Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Rhenium and Base Co-catalyzed [3+2] Annulations of N-H Ketimines and Alkynes to Access Unprotected Tertiary Indenamines through C-H Bond Activation

Xiqing Jin, Xiaoxu Yang, Yunhui Yang, Congyang Wang*

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

E-mail: wangcy@iccas.ac.cn.

1. General Information

Unless otherwise noted, all reactions were carried out in oven-dried reaction vessels with Teflon screw caps under a nitrogen atmosphere by using standard Schlenk techniques. Reaction temperatures are recorded on the temperature of the bath oil surrounding the Schlenk tubes. Anhydrous solvents were purified and dried following standard procedures. All commercially available reagents were used as received. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Flash column chromatography was performed on silica gel (200-300 mesh).

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 AV or 500 AV spectrometers. Chemical shifts for protons are quoted in parts per million downfield from tetramethylsilane and are referenced to the solvent peak (for $CDCl_3$, ^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.16 ppm); Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J*, Hz). The mass spectra (MS) were recorded on a LC-MS2010 spectrometer or a GCMS-QP2010-SE (SHIMADZU). The high resolution mass spectra (HRMS) were recorded on a GCT-MS Micromass UK spectrometer or a Bruker Apex IV FTMS.

2. General Procedure for the Preparation of N-H Ketimines

All the imines are prepared according to the general procedures above.[1-4]

General procedure A for the synthesis of N–H diarylimine

In an oven-dried Schlenk tube under N_2 atmosphere, a mixture of the aryl nitrile (20 mmol) and the aryl Grignard reagent (20 mmol) was stirred in THF (20 mL) at 80 ℃ for 12 h. The reaction mixture was cooled to room temperature and then treated with $Na_2SO_4 \cdot 10H_2O$ (10 mmol). After stirring vigorously for 0.5 h, the mixture was diluted with Et_2O (80 mL) and the resulting suspension was filtrated through Celite. The volatile materials were evaporated under vacuum. The residue was further purified by flash column chromatography, with 1.5 mL of TEA added into every 100 mL of eluent (PE/EA).

General procedure B for the synthesis of N–H arylalkylimines

A stirred solution of the aryl nitrile (20 mmol) in THF (20 mL) under a positive atmosphere of N_2 was cooled to -78 ℃ and the alkyllithium reagent (32 mmol) was added dropwise over 0.5 h. The mixture was stirred at -78 ℃ for 2 h, quenched with anhydrous MeOH (5 mL) and then stirred at room temperature for 2 h. The resulting suspension was filtrated through Celite and the solvent was removed by rotary evaporation. The residue was purified by vacuum distillation.

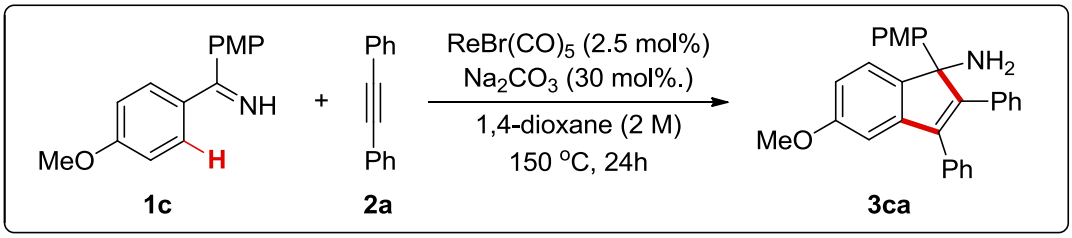
3. General Procedure for the Preparation of Alkynes

Alkynes **2a**, **2b**, **2c**, **2j**, **2k**, **2l** are commercially available (from Alfa Aesar) and used as received. Other alkynes are prepared according to the literatures: [5,6]

A round bottom flask with a magnetic stir bar is fitted with a rubber septum and flame dried under vacuum. The flask is purged with nitrogen, and charged with $PdCl_2(PPh_3)_2$ (6 mol%), CuI (10 mol%) and aryliodide or bromide (1 equiv). Septum is parafilmed after solids are added. While stirring, dry benzene (0.20 M) is added by syringe under nitrogen atomosphere. DBU (6 equiv) is then added by syringe under nitrogen. Ice-chilled thrimethylsilylethynylene (0.50 equiv) is then added by syringe, followed immediately by distilled water (40 mol%). The reaction flask is covered in aluminum foil and left stirring at a high rate of speed for 18 h, at the end of which the reaction mixture is partitioned in ethyl ether and distilled water. The organic layer is washed with 10% HCl three times, saturated aqueous NaCl, dried over $MgSO_4$, gravity-filtered and the solvent removed in vacuo. The crude product is purified by silica gel column chromatography.

1,2-bis(4-fluorophenyl)ethyne (**2d**)[5], 1,2-bis(4-chlorophenyl)ethyne (**2e**)[5], 1,2-bis(4-bromophenyl)ethyne (**2f**)[5], 1,2-bis(2-fluorophenyl)ethyne (**2g**)[5], 1,2-bis(3-methylphenyl)ethyne (**2h**)[6] and 1,2-bis(4-fluorophenyl)ethyne (**2i**)[5] are all prepared according to the literatures. And the spectra data are in agreement with the known compounds in literatures.

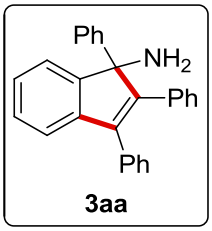
4. Typical Procedure for [3+2] Annulations of N-H Ketimines and Alkynes



A oven-dried Teflon-screw-capped tube was equipped with a magnetic stir bar. $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl)methanimine **1c** (1.0 mmol, 135.2 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg), and 1,4-dioxane (2.0 mL) were added into the reaction vessel under nitrogen. Then the Teflon cap was screwed up and the reaction mixture was stirred at 150 °C for 24 h. After completion of the reaction, the crude mixture was cooled down. The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ca** as a light-yellow solid.

5. Characterization Data for Unprotected tertiary Indenamines

1,2,3-triphenyl-1*H*-inden-1-amine (3aa)



3aa

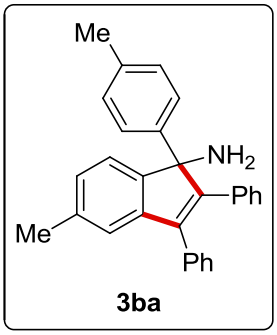
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), diphenylmethanimine **1a** (1.0 mmol, 181.1 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3aa** in 94% isolated yield as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.40-7.42 (m, 2H), 7.16-7.34 (m, 9H), 7.09-7.13 (m, 1H), 6.97-7.06 (m, 3H), 6.85-6.87 (m, 2H), 1.80 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 151.1, 142.9, 142.8, 139.4, 135.1,134.5, 129.7, 129.5, 128.7, 128.0, 127.7, 127.6, 127.3, 126.9, 126.8, 125.6, 123.2, 121.0, 71.7;

HRMS (ESI): Caculated for $C_{27}H_{20}N^+$ ($[M-2H+H]^+$): 358.15902, found: 358.15862.

5-methyl-2,3-diphenyl-1-(*p*-tolyl)-1*H*-inden-1-amine (3ba)



3ba

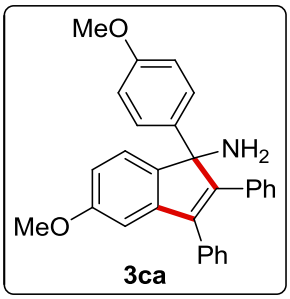
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), di-*p*-tolylmethanimine **1b** (1.0 mmol, 209.1 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ba** in 97% isolated yield as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.44 (m, 4H), 7.35-7.38 (m, 2H), 7.20-7.33 (m, 1H), 7.01-7.11 (m, 7H), 6.96-6.98 (m, 1H), 6.86-6.88 (m, 2H), 2.31-2.32 (m, 6H), 1.81 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 150.6, 143.0, 140.0, 139.3, 137.5, 136.4, 135.4, 134.7, 129.8, 129.6, 129.5, 128.7, 128.0, 127.6, 127.5, 127.2, 125.5, 122.9, 121.7, 71.3, 21.7, 21.2;

HRMS (ESI): Caculated for $C_{29}H_{26}N^+$ ($[M+H]^+$): 388.20598, found: 388.20631.

5-methoxy-1-(4-methoxyphenyl)-2,3-diphenyl-1*H*-inden-1-amine (3ca)



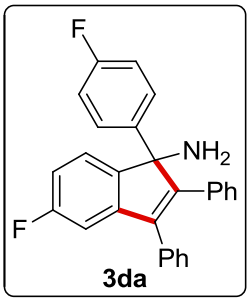
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl)methanimine **1c** (1.0 mmol, 241.1 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 °C for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ca** in 95% isolated yield as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.9 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.09 – 6.98 (m, 3H), 6.90 – 6.79 (m, 5H), 6.69 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 1.80 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 158.6, 152.5, 145.5, 144.2, 138.8, 135.1, 135.0, 134.6, 129.7, 129.5, 128.7, 128.0, 127.6, 127.3, 126.8, 123.7, 114.0, 111.6, 107.4, 70.8, 55.6, 55.3.

HRMS (ESI): Caculated for $C_{29}H_{26}O_2N^+$ ($[M+H]^+$): 420.19581, found: 420.19592.

5-fluoro-1-(4-fluorophenyl)-2,3-diphenyl-1*H*-inden-1-amine (3da)



Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-fluorophenyl)methanimine **1d** (1.0 mmol, 217.1 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 °C for 24 h. After the workup,

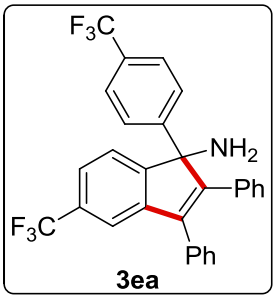
the product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ca** in 98% isolated yield as a yllew-white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.53 (m, 2H), 7.30-7.38 (m, 5H), 7.10-7.14 (m, 2H), 7.05-7.09 (m, 2H), 6.96-7.01 (m, 3H), 6.81-6.86 (m, 3H), 1.81 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (q, $^2J_{C\text{-}F}$ = 243.1 Hz), 162.1 (q, $^2J_{C\text{-}F}$ = 243.9 Hz), 152.8, 148.2, 144.9 (d, $^4J_{C\text{-}F}$ = 8.6 Hz), 138.6 (d, $^5J_{C\text{-}F}$ = 3.0 Hz), 138.3 (d, $^5J_{C\text{-}F}$ = 3.0 Hz), 134.5, 134.1, 129.6, 129.4, 128.9, 128.2, 128.0, 127.7, 127.4 (d, $^4J_{C\text{-}F}$ = 8.0 Hz), 124.2 (d, $^4J_{C\text{-}F}$ = 9.1 Hz), 115.6 (d, $^3J_{C\text{-}F}$ = 21.0 Hz), 113.2 (d, $^3J_{C\text{-}F}$ = 23.0 Hz), 108.6 (d, $^3J_{C\text{-}F}$ = 24.0 Hz), 70.9;

HRMS (ESI): Caculated for $C_{27}H_{20}NF_2^+$ ($[M+H]^+$): 396.15583, found: 396.15634.

2,3-diphenyl-5-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-inden-1-amine (3ea)



3ea

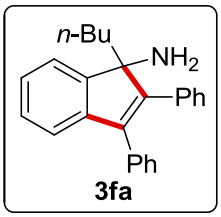
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-(trifluoromethyl)phenyl)methanimine **1e** (1.0 mmol, 371.1 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 °C for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ea** in 56% isolated yield as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.54 (s, 1H), 7.49 - 7.34 (m, 6H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 1.89 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 152.0, 146.4, 143.6, 139.2, 134.0, 133.5, 130.8 (q, $^3J_{C\text{-}F}$ = 31.8 Hz), 129.7 (q, $^3J_{C\text{-}F}$ = 31.8 Hz), 129.6, 129.4, 129.1, 128.4, 128.3, 128.0, 126.1, 126.0 (q, $^4J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $^2J_{C\text{-}F}$ = 270.8 Hz), 124.3 (q, $^2J_{C\text{-}F}$ = 270.3 Hz), 124.1 (q, $^4J_{C\text{-}F}$ = 3.9 Hz), 123.5 , 118.1 (q, ^4J = 3.7 Hz), 71.6;

HRMS (EI): Caculated for $C_{29}H_{19}F_6N$: 495.1422, found: 495.1419.

1-butyl-2,3-diphenyl-1*H*-inden-1-amine (3fa)



3fa

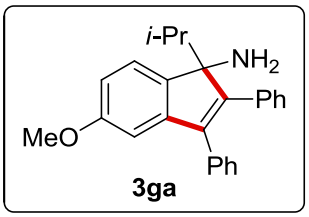
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), 1-phenylpentan-1-imine **1f** (1.0 mmol, 161.1 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, the product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3fa** in 54% isolated yield as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.48 (m, 1H), 7.22-7.33 (m, 13H), 1.95-2.02 (m, 1H), 1.84-1.91 (m, 1H), 1.64 (s, 2H), 1.12-1.24 (3H), 0.75-0.89 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 149.4, 143.3, 139.6, 135.7, 135.0, 129.7, 129.5, 128.34, 128.26, 127.6, 127.30, 127.28, 126.2, 121.9, 120.7, 69.6, 38.3, 26.0, 22.9, 14.0;

HRMS (ESI): Caculated for $C_{25}H_{24}N^+([M-2H+H]^+)$: 338.19032, found: 338.19008.

1-butyl-2,3-diphenyl-1*H*-inden-1-amine (3ga)



3ga

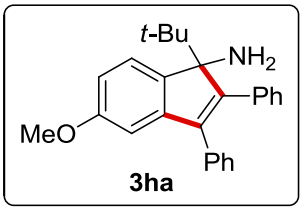
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), 2-methyl-1-(4-methoxyphenyl) propan-1-imine **1g** (1.0 mmol, 177.2 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ga** in 86% isolated yield as a yellow-white solid.

^{1}H NMR (MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 1H), 7.31 (dd, J_1 = 8.4 Hz, J_2 = 2 Hz, 2H), 7.21-7.27 (m, 8H), 6.81 (d, J = 2.4 Hz, 1H), 6.76 (dd, J_1 = 8 Hz, J_2 = 2.4 Hz, 1H), 3.78 (s, 3H), 1.99-2.08 (m, 1H), 1.69 (s, 2H), 1.18 (d, J = 6.8 Hz, 3H), 0.62 (d, J = 6.8 Hz, 3H);

^{13}C NMR (MHz, $CDCl_3$) δ 159.7, 151.0, 145.4, 141.0, 139.7, 136.2, 134.9, 129.8, 129.5, 128.4, 128.2, 127.3, 123.7, 110.5, 107.1, 72.0, 55.6, 34.5, 17.4, 17.3;

HRMS (ESI): Caculated for $C_{25}H_{26}ON^+$ ($[M+H]^+$): 356.20089, found: 356.20020.

1-butyl-5-methoxy-2,3-diphenyl-1*H*-inden-1-amine (3ha)



3ha

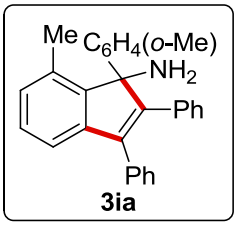
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), 1-(4-methoxyphenyl)-2,2-dimethyl propan-1-imine **1h** (1.0 mmol, 191.1 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 °C for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ha** in 60% isolated yield as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 1H), 7.16-7.29 (m, 8H), 7.11-7.13 (m, 2H), 6.71-6.73 (m, 2H), 3.74 (s, 3H), 1.83 (s, 2H), 0.88 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 150.8, 145.7, 142.0, 140.7, 138.6, 134.9, 129.52, 129.50, 128.2, 127.0, 126.9, 125.2, 109.9, 106.6, 74.9, 55.5, 38.0, 26.5;

HRMS (ESI): Caculated for $C_{26}H_{28}ON^+$ ($[M+H]^+$): 370.21654, found: 370.21680.

7-methyl-2,3-diphenyl-1-(o-tolyl)-1*H*-inden-1-amine (3ia)



3ia

Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol%, 10.2 mg), di-*o*-tolylmethanimine **1i** (1.0 mmol, 209.1 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 °C for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ia** in 82% isolated yield as a yellow-white solid.

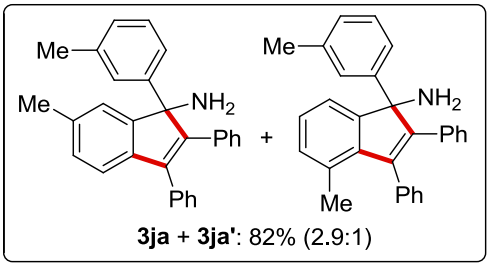
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 1H), 7.18-7.32 (m, 9H), 6.99-7.09

(m, 4H), 6.93-6.95 (m, 1H), 6.71 (d, *J* = 7.6 Hz, 2H), 1.97 (s, 3H), 1.79-1.84 (m, 5H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 147.9, 144.3, 139.3, 139.0, 136.0, 135.3, 134.6, 134.1, 131.8, 130.0, 129.5, 128.9, 128.7, 128.6, 127.9, 127.5, 127.4, 127.3, 126.0, 119.1, 72.0, 19.5, 17.8;

HRMS (ESI): Caculated for $C_{29}H_{26}N^+([M+H]^+)$: 388.20598, found: 388.20655.

6-methyl-2,3-diphenyl-1-(*m*-tolyl)-*1H*-inden-1-amine (3ja) and 4-methyl-2,3-diphenyl-1-(*m*-tolyl)-1H-inden-1-amine (3ja')



Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), di-m-tolylmethanimine **1j** (1.0 mmol, 209.3 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (1.5 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, the product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ja** and **3ja'** in 82% isolated yield as a yellow oily liquid. **3ja**:**3ja'** = 3:1 (determined by ^{1}H NMR).

Data of the major isomer **3ja**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 3H), 7.40 – 7.28 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.11 – 7.01 (m, 6H), 6.85 (d, *J* = 7.7 Hz, 2H), 2.33 (s, 3H), 2.29 (s, 3H), 1.81 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 150.3, 142.9, 140.2, 139.3, 138.3, 136.7, 135.4, 134.7, 129.7, 129.6, 128.7, 128.6, 128.3, 128.1, 127.7, 127.6, 127.1, 126.2, 124.1, 122.8, 120.8, 71.5, 21.9, 21.6.

Data of the mixture of **3ja** and **3ja'**:

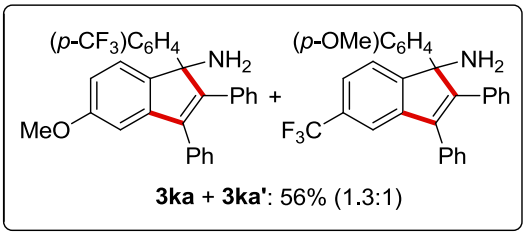
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 153.3, 151.7, 150.3, 142.9, 142.8, 141.2, 140.3, 140.2, 139.3, 138.3, 138.2, 138.1, 136.7, 135.4, 134.7, 134.6, 132.3, 131.0, 130.2, 129.73, 129.69, 129.6, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.8, 127.73, 127.69, 127.6, 127.3, 127.1, 127.0, 126.7, 126.2, 124.1, 122.8, 121.0, 120.8, 71.5, 71.1, 21.9,

21.6, 20.3.

HRMS (ESI): Caculated for $C_{29}H_{26}N^+([M+H]^+)$: 388.20598, found: 388.20566.

5-methoxy-2,3-diphenyl-1-(4-(trifluoromethyl)phenyl)-*1H*-inden-1-amine (3ka)

1-(4-methoxyphenyl)-2,3-diphenyl-5-(trifluoromethyl)-*1H*-inden-1-amine (3ka')



Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol%, 10.2 mg), (4-methoxyphenyl)(4-(trifluoro methyl)phenyl)methanimine **1k** (1.0 mmol, 279.3 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 °C for 24 h. After the workup, the product was pre-absorbed on silica gel and purified by flash column chromatography affording products **3ka** and **3ka'** in 56% isolated yield as yellow-white solid. The ratio of **3ka**:**3ka'** was 1.3:1 determined by ^{1}H NMR analysis.

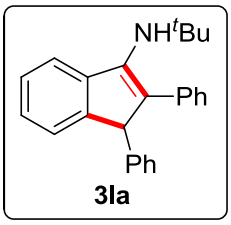
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.51 (s, 0.5H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.45 – 7.30 (m, 6H), 7.16 – 7.05 (m, 3.5H), 6.90 – 6.84 (m, 2.4H), 6.82 (d, *J* = 7.2 Hz, 1H), 6.71 (dd, *J* = 8.2, 2.3 Hz, 0.6H), 3.81 (s, 1.3H), 3.78 (s, 1.7H), 1.79 (s, 2H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 159.0, 156.7, 152.7, 151.8, 148.0, 144.6, 144.3, 143.5, 139.8, 138.3, 134.7, 134.4, 134.1, 134.0, 133.4, 130.12 (q, $^3J_{C-F}$ = 31.9 Hz), 129.7, 129.6, 129.5, 129.4, 129.1 (q, $^3J_{C-F}$ = 32.2 Hz), 129.0, 128.9, 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 126.8, 126.0, 125.7 (q, $^4J_{C-F}$ = 3.6 Hz), 124.5 (q, $^2J_{C-F}$ = 272.3 Hz), 124.4 (q, $^2J_{C-F}$ = 272.0 Hz), 123.9, 123.8 (q, $^4J_{C-F}$ = 4.0 Hz), 123.4, 117.7 (q, $^4J_{C-F}$ = 3.8 Hz), 114.3, 111.8, 107.7, 71.4, 71.0, 55.6, 55.3.

HRMS (ESI): Caculated for $C_{29}H_{23}F_3NO^+([M+H]^+)$: 458.17263, found: 458.17246.

***N*-(*tert*-butyl)-1,2-diphenyl-*1H*-inden-3-amine (3la)**

Following the general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 2.5 mol %, 16.3 mg),



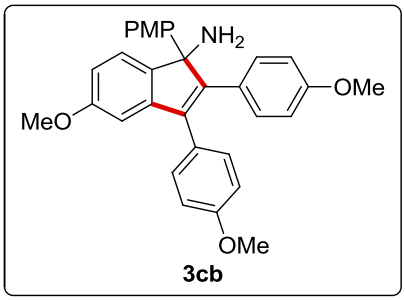
N-*tert*-butyl-1-phenylmethanimine (**1l**) (1.0 mmol, 161.2 mg), diphenylacetylene **2a** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, the product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3la** in 54% isolated yield as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.21-7.35 (m, 6H), 7.08-7.18 (m, 6H), 7.03-7.04 (m, 2H), 4.87 (s, 1H), 1.13 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 144.5, 143.4, 140.6, 137.2, 136.8, 129.0, 128.6, 128.4, 128.3, 126.6, 126.5, 125.6, 124.0, 120.1, 56.8, 55.1, 31.2;

HRMS (ESI): Caculated for $C_{25}H_{26}N^+$ ($[M+H]^+$):340.2060 , found: 340.2059.

5-methoxy-1,2,3-tris(4-methoxyphenyl)-1*H*-inden-1-amine (3cb)



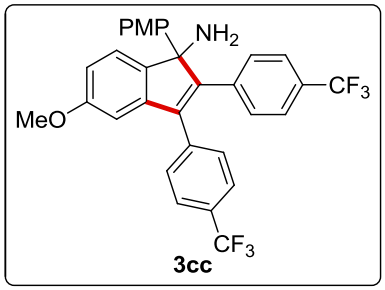
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl) methanimine **1c** (1.0 mmol, 241.1 mg), 1,2-bis(4-methoxyphenyl)ethyne **2b** (1.0 mmol, 238.1 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3cb** in 96% isolated yield as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 6.86 – 6.78 (m, 4H), 6.66 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.61 (d, *J* = 8.9 Hz, 1H), 3.82 (s, 2H), 3.78 (s, 2H), 3.76 (s, 2H), 3.69 (s, 2H), 1.78 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 159.0, 158.6, 158.5, 151.3, 145.5, 144.6, 137.4, 135.5, 130.9, 130.7, 127. 6, 127.0, 126.7, 123.6, 114.2, 114.0, 113.6, 111.2, 107.1, 77.5, 77.2, 76.8, 70.5, 55.6, 55.3, 55.3, 55.1.

HRMS (ESI): Caculated for $C_{31}H_{30}O_4N^+$ ($[M+H]^+$): 480.21693, found: 480.21744.

5-methoxy-1-(4-methoxyphenyl)-2,3-bis(4-(trifluoromethyl)phenyl)-1*H*-inden-1-amine (3cc)



3cc

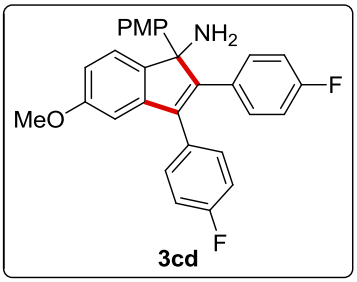
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl)methanimine **1c** (1.0 mmol, 241.1 mg), 1,2-bis(4-(trifluoro methyl)phenyl)-ethyne **2c** (1.0 mmol, 314.1 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3cc** in 93% isolated yield as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.75 (dd, J_1= 8.0 Hz, J_2 = 2.4 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 1.82 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 158.9, 152.3, 145.6, 143.2, 139.0, 138.4, 138.1, 133.9, 130.1 (q, $^3J_{C\text{-}F}$ = 32.3 Hz), 129.9, 129.8, 129.5 (q, $^3J_{C\text{-}F}$ = 32.2 Hz), 126.8, 125.9 (q, $^4J_{C\text{-}F}$ = 3.6 Hz), 125.1 (q, $^4J_{C\text{-}F}$ = 3.7 Hz), 124.2 (q, $^2J_{C\text{-}F}$ = 270.5 Hz), 124.1 (q, $^2J_{C\text{-}F}$ = 270.4 Hz), 124.0, 114.2, 112.4, 107.5, 71.2, 55.6, 55.3;

HRMS (ESI): Caculated for $C_{31}H_{24}O_2NF_6^+$ ($[M+H]^+$): 556.17057, found: 556.17157.

2,3-bis(4-fluorophenyl)-5-methoxy-1-(4-methoxyphenyl)-1*H*-inden-1-amine (3cd)



3cd

Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl) methanimine **1c** (1.0 mmol, 241.1 mg), 1,2-bis(4-fluoro phenyl)ethyne **2d** (1.0 mmol, 214.1 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction

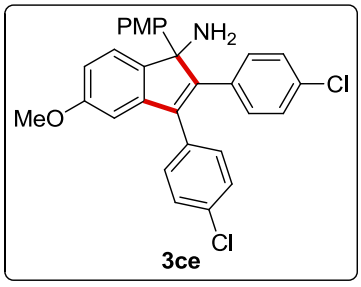
mixture was stirred at 150 °C for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3cd** in 96% isolated yield as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.40 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.05 (m, 2H), 6.81-6.84 (m, 5H), 6.76 (td, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 2H), 6.70 (dd, J_1 = 8.2 Hz, J = 2.4 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 1.78 (s, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, $^2J_{C-F}$ = 245.7 Hz), 162.0 (d, $^2J_{C-F}$ = 246.3 Hz), 159.9, 158.7, 151.7, 145.5, 144.0, 137.9, 134.5, 131.4 (d, $^4J_{C-F}$ = 7.7 Hz), 131.2 (d, $^4J_{C-F}$ = 7.8 Hz), 130.7 (d, $^5J_{C-F}$ = 3.3 Hz), 130.5 (d, $^5J_{C-F}$ = 3.5 Hz), 126.8, 123.8, 115.9 (d, $^3J_{C-F}$ = 21.3 Hz), 115.2 (d, $^3J_{C-F}$ = 21.0 Hz), 114.7, 111.7, 107.3, 70.8, 55.6, 55.3;

HRMS (ESI): Caculated for $C_{29}H_{24}O_2NF_2^+$ ($[M+H]^+$): 456.17696, found: 456.17761.

2,3-bis(4-chlorophenyl)-5-methoxy-1-(4-methoxyphenyl)-1*H*-inden-1-amine (3ce)



3ce

Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl) methanimine **1c** (1.0 mmol, 241.1 mg), 1,2-bis(4-chlorophenyl)ethyne **2e** (1.0 mmol, 246.0 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 °C for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ce** in 95% isolated yield as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.38 (m, 6H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.04 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 2H), 6.77-6.83 (m, 5H), 6.70 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 1.78 (s, 2H);

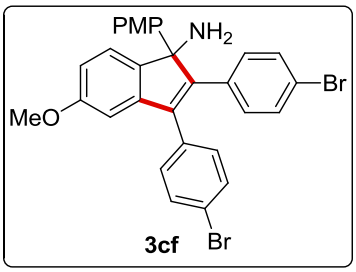
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 158.7, 151.7, 145.5, 143.6, 138.2, 134.3, 133.7, 133.4, 133.2, 132.9, 130.9, 130.8, 129.1, 128.4, 126.8, 123.8, 114.1, 112.0, 107.3, 70.8, 55.6, 55.3;

HRMS (ESI): Caculated for $C_{29}H_{22}Cl_2O_2N^+$ ($[M-2H+H]^+$): 486.10220, found:

486.10230.

2,3-bis(4-bromophenyl)-5-methoxy-1-(4-methoxyphenyl)-1*H*-inden-1-amine (3cf)

Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl) methanimine **1c** (1.0 mmol, 241.1 mg), 1,2-bis(4-bromophenyl)ethyne **2f** (1.0 mmol, 178.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3cf** in 78% isolated yield as a solid.



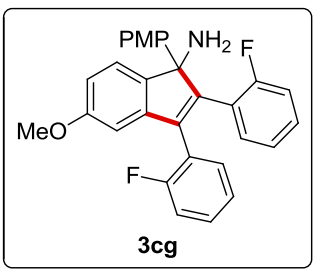
3cf

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.79-6.83 (m, 3H), 6.69-6.73 (m, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 1.77 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 158.7, 151.7, 145.5, 143.5, 138.2, 134.2, 133.6, 133.3, 132.1, 131.4, 131.2, 131.1, 126.7, 123.8, 121.9, 121.8, 114.1, 112.0, 107.2, 70.8, 55.6, 55.3;

HRMS (ESI): Caculated for $C_{29}H_{22}Br_2O_2N^+$ ($[M-2H+H]^+$): 574.00117, found: 574.00163.

2,3-bis(2-fluorophenyl)-5-methoxy-1-(4-methoxyphenyl)-1*H*-inden-1-amine (3cg)



3cg

Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl)methanimine **1c** (1.0 mmol, 241.1 mg), 1,2-bis(2-fluorophenyl)ethyne **2g** (1.0 mmol, 214.1 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, the product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ca** in 76% yield as a

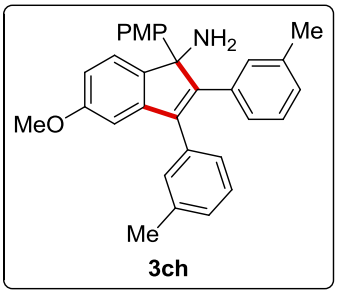
solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.17 (m, 2H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.11 – 6.98 (m, 3H), 6.88 – 6.74 (m, 4H), 6.72 (d, *J* = 6.8 Hz, 2H), 6.66 (t, *J* = 6.9 Hz, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 1.88 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1 (d, $^2J_{C-F}$ = 245.1 Hz), 160.0, 158.6, 149.2, 145.1, 143.8, 133.3, 131.0, 130.84 (d, $^5J_{C-F}$ = 2.6 Hz), 129.7 (d, $^4J_{C-F}$ = 8.0 Hz), 129.4 (d, $^4J_{C-F}$ = 8.1 Hz), 127.2, 124.0 (d, $^5J_{C-F}$ = 3.3 Hz), 123.7, 123.5 (d, $^5J_{C-F}$ = 3.2 Hz), 122.34 (d, $^3J_{C-F}$ = 16.0 Hz), 122.28 (d, $^3J_{C-F}$ = 16.2 Hz), 115.8 (d, $^3J_{C-F}$ = 21.7 Hz), 115.4 (d, $^3J_{C-F}$ = 21.5 Hz), 113.7, 111.8, 107.3, 71.8, 55.5, 55.2.

HRMS (ESI): Caculated for $C_{29}H_{24}O_2NF_2^+$ ($[M+H]^+$): 456.17696, found: 456.17698.

5-methoxy-1-(4-methoxyphenyl)-2,3-di-*m*-tolyl-1*H*-inden-1-amine (3ch)



3ch

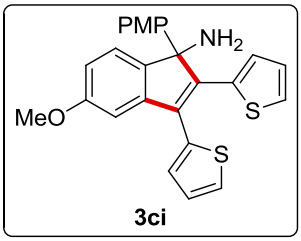
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl) methanimine **1c** (1.0 mmol, 241.1 mg), 1,2-di-*m*-tolylethyne **2h** (1.0 mmol, 206.1 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, the product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ch** in 84% isolated yield as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.89-6.96 (m, 2H), 6.81-6.84 (m, 3H), 6.65-6.69 (m, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 2.32 (s, 3H), 2.07 (s, 3H), 1.80 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 158.5, 152.4, 145.5, 144.5, 138.7, 138.1, 137.3, 135.3, 135.1, 134.5, 130.4, 130.0, 128.5, 128.3, 128.0, 127.8, 126.82, 126.77, 126.6, 123.6, 114.0, 111.4, 107.5, 70.7, 55.6, 55.3, 21.6, 21.5;

HRMS (EI): Caculated for $C_{31}H_{30}O_2N^+$ ($[M+H]^+$): 448.22711, found: 448.22757.

