Supporting Information

Functionalized Imidazoliniums from Three-Component Domino Reaction of *N*-Formylmethylcarboxamides with Amines and Isocyanides

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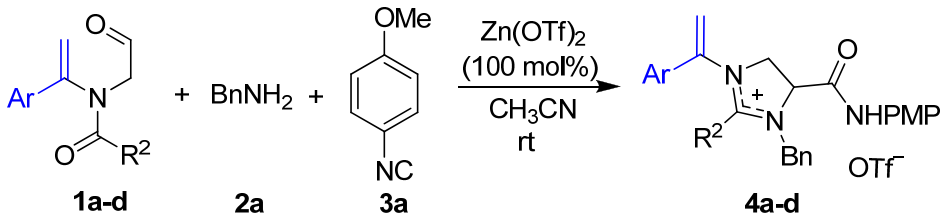
1. General Information

Unless otherwise noted, all reactions were carried out in oven dried glasswares. Anhydrous solvents were purified and dried following standard procedures. All commercially available reagents were used as received. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Flash column chromatography was performed on silica gel (200-300 mesh).

Melting points were uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECX-400 400 MHz spectrometers. ^{1}H NMR chemical shifts were reported relative to residual DMSO-d_6 (2.50 ppm), $CDCl_3$ (7.26 ppm) or acetone-d_6 (2.05 ppm). ^{13}C NMR chemical shifts were reported relative to the central line of DMSO-d_6 (39.52 ppm), $CDCl_3$ (77.16 ppm) or acetone-d_6 (29.84 ppm, 206.26 ppm). Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constant (*J*, Hz). Low-resolution mass spectra (MS) were recorded on a Shimadzu GC-MS QP 2010 Plus spectrometer. The high resolution mass spectra (HRMS) were recorded on a Shimadzu LCMS-IT-TOF spectrometer or a Thermo Exactive spectrometer. Infrared spectra were recorded using a PerkinElmer Spectrum 100 FT-IR spectrometer with KBr pellets in the 4000-400 cm^{-1} region.

2. Scope of Substrates

2.1. General Procedure for the Synthesis of 2-Imidazolinium Salts 4a-d

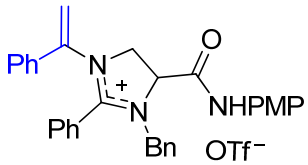


Scheme S1. Synthesis of 2-imidazolinium salts **4a-d**

To a solution of **1** (0.3 mmol), **2a** (36 μL, 0.33 mmol) and 4-methoxyphenyl isocyanide **3** (79.6 mg, 0.36 mmol) in CH_3CN (15 mL) was added $Zn(OTf)_2$ (109.1 mg，0.3 mmol), the resulting mixture was stirred at room temperature for 1 h to 2 h, After completion of the reaction (monitored by TLC), the reaction was quenched by saturated $NaHCO_3$ solution (5 mL) and extracted with dichloromethane (4×15 mL). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (acetone/petroleum ether) to afford product **4a-d**.

2.2. Characterization Data for 2-Imidazolinium Salts 4a-d

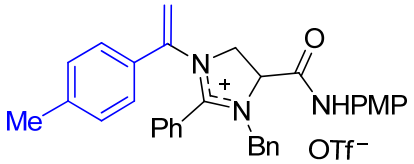
1-benzyl-5-(4-methoxyphenylcarbamoyl)-2-methyl-3-(1-phenylvinyl)-4,5-dihydro-1*H*-imidazol-3-ium triflate (4a)



Colorless solid (162 mg, yield: 85%). **m.p.** 181 – 182 °C; **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.75 (s, 1H), 7.75 (d, J = 7.1 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.60 – 7.54 (m, 6H), 7.40 – 7.30 (m, 8H), 6.92 (d, J = 9.1 Hz, 2H), 5.80 (d, J = 1.5 Hz, 1H), 5.66

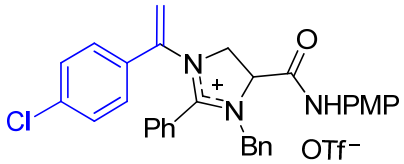
(d, *J* = 1.5 Hz, 1H), 5.24 (dd, *J* = 11.7, 4.8 Hz, 1H), 4.99 (t, *J* = 11.7 Hz, 1H), 4.90 (d, *J* = 15.5 Hz, 1H), 4.72 (d, *J* = 15.5 Hz, 1H), 4.57 (dd, *J* = 11.7, 4.7 Hz, 1H), 3.80 (s, 3H); **^{19}F NMR** (376 MHz, Acetone-d_6) δ -78.77; **^{13}C NMR** (100 MHz, Acetone-d_6) δ 168.3, 165.9, 157.7, 143.1, 134.9, 134.0, 133.6, 131.9, 130.5, 130.3, 129.8, 129.7, 129.6, 129.5, 127.0, 123.3, 122.45, 122.36, 115.8, 114.7, 63.4, 57.2, 55.7, 52.2; **IR** (KBr, cm^{-1}) ν 1692, 1573, 1551, 1513, 1283, 1257, 1241, 1170, 1155, 1030; **MS** (ESI) 488 [M-OTf]$^+$; **Anal.** Calcd. for: C: 62.16, H: 4.74, N: 6.59. found: C: 62.30, H: 4.79, N: 6.52.

1-benzyl-5-(4-methoxyphenylcarbamoyl)-2-methyl-3-(1-p-tolylvinyl)-4,5-dihydro-1*H*-imidazol-3-ium triflate (4b)



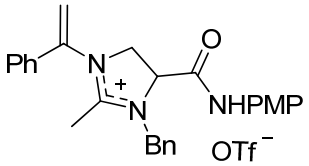
Yellow oil (158 mg, yield: 81%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.76 (s, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.68 – 7.63 (m, 1H), 7.60 – 7.55 (m, 4H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.30 (m, 5H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.76 (d, *J* = 1.4 Hz, 1H), 5.58 (d, *J* = 1.3 Hz, 1H), 5.24 (dd, *J* = 11.6, 4.8 Hz, 1H), 4.95 (d, *J* = 11.7 Hz, 1H), 4.89 (d, *J* = 15.3 Hz, 1H), 4.72 (d, *J* = 15.5 Hz, 1H), 4.53 (dd, *J* = 11.7, 4.8 Hz, 1H), 3.79 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 168.4, 165.9, 157.7, 143.0, 140.7, 134.0 133.6, 131.93, 131.86 130.4, 130.3, 129.8, 129.65, 129.60, 129.5, 126.9, 123.3, 122.5, 115.0, 114.7, 63.4, 57.1, 55.7, 52.1; **IR** (KBr, cm^{-1}) ν 1689, 1555, 1513, 1248, 1162, 1031; **HRMS** (ESI) calcd. for $C_{33}H_{32}N_3O_2$ [M-OTf]$^+$ 502.2489, found 502.2484.

1-benzyl-3-(1-(4-chlorophenyl)vinyl)-5-(4-methoxyphenylcarbamoyl)-2-methyl-4,5-dihydro-1*H*-imidazol-3-ium triflate (4c)



Yellow oil (165 mg, yield: 82%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.76 (s, 1H), 7.77 – 7.74 (m, 2H), 7.67 – 7.63 (m, 1H), 7.61 – 7.55 (m, 6H), 7.39 – 7.30 (m, 7H), 6.92 (d, J = 9.0 Hz, 2H), 5.84 (d, J = 1.7 Hz, 1H), 5.72 (d, J = 1.7 Hz, 1H), 5.24 (dd, J = 11.6, 4.6 Hz, 1H), 5.01 (t, J = 11.6 Hz, 1H), 4.90 (d, J = 15.4 Hz, 1H), 4.72 (d, J = 15.4 Hz, 1H), 4.59 (dd, J = 11.6, 4.6 Hz, 1H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 168.3, 165.9, 157.7, 142.2, 135.8, 134.1, 133.9, 133.5, 131.9, 130.4, 129.80, 129.77, 129.7, 129.6, 128.8, 123.2, 122.5, 122.4, 116.4, 114.7, 63.4, 57.2, 55.7, 52.2; **IR** (KBr, cm^{-1}) ν 1687, 1560, 1513, 1249, 1165, 1031; **HRMS** (ESI) calcd. for $C_{32}H_{29}ClN_2O_3$ [M-OTf]$^+$ 522.1943, found 522.1936.

1-benzyl-5-(4-methoxyphenylcarbamoyl)-2-methyl-3-(1-phenylvinyl)-4,5-dihydro-1*H*-imidazol-3-ium triflate (4d)

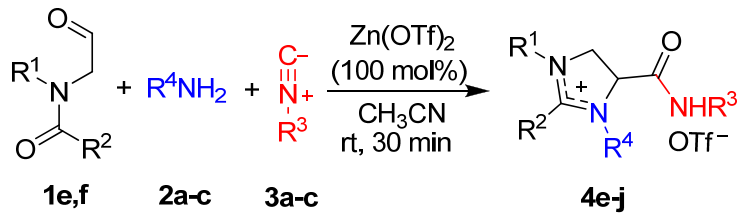


Yellow oil (152 mg, yield: 88%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.72 (s, 1H), 7.68 – 7.66 (m, 2H), 7.52 – 7.46 (m, 7H), 7.37 – 7.30 (m, 4H), 6.86 (d, J = 9.0 Hz, 2H), 6.09 (d, J = 1.1 Hz, 1H), 5.79 (d, J = 1.1 Hz, 1H), 5.13 – 5.07 (m, 2H), 4.88 (d, J = 15.7 Hz, 1H), 4.58 (t, J = 11.6 Hz, 1H), 4.24 (dd, J = 11.4, 5.5 Hz, 1H), 3.75 (s, 3H), 2.53 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 169.1, 165.8, 157.4, 142.3, 134.0, 133.8, 131.8, 130.8, 130.0, 129.6, 129.4, 129.3, 126.7, 122.4, 116.3, 114.5, 63.4, 55.9, 55.6, 51.4, 12.9; **IR** (KBr, cm^{-1}) ν 1690, 1592, 1513, 1258, 1174, 1032; **HRMS** (ESI) calcd. for $C_{27}H_{28}N_3O_2$ [M-OTf]$^+$ 426.2176, found 426.2172.

2.3. General Procedure for the Synthesis of 2-Imidazolinium Salts 4e-j

Substrates **1e** and **1f** was synthesized according to literature procedure[2,3].

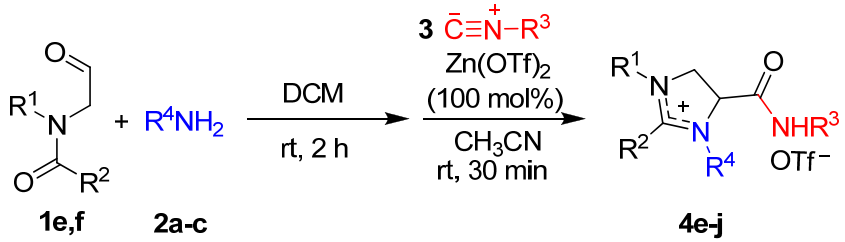
Method A: One-pot Manner



Scheme S2. Synthesis of 2-imidazolinium salts **4e-j**

To a solution of **1** (0.3 mmol), **2** (0.33 mmol) and isocyanide **3** (0.36 mmol) in CH_3CN (15 mL) was added $Zn(OTf)_2$ (109.1 mg，0.3 mmol), the resulting mixture was stirred at room temperature for 30 minutes, After completion of the reaction (monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ solution (5 mL) and extracted with dichloromethane (4×15 mL). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (acetone/petroleum ether) to afford product **4e-j**.

Method B: **Step-wise Manner**



Scheme S3. Synthesis of 2-imidazolinium salts **4e-j**

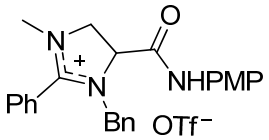
To a solution of **1** (0.3 mmol) in dichloromethane (5 mL) was added amine **2** (0.33 mmol). The reaction mixture was stirred at ambient temperature for 2 h, and then dichloromethane was removed under reduced pressure and dried *in vacuo* for another 10 min to give the corresponding imine.

The imine was dissolved in acetonitrile (15 mL) at ambient temperature, isocyanide **3** (0.36 mmol) and $Zn(OTf)_2$ (109.1 mg，0.3 mmol) was added subsequently. After completion of the reaction (monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ solution (5 mL). The resulting mixture was then extracted with dichloromethane (4×15 mL). The combined organic extracts were washed with brine,

dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (acetone/petroleum ether) to give product **4e-j**.

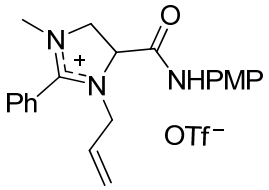
2.4. Characterization Data for 2-Imidazolinium Salts 4e-j

1-benzyl-5-(4-methoxyphenylcarbamoyl)-3-methyl-2-phenyl-4,5-dihydro-1*H*-imidazol-3-ium triflate (4e)



Yellow oil (155 mg, yield: 94%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.76 (s, 1H), 7.79 – 7.72 (m, 5H), 7.55 (d, J = 9.0 Hz, 2H), 7.29 – 7.28 (m, 5H), 6.88 (d, J = 9.0 Hz, 2H), 5.04 (dd, J = 12.1, 6.5 Hz, 1H), 4.71 – 4.53 (m, 3H), 4.28 (dd, J = 12.0, 6.5 Hz, 1H), 3.76 (s, 3H), 3.14 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 167.4, 165.2, 156.7, 133.4, 133.2, 131.3, 130.0, 128.9, 128.7, 128.4, 128.2, 122.1, 121.6, 113.9, 62.0, 55.2, 54.9, 50.6; **IR** (KBr, cm^{-1}) ν 1694, 1602, 1552, 1513, 1251, 1168, 1031; **HRMS** (ESI) calcd. for $C_{25}H_{26}N_3O_2$ $[M\text{-}OTf]^+$ 400.2020, found 400.2014.

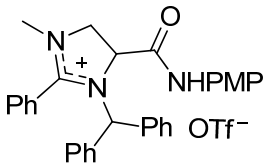
1-allyl-5-(4-methoxyphenylcarbamoyl)-3-methyl-2-phenyl-4,5-dihydro-1*H*-imidazol-3-ium triflate (4f)



Yellow oil (134 mg, yield: 89%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.87 (s, 1H), 7.81 – 7.76 (m, 5H), 7.66– 7.64 (m, 2H), 6.92 – 6.90 (m, 2H), 5.88 – 5.78 (m, 1H), 5.27 (dd, J = 17.1, 1.1 Hz, 1H), 5.20 – 5.16 (m, 2H), 4.59 (t, J = 12.1 Hz, 1H), 4.27 (dd, J = 11.9, 6.6 Hz, 1H), 4.07 (dd, J = 16.1, 5.5 Hz, 1H), 3.96 (dd, J = 16.1, 6.7 Hz, 1H), 3.78 (s, 3H), 3.13 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 167.9, 166.1, 157.4, 134.0, 132.2, 131.5, 130.6, 129.4, 123.4, 122.8, 122.2, 120.5, 120.3, 114.6,

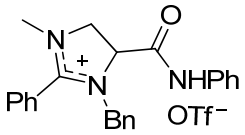
62.8, 55.9, 55.6, 50.3, 34.9; **IR** (KBr, cm^{-1}) ν 1695, 1603, 1514, 1253, 1174, 1035; **MS** (CI) 350 $[M\text{-}OTf]^+$ (100), 199 (97); **HRMS** (ESI) calcd. for $C_{21}H_{24}N_3O_2$ $[M\text{-}OTf]^+$ 350.1863, found 350.1859.

1-benzhydryl-5-(4-methoxyphenylcarbamoyl)-3-methyl-2-phenyl-4,5-dihydro-1*H*-imidazol-3-ium triflate (4g)



Yellow oil (80 mg, yield: 43%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.02 (s, 1H), 7.78 – 7.61 (m, 3H), 7.44 – 7.40 (m, 4H), 7.33 – 7.15 (m, 11H), 6.83 (d, J = 9.1 Hz, 2H), 6.21 (s, 1H), 5.26 (dd, J = 11.5, 4.6 Hz, 1H), 4.80 (t, J = 11.9 Hz, 1H), 4.18 (dd, J = 12.2, 4.5 Hz, 1H), 3.76 (s, 3H), 3.12 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 168.9, 166.5, 157.2, 136.6, 133.4, 131.9, 131.4, 130.5, 130.2, 129.6, 129.5, 129.3, 129.1, 128.8, 128.4, 123.4, 122.2, 66.4, 62.6, 56.4, 55.6, 35.0; **IR** (KBr, cm^{-1}) ν 1694, 1622, 1513, 1253, 1171, 1032; **HRMS** (ESI) calcd. for $C_{31}H_{30}N_3O_2$ $[M\text{-}OTf]^+$ 476.2333, found 476.2329.

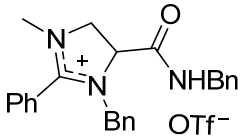
1-benzyl-3-methyl-2-phenyl-5-(phenylcarbamoyl)-4,5-dihydro-1*H*-imidazol-3-ium triflate (4h)



Yellow oil (149 mg, yield: 96%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.84 (s, 1H), 7.80 – 7.75 (m, 5H), 7.67 (d, J = 7.8 Hz, 2H), 7.35 – 7.25 (m, 7H), 7.13 (t, J = 7.4 Hz, 1H), 5.08 (dd, J = 12.2, 6.3 Hz, 1H), 4.71 – 4.55 (m, 3H), 4.30 (dd, J = 12.1, 6.2 Hz, 1H), 3.15 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 168.1, 166.3, 139.0, 134.1, 133.9, 130.7, 129.6, 129.5, 129.4, 129.1, 128.9, 125.2, 122.8, 120.6, 62.6, 56.0, 51.3, 35.0; **IR** (KBr, cm^{-1}) ν 1699, 1601, 1554, 1252, 1163, 1031; **MS** (CI) 370 $[M\text{-}OTf]^+$ (74), 249 (100), 159 (76), 91 (97); **HRMS** (ESI) calcd. for $C_{24}H_{24}N_3O$ $[M\text{-}OTf]^+$

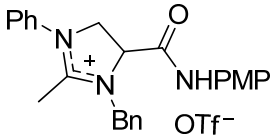
370.1914, found 370.1909.

1-benzyl-5-(benzylcarbamoyl)-3-methyl-2-phenyl-4,5-dihydro-1*H*-imidazol-3-ium triflate (4i)



Yellow oil (154 mg, yield: 96%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.40 (t, J = 5.7 Hz, 1H), 7.80 – 7.72 (m, 5H), 7.35 – 7.22 (m, 11H), 4.89 (dd, J = 12.3, 7.0 Hz, 1H), 4.61 (d, J = 15.7 Hz, 1H), 4.54 (t, J = 12.1 Hz, 1H), 4.46 – 4.34 (m, 3H), 4.18 (dd, J = 11.9, 7.0 Hz, 1H), 3.10 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 168.0, 167.9, 139.1, 133.85, 133.80, 130.6, 129.6, 129.4, 129.22, 129.17, 128.9, 128.5, 128.0, 123.4, 122.8, 120.2, 61.8, 55.7, 51.1, 43.9, 35.0; **IR** (KBr, cm^{-1}) ν 1692, 1602, 1259, 1171, 1034; **HRMS** (ESI) calcd. for $C_{25}H_{26}N_3O$ $[M\text{-}OTf]^+$ 384.2070, found 384.2064.

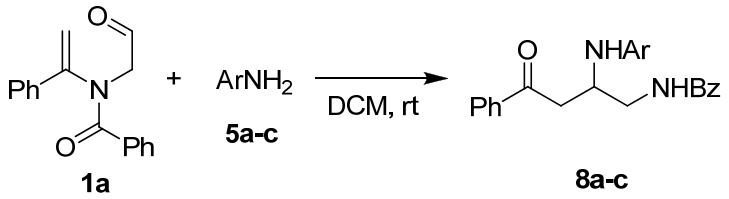
1-benzyl-5-(4-methoxyphenylcarbamoyl)-2-methyl-3-phenyl-4,5-dihydro-1*H*-imidazol-3-ium triflate (4j)



Yellow oil (128 mg, yield: 78%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.74 (s, 1H), 7.65 – 7.49 (m, 10H), 7.38 – 7.30 (m, 7H), 6.86 (d, J = 9.1 Hz, 2H), 5.16 – 5.07 (m, 2H), 4.91 – 4.72 (m, 3H), 4.52 (dd, J = 11.2, 6.8 Hz, 1H), 3.76 (s, 3H), 2.55 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 168.3, 165.7, 157.4, 136.7, 133.8, 131.8, 130.9, 130.5, 129.7, 129.4, 129.3, 126.9, 123.3, 122.4, 120.2, 114.5, 63.2, 56.8, 55.6, 51.3, 12.9; **IR** (KBr, cm^{-1}) ν 1513, 1252, 1173, 1035; **HRMS** (ESI) calcd. for $C_{25}H_{26}N_3O_2$ $[M\text{-}OTf]^+$ 400.2020, found 400.2016.

3. Synthesis and Characterization for β-Amino-γ-benzamido Ketones 8a-c

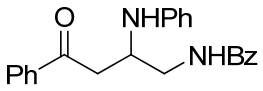
Compound **1a-d** was synthesized according to our previous reported procedure[1].



Scheme S4. Synthesis of β-amino-γ-benzamido ketone **8a-c**

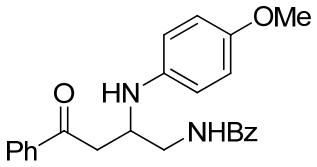
General procedure: To a solution of **1a** (79.6 mg, 0.3 mmol) in DCM (5 mL) was added aromatic amine **5** (0.33 mmol) and $Zn(OTf)_2$ (109.1 mg, 0.3 mmol). The reaction mixture was stirred at ambient temperature until the disappearance of **1a** (monitored by TLC), and then concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford product **8a-c**.

***N*-(4-oxo-4-phenyl-2-(phenylamino)butyl)benzamide (8a)**



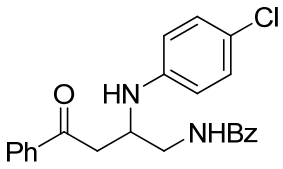
Colorless solid (59 mg, yield: 55%). **m.p.** 163 – 165 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.63 (t, J = 5.8 Hz, 1H), 7.93 – 7.91 (m, 2H), 7.81 – 7.79 (m, 2H), 7.64–7.60 (m, 1H), 7.53 – 7.42 (m, 5H), 7.06 (t, J = 7.9 Hz, 2H), 6.67 (d, J = 7.7 Hz, 2H), 6.51 (t, J = 7.2 Hz, 1H), 5.57 (d, J = 8.4 Hz, 1H), 4.25 – 4.16 (m, 1H), 3.63 – 3.57 (m, 1H), 3.30 – 3.23 (m, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 198.5, 166.8, 147.9, 136.9, 134.5, 133.2, 131.2, 129.0, 128.7, 128.3, 128.0, 127.2, 115.8, 112.4, 48.8, 42.7, 41.3; **IR** (KBr, cm^{-1}) ν 3380, 1682, 1636, 1603, 1523; **HRMS** (ESI) calcd. for $C_{23}H_{23}O_2N_2$ $[M+H]^+$ 359.1754, Found 359.1751.

***N*-(2-(4-methoxyphenylamino)-4-oxo-4-phenylbutyl)benzamide (8b)**



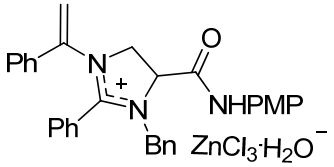
Yellow solid (49 mg, yield: 42%). **m.p.** 119 – 121 °C; **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.99 – 7.97 (m, 3H), 7.85– 7.83 (m, 2H), 7.62 – 7.57 (m, 1H), 7.51 – 7.46 (m, 3H), 7.42 (t, *J* = 7.4 Hz, 2H), 6.80 – 6.60 (m, 4H), 4.72 (d, *J* = 7.8 Hz, 1H), 4.29 – 4.26 (m, 1H), 3.82 – 3.75 (m, 1H), 3.66 (s, 3H), 3.60 – 3.54 (m, 1H), 3.40 – 3.29 (m, 2H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 199.3, 168.1, 152.8, 143.0, 138.3, 135.9, 133.8, 131.9, 129.4, 129.1, 128.9, 128.0, 115.5, 115.2, 55.8, 52.0, 44.1, 42.0; **IR** (KBr, cm^{-1}) ν 3374, 1677, 1638, 1514; **MS** (CI) 388 $[M]^+$ (5), 160 (35), 105 (100); **HRMS** (ESI) calcd. for $C_{24}H_{25}N_2O_3$ $[M+H]^+$ 389.1860, found 389.1856.

***N*-(2-(4-chlorophenylamino)-4-oxo-4-phenylbutyl)benzamide (8c)**



Colorless solid (52 mg, yield: 42%). **m.p.** 160 – 161 °C; **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.29 (m, 5H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.65 – 6.57 (m, 1H), 5.13 (d, *J* = 8.5 Hz, 1H), 5.08 – 5.01 (m, 2H), 4.26 – 4.21 (m, 1H), 3.53 – 3.47 (m, 1H), 3.37 – 3.31 (m, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 199.1, 157.9, 147.7, 138.1, 138.0, 133.9, 129.5, 129.4, 129.1, 128.8, 128.6, 121.0, 114.9, 66.6, 50.7, 44.8, 41.6; **IR** (KBr, cm^{-1}) ν 3391, 1679, 1634, 1601, 1536; **HRMS** (ESI) calcd. for $C_{23}H_{22}{}^{35}ClN_2O_2$ $[M+H]^+$, $C_{23}H_{22}{}^{37}ClN_2O_2$ $[M+2+H]^+$ 393.1364, 395,1340, found 393.1359, 393.1331.

