SUPPORTING INFORMATION

Diaryliodonium Salts as Efficient Lewis Acid Catalysts for Direct Three Component Mannich Reactions

Yanxia Zhang,[a,b] Jianwei Han*[b] and Zhen-Jiang Liu*[a]

a. School of Chemical and Environmental Engineering, Shanghai Institute of Technology,100 Haiquan Road, Shanghai 201418, P. R. China. Fax: (+86)-21- 60877231; Tel: (+86)-21- 60877227; E-mail: zjliu@sit.edu.cn

b. Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, 345 Ling Ling Road, Shanghai 200237, P. R. China. Fax: (+86)-21- 54925383; Tel: (+86)-21- 54925551; E-mail: jianweihan@sioc.ac.cn

Table of Contents

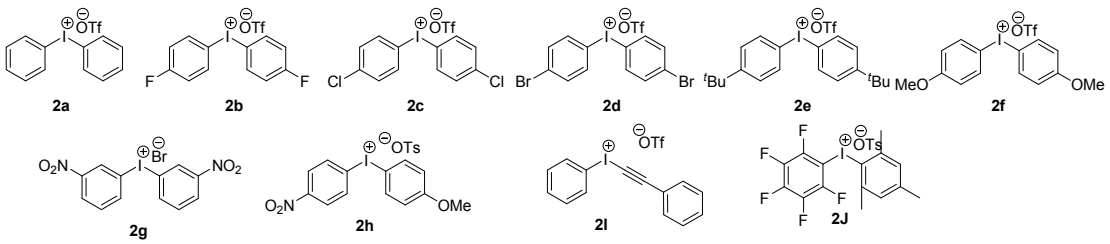
Part 1. General Information

a. Methods:

NMR spectrum: ^{1}H and ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 300 spectrometer, operating at 300 MHz for ^{1}H NMR; 75 MHz for ^{13}C NMR; 282 MHz for ^{19}F NMR. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HPLC analyses were on an Thermo Scientific Ultimate 3000 series with DAICEL chiral columns. Mass spectra were recorded by the State Key Laboratory of Organometallic Chemistry of Shanghai Institute of Organic Chemistry.

Chromatography: Column chromatography was performed with silica gel (300-400 mesh ASTM; Huanghai).

b. Materials: All solvents were dried and/or distilled by standard methods. Aniline and benzaldehyde distilled by standard methods, other reagents were purchased from commercial sources (Adamas, Acros and Aldrich) and used without further purification. All the diaryliodonium salts were synthesized according to the literature procedures. Salts **2a, 2b, 2c, 2d, 2e**were prepared from iodine and the corresponding arene in the presence of *m*CPBA and TfOH described by Olofsson and co-workers.[1] Salt **2f** was synthesized by situ anion exchange described by Olofsson and co-workers.[2] Salt **2g** was prepared from the corresponding arene with sodium metaperiodate as the coupling reagent in acidic media described by Skulski and co-workers.[3] Salt **2h** was prepared from oxidation of an iodoarene with mCPBA in the presence of TsOH followed by reaction with an arene by Olofsson and co-workers.[4] Salt **2i** were prepared from the corresponding Koser's reagent and phenylacetylene described by Gerald F. Korse and co-workers.[5] Salt **2j** was synthesized by Viktor V. Zhdankin and co-workers.[6]



Part 2. Experimental Section

a. Typical procedure for three components Mannich reaction (Table 1)

$PhCOCH_3$ (**9a**, 1.0mmol, 1.0 equiv.), PhCHO (**10a,** 1.0 mmol, 1.0 equiv.) and $PhNH_2$(**11a,** 1.0 mmol,1.0 equiv)were added into hydrogenated tube under free-solvent , and then added catalyst. The mixture was stirred under at room temperature for 24 h, the solvents were removed via a rotary evaporator. The residue was purified with silica gel chromatography (ethyl acetate/petroleum ether=1:30) to provide pure products.

b. Screen solvents for three components Mannich reaction[a]

Entry	Solvent	Time (h)	Yield (%)[b]
1	hexane	24	50
2	ethanol	24	56
3	ethyl acetate	24	49
4	chloroform	24	83
5	acetonitrile	24	50
6	methanol	24	76
7	water	24	48
8	Free-solvent	24	86

Unless otherwise specified, reaction conditions: **9a** (1 mmol), **10a** (1 mmol), **11a** (1 mmol) in the presence of iodonium salt **8a** (0.1 mmol) in solvent (1 mL) at room temperature for 24 hours. [b] Isolated yield.

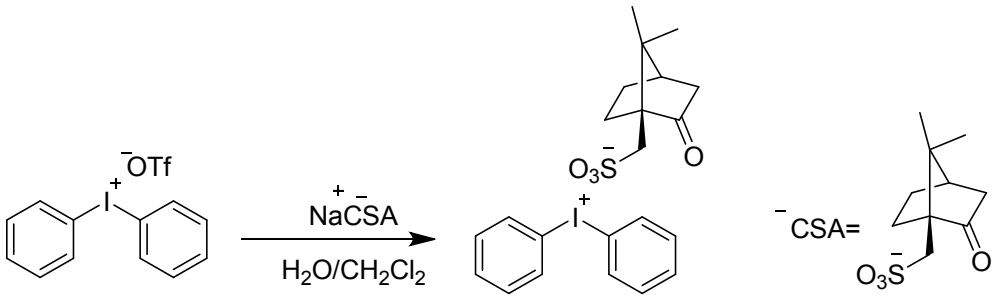
c. Screen catalyst loading for Mannich reaction of three components[a]

entry	Catalyst Loading (mol%)	Time(h)	Yield(%)[b]
1	0.0	24	0
2	5.0	24	50
3	7.5	24	68
4	10.0	24	86
5	12.5	24	80

[a] Unless otherwise specified, reaction conditions: **9a** (1 mmol), **10a** (1 mmol), **11a** (1 mmol) in the presence of iodonium salt **8a** at room temperature for 24 hours. [b] Isolated yield.

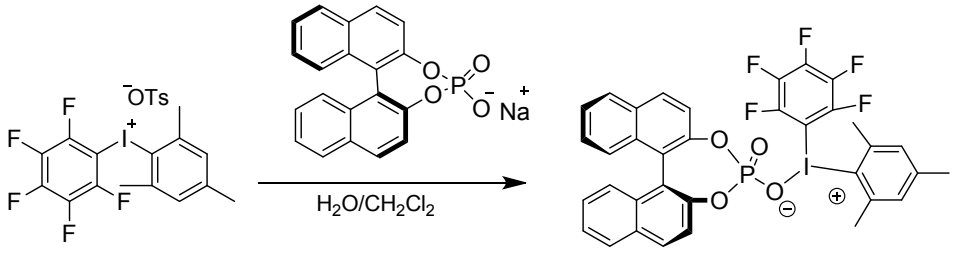
d. Synthesis of the Chiral Diaryliodonium Salt

1.



A solution of diphenyliodonium triflate (1.00 g, 2.3mmol) in dichloromethane (75 ml) was treated with a solution of sodium (1*D*)-camphor-10-sulfonate (2.87g, 11.3mmol) in water (10 ml) at room temperature. After separation of the phases, the aqueous phase was extracted thrice with dichloromethane(10 ml × 3). The combined organic extracts were concentrated to dryness. The material obtained was dissolved in dichloromethane(10 ml) and the procedure outlined repeated. After a total of three such treatments, complete anion exchange was accomplished (as determined by ^{1}H NMR). The crude material was triturated with diethyl ether, to yield the salt (0.94 g, 79%) as an off-white solid after isolation by filtration and several washes with diethyl ether.

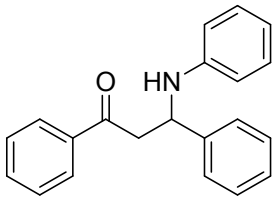
2.



A solution of mesityl(perfluorophenyl)iodonium salts (0.16 g, 0.28 mmol) in dichloromethane (10 ml) was treated with a solution of sodium (*R*)-(-)-1,1'-binaphthyl-2,2'-diylhydrogenphosphate (0.11g, 0.28mmol) in water(10ml) at room temperature. After separation of the phases, the aqueous phase was extracted thrice with dichloromethane(10 ml × 3). The combined organic extracts were concentrated to dryness. The material obtained was dissolved in dichloromethane (10 ml) and the procedure outlined repeated. After a total of three such treatments, complete anion exchange was accomplished (as determined by ^{1}H NMR). The crude material was triturated with diethyl ether, to yield the salt (0.17g, 80%) as an off-white solid after isolation by filtration and several washes with diethyl ether.

Part 3. Characterization of the Products

1,3-diphenyl-3-(phenylamino)propan-1-one(12a)

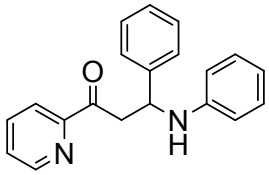


The product (93% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.89 (d, 2H), 7.60-7.53 (t, 1H), 7.50-7.40 (m, 4H), 7.35-7.30 (t, 2H), 7.25-7.20 (t, 1H), 7.15-7.06 (t, 2H), 6.73-6.64 (t, 1H) , 6.61-6.55 (d, 2H), 5.00(t, 1H) 3.60-3.40(m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.49, 147.14, 143.16, 136.84, 133.69, 129.34, 129.06, 128.94, 128.44, 127.59, 126.59, 118.00, 102.99, 54.99, 46.54.

3-phenyl-3-(phenylamino)-1-(pyridine-2-yl)propan-1-one(12b)

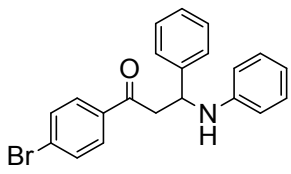


The product (83% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80-8.72 (d, 1H), 8.10-8.02 (d, 1H), 7.89-7.80 (t, 1H), 7.55-7.47 (d, 3H), 7.40-7.30 (t, 2H),7.30-7.20 (t, 1H), 7.05-7.02 (t, 2H), 6.68-6.60 (t, 1H), 6.56-6.50 (d, 2H), 5.10-5.00(m, 1H), 3.85-3.52 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.06, 153.45, 149.14, 147.23, 143.41, 137.38, 129.28, 128.94, 127.63, 127.42, 126.63, 122.55, 117.55, 113.66, 55.56, 46.11.

1-(4-bromophenyl)-3-phenyl-3-(phenylamino)propan-1-one(12c)

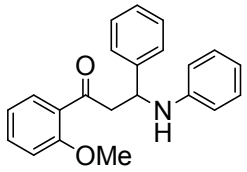


The product (90% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[9]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.72 (d, 2H), 7.63-7.55 (d, 2H), 7.47-7.40 (d, 2H), 7.38-7.30 (t, 2H), 7.30-7.27 (d, 1H), 7.17-7.07 (t, 2H), 6.74-6.65 (t, 1H), 6.63-6.53 (t, 2H), 5.08-5.00 (t, 1H), 3.52-3.38 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.51, 147.05, 142.93, 135.60, 132.23, 129.93, 129.11, 127.71, 126.57, 118.13, 114.03, 54.90, 46.39.

1-(2-methoxyphenyl)-3-phenyl-3-(phenylamino)propan-1-one(12d)

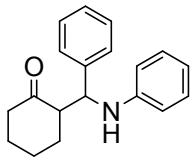


The product (85% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.62 (m, 1H), 7.53-7.42 (m, 3H), 7.37-7.30 (t, 2H), 7.25-7.21 (d, 1H), 7.13-7.05 (t, 2H), 7.03-6.95 (t, 2H), 6.70-6.63 (t, 1H), 6.57-6.50 (d, 2H), 5.02-4.95 (dd, 1H), 3.95 (s, 3H), 3.60-3.32 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.85, 158.67, 147.43, 143.61, 134.12, 130.84, 129.25, 128.89, 127.30, 126.60, 121.14, 117.64, 113.87, 111.72, 55.78, 55.21, 51.71.

2-(phenyl(phenylamino)methyl)cyclohexanone(12e)

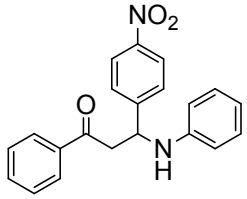


The product (99% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.36 (t, 2H), 7.36-7.28 (m, 2H), 7.28-7.20 (m, 1H), 7.14-7.05 (m, 2H), 6.72-6.63 (m, 1H), 6.63-6.53 (t, 2H), 4.88-4.60 (m, 1H), 2.90-2.70 (m, 1H), 2.50-2.25 (m, 2H), 2.10-1.60 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 213.36, 211.60, 147.44, 141.93, 129.30, 129.25, 128.71, 128.61, 127.75, 127.50, 127.41, 127.24, 121,12, 117.90, 117.73, 114.29, 113.82, 58.18, 57.73, 57.44, 56.87, 42.66, 42.25, 42.02, 31.55, 28.89, 28.16, 27.28, 25.10, 23.89.

3-(4-nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one(12f)

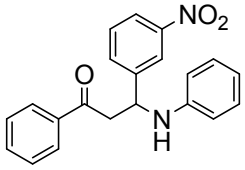


The product (67％ yield) as a yellow solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[10]

^{1}H NMR (300MHz, $CDCl_3$) δ 8.05-7.95 (m, 3H), 7.87-7.80 (d, 1H), 7.63-7.53 (m, 2H), 7.53-7.44 (m, 2H), 7.44-7.35 (t, 1H), 7.12-7.02 (t, 2H), 6.71-6.62 (t, 1H), 6.50-6.42 (d, 2H), 5.62-5.53 (m, 1H), 3.85-3.72 (m, 1H), 3.45-3.33 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.46, 148.93, 146.29, 138.54, 136.49, 134.06, 133.98, 129.46, 129.31, 129.03, 128.63, 128.55, 125.21, 118.45, 113.65, 51.06, 44.99.

3-(3-nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one(12g)

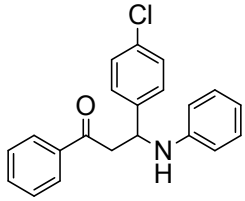


The product (76% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37-8.32 (s, 1H), 8.14-8.07 (d, 1H), 7.95-7.90 (d, 2H), 7.87-7.80 (d, 1H), 7.65-7.55 (t, 1H), 7.55-7.43 (q, 3H), 7.17-7.07 (t, 2H), 6.78-6.68 (t, 1H), 6.60-6.50 (d, 2H), 5.17-5.10 (t, 1H), 3.58-3.51 (d, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.54, 148.89, 146.51, 145.69, 136.50, 134.04, 133.24, 130.01, 129.51, 129.08, 128.39, 122.74, 121.70, 118.66, 114.05, 54.25, 46.07.

3-(4-chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one(12h)

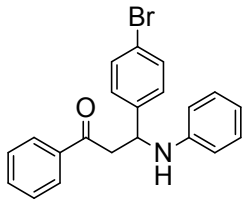


The product (96% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95-7.90 (d, 2H), 7.63-7.55 (t, 1H), 7.50-7.37 (m, 4H), 7.34-7.25 (t, 2H), 7.15-7.07 (t, 2H), 6.75-6.67 (t, 1H), 6.60-6.50 (d, 2H), 5.05-4.95(t, 1H), 3.58-3.41 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.09, 146.57, 141.48, 136.69, 133.85, 133.23, 129.40, 129.20, 129.00, 128.41, 128.13, 118.55, 114.31, 54.61, 46.23.

3-(4-bromophenyl)-1-phenyl-3-(phenylamino)propan-1-one(12i)

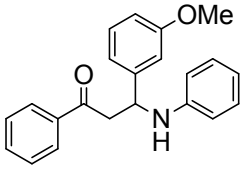


The product (96% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95-7.87 (d, 2H), 7.65-7.55 (t, 1H), 7.52-7.42 (t, 4H), 7.40-7.30 (d, 2H), 7.15-7.07 (t, 2H), 6.75-6.65 (t, 1H), 6.60-6.50 (d, 2H), 5.05-4.90(t, 1H), 3.55-3.35 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.09, 146.86, 142.27, 136.70, 133.85, 132.14, 129.39, 129.00, 128.43, 128.41, 121.26, 118.30, 114.06, 54.42, 46.30.

3-(3-methoxyphenyl)-1-phenyl-3-(phenylamino)propan-1-one(12j)

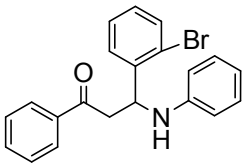


The product (88% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.87 (d, 2H), 7.64-7.54 (t, 1H), 7.52-7.43 (t, 2H), 7.34-7.23 (t, 1H), 7.17-6.98 (m, 4H), 6.85-6.76 (d, 1H), 6.75-6.65 (t, 1H), 6.65-6.55 (d, 2H), 5.05-4.96 (t, 1H), 3.79 (s, 3H), 3.60-3.35 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.47, 160.21, 147.25, 145.12, 136.89, 133.71, 130.13, 129.35, 128.96, 128.47, 118.87, 118.03, 114.05, 112.74, 112.42, 55.45, 55.04, 46.56.

3-(2-bromophenyl)-1-phenyl-3-(phenylamino)propan-1-one(12k)

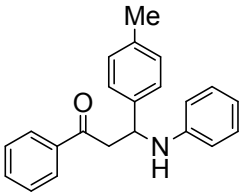


The product (69% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05-7.95 (d, 2H), 7.64-7.52 (q, 3H), 7.51-7.41 (t, 2H), 7.25-7.19 (m, 1H), 7.15-7.05 (q, 3H), 6.72-6.61 (t, 1H), 6.52-6.43 (d, 2H), 5.31-5.20 (dd, 1H), 3.70-3.57 (q, 1H), 3.35-3.21 (q, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.76, 146.64, 141.21, 133.83, 133.32, 129.33, 129.15, 128.94, 128.65, 128.50, 128.32, 122.82, 118.08, 113.85, 54.46, 44.04.

1-phenyl-3-(phenylamino)-3-(*p*-tolyl)propan-1-one(12l)



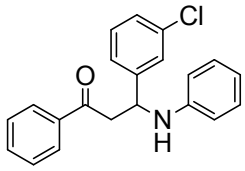
The product (94% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.90 (d, 2H), 7.65-7.55 (q, 1H), 7.50-7.41 (t, 2H), 7.40-7.32 (d, 2H), 7.20-7.05 (q, 4H), 6.74-6.66 (t, 1H), 6.64-6.56 (d, 2H), 5.05-4.95 (t, 1H), 3.60-3.40 (m, 2H), 2.36-

2.30 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.53, 146.92, 139.90, 137.25, 136.86, 133.66, 129.74, 129.34, 128.98, 128.45, 126.57, 118.22, 114.28, 54.96, 46.47, 21.34.

3-(3-chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one(12m)

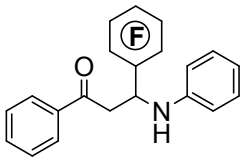


The product (87% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.87 (d, 2H), 7.64-7.55 (t, 1H), 7.53-7.43 (t, 3H), 7.40-7.33 (d, 1H), 7.33-7.20 (m, 2H), 7.17-7.07 (t, 2H), 6.75-6.66 (t, 1H), 6.60-6.53 (d, 2H), 5.05-4.92 (t, 1H), 3.58-3.37 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.98, 146.89, 145.55, 136.69, 134.92, 133.84, 130.36, 129.40, 129.00, 128.42, 127.82, 126.77, 124.89, 118.32, 114.05, 54.60, 46.38.

3-(polyfluorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (12n)



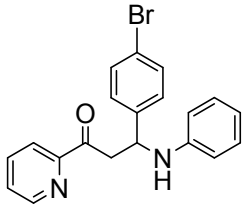
The product (45% yield) as a yellow solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.92 (d, 2H), 7.67-7.57 (t, 1H), 7.55-7.45 (t, 2H), 7.24-7.14 (t, 2H), 6.83-6.67 (m, 3H), 5.71-5.57 (t, 1H), 3.85-3.65 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.37, 145.78, 136.31, 134.00, 129.77, 129.07, 128.29, 119.45, 113.93, 45.50, 43.78.

^{19}F NMR (282 MHz, $CDCl_3$) δ -161.80 (td, J_F = 24.0, 9.0 Hz, 2F), -155.40 (t, J_F = 21.0Hz, 1F), -144.05 (dd, J_F = 21.0, 6.0 Hz, 2F)

3-(4-bromophenyl)-3-(phenylamino)-1-(pyridine-2-yl)propan-1-one(12o)

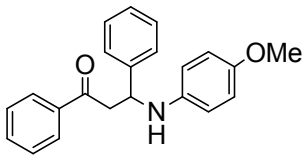


The product (94% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80-8.70 (d, 1H), 8.10-7.97 (d, 1H), 7.93-7.78 (t, 1H), 7.60-7.30 (m, 5H), 7.13-7.00 (t, 2H), 6.70-6.60 (t, 1H), 6.53-6.38 (d, 2H), 5.10-4.88 (m, 1H), 3.80-3.45 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.70, 153.31, 149.14, 146.87, 142.50, 137.42, 132.01, 129.31, 128.44, 127.72, 122.57, 121.12, 117.85, 113.68, 54.99, 45.86.

