Supporting Information

Ruthenium-Catalyzed Reductive Amination of Ketones with Nitroarenes and Nitriles

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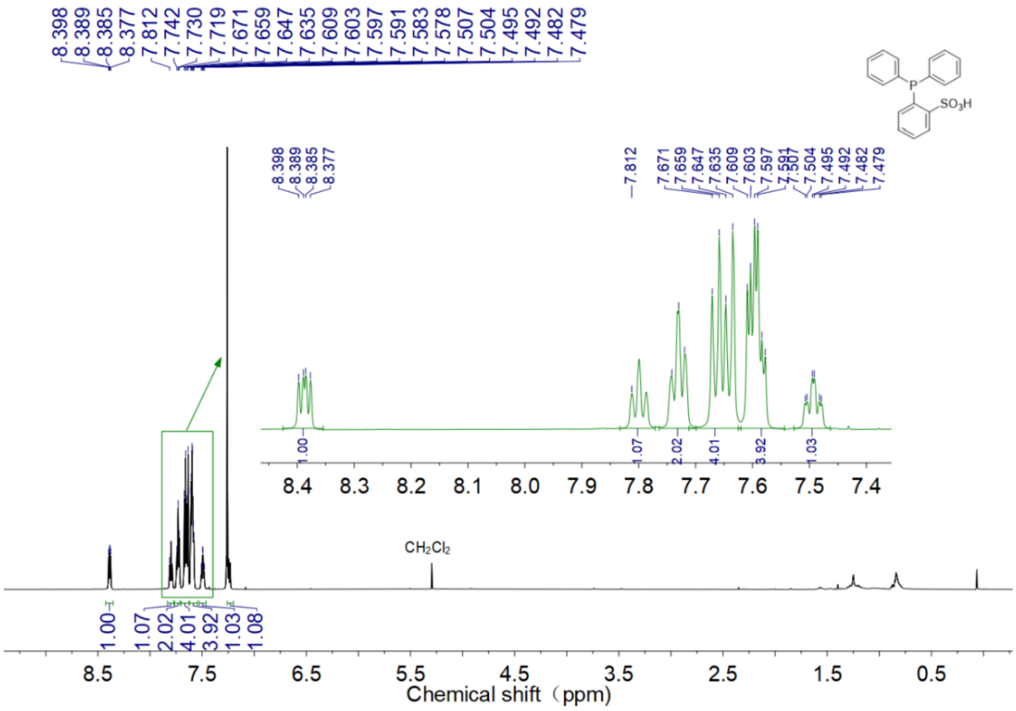
1. General Experimental Information

Unless specified, all substrates, Ru precursor was obtained commercially and their purity has been checked before use. All reactions were done under argon using a standard glove box and the solvents were dried before use unless otherwise noted. In particular, the Schlenk techniques were used in the synthesis of the Ru catalyst. All catalytic reactions were carried out in 25 mL autoclaves (Wuzhou Dingchuang (Beijing) Technology Co., Ltd.). GC-7890B equipped with a capillary column (DB-FFAP, 30 m × 0.32 mm) using a flame ionization detector. GC-MS was performed using Shimadzu GCMS-QP2020, column Rtx-5MS 30 m × 0.25 mm × 0.25 µm. GC was recorded on an Agilent 8890N instrument. ^{1}H, ^{13}C, ^{31}P NMR data were recorded on a Bruker ASCEND spectrometer (^{1}H, 600 MHz; $^{13}C\{^{1}H\}$, 151 MHz) using $CDCl_3$ as solvents. ^{1}H NMR and ^{13}C NMR, chemical shift δ is given relative to TMS and referenced to the solvent signal. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, coupling constant (s) *J* are reported in Hz and relative integrations are reported. Column chromatography was performed using silica gel.

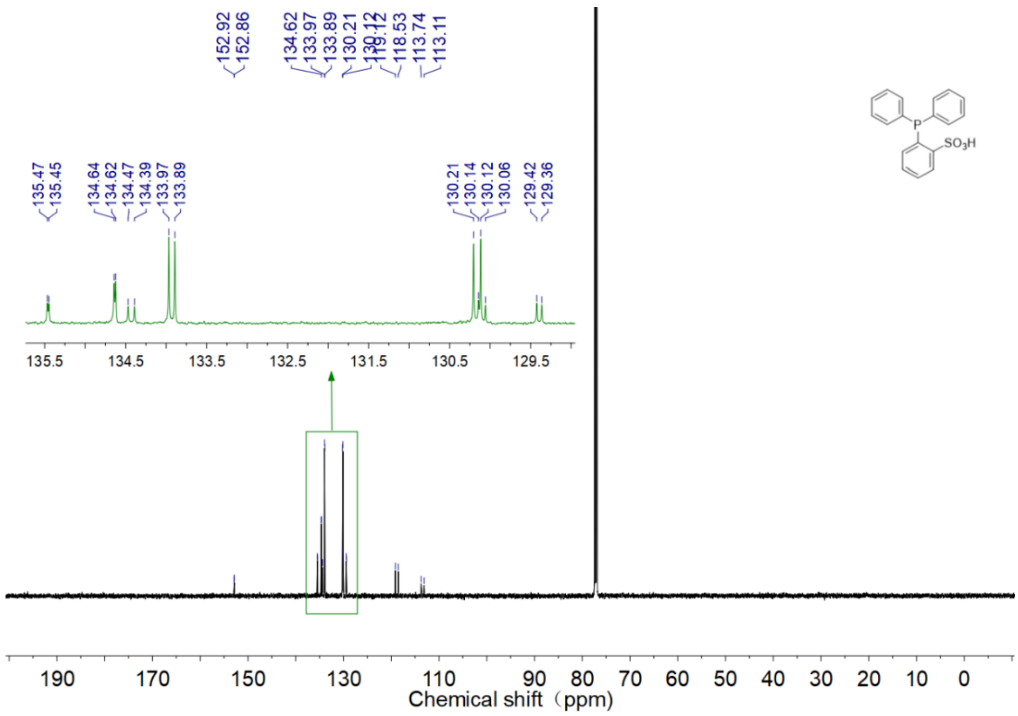
2. Preparation and characterization of Ru(dppbsa)

<u>Preparation of dppbsa Ligand</u>

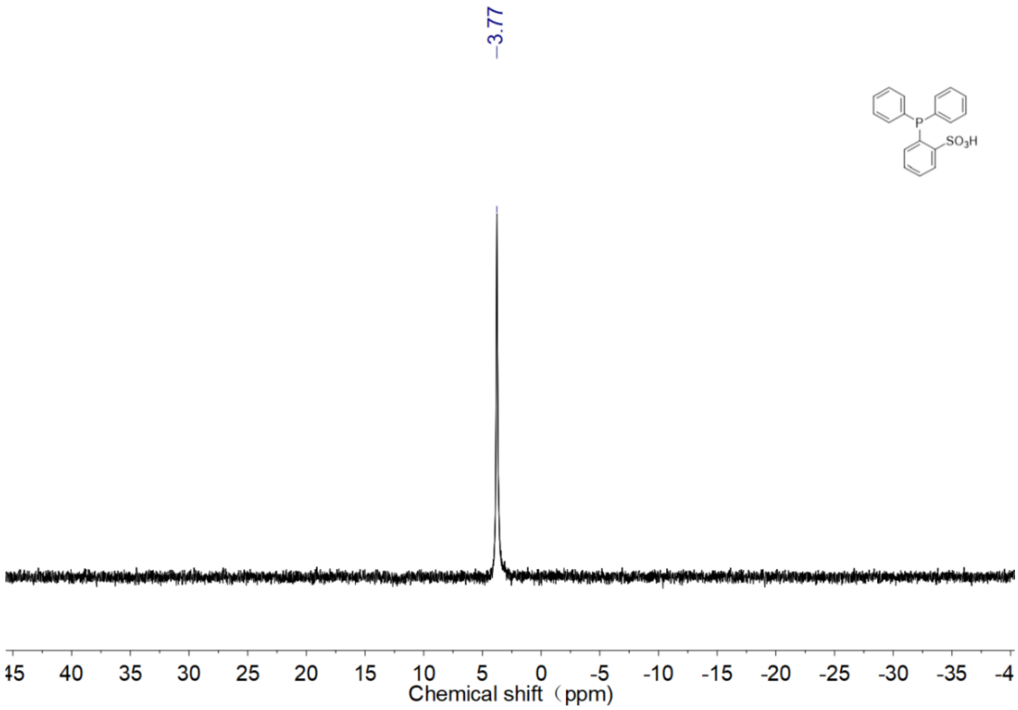
According to the literature,[S1] benzenesulfonic acid (0.80 g, 5 mmol) was dissolved in a Schleck tube with 25 mL of THF, *n*-BuLi (2.5 M in hexanes; 4 mL, 10 mmol) was added at 0 °C. After stirring for 1 h at room temperature; the solution was cooled to 0 °C again, a solution of chlorodi-phenylphosphane (1.10 g, 5 mmol) in THF (10 mL) was added dropwise to the Schleck tube and stirred at room temperature overnight. After the reaction, the solvent was removed in vacuo to obtain a pale-yellow solid. The solid was dissolved in dichloromethane (50 mL) and extracted with aqueous HCl (2 M, 30 mL), and then deionized water (30 mL) was added twice. The crude product was dissolved in dichloromethane and recrystallized with ether at -32 °C to obtain 1.05 g of white solid with a yield of 62%. **^{1}H NMR** (600 MHz, 298K, $CDCl_3$): δ = 8.39 (m, 1H), 7.80 (m, 1H), 7.73 (m, 2H), 7.66 (m, 2H), 7.64 (m, 2H), 7.59 (m, 4H), 7.49 (m, 1H), 7.25 (m, 1H), N.O. (-SO_3H). **^{13}C{^{1}H} NMR** (151 MHz, 298K, $CDCl_3$): δ = 152.9 (J_{PC} = 8.9 Hz, *i*-Ph-SO_3H), 135.5 (J_{PC} = 3.2 Hz, *i*-Ph), 134.6 (J_{PC} = 3.0 Hz, 2 × *i*-Ph), 134.5, 134.4, 134.0, 133.9, 130.2, 130.1 (4), 130.1 (1), 130.0 (5), 129.4 (2), 129.3 (6), 119.1, 118.5, 113.7, 113.1 (Ph). **^{31}P{^{1}H} NMR** (243 MHz, 298K, $CDCl_3$): δ = 3.8.



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of dppbsa



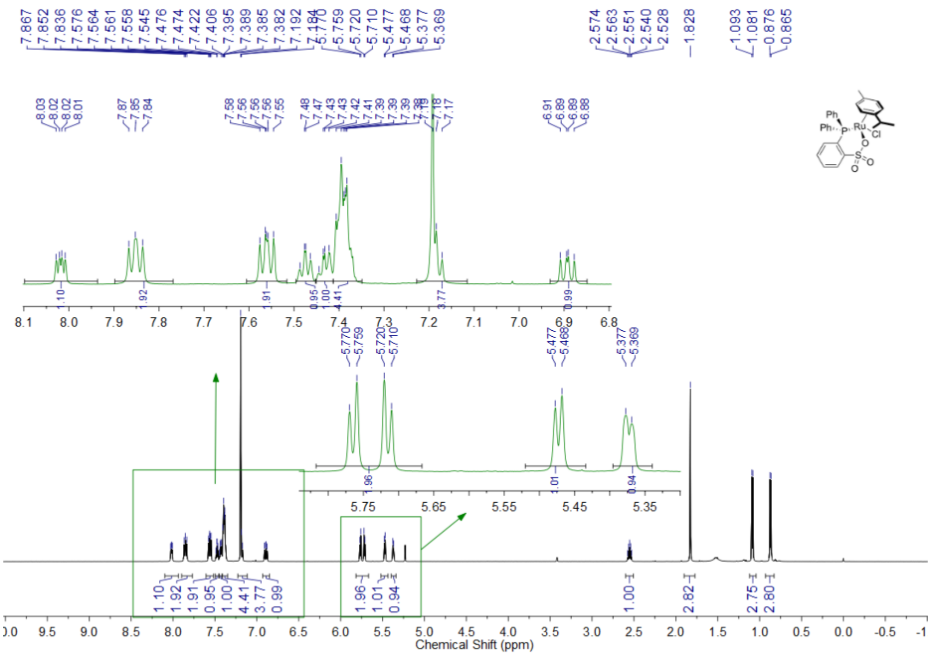
^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of dppbsa



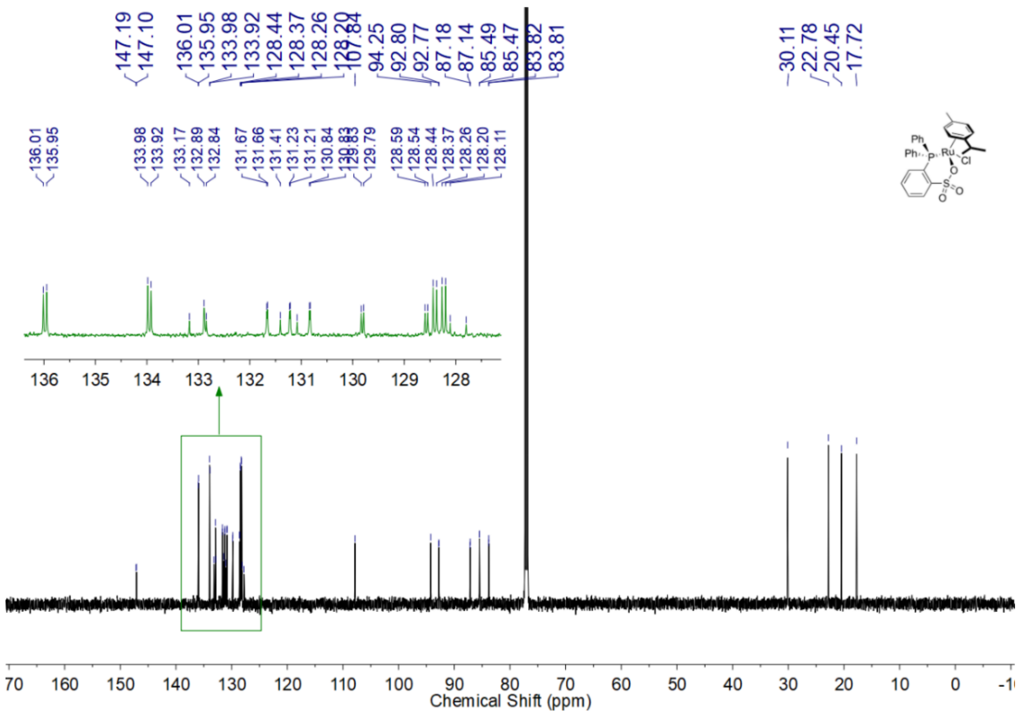
^{31}P NMR (243 MHz, $CDCl_3$, 298 K) of dppbsa

Preparation of Ru(dppbsa) Complex

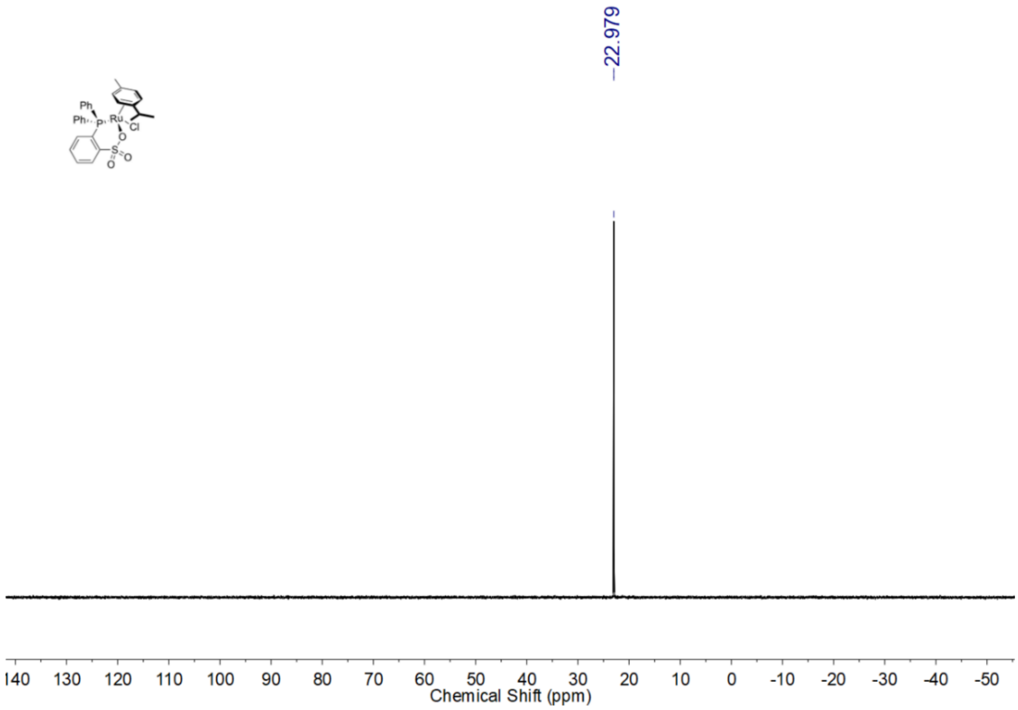
According to the literature,[S2] dppbsa ligand (164.2 mg, 0.46 mmol) and *t*-BuOK (58.2 mg, 0.51 mmol, 1.1 equiv.) were added to a 25 mL Schlenk tube, 10 mL of degassed MeOH was added, and the mixture was stirred at room temperature for 30 min; [Ru(*p*-cymene)Cl_2]$_2$ (144.5 mg, 0.22 mmol, 0.5 equiv.) was added and stirred at room temperature for 16 h; after the MeOH was removed in vacuo, the solid was dissolved in dichloromethane. Filter and recrystallize in *n*-hexane/dichloromethane solution to obtain 262.2 mg of dark red solid, with a yield of 90%. **^{1}H NMR** (600 MHz, 298 K, $CDCl_3$): δ = 8.08 (m, 1H), 7.92 (m, 2H), 7.64 (m, 1H), 7.62 (m, 1H), 7.54 (m, 1H), 7.50 (m, 1H), 7.46 (m, 4H), 7.44 (m, 1H), 7.25 (m, 1H), 6.96 (m, 1H), 5.83 (d, $^{3}J_{HH}$ = 6.5 Hz, 1H), 5.78 (d, $^{3}J_{HH}$ = 6.5 Hz, 1H), 5.54 (d, $^{3}J_{HH}$ = 5.5 Hz, 1H), 5.44 (d, $^{3}J_{HH}$ = 5.5 Hz, 1H), 2.62 (sept, $^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{HH}$ = 6.8 Hz, 1H), 1.89 (s, 3H, CH_3), 1.15 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H), 0.94 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, 298K, $CDCl_3$): δ = 147.2 (J_{PC} = 12.8 Hz, *i*-Ph-SO_3Ru), 136.1 (J_{PC} = 9.8 Hz), 134.1 (J_{PC} = 9.8 Hz), 133.3, 133.0(0), 132.9(6), 131.8 (J_{PC} = 2.5 Hz), 131.5, 131.3 (J_{PC} = 2.0 Hz), 131.2, 131.0 (J_{PC} = 2.5 Hz), 129.9 (J_{PC} = 6.8 Hz), 128.7 (J_{PC} = 8.3 Hz), 128.5 (J_{PC} = 9.7 Hz), 128.4 (J_{PC} = 10.3 Hz), 128.2, 128.1, 108.0, 94.4, 92.9 (J_{PC} = 5.3 Hz), 87.3 (J_{PC} = 7.7 Hz), 85.6 (J_{PC} = 2.2 Hz), 83.9 (J_{PC} = 2.2 Hz), 30.2, 22.9, 20.5, 17.8. **^{31}P{^{1}H} NMR** (243 MHz, 298K, $CDCl_3$): δ = 22.9.



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of Ru(dppbsa)



^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of Ru(dppbsa)



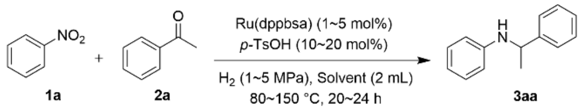
^{31}P NMR (243 MHz, $CDCl_3$, 298 K) of Ru(dppbsa)

3. Ruthenium-catalyzed Reductive Amination Reactions

General Procedure: In a typical experiment, combination of substrate, Ru(dppbsa) (3.7 mg, 6 µmol) and *p*-TsOH (6.8 mg, 40 µmol) was dissolved in toluene (2 mL) in a reaction vessel equipped with a Teflon lining and a stir bar in the glove box. After addition of the above reactants, the reaction vessel was filled with H_2. The solution was stirred at 120 °C. At the end of the reaction, the pressure of reaction vessel was gradually released, and the reaction mixture was diluted with ethyl acetate (20 mL) for analysis. The structures of the products were determined by GC-MS analysis, and yields determined by GC analysis. For some selected examples, the solvent was removed under vacuum to provide a crude product for ^{1}H NMR (600 MHz, 298 K, $CDCl_3$) analysis. The structures of the products were determined by ^{1}H NMR and ^{13}C NMR, with spectra matching those reported in the literature or authentic samples[S3,4].

Screening Conditions for Catalytic Reductive Amination of Acetophenone (2a) with nitrobenzene (1a).

Table 1. Reductive amination of acetophenone (**2a**) with nitrobenzene (**1a**).[a]

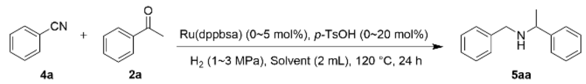


Entry	**2a** (equiv.)	[Ru] (mol%)	T (℃)	Solvent	Conv. (%)	Yield (%)
1	2	5	150	Toluene	98	40
2	5	5	150	Toluene	100	55
3	10	5	150	Toluene	99	60
4	20	5	150	Toluene	100	78
5	25	5	150	Toluene	100	69
6	30	5	150	Toluene	100	66
7[b]	20	5	150	Toluene	100	67
8[c,d]	20	5	120	toluene	100	50
9	20	5	120	Toluene	100	76
10	20	5	80	Toluene	100	40
11	20	5	120	THF	100	63
12	20	5	120	Heptane	100	50
13	20	5	120	*t*-BuOH	100	48
14	20	5	120	Anisole	100	36
15	20	3	120	Toluene	100	81
16	20	1	120	Toluene	100	9
17[c]	20	3	120	Toluene	100	91
18[c,d]	20	3	120	Toluene	100	62

[a] **General conditions**: **1a** (0.2 mmol), H_2 (1 MPa), *p*-TsOH (10 mol%), 24 h, under argon, in autoclave; yields were determined by GC where biphenyl is severed as the internal standard; [b] H_2 (3 MPa), 2-phenylethanol (**6a**) was detected with 55% GC yield; [c] H_2 (5 MPa), **6a** was detected with 58% GC yield; [d] *p*-TsOH (20 mol%); [e] 20 h. THF: tetrahydrofuran.

Screening Conditions for Catalytic Reductive Amination of Acetophenone (2a) with benzonitrile (4a).

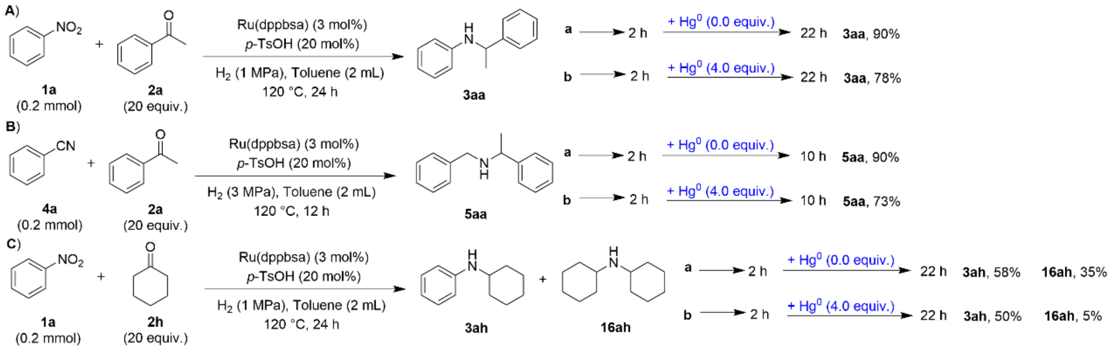
Table S2. Reductive amination of acetophenone (**2a**) with benzonitrile (**4a**).[a]



Entry	[Ru] (mol%)	H_2 (MPa)	Time (h)	Conv. (%)	Yield (%)
1	3	1	24	100	72
2	5	1	24	100	70
3	3	3	24	100	89
4	3	3	12	100	90
5	3	3	10	100	77

[a] General conditions: **4a** (0.2 mmol), **2a** (20 equiv.), *p*-TsOH (20 mol%), 120 °C, toluene (2 mL), under argon, in autoclave; yields determined by GC using biphenyl as the internal standard.

4. Amalgamation experiments



Scheme S1 Amalgamation experiments

5. Detection of *p*-cymene

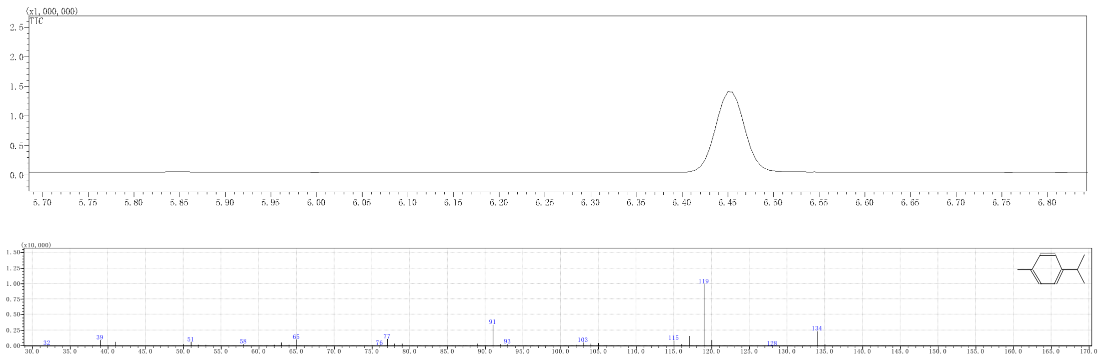


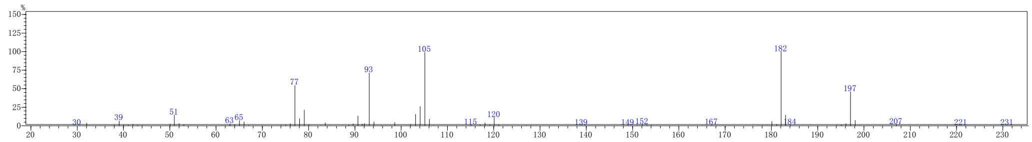
Fig. S1 GC-MS analysis of *p*-cymene in the evaluation of catalytic performance

6. NMR, GC and GC-MS Data

1. *N*-(1-Phenylethyl) Aniline (3aa)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Yellow liquid, Yield: 32.7 mg, 83%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.39 (d, $^3J_{HH}$ = 4.0 Hz, 2H, Ph), 7.31 (d, $^3J_{HH}$ = 6.8 Hz, 2H, Ph), 7.21 (m, 6H, Ph), 4.51 (s, 1H, NH), 3.47 (q, $^3J_{HH}$ = 7.0 Hz, 1H, CH), 1.20 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 135.0, 133.9, 129.2 (2C), 128.9 (2C), 128.7 (2C), 128.6 (2C), 124.5 (2C), 64.6, 19.1.

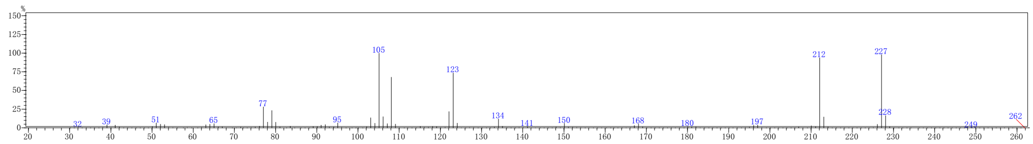
GC-MS (m/z): Calcd. 197; Found 197.



2. *N*-(4-Methoxyphenyl)-*N*-(1-Phenylethyl) Amine (3ba)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 36.8 mg, 81%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.27 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ph), 7.22 (t, $^3J_{HH}$ = 7.7 Hz, 2H, Ph), 7.12 (m, 1H, Ph), 6.60 (m, 2H, Ph), 6.38 (m, 2H, Ph), 4.32 (q, $^3J_{HH}$ = 6.6 Hz, 1H, CH), 3.77 (s, 1H, NH), 3.59 (s, 3H, CH_3), 1.40 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 152.0, 145.4, 141.5, 128.6 (2C), 126.8, 125.9 (2C), 114.8 (2C), 114.6 (2C), 55.7, 54.3, 25.1.

GC-MS (m/z): Calcd. 227; Found 227.

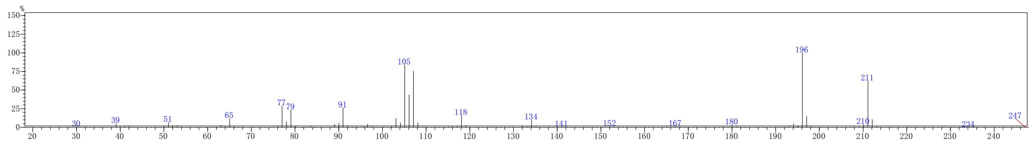


3. 4-Methyl-*N*-(1-Phenylethyl) Aniline (3ca)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 36.3 mg, 86%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.27 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Ph), 7.21 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ph), 7.12 (m, 1H, Ph), 6.81 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ph), 6.35 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 4.36 (q, $^3J_{HH}$ = 6.7 Hz, 1H, CH), 3.90 (s, 1H, NH), 2.09 (s, 3H, CH_3), 1.41 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR**

(151 MHz, $CDCl_3$, 298 K): δ = 144.3, 143.8, 128.5 (2C), 127.5 (2C), 125.7 (2C), 124.8 (2C), 112.4 (2C), 52.7, 23.9, 19.3.

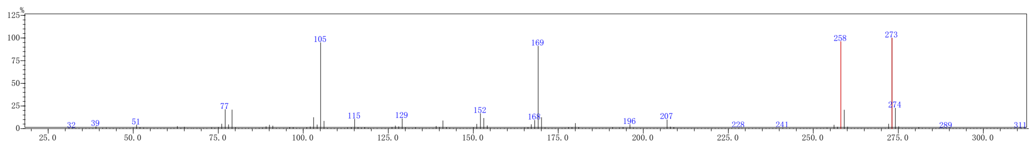
GC-MS (m/z): Calcd. 211; Found 211.



4. ***N*-(1-Phenylethyl)-[1,1'-Biphenyl]-4-Amine (3da)**

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 38.2 mg, 70%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.39 (d, $^3J_{HH}$ = 7.1 Hz, 2H, Ph), 7.32 (d, $^3J_{HH}$ = 7.1 Hz, 2H, Ph), 7.29 (m, 2H, Ph), 7.27 (m, 2H, Ph), 7.25 (m, 3H, Ph), 7.18 (s, 3H, Ph), 6.62 (s, 1H, NH), 4.46 (q, $^3J_{HH}$ = 6.9 Hz, 1H, CH), 2.10 (s, 3H, CH_3), 1.54 (d, $^3J_{HH}$ = 5.7 Hz, 3H, CH_3).

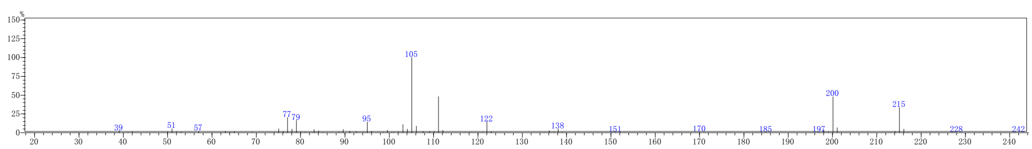
GC-MS (m/z): Calcd. 273; Found 273.



5. **4-Fluoro-*N*-(1-Phenylethyl) Aniline (3ea)**

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 33.1 mg, 77%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.24 (m, 4H, Ph), 7.15 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ph), 6.75 (m, 2H, Ph), 6.30 (m, 2H, Ph), 4.33 (q, $^3J_{HH}$ = 6.7 Hz, 1H, CH), 3.96 (s, 1H, NH), 1.42 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 155.7 (d, J_F = 251.3 Hz), 144.9, 143.4, 128.7 (2C), 127.0 (2C), 125.8 (2C), 115.5 (d, J_F = 23.8 Hz, 2C) 114.2 (d, J_F = 8.0 Hz), 54.2, 25.0. ^{19}F NMR (564 MHz, $CDCl_3$, 298 K): δ = -125.8.

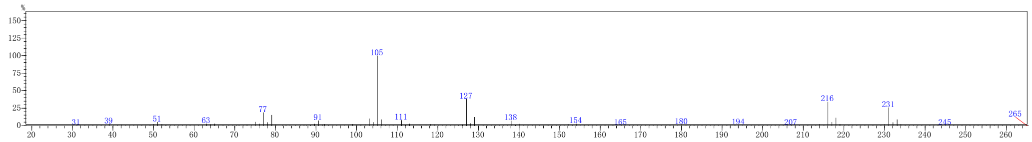
GC-MS (m/z): Calcd. 215; Found 215.



6. **4-Chloro-*N*-(1-Phenylethyl) Aniline (3fa)**

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 33.7 mg, 73%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.31 (m, 4H, Ph), 7.23 (m, 1H, Ph), 7.01 (m, 2H, Ph), 6.44 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Ph), 4.43 (q, $^3J_{HH}$ = 6.7 Hz, 1H, CH), 1.52 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 145.3, 144.3, 128.9 (2C), 128.7 (2C), 127.1, 125.8 (2C), 124.1 (2C), 114.7, 53.9, 24.7.

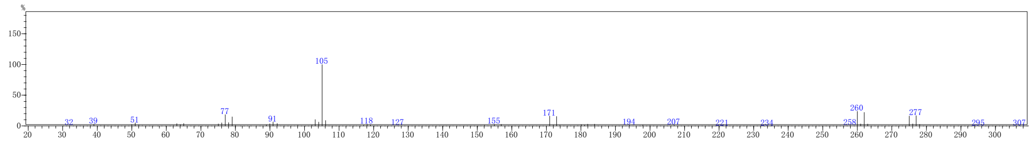
GC-MS (m/z): Calcd. 231; Found 231.



7. 4-Bromo-*N*-(1-Phenylethyl) Aniline (3ga)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 30.5 mg, 55%. **^1H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.22 (m, 2H, Ph), 7.13 (m, 4H, Ph), 7.05 (d, $^3J_{HH}$ = 8.8 Hz, 1H, Ph), 6.27 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Ph), 4.32 (q, $^3J_{HH}$ = 6.8 Hz, 1H, CH), 3.97 (s, 1H, NH), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 146.2, 144.6, 131.8 (2C), 128.8 (2C), 127.1, 125.8 (2C), 114.9 (2C), 108.9, 53.9, 24.7.

