BAr^F_3-Catalyzed Imine Hydroboration with Pinacolborane Not Requiring the Assistance of an Additional Lewis Base

Qin Yin,[†,§] Yashar Soltani,[†,‡,§] Rebecca L. Melen,[*,‡] and Martin Oestreich [*]

[†]*Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 115, 10623 Berlin, Germany*

[‡]*School of Chemistry, Cardiff University, Main Building, Cardiff, CF10 3AT, Cymru/Wales, United Kingdom*

Supporting Information

Table of Contents

1 General Information

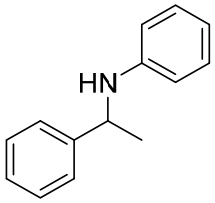
Reactions were generally performed in a GLC-vial, using an *MBraun* glove box under a static pressure of argon unless otherwise stated. Pinacolborane (HBpin) was purchased from *Sigma-Aldrich* and distilled prior to use. Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] was purchased from *Boulder Scientific Company* and sublimed twice before use. Tris[3,5-bis(trifluoromethyl)phenyl]-borane ($BAr^F{}_3$) was prepared according to a reported procedure.[1] Technical grade solvents for extraction or chromatography (cyclohexane, CH_2Cl_2, and ethyl acetate) were distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Grace* using the indicated solvents. ^1H, ^{13}C, ^{11}B, and ^{19}F spectra were recorded in $CDCl_3$, C_6D_6, or CD_2Cl_2 on a *Bruker* Avence III 500 MHz instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^1H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR; C_6D_5H: δ = 7.16 ppm for ^1H NMR and C_6D_6: δ = 128.06 ppm for ^{13}C NMR; $CDHCl_2$: δ = 5.32 ppm for ^1H NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplett, q = quartet, sept = septet, m = multiplet, br = broad signal), coupling constants (Hz), and integration. Gas-liquid chromatography (GLC) was performed on an *Agilent Technologies* 7820A gas chromatograph equipped with a FS-SE-54 capillary column (30 m × 0.32 mm, 0.25 µm film thickness) by *CS-Chromatographie Service* using the following program: N_2 carrier gas, injection temperature 240 °C, detector temperature 300 °C, flow rate: 1.74 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Infrared (IR) spectra were recorded on an *Agilent Technologies* Cary 630 FT-IR spectrometer equipped with an ATR unit and the signals are reported in wavenumbers (cm^{-1}). Mass spectra (MS) were obtained from the Analytical Facility at the School of Chemistry, Cardiff University.

2 General Procedure for the Catalytic Imine Hydroboration

In a glove box, a 2-mL GLC-vial equipped with a stirring bar is charged with BAr^F_3 (1.0 mol %), imine (1.0 equiv), and HBpin (1.2 equiv). Benzene (1 M) is added to the reaction, and the resulting mixture is stirred for 18 h at room temperature. The resulting yellow orange solution is then diluted with CH_2Cl_2 (ca. 3 mL) and washed with water (3×5 mL). The combined organic layers are washed with brine (5.0 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The conversion is determined by GLC-MS analysis of the crude material. The crude mixture is further purified by flash-column chromatography on silica gel using the indicated eluent.

3 Characterization Data

3.1 *N*-(1-Phenylethyl)aniline (4a)

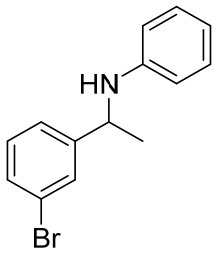


4a
$C_{14}H_{15}N$
M = 197.28

Prepared from (*E*)-*N*,1-diphenylethan-1-imine (**2a**, 0.2 mmol, 39.4 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4a** (34.5 mg, 87%) as colorless oil.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.38 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.30–7.23 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 8.6 Hz, 2H), 4.52 (q, *J* = 6.7 Hz, 1H), 4.16 (brs, 1H), 1.55 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.3, 145.2, 129.2, 128.7, 127.0, 125.9, 117.4, 113.4, 53.6, 25.1.

3.2 *N*-(1-(3-Bromophenyl)ethyl)aniline (4b)

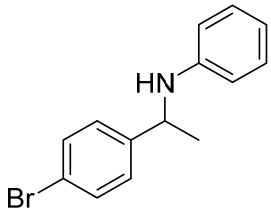


4b
$C_{14}H_{14}BrN$
M = 276.17 g/mol

Prepared from (*E*)-1-(3-bromophenyl)-*N*-phenylethan-1-imine (**2b**, 54.9 mg, 0.2 mmol) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4b** (42.3 mg, 77%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.30–7.24 (m, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.41 (d, *J* = 8.5 Hz, 2H), 4.35 (q, *J* = 6.7 Hz, 1H), 4.15 (brs, 1H), 1.42 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.0, 146.9, 130.4, 130.2, 129.3, 129.2, 124.7, 123.0, 117.9, 113.6, 53.5, 25.2.[2]

3.3 *N*-(1-(4-Bromophenyl)ethyl)aniline (4c)



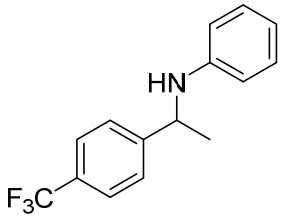
4c
$C_{14}H_{14}BrN$
M = 276.17 g/mol

Prepared from (*E*)-1-(4-bromophenyl)-*N*-phenylethan-1-imine (**2c**, 55.4 mg, 0.2 mmol) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4c** (53.4 mg, 96%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.17–7.11 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 2H), 4.47 (q, *J* = 6.7 Hz, 1H), 4.29 (brs, 1H), 1.53 (d, *J*

= 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.8, 144.3, 131.9, 129.3, 127.8, 120.7, 117.9, 113.7, 53.4, 25.1.[2]

3.4 *N*-(1-(4-(Trifluoromethyl)phenyl)ethyl)aniline (4d)

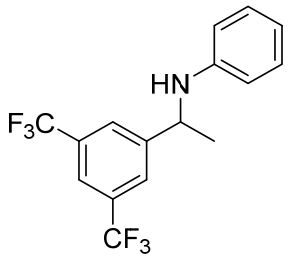


4d
$C_{15}H_{14}F_3N$
M =265.27 g/mol

Prepared from (*E*)-*N*-phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-imine (**2d**, 52.6 mg, 0.2 mmol) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4d** (47.5 mg, 90%) as light yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.02 (t, *J* = 8.0 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 7.7 Hz, 2H), 4.44 (q, *J* = 6.8 Hz, 1H), 4.30 (brs, 1H), 1.44 (d, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.4, 146.6, 129.3 (q, *J* = 32.3 Hz), 129.3, 126.3, 125.7 (q, *J* = 3.8 Hz), 118.0, 113.6, 53.6, 25.0.[2]

3.5 *N*-(1-(3,5-Bis(trifluoromethyl)phenyl)ethyl)aniline (4e)

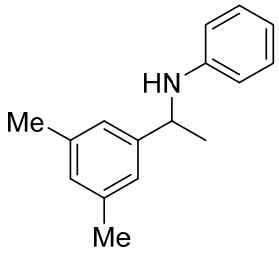


4e
$C_{16}H_{13}F_6N$
M = 333.27 g/mol

Prepared from (*E*)-1-(3,5-bis(trifluoromethyl)phenyl)-*N*-phenylethan-1-imine (**2e**, 0.2 mmol, 66.5 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (18/1) as eluent to afford **4e** (56.0 mg, 84%) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (s, 2H), 7.78 (s, 1H), 7.14 (t, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 7.7 Hz, 2H), 4.59 (q, *J* = 6.7 Hz, 1H), 4.32 (brs, 1H), 1.57 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 148.3, 146.4, 132.2 (q, *J* = 33.3 Hz), 129.5, 126.4, 123.5 (q, *J* = 272.9 Hz), 121.4, 118.6, 113.8, 53.8, 25.1.[2]

3.6 *N*-(1-(3,5-Dimethylphenyl)ethyl)aniline (4f)

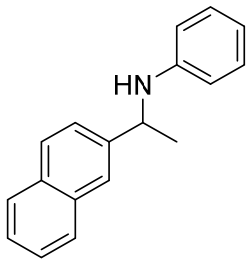


4f
$C_{16}H_{19}N$
M=225.33 g/mol

Prepared from (*E*)-1-(3,5-dimethylphenyl)-*N*-phenylethan-1-imine (**2f**, 0.2 mmol, 45.2 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4f** (43.1 mg, 95%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.11 (m, 2H), 7.02 (s, 2H), 6.91 (s, 1H), 6.73–6.67 (m, 1H), 6.61–6.56 (m, 2H), 4.44 (q, *J* = 6.7 Hz, 1H), 4.28 (br s, 1H), 2.34 (s, *J* = 0.5 Hz, 6H), 1.54 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.3, 145.2, 138.2, 129.2, 128.7, 123.8, 117.4, 113.6, 53.8, 25.0, 21.5.[2]

3.7 *N*-(1-(Naphthalen-2-yl)ethyl)aniline (4g)

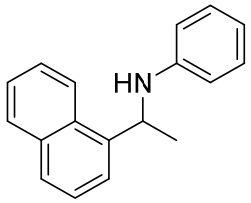


4g
$C_{18}H_{17}N$
M = 247.33 g/mol

Prepared from (*E*)-1-(naphthalen-2-yl)-*N*-phenylethan-1-imine (**2g**, 0.2 mmol, 49.6 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4g** (46.0 mg, 92%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.82 (m, 4H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.52–7.45 (m, 2H), 7.13 (t, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 2H), 4.68 (q, *J* = 6.7 Hz, 1H), 4.45 (br s, 1H), 1.64 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.2, 142.7, 133.7, 132.9, 129.3, 128.6, 128.0, 127.8, 126.1, 125.7, 124.6, 124.5, 117.7, 113.7, 54.1, 25.0.[3]

3.8 *N*-(1-(Naphthalen-1-yl)ethyl)aniline (4h)

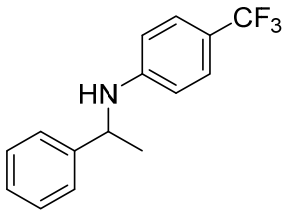


4h
$C_{18}H_{17}N$
M=247.33 g/mol

Prepared from (*E*)-1-(naphthalen-1-yl)-*N*-phenylethan-1-imine (**2h**, 0.2 mmol, 49.8 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4h** (49.9 mg, 99%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.63–7.51 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.14–7.07 (m, 2H), 6.72–6.66 (m, 1H), 6.54 (d, *J* = 7.6, 2H), 5.33 (q, *J* = 6.4 Hz, 1H), 4.41 (s, 1H), 1.70 (d, *J* = 7.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.1, 140.0, 134.2, 130.9, 129.3, 127.6, 126.2, 126.0, 125.6, 122.7, 122.5, 117.5, 113.5, 49.7, 23.7.[4]

3.9 *N*-(1-Phenylethyl)-4-(trifluoromethyl)aniline (4i)

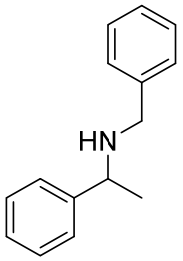


4i
$C_{15}H_{14}F_3N$
M=265.27 g/mol

Prepared from (*E*)-1-phenyl-*N*-(4-(trifluoromethyl)phenyl)ethan-1-imine (**2i**, 0.2 mmol, 51.8 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4i** (15.6 mg, 30%) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.31 (m, 6H), 7.28–7.24 (m, 1H), 6.53 (d, *J* = 7.8 Hz, 2H), 4.52 (q, *J* = 6.7 Hz, 1H), 1.55 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 149.5, 144.2, 129.0, 127.4, 126.6 (q, *J* = 3.7 Hz), 125.9, 125.0 (q, *J* = 269.8 Hz), 118.6, 112.8, 53.6, 24.9.[2]

3.10 *N*-Benzyl-1-phenylethanamine (4k)

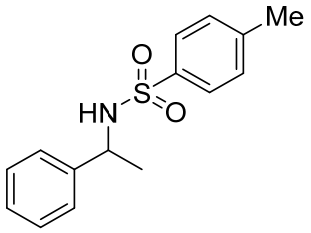


4k
$C_{15}H_{17}N$
M = 211.30 g/mol

Prepared from (*E*)-*N*-benzyl-1-phenylethan-1-imine (**2k**, 0.2 mmol, 42.9 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (10/1) as eluent to afford **4k** (35.9 mg, 83%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.18 (m, 10H), 3.78 (q, *J* = 6.6 Hz, 1H), 3.63 (AB, *J* = 13.2 Hz, 1H), 3.56 (BA, *J* = 13.2 Hz, 1H), 2.61 (brs, 1H), 1.35 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.9, 139.9, 128.7, 128.6, 128.4, 127.3, 127.3, 126.9, 57.7, 51.6, 24.3.[5]

3.11 4-Methyl-*N*-(1-phenylethyl)benzenesulfonamide (4l)

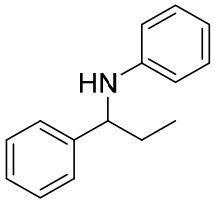


4l
$C_{15}H_{17}NO_2S$
M=275.37 g/mol

Prepared from 4-methyl-*N*-(1-phenylethylidene)benzenesulfonamide (**2l**, 0.2 mmol, 55.1 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4l** (38.4 mg, 70%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.19–7.16 (m, 4H), 7.11–7.09 (m, 2H), 5.12 (brs, 1H), 4.49–4.42 (m, 1H), 2.38 (s, 3H), 1.41 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.2, 142.2, 137.7, 129.5, 128.6, 127.5, 127.2, 126.2, 53.7, 23.7, 21.6.[6]

3.12 *N*-(1-Phenylpropyl)aniline (4m)

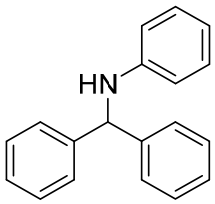


4m
$C_{15}H_{17}N$
M=211.30 g/mol

Prepared from (*E*)-*N*,1-diphenylpropan-1-imine (**2m**, 0.2 mmol, 41.8 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4m** (35.1 mg, 83%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.30 (m, 4H), 7.26–7.21 (m, 1H), 7.13 – 7.08 (m, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 2H), 4.35 (br s, 1H), 4.24 (t, *J* = 6.7 Hz, 1H), 1.95–1.78 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.3, 143.8, 129.2, 128.6, 127.1, 126.7, 117.5, 113.6, 60.1, 31.7, 11.0.[2]

3.13 *N*-Benzhydrylaniline (4n)

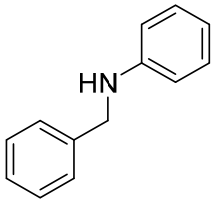


4n
$C_{19}H_{17}N$
M=259.34 g/mol

Prepared from *N*,1,1-triphenylmethanimine (**2n**, 0.2 mmol, 51.8 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4n** (49.2 mg, 94%) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.45 (m, 10H), 7.37–7.30 (m, 2H), 6.92 (t, *J* = 6.6 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 2H), 5.72 (s, 1H), 4.46 (brs, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 147.3, 142.9, 129.2, 128.9, 127.5, 127.4, 117.8, 113.6, 63.2.[7]

3.14 *N*-benzylaniline (4o)

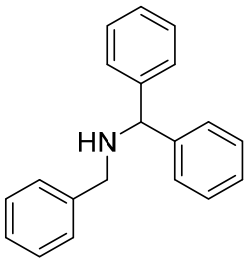


4o
$C_{13}H_{13}N$
M=183.24 g/mol

Prepared from (*E*)-*N*,1-diphenylmethanimine (**2o**, 0.2 mmol, 36.5 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4o** (31.7 mg, 86%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.27 (m, 5H), 7.21 (t, *J* = 7.6 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 2H), 4.36 (brs, 1H), 4.36 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.0, 139.4, 129.4, 128.8, 127.7, 127.4, 117.9, 113.2, 48.6.[8]

3.15 *N*-Benzyl-1,1-diphenylmethanamine (4p)

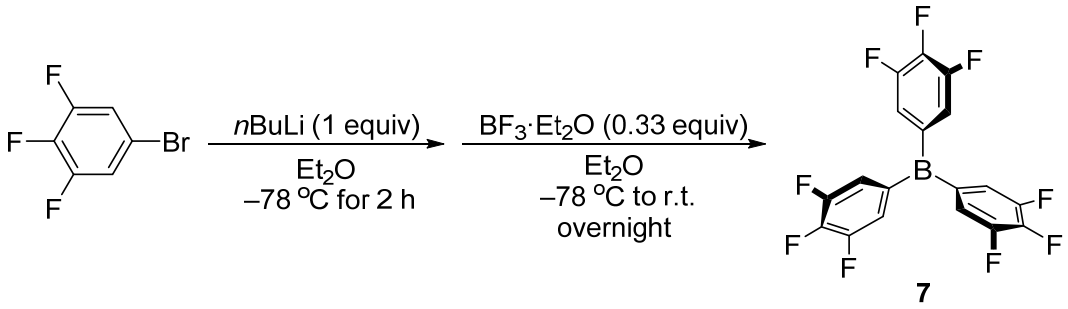


4p
$C_{20}H_{19}N$
M = 273.37 g/mol

Prepared from (*E*)-*N*-benzhydryl-1-phenylmethanimine (**2p**, 0.2 mmol, 55.1 mg) and HBpin (30.7 mg, 0.24 mmol, 1.2 equiv) according to the General Procedure. The title compound was purified by flash-column chromatography using cyclohexane/TBME (25/1) as eluent to afford **4p** (47.9 mg, 86%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.42 (m, 4H), 7.33–7.18 (m, 11H), 4.86 (s, 1H), 3.75 (s, 2H), 2.04 (br s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.9, 140.3, 128.6, 128.5, 128.4, 127.5, 127.2, 127.1, 66.5, 51.9.[9]

4 Synthesis of Tris(3,4,5-trifluorophenyl)borane (7)



Scheme S1. Synthesis of tris(3,4,5-trifluorophenyl)borane (**7**).

5-Bromo-1,2,3-trifluorobenzene (3.5 mL, 29.4 mmol, 1 equiv) was dissolved in diethylether (50 mL) under nitrogen. The resulting solution was stirred and cooled to –78 °C, and a solution of *n*BuLi (20 mL, 1.47 M, 29.4 mmol, 1 equiv) was added slowly. The resulting yellow solution was stirred for 2 h and turned white. To the still cool mixture, $BF_3{\cdot}OEt_2$ (1.2 mL, 9.8 mmol, 0.33 equiv) was added dropwise and, after stirring for another 2 h, the cooling setup was removed. The reaction was stirred overnight, the solvent was then removed in vacuo, and the resulting solid was sublimed at 120 °C under vacuum yielding pale yellow oily crystals that were washed with pentane (3x3 mL), dried, and resublimed to afford **7** (0.65 g, 16%) as a pale yellow crystal.

Lewis acidity (Gutmann–Beckett method): 79.07 AN (in C_6D_6).[10]

HRMS (TOF EI) for $C_{18}H_6F_9B^+$: calculated 404.0413, found 404.0529. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (t, *J* = 7.4 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3 (ddd, *J* = 254.0, 9.6, 2.7 Hz, *m*C), 143.0 (dt, *J* = 260.9, 15.0 Hz, *p*C), 136.5–136.0 (m, C-B), 122.0 (dd, *J* = 13.6, 5.4 Hz, *o*C). ^{11}B NMR (128 MHz, $CDCl_3$): δ 64.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -133.2 (d, *J* = 20.1 Hz, *m*F), -152.4 (t, *J* = 20.1 Hz, *p*F).

5 Molecular Structure and X-Ray Data of Compound 7 (CCDC 1549490)

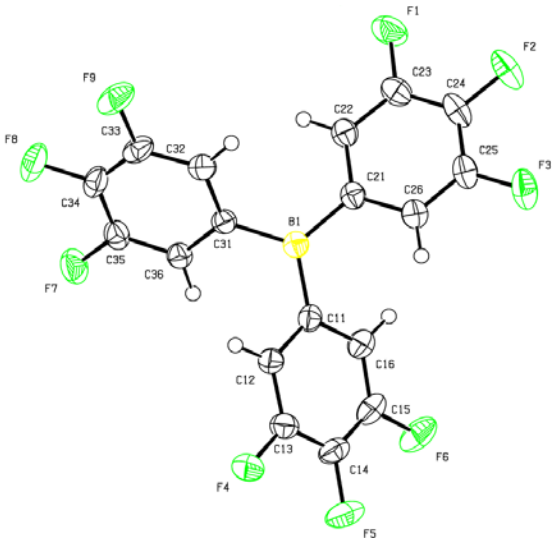


Table S1. Crystal data for **7**.

Bond precision: C-C = 0.0030 A Wavelength=1.54178

Cell: a=9.6716(3) b=12.3184(4) c=13.4558(5)

alpha=90 beta=100.288(3) gamma=90 Temperature: 150 K

Calculated Reported Volume 1577.33(9) 1577.34(9)

Space group P 21/n P 21/n Hall group -P 2yn -P 2yn

Moiety formula C18 H6 B F9 C18 H6 B F9 Sum formula C18 H6 B F9 C18 H6 B F9

Mr 404.04 404.04 Dx,g cm-3 1.701 1.701

Z 4 4 Mu (mm-1) 1.558 1.558

F000 800.0 800.0 F000’ 803.87

h,k,lmax 12,15,16 11,14,16 Nref 3194 3086

Tmin,Tmax 0.775,0.915 0.544,1.000 Tmin’ 0.620

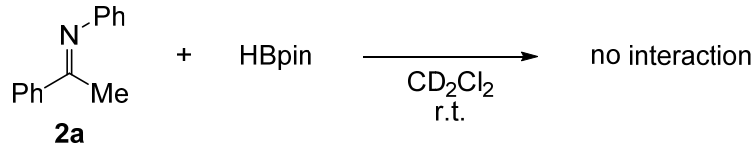
Correction method= # Reported T Limits: Tmin=0.544 Tmax=1.000

AbsCorr = GAUSSIAN Data completeness= 0.966 Theta(max)= 73.906

R(reflections)= 0.0443(2480) wR2(reflections)= 0.1305(3086)

S = 1.015 Npar= 253

6 NMR Spectroscopic Measurements



Scheme S2. Probing the interaction between ketimine (**2a**) and HBpin.

In a glove box, ketimine (**2a**, 9.8 mg, 0.05 mmol, 1.0 equiv) and HBpin (6.4 mg, 0.05 mmol, 1.0 equiv) were dissolved in CD_2Cl_2 (0.5 mL) in a dried J. Young NMR tube. The reaction mixture was shaken for 30 min and monitored by ^{1}H NMR and ^{11}B NMR spectroscopy. Analysis of both ^{1}H NMR and ^{11}B NMR spectra did not show any interaction between **2a** and HBpin.

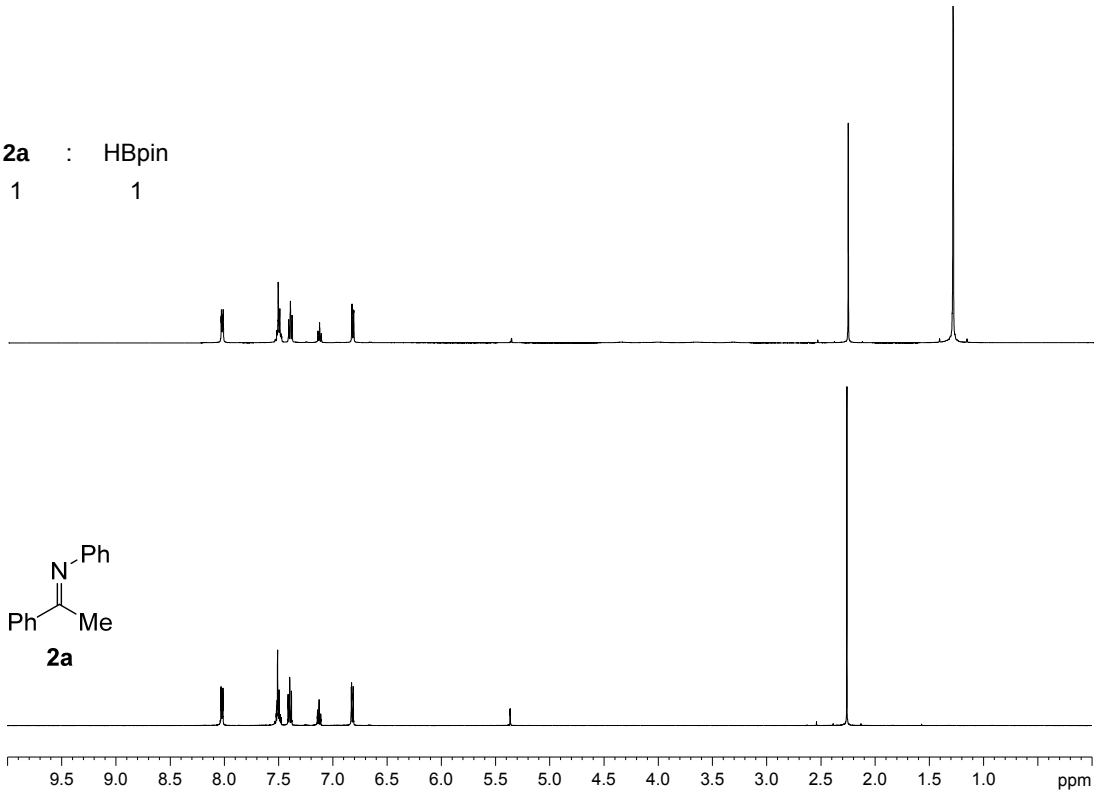


Figure S1. Monitoring the interaction of ketimine (**2a**) and HBpin by ^{1}H NMR spectroscopy (500 MHz, CD_2Cl_2).