3-((4-methoxyphenyl)amino)-1,3-diphenylpropan-1-one(12p)

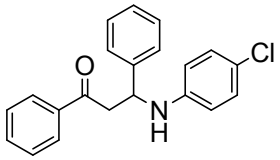


The product (90% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[13]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95-7.87 (d, 2H), 7.60-7.53 (m, 1H), 7.50-7.42 (m, 4H), 7.37-7.30 (t, 2H), 7.25-7.22 (d, 1H), 6.72-6.67 (d, 2H), 6.60-6.53 (d, 2H), 4.98-4.91 (dd, 1H), 3.70 (s, 3H), 3.55-3.40 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.55, 152.76, 143.14, 140.95, 136.90, 133.63, 129.02, 128.91, 128.81, 128.42, 127.60, 126.74, 115.87, 114.91, 56.20, 55.90, 46.52.

4-bromo-2,3,5,6-tetrafluoro-1,1'-biphenyl (12q)

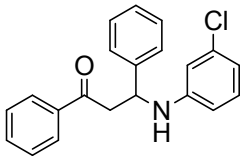


The product (86% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.87 (d, 2H), 7.65-7.55 (t, 1H), 7.50-7.40 (q, 4H), 7.37-7.30 (t, 2H), 7.25-7.20 (m, 1H), 7.07-7.00 (d, 2H), 6.55-6.42 (d, 2H), 5.00-4.90 (t, 1H), 3.57-3.35 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.37, 145.67, 142.62, 136.74, 133.79, 129.14, 128.97, 128.42, 127.75, 126.52, 115.23, 55.16, 46.42.

3-((3-chlorophenyl)amino)-1,3-diphenylpropan-1-one(12r)



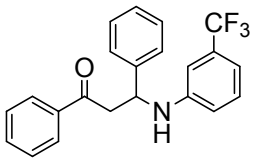
The product (89% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[14]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.87 (d, 2H), 7.64-7.55 (t, 1H), 7.52-7.40 (t, 4H), 7.40-7.32 (t, 2H), 7.32-7.26 (d, 1H), 7.05-6.95 (t, 1H), 6.70-6.60 (d, 1H), 6.60-6.52 (s, 1H), 6.47-6.40 (dd, 1H), 5.08-4.95 (t, 1H), 3.60-3.35 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.28, 148.39, 142.56, 136.76, 135.01, 133.81, 130.34, 129.17, 128.99,

128.44, 127.79, 126.51, 117.90, 113.81, 112.17, 54.83, 46.35.

1,3-diphenyl-3-((3-(trifluoromethyl)phenyl)amino)propan-1-one(12s)

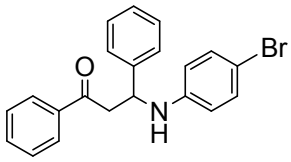


The product (76% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.87 (d, 2H), 7.65-7.55 (t, 1H), 7.53-7.41 (t, 4H), 7.40-7.32 (t, 2H), 7.30-7.22 (m, 1H), 7.22-7.13 (t, 1H), 6.95-6.87 (d, 1H), 6.85-6.77 (s, 1H), 6.73-6.65 (d, 1H), 5.10-5.00 (t, 1H), 3.60-3.40 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.30, 147.32, 142.38, 136.56, 133.86, 129.77, 129.20, 129.00, 128.44, 127.85, 126.47, 116.61, 114.37, 110.55, 54.86, 46.35.

3-((4-bromophenyl)amino)-1,3-diphenylpropan-1-one(12t)

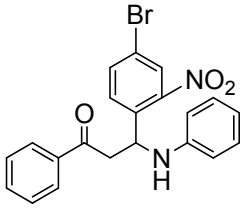


The product (98% yield) as a white solid was purified with silica gel chromatography (ethyl acetate/petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.87 (d, 2H), 7.63-7.55 (t, 1H), 7.50-7.38 (q, 4H), 7.37-7.30 (t, 2H), 7.26-7.23 (m, 1H), 7.20-7.13 (d, 2H), 6.50-6.42 (d, 2H), 5.00-4.90 (t, 1H), 3.58-3.40 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.36, 149.87, 142.26, 136.72, 133.80, 132.04, 129.14, 128.97, 128.42, 127.82, 126.58, 115.99, 55.36, 46.25.

3-(4-bromo-2-nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one(12u)

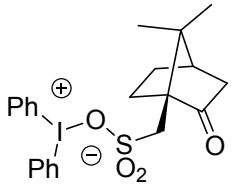


The product (83% yield) as a yellow liquid was purified with silica gel chromatography (ethyl acetate/petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15-8.07 (s, 1H), 8.01-7.94 (d, 2H), 7.80-7.72 (d, 1H), 7.68-7.55 (q, 2H), 7.53-7.43 (t, 2H), 7.15-7.05 (t, 2H), 6.75-6.65 (t, 1H), 6.51-6.41 (d, 2H), 5.60-5.50 (dd, 1H), 3.83-3.70 (m, 1H), 3.48-3.33 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.13, 149.29, 146.01, 137.69, 137.10, 136.36, 134.12, 131.13, 129.55, 129.09, 128.58, 128.04, 121.60, 118.74, 115.35, 113.88, 50.80, 44.65.

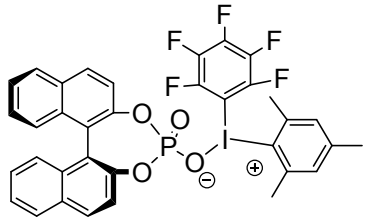
diphenyliodonium (1*D*)-camphor-10-sulfonate (8o)



The product (93% yield) as an off-white solid after isolation by filtration and several washes with diethyl ether. The analytical data is corresponding to those described in the literature.[15]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-8.00 (d, 4H), 7.58-7.48 (t, 2H), 7.47-7.35 (t, 4H), 3.15-3.05 (d, 1H), 2.57-2.47 (d, 1H), 2.47-2.40 (m, 1H), 2.30-2.18 (m, 1H), 1.98-1.75 (m, 3H), 1.50-1.36 (m, 1H), 1.27-1.18 (m, 1H), 0.95-0.90 (s, 3H), 0.73-0.67 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 217.04, 135.22, 131.54, 123.52, 115.60, 58.40, 47.72, 47.01, 42.80, 42.47, 26.93, 24.20, 19.90, 19.69.



The product (80% yield) as an off-white solid after isolation by filtration and several washes with diethyl ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.75 (t, 4H), 7.45-7.31 (m, 4H), 7.30-7.15 (m, 4H), 6.76-6.64 (s, 2H), 2.67-2.45 (s, 6H), 2.15-2.05 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.64, 148.51, 142.58, 141.43, 132.33, 131.00, 129.98, 129.22, 128.08, 126.97, 125.87, 124.67, 121.75, 121.72, 121.39, 121.35, 26.51, 20.86.

^{19}F NMR (282 MHz, $CDCl_3$) δ -157.57 (m, 2F), -146.80 (m, 1F), -122.45 (m, 2F)

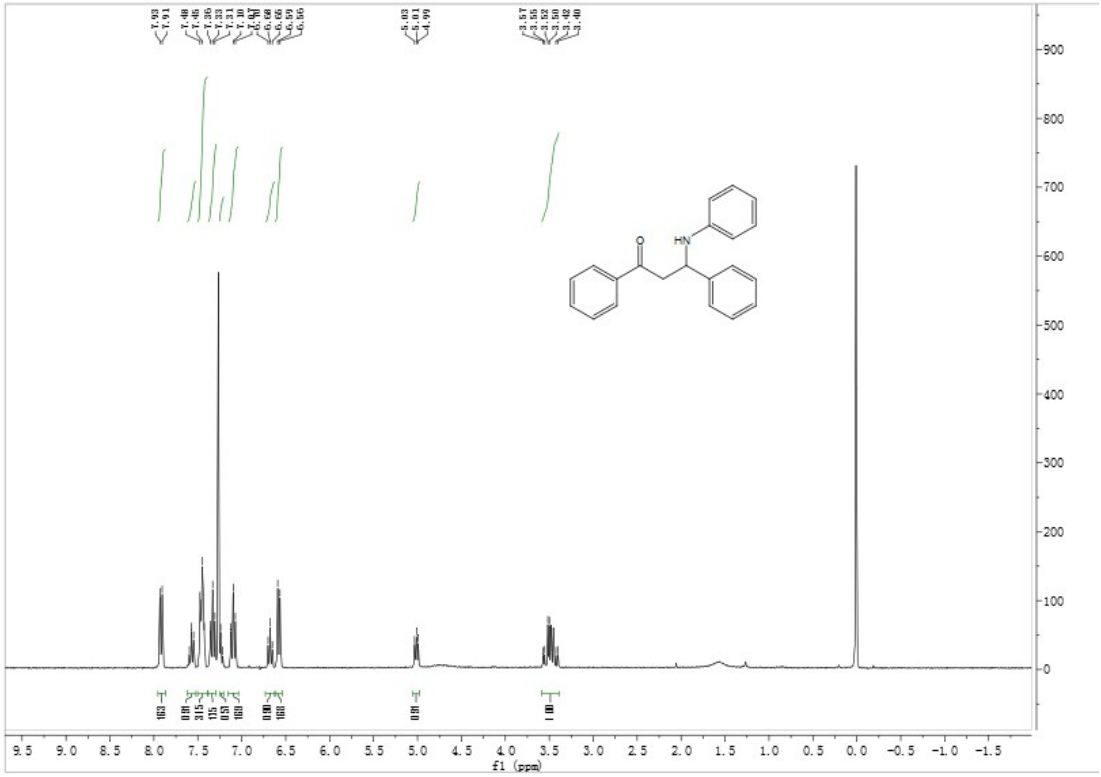
HRMS(ESI): calcd for $C_{15}H_{11}F_5I^+$([M-anion]+):412.9820, found 412.9819

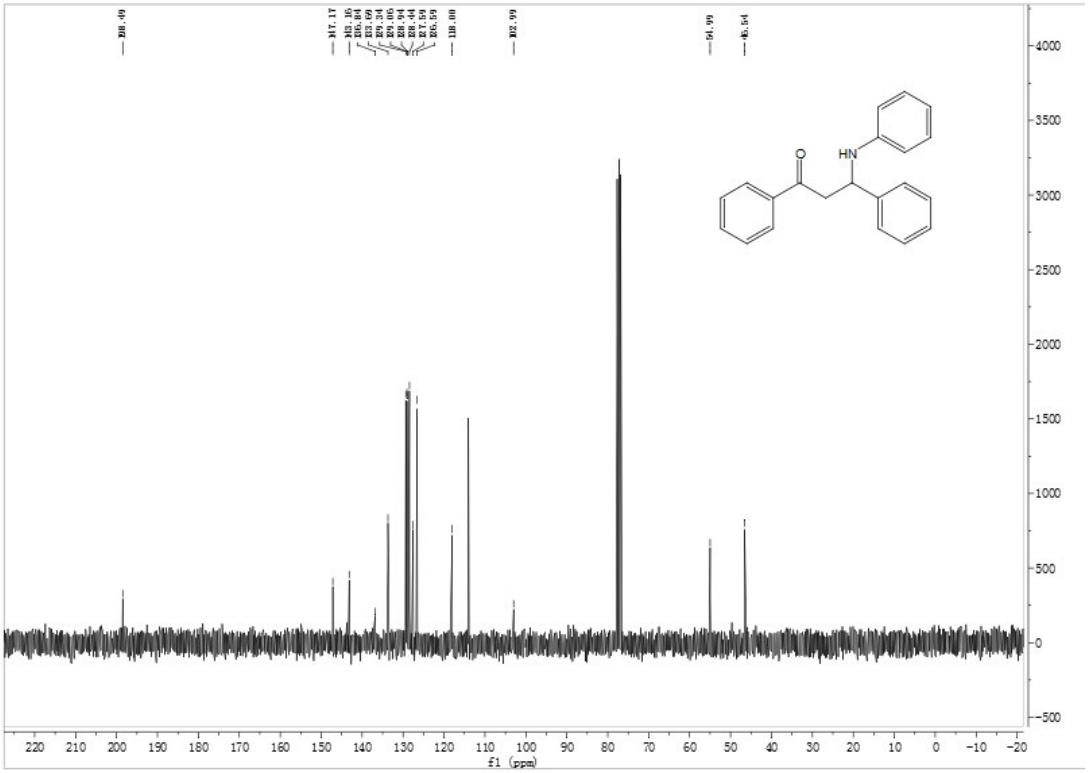
Part 4. References

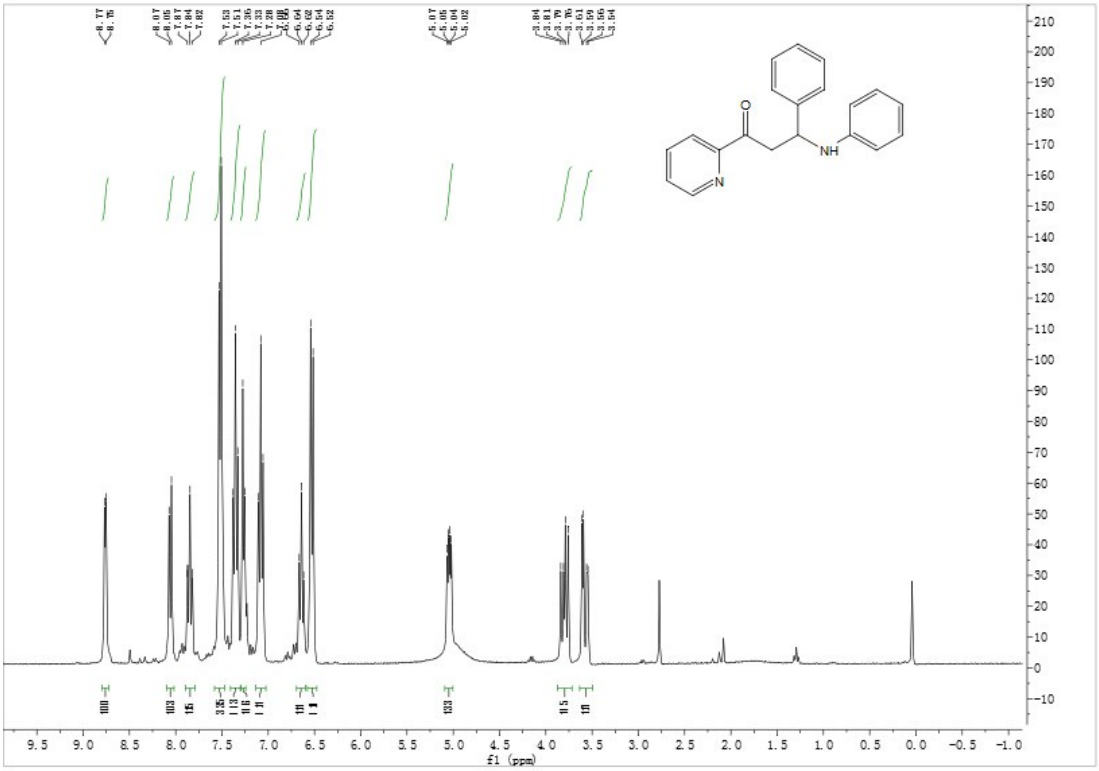
1. M. Bielawski, Z. Zhu and B. Olofsson, *Adv. Synth. Catal.,* **2007**, *349*, 2610.
2. M. Zhu, N. Jalalian and B. Olofsson, *Synlett.,* **2008**, *4*, 592.
3. L. Kraszkiewicz, and L. Skulski, *Synthesis.,* **2008**, *15*, 2373.
4. Tue B. Petersen, Rehan Khan, and Berit Olofsson*, *Org. Lett.,* **2011**, 13, 3462-3465
5. Louis Rebrovic and Gerald F. Koser*, *J. Org. Chem.,* **1984**, 49*,* 4700-4702
6. Aleksandra A. Zagulyaeva and Viktor V. Zhdankin, *J. Org. Chem.,* **2010**, 75, 2119–2122
7. Muthusamy Poomalai Pachamuthu, Anand Ramanathan*c, *Green Chem.,* **2013**, 15, 2158–2166
8. Kshama Kundu and Sandip K. Nayak* , *RSC Adv.,* **2012**, 2, 480–486
9. N. G. Kozlov and L. I. Basalaeva , *Russian Journal of General Chemistry.,* **2004**, 74, 1003-1008
10. X. Zhang et al. *Journal of Organometallic Chemistry.,* **2014**, 749, 241-245

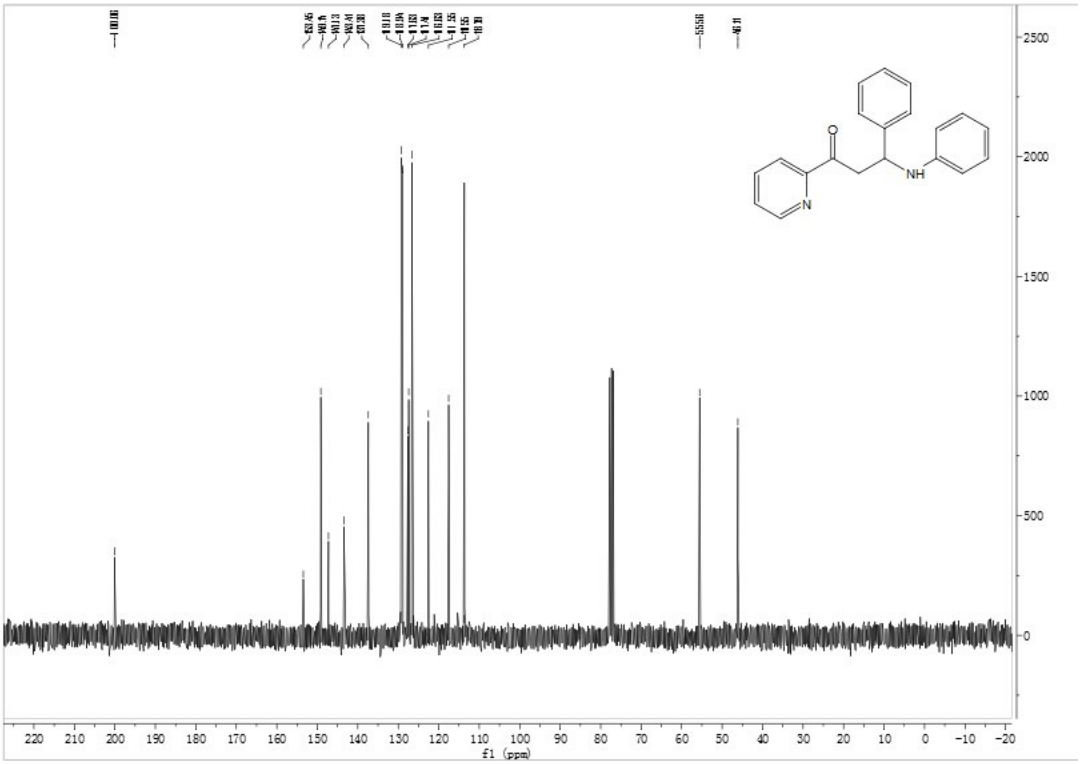
11. Ningbo Li, Xinhua Xu, *Dalton Trans.,* **2014**, 43, 11696–11708
12. Hashem Sharghi and Mahboubeh Jokar, *Can. J. Chem.,* **2009**, 88, 14-26
13. Maximillian Böhm and Rainer Mahrwald, *Eur. J. Org. Chem.,* **2013**, 1046–1049
14. AbuT. Khan and Lokman H. Choudhung, *Eur. J. Org. Chem.,* **2008**, 834-839
15. Per-Ola Norrby and Berit Olofsson, *Chem. Eur. J.* **2010**, 16, 8251 – 8254

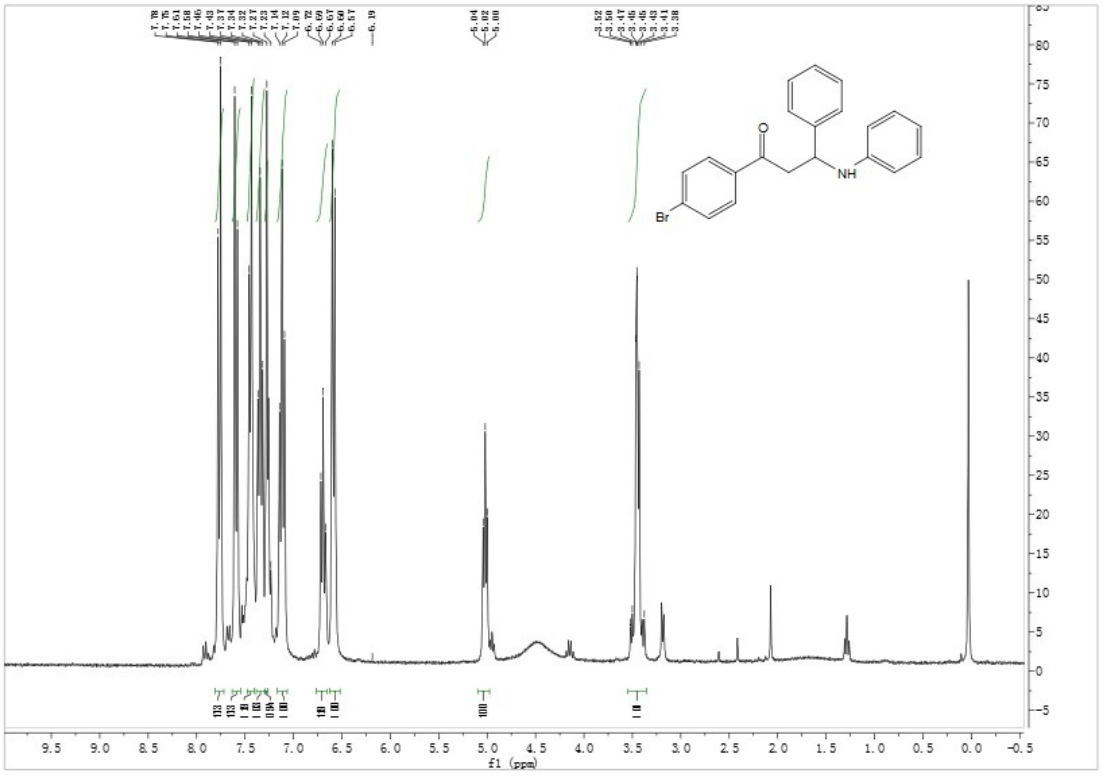
Part 5. Copies of ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR Spectra

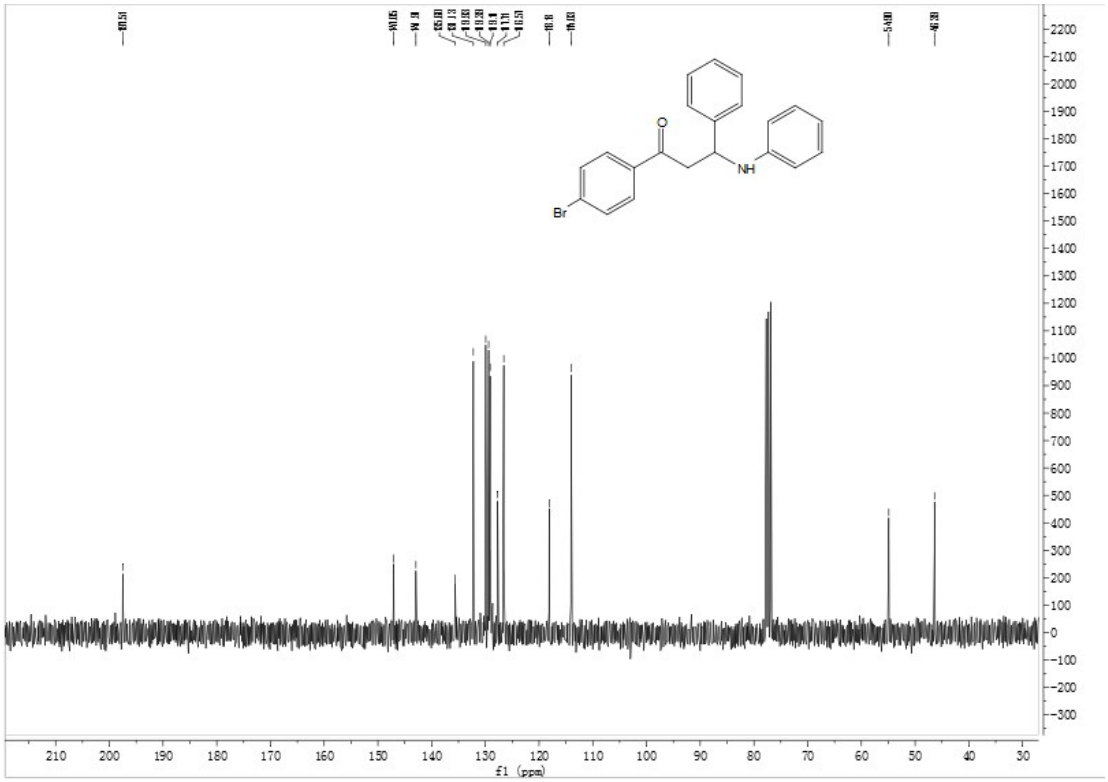


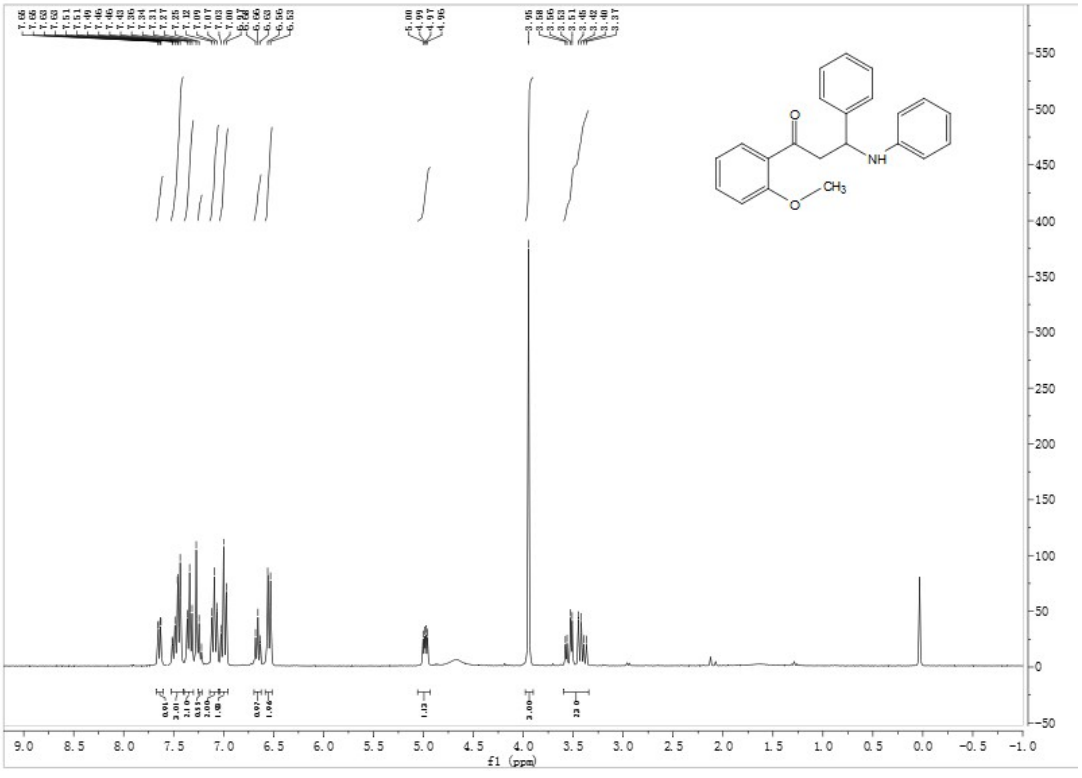

198.49
147.17
143.16
135.84
133.60
129.34
129.05
128.94
128.44
127.55
126.59
118.00
102.99
54.99
45.64
O
HN
f1 (ppm)

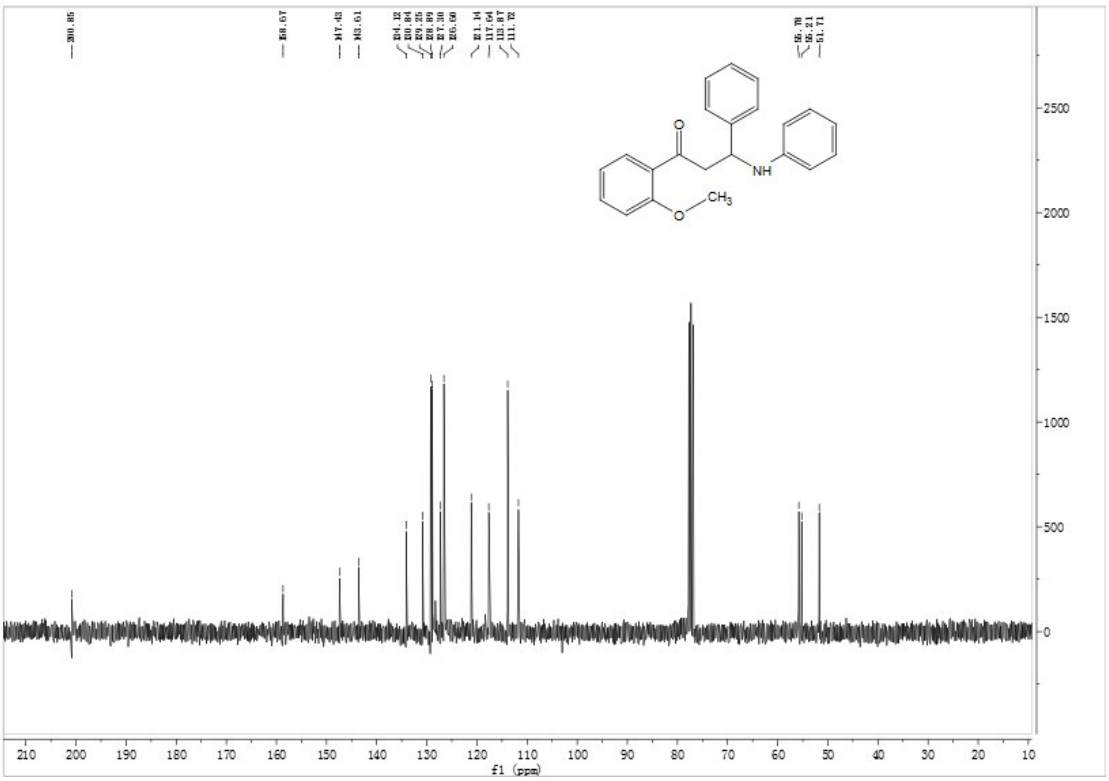

8.77
8.76
8.07
8.06
7.87
7.84
7.82
7.53
7.51
7.36
7.33
7.28
6.64
6.62
6.54
6.52
5.07
5.06
5.04
5.02
3.84
3.81
3.79
3.76
3.61
3.59
3.55
3.54
O
NH
N
f1 (ppm)

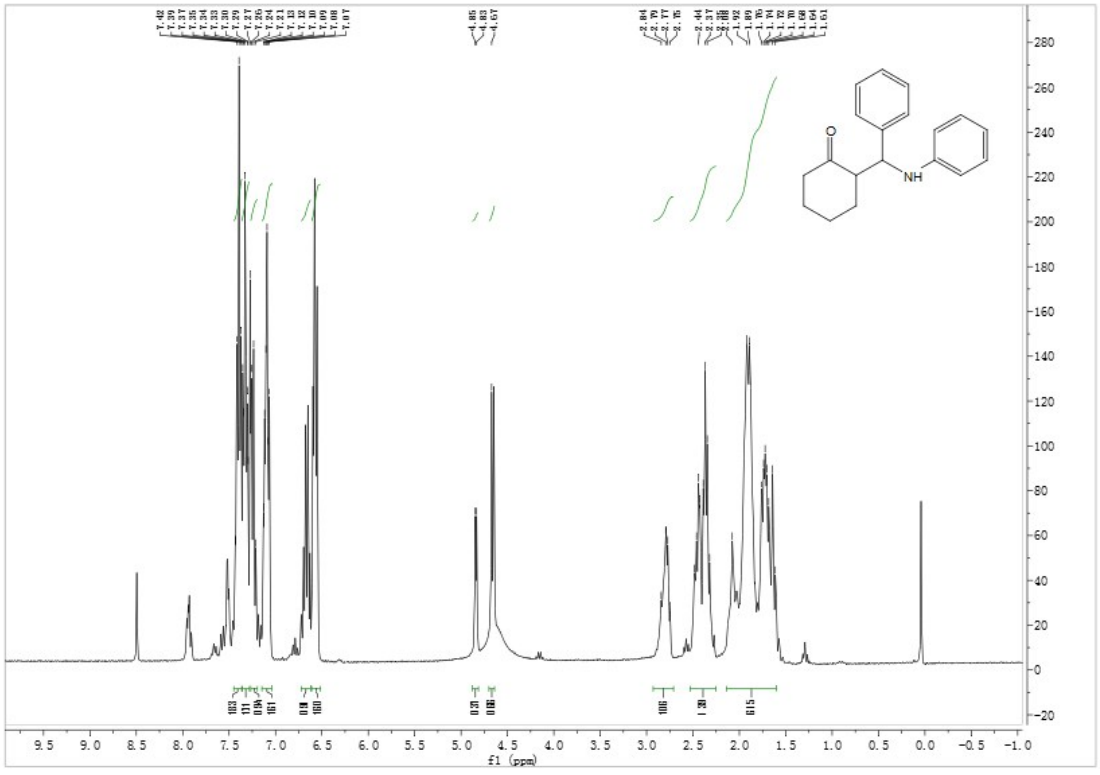

O
NH
N
f1 (ppm)

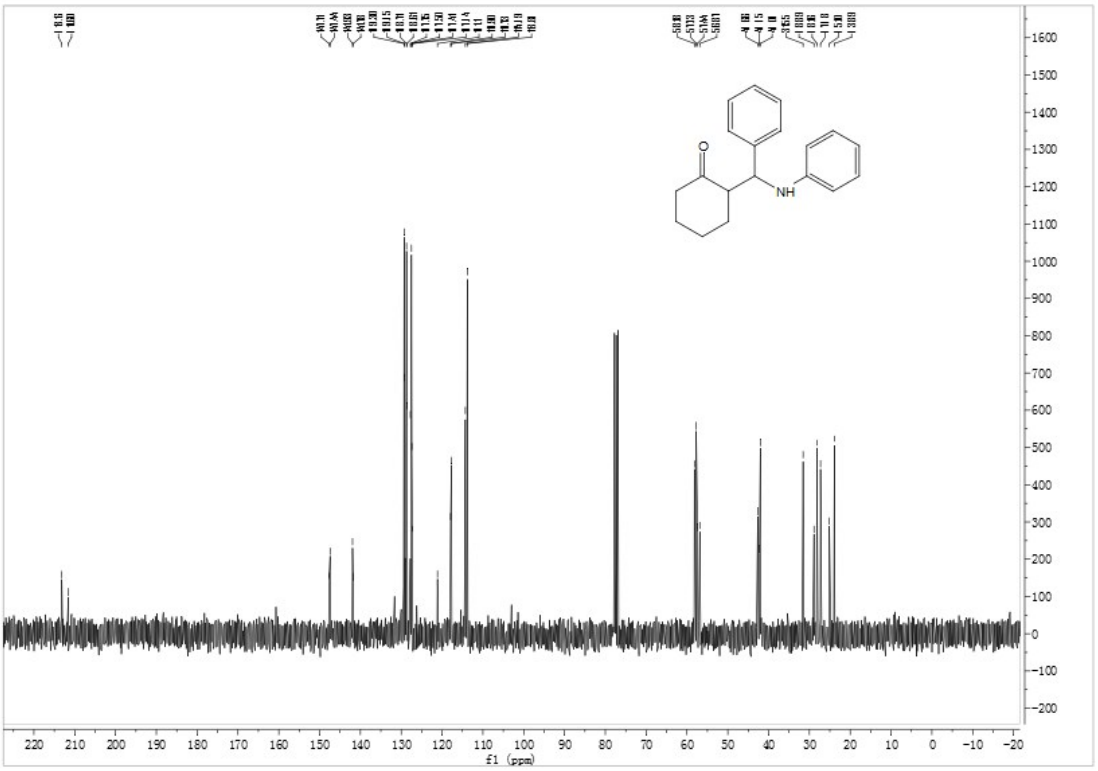

O
NH
Br
f1 (ppm)

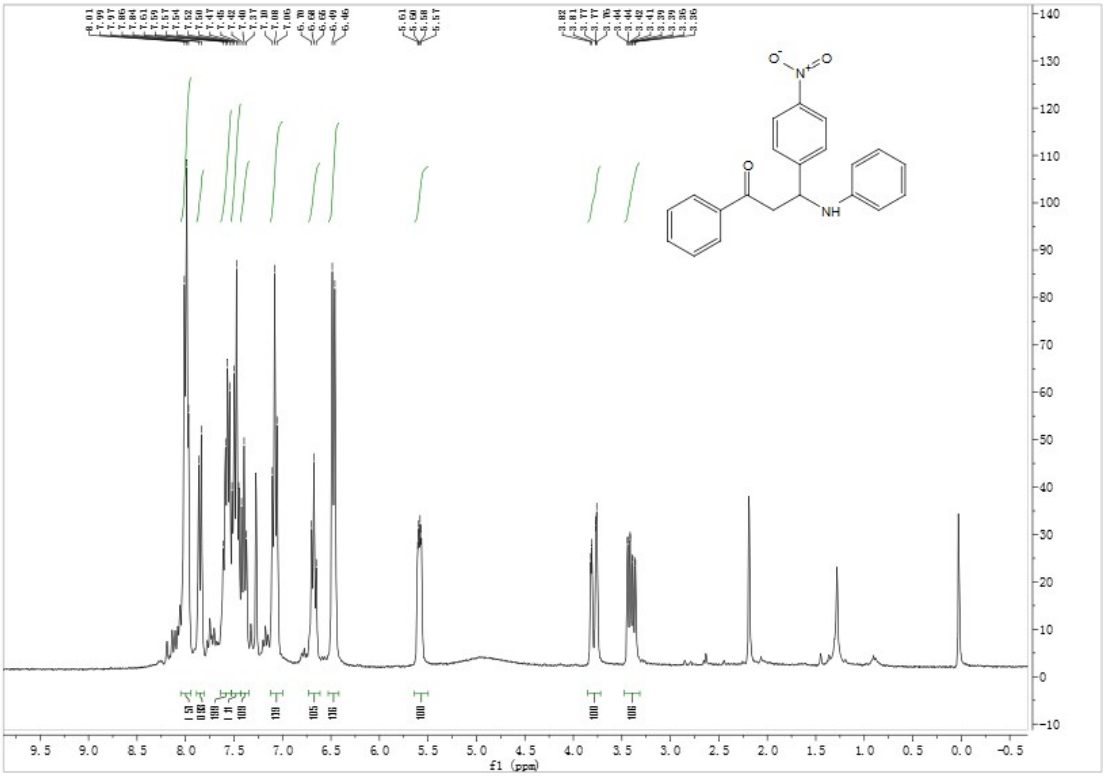

O
NH
Br
f1 (ppm)

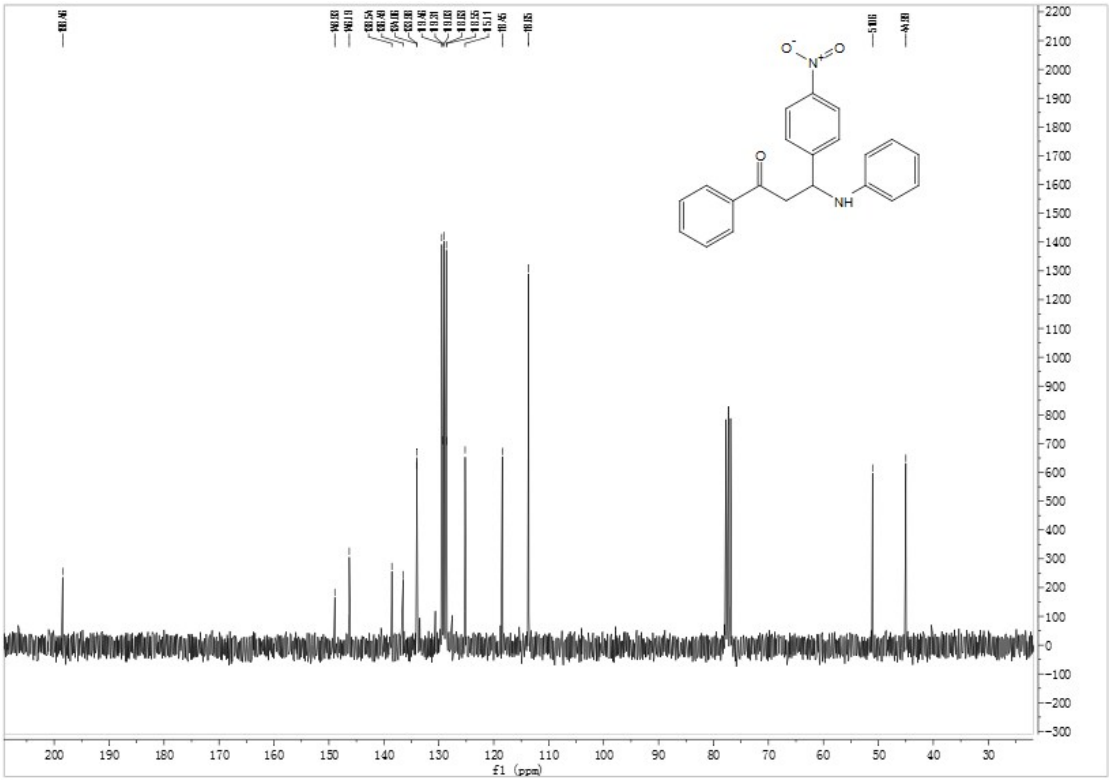

O
NH
CH3
O
f1 (ppm)

