Supplementary Information for:

Synthesis and Reactivity of Fluorinated Triaryl Aluminium Complexes

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Contents

S1 Experimental procedure and compound characterization

S1.1 General experimental

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using standard Schlenk and glove box techniques. With the exception of THF, Et_2O and deuterated solvents, all solvents used were dried by passing through an alumina column incorporated into an MB SPS-800 solvent purification system, degassed and finally stored in an ampoule fitted with a Teflon valve under a dinitrogen atmosphere. THF was dried over molten potassium for three days and distilled over argon, whereas Et_2O was dried over sodium wire and benzophenone before being distilled over argon. Deuterated solvents were dried over calcium hydride, distilled, freeze-pump-thawed degassed and stored over 3 Å molecular sieves in a glove box. Starting materials were purchased from commercial suppliers and used as received. ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F, and ^{11}B NMR spectra were recorded on a Bruker Avance 400 or 500 MHz spectrometer. Chemical shifts are expressed as parts per million (ppm, δ) and are referenced to $CDCl_3$ (7.26/77.16 ppm) or C_6D_6 (7.16/128.06 ppm) as internal standards. Multinuclear NMR spectra were referenced to $BF_3{\cdot}Et_2O/CDCl_3$ (^{11}B), $CFCl_3$ (^{19}F). The description of signals includes s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, ov dd = overlapping doublet of doublets, and m = multiplet. All coupling constants are absolute values and are expressed in Hertz (Hz). IR-Spectra were measured on a Shimadzu IR Affinity-1 photospectrometer. The description of signals includes s = strong, m = medium, w = weak, sh = shoulder, and br = broad. Mass spectra were measured by the School of Chemistry in Cardiff University on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer.

Note 1: the aluminium compounds prepared in this manuscript are potentially shock and thermally sensitive due to the potential formation of benzyne intermediates. Appropriate care should be taken.

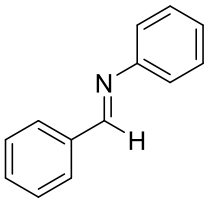
Note 2: due to the potential for benzyne formation, lack of in-house elemental analysis (EA) facilities, and the closure of our laboratory as well as the external EA facilities due to the COVID19 pandemic, some elemental analyses of the samples were not performed. For these compounds bulk purity was determined by multinuclear NMR spectroscopy with any residual solvent or starting material accounted for.

S1.2 Synthesis of imines

General procedure 2

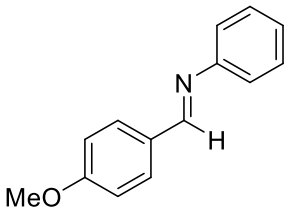
In accordance with the literature known procedure,[1] the necessary aldehyde (10 mmol) was dissolved in CH_2Cl_2 (10 mL) along with 3 Å molecular sieves. To this the required amine (10 mmol) was added. The reaction was left at ambient temperature for two hours at which point $MgSO_4$ was added with subsequent filtration. Volatiles were removed *in vacuo* to leave the pure imine in quantitative yields.

Synthesis of N,1-diphenylmethanimine



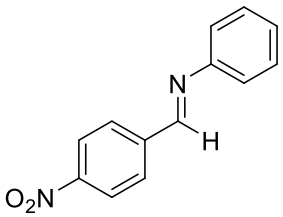
Synthesized in accordance with general procedure 2 using benzaldehyde (1.06 g, 10 mmol, 1.0 equiv) and aniline (933 mL, 10 mmol, 1.0 equiv). Yield: 1.74 g, 9.60 mmol, 96%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 8.46 (s, 1H, N=CH), 7.92 (dd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 2.8 Hz, 2H, Ar–H), 7.61–7.43 (m, 3H, Ar–H), 7.41 (t, $^3J_{HH}$ = 7.7 Hz, 2H, Ar–H), 7.23 (d, $^3J_{HH}$ = 8.4 Hz, 3H, Ar–H).

Synthesis of 1-(4-methoxyphenyl)-N-phenylmethanimine



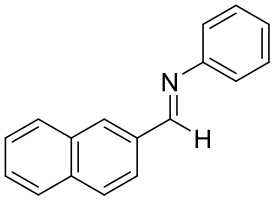
Synthesized in accordance with general procedure 2 using 4-methoxybenzaldehyde (1.36 g, 10 mmol, 1.0 equiv) and aniline (933 mL, 10 mmol, 1.0 equiv). Yield: 2.04 g, 9.67 mmol, 96.7%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 8.39 (s, 1H, N=CH), 7.86 (d, $^3J_{HH}$ = 8.9 Hz, 2H, Ar–H), 7.50–7.33 (m, 2H, Ar–H), 7.25–7.18 (m, 3H, Ar–H), 6.99 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar–H), 3.88 (s, 3H, OMe).