5-methoxy-1-(4-methoxyphenyl)-2,3-di(thiophen-2-yl)-1*H*-inden-1-amine (3ci)



3ci

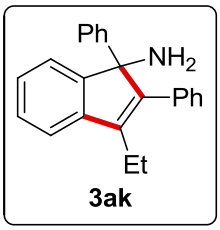
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl) methanimine **1c** (1.0 mmol, 241.1 mg), 1,2-di(thiophen -2-yl)ethyne **2i** (1.0 mmol, 190.0 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ci** in 94% isolated yield as a brown oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.49 (m, 3H), 7.20-7.22 (m, 1H), 7.16 (dd, J_1 = 5.2 H, J_2 = 3.6 Hz, 1H), 7.10-7.12 (m, 2H), 6.79-6.83 (m, 4H), 6.66-6.73 (m, 2H), 3.74 (s, 3H), 3.72 (s, 3H), 1.90 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 158.8, 148.2, 144.4, 144.0, 135.9, 135.1, 134.6, 131.2, 128.2, 128.1, 127.8, 127.0, 126.8, 126.7, 123.7, 114.0, 112.2, 107.0, 70.7, 55.5, 55.2;

HRMS (EI): Caculated for $C_{25}H_{22}O_2NS_2^+$ ($[M+H]^+$): 432.10865, found: 432.10920.

3-methyl-1,2-diphenyl-1*H*-inden-1-amine (3ak) [3]



3ak

Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), diphenylmethanimine **1a** (1.0 mmol, 181.1 mg), but-1-yn-1-ylbenzene **2k** (1.0 mmol, 130.1 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After workup, the crude reaction mixture was checked by ^{1}H NMR analysis and only one regioisomer was detected. Then the product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ak** in 79% isolated yield as a solid. The spectra data of **3ak** is in agreement with the known compound in literature.[3]

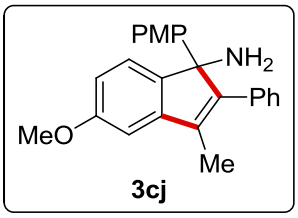
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 3H), 7.31 – 7.09 (m, 9H), 6.96 – 6.87 (m, 2H), 2.75 – 2.39 (m, 2H), 1.75 (s, 2H), 1.26 (t, J = 7.6 Hz, 3H).;

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 150.3, 143.2, 142.5, 140.4, 135.2, 129.3,

128.4, 128.2, 127.7, 127.4, 126.8, 126.4, 125.9, 123.0, 120.0, 71.8, 19.5, 13.8.;

HRMS (EI): Caculated for $C_{23}H_{22}N^+$ ($[M+H]^+$): 312.17468, found: 312.17422.

5-methoxy-1-(4-methoxyphenyl)-3-methyl-2-phenyl-1*H*-inden-1-amine (3cj)



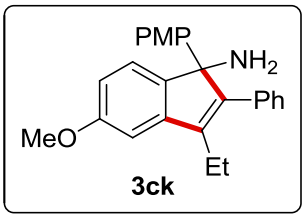
Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl)methanimine **1c** (1.0 mmol, 241.1 mg), prop-1-yn-1-ylbenzene **2j** (1.0 mmol, 116.1 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3cj** in 87% isolated yield as a solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.34 (m, 2H), 7.21-7.29 (m, 3H), 7.08 (d, *J* = 4.4 Hz, 1H), 7.00-7.04 (m, 2H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.78-6.82 (m, 2H), 6.70 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 2.18 (s, 3H), 1.74 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 158.4, 151.7, 145.6, 145.4, 135.2, 134.9, 133.8, 129.3, 128.1, 127.3, 126.9, 123.1, 113.7, 111.0, 106.0, 70.8, 55.5, 55.2, 11.8;

HRMS (EI): Caculated for $C_{24}H_{24}O_2N^+$ ($[M+H]^+$): 358.18016, found: 358.18060.

3-ethyl-5-methoxy-1-(4-methoxyphenyl)-2-phenyl-1*H*-inden-1-amine (3ck)



Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl)methanimine **1c** (1.0 mmol, 241.1 mg), but-1-yn-1-ylbenzene **2k** (3.0 mmol, 260.2 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 ^oC for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3ck** in 78% isolated yield as a solid.

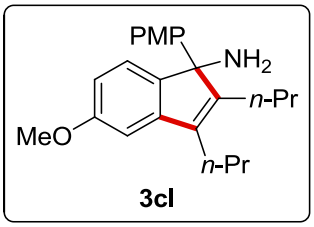
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-7.25 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.90-6.93 (m, 3H), 6.76 (d, *J* = 7.8 Hz, 2H), 6.66 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 3.82 (s, 3H),

3.75 (s, 3H), 2.45-2.60 (m, 2H), 1.70 (s, 2H), 1.24 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 158.4, 151.8, 145.7, 144.7, 139.6, 135.3, 134.7, 129.3, 128.2, 127.4, 127.0, 123.4, 113.7, 110.7, 106.6, 70.8, 55.6, 55.2, 19.4, 13.8;

HRMS (EI): Caculated for $C_{25}H_{26}O_2N^+$ ($[M+H]^+$): 372.19581, found: 372.19617.

5-methoxy-1-(4-methoxyphenyl)-2,3-dipropyl-1*H*-inden-1-amine (3cl)



3cl

Following the general procedure: $ReBr(CO)_5$ (0.025 mmol, 2.5 mol %, 10.2 mg), bis(4-methoxyphenyl)methanimine **1c** (1.0 mmol, 241.1 mg), oct-4-yne **2l** (1.0 mmol, 110.1 mg), Na_2CO_3 (0.3 mmol, 30 mol%, 31.8 mg) and 1,4-dioxane (2.0 mL) were added into reaction vessel with a Teflon screw cap under nitrogen. The reaction mixture was stirred at 150 °C for 24 h. After the workup, The product was pre-absorbed on silica gel and purified by flash column chromatography affording product **3cl** in 78% isolated yield as a brown oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.74-6.77 (m, 3H), 6.58 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 2.44-2.47 (m, 2H), 2.14-2.22 (m, 1H), 1.96-2.08 (m, 1H), 1.61-1.70 (m, 4H), 1.26-1.39 (m, 1H), 1.08-1.21 (m, 1H), 1.01 (t, *J* = 7.3 Hz, 3H), 0.82 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 158.4, 152.4, 146.2, 145.7, 136.3, 135.2, 126.9, 122.4, 113.5, 109.4, 105.9, 70.2, 55.5, 55.2, 28.0, 27.7, 23.1, 22.1, 14.9, 14.5;

HRMS (EI): Caculated for $C_{23}H_{30}O_2N^+$ ($[M+H]^+$) : 352.22711, found: 352.22755.

In addition, we have conducted the reactions of ketimine **1c** with phenylacetylene and silyl-substituted alkyne (TMSC≡CPh) under the standard reaction conditions. Unfortunately, no reaction took place with phenylacetylene and the expected [3+2] annulation product was only detected in a very low yield (14%) by ^{1}H NMR for the silyl-substituted alkyne (TMSC≡CPh), which might be ascribed to the increased steric hindrance of the silyl-substituted alkyne.

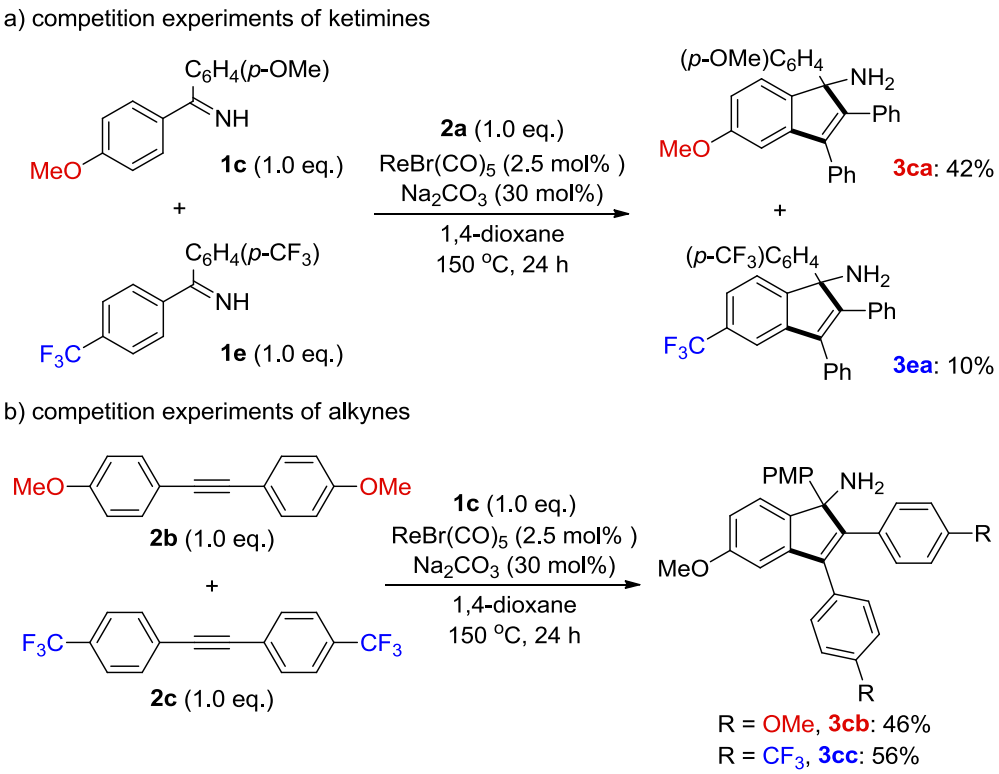
6. Mechanistic Studies

6.1 Competition Experiments

In order to explore the possible reaction mechanism, two competition experiments were conducted (**Scheme S1**).

First, equal molar amounts of ketimines **1c** and **1e** bearing OMe and CF_3 groups at the *para*-position respectively, were treated with an inadequate amount of alkyne **2a** under standard conditions (**Scheme S1a**). The amine **3ca** derived from **1c** turned out to be the major product (**Figure S1**), which suggested the existence of the electron-donating group in ketimines facilitated the reaction.

On the other hand, equal molar amounts of alkynes **2b** and **2c** with OMe and CF_3 groups at the *para*-position respectively, were treated with ketimine **1c** under standard conditions (**Scheme S1b**). It was found that the reaction favored alkyne **2c** bearing the electron-withdrawing group CF_3 slightly (**Figure S2**).



Scheme S1. Competition Reactions

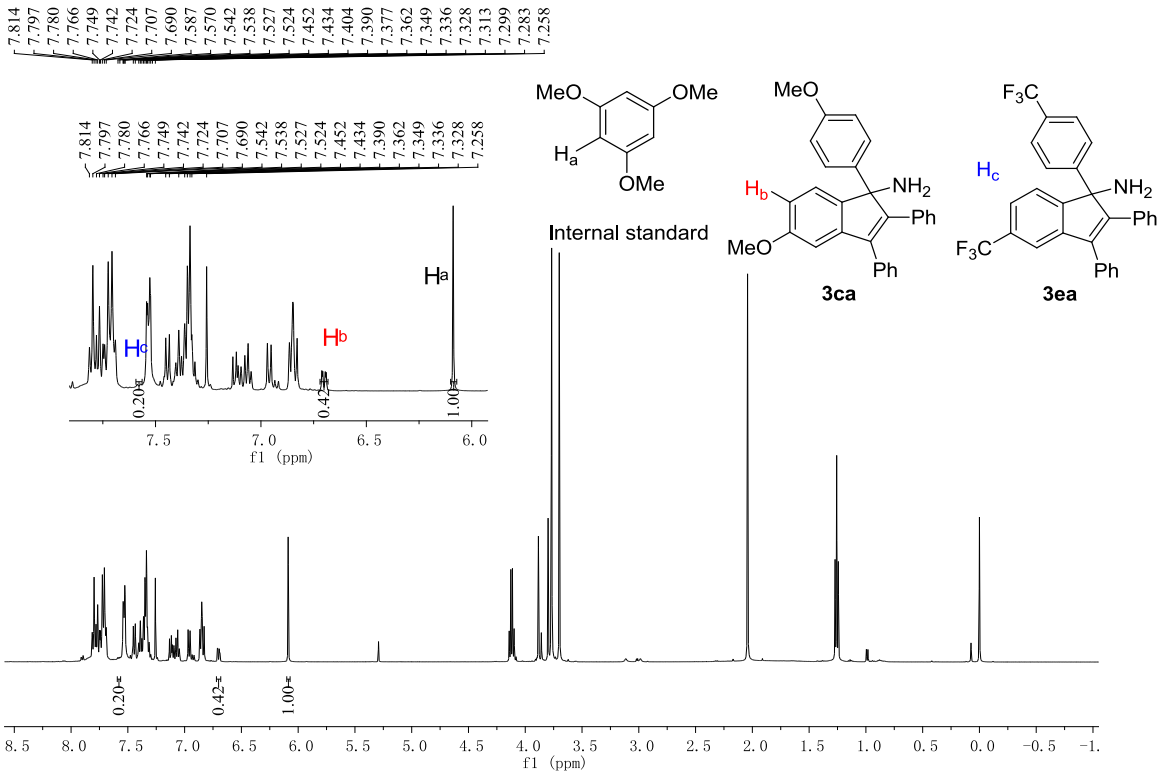


Figure S1. Crude ^{1}H NMR Spectra of the Competition Reactions **Scheme S1a**

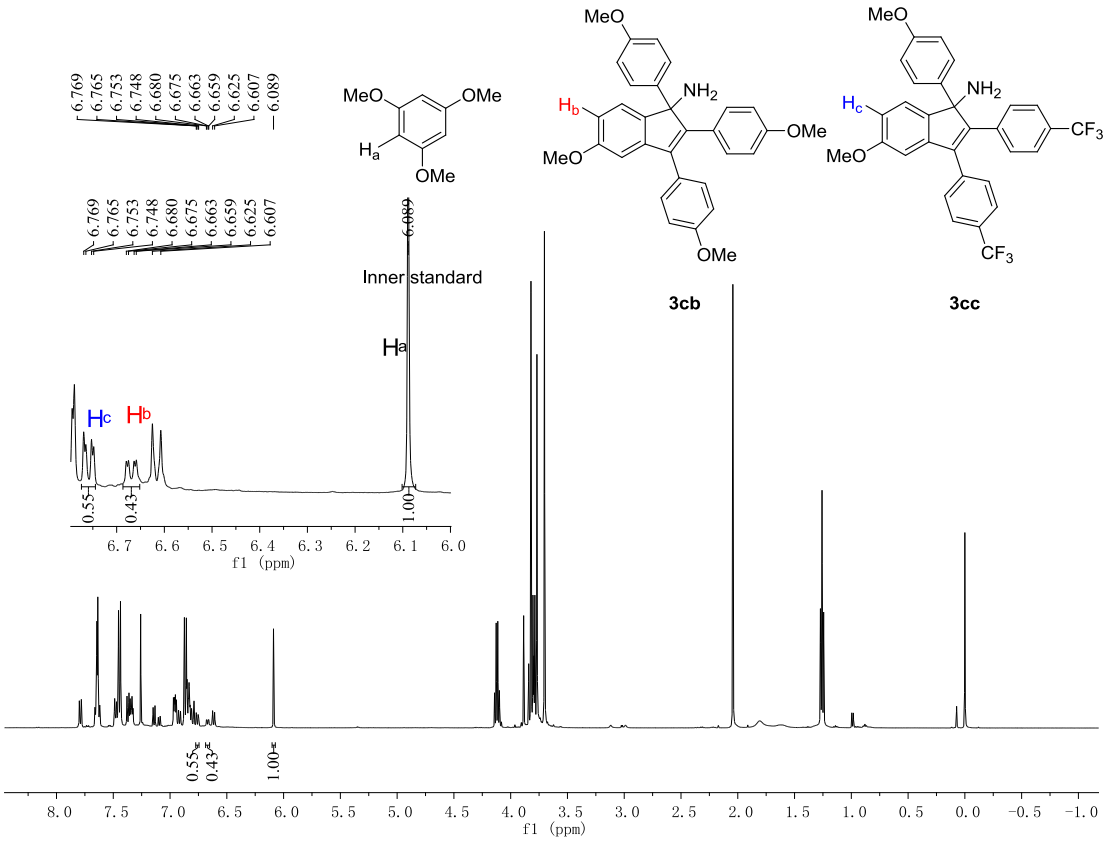
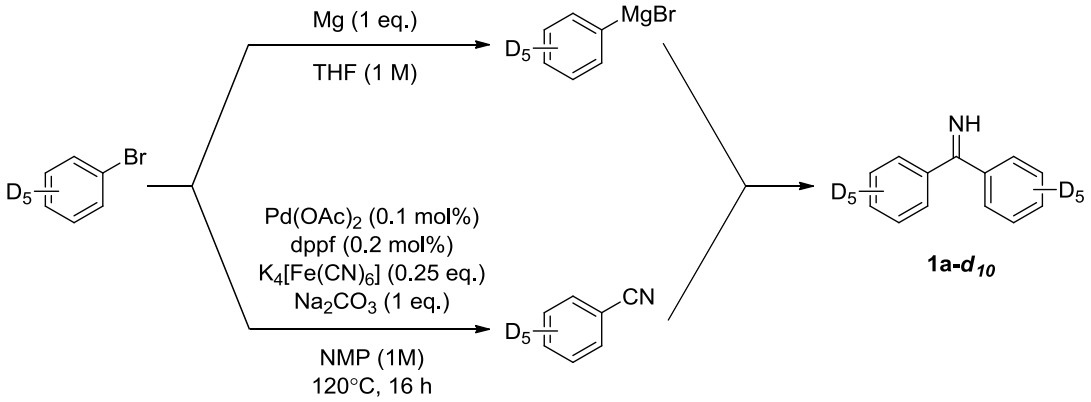


Figure S2. Crude ^{1}H NMR Spectra of the Competition Reactions **Scheme S1b**

6.2 Deuterium-labeling Experiments

Deuterated N-H ketimine **1a-*d*$_{10}$** was prepared from commercially available bromobenzene-d_5 (Alfa Aesar, >99% D) according to the following **Scheme S2**.[1,7]



Scheme S2. Preparation of Deuterated Ketimine **1a-*d*$_{10}$**

Dipentadeuterophenylmethanimine (**1a-*d*$_{10}$**)

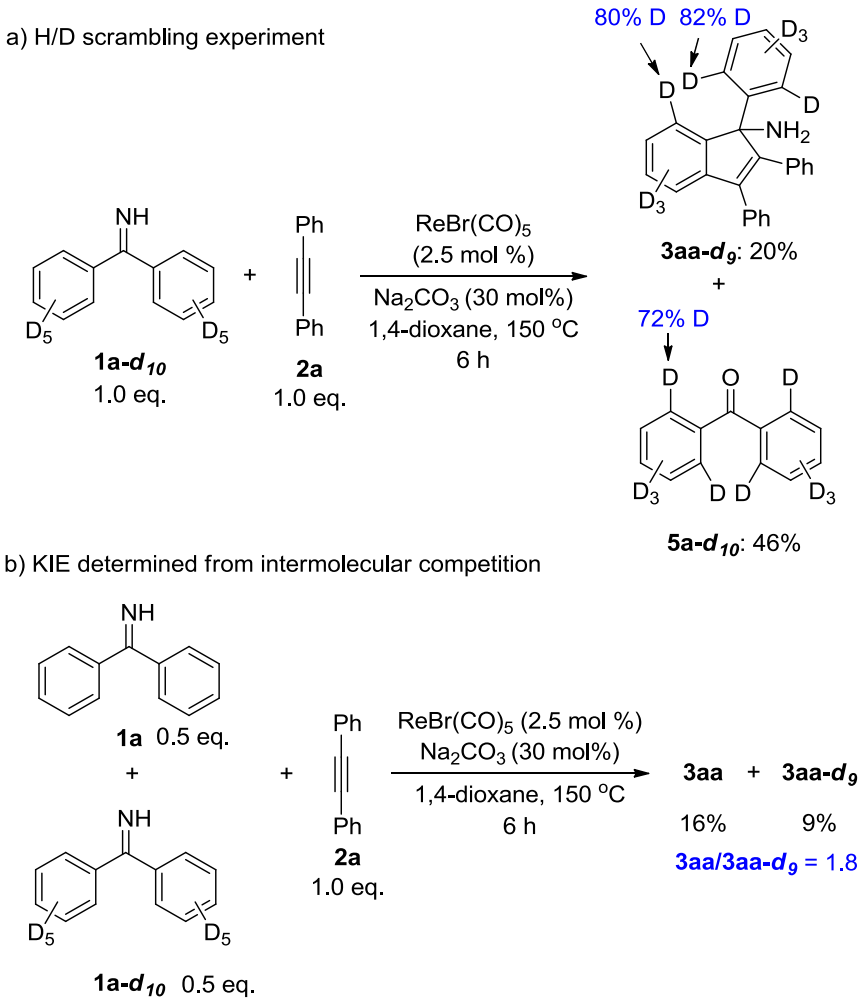
Pentadeuterobenzonitrile was synthesized from bromobenzene-d_5 (20 mmol, 3.24 g) by a known procedure and then treated with (Ph-d_5)MgBr (20 mmol) following the previously described general procedure A for the synthesis of N–H diaryl imines. After workup, the title compound was isolated by column chromatography (PE/Et_2O/TEA = 100/10/1.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (br, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 139.3, 129.8 (t), 128.3 (t), 127.9 (t).

With the deuterated ketimine **1a-*d*$_{10}$** in hand, H/D scrambling experiment and intermolecular KIE experiment were conducted (**Scheme S3**). Firstly, a solution of **1a-*d*$_{10}$** (1.0 eq.), **2a** (1.0 eq.), $ReBr(CO)_5$ (2.5 mol%) and Na_2CO_3 (0.3 eq.) in 1,4-dioxane (0.5 M) was stirred at 150℃ for 6 h under N_2 atmosphere. After workup, the product **3aa-*d*$_9$** and by-product **5a-*d*$_{10}$** was purified by the column chromatography to reveal the isolated yields to be 20% and 46% respectively. The ^{1}H NMR spectra of **3aa-*d*$_9$** (Figure 1) indicated there is around 20% deuterium loss at the *ortho*-position of the product. And there is also 28% deuterium loss at the *ortho*-position of the byproduct **5a-*d*$_{10}$** (Figure S4). Therefore, the C−H activation step might be a reversible process.

Then the intermolecular competition experiment was conducted. Equivalent **1a** and **1a-*d*$_{10}$** (0.5 eq.) was added to a solution of **2a** (1.0 eq.) in 1,4-dioxane (0.5 M) under standard conditions. After 6 h, the product (**3aa** and **3aa-*d*$_9$**) was isolated by column chromatography. The ^{1}H NMR spectra showed that the ratio between **3aa** and **3aa-*d*$_9$** is 1.8 (Figure S5, 0.64/0.36).



Scheme S3. Deuterium-labeling Experiments

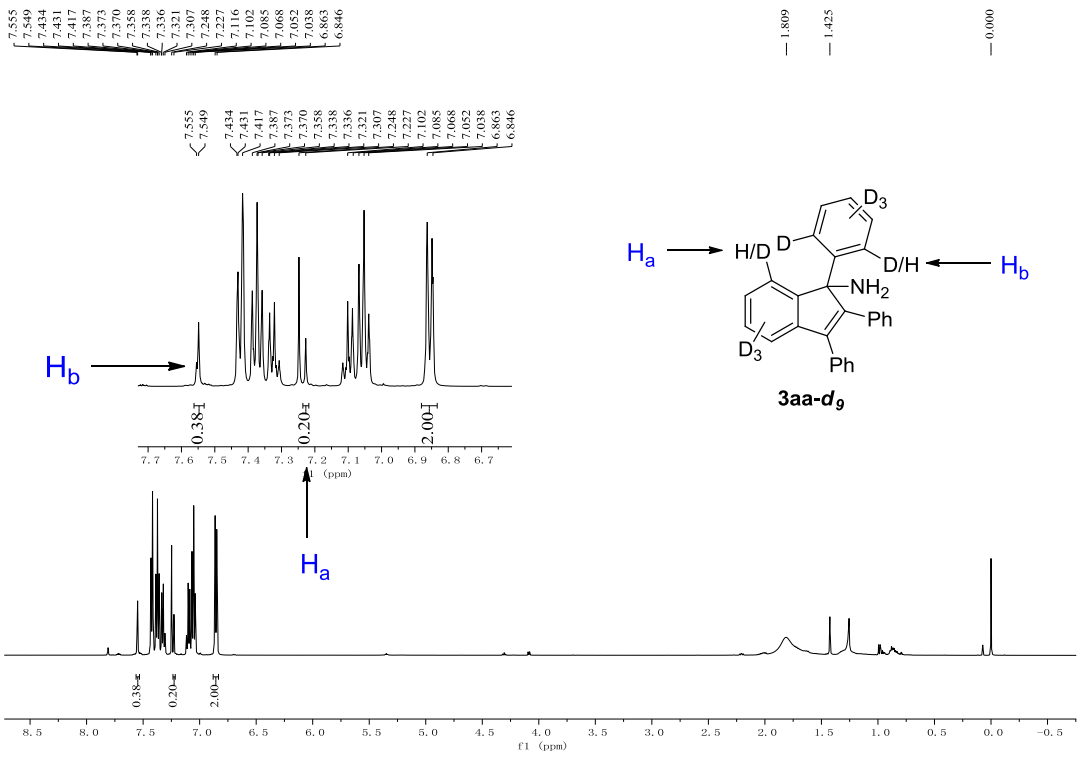


Figure S3. ^{1}H NMR Spectra of **3aa-*d*$_9$**

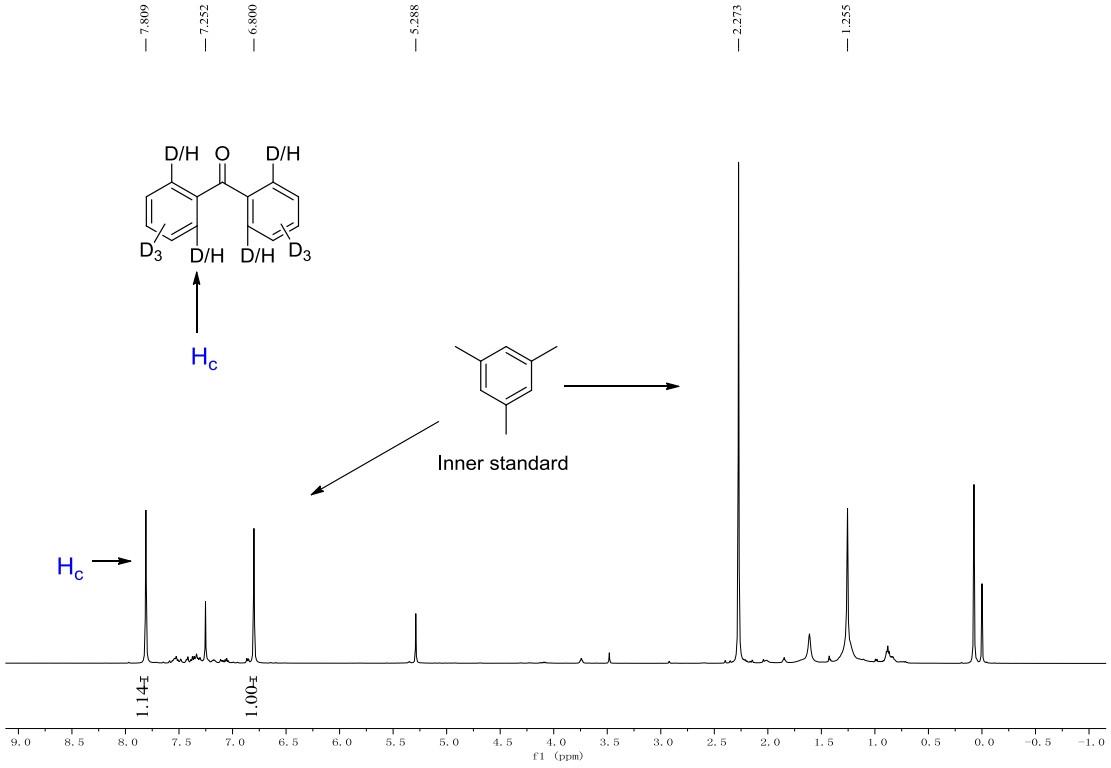


Figure S4. ^{1}H NMR Spectra of **5a-*d*$_{10}$**

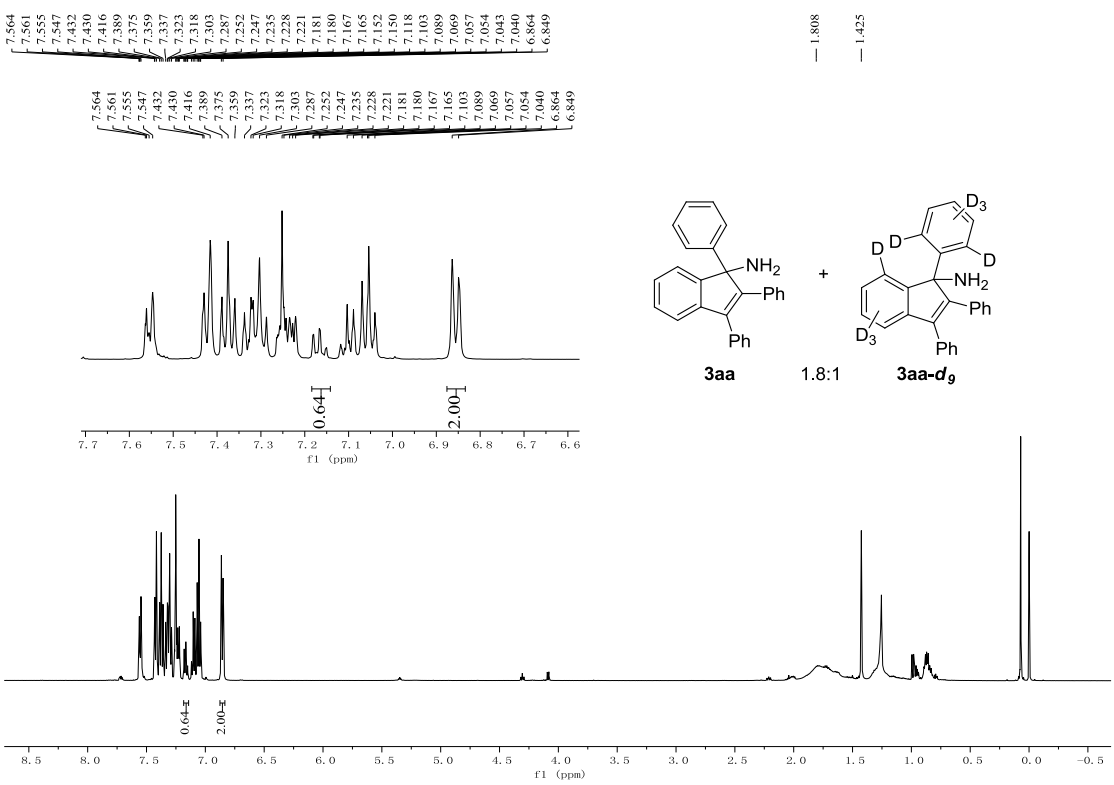
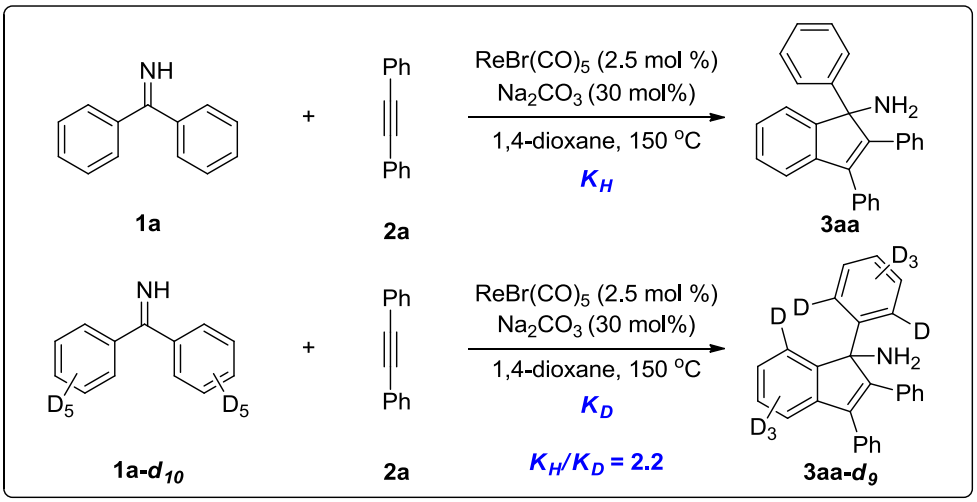


Figure S5. ^{1}H NMR Spectra of the Mixture of **3aa** and **3aa-*d*$_9$**

In addition, two parallel reactions of **2a** with **1a** and **1a-*d*$_{10}$** respectively were performed to determine the corresponding KIE value (**Scheme S4**). **1a** (0.2 mmol, 36.2 mg) and **1a-*d*$_{10}$** (0.2 mmol, 38.2 mg) were placed in an oven-dried Schlenk tube respectively, and then treated with the same mixture of **2a** (0.2 mmol, 35.6 mg), $Re(CO)_5Br$ (0.005 mmol, 2.0 mg), 1,3,5-trimethoxybenzene (internal standard, 0.067 mmol, 11.2 mg) in anhydrous dioxane (0.5 M) at 150 ℃ under N_2 atmosphere. Each reaction was sampled at the following indicated points and analyzed by GC. The GC yields were calculated after calibrating the response of GC.