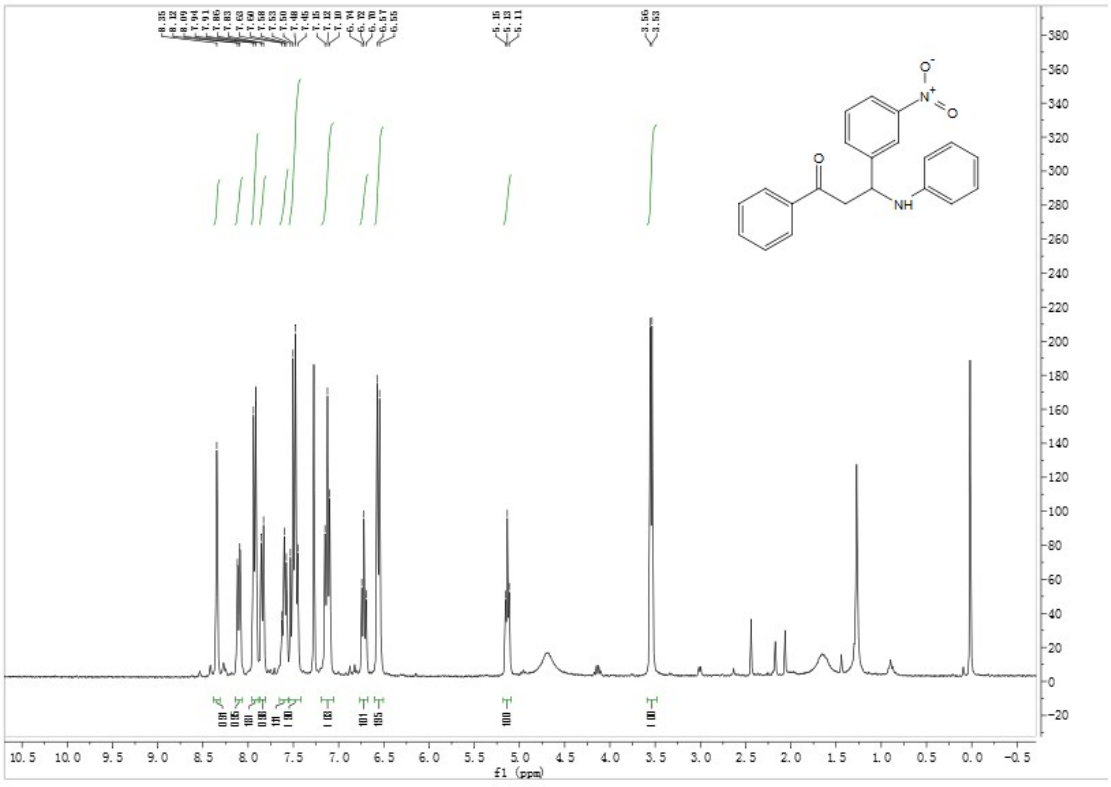

200.85
158.67
147.43
143.51
134.32
130.84
129.25
128.89
127.30
120.60
83.14
117.64
113.87
111.92
56.78
55.21
51.71
O
NH
CH3
O
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

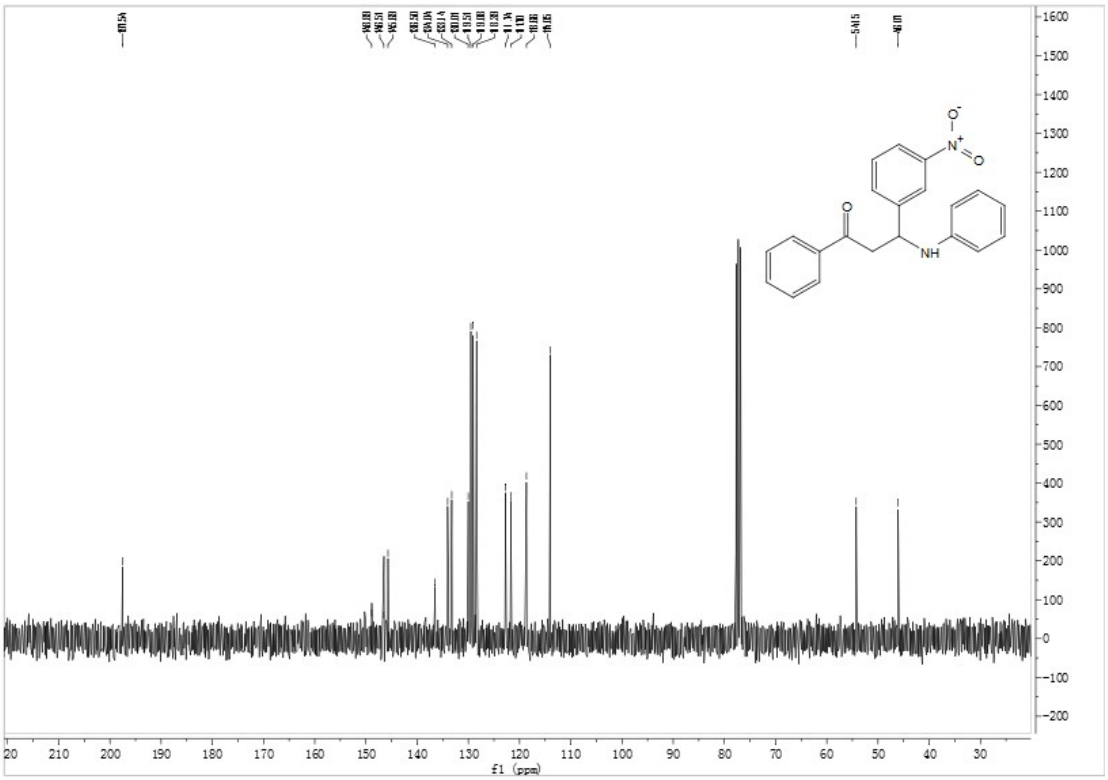

7.42
7.39
7.37
7.35
7.34
7.33
7.30
7.29
7.27
7.26
7.24
7.21
7.13
7.12
7.10
7.09
7.08
7.07
4.85
4.83
4.67
2.84
2.79
2.77
2.76
2.44
2.37
2.08
1.92
1.89
1.76
1.74
1.72
1.70
1.68
1.64
1.63
1.61
O
NH
1.83
1.71
1.94
1.61
1.08
1.00
0.78
0.88
1.08
1.30
3.15
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

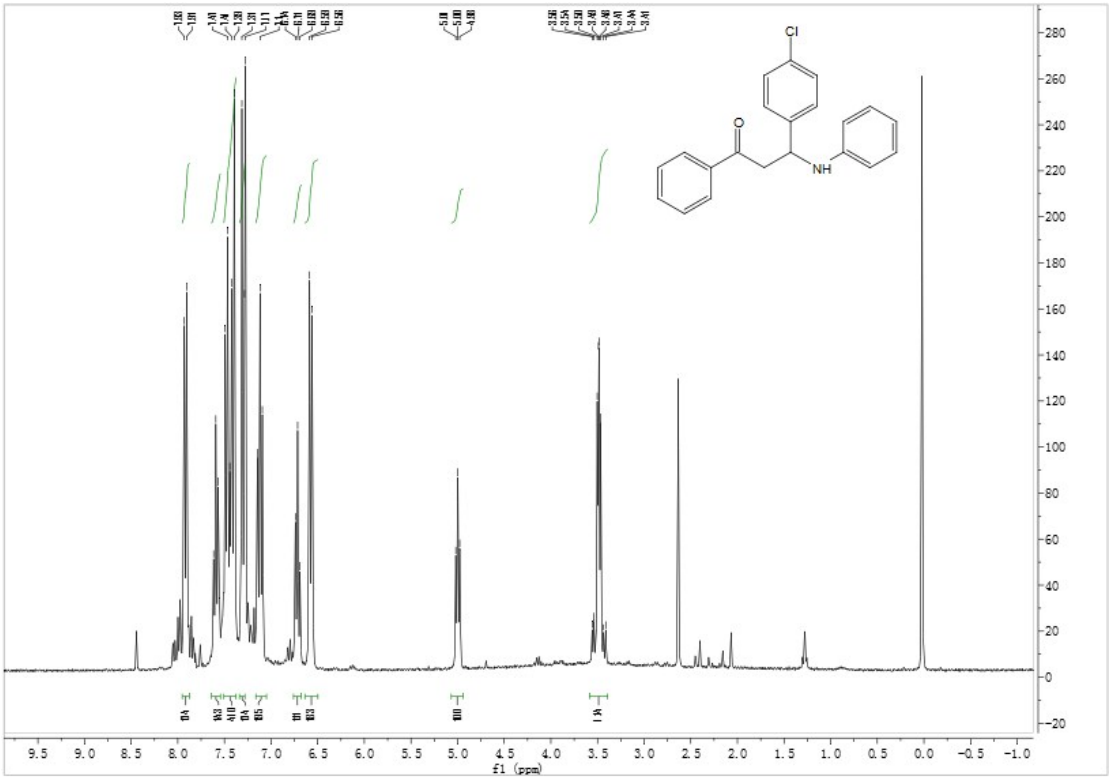

O
NH
f1 (ppm)

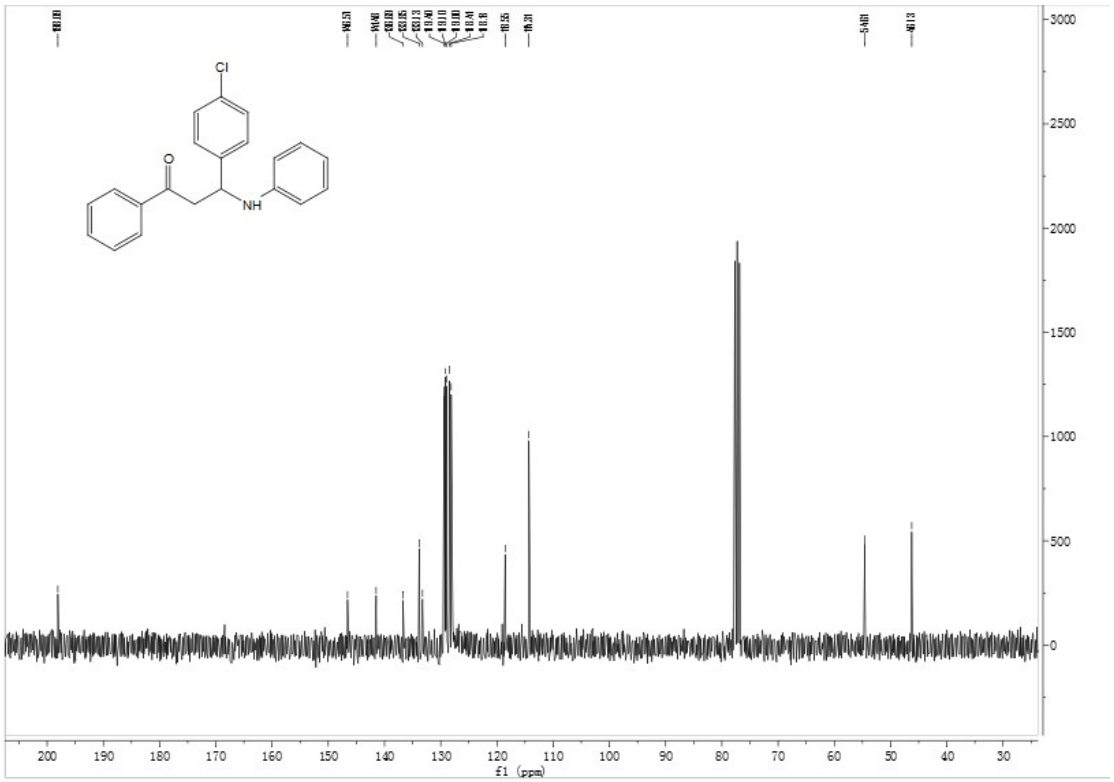

O
N+
O
O
NH
f1 (ppm)

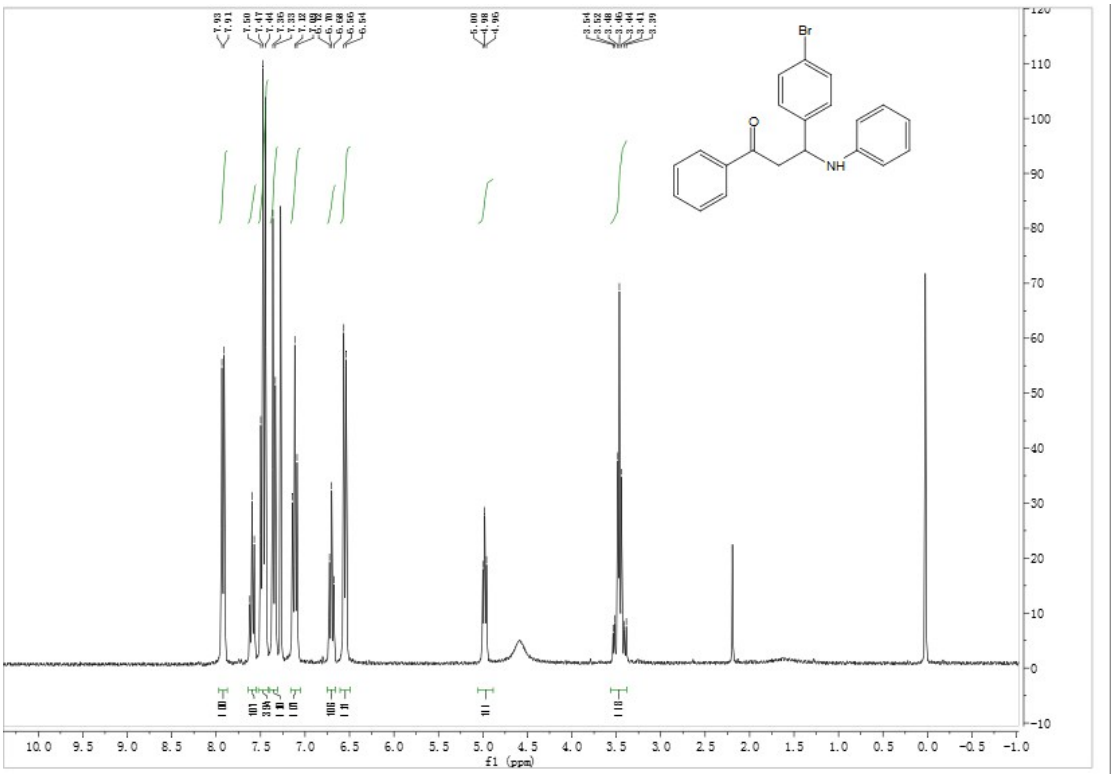

O
NH
f1 (ppm)

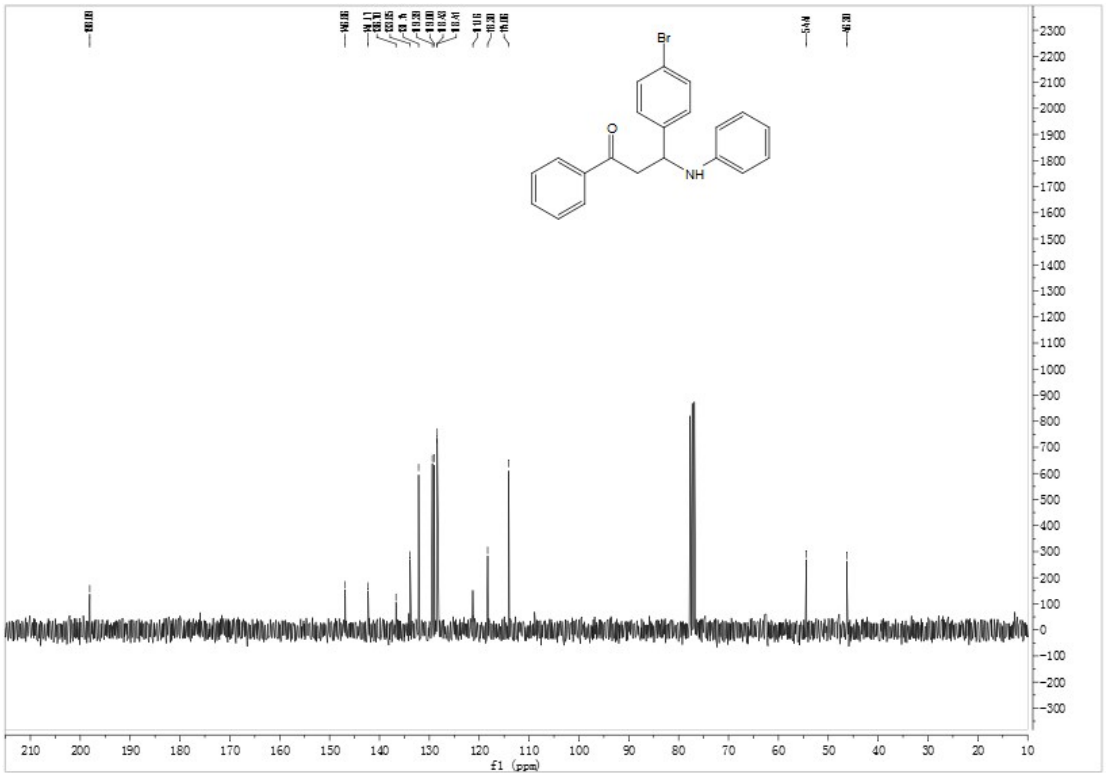

O
NH
f1 (ppm)

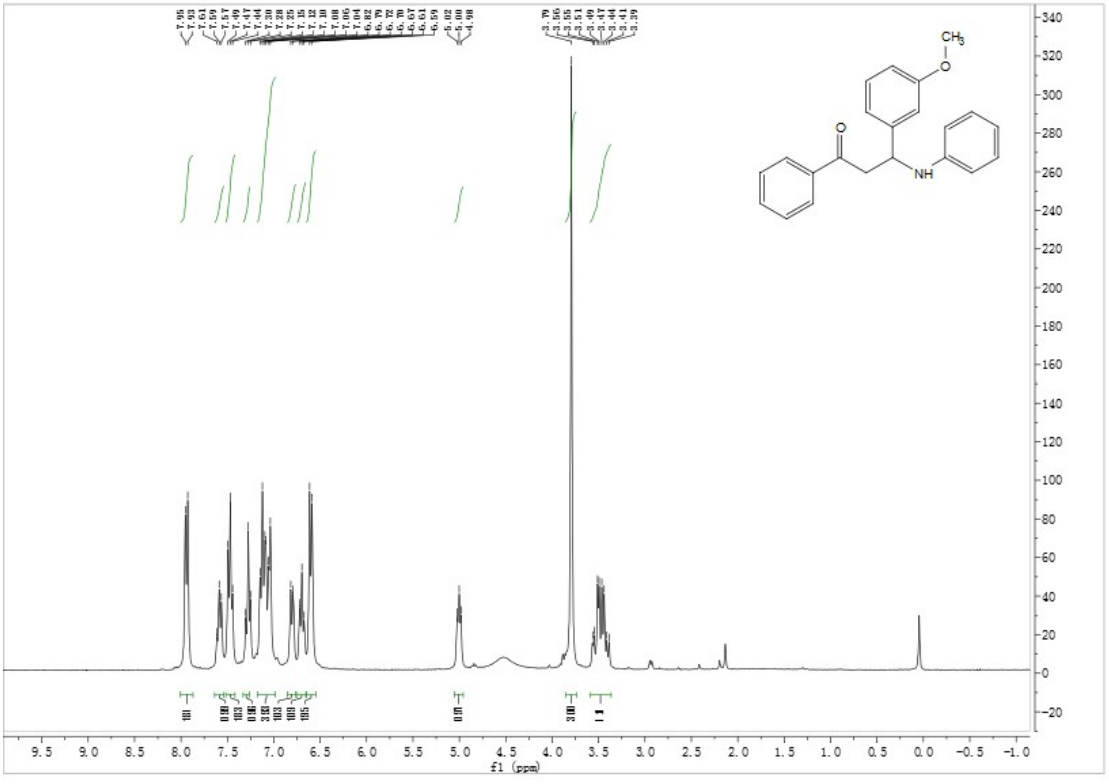

O
N+
O-
O
NH
f1 (ppm)

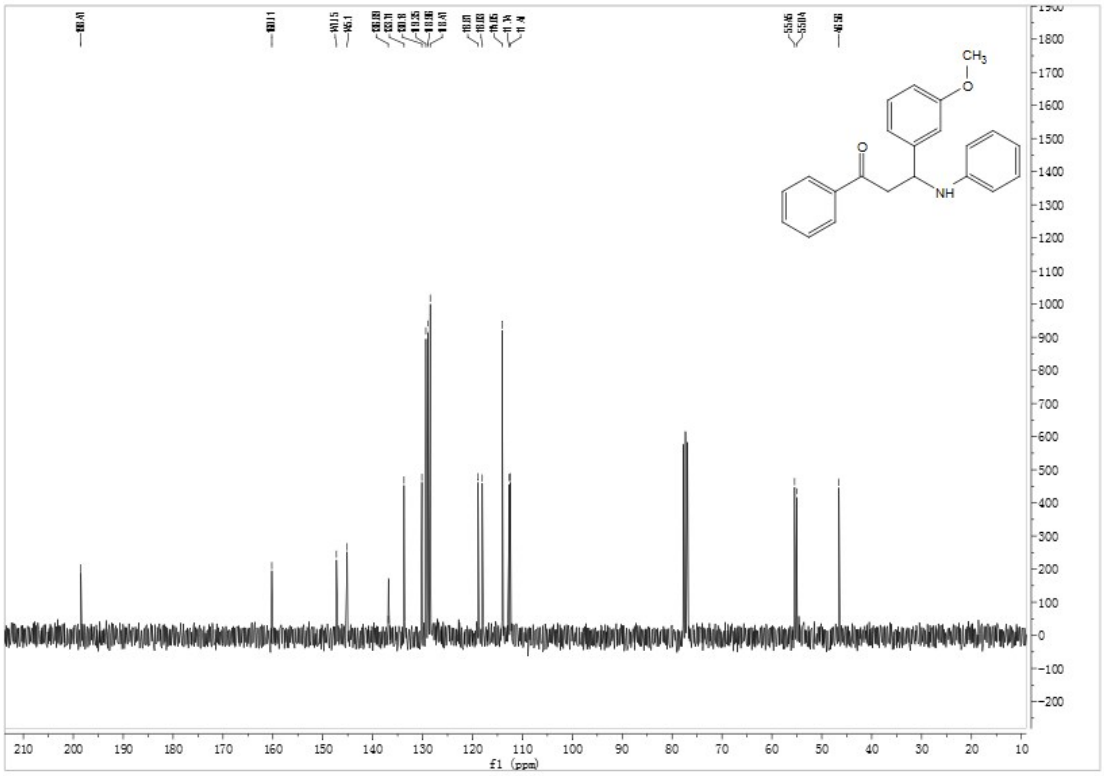

Cl
O
NH
f1 (ppm)

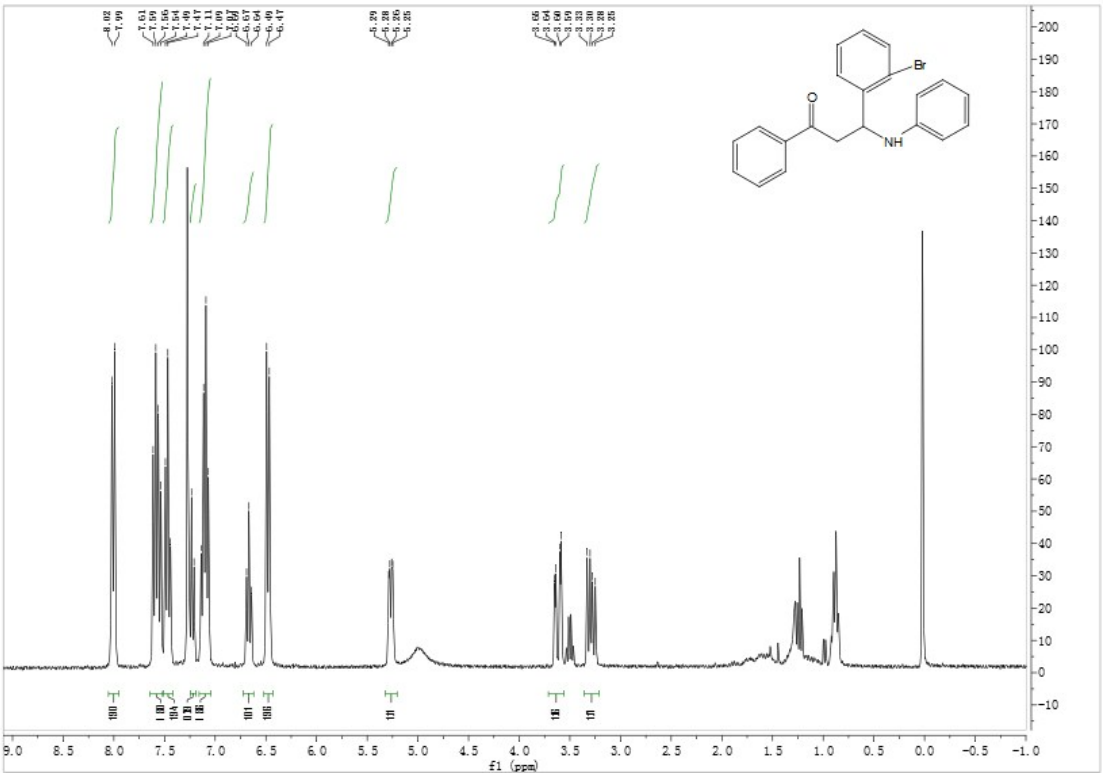

Cl
O
NH
f1 (ppm)

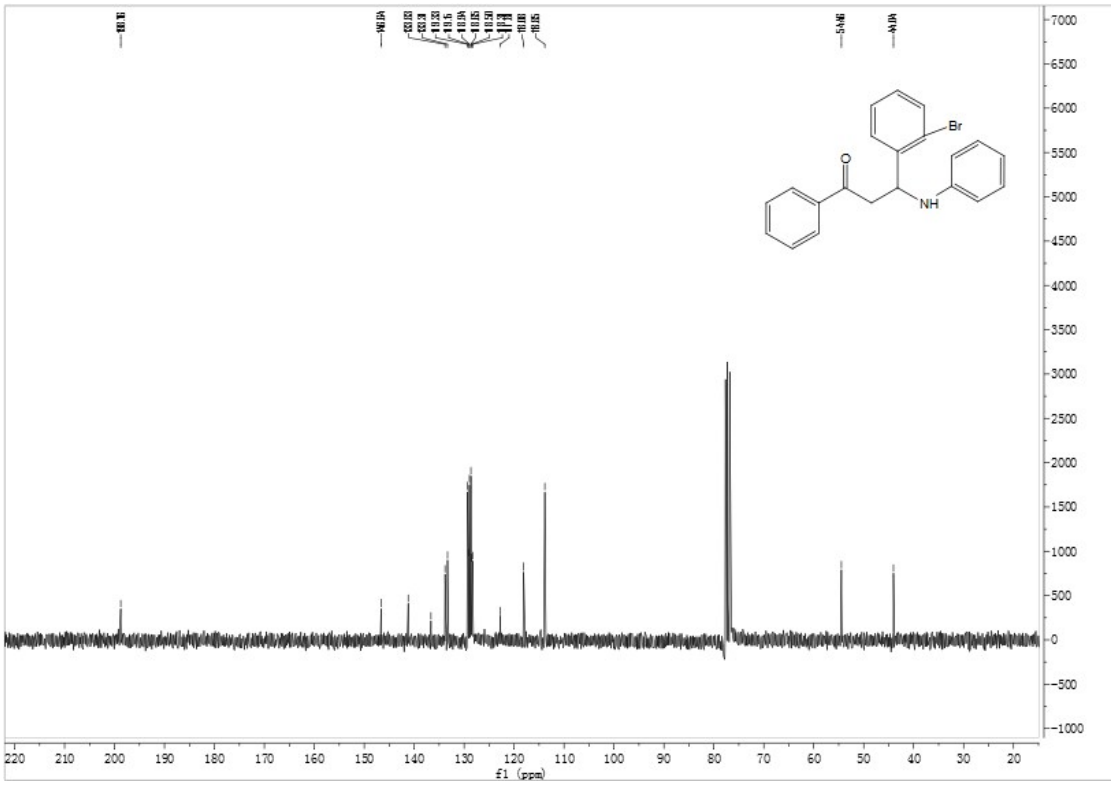

Br
O
NH
f1 (ppm)

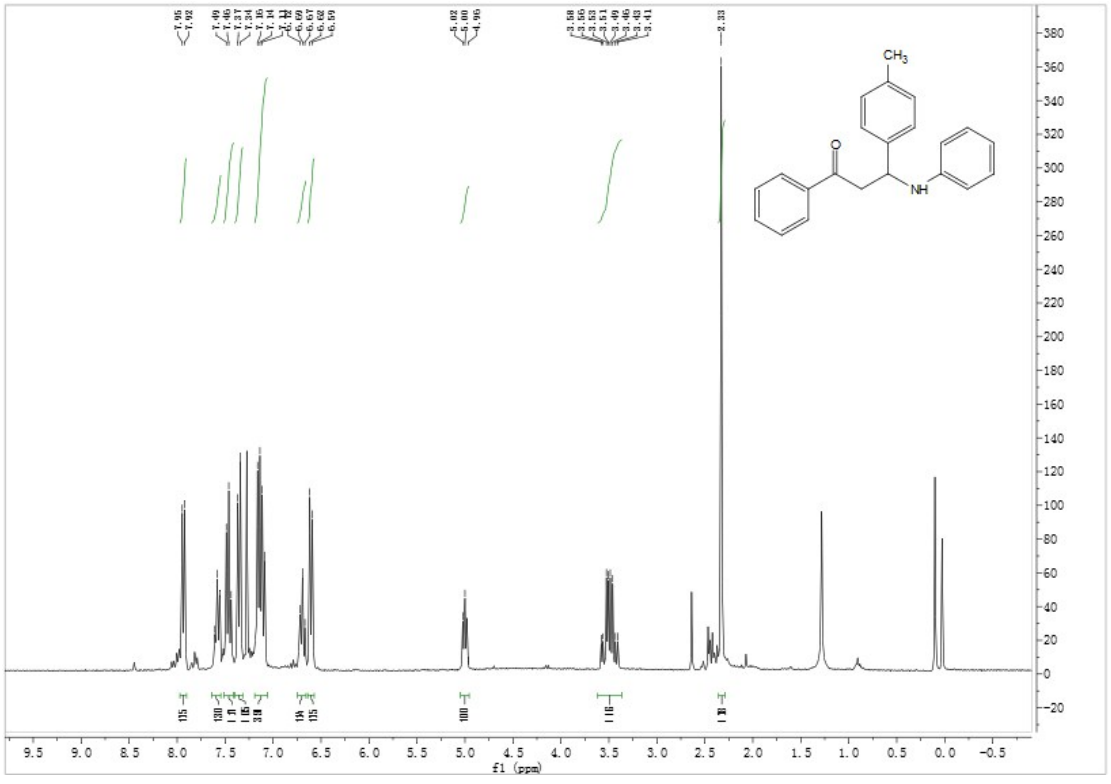

Br
O
NH
f1 (ppm)

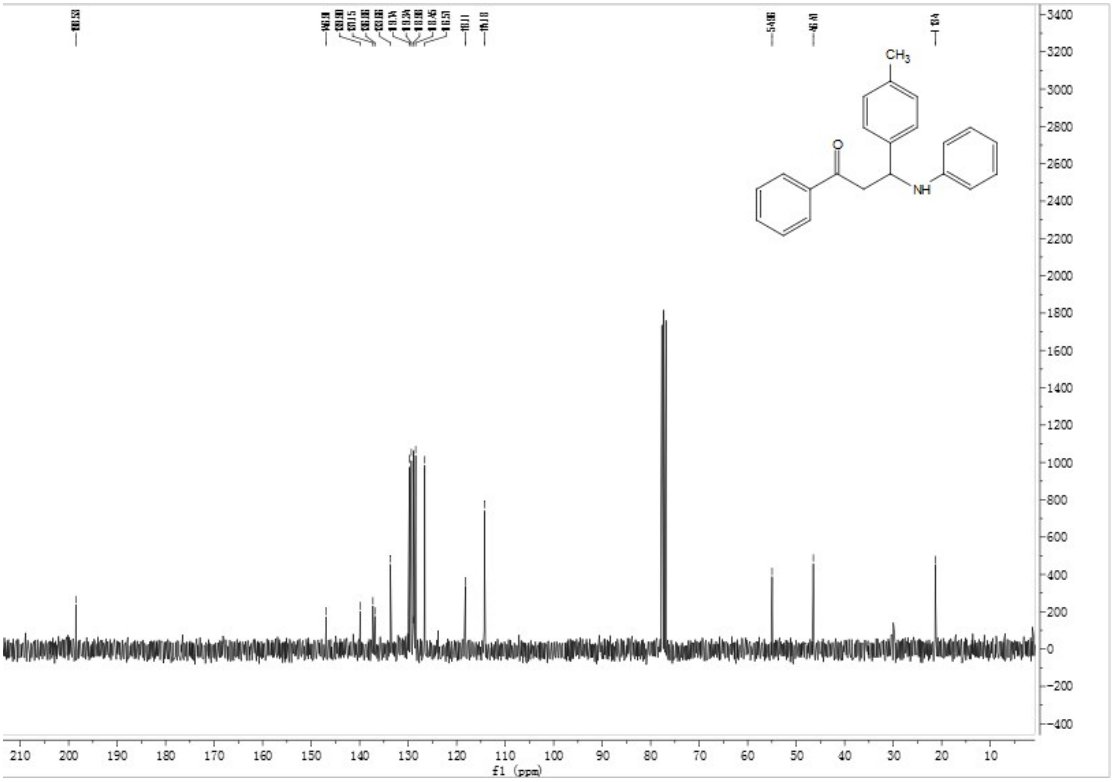

CH3
O
O
NH
f1 (ppm)

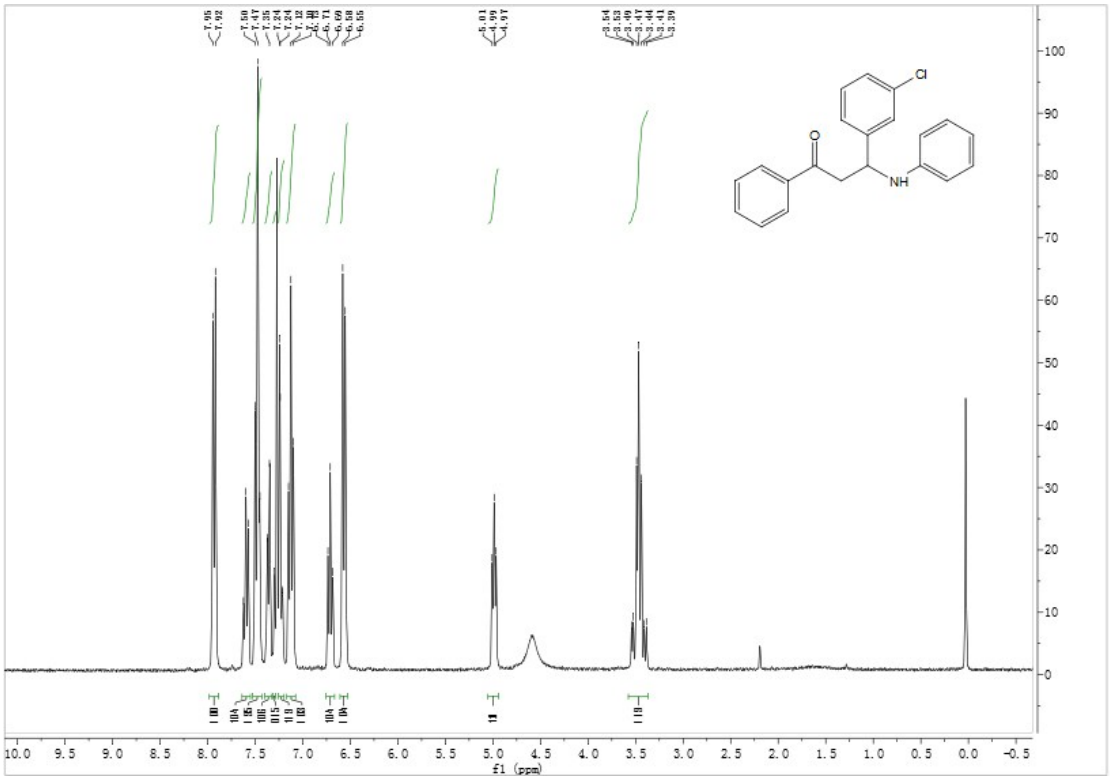

CH3
O
O
NH
f1 (ppm)

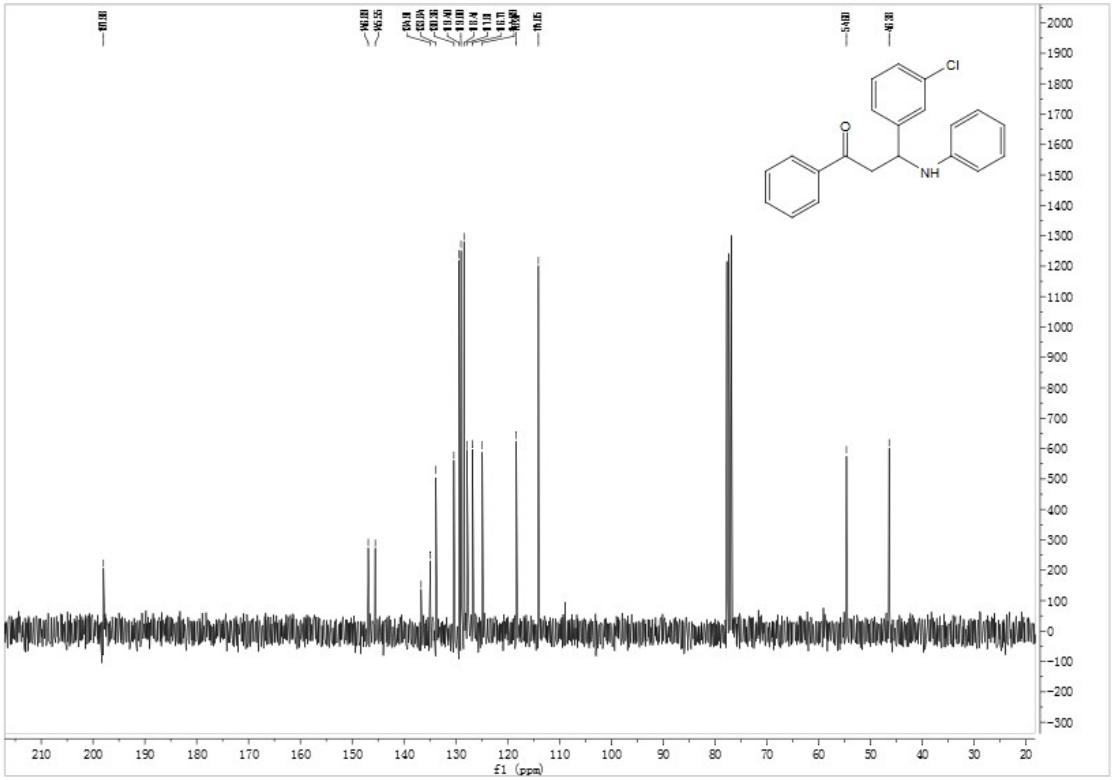

Br
O
NH
f1 (ppm)