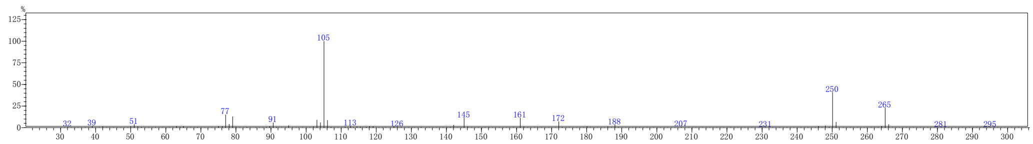
GC-MS (m/z): Calcd. 276; Found 277.



8. *N*-(1-Phenylethyl)-4-(Trifluoromethyl) Aniline (3ha)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 34.5 mg, 65%. **^1H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.25 (m, 5H, Ph), 7.18 (m, 2H, Ph), 6.45 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph), 4.44 (q, $^3J_{HH}$ = 6.8 Hz, 1H, CH), 1.47 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3). ^{19}F NMR (564 MHz, $CDCl_3$, 298 K): δ = -61.1.

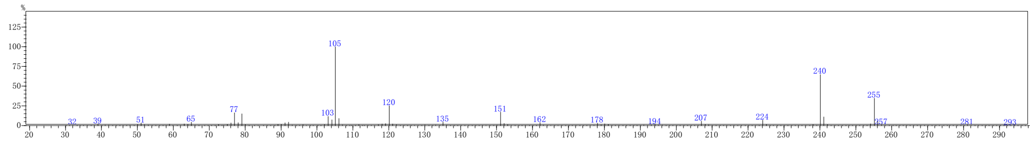
GC-MS (m/z): Calcd. 265; Found 265.



9. Methyl-4-((1-Phenylethyl) Amino) Benzoate (3ia)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 34.6 mg, 68%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.70 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Ph), 7.24 (m, 4H, Ph), 7.16 (m, 1H, Ph), 6.40 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph), 4.47 (q, $^3J_{HH}$ = 6.6 Hz, 1H, CH), 3.79 (s, 1H, NH), 3.73 (s, 3H, CH_3), 1.46 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 167.2, 150.8, 144.0, 131.4 (2C), 128.8 (2C), 127.2, 125.7 (2C), 118.5, 112.3 (2C), 53.2, 51.5, 24.6.

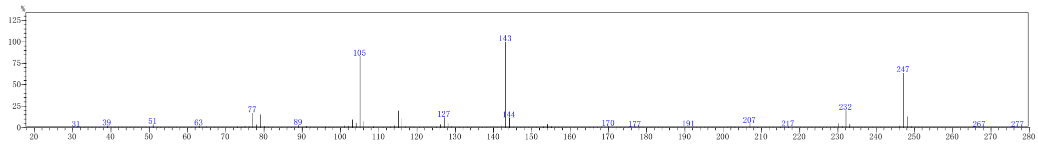
GC-MS (m/z): Calcd. 255; Found 255.



10. *N*-(1-Phenylethyl) Naphthalen-1-Amine (3ja)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Brown liquid, Yield: 31.6 mg, 64%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.77 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ph), 7.26 (m, 5H, Ph), 7.16 (m, 3H, Ph), 7.05 (d, $^3J_{HH}$ = 7.1 Hz, 1H, Ph), 6.51 (d, $^3J_{HH}$ = 9.7 Hz, 1H, Ph), 5.56 (dd, $^3J_{HH}$ = 9.8, 4.8 Hz, 1H, Ph), 4.24 (t, $^3J_{HH}$ = 4.5 Hz, 1H, CH), 3.66 (m, 1H, NH), 1.00 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 157.5, 144.1, 133.9, 130.0, 128.9, 128.1 (2C), 127.8, 127.7, 127.6 (2C), 127.4 (2C), 127.1, 126.3, 123.3, 42.6, 13.3.

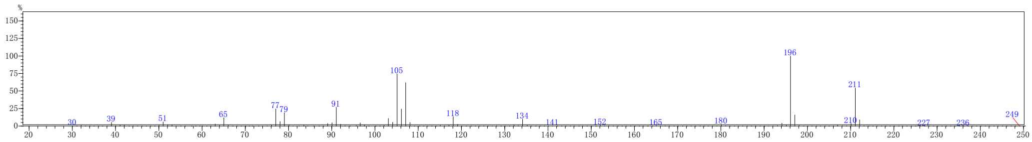
GC-MS (m/z): Calcd. 247; Found 247.



11. 3-Methyl-*N*-(1-Phenylethyl) Aniline (3ka)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 23.2 mg, 55%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.36 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 7.30 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ph), 7.21 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ph), 6.97 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Ph), 6.47 (d, $^3J_{HH}$ = 7.4 Hz, 1H, Ph), 6.37 (s, 1H, Ph), 6.31 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ph), 4.47 (q, $^3J_{HH}$ = 6.7 Hz, 1H, CH), 4.05 (s, 1H, NH), 2.20 (s, 3H, CH_3), 1.50 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 147.1, 145.2, 138.8, 128.9, 128.6 (2C), 126.8, 125.8 (2C), 118.3, 114.2, 110.4, 53.5, 24.8, 21.5 (2C).

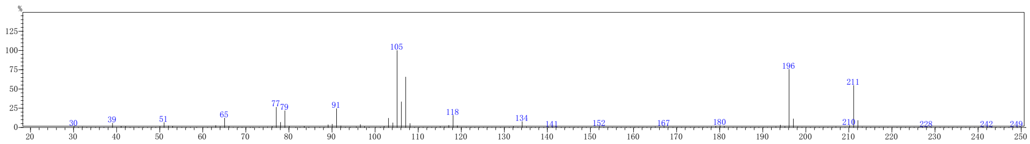
GC-MS (m/z): Calcd. 211; Found 211.



12. 2-Methyl-*N*-(1-Phenylethyl) Aniline (3la)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 31.7 mg, 75%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.26 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ph), 7.21 (t, $^3J_{HH}$ = 7.4 Hz, 2H, Ph), 7.12 (m, 1H, Ph), 6.95 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Ph), 6.86 (t, $^3J_{HH}$ = 8.1 Hz, 1H, Ph), 6.51 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ph), 6.28 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ph), 4.44 (q, $^3J_{HH}$ = 6.4 Hz, 1H, CH), 3.75 (s, 1H, NH), 2.13 (s, 3H, CH_3), 1.46 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 148.2, 145.9, 144.9, 132.9 (2C), 131.5 (2C), 129.9 (2C), 128.7, 119.8, 114.0, 56.2, 28.1, 20.5 (2C).

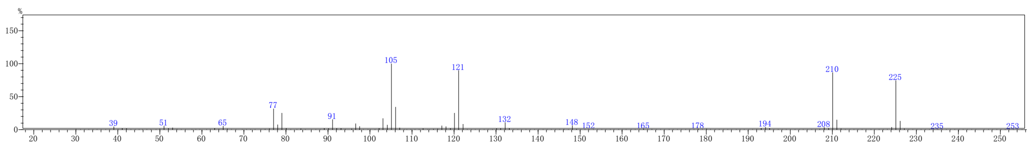
GC-MS (m/z): Calcd. 211; Found 211.



13. 2,4-Dimethyl-*N*-(1-Phenylethyl) Aniline (3ma)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 38.3 mg, 85%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.27 (d, $^3J_{HH}$ = 7.3 Hz, 2H, Ph), 7.22 (t, $^3J_{HH}$ = 7.3 Hz, 2H, Ph), 7.12 (t, $^3J_{HH}$ = 7.1 Hz, 1H, Ph), 6.79 (s, 1H, Ph), 6.67 (d, $^3J_{HH}$ = 8.7 Hz, 1H, Ph), 6.20 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Ph), 4.42 (q, $^3J_{HH}$ = 6.7 Hz, 1H, CH), 3.64 (s, 1H, NH), 2.10 (d, $^3J_{HH}$ = 11.9 Hz, 6H, CH_3), 1.46 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 145.4, 142.9, 130.9, 128.6 (2C), 127.2 (2C), 126.8, 125.8 (2C), 121.8, 111.3, 53.57, 25.3, 17.6 (2C).

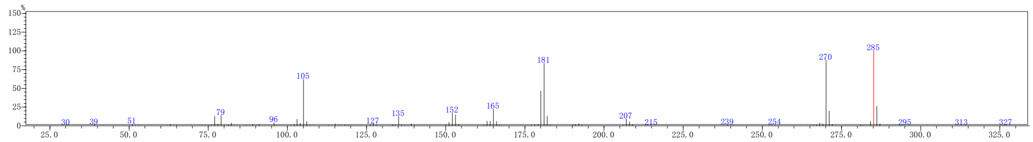
GC-MS (m/z): Calcd. 225; Found 225.



14. *N*-(1-Phenylethyl)-*9H*-Fluoren-2-Amine (3na)

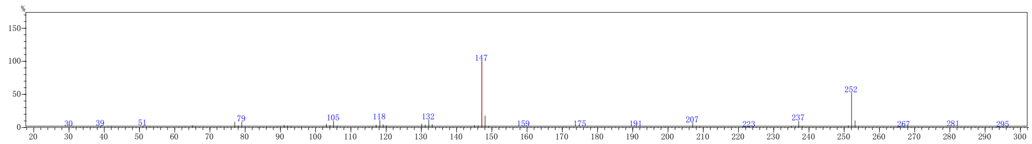
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 38.2 mg, 67%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.46 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, Ph), 7.38 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, Ph), 7.29 (m, 3H, Ph), 7.22 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ph), 7.16 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, Ph), 7.12 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, Ph), 7.03 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, Ph), 6.57 (s, 1H, Ph), 6.43 (dd, $^{3}J_{HH}$ = 8.3, 1.5 Hz, 1H, Ph), 4.44 (q, $^{3}J_{HH}$ = 6.6 Hz, 1H, CH), 4.06 (s, 1H, NH), 3.61 (dd, $^{3}J_{HH}$ = 27.1, 21.5 Hz, 2H, CH_2), 1.42 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 146.8, 145.2, 145.0, 142.4, 142.2, 131.9, 128.7 (2C), 127.0, 126.6, 125.9 (2C), 124.8, 124.7, 120.6, 118.4, 112.5, 109.9, 53.7, 37.0, 25.0.

GC-MS (m/z): Calcd. 285; Found 285.



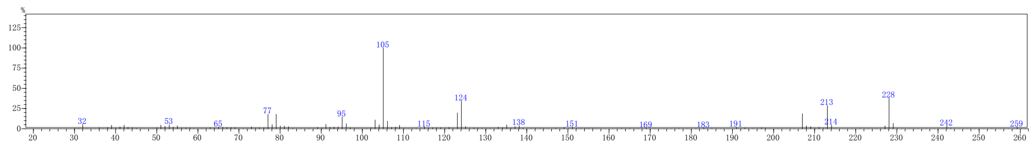
15. *N*-(1-Phenylethyl)-1,2,3,4-Tetrahydroquinolin-7-Amine (3oa)

GC-MS (m/z): Calcd. 252; Found 252.



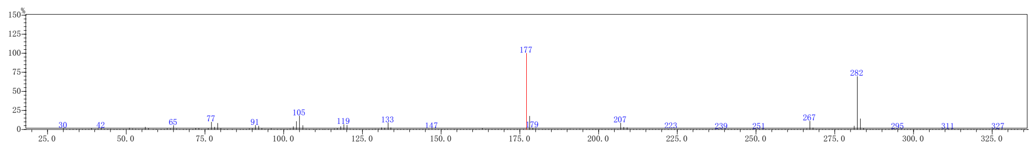
16. 5-Methoxy-*N*-(1-Phenylethyl) Pyridin-2-Amine (3pa)

GC-MS (m/z): Calcd. 228; Found 228.



17. 4-Morpholino-*N*-(1-Phenylethyl) Aniline (3qa)

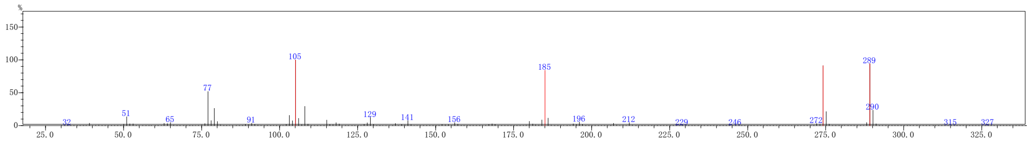
GC-MS (m/z): Calcd. 282; Found 282.



18. 4-Phenoxy-*N*-(1-Phenylethyl) Aniline (3ra)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 36.4 mg, 63%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.27 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H, Ph), 7.22 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ph), 7.13 (m, 3H, Ph), 6.87 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ph), 6.79 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ph), 6.71 (m, 2H, Ph), 6.39 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ph), 4.34 (q, $^3J_{HH}$ = 6.7 Hz, 1H, CH), 3.90 (s, 1H, NH), 1.41 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 159.0, 147.6, 145.2, 143.9, 129.5 (2C), 128.7 (2C), 127.0, 125.9 (2C), 121.9, 121.0 (2C), 117.2 (2C), 114.3 (2C), 54.1, 25.1.

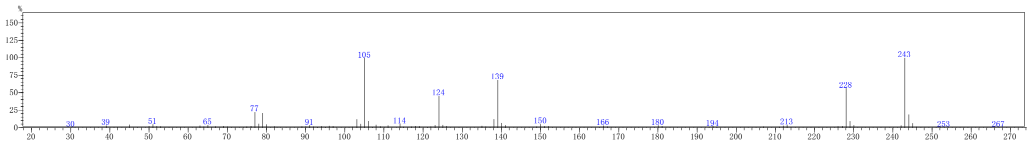
GC-MS (m/z): Calcd. 289; Found 289.



19. 4-(Methylthio)-*N*-(1-Phenylethyl) Aniline (3sa)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 36.9 mg, 76%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.23 (m, 4H, Ph), 7.13 (t, $^3J_{HH}$ = 7.1 Hz, 1H, Ph), 7.03 (dt, $^3J_{HH}$ = 8.8, 2.5 Hz, 2H, Ph), 6.36 (dt, $^3J_{HH}$ = 8.6, 2.4 Hz, 2H, Ph), 4.36 (q, $^3J_{HH}$ = 6.7 Hz, 1H, CH), 4.02 (s, 1H, NH), 2.26 (s, 3H, CH_3), 1.41 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 146.0, 144.9, 131.3 (2C), 128.7 (2C), 127.0, 125.8 (2C), 124.2, 114.0 (2C), 53.6, 24.9, 19.1.

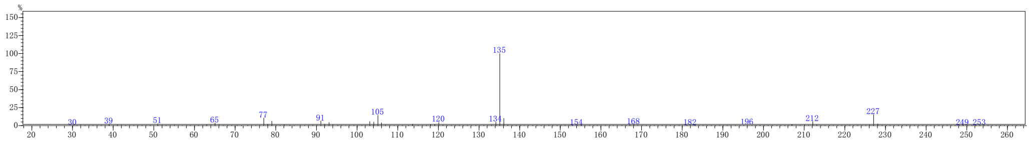
GC-MS (m/z): Calcd. 243; Found 243.



20. *N*-(1-(4-Methoxyphenyl) Ethyl) Aniline (3ab)

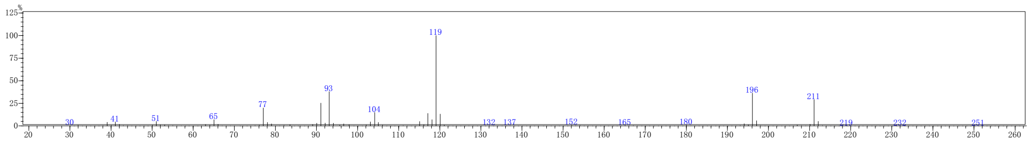
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 23.6 mg, 52%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.29 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ph), 7.10 (m, 2H, Ph), 6.86 (m, 2H, Ph), 6.66 (t, $^3J_{HH}$ = 7.1 Hz, 2H, Ph), 6.54 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ph), 4.46 (q, $^3J_{HH}$ = 6.7 Hz, 1H, CH), 3.79 (s, 3H, CH_3), 1.51 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 158.5, 151.3, 147.1, 137.1, 129.1 (2C), 126.9 (2C), 114.0 (2C), 113.3, 113.0, 55.2, 52.9, 24.9.

GC-MS (m/z): Calcd. 227; Found 227.



21. *N*-(1-(*p*-Tolyl) Ethyl) Aniline (3ac)

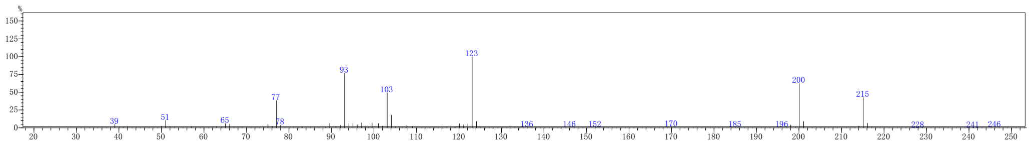
GC-MS (m/z): Calcd. 211; Found 211.



22. *N*-(1-(4-Fluorophenyl) Ethyl) Aniline (3ad)

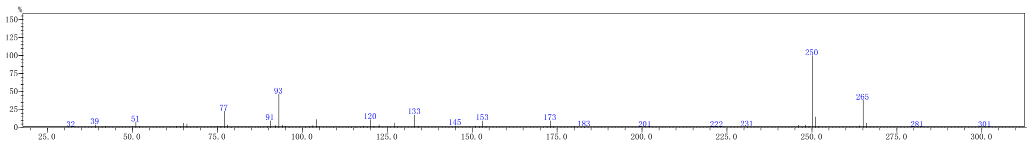
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 29.2 mg, 68%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.34 (m, 2H, Ph), 7.10 (m, 2H, Ph), 7.00 (t, $^{3}J_{HH}$ = 8.6 Hz, 2H, Ph), 6.68 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, Ph), 6.51 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, Ph), 4.47 (q, $^{3}J_{HH}$ = 7.2 Hz, 1H, CH), 4.34 (m, 1H, NH), 1.51 (d, $^{3}J_{HH}$ = 7.1 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 161.7 (d, J_F = 261.3 Hz), 150.8, 140.7, 130.0 (d, J_F = 7.8 Hz), 129.1 (2C), 128.6 (d, J_F = 8.6 Hz), 128.3, 127.4 (d, J_F = 8.5 Hz), 115.4 (d, J_F = 22.2 Hz), 114.4 (d, J_F = 22.8 Hz), 113.5, 66.7, 25.0. ^{19}F NMR (564 MHz, $CDCl_3$, 298 K): δ = -115.8.

GC-MS (m/z): Calcd. 215; Found 215.



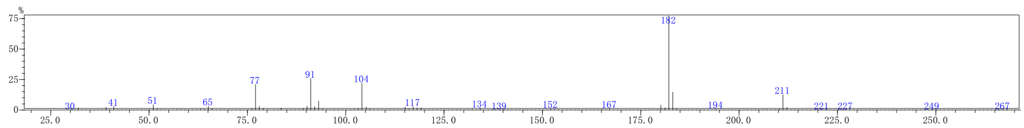
23. *N*-(1-(4-(Trifluoromethyl) Phenyl) Ethyl) Aniline (3ae)

GC-MS (m/z): Calcd. 265; Found 265.



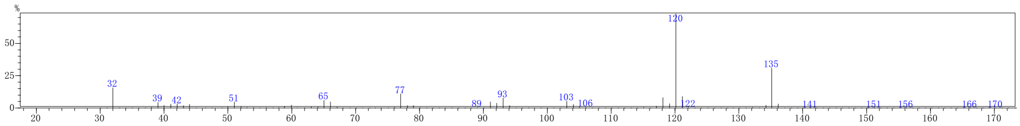
24. *N*-(1-Phenylpropyl) Aniline (3af)

GC-MS (m/z): Calcd. 211; Found 211.



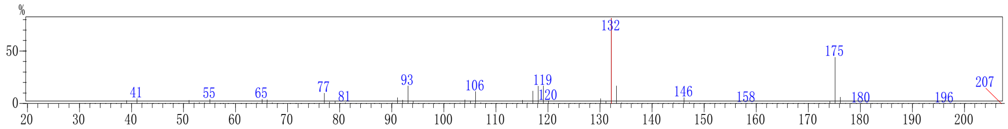
25. *N*-Isopropylaniline (3ag)

GC-MS (m/z): Calcd. 135; Found 135.



26. *N*-cyclohexylaniline (3ah)

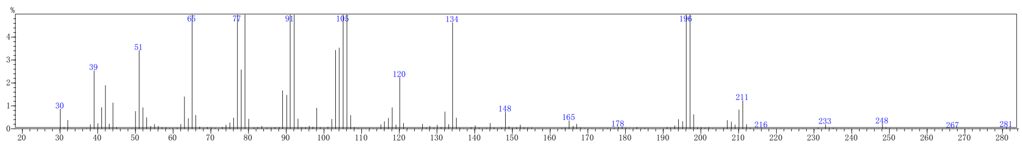
GC-MS (m/z): Calcd. 175; Found 175.



27. *N*-Benzyl-1-Phenylethan-1-Amine (5aa)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 35.0 mg, 83%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.39 (m, 4H, Ph), 7.36 (d, $^3J_{HH}$ = 5.9 Hz, 1H, Ph), 7.34 (s, 1H, Ph), 7.33 (m, 2H, Ph), 7.31 (m, 1H, Ph), 7.28 (t, $^3J_{HH}$ = 5.4 Hz, 1H), 3.85 (q, $^3J_{HH}$ = 7.2 Hz, 1H, CH), 3.67 (dd, $^3J_{HH}$ = 39.0, 13.1 Hz, 2H, CH_2), 1.71 (s, 1H, NH), 1.41 (d, $^3J_{HH}$ = 7.7 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 145.4, 140.5, 128.5 (2C), 128.3 (2C), 128.1, 127.0, 126.9, 126.7 (2C), 57.5 (2C), 51.6, 24.4.

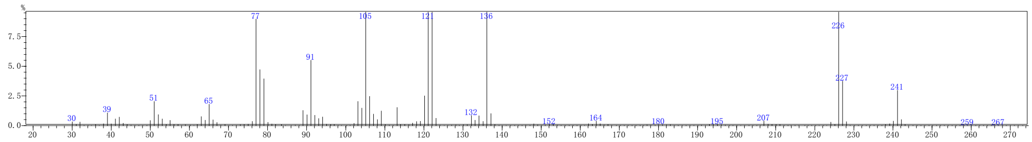
GC-MS (m/z): Calcd. 211; Found 211.



28. *N*-(4-Methoxybenzyl)-1-Phenylethan-1-Amine (5ba)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 35.2 mg, 73%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.26 (m, 4H, Ph), 7.17 (m, 1H, Ph), 7.11 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Ph), 6.76 (m, 2H, Ph), 3.72 (m, 1H, CH), 3.70 (s, 3H, CH_3), 3.48 (q, $^3J_{HH}$ = 12.9 Hz, 2H, CH_2), 1.53 (s, 1H, NH), 1.28 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 158.6, 145.6, 132.8, 129.3 (2C), 128.4 (2C), 126.9, 126.7 (2C), 113.8 (2C), 57.4, 55.3, 51.0, 24.5.

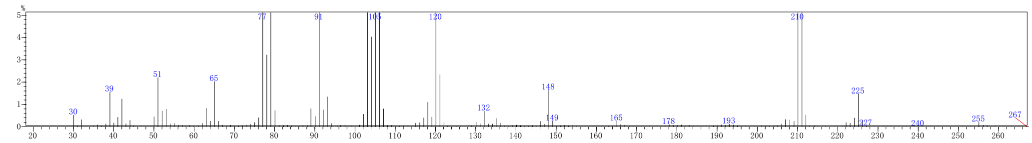
GC-MS (m/z): Calcd. 241; Found 241.



29. *N*-(4-Methylbenzyl)-1-Phenylethan-1-Amine (5ca)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 324.7 mg, 77%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.26 (d, $^3J_{HH}$ = 7.3 Hz, 3H, Ph), 7.14 (d, $^3J_{HH}$ = 7.9 Hz, 3H, Ph), 7.08 (d, $^3J_{HH}$ = 7.3 Hz, 1H, Ph), 7.04 (m, 2H, Ph), 3.72 (q, $^3J_{HH}$ = 8.0 Hz, 1H, CH), 3.51 (dd, $^3J_{HH}$ = 40.2, 13.1 Hz, 2H, CH_2), 2.25 (s, 3H, CH_3), 1.67 (s, 1H, NH), 1.28 (d, $^3J_{HH}$ = 6.7 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 145.5, 137.2, 136.5, 136.4, 129.1 (2C), 128.4, 128.1 (2C), 126.9, 126.7, 52.7, 51.3, 24.4, 21.1.

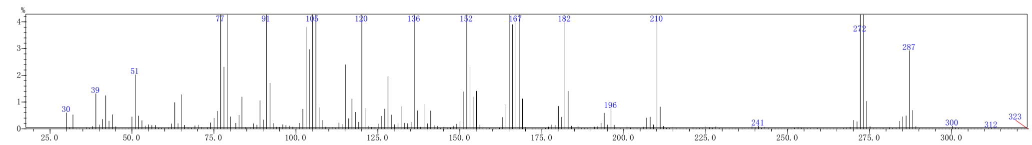
GC-MS (m/z): Calcd. 225; Found 225.



30. *N*-([1,1'-Biphenyl]-4-Ylmethyl)-1-Phenylethan-1-Amine (5da)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 37.9 mg, 66%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.48 (m, 3H, Ph), 7.44 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph), 7.32 (m, 3H, Ph), 7.25 (m, 5H, Ph), 7.16 (m, 1H, Ph), 3.74 (q, $^3J_{HH}$ = 6.2 Hz, 1H, CH), 3.57 (dd, $^3J_{HH}$ = 34.9, 13.3 Hz, 2H, CH_2), 1.73 (s, 1H, NH), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 141.0, 139.9, 128.85 (2C), 128.81, 128.6, 128.5, 127.5, 127.36, 127.34, 127.21 (2C), 127.20, 127.15, 127.12, 127.0, 126.8 (2C), 57.6, 51.3, 24.5.

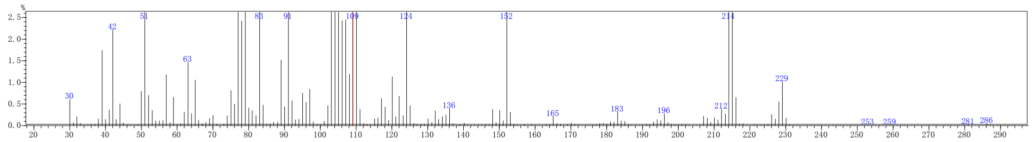
GC-MS (m/z): Calcd. 287; Found 287.



31. *N*-(4-Fluorobenzyl)-1-Phenylethan-1-Amine (5ea)

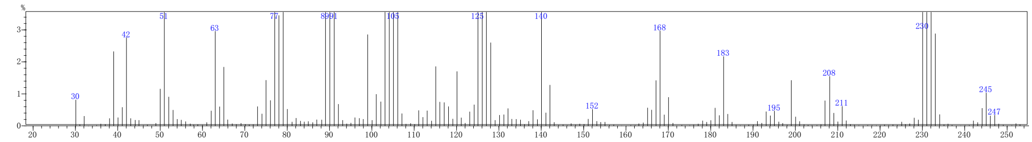
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 31.1 mg, 68%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.35 (d, $^3J_{HH}$ = 5.0 Hz, 4H, Ph), 7.30 (m, 1H, Ph), 7.24 (m, 2H, Ph), 6.99 (m, 2H, Ph), 3.80 (q, $^3J_{HH}$ = 6.4 Hz, 1H, CH), 3.59 (dd, $^3J_{HH}$ = 31.0, 13.2 Hz, 2H, CH_2), 1.71 (s, 1H, NH), 1.38 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 161.9 (d, J_F = 260.4 Hz), 145.2, 129.7 (d, J_F = 8.5 Hz), 128.5 (2C), 127.0, 126.7 (2C), 115.2 (2C), 115.0 (2C), 57.5 (d, J_F = 4.5 Hz), 50.8, 24.4. ^{19}F NMR (564 MHz, $CDCl_3$, 298 K): δ = -115.9.

GC-MS (m/z): Calcd. 229; Found 229.



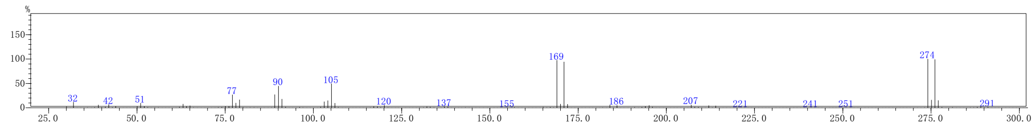
32. *N*-(4-Chlorobenzyl)-1-Phenylethan-1-Amine (5fa)

GC-MS (m/z): Calcd. 245; Found 245.



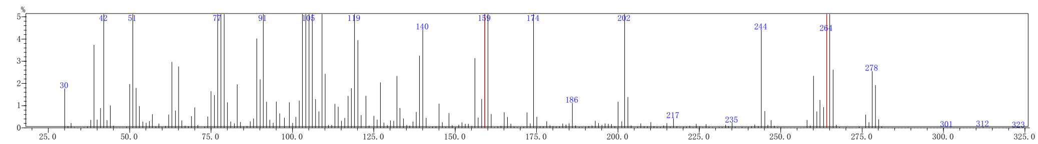
33. *N*-(4-Bromobenzyl)-1-Phenylethan-1-Amine (5ga)

GC-MS (m/z): Calcd. 276; Found 276.



34. 1-Phenyl-*N*-(4-(Trifluoromethyl) Benzyl) Ethan-1-Amine (5ha)

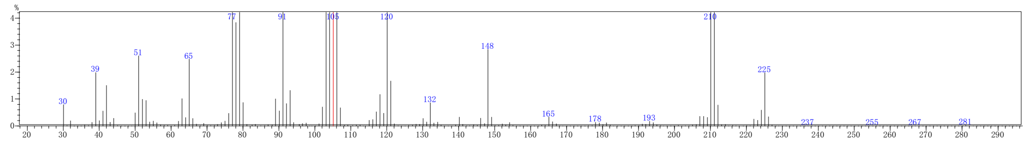
GC-MS (m/z): Calcd. 279; Found 278.



35. *N*-(3-Methylbenzyl)-1-Phenylethan-1-Amine (5ia)

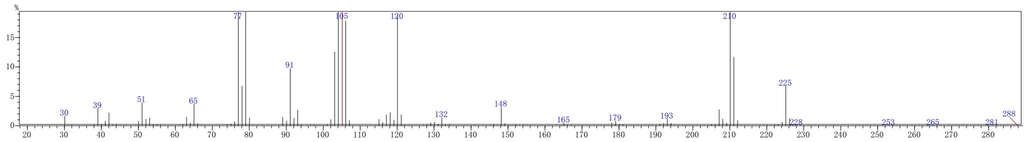
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 29.3 mg, 65%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.27 (m, 2H, Ph), 7.19 (m, 1H, Ph), 7.13 (m, 2H, Ph), 7.04 (m, 2H, Ph), 6.99 (m, 2H, Ph), 3.74 (q, $^3J_{HH}$ = 6.1 Hz, 2H, CH_2), 3.51 (dd, $^3J_{HH}$ = 37.1, 12.9 Hz, 1H, CH), 2.27 (d, $^3J_{HH}$ = 8.2 Hz, 3H, CH_3), 1.75 (s, 1H, NH), 1.30 (d, $^3J_{HH}$ = 8.2 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 140.1, 138.0, 128.9, 128.9, 128.5, 128.32, 128.30, 127.7, 127.6, 126.9, 126.7, 125.2, 53.1, 51.6, 24.4, 21.4.

GC-MS (m/z): Calcd. 225; Found 225.



36. *N*-(2-Methylbenzyl)-1-Phenylethan-1-Amine (5ja)

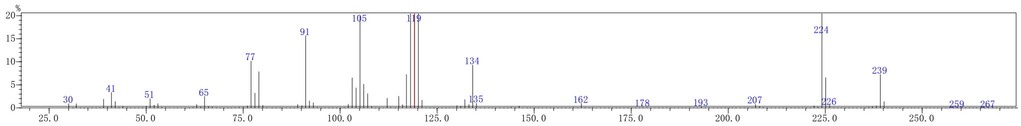
GC-MS (m/z): Calcd. 225; Found 225.



37. *N*-(2,4-Dimethylbenzyl)-1-Phenylethan-1-Amine (5ka)

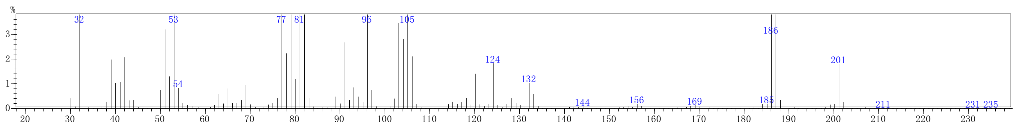
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 39.7 mg, 83%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.53 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Ph), 7.48 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ph), 7.39 (m, 1H, Ph), 7.29 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ph), 7.11 (s, 2H, Ph), 3.98 (q, $^3J_{HH}$ = 6.6 Hz, 1H, CH), 3.72 (t, $^3J_{HH}$ = 13.1 Hz, 2H, CH_2), 2.41 (d, $^3J_{HH}$ = 30.3 Hz, 6H, CH_3), 1.80 (s, 1H, NH), 1.52 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 145.9, 136.5, 136.4, 135.7, 131.2, 128.8, 128.5 (2C), 127.0, 126.8 (2C), 126.6, 58.2, 49.5, 24.7, 21.1, 18.9.

GC-MS (m/z): Calcd. 239; Found 239.



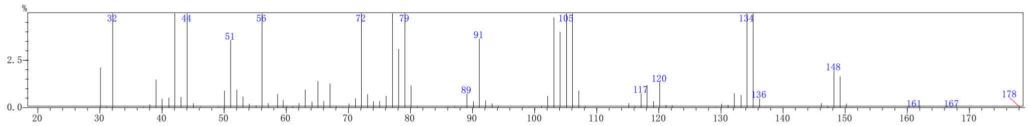
38. *N*-(Furan-2-Ylmethyl)-1-Phenylethan-1-Amine (5la)

GC-MS (m/z): Calcd. 201; Found 201.



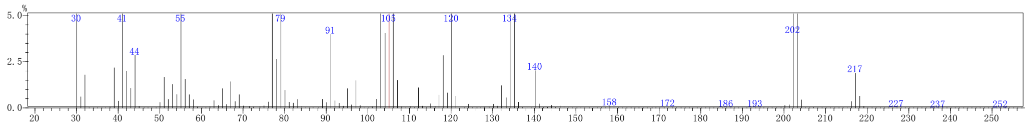
39. *N*-Ethyl-1-Phenylethan-1-Amine (5ma)

GC-MS (m/z): Calcd. 149; Found 149.



40. *N*-(Cyclohexylmethyl)-1-Phenylethan-1-Amine (5na)

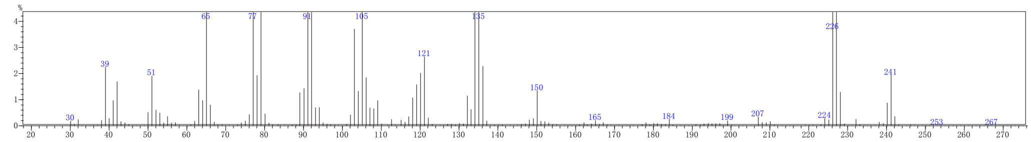
GC-MS (m/z): Calcd. 217; Found 217.



41. *N*-Benzyl-1-(4-Methoxyphenyl)-Ethan-1-Amine (5ab)

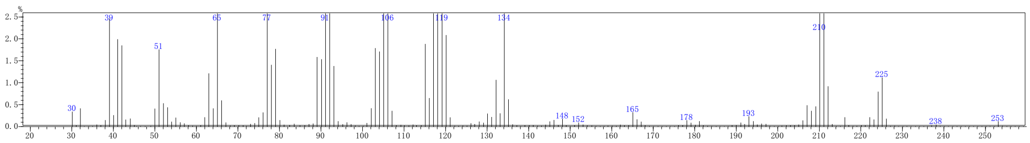
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Yellow liquid, Yield: 30.4 mg, 63%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.91 (dt, $^{3}J_{HH}$ = 8.8, 2.8 Hz, 3H, Ph), 7.18 (dt, $^{3}J_{HH}$ = 8.7, 2.8 Hz, 2H, Ph), 6.91 (dt, $^{3}J_{HH}$ = 8.9, 2.4 Hz, 2H, Ph), 6.84 (dt, $^{3}J_{HH}$ = 8.7, 2.8 Hz, 2H, Ph), 3.85 (s, 1H, CH), 3.78 (s, 4H, CH_3, CH), 1.64 (s, 1H, NH), 1.30 (d, $^{3}J_{HH}$ = 7.2 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 197.8, 163.3, 157.9, 138.8, 130.3 (2C), 127.7 (2C), 113.8 (2C), 113.6 (2C), 55.4, 46.8, 35.0, 21.8.

GC-MS (m/z): Calcd. 241; Found 241.



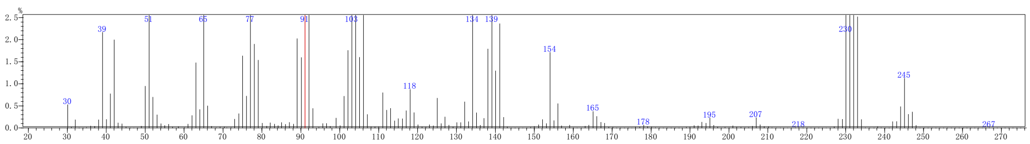
42. *N*-Benzyl-1-(*p*-Tolyl)-Ethan-1-Amine (5ac)

GC-MS (m/z): Calcd. 225; Found 225.



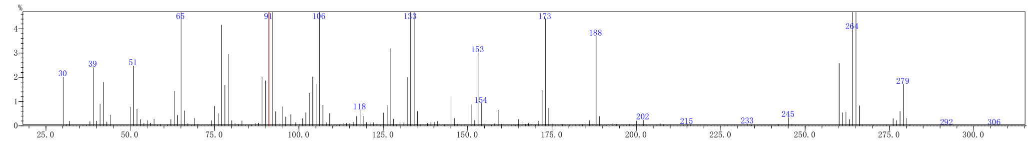
43. *N*-Benzyl-1-(4-Chlorophenyl) Ethan-1-Amine (5ai)

GC-MS (m/z): Calcd. 245; Found 245.



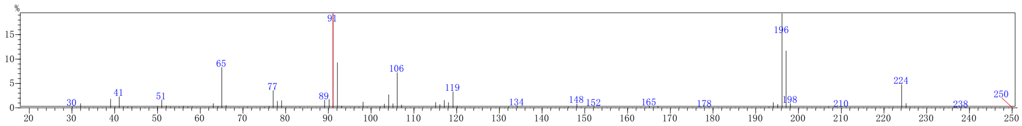
44. *N*-Benzyl-1-(4-(Trifluoromethyl) Phenyl) Ethan-1-Amine (5ae)

GC-MS (m/z): Calcd. 279; Found 279.



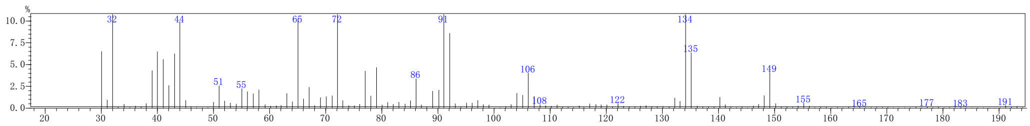
45. *N*-Benzyl-1-Phenylpropan-1-Amine (5af)

GC-MS (m/z): Calcd. 225; Found 224.



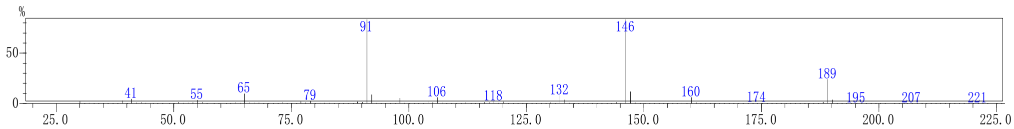
46. *N*-Benzylpropan-2-Amine (5ag)

GC-MS (m/z): Calcd. 149; Found 149.



47. *N*-benzylcyclohexanamine (5ah)

GC-MS (m/z): Calcd. 189; Found 189.



7. References

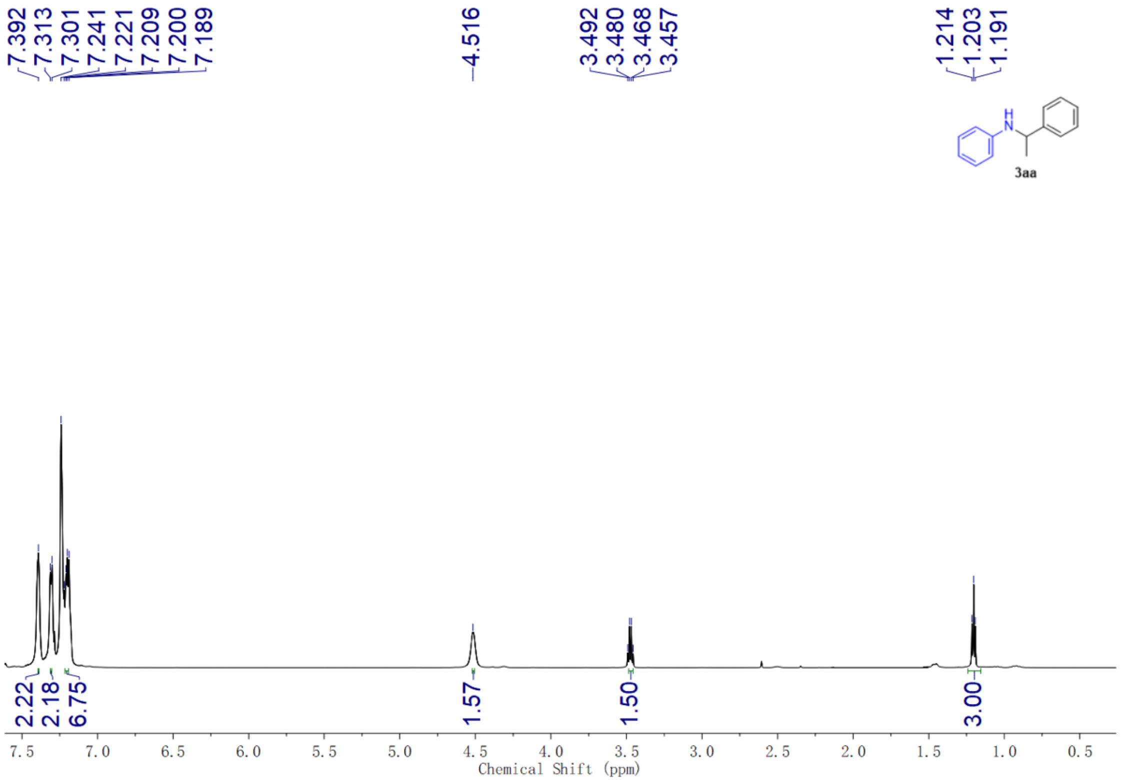
(1) L. Piche, J. C. Daigle, R. Poli and J. P.Claverie, *Eur. J. Inorg. Chem.* 2010, **2010**, 4595–4601.

(2) B. Sundararaju, Z. Tang, M. Achard, G. V. M. Sharma, L. Toupet and C. Bruneau, *Adv. Synth. Catal.*, 2010, **352**, 3141–3146.

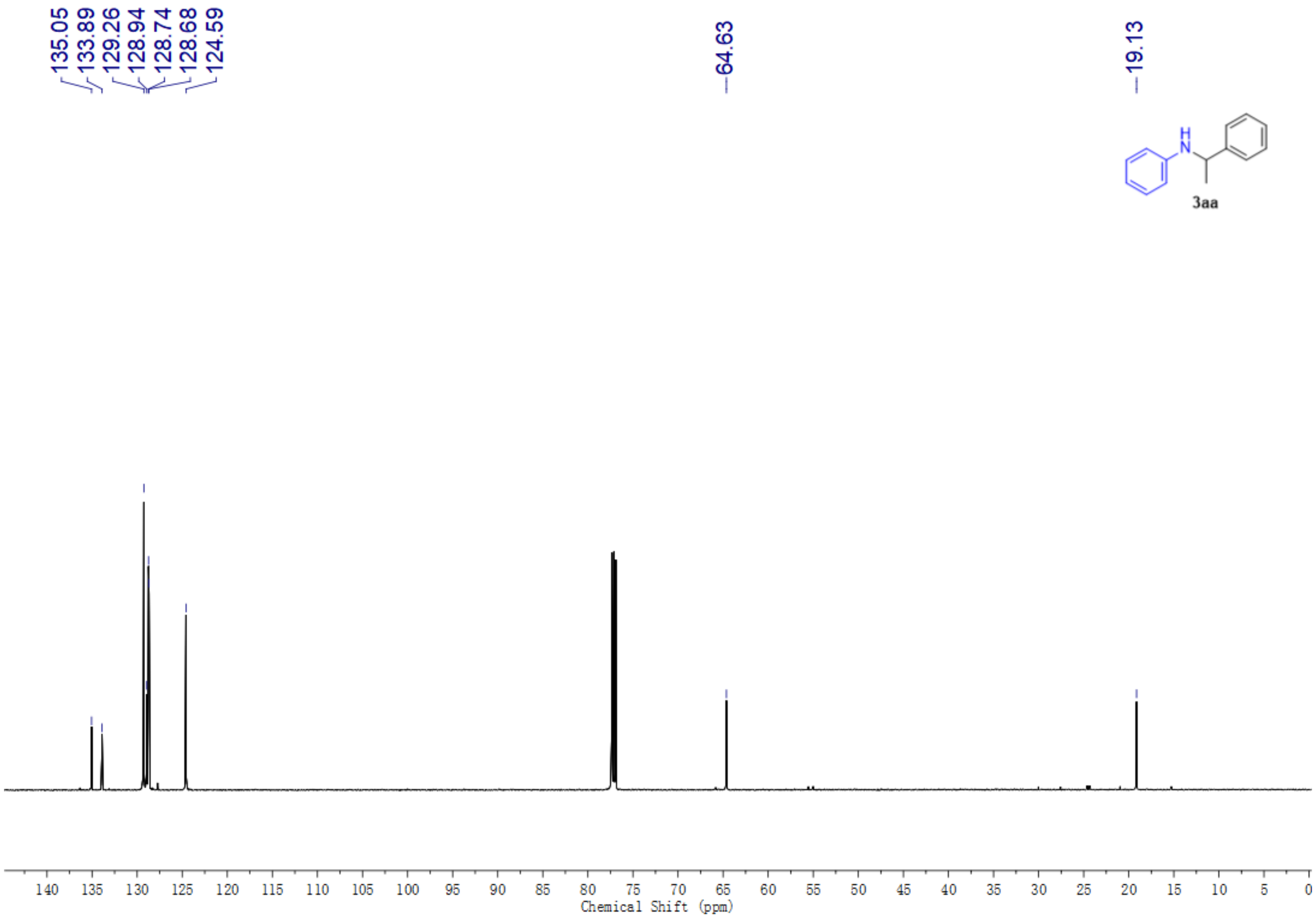
(3) J. D. Grayson, F. M. Dennis, C. C. Robertson and B. M. Partridge, *J. Org. Chem.*, 2021, **86**, 9883−9897.

(4) Y. J. Su, M. Lu, B. L. Dong, H. Chen and X. D. Shi, *Adv. Synth. Catal.*, 2014, **356**, 692-696.

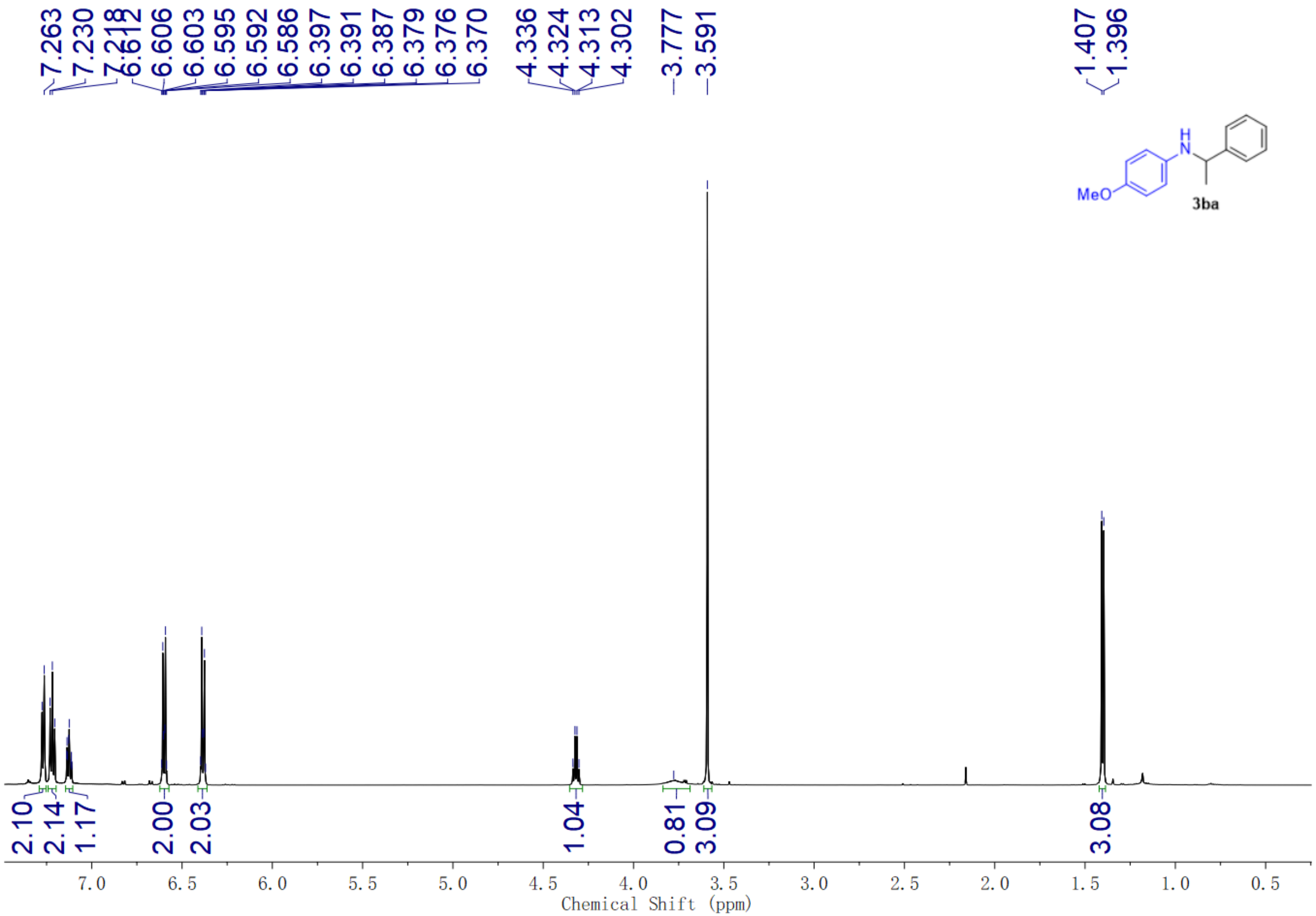
8. NMR Spectra



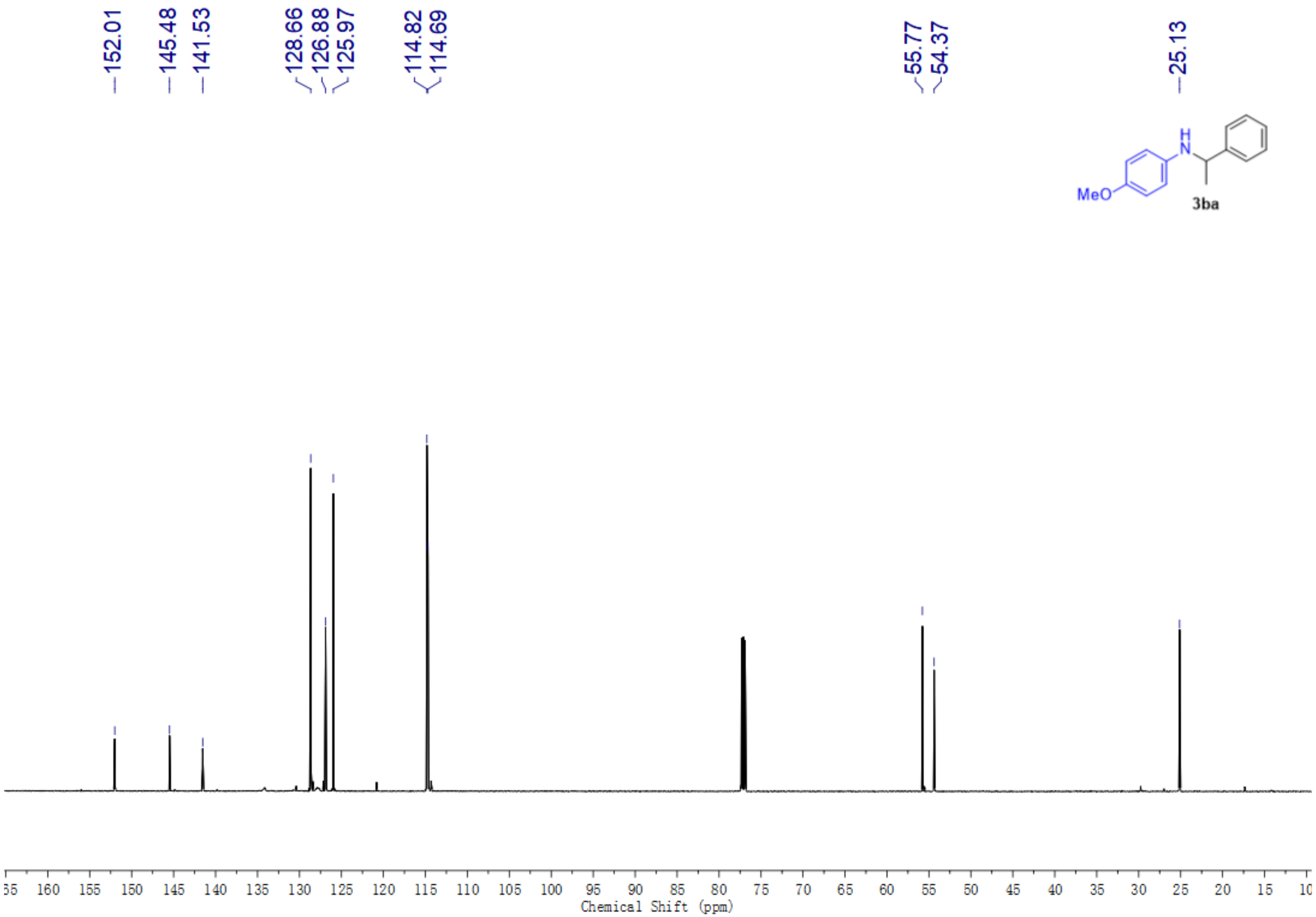
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3aa**



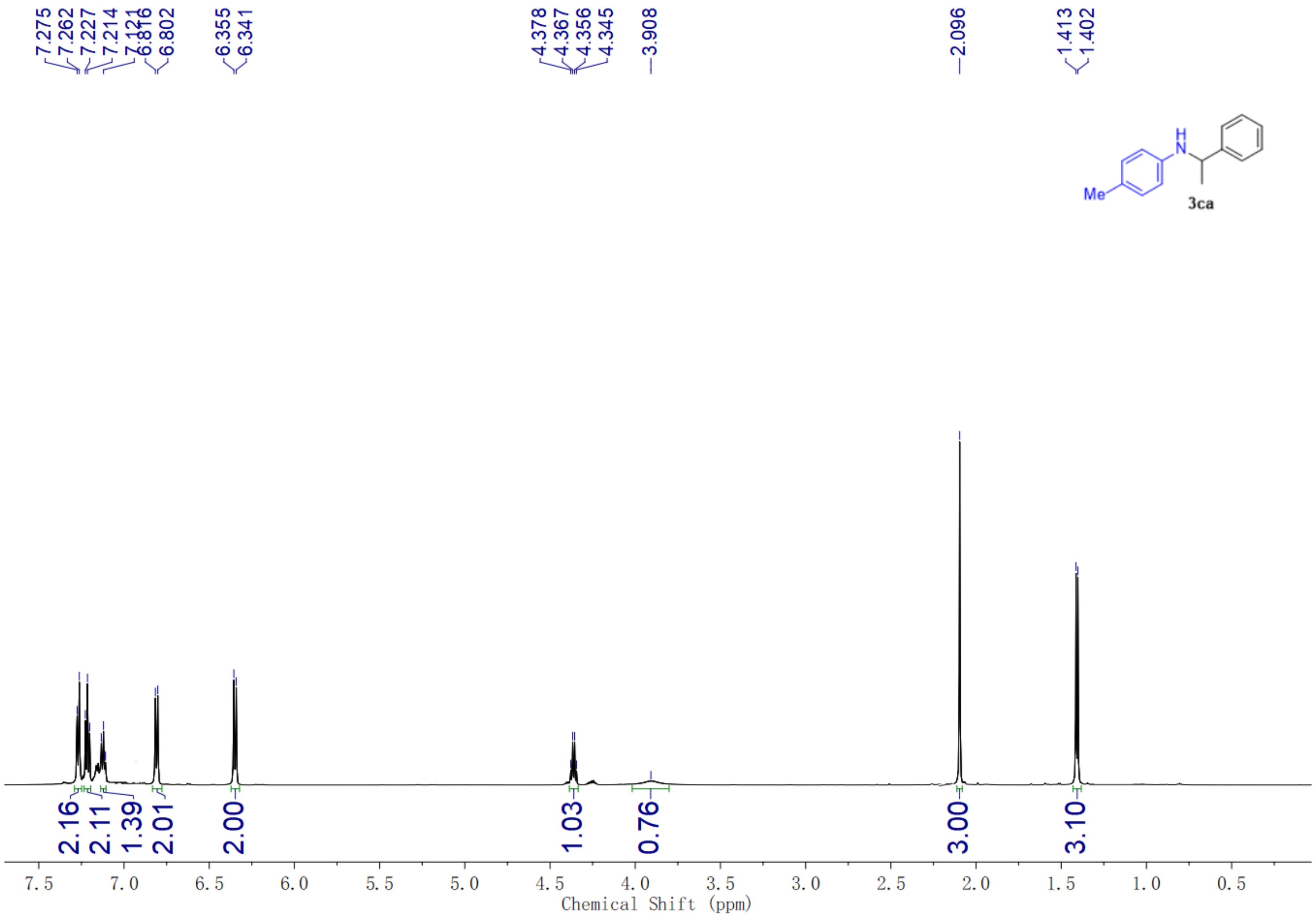
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3aa**



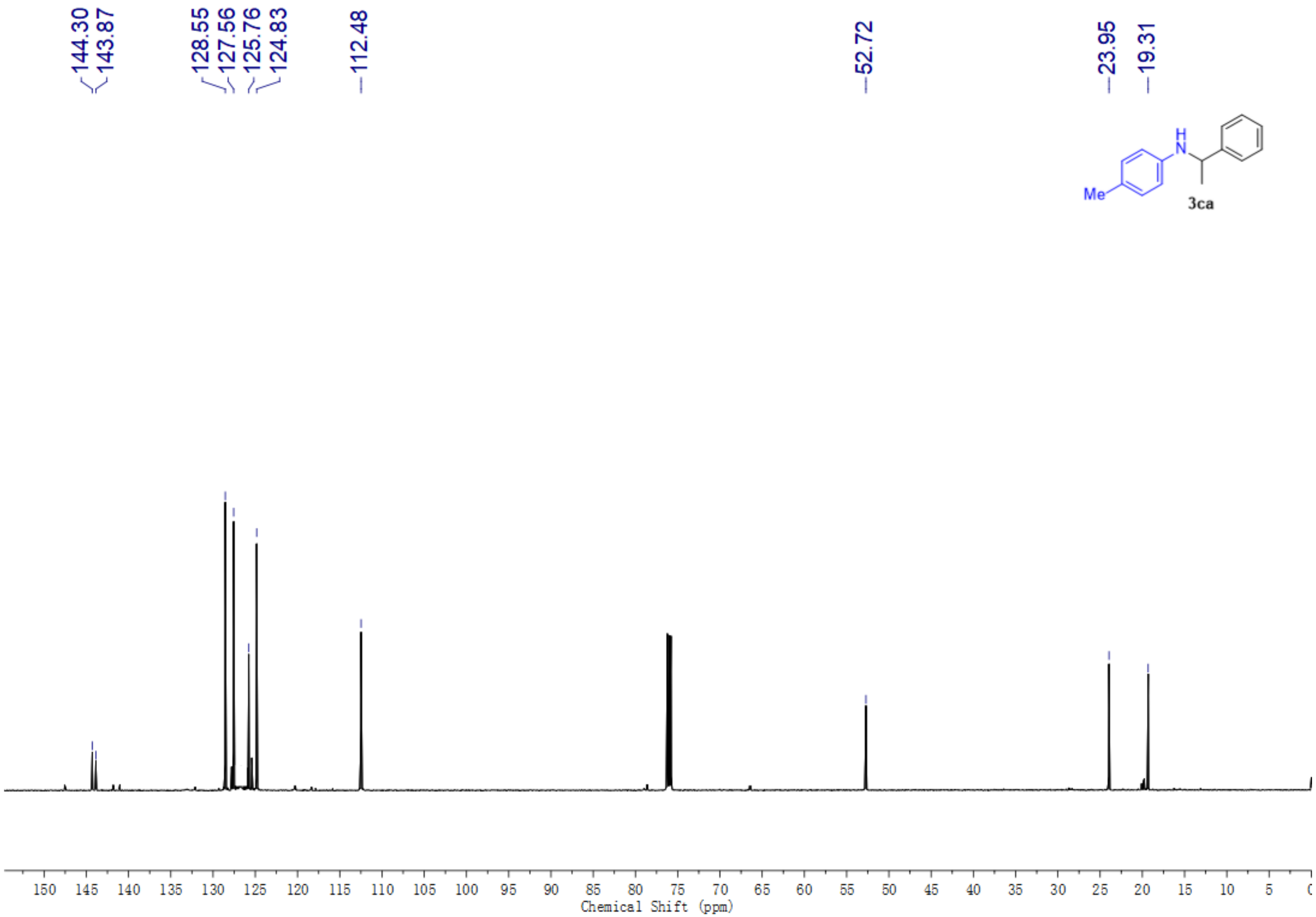
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3ba**



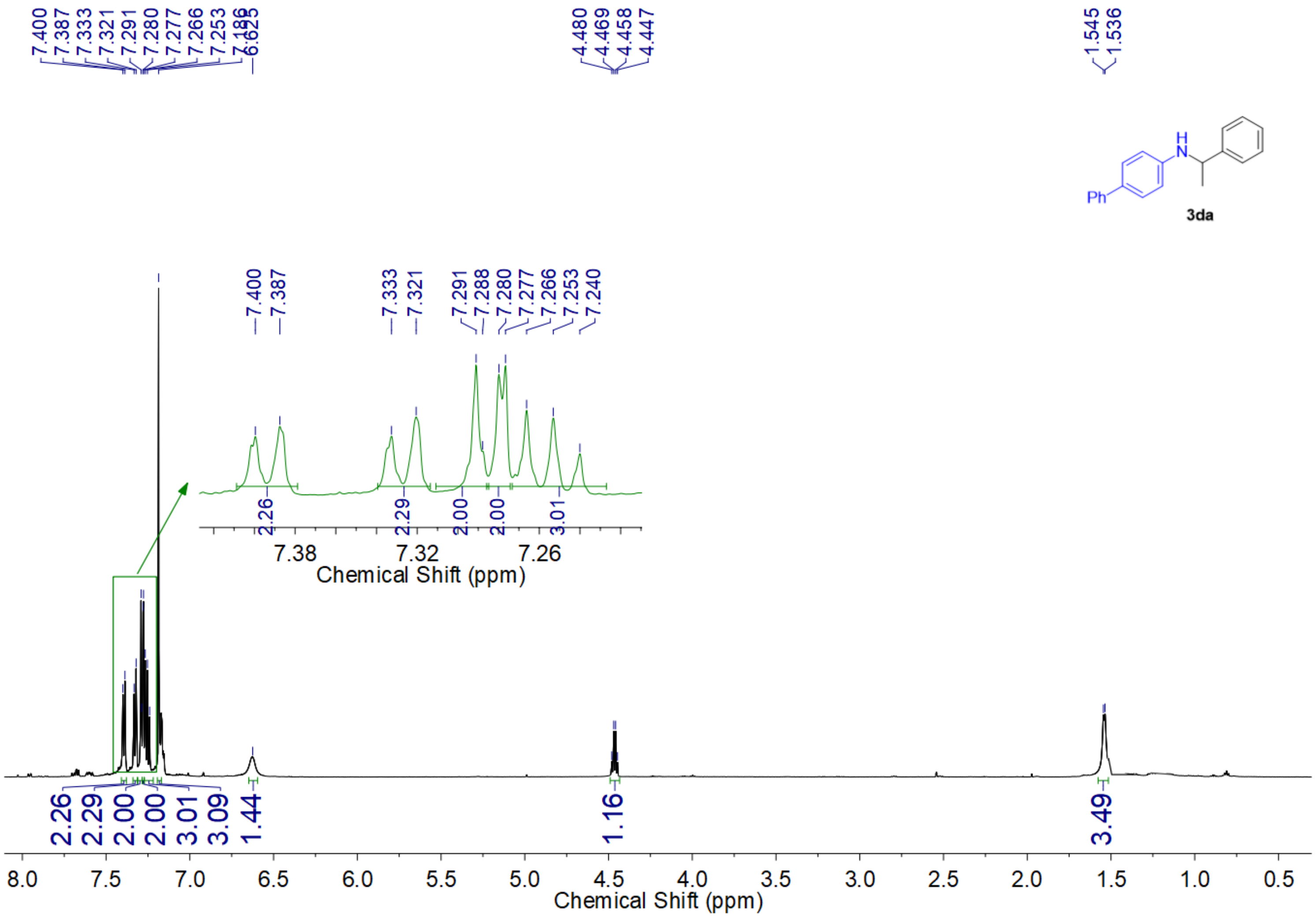
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ba**



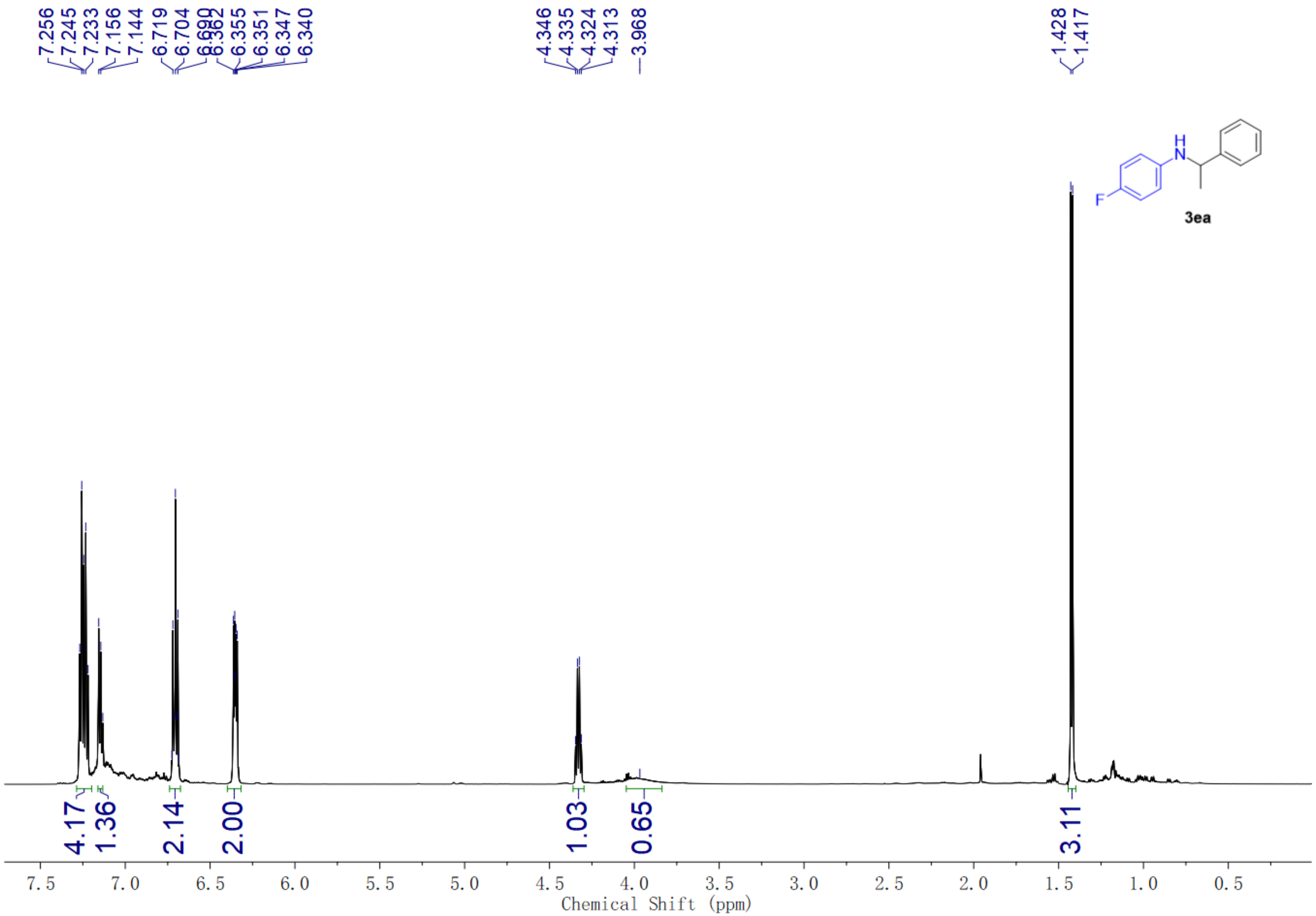
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3ca**



