Supporting Information

Visible-light-induced thiol-mediated transfer hydrogenation/deuteration of activated alkenes, imines and azo compounds

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1. General Information

All reagents and solvents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros and Energy Chemical. All commercial reagents were used as supplied unless otherwise stated. Organic solutions were concentrated by rotary evaporation below 45 °C. All reactions were monitored by TLC, GC-MS. Analytical thin-layer chromatography was performed using Merck Kieselgel 60 F254 0.20 mm precoated glass-backed silica gel plates. Visualization of the chromatogram was performed by UV absorbance (λmax = 254 nm) and/or by staining with aqueous potassium permanganate. Flash column chromatography was performed using silica gel (EM 60 F254 300 - 400 mesh) with the appropriate solvent system.

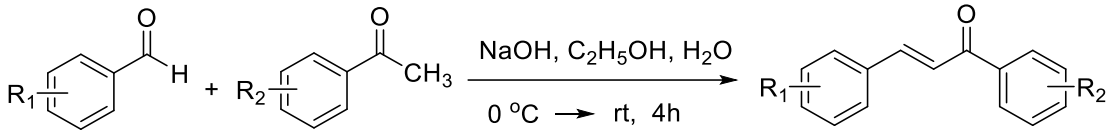
The photoreactor used in this research was bought from Taobao (www.taobao.com) (Fig. S1: blue LED, 50W, 450 nm).

Proton nuclear magnetic resonance (1H NMR) spectra were recorded on a Bruker DPX 400 (400 MHz) or Avance 500 (500 MHz) spectrometer. Chemical shifts (δ) are recorded in parts per million (ppm) and are quoted to the nearest 0.01 ppm relative to the residual solvent protons (CDCl3 = 7.26 ppm). Coupling constants (J) are quoted in Hertz (Hz), and data reported as follows: Chemical shift (multiplicity, coupling constant, number of protons). Coupling constants were reported to the nearest 0.1 Hz and multiplicity reported according to the following: s =singlet, d = doublet, t = triplet, q = quartet, qui = quintet m = multiplet, br = broad, with associated combinations e.g. dd = doublet of doublets Carbon nuclear magnetic resonance (13C NMR) spectra were recorded on a Bruker AVANCE 500 (125 MHz) spectrometer. Chemical shifts (δ) are recorded in parts per million (ppm) and are quoted to the nearest 0.1 ppm relative to the residual solvent protons (CDCl3 = 77.2 ppm). High - resolution mass spectra were recorded on a micrOTOF-Q II 10410 mass spectrometer.

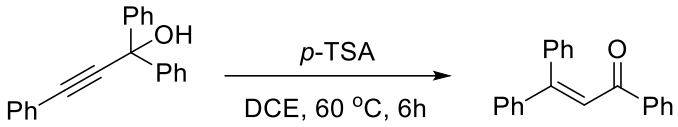
Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification.

2. General Procedure for Preparation of Material

General Procedure for Preparation of α,β-unsaturated Ketones[1]

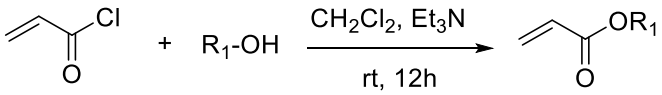


To a solution of NaOH (20 mmol, 2.0 equiv, 0.80 g) in H_2O (10 mL) and aromatic ketone (10 mmol, 1.0 equiv, 1.20 g) in 12 mL ethanol at 0 °C was added gradually aromatic aldehyde (10 mmol, 1.0 equiv, 1.06 g). The mixture was then allowed to warm to room temperature and stirred for 4 h, after which a precipitate of the product formed. The crude product was collected by suction filtration on a Buchner funnel and washed repeatedly with cold water. Further recrystallization from ethanol or purification by silica gel column chromatography afforded corresponding α,β-unsaturated ketones.



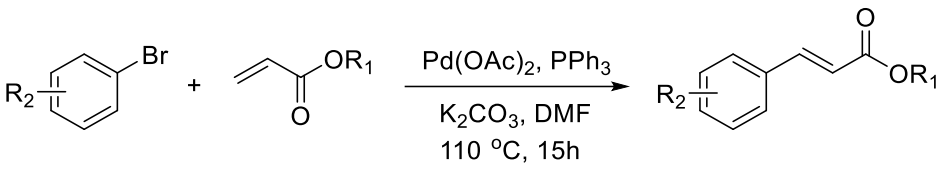
The corresponding 1,1,3-triphenylprop-2-yn-1-ol (10 mmol, 1.0 equiv, 2.84 g) and *p*-toluenesulphonicacid (3 mmol, 0.3 equiv, 0.52 g) were dissolved in dry DCE (20 mL) under nitrogen atmosphere. The reaction mixture was stirred at 60 °C (oil bath) for 6 h. The solvent was removed under reduced pressure and the resultant crude product was purified by silica gel column chromatography.

General Procedure for Preparation of Acrylate[2]



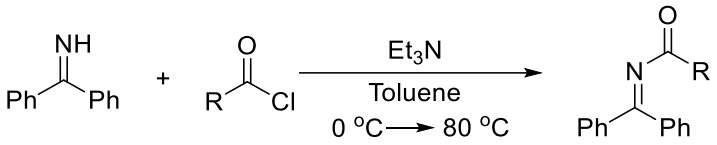
Derivative of alcohol or phenol (10 mmol, 1.0 equiv, 0.95 g) was mixed with Et_3N (15 mmol, 1.5 equiv, 1.51 g) in dry CH_2Cl_2 (20 mL) and cooled to 0 °C in an ice-water bath. Then acryloyl chloride (12 mmol, 1.2 equiv, 1.09 g) was added dropwise. The mixture was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to get the desired product.

General Procedure for Preparation of Cinnamic esters[3]



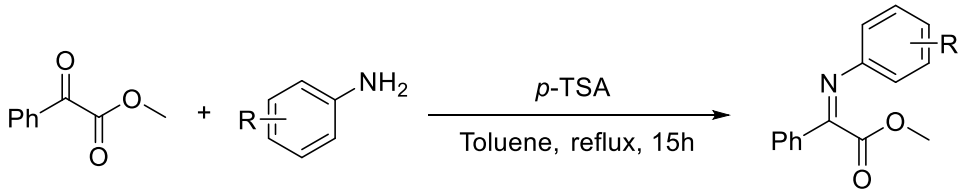
Bromobenzene (10 mmol, 1.0 equiv, 1.57 g), acrylate (12 mmol, 1.2 equiv, 1.03 g) were added to a solution of $Pd(OAc)_2$ (1 mmol, 10 mol%, 0.23 g), PPh_3 (2 mmol, 20 mol%, 0.52 g) and K_2CO_3 (20 mmol, 2.0 equiv, 2.76 g) in dry DMF (20 mL) under nitrogen at 110 °C (oil bath) for 15 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (3 × 30 mL). The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

General Procedure for Preparation of *N*-acylimine[4]



A solution of benzophenone imine (10 mmol, 1.0 equiv, 1.81 g) was dissolved in toluene (20 mL) under nitrogen flow. Triethylamine (20 mmol, 2.0 equiv, 2.02 g) and corresponding acyl chloride (10 mmol, 1.0 equiv, 1.41 g) were added at room temperature. The resulting mixture was stirred for 2 h at 80 ºC (oil bath). After the mixture was cooled to room temperature, saturated ammonium chloride solution was added and the mixture was extracted with DCM (3 × 30 mL), and combined organic layer was evaporated in vacuo. The resulting solid was washed with cold hexane to afford desired products as a white solid.

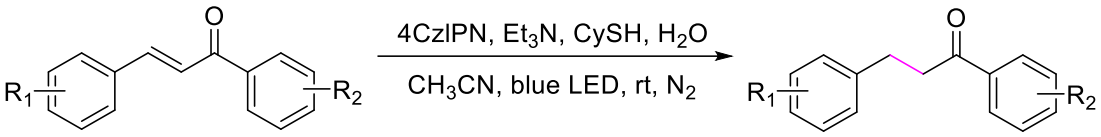
General Procedure for Preparation of α-aryl imino ester[5]



The mixture of anisidine (10.5 mmol, 1.05 equiv, 0.98 g), methyl benzoylformate (10 mmol, 1.0 equiv, 1.64 g) and *p*-toluenesulfonic acid (0.5 mmol, 5 mol%, 0.086 g) in toluene (20 mL) was refluxed (oil bath) overnight with azeotropic removal of water. The solvent was evaporated and the residue was purified by flash column chromatography to give the corresponding α-aryl imino ester.

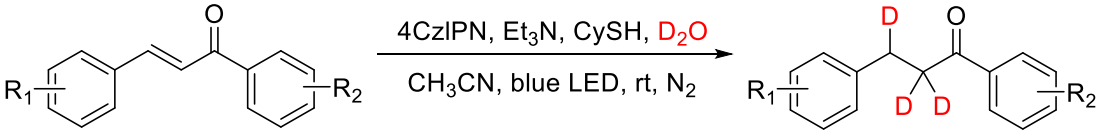
3. General Experimental Procedures

General Procedure for the Photochemical Hydrogenation



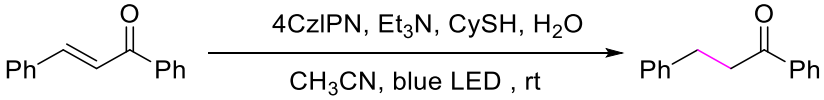
Unsaturated compound (0.2 mmol, 1.0 equiv.), 4CzIPN (0.01 mmol, 5 mol%) were placed in a 10.0 mL quartz test tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), Et_3N (0.3 mmol, 1.5 equiv.), CySH (0.24 mmol, 1.2 equiv.), H_2O (3.0 mmol, 15.0 equiv.) and CH_3CN (2 mL) were sequentially added under nitrogen atmosphere. The quartz test tube was sealed and placed approximately 3 cm from two 50W blue LEDs (λ=450 nm). This mixture was then stirred and irradiated for 12 h at room temperature. The reaction mixture was evaporated and purified directly by column chromatography to afford the product.

General Procedure for the Photochemical Deuteration



Unsaturated compound (0.2 mmol, 1.0 equiv.), 4CzIPN (0.01 mmol, 5 mol%) were placed in a 10.0 mL quartz test tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), Et_3N (0.3 mmol, 1.5 equiv.), CySH (0.24 mmol, 1.2 equiv.), D_2O (3.0 mmol, 15.0 equiv.) and CH_3CN (2 mL) were sequentially added under nitrogen atmosphere. The quartz test tube was sealed and placed approximately 3 cm from two 50W blue LEDs (λ=450 nm). This mixture was then stirred and irradiated for 12 h at room temperature. The reaction mixture was evaporated and purified directly by column chromatography to afford the produc

4. Gram-Scale Synthesis



(*E*)-1,3-Diphenyl-2-propenone (10.0 mmol, 1.0 equiv, 2.08 g), 4CzIPN (0.5 mmol, 5 mol%, 0.39 g), were placed in a 50.0 mL quartz test tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), Et_3N (15.0 mmol, 1.5 equiv, 1.52 g), CySH (12.0 mmol, 1.2 equiv, 1.39 g),

H_2O (150 mmol, 15.0 equiv, 2.70 g) and CH_3CN (20 mL) were sequentially added under nitrogen atmosphere. The quartz test tube was sealed and placed approximately 3 cm from two 50W blue LEDs (λ=450 nm). This mixture was then stirred and irradiated for 12 h at room temperature. The reaction mixture was evaporated and purified directly by column chromatography to afford the product (71%, 1.48 g).

5. Ultraviolet Absorption and Fluorescence Quenching Experiments

UV/Vis absorption spectra were recorded on a SHIMADZU UV-2600 spectrophotometer. $1*10^{-3}$ mol/L^{-1} different solutions using MeCN as the solvent were prepared. The samples were measured in Surui® fluorescence quartz cuvettes (chamber volume = 3.500 mL, H ×W ×D = 48 mm × 12.5 mm × 12.5 mm, path length = 10 mm)

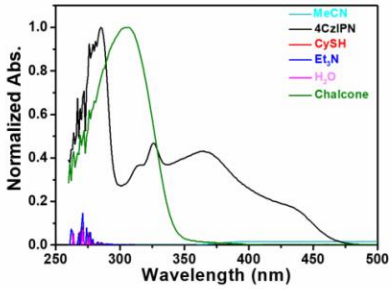
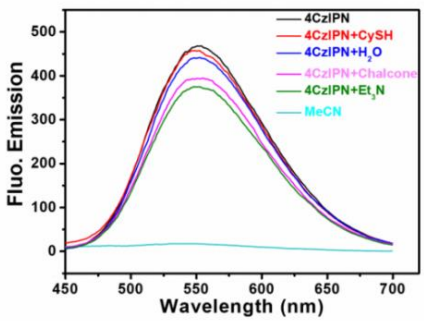


Fig. S2 UV-Vis absorption spectrum

The fluorescence spectrum is recorded on the burker F-7000. Different solutions using MeCN as the solvent were prepared. The samples were measured in Surui® fluorescence quartz cuvettes (chamber volume = 3.500 mL, H × W × D = 48 mm × 12.5 mm × 12.5 mm, path length = 10 mm). The following parameters were set: data interval = 0.5 nm, scan-speed = 500 nm/min, excitation wavelength λ_{ex} = 330 nm.



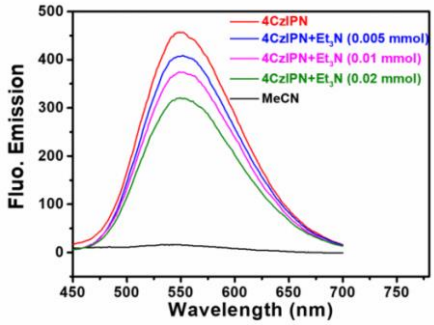


Fig. S3 Fluorescence spectrum (1)

Fig. S4 Fluorescence spectrum (2)

6. Cyclic Voltammetry Measurement

Cyclic voltammograms were recorded using an Autolab potentiostat. The sample was prepared using 0.025 mmol of ketone **56** in 5 mL of a 0.1 M solution of $N(n\text{Bu})_4PF_6$ in dry, degassed MeCN. Measurements used a glassy carbon working electrode, a platinum counter electrode, and a saturated calomel electrode with scan rates of 100 and 250 mV/s.

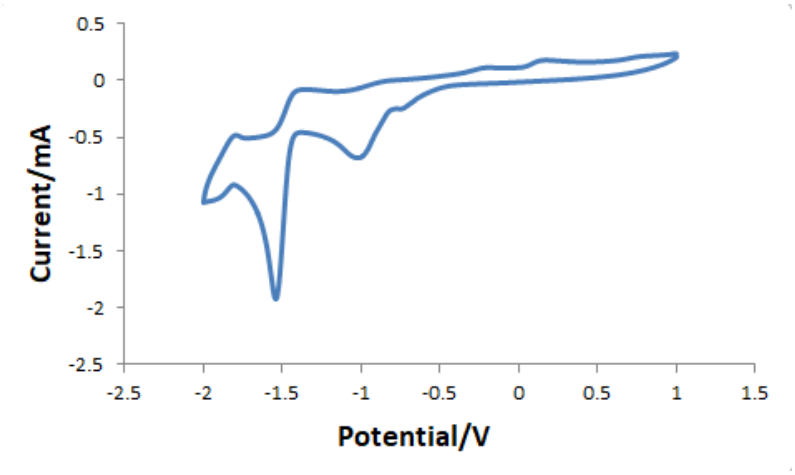
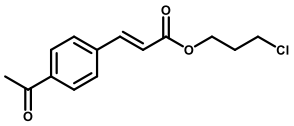
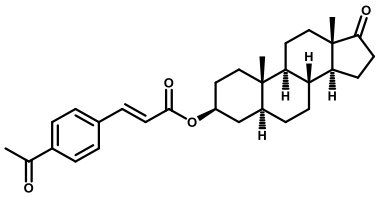


Fig. S5 Cyclic voltammograms of ketone **56** in MeCN

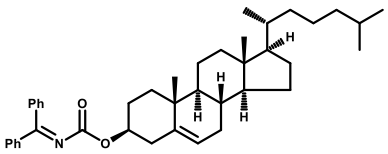
7 Characterization Data of all Substrates



3-chloropropyl (*E*)-3-(4-acetylphenyl)acrylate (S1): yellow liquid; EtOAc/PE = 1/1, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.91-7.89 (m, 2H), 7.63 (d, *J* = 16.0 Hz, 1H), 7.55-7.53 (m, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.33 (t, *J* = 6.0 Hz, 2H), 3.71 (t, *J* = 6.0 Hz, 2H), 2.55 (s, 3H), 1.93-1.90 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 197.5, 166.8, 143.4, 138.7, 138.0, 128.8, 128.1, 120.5, 61.8, 59.0, 31.8, 26.6. HR-MS (ESI) m/z: Calculated for $C_{14}H_{16}ClO_3^+$[M + H]$^+$: 267.0782. Found: 267.0789.



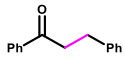
(3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (*E*)-3-(4-acetylphenyl)acrylate (S2): white solid; EtOAc/PE = 1/8, v/v. m.p. 171.8-172.5 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 16.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 4.88-4.80 (m, 1H), 2.61 (s, 3H), 2.47-2.40 (m, 1H), 2.11-2.02 (m, 1H), 1.96-1.90 (m, 2H), 1.82-1.76 (m, 3H), 1.72-1.65 (m, 3H), 1.60-1.52 (m, 2H), 1.47-1.44 (m, 1H), 1.37-1.24 (m, 6H), 1.12-1.05 (m, 1H), 1.04-0.97 (m, 1H), 0.88 (s, 3H), 0.86 (s, 3H), 0.77-0.70 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 197.3, 166.0, 142.8, 138.9, 138.0, 128.9, 128.1, 121.3, 74.0, 54.4, 51.4, 47.8, 44.7, 36.8, 35.9, 35.7, 35.1, 34.0, 31.6, 30.8, 28.3, 27.5, 26.7, 21.8, 20.5, 13.8, 12.3. HR-MS (ESI) m/z: Calculated for $C_{30}H_{39}O_4^+$[M + H]$^+$: 463.2843. Found: 463.2824.



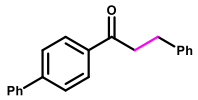
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (diphenylmethylene)carbamate: white solid; m.p. 170.9-171.7 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.60-7.57 (m, 2H), 7.50-7.46 (m, 4H), 7.42-7.39 (m, 4H), 5.32-5.31 (m, 1H), 4.56-4.46 (m, 1H), 2.15-2.14 (m, 1H), 2.02-1.93 (m, 2H), 1.86-1.78 (m, 2H), 1.71-1.67 (m, 1H), 1.56-1.40 (m, 8H), 1.36-1.33 (m, 3H), 1.28-1.24 (m, 1H), 1.18-1.08 (m, 7H), 1.03-1.00 (m, 3H), 0.96 (s, 3H), 0.92-0.91 (m,

3H), 0.88 (s, 3H), 0.86 (s, 3H), 0.67 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 171.0, 162.1, 139.5, 132.4, 130.1, 128.3, 128.2, 122.7, 76.0, 56.7, 56.2, 50.0, 42.3, 39.8, 39.6, 37.9, 37.0, 36.5, 36.2, 35.8, 31.9, 28.2, 28.0, 27.6, 24.3, 23.9, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9. HR-MS (ESI) m/z: Calculated for $C_{41}H_{56}NO_2^+$[M + H]$^+$: 594.4306. Found: 594.4281.

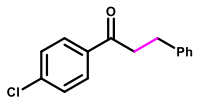
8 Characterization data of all products



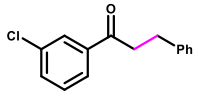
1,3-diphenylpropan-1-one (2): white solid (34.4 mg, 82% yield); EtOAc/PE = 1/20, v/v. m.p. 67.8-68.1 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 7.2 Hz, 2H), 7.57-7.53 (m, 1H), 7.47-7.43 (m, 2H), 7.32-7.19 (m, 5H), 3.31 (t, *J* = 8.4 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.3, 141.3, 136.9, 133.1, 128.6, 128.5, 128.4, 128.1, 126.2, 40.5, 30.2. HR-MS (ESI) m/z: Calculated for $C_{15}H_{15}O^{+}[M + H]^{+}$: 211.1117. Found: 211.1114.



1-([1,1'-biphenyl]-4-yl)-3-phenylpropan-1-one (3): white solid (29.7 mg, 52% yield); EtOAc/PE = 1/20, v/v. m.p. 117.6-118.5 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.05 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 6.8 Hz, 2H), 7.50-7.46 (m, 2H), 7.43-7.39 (m, 1H), 7.35-7.28 (m, 4H), 7.25-7.22 (m, 1H), 3.35 (t, *J* = 8.0 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 198.9, 145.8, 141.4, 139.9, 135.6, 129.0, 128.7, 128.6, 128.5, 128.3, 127.3, 127.2, 126.2, 40.6, 30.2. HR-MS (ESI) m/z: Calculated for $C_{21}H_{19}O^{+}[M + H]^{+}$: 287.1430. Found: 287.1426.

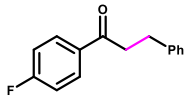


1-(4-chlorophenyl)-3-phenylpropan-1-one (4): white solid (30.7 mg, 63% yield); EtOAc/PE = 1/20, v/v. m.p. 72.4-72.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.32-7.29 (m, 2H), 7.25-7.21 (m, 3H), 3.26 (t, *J* = 8.0 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 193.2, 136.3, 134.8, 130.4, 124.7, 124.2, 123.8, 123.7, 121.5, 35.7, 25.3. HR-MS (ESI) m/z: Calculated for $C_{15}H_{14}ClO^{+}[M + H]^{+}$: 245.0728. Found: 245.0722.

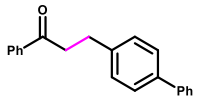


1-(3-chlorophenyl)-3-phenylpropan-1-one (5): yellow liquid (25.4 mg, 52% yield); EtOAc/PE = 1/20, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.92-7.91 (m, 1H), 7.83-7.81 (m, 1H), 7.53-7.51 (m, 1H), 7.41-7.37 (m, 1H), 7.32-7.28 (m, 2H), 7.25-7.21 (m, 3H), 3.28 (t, *J* = 8.0 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 197.9, 141.0, 138.4, 135.0, 133.0, 130.0, 128.6, 128.4, 128.2,

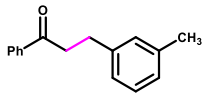
126.3, 126.1, 40.6, 30.0. HR-MS (ESI) m/z: Calculated for $C_{15}H_{14}ClO^+[M + H]^+$: 245.0728. Found: 245.0732.



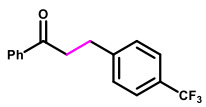
1-(4-fluorophenyl)-3-phenylpropan-1-one (6): yellow liquid (37.9 mg, 83% yield); EtOAc/PE = 1/20, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.92-7.88 (m, 2H), 7.24-7.21 (m, 2H), 7.18-7.13 (m, 3H), 7.06-7.02 (m, 2H), 3.20 (t, *J* = 8.0 Hz, 2H), 2.98 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 197.6, 165.7 (d, *J* = 253.8 Hz), 141.2, 133.3 (d, *J* = 2.5 Hz), 130.7, 130.6, 128.4, 126.2, 115.7 (d, *J* = 21.3 Hz), 40.4, 30.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ (ppm) -105.3. HR-MS (ESI) m/z: Calculated for $C_{15}H_{14}FO^+[M + H]^+$: 229.1023. Found: 229.1014.



3-([1,1'-biphenyl]-4-yl)-1-phenylpropan-1-one (7): white solid (40.1 mg, 70% yield); EtOAc/PE = 1/20, v/v. m.p. 48.0-49.5 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J* = 7.2 Hz, 2H), 7.61-7.55 (m, 5H), 7.50-7.43 (m, 4H), 7.36-7.34 (m, 3H), 3.36 (t, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.2, 141.0, 140.5, 139.2, 136.9, 133.1, 128.9, 128.8, 128.7, 128.1, 127.3, 127.1, 127.0, 40.4, 29.8. HR-MS (ESI) m/z: Calculated for $C_{21}H_{19}O^+[M + H]^+$: 287.1430. Found: 287.1436.

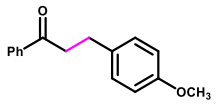


1-phenyl-3-(m-tolyl)propan-1-one (8): yellow solid (22.4 mg, 50% yield); EtOAc/PE = 1/20, v/v. m.p. 68.2-69.3 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.98 (d, *J* = 7.2 Hz, 2H), 7.58-7.55 (m, 1H), 7.48-7.44 (m, 2H), 7.22-7.19 (m, 1H), 7.09-7.03 (m, 3H), 3.31 (t, *J* = 8.0 Hz, 2H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.35 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.3, 141.3, 138.2, 136.9, 133.1, 129.3, 128.6, 128.5, 128.1, 126.9, 125.4, 40.6, 30.1, 21.4. HR-MS (ESI) m/z: Calculated for $C_{16}H_{17}O^+[M + H]^+$: 225.1274. Found: 225.1271.

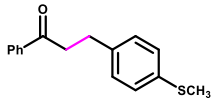


1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (9): yellow liquid (39.5 mg, 71% yield); EtOAc/PE = 1/20, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 7.6 Hz, 2H), 7.59-7.54 (m, 3H), 7.48-7.44 (m, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 3.33 (t, *J* = 7.2 Hz, 2H), 3.14 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 198.6,

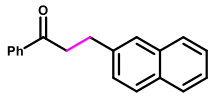
145.5, 136.7, 133.3, 128.8, 128.7, 128.3 (q, *J* = 32.5 Hz), 128.0, 125.5 (q, *J* = 3.75 Hz), 124.3 (q, *J* = 270 Hz), 39.8, 29.8. **^{19}F NMR** (471 MHz, $CDCl_3$) δ (ppm) -62.3. HR-MS (ESI) m/z: Calculated for $C_{16}H_{14}F_3O^+[M + H]^+$: 279.0991. Found: 279.0988.



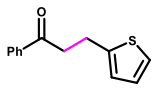
3-(4-methoxyphenyl)-1-phenylpropan-1-one (10): white solid (24.9 mg, 52% yield); EtOAc/PE = 1/10, v/v. m.p. 58.6-59.7 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 8.0 Hz, 2H), 7.57-7.54 (m, 1H), 7.47-7.44 (m, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 3.27 (t, *J* = 7.5 Hz, 2H), 3.02 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.4, 158.0, 136.9, 133.3, 133.1, 129.4, 128.6, 128.1, 114.0, 55.3, 40.7, 29.3. HR-MS (ESI) m/z: Calculated for $C_{16}H_{17}O_2^+[M + H]^+$: 241.1223. Found: 241.1218.



3-(4-(methylthio)phenyl)-1-phenylpropan-1-one (11): yellow liquid (34.8 mg, 68% yield); EtOAc/PE = 1/20, v/v. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 8.0 Hz, 2H), 7.57-7.55 (m, 1H), 7.47-7.44 (m, 2H), 7.22-7.18 (m, 4H), 3.28 (t, *J* = 8.0 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), 2.47 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.1, 138.4, 136.9, 135.8, 133.1, 129.0, 128.6, 128.1, 127.3, 40.4, 29.6, 16.3. HR-MS (ESI) m/z: Calculated for $C_{16}H_{17}OS^+[M + H]^+$: 257.0995. Found: 257.0990.

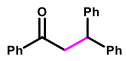


3-(naphthalen-2-yl)-1-phenylpropan-1-one (12): yellow solid (37.9 mg, 73% yield); EtOAc/PE = 1/20, v/v. m.p. 66.7-67.8 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 7.99 (d, *J* = 7.0 Hz, 2H), 7.83-7.80 (m, 3H), 7.71-7.70 (m, 1H), 7.59-7.56 (m, 1H), 7.48-7.40 (m, 5H), 3.41 (t, *J* = 8.0 Hz, 2H), 3.25 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.2, 138.8, 136.9, 133.7, 133.1, 132.1, 128.7, 128.2, 128.1, 127.7, 127.5, 127.2, 126.6, 126.1, 125.4, 40.4, 30.3. HR-MS (ESI) m/z: Calculated for $C_{19}H_{17}O^+[M + H]^+$: 261.1274. Found: 261.1284.

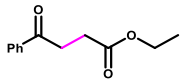


3-phenyl-1-(thiophen-2-yl)propan-1-one (13): yellow liquid (27.7 mg, 64% yield); EtOAc/PE = 1/10, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.69-7.68 (m, 1H), 7.63-7.61 (m, 1H), 7.32-7.28 (m, 2H), 7.26-7.19 (m, 3H), 7.12-7.10 (m, 1H), 3.23 (t, *J* = 8.0 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 192.2,

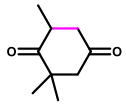
144.2, 141.0, 133.6, 131.8, 128.6, 128.5, 128.1, 126.2, 41.2, 30.4. HR-MS (ESI) m/z: Calculated for $C_{13}H_{13}OS^+[M + H]^+$: 217.0682. Found: 217.0687.



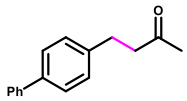
1,3,3-triphenylpropan-1-one (14): yellow solid (55.5 mg, 97% yield); EtOAc/PE = 1/20, v/v. m.p. 90.5-91.7 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.97-7.95 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.44 (m, 2H), 7.30-7.29 (m, 8H), 7.23-7.18 (m, 2H), 4.87 (t, *J* = 7.2 Hz, 1H), 3.77 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 198.0, 144.2, 137.1, 133.1, 128.7, 128.6, 128.1, 127.9, 126.4, 46.0, 44.8. HR-MS (ESI) m/z: Calculated for $C_{21}H_{19}O^+[M + H]^+$: 287.1430. Found: 287.1436.



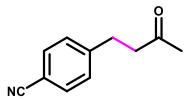
ethyl 4-oxo-4-phenylbutanoate (15): yellow liquid (30.1 mg, 73% yield); EtOAc/PE = 1/10, v/v. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 7.98 (d, *J* = 7.5 Hz, 2H), 7.58-7.55 (m, 1H), 7.48-7.45 (m, 2H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.31 (t, *J* = 7.0 Hz, 2H), 2.75 (t, *J* = 6.5 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 198.2, 172.9, 136.6, 133.2, 128.6, 128.0, 60.7, 33.4, 28.3, 14.2. HR-MS (ESI) m/z: Calculated for $C_{12}H_{15}O_3^+[M + H]^+$: 207.1016. Found: 207.1012.



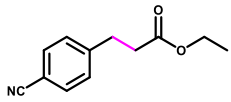
2,2,6-trimethylcyclohexane-1,4-dione (16): white solid (19.1 mg, 62% yield); EtOAc/PE = 1/10, v/v. m.p. 67.2-68.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 3.05-2.95 (m, 1H), 2.78-2.76 (m, 1H), 2.73-2.71 (m, 1H), 2.51 (d, *J* = 15.6 Hz, 1H), 2.37-2.29 (m, 1H), 1.20 (s, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.11 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 214.1, 208.0, 52.8, 44.9, 39.8, 26.5, 25.6, 14.6. HR-MS (ESI) m/z: Calculated for $C_9H_{15}O_2^+[M + H]^+$: 155.1067. Found: 155.1061.



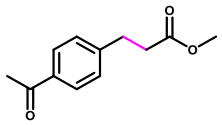
4-([1,1'-biphenyl]-4-yl)butan-2-one (17): yellow solid (16.6 mg, 37% yield); EtOAc/PE = 1/10, v/v. m.p. 61.6-62.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.57 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.17 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 207.9, 141.0, 140.1, 139.1, 128.8, 128.7, 127.3, 127.1, 127.0, 45.1, 30.1, 29.4. HR-MS (ESI) m/z: Calculated for $C_{16}H_{17}O^+[M + H]^+$: 225.1274. Found: 225.1265.



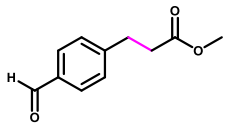
4-(3-oxobutyl)benzonitrile (18): yellow liquid (25.3 mg, 73% yield); EtOAc/PE = 1/10, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.55 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.14 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 206.8, 146.8, 132.3, 129.2, 118.9, 110.1, 44.2, 30.1, 30.0. HR-MS (ESI) m/z: Calculated for $C_{11}H_{12}NO^+$[M + H]$^+$: 174.0913. Found: 174.0916.



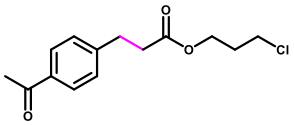
ethyl 3-(4-cyanophenyl)propanoate (19): yellow liquid (32.9 mg, 81% yield); EtOAc/PE = 1/10, v/v. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 7.57 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.22 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 172.2, 146.2, 132.3, 129.2, 118.9, 110.3, 60.7, 35.1, 30.9, 14.2. HR-MS (ESI) m/z: Calculated for $C_{12}H_{14}NO_2^+$[M + H]$^+$: 204.1019. Found: 204.1011.



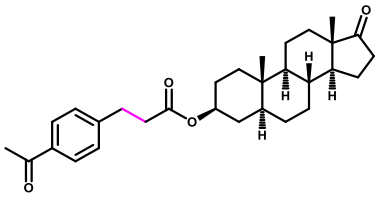
methyl 3-(4-acetylphenyl)propanoate (20): yellow liquid (32.9 mg, 80% yield); EtOAc/PE = 1/10, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.66 (s, 3H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.57 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 197.8, 172.9, 146.2, 135.5, 128.7, 128.5, 51.7, 35.1, 30.8, 26.6. HR-MS (ESI) m/z: Calculated for $C_{12}H_{15}O_3^+$[M + H]$^+$: 207.1016. Found: 207.1022.



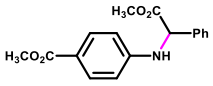
methyl 3-(4-formylphenyl)propanoate (21): yellow liquid (23.0 mg, 60% yield); EtOAc/PE = 1/10, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.98 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.67 (s, 3H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 191.9, 172.8, 147.8, 134.9, 130.1, 129.0, 51.8, 35.0, 31.0. HR-MS (ESI) m/z: Calculated for $C_{11}H_{13}O_3^+$[M + H]$^+$: 193.0859. Found: 193.0855.



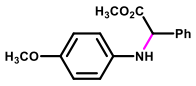
3-chloropropyl 3-(4-acetylphenyl)propanoate (22): yellow liquid (38.1 mg, 71% yield); EtOAc/PE = 1/1, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 4.22 (t, *J* = 6.0 Hz, 2H), 3.61 (t, *J* = 5.6 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.57 (s, 3H), 1.86-1.79 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 197.9, 172.9, 146.1, 135.5, 128.7, 128.6, 61.6, 59.1, 35.3, 31.7, 30.8, 26.6. HR-MS (ESI) m/z: Calculated for $C_{14}H_{18}ClO_3^+$[M + H]$^+$: 269.0939. Found: 269.0932.



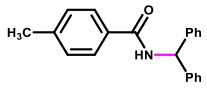
(3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-(4-acetylphenyl)propanoate (23): white solid (70.5 mg, 76% yield); EtOAc/PE = 1/8, v/v. m.p. 143.5-144.7 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.71-4.63 (m, 1H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 2.45-2.38 (m, 1H), 2.09-2.00 (m, 1H), 1.94-1.87 (m, 1H), 1.79-1.74 (m, 4H), 1.65-1.61 (m, 1H), 1.57-1.42 (m, 4H), 1.35-1.18 (m, 7H), 1.03-0.94 (m, 2H), 0.84 (s, 3H), 0.82 (s, 3H), 0.72-0.66 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 197.7, 172.0, 146.3, 135.4, 128.6, 128.5, 73.8, 54.3, 51.4, 47.8, 44.7, 36.7, 35.8, 35.6, 35.0, 33.9, 31.5, 31.0, 30.8, 28.3, 27.4, 26.6, 21.8, 20.5, 13.8, 12.2. HR-MS (ESI) m/z: Calculated for $C_{30}H_{41}O_4^+$[M + H]$^+$: 465.2999. Found: 564.3016.



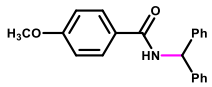
methyl 4-((2-methoxy-2-oxo-1-phenylethyl)amino)benzoate (24): white solid (54.4 mg, 91% yield); EtOAc/PE = 1/8, v/v. m.p. 144.2-145.9 ℃. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ (ppm) 7.64 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.35-7.32 (m, 2H), 7.29-7.26 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 2H), 5.34 (d, *J* = 8.0 Hz, 1H), 3.68 (s, 3H), 3.60 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ (ppm) 172.1, 166.7, 151.6, 137.6, 131.2, 129.2, 128.7, 128.1, 117.7, 112.6, 59.6, 52.9, 51.8. HR-MS (ESI) m/z: Calculated for $C_{17}H_{18}NO_4^+$[M + H]$^+$: 300.1230. Found: 300.1236.



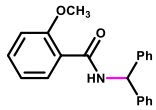
methyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (25): yellow solid (43.9 mg, 81% yield); EtOAc/PE = 1/10, v/v. m.p. 98.7-100.1 ℃. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ (ppm) 7.50 (d, *J* = 7.2 Hz, 2H), 7.38-7.34 (m, 2H), 7.32-7.28 (m, 1H), 6.70-6.63 (m, 4H), 5.95 (d, *J* = 8.4 Hz, 1H), 5.17 (d, J = 8.8 Hz, 1H), 3.62 (s, 3H), 3.61 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ (ppm) 172.9, 151.9, 141.5, 138.4, 129.0, 128.4, 128.0, 114.9, 114.8, 60.9, 55.7, 52.6. HR-MS (ESI) m/z: Calculated for $C_{16}H_{18}NO_3^+$[M + H]$^+$: 272.1281. Found: 272.1277.



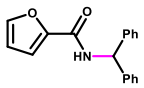
N-**benzhydryl-4-methylbenzamide (26):** white solid (51.8 mg, 86% yield); EtOAc/PE = 1/10, v/v. m.p. 176.1-177.9 ℃. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ (ppm) 9.17 (d, *J* = 9.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.37-7.32 (m, 8H), 7.28-7.25 (m, 4H), 6.41 (d, *J* = 9.2 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ (ppm) 166.3, 142.9, 141.7, 132.0, 129.2, 128.8, 128.2, 128.1, 127.4, 56.7, 21.4. HR-MS (ESI) m/z: Calculated for $C_{21}H_{20}NO^+$[M + H]$^+$: 302.1539. Found: 302.1544.



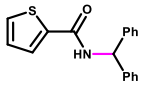
N-**benzhydryl-4-methoxybenzamide (27):** white solid (60.2 mg, 95% yield); EtOAc/PE = 1/5, v/v. m.p. 196.4-197.9 ℃. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ (ppm) 9.05 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.32-7.26 (m, 8H), 7.21-7.18 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 8.8 Hz, 1H), 3.74 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ (ppm) 165.8, 162.2, 143.0, 130.0, 128.8, 128.1, 127.4, 127.0, 113.9, 56.7, 55.8. HR-MS (ESI) m/z: Calculated for $C_{21}H_{20}NO_2^+$[M + H]$^+$: 318.1489. Found: 318.1486.



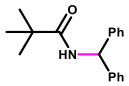
N-**benzhydryl-2-methoxybenzamide (28):** yellow solid (57.7 mg, 91% yield); EtOAc/PE = 1/5, v/v. m.p. 116.1-117.5 ℃. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ (ppm) 9.00 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.50-7.46 (m, 1H), 7.40-7.34 (m, 8H), 7.27-7.24 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.05-7.02 (m, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ (ppm) 165.0, 157.4, 143.0, 132.6, 130.6, 129.0, 127.6, 127.5, 124.0, 121.0, 112.6, 57.0, 56.5. HR-MS (ESI) m/z: Calculated for $C_{21}H_{20}NO_2^+$[M + H]$^+$: 318.1489. Found: 318.1482.



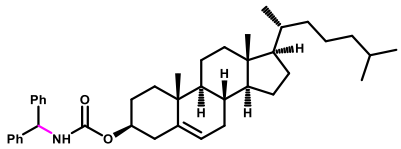
***N*-benzhydrylfuran-2-carboxamide (29):** white solid (50.4 mg, 91% yield); EtOAc/PE = 1/10, v/v. m.p. 128.6-129.7 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 9.18 (d, *J* = 6.8 Hz, 1H), 7.87-7.85 (m, 1H), 7.38-7.34 (m, 8H), 7.30-7.24 (m, 3H), 6.64-6.63 (m, 1H), 6.38 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 157.7, 148.0, 145.7, 142.5, 128.8, 128.1, 127.5, 114.4, 112.3, 56.1. HR-MS (ESI) m/z: Calculated for $C_{18}H_{16}NO_2^+$[M + H]$^+$: 278.1176. Found: 278.1171.



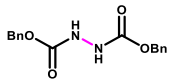
***N*-benzhydrylthiophene-2-carboxamide (30):** white solid (56.3 mg, 96% yield); EtOAc/PE = 1/10, v/v. m.p. 174.3-175.6 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 9.29 (d, *J* = 8.8 Hz, 1H), 8.04-8.03 (m, 1H), 7.78-7.77 (m, 1H), 7.36-7.35 (m, 8H), 7.29-7.26 (m, 2H), 7.17-7.15 (m, 1H), 6.39 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 161.1, 142.5, 140.2, 131.6, 129.2, 128.8, 128.4, 128.2, 127.6, 56.7. HR-MS (ESI) m/z: Calculated for $C_{18}H_{16}NOS^+$[M + H]$^+$: 294.0947. Found: 294.0955.



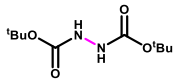
***N*-benzhydrylpivalamide (31):** white solid (29.9 mg, 56% yield); EtOAc/PE = 1/10, v/v. m.p. 143.8-144.9 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.21 (d, *J* = 8.8 Hz, 1H), 7.34-7.31 (m, 4H), 7.27-7.24 (m, 6H), 6.17 (d, *J* = 8.8 Hz, 1H), 1.15 (s, 9H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 177.1, 143.1, 128.7, 128.0, 127.3, 56.1, 38.6, 27.8. HR-MS (ESI) m/z: Calculated for $C_{18}H_{22}NO^+$[M + H]$^+$: 268.1696. Found: 268.1691.



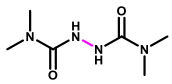
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl benzhydrylcarbamate (32): yellow oil (98.8 mg, 83% yield); EtOAc/PE = 1/10, v/v. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.31-7.27 (m, 4H), 7.23-7.21 (m, 6H), 5.94-5.93 (m, 1H), 5.34-5.26 (m, 1H), 5.26 (s, 1H), 4.51-4.45 (m, 1H), 2.38-2.31 (m, 1H), 2.00-1.91 (m, 3H), 1.86-1.80 (m, 3H), 1.58-1.40 (m, 8H), 1.36-1.28 (m, 4H), 1.14-1.06 (m, 7H), 1.00-0.98 (m, 4H), 0.90-0.89 (m, 4H), 0.84 (d, J = 6.4 Hz, 6H), 0.65 (s, 3H).**^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 155.4, 141.9, 139.8, 128.6, 127.4, 127.3, 122.5, 74.7, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.5, 37.0, 36.5, 36.2, 35.8, 31.9, 31.8, 28.2, 28.1, 28.0, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9. HR-MS (ESI) m/z: Calculated for $C_{41}H_{58}NO_2^+$[M + H]$^+$: 596.4462. Found: 596.4489.



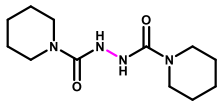
dibenzyl hydrazine-1,2-dicarboxylate (33): yellow solid (27.0 mg, 45% yield); EtOAc/PE = 1/2, v/v. m.p. 65.6-66.9 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 9.25 (s, 2H), 7.38-7.36 (m, 6H), 7.34-7.30 (m, 4H), 5.09 (s, 4H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 157.0, 137.0, 128.9, 128.5, 128.3, 66.4. HR-MS (ESI) m/z: Calculated for $C_{16}H_{17}N_2O_4^+$[M + H]$^+$: 301.1183. Found: 301.1177.



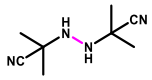
di-*tert*-butyl hydrazine-1,2-dicarboxylate (34): white solid (45.5 mg, 98% yield); EtOAc/PE = 1/3, v/v. m.p. 112.5-113.8 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.58 (s, 2H), 1.39 (s, 18H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 155.8, 81.5, 28.2. HR-MS (ESI) m/z: Calculated for $C_{10}H_{21}N_2O_4^+$[M + H]$^+$: 233.1496. Found: 233.1491.



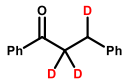
N^1,*N*^{1},*N*^{2},*N*^{2}**-tetramethylhydrazine-1,2-dicarboxamide (35):** white solid (33.8 mg, 97% yield); EtOAc/PE = 1/4, v/v. m.p. 198.9-200.1 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.92 (s, 2H), 2.80 (s, 12H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 159.1, 36.3. HR-MS (ESI) m/z: Calculated for $C_6H_{15}N_4O_2^+$[M + H]$^+$: 175.1190. Found: 175.1196.



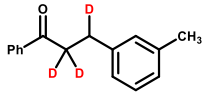
N′**-(piperidine-1-carbonyl)piperidine-1-carbohydrazide (36):** white solid (47.2 mg, 93% yield); EtOAc/PE = 1/4, v/v. m.p. 179.3-180.6 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.02 (s, 2H), 3.29-3.28 (m, 8H), 1.56-1.53 (m, 4H), 1.43-1.41 (m, 8H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 158.3, 44.9, 25.8, 24.6. HR-MS (ESI) m/z: Calculated for $C_{12}H_{23}N_4O_2^+$[M + H]$^+$: 255.1816. Found: 255.1822.



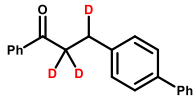
2,2'-(hydrazine-1,2-diyl)bis(2-methylpropanenitrile) (37): white solid (18.6 mg, 56% yield); EtOAc/PE = 1/10, v/v. m.p. 95.6-96.9 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 4.80 (s, 2H), 1.35 (s, 12H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 123.8, 53.8, 25.5. HR-MS (ESI) m/z: Calculated for $C_8H_{15}N_4^+$[M + H]$^+$: 167.1291. Found: 167.1288.



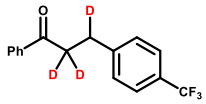
1,3-diphenylpropan-1-one-2,2,3-*d*$_3$ (38): white solid (26.4 mg, 62% yield); EtOAc/PE = 1/20, v/v. m.p. 61.4-62.6 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.94-7.92 (m, 2H), 7.54-7.50 (m, 1H), 7.44-7.40 (m, 2H), 7.30-7.22 (m, 4H), 7.20-7.17 (m, 1H), 3.27-3.23 (m, 0.24H, 88%D), 3.06-3.02 (m, 1.10H, 90%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.4, 141.3, 136.9, 133.1, 128.7, 128.6, 128.5, 128.1, 126.2, 40.4-39.4 (m), 30.1-29.6 (m). HR-MS (ESI) m/z: Calculated for $C_{15}H_{12}D_3O^+[M + H]^+$: 214.1306. Found: 214.1309.



1-phenyl-3-(*m*-tolyl)propan-1-one-2,2,3-*d*$_3$ (39): yellow solid (23.6 mg, 52% yield); EtOAc/PE = 1/20, v/v. m.p. 67.2-68.5 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.99 (d, *J* = 7.6 Hz, 2H), 7.59-7.56 (m, 1H), 7.50-7.46 (m, 2H), 7.24-7.21 (m, 1H), 7.10-7.05 (m, 3H), 3.32-3.27 (m, 0.24H, 88%D), 3.07-3.04 (m, 1.08H, 92%D), 2.37 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.4, 141.2, 138.1, 137.0, 133.1, 129.3, 128.6, 128.5, 128.1, 126.9, 125.4, 40.4-39.5 (m), 30.1-29.6 (m), 21.5. HR-MS (ESI) m/z: Calculated for $C_{16}H_{14}D_3O^+[M + H]^+$: 228.1462. Found: 228.1455.

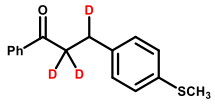


3-([1,1'-biphenyl]-4-yl)-1-phenylpropan-1-one-2,2,3-*d*$_3$ (40): white solid (39.9 mg, 69% yield); EtOAc/PE = 1/20, v/v. m.p. 57.9-59.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.01-7.99 (m, 2H), 7.62-7.60 (m, 2H), 7.58-7.55 (m, 3H), 7.50-7.44 (m, 4H), 7.37-7.35 (m, 3H), 3.37-3.32 (m, 0.21H, 90%D), 3.15-3.12 (m, 1.07H, 93%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.3, 141.0, 140.4, 139.2, 136.9, 133.1, 128.9, 128.8, 128.7, 128.1, 127.3, 127.2, 127.1, 40.1-39.4 (m), 29.7-29.2 (m). HR-MS (ESI) m/z: Calculated for $C_{21}H_{16}D_3O^+[M + H]^+$: 290.1619. Found: 290.1626.

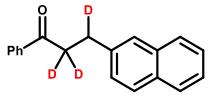


1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one-2,2,3-*d*$_3$ (41): yellow liquid (35.9 mg, 64% yield); EtOAc/PE = 1/20, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 7.6 Hz, 2H), 7.59-7.54 (m, 3H), 7.48-7.44 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.33-3.29 (m, 0.28H, 86%D), 3.14-3.11 (m, 1.05H, 95%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 198.7, 145.5, 136.7, 133.3, 128.8, 128.7. 128.5 (q, *J* = 32.5 Hz), 128.0, 125.4 (q, *J* = 3.75 Hz), 124.4 (q, *J* = 270 Hz), 39.7-38.7 (m), 29.7-29.2 (m). **^{19}F**

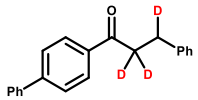
NMR (471 MHz, CDCl3) δ (ppm) -62.3. HR-MS (ESI) m/z: Calculated for $C_{16}H_{11}D_3F_3O^+[M + H]^+$: 282.1180. Found: 282.1188.



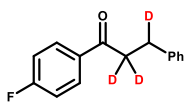
3-(4-(methylthio)phenyl)-1-phenylpropan-1-one-2,2,3-*d*$_3$ (42): yellow liquid (24.3 mg, 47% yield); EtOAc/PE = 1/20, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, *J* = 8.0 Hz, 2H), 7.57-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.23-7.17 (m, 4H), 3.28-3.24 (m, 0.27H, 87%D), 3.05-3.01 (m, 1.09H, 91%D), 2.46 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.2, 138.3, 136.9, 135.8, 133.1, 129.0, 128.7, 128.1, 127.3, 40.3-39.3 (m), 29.5-29.0 (m), 16.3. HR-MS (ESI) m/z: Calculated for $C_{16}H_{14}D_3OS^+[M + H]^+$: 260.1183. Found: 260.1177.



3-(naphthalen-2-yl)-1-phenylpropan-1-one-2,2,3-*d*$_3$ (43): white solid (32.1 mg, 61% yield); EtOAc/PE = 1/20, v/v. m.p. 58.5-59.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J* = 7.2 Hz, 2H), 7.85-7.81 (m, 3H), 7.72-7.71 (m, 1H), 7.59-7.55 (m, 1H), 7.49-7.41 (m, 5H), 3.40-3.35 (m, 0.32H, 84%D), 3.27-3.24 (m, 1.09H, 91%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.3, 138.8, 136.9, 133.7, 133.1, 132.2, 128.7, 128.2, 128.1, 127.7, 127.5, 127.2, 126.6, 126.1, 125.4, 40.3-39.5 (m), 30.3-29.7 (m). HR-MS (ESI) m/z: Calculated for $C_{19}H_{14}D_3O^+[M + H]^+$: 264.1462. Found: 264.1466.

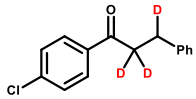


1-([1,1'-biphenyl]-4-yl)-3-phenylpropan-1-one-2,2,3-*d*$_3$ (44): white solid (28.9 mg, 50% yield); EtOAc/PE = 1/20, v/v. m.p. 119.7-120.6 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.59 (d, J = 7.6 Hz, 2H), 7.45-7.42 (m, 2H), 7.38-7.35 (m, 1H), 7.31-7.24 (m, 4H), 7.21-7.18 (m, 1H), 3.30-3.25 (m, 0.38H, 81%D), 3.08-3.05 (m, 1.06H, 94%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 199.0, 145.8, 141.3, 139.9, 135.6, 129.0, 128.7, 128.6, 128.5, 128.3, 127.3, 127.2, 126.2, 40.5-39.5 (m), 30.2-29.7 (m). HR-MS (ESI) m/z: Calculated for $C_{21}H_{16}D_3O^+[M + H]^+$: 290.1619. Found: 290.1612.

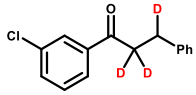


1-(4-fluorophenyl)-3-phenylpropan-1-one-2,2,3-*d*$_3$ (45): yellow liquid (25.4 mg, 55% yield); EtOAc/PE = 1/20, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.98-7.94 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.18 (m, 3H), 7.12-7.07 (m, 2H), 3.25-3.21 (m, 0.30H,

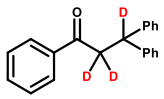
85%D), 3.05-3.02 (m, 1.10H, 90%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 197.7, 165.8 (d, *J* = 253.75 Hz), 141.1, 133.4 (d, *J* = 2.5 Hz), 130.7, 130.6, 128.6, 126.2, 115.7 (d, J = 22.5 Hz), 40.3-39.5 (m), 30.1-29.6 (m). **^{19}F NMR** (471 MHz, CDCl3) δ (ppm) -105.2. HR-MS (ESI) m/z: Calculated for $C_{15}H_{11}D_3FO^+$[M + H]$^+$: 232.1211. Found: 232.1216.



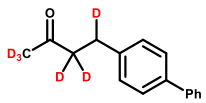
1-(4-chlorophenyl)-3-phenylpropan-1-one-2,2,3-*d*$_3$ (46): white solid (20.2 mg, 41% yield); EtOAc/PE = 1/20, v/v. m.p. 72.6-73.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.88-7.86 (m, 2H), 7.41-7.39 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.19 (m, 3H), 3.25-3.20 (m, 0.32H, 84%D), 3.05-3.02 (m, 1.10H, 90%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 198.1, 141.0, 139.5, 135.2, 129.5, 129.0, 128.6, 128.4, 126.3, 40.4-39.4 (m), 30.0-29.5 (m). HR-MS (ESI) m/z: Calculated for $C_{15}H_{11}D_3ClO^+$[M + H]$^+$: 248.0916. Found: 248.0912.



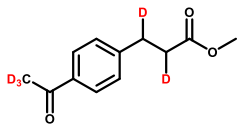
1-(3-chlorophenyl)-3-phenylpropan-1-one-2,2,3-*d*$_3$ (47): yellow liquid (15.8 mg, 32% yield); EtOAc/PE = 1/20, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.91-7.90 (m, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.52-7.50 (m, 1H), 7.40-7.36 (m, 1H), 7.31-7.28 (m, 2H), 7.24-7.20 (m, 3H), 3.26-3.22 (m, 0.40H, 80%D), 3.06-3.03 (m, 1.06H, 94%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 198.0, 141.0, 138.4, 135.0, 133.0. 129.9, 128.6, 128.4, 128.2, 126.3, 126.1, 40.5-39.5 (m), 29.9-29.4 (m). HR-MS (ESI) m/z: Calculated for $C_{15}H_{11}D_3ClO^+$[M + H]$^+$: 248.0916. Found: 248.0919.



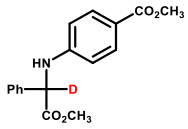
1,3,3-triphenylpropan-1-one-2,2,3-*d*$_3$ (48): white solid (55.5 mg, 96% yield); EtOAc/PE = 1/20, v/v. m.p. 92.9-93.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 7.6 Hz, 2H), 7.44-7.41 (m, 1H), 7.34-7.30 (m, 2H), 7.22-7.18 (m, 8H), 7.12-7.09 (m, 2H), 4.81-4.80 (m, 0.11H, 89%D), 3.67-3.63 (m, 0.30H, 85%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 198.2, 144.3, 137.2, 133.2, 128.8, 128.7, 128.2, 128.0, 126.6, 46.1-45.5 (m), 44.8-43.7 (m). HR-MS (ESI) m/z: Calculated for $C_{21}H_{16}D_3O^+$[M + H]$^+$: 290.1619. Found: 290.1610.



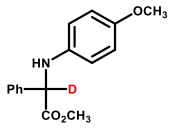
4-([1,1'-biphenyl]-4-yl)butan-2-one-1,1,1,3,3,4-*d*$_6$ (49): white solid (12.9 mg, 28% yield); EtOAc/PE = 1/10, v/v. m.p. 63.5-64.7 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.57-7.55 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43-7.39 (m, 2H), 7.34-7.30 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.93-2.90 (m, 1.01H, 99%D), 2.78-2.74 (m, 0.33H, 84%D), 2.14-2.10 (m, 0.67H, 78%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 208.1, 141.0, 140.1, 139.2, 128.8, 128.7, 127.3, 127.1, 127.0, 44.8-44.2 (m), 29.9-29.5 (m), 29.3-28.8 (m). HR-MS (ESI) m/z: Calculated for $C_{16}H_{11}D_6O^+$[M + H]$^+$: 231.1651. Found: 231.1659.



methyl 3-(4-(acetyl-*d*$_3$)phenyl)propanoate-2,3-*d*$_2$ (50): yellow liquid (30.0 mg, 71% yield) ; EtOAc/PE = 1/10, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.66 (s, 3H), 3.01-2.97 (m, 1.05H, 95%D), 2.65-2.62 (m, 1.14H, 86%D), 2.57-2.53 (m, 0.63H, 79%D). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 197.7, 172.8, 146.1, 135.5, 128.6, 128.5, 51.6, 35.0-24.5 (m), 30.8-30.2 (m), 26.1-25.6 (m). HR-MS (ESI) m/z: Calculated for $C_{12}H_{10}D_5O_3^+$[M + H]$^+$: 212.1330. Found: 212.1337.

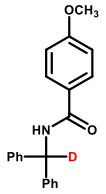


methyl 4-((2-methoxy-2-oxo-1-phenylethyl-1-*d*)amino)benzoate (51): white solid (54.0 mg, 90% yield); EtOAc/PE = 1/8, v/v. m.p. 150.3-151.6 ℃. **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ (ppm) 7.75-7.73 (m, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.41-7.38 (m, 2H), 7.34-7.31 (m, 1H), 7.24 (s, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 5.41 (d, *J* = 8.0 Hz, 0.11H, 89%D), 3.74 (s, 3H), 3.66 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ (ppm) 172.1, 166.8, 151.6, 137.6, 131.3, 129.2, 128.7, 128.1, 117.8, 112.6, 59.7-59.2 (m), 52.8, 51.7. HR-MS (ESI) m/z: Calculated for $C_{17}H_{17}DNO_4^+$[M + H]$^+$: 301.1293. Found: 301.1299.

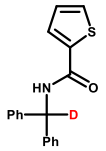


methyl 2-((4-methoxyphenyl)amino)-2-phenylacetate-*d* (52): white solid (40.8 mg, 75% yield); EtOAc/PE = 1/10, v/v. m.p. 100.7-101.9 ℃. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ (ppm) 7.43 (d, *J* = 7.2 Hz, 2H), 7.27-7.24 (m, 2H), 7.21-7.19 (m, 1H), 6.59-6.57 (m, 4H), 5.09 (d, *J* = 8.4 Hz, 0.1H, 90%D), 5.85 (s, 1H), 3.51 (s, 6H). **^{13}C**

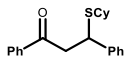
NMR (125 MHz, DMSO-d_6) δ (ppm) 177.7, 156.7, 146.2, 143.2, 133.8, 133.2, 132.8, 119.7, 119.6, 65.8-65.3 (m), 60.4, 57.3. HR-MS (ESI) m/z: Calculated for $C_{16}H_{17}DNO_3^+[M + H]^+$: 273.1344. Found: 272.1340.



N-**(diphenylmethyl-*d*)-4-methoxybenzamide (53):** white solid (26.1 mg, 41% yield); EtOAc/PE = 1/5, v/v. m.p. 191.7-192.8 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.12 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.39-6.33 (m, 8H), 6.27-6.24 (m, 2H), 6.01 (d, *J* = 8.8 Hz, 2H), 5.44 (d, J = 8.4 Hz, 0.09H, 91%D), 2.81 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 165.9, 162.2, 142.9, 130.0, 128.8, 128.1, 127.4, 127.0, 113.9, 56.7-56.3 (m), 55.8. HR-MS (ESI) m/z: Calculated for $C_{21}H_{19}DNO_2^+[M + H]^+$: 319.1551. Found: 319.1558.



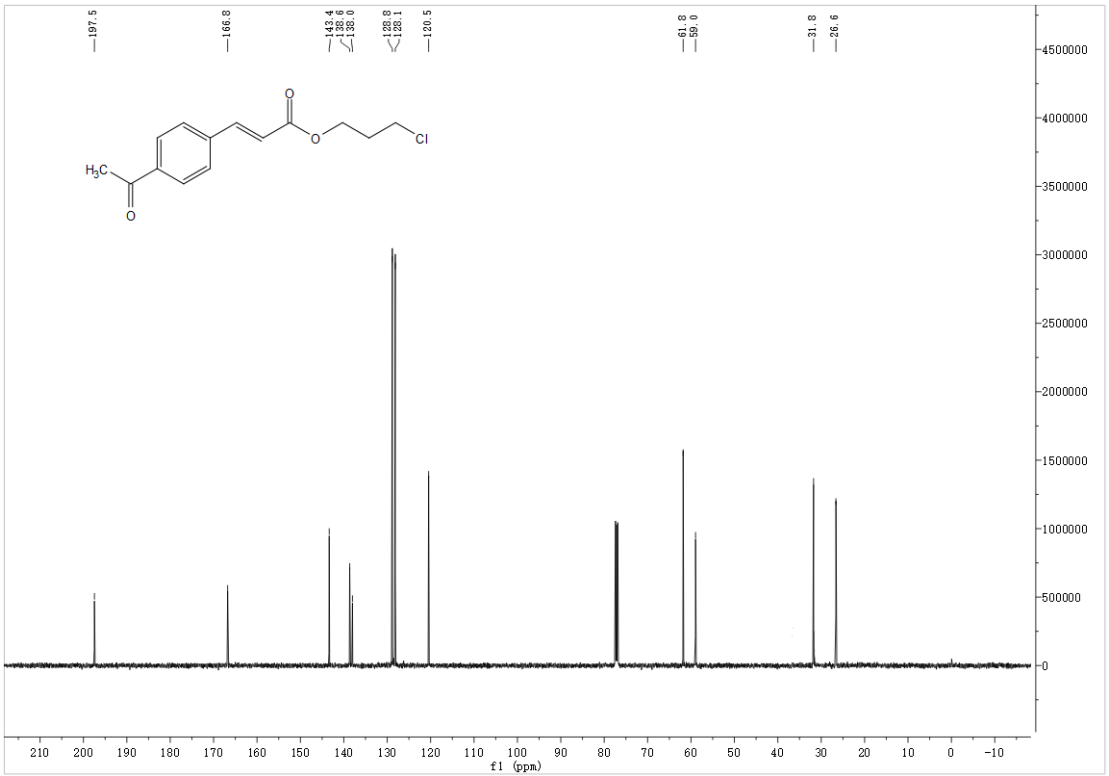
N-**(diphenylmethyl-*d*)thiophene-2-carboxamide (54):** white solid (42.9 mg, 73% yield); EtOAc/PE = 1/10, v/v. m.p. 176.4-177.7 ℃. **^{1}H NMR** (500 MHz, DMSO-d_6) δ (ppm) 9.17 (s, 1H), 7.93-7.92 (m, 1H), 7.60-7.59 (m, 1H), 7.25-7.19 (m, 8H), 7.13-7.10 (m, 2H), 7.01-7.00 (m, 1H), 6.31-6.28 (m, 0.12H, 88%D). **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm) 161.2, 142.5, 140.2, 131.6, 129.2, 128.9, 128.4, 128.2, 127.6, 56.8-56.3 (m). HR-MS (ESI) m/z: Calculated for $C_{18}H_{15}DNOS^+[M + H]^+$: 295.1010. Found: 295.1016.



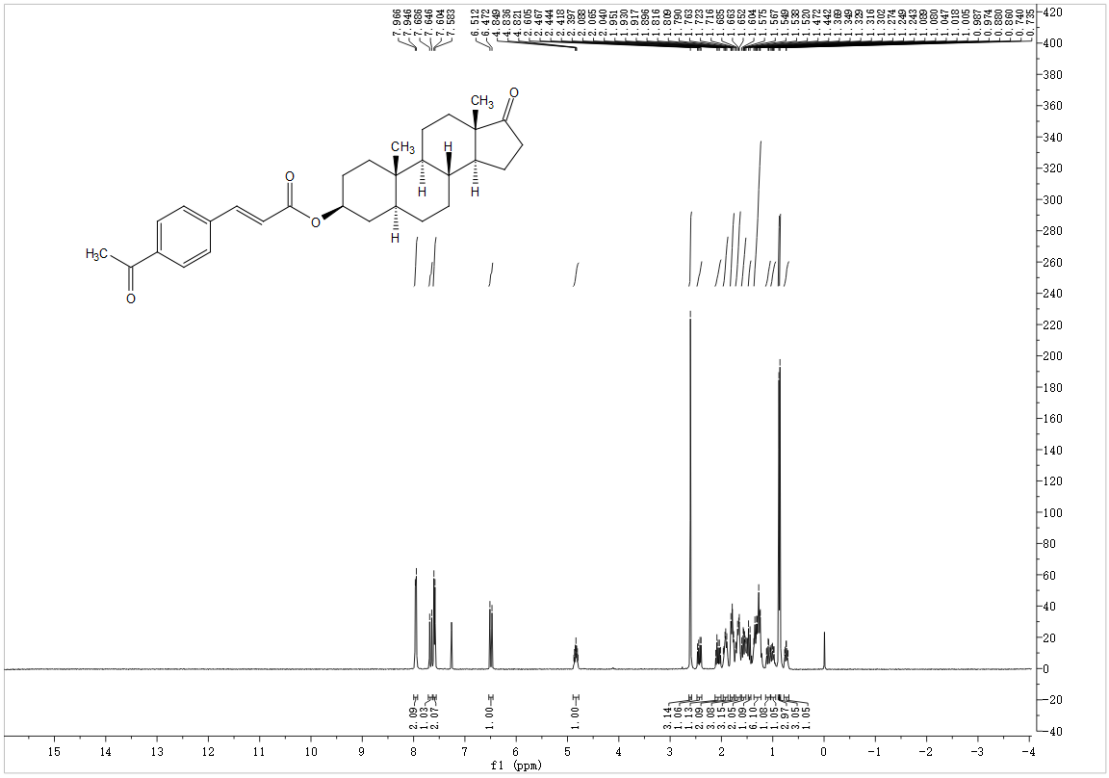
3-(cyclohexylthio)-1,3-diphenylpropan-1-one (56): colorless oil (59.0 mg, 91% yield ; EtOAc/PE = 1/10, v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.91-7.89 (m, 2H), 7.51-7.47 (m, 3H), 7.41-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.22-7.18 (m, 1H), 4.71 (t, *J* = 6.8 Hz, 1H), 3.53 (d, *J* = 6.8 Hz, 2H), 2.52-2.45 (m, 1H), 2.06-2.02 (m, 1H), 1.77-1.74 (m, 2H), 1.66-1.63 (m, 1H), 1.55-1.52 (m, 1H), 1.43-1.34 (m, 1H), 1.33-1.25 (m, 1H), 1.24-1.12 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm) 196.9, 143.1, 137.0, 133.2, 128.6, 128.5, 128.1, 127.8, 127.1, 46.0, 43.2, 43.0, 33.7, 33.3, 25.9. HR-MS (ESI) m/z: Calculated for $C_{21}H_{25}OS^+[M + H]^+$: 325.1621. Found: 325.1622.

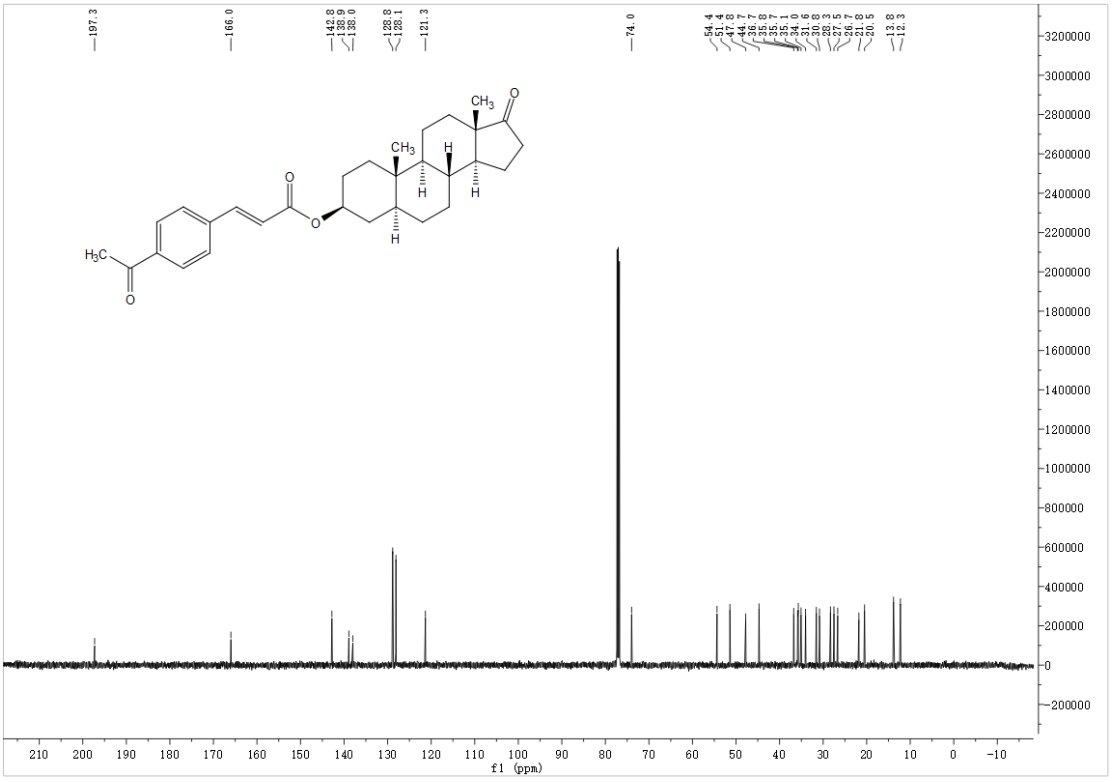
9 Copies of NMR Spectra of all Substrates

Substrate (S1)

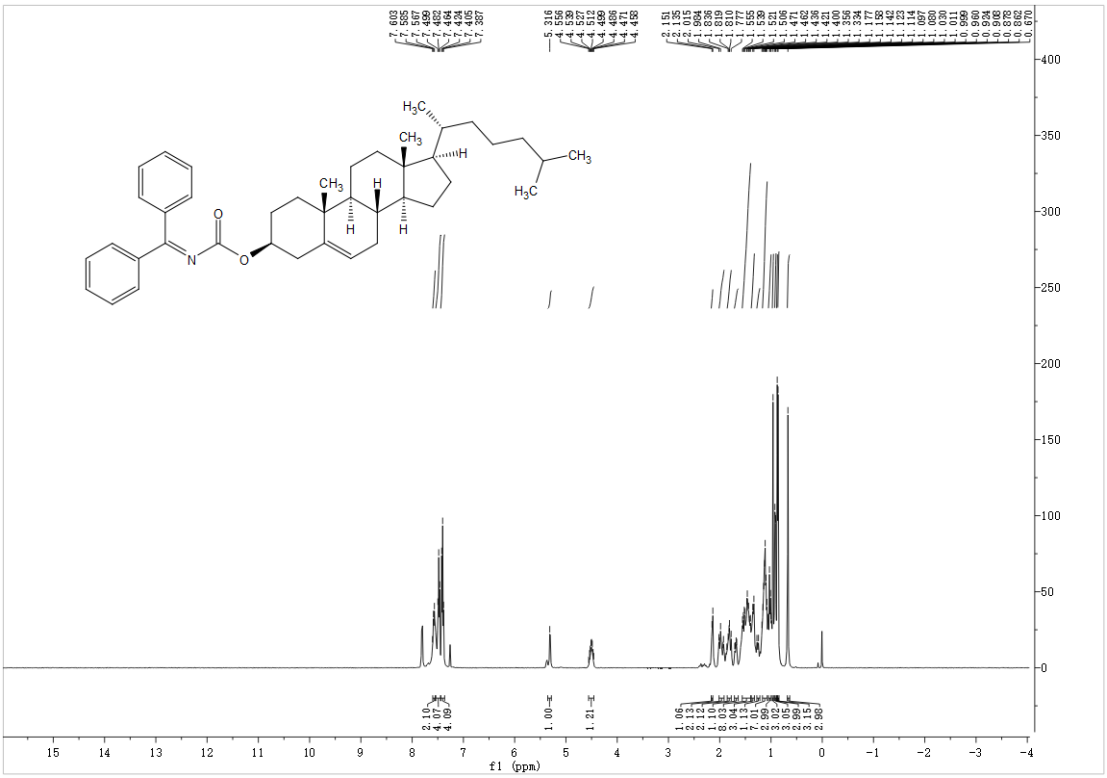


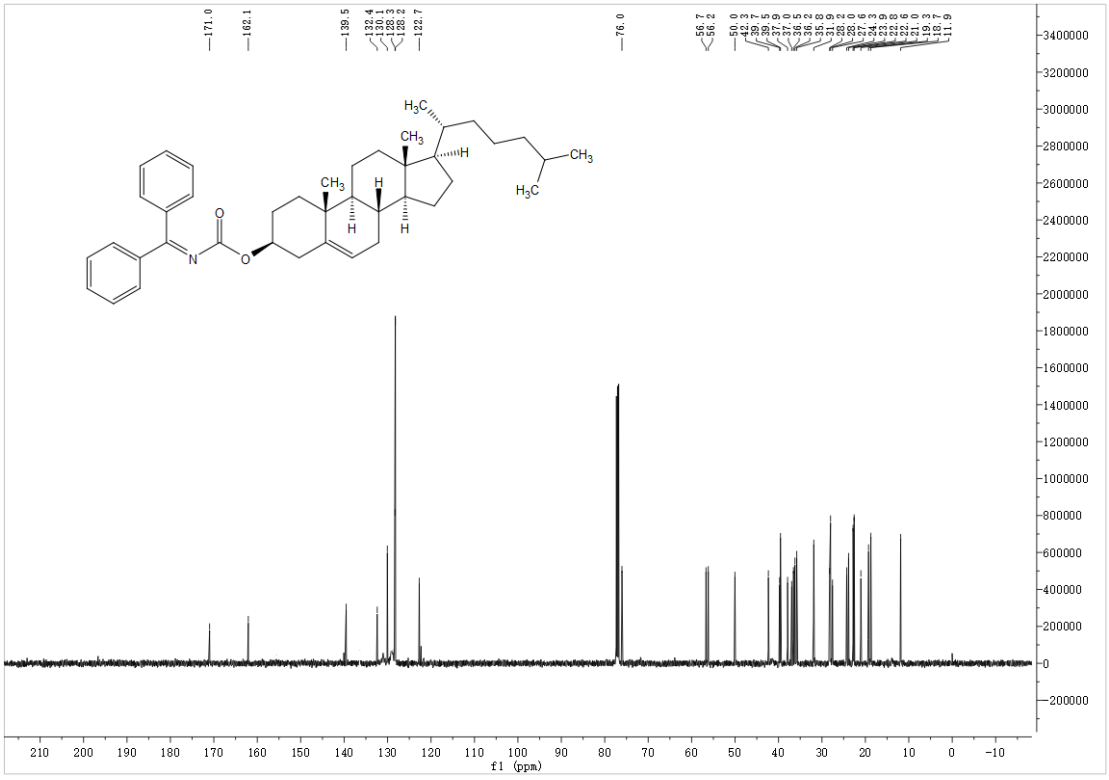
Substrate (S2)





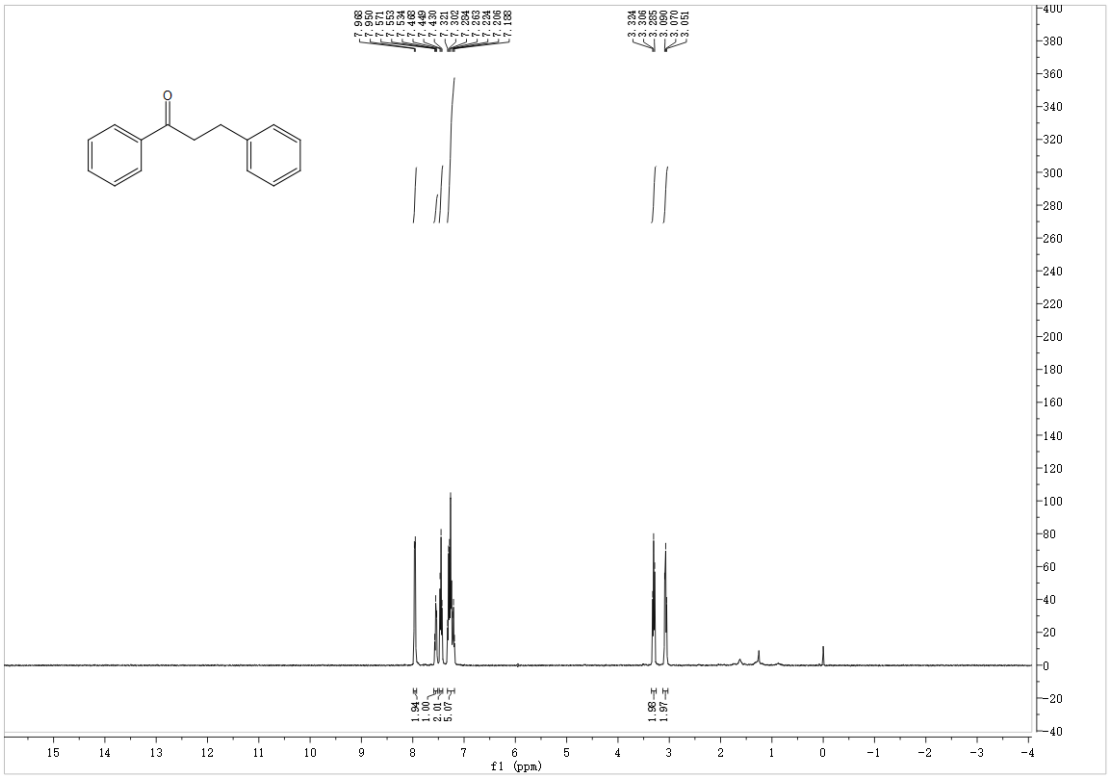
Substrate (S3)

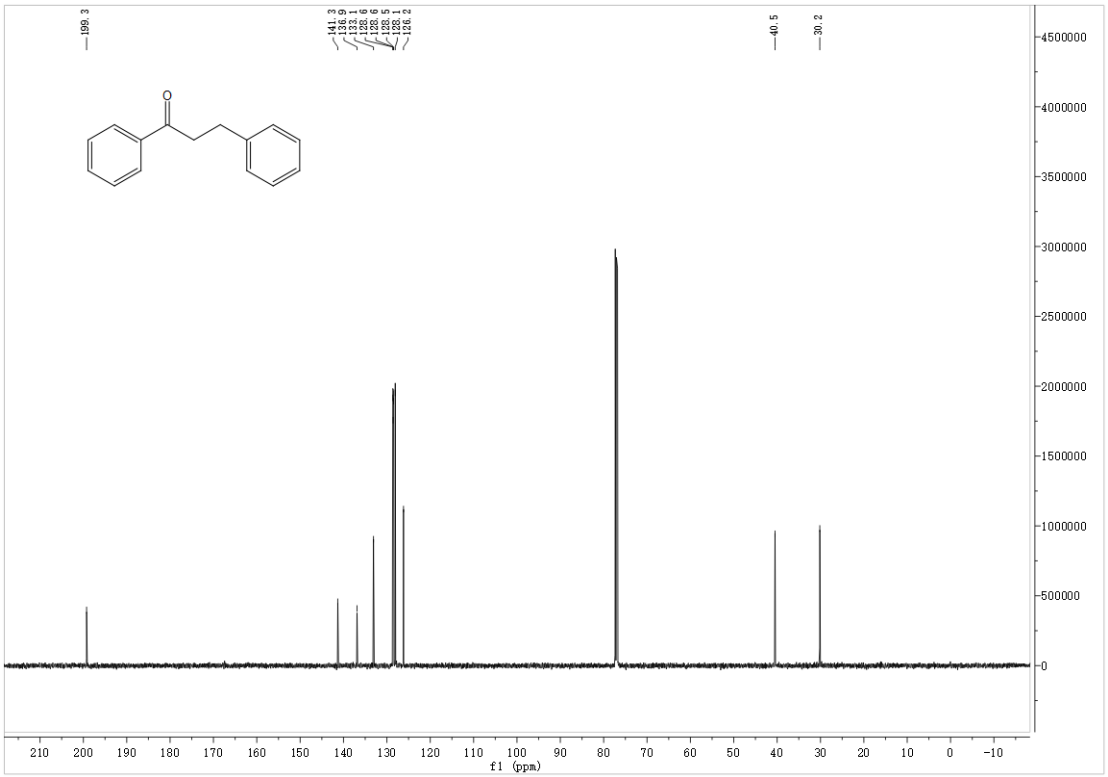




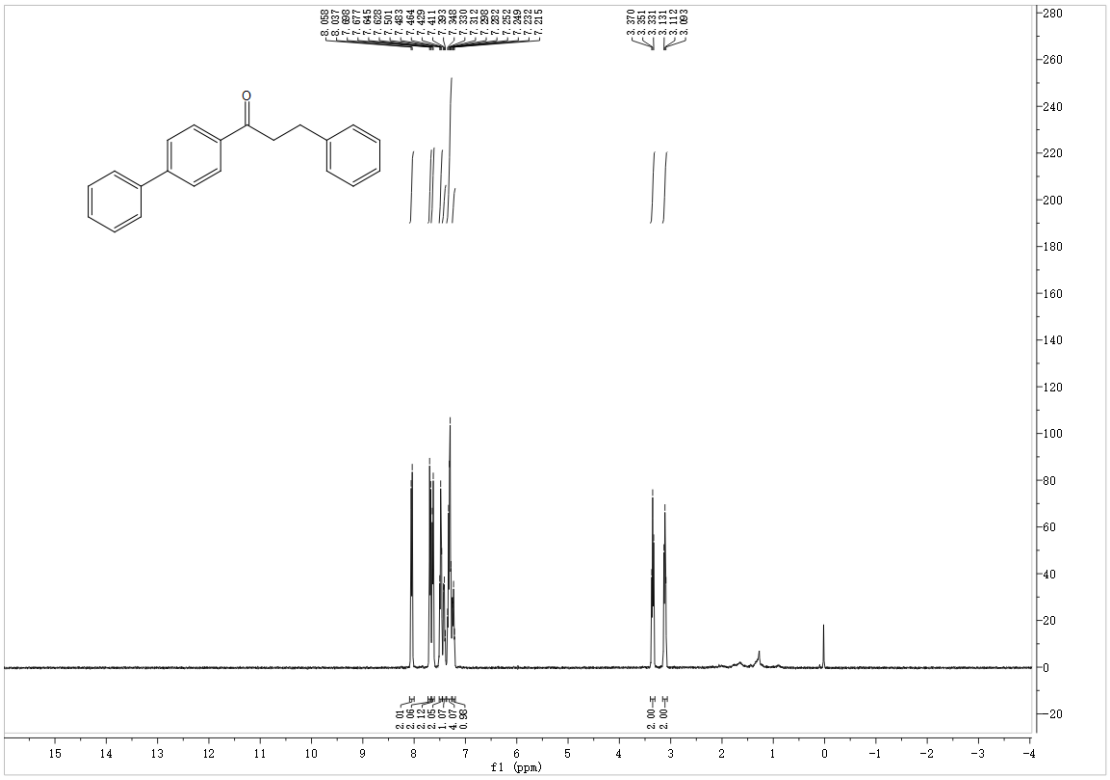
9. Copies of NMR Spectra of all Products

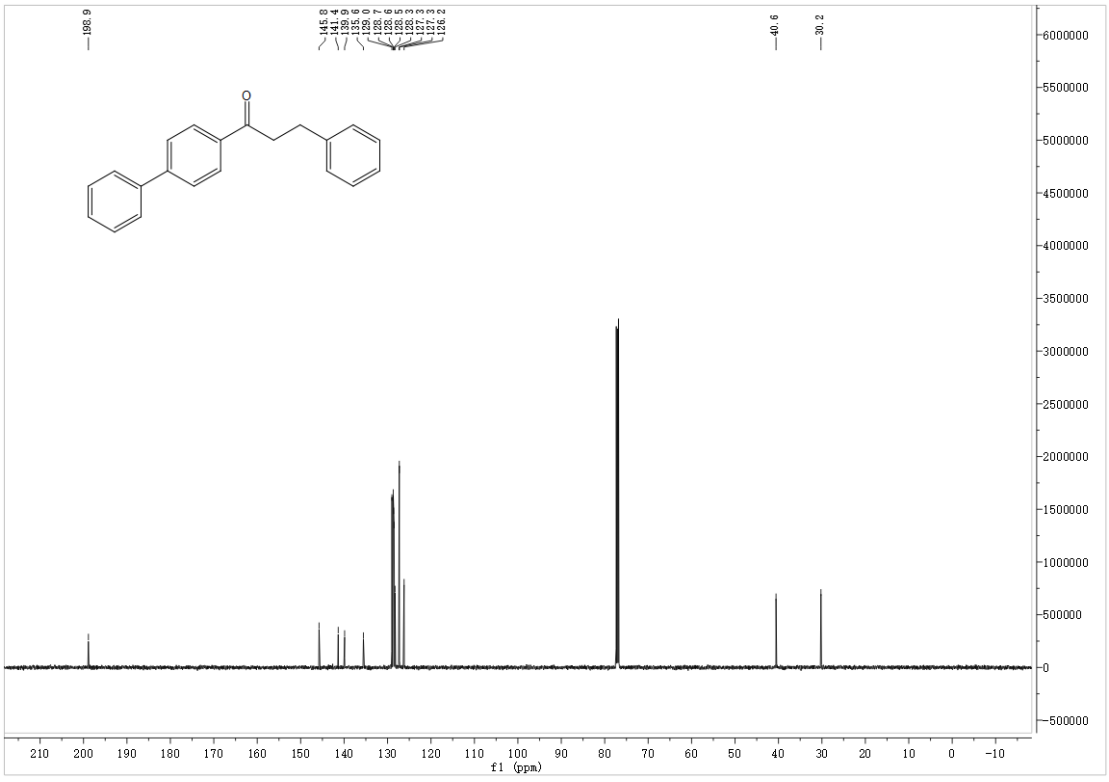
Product (**2**)



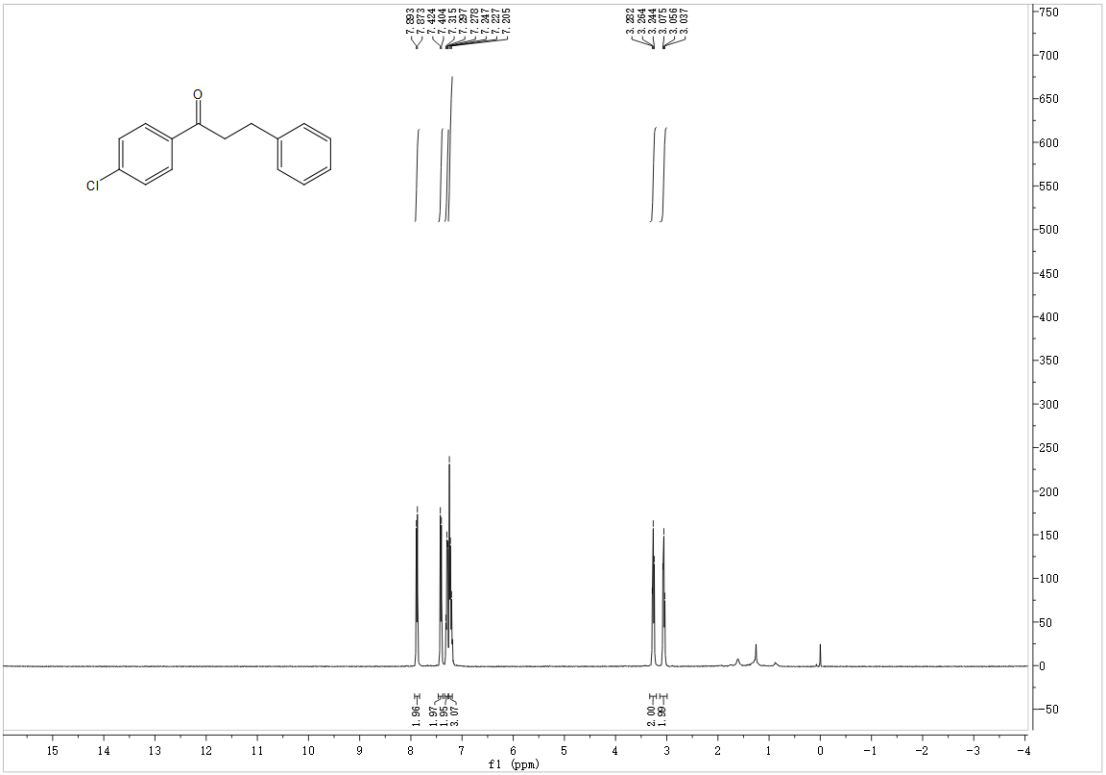


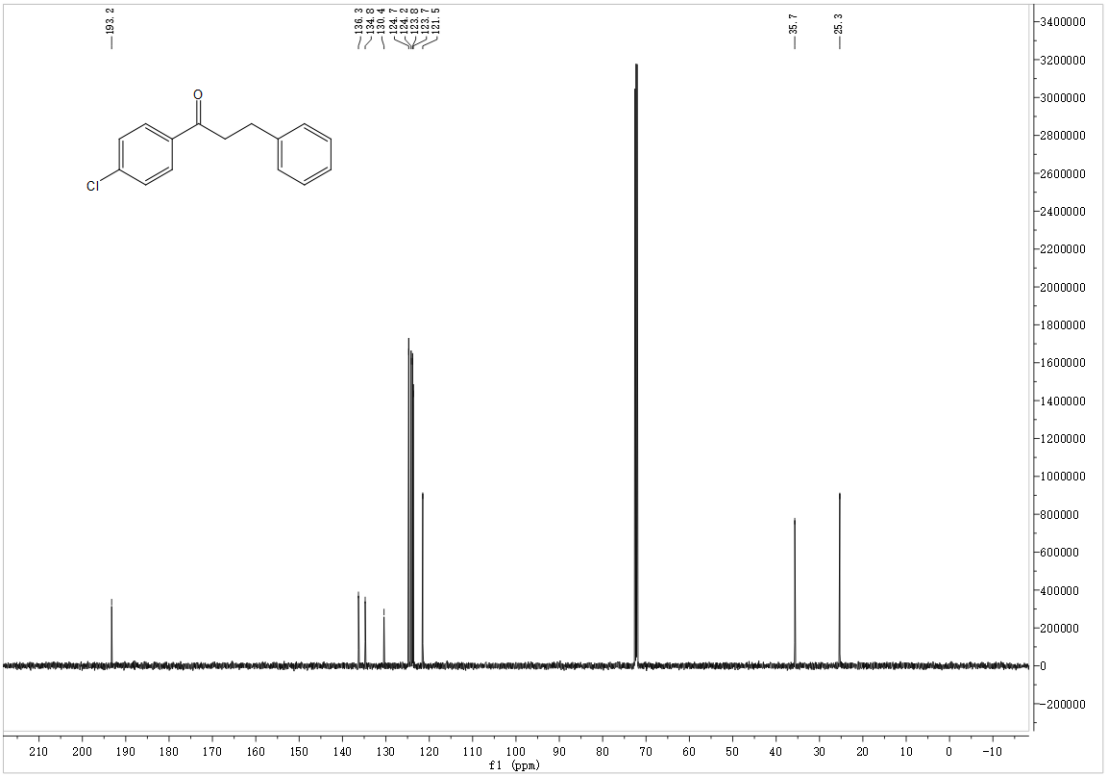
Product (**3**)



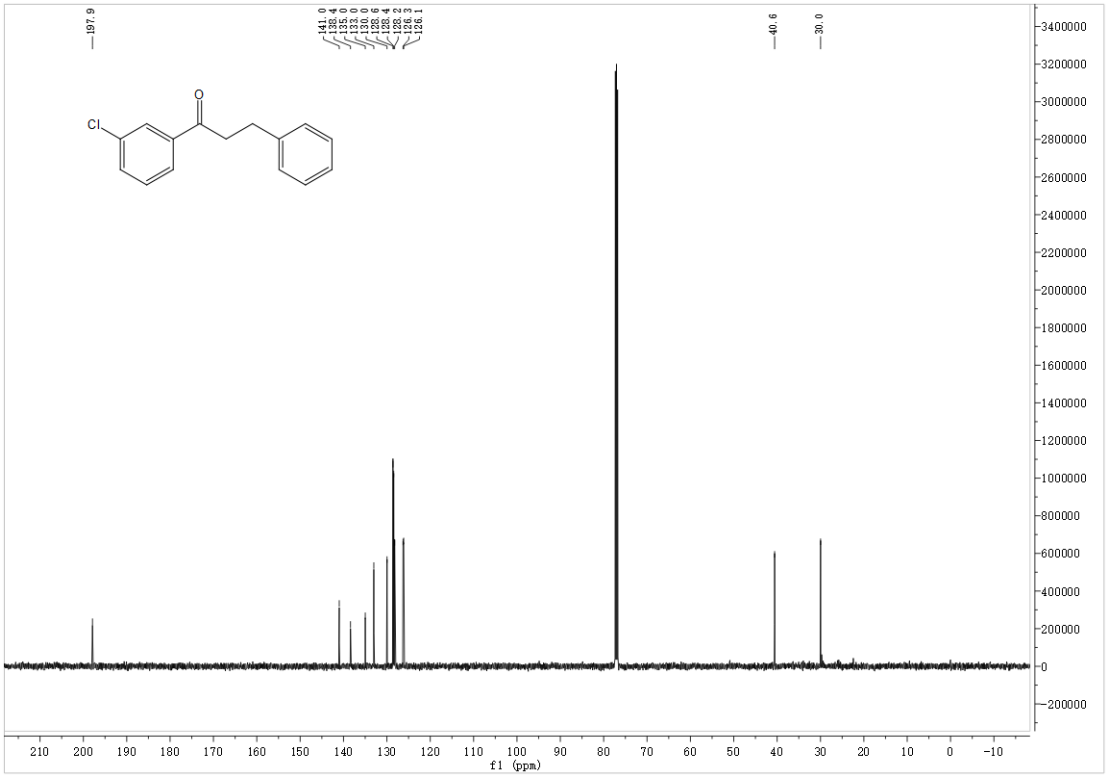


Product (**4**)


7.893
7.873
7.454
7.404
7.315
7.297
7.278
7.247
7.227
7.205
3.252
3.234
3.244
3.075
3.056
3.037
O
Cl
1.96
1.97
1.95
3.07
2.00
1.89
f1 (ppm)

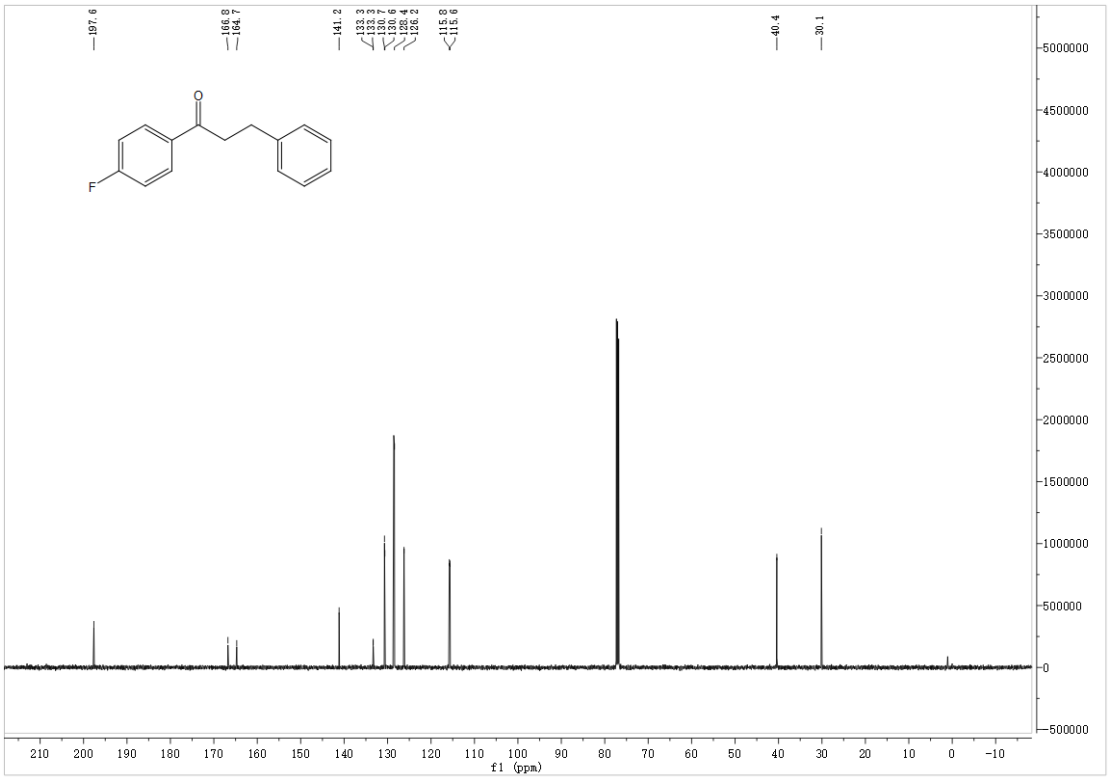

193.2
136.3
134.8
130.4
124.7
124.3
123.8
123.7
121.5
35.7
25.3
O
Cl
f1 (ppm)

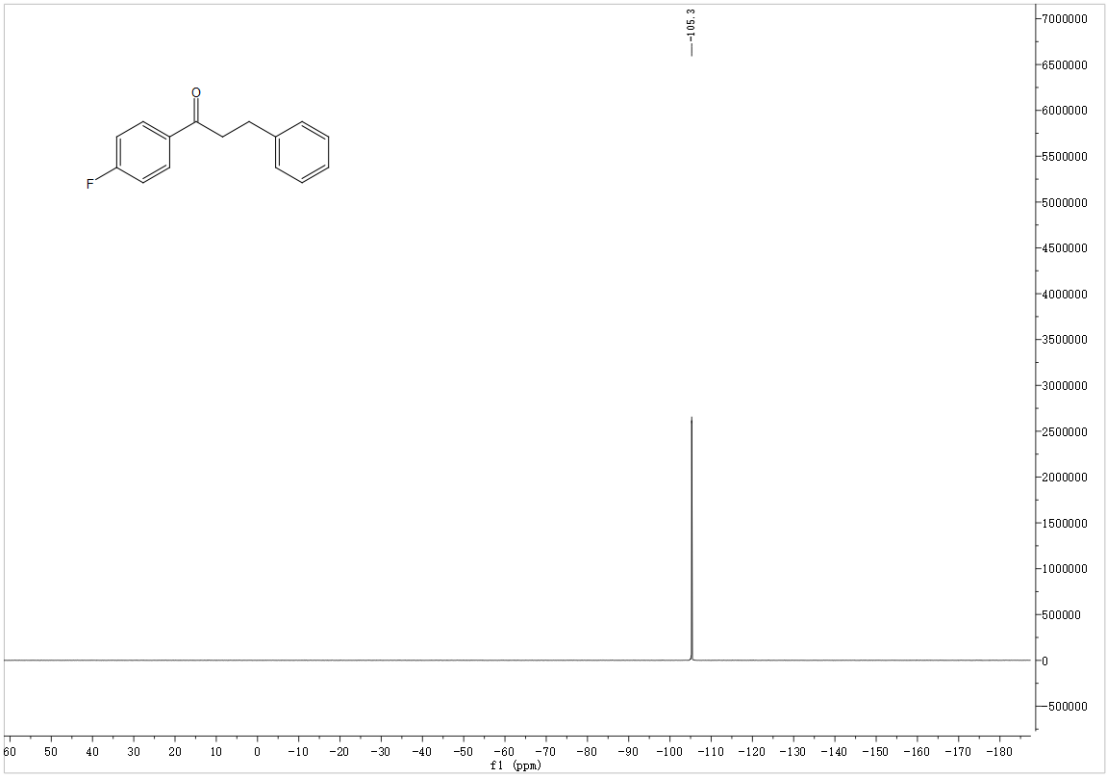
Product (**5**)



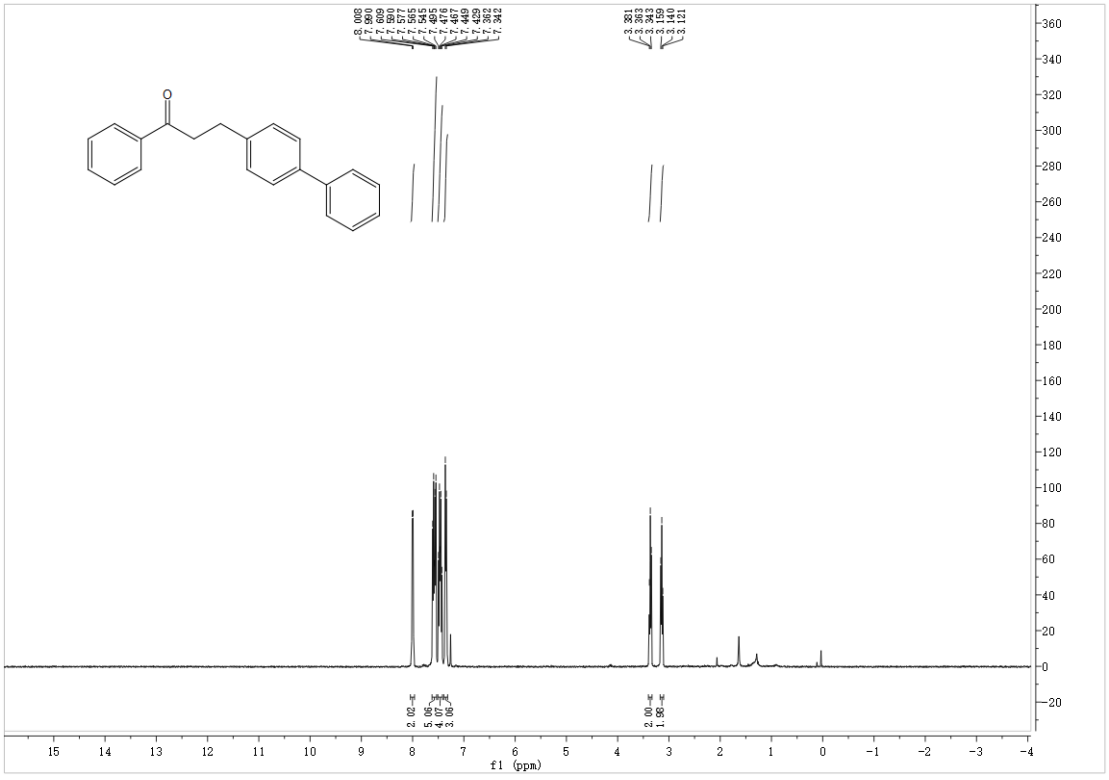
Product (**6**)

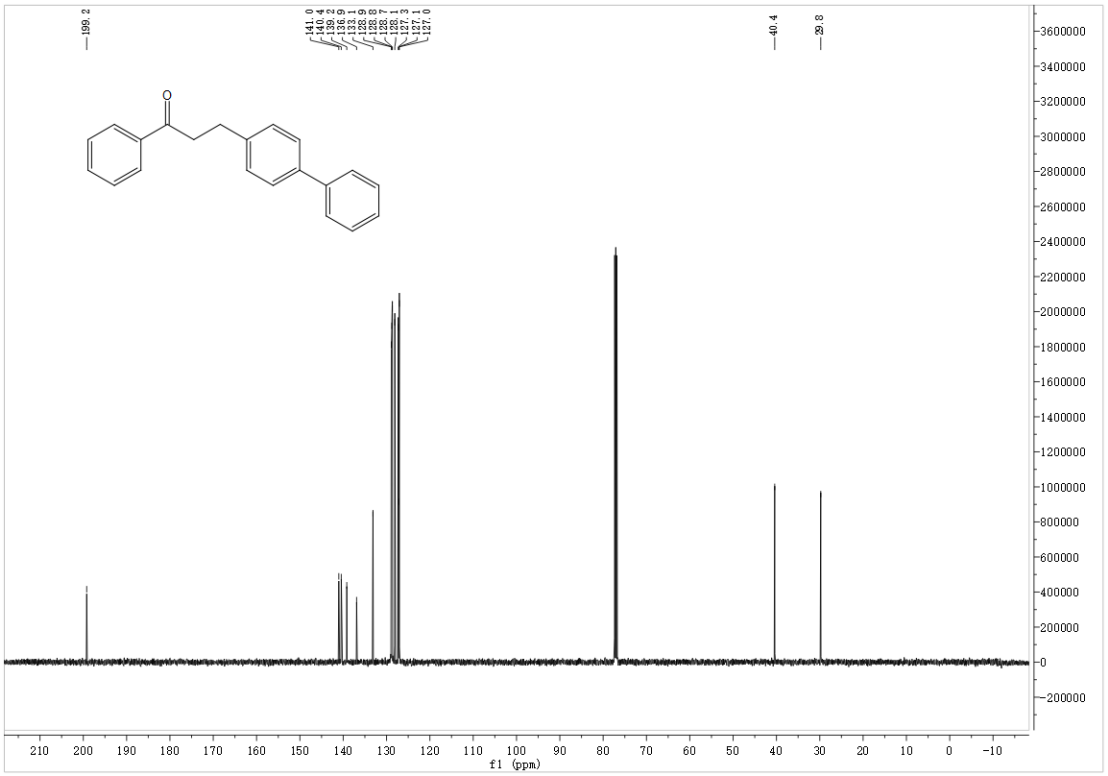

7.918
7.908
7.898
7.888
7.884
7.241
7.233
7.205
7.177
7.138
7.149
7.139
7.055
7.035
7.015
3.214
3.195
3.175
3.004
2.984
2.965
O
F
1.99
1.92
3.02
2.02
2.00
2.00
f1 (ppm)


197.6
166.8
164.7
141.2
133.3
133.3
130.7
130.6
128.4
126.2
115.8
115.6
40.4
30.1
O
F
f1 (ppm)

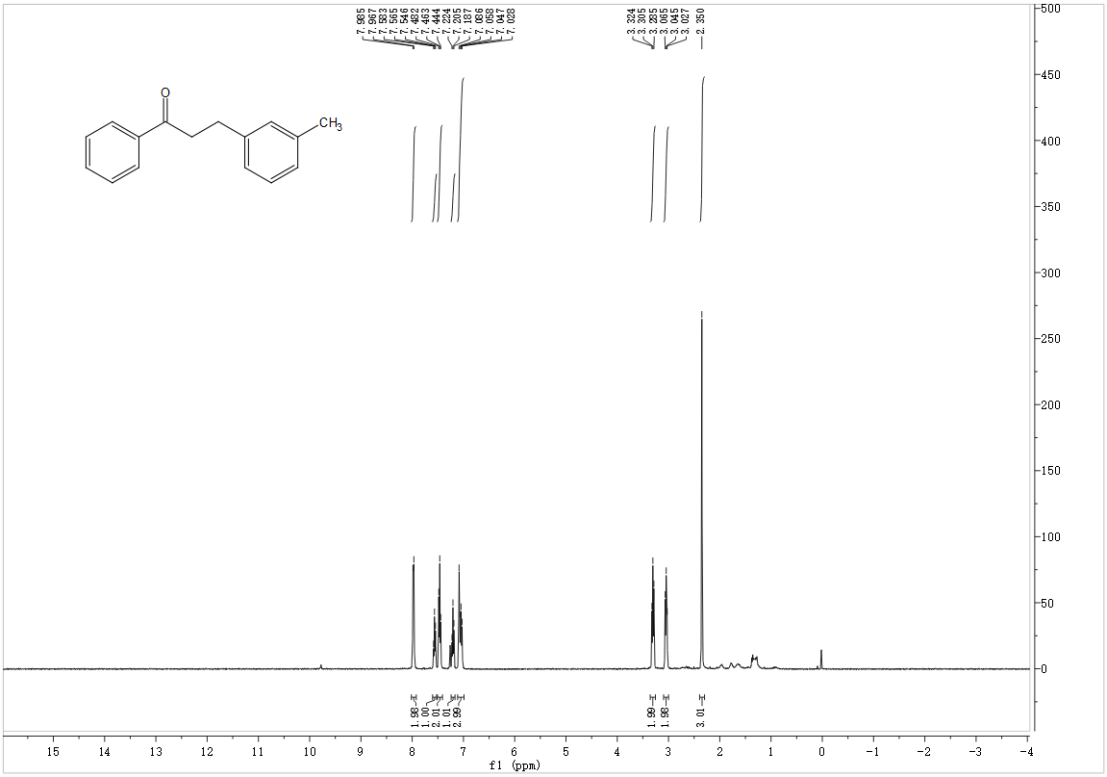

-105.3
O
F
f1 (ppm)

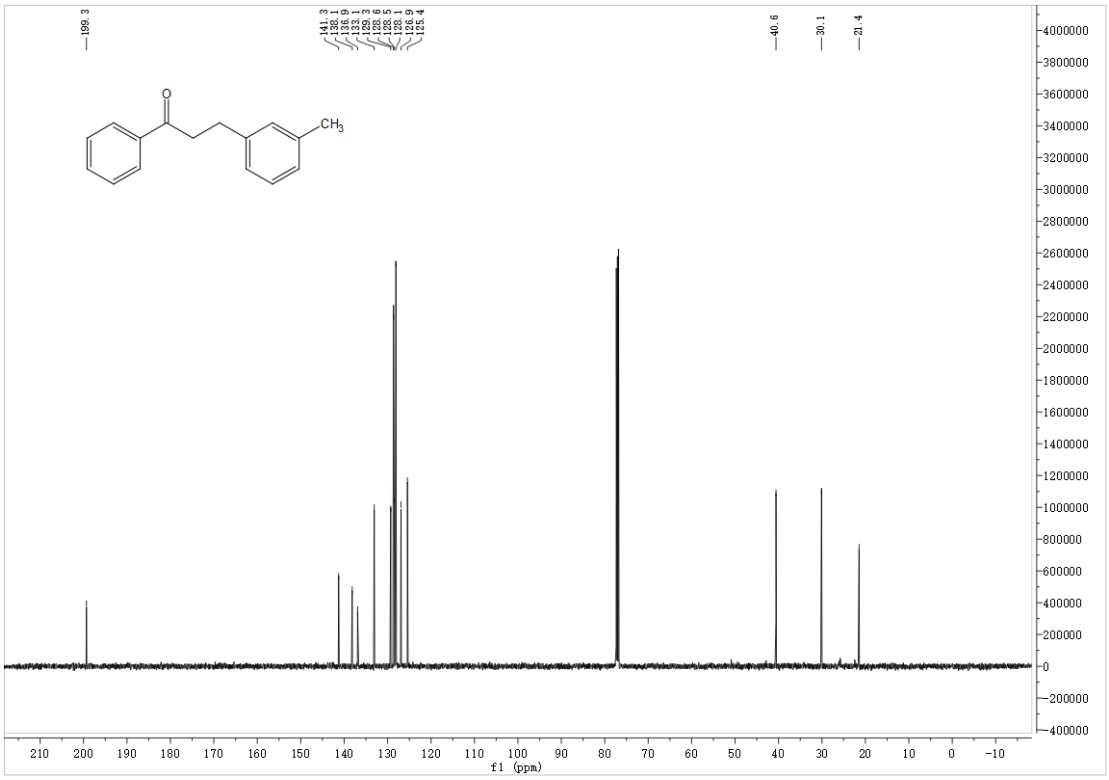
Product (**7**)


8.008
7.990
7.609
7.590
7.577
7.565
7.545
7.495
7.476
7.467
7.449
7.429
7.382
7.342
3.301
3.283
3.263
3.243
3.159
3.140
3.121
O
2.02
5.98
4.07
3.98
2.00
1.98
f1 (ppm)

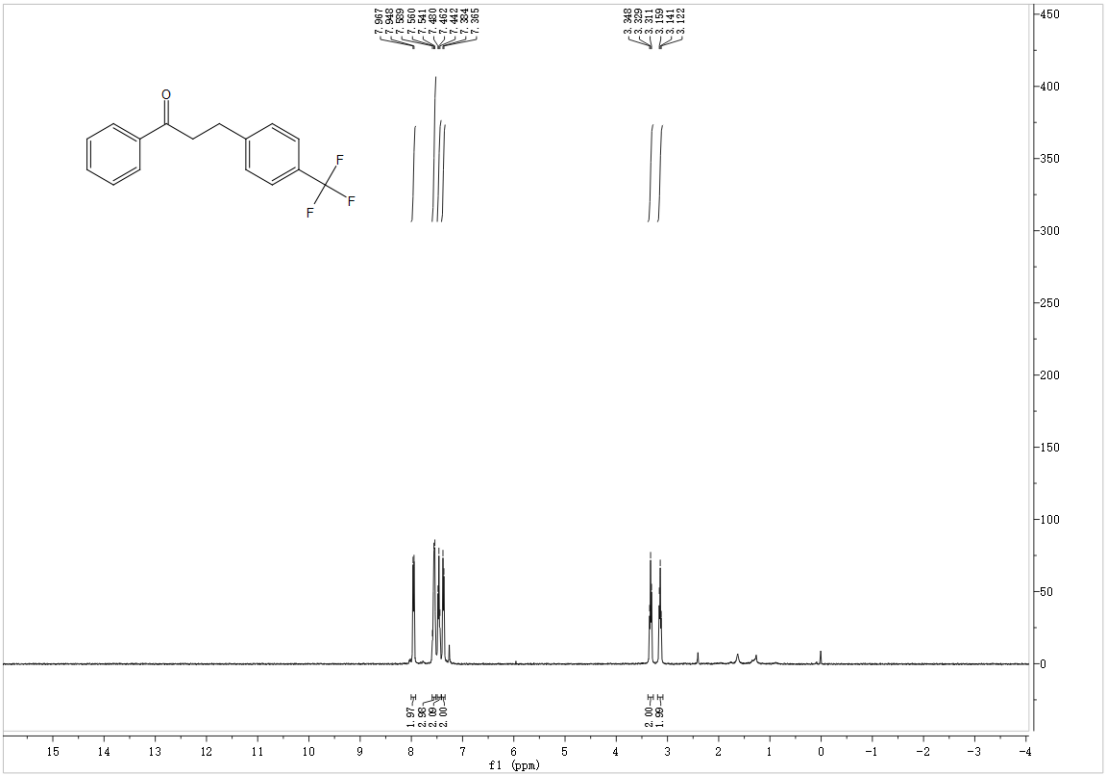

199.2
141.0
140.4
139.2
136.9
133.1
129.0
128.8
128.7
128.1
127.3
127.1
127.0
40.4
29.8
O
f1 (ppm)

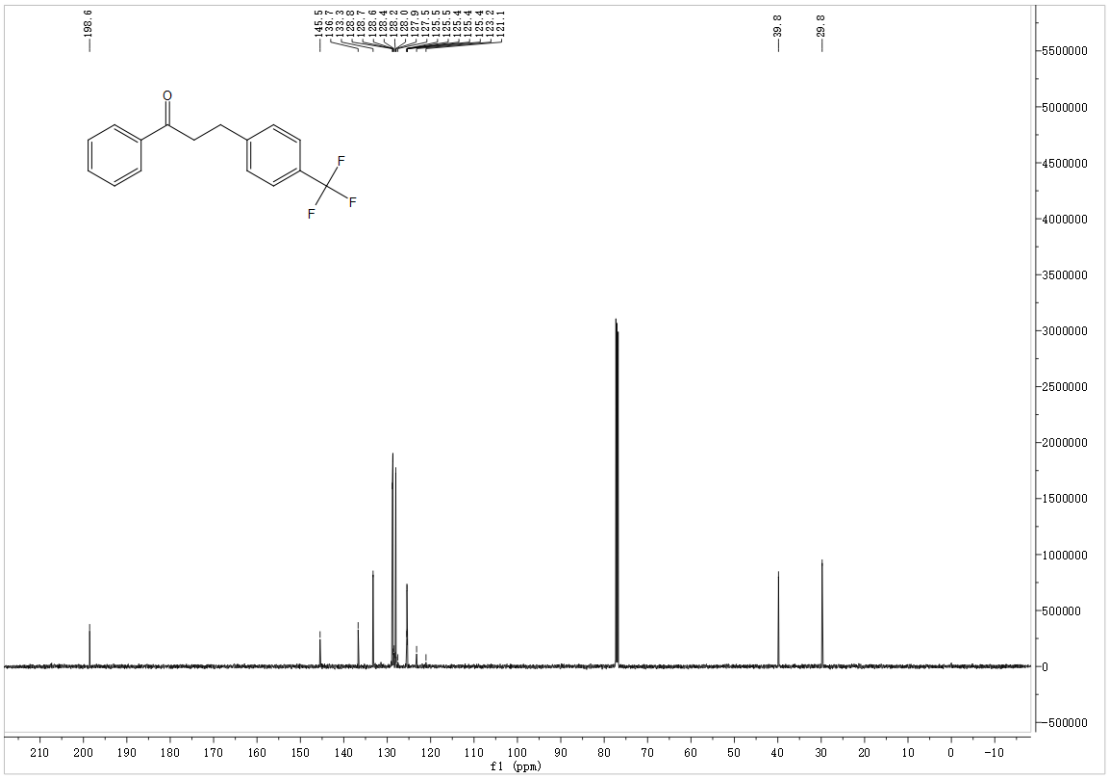
Product (**8**)

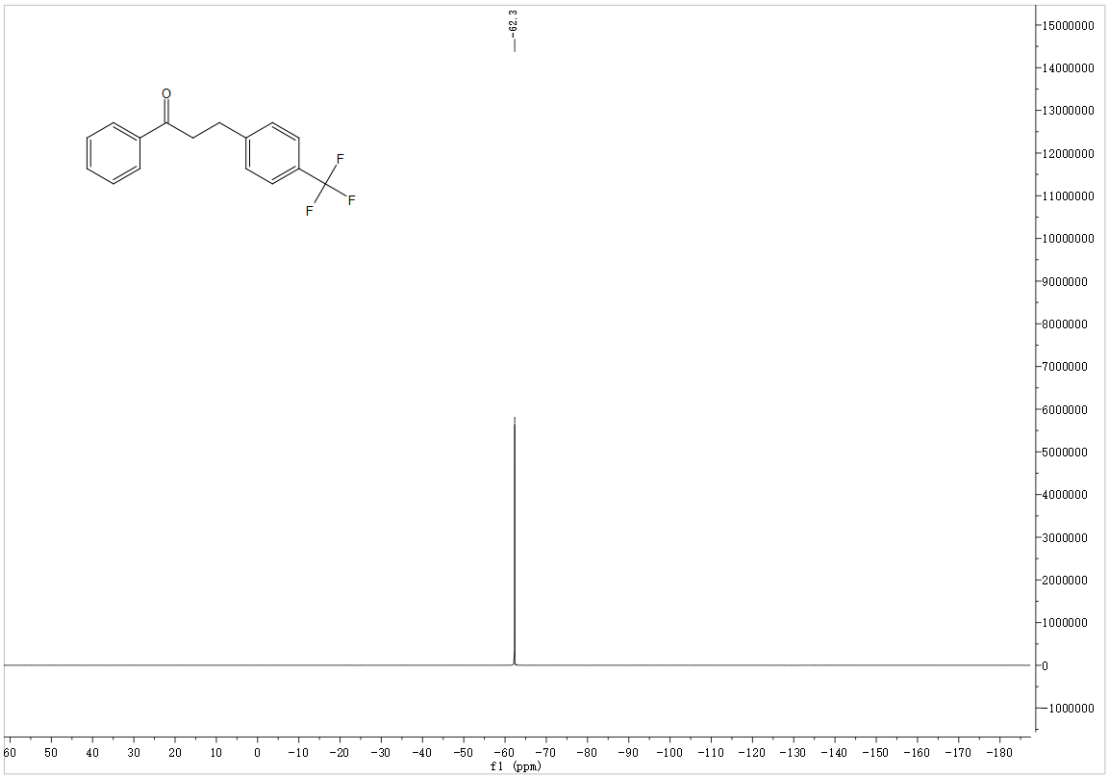

7.965
7.963
7.583
7.565
7.546
7.483
7.444
7.224
7.215
7.187
7.036
7.008
6.947
7.028
3.324
3.305
3.285
3.065
3.045
3.027
2.350
1.98
1.00
2.01
2.01
2.89
1.99
1.98
3.01
O
CH3
f1 (ppm)


199.3
141.3
136.9
133.1
129.3
128.5
128.1
126.9
125.4
40.6
30.1
21.4
O
CH3
f1 (ppm)

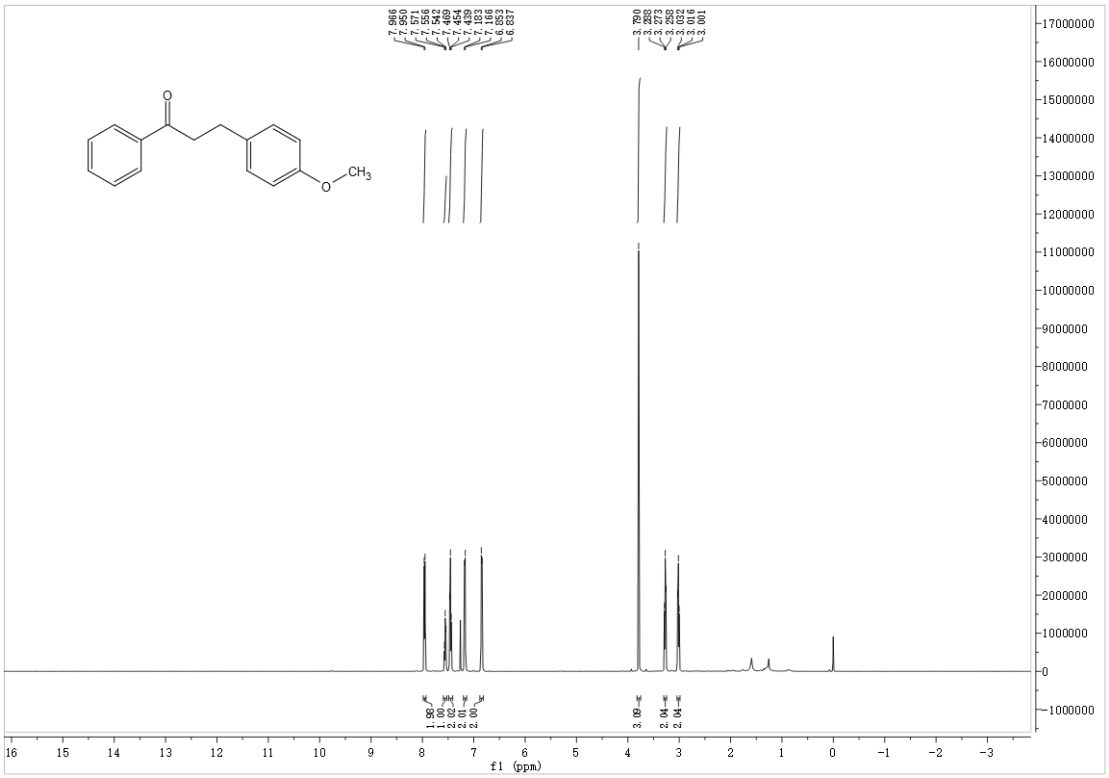
Product (**9**)

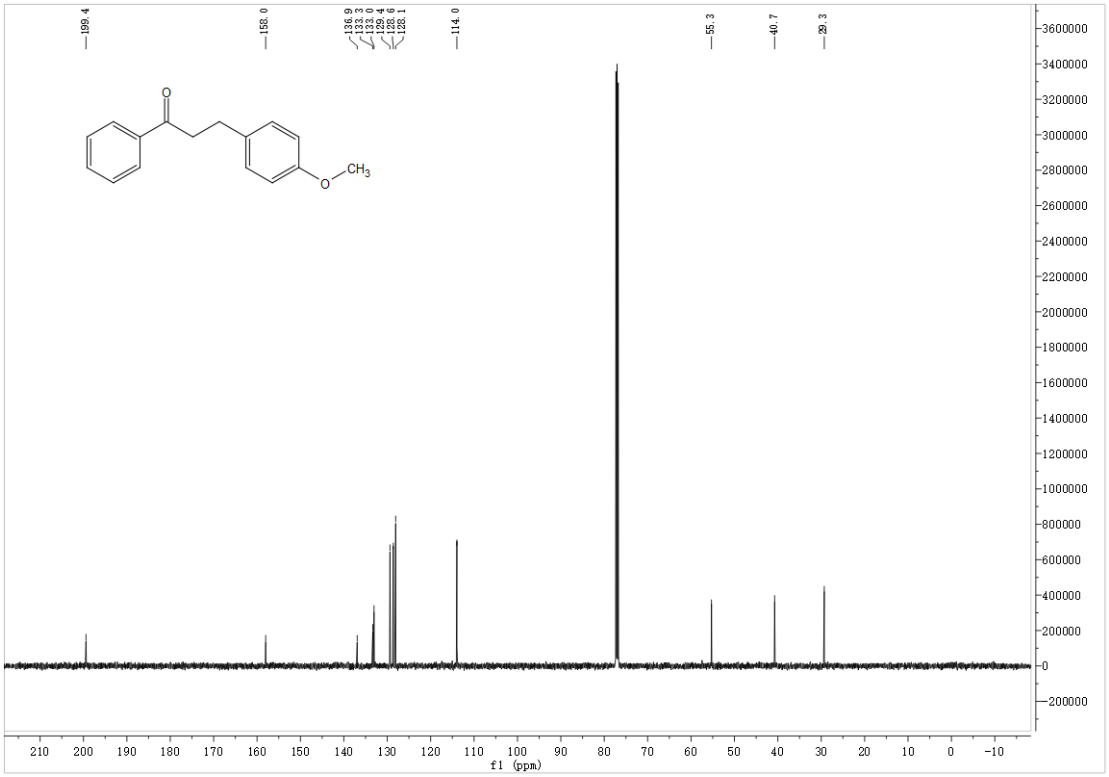

7.967
7.963
7.560
7.541
7.460
7.442
7.384
7.365
3.348
3.329
3.311
3.159
3.141
3.122
O
F
F
F
1.97
2.88
2.00
2.00
1.99
f1 (ppm)


198.6
145.5
136.7
133.3
128.9
128.7
128.6
128.4
128.2
128.0
127.9
127.5
125.5
125.5
125.4
125.4
123.2
121.1
39.8
29.8
O
F
F
F
f1 (ppm)

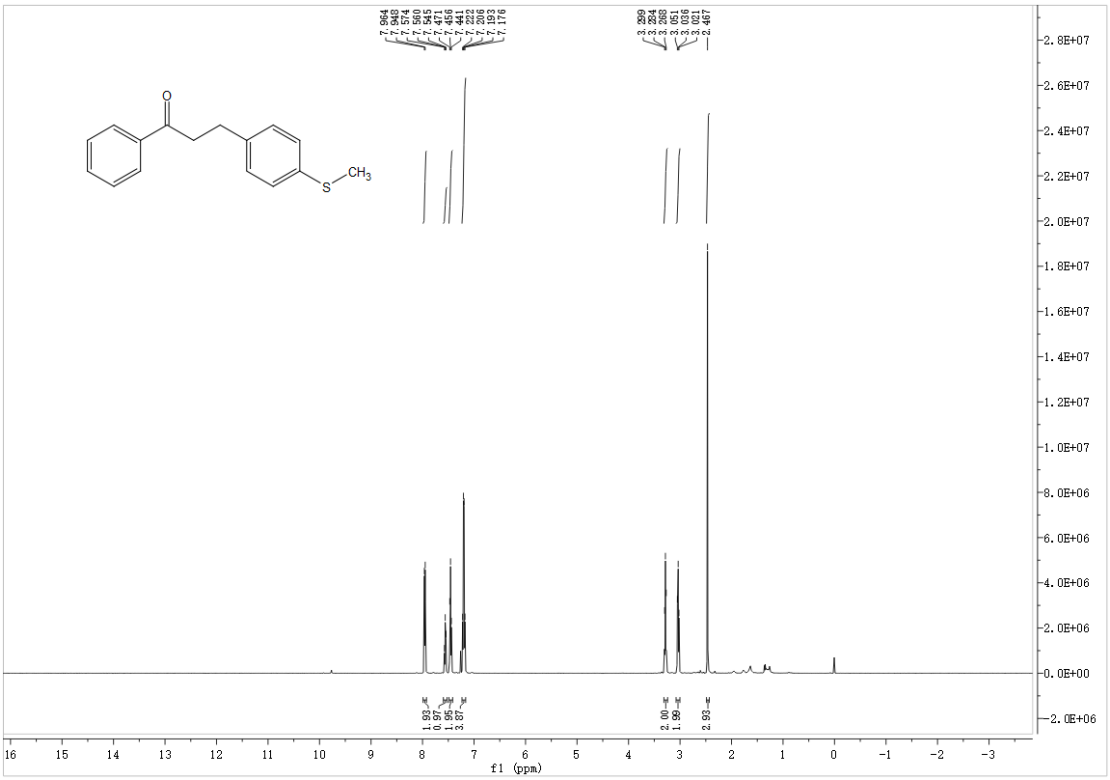

-62.3
O
F
F
F
f1 (ppm)

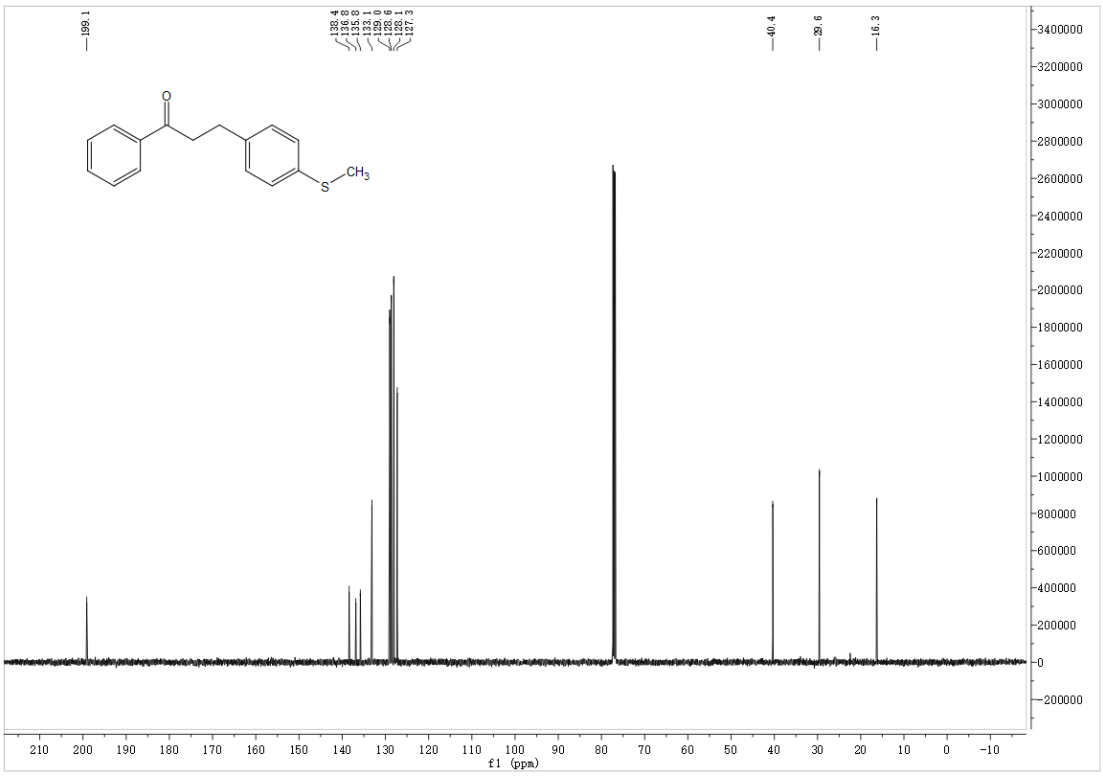
Product (**10**)


7.966
7.950
7.571
7.558
7.542
7.469
7.454
7.439
7.183
7.165
6.853
6.837
3.709
3.288
3.273
3.259
3.032
3.016
3.001
O
O
CH3
1.98
1.00
2.02
2.01
2.00
3.09
2.04
2.04
f1 (ppm)

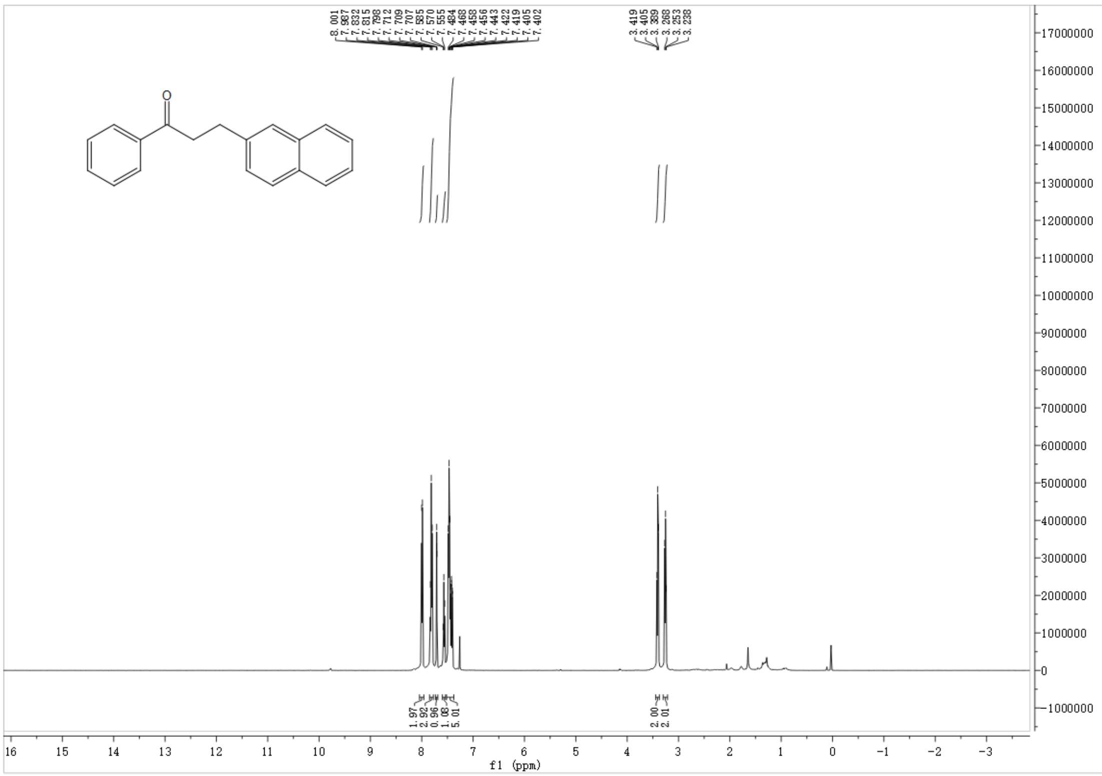

199.4
158.0
136.9
133.3
133.0
129.4
128.6
128.1
114.0
55.3
40.7
29.3
O
O
CH3
f1 (ppm)

Product (**11**)

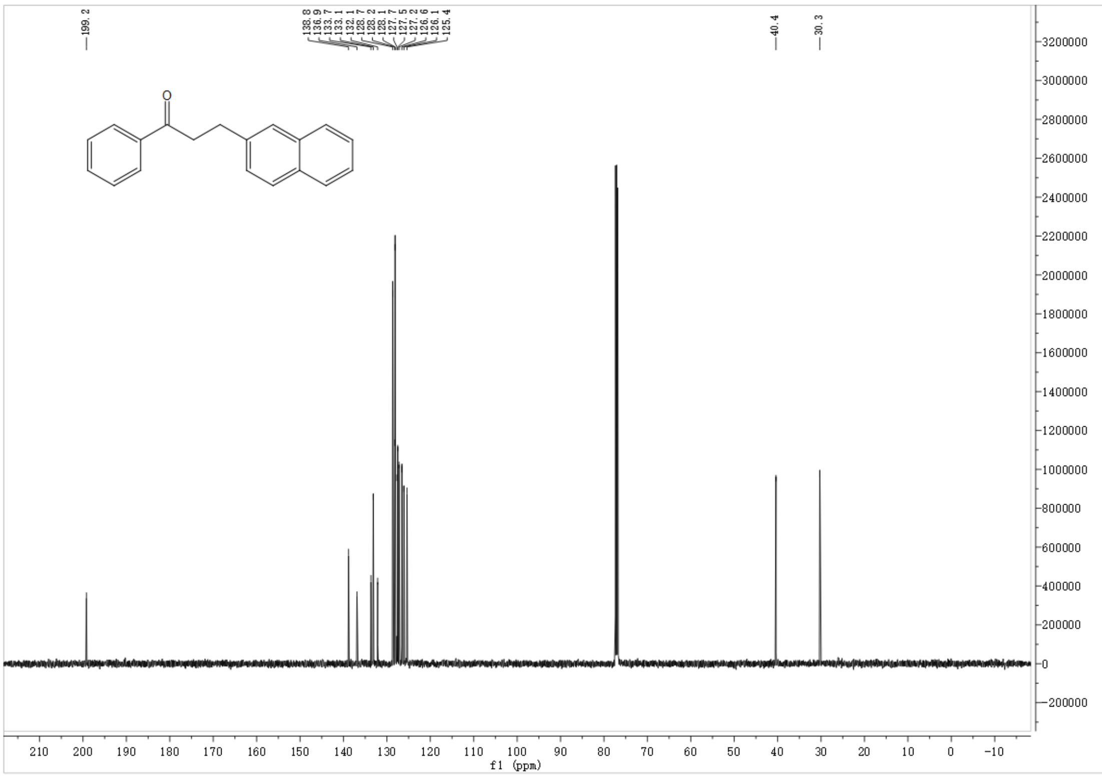

7.964
7.948
7.574
7.560
7.545
7.471
7.456
7.441
7.222
7.206
7.193
7.176
3.299
3.284
3.268
3.051
3.035
3.021
2.467
O
S
CH3
1.93
0.97
1.95
3.87
2.00
1.99
2.93
f1 (ppm)


199.1
138.4
136.8
135.8
133.1
129.0
128.6
128.1
127.3
40.4
29.6
16.3
O
S
CH3
f1 (ppm)

Product (**12**)

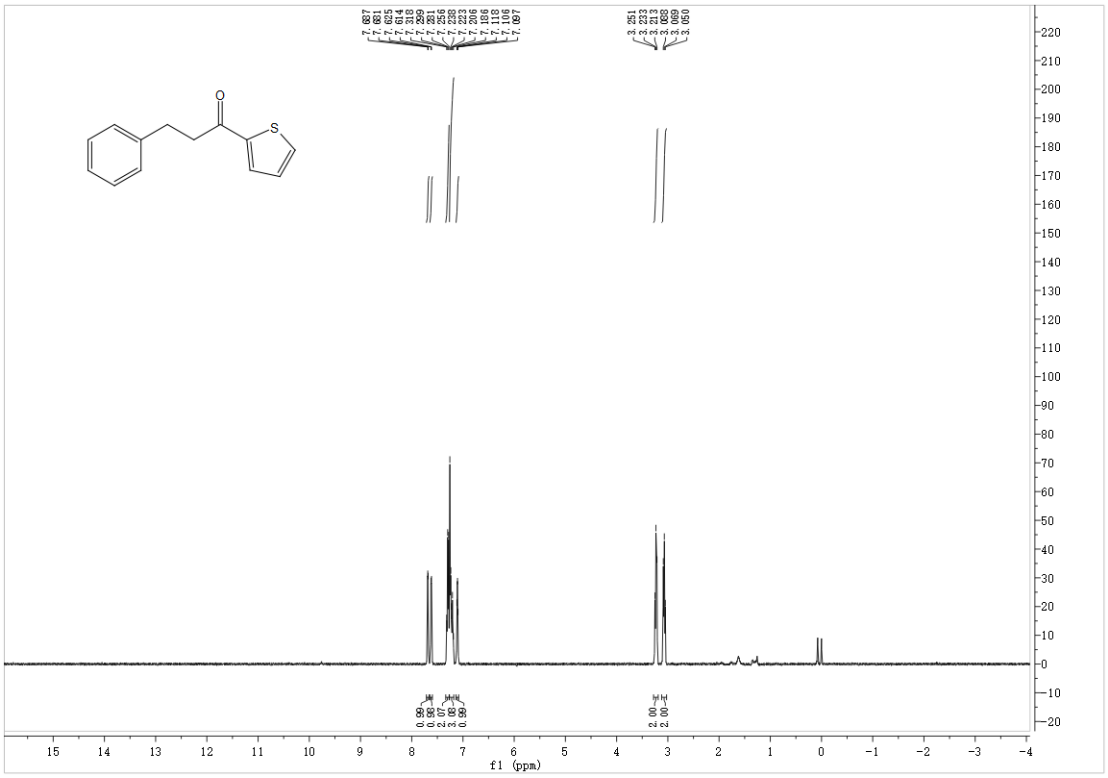


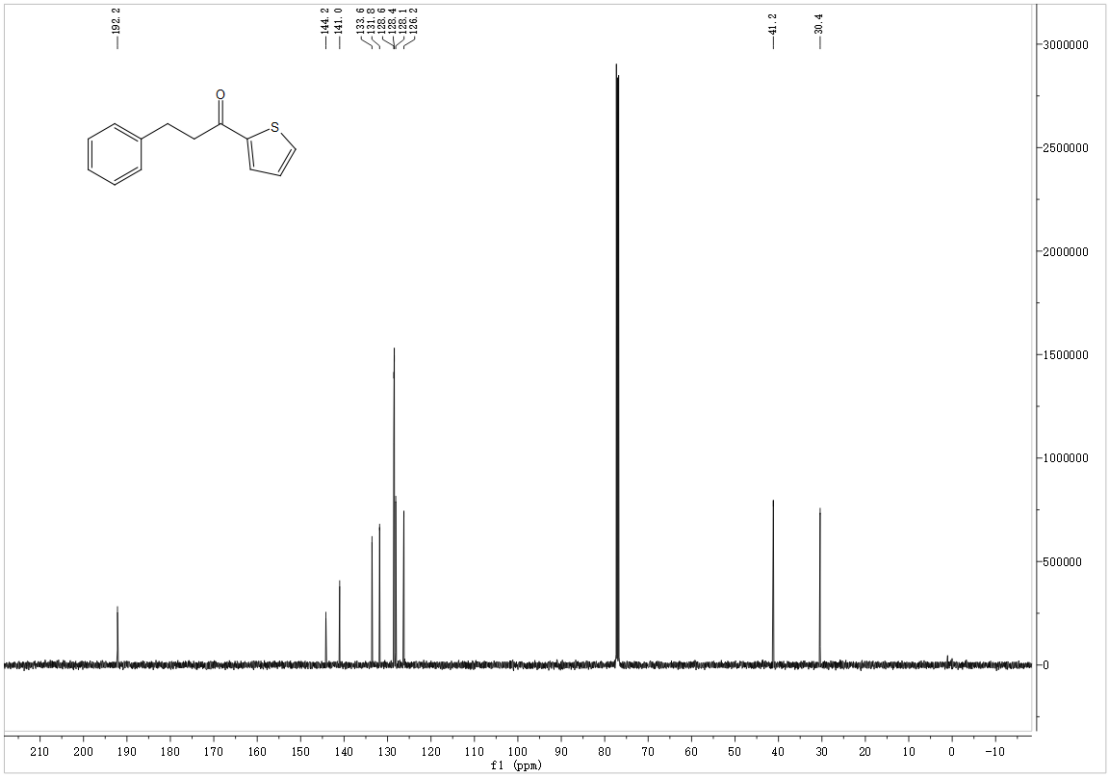
8.001
7.987
7.832
7.815
7.798
7.712
7.709
7.707
7.585
7.570
7.555
7.484
7.468
7.458
7.456
7.443
7.422
7.419
7.405
7.402
3.419
3.405
3.389
3.268
3.253
3.238
O
1.97
2.92
0.96
1.08
5.01
2.00
2.01
f1 (ppm)



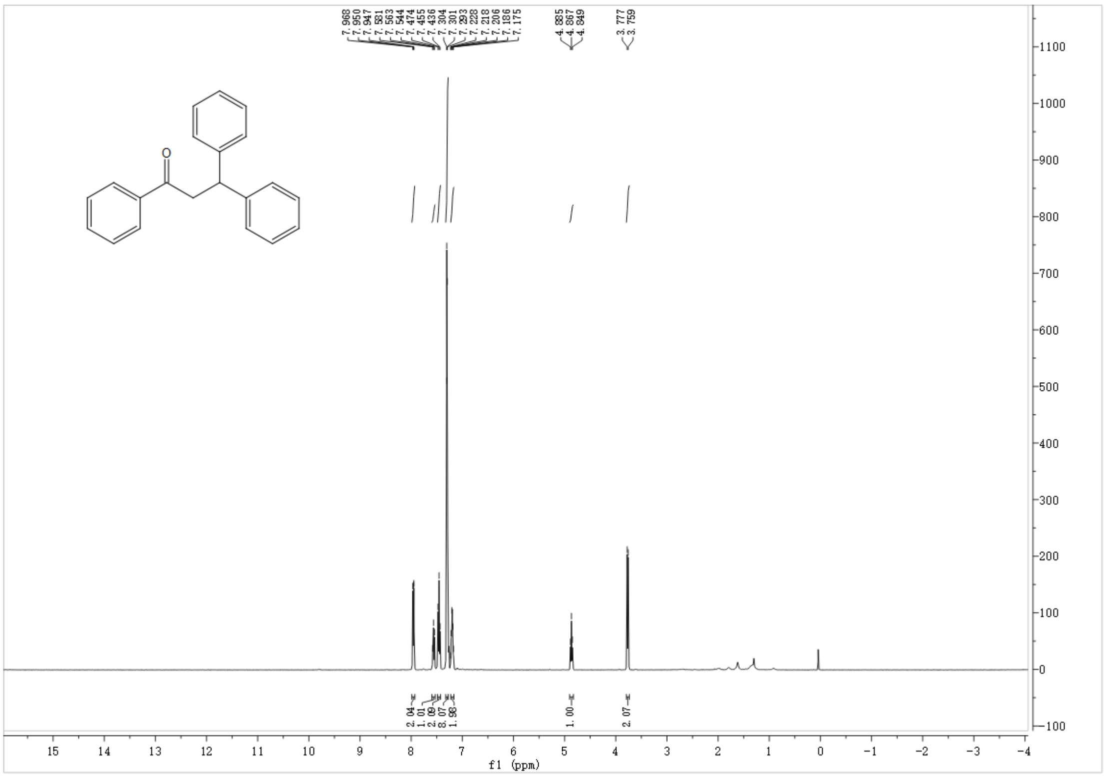
199.2
138.8
136.9
133.7
133.1
132.1
128.7
128.2
128.1
127.7
127.5
127.2
126.6
126.1
125.4
40.4
30.3
O
f1 (ppm)

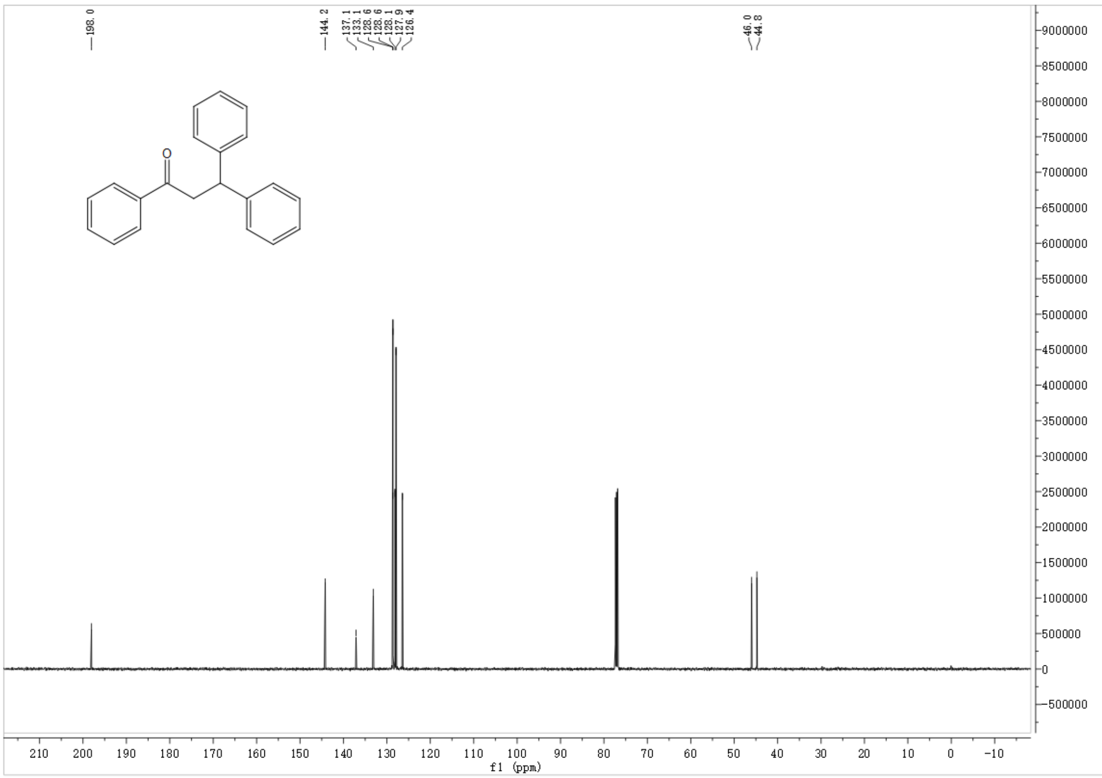
Product (**13**)


7.687
7.681
7.665
7.615
7.614
7.318
7.299
7.291
7.256
7.238
7.233
7.208
7.188
7.118
7.106
7.097
3.251
3.213
3.083
3.069
3.050
O
S
0.98
0.98
2.07
3.98
0.99
2.00
2.00
f1 (ppm)

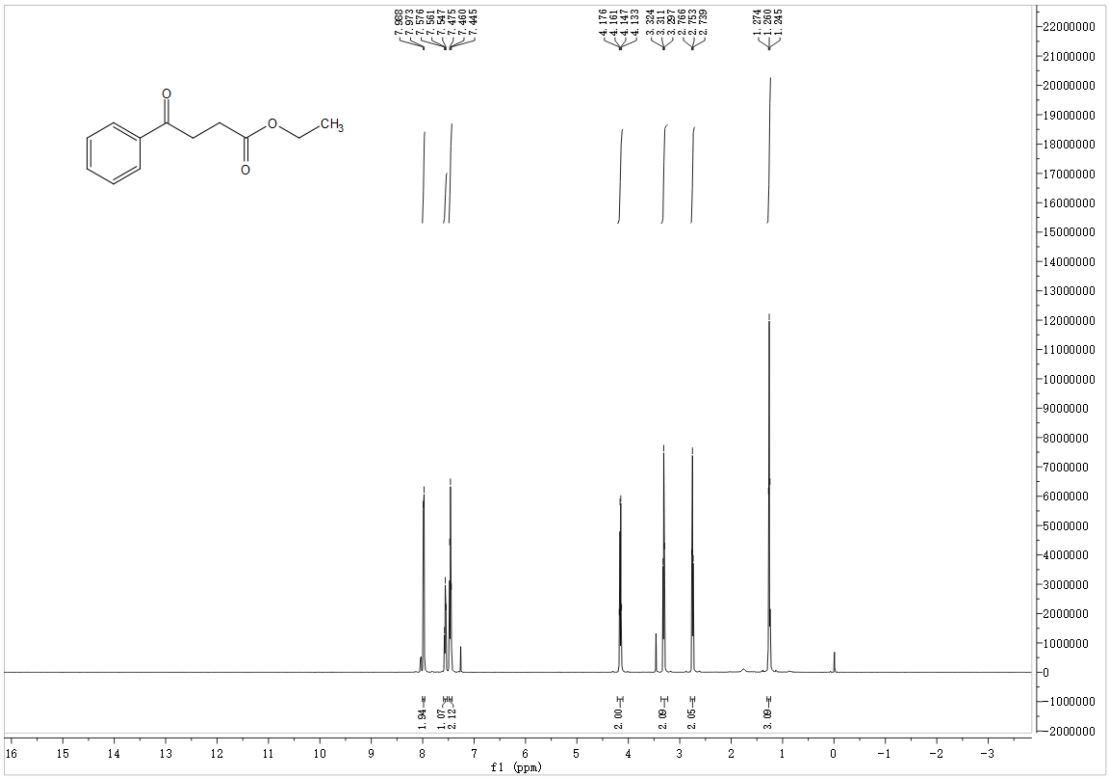

192.2
144.2
141.0
133.6
131.8
128.6
128.4
128.1
126.2
41.2
30.4
O
S
f1 (ppm)

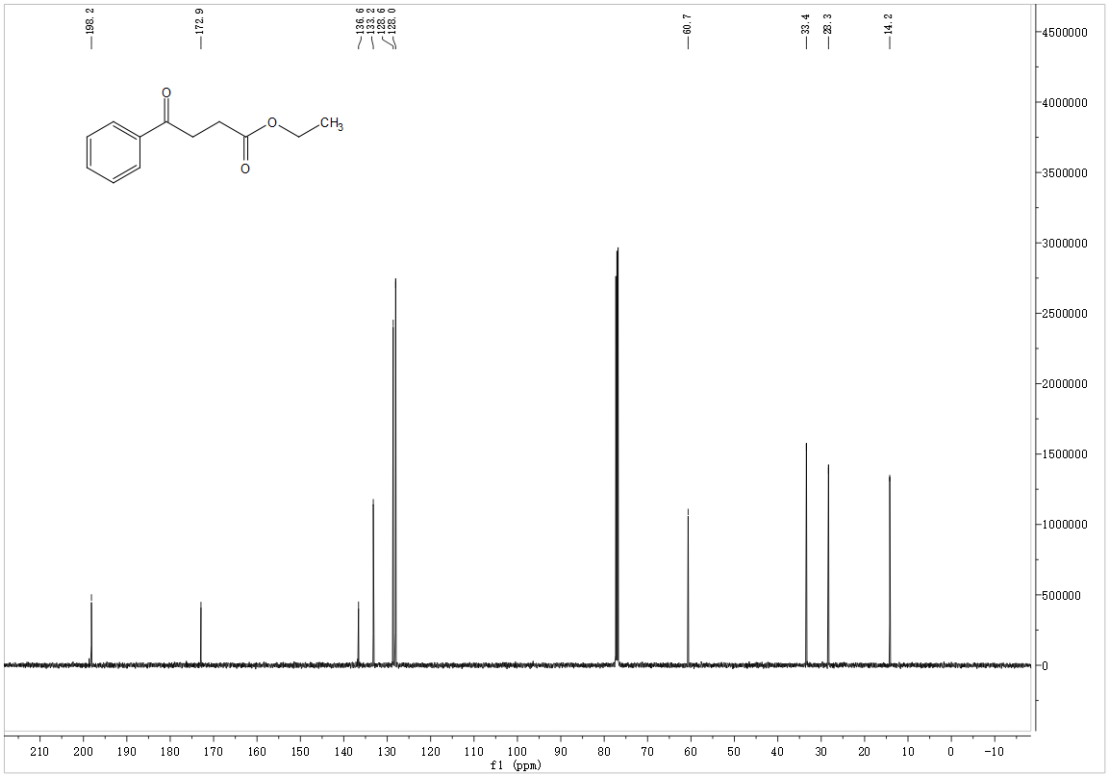
Product (**14**)


7.968
7.950
7.947
7.581
7.563
7.544
7.474
7.455
7.436
7.304
7.301
7.293
7.228
7.218
7.206
7.186
7.175
4.885
4.867
4.849
3.777
3.759
O
2.04
1.01
2.09
8.07
1.98
1.00
2.07
f1 (ppm)

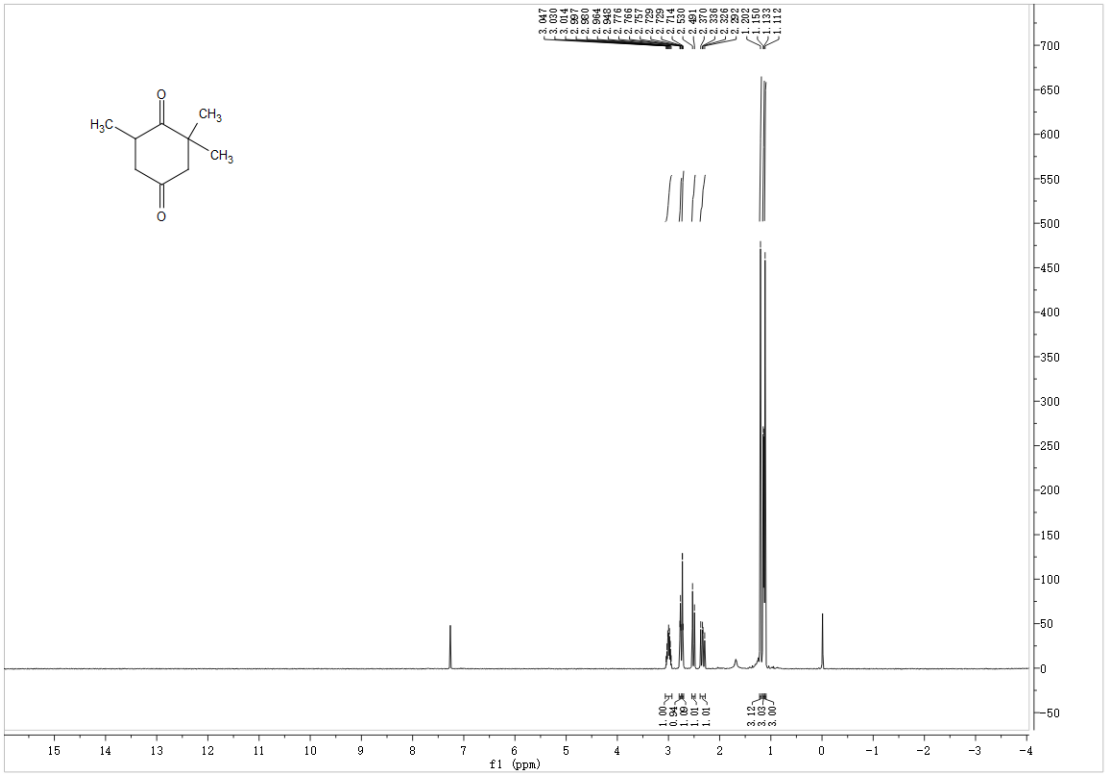

198.0
144.2
137.1
133.1
128.6
128.1
127.9
126.4
46.0
44.8
O
f1 (ppm)

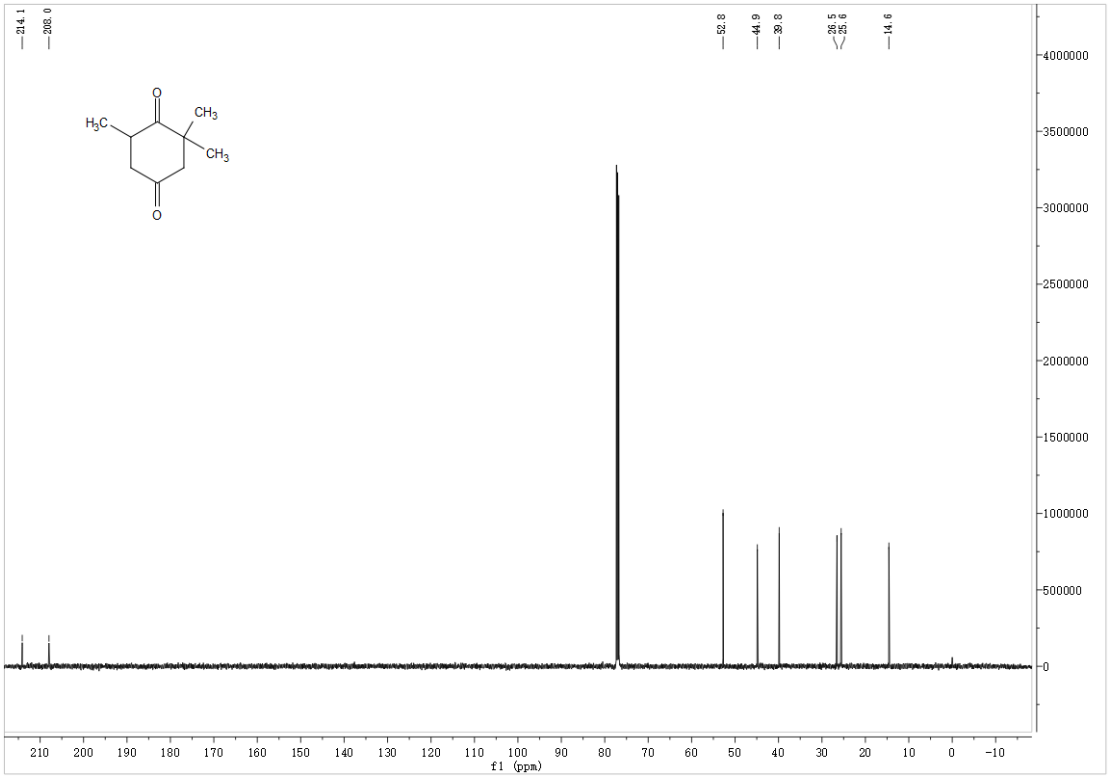
Product (**15**)


7.988
7.973
7.576
7.561
7.547
7.475
7.460
7.445
4.176
4.161
4.147
4.133
3.324
3.311
3.297
2.768
2.753
2.739
1.274
1.260
1.245
1.94
1.07
2.12
2.00
2.09
2.05
3.09
f1 (ppm)


198.2
172.9
136.6
133.2
128.6
128.0
60.7
33.4
28.3
14.2
f1 (ppm)

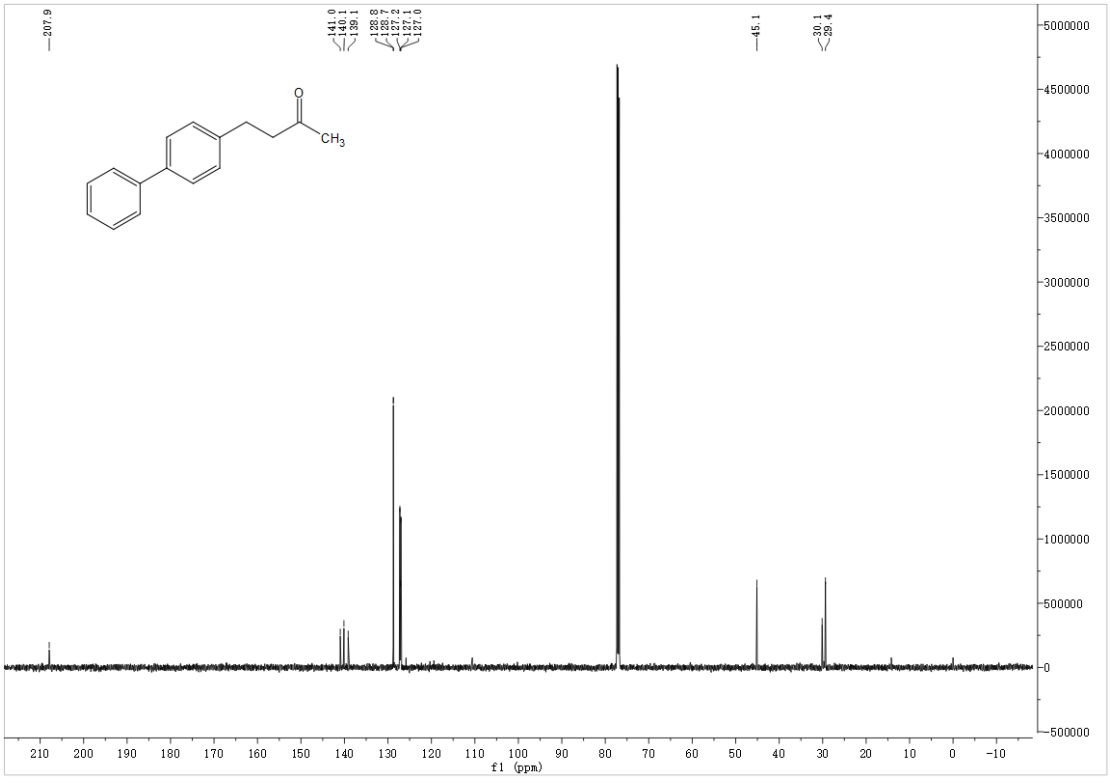
Product (**16**)


H3C
CH3
CH3
O
O
f1 (ppm)


214.1
208.0
52.8
44.9
39.8
26.5
25.6
14.6
H3C
CH3
CH3
O
O
f1 (ppm)

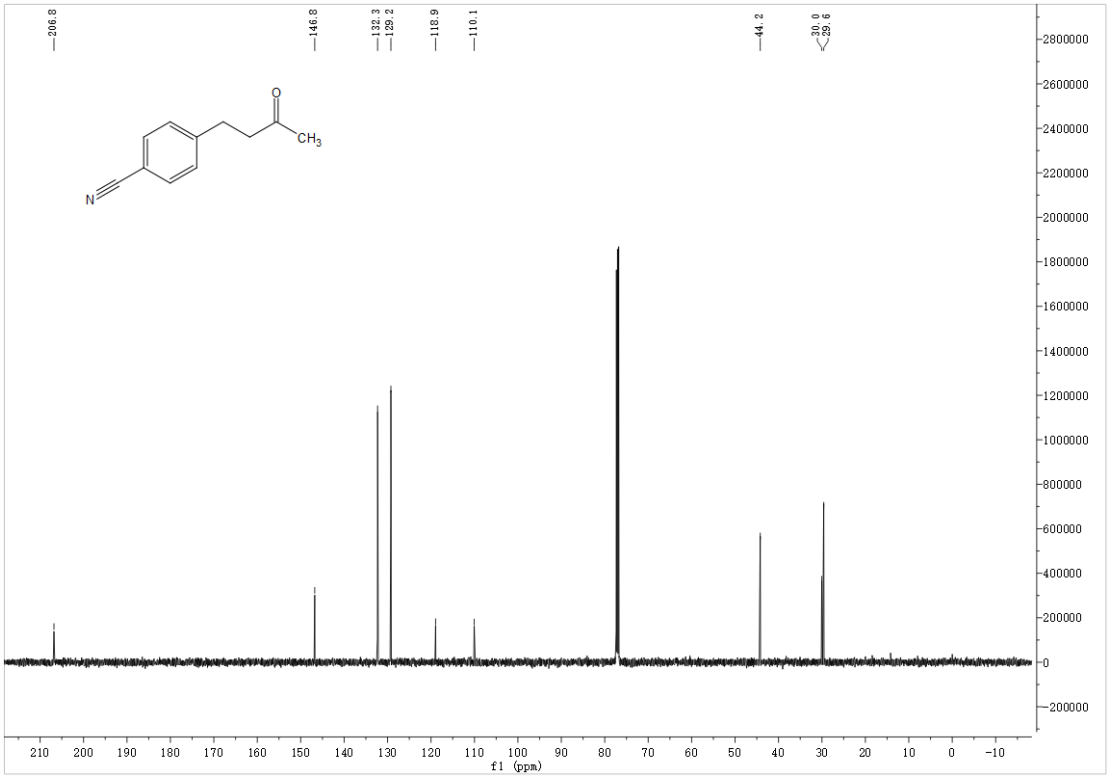
Product (**17**)


7.853
7.844
7.599
7.589
7.449
7.430
7.411
7.350
7.331
7.313
7.271
7.252
2.965
2.947
2.928
2.823
2.804
2.175
2.107
O
CH3
2.11
1.98
2.08
1.07
2.00
2.11
1.99
3.03
f1 (ppm)

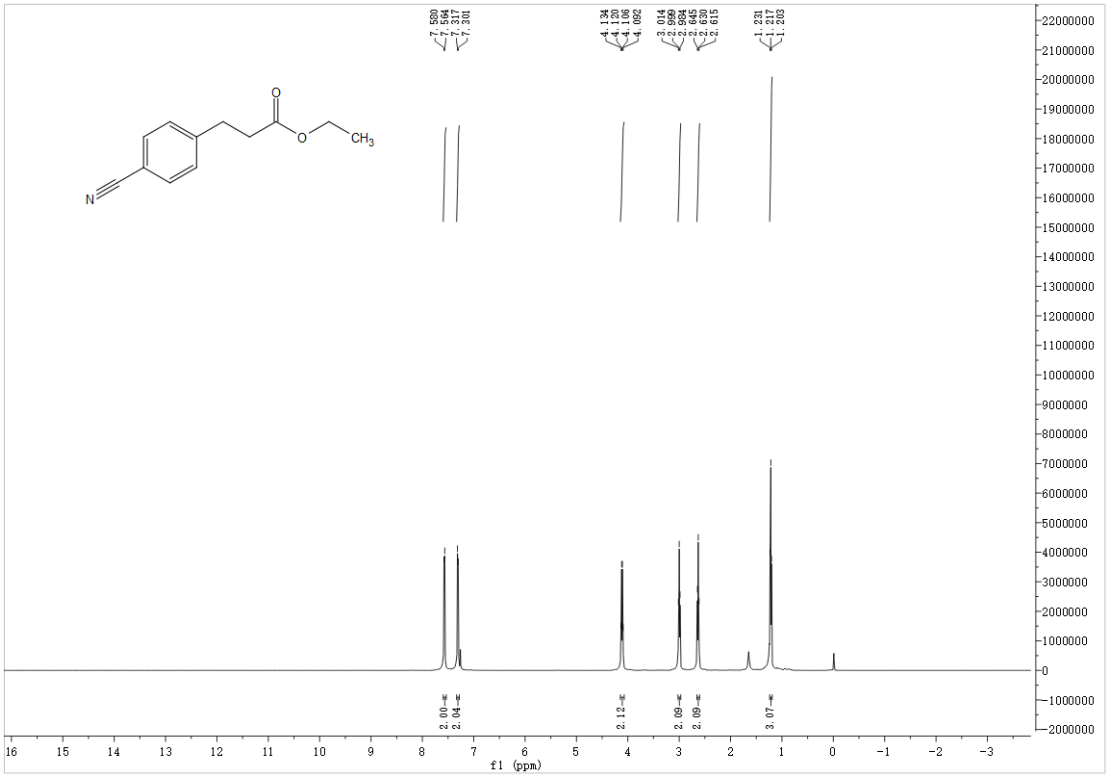

207.9
141.0
140.1
139.1
128.8
128.7
127.2
127.1
127.0
45.1
30.1
29.4
O
CH3
f1 (ppm)

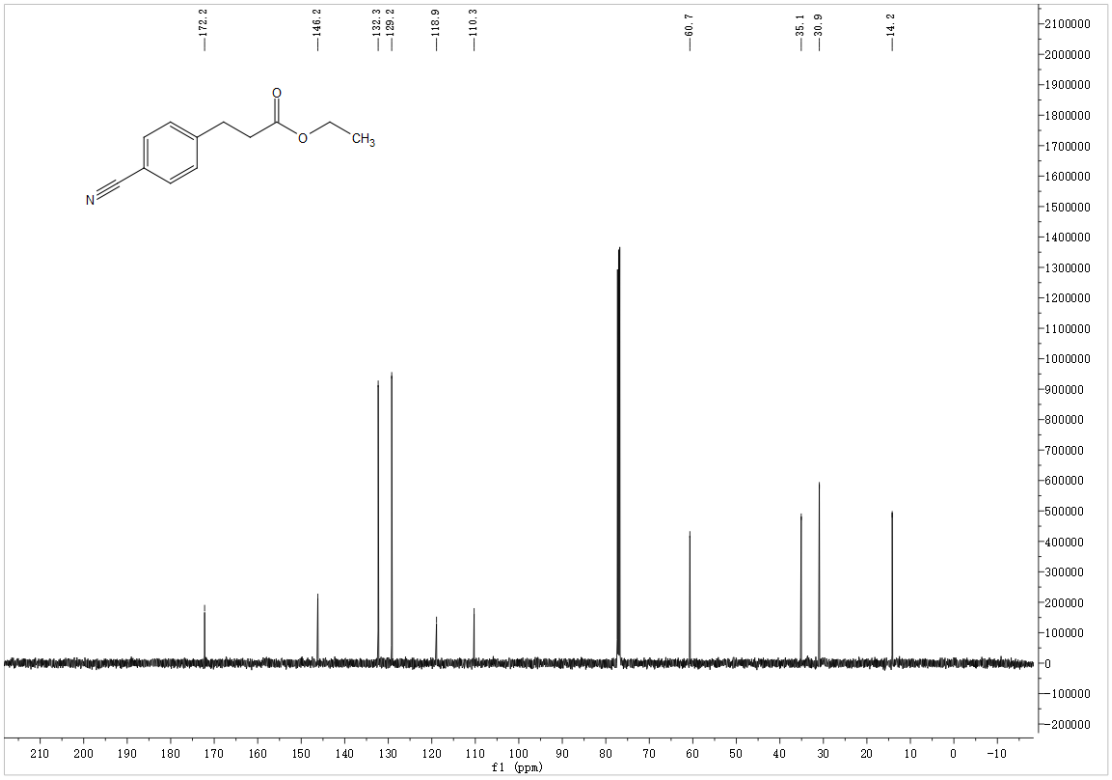
Product (**18**)


7.564
7.543
7.294
7.274
2.958
2.940
2.922
2.750
2.771
2.753
2.140
O
CH3
N
2.00
2.04
2.11
2.08
3.08
f1 (ppm)

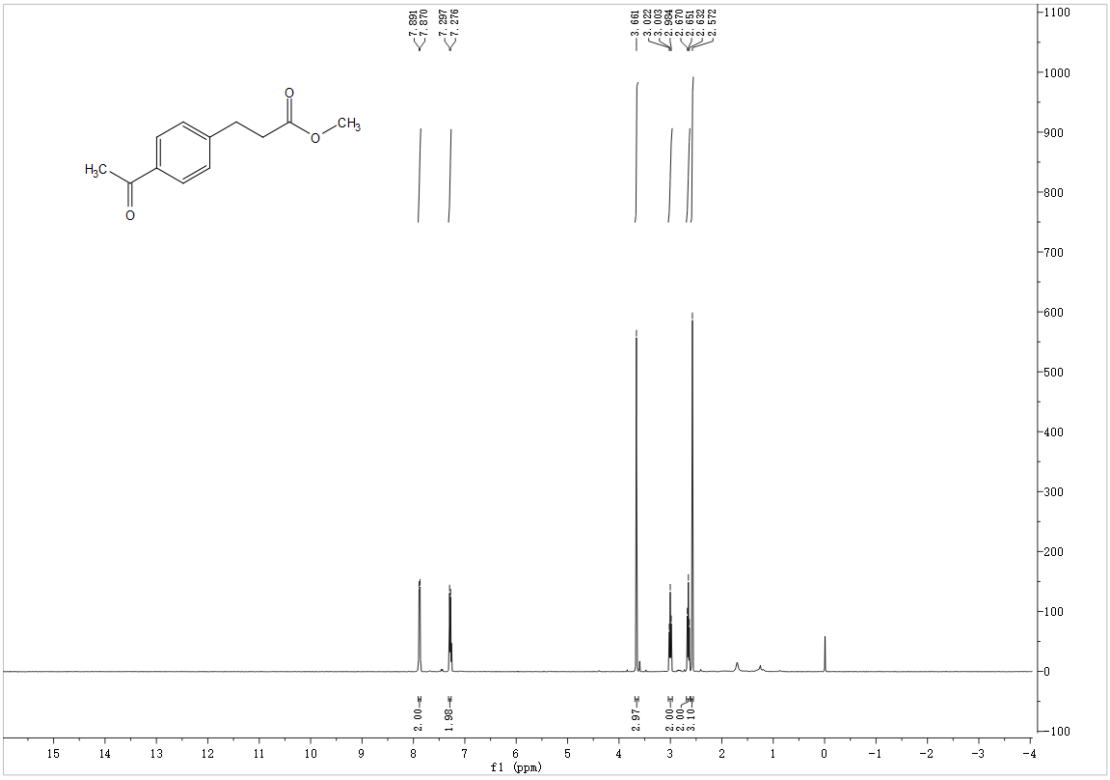

206.8
146.8
132.3
129.2
118.9
110.1
44.2
30.0
29.6
O
CH3
N
f1 (ppm)

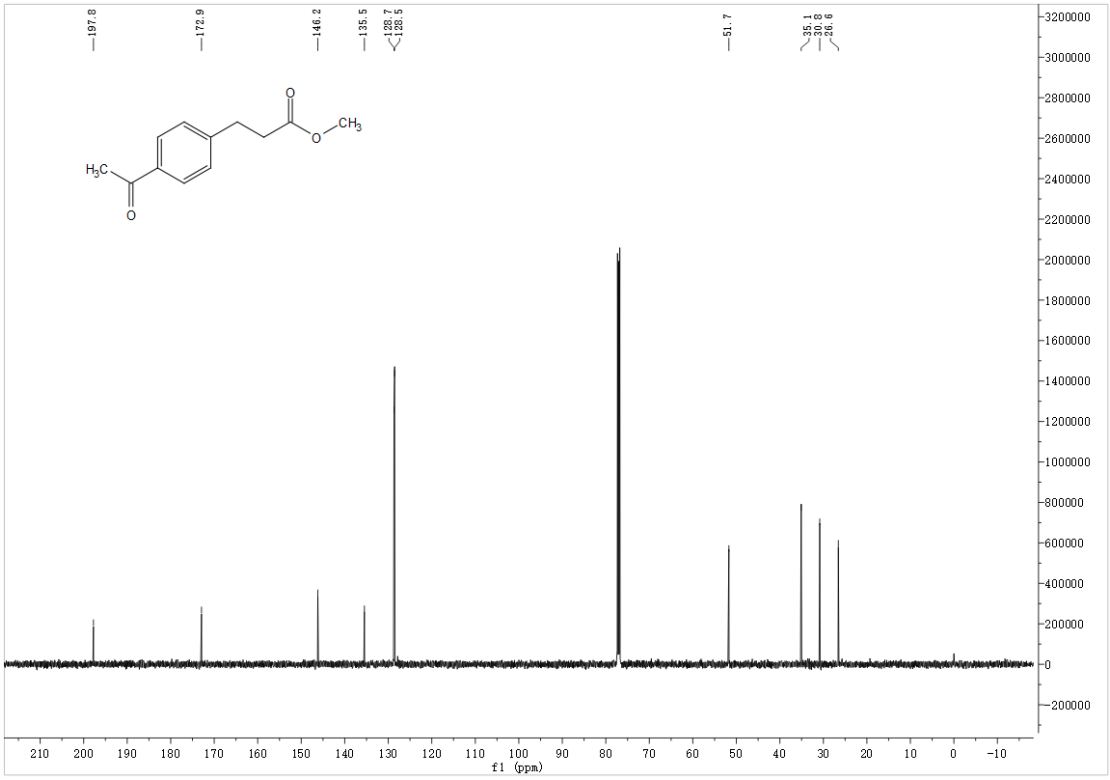
Product (**19**)


7.580
7.564
7.317
7.301
4.134
4.120
4.106
4.092
3.014
2.999
2.984
2.645
2.630
2.615
1.231
1.217
1.203
2.00
2.04
2.13
2.09
2.09
3.07
f1 (ppm)

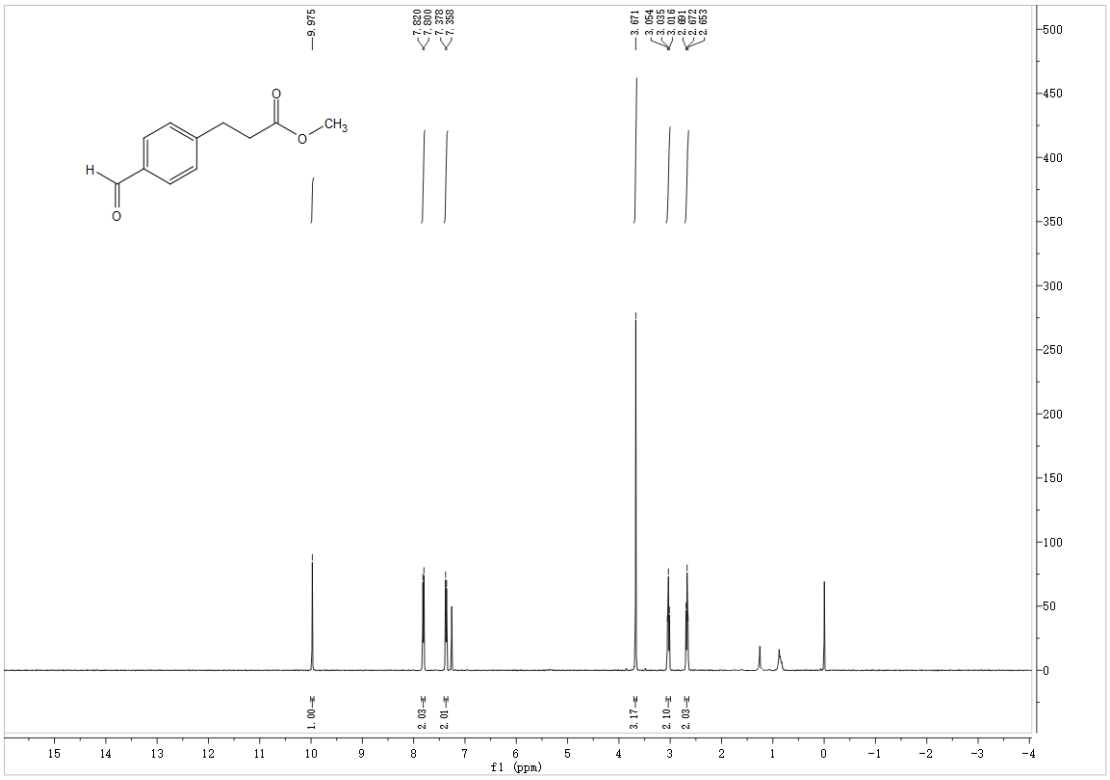

172.2
146.2
132.3
129.2
118.9
110.3
60.7
35.1
30.9
14.2
f1 (ppm)

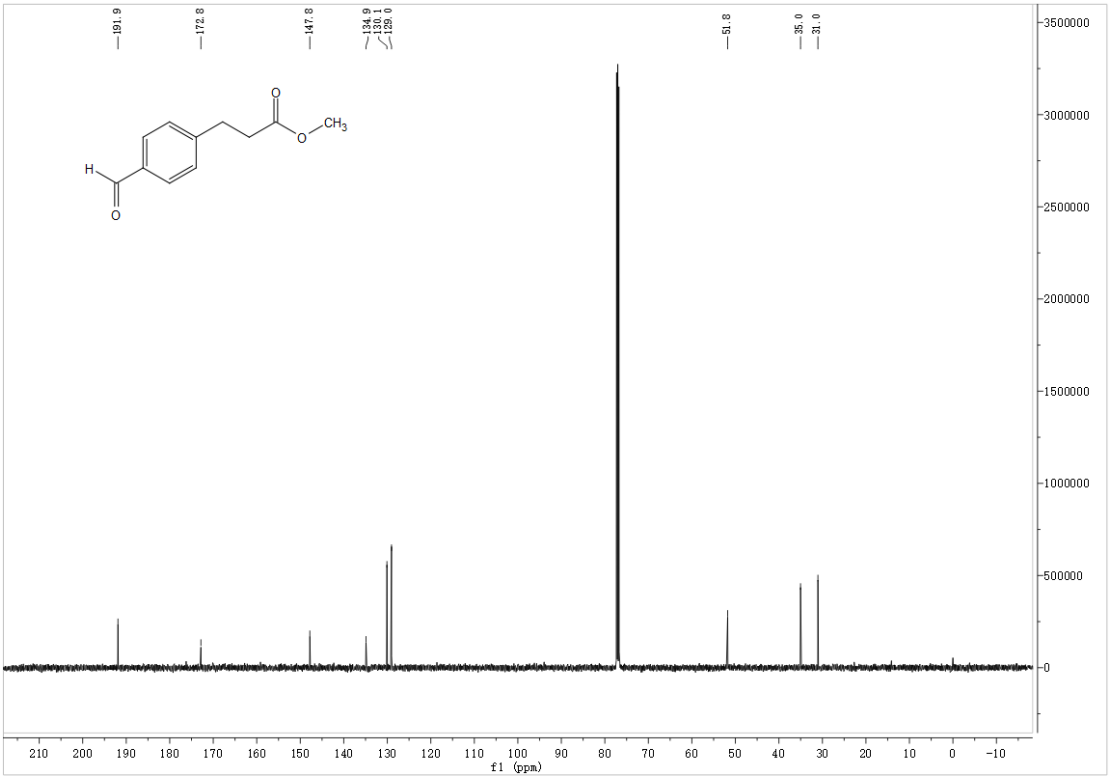
Product (**20**)


7.891
7.870
7.297
7.276
3.661
3.022
3.003
2.984
2.670
2.651
2.632
2.572
O
O
CH3
H3C
O
2.00
1.98
2.97
2.00
2.00
3.10
f1 (ppm)

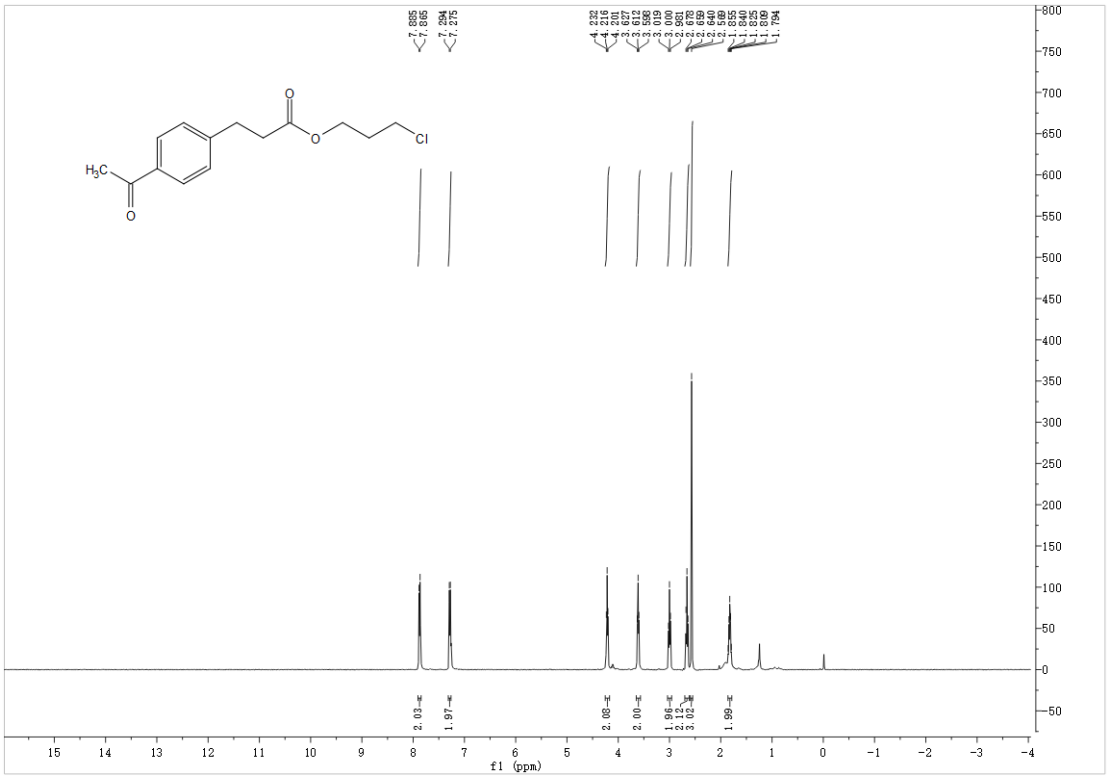

197.8
172.9
146.2
135.5
128.7
128.5
51.7
35.1
30.8
26.6
O
O
CH3
H3C
O
f1 (ppm)

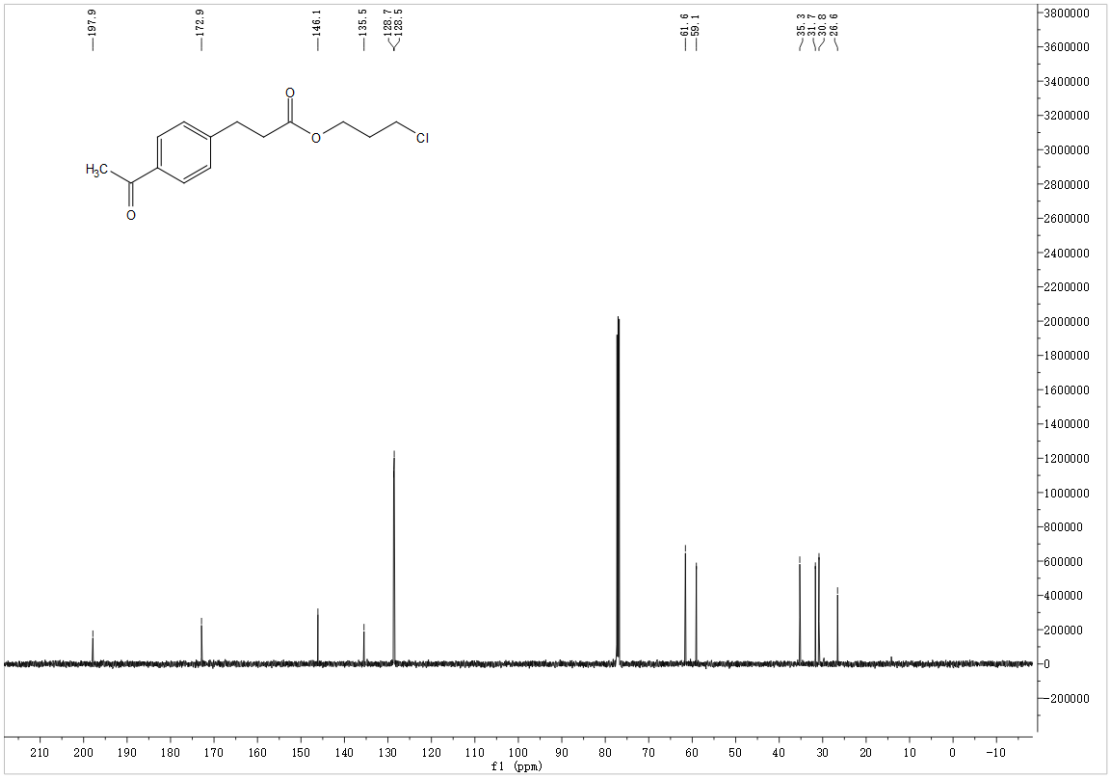
Product (**21**)


9.975
7.820
7.800
7.378
7.358
3.671
3.054
3.035
3.015
2.691
2.672
2.653
1.00
2.03
2.01
3.17
2.10
2.03
f1 (ppm)


191.9
172.8
147.8
134.9
130.1
129.0
51.8
35.0
31.0
f1 (ppm)

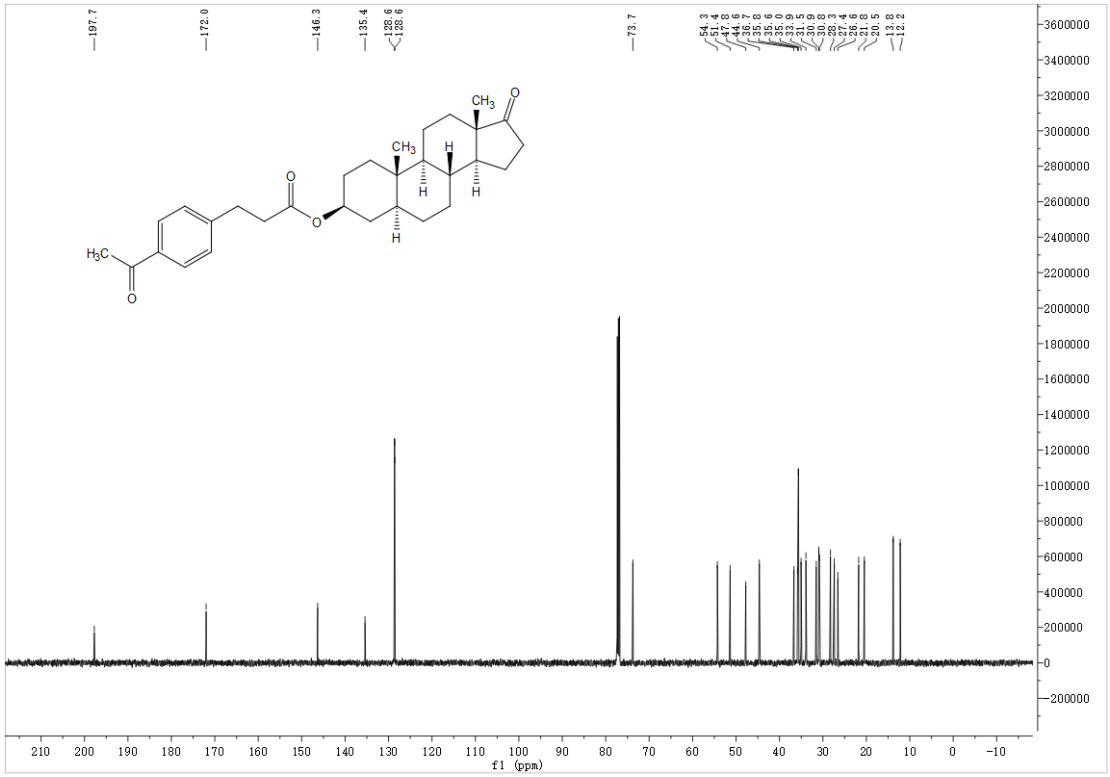
Product (**22**)


7.885
7.865
7.294
7.275
4.232
4.216
4.201
3.627
3.612
3.598
3.139
3.119
3.000
2.981
2.678
2.660
2.640
2.569
1.855
1.840
1.825
1.809
1.794
O
O
Cl
H3C
O
2.03
1.97
2.08
2.00
1.96
2.12
3.02
1.99
f1 (ppm)

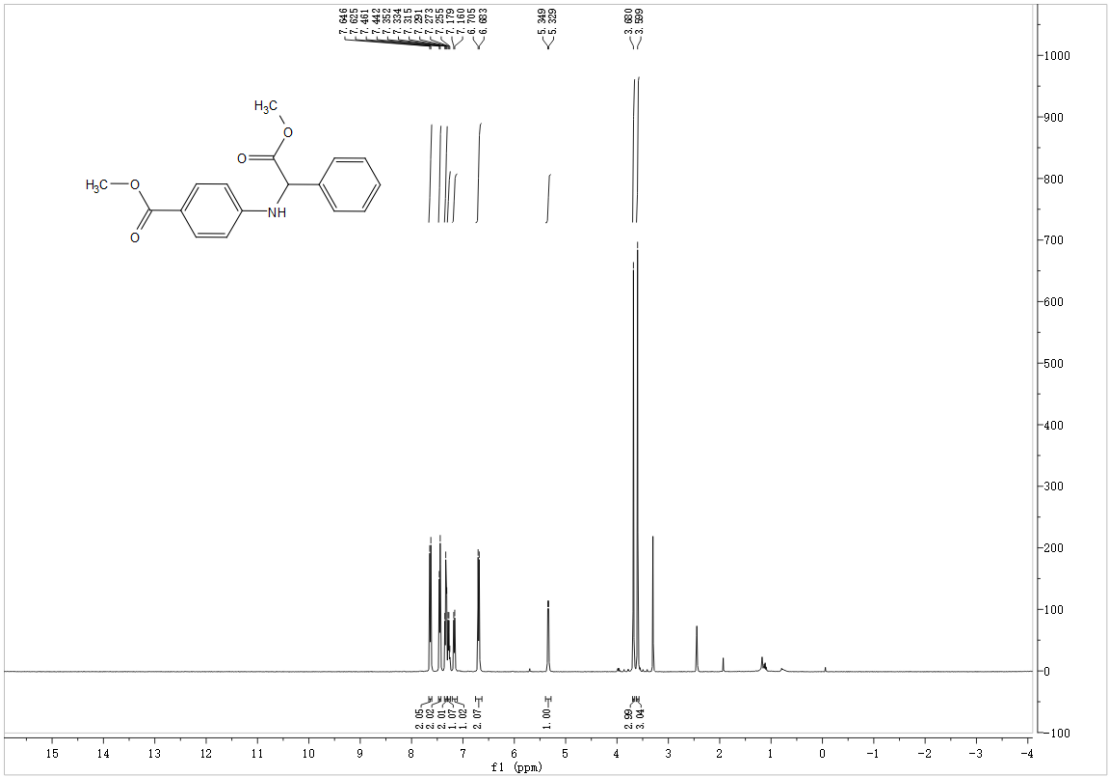

197.9
172.9
146.1
135.5
128.7
128.5
61.6
59.1
35.3
31.7
30.8
26.6
O
O
Cl
H3C
O
f1 (ppm)

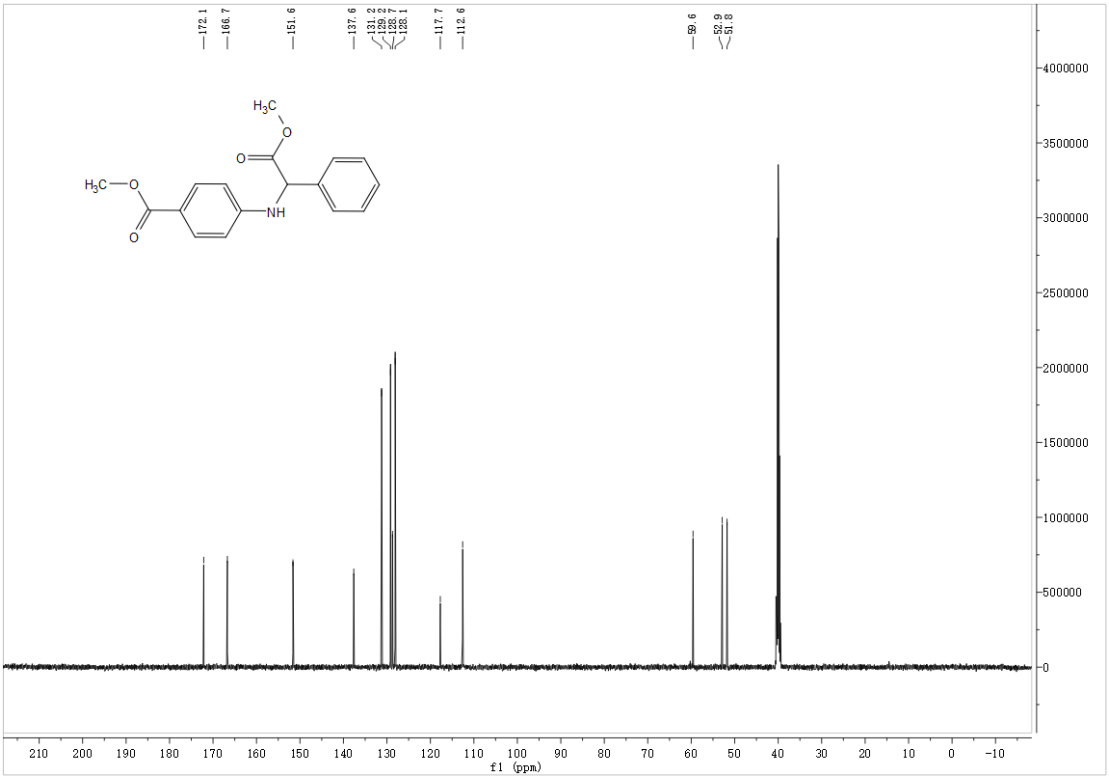
Product (**23**)


CH3
O
CH3
H
H
H
H
O
O
H3C
O
f1 (ppm)

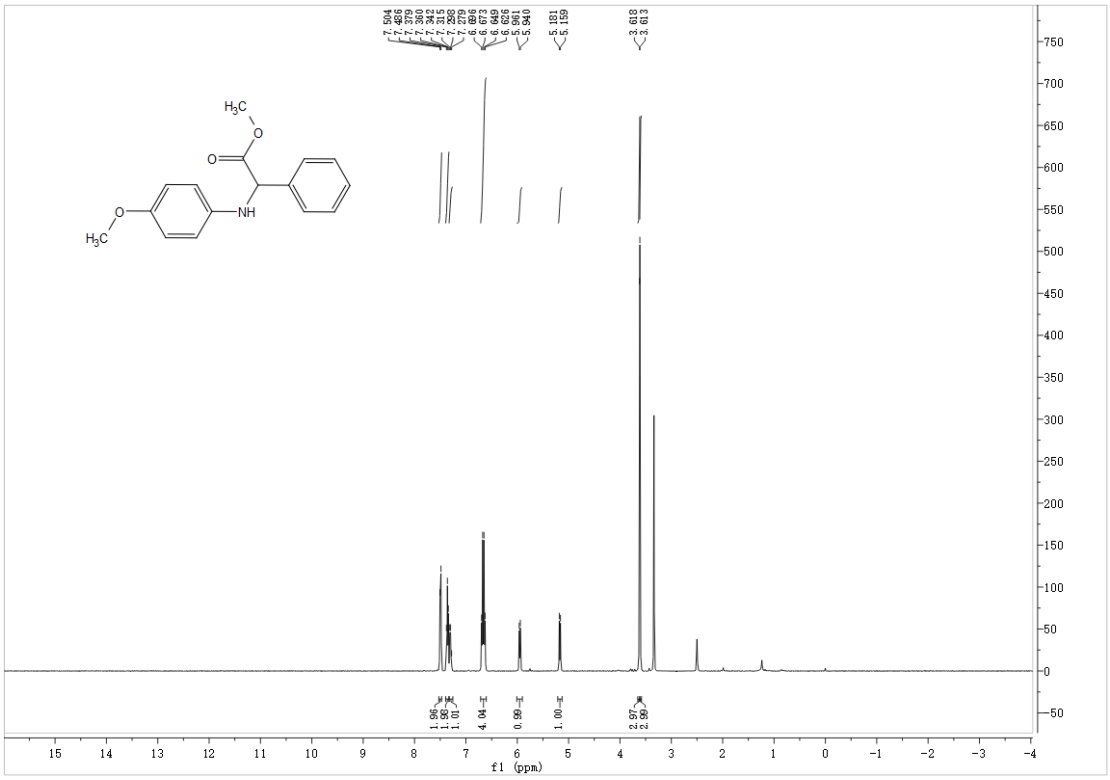

197.7
172.0
146.3
135.4
128.6
128.6
73.7
CH3
O
CH3
H
H
H
H
O
O
H3C
O
f1 (ppm)

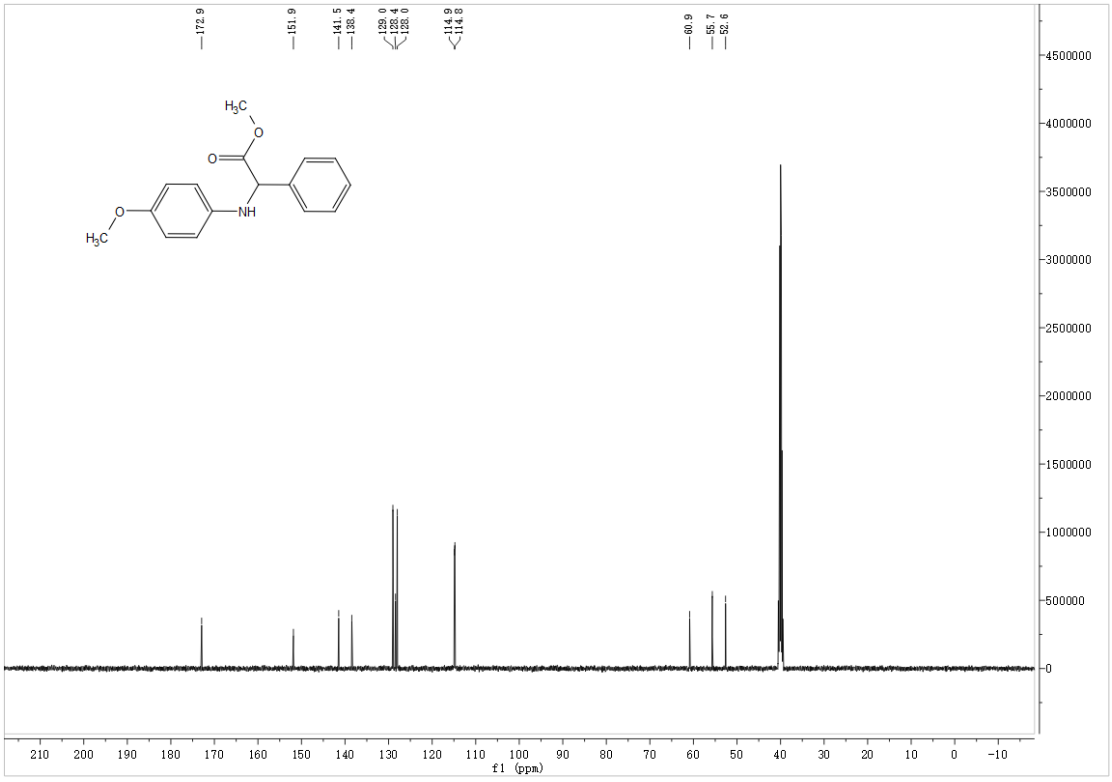
Product (**24**)


7.646
7.625
7.491
7.464
7.352
7.334
7.315
7.301
7.273
7.255
7.179
7.160
6.705
6.683
5.349
5.329
3.880
3.599
H3C
O
O
H3C
O
O
NH
O
2.05
2.02
2.01
1.07
1.02
2.07
1.00
2.99
3.04
f1 (ppm)

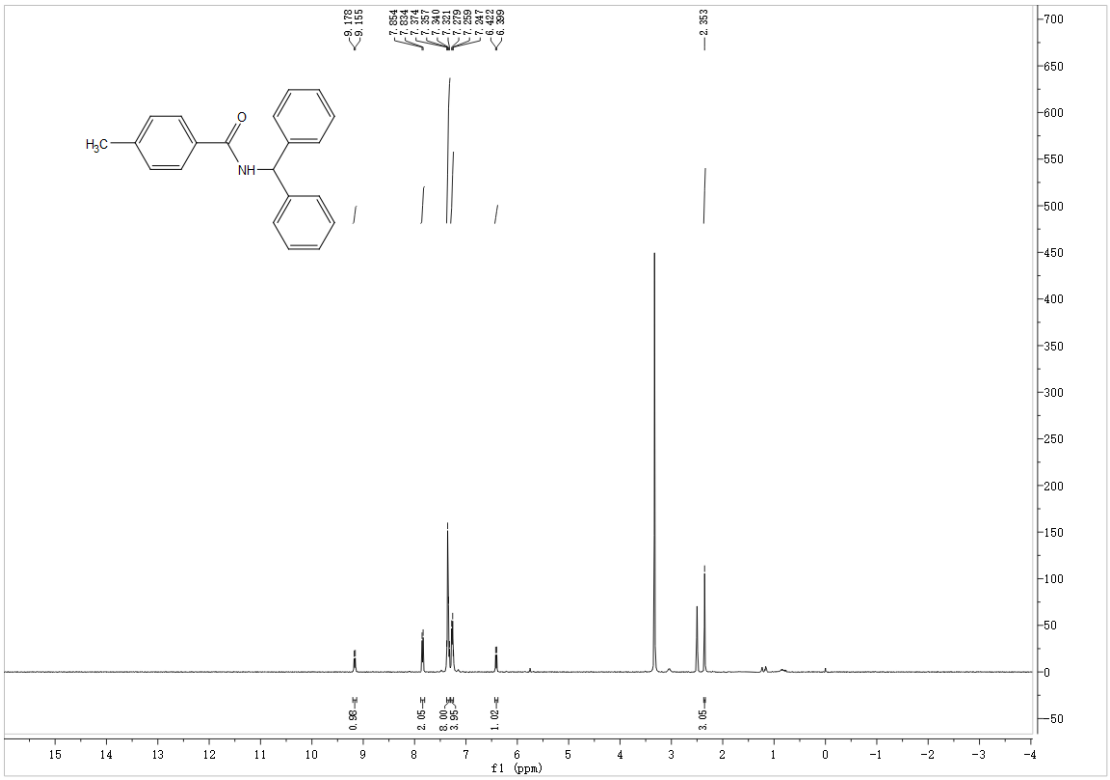

172.1
166.7
151.6
137.6
131.2
129.2
128.7
126.1
117.7
112.6
59.6
52.9
51.8
H3C
O
O
H3C
O
O
NH
O
f1 (ppm)

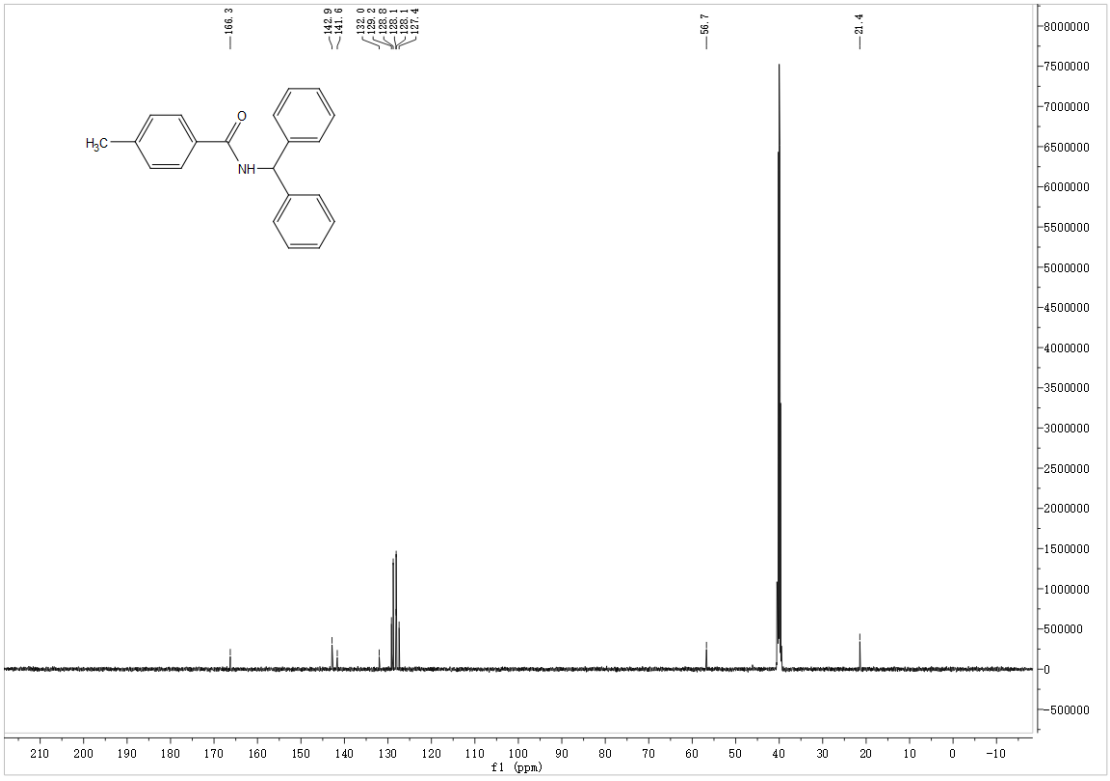
Product (**25**)


7.504
7.488
7.379
7.360
7.342
7.315
7.288
7.278
6.696
6.673
6.649
6.626
6.581
5.940
5.181
5.159
3.618
3.613
1.96
1.98
1.01
4.04
0.99
1.00
2.97
2.89
f1 (ppm)

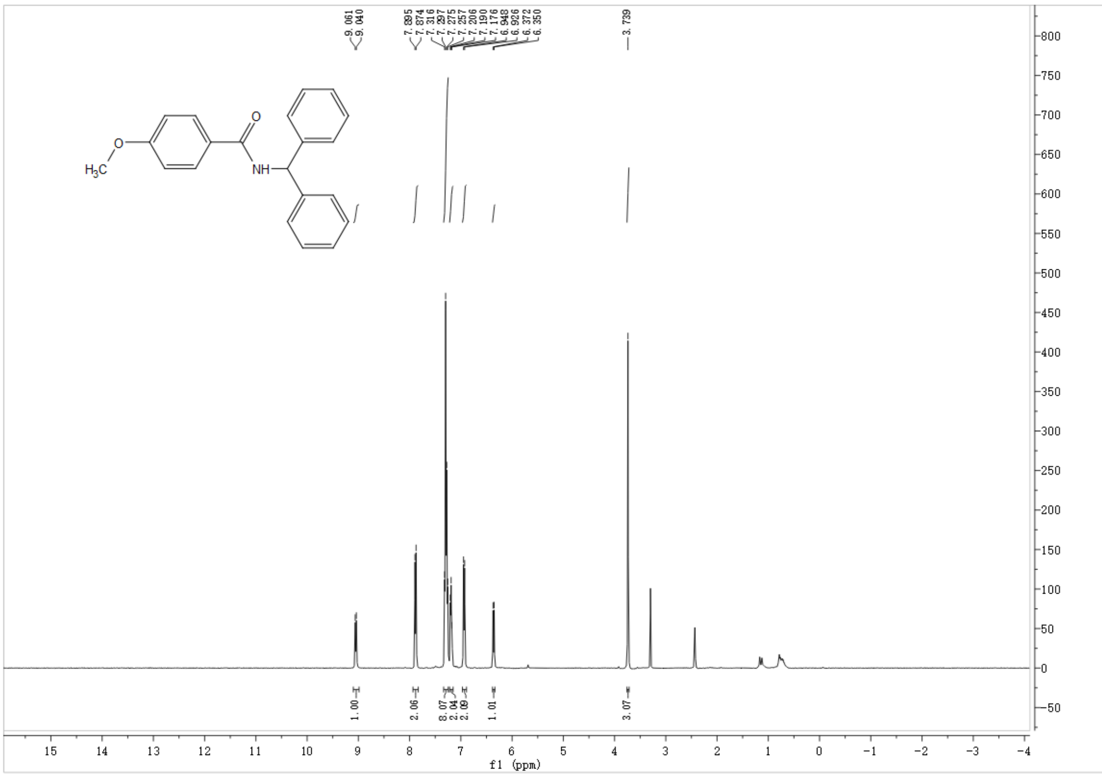

172.9
151.9
141.5
138.4
129.0
128.4
120.0
114.9
114.8
60.9
55.7
52.6
f1 (ppm)

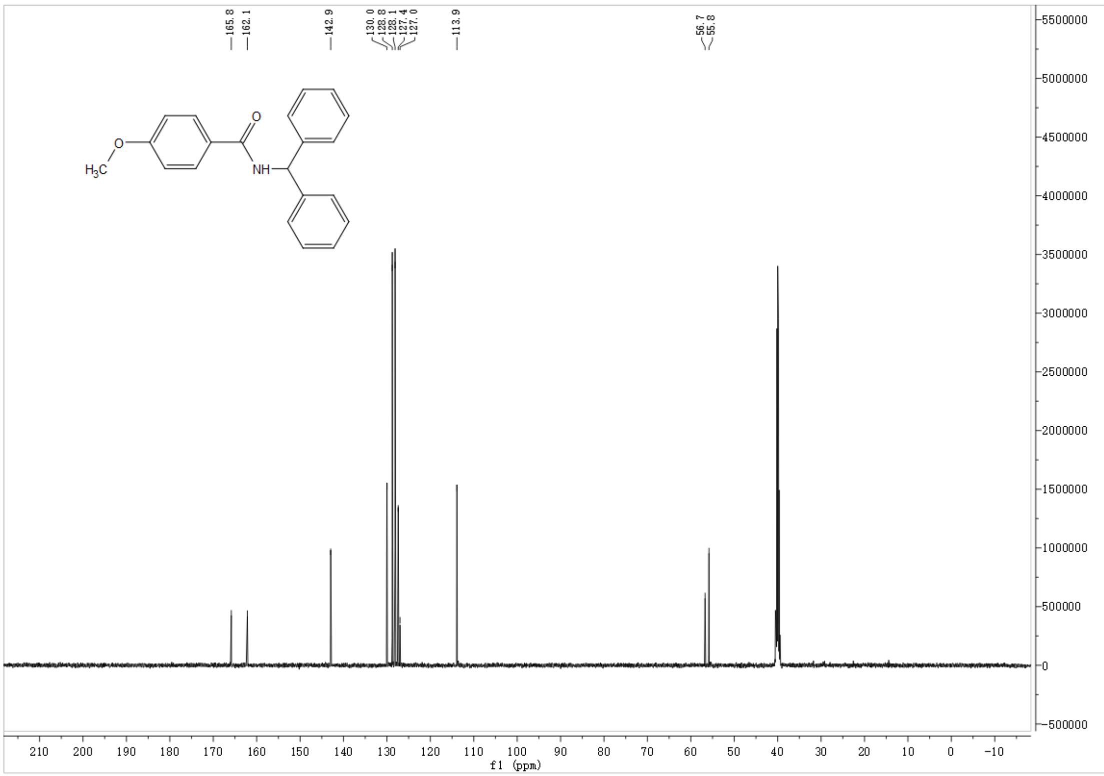
Product (**26**)


9.178
9.155
7.654
7.634
7.374
7.357
7.340
7.321
7.279
7.259
7.247
6.472
6.369
2.353
0.98
2.05
8.00
3.95
1.02
3.05
f1 (ppm)

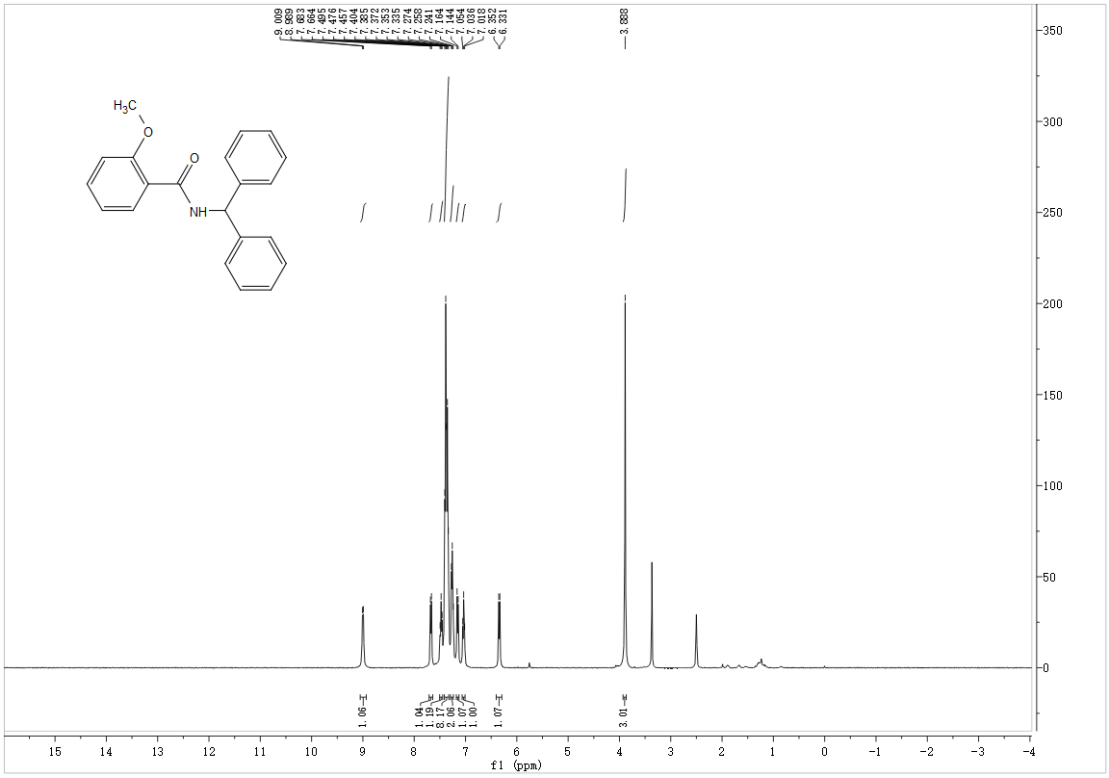

166.3
142.9
141.6
132.0
129.2
128.8
128.1
127.1
127.4
56.7
21.4
f1 (ppm)

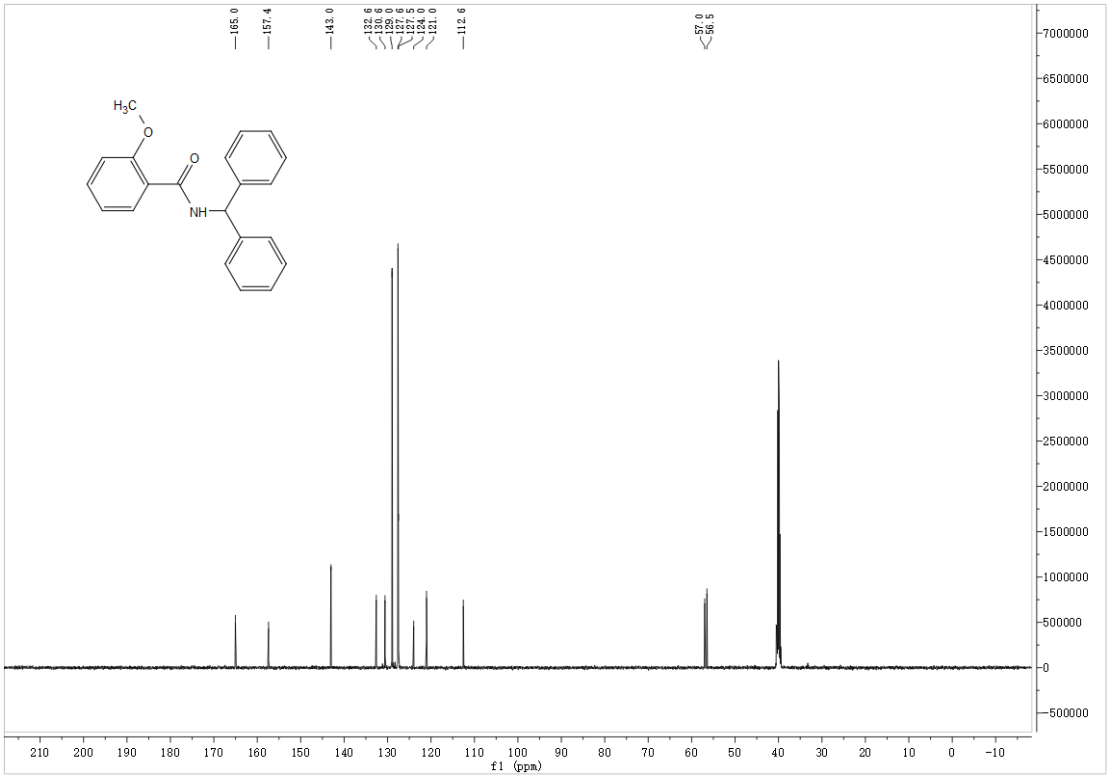
Product (**27**)



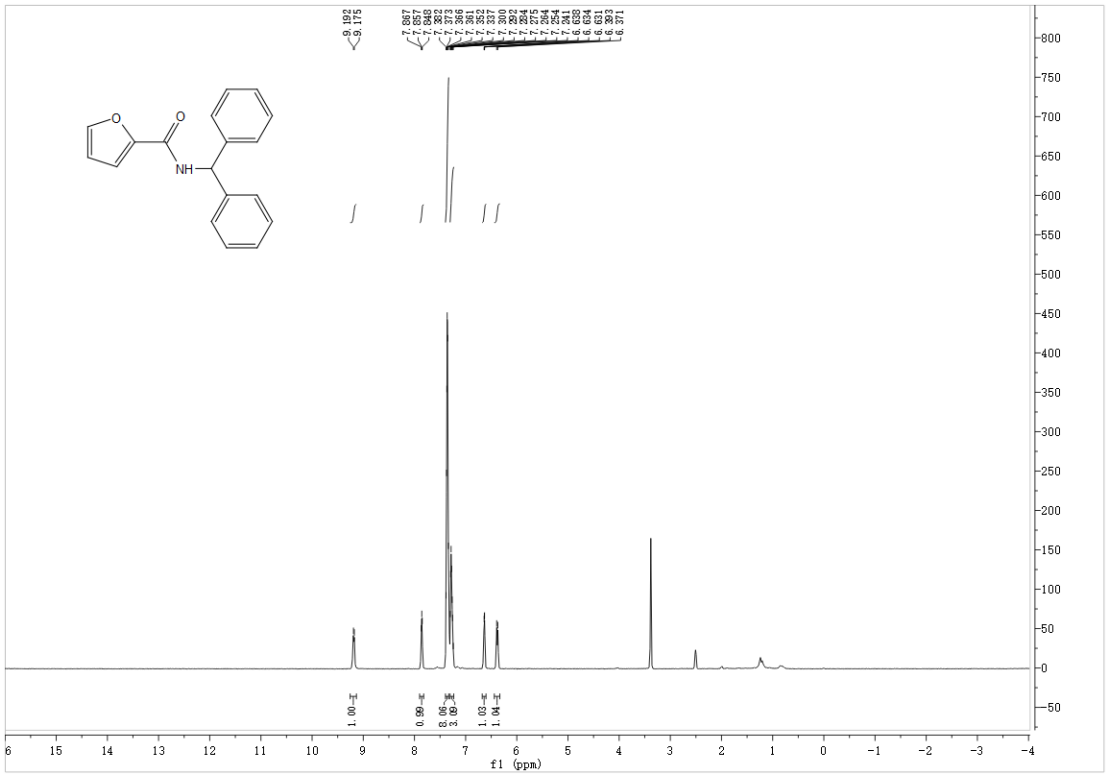


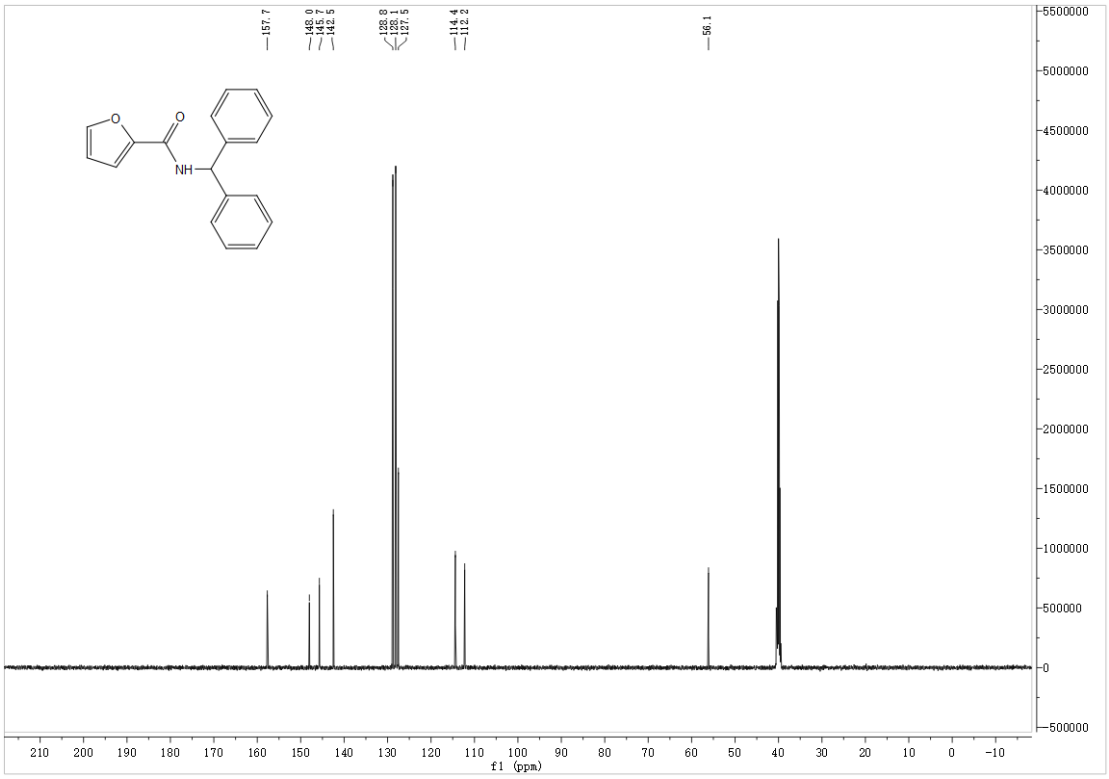
Product (**28**)


9.009
8.999
8.883
7.694
7.495
7.476
7.457
7.404
7.395
7.372
7.353
7.335
7.274
7.265
7.041
7.164
7.144
7.105
7.036
7.018
6.352
6.331
3.888
H3C
O
O
NH
1.06
1.04
1.19
8.17
2.06
1.07
1.00
1.07
3.01
f1 (ppm)

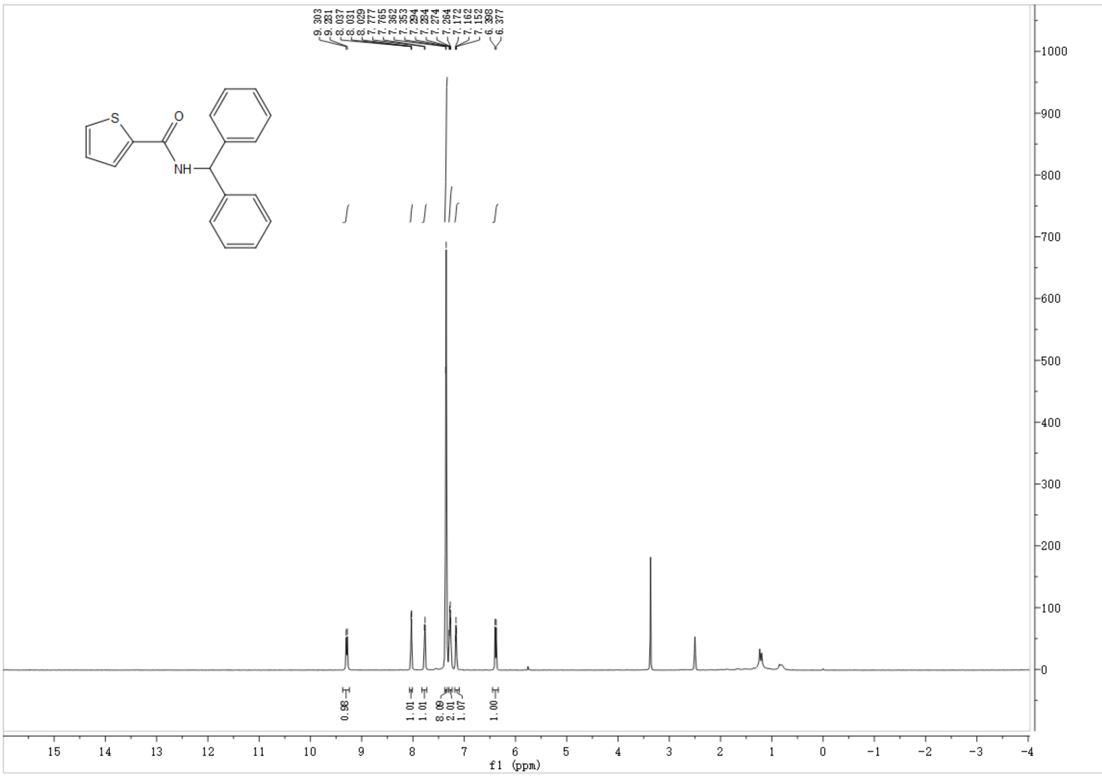

165.0
157.4
143.0
132.6
130.6
129.0
127.6
127.5
124.0
121.0
112.6
57.0
56.5
H3C
O
O
NH
f1 (ppm)

Product (**29**)

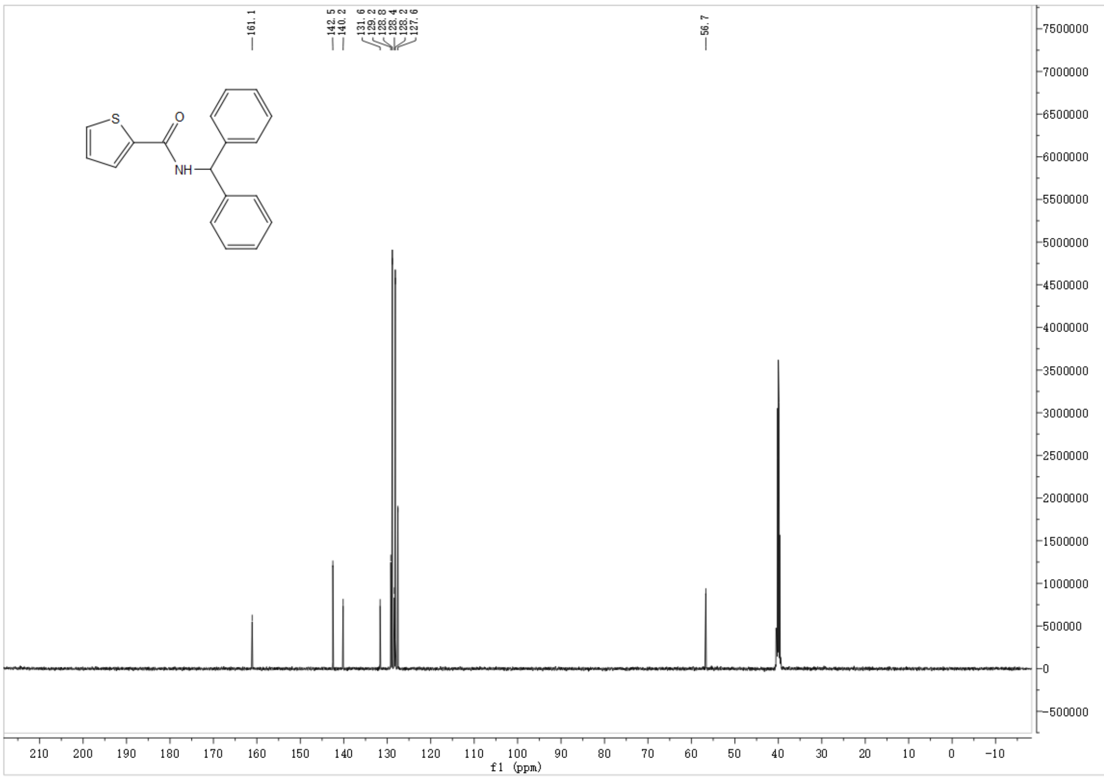

9.192
9.175
7.697
7.695
7.648
7.382
7.373
7.368
7.361
7.352
7.337
7.300
7.293
7.284
7.275
7.264
7.254
7.241
6.638
6.634
6.631
6.393
6.371
1.00
0.99
8.06
3.09
1.03
1.04
f1 (ppm)


157.7
148.0
145.7
142.5
128.8
128.1
127.5
114.4
112.2
56.1
f1 (ppm)

Product (**30**)

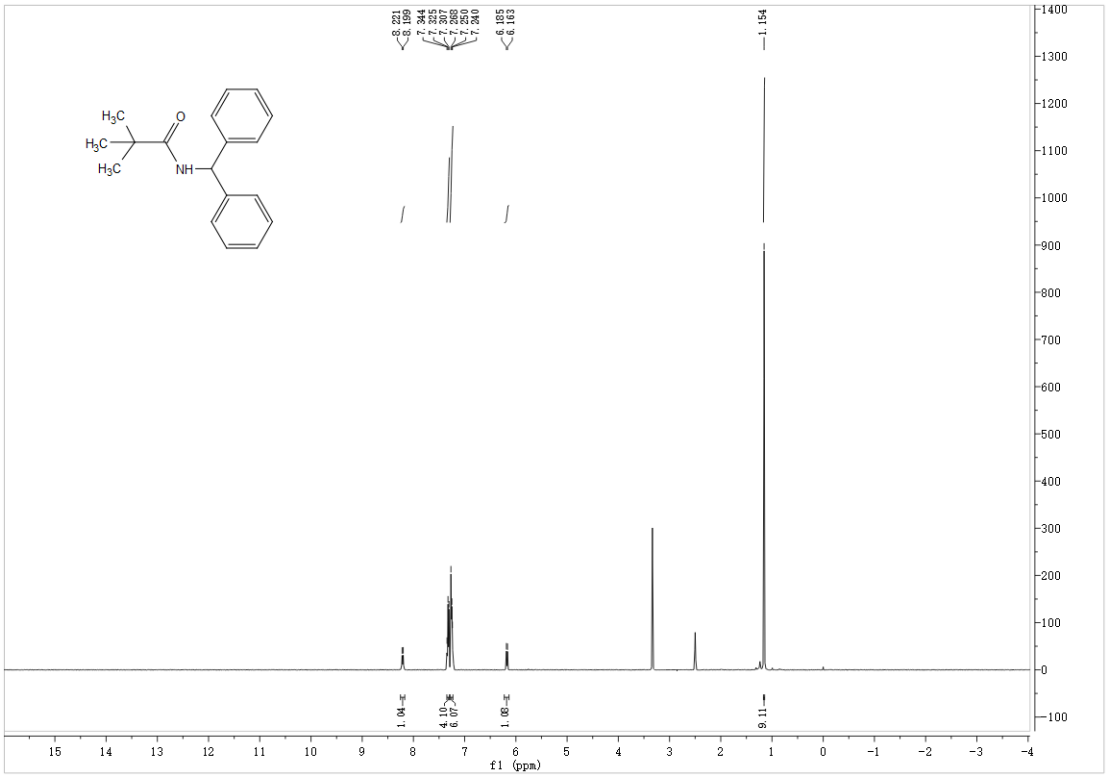


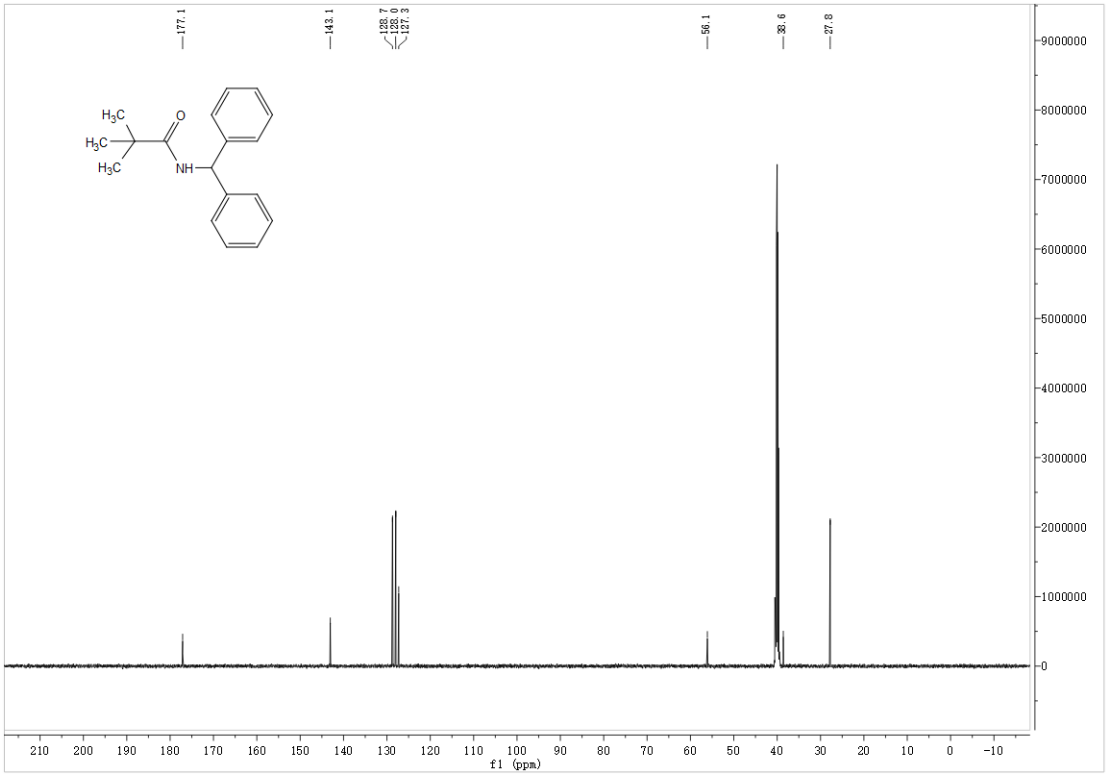
9.303
9.281
8.037
8.031
8.029
7.777
7.765
7.362
7.353
7.294
7.284
7.274
7.264
7.172
7.162
7.152
6.398
6.377
S
O
NH
0.98
1.01
1.01
8.09
2.01
1.07
1.00
f1 (ppm)



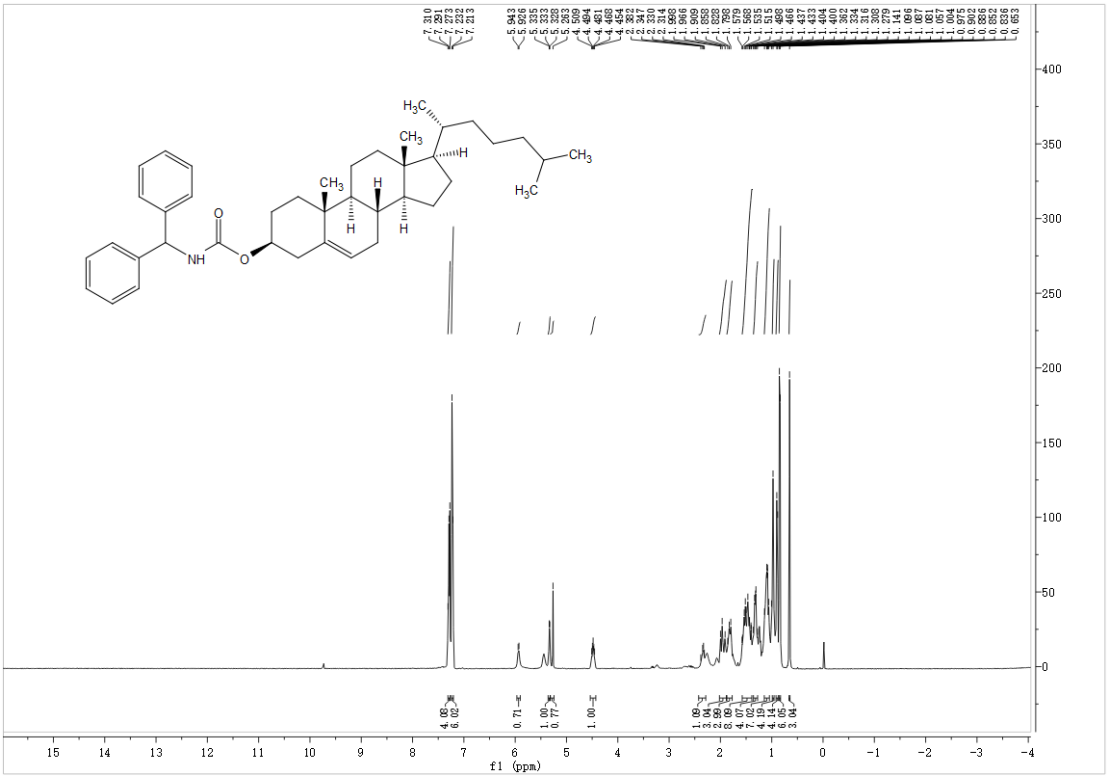
161.1
142.5
140.2
131.6
129.2
128.8
128.4
128.2
127.6
56.7
S
O
NH
f1 (ppm)

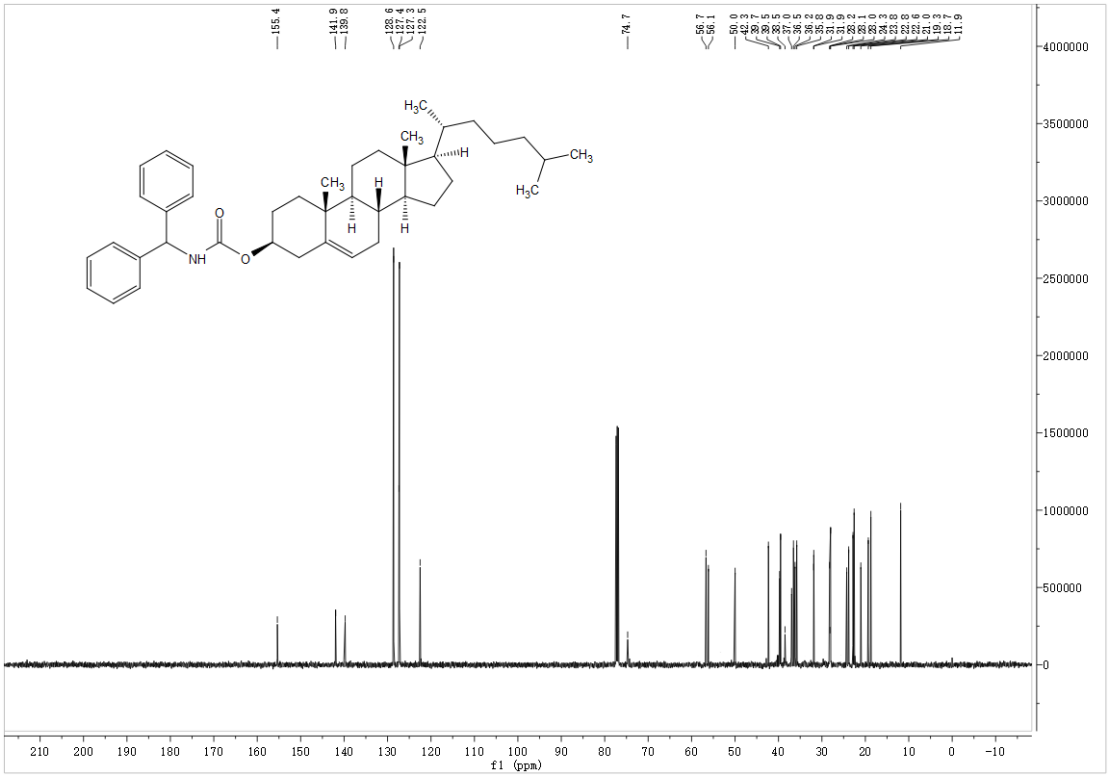
Product (**31**)


8.221
8.199
7.344
7.335
7.307
7.288
7.250
7.240
6.185
6.163
1.154
1.04
4.10
6.07
1.00
9.11
f1 (ppm)


177.1
143.1
128.7
128.0
127.3
56.1
38.6
27.8
f1 (ppm)

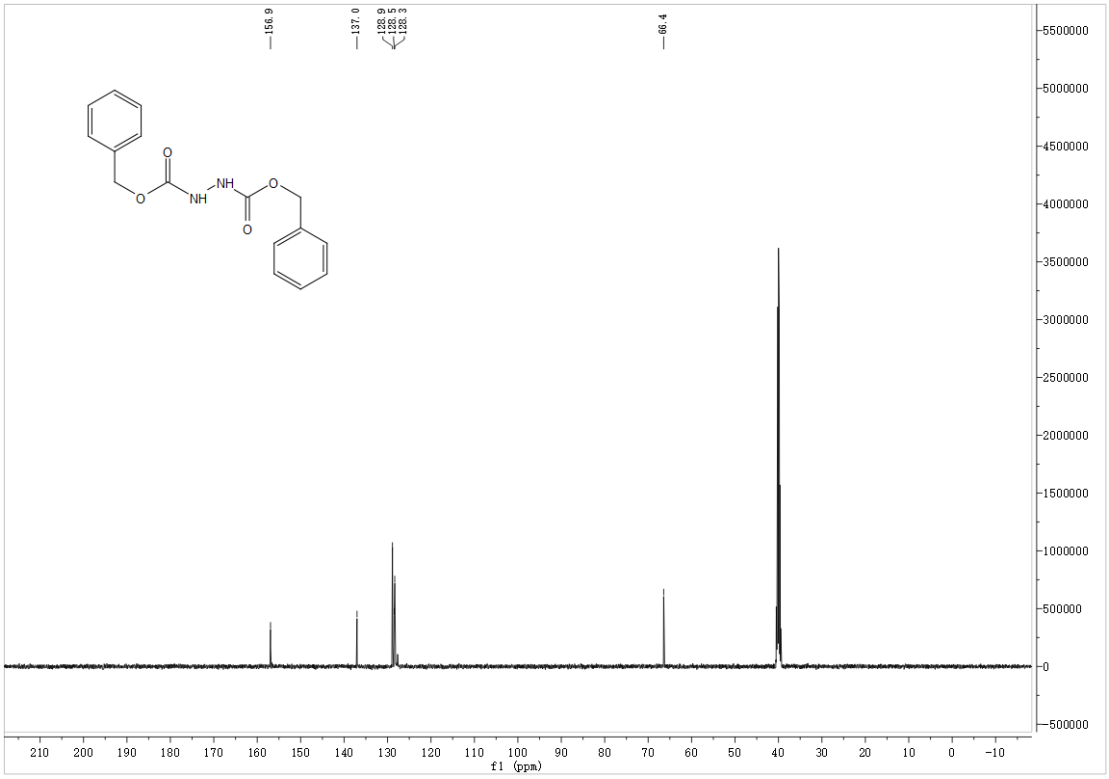
Product (**32**)



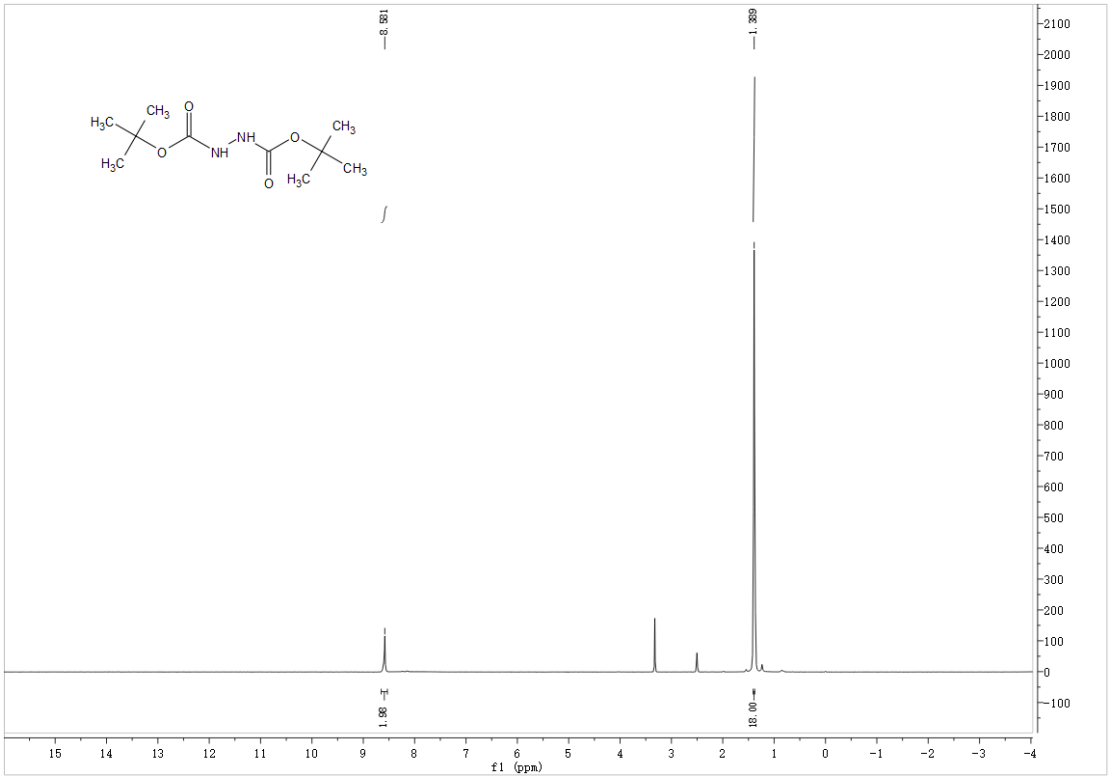


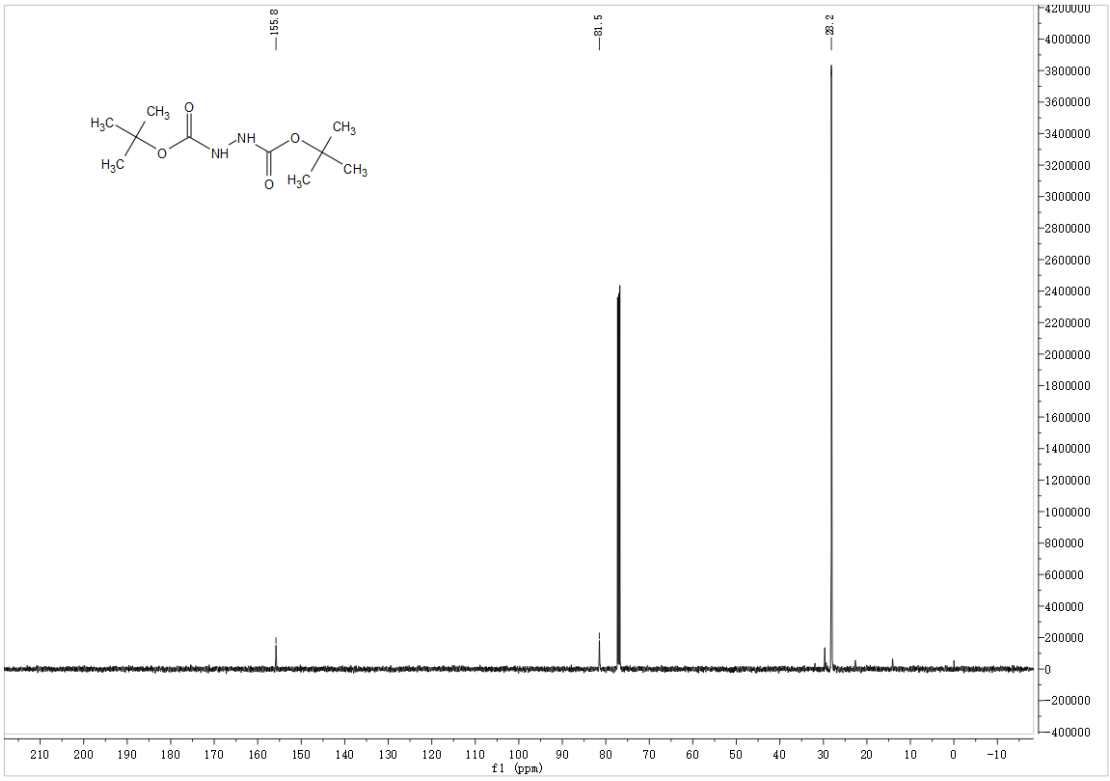
Product (**33**)


9.245
7.376
7.370
7.364
7.336
7.330
7.322
5.093
1.24
0.02
4.06
4.00
f1 (ppm)

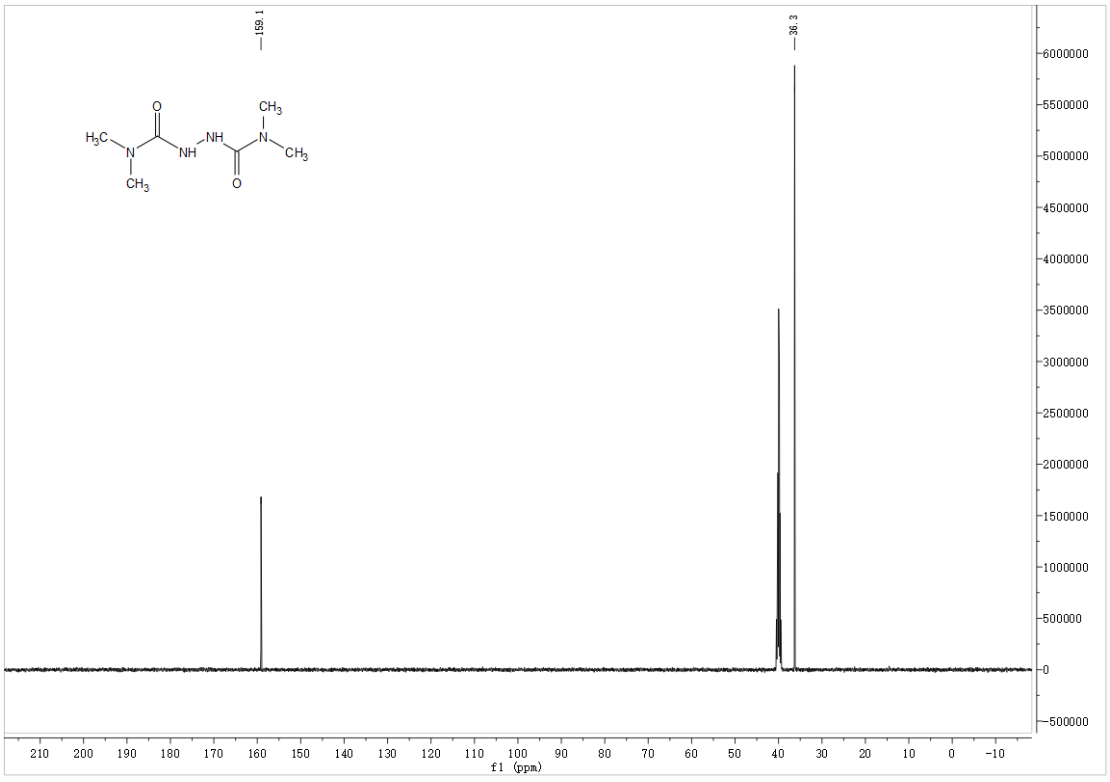

156.9
137.0
128.9
128.5
128.3
66.4
f1 (ppm)

Product (**34**)

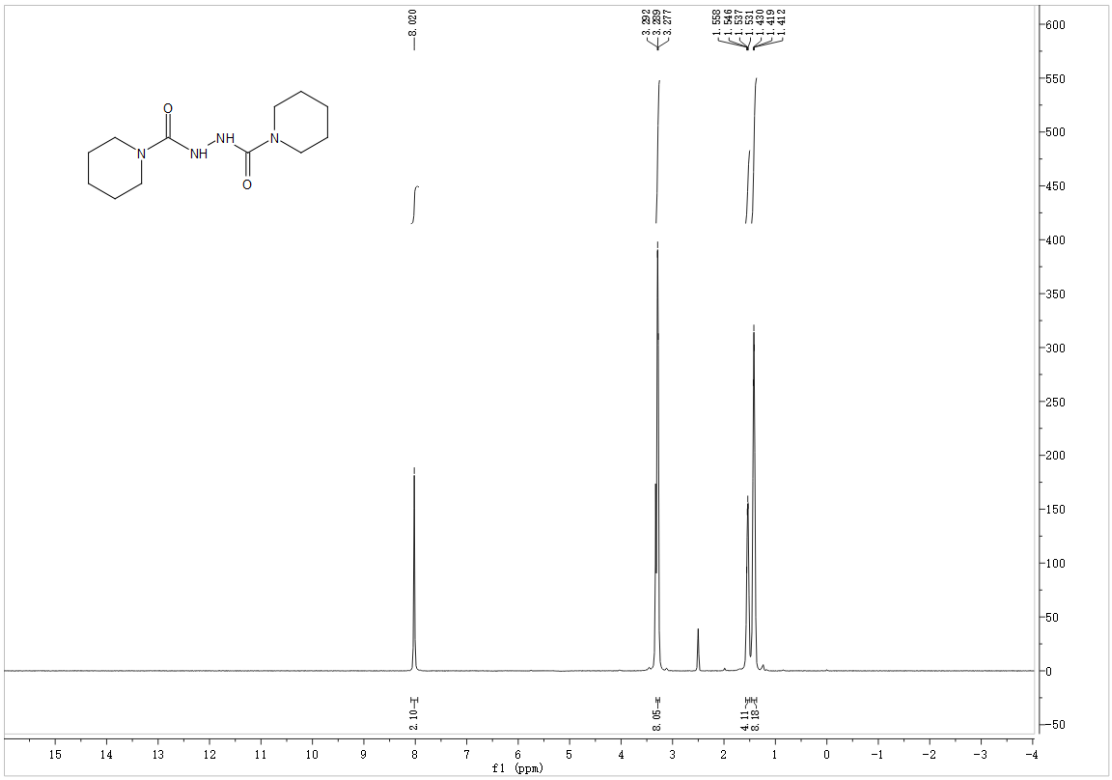


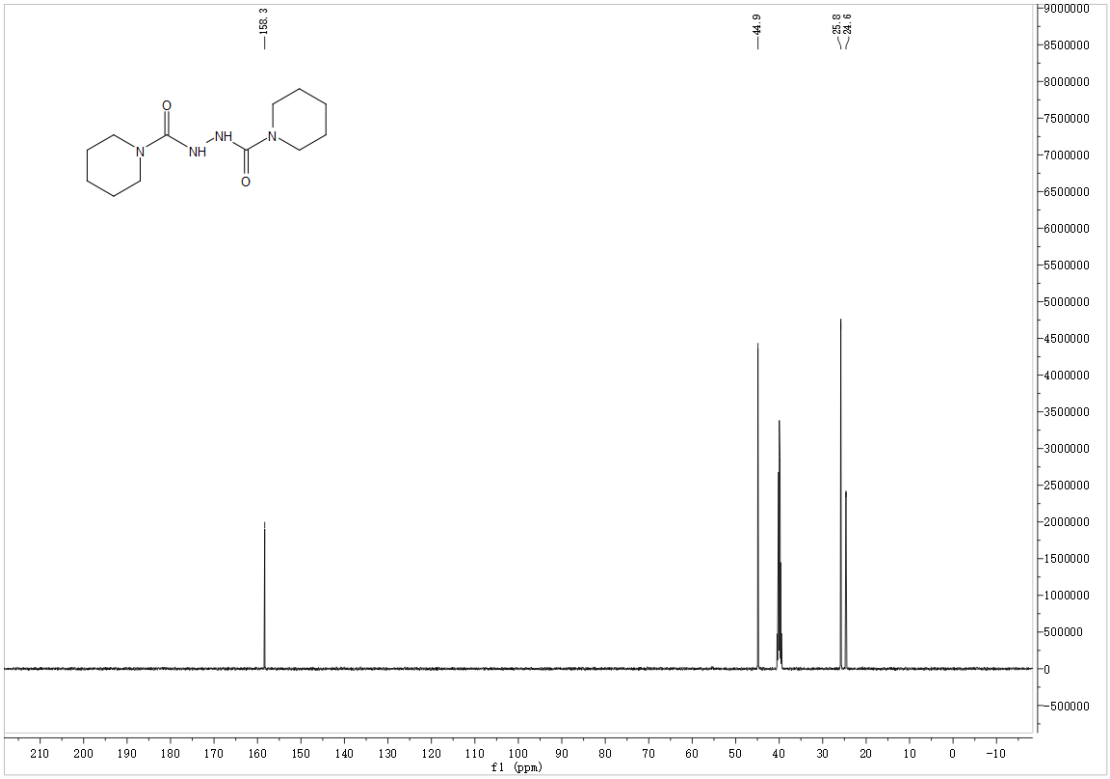


Product (**35**)

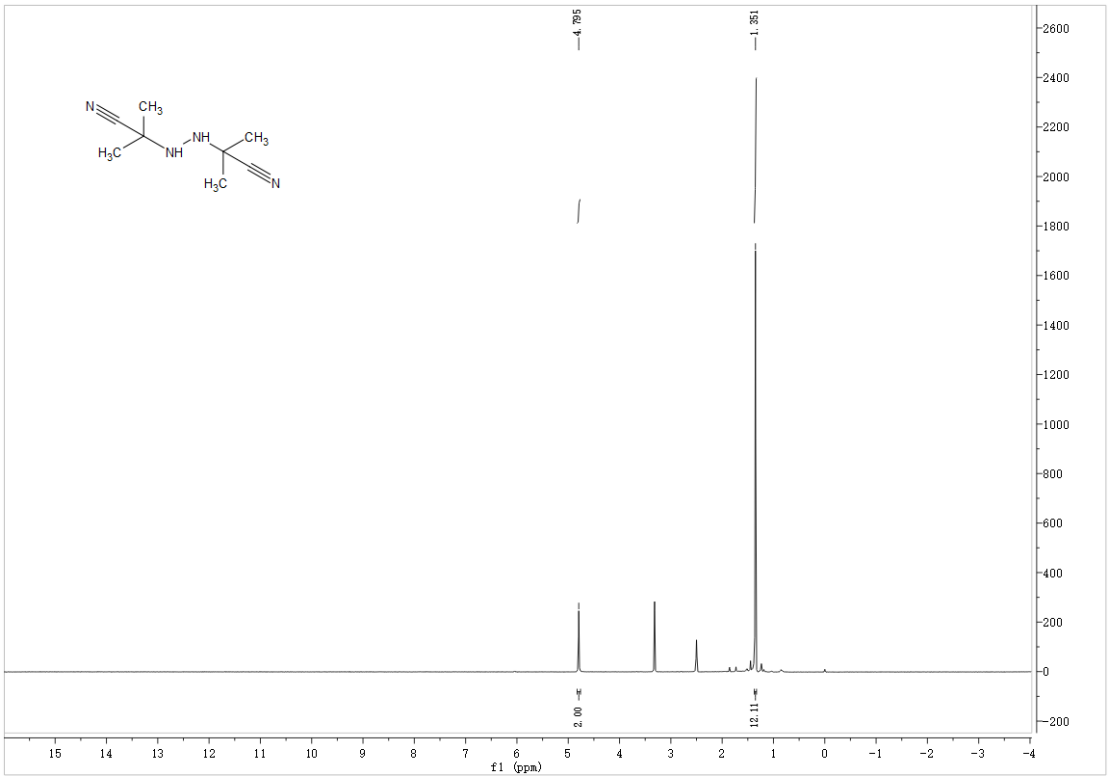


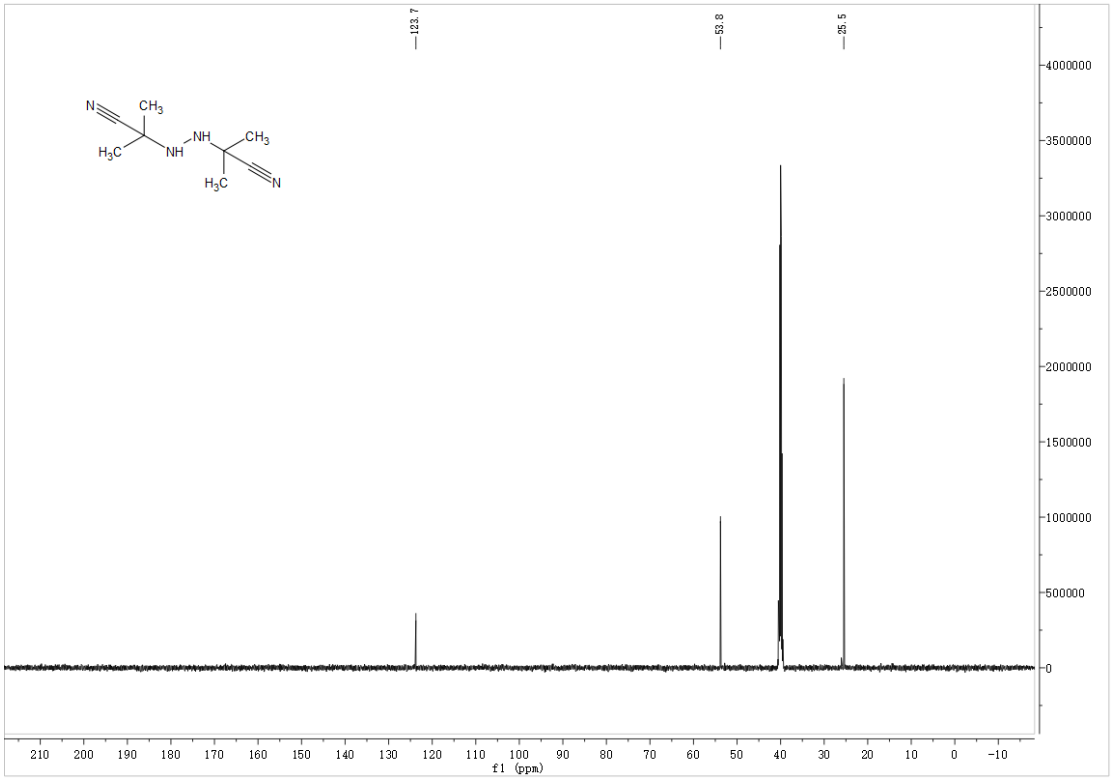
Product (**36**)


8.020
3.292
3.280
3.277
1.568
1.547
1.537
1.531
1.430
1.419
1.412
2.10
8.05
4.11
8.18
f1 (ppm)

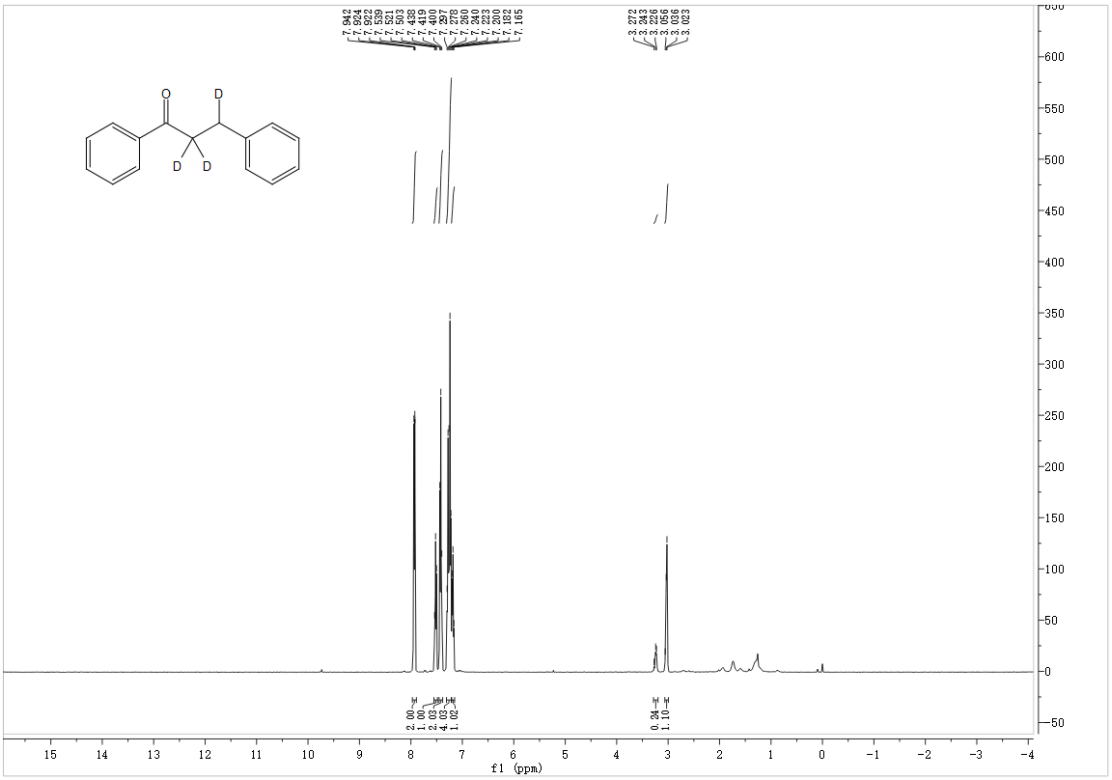

158.3
44.9
25.8
24.6
f1 (ppm)

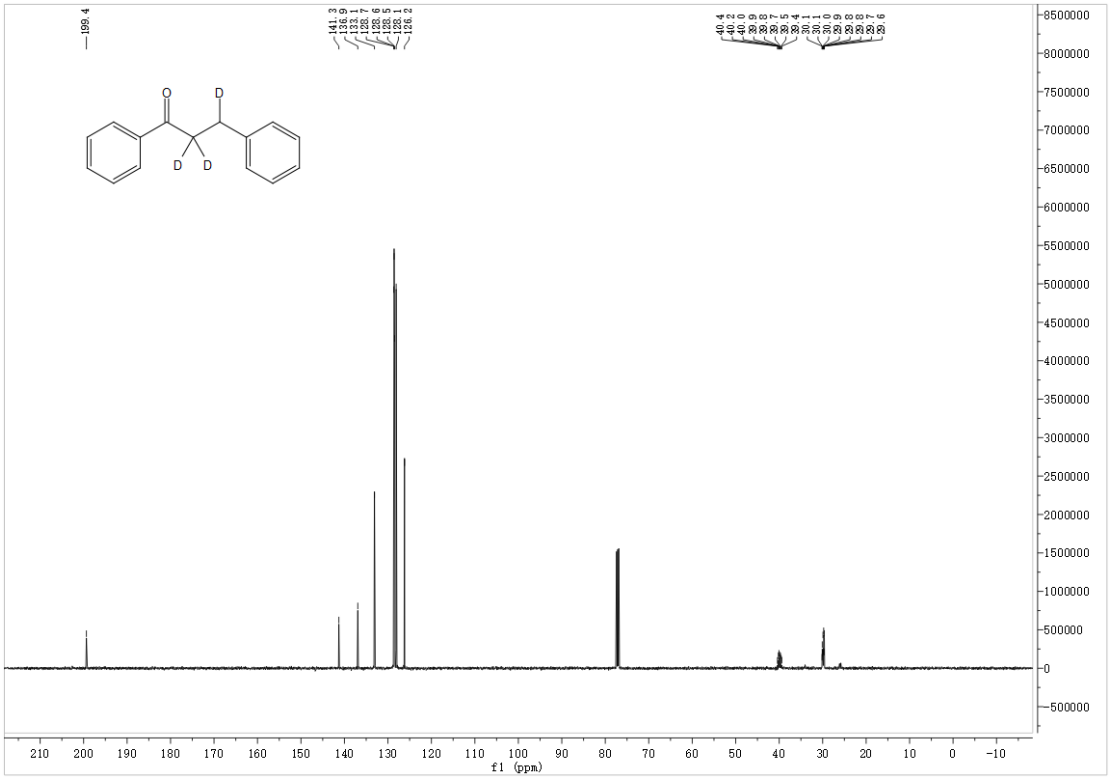
Product (**37**)



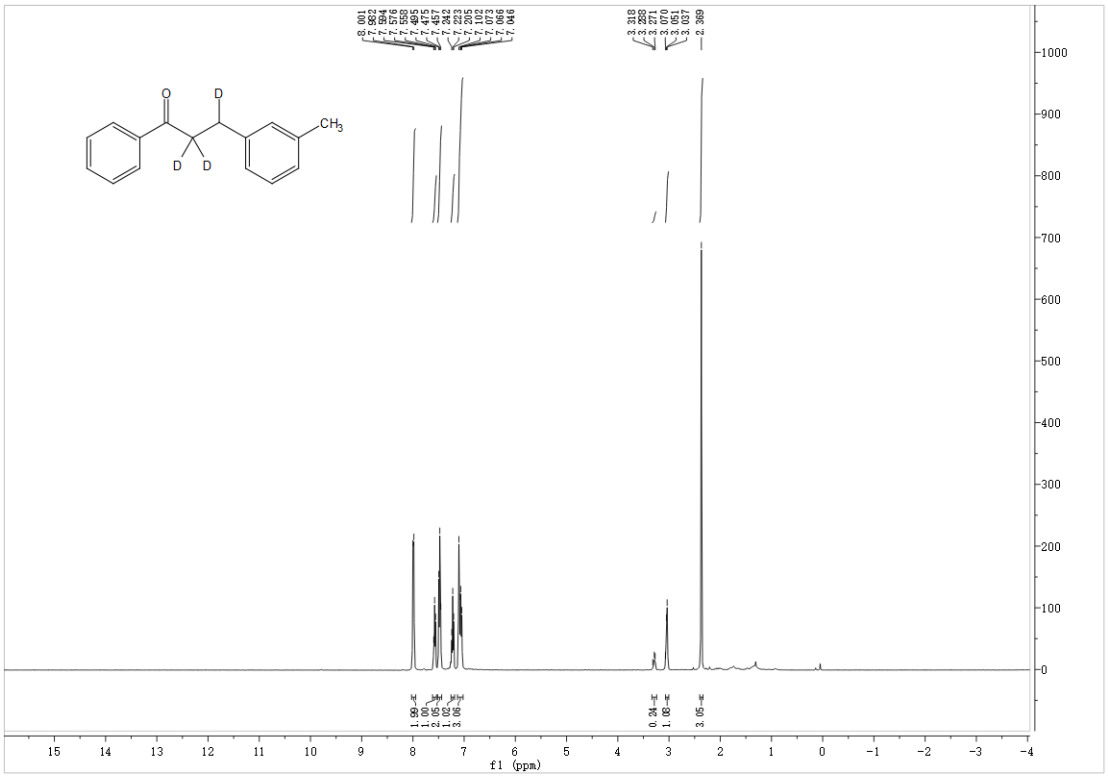


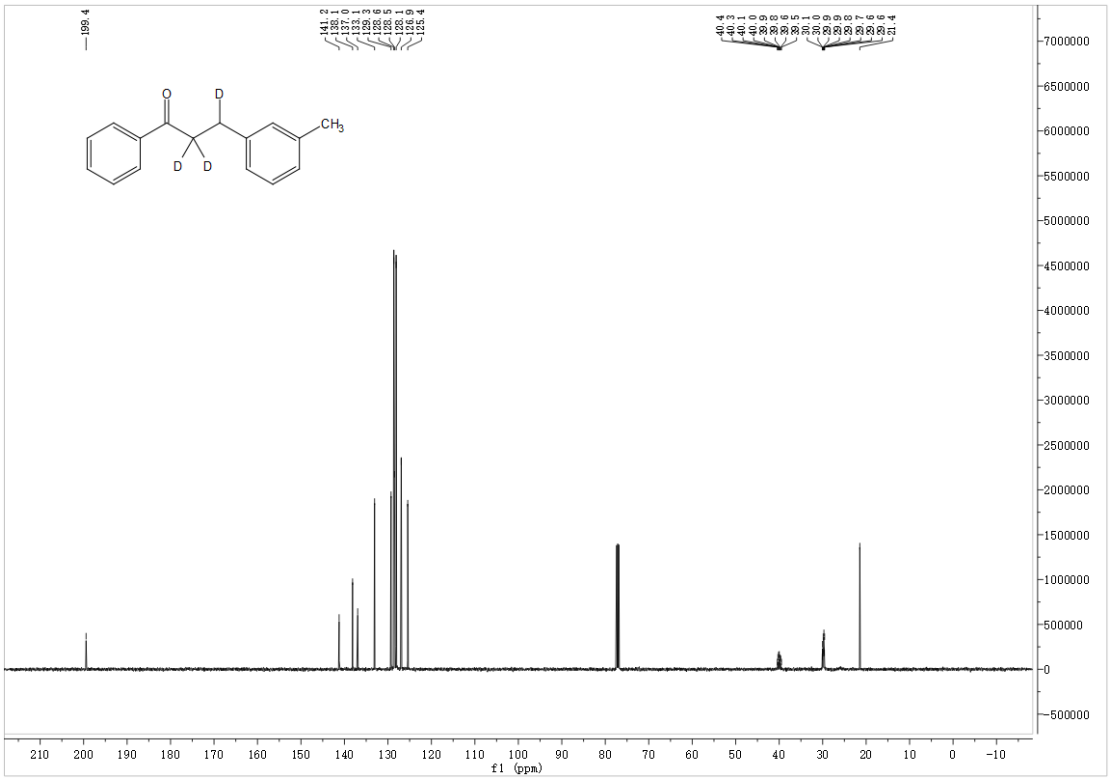
Product (**38**)


7.942
7.924
7.922
7.539
7.521
7.503
7.438
7.419
7.410
7.297
7.278
7.260
7.240
7.223
7.200
7.182
7.165
3.272
3.243
3.226
3.056
3.036
3.023
O
D
D
D
2.00
1.00
1.03
4.11
1.02
0.24
1.10
f1 (ppm)

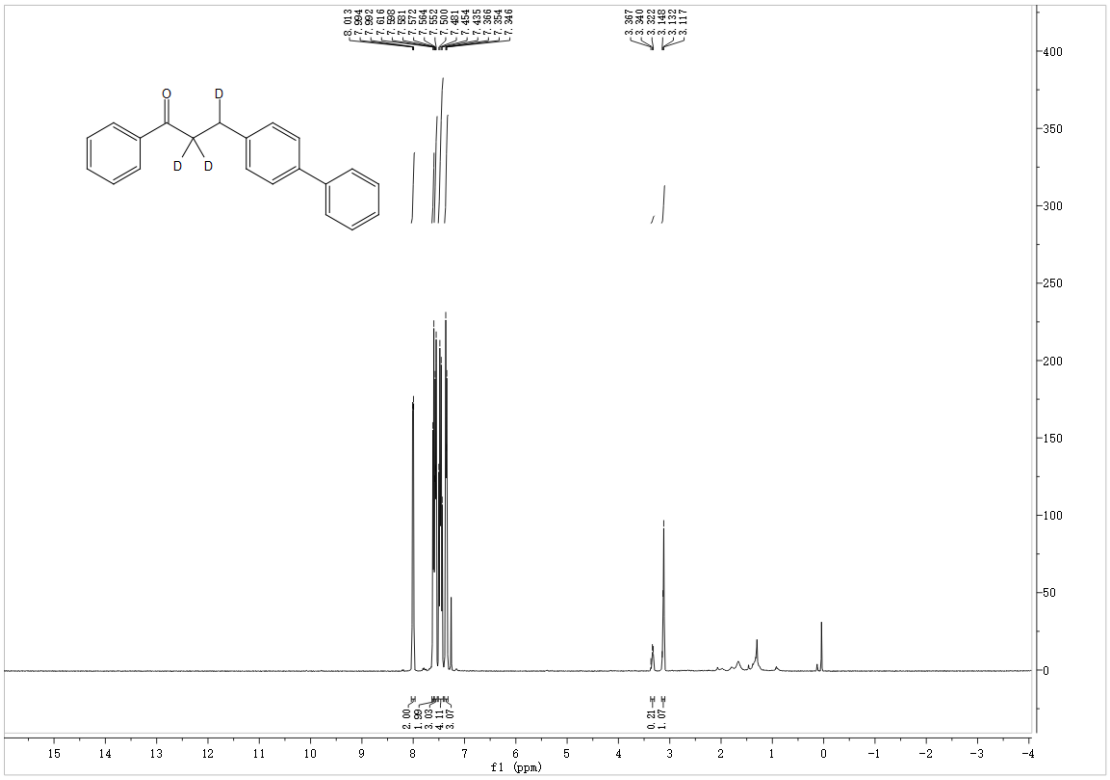

199.4
141.3
136.9
133.1
128.7
128.6
128.5
128.1
126.2
40.4
40.2
40.0
39.9
39.8
39.7
39.5
39.4
30.1
30.0
29.9
29.8
29.7
29.6
O
D
D
D
f1 (ppm)

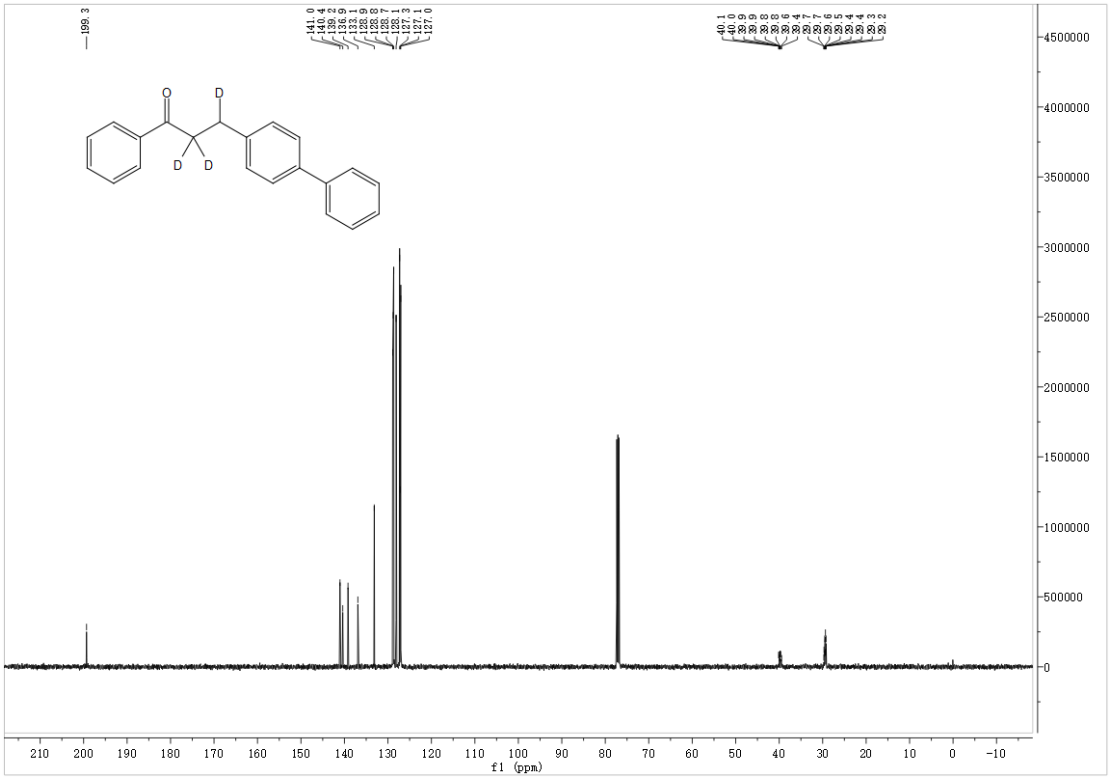
Product (**39**)


8.001
7.982
7.894
7.576
7.558
7.485
7.475
7.457
7.232
7.223
7.205
7.102
7.073
7.069
7.046
3.318
3.303
3.271
3.070
3.051
3.037
2.389
O
D
D
D
CH3
1.99
1.00
2.05
1.57
3.06
0.24
1.08
3.05
f1 (ppm)

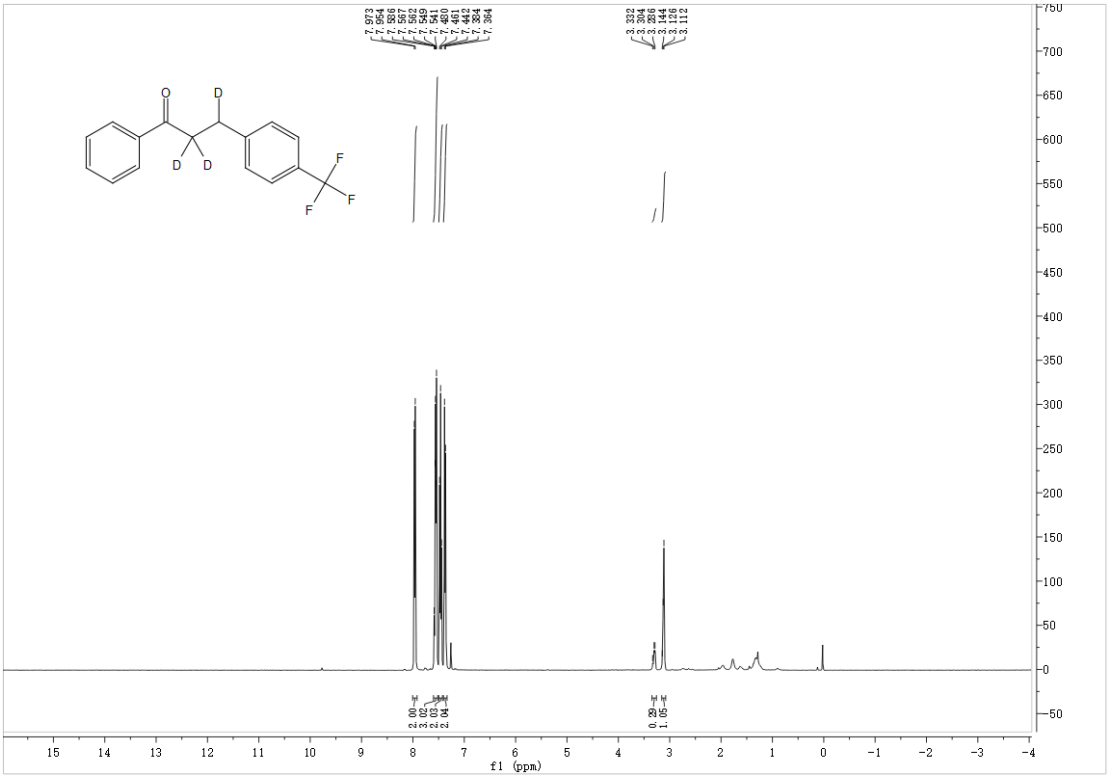

199.4
141.2
138.1
137.0
133.1
129.3
128.5
128.5
128.1
126.9
125.4
40.4
40.3
40.1
40.0
39.9
39.8
39.6
39.5
30.1
30.0
29.9
29.9
29.8
29.7
29.6
29.6
21.4
O
D
D
D
CH3
f1 (ppm)

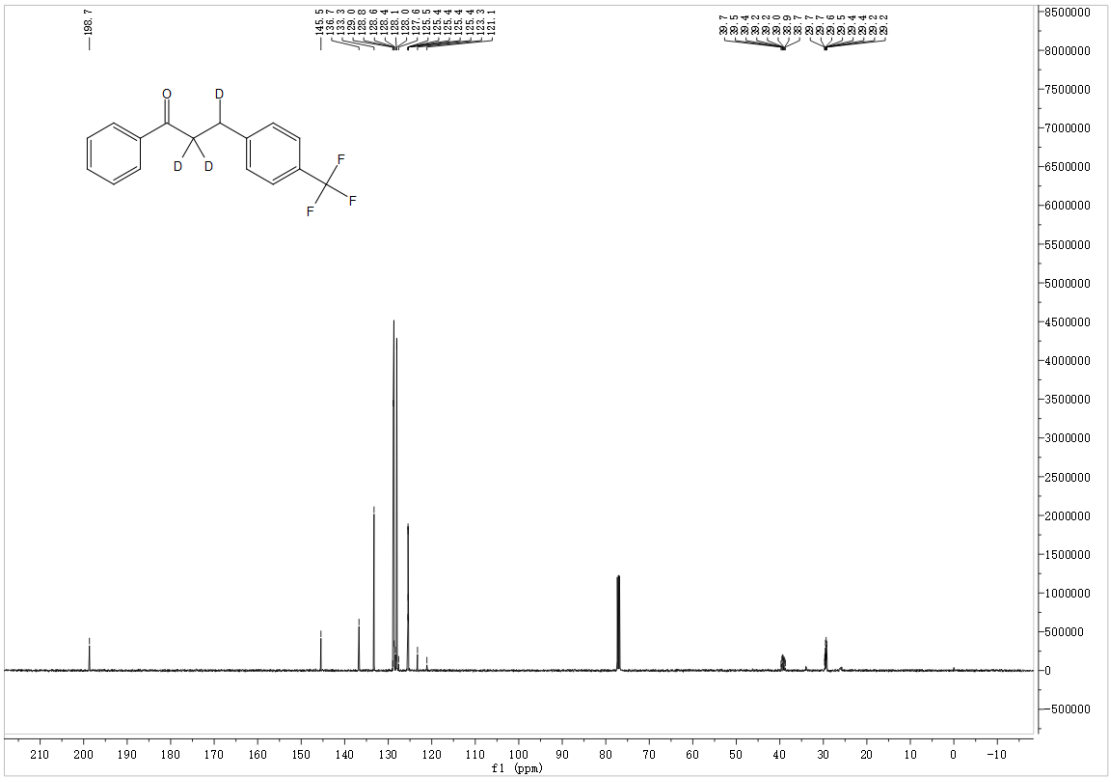
Product (**40**)

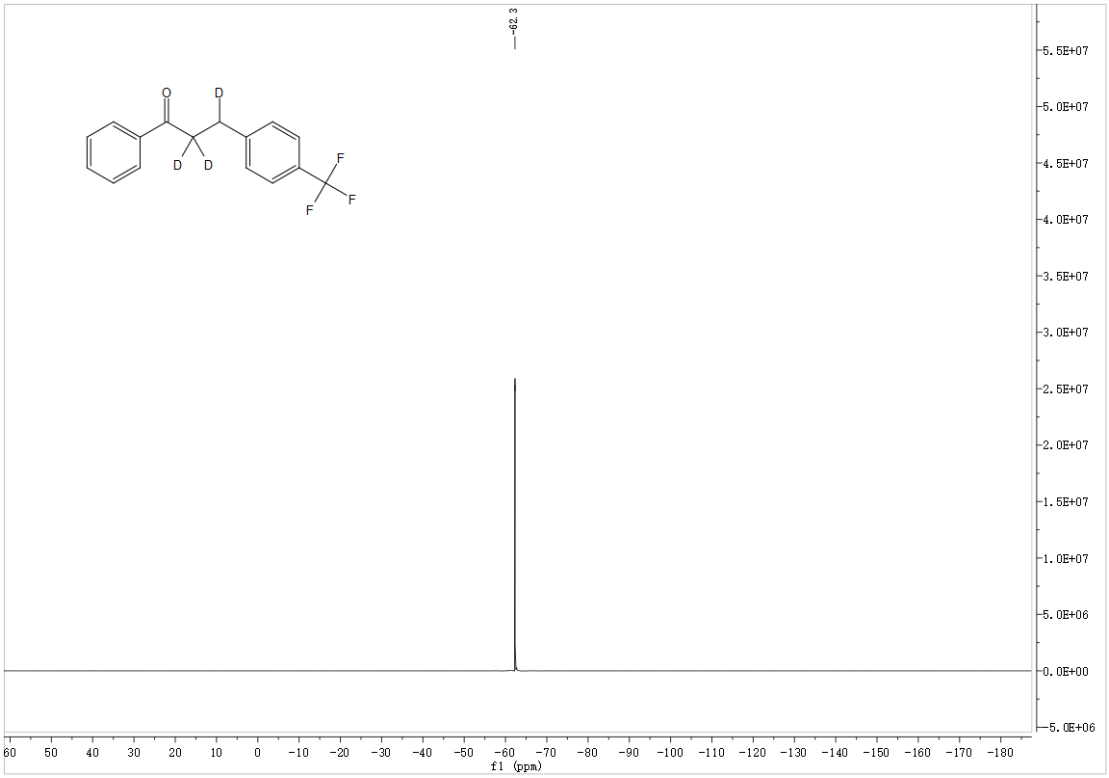




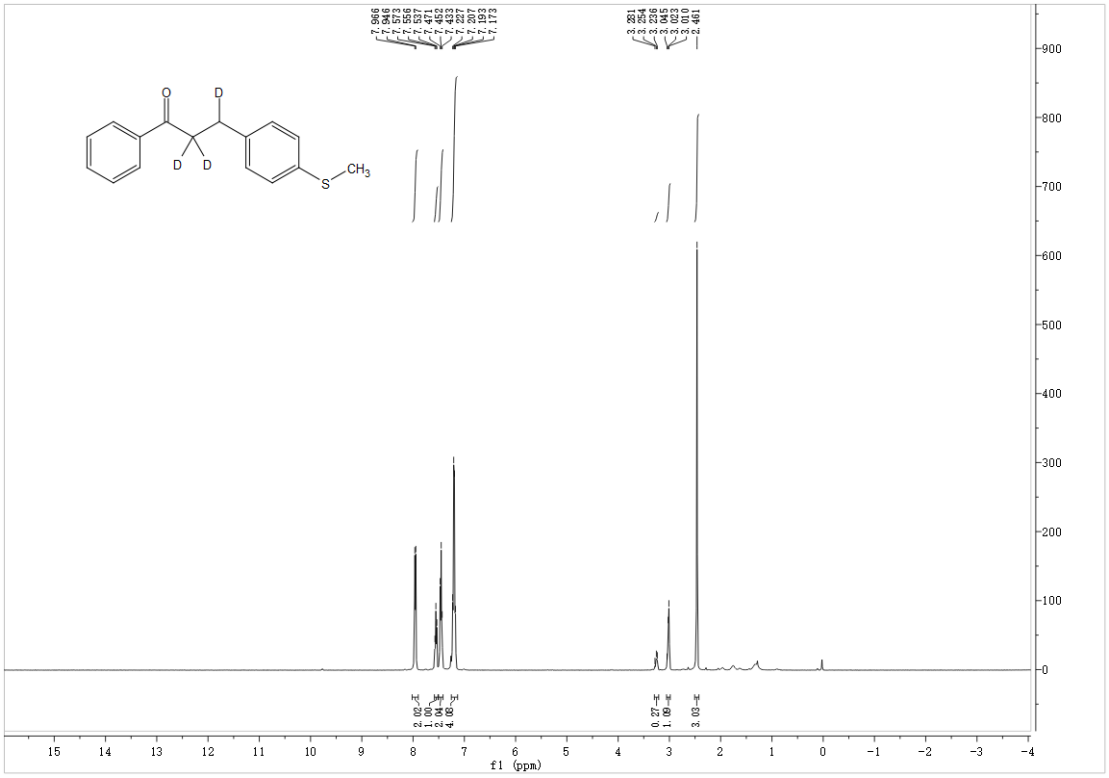
Product (**41**)

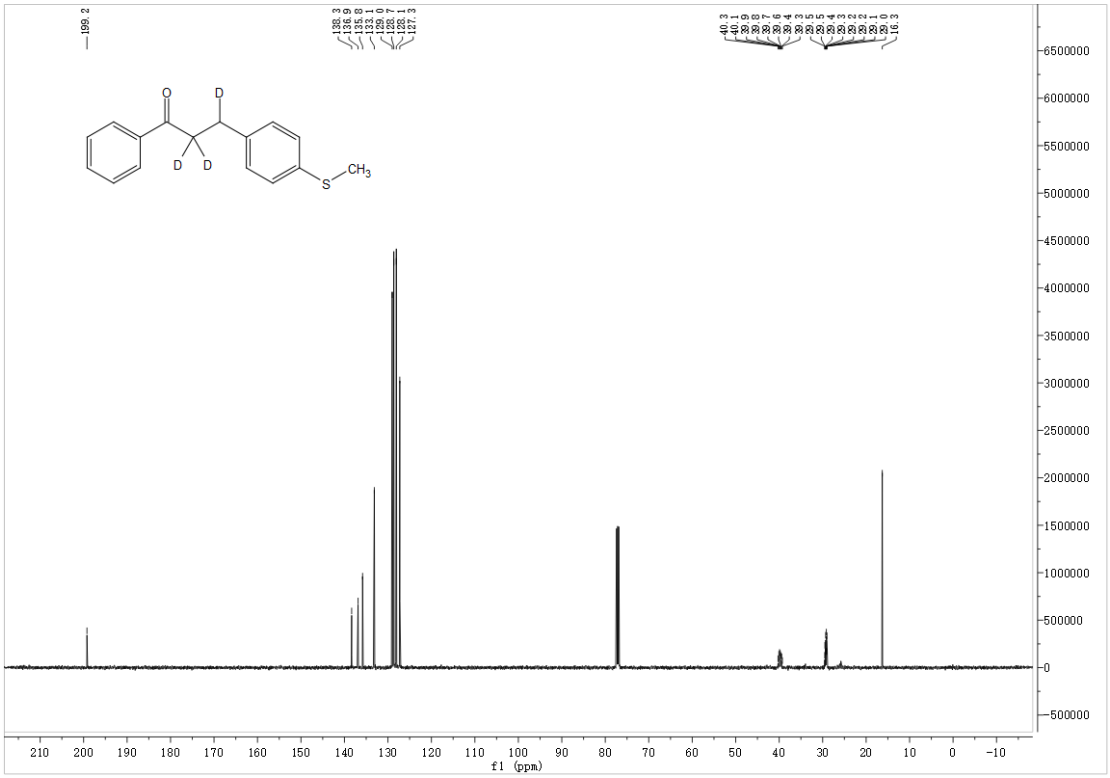

7.973
7.964
7.955
7.567
7.562
7.549
7.541
7.461
7.442
7.384
7.364
3.332
3.304
3.285
3.144
3.125
3.112
O
D
D
D
F
F
F
2.00
2.02
2.03
2.04
0.29
1.05
f1 (ppm)


198.7
145.5
136.7
133.3
129.0
128.8
128.6
128.4
128.1
127.6
127.0
125.5
125.4
125.4
125.4
125.4
123.3
121.1
30.7
30.5
30.4
30.2
30.0
29.9
29.7
29.7
29.6
29.5
29.4
29.2
29.2
O
D
D
D
F
F
F
f1 (ppm)

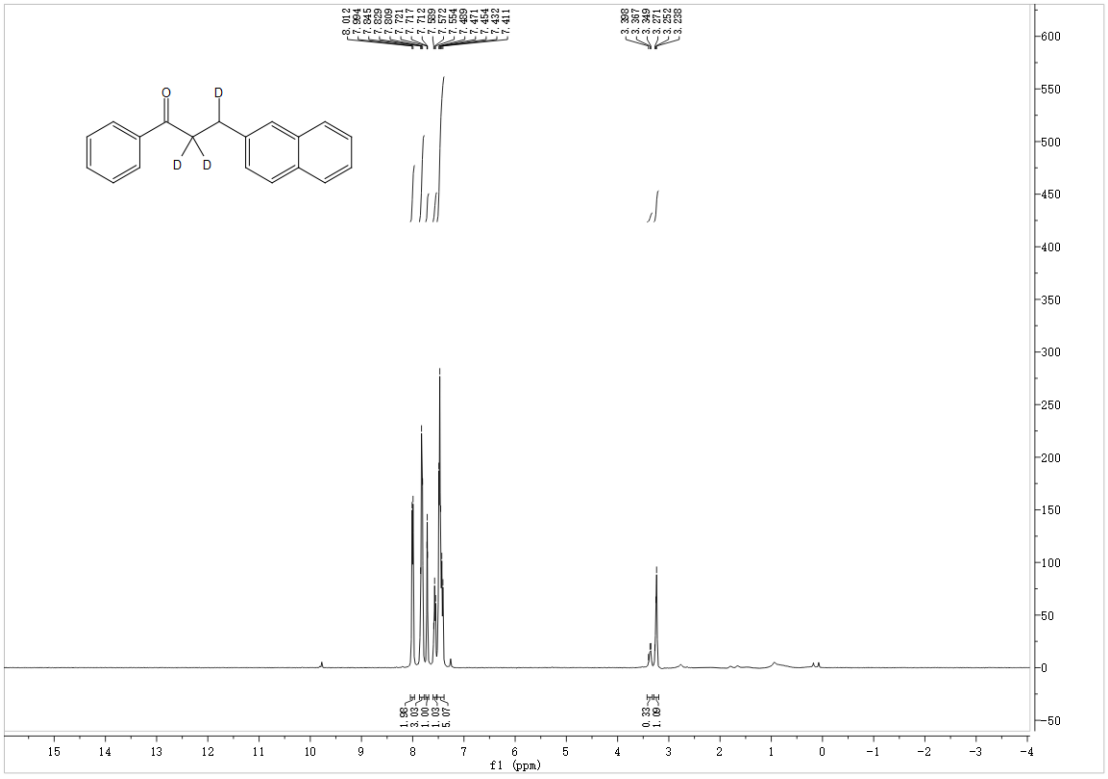

-62.3
O
D
D
D
F
F
F
f1 (ppm)

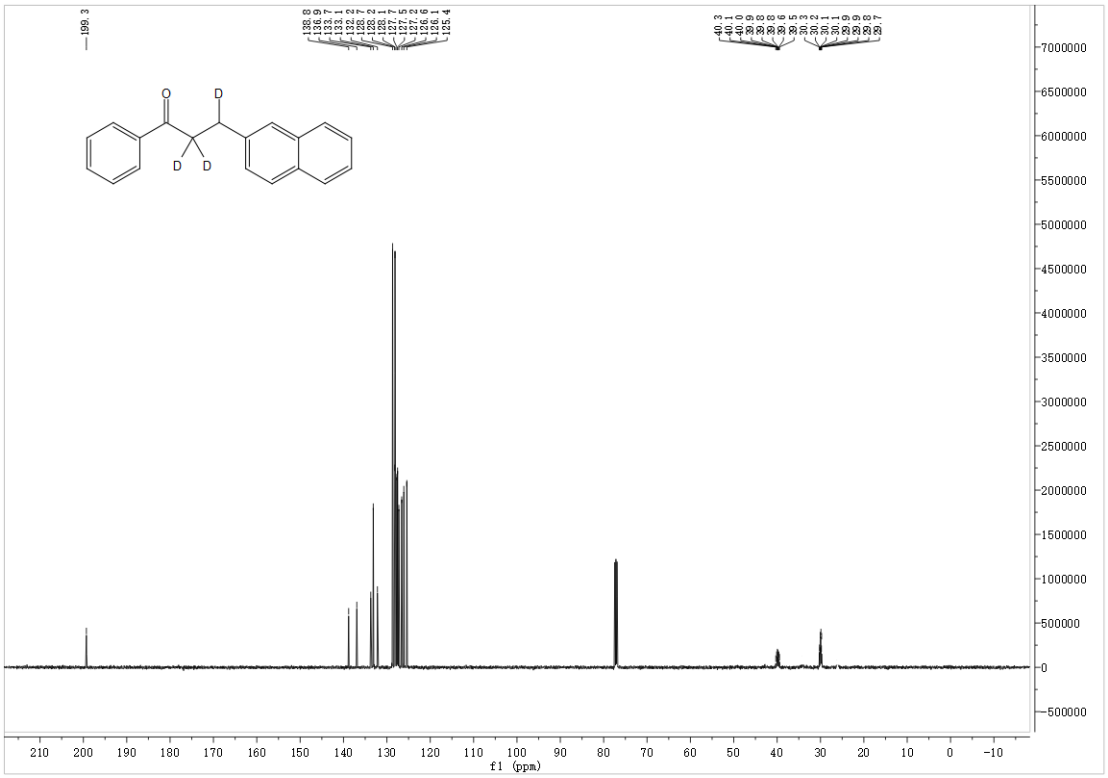
Product (**42**)


7.966
7.946
7.573
7.555
7.537
7.471
7.452
7.433
7.227
7.207
7.193
7.173
3.281
3.265
3.236
3.045
3.023
3.010
2.461
O
D
D
D
S
CH3
2.02
2.00
1.04
4.00
0.27
1.09
3.03
f1 (ppm)

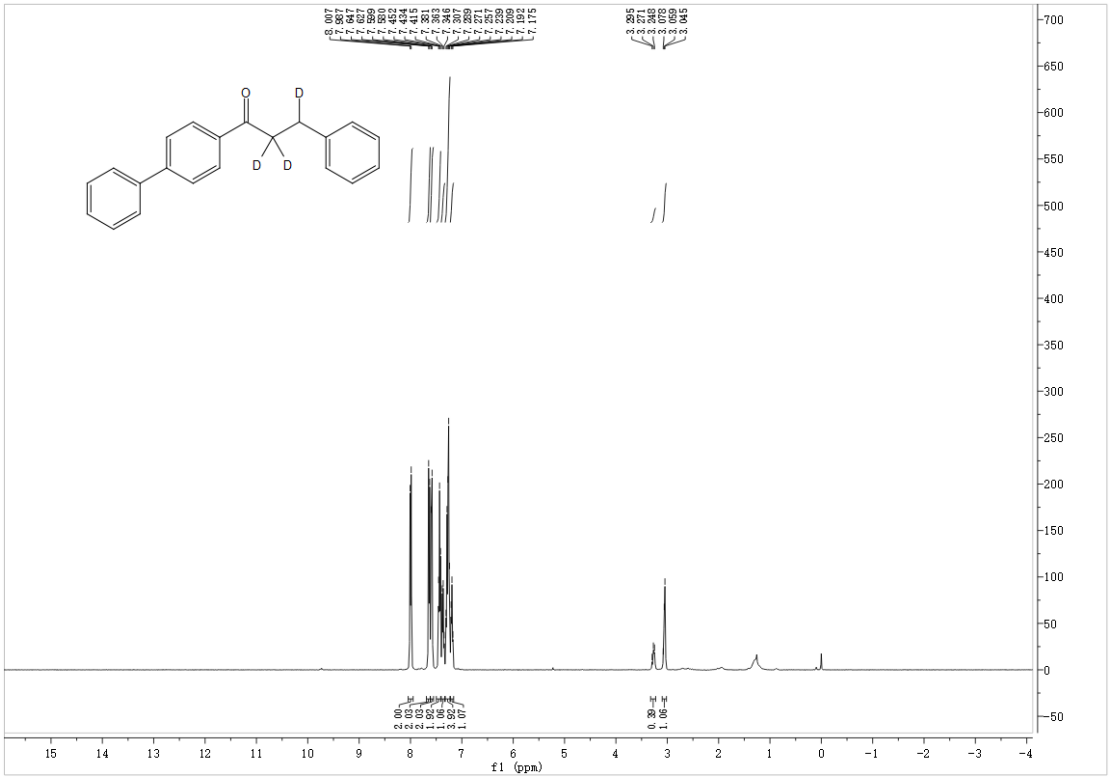

199.2
138.3
136.9
135.8
133.1
129.0
128.7
128.1
127.3
40.3
40.1
39.9
39.8
39.7
39.6
39.4
39.3
29.5
29.4
29.3
29.2
29.1
29.0
16.3
O
D
D
D
S
CH3
f1 (ppm)

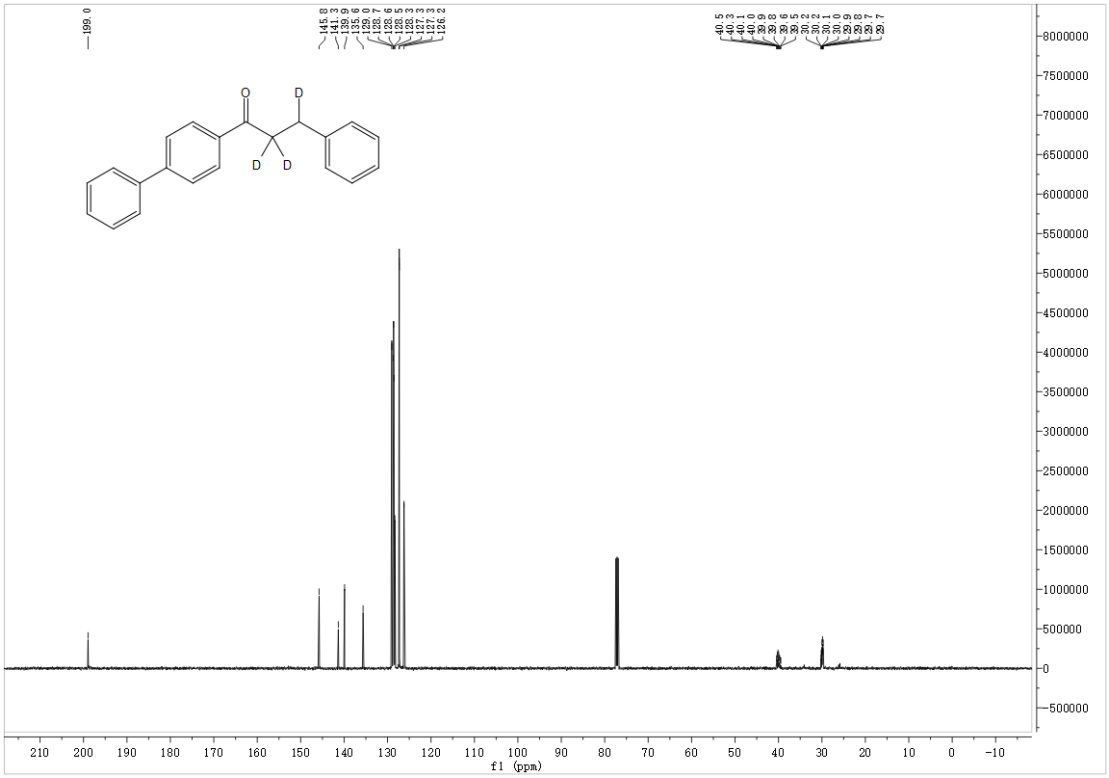
Product (**43**)


8.012
7.994
7.845
7.829
7.721
7.717
7.712
7.588
7.572
7.564
7.489
7.471
7.454
7.432
7.411
3.398
3.387
3.349
3.271
3.252
3.238
1.96
3.03
1.00
1.03
5.07
0.33
1.89
O
D
D
D
f1 (ppm)

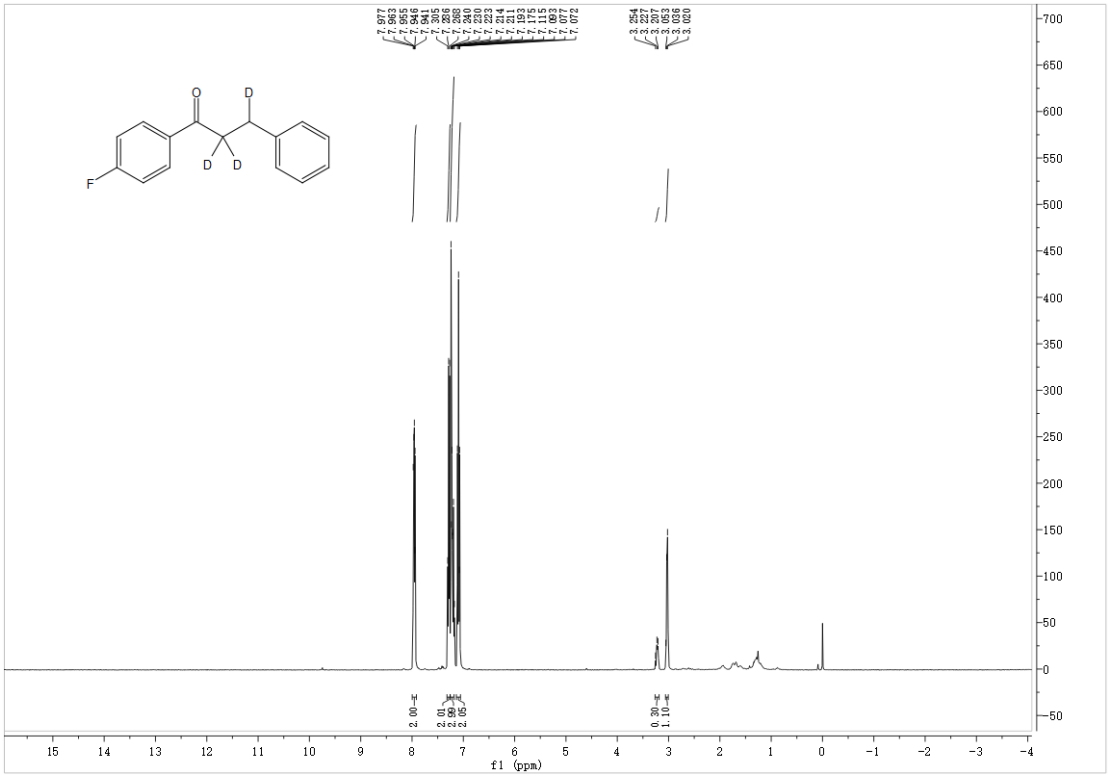


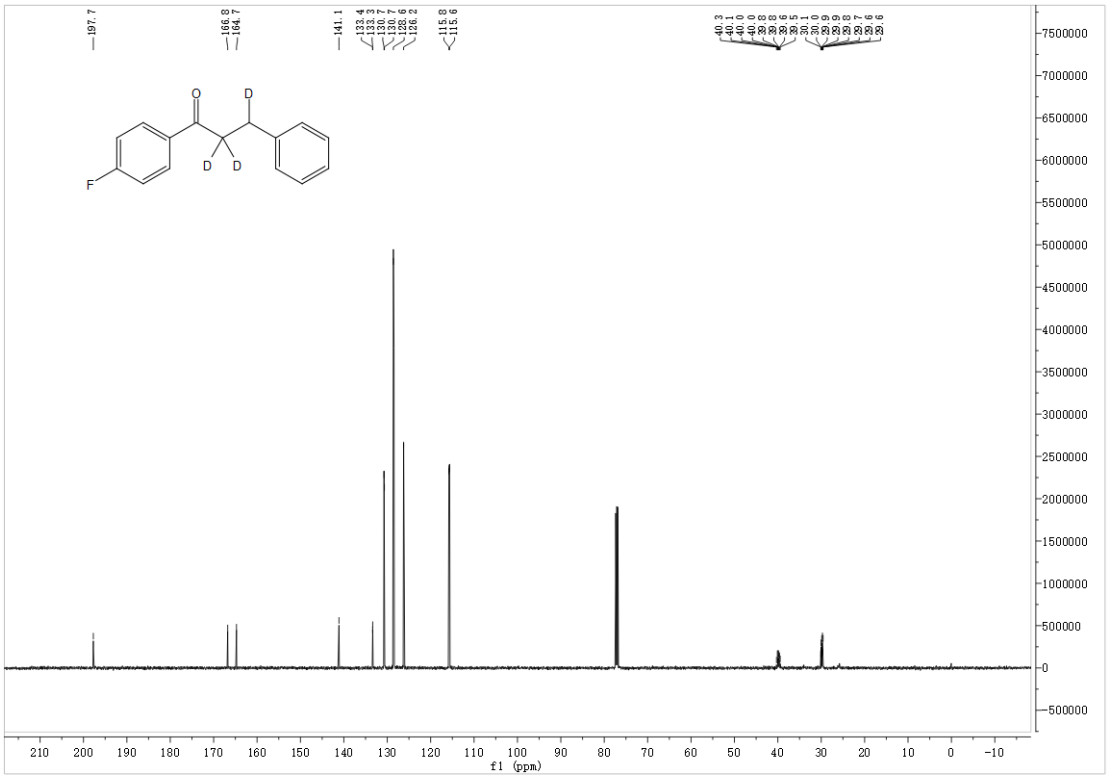
Product (**44**)





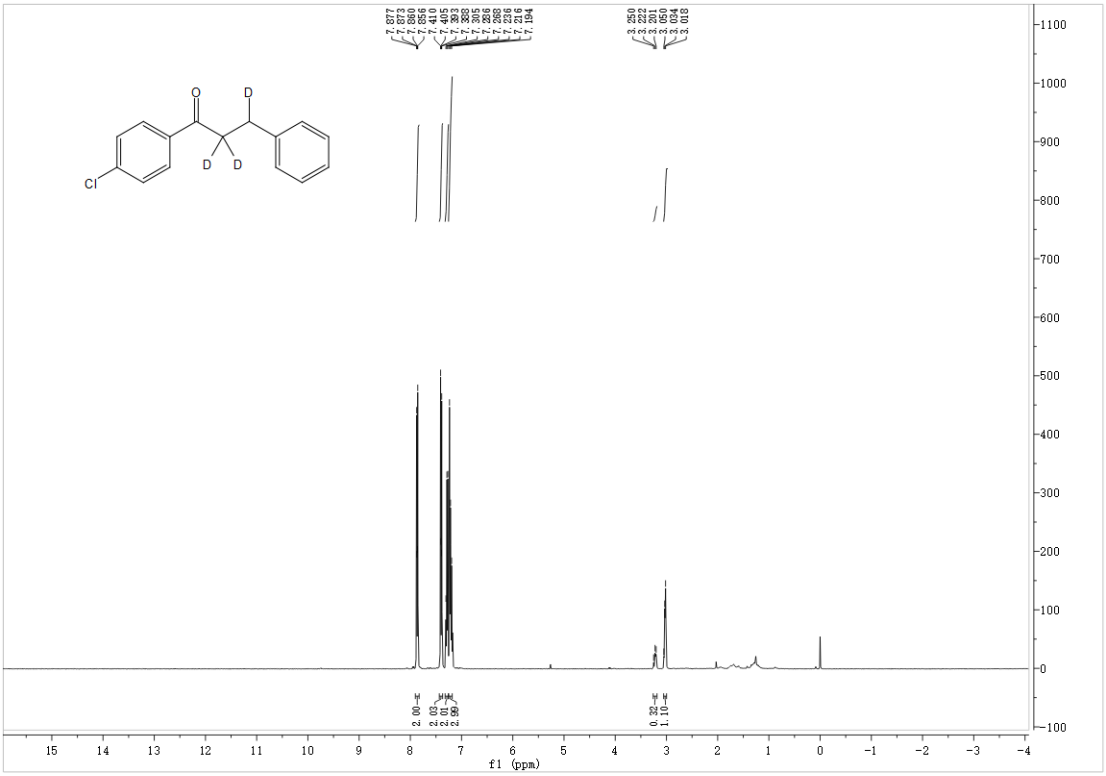
Product (**45**)

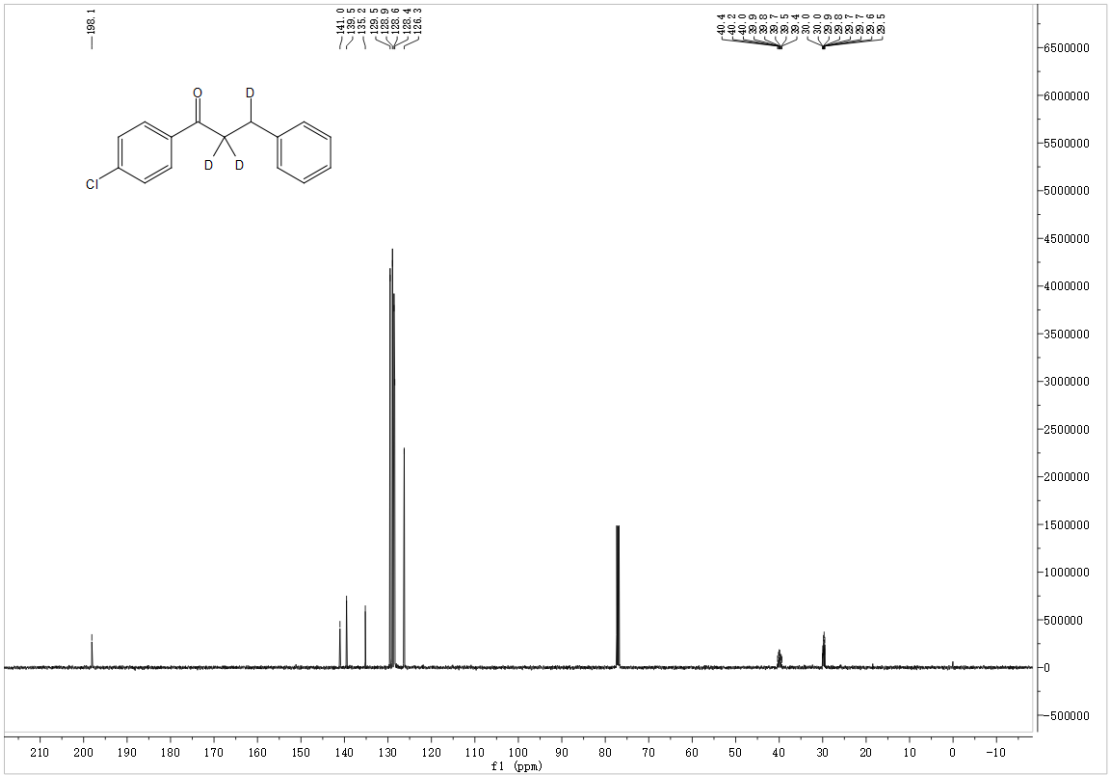



197.7
166.8
164.7
141.1
133.4
133.3
130.7
130.7
128.6
126.2
115.8
115.6
O
D
D
D
F
f1 (ppm)