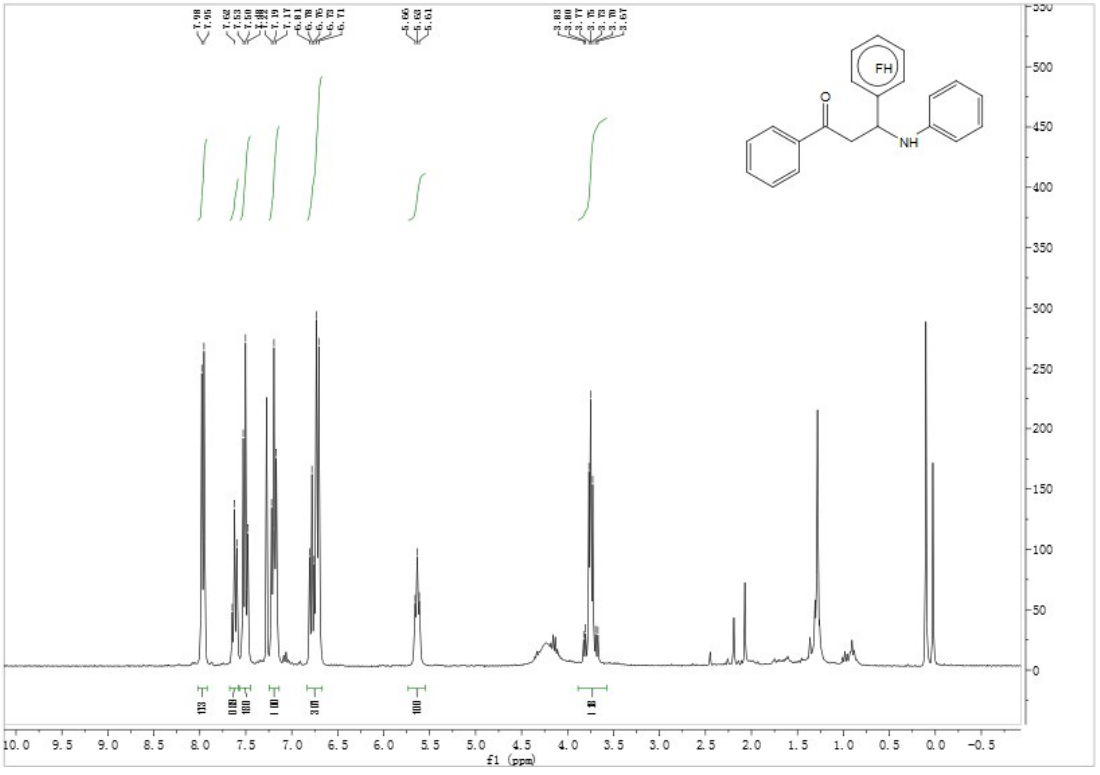

Br
O
NH
f1 (ppm)

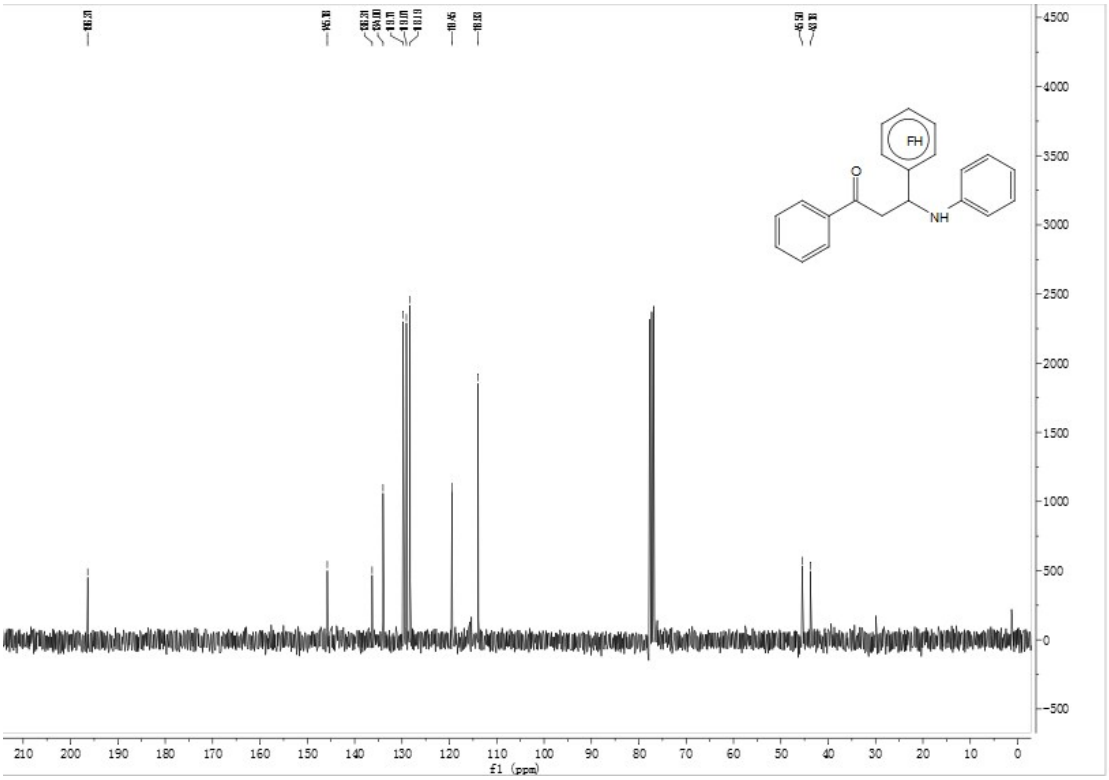

CH3
O
NH
f1 (ppm)

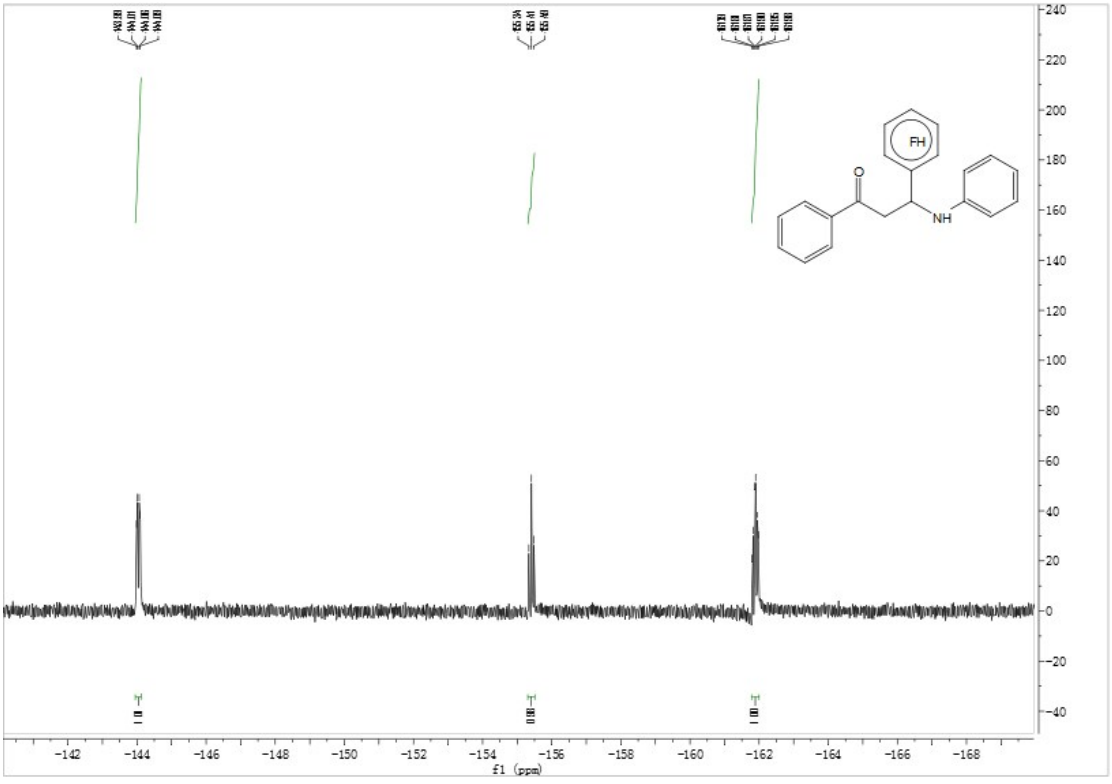

CH3
O
NH
f1 (ppm)

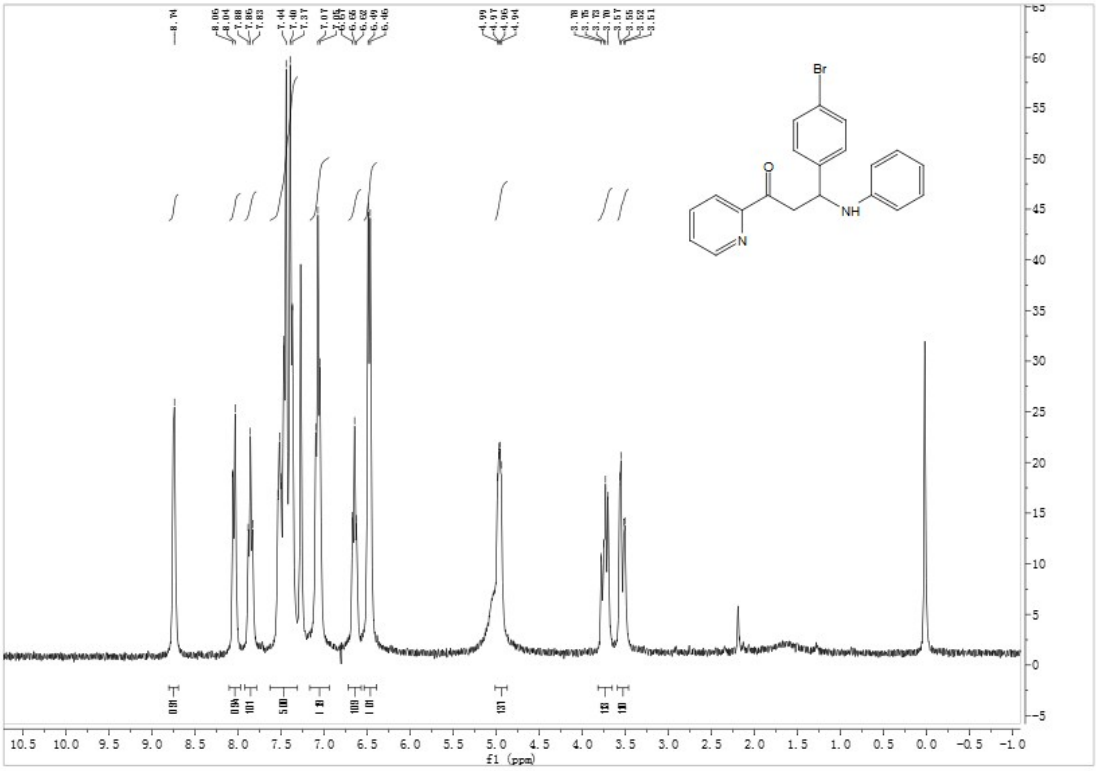

Cl
O
NH
f1 (ppm)

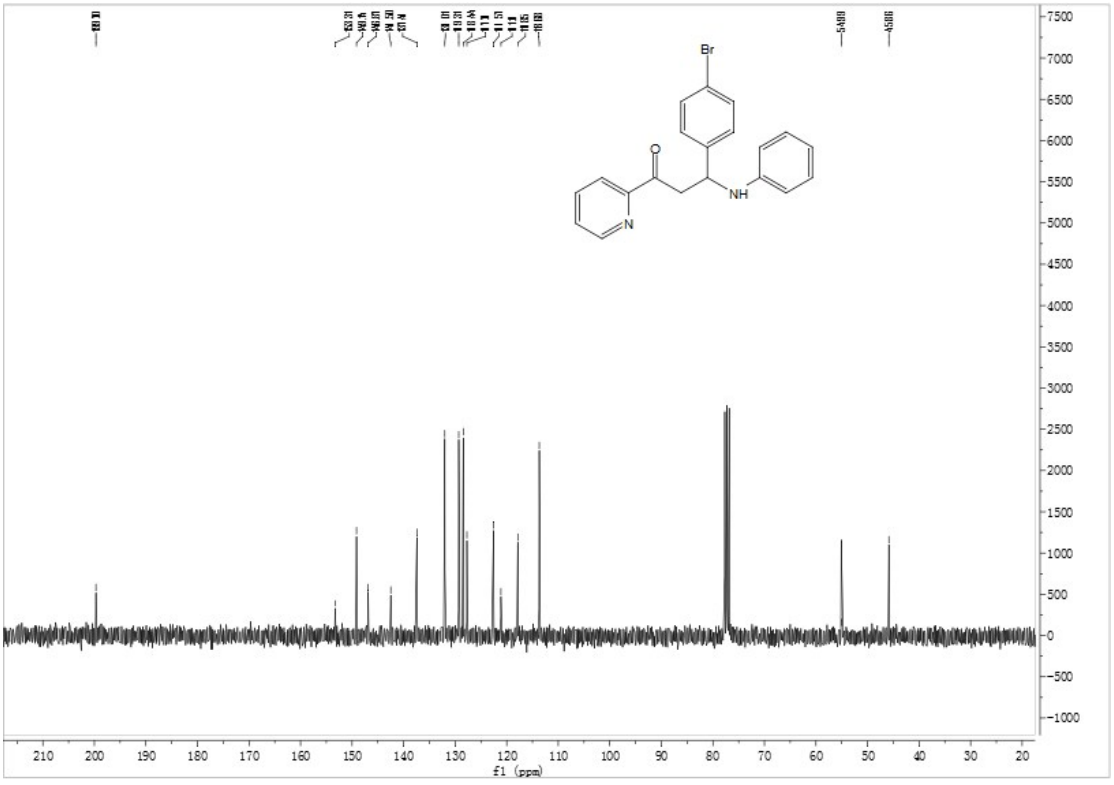

Cl
O
NH
f1 (ppm)

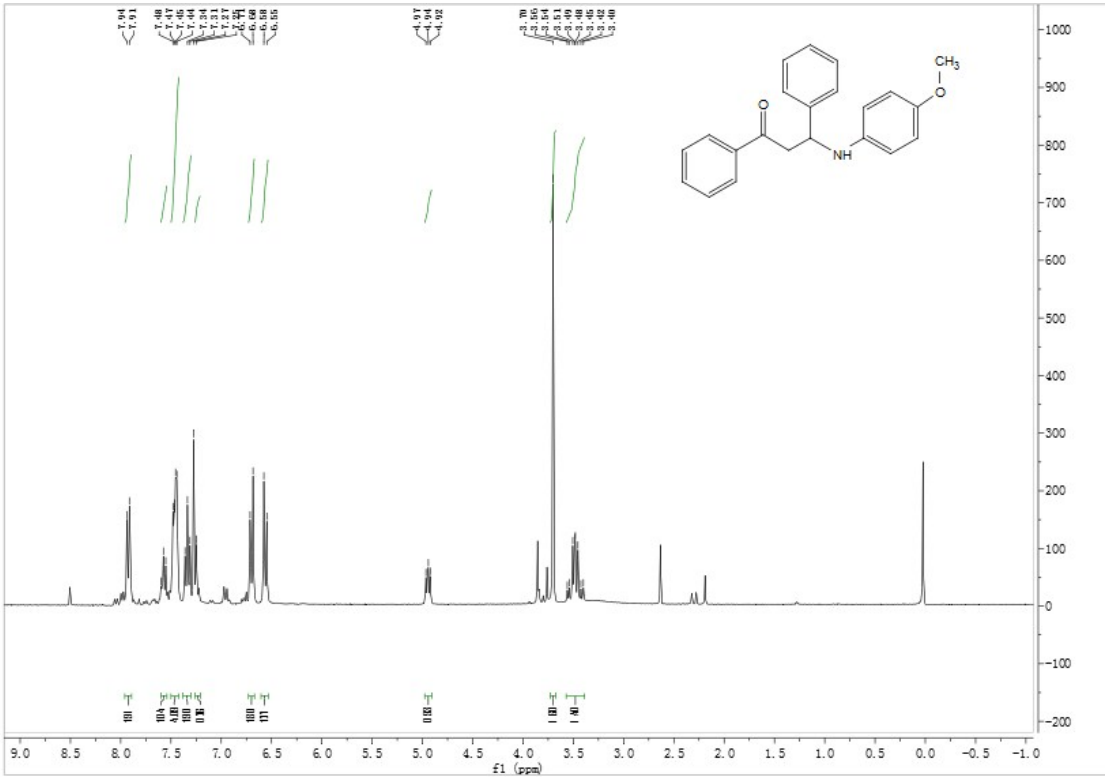

FH
O
NH
f1 (ppm)

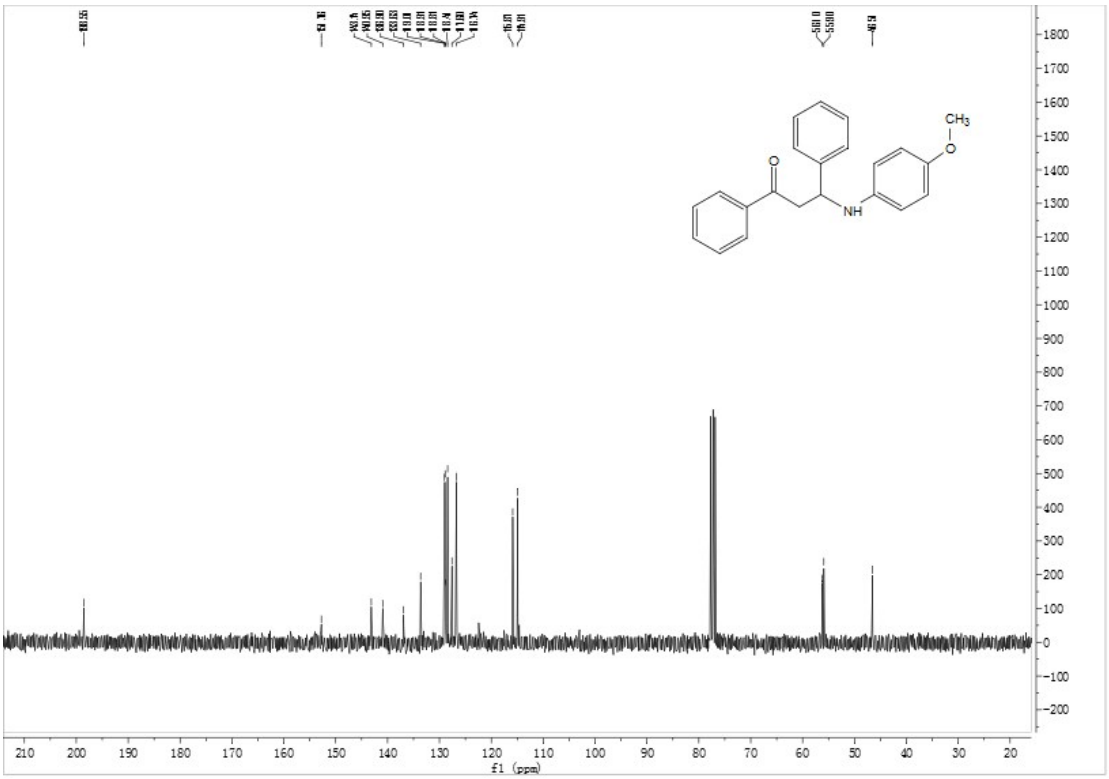

FH
O
NH
f1 (ppm)

