Supporting Information

Silver(I)-catalysed carboxylative cyclisation of primary propargylic amines in neat water using potassium bicarbonate as the carboxyl source: environment-friendly synthesis of Z-5-alkylidene-1,3-oxazolidin-2-ones

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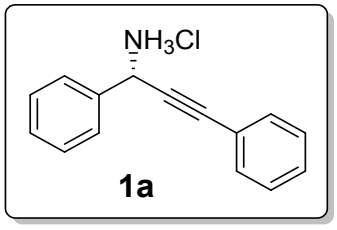
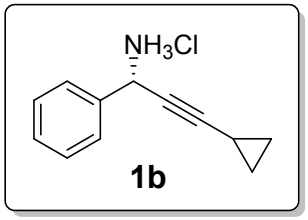
Melting points were measured on an SGW X-4 microscope apparatus which was uncorrected. Specific optical rotation was measured on a Rudolph AUTOPOL IV polarimeter. All reagents and solvents are commercially available and were used as purchased, without further purification. Mass spectra were measured on an LTQ Orbitrap XL type high resolution mass spectrometer (EI ion source) and an 6500-Qtrap liquid chromatograph-mass spectrometer (ESI ion source). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Advanced III HD 400. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad).

Typical Procedure for the Preparation of Propargylic amine 1: To a cooled (-78 °C) solution of *N*-sulfinylimine (1.0 mmol) in CH_2Cl_2 (5 mL) under Ar was added dropwise a freshly prepared ethereal solution of alkynyl Grignard reagent (2−3 mmol), and the solution was stirred at the same temperature for 2 h, then gradually warmed to rt and stirred overnight. The reaction was quenched by sat. aq NH_4Cl, extracted with EtOAc, and the combined organic phase was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography eluted with EtOAc/PE. The pure product was dissolved in a 2M HCl/MeOH solution and stirred at room temperature for 1 h, the solvent was removed under vacuo and the residue was triturated with EtOAc to afford propargylic amine hydrochloride as a white solid after filtration. In some cases the salt has an appreciable solubility in EtOAc, it was extracted into water, the aqueous phase was basified with sat. $NaHCO_3$ and extracted with EtOAc for three times. Free propargylic amine was isolated as colorless oil after concentration.



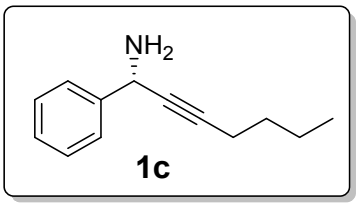
1a

1a: White solid (89%), M.P.: 156 – 157 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.23 (s, 3H), 7.72 (d, J = 7.8 Hz, 2H), 7.51 – 7.42(m, 8H), 5.67 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.4, 132.0, 129.9, 129.7, 129.3, 128.6, 121.4, 114.9, 87.7, 85.2, 45.8; HR-MS (ESI$^+$): *m/z* calcd for $C_{15}H_{13}N$ $[M + H]^+$ 208.1126, found 208.1126.

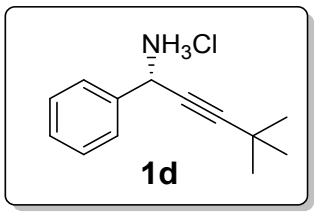


1b

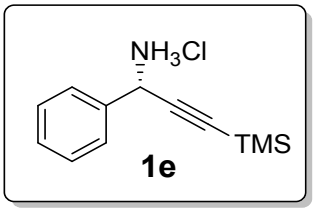
1b: White solid (87%), M.P.: 171 – 172 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.05 (s, 3H), 7.62 – 7.59 (m, 2H), 7.36 – 7.44 (m, 3H), 5.27 (d, *J* = 5.2 Hz, 1H), 1.44 – 1.37 (m, 1H), 0.85 – 0.80 (m, 2H), 0.67-0.63 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.9, 129.5, 129.1, 128.4, 92.2, 71.1, 45.5, 8.5, -0.5; $[\alpha]_D^{20}$ –28.5 (*c* 0.20, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{12}H_{13}N$ $[M + H]^+$ 172.1126, found 172.1118.



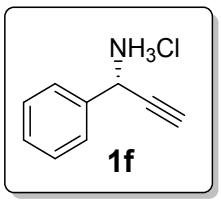
1c: colorless oil (91%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.53 (m, 2H), 7.39 – 7.27 (m, 3H), 4.78 (s, 1H), 2.27 (td, *J* = 7.0, 2.1 Hz, 2H), 1.56 – 1.43 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); HR-MS (ESI$^+$): *m/z* calcd for $C_{13}H_{17}N$ $[M + H]^+$ 188.1439, found 188.1438.



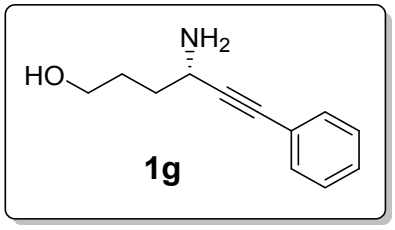
1d: White solid (90%), M.P.: 162 – 163 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.94 (s, 3H), 7.62 – 7.59 (m, 2H), 7.46 – 7.38 (m, 3H), 5.33 (s, 1H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.9, 129.5, 129.1, 128.5, 97.0, 74.5, 45.4, 30.8, 27.6; $[\alpha]_D^{20}$ –40.0 (*c* 0.10, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{13}H_{17}N$ $[M + H]^+$ 188.1439, found 188.1438.



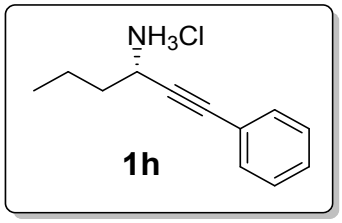
1e: White solid (90%); ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.63 – 7.60 (m, 2H), 7.51 – 7.49 (m, 3H), 5.38 (s, 1H), 0.25 (s, 9H);



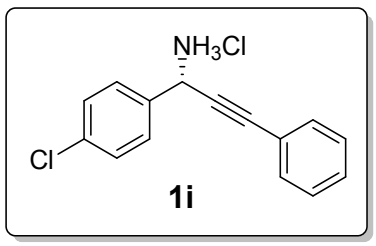
1f: White solid (89%), M.P.: 142 – 143 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.14 (s, 3H), 7.65 – 7.62 (m, 2H), 7.47 – 7.41 (m, 3H), 5.41 (s, 1H), 3.94 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.1, 129.7, 129.2, 128.5, 80.0, 79.5, 45.0; HR-MS (ESI$^+$): *m/z* calcd C_9H_9N for $[M + H]^+$ 132.0813, found 132.0814.



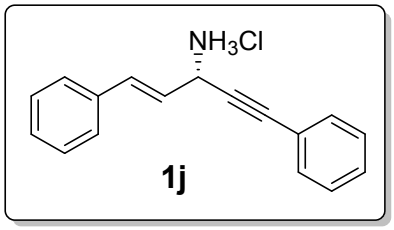
1g: colorless oil (86%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.40 (m, 2H), 7.33 – 7.30 (m, 3H), 3.83 – 3.79 (m, 1H), 3.72 – 3.66 (m, 2H), 2.07 – 1.89 (m, 4H), 1.82 – 1.74 (m, 2H); HR-MS (ESI$^+$): *m/z* calcd for $C_{12}H_{15}NO$ $[M + H]^+$ 190.1232, found 190.1234.



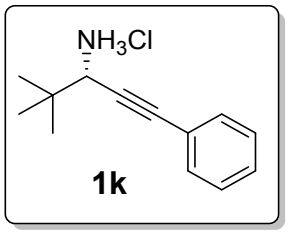
1h: White solid (90%), M.P.: 169 – 170 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 3H), 7.46 – 7.38 (m, 5H), 4.27 (s, 1H), 1.88 – 1.73 (m, 2H), 1.55 – 1.42 (m, 2H), 0.92 (t, J = 7.36 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 131.9, 129.7, 129.3, 121.6, 86.3, 85.9, 42.7, 35.4, 18.8, 13.8; $[\alpha]_D^{20}$ +33.0 (c 0.20, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{12}H_{15}N$ $[M + H]^+$ 174.1283, found 174.1275.



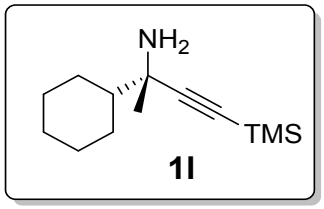
1i: White solid (92%), M.P.: 160 – 161 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.33 (s, 3H), 7.78 – 7.74 (m, 2H), 7.57 – 7.39 (m, 7H), 5.72 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 134.44, 134.41, 132.0, 130.7, 129.9, 129.3, 129.2, 121.3, 87.9, 84.9, 45.1; $[\alpha]_D^{20}$ −6.5 (c 0.20, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{15}H_{12}NCl$ $[M + H]^+$ 242.0737, found 242.0731.



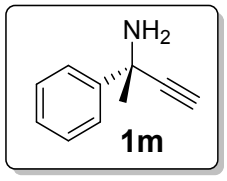
1j: White solid (89%), M.P.: 153 – 154 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 3H), 7.54 – 7.30 (m, 10H), 6.97 (d, J = 15.8 Hz, 1H), 6.45 (dd, J = 15.8, 6.5 Hz, 1H), 5.22 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.5, 135.0, 132.0, 129.9, 129.3, 129.2, 127.2, 123.0, 121.4, 87.7, 84.2, 44.1; $[\alpha]_D^{20}$ +8.0 (c 0.20, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{17}H_{15}N$ [M + H]$^+$ 234.1283, found 234.1271.



1k: White solid (91%), M.P.: 164 – 165 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 (s, 3H), 7.48 – 7.39 (m, 5H), 4.13 (d, J = 5.0 Hz, 1H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 131.9, 129.7, 129.3, 121.6, 87.1, 84.8, 52.4, 34.8, 26.2; $[\alpha]_D^{20}$ –12.0 (c 0.10, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{13}H_{17}N$ [M + H]$^+$ 188.1439, found 188.1432.

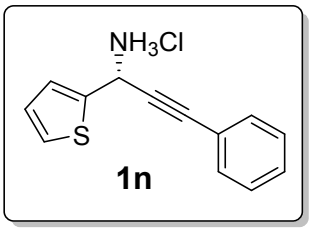


1l: colorless oil (73%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.88 – 1.59 (m, 7H), 1.18 (s, 3H), 1.17 – 0.97 (m, 4H), 0.10 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 114.7, 84.2, 51.9, 48.6, 27.8, 27.7, 27.4, 26.51, 26.47, 26.42, 0.7; $[\alpha]_D^{20}$ +13.0 (c 0.20, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{13}H_{25}NSi$ [M + H]$^+$ 224.1835, found 224.1828.

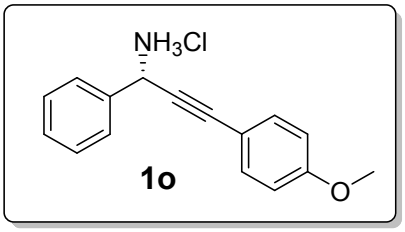


1m: colorless oil (72%); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 – 7.74 (m, 2H), 7.40 – 7.28 (m, 3H), 2.56 (s, 1H), 1.71 (s, 3H); ^{13}C NMR (100 MHz,

Chloroform-*d*) δ 145.5, 128.3, 127.3, 125.3, 90.4, 70.8, 51.8, 33.8; $[\alpha]_D^{20}$ −16.0 (*c* 0.20, $CHCl_3$); HR-MS (ESI^+): *m/z* calcd for $C_{10}H_{11}N$ $[M + H]^+$ 146.0970, found 146.0971.

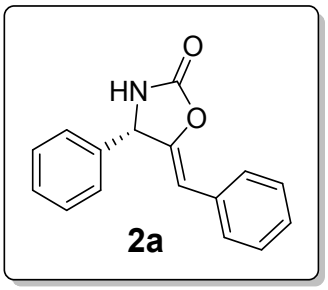


1n: White solid (92%), M.P.: 144 – 145 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 9.39 (s, 3H), 7.64 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.56 – 7.34 (m, 6H), 7.10 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.02 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.7, 132.0, 130.0, 129.3, 129.1, 128.2, 127.8, 121.1, 87.0, 85.0, 41.1; $[\alpha]_D^{20}$ +5.0 (*c* 0.20, $CHCl_3$); HR-MS (ESI^+): *m/z* calcd for $C_{13}H_{11}NS$ $[M + H]^+$ 214.0691, found 214.0683.



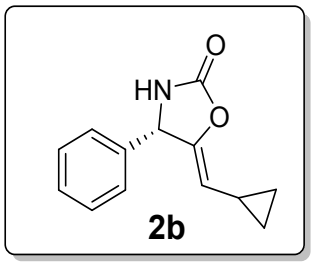
1o: White solid (90%), M.P.: 186 – 187 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 9.02 (s, 3H), 7.70 (d, *J* = 6.8 Hz, 2H), 7.58 – 7.39 (m, 5H), 7.00 (d, *J* = 8.3 Hz, 2H), 5.66 (s, 1H), 3.80 (s, 3H).; ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.6, 133.7, 132.3, 129.8, 129.4, 128.5, 115.0, 113.2, 88.0, 83.7, 55.8, 46.0; $[\alpha]_D^{20}$ +12.0 (*c* 0.10, $CHCl_3$); HR-MS (ESI^+): *m/z* calcd for $C_{13}H_{11}NS$ $[M + H]^+$ 274.0993, found 274.0983.

Typical Procedure for the Preparation of Z-5-alkylidene-1,3-oxazolidin-2-ones: $KHCO_3$ (6 mmol) and Ag_2CO_3 (0.02 mmol) were added to water (5 mL) and stirred at 50 °C, followed by dropwise addition of a solution of propargylic amine hydrochloride (1.0 mmol in 5 mL water), at a rate that no excessive emulsion was formed. The reaction was monitored by TLC. The reaction mixture was extracted with ethyl acetate, the organic phase was washed with 1 N HCl to recover the unreacted propargylic amine. The organic layer was washed with water and brine, dried over Na_2SO_4, concentrated in vacuo, and purified by flash column chromatography.



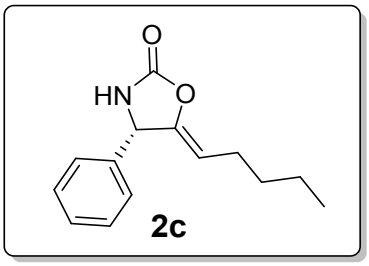
2a

2a: White solid, M.P.: 170 – 171 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.20 (m, 10H), 5.71 (s, 1H), 5.55 (s, 1H), 5.31 (s, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.8, 148.8, 138.7, 133.2, 129.3, 129.2, 128.4, 128.3, 127.1, 127.0, 104.9, 60.6. $[\alpha]_D^{20}$ +96.5 (*c* 0.10, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{16}H_{13}NO_2$ [M + H]$^+$ 252.1019, found 252.1018.



2b

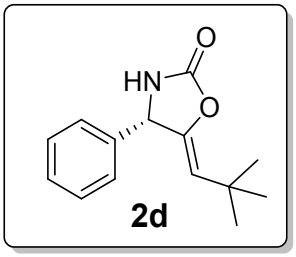
2b: White solid, M.P.: 165 – 166 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.32 (m, 5H), 5.70 (s, 1H), 5.38 (s, 1H), 3.92 (dd, *J* = 9.3 Hz, 1H), 1.74 – 1.67 (m, 1H), 0.80 – 0.69 (m, 2H), 0.35 – 0.22 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.3, 148.1, 139.3, 129.1, 128.9, 126.8, 109.0, 59.6, 7.8, 6.7, 6.6; $[\alpha]_D^{20}$ −52.2 (*c* 0.10, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{13}H_{13}NO_2$ [M + H]$^+$ 216.1019, found 216.1020.



2c

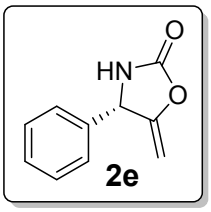
2c: White solid, M.P.: 106 – 107 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.32 (m, 5H), 5.87 (s, 1H), 5.37 (s, 1H), 4.42 (dt, *J* = 7.6, 2.1 Hz, 1H), 2.19 – 2.08 (m, 2H), 1.35-1.25 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.3, 148.5, 139.4, 129.1, 128.9, 126.8, 105.2, 59.5, 31.3, 24.6, 22.1, 13.8; $[\alpha]_D^{20}$ −15.0 (*c* 0.60, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{14}H_{17}NO_2$ [M + H]$^+$232.1332,

found 232.1334.



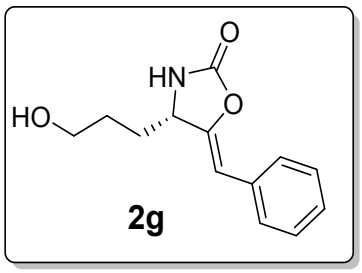
2d

2d: White solid, M.P.: 152 – 153 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 5H), 5.64 (s, 1H), 5.32 (s, 1H), 4.34 (d, *J* = 2.0 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2, 146.7, 139.7, 129.1, 128.9, 126.9, 115.1, 60.0, 30.2, 29.7; $[\alpha]_D^{20}$ −65.0 (*c* 0.30, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{14}H_{17}NO_2$ [M + H]$^+$ 232.1332, found 232.1335.



2e

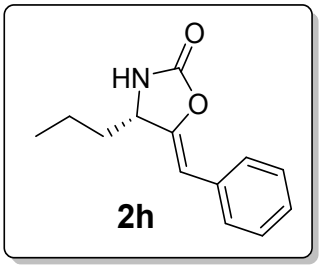
2e: White solid, M.P.: 117 – 118 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.33 (m, 5H), 6.04 (s, 1H), 5.41 (t, *J* = 2.4 Hz, 1H), 4.78 (m, 1H), 4.13 (q, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.11, 155.95, 151.7, 138.7, 129.2, 129.1, 126.7, 88.4, 59.8; $[\alpha]_D^{20}$ −16.0 (*c* 0.10, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{10}H_{19}NO_2$ [M + H]$^+$ 176.0707, found 176.0710.



2g

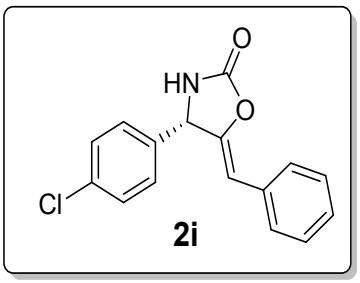
2g: White solid, M.P.: 159 – 160 °C; ^{1}H NMR (400 MHz, MeOD) δ 7.56 (d, *J* = 5.0 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.21 – 7.17 (m, 1H), 5.63 (d, *J* = 2.0 Hz, 1H), 4.65 – 4.63 (m, 1H), 3.63 (t, *J* = 6.2 Hz, 2H), 1.94 – 1.88 (m, 1 H), 1.71 – 1.78 (m, 1H), 1.70 – 1.63 (m, 2H). ^{13}C NMR (100 MHz, MeOD) δ 149.4, 133.9, 127.9, 127.8, 126.2, 101.8, 61.0, 56.3, 32.4, 26.9; $[\alpha]_D^{20}$ −75.2 (*c* 0.06, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for

$C_{13}H_{15}NO_3$ $[M + H]^+$ 234.1125, found 234.1127.



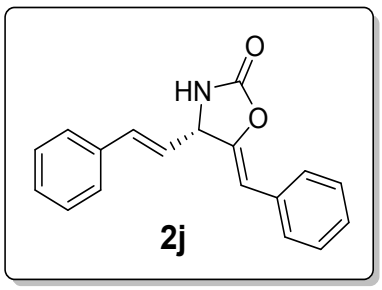
2h

2h: White solid, M.P.: 134 – 135 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.36 – 7.20 (m, 3H), 6.54 (s, 1H), 5.49 (s, 1H), 4.56 (t, *J* = 5.8 Hz, 1H), 1.70 – 1.80 (m, 2H), 1.53 – 1.43 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.5, 148.9, 133.4, 128.4, 128.3, 126.8, 102.7, 56.5, 38.5, 18.0, 13.7; $[\alpha]_D^{20}$ –43.0 (*c* 1.00, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{13}H_{15}NO_2$ $[M + H]^+$ 218.1176, found 218.1173.



2i

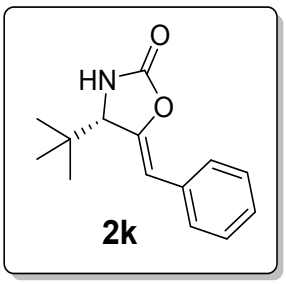
2i: White solid, M.P.: 159 – 160 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.20 (m, 7H), 5.92 (s, 1H), 5.54 (s, 1H), 5.28 (s, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.5, 148.3, 137.2, 132.9, 129.5, 128.5, 128.44, 128.35, 127.2, 105.2, 60.0; $[\alpha]_D^{20}$ +83.0 (*c* 0.40, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{16}H_{12}NClO_2$ $[M + H]^+$ 286.0629, found 286.0627.



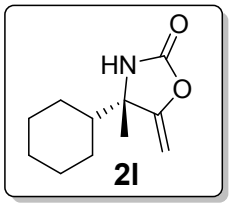
2j

2j: White solid, M.P.: 173 – 174 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.47 – 7.28 (m, 8 H), 6.72 (d, *J* = 15.6 Hz, 1H), 6.17 (q, *J* = 15.6 Hz, 1H), 5.59 (s, 1H), 5.54 (d, *J* = 2.0 Hz, 1H), 5.19 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR

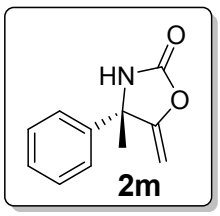
(100 MHz, Chloroform-*d*) δ 155.8, 147.2, 135.2, 135.0, 133.2, 128.8, 128.7, 128.5, 128.3, 127.1, 126.8, 125.3, 104.5, 59.5; $[\alpha]_D^{20}$ −25.0 (*c* 0.12, $CHCl_3$); HR-MS (ESI^+): *m/z* calcd for $C_{18}H_{15}NO_2$ $[M + H]^+$ 278.1176, found 278.1173.



2k: White solid, M.P.: 214 – 215 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.59 (m, 2H), 7.36 – 7.27 (m, 3H), 6.41 (br, 1H), 5.57 (s, 1H), 4.12 (s, 1H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.7, 146.6, 133.3, 128.6, 128.4, 127.0, 105.8, 66.1, 35.8, 24.9; $[\alpha]_D^{20}$ −128.0 (*c* 0.18, $CHCl_3$); HR-MS (ESI^+): *m/z* calcd for $C_{14}H_{17}NO_2$ $[M + H]^+$ 232.1338, found 232.1329.

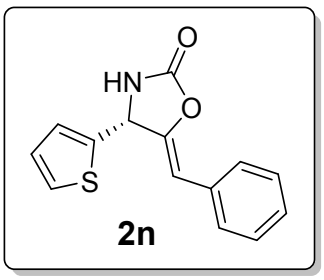


2l: colorless liquid, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.06 (br, 1H), 4.67 (s, 1H), 4.16 (s, 1H), 1.83 (m, 1H), 1.41 (s, 3H), 1.39 – 0.94 (m, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.8, 156.5, 84.9, 64.4, 47.5, 26.6, 26.3, 26.1, 26.0, 25.9, 25.5; $[\alpha]_D^{20}$ −69.0 (*c* 0.60, $CHCl_3$); HR-MS (ESI^+): *m/z* calcd for $C_{11}H_{17}NO_2$ $[M + H]^+$ 196.1338, found 196.1337.



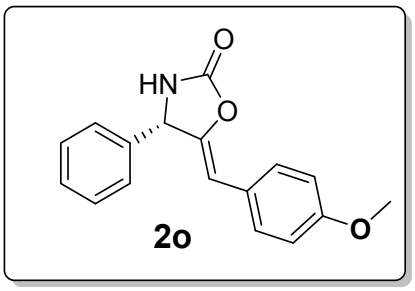
2m: White solid, M.P.: 126 – 128 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.27 (m, 5H), 6.35 (br, 1H), 4.76 (d, *J* = 3.4 Hz, 1H), 4.23 (d, *J* = 3.2 Hz, 1H), 1.89 (s, 3H); ^1H NMR (400 MHz, Chloroform-*d*) δ 161.0, 155.4, 142.3, 128.9, 128.2, 125.0, 87.1, 63.2, 28.3; $[\alpha]_D^{20}$ −52.0 (*c* 0.10, $CHCl_3$); HR-MS (ESI^+): *m/z* calcd for $C_{11}H_{11}NO_2$

$[M + H]^+$ 190.0863, found 190.0867.



2n

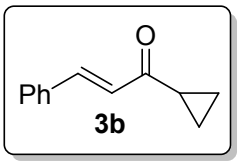
2n: White solid, M.P.: 157 – 158 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.54 (m, 2H), 7.39 – 7.31 (m, 3H), 7.25-7.18 (m, 2H), 7.05 – 7.03 (m, 1H), 5.88 (d, J = 2.0 Hz, 1H), 5.72 (br, 1H), 5.48 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.2, 147.89, 142.0, 133.0, 128.5, 128.4, 127.2, 127.1, 127.0, 126.6, 105.2, 56.0; $[\alpha]_D^{20}$ +16.0 (*c* 0.15, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{14}H_{11}NSO_2$ $[M + H]^+$ 258.0589, found 258.0583.



2o

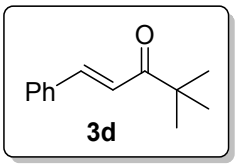
2o: White solid, M.P.: 154 – 155 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.40 (m, 7H), 6.86 (d, J = 8.5 Hz, 2H), 6.00 (s, 1H), 5.54 (s, 1H), 5.27 (s, 1H), 3.81 (s, 3H).; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.6, 156.0, 147.2, 139.0, 129.7, 129.3, 129.2, 127.1, 126.0, 113.9, 104.5, 60.6, 55.3.; $[\alpha]_D^{20}$ +103.0 (*c* 0.20, $CHCl_3$); HR-MS (ESI$^+$): *m/z* calcd for $C_{14}H_{11}NSO_2$ $[M + H]^+$ 282.1125, found 282.1131.

Typical Procedure for Ag-catalysed C–N cleavage of propargylic amines: $KHCO_3$ (6 mmol), $AgNO_3$ (0.05 mmol) and propargylic amine (1.0 mmol) were added to 95% EtOH (5 mL) and stirred at 70 °C. The reaction was monitored by TLC. After completion, the solvent was removed in vacuo. The residue was dissolved in MTBE and washed with 1 N HCl. The organic layer was dried with Na_2SO_4, concentrated in vacuo, and purified by flash column chromatography.



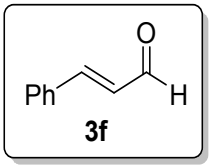
3b

3b: Yellow liquid (59%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 16.1 Hz, 1H), 7.60 – 7.58 (m, 2H), 7.43 – 7.40 (m, 3H), 6.90 (d, *J* = 16.1 Hz, 1H), 2.29 – 2.26 (m, 1H), 1.18 (dt, *J* = 6.8, 3.4 Hz, 2H), 1.00 (dt, *J* = 7.3, 3.7 Hz, 2H).



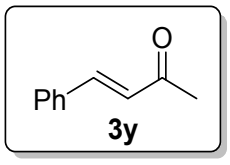
3d

3d: Yellow liquid (61%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 15.6 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.42 – 7.36 (m, 3H), 7.16 (d, *J* = 15.6 Hz, 1H), 1.26 (s, 9H)



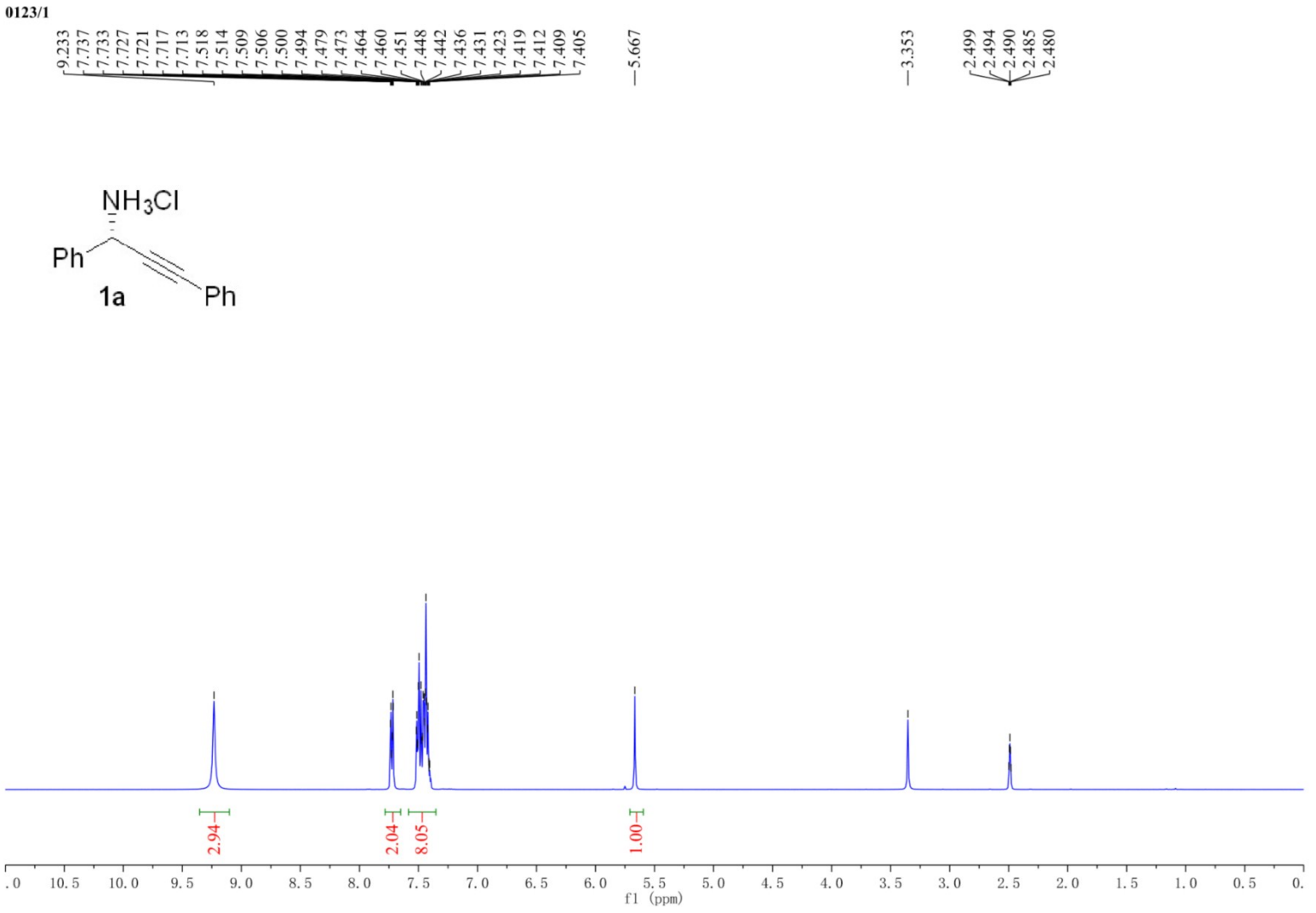
3f

3f: Yellow liquid (66%); ^{1}H NMR (400 MHz, Chloroform-*d*) 9.74 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.43 (m, 6H), 6.75 (dd, *J* = 16.0, 7.7 Hz, 1H);