Synthesis of 1-(4-nitrophenyl)-N-phenylmethanimine



Synthesized in accordance with general procedure 2 using 4-nitrobenzaldehyde (1.51 g, 10 mmol, 1.0 equiv) and aniline (933 mL, 10 mmol, 1.0 equiv). Yield: 2.11 g, 9.32 mmol, 93.2%. Spectroscopic analyses agree with literature values.[2] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 8.49 (s, 1H, CH=N), 8.26 (d, $^3J_{HH}$ = 9.0 Hz, 2H, Ar–H), 8.01 (d, $^3J_{HH}$ = 9.3 Hz, 2H, Ar–H), 7.41–7.33 (m, 2H, Ar–H), 7.23 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar–H), 7.20 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar–H).

Synthesis of 1-(naphthalen-2-yl)-N-phenylmethanimine



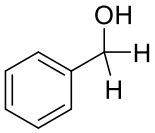
Synthesized in accordance with general procedure 2 using 4-napthaldehyde (1.56 g, 10 mmol, 1.0 equiv) and aniline (933 mL, 10 mmol, 1.0 equiv). Yield: 2.18 g, 9.43 mmol, 94.3%. Spectroscopic analyses agree with literature values.[2] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 8.63 (s, 1H, CH=N), 8.21 (s, 1H, Ar–H), 8.18 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, Ar–H), 7.94 (t, $^3J_{HH}$ = 8.1 Hz, 2H, Ar–H), 7.89 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar–H), 7.59–7.51 (m, 2H, Ar–H), 7.43 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, Ar–H), 7.31–7.22 (m, 3H, Ar–H).

S1.3 Synthesis of reduction products

General procedure 3

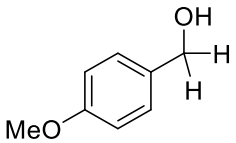
In an NMR tube, pinacol borane (35 µL, 240 µmol, 1.2 equiv) and the substrate (200 µmol, 1.0 equiv) were combined in deuterated chloroform (0.7 mL). To this, tris(3,4,5-trifluorophenyl)alane etherate (10 mg, 10 mol%, 20 µmol, 0.1 equiv) was added, and the NMR tube sealed. The mixture was heated to 70 °C and conversion was monitored *via in situ* ^{1}H NMR spectroscopy until the desired boronate ester had been formed in >95% yield. Upon completion of the reaction, the catalyst was removed (and for compounds **6**–**8**, the boronate ester was hydrolyzed) by washing with 1 M NaOH (3 × 10 mL) and was further purified using flash column chromatography.

Synthesis of phenylmethanol (**6a**)



Synthesized in accordance with general procedure 3 using benzaldehyde (21 µL, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 21 mg, 193 µmol, 97%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.39–7.34 (m, 4H, Ar–H), 7.31 (t, $^3J_{HH}$ = 6.7 Hz, 1H, Ar–H), 4.63 (s, 2H, CH_2), 2.71 (br, 1H, OH). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 140.9 (s, Ar), 128.6 (s, Ar), 127.6 (s, Ar), 127.0 (s, Ar), 65.1 (s).

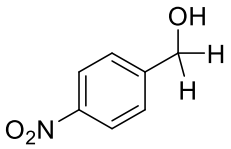
Synthesis of (4-methoxyphenyl)methanol (**6b**)



Synthesized in accordance with general procedure 3 using 4-methoxybenzaldehyde (24 µL, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 24 mg, 174 µmol, 87%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.30 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar–H), 6.90

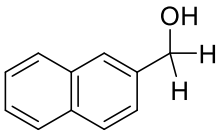
(d, $^3J_{HH}$ = 8.7 Hz, 2H, Ar–H), 4.62 (s, 2H, CH_2), 3.81 (s, 3H, OMe). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 159.4 (s, Ar), 133.3 (s, Ar), 128.8 (s, Ar), 114.1 (s, Ar), 65.2 (s), 55.5 (s).