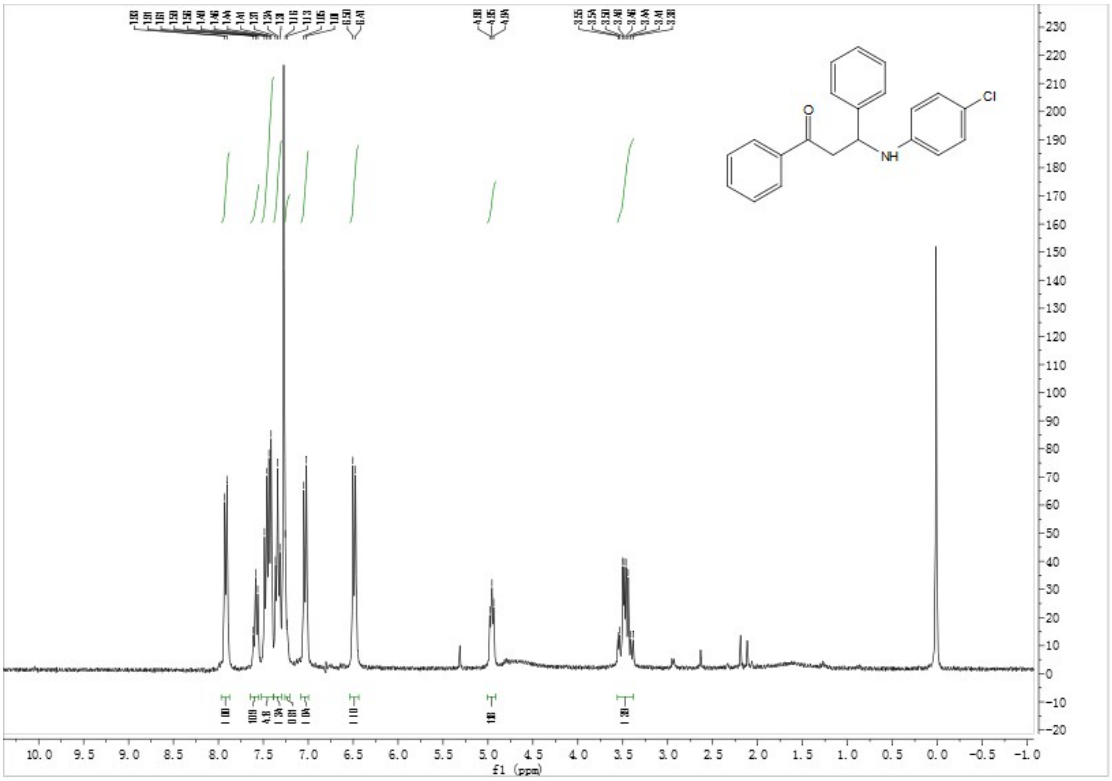

FH
O
NH
f1 (ppm)

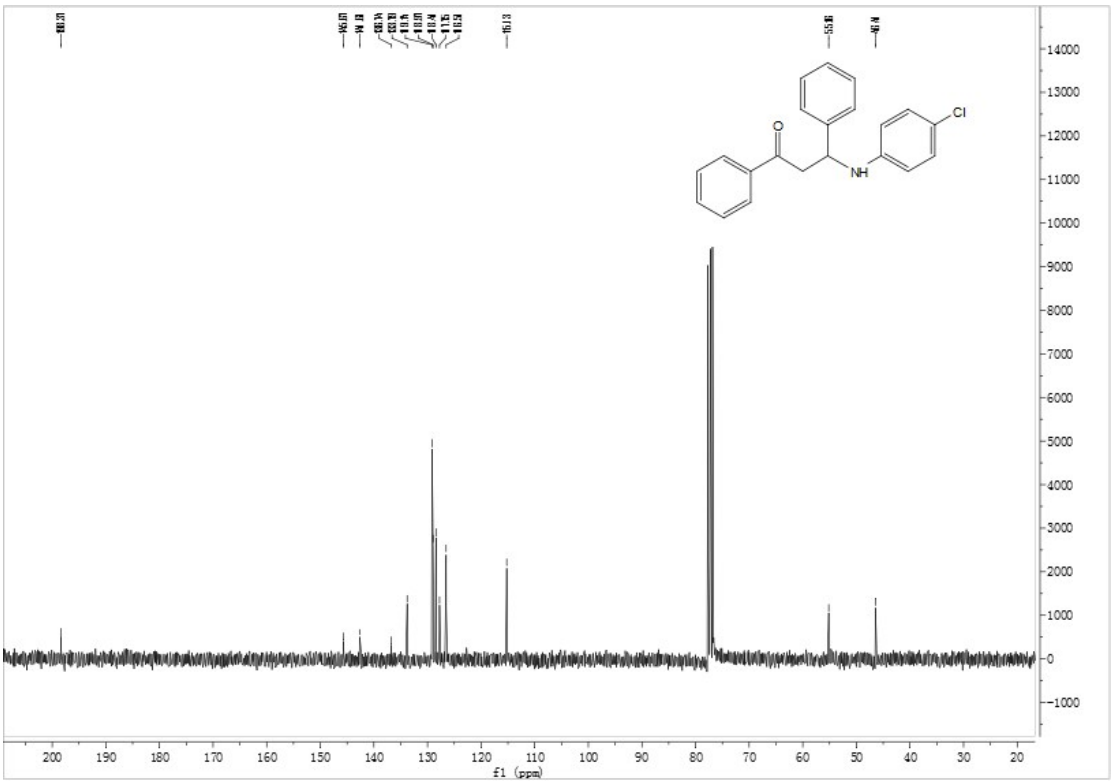

Br
O
NH
N
f1 (ppm)

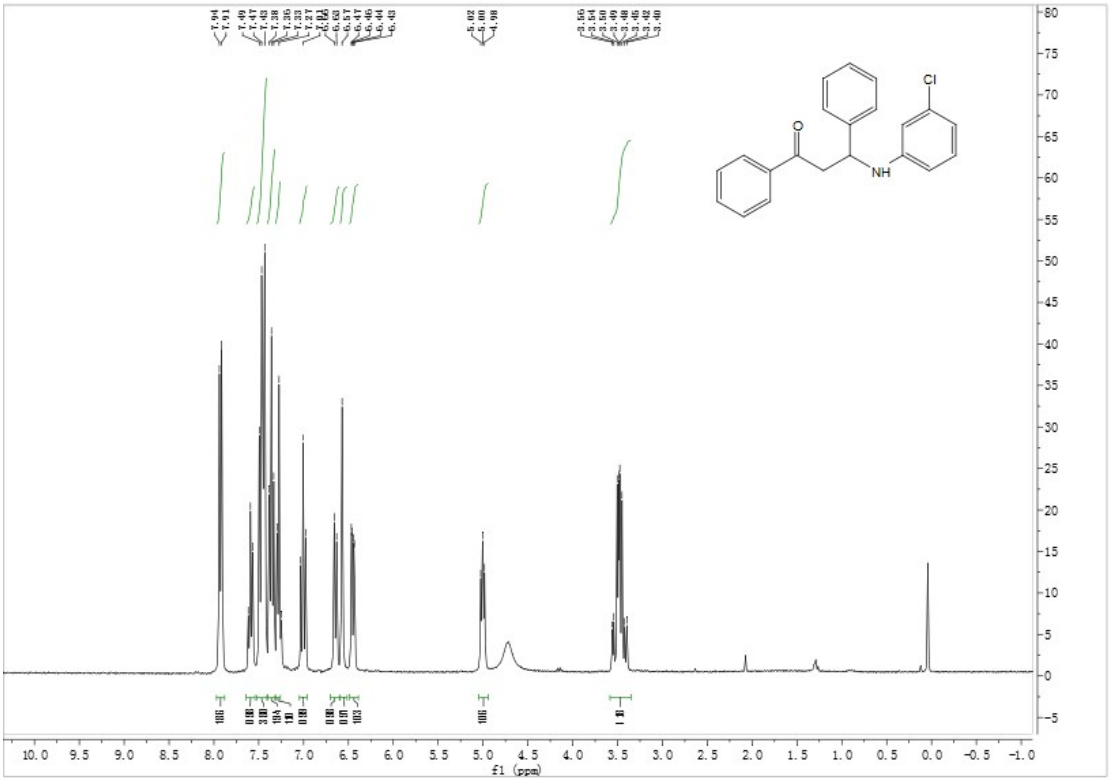

Br
O
NH
N
f1 (ppm)

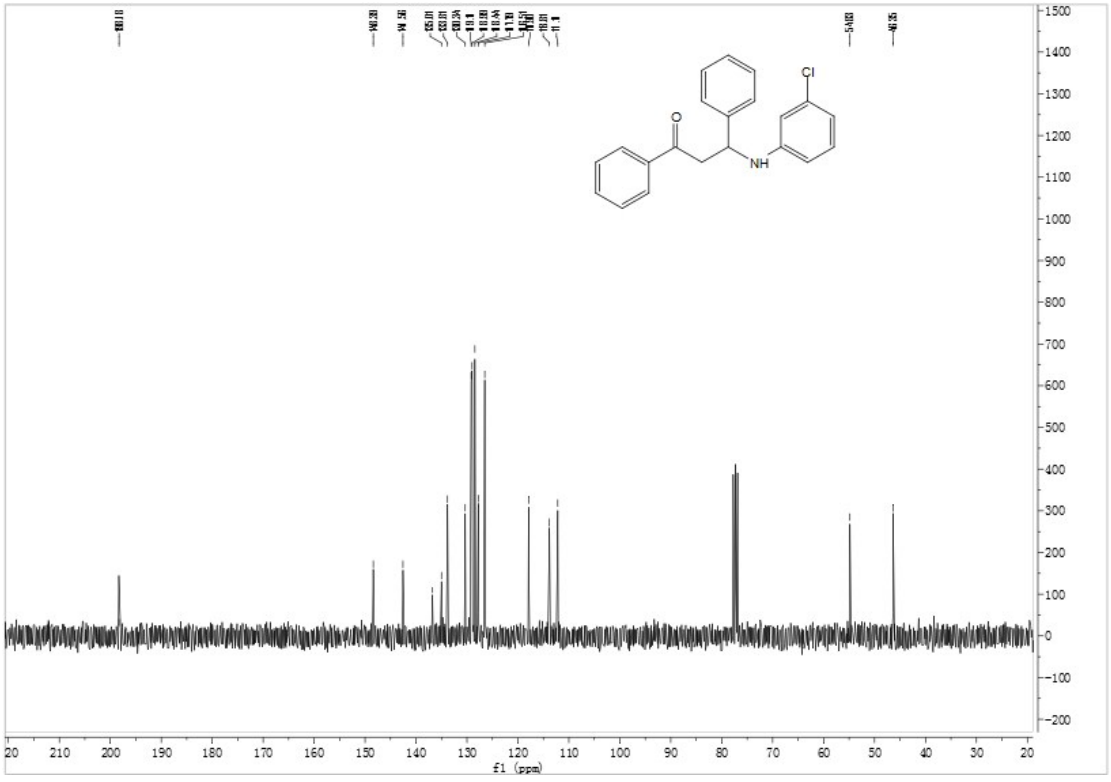

CH3
O
O
NH
f1 (ppm)

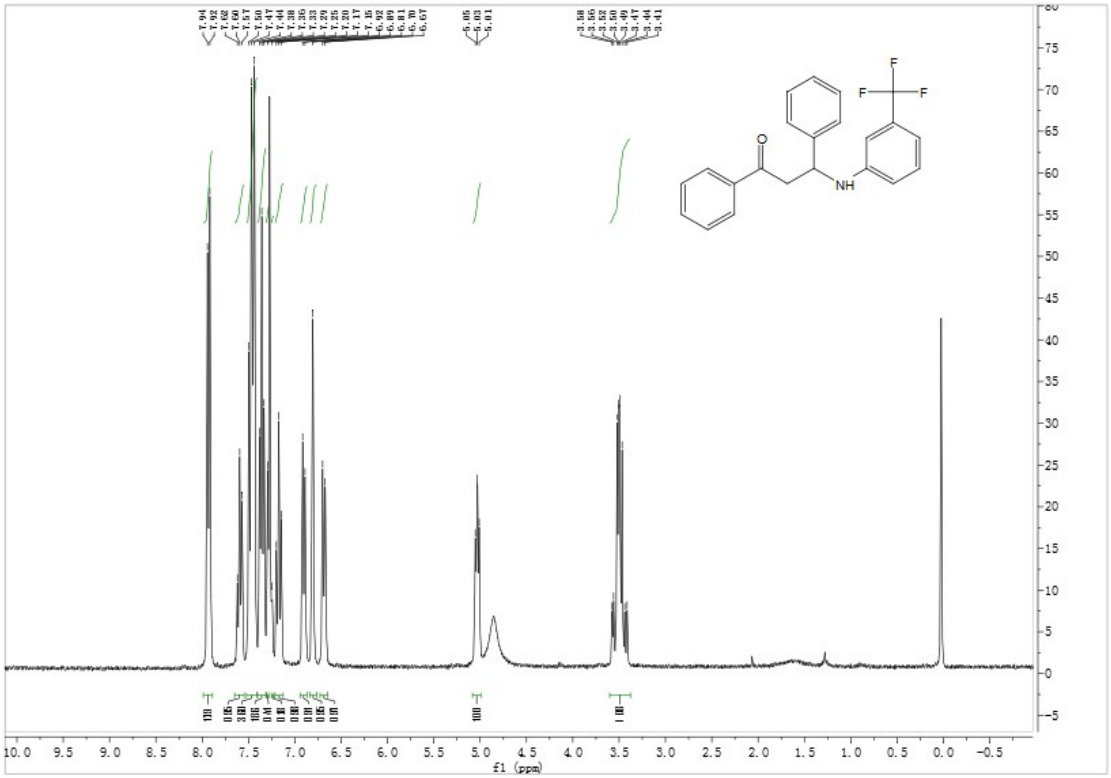

CH3
O
O
NH
f1 (ppm)

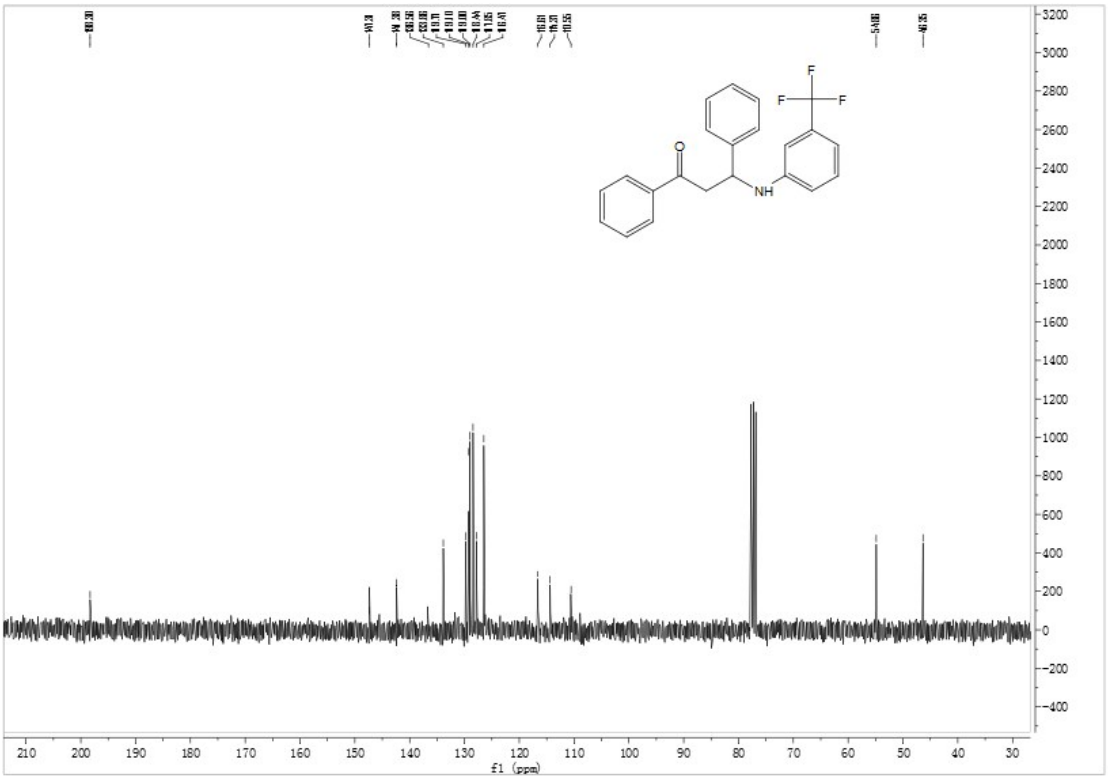

O
NH
Cl
f1 (ppm)

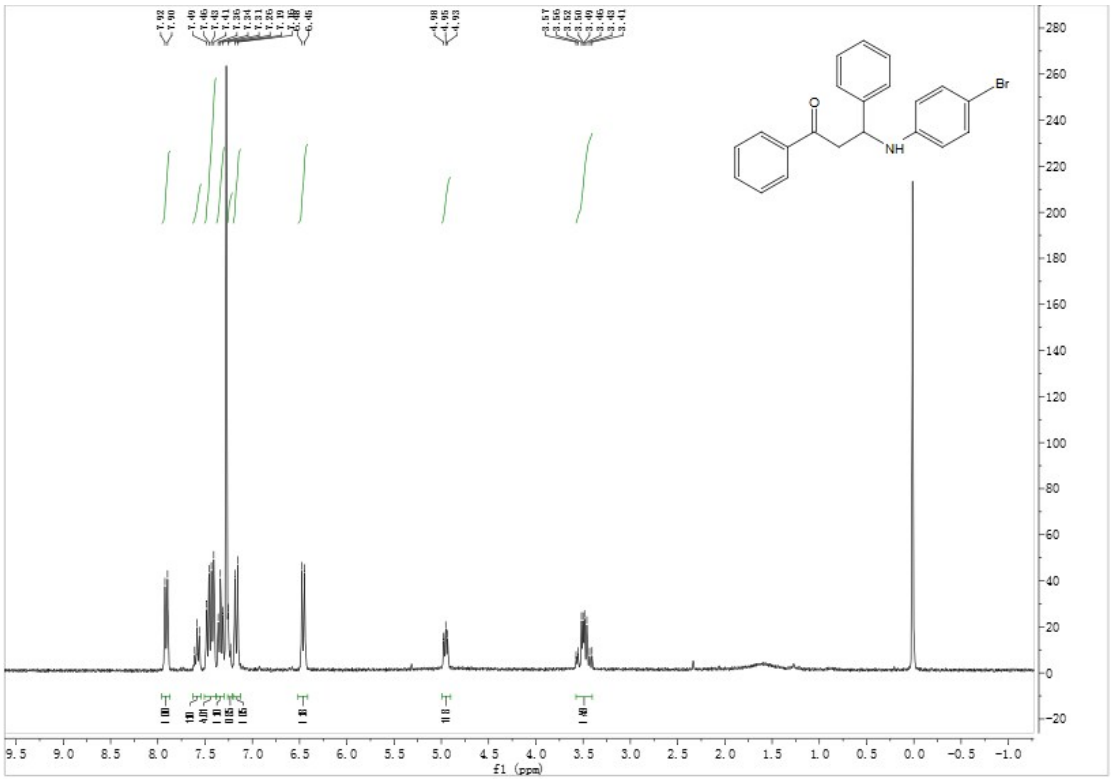

O
NH
Cl
f1 (ppm)

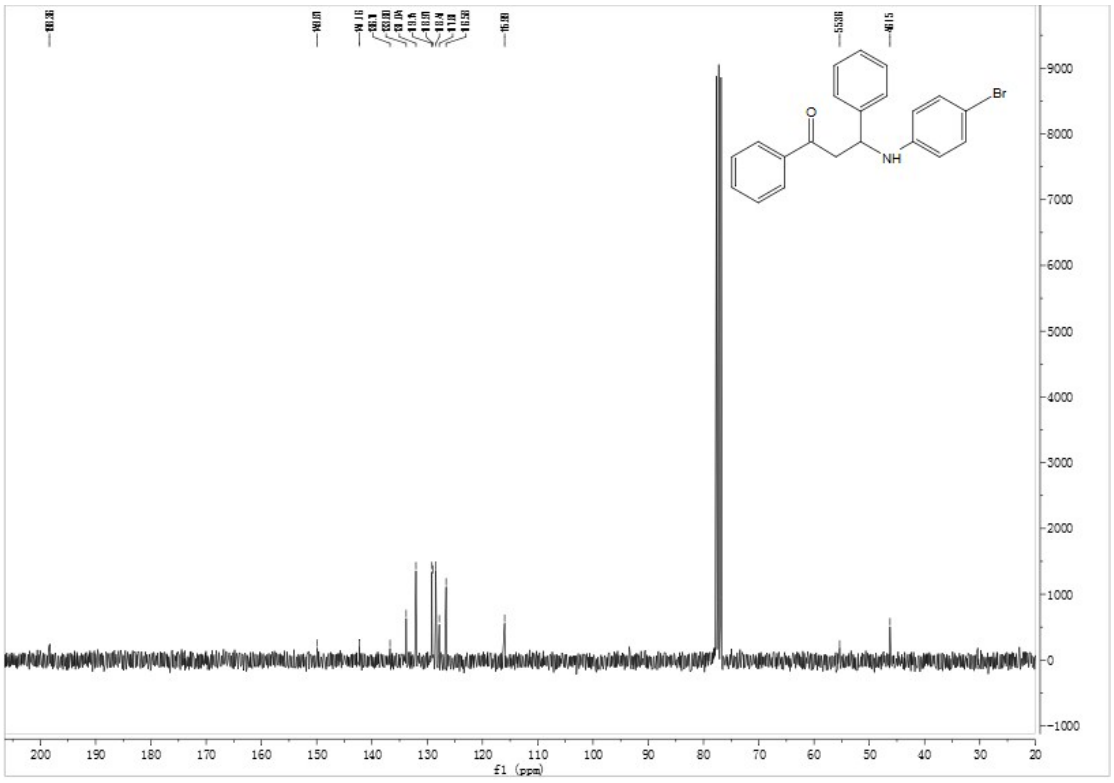

Cl
O
NH
f1 (ppm)