3y

3y: Yellow liquid (72%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.41 (m, 6H), 6.74 (d, *J* = 16.4 Hz, 1H), 2.41 (s, 3H).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7.733
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7.721
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7.509
7.506
7.500
7.494
7.479
7.473
7.464
7.460
7.451
7.448
7.442
7.436
7.431
7.423
7.419
7.412
7.409
7.405
5.667
3.353
2.499
2.494
2.490
2.485
2.480
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Ph
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Ph
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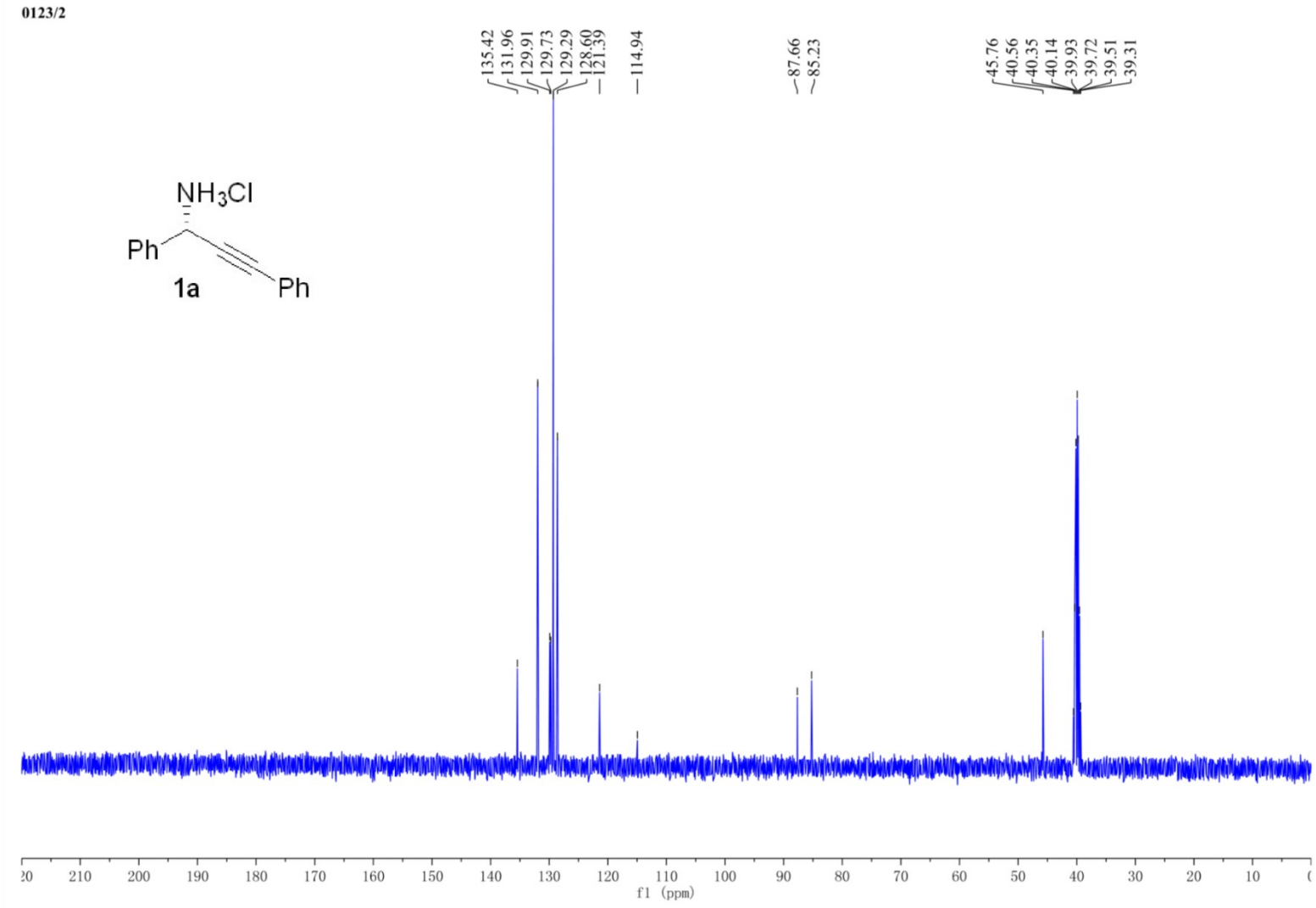
1.00
f1 (ppm)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129.29
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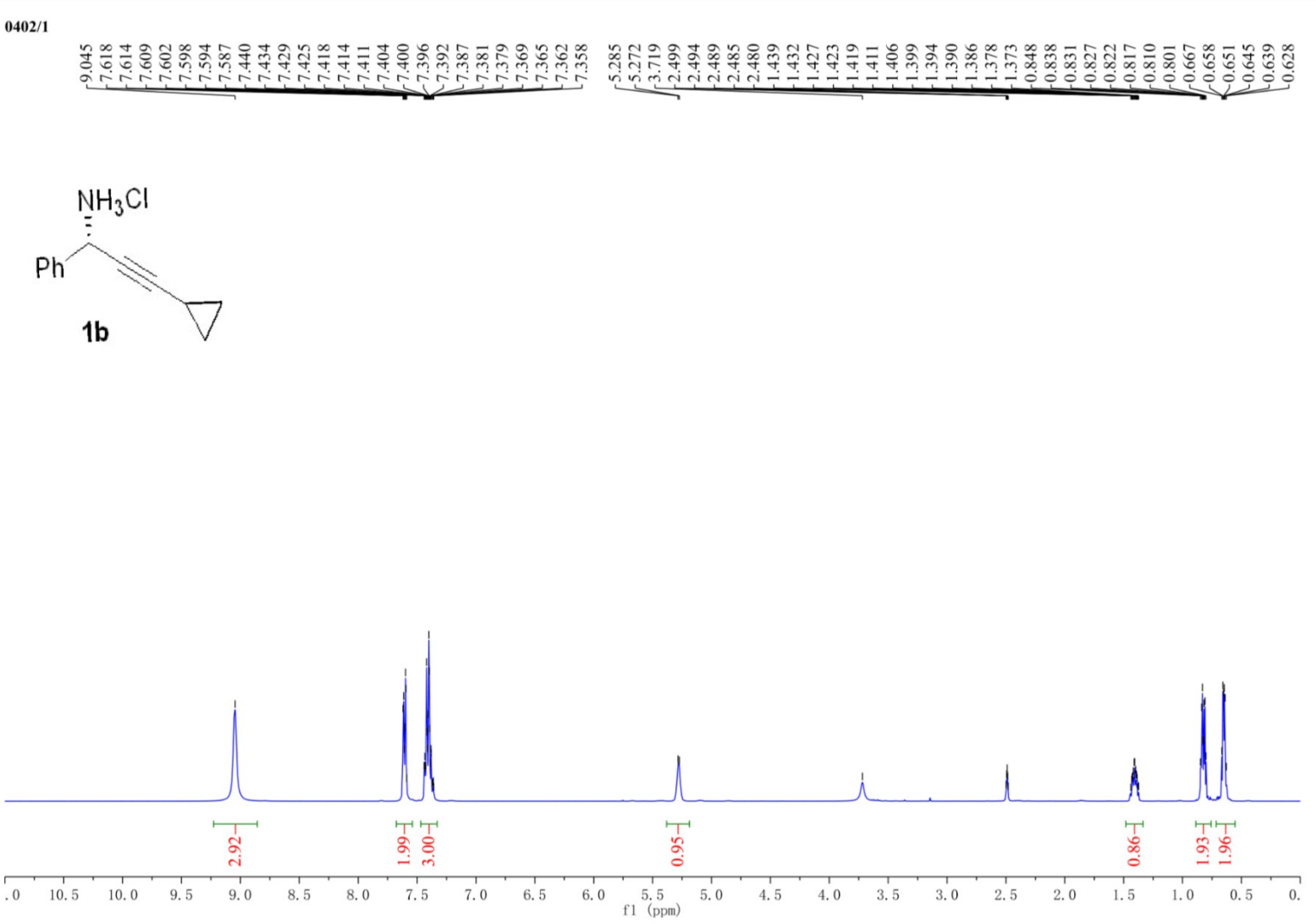
40.14
39.93
39.72
39.51
39.31
NH3Cl
Ph
Ph
1a
f1 (ppm)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7.414
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7.404
7.400
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7.392
7.387
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7.379
7.369
7.365
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7.358
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3.719
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2.489
2.485
2.480
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1.432
1.427
1.423
1.419
1.411
1.406
1.399
1.394
1.390
1.386
1.378
1.373
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0.831
0.827
0.822
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0.810
0.801
0.667
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0.651
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0.639
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Ph
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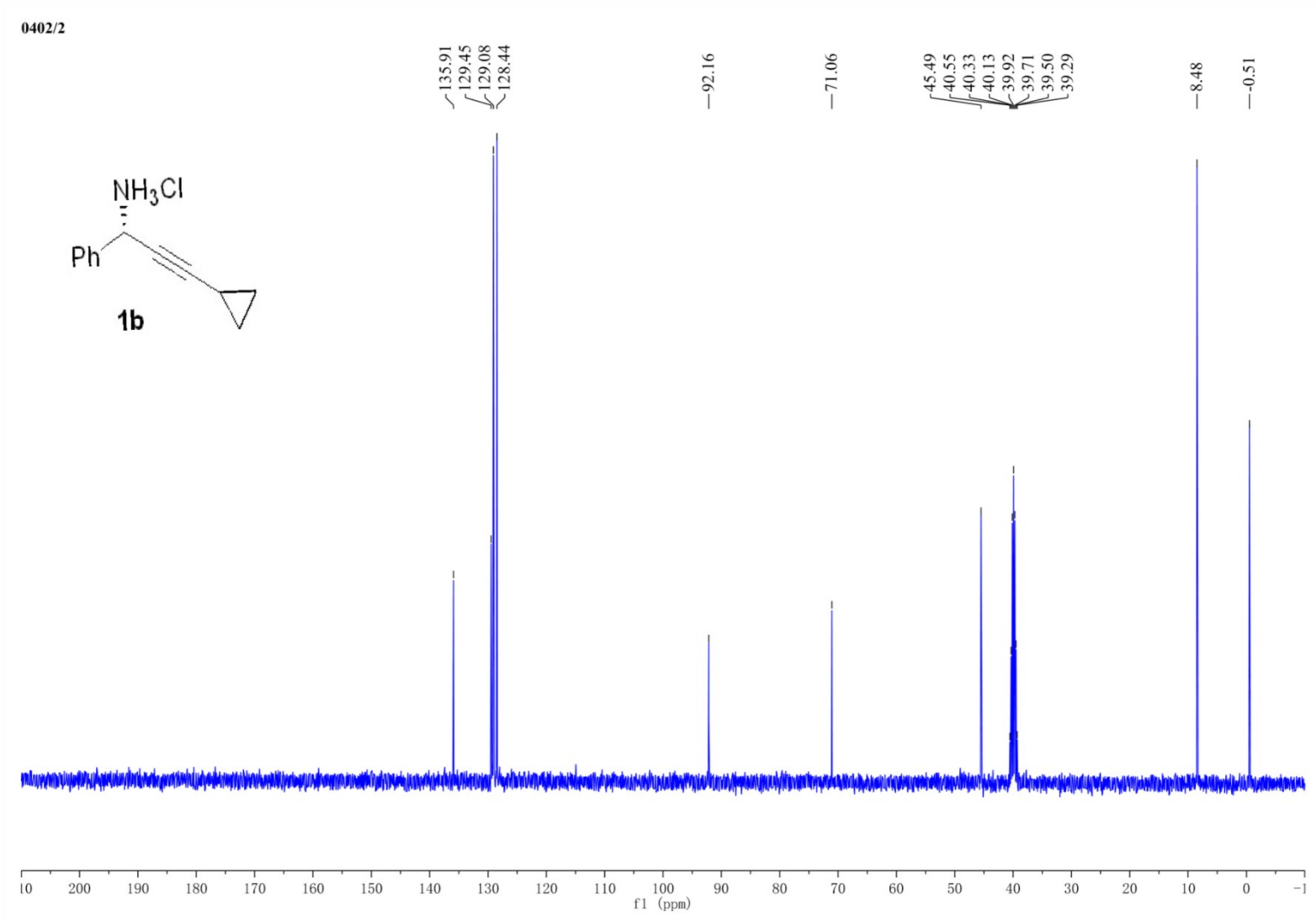
1.96
f1 (ppm)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39.29
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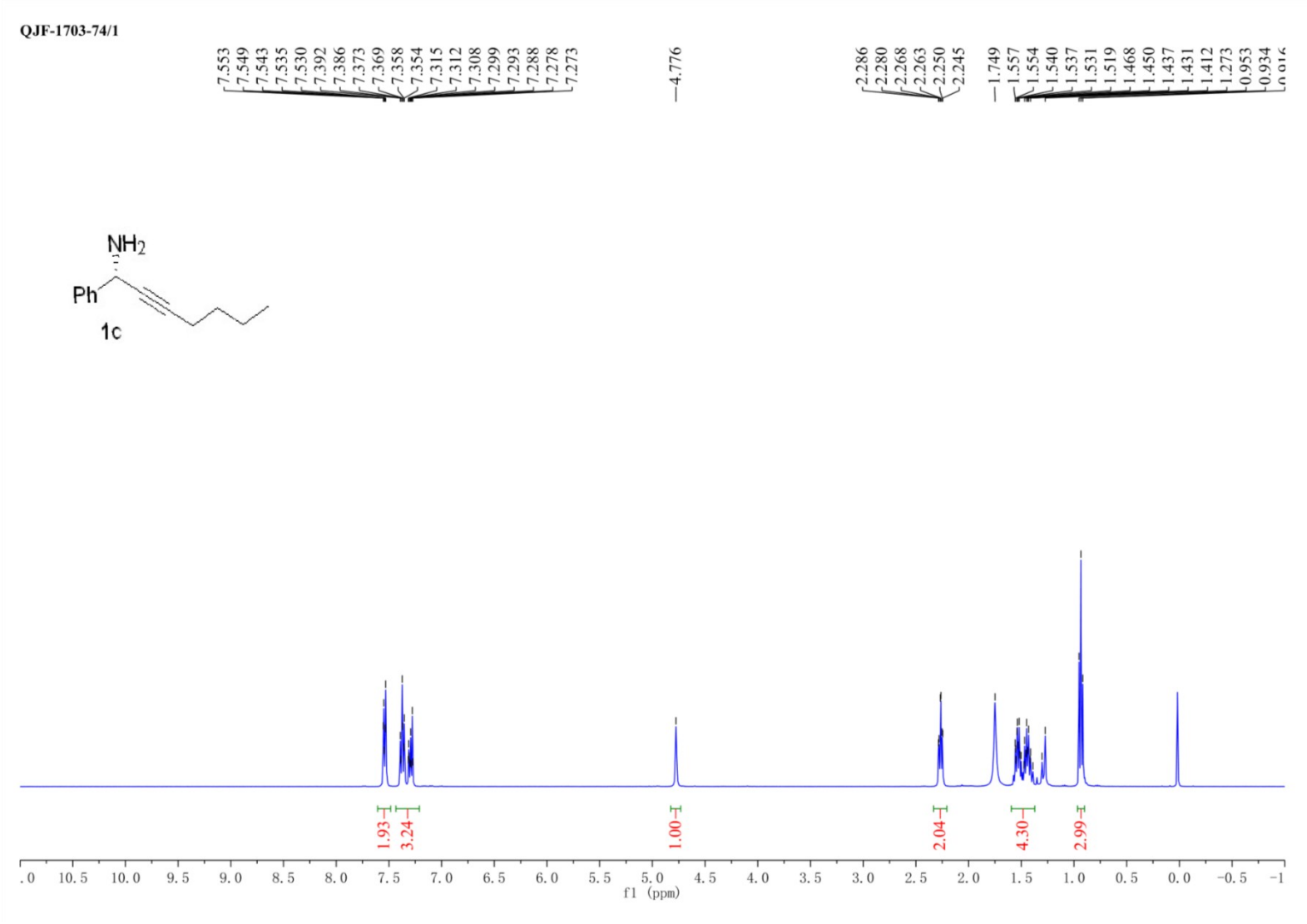
NH3Cl
Ph
1b
f1 (ppm)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7.299
7.293
7.288
7.278
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2.263
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2.245
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1.554
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Ph
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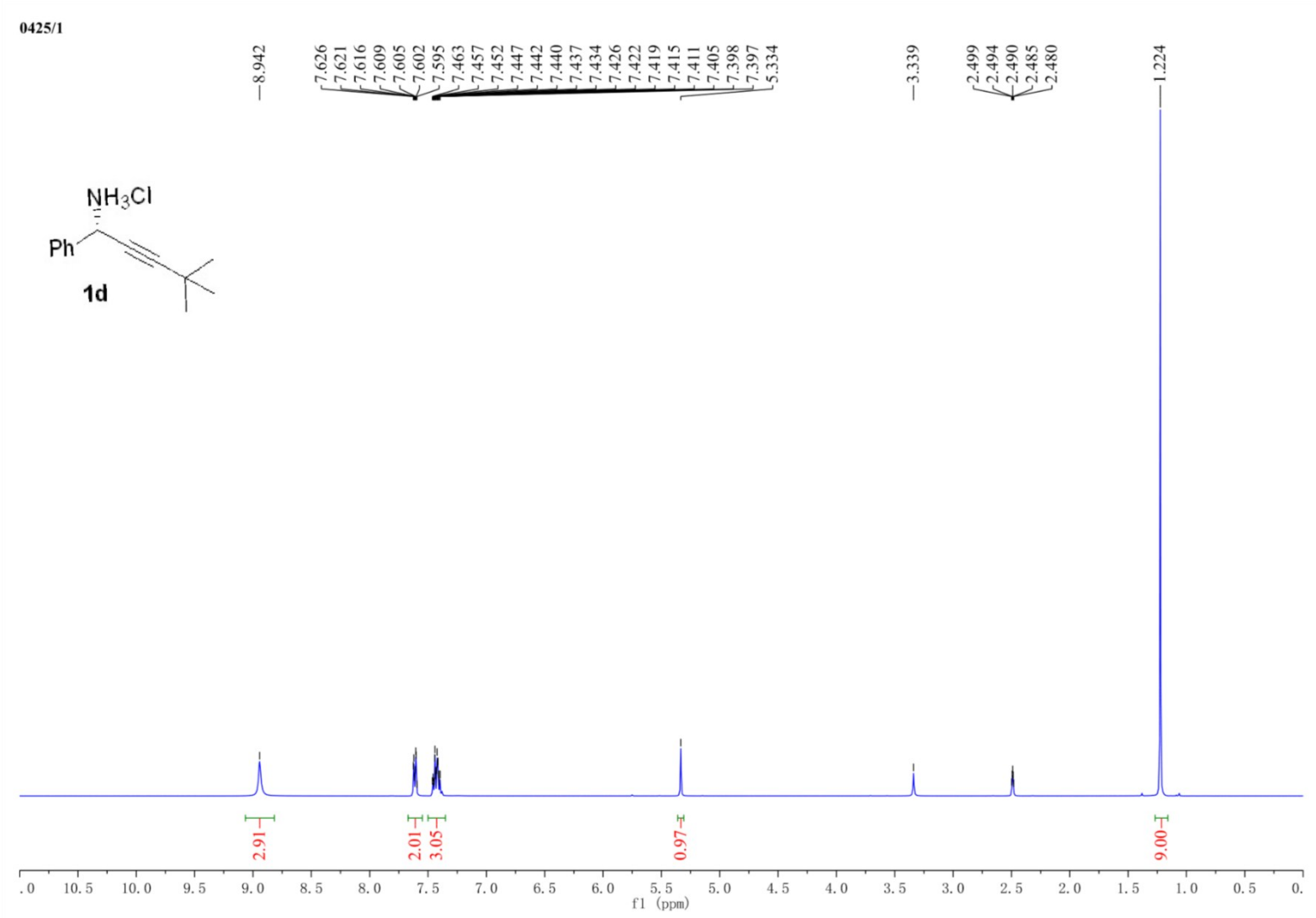
2.99
f1 (ppm)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7.616
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7.595
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7.452
7.447
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7.437
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7.426
7.422
7.419
7.415
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7.397
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2.490
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Ph
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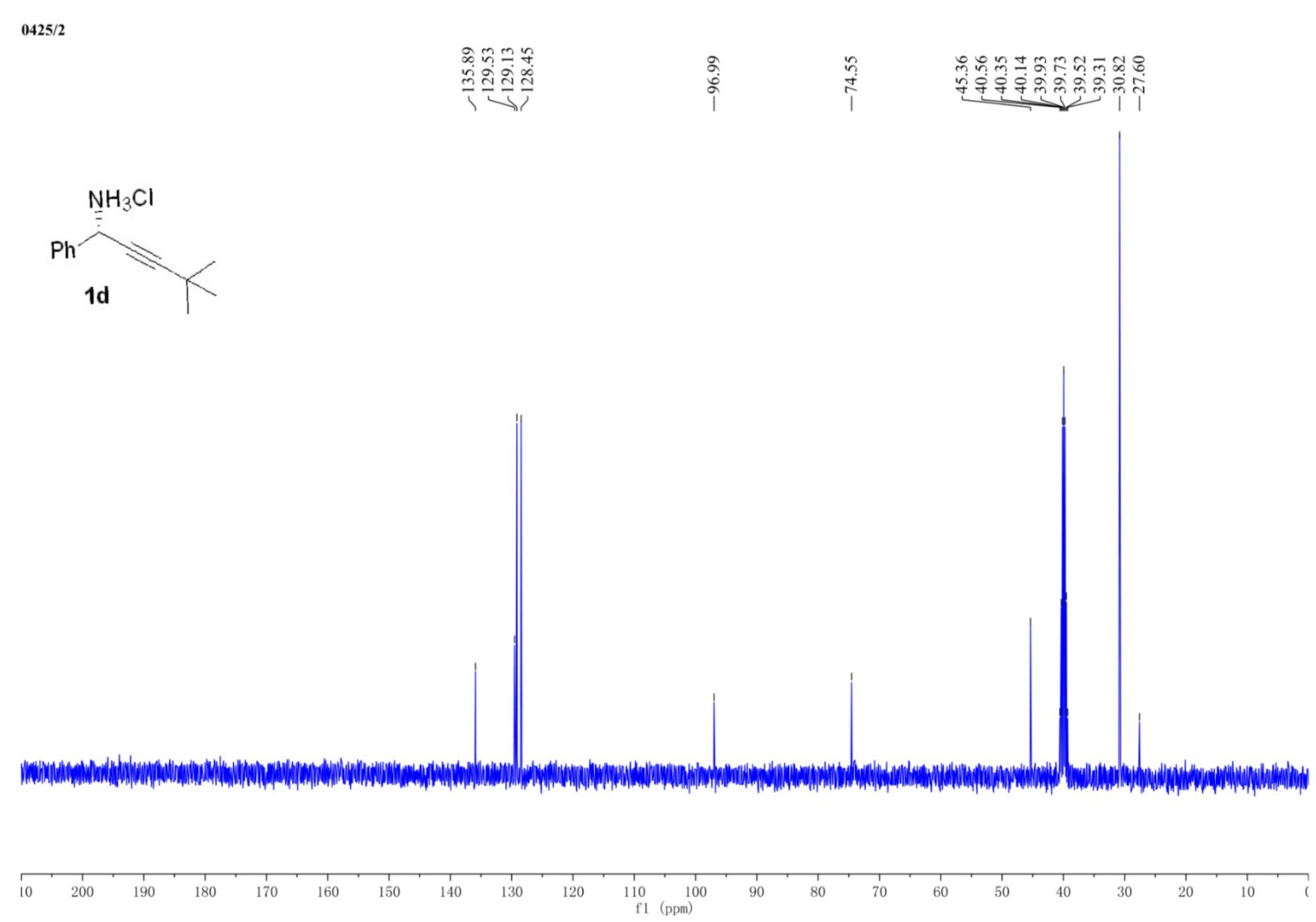
9.00
f1 (ppm)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129.13
128.45
96.99
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45.36
40.56
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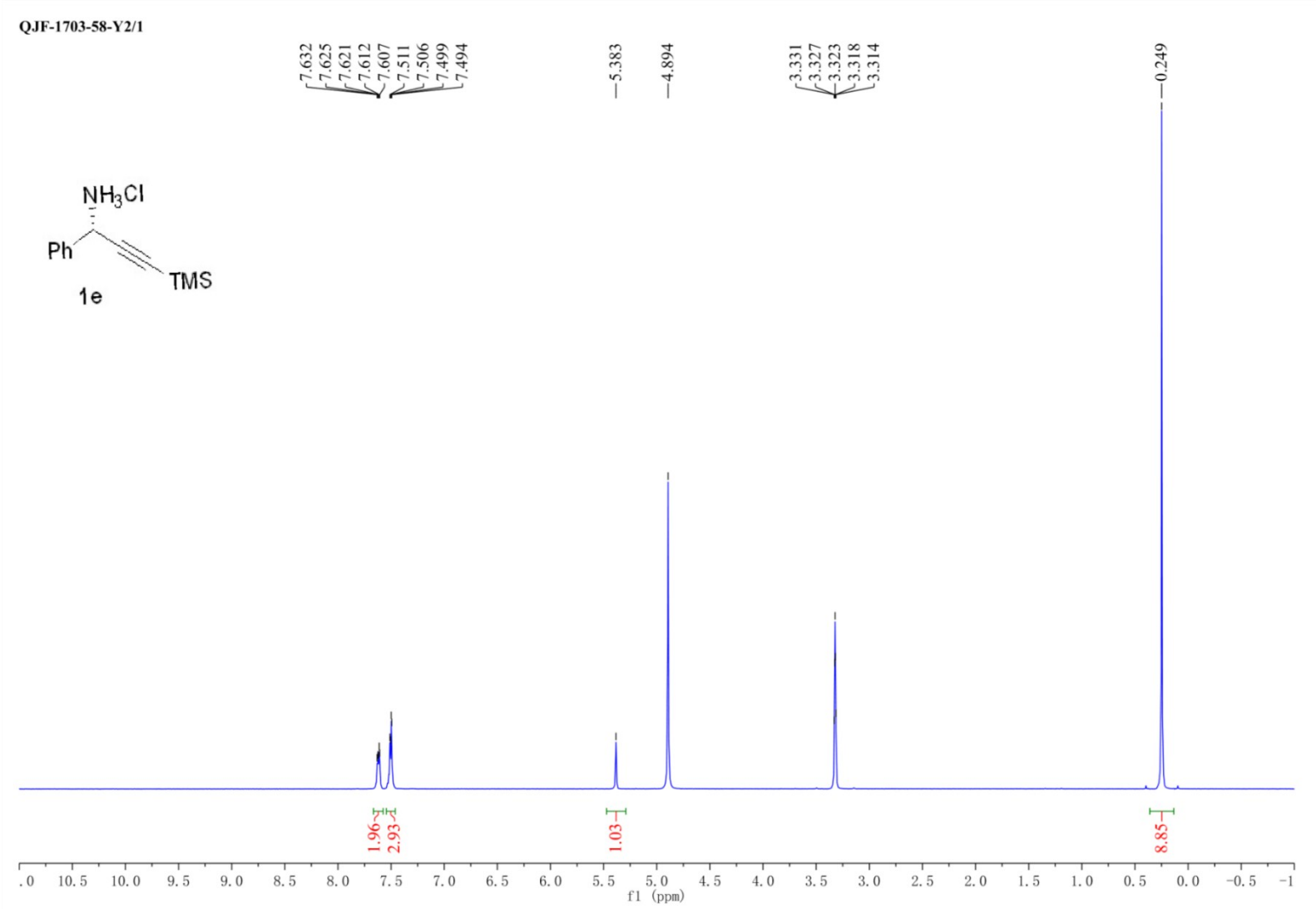
30.82
27.60
NH3Cl
Ph
1d
f1 (ppm)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7.506
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3.327
3.323
3.318
3.314
0.249
NH3Cl
Ph
TMS
1e
1.96
2.93
1.03
8.85
f1 (ppm)

0433/1

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7.647
7.642
7.627
7.623
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7.462
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7.432
7.428
7.422
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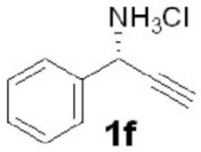
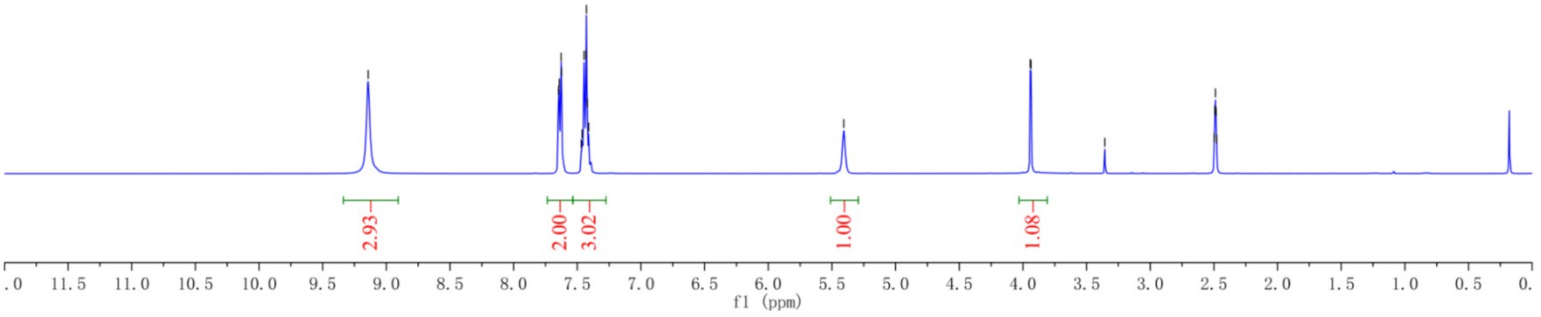
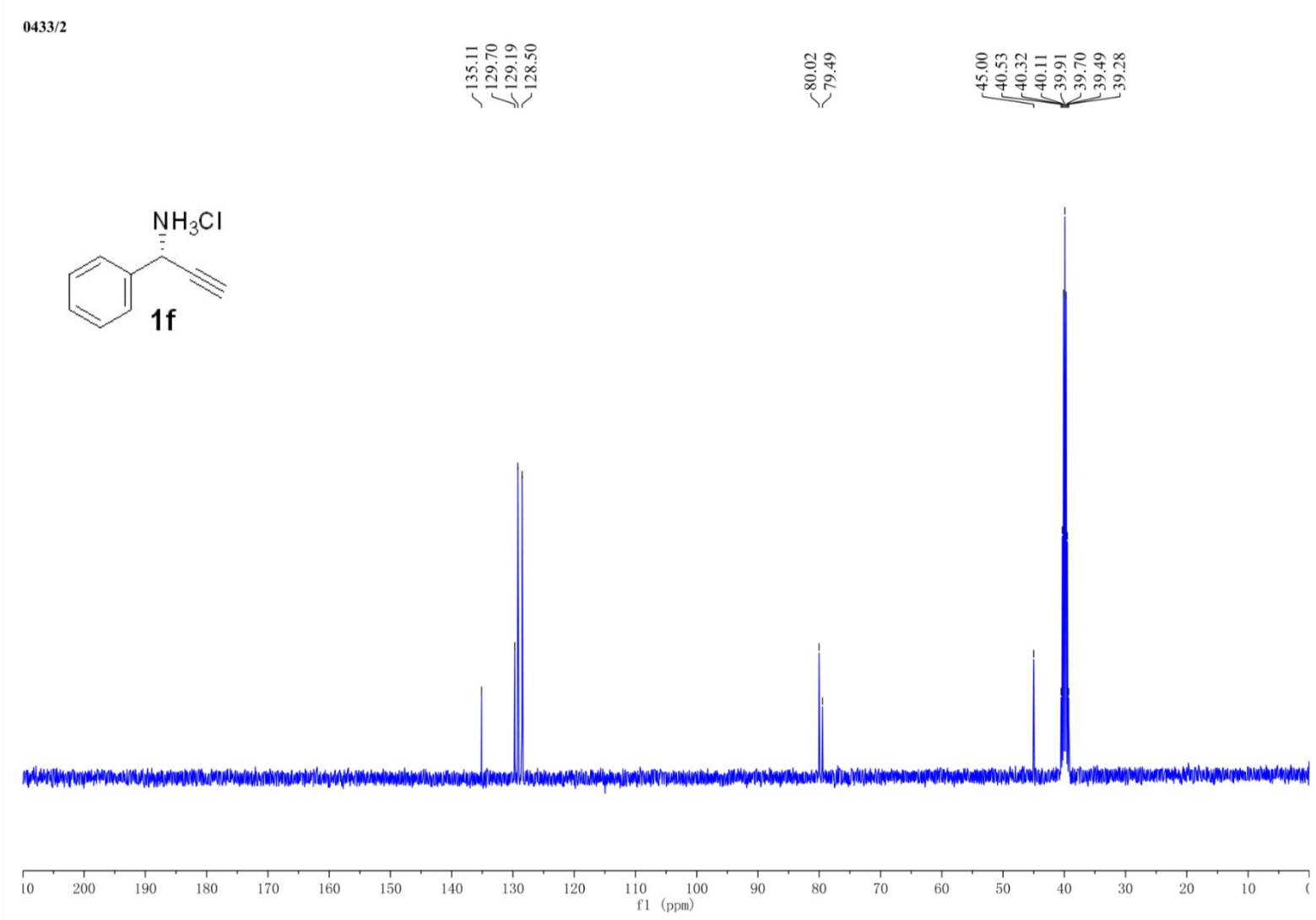
2.479