4. Characterization Data for 2-Imidazolinium Chloride•$ZnCl_2$•H_2O and $[Cu(PMPNC)_4]PF_6$ Complex



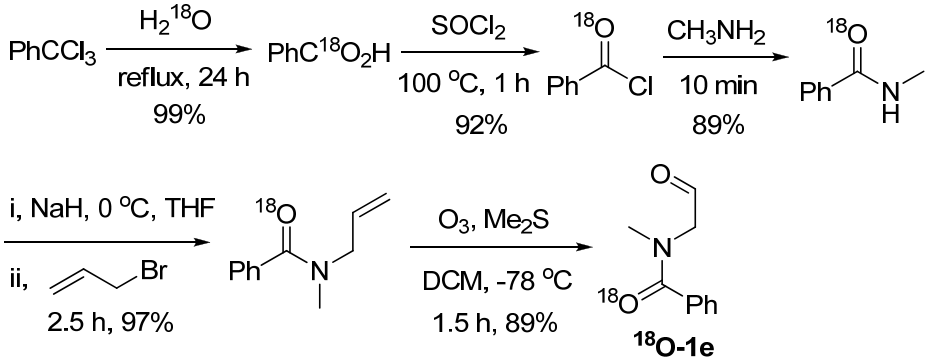
Yellow solid (105 mg, yield: 52%). **m.p.** 177 – 178 °C; **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.70 (s, 1H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.61 – 7.51 (m, 7H), 7.42 – 7.25

(m, 8H), 6.90 – 6.87 (m, 2H), 5.78 (d, J = 1.6 Hz, 1H), 5.68 (d, J = 1.6 Hz, 1H), 5.51 (dd, J = 11.7, 5.7 Hz, 1H), 5.08 (t, J = 11.7 Hz, 1H), 4.97 (d, J = 15.6 Hz, 1H), 4.75 (d, J = 15.6 Hz, 1H), 4.56 (dd, J = 11.7, 5.8 Hz, 1H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 168.3, 165.7, 157.7, 143.1, 134.8, 133.9, 133.7, 131.8, 130.5, 130.2, 129.8, 129.72, 129.66 129.6, 129.4, 127.1, 123.3, 122.5, 115.9, 114.6, 64.1, 57.2, 55.7, 52.5; **IR** (KBr, cm^{-1}) ν 1697, 1563, 1542, 1512, 1239; **MS** (ESI) 488 [M-$ZnCl_3$•H_2O]$^+$; **Anal**. Calcd. for: C: 56.66, H: 4.75, N: 6.19. found: C: 56.43, H: 4.74, N: 6.05.

Cu(PMPNC)$_4$•PF_6

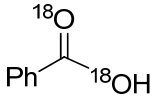
Yellow solid (65 mg, yield: 97%). **m.p.** 178 – 179 °C; **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.68 (d, J = 9.0 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H); **^{19}F NMR** (376 MHz, Acetone-d_6) δ -71.6, -73.5; **^{13}C NMR** (100 MHz, Acetone-d_6) δ 162.2, 129.3, 116.0, 56.3; **IR** (KBr, cm^{-1}) ν 2165, 1602, 1505, 1263, 1024, 846.

5. Synthesis and Characterization of ^{18}O-1e



Scheme S5. Synthesis of **^{18}O-1e**

PhC^{18}O$_2$H[4]

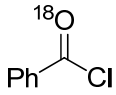


In a sealed tube, α, α, α-trichlorotoluene (2.5 g, 12.5 mmol) and $H_2{}^{18}O$ (1 g，50 mmol) were heated at 120 °C for 24 h. The reaction mixture was concentrated *in vavuo* to remove excess water and HCl, then a solution of NaOH (0.15 M, 75 mL) was added to the crude mixture. The aqueous phase was washed with AcOEt, acidified with an

aqueous HCl (1 N) solution and extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried upon anhydrous Na_2SO_4, filtered, concentrated *in vacuo* to afford benzoic acid (1.568 g, yield: 99%) as colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 (br, 1H), 8.15 – 8.12 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 134.0, 130.4, 129.4, 128.6; **MS** (CI) 127 $[M+1]^+$ (10), 126 $[M]^+$ (100), 107 (90); **HRMS** (ESI) calcd. for $C_7H_5{}^{18}O_2$ $[M-H]^-$ 125.0369, found 125.0371.

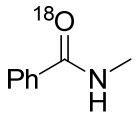
PhC^{18}OCl[4]



^{18}O-Labeled benzoic acid (1.32 g, 10.47 mmol) was placed in a 15 mL round bottomed flask and $SOCl_2$ (1.58 g, 13.2 mmol) was added drop by drop. The mixture was heated gently for 1 h at 100 ^{o}C (1.5 mL $SOCl_2$ was added after 20 min to make a clear solution), cooled, and then distilled (about 70 ^{o}C) at atmospheric pressure to remove excess $SOCl_2$. A vacuum was applied and the bath temperature was slowly increased to 130 ^{o}C to give one fraction of PhC^{18}OCl (1.379 g, yield: 92%) as colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.6, 135.5, 133.4, 131.6, 129.1.

^{18}O-labled-*N*-methylbenzamide

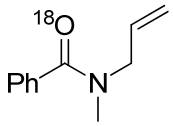


To a solution of PhC^{18}OCl (1.426 g, 10 mmol) in Et_2O (25 mL) was added aqueous CH_3NH_2 solution (15 mL) slowly at ambient temperature. The reaction mixture was stirred for another 1 h, and then concentrated *in vacuo* to afford the crude ^{18}O-labled-*N*-methylbenzamide product (1.22 g, yield: 89%) as colorless solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (s, 1H), 7.84 – 7.82 (m, 2H),, 7.52 – 7.42 (m, 3H), 2.81 (d, *J* = 4.6 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.3, 134.5, 130.4,

127.7, 126.6, 25.7; **MS** (CI) 138 $[M+1]^+$ (8), 137 $[M]^+$ (38), 107 (100); **HRMS** (ESI) calcd. for $C_8H_{10}N^{18}O$ $[M+H]^+$ 138.0799, found 138.0799.

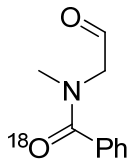
^{18}O-labled-*N*-allyl-*N*-methylbenzamide



To a solution of ^{18}O-labled-*N*-methylbenzamide (686 mg, 10 mmol) in dry THF (10 mL) was added NaH (240 mg, 10 mmol) at 0 ^{o}C. The reaction mixture was stirred for 15 min, and then allyl bromide (1.21 g, 10 mmol) was added drop by drop. The resulting mixture was allowed to warm to room temperature and stirred for another 1 h, then quenched with ice water, extracted with EtOAc (3×15 mL), the combined organic extracts were dried over anhydrous Na_2SO_4. After filtration and concentration *in vavuo*, the residue was subject to silica gel column chromatography (petroleum ether/EtOAc) to give ^{18}O-labled-*N*-allyl-*N*-methylbenzamide (863 mg, yield: 97%) as yellow oil.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 – 7.37 (m, 5H), 5.89 - 5.79 (m, 1H), 5.22 – 5.18 (m, 2H), 2.91 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 136.3, 133.3, 129.1, 128.1, 116.8; **MS** (CI) 178 $[M+1]^+$ (3), 177 $[M]^+$ (10), 162 (13), 107 (100); **HRMS** (ESI) calcd. for $C_{11}H_{14}N^{18}O$ $[M+H]^+$ 178.1112, found 178.1111.

^{18}O-labled-*N*-(2-oxoethyl)-*N*-phenylacetamide (^{18}O-1e)



^{18}O-labled-*N*-allyl-*N*-methylbenzamide (709 mg, 4 mmol) was dissolved in CH_2Cl_2/MeOH (v:v = 5:1) (48 mL). After cooling to -78 ^{o}C, ozone and oxygen gas were bubbled into the solution, After 2 h, the ozone was evacuated with nitrogen for 15 min at -78 ^{o}C, and dimethyl sulfide (5.0 mL) was added. The resulting solution was allowed to warm to room temperature over 1 h. The clear solution was

concentrated *in vacuo* and then purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to afford substrate **^{18}O-1e** (789 mg, yield: 89%) as yellow oil.

Yellow oil (789 mg, yield: 89%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.56 (s, 1H), 7.46 – 7.40 (m, 5H), 4.24 (s, 2H), 2.98 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 198.1, 170.5, 135.5, 129.0, 127.8, 126.2; **IR** (KBr, cm^{-1}) ν 1731, 1634, 1398; **HRMS** (ESI) calcd. for $C_{18}H_{11}NO^{18}O$ $[M+H]^+$ 180.0910, found 180.0908.

6. HRMS Spectra for ^{18}O-1e and ^{18}O-4e

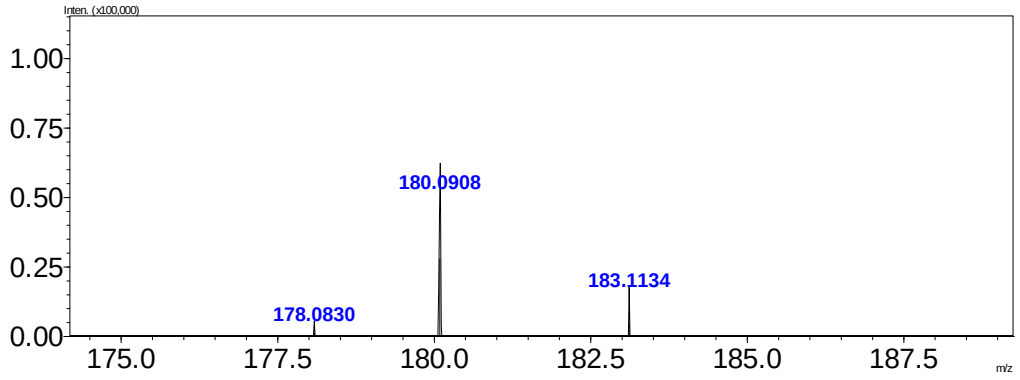


Figure S1. HRMS spectra of **^{18}O-1e**

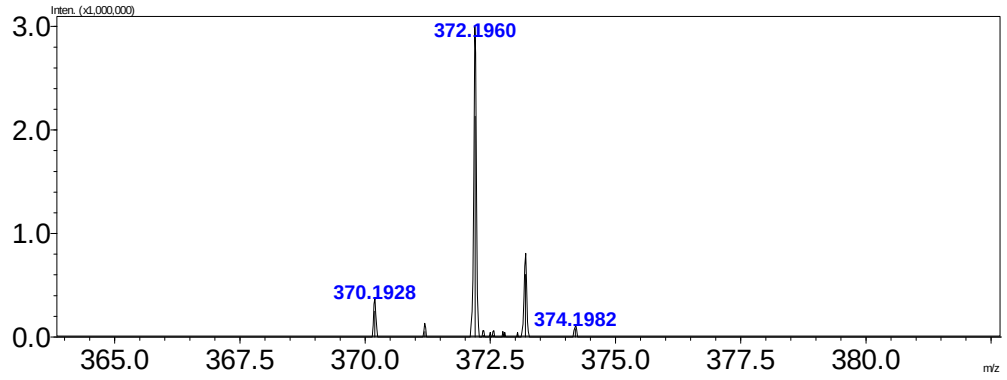


Figure S2. HRMS spectra of **^{18}O-4e**

7. Crystallographic Data

Crystal data and structure refinement for **4a**

Identification code	**4a**
Empirical formula	$C_{33}H_{30}F_3N_3O_5S$

Formula weight	637.66
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.012(2) Å α = 102.467(3)°
	b = 13.115(4) Å β = 104.463(4)°
	c = 15.516(5) Å γ = 98.556(3)°
Volume	1505.7(8) $Å^3$
Z	2
Calculated density	1.407 Mg/m^3
Absorption coefficient	0.173 mm^{-1}
F(000)	664
Crystal size	0.39 × 0.37 × 0.33 mm
Theta range for data collection	2.64 to 27.51°
Limiting indices	-10<=h<=10, -16<=k<=17, -20<=l<=20
Reflections collected/unique	19349/6868[R(int) = 0.0407]
Completeness to theta = 27.48°	99.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.6542
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6868/0/407
Goodness-of-fit on F^2	1.112
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1246
R indices (all data)	R1 = 0.0530, wR2 = 0.1286
Largest diff. peak and hole	0.328 and -0.433 e. $Å^{-3}$

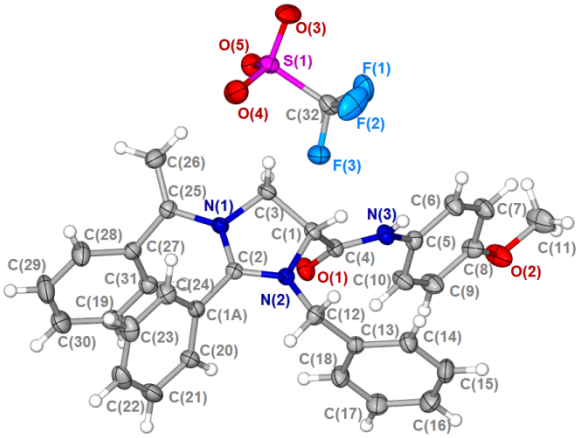


Figure S3. ORTEP presentation of **4a**

Crystal data and structure refinement for $Cu(PMPNC)_4•PF_6$	
Identification code	$Cu(PMPNC)_4•PF_6$
Empirical formula	$C_{32}H_{28}CuF_6N_4O_3P$
Formula weight	741.09
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2/n
Unit cell dimensions	a = 16.002(10) Å α = 90°
	b = 6.542(4) Å β = 90.151(9)°
	c = 16.026(10) Å γ = 90°
Volume	1678.0(18) $Å^3$
Z	2
Calculated density	1.467 Mg/m^3
Absorption coefficient	0.774 mm^{-1}
F(000)	756
Crystal size	0.31 × 0.11 × 0.07 mm
Theta range for data collection	3.11 to 27.39°
Limiting indices	-20<=h<=20, -8<=k<=8, -20<=l<=20

Reflections collected/unique	11265/3673[R(int) = 0.0651]
Completeness to theta = 27.48°	96.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.5733
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3673/0/221
Goodness-of-fit on F^2	1.222
Final R indices [I>2sigma(I)]	R1 = 0.0807, wR2 = 0.1849
R indices (all data)	R1 = 0.0901, wR2 = 0.1923
Largest diff. peak and hole	0.543 and -0.462 e. $Å^{-3}$

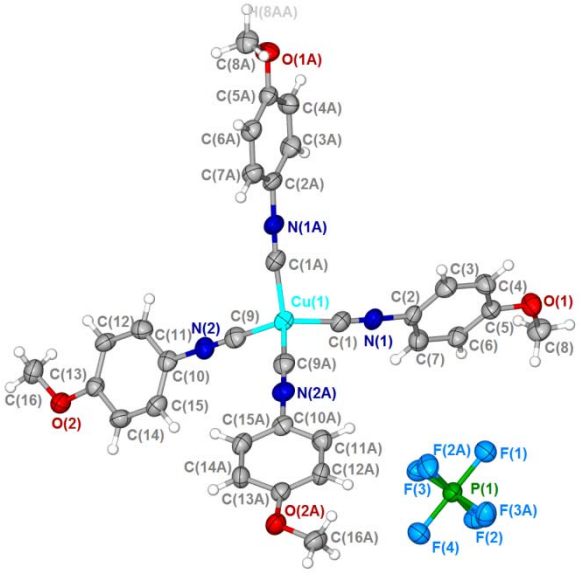


Figure S4. ORTEP presentation of $Cu(PMPNC)_4•PF_6$

Crystal data and structure refinement for 2-imidazolinium chloride•$ZnCl_2$•H_2O complex

Identification code	2-imidazolinium chloride•$ZnCl_2$•H_2O
Empirical formula	$C_{32}H_{23}Cl_3N_3O_3Zn$
Formula weight	678.33
Temperature	173(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 17.046(3) Å α = 90°
	b = 8.1172(16) Å β = 108.30(3)°
	c = 24.185(5) Å γ = 90°
Volume	3177.2(11) $Å^3$
Z	4
Calculated density	1.418 Mg/m^3
Absorption coefficient	1,062 mm^{-1}
F(000)	1400
Crystal size	0.27 × 0.23 × 0.10 mm
Theta range for data collection	1.77 to 27.48°
Limiting indices	-22<=h<=21, -10<=k<=8, -31<=l<=31
Reflections collected/unique	22011/7276[R(int) = 0.0967]
Completeness to theta = 27.48°	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.5652
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7276/0/380
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0553, wR2 = 0.1187
R indices (all data)	R1 = 0.0745, wR2 = 0.1262
Largest diff. peak and hole	0.465 and -0.382 e. $Å^{-3}$

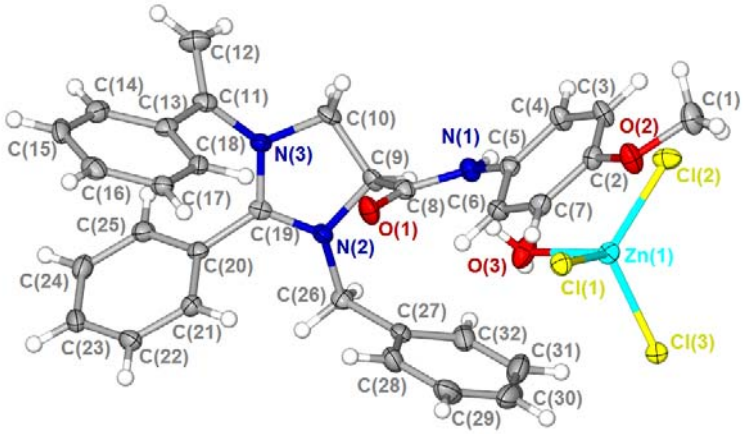
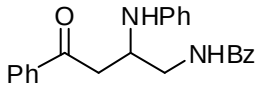


Figure S5. ORTEP presentation of 2-imidazolinium chloride•$ZnCl_2$•H_2O complex

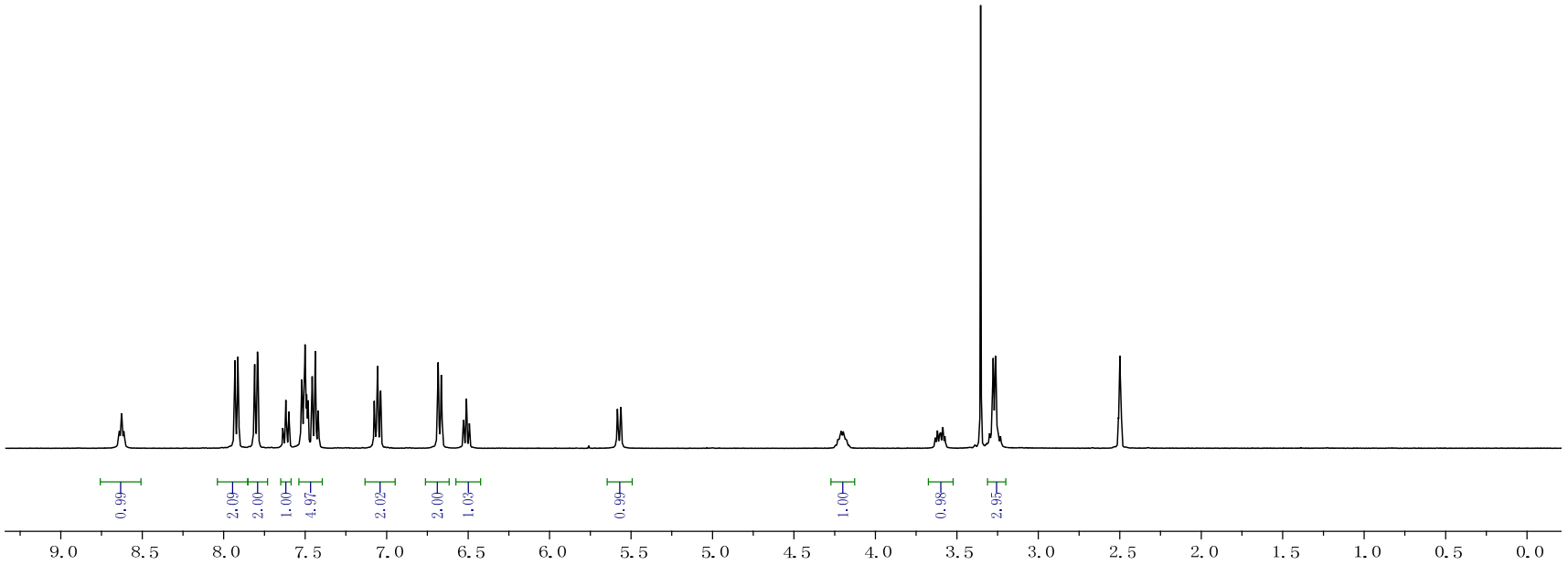
8. References

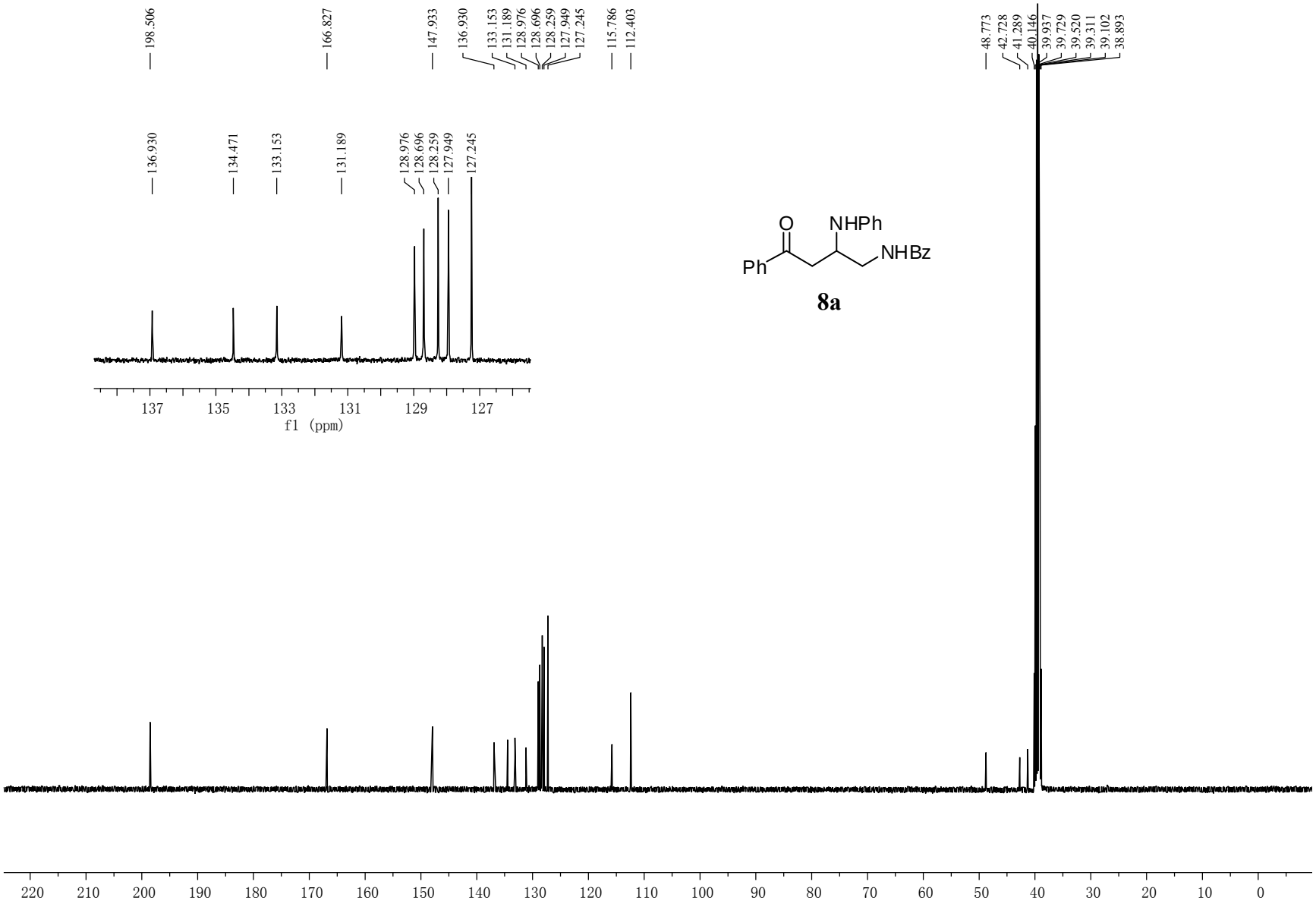
1. C.-H. Lei, D.-X. Wang, L. Zhao, J. Zhu and M.-X. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 4708-4711.
2. N. Ohmura, A. Nakamura, A. Hamasaki and M. Tokunaga, *Eur. J. Org. Chem.*, 2008, 5042-5045.
3. S. Hanada, T. Ishida, Y. Motoyama and H. Nagashima, *J. Org. Chem.*, 2007, **72**, 7551-7559.
4. M. Kobayashi and R. Kiritani, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1782-1784.