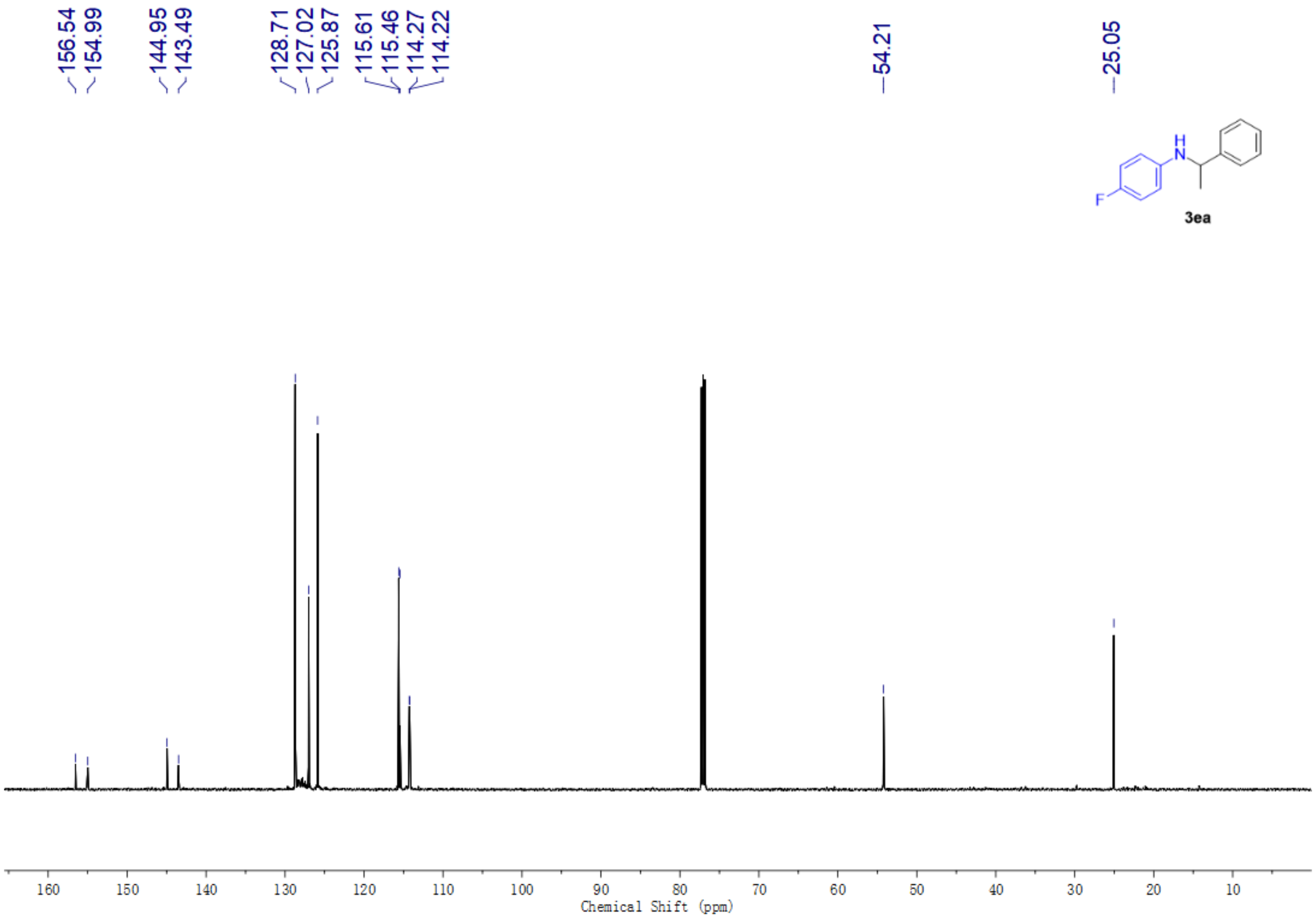
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ca**



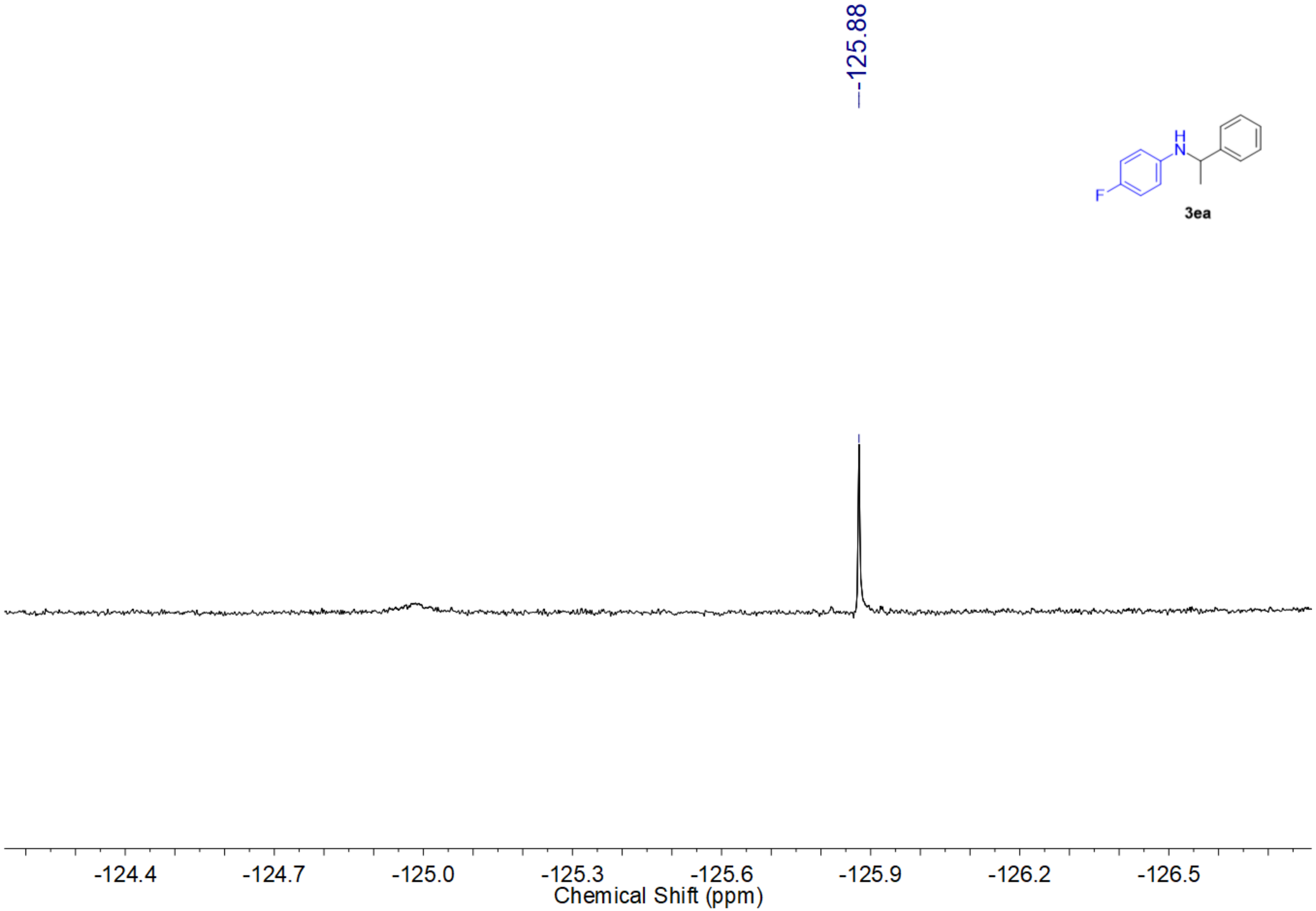
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3da**



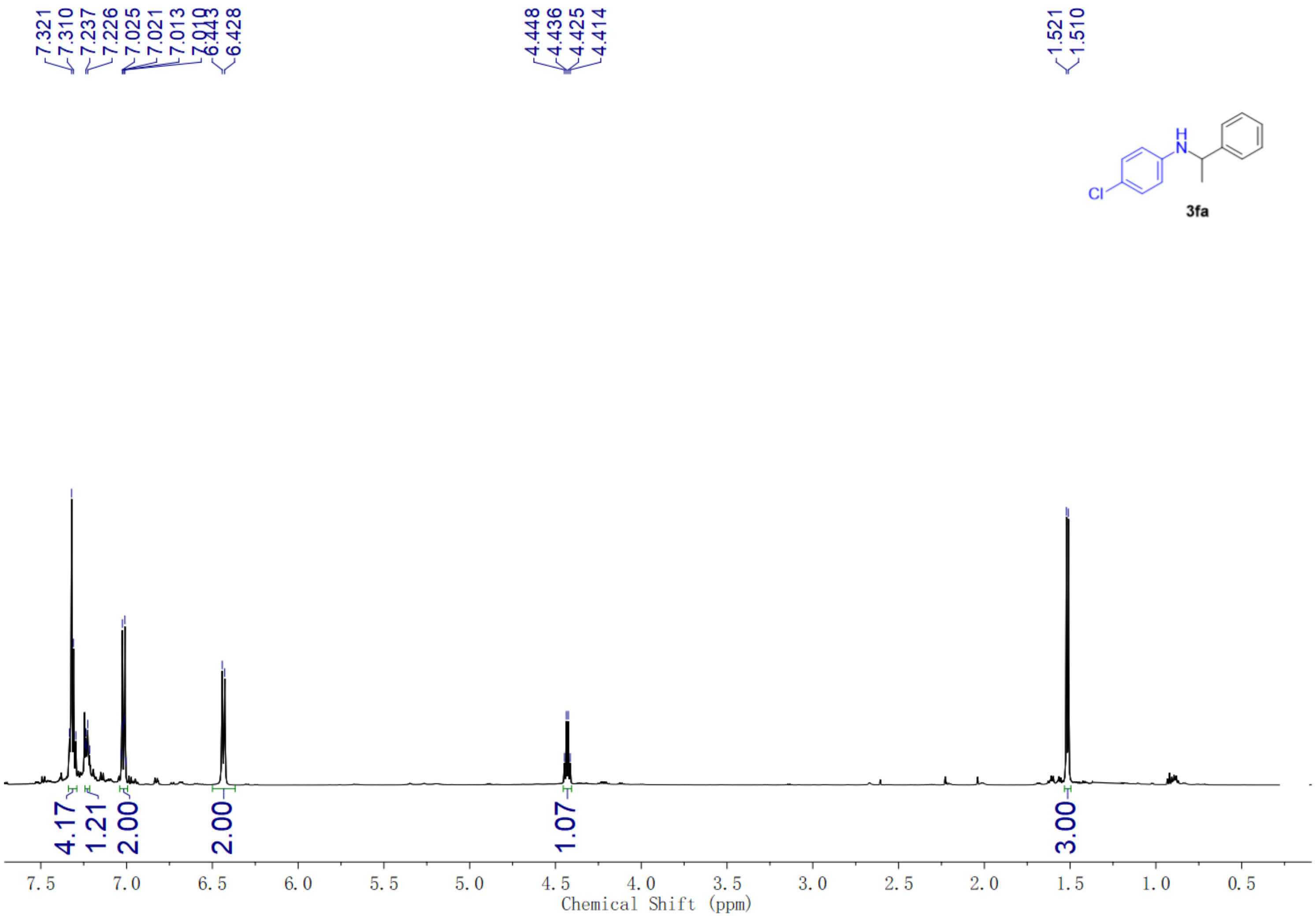
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **3ea**



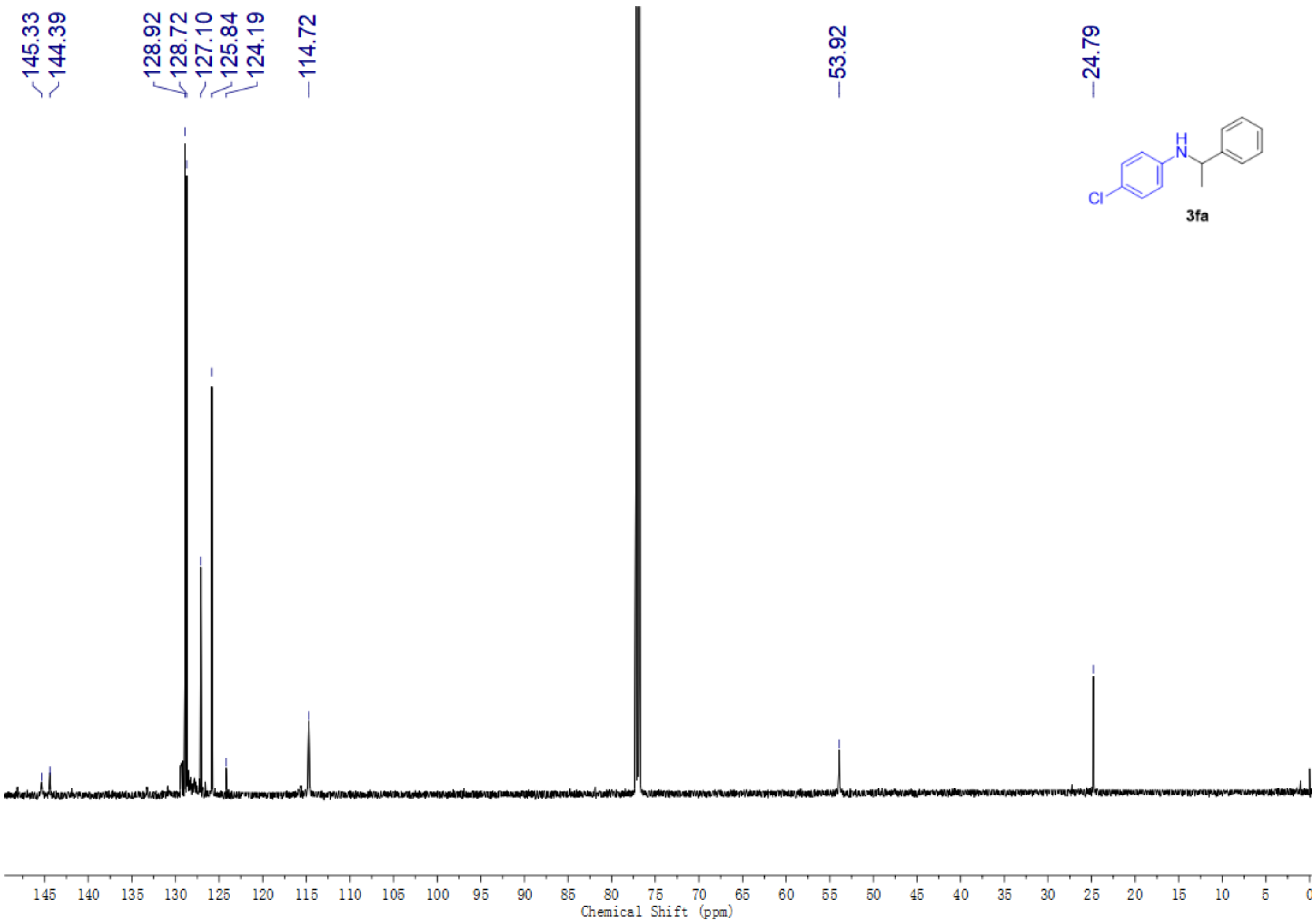
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ea**



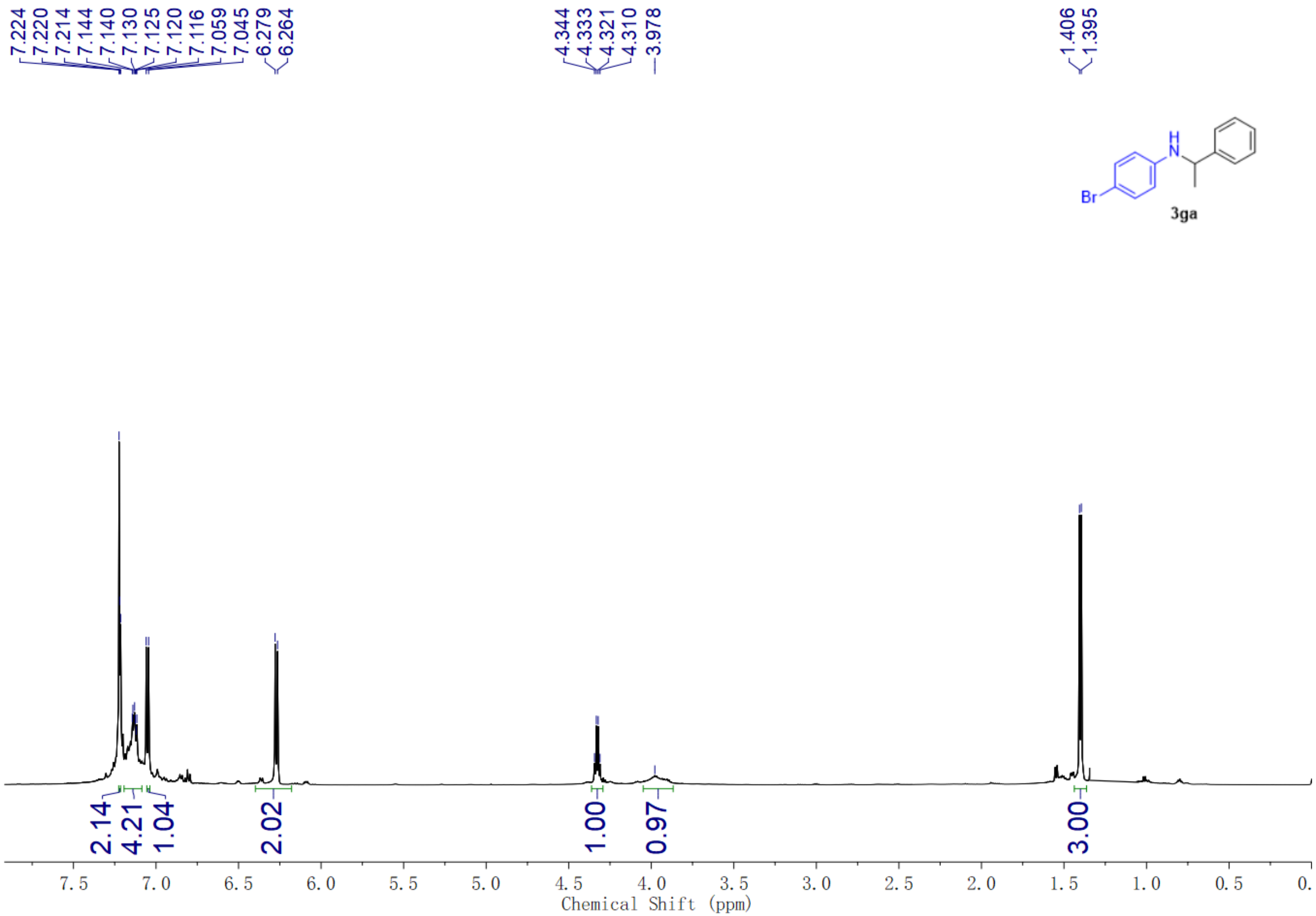
^{19}F NMR (564 MHz, 298 K, $CDCl_3$) of **3ea**



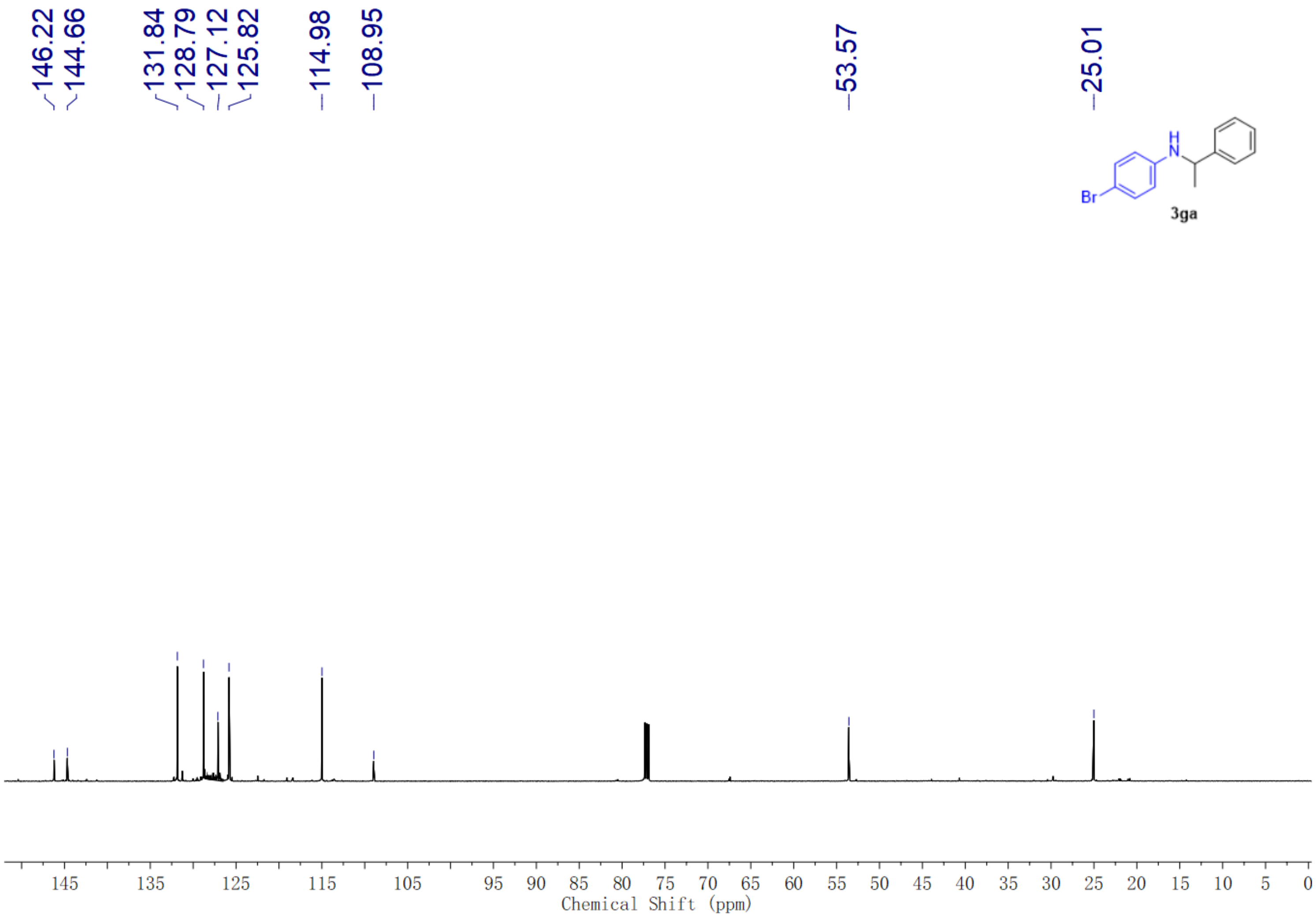
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3fa**



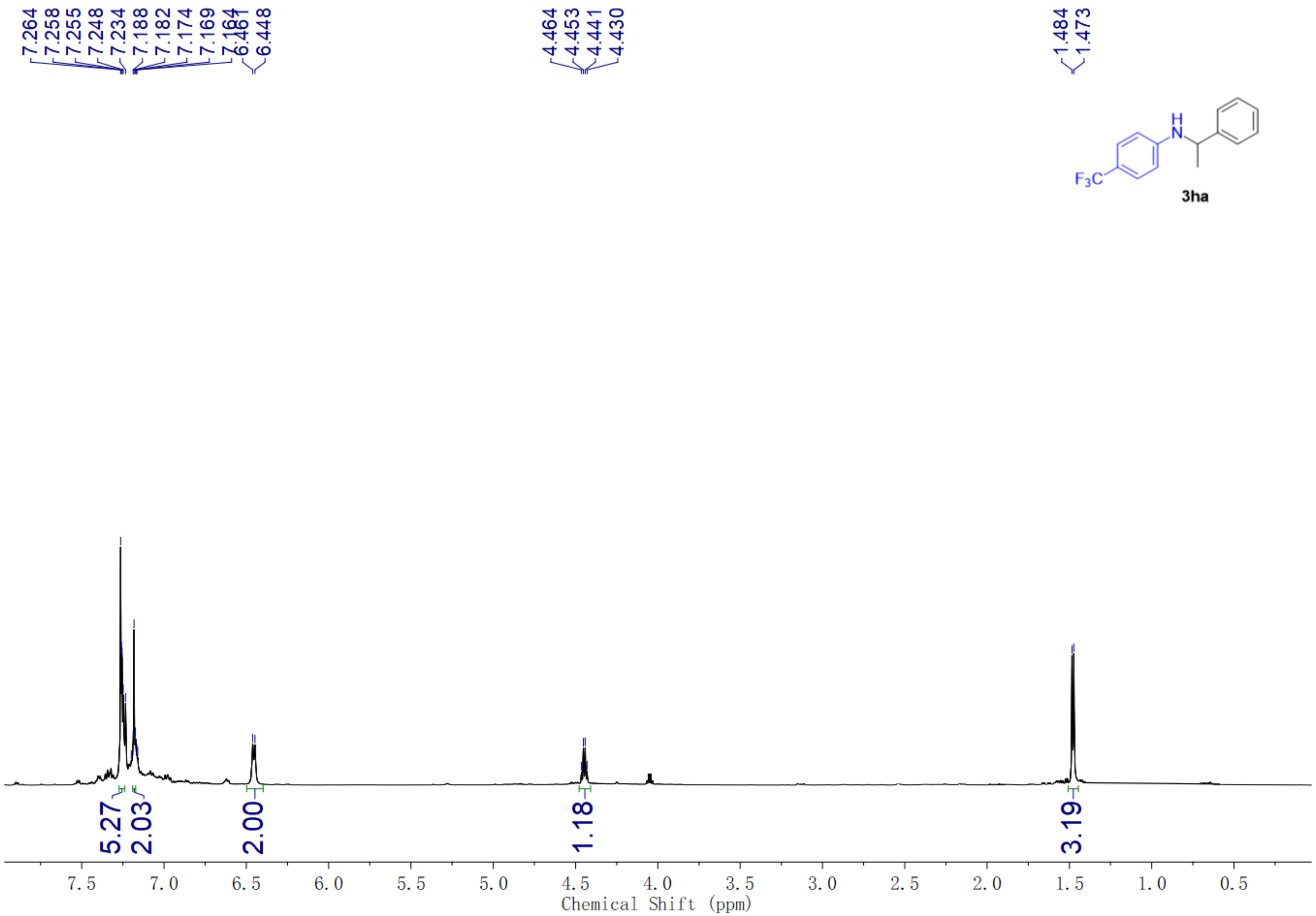
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3fa**



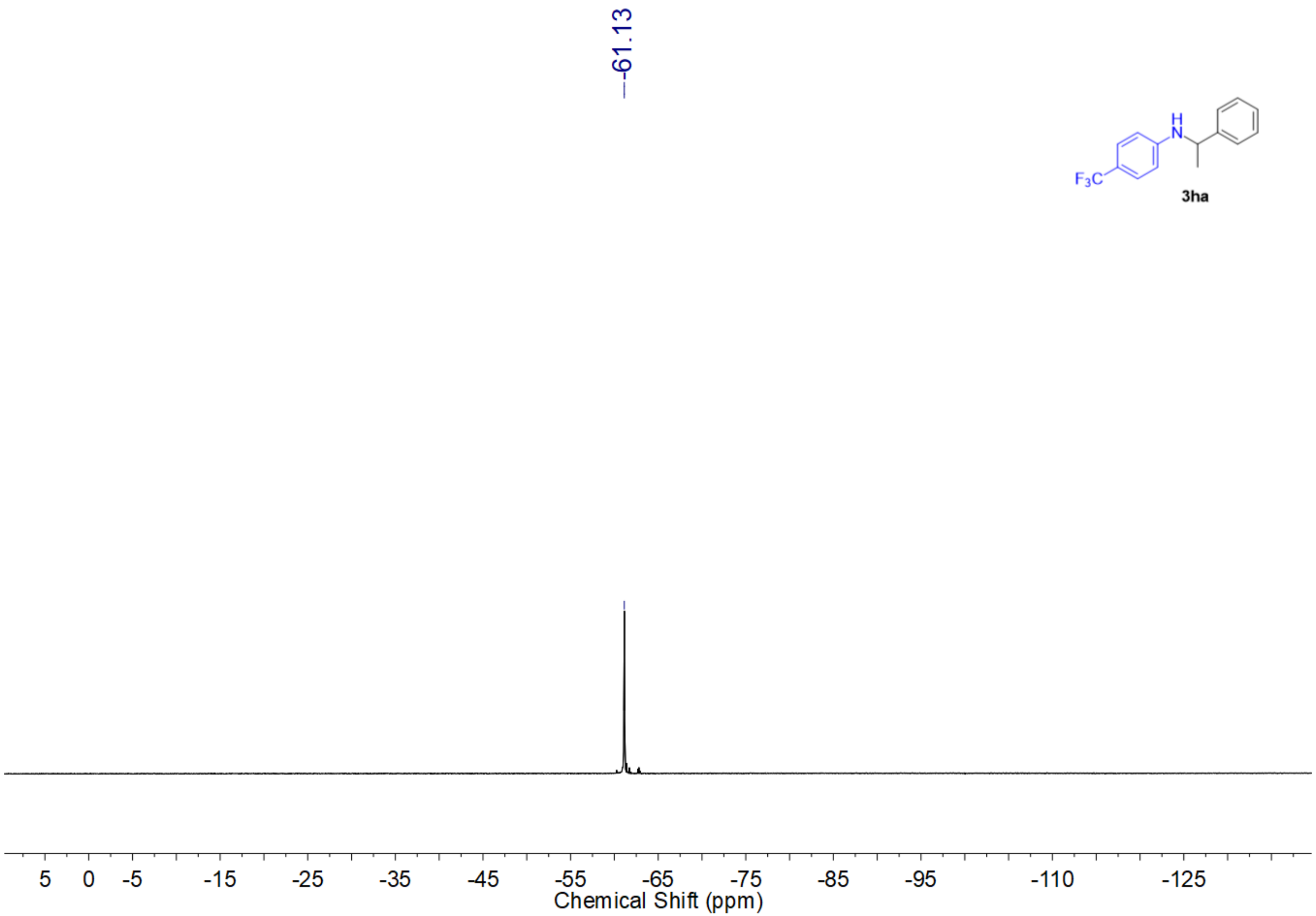
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **3ga**



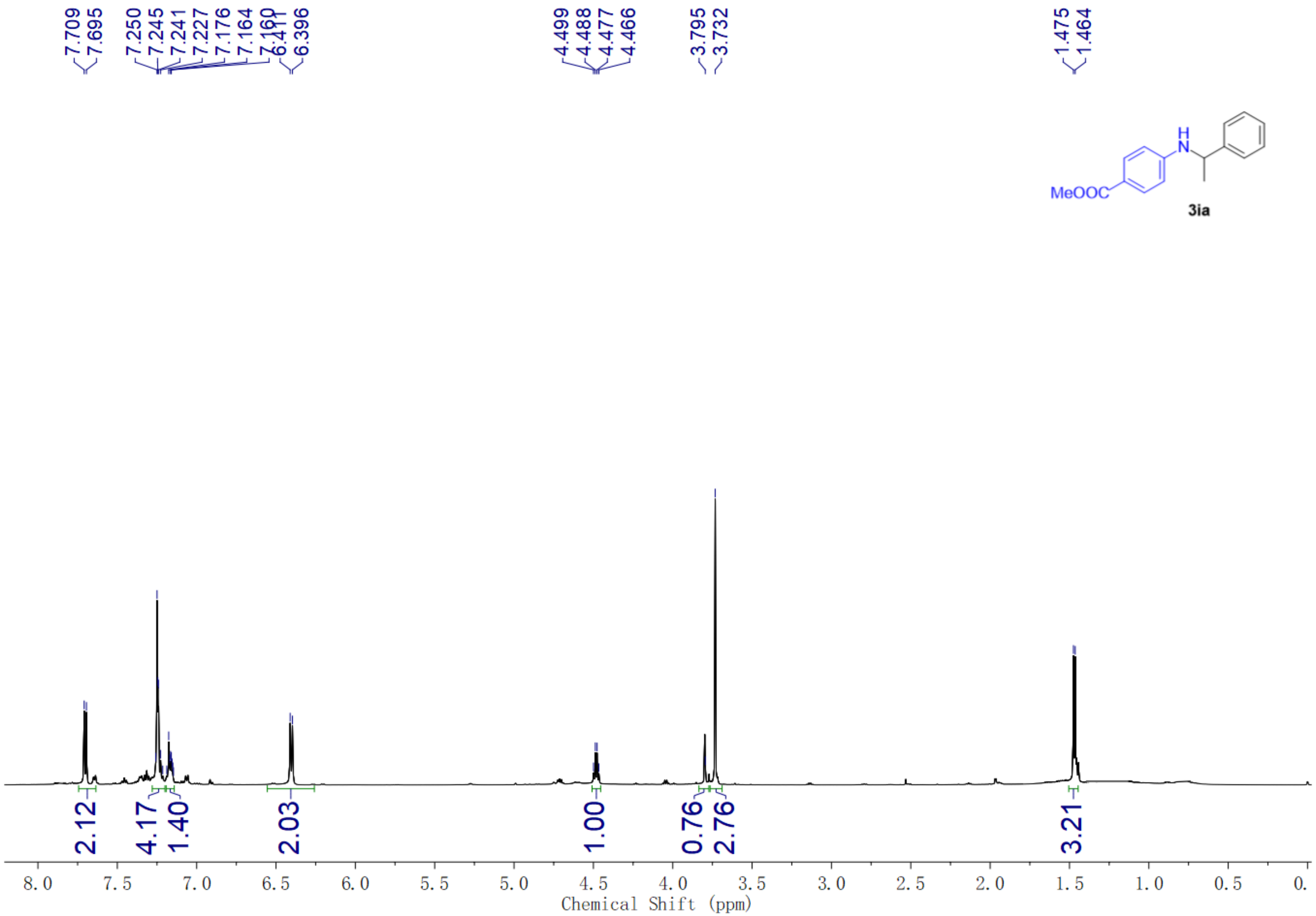
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ga**



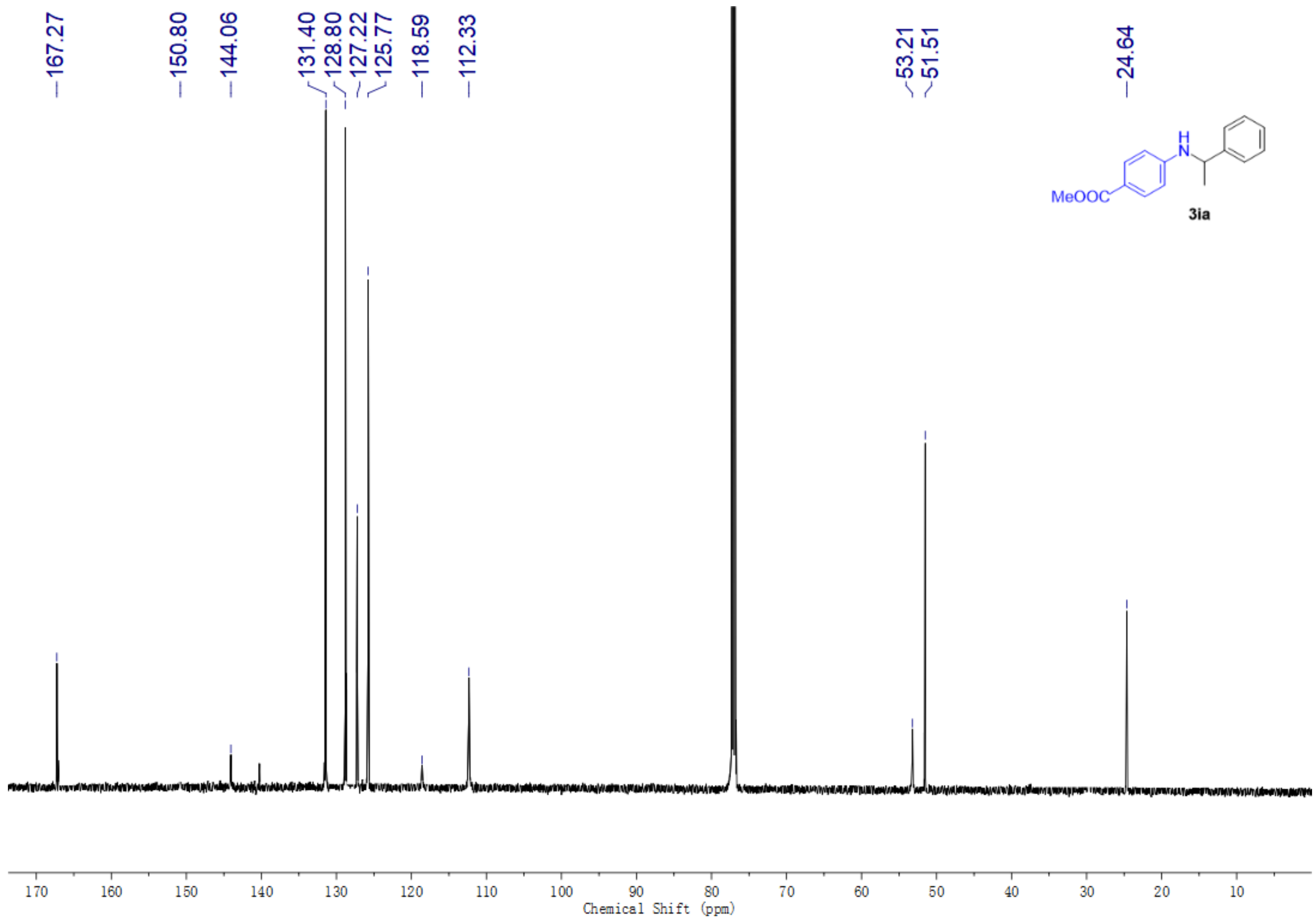
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3ha**



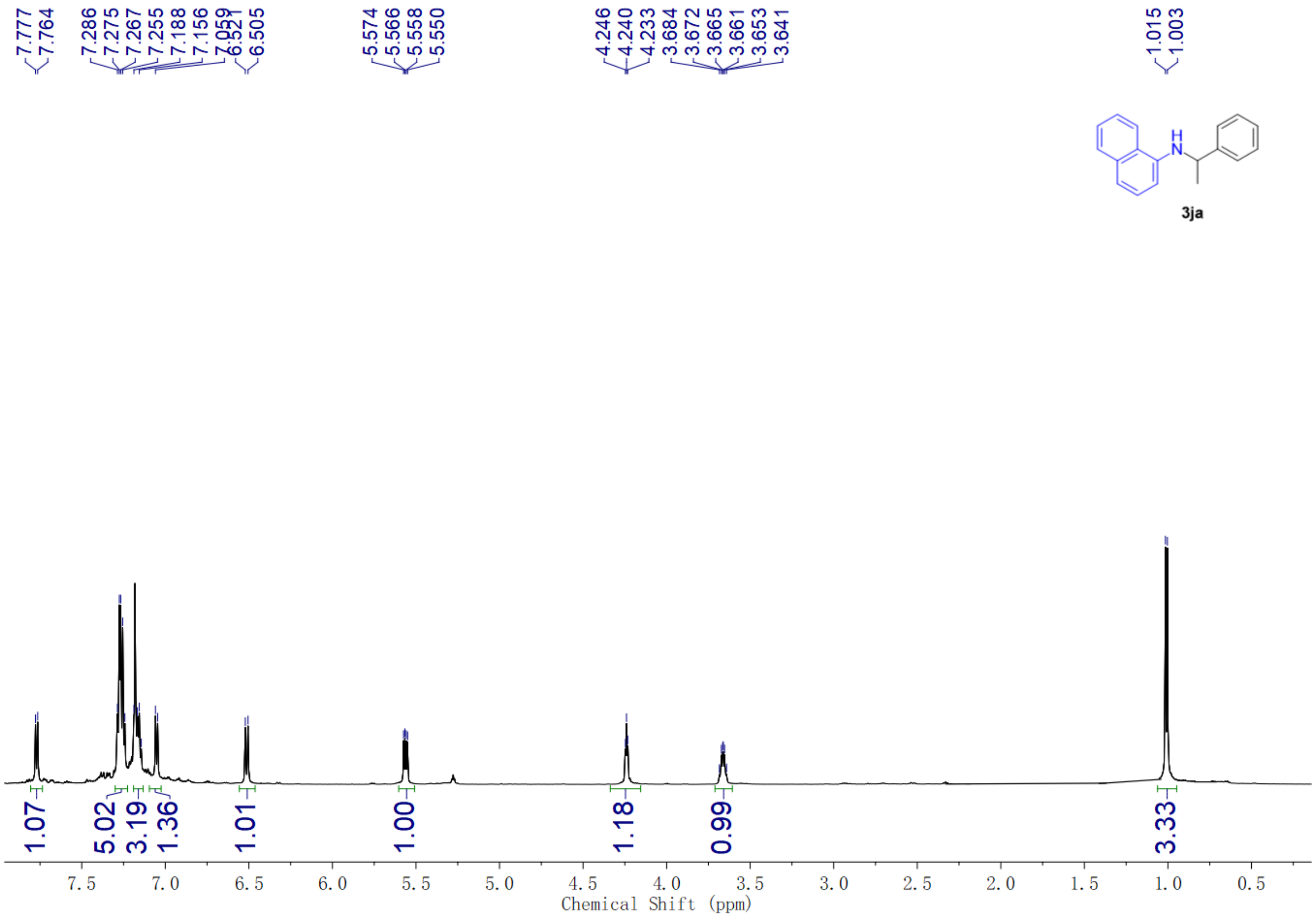
^{19}F NMR (564 MHz, 298 K, $CDCl_3$) of **3ha**



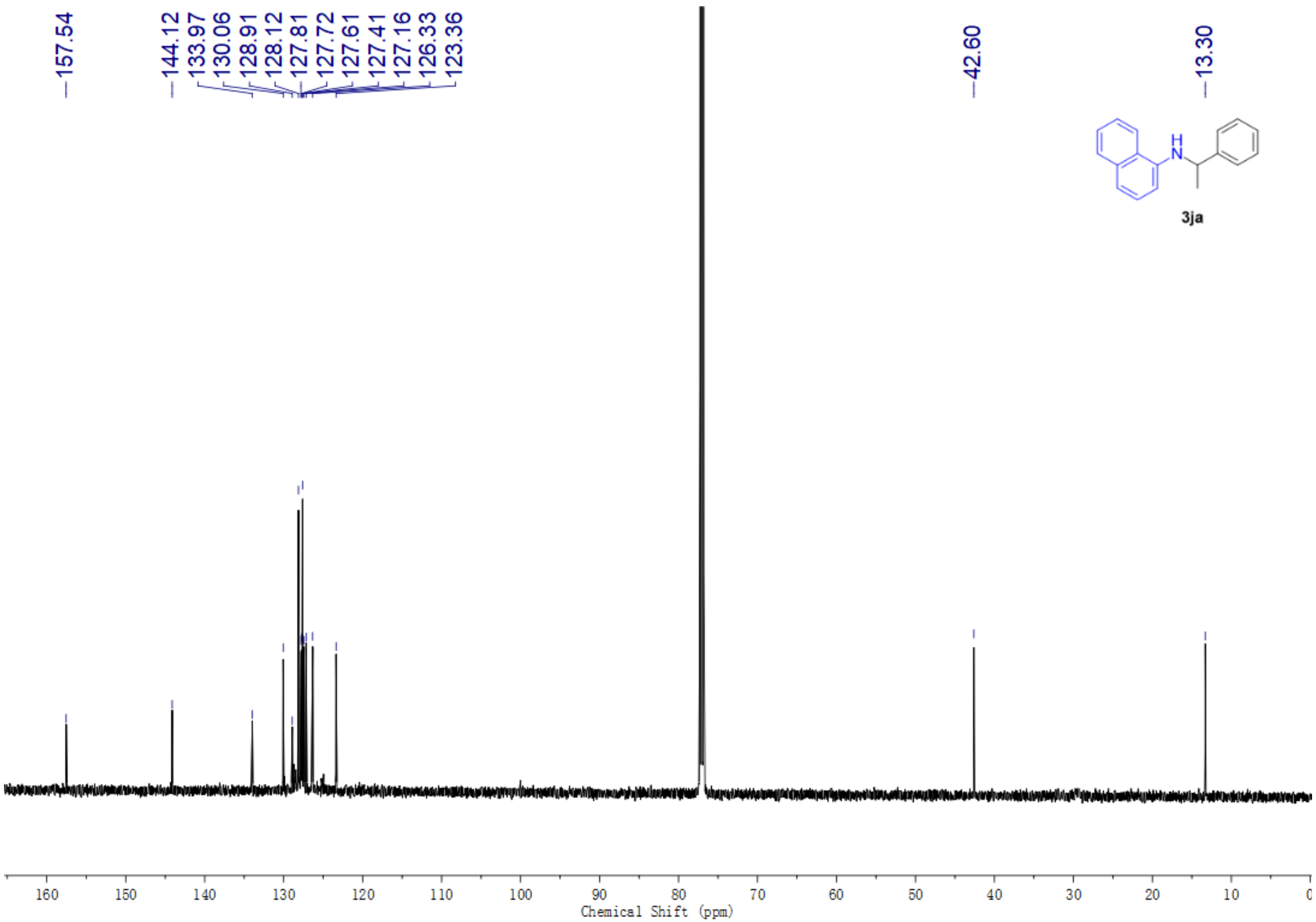
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **3ia**



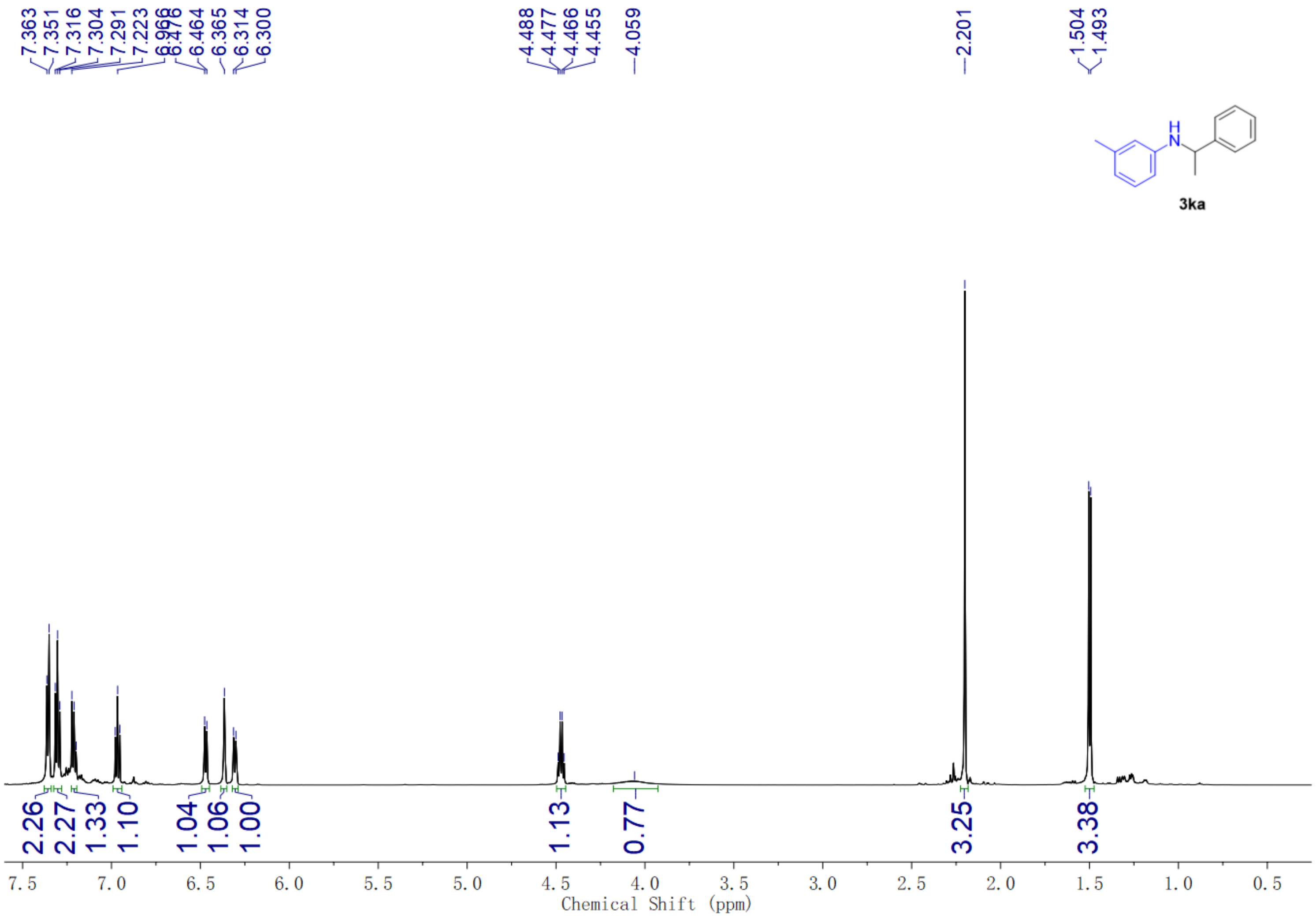
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ia**



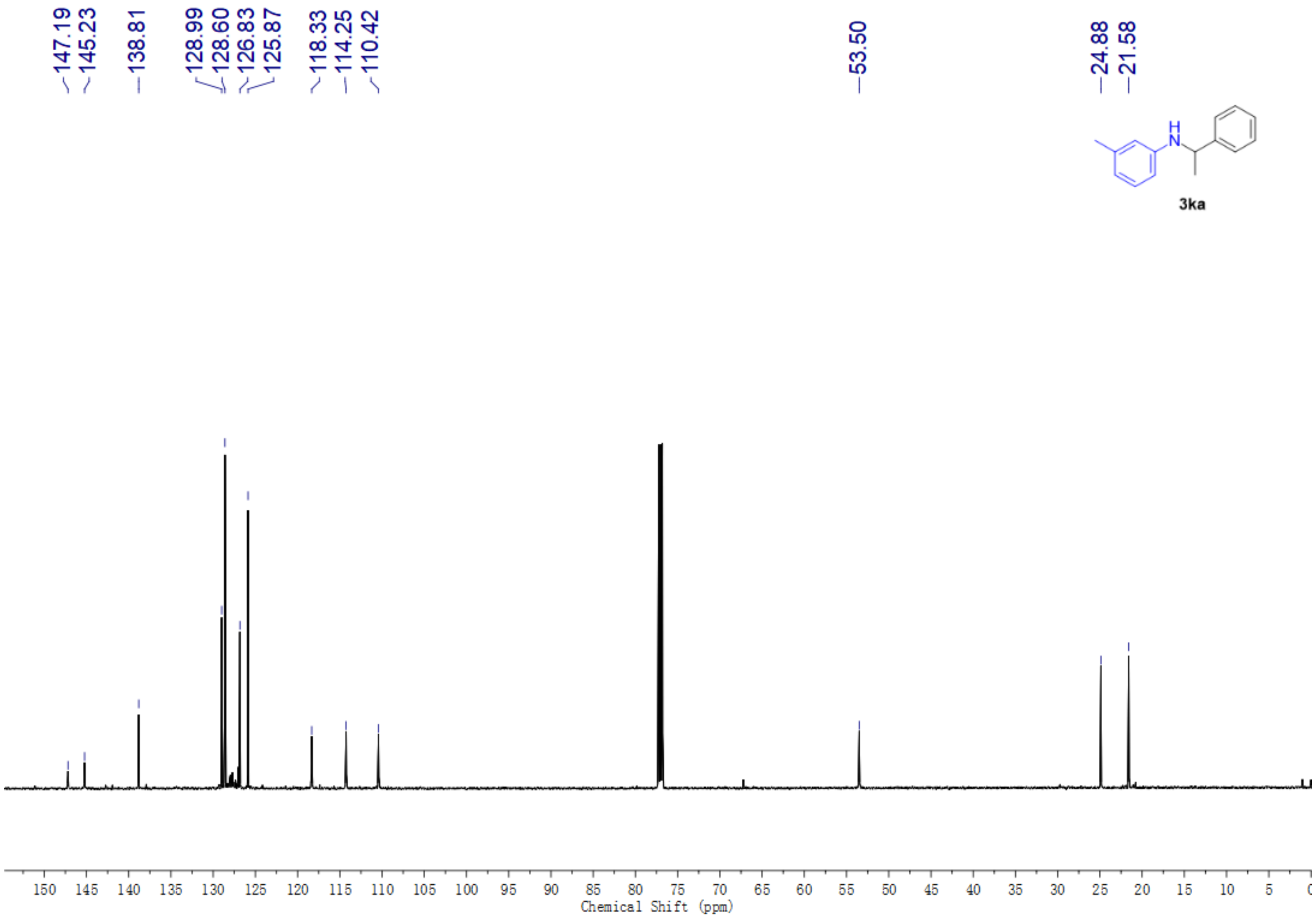
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3ja**



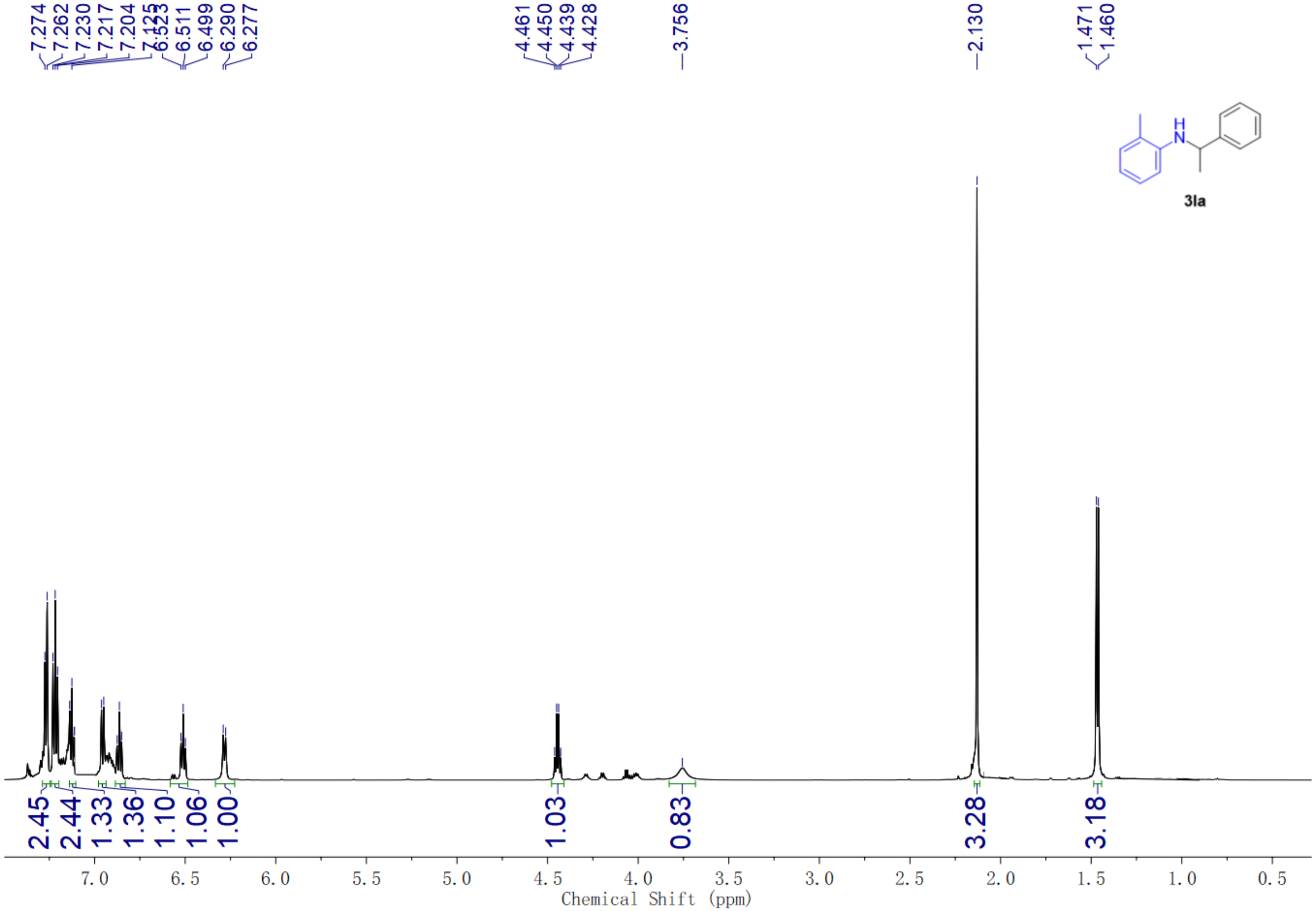
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ja**



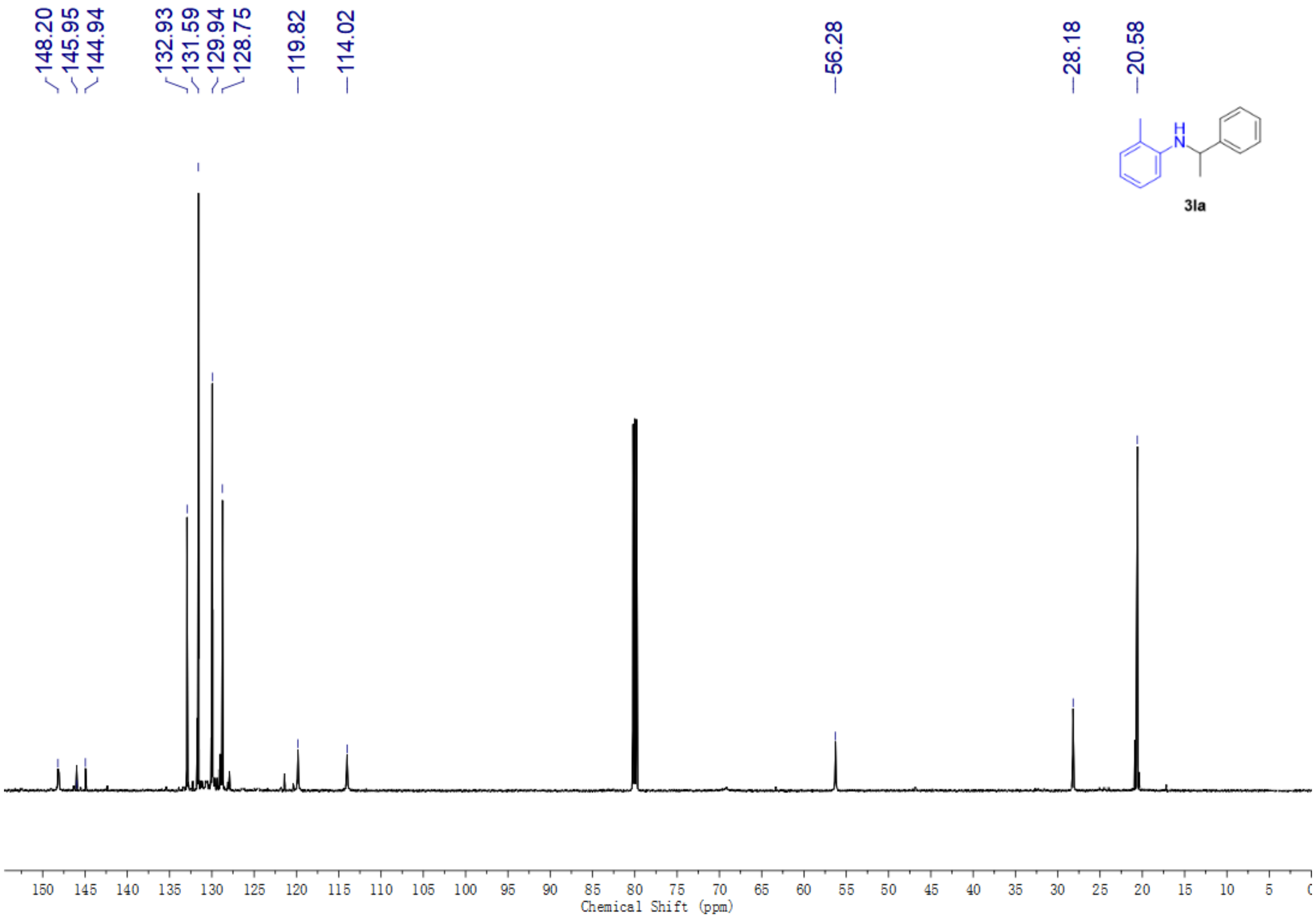
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3ka**



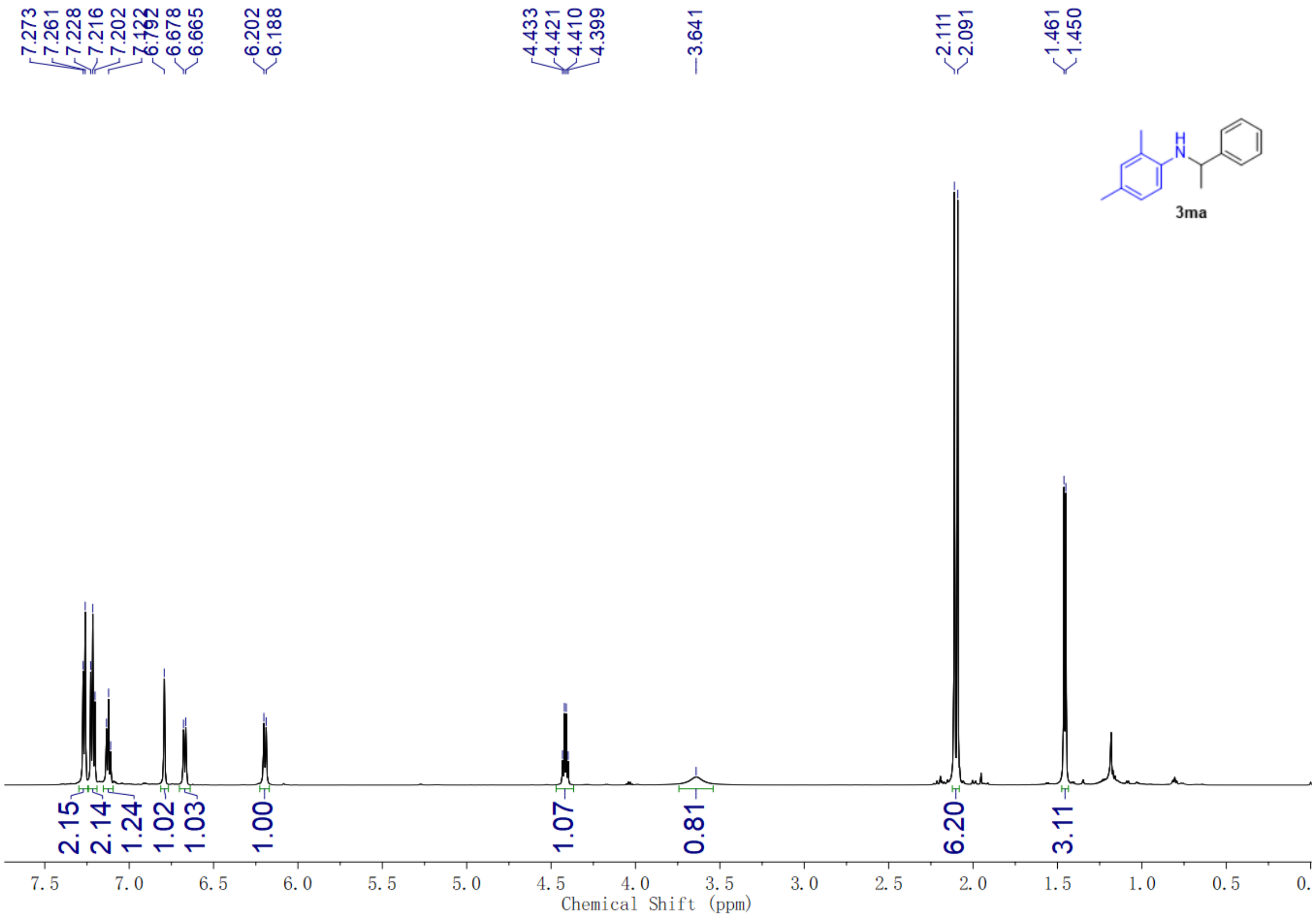
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ka**



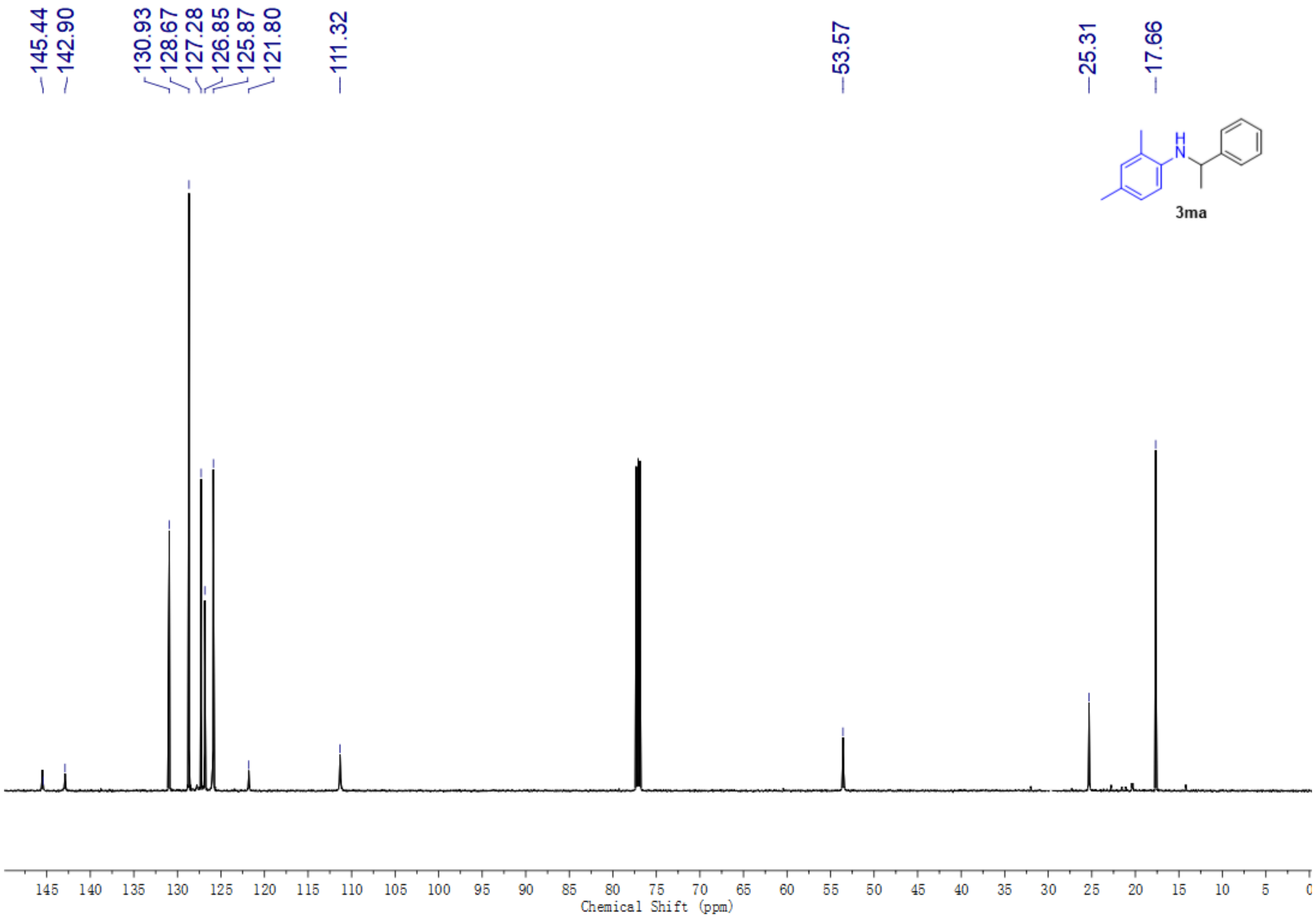
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3la**



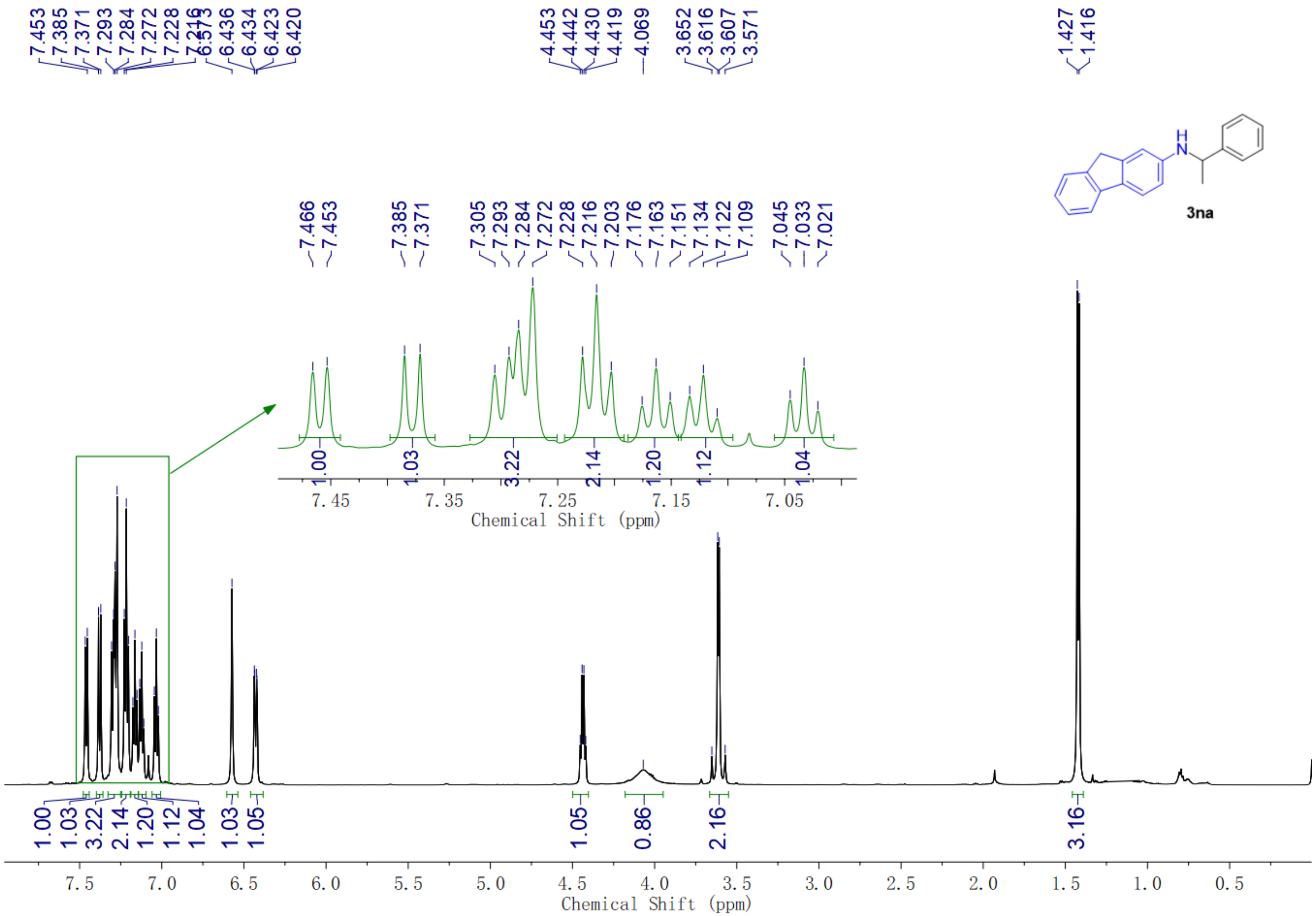
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3la**



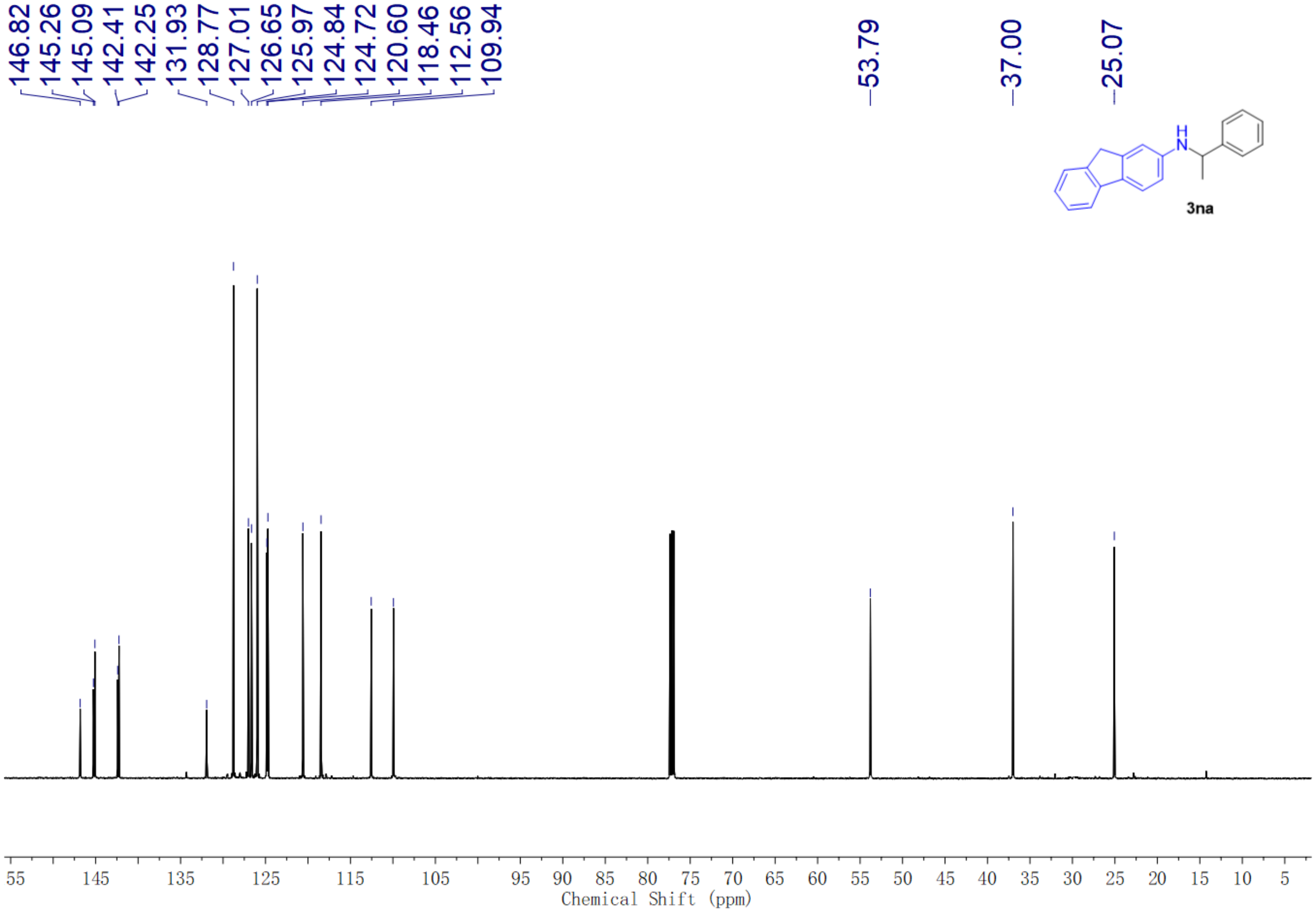
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **3ma**



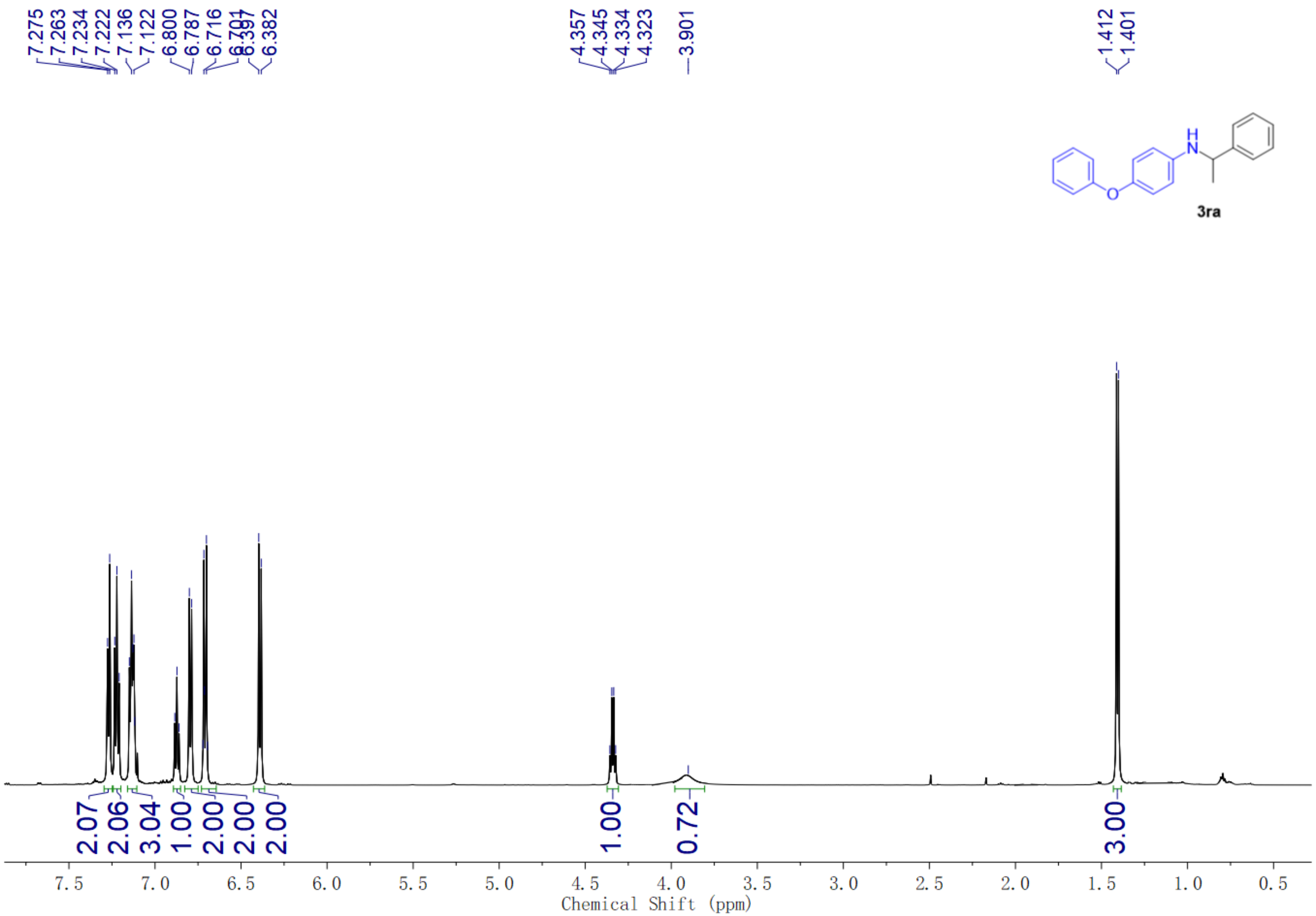
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ma**



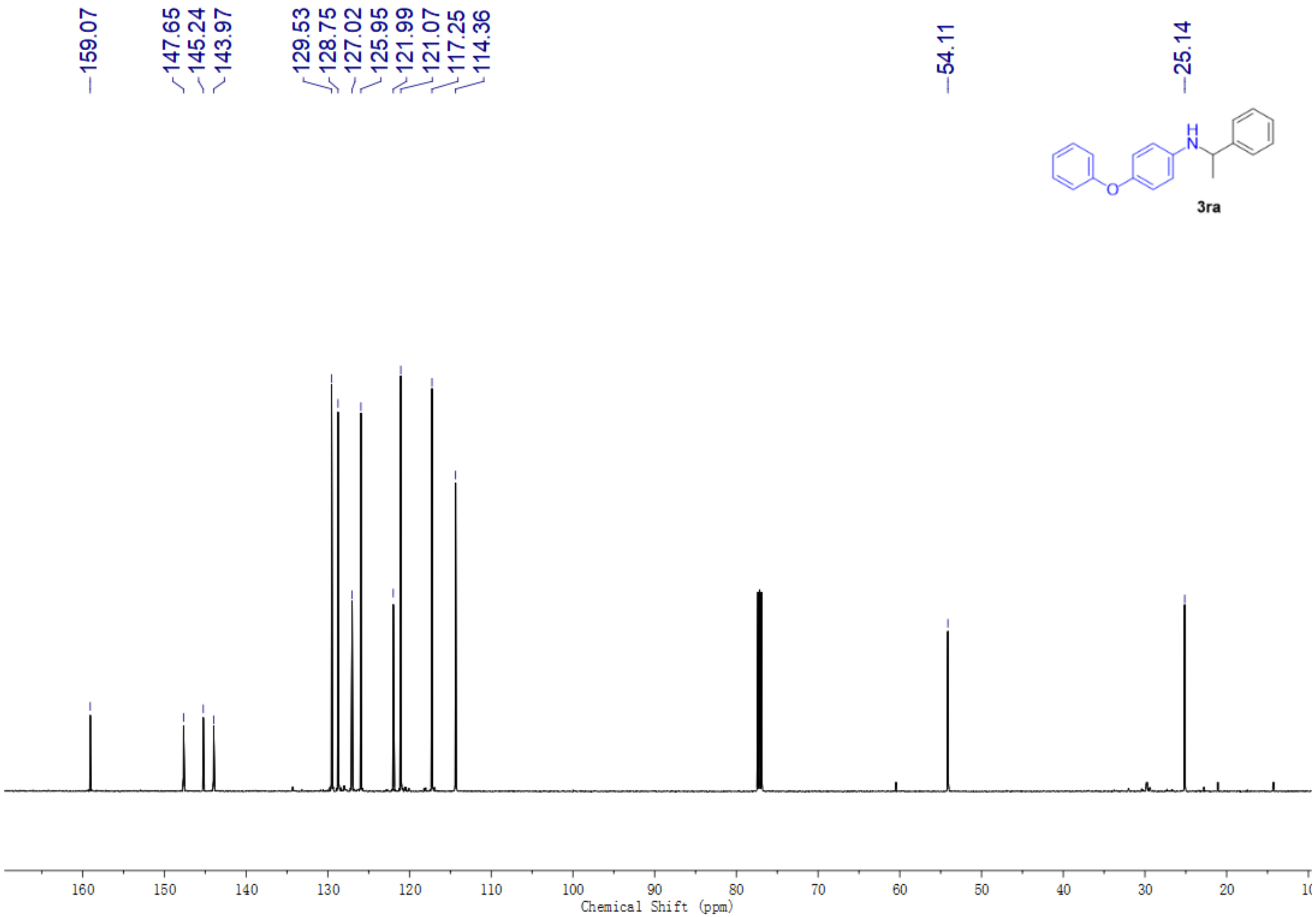
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3na**



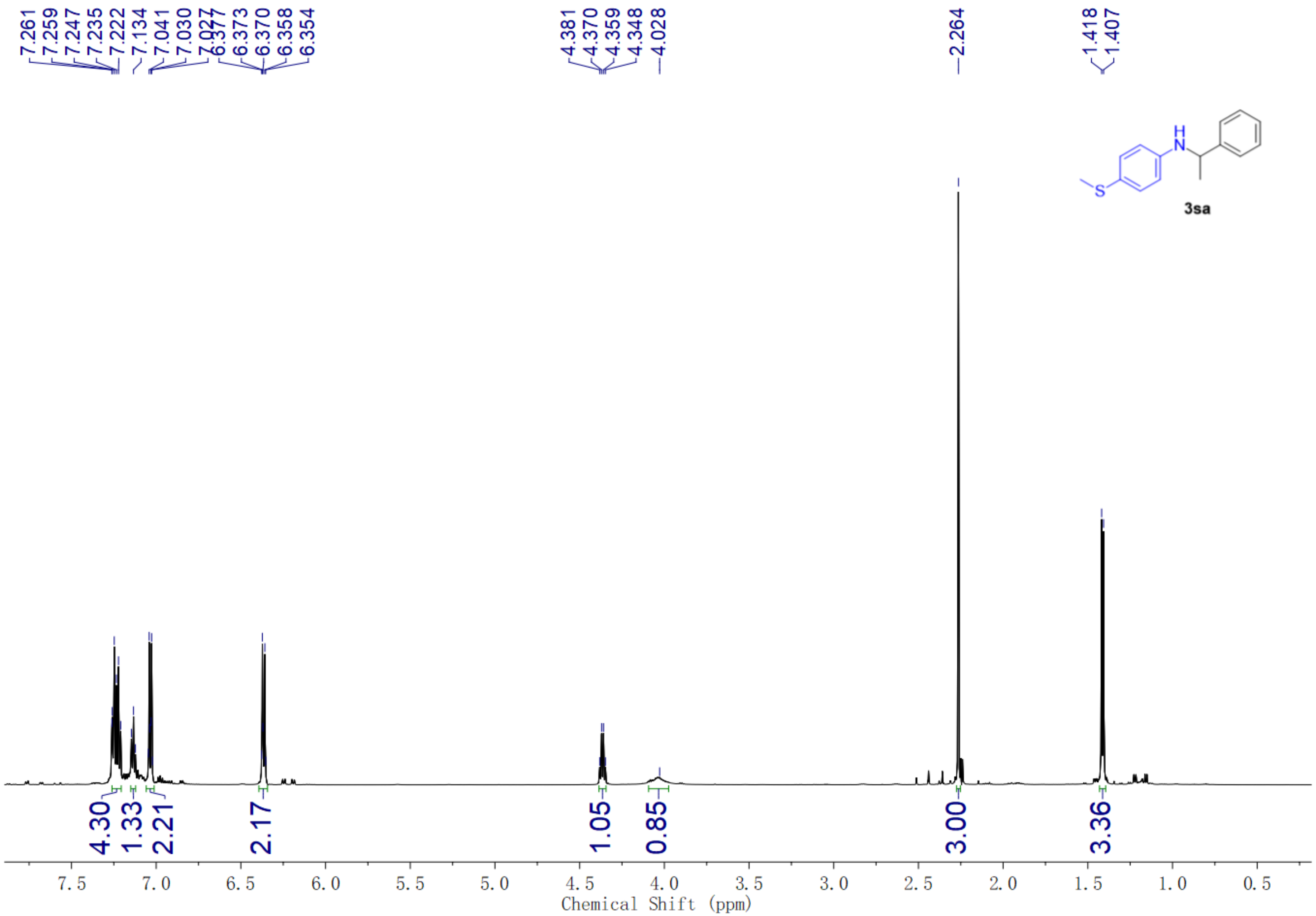
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3na**



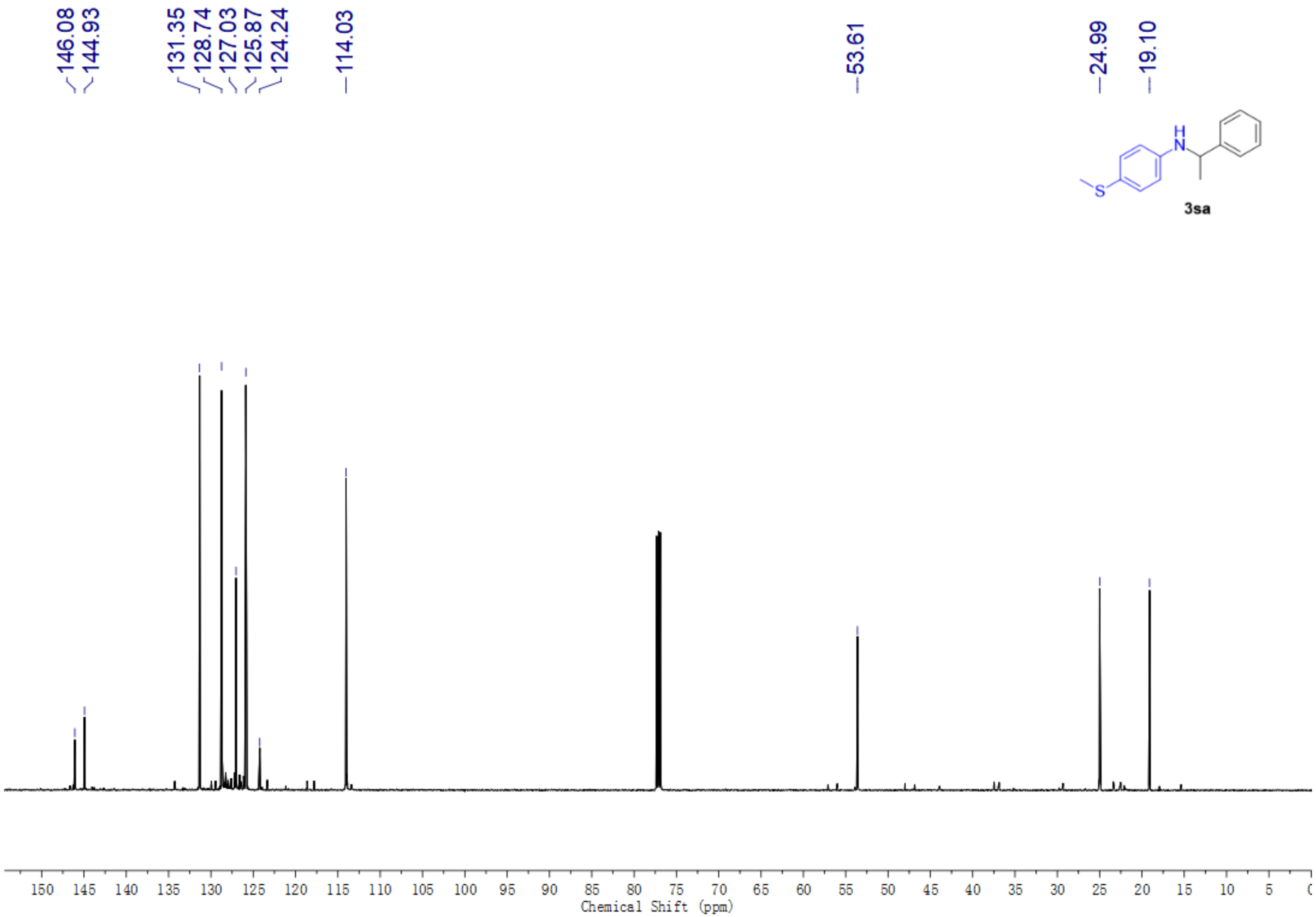
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3ra**



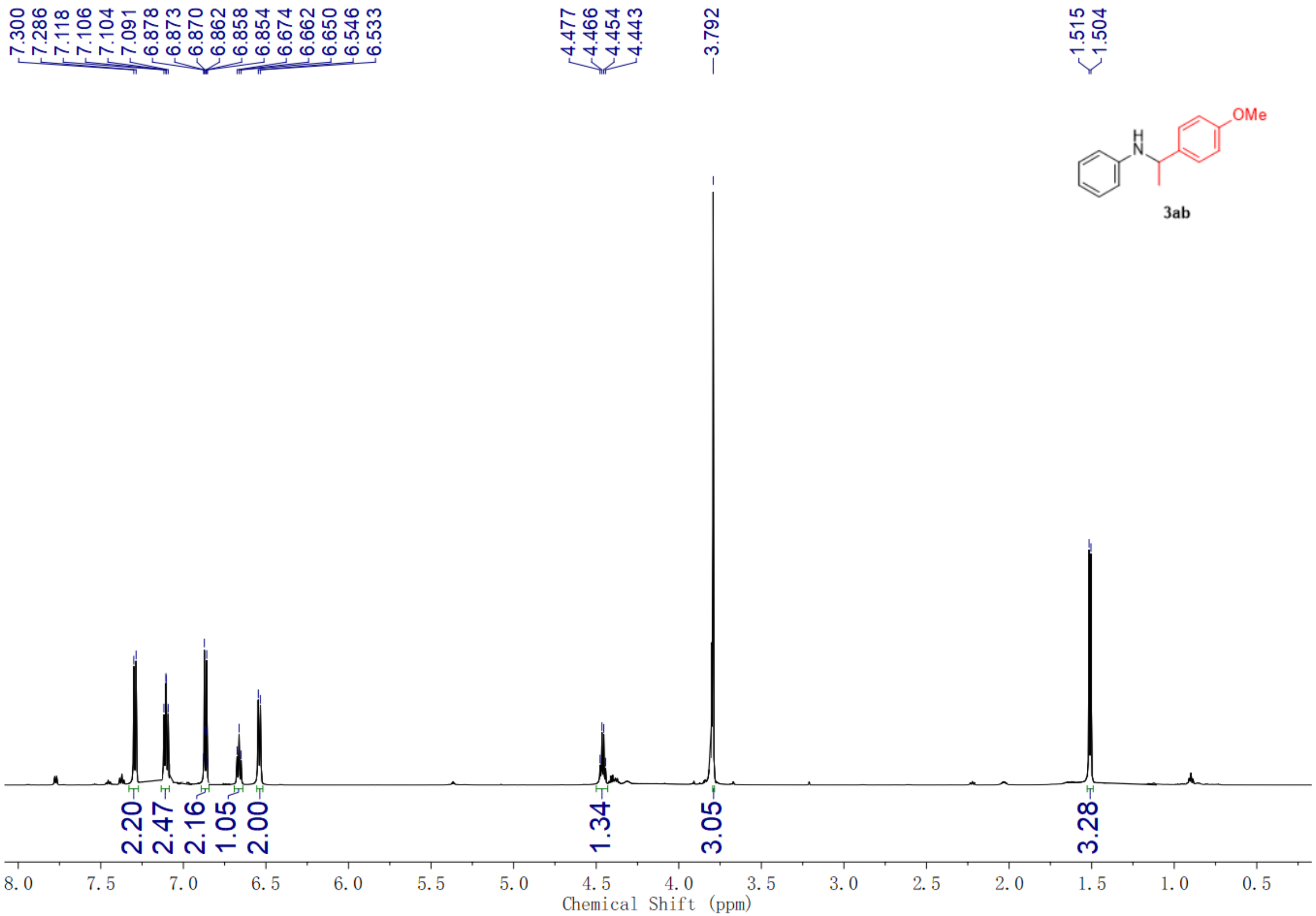
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ra**



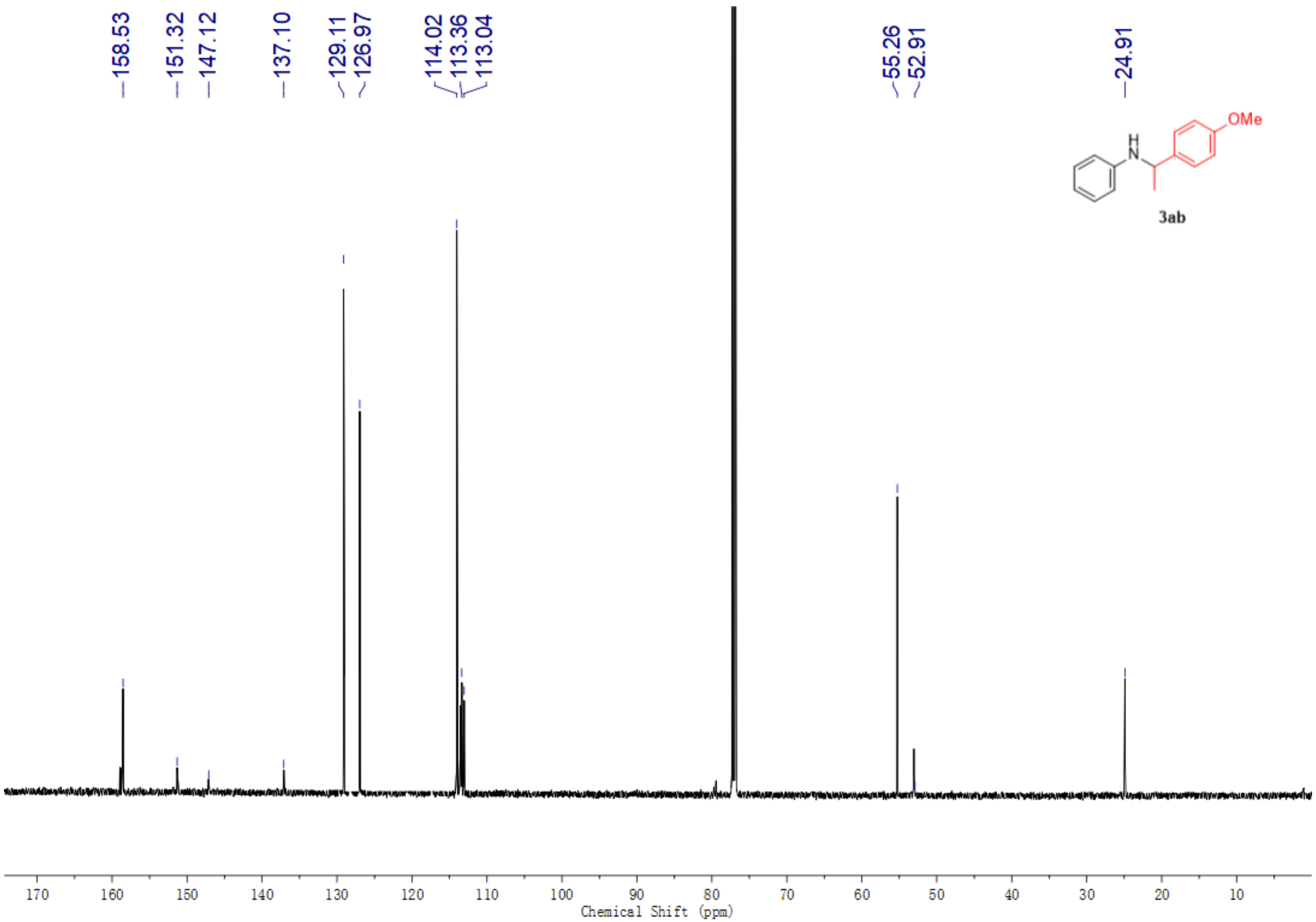
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3sa**



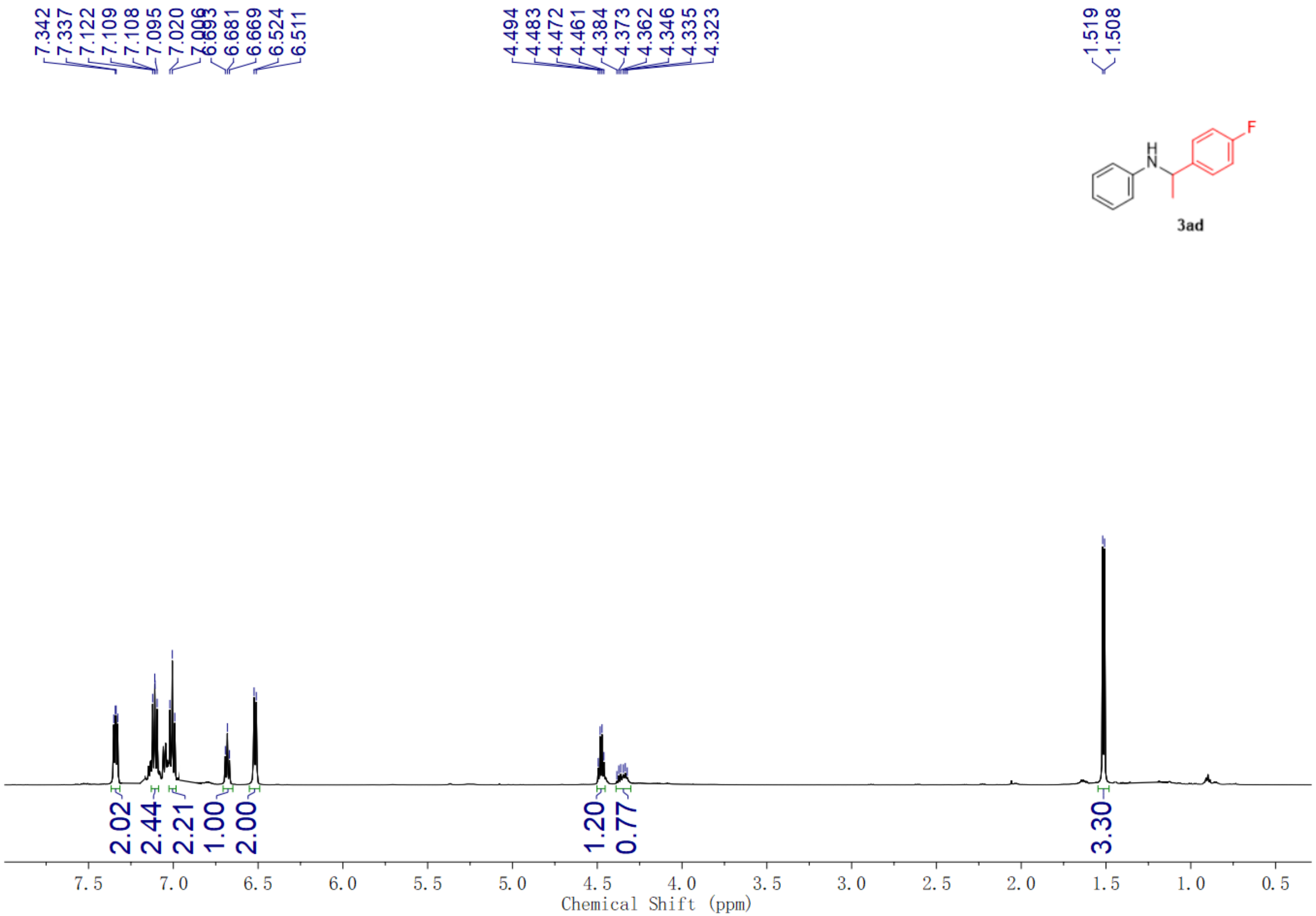
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3sa**



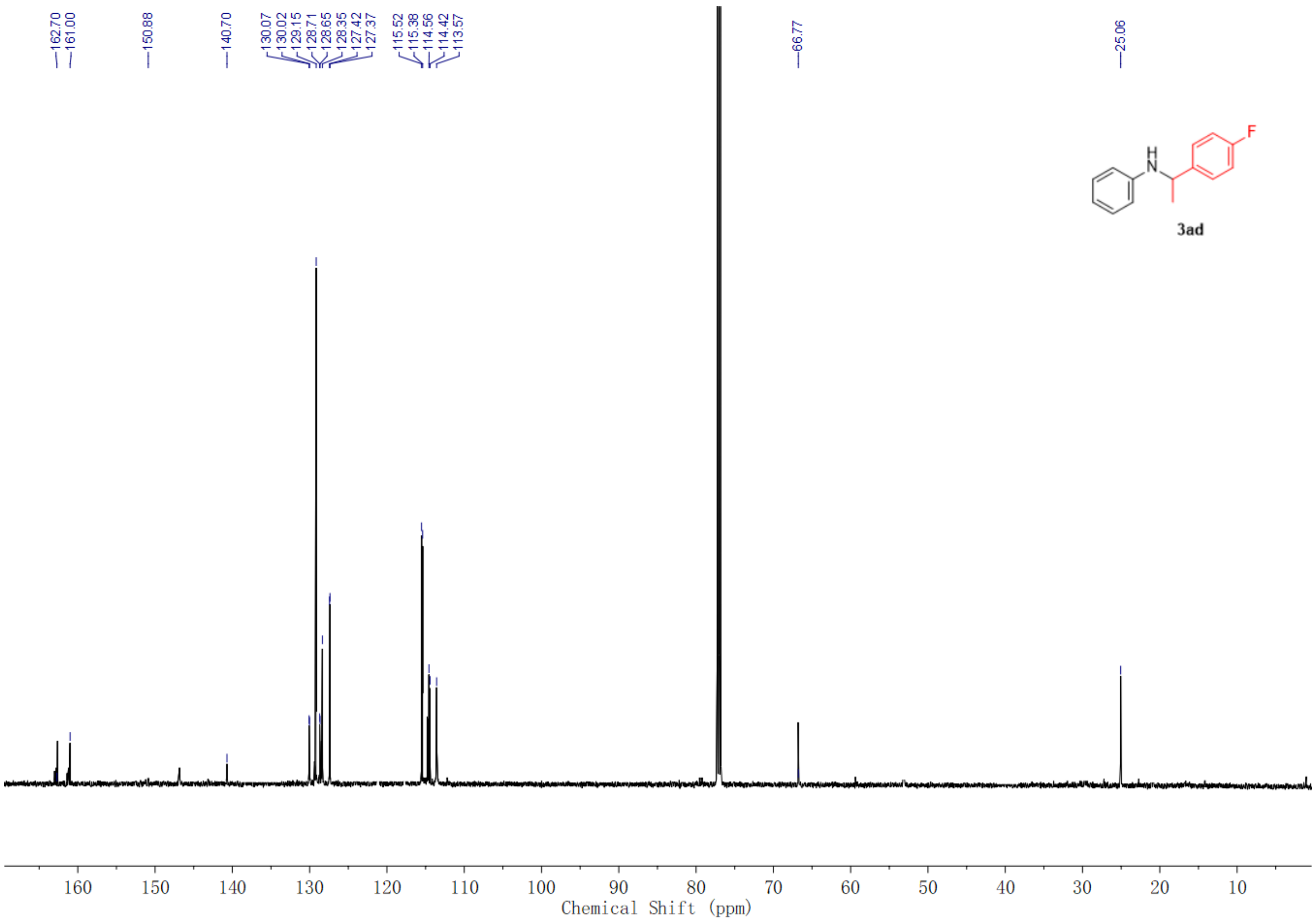
^1H NMR (600 MHz, 298K, $CDCl_3$) of **3ab**



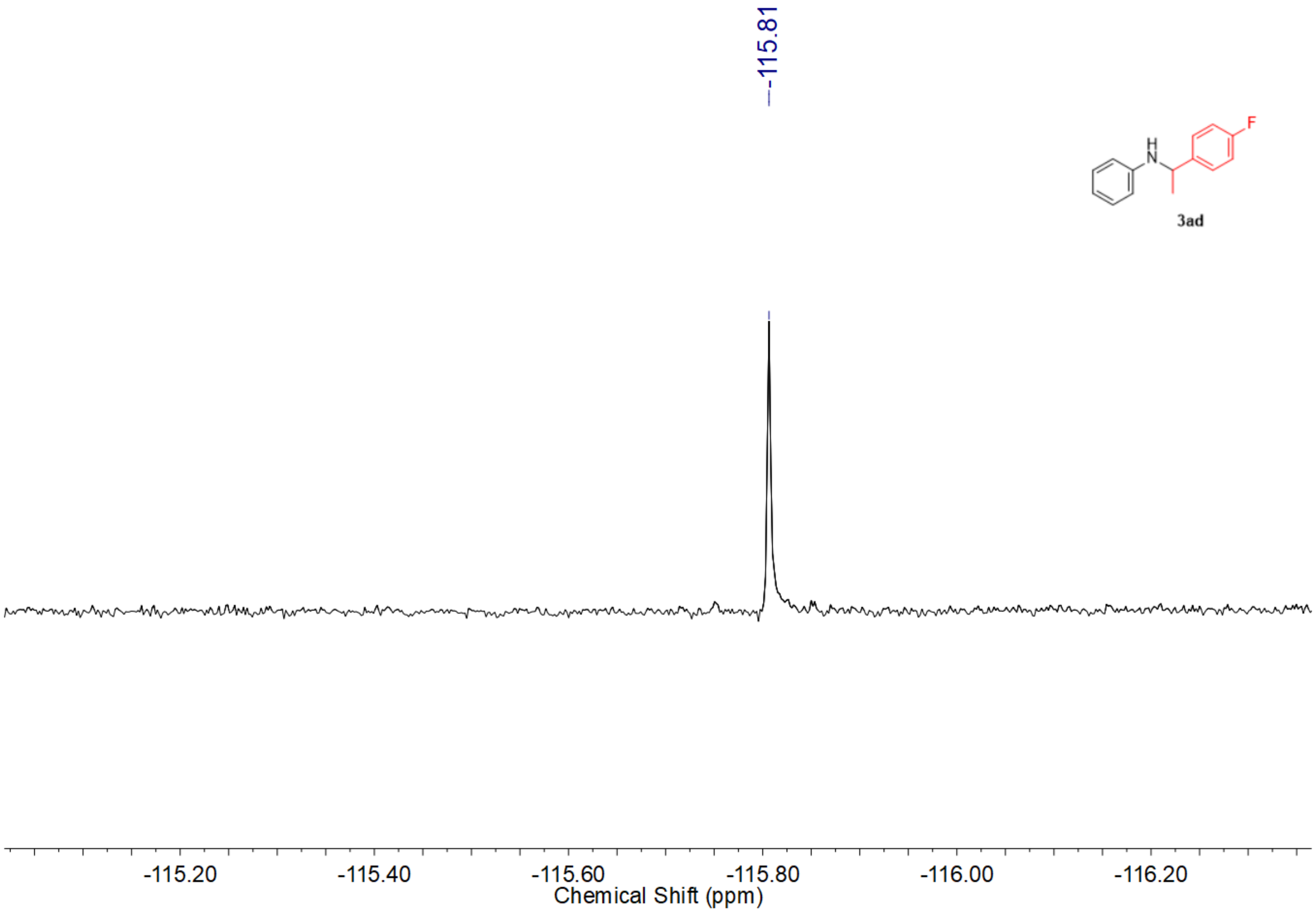
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ab**



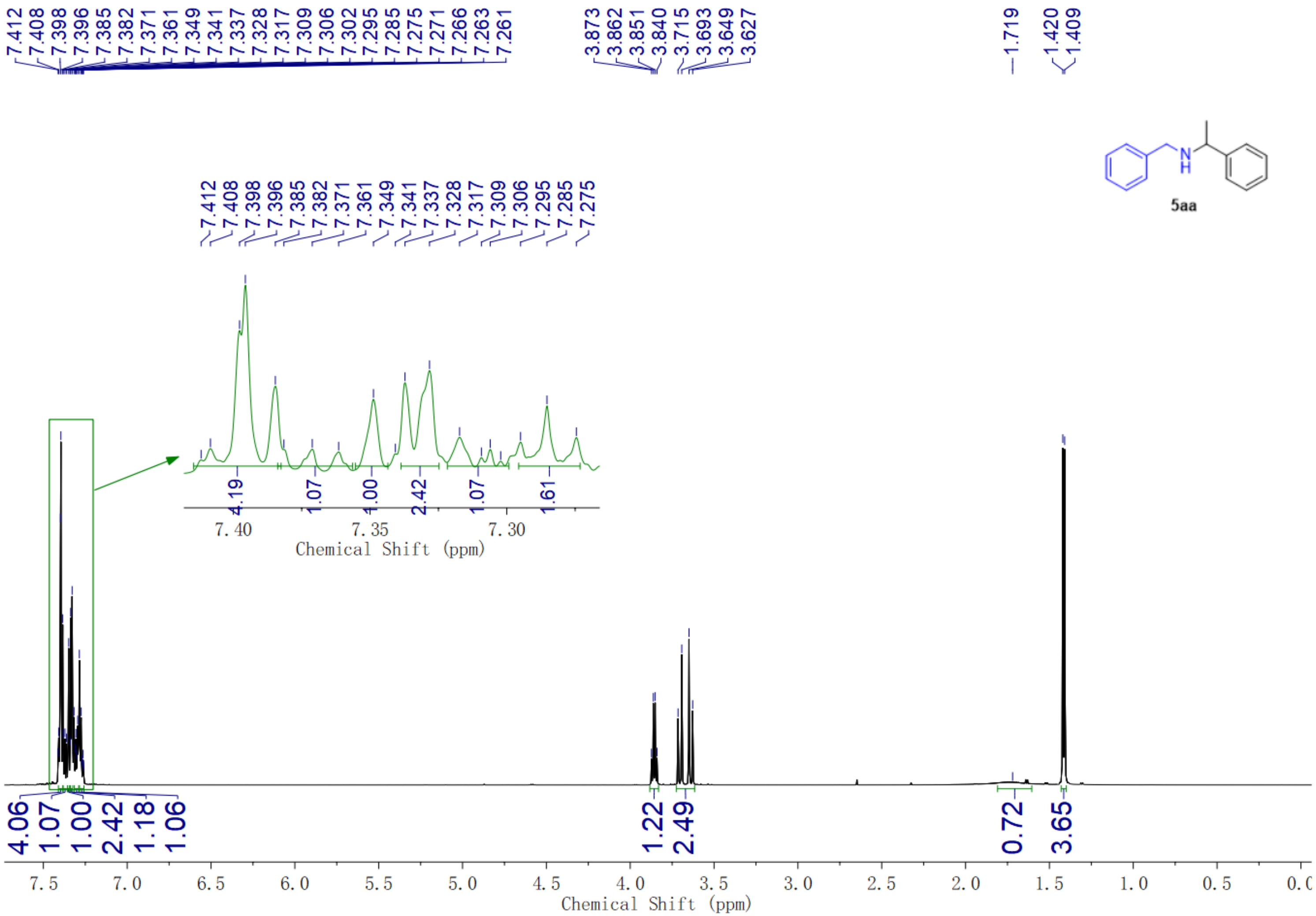
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **3ad**



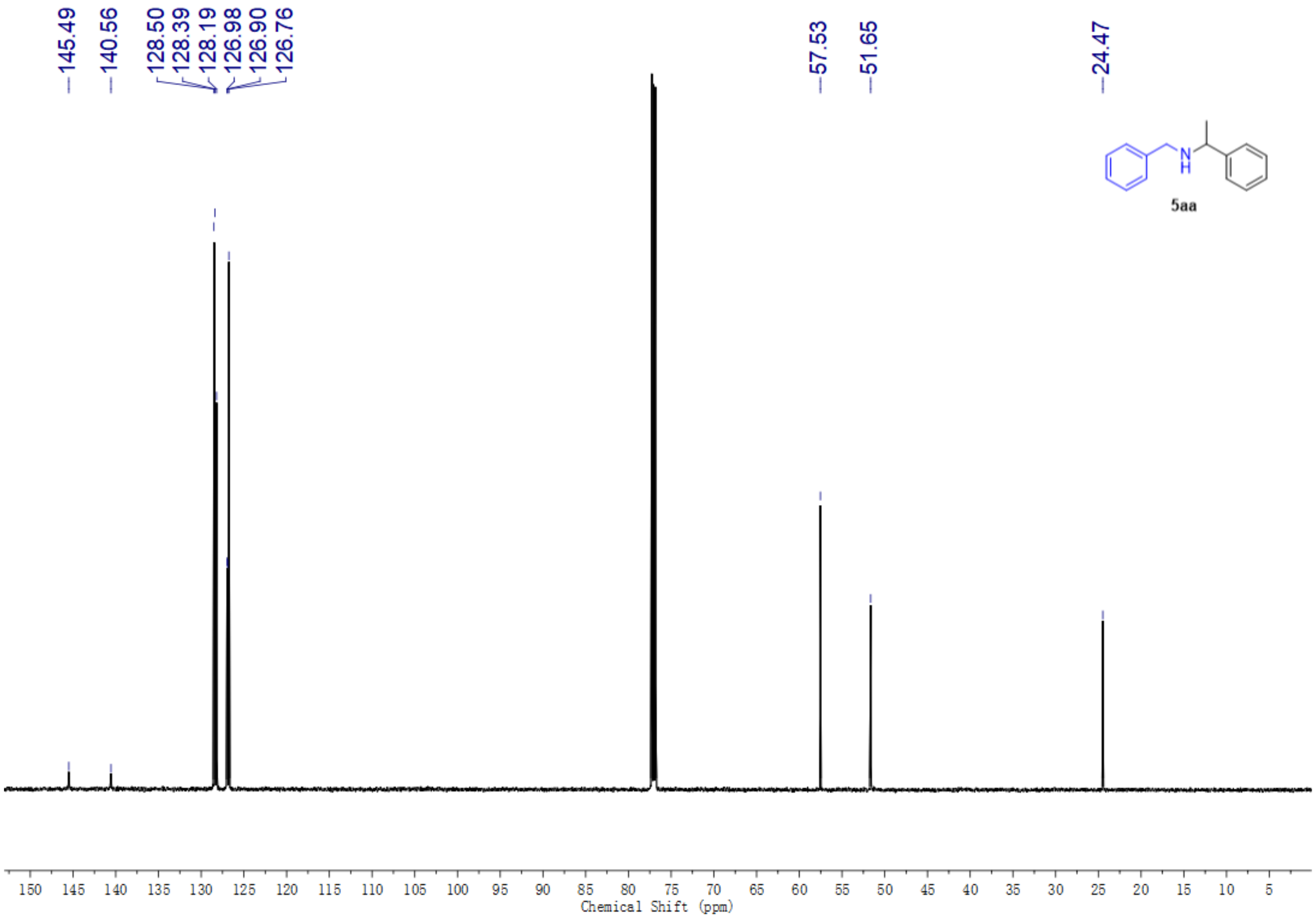
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **3ad**



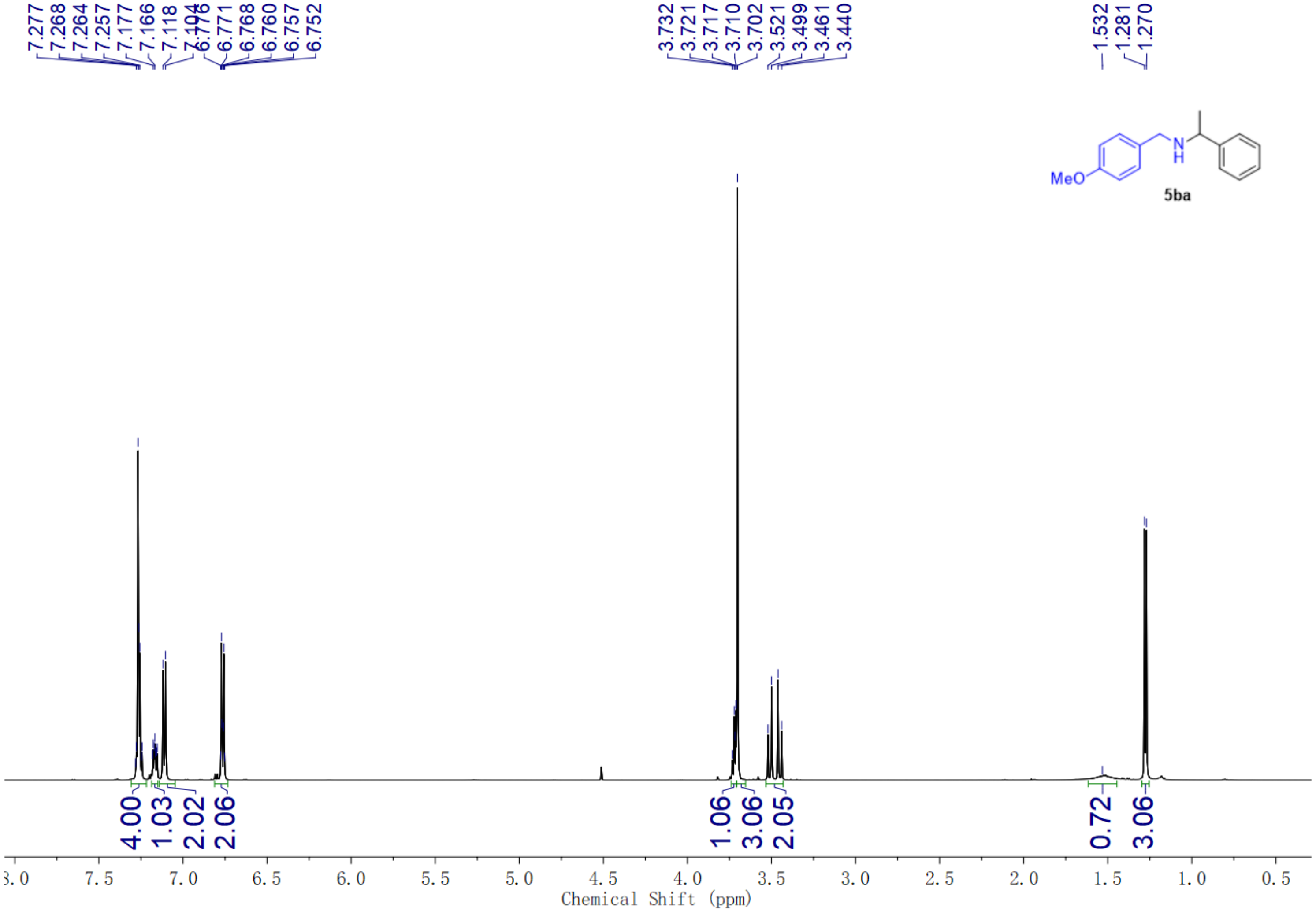
^{19}F NMR (564 MHz, 298 K, $CDCl_3$) of **3ha**



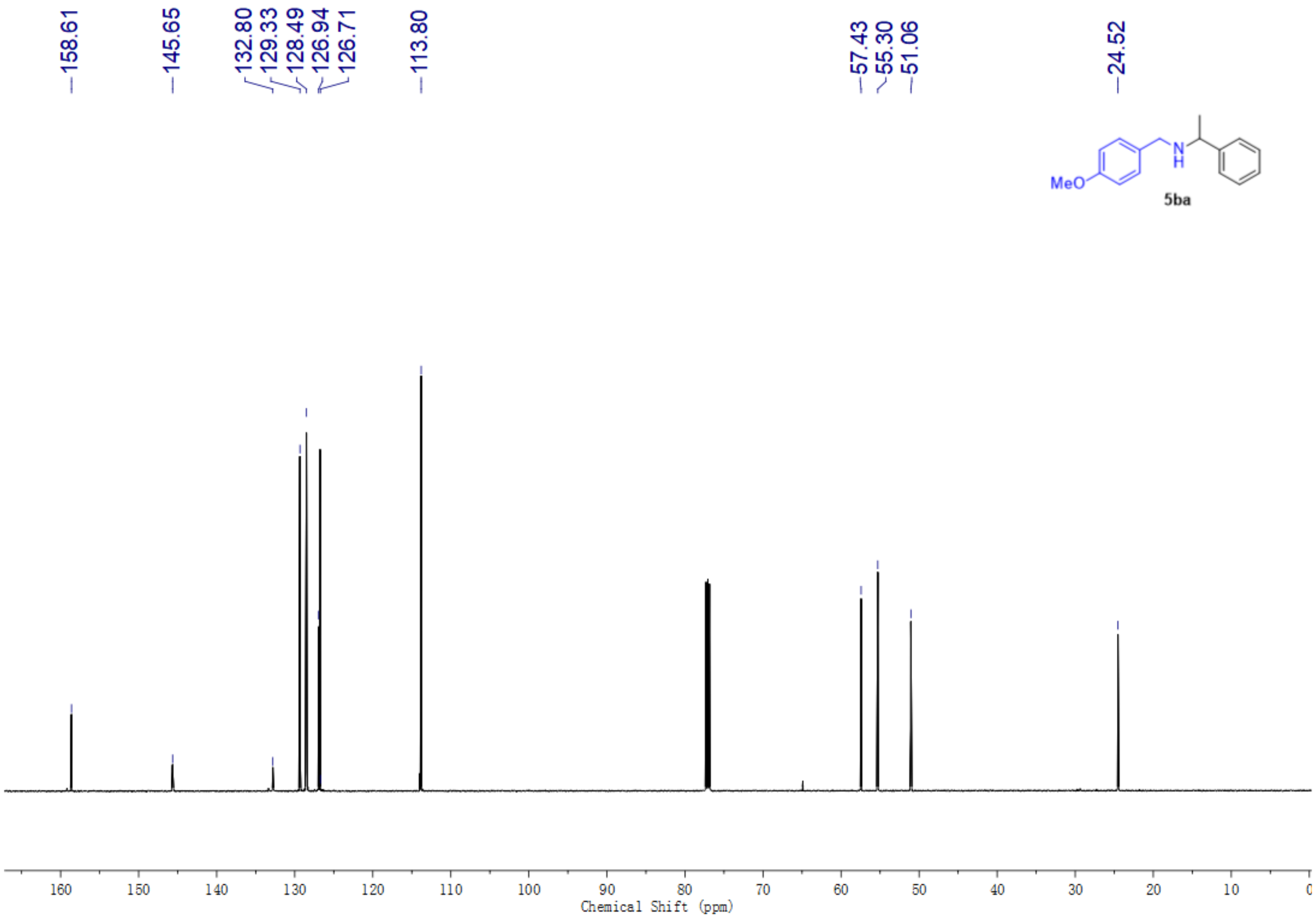
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **5aa**



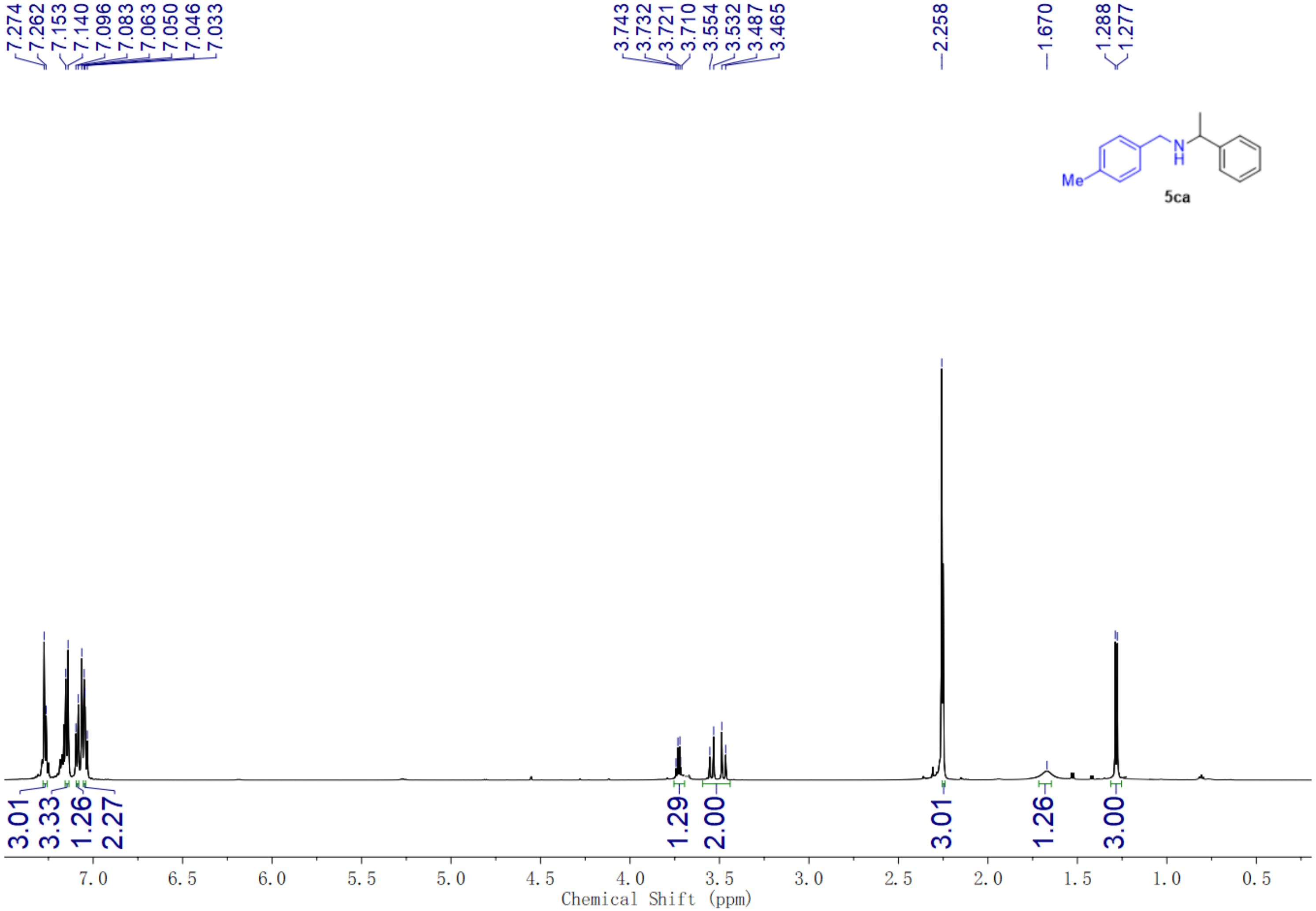
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **5aa**



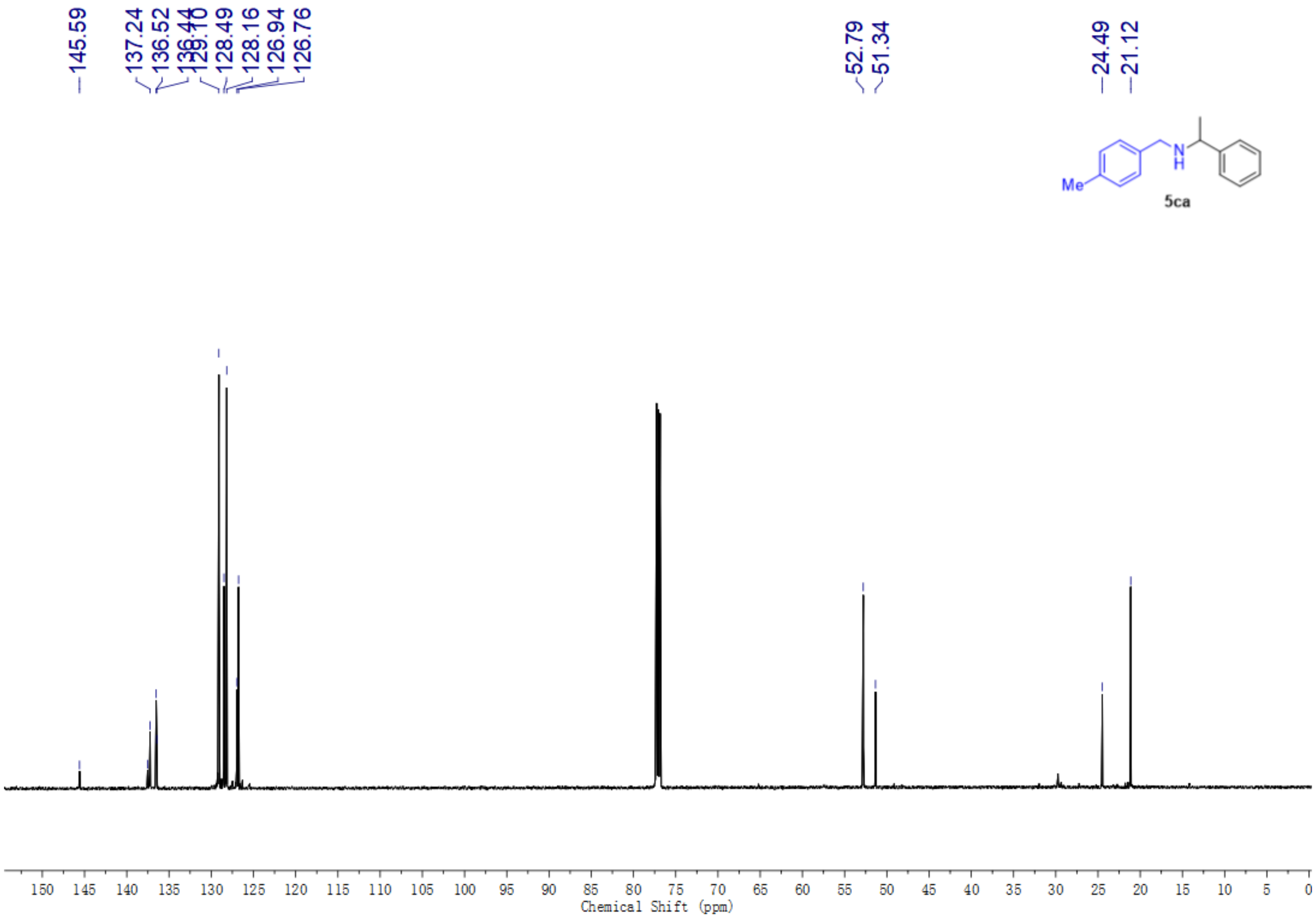
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **5ba**



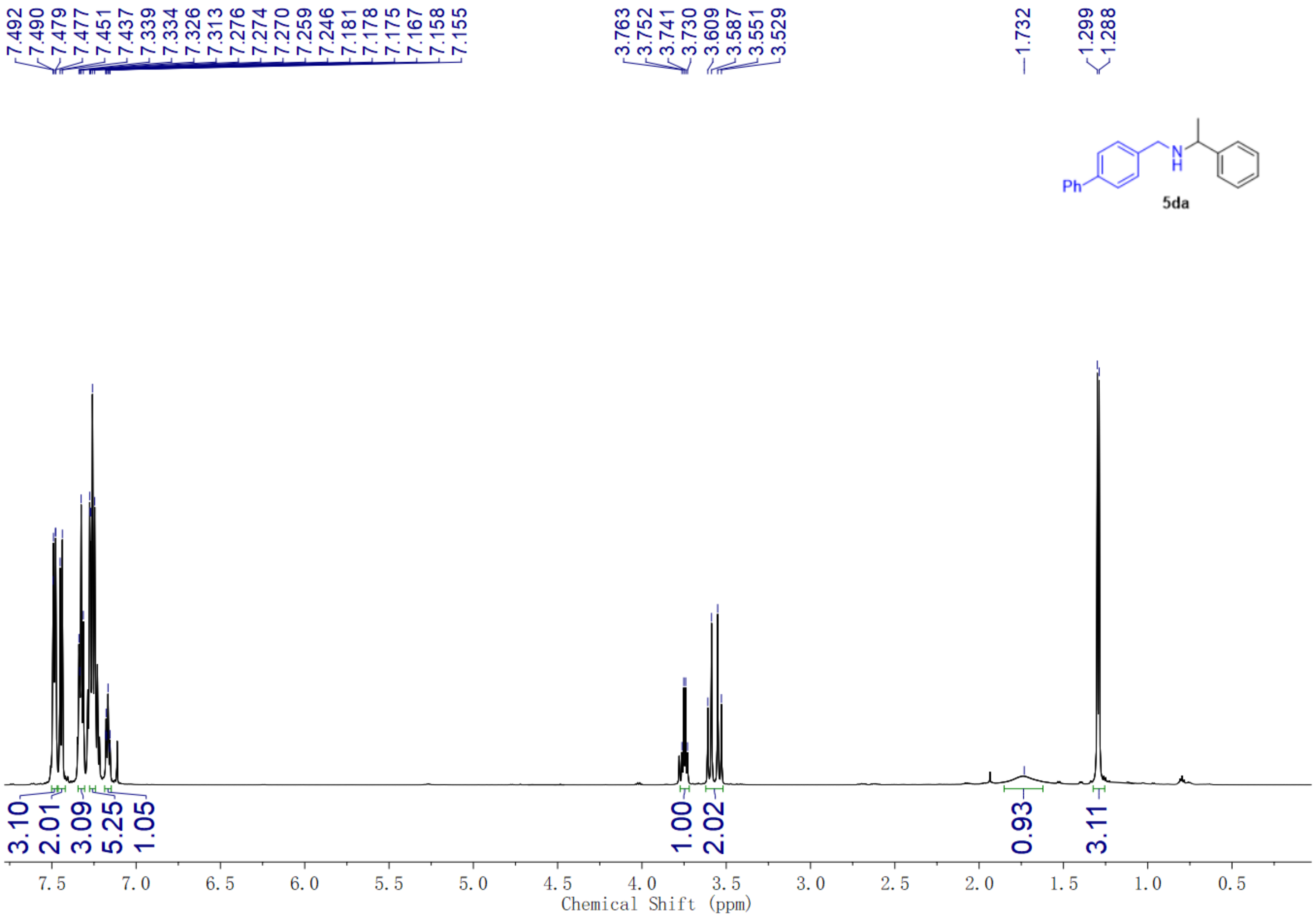
[13]C NMR (151 MHz, 298 K, $CDCl_3$) of **5ba**



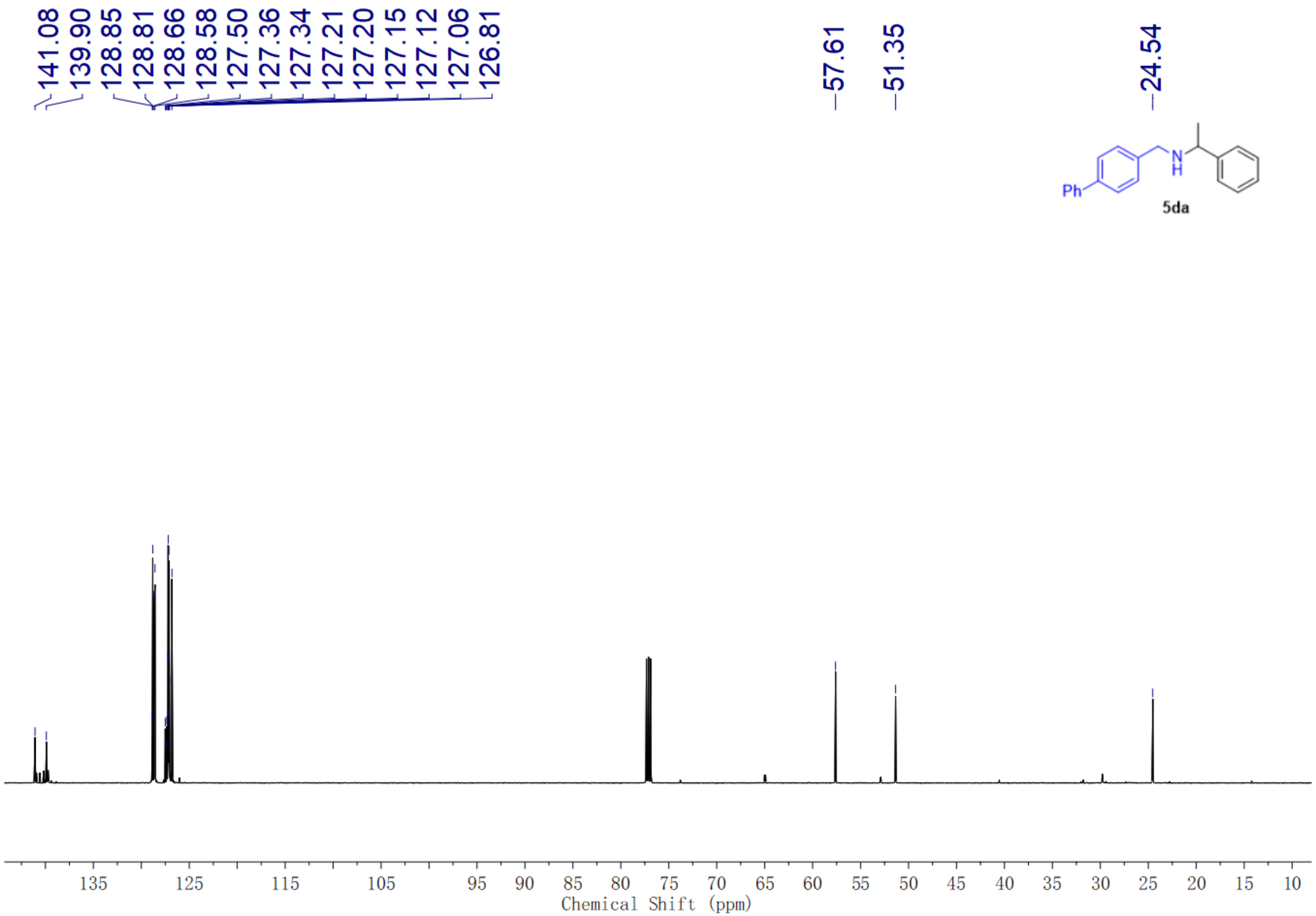
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **5ca**



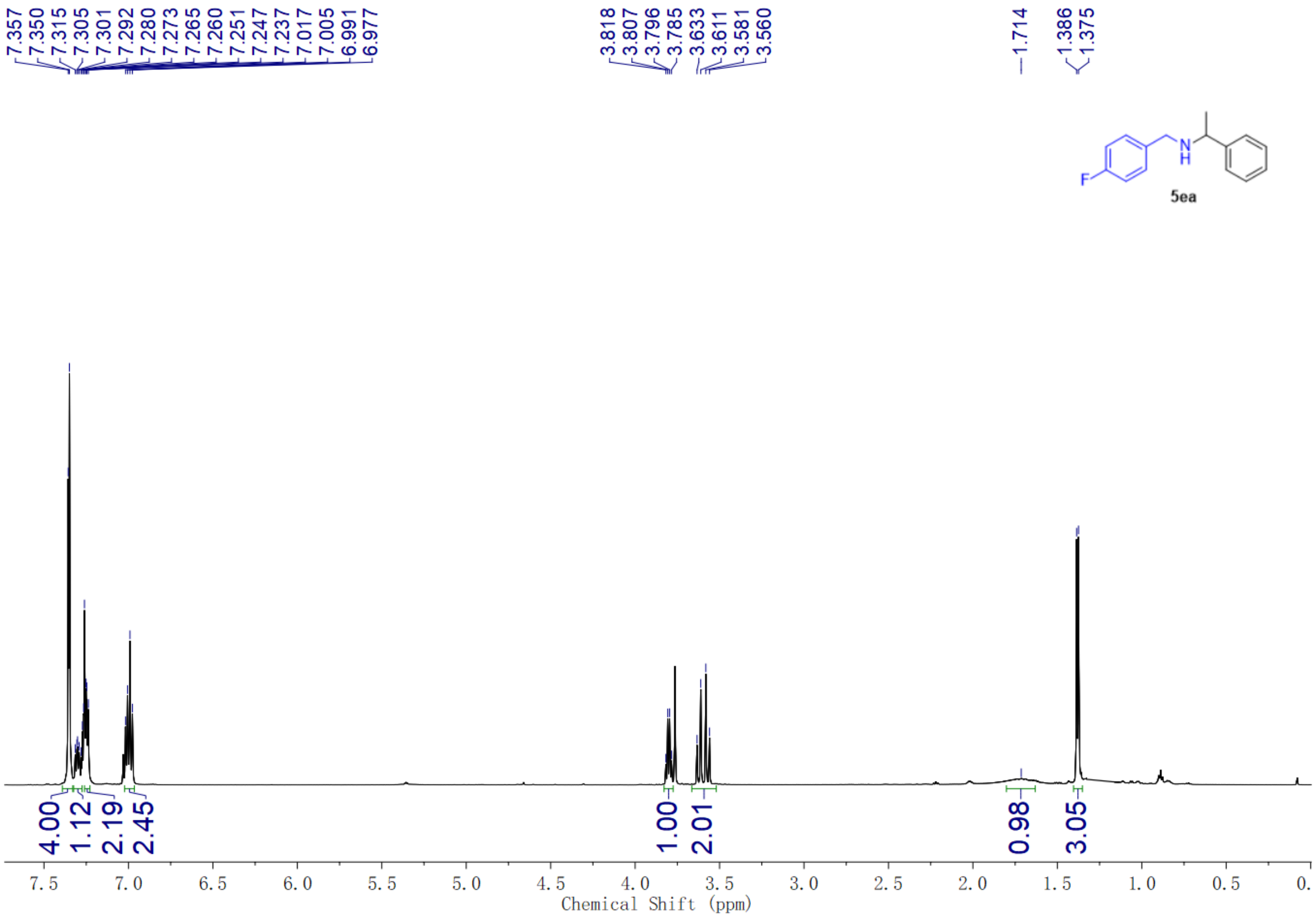
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **5ca**



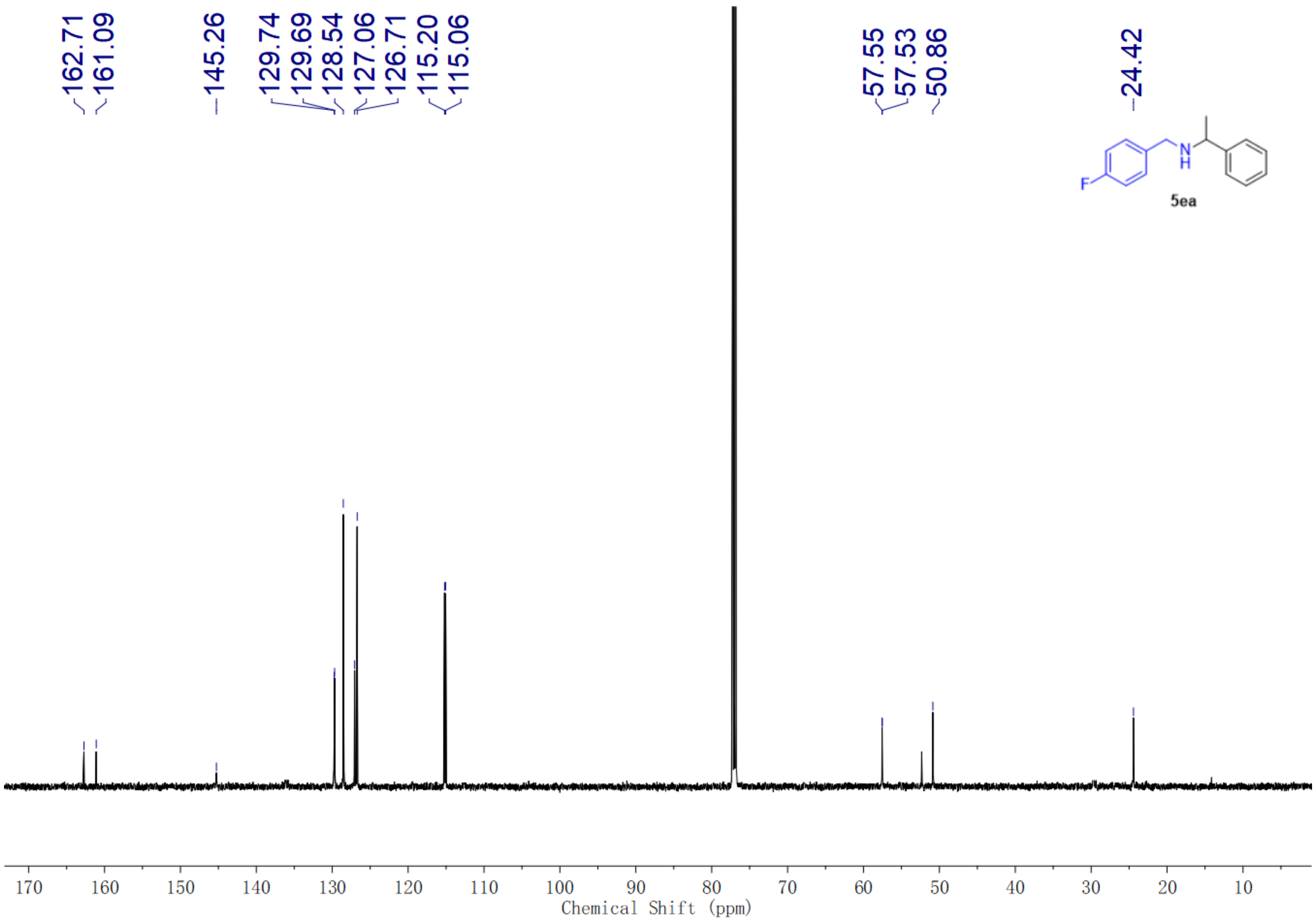
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **5da**



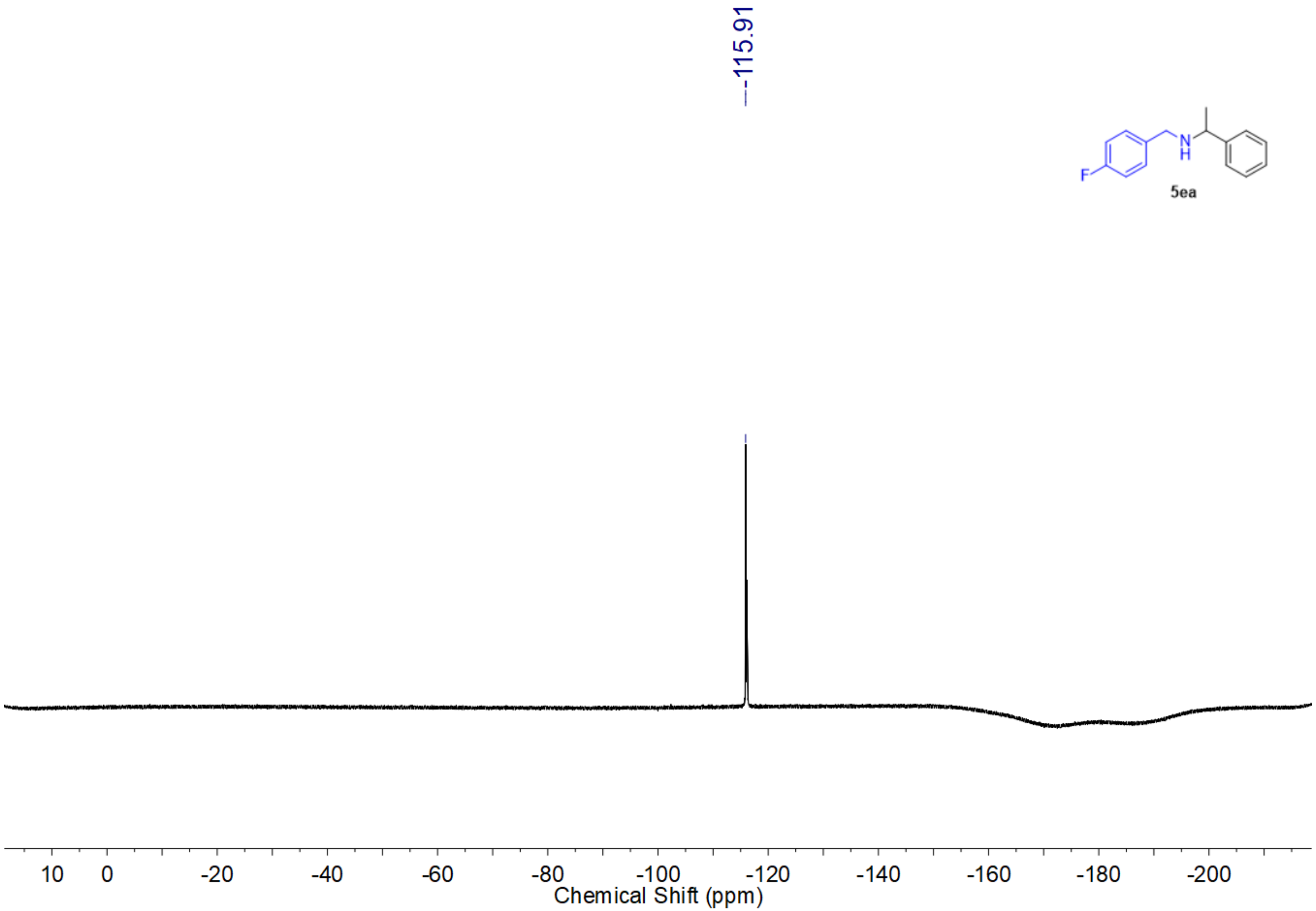
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **5da**



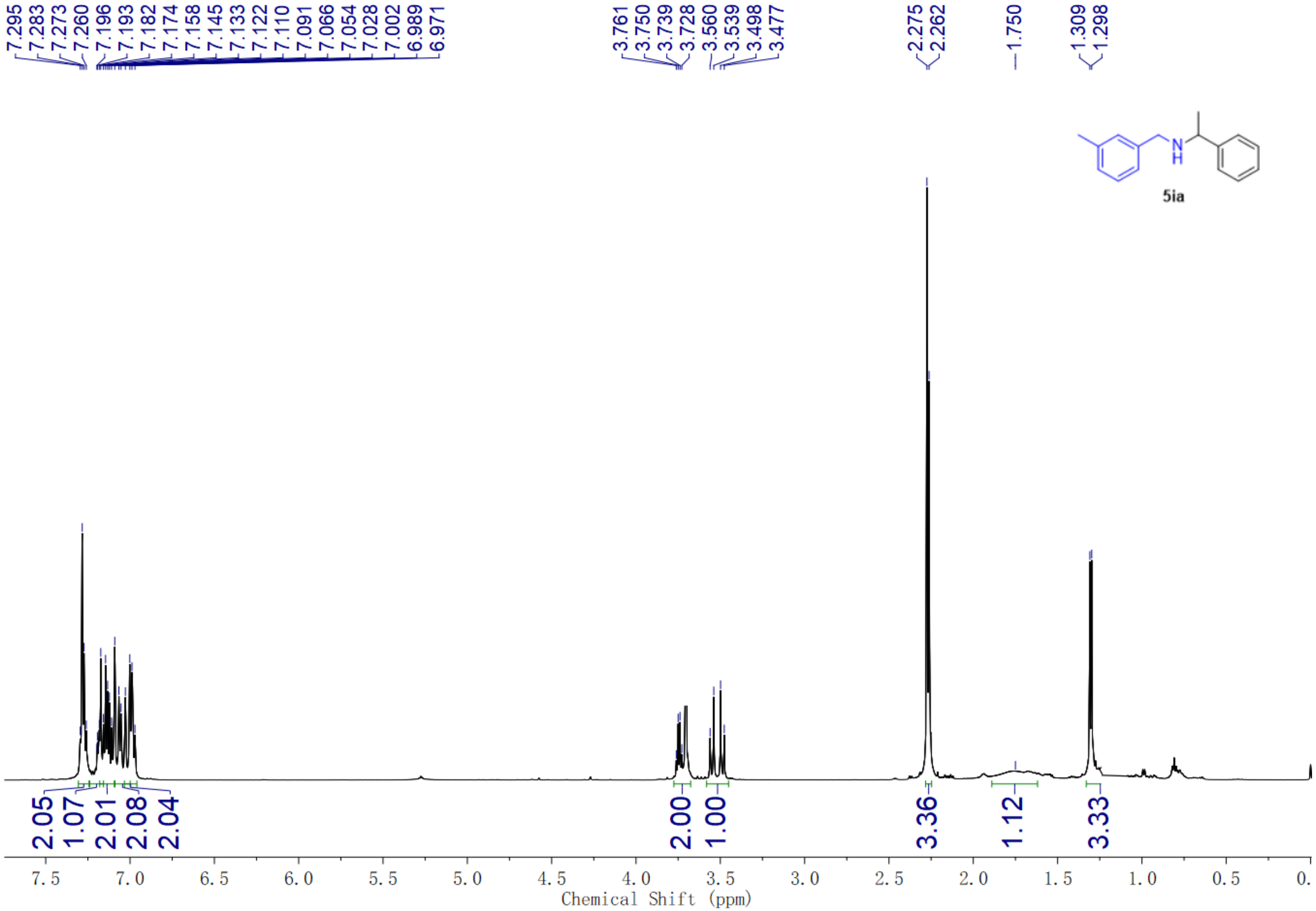
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **5ea**



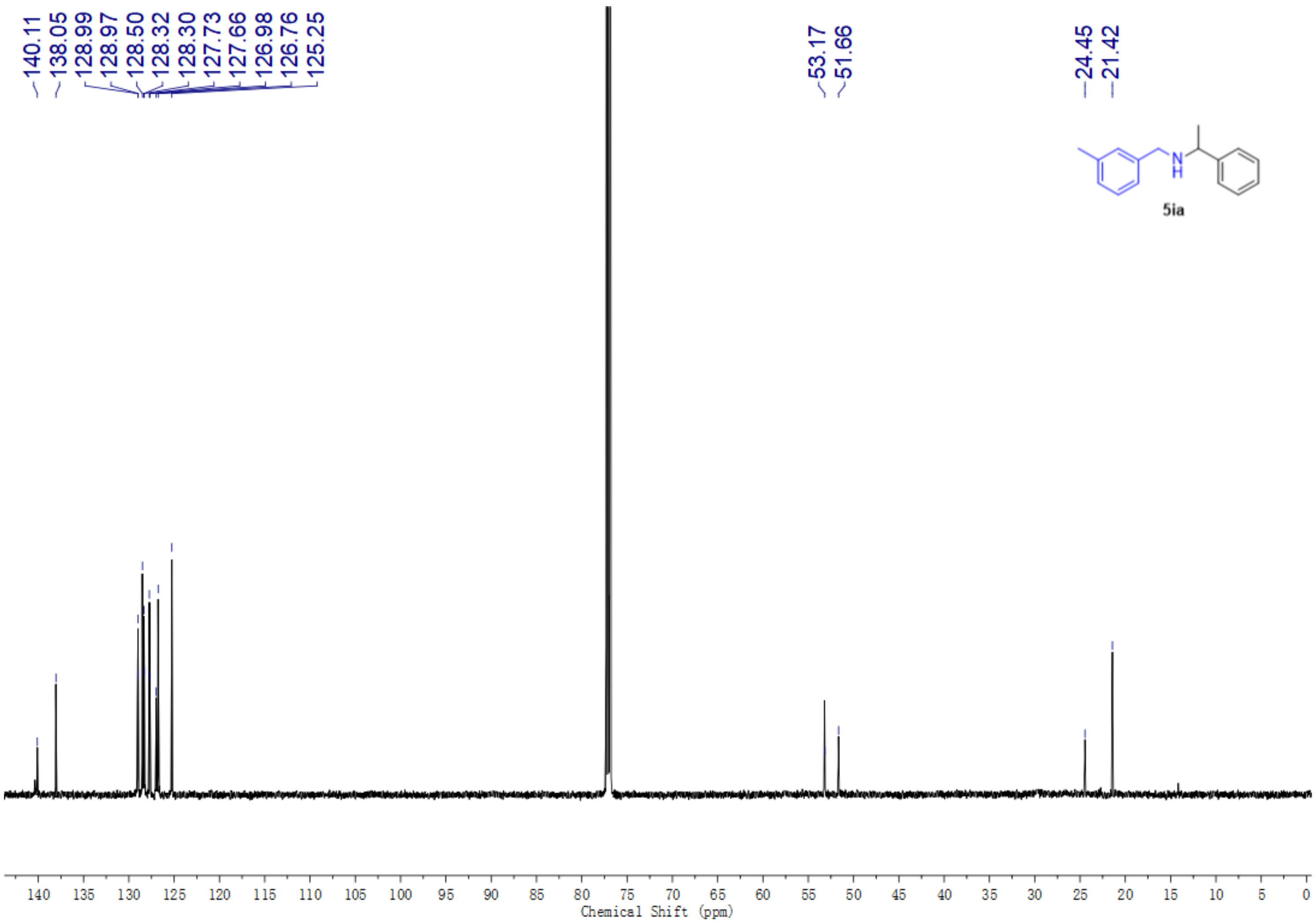
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **5ea**



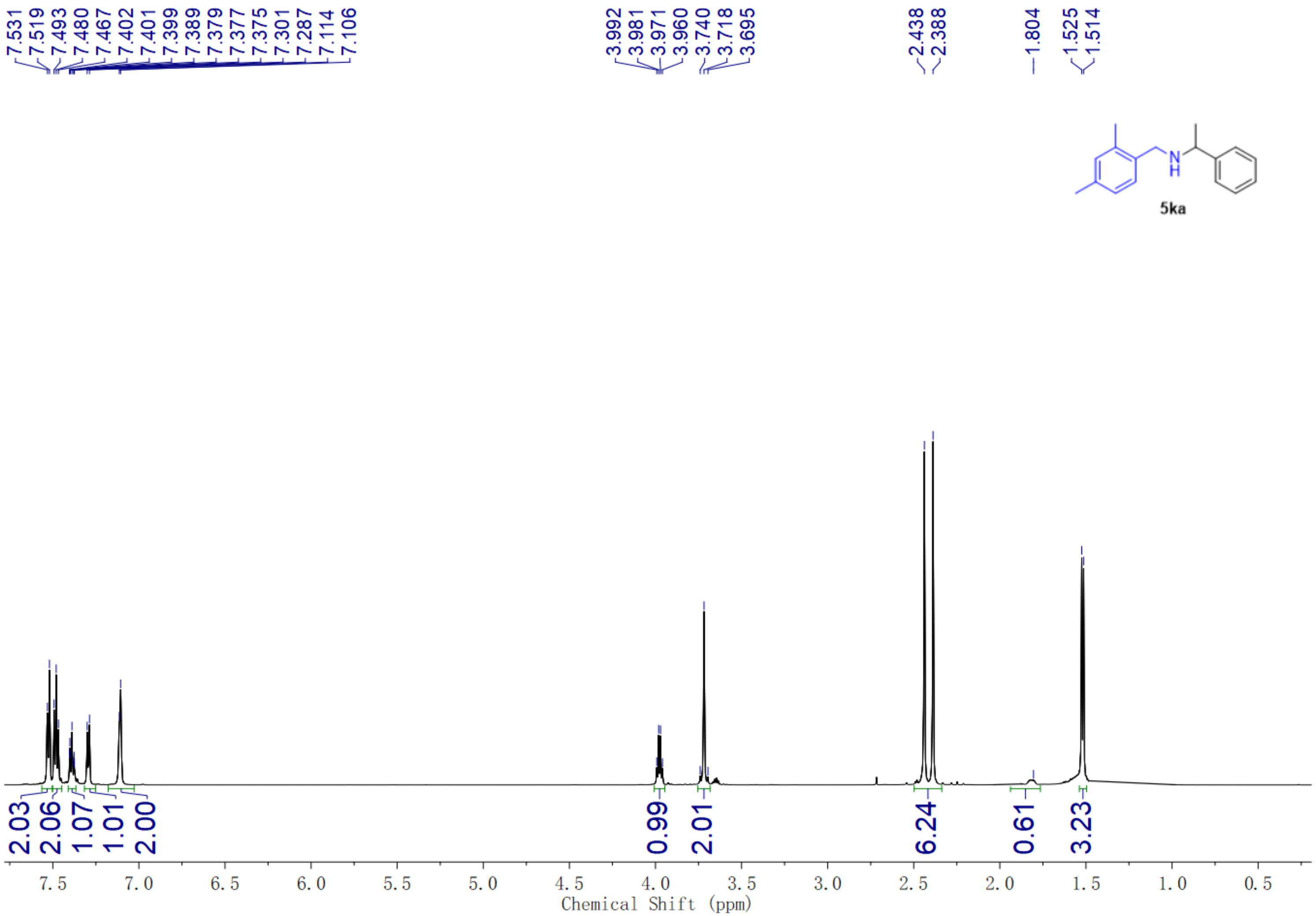
^{19}F NMR (564 MHz, 298 K, $CDCl_3$) of **5ea**



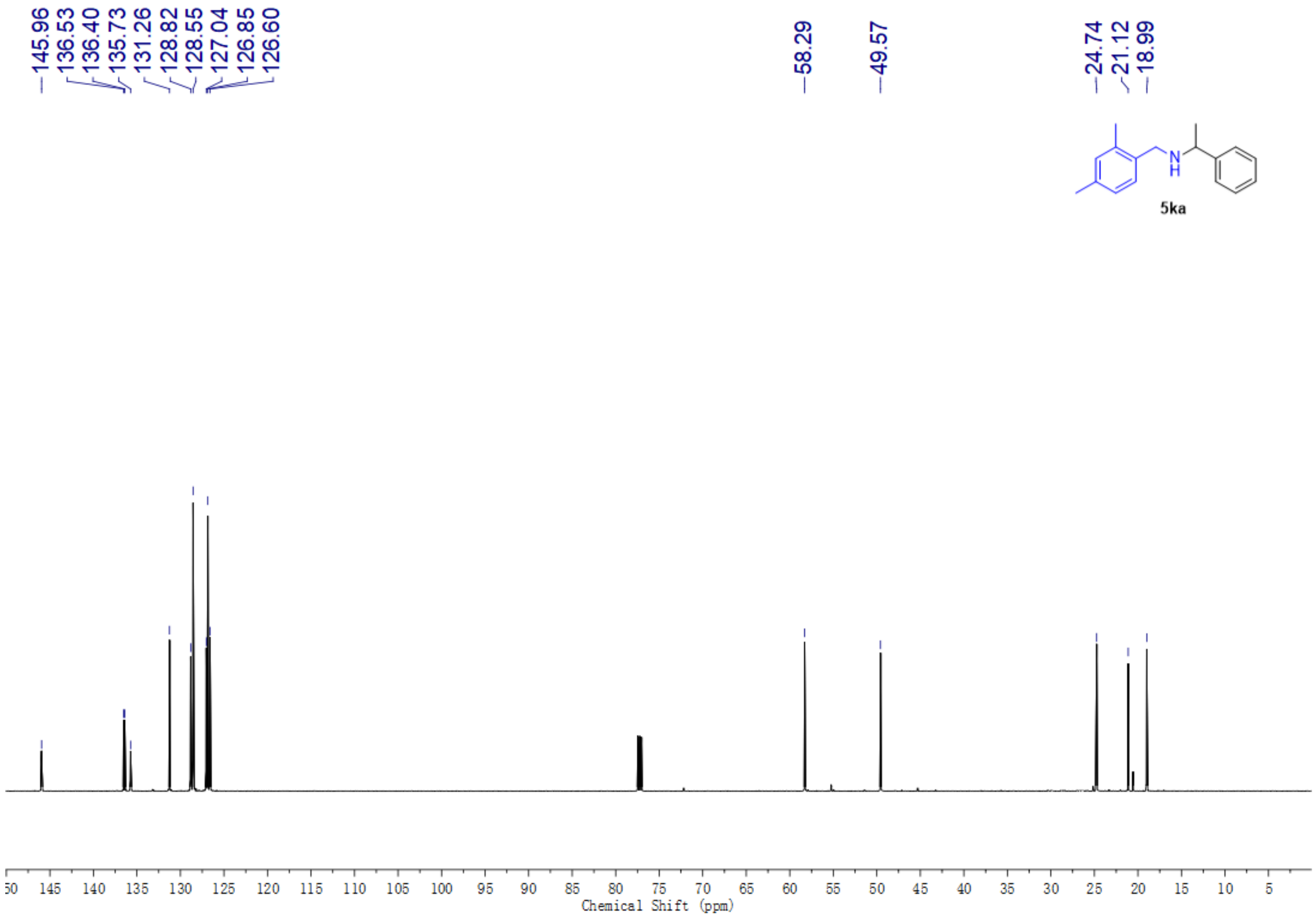
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **5ia**



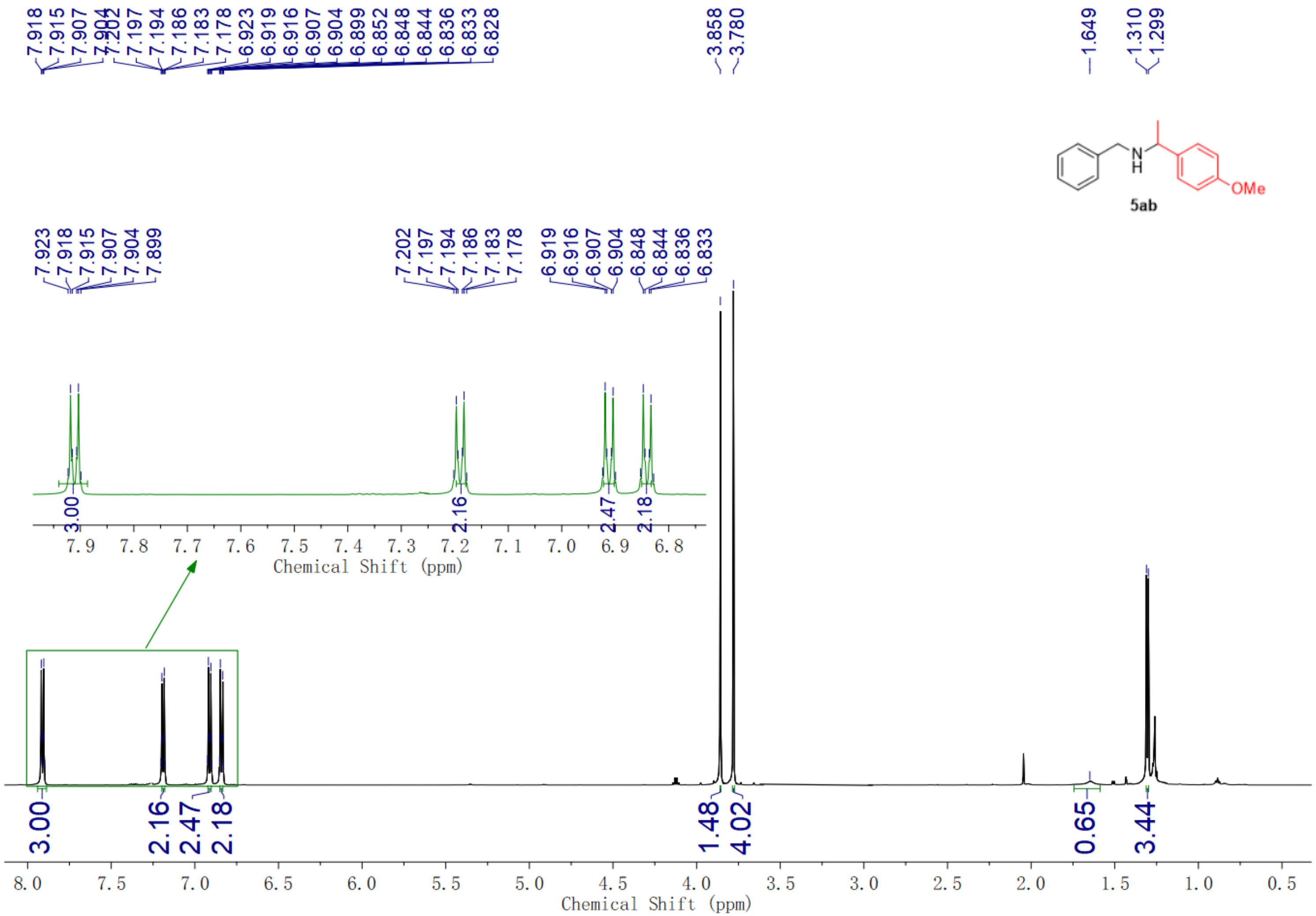
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **5ia**



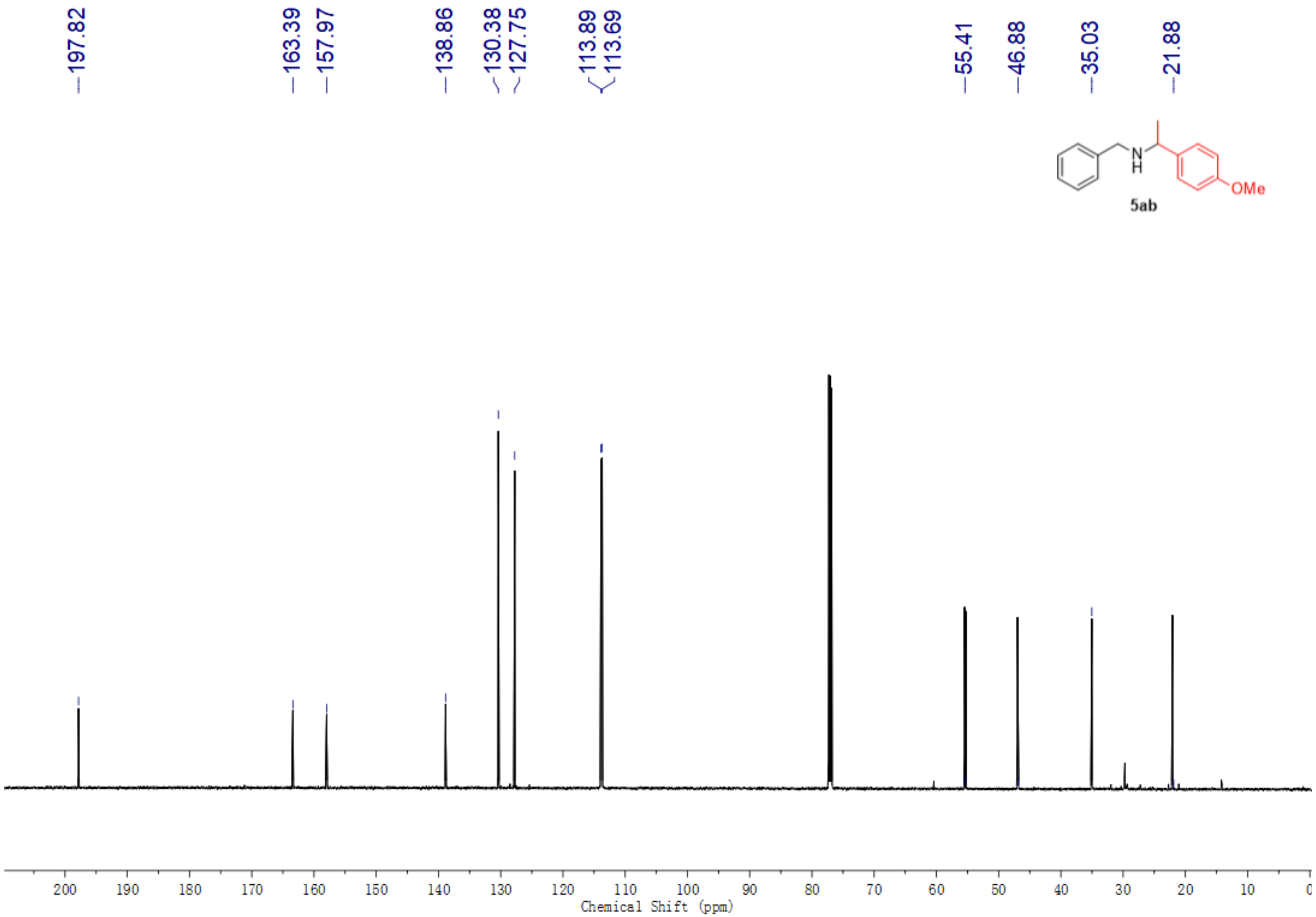
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **5ka**



^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **5ka**



^1H NMR (600 MHz, 298K, $CDCl_3$) of **5ab**



^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **5ab**