Supporting Information

σ-bond Hydroboration of Cyclopropanes

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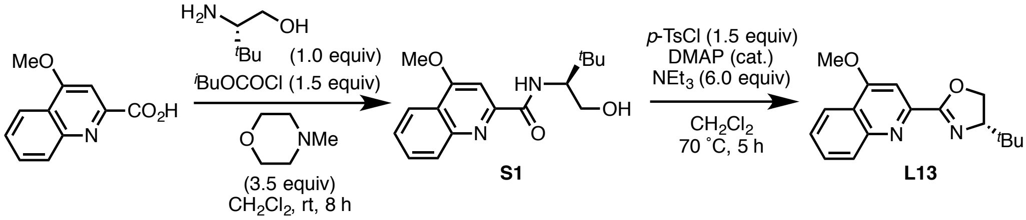
1. General

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. $[Ir(OMe)(cod)]_2$, [Ir(cod)(acac)], $PdCl_2(dppf)\cdot CH_2Cl_2$ and cyclopropylbenzene (**1o**) were obtained from Wako Chemicals. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (HBpin) and quinoline (**L6**) were obtained from TCI. $[Ir(OMe)(cod)]_2$, (*S*)-4-(*tert*-butyl)-2-(2-(diphenylphosphaneyl)phenyl)-4,5-dihydrooxazole (**L4**) and 2,2'-biquinoline (**L7**) were obtained from Sigma-Aldrich. (*S*)-4-(*tert*-Butyl)-2-(quinolin-2-yl)-4,5-dihydrooxazole (^{t}BuQuinox: **L1**),[1] (*S*)-4-(*tert*-butyl)-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L2**),[2] (*S*)-4-(*tert*-butyl)-2-(isoquinolin-1-yl)-4,5-dihydrooxazole (**L3**),[3] (4*S*,4'*S*)-4,4'-di-*tert*-butyl-4,4',5,5'-tetrahydro-2,2'-bioxazole (**L5**),[4] (*S*)-4-isopropyl-2-(quinolin-2-yl)-4,5-dihydrooxazole (^{i}PrQuinox: **L8**),[5] (*S*)-4-methyl-2-(quinolin-2-yl)-4,5-dihydrooxazole (MeQuinox: **L9**),[6] 2-(quinolin-2-yl)-4,5-dihydrooxazole (Quinox: **L10**),[6] (*S*)-4-phenyl-2-(quinolin-2-yl)-4,5-dihydrooxazole (PhQuinox: **L11**),[7] 4,4-dimethyl-2-(quinolin-2-yl)-4,5-dihydrooxazole (Me_2Quinox: **L12**),[8] (*S*)-4-(*tert*-butyl)-2-(6-methylpyridin-2-yl)-4,5-dihydrooxazole (**L17**),[9] (4*S*,4'*S*)-4,4'-diisopropyl-4,4',5,5'-tetrahydro-2,2'-bioxazole (**L18**),[10] 4-methylquinoline-2-carbonitrile,[10] 4-(trifluoromethyl)quinolin-2(1*H*)-one,[11] 5-methoxyquinoline-2-carbonitrile,[12] *N*-cyclopropyl-2,2,2-trifluoroacetamide (**1d**),[13] methyl cyclopropylcarbamate (**1h**),[14] 1-cyclopropyl-4-methylbenzene (**1p**),[15] 1-chloro-4-cyclopropylbenzene (**1q**),[16] 1-cyclopropylnaphthalene (**1r**),[17] *N*-cyclopropylbenzamide (**1t**),[18] *N*-((1*S*,2*R*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)pivalamide (**4a**),[13] *N*-(prop-1-en-2-yl)benzamide,[19] 4,4,5,5-tetramethyl-2-(2-phenylallyl)-1,3,2-dioxaborolane,[20] 4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-*d* (DBpin)[21–23] were synthesized by known procedures and the spectra matched those of reported compounds in the literature. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in dried glassware using standard vacuum-line techniques. All hydroboration reactions were performed in 20-mL glass vessel tubes equipped with a J. Young® O-ring tap and heated in an oil bath or an 8-well reaction block (heater + magnetic stirrer). All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm) or phosphomolybdic acid/sulfuric acid solution. Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh) or Biotage Isolera® equipped with Biotage SNAP Cartridge KP-Sil columns using hexane/ethyl acetate as eluents. Medium pressure liquid chromatography (MPLC) was performed using Yamazen W-prep 2XY. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative gel permeation chromatography (GPC) was performed with a JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. LCMS analysis was conducted on an Agilent 6100 instrument equipped with Poroshell 120 EC-C18 column (2.1x100 mm, 2.7 μm) using acetonitrile/5 mM $HCOONH_4$ in water as an eluent. High-resolution mass spectra (HRMS) were obtained from Thermo Fisher Scientific Exactive (ESI) and JEOL JMS-T100TD instrument (DART). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 spectrometer (^{1}H 600 MHz, ^{13}C 151 MHz), a JEOL JNM-ECA-500 spectrometer (^{1}H 500 MHz, ^{13}C 126 MHz), a JEOL JNM-ECA-400 spectrometer (^{1}H 400 MHz, ^{13}C 101 MHz) and a JEOL JNM-ECS-400 (^{1}H 400 MHz, ^{19}F 376 MHz). Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or $(CD_3)_2SO$ (for solvent residual signal; δ 2.50 ppm) or $(CD_3)_2CO$ (for solvent residual signal; δ 2.05 ppm) or D_2O (for solvent residual signal; δ 4.79 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm) or $(CD_3)_2SO$ (δ 39.5 ppm) or $(CD_3)_2CO$ (δ 29.84 ppm). Chemical shifts for ^{19}F NMR are expressed in ppm relative to fluorobenzene (δ –113.6 ppm) as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, quin = quintet, sep = septet, m = multiplet, brs = broad singlet), coupling constant (Hz), and integration.

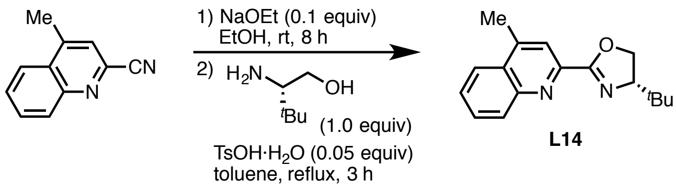
2. Preparation of Ligands



(*S*)-4-(*tert*-Butyl)-2-(4-methoxyquinolin-2-yl)-4,5-dihydrooxazole (L13)

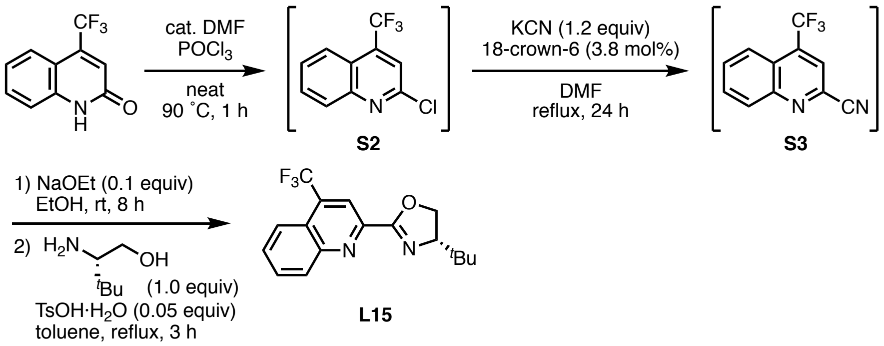
To a mixture of 4-methoxyquinoline-2-carboxylic acid (201 mg, 1.0 mmol) and 4-methylmorpholine (0.22 mL, 2.0 mmol) in dichloromethane (15 mL) was slowly added isobutyl chloroformate (0.20 mL, 1.5 mmol) at 0 °C and the resultant mixture was stirred at the same temperature for 30 min. (*S*)-2-Amino-3,3-dimethylbutan-1-ol (153 mg, 1.0 mmol) in dichloromethane (10 mL) and 4-methylmorpholine (0.16 mL, 1.5 mmol) were slowly added at 0 ˚C. The reaction mixture was stirred at room temperature for 8 h. The reaction mixture was diluted with saturated aqueous NH_4Cl and extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product **S1** was used in the next step without further purification.

To a solution of the crude amide **S1**, *N*,*N*-dimethylpyridin-4-amine (DMAP: 13.3 mg, 0.11 mmol) and 4-toluenesulfonyl chloride (*p*-TsCl: 292 mg, 1.5 mmol) in dichloromethane (40 mL) was slowly added triethylamine (0.85 mL, 6.1 mmol), then the reaction mixture was stirred at 70 °C for 5 h. After cooling to room temperature, the reaction mixture was diluted with H_2O and extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by Isolera® (hexane/ethyl acetate = 1:1). The collected fractions were purified again by PTLC ($CHCl_3$/acetone = 10:1) to afford **L13** (38.1 mg, 13% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 11.4, 8.4 Hz, 2H), 7.72 (td, *J* = 7.2, 1.8 Hz, 1H), 7.62 (s, 1H), 7.56 (dd, *J* = 8.4, 7.2 Hz, 1H), 4.54 (t, *J* = 9.0 Hz, 1H), 4.41 (t, *J* = 8.4 Hz, 1H), 4.21–4.10 (m, 4H), 1.01 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1, 162.6, 148.5, 148.1, 130.2, 129.9, 126.9, 121.8, 121.7, 99.7, 76.4, 69.6, 56.1, 34.1, 26.0; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{21}N_2O_2$ $[M+H]^+$: 285.1598, found 285.1599.



(*S*)-4-(*tert*-Butyl)-2-(4-methylquinolin-2-yl)-4,5-dihydrooxazole (L14)

To a solution of 4-methylquinoline-2-carbonitrile[10] (86.5 mg, 0.51 mmol) in EtOH (3.0 mL) was added NaOEt (3.5 mg, 0.05 mmol). The reaction mixture was stirred at room temperature for 8 h. After adding acetic acid (5.0 mL) to this mixture, the volatiles were removed *in vacuo*. The residue was diluted with dichloromethane (10 mL) and washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. A mixture of the crude product, (*S*)-2-amino-3,3-dimethylbutanol (60.0 mg, 0.51 mmol) and *p*-TsOH·H_2O (3.7 mg, 0.022 mmol) in toluene (5.0 mL) was refluxed for 3 h. After cooling to room temperature, saturated aqueous $NaHCO_3$ (10 mL) was added to the mixture, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 3:1 to 1:3) to give **L14** (74.8 mg, 55% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, J = 8.4 Hz, 1H), 8.11 (s, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.74 (td, J = 6.9, 1.2 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 4.53 (dd, J = 10.2, 9.0 Hz, 1H), 4.40 (t, J = 9.0 Hz, 1H), 4.18 (dd, J = 10.2, 8.4 Hz, 1H), 2.76 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9, 147.4, 146.6, 145.1, 130.9, 129.6, 128.8, 127.6, 123.6, 121.4, 76.5, 69.5, 34.1, 26.0, 18.7; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{21}N_2O$ [M+H]$^+$: 269.1648, found 269.1646.



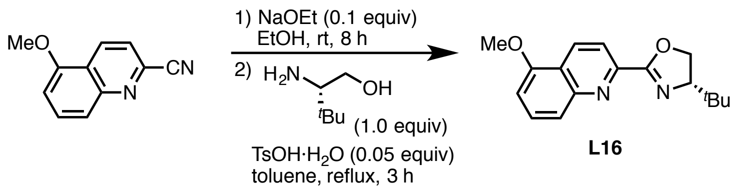
(*S*)-4-(*tert*-Butyl)-2-(4-(trifluoromethyl)quinolin-2-yl)-4,5-dihydrooxazole (L15)

To a 20 mL glass vessel with a magnetic stirring bar were placed 4-(trifluoromethyl)quinolin-2(1*H*)-one[11] (500 mg, 2.3 mmol), DMF (cat.) and $POCl_3$ (5 mL). The mixture was stirred at 90 °C for 1 h. After cooling to room temperature, the solution was concentrated *in vacuo* and poured into an ice-cold solution of $NaHCO_3$. The mixture was extracted with dichloromethane, then the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product **S2** weighed 474 mg (87% yield) and was used in the next step without further purification.

To a 20-mL glass vessel with a magnetic stirring bar were placed 2-chloro-4-(trifluoromethyl)quinoline (**S2**: 474 mg, 2.0 mmol), KCN (159 mg, 2.4 mmol), and 18-crown-6 (20.4 mg, 0.08 mmol) in DMF (6.0 mL). The mixture was stirred under reflux for 24 h. After cooling to room temperature, it was poured into ice/water (20 mL), and was allowed to stand at room temperature for 12 h;

then the formed solid was filtered and dried under reduced pressure. The crude product **S3** weighed 123 mg (27 % yield) was used in the next step without further purification.

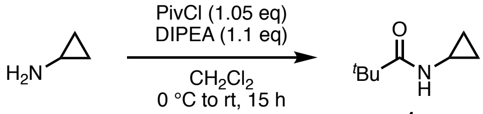
The synthetic procedure of **L15** is the same as that of **L14**, but 4-(trifluoromethyl)quinoline-2-carbonitrile (**S3**: 123 mg, 0.55 mmol) was used. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5:1) to give **L15** (128 mg, 72% yield) as a pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.86 (t, *J* = 7.2 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 4.57 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.43 (t, *J* = 8.4 Hz, 1H), 4.21 (dd, *J* = 10.2, 8.4 Hz, 1H), 1.02 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 148.3, 146.6, 134.9 (q, $J_{C–F}$ = 32.3 Hz), 131.2, 130.7, 129.5, 123.9, 123.4, 123.2 (q, $J_{C–F}$ = 273 Hz), 118.3 (q, $J_{C–F}$ = 4.8 Hz), 76.7, 69.9, 34.1, 25.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.9; HRMS (ESI) *m/z* calcd for $C_{17}H_{18}F_3N_2O$ $[M+H]^+$: 323.1366, found 323.1366.



(*S*)-4-(*tert*-Butyl)-2-(5-methoxyquinolin-2-yl)-4,5-dihydrooxazole (L16)

The synthetic procedure of **L16** is the same as that of **L14**, but 5-methoxyquinoline-2-carbonitrile[12] (270 mg, 1.5 mmol) was used. The residue was purified by MPLC (hexane/ethyl acetate = 3:1 to 1:3). The obtained solid was crystallized from hexane to give **L16** (310 mg, 74% yield) as a light yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 7.8 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 4.53 (dd, *J* = 9.6, 8.4 Hz, 1H), 4.39 (t, *J* = 8.4 Hz, 1H), 4.18 (dd, *J* = 9.6, 8.4 Hz, 1H), 4.02 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.8, 154.9, 148.4, 147.3, 131.5, 129.8, 122.4, 121.3, 120.1, 105.4, 76.6, 69.6, 55.8, 34.1, 26.0; HRMS (ESI) *m/z* calcd for $C_{17}H_{21}N_2O_2$ $[M+H]^+$: 285.1598, found 285.1592.

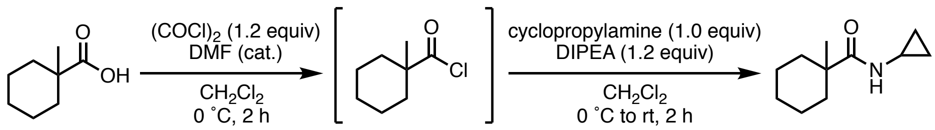
3. Preparation of Substituted Cyclopropanes



1a

N-Cyclopropylpivalamide (1a) [13]

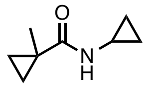
To a solution of cyclopropylamine (10.0 mL, 0.14 mol) and *N,N*-diisopropylethylamine (DIPEA: 27.2 mL, 0.16 mol) in dichloromethane (100 mL) was slowly added a solution of pivaloyl chloride (PivCl: 18.6 mL, 0.15 mol) in dichloromethane (50 mL) from a dropping funnel at 0 °C. The reaction mixture was stirred at room temperature for 15 h. To the reaction mixture was added saturated aqueous $NaHCO_3$ (40 mL), which was then extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1 to 1:2). The obtained solid was crystallized from hexane to give **1a** (18.3 g, 90% yield) as white needles. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.71 (brs, 1H), 2.72–2.68 (m, 1H), 1.17 (s, 9H), 0.78–0.75 (m, 2H), 0.47–0.44 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.8, 38.4, 27.5, 22.7, 6.6; HRMS (ESI) *m*/*z* calcd for $C_8H_{15}NO$ $[M+H]^+$: 142.1226, found 142.1223.



S4 1b

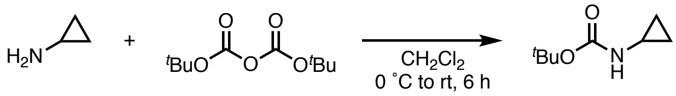
N-Cyclopropyl-1-methylcyclohexane-1-carboxamide (1b)

To a solution of 1-methylcyclohexane-1-carboxylic acid (1.1 g, 9.5 mmol) and *N*,*N*-dimethylformamide (DMF: 0.10 mL) in dichloromethane (50 mL) was slowly added $(COCl)_2$ (0.97 mL, 11.4 mmol) at 0 ˚C. The reaction mixture was stirred at 0 ˚C for 2 h, upon which it was evaporated *in vacuo*. The crude product **S4** and DIPEA (2.0 mL, 11.4 mmol) were dissolved in dichloromethane (50 mL). To this solution was slowly added cyclopropylamine (1.5 mL, 9.5 mmol) at 0 ˚C. The reaction mixture was stirred at room temperature for 2 h. The mixture was extracted with dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by Isolera® (hexane/ethyl acetate = 2:1 to 0:1). The obtained solid was washed with hexane to afford **1b** (1.5 g, 87% yield) as an orange solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.70 (brs, 1H), 2.74–2.68 (m, 1H), 1.89–1.81 (m, 2H), 1.57–1.50 (m, 2H), 1.49–1.37 (m, 3H), 1.36–1.27 (m, 3H), 1.11 (s, 3H), 0.80–0.74 (m, 2H), 0.47–0.42 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.1, 42.4, 35.6, 26.2, 25.8, 22.8, 22.7, 6.7; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{19}NNaO$ $[M+Na]^+$: 204.1359, found 204.1364.



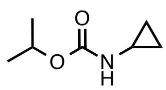
***N*-Cyclopropyl-1-methylcyclopropane-1-carboxamide (1c)**

The synthetic procedure of **1c** is the same as that of **1b**, but 1-methylcyclopropane-1-carboxylic acid (619 mg, 6.2 mmol) was used. The residue was purified by Isolera® (hexane/ethyl acetate = 2:1 to 0:1). The obtained solid was crystallized from hexane to afford **1c** (289 mg, 34% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.83 (brs, 1H), 2.74–2.68 (m, 1H), 1.27 (s, 3H), 1.21–1.17 (m, 2H), 0.79–0.74 (m, 2H), 0.56–0.53 (m, 2H), 0.51–0.47 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 23.0, 19.7, 18.9, 16.0, 6.6; HRMS (ESI) *m*/*z* calcd for $C_8H_{13}NNaO$ $[M+Na]^+$: 162.0889, found 162.0886.



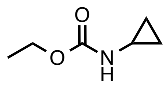
***tert*-Butyl cyclopropylcarbamate (1e)**[13]

To a solution of cyclopropylamine (0.56 mL, 8.0 mmol) in dichloromethane (30 mL) was slowly added di-*tert*-butyl dicarbonate (1.8 mL, 8.0 mmol) at 0 ˚C. The reaction mixture was stirred at room temperature for 6 h. The mixture was extracted with dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by Isolera® (hexane/ethyl acetate = 2:1 to 0:1). The obtained solid was washed with hexane to afford **1e** (950 mg, 75% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.73 (brs, 1H), 2.53 (m, 1H), 1.44 (s, 9H), 0.72–0.64 (m, 2H), 0.52–0.44 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6, 79.4, 28.4, 22.8, 6.7; HRMS (ESI) *m*/*z* calcd for $C_8H_{15}NNaO_2$ $[M+Na]^+$: 180.0995, found 180.0996.



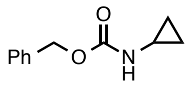
Isopropyl cyclopropylcarbamate (1f)

The synthetic procedure of **1f** is the same as that of **1a**, but cyclopropylamine (0.31 mL, 4.5 mmol) and isopropyl carbonochloridate (0.57 mL, 5.0 mmol) were used. The residue was purified by Isolera® (hexane/ethyl acetate = 2:1 to 0:1) to afford **1f** (400 mg, 62% yield) as a white solid. ^{1}H NMR (600 MHz, 50 ˚C, $CDCl_3$) δ 4.91 (sep, J = 6.6 Hz, 1H), 4.70 (brs, 1H), 2.60–2.54 (m, 1H), 1.22 (d, J = 6.6 Hz, 6H), 0.73–0.65 (m, 2H), 0.53–0.45 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 67.9, 22.9, 22.1, 6.7; HRMS (ESI) *m*/*z* calcd for $C_7H_{13}NNaO_2$ $[M+Na]^+$: 166.0838, found 166.0839.



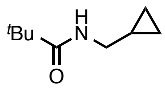
Ethyl cyclopropylcarbamate (1g)[14]

The synthetic procedure of **1g** is the same as that of **1a**, but cyclopropylamine (0.31 mL, 4.5 mmol) and ethyl carbonochloridate (0.47 mL, 5.0 mmol) were used. The residue was purified by Isolera® (hexane/ethyl acetate = 2:1 to 0:1) to afford **1g** (530 mg, 91% yield) as a white solid. ^{1}H NMR (600 MHz, 50 ˚C, $CDCl_3$) δ 4.73 (brs, 1H), 4.12 (q, J = 6.9 Hz, 2H), 2.61–2.54 (m, 1H), 1.24 (t, J = 6.9 Hz, 3H), 0.74–0.65 (m, 2H), 0.55–0.45 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 60.6, 22.9, 14.5, 6.6; HRMS (ESI) *m*/*z* calcd for $C_6H_{11}NNaO_2$ $[M+Na]^+$: 152.0682, found 152.0682.



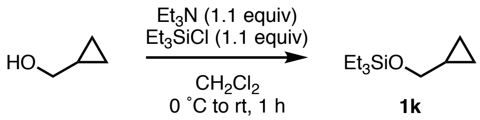
Benzyl cyclopropylcarbamate (1i)[14]

The synthetic procedure of **1i** is the same as that of **1a**, but cyclopropylamine (0.50 mL, 7.2 mmol) and benzyl carbonochloridate (1.1 mL, 7.5 mmol) were used. The residue was purified by Isolera® (hexane/ethyl acetate = 5:1 to 0:1). The obtained solid was washed with hexane to afford **1i** (350 mg, 25% yield) as a white solid. ^{1}H NMR (500 MHz, 60 ˚C, $CDCl_3$) δ 7.36–7.26 (m, 5H), 5.10 (s, 2H), 4.81 (brs, 1H), 2.64–2.57 (m, 1H), 0.78–0.65 (m, 2H), 0.57–0.46 (m, 2H); ^{13}C NMR (126 MHz, 60 ˚C, $CDCl_3$) δ 157.1, 136.8, 128.5, 128.1, 66.7, 23.3, 6.9; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{13}NNaO_2$ $[M+Na]^+$: 214.0838, found 214.0833.



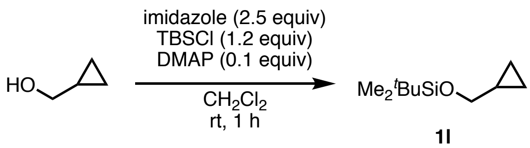
***N*-(Cyclopropylmethyl)pivalamide (1j)**

The synthetic procedure of **1j** is the same as that of **1a**, but cyclopropylmethanamine (1.0 mL, 11.7 mmol) was used. The residue was purified by Isolera® (hexane/ethyl acetate = 2:1 to 0:1). The obtained solid was crystallized from hexane to afford **1j** (1.4 g, 77% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.69 (brs, 1H), 3.10 (dd, J = 6.9, 5.5 Hz, 2H), 1.21 (s, 9H), 0.98–0.90 (m, 1H), 0.53–0.47 (m, 2H), 0.23–0.17 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 44.3, 38.6, 27.6, 10.7, 3.2; HRMS (ESI) *m*/*z* calcd for $C_9H_{17}NNaO$ $[M+Na]^+$: 178.1202, found 178.1200.



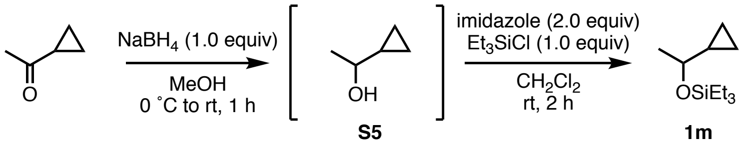
(Cyclopropylmethoxy)triethylsilane (1k)

To a mixture of cyclopropylmethanol (0.41 mL, 5.0 mmol) and triethylamine (0.77 mL, 5.5 mmol) in dichloromethane (15 mL) was added chlorotriethylsilane (0.92 mL, 5.5 mmol) at 0 ˚C. The mixture was stirred at room temperature for 1 h. The mixture was extracted with dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10:1) to give **1k** (800 mg, 85% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.46 (d, J = 6.6 Hz, 2H), 1.08–0.93 (m, 10H), 0.61 (q, J = 8.3 Hz, 6H), 0.52–0.46 (m, 2H), 0.21–0.16 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 67.4, 13.3, 6.8, 4.5, 2.8; HRMS (ESI) *m*/*z* calcd for $C_{10}H_{22}NaOSi$ $[M+Na]^+$: 209.1332, found 209.1333.



***tert*-Butyl(cyclopropylmethoxy)dimethylsilane (1l)**

To a mixture of cyclopropylmethanol (0.41 mL, 5.0 mmol), 1*H*-imidazole (851 mg, 12.5 mmol) and *N*,*N*-dimethylpyridin-4-amine (DMAP: 61.1 mg, 0.50 mmol) in dichloromethane (20 mL) was added *tert*-butylchlorodimethylsilane (TBSCl: 904 mg, 6.0 mmol) in dichloromethane (5.0 mL). The mixture was stirred at room temperature for 1 h. The mixture was extracted with dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10:1) to give **1l** (604 mg, 65% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.49 (d, J = 6.0 Hz, 2H), 1.05–0.97 (m, 1H), 0.90 (s, 9H), 0.49–0.42 (m, 2H), 0.21–0.15 (m, 2H), 0.06 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 67.5, 26.0, 18.5, 13.3, 2.6, –5.1; HRMS (ESI) *m*/*z* calcd for $C_{10}H_{22}NaOSi$ $[M+Na]^+$: 209.1332, found 209.1332.

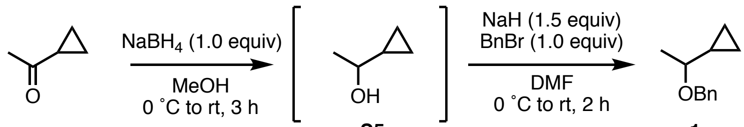


(1-Cyclopropylethoxy)triethylsilane (1m)[24]

A Schlenk tube containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. After adding 1-cyclopropylethan-1-one (0.40

mL, 4.0 mmol) and MeOH (3.0 mL), $NaBH_4$ (151 mg, 4.0 mmol) was added to the mixture at 0 ˚C. After stirring at room temperature for 1 h, H_2O (5.0 mL) was added. The mixture was extracted with dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude alcohol **S5** was used without further purification in the next step.

To a mixture of the crude alcohol **S5** and 1*H*-imidazole (545 mg, 8.0 mmol) in dichloromethane (10 mL) was added chlorotriethylsilane (0.67 mL, 4.0 mmol) at room temperature. After stirring at room temperature for 2 h, the mixture was extracted with dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10:1) to give **1m** (628 mg, 78% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.24–3.18 (m, 1H), 1.22 (d, J = 6.0 Hz, 3H), 0.96 (t, J = 8.2 Hz, 9H), 0.91–0.83 (m, 1H), 0.58 (q, J = 8.2 Hz, 6H), 0.47–0.39 (m, 2H), 0.29–0.23 (m, 1H), 0.17–0.10 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 72.3, 23.9, 19.1, 6.9, 5.0, 3.3, 2.0; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{24}NaOSi$ $[M+Na]^+$: 223.1489, found 223.1300.

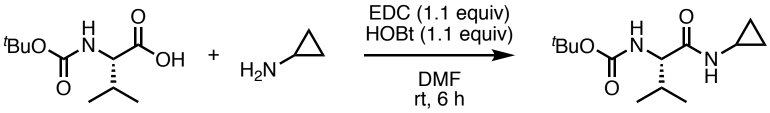


((1-Cyclopropylethoxy)methyl)benzene (1n)

A Schlenk tube containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. After adding 1-cyclopropylethan-1-one (0.40 mL, 4.0 mmol) and MeOH (3.0 mL), $NaBH_4$ (151 mg, 4.0 mmol) was added to the mixture at 0 ˚C. After stirring for 3 h at room temperature, H_2O (5.0 mL) was added. The mixture was extracted with dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude alcohol **S5** was used without further purification in the next step.

A two-necked flask containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. After adding the crude alcohol **S5** and DMF (10 mL), NaH (60%, dispersion in paraffin liquid: 240 mg, 6.0 mmol) was added to the mixture at 0 ˚C and stirred for 15 min. To the mixture was added (bromomethyl)benzene (0.48 mL, 4.0 mmol) at the same temperature. After stirring for 2 h at room temperature, H_2O (5.0 mL) was added, then the mixture was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by Isolera® (hexane/ethyl acetate = 10:1) to give **1n** (503 mg, 71% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.30 (m, 4H), 7.28–7.23 (m, 1H), 4.66 (d, J = 12 Hz, 1H), 4.57 (d, J = 12 Hz, 1H), 2.90–2.82 (m, 1H), 1.29 (d, J = 6.5 Hz, 3H), 0.94–

0.85 (m, 1H), 0.64–0.56 (m, 1H), 0.50–0.42 (m, 1H), 0.39–0.31 (m, 1H), 0.11–0.03 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2, 128.3, 127.5, 127.3, 79.1, 70.1, 20.2, 16.4, 4.7, 1.0; HRMS (ESI) *m*/*z* calcd for $C_{12}H_{16}NaO$ $[M+Na]^+$: 199.1093, found 199.1092.

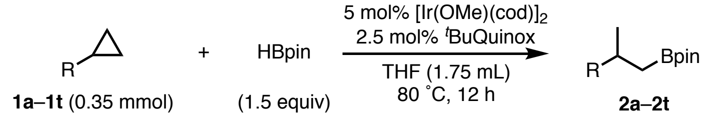


1s

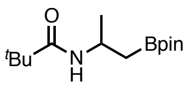
***tert*-Butyl (*R*)-(1-(cyclopropylamino)-3-methyl-1-oxobutan-2-yl)carbamate (1s)**

To a 30-mL round-bottom flask, (*tert*-butoxycarbonyl)-*D*-valine (869 mg, 4.0 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC: 843 mg, 4.4 mmol), 1-hydroxybenzotriazole (HOBt: 595 mg, 4.4 mmol) and DMF (15 mL) were added. After adding cyclopropylamine (0.28 mL, 4.0 mmol), the mixture was stirred at room temperature for 6 h. To the mixture was added saturated aqueous $NaHCO_3$, then the mixture was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by Isolera® (hexane/ethyl acetate = 2:1 to 0:1). The obtained solid was crystallized from hexane and ethyl acetate to afford **1s** (715 mg, 72% yield) as a white solid. ^{1}H NMR (600 MHz, 90 ˚C, $(CD_3)_2SO$) δ 7.62 (brs, 1H), 6.08 (brs, 1H), 3.72–3.68 (m, 1H), 2.67–2.61 (m, 1H), 1.93–1.86 (m, 1H), 1.40 (s, 9H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 3H), 0.65–0.59 (m, 2H), 0.46–0.37 (m, 2H); ^{13}C NMR (151 MHz, 90 ˚C, $(CD_3)_2SO$) δ 171.8, 154.8, 77.7, 59.4, 30.2, 27.7, 21.7, 18.6, 17.6, 5.1, 5.0; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{24}N_2NaO_3$ $[M+Na]^+$: 279.1679, found 279.1675.

4. Procedure for Ir-Catalyzed Hydroboration of Monosubstituted Cyclopropanes

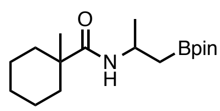


A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. To this vessel were added cyclopropane (0.35 mmol) and (*S*)-4-(*tert*-butyl)-2-(quinolin-2-yl)-4,5-dihydrooxazole (^{t}BuQuinox: 2.2 mg, 8.8 μmol) under nitrogen, after which it was introduced inside an argon atmosphere glovebox. In the glovebox, $[Ir(OMe)(cod)]_2$ (11.6 mg, 0.018 mmol) and THF (1.0 mL) were added. After 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin: 76.2 μL, 0.53 mmol) and THF (0.75 mL) were added, the glass vessel was sealed with the O-ring tap and then taken out of the glovebox. The mixture was stirred at 80 ˚C for 12 h, cooled to room temperature and concentrated *in vacuo*. The residue was purified by MPLC to give the hydroboration product **2**. The branch/linear ratio was determined by ^{1}H NMR analysis of the crude product.



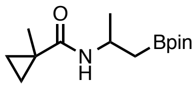
***N*-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)pivalamide (2a)**

The reaction was performed for 3 h. Purification by MPLC (hexane/ethyl acetate = 3:1 to 1:1) gave **2a** (64.5 mg, 68% yield, branch/linear = >95:5) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.27 (d, J = 6.6 Hz, 1H), 4.25–4.17 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H), 1.17 (s, 9H), 1.14–1.00 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 83.4, 41.7, 38.5, 27.5, 25.0, 24.7, 22.8; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{28}BNNaO_3$ $[M+Na]^+$: 292.2054, found 292.2049.



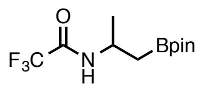
1-Methyl-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)cyclohexane-1-carboxamide (2b)

The reaction was performed for 24 h. Purification by MPLC (hexane/ethyl acetate = 3:1 to 1:1) gave **2b** (73.7 mg, 68% yield, branch/linear = 96:4) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.32 (d, J = 7.8 Hz, 1H), 4.30–4.22 (m, 1H), 1.97–1.87 (m, 2H), 1.58–1.36 (m, 5H), 1.35–1.18 (m, 15H), 1.16–1.01 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 83.3, 42.5, 41.6, 35.7, 35.6, 26.8, 25.9, 25.0, 24.7, 23.1, 23.0, 22.8, 18.9; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{32}BNNaO_3$ $[M+Na]^+$: 332.2367, found 332.2367.



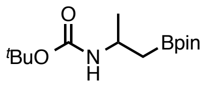
1-Methyl-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)cyclopropane-1-carboxamide (2c)

Purification by MPLC (hexane/ethyl acetate = 3:1 to 1:1); the collected fractions were purified again by GPC to give **2c** (51.0 mg, 55% yield, branch/linear = 92:8) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.41 (d, J = 6.6 Hz, 1H), 4.30–4.21 (m, 1H), 1.33–1.22 (m, 15H), 1.20–1.00 (m, 7H), 0.55–0.48 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 83.3, 42.0, 24.9, 24.6, 22.9, 19.5, 18.9, 15.6, 15.5; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{26}BNNaO_3$ $[M+Na]^+$: 290.1898, found 290.1892.



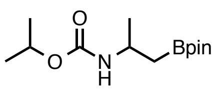
2,2,2-Trifluoro-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)acetamide (2d)

Purification by MPLC (hexane/ethyl acetate = 3:1 to 1:1) gave **2d** (42.4 mg, 43% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (brs, 1H), 4.33–4.25 (m, 1H), 1.27 (s, 12H), 1.24–1.08 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0 (q, $J_{C–F}$ = 36.0 Hz), 116.0 (q, $J_{C–F}$ = 286.1 Hz), 83.8, 43.1, 24.8, 24.7, 22.3, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –76.9; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{19}BF_3NNaO_3$ $[M+Na]^+$: 304.1302, found 304.1301.



***tert*-Butyl (1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate (2e)[25]**

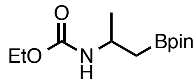
Purification by MPLC (hexane/EtOAc = 3:1 to 1:1) gave **2e** (60.0 mg, 60% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.72 (brs, 1H), 3.96–3.84 (m, 1H), 1.44 (s, 9H), 1.25 (s, 12H), 1.15 (d, J = 6.3 Hz, 3H), 1.09–0.99 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.1, 83.2, 78.6, 43.6, 28.4, 24.8, 24.7, 23.3, 20.0; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{28}BNNaO_4$ $[M+Na]^+$: 308.2004, found 308.2000.



Isopropyl (1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate (2f)

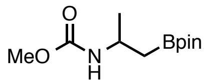
Purification by MPLC (hexane/ethyl acetate = 3:1 to 1:1) gave **2f** (52.0 mg, 55% yield) as a colorless oil. ^{1}H NMR (600 MHz, 60 ˚C, $CDCl_3$) δ 4.94–4.85 (m, 1H), 4.72 (brs, 1H), 3.97–3.87 (m, 1H), 1.27–

0.98(m, 23H); ^{13}C NMR (151 MHz, 60 ˚C, $CDCl_3$) δ 155.5, 83.3, 67.5, 44.1, 24.9, 24.8, 23.3, 22.2; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{26}BNO_4Na$ $[M+Na]^+$: 294.1847, found 294.1843.



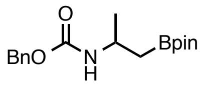
Ethyl (1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate (2g)

Purification by MPLC (hexane/ethyl acetate = 3:1 to 1:1) gave **2g** (42.8 mg, 48% yield) as a colorless oil. ^{1}H NMR (600 MHz, 50 ˚C, $CDCl_3$) δ 4.82 (brs, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.99–3.89 (m, 1H), 1.26–1.21 (m, 15H), 1.16 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 83.3, 60.3, 43.9, 24.9, 24.7, 23.2, 14.7; HRMS (ESI) *m*/*z* calcd for $C_{12}H_{24}BNNaO_4$ $[M+Na]^+$: 280.1691, found 280.1694.



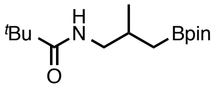
Methyl (1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate (2h)

The reaction was performed for 22 h. Purification by MPLC (hexane/ethyl acetate = 3:1 to 1:1) gave **2h** (27.5 mg, 32% yield) as a colorless oil. ^{1}H NMR (600 MHz, 60 ˚C, $CDCl_3$) δ 4.86 (brs, 1H), 3.98–3.89 (m, 1H), 3.64 (s, 3H), 1.24 (s, 12H), 1.16 (d, *J* = 6.6 Hz, 3H), 1.05 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (151 MHz, 60 ˚C, $CDCl_3$) δ 156.3, 83.4, 51.7, 44.3, 24.9, 24.8, 23.2, 20.0; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{22}BNNaO_4$ $[M+Na]^+$: 266.1534, found 266.1535.



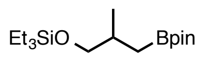
Benzyl (1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate (2i)

Purification by MPLC (hexane/ethyl acetate = 5:1 to 1:1) gave **2i** (46.0 mg, 41% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5H), 5.14–4.98 (m, 3H), 4.03–3.95 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.18 (d, *J* = 7.2 Hz, 3H), 1.08 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 137.0, 128.4, 128.0, 127.9, 83.3, 66.2, 44.2, 24.8, 24.7, 23.1, 19.8; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{26}BNNaO_4$ $[M+Na]^+$: 342.1847, found 342.1847.



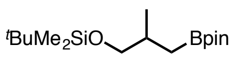
***N*-(2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide (2j)**

The reaction was performed using (acetylacetonato)(1,5-cyclooctadiene)iridium(I) ([Ir(cod)(acac)]: 7.1 mg, 0.018 mmol). Purification by MPLC (hexane/ethyl acetate = 3:1 to 1:1) gave **2j** (65.1 mg, 66% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (brs, 1H), 3.20–3.05 (m, 2H), 1.96–1.84 (m, 1H), 1.254 (s, 6H), 1.250 (s, 6H), 1.20 (s, 9H), 0.94 (d, J = 6.8 Hz, 3H), 0.84 (dd, J = 15.6, 5.6 Hz, 1H), 0.71 (dd, J = 15.6, 8.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 83.2, 47.0, 38.7, 29.7, 27.7, 24.9, 24.7, 20.2; HRMS (ESI) m/z calcd for $C_{15}H_{30}BNNaO_3$ $[M+Na]^+$: 306.2211, found 306.2208.



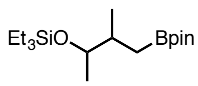
Triethyl(2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane (2k)

The reaction was performed using [Ir(cod)(acac)] (7.1 mg, 0.018 mmol). Purification by MPLC (hexane/ethyl acetate = 20:1 to 10:1) gave **2k** (58.0 mg, 53% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 (dd, J = 10, 6.0 Hz, 1H), 3.31 (dd, J = 10, 7.5 Hz, 1H), 1.91–1.81 (m, 1H), 1.24 (s, 12H), 0.99–0.84 (m, 13H), 0.62–0.54 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 82.8, 69.8, 32.3, 24.9, 24.8, 19.0, 6.8, 4.4; HRMS (ESI) m/z calcd for $C_{16}H_{35}BNaO_3Si$ $[M+Na]^+$: 337.2341, found 337.2344.



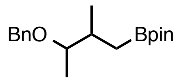
***tert*-Butyldimethyl(2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane (2l)**[26]

The reaction was performed using [Ir(cod)(acac)] (7.1 mg, 0.018 mmol) for 19 h. Purification by MPLC (hexane/ethyl acetate = 20:1 to 10:1) gave **2l** (58.1 mg, 53% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.43 (dd, J = 9.7, 6.1 Hz, 1H), 3.31 (dd, J = 9.7, 7.6 Hz, 1H), 1.88–1.80 (m, 1H), 1.24 (s, 12H), 0.92 (d, J = 6.4 Hz, 3H), 0.90–0.83 (m, 10H), 0.58 (dd, J = 15.8, 9.0 Hz, 1H), 0.03 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 82.9, 70.1, 32.3, 26.0, 24.9, 24.8, 19.0, 18.4, –5.3; HRMS (ESI) m/z calcd for $C_{16}H_{35}BNaO_3Si$ $[M+Na]^+$: 337.2341, found 337.2344.



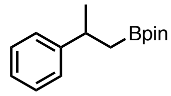
Triethyl((3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)oxy)silane (2m)

The reaction was performed using [Ir(cod)(acac)] (7.1 mg, 0.018 mmol). Purification by MPLC (hexane/ethyl acetate = 20:1 to 10:1) gave **2m** (57.5 mg, 50% yield, *d.r.* = 1:1) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.66–3.60 (m, 1H), 1.79–1.66 (m, 1H), 1.26–1.22 (m, 13H), 1.07 (d, J = 6.0 Hz, 2H), 1.04 (d, J = 6.0 Hz, 1H), 0.99–0.91 (m, 9H), 0.90–0.86 (m, 3H), 0.68–0.54 (m, 7H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 82.8, 73.2, 72.9, 36.8, 36.7, 24.9, 24.7, 20.5, 19.3, 17.3, 17.1, 6.9, 5.14, 5.09; HRMS (ESI) m/z calcd for $C_{17}H_{37}BNaO_3Si$ $[M+Na]^+$: 351.2497, found 351.2500.



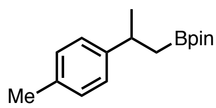
2-(3-(Benzyloxy)-2-methylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)

The reaction was performed using [Ir(cod)(acac)] (7.1 mg, 0.018 mmol). Purification by MPLC (hexane/ethyl acetate = 20:1 to 10:1) gave **2n** (53.5 mg, 50% yield, *d.r.* = 62:38) as a colorless oil. The diastereoselectivity was determined by ^{1}H NMR analysis. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.29 (m, 4H), 7.27–7.22 (m, 1H), 4.58–4.46 (m, 2H), 3.38–3.32 (m, 0.62H), 3.32–3.27 (m, 0.38H), 2.03–1.95 (m, 1H), 1.23 (s, 7.5H), 1.22 (s, 4.5H), 1.13–1.09 (m, 3H), 0.99–0.89 (m, 4H), 0.71–0.65 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.5, 128.2, 127.6, 127.5, 127.19, 127.16, 82.9, 79.9, 79.7, 70.49, 70.46, 34.2, 34.1, 25.0, 24.85, 24.78, 24.7, 18.1, 17.3, 15.6, 15.4; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{29}BNaO_3$ $[M+Na]^+$: 327.2102, found 327.2097.



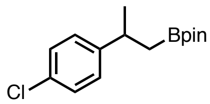
4,4,5,5-Tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane(2o)[27]

The reaction was performed for 36 h. Purification by MPLC (hexane/ethyl acetate = 20:1 to 10:1) gave **2o** (38.0 mg, 44% yield, branch/linear = 91:9) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.22 (m, 4H), 7.16–7.12 (m, 1H), 3.06–2.99 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.20–1.10 (m, 14H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.3, 128.2, 126.6, 125.6, 83.0, 35.8, 24.9, 24.8, 24.7; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{23}BNaO_2$ $[M+Na]^+$: 269.1683, found 269.1685.



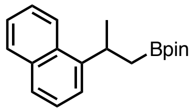
4,4,5,5-Tetramethyl-2-(2-(*p*-tolyl)propyl)-1,3,2-dioxaborolane (2p)[28]

The reaction was performed for 36 h. Purification by MPLC (hexane/ethyl acetate = 10:1 to 1:1) gave **2p** (33.1 mg, 36% yield, branch/linear = 91:9) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 3.04–2.96 (m, 1H), 2.30 (s, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.20–1.06 (m, 14H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3, 135.0, 128.8, 126.4, 83.0, 35.3, 24.9, 24.8, 24.7, 20.9; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{25}BNaO_2$ $[M+Na]^+$: 283.1840, found 283.1839.



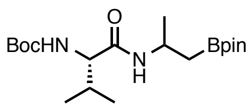
2-(2-(4-Chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q)[29]

The reaction was performed for 36 h. Purification by MPLC (hexane/ethyl acetate = 10:1 to 1:1) gave **2q** (33.0 mg, 34% yield, branch/linear = 91:9) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 3.04–2.97 (m, 1H), 1.25 (d, *J* = 7.2 Hz, 3H), 1.162 (s, 6H), 1.158 (s, 6H), 1.13–1.09 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 131.2, 128.2, 128.0, 83.1, 35.3, 24.8, 24.74, 24.69; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{22}BClNaO_2$ $[M+Na]^+$: 303.1294, found 303.1299.



4,4,5,5-Tetramethyl-2-(2-(naphthalen-1-yl)propyl)-1,3,2-dioxaborolane (2r)[30]

The reaction was performed for 36 h. Purification by MPLC (hexane/ethyl acetate = 20:1 to 10:1) gave **2r** (53.3 mg, 51% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.69–7.65 (m, 1H), 7.52–7.48 (m, 1H), 7.47–7.41 (m, 3H), 3.96–3.86 (m, 1H), 1.44–1.34 (m, 4H), 1.27 (dd, *J* = 15.6, 9.0 Hz, 1H), 1.15 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.3, 133.8, 131.3, 128.7, 126.1, 125.6, 125.5, 125.1, 123.6, 122.1, 83.0, 30.0, 24.9, 24.7, 24.6, 24.4; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{25}BNaO_2$ $[M+Na]^+$: 319.1840, found 319.1841.

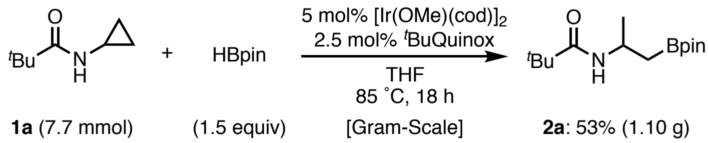


***tert*-Butyl((2*R*)-3-methyl-1-oxo-1-((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)amino)butan-2-yl)carbamate (2s)**

The reaction was performed for 16 h. Purification by MPLC (hexane/ethyl acetate = 2:1 to 1:1); the collected fractions were purified again by GPC to give **2s** (57.9 mg, 43% yield, *d.r.* = 53:47) as a colorless oil. The diastereoselectivity was determined by ^{1}H NMR analysis. ^{1}H NMR (600 MHz, 60 °C, $CDCl_3$) δ 6.17 (brs, 0.47H), 6.12 (brs, 0.53H), 5.06 (brs, 1H), 4.26–4.18 (m, 1H), 3.85–3.78 (m, 1H), 2.15–2.06 (m, 1H), 1.44 (s, 9H), 1.27–1.23 (m, 12H), 1.16 (d, *J* = 7.2 Hz, 3H), 1.08–1.05 (m, 2H), 0.950 (d, *J* = 7.2 Hz, 1.6H), 0.947 (d, *J* = 7.1 Hz, 1.4H), 0.91 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, 60 °C, $CDCl_3$) δ 170.0, 169.9, 83.5, 83.4, 42.3, 42.2, 31.2, 28.4, 24.90, 24.88, 24.7, 22.7, 22.6, 19.2, 19.0, 17.8; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{37}BN_2NaO_5$ $[M+Na]^+$: 407.2688, found 407.2682.

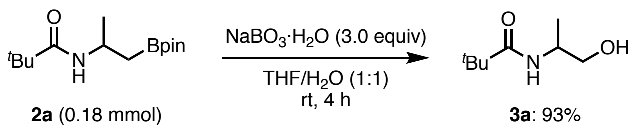
5. Synthetic Application

5-1. Gram-scale Reaction



A 100-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun *in vacuo* and filled with nitrogen after cooling to room temperature. To this vessel were added *N*-cyclopropylpivalamide (**1a**: 1.1 g, 7.7 mmol) and (*S*)-4-(*tert*-butyl)-2-(quinolin-2-yl)-4,5-dihydrooxazole (^{t}BuQuinox: 49.0 mg, 0.19 mmol), after which it was introduced inside an argon atmosphere glovebox. In the glovebox, $[Ir(OMe)(cod)]_2$ (255 mg, 0.39 mmol) and THF (20 mL) were added. After 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin: 1.68 L, 11.6 mmol) and THF (18 mL) were added, the glass vessel was sealed with the O-ring tap and then taken out of the glovebox. The mixture was stirred in oil bath at 85 ˚C for 18 h, cooled to room temperature and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 3:1). The collected fractions were purified again by silica gel column chromatography (hexane/ethyl acetate = 3:1 to 1:1) to afford **2a** (1.10 g, 53% yield) as a white solid.

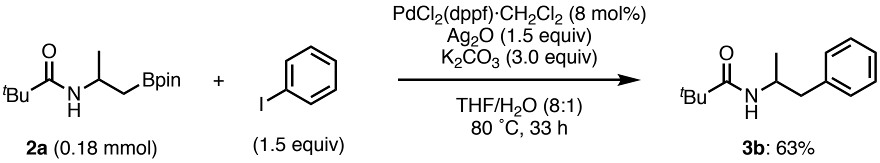
5-2. Oxidation of 2a



To a screw cap 20-mL glass vessel containing a magnetic stirring bar were added **2a** (48.5 mg, 0.18 mmol), $NaBO_3{\cdot}H_2O$ (54.0 mg, 0.54 mmol), THF (1.5 mL) and H_2O (1.5 mL). The mixture was stirred at room temperature for 4 h under air, upon which it was diluted with ethyl acetate. The mixture was extracted with ethyl acetate, the organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The resultant residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to afford the corresponding alcohol **3a** (28.6 mg, 93% yield) as a colorless oil.

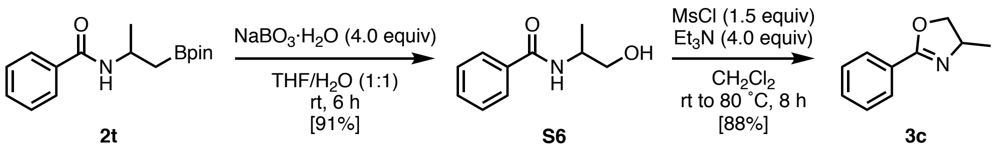
***N*-(1-Hydroxypropan-2-yl)pivalamide (3a)**[31] ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.81 (brs, 1H), 4.09–4.00 (m, 1H), 3.68–3.62 (m, 1H), 3.53 (dd, J = 10.8, 6.0 Hz, 1H), 1.21 (s, 9H), 1.18 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.5, 67.4, 47.7, 38.6, 27.5, 17.0; HRMS (ESI) *m/z* calcd for $C_8H_{17}NO_2Na$ $[M+Na]^+$: 182.1152, found 182.1149.

5-3. Suzuki–Miyaura Coupling of 2a with Iodobenzene



A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. A mixture of **2a** (48.5 mg, 0.18 mmol), iodobenzene (55.1 mg, 0.27 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (11.8 mg, 0.014 mmol), Ag_2O (62.6 mg, 0.27 mmol), K_2CO_3 (74.6 mg, 0.54 mmol), water (0.20 mL) in THF (1.6 mL) was placed into the glass vessel under nitrogen atmosphere, then the glass vessel was sealed with the O-ring tap. The mixture was stirred at 80 °C for 33 h in a heating block. After cooling to room temperature, the mixture was passed through a short pad of silica gel with ethyl acetate and the filtrate was concentrated *in vacuo*. The resultant residue was purified by MPLC (hexane/ethyl acetate = 3:1 to 1:1) to give **3b** (25.0 mg, 63% yield) as a white solid. ***N*-(1-Phenylpropan-2-yl)pivalamide (3b)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 6.8 Hz, 2H), 7.24–7.15 (m, 3H), 5.38 (d, J = 5.2 Hz, 1H), 4.31–4.19 (m, 1H), 2.83–2.72 (m, 2H), 1.14–1.10 (m, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 138.0, 129.5, 128.3, 126.4, 45.7, 42.4, 38.5, 27.5, 20.1; HRMS (ESI) *m/z* calcd for $C_{14}H_{21}NONa$ $[M+Na]^+$: 242.1515, found 242.1511.

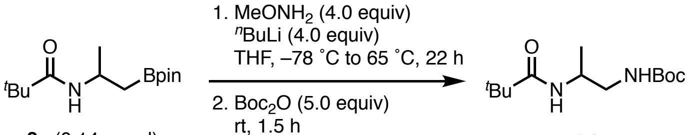
5-4. Sequential Oxidation/Mesylation/Cyclization to Oxazoline



To a screw cap 20-mL glass vessel containing a magnetic stirring bar were added **2t** (13.0 mg, 0.045 mmol), $NaBO_3\cdot H_2O$ (17.9 mg, 0.18 mmol), THF (1.0 mL) and H_2O (1.0 mL). The mixture was stirred at room temperature for 6 h under air. The mixture was diluted with saturated aqueous NH_4Cl. The mixture was extracted with ethyl acetate, then the organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The resultant residue was purified by PTLC (hexane/ethyl acetate = 1:3) to afford the corresponding alcohol **S6** (7.4 mg, 91% yield) as a white solid. ***N*-(1-Hydroxypropan-2-yl)benzamide (S6)** [32] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 8.4 Hz, 2H), 6.26 (brs, 1H), 4.34–4.26 (m, 1H), 3.83–3.78 (m, 1H), 3.67 (dd, J = 10.8, 6.0 Hz, 1H), 2.61 (brs, 1H), 1.31 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 134.3, 131.6, 128.6, 126.9, 67.0, 48.1, 17.1; HRMS (ESI) *m/z* calcd for $C_{10}H_{13}NNaO_2$ $[M+Na]^+$: 202.0838 found 202.0839.

To a 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was added the alcohol **S6** (25.0 mg, 0.14 mmol) in dichloromethane (1.0 mL). To the solution were added methanesulfonyl chloride (MsCl: 16.2 μL, 0.21 mmol) and triethylamine (77.8 μL, 0.56 mmol) at room temperature, which was stirred for 20 min. Then, the mixture was stirred at 80 ˚C for 8 h, cooled to room temperature and concentrated *in vacuo*. The resultant residue was purified by PTLC (hexane/ethyl acetate = 5:1) to afford **3c** (19.7 mg, 88% yield) as a colorless oil. **4-Methyl-2-phenyl-4,5-dihydrooxazole (3c)**[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.92 (m, 2H), 7.50–7.37 (m, 3H), 4.53 (dd, J = 9.6, 8.0 Hz, 1H), 4.44–4.33 (m, 1H), 3.96 (t, J = 8.0 Hz, 1H), 1.37 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 131.2, 128.3, 128.2, 127.8, 74.0, 62.0, 21.5; HRMS (ESI) *m*/*z* calcd for $C_{10}H_{12}NO$ $[M+H]^+$: 162.0913 found 162.0913.

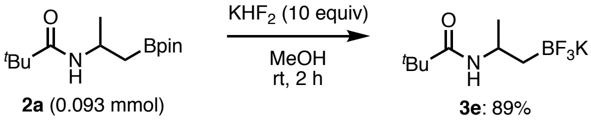
5-5. Amination of 2a



2a (0.14 mmol) **3d**

Amination was performed according to the literature procedure.[34] A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. *O*-Methylhydroxylamine (1.0 g, 2.6% THF solution) was placed in the tube and cooled to –78 ˚C. ^{n}BuLi (1.6 M in hexane, 0.35 mL, 0.56 mmol) was added dropwise, then stirred for 30 min at –78 ˚C. **2a** (38.0 mg, 0.14 mmol) in THF (0.20 mL) was added to the solution at the same temperature, then the mixture was warmed to room temperature; thereafter the mixture was stirred at 65 ˚C for 22 h. The mixture was cooled to room temperature, and Boc_2O (0.16 mL, 0.71 mmol) was added and stirred for 1.5 h at room temperature. The reaction was quenched with water. The mixture was extracted with ethyl acetate, and the organic layers were washed by brine, dried over Na_2SO_4 and concentrated *in vacuo*. The resultant residue was purified by Isolera® (hexane/ethyl acetate = 3:1 to 1:1) to give **3d** (13.8 mg, 38% yield) as a white solid. ***tert*-Butyl (2-pivalamidopropyl)carbamate (3d)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (brs, 0.21H), 6.36 (brs, 0.79H), 4.94 (brs, 0.79H), 4.69 (brs, 0.21H), 4.02–3.91 (m, 0.79H), 3.88–3.79 (m, 0.21H), 3.29–3.08 (m, 2H), 1.43 (s, 9H), 1.23–1.10 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 157.2, 79.7, 47.2, 47.0, 46.3, 45.5, 38.5, 28.4, 27.5, 18.9, 18.2; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{26}N_2NaO_3$ $[M+Na]^+$: 281.1836 found 281.1837.

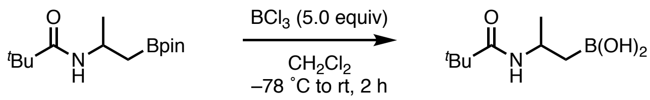
5-6. Synthesis of Potassium Trifluoroborate Salt 3e



2a (0.093 mmol) **3e**: 89%

To a solution of **2a** (25.0 mg, 0.093 mmol) in MeOH (0.50 mL) was added KHF_2 (2.0 mL of saturated aqueous solution (4.0–4.5 M), 0.93 mmol) dropwise at room temperature. The solution was stirred at room temperature for 2 h, then concentrated *in vacuo*. To the residue was added 60% aqueous MeOH, which was then concentrated *in vacuo*. This procedure was repeated twice. The resultant white solid was dissolved in acetone (0.10 mL), then ether was added. The precipitate was washed with ether, and the resultant precipitate was dissolved in acetone, and concentrated *in vacuo* overnight to afford potassium trifluoroborate **3e** (33.0 mg, 89% yield) as a white solid. ***N*-(1-(Trifluoro-λ^4-boraneyl)propan-2-yl)pivalamide, potassium salt (3e)** ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 6.78 (brs, 1H), 3.88–3.81 (m, 1H), 1.12–1.07 (m, 12H), 0.44–0.35 (m, 1H), 0.34–0.25 (m, 1H); ^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 177.3, 44.9, 38.9, 28.1, 27.1, 23.8; HRMS (ESI) *m/z* calcd for $C_8H_{16}BF_3NO$ $[M–K]^-$: 210.1272 found 210.1278.

5-7. Synthesis of Alkylboronic Acid 3f

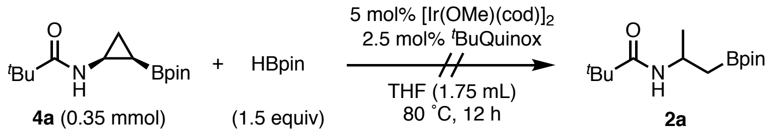


2a (0.098 mmol) **3f**: >99%

Conversion to boronic acid was performed according to a literature procedure.[35] A 10-mL Schlenk tube containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. **2a** (26.5 mg, 0.098 mmol) and dichloromethane (0.30 mL) were added to the tube under nitrogen. After the solution was cooled to –78 ˚C, BCl_3 (1 M in heptane, 0.49 mL, 0.49 mmol) was added dropwise. The mixture was stirred at the same temperature for 1 h, then allowed to warm to room temperature and stirred for 1 h. The mixture was concentrated *in vacuo*. After adding MeOH (1.0 mL) to the residue, the mixture was further concentrated *in vacuo*. This procedure was repeated twice. The residue was treated with water, and washed with diethyl ether. The resulting aqueous solution was concentrated *in vacuo* to afford the corresponding boronic acid **3f** (18.9 mg, >99% yield) as a white solid. **(2-Pivalamidopropyl)boronic acid (3f)** ^{1}H NMR (500 MHz, D_2O) δ 3.86–3.77 (m, 1H), 1.21–1.14 (m, 12H), 0.91 (dd, *J* = 14.5, 6.0 Hz, 1H), 0.68 (dd, *J* = 14.5, 9.0 Hz, 1H); ^{13}C NMR (126 MHz, D_2O) δ 181.4, 45.8, 38.1, 26.2, 23.8, 22.1; HRMS (ESI) *m/z* calcd for $C_8H_{17}BNO_3$ $[M–H]^-$: 186.1296 found 186.1299.

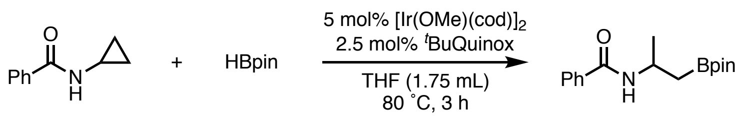
6. Mechanistic Consideration

6-1. Reaction of Plausible Reaction Intermediate 4a



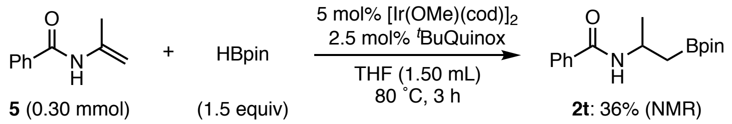
A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. To the veseel were added *N*-((1*S*,2*R*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)pivalamide (**4a**: 93.5 mg, 0.35 mmol) and (*S*)-4-(tert-butyl)-2-(quinolin-2-yl)-4,5-dihydrooxazole (^{t}BuQuinox: 2.2 mg, 8.8 μmol), then it was introduced inside an argon atmosphere glovebox. In the glovebox, $[Ir(OMe)(cod)]_2$ (11.6 mg, 0.018 mmol) and THF (1.0 mL) were added. After 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin: 76.2 μL, 0.53 mmol) and THF (0.75 mL) were added, the glass vessel was sealed with the O-ring tap and then taken out of the glovebox. The mixture was stirred at 80 ˚C for 12 h, cooled to room temperature and concentrated *in vacuo*. According to ^{1}H NMR and LCMS analysis, no reaction occurred and starting material **4a** remained.

6-2. Hydroboration of 1t or 5



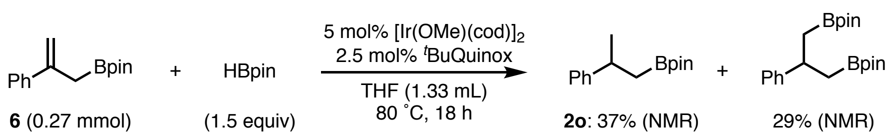
A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. To the vessel were added *N*-cyclopropylbenzamide (**1t**: 56.4 mg, 0.35 mmol) and (*S*)-4-(*tert*-butyl)-2-(quinolin-2-yl)-4,5-dihydrooxazole (^{t}BuQuinox: 2.2 mg, 8.8 μmol), then it was introduced inside an argon atmosphere glovebox. In the glovebox, $[Ir(OMe)(cod)]_2$ (11.6 mg, 0.018 mmol) and THF (1.0 mL) were added. After 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin: 76.2 μL, 0.53 mmol) and THF (0.75 mL) were added, the glass vessel was sealed with the O-ring tap and then taken out of the glovebox. The mixture was stirred at 80 ˚C for 3 h, cooled to room temperature and concentrated *in vacuo*. ^{1}H NMR yield was 44% determined by using dibromomethane as an internal standard. The residue was purified by MPLC (hexane/ethyl acetate = 3:1 to 1:1) to give **2t** (31.0 mg, 36% yield) as a colorless oil. ***N*-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzamide (2t)** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 4.51–

4.42 (m, 1H), 1.30–1.12 (m, 17H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 135.2, 131.1, 128.4, 126.8, 83.5, 42.5, 25.0, 24.7, 23.0; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{25}BNO_3$ $[M+H]^+$: 290.1922, found 290.1920.



A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. To the vessel were added *N*-(prop-1-en-2-yl)benzamide[36] (**5**: 48.4 mg, 0.30 mmol) and (*S*)-4-(*tert*-butyl)-2-(quinolin-2-yl)-4,5-dihydrooxazole (^{t}BuQuinox: 1.9 mg, 7.5 μmol), the vessel was introduced inside an argon atmosphere glovebox. In the glovebox, $[Ir(OMe)(cod)]_2$ (9.9 mg, 0.015 mmol) and THF (1.0 mL) were added. After 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin: 65.3 μL, 0.45 mmol) and THF (0.50 mL) were added, the glass vessel was sealed with the O-ring tap and then taken out of the glovebox. The mixture was stirred at 80 ˚C for 3 h, cooled to room temperature and concentrated *in vacuo*. ^{1}H NMR yield of **2t** was 36% determined by using dibromomethane as an internal standard. This result indicate that the hydroboration of cyclopropanes proceeds through Ir-catalyzed hydroboration of the corresponding olefin which is generated via C–C bond cleavage.

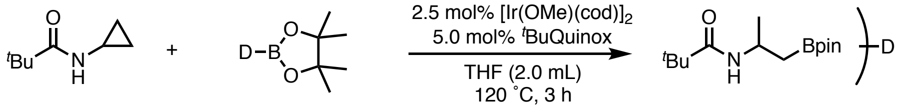
6-3. Hydroboration of 6



A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. To the vessel was added (*S*)-4-(*tert*-butyl)-2-(quinolin-2-yl)-4,5-dihydrooxazole (^{t}BuQuinox: 1.7 mg, 6.7 μmol), the vessel was introduced inside an argon atmosphere glovebox. In the glovebox, $[Ir(OMe)(cod)]_2$ (8.8 mg, 13.5 μmol) and THF (0.50 mL) were added. After 4,4,5,5-tetramethyl-2-(2-phenylallyl)-1,3,2-dioxaborolane[37] (**6**: 65.0 mg, 0.27 mmol) in THF (0.33 mL), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin: 58.0 μL, 0.40 mmol) and THF (0.50 mL) were added, the glass vessel was sealed with the O-ring tap and then taken out of the glovebox. The mixture was stirred at 80 ˚C for 18 h, cooled to room temperature and concentrated *in vacuo*. ^{1}H NMR yield of **2o** was 37% determined by using dibromomethane as an internal standard. ^{1}H NMR analysis of the crude product indicated that 2,2'-(2-phenylpropane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[38] is formed in 29% NMR yield determined by using dibromomethane as an internal standard. The residue was purified by PTLC (hexane/ethyl acetate = 10:1) to give **2o** (21.9 mg, 33% yield) as a colorless oil.

6-4. Deuterium Labeling Experiments

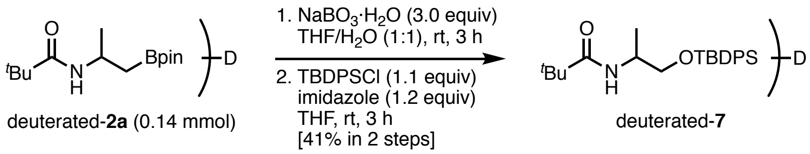
6-4-1. Hydroboration of 1a with DBpin



1a (0.35 mmol) (1.5 equiv_98 atom %D) deuterated-**2a**: 40%

A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. To the glass vessel were added ^{t}BuQuinox (4.5 mg, 0.018 mmol), [Ir(OMe)(cod)]$_2$ (5.9 mg, 8.9 μmol) and THF (1.0 mL) under nitrogen, then the mixture was stirred at room temperature for 15 min. *N*-cyclopropylpivalamide (**1a**: 50.0 mg, 0.35 mmol), DBpin[21, 22] (77.1 μL, 0.53 mmol) and THF (1.0 mL) were added to the mixture under nitrogen, and the glass vessel was sealed with the O-ring tap. The mixture was stirred at 120 ˚C for 3 h. After cooling to room temperature, the mixture was concentrated *in vacuo*. The residue was purified by MPLC (hexane/ethyl acetate = 3:1 to 1:1) to give the corresponding product deuterated-**2a** (38.3 mg, 40% yield).

6-4-2. Oxidation of Deuterated-2a and Silylation to Deuterated-7



deuterated-**2a** (0.14 mmol) deuterated-**7**

To a solution of the deuterated-**2a** (38.0 mg, 0.14 mmol) in THF (2.0 mL) and H_2O (2.0 mL) was added $NaBO_3 \cdot H_2O$ (42.1 mg, 0.42 mmol). The mixture was stirred at room temperature for 3 h. The mixture was diluted with H_2O (5.0 mL) and extracted with ethyl acetate, the combined organic layers were dried over Na_2SO_4, filtered and the filtrate was concentrated *in vacuo*. The crude alcohol was used in the next step without further purification.

To a solution of the crude alcohol and imidazole (14.4 mg, 0.21 mmol) in THF (5.0 mL) was added *tert*-butylchlorodiphenylsilane (TBDPSCl: 47.4 μL, 0.18 mmol). The reaction mixture was stirred at room temperature for 3 h. The mixture was diluted with H_2O (5.0 mL) and extracted with ethyl acetate, the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by MPLC (hexane/ethyl acetate = 4:1 to 1:1) to give the corresponding product deuterated-**7** (23.1 mg, 41% yield) as a colorless oil. According to the ^{2}H NMR of deuterated-**7**, D atom was distributed in the product structure as shown below (Figure S1). This incorporation of deuterium indicates that there is equilibrium via a reversible migratory insertion and that hydroboration proceeds through *in-situ* olefin formation.

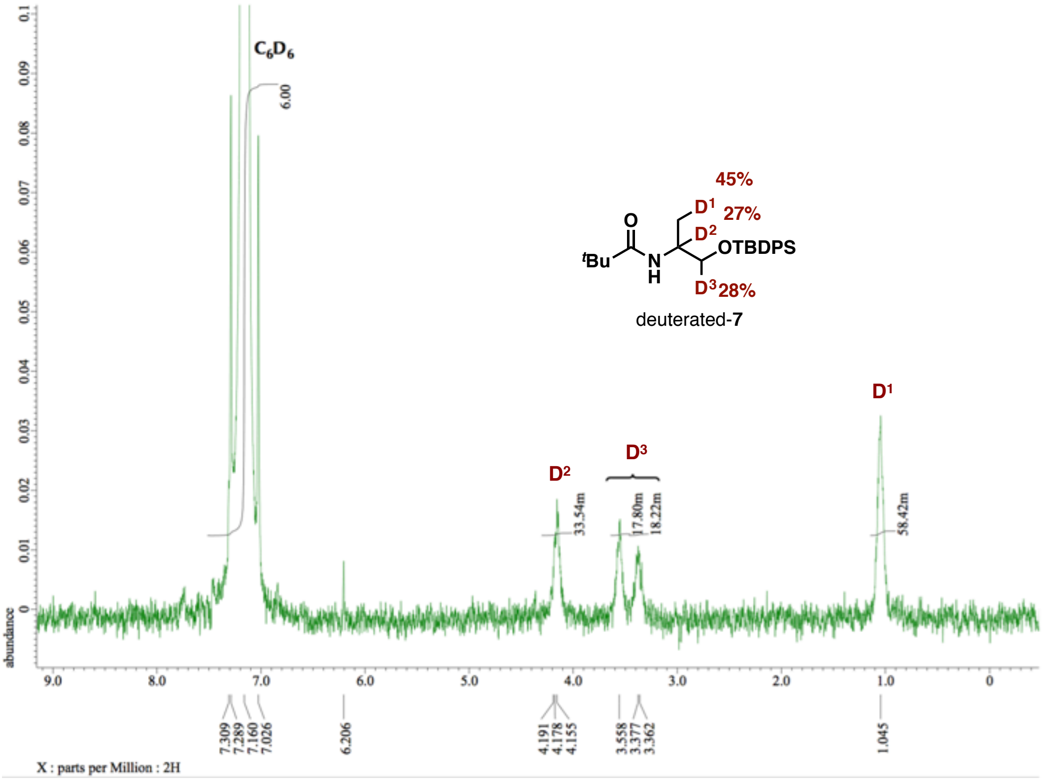
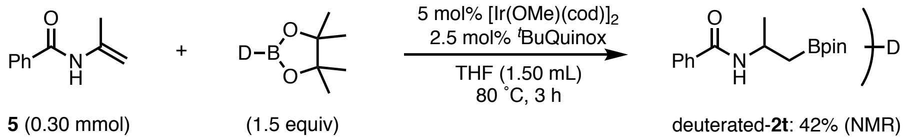


Figure **S1**. ^{2}H NMR of deuterated-**7**

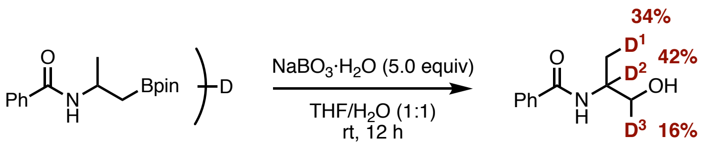
6-4-3. Hydroboration of 5 with DBpin



A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. To the glass vessel were added ^{t}BuQuinox (1.9 mg, 7.5 μmol), $[Ir(OMe)(cod)]_2$ (9.9 mg, 15 μmol) and THF (1.0 mL) under nitrogen, then the mixture was stirred at room temperature for 5 min. *N*-(prop-1-en-2-yl)benzamide[39] (**5**: 48.4 mg, 0.30 mmol), DBpin (3.3 M solution in THF: 136 μL, 0.45 mmol)[23] and THF (0.50 mL) were added to the mixture under nitrogen, and the glass vessel was sealed with the O-ring tap.

The mixture was stirred at 80 ˚C for 3 h. After cooling to room temperature, the mixture was concentrated *in vacuo*. ^{1}H NMR yield of deuterated-**2t** was 42% determined by using dibromomethane as an internal standard. The residue was purified by PTLC (hexane/ethyl acetate = 3:1). The obtained crude product deuterated-**2t** was used in the next step without further purification.

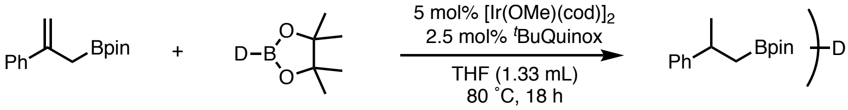
6-4-4. Oxidation of Deuterated-2t to Deuterated-8



deuterated-**2a** (74 μmol) deuterated-**8**: 64%

To a solution of the crude product deuterated-**2t** weighted 23.3 mg (73.5 μmol) in THF (2.0 mL) and H_2O (2.0 mL) was added $NaBO_3 \cdot 4H_2O$ (56.5 mg, 0.38 mmol). The mixture was stirred at room temperature for 3 h. The mixture was diluted with H_2O (5.0 mL) and extracted with ethyl acetate, the combined organic layers were dried over Na_2SO_4, filtered and the filtrate was concentrated *in vacuo*. The residue was purified by PTLC (hexane/ethyl acetate = 1:3) to afford the corresponding product deuterated-**8**[32] (8.4 mg, 64% yield) as a white solid. **Deuterated-8** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 8.4 Hz, 2H), 6.29 (brs, 1H), 4.35–4.24 (m, 0.58H), 3.84–3.75 (m, 0.90H), 3.71–3.62 (m, 0.94H), 2.69 (brs, 1H), 1.33–1.21 (m, 2.66H).

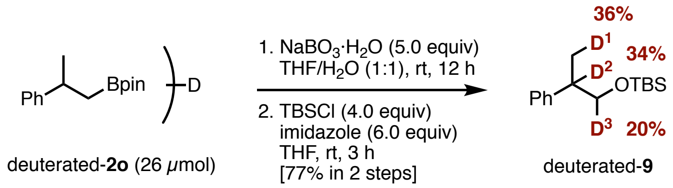
6-4-5. Hydroboration of 6 with DBpin



6 (0.27 mmol) (1.5 equiv) deuterated-**2o**: 19% (NMR)

A 20-mL glass vessel tube equipped with a J. Young® O-ring tap containing a magnetic stirring bar was dried with a heat gun under reduced pressure and filled with nitrogen after cooling to room temperature. To the glass vessel were added ^{t}BuQuinox (1.7 mg, 6.7 μmol), $[Ir(OMe)(cod)]_2$ (8.8 mg, 13.5 μmol) and THF (1.0 mL) under nitrogen, then the mixture was stirred at room temperature for 15 min. 4,4,5,5-Tetramethyl-2-(2-phenylallyl)-1,3,2-dioxaborolane[37] (**6**: 65.0 mg, 0.27 mmol), DBpin (3.3 M solution in THF: 123 μL, 0.41 mmol)[23] and THF (0.33 mL) were added to the mixture under nitrogen, and the glass vessel was sealed with the O-ring tap. The mixture was stirred at 80 ˚C for 18 h. After cooling to room temperature, the mixture was concentrated *in vacuo*. The residue was purified by PTLC (hexane/ethyl acetate = 9:1). ^{1}H NMR yield of deuterated-**2o** was 19% determined by using dibromomethane as an internal standard. The obtained crude product deuterated-**2o** was used in the next step without further purification.

6-4-6. Oxidation of Deuterated-2o and Silylation to Deuterated-9



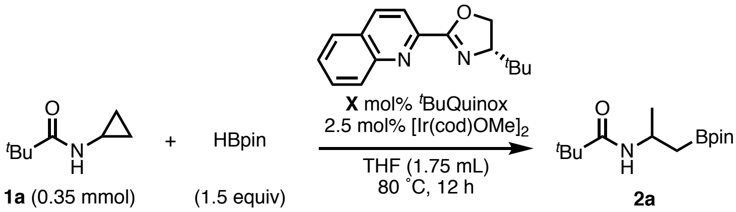
To a solution of the crude product deuterated-**2o** (26 µmol) in THF (1.0 mL) and H_2O (1.0 mL) was added $NaBO_3{\cdot}4H_2O$ (19.7 mg, 0.13 mmol). The mixture was stirred at room temperature for 12 h. The mixture was diluted with H_2O (5.0 mL) and extracted with ethyl acetate, the combined organic layers were dried over Na_2SO_4, filtered and the filtrate was concentrated *in vacuo*. The crude alcohol was used in the next step without further purification.

To a solution of the crude alcohol and imidazole (14.4 mg, 0.21 mmol) in THF (5.0 mL) was added *tert*-butyldimethylchlorosilane (TBSCl: 15.7 mg, 0.10 mmol). The reaction mixture was stirred at room temperature for 6 h. The mixture was diluted with H_2O (5.0 mL) and extracted with ethyl acetate, the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by PTLC (hexane/ethyl acetate = 30:1) to afford the corresponding product deuterated-**9** (5.0 mg, 77% yield) as a colorless oil. **Deuterated-9** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 2H), 7.24–7.16 (m, 3H), 3.72–3.64 (m, 0.88H), 3.61–3.54 (m, 0.92H), 2.95–2.83 (m, 0.66H), 1.30–1.24 (m, 2.64H), 0.86 (s, 9H), –0.03 (s, 3H), –0.04 (s, 3H).

The spectra of **9** are in accordance with those of the compounds reported in the literature.[40]

7. Effect of Reaction Parameters

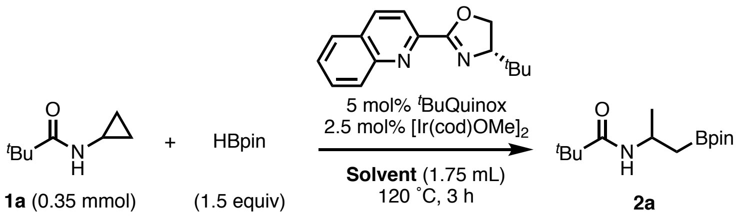
7-1. Investigation of the Ratio of $[Ir(cod)OMe]_2$ and ^{t}BuQuinox



Entry	X	Ir/Ligand	NMR Yield (%)[a]
1	1.25	4:1	73
2	2.5	2:1	69
3	5.0	1:1	38
4	7.5	2:3	10

[a] CH_2Br_2 was used as an internal standard.

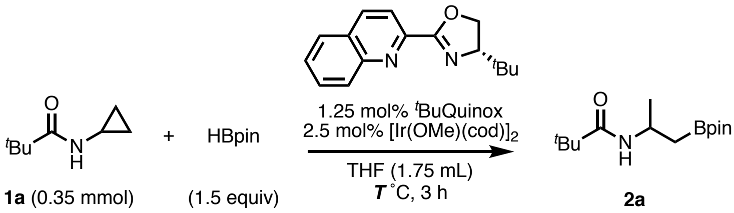
7-2. Investigation of Solvents



Entry	Solvent	NMR Yield (%)[a]
1	THF	56
2	cyclohexane	50
3	^{t}BuOMe	8
4	octane	42
5	cyclopentyl methyl ether	<5

[a] CH_2Br_2 was used as an internal standard.

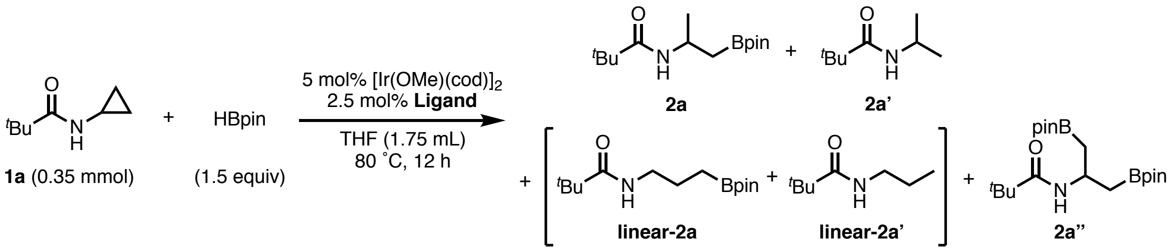
7-3. Investigation of Reaction Temperature



Entry	*T*	NMR Yield (%)[a]
1	120	70
2	80	73
3	50	14
4[b]	50	70
5	rt	<5

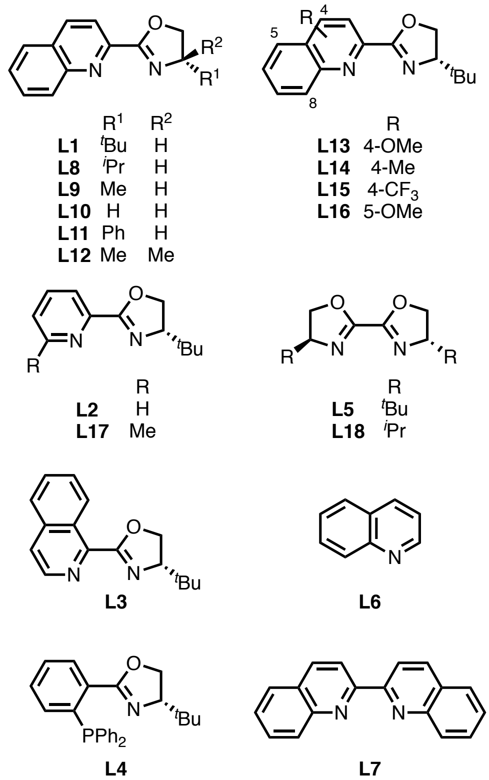
[a]CH_2Br_2 was used as an internal standard.
[b]64 h.

7-4. Investigation of Ligands

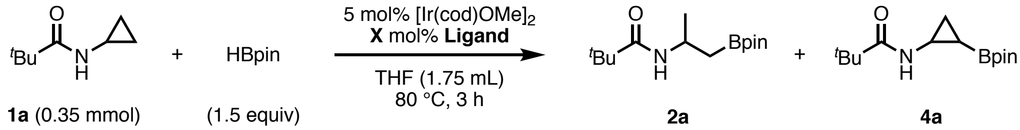


Entry	Ligand	2a	1a	2a'	linear-2a+linear-2a'	2a''
		NMR Yield (%)[a]				
1	^{t}BuQuinox (**L1**)	69	2	19	4	6
2	**L2**	<1	90	<1	7	<1
3	**L3**	<1	74	4	14	<1
4	**L4**	<1	65	3	8	<1
5	**L5**	<1	54	6	22	<1
6[c]	**L6**	<1	75	4	11	<1
7	**L7**	<1	88	<5	<10	<5
8	**L8**	69	2	7	3	12
9	**L9**	49	16	18	4	8
10	**L10**	14	70	2	6	8
11	**L11**	13	55	16	10	2
12	**L12**	25	62	12	5	<5
13[b]	**L13**	69	8	<5	4	20
14[b]	**L14**	69	<5	16	3	15
15[b]	**L15**	30	49	7	11	15
16	**L16**	67	<1	19	4	9
17	**L17**	<1	59	6	7	<1
18	**L18**	<1	54	6	22	<1
19	dppe	<1	69	<1	5	<1
20	dppf	<1	74	<1	7	<1
21	BINAP	<1	90	<1	4	<1

[a]CH_2Br_2 was used as an internal standard.
[b]The reaction was performed with 2.5 mol% of $[Ir(OMe)(cod)]_2$ and 5 mol% of ligand at 120 ˚C for 3 h.
[c]20 mol% ligand was used.



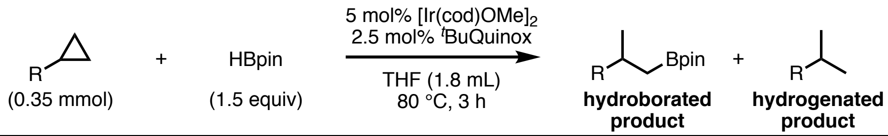
7-5. Reinvestigation of Ligands



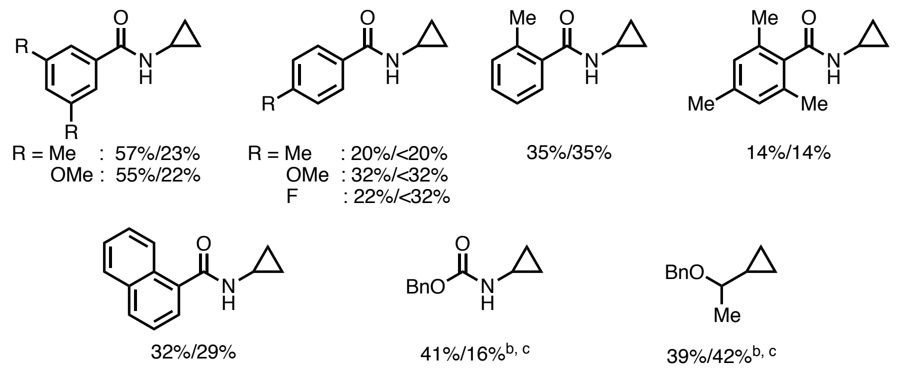
Entry	**Ligand** (**X** mol%)	NMR Yield (%)[a] **2a**	**1a**	**4a**
1	^{t}BuQuinox (2.5)	75	4	0
2	2,9-Me_2phen (5)	0	94	0
3	3,4,7,8-Me_4phen (5)	0	58	41

[a]CH_2Br_2 was used as an internal standard.

7-6. Examples for the ratio of hydroborated and hydorogenated products



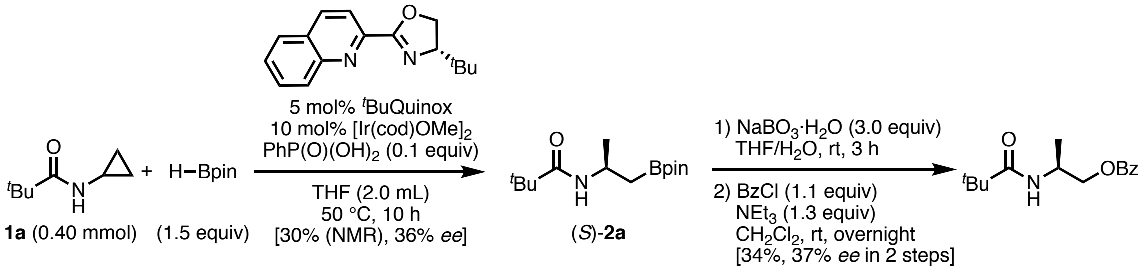
NMR Yield (**hydroborated/hydrogenated**)[a]



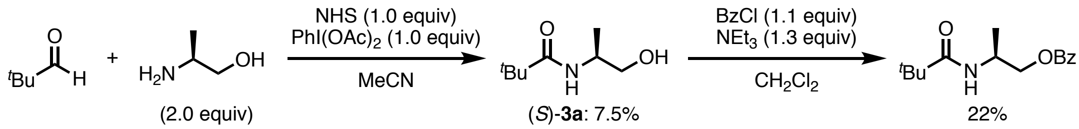
[a]CH_2Br_2 was used as an internal standard.
[b]Isolated yield.
[c]11 h.

8. Attempt toward Enantioselective Hydroboration

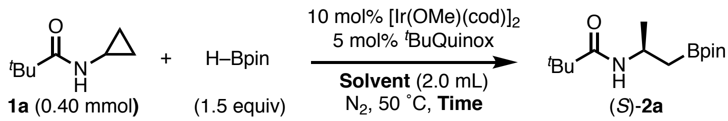
8-1. Optimized Conditions



8-2. Synthesis of Authentic Sample: For Determination of Absolute Configuration of 2a



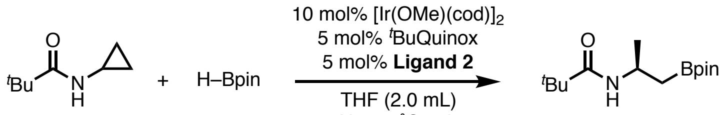
8-3. Effect of Solvent



Entry	**Solvent**	**Time**	Yield of (*S*)-**2a** (%)[a]	*ee* (%)
1	THF	3 h	53	15
2	hexane	10 h	37	13
3	CF_2CH_2OH	10 h	0	–
4	^{t}BuOH	10 h	0	–
5	cyclohexane	10 h	9	9
6	^{t}BuOMe	10 h	0	–
7	CPME	3 h	10	11

[a] CH_2Br_2 was used as an internal standard.

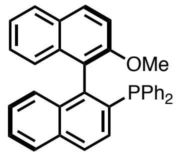
8-4. Effect of Co-ligand



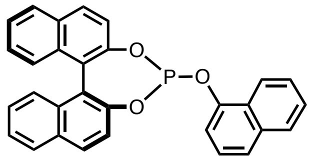
1a (0.40 mmol) (1.5 equiv) (*S*)-**2a**

Entry	**Ligand 2**	Yield of (*S*)-**2a** (%)[a]	*ee* (%)
1	none	53	15
2	**L19**	5	16
3	**L20**	8	24
4	**L21**	6	7
5	**L4**	16	15
6	**L22**	52	13
7	**L23**	0	–
8	**L24**	33	7
9	**L25**	51	15

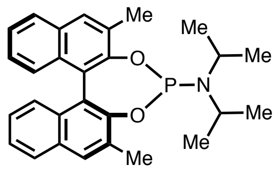
[a]CH_2Br_2 was used as an internal standard.



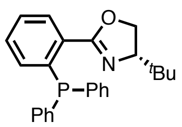
L19



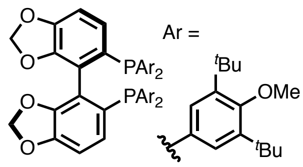
L20



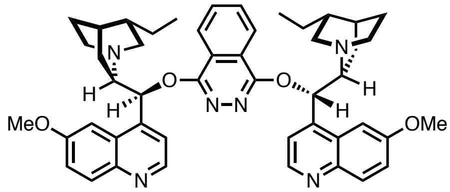
L21



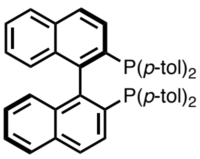
L4



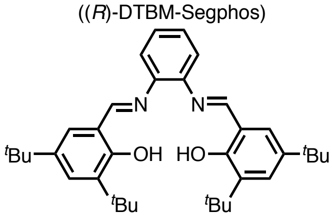
L22
((*R*)-DTBM-Segphos)



L23
((DHQD)$_2$PHAL)

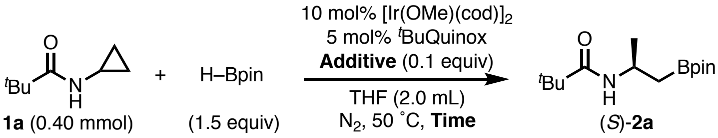


L24
((*S*)-T-BINAP)



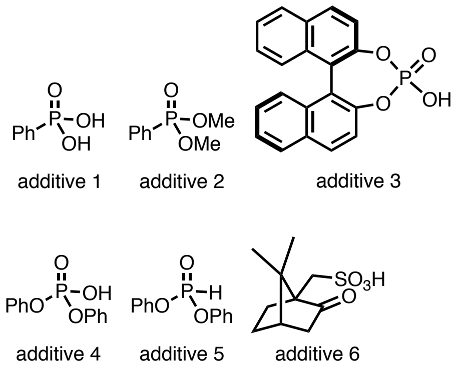
L25

8-5. Effect of Additive



Entry	**Additive**	**Time**	Yield of (*S*)-**2a** (%)[a]	*ee* (%)
1	none	3 h	53	15
2	$B(C_6F_5)_3$	3 h	0	–
3	$Sc(OTf)_4$	3 h	0	–
4	KBF_4	3 h	64	16
5	Rb_2CO_3	3 h	0	–
6	additive 1	10 h	30	36
7	additive 2	10 h	57	18
8	additive 3	10 h	36	28
9	additive 4	3 h	<30	32
10	additive 5	3 h	19	17
11	TsOH	3 h	0	–
12	additive 6	3 h	0	–
13	PinBOH[c]	16 h	41	14
14	PinBOH[c,d]	10 h	21	46

[a] CH_2Br_2 was used as an internal standard.
[b] 0.2 equiv of additive were used.
[c] 2.0 M solution of PinBOH was used.
[d] 2-MeTHF was used instead of THF.



9. The Detailed Explanation of Calculations for Difference in Activation Energy using ^{t}BuQuinox vs. L2 or L10

$\boxed{\Delta G_a(\mathbf{C-C})}$ of L2 and L10 ligands computed with a model reactant

In the cases of L2 and L10, B' is stable compared to B. Therefore, $\boxed{\Delta G_a(\mathrm{C-C})}$ of L2 and L10 were computed with

$$\boxed{\Delta G_a(\mathrm{C-C}) = \Delta G_a(\mathbf{B'} \rightarrow \mathbf{B}) + \Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}}),}$$

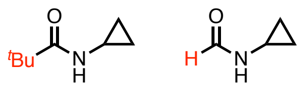
where $\boxed{\Delta G_a(\mathbf{B'} \rightarrow \mathbf{B})}$ and $\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$ are the activation free energies from B' to B and from B to TS_{BC}, respectively. $\boxed{\Delta G_a(\mathbf{B'} \rightarrow \mathbf{B})}$ and $\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$ are summarized in the following table.

Ligand	$\boxed{\Delta G_a(\mathbf{B'} \rightarrow \mathbf{B})}$[a)]	$\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$[a)]
L2	5.0	38.5
L10	7.5	32.5

a) Unit: kcal/mol

Because B is stable compared to B' in the case of L1, the activation step from B' to B is one of the reasons why $\boxed{\Delta G_a(\mathrm{C-C})}$ of L2 and L10 is large compared to $\boxed{\Delta G_a(\mathrm{C-C})}$ of L1.

$\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$ of L2 and L10 are still large compared to $\boxed{\Delta G_a(\mathrm{C-C})}$ of L1 (22.7 kcal/mol). To elucidate the origin of large $\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$, we computed $\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$ using the following model reactant.



1a **Model**

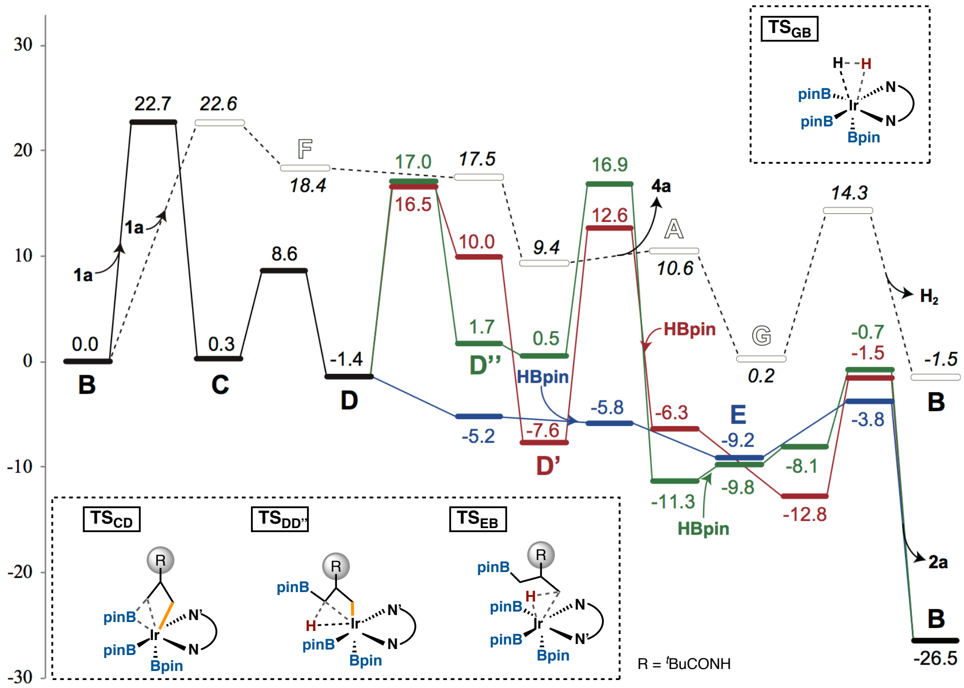
In the model reactant, we replaced ^{t}Bu group by H. We computed $\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$ of L2 and L10 ligands using the original (**1a**) and model reactants, as follows:

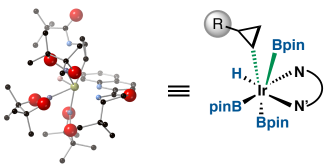
Ligand	1a[a)]	model[a)]
L1	22.7	20.8
L2	38.5	21.1
L10	32.5	15.8

a) Unit: kcal/mol

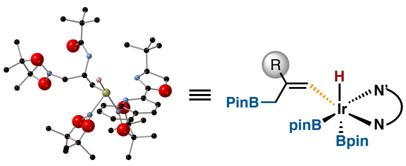
As a comparison, we also summarized $\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$ of L1 in the same table. In the case of 1a, $\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$ of L2 and L10 are around 10 kcal/mol larger than that of L1. On the other hand, when we employed model reactant, the difference in $\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$ becomes small among L1, L2, and L10 ligands. From the results, we concluded that the large $\boxed{\Delta G_a(\mathbf{B} \rightarrow \mathbf{TS_{BC}})}$ of L2 and L10 comes from the bulkiness of **1a**.

10. Chemical Structures of Calculated energies (Figure 3B)

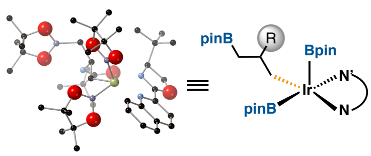




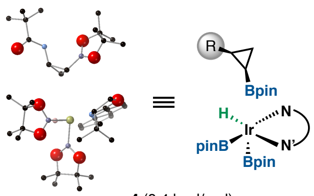
e1 (17.5 kcal/mol)



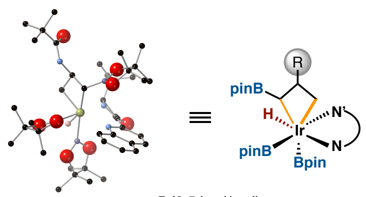
e2 (10.0 kcal/mol)



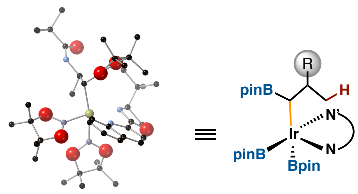
e3 (-5.2 kcal/mol)



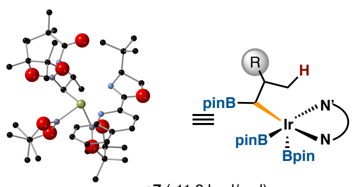
e4 (9.4 kcal/mol)



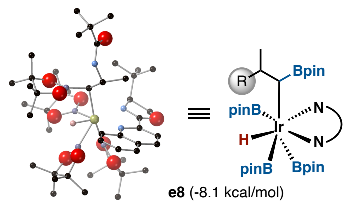
e5 (0.5 kcal/mol)



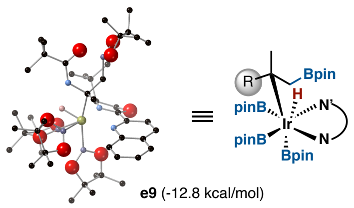
e6 (16.9 kcal/mol)



e7 (-11.3 kcal/mol)



e8 (-8.1 kcal/mol)



e9 (-12.8 kcal/mol)

11. Computational Details

All geometries were optimized by the DFT method with B3PW91 functional.[41–44] For the optimization, the employed basis sets are cc-pVDZ-pp for Ir,[45] 6-31G* for B, O, and N, and 6-31G for C atoms. [46,47] About H atoms, we employed two types of basis set, 6-311G** and 6-31G.[48] The former one was employed for the H atom that are attached to cyclopropane group and boron atom, and the latter one was employed for other hydrogens. The optimized structures were verified by frequency calculations as minima (no imaginary frequency) or transition structures (one imaginary frequency). We employed the frequency calculation data for the thermal correction. After the optimization, we computed free energy changes with spin-component-scaled MP2 (SCS-MP2) method[49] with larger basis set. In the basis set, 6-311G* was employed for B, and 6-311+G* was employed for O and N atoms.[48] For the carbon atoms of cyclopropane group, 6-311G* was employed and 6-31G* was employed for other carbon atoms.:[46–48] About H atoms, we employed 6-311G** and 6-31G. All calculations were carried out with the Gaussian09 program package.[49]

Cartesian Coordinates (unit: angstrom)

Geometry A

Element	X	Y	Z
Ir	-0.310276	-0.071909	-0.732535
B	1.653650	-0.231391	-1.188926
O	2.068717	0.210129	-2.454341
O	2.749504	-0.760654	-0.492880
C	3.387944	-0.349483	-2.724719
C	3.962486	-0.542344	-1.277839
C	4.160177	0.627507	-3.606631
C	3.168054	-1.675839	-3.463100
C	4.639603	0.717936	-0.727863
C	4.876264	-1.752134	-1.100068
H	5.183560	0.275161	-3.783090
H	3.658928	0.716420	-4.576009
H	4.202005	1.622517	-3.157427
H	2.577252	-1.481789	-4.363770
H	4.114932	-2.139733	-3.761002
H	2.609153	-2.379469	-2.838513

H	4.835460	0.575190	0.340174
H	5.593709	0.917166	-1.228029
H	3.991558	1.591734	-0.844706
H	5.767000	-1.668128	-1.734148
H	5.206648	-1.813615	-0.057649
H	4.355809	-2.680859	-1.343611
B	0.138311	-1.194784	0.836674
O	0.264107	-2.582162	0.835267
O	0.283295	-0.683241	2.130377
C	0.332071	-3.040058	2.217868
C	0.809437	-1.749528	2.978435
C	1.294933	-4.222427	2.284437
C	-1.080598	-3.484673	2.614669
C	2.334152	-1.592258	2.999932
C	0.237448	-1.576430	4.382588
H	1.432687	-4.561212	3.318279
H	0.888877	-5.056596	1.702804
H	2.268269	-3.961233	1.863848
H	-1.419366	-4.248592	1.907780
H	-1.105739	-3.910078	3.623994
H	-1.780828	-2.644831	2.569500
H	2.577181	-0.601022	3.397168
H	2.811229	-2.344687	3.637528
H	2.741834	-1.661535	1.987361
H	0.564785	-2.388521	5.042657
H	0.590850	-0.630323	4.805696
H	-0.854648	-1.552382	4.369568
N	-2.467985	0.345558	-0.891312
C	-2.728215	1.582360	-0.631662
C	-3.658363	-0.248549	-1.546084
C	-1.776945	2.450432	0.052166
O	-3.936581	2.072719	-0.993207

C	-4.629832	0.960137	-1.654242
H	-3.352649	-0.594025	-2.541315
C	-4.229328	-1.479931	-0.779366
C	-2.148700	3.749248	0.461887
N	-0.569541	1.895575	0.266826
H	-5.574206	0.814253	-1.127086
H	-4.828780	1.266959	-2.683575
C	-3.210232	-2.633162	-0.835181
C	-4.524297	-1.118832	0.686824
C	-5.522706	-1.935858	-1.488351
C	-1.237855	4.510579	1.151928
H	-3.141894	4.110131	0.226128
C	0.347318	2.643592	0.977541
H	-3.000739	-2.920604	-1.873001
H	-2.258670	-2.363568	-0.369991
H	-3.616255	-3.510815	-0.317567
H	-5.253088	-0.302938	0.777354
H	-4.939723	-1.988781	1.208328
H	-3.606021	-0.820093	1.203415
H	-5.898396	-2.850548	-1.016115
H	-6.322997	-1.187876	-1.431724
H	-5.335210	-2.160724	-2.546077
C	0.039861	3.969433	1.438003
H	-1.482611	5.513971	1.485405
C	1.623578	2.098505	1.263006
C	1.019898	4.697643	2.161033
C	2.549658	2.832369	1.974643
H	1.838288	1.094681	0.922571
C	2.252389	4.140953	2.426027
H	0.777589	5.700251	2.501208
H	3.521129	2.400314	2.189615
H	2.997788	4.702670	2.979837

H	-0.302132	-1.426408	-1.544958

Geometry B

Element	X	Y	Z
Ir	-0.059914	0.354253	-0.157219
B	-1.602789	-0.860411	-0.660050
O	-2.952888	-0.477692	-0.521134
O	-1.542222	-2.098846	-1.303241
C	-3.796066	-1.630653	-0.827646
C	-2.870013	-2.457310	-1.783238
C	-5.096314	-1.134444	-1.453848
C	-4.078394	-2.345644	0.498032
C	-2.958903	-2.003738	-3.245942
C	-3.028357	-3.972252	-1.686304
H	-5.731451	-1.975253	-1.756922
H	-5.652587	-0.539481	-0.721324
H	-4.908038	-0.507594	-2.329189
H	-4.578324	-1.647381	1.177539
H	-4.729396	-3.215579	0.357960
H	-3.141873	-2.660273	0.966009
H	-2.140913	-2.463306	-3.808812
H	-3.907354	-2.300163	-3.707577
H	-2.852036	-0.917096	-3.323260
H	-4.046017	-4.280718	-1.954090
H	-2.332799	-4.458903	-2.378006
H	-2.804250	-4.326741	-0.678033
B	0.020180	-0.728117	1.504571
O	-0.828186	-1.759172	1.909396
O	0.940999	-0.434333	2.524261
C	-0.605851	-2.023089	3.325268
C	0.852719	-1.480197	3.540757
C	-0.778111	-3.519768	3.569145

C	-1.663798	-1.231296	4.102972
C	1.932387	-2.518238	3.215190
C	1.113260	-0.849143	4.905780
H	-0.539912	-3.779797	4.607402
H	-1.817902	-3.805303	3.377933
H	-0.140003	-4.102645	2.901644
H	-2.655883	-1.523999	3.745552
H	-1.610315	-1.428777	5.179290
H	-1.547609	-0.156373	3.935140
H	2.911112	-2.026548	3.233258
H	1.946164	-3.331644	3.948850
H	1.779092	-2.930344	2.214225
H	0.996945	-1.587180	5.708344
H	2.138906	-0.467144	4.942010
H	0.436089	-0.013139	5.094938
N	-1.163704	2.239506	-0.363764
C	-0.399114	3.120198	-0.923249
C	-2.567541	2.678315	-0.556900
C	1.058034	3.096184	-0.788766
O	-0.989571	4.121918	-1.615666
C	-2.419550	3.765945	-1.644265
H	-3.138168	1.814268	-0.907145
C	-3.207687	3.170483	0.779889
C	1.862288	4.139127	-1.299320
N	1.530265	2.039254	-0.112769
H	-2.982612	4.680207	-1.456496
H	-2.637511	3.396118	-2.650740
C	-3.130818	2.040493	1.823595
C	-2.488585	4.415848	1.331404
C	-4.688612	3.499048	0.499773
C	3.216737	4.097399	-1.066217
H	1.397113	4.942756	-1.856053

C	2.874296	2.005879	0.162399
H	-3.556582	1.112218	1.432084
H	-2.092072	1.831796	2.096088
H	-3.676582	2.332841	2.729267
H	-2.543705	5.273186	0.649379
H	-2.953190	4.719226	2.276964
H	-1.433760	4.201731	1.536455
H	-5.180674	3.821364	1.424622
H	-4.805628	4.308413	-0.232290
H	-5.221208	2.616853	0.124708
C	3.761823	3.032084	-0.307035
H	3.872262	4.875746	-1.444227
C	3.389966	0.944453	0.948535
C	5.142252	2.948479	0.011660
C	4.735087	0.905963	1.252010
H	2.695273	0.198264	1.320237
C	5.620085	1.906093	0.776555
H	5.811118	3.722969	-0.352297
H	5.123152	0.097730	1.863043
H	6.675890	1.849252	1.021266
B	1.155686	-1.114557	-0.845296
O	1.669825	-0.935975	-2.137303
O	1.634728	-2.304807	-0.299975
C	2.256617	-2.197523	-2.579841
C	2.608318	-2.894412	-1.214819
C	3.452076	-1.885439	-3.476557
C	1.175602	-2.938857	-3.373590
C	4.001573	-2.528751	-0.692180
C	2.420839	-4.409758	-1.197962
H	3.960212	-2.805427	-3.789562
H	3.104061	-1.366597	-4.375894
H	4.173501	-1.238351	-2.972253

H	0.865295	-2.308934	-4.213945
H	1.544267	-3.890484	-3.772515
H	0.299343	-3.118190	-2.745368
H	4.098980	-2.888020	0.337565
H	4.793037	-2.989014	-1.293918
H	4.145525	-1.444775	-0.689740
H	3.081724	-4.896687	-1.924964
H	2.665522	-4.797365	-0.203281
H	1.386881	-4.680723	-1.420820

Geometry C

Element	X	Y	Z
Ir	-0.043610	0.035235	-0.275700
B	-1.977362	-0.294259	0.703003
O	-3.094849	0.195960	0.023727
O	-2.367769	-1.191294	1.682464
C	-4.306708	-0.287276	0.686190
C	-3.771966	-1.538939	1.465900
C	-5.356442	-0.588506	-0.379395
C	-4.787925	0.839993	1.604310
C	-3.778986	-2.824755	0.631635
C	-4.429607	-1.791101	2.819265
H	-6.264009	-1.004095	0.073766
H	-5.627995	0.335814	-0.899545
H	-4.980939	-1.295088	-1.122392
H	-4.989092	1.730781	1.000685
H	-5.708293	0.569447	2.132302
H	-4.016474	1.097524	2.334631
H	-3.192924	-3.584150	1.156784
H	-4.795368	-3.204817	0.481675
H	-3.313281	-2.663145	-0.344502
H	-5.494844	-2.019683	2.696982

H	-3.950430	-2.648509	3.302169
H	-4.331896	-0.931354	3.485542
B	-0.475587	0.804807	1.654239
O	-1.080539	2.041648	1.924083
O	0.104386	0.298866	2.815503
C	-0.711968	2.473438	3.274162
C	-0.269664	1.123704	3.956087
C	-1.925843	3.146912	3.910089
C	0.426745	3.490023	3.136798
C	-1.408731	0.399303	4.681074
C	0.941104	1.242987	4.880481
H	-1.706864	3.452506	4.939705
H	-2.188550	4.043996	3.339589
H	-2.794288	2.485387	3.921065
H	0.086190	4.324821	2.515537
H	0.724157	3.891200	4.111441
H	1.303582	3.045780	2.659045
H	-1.053891	-0.586269	4.996635
H	-1.740034	0.950306	5.567806
H	-2.257090	0.240834	4.011801
H	0.725955	1.903878	5.728427
H	1.192306	0.254507	5.278135
H	1.815895	1.624377	4.349362
N	-1.028057	1.888327	-1.364506
C	-1.878646	1.416957	-2.201059
C	-1.471286	3.284011	-1.049121
C	-1.814137	0.076493	-2.773565
O	-2.933303	2.188040	-2.568134
C	-2.907833	3.300565	-1.615077
H	-1.469388	3.381342	0.040101
C	-0.560454	4.399600	-1.657455
C	-2.415468	-0.150621	-4.034160

N	-1.167163	-0.852227	-2.060165
H	-3.173964	4.202948	-2.164062
H	-3.660229	3.086173	-0.851835
C	0.851269	4.322863	-1.058323
C	-0.467179	4.274588	-3.189279
C	-1.162453	5.771016	-1.276705
C	-2.309552	-1.389704	-4.608596
H	-2.928609	0.669853	-4.518714
C	-1.111977	-2.126706	-2.597518
H	0.824787	4.429759	0.031849
H	1.331486	3.374179	-1.299325
H	1.477143	5.127062	-1.462303
H	-1.448403	4.344274	-3.674045
H	0.159256	5.079305	-3.591487
H	-0.007527	3.322128	-3.474439
H	-0.490546	6.570765	-1.608517
H	-2.138216	5.953674	-1.741828
H	-1.279273	5.862063	-0.189309
C	-1.649920	-2.420365	-3.897147
H	-2.730337	-1.595326	-5.587779
C	-0.543129	-3.186735	-1.851778
C	-1.537343	-3.733706	-4.421658
C	-0.463376	-4.457481	-2.385537
H	-0.211664	-2.991456	-0.840800
C	-0.945949	-4.736589	-3.685121
H	-1.936242	-3.932042	-5.412187
H	-0.032467	-5.257545	-1.792467
H	-0.864267	-5.739803	-4.090413
B	0.831824	-1.540477	0.676994
O	0.194673	-2.689209	1.151911
O	2.212309	-1.648030	0.917085
C	1.126056	-3.453447	1.975414

C	2.515870	-2.985448	1.418820
C	0.826520	-4.940062	1.800886
C	0.879317	-3.033966	3.427846
C	3.003504	-3.812851	0.223462
C	3.619379	-2.876369	2.467961
H	1.534839	-5.551323	2.372341
H	-0.181671	-5.153156	2.170303
H	0.874904	-5.242182	0.752082
H	-0.169542	-3.228212	3.671667
H	1.511894	-3.595359	4.124160
H	1.053912	-1.962821	3.551545
H	3.869609	-3.316140	-0.225288
H	3.305331	-4.821676	0.525154
H	2.229493	-3.890896	-0.545946
H	3.815190	-3.850023	2.932430
H	4.547363	-2.535737	1.997490
H	3.351988	-2.161523	3.248917
H	2.121688	0.687771	1.276285
H	2.053293	-1.040746	-1.684801
C	7.057733	1.798285	0.021526
C	6.315309	0.685395	-0.748583
H	7.031493	2.728372	-0.552958
H	6.588809	1.982576	0.995886
H	8.102562	1.510970	0.192058
C	6.310873	-0.604028	0.086146
C	7.028236	0.430006	-2.093903
H	5.810922	-1.426487	-0.440625
H	7.342930	-0.919736	0.279989
H	5.825017	-0.456491	1.058530
H	8.072559	0.141243	-1.922449
H	6.536294	-0.375524	-2.652701
H	7.003905	1.336082	-2.705637

C	4.905545	1.234803	-1.084591
O	4.804011	2.276699	-1.747096
N	3.827294	0.542216	-0.634284
H	3.941315	-0.301558	-0.089502
C	2.455865	0.953851	-0.875204
H	2.544460	1.892095	-1.426244
C	1.634244	1.127376	0.408993
H	1.389368	2.170755	0.615242
C	1.590293	-0.052276	-1.639365
H	1.348527	0.277804	-2.656401

Geometry D

Element	X	Y	Z
Ir	-0.971343	0.042188	-0.336574
B	-1.819856	-0.105835	1.455088
O	-1.368093	0.566205	2.588062
O	-3.010985	-0.780960	1.715802
C	-2.135550	0.082975	3.733081
C	-3.463596	-0.415327	3.054340
C	-2.304917	1.234966	4.719502
C	-1.318253	-1.048457	4.365880
C	-4.508207	0.693928	2.885720
C	-4.095720	-1.645000	3.699843
H	-2.924721	0.933834	5.572372
H	-1.323081	1.533265	5.101114
H	-2.760473	2.107024	4.244263
H	-0.338954	-0.652434	4.653470
H	-1.805488	-1.451904	5.260449
H	-1.155532	-1.852892	3.643411
H	-5.303807	0.330639	2.227597
H	-4.954678	0.981431	3.843869
H	-4.064905	1.582131	2.424748

H	-4.389309	-1.439113	4.736034
H	-4.993073	-1.930900	3.141055
H	-3.406580	-2.491911	3.688617
B	-0.506304	-1.887863	-0.002643
O	-0.402613	-2.560493	1.219569
O	-0.113972	-2.754618	-1.042319
C	0.308598	-3.815976	1.028456
C	0.089646	-4.098063	-0.501759
C	-0.289198	-4.861036	1.968761
C	1.774710	-3.562464	1.398209
C	-1.180826	-4.907282	-0.784550
C	1.275923	-4.728011	-1.225620
H	0.169780	-5.844004	1.809434
H	-0.104165	-4.565056	3.006575
H	-1.369172	-4.948999	1.831548
H	1.817987	-3.188488	2.425868
H	2.371957	-4.479319	1.336661
H	2.219107	-2.802077	0.749802
H	-1.358299	-4.915820	-1.865199
H	-1.079828	-5.944821	-0.447898
H	-2.051031	-4.461651	-0.294235
H	1.524578	-5.707198	-0.799298
H	1.025874	-4.869526	-2.282272
H	2.155914	-4.084957	-1.176051
N	-1.352974	2.254582	-0.965941
C	-2.619962	2.374356	-0.755129
C	-0.767409	3.618891	-0.847748
C	-3.571211	1.290169	-0.994629
O	-3.092496	3.578321	-0.355560
C	-1.879726	4.377658	-0.098241
H	0.160429	3.568927	-0.268508
C	-0.422034	4.225823	-2.250691

C	-4.953295	1.553514	-1.101080
N	-3.010343	0.080821	-1.160415
H	-2.075492	5.386390	-0.460719
H	-1.727840	4.390391	0.985100
C	0.596289	3.323863	-2.972439
C	-1.674348	4.374358	-3.135175
C	0.229179	5.606157	-2.019168
C	-5.796359	0.527519	-1.453254
H	-5.312034	2.556467	-0.907749
C	-3.834106	-0.938215	-1.589354
H	1.533277	3.279675	-2.408766
H	0.208069	2.307547	-3.098294
H	0.814369	3.731142	-3.967483
H	-2.430272	5.029199	-2.685839
H	-1.391887	4.813482	-4.099577
H	-2.135654	3.401185	-3.338639
H	0.548680	6.030780	-2.978505
H	-0.465687	6.322384	-1.562933
H	1.107846	5.511174	-1.372290
C	-5.248779	-0.746675	-1.740307
H	-6.866916	0.684485	-1.539265
C	-3.271629	-2.193525	-1.924904
C	-6.050360	-1.828742	-2.188836
C	-4.077733	-3.215130	-2.382834
H	-2.200056	-2.322400	-1.821721
C	-5.477492	-3.040643	-2.506871
H	-7.121239	-1.676658	-2.288212
H	-3.634048	-4.168456	-2.649041
H	-6.094238	-3.861869	-2.857583
B	3.872650	-0.845855	-1.068506
O	4.477232	-1.620754	-2.030121
O	4.592733	-0.815284	0.111036

C	5.620844	-2.303412	-1.424284
C	5.907915	-1.420399	-0.151875
C	6.746984	-2.340956	-2.454501
C	5.171265	-3.727116	-1.086635
C	6.878333	-0.268297	-0.429110
C	6.337770	-2.189565	1.092570
H	7.649991	-2.796975	-2.033030
H	6.430618	-2.941984	-3.312762
H	6.992934	-1.340907	-2.817746
H	4.799313	-4.205435	-1.997654
H	5.999368	-4.326411	-0.694004
H	4.363798	-3.724222	-0.349510
H	6.915176	0.391310	0.442729
H	7.891533	-0.637271	-0.618206
H	6.555927	0.324105	-1.290924
H	7.292896	-2.699459	0.923544
H	6.467694	-1.493266	1.927055
H	5.590704	-2.930228	1.385152
H	1.300669	-0.446850	1.115824
H	2.749079	0.431592	-2.341266
C	3.442765	4.324117	2.689116
C	4.154558	3.440753	1.643259
H	2.848783	5.092326	2.187360
H	2.770617	3.726281	3.316230
H	4.180438	4.808061	3.340587
C	4.936882	2.331615	2.363220
C	5.122199	4.311126	0.810934
H	5.493000	1.699619	1.661595
H	5.666791	2.782645	3.045608
H	4.275417	1.692632	2.960752
H	5.866324	4.781315	1.465272
H	5.653232	3.707483	0.065017

H	4.566535	5.094766	0.287439
C	3.065988	2.919242	0.673153
O	2.276263	3.737109	0.162144
N	3.040460	1.599188	0.389955
H	3.675575	0.978502	0.874769
C	1.965362	0.959691	-0.383269
H	1.526030	1.776213	-0.954529
C	0.881402	0.401896	0.558169
H	0.685452	1.176085	1.311258
C	2.544320	-0.065611	-1.381152
H	1.767795	-0.806335	-1.614831

Geometry D’

Element	X	Y	Z
Ir	0.896380	-0.093413	-0.454892
B	2.919270	-0.322394	-0.091899
O	3.453452	-0.669740	1.144974
O	3.940109	-0.007780	-0.992473
C	4.895301	-0.441764	1.120798
C	5.209289	-0.453360	-0.416902
C	5.570869	-1.547387	1.927392
C	5.140145	0.920239	1.781332
C	5.470784	-1.859289	-0.967938
C	6.309183	0.505496	-0.863306
H	6.662957	-1.461906	1.877107
H	5.270320	-1.469546	2.977437
H	5.275294	-2.534140	1.565513
H	4.710938	0.904161	2.788137
H	6.208442	1.148370	1.864293
H	4.651557	1.722697	1.219487
H	5.502145	-1.807266	-2.061137
H	6.424480	-2.265365	-0.613109

H	4.658585	-2.534762	-0.685615
H	7.273248	0.229454	-0.420127
H	6.411594	0.459945	-1.952584
H	6.081820	1.538383	-0.587066
B	0.890218	-2.126968	-0.553139
O	2.024775	-2.950361	-0.581525
O	-0.251633	-2.920067	-0.759523
C	1.652197	-4.248620	-1.130245
C	0.131555	-4.330139	-0.764090
C	2.530290	-5.322892	-0.494596
C	1.902416	-4.184066	-2.642382
C	-0.114954	-4.872011	0.648385
C	-0.744427	-5.066571	-1.773182
H	2.220850	-6.324339	-0.816595
H	3.570980	-5.175859	-0.801893
H	2.491151	-5.275175	0.596028
H	2.948757	-3.914018	-2.814759
H	1.705664	-5.145457	-3.129268
H	1.275995	-3.417349	-3.108450
H	-1.162259	-4.697215	0.915903
H	0.081325	-5.948007	0.709760
H	0.520797	-4.359062	1.376966
H	-0.444182	-6.117646	-1.859499
H	-1.788331	-5.036411	-1.444335
H	-0.689718	-4.603364	-2.760882
N	1.353029	2.132100	-0.549336
C	1.434864	2.615498	0.647452
C	2.231834	2.978797	-1.412152
C	0.967987	1.899815	1.821288
O	2.107841	3.785569	0.822320
C	2.448381	4.228873	-0.530827
H	3.166006	2.405750	-1.502961

C	1.744686	3.282320	-2.855617
C	0.965284	2.530571	3.087245
N	0.621319	0.613037	1.607914
H	1.776927	5.055063	-0.787463
H	3.478234	4.585335	-0.508404
C	1.822861	2.001992	-3.707693
C	0.310433	3.834921	-2.880759
C	2.709639	4.327082	-3.462646
C	0.579233	1.813007	4.189629
H	1.279869	3.564556	3.153584
C	0.220845	-0.116763	2.712738
H	2.848834	1.618642	-3.742515
H	1.196362	1.208090	-3.295690
H	1.497885	2.214436	-4.733421
H	0.209800	4.760399	-2.300777
H	0.016496	4.062036	-3.912020
H	-0.399734	3.099860	-2.488631
H	2.460369	4.491522	-4.516911
H	2.646996	5.297824	-2.955375
H	3.748545	3.977628	-3.416882
C	0.193903	0.457802	4.028673
H	0.566875	2.261621	5.177736
C	-0.170853	-1.467925	2.554323
C	-0.211404	-0.342042	5.126747
C	-0.563866	-2.218654	3.643552
H	-0.158795	-1.880030	1.553907
C	-0.582949	-1.656997	4.940908
H	-0.223034	0.103229	6.117235
H	-0.866115	-3.250207	3.500127
H	-0.892011	-2.262259	5.786808
B	-3.996347	-0.361331	-0.069738
O	-4.957148	-0.968442	0.781588

