Supporting Information

Concise asymmetric synthesis of (−)-Bao Gong Teng A via Evans chiral auxiliary-based 1,3-dipolar cycloaddition

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Table of contents

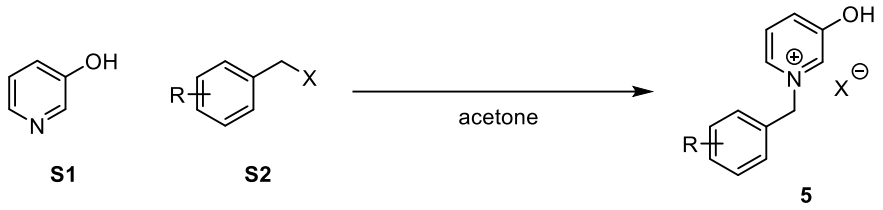
1. General Information

All moisture-sensitive reactions were performed under an atmosphere of nitrogen, and the starting materials were azeotropically dried with benzene before use. All reagents were purchased and used without further purification unless otherwise specified. TLC analyses were conducted on Huanghai precoated silica gel $HSGF_{254}$ (0.2 mm layer thickness) purchased from Yantai Jiangyou Silica gel Development Co., Ltd. Visualization was accomplished with UV light, exposure to iodine, stained with ethanolic solution of phosphomolybdic acid or basic solution of $KMnO_4$. Column chromatography was performed over silica gel (AR, 100-200 mesh or 300-400 mesh) purchased from Shanghai Titan Scientific Co., Ltd. Anhydrous tetrahydrofuran (THF), dichloromethane (DCM), ethyl acetate (EtOAc), toluene, acetonitrile (MeCN) and triethylamine (Et_3N) were purchased from Shanghai Titan Scientific Co., Ltd. and used without further drying.

Specific Rotation (OR) was measured on Rudolph Research Analytical AUTOPOL IV Automatic Polarimeter. Infrared (IR) spectra were recorded on a SHIMADZU IRAffinity-1S Instrument, and only selected peaks are reported in wavenumbers (cm^{-1}). ^1H and ^{13}C NMR spectra were collected on a Bruker AVANCE NEO 400 MHz and 600 MHz NMR Spectrometer using residue solvent peaks as an internal standard (^1H NMR: DMSO-*d6* at 2.50 ppm, methanol-*d4* at 3.31 ppm, $CDCl_3$ at 7.26 ppm, acetone-*d6* at 2.05 ppm; ^{13}C NMR: DMSO-*d6* at 39.52 ppm, methanol-*d4* at 49.00 ppm, $CDCl_3$ at 77.00 ppm, acetone-*d6* at 29.84 ppm), coupling constant *J* are given in Hz. The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, hept = heptet, m = multiplet, and br = broad), *J* values (Hz), and integration. High resolution mass spectra (HRMS) were acquired by Agilent 6545 Accurate-Mass Q-TOF LC/MS System. Melting points (MP) were determined on a INESA SGW X-4A Micro melting point apparatus, and the temperature range is reported in Celsius degrees (℃). X-ray structure was determined on a Bruker D8 Venture X-ray Diffraction meter.

2. General Procedures for the Preparation of Pyridinium Salt 5 and *N*-Acryloyloxazolidinone 6

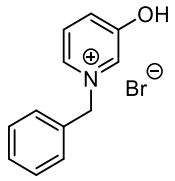
Pyridinium Salt 5.



S1 **S2** **5**

A mixture of 3-hydroxypyridine **S1** (1.0 eq.) and benzyl halide **S2** (1.1 eq.) in acetone (1.2 M) was refluxed overnight. After removing the solvent by evaporation, the resultant crude product was recrystallized from acetonitrile to afford crystalline pyridinium salt **5** as a pure product.

Pyridinium salt 5a.



5a

According to the general procedures, **5a** (24.7 g, 87% yield, a white crystal) was synthesized from 3-hydroxypyridine **S1** (10.1 g, 106 mmol) and corresponding benzyl halide (13.4 mL, 113 mmol).

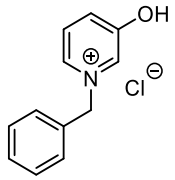
TLC: R_f = 0.38 (CH_2Cl_2 / MeOH, 9:1 v/v).

^{1}H NMR (600 MHz, DMSO-*d6*): δ 12.02 (brs, 1H), 8.78–8.68 (m, 2H), 8.02–7.91 (m, 2H), 7.59–7.50 (m, 2H), 7.48–7.39 (m, 3H), 5.79 (s, 2H).

Mp: 147–149 ℃.

The spectroscopic data of pyridinium salt **5a** were in accordance with those reported in literature.[1]

Pyridinium salt 5b.



5b

According to the general procedures, **5b** (10.8 g, 66% yield, a white crystal) was synthesized from 3-hydroxypyridine **S1** (7.02 g, 73.8 mmol) and corresponding benzyl halide (9.30 mL, 80.8 mmol).

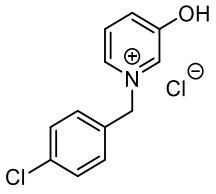
TLC: R_f = 0.35 (CH_2Cl_2 / MeOH, 9:1 v/v).

^{1}H NMR (600 MHz, DMSO-*d6*): δ 12.48 (brs, 1H), 8.83 (m, 1H), 8.73 (m, 1H), 8.11 (m, 1H), 7.95 (dd, *J* = 8.7, 5.9 Hz, 1H), 7.56–7.52 (m, 2H), 7.46–7.38 (m, 3H), 5.79 (s, 2H).

Mp: 131–133 ℃.

The spectroscopic data of pyridinium salt **5b** were in accordance with those reported in literature.[2]

Pyridinium salt 5c.



5c

According to the general procedures, **5c** (15.7 g, 73% yield, a white crystal) was synthesized from 3-hydroxypyridine **S1** (8.01 g, 84.3 mmol) and corresponding benzyl halide (11.9 mL, 93.1 mmol).

TLC: R_f = 0.32 (CH_2Cl_2 / MeOH, 9:1 v/v).

IR (KBr): 3024, 2814, 2606, 2517, 1584, 1512, 1493, 1458, 1312, 1274, 1153, 1032, 812 cm^{-1}.

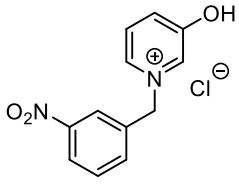
^{1}H NMR (600 MHz, methanol-*d4*): δ 8.57–8.51 (m, 2H), 7.96 (ddd, *J* = 8.7, 2.4, 1.1 Hz, 1H), 7.92 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.53–7.46 (m, 4H), 5.75 (s, 2H), a signal due to proton (OH) was not observed.

^{13}C NMR (150 MHz, methanol-*d4*): δ 159.4, 137.0, 136.8, 134.0, 133.5, 133.1, 131.8 (2C), 130.8 (2C), 130.1, 64.8.

HRMS (ESI+): *m/z* calculated for $C_{12}H_{11}ClNO^+$ $[M–Cl]^+$ 220.0524, found *m/z* 220.0526.

Mp: 178–180 ℃.

Pyridinium salt 5d.



5d

According to the general procedures, **5d** (4.86 g, 69% yield, a white crystal) was synthesized from 3-hydroxypyridine **S1** (2.51 g, 26.4 mmol) and corresponding benzyl halide (5.01 g, 29.2 mmol).

TLC: R_f = 0.28 (CH_2Cl_2 / MeOH, 9:1 v/v).

IR (KBr): 3055, 2964, 2839, 2635, 2365, 1558, 1543, 1506, 1489, 1346, 1312, 772 cm^{-1}.

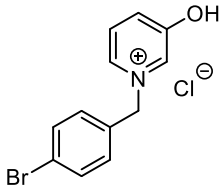
^{1}H NMR (600 MHz, methanol-*d4*): δ 8.62 (m, 1H), 8.59 (m, 1H), 8.43 (m, 1H), 8.34 (ddd, *J* = 8.3, 2.2, 0.9 Hz, 1H), 7.99 (ddd, *J* = 8.7, 2.4, 1.0 Hz, 1H), 7.94 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.90 (m, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 5.90 (s, 2H), a signal due to proton (OH) was not observed.

^{13}C NMR (150 MHz, methanol-*d4*): δ 159.9, 150.2, 136.72, 136.70, 136.0, 134.3, 133.5, 132.0, 130.2, 125.6, 124.9, 64.4.

HRMS (ESI+): *m/z* calculated for $C_{12}H_{11}N_2O_3^+$ $[M–Cl]^+$ 231.0764, found *m/z* 231.0766.

Mp: 215–217 ℃.

Pyridinium salt 5e.



5e

According to the general procedures, **5e** (4.22 g, 63% yield, a white crystal) was synthesized from 3-hydroxypyridine **S1** (2.11 g, 22.2 mmol) and corresponding benzyl halide (5.00 g, 24.3 mmol).

TLC: R_f = 0.33 (CH_2Cl_2 / MeOH, 9:1 v/v).

IR (KBr): 3026, 2714, 2614, 2527, 1589, 1512, 1489, 1317, 1271, 1153, 1016, 762 cm^{-1}.

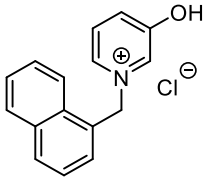
^{1}H NMR (600 MHz, methanol-*d4*): δ 8.56–8.52 (m, 2H), 7.97 (ddd, *J* = 8.7, 2.4, 1.0 Hz, 1H), 7.92 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.66–7.62 (m, 2H), 7.46–7.41 (m, 2H), 5.75 (s, 2H), a signal due to proton (OH) was not observed.

^{13}C NMR (150 MHz, methanol-*d4*): δ 159.4, 136.9, 134.0, 133.9, 133.8 (2C), 133.2, 131.9 (2C), 130.1, 125.1, 64.8.

HRMS (ESI+): *m/z* calculated for $C_{12}H_{11}{}^{79}BrNO^+$ $[M–Cl]^+$ 264.0019, found *m/z* 264.0021.

Mp: 195–197 ℃.

Pyridinium salt 5f.



5f

According to the general procedures, **5f** (28.6 g, 82% yield, a white crystal) was synthesized from 3-hydroxypyridine **S1** (12.2 g, 128 mmol) and corresponding benzyl halide (24.9 g, 141 mmol).

TLC: R_f = 0.41 (CH_2Cl_2 / MeOH, 9:1 v/v).

IR (KBr): 3021, 2684, 2575, 2509, 1584, 1574, 1510, 1329, 1310, 1275, 1146, 1028, 789 cm^{-1}.

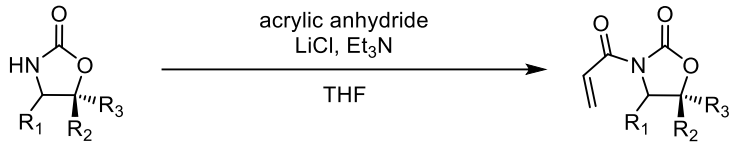
^{1}H NMR (600 MHz, methanol-*d4*): δ 8.49 (d, *J* = 5.8 Hz, 1H), 8.44 (m, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 8.02 (m, 1H), 7.98 (m, 1H), 7.94 (ddd, *J* = 8.7, 2.4, 1.0 Hz, 1H), 7.89 (dd, *J* = 8.7, 5.9 Hz, 1H), 7.66–7.58 (m, 4H), 6.29 (s, 2H), a signal due to proton (OH) was not observed.

^{13}C NMR (150 MHz, methanol-*d4*): δ 159.5, 136.6, 135.7, 133.6, 133.2, 132.4, 132.3, 130.9, 130.5, 129.9, 129.3, 129.0, 127.9, 126.7, 123.4, 63.3.

HRMS (ESI+): *m/z* calculated for $C_{16}H_{14}NO^+$ $[M–Cl]^+$ 236.1070, found *m/z* 236.1072.

Mp: 219–221 ℃.

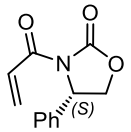
***N*-Acryloyloxazolidinone 6.**



S3 **6**

To a stirred solution of oxazolidinone **S3** (1.0 eq.) in THF (0.5 M) was added LiCl (1.3 eq.) at room temperature. After the mixture was cooled to -20 ℃, Et_3N (1.9 eq.) was added slowly into the mixture via syringe. After stirring for 30 min at the same temperature, acrylic anhydride (ca. 1.4 eq.) was added dropwise into the mixture via syringe. The mixture was stirred for 0.5 h at 0 ℃ and then kept at 10 ℃ for another 5 h. The reaction was checked by TLC detection, and the mixture was quenched by saturated aqueous NH_4Cl. After removing most of the THF by evaporation, the mixture was diluted with EtOAc and extracted with EtOAc three times. The combined extracts were washed with saturated aqueous $NaHCO_3$, brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure. The resultant crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether = 8% → 15%) to afford *N*-acryloyloxazolidinone **6** as a pure product.

***N*-Acryloyloxazolidinone (*S*)-6a.**



***(S)*-6a**

According to the general procedures, ***(S)*-6a** (2.03 g, 76% yield, a white solid) was synthesized from corresponding oxazolidinone (2.01 g, 12.3 mmol) and acrylic anhydride (1.95 mL, 16.9 mmol).

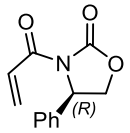
TLC: R_f = 0.68 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{25}_{D}$ = +138.5 (c = 0.40, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 17.0, 10.4 Hz, 1H), 7.41–7.37 (m, 2H), 7.37–7.31 (m, 3H), 6.49 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.89 (dd, *J* = 10.4, 1.7 Hz, 1H), 5.50 (dd, *J* = 8.8, 3.8 Hz, 1H), 4.73 (t, *J* = 8.8 Hz, 1H), 4.31 (dd, *J* = 8.8, 3.8 Hz, 1H).

The spectroscopic data of *N*-acryloyloxazolidinone ***(S)*-6a** were in accordance with those reported in literature.[3]

***N*-Acryloyloxazolidinone *(R)*-6a.**



***(R)*-6a**

According to the general procedures, ***(R)*-6a** (2.52 g, 79% yield, a white solid) was synthesized from corresponding oxazolidinone (2.41 g, 14.8 mmol) and acrylic anhydride (2.30 mL, 19.9 mmol).

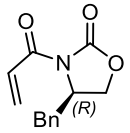
TLC: R_f = 0.68 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{27}_{D}$ = –146.2 (c = 0.40, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 17.0, 10.4 Hz, 1H), 7.41–7.36 (m, 2H), 7.37–7.31 (m, 3H), 6.49 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.89 (dd, *J* = 10.4, 1.7 Hz, 1H), 5.50 (dd, *J* = 8.8, 3.8 Hz, 1H), 4.73 (t, *J* = 8.8 Hz, 1H), 4.31 (dd, *J* = 8.8, 3.8 Hz, 1H).

The spectroscopic data of *N*-acryloyloxazolidinone ***(R)*-6a** were in accordance with those reported in literature.[4]

***N*-Acryloyloxazolidinone 6b.**



6b

According to the general procedures, **6b** (893 mg, 68% yield, a white solid) was synthesized from corresponding oxazolidinone (1.00 g, 5.64 mmol) and acrylic anhydride (910 μL, 7.89 mmol).

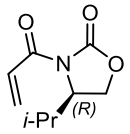
TLC: R_f = 0.61 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{25}_{D}$ = –95.7 (c = 0.40, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 16.9, 10.4 Hz, 1H), 7.37–7.31 (m, 2H), 7.28 (m, 1H), 7.25–7.20 (m, 2H), 6.61 (dd, *J* = 16.9, 1.8 Hz, 1H), 5.94 (dd, *J* = 10.4, 1.8 Hz, 1H), 4.74 (ddt, *J* = 9.6, 7.6, 3.4 Hz, 1H), 4.28–4.17 (m, 2H), 3.35 (dd, *J* = 13.4, 3.4 Hz, 1H), 2.81 (dd, *J* = 13.4, 9.6 Hz, 1H).

The spectroscopic data of *N*-acryloyloxazolidinone **6b** were in accordance with those reported in literature.[5]

N-Acryloyloxazolidinone 6c.



6c

According to the general procedures, **6c** (810 mg, 58% yield, a white solid) was synthesized from corresponding oxazolidinone (992 mg, 7.68 mmol) and acrylic anhydride (1.25 mL, 10.8 mmol).

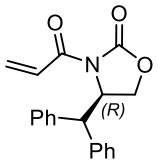
TLC: R_f = 0.60 (Petroleum ether / EtOAc, 3:1 v/v).

OR: $[\alpha]^{24}_D$ = –91.4 (c = 0.40, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 17.0, 10.5 Hz, 1H), 6.54 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.89 (dd, *J* = 10.5, 1.8 Hz, 1H), 4.50 (ddd, *J* = 8.4, 4.0, 3.1 Hz, 1H), 4.30 (dd, *J* = 9.1, 8.4 Hz, 1H), 4.23 (dd, *J* = 9.1, 3.1 Hz, 1H), 2.42 (heptd, *J* = 7.0, 4.0 Hz, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H).

The spectroscopic data of *N*-acryloyloxazolidinone **6c** were in accordance with those reported in literature.[6]

N-Acryloyloxazolidinone 6d.



6d

According to the general procedures, **6d** (381 mg, 31% yield, a white solid) was synthesized from corresponding oxazolidinone (1.02 g, 4.03 mmol) and acrylic anhydride (640 μL, 5.55 mmol).

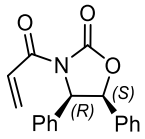
TLC: R_f = 0.70 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{25}_D$ = –196.9 (c = 0.20, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 17.0, 10.5 Hz, 1H), 7.36–7.28 (m, 6H), 7.15–7.09 (m, 4H), 6.50 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.87 (dd, *J* = 10.5, 1.8 Hz, 1H), 5.38 (ddd, *J* = 8.2, 5.6, 2.7 Hz, 1H), 4.75 (d, *J* = 5.6 Hz, 1H), 4.48 (dd, *J* = 9.2, 8.2 Hz, 1H), 4.43 (dd, *J* = 9.2, 2.7 Hz, 1H).

The spectroscopic data of *N*-acryloyloxazolidinone **6d** were in accordance with those reported in literature.[7]

N-Acryloyloxazolidinone 6e.



6e

According to the general procedures, **6e** (325 mg, 53% yield, a white solid) was synthesized from corresponding oxazolidinone (500 mg, 2.09 mmol) and acrylic anhydride (340 μL, 2.95 mmol).

TLC: R_f = 0.58 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{22}_D$ = +35.0 (c = 0.20, $CHCl_3$).

IR (KBr): 3068, 3032, 2918, 1769, 1695, 1614, 1404, 1340, 1305, 1244, 997 cm^{-1}.

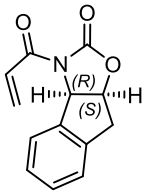
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 17.0, 10.5 Hz, 1H), 7.16–7.07 (m, 6H), 7.01–6.95 (m, 2H), 6.90–6.86 (m, 2H), 6.53 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.97–5.92 (m, 2H), 5.73 (*d*, *J* = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 153.6, 134.3, 132.7, 132.4, 128.5, 128.3 (2C), 128.2, 128.1 (2C), 127.2, 126.6 (2C), 126.1 (2C), 80.5, 63.0.

HRMS (ESI+): *m/z* calculated for $C_{18}H_{16}NO_3^+$ $[M+H]^+$ 294.1125, found *m/z* 294.1125.

Mp: 113–115 ℃.

N-Acryloyloxazolidinone 6f.



6f

According to the general procedures, **6f** (378 mg, 58% yield, a white solid) was synthesized from corresponding oxazolidinone (500 mg, 2.85 mmol) and acrylic anhydride (460 μL, 3.99 mmol).

TLC: R_f = 0.51 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{21}_D$ = –442.6 (c = 0.20, $CHCl_3$).

IR (KBr): 3068, 3034, 2930, 1771, 1683, 1620, 1477, 1409, 1363, 1253, 1126, 766 cm^{-1}.

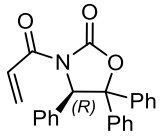
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 16.9, 10.4 Hz, 1H), 7.35 (m, 1H), 7.30–7.27 (m, 2H), 6.63 (dd, *J* = 16.9, 1.9 Hz, 1H), 6.01 (d, *J* = 6.9 Hz, 1H), 5.93 (dd, *J* = 10.4, 1.9 Hz, 1H), 5.32 (ddd, *J* = 7.1, 4.8, 2.5 Hz, 1H), 3.42–3.39 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 165.3, 152.9, 139.4, 139.0, 131.9, 129.9, 128.2, 127.40, 127.36, 125.2, 78.2, 63.2, 38.0.

HRMS (ESI+): *m/z* calculated for $C_{13}H_{12}NO_3^+$ $[M+H]^+$ 230.0812, found *m/z* 230.0810.

Mp: 134–136 ℃.

N-Acryloyloxazolidinone 6g.



6g

According to the general procedures, **6g** (385 mg, 72% yield, a light red foamy solid) was synthesized from corresponding oxazolidinone (455 mg, 1.44 mmol) and acrylic anhydride (230 μL, 2.00 mmol).

TLC: R_f = 0.66 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{26}_D$ = +228.8 (c = 0.20, $CHCl_3$).

IR (KBr): 3062, 3034, 2922, 1782, 1693, 1620, 1450, 1406, 1331, 1246, 1172, 993 cm^{-1}.

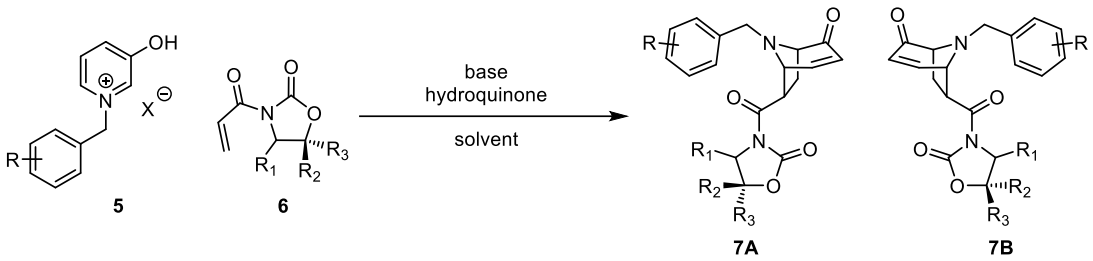
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.61 (m, 2H), 7.51 (dd, *J* = 17.0, 10.5 Hz, 1H), 7.47–7.35 (m, 3H), 7.16–6.97 (m, 10H), 6.47 (dd, *J* = 17.0, 1.7 Hz, 1H), 6.28 (s, 1H), 5.86 (dd, *J* = 10.5, 1.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 152.6, 141.7, 137.9, 135.6, 132.3, 129.0 (2C), 128.9, 128.3 (2C), 128.2, 127.7 (2C), 127.50, 127.47 (2C), 127.2, 126.2 (2C), 126.0 (2C), 89.2, 66.1.

HRMS (ESI+): *m/z* calculated for $C_{24}H_{20}NO_3^+$ $[M+H]^+$ 370.1438, found *m/z* 370.1441.

3. Optimization Studies of the 1,3-Dipolar Cycloaddition

General Procedures



To a stirred solution of pyridinium salt **5**, *N*-acryloyloxazolidinone **6** and hydroquinone (0.1 eq.) in solvent (concentration) was added base (2.3 eq.) slowly at room temperature. After stirring for a certain period of time at the same temperature, the reaction mixture was filtered through a pad of Kiesslguhr, and the residue was washed with EtOAc three times. The filtrate and the washings were concentrated under reduced pressure. The residual oil was pre-purified by column chromatography on silica gel (EtOAc/petroleum ether = 50%) to afford a mixture of cycloadduct **7A** and **7B** as a crude product. The NMR yield of cycloadduct **7A** and **7B** were determined by ^{1}H NMR spectra of crude product based on pyridinium salt **5** or *N*-acryloyloxazolidinone **6** using dibromomethane as internal standard.

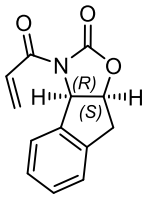
Table S1. All results of optimization studies with pyridinium salt **5** and *N*-acryloyloxazolidinone **6**

entry	**5**	equiv. of **5**	**6**	equiv. of **6**	base	solv.	conc.	time	NMR yield (**7A**)	d.r. of **7A** / **7B**
1	R = H X = Br	1.0	R_1 = (*S*)-Ph R_2 = H, R_3 = H	1.5	Et_3N	EtOAc	0.2 M	7 d	11%	1/3
2	R = H X = Br	1.0	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.5	Et_3N	EtOAc	0.2 M	7 d	34%	3/1
3	R = H X = Br	1.0	*N*-acryloyl-(*2S*)-bornane-10,2-sultam	1.3	Et_3N	EtOAc	0.2 M	5 d	messy N.D.	N.D.
4	R = H X = Cl	1.0	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.4	Et_3N	EtOAc	0.2 M	7 d	36%	3/1
5	R = *p*-Cl X = Cl	1.0	R_1 = (*S*)-Ph R_2 = H, R_3 = H	1.4	Et_3N	EtOAc	0.2 M	5 d	14%	1/4
6	R = *p*-Cl X = Cl	1.0	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.4	Et_3N	EtOAc	0.2 M	5 d	45%	4/1

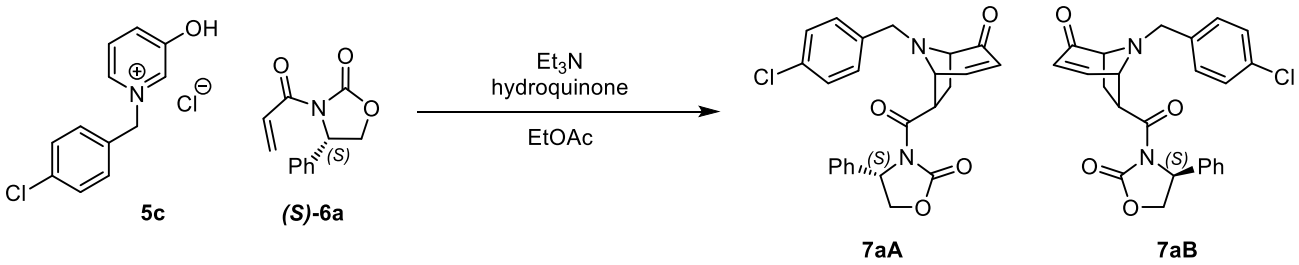
(continued Table)

entry	**5**	equiv. of **5**	**6**	equiv. of **6**	base	solv.	conc.	time	NMR yield (**7A**)	d.r. of **7A** / **7B**
7	R = *p*-Cl X = Cl	1.0	R_1 = (*R*)-Bn R_2 = H, R_3 = H	1.4	Et_3N	EtOAc	0.2 M	5 d	23%	1/1
8	R = *p*-Cl X = Cl	1.0	R_1 = (*R*)-^{i}Pr R_2 = H, R_3 = H	1.4	Et_3N	EtOAc	0.2 M	5 d	21%	1/1
9	R = *p*-Cl X = Cl	1.0	R_1 = (*R*)-$CHPh_2$ R_2 = H, R_3 = H	1.4	Et_3N	EtOAc	0.2 M	5 d	29%	1/1
10	R = *p*-Cl X = Cl	1.0	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.4	NMM	EtOAc	0.2 M	5 d	43%	4/1
11	R = *p*-Cl X = Cl	1.0	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.4	DBU	EtOAc	0.2 M	5 d	49%	4/1
12	R = *p*-Cl X = Cl	1.0	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.4	Et_3N	MeCN	0.2 M	5 d	38%	4/1
13	R = *p*-Cl X = Cl	1.0	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.4	Et_3N	toluene	0.2 M	5 d	22%	4/1
14	R = *p*-Cl X = Cl	1.4	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.0	Et_3N	EtOAc	0.2 M	10 d	41%	4/1
15	R = *p*-Cl X = Cl	1.2	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.0	Et_3N	EtOAc	0.5 M	10 d	74%	4/1
16	R = *p*-Cl X = Cl	1.2	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.0	Et_3N	EtOAc	0.5 M	2 d	70%	4/1
17	R = *m*-NO_2 X = Cl	1.2	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.0	Et_3N	EtOAc	0.2 M	5 d	10%	3/2
18	R = *p*-Br X = Cl	1.2	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.0	Et_3N	EtOAc	0.2 M	5 d	43%	3/1
19	R = 1-Napht X = Cl	1.4	R_1 = (*R*)-Ph R_2 = H, R_3 = H	1.0	Et_3N	EtOAc	0.2 M	5 d	44%	3/1
20	R = *p*-Cl X = Cl	1.4	R_1 = (*R*)-Ph R_2 = Ph, R_3 = H	1.0	Et_3N	EtOAc	0.2 M	5 d	47%	5/1

(continued Table)

entry	**5**	equiv. of **5**	**6**	equiv. of **6**	base	solv.	conc.	time	NMR yield (**7A**)	d.r. of **7A** / **7B**
21	R = *p*-Cl X = Cl	1.4		1.0	Et_3N	EtOAc	0.2 M	5 d	32%	3/2
22	R = *p*-Cl X = Cl	1.4	R_1 = (*R*)-Ph R_2 = Ph, R_3 = Ph	1.0	Et_3N	EtOAc	0.2 M	5 d	37%	2/1

Cycloadduct 7aA and 7aB.