1f

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45.00
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40.32
40.11
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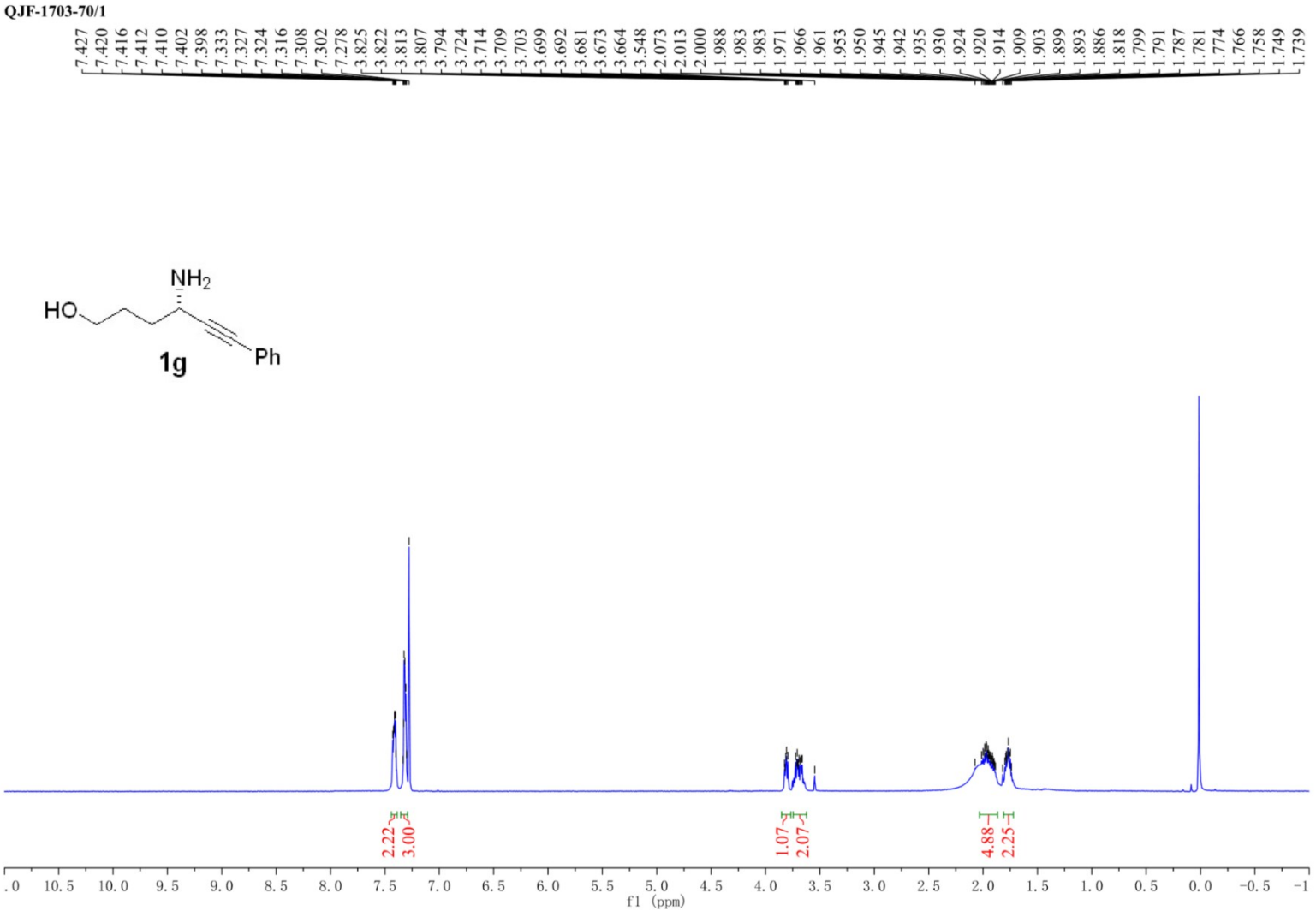
39.49
39.28
NH3Cl
1f
f1 (ppm)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3.822
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3.807
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3.724
3.714
3.709
3.703
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3.692
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1.818
1.799
1.791
1.787
1.781
1.774
1.766
1.758
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HO
Ph
1g
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2.07
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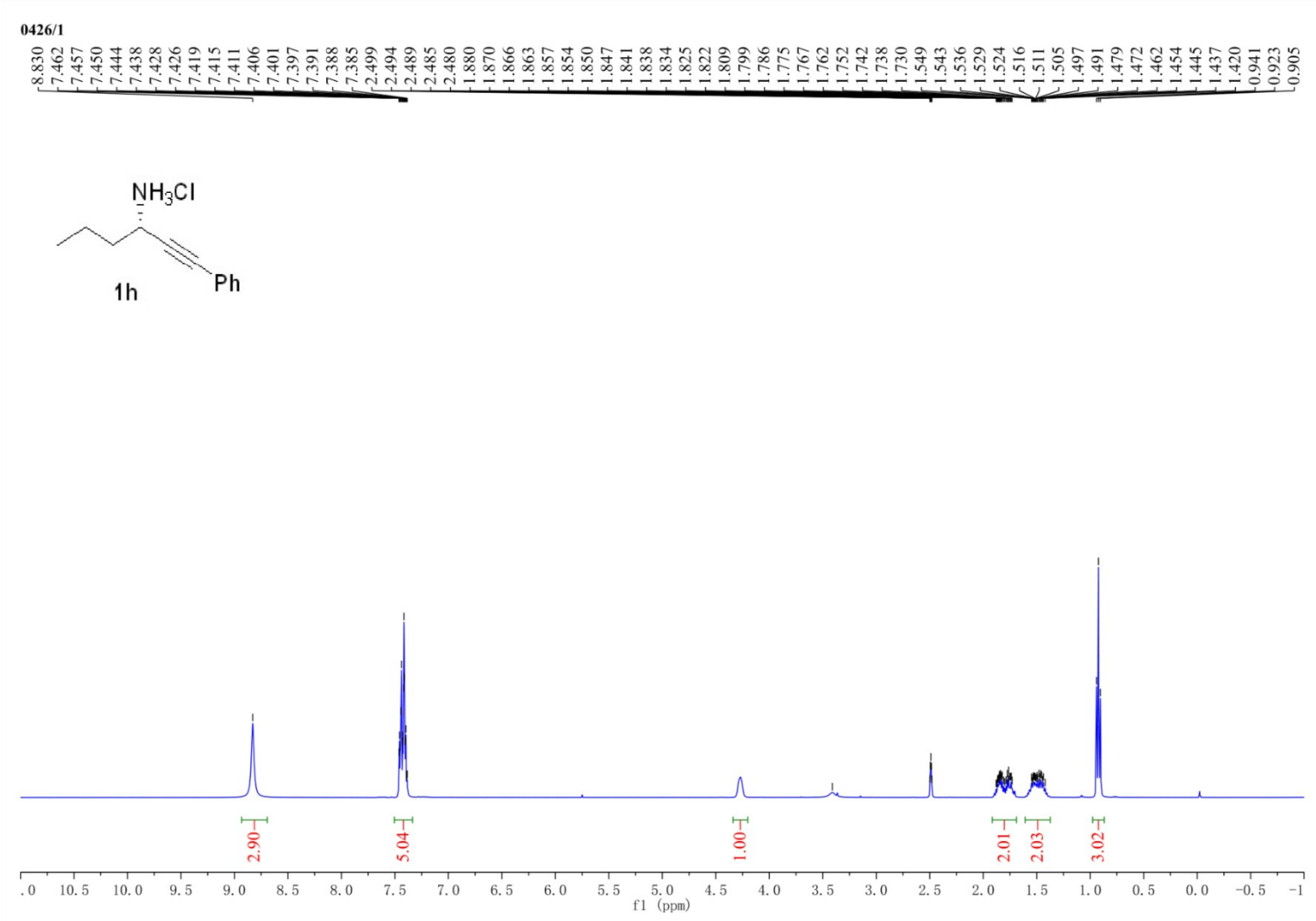
2.25
f1 (ppm)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7.388
7.385
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2.494
2.489
2.485
2.480
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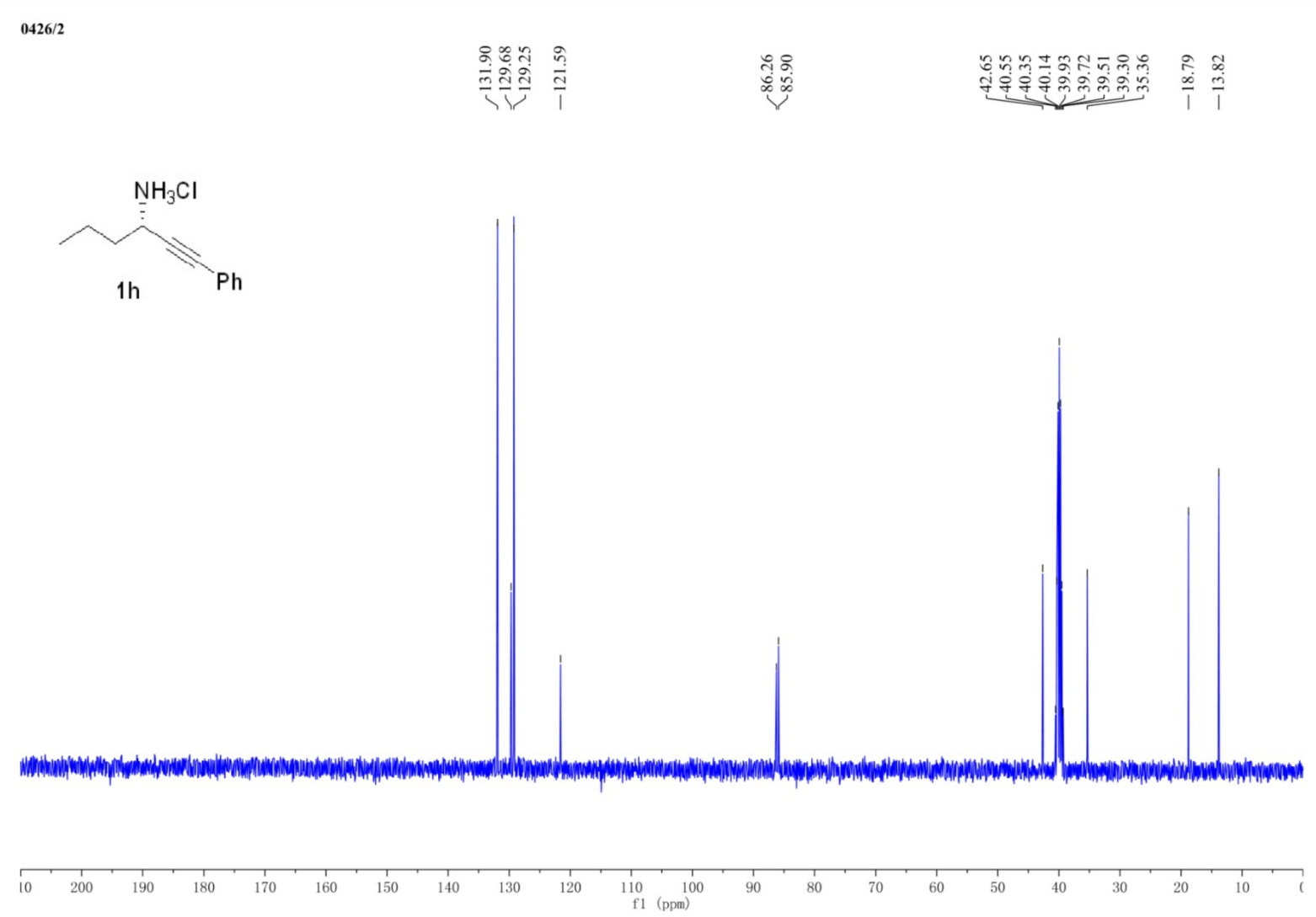
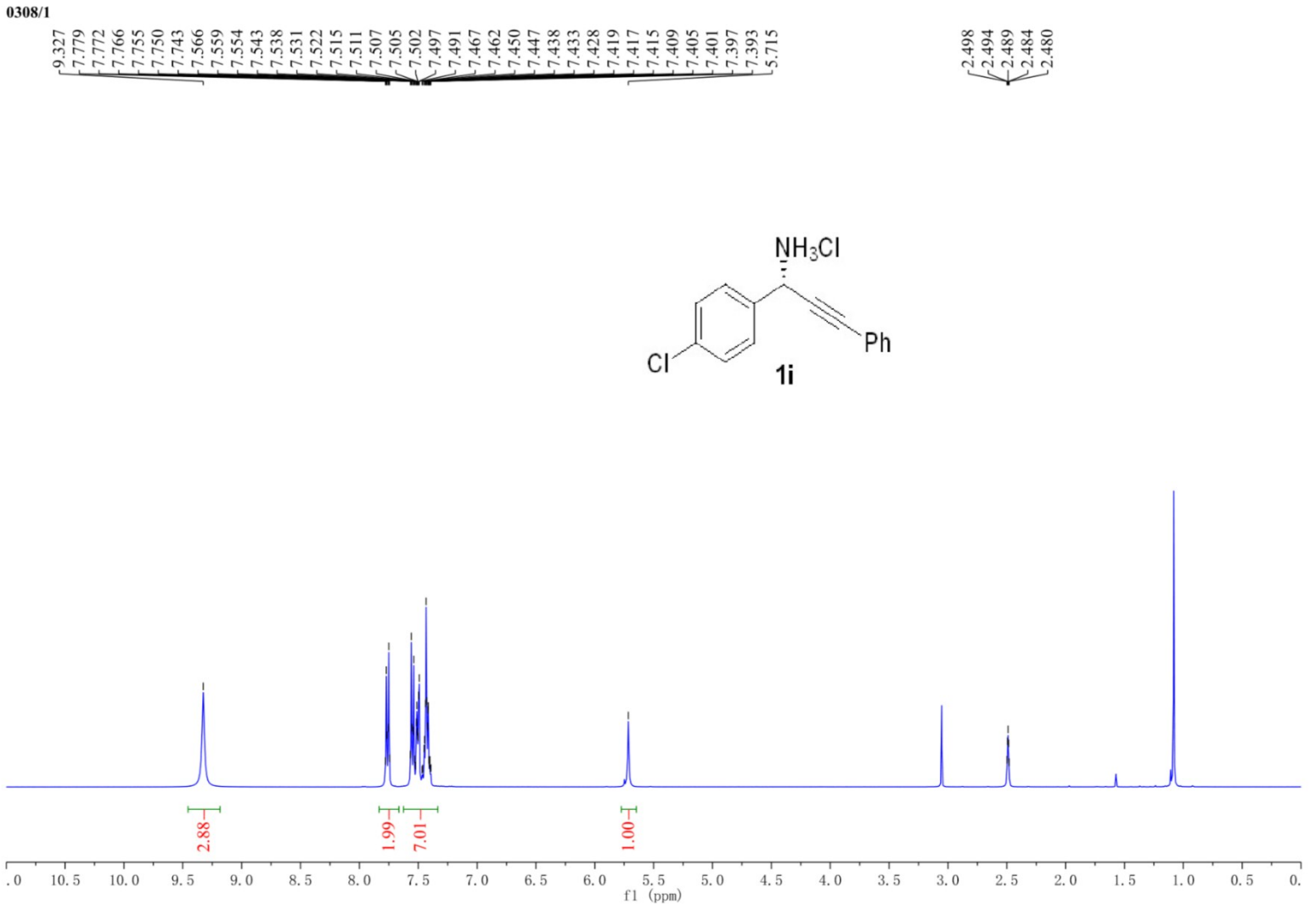
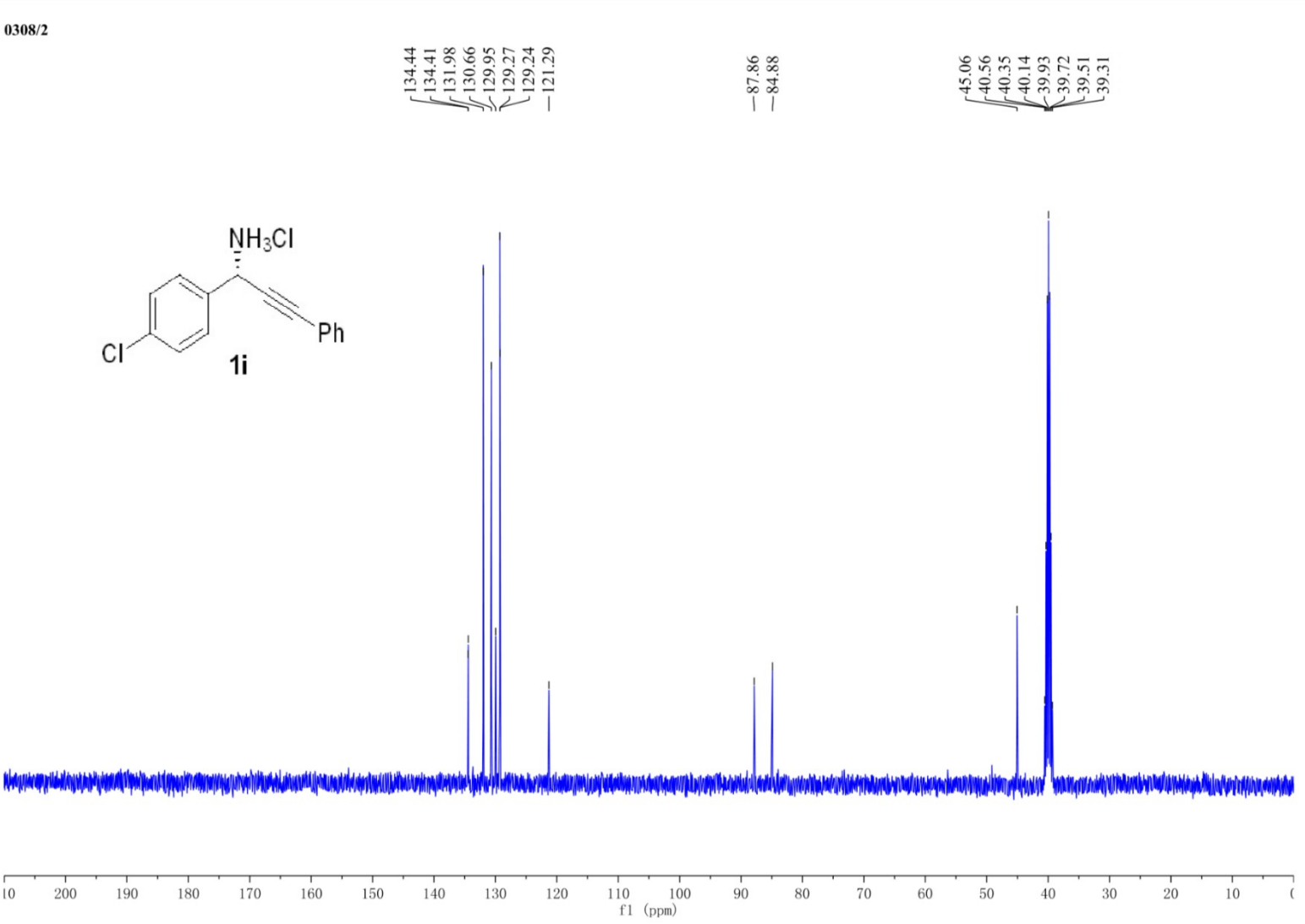
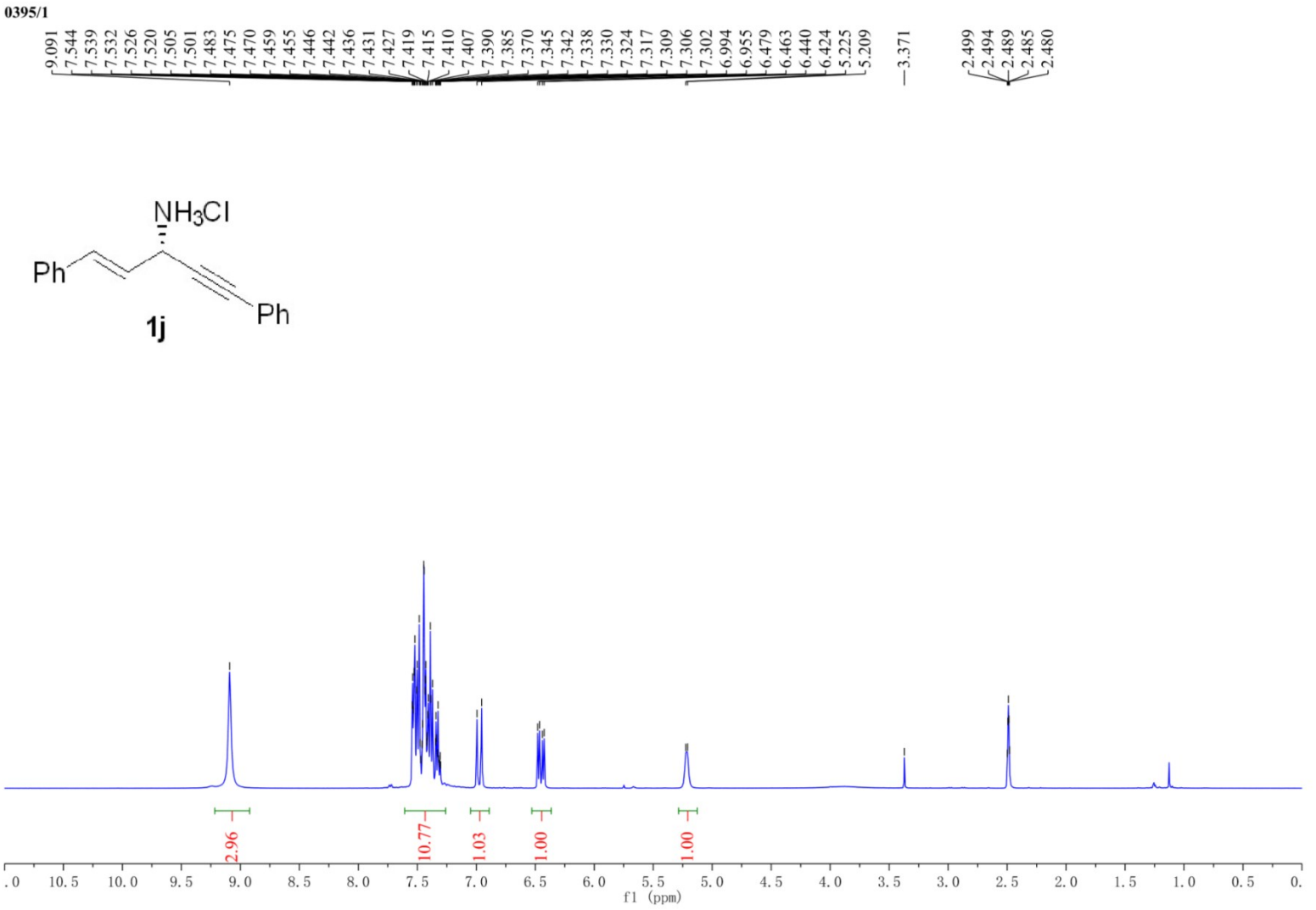
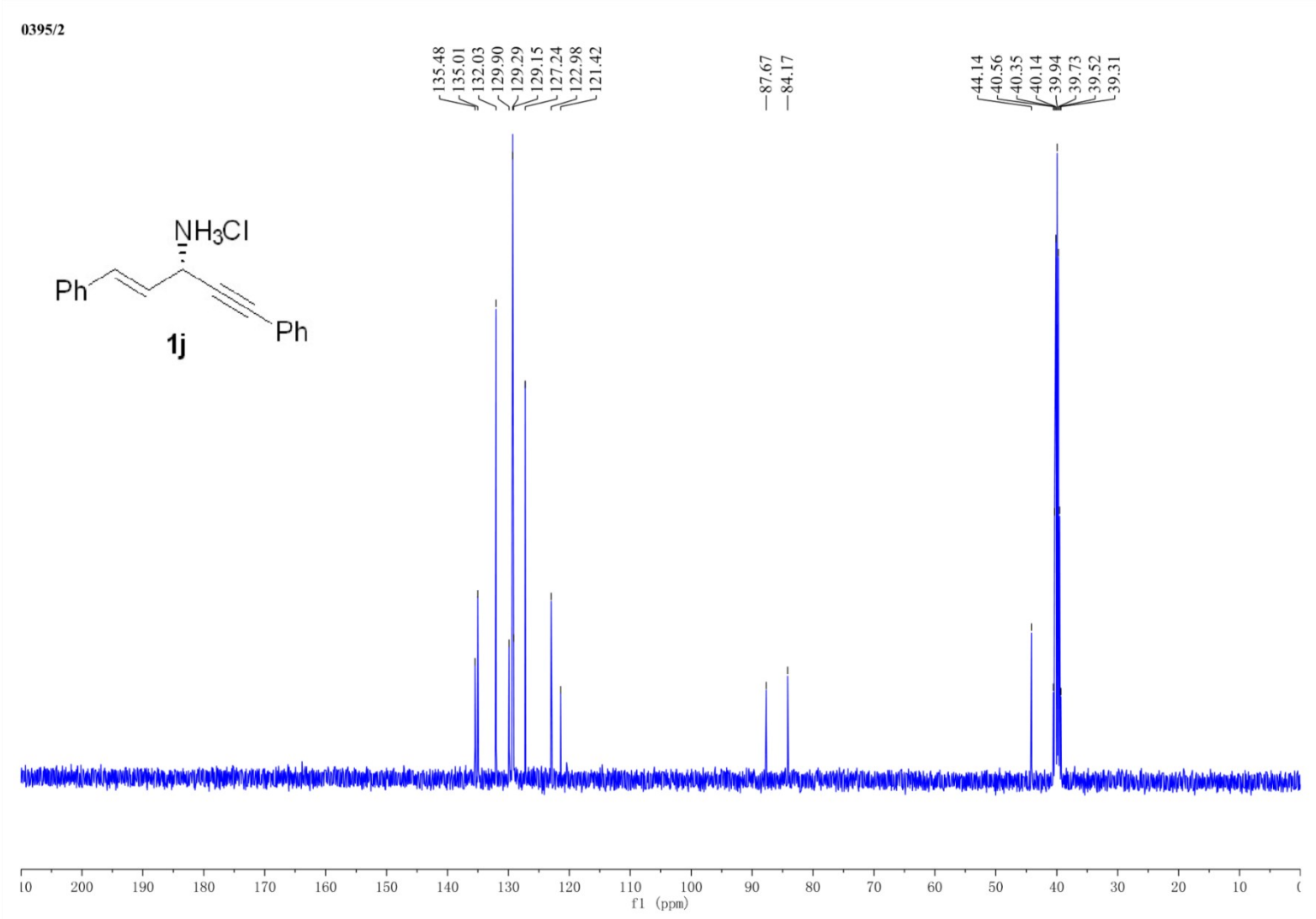
1.870
1.866
1.863
1.857
1.854
1.850
1.847
1.841
1.838
1.834
1.825
1.822
1.809
1.799
1.786
1.775
1.767
1.762
1.752
1.742
1.738
1.730
1.549
1.543
1.536
1.529
1.524
1.516
1.511
1.505
1.497
1.491
1.479
1.472
1.462
1.454
1.445
1.437
1.420
0.941
0.923
0.905
NH3Cl
Ph
1h
2.90
5.04
1.00
2.01
2.03
3.02
f1 (ppm)

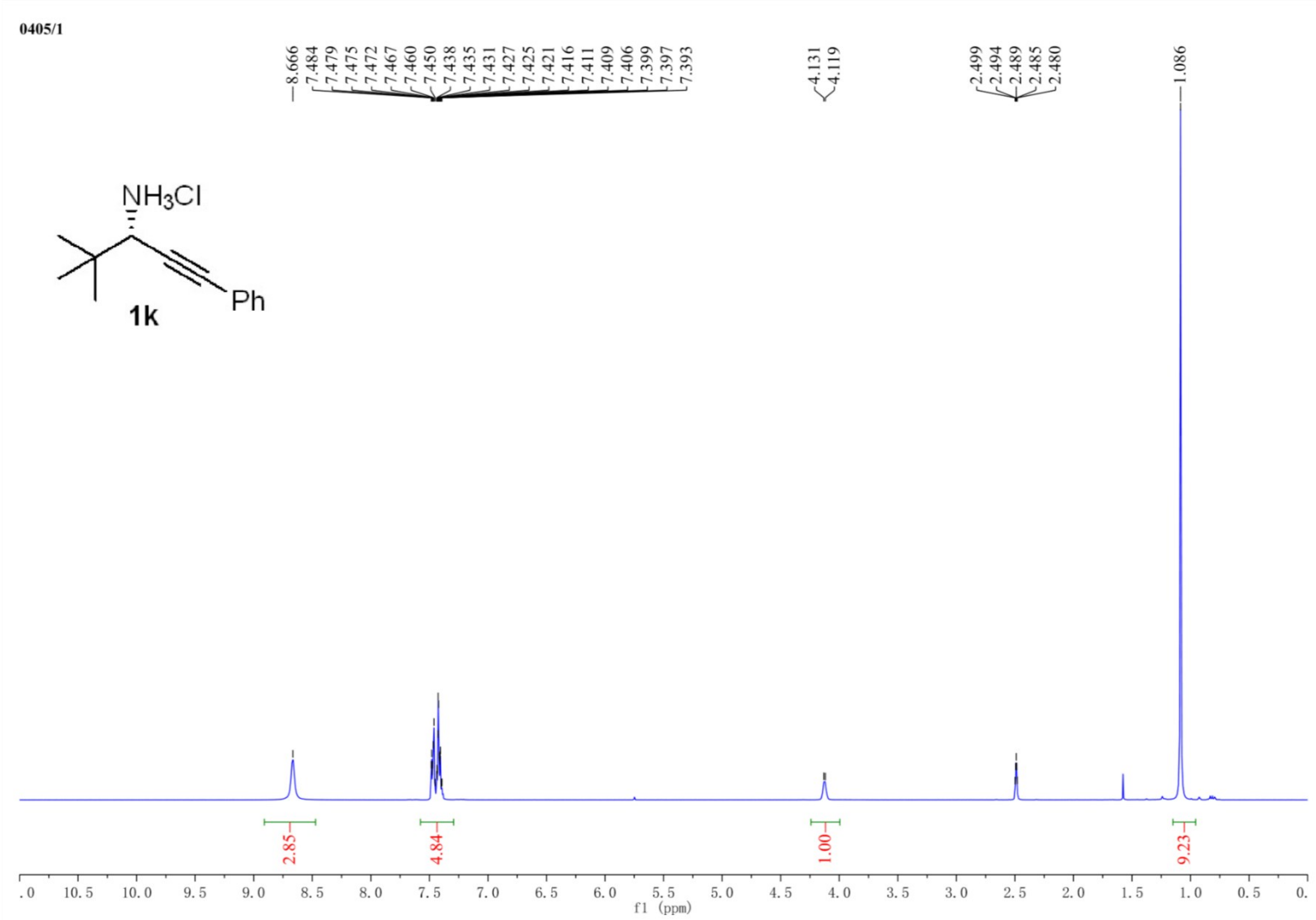

0426/2
131.90
129.68
129.25
121.59
86.26
85.90
42.65
40.55
40.35
40.14
39.93
39.72
39.51
39.30
35.36
18.79
13.82
NH3Cl
Ph
1h
f1 (ppm)

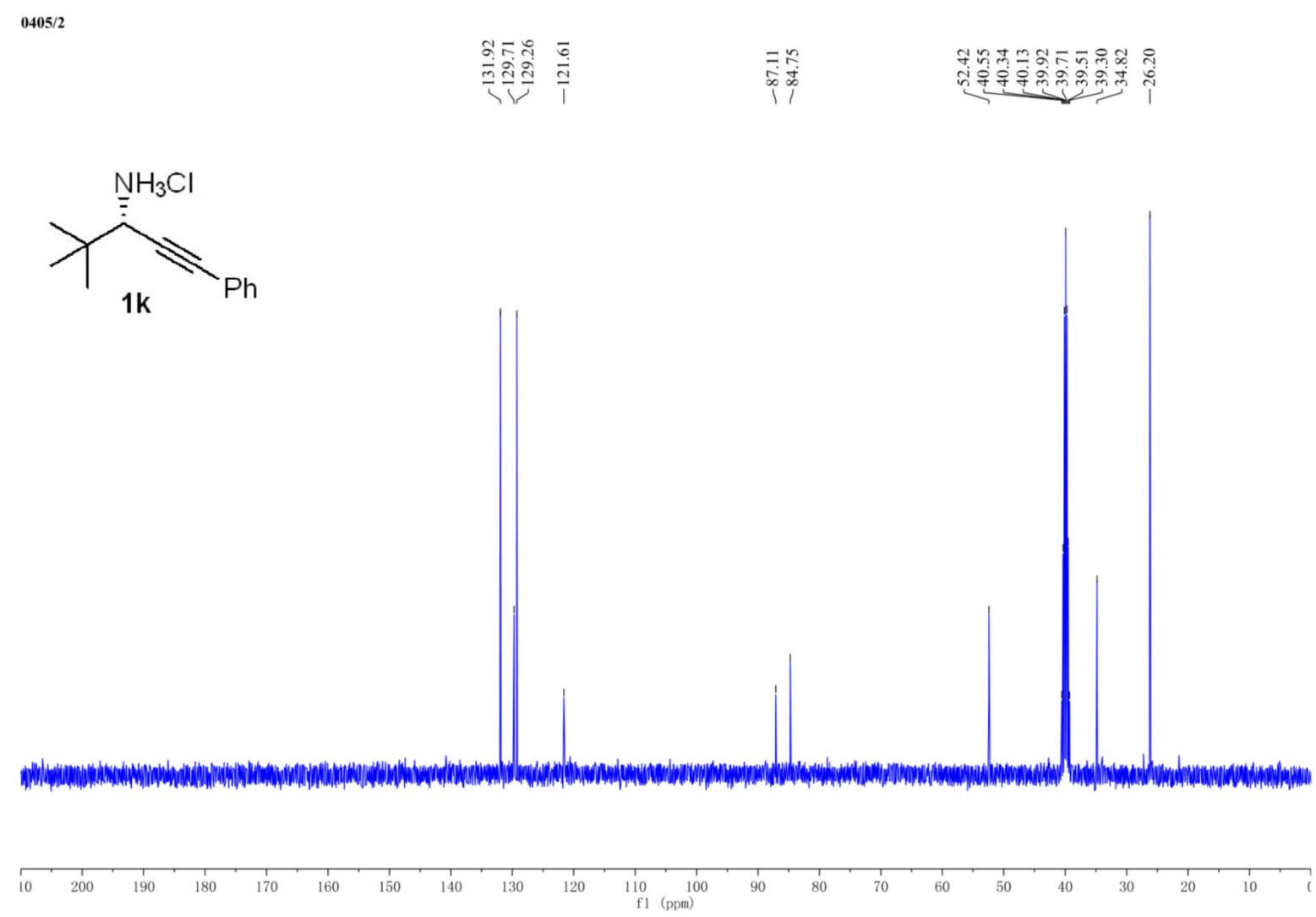

0308/1
9.327
7.779
7.772
7.766
7.755
7.750
7.743
7.566
7.559
7.554
7.543
7.538
7.531
7.522
7.515
7.511
7.507
7.505
7.502
7.497
7.491
7.467
7.462
7.450
7.447
7.438
7.433
7.428
7.419
7.417
7.415
7.409
7.405
7.401
7.397
7.393
5.715
2.498
2.494
2.489
2.484
2.480
NH3Cl
Cl
Ph
1i
2.88
1.99
7.01
1.00
f1 (ppm)

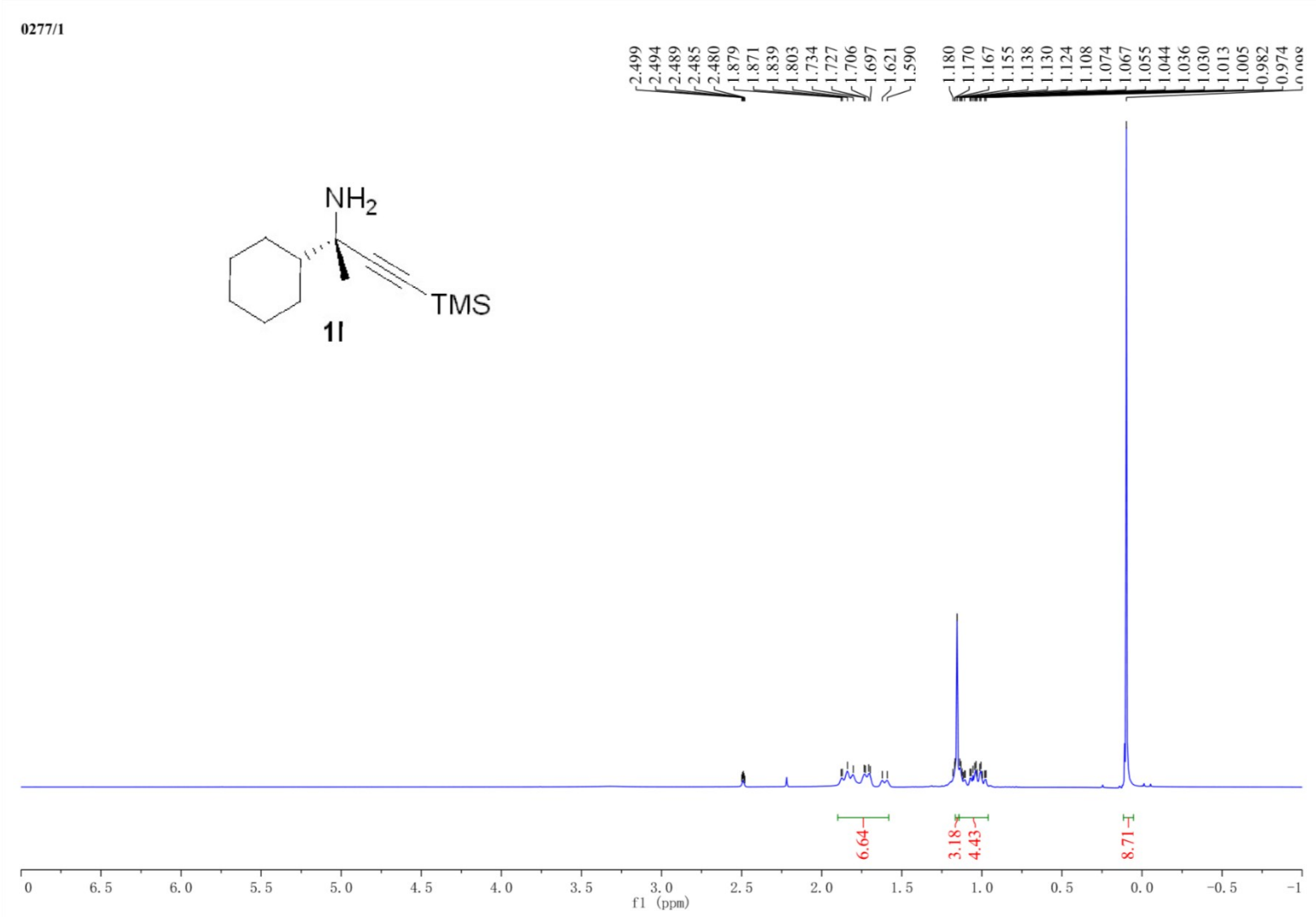

0308/2
134.44
134.41
131.98
130.66
129.95
129.27
129.24
121.29
87.86
84.88
45.06
40.56
40.35
40.14
39.93
39.72
39.51
39.31
NH3Cl
Cl
Ph
1i
f1 (ppm)

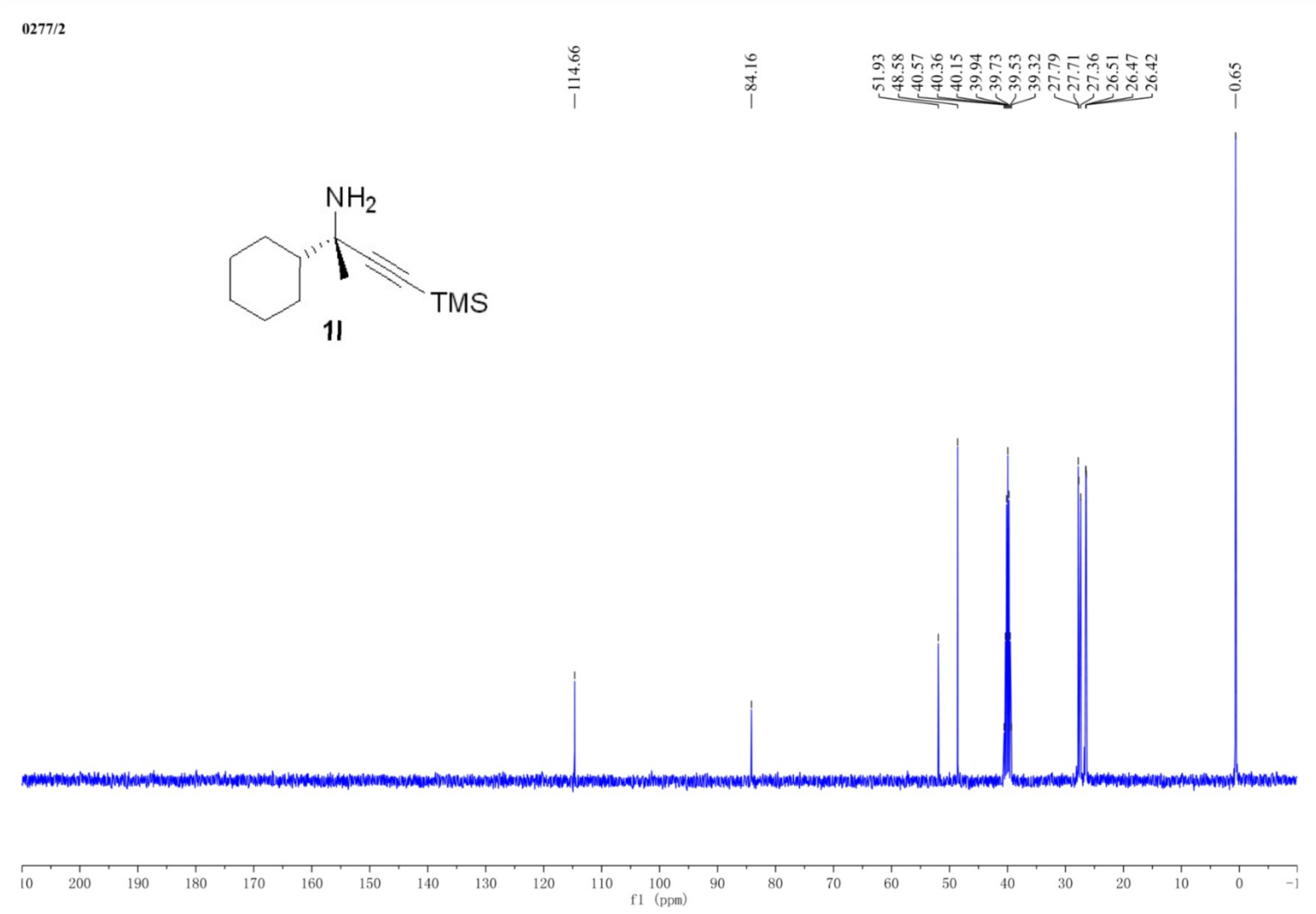

0395/1
9.091
7.544
7.539
7.532
7.526
7.520
7.505
7.501
7.483
7.475
7.470
7.459
7.455
7.446
7.442
7.436
7.431
7.427
7.419
7.415
7.410
7.407
7.390
7.385
7.370
7.345
7.342
7.338
7.330
7.324
7.317
7.309
7.306
7.302
6.994
6.955
6.479
6.463
6.440
6.424
5.225
5.209
3.371
2.499
2.494
2.489
2.485
2.480
NH3Cl
Ph
Ph
1j
2.96
10.77
1.03
1.00
1.00
f1 (ppm)


0395/2
135.48
135.01
132.03
129.90
129.29
129.15
127.24
122.98
121.42
87.67
84.17
44.14
40.56
40.35
40.14
39.94
39.73
39.52
39.31
NH3Cl
Ph
Ph
1j
f1 (ppm)

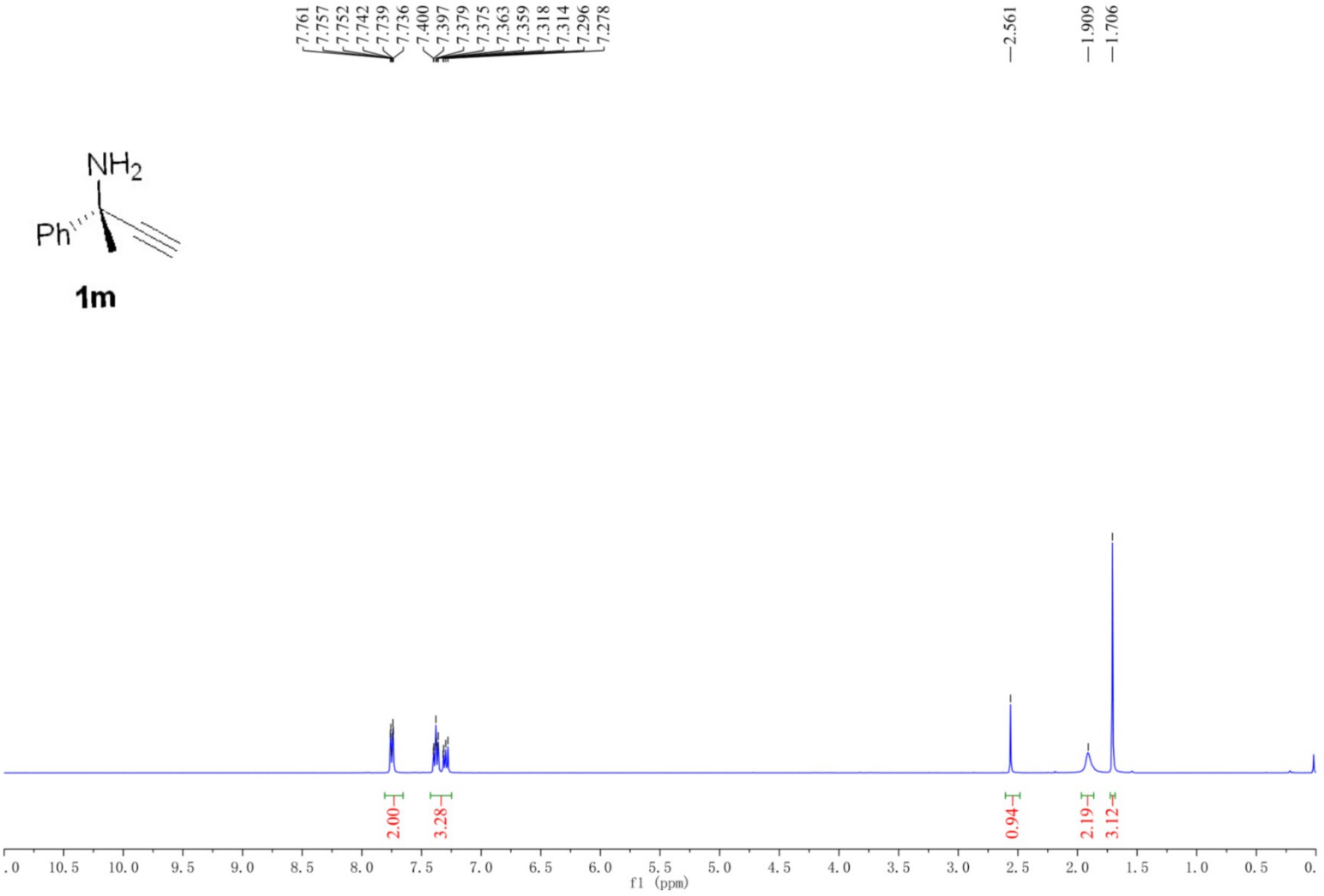

0405/1
8.666
7.484
7.479
7.475
7.472
7.467
7.460
7.450
7.438
7.435
7.431
7.427
7.425
7.421
7.416
7.411
7.409
7.406
7.399
7.397
7.393
4.131
4.119
2.499
2.494
2.489
2.485
2.480
1.086
NH3Cl
Ph
1k
2.85
4.84
1.00
9.23
f1 (ppm)


0405/2
131.92
129.71
129.26
121.61
87.11
84.75
52.42
40.55
40.34
40.13
39.92
39.71
39.51
39.30
34.82
26.20
NH3Cl
Ph
1k
f1 (ppm)

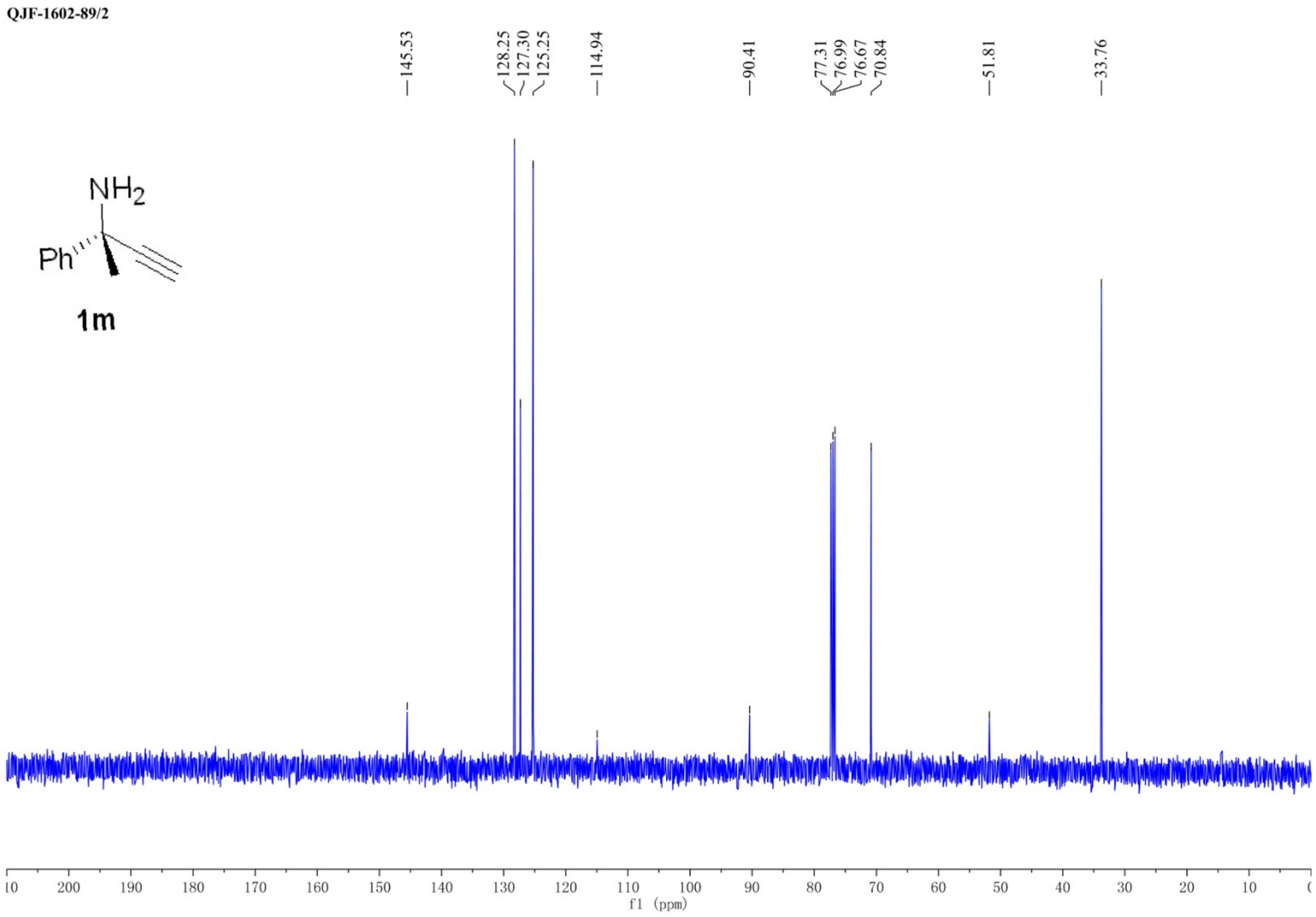

0277/1
2.499
2.494
2.489
2.485
2.480
1.879
1.871
1.839
1.803
1.734
1.727
1.706
1.697
1.621
1.590
1.180
1.170
1.167
1.155
1.138
1.130
1.124
1.108
1.074
1.067
1.055
1.044
1.036
1.030
1.013
1.005
0.982
0.974
NH2
TMS
1l
6.64
3.18
4.43
8.71
0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

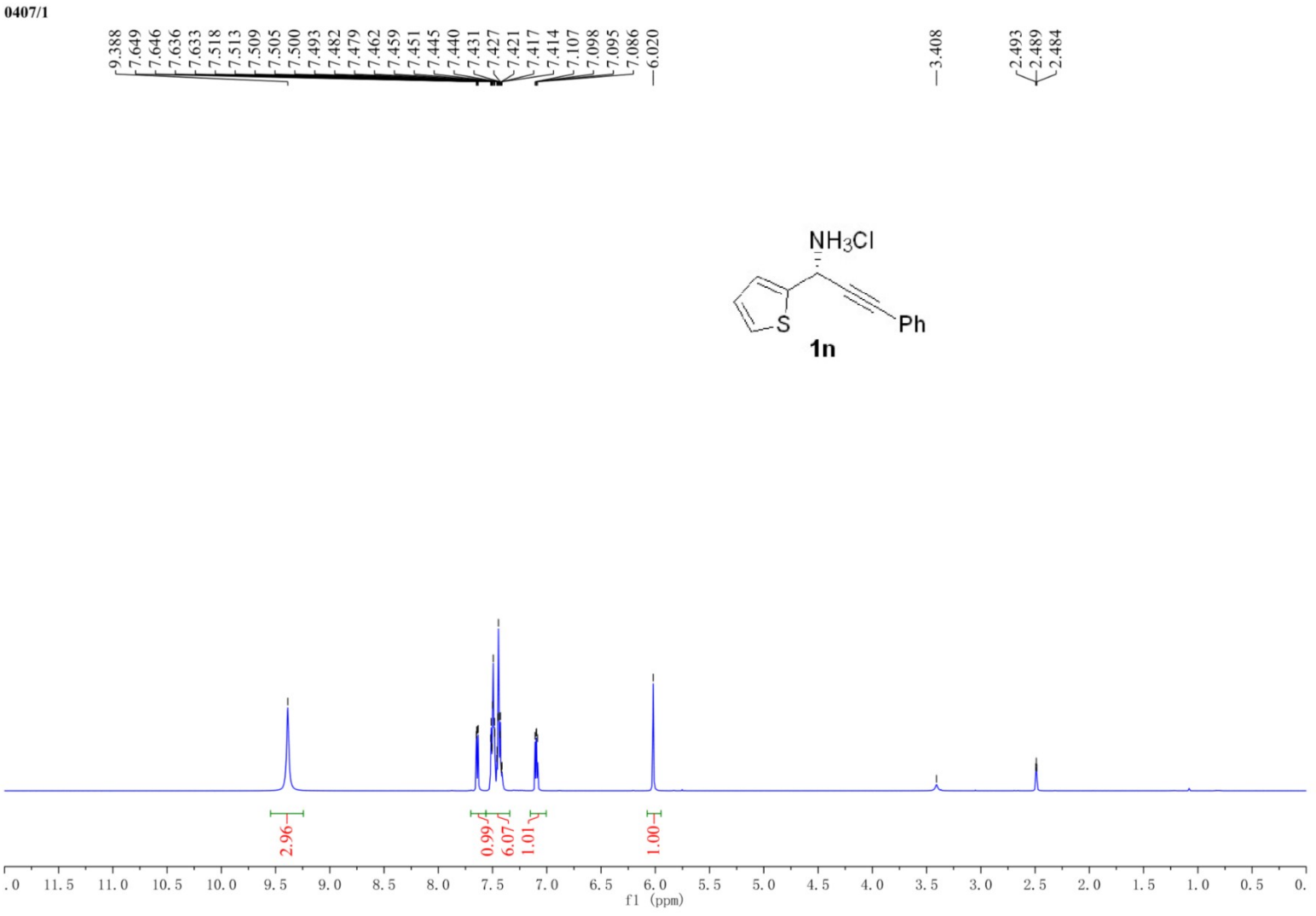

0277/2
114.66
84.16
51.93
48.58
40.57
40.36
40.15
39.94
39.73
39.53
39.32
27.79
27.71
27.36
26.51
26.47
26.42
0.65
NH2
TMS
1l
f1 (ppm)

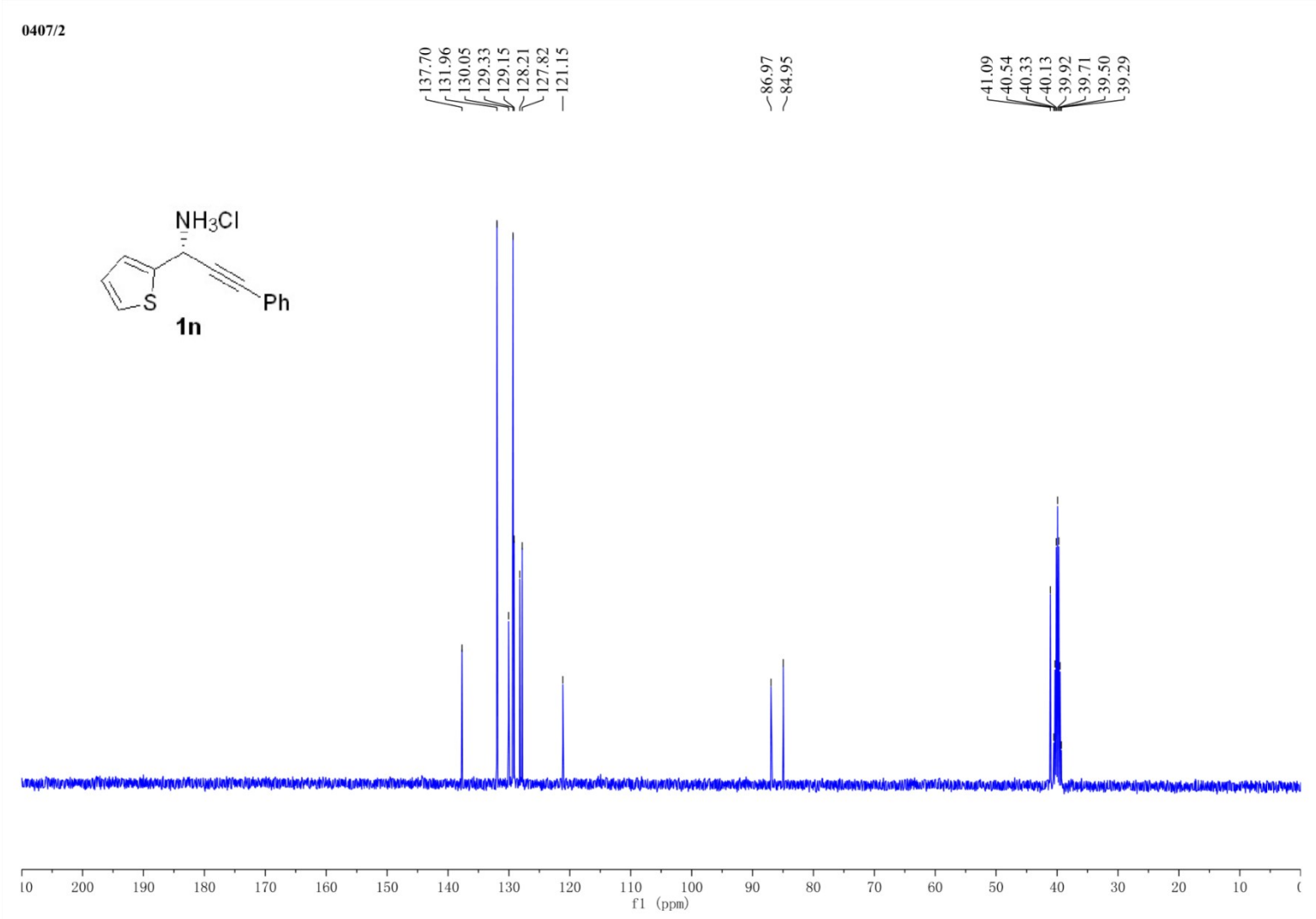
QJF-1602-89/1

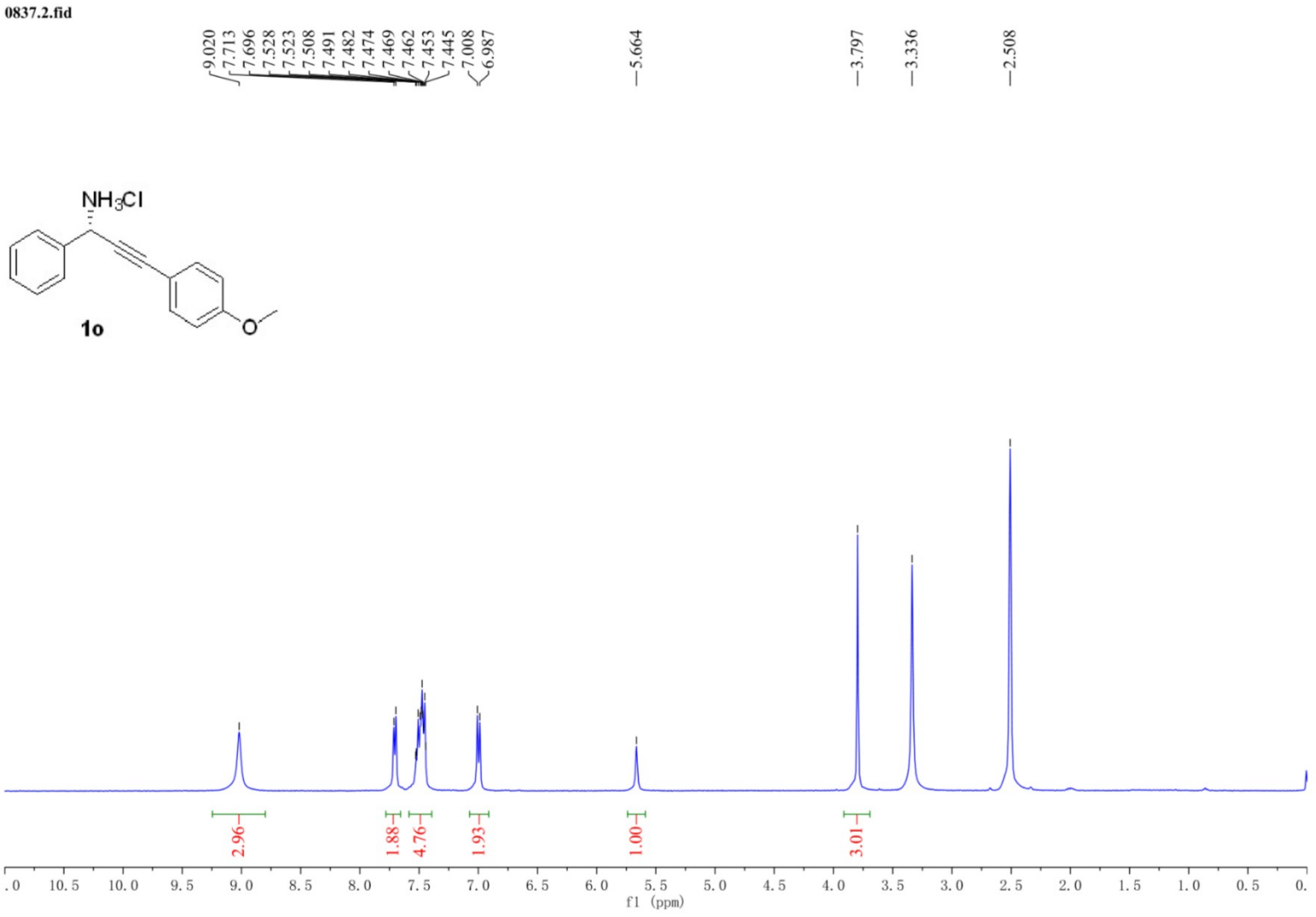


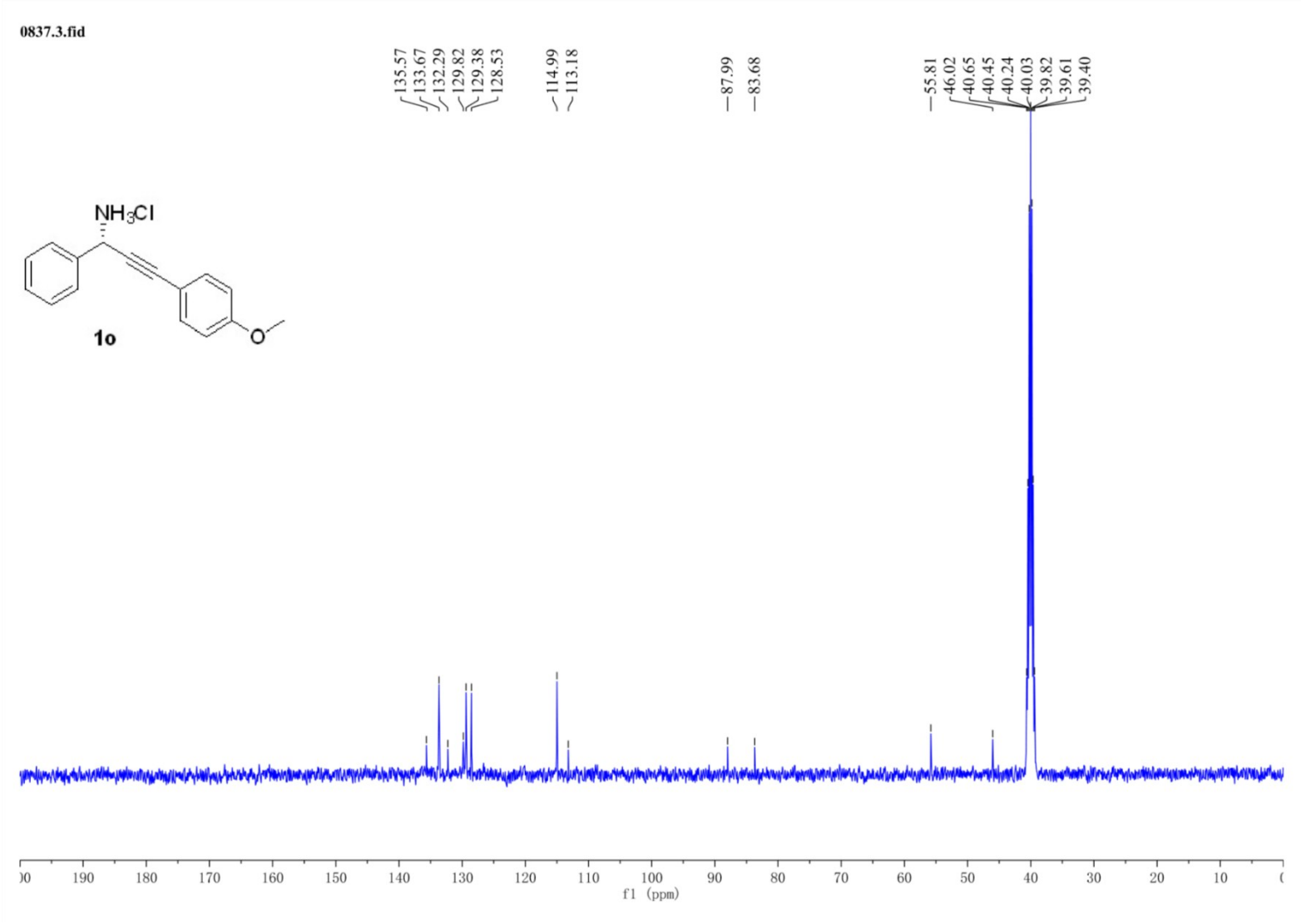
1m


QJF-1602-89/2
145.53
128.25
127.30
125.25
114.94
90.41
77.31
76.99
76.67
70.84
51.81
33.76
NH2
Ph
1m
f1 (ppm)

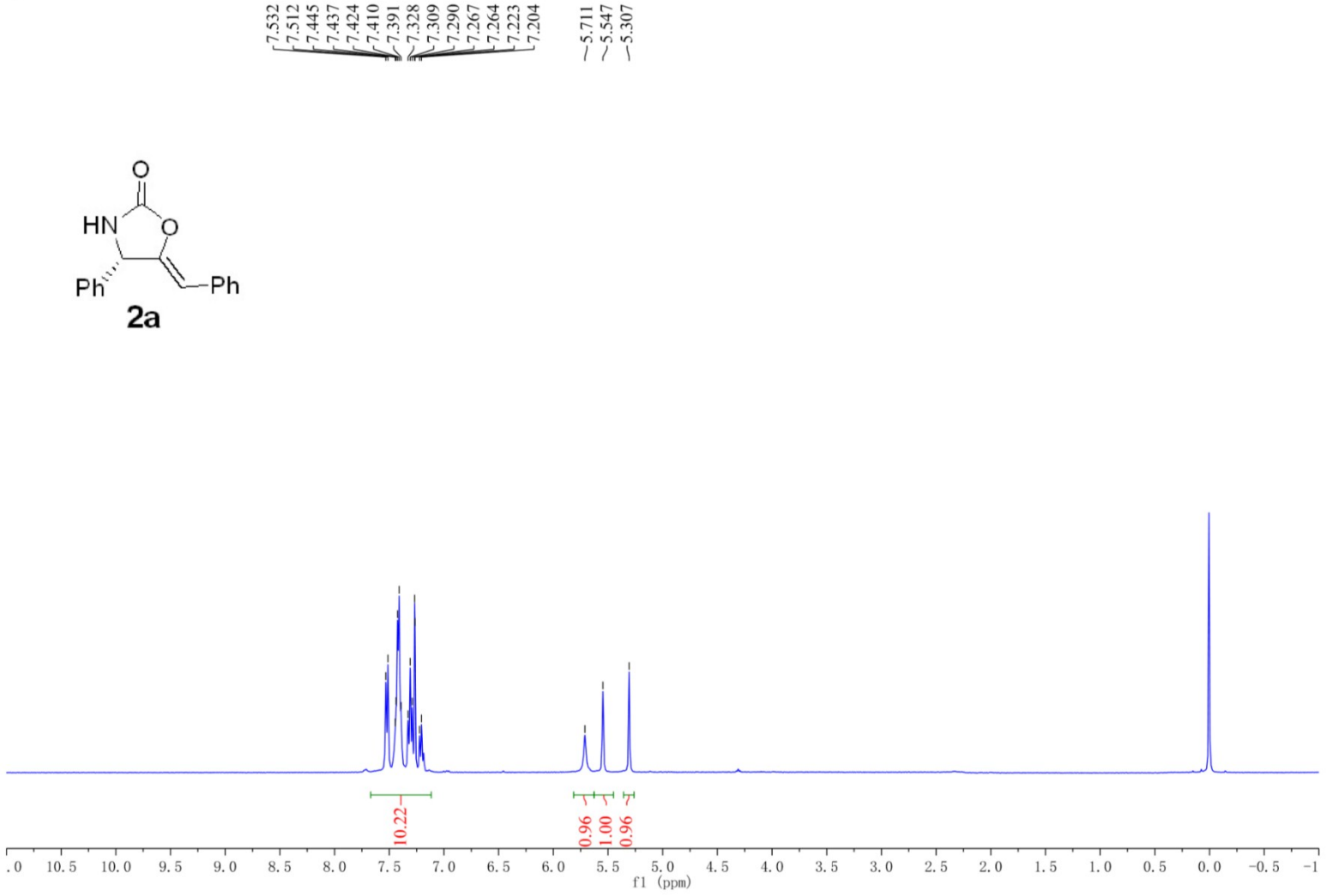

0407/1
9.388
7.649
7.646
7.636
7.633
7.518
7.513
7.509
7.505
7.500
7.493
7.482
7.479
7.462
7.459
7.451
7.445
7.440
7.431
7.427
7.421
7.417
7.414
7.107
7.098
7.095
7.086
6.020
3.408
2.493
2.489
2.484
NH3Cl
S
Ph
1n
2.96
0.99
6.07
1.01
1.00
f1 (ppm)

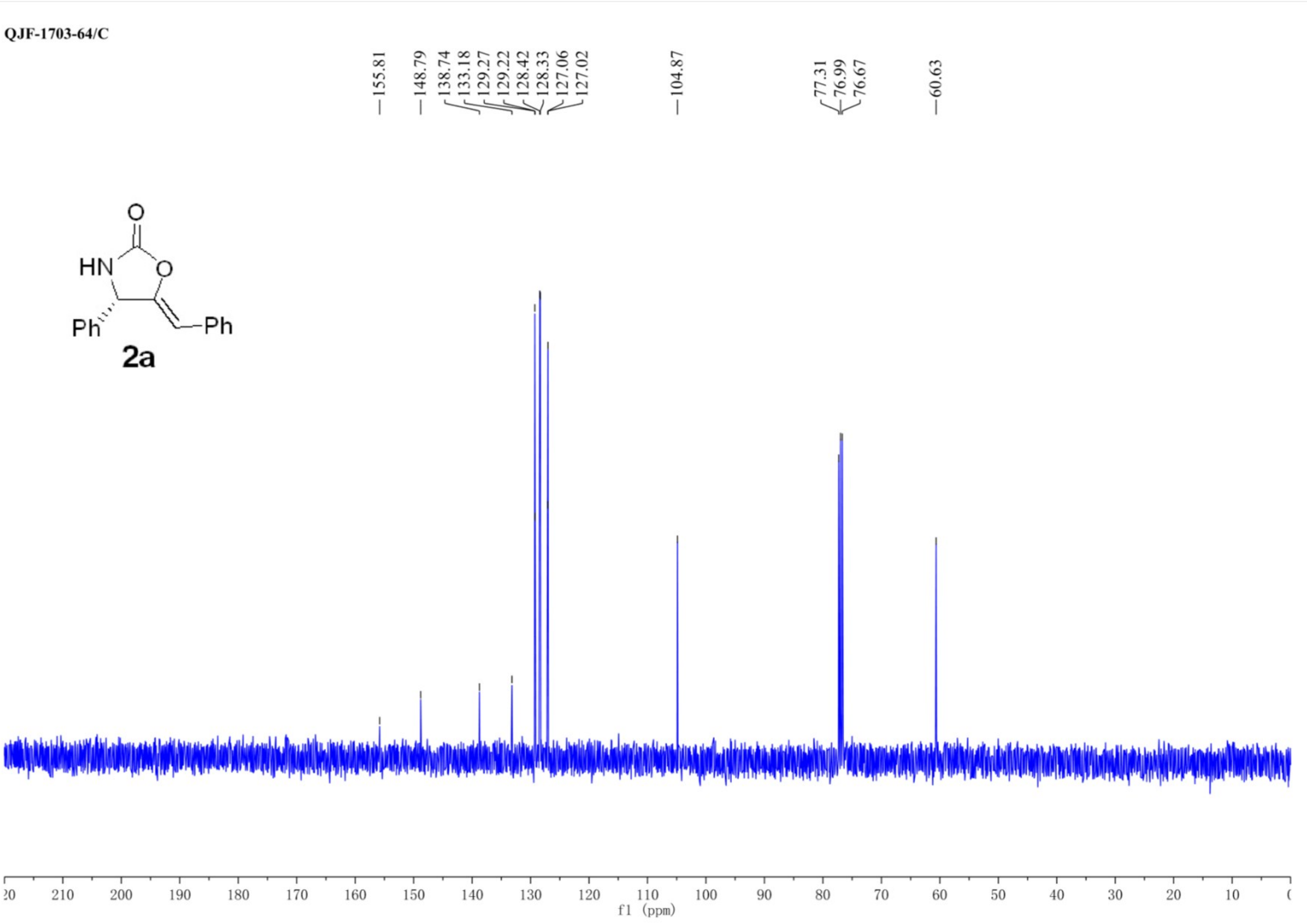

0407/2
137.70
131.96
130.05
129.33
129.15
128.21
127.82
121.15
86.97
84.95
41.09
40.54
40.33
40.13
39.92
39.71
39.50
39.29
NH3Cl
S
Ph
1n
f1 (ppm)


0837.2.fid
9.020
7.713
7.696
7.528
7.523
7.508
7.491
7.482
7.474
7.469
7.462
7.453
7.445
7.008
6.987
5.664
3.797
3.336
2.508
NH3Cl
1o
O
2.96
1.88
4.76
1.93
1.00
3.01
f1 (ppm)

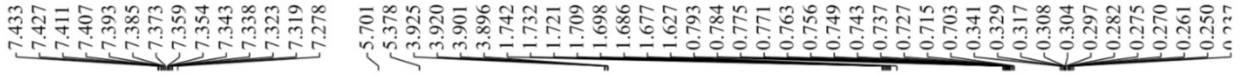

0837.3.fid
135.57
133.67
132.29
129.82
129.38
128.53
114.99
113.18
87.99
83.68
55.81
46.02
40.65
40.45
40.24
40.03
39.82
39.61
39.40
NH3Cl
1o
O
f1 (ppm)

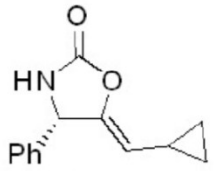
QJF-1703-64/2


7.532
7.512
7.445
7.437
7.424
7.410
7.391
7.328
7.309
7.290
7.267
7.264
7.223
7.204
5.711
5.547
5.307
O
HN
O
Ph
Ph
2a
10.22
0.96
1.00
0.96
f1 (ppm)

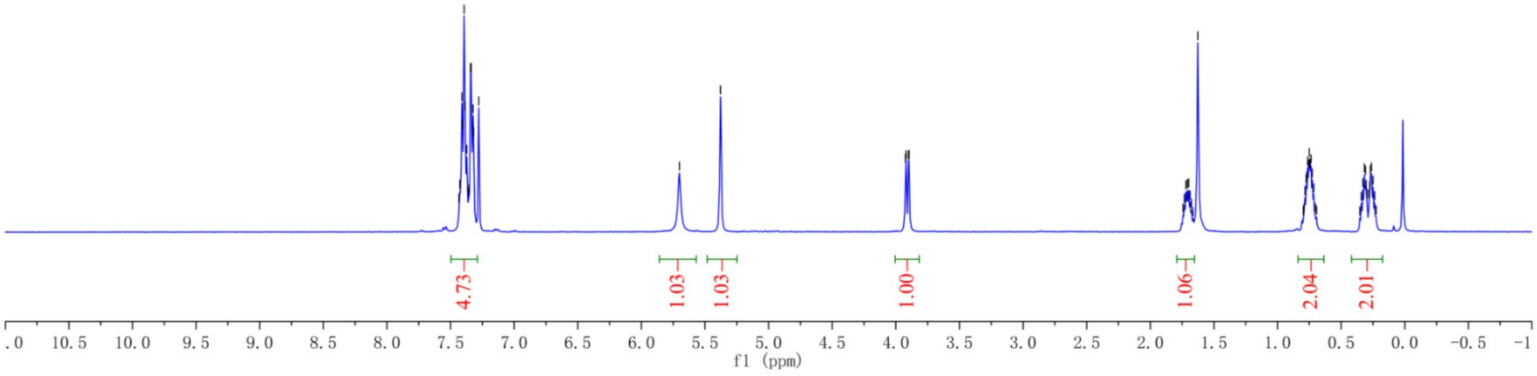

QJF-1703-64/C
155.81
148.79
138.74
133.18
129.27
129.22
128.42
128.33
127.06
127.02
104.87
77.31
76.99
76.67
60.63
O
HN
O
Ph
Ph
2a
f1 (ppm)

QJF-1703-69/2

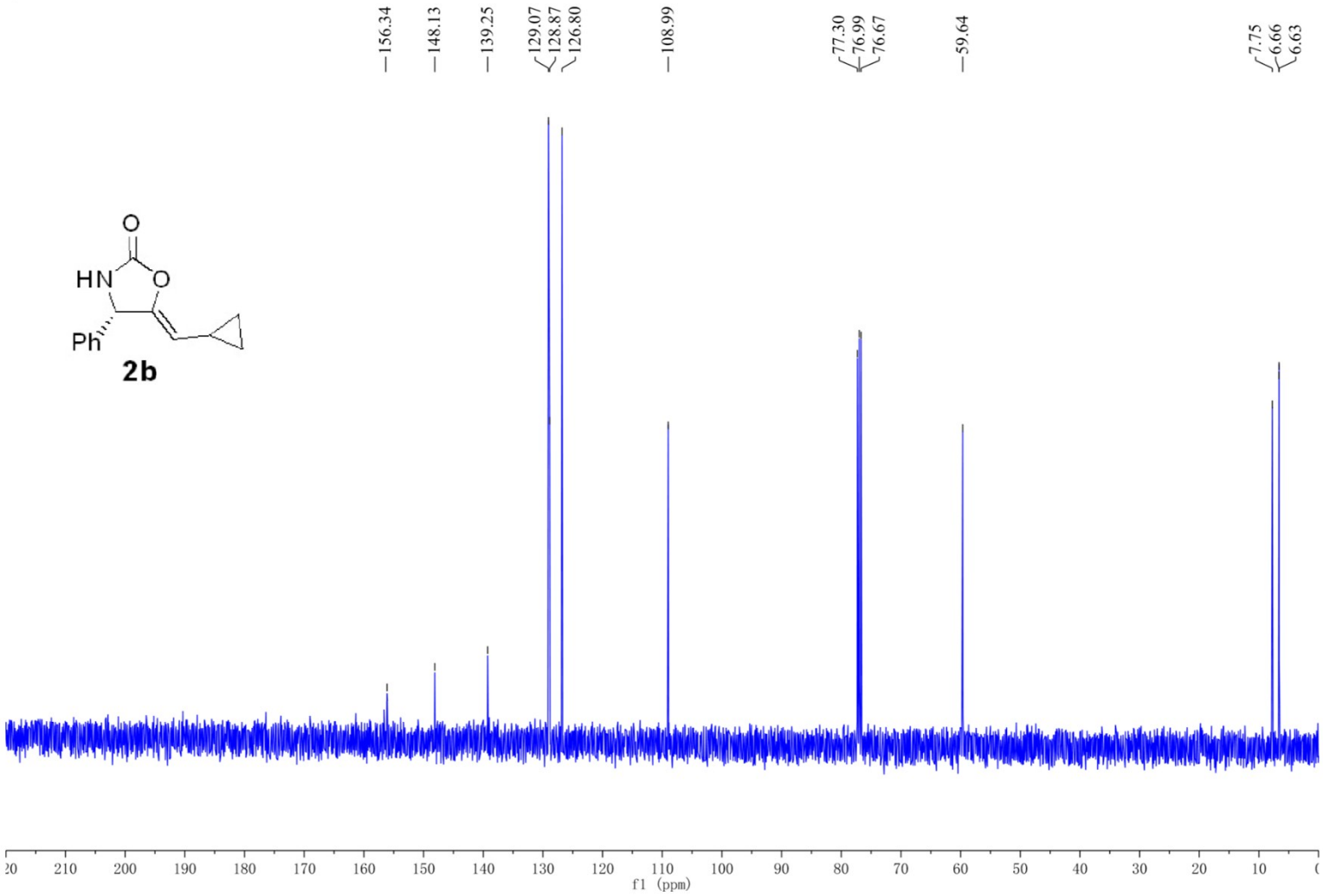


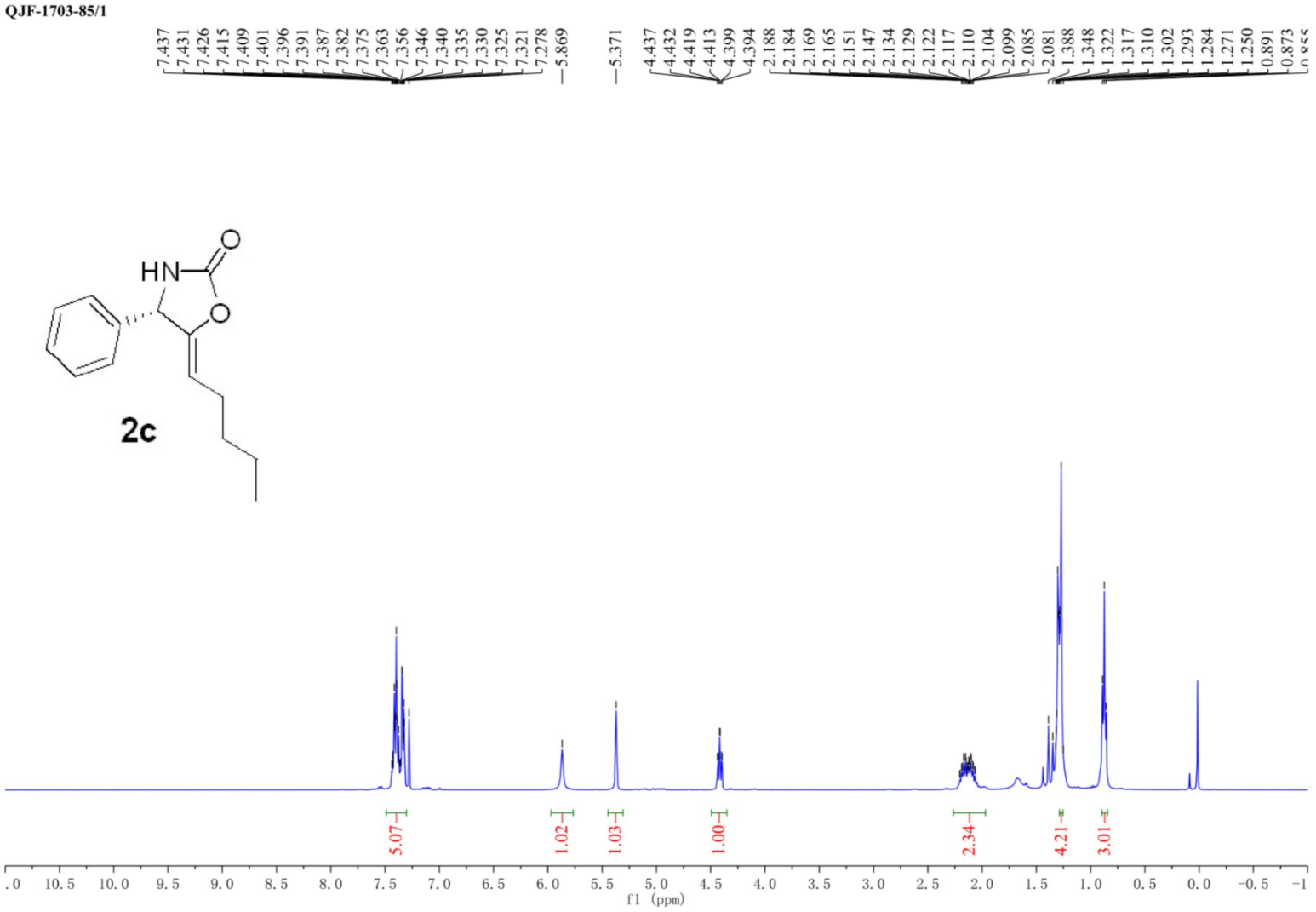


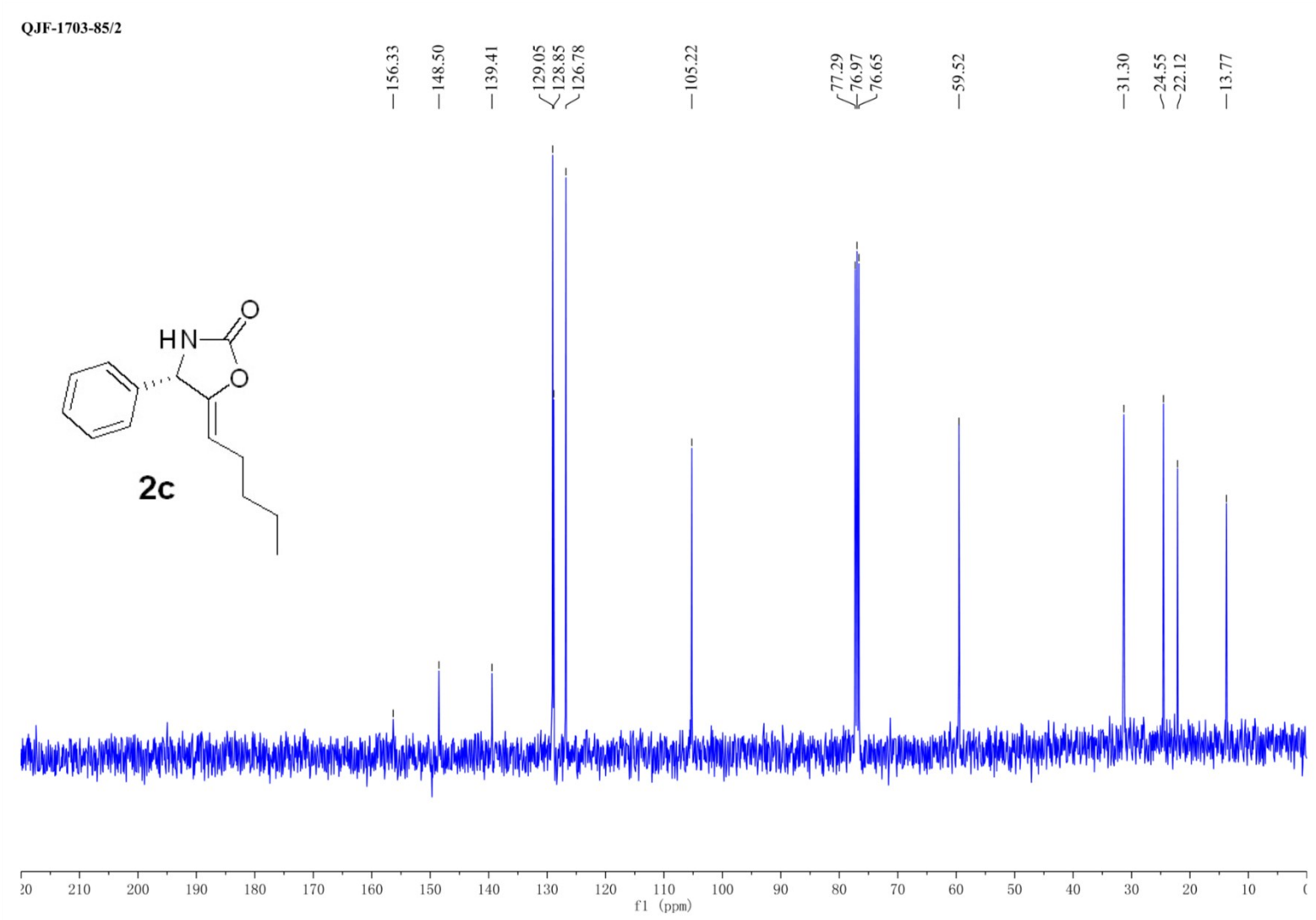
2b

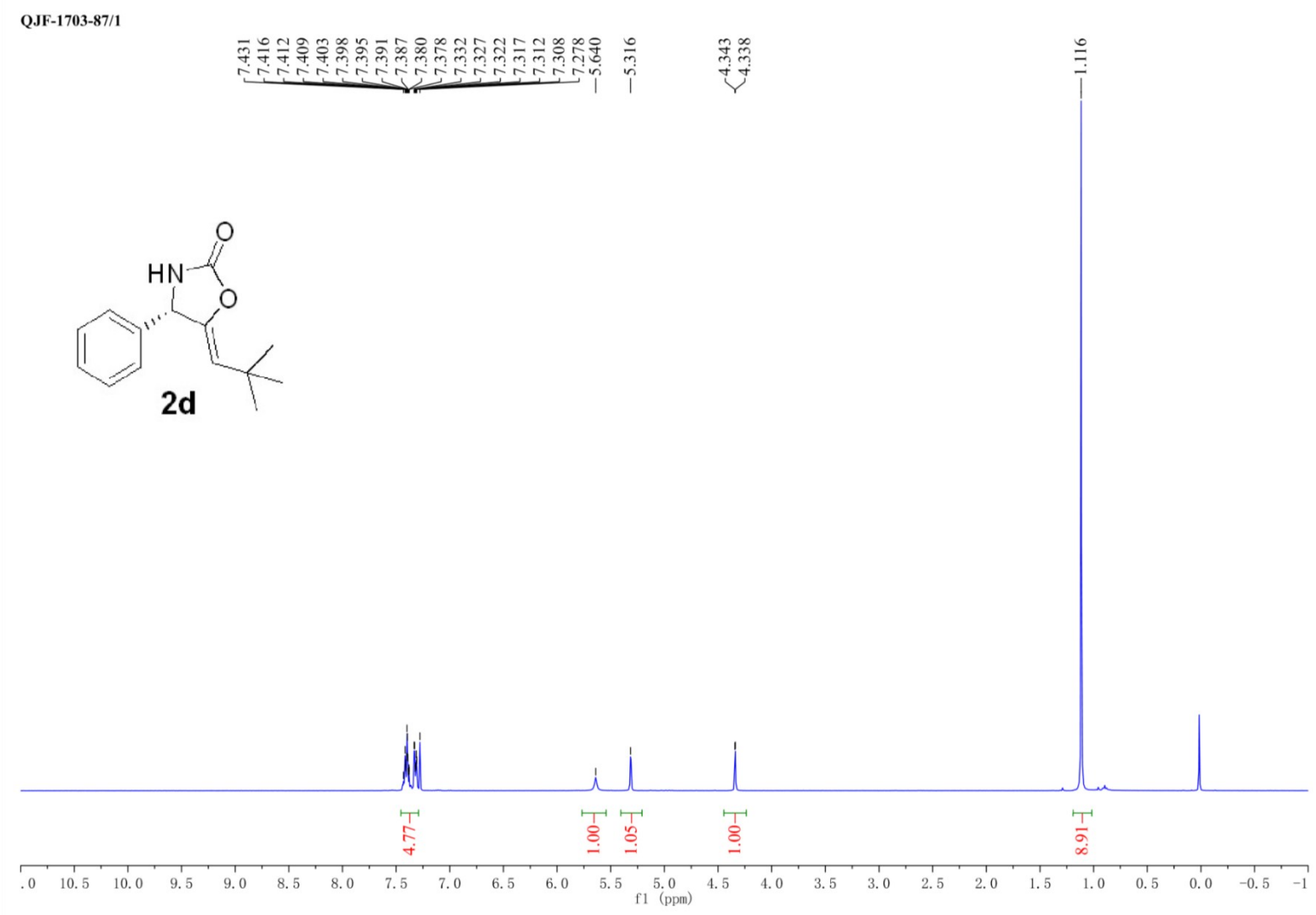


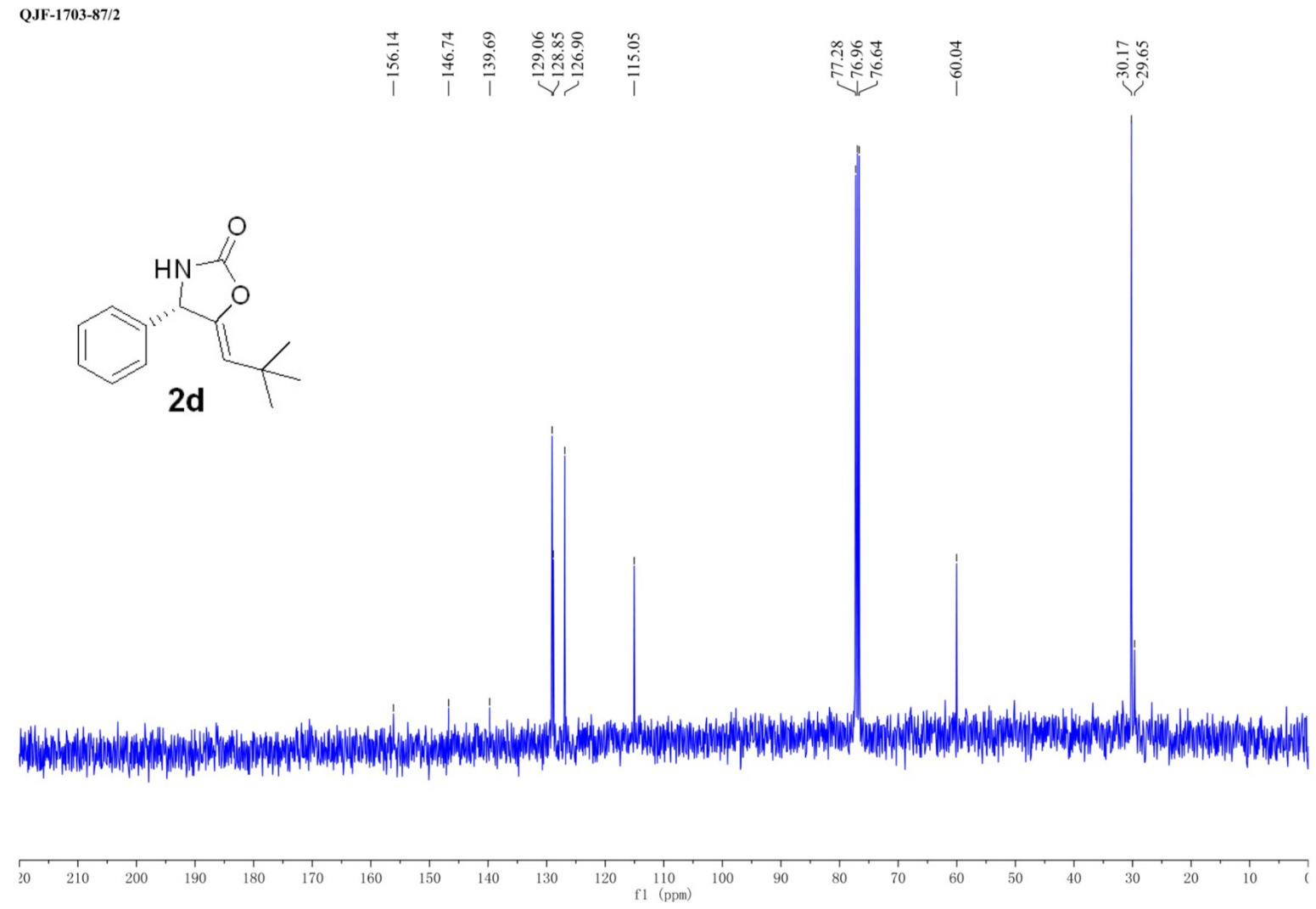
QJF-1703-69/2


156.34
148.13
139.25
129.07
128.87
126.80
108.99
77.30
76.99
76.67
59.64
7.75
6.66
6.63
O
HN
O
Ph
2b
f1 (ppm)

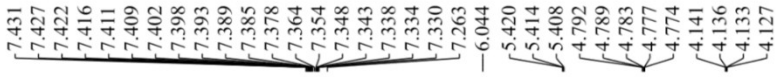

QJF-1703-85/1
7.437
7.431
7.426
7.415
7.409
7.401
7.396
7.391
7.387
7.382
7.375
7.363
7.356
7.346
7.340
7.335
7.330
7.325
7.321
7.278
5.869
5.371
4.437
4.432
4.419
4.413
4.399
4.394
2.188
2.184
2.169
2.165
2.151
2.147
2.134
2.129
2.122
2.117
2.110
2.104
2.099
2.085
2.081
1.388
1.348
1.322
1.317
1.310
1.302
1.293
1.284
1.271
1.250
0.891
0.873
HN
O
O
2c
5.07
1.02
1.03
1.00
2.34
4.21
3.01
f1 (ppm)

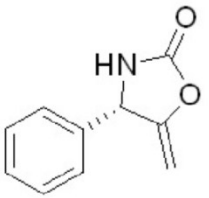

QJF-1703-85/2
156.33
148.50
139.41
129.05
128.85
126.78
105.22
77.29
76.97
76.65
59.52
31.30
24.55
22.12
13.77
HN
O
O
2c
f1 (ppm)


QJF-1703-87/1
7.431
7.416
7.412
7.409
7.403
7.398
7.395
7.391
7.387
7.380
7.378
7.332
7.327
7.322
7.317
7.312
7.308
7.278
5.640
5.316
4.343
4.338
1.116
HN
O
O
2d
4.77
1.00
1.05
1.00
8.91
f1 (ppm)

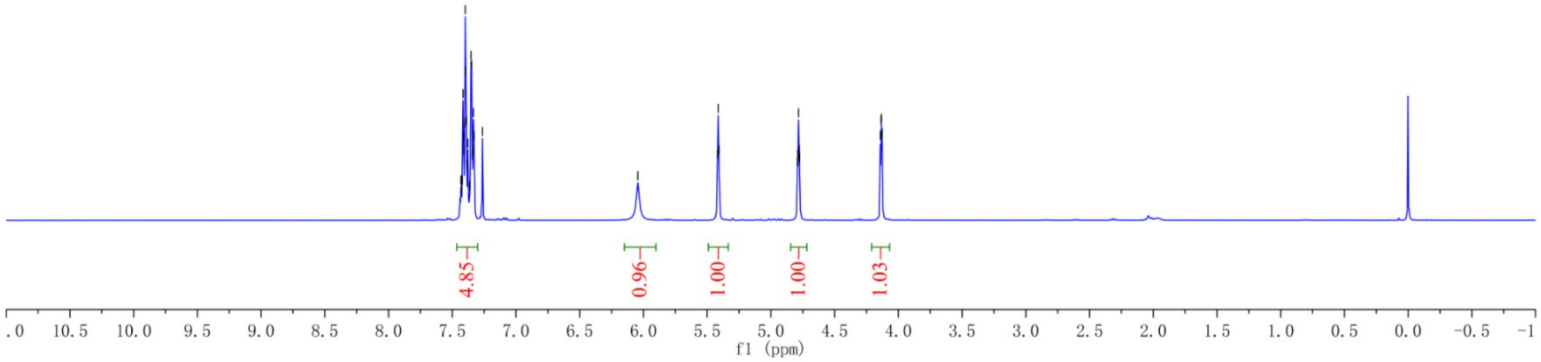

QJF-1703-87/2
156.14
146.74
139.69
129.06
128.85
126.90
115.05
77.28
76.96
76.64
60.04
30.17
29.65
HN
O
O
2d
f1 (ppm)

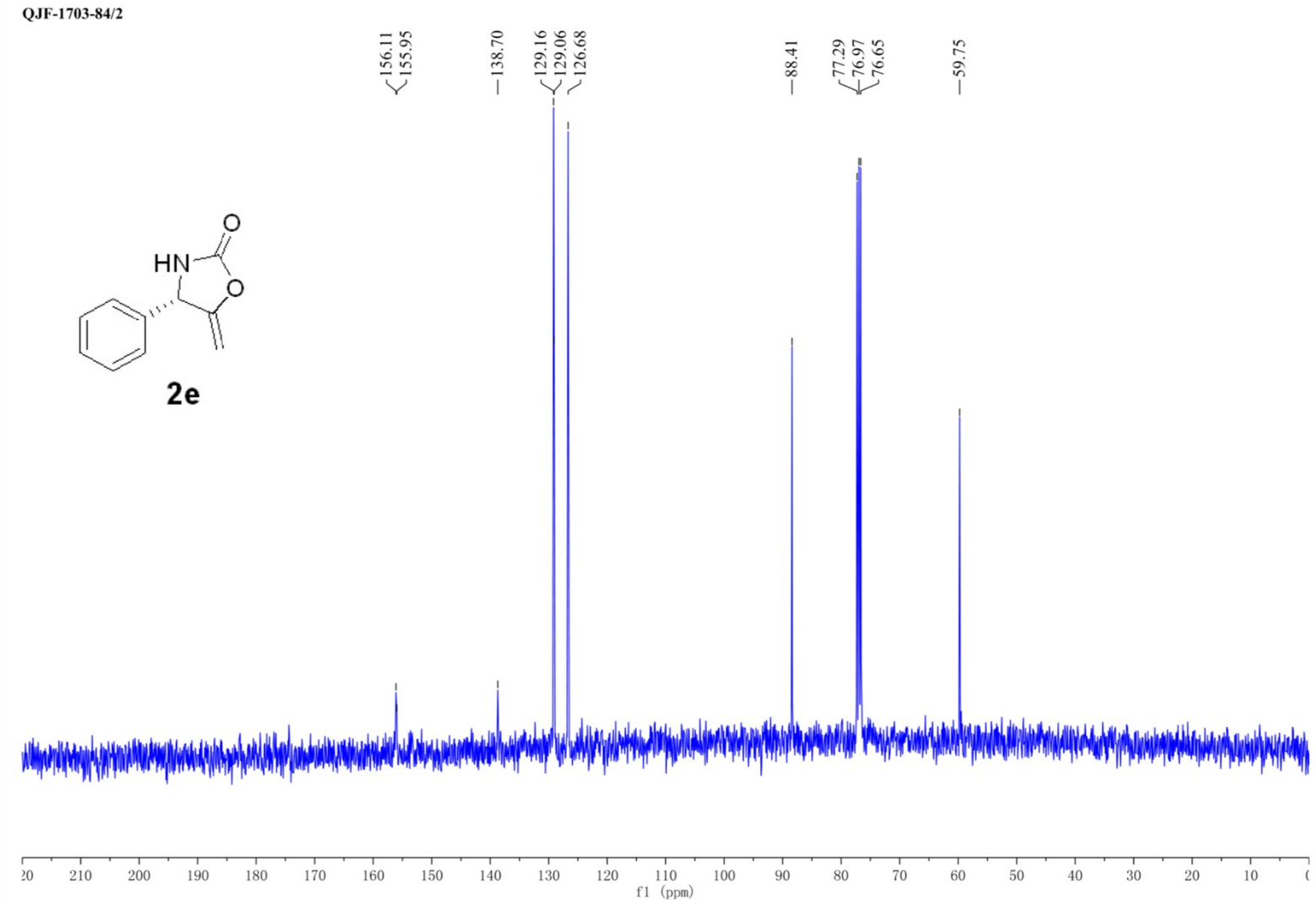
QJF-1703-84/1

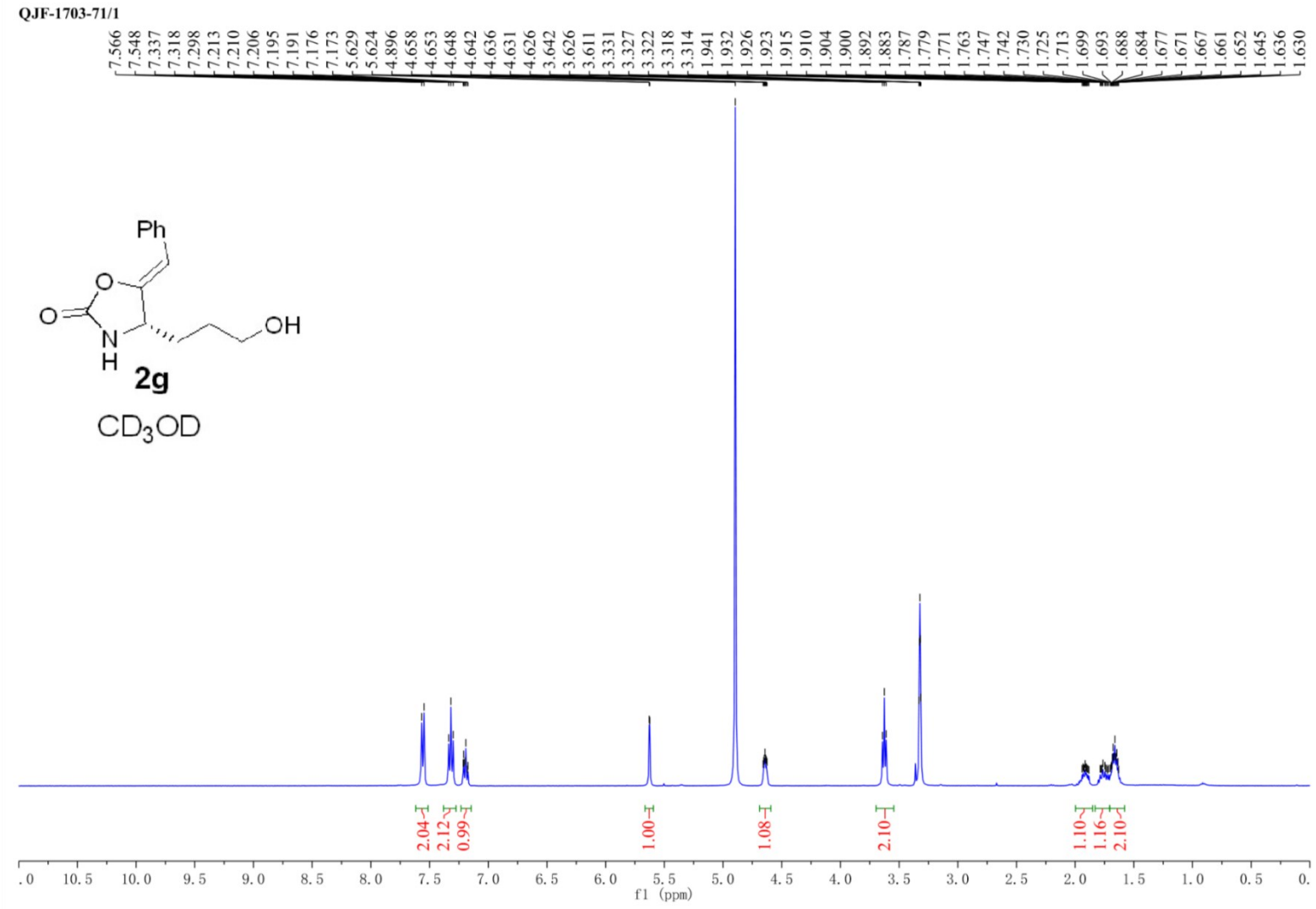


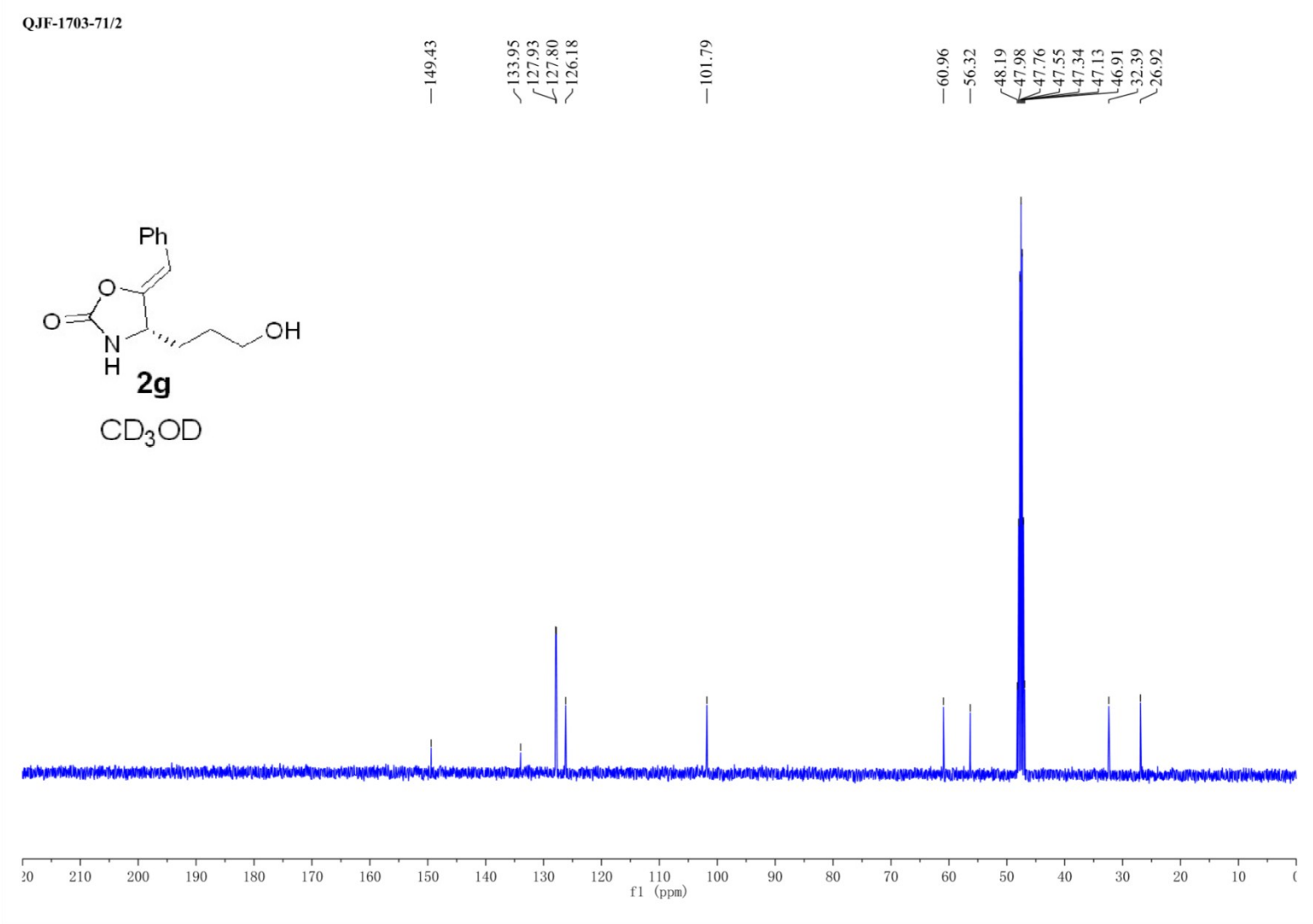


2e

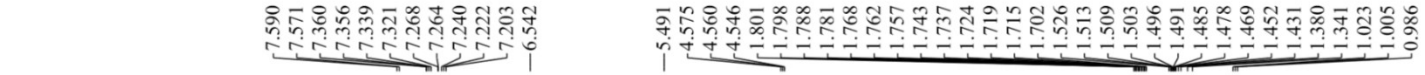


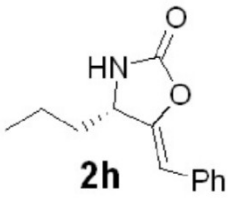

QJF-1703-84/2
156.11
155.95
138.70
129.16
129.06
126.68
88.41
77.29
76.97
76.65
59.75
HN
O
O
2e
f1 (ppm)


QJF-1703-71/1
7.566
7.548
7.337
7.318
7.298
7.213
7.210
7.206
7.195
7.191
7.176
7.173
5.629
5.624
4.896
4.658
4.653
4.648
4.642
4.636
4.631
4.626
3.642
3.626
3.611
3.331
3.327
3.322
3.318
3.314
1.941
1.932
1.926
1.923
1.915
1.910
1.904
1.900
1.892
1.883
1.787
1.779
1.771
1.763
1.747
1.742
1.730
1.725
1.713
1.699
1.693
1.688
1.684
1.677
1.671
1.667
1.661
1.652
1.645
1.636
1.630
Ph
O
O
N
H
OH
2g
CD3OD
2.04
2.12
0.99
1.00
1.08
2.10
1.10
1.16
2.10
f1 (ppm)

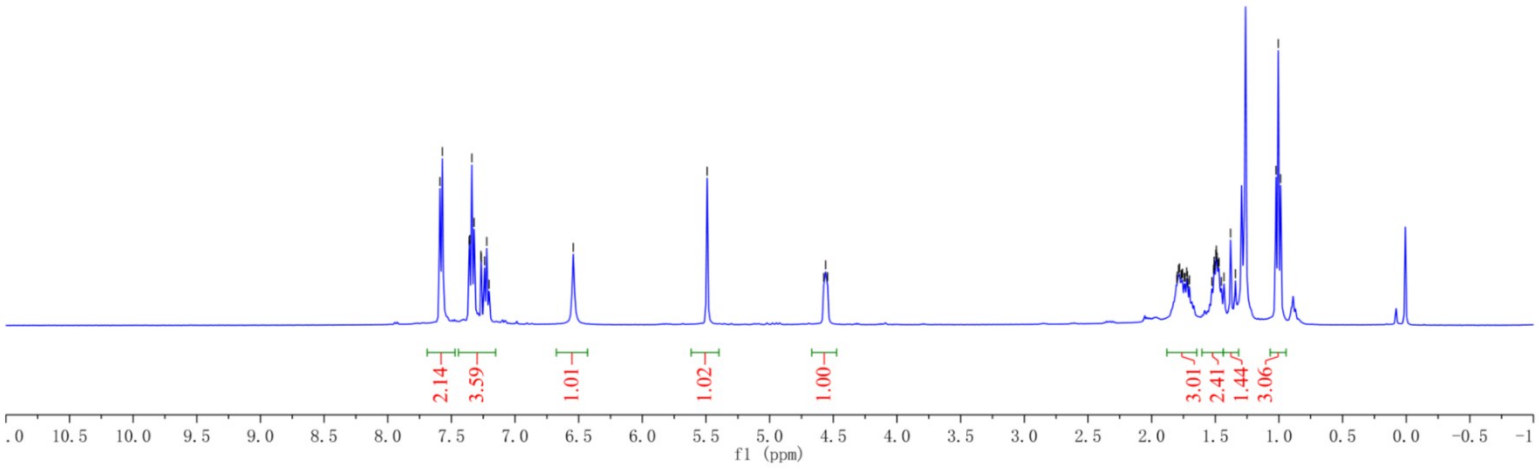

QJF-1703-71/2
149.43
133.95
127.93
127.80
126.18
101.79
60.96
56.32
48.19
47.98
47.76
47.55
47.34
47.13
46.91
32.39
26.92
Ph
O
O
N
H
OH
2g
CD3OD
f1 (ppm)

QJF-1703-91/1

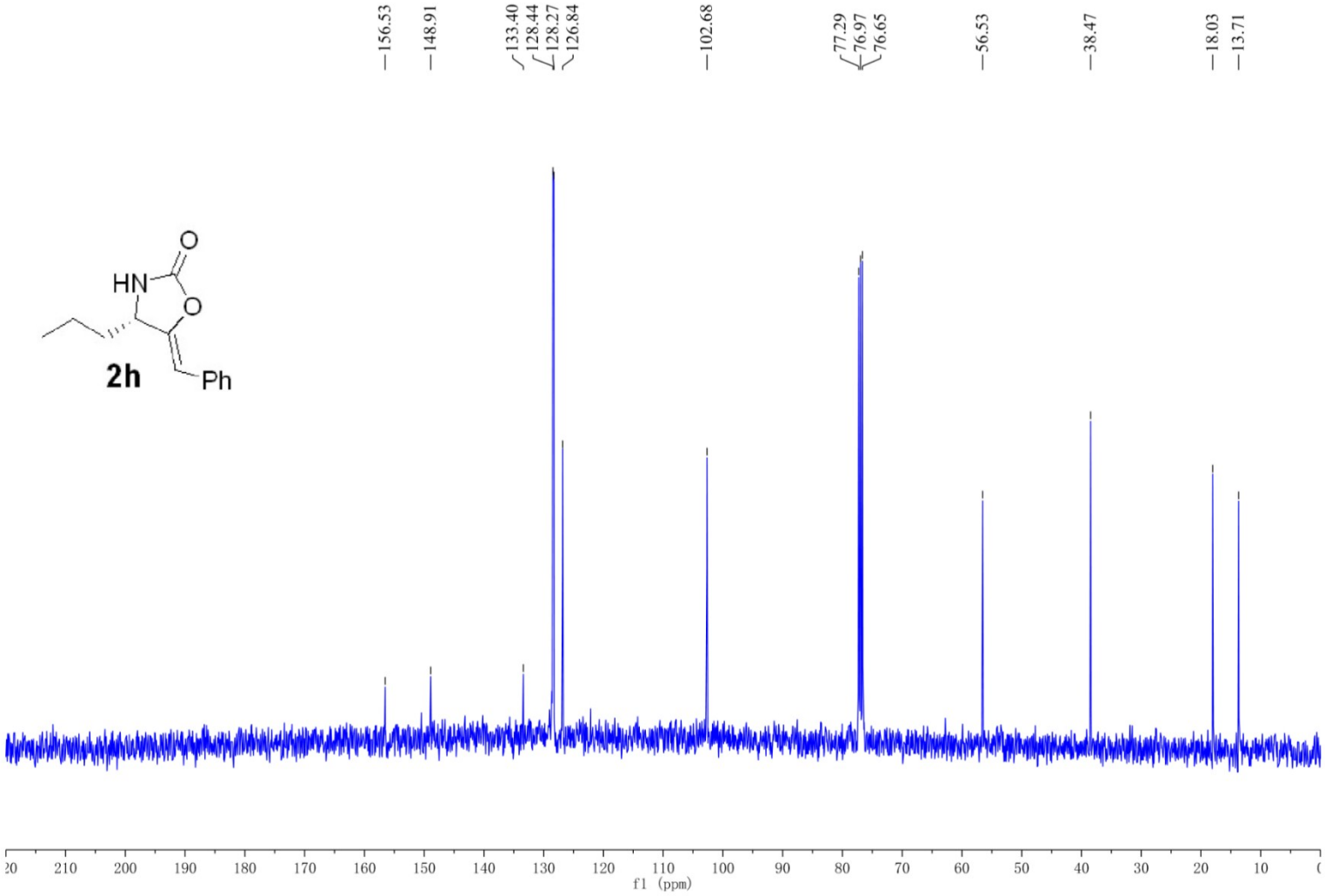




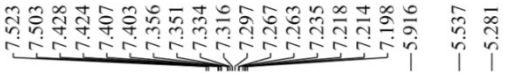
2h

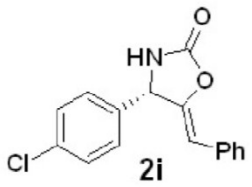


QJF-1703-91/2

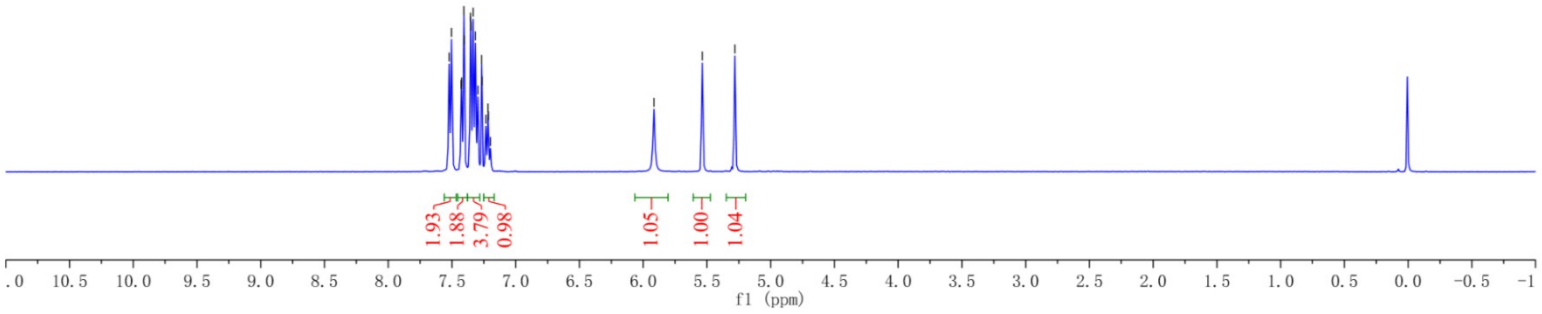

156.53
148.91
133.40
128.44
128.27
126.84
102.68
77.29
76.97
76.65
56.53
38.47
18.03
13.71
HN
O
O
Ph
2h
f1 (ppm)

QJF-1703-90/1

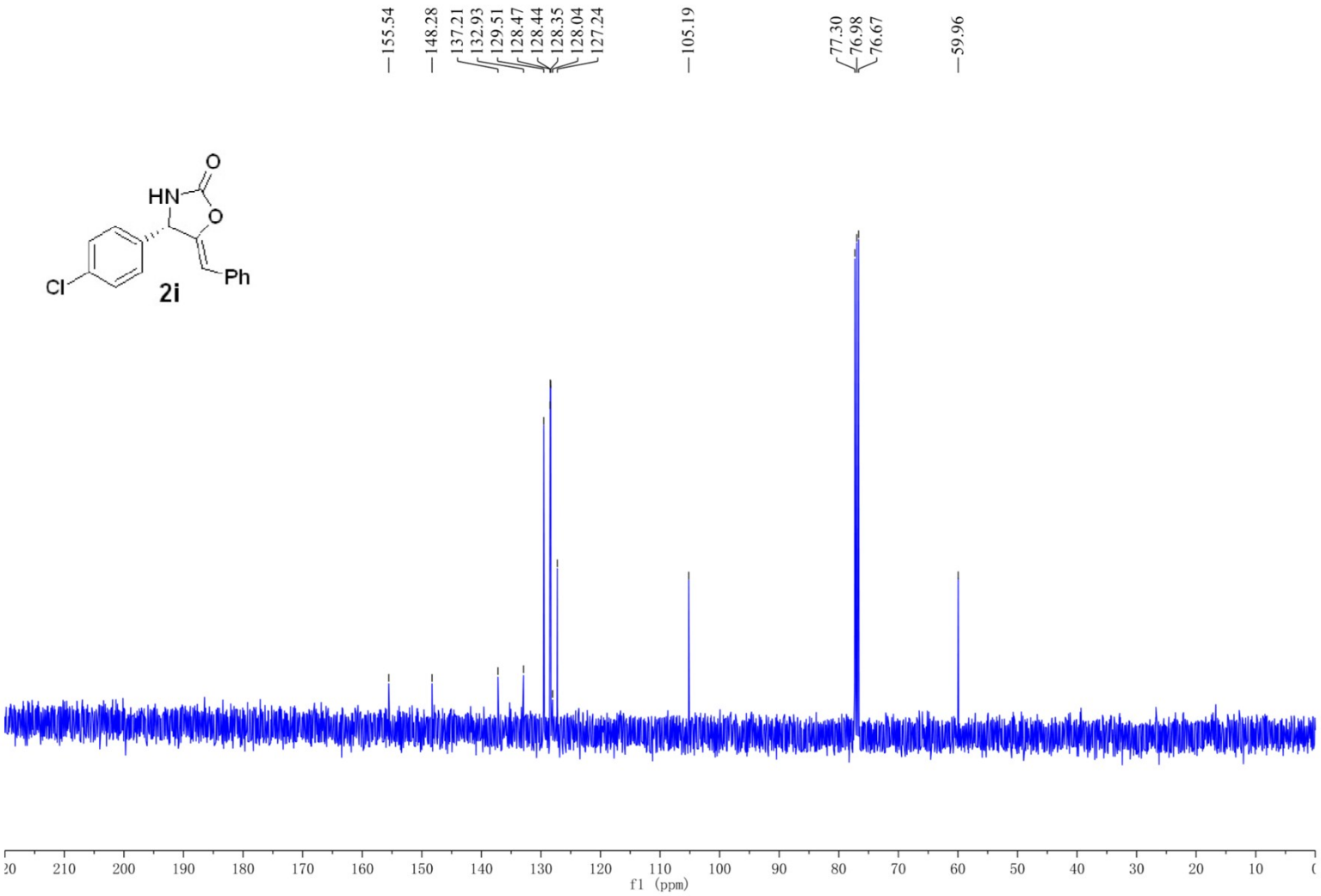


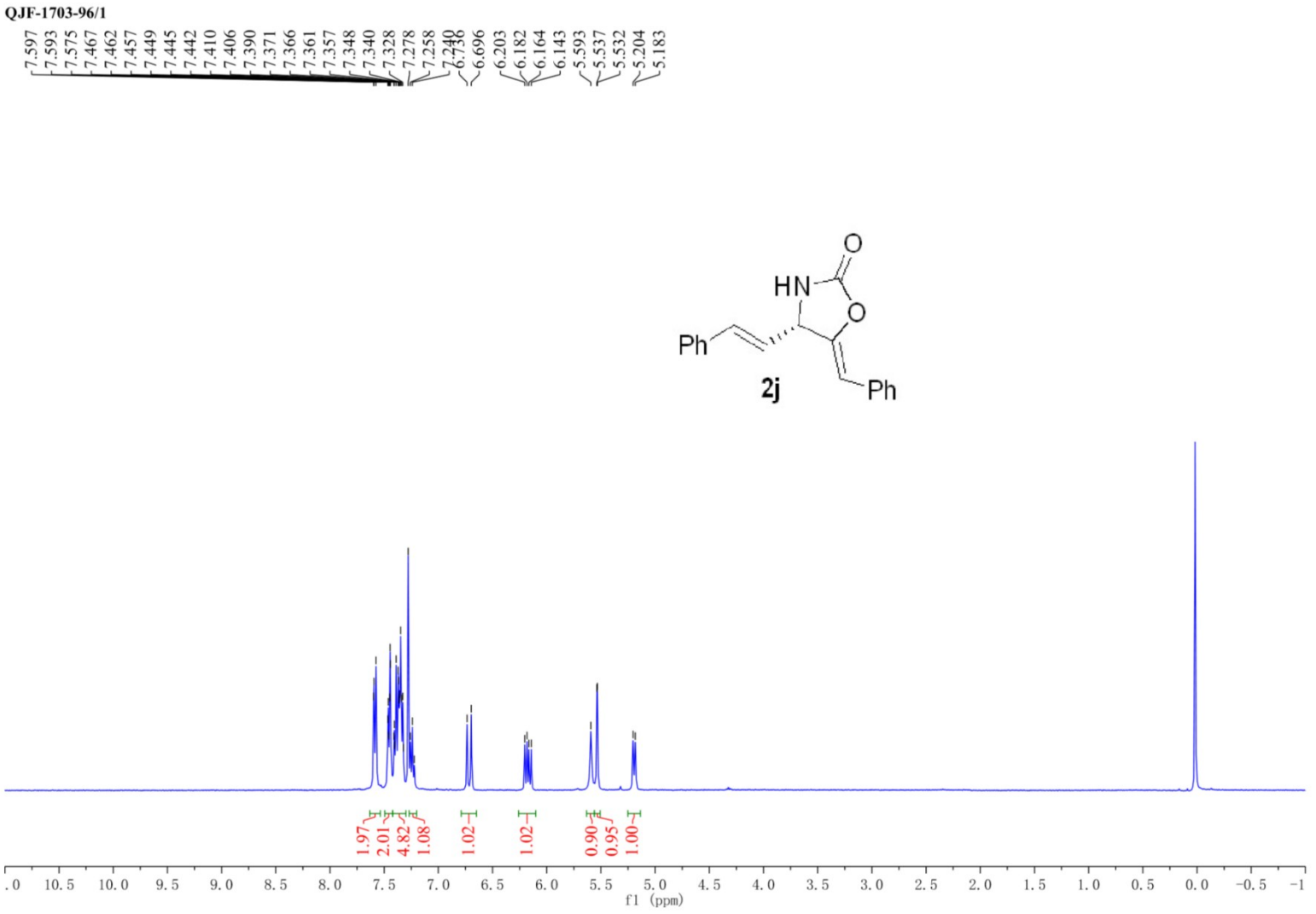


2i

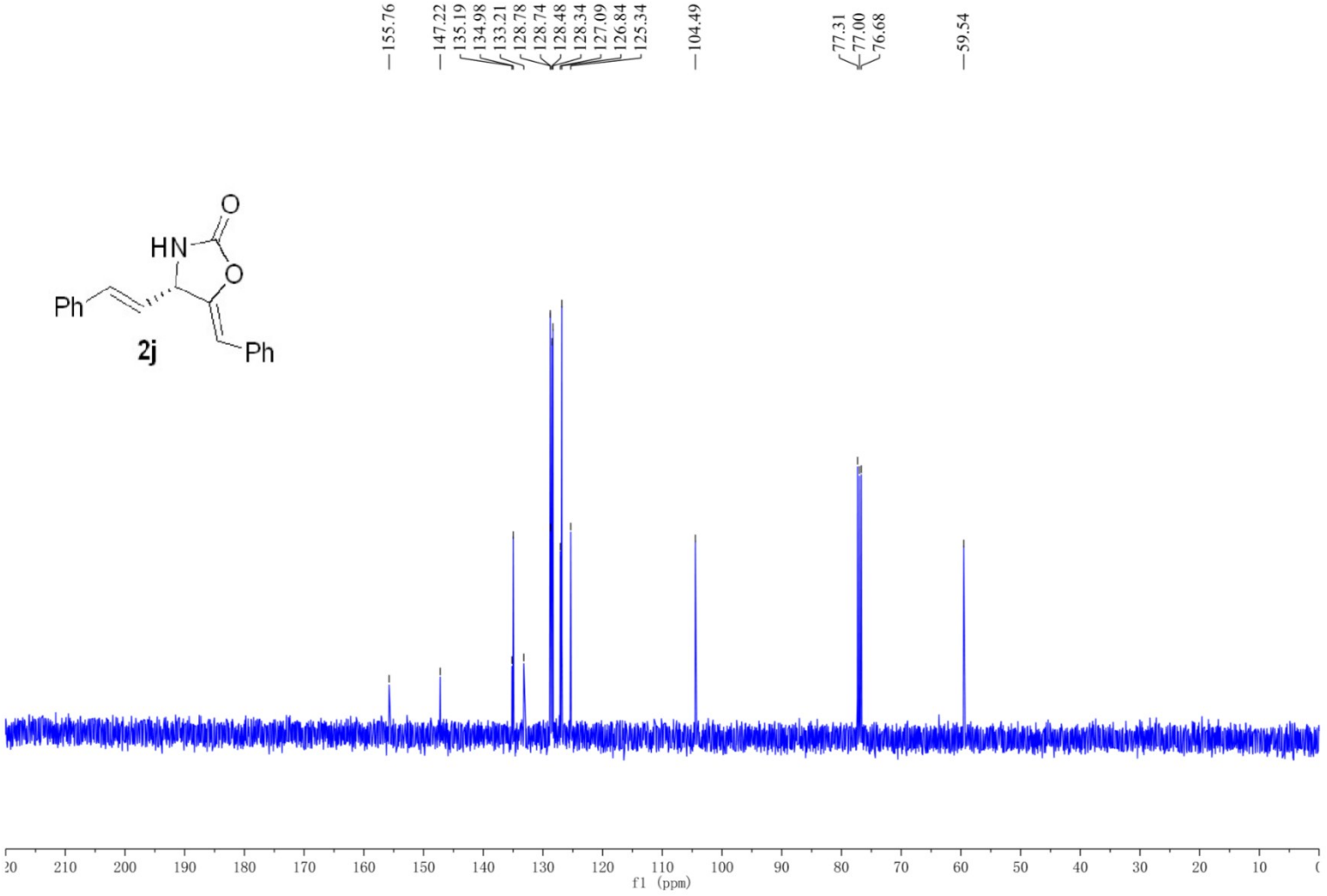


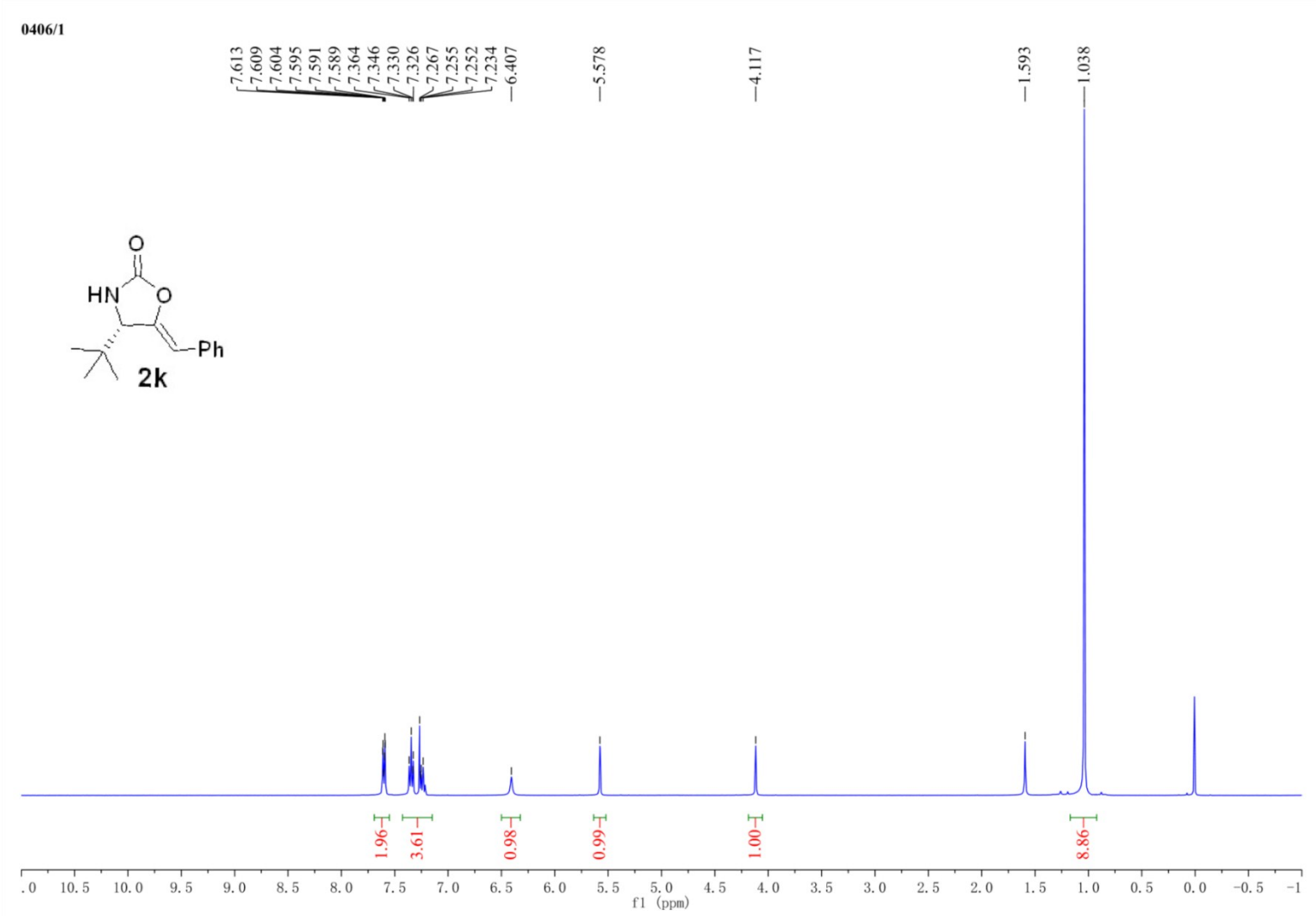
QJF-1703-90/2

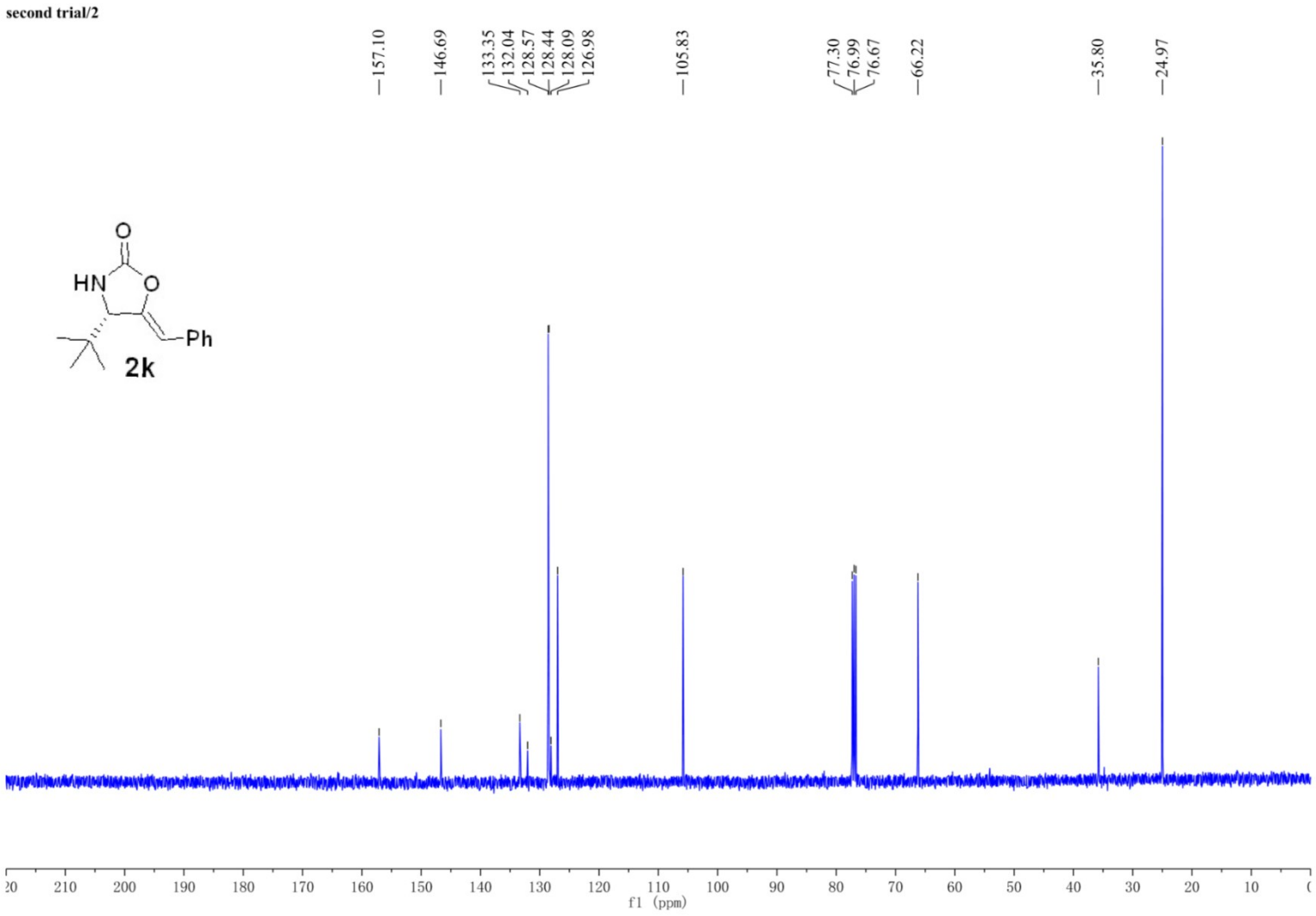

155.54
148.28
137.21
132.93
129.51
128.47
128.44
128.35
128.04
127.24
105.19
77.30
76.98
76.67
59.96
O
HN
O
Cl
Ph
2i
f1 (ppm)


QJF-1703-96/1
7.597
7.593
7.575
7.467
7.462
7.457
7.449
7.445
7.442
7.410
7.406
7.390
7.371
7.366
7.361
7.357
7.348
7.340
7.328
7.278
7.258
7.240
6.738
6.696
6.203
6.182
6.164
6.143
5.593
5.537
5.532
5.204
5.183
O
HN
O
Ph
Ph
2j
1.97
2.01
4.82
1.08
1.02
1.02
0.90
0.95
1.00
f1 (ppm)

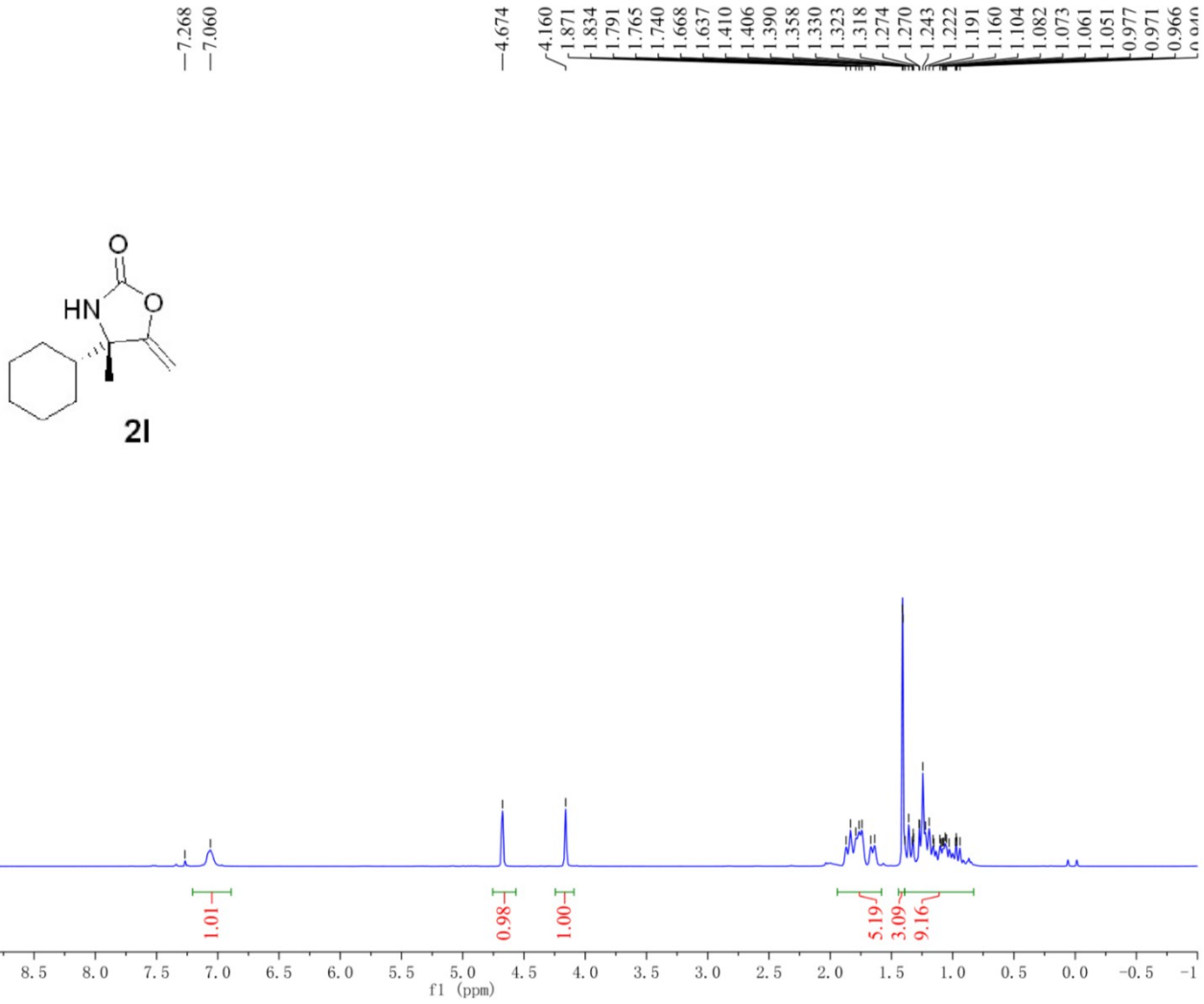
QJF-1703-96/2

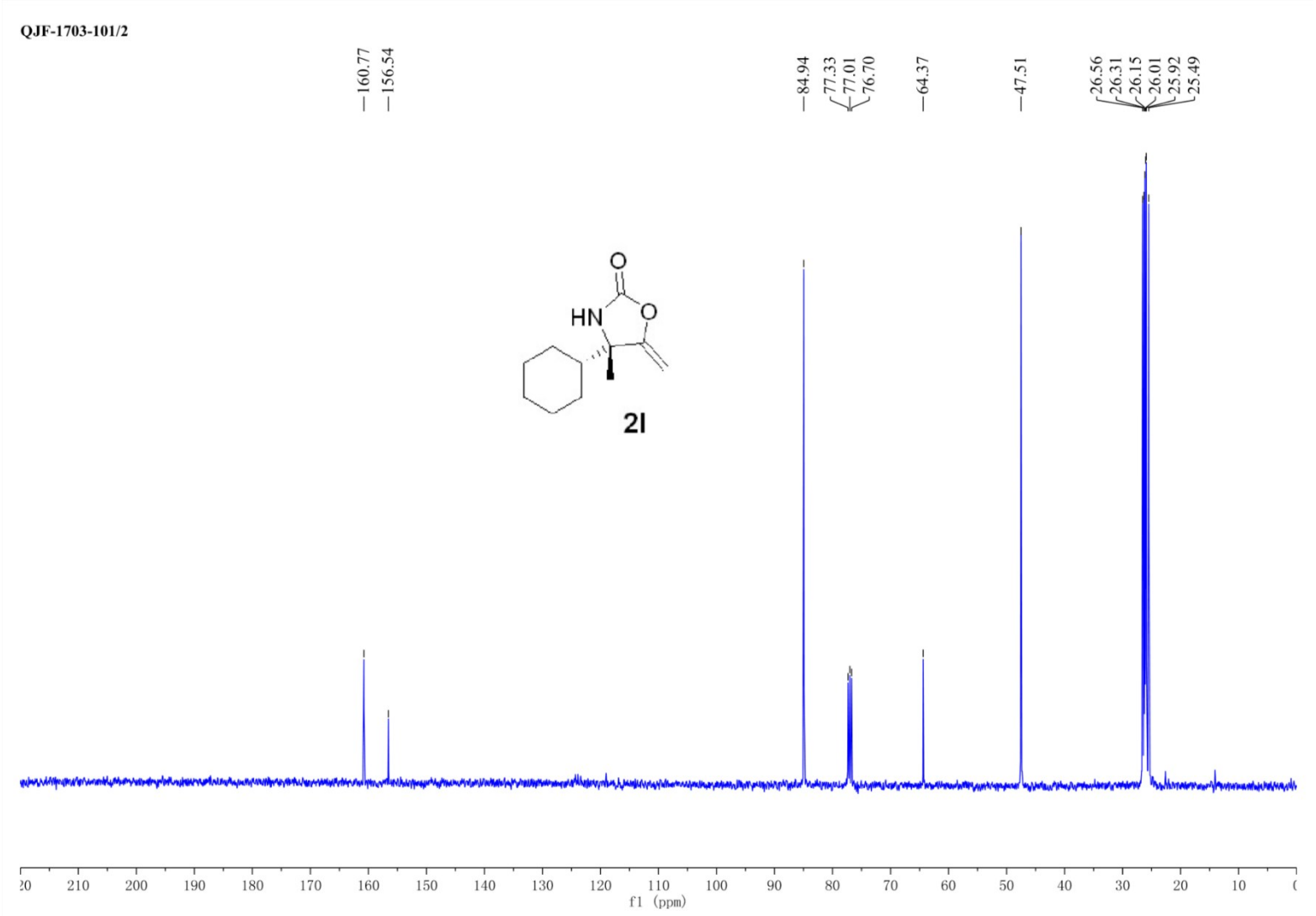

155.76
147.22
135.19
134.98
133.21
128.78
128.74
128.48
128.34
127.09
126.84
125.34
104.49
77.31
77.00
76.68
59.54
HN
O
O
Ph
Ph
2j
f1 (ppm)


0406/1
7.613
7.609
7.604
7.595
7.591
7.589
7.364
7.346
7.330
7.326
7.267
7.255
7.252
7.234
6.407
5.578
4.117
1.593
1.038
HN
O
O
Ph
2k
1.96
3.61
0.98
0.99
1.00
8.86
f1 (ppm)

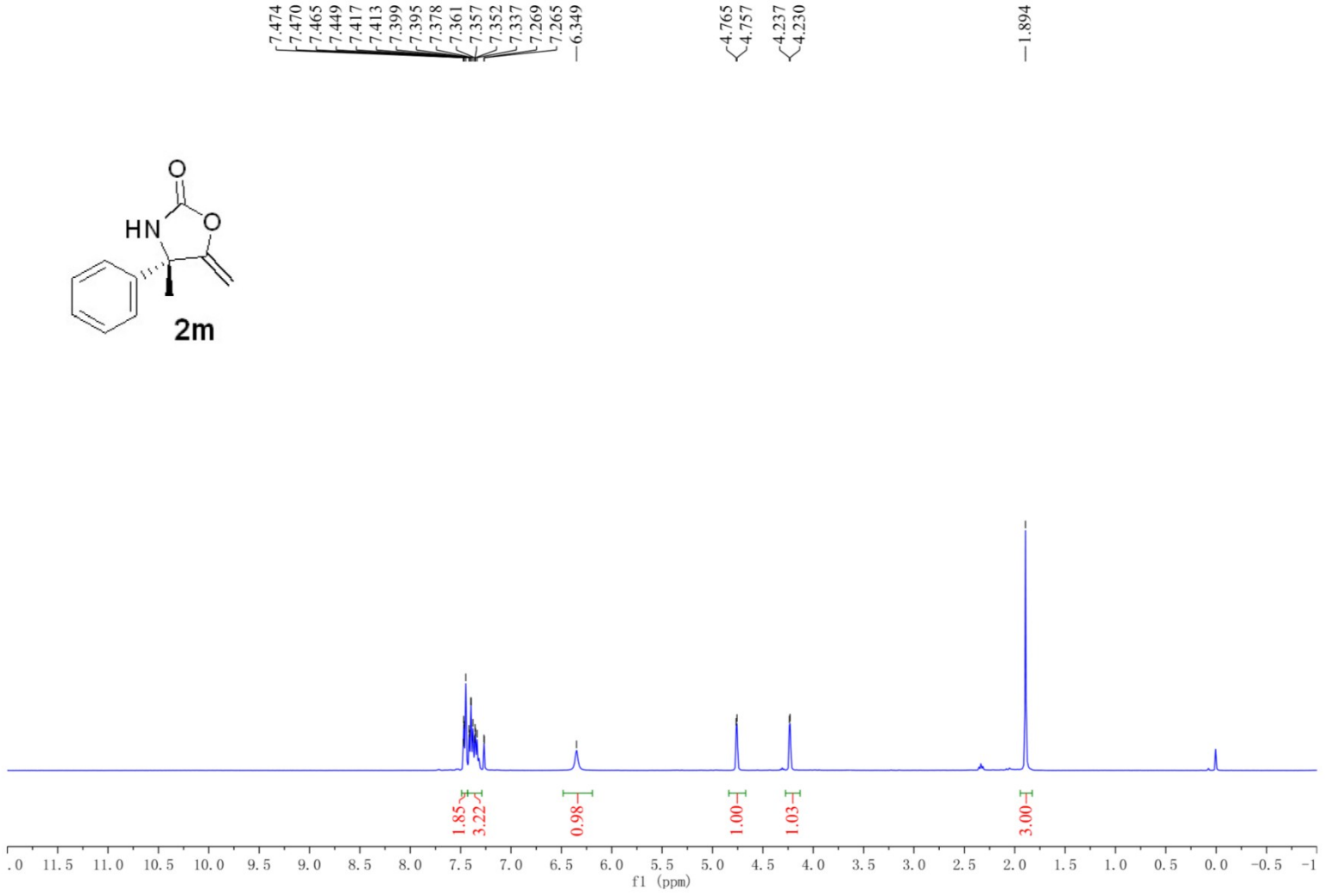

second trial/2
157.10
146.69
133.35
132.04
128.57
128.44
128.09
126.98
105.83
77.30
76.99
76.67
66.22
35.80
24.97
O
HN
O
Ph
2k
f1 (ppm)

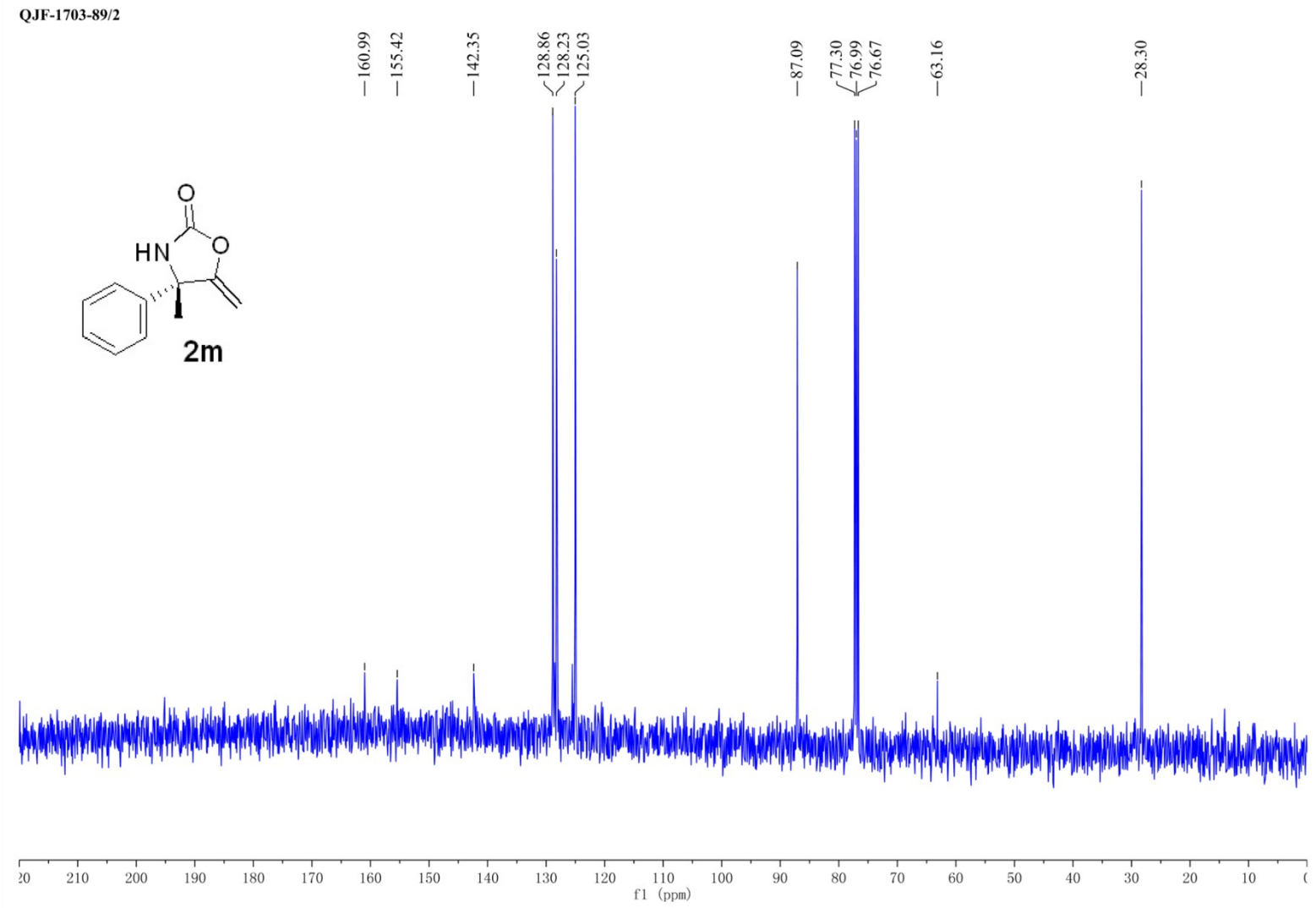
QJF-1703-101/1

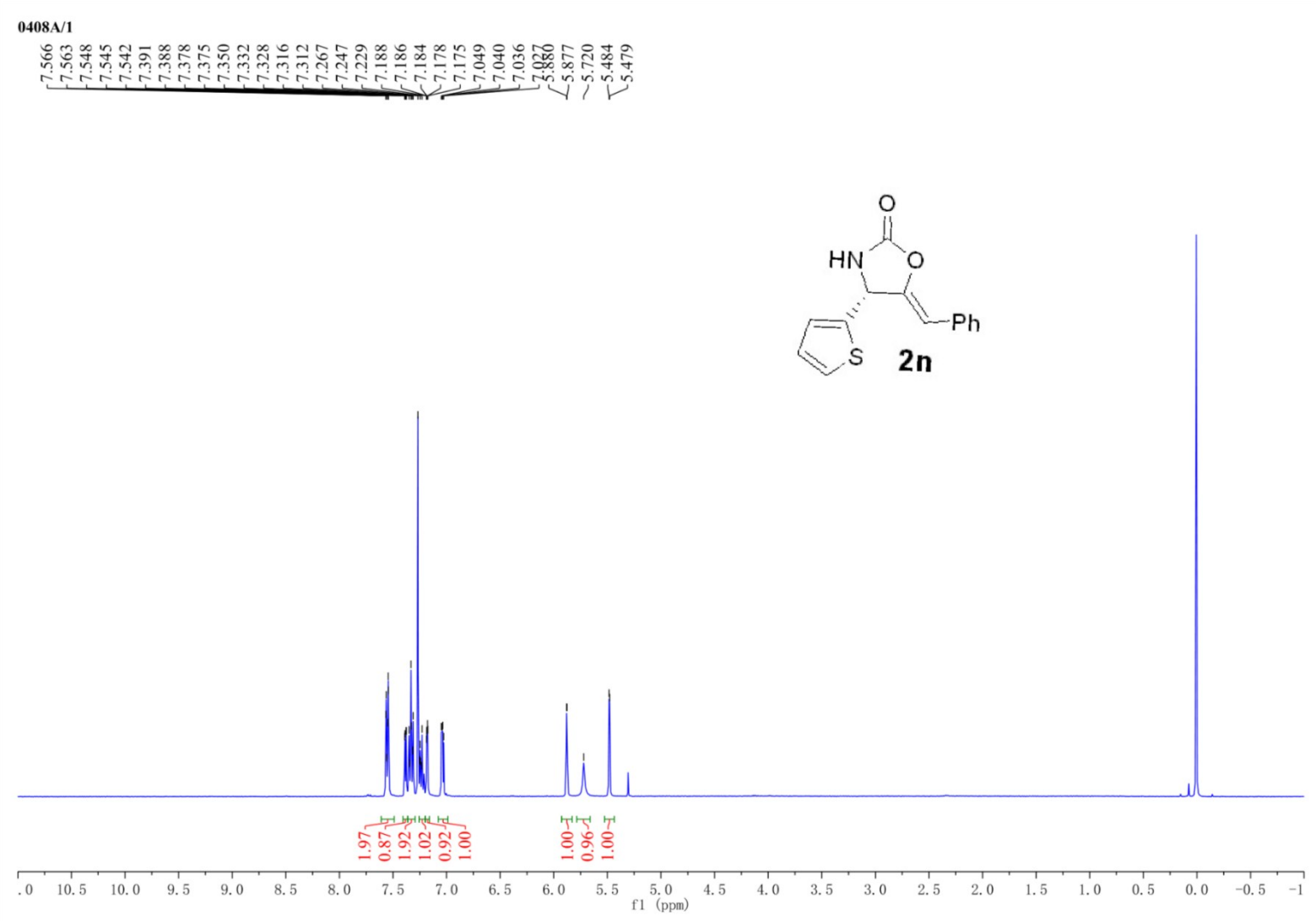


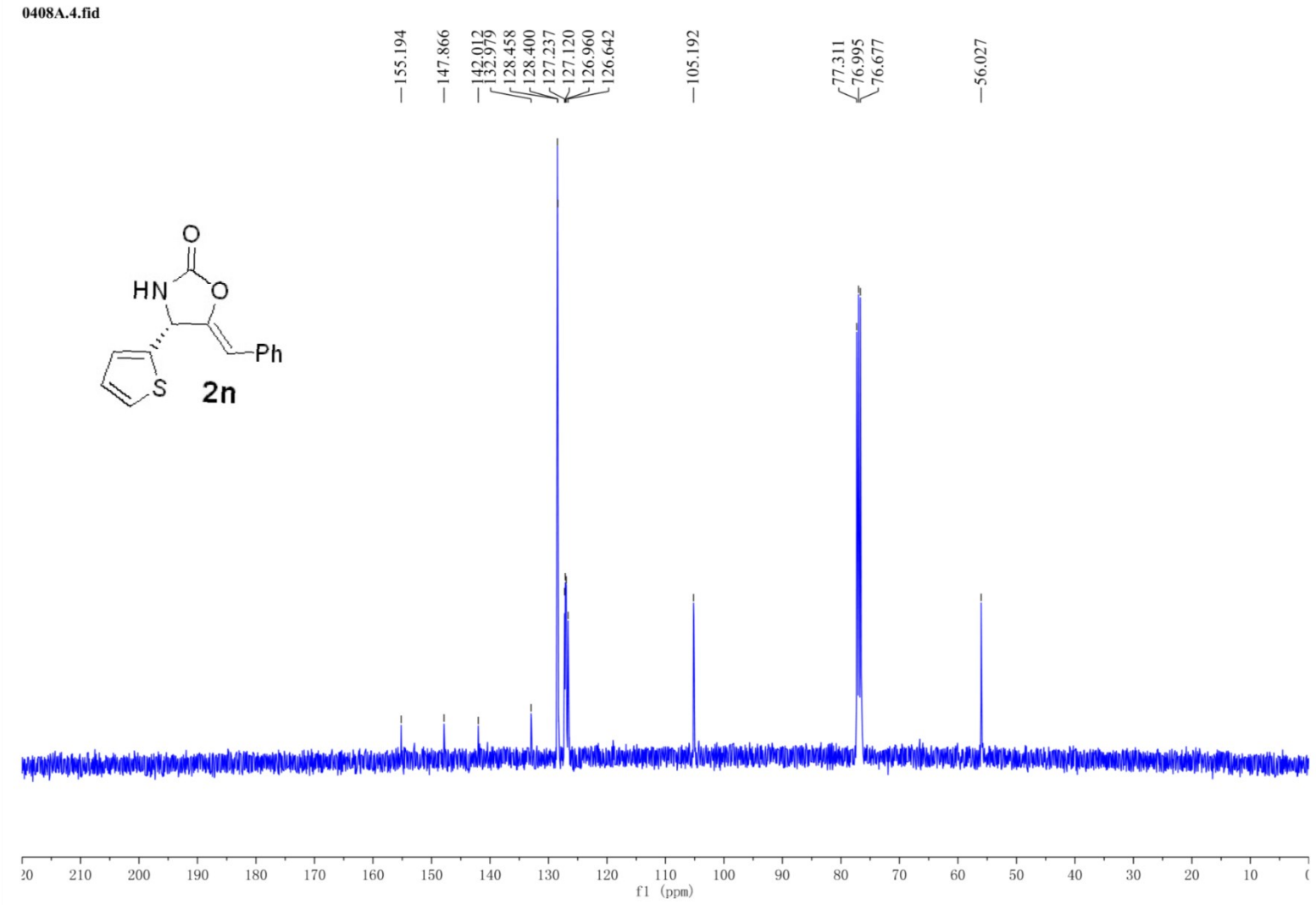

QJF-1703-101/2
160.77
156.54
84.94
77.33
77.01
76.70
64.37
47.51
26.56
26.31
26.15
26.01
25.92
25.49
HN
O
O
2l
f1 (ppm)

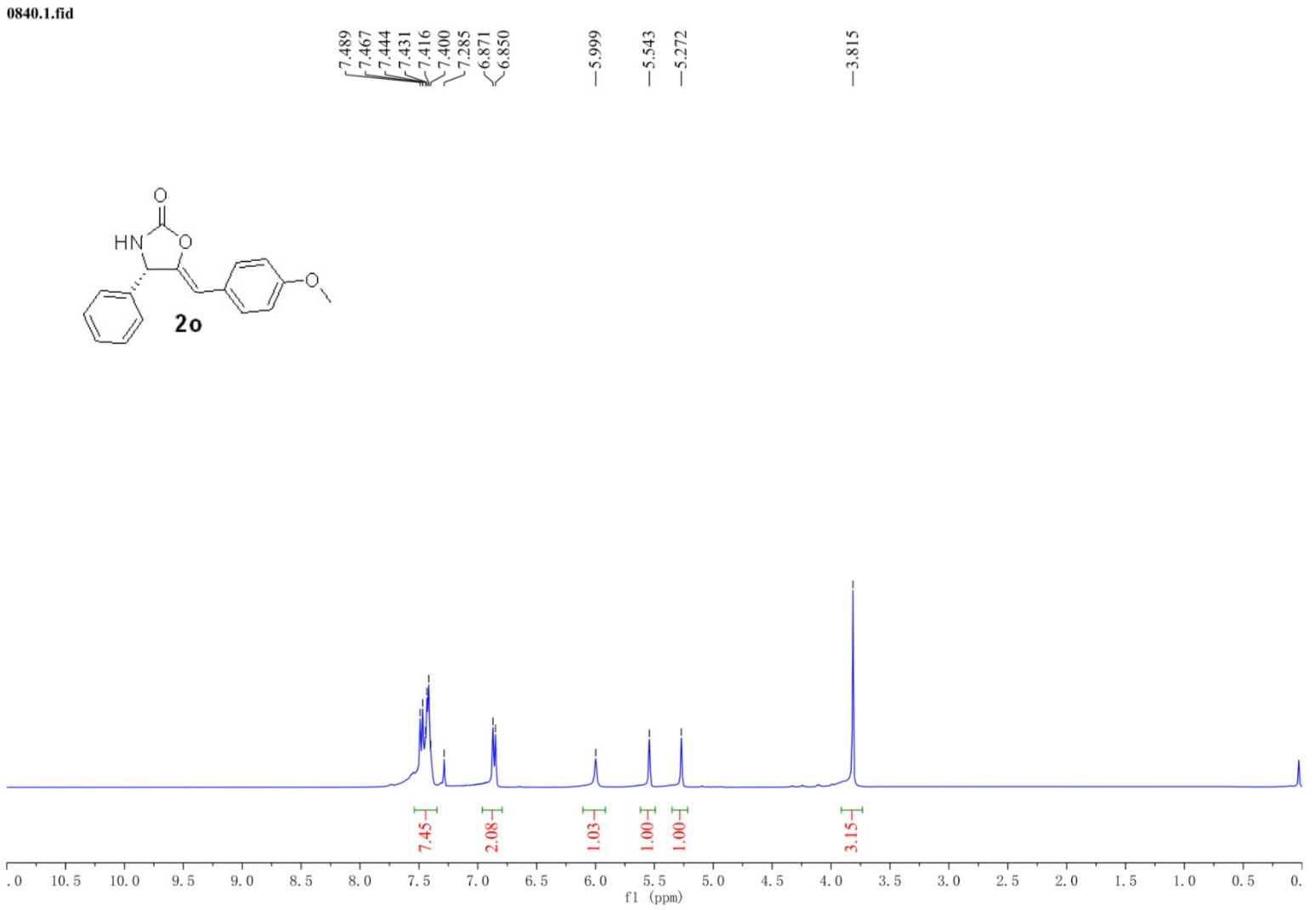
QJF-1703-89/1

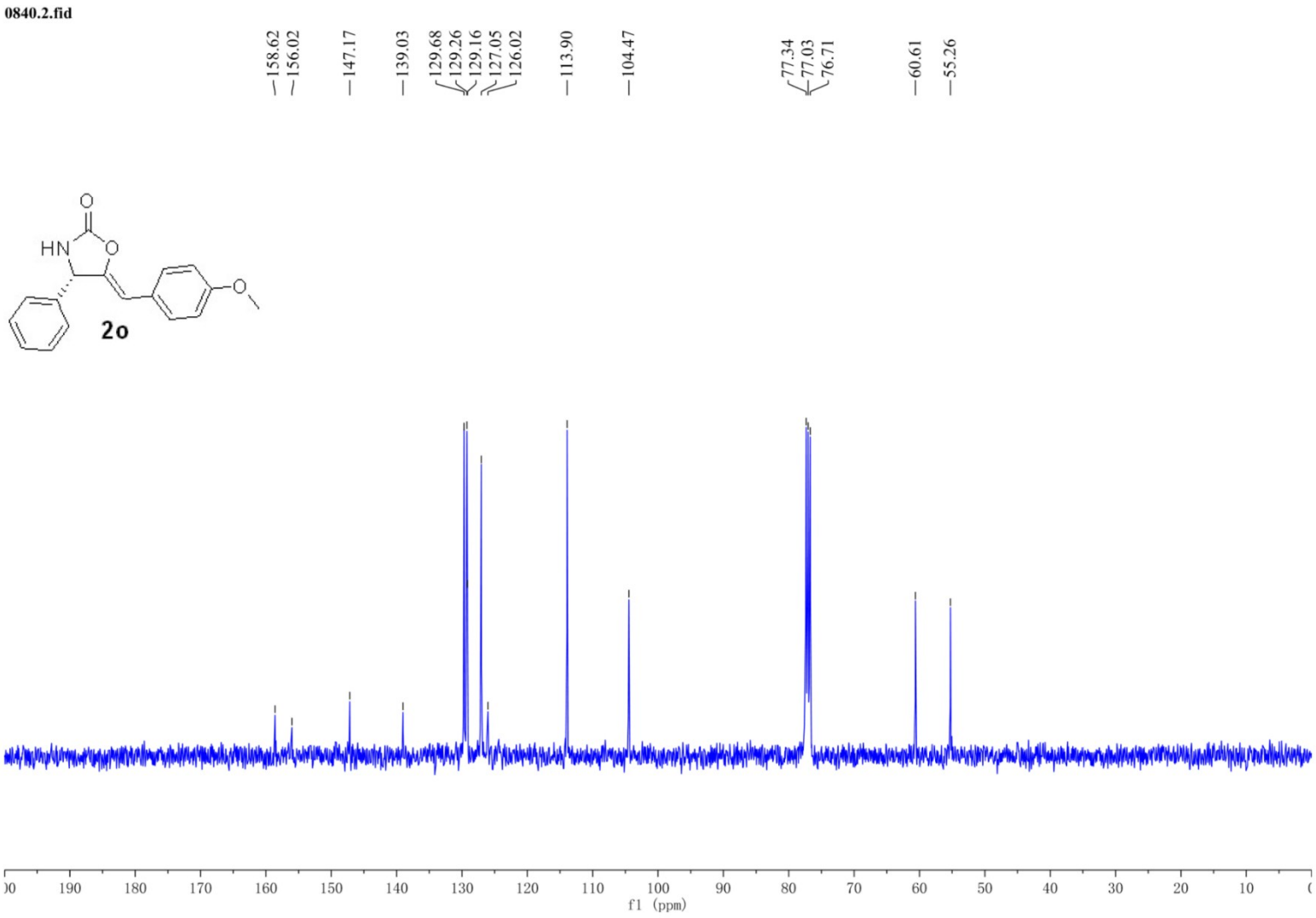

7.474
7.470
7.465
7.449
7.417
7.413
7.399
7.395
7.378
7.361
7.357
7.352
7.337
7.269
7.265
6.349
4.765
4.757
4.237
4.230
1.894
HN
O
O
2m
1.85
3.22
0.98
1.00
1.03
3.00
f1 (ppm)


QJF-1703-89/2
160.99
155.42
142.35
128.86
128.23
125.03
87.09
77.30
76.99
76.67
63.16
28.30
HN
O
O
2m
f1 (ppm)

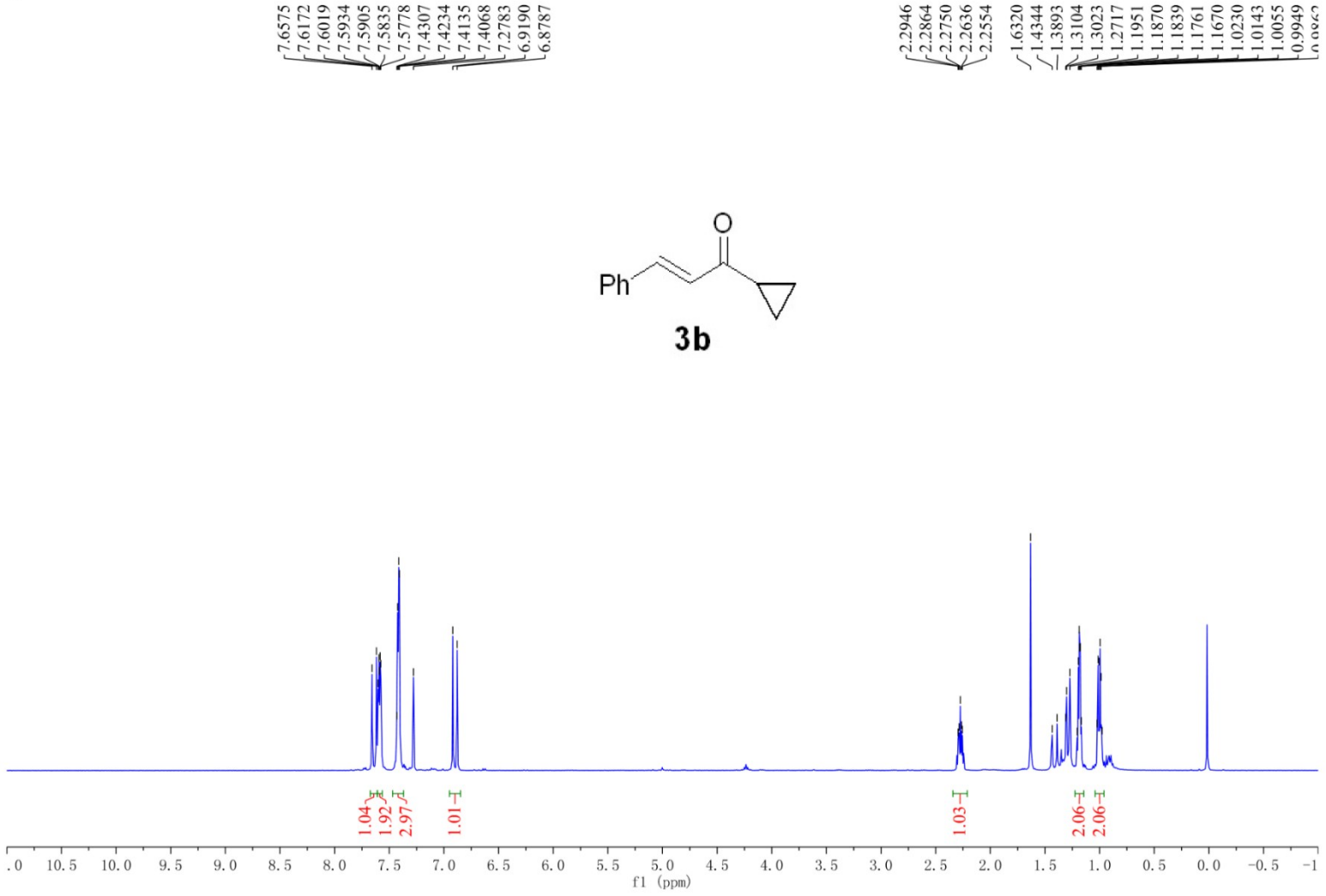

0408A/1
7.566
7.563
7.548
7.545
7.542
7.391
7.388
7.378
7.375
7.350
7.332
7.328
7.316
7.312
7.267
7.247
7.229
7.188
7.186
7.184
7.178
7.175
7.049
7.040
7.036
5.880
5.877
5.720
5.484
5.479
HN
O
O
Ph
S
2n
1.97
0.87
1.92
1.02
0.92
1.00
1.00
0.96
1.00
f1 (ppm)


0408A.4.fid
155.194
147.866
142.012
132.979
128.458
128.400
127.237
127.120
126.960
126.642
105.192
77.311
76.995
76.677
56.027
O
HN
O
Ph
S
2n
f1 (ppm)

