compound **52**



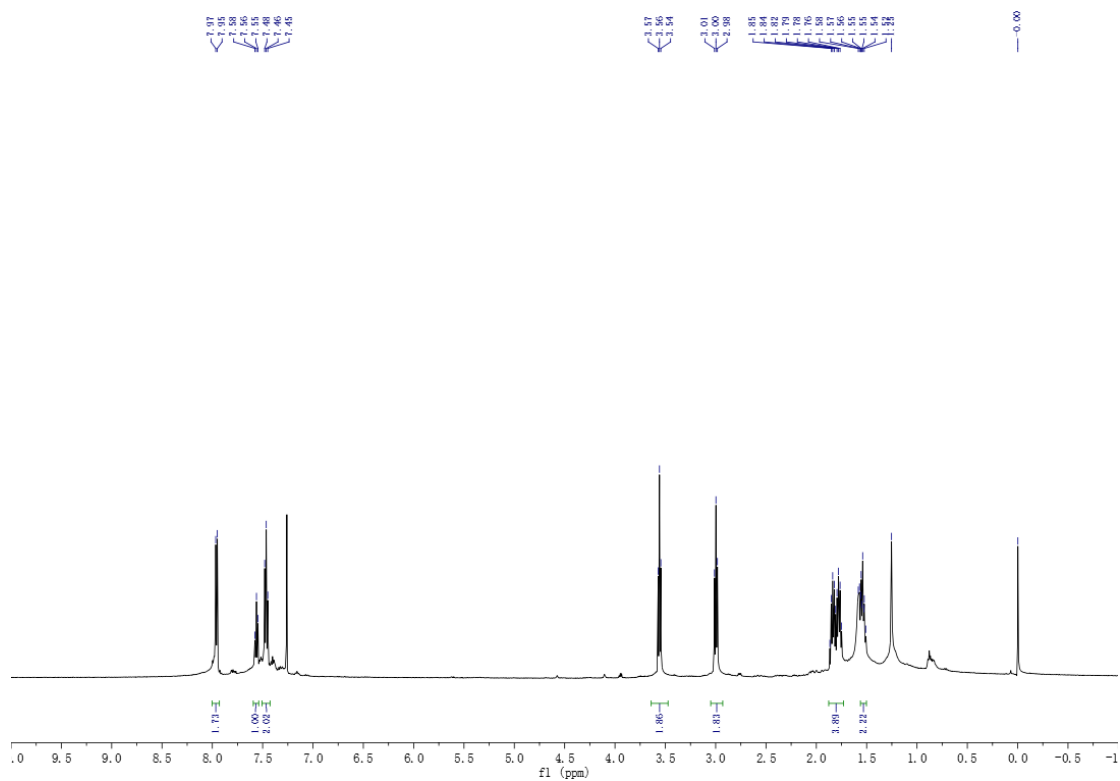
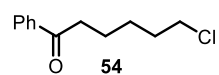
¹³C NMR of compound **52**