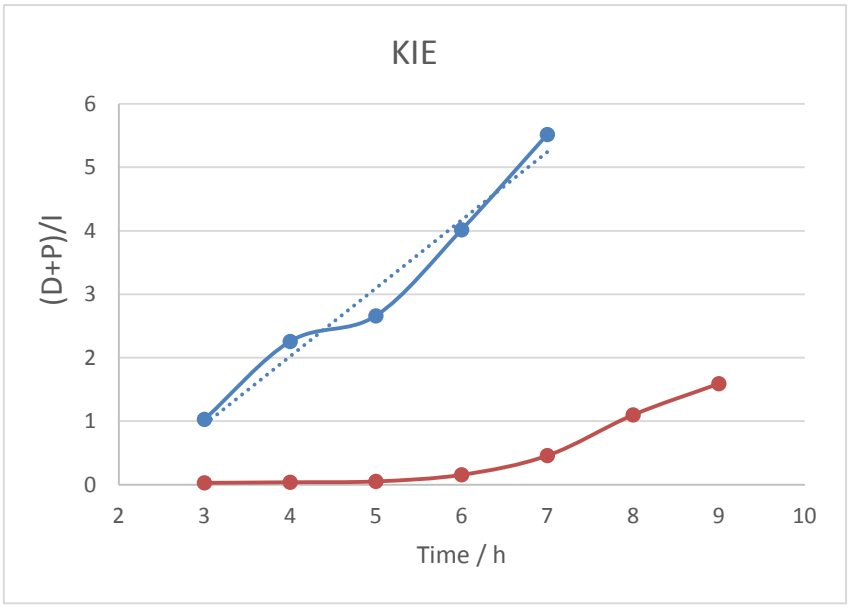
Scheme S4. KIE Experiments

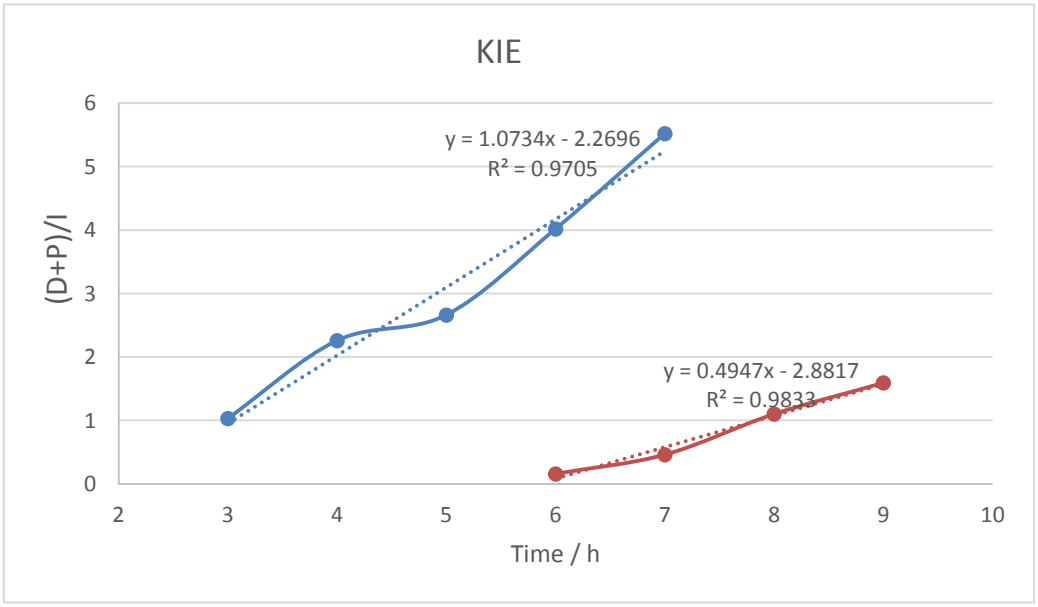
KIE-H

ENTRY	Time/h	Inner Standard	de-NH_2	P	(D+P)/I
5	3	49.23	16.35	34.42	1.031282
6	4	30.69	22.49	46.82	2.25839
7	5	27.31	21.34	51.35	2.661662
8	6	19.93	29.38	50.69	4.017561
9	7	15.34	16.76	67.9	5.518905

KIE-D

ENTRY	Time	Inner Standard	de-NH_2	P	(D+P)/I
2	3	96.98	1.71	1.31	0.03114
3	4	96.08	1.72	2.2	0.040799
4	5	94.88	2.45	2.67	0.053963
5	6	86.35	5.71	7.94	0.158078
6	7	68.46	12.91	18.63	0.460707
7	8	47.58	16.28	36.14	1.101723
8	9	38.56	14.16	47.28	1.593361





$$\text{KIE} = \frac{K_H}{K_D} = 2.2$$

Thus, the KIE value from the two parallel reactions was determined to be 2.2, which indicated that the cleavage of the C–H bond might be involved in the rate-determining step of the reaction.

7. References

[1] R. He, Z.-T. Huang, Q.-Y. Zheng and C. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 4950.

[2] C. J. Thoman and I. M. Hunsberger, *J. Org. Chem.*, 1968, **33**, 2852.

[3] Z.-M. Sun, S.-P. Chen and P. Zhao, *Chem. Eur. J*, 2010, **16**, 2619.

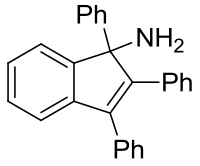
[4] M. Chafeev, N. Chakka, J.-J. Cadieux, J. Fu, R. Kamboj, V. Kodumuru, J. Langille, S. Liu, J. Sun, S. Sviridov and Z. Zhang, US2008234384 (A1), 2008-09-25.

[5] J. H. Lee, S. Gupta,; W. Jeong, Y. H. Rhee, J. Park, *Angew. Chem. Int. Ed.* 2012, **51**, 10851.

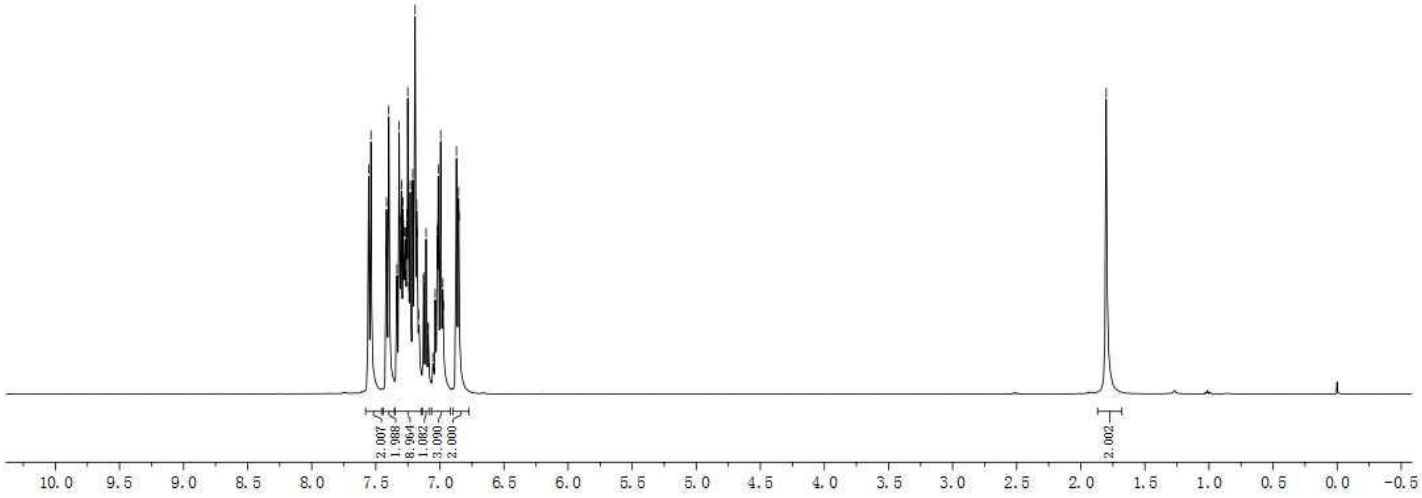
[6] C.-C. Tai, M.-S. Yu, Y.-L. Chen, W.-H. Chuang, T.-H. Lin, G. P. A. Yapc and T.-G. Ong, *Chem. Commun.*, 2014, **50**, 4344.

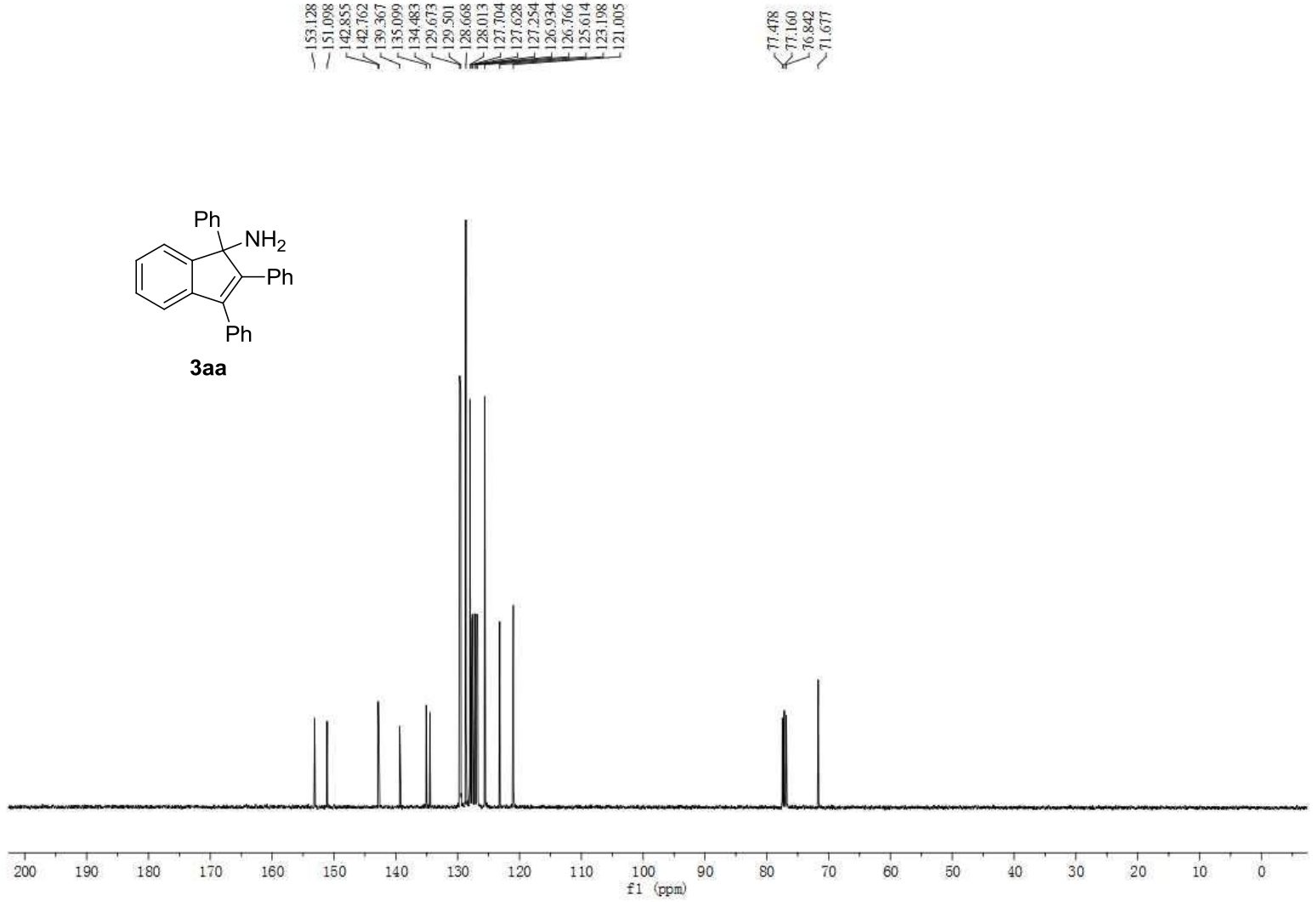
[7] T. Schareina, A. Zapf and M. Bller, *J. Organomet. Chem.* 2004, **689**, 4576.

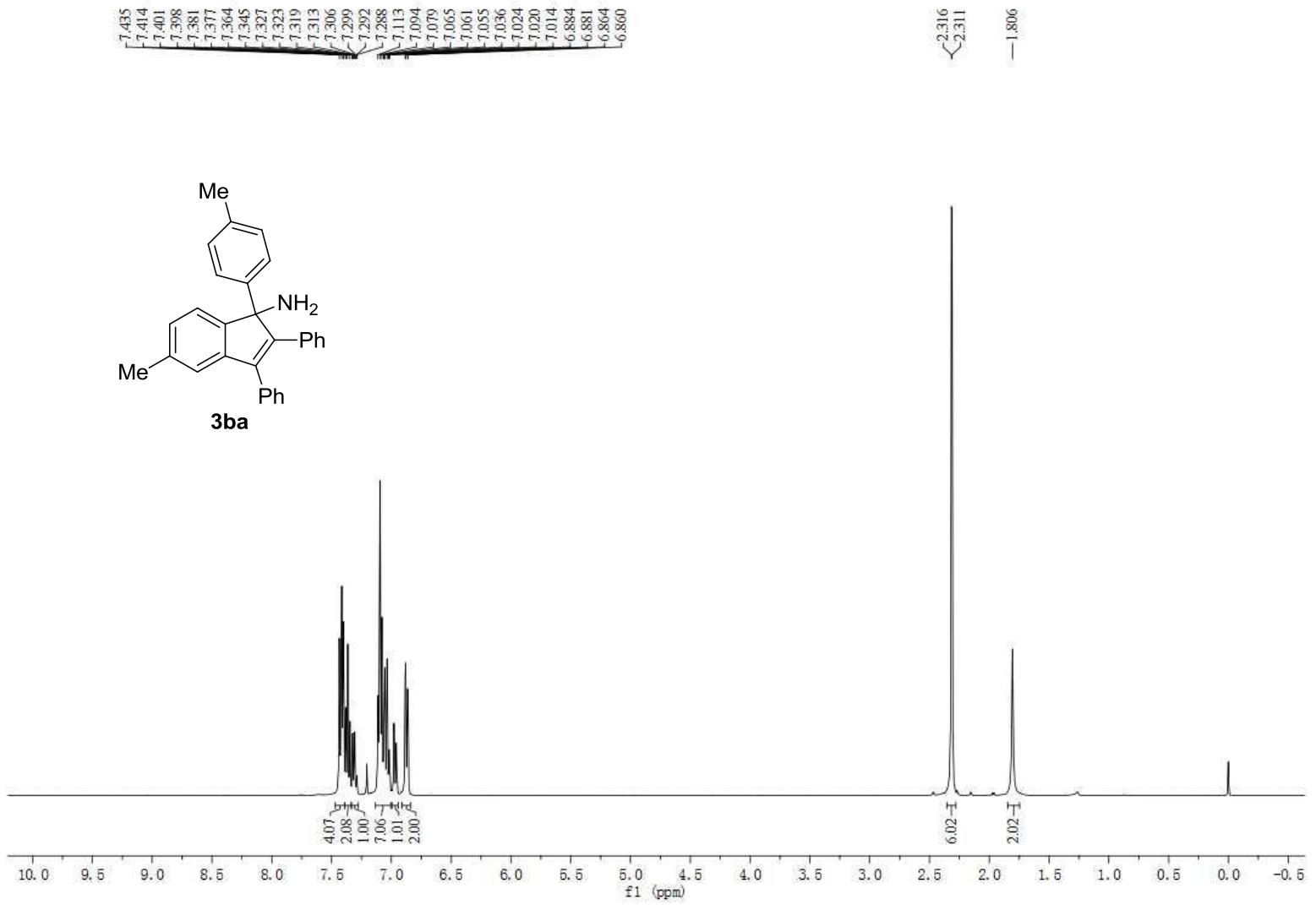
8. ^{1}H NMR and ^{13}C NMR Spectra of Products

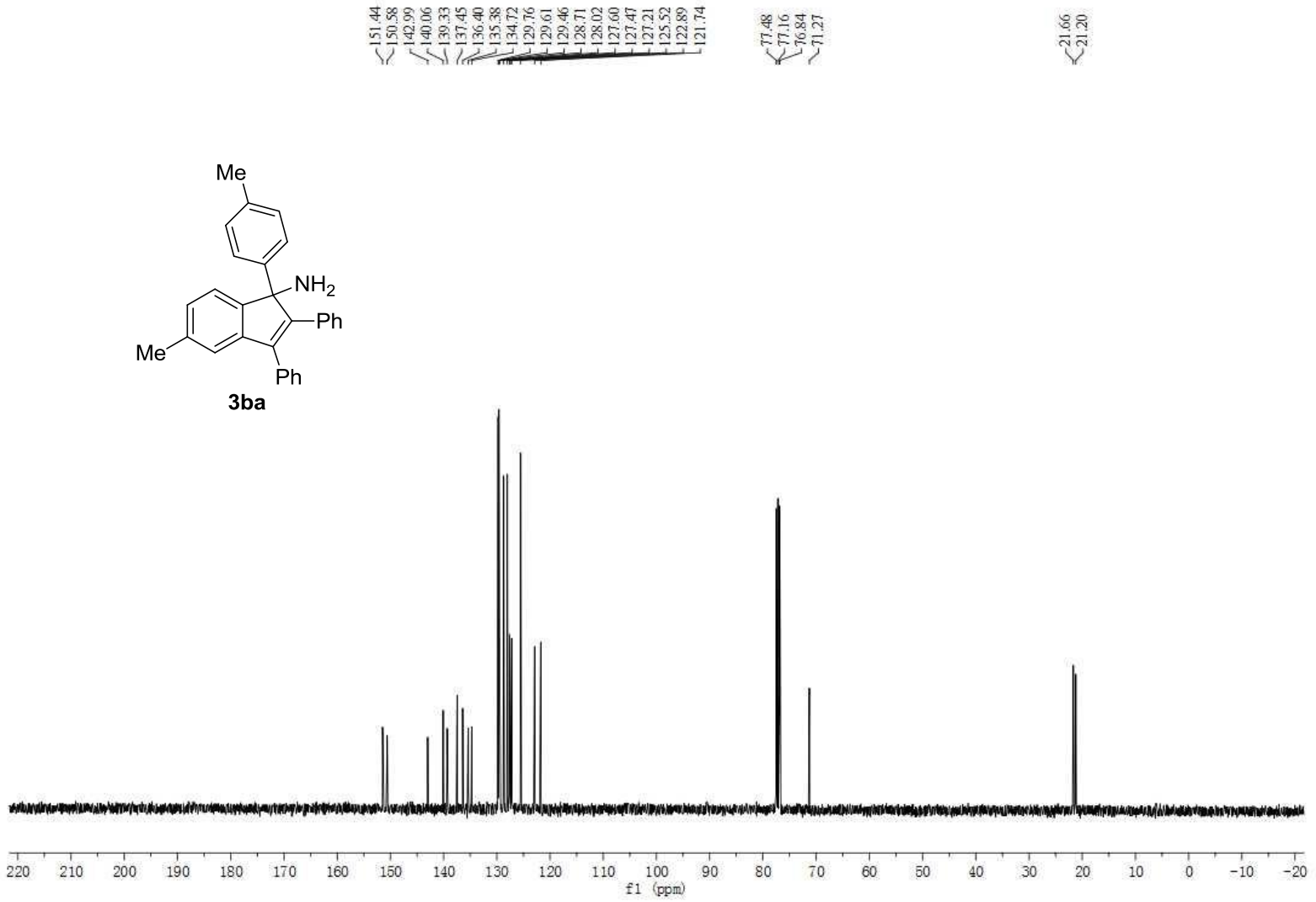


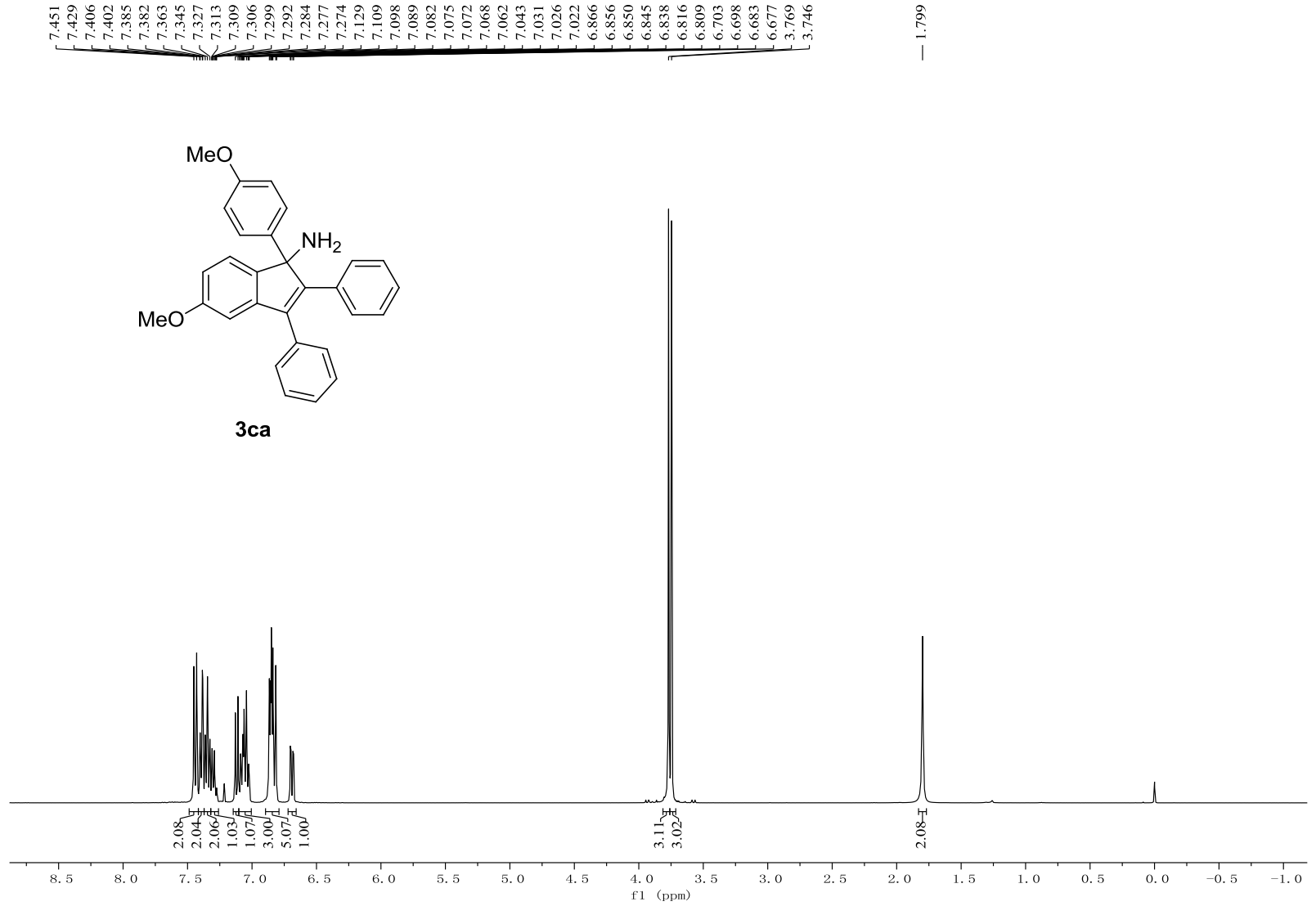
3aa

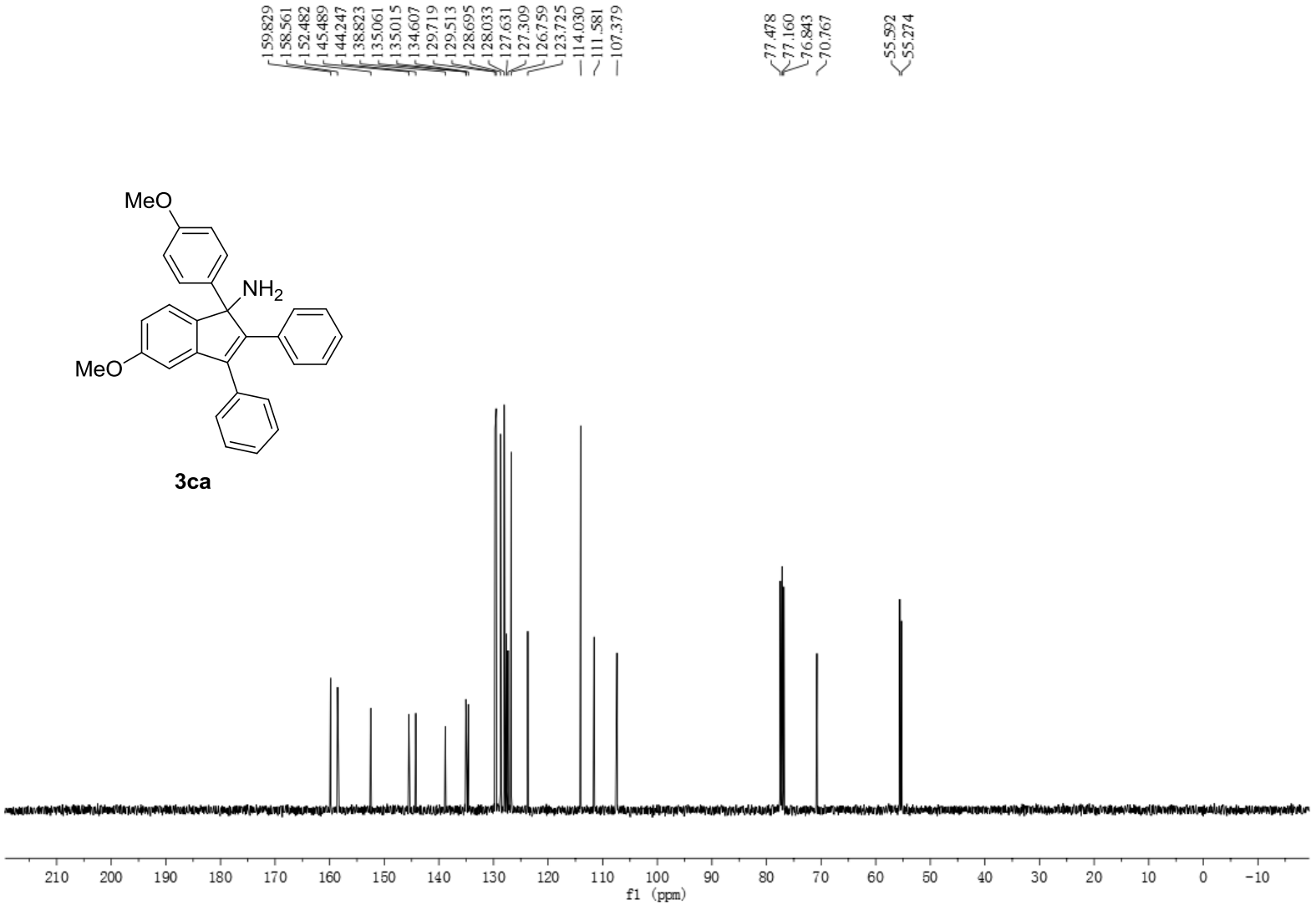



153.128
151.098
142.855
142.762
139.367
135.099
134.483
129.673
129.501
128.668
128.013
127.704
127.628
127.254
126.934
126.766
125.614
123.198
121.005
77.478
77.160
76.842
71.677
Ph
NH2
Ph
Ph
3aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

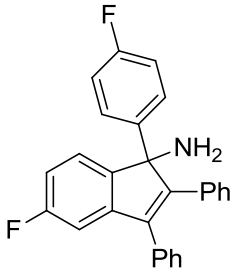

7.435
7.414
7.401
7.398
7.381
7.377
7.364
7.345
7.327
7.323
7.319
7.313
7.306
7.299
7.292
7.288
7.113
7.094
7.079
7.065
7.061
7.055
7.036
7.024
7.020
7.014
6.884
6.881
6.864
6.860
2.316
2.311
1.806
Me
NH2
Ph
Me
Ph
3ba
4.07
2.08
1.00
7.06
1.01
2.00
6.02
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


151.44
150.58
142.99
140.06
139.33
137.45
136.40
135.38
134.72
129.76
129.61
129.46
128.71
128.02
127.60
127.47
127.21
125.52
122.89
121.74
77.48
77.16
76.84
71.27
21.66
21.20
Me
NH2
Ph
Me
Ph
3ba
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

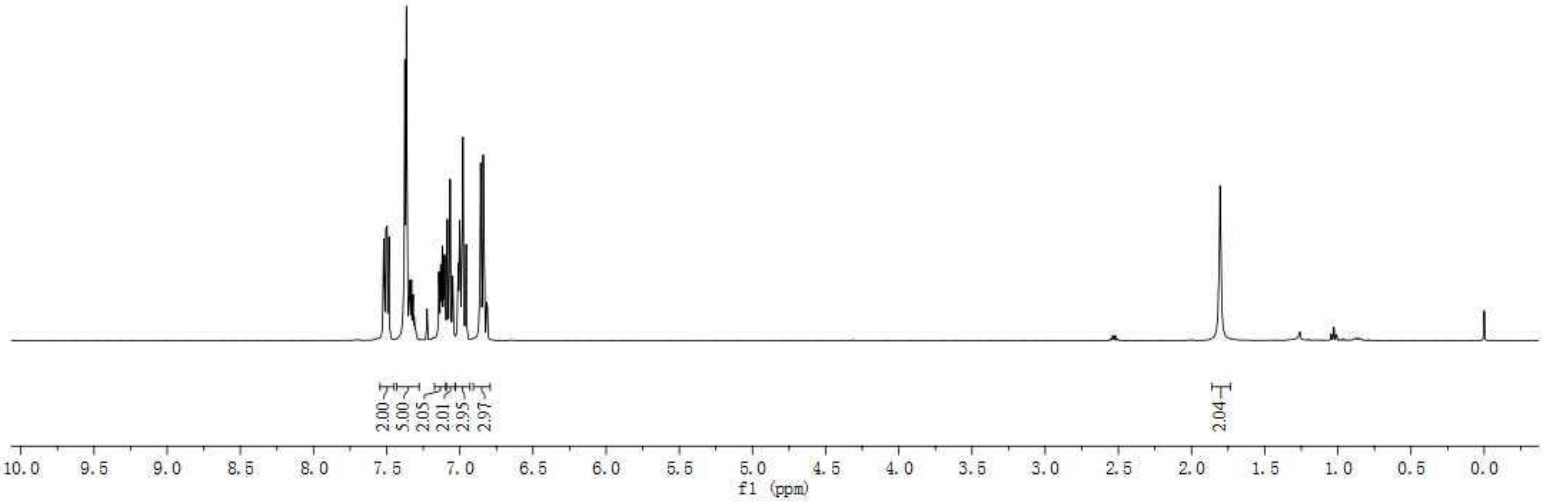

7.451
7.429
7.406
7.402
7.385
7.382
7.363
7.345
7.327
7.313
7.309
7.306
7.299
7.292
7.284
7.277
7.274
7.129
7.109
7.098
7.089
7.082
7.075
7.072
7.068
7.062
7.043
7.031
7.026
7.022
6.866
6.856
6.850
6.845
6.838
6.816
6.809
6.703
6.698
6.683
6.677
3.769
3.746
1.799
MeO
NH2
MeO
3ca
2.08
2.04
2.06
1.03
1.07
3.00
5.07
1.00
3.11
3.02
2.08
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)

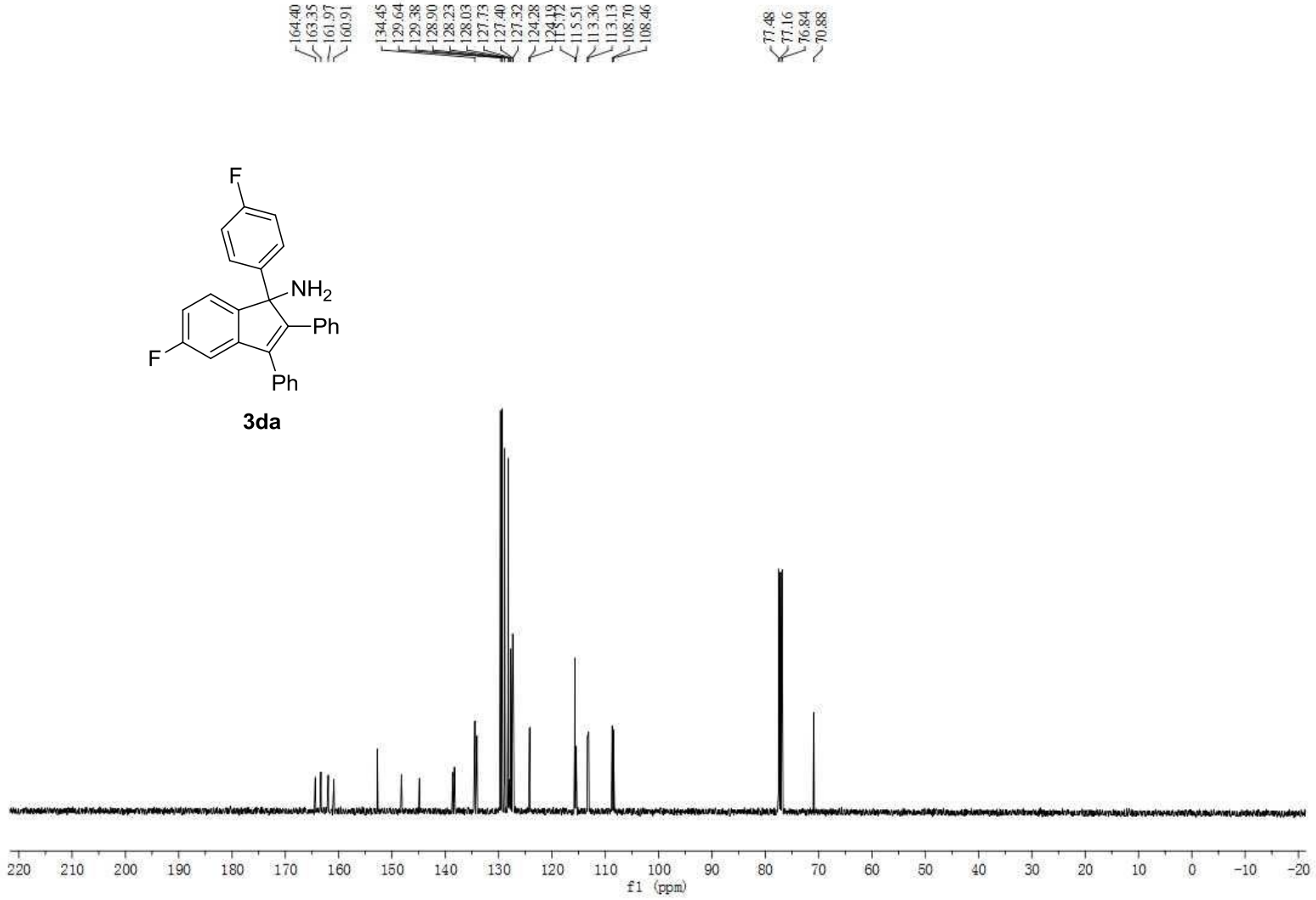

159.829
158.561
152.482
145.489
144.247
138.823
135.061
135.015
134.607
129.719
129.513
128.695
128.033
127.631
127.309
126.759
123.725
114.030
111.581
107.379
77.478
77.160
76.843
70.767
55.592
55.274
MeO
NH2
MeO
3ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