According to the general procedures, cycloadduct **7aA** (minor, 14% NMR yield calculated from internal standard when carried with 0.5 mmol of **5c** in entry 5) was synthesized from pyridinium salt **5c** (1.56 g, 6.08 mmol, 1.2 eq.) and *N*-acryloyloxazolidinone **(*S*)-6a** (1.10 g, 5.06 mmol, 1.0 eq.). The resultant crude oil was purified by column chromatography on silica gel (120 g, EtOAc/petroleum ether = 5% → 10% → 25%) to afford cycloadduct **7aA** (252 mg, 11%) as a slightly yellow crystal, and cycloadduct **7aB** (1.08 g, 49%) as a slightly yellow foamy solid.

Cycloadduct **7aA**:

TLC: R_f = 0.49 (Toluene / Et_2O, 2:1 v/v).

OR: $[\alpha]^{28}_D$ = +73.1 (c = 0.20, $CHCl_3$).

IR (KBr): 3014, 2987, 2952, 1780, 1704, 1680, 1480, 1389, 1319, 1250, 1062, 887 cm^{-1}.

^{1}H NMR (600 MHz, acetone-*d6*): δ 7.45–7.40 (m, 4H), 7.36 (m, 1H), 7.32–7.29 (m, 2H), 7.26–7.23 (m, 2H), 7.22 (dd, *J* = 9.8, 5.1 Hz, 1H), 6.02 (dd, *J* = 9.8, 1.5 Hz, 1H), 5.63 (dd, *J* = 8.8, 3.8 Hz, 1H), 4.83 (t, *J* = 8.8 Hz, 1H), 4.29 (dd, *J* = 8.8, 3.8 Hz, 1H), 4.12 (d, *J* = 5.1 Hz, 1H), 3.98 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.75 (d, *J* = 14.1 Hz, 1H), 3.71 (d, *J* = 14.1 Hz, 1H), 3.47 (d, *J* = 7.9 Hz, 1H), 2.85 (ddd, *J* = 13.6, 7.9, 4.3 Hz, 1H), 1.84 (dd, *J* = 13.6, 9.2 Hz, 1H).

^{13}C NMR (100 MHz, acetone-*d6*): δ 198.7, 171.9, 155.0, 150.6, 141.0, 138.6, 133.1, 130.6 (2C), 129.8 (2C), 129.2 (2C), 129.1, 127.9, 126.9 (2C), 71.3, 69.5, 62.4, 58.8, 52.1, 49.4, 27.8.

HRMS (ESI+): *m/z* calculated for $C_{24}H_{22}ClN_2O_4^+$ $[M+H]^+$ 437.1263, found *m/z* 437.1264.

Mp: 264–266 ℃.

Cycloadduct **7aB**:

TLC: R_f = 0.41 (Toluene / Et_2O, 2:1 v/v).

OR: $[\alpha]^{26}_D$ = +112.3 (c = 0.20, $CHCl_3$).

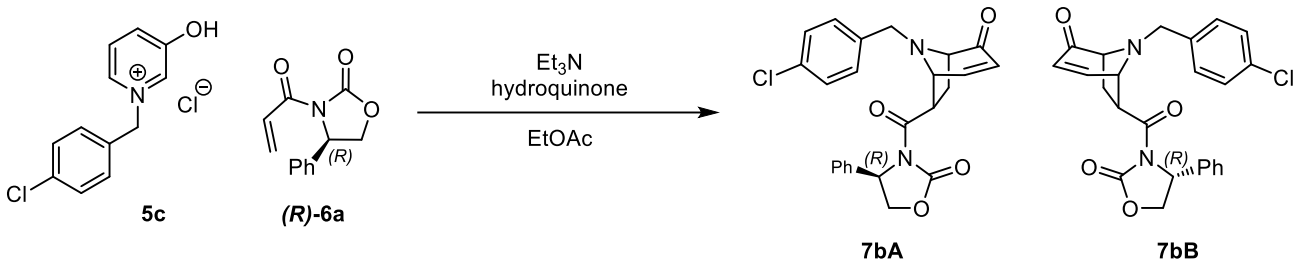
IR (KBr): 3031, 2941, 2922, 1789, 1712, 1685, 1455, 1406, 1380, 1319, 1197, 1056, 758 cm^{-1}.

^{1}H NMR (600 MHz, acetone-*d6*): δ 7.42–7.35 (m, 5H), 7.24 (dd, *J* = 9.8, 5.0 Hz, 1H), 7.22–7.18 (m, 2H), 7.07–7.03 (m, 2H), 6.02 (dd, *J* = 9.8, 1.5 Hz, 1H), 5.61 (dd, *J* = 8.8, 4.1 Hz, 1H), 4.88 (t, *J* = 8.8 Hz, 1H), 4.30 (dd, *J* = 8.8, 4.1 Hz, 1H), 4.04 (d, *J* = 5.0 Hz, 1H), 3.91 (dd, *J* = 9.1, 4.0 Hz, 1H), 3.69 (d, *J* = 13.8 Hz, 1H), 3.63 (d, *J* = 13.8 Hz, 1H), 3.45 (d, *J* = 8.0 Hz, 1H), 3.00 (ddd, *J* = 13.5, 8.0, 4.0 Hz, 1H), 1.72 (dd, *J* = 13.5, 9.1 Hz, 1H).

^{13}C NMR (100 MHz, acetone-*d6*): δ 198.8, 171.7, 155.1, 150.3, 140.9, 138.4, 133.0, 130.7 (2C), 129.8 (2C), 129.1 (2C), 129.0, 127.8, 126.9 (2C), 71.3, 69.7, 63.1, 58.7, 52.0, 49.4, 26.5.

HRMS (ESI+): *m/z* calculated for $C_{24}H_{22}ClN_2O_4^+$ $[M+H]^+$ 437.1263, found *m/z* 437.1265.

Cycloadduct 7bA and 7bB.



According to the general procedures, cycloadduct **7bA** (major, 70% NMR yield calculated from internal standard when carried with 0.6 mmol of **5c** in entry 16) was synthesized from pyridinium salt **5c** (5.66 g, 22.1 mmol, 1.2 eq.) and *N*-acryloyloxazolidinone **(*R*)-6a** (4.00 g, 18.4 mmol, 1.0 eq.). The resultant crude oil was purified by column chromatography on silica gel (220 g, EtOAc/petroleum ether = 5% → 10% → 25%) to afford cycloadduct **7bA** (4.76 g, 59%) as a slightly yellow foamy solid, and cycloadduct **7bB** (1.16 g, 14%) as a slightly yellow crystal.

Cycloadduct **7bA**:

TLC: R_f = 0.41 (Toluene / Et_2O, 2:1 v/v).

OR: $[\alpha]^{21}_D$ = –102.2 (c = 0.18, $CHCl_3$).

IR (KBr): 3030, 2922, 2849, 1782, 1732, 1682, 1456, 1384, 1234, 1198, 1015, 707 cm^{-1}.

^{1}H NMR (600 MHz, acetone-*d6*): δ 7.43–7.35 (m, 5H), 7.24 (dd, *J* = 9.8, 5.0 Hz, 1H), 7.22–7.18 (m, 2H), 7.07–7.03 (m, 2H), 6.02 (dd, *J* = 9.8, 1.5 Hz, 1H), 5.61 (dd, *J* = 8.8, 4.1 Hz, 1H), 4.88 (t, *J* = 8.8 Hz, 1H), 4.30 (dd, *J* = 8.8, 4.1 Hz, 1H), 4.04 (d, *J* = 5.0 Hz, 1H), 3.91 (dd, *J* = 9.1, 4.0 Hz, 1H), 3.69 (d, *J* = 13.8 Hz, 1H), 3.63 (d, *J* = 13.8 Hz, 1H), 3.45 (d, *J* = 8.0 Hz, 1H), 3.00 (ddd, *J* = 13.5, 8.0, 4.0 Hz, 1H), 1.72 (dd, *J* = 13.5, 9.1 Hz, 1H).

^{13}C NMR (100 MHz, acetone-*d6*): δ 198.8, 171.7, 155.1, 150.3, 140.9, 138.4, 133.0, 130.7 (2C), 129.8 (2C), 129.2 (2C), 129.1, 127.8, 126.9 (2C), 71.3, 69.7, 63.1, 58.7, 52.0, 49.4, 26.5.

HRMS (ESI+): *m/z* calculated for $C_{24}H_{22}ClN_2O_4^+$ $[M+H]^+$ 437.1263, found *m/z* 437.1267.

Cycloadduct **7bB**:

TLC: R_f = 0.49 (Toluene / Et_2O, 2:1 v/v).

OR: $[\alpha]^{27}_D$ = –66.5 (c = 0.20, $CHCl_3$).

IR (KBr): 3009, 2994, 2941, 1788, 1712, 1681, 1491, 1388, 1319, 1220, 1083, 858 cm^{-1}.

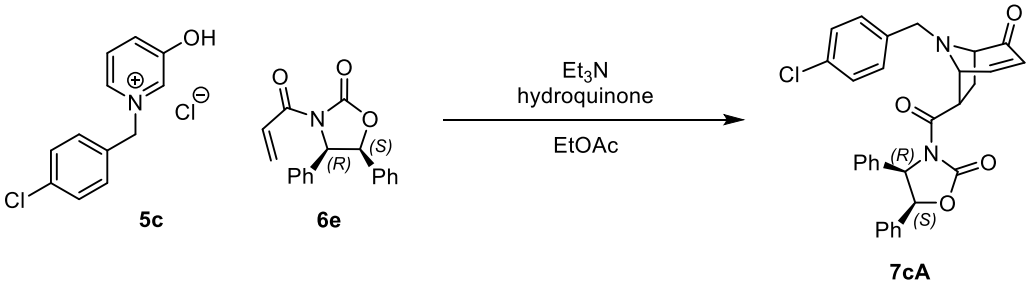
^{1}H NMR (600 MHz, acetone-*d6*): δ 7.44–7.40 (m, 4H), 7.36 (m, 1H), 7.32–7.29 (m, 2H), 7.26–7.23 (m, 2H), 7.22 (dd, *J* = 9.8, 5.1 Hz, 1H), 6.02 (dd, *J* = 9.8, 1.5 Hz, 1H), 5.63 (dd, *J* = 8.8, 3.8 Hz, 1H), 4.83 (t, *J* = 8.8 Hz, 1H), 4.29 (dd, *J* = 8.8, 3.8 Hz, 1H), 4.12 (d, *J* = 5.1 Hz, 1H), 3.98 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.75 (d, *J* = 14.1 Hz, 1H), 3.71 (d, *J* = 14.1 Hz, 1H), 3.47 (d, *J* = 7.9 Hz, 1H), 2.85 (ddd, *J* = 13.6, 7.9, 4.3 Hz, 1H), 1.84 (dd, *J* = 13.6, 9.2 Hz, 1H).

^{13}C NMR (100 MHz, acetone-*d6*): δ 198.7, 171.9, 155.0, 150.6, 141.0, 138.6, 133.1, 130.6 (2C), 129.8 (2C), 129.2 (2C), 129.1, 127.9, 126.9 (2C), 71.3, 69.5, 62.4, 58.8, 52.1, 49.4, 27.8.

HRMS (ESI+): *m/z* calculated for $C_{24}H_{22}ClN_2O_4^+$ $[M+H]^+$ 437.1263, found *m/z* 437.1269.

Mp: 271–272 ℃.

Cycloadduct 7cA.



According to the general procedures, cycloadduct **7cA** (major, 47% NMR yield calculated from internal standard) in entry 20 was synthesized from pyridinium salt **5c** (180 mg, 702 μmol, 1.4 eq.) and *N*-acryloyloxazolidinone **6e** (147 mg, 501 μmol, 1.0 eq.). The resultant crude oil was purified by

column chromatography on silica gel (4 g, EtOAc/petroleum ether = 5% → 10% → 13% → 25%) to afford single cycloadduct **7cA** (88.1 mg, 34% isolated yield) as a slightly yellow crystal.

TLC: R_f = 0.39 (Toluene / Et_2O, 2:1 v/v).

OR: $[\alpha]^{25}_D$ = –5.6 (c = 0.20, $CHCl_3$).

IR (KBr): 3103, 2973, 1868, 1785, 1704, 1408, 1377, 1341, 1268, 1208, 1151, 1040, 727 cm^{-1}.

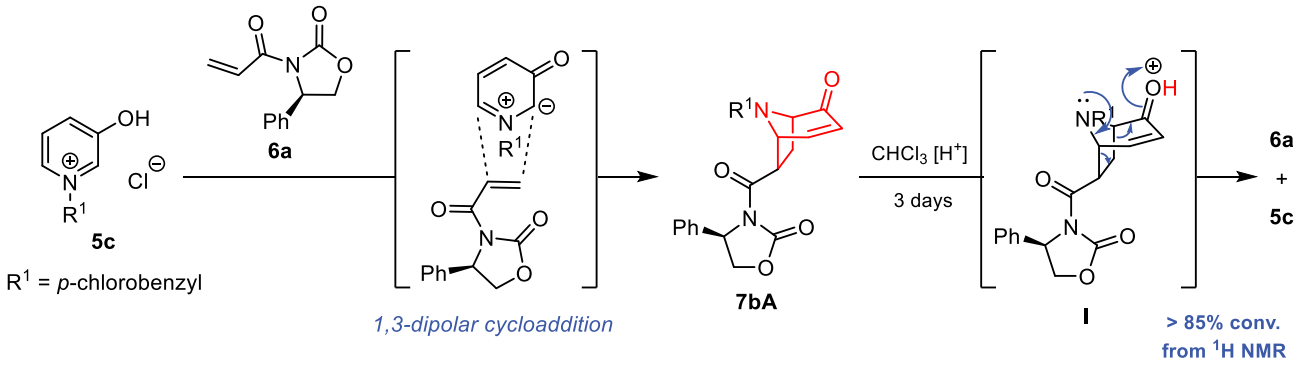
^{1}H NMR (600 MHz, acetone-*d6*): δ 7.32 (dd, *J* = 9.8, 5.0 Hz, 1H), 7.19–7.16 (m, 2H), 7.15–7.05 (m, 10H), 6.97–6.94 (m, 2H), 6.21 (d, *J* = 8.0 Hz, 1H), 6.06 (dd, *J* = 9.8, 1.5 Hz, 1H), 5.95 (d, *J* = 8.0 Hz, 1H), 4.12 (d, *J* = 5.0 Hz, 1H), 3.99 (dd, *J* = 9.1, 4.1 Hz, 1H), 3.73 (d, *J* = 13.8 Hz, 1H), 3.67 (d, *J* = 13.8 Hz, 1H), 3.49 (d, *J* = 8.0 Hz, 1H), 3.01 (ddd, *J* = 13.5, 8.0, 4.1 Hz, 1H), 1.81 (dd, *J* = 13.5, 9.1 Hz, 1H).

^{13}C NMR (100 MHz, acetone-*d6*): δ 198.7, 171.4, 154.9, 150.4, 138.4, 136.6, 134.8, 133.0, 130.7 (2C), 129.2 (2C), 128.99 (2C), 128.96, 128.7 (2C), 128.6, 128.0, 127.7 (2C), 127.2 (2C), 81.2, 69.9, 63.6, 62.7, 52.0, 49.4, 27.1.

HRMS (ESI+): *m/z* calculated for $C_{30}H_{26}ClN_2O_4^+$ $[M+H]^+$ 513.1576, found *m/z* 513.1569.

Mp: 285–286 ℃.

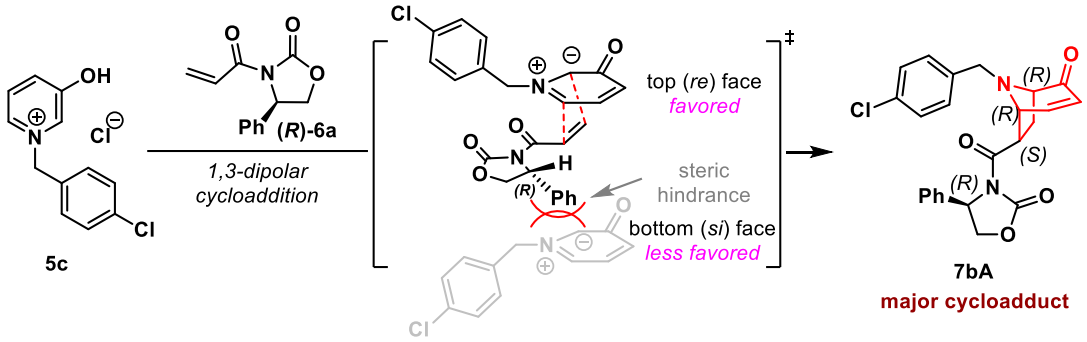
Note: The cycloadducts obtained by this 1,3-dipole cycloaddition were sensitive to acidic conditions (such as chloroform condition, which is considered slightly acidic). For instance, 0.1 mmol of cycloadduct **7bA** was dissolved in chloroform as a 0.1 M solution, and dibromomethane was added as internal standard. After stewing for 3 days, cycloadduct **7bA** underwent a reverse ring-open process to afford pyridinium salt **5c** and *N*-acryloyloxazolidinone **(*R*)-6a** (both of **5c** and **(*R*)-6a** are starting material) with approximately 85% conversion by NMR analysis. Thus, the lower isolated yield of cycloadducts was attributed to the instability, which likely decomposed partly under the purification by silica gel (even 0.01% of Et_3N was added when purification).



Scheme S1. Reverse ring-opening process of cycloadducts under acidic condition

The possible transition state for the 1,3-dipolar cycloaddition:

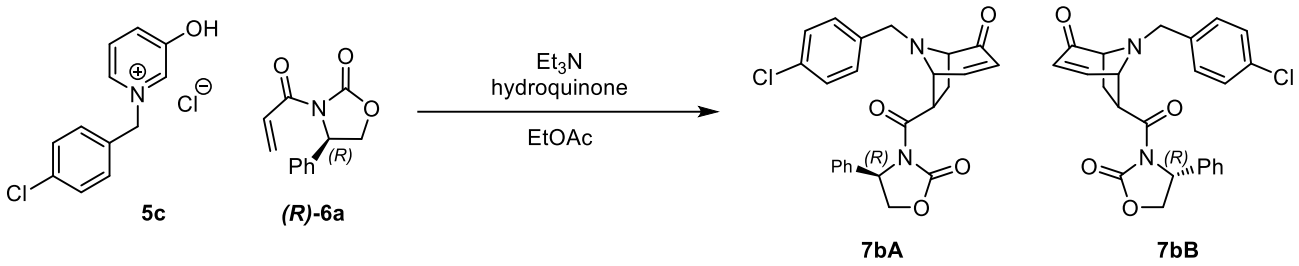
A plausible transition state for the cycloaddition reaction is depicted in Scheme S2. The approach of pyridinium salt **5c** to the olefin moiety of (*R*)-3-acryloyl-4-phenyloxazolidin-2-one **(*R*)-6a** from the *si* face is hindered by the steric effect of the phenyl group. Consequently, the *re* face approach is more favorable, leading to the formation of the major cycloadduct **7bA**.



Scheme S2. The possible transition state for the 1,3-dipolar cycloaddition

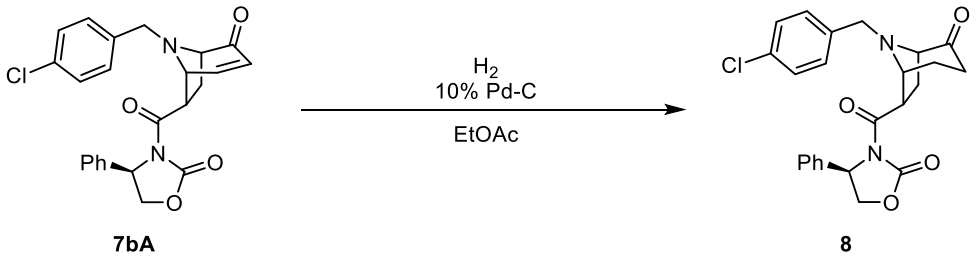
4. Synthetic Procedures of (−)-Bao Gong Teng A

Cycloadduct 7bA.



To a stirred solution of pyridinium salt **5a** (38.8 g, 151 mmol, 1.2 eq.), *N*-acryloyloxazolidinone **(*R*)-6a** (27.4 g, 126 mmol, 1.0 eq.) and hydroquinone (1.39 g, 12.6 mmol, 0.1 eq.) in EtOAc (300 mL) was added Et_3N (35.2 mL, 252 mol, 2.0 eq.) slowly at room temperature. After stirring for 2 days at the same temperature, the reaction mixture was filtered through a pad of Kiesslguhr, and the residue was washed with EtOAc (200 mL) three times. The filtrate and the washings were concentrated under reduced pressure. The residual oil was purified by column chromatography on silica gel (800 g, EtOAc/petroleum ether = 5% → 10% → 25%) to afford cycloadduct **7bA** (28.6 g, 52%) as a slightly yellow foamy solid, and cycloadduct **7bB** (5.73 g, 10%) as a slightly yellow crystal.

Ketone 8.



To a stirred solution of cycloadduct **7bA** (4.76 g, 10.9 mmol) in EtOAc (55 mL) was added 10% Pd/C (190 mg, 4.0 wt%) at room temperature. The suspension was degassed under reduced pressure and purged with hydrogen (1 atm) several times. After stirring under a hydrogen atmosphere for 24 h at the same temperature, the mixture was filtered through a pad of Kiesslguhr, the residue was washed with EtOAc (30 mL). The filtrate and the washings were combined and concentrated. The residual oil was purified by column chromatography on silica gel (80 g, EtOAc/petroleum ether = 15% → 25%) to afford ketone **8** (4.77 g, quant.) as a white foamy solid.

TLC: R_f = 0.46 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{24}_D$ = –95.3 (c = 0.20, $CHCl_3$).

IR (KBr): 3032, 2949, 1778, 1705, 1490, 1456, 1384, 1323, 1234, 1201, 1107, 1014, 759 cm^{-1}.

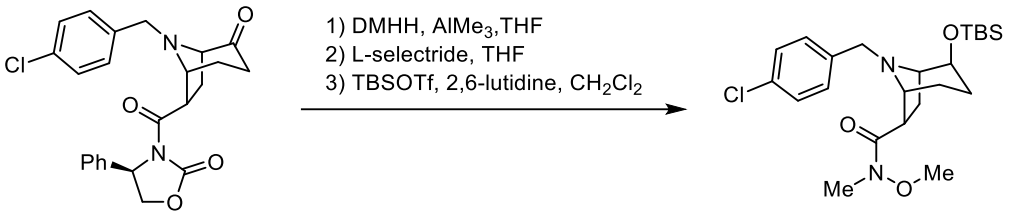
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44–7.36 (m, 3H), 7.31–7.27 (m, 2H), 7.11–7.06 (m, 2H), 6.92–6.88 (m, 2H), 5.48 (dd, *J* = 8.9, 3.7 Hz, 1H), 4.72 (t, *J* = 8.9 Hz, 1H), 4.33 (dd, *J* = 8.9, 3.7 Hz, 1H), 4.06 (dd, *J* = 9.2, 5.5 Hz, 1H), 3.56 (d, *J* = 13.8 Hz, 1H), 3.47 (d, *J* = 13.8 Hz, 1H), 3.43 (d, *J* = 7.6 Hz, 1H), 3.37 (m, 1H), 2.91 (m, 1H), 2.50 (ddd, *J* = 17.1, 11.1, 9.2 Hz, 1H), 2.37 (dd, *J* = 17.1, 6.7 Hz, 1H), 2.27 (m, 1H), 2.18 (m, 1H), 1.96 (dd, *J* = 14.0, 9.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 209.3, 173.2, 153.7, 138.8, 136.5, 132.5, 129.4 (2C), 129.3 (2C), 128.9, 128.4 (2C), 126.0 (2C), 70.4, 70.1, 61.4, 58.0, 52.5, 46.2, 33.1, 29.1, 28.7.

HRMS (ESI+): *m/z* calculated for $C_{24}H_{24}ClN_2O_4^+$ $[M+H]^+$ 439.1419, found *m/z* 439.1425.

Note: According to the same procedures, ketone **8** (18.5 g, 99%) was synthesized from cycloadduct **7bA** (18.7 g, 42.8 mmol) as a white foamy solid.

Weinreb amide 9.



8 **9**

To a stirred suspension of *N*,*O*-dimethylhydroxylamine hydrochloride (DMHH, 2.65 g, 27.2 mmol, 2.5 eq., dried by heater in vacuum for 30 min) in THF (15 mL) was added $AlMe_3$ (15.2 mL, 30.4 mmol, 2.8 eq., 2.0 M solution in Hexane) dropwise at 0 ℃. After stirring for 30 min at room temperature, the mixture was cooled to −20 ℃ and added a solution of ketone **8** (4.77 g, 10.9 mmol, 1.0 eq.) in THF (10 mL) via syringe slowly. After stirring for 30 min at the same temperature, the mixture was stirred for another 10 h at 0 ℃. The reaction was checked by TLC detection, and the mixture was quenched with saturated aqueous Rochelle's salt (30 mL) and H_2O (10 mL) at 0 ℃. The mixture was stirring for additional 1 h at the same temperature, filtered through a pad of Kiesslguhr, washed with EtOAc (25 mL), and the filtrate was extracted with EtOAc (30 mL) three times. The combined extracts were washed with brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure, and the residual oil was partly purified by column chromatography on silica gel (40 g, EtOAc/CH_2Cl_2 = 10% → 30%). The resultant crude Weinreb amide was used for the next reaction without further purification.

To a stirred solution of the crude Weinreb amide in THF (55 mL) was added L-selectride (21.7 mL, 21.7 mmol, 2.0 eq., 1.0 M solution in THF) dropwise at −78 °C. After stirring for 20 h at the same

temperature, the mixture was quenched with saturated aqueous NH_4Cl (30 mL). After removing most of the THF by evaporation, the mixture was diluted with EtOAc (20 mL) and extracted with EtOAc (30 mL) three times. The combined extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residual oil was partly purified by column chromatography on silica gel (25 g, EtOAc/CH_2Cl_2 = 15% → 50%). The resultant crude alcohol was used for the next reaction without further purification.

To a stirred solution of the crude alcohol in CH_2Cl_2 (90 mL) was added 2,6-lutidine (3.15 mL, 27.0 mmol, 2.5 eq.) and TBSOTf (4.25 mL, 18.5 mmol, 1.7 eq.) slowly at −40 ℃. After stirring for 12 h at the same temperature, the mixture was quenched with saturated aqueous $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (45 mL) three times. The combined extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residual oil was purified by column chromatography on silica gel (120 g, EtOAc/petroleum ether = 3% → 10% → 20%) to afford Weinreb amide **9** (2.03 g, 41% in 3 steps) as a colorless oil.

TLC: R_f = 0.42 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{20}_D$ = –82.9 (c = 0.20, $CHCl_3$).

IR (KBr): 2954, 2935, 2856, 1668, 1650, 1489, 1471, 1373, 1260, 1093, 1016, 800 cm^{-1}.

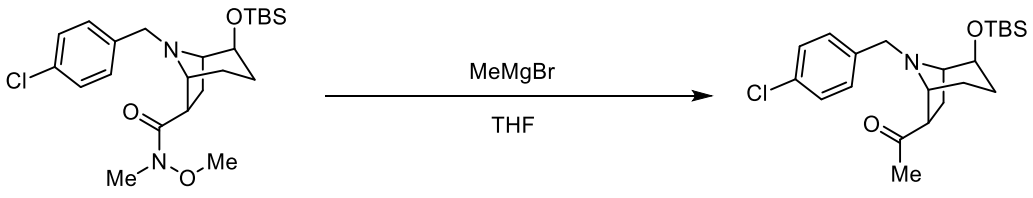
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41–7.38 (m, 2H), 7.23–7.20 (m, 2H), 3.81 (d, *J* = 15.0 Hz, 1H), 3.75 (d, *J* = 15.0 Hz, 1H), 3.66 (s, 3H), 3.63 (m, 1H), 3.34 (m, 1H), 3.22 (m, 1H), 3.21 (s, 3H), 3.07 (m, 1H), 2.60 (dt, *J* = 13.4, 6.8 Hz, 1H), 2.10 (tdd, *J* = 12.9, 5.4, 2.7 Hz, 1H), 1.77 (m, 1H), 1.58 (dd, *J* = 13.4, 9.3 Hz, 1H), 1.52 (dd, *J* = 14.7, 5.4 Hz, 1H), 1.33 (m, 1H), 0.91 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 139.3, 131.7, 129.5 (2C), 127.9 (2C), 70.4, 65.7, 63.5, 60.8, 55.2, 43.2, 32.9, 28.3, 26.9, 25.94, 25.90 (3C), 18.2, –4.7, –4.9.

HRMS (ESI+): *m/z* calculated for $C_{23}H_{38}ClN_2O_3Si^+$ $[M+H]^+$ 453.2335, found *m/z* 453.2353.

Note: According to the same procedures, Weinreb amide **9** (5.37 g, 35% in 3 steps) was synthesized from ketone **8** (14.7 g, 33.5 mmol) as a colorless oil.

Methyl ketone 10.



9 **10**

To a stirred solution of Weinreb amide **9** (1.83 g, 4.04 mmol, 1.0 eq.) in THF (40 mL) was added methylmagnesium bromide (14.1 mL, 14.1 mmol, 3.5 eq., 1.0 M solution in THF) slowly at 0 ℃. After stirring for 12 h at room temperature, the mixture was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with Et_2O (35 mL) and EtOAc (35 mL) three times. The combined extracts were washed with brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (80 g, EtOAc/petroleum ether = 3% → 7% → 20%) to afford methyl ketone **10** (1.56 g, 95%) as a colorless oil.

TLC: R_f = 0.63 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{26}_D$ = –63.7 (c = 0.20, $CHCl_3$).

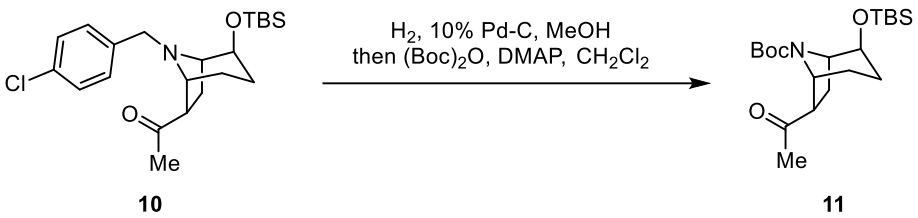
IR (KBr): 2951, 2931, 2856, 1711, 1489, 1471, 1360, 1256, 1167, 1096, 1026, 860 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.3 Hz, 0.4H), 7.31 (d, *J* = 8.3 Hz, 1.6H), 7.26 (d, *J* = 8.3 Hz, 0.4H), 7.22 (d, *J* = 8.3 Hz, 1.6H), 3.77 (d, *J* = 14.9 Hz, 0.8H), 3.74 (d, *J* = 14.9 Hz, 0.8H), 3.71 (d, *J* = 14.5 Hz, 0.2H), 3.653 (d, *J* = 14.5 Hz, 0.2H), 3.647 (m, 0.2H), 3.62 (m, 0.8H), 3.46 (m, 0.2H), 3.41 (m, 0.2H), 3.38 (m, 0.8H), 3.23 (m, 0.8H), 3.09 (m, 0.2H), 2.86 (dd, *J* = 9.1, 5.7 Hz, 0.8H), 2.44 (dt, *J* = 13.2, 6.3 Hz, 0.8H), 2.21–2.11 (m, 1H), 2.18 (s, 0.6H), 2.16 (s, 2.4H), 2.09–2.02 (m, 0.4H), 1.92 (m, 0.2H), 1.80–1.67 (m, 1H), 1.59–1.50 (m, 1.6H), 1.28 (m, 0.8H), 1.22 (m, 0.2H), 0.91 (s, 7.2H), 0.89 (s, 1.8H), 0.03 (s, 2.4H), 0.01 (s, 2.4H), 0.00 (s, 0.6H), –0.01 (s, 0.6H), as a 4:1 mixture of two rotamers observed in NMR.

^{13}C NMR (150 MHz, $CDCl_3$): δ 209.5 (0.8C), 207.4 (0.2C), 139.0 (0.8C), 138.4 (0.2C), 132.2 (0.2C), 131.9 (0.8C), 129.52 (0.4C), 129.46 (1.6C), 128.2 (0.4C), 128.1 (1.6C), 70.6 (0.2C), 70.2 (0.8C), 65.1 (0.8C), 64.9 (0.2C), 62.1 (0.2C), 60.6 (0.8C), 56.2 (0.2C), 54.5 (0.8C), 54.4 (0.8C), 53.7 (0.2C), 29.8 (0.2C), 28.6 (0.8C), 27.5 (0.8C), 25.89 (0.6C), 25.87 (2.4C), 25.8 (0.8C), 25.3 (0.8C), 24.9 (0.2C), 24.5 (0.2C), 24.1 (0.2C), 18.2 (0.2C), 18.1 (0.8C), –4.7, –4.9, as a 4:1 mixture of two rotamers observed in NMR.

HRMS (ESI+): *m/z* calculated for $C_{22}H_{35}ClNO_2Si^+$ $[M+H]^+$ 408.2120, found *m/z* 408.2148.

Carbamate 11.



10 **11**

To a stirred solution of methyl ketone **10** (1.12 g, 2.74 mmol, 1.0 eq.) in MeOH (28 mL) was added 10% Pd/C (56.4 mg, 5.0 wt%) at room temperature. The suspension was degassed under reduced

pressure and purged with hydrogen (1 atm) several times. After stirring under a hydrogen atmosphere for 24 h at the same temperature, the mixture was filtered through a pad of Kiesslguhr, the residue was washed with EtOAc (30 mL). The filtrate and the washings were combined and concentrated. The resultant crude oil was redissolved in CH_2Cl_2 (34 mL) and added DMAP (335 mg, 2.74 mmol, 1.0 eq.) and $(Boc)_2O$ (2.85 mL, 13.7 mmol, 5.0 eq.) at room temperature. After stirring for 15 h at the same temperature, the mixture was concentrated under reduced pressure. The residual oil was purified by column chromatography on silica gel (40 g, EtOAc/petroleum ether = 3% → 7% → 15%) to afford carbamate **11** (864 mg, 82%) as a colorless oil.

TLC: R_f = 0.67 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{25}_D$ = +18.2 (c = 0.22, $CHCl_3$).

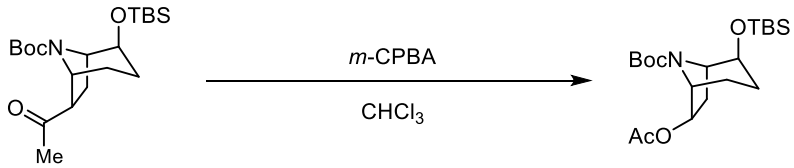
IR (KBr): 2954, 2856, 1717, 1699, 1423, 1364, 1306, 1260, 1169, 1109, 1030, 837 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.52 (s, 0.55H), 4.35 (s, 0.45H), 4.30 (m, 0.45H), 4.21 (m, 0.55H), 3.68 (m, 0.45H), 3.64 (m, 0.55H), 2.87– 2.80 (m, 1H), 2.31 (m, 0.55H), 2.19 (s, 1.65H), 2.18–2.04 (m, 1.45H), 2.15 (s, 1.35H), 1.77–1.66 (m, 1.55H), 1.58–1.34 (m, 2.45H), 1.42 (s, 9H), 0.89 (s, 4.95H), 0.88 (s, 4.05H), 0.07 (s, 3H), 0.04 (s, 3H), as a 11:9 mixture of two rotamers observed in NMR.

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.9 (0.45C), 207.7 (0.55C), 153.9 (0.55C), 152.8 (0.45C), 79.3 (0.55C), 78.8 (0.45C), 69.0 (0.45C), 68.8 (0.55C), 59.6 (0.55C), 58.2 (0.45C), 55.9 (0.45C), 55.5 (0.55C), 53.8 (0.45C), 53.0 (0.55C), 28.43 (1.35C), 28.37 (1.65C), 28.1, 27.9, 27.3 (0.45C), 27.1 (0.55C), 26.9 (0.45C), 25.9 (1.65C), 25.8 (1.35C), 25.5 (0.55C), 18.14 (0.55C), 18.09 (0.45C), –4.7 (0.55C), –4.9 (0.45C), –5.0 (0.55C), –5.10 (0.45C), as a 11:9 mixture of two rotamers observed in NMR.

HRMS (ESI+): *m/z* calculated for $C_{20}H_{37}NO_4SiNa^+$ $[M+Na]^+$ 406.2384, found *m/z* 406.2387.

Acetate 12.



11 **12**

To a stirred solution of carbamate **11** (790 mg, 2.06 mmol, 1.0 eq.) in $CHCl_3$ (20 mL) was added *m*-CPBA (889 mg, 5.15 mmol, 2.5 eq., dissolved in 4 mL $CHCl_3$) at room temperature. After stirring for 5 days at the same temperature, the mixture was quenched with saturated aqueous Na_2CO_3 (5 mL), saturated aqueous $Na_2S_2O_3$ (15 mL) and extracted with CH_2Cl_2 (20 mL) three times. The combined extracts were washed with brine and dried over Na_2SO_4. The filtrate was concentrated under reduced

pressure. The residual oil was purified by column chromatography on silica gel (30 g, EtOAc/petroleum ether = 3% → 5% → 10%) to afford acetate **12** (394 mg, 48%, after 2 recycles of recovery carbamate **11**, the total yield of acetate **12** achieved 617 mg, 75%) as a colorless oil.

TLC: R_f = 0.71 (Petroleum ether / EtOAc, 2:1 v/v).

OR: $[\alpha]^{25}_D$ = –15.6 (c = 0.10, $CHCl_3$).

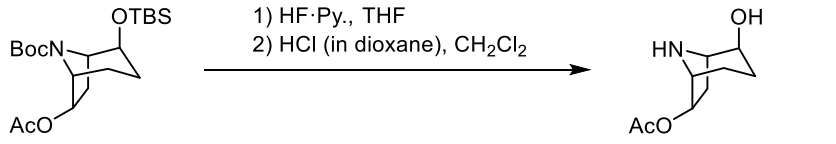
IR (KBr): 2953, 2930, 2857, 1742, 1699, 1427, 1366, 1310, 1248, 1177, 1111, 1026, 837 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.04 (dd, *J* = 7.2, 2.6 Hz, 0.45H), 5.02 (dd, *J* = 7.3, 2.5 Hz, 0.55H), 4.33 (m, 0.55H), 4.29 (m, 0.45H), 4.25 (m, 0.45H), 4.07 (m, 055H), 3.64 (m, 0.55H), 3.60 (m, 0.45H), 2.08–1.94 (m, 2H), 2.03 (s, 1.65H), 2.01 (s, 1.35H), 1.88–1.78 (m, 1H), 1.67–1.61 (m, 1H), 1.55–1.42 (m, 2H), 1.46 (s, 4.05H), 1.45 (s, 4.95H), 0.89 (s, 4.05H), 0.88 (s, 4.95H), 0.073 (s, 1.65H), 0.065 (s, 1.35H), 0.039 (s, 1.65H), 0.037 (s, 1.35H), as a 11:9 mixture of two rotamers observed in NMR.

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.04 (0.45C), 171.00 (0.55C), 154.1 (0.45C), 153.5 (0.55C), 79.2 (0.45C), 78.7 (0.55C), 77.1 (0.55C), 76.3 (0.45C), 68.8 (0.55C), 68.7 (0.45C), 59.8 (0.55C), 59.2 (0.45C), 58.5 (0.55C), 58.0 (0.45C), 35.8 (0.45C), 34.9 (0.55C), 28.5 (1.65C), 28.5 (1.35C), 25.92 (1.35C), 25.88 (0.55C), 25.79 (1.65C), 25.75 (0.45C), 23.90 (0.45C), 23.87 (0.55C), 21.2 (0.45C), 21.1 (0.55C), 18.2 (0.45C), 18.1 (0.55C), –4.7 (0.45C), –4.9 (0.55C), –5.0 (0.45C), –5.1 (0.55C), as a 11:9 mixture of two rotamers observed in NMR.

HRMS (ESI+): *m/z* calculated for $C_{20}H_{37}NO_5SiNa^+$ $[M+Na]^+$ 422.2333, found *m/z* 422.2340.

(−)-Bao Gong Teng A (1).



12 (−)-Bao Gong Teng A (**1**)

Acetate **12** (311 mg, 778 μmol, 1.0 eq.) in a PP tube was added HF–pyridine/THF (1/5 v/v, 7.5 mL), and the mixture was stirred at room temperature for 12 h. Then, the mixture was poured into saturated aqueous $NaHCO_3$ (25 mL) slowly at 0 ℃, and the aqueous mixture was extracted with EtOAc (30 mL) three times. The combined extracts were washed with brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure, and the residual oil was partly purified by column chromatography on silica gel (12 g, EtOAc/petroleum ether = 3% → 6% → 10% → 20%). The resultant alcohol was used for the next reaction without further purification.

To a stirred solution of resultant alcohol in CH_2Cl_2 (7 mL) was added HCl solution (973 μL, 3.89 mmol, 5.0 eq., 4.0 M solution in dioxane) at room temperature. After stirring for 5 h at the same temperature, the reaction mixture was concentrated under reduced pressure, and diluted with CH_2Cl_2

(6 mL). The mixture was washed with saturated aqueous $NaHCO_3$ (4 mL) and extracted with CH_2Cl_2 (9 mL) three times. The combined extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residual oil was quickly purified by column chromatography on silica gel (6 g, MeOH/CH_2Cl_2 = 3% → 5% → 10%) to afford (−)-Bao Gong Teng A (**1**) (104 mg, 72% in 2 steps) as a colorless oil.

TLC: R_f = 0.11 (CH_2Cl_2 / MeOH, 9:1 v/v).

OR: $[\alpha]^{23}_D$ = –16.4 (c = 0.31, H_2O), {lit.[8] $[\alpha]^{23}_D$ = –7.5 (c = 0.34, H_2O)}.

IR (KBr): 3361, 3140, 3033, 2940, 2855, 1730, 1650, 1437, 1380, 1245, 1180, 1091, 1026, 860 cm^{-1}.

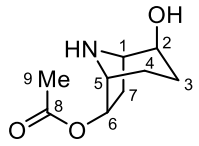
^{1}H NMR (600 MHz, $CDCl_3$): δ 5.13 (dd, *J* = 7.0, 2.3 Hz, 1H), 3.60–3.54 (m, 2H), 3.32 (m, 1H), 2.17 (dd, *J* = 14.7, 7.0 Hz, 1H), 2.04 (s, 3H), 1.88 (m, 1H), 1.79 (ddd, *J* = 14.7, 6.6, 2.3 Hz, 1H), 1.63–1.45 (m, 3H), a signal due to proton (OH, NH) was not observed.

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 77.9, 67.4, 61.1, 60.6, 37.1, 24.9, 24.6, 21.2.

HRMS (ESI+): *m/z* calculated for $C_9H_{16}NO_3^+$ $[M+H]^+$ 186.1125, found *m/z* 186.1130.

The spectroscopic data of synthetic (–)-Bao Gong Teng A (**1**) were identical to those of the natural product.

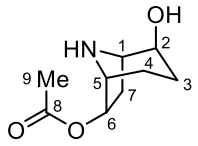
Table S2. Comparison of ^{1}H NMR spectroscopic data of natural and synthetic (–)-Bao Gong Teng A



(–)-Bao Gong Teng A (**1**)

No.	**Natural** [9] δ ^{1}H [ppm; mult; *J* (Hz)] 90 MHz, $CDCl_3$	**Huang's synthetic** [10] δ ^{1}H [ppm; mult; *J* (Hz)] 400 MHz, $CDCl_3$	**Our synthetic** δ ^{1}H [ppm; mult; *J* (Hz)] 600 MHz, $CDCl_3$
1	3.6–3.4 (1H, m)	3.58–3.53 (1H, m)	3.60–3.54 (1H, m)
2	3.4–3.2 (1H, m)	3.30 (1H, m)	3.32 (1H, m)
3	2.4–1.0 (2H, m)	1.88 (1H, m) 1.59–1.48 (1H, m)	1.88 (1H, m) 1.63–1.45 (1H, m)
4	2.4–1.0 (2H, m)	1.59–1.48 (2H, m)	1.63–1.45 (2H, m)
5	3.6–3.4 (1H, m)	3.58–3.53 (1H, m)	3.60–3.54 (1H, m)
6	5.2–5.0 (1H, dd, 8, 3–4)	5.13 (1H, dd, 7.0, 2.1)	5.13 (1H, dd, 7.0, 2.3)
7	2.4–1.0 (2H, m)	2.16 (1H, dd, 14.7, 7.0) 1.78 (1H, ddd, 14.7, 6.7, 2.1)	2.17 (1H, dd, 14.7, 7.0) 1.79 (1H, ddd, 14.7, 6.6, 2.3)
8	–	–	–
9	1.98 (3H, s)	2.04 (3H, s)	2.04 (3H, s)
OH	2.8–2.6 (1H, brs)	2.65 (1H, brs)	not observed
NH	2.8–2.6 (1H, brs)	2.65 (1H, brs)	not observed

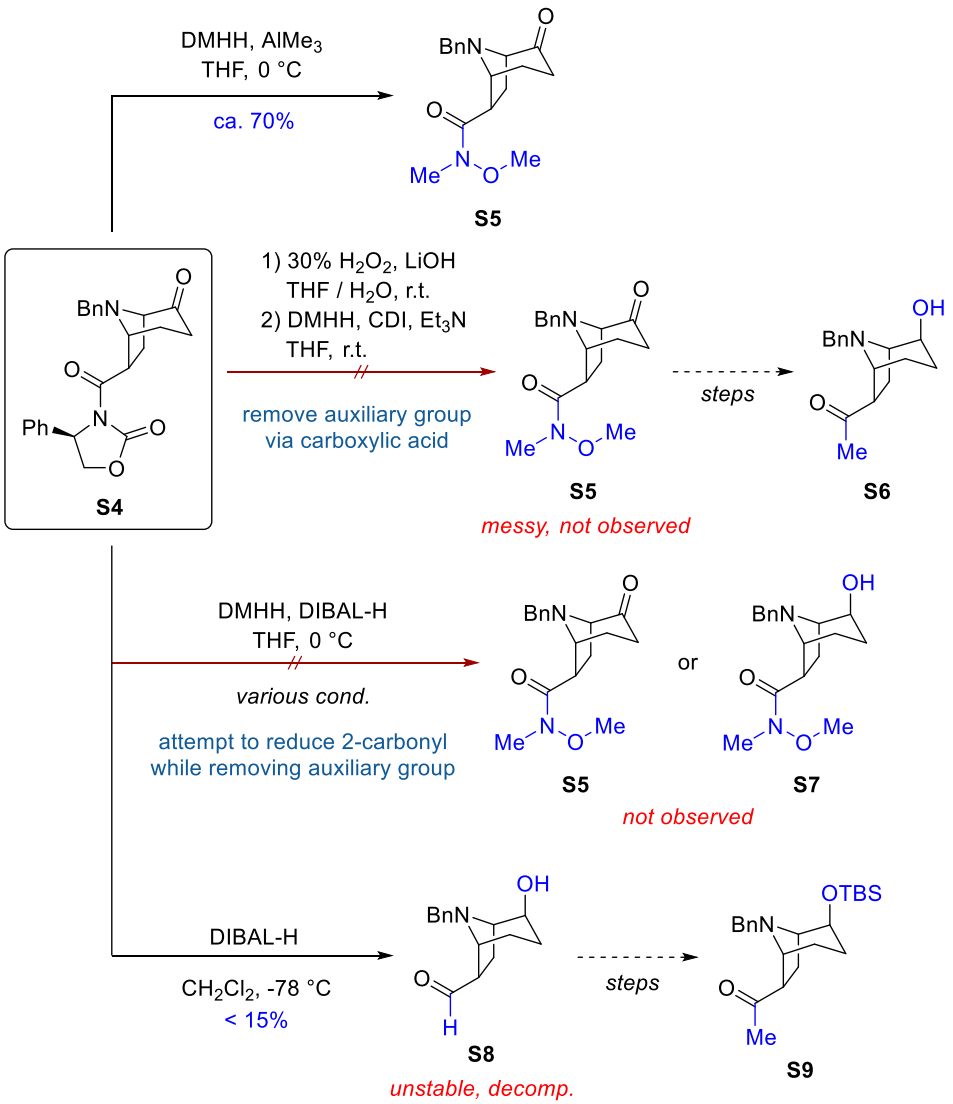
Table S3. Comparison of ^{13}C NMR spectroscopic data of natural and synthetic (–)-Bao Gong Teng A



(–)-Bao Gong Teng A (**1**)

No.	**Natural** [11] ***Benzoate derivative*** δ ^{13}C (ppm) 23 MHz, $CDCl_3$	**Huang's synthetic** [10] δ ^{13}C (ppm) 100 MHz, $CDCl_3$	**Our synthetic** δ ^{13}C (ppm) 100 MHz, $CDCl_3$
1	60.2	60.8	60.6
2	66.6	67.7	67.4
3	23.4	25.3	24.9
4	22.9	25.0	24.6
5	60.2	61.4	61.1
6	74.7	78.3	77.9
7	34.0	37.4	37.1
8	171.3	170.9	170.8
9	20.4	21.5	21.2

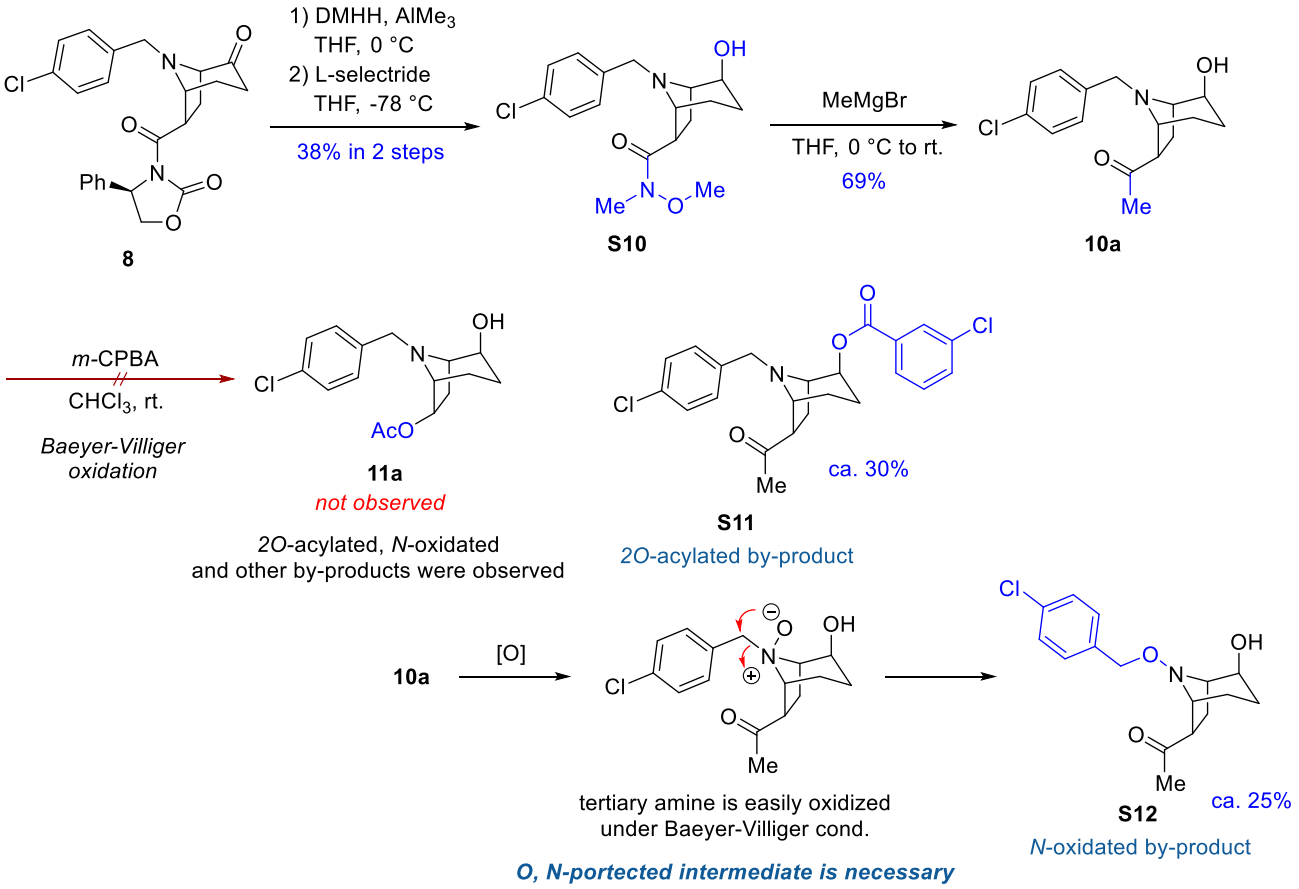
Summary of failed approaches to the synthesis of (–)-Bao Gong Teng A.



Scheme S3. Attempts to remove the oxazolidinone auxiliary

We attempted several ways to remove the oxazolidinone auxiliary after selective construction of 8-azabicyclo[3.2.l]octane skeleton. As we described in the main text (Scheme 3), a model transamination process of ketone **S4** was conducted by using *N*,*O*-dimethylhydroxylamine hydrochloride (DMHH) and $AlMe_3$, the desired Weinreb amide **S5** can be obtained in approximately 70% yield. We also attempted to remove the oxazolidinone moiety via carboxylic acid intermediate, after the treatment of ketone **S4** with 30% H_2O_2 and LiOH, the crude carboxylic acid was treated with DMHH and CDI. However, the reaction mixture became messy and no desired product was observed. Additionally, to achieve an efficient approach to 2-hydroxylated 8-azabicyclo[3.2.1]octane intermediate **S7**, we attempted to reduce the 2-carbonyl group while removing the oxazolidinone auxiliary, but it all failed to provide satisfactory results under various conditions including the use of DMHH/DIBAL-H with

several experiments. Furthermore, we also tried to remove the oxazolidinone auxiliary by single use of DIBAL-H to afford 2-hydroxy aldehyde **S8**, the low yield of desired aldehyde **S8** was attributed to its instability, which likely decomposed under the post-treatment and purification. Given these issues, we chose to proceed with the method outlined in the main text (Scheme 3) for its better yield and reliability.

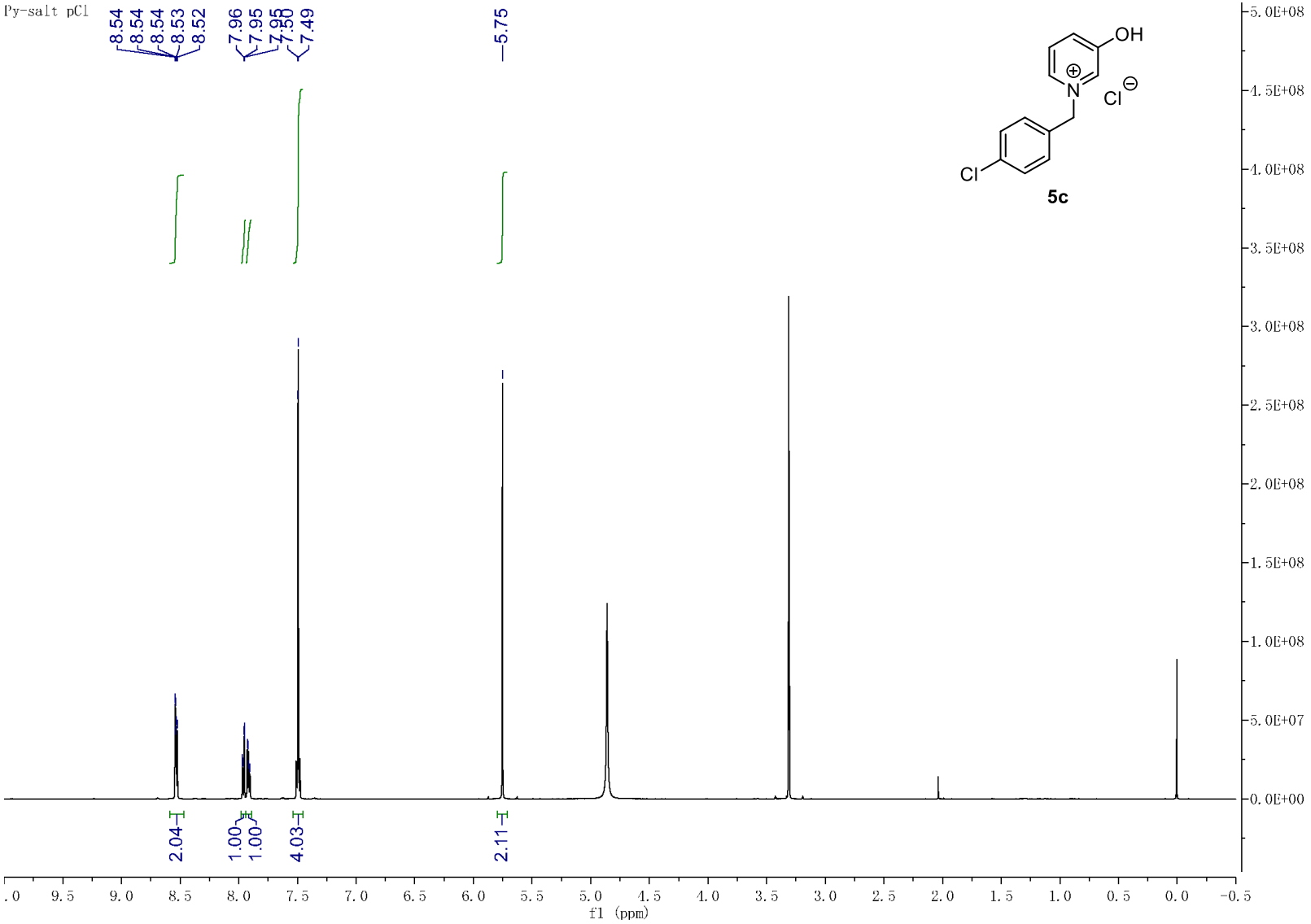


Scheme S4. Failed attempts to *6O*-acetyl intermediate **11a** via direct Baeyer–Villiger oxidation

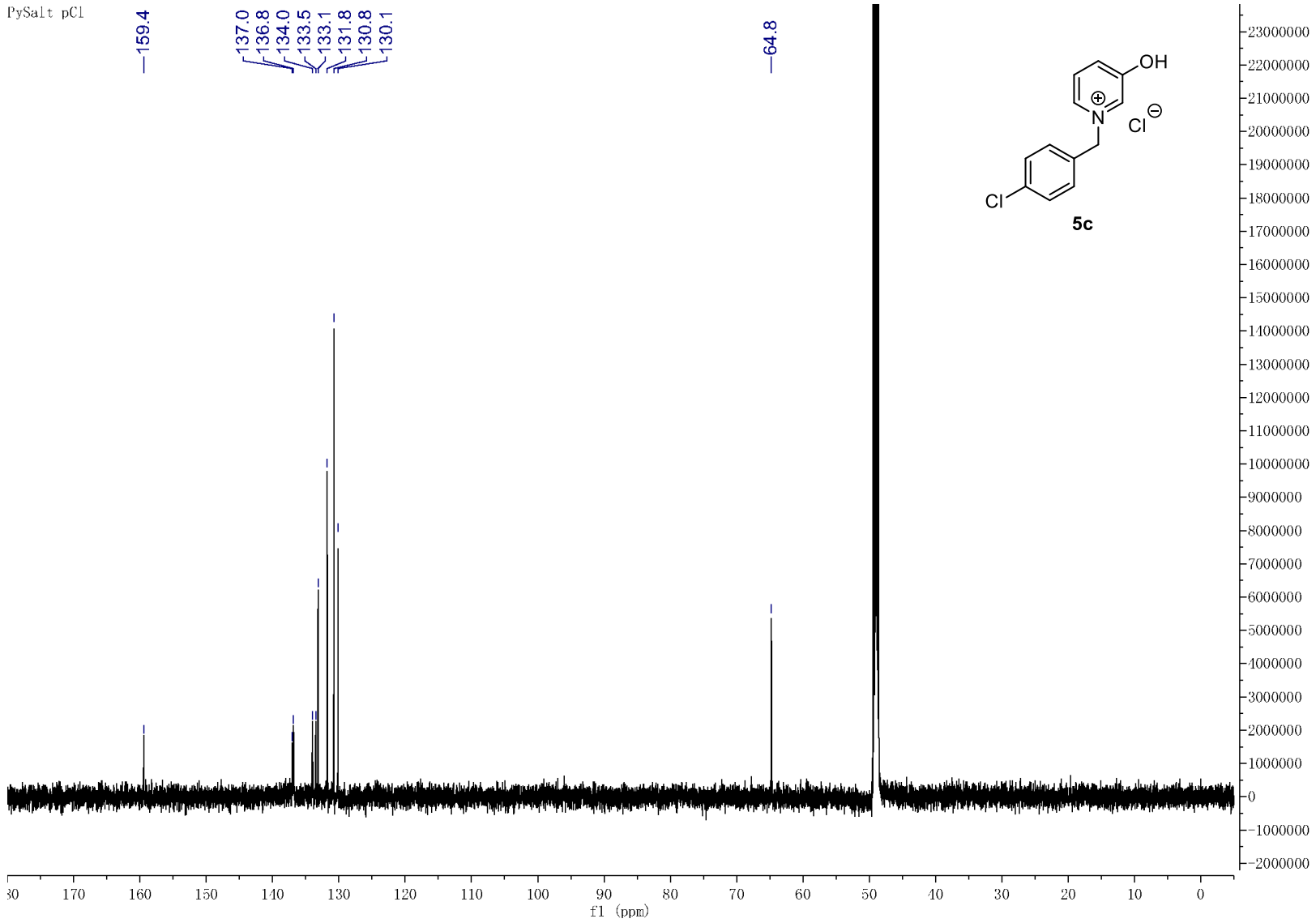
After removal of the oxazolidinone auxiliary group and stereoselective reduction of the C2 carbonyl group of ketone **8**, we afforded Weinreb amide **S10** in a 2-step yield of 38%. The following methylation of Weinreb amide **S10** gave methyl ketone **10a**, which was thought to be the precursor of introducing the 6-acetoxy group in our initial plan, in 68% yield. Regrettably, the Baeyer−Villiger oxidation process similar to that reported in the literature did not achieve for methyl ketone **10a**,[1] no desired acetate **11a** was observed. Instead, *2O*-acylated by-product **S11** and *N*-oxidated by-product **S12** were obtained under the Baeyer−Villiger condition. Thus, considering the nitrogen atom of benzyl-substituted tertiary amine moiety is easily oxidized,[12] we had better replace an electron-withdrawing group (such as *t*-butyloxy carbonyl group) to prevent the oxidation of the nitrogen atom. And a protected 2-hydroxy group (such as silyl group) is needed to prevent the *O*-acylation.

5. ^{1}H NMR and ^{13}C NMR Spectra

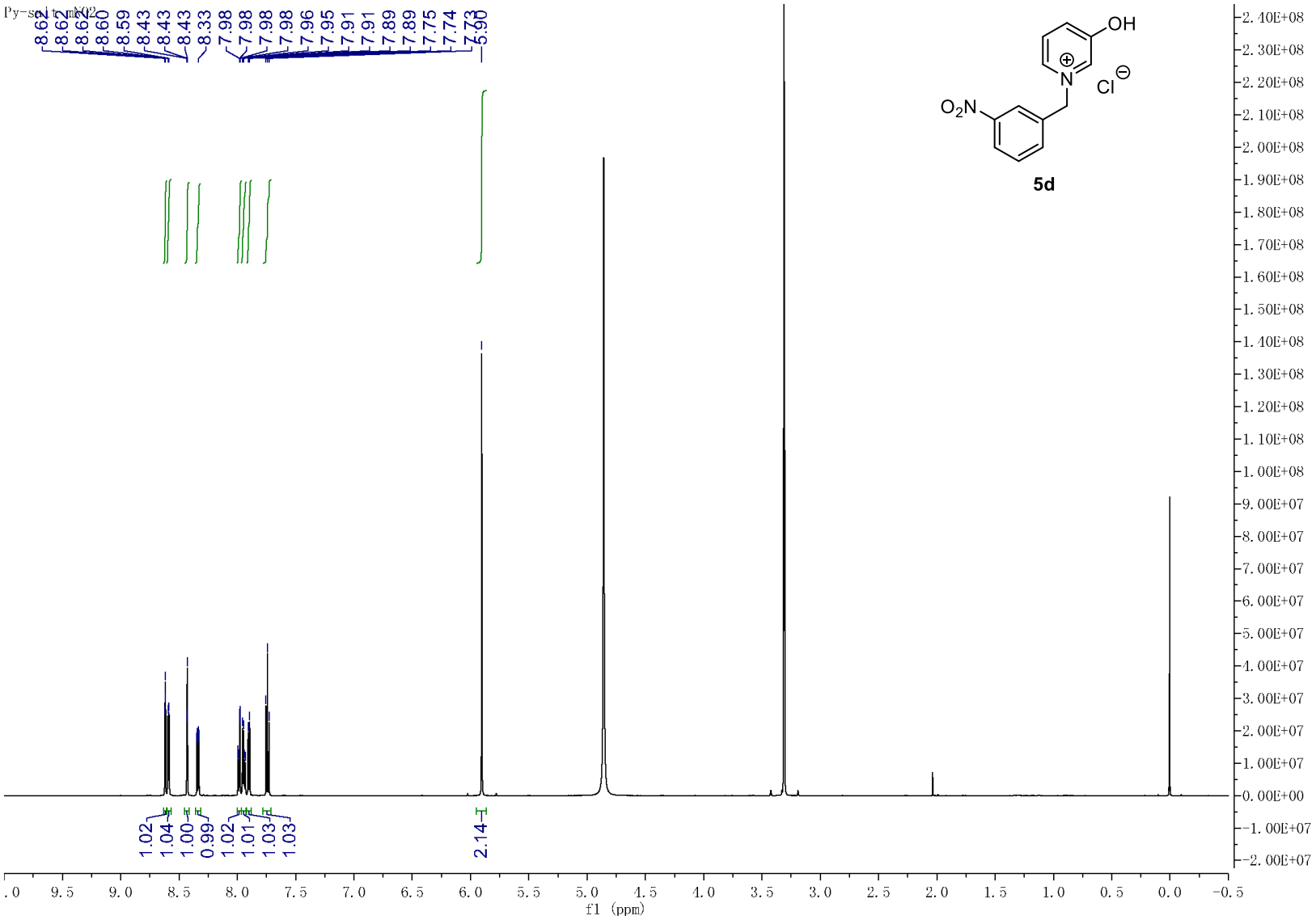
^{1}H NMR of **5c** (600 MHz, methanol-*d4*)



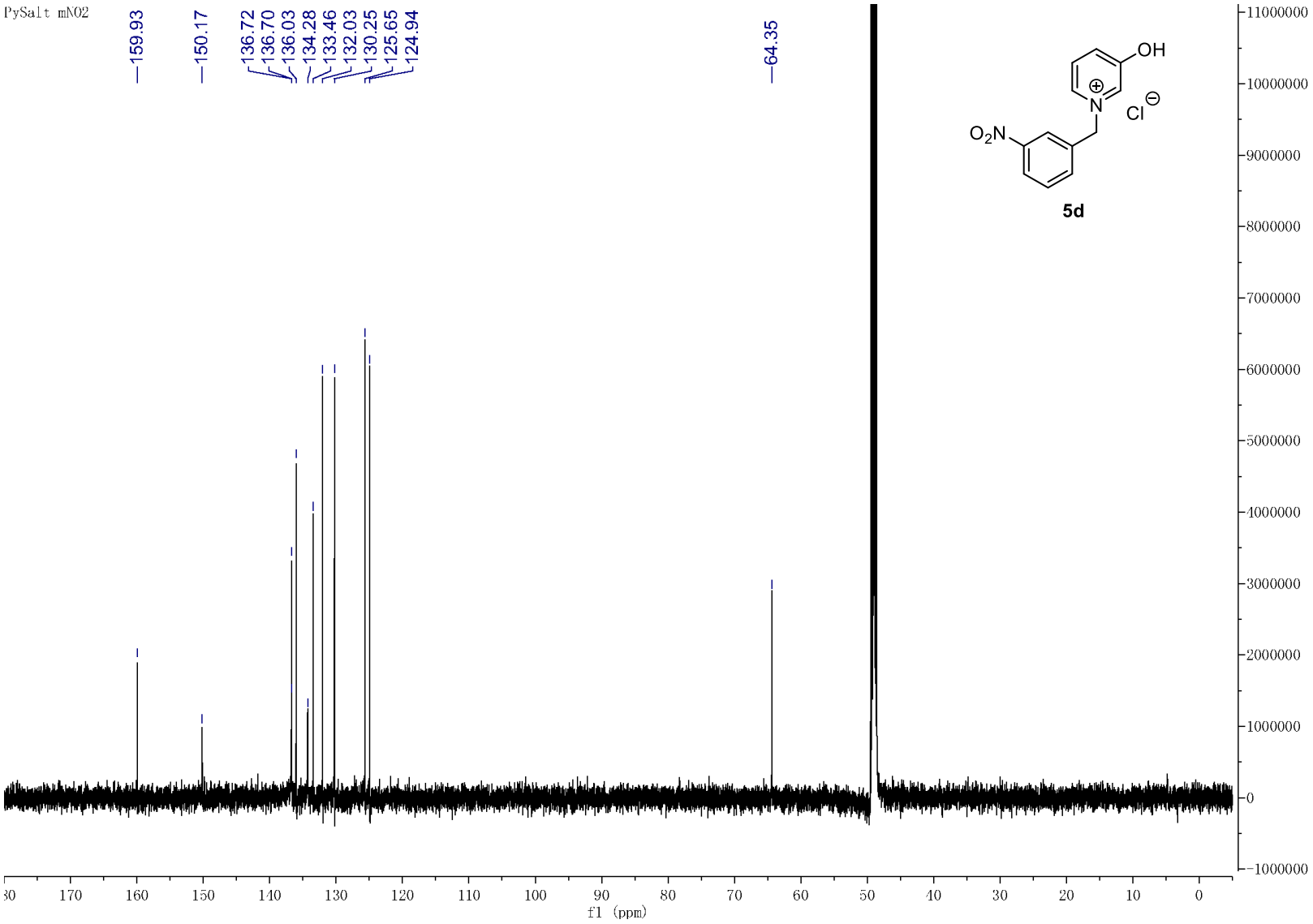
^{13}C NMR of **5c** (150 MHz, methanol-*d4*)



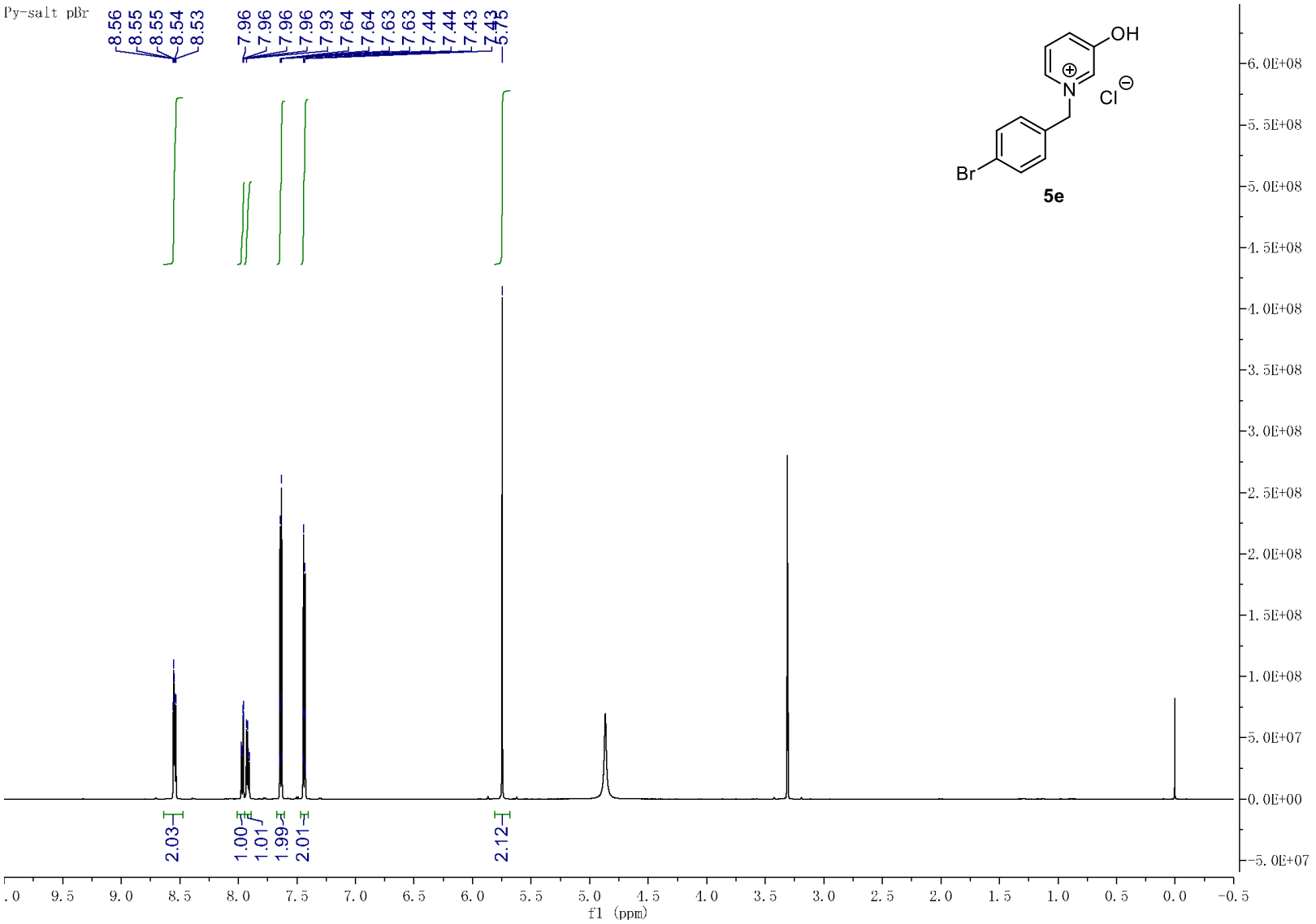
^{1}H NMR of **5d** (600 MHz, methanol-*d4*)



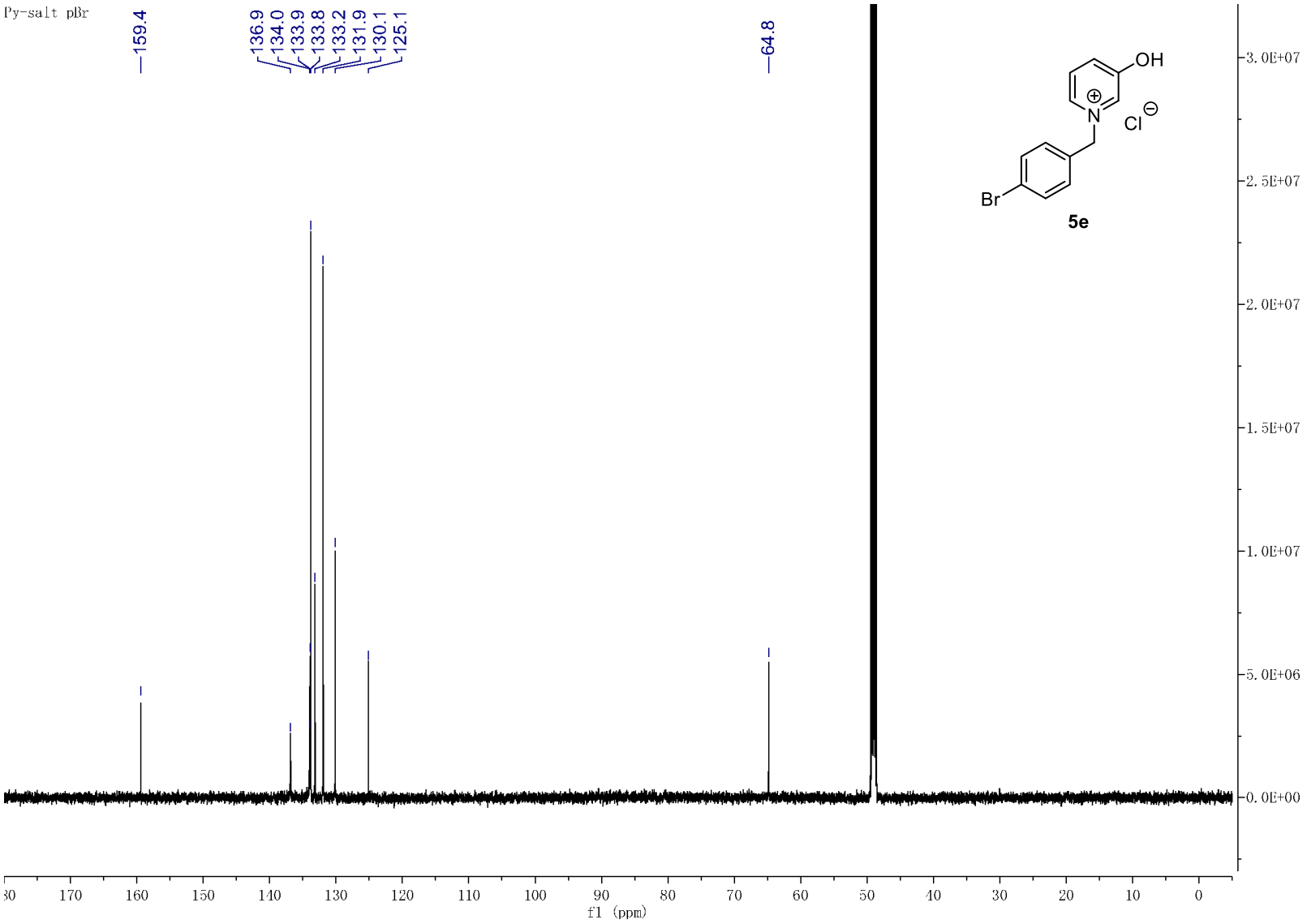
^{13}C NMR of **5d** (150 MHz, methanol-*d4*)



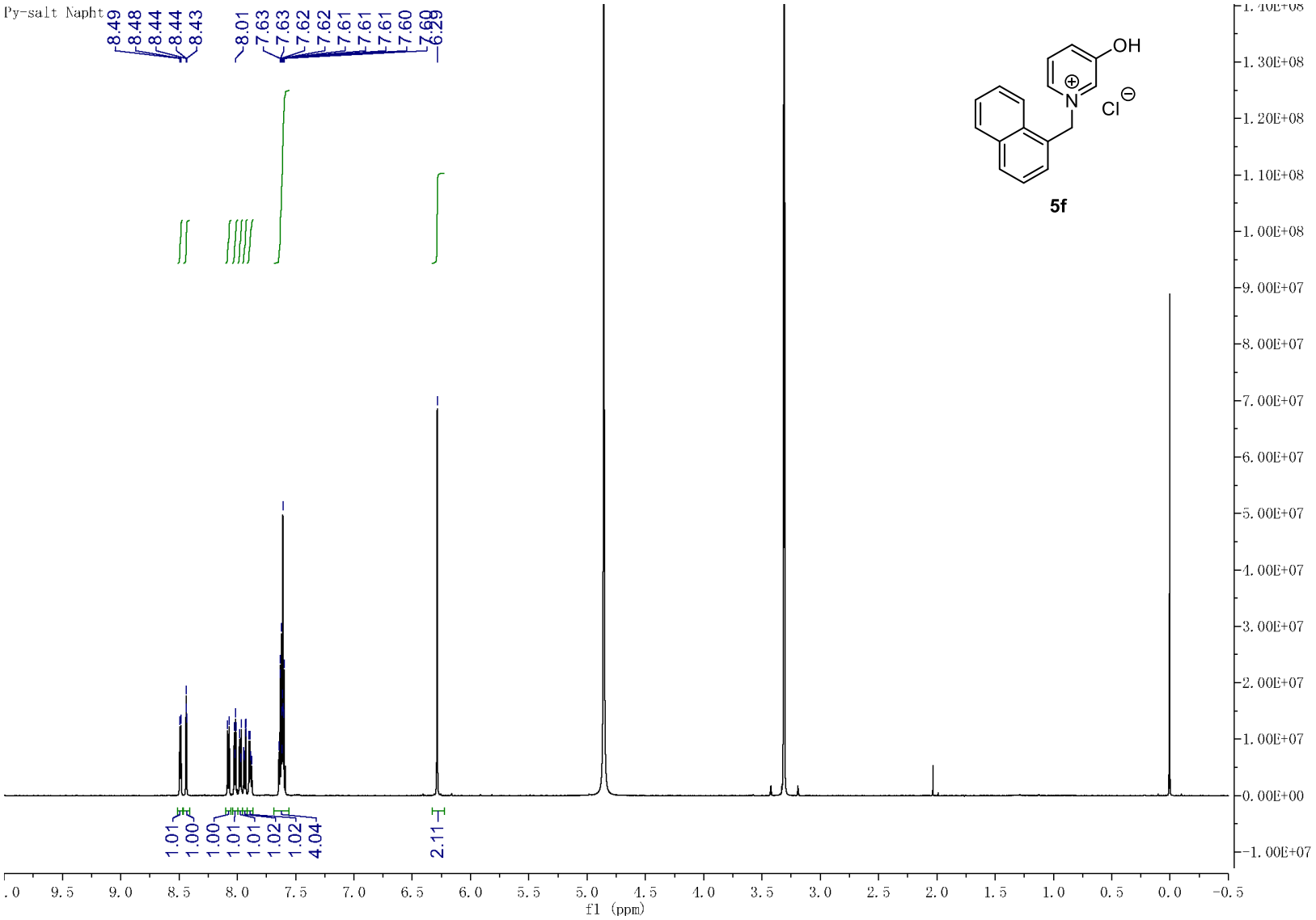
^{1}H NMR of **5e** (600 MHz, methanol-*d4*)



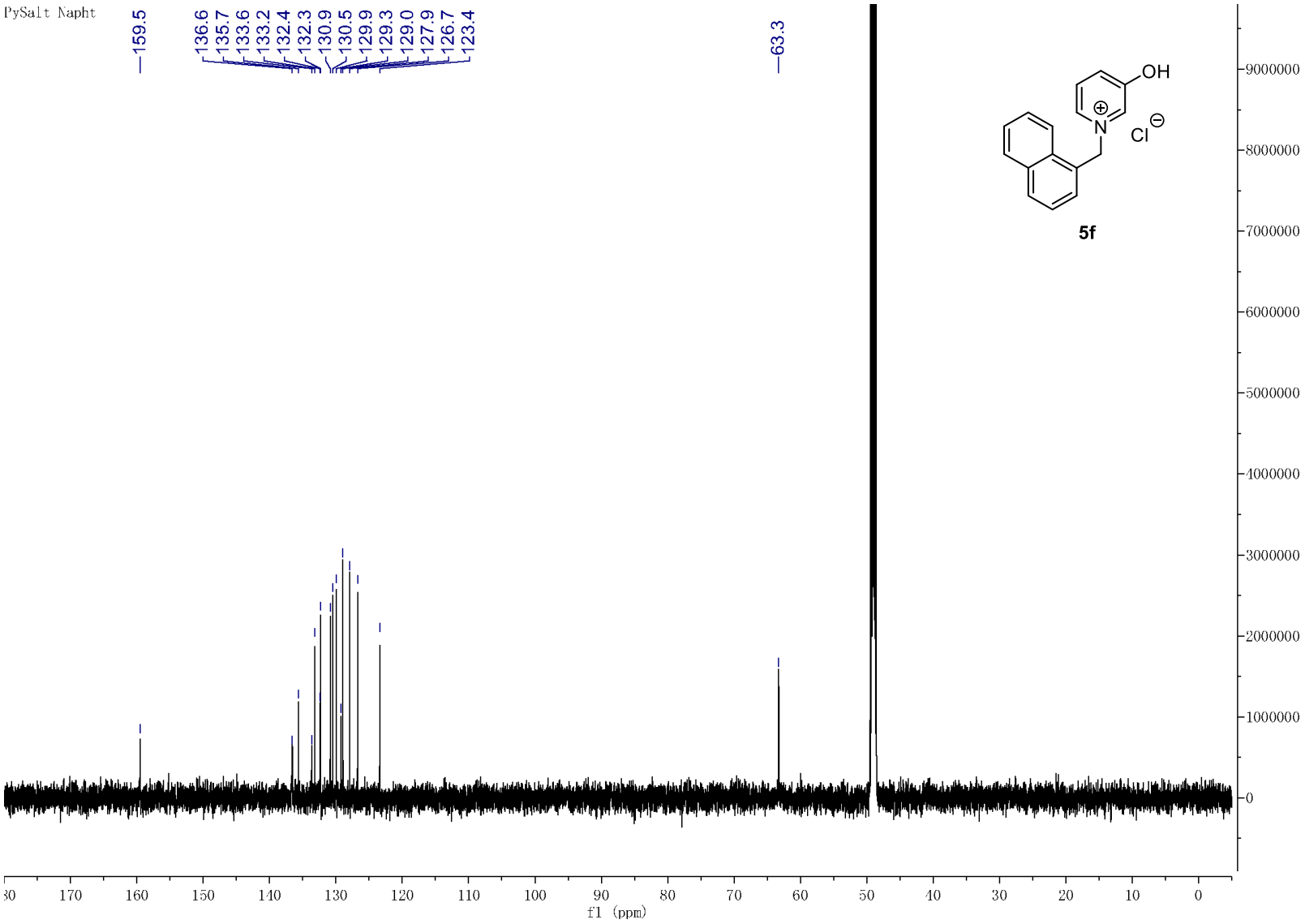
^{13}C NMR of **5e** (150 MHz, methanol-*d4*)



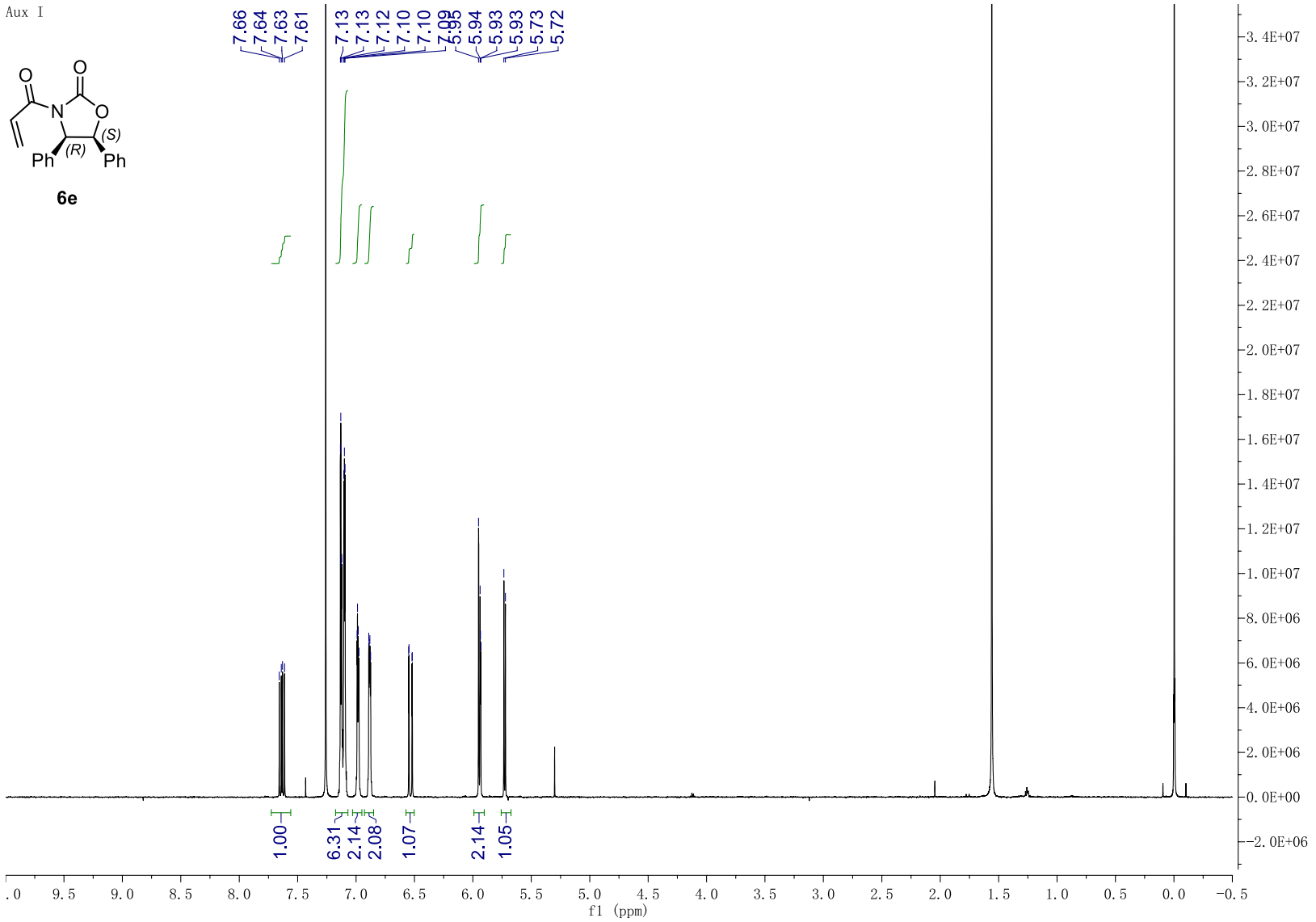
^{1}H NMR of **5f** (600 MHz, methanol-*d4*)