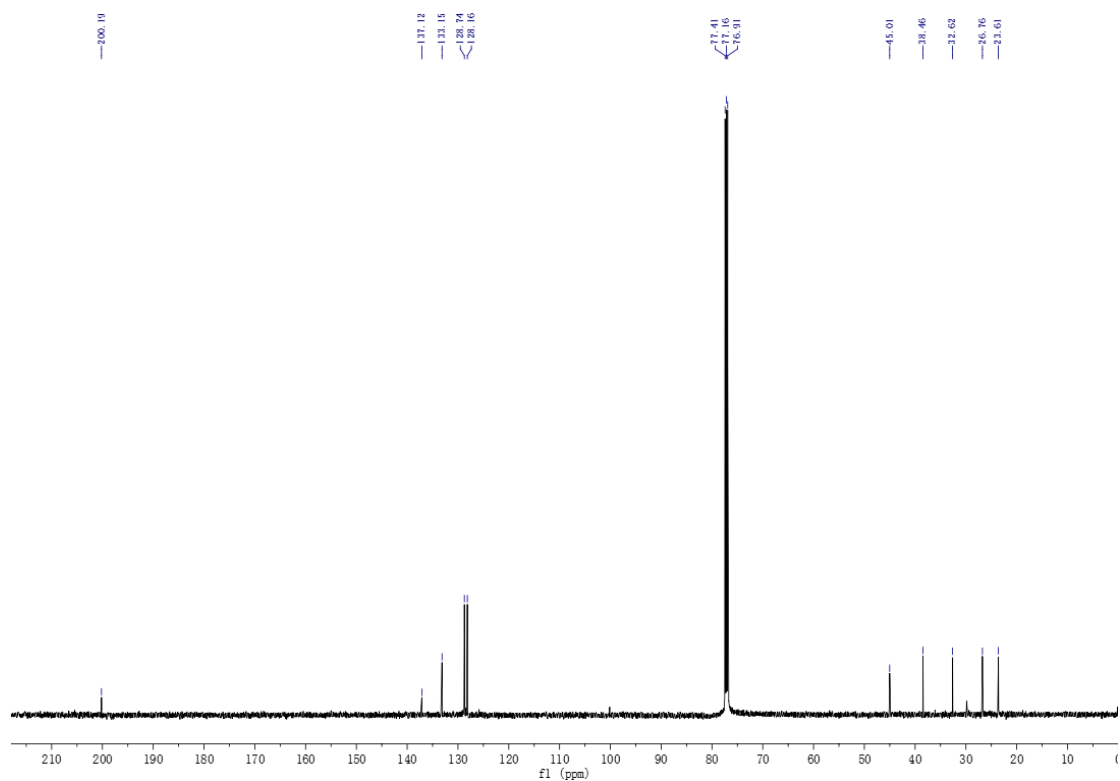
¹H NMR of compound **53**



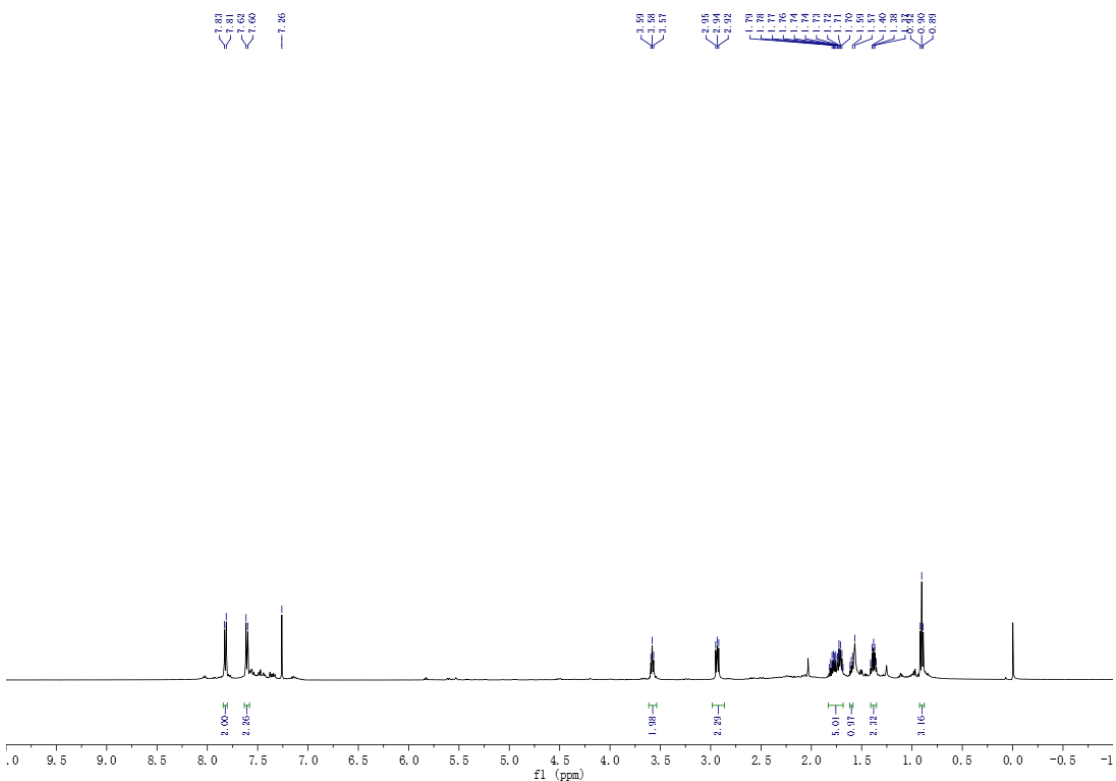
¹³C NMR of compound **53**



¹H NMR of compound **54**

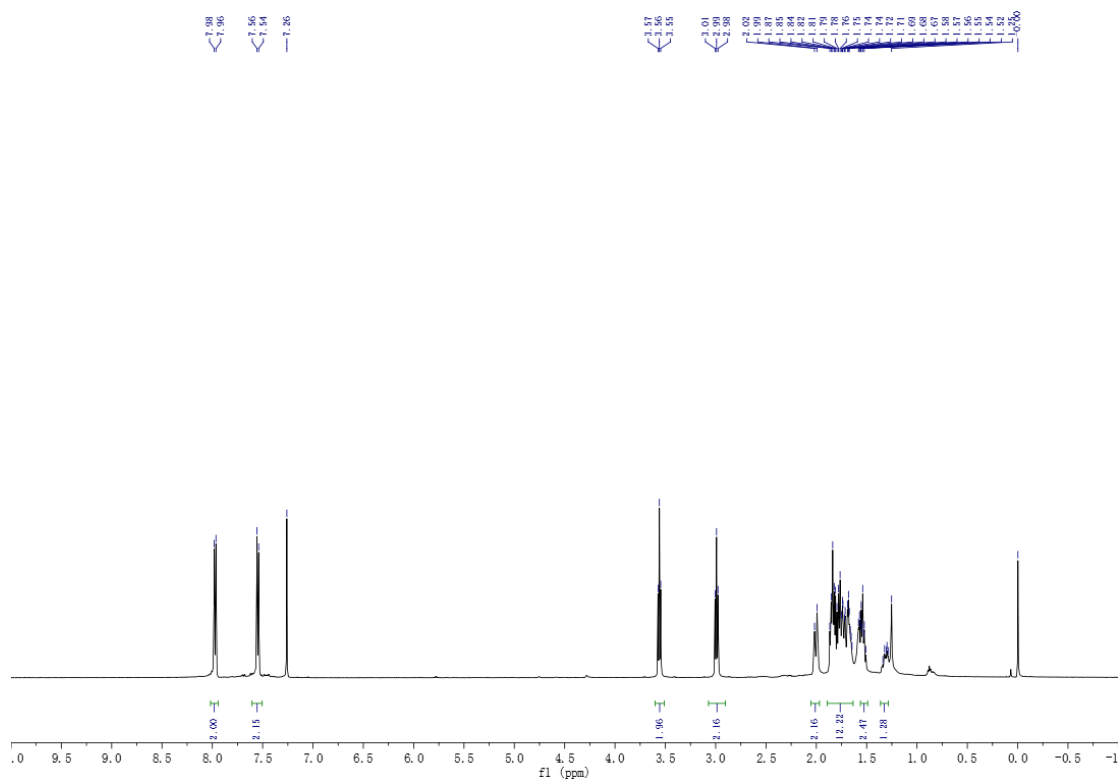
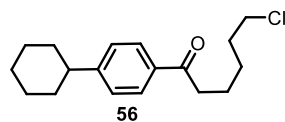