9. Copies of ^{1}H and ^{13}C NMR Spectra



8a

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40.146
39.937
39.729
39.520
39.311
39.102
38.893
136.930
134.471
133.153
131.189
128.976
128.696
128.259
127.949
127.245
137
135
133
131
129
127
f1 (ppm)
O
NHPh
NHBz
Ph
8a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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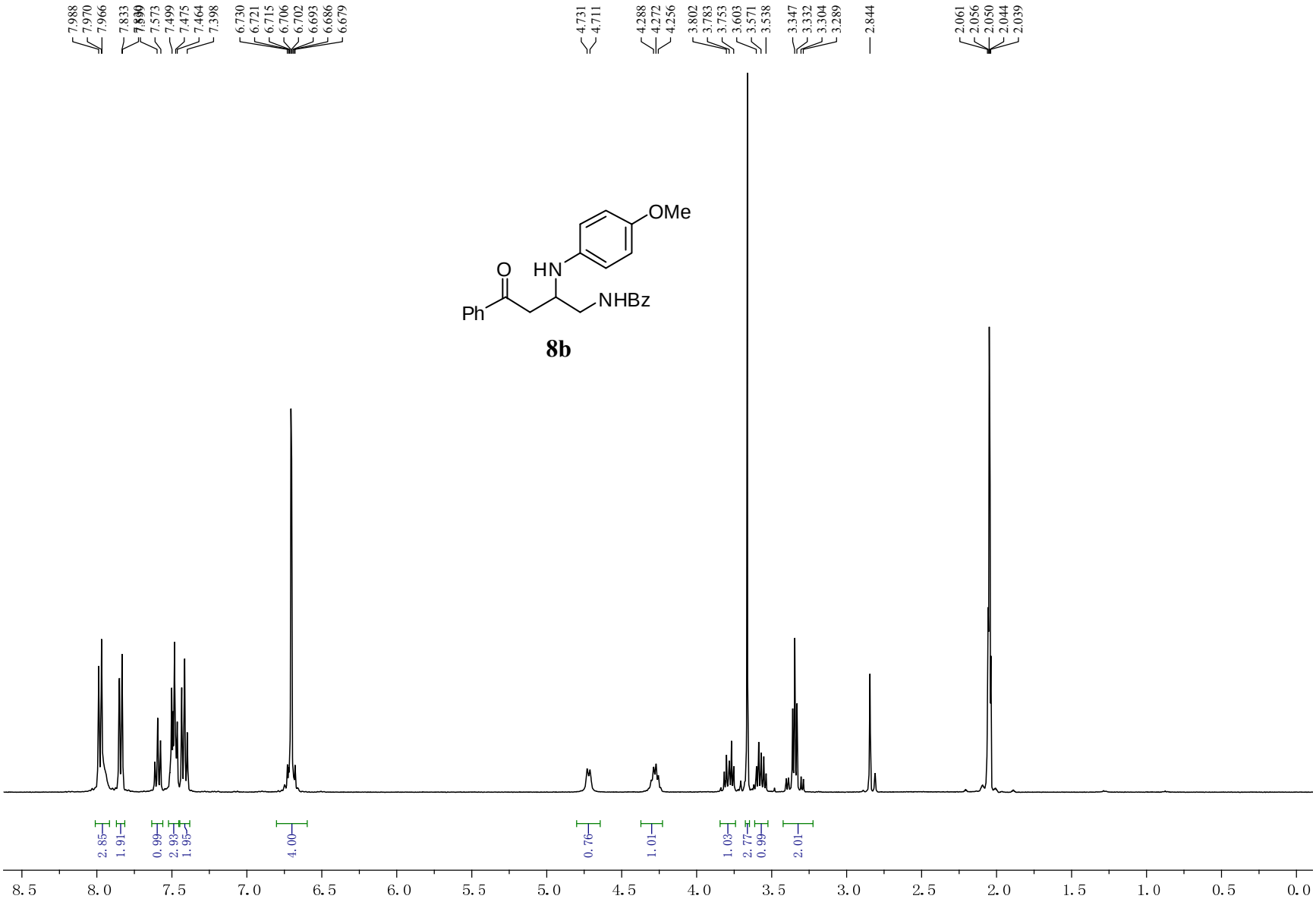
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7.966
7.833
7.573
7.499
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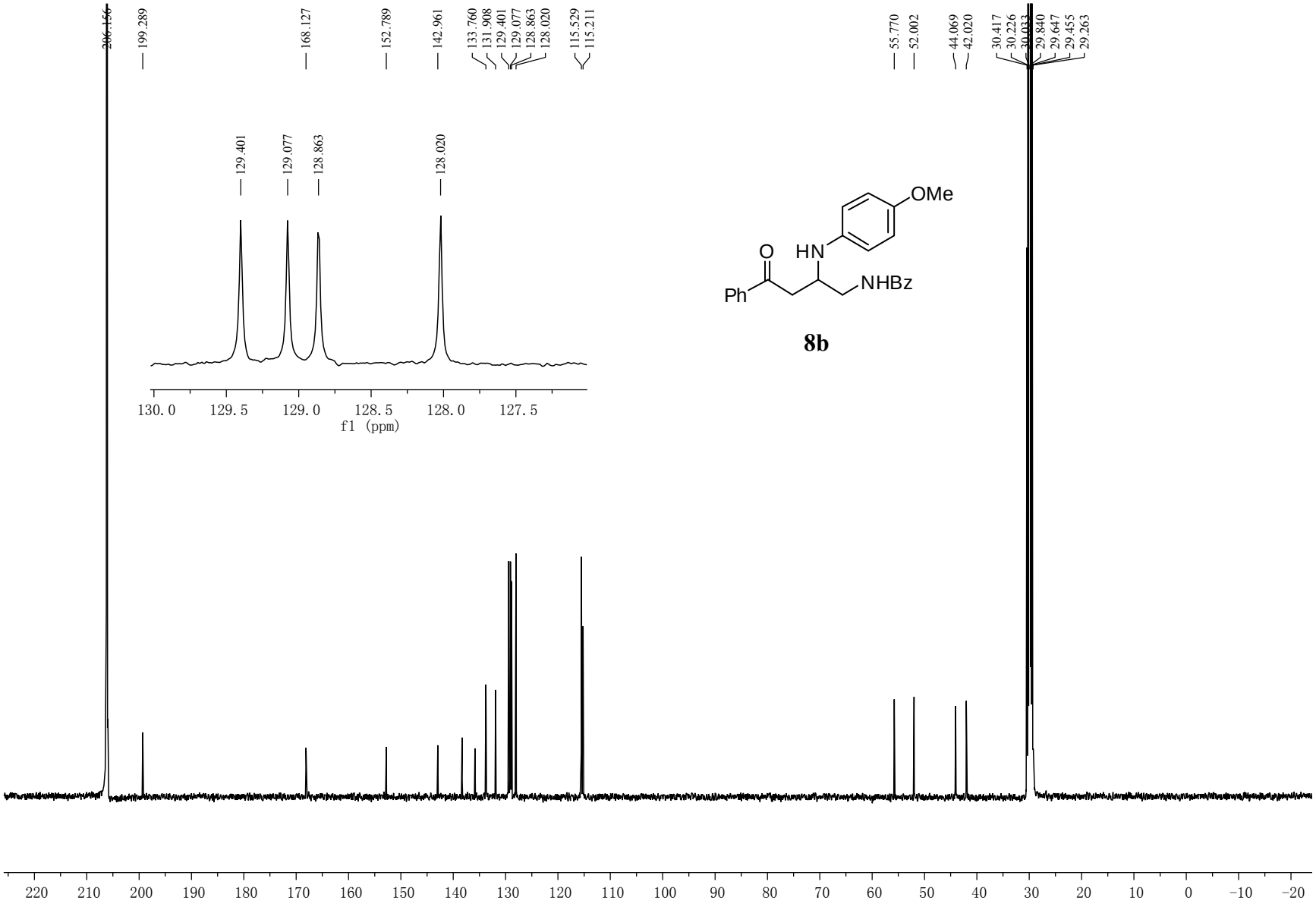
7.464
7.398
6.730
6.721
6.715
6.706
6.702
6.693
6.686
6.679
4.731
4.711
4.288
4.272
4.256
3.802
3.783
3.753
3.603
3.571
3.538
3.347
3.332
3.304
3.289
2.844
2.061
2.056
2.050
2.044
2.039
OMe
HN
O
NHBz
Ph
8b
2.85
1.91
0.99
2.93
1.95
4.00
0.76
1.01
1.03
2.77
0.99
2.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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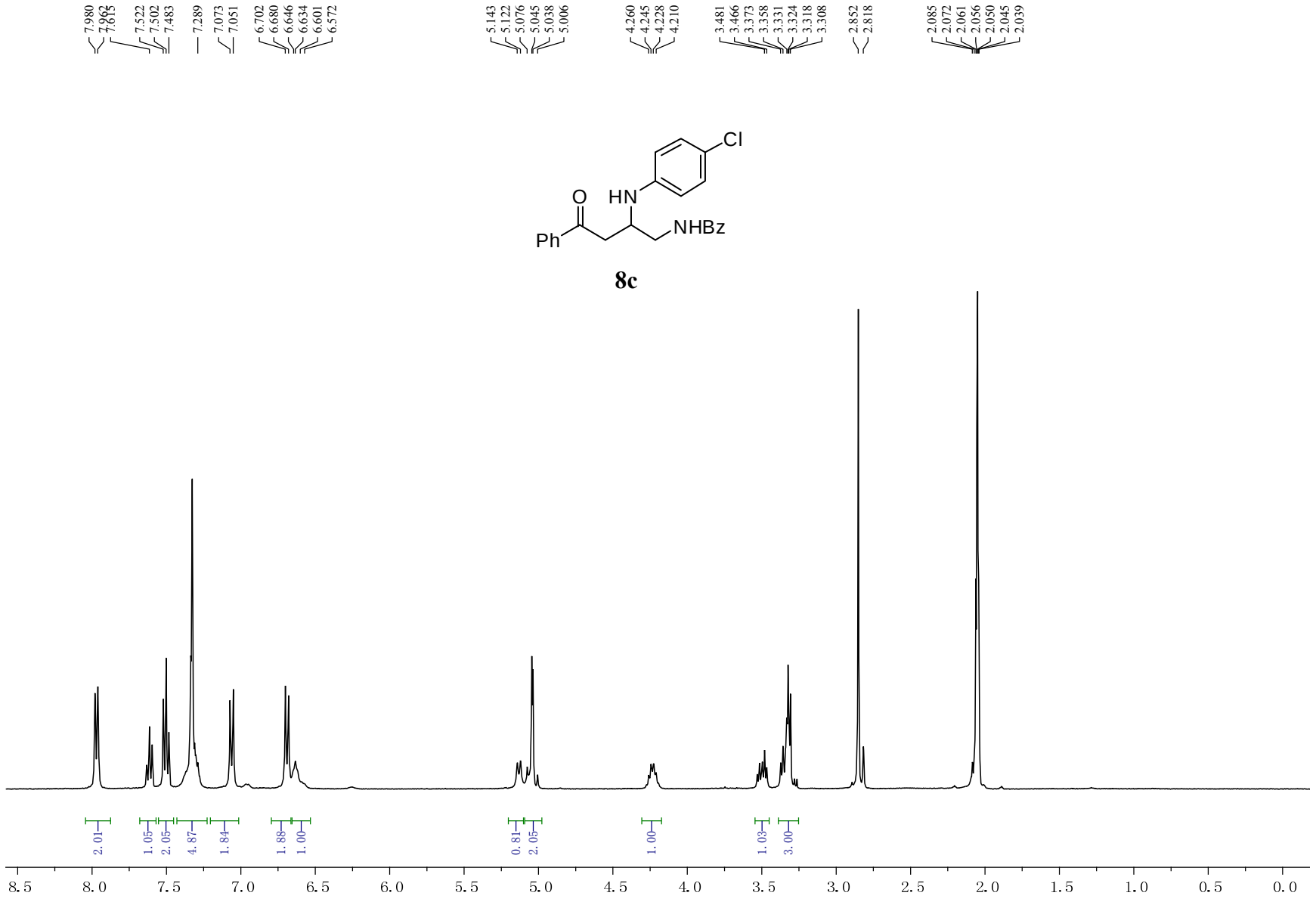
168.127
152.789
142.961
133.760
131.908
129.401
129.077
128.863
128.020
115.529
115.211
55.770
52.002
44.069
42.020
30.417
30.226
30.033
29.840
29.647
29.455
29.263
129.401
129.077
128.863
128.020
130.0
129.5
129.0
128.5
128.0
127.5
f1 (ppm)
OMe
HN
O
Ph
NHBz
8b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20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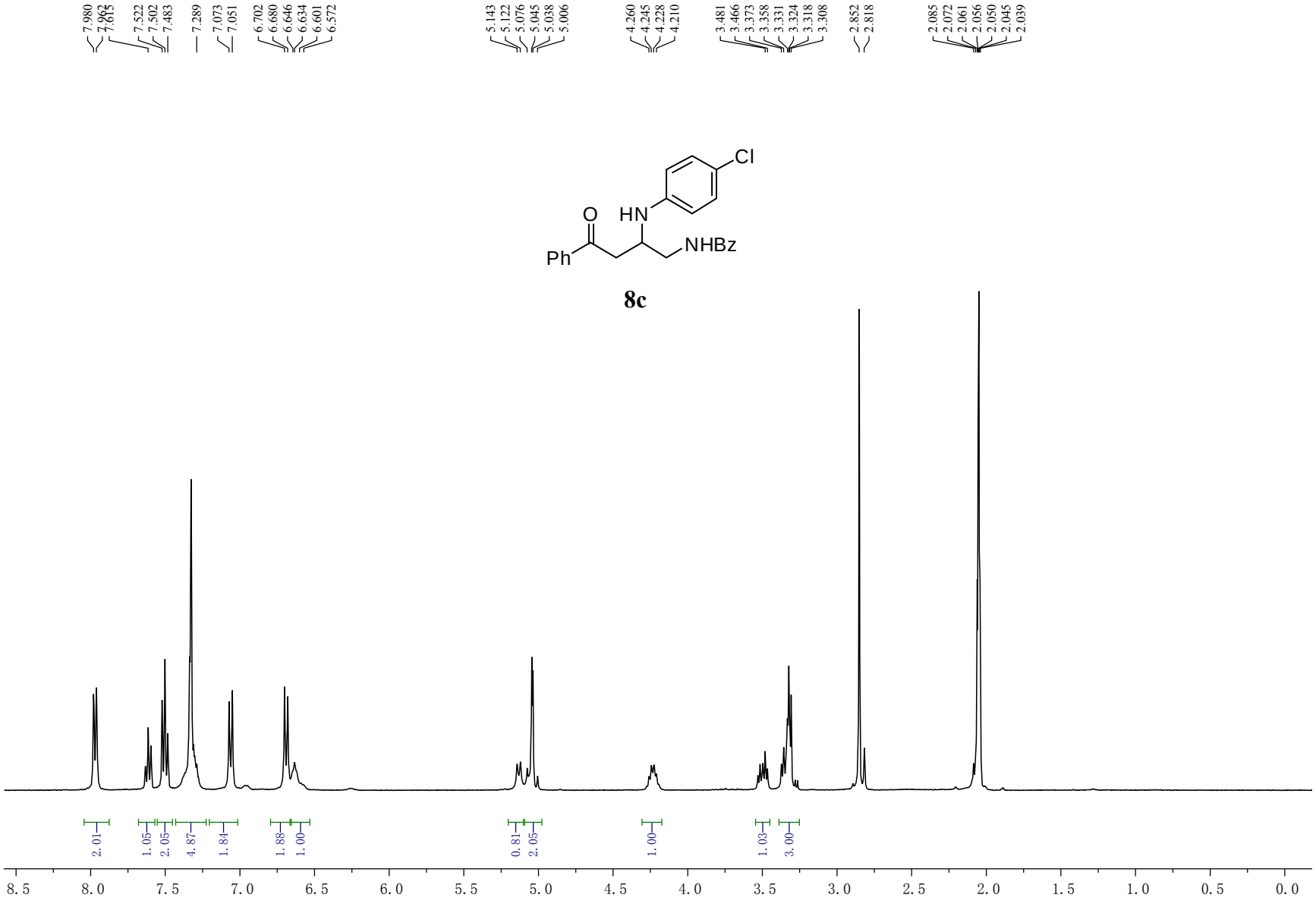
7.962
7.615
7.522
7.502
7.483
7.289
7.073
7.051
6.702
6.680
6.646
6.634
6.601
6.572
5.143
5.122
5.076
5.045
5.038
5.006
4.260
4.245
4.228
4.210
3.481
3.466
3.373
3.358
3.331
3.324
3.318
3.308
2.852
2.818
2.085
2.072
2.061
2.056
2.050
2.045
2.039
Cl
HN
O
NHBz
Ph
2.01
1.05
2.05
4.87
1.84
1.88
1.00
0.81
2.05
1.00
1.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

8c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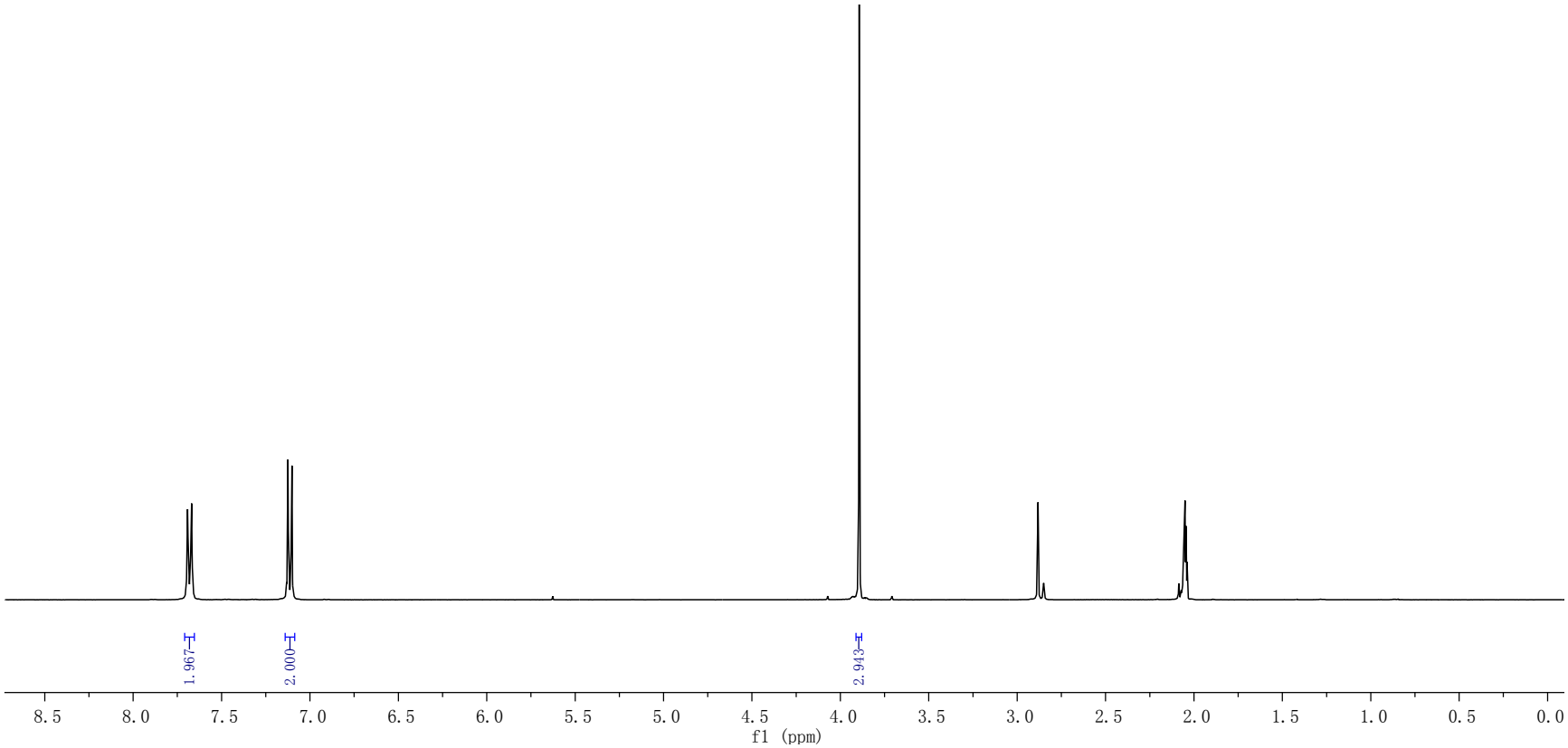
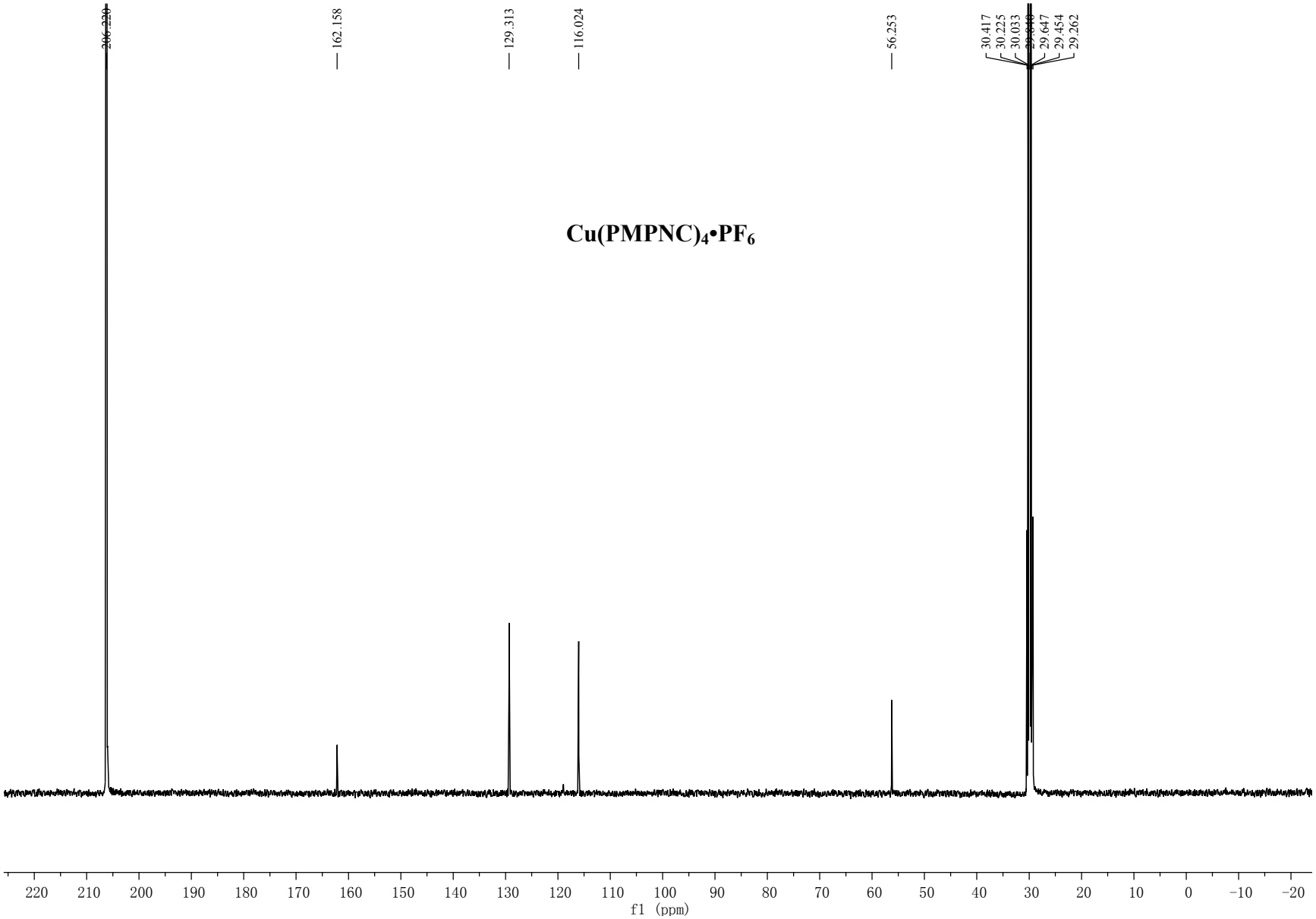
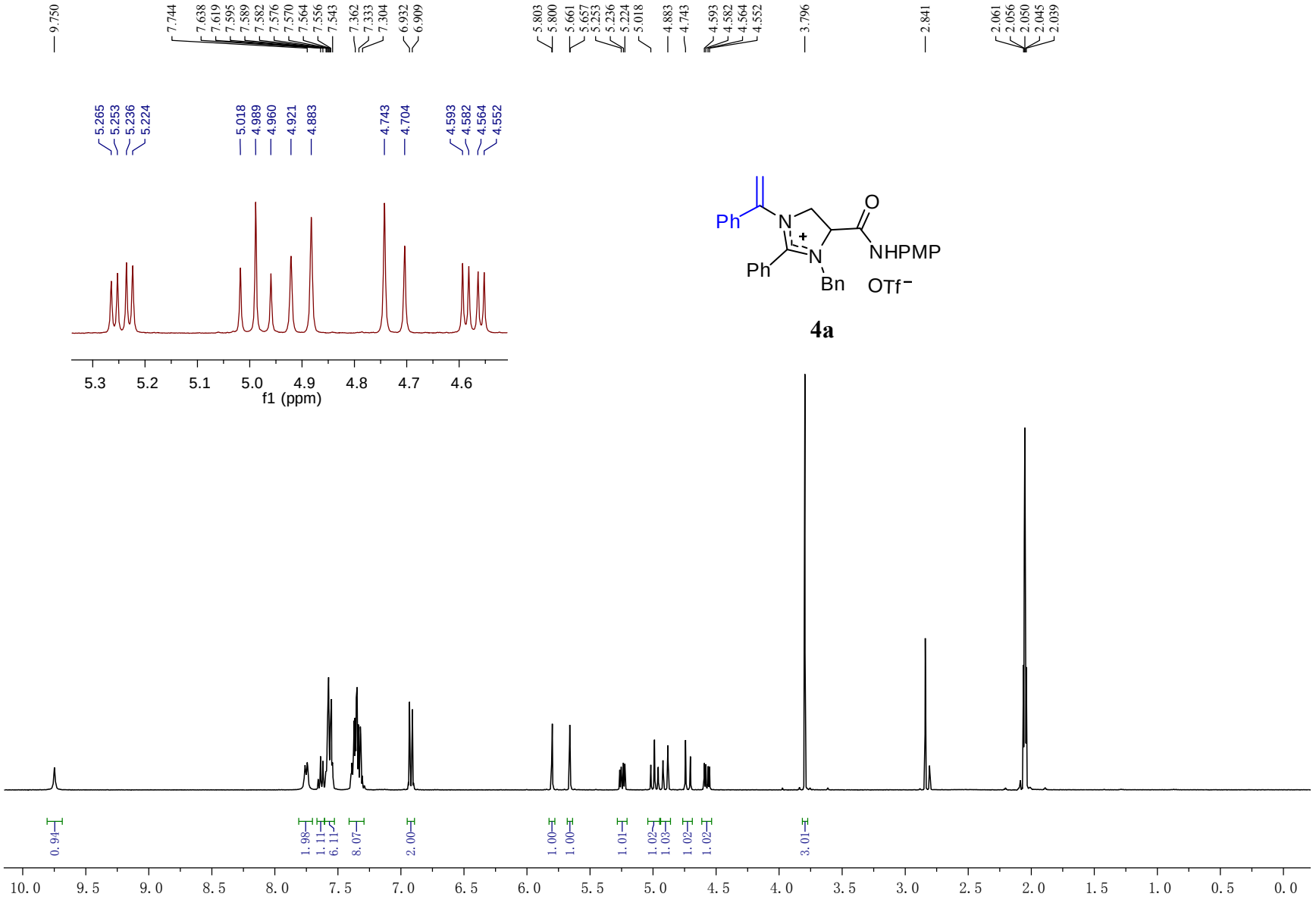
7.962
7.615
7.522
7.502
7.483
7.289
7.073
7.051
6.702
6.680
6.646
6.634
6.601
6.572
5.143
5.122
5.076
5.045
5.038
5.006
4.260
4.245
4.228
4.210
3.481
3.466
3.373
3.358
3.331
3.324
3.318
3.308
2.852
2.818
2.085
2.072
2.061
2.056
2.050
2.045
2.039
Cl
HN
O
NHBz
Ph
2.01
1.05
2.05
4.87
1.84
1.88
1.00
0.81
2.05
1.00
1.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

8c

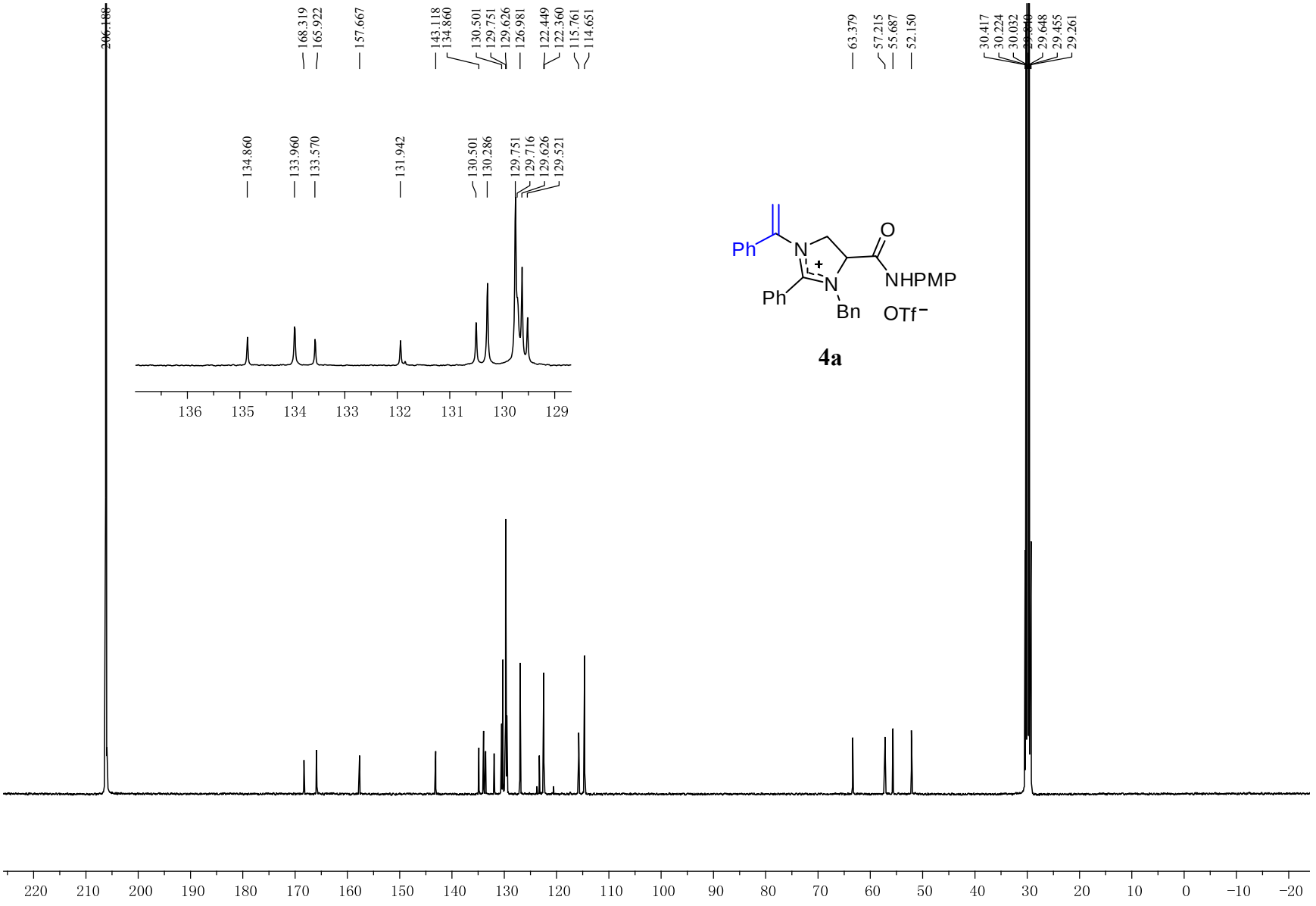
$Cu(PMPNC)_4•PF_6$




206.220
162.158
129.313
116.024
56.253
30.417
30.225
30.033
29.840
29.647
29.454
29.262
Cu(PMPNC)4•PF6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)


9.750
7.744
7.638
7.619
7.595
7.589
7.582
7.576
7.570
7.564
7.556
7.543
7.362
7.333
7.304
6.932
6.909
5.803
5.800
5.661
5.657
5.253
5.236
5.224
5.018
4.883
4.743
4.593
4.582
4.564
4.552
3.796
2.841
2.061
2.056
2.050
2.045
2.039
5.265
5.253
5.236
5.224
5.018
4.989
4.960
4.921
4.883
4.743
4.704
4.593
4.582
4.564
4.552
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
f1 (ppm)
Ph
N
O
NHPMP
Ph
N
Bn
OTf⁻
0.94
1.98
1.11
6.11
8.07
2.00
1.00
1.00
1.01
1.02
1.03
1.02
1.02
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

4a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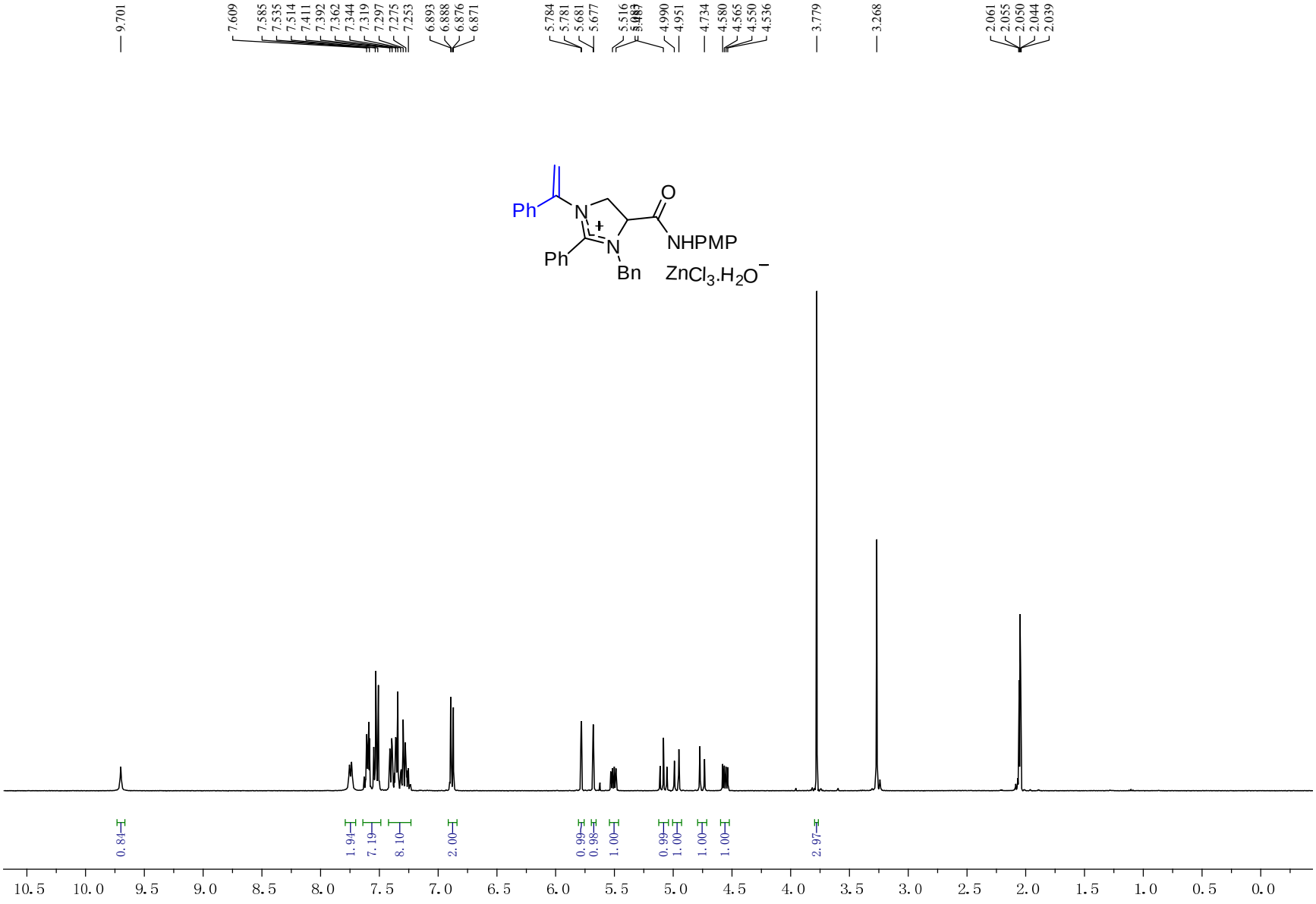
168.319
165.922
157.667
143.118
134.860
130.501
129.751
129.626
126.981
122.449
122.360
115.761
114.651
63.379
57.215
55.687
52.150
30.417
30.224
30.032
29.648
29.455
29.261
134.860
133.960
133.570
131.942
130.501
130.286
129.751
129.716
129.626
129.521
136
135
134
133
132
131
130
129
Ph
N
+
N
O
NHPMP
Ph
Bn
OTf⁻
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20

4a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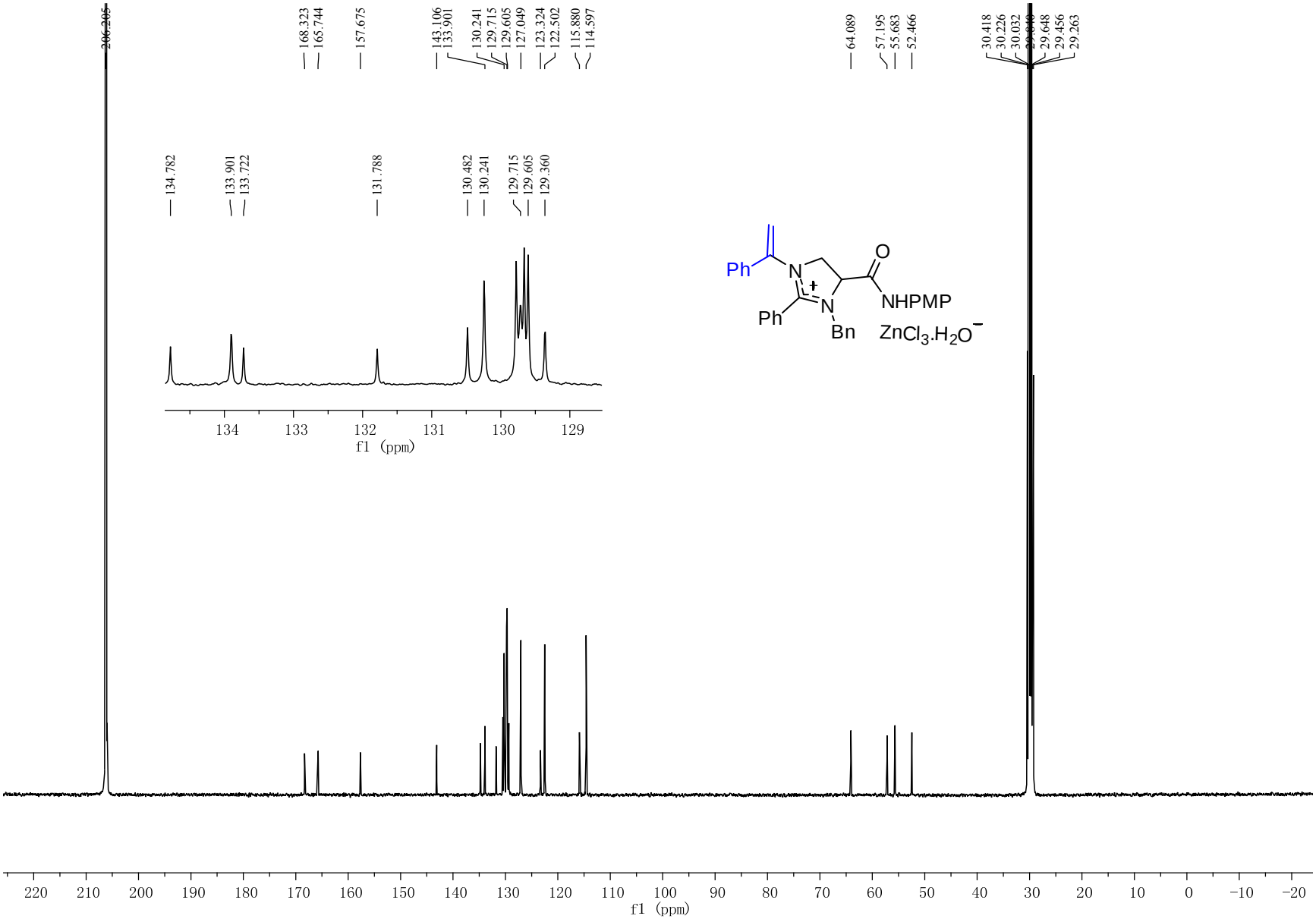
7.609
7.585
7.535
7.514
7.411
7.392
7.362
7.344
7.319
7.297
7.275
7.253
6.893
6.888
6.876
6.871
5.784
5.781
5.681
5.677
5.516
4.990
4.951
4.734
4.580
4.565
4.550
4.536
3.779
3.268
2.061
2.055
2.050
2.044
2.039
Ph
N
O
NHPMP
Ph
N
Bn
ZnCl3.H2O−
0.84
1.94
7.19
8.10
2.00
0.99
0.98
1.00
0.99
1.00
1.00
1.00
2.97
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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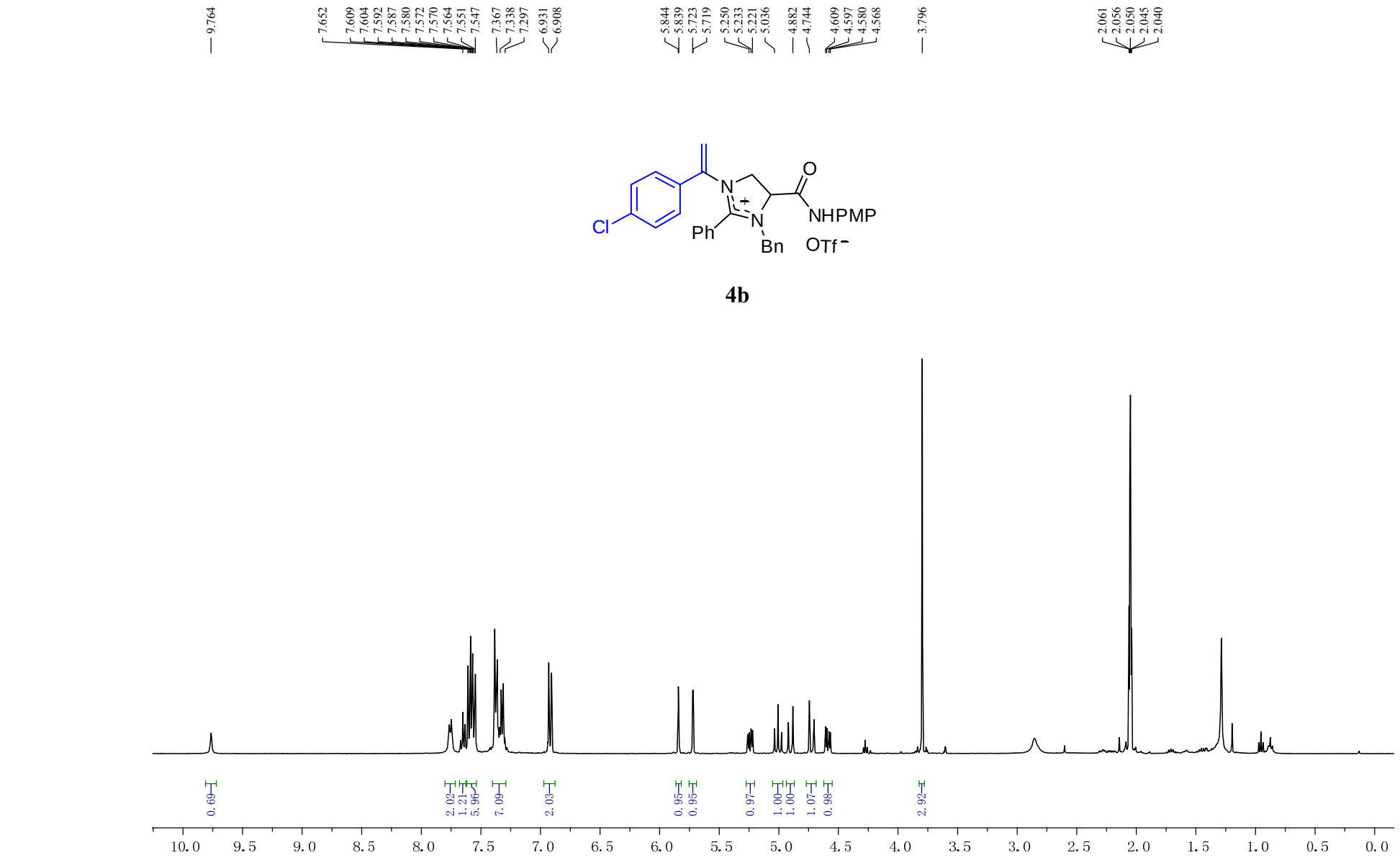
168.323
165.744
157.675
143.106
133.901
130.241
129.715
129.605
127.049
123.324
122.502
115.880
114.597
64.089
57.195
55.683
52.466
30.418
30.226
30.032
29.648
29.456
29.263
134.782
133.901
133.722
131.788
130.482
130.241
129.715
129.605
129.360
134
133
132
131
130
129
f1 (ppm)
Ph
N
O
NHPMP
Ph
N
Bn
ZnCl3.H2O−
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)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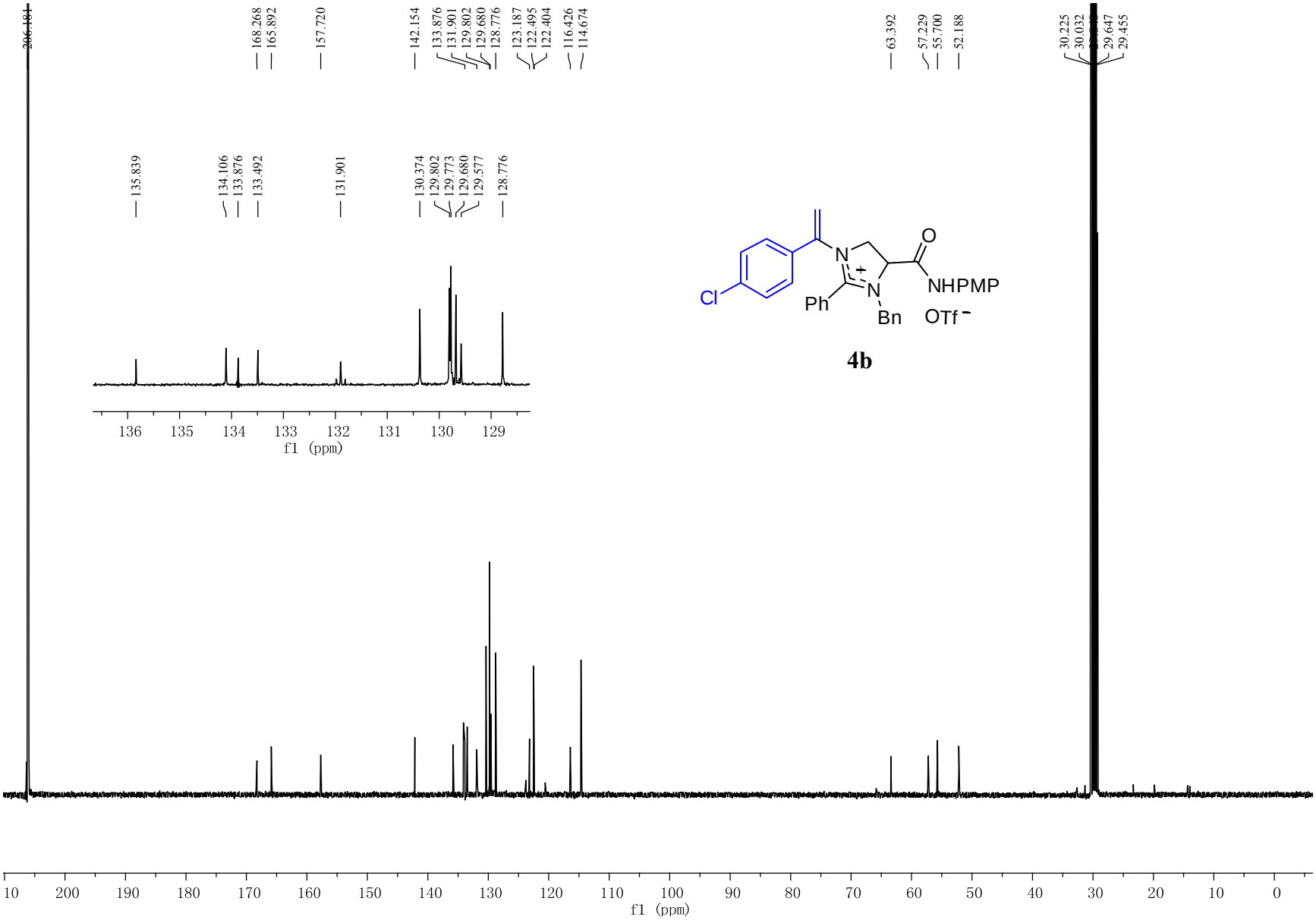
7.609
7.604
7.592
7.587
7.580
7.572
7.570
7.564
7.551
7.547
7.367
7.338
7.297
6.931
6.908
5.844
5.839
5.723
5.719
5.250
5.233
5.221
5.036
4.882
4.744
4.609
4.597
4.580
4.568
3.796
2.061
2.056
2.050
2.045
2.040
Cl
Ph
N
N
O
NHPMP
Bn
OTf
0.69
2.02
1.21
5.96
7.09
2.03
0.95
0.95
0.97
1.00
1.00
1.07
0.98
2.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

4b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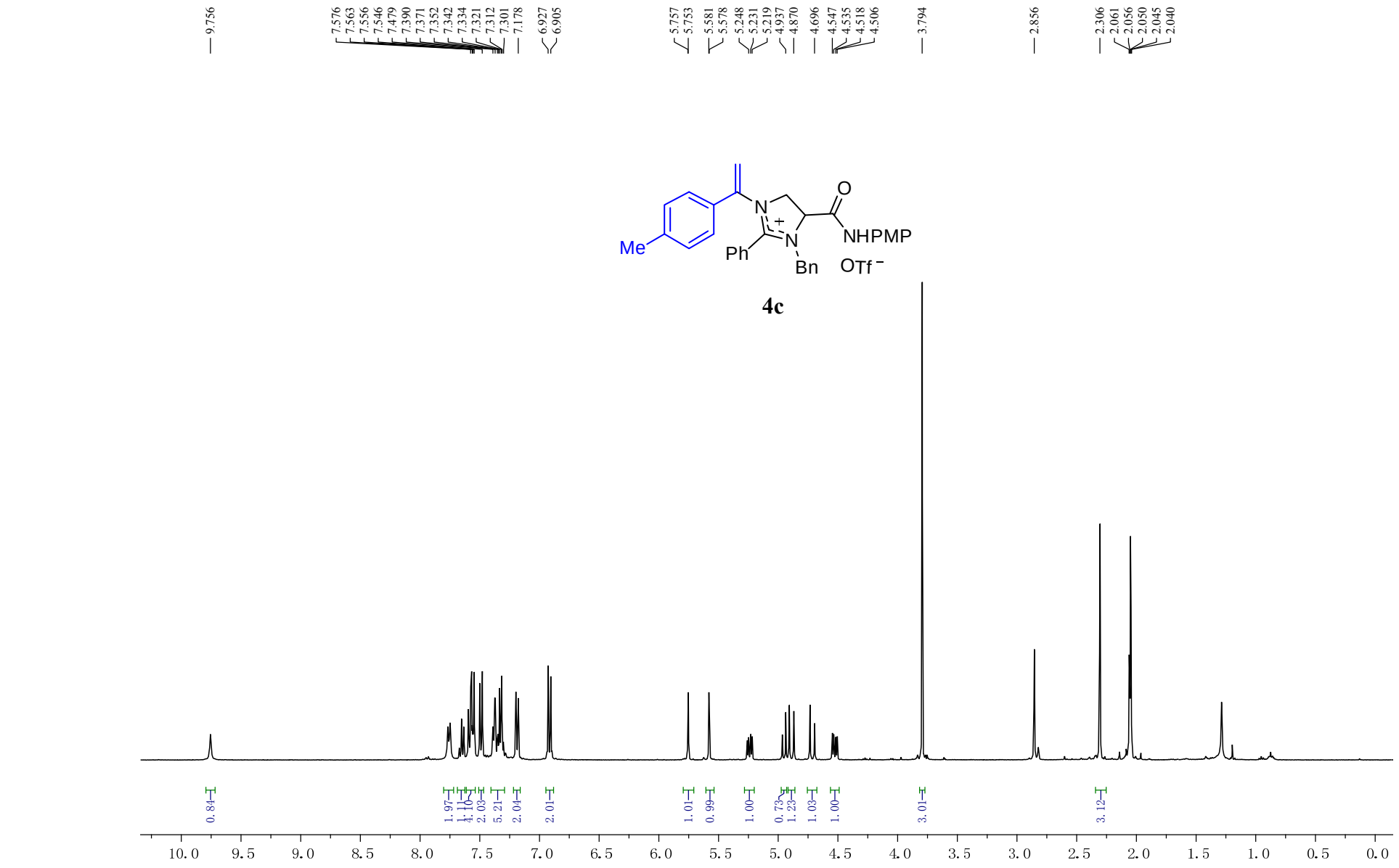
168.268
165.892
157.720
142.154
133.876
131.901
129.802
129.680
128.776
123.187
122.495
122.404
116.426
114.674
63.392
57.229
55.700
52.188
30.225
30.032
29.647
29.455
135.839
134.106
133.876
133.492
131.901
130.374
129.802
129.773
129.680
129.577
128.776
136 135 134 133 132 131 130 129
f1 (ppm)
Cl
Ph
N
N
O
NHPMP
Bn
OTf⁻
4b
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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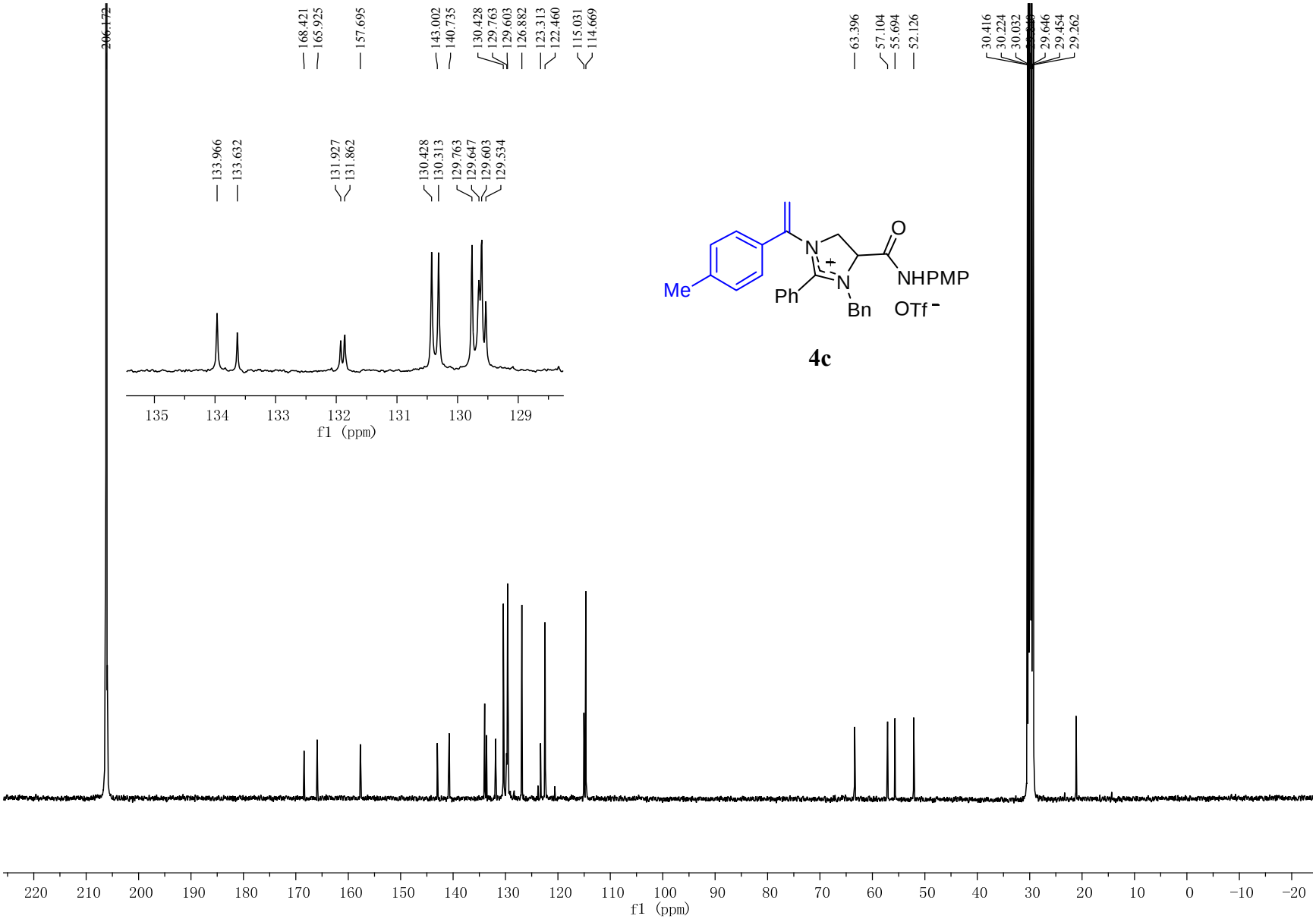
7.563
7.556
7.546
7.479
7.390
7.371
7.352
7.342
7.334
7.321
7.312
7.301
7.178
6.927
6.905
5.757
5.753
5.581
5.578
5.248
5.231
5.219
4.937
4.870
4.696
4.547
4.535
4.518
4.506
3.794
2.856
2.306
2.061
2.056
2.050
2.045
2.040
Me
Ph
N
N
O
NHPMP
Bn
OTf⁻
0.84
1.97
1.10
2.03
5.21
2.04
2.01
1.01
0.99
1.00
0.73
1.23
1.03
1.00
3.01
3.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

4c


206.172
168.421
165.925
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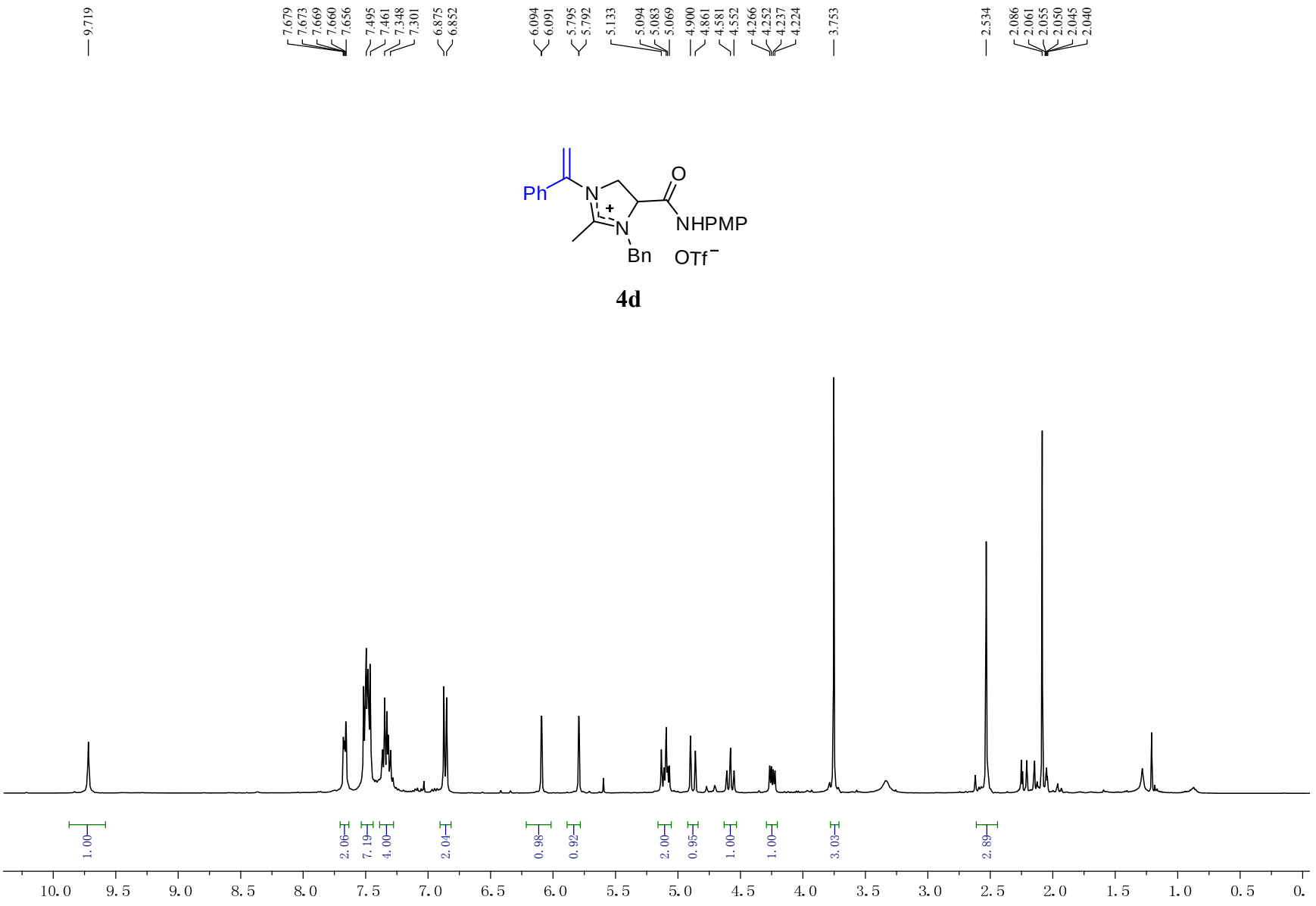
143.002
140.735
130.428
129.763
129.603
126.882
123.313
122.460
115.031
114.669
63.396
57.104
55.694
52.126
30.416
30.224
30.032
29.646
29.454
29.262
133.966
133.632
131.927
131.862
130.428
130.313
129.763
129.647
129.603
129.534
135
134
133
132
131
130
129
f1 (ppm)
Me
Ph
N
N
O
NHPMP
Bn
OTf
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

4c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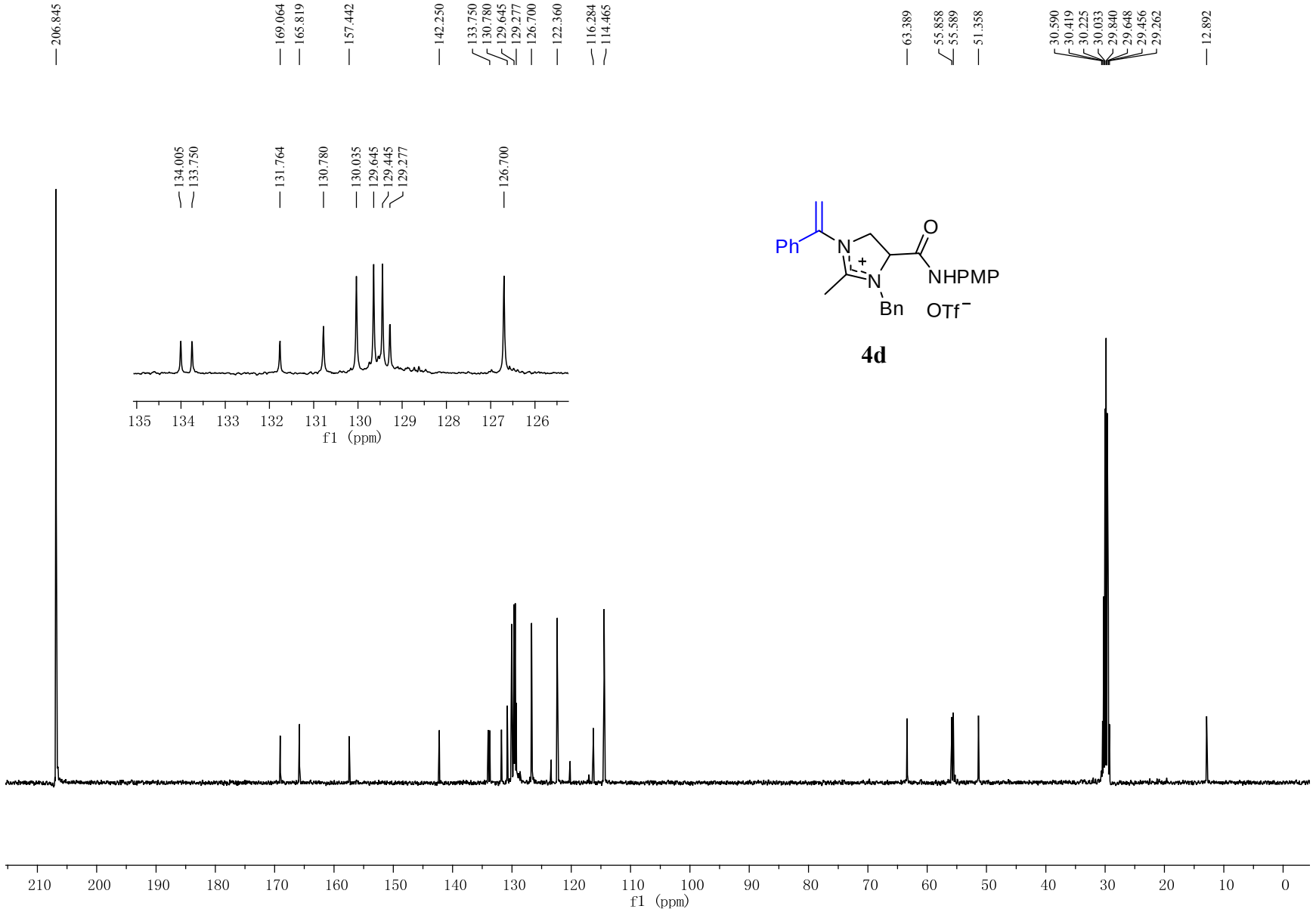
7.679
7.673
7.669
7.660
7.656
7.495
7.461
7.348
7.301
6.875
6.852
6.094
6.091
5.795
5.792
5.133
5.094
5.083
5.069
4.900
4.861
4.581
4.552
4.266
4.252
4.237
4.224
3.753
2.534
2.086
2.061
2.055
2.050
2.045
2.040
Ph
N
O
NHPMP
N
Bn
OTf⁻
1.00
2.06
7.19
4.00
2.04
0.98
0.92
2.00
0.95
1.00
1.00
3.03
2.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.

4d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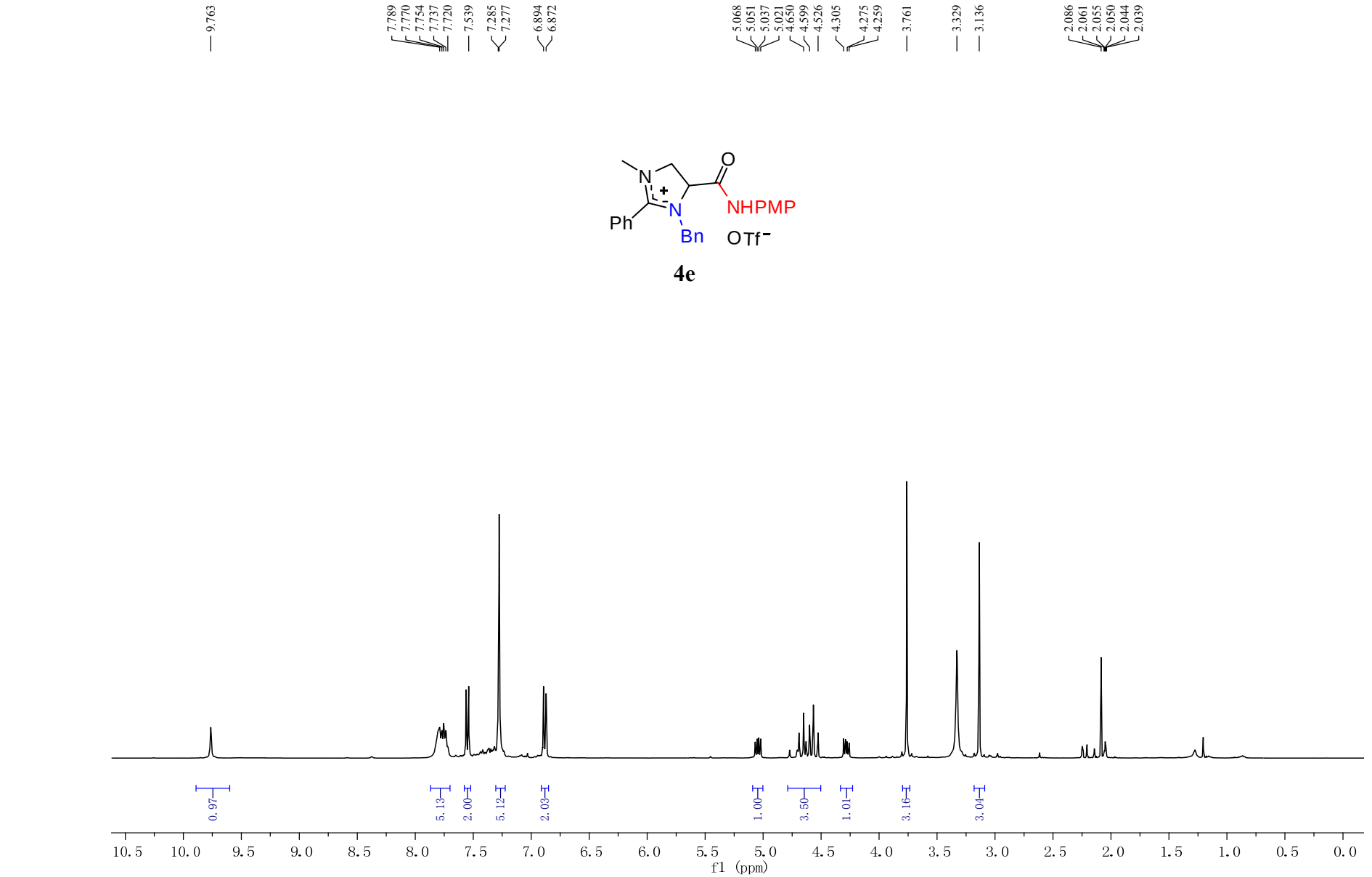
133.750
130.780
129.645
129.277
126.700
122.360
116.284
114.465
63.389
55.858
55.589
51.358
30.590
30.419
30.225
30.033
29.840
29.648
29.456
29.262
12.892
134.005
133.750
131.764
130.780
130.035
129.645
129.445
129.277
126.700
135 134 133 132 131 130 129 128 127 126
f1 (ppm)
Ph
N
O
NHPMP
N
Bn
OTf⁻
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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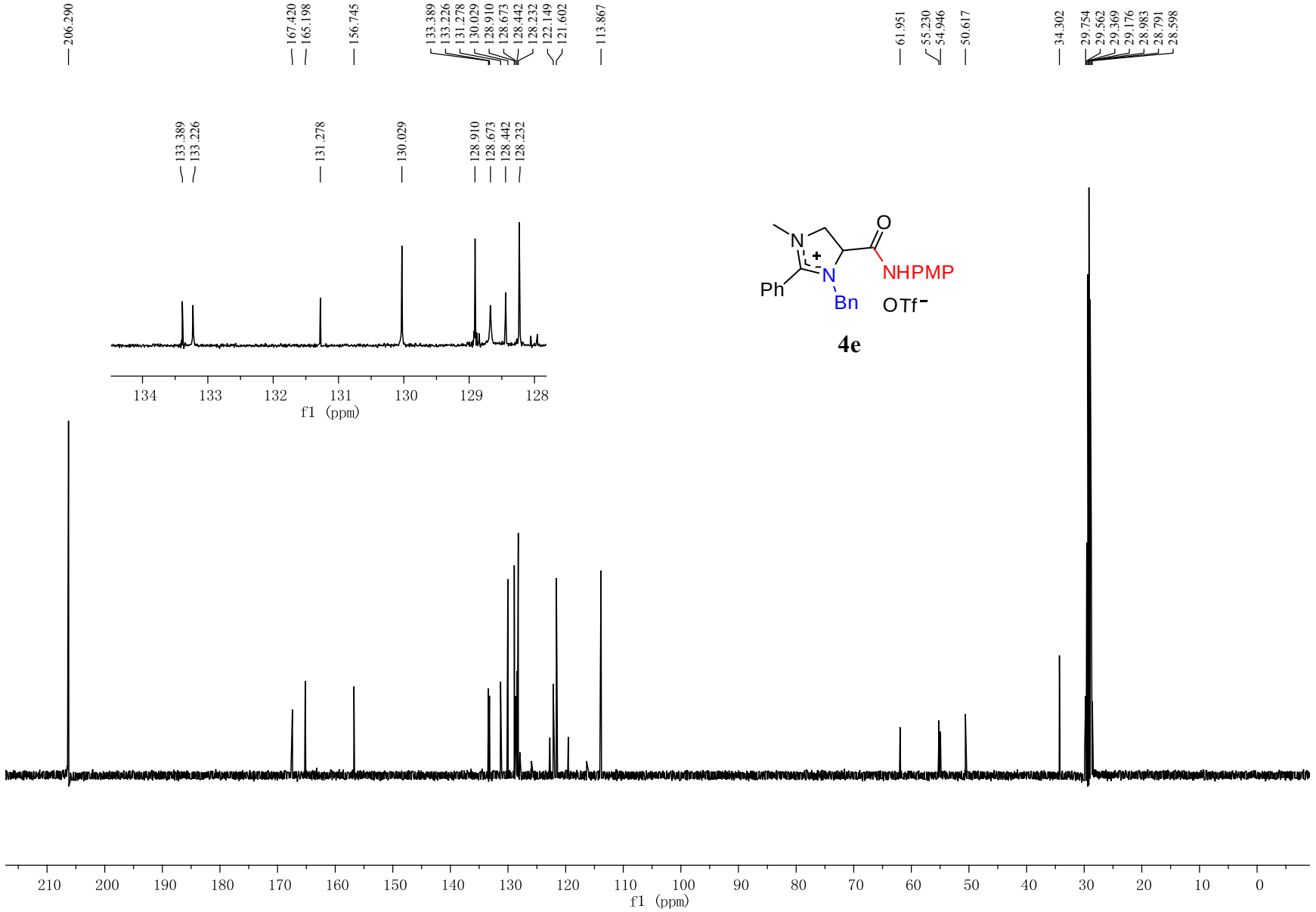
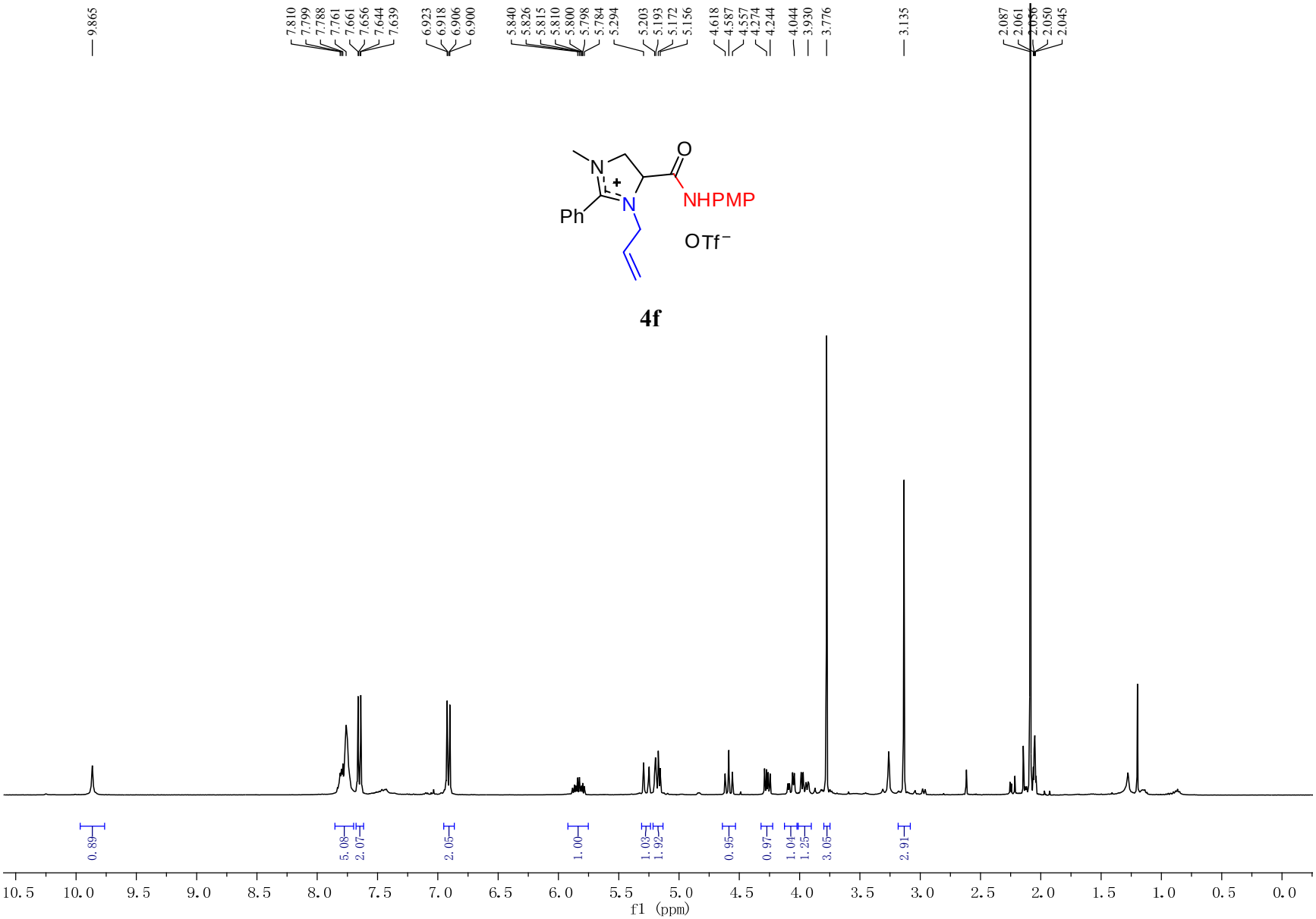
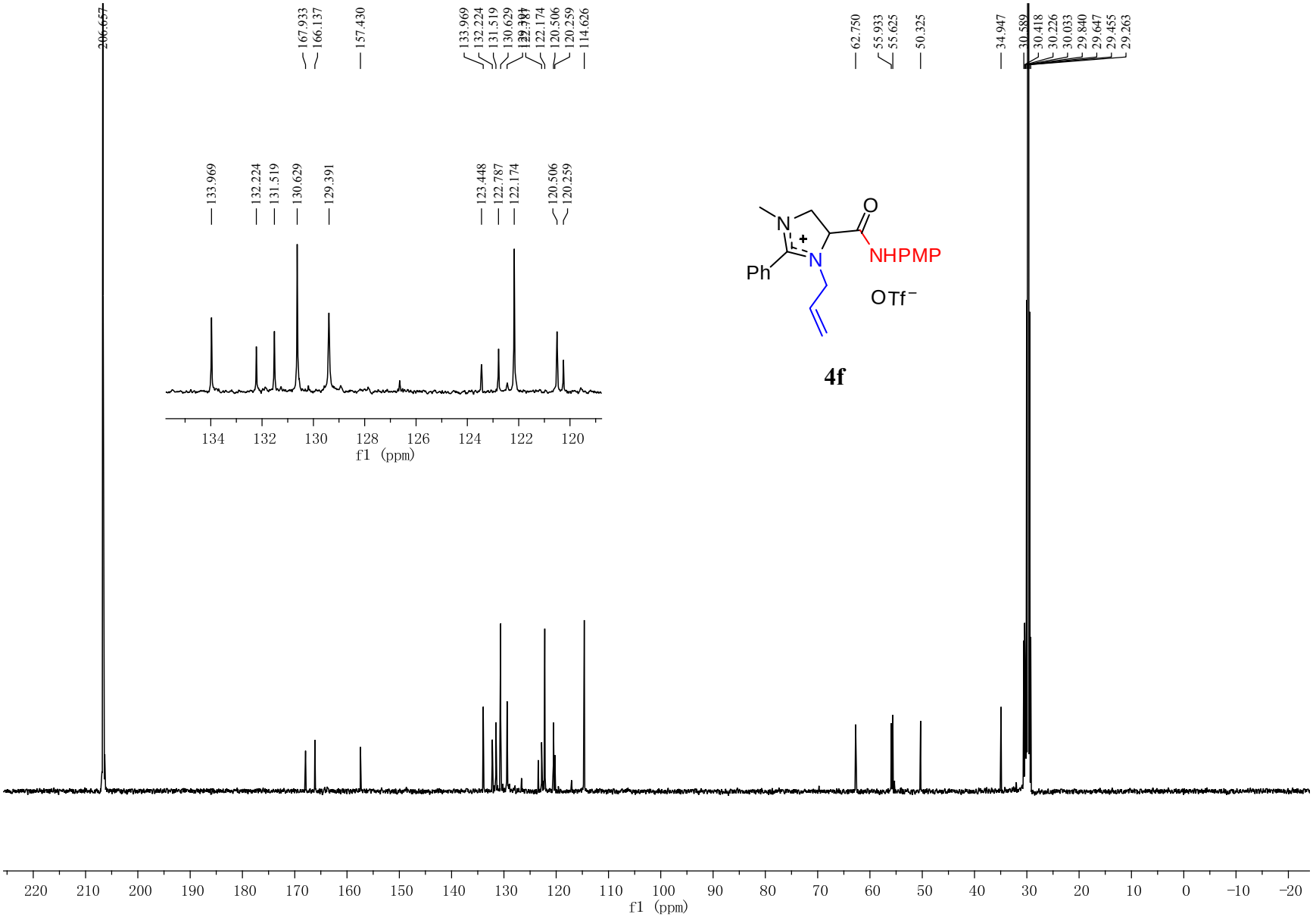
7.770
7.754
7.737
7.720
7.539
7.285
7.277
6.894
6.872
5.068
5.051
5.037
5.021
4.650
4.599
4.526
4.305
4.275
4.259
3.761
3.329
3.136
2.086
2.061
2.055
2.050
2.044
2.039
O
N
NHPMP
Ph
N
Bn
OTf⁻
0.97
5.13
2.00
5.12
2.03
1.00
3.50
1.01
3.16
3.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