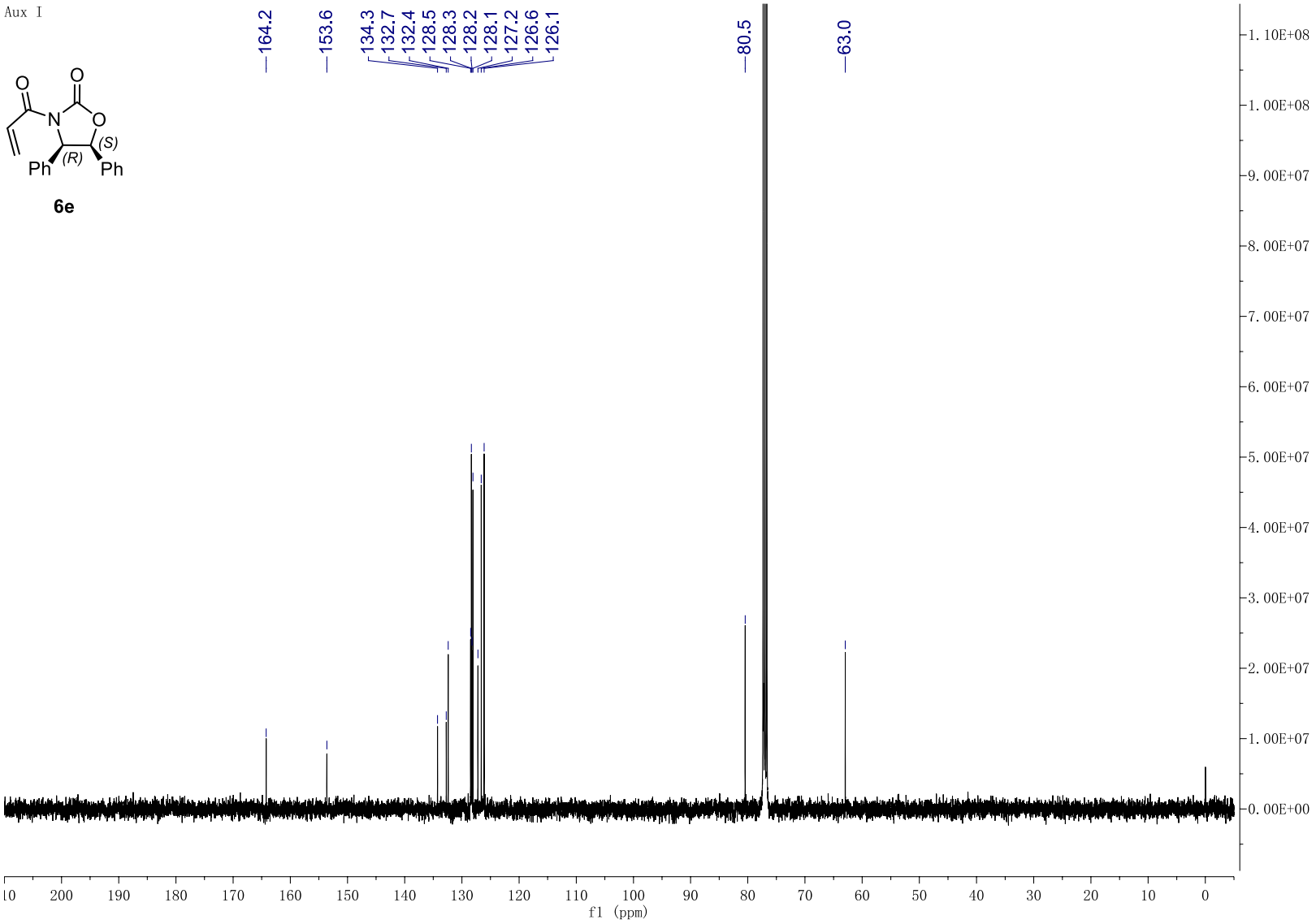
^{13}C NMR of **5f** (150 MHz, methanol-*d4*)



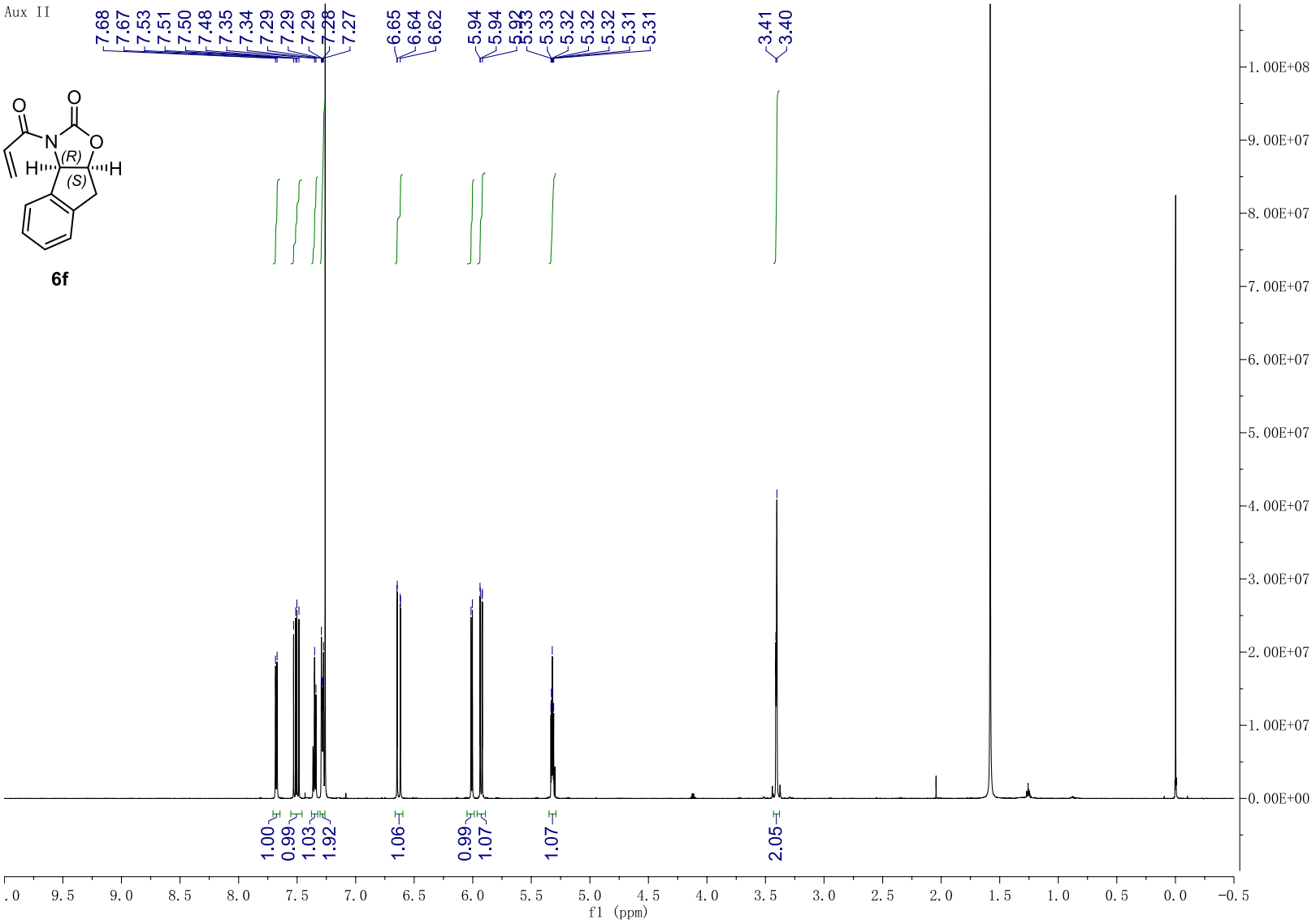
^{1}H NMR of **6e** (600 MHz, $CDCl_3$)



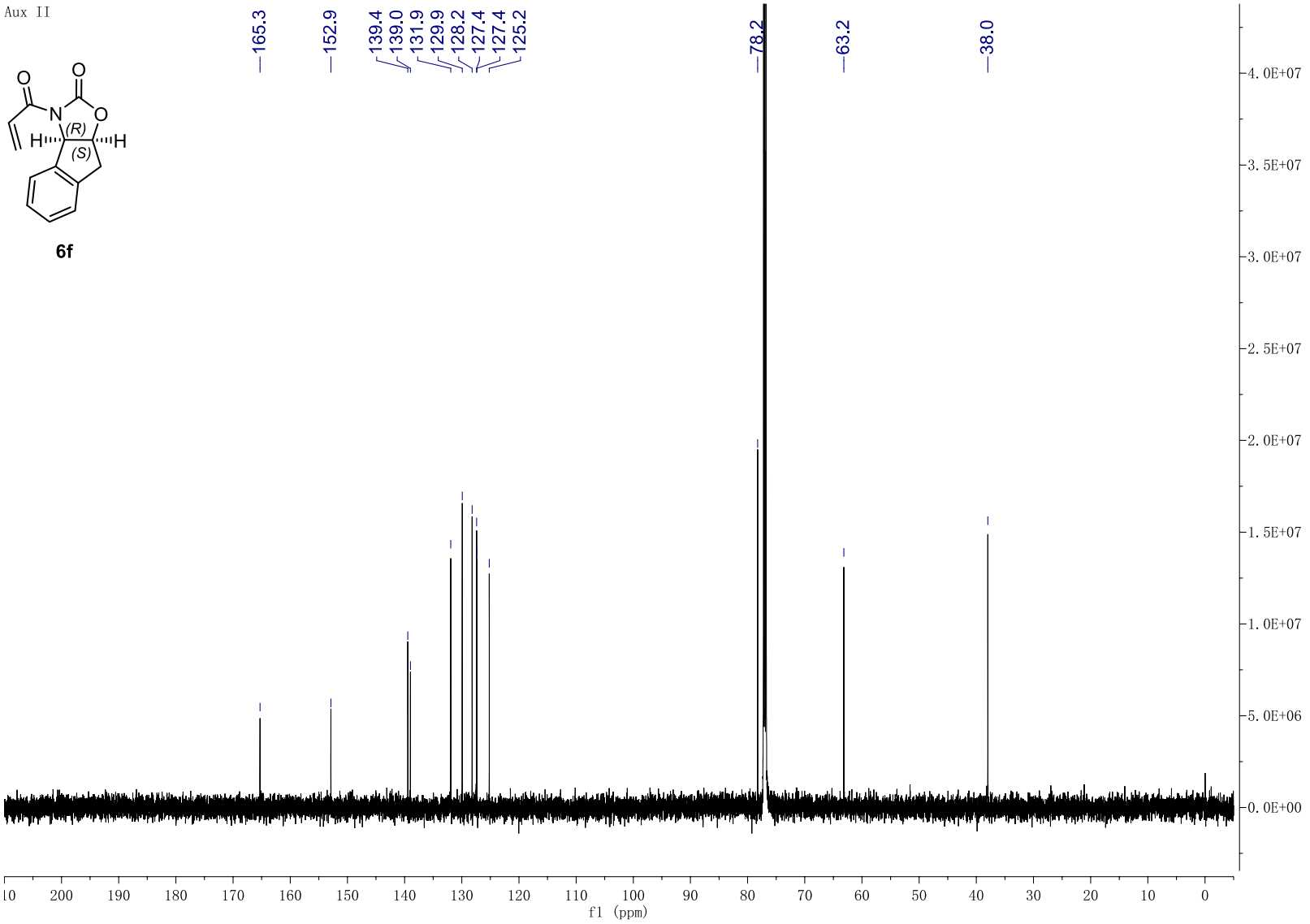
^{13}C NMR of **6e** (100 MHz, $CDCl_3$)



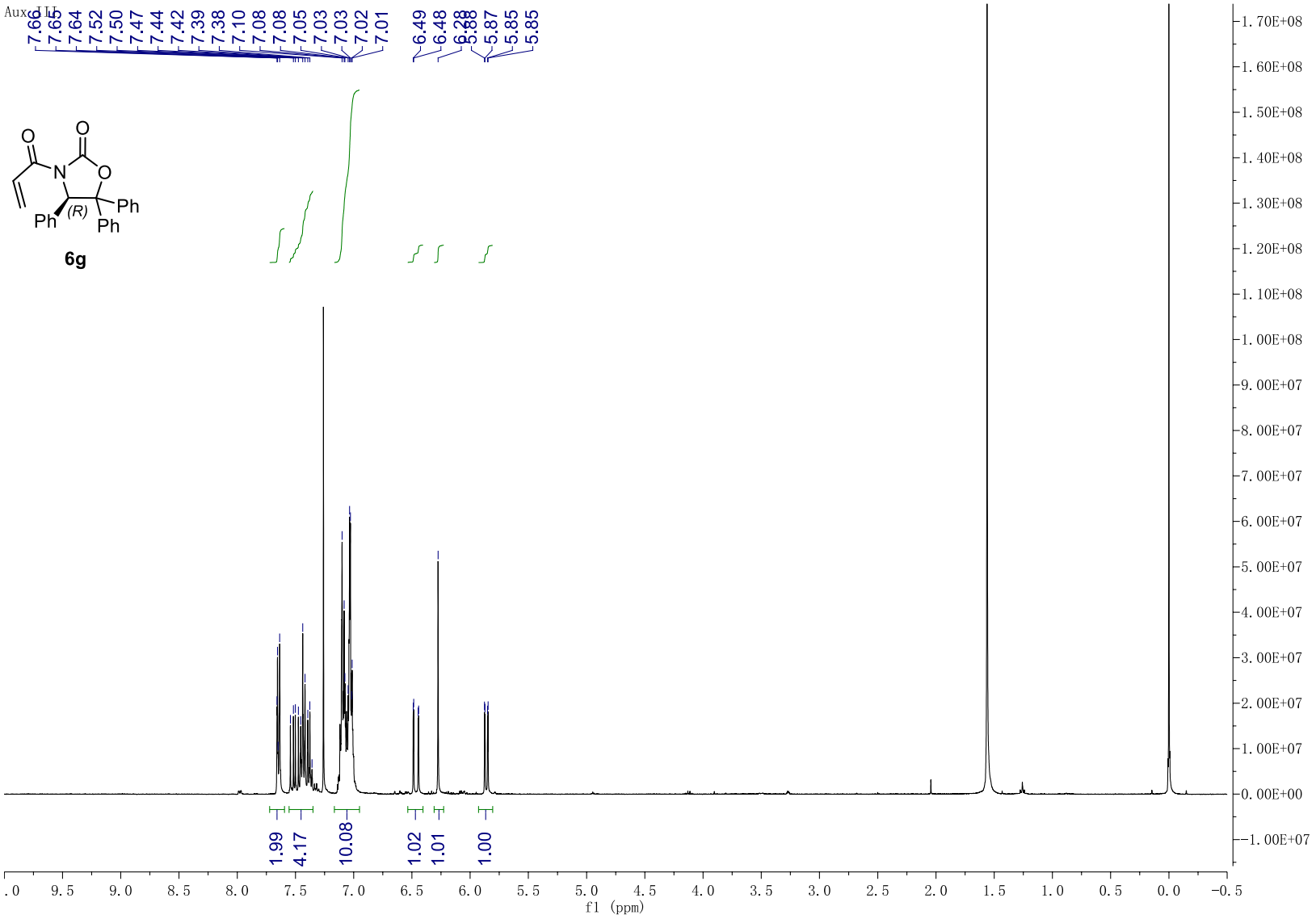
^{1}H NMR of **6f** (600 MHz, $CDCl_3$)



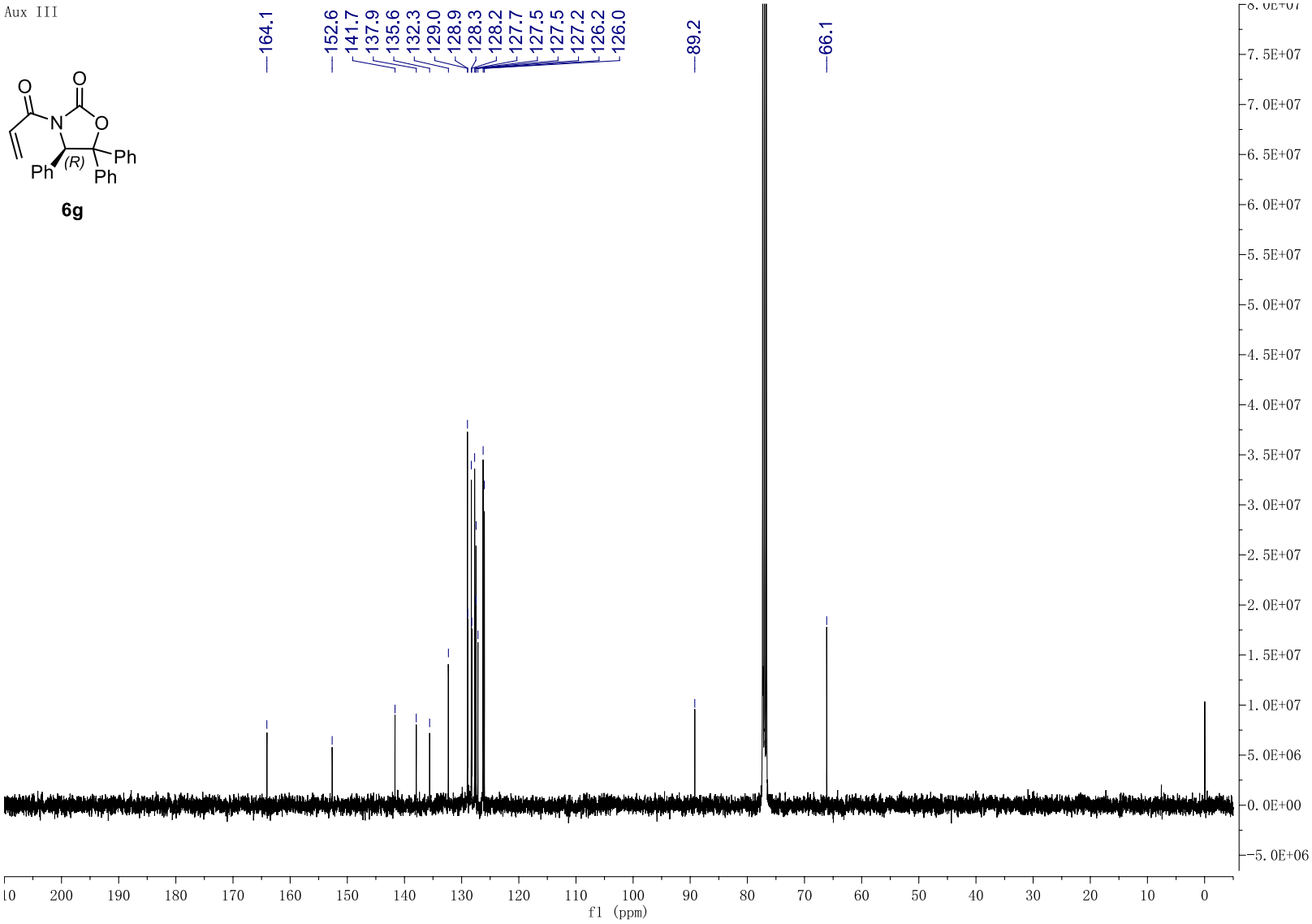
^{13}C NMR of **6f** (150 MHz, $CDCl_3$)



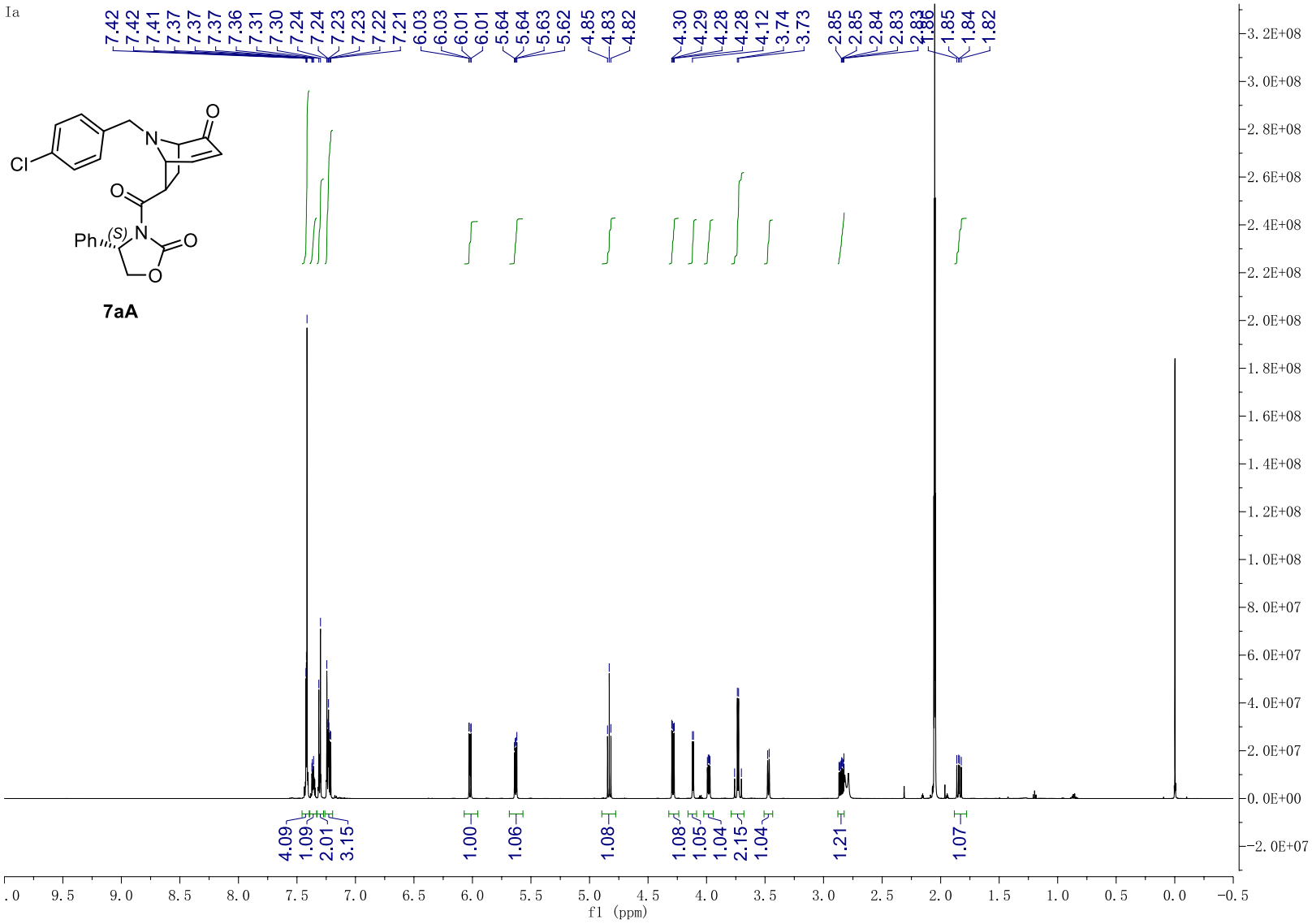
^{1}H NMR of **6g** (400 MHz, $CDCl_3$)



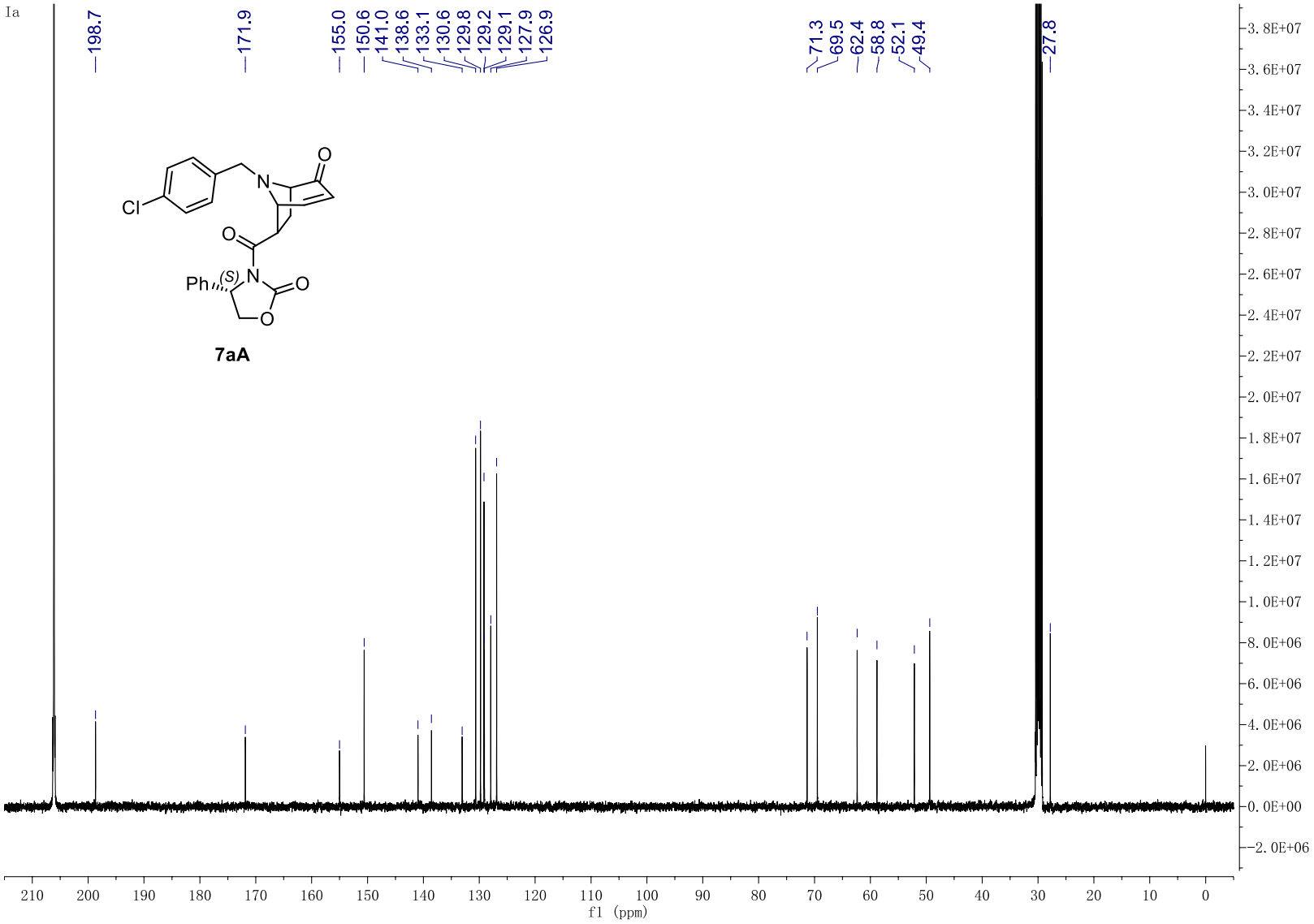
^{13}C NMR of **6g** (100 MHz, $CDCl_3$)