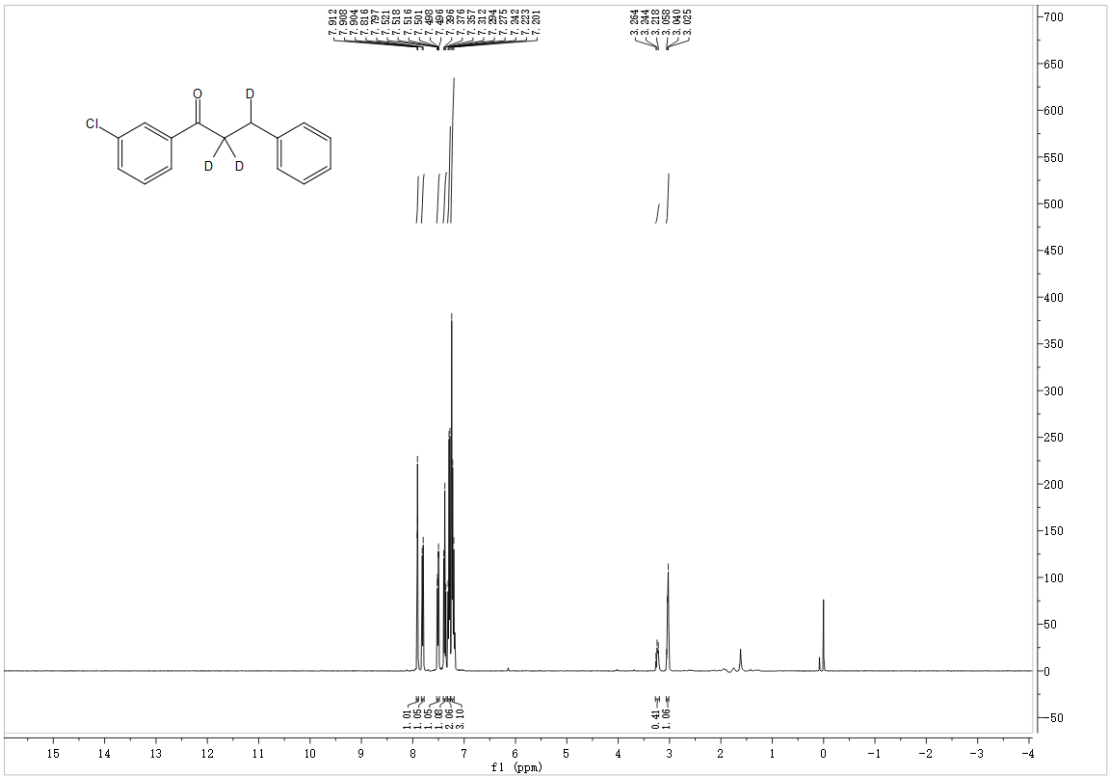

-105.2
O
D
D
D
F
f1 (ppm)

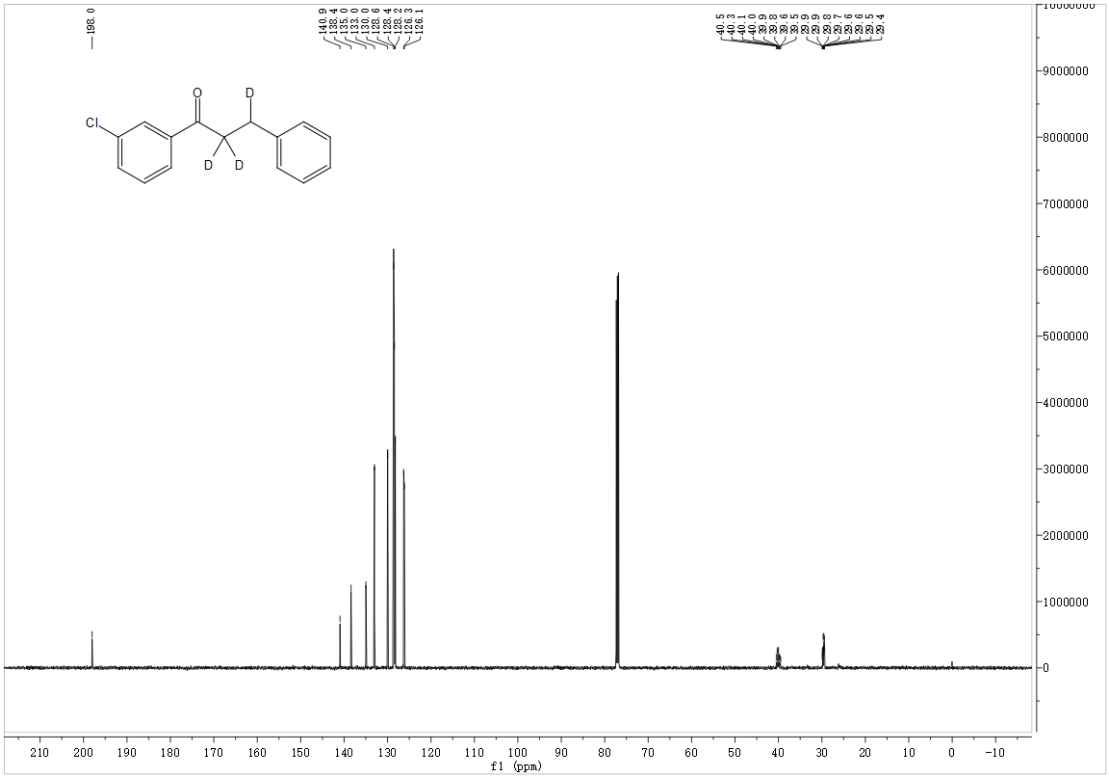
Product (**46**)



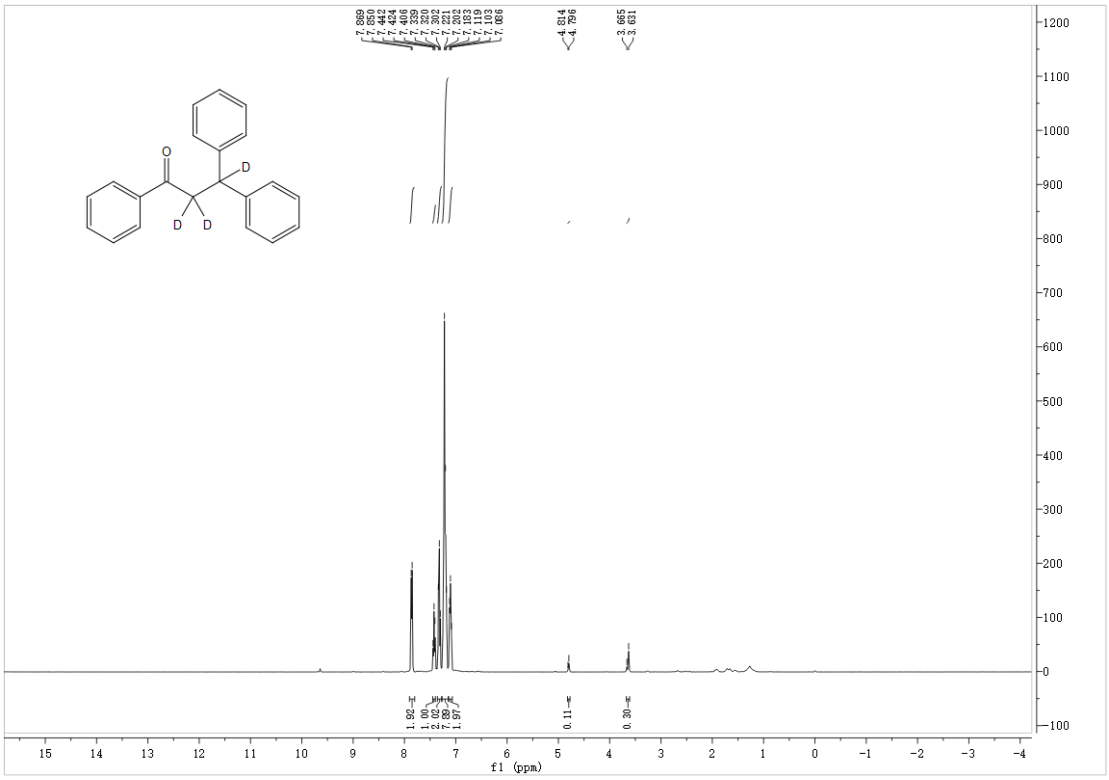


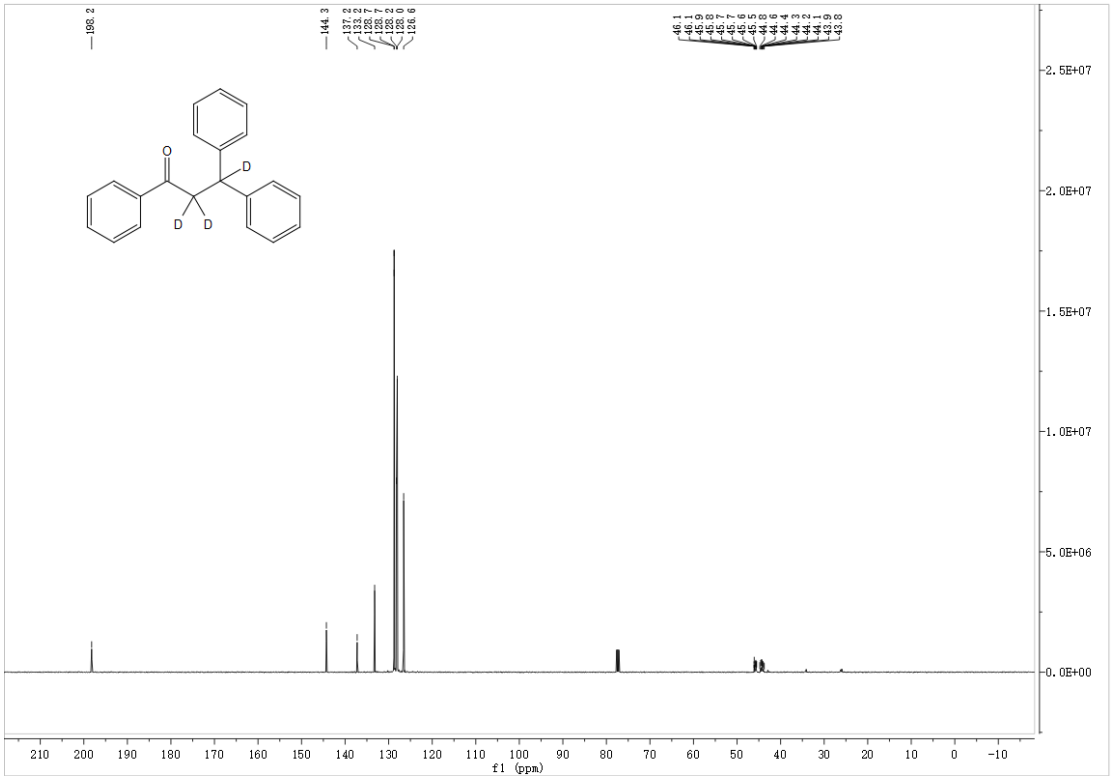
Product (**47**)



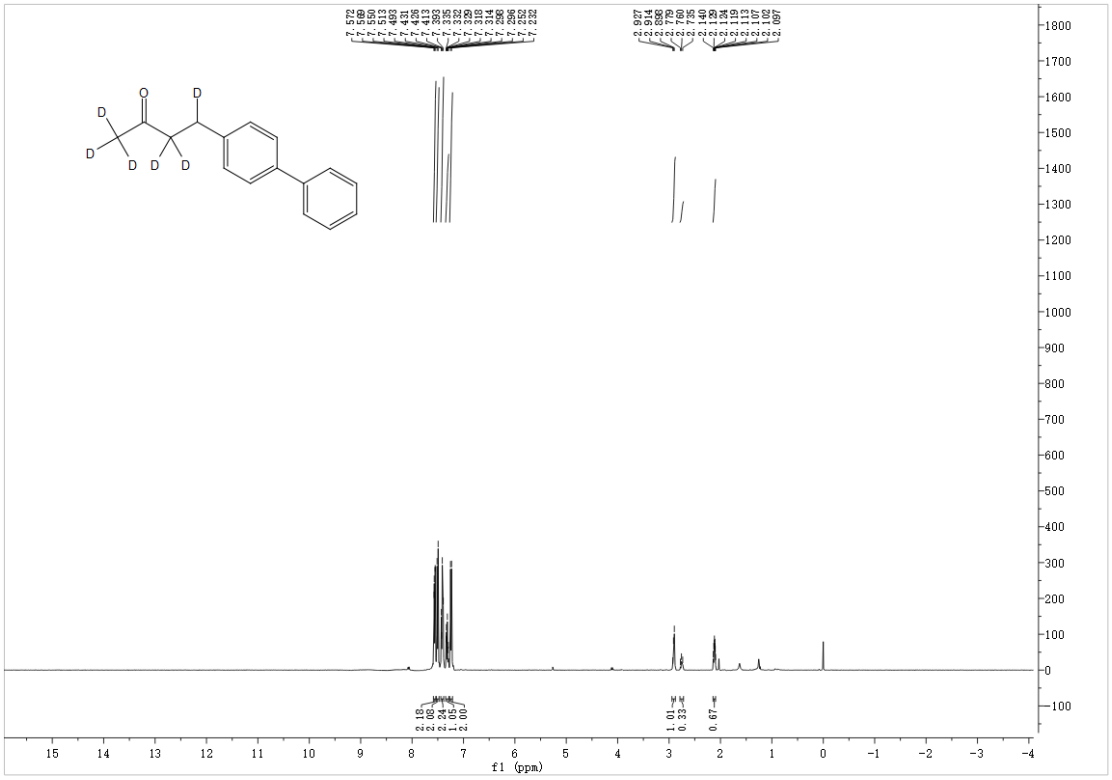


Product (**48**)

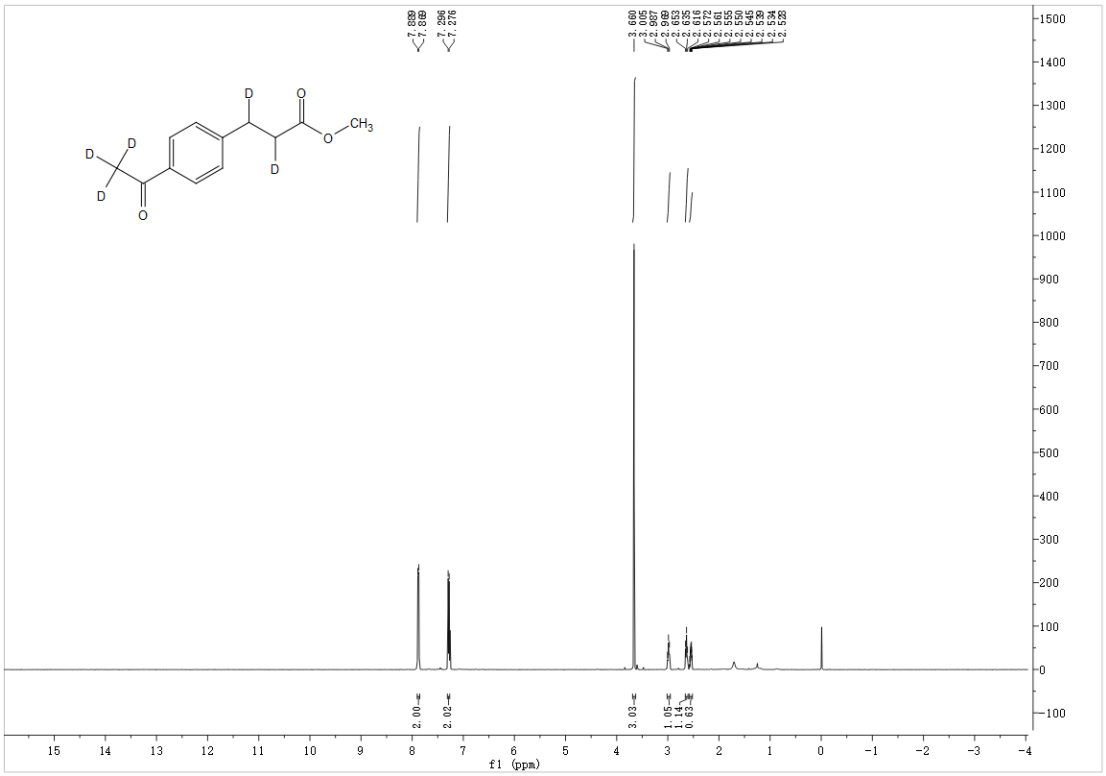


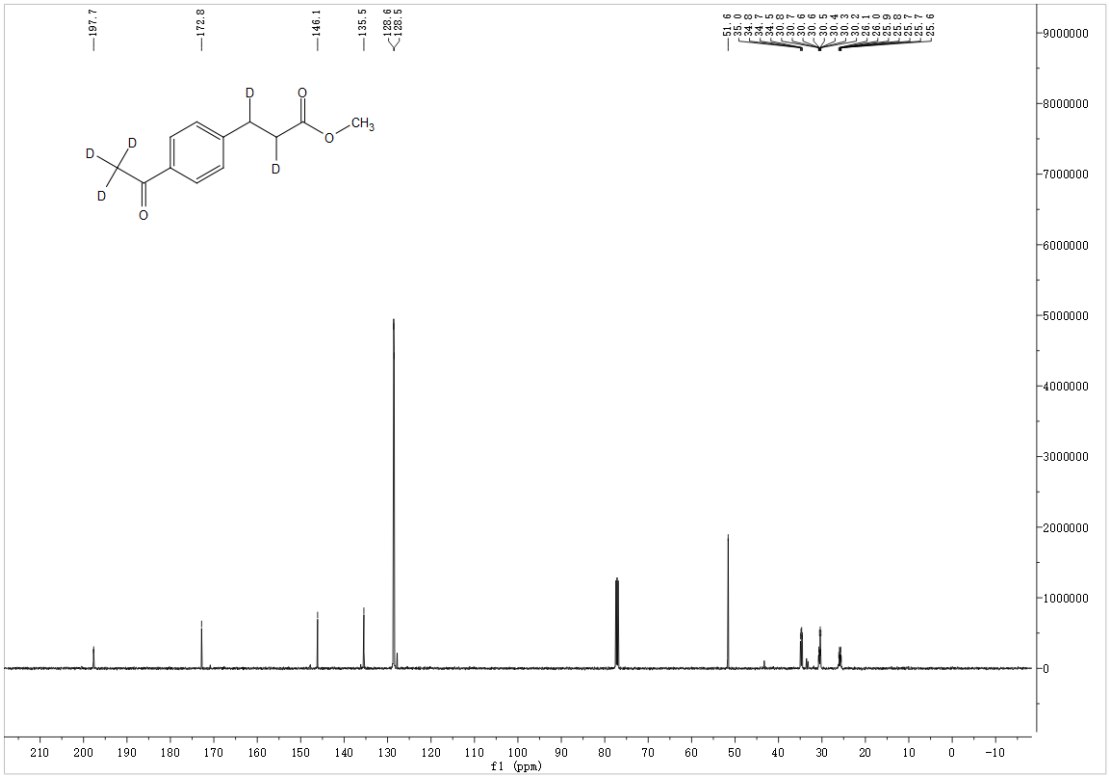


Product (**49**)

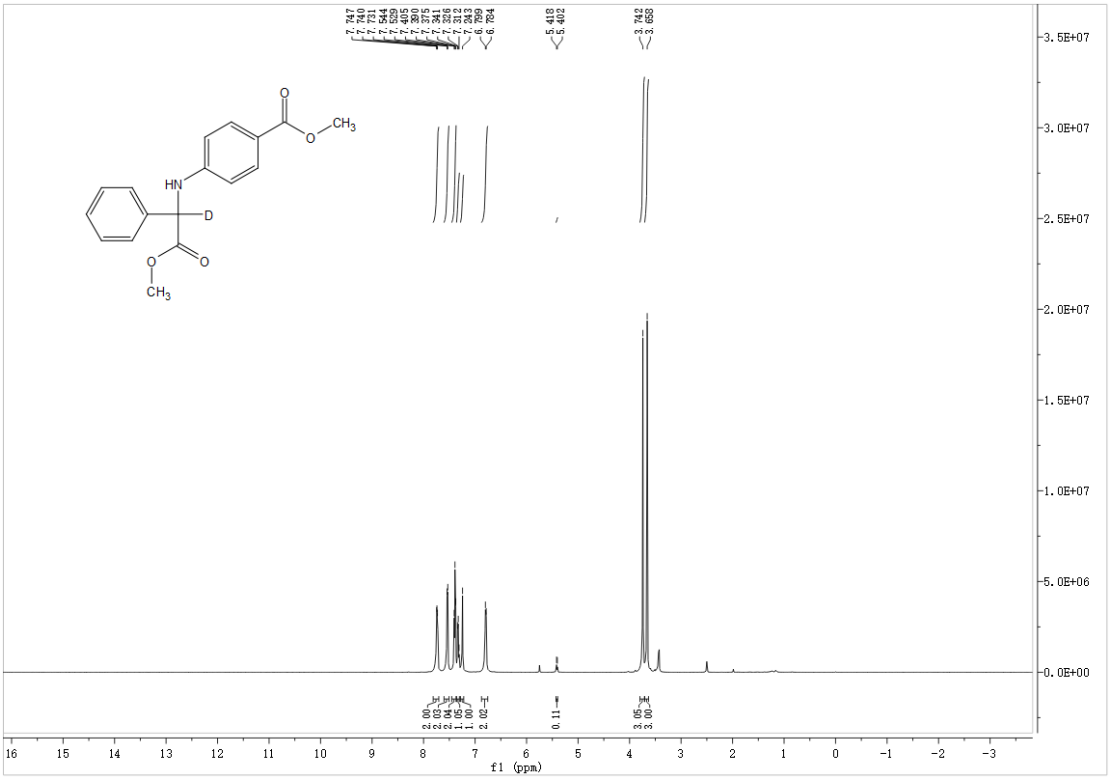


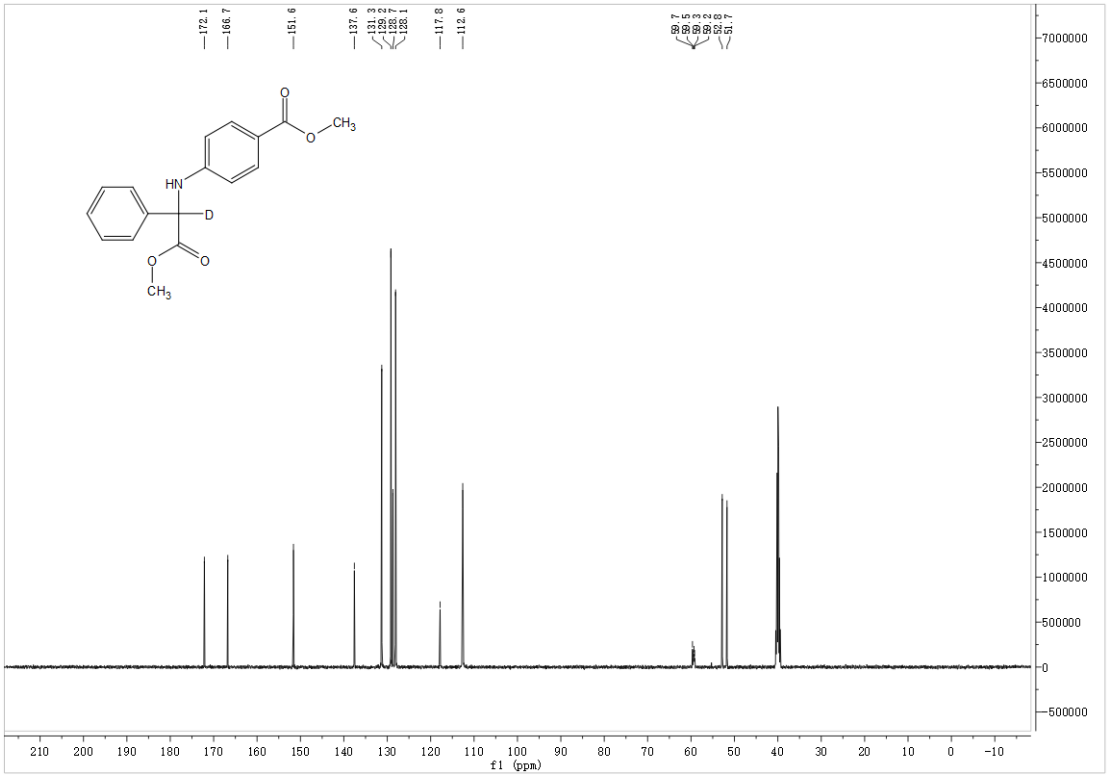
Product (**50**)


7.889
7.880
7.296
7.276
3.660
3.655
3.007
2.999
2.653
2.635
2.610
2.572
2.561
2.555
2.550
2.545
2.539
2.534
2.520
D
O
CH3
D
D
D
D
O
2.00
2.02
3.03
1.05
1.14
0.63
f1 (ppm)

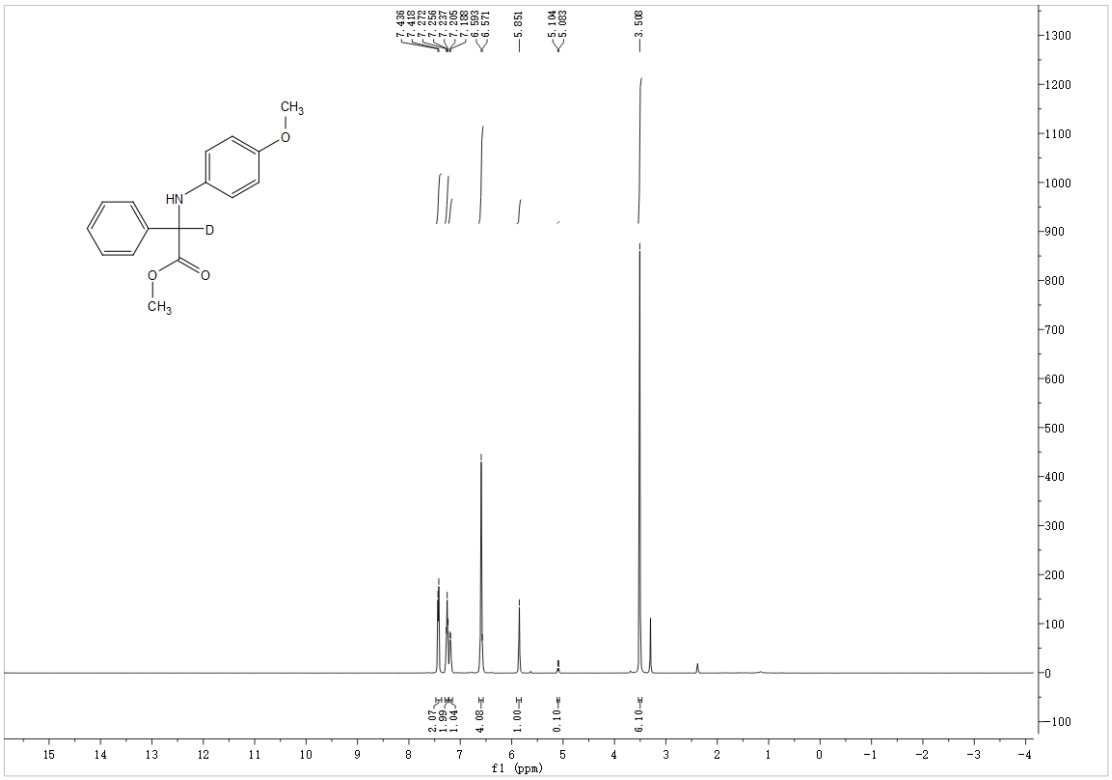

197.7
172.8
146.1
135.5
128.6
128.5
51.6
35.0
34.8
34.7
34.5
30.8
30.7
30.6
30.5
30.4
30.3
30.2
30.1
26.0
25.9
25.8
25.7
25.6
D
O
CH3
D
D
D
D
O
f1 (ppm)

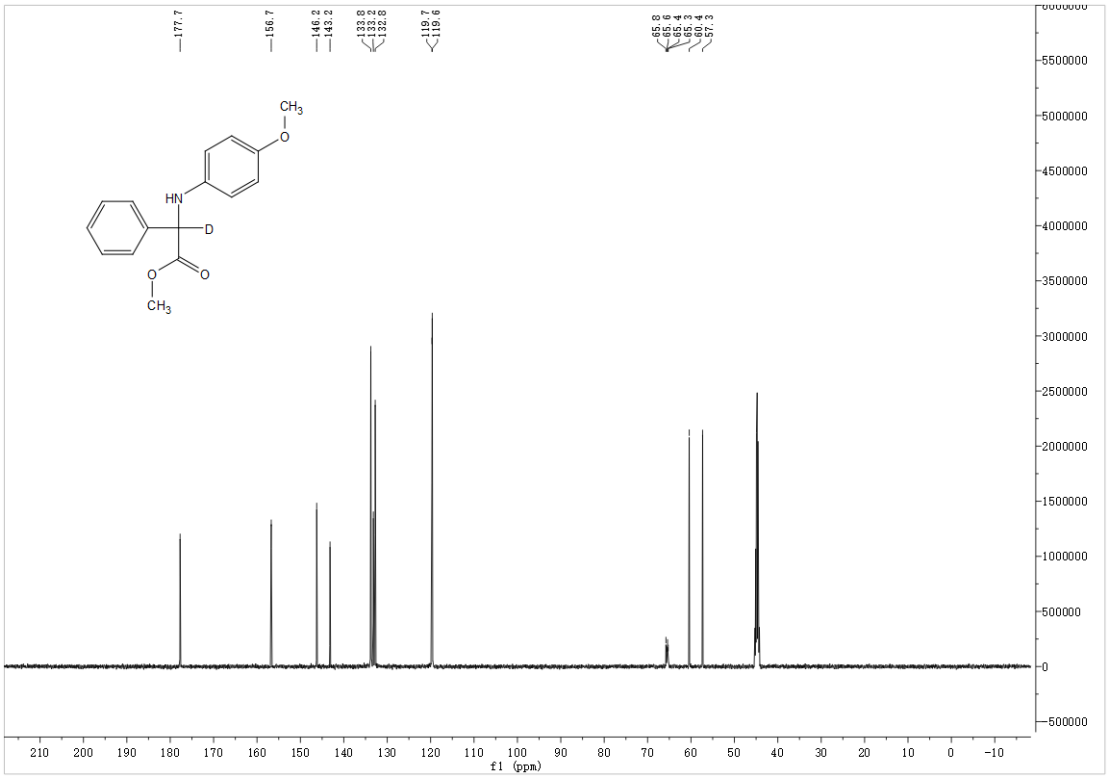
Product (**51**)


7.747
7.740
7.731
7.544
7.529
7.495
7.390
7.375
7.341
7.316
7.312
7.243
6.799
6.784
5.418
5.402
3.742
3.658
HN
D
O
CH3
f1 (ppm)

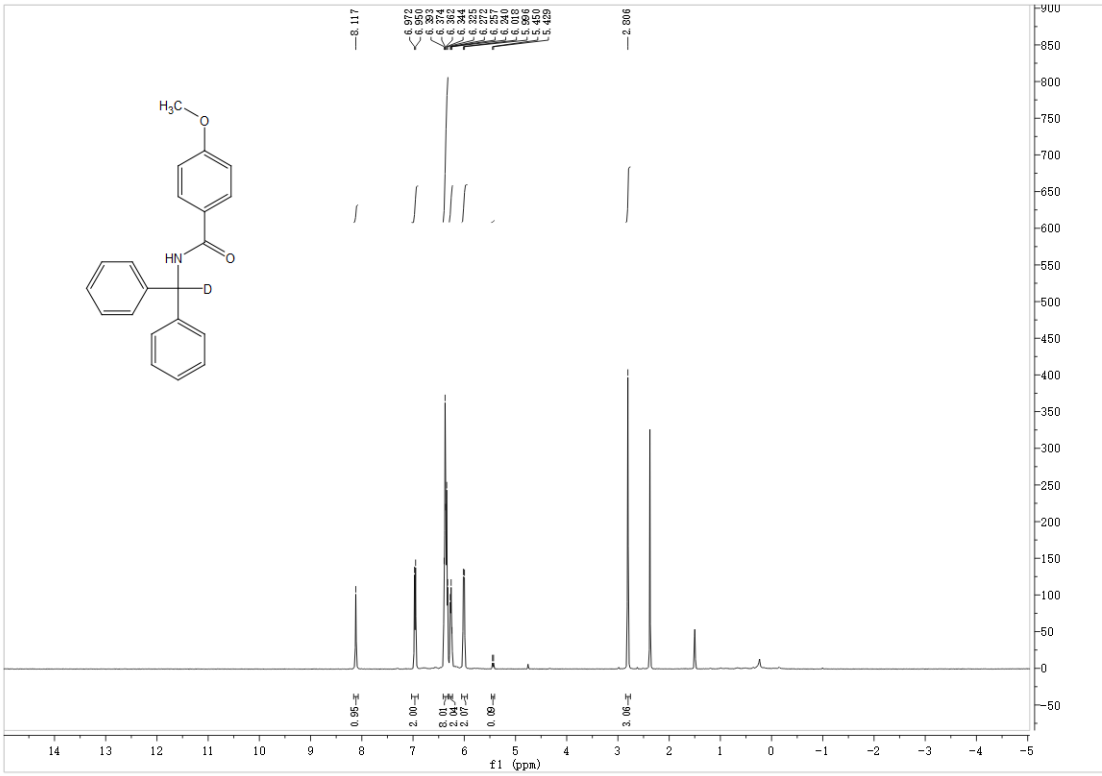

172.1
166.7
151.6
137.6
131.3
129.2
128.7
128.1
117.8
112.6
59.7
59.5
59.3
59.2
52.8
51.7
HN
D
O
CH3
f1 (ppm)

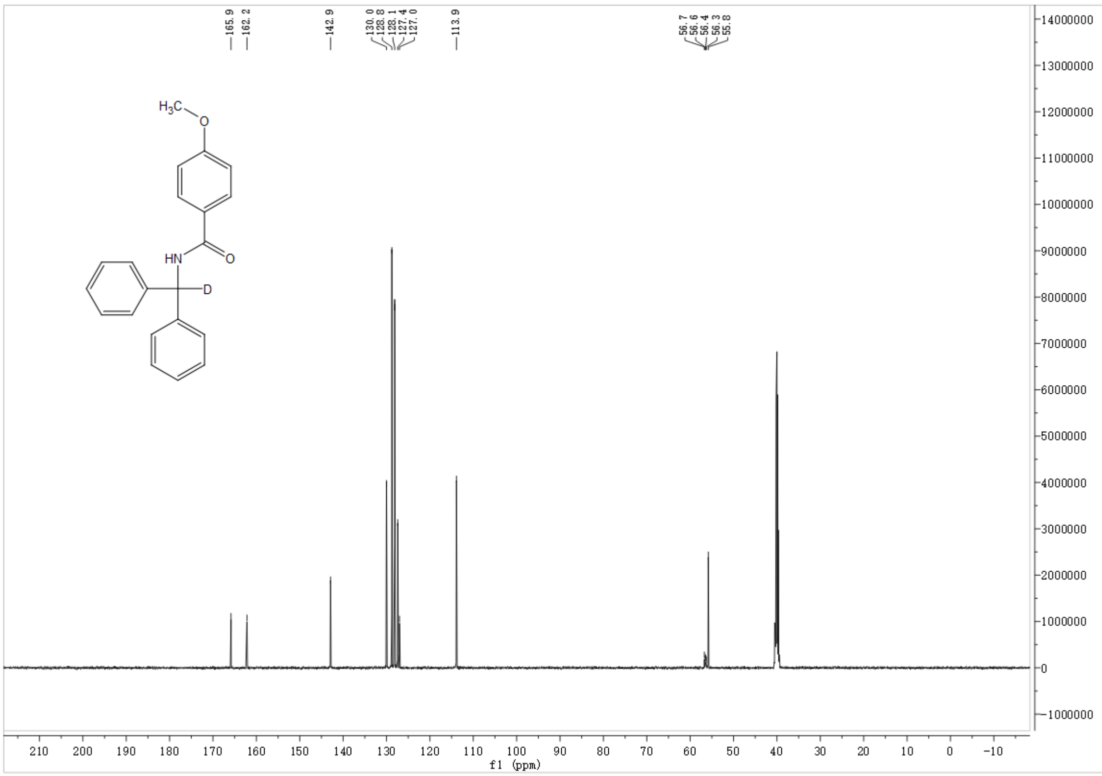
Product (**52**)


7.436
7.418
7.272
7.256
7.237
7.205
7.188
6.593
6.571
5.851
5.104
5.083
3.508
CH3
O
HN
D
O
O
CH3
2.07
1.99
1.04
4.08
1.00
0.10
6.10
f1 (ppm)

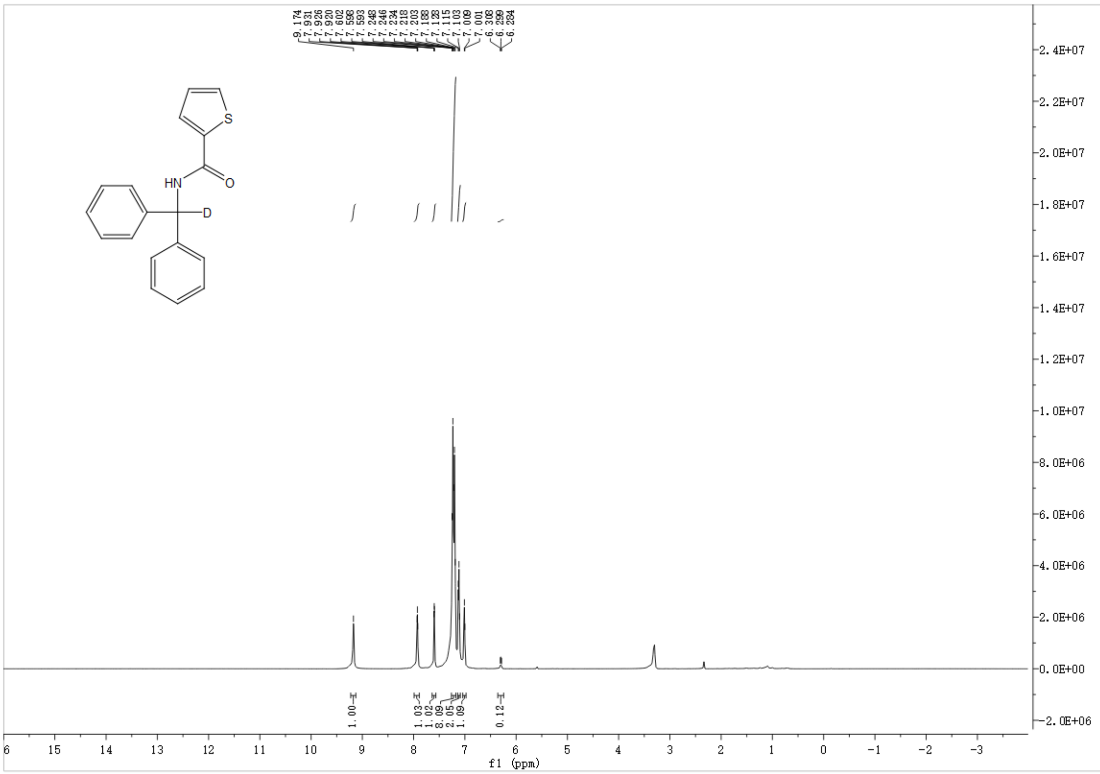

177.7
156.7
146.2
143.2
133.8
133.2
132.8
119.7
119.6
65.8
65.6
65.4
65.3
65.4
57.3
CH3
O
HN
D
O
O
CH3
f1 (ppm)

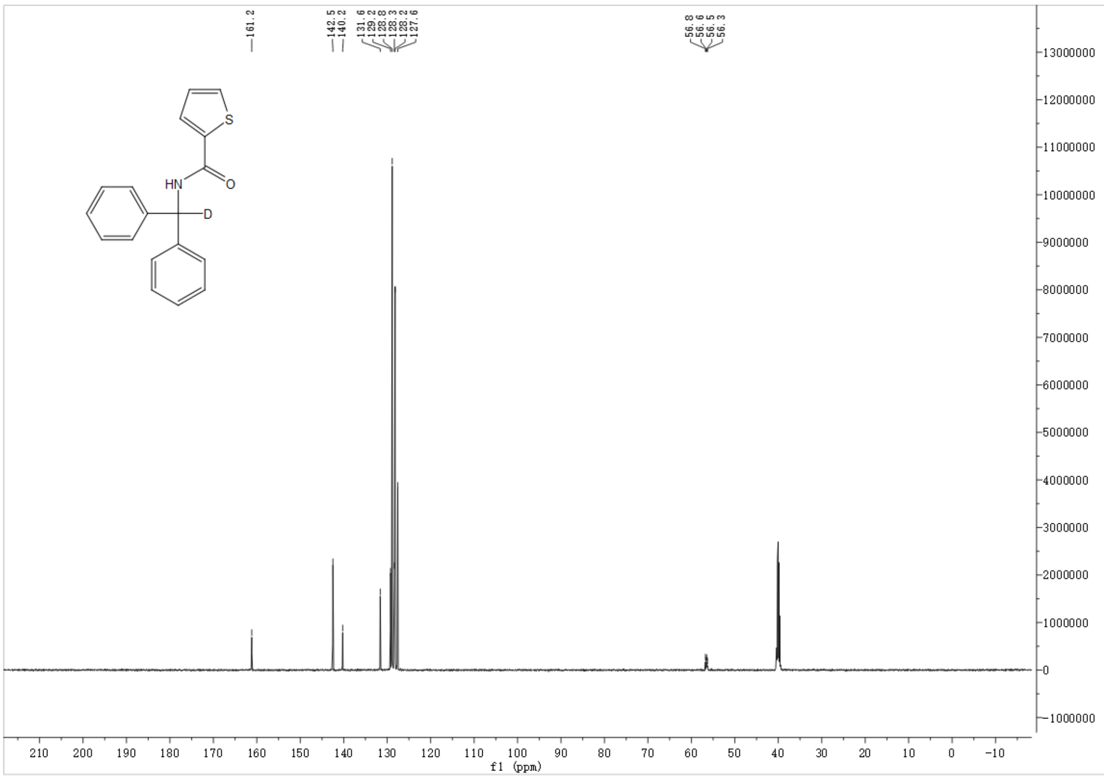
Product (**53**)



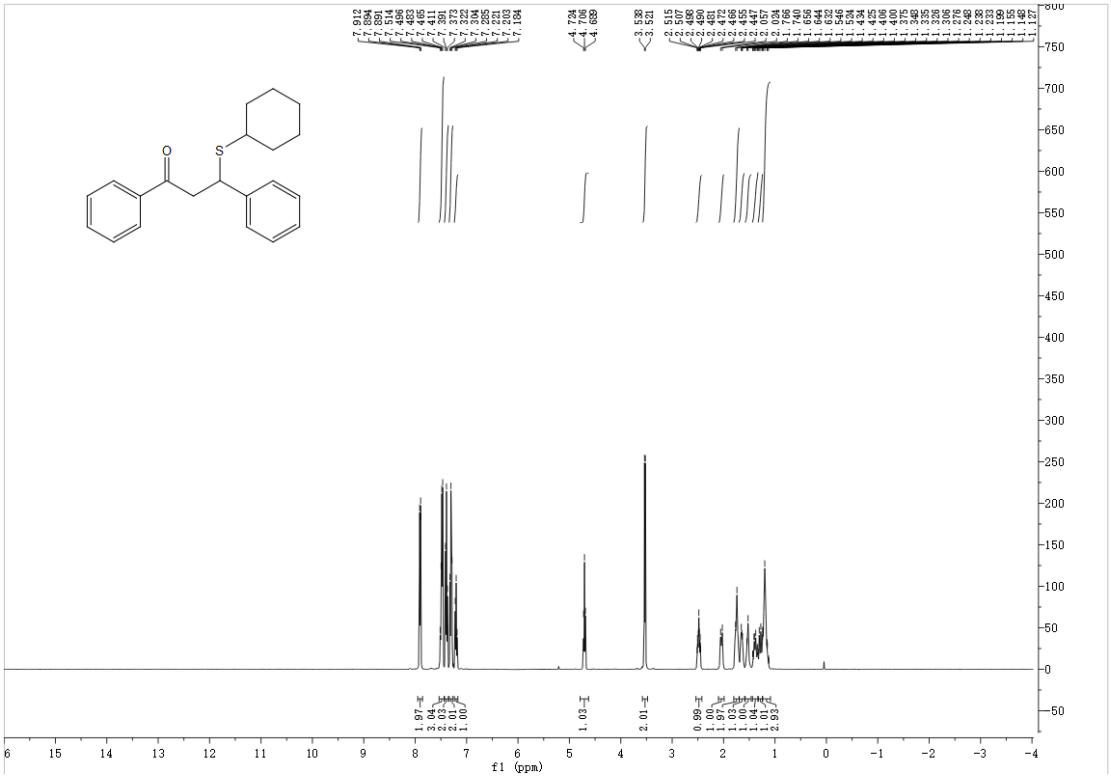


Product (**54**)





Product (**56**)


O
S
f1 (ppm)


196.9
143.1
137.0
133.2
128.6
128.5
128.1
127.8
127.1
46.0
43.2
43.0
33.7
33.3
25.9
O
S
f1 (ppm)

Reference

(1) Li, H.-C. et al. Transition-Metal-Free Highly Chemoselective and Stereoselective Reduction with Se/DMF/H_2O System. *Org. Lett.* **20**, 5573-5577 (2018).

(2) Zhang, J., Zhang, S. & Zou, H. Acid- and Base-Switched Palladium-Catalyzed γ-C(sp3)–H Alkylation and Alkenylation of Neopentylamine. *Org. Lett.* **23**, 3466-3471 (2021).

(3) Sim, J., Ryou, B., Choi, M., Lee, C. & Park, C.-M. Electrochemical C(sp^3)–H Functionalization of γ-Lactams Based on Hydrogen Atom Transfer. *Org. Lett*. **24**, 4264-4269 (2022).

(4) Zhang, K., Liu, X.-F., Zhang, W.-Z., Ren, W.-M. & Lu, X.-B. Electrocarboxylation of *N*-Acylimines with Carbon Dioxide: Access to Substituted α-Amino Acids. *Org. Lett.* **24**, 3565-3569 (2022).

(5) Zhong, Y. et al. H_2O/D_2O as the only H/D source for photocatalytic phosphine-mediated radical transfer hydrogenation/deuteration of α-aryl imino esters. *Org. Chem. Front.* **11**, 2793-2799 (2024).