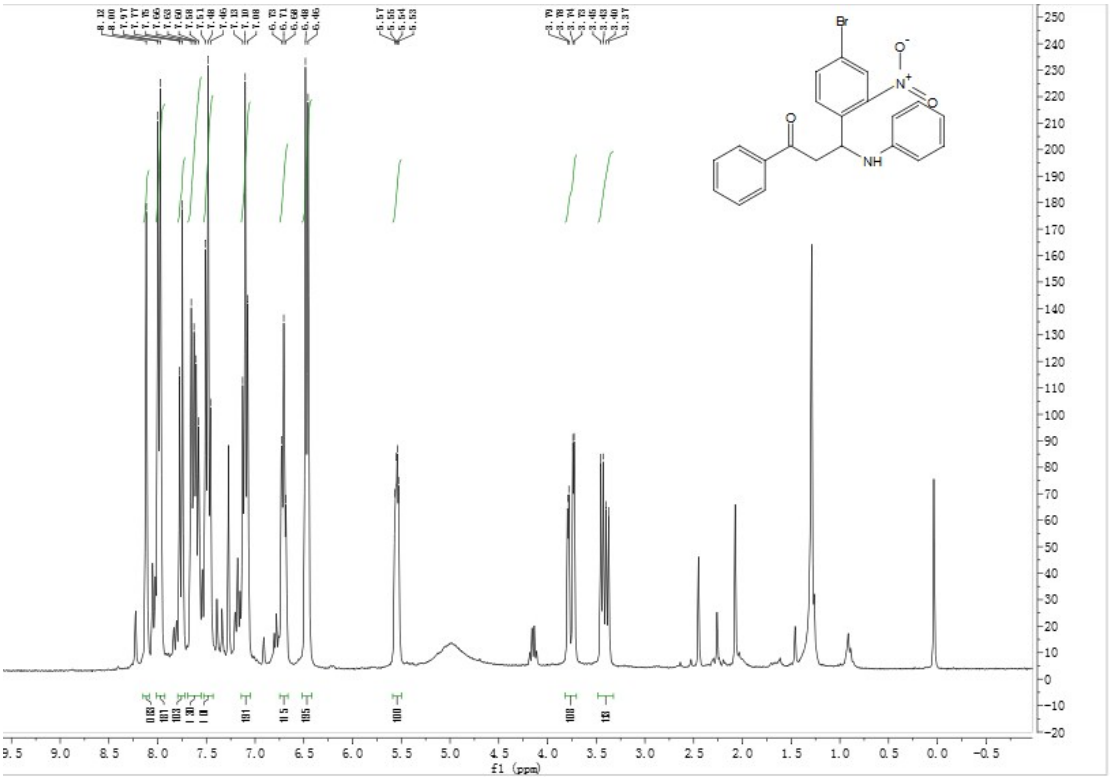

Cl
O
NH
f1 (ppm)

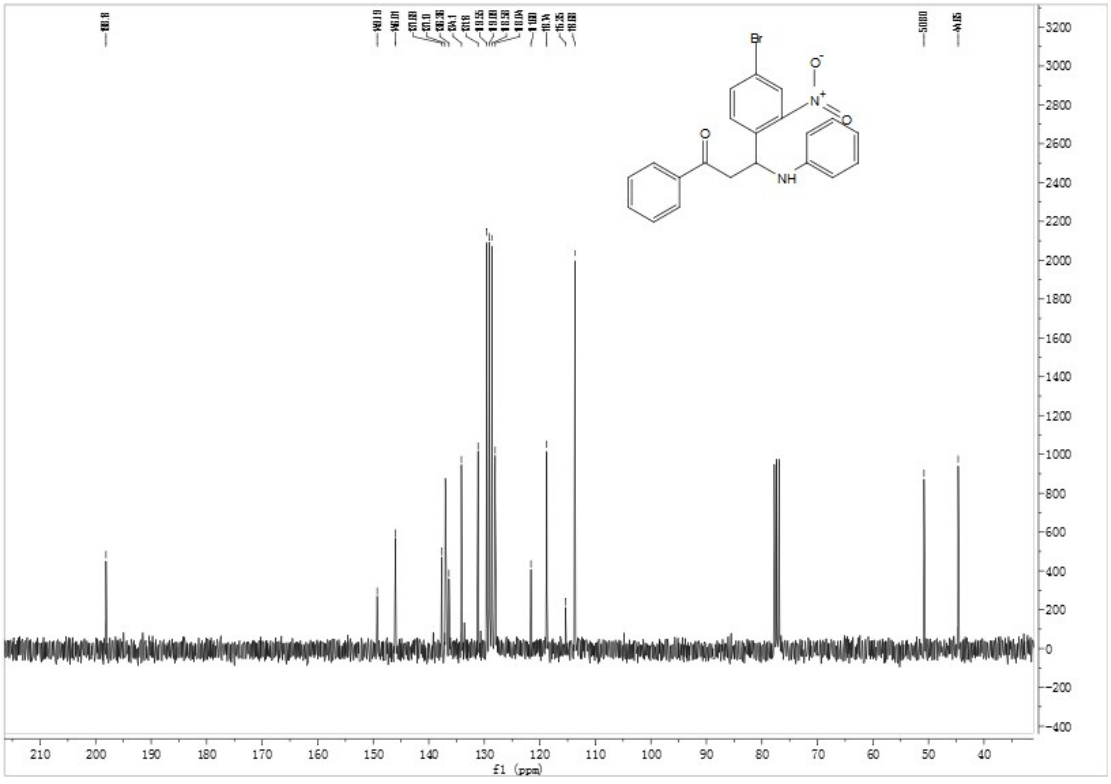

F
F
F
O
NH
f1 (ppm)

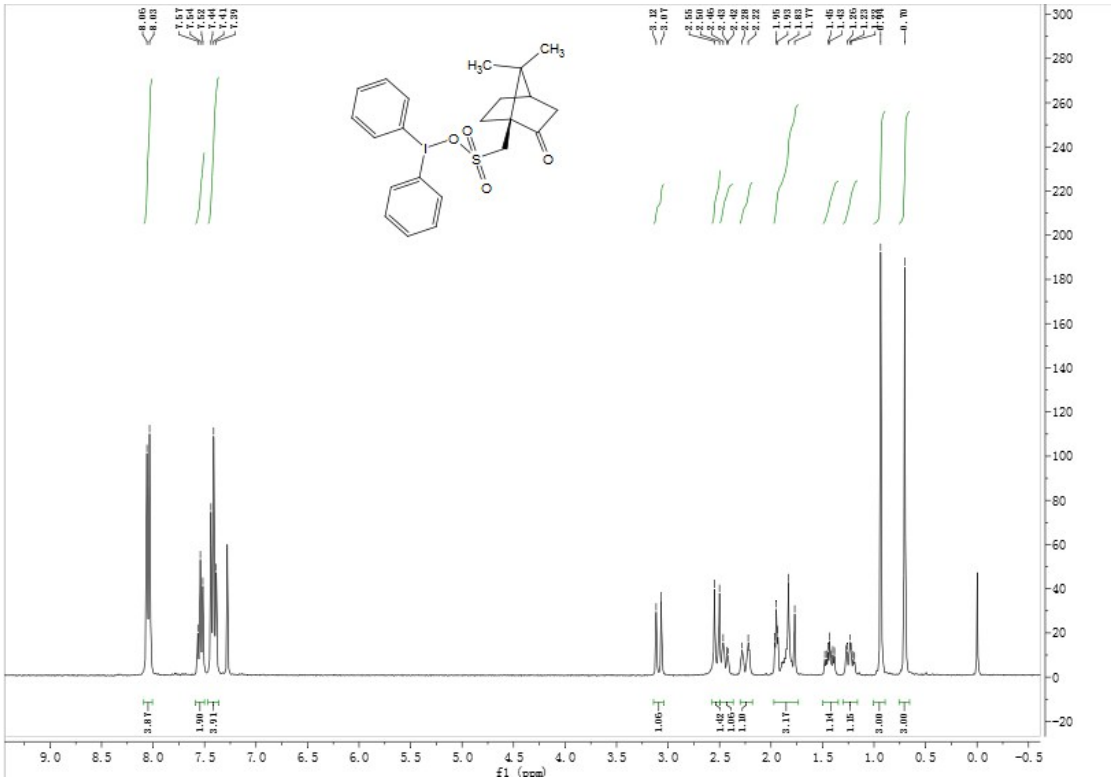

F
F
F
O
NH
f1 (ppm)

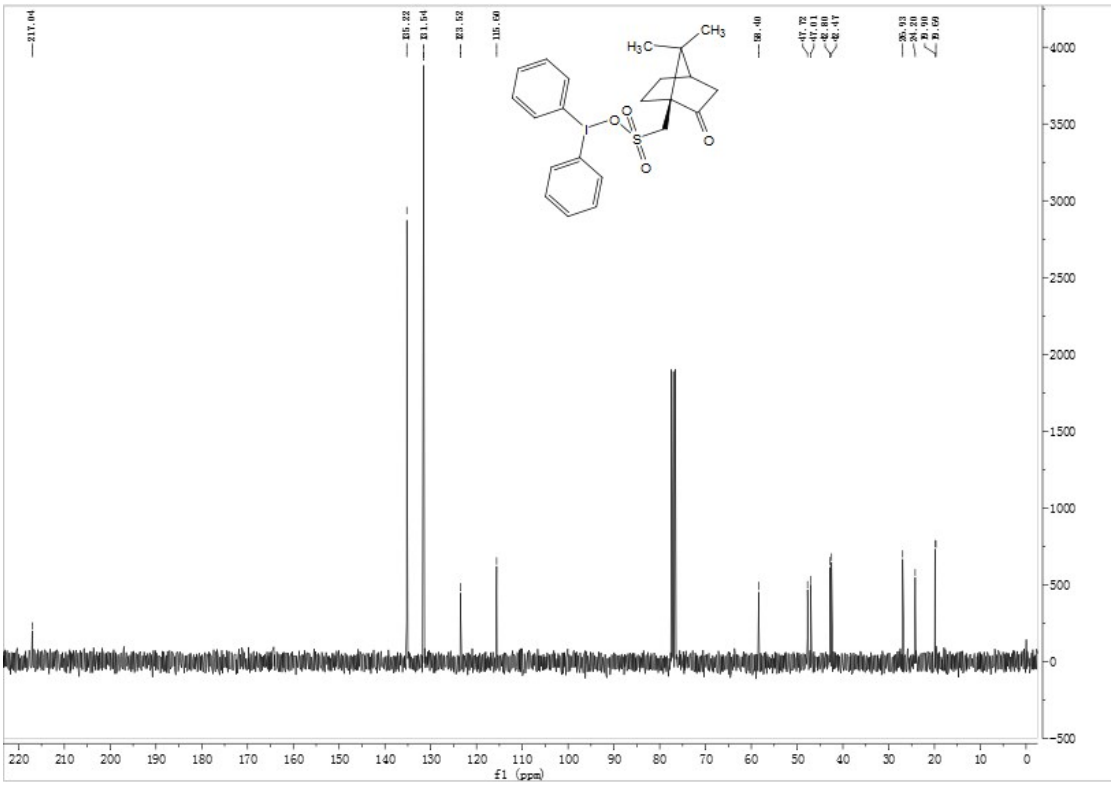

O
NH
Br
f1 (ppm)

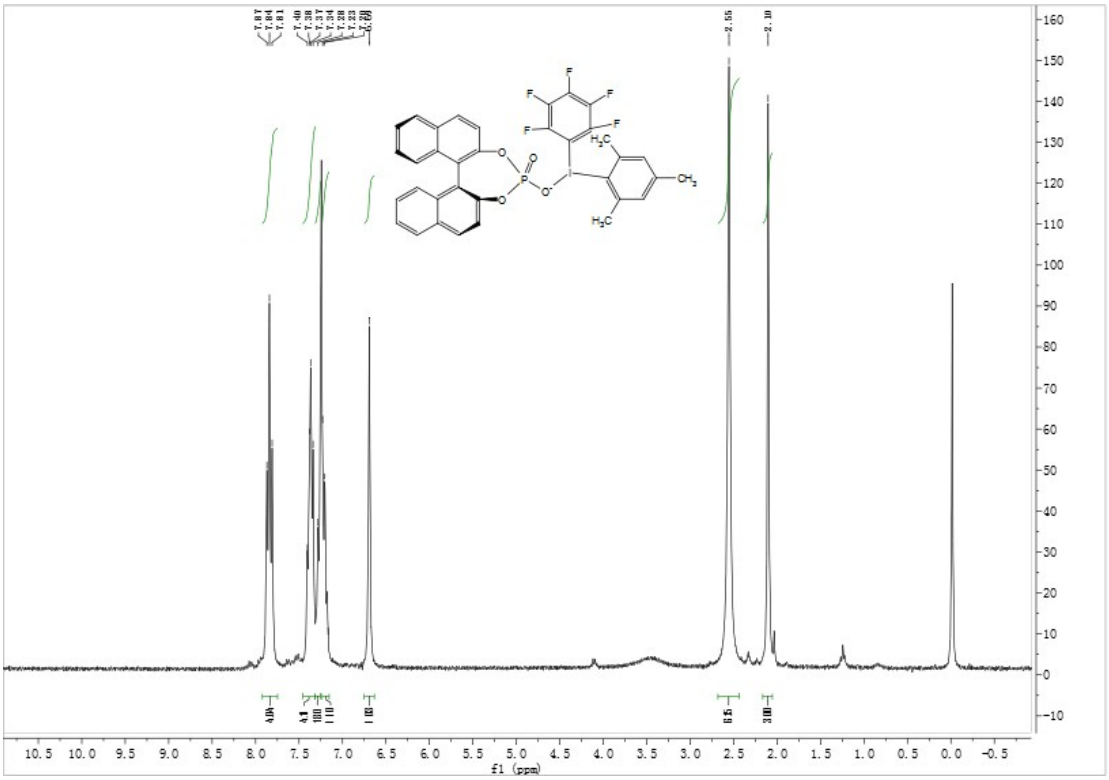

O
NH
Br
f1 (ppm)

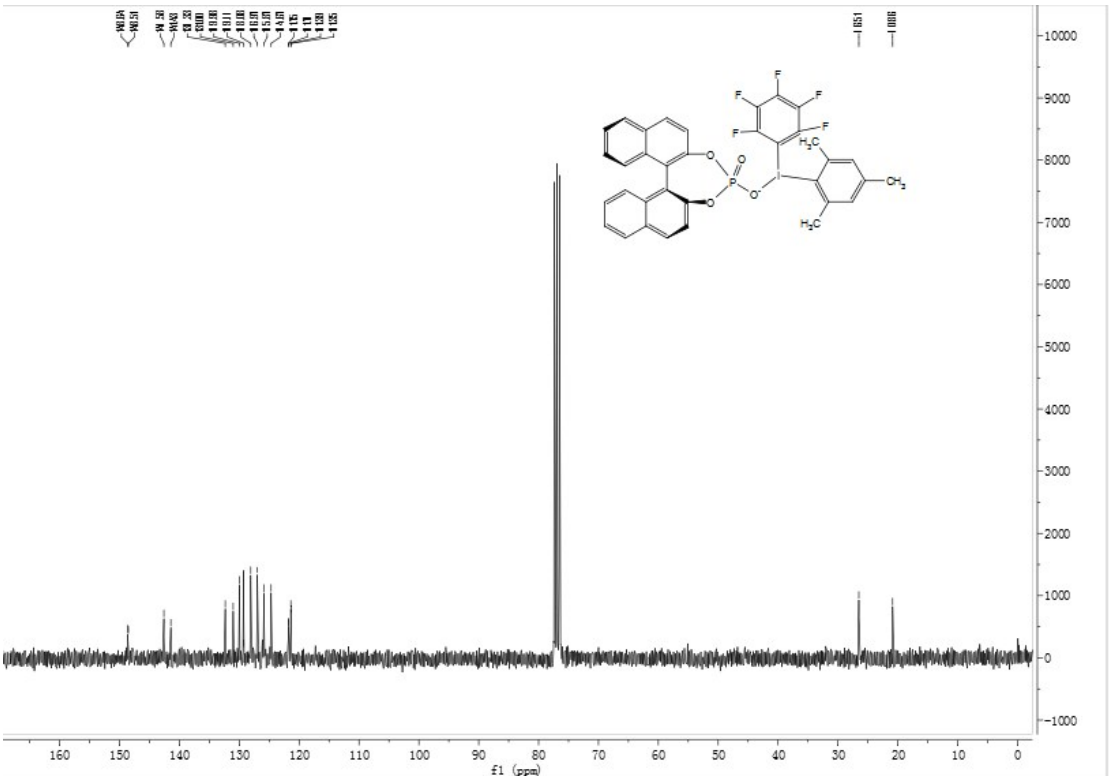

Br
O
N
O
O
NH
f1 (ppm)

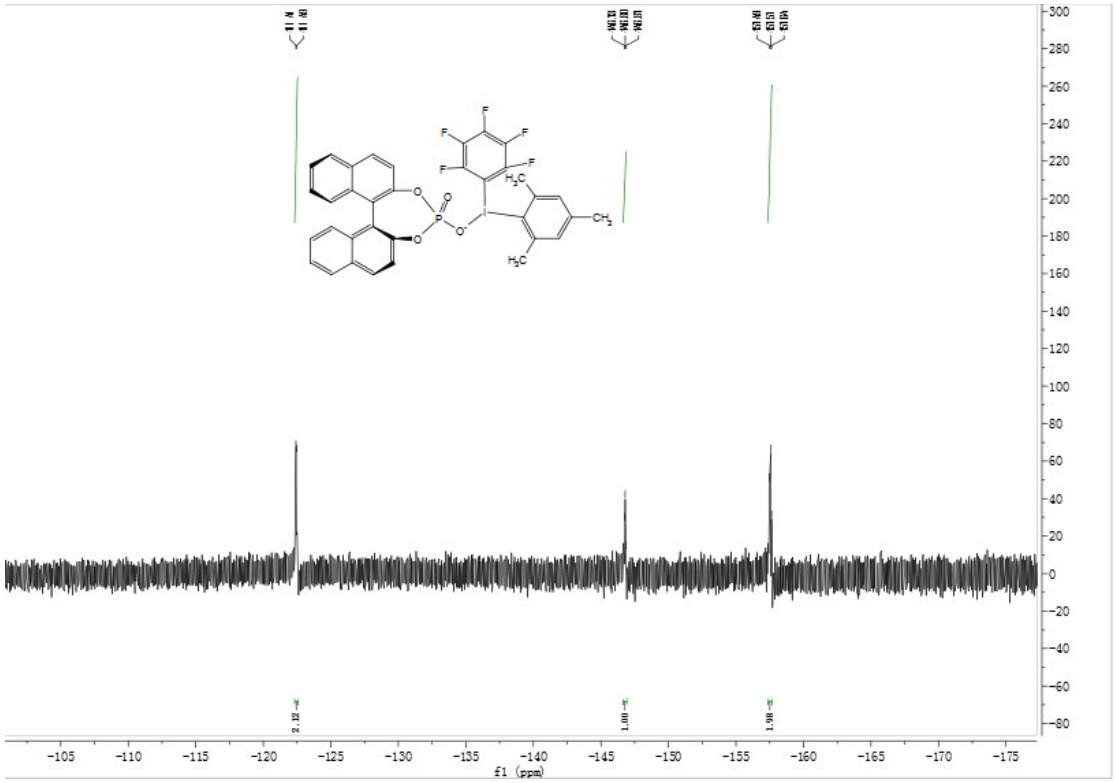

Br
O
N
O
O
NH
f1 (ppm)


8.05
8.03
7.57
7.54
7.52
7.44
7.41
7.39
3.12
3.07
2.55
2.50
2.45
2.42
2.28
2.22
1.95
1.93
1.83
1.77
1.46
1.43
1.25
1.23
0.94
0.70
H3C
CH3
O
S
O
O
O
I
3.87
1.90
3.91
1.06
1.02
1.05
1.10
3.17
1.04
1.15
3.00
3.00
f1 (ppm)


217.04
135.22
131.54
123.52
115.60
60.40
47.72
47.01
42.80
42.47
26.93
24.20
19.90
19.69
H3C
CH3
O
S
O
O
O
I
f1 (ppm)


f1 (ppm)


f1 (ppm)


F
F
F
F
F
H3C
O
O
P
O
O
I
CH2
H3C
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
f1 (ppm)