¹³C NMR of compound **54**

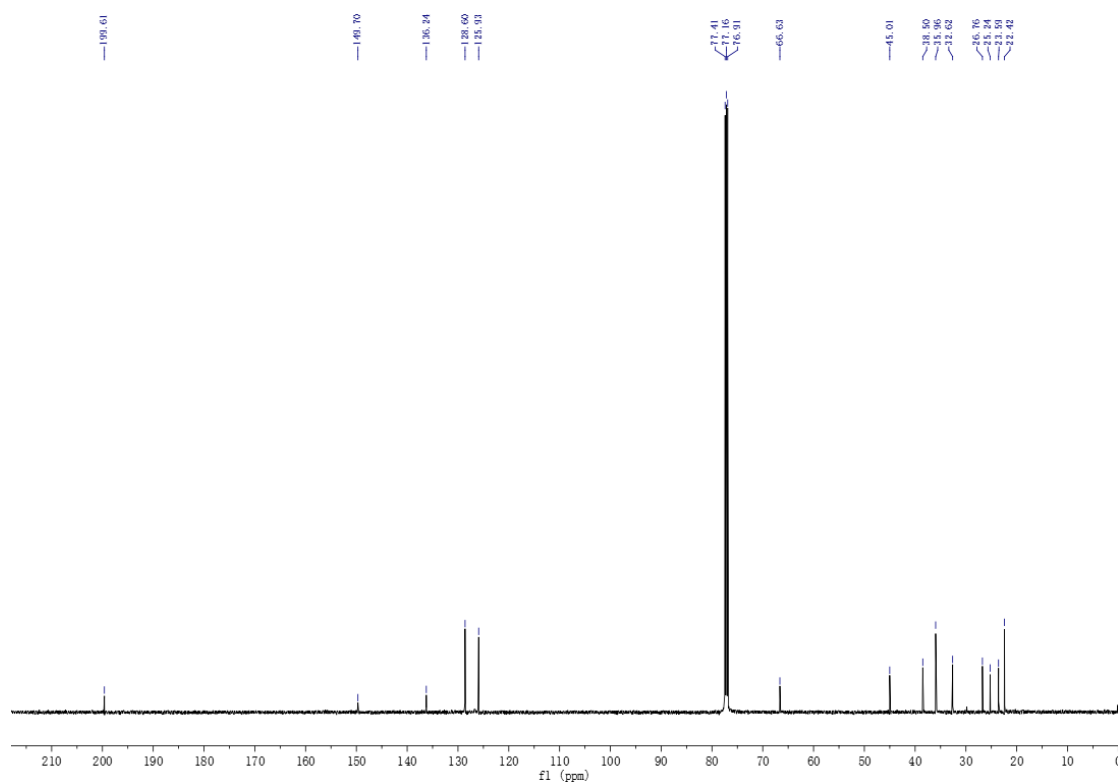


¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis is labeled 'f1 (ppm)' and ranges from 0 to 210. The spectrum shows several peaks with their chemical shifts labeled: 199.29, 135.80, 132.07, 129.70, 128.30, 77.41, 77.16, 76.91, 41.22, 36.39, 36.32, 35.92, 31.02, 30.92, 10.63. A large solvent peak is visible at 77 ppm.

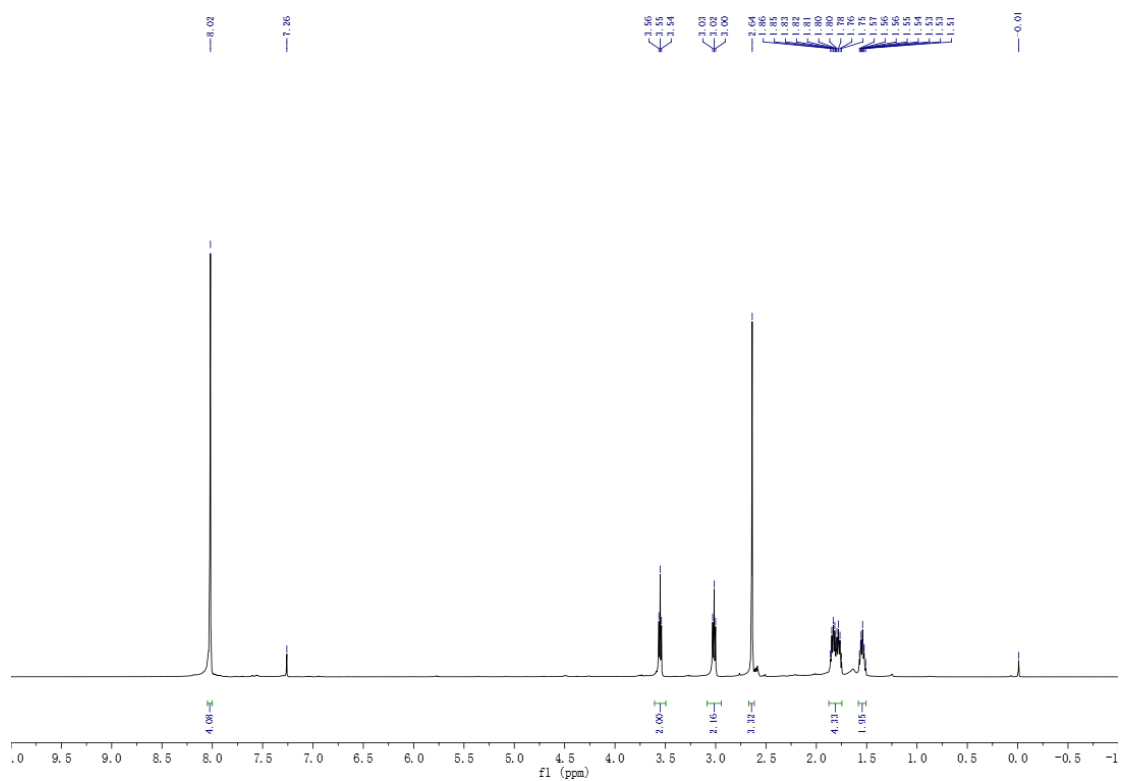
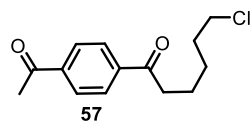
S135