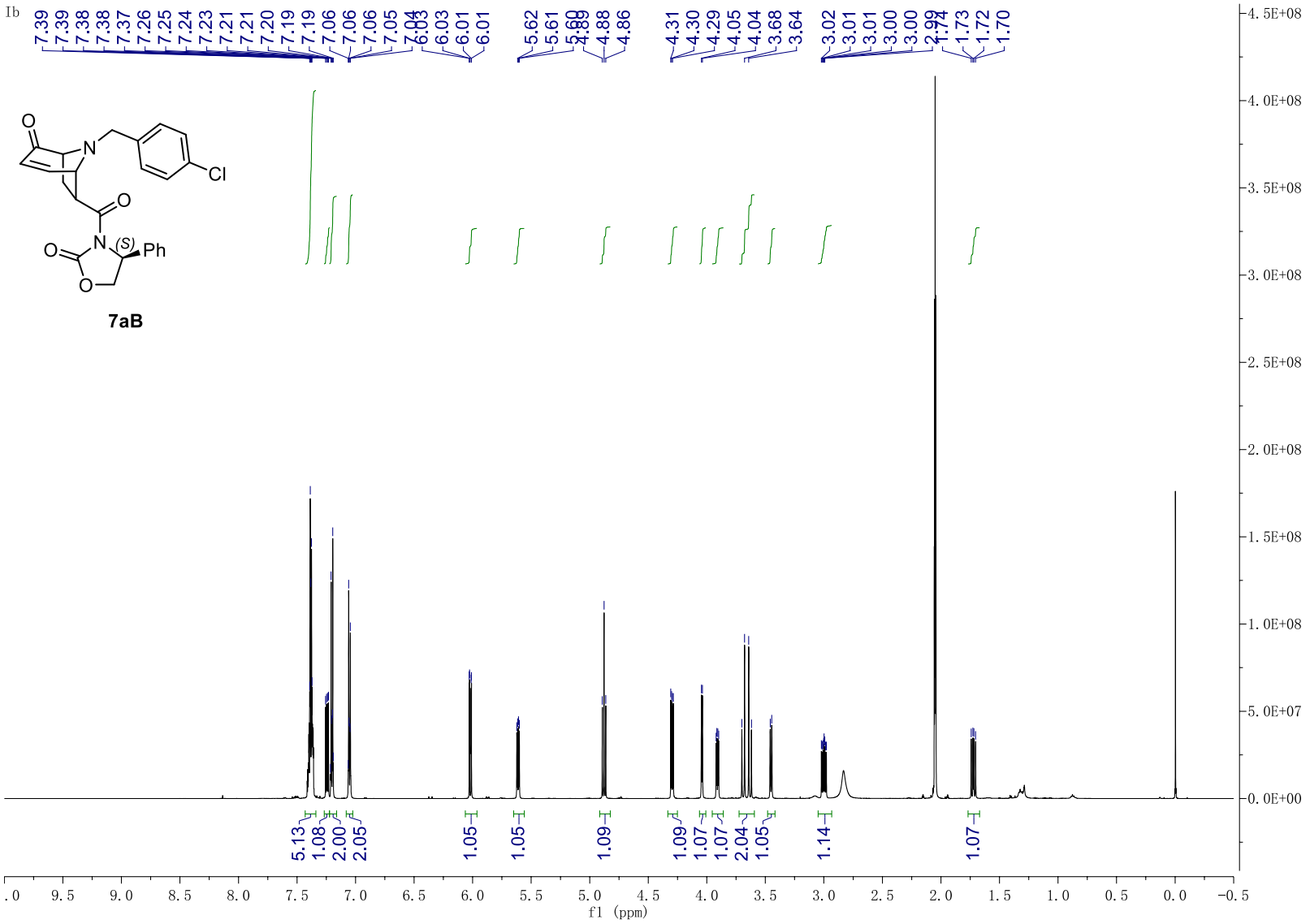
^{1}H NMR of **7aA** (600 MHz, acetone-*d6*)



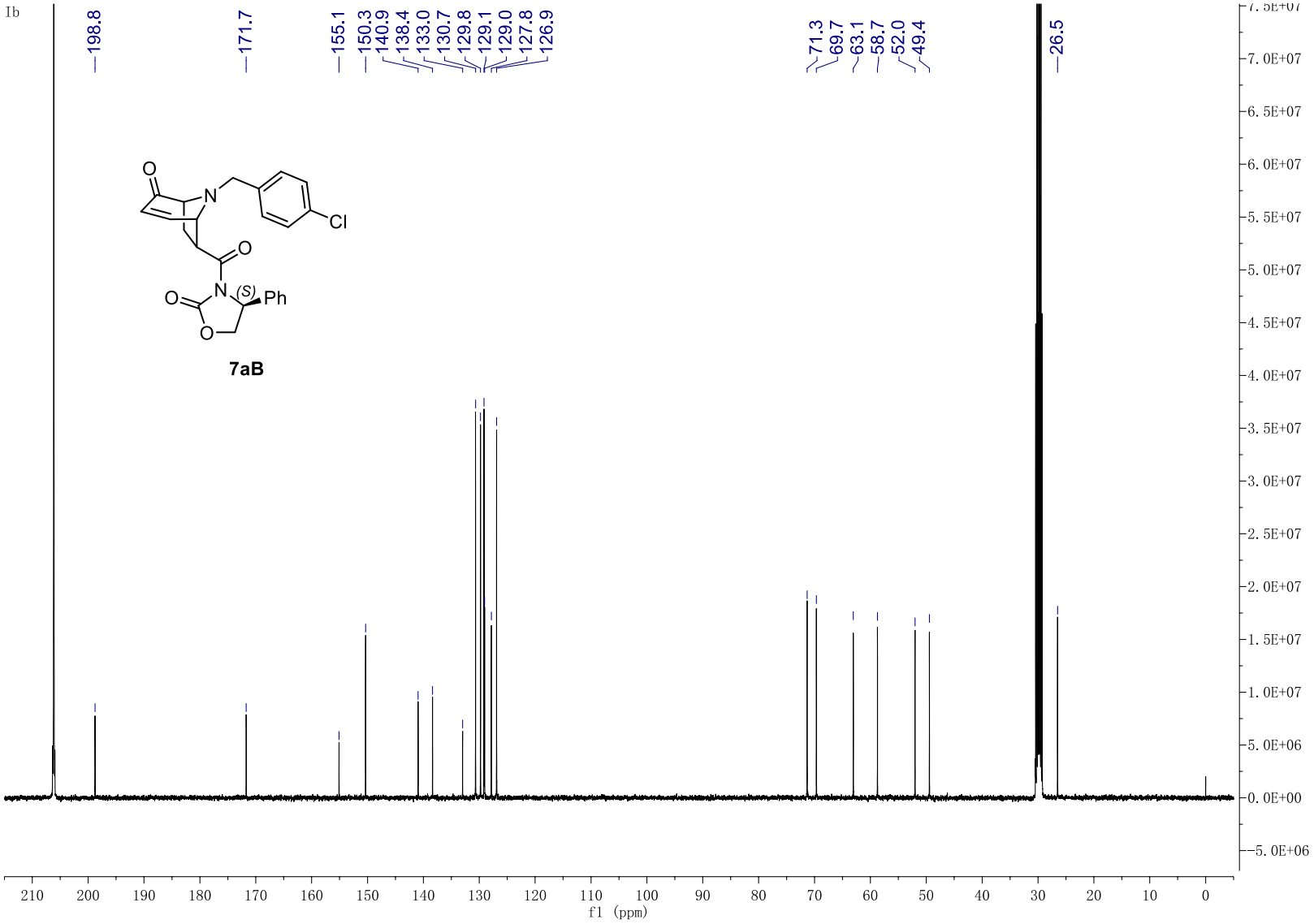
^{13}C NMR of **7aA** (100 MHz, acetone-*d6*)



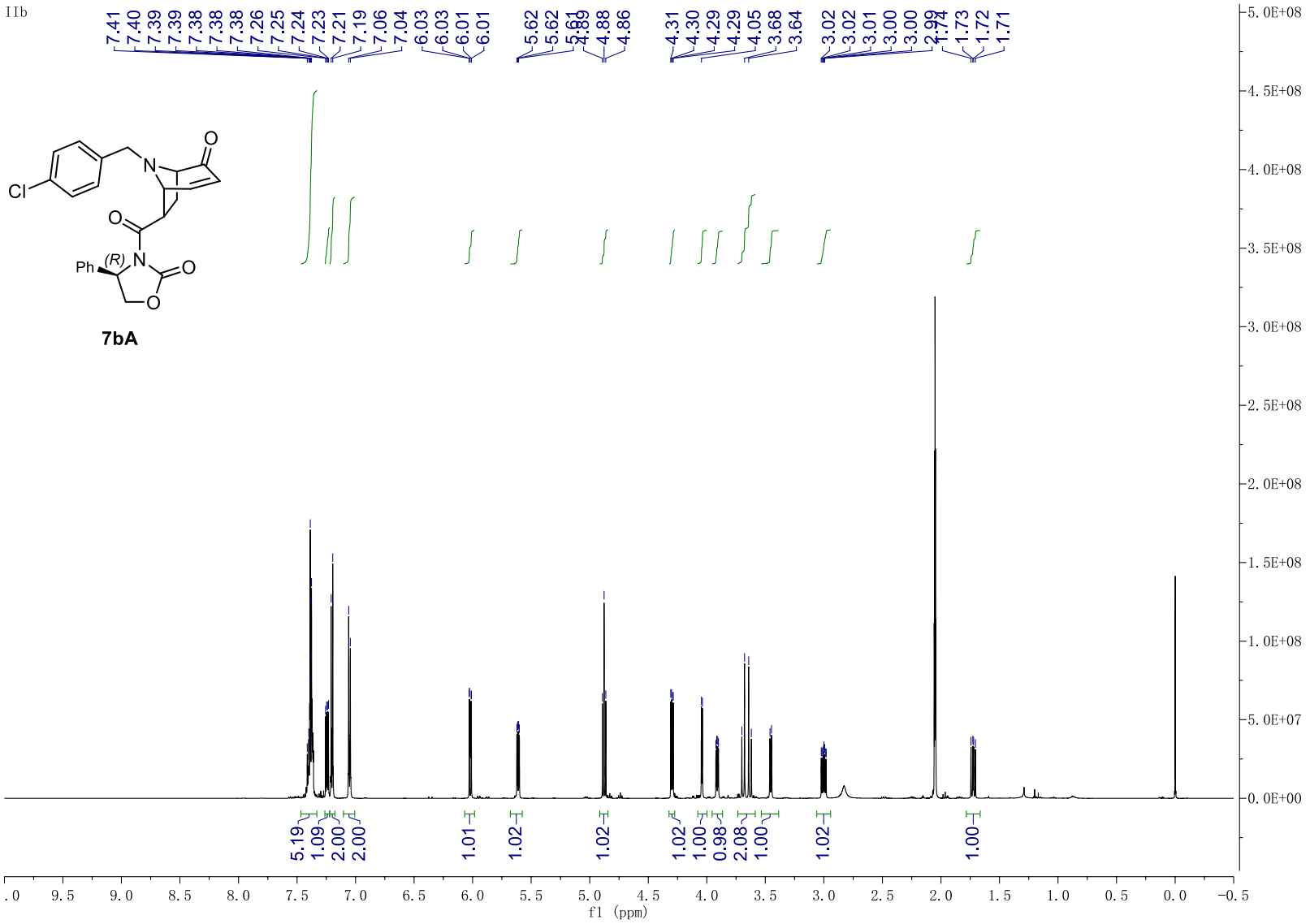
^{1}H NMR of **7aB** (600 MHz, acetone-*d6*)



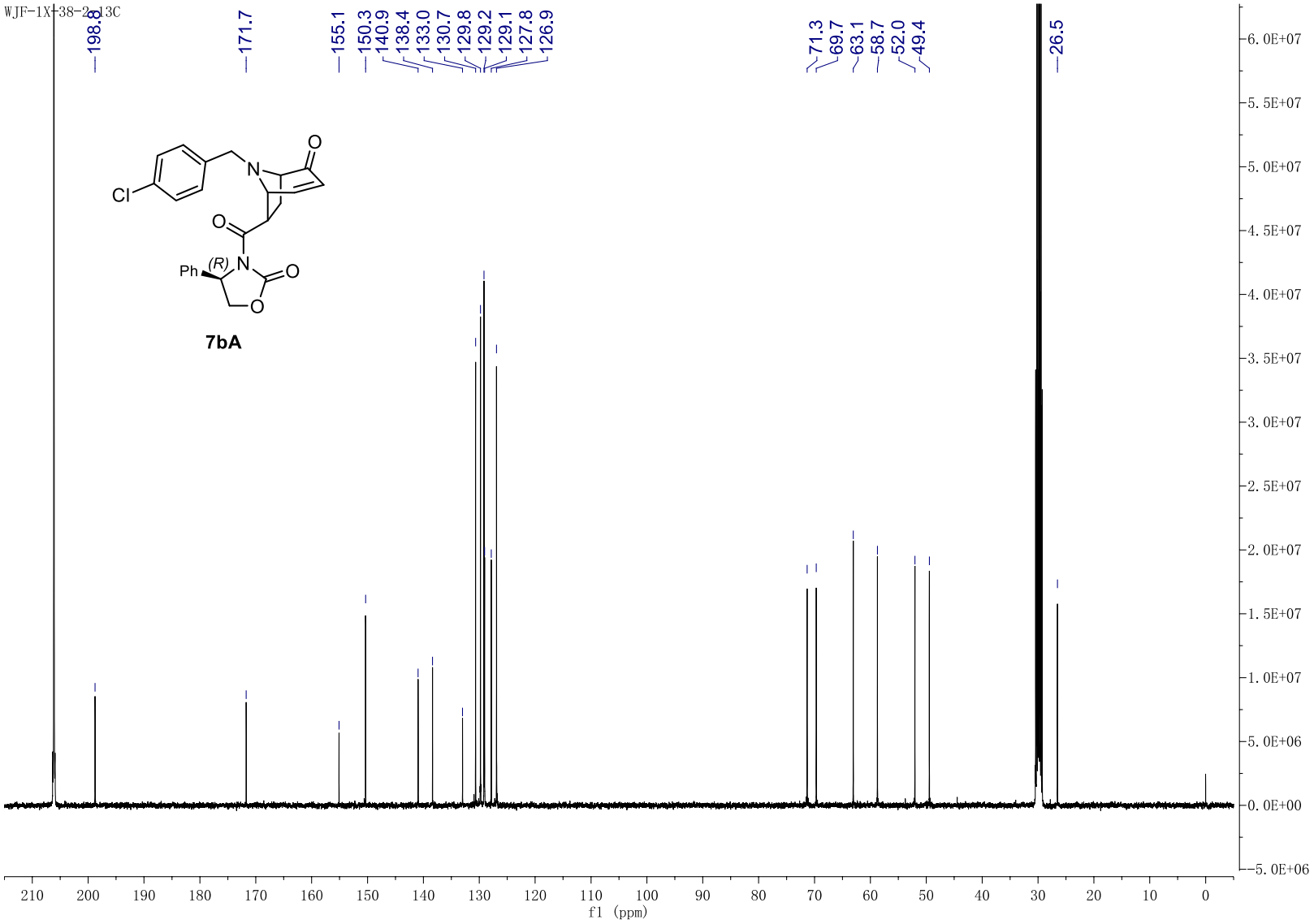
^{13}C NMR of **7aB** (100 MHz, acetone-*d6*)



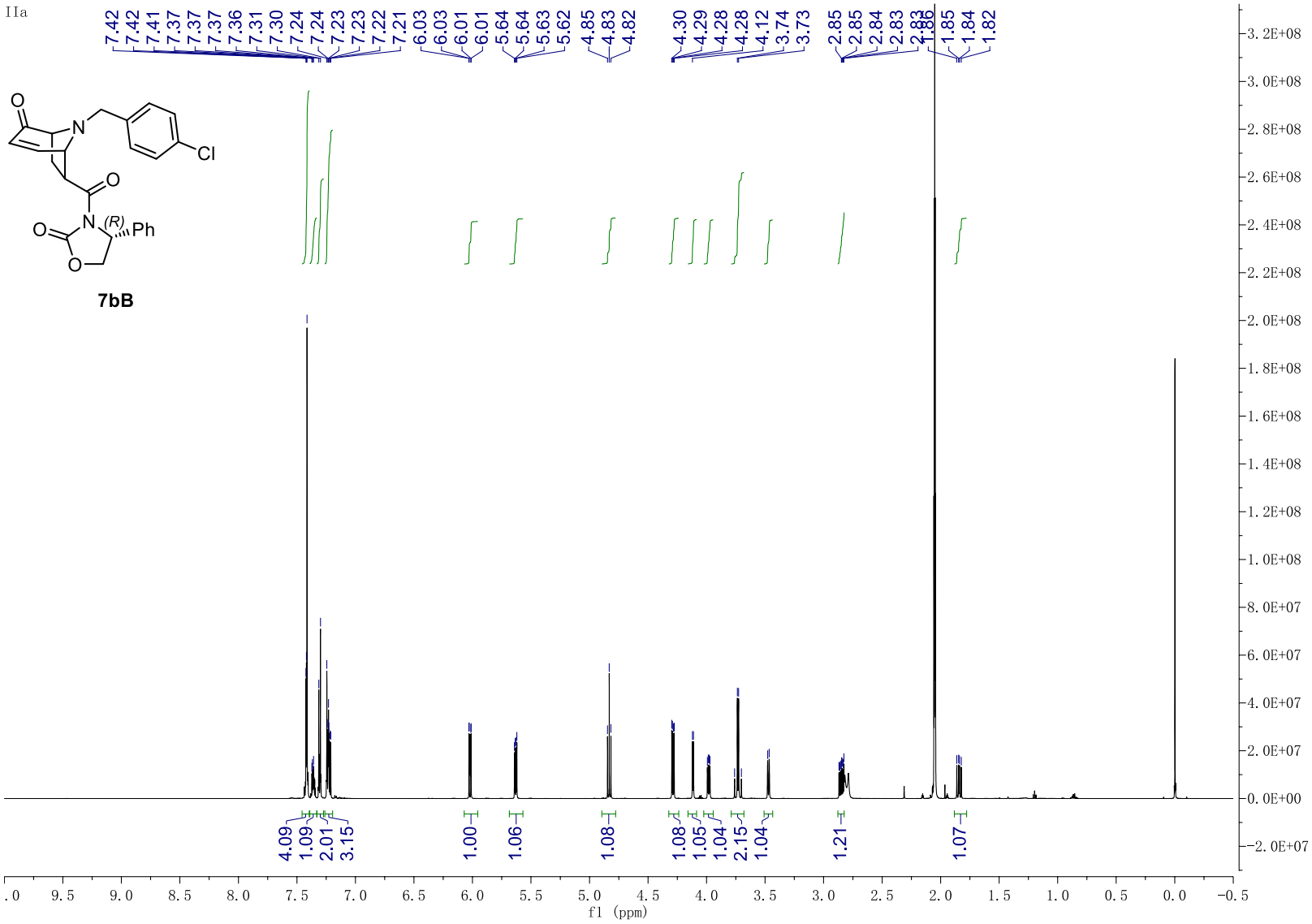
^{1}H NMR of **7bA** (600 MHz, acetone-*d6*)



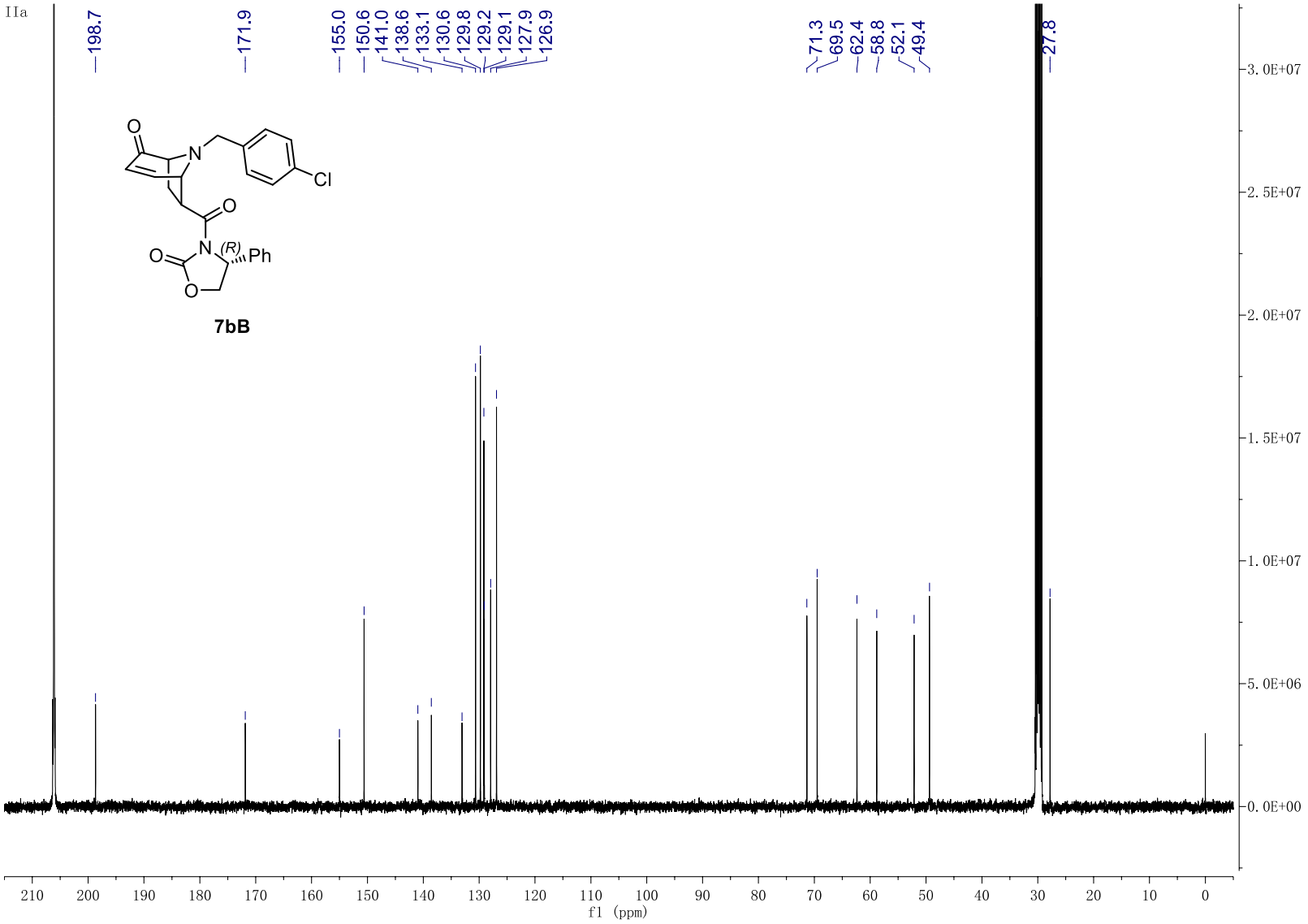
^{13}C NMR of **7bA** (100 MHz, acetone-*d6*)



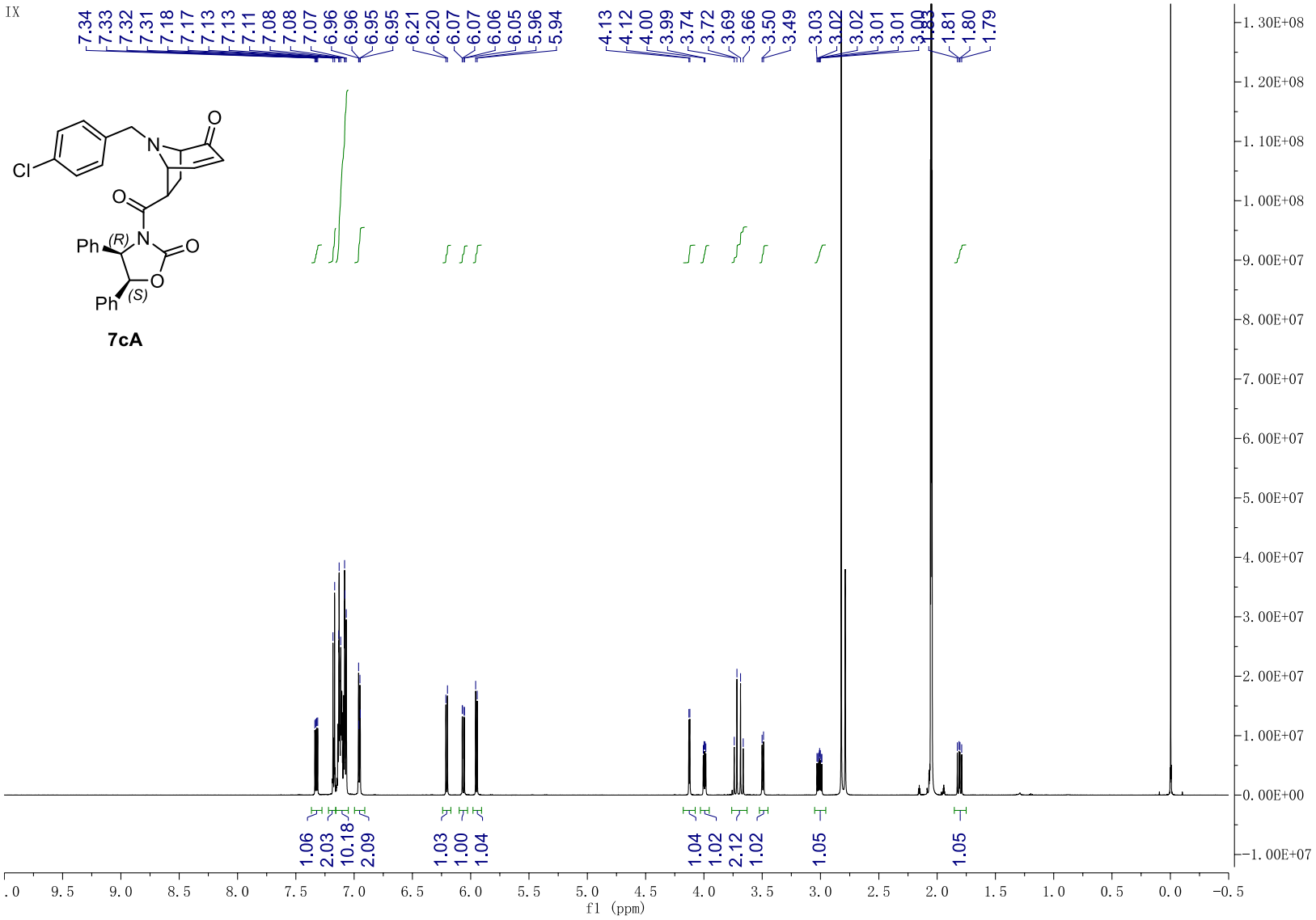
^{1}H NMR of **7bB** (600 MHz, acetone-*d6*)



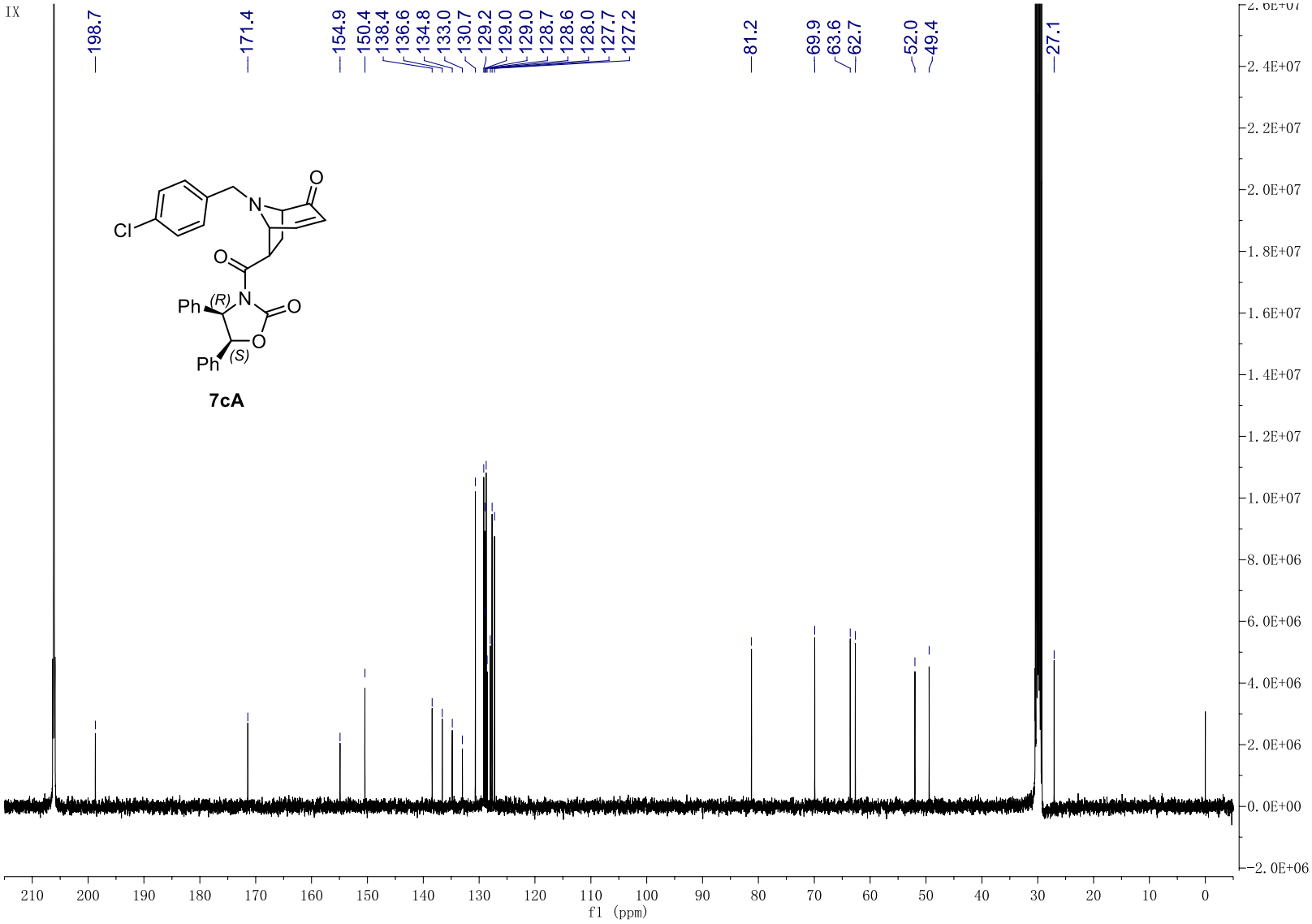
^{13}C NMR of **7bB** (100 MHz, acetone-*d6*)