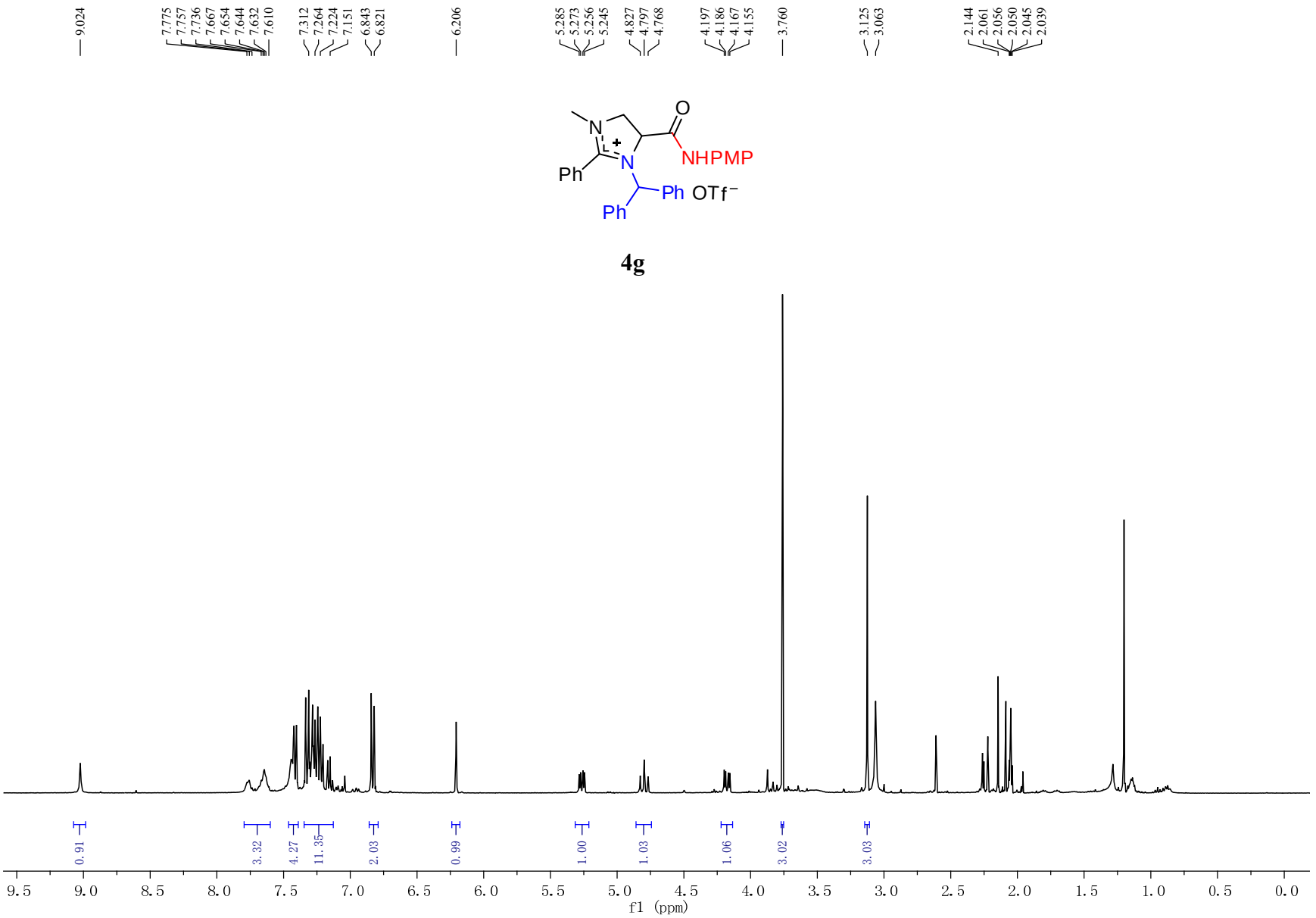
4e


206.290
167.420
165.198
156.745
133.389
133.226
131.278
130.029
128.910
128.673
128.442
128.232
122.149
121.602
113.867
61.951
55.230
54.946
50.617
34.302
29.754
29.562
29.369
29.176
28.983
28.791
28.598
f1 (ppm)
Ph
N
O
NHPMP
Bn
OTf⁻
4e

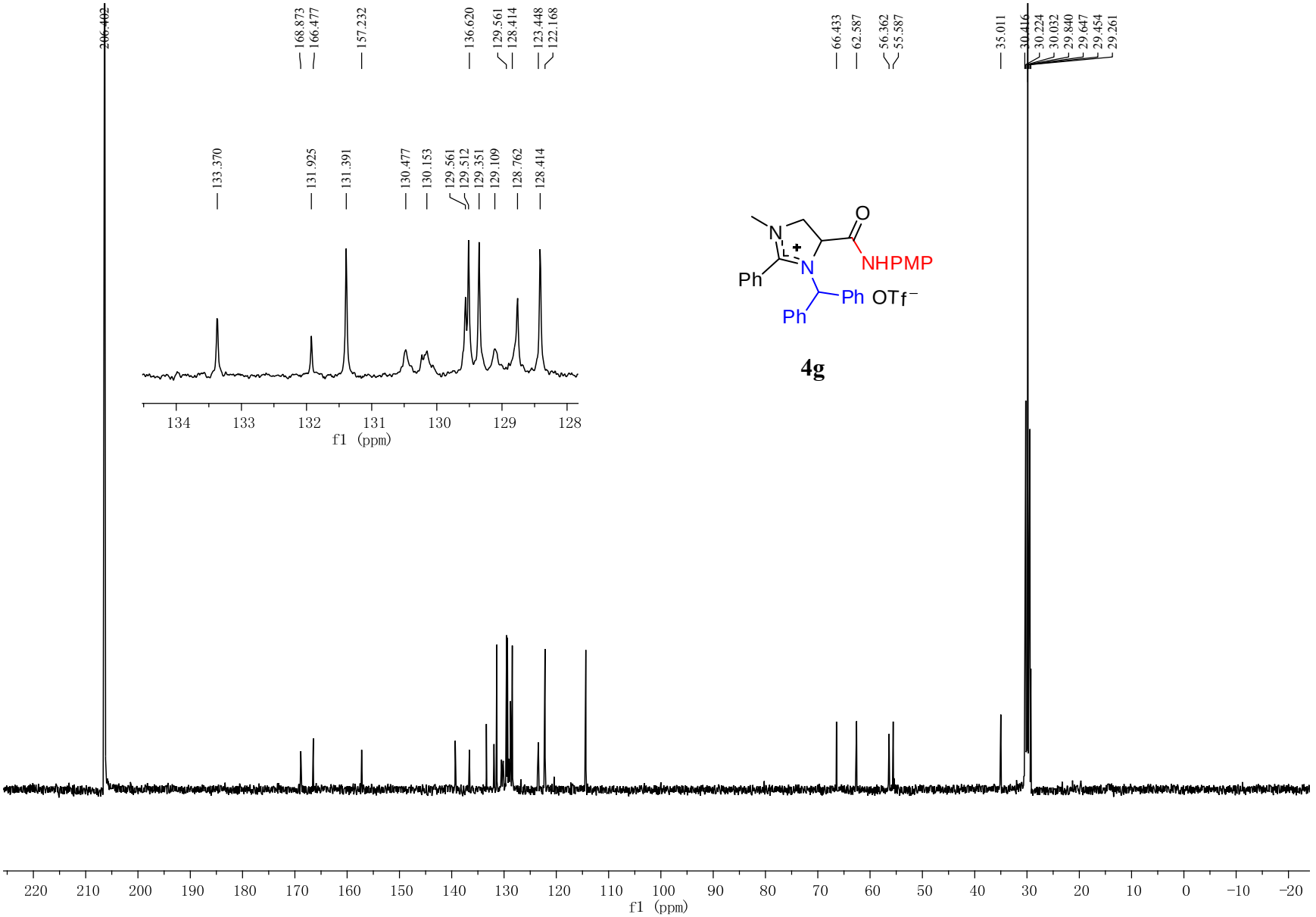

9.865
7.810
7.799
7.788
7.761
7.661
7.656
7.644
7.639
6.923
6.918
6.906
6.900
5.840
5.826
5.815
5.810
5.800
5.798
5.784
5.294
5.203
5.193
5.172
5.156
4.618
4.587
4.557
4.274
4.244
4.044
3.930
3.776
3.135
2.087
2.061
2.036
2.050
2.045
O
N
N
Ph
NHPMP
OTf⁻
0.89
5.08
2.07
2.05
1.00
1.03
1.92
0.95
0.97
1.04
1.25
3.05
2.91
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4f

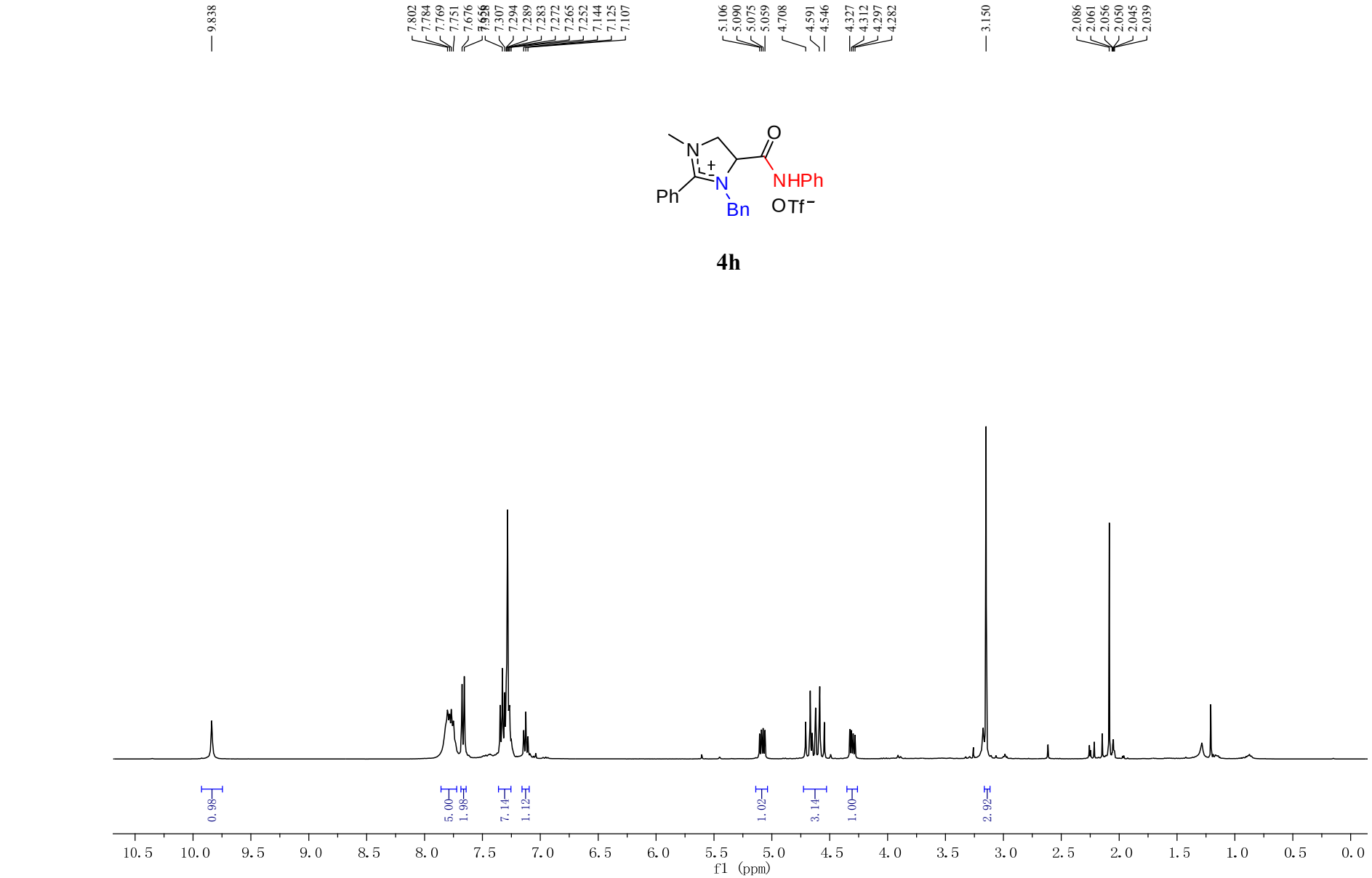

206.657
167.933
166.137
157.430
133.969
132.224
131.519
130.629
129.391
123.448
122.787
122.174
120.506
120.259
114.626
62.750
55.933
55.625
50.325
34.947
30.589
30.418
30.226
30.033
29.840
29.647
29.455
29.263
f1 (ppm)
Ph
N
O
NHPMP
OTf⁻
4f


9.024
7.775
7.757
7.736
7.667
7.654
7.644
7.632
7.610
7.312
7.264
7.224
7.151
6.843
6.821
6.206
5.285
5.273
5.256
5.245
4.827
4.797
4.768
4.197
4.186
4.167
4.155
3.760
3.125
3.063
2.144
2.061
2.056
2.050
2.045
2.039
O
N
NHPMP
Ph
N
Ph
Ph
OTf⁻
0.91
3.32
4.27
11.35
2.03
0.99
1.00
1.03
1.06
3.02
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

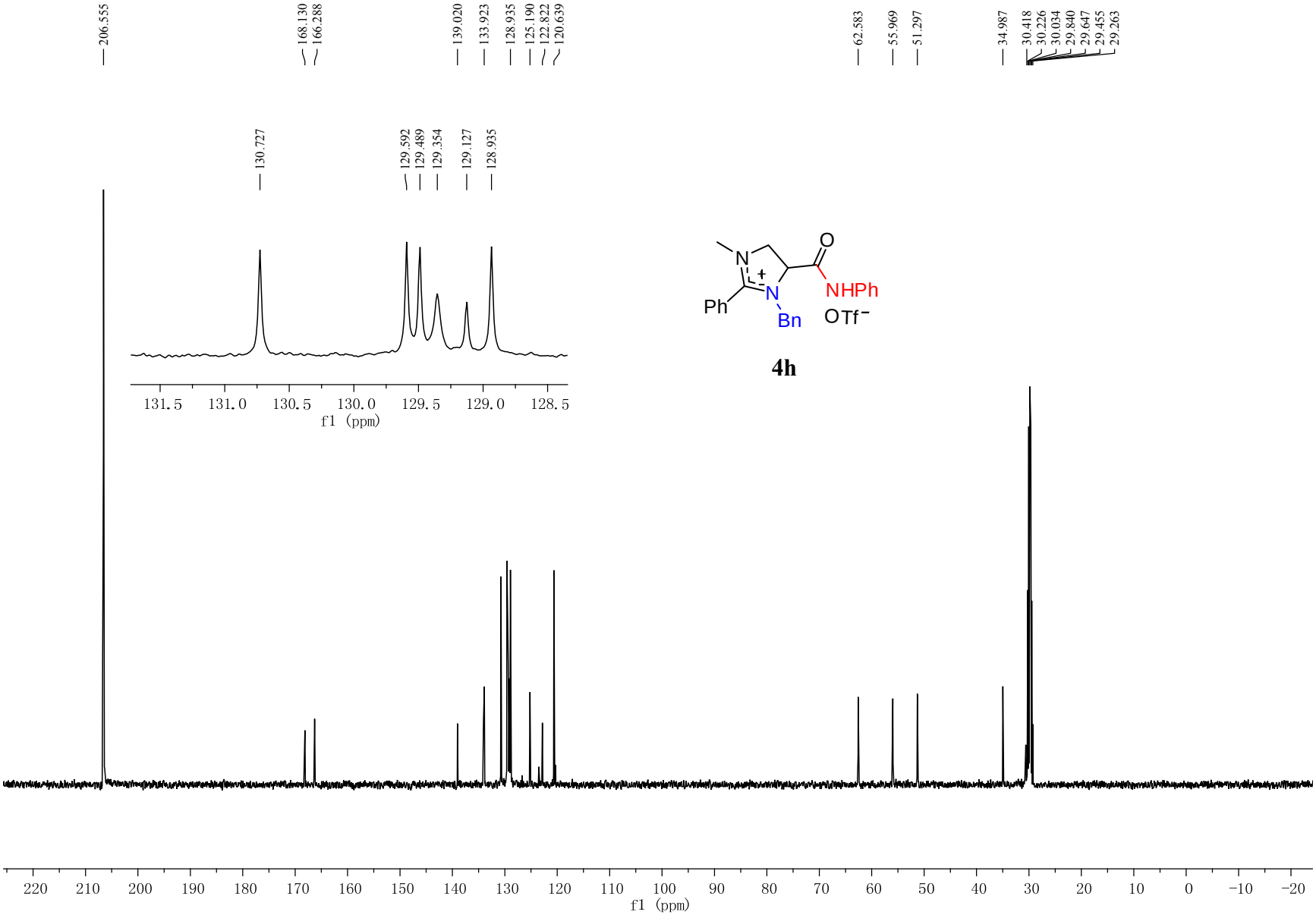
4g

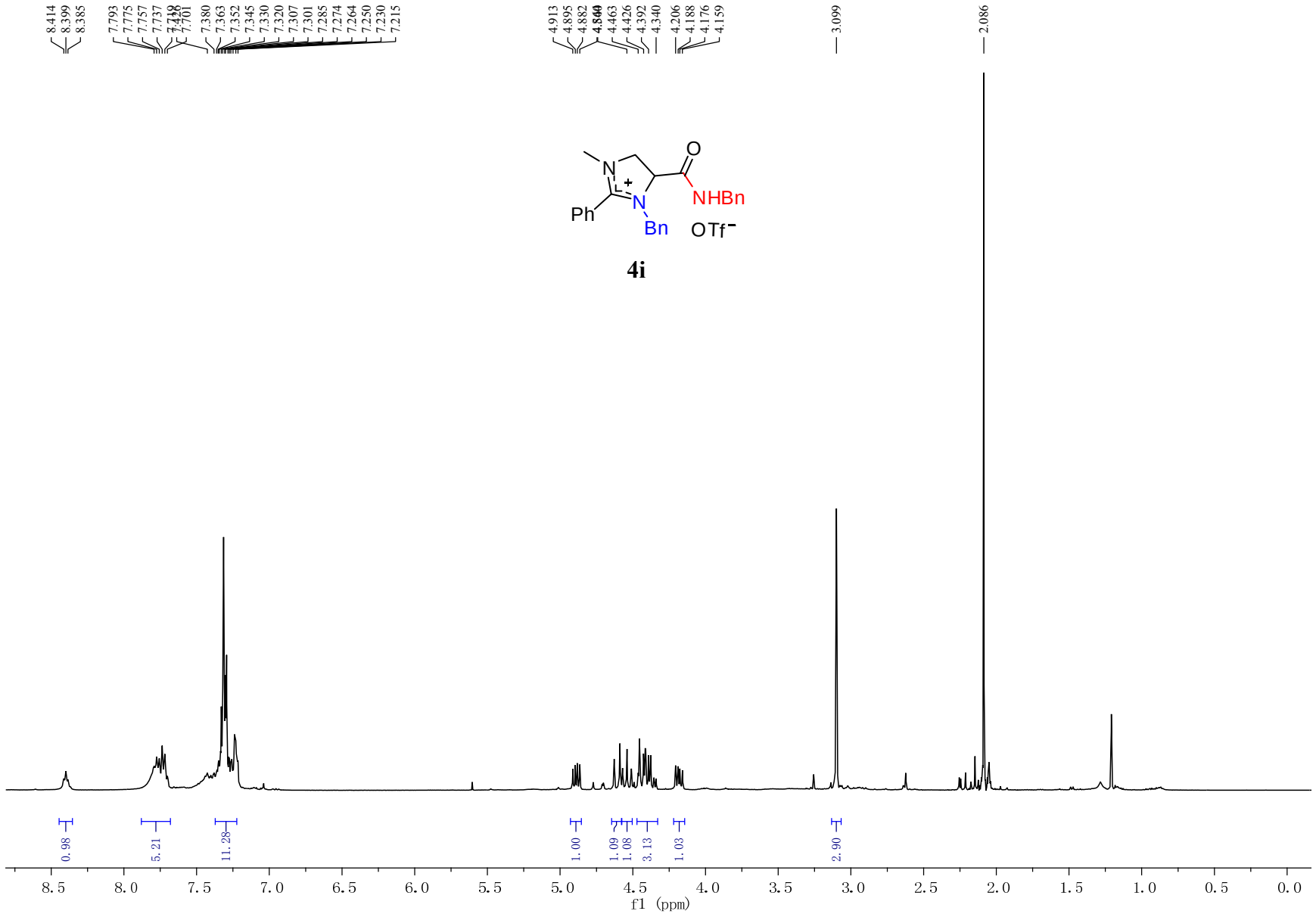

206.402
168.873
166.477
157.232
136.620
129.561
128.414
123.448
122.168
66.433
62.587
56.362
55.587
35.011
30.416
30.224
30.032
29.840
29.647
29.454
29.261
133.370
131.925
131.391
130.477
130.153
129.561
129.512
129.351
129.109
128.762
128.414
134
133
132
131
130
129
128
f1 (ppm)
O
N
Ph
N
NHPMP
Ph
Ph
OTf⁻
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

4g

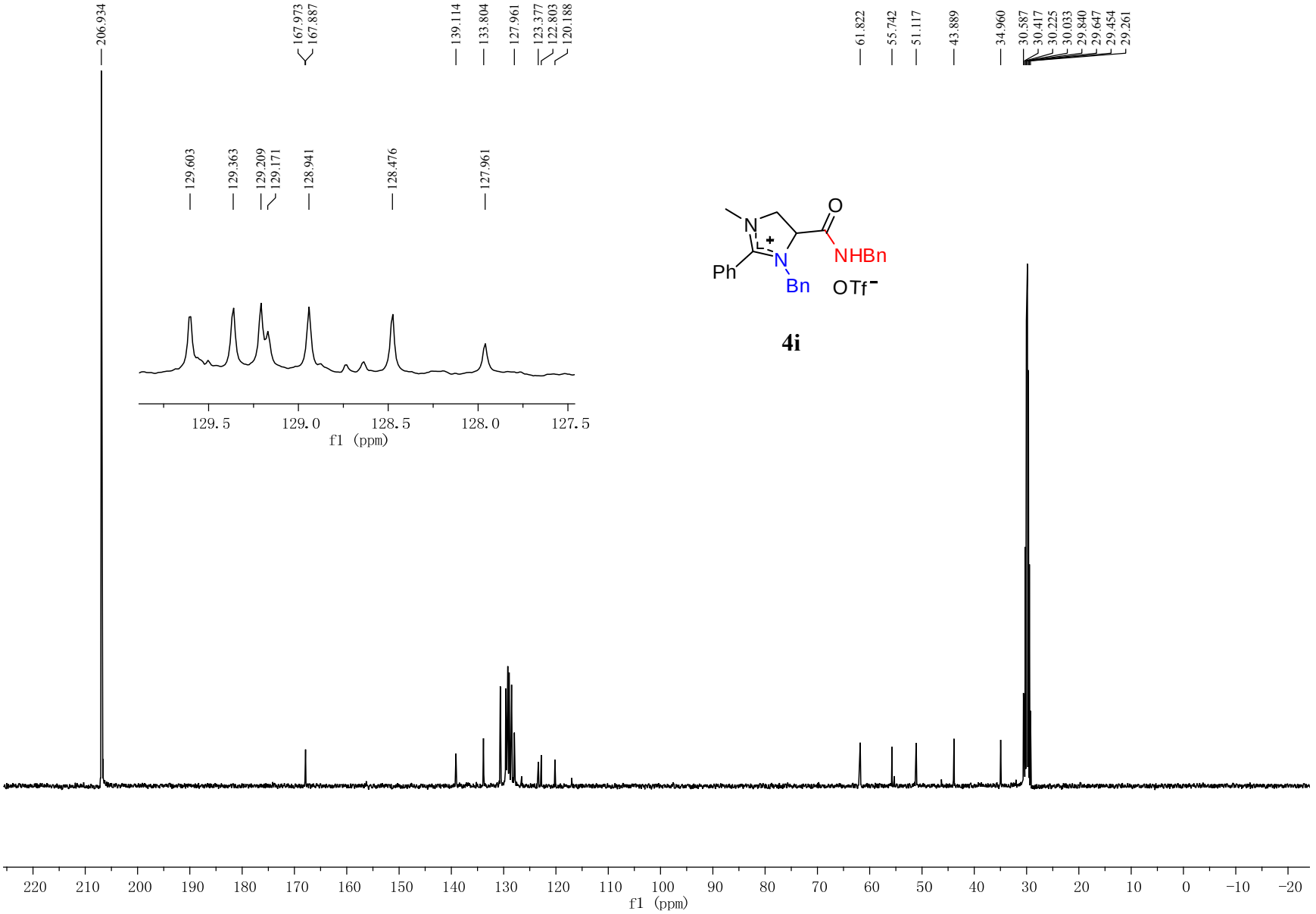

9.838
7.802
7.784
7.769
7.751
7.676
7.656
7.628
7.307
7.294
7.289
7.283
7.272
7.265
7.252
7.144
7.125
7.107
5.106
5.090
5.075
5.059
4.708
4.591
4.546
4.327
4.312
4.297
4.282
3.150
2.086
2.061
2.056
2.050
2.045
2.039
O
N
+
N
NHPh
Ph
Bn
OTf⁻
0.98
5.00
1.98
7.14
1.12
1.02
3.14
1.00
2.92
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

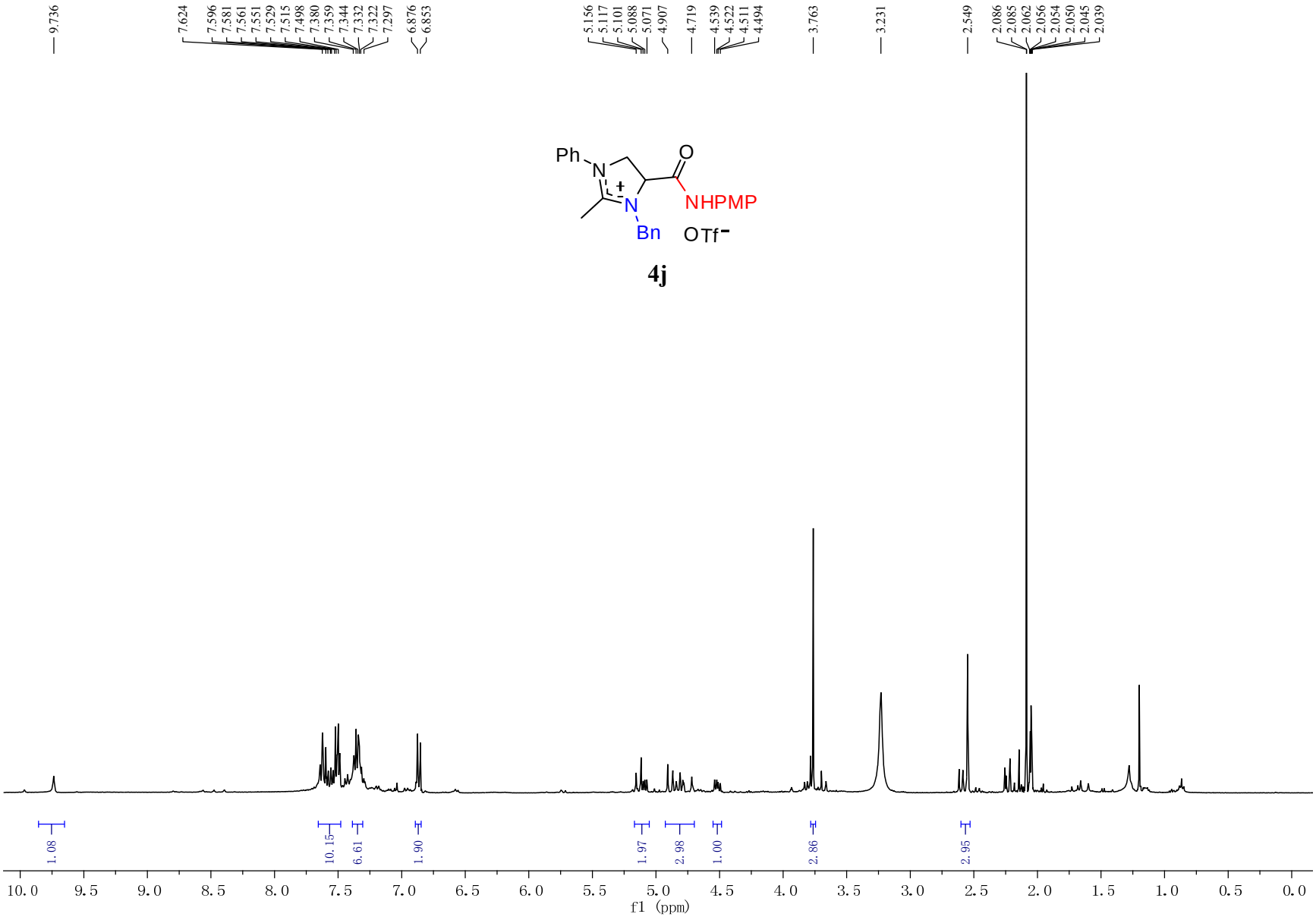
4h


206.555
168.130
166.288
139.020
133.923
128.935
125.190
122.822
120.639
62.583
55.969
51.297
34.987
30.418
30.226
30.034
29.840
29.647
29.455
29.263
130.727
129.592
129.489
129.354
129.127
128.935
131.5
131.0
130.5
130.0
129.5
129.0
128.5
f1 (ppm)
O
N
+
N
NHPh
Ph
Bn
OTf⁻
4h
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

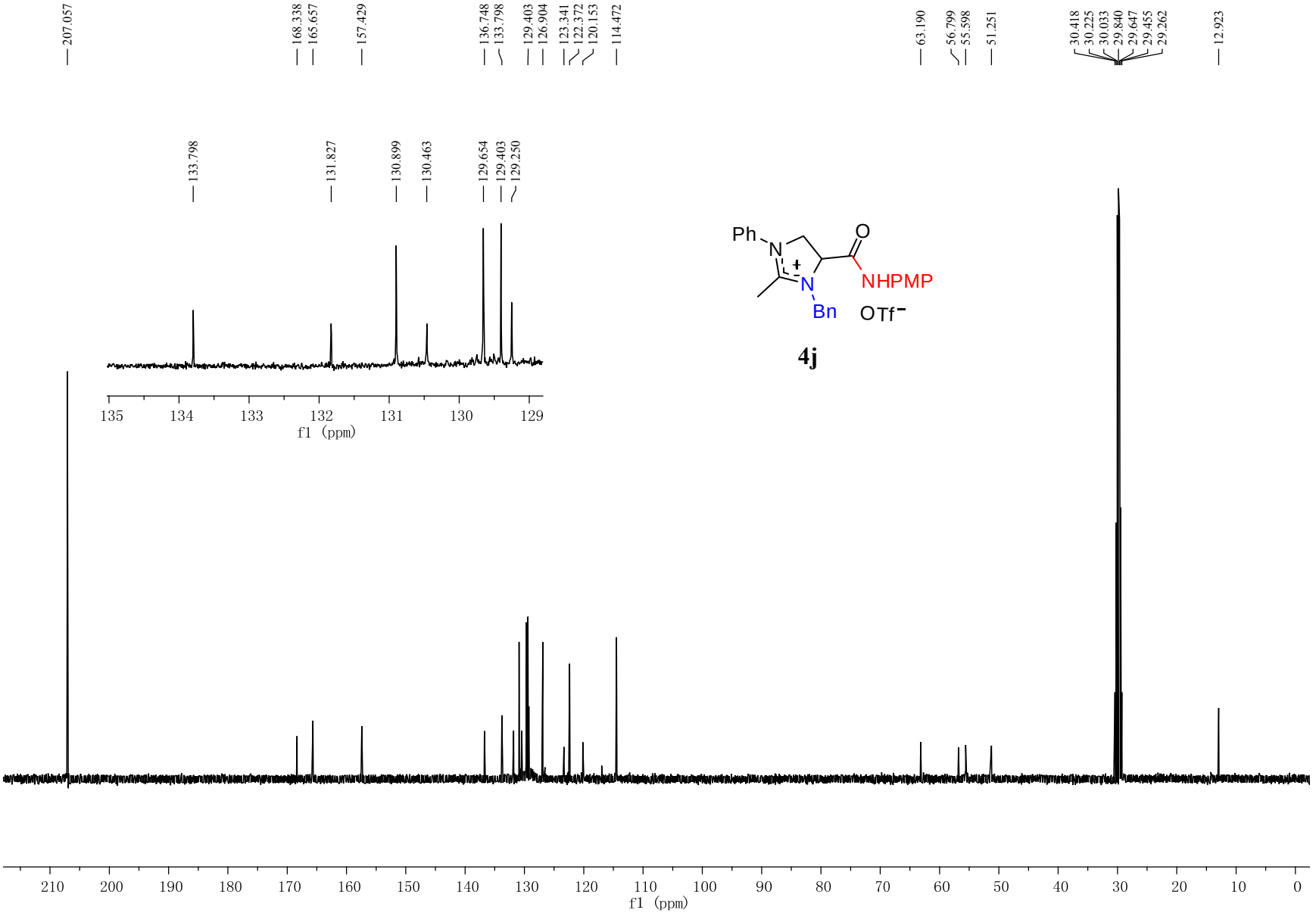

8.414
8.399
8.385
7.793
7.775
7.757
7.737
7.701
7.380
7.363
7.352
7.345
7.330
7.320
7.307
7.301
7.285
7.274
7.264
7.250
7.230
7.215
4.913
4.895
4.882
4.463
4.426
4.392
4.340
4.206
4.188
4.176
4.159
3.099
2.086
O
N
Ph
N
Bn
NHBn
OTf⁻
0.98
5.21
11.28
1.00
1.09
1.08
3.13
1.03
2.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

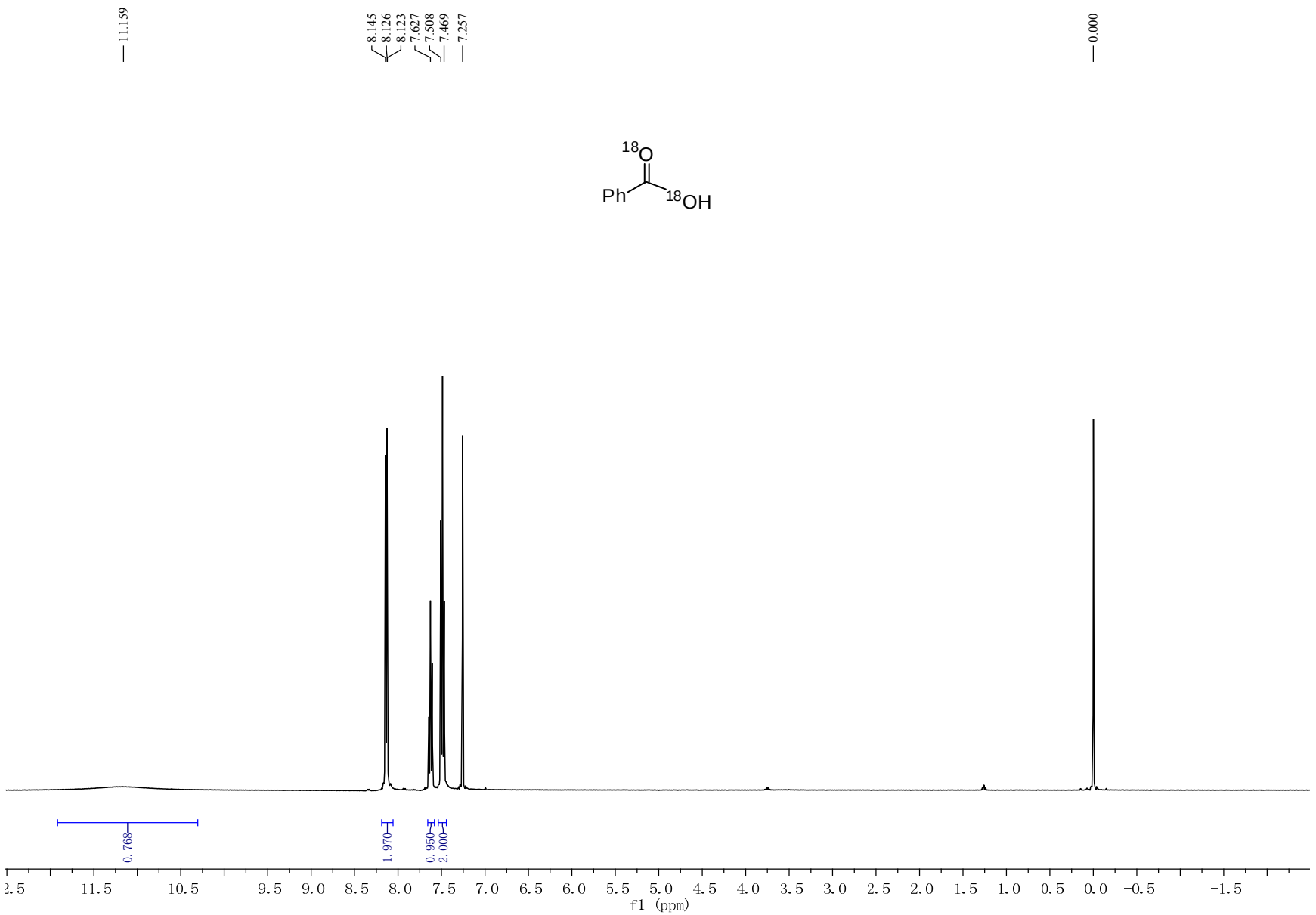
4i

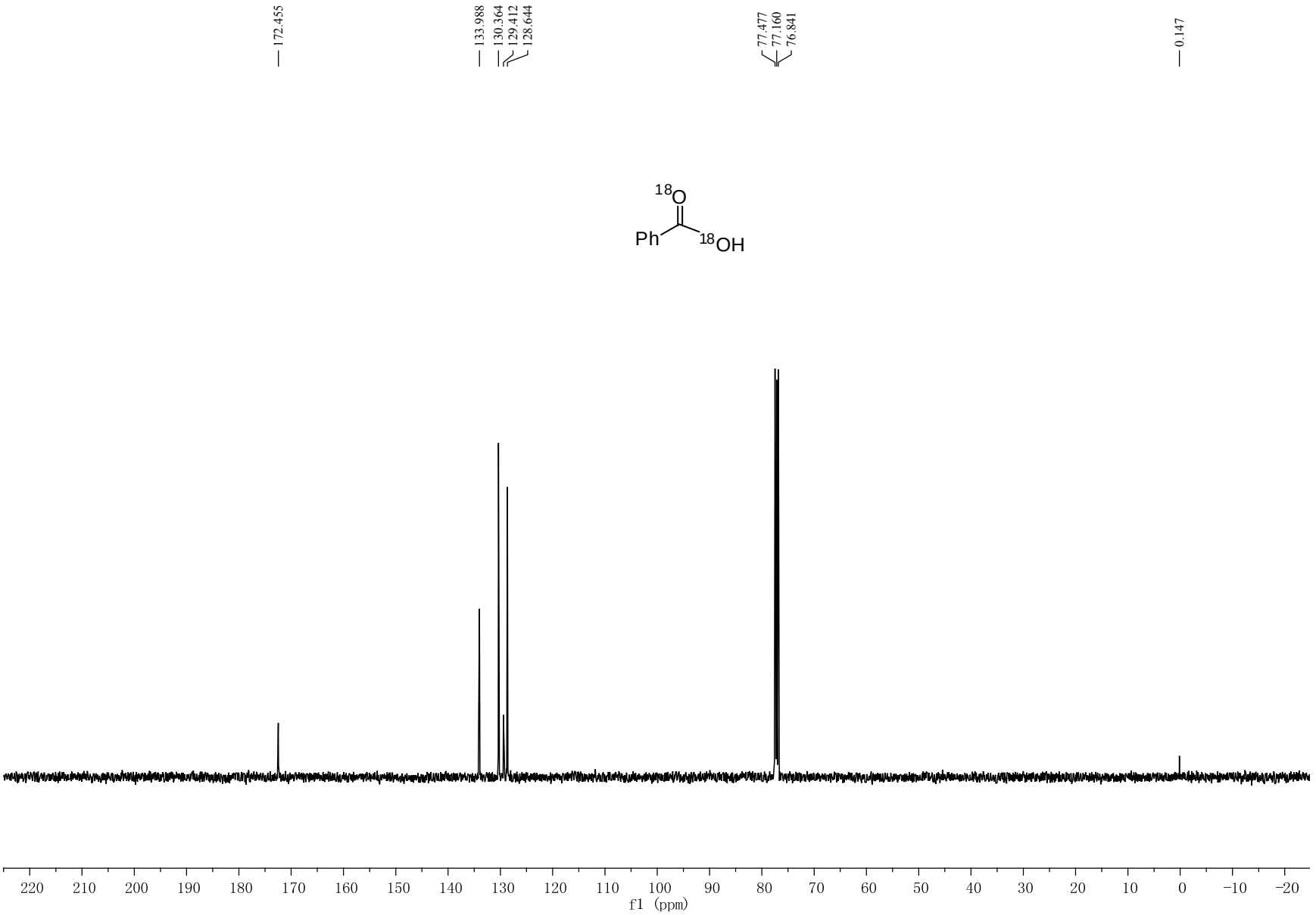

206.934
167.973
167.887
139.114
133.804
127.961
123.377
122.803
120.188
61.822
55.742
51.117
43.889
34.960
30.587
30.417
30.225
30.033
29.840
29.647
29.454
29.261
129.603
129.363
129.209
129.171
128.941
128.476
127.961
129.5
129.0
128.5
128.0
127.5
f1 (ppm)
O
N
Ph
N
Bn
NHBn
OTf
4i
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

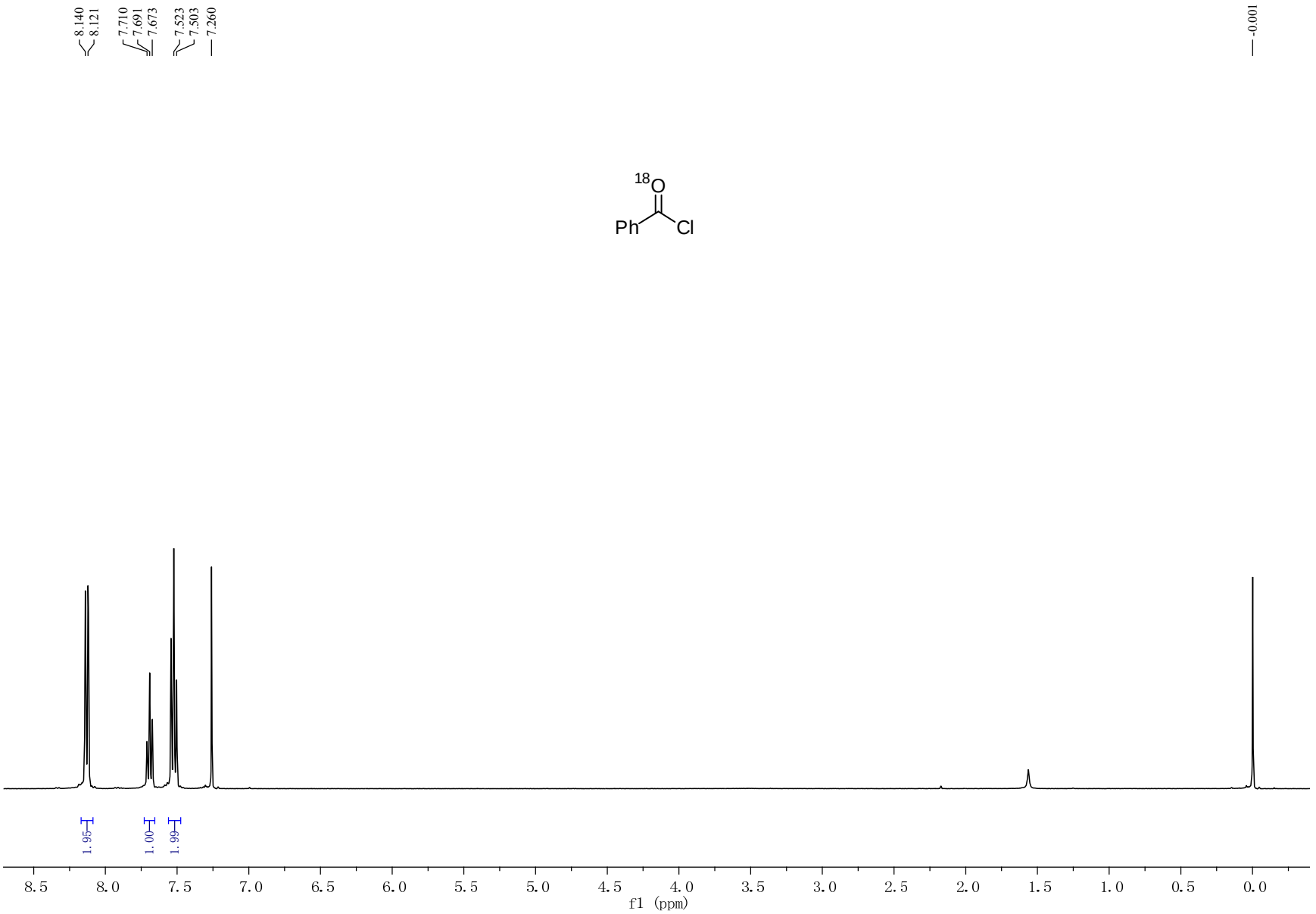

9.736
7.624
7.596
7.581
7.561
7.551
7.529
7.515
7.498
7.380
7.359
7.344
7.332
7.322
7.297
6.876
6.853
5.156
5.117
5.101
5.088
5.071
4.907
4.719
4.539
4.522
4.511
4.494
3.763
3.231
2.549
2.086
2.085
2.062
2.056
2.054
2.050
2.045
2.039
Ph
N
O
NHPMP
N
Bn
OTf
1.08
10.15
6.61
1.90
1.97
2.98
1.00
2.86
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