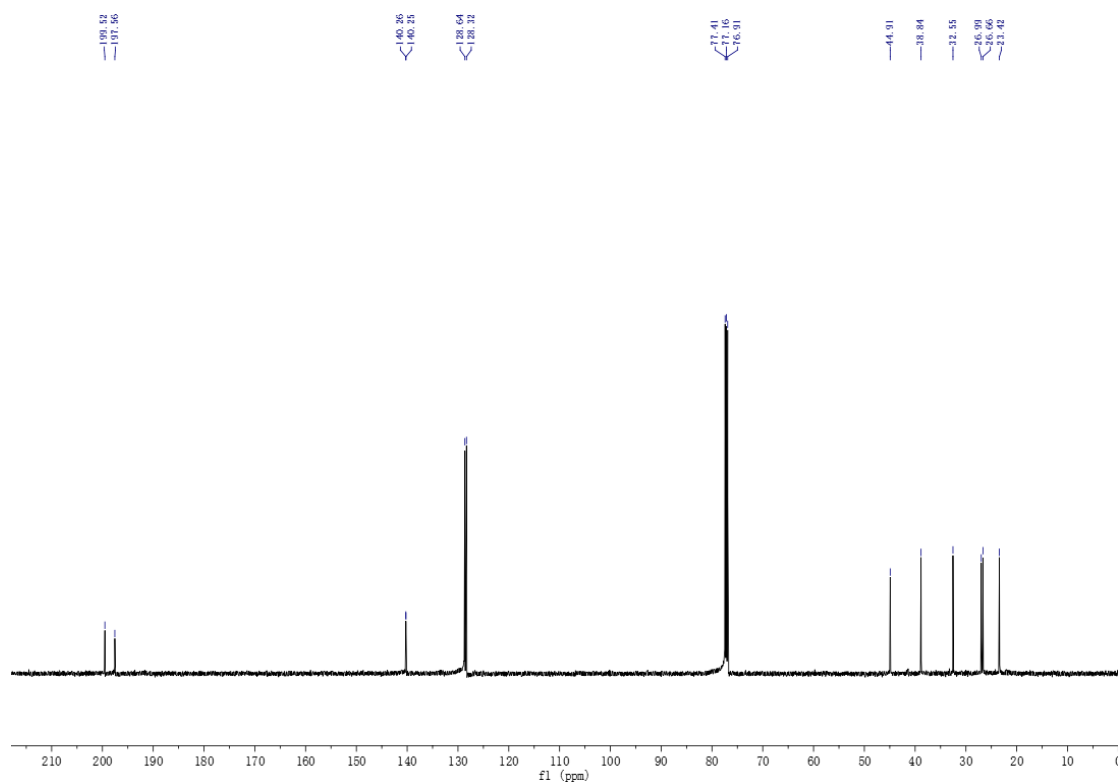
¹H NMR of compound **56**



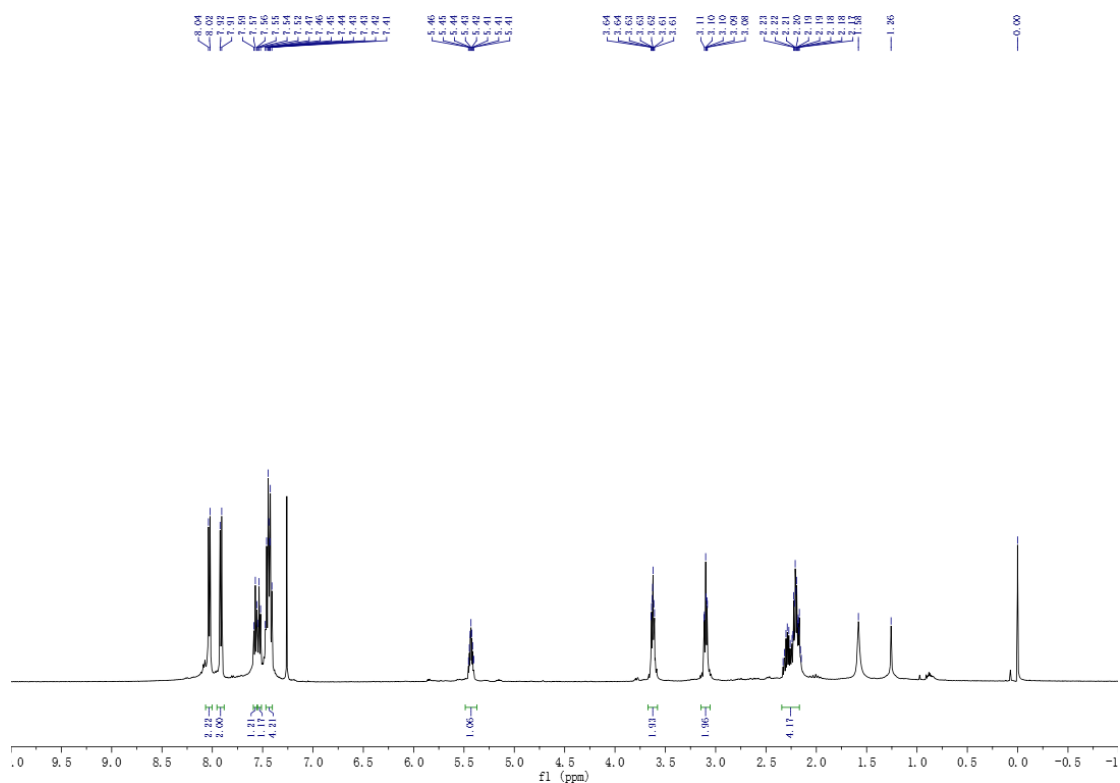
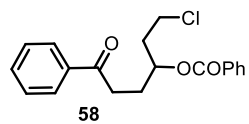
¹³C NMR of compound **56**



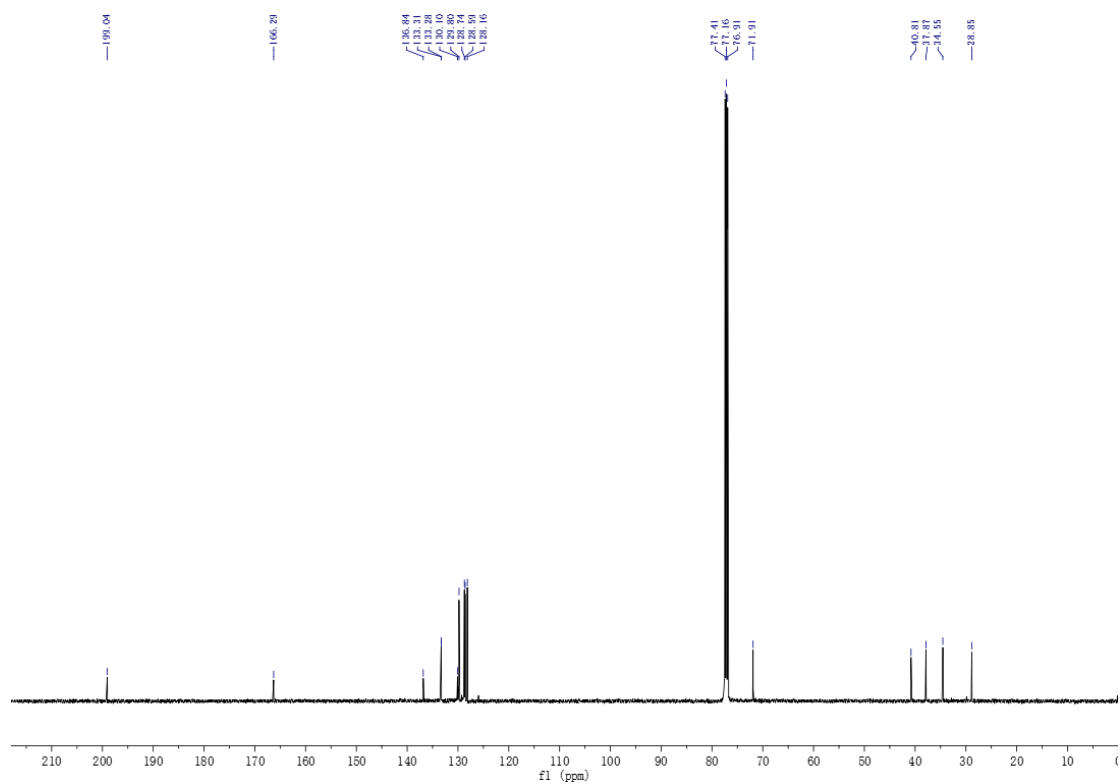
¹H NMR of compound **57**



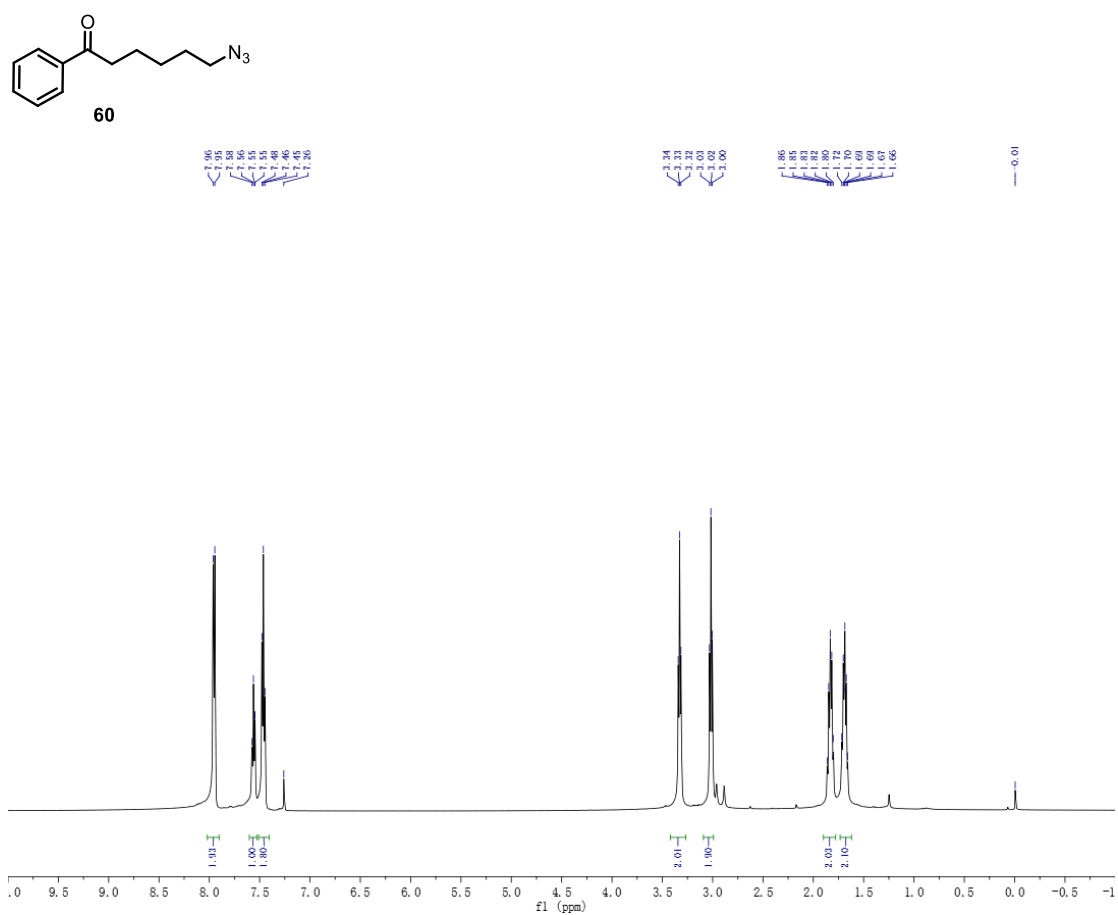
¹³C NMR of compound **57**



¹H NMR of compound **58**



¹³C NMR of compound **58**



¹H NMR of compound **60**