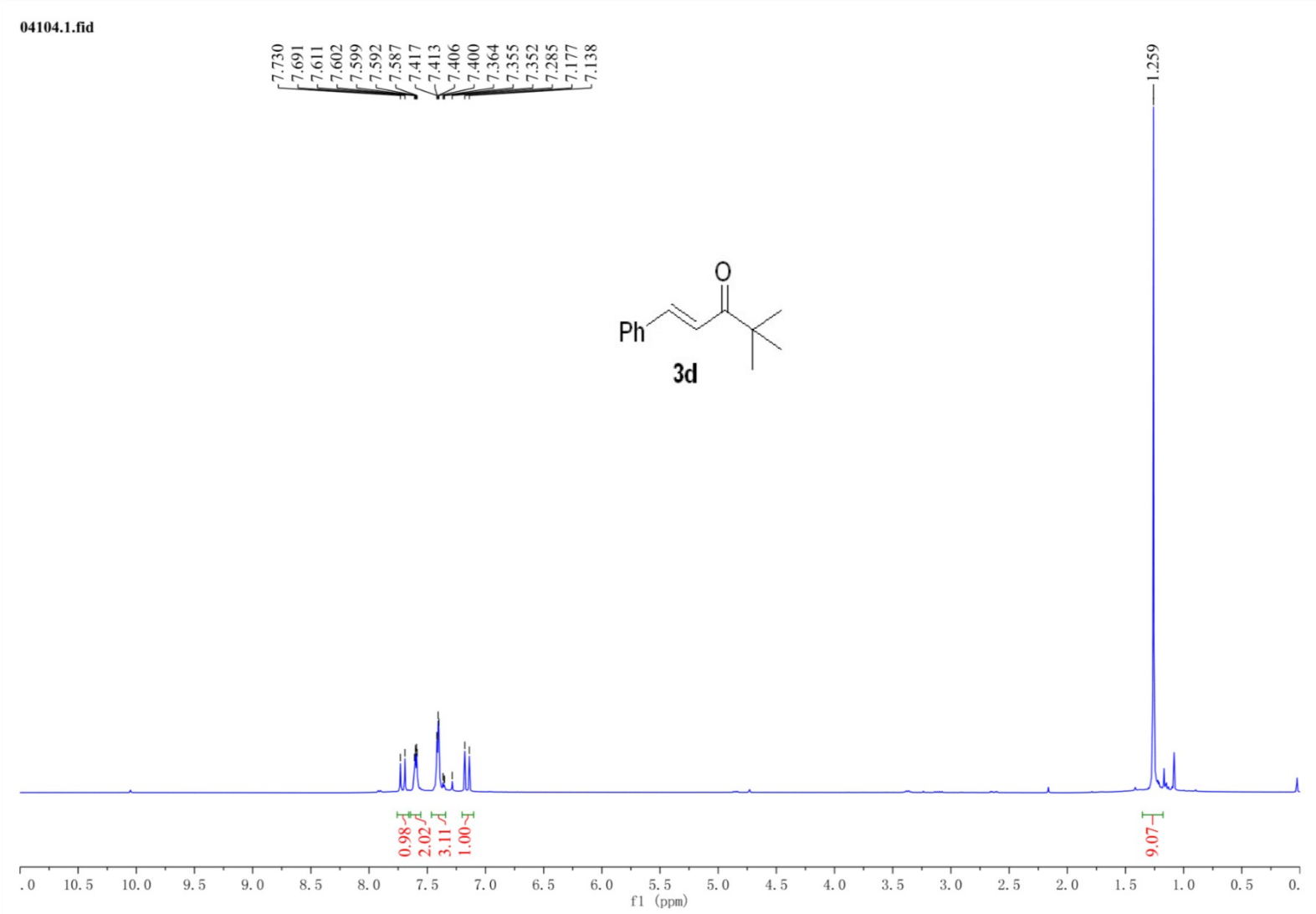

0840.1.fid
7.489
7.467
7.444
7.431
7.416
7.400
7.285
6.871
6.850
5.999
5.543
5.272
3.815
HN
O
O
O
2o
7.45
2.08
1.03
1.00
1.00
3.15
f1 (ppm)


0840.2.fid
158.62
156.02
147.17
139.03
129.68
129.26
129.16
127.05
126.02
113.90
104.47
77.34
77.03
76.71
60.61
55.26
HN
O
O
O
2o
f1 (ppm)

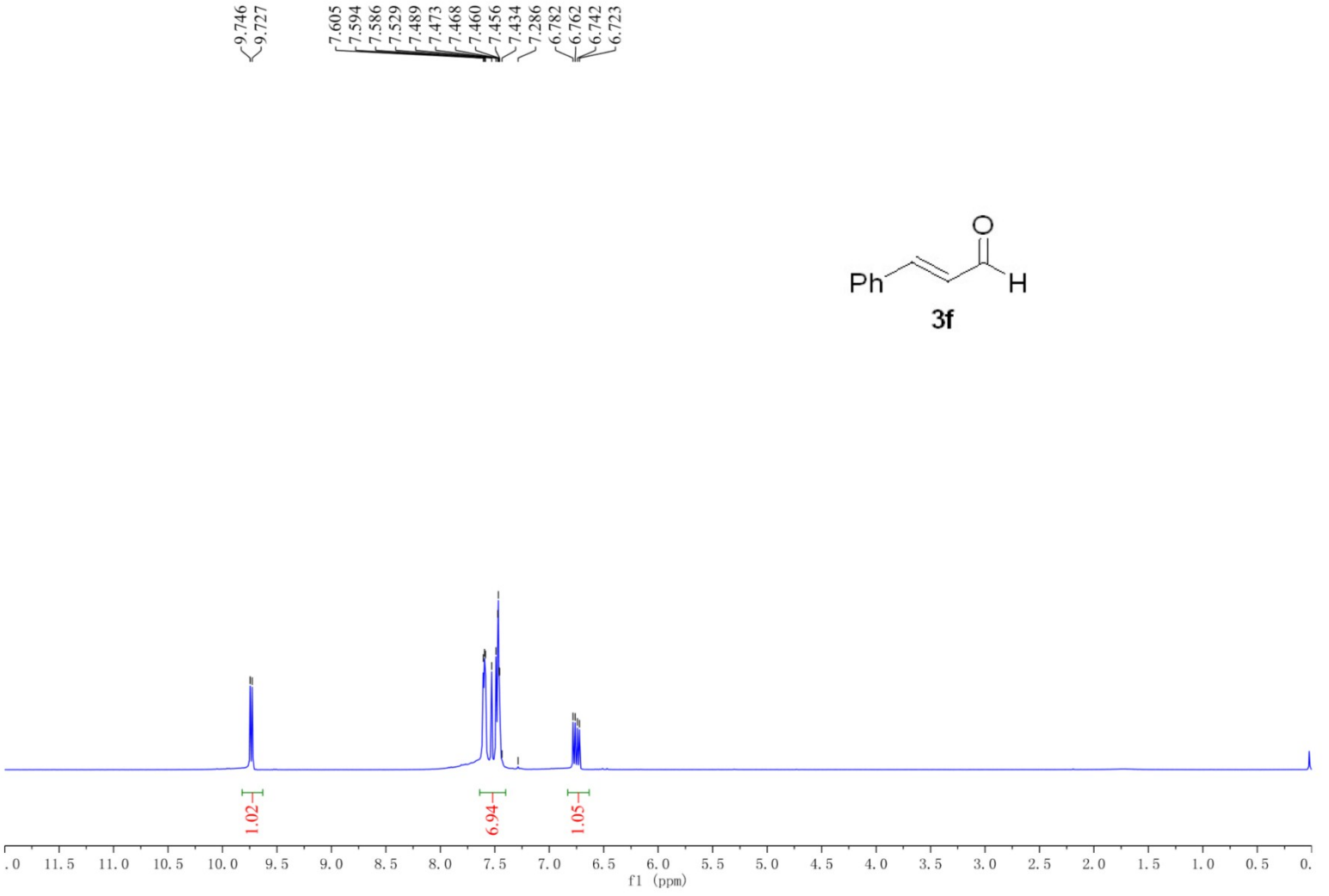
QJF-1703-69/1



3b

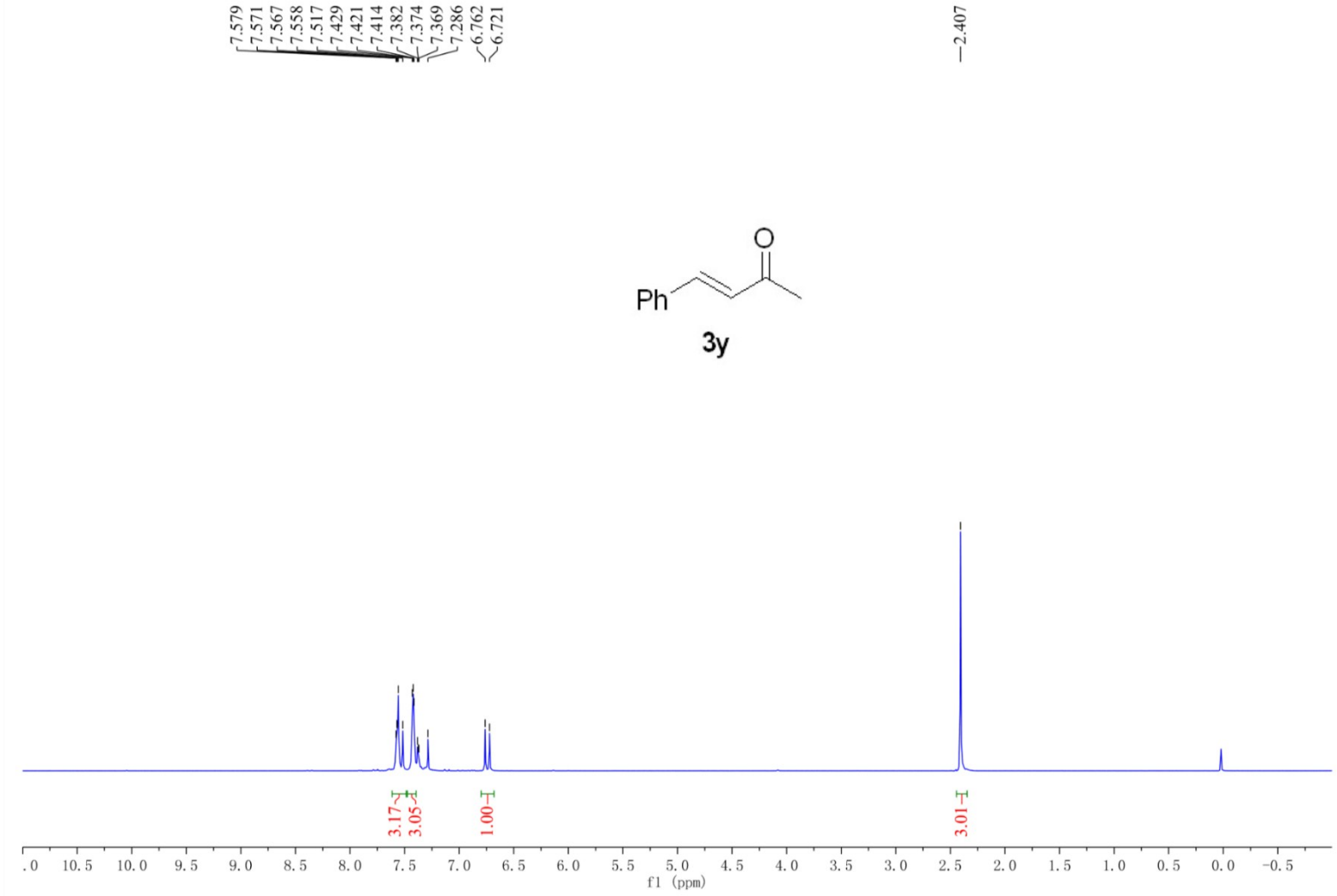

04104.1.fid
7.730
7.691
7.611
7.602
7.599
7.592
7.587
7.417
7.413
7.406
7.400
7.364
7.355
7.352
7.285
7.177
7.138
1.259
O
Ph
3d
0.98
2.02
3.11
1.00
9.07
f1 (ppm)

04102.1.fid



3f

04103.1.fid

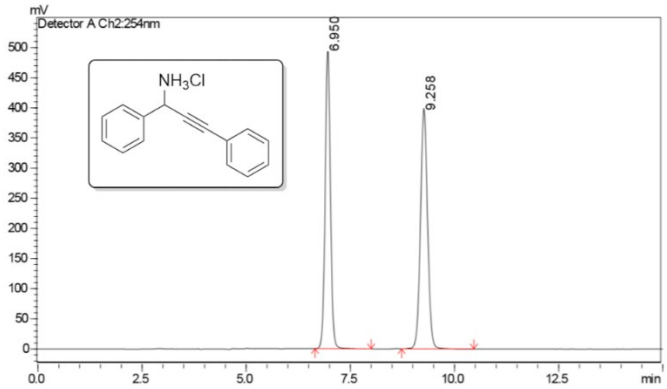

7.579
7.571
7.567
7.558
7.517
7.429
7.421
7.414
7.382
7.374
7.369
7.286
6.762
6.721
2.407
Ph
O
3y
3.17
3.05
1.00
3.01
f1 (ppm)

DAICEL CHIRAL TECHNOLOGIES (CHINA) CO., LTD.

No. 32, Hexiang Road, WaiGaoQiao Freetradezone, Shanghai, 200131, China
Tel: 021-50460086 Fax: 021-50462321 Web: www.daicelchiraltech.cn

Column	:	CHIRALPAK® AY-H
Column size	:	0.46 cm I.D. ×25 cm L ×5 μm
Injection	:	2 μl
Mobile phase	:	n-Hexane/Isopropanol /Diethylamine = 90/10/0.1(v/v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35℃
Sample solution	:	1.0 mg/ml in EtOH10% Hexane90%
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-02
Sample structure		B190635N 1-1 本次分析结果仅代表来样 建议使用中性流动相溶解样品

< Chromatogram >



<Column Performance Report>

Peak No.	Time	Area	Area %	Plate number	Tailing	Resolution
1	6.950	4371630	48.0400	11417.354	1.084	--
2	9.258	4728354	51.9600	12190.135	1.083	7.752

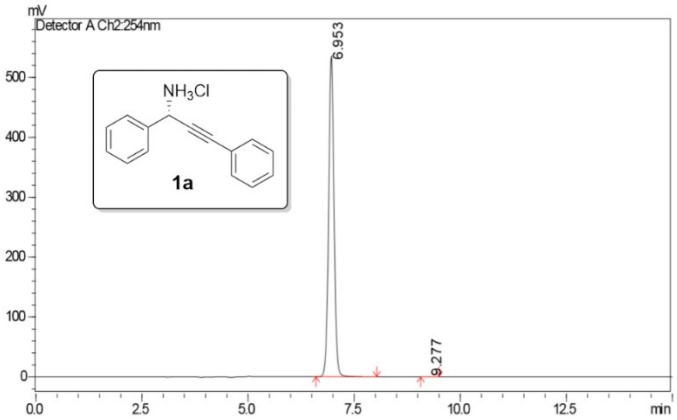
Testing date：2019-06-26 Tested by：Feng Xiaowan Confirmed by：Wang Yanlin

DAICEL CHIRAL TECHNOLOGIES (CHINA) CO., LTD.

No. 32, Hexiang Road, WaiGaoQiao Freetradezone, Shanghai, 200131, China
Tel: 021-50460086 Fax: 021-50462321 Web: www.daicelchiraltech.cn

Column	:	CHIRALPAK® AY-H
Column size	:	0.46 cm I.D. ×25 cm L ×5 μm
Injection	:	2 μl
Mobile phase	:	n-Hexane/Isopropanol /Diethylamine = 90/10/0.1(v/v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35℃
Sample solution	:	0.5 mg/ml in EtOH10% Hexane90%
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-02
Sample structure		B190636N 1-2 本次分析结果仅代表来样 建议使用中性流动相溶解样品

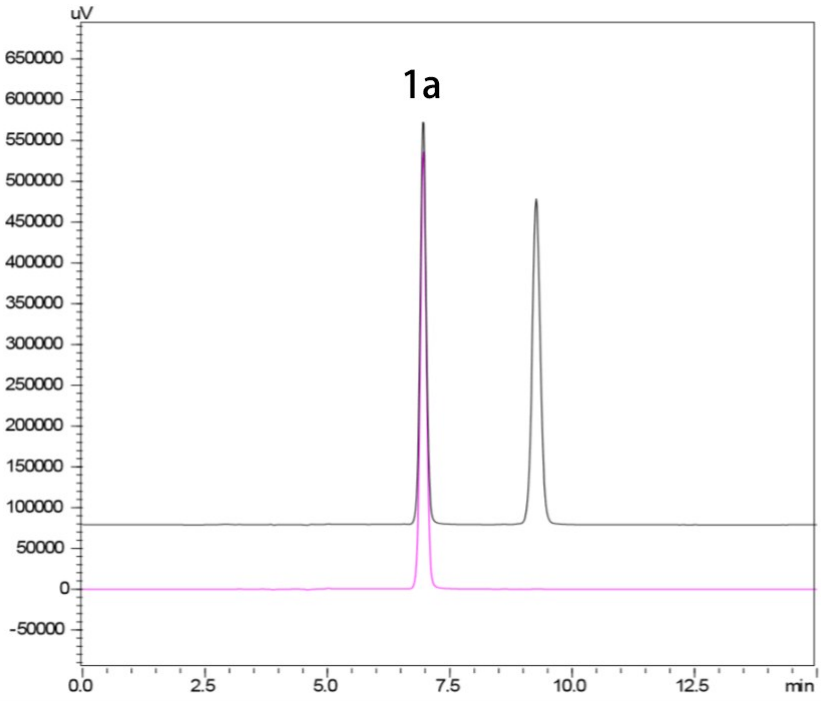
< Chromatogram >



<Column Performance Report>

Peak No.	Time	Area	Area %	Plate number	Tailing	Resolution
1	6.953	4729101	99.9726	11808.869	1.084	--
2	9.277	1296	0.0274	13312.546	1.057	8.046

Testing date: 2019-06-26 Tested by: Feng Xiaowan Confirmed by: Wang Yanlin

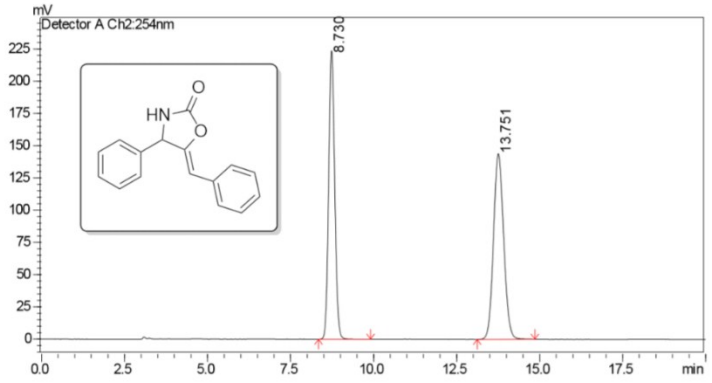

uV
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
1a
0.0
2.5
5.0
7.5
10.0
12.5
min

DAICEL CHIRAL TECHNOLOGIES (CHINA) CO., LTD.

No. 32, Hexiang Road, WaiGaoQiao Freetradezone, Shanghai, 200131, China
Tel: 021-50460086 Fax: 021-50462321 Web: www.daicelchiraltech.cn

Column	:	CHIRALCEL® OJ-H
Column size	:	0.46 cm I.D. ×25 cm L ×5 µm
Injection	:	3 µl
Mobile phase	:	n-Hexane / Ethanol = 75/25 (v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35℃
Sample solution	:	0.4 mg/ml in MeOH10% EtOH20% Hexane70%
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-01
Sample structure		B190631N A-1 本次分析结果仅代表来样 建议使用中性流动相溶解样品

< Chromatogram >



<Column Performance Report>

Peak No.	Time	Area	Area %	Plate number	Tailing	Resolution
1	8.730	2840147	48.0386	10535.831	1.111	--
2	13.751	3072078	51.9614	9489.267	1.107	11.098

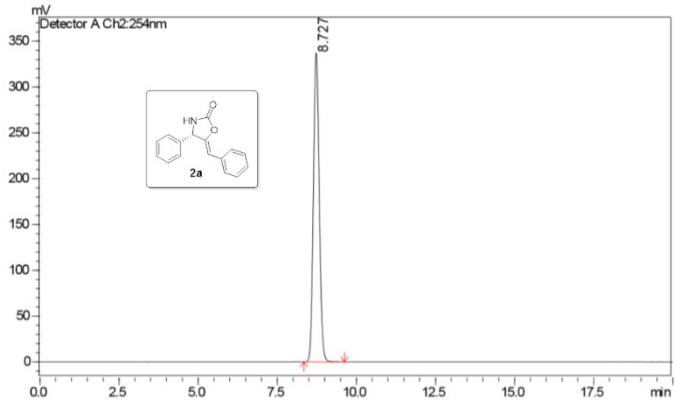
Testing date：2019-06-24 Tested by：Feng Xiaowan Confirmed by：Wang Yanlin

DAICEL CHIRAL TECHNOLOGIES (CHINA) CO., LTD.

No. 32, Hexiang Road, WaiGaoQiao Freetradezone, Shanghai, 200131, China
Tel: 021-50460086 Fax: 021-50462321 Web: www.daicelchiraltech.cn

Column	:	CHIRALCEL® OJ-H
Column size	:	0.46 cm I.D. ×25 cm L ×5 μm
Injection	:	2 μl
Mobile phase	:	n-Hexane / Ethanol = 75/25 (v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35℃
Sample solution	:	0.3 mg/ml in MeOH10% EtOH20% Hexane70%
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-01
Sample structure		B190632N A-2 本次分析结果仅代表来样 建议使用中性流动相溶解样品

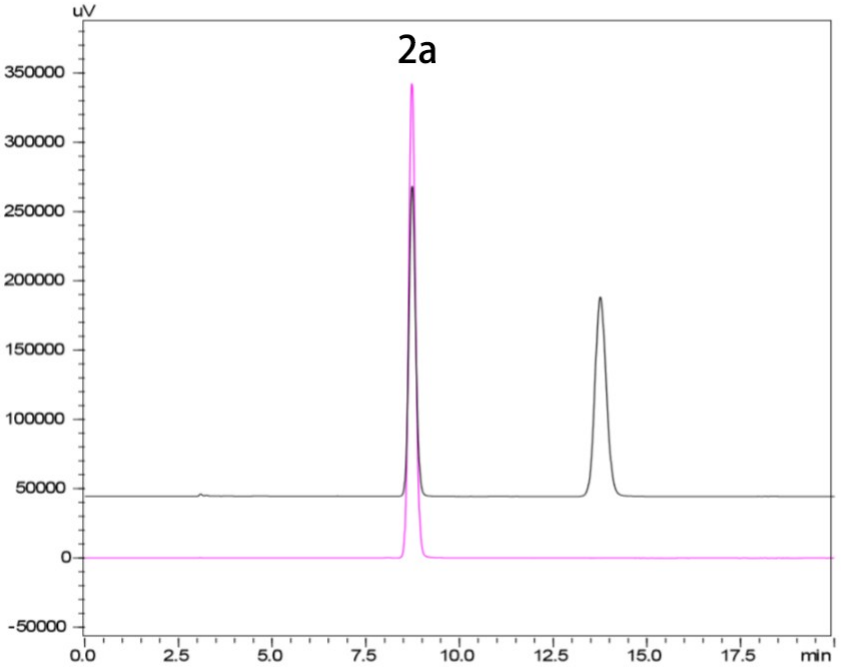
< Chromatogram >



<Column Performance Report>

Peak No.	Time	Area	Area %	Plate number	Tailing	Resolution
1	8.727	4340493	100.0000	10268.065	1.120	--

Testing date：2019-06-24 Tested by：Feng Xiaowan Confirmed by：Wang Yanlin


2a
uV
350000
300000
250000
200000
150000
100000
50000
0
-50000
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
min

DAICEL CHIRAL TECHNOLOGIES (CHINA) CO., LTD.

No. 32, Hexiang Road, WaiGaoQiao Freetradezone, Shanghai, 200131, China
Tel: 021-50460086 Fax: 021-50462321 Web: www.daicelchiraltech.cn

Column	:	CHIRALPAK® AY-H
Column size	:	0.46 cm I.D. ×25 cm L ×5 μm
Injection	:	2 μl
Mobile phase	:	n-Hexane/Isopropanol /Diethylamine = 95/5/0.1(v/v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35℃
Sample solution	:	1.0 mg/ml in Mobile phase（超声）
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-02
Sample structure		B190637N 4-1
		本次分析结果仅代表来样 建议使用中性流动相溶解样品

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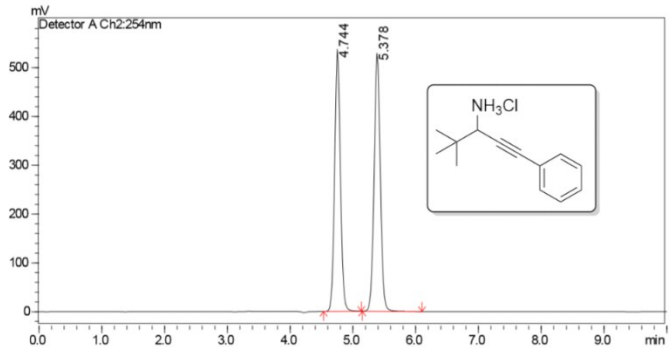

<Column Performance Report>

Peak No.	Time	Area	Area %	Plate number	Tailing	Resolution
1	4.744	3442260	48.6124	9521.973	1.172	--
2	5.378	3638780	51.3876	10490.662	1.114	3.131

Testing date：2019-06-26 Tested by：Feng Xiaowan Confirmed by：Wang Yanlin

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Injection	:	2 μl
Mobile phase	:	n-Hexane/Isopropanol /Diethylamine = 95/5/0.1(v/v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35℃
Sample solution	:	0.5 mg/ml in Mobile phase
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-02
Sample structure		B190638N 4-2 本次分析结果仅代表来样 建议使用中性流动相溶解样品

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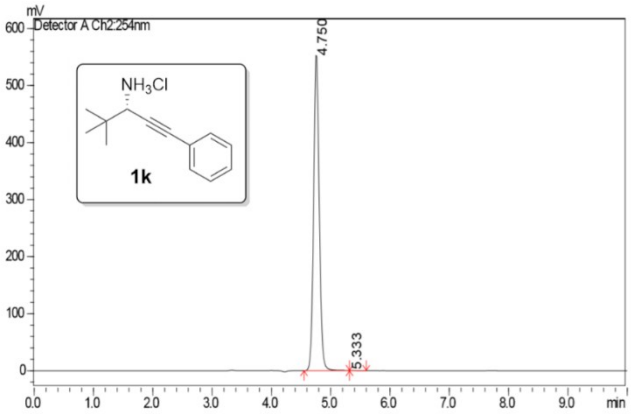
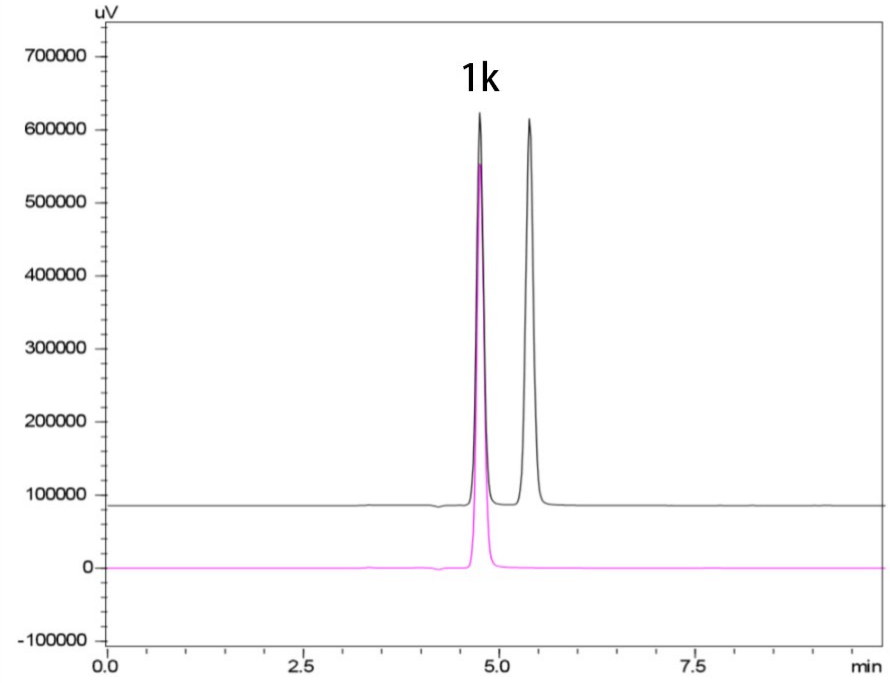


<Column Performance Report>

Peak No.	Time	Area	Area %	Plate number	Tailing	Resolution
1	4.750	3658375	99.9107	8981.643	1.177	--
2	5.333	3270	0.0893	--	--	--

Testing date：2019-06-26 Tested by：Feng Xiaowan Confirmed by：Wang Yanlin


uV
700000
600000
500000
400000
300000
200000
100000
0
-100000
0.0
2.5
5.0
7.5
min
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Column	:	CHIRALCEL® OJ-H
Column size	:	0.46 cm I.D. ×25 cm L ×5 μm
Injection	:	2 μl
Mobile phase	:	n-Hexane / Ethanol = 95/5 (v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35℃
Sample solution	:	0.5 mg/ml in MeOH10% EtOH20% Hexane70%
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-01
Sample structure		B190633N D-1 本次分析结果仅代表来样 建议使用中性流动相溶解样品

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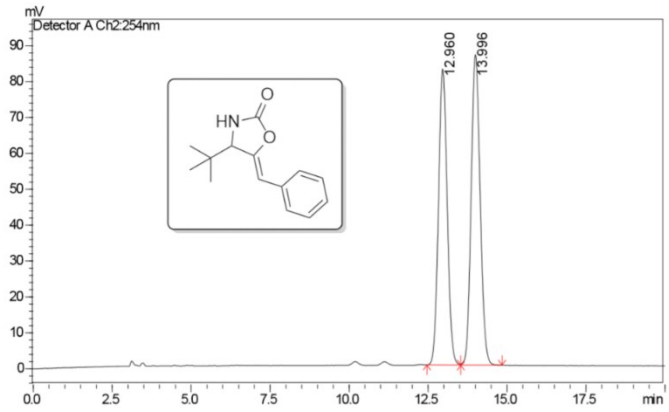

<Column Performance Report>

Peak No.	Time	Area	Area %	Plate number	Tailing	Resolution
1	12.960	1583604	48.0095	10214.769	1.074	--
2	13.996	1714915	51.9905	11241.287	1.122	1.990

Testing date: 2019-06-24 Tested by: Feng Xiaowan Confirmed by: Wang Yanlin

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Column size	:	0.46 cm I.D. ×25 cm L ×5 μm
Injection	:	2 μl
Mobile phase	:	n-Hexane / Ethanol = 95/5 (v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35℃
Sample solution	:	0.5 mg/ml in MeOH10% EtOH20% Hexane70%
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-01

Sample structure: B190634N D-2

本次分析结果仅代表来样 建议使用中性流动相溶解样品

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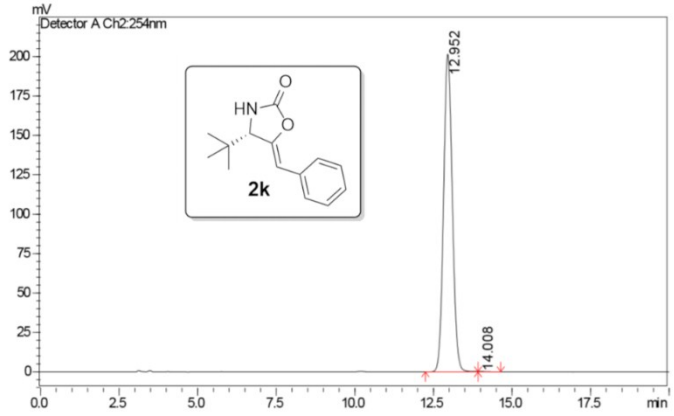

<Column Performance Report>

Peak No.	Time	Area	Area %	Plate number	Tailing	Resolution
1	12.952	3901445	99.8697	10178.434	1.097	--
2	14.008	5089	0.1303	3967.697	--	1.505

Testing date: 2019-06-24 Tested by: Feng Xiaowan Confirmed by: Wang Yanlin

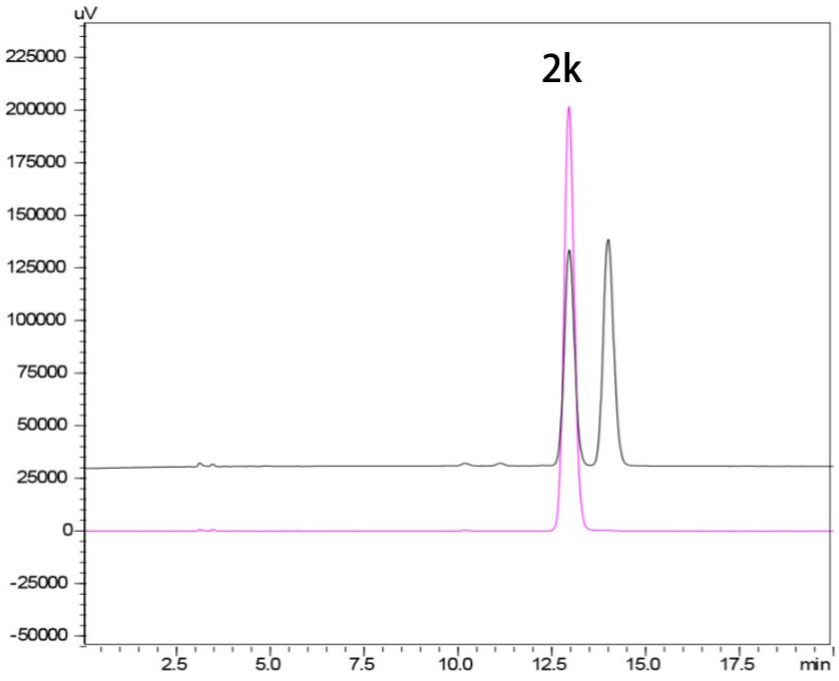

Table S1. Summary of Chiral HPLC Analysis

compound	column	$t_{R\,(S)}$ (min)	$t_{R\,(R)}$ (min)	ee (%)
1a	Chiralpak AY-H	6.95	9.26	99.94
2a	Chiralcel OJ-H	8.73	13.75	100
1k	Chiralpak AY-H	4.74	5.38	99.82
2k	Chiralcel OJ-H	12.96	14.00	99.74