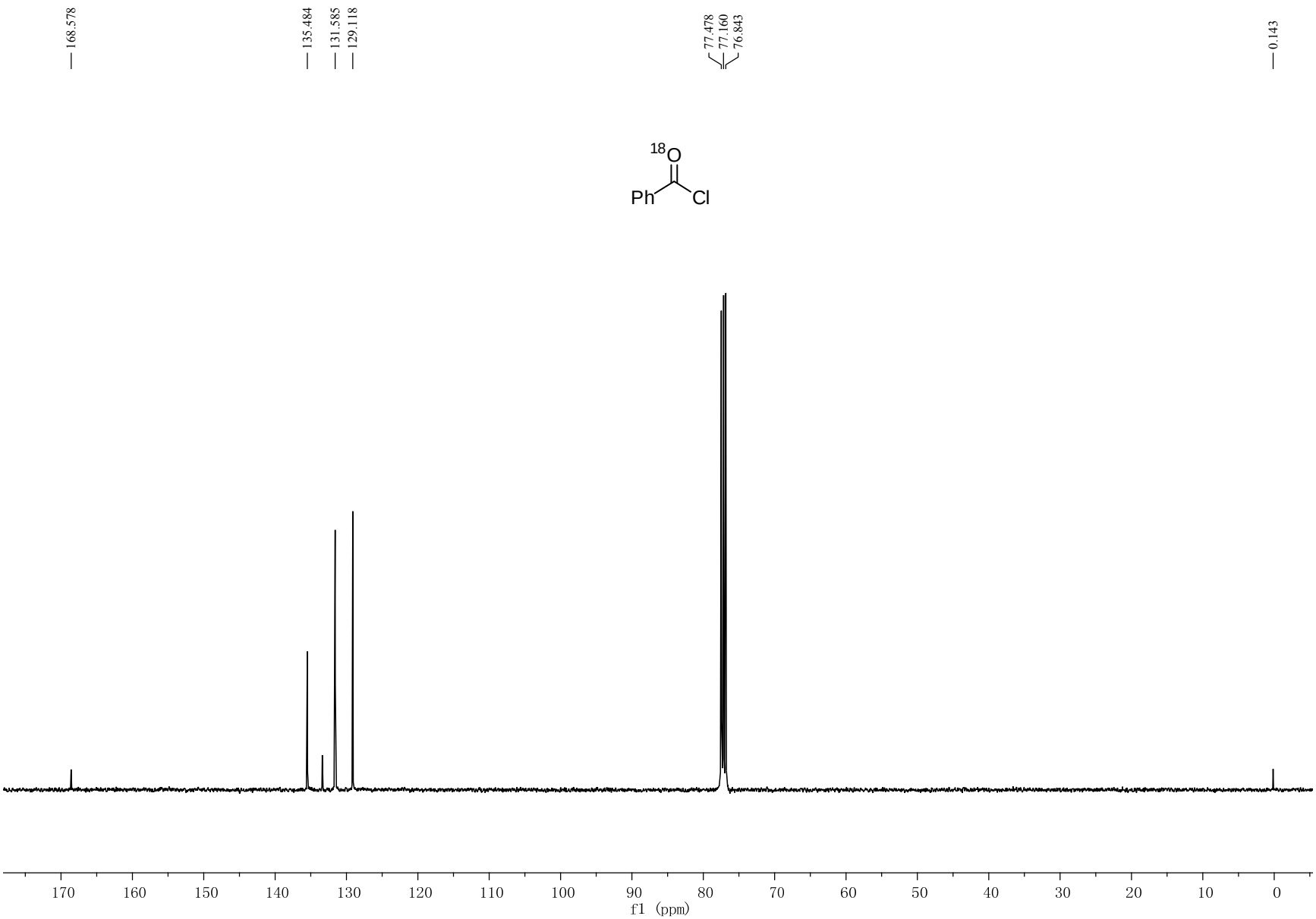
4j

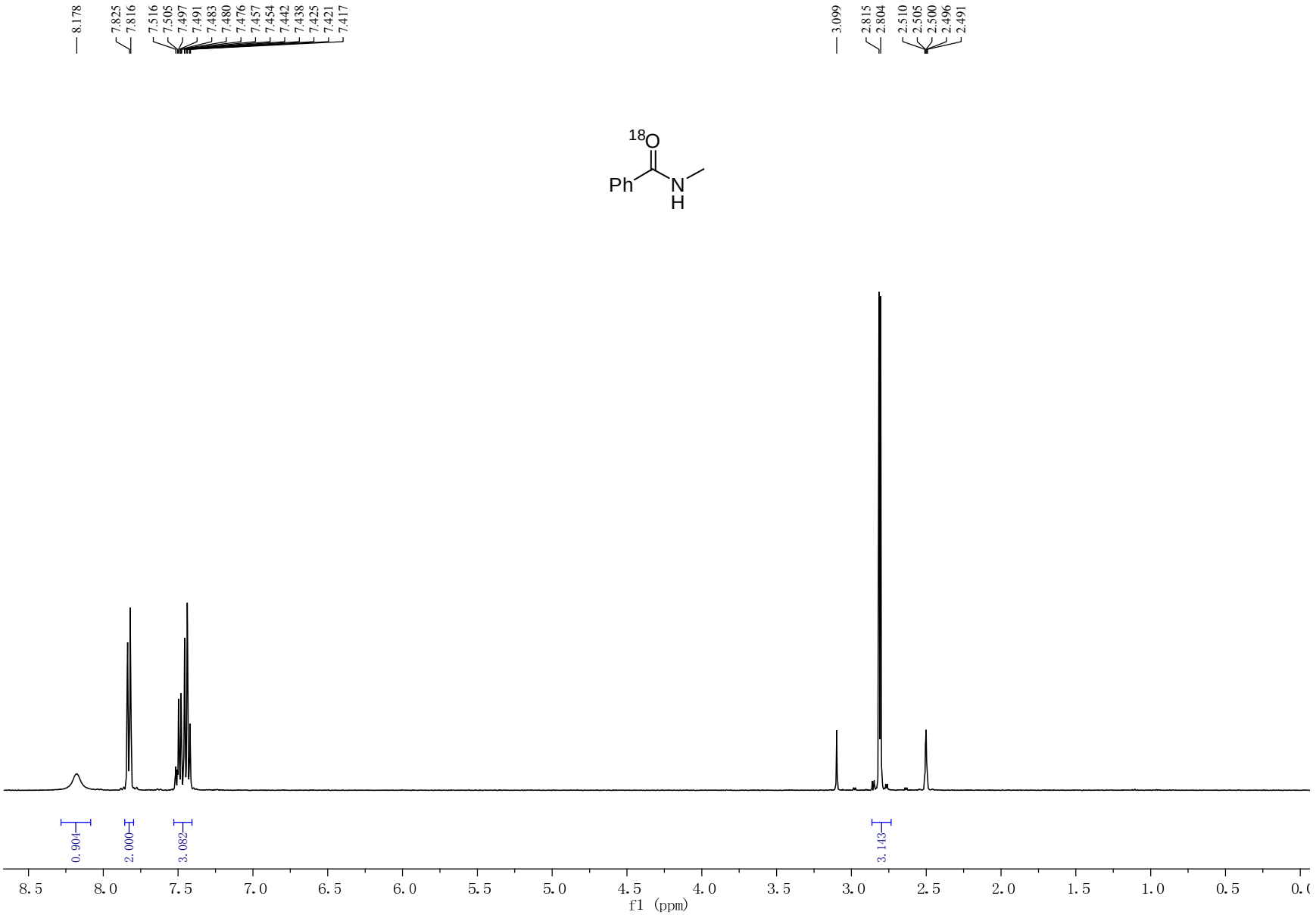

207.057
168.338
165.657
157.429
136.748
133.798
129.403
126.904
123.341
122.372
120.153
114.472
63.190
56.799
55.598
51.251
30.418
30.225
30.033
29.840
29.647
29.455
29.262
12.923
133.798
131.827
130.899
130.463
129.654
129.403
129.250
135
134
133
132
131
130
129
f1 (ppm)
Ph
N
O
NHPMP
N
Bn
OTf⁻
4j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

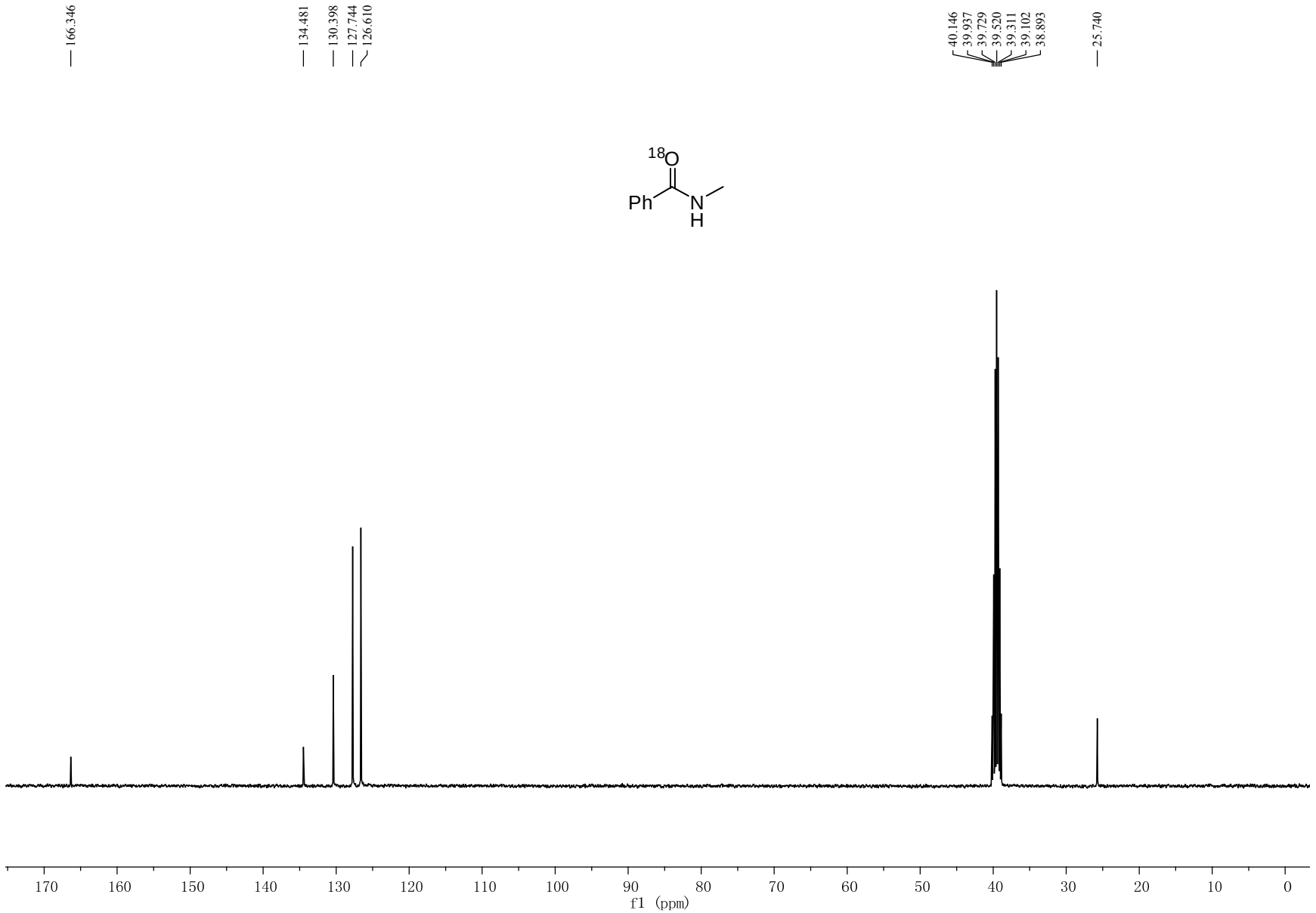

11.159
8.145
8.126
8.123
7.627
7.508
7.469
7.257
0.000
18O
Ph
18OH
0.768
1.970
0.950
2.000
f1 (ppm)

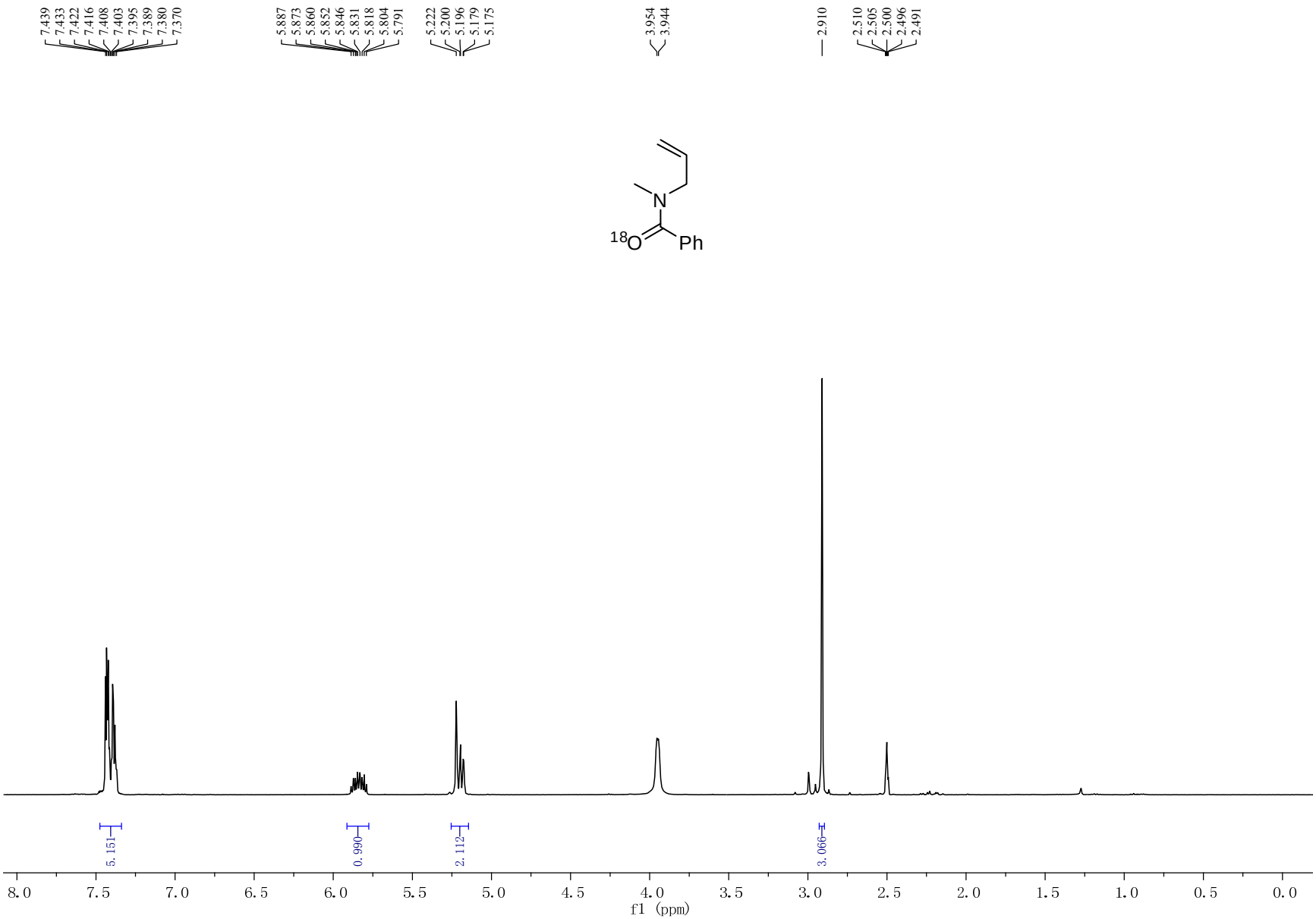

172.455
133.988
130.364
129.412
128.644
77.477
77.160
76.841
0.147
18O
Ph
18OH
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

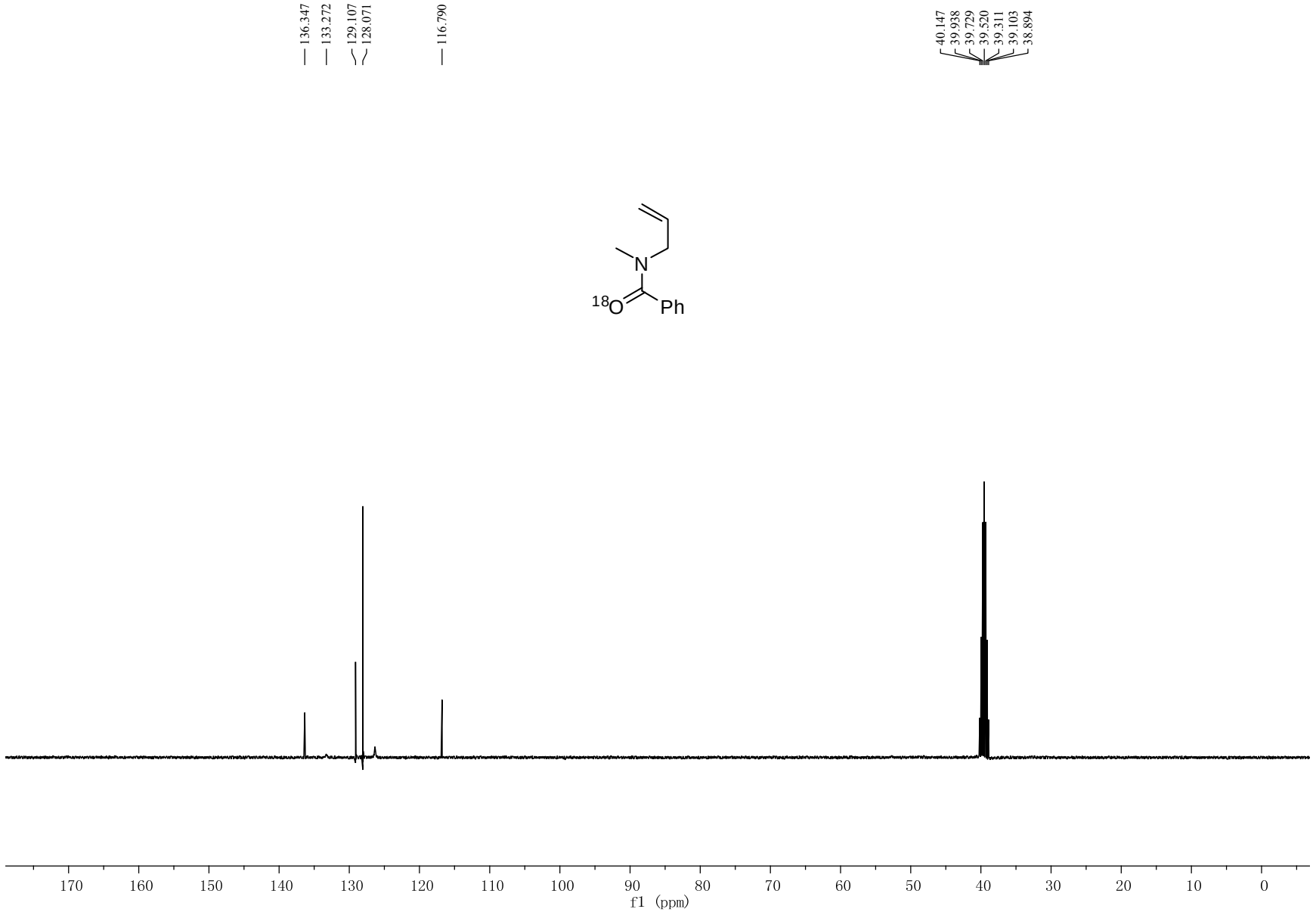

8.140
8.121
7.710
7.691
7.673
7.523
7.503
7.260
-0.001
18O
Ph
Cl
1.95
1.00
1.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

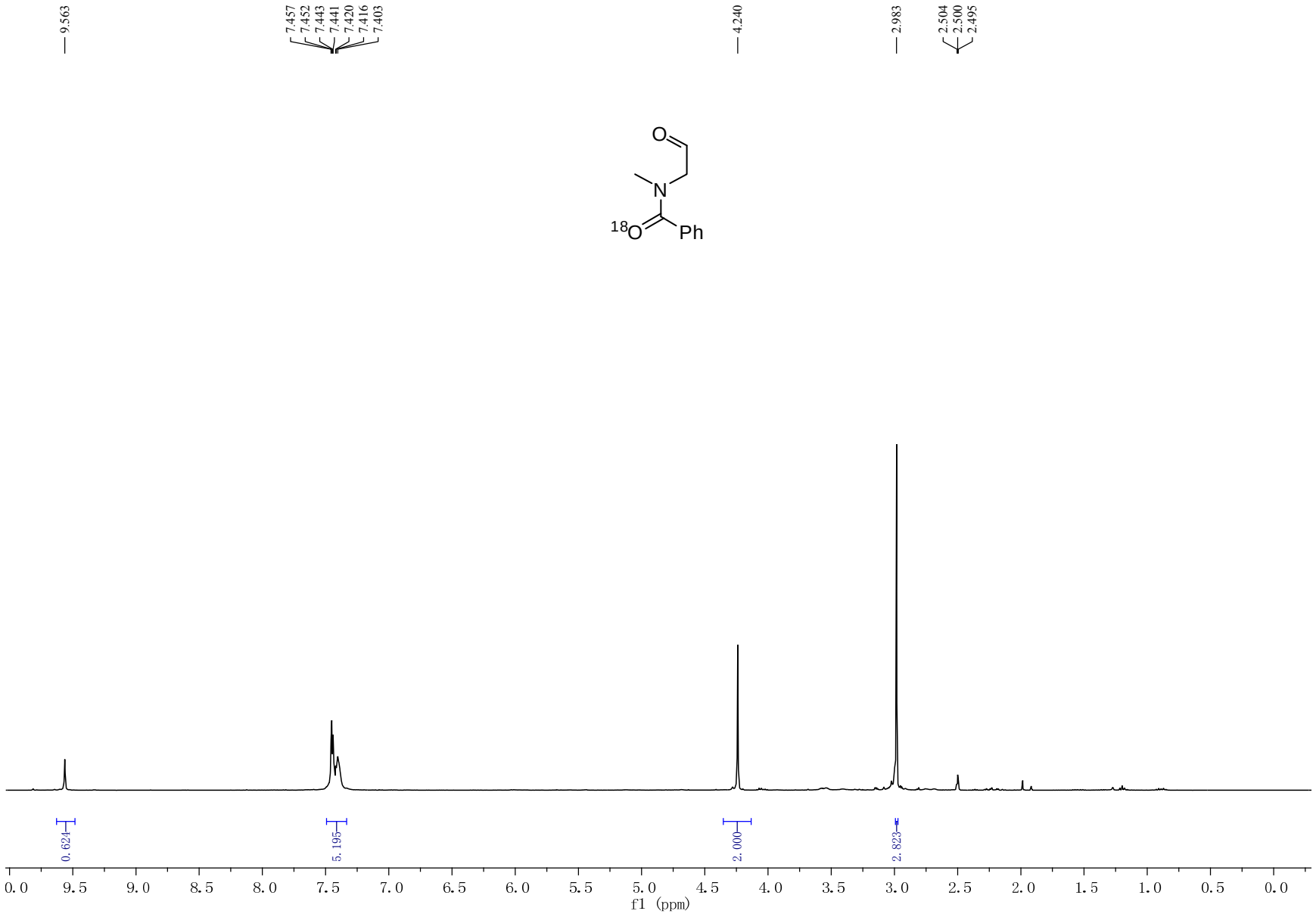

168.578
135.484
131.585
129.118
77.478
77.160
76.843
0.143
18O
Ph
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

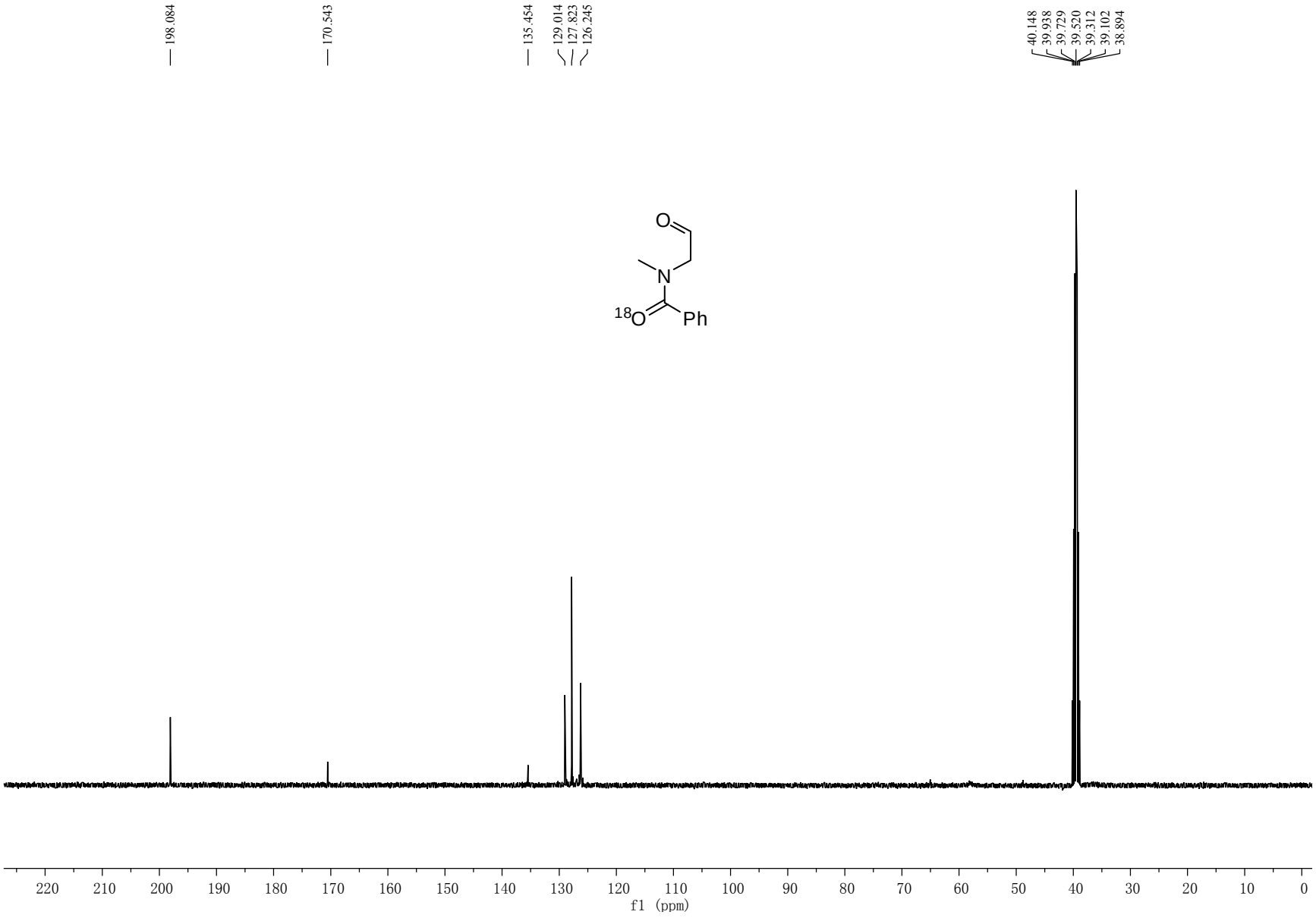

8.178
7.825
7.816
7.516
7.505
7.497
7.491
7.483
7.480
7.476
7.457
7.454
7.442
7.438
7.425
7.421
7.417
3.099
2.815
2.804
2.510
2.505
2.500
2.496
2.491
18O
Ph
N
H
0.904
2.000
3.082
3.143
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


166.346
134.481
130.398
127.744
126.610
40.146
39.937
39.729
39.520
39.311
39.102
38.893
25.740
18O
Ph
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.439
7.433
7.422
7.416
7.408
7.403
7.395
7.389
7.380
7.370
5.887
5.873
5.860
5.852
5.846
5.831
5.818
5.804
5.791
5.222
5.200
5.196
5.179
5.175
3.954
3.944
2.910
2.510
2.505
2.500
2.496
2.491
N
18O
Ph
5.151
0.990
2.112
3.066
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


136.347
133.272
129.107
128.071
116.790
40.147
39.938
39.729
39.520
39.311
39.103
38.894
N
18O
Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.563
7.457
7.452
7.443
7.441
7.420
7.416
7.403
4.240
2.983
2.504
2.500
2.495
O
N
18O
Ph
0.624
5.195
2.000
2.823
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.084
170.543
135.454
129.014
127.823
126.245
40.148
39.938
39.729
39.520
39.312
39.102
38.894
O
N
18O
Ph
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)