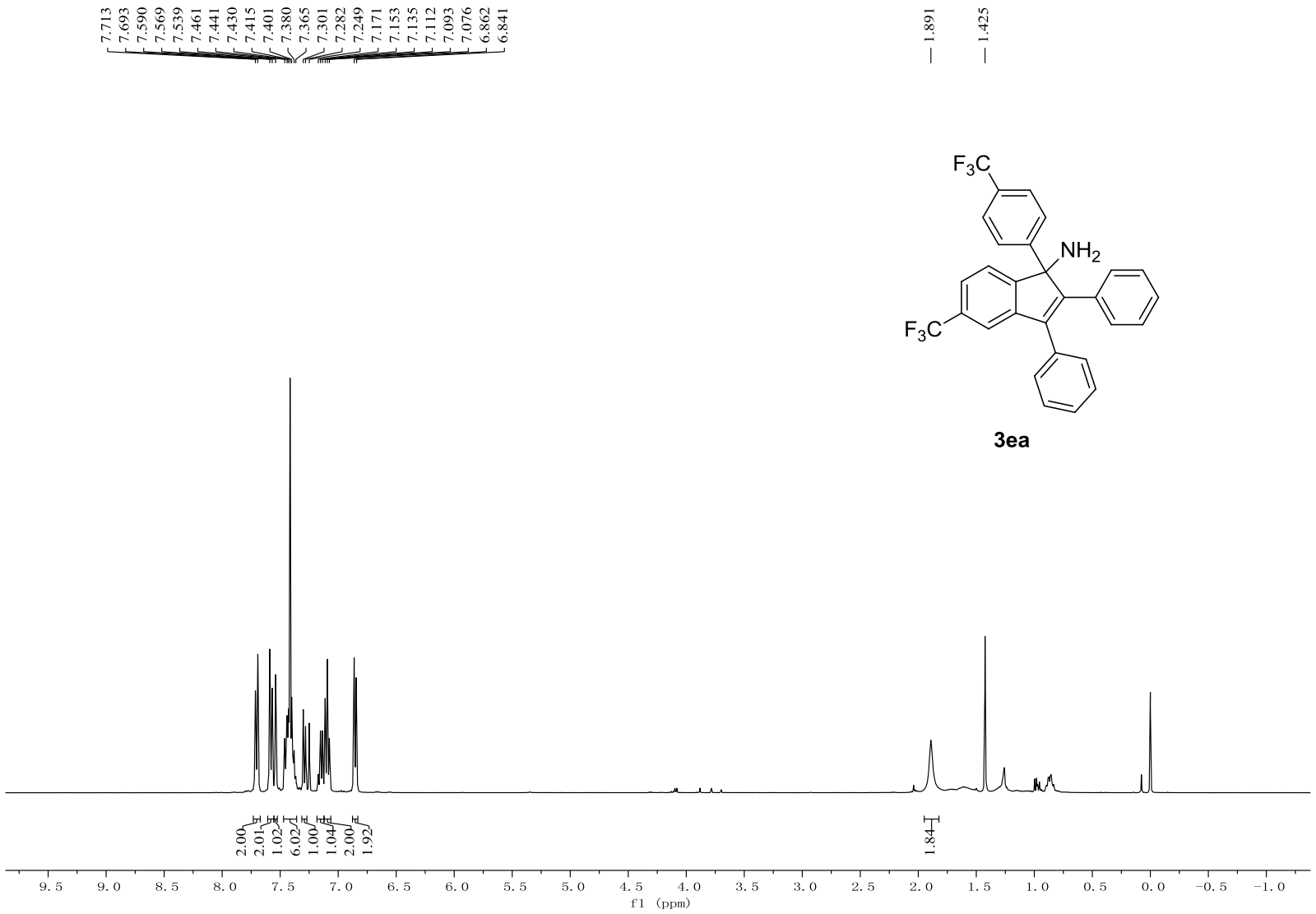

7.527
7.520
7.514
7.506
7.501
7.497
7.489
7.484
7.476
7.375
7.365
7.350
7.346
7.340
7.330
7.323
7.319
7.312
7.308
7.304
7.297
7.144
7.138
7.131
7.123
7.120
7.110
7.105
7.102
7.098
7.085
7.070
7.066
7.053
7.049
7.045
7.011
7.005
7.000
6.995
6.988
6.979
6.962
6.957
6.860
6.858
6.855
6.840
6.837
6.817
6.811
1.805

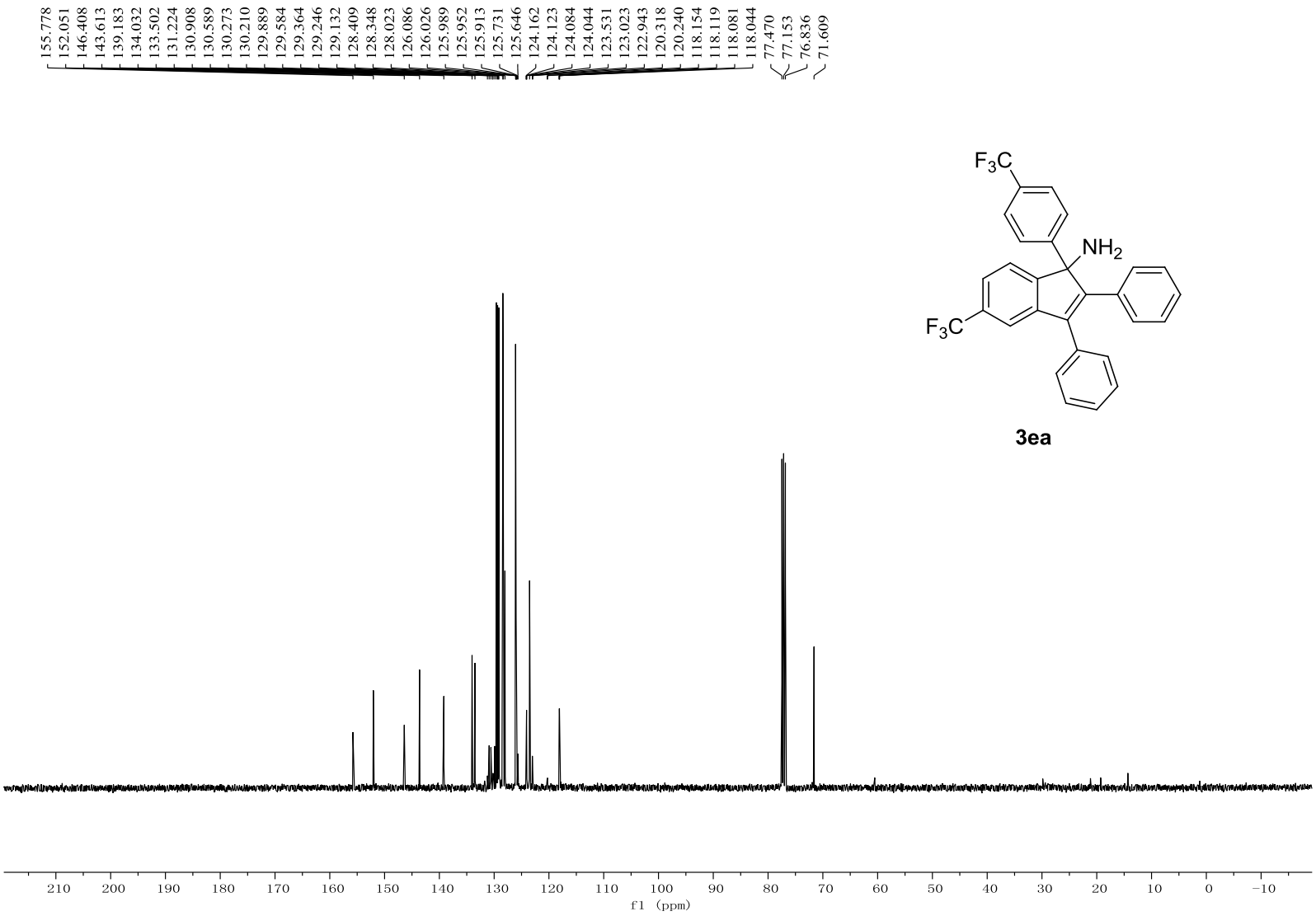

F
NH2
Ph
F
Ph

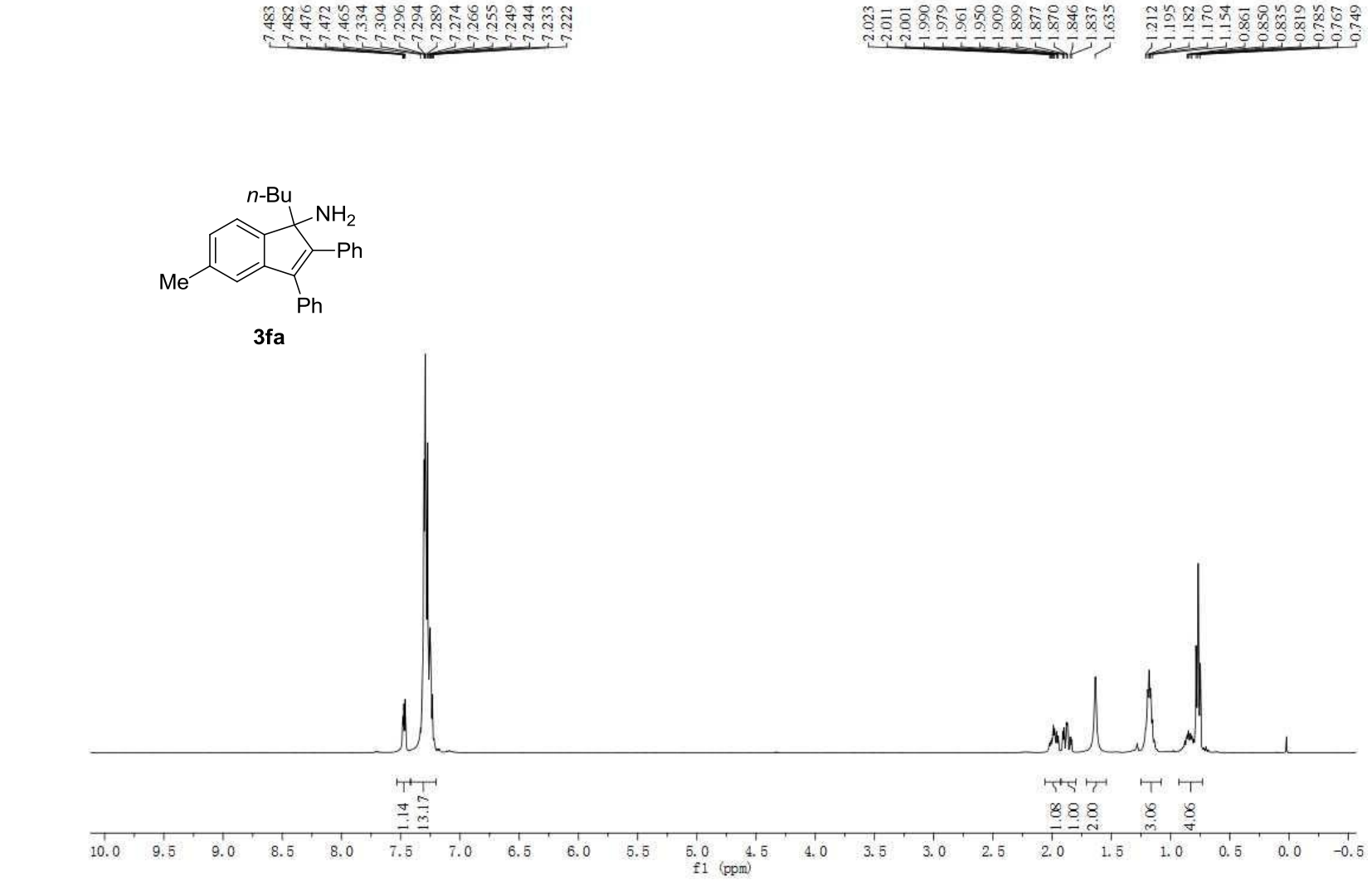
3da

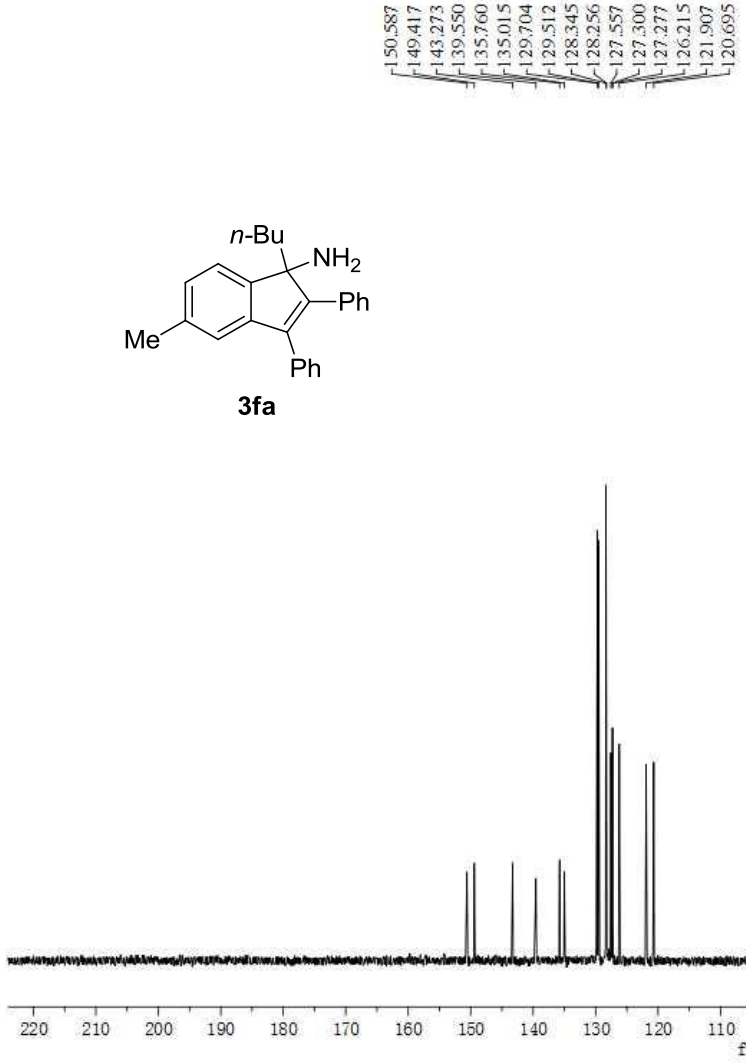

2.00
5.00
2.05
2.01
2.95
2.97
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.40
163.35
161.97
160.91
134.45
129.64
129.38
128.90
128.23
128.03
127.73
127.40
127.32
124.28
124.13
123.72
115.51
113.36
113.13
108.70
108.46
77.48
77.16
76.84
70.88
F
NH2
Ph
F
Ph
3da
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

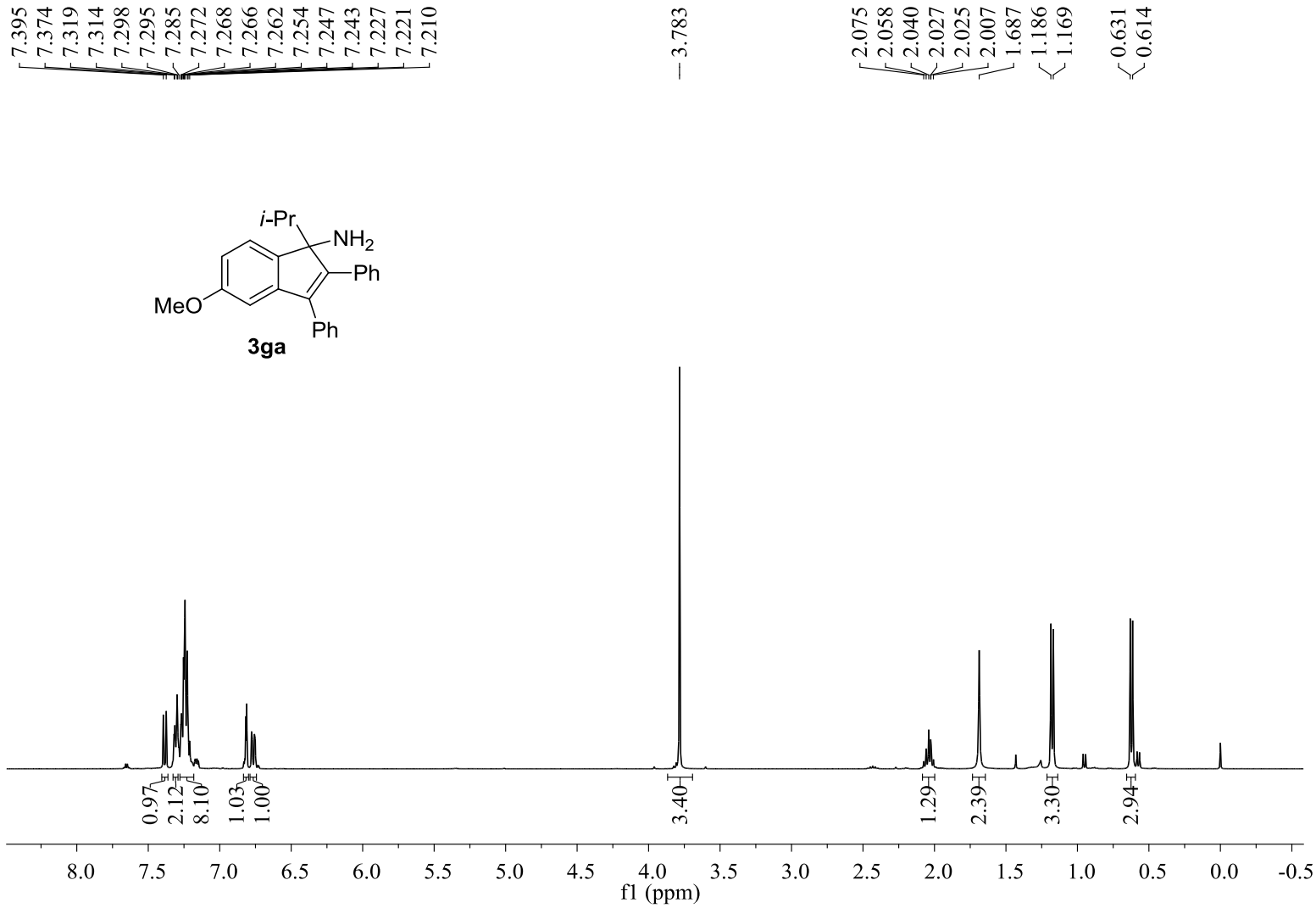

7.713
7.693
7.590
7.569
7.539
7.461
7.441
7.430
7.415
7.401
7.380
7.365
7.301
7.282
7.249
7.171
7.153
7.135
7.112
7.093
7.076
6.862
6.841
1.891
1.425
F3C
NH2
F3C
3ea
2.00
2.01
1.02
6.02
1.00
1.04
2.00
1.92
1.84
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

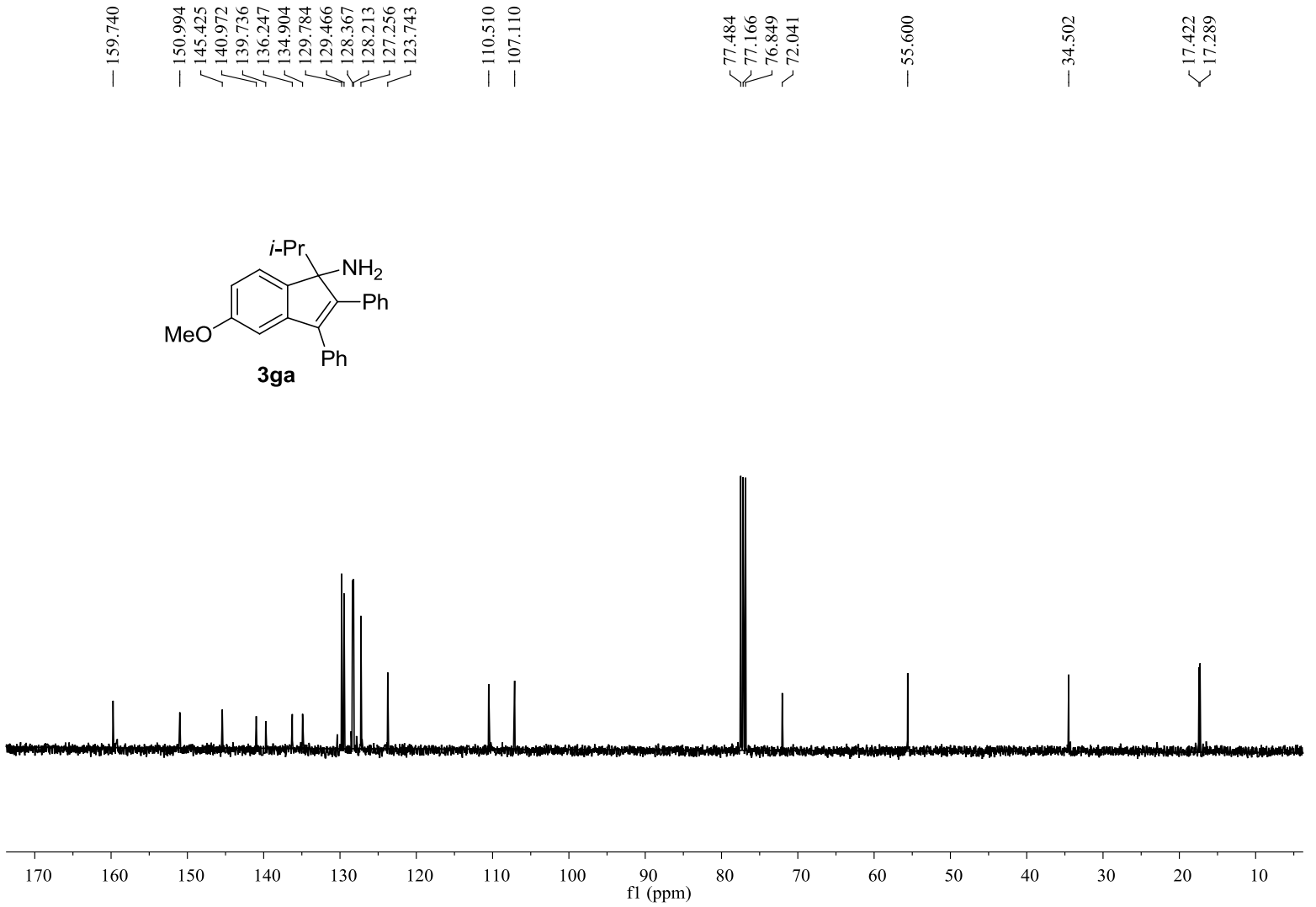

155.778
152.051
146.408
143.613
139.183
134.032
133.502
131.224
130.908
130.589
130.273
130.210
129.889
129.584
129.364
129.246
129.132
128.409
128.348
128.023
126.086
126.026
125.989
125.952
125.913
125.731
125.646
124.162
124.123
124.084
124.044
123.531
123.023
122.943
120.318
120.240
118.154
118.119
118.081
118.044
77.470
77.153
76.836
71.609
F3C
NH2
F3C
3ea
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

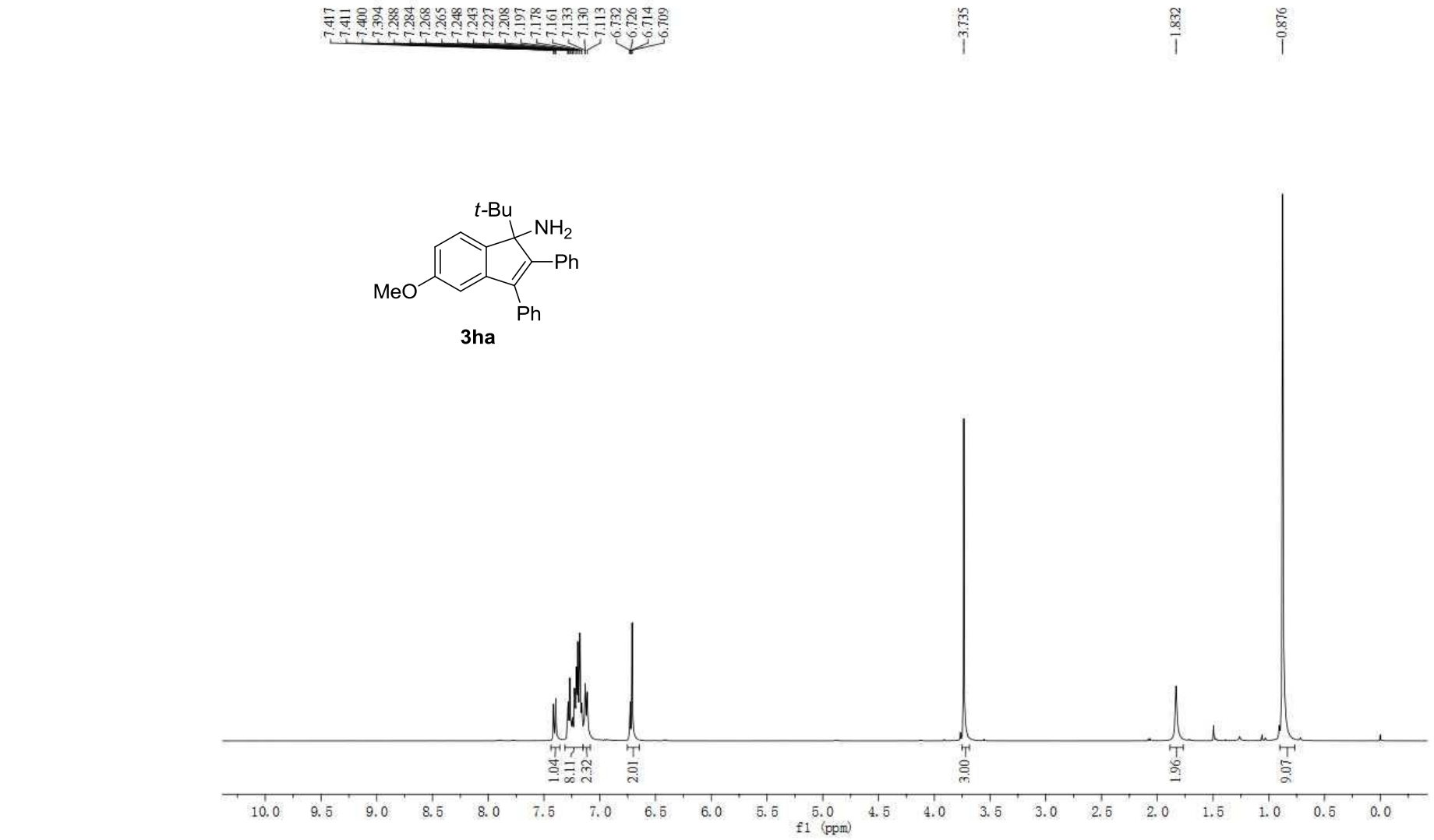

7.483
7.482
7.476
7.472
7.465
7.334
7.304
7.296
7.294
7.289
7.274
7.266
7.255
7.249
7.244
7.233
7.222
2.023
2.011
2.001
1.990
1.979
1.961
1.950
1.909
1.899
1.887
1.870
1.846
1.837
1.635
1.212
1.195
1.182
1.170
1.154
0.861
0.850
0.835
0.819
0.785
0.767
0.749
n-Bu
NH2
Ph
Me
Ph
3fa
1.14
13.17
1.08
1.00
2.00
3.06
4.06
10.0
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
f1 (ppm)

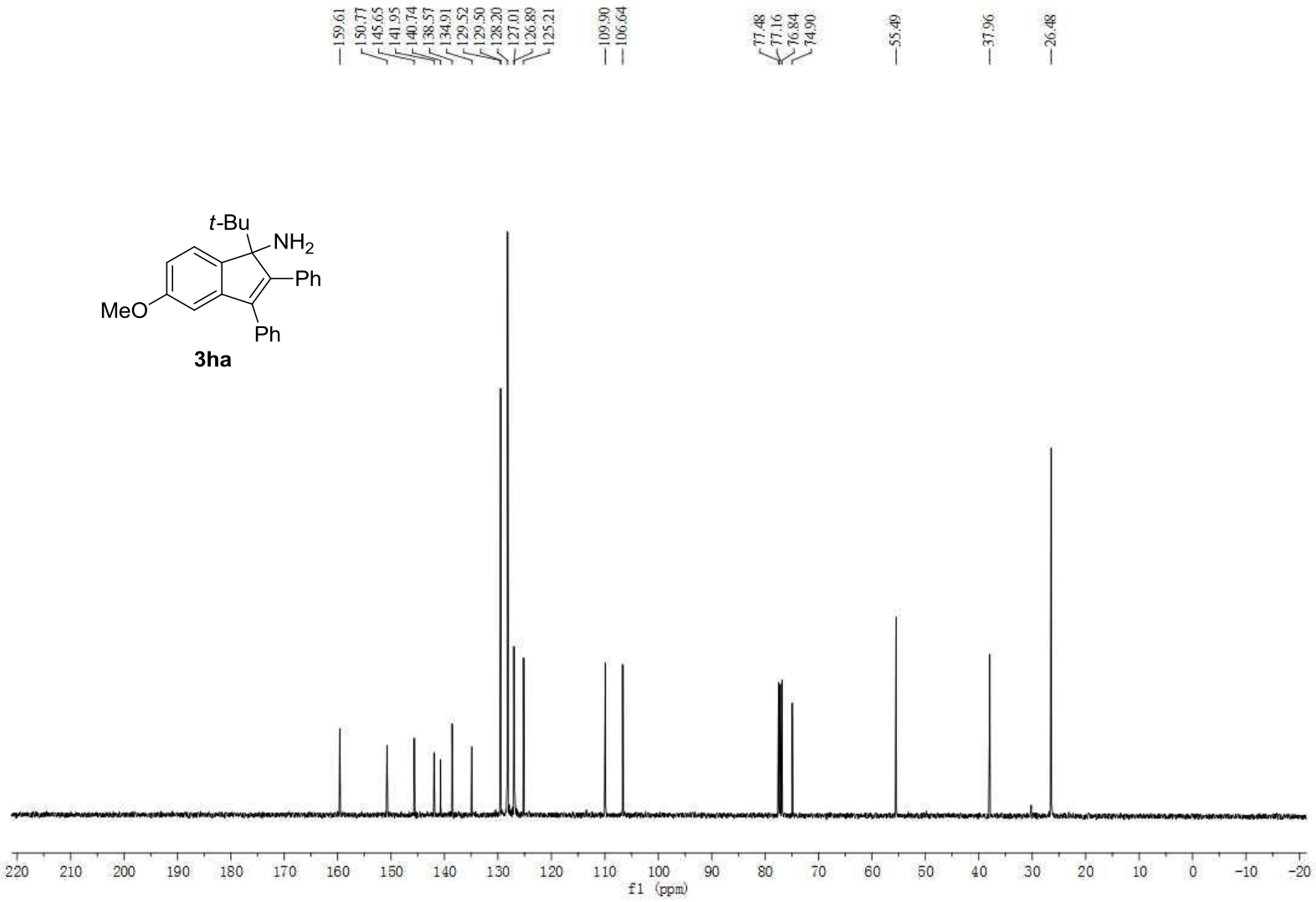

150.587
149.417
143.273
139.550
135.760
135.015
129.704
129.512
128.345
128.256
127.557
127.300
127.277
126.215
121.907
120.695
77.477
77.160
76.842
69.639
38.355
25.973
22.910
13.987
n-Bu
NH2
Ph
Me
Ph
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

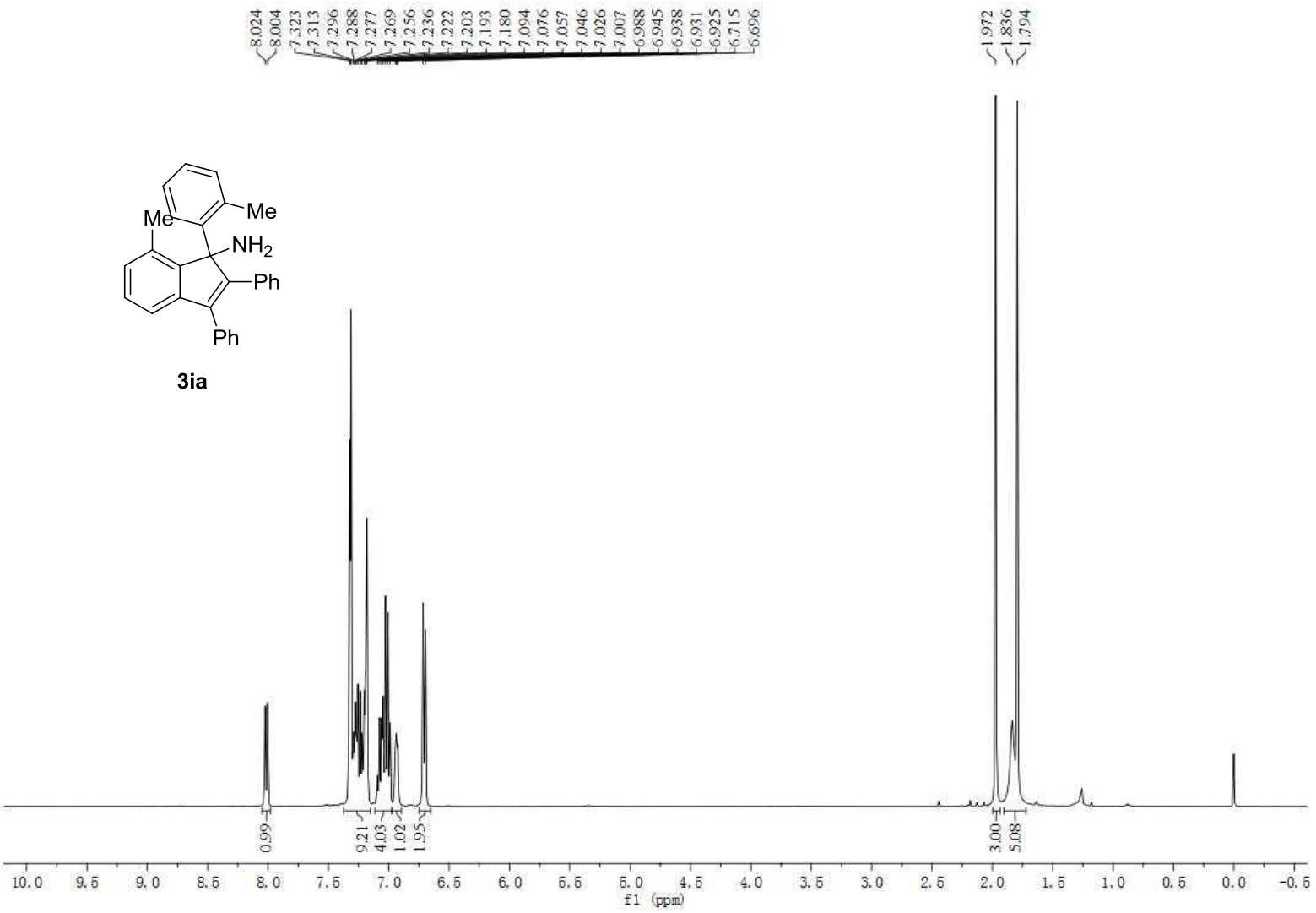
3fa

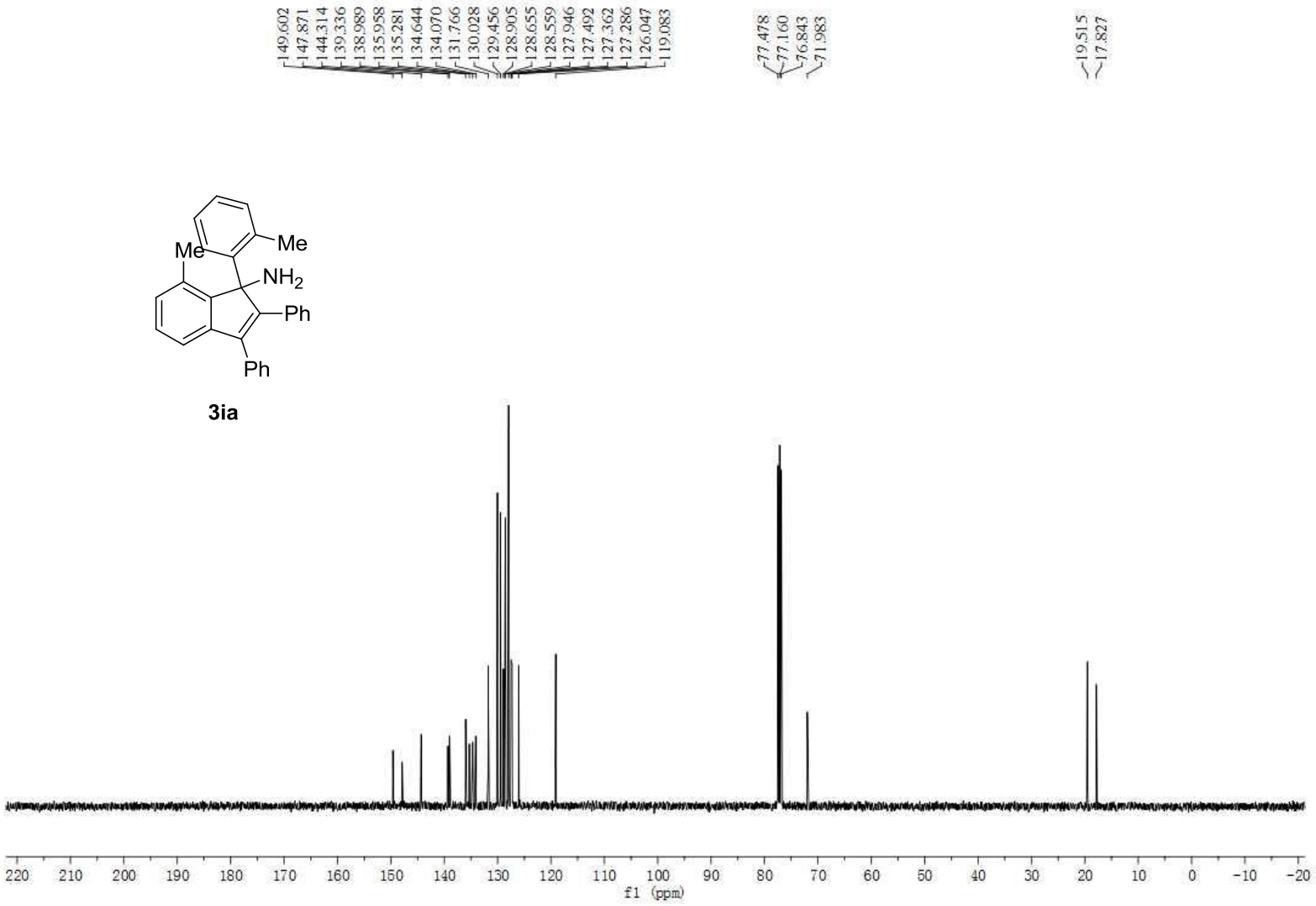

7.395
7.374
7.319
7.314
7.298
7.295
7.285
7.272
7.268
7.266
7.262
7.254
7.247
7.243
7.227
7.221
7.210
3.783
2.075
2.058
2.040
2.027
2.025
2.007
1.687
1.186
1.169
0.631
0.614
i-Pr
NH2
Ph
MeO
Ph
3ga
0.97
2.12
8.10
1.03
1.00
3.40
1.29
2.39
3.30
2.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

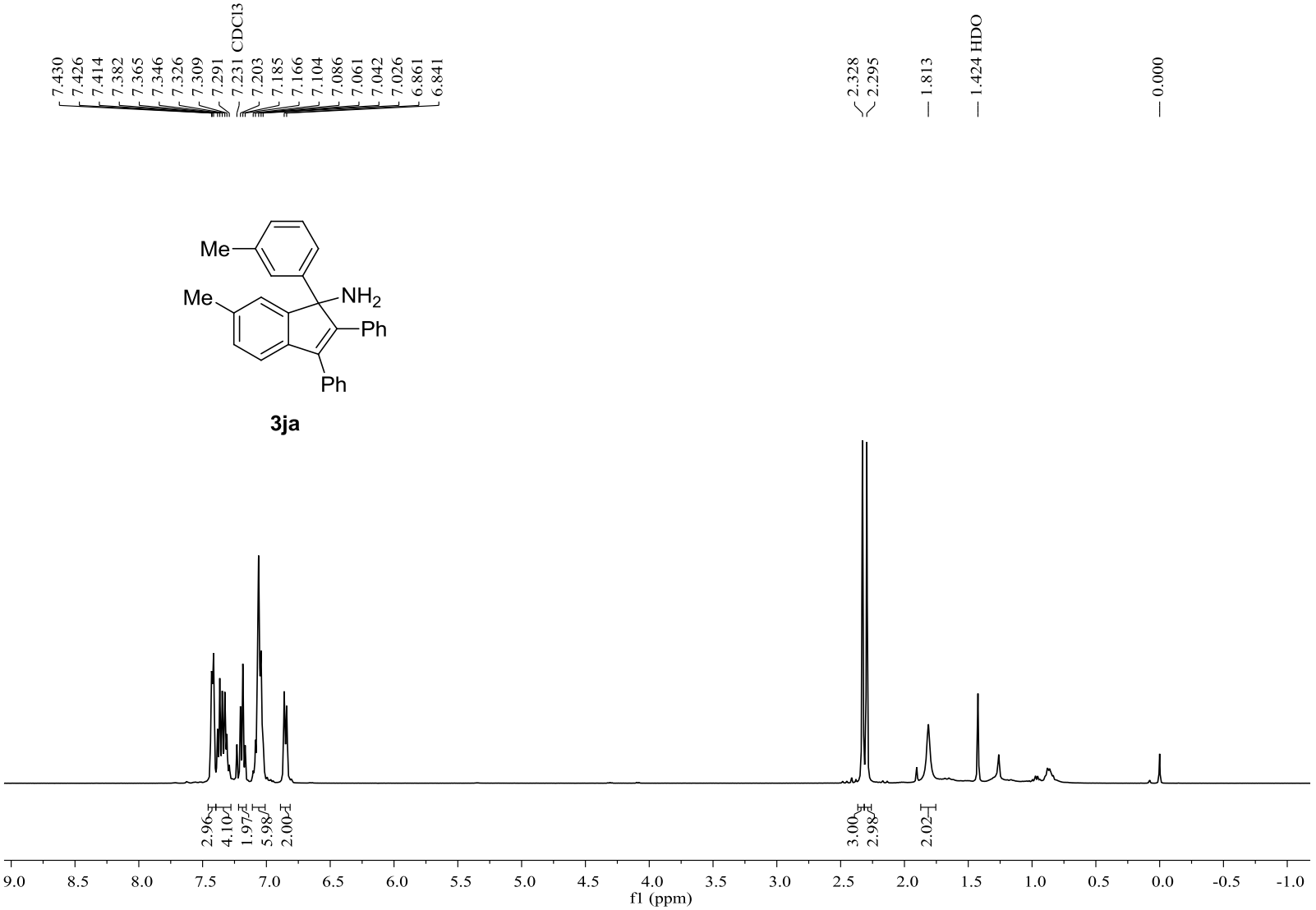

159.740
150.994
145.425
140.972
139.736
136.247
134.904
129.784
129.466
128.367
128.213
127.256
123.743
110.510
107.110
77.484
77.166
76.849
72.041
55.600
34.502
17.422
17.289
i-Pr
NH2
Ph
MeO
Ph
3ga
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

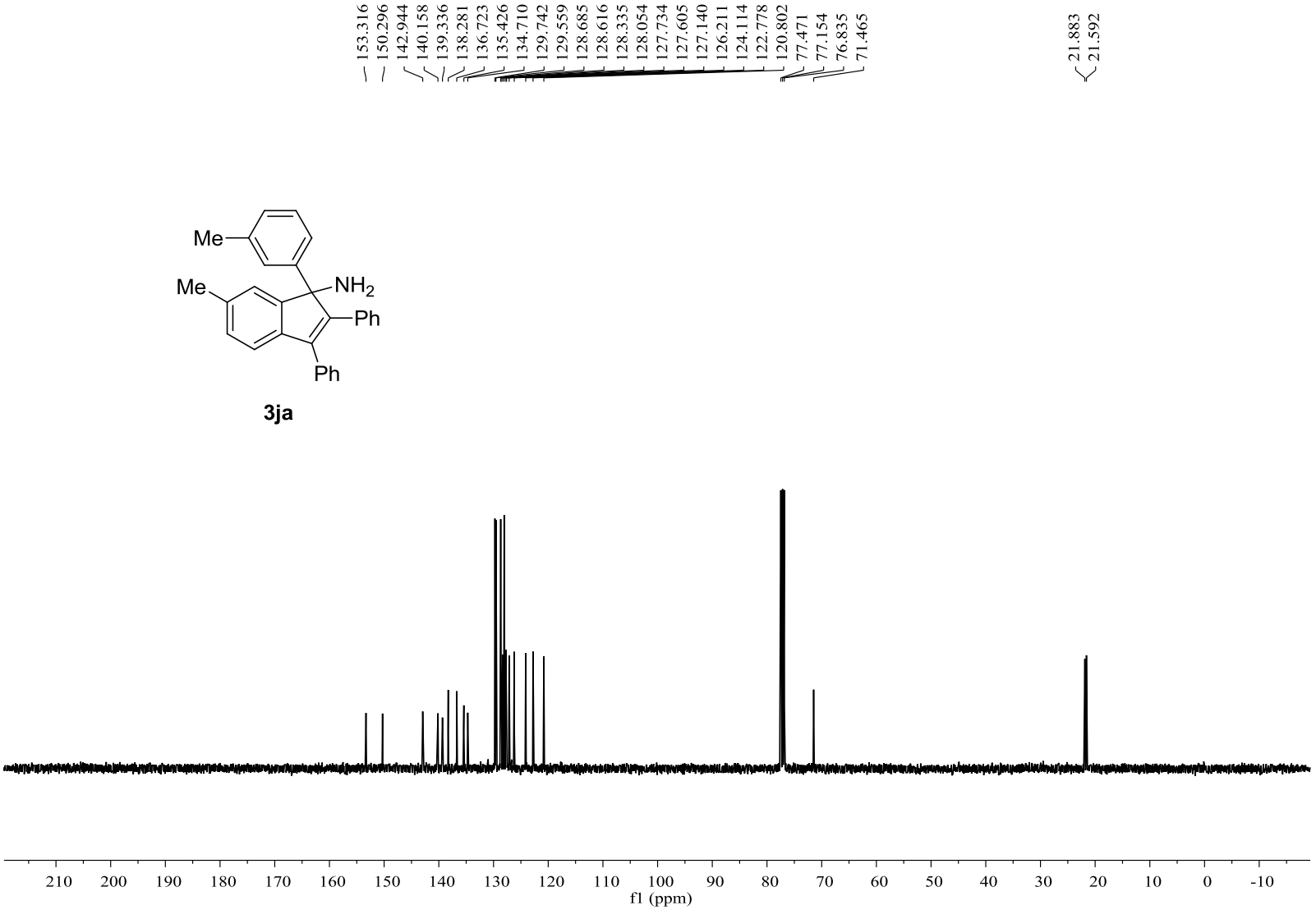

7.417
7.411
7.400
7.394
7.288
7.284
7.268
7.265
7.248
7.243
7.227
7.208
7.197
7.178
7.161
7.133
7.130
7.113
6.732
6.726
6.714
6.709
3.735
1.832
0.876
t-Bu
NH2
Ph
MeO
Ph
3ha
1.04
8.11
2.32
2.01
3.00
1.96
9.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

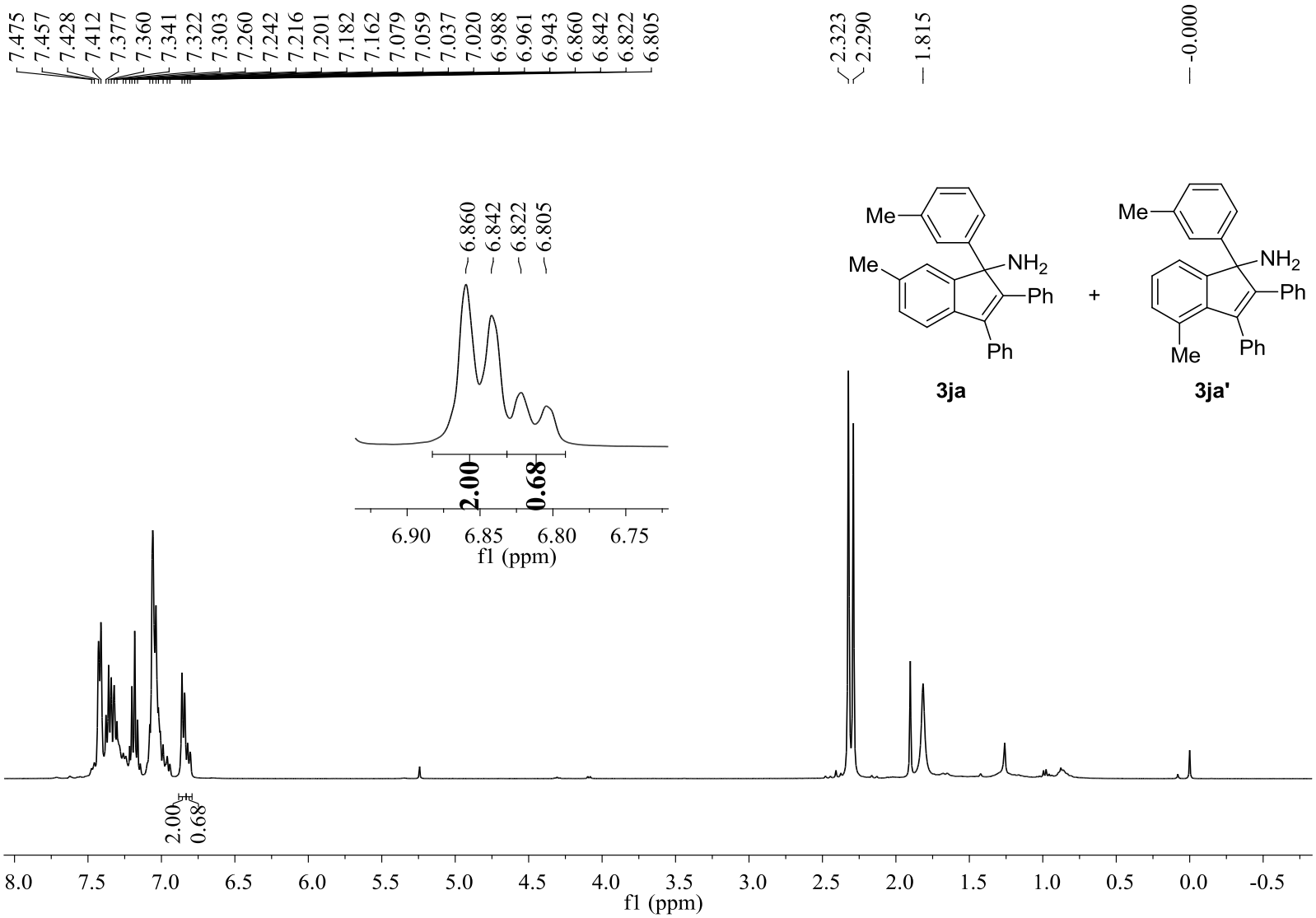

159.61
150.77
145.65
141.95
140.74
138.57
134.91
129.52
129.50
128.20
127.01
126.89
125.21
109.90
106.64
77.48
77.16
76.84
74.90
55.49
37.96
26.48
t-Bu
NH2
Ph
MeO
Ph
3ha
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

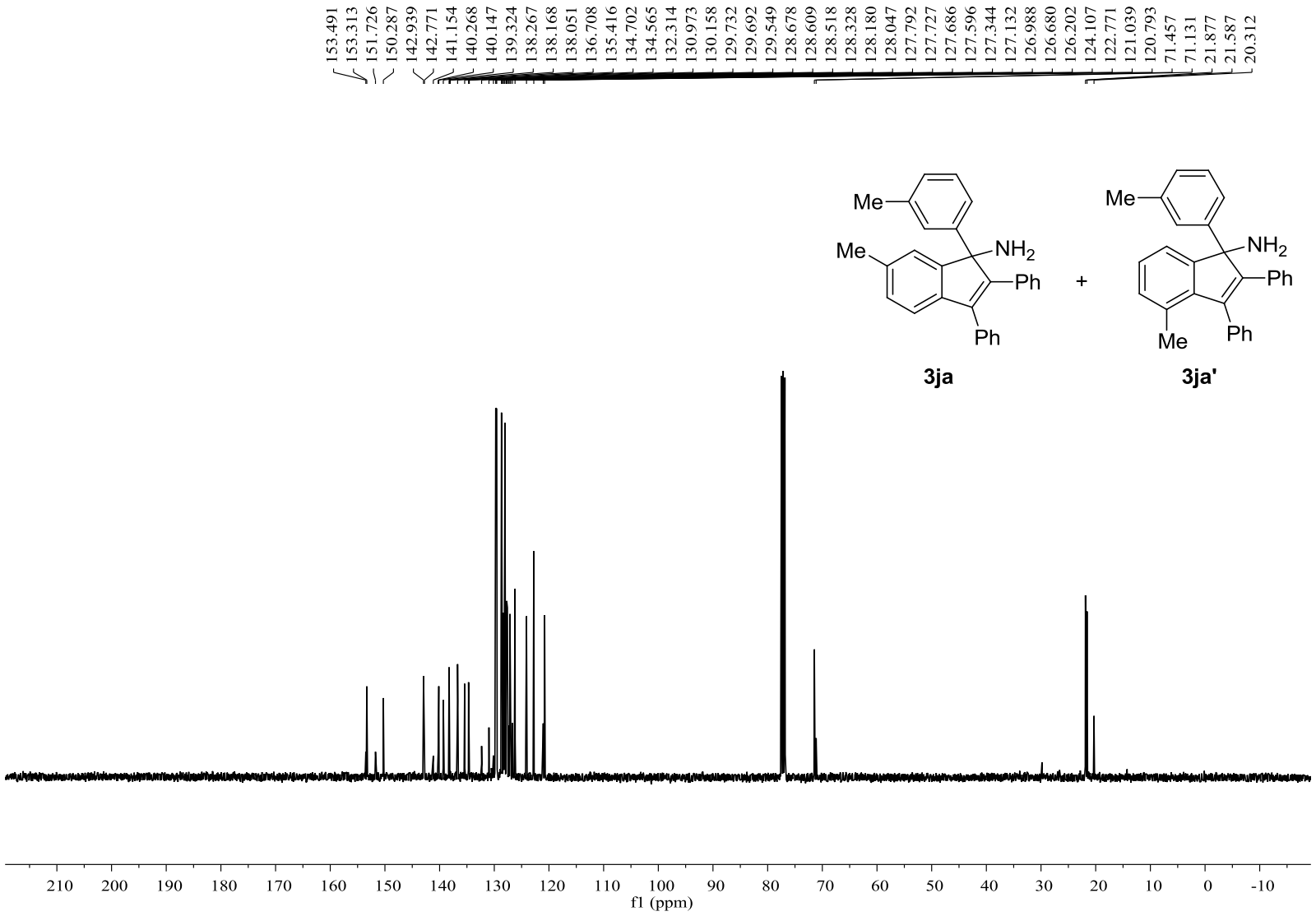

8.024
8.004
7.323
7.313
7.296
7.288
7.277
7.269
7.256
7.236
7.222
7.203
7.193
7.180
7.094
7.076
7.057
7.046
7.026
7.007
6.988
6.945
6.938
6.931
6.925
6.715
6.696
1.972
1.836
1.794
Me
Me
NH2
Ph
Ph
3ia
0.99
9.21
4.03
1.02
1.95
3.00
5.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

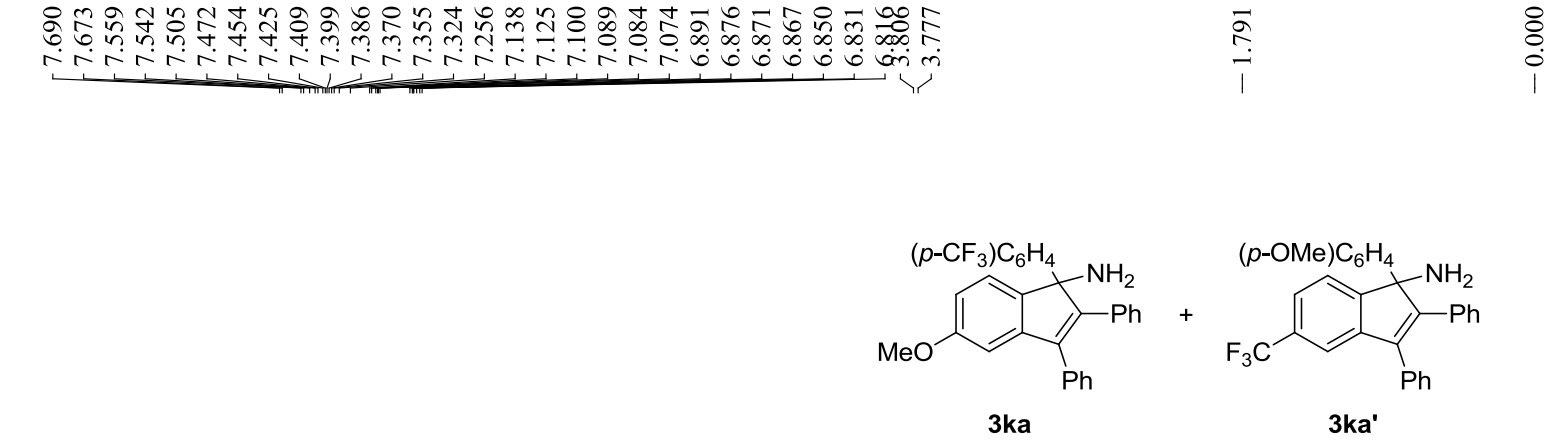

149.602
147.871
144.314
139.336
138.989
135.958
135.281
134.644
134.070
131.766
130.028
129.456
128.905
128.655
128.559
127.946
127.492
127.362
127.286
126.047
119.083
77.478
77.160
76.843
71.983
19.515
17.827
Me
Me
NH2
Ph
Ph
3ia
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

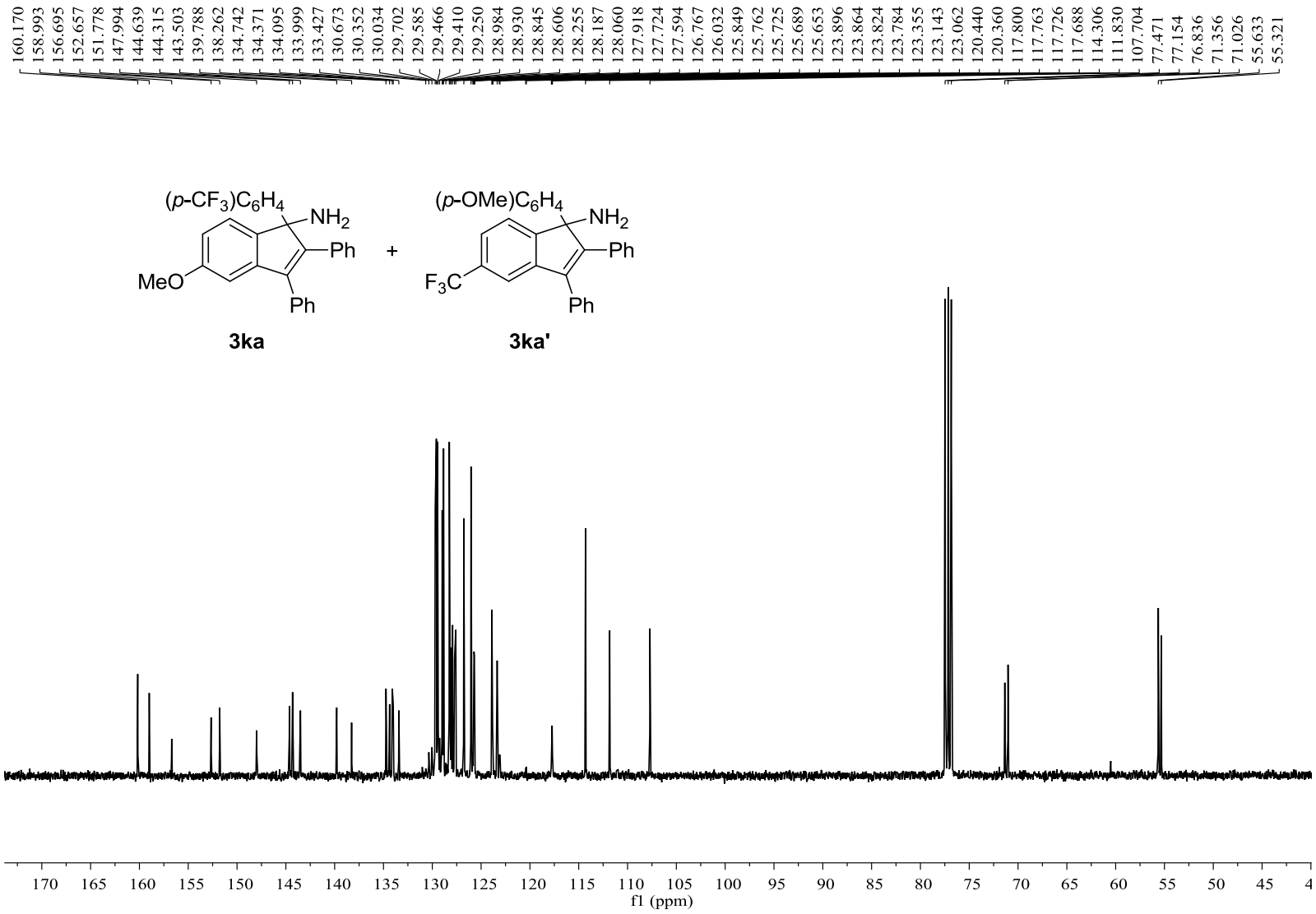

7.430
7.426
7.414
7.382
7.365
7.346
7.326
7.309
7.291
7.231 CDCl3
7.203
7.185
7.166
7.104
7.086
7.061
7.042
7.026
6.861
6.841
2.328
2.295
1.813
1.424 HDO
0.000
Me
Me
NH2
Ph
Ph
3ja
2.96
4.10
1.97
5.98
2.00
3.00
2.98
2.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

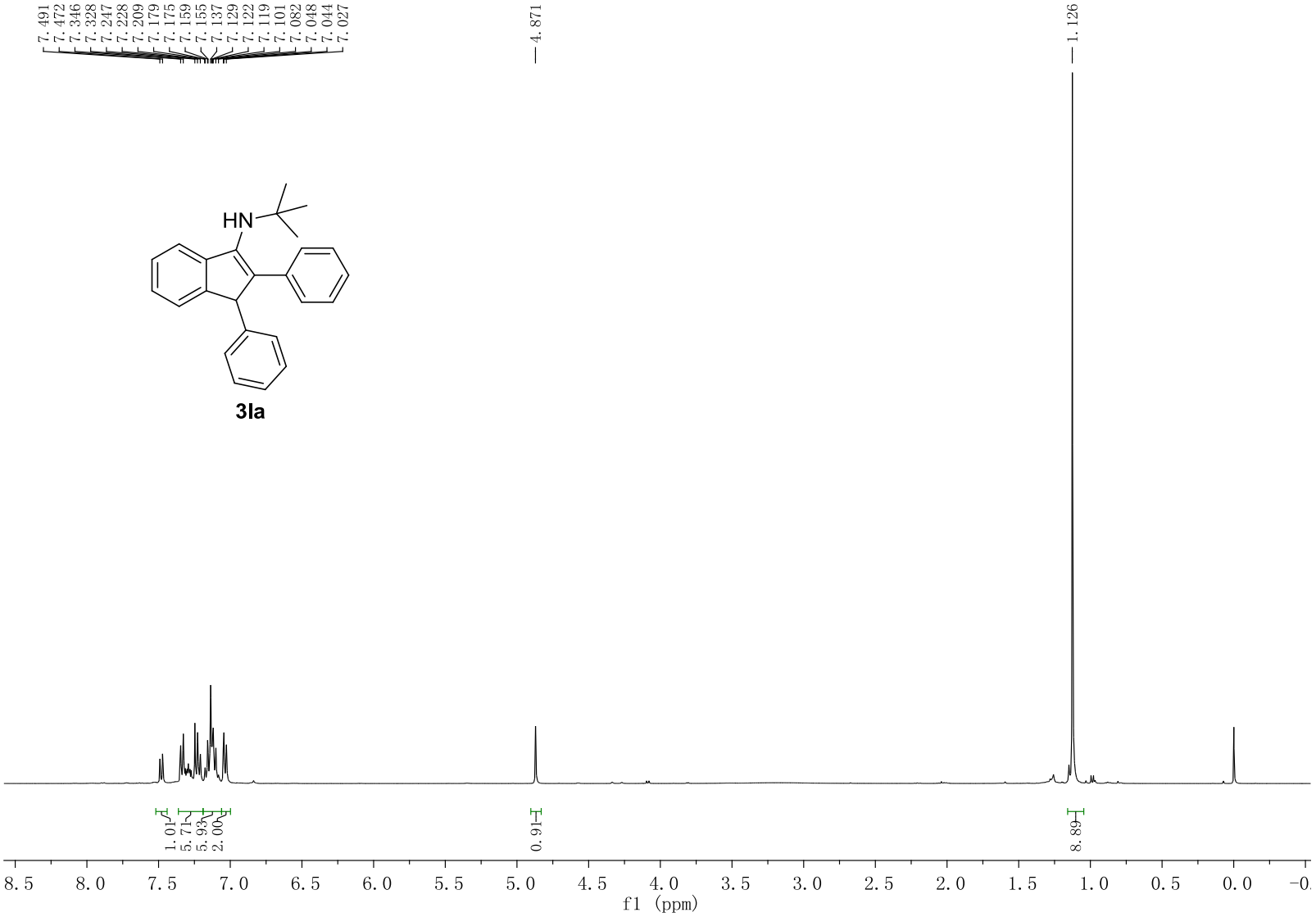

153.316
150.296
142.944
140.158
139.336
138.281
136.723
135.426
134.710
129.742
129.559
128.685
128.616
128.335
128.054
127.734
127.605
127.140
126.211
124.114
122.778
120.802
77.471
77.154
76.835
71.465
21.883
21.592
Me
Me
NH2
Ph
Ph
3ja
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