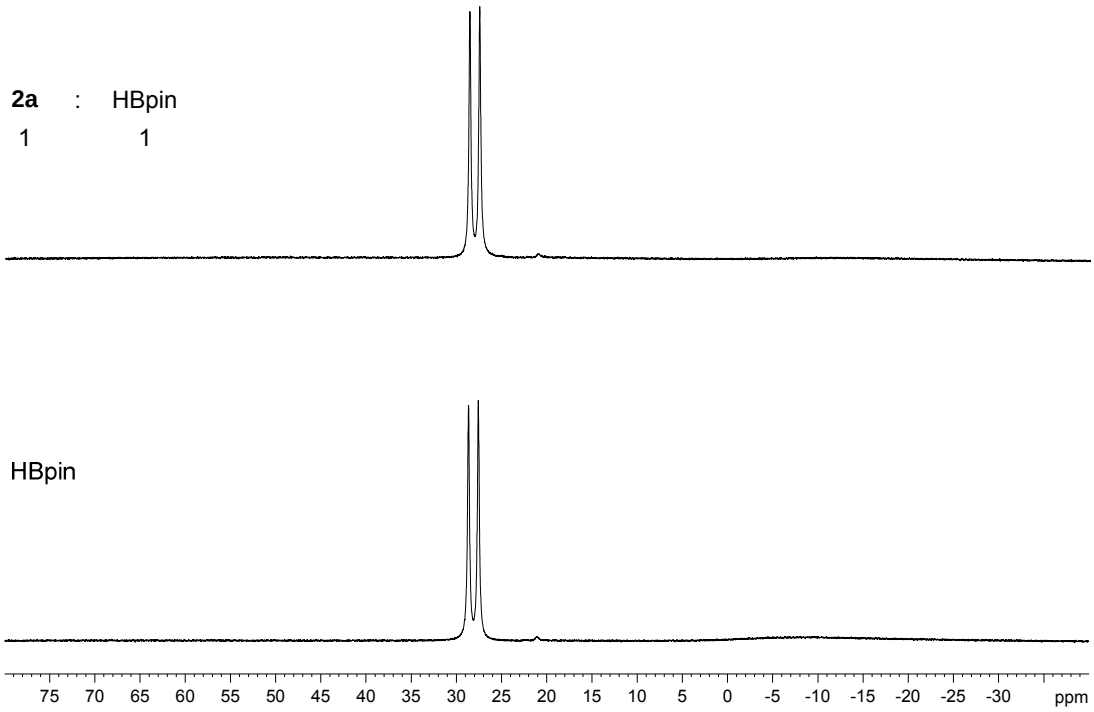
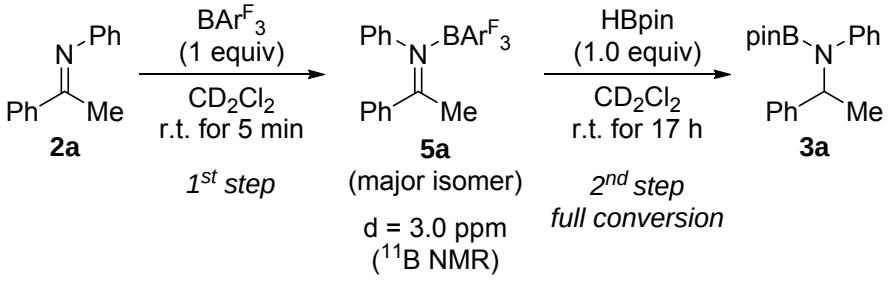


Figure S2. Monitoring the interaction of ketimine (**2a**) and HBpin by ^{11}B NMR spectroscopy (160 MHz, CD_2Cl_2).



Scheme S3. Probing the stoichiometric reaction of ketimine (**2a**) and HBpin in the presence of BAr^F_3.

Step 1: Generation of Lewis pair **5a**

In a glove box, ketimine (**2a**, 7.8 mg, 0.04 mmol, 1.0 equiv) and BAr^F_3 (26.0 mg, 0.04 mmol, 1.0 equiv) were dissolved in CD_2Cl_2 (0.5 mL) in a dried J. Young NMR tube. The reaction mixture was shaken for 5 min and monitored by ^{1}H NMR, ^{19}F NMR, and ^{11}B NMR spectroscopy. Formation of the corresponding Lewis pair **5a** was observed; **5a** was assigned to be the thermodynamically more stable isomer by 2D NMR measurements (H,H-NOESY, H,H-COSY, H,C-HSQC, H,C-HMBC).

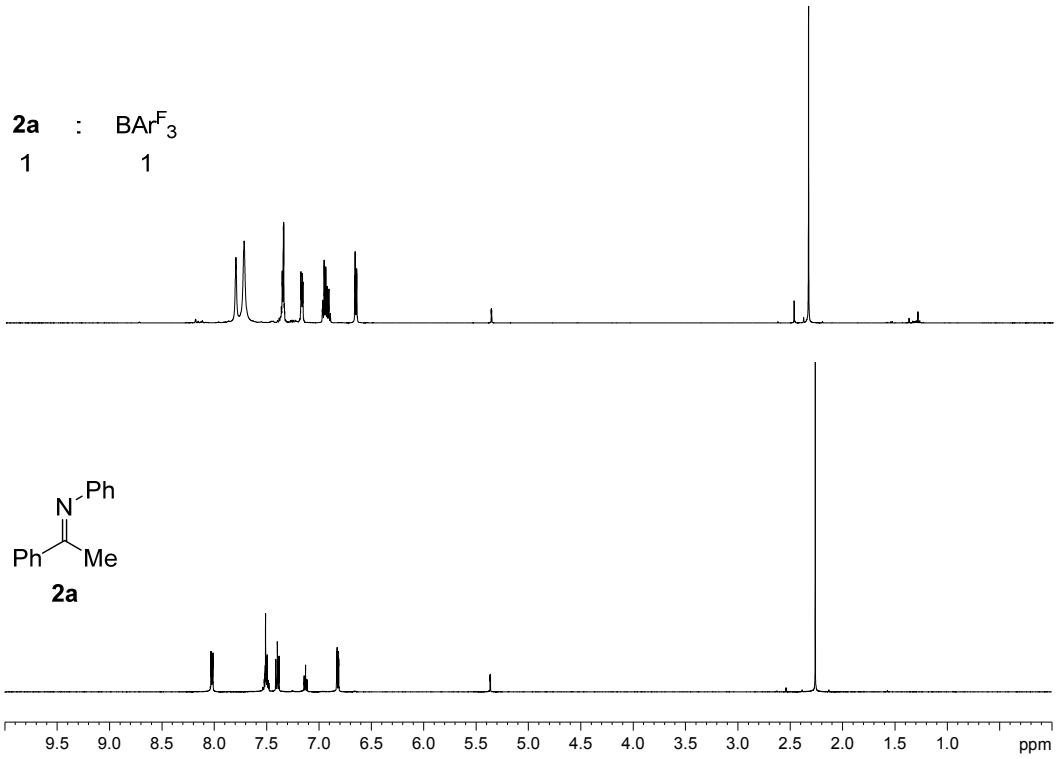


Figure S3. Monitoring the interaction of ketimine (**2a**) and BAr^F_3 by ^1H NMR spectroscopy (500 MHz, CD_2Cl_2).

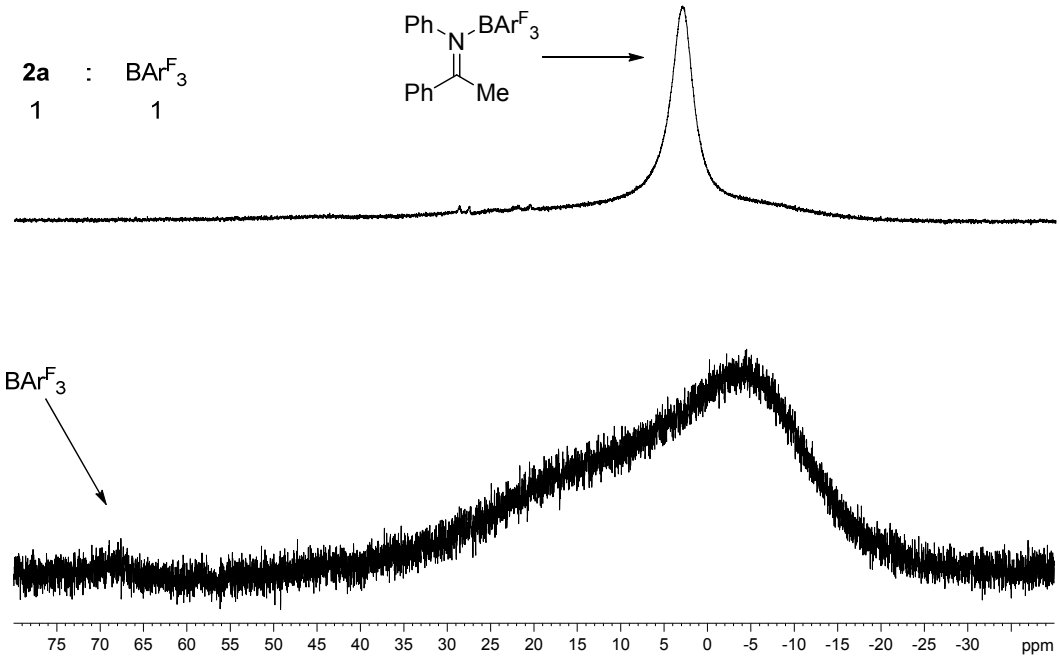


Figure S4. Monitoring the interaction of ketimine (**2a**) and BAr^F_3 by ^{11}B NMR spectroscopy (160 MHz, CD_2Cl_2).

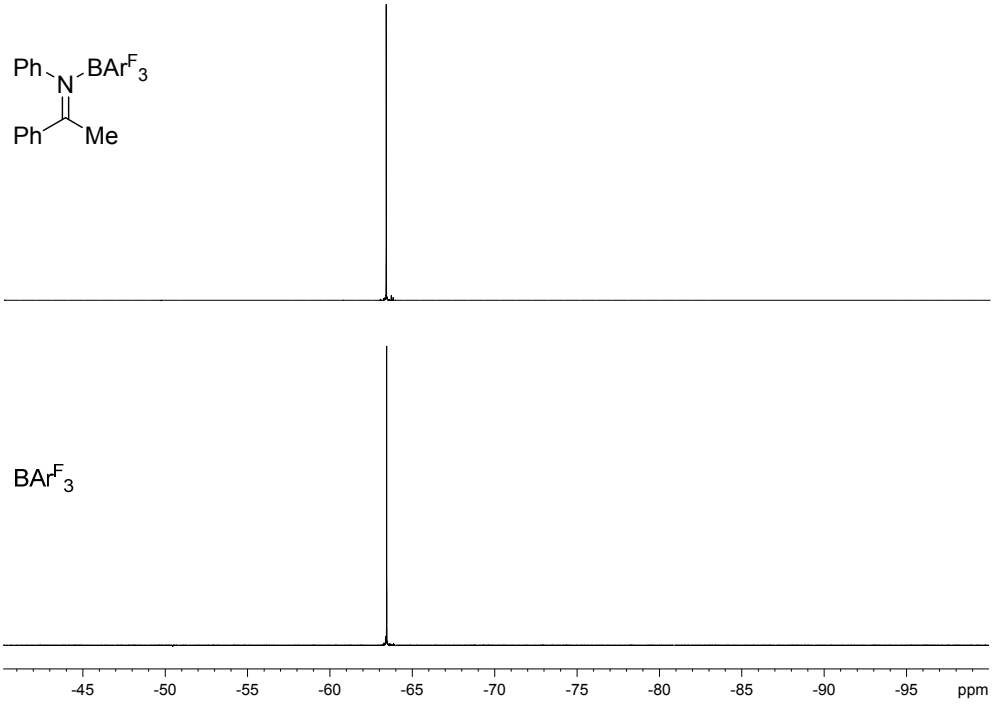


Figure S5. Monitoring the interaction of ketimine (**2a**) and BAr^F_3 by ^{19}F NMR spectroscopy (471 MHz, CD_2Cl_2).

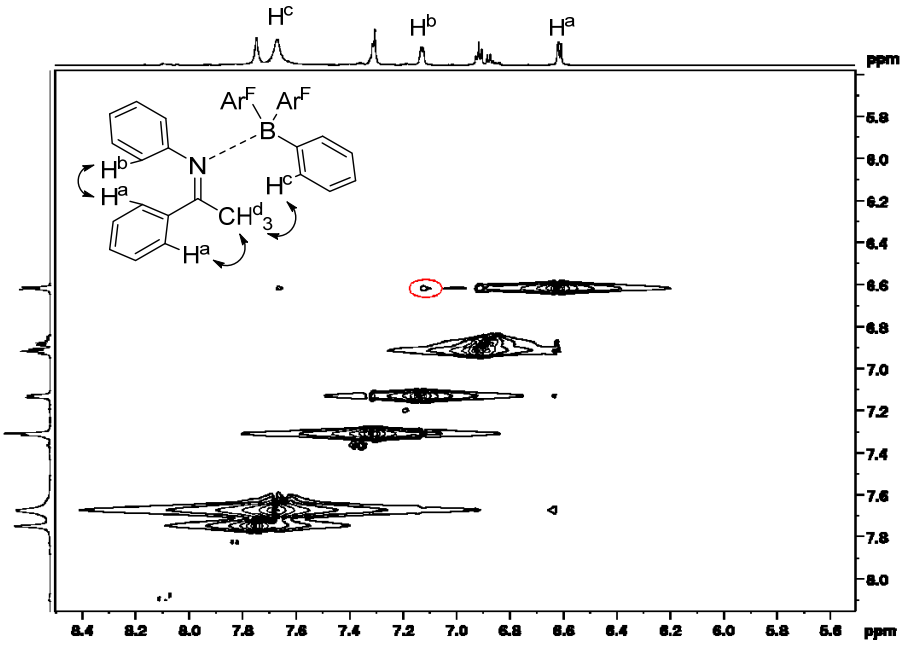


Figure S6. Part of a H,H-NOESY spectroscopy (700 MHz, CD_2Cl_2, 600 ms mixing time) showing NOEs from H^a and H^b. The correlations between H^a and H^d, H^c and H^d, H^c and H^b are also observed (not shown).

Step 2: HBpin (5.1 mg, 0.04 mmol, 1.0 equiv) was added to the in-situ generated Lewis adduct **5a**. The resulting mixture was then immediately monitored by ^{1}H NMR and ^{11}B NMR spectroscopy. Formation of traces amount of hydroboration product **3a** were observed, and full conversion was reached after 17 h, and BAr^{F}_{3} was recovered.

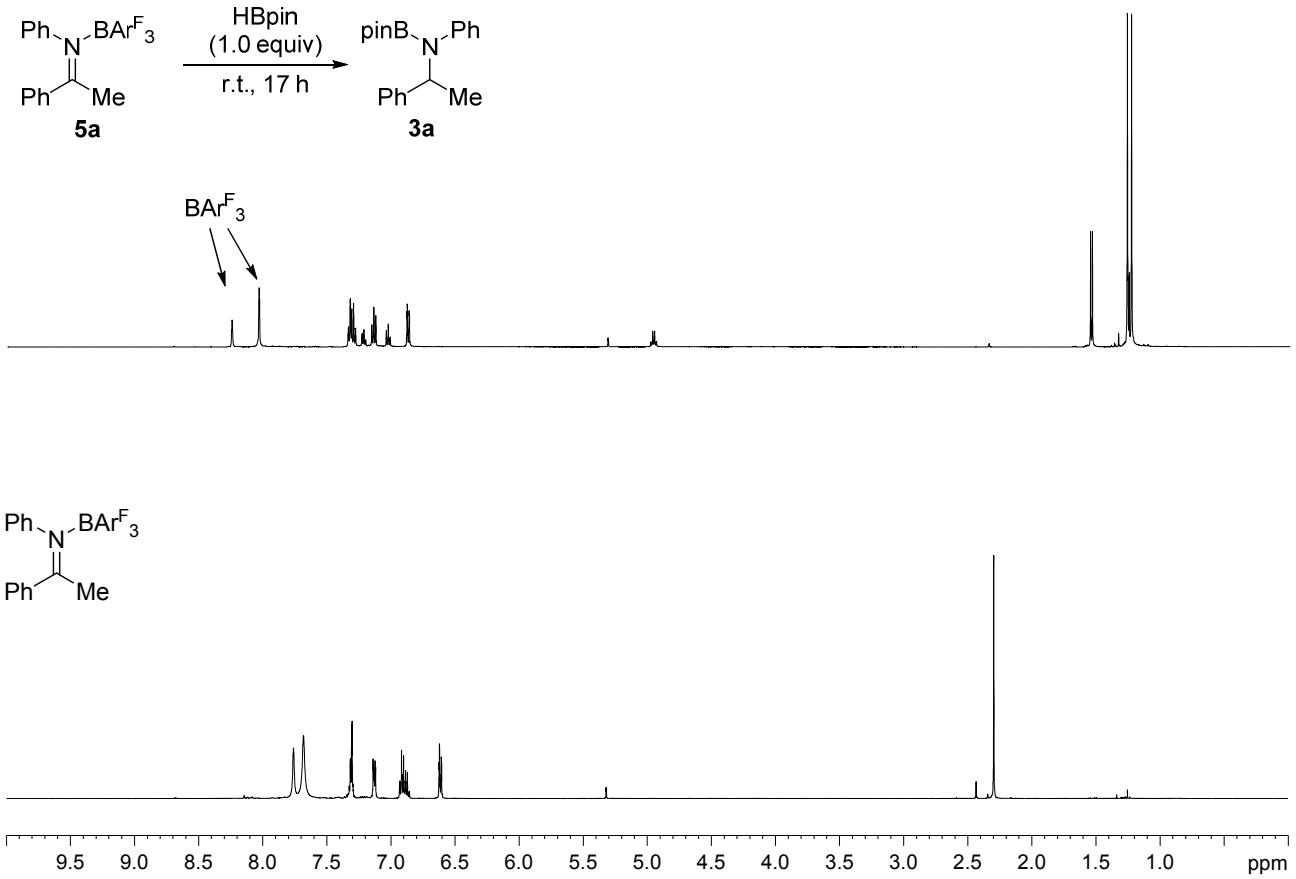


Figure S7. Monitoring the reaction of in situ generated Lewis adduct **5a** with HBpin (1 equiv) by ^{1}H NMR spectroscopy (500 MHz, CD_2Cl_2).

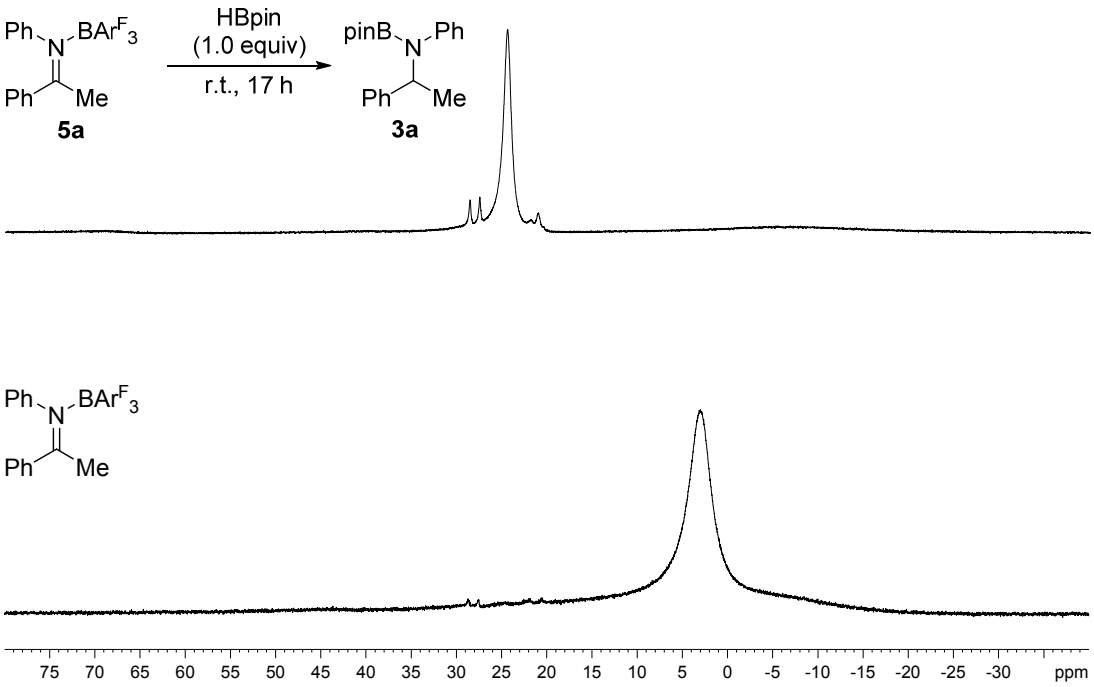
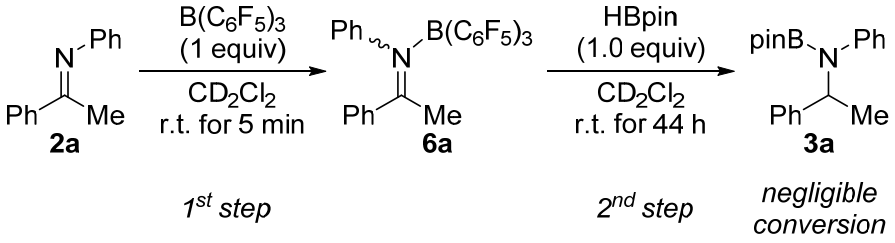


Figure S8. Monitoring the reaction of in-situ generated Lewis adduct **5a** with HBpin (1 equiv) by ^{11}B NMR spectroscopy (160 MHz, CD_2Cl_2).



Scheme S4. Probing the stoichiometric reaction of ketimine (**2a**) and HBpin in the presence of $B(C_6F_5)_3$.

Step 1: Generation of Lewis pair **6a**

In a glove box, ketimine (**2a**, 5.0 mg, 0.026 mmol, 1.0 equiv) and $B(C_6F_5)_3$ (13.1 mg, 0.026 mmol, 1.0 equiv) were dissolved in CD_2Cl_2 (0.5 mL) in a dried J. Young NMR tube. The reaction mixture was shaken for 5 min and monitored by ^{1}H NMR, ^{19}F NMR, and ^{11}B NMR spectroscopy. Formation of the corresponding Lewis pair **6a** was observed. Restricted rotation around the B−N and B−C bonds was seen in the ^{19}F NMR spectrum; we ascribe this to the steric bulk of $B(C_6F_5)_3$.[11]

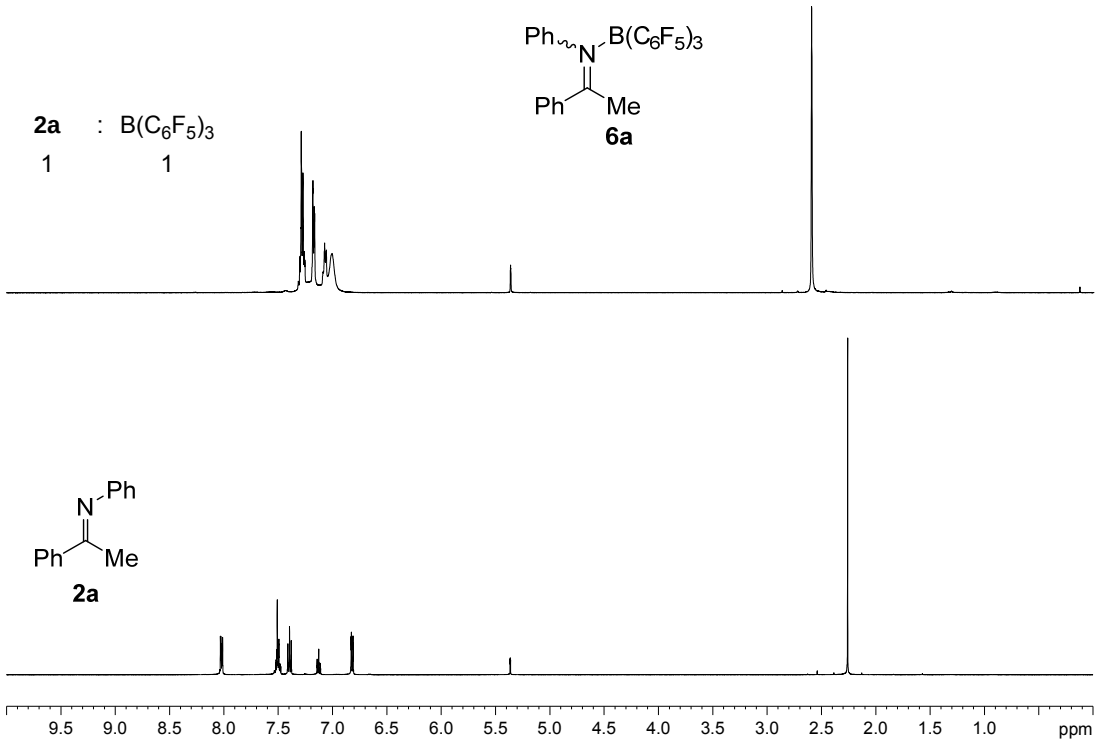


Figure S9. Monitoring the interaction of ketimine (**2a**) and $B(C_6F_5)_3$ by ^1H NMR spectroscopy (500 MHz, CD_2Cl_2).

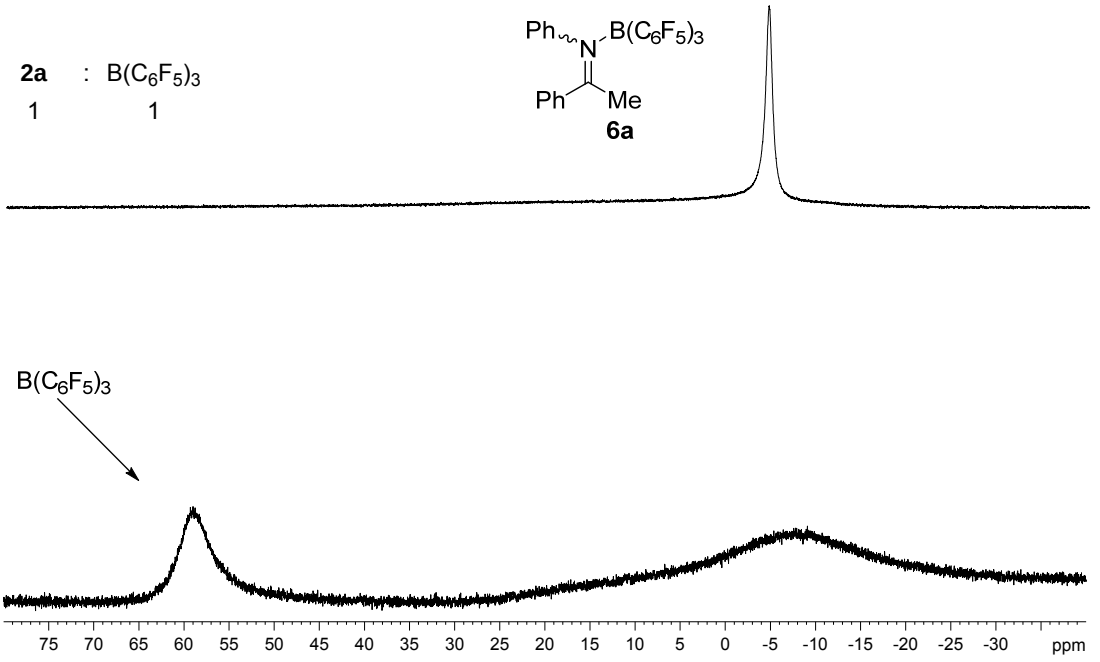


Figure S10. Monitoring the interaction of ketimine (**2a**) and $B(C_6F_5)_3$ by ^{11}B NMR spectroscopy (160 MHz, CD_2Cl_2).

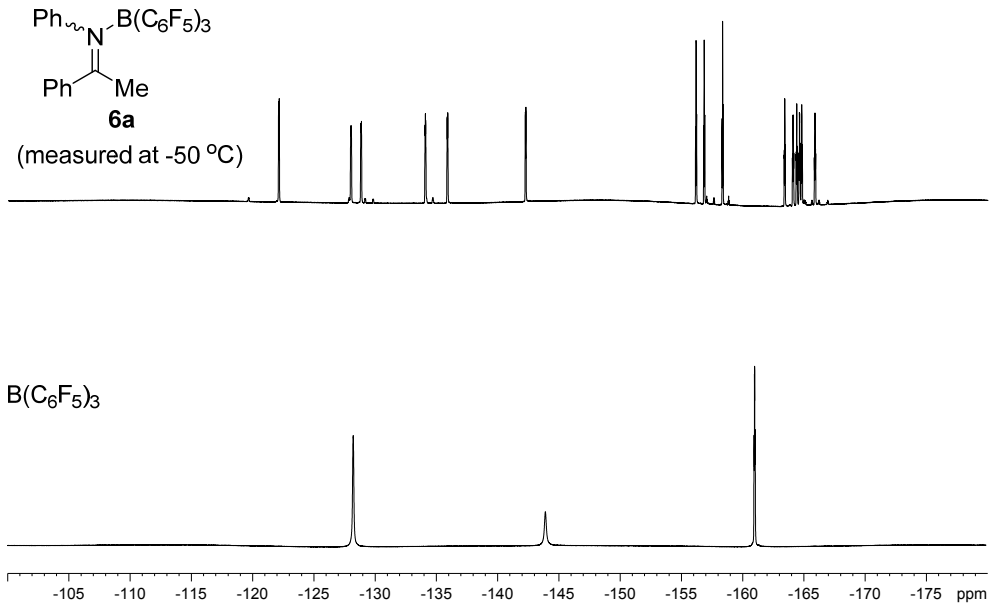


Figure S11. Monitoring the interaction of ketimine (**2a**) and $B(C_6F_5)_3$ by ^{19}F NMR spectroscopy (471 MHz, CD_2Cl_2).

Step 2: HBpin (3.3 mg, 0.026 mmol, 1.0 equiv) was added to the in-situ generated Lewis adduct **6a**. The resulting mixture was then immediately monitored by ^{1}H NMR and ^{11}B NMR spectroscopy. Formation of only traces amounts of hydroboration product **3a** was observed after 44 h.

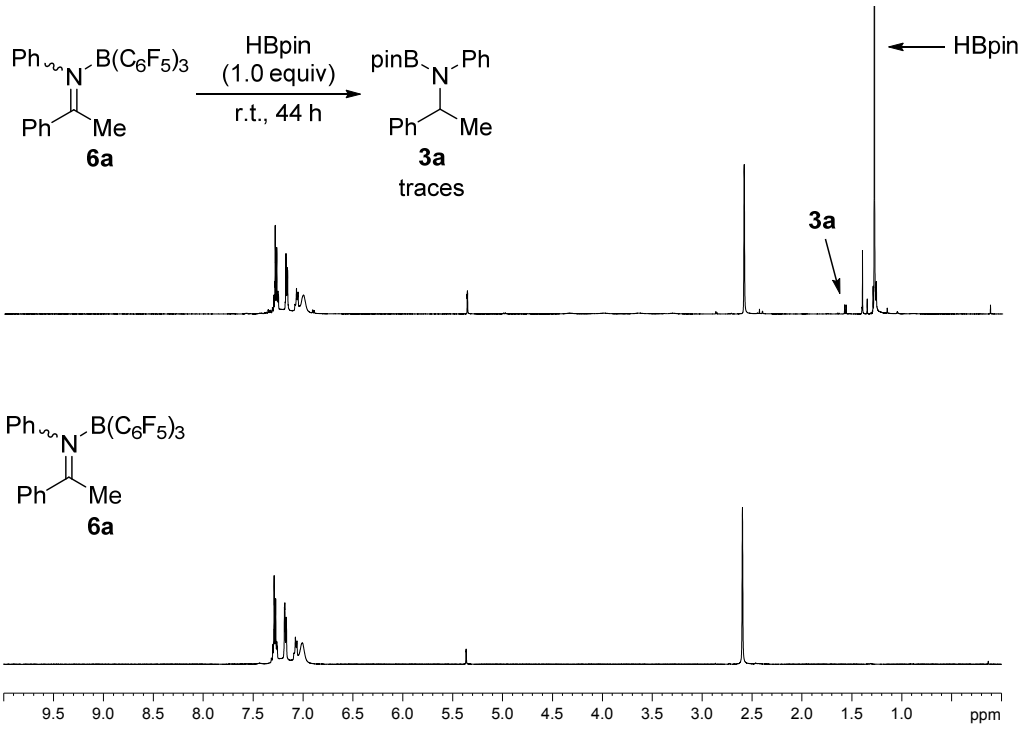


Figure S12. Monitoring the reaction of in situ generated Lewis adduct **6a** with HBpin (1 equiv) by ^{1}H NMR spectroscopy (500 MHz, CD_2Cl_2).

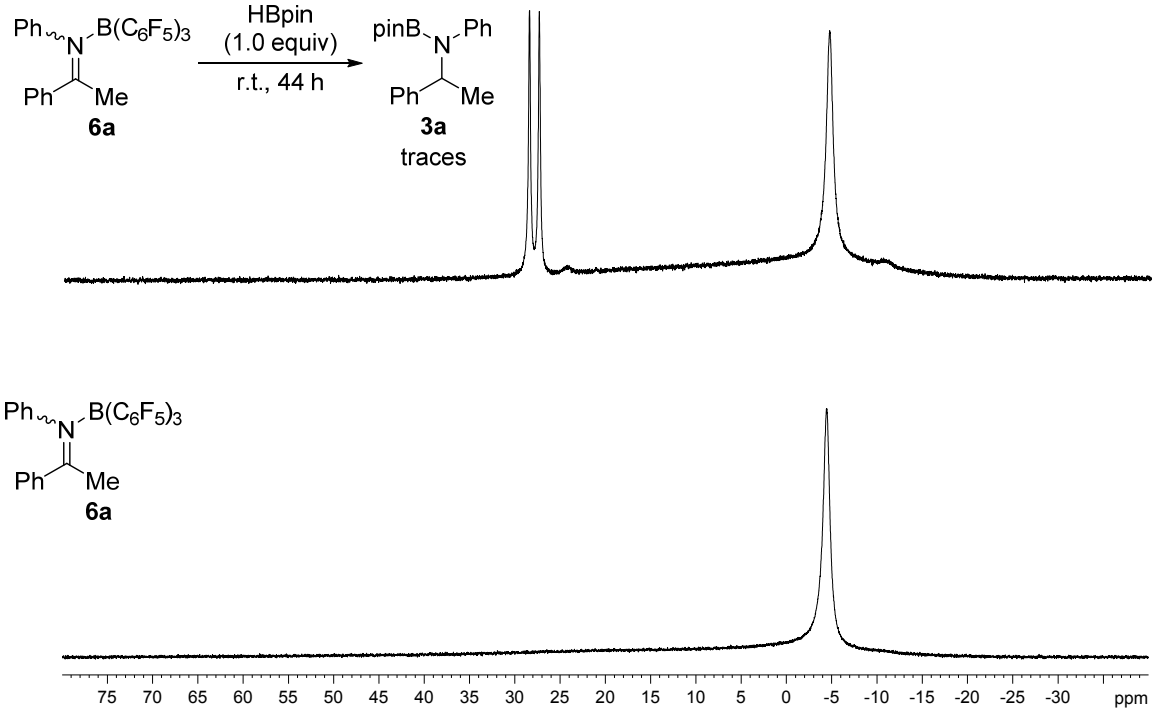
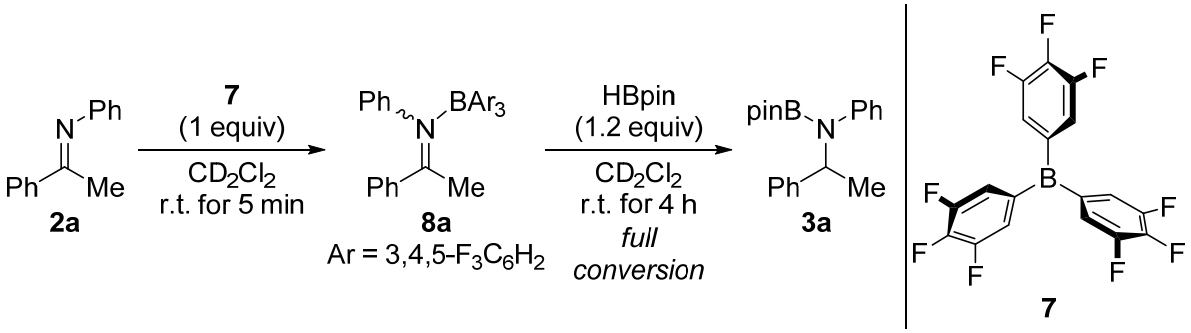


Figure S13. Monitoring the reaction of in situ generated Lewis adduct **6a** with HBpin (1 equiv) by ^{11}B NMR spectroscopy (160 MHz, CD_2Cl_2).



Scheme S5. Probing the stoichiometric reaction of ketimine (**2a**) and HBpin in the presence of **7**.

Step 1: Generation of Lewis pair **8a**

In a glove box, ketimine (**2a**, 5.0 mg, 0.026 mmol, 1.0 equiv) and **7** (10.0 mg, 0.026 mmol, 1.0 equiv) were dissolved in CD_2Cl_2 (0.5 mL) in a dried J. Young NMR tube. The reaction mixture was shaken for 5 min and monitored by ^1H NMR, ^{19}F NMR, and ^{11}B NMR spectroscopy. Formation of the corresponding Lewis pair **8a** was observed. **8a** is a mixture of *cis* and *trans* adducts.

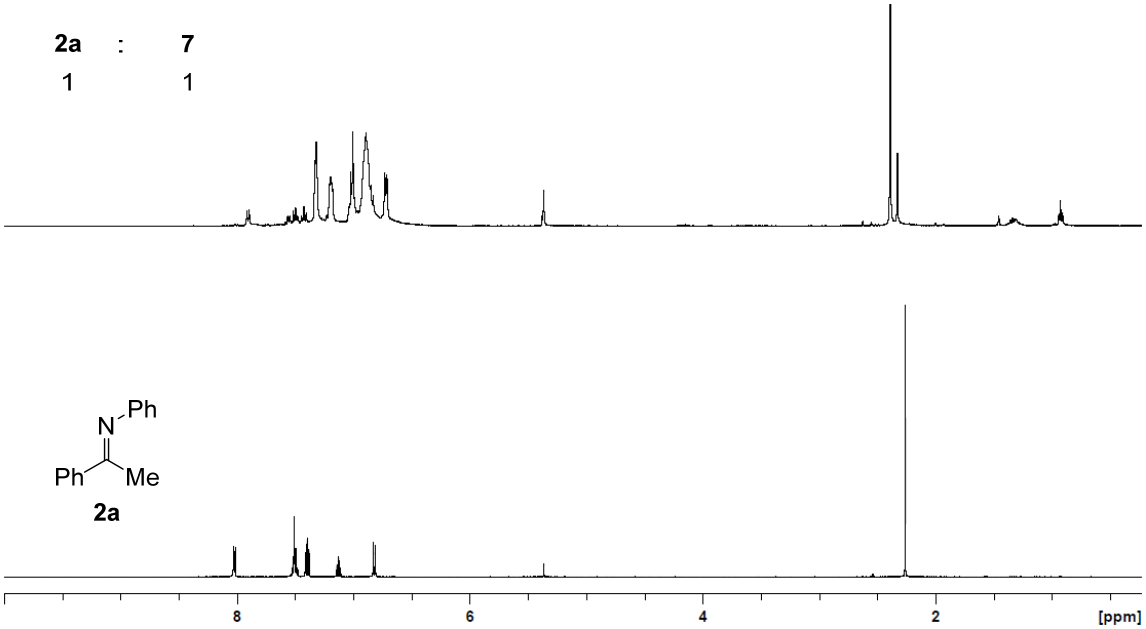


Figure S14. Monitoring the interaction of ketimine (**2a**) and **7** by ^{1}H NMR spectroscopy (400 MHz, CD_2Cl_2; For ^{1}H NMR spectroscopy of **2a**: 500 MHz, CD_2Cl_2).

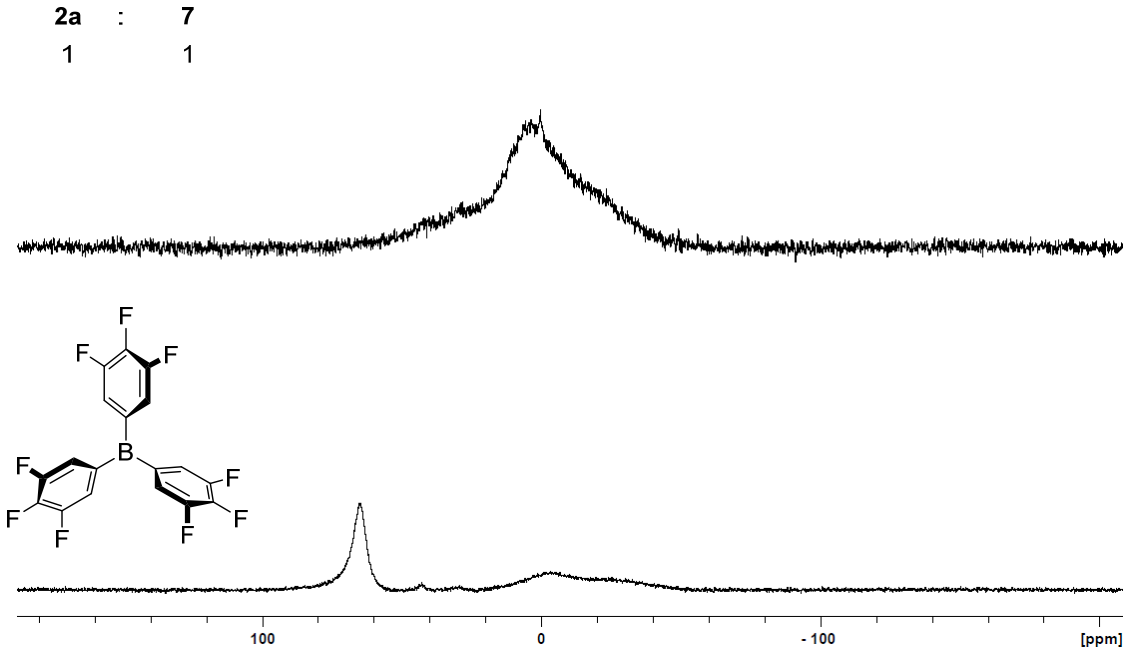


Figure S15. Monitoring the interaction of ketimine (**2a**) and **7** by ^{11}B NMR spectroscopy (128 MHz, CD_2Cl_2).

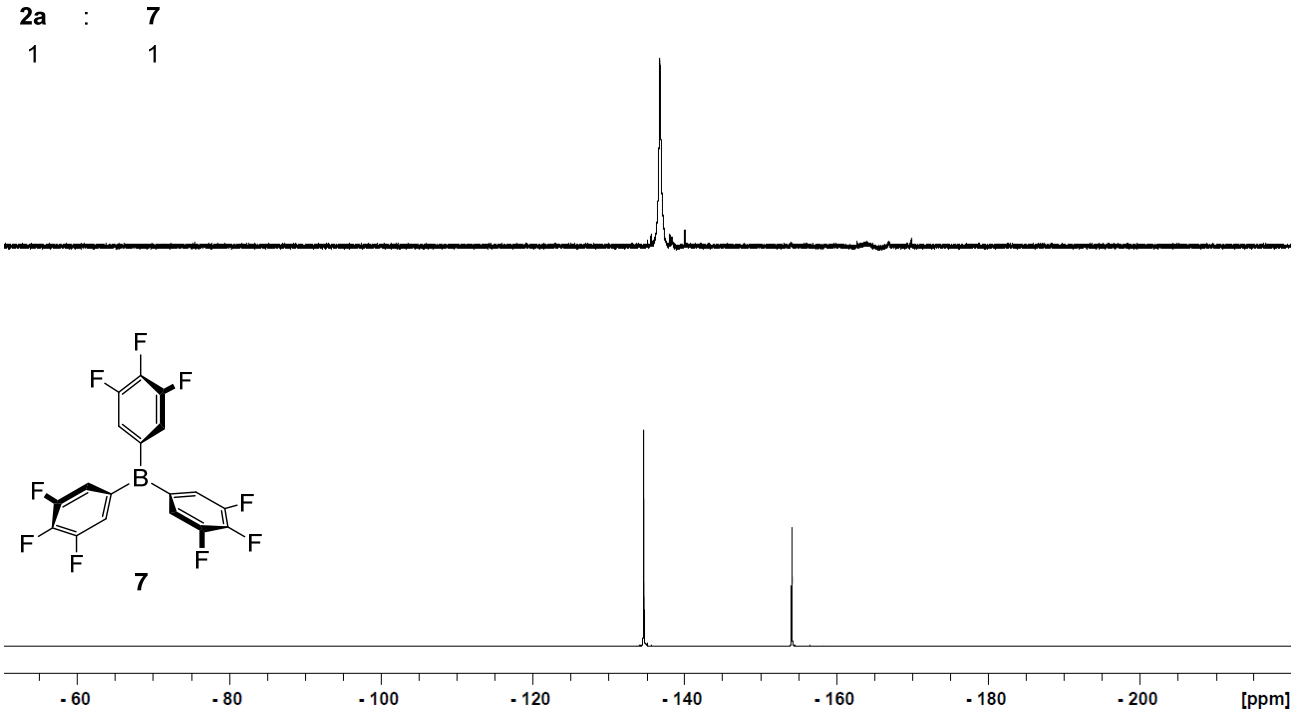


Figure S16. Monitoring the interaction of ketimine (**2a**) and **7** by ^{19}F NMR spectroscopy (376 MHz, CD_2Cl_2).

Step 2: HBpin (4.0 mg, 0.026 mmol, 1.2 equiv) was added to the in-situ generated Lewis adduct **8a**. The resulting mixture was then immediately monitored by ^{1}H NMR and ^{11}B NMR spectroscopy. Formation of traces amount of hydroboration product **3a** were observed, and full conversion was reached after 4 h. Borane catalyst **7** was recovered after the reaction, judged from ^{11}B NMR and ^{19}F NMR spectroscopy.

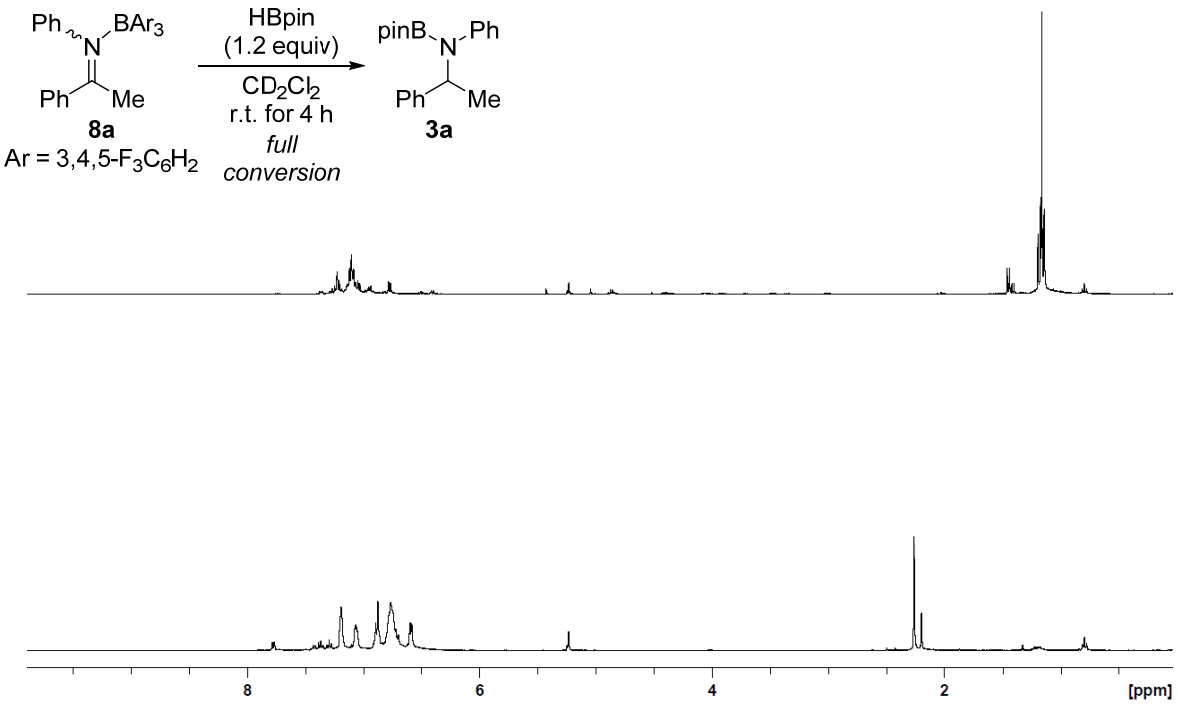


Figure S17. Monitoring the reaction of in situ generated Lewis adduct **8a** with HBpin (1.2 equiv) by ^{1}H NMR spectroscopy (500 MHz, CD_2Cl_2).

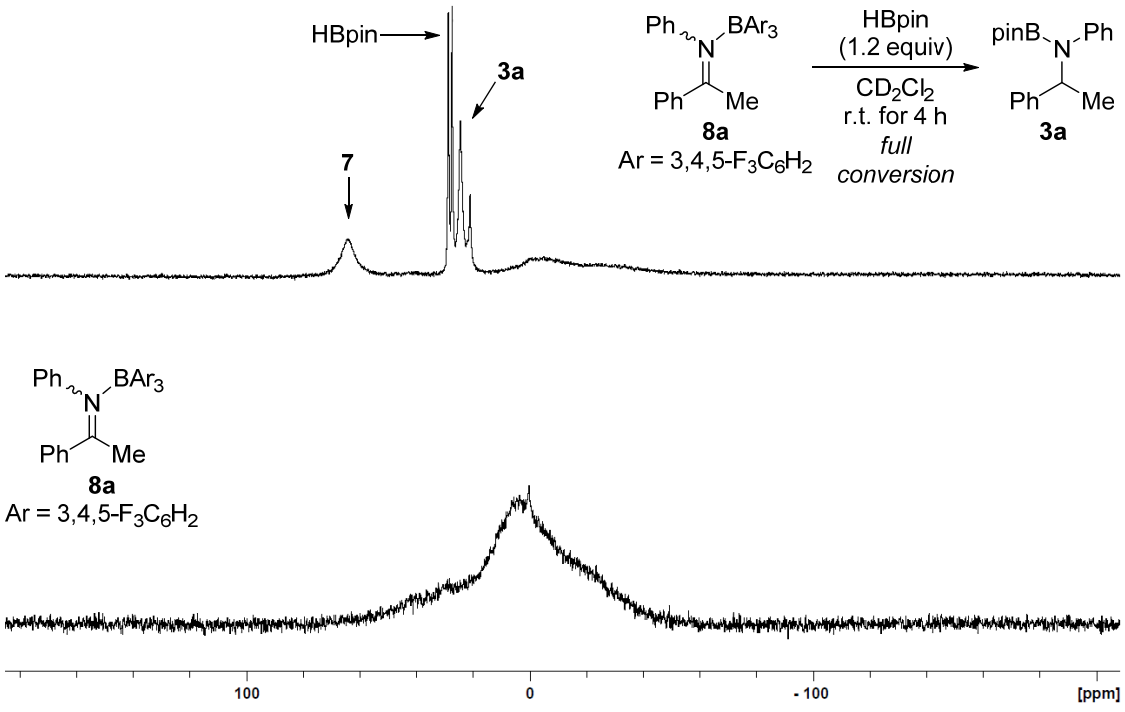


Figure S18. Monitoring the reaction of in-situ generated Lewis adduct **8a** with HBpin (1.2 equiv) by ^{11}B NMR spectroscopy (128 MHz, CD_2Cl_2).

7 NMR Spectra

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(1-phenylethyl)aniline (**4a**).

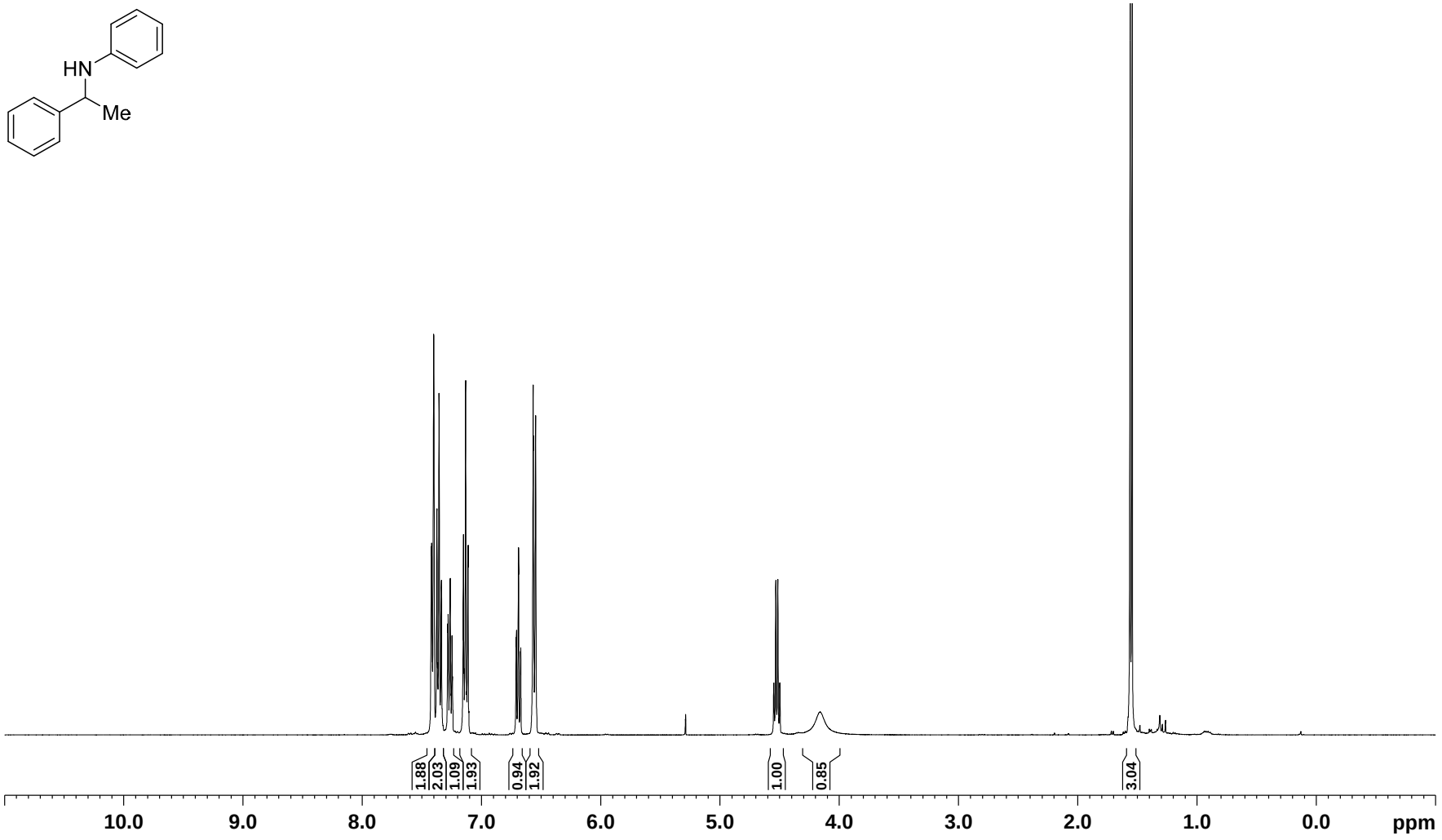


Figure S20. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(1-phenylethyl)aniline (**4a**).

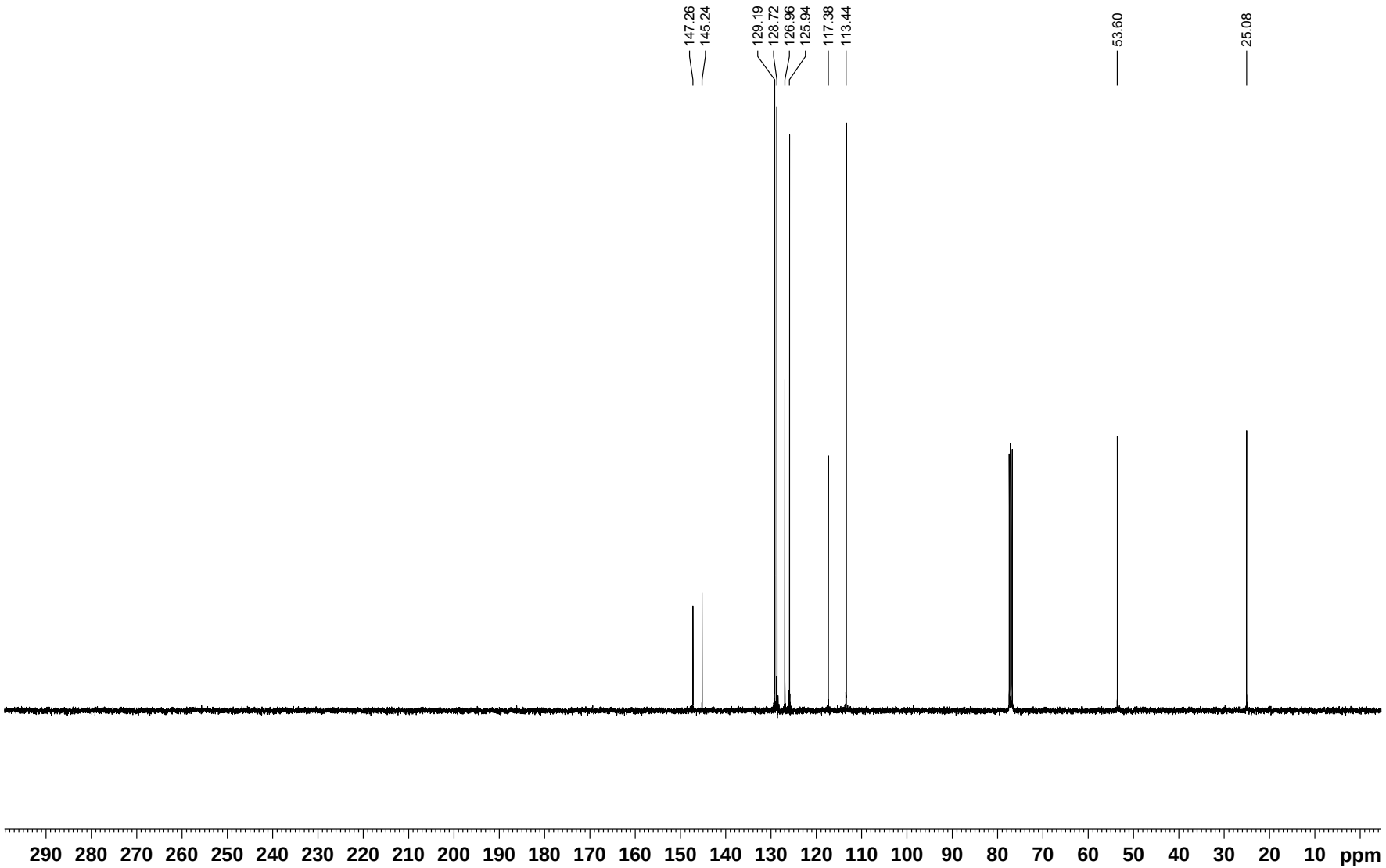


Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) of *N*-(1-(3-bromophenyl)ethyl)aniline (**4b**).

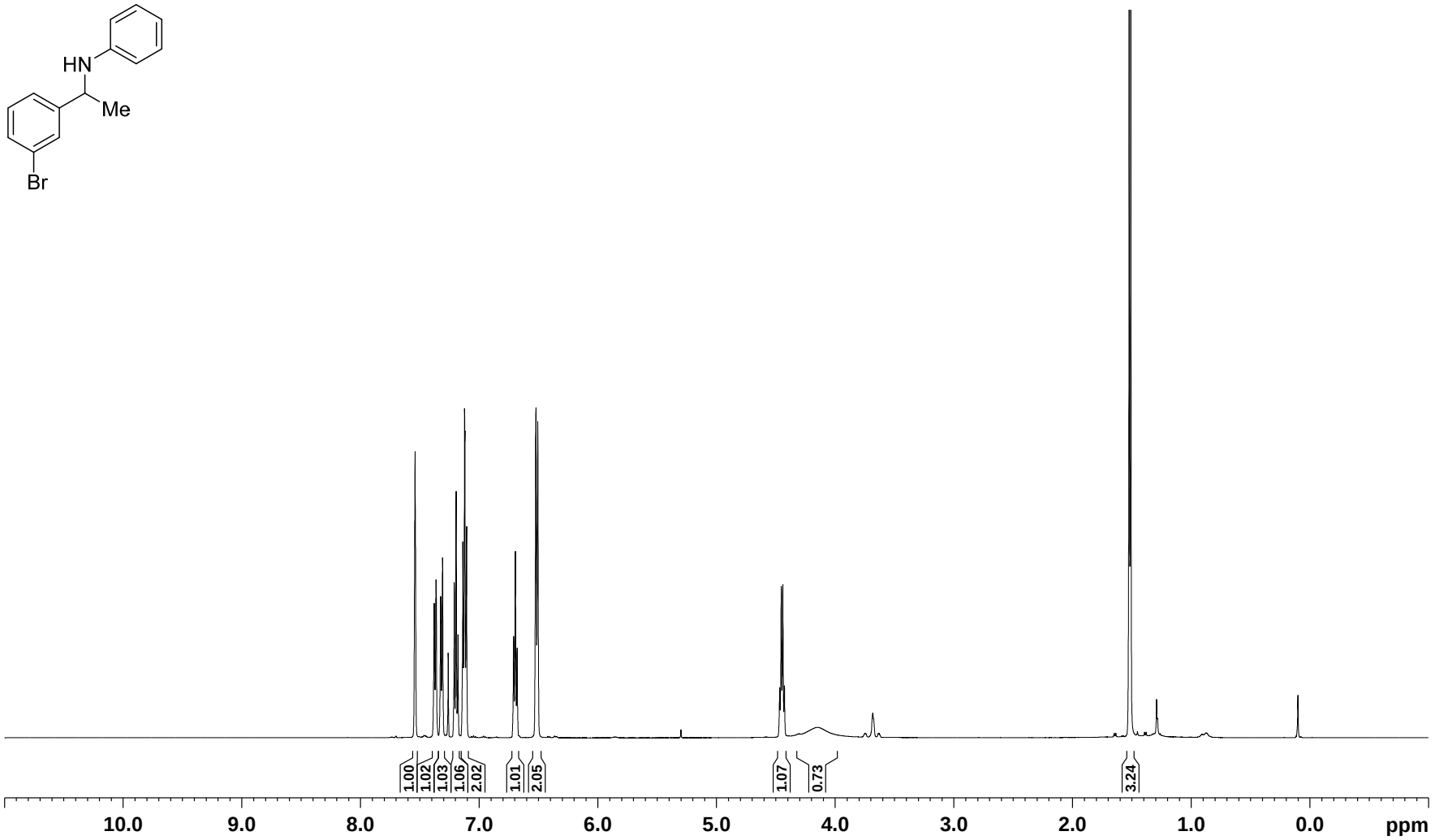


Figure S22. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of *N*-(1-(3-bromophenyl)ethyl)aniline (**4b**).

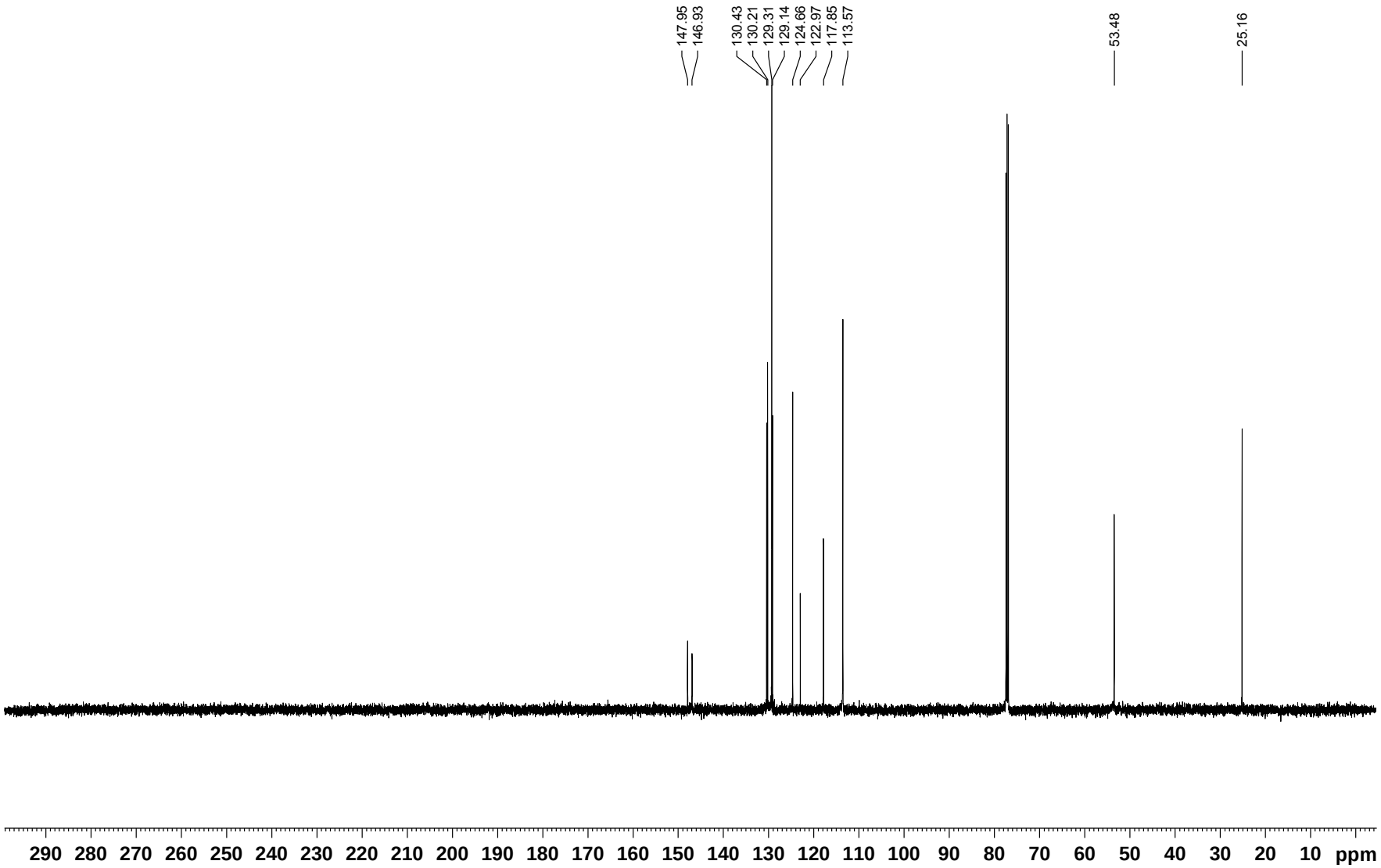


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(1-(4-bromophenyl)ethyl)aniline (**4c**).

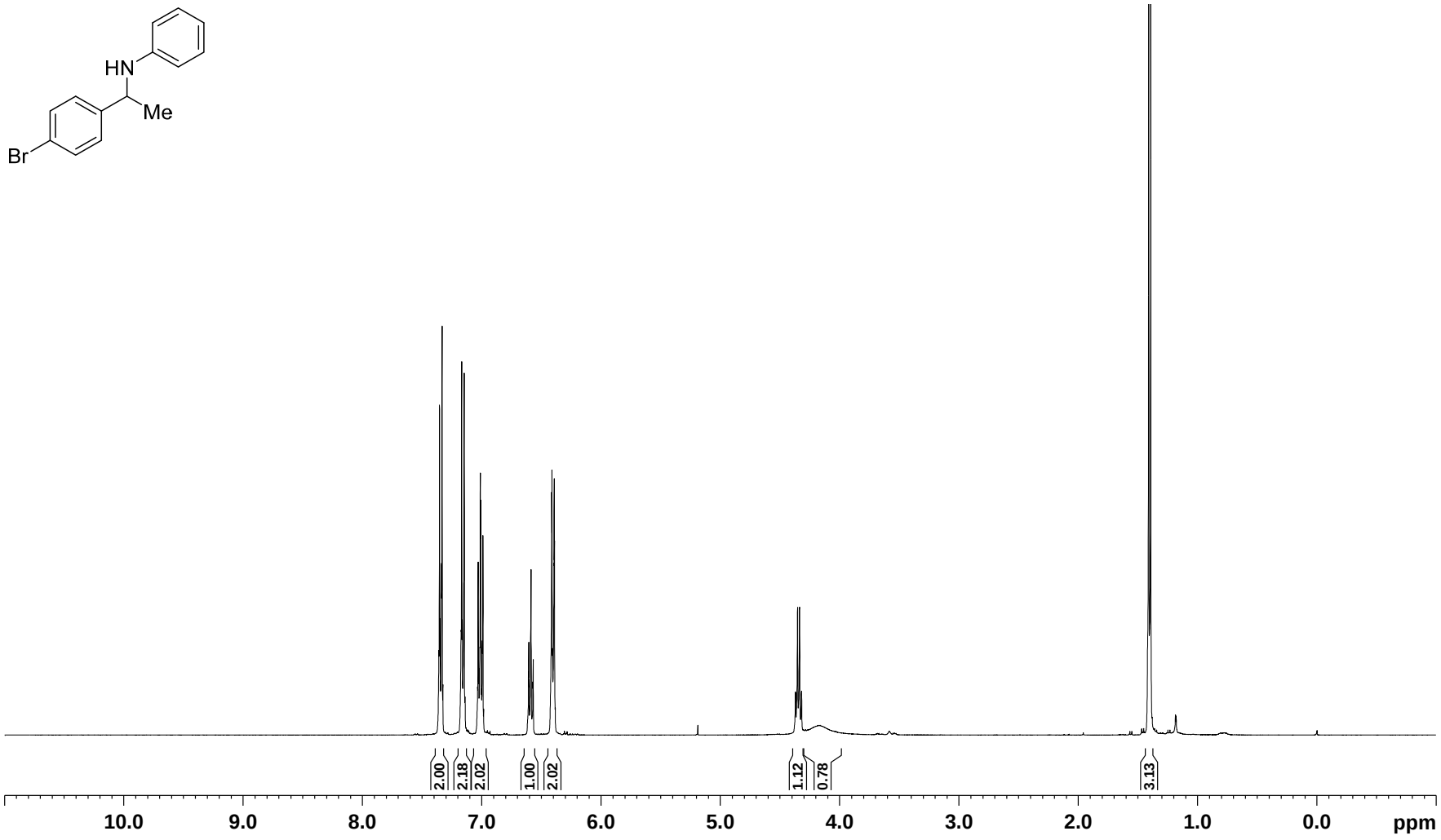


Figure S24. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(1-(4-bromophenyl)ethyl)aniline (**4c**).

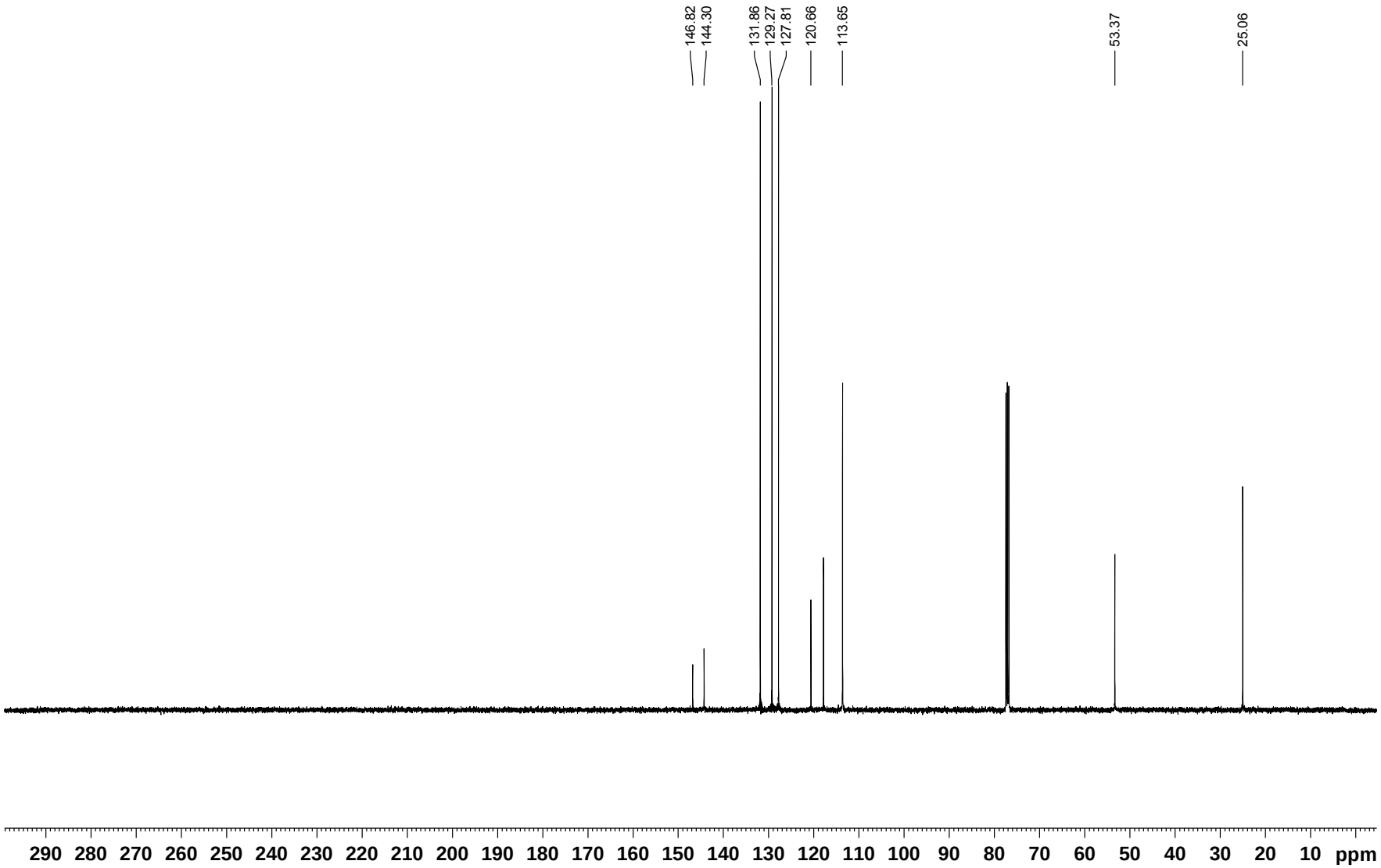


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(1-(4-(trifluoromethyl)phenyl)ethyl)aniline (**4d**).

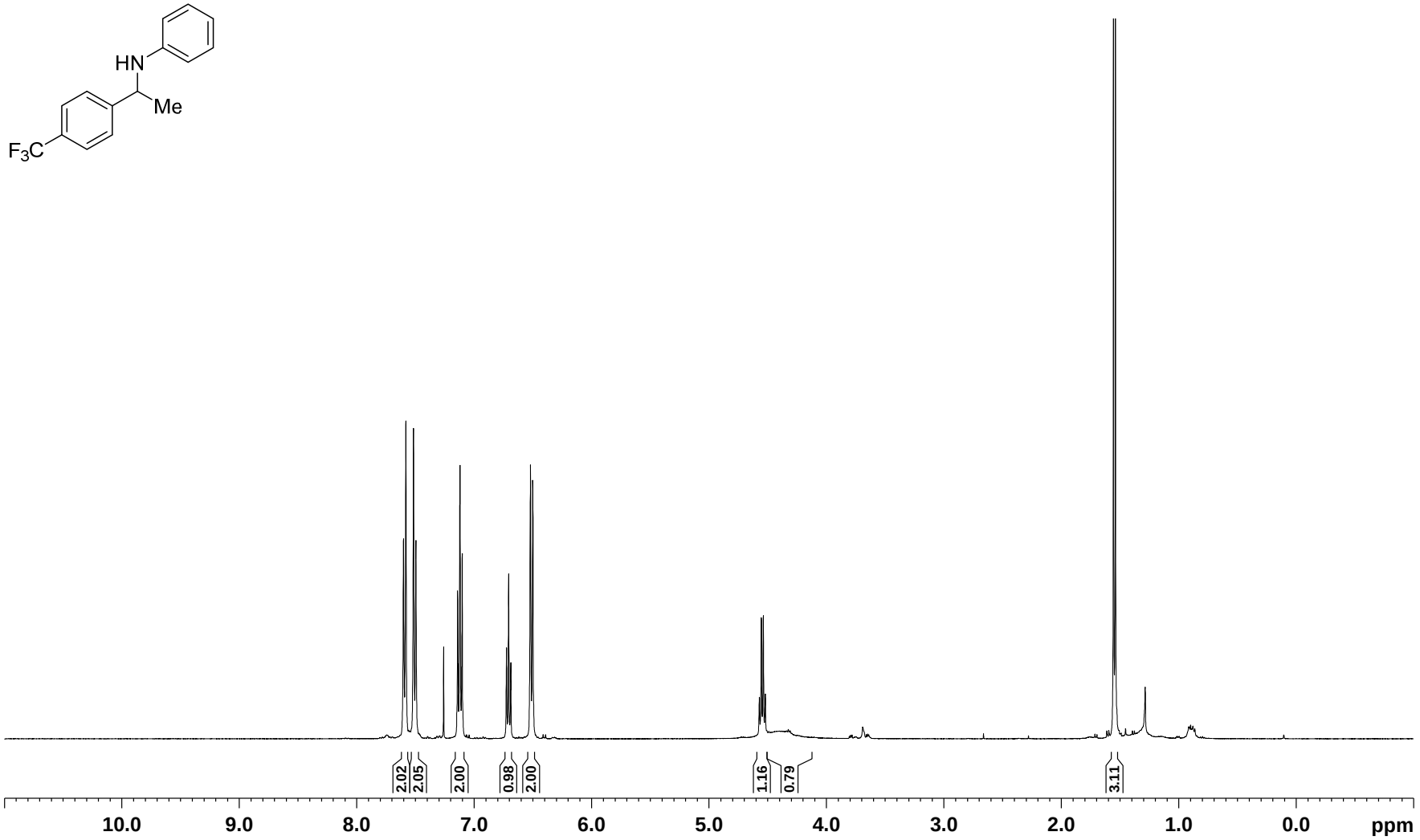


Figure S26. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(1-(4-(trifluoromethyl)phenyl)ethyl)aniline (**4d**).

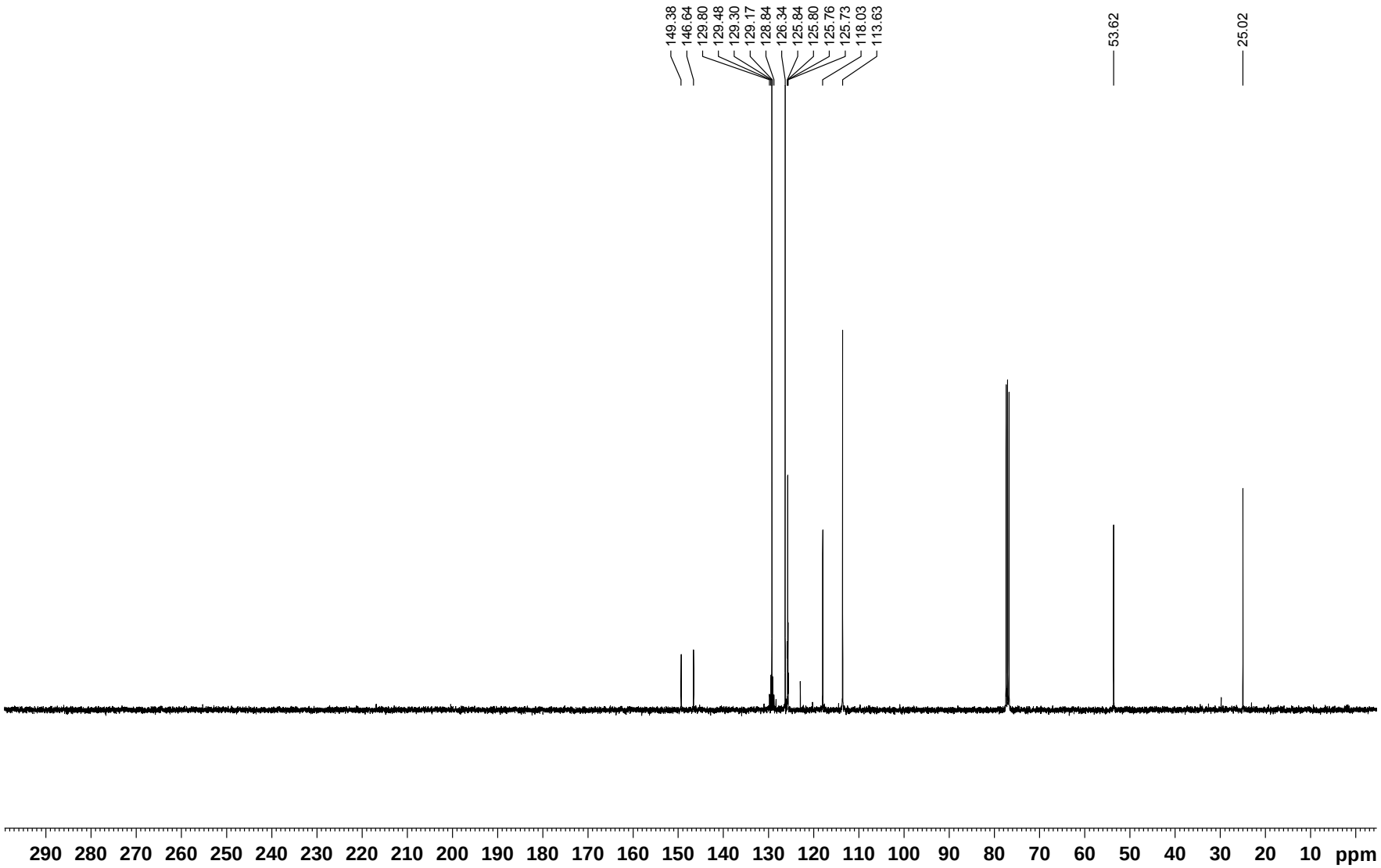


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(1-(3,5-bis(trifluoromethyl)phenyl)ethyl)aniline (**4e**).

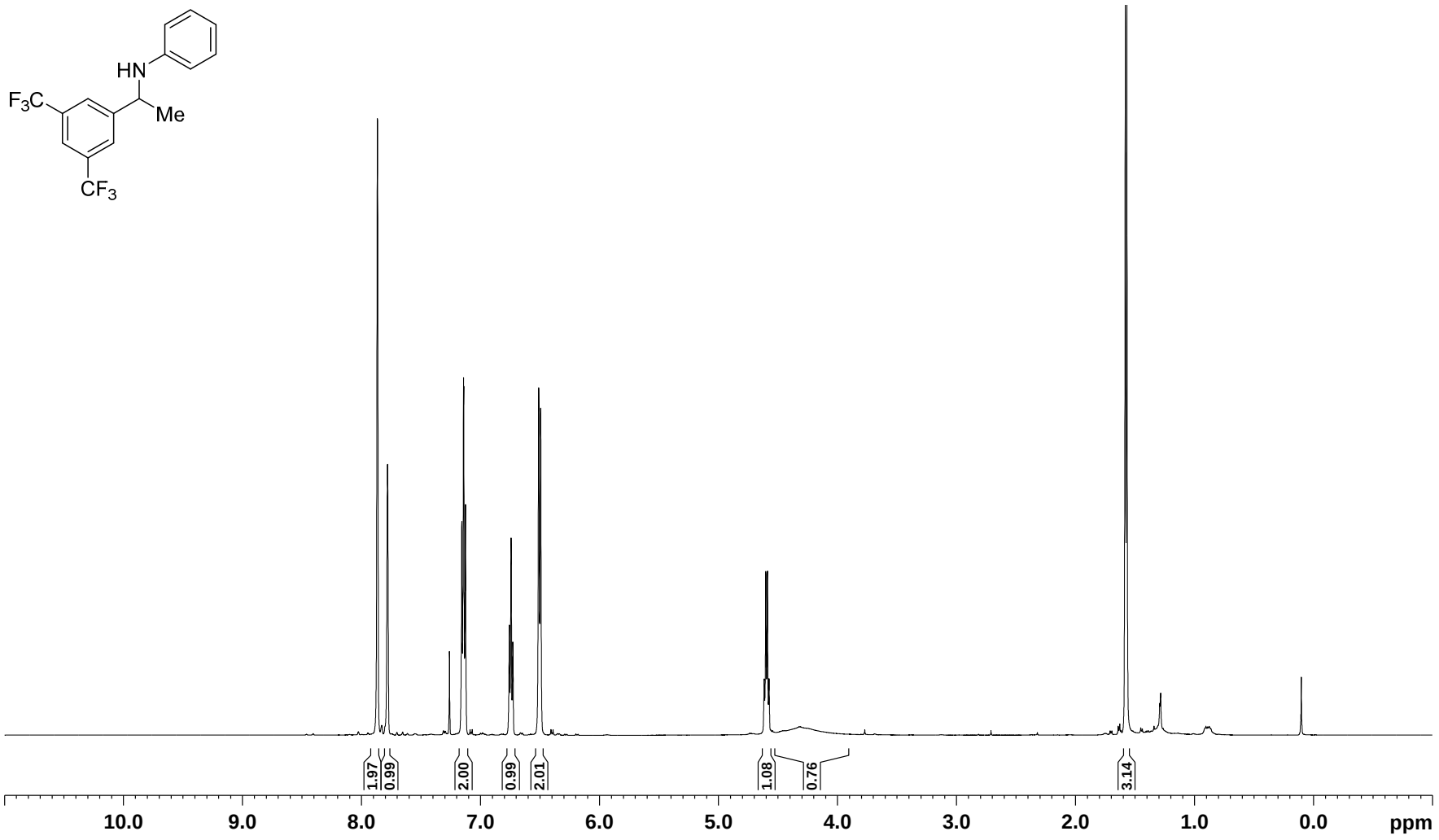


Figure S28. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(1-(3,5-bis(trifluoromethyl)phenyl)ethyl)aniline (**4e**).

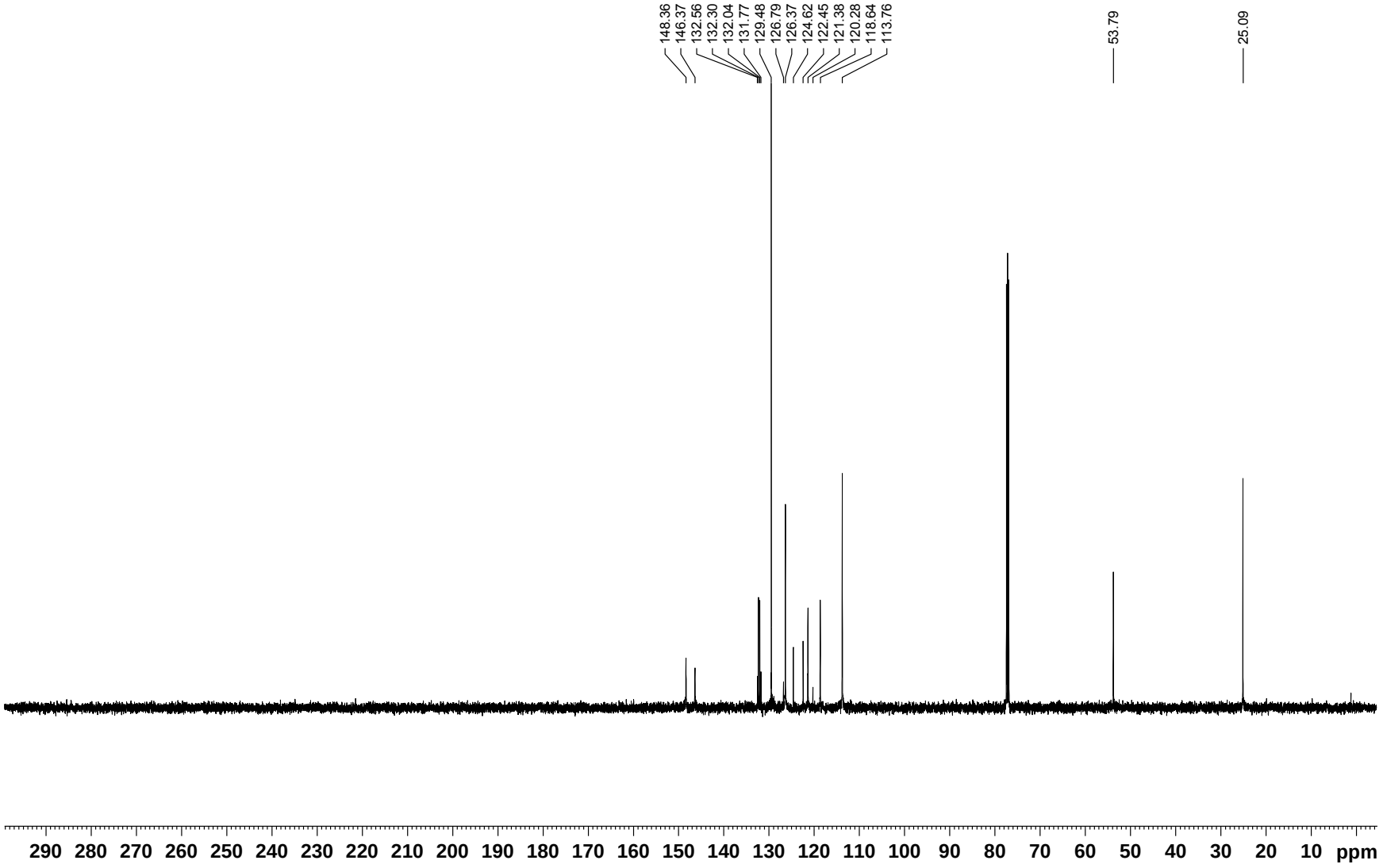


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(1-(3,5-dimethylphenyl)ethyl)aniline (**4f**).

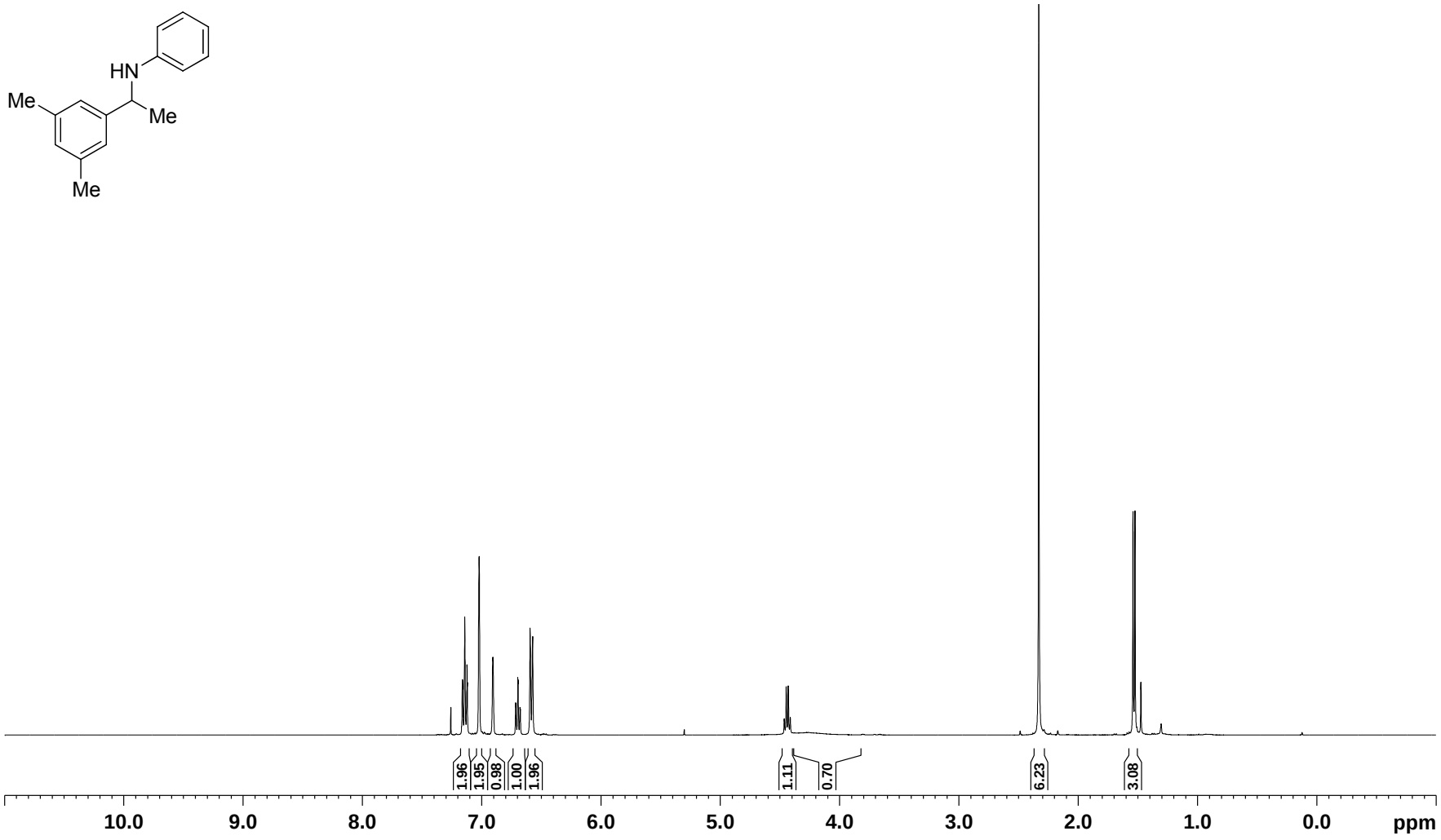


Figure S30. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(1-(3,5-dimethylphenyl)ethyl)aniline (**4f**).

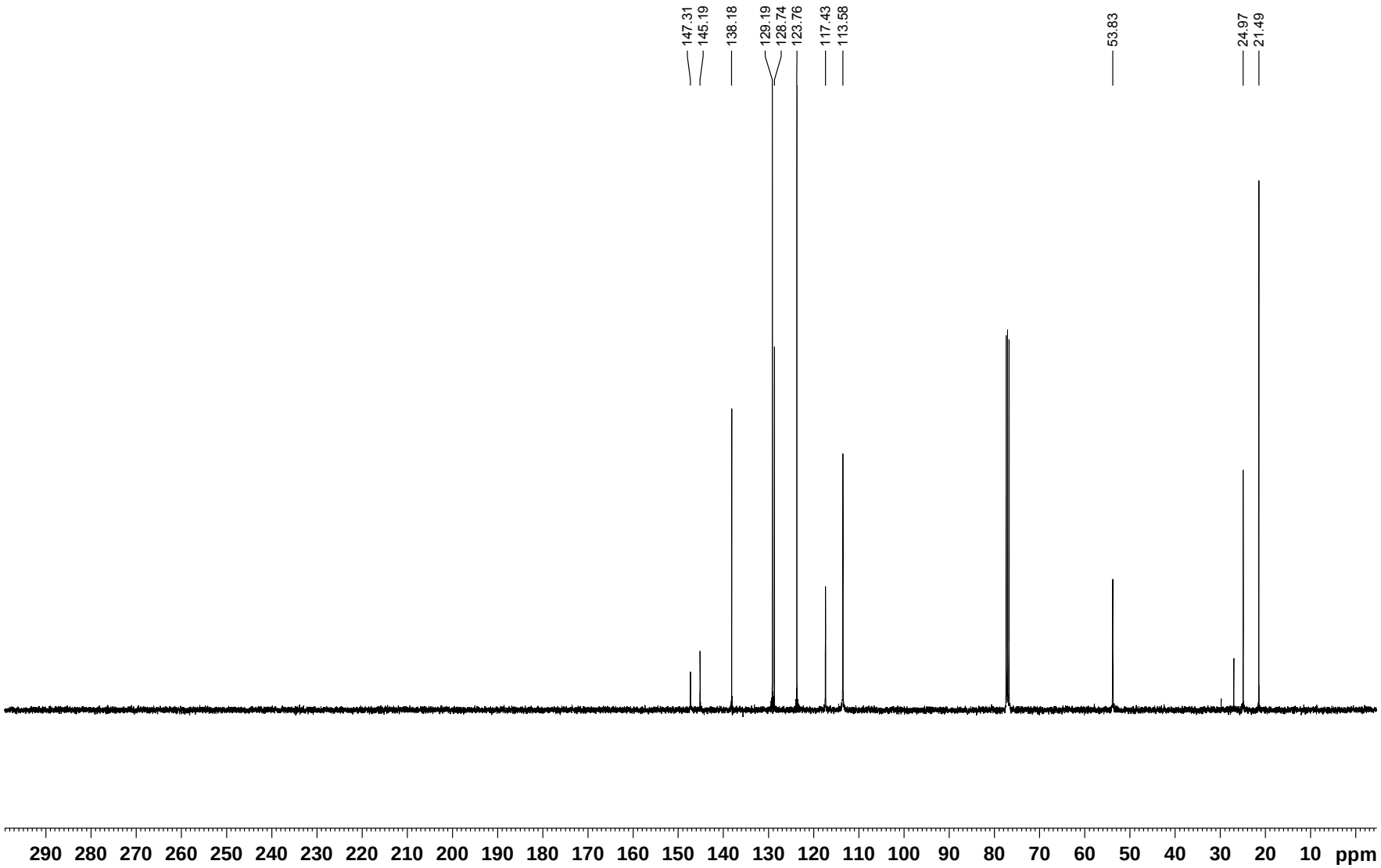


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(1-(naphthalen-2-yl)ethyl)aniline (**4g**).

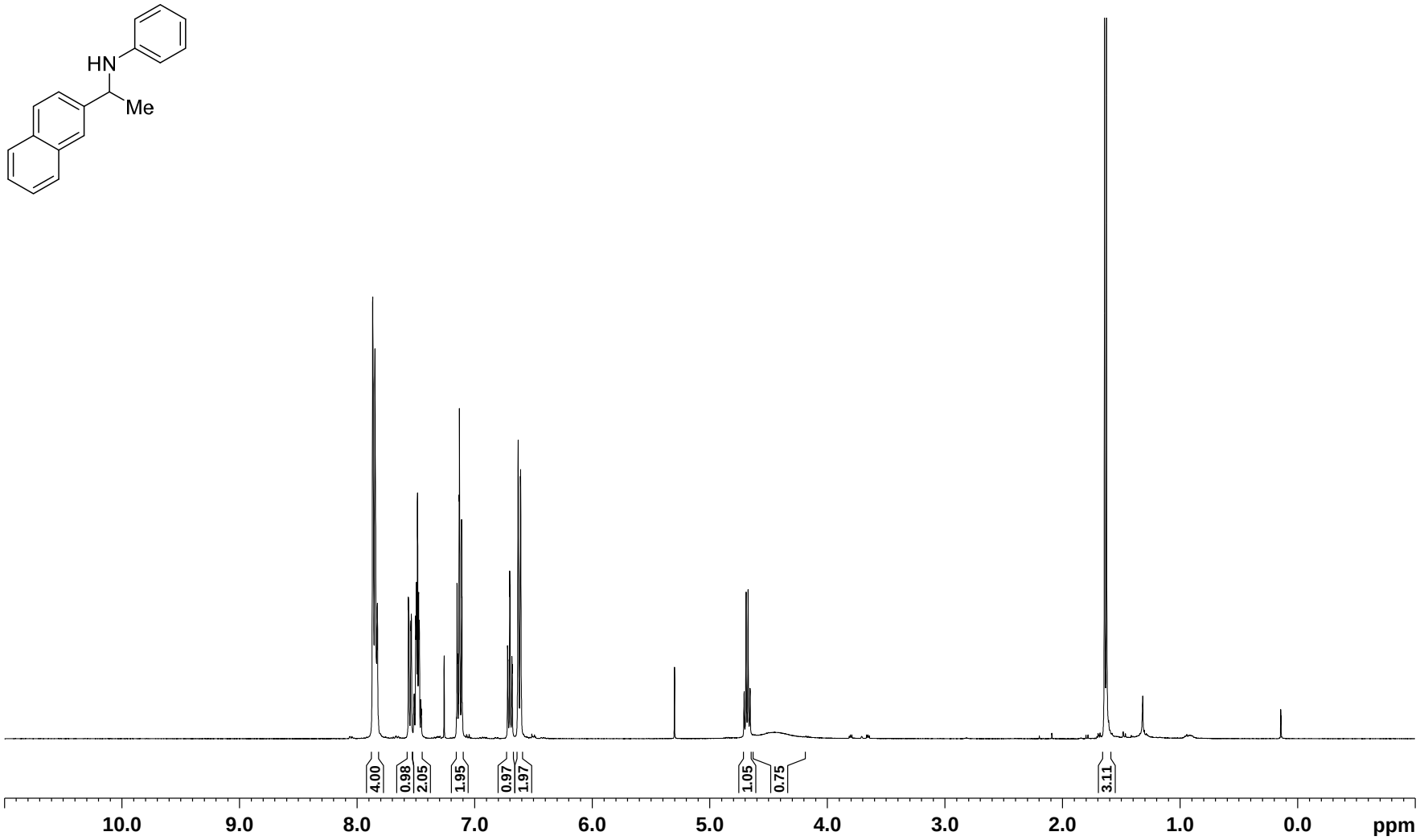


Figure S32. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(1-(naphthalen-2-yl)ethyl)aniline (**4g**).

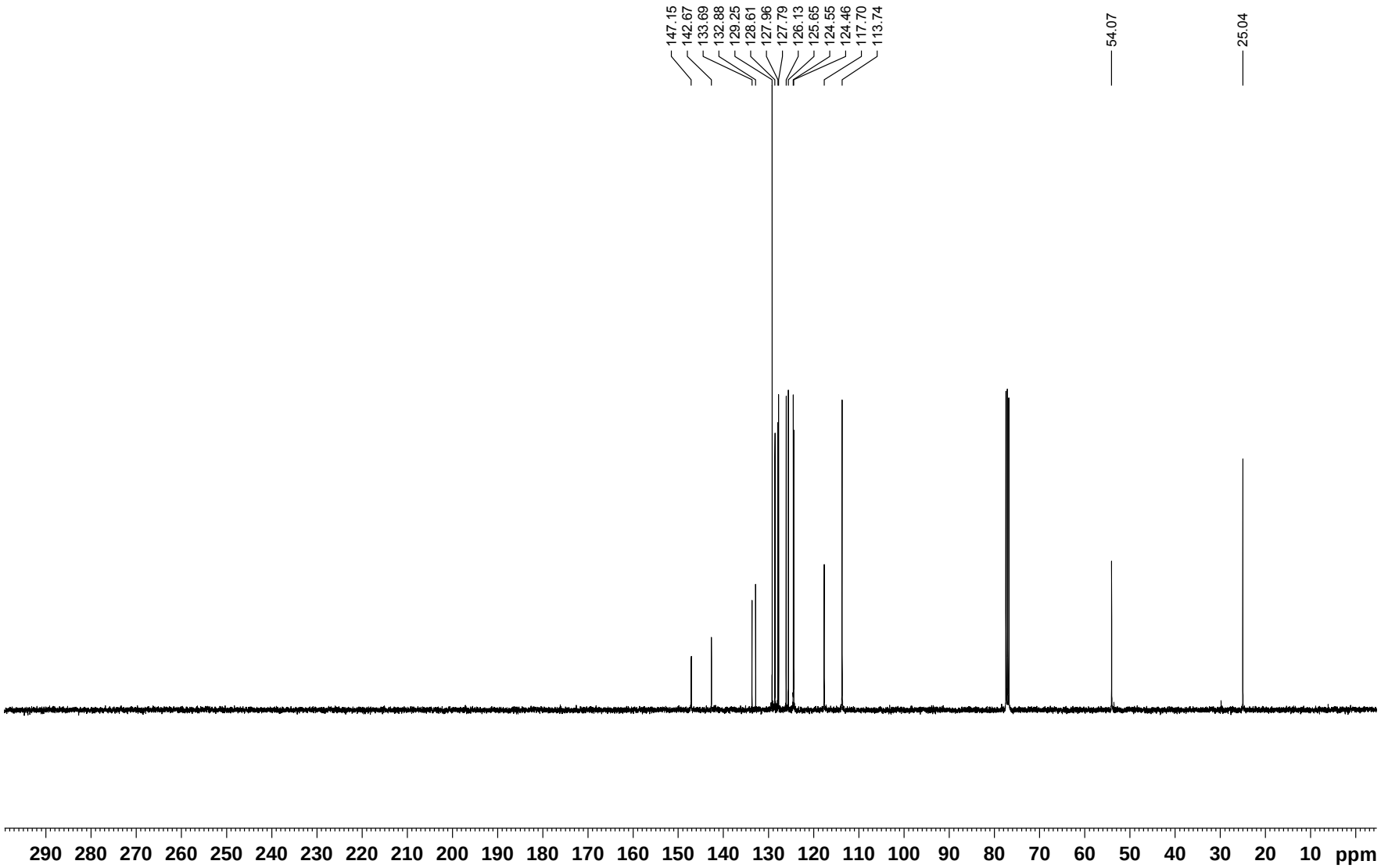


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(1-(naphthalen-1-yl)ethyl)aniline (**4h**).