O	-4.463989	-0.373766	-1.411070
C	-5.994505	-1.533442	-0.053917
C	-5.879210	-0.680447	-1.372413
C	-7.330254	-1.412809	0.678452
C	-5.651101	-3.013757	-0.277592
C	-6.665602	0.636414	-1.296291
C	-6.239931	-1.424622	-2.657388
H	-8.157695	-1.778488	0.058314
H	-7.298985	-2.013286	1.594161
H	-7.532215	-0.377575	0.963341
H	-5.536117	-3.496296	0.698576
H	-6.434653	-3.538780	-0.835718
H	-4.705772	-3.111516	-0.820367
H	-6.364292	1.272003	-2.135861
H	-7.746779	0.468005	-1.360103
H	-6.443708	1.168512	-0.367436
H	-7.284884	-1.757025	-2.642516
H	-6.106115	-0.757439	-3.515845
H	-5.593964	-2.293360	-2.803618
H	-1.039271	-1.008926	-2.200673
H	-2.257496	-0.664940	1.243759
C	-1.898605	4.373249	0.447945
C	-3.162779	3.526930	0.654891
H	-1.063018	4.019488	1.062086
H	-1.587992	4.400679	-0.603026
H	-2.108477	5.405685	0.748005
C	-4.311116	4.098913	-0.207577
C	-3.569124	3.562997	2.146583
H	-5.220899	3.508664	-0.075207
H	-4.513961	5.134009	0.089591
H	-4.048296	4.091478	-1.271704
H	-3.791491	4.594591	2.442408

H	-4.455277	2.946027	2.315206
H	-2.760252	3.188808	2.784636
C	-2.992890	2.050600	0.268730
O	-4.000733	1.301672	0.441061
N	-1.828651	1.606363	-0.227426
H	-1.090136	2.277991	-0.396429
C	-1.570425	0.233986	-0.573641
H	1.455061	-0.448143	-1.883743
C	-0.922884	-0.018457	-1.779456
H	-0.784992	0.791100	-2.489474
C	-2.440884	-0.718850	0.164125
H	-2.217736	-1.733615	-0.165841

Geometry D''

Element	X	Y	Z
Ir	-0.296769	0.087961	-0.029556
B	-2.398285	-0.081746	-0.494865
O	-3.121868	0.473792	-1.538070
O	-3.253627	-0.504265	0.522042
C	-4.522614	0.623672	-1.137818
C	-4.644204	-0.351078	0.096526
C	-5.404717	0.266968	-2.332521
C	-4.721858	2.099537	-0.777742
C	-5.154435	-1.749905	-0.260641
C	-5.443728	0.202214	1.275634
H	-6.466393	0.356321	-2.074724
H	-5.194247	0.957034	-3.155668
H	-5.217230	-0.748370	-2.687298
H	-4.459710	2.712717	-1.645241
H	-5.762048	2.310132	-0.506913
H	-4.075242	2.399509	0.050630
H	-5.073210	-2.392330	0.622382

H	-6.203618	-1.731083	-0.573997
H	-4.553477	-2.196463	-1.054774
H	-6.490853	0.368911	0.997530
H	-5.423730	-0.519773	2.098516
H	-5.025214	1.141402	1.643150
B	-0.868049	-1.173845	-1.608710
O	-1.266121	-2.513585	-1.523895
O	-0.669494	-0.807225	-2.934172
C	-1.426844	-3.055306	-2.873689
C	-0.682831	-1.994301	-3.775305
C	-2.930604	-3.131471	-3.150347
C	-0.826817	-4.459911	-2.900434
C	-1.398203	-1.639301	-5.079116
C	0.776480	-2.358108	-4.077257
H	-3.139170	-3.556661	-4.137781
H	-3.398721	-3.771765	-2.395800
H	-3.381735	-2.137601	-3.093184
H	-1.384410	-5.107804	-2.216035
H	-0.889483	-4.893476	-3.905310
H	0.218742	-4.457016	-2.585419
H	-0.820237	-0.874199	-5.607349
H	-1.485746	-2.513758	-5.734505
H	-2.394201	-1.233488	-4.890528
H	0.846694	-3.213451	-4.758198
H	1.259417	-1.498048	-4.551704
H	1.330408	-2.590007	-3.164166
N	-0.757472	-1.151692	1.821357
C	-1.237323	-0.360656	2.716421
C	-1.240351	-2.534045	2.153193
C	-1.252211	1.093775	2.601648
O	-1.953721	-0.883096	3.740687
C	-2.158204	-2.284547	3.381762

H	-1.828098	-2.847237	1.283178
C	-0.179665	-3.647170	2.429345
C	-1.536846	1.905153	3.722947
N	-1.083969	1.566894	1.358885
H	-1.896079	-2.878694	4.256521
H	-3.219425	-2.408391	3.153359
C	0.638763	-3.968227	1.166797
C	0.767564	-3.262495	3.578740
C	-0.966657	-4.930444	2.796848
C	-1.672162	3.258900	3.546288
H	-1.646598	1.435268	4.691799
C	-1.298552	2.913618	1.147073
H	-0.008788	-4.054266	0.288076
H	1.397917	-3.210569	0.978740
H	1.170637	-4.916962	1.306148
H	0.230480	-3.059273	4.514030
H	1.469788	-4.081370	3.770089
H	1.368105	-2.385896	3.319385
H	-0.261161	-5.755086	2.946226
H	-1.549481	-4.832717	3.720217
H	-1.650166	-5.216936	1.987196
C	-1.587191	3.798996	2.238207
H	-1.873533	3.916805	4.385685
C	-1.295930	3.427797	-0.171921
C	-1.821607	5.172406	1.971941
C	-1.566725	4.761692	-0.398258
H	-1.097806	2.737496	-0.981624
C	-1.816756	5.646330	0.677468
H	-2.024581	5.836908	2.806558
H	-1.588480	5.137993	-1.415696
H	-2.013779	6.694799	0.478788
B	2.297645	1.829497	-0.089169

O	2.075434	3.187065	0.069673
O	3.243998	1.587271	-1.089103
C	2.743477	3.889423	-1.025169
C	3.853103	2.864759	-1.454426
C	3.260757	5.221408	-0.488604
C	1.706976	4.127744	-2.126822
C	5.139673	3.002706	-0.633512
C	4.175687	2.837576	-2.945509
H	3.827997	5.761121	-1.255864
H	2.412674	5.845374	-0.189081
H	3.898267	5.079497	0.387040
H	0.882359	4.713261	-1.713729
H	2.137032	4.681504	-2.968074
H	1.302967	3.180516	-2.497428
H	5.799880	2.159702	-0.857834
H	5.674799	3.927176	-0.874742
H	4.922216	2.992824	0.439079
H	4.575593	3.802588	-3.277674
H	4.932761	2.071290	-3.141923
H	3.291979	2.597290	-3.540498
H	1.759944	-0.647885	-1.620548
H	1.576466	0.968796	1.819609
C	6.055321	-3.430026	0.162619
C	5.843242	-1.985387	0.664741
H	5.649873	-4.139511	0.889218
H	5.548391	-3.591751	-0.796613
H	7.124723	-3.630620	0.023254
C	6.366646	-0.993886	-0.384238
C	6.604499	-1.788813	1.992962
H	6.256609	0.043692	-0.048065
H	7.434878	-1.171360	-0.556780
H	5.854194	-1.110301	-1.347178

H	7.673747	-1.989796	1.852888
H	6.494062	-0.761568	2.361505
H	6.209319	-2.469917	2.751790
C	4.333263	-1.840638	0.982931
O	3.819032	-2.606986	1.813330
N	3.628718	-0.877501	0.337627
H	4.075931	-0.271261	-0.336966
C	2.186485	-0.704143	0.505257
H	1.927020	-1.342574	1.348204
C	1.343907	-1.080714	-0.709043
H	1.195933	-2.153120	-0.838715
C	1.660637	0.705770	0.758669
H	-0.057193	1.042982	-1.236521

Geometry E

Element	X	Y	Z
Ir	-0.715431	0.126655	0.094476
B	-0.956557	2.129345	-0.208296
O	-1.694426	2.989527	0.607751
O	-0.283712	2.853352	-1.182773
C	-1.760474	4.294953	-0.055873
C	-0.458626	4.280073	-0.928148
C	-1.813355	5.384781	1.010536
C	-3.047289	4.298905	-0.887819
C	0.783046	4.764442	-0.173482
C	-0.567368	4.996036	-2.271412
H	-1.800332	6.379249	0.549193
H	-2.740410	5.293247	1.586771
H	-0.970385	5.313103	1.702266
H	-3.899910	4.122221	-0.224093
H	-3.195681	5.257785	-1.396540
H	-3.022593	3.494002	-1.627183

H	1.670938	4.528464	-0.767256
H	0.751982	5.846344	-0.000416
H	0.874368	4.257401	0.792978
H	-0.769138	6.065041	-2.132861
H	0.379869	4.894020	-2.810053
H	-1.357971	4.562231	-2.887117
B	-2.736595	-0.731664	0.149110
O	-4.003437	-0.270390	-0.188488
O	-2.832658	-1.992667	0.738090
C	-5.019262	-1.227557	0.272489
C	-4.173558	-2.528922	0.511753
C	-6.098050	-1.350672	-0.801125
C	-5.646829	-0.659108	1.547880
C	-4.077531	-3.431410	-0.723092
C	-4.579094	-3.351517	1.732040
H	-6.871726	-2.061856	-0.488475
H	-6.573222	-0.376578	-0.954362
H	-5.688556	-1.684649	-1.755894
H	-6.024845	0.346345	1.339271
H	-6.482977	-1.280531	1.887050
H	-4.917710	-0.583757	2.356397
H	-3.350661	-4.224896	-0.523887
H	-5.040478	-3.895585	-0.962405
H	-3.721270	-2.866499	-1.588863
H	-5.597023	-3.742924	1.620445
H	-3.898198	-4.202277	1.837452
H	-4.529485	-2.763152	2.650902
N	-0.784359	0.210924	2.260600
C	-0.135206	-0.752616	2.825487
C	-0.954442	1.286937	3.291730
C	0.171797	-2.015170	2.166866
O	0.307129	-0.557853	4.090487

C	0.121032	0.880916	4.317988
H	-0.735726	2.244892	2.813962
C	-2.389549	1.363472	3.913244
C	0.631052	-3.120255	2.924252
N	-0.036703	-2.032722	0.850568
H	-0.169335	1.006601	5.359270
H	1.086232	1.364254	4.135065
C	-3.415849	1.788497	2.852393
C	-2.803561	0.012466	4.526438
C	-2.377427	2.452267	5.011187
C	0.854213	-4.310103	2.279185
H	0.785980	-3.002304	3.989161
C	0.188876	-3.213934	0.189958
H	-3.195998	2.788077	2.473708
H	-3.413898	1.122045	1.989108
H	-4.419558	1.788636	3.295481
H	-2.119371	-0.315063	5.318296
H	-3.802729	0.101001	4.969300
H	-2.842849	-0.769692	3.760301
H	-3.399801	2.613160	5.372069
H	-1.767325	2.182080	5.881242
H	-2.011214	3.407122	4.614140
C	0.631418	-4.392912	0.881436
H	1.195133	-5.186850	2.821349
C	-0.031188	-3.280942	-1.208398
C	0.832367	-5.592194	0.150485
C	0.175085	-4.463789	-1.888075
H	-0.403704	-2.401045	-1.718812
C	0.609801	-5.628394	-1.209938
H	1.163594	-6.479186	0.683017
H	-0.005497	-4.504137	-2.957188
H	0.763861	-6.548920	-1.763837

B	3.829789	-1.070197	-0.899911
O	4.487412	-1.964029	-1.714631
O	4.229200	-1.165865	0.419228
C	5.237531	-2.887259	-0.865811
C	5.382879	-2.072147	0.474352
C	6.551972	-3.219958	-1.566118
C	4.379560	-4.147184	-0.720825
C	6.635194	-1.191372	0.512022
C	5.280175	-2.900627	1.751197
H	7.177473	-3.867451	-0.941019
H	6.340370	-3.749347	-2.500466
H	7.114070	-2.316643	-1.811819
H	4.164254	-4.543167	-1.717801
H	4.894133	-4.922156	-0.142686
H	3.425382	-3.922120	-0.236931
H	6.583194	-0.534696	1.385924
H	7.547666	-1.791306	0.590351
H	6.703614	-0.565084	-0.382711
H	6.088829	-3.638600	1.802434
H	5.363856	-2.242772	2.622299
H	4.322396	-3.421266	1.813161
H	1.895351	-0.648544	-1.803339
H	1.308734	1.598266	1.211392
C	5.013696	4.984768	0.298386
C	5.310390	3.484655	0.092384
H	4.724061	5.439469	-0.652504
H	4.192960	5.129012	1.011378
H	5.901598	5.497982	0.687483
C	5.654232	2.842353	1.445191
C	6.499314	3.330742	-0.880760
H	5.928817	1.785601	1.340656
H	6.514816	3.357348	1.888789

H	4.820369	2.921358	2.153443
H	7.386631	3.838617	-0.483125
H	6.749838	2.274093	-1.035400
H	6.244523	3.767847	-1.850568
C	4.069741	2.872266	-0.610842
O	3.651077	3.387991	-1.658330
N	3.484235	1.791387	-0.038390
H	3.928309	1.349498	0.753920
C	2.306840	1.106563	-0.596639
H	1.824486	1.850517	-1.231746
C	2.768909	-0.068237	-1.477776
H	3.199189	0.338186	-2.403471
C	1.346789	0.731395	0.536749
H	1.791576	-0.091866	1.118095
H	-0.118554	0.079278	-1.370653
B	-1.740774	0.011600	-1.731836
O	-1.844551	-1.128697	-2.554888
O	-2.230480	1.119640	-2.412288
C	-2.079126	-0.679210	-3.927296
C	-2.763362	0.718197	-3.707317
C	-2.938752	-1.717842	-4.640810
C	-0.704434	-0.576935	-4.599802
C	-4.285345	0.640669	-3.574043
C	-2.380285	1.781582	-4.734996
H	-3.173526	-1.393204	-5.661088
H	-2.394519	-2.666050	-4.703684
H	-3.875097	-1.897993	-4.108089
H	-0.206453	-1.550467	-4.543826
H	-0.789404	-0.296030	-5.654786
H	-0.071434	0.158391	-4.093956
H	-4.662096	1.618076	-3.257444
H	-4.761154	0.376963	-4.525002

H	-4.567956	-0.084458	-2.810264
H	-2.683782	1.477848	-5.743913
H	-2.892454	2.719183	-4.496493
H	-1.305915	1.975192	-4.729619

Geometry F

Element	X	Y	Z
Ir	-0.187944	-0.058574	-0.404755
H	1.164992	0.723744	-0.105478
C	2.170609	0.174232	-2.785076
C	0.745644	-0.045034	-2.355505
C	1.501747	-1.132786	-3.108840
B	0.814926	-1.745837	0.105129
B	-1.633667	-0.008644	1.229099
B	0.592097	0.678092	1.405090
N	3.272501	0.212889	-1.869494
N	-1.489682	1.721860	-1.442681
N	-1.721735	-1.038659	-1.581217
O	2.204345	-1.916040	0.050118
O	0.213057	-2.941680	0.493936
O	-2.908568	0.429046	0.870363
O	-1.602838	-0.313510	2.584755
O	4.410845	1.750496	-3.110764
O	-2.796495	-0.840420	-3.561477
O	0.381574	1.970175	1.909377
O	1.529601	0.012991	2.192736
C	2.539398	-3.308923	0.359764
C	1.233099	-3.815092	1.067516
C	3.781859	-3.336017	1.246255
C	2.825966	-4.022791	-0.964971
C	1.223573	-3.559923	2.578830
C	0.862873	-5.266660	0.775074

C	-3.672568	0.731406	2.079799
C	-2.929885	-0.113547	3.179254
C	-5.129865	0.344079	1.844069
C	-3.556453	2.246175	2.289957
C	-3.530950	-1.499545	3.432410
C	-2.766634	0.605166	4.518388
C	6.790889	0.505849	-2.052493
C	5.578546	0.906060	-1.182970
C	5.811315	2.322689	-0.617079
C	5.414727	-0.101165	-0.038781
C	4.360571	0.988568	-2.134396
C	1.418413	2.262143	2.898789
C	1.856119	0.824938	3.361660
C	0.813756	3.138625	3.991168
C	2.528526	3.023551	2.165829
C	1.046008	0.286592	4.543153
C	3.348891	0.677204	3.650719
C	-1.450198	3.092016	-1.358864
C	-2.305813	1.190756	-2.353706
C	-0.577400	3.707353	-0.427903
C	-2.262930	3.926421	-2.201669
C	-3.138742	1.934567	-3.224344
C	-2.280440	-0.263567	-2.449173
C	-0.512869	5.082140	-0.337971
C	-2.172054	5.336679	-2.080433
C	-3.120657	3.303317	-3.140491
C	-1.310965	5.906517	-1.167609
C	-2.249171	-2.205824	-3.537304
C	-1.959616	-2.444302	-2.047526
C	-3.137463	-3.179893	-1.323820
C	-2.898362	-3.215969	0.189868
C	-4.493635	-2.495329	-1.587716

C	-3.171125	-4.630482	-1.853008
H	3.979630	-4.353237	1.604476
H	4.656352	-3.005018	0.678778
H	3.664614	-2.673932	2.105856
H	3.617650	-3.486850	-1.498030
H	3.161147	-5.052549	-0.800092
H	1.940298	-4.044528	-1.607049
H	0.217971	-3.761565	2.960583
H	1.932437	-4.208321	3.104972
H	1.459071	-2.513651	2.789388
H	1.639329	-5.947790	1.142238
H	-0.072491	-5.516086	1.286681
H	0.723687	-5.442071	-0.294421
H	-5.733858	0.526984	2.740456
H	-5.539918	0.950387	1.029836
H	-5.227177	-0.707712	1.566140
H	-3.953261	2.754110	1.405453
H	-4.124604	2.582182	3.164046
H	-2.510497	2.544662	2.405565
H	-2.838409	-2.071361	4.058055
H	-4.490010	-1.426415	3.957074
H	-3.681502	-2.055110	2.506334
H	-3.746114	0.832033	4.955702
H	-2.227560	-0.038936	5.220329
H	-2.210085	1.537941	4.410365
H	6.668841	-0.507345	-2.454665
H	6.890669	1.198269	-2.892761
H	7.710481	0.529502	-1.454822
H	4.987037	2.627363	0.038499
H	6.740775	2.351986	-0.035118
H	5.880370	3.042449	-1.437590
H	6.303743	-0.080410	0.603203

H	4.543473	0.117971	0.588469
H	5.309152	-1.122186	-0.422424
H	3.245486	-0.423494	-1.079055
H	2.358422	0.870658	-3.594830
H	0.087736	0.502536	-3.035734
H	1.268366	-1.346349	-4.151730
H	1.845460	-1.993039	-2.546398
H	1.550274	3.347220	4.775700
H	0.495729	4.094272	3.561561
H	-0.056909	2.664288	4.448171
H	2.112772	3.938755	1.732478
H	3.341294	3.305264	2.842977
H	2.942383	2.422505	1.351052
H	1.323709	-0.757907	4.716758
H	1.249494	0.851429	5.459428
H	-0.020451	0.314192	4.319917
H	3.645784	1.313275	4.493038
H	3.565757	-0.361308	3.920301
H	3.960325	0.934800	2.784156
H	0.007416	3.074189	0.226555
H	-3.759877	1.408048	-3.937560
H	0.159527	5.540730	0.379757
H	-2.789197	5.956391	-2.724504
H	-3.741823	3.913914	-3.788388
H	-1.241312	6.986140	-1.082470
H	-2.998866	-2.864462	-3.972242
H	-1.342242	-2.201064	-4.149478
H	-1.040224	-3.010092	-1.884739
H	-1.942399	-3.678663	0.439216
H	-2.879312	-2.200525	0.588347
H	-3.709481	-3.771830	0.677264
H	-4.759603	-2.468694	-2.650148

H	-5.283481	-3.047384	-1.064186
H	-4.494084	-1.470349	-1.201640
H	-3.954529	-5.192749	-1.331990
H	-3.389325	-4.687186	-2.926479
H	-2.216330	-5.138104	-1.669359

Geometry G

Element	X	Y	Z
Ir	-0.193607	-0.312084	-0.465194
H	-0.382391	0.254510	-1.911419
B	1.179452	1.233982	-0.552879
O	2.337842	1.424800	0.210030
O	1.026165	2.296729	-1.448501
C	2.849769	2.774471	-0.037737
C	2.232523	3.110742	-1.439906
C	4.375072	2.739380	0.000667
C	2.317454	3.670188	1.086156
C	3.093011	2.638387	-2.617706
C	1.835156	4.572259	-1.634483
H	4.790432	3.729152	-0.223530
H	4.711985	2.449916	1.001714
H	4.780896	2.023067	-0.717102
H	2.675396	3.287598	2.047009
H	2.666990	4.702938	0.977709
H	1.224608	3.655505	1.104073
H	2.515203	2.754458	-3.540235
H	4.015206	3.222902	-2.710500
H	3.340661	1.578894	-2.513930
H	2.711736	5.229139	-1.584146
H	1.374858	4.694416	-2.620428
H	1.112699	4.892950	-0.880553
B	-1.337717	1.365958	0.103779

O	-1.076718	2.363907	1.043635
O	-2.584313	1.582600	-0.482646
C	-2.283984	3.172818	1.221790
C	-3.044993	2.921343	-0.123757
C	-1.871703	4.619640	1.473776
C	-3.018181	2.610070	2.444211
C	-2.598870	3.856839	-1.253373
C	-4.566744	2.899867	-0.016703
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H	-1.314535	4.685147	2.414124
H	-1.231987	4.996988	0.673098
H	-2.340465	2.628208	3.303344
H	-3.906888	3.200778	2.692167
H	-3.322610	1.573149	2.271320
H	-3.030609	3.501598	-2.194532
H	-2.933839	4.886634	-1.086922
H	-1.510090	3.842336	-1.358422
H	-4.952443	3.875381	0.302668
H	-4.996422	2.668773	-0.996783
H	-4.908230	2.138089	0.687951
N	-0.097042	-1.334605	1.516284
C	-0.975390	-2.272737	1.617631
C	0.874226	-1.527990	2.634924
C	-2.102002	-2.399821	0.706375
O	-0.805963	-3.212605	2.582019
C	0.557194	-2.972607	3.075048
H	1.874418	-1.454704	2.202843
C	0.746460	-0.479209	3.783857
C	-3.132514	-3.339298	0.941473
N	-2.058506	-1.581032	-0.351817
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C	1.051225	0.924883	3.242682
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C	1.803578	-0.824530	4.856736
C	-4.165076	-3.423758	0.041145
H	-3.078108	-3.968644	1.820590
C	-3.081963	-1.656071	-1.268634
H	2.031037	0.954133	2.757088
H	0.313086	1.246268	2.505391
H	1.049968	1.647101	4.069734
H	-0.919989	-1.475726	4.832068
H	-0.708334	0.236271	5.226254
H	-1.418570	-0.221992	3.672526
H	1.792177	-0.057226	5.639241
H	1.620117	-1.789606	5.344418
H	2.811119	-0.843958	4.422685
C	-4.167069	-2.579970	-1.098213
H	-4.976272	-4.130768	0.184577
C	-3.064186	-0.817979	-2.411479
C	-5.193967	-2.629202	-2.075740
C	-4.076926	-0.894921	-3.344239
H	-2.243421	-0.119833	-2.508472
C	-5.149900	-1.804310	-3.179488
H	-6.011247	-3.331331	-1.939015
H	-4.052852	-0.248142	-4.214968
H	-5.936729	-1.849034	-3.925623
H	0.431464	-1.677084	-1.305619
B	1.695368	-1.274295	-0.961713
O	2.329003	-2.141911	-0.064620
O	2.527076	-0.978828	-2.037979
C	3.728817	-2.274139	-0.468370
C	3.661680	-1.896275	-1.991198
C	4.174573	-3.706392	-0.183056

C	4.542332	-1.283587	0.368859
C	3.299296	-3.084575	-2.891366
C	4.896080	-1.184183	-2.534048
H	5.196201	-3.875690	-0.542856
H	4.164243	-3.885864	0.897283
H	3.510945	-4.435111	-0.654130
H	4.433059	-1.539446	1.428543
H	5.608392	-1.323658	0.120706
H	4.169387	-0.266060	0.228872
H	3.066343	-2.707657	-3.891883
H	4.124690	-3.799959	-2.971842
H	2.415174	-3.606615	-2.512318
H	5.779159	-1.830681	-2.469317
H	4.737662	-0.928053	-3.586503
H	5.097911	-0.260907	-1.987084

12. References

[1] He, W.; Yip, K.-T.; Zhu, N.-Y.; Yang, D. Pd(II)/^{t}Bu-quinolineoxazoline: An Air-Stable and Modular Chiral Catalyst System for Enantioselective Oxidative Cascade Cyclization. *Org. Lett.* **2009**, *11*, 5626–5628.

[2] Holder, J. C.; Zou, L.; Marziale, A. N.; Liu, P.; Lan, Y.; Gatti, M.; Kikushima, K.; Houk, K. N.; Stoltz, B. M. Mechanism and Enantioselectivity in Palladium-Catalyzed Conjugate Addition of Arylboronic Acids to β-Substituted Cyclic Enones: Insights from Computation and Experiment. *J. Am. Chem. Soc.* **2013**, *135*, 14996–15007.

[3] Binder, J. T.; Cordier, C. J.; Fu, G. C. Catalytic Enantioselective Cross-Couplings of Secondary Alkyl Electrophiles with Secondary Alkylmetal Nucleophiles: Negishi Reactions of Racemic Benzylic Bromides with Achiral Alkylzinc Reagents. *J. Am. Chem. Soc.* **2012**, *134*, 17003–17006.

[4] Crisci, A. G. D.; Chung, K.; Oliver, A. G.; Solis-Ibarra, D. R.; Waymouth, M. Chemoselective Oxidation of Polyols with Chiral Palladium Catalysts. *Organometallics* **2013**, *32*, 2257–2266.

[5] Hassani, R.; Requet, A.; Marque, S.; Gaucher, A.; Prim, D.; Kacem, Y.; Hassine, B. B. Efficacious and Rapid Metal- and Solvent-Free Synthesis of Enantiopure Oxazolines. *Tetrahedron: Asymmetry* **2014**, *25*, 1275–1279.

[6] Guo, J.; Liu, H.; Bi, J.; Zhang, C.; Zhang, H.; Bai, C.; Hu, Y.; Zhang, X. Pyridine–Oxazoline and Quinoline–Oxazoline Ligated Cobalt Complexes: Synthesis, Characterization, and 1,3-Butadiene Polymerization Behaviors. *Inorg. Chim. Acta* **2015**, *435*, 305–312.

[7] Jiang, F.; Wu, Z.; Zhang, W. Pd-Catalyzed Asymmetric Aza-Wacker-Type Cyclization Reaction of Olefinic Tosylamides. *Tetrahedron Lett.* **2010**, *51*, 5124–5126.

[8] Michel, B. W.; Camelio, A. M.; Cornell, C. N.; Sigman, M. S. A General and Efficient Catalyst System for a Wacker-Type Oxidation Using TBHP as the Terminal Oxidant: Application to Classically Challenging Substrates. *J. Am. Chem. Soc.* **2009**, *131*, 6076–6077.

[9] Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. Cyclopropanation with Diazomethane and Bis(oxazoline)palladium(II) Complexes. *J. Org. Chem.* **1997**, *62*, 3375–3389.

[10] Shuman, R. T.; Ornstein, P. L.; Paschal, J. W.; Gesellchen, P. D. An Improved Synthesis of Homoproline and Derivatives. *J. Org. Chem.* **1990**, *55*, 738–741.

[11] Oeveren, A. V.; Motamedi, M.; Mani, N. S.; Marschke, K. B.; López, F. J.; Schrader, W. T.; Negro-Vilar, A.; Zhi, L. Discovery of 6-*N*,*N*-Bis(2,2,2-trifluoroethyl)amino-4-trifluoromethylquinolin-2(1H)-one as a Novel Selective Androgen Receptor Modulator. *J. Med. Chem.* **2006**, *49*, 6143–6146.

[12] Spadoni, G.; Bedini, A.; Lucarini, S.; Mari, M.; Caignard, D.-H.; Boutin, J. A.; Delagrange, P.; Lucini, V.; Scaglione, F.; Lodola, A.; Zanardi, F.; Pala, D.; Mor, M.; Rivara, S. Highly Potent and Selective MT_2 Melatonin Receptor Full Agonists from Conformational Analysis of 1-Benzyl-2-acylaminomethyl-tetrahydroquinolines. *J. Med. Chem.* **2015**, *58*, 7512–7525.

[13] Miyamura, S.; Araki, M.; Suzuki, T.; Yamaguchi, J.; Itami, K. Stereodivergent Synthesis of Arylcyclopropylamines by Sequential C–H Borylation and Suzuki–Miyaura Coupling. *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 846–851.

[14] Shaw, M. H.; McCreanor, N. G.; Whittingham, W. G.; Bower, J. F. Reversible C–C Bond Activation Enables Stereocontrol in Rh-Catalyzed Carbonylative Cycloadditions of Aminocyclopropanes. *J. Am. Chem. Soc.* **2015**, *137*, 463–468.

[15] Toro, J. M. S.; Hartog, T. D.; Chen, P. Cyclopropanation of Styrenes and Stilbenes Using Lithiomethyl Trimethylammonium Triflate as Methylene Donor. *Chem. Commun.* **2014**, *50*, 10608–10610.

[16] Zhou, Y.-Y.; Uyeda, C. Reductive Cyclopropanations Catalyzed by Dinuclear Nickel Complexes. *Angew. Chem., Int. Ed. Engl.* **2016**, *55*, 3171–3175.

[17] Molander, G. A.; Beaumard, F.; Niethamer, T. K. Cross-Coupling of Mesylated Phenol Derivatives with Potassium Cyclopropyltrifluoroborate. *J. Org. Chem.* **2011**, *76*, 8126–8130.

[18] Lin, J.-P.; Long, Y.-Q. Transition Metal-Free One-Pot Synthesis of 2-Substituted 3-Carboxy-4-Quinolone and Chromone Derivatives. *Chem. Commun.* **2013**, *49*, 5313–5315.

[19] Wolfe, J. P.; Ney, J. E. A New, Mild Synthesis of N-Sulfonyl Ketimines via the Palladium-Catalyzed Isomerization of Aziridines. *Org. Lett.* **2003**, *5*, 4607–4610.

[20] Ma, W.; Fang, J.; Ren, J.; Wang, Z. Lewis Acid Catalyzed Formal Intramolecular [3 + 3] Cross-Cycloaddition of Cyclopropane 1,1-Diesters for Construction of Benzobicyclo[2.2.2]octane Skeletons. *Org. Lett.* **2015**, *17*, 4180–4183.

[21] Wei, C. S.; Jiménez-Hoyos, C. A.; Videa, M. F.; Hartwig, J. F.; Hall, M. B. Origins of the Selectivity for Borylation of Primary over Secondary C–H Bonds Catalyzed by Cp*-Rhodium Complexes. *J. Am. Chem. Soc.* **2010**, *132*, 3078–3091.

[22] Lessard, S.; Peng, F.; Hall, D. G. α-Hydroxyalkyl Heterocycles via Chiral Allylic Boronates: Pd-Catalyzed Borylation Leading to a Formal Enantioselective Isomerization of Allylic Ether and Amine. *J. Am. Chem. Soc.* **2009**, *131*, 9612–9613.

[23] Lahiri, N.; Lotfizadeh, N.; Tsuchikawa, R.; Deshpande, V. V.; Louie, J. Hexaaminobenzene as a building block for a Family of 2D Coordination Polymers. *J. Am. Chem. Soc.* **2017**, *139*, 19–22.

[24] Koller, J.; Bergman, R. G. Controlled Hydrosilylation of Carbonyls and Imines Catalyzed by a Cationic Aluminum Alkyl Complex. *Organometallics* **2012**, *31*, 2530–2533.

[25] Ursinyova, N.; Bedford, R. B.; Gallagher, T. Copper-Catalyzed Borylation of Cyclic Sulfamidates: Access to Enantiomerically Pure (β-and γ-Amino-alkyl)boronic Esters. *Eur. J. Org. Chem.* **2016**, 673–677.

[26] Yamamoto, Y.; Fujikawa, R.; Umemoto, T.; Miyaura, N. Iridium-Catalyzed Hydroboration of Alkenes with Pinacolborane. *Tetrahedron* **2004**, *60*, 10695–10700.

[27] Wen, Y.; Xie, J.; Deng, C.; Li, C. Selective Synthesis of Alkylboronates by Copper(I)-Catalyzed Borylation of Allyl or Vinyl Arenes. *J. Org. Chem.* **2015**, *80*, 4142–4147.

[28] Zhang, L.; Zuo, Z.; Wan, X.; Huang, Z. Cobalt-Catalyzed Enantioselective Hydroboration of 1,1-Disubstituted Aryl Alkenes. *J. Am. Chem. Soc.* **2014**, *136*, 15501–15504.

[29] Mazet, C.; Gérard, D. Highly Regio- and Enantioselective Catalytic Asymmetric Hydroboration of α-Substituted Styrenyl Derivatives. *Chem Commun.* **2011**, *47*, 298–300.

[30] Corberán, R.; Mszar, N. W.; Hoveyda, A. H. NHC-Cu-Catalyzed Enantioselective Hydroboration of Acyclic and Exocyclic 1,1-Disubstituted Aryl Alkenes. *Angew. Chem., Int. Ed. Engl.* **2011**, *50*, 7079–7082.

[31] Yao, H.; Tang, Y.; Yamamoto, K. Metal-Free Oxidative Amide Formation with *N*-Hydroxysuccinimide and Hypervalent Iodine Reagents. *Tetrahedron Lett.* **2012**, *53*, 5094–5098.

[32] Minato, D.; Arimoto, H.; Nagasue, Y.; Demizu, Y.; Onomura, O. Asymmetric Electrochemical Oxidation of 1,2-Diols, Aminoalcohols, and Aminoaldehydes in the Presence of Chiral Copper Catalyst. *Tetrahedron* **2008**, *64*, 6675–6683.

[33] Martin, A.; Casto, K.; Morris, W.; Morgan, J. B. Phosphine-Catalyzed Heine Reaction. *Org. Lett.* **2011**, *13*, 5444–5447.

[34] Mlynarski, S. N.; Karns, A. S.; Morken, J. P. Direct Stereospecific Amination of Alkyl and Aryl Pinacol Boronates. *J. Am. Chem. Soc.* **2012**, *134*, 16449–16451.

[35] Hu, N.; Zhao, G.; Zhang, Y.; Liu, X.; Li, G.; Tang, W. Synthesis of Chiral α-Amino Tertiary Boronic Esters by Enantioselective Hydroboration of α-Arylenamides. *J. Am. Chem. Soc.* **2015**, *137*, 6746–6749.

[36] Wolfe, J. P.; Ney, J. E. A New, Mild Synthesis of N-Sulfonyl Ketimines via the Palladium-Catalyzed Isomerization of Aziridines. *Org. Lett.* **2003**, *5*, 4607–4610.

[37] Ma, W.; Fang, J.; Ren, J.; Wang, Z. Lewis Acid Catalyzed Formal Intramolecular [3 + 3] Cross-Cycloaddition of Cyclopropane 1,1-Diesters for Construction of Benzobicyclo[2.2.2]octane Skeletons. *Org. Lett.* **2015**, *17*, 4180–4183.

[38] Palmer, W. N.; Obligacion, J. V.; Pappas, I.; Chirik, P. J. Cobalt-Catalyzed Benzylic Borylation: Enabling Polyborylation and Functionalization of Remote, Unactivated C(sp^3)–H Bonds. *J. Am. Chem. Soc.* **2016**, *138*, 766–769.

[39] Yang, T.; Fan, X.; Zhao, X.; Yu, W. Iron-Catalyzed Acyl Migration of Tertiary α-Azidyl Ketones: Synthetic Approach toward Enamides and Isoquinolones. *Org. Lett.* **2018**, *20*, 1875–1879.

[40] Toriyama, F.; Cornella, J.; Wimmer, L.; Chen, T.-G.; Dixon, D. D.; Creech, G.; Baran, P. S. Redox-Active Esters in Fe-Catalyzed C–C Coupling. *J. Am. Chem. Soc.* **2016**, *138*, 11132–11135.

[41] Becke, D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.

[42] Becke, D. *J.* Density-Functional Thermochemistry. III. The Role of Exact Exchange. *Chem. Phys*. **1993**, *98*, 5648–5652.

[43] Perdew J. P.; Wang, Y. Accurate and Simple Analytic Representation of the Electron-Gas Correlation Energy. *Phys. Rev. B* **1992**, *45*, 13244–13249.

[44] Figgen, D.; Peterson, K. A.; Dolg, M.; Stoll, H. Energy-Onsistent Pseudopotentials and Correlation Consistent Basis Sets for the Elements Hf–Pt. *J. Chem. Phys*. **2009**, *130*, 164108.

[45] Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theor. Chim. Acta* **1973**, *28*, 213–222.

[46] Wehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys*. **1972**, *56*, 2257–2261.

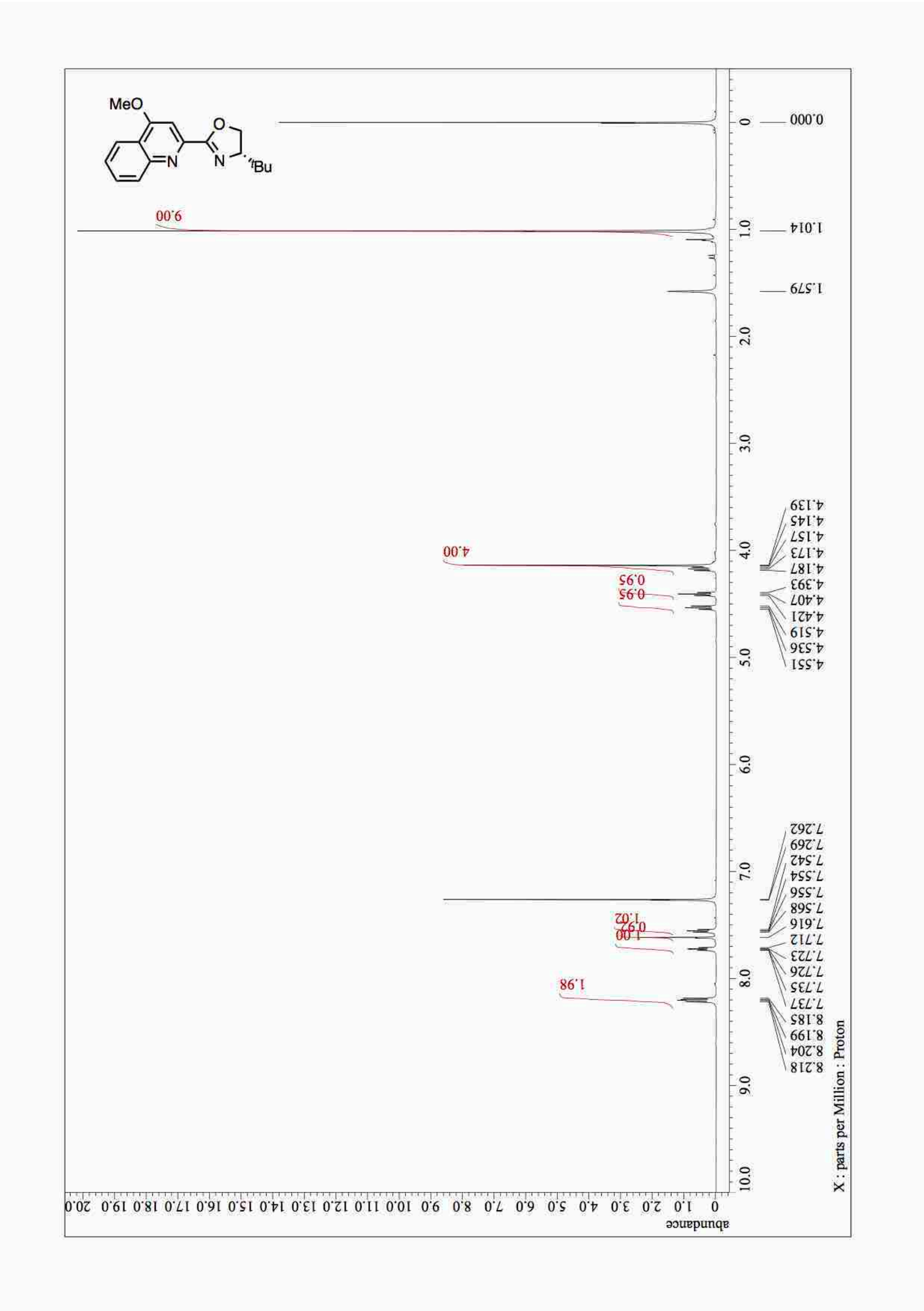
[47] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self‐Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys*. **1980**, *72*, 650–654.

[48] Grimme, S. Improved Second-Order Møller-Plesset Perturbation Theory by Separate Scaling of Parallel- and Antiparallel-Spin Pair Correlation Energies. *J. Chem. Phys.* **2003**, *118*, 9095–9102.

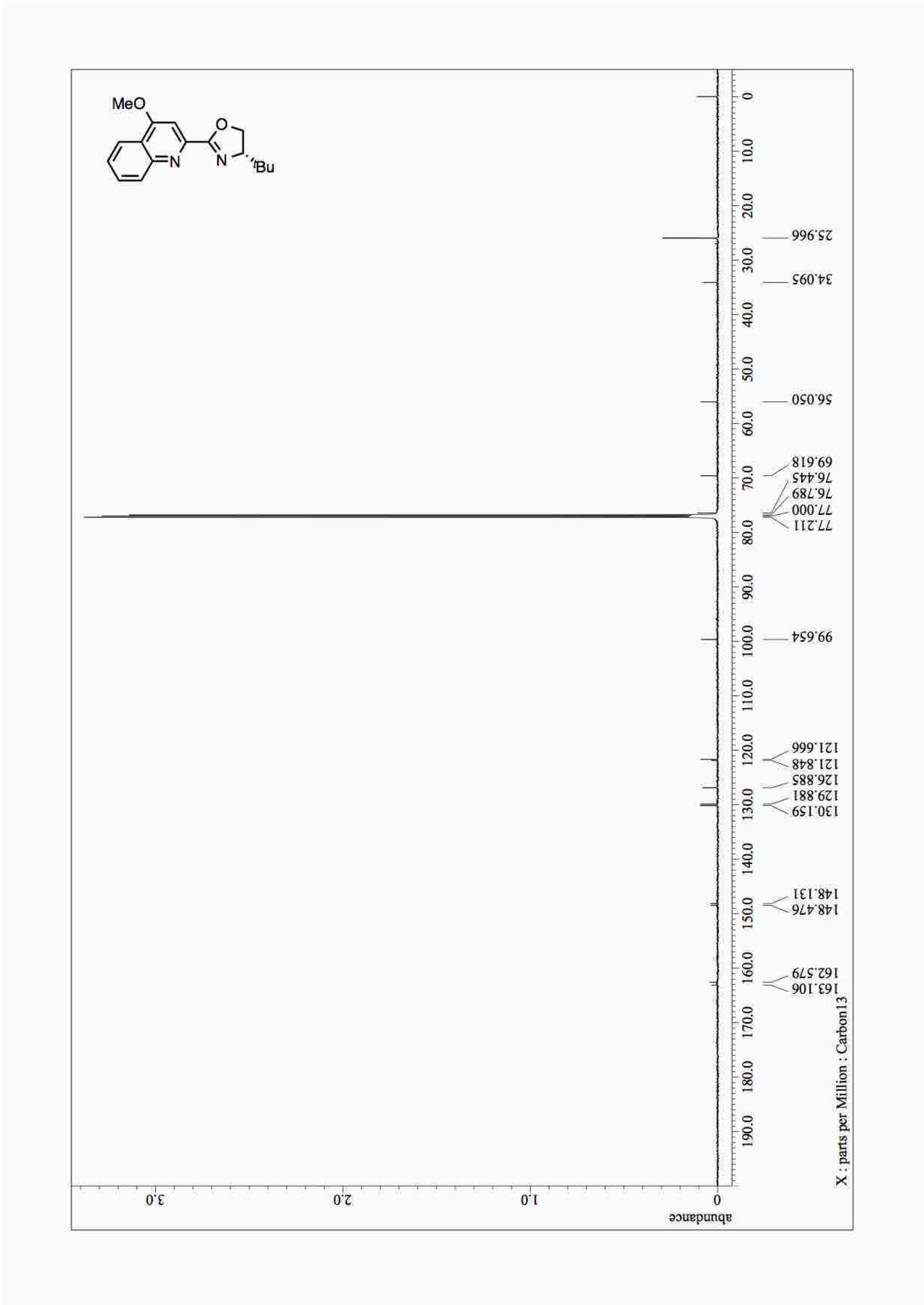
[49] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

13. ^{1}H, ^{13}C and ^{19}F NMR Spectra

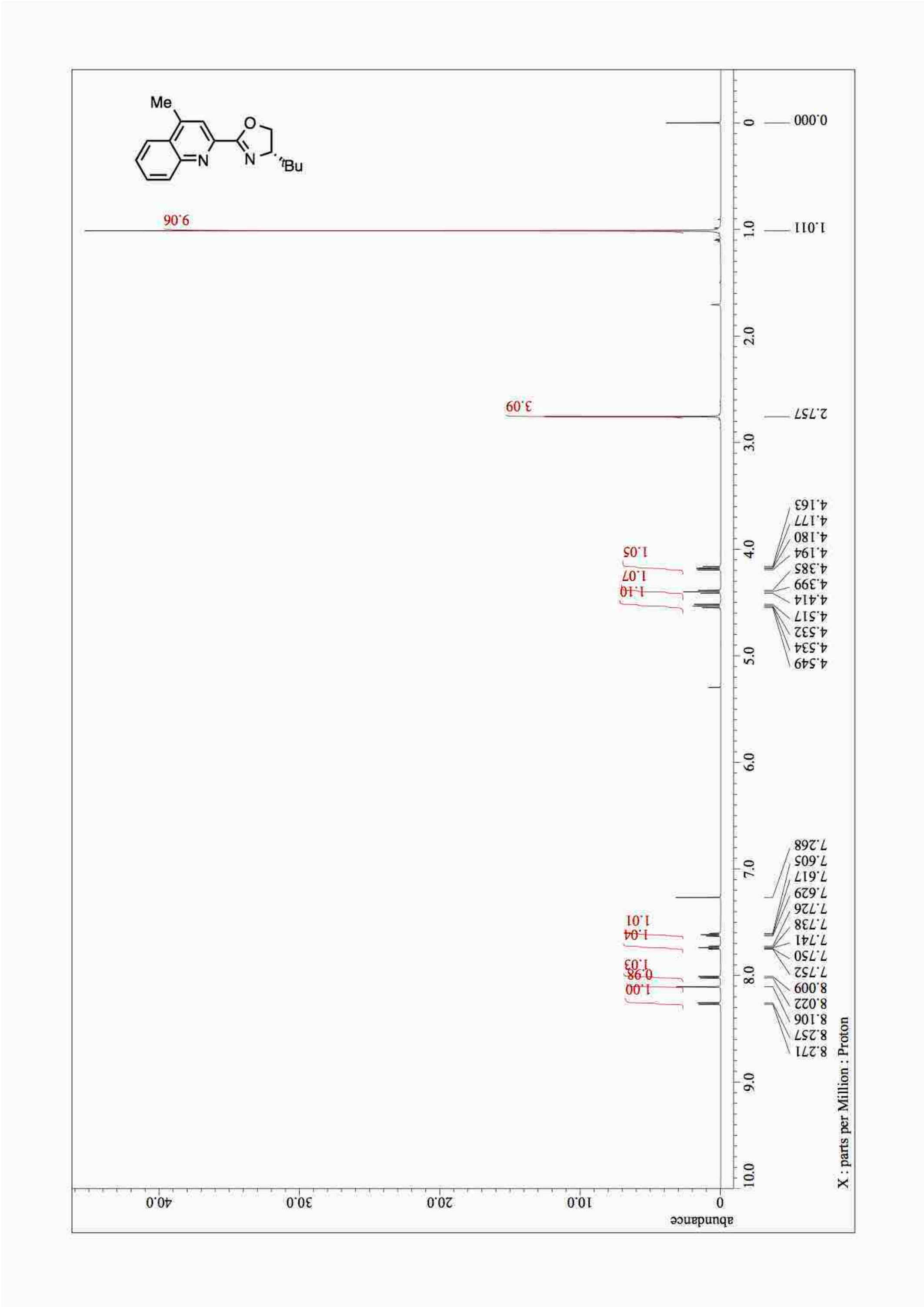
^{1}H NMR of **L13** (600 MHz, $CDCl_3$)



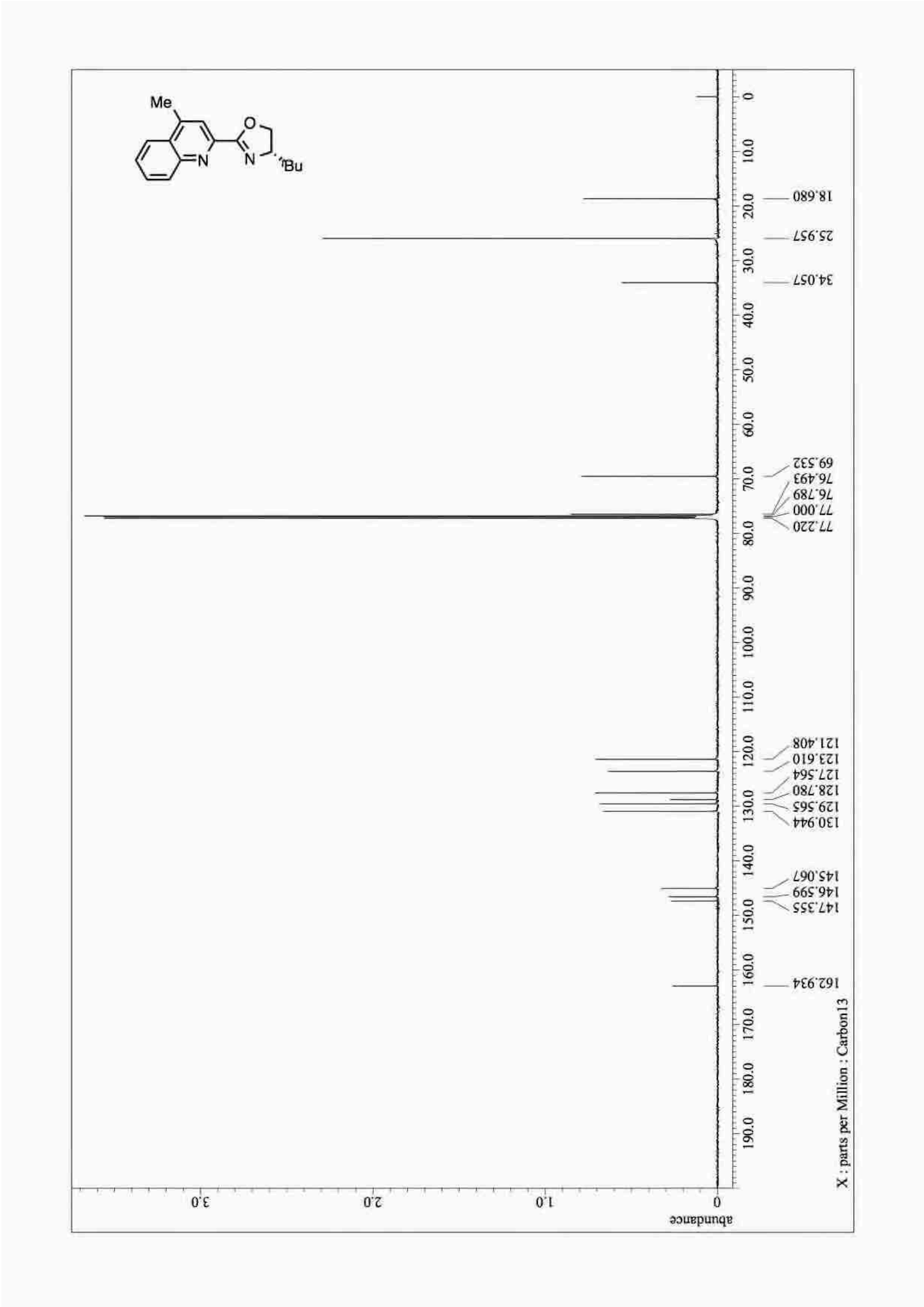
^{13}C NMR of **L13** (151 MHz, $CDCl_3$)



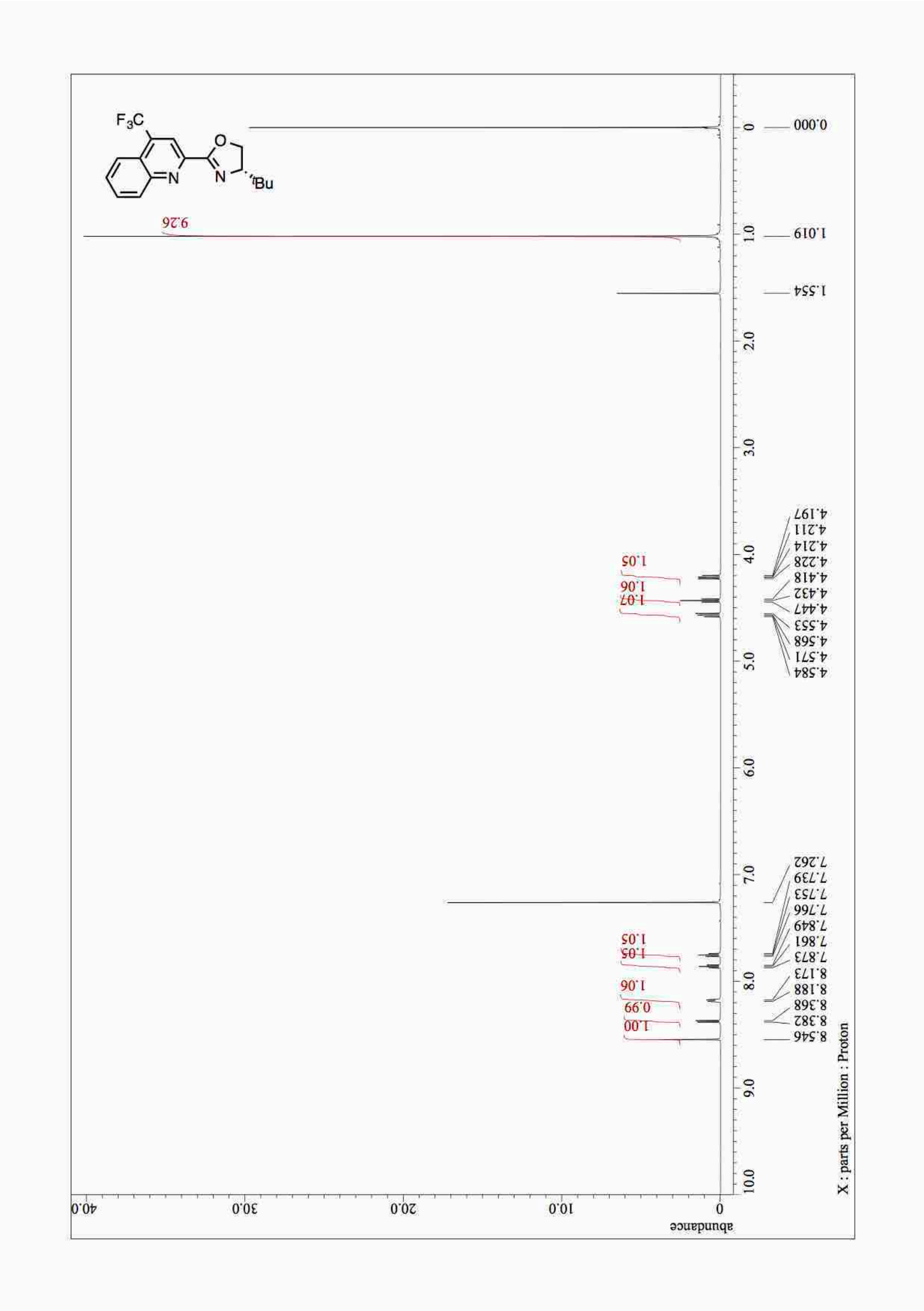
[1]H NMR of **L14** (600 MHz, $CDCl_3$)



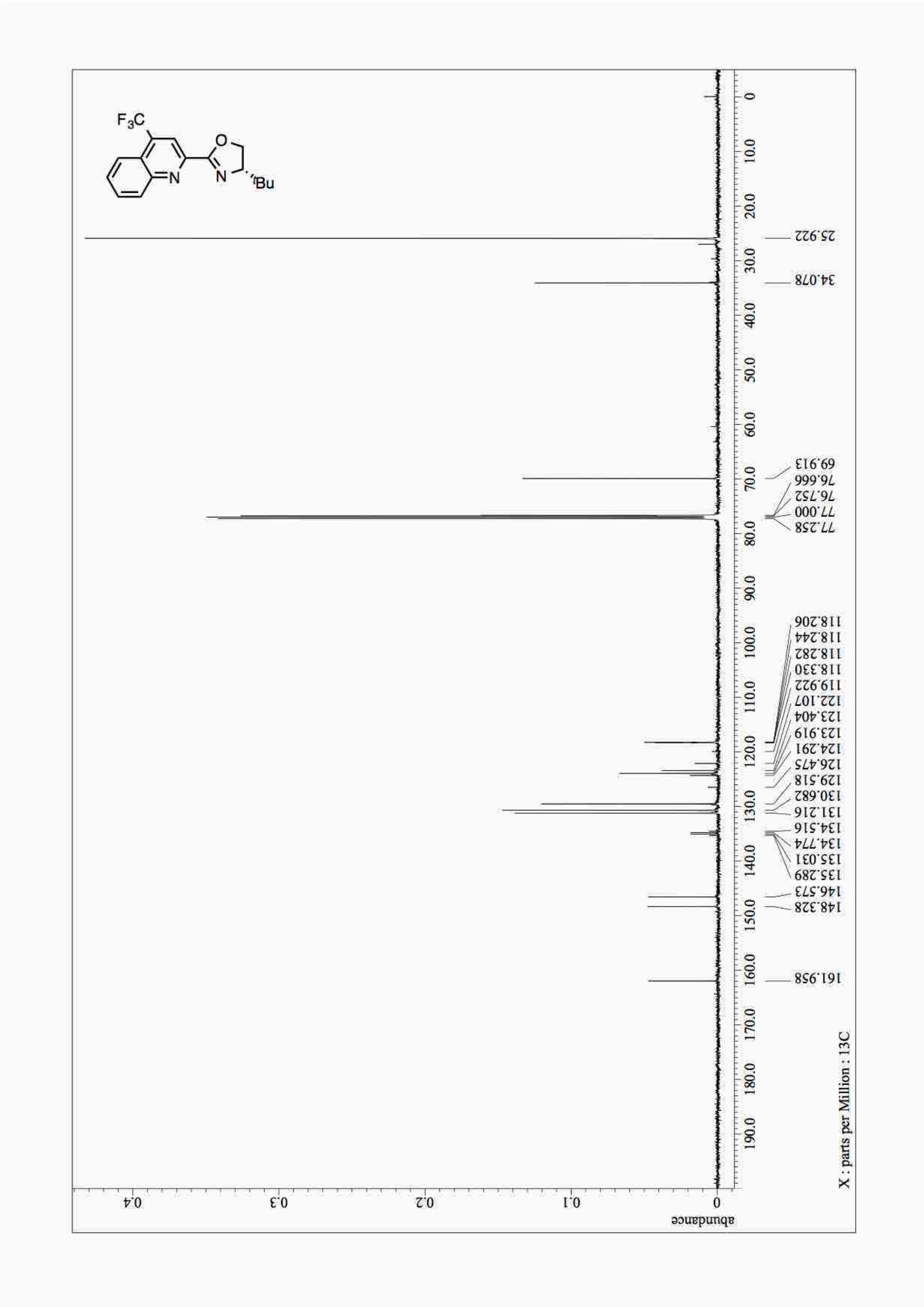
^{13}C NMR of **L14** (151 MHz, $CDCl_3$)



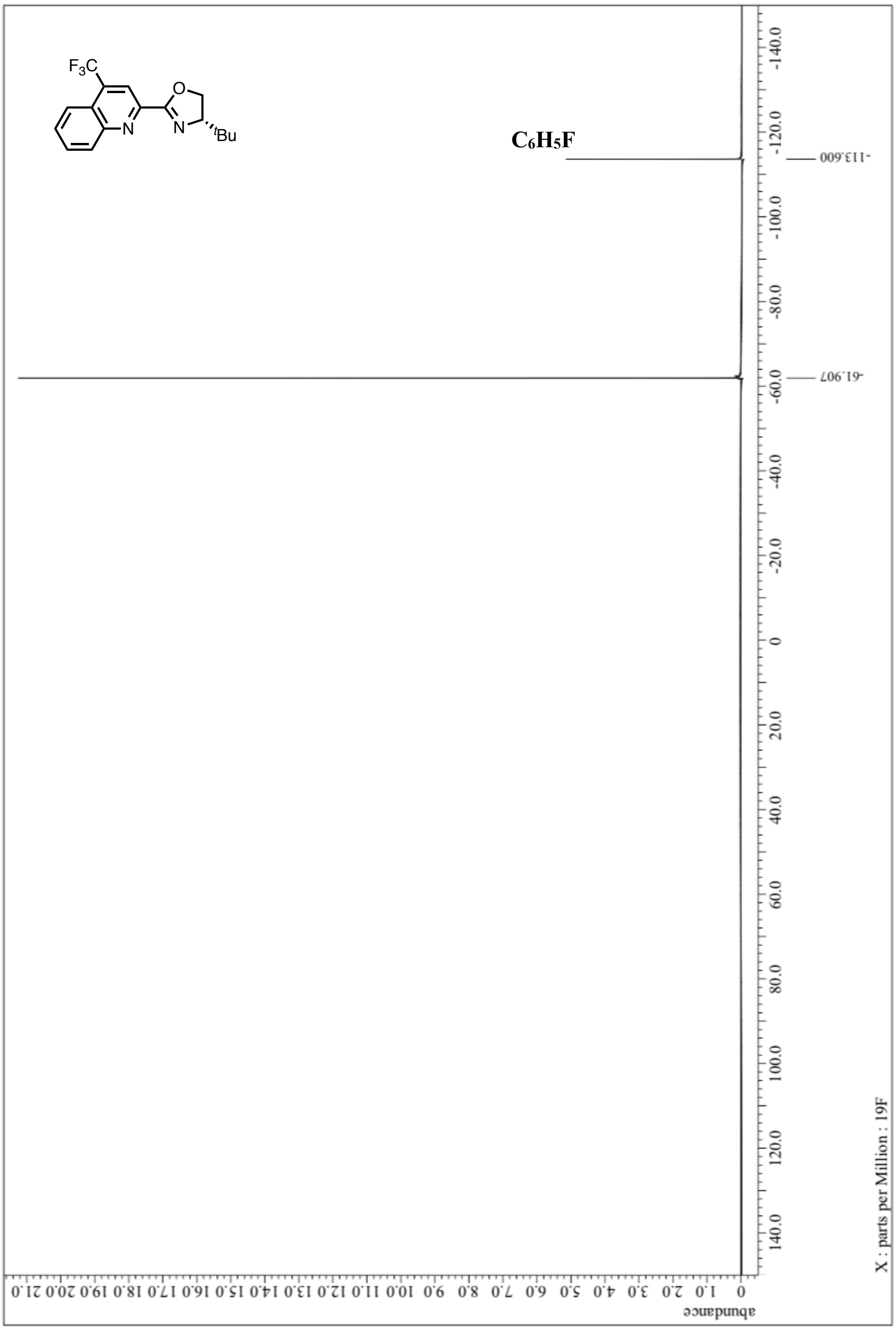
[1]H NMR of **L15** (600 MHz, $CDCl_3$)