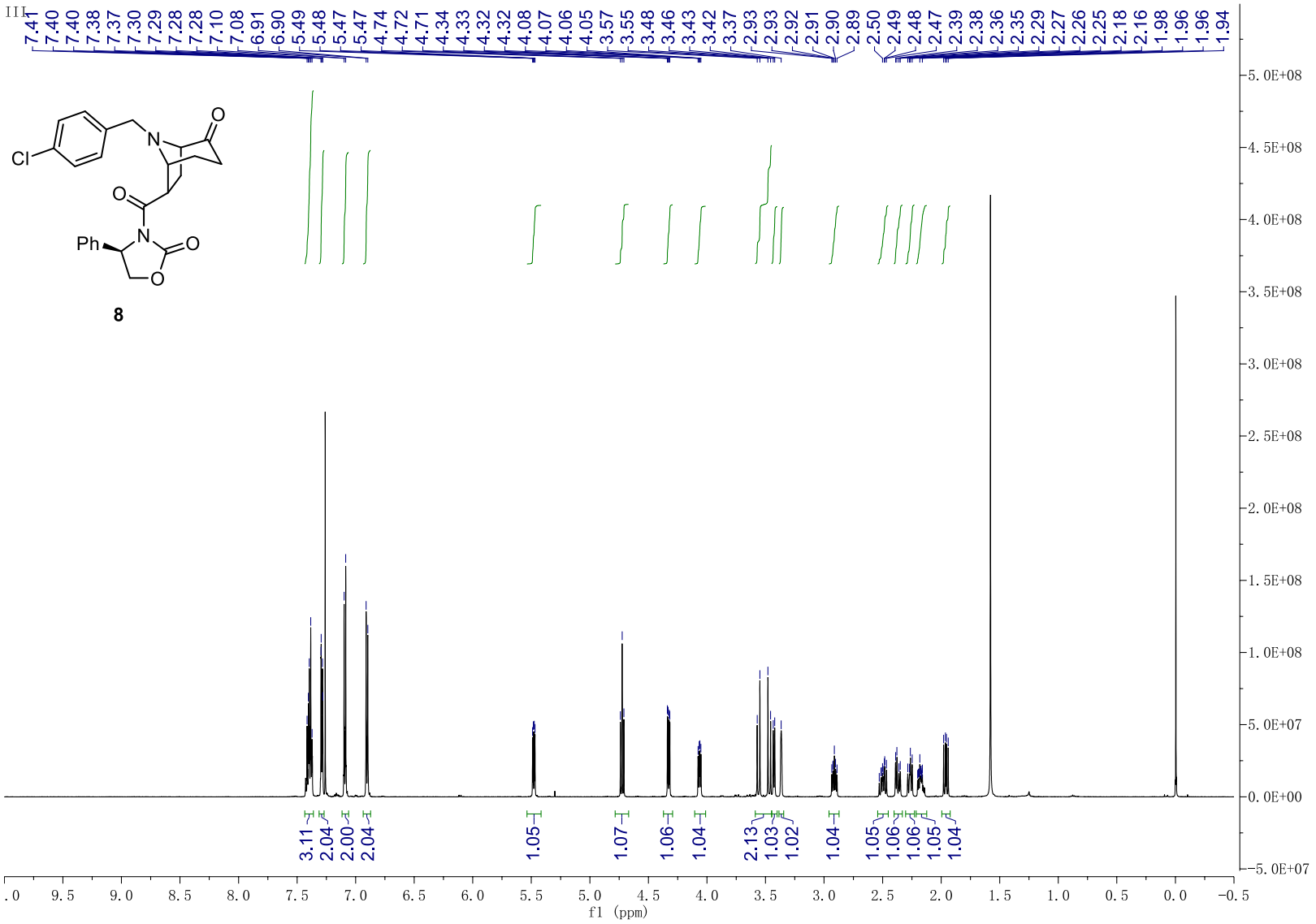
^{1}H NMR of **7cA** (600 MHz, acetone-*d6*)



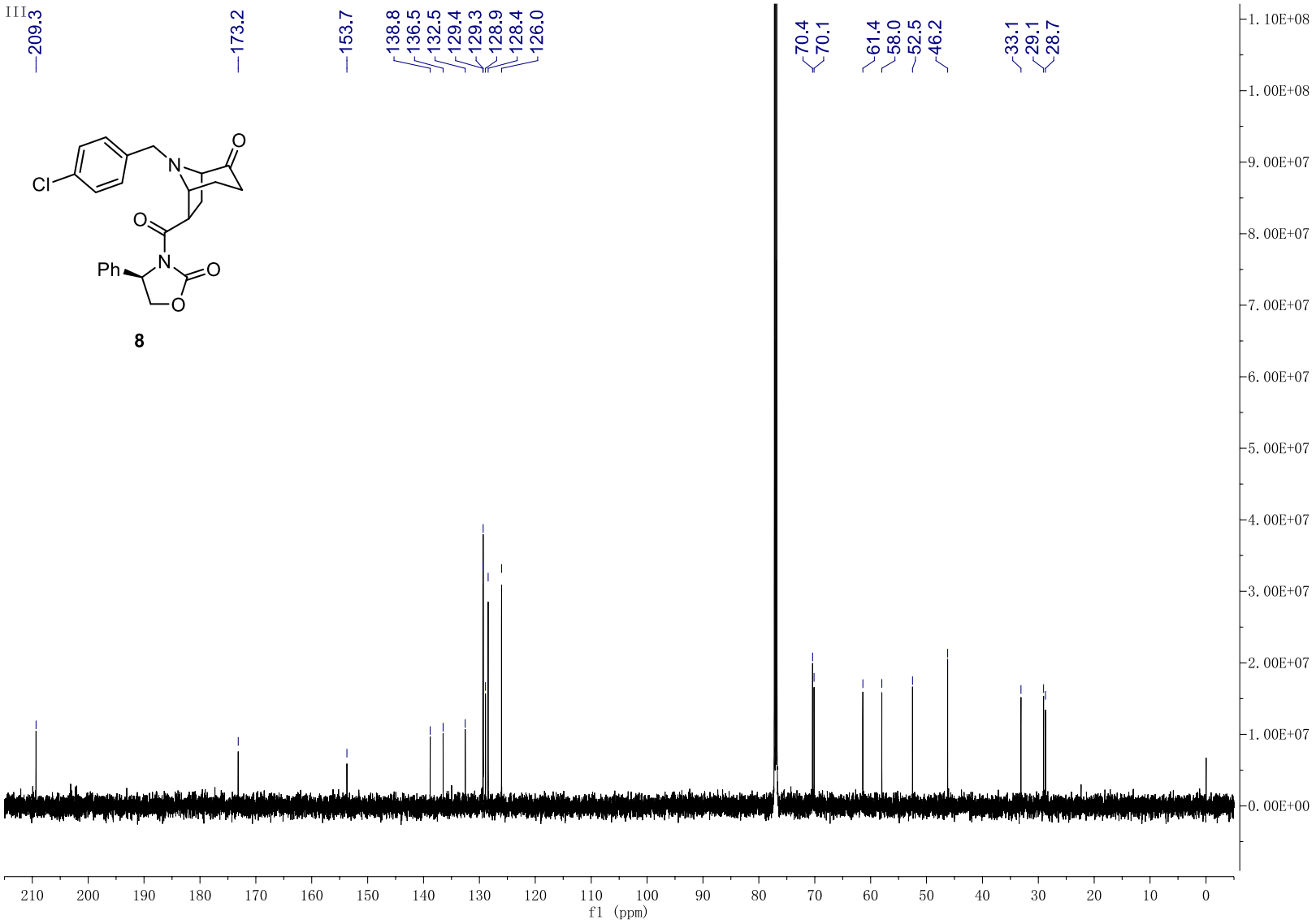
^{13}C NMR of **7cA** (100 MHz, acetone-*d6*)



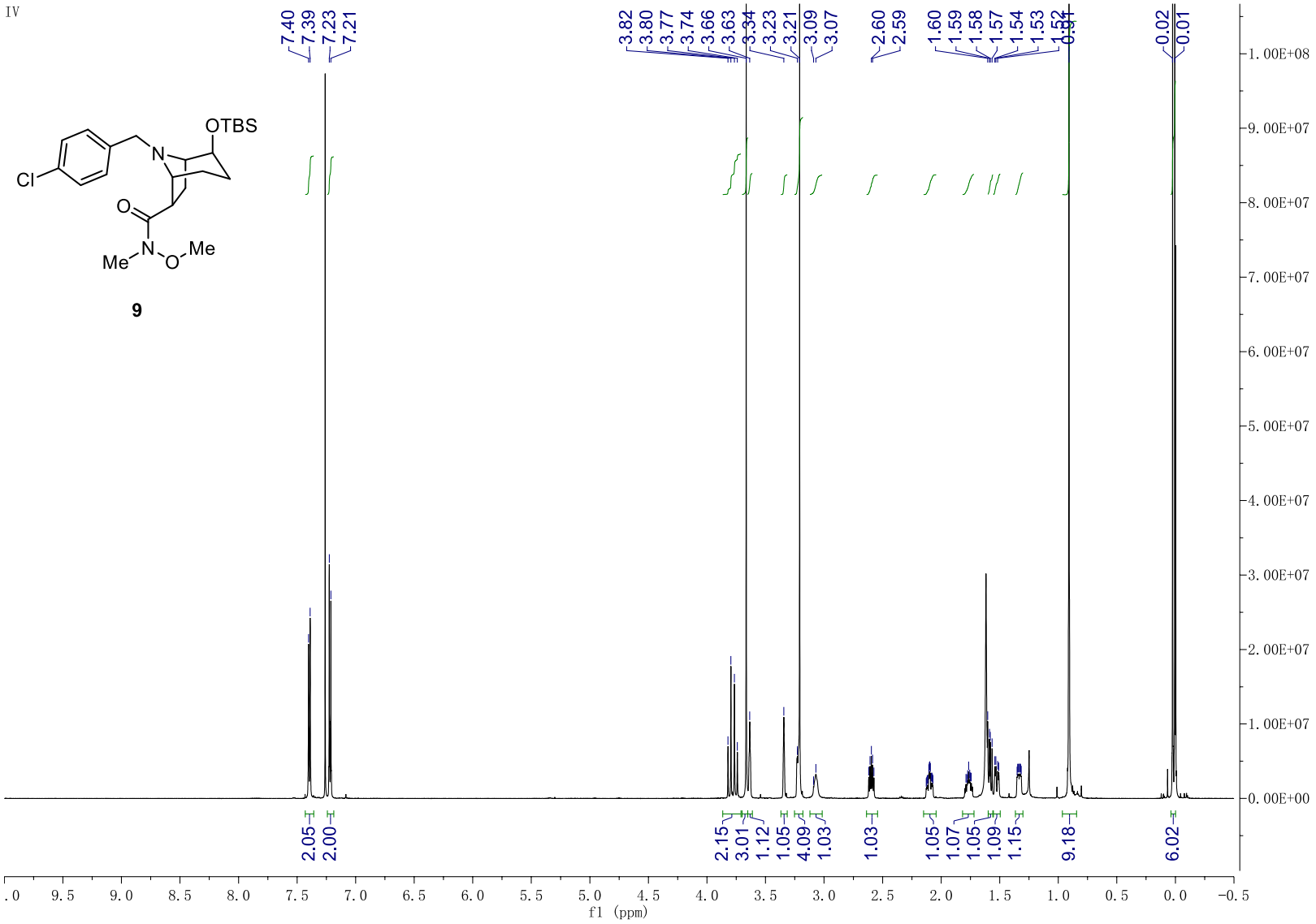
^{1}H NMR of **8** (600 MHz, $CDCl_3$)



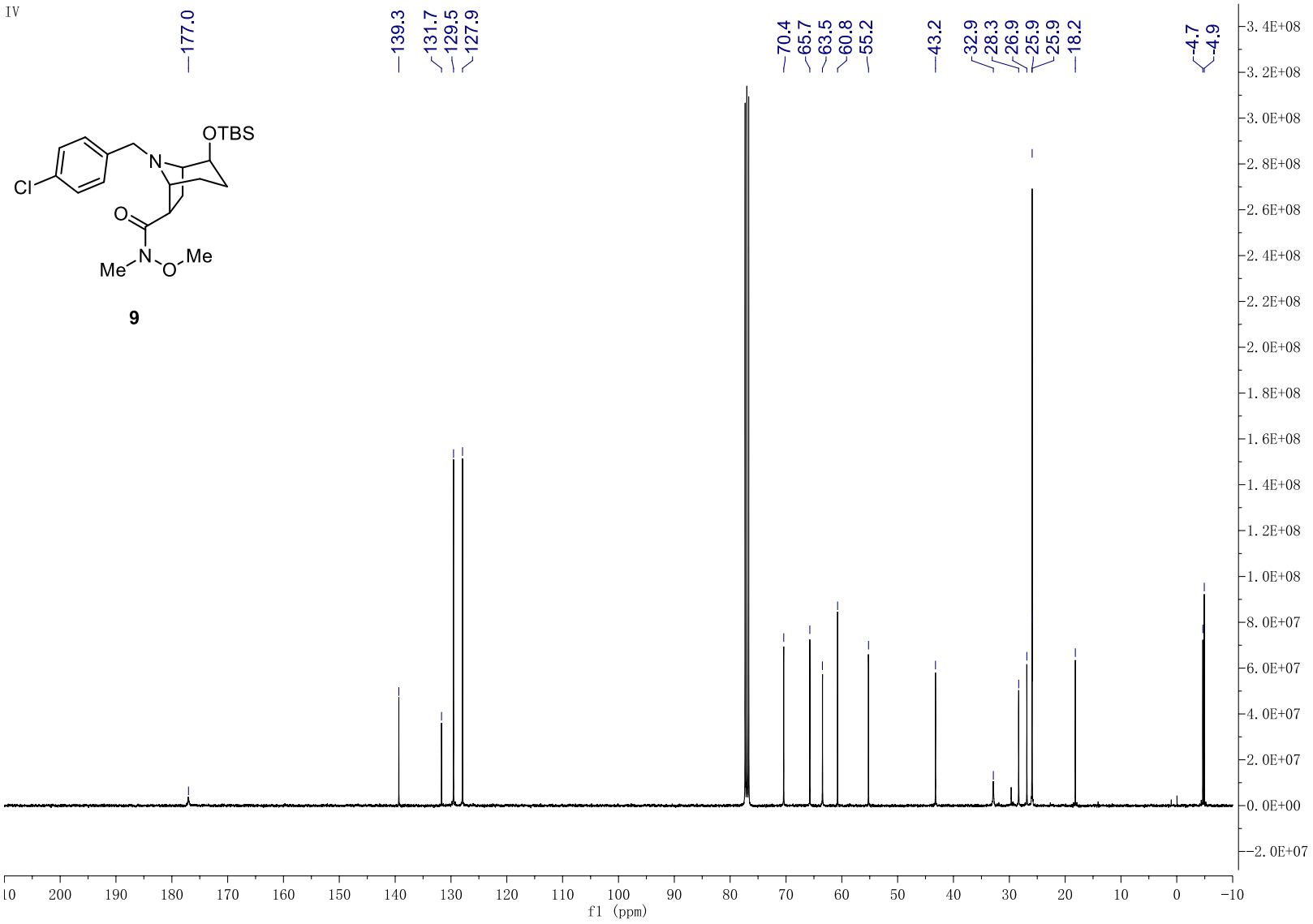
^{13}C NMR of **8** (150 MHz, $CDCl_3$)



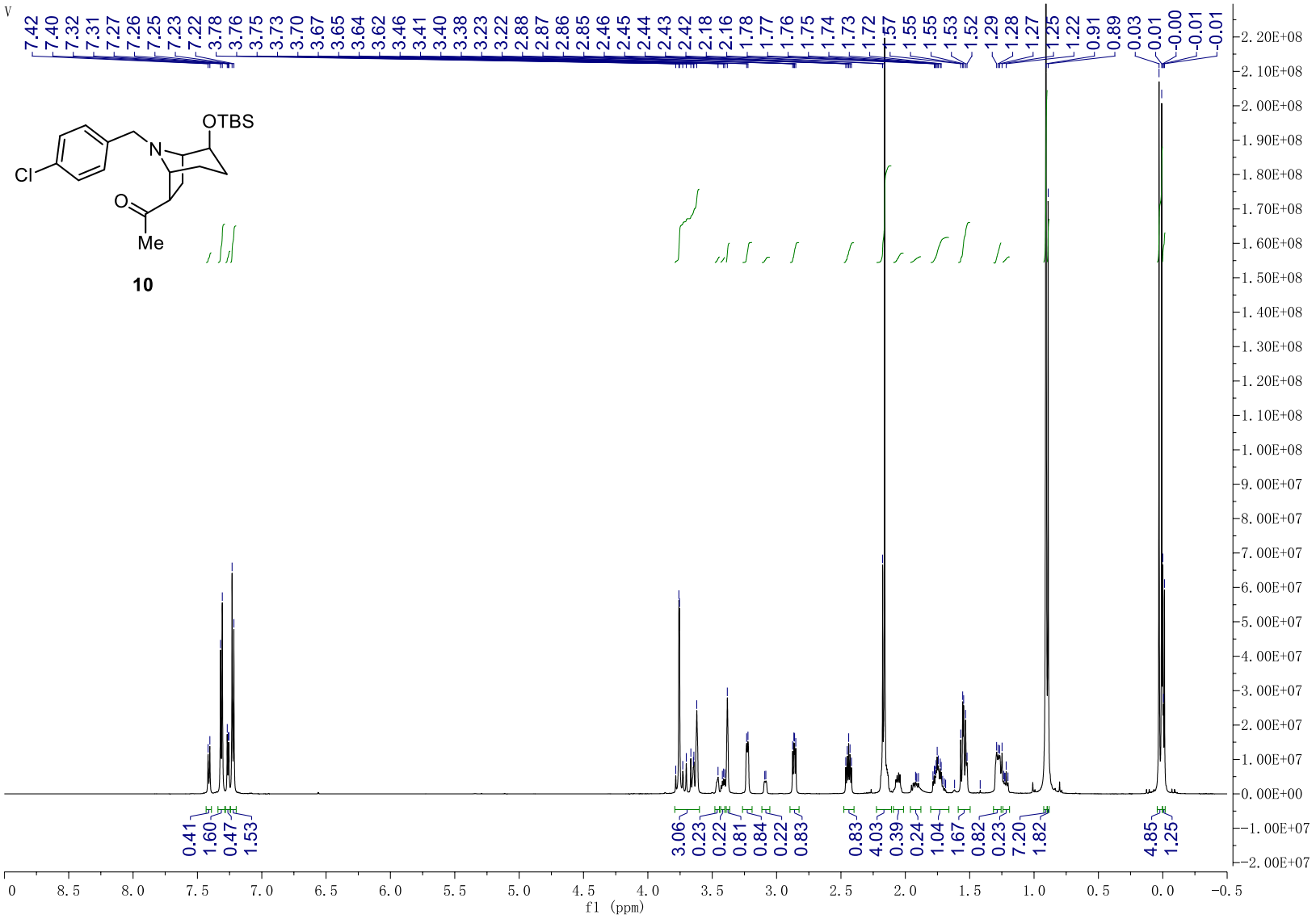
^{1}H NMR of **9** (600 MHz, $CDCl_3$)



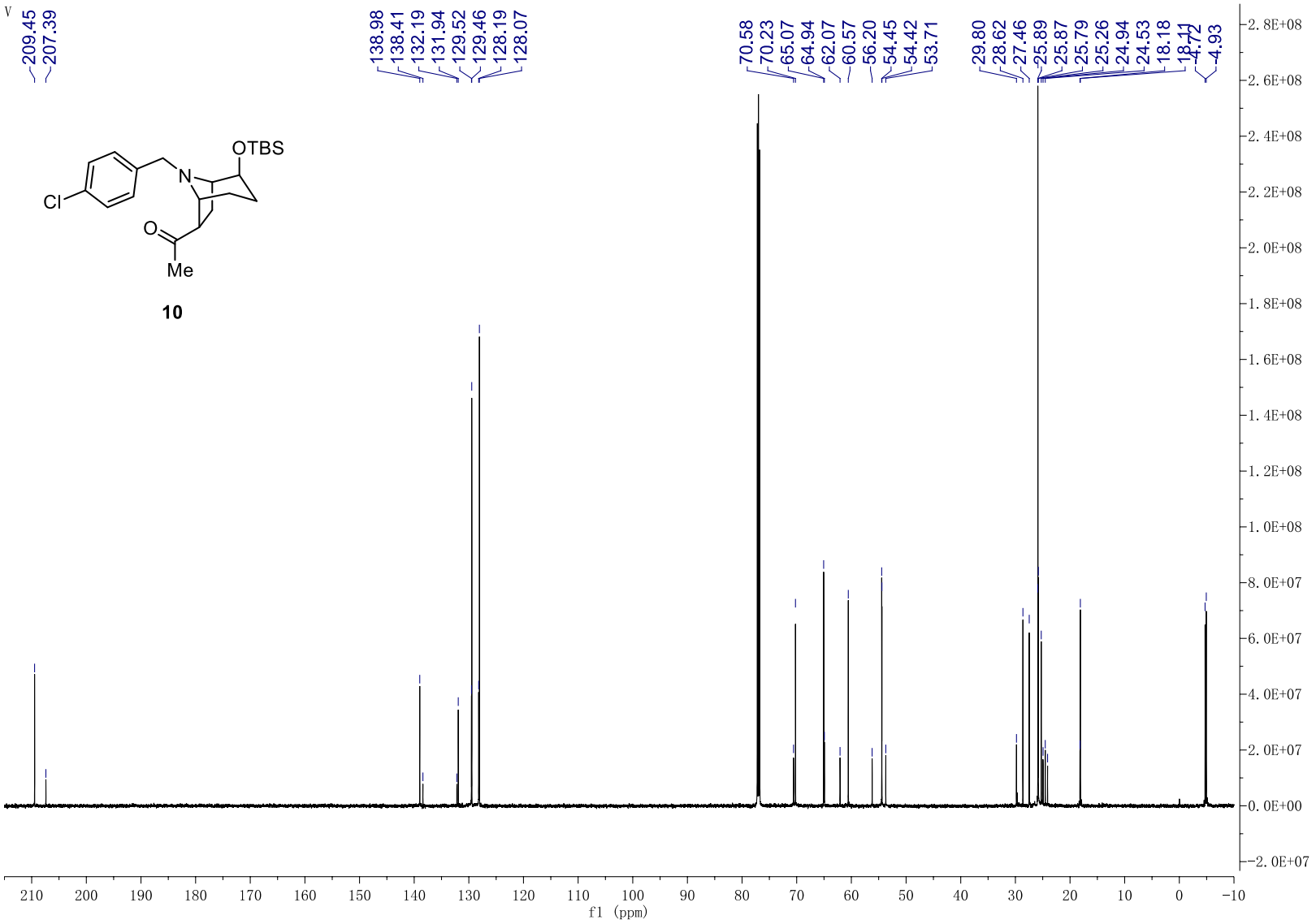
^{13}C NMR of **9** (100 MHz, $CDCl_3$)



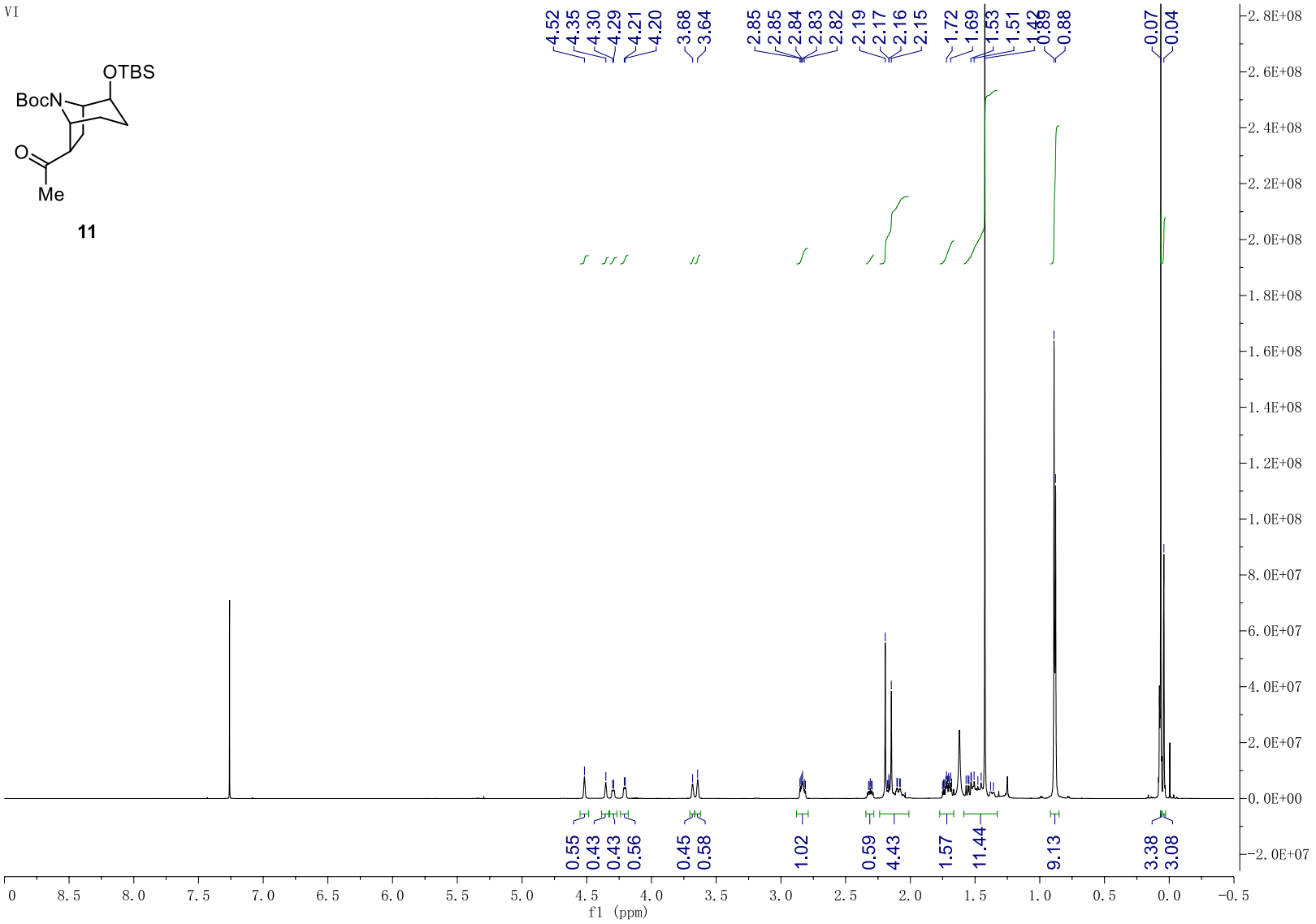
^{1}H NMR of **10** (600 MHz, $CDCl_3$)



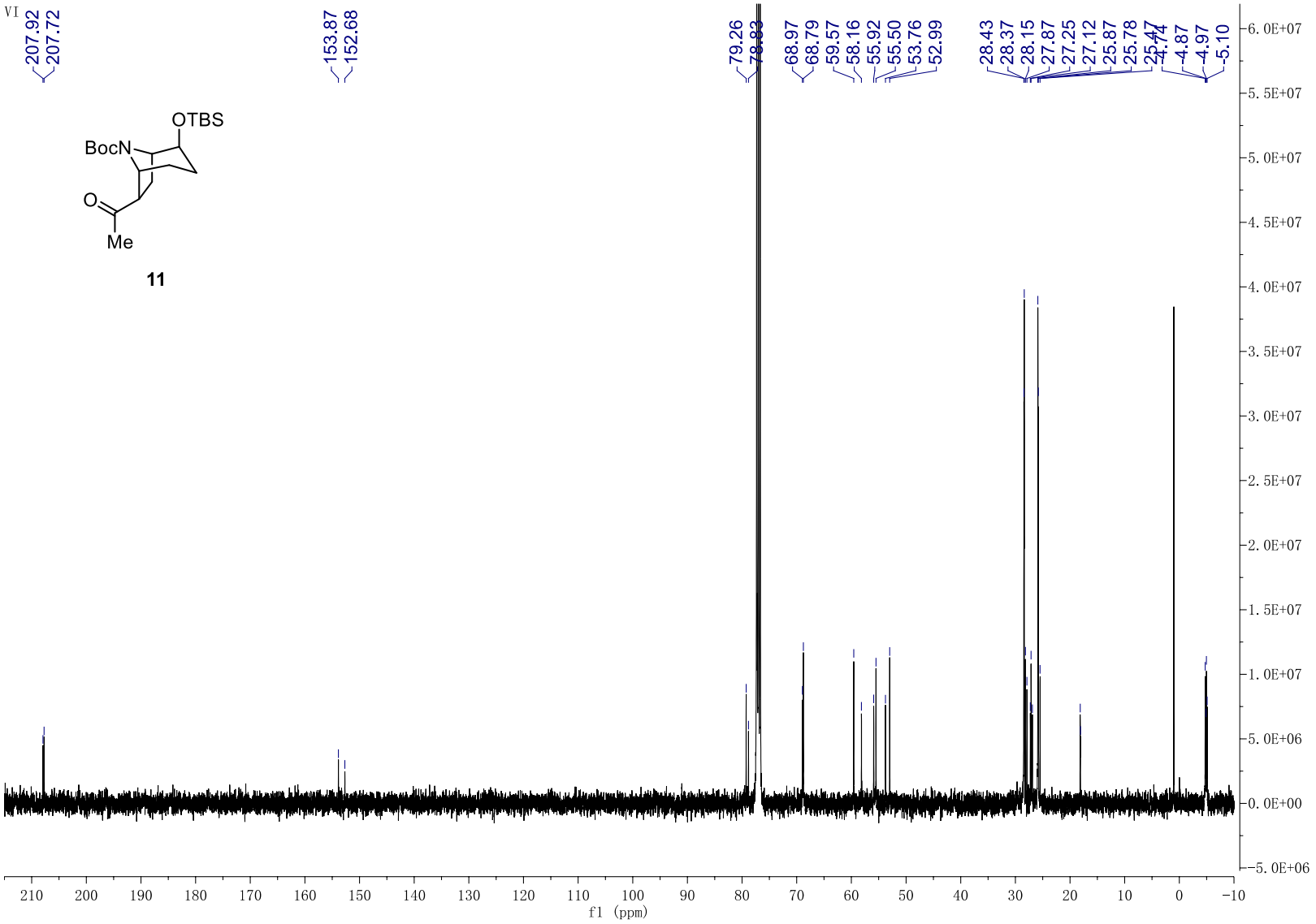
^{13}C NMR of **10** (150 MHz, $CDCl_3$)