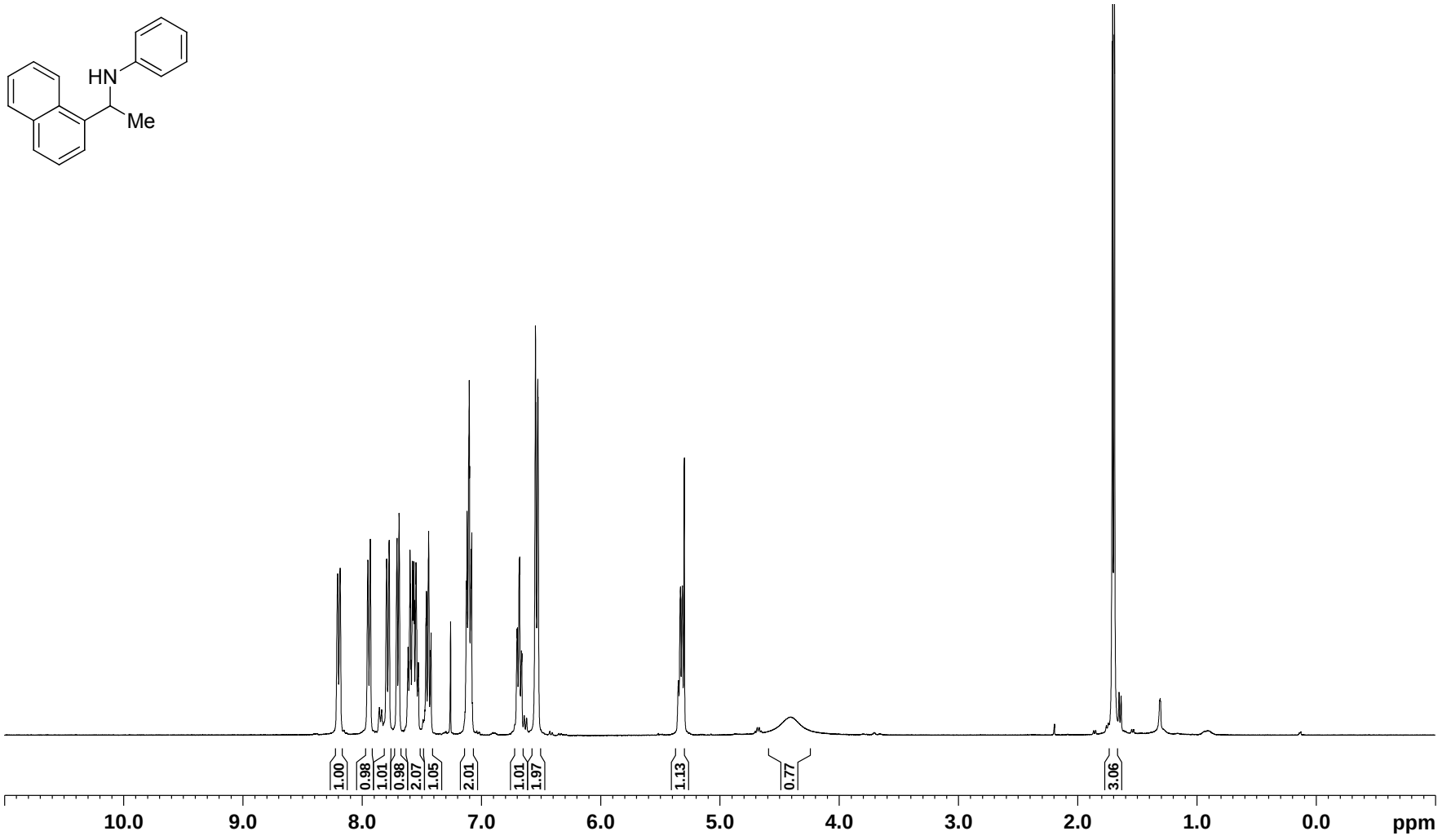


Figure S34. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(1-(naphthalen-1-yl)ethyl)aniline (**4h**).

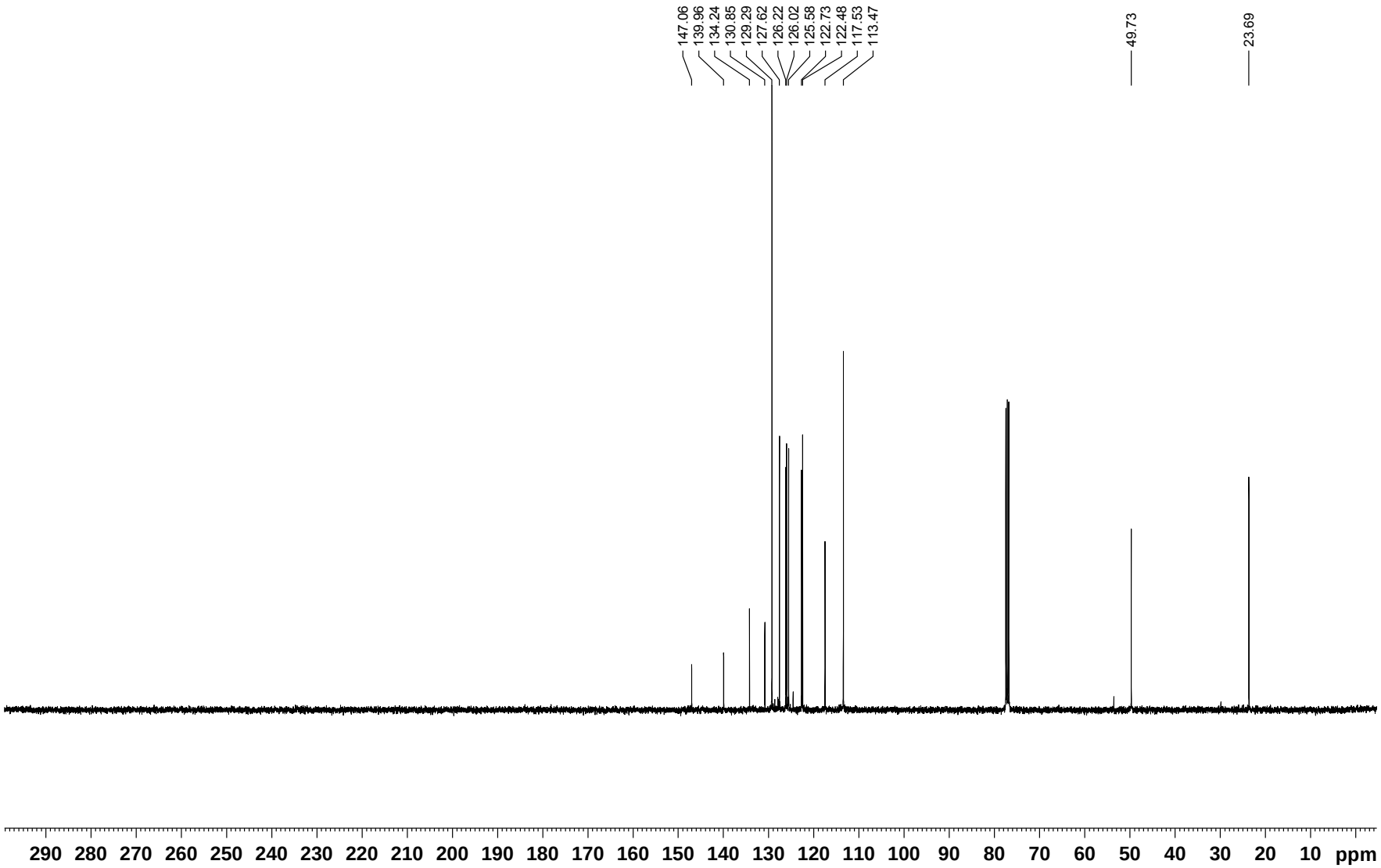


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(1-phenylethyl)-4-(trifluoromethyl)aniline (**4i**).

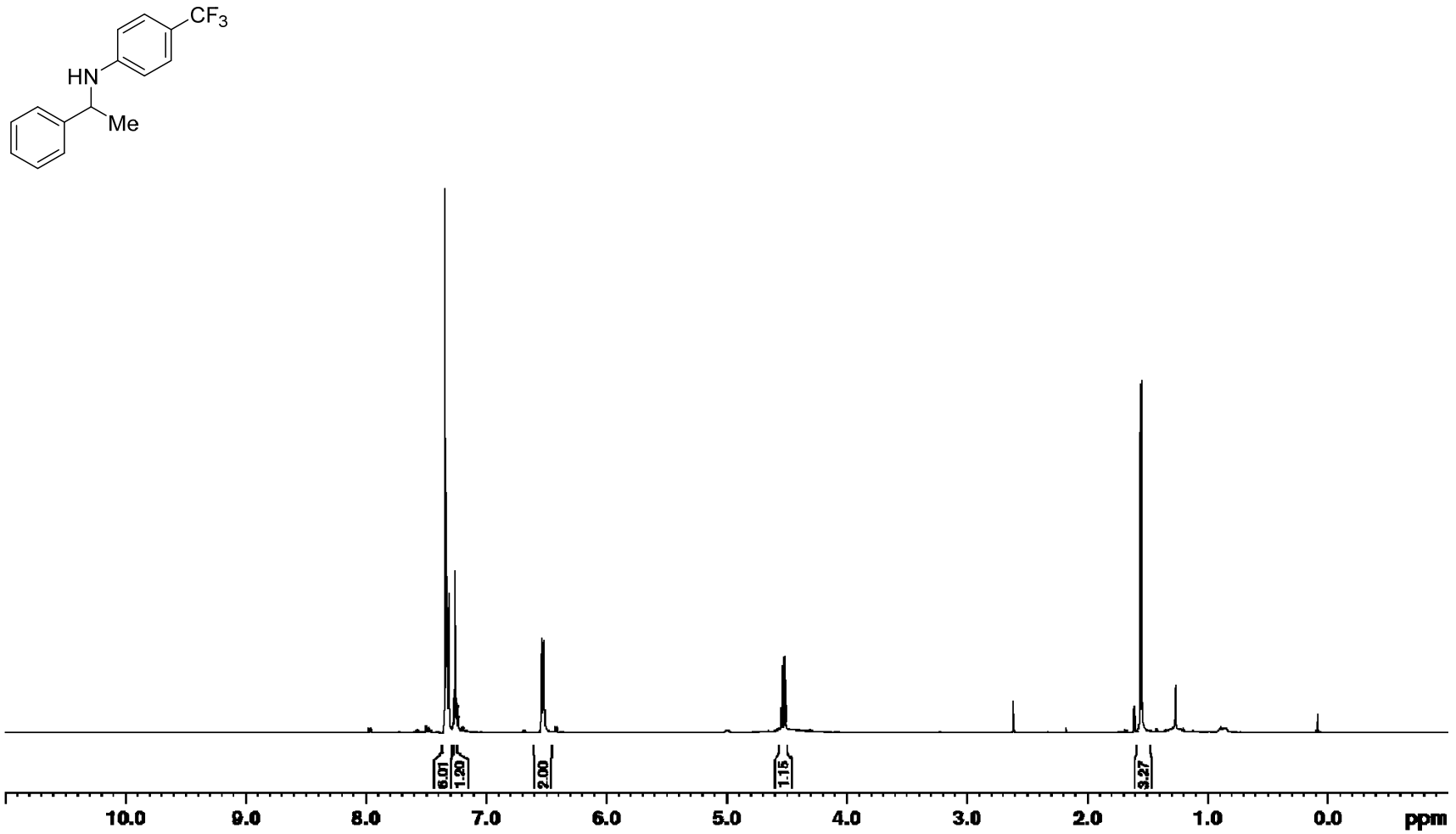


Figure S36. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(1-phenylethyl)-4-(trifluoromethyl)aniline (**4i**).

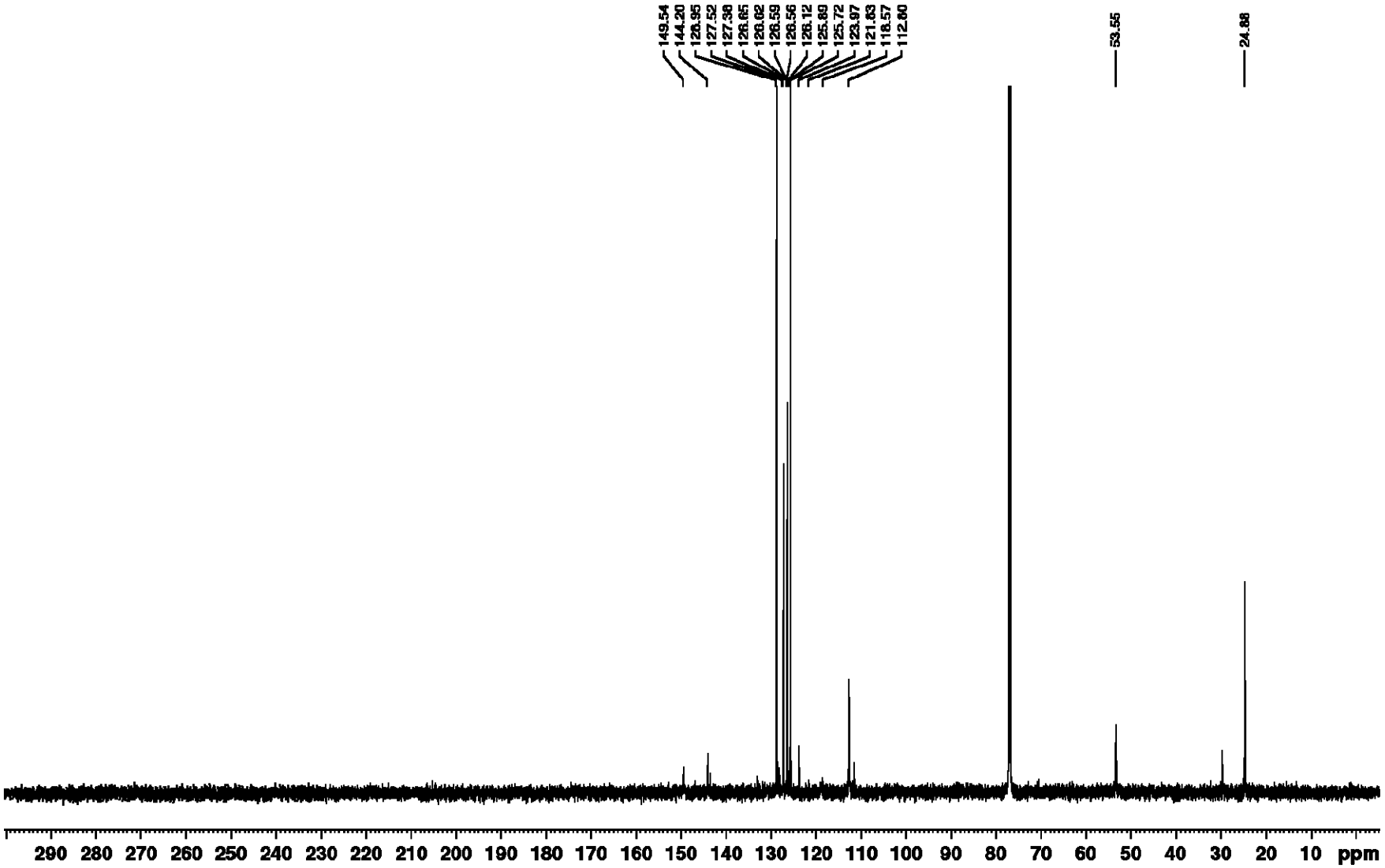


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-benzyl-1-phenylethanamine (**4k**).

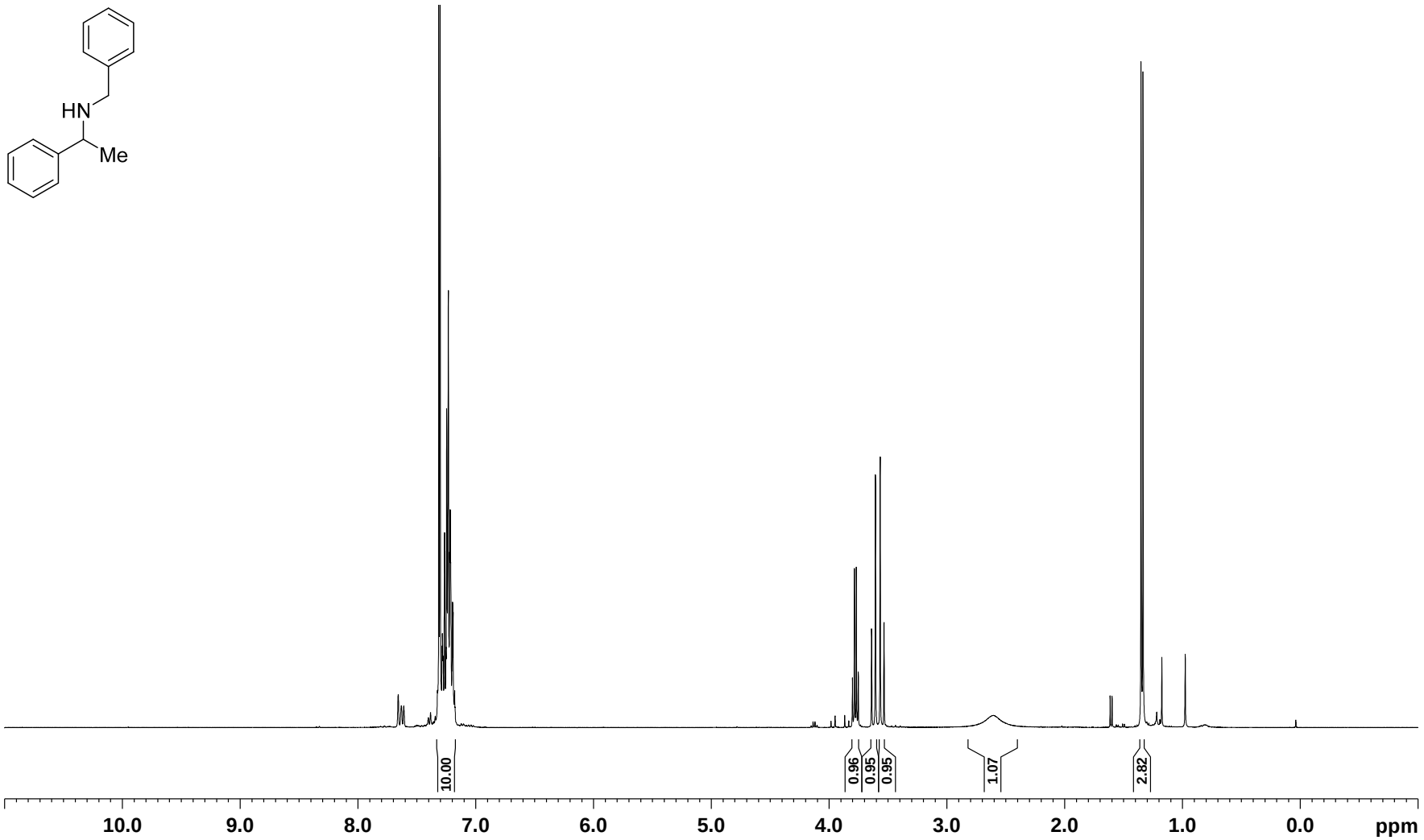


Figure S38. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-benzyl-1-phenylethanamine (**4k**).

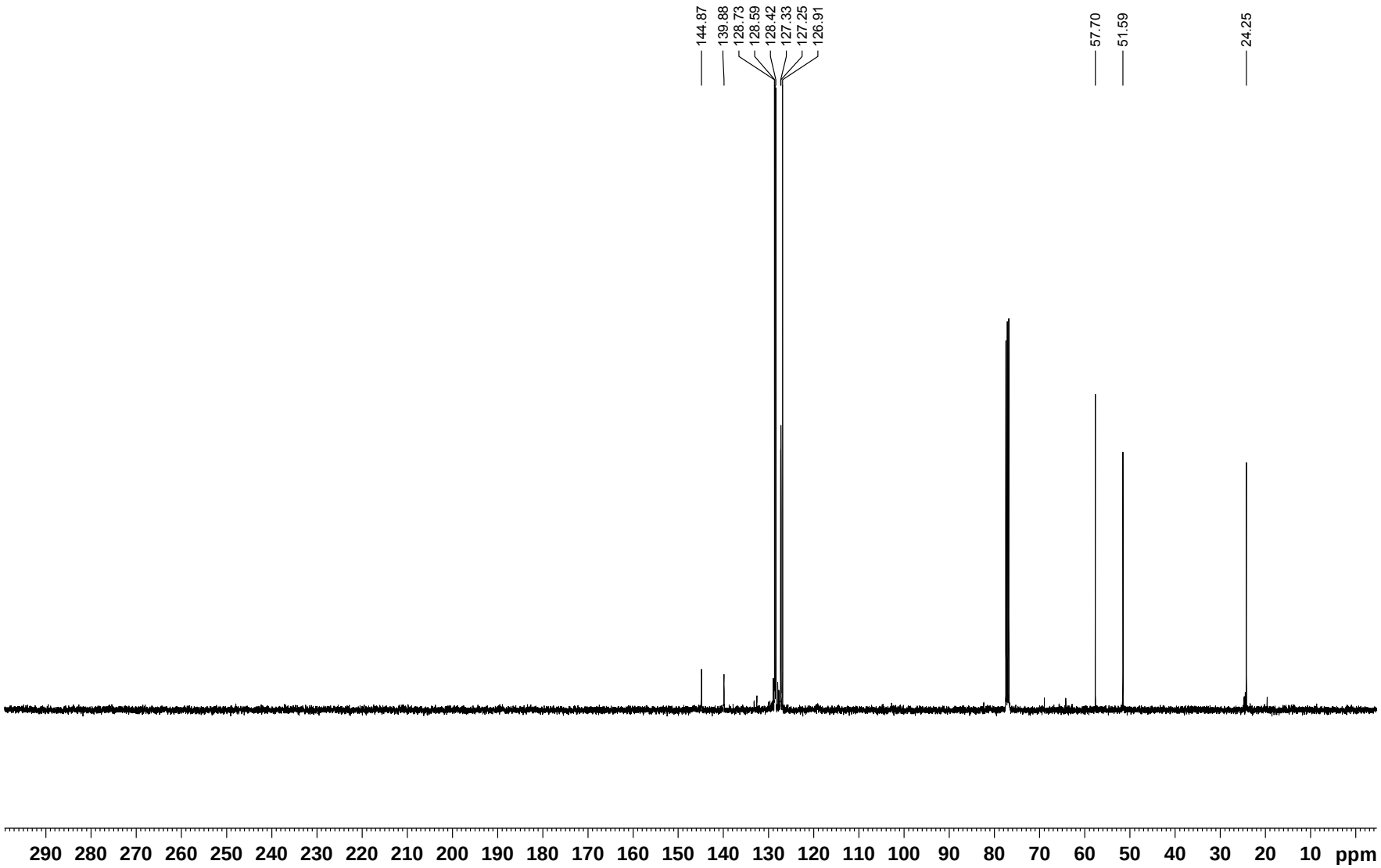


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of 4-methyl-*N*-(1-phenylethyl)benzenesulfonamide (**4l**).

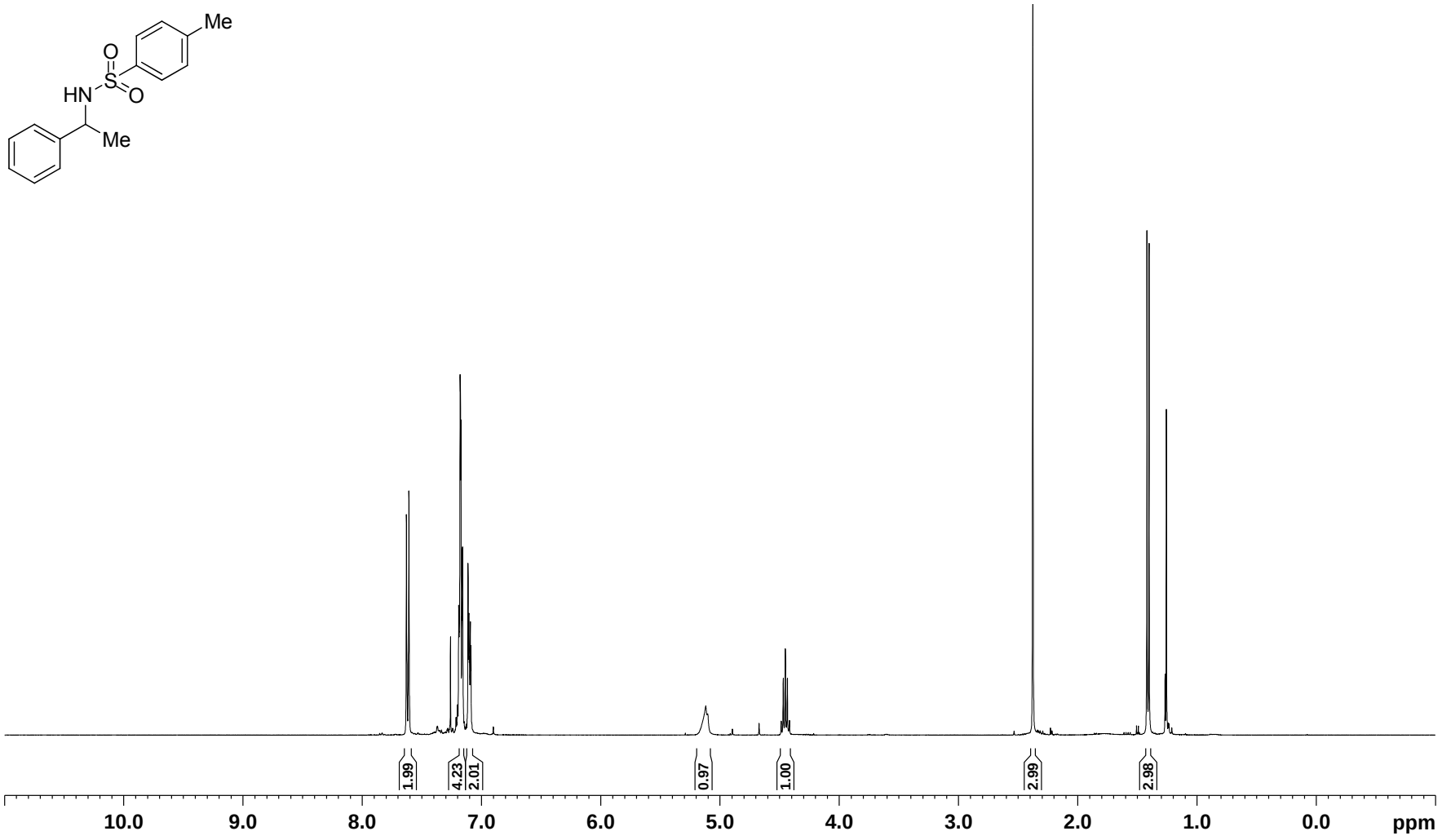


Figure S40. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 4-methyl-*N*-(1-phenylethyl)benzenesulfonamide (**4l**).

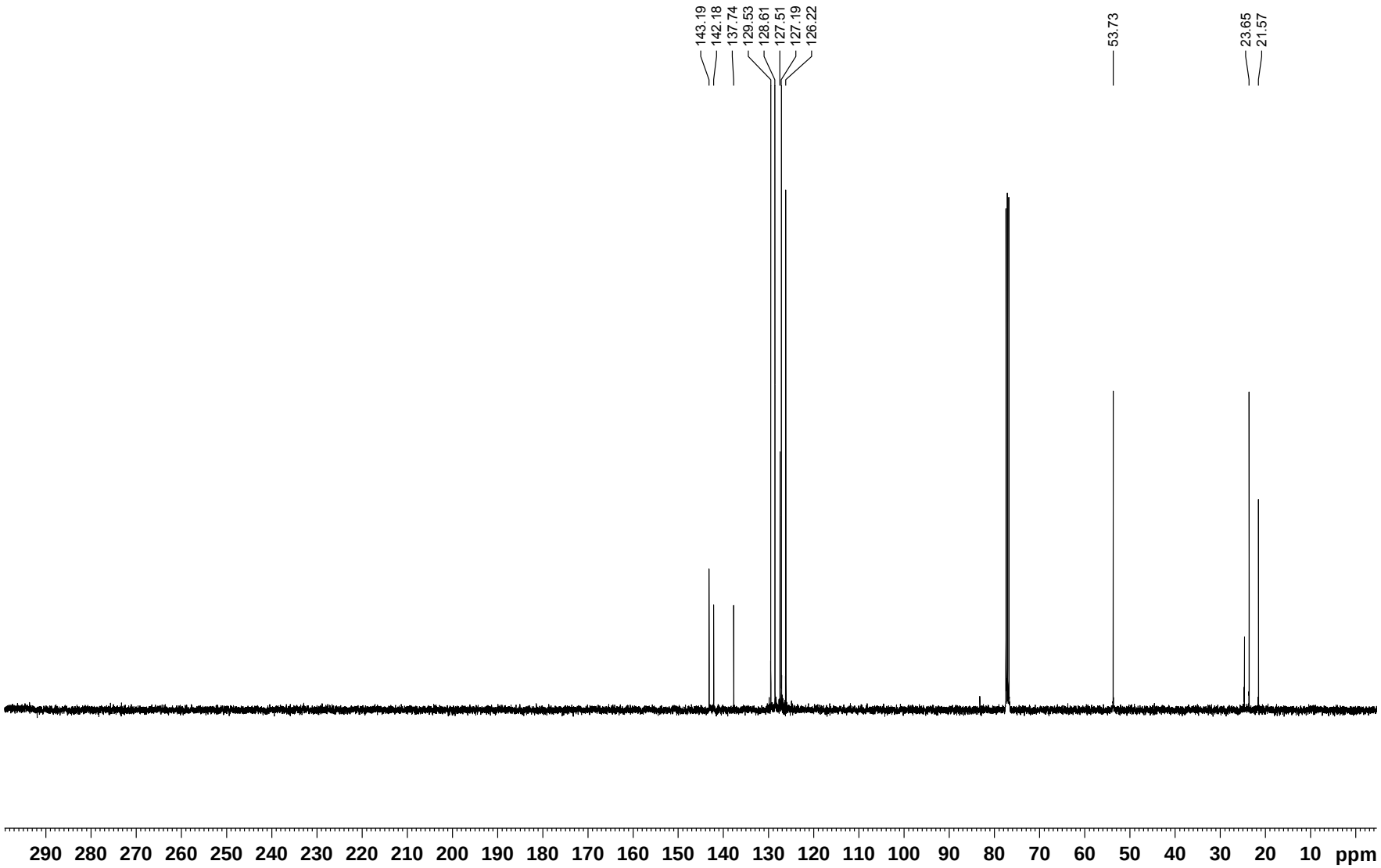


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(1-phenylpropyl)aniline (**4m**).

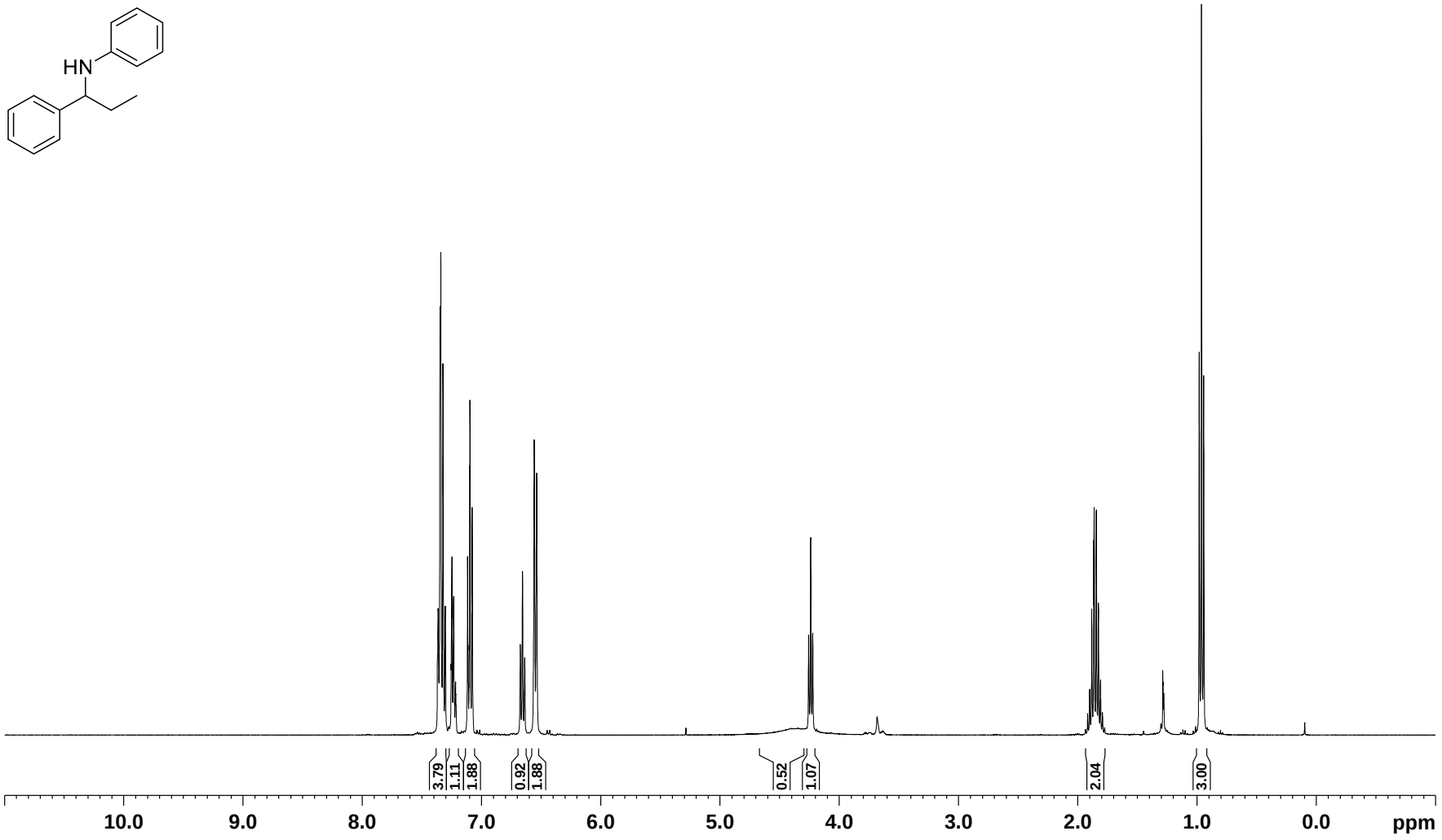


Figure S42. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(1-phenylpropyl)aniline (**4m**).

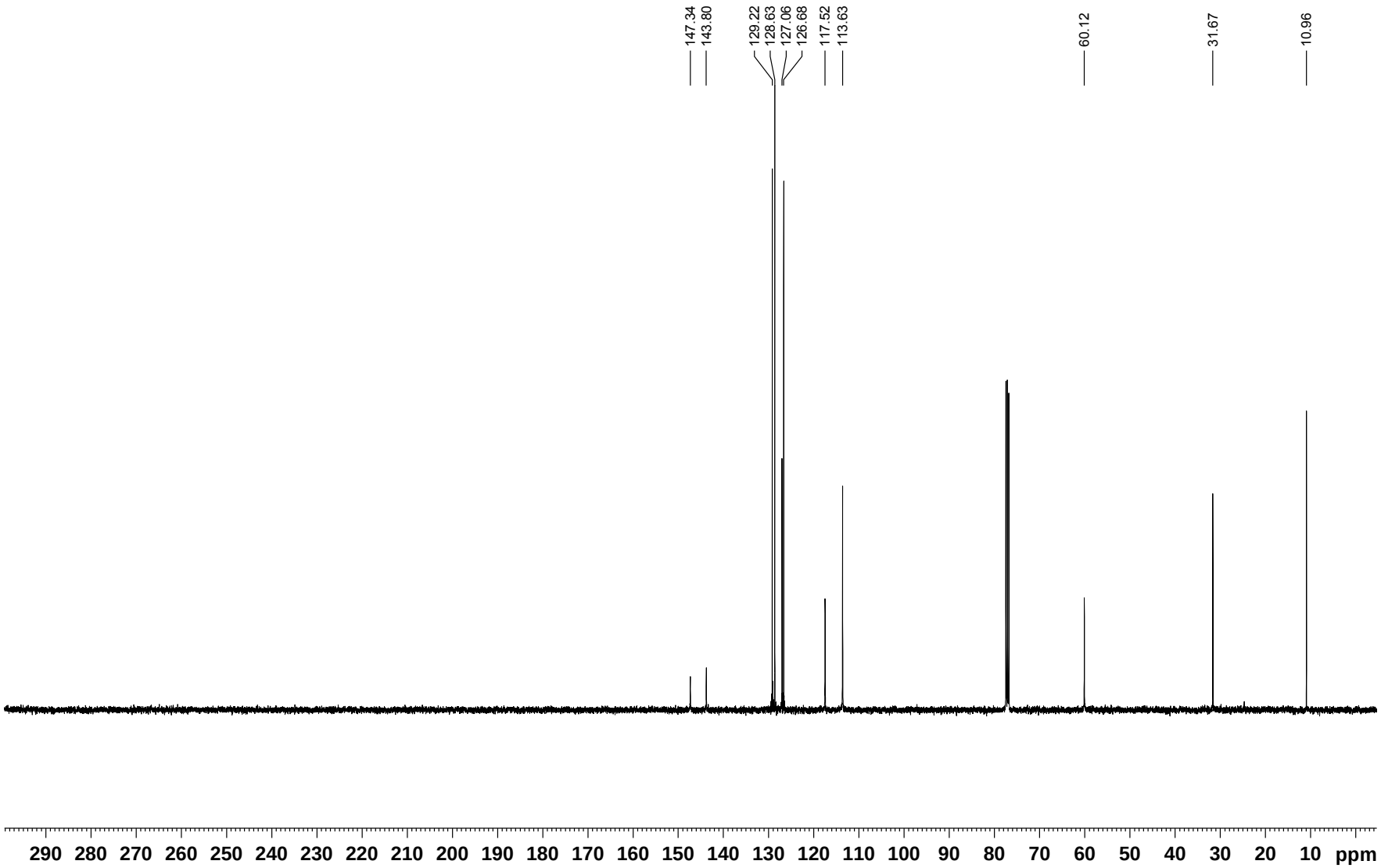


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-benzhydrylaniline (**4n**).

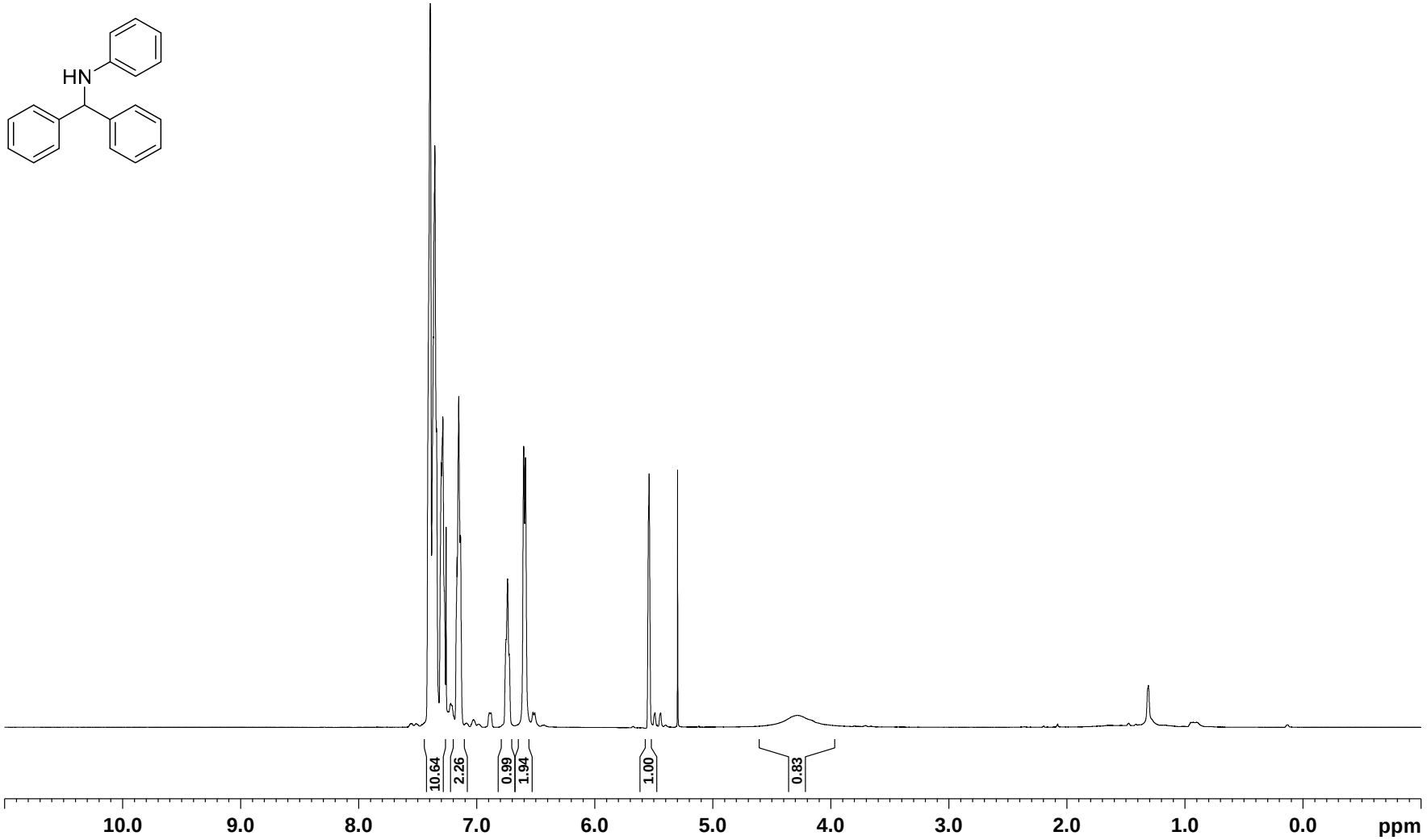


Figure S44. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-benzhydrylaniline (**4n**).

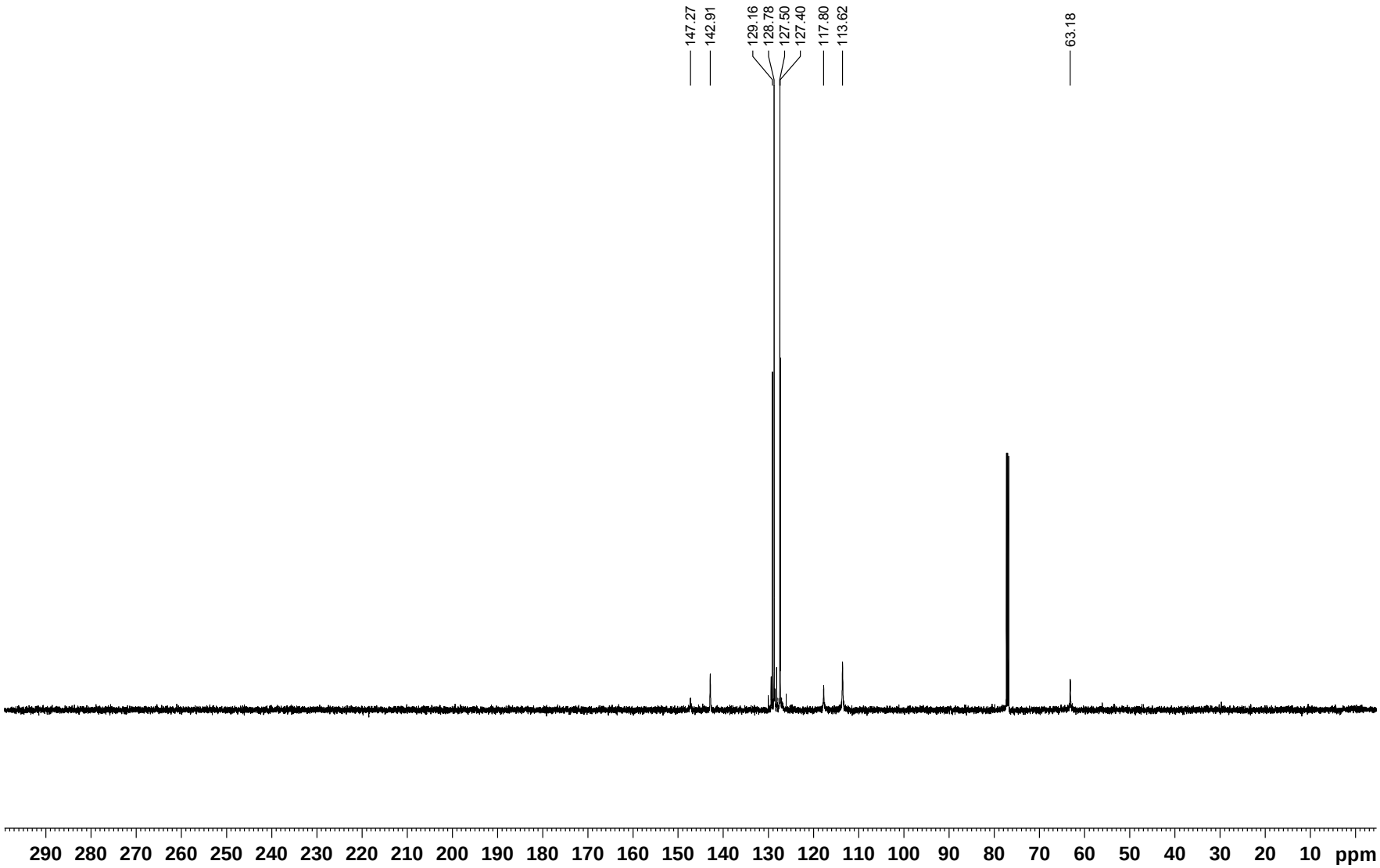


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-benzylaniline (**4o**).

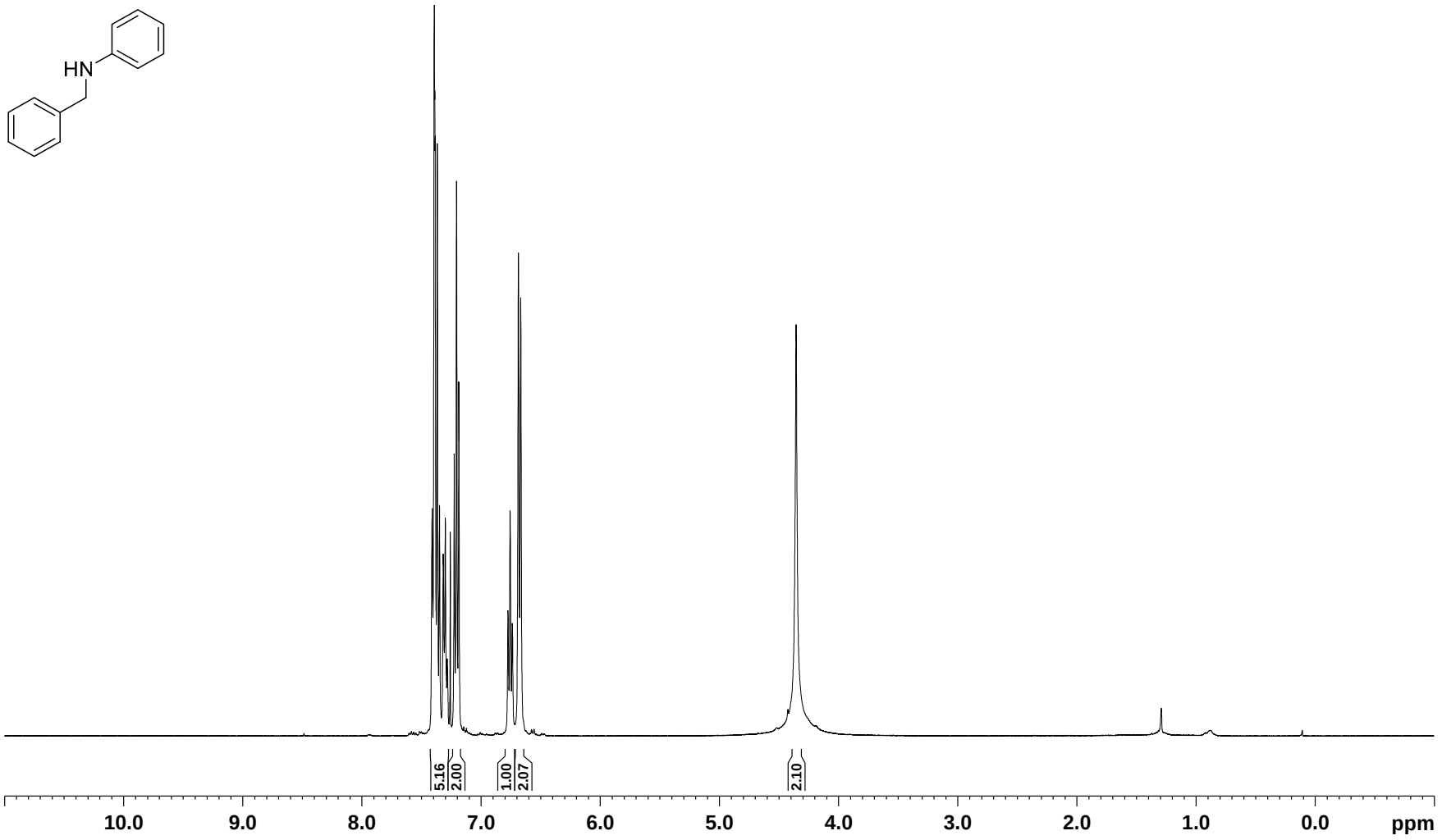


Figure S46. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-benzylaniline (**4o**).

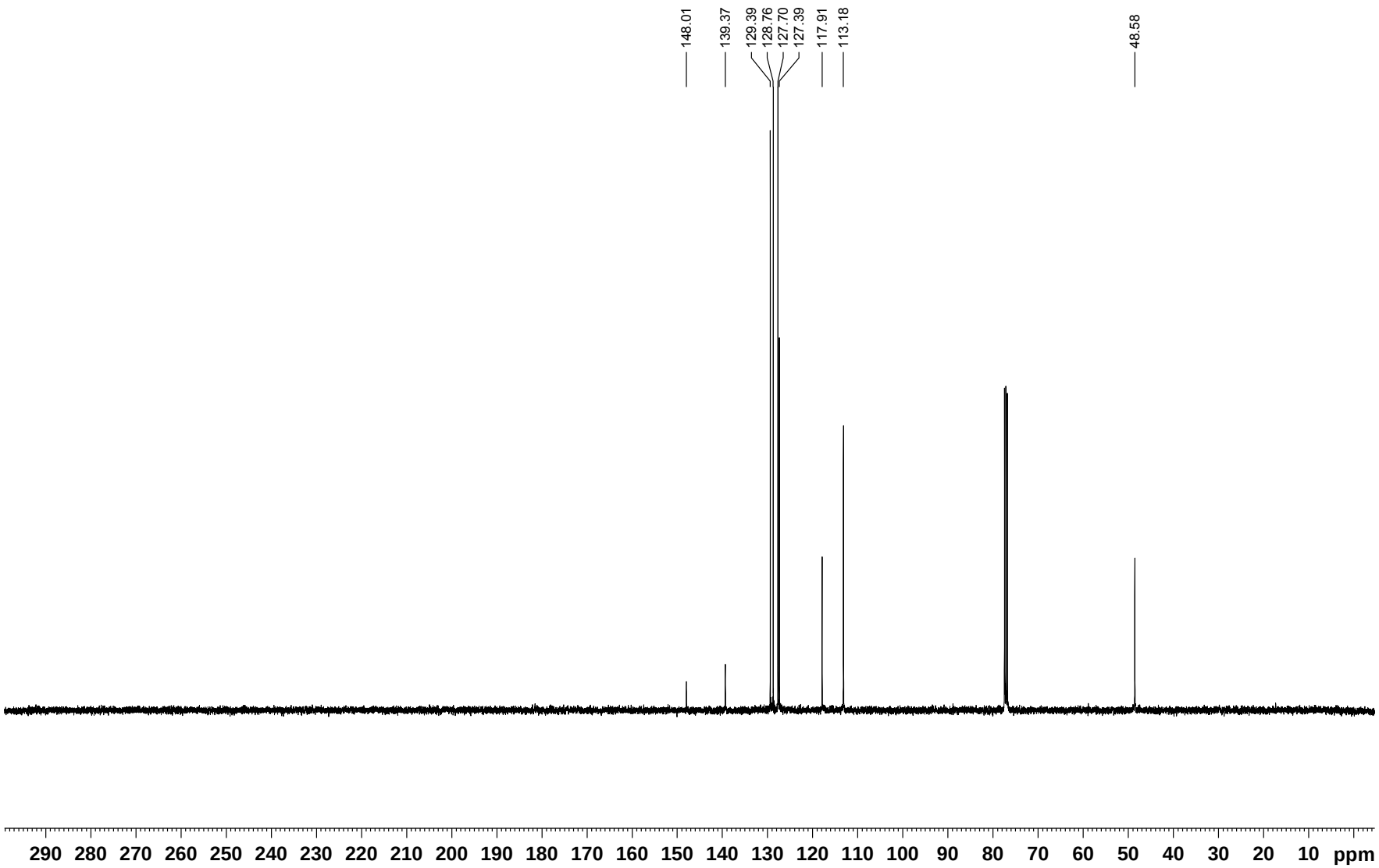


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) of *N*-benzyl-1,1-diphenylmethanamine (**4p**).

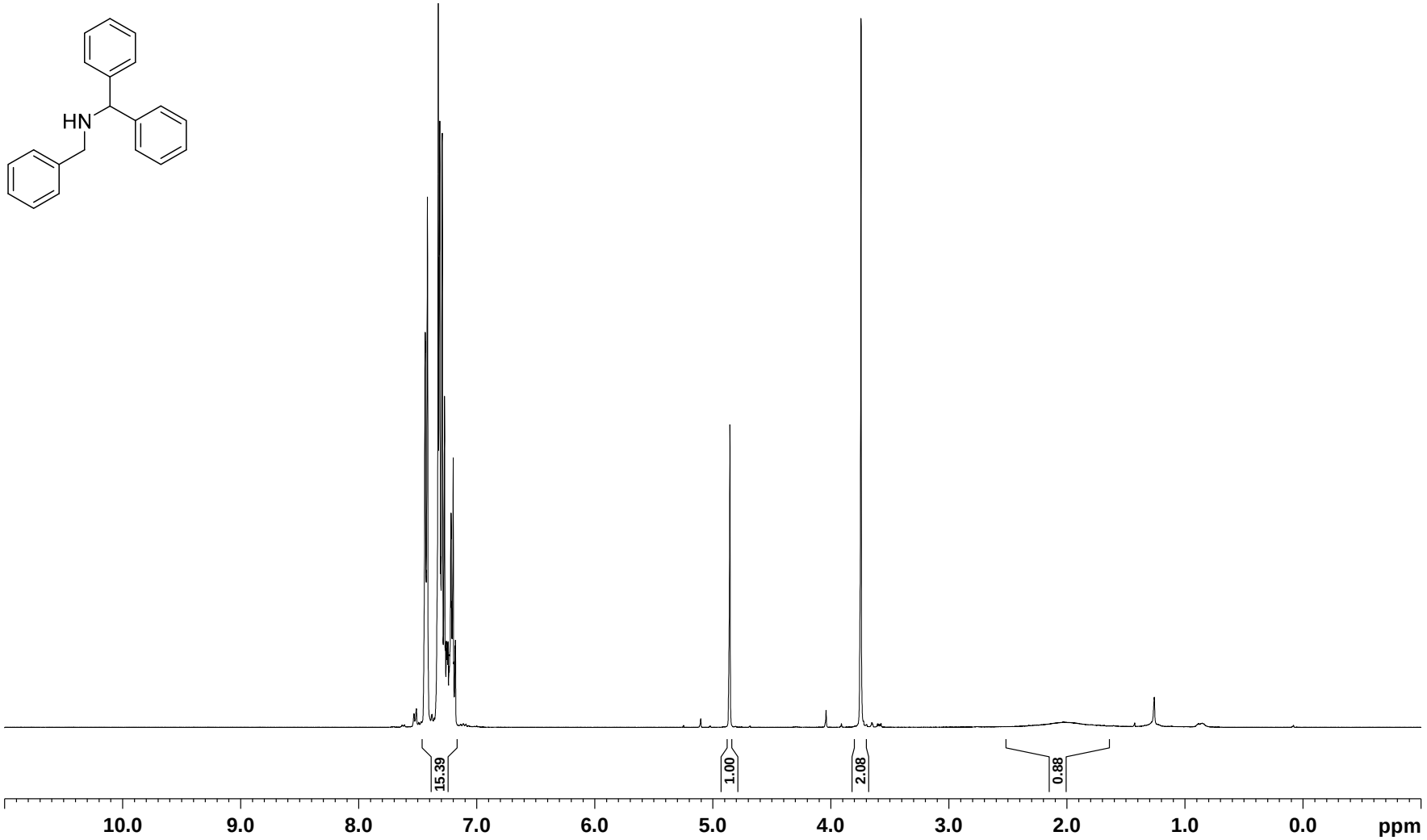


Figure S48. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of *N*-benzyl-1,1-diphenylmethanamine (**4p**).

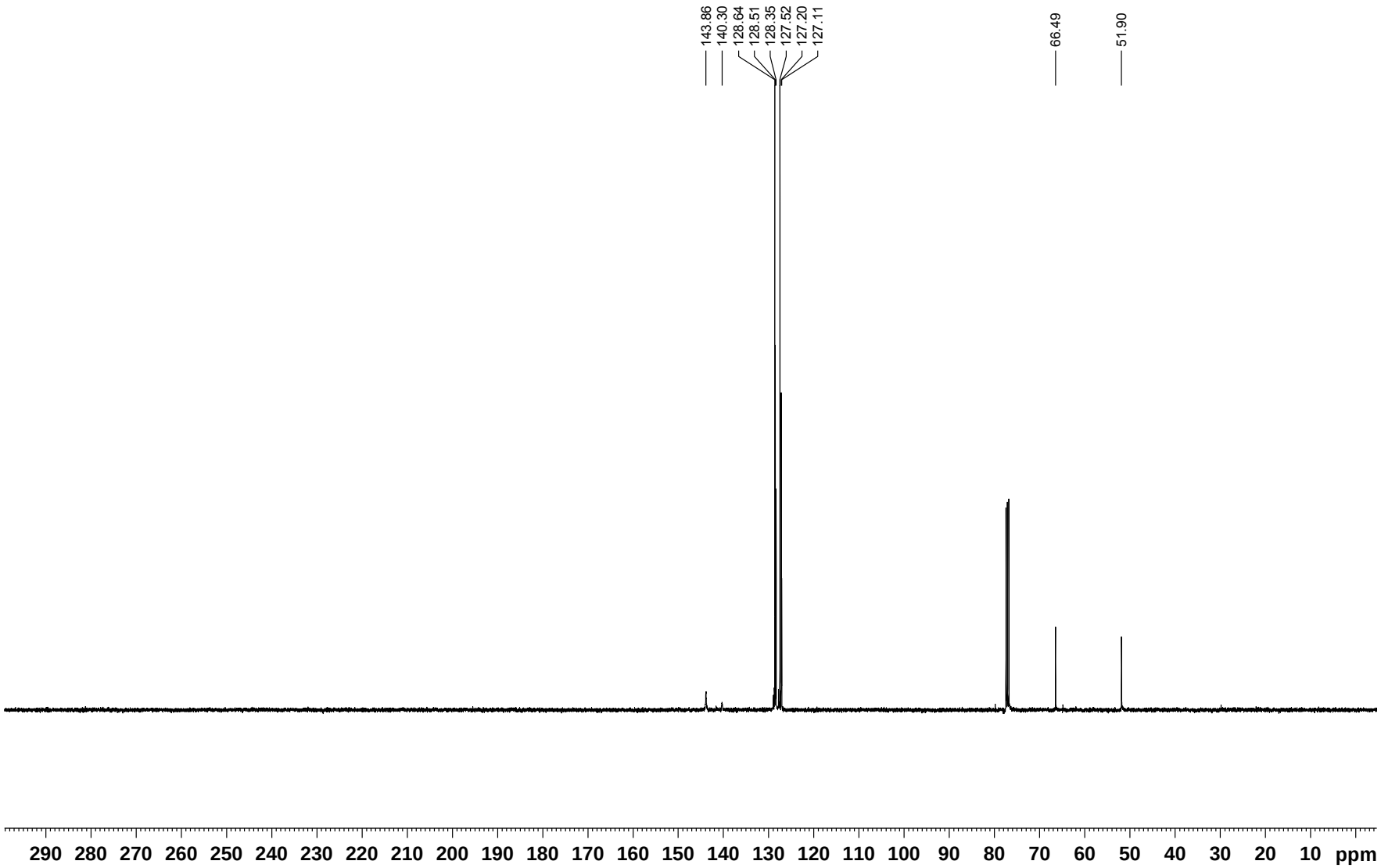


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) of tris(3,4,5-trifluorophenyl)borane (**7**).

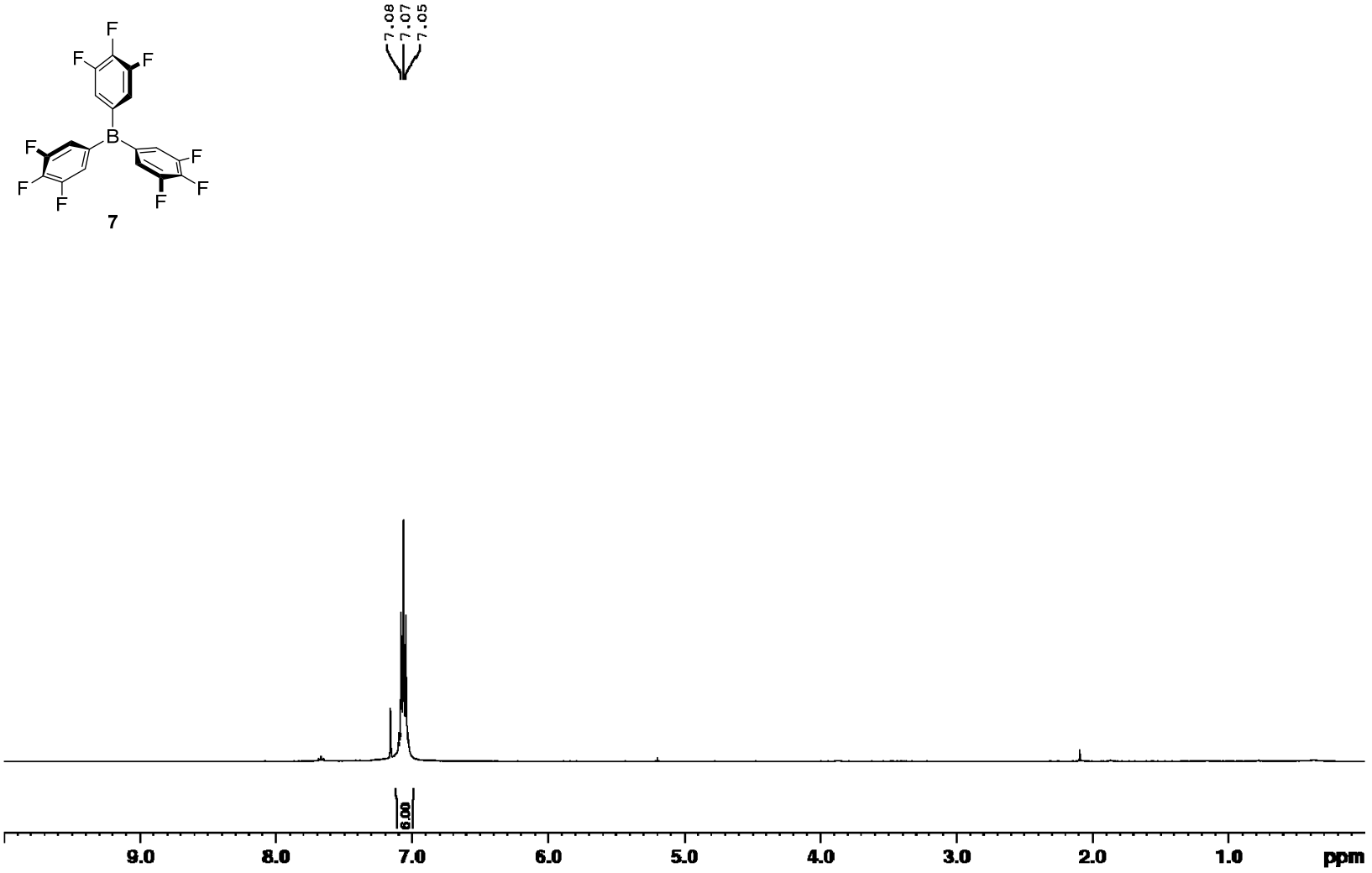


Figure S50. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of tris(3,4,5-trifluorophenyl)borane (**7**).

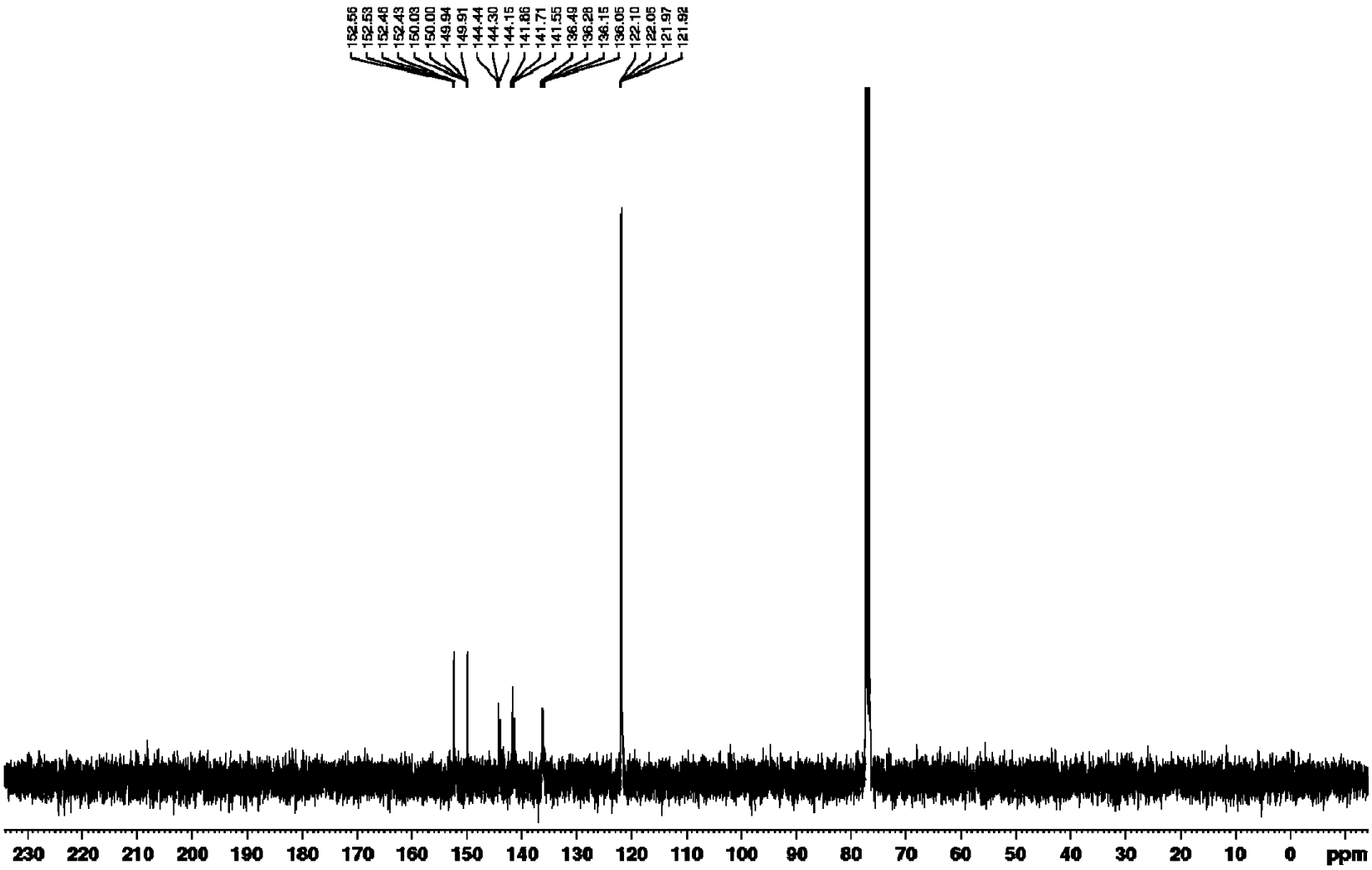


Figure S51. ^{11}B NMR (128 MHz, $CDCl_3$) of tris(3,4,5-trifluorophenyl)borane (**7**).

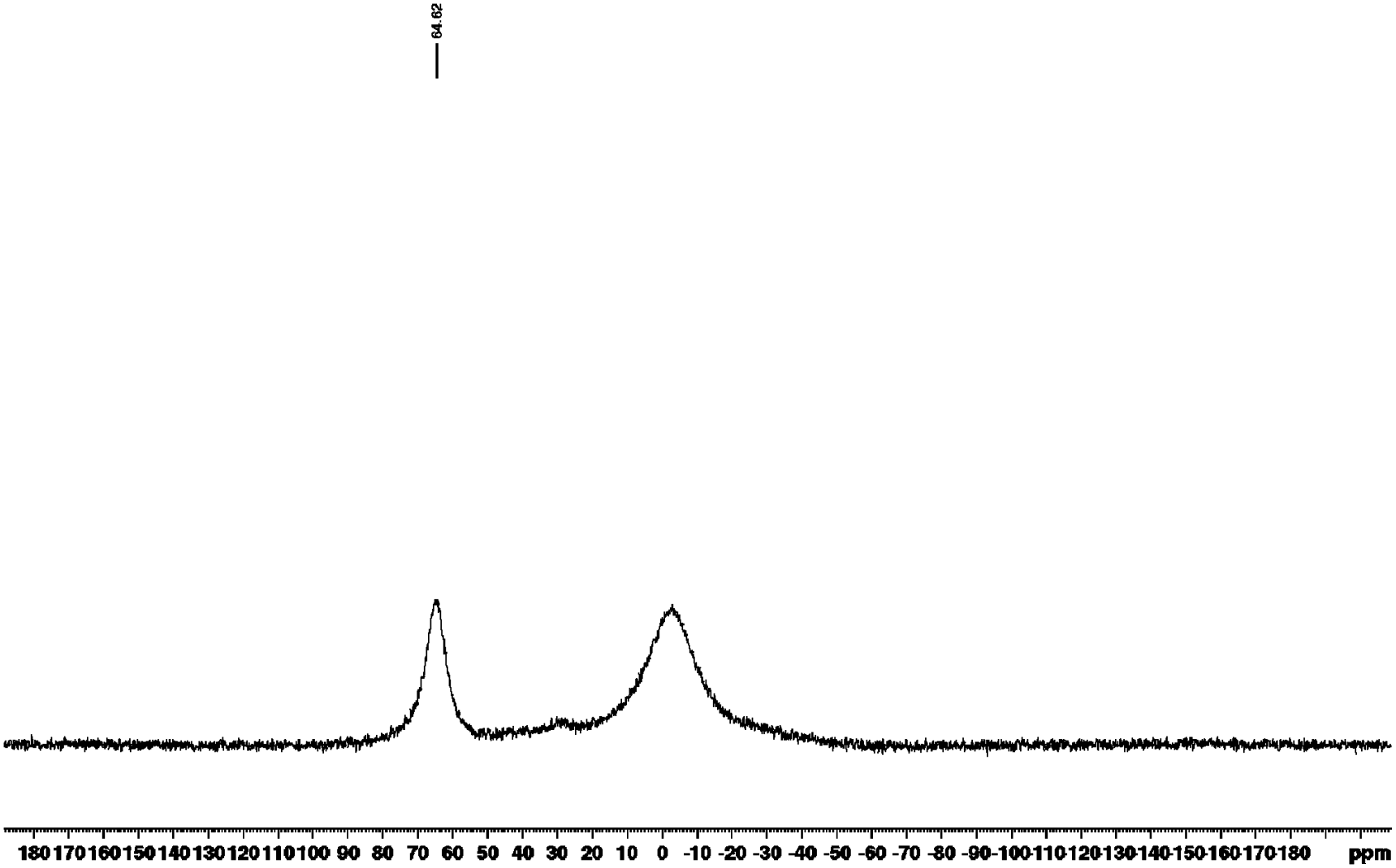
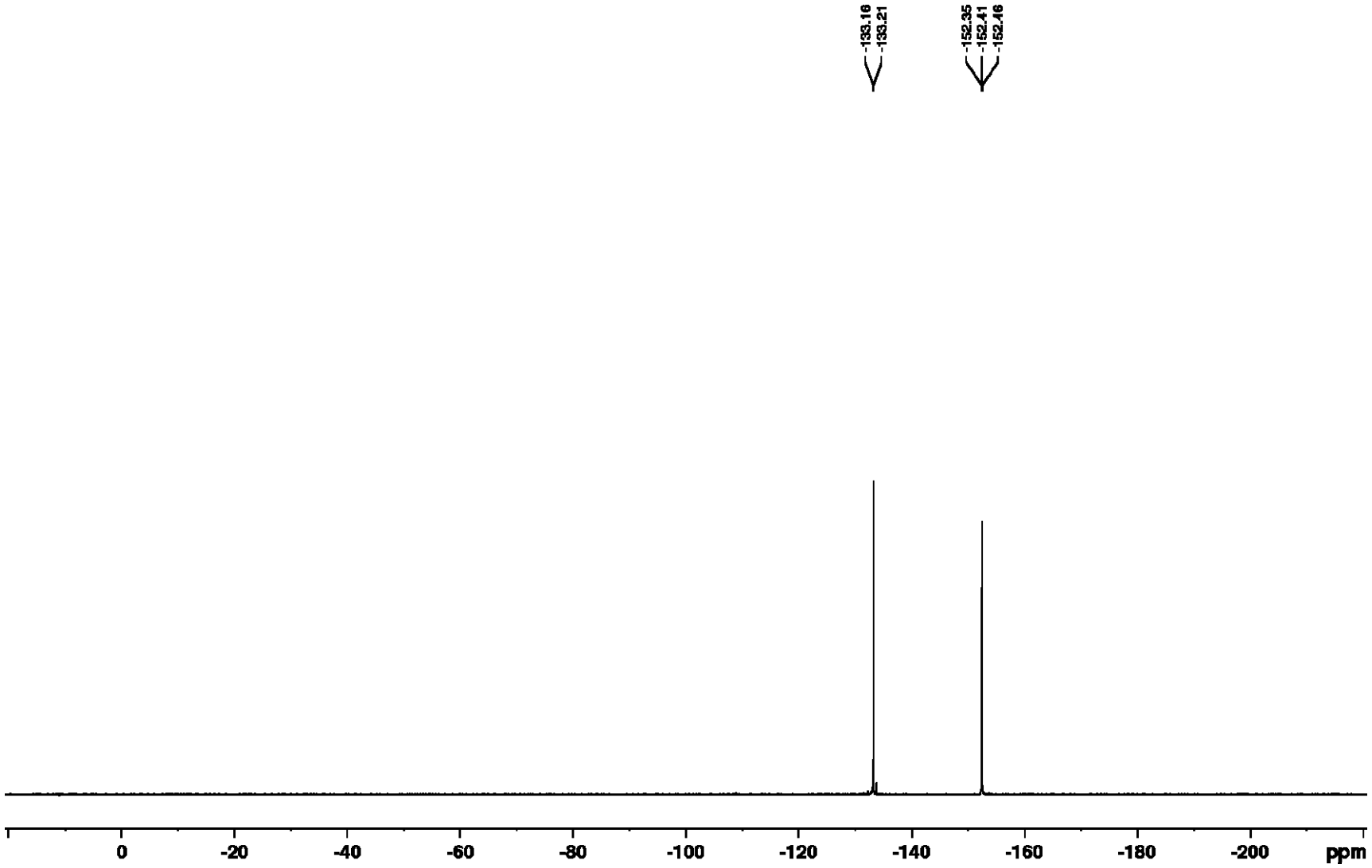


Figure S52. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of tris(3,4,5-trifluorophenyl)borane (**7**).



8 References

(1) Herrington, T. J.; Thom, A. J. W.; White, A. J. P.; A. E. Ashley, *Dalton Trans.* **2012**, *41*, 9019–9022.

(2) Lefranc, A.; Qu, Z.-W.; Grimme, S.; Oestreich, M. *Chem.—Eur. J.* **2016**, *22*, 10009–10016.

(3) Wang, Z.; Ye, X.; Wei, S.; Wu, P.; Zhang, A.; Sun, J. *Org. Lett.* **2006**, *8*, 999–1001.

(4) Hu, A.; Ogasawara, M.; Sakamoto, T.; Okada, A.; Nakajima, K.; Takahashi, T.; Lin, W. *Adv. Synth. Catal.* **2006**, *348*, 2051–2056.

(5) Sato, Y.; Kayaki, Y.; Ikariya, T. *Organometallics* **2016**, *35*, 1257–1264.

(6) Wallach, D. R.; Chisholm, J. D. *J. Org. Chem*. **2016**, *81*, 8035−8042.

(7) Xu, Q.; Xie, H.; Zhang, E.-L.; Ma, X.; Chen, J.; Yu, X.-C.; Li, H. *Green Chem*. **2016**, *18*, 3940–3944.

(8) Mueller, A. L.; Bleith, T.; Roth, T.; Wadepohl, H.; Gade, L. H. *Inorg. Chem*. **2015**, *54*, 5079−5084.

(9) Likhar, P. R.; Arundhathi, R.; Kantam, M. L.; Prathima, P. S.; *Eur. J. Org. Chem*. **2009**, 5383–5389.

(10) Beckett, M. A.; Strickland, G. C.; Holland, J. R.; Varma, K. S. *Polym. Commun*. **1996**, *37*, 4629–4631.

(11) Blackwell, J. M.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 1400–1407.