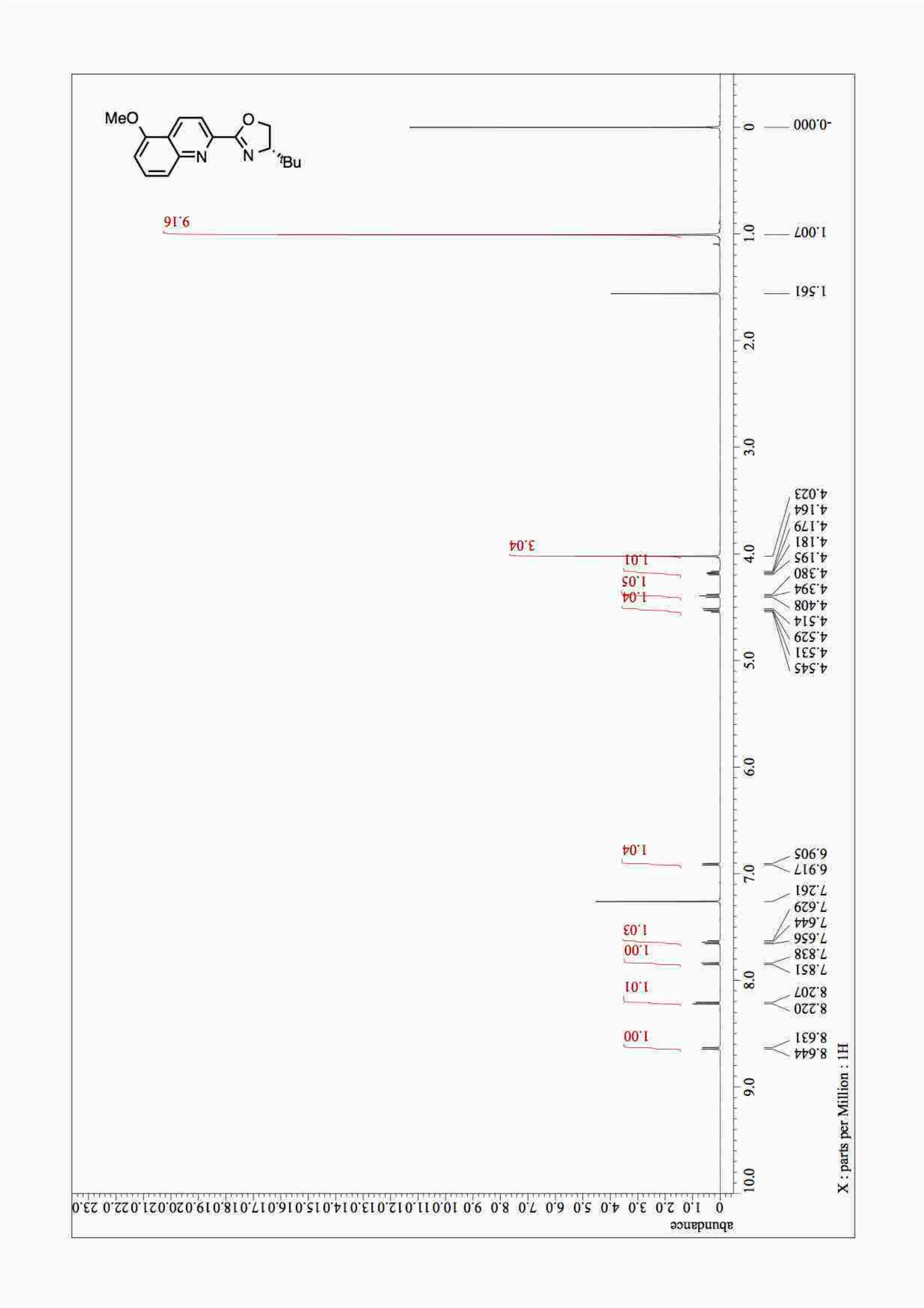
^{13}C NMR of **L15** (126 MHz, $CDCl_3$)



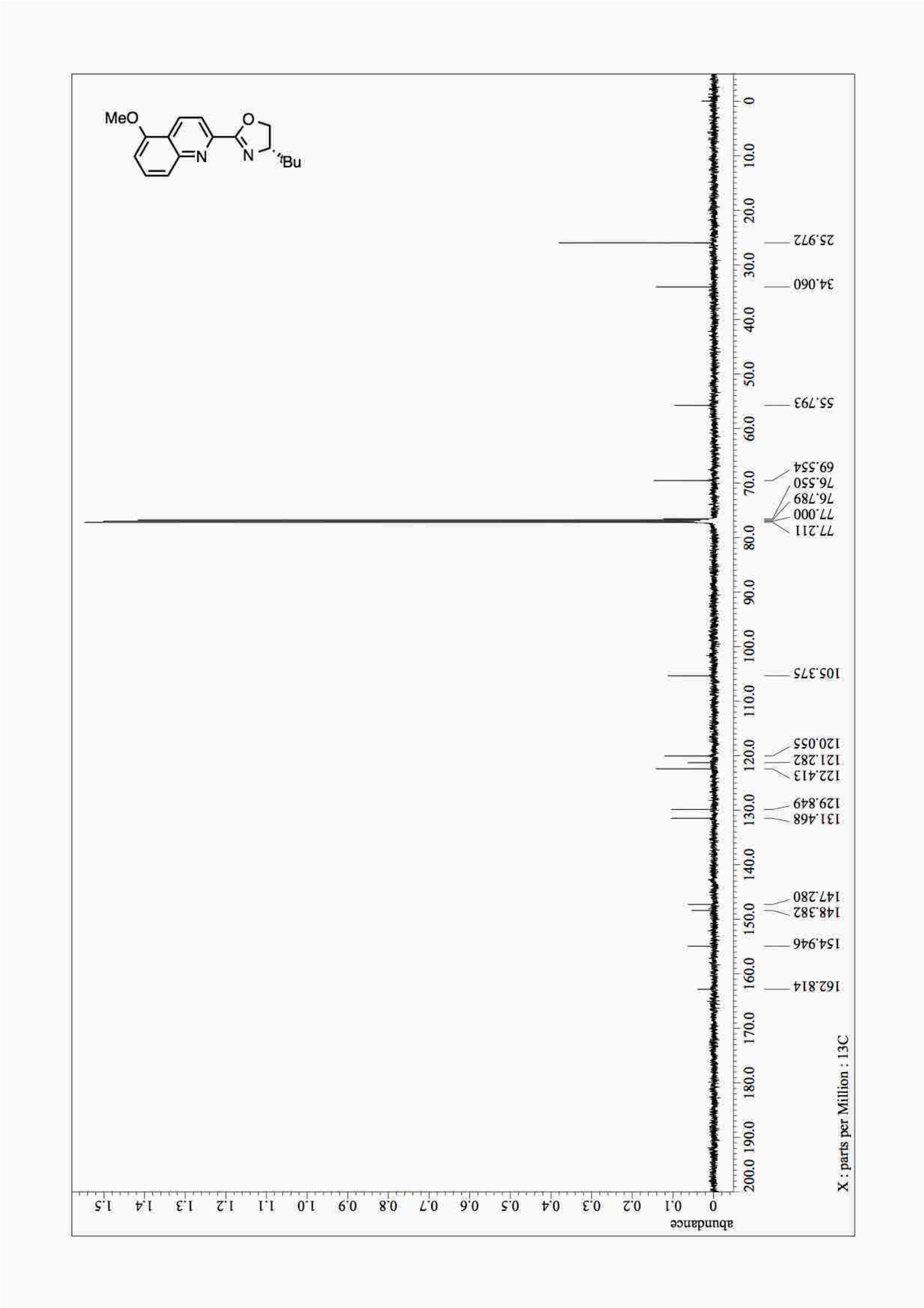
^{19}F NMR of **L15** (376 MHz, $CDCl_3$)



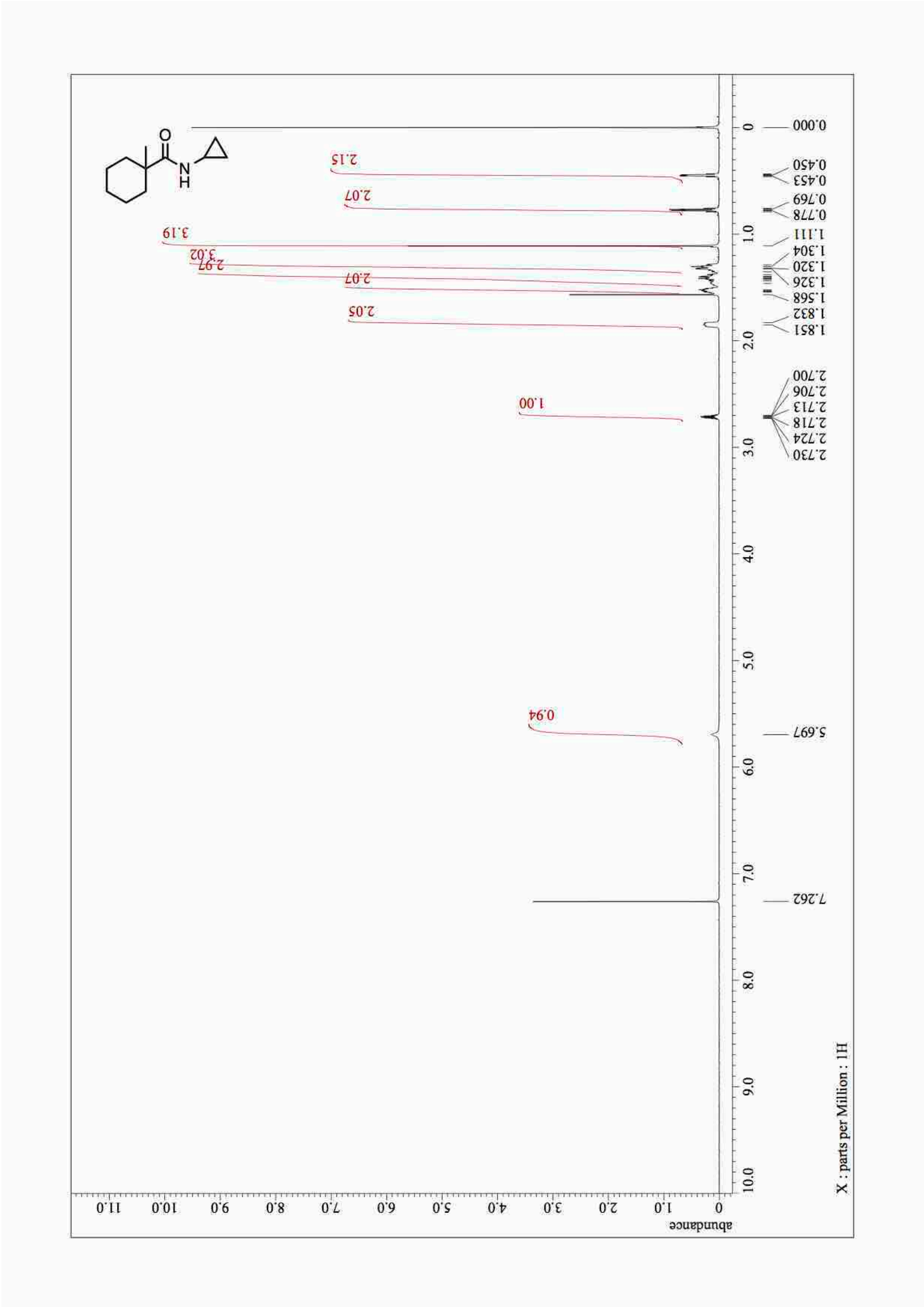
^{1}H NMR of **L16** (600 MHz, $CDCl_3$)



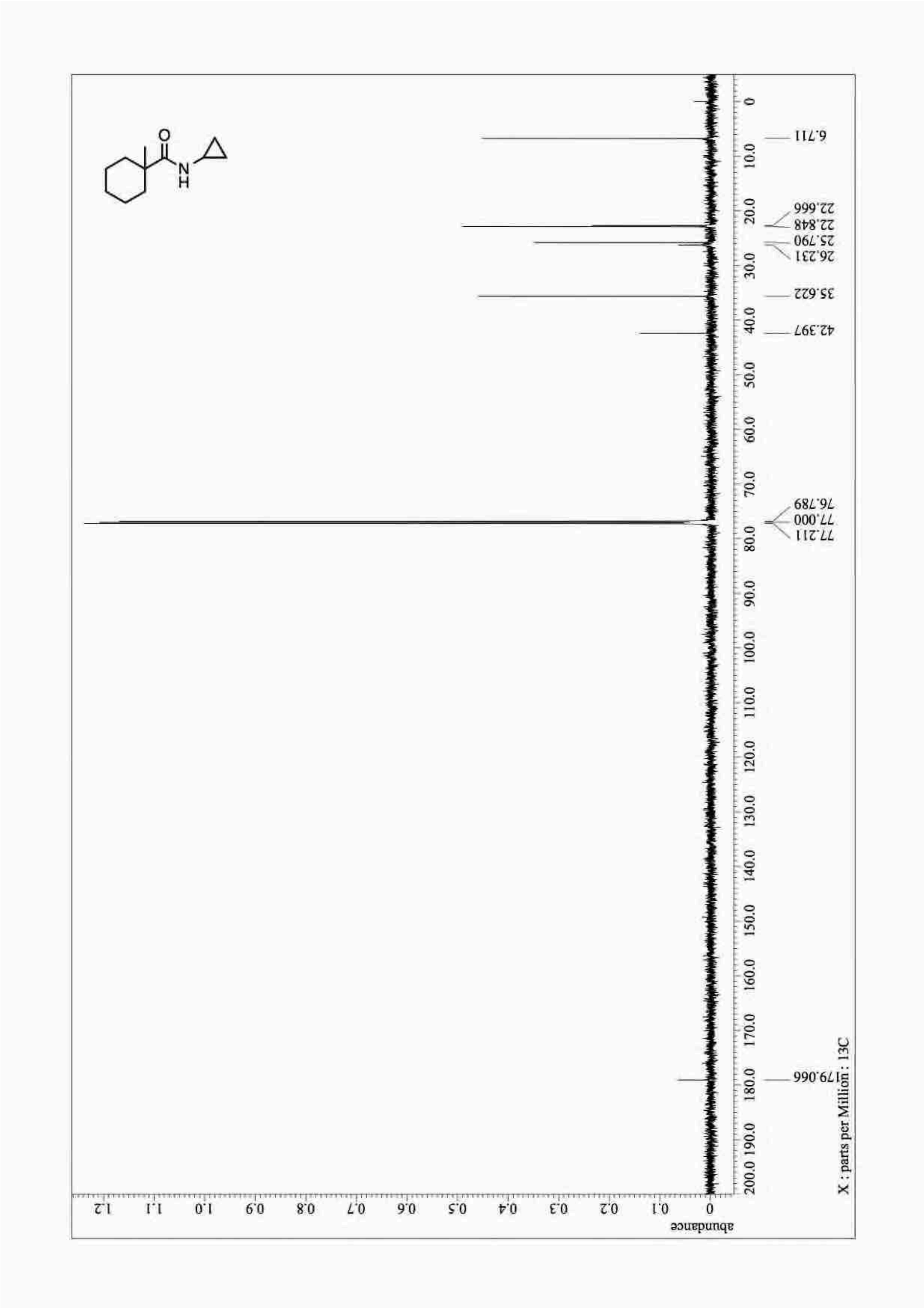
^{13}C NMR of **L16** (151 MHz, $CDCl_3$)



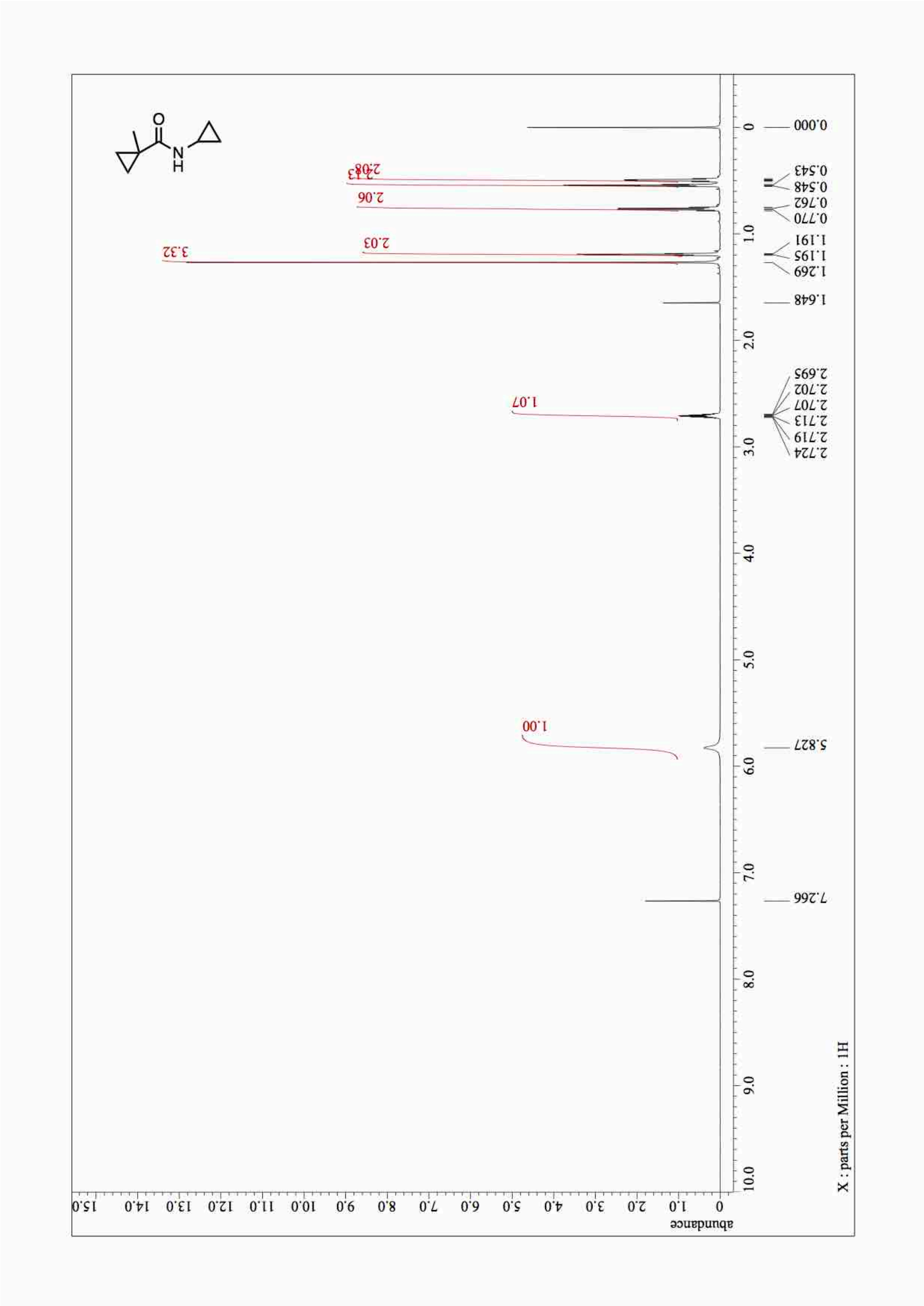
[1]H NMR of **1b** (600 MHz, $CDCl_3$)



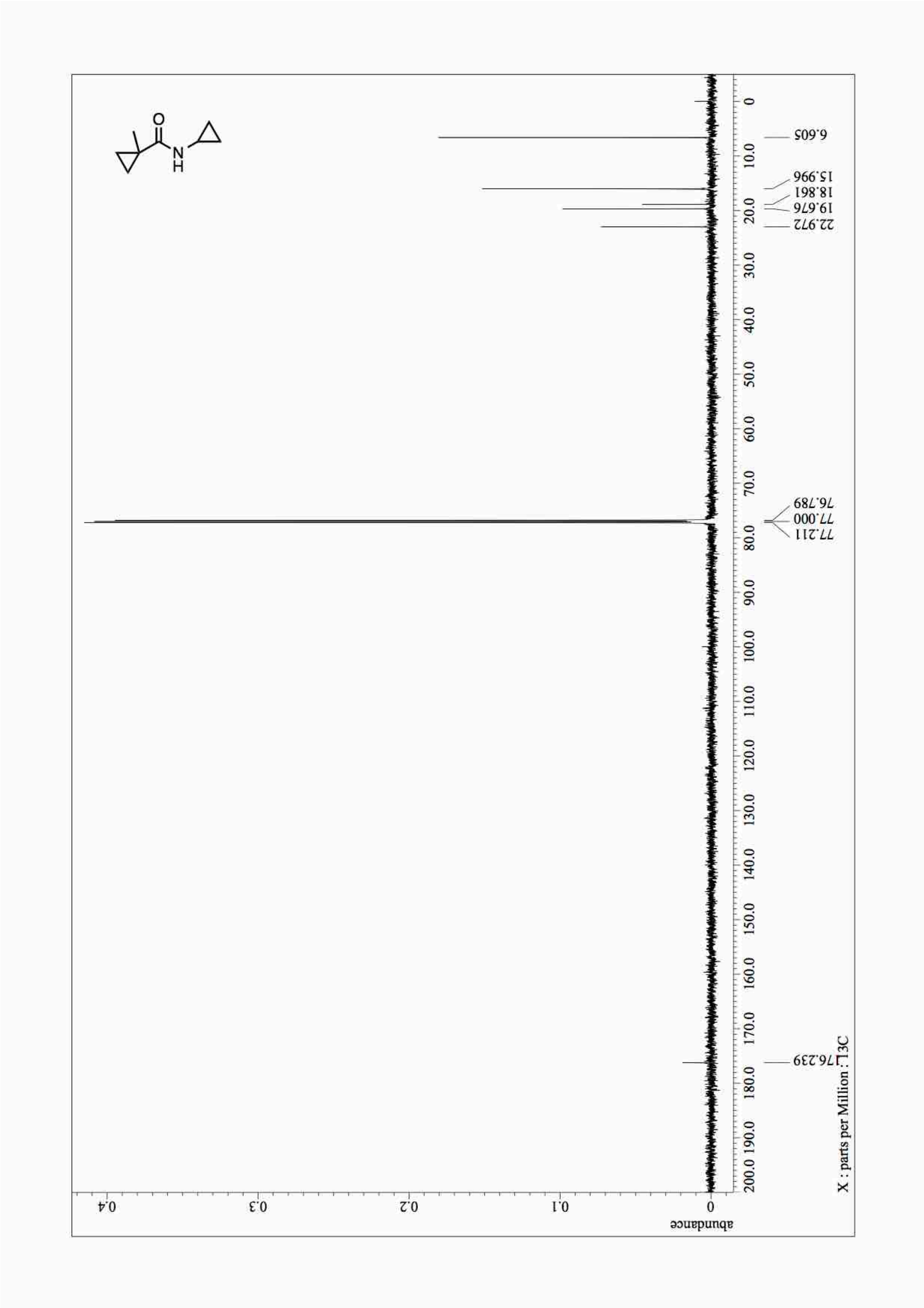
^{13}C NMR of **1b** (151 MHz, $CDCl_3$)



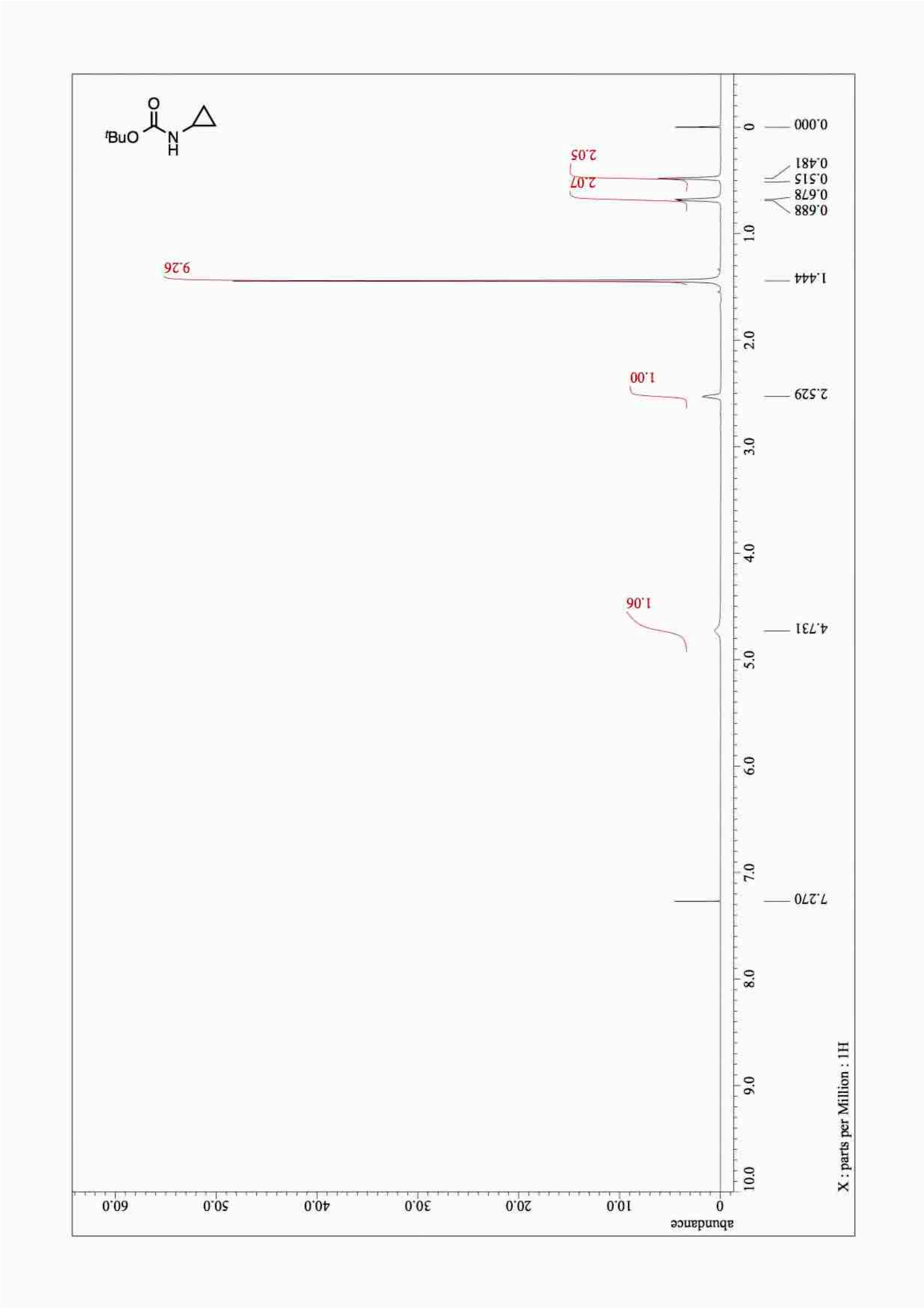
^{1}H NMR of **1c** (600 MHz, $CDCl_3$)



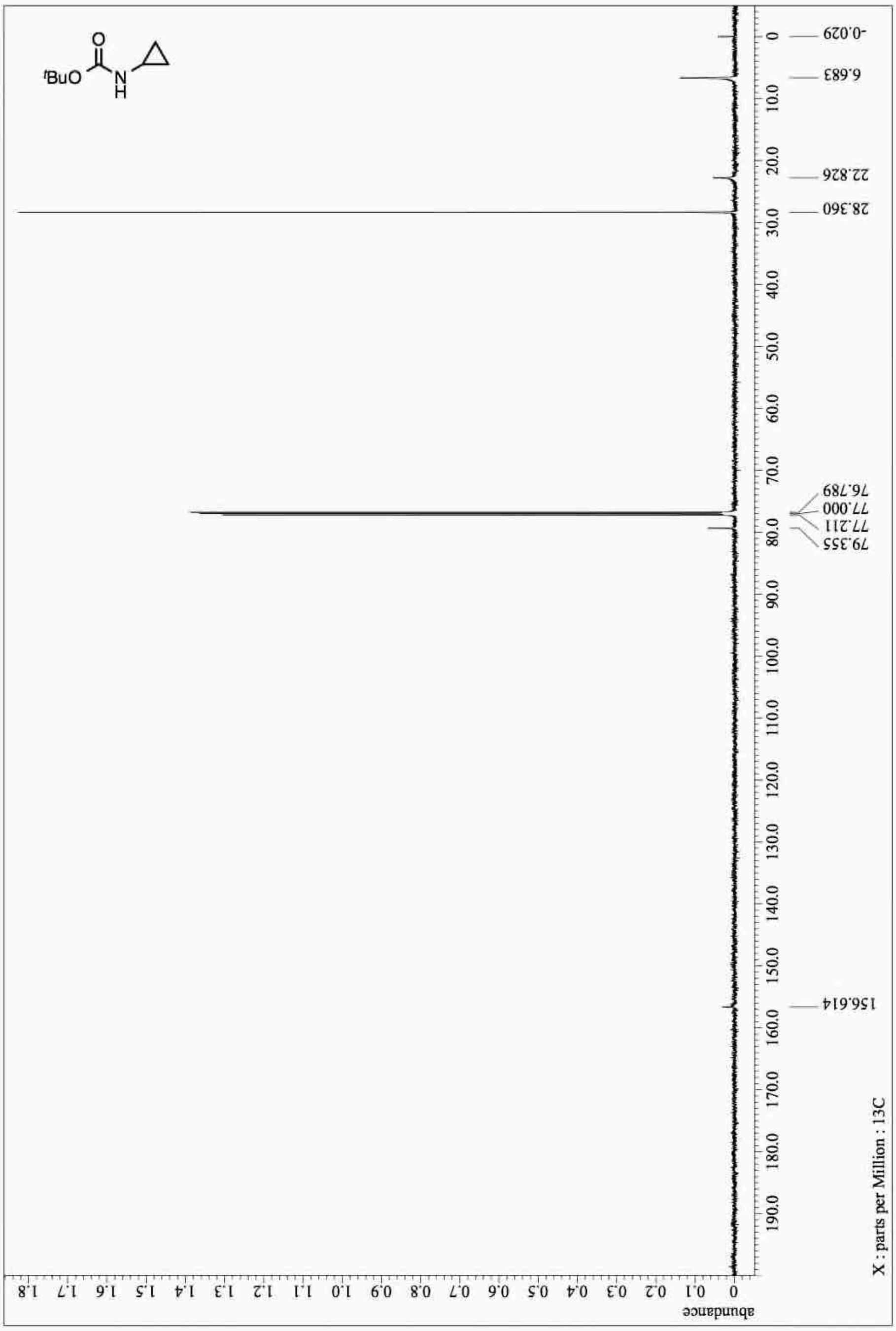
^{13}C NMR of **1c** (151 MHz, $CDCl_3$)



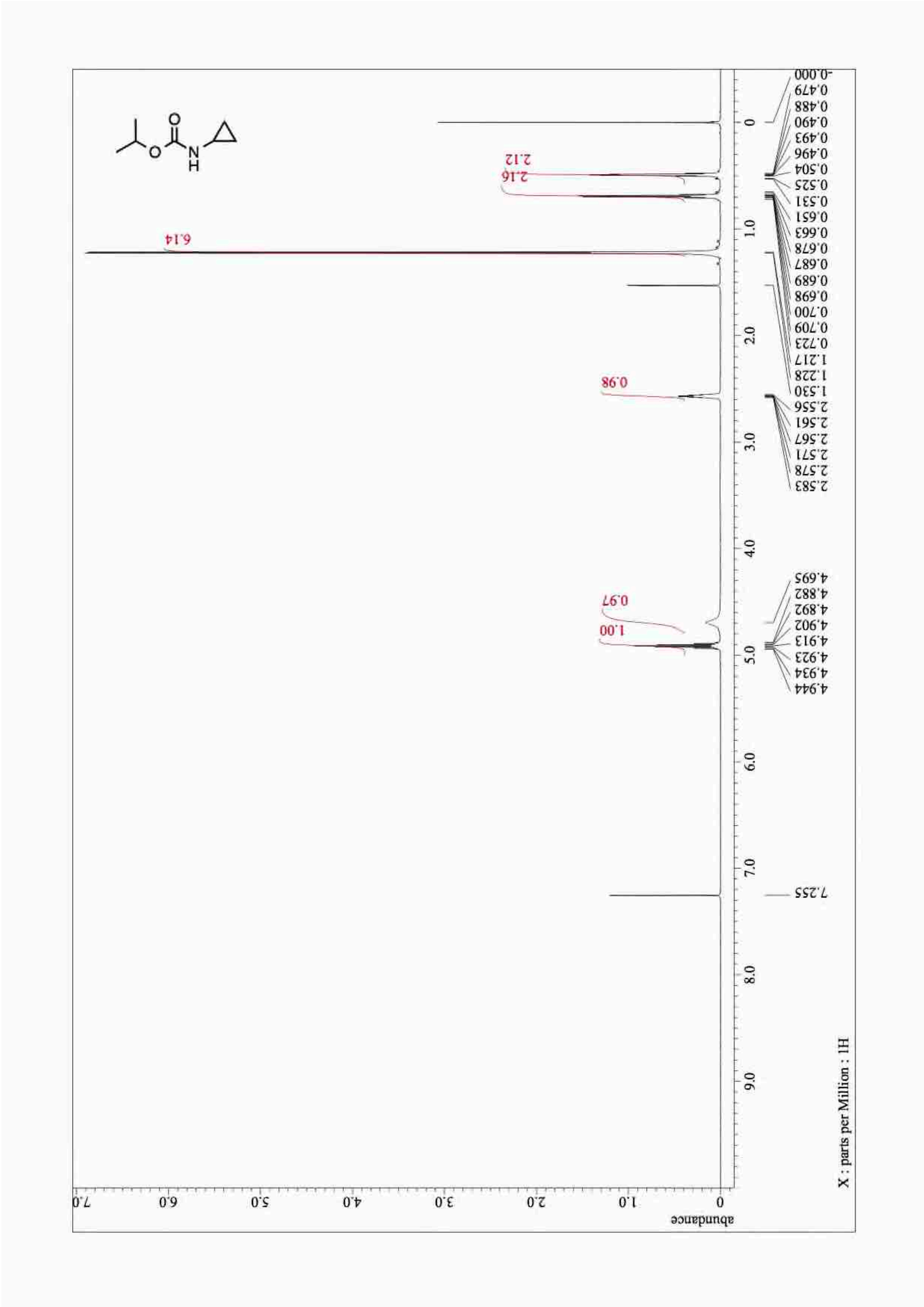
^{1}H NMR of **1e** (600 MHz, $CDCl_3$)



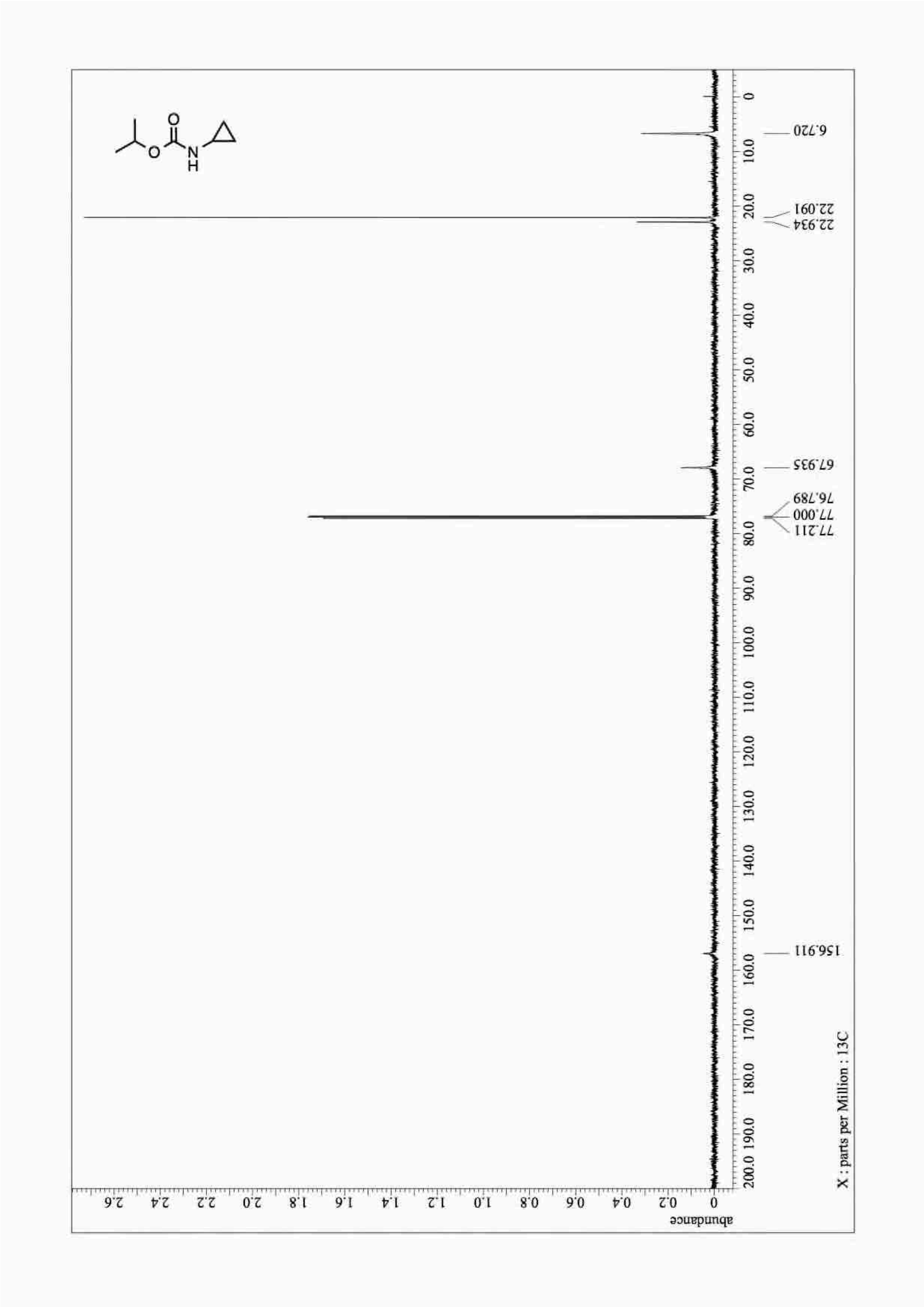
^{13}C NMR of **1e** (151 MHz, $CDCl_3$)



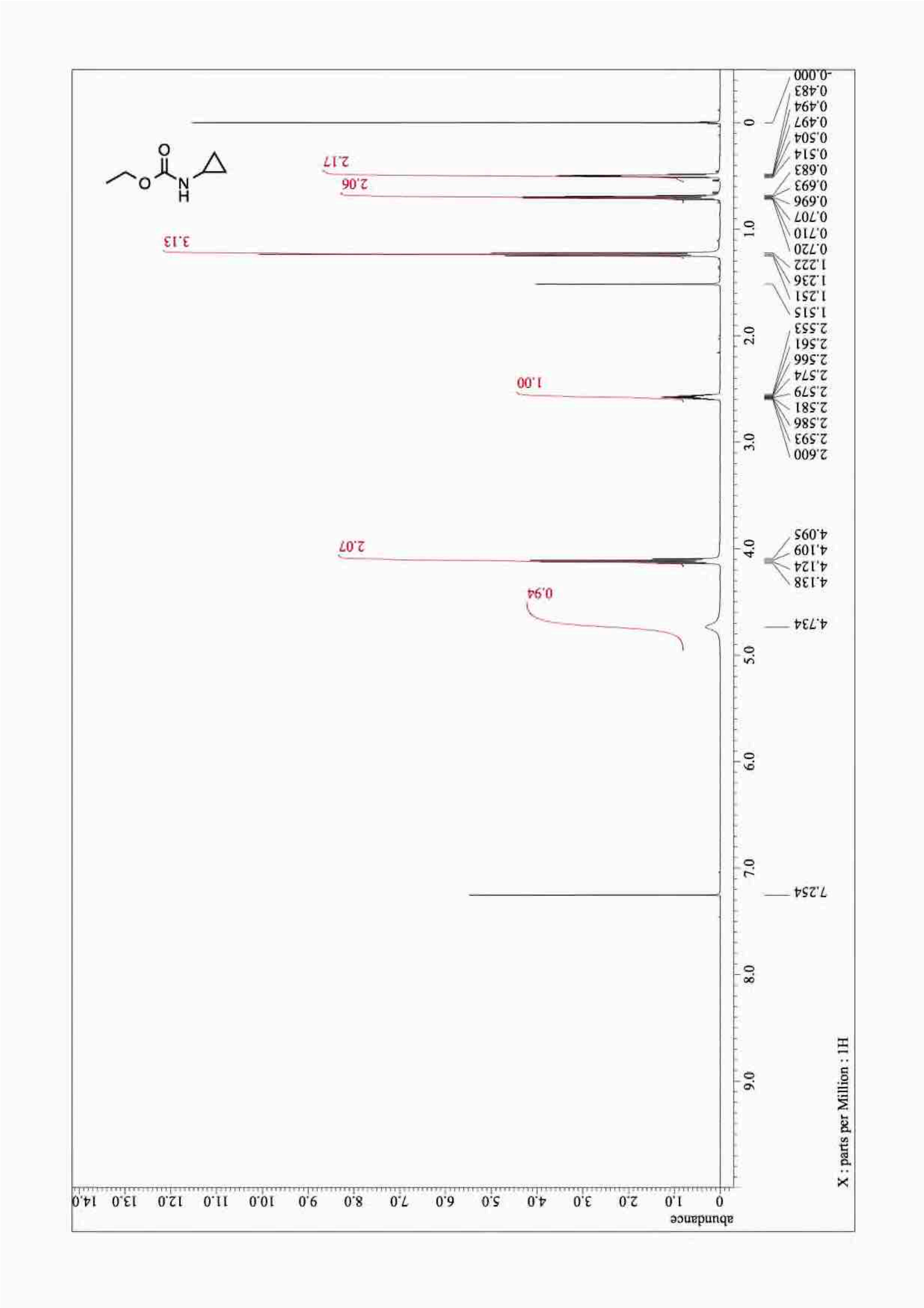
[1]H NMR of **1f** (600 MHz, 50 ˚C, $CDCl_3$)



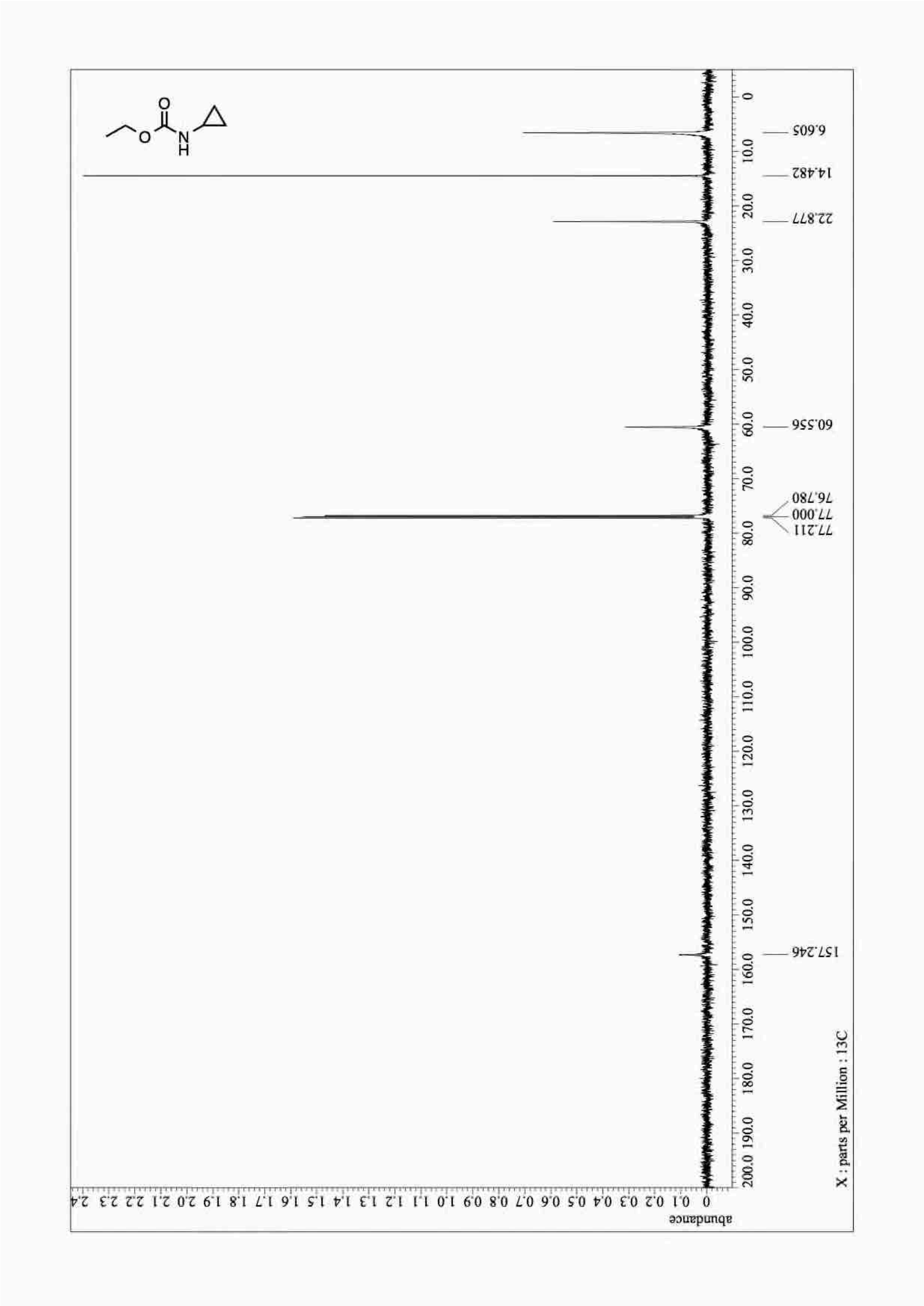
^{13}C NMR of **1f** (151 MHz, $CDCl_3$)



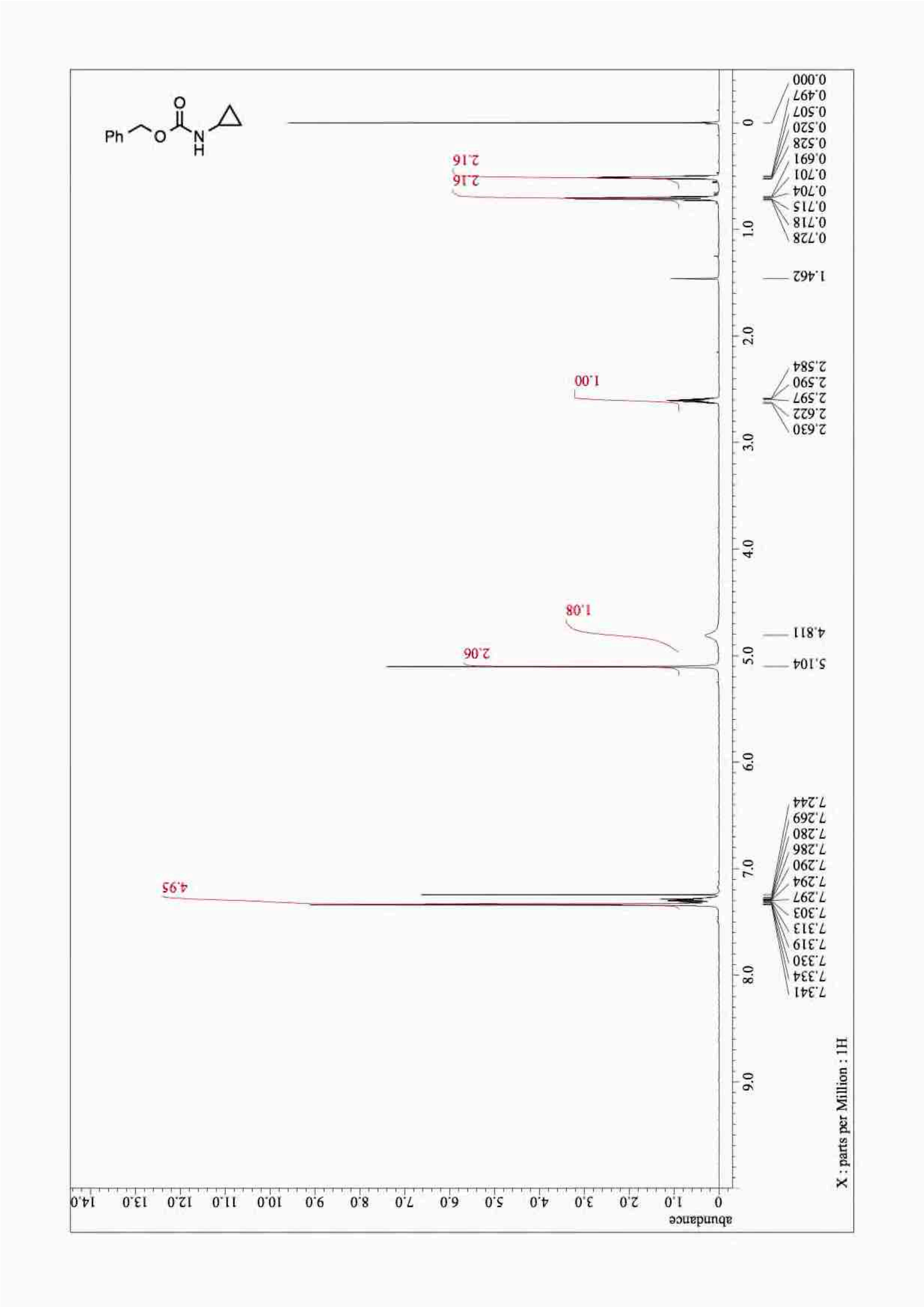
^{1}H NMR of **1g** (600 MHz, 50 ˚C, $CDCl_3$)



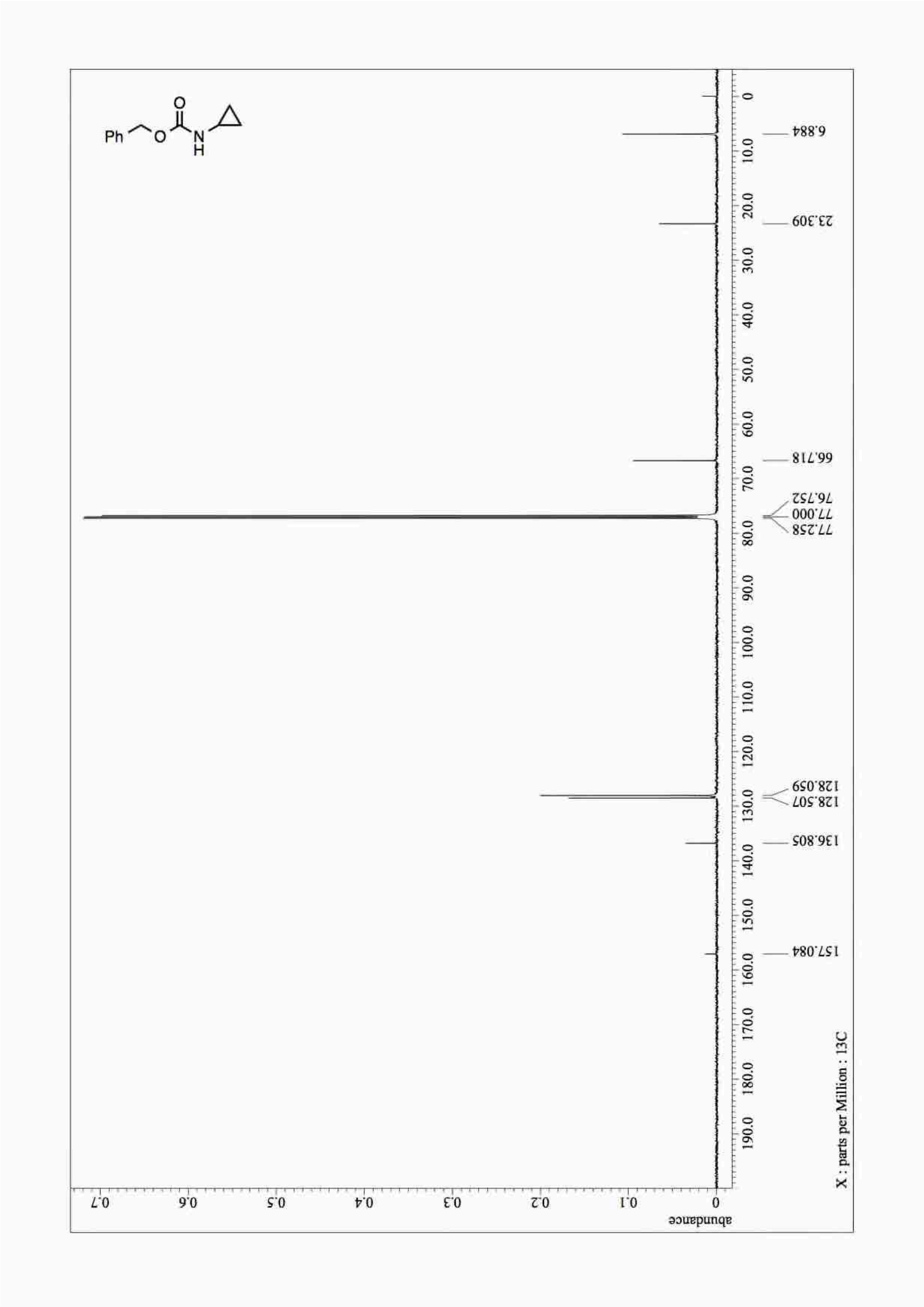
^{13}C NMR of **1g** (151 MHz, $CDCl_3$)



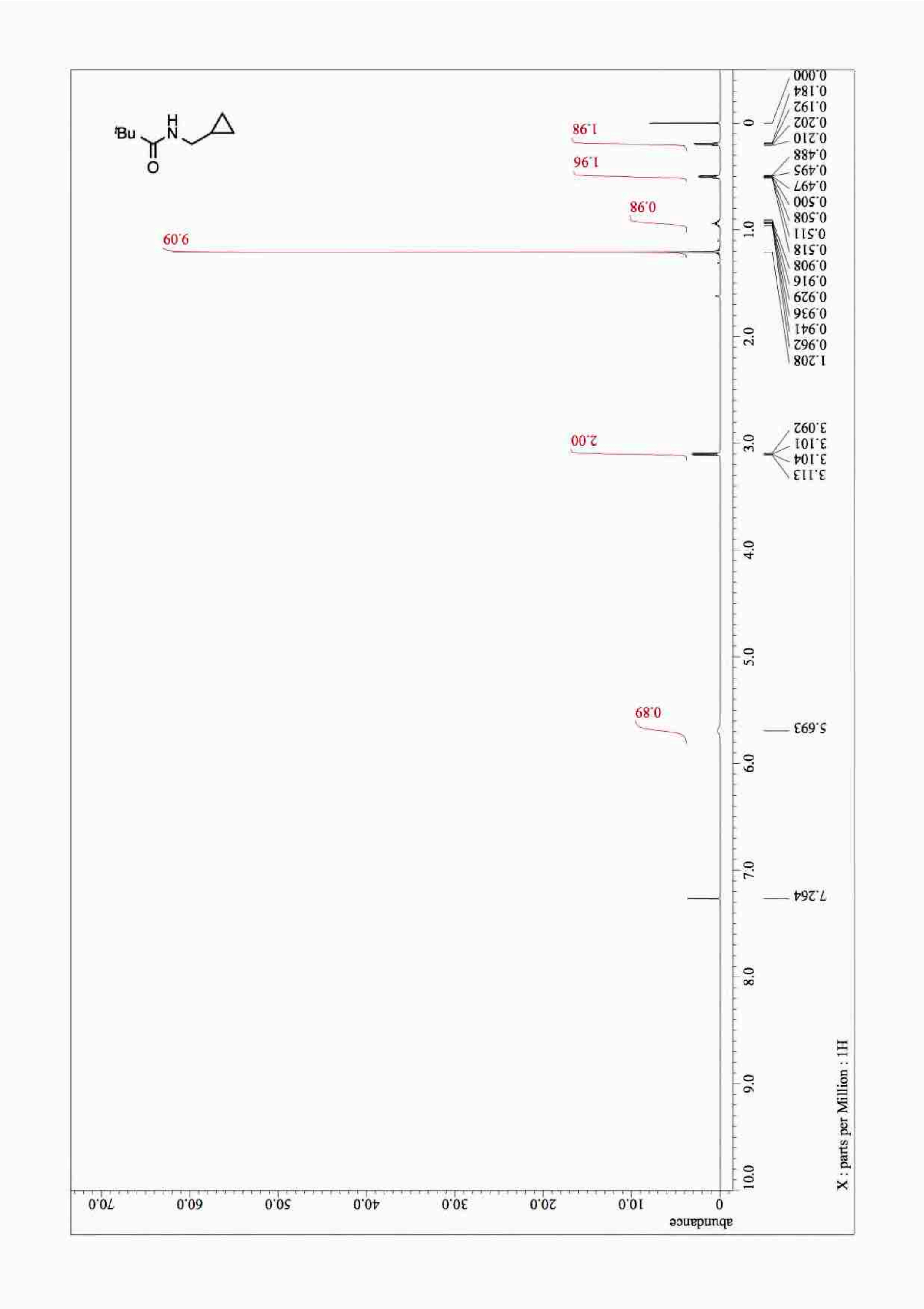
^{1}H NMR of **1i** (500 MHz, 60 ˚C, $CDCl_3$)



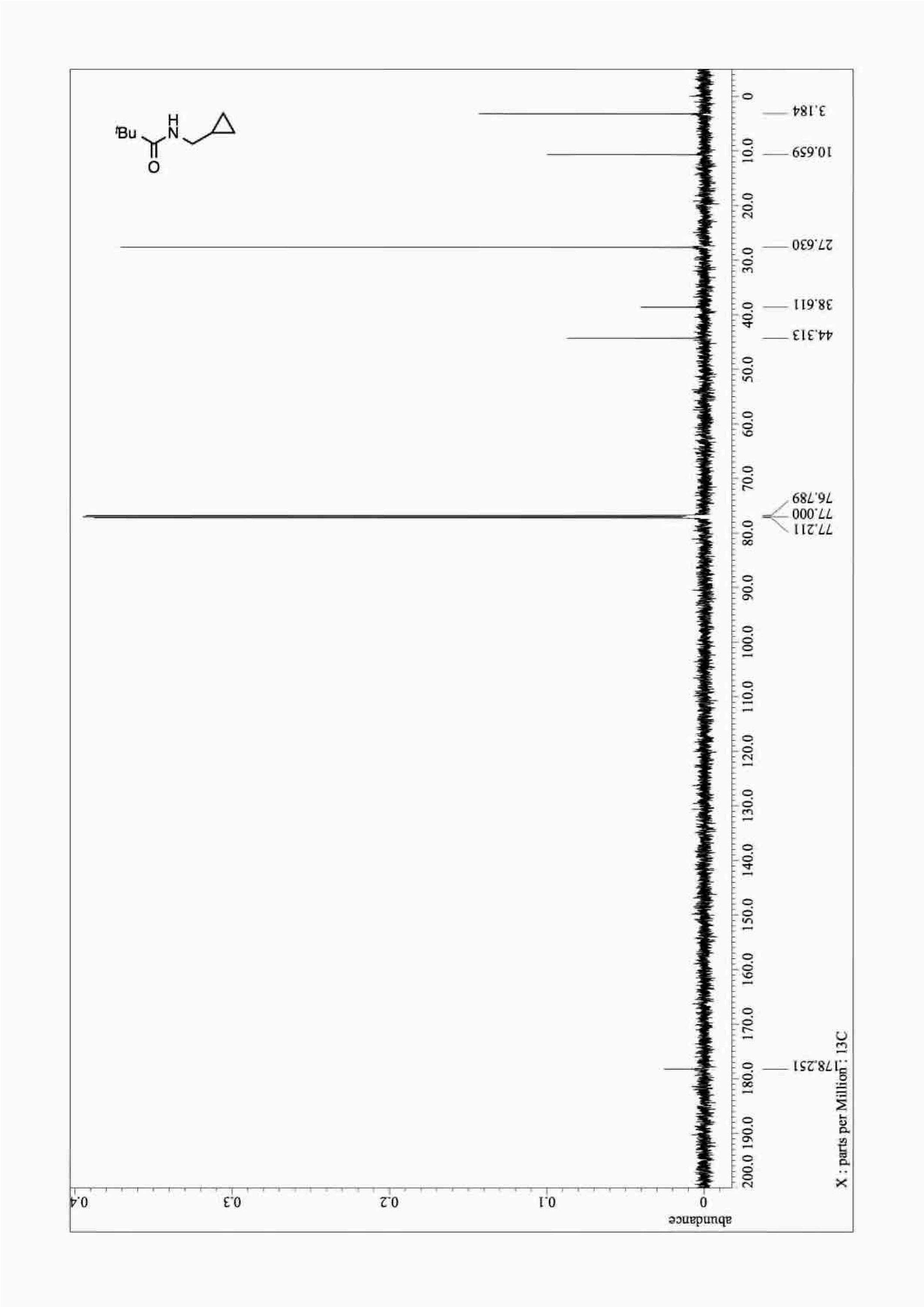
^{13}C NMR of **1i** (126 MHz, 60 ˚C, $CDCl_3$)



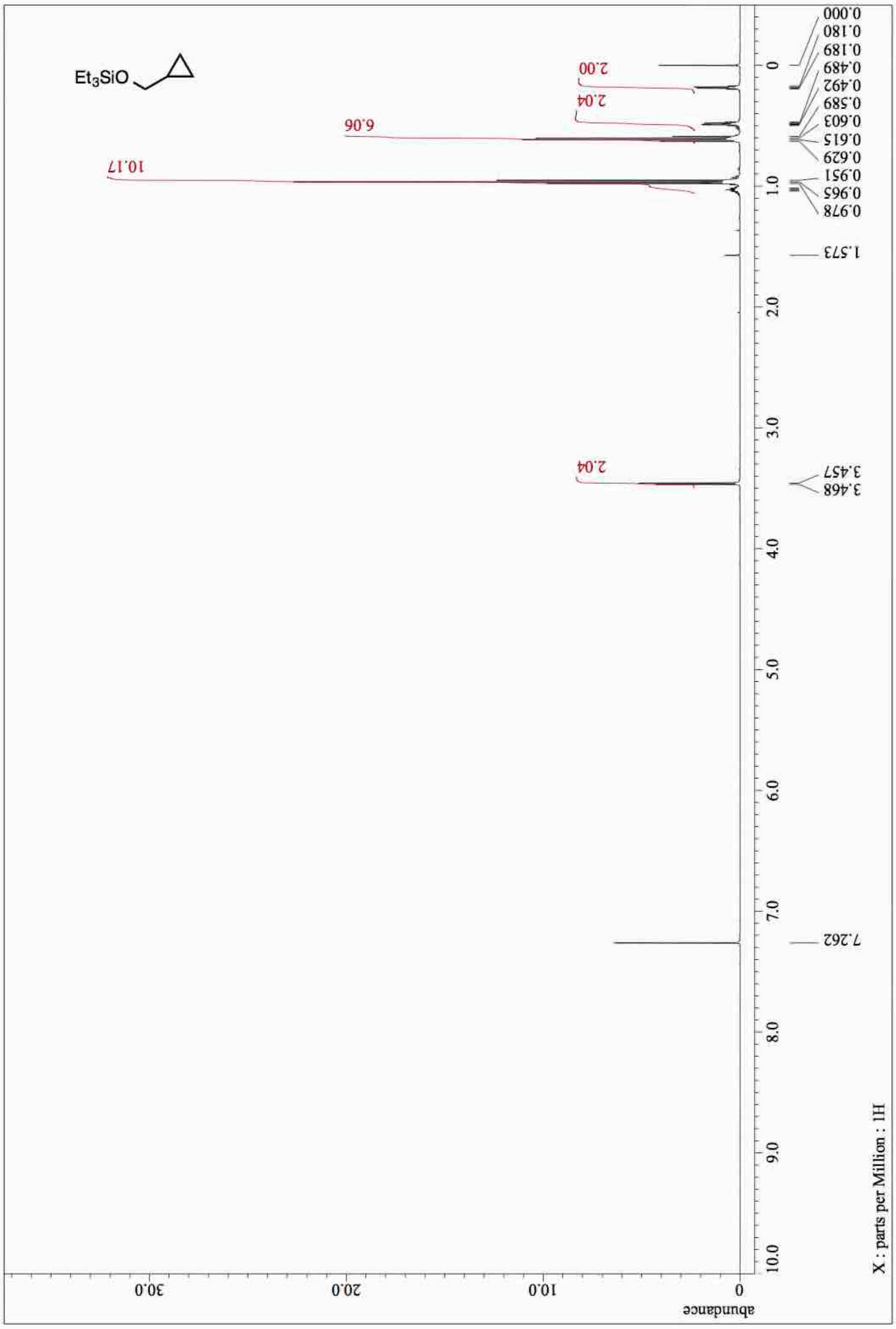
^{1}H NMR of **1j** (600 MHz, $CDCl_3$)



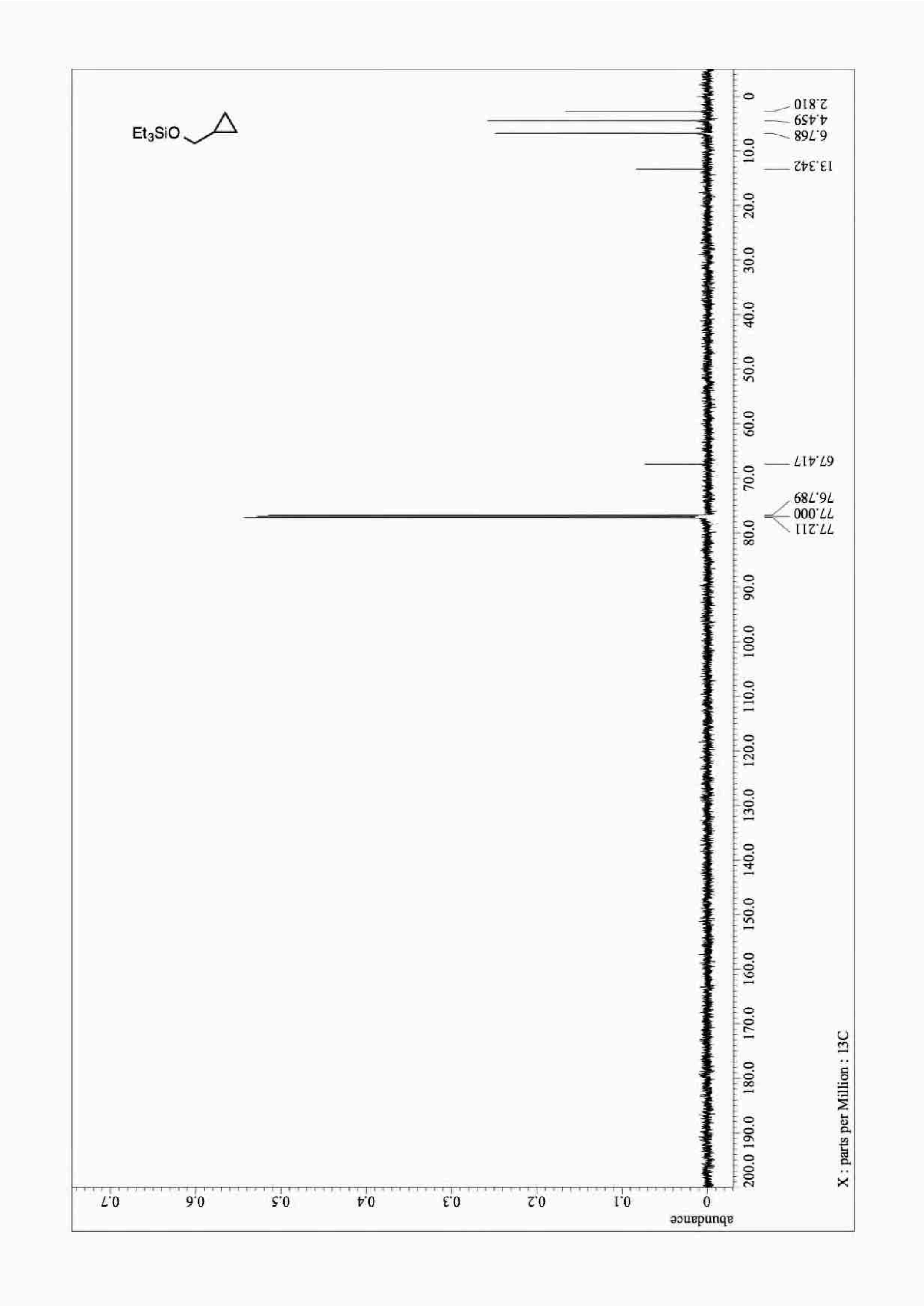
^{13}C NMR of **1j** (151 MHz, $CDCl_3$)



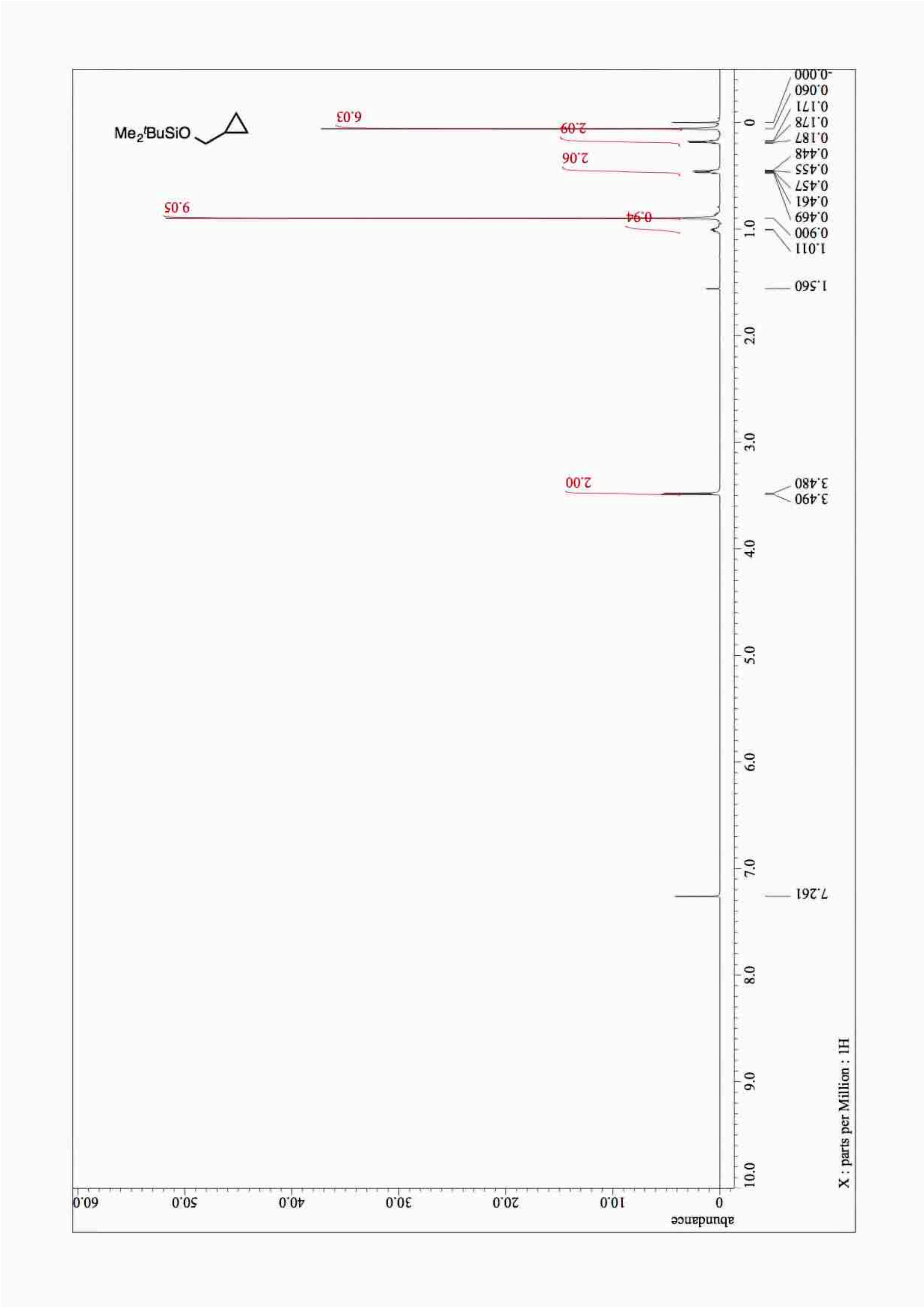
[1]H NMR of **1k** (600 MHz, $CDCl_3$)



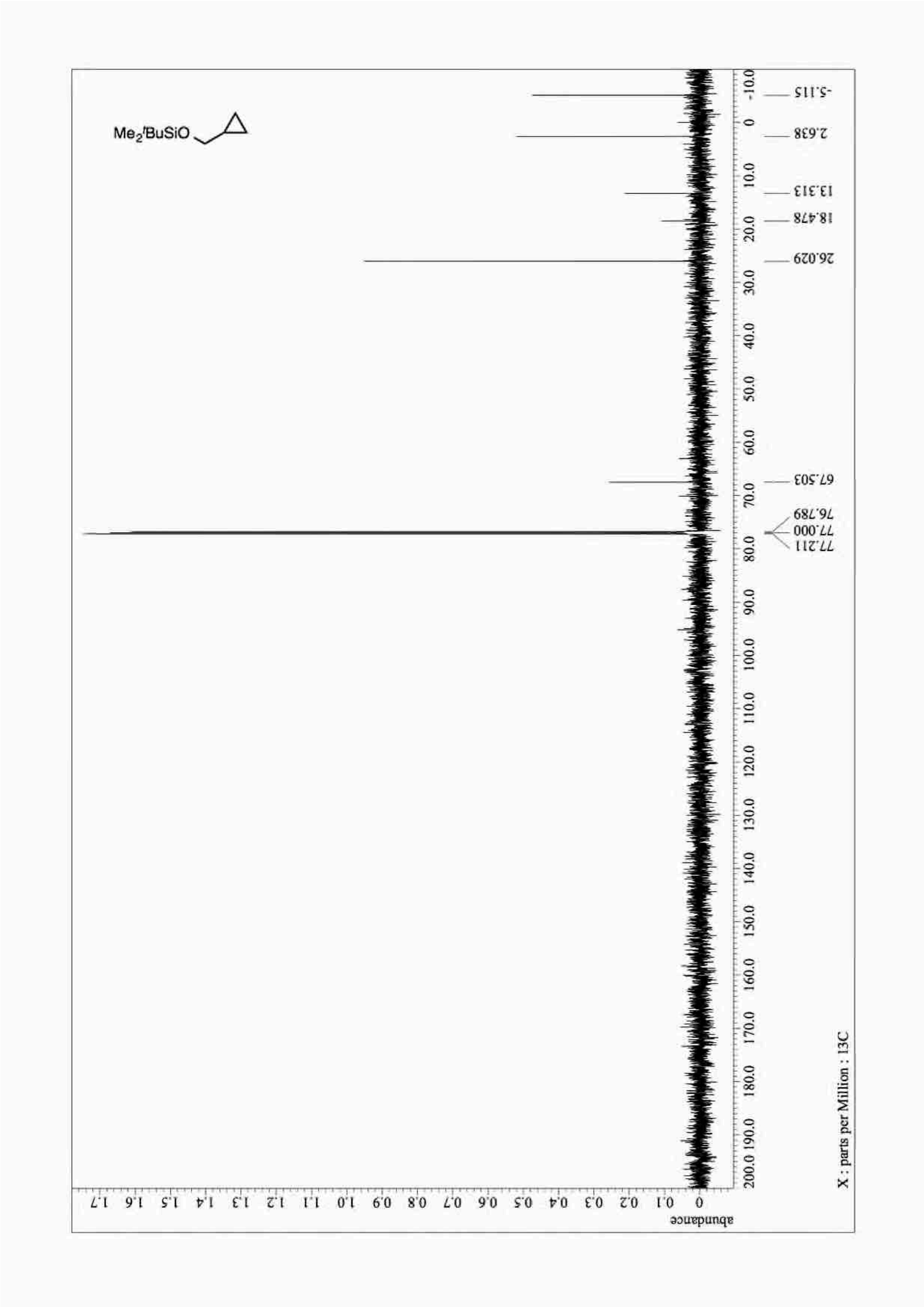
^{13}C NMR of **1k** (151 MHz, $CDCl_3$)



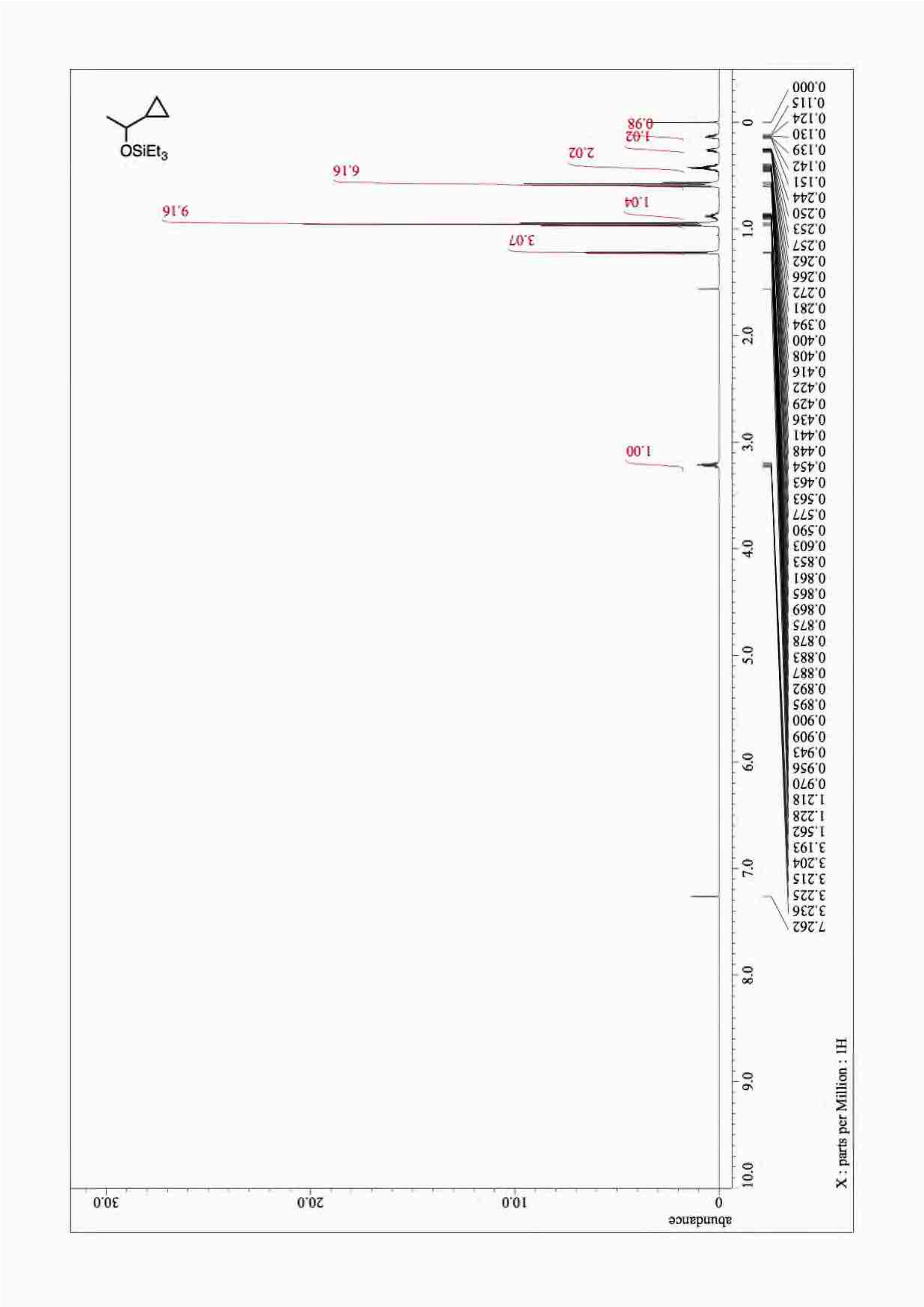
[1]H NMR of **1l** (600 MHz, $CDCl_3$)



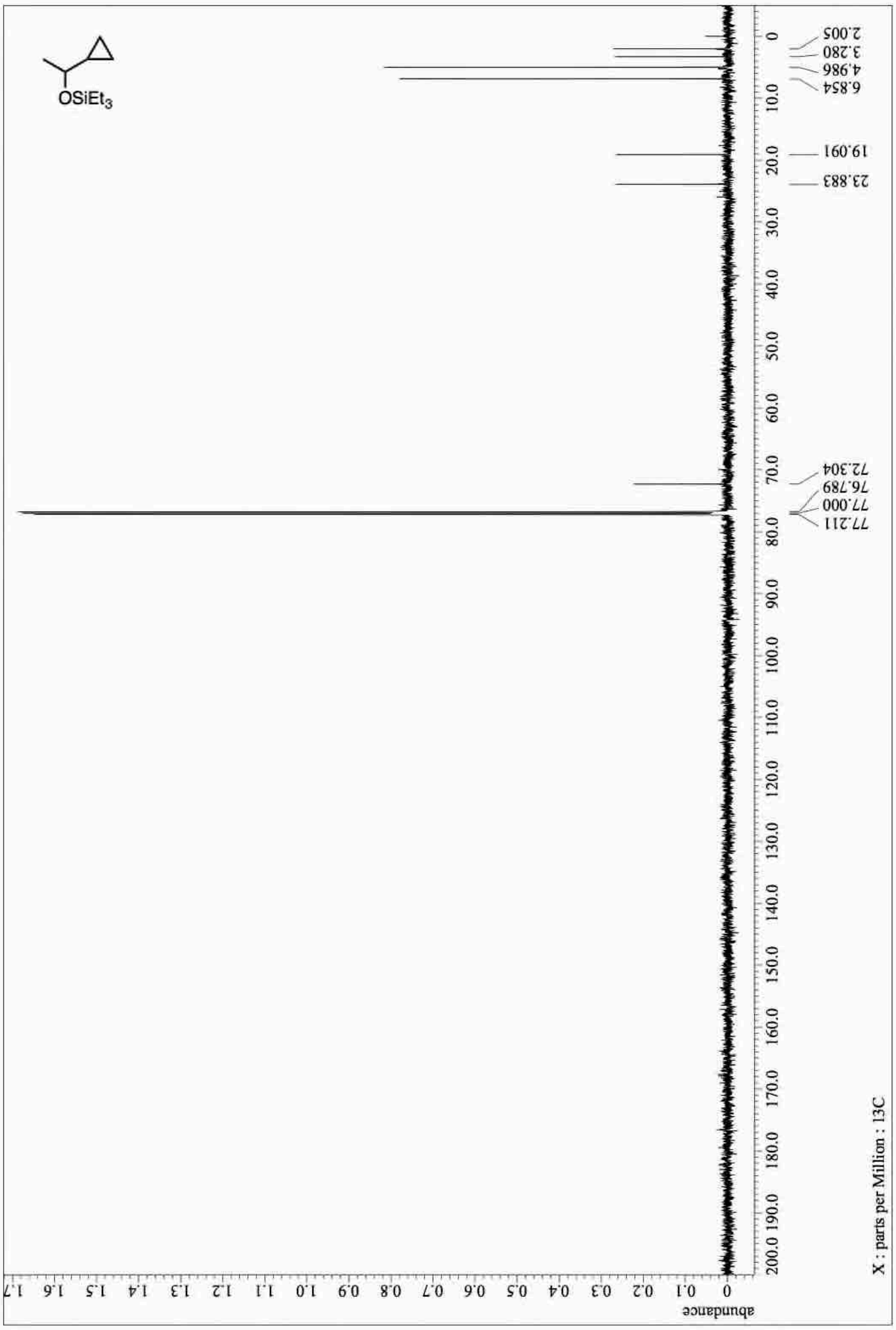
^{13}C NMR of **1l** (151 MHz, $CDCl_3$)



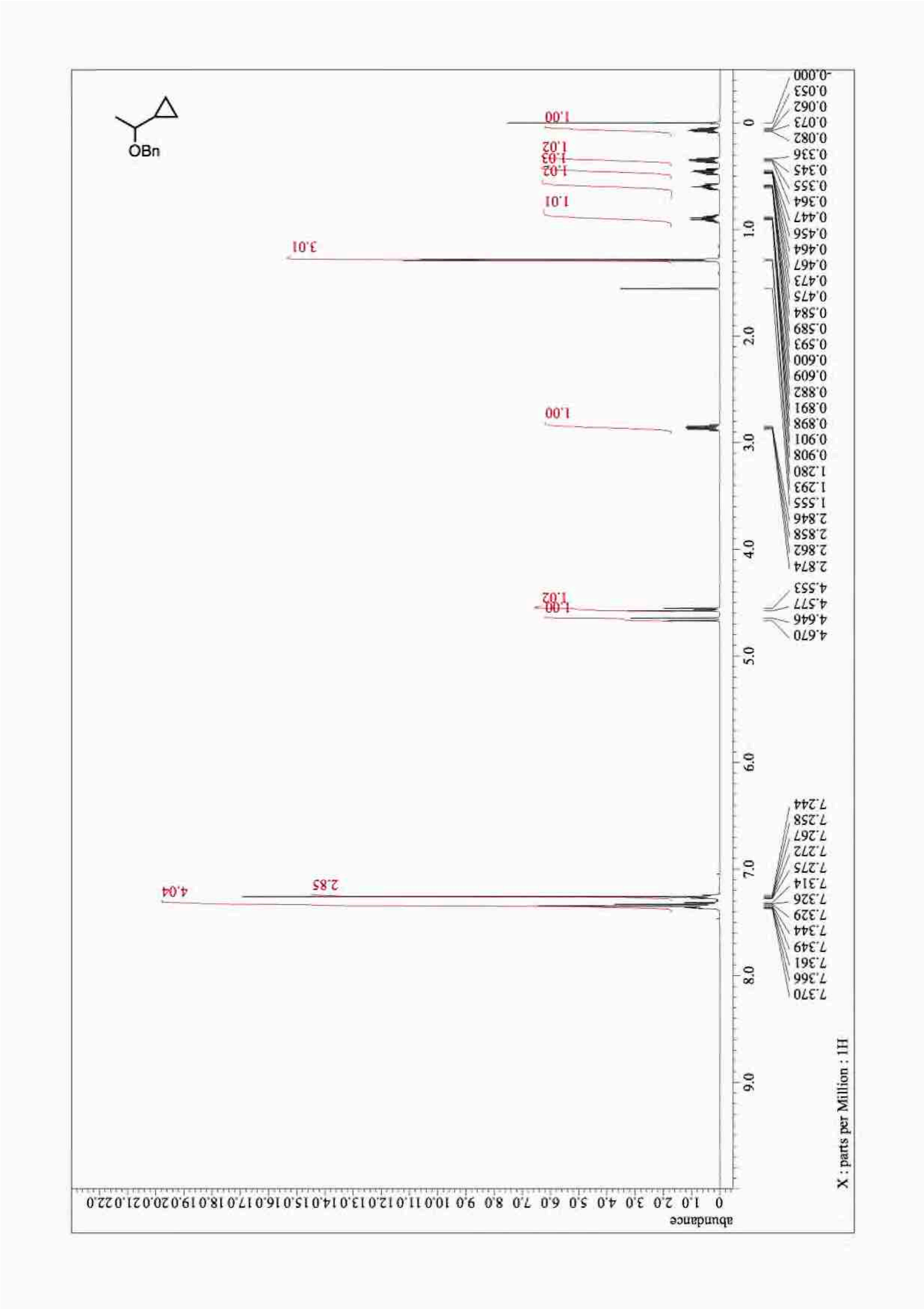
[1]H NMR of **1m** (600 MHz, $CDCl_3$)



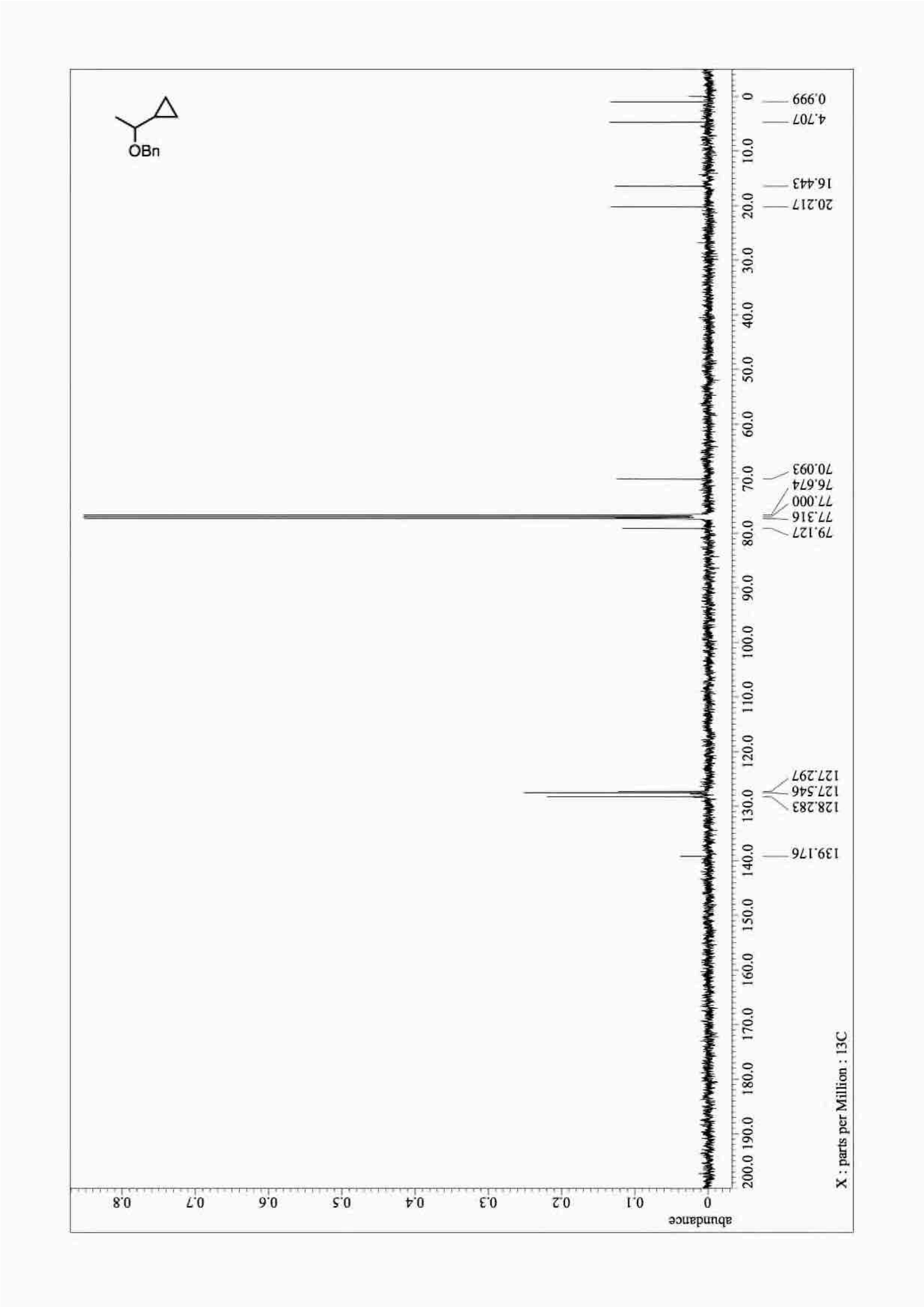
^{13}C NMR of **1m** (151 MHz, $CDCl_3$)



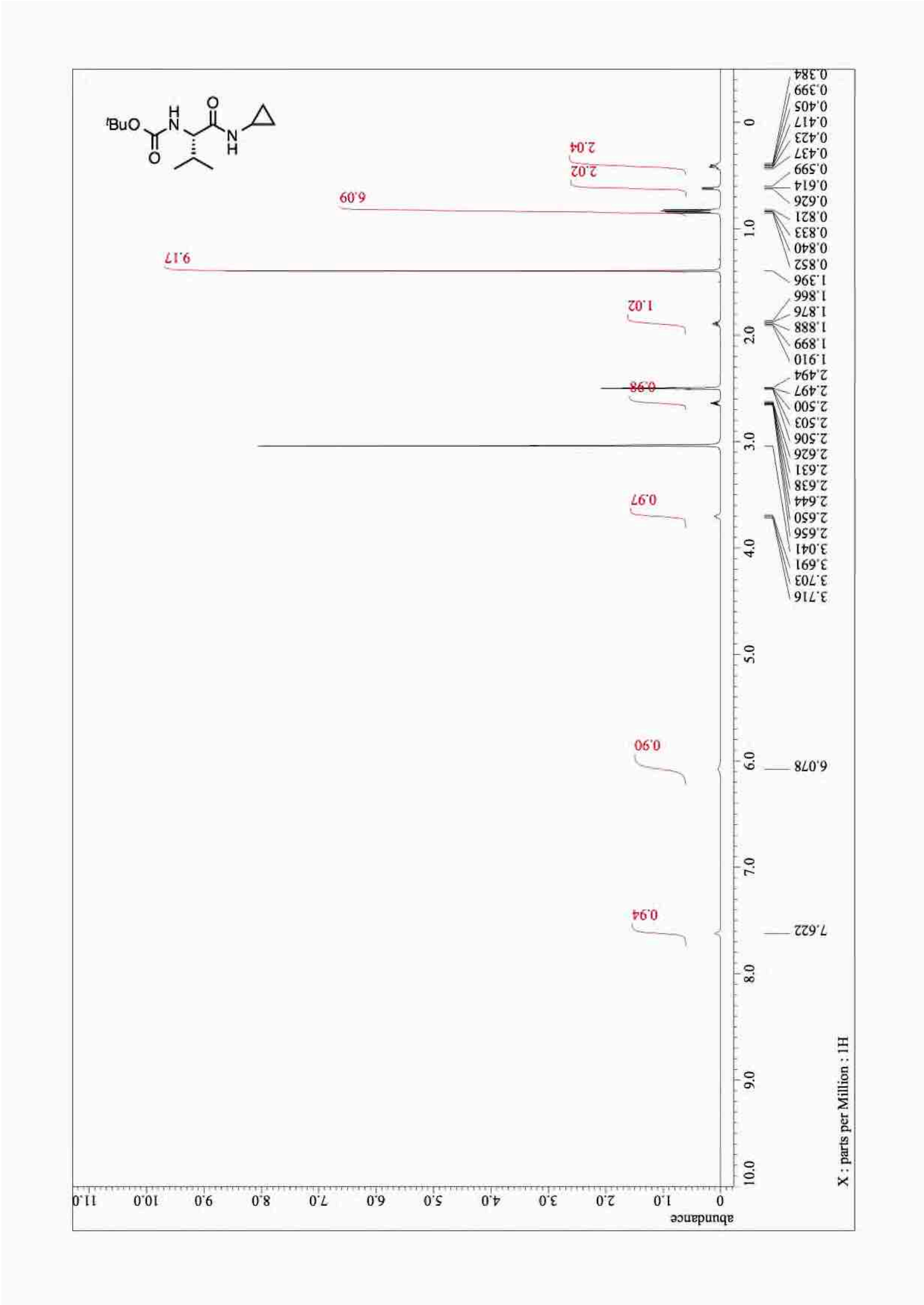
^{1}H NMR of **1n** (500 MHz, $CDCl_3$)



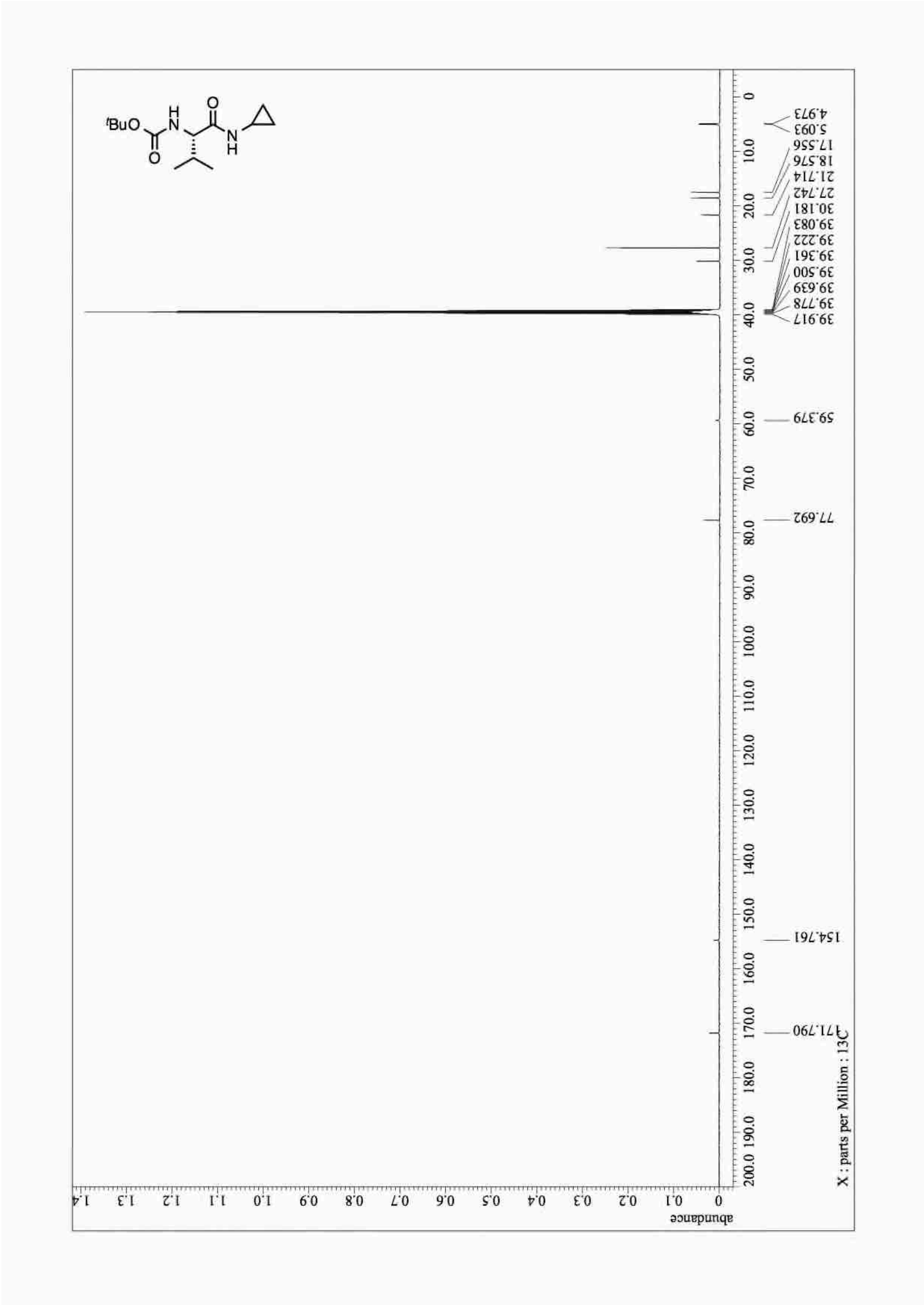
^{13}C NMR of **1n** (151 MHz, $CDCl_3$)



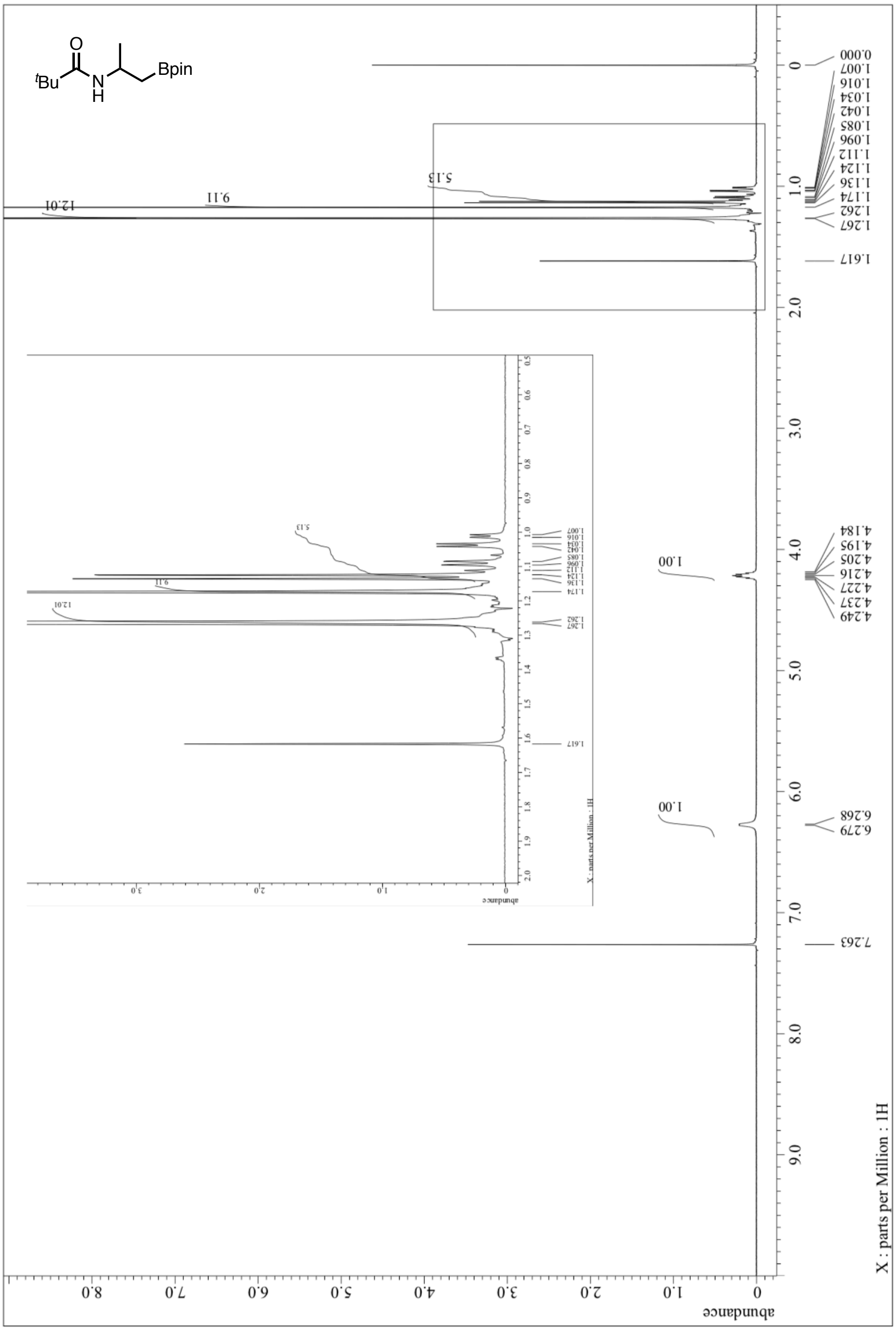
[1]H NMR of **1s** (600 MHz, 90 ˚C, $(CD_3)_2SO$)



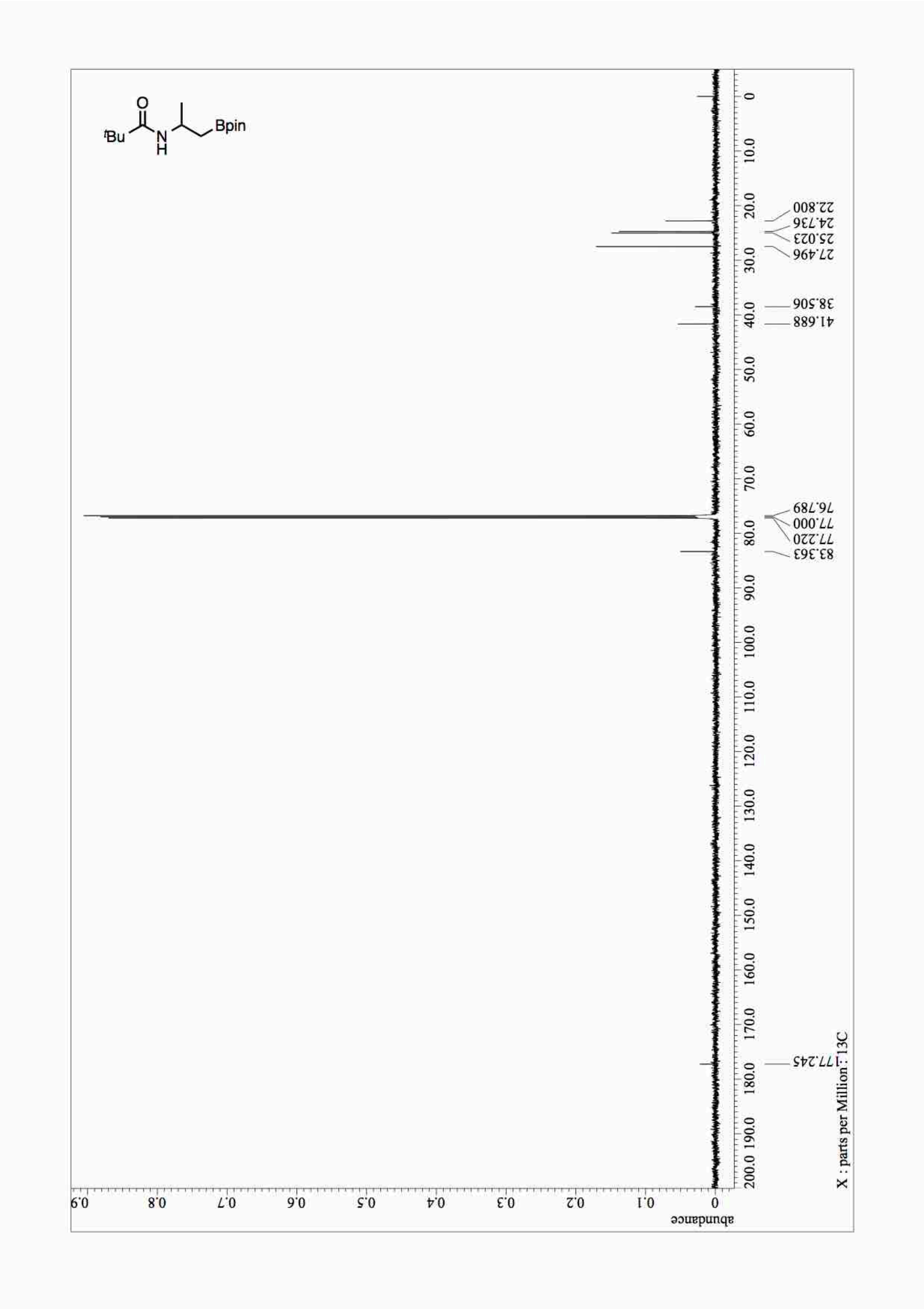
^{13}C NMR of **1s** (151 MHz, 90 °C, $(CD_3)_2SO$)



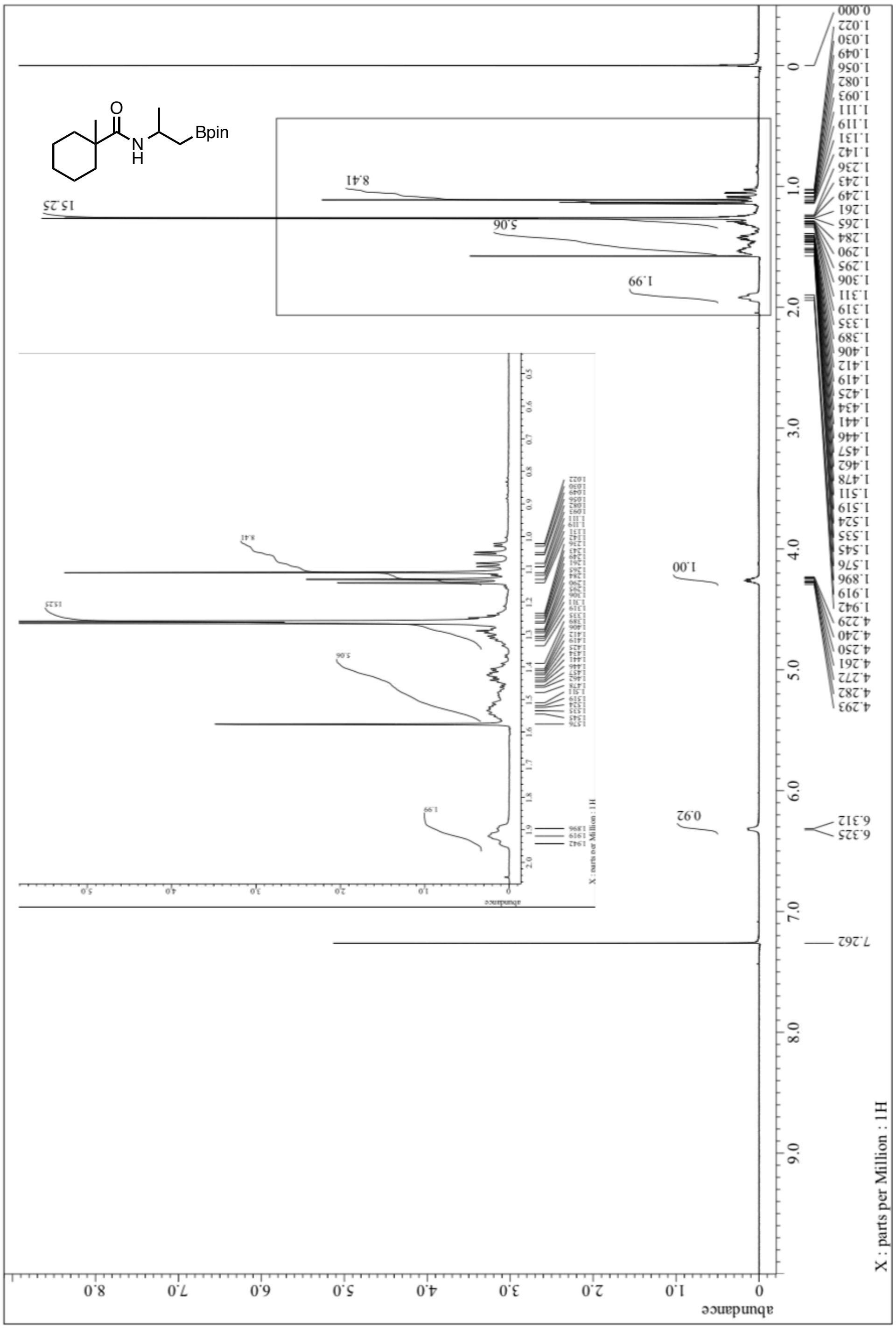
^{1}H NMR of **2a** (600 MHz, $CDCl_3$)



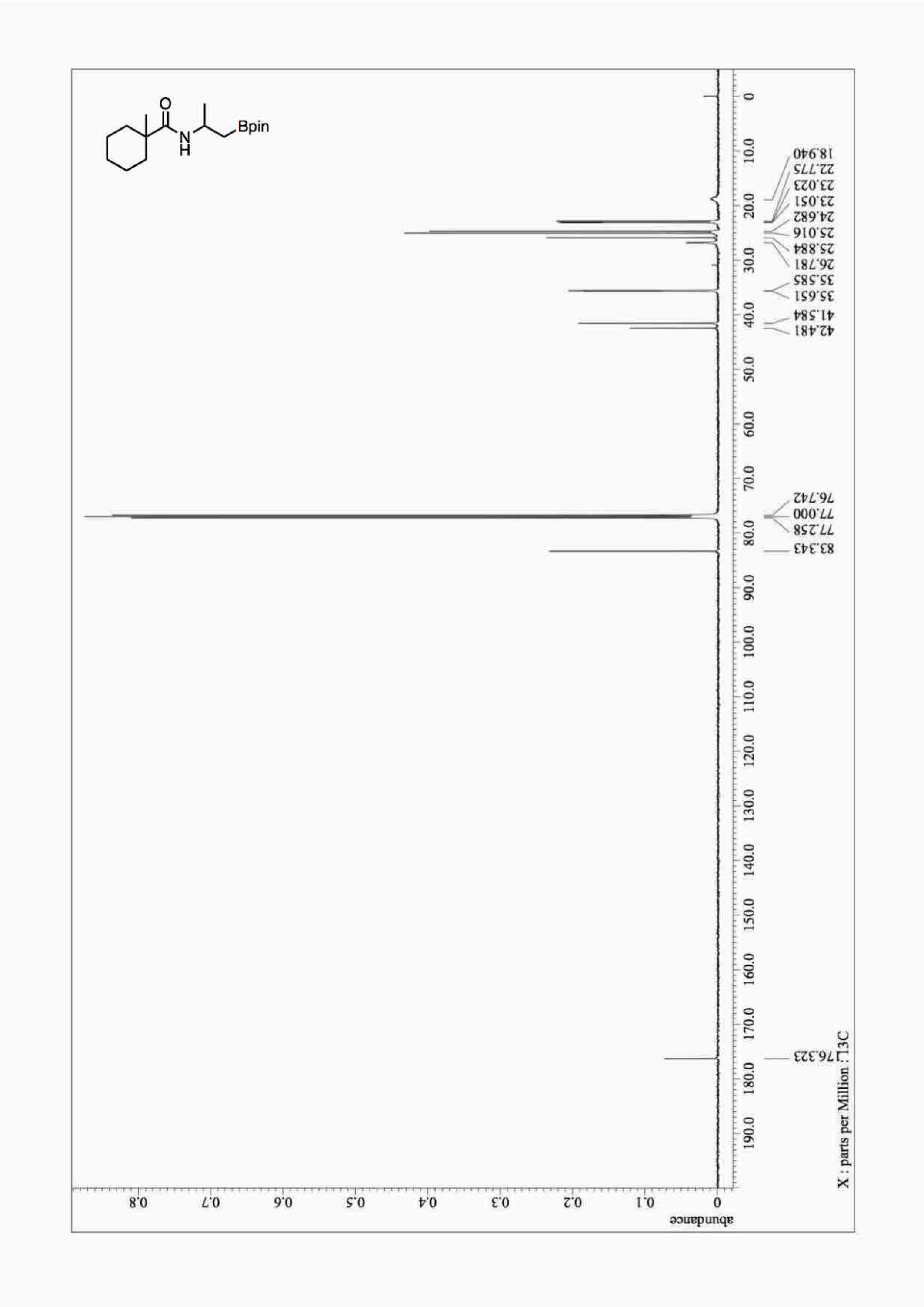
^{13}C NMR of **2a** (151 MHz, $CDCl_3$)



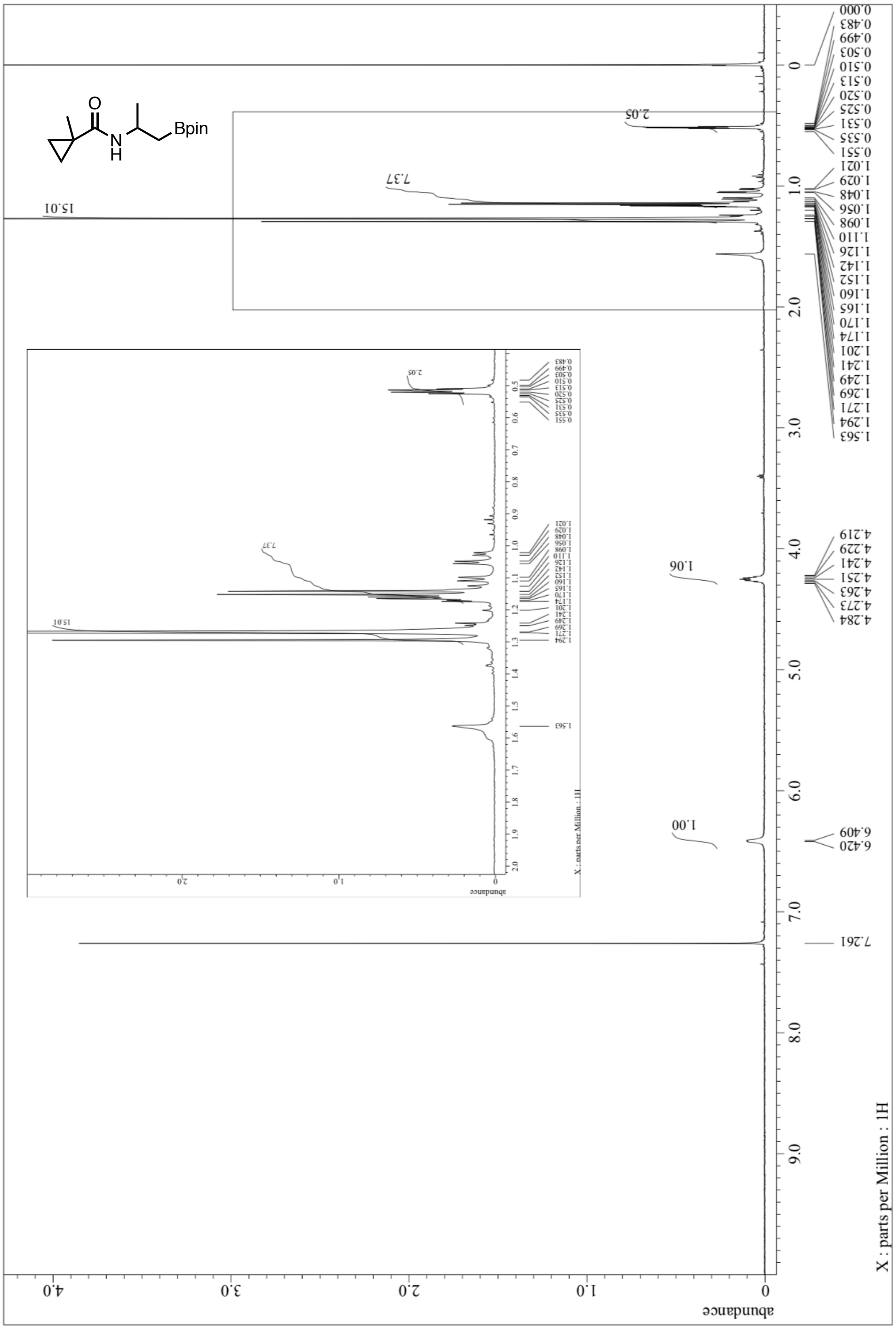
[1]H NMR of **2b** (600 MHz, $CDCl_3$)



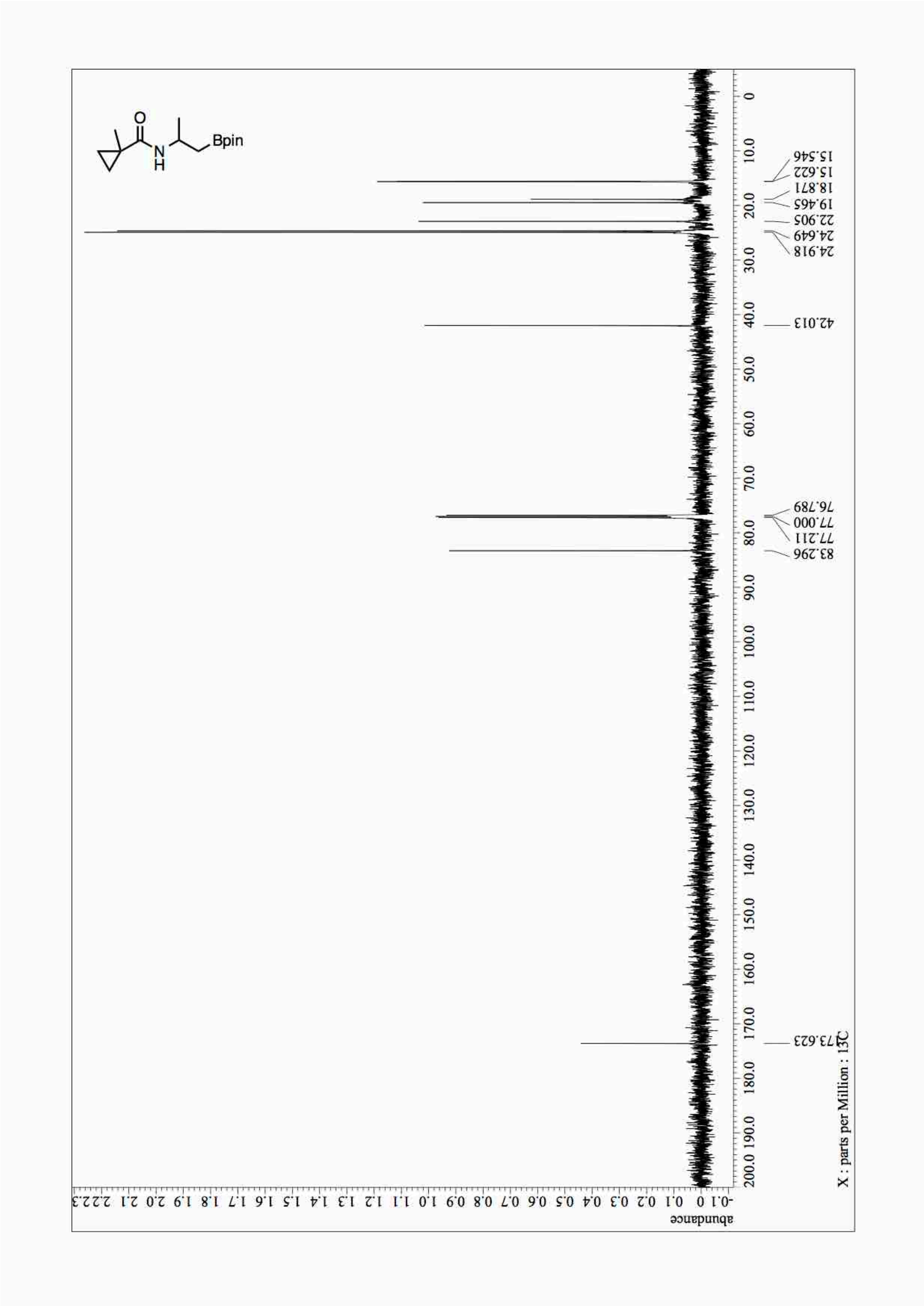
^{13}C NMR of **2b** (126 MHz, $CDCl_3$)



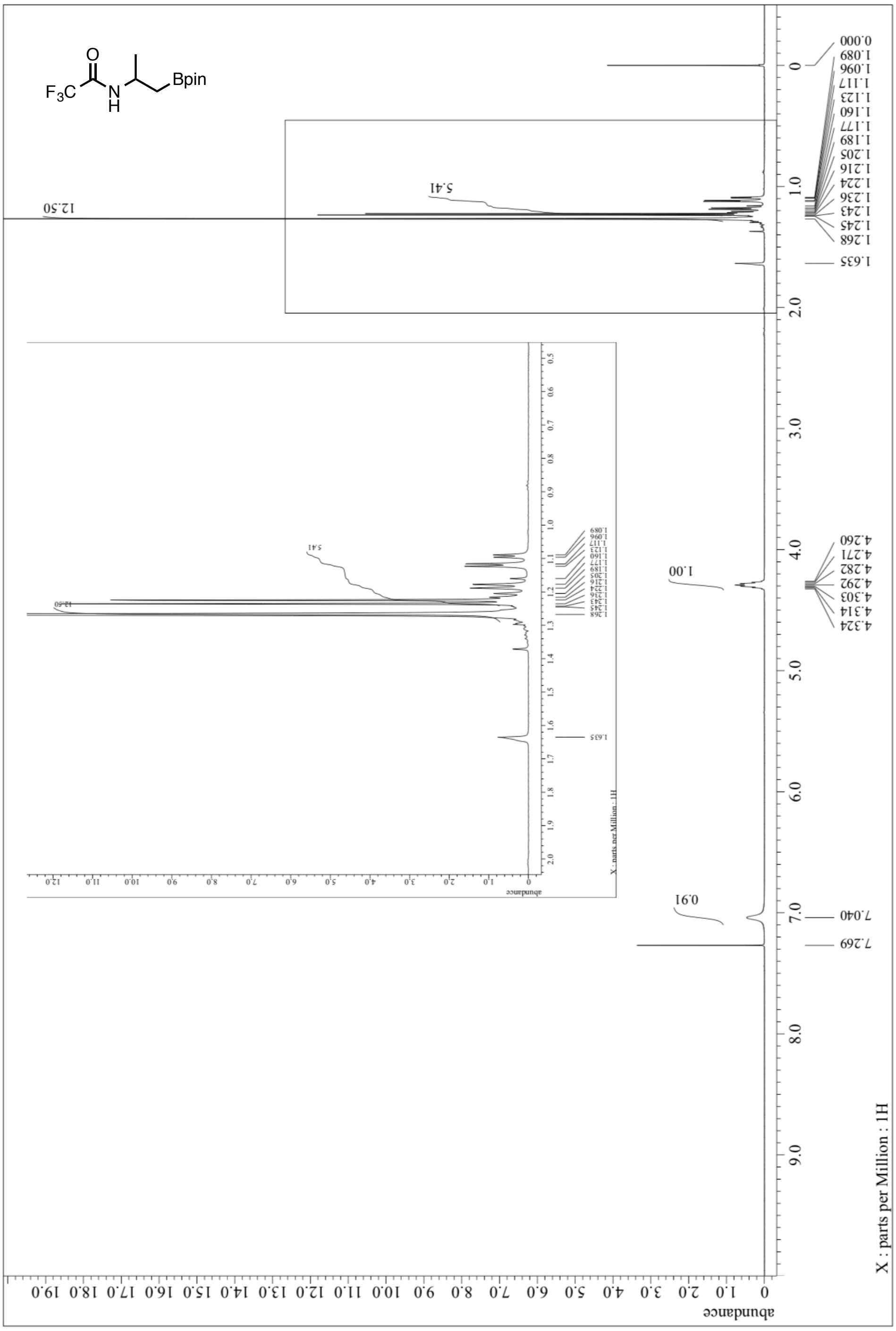
[1]H NMR of **2c** (600 MHz, $CDCl_3$)



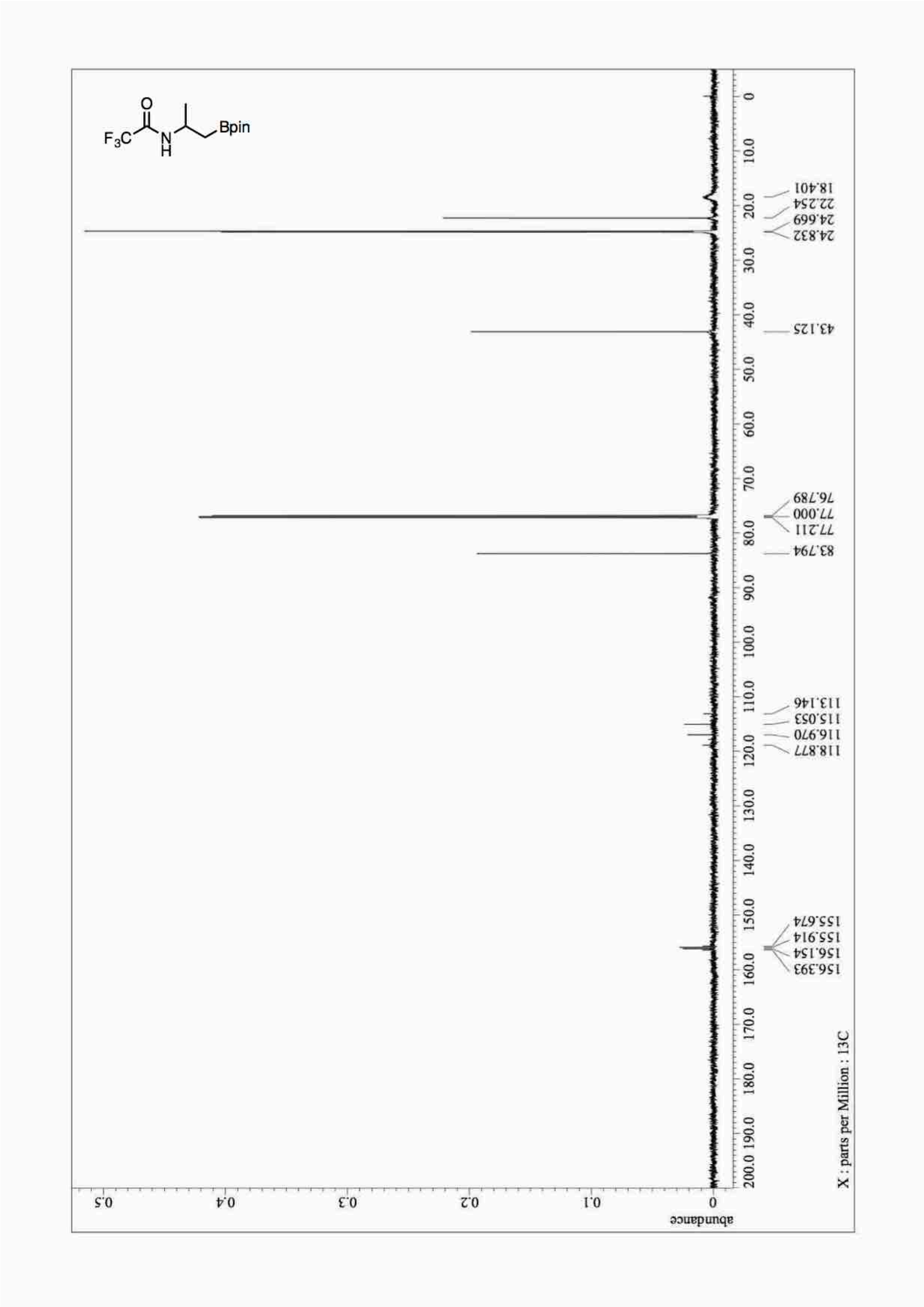
^{13}C NMR of **2c** (151 MHz, $CDCl_3$)



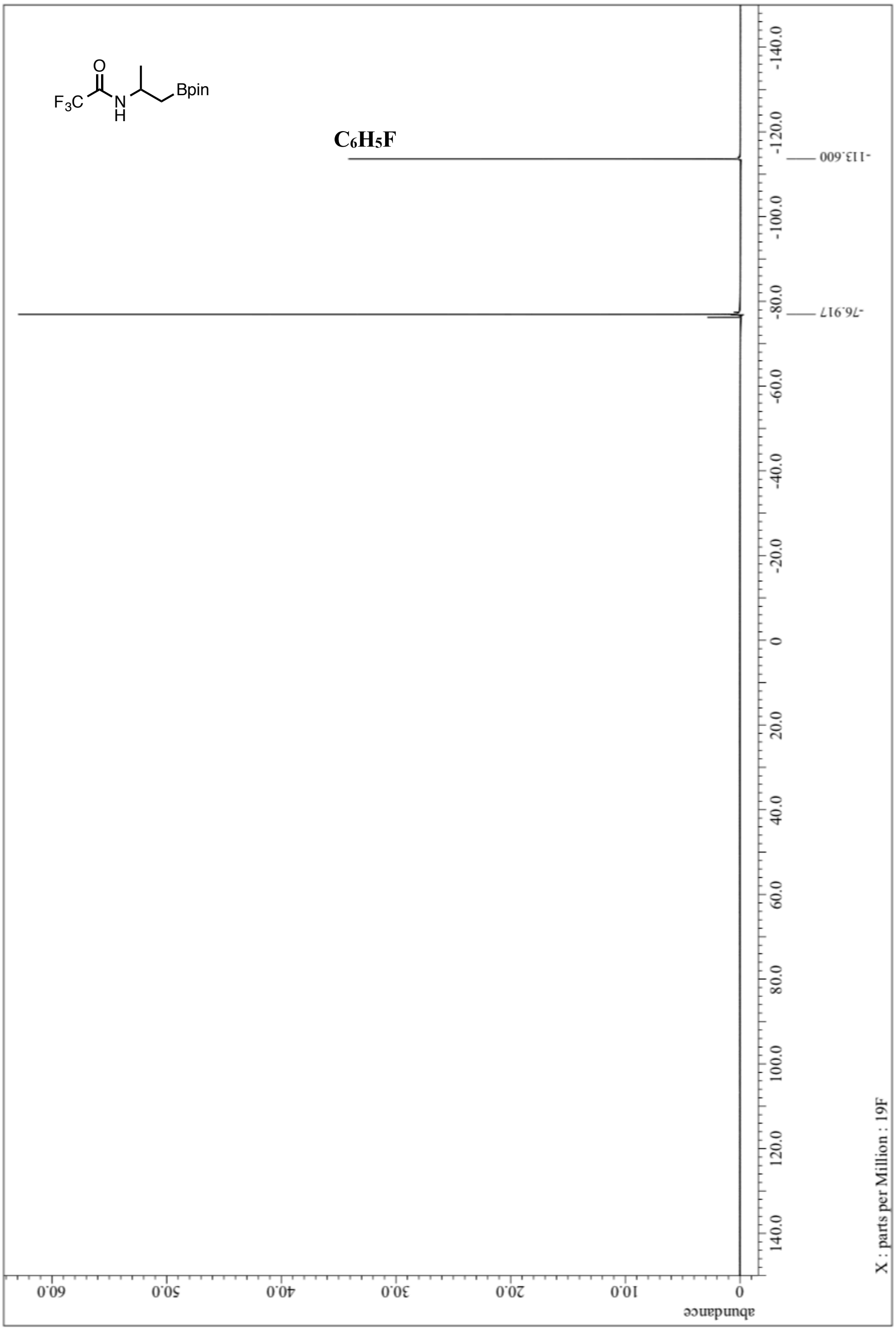
[1]H NMR of **2d** (600 MHz, $CDCl_3$)



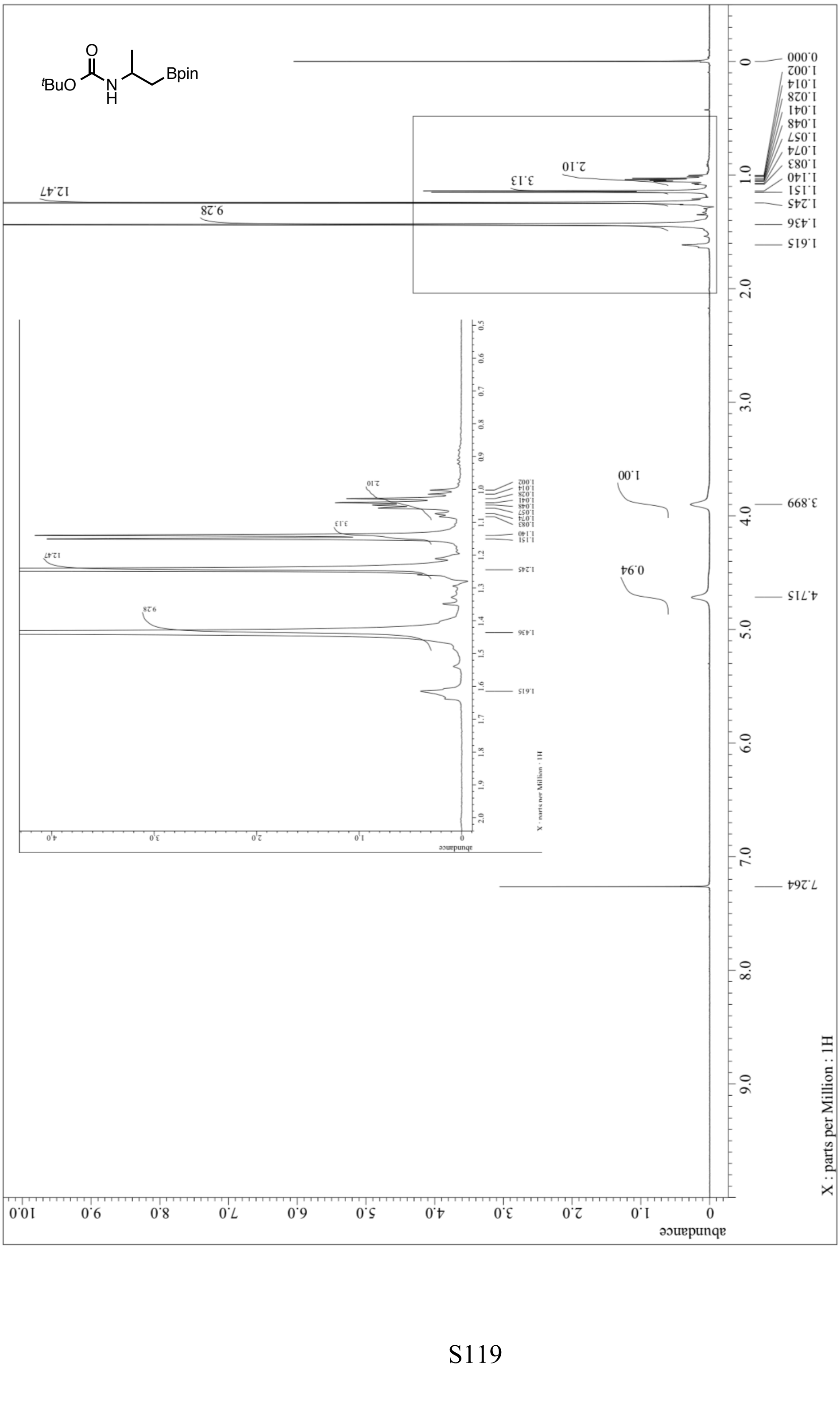
^{13}C NMR of **2d** (151 MHz, $CDCl_3$)



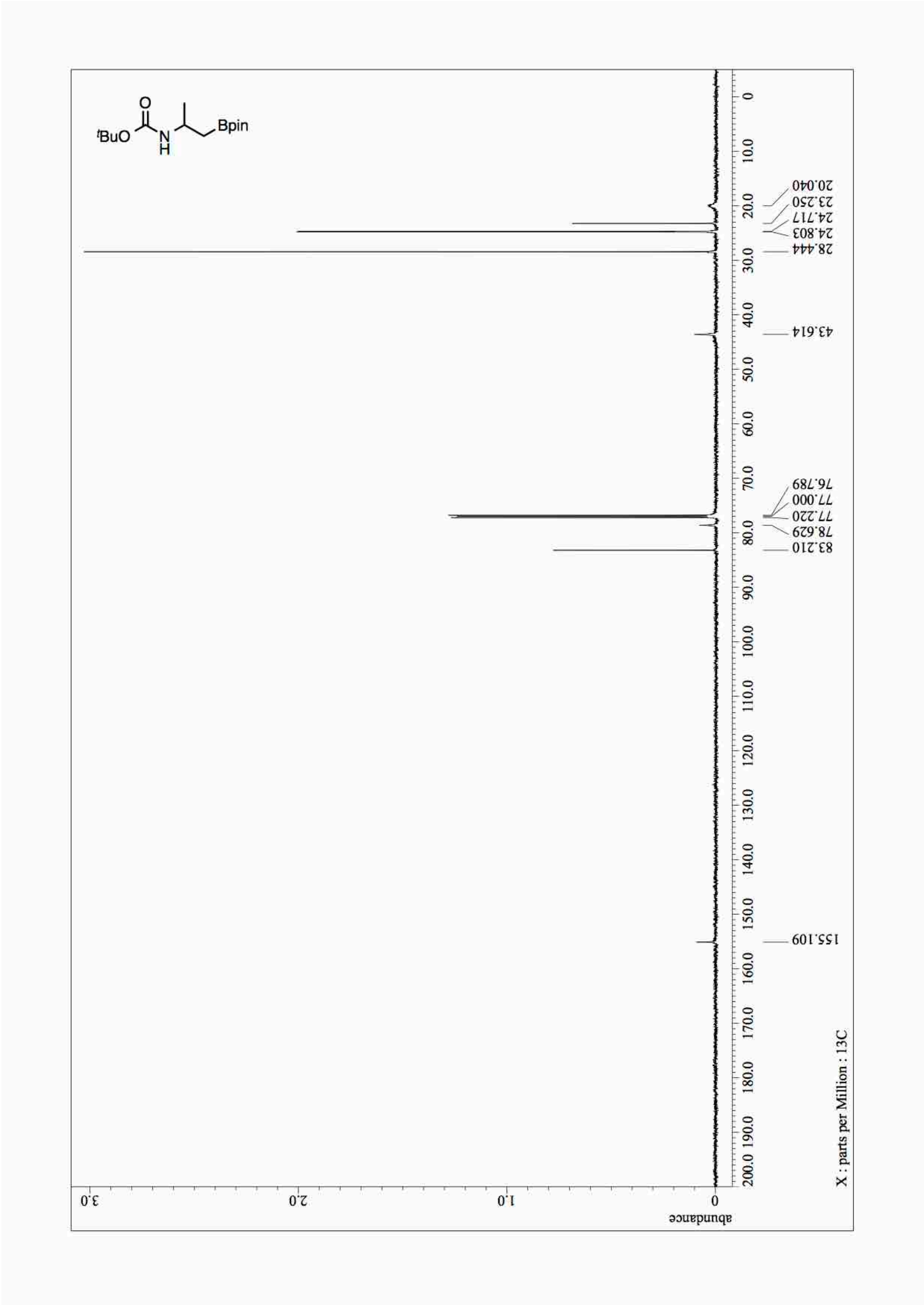
[19]F NMR of **2d** (376 MHz, $CDCl_3$)



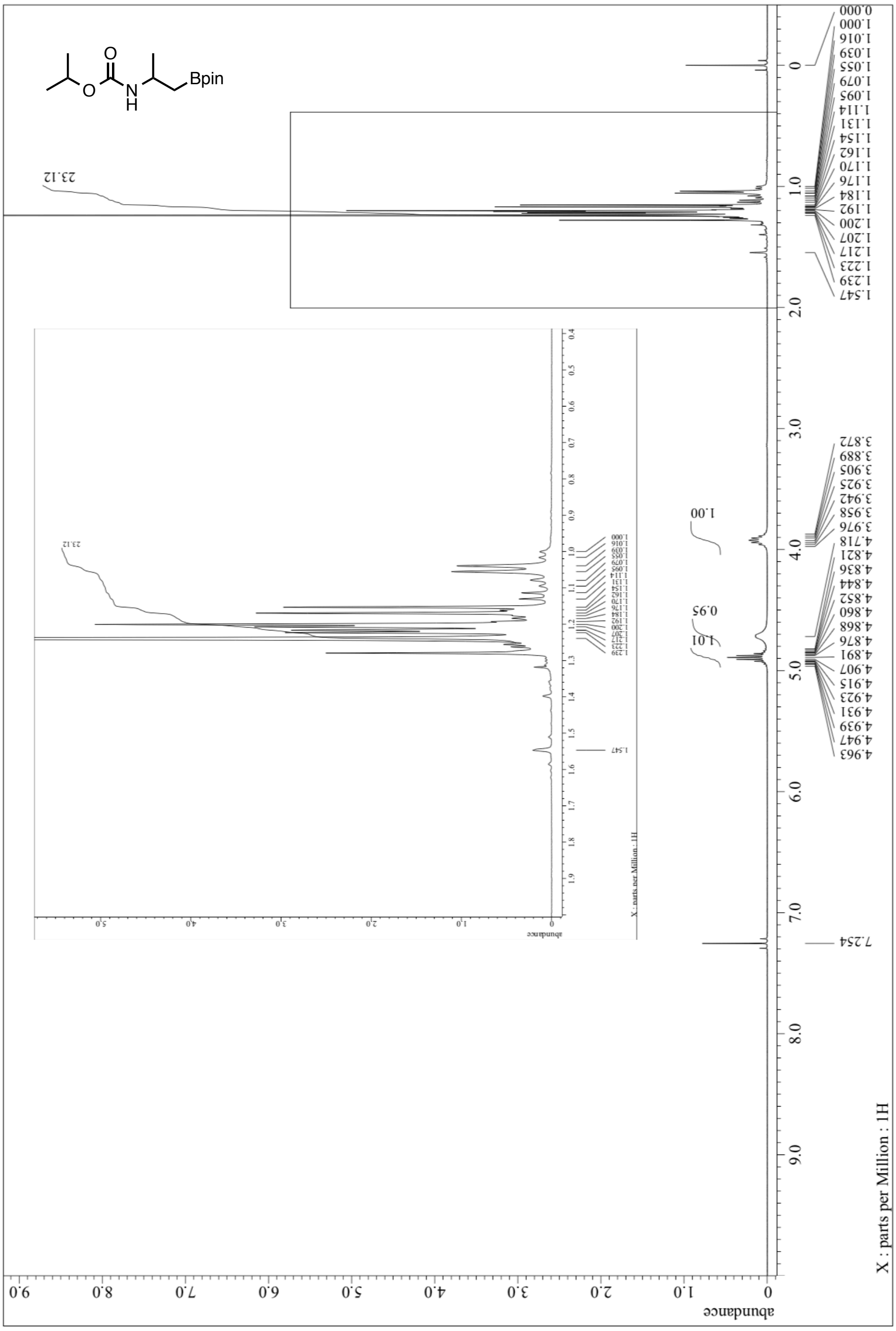
[1]H NMR of **2e** (600 MHz, $CDCl_3$)



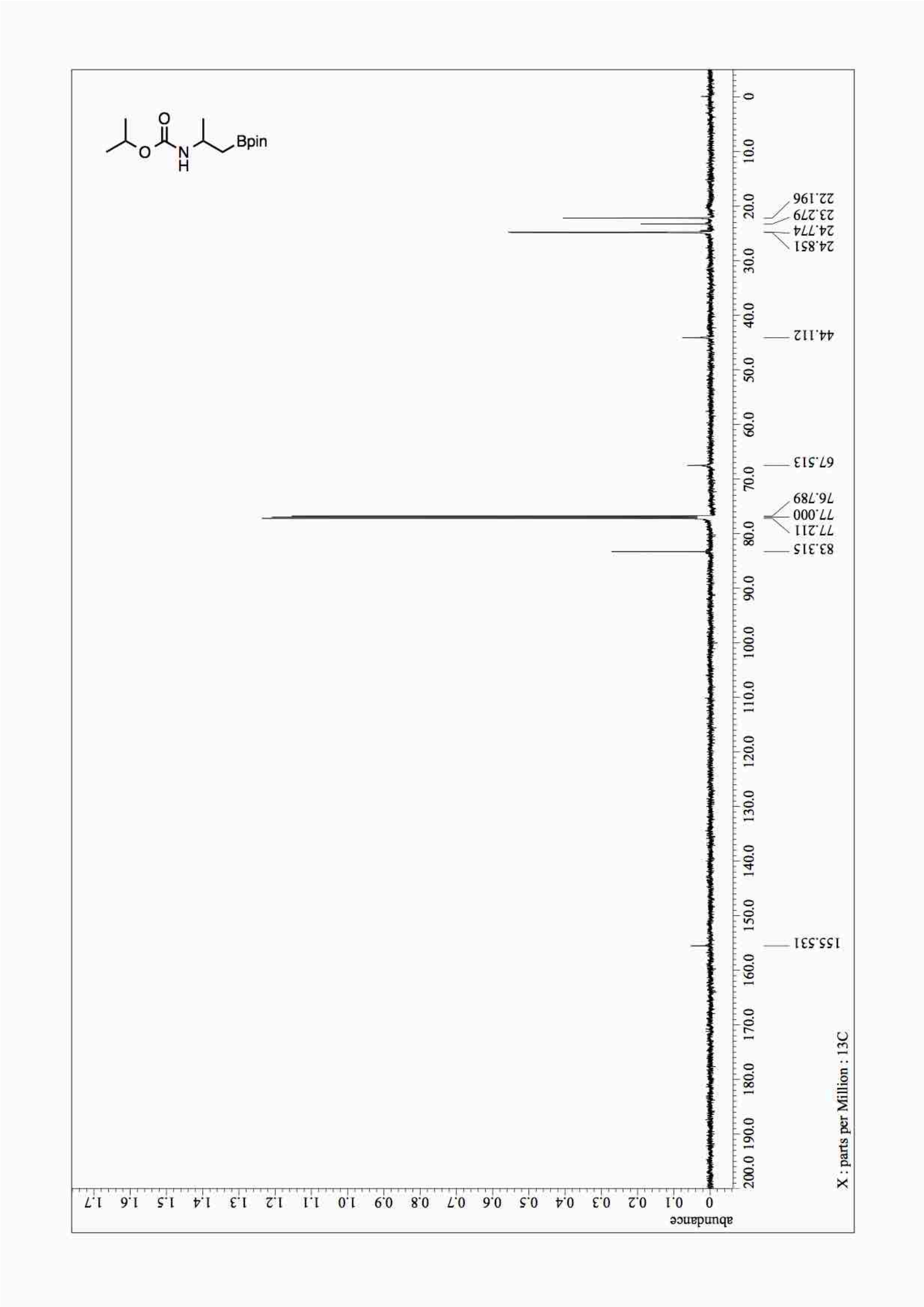
^{13}C NMR of **2e** (151 MHz, $CDCl_3$)



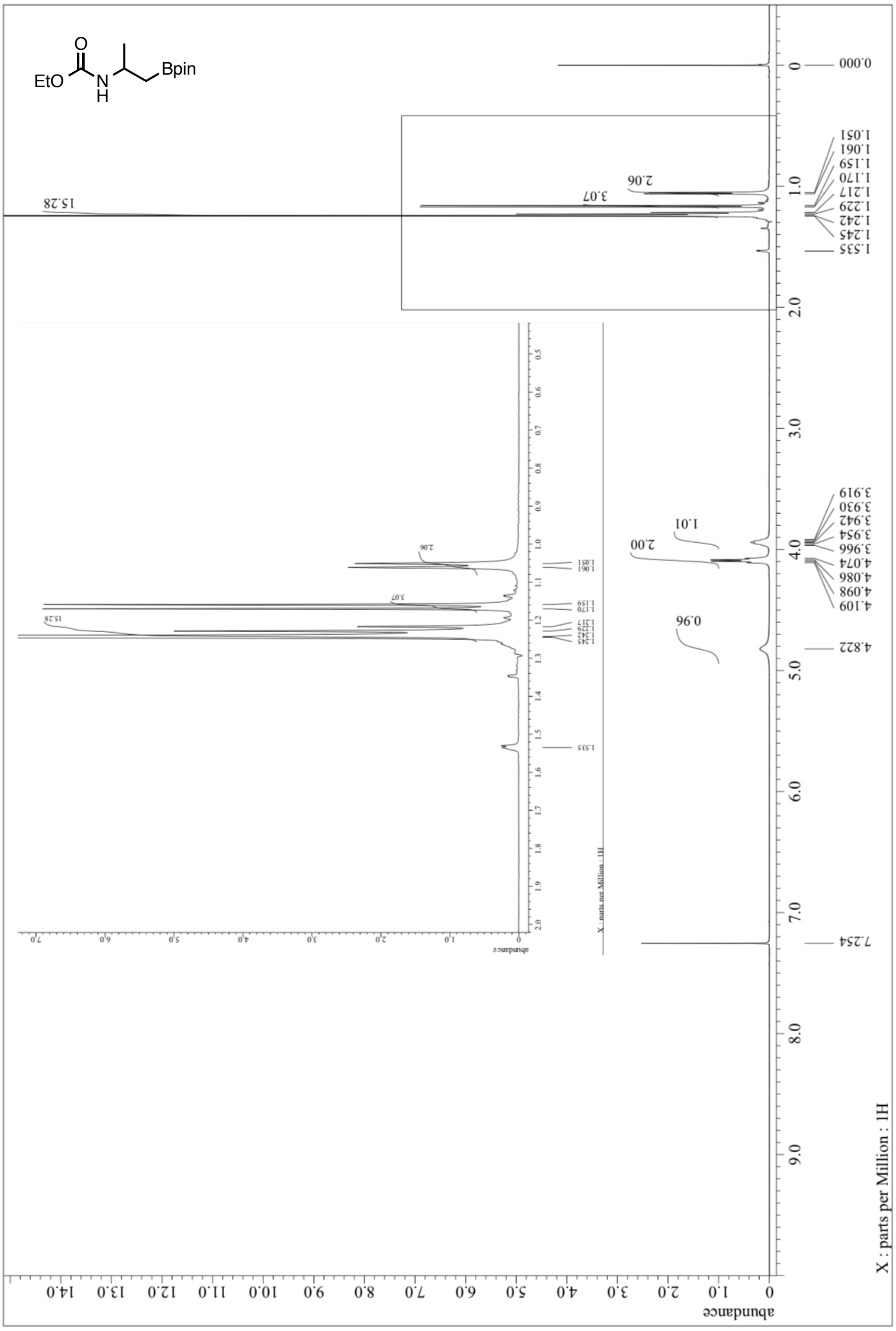
[1]H NMR of **2f** (600 MHz, 60 ˚C, $CDCl_3$)



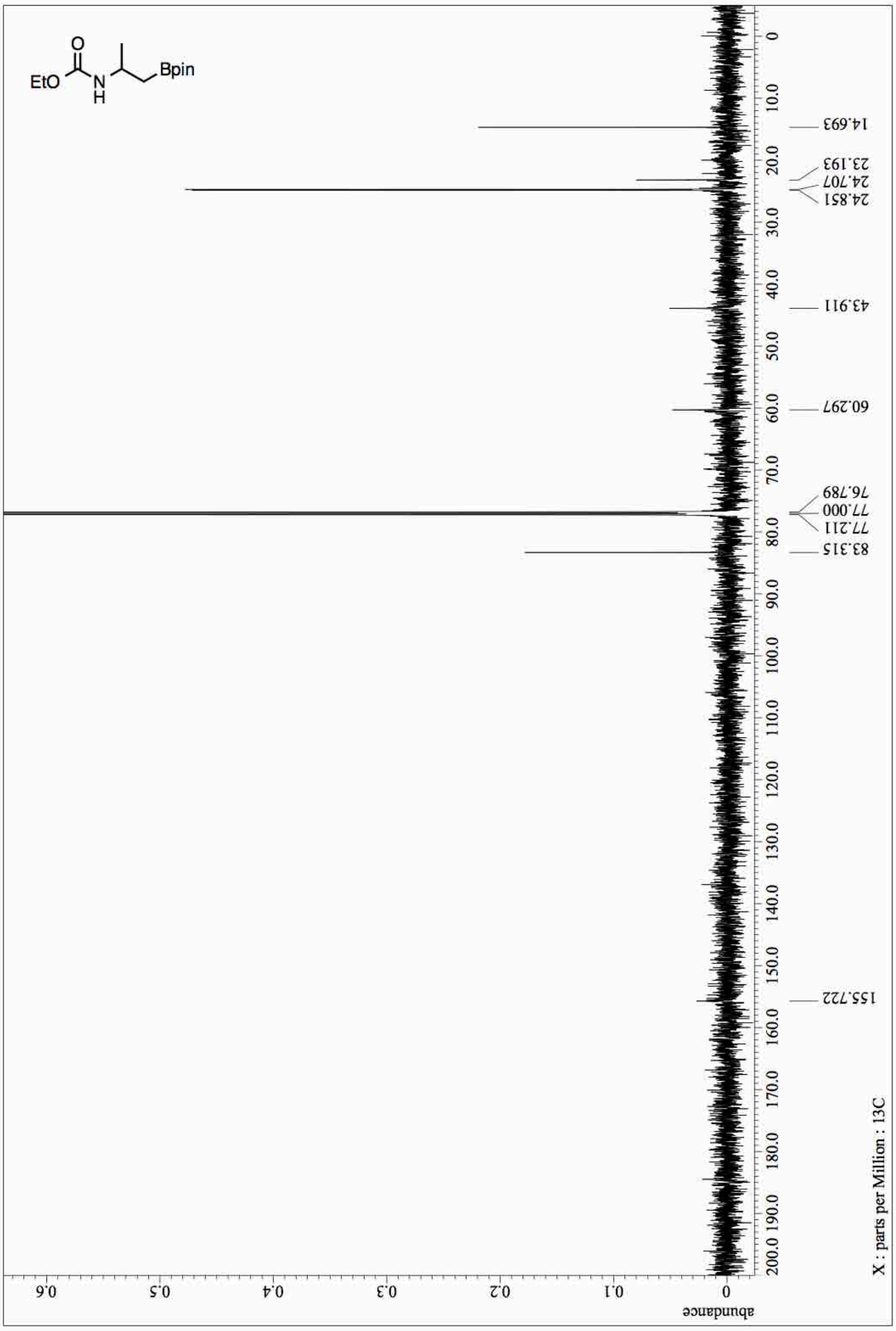
^{13}C NMR of **2f** (151 MHz, 60 ˚C, $CDCl_3$)



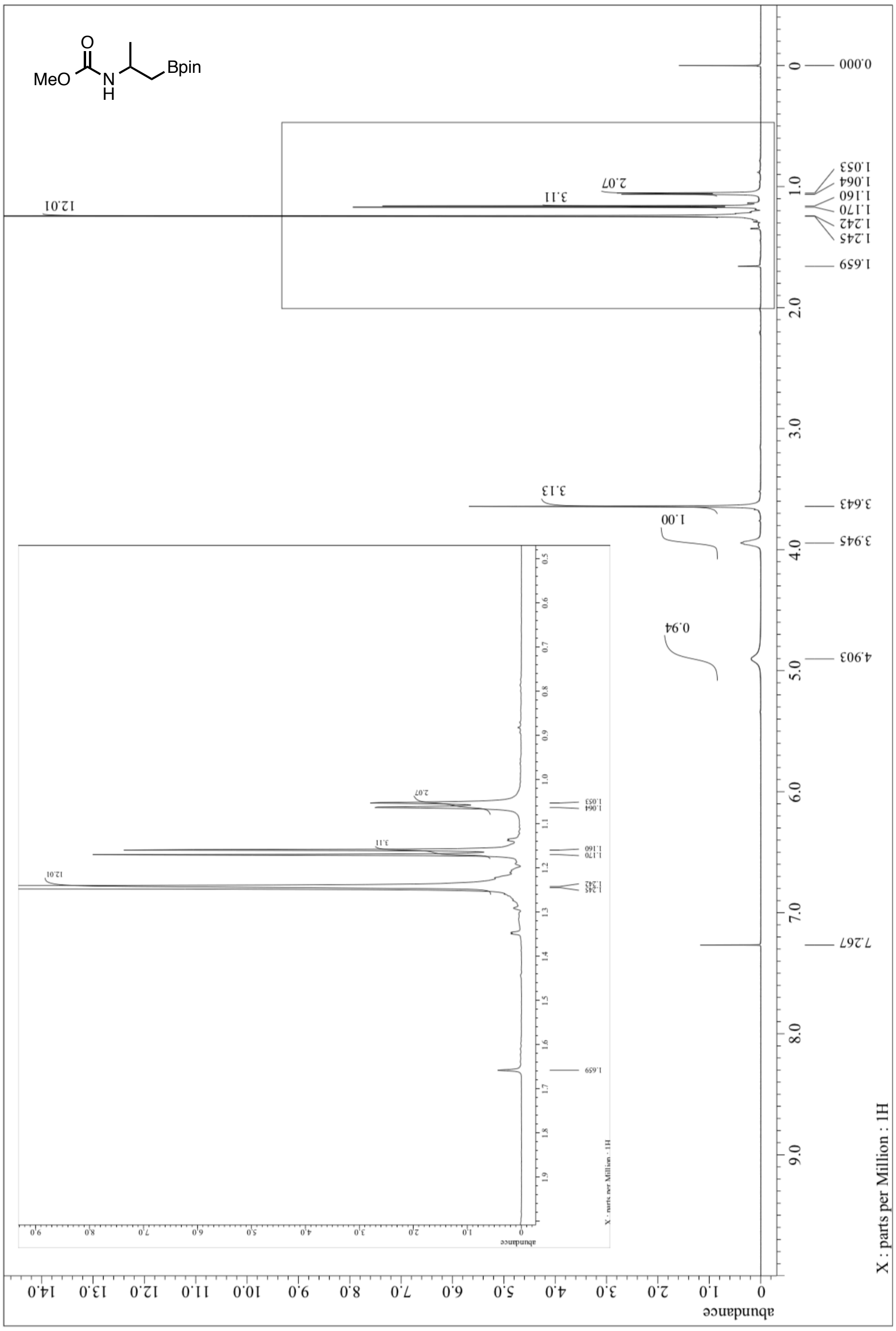
[1]H NMR of **2g** (600 MHz, 50 ˚C, $CDCl_3$)



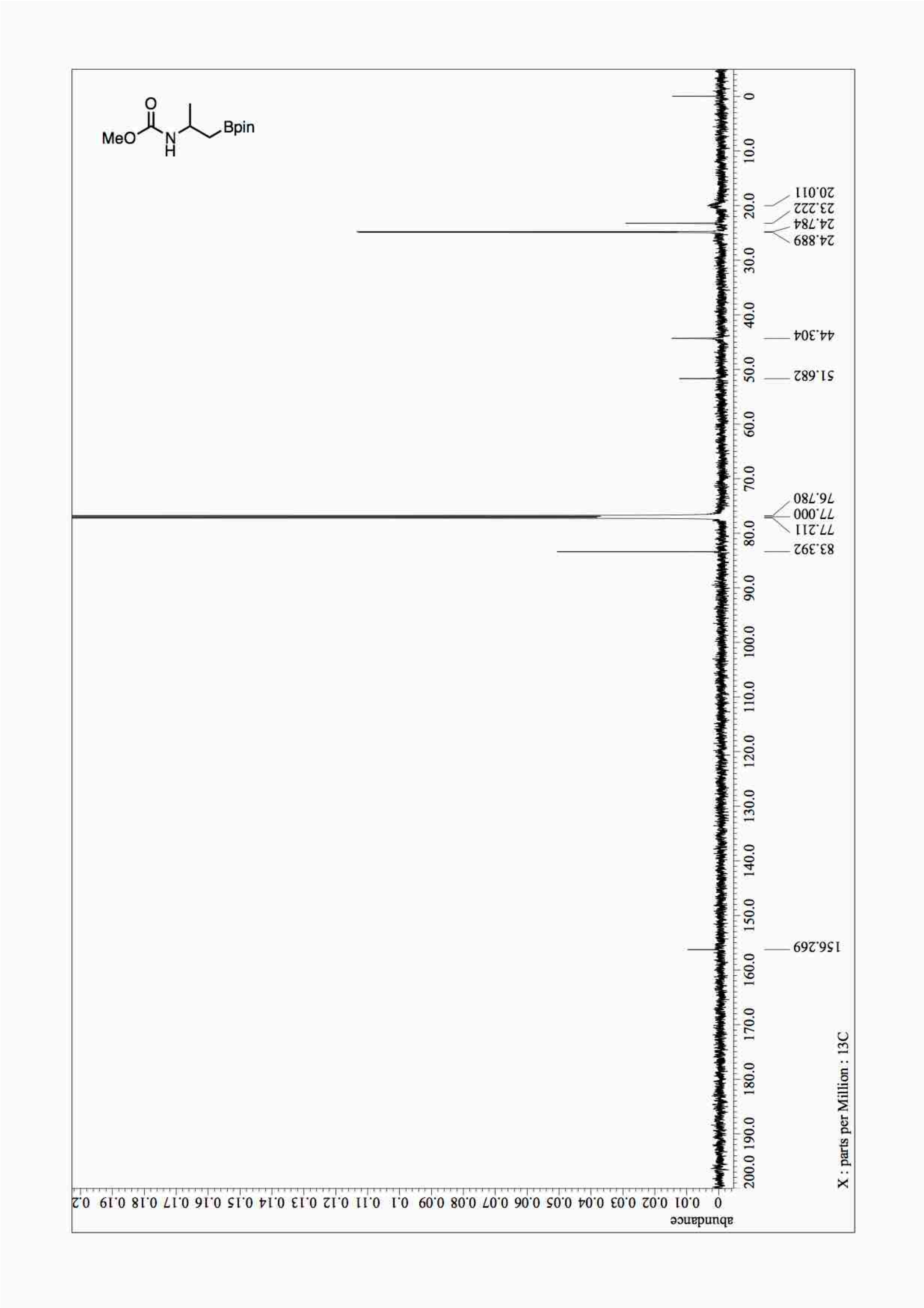
^{13}C NMR of **2g** (151 MHz, $CDCl_3$)



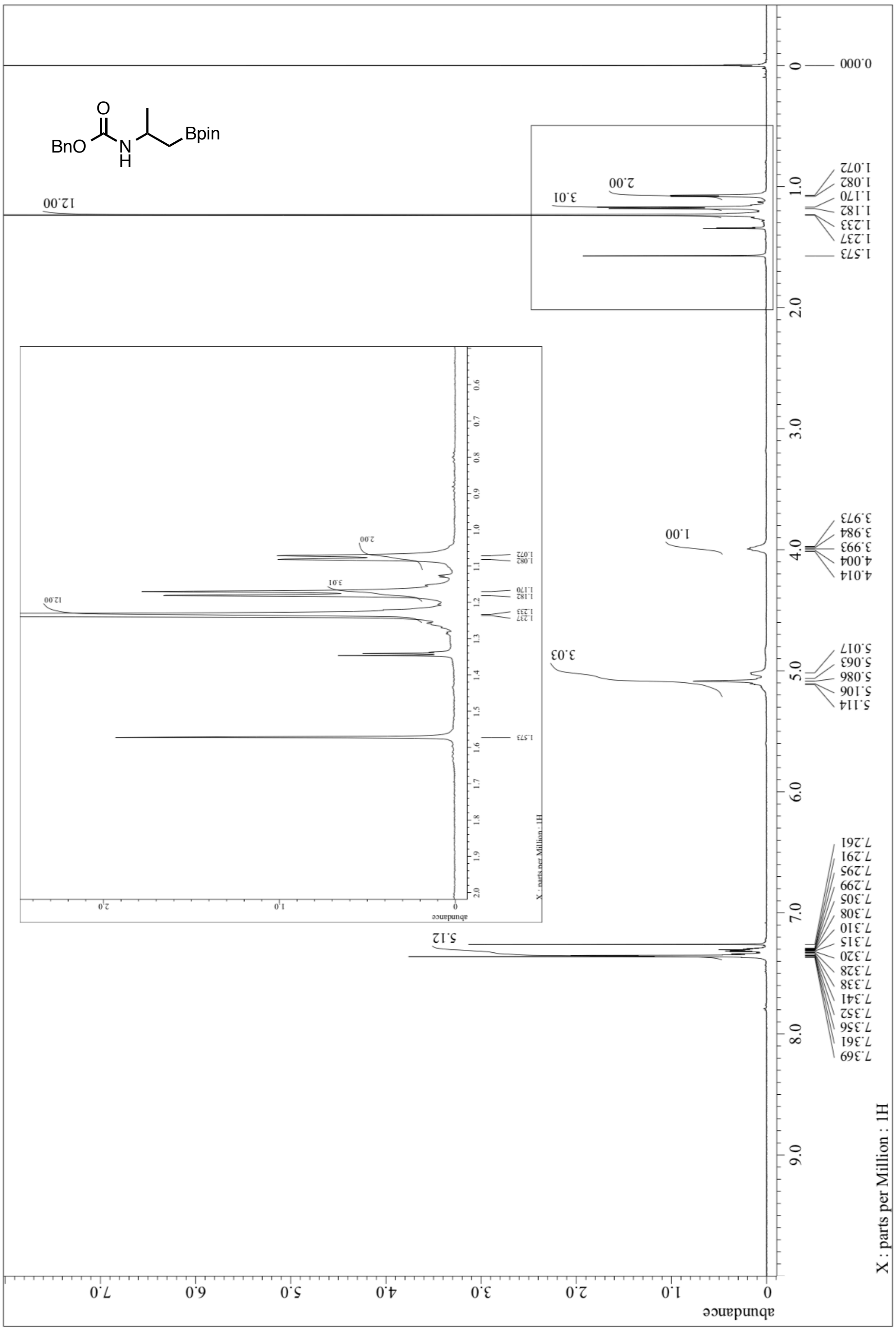
^{1}H NMR of **2h** (600 MHz, $CDCl_3$)



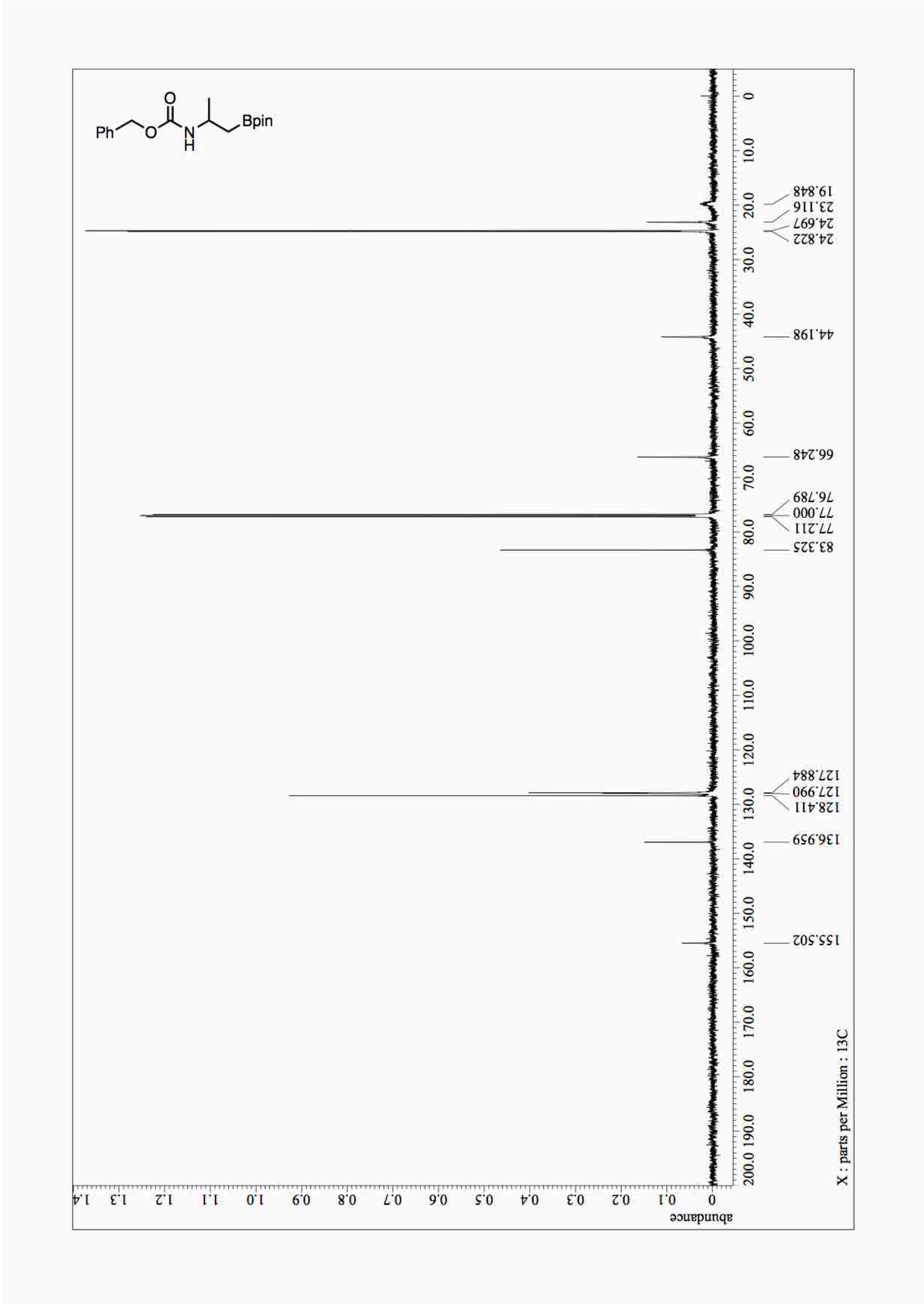
^{13}C NMR of **2h** (151 MHz, $CDCl_3$)



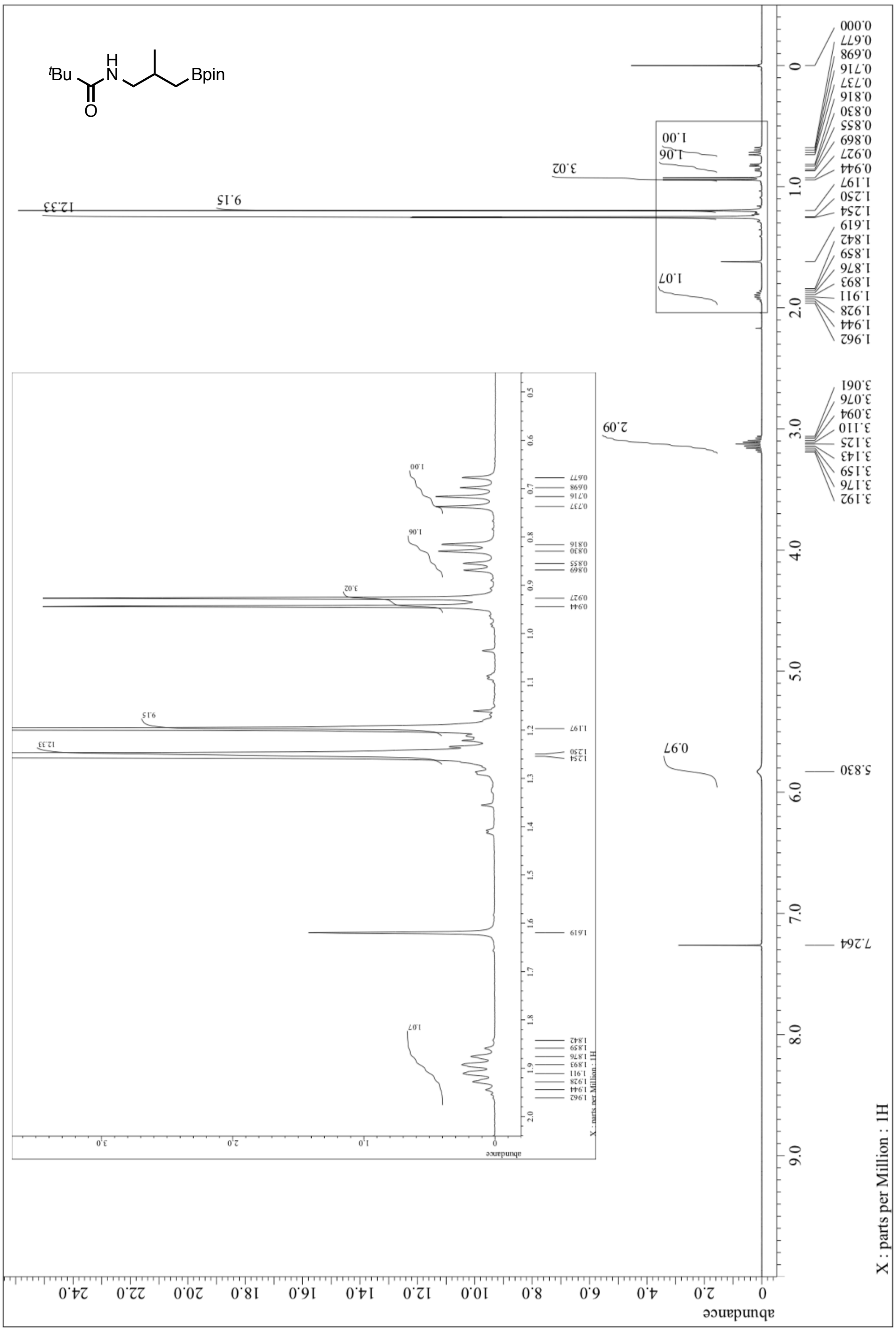
^{1}H NMR of **2i** (600 MHz, 60 ˚C, $CDCl_3$)



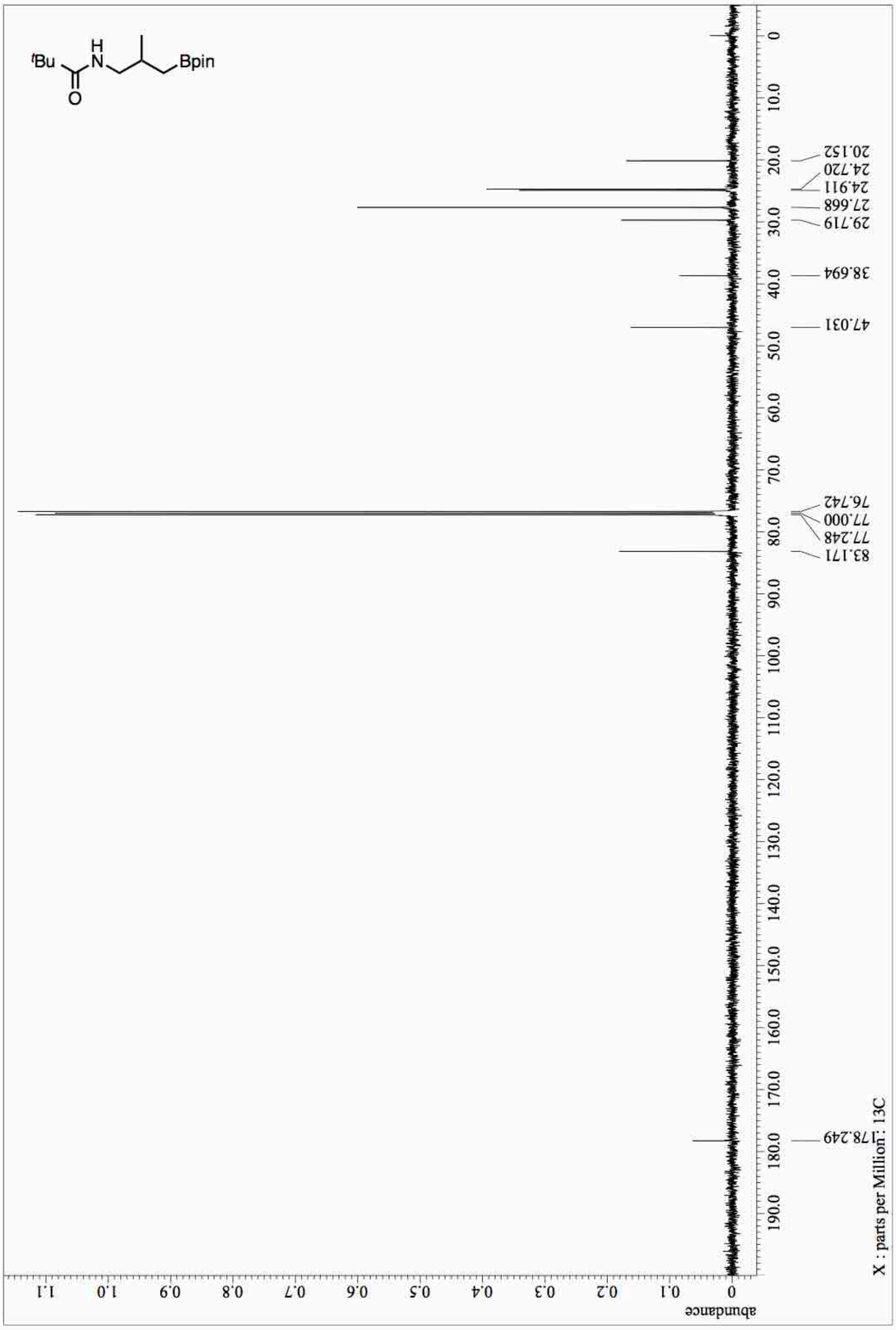
^{13}C NMR of **2i** (151 MHz, 60 ˚C, $CDCl_3$)



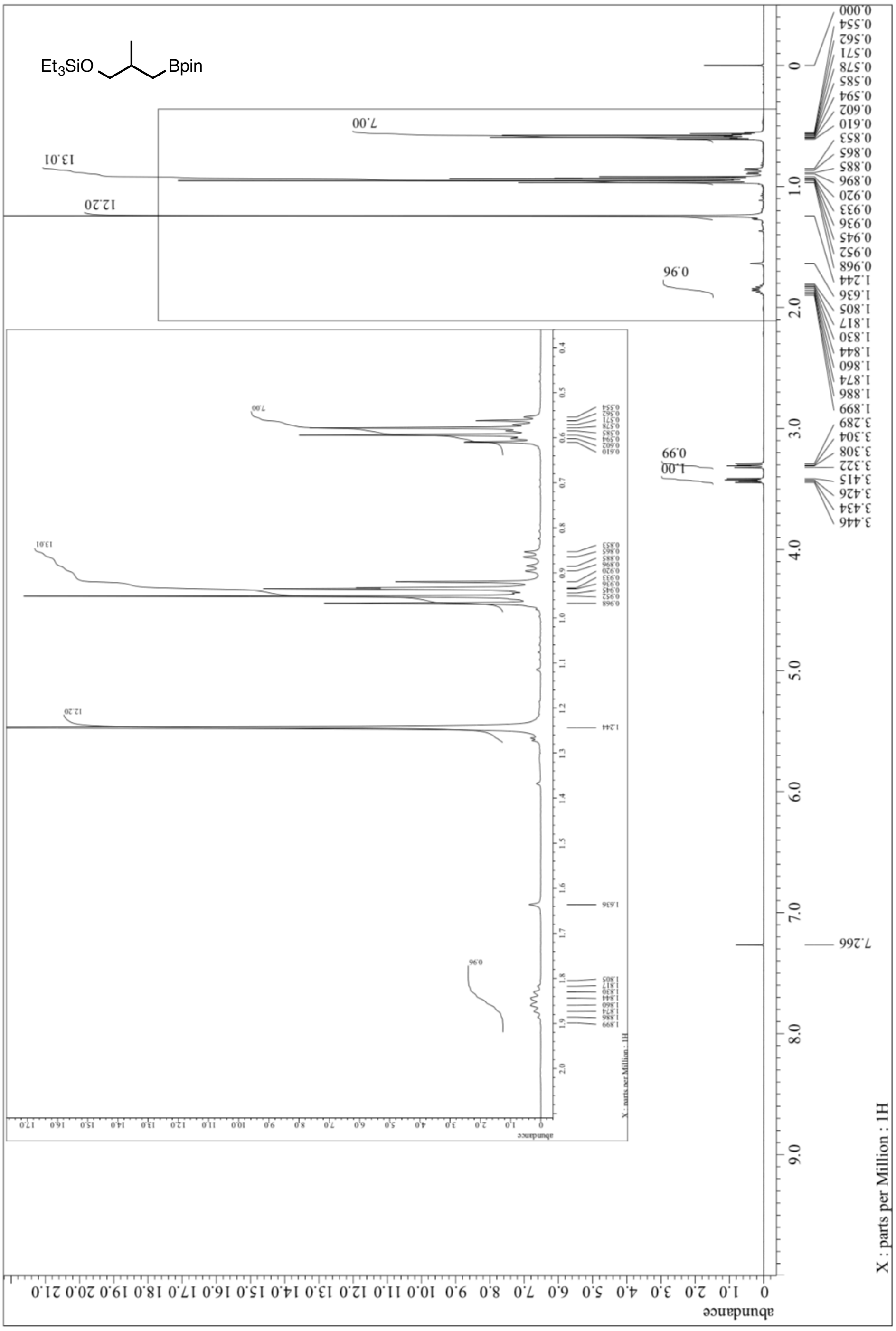
^{1}H NMR of **2j** (400 MHz, $CDCl_3$)



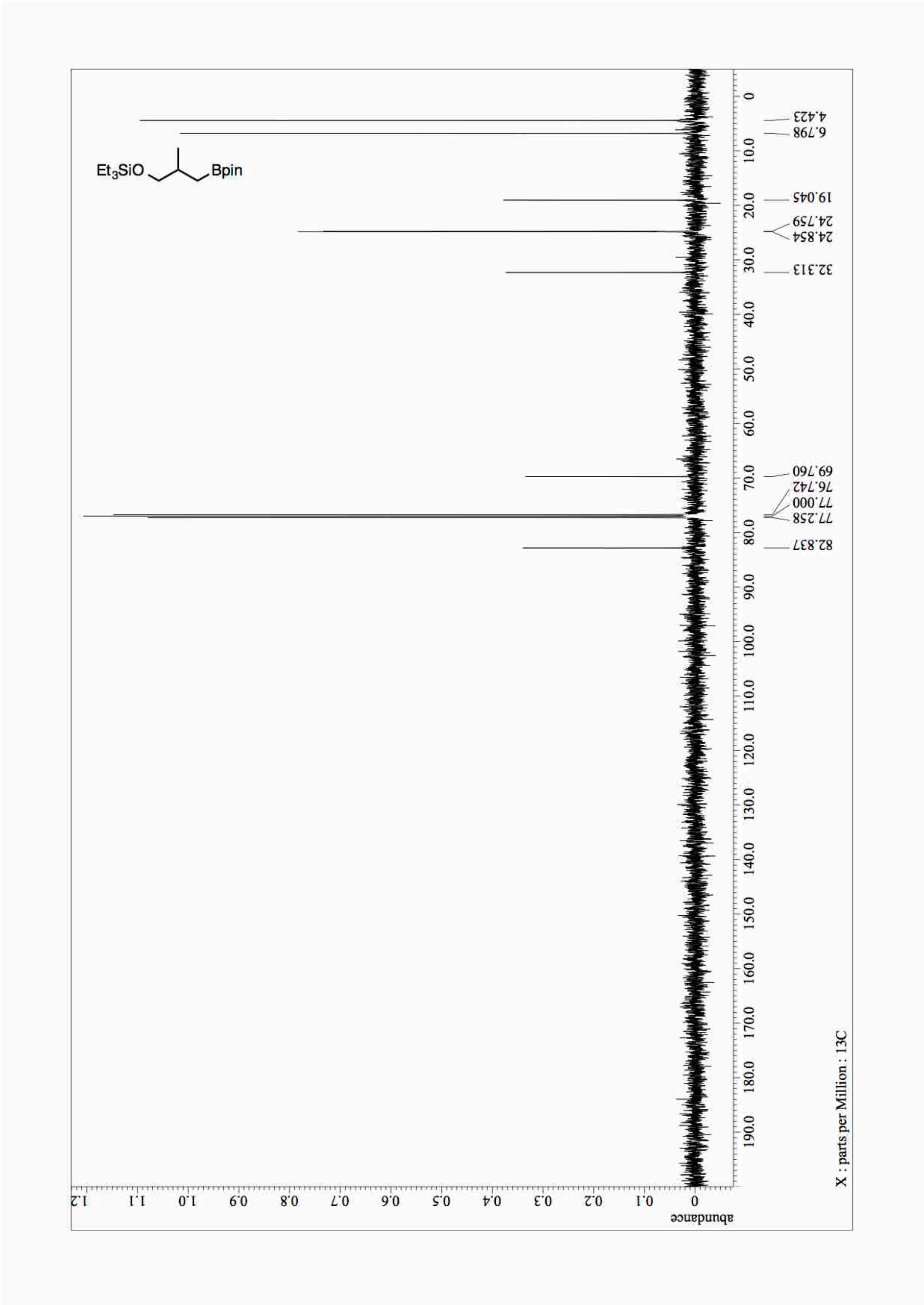
^{13}C NMR of **2j** (126 MHz, $CDCl_3$)



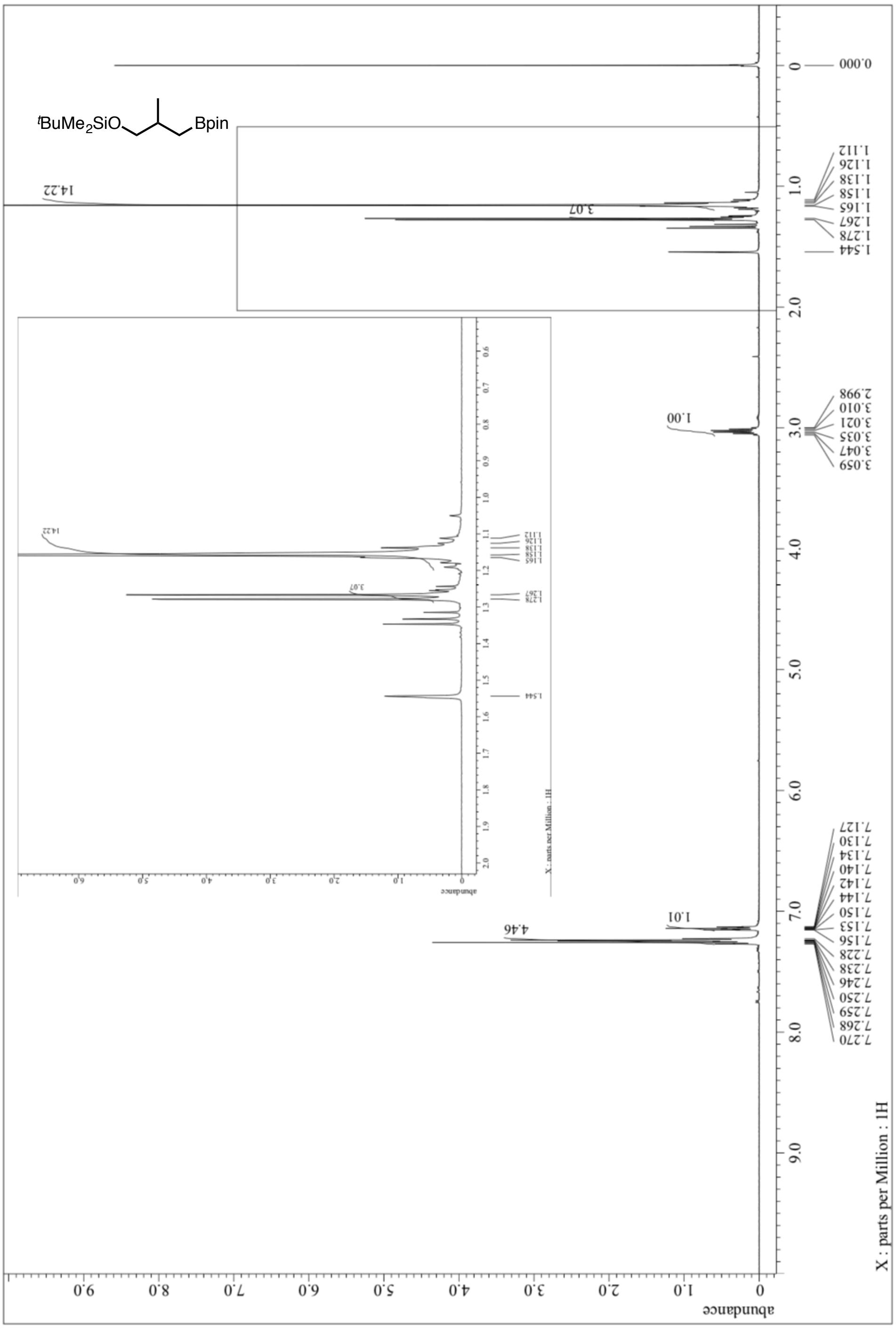
^{1}H NMR of **2k** (500 MHz, $CDCl_3$)



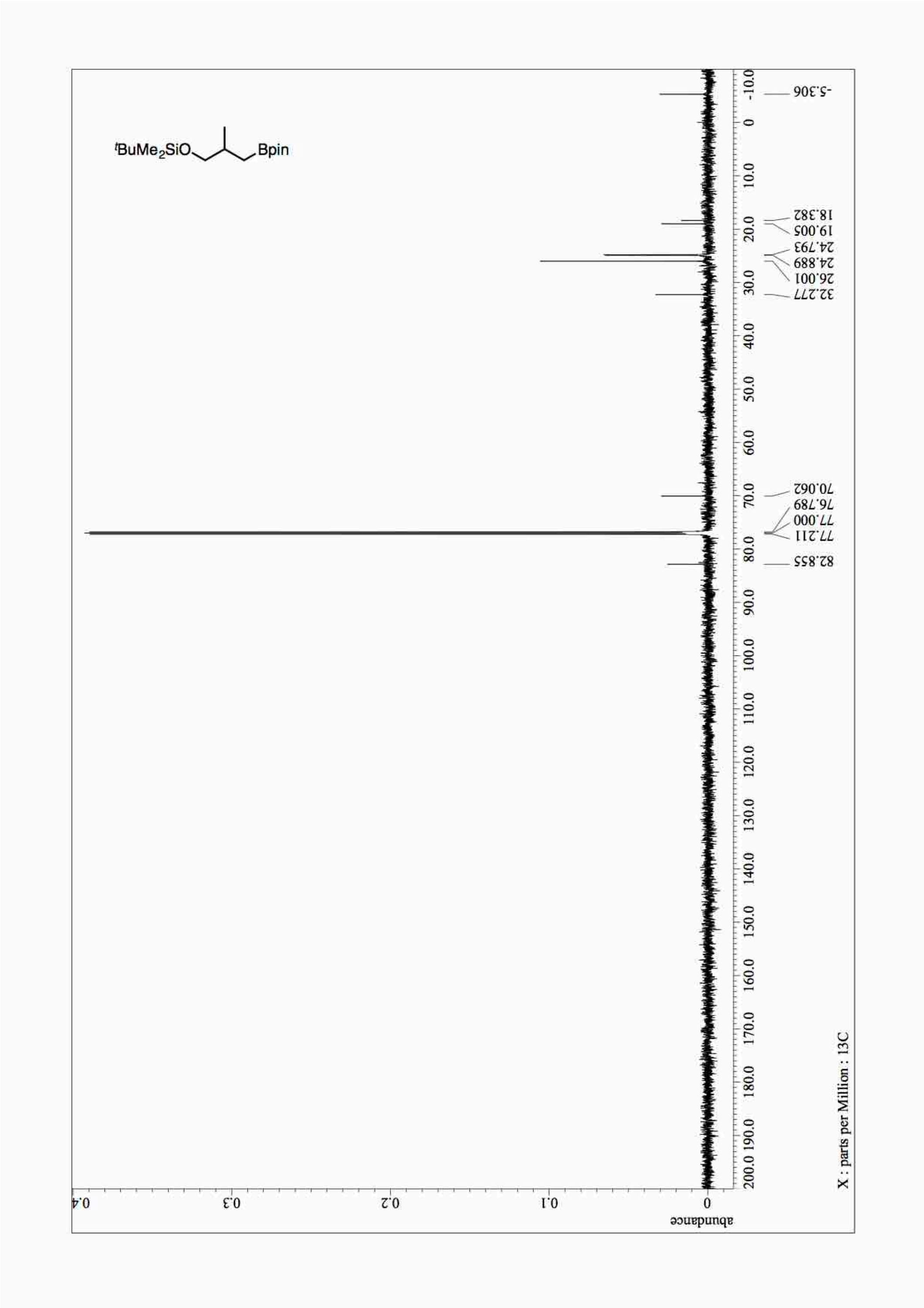
^{13}C NMR of **2k** (126 MHz, $CDCl_3$)



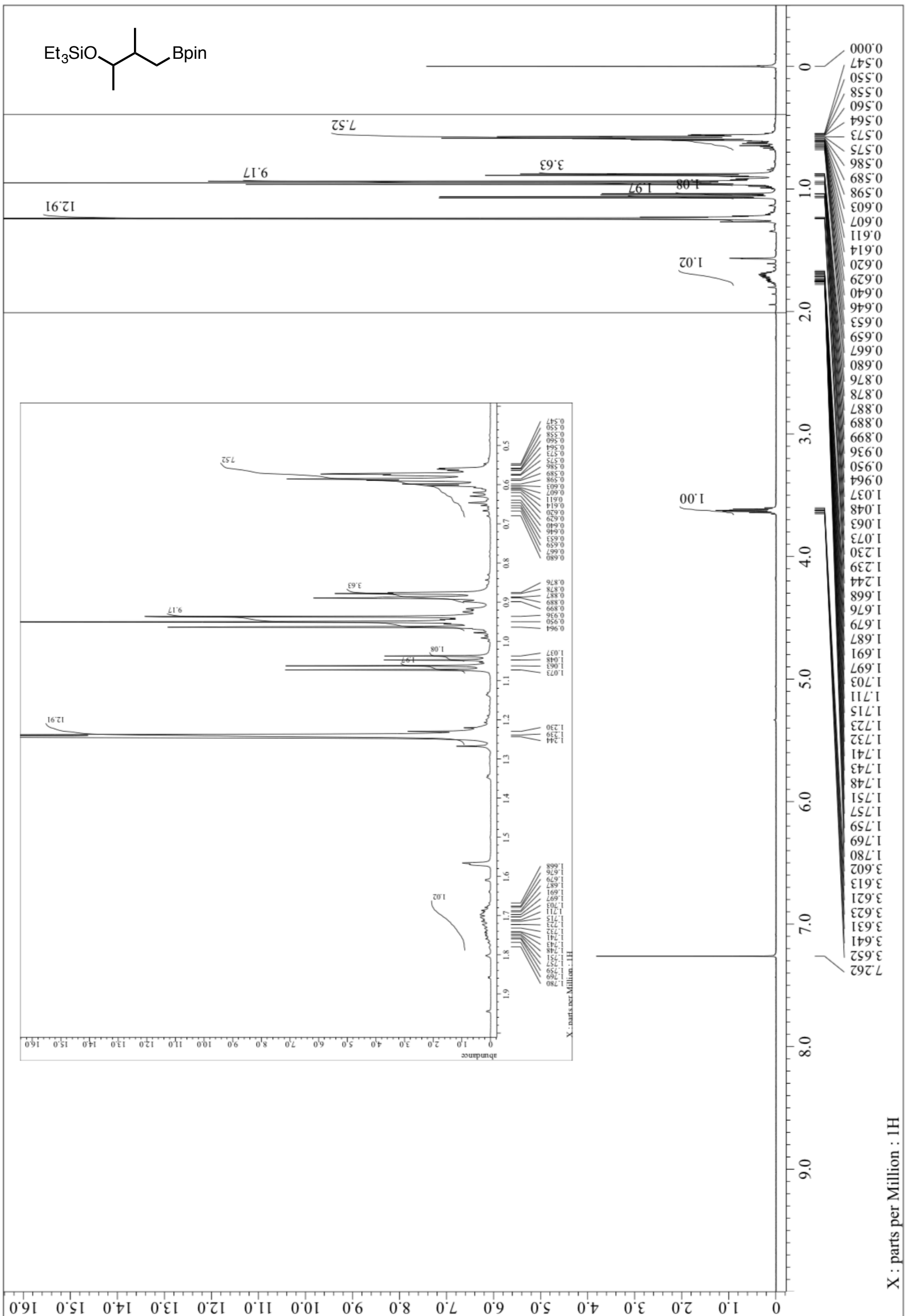
^{1}H NMR of **2l** (600 MHz, $CDCl_3$)



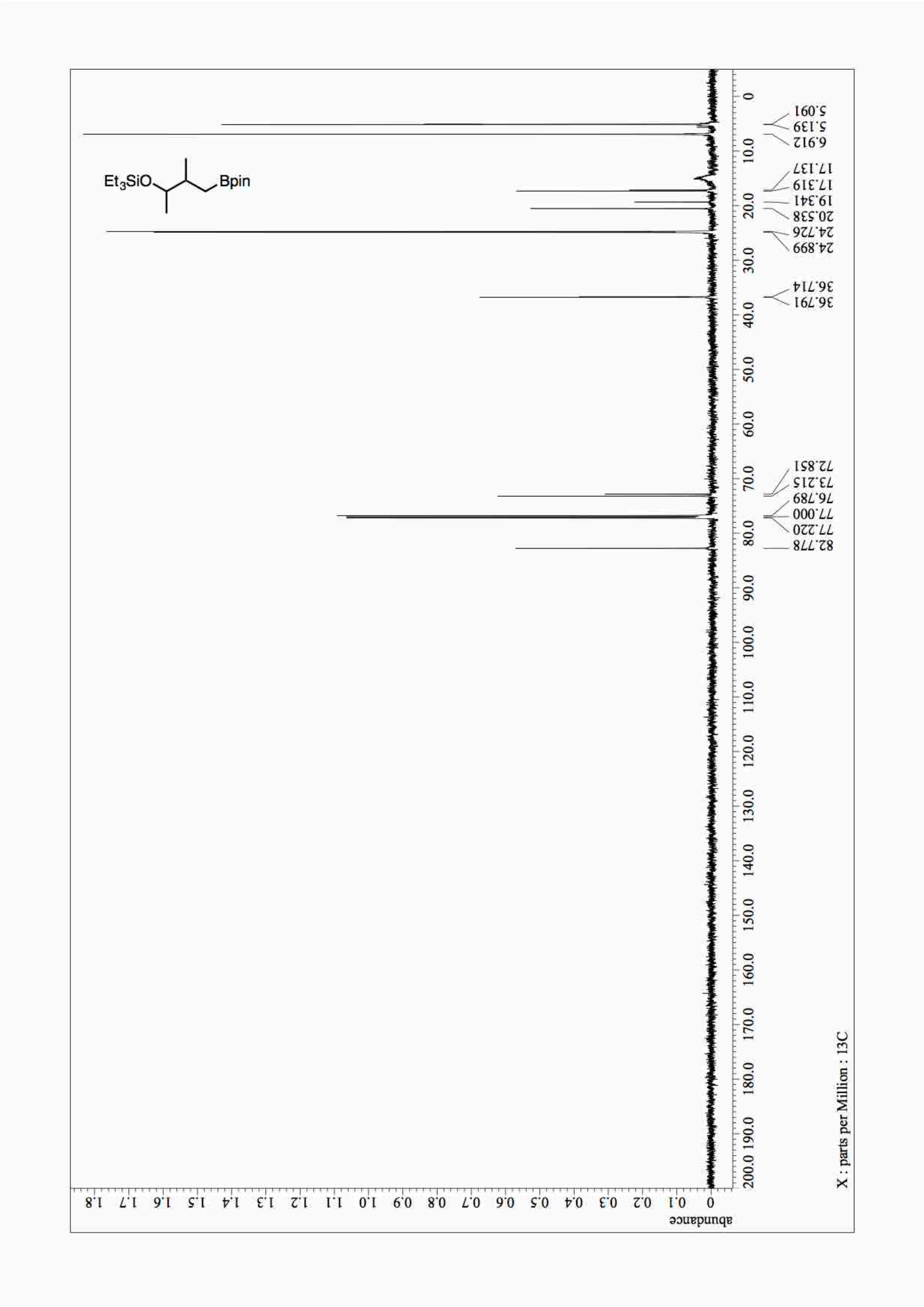
^{13}C NMR of **2l** (151 MHz, $CDCl_3$)



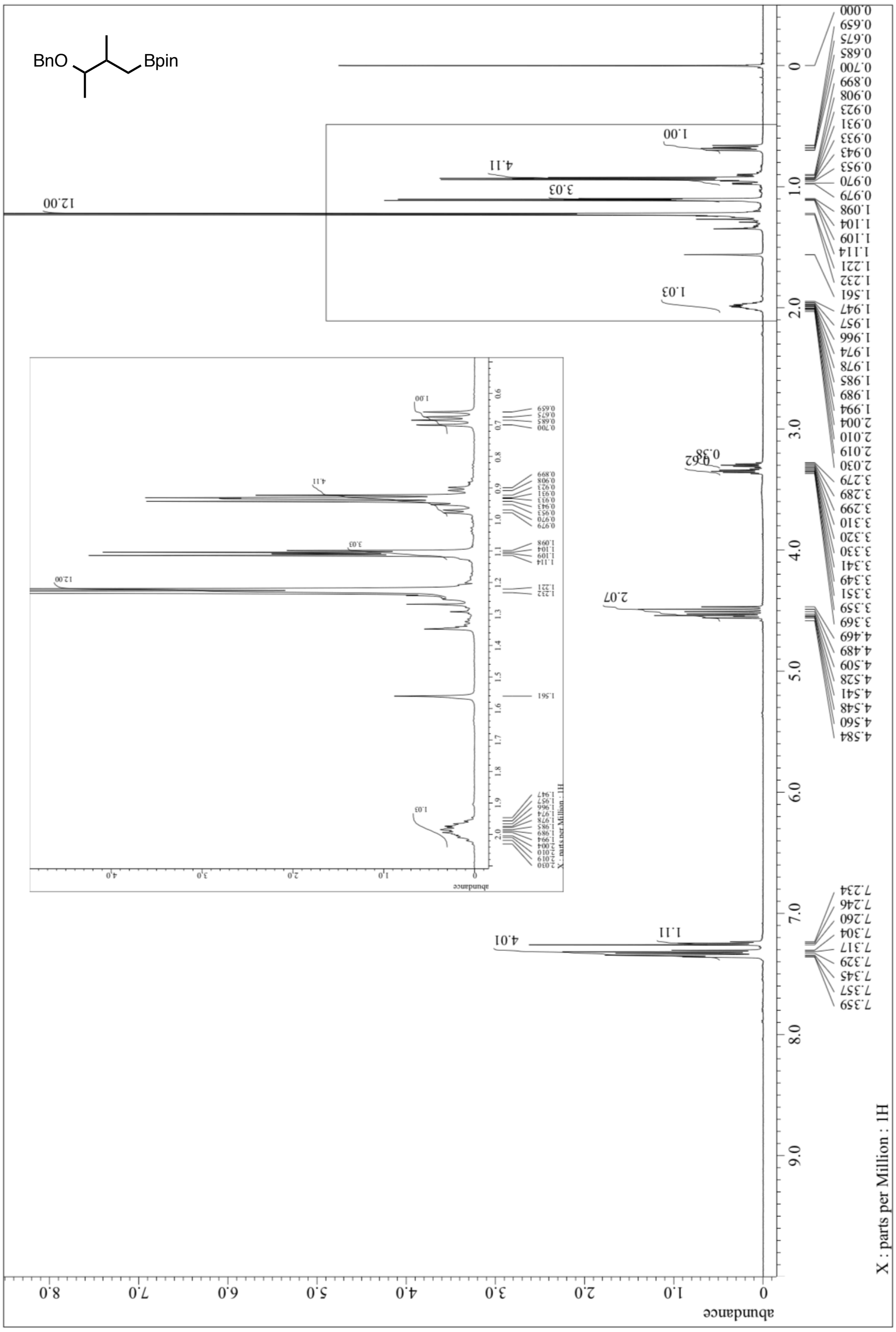
^{1}H NMR of **2m** (600 MHz, CDCl$_3$)



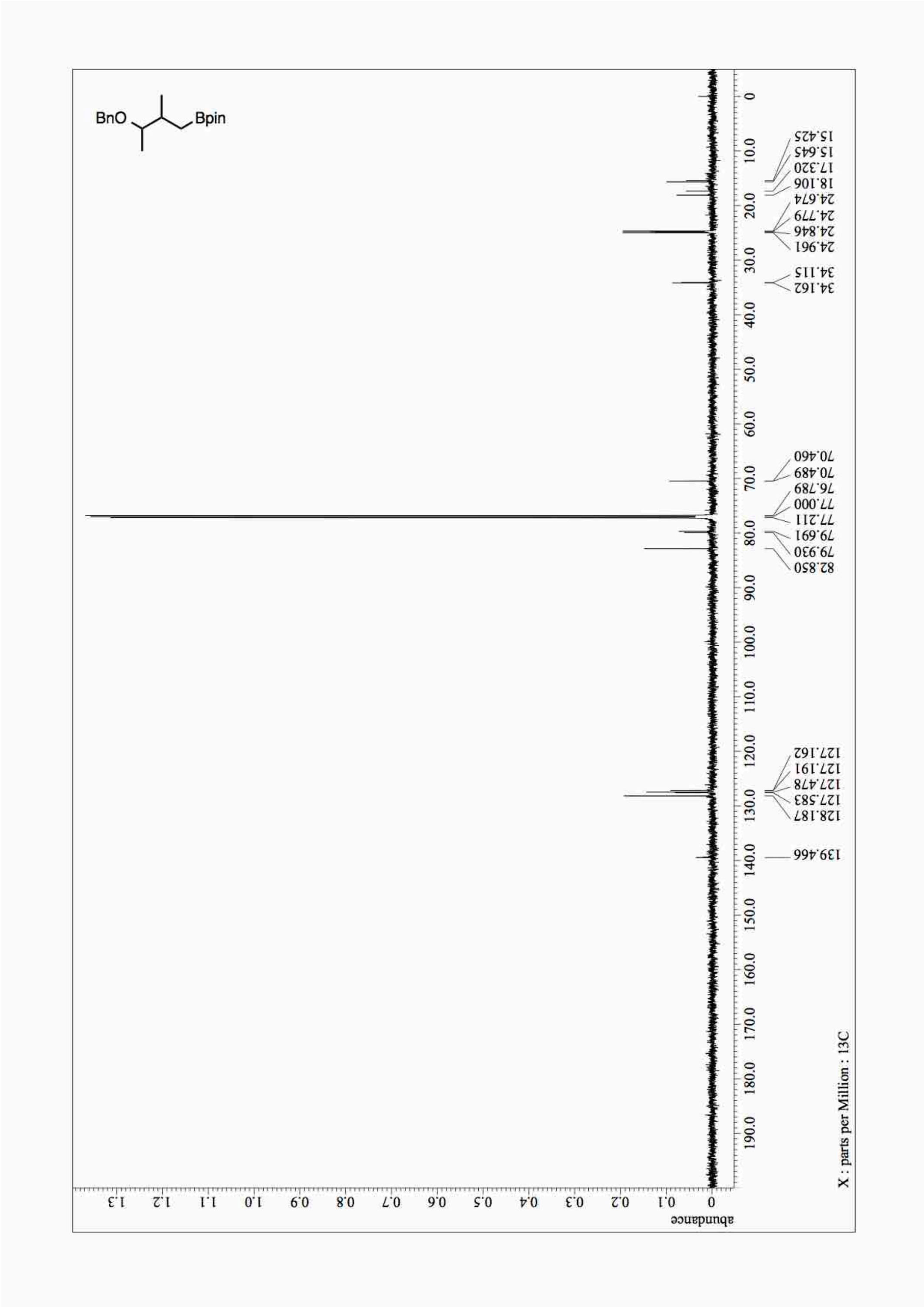
^{13}C NMR of **2m** (151 MHz, $CDCl_3$)



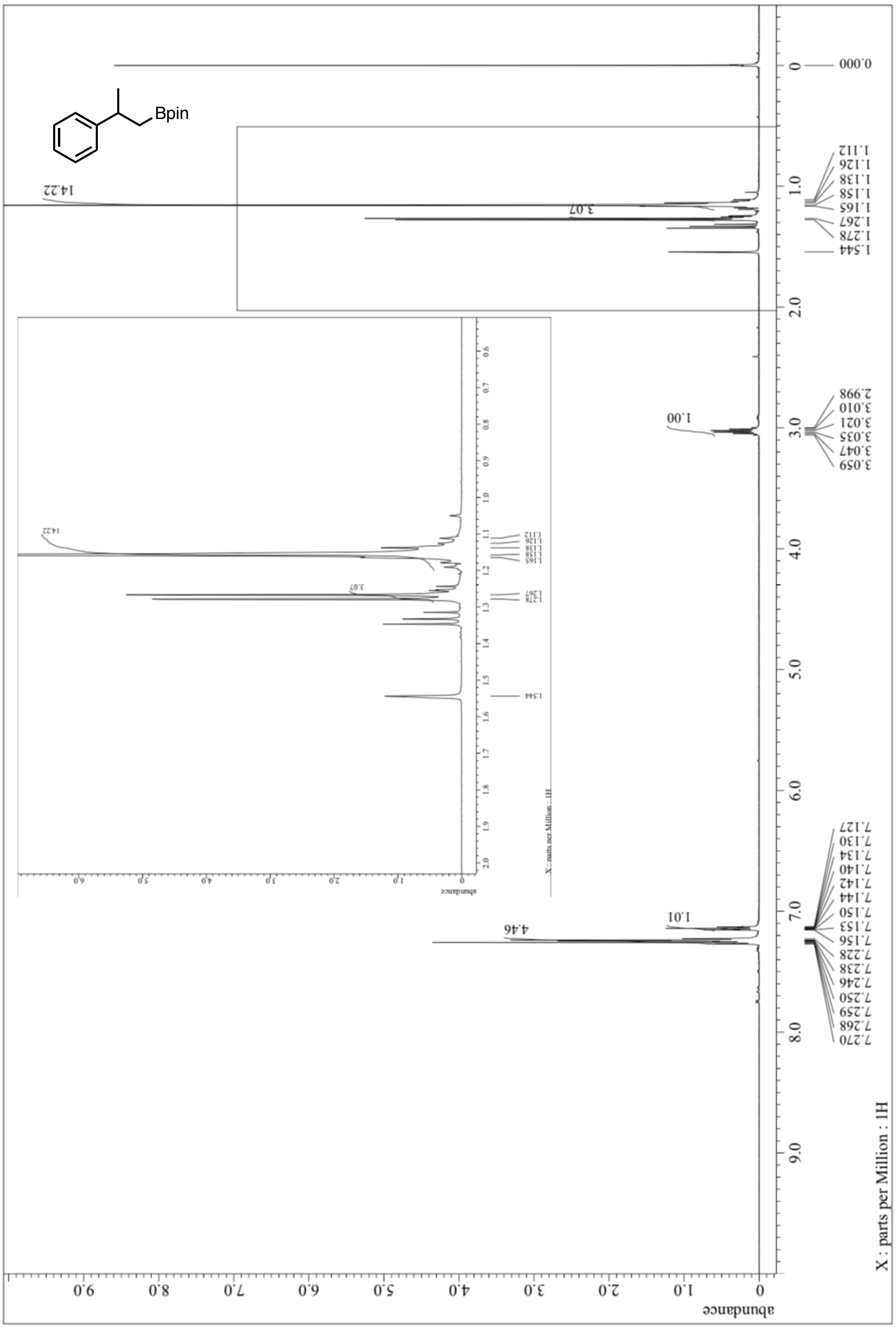
[1]H NMR of **2n** (600 MHz, $CDCl_3$)



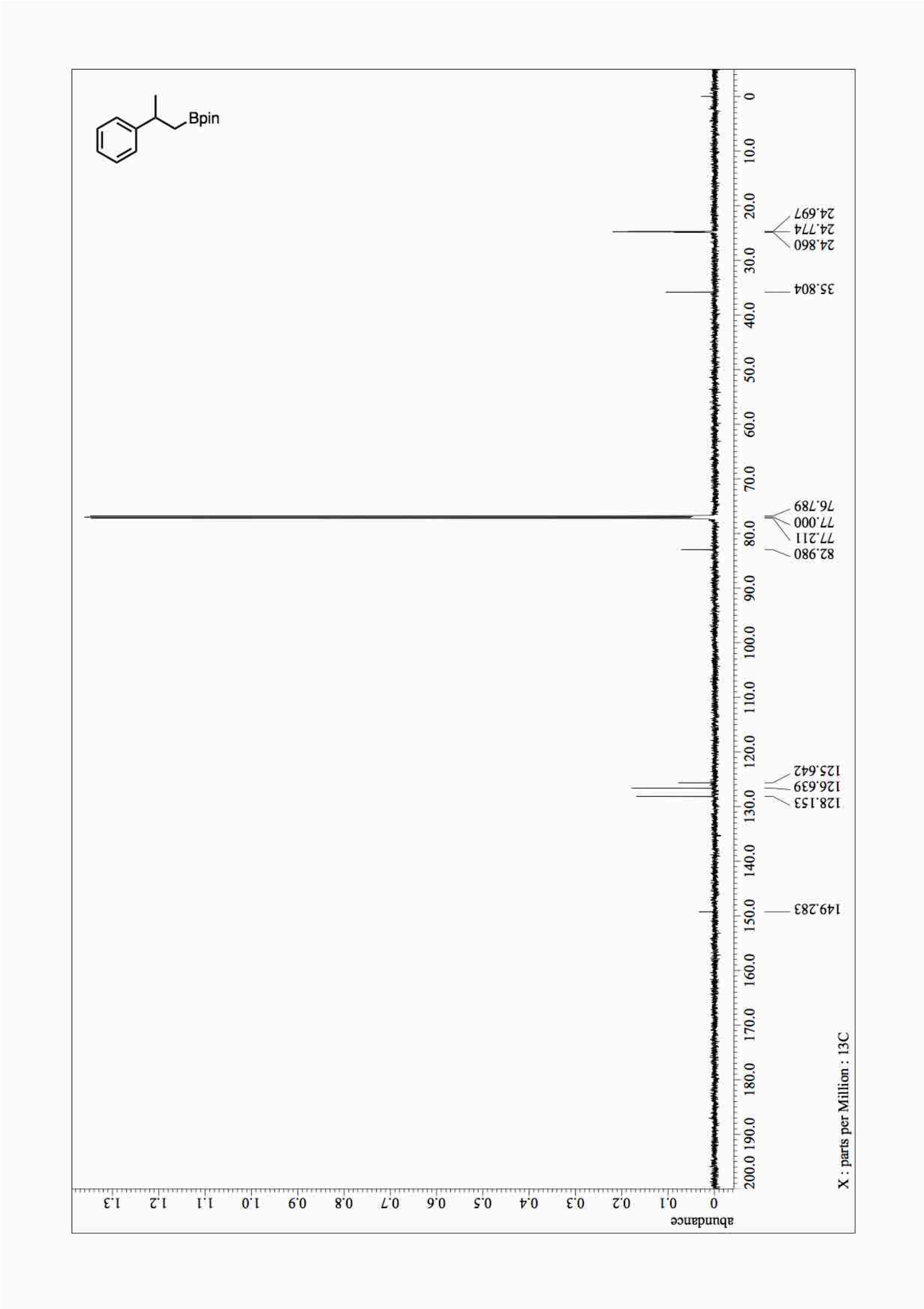
^{13}C NMR of **2n** (151 MHz, $CDCl_3$)



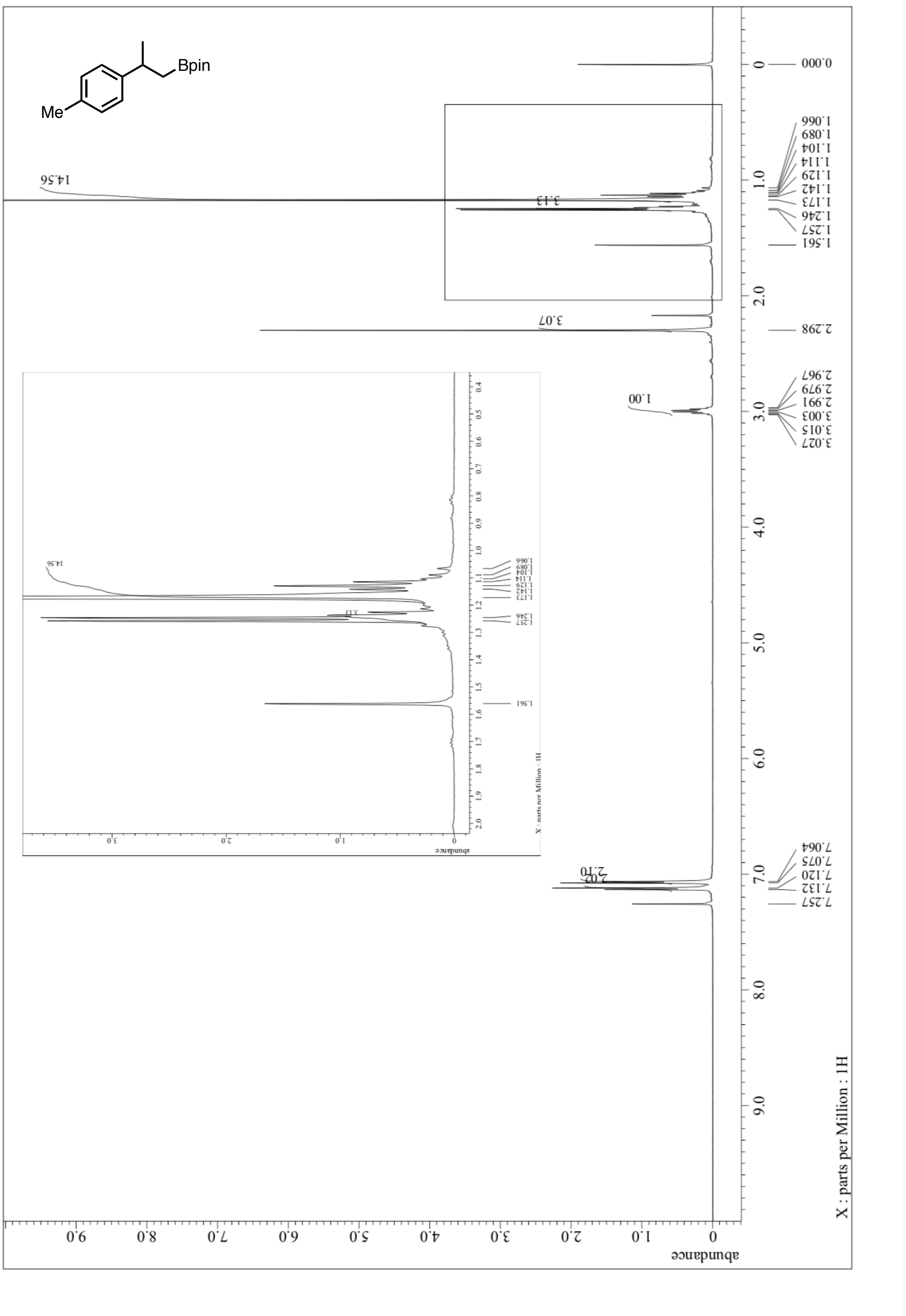
[1]H NMR of **2o** (600 MHz, $CDCl_3$)



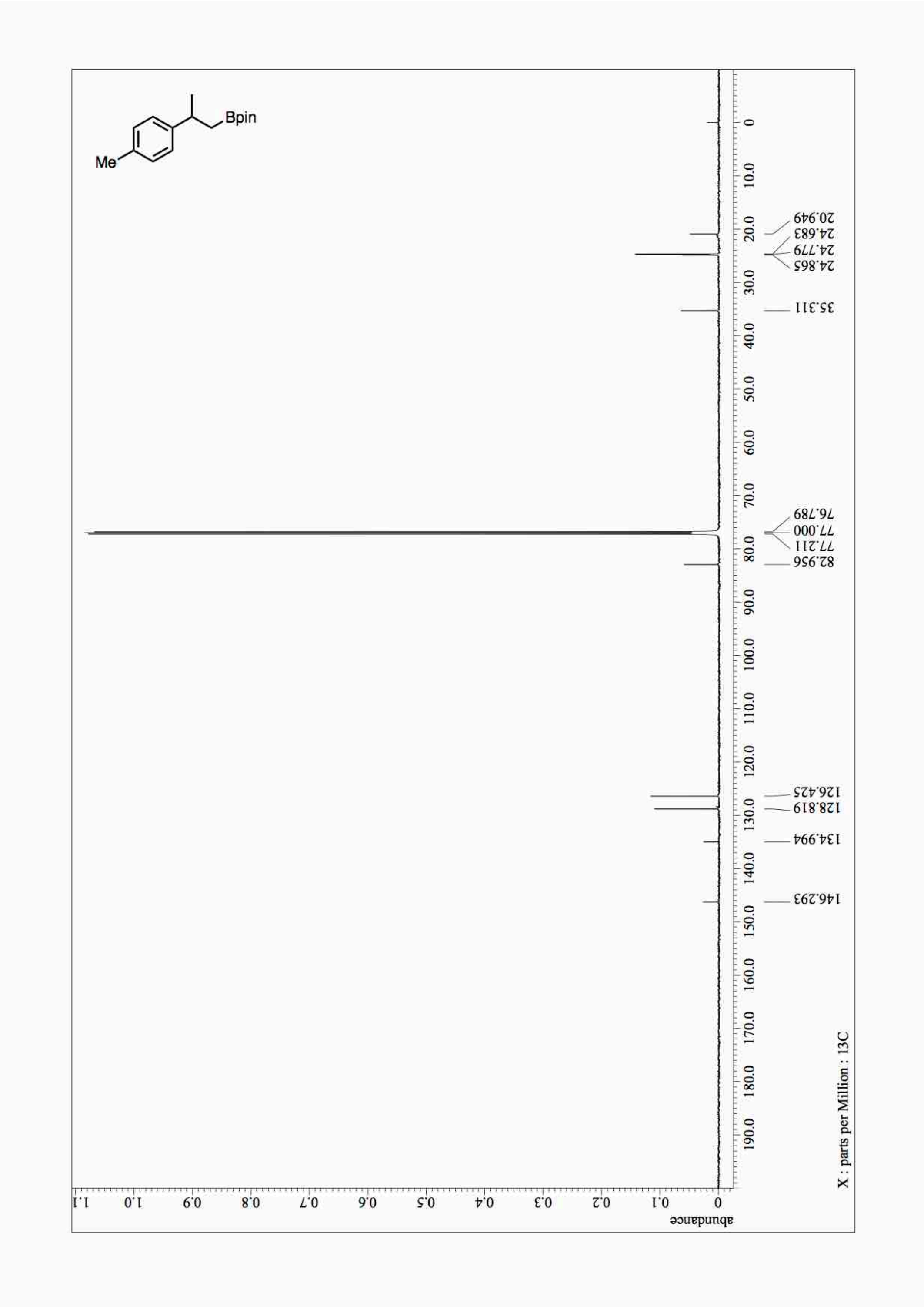
^{13}C NMR of **2o** (151 MHz, $CDCl_3$)



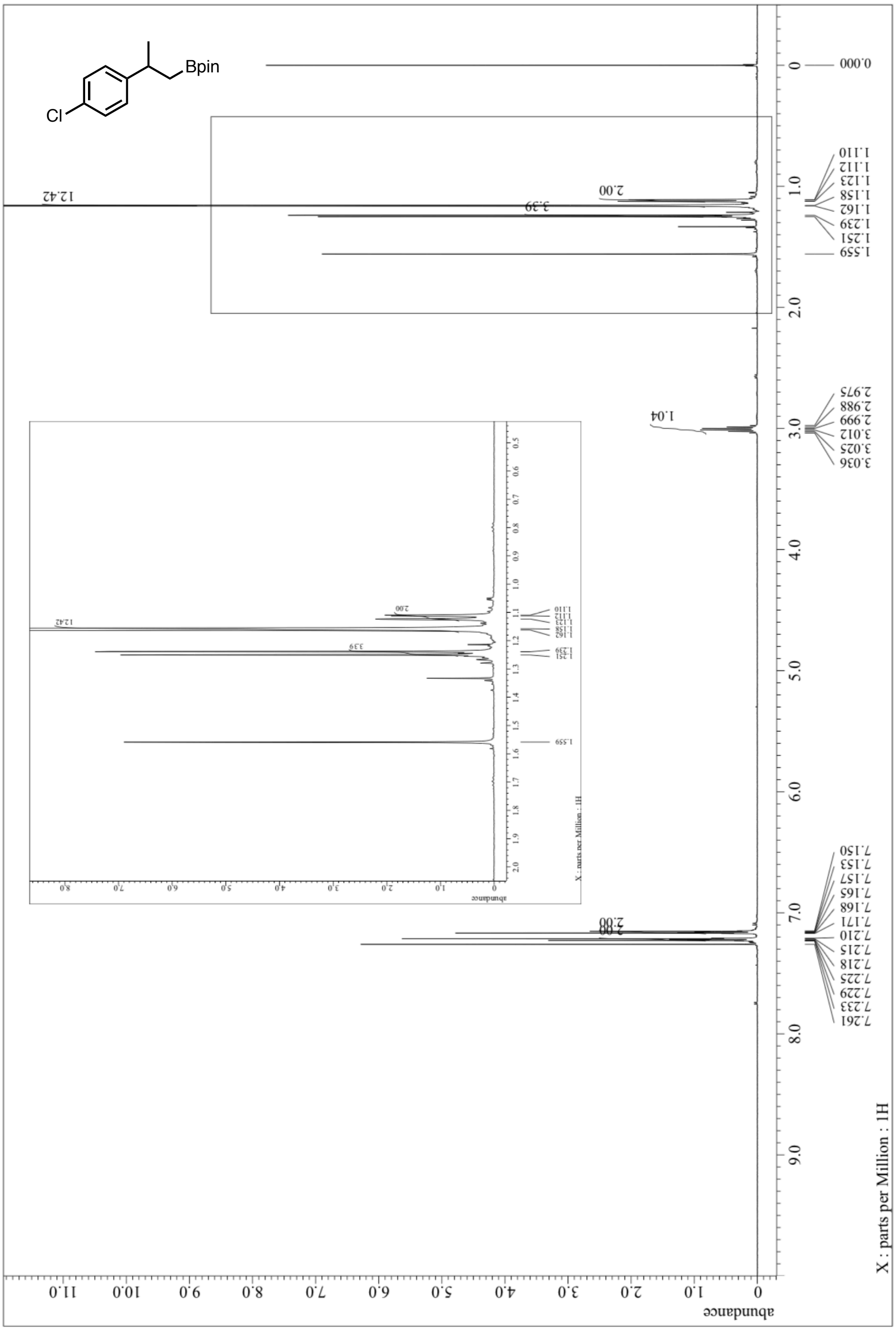
^{1}H NMR of **2p** (600 MHz, $CDCl_3$)



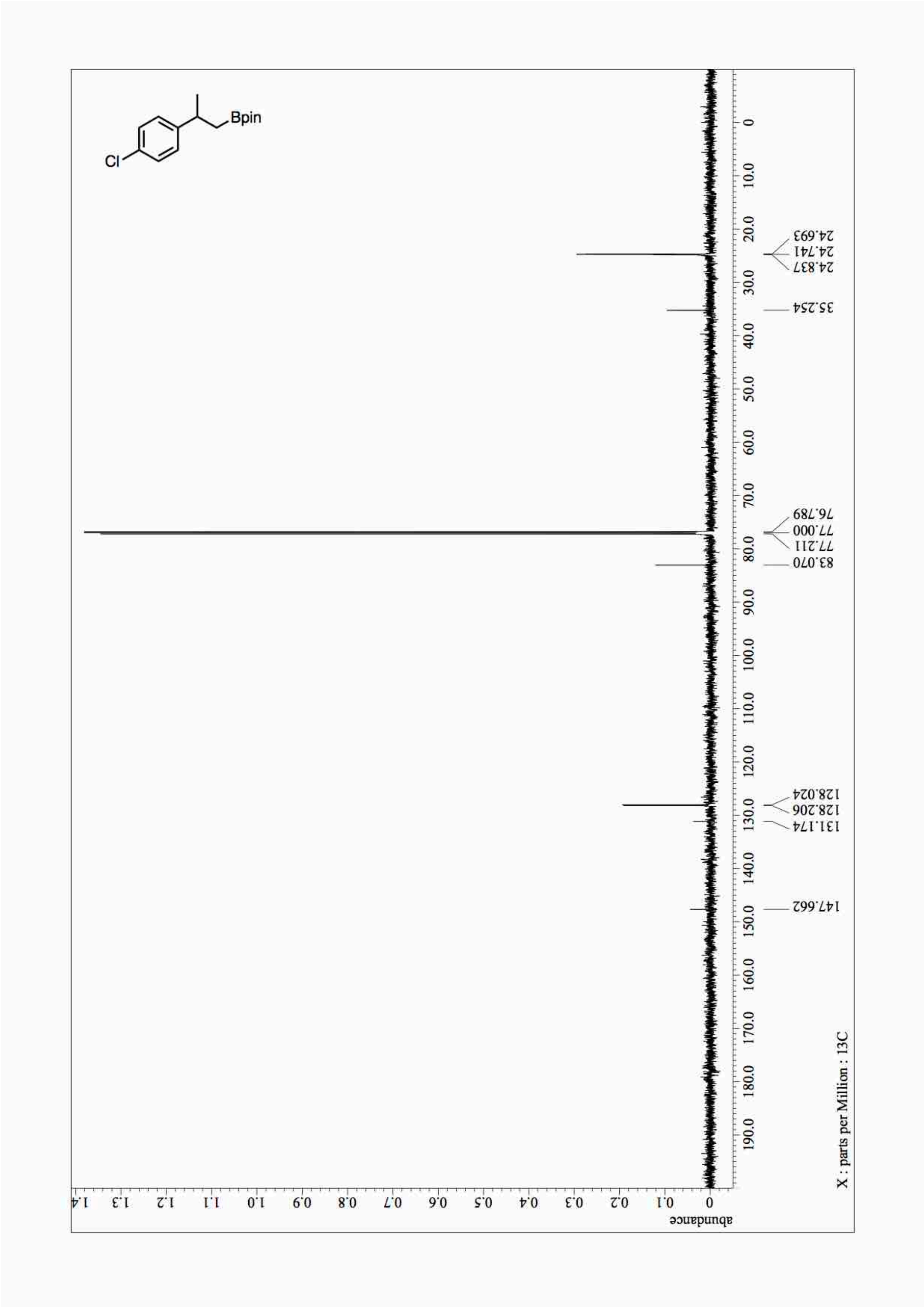
^{13}C NMR of **2p** (151 MHz, $CDCl_3$)



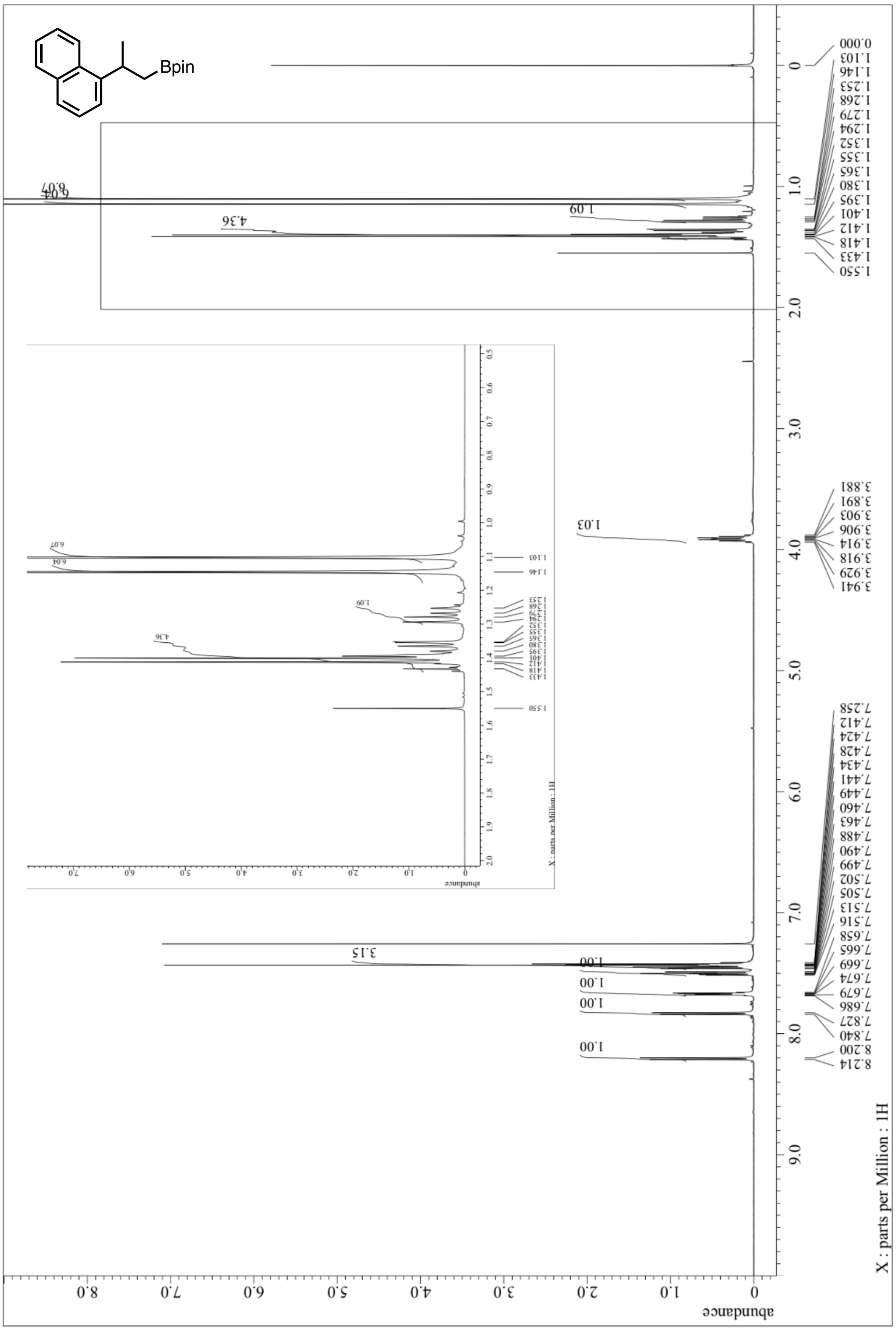
^{1}H NMR of **2q** (600 MHz, $CDCl_3$)



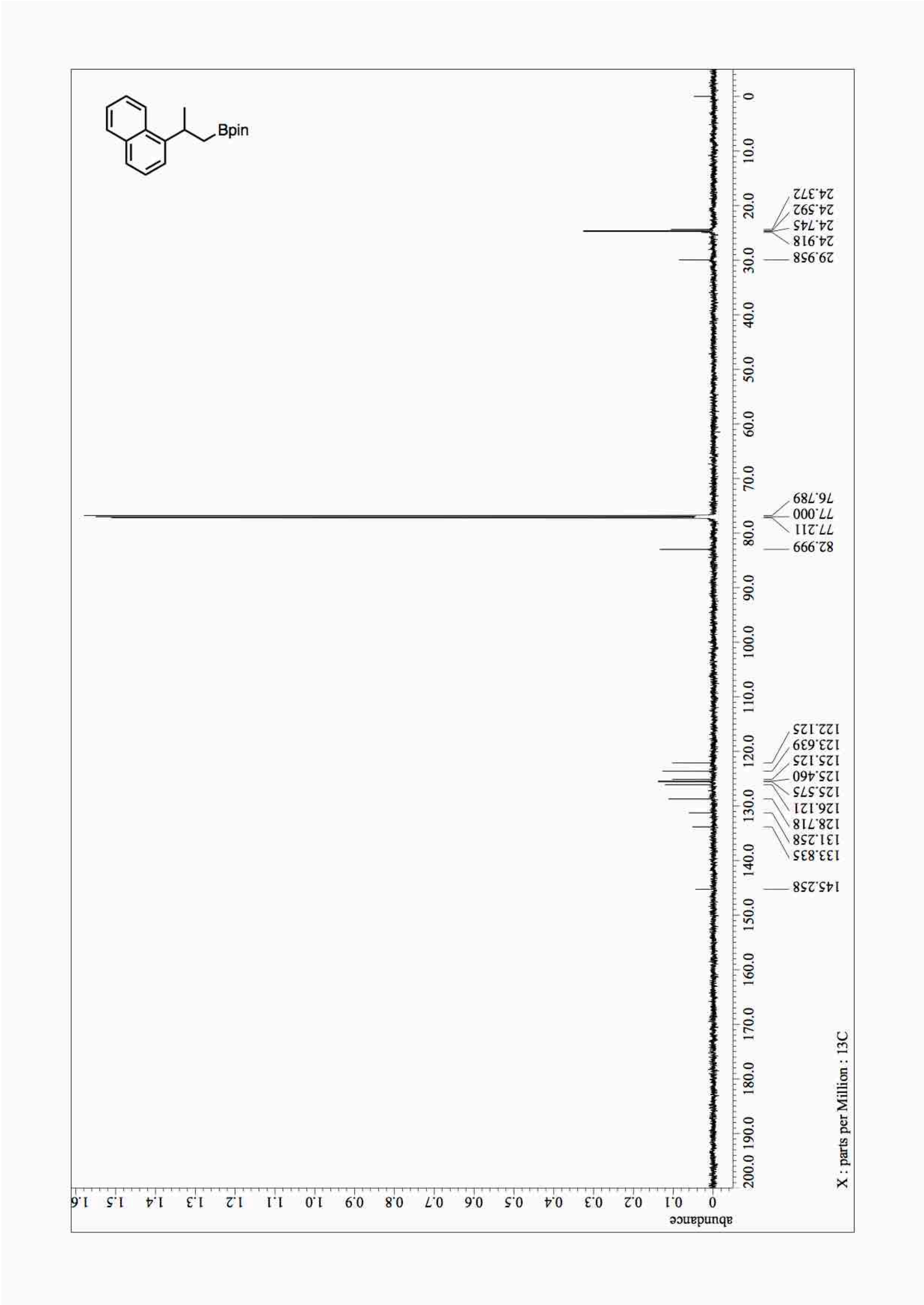
^{13}C NMR of **2q** (151 MHz, $CDCl_3$)



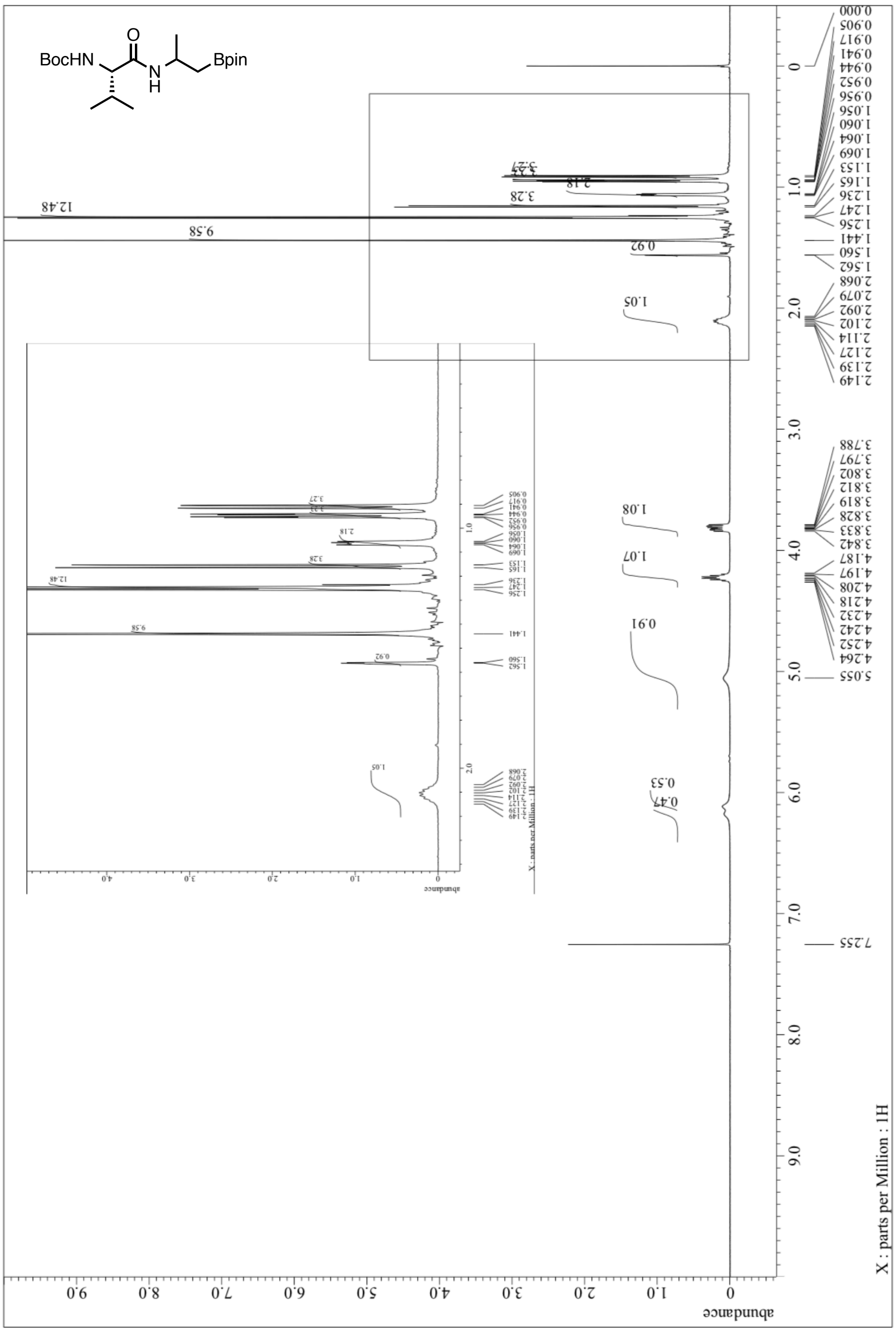
[1]H NMR of **2r** (600 MHz, $CDCl_3$)



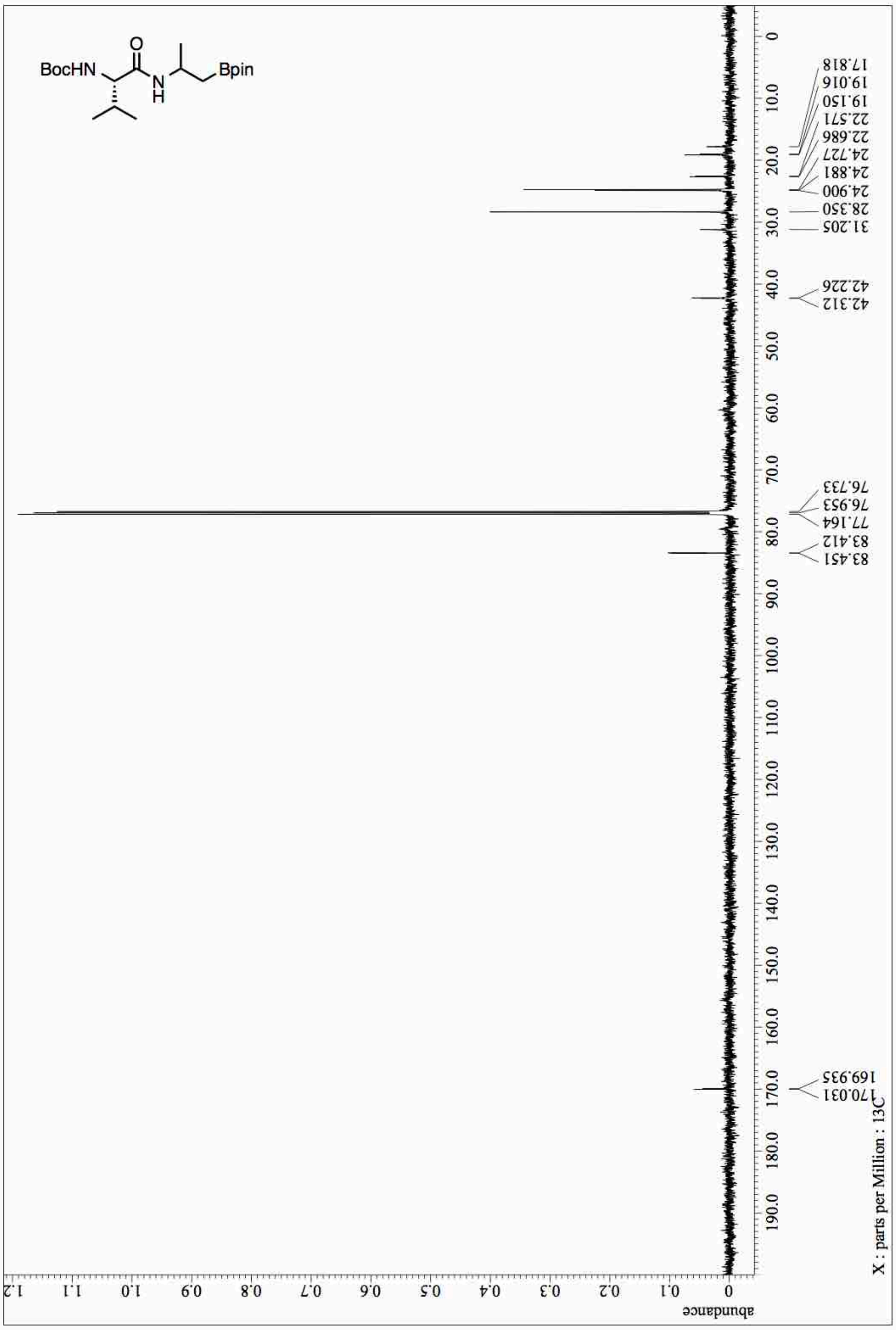
^{13}C NMR of **2r** (151 MHz, $CDCl_3$)



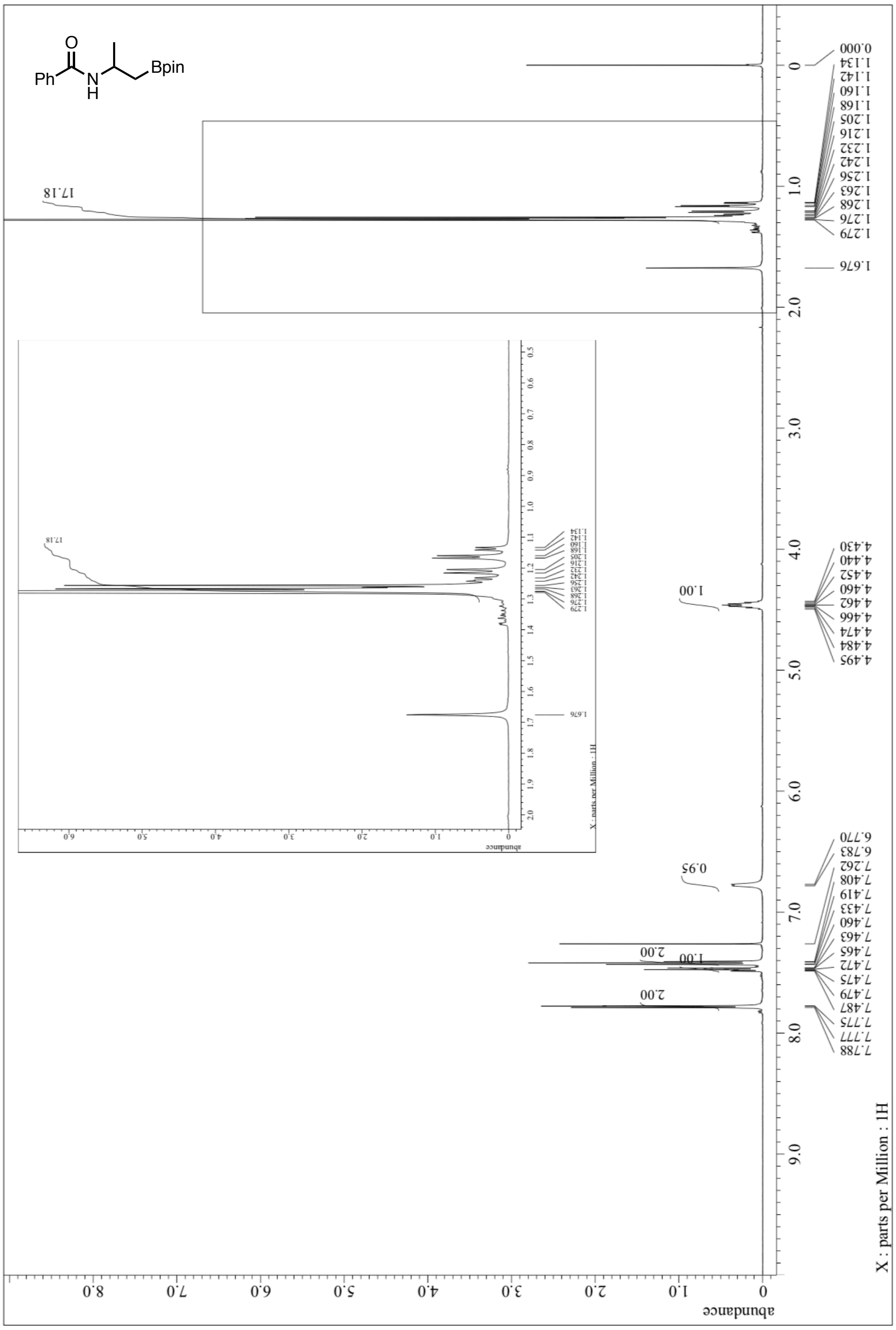
^{1}H NMR of **2s** (600 MHz, 60 ˚C, $CDCl_3$)



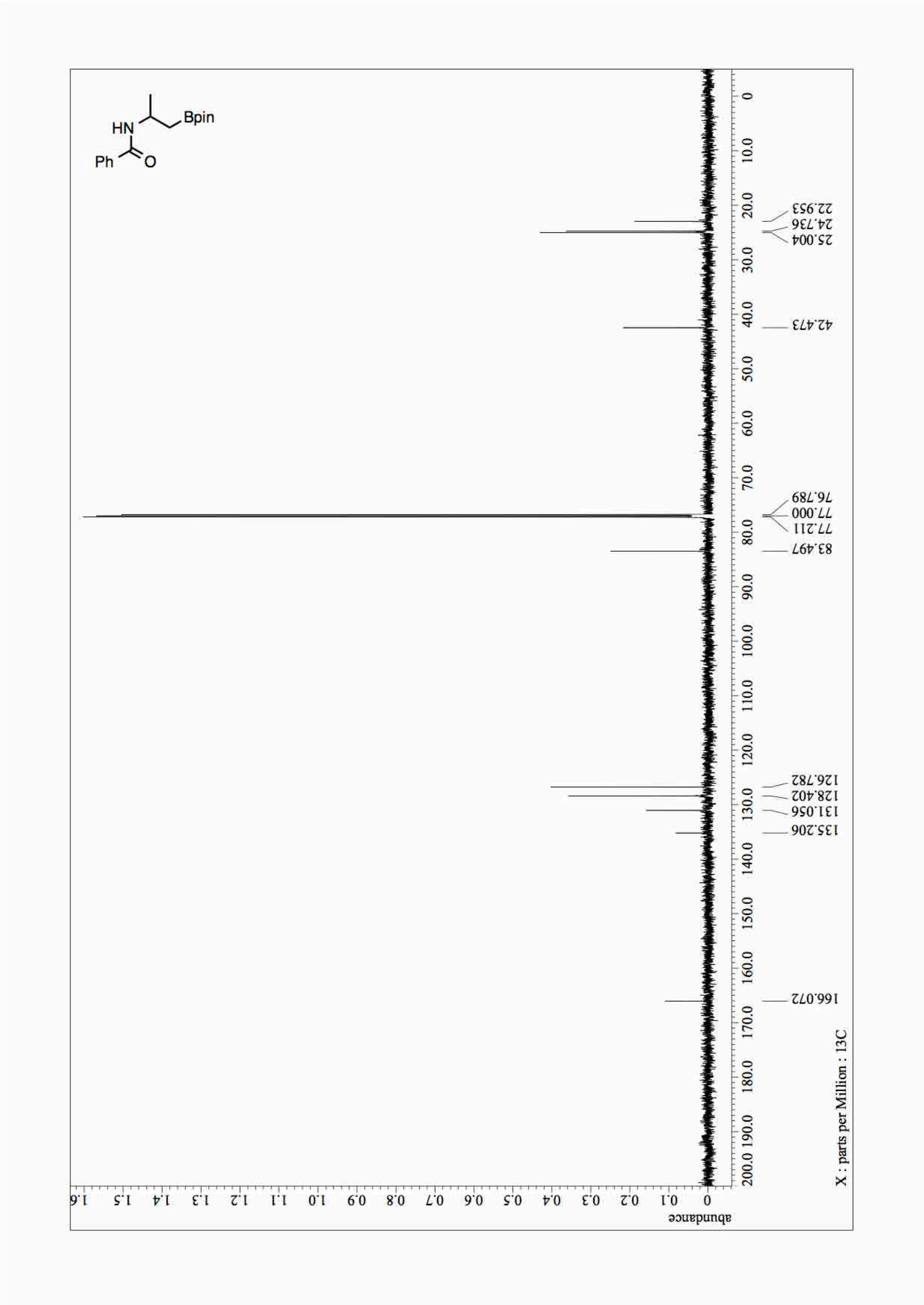
^{13}C NMR of **2s** (151 MHz, 60 ˚C, $CDCl_3$)



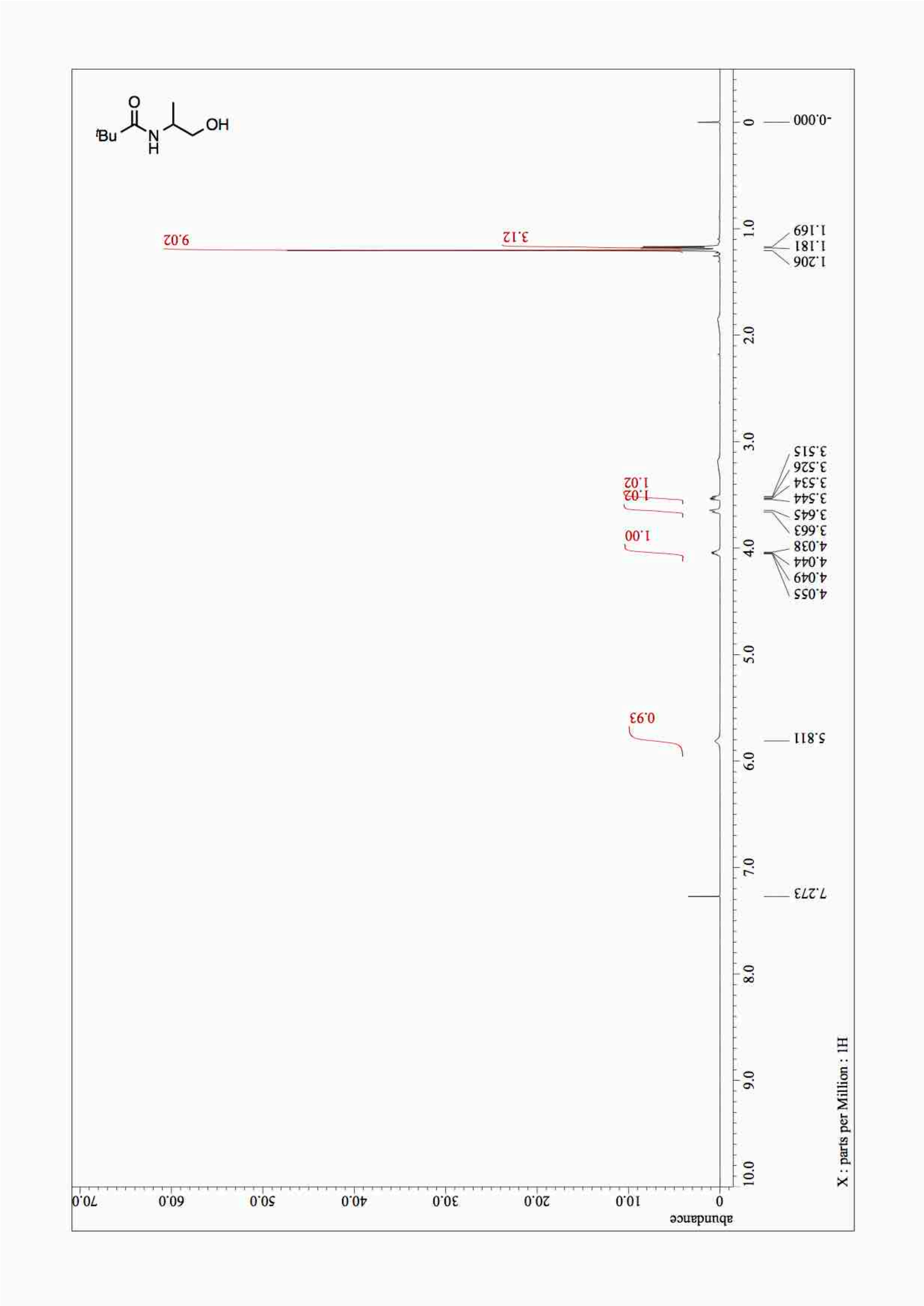
[1]H NMR of **2t** (600 MHz, $CDCl_3$)



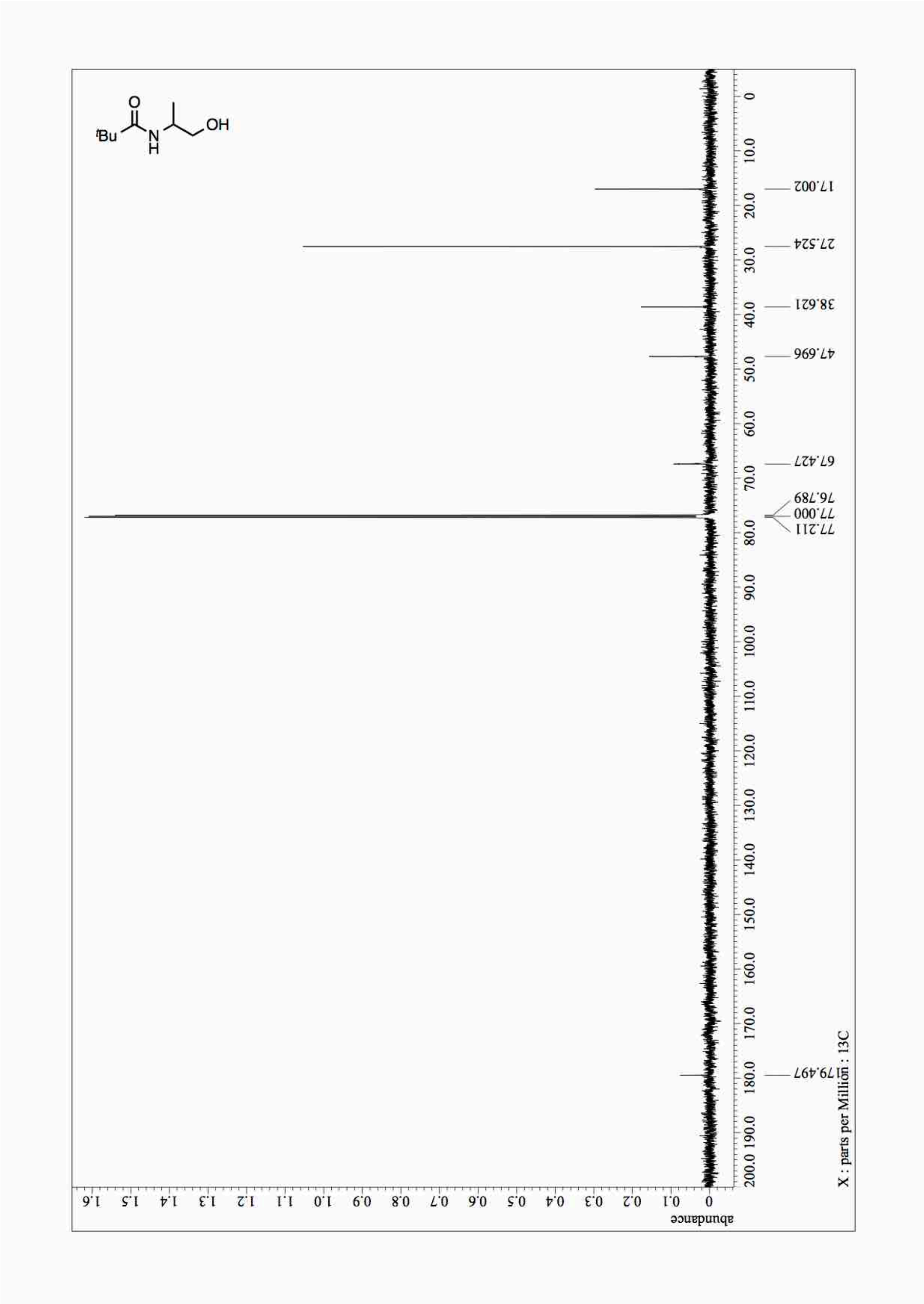
^{13}C NMR of **2t** (126 MHz, $CDCl_3$)



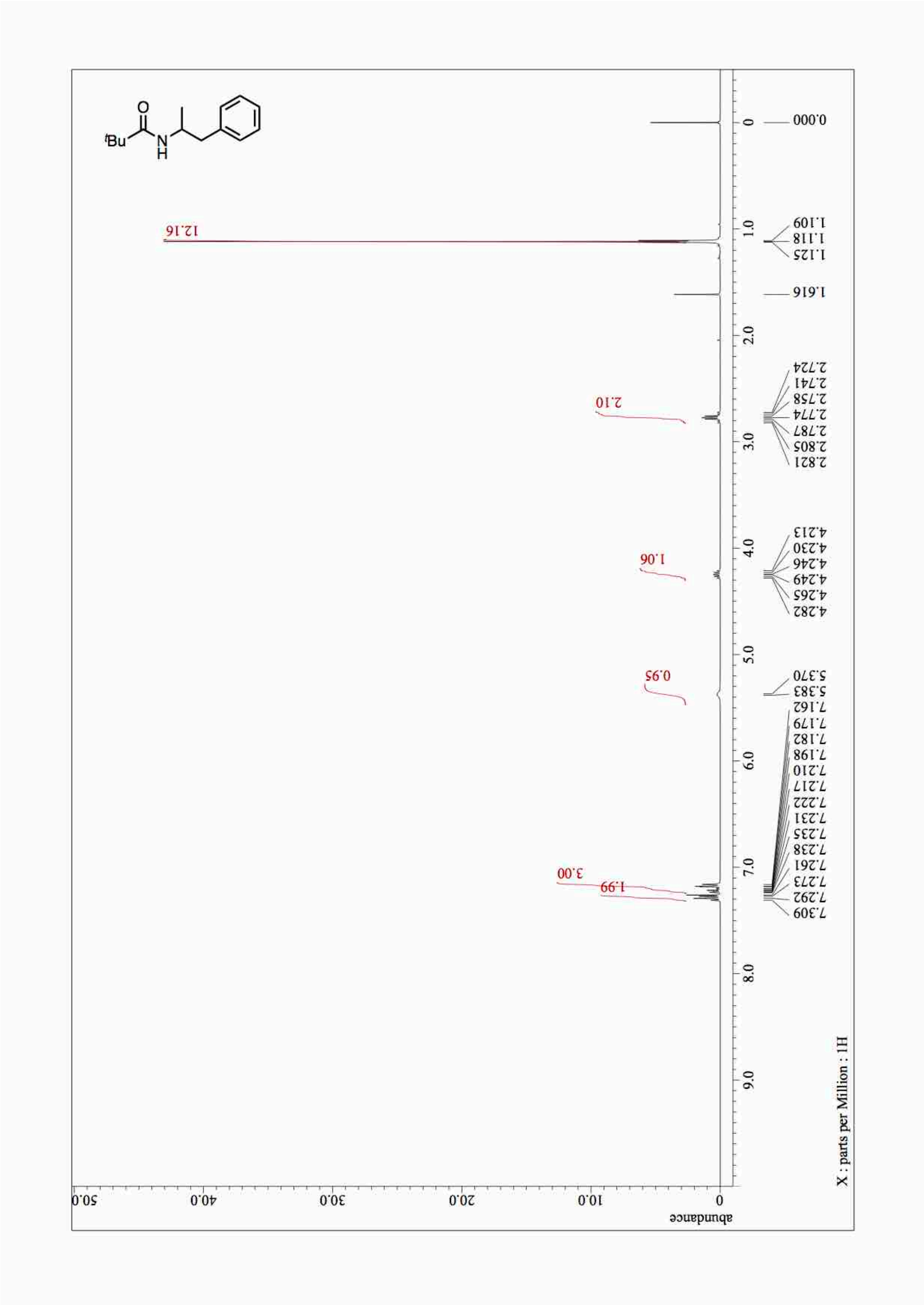
^{1}H NMR of **3a** (600 MHz, $CDCl_3$)



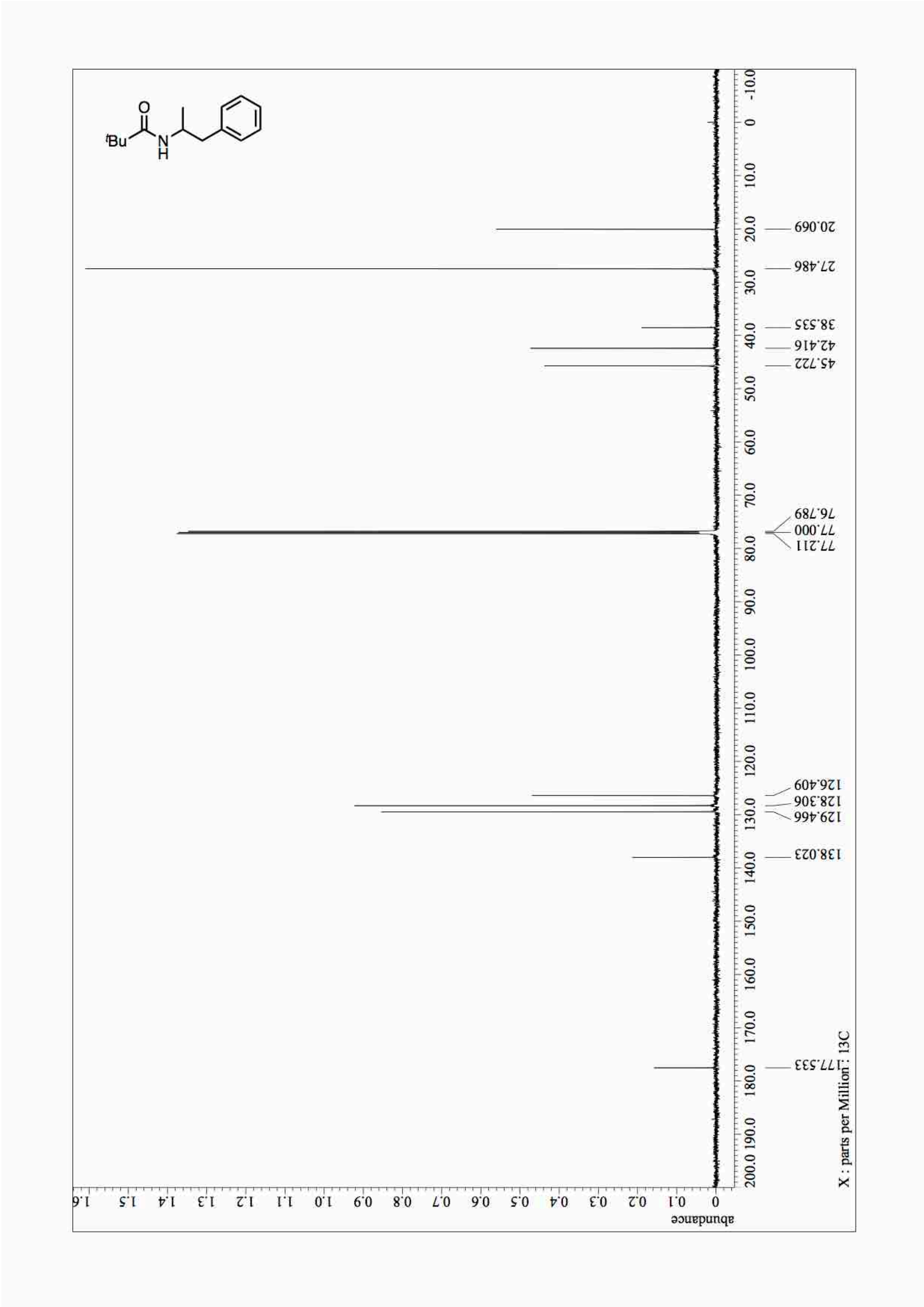
^{13}C NMR of **3a** (151 MHz, $CDCl_3$)



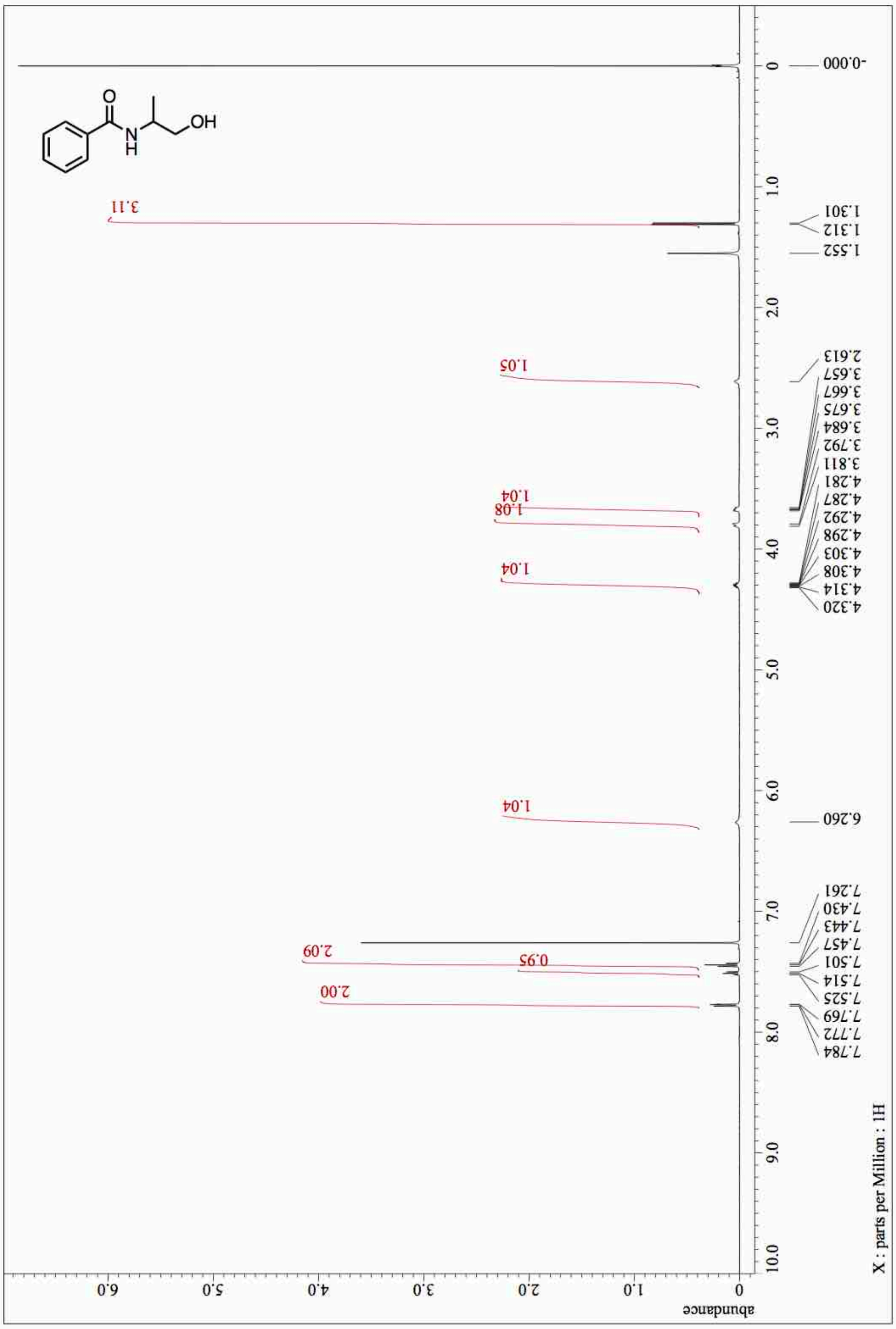
^{1}H NMR of **3b** (400 MHz, $CDCl_3$)



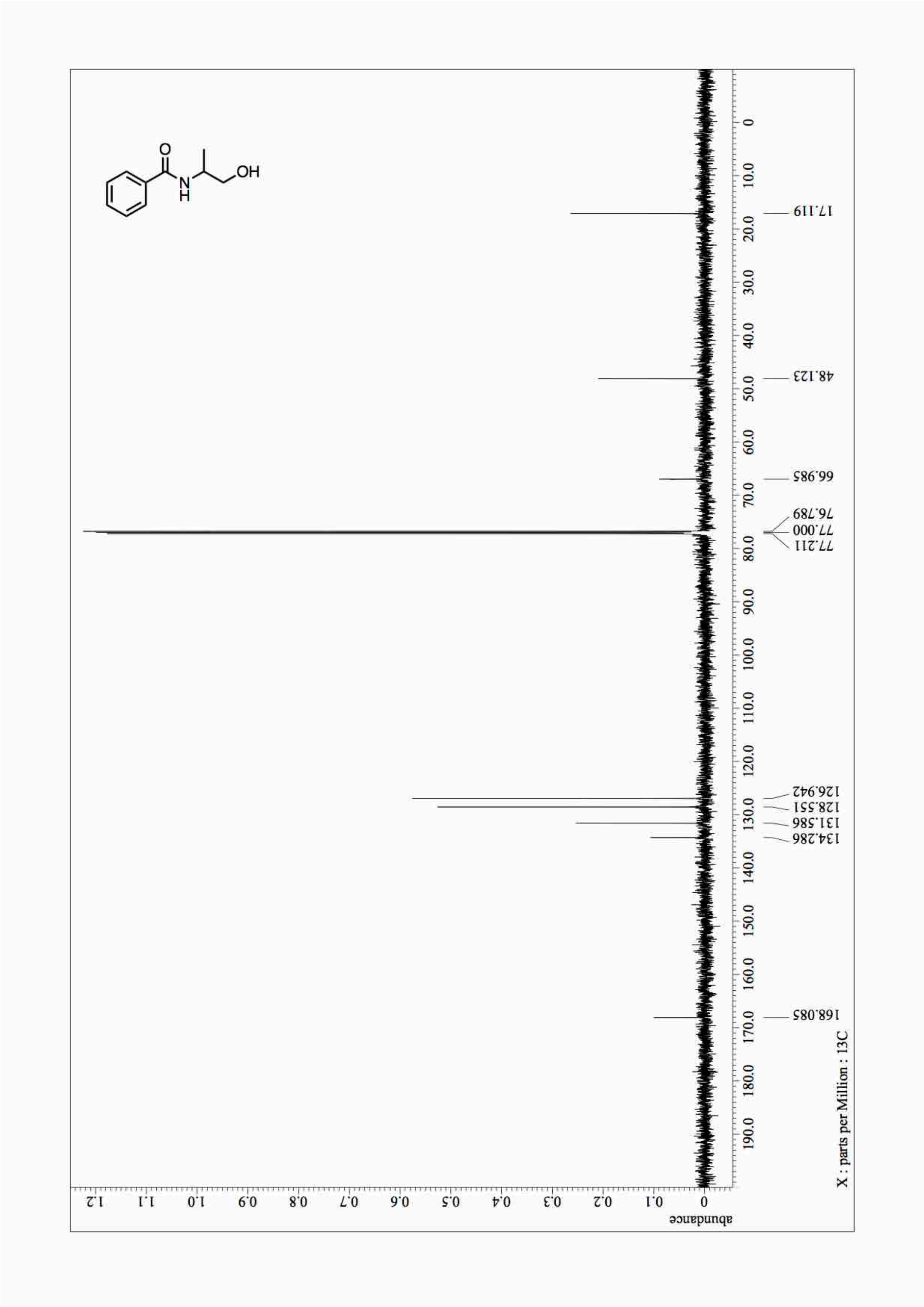
^{13}C NMR of **3b** (151 MHz, $CDCl_3$)



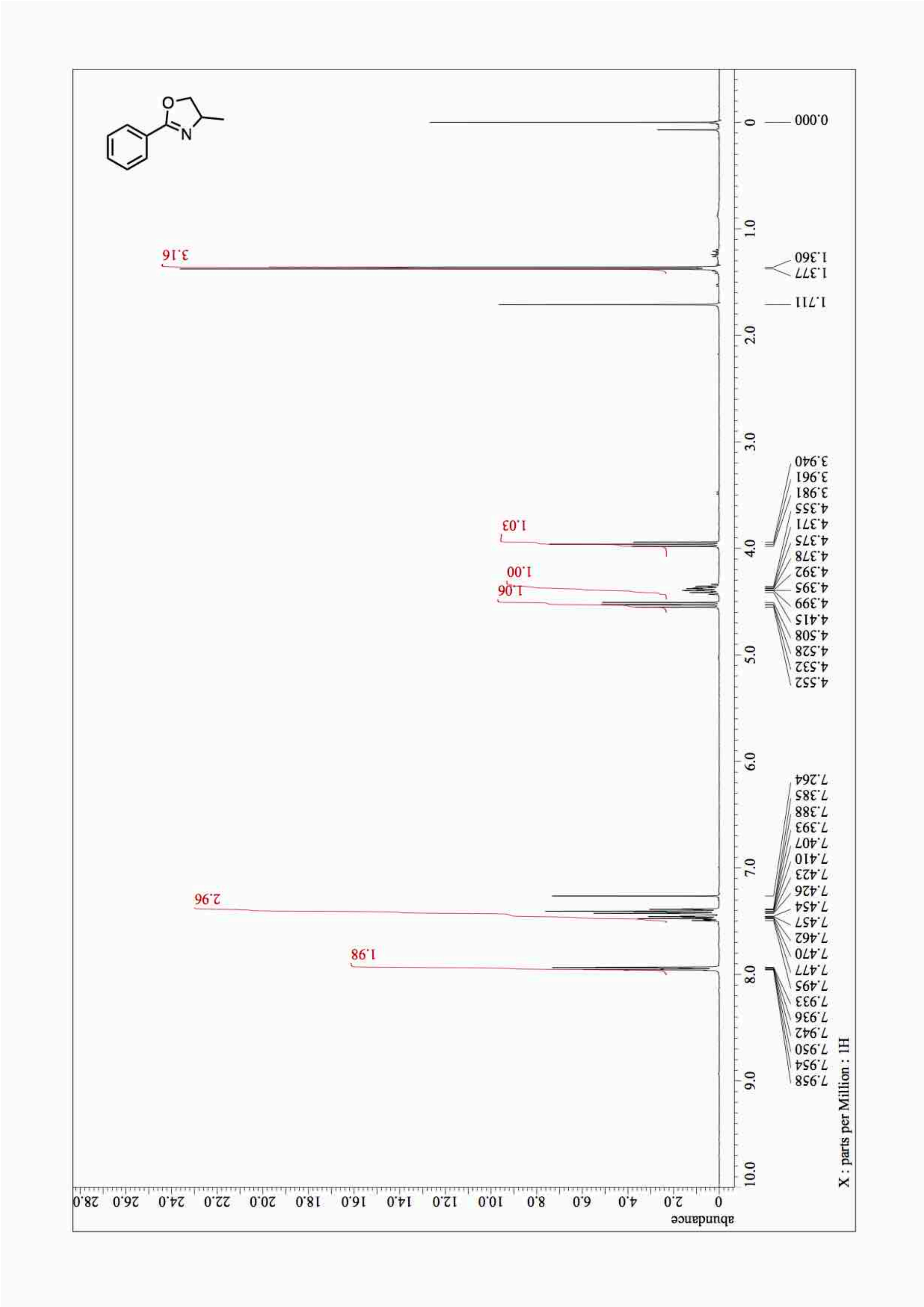
[1]H NMR of **S6** (600 MHz, $CDCl_3$)



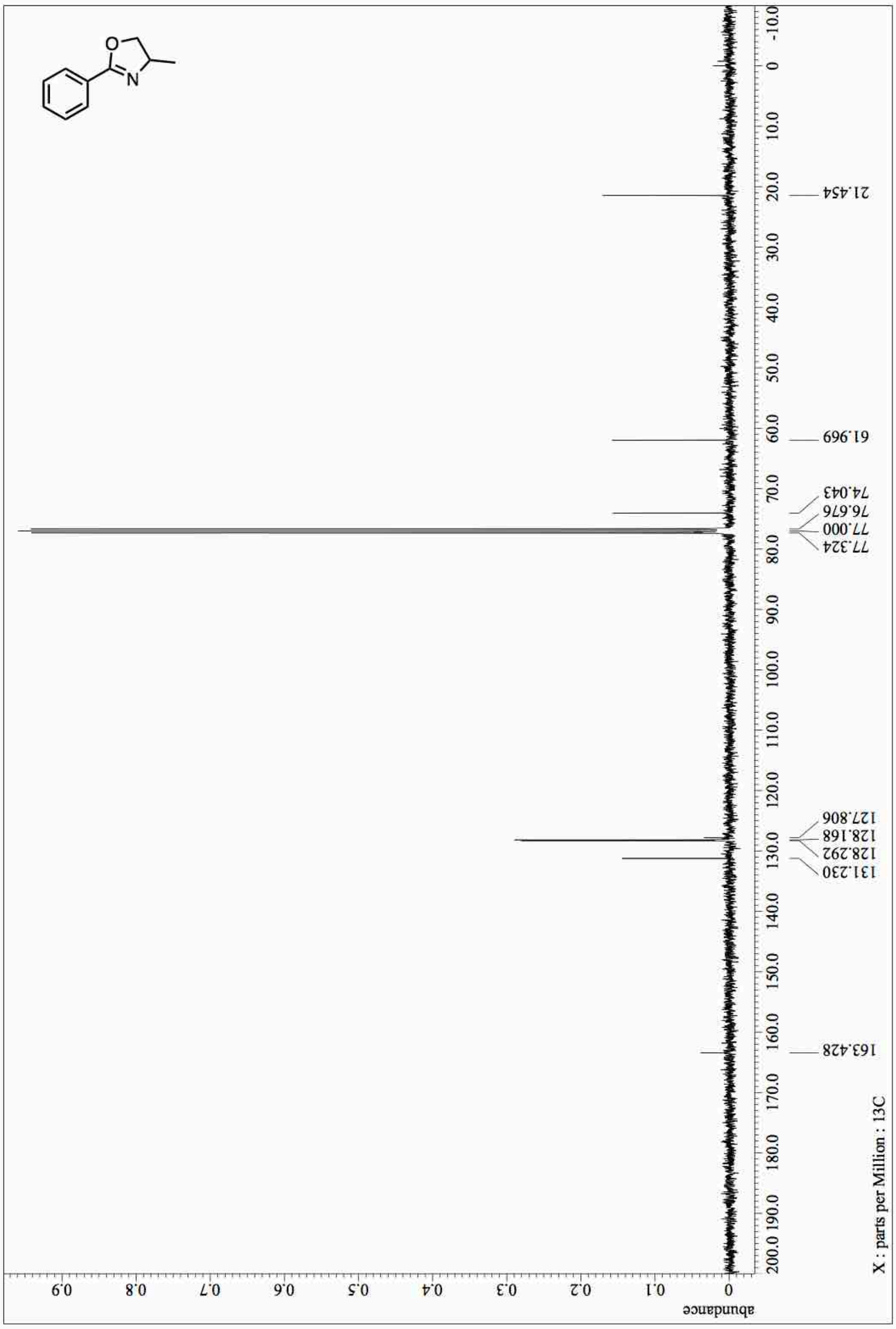
^{13}C NMR of **S6** (151 MHz, $CDCl_3$)



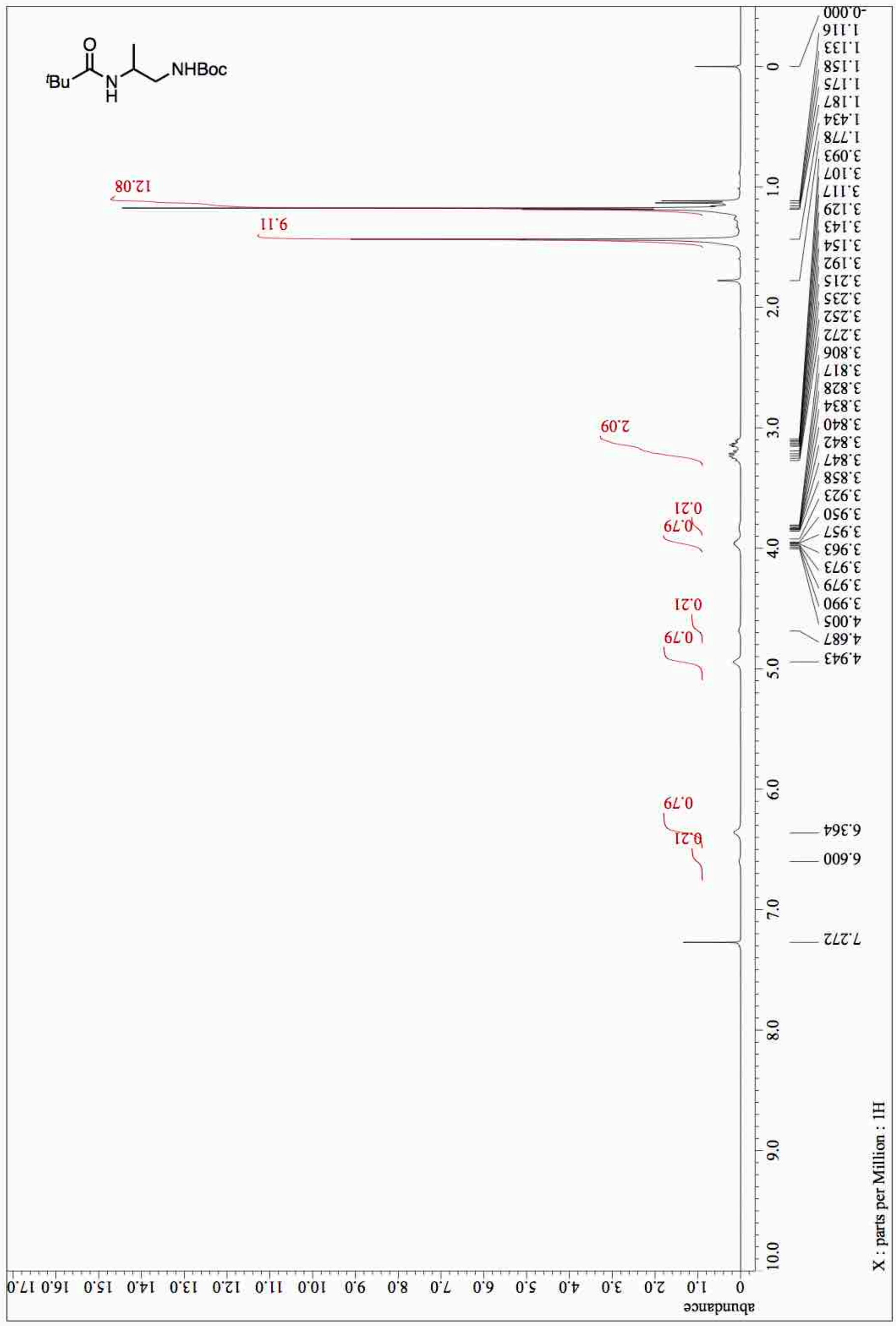
^{1}H NMR of **3c** (400 MHz, $CDCl_3$)



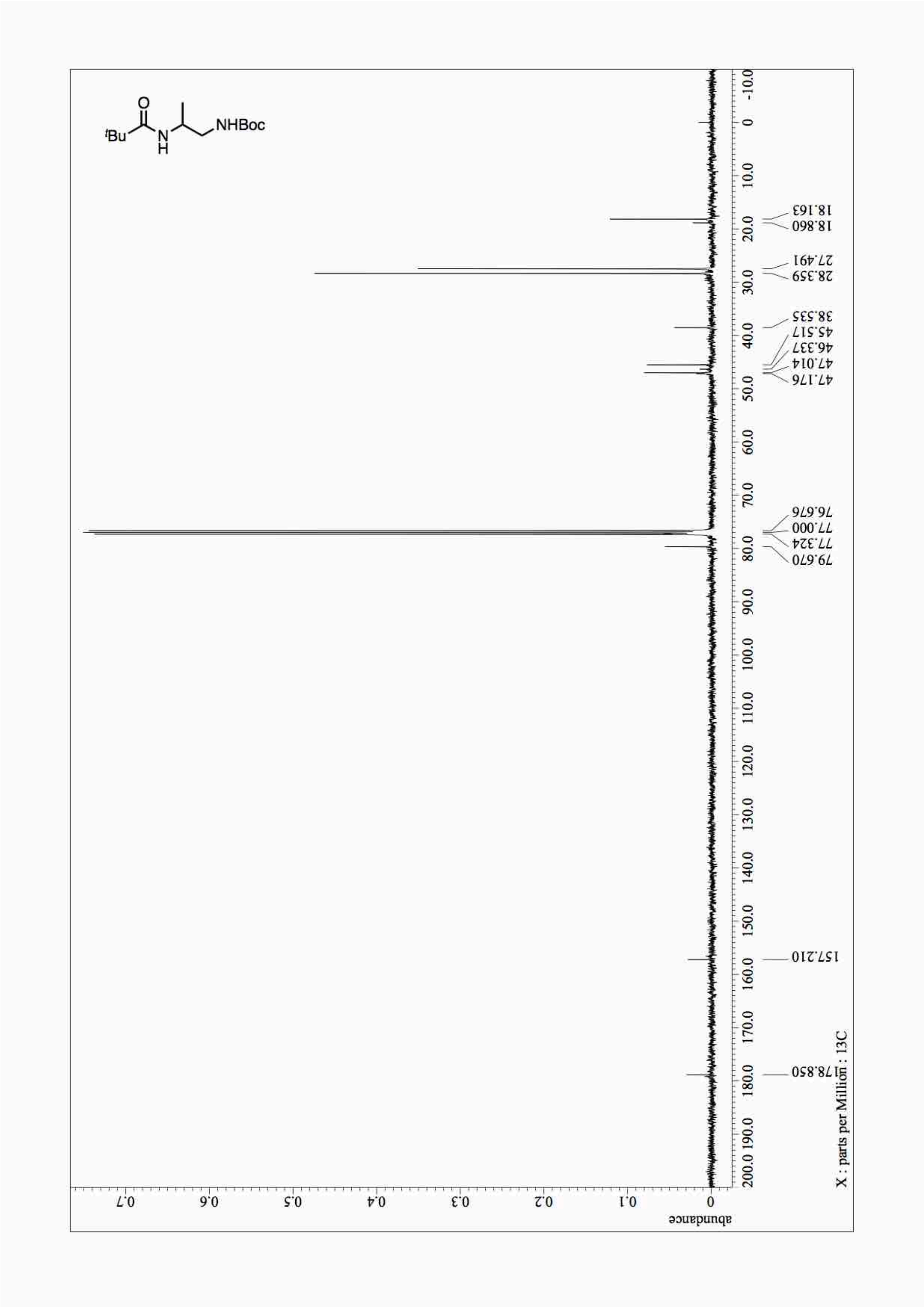
^{13}C NMR of **3c** (101 MHz, $CDCl_3$)



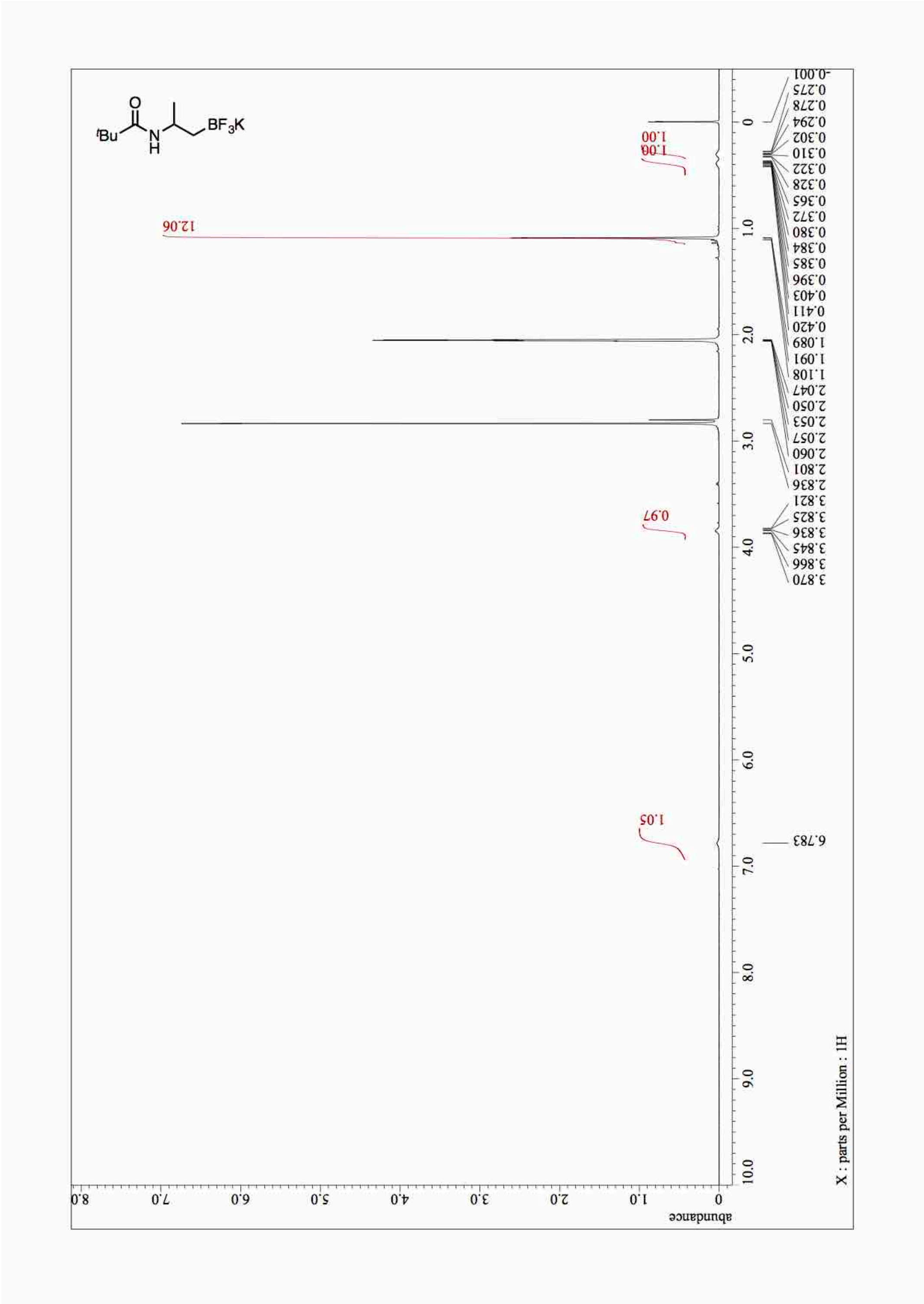
[1]H NMR of **3d** (400 MHz, $CDCl_3$)



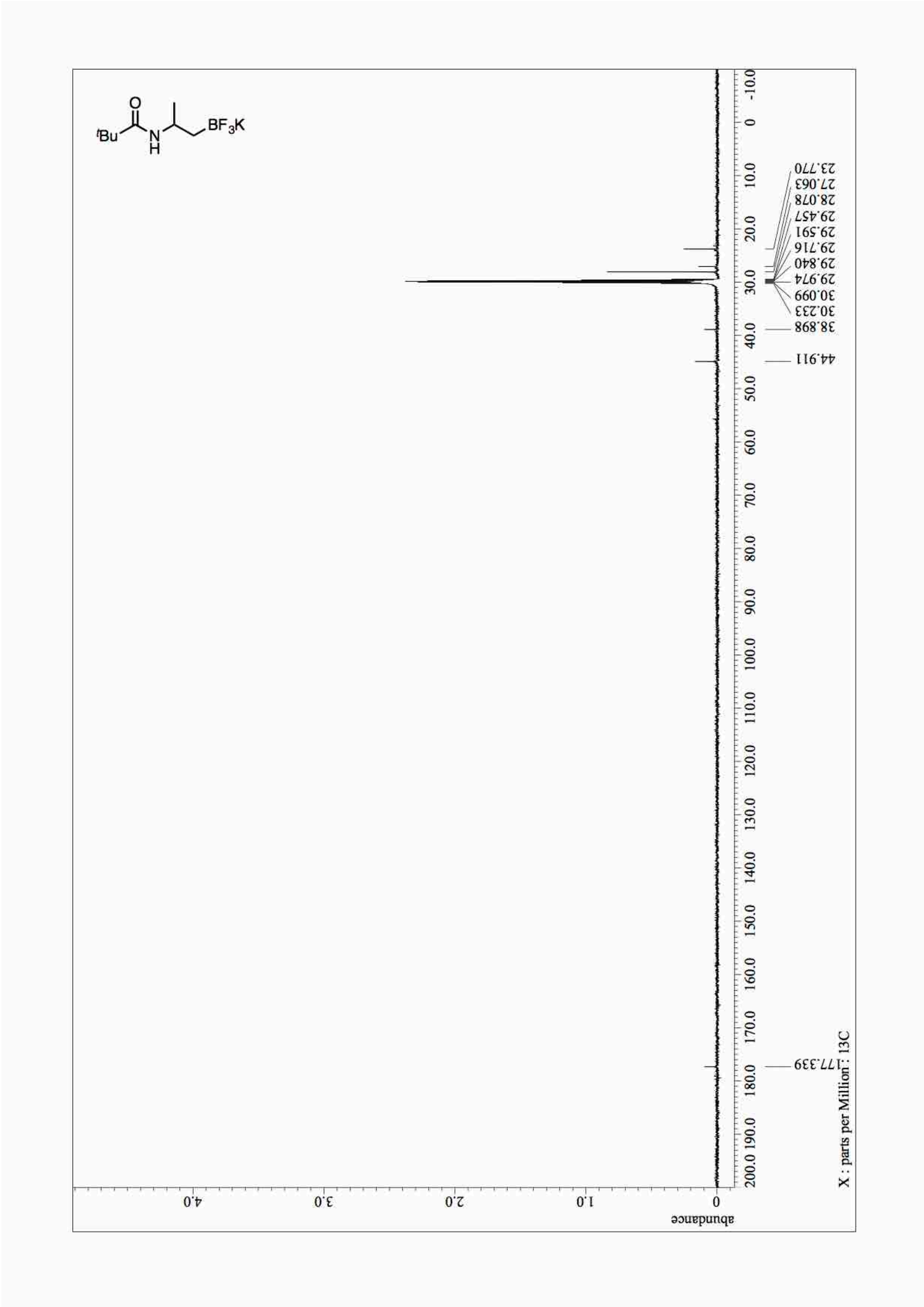
^{13}C NMR of **3d** (101 MHz, $CDCl_3$)



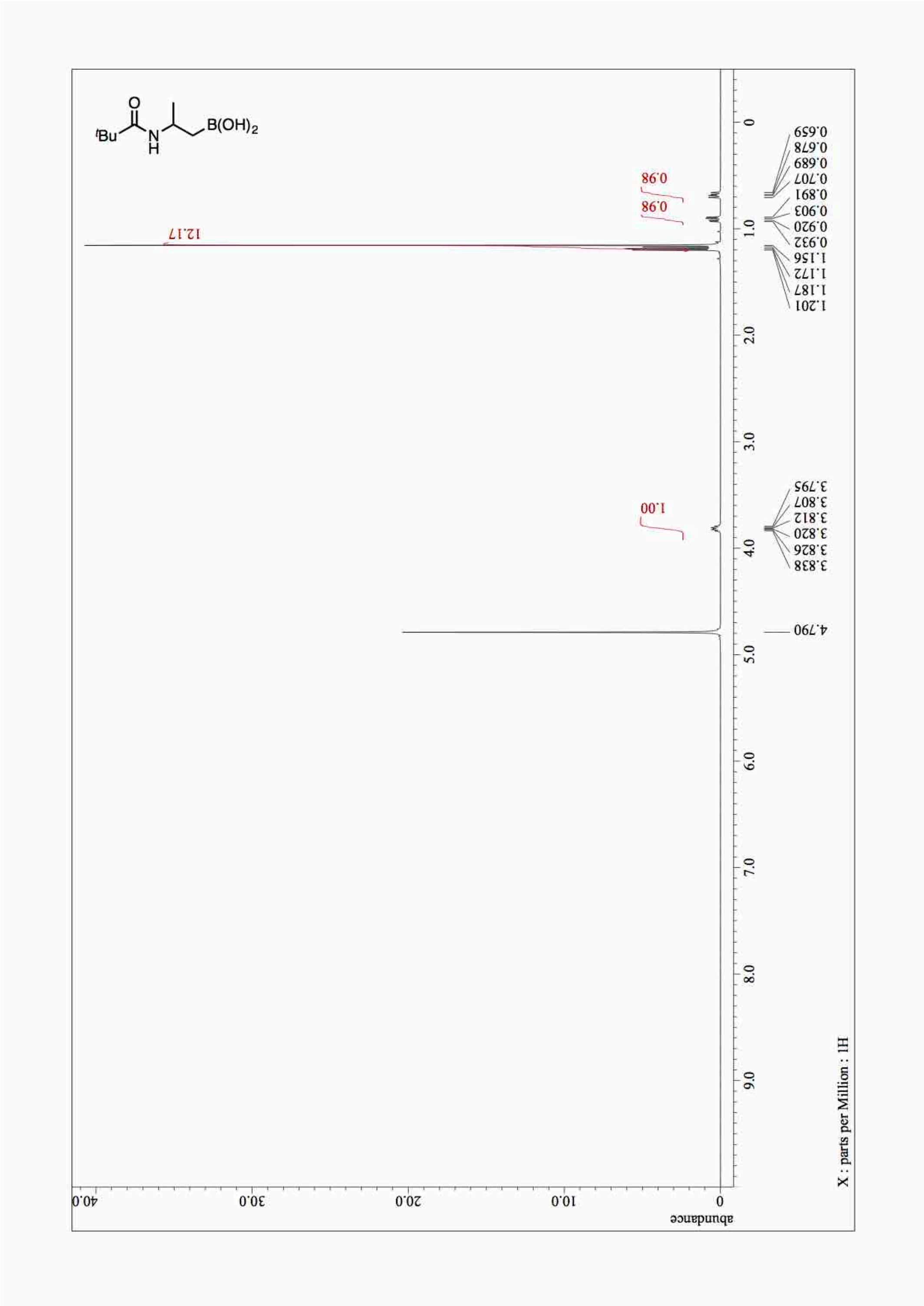
^{1}H NMR of **3e** (600 MHz, $(CD_3)_2CO$)



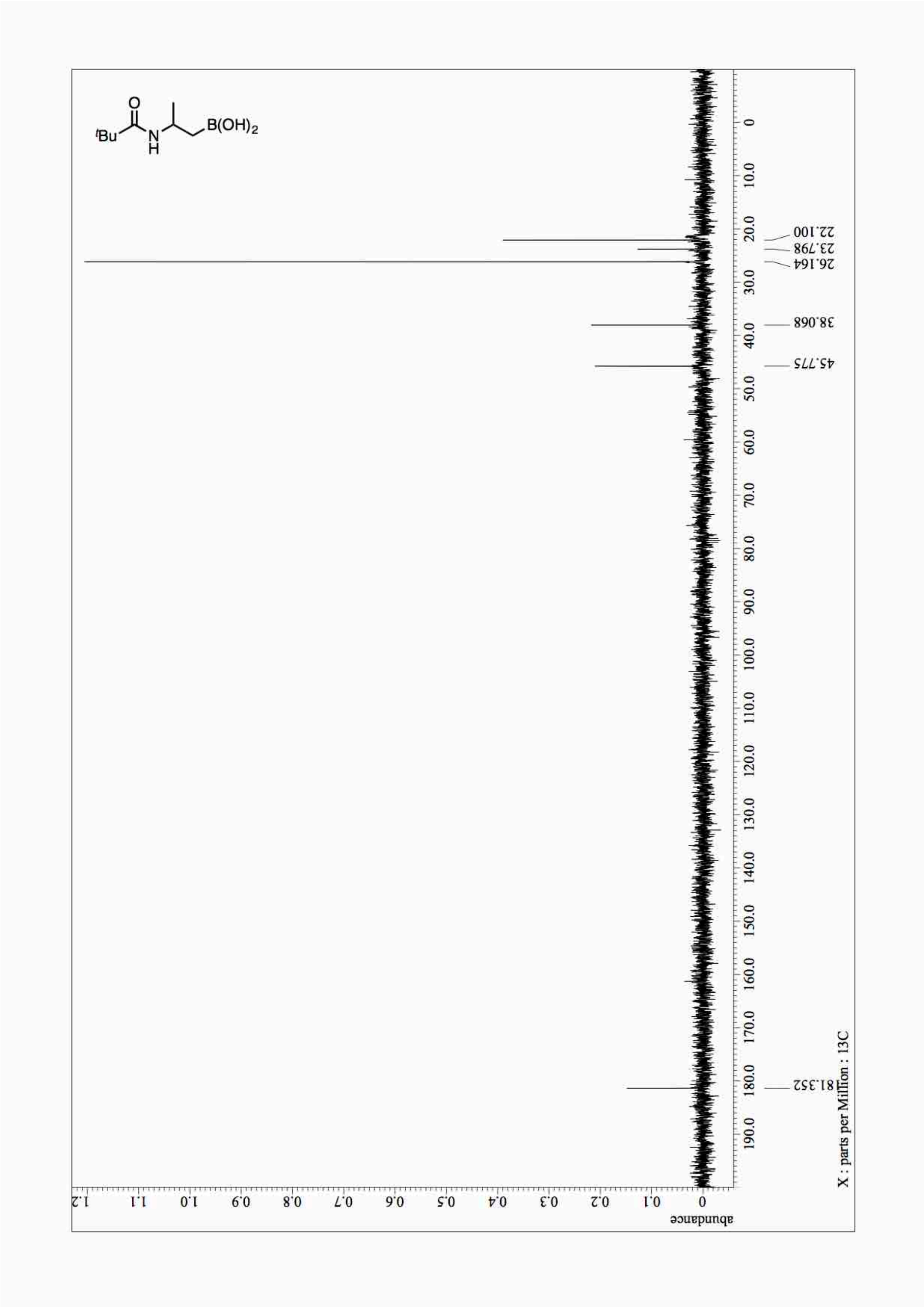
^{13}C NMR of **3e** (151 MHz, $(CD_3)_2CO$)



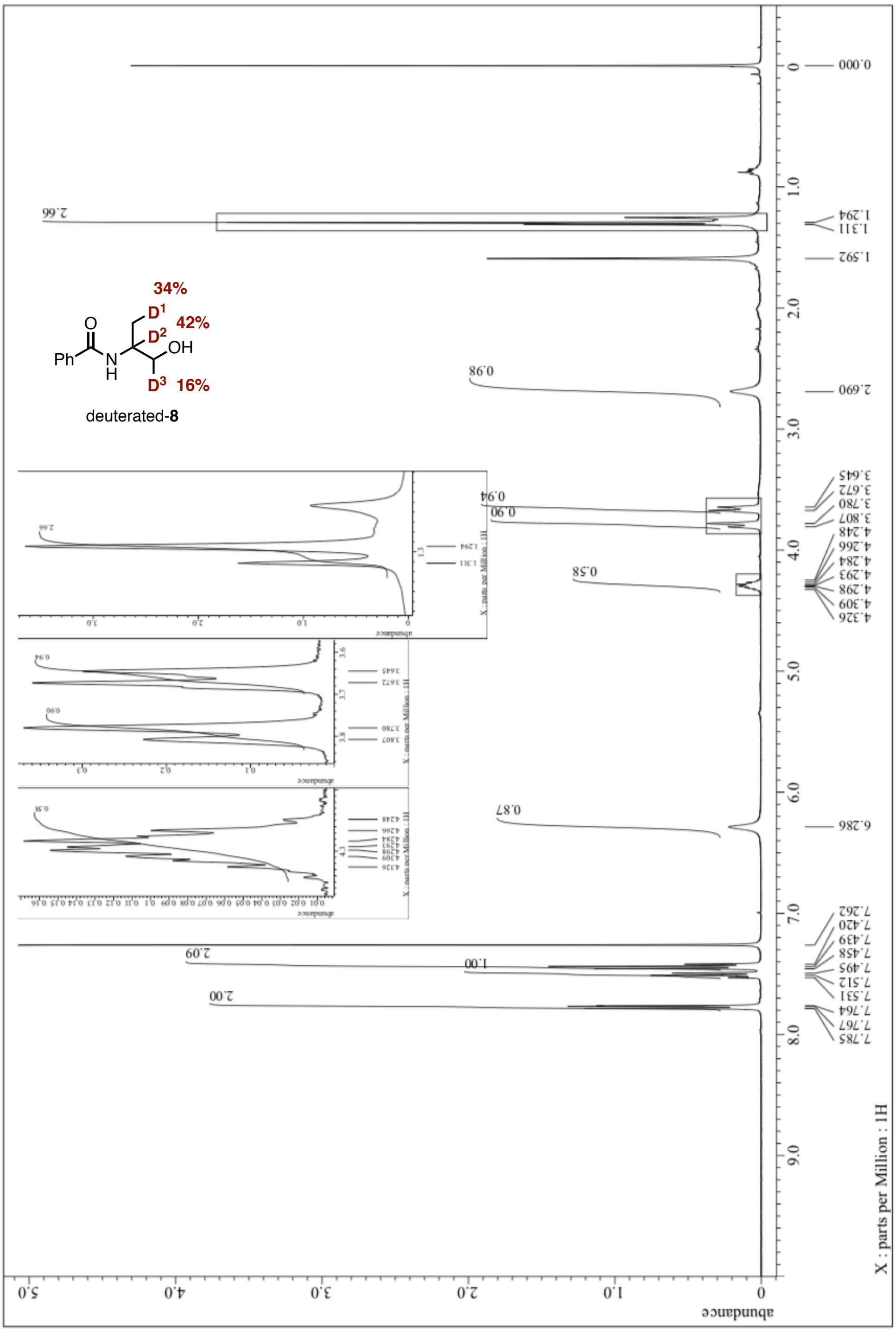
^{1}H NMR of **3f** (500 MHz, D_2O)



^{13}C NMR of **3f** (126 MHz, D_2O)



^{1}H NMR of deuterated-**8** (400 MHz, $CDCl_3$)



^{1}H NMR of deuterated-**9** (400 MHz, $CDCl_3$)