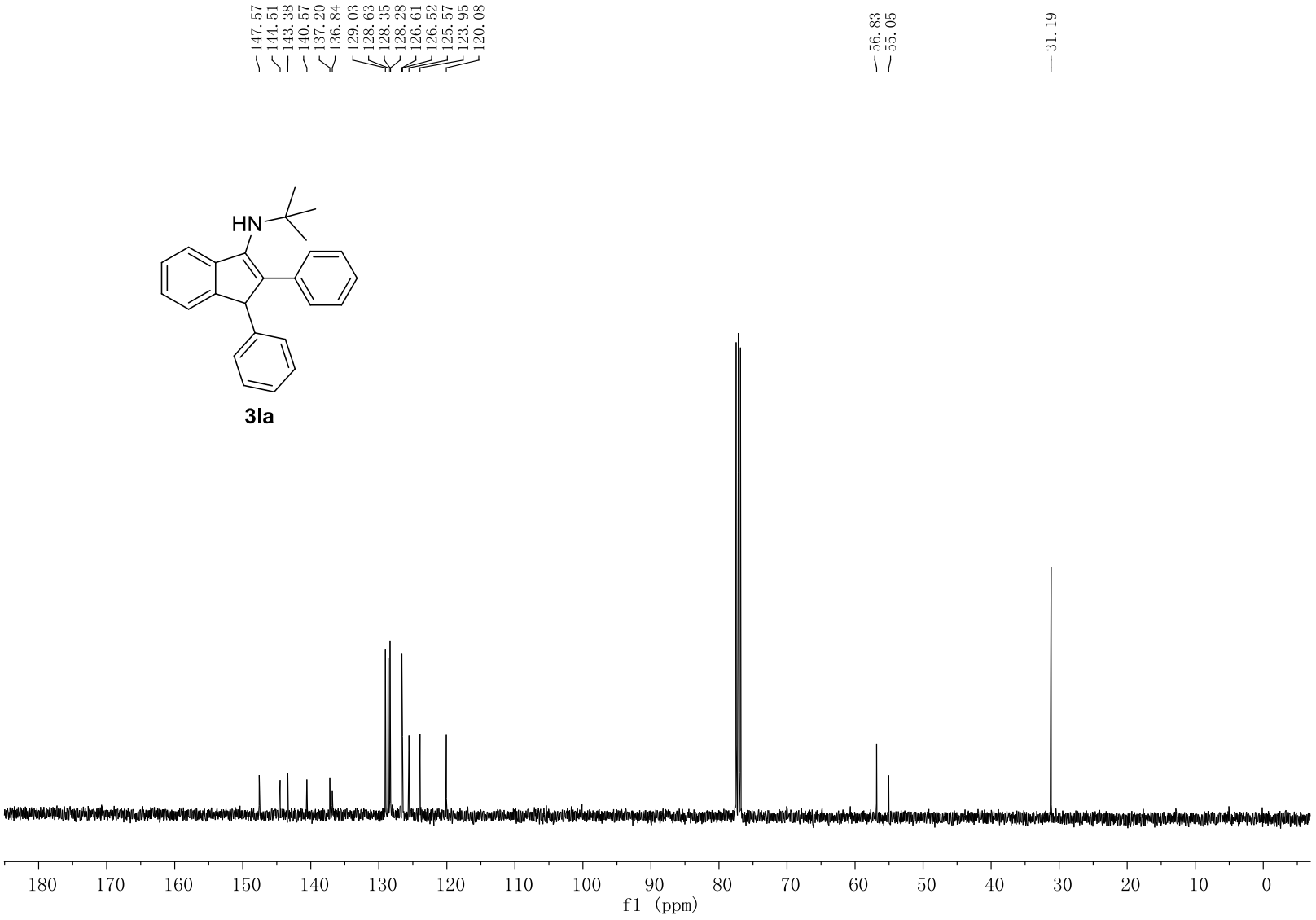

7.475
7.457
7.428
7.412
7.377
7.360
7.341
7.322
7.303
7.260
7.242
7.216
7.201
7.182
7.162
7.079
7.059
7.037
7.020
6.988
6.961
6.943
6.860
6.842
6.822
6.805
2.323
2.290
1.815
-0.000
6.860
6.842
6.822
6.805
2.00
0.68
6.90
6.85
6.80
6.75
f1 (ppm)
Me
NH2
Ph
Ph
3ja
+
Me
NH2
Ph
Me
Ph
3ja'
2.00
0.68
8.0
7.5
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
f1 (ppm)

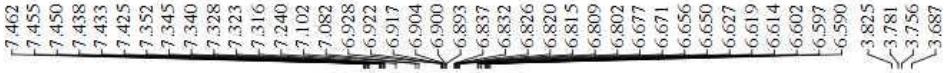

153.491
153.313
151.726
150.287
142.939
142.771
141.154
140.268
140.147
139.324
138.267
138.168
138.051
136.708
135.416
134.702
134.565
132.314
130.973
130.158
129.732
129.692
129.549
128.678
128.609
128.518
128.328
128.180
128.047
127.792
127.727
127.686
127.596
127.344
127.132
126.988
126.680
126.202
124.107
122.771
121.039
120.793
71.457
71.131
21.877
21.587
20.312
Me
Me
NH2
Ph
Ph
3ja
+
Me
NH2
Ph
Me
Ph
3ja'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

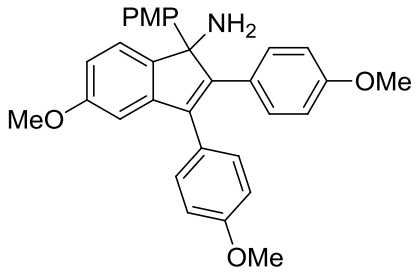

7.690
7.673
7.559
7.542
7.505
7.472
7.454
7.425
7.409
7.399
7.386
7.370
7.355
7.324
7.256
7.138
7.125
7.100
7.089
7.084
7.074
6.891
6.876
6.871
6.867
6.850
6.831
6.816
3.806
3.777
1.791
0.000
(p-CF3)C6H4
NH2
Ph
MeO
Ph
+
(p-OMe)C6H4
NH2
Ph
F3C
Ph
3ka
3ka'
1.07
1.13
0.48
0.91
5.90
3.51
2.30
1.09
0.57
1.33
1.67
2.13
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
f1 (ppm)


160.170
158.993
156.695
152.657
151.778
147.994
144.639
144.315
143.503
139.788
138.262
134.742
134.371
134.095
133.999
133.427
130.673
130.352
130.034
129.702
129.585
129.466
129.410
129.250
128.984
128.930
128.845
128.606
128.255
128.187
128.060
127.918
127.724
127.594
126.767
126.032
125.849
125.762
125.725
125.689
125.653
123.896
123.864
123.824
123.784
123.355
123.143
123.062
120.440
120.360
117.800
117.763
117.726
117.688
114.306
111.830
107.704
77.471
77.154
76.836
71.356
71.026
55.633
55.321
(p-CF3)C6H4
NH2
Ph
MeO
Ph
3ka
+
(p-OMe)C6H4
NH2
Ph
F3C
Ph
3ka'
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
4
f1 (ppm)

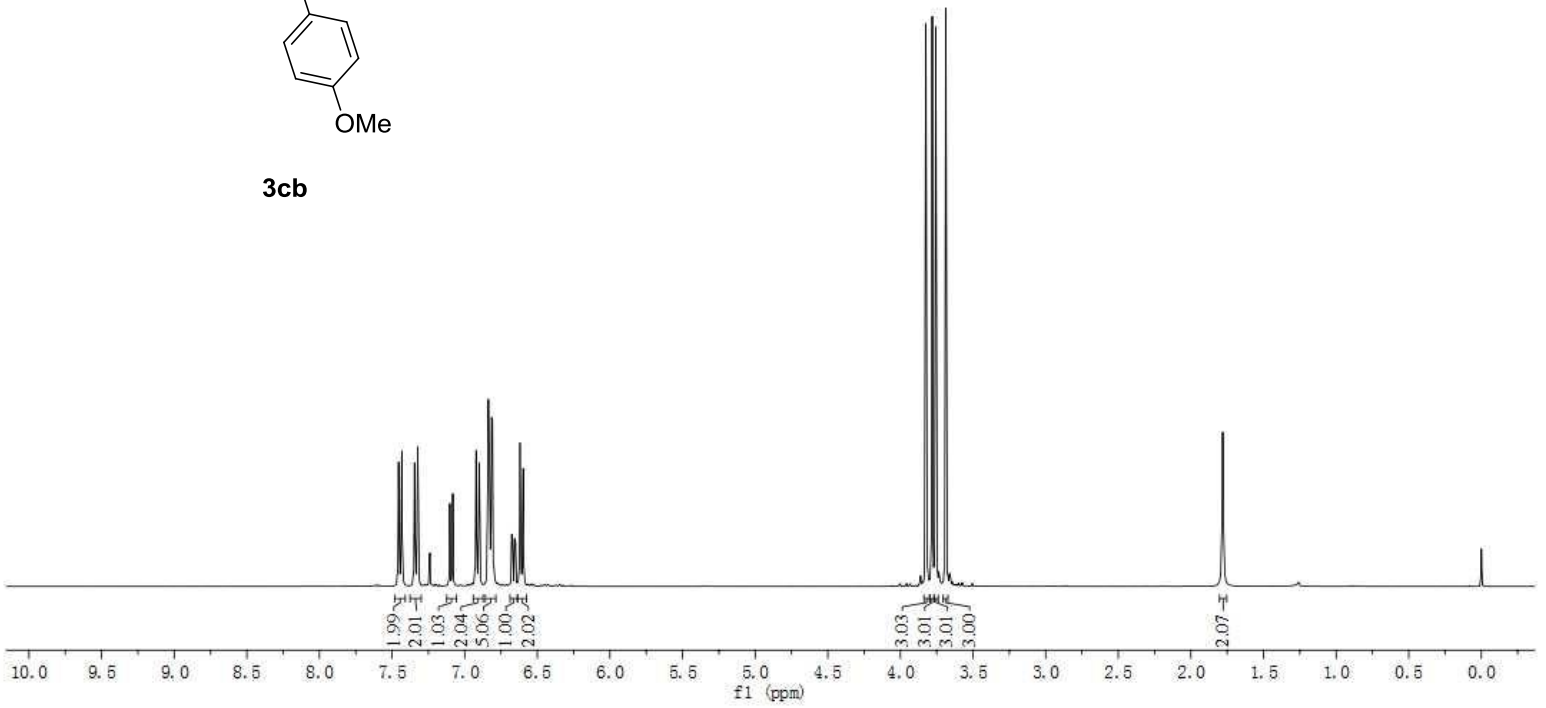

7.491
7.472
7.346
7.328
7.247
7.228
7.209
7.179
7.175
7.159
7.155
7.137
7.129
7.122
7.119
7.101
7.082
7.048
7.044
7.027
4.871
1.126
HN
3Ia
1.01
5.71
5.93
2.00
0.91
8.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

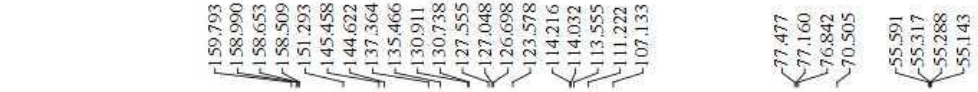

147.57
144.51
143.38
140.57
137.20
136.84
129.03
128.63
128.35
128.28
126.61
126.52
125.57
123.95
120.08
56.83
55.05
31.19
HN
3la
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

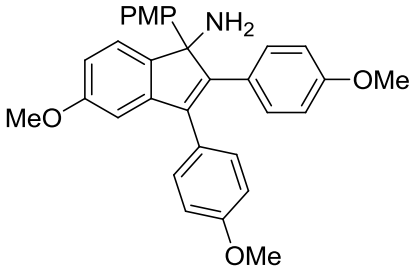

7.462
7.455
7.450
7.438
7.433
7.425
7.352
7.345
7.340
7.328
7.323
7.316
7.240
7.102
7.082
6.928
6.922
6.917
6.904
6.900
6.893
6.837
6.832
6.826
6.820
6.815
6.809
6.802
6.677
6.671
6.656
6.650
6.627
6.619
6.614
6.602
6.597
6.590
3.825
3.781
3.756
3.687
1.781


PMP
NH2
OMe
MeO
OMe

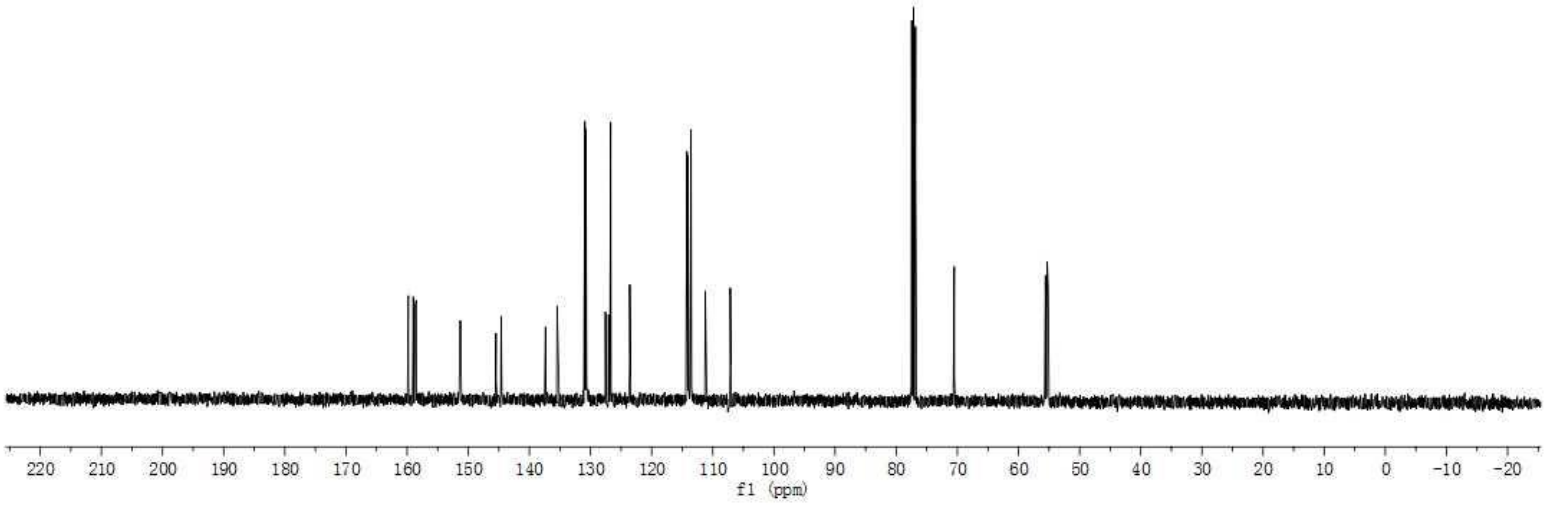
3cb

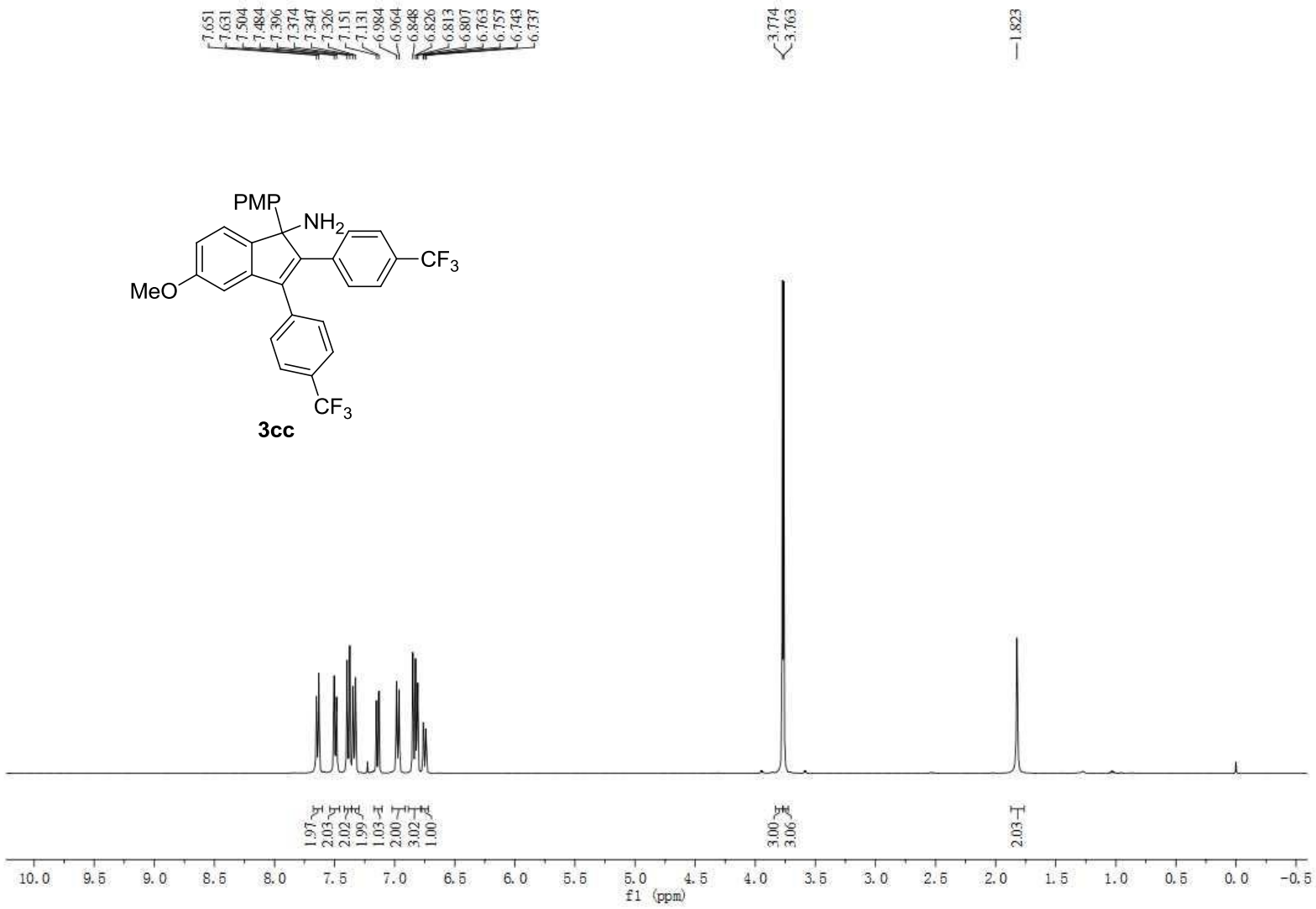

1.99
2.01
1.03
2.04
5.06
1.00
2.02
3.03
3.01
3.01
3.00
2.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

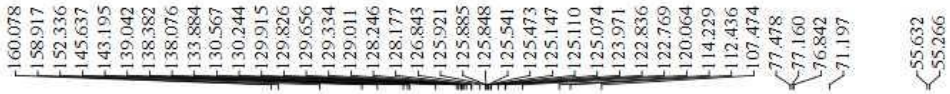

159.793
158.990
158.653
158.509
151.293
145.458
144.622
137.364
135.466
130.911
130.738
127.555
127.048
126.698
123.578
114.216
114.032
113.555
111.222
107.133
77.477
77.160
76.842
70.505
55.591
55.317
55.288
55.143

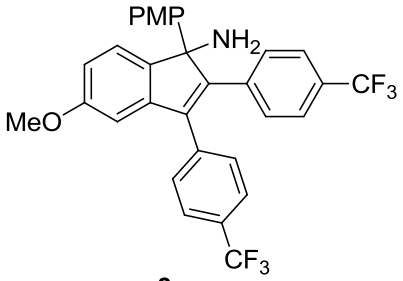

PMP
NH2
OMe
MeO
OMe

3cb

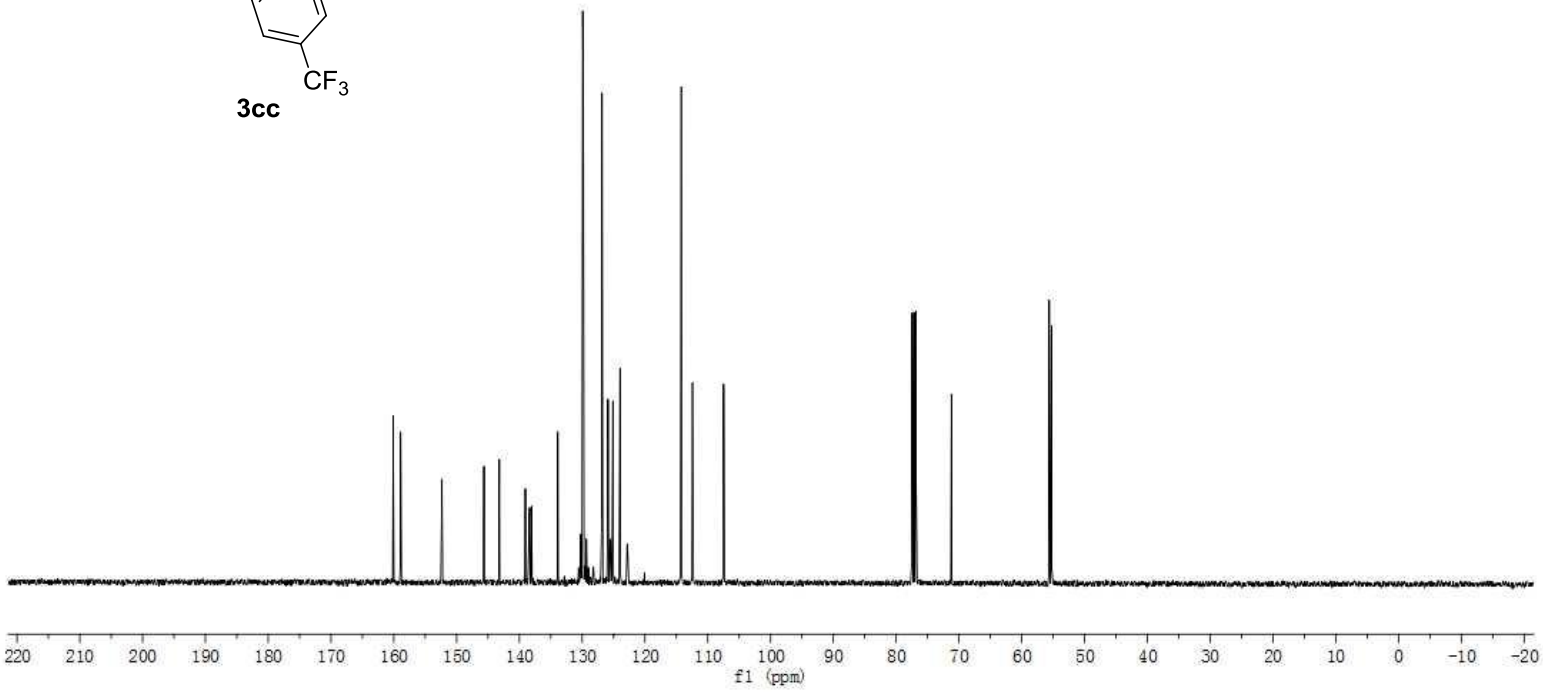

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

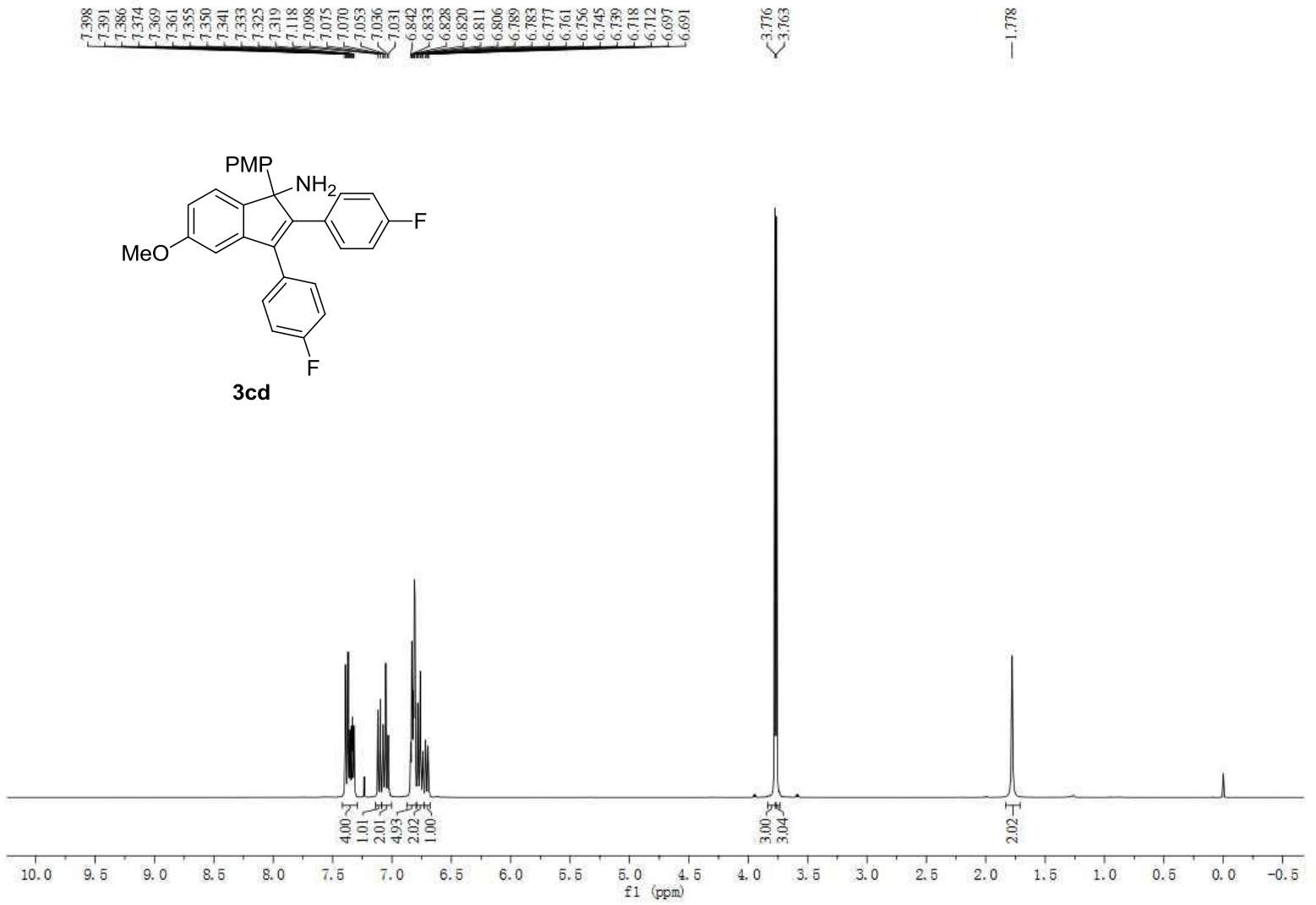

7.651
7.631
7.504
7.484
7.396
7.374
7.347
7.326
7.151
7.131
6.984
6.964
6.848
6.826
6.813
6.807
6.763
6.757
6.743
6.737
3.774
3.763
1.823
PMP
NH2
CF3
MeO
CF3
3cc
1.97
2.03
2.02
1.99
1.03
2.00
3.02
1.00
3.00
3.06
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

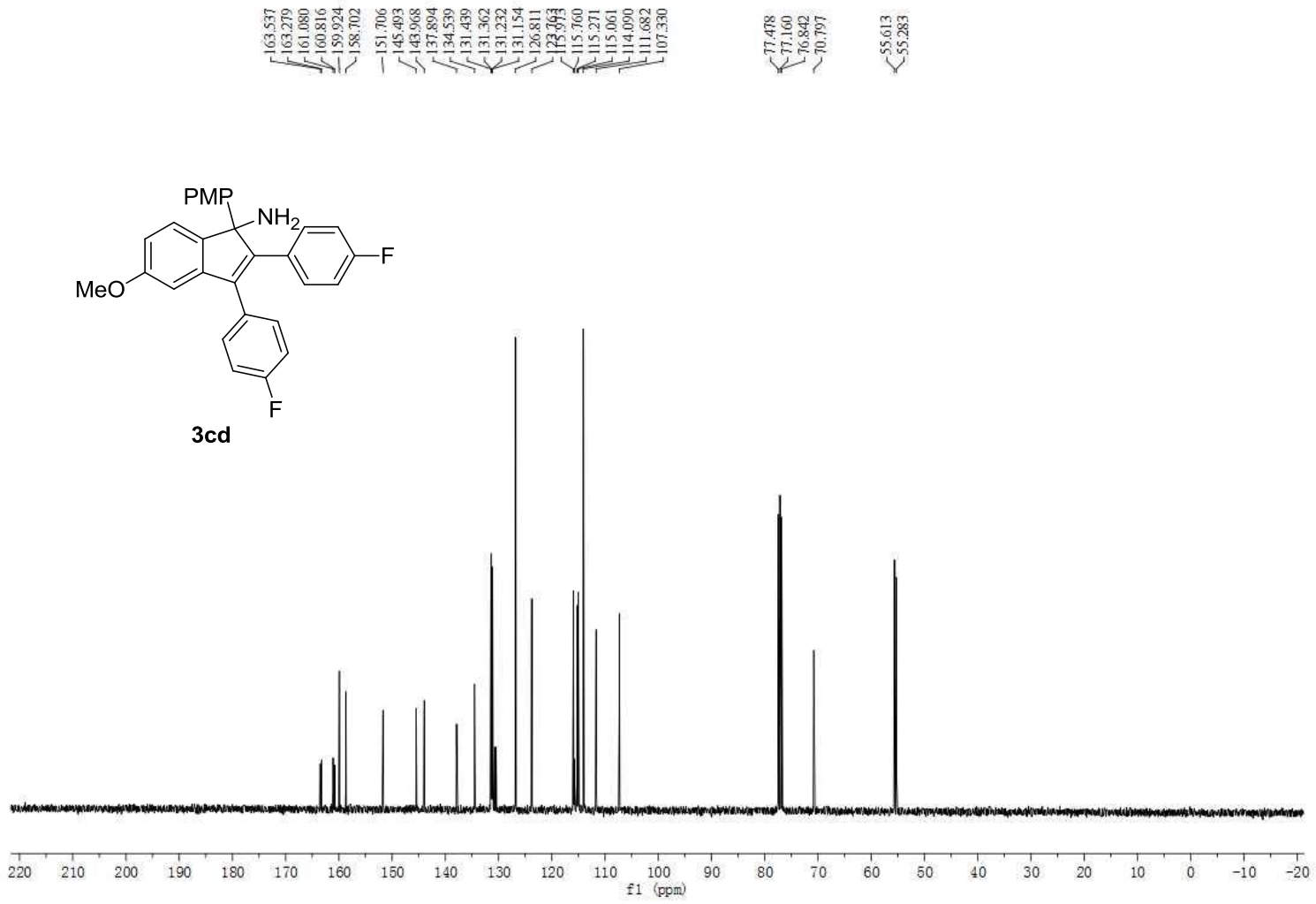

160.078
158.917
152.336
145.637
143.195
139.042
138.382
138.076
133.884
130.567
130.244
129.915
129.826
129.656
129.334
129.011
128.246
128.177
126.843
125.921
125.885
125.848
125.541
125.473
125.147
125.110
125.074
123.971
122.836
122.769
120.064
114.229
112.436
107.474
77.478
77.160
76.842
71.197
55.632
55.266

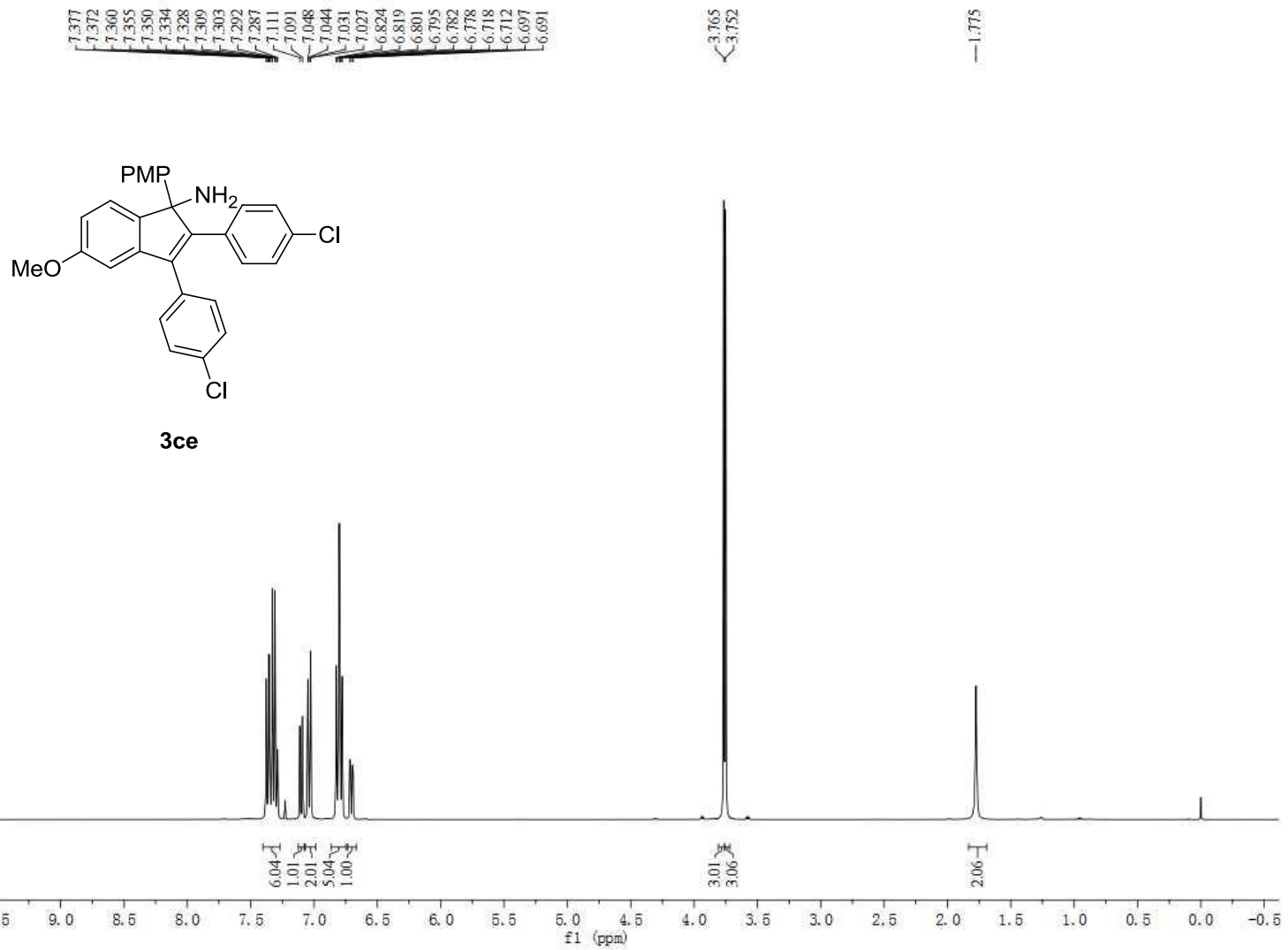

PMP
NH2
CF3
MeO
CF3

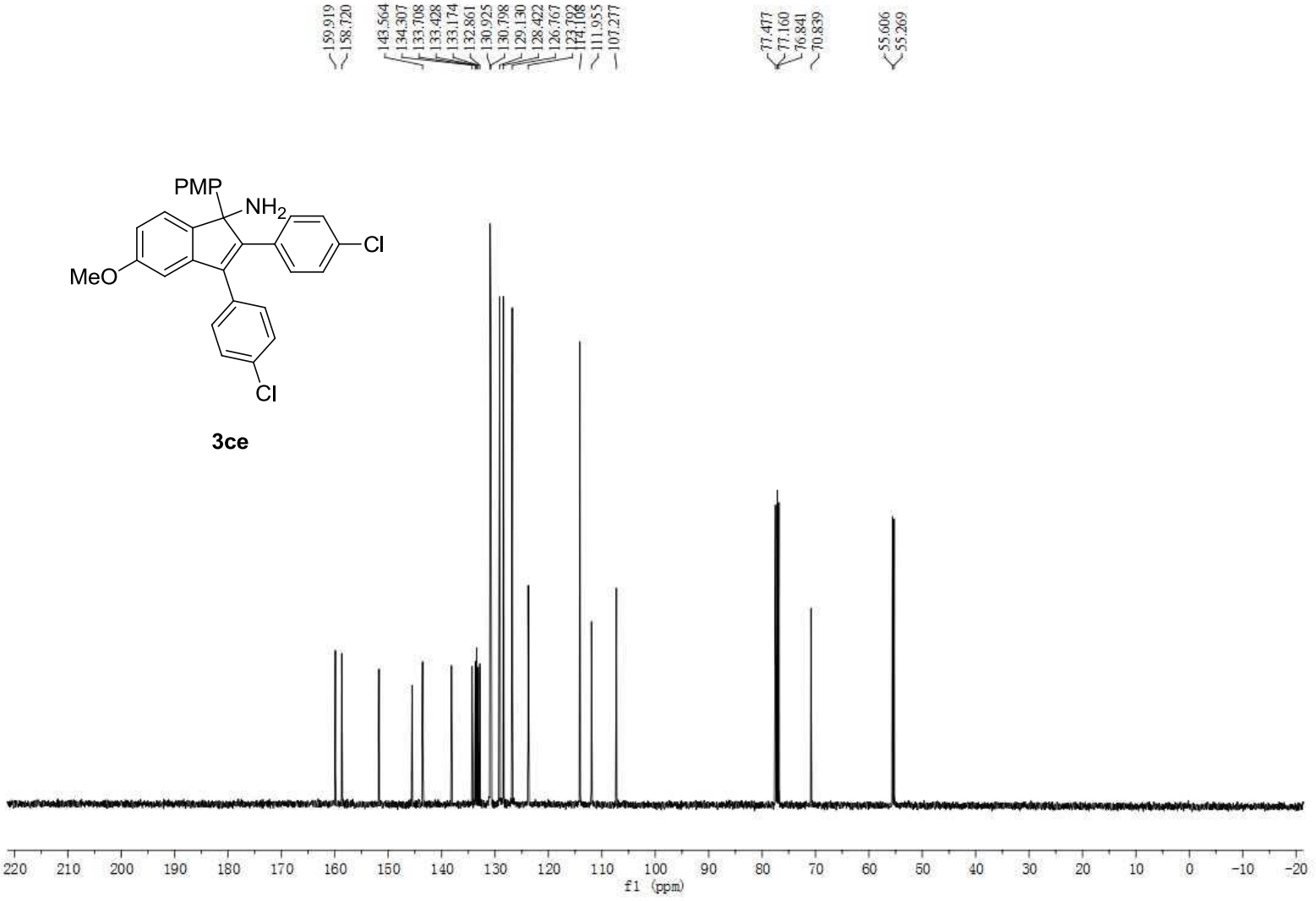
3cc

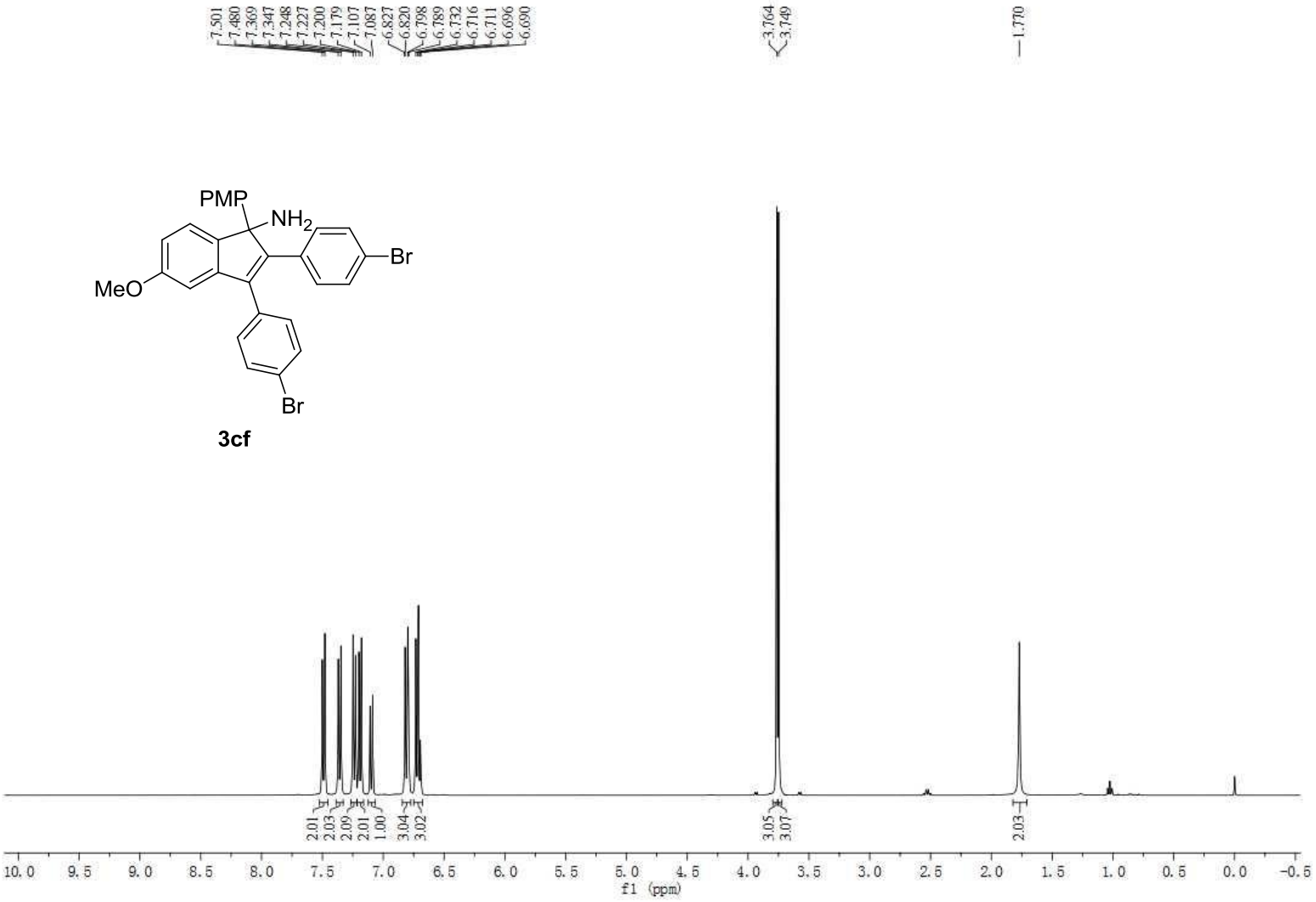

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.398
7.391
7.386
7.374
7.369
7.361
7.355
7.350
7.341
7.333
7.325
7.319
7.118
7.098
7.075
7.070
7.053
7.036
7.031
6.842
6.833
6.828
6.820
6.811
6.806
6.789
6.783
6.777
6.761
6.756
6.745
6.739
6.718
6.712
6.697
6.691
3.776
3.763
1.778
PMP
NH2
F
MeO
F
3cd
4.00
1.01
2.01
4.93
2.02
1.00
3.00
3.04
2.02
10.0
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
f1 (ppm)

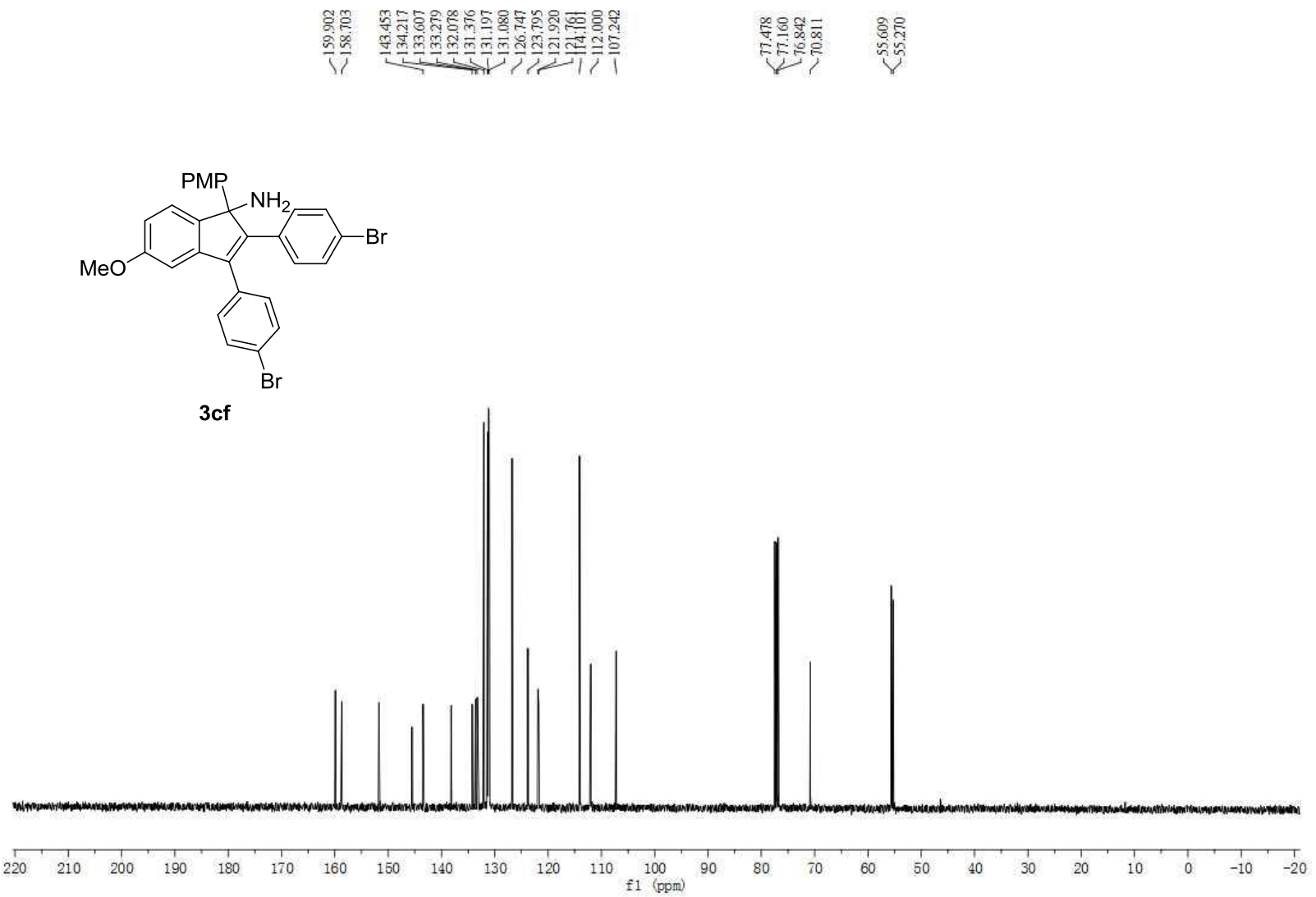

163.537
163.279
161.080
160.816
159.924
158.702
151.706
145.493
143.968
137.894
134.539
131.439
131.362
131.232
131.154
126.811
123.763
115.973
115.760
115.271
115.061
114.090
111.682
107.330
77.478
77.160
76.842
70.797
55.613
55.283
PMP
NH2
F
MeO
F
3cd
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.377
7.372
7.360
7.355
7.350
7.334
7.328
7.309
7.303
7.292
7.287
7.111
7.091
7.048
7.044
7.031
7.027
6.824
6.819
6.801
6.795
6.782
6.778
6.718
6.712
6.697
6.691
3.765
3.752
1.775
PMP
NH2
Cl
MeO
Cl
3ce
6.04
1.01
2.01
5.04
1.00
3.01
3.06
2.06
10.0 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
f1 (ppm)

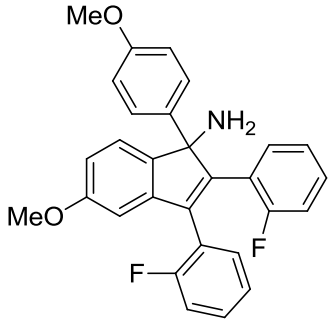

159.919
158.720
143.564
134.307
133.708
133.428
133.174
132.861
130.925
130.798
129.130
128.422
126.767
111.955
107.277
77.477
77.160
76.841
70.839
55.606
55.269
PMP
NH2
Cl
MeO
Cl
3ce
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.501
7.480
7.369
7.347
7.248
7.227
7.200
7.179
7.107
7.087
6.827
6.820
6.798
6.789
6.732
6.716
6.711
6.696
6.690
3.764
3.749
1.770
PMP
NH2
Br
MeO
Br
2.01
2.03
2.09
2.01
1.00
3.04
3.02
3.05
3.07
2.03
10.0
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
f1 (ppm)

3cf

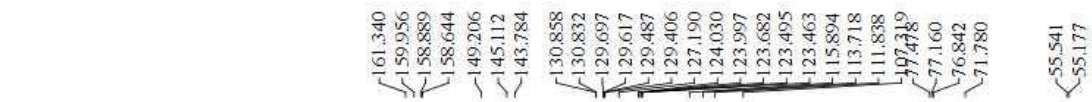

159.902
158.703
143.453
134.217
133.607
133.279
132.078
131.376
131.197
131.080
126.747
123.795
121.920
121.761
121.181
112.000
107.242
77.478
77.160
76.842
70.811
55.609
55.270
PMP
NH2
Br
MeO
Br
3cf
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

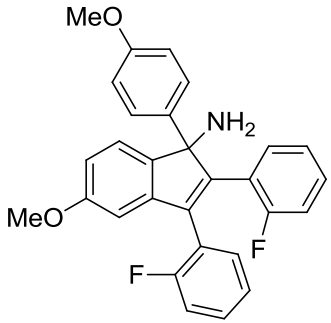

7.343
7.321
7.297
7.290
7.283
7.275
7.268
7.245
7.241
7.232
7.226
7.212
7.206
7.193
7.189
7.146
7.124
7.105
7.101
7.092
7.087
7.067
7.062
7.053
7.049
7.025
6.849
6.839
6.821
6.802
6.794
6.772
6.765
6.738
6.732
6.715
6.676
6.658
6.642
3.735
3.729
1.879


MeO
NH2
MeO
F
F

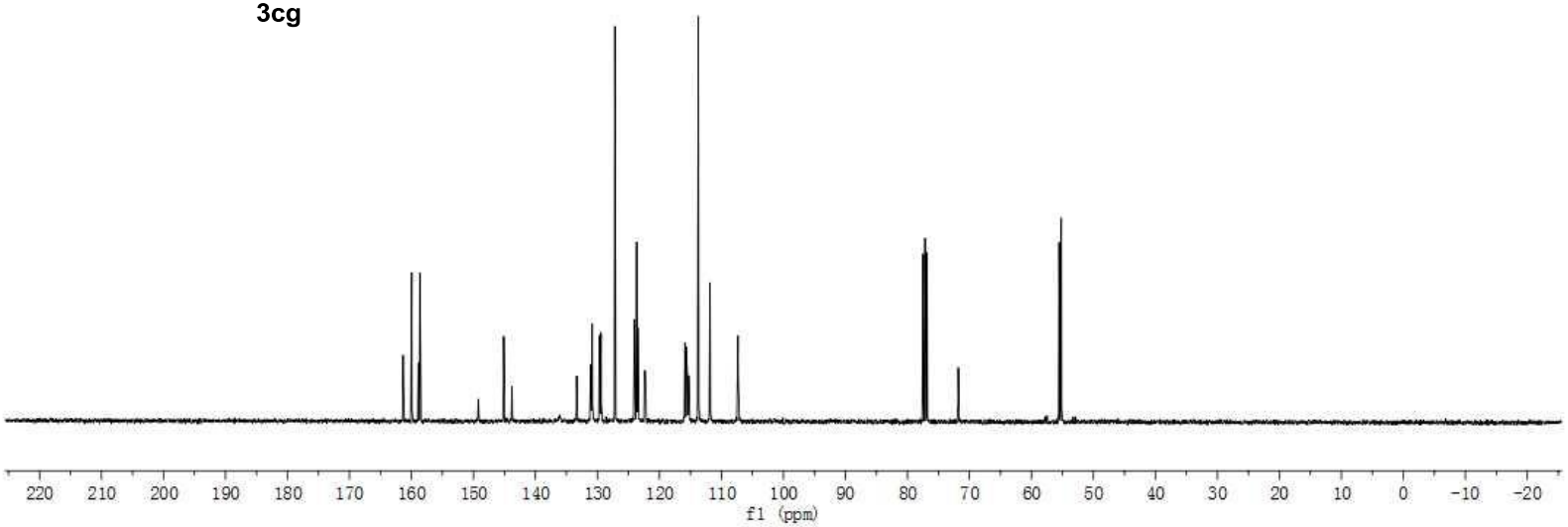
3cg

2.12
1.87
1.06
2.97
4.00
1.94
1.00
5.98
2.02
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
f1 (ppm)

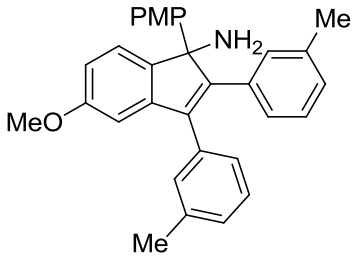

161.340
159.956
158.889
158.644
149.206
145.112
143.784
130.858
130.832
129.697
129.617
129.487
129.406
127.190
124.030
123.997
123.682
123.495
123.463
115.894
113.718
111.838
77.160
76.842
71.780
55.541
55.177


MeO
NH2
MeO
F
F

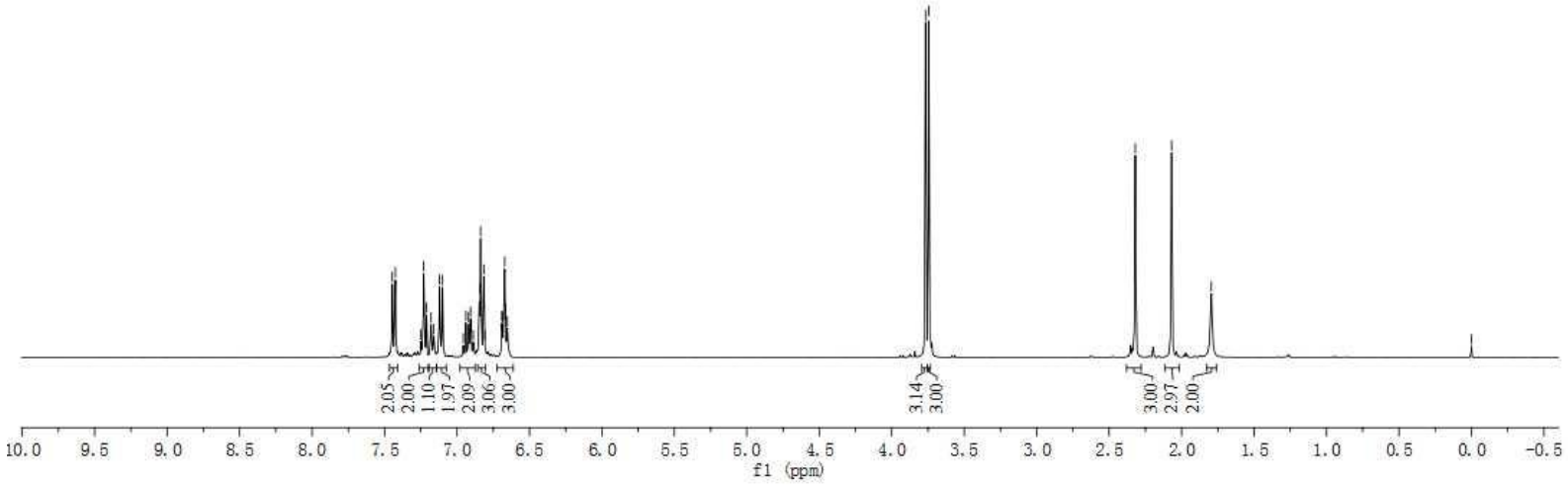
3cg


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

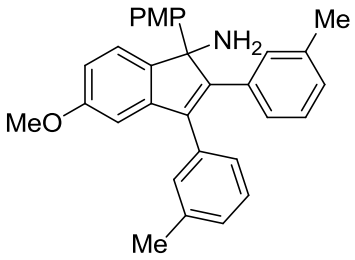

7.447
7.425
7.248
7.229
7.211
7.178
7.160
7.120
7.100
6.957
6.939
6.920
6.907
6.888
6.844
6.837
6.815
6.807
6.691
6.685
6.671
6.665
6.652
3.766
3.745
2.319
2.070
1.795
0.000


PMP
NH2
Me
MeO
Me

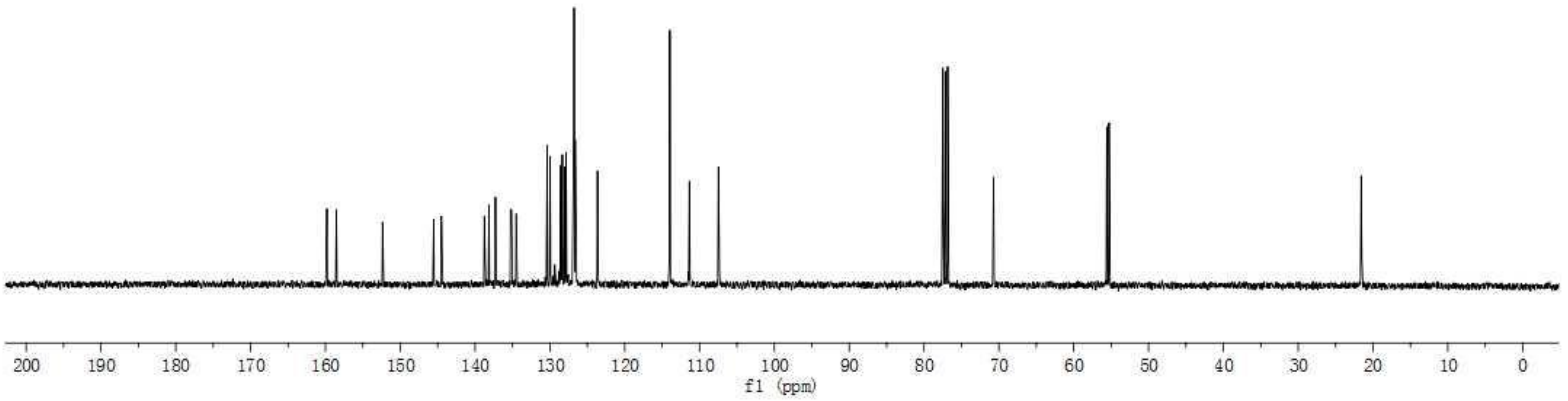
3ch

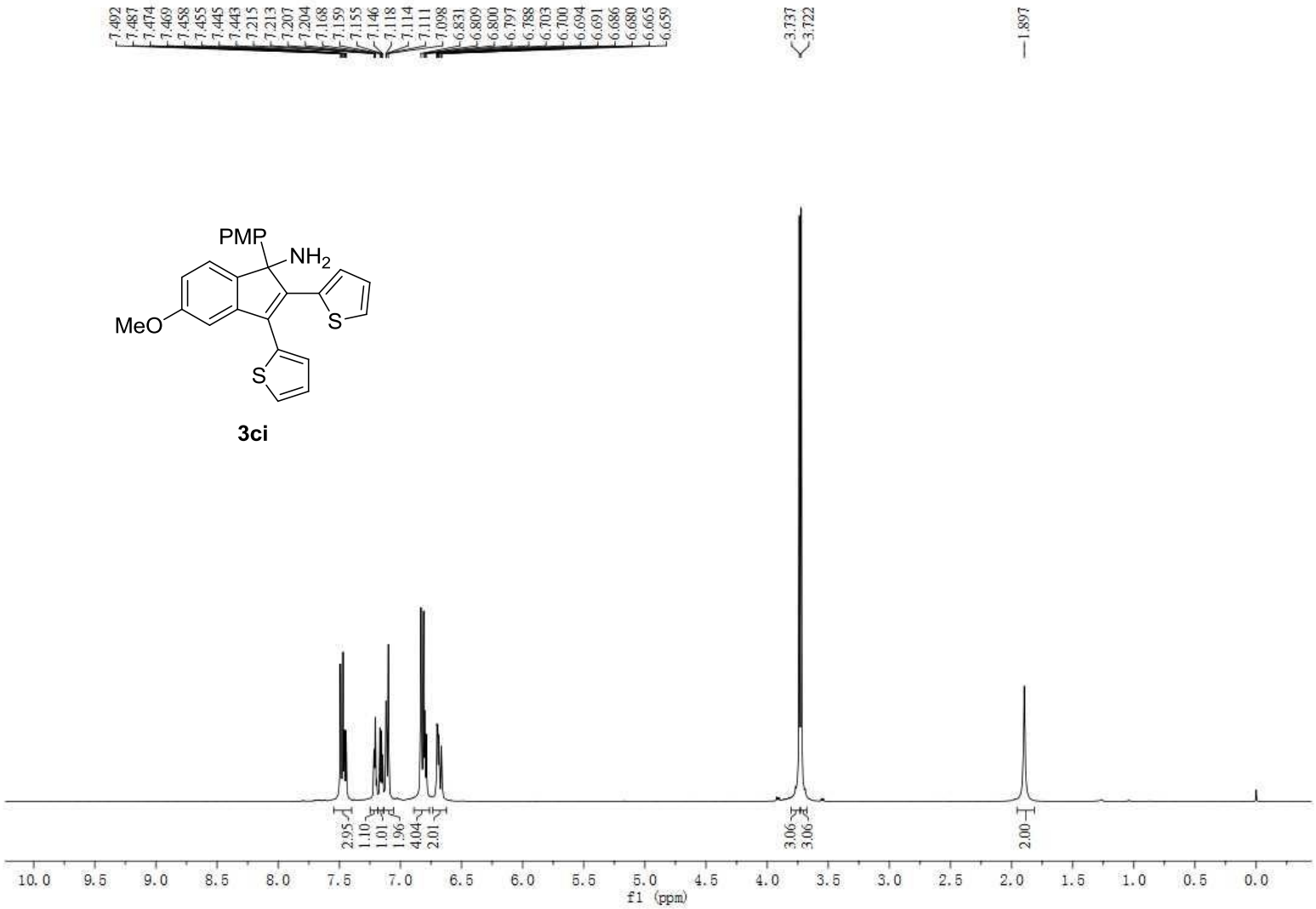

2.05
2.00
1.10
1.97
2.09
3.06
3.00
3.14
3.00
3.00
2.97
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


159.80
158.54
152.36
145.52
144.50
130.36
129.97
128.53
128.34
128.01
127.83
126.82
126.77
126.61
111.36
107.48
77.48
77.16
76.84
70.71
55.58
55.28
21.58
21.51

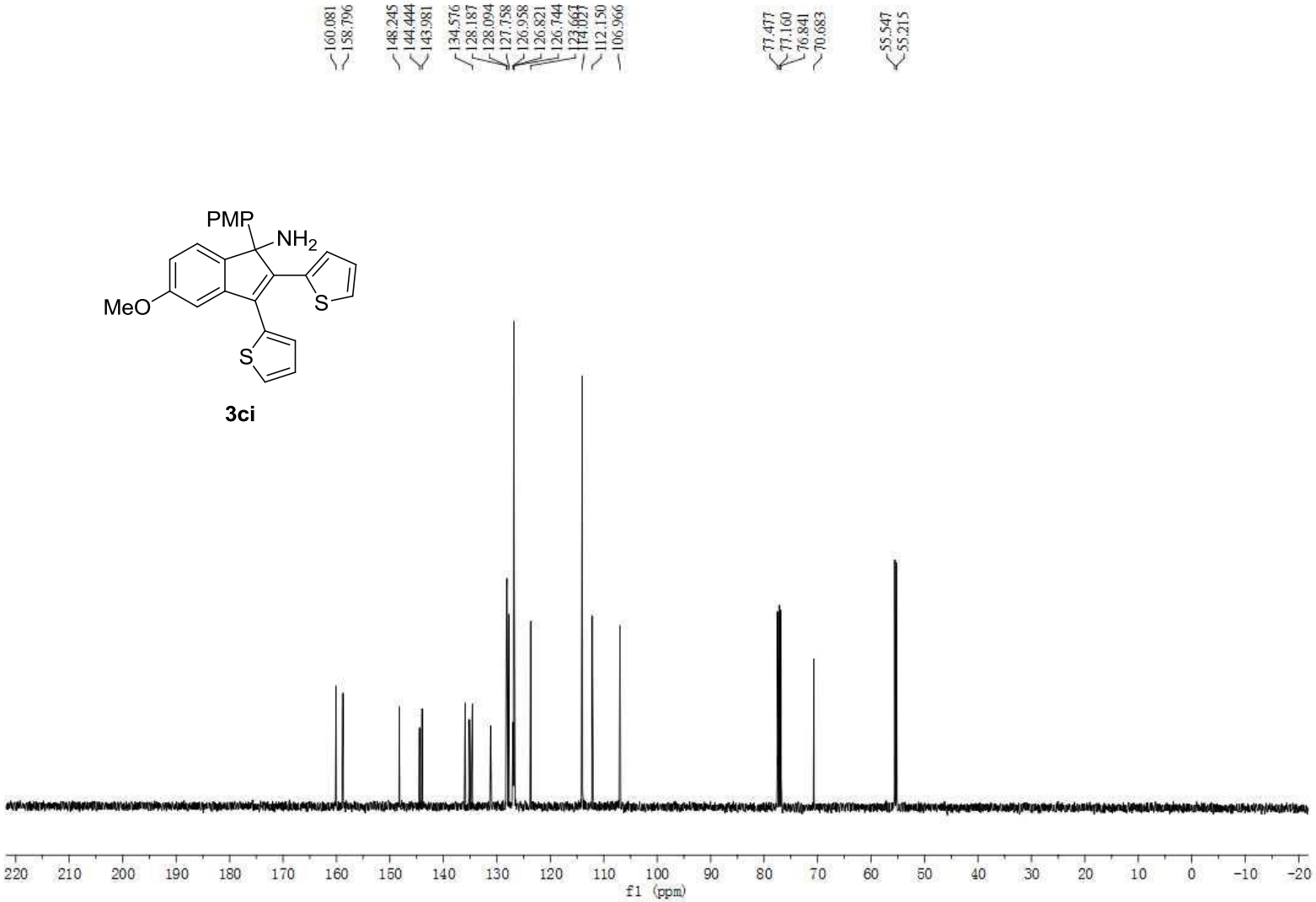

PMP
NH2
Me
MeO
Me

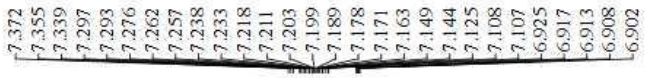
3ch

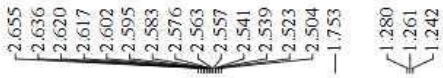

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

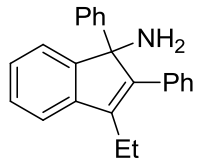

7.492
7.487
7.474
7.469
7.458
7.455
7.445
7.443
7.215
7.213
7.207
7.204
7.168
7.159
7.155
7.146
7.118
7.114
7.111
7.098
6.831
6.809
6.800
6.797
6.788
6.703
6.700
6.694
6.691
6.686
6.680
6.665
6.659
3.737
3.722
1.897
PMP
NH2
MeO
S
S
2.95
1.10
1.01
1.96
4.04
2.01
3.06
3.06
2.00
10.0
9.5
9.0
8.5
8.0
7.5
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
f1 (ppm)

3ci

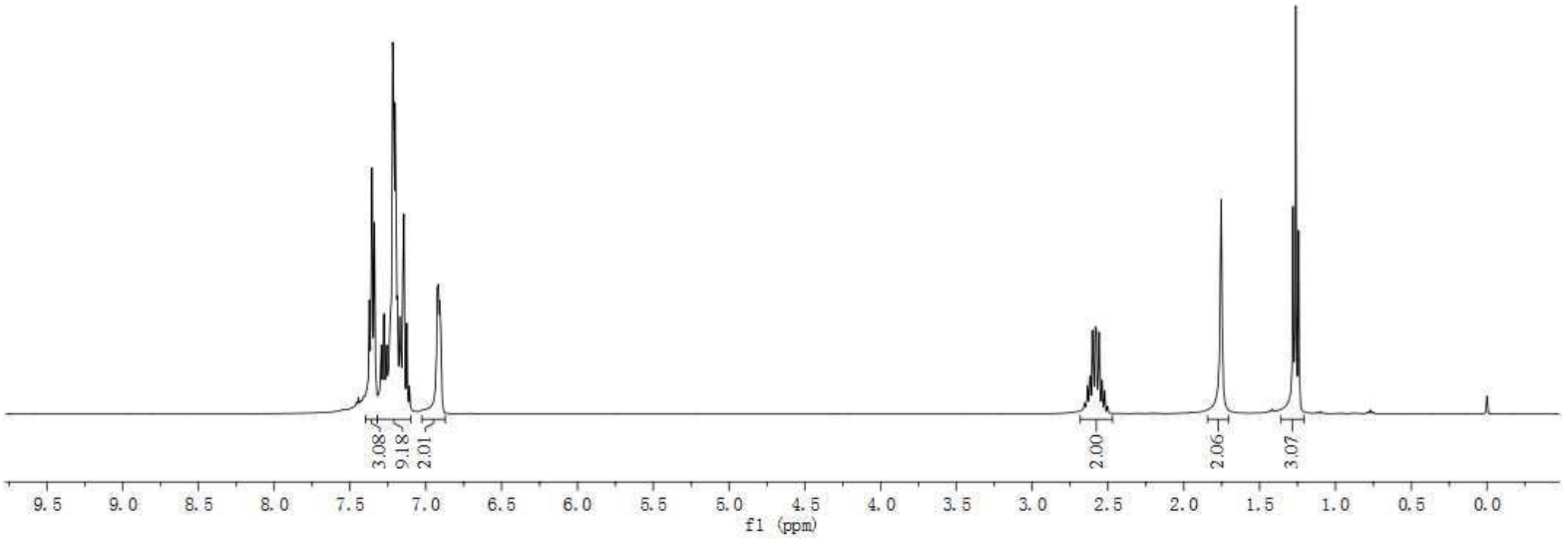

160.081
158.796
148.245
144.444
143.981
134.576
128.187
128.094
127.758
126.958
126.821
126.744
112.150
106.966
77.477
77.160
76.841
70.683
55.547
55.215
PMP
NH2
MeO
S
S
3ci
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

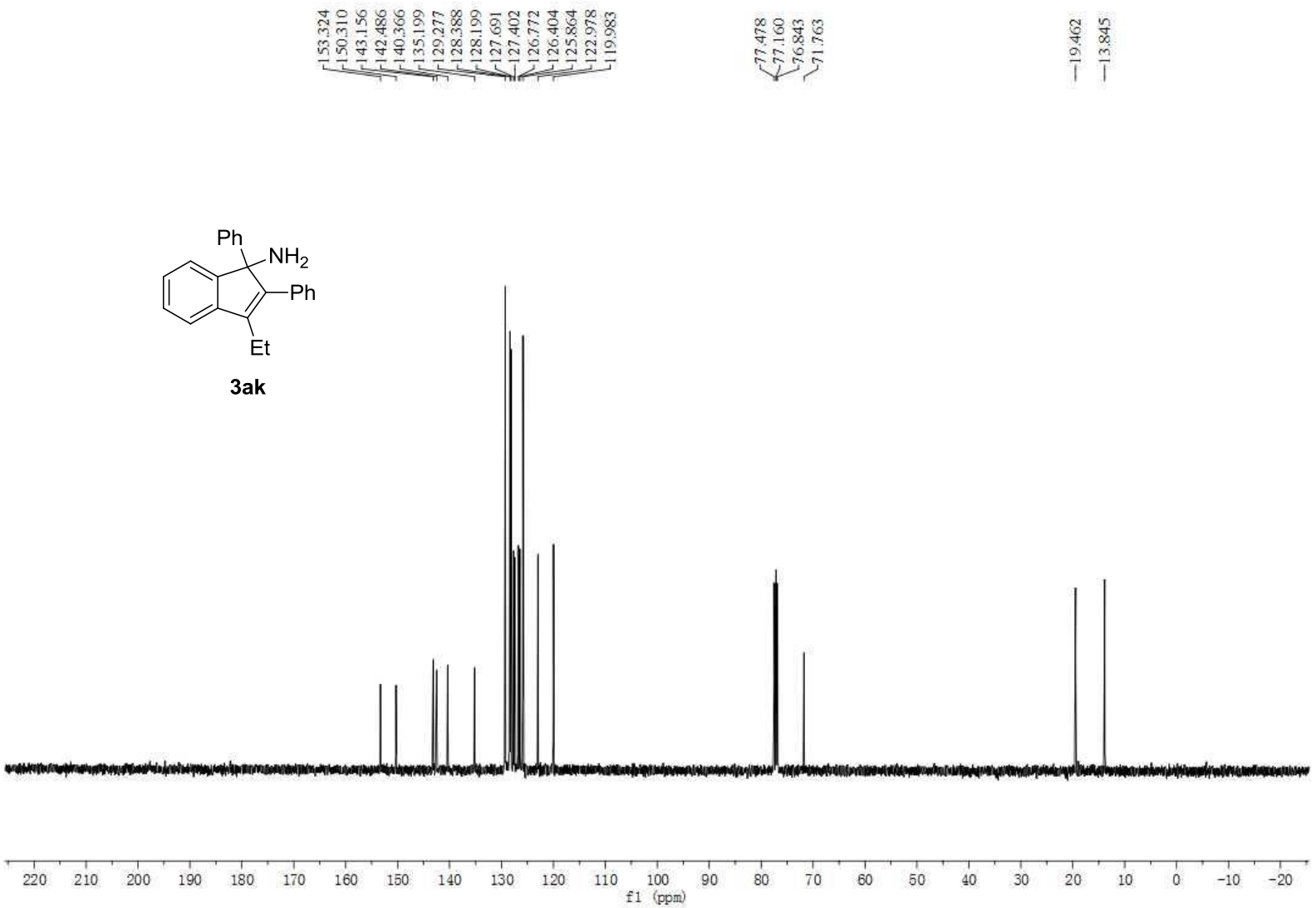

7.372
7.355
7.339
7.297
7.293
7.276
7.262
7.257
7.238
7.233
7.218
7.211
7.203
7.199
7.189
7.178
7.171
7.163
7.149
7.144
7.125
7.108
7.107
6.925
6.917
6.913
6.908
6.902

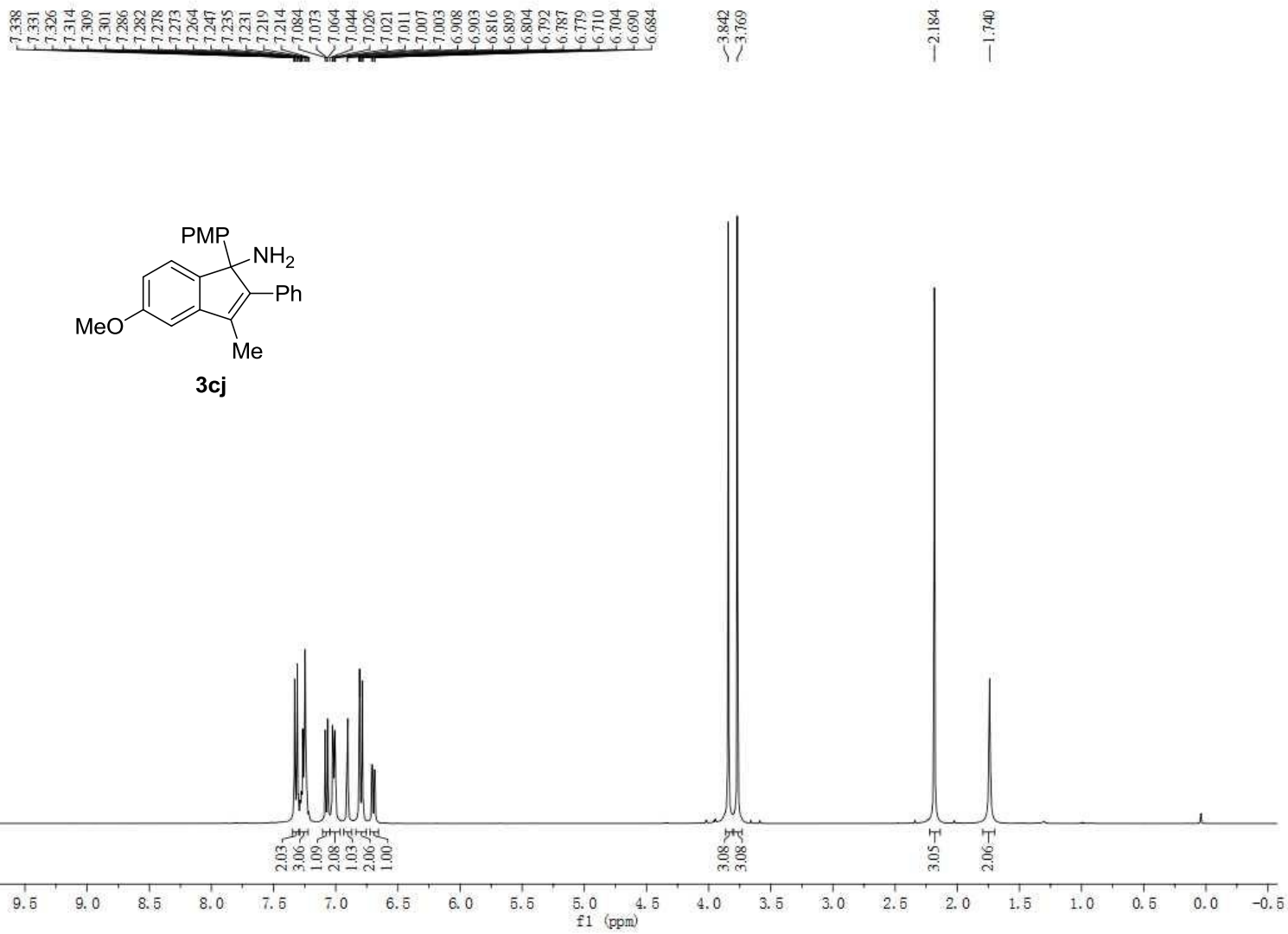

2.655
2.636
2.620
2.617
2.602
2.595
2.583
2.576
2.563
2.557
2.541
2.539
2.523
2.504
1.753
1.280
1.261
1.242

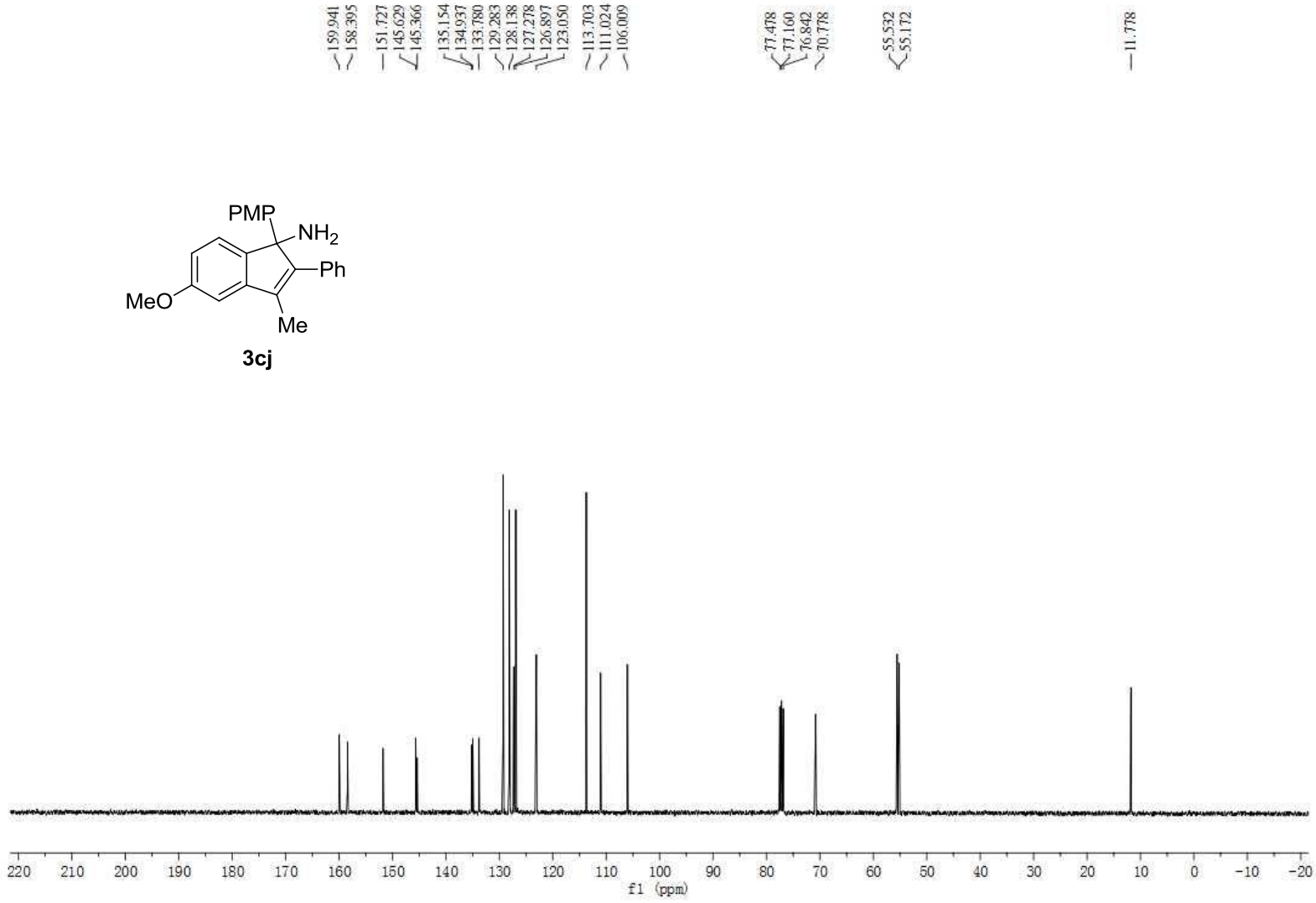

Ph
NH2
Ph
Et

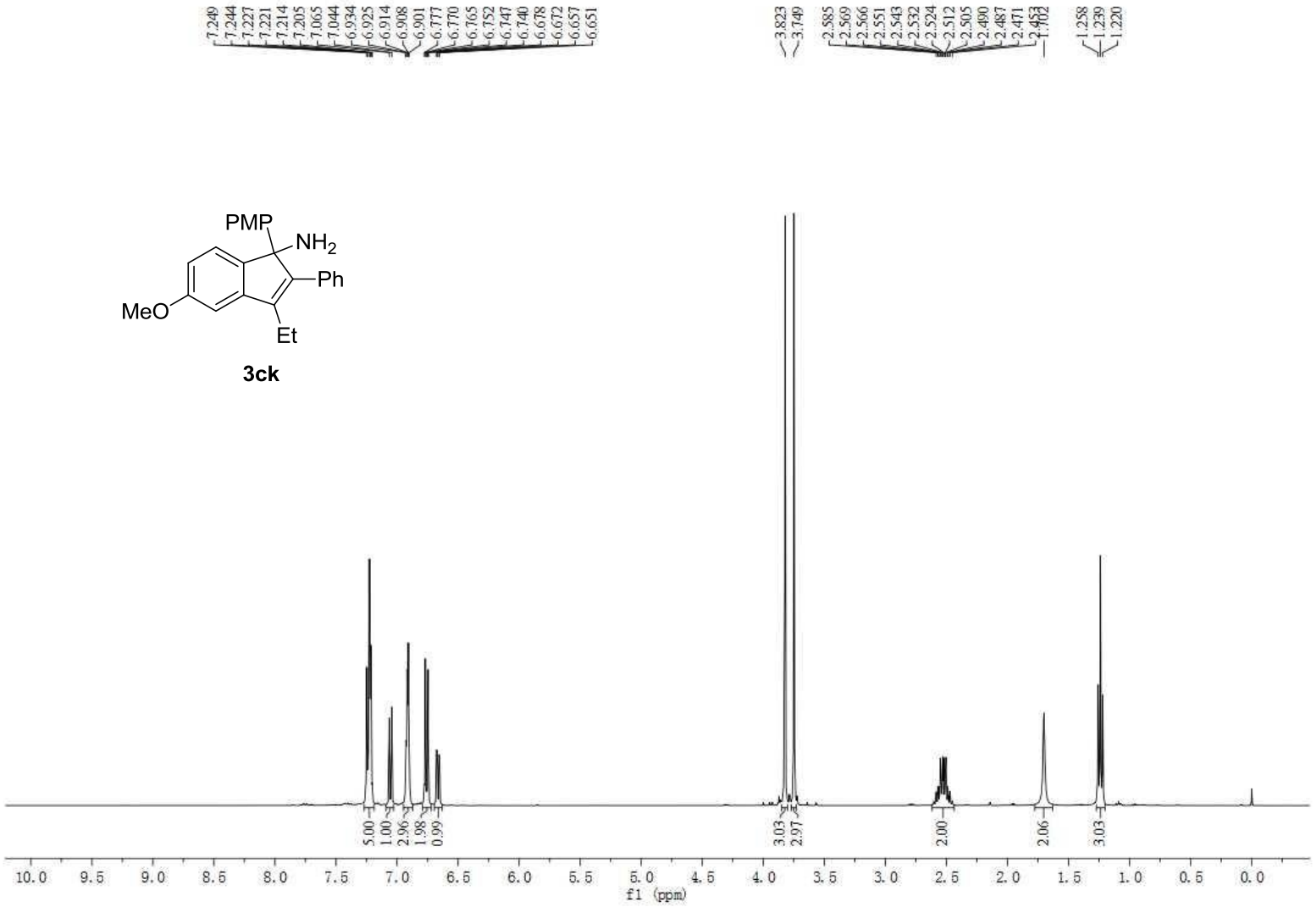
3ak

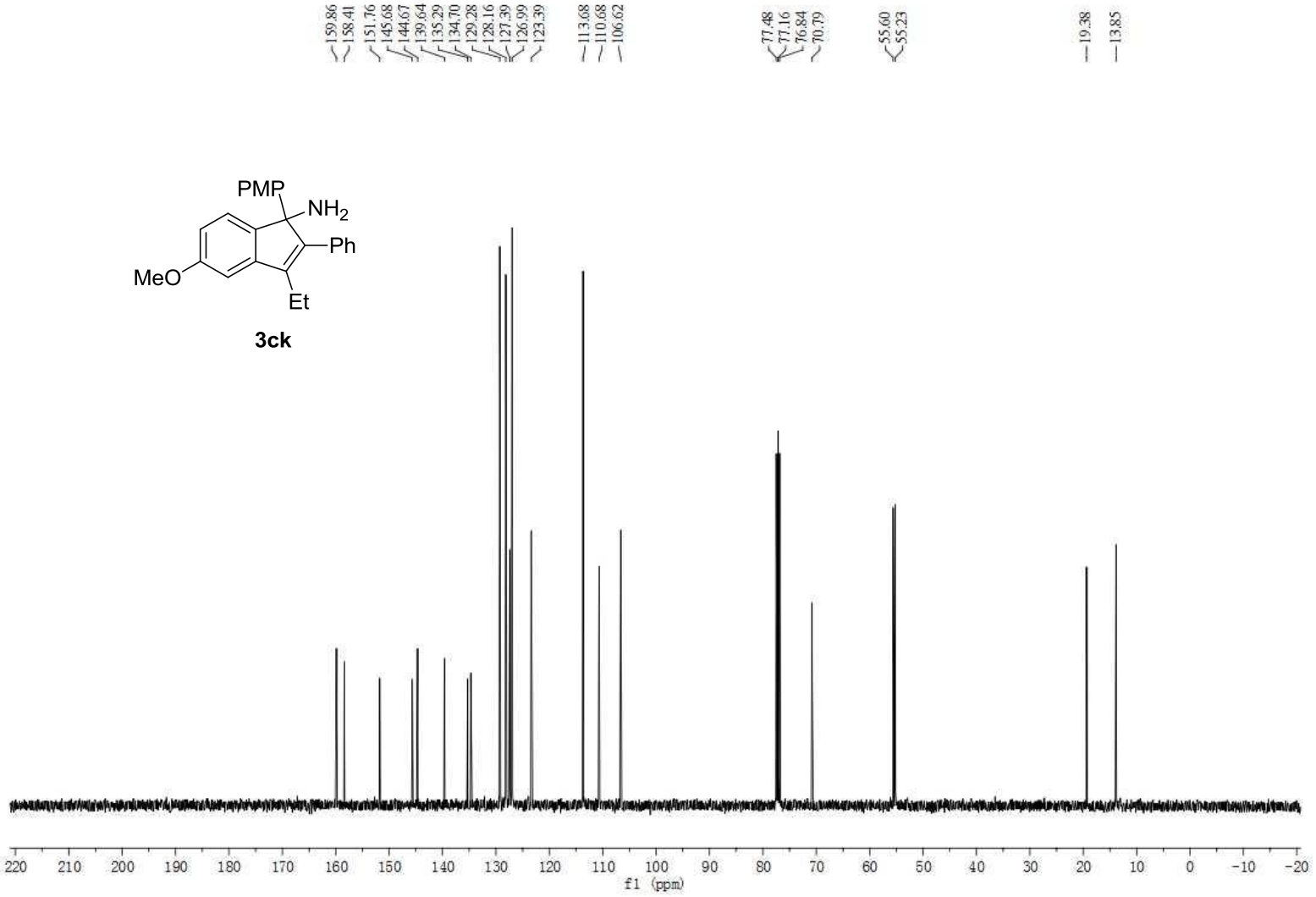

3.08
9.18
2.01
2.00
2.06
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

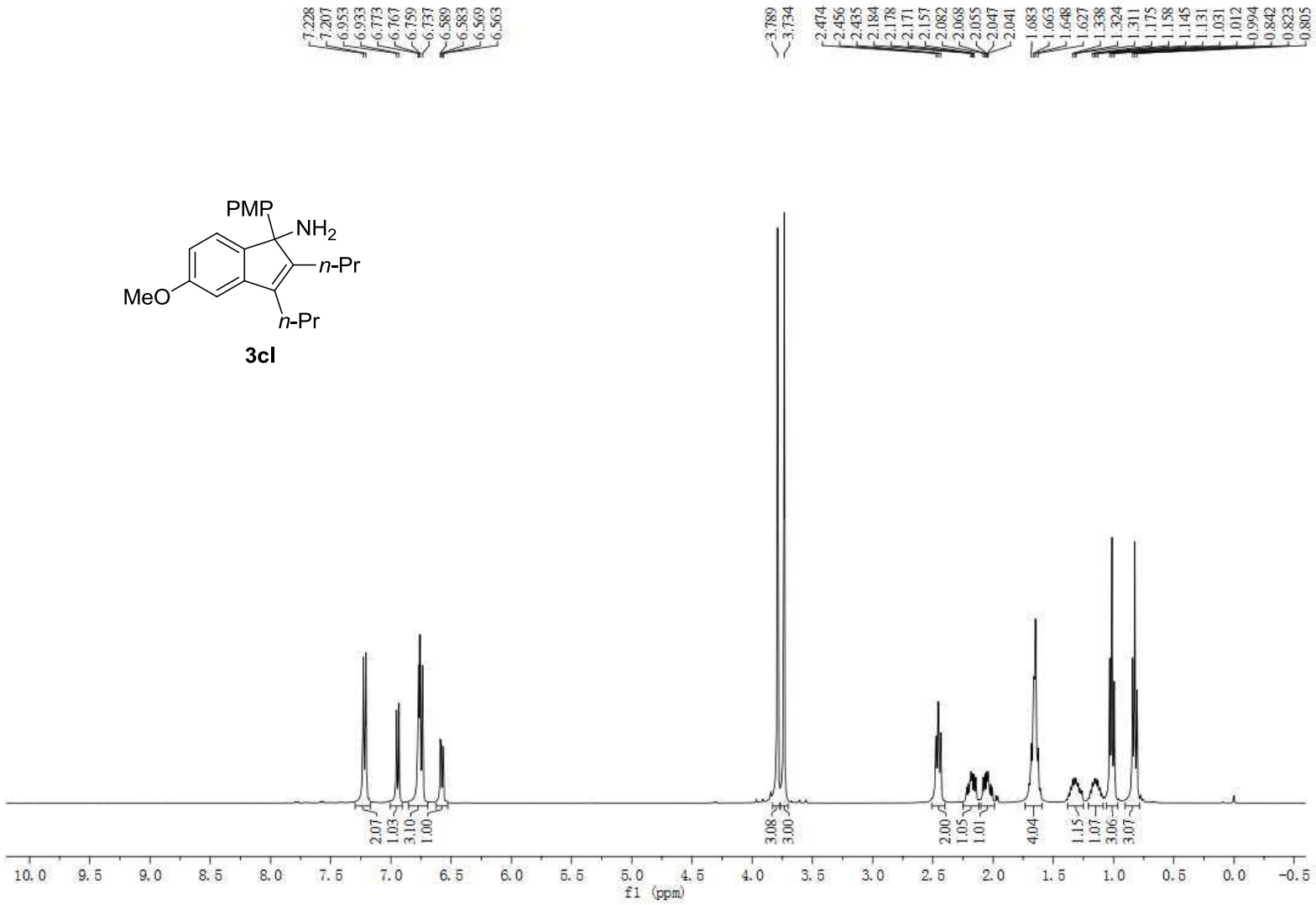

153.324
150.310
143.156
142.486
140.366
135.199
129.277
128.388
128.199
127.691
127.402
126.772
126.404
125.864
122.978
119.983
77.478
77.160
76.843
71.763
19.462
13.845
Ph
NH2
Ph
Et
3ak
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

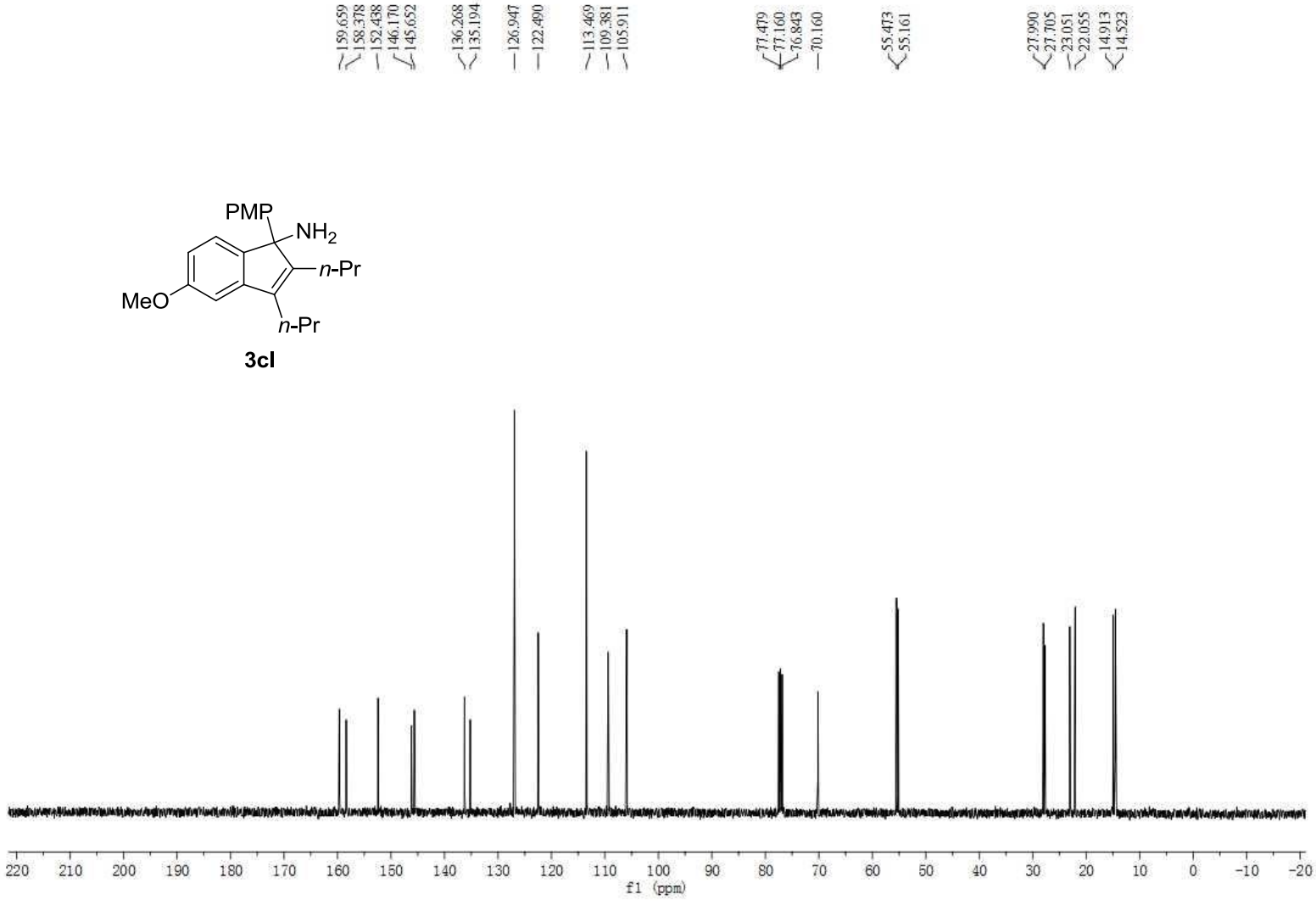

7.338
7.331
7.326
7.314
7.309
7.301
7.286
7.282
7.278
7.273
7.264
7.247
7.235
7.231
7.219
7.214
7.084
7.073
7.064
7.044
7.026
7.021
7.011
7.007
7.003
6.908
6.903
6.816
6.809
6.804
6.792
6.787
6.779
6.710
6.704
6.690
6.684
3.842
3.769
2.184
1.740
PMP
NH2
Ph
MeO
Me
3cj
2.03
3.06
1.09
2.08
1.03
2.06
1.00
3.08
3.08
3.05
2.06
10.0
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
f1 (ppm)


159.941
158.395
151.727
145.629
145.366
135.154
134.937
133.780
129.283
128.138
127.278
126.897
123.050
113.703
111.024
106.009
77.478
77.160
76.842
70.778
55.532
55.172
11.778
PMP
NH2
Ph
MeO
Me
3cj
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.249
7.244
7.227
7.221
7.214
7.205
7.065
7.044
6.934
6.925
6.914
6.908
6.901
6.777
6.770
6.765
6.752
6.747
6.740
6.678
6.672
6.657
6.651
3.823
3.749
2.585
2.569
2.566
2.551
2.543
2.532
2.524
2.512
2.505
2.490
2.487
2.471
1.258
1.239
1.220
PMP
NH2
Ph
MeO
Et
3ck
5.00
1.00
2.96
1.98
0.99
3.03
2.97
2.00
2.06
3.03
10.0
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
f1 (ppm)


159.86
158.41
151.76
145.68
144.67
139.64
135.29
134.70
129.28
128.16
127.39
126.99
123.39
113.68
110.68
106.62
77.48
77.16
76.84
70.79
55.60
55.23
19.38
13.85
PMP
NH2
Ph
MeO
Et
3ck
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.228
7.207
6.953
6.933
6.773
6.767
6.759
6.737
6.589
6.583
6.569
6.563
3.789
3.734
2.474
2.456
2.435
2.184
2.178
2.171
2.157
2.082
2.068
2.055
2.047
2.041
1.683
1.663
1.648
1.627
1.338
1.324
1.311
1.175
1.158
1.145
1.131
1.031
1.012
0.994
0.842
0.823
0.805
PMP
NH2
n-Pr
MeO
n-Pr
3cl
2.07
1.03
3.10
1.00
3.08
3.00
2.00
1.05
1.01
4.04
1.15
1.07
3.06
3.07
10.0
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
f1 (ppm)


159.659
158.378
152.438
146.170
145.652
136.268
135.194
126.947
122.490
113.469
109.381
105.911
77.479
77.160
76.843
70.160
55.473
55.161
27.990
27.705
23.051
22.055
14.913
14.523
PMP
NH2
n-Pr
MeO
n-Pr
3cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)