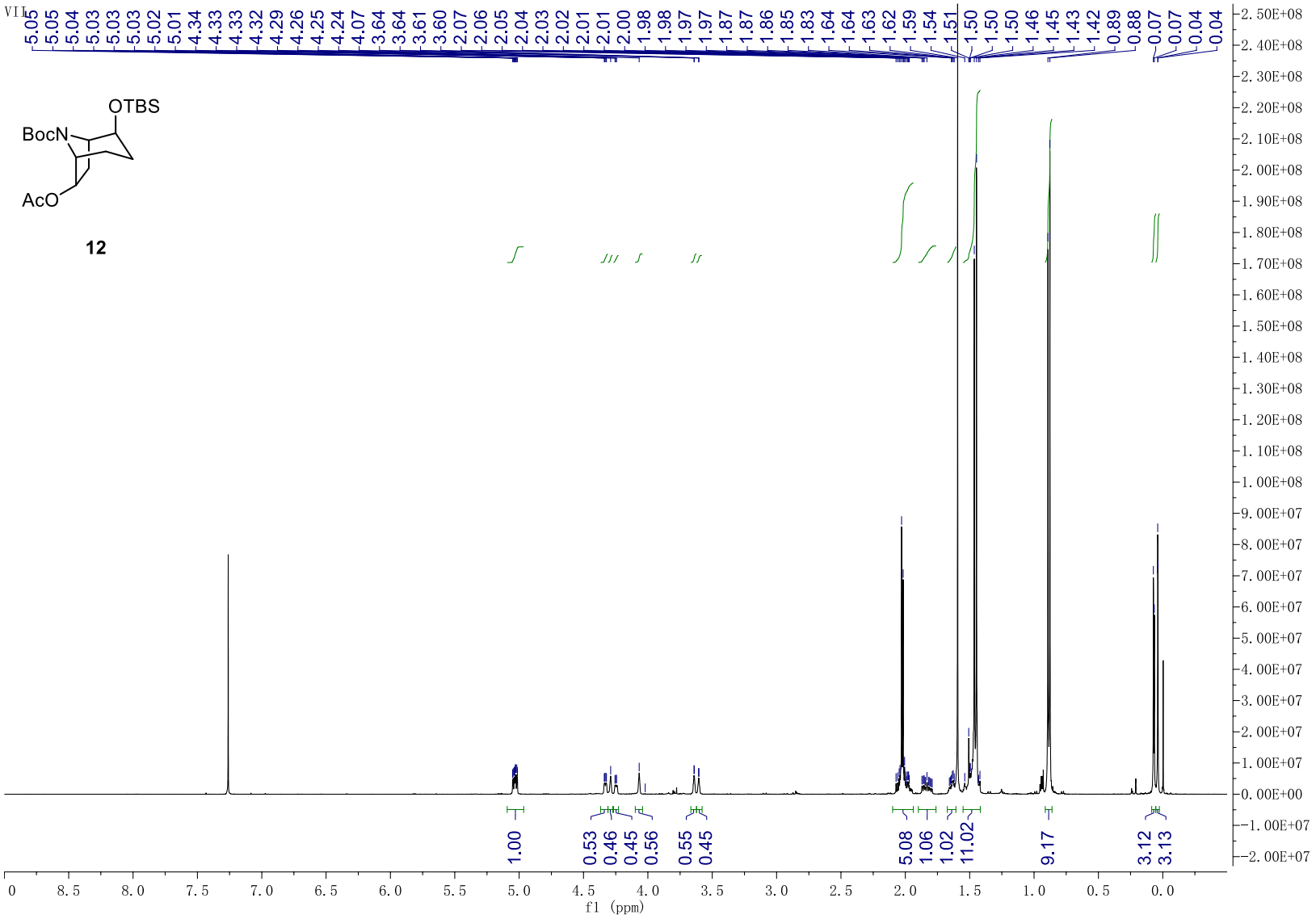
^{1}H NMR of **11** (600 MHz, $CDCl_3$)



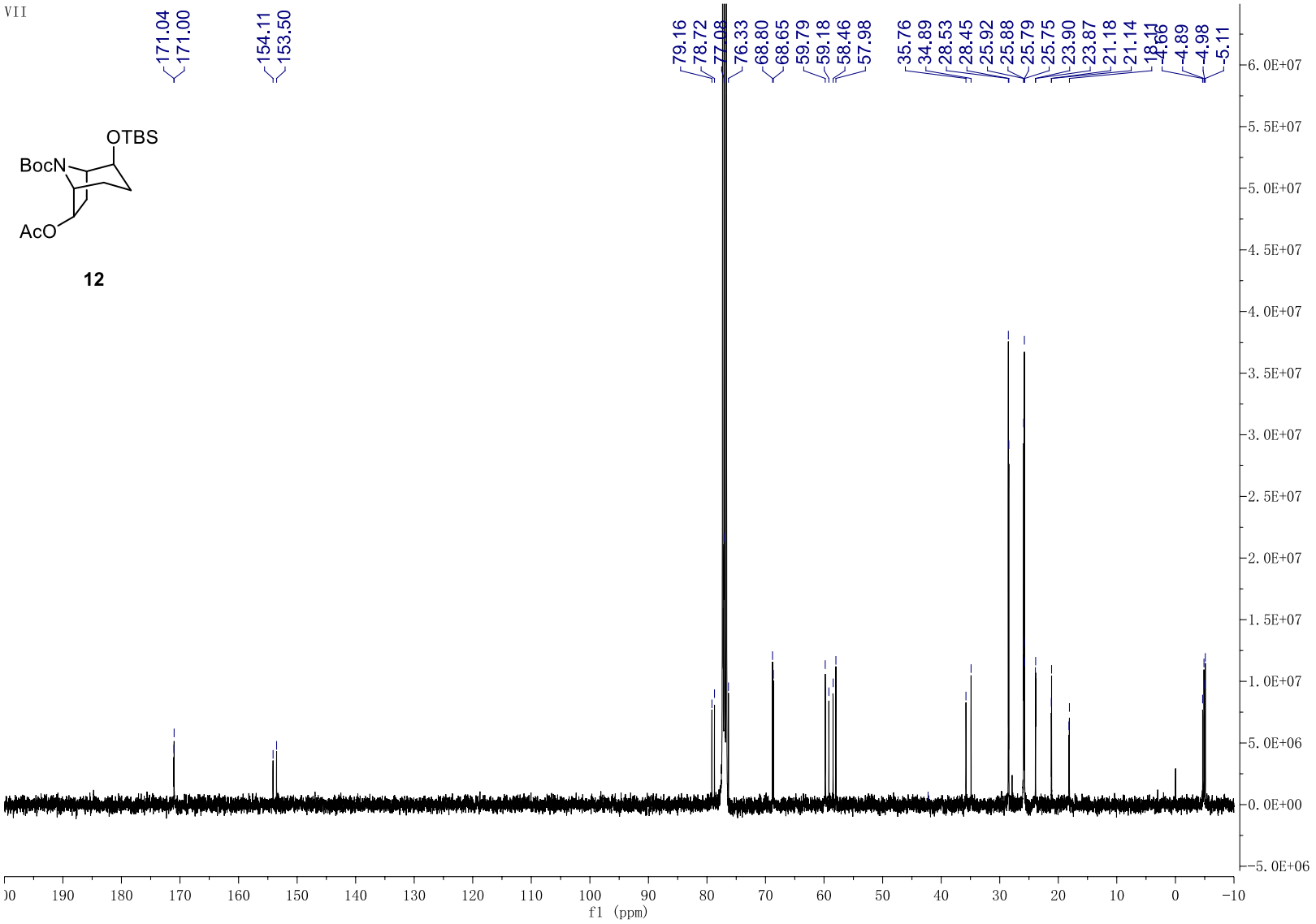
^{13}C NMR of **11** (100 MHz, $CDCl_3$)



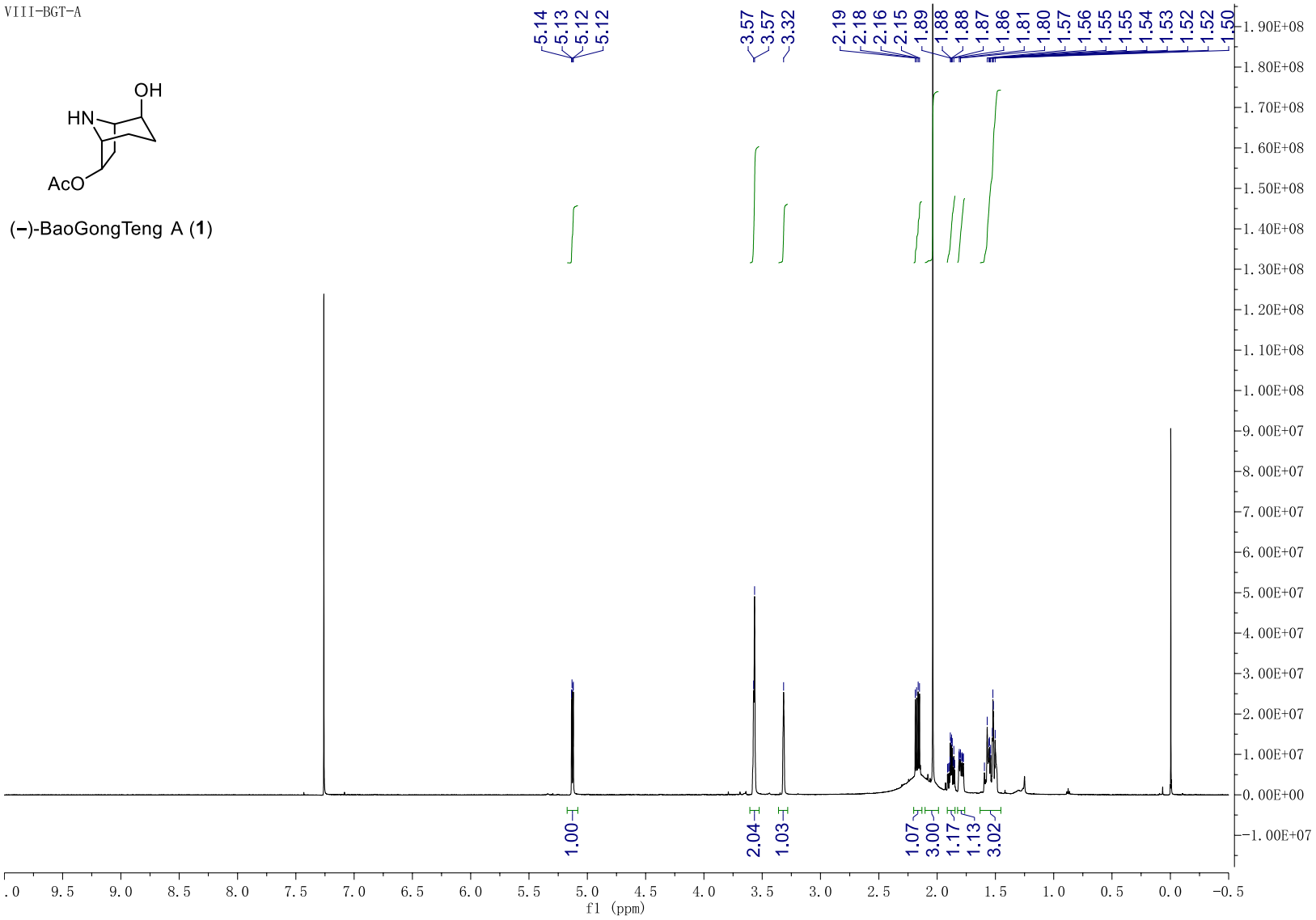
^{1}H NMR of **12** (600 MHz, $CDCl_3$)



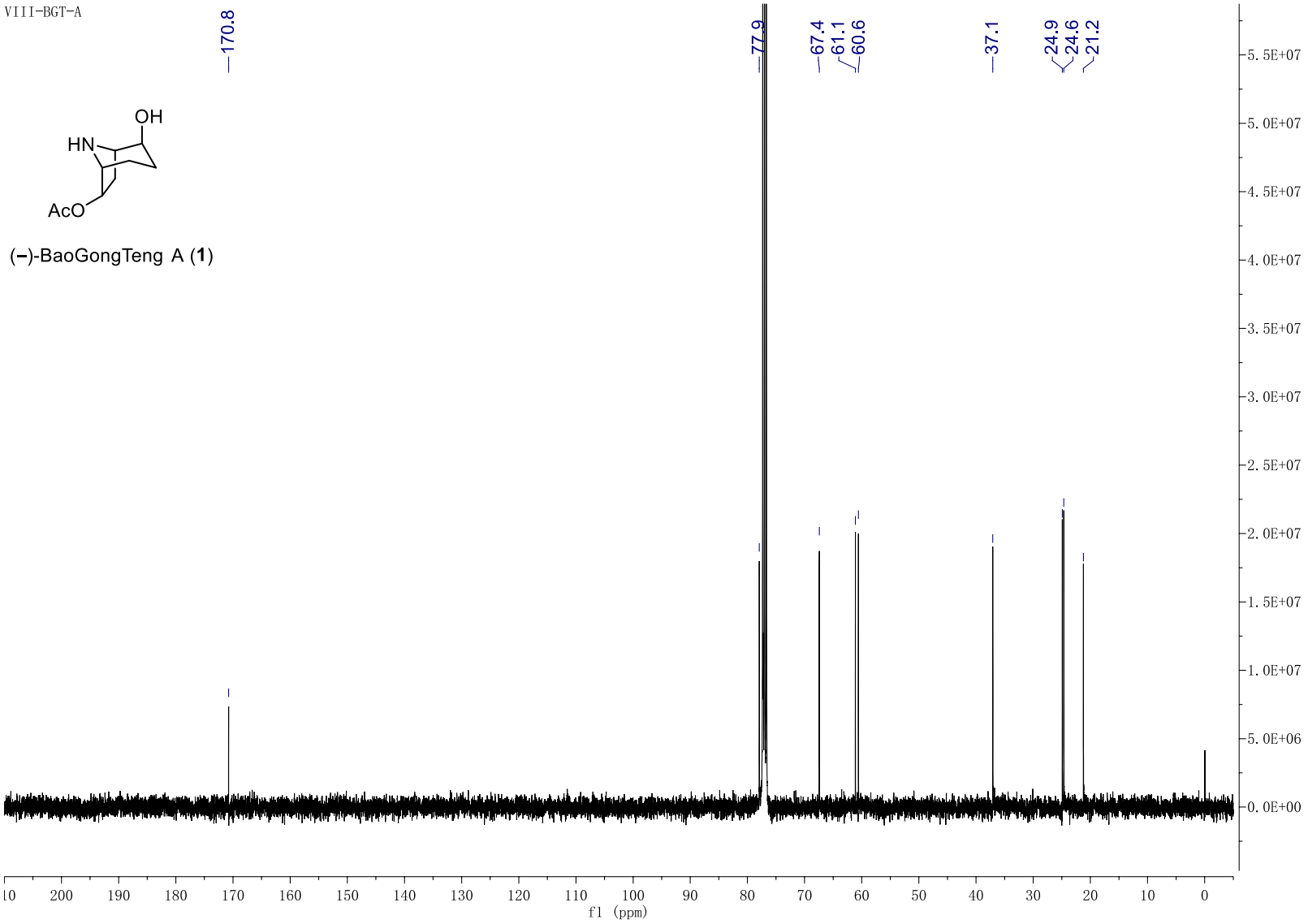
^{13}C NMR of **12** (100 MHz, $CDCl_3$)



^{1}H NMR of (–)-Bao Gong Teng A (**1**) (600 MHz, $CDCl_3$)



^{13}C NMR of (–)-Bao Gong Teng A (**1**) (100 MHz, $CDCl_3$)



6. X-ray Crystal Data of Cycloadduct 7aA, 7bB and 7cA

The absolute configuration of cycloadduct **7aA**, **7bB** and **7cA** were determined by X-ray diffraction. The X-ray crystallography data have been deposited in Cambridge Crystallography Data Center (CCDC 2395526 (**7aA**), CCDC 2395527 (**7bB**) and CCDC 2402960 (**7cA**)). The absolute configuration of other cycloadducts was assumed by analogy.

The single crystal sample for X-ray analysis was obtained by recrystallization from a mixed solvent of ethyl ether and petroleum ether by slow evaporation. A suitable crystal was selected and the data were collected on a d8 venture system (Cu kα, λ = 1.54178 Å). The crystal was kept at 300(2) K during data collection.

X-ray Crystal Structure of Cycloadduct 7aA.

Experimental parameters pertaining to single crystal X-ray analysis of cycloadduct **7aA** are given in Table S5. The ORTEP diagram of cycloadduct **7aA** is shown as follows.

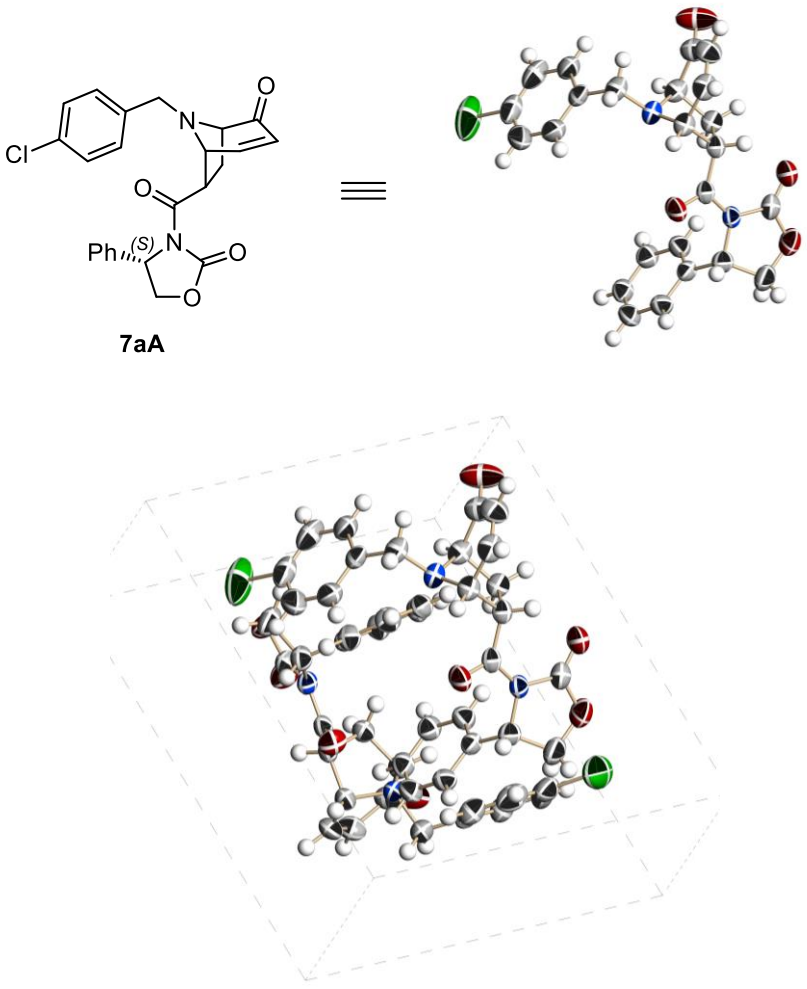


Figure S1. Thermal ellipsoids are shown at 50% probability for cycloadduct **7aA**

Table S4. Crystal data and structure refinement for cycloadduct **7aA**

Identification code	**7aA**	
Chemical formula	$C_{24}H_{21}ClN_2O_4$	
Formula weight	436.88 g/mol	
Temperature	306(2) K	
Wavelength	1.54178 Å	
Crystal size	0.100 x 0.100 x 0.150 mm	
Crystal habit	clear light colourless block	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 12.5837(3) Å	α = 90°
	b = 6.1999(2) Å	β = 96.4440(10)°
	c = 13.8988(3) Å	γ = 90°
Volume	1077.50(5) $Å^3$	
Z	2	
Density (calculated)	1.347 g/cm^3	
Absorption coefficient	1.851 mm^{-1}	
F(000)	456	
Diffractometer	d8 venture	
Theta range for data collection	3.20 to 65.13 °	
Index ranges	-14<=h<=14, -7<=k<=7, -16<=l<=16	
Reflections collected	16093	
Independent reflections	3666 [R(int) = 0.0535]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	

Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	3666 / 1 / 280	
Goodness-of-fit on F2	1.055	
Final R indices	3186 data; I>2σ(I)	R1 = 0.0372, wR2 = 0.0846
	all data	R1 = 0.0458, wR2 = 0.0903
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0325P)^2+0.1682P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.080(15)	
Largest diff. peak and hole	0.109 and -0.193 eÅ^{-3}	
R.M.S. deviation from mean	0.031 eÅ^{-3}	

X-ray Crystal Structure of Cycloadduct 7bB.

Experimental parameters pertaining to single crystal X-ray analysis of cycloadduct **7bB** are given in Table S4. The ORTEP diagram of cycloadduct **7bB** is shown as follows.

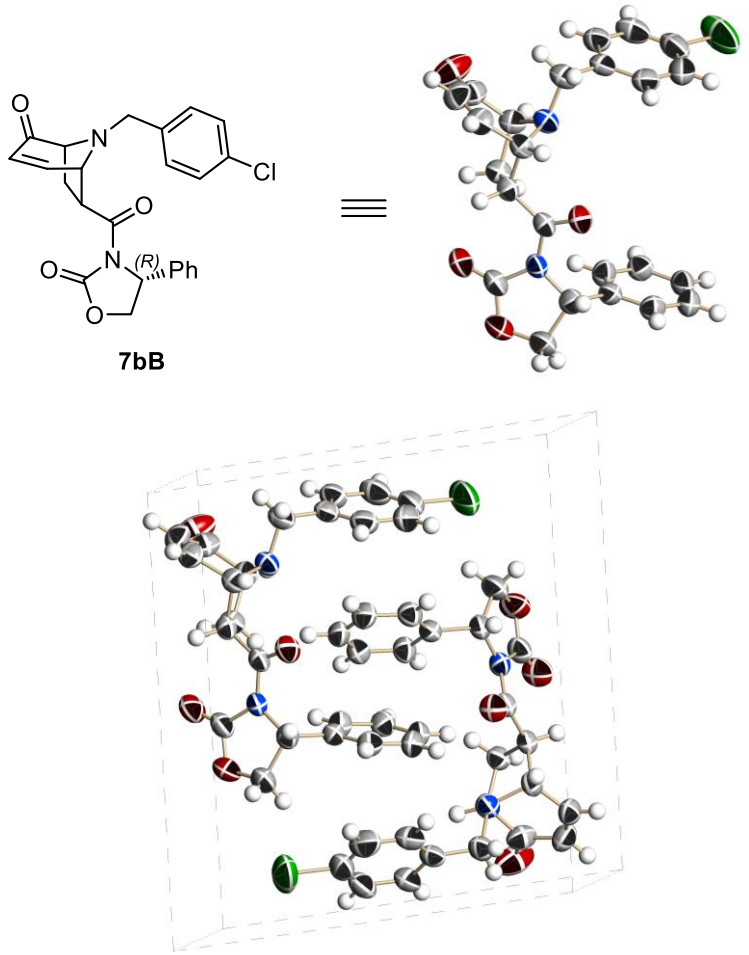


Figure S2. Thermal ellipsoids are shown at 50% probability for cycloadduct **7bB**

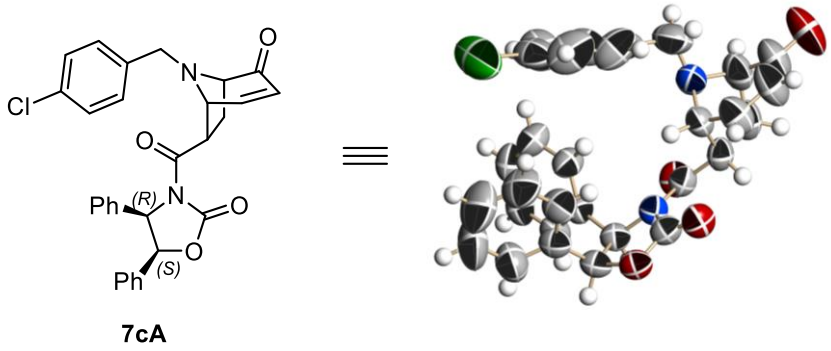
Table S5. Crystal data and structure refinement for cycloadduct **7bB**

Identification code	**7bB**	
Chemical formula	$C_{24}H_{21}ClN_2O_4$	
Formula weight	436.88 g/mol	
Temperature	303(2) K	
Wavelength	1.54178 Å	
Crystal size	0.100 x 0.100 x 0.150 mm	
Crystal habit	clear light colourless plate	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 12.5846(3) Å	α = 90°
	b = 6.2016(2) Å	β = 96.423(2)°
	c = 13.8899(4) Å	γ = 90°
Volume	1077.23(5) $Å^3$	
Z	2	
Density (calculated)	1.347 g/cm^3	
Absorption coefficient	1.852 mm^{-1}	
F(000)	456	
Diffractometer	d8 venture	
Theta range for data collection	3.20 to 65.39 °	
Index ranges	-14<=h<=14, -7<=k<=7, -16<=l<=16	
Reflections collected	16849	
Independent reflections	3692 [R(int) = 0.0705]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	

Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	3692 / 1 / 280	
Goodness-of-fit on F2	1.040	
Final R indices	2953 data; I>2σ(I)	R1 = 0.0474, wR2 = 0.1101
	all data	R1 = 0.0624, wR2 = 0.1211
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0511P)^2+0.2180P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.08(2)	
Largest diff. peak and hole	0.141 and -0.208 eÅ^{-3}	
R.M.S. deviation from mean	0.043 eÅ^{-3}	

X-ray Crystal Structure of Cycloadduct 7cA.

Experimental parameters pertaining to single crystal X-ray analysis of cycloadduct **7cA** are given in Table S6. The ORTEP diagram of cycloadduct **7cA** is shown as follows.



7cA

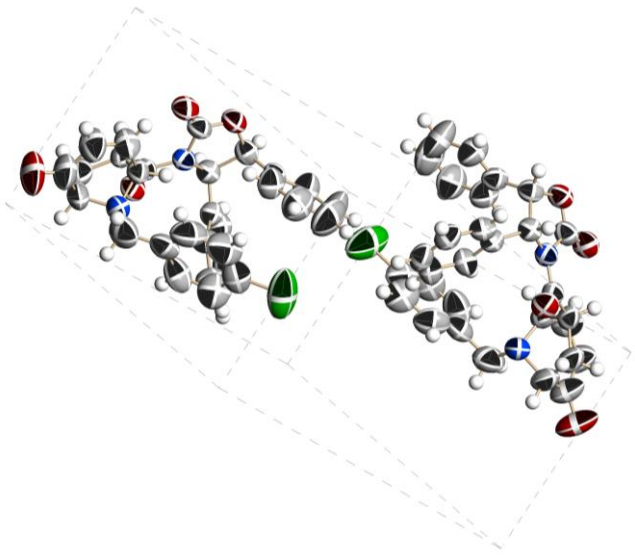


Figure S3. Thermal ellipsoids are shown at 50% probability for cycloadduct **7cA**

Table S6. Crystal data and structure refinement for cycloadduct **7cA**

Identification code	**7cA**
Chemical formula	$C_{30}H_{25}ClN_2O_4$
Formula weight	512.97 g/mol
Temperature	301(2) K
Wavelength	1.54184 Å
Crystal size	0.170 x 0.170 x 0.380 mm
Crystal habit	clear light colourless block
Crystal system	monoclinic
Unit cell dimensions	a = 12.6891(4) Å α = 90°
	b = 8.3323(3) Å β = 111.1558(18)°
	c = 13.3055(5) Å γ = 90°
Volume	1311.97(9) $Å^3$
Z	2
Density (calculated)	1.299 g/cm^3
Absorption coefficient	1.603 mm^{-1}
F(000)	536
Diffractometer	d8 venture
Theta range for data collection	3.56 to 65.14 °
Index ranges	-14<=h<=14, -9<=k<=9, -15<=l<=15
Reflections collected	26516
Independent reflections	4439 [R(int) = 0.1043]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7720 and 0.5810
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)

Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	4439 / 1 / 334	
Goodness-of-fit on F2	1.024	
Δ/σmax	0.001	
Final R indices	3226 data; I>2σ(I)	R1 = 0.0524, wR2 = 0.1385
	all data	R1 = 0.0818, wR2 = 0.1548
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0761P)^2+0.1619P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.106(17)	
Largest diff. peak and hole	0.220 and -0.272 eÅ^{-3}	
R.M.S. deviation from mean	0.036 eÅ^{-3}	

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