Synthesis of (4-nitrophenyl)methanol (**6c**)



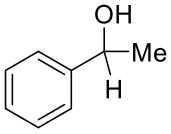
Synthesized in accordance with general procedure 3 using 4-nitrobenzaldehyde (31 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a yellow solid. Yield: 27 mg, 176 µmol, 88%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 8.22 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar–H), 7.54 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar–H), 4.84 (d, $^3J_{HH}$ = 5.5 Hz, 2H, CH_2), 1.90 (t, $^3J_{HH}$ = 5.5 Hz, 1H, OH). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 148.2 (s, Ar), 147.5 (s, Ar) 127.1 (s, Ar), 123.9 (s, Ar), 64.2 (s).

Synthesis of napthalen-2-ylmethanol (**6d**)



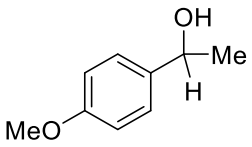
Synthesized in accordance with general procedure 3 using 2-napthaldehyde (31 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 28 mg, 177 µmol, 89%. Spectroscopic analyses agree with literature values.[3] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.87–7.81 (m, 4H, Ar–H), 7.51–7.46 (m, 3H, Ar–H), 4.87 (d, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2), 1.73 (t, $^3J_{HH}$ = 6.0 Hz, 1H, OH). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 138.4 (s, Ar), 133.5 (s, Ar), 133.1 (s, Ar), 128.5 (s, Ar), 128.0 (s, Ar), 127.9 (s, Ar), 126.4 (s, Ar), 126.1 (s, Ar), 125.6 (s, Ar), 125.3 (s, Ar), 65.7 (s).

Synthesis of 1-phenylethanol (**7a**)



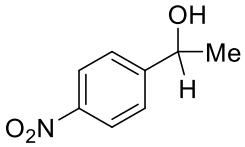
Synthesized in accordance with general procedure 3 using acetophenone (23 µL, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 23 mg, 188 µmol, 94%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.41–7.32 (m, 4H, Ar–H), 7.32–7.24 (m, 1H, Ar–H), 4.90 (q, $^3J_{HH}$ = 6.4 Hz, 1H, CH_2), 1.92 (br, 1H, OH), 1.50 (d, $^3J_{HH}$ = 6.5 Hz, 3H, Me). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 145.9 (s, Ar), 128.6 (s, Ar), 127.6 (s, Ar), 125.5 (s, Ar), 70.5 (s), 25.3 (s).

Synthesis of 1-(4-methoxyphenyl)ethanol (**7b**)



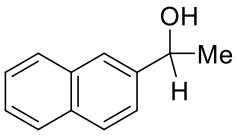
Synthesized in accordance with general procedure 3 using 4-methoxyacetophenone (28 µL, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 29 mg, 191 µmol, 95%. Spectroscopic analyses agree with literature values.[4] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.31 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar–H), 6.89 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar–H), 4.86 (q, $^3J_{HH}$ = 6.4 Hz, 1H, CH_2), 3.81 (s, 3H, OMe), 1.74 (br, 1H, OH), 1.48 (d, $^3J_{HH}$ = 6.4 Hz, 3H, Me). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 159.0 (s, Ar), 138.0 (s, Ar), 126.7 (s, Ar), 113.9 (s, Ar), 70.0 (s), 55.3 (s), 25.0 (s).

S*ynthesis of 1-(4-nitrophenyl)ethanol* (**7c**)



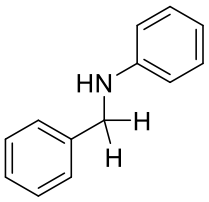
Synthesized in accordance with general procedure 3 using 4-nitroacetophenone (33 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a yellow solid. Yield: 29 mg, 174 µmol, 87%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 8.20 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar–H), 7.54 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar–H), 5.02 (q, $^3J_{HH}$ = 6.5 Hz, 1H, CH_2), 2.05 (br, 1H, OH), 1.52 (d, $^3J_{HH}$ = 6.5 Hz, 3H, Me). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 153.2 (s, Ar), 147.3 (s, Ar), 126.3 (s, Ar), 123.9 (s, Ar), 69.7 (s), 25.7 (s).

Synthesis of 1-(napthalen-2-yl)ethanol (**7d**)



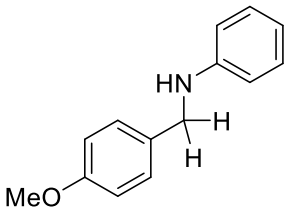
Synthesized in accordance with general procedure 3 using 2-acetylnapthalene (36 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 32 mg, 186 µmol, 93%. Spectroscopic analyses agree with literature values.[4] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.88–7.79 (m, 4H, Ar–H), 7.54–7.43 (m, 3H, Ar–H), 5.08 (qd, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 3.3 Hz, 1H, CH_2), 1.92 (d, $^3J_{HH}$ = 3.5 Hz, 1H, OH), 1.59 (d, $^3J_{HH}$ = 6.5 Hz, 3H, Me). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 143.3 (s, Ar), 133.5 (s, Ar), 133.1 (s, Ar), 128.5 (s, Ar), 128.1 (s, Ar), 127.8 (s, Ar), 126.3 (s, Ar), 125.9 (s, Ar), 123.9 (s, Ar), 123.9 (s, Ar), 70.7 (s), 25.3 (s).

Synthesis of N-benzylaniline (**8a**)



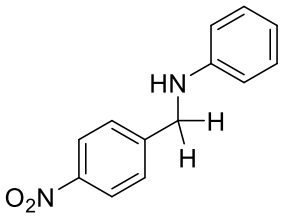
Synthesized in accordance with general procedure 3 using *N*,1-diphenylmethanimine (36 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 33 mg, 180 µmol, 90%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.41–7.33 (m, 4H, Ar–H), 7.32–7.26 (m, 1H, Ar–H), 7.19 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, Ar–H), 6.73 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar–H), 6.69–6.64 (m, 2H, Ar–H), 4.34 (s, 2H, CH_2), 4.03 (br, 1H, NH). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 148.3 (s, Ar), 139.6 (s, Ar), 129.4 (s, Ar), 128.8 (s, Ar), 127.7 (s, Ar), 127.4 (s, Ar), 117.7 (s, Ar), 113.0 (s, Ar), 48.5 (s).

Synthesis of N-(4-methoxybenzyl)aniline (**8b**)



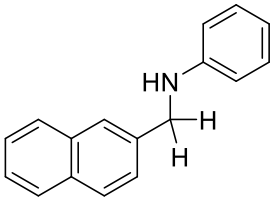
Synthesized in accordance with general procedure 3 using 1-(4-methoxyphenyl)-*N*-phenylmethanimine (42 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 38 mg, 178 µmol, 89%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.30 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar–H), 7.19 (t, $^3J_{HH}$ = 7.8 Hz, 2H, Ar–H), 6.89 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar–H), 6.72 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar–H), 6.65 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar–H), 4.26 (s, 2H, CH_2), 3.95 (br, 1H, NH), 3.81 (s, 3H, OMe). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 159.0 (s, Ar), 148.3 (s, Ar), 131.5 (s, Ar), 129.4 (s, Ar), 128.9 (s, Ar), 117.6 (s, Ar), 114.2 (s, Ar), 113.0 (s, Ar), 55.4 (s), 47.9 (s).

Synthesis of N-(4-nitrobenzyl)aniline (**8c**)



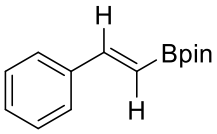
Synthesized in accordance with general procedure 3 using 1-(4-nitrophenyl)-*N*-phenylmethanimine (45 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 35 mg, 153 µmol, 77%. Spectroscopic analyses agree with literature values.[5] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 8.20 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar–H), 7.55–7.53 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar–H), 7.17 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, Ar–H), 6.75 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar–H), 6.58 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar–H), 4.48 (s, 2H, CH_2), 4.25 (br, 1H, NH). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 147.6 (s, Ar), 147.4 (s, Ar), 147.2 (s, Ar), 129.5 (s, Ar), 127.8 (s, Ar), 124.0 (s, Ar), 118.4 (s, Ar), 113.0 (s, Ar), 47.8 (s).

Synthesis of N-(napthalen-2-ylmethyl)aniline (**8d**)



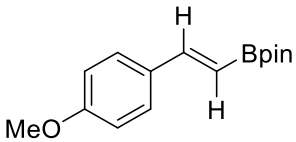
Synthesized in accordance with general procedure 3 using 1-(naphthalen-2-yl)-*N*-phenylmethanimine (46 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colorless oil. Yield: 42 mg, 180 µmol, 90%. Spectroscopic analyses agree with literature values.[5] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.85–7.80 (m, 4H, Ar–H), 7.51–7.44 (m, 3H, Ar–H), 7.22–7.17 (m, 2H, Ar–H), 6.74 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, Ar–H), 6.69 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H, Ar–H), 4.51 (s, 2H, CH_2), 4.16 (s, 1H, NH). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 148.2 (s, Ar), 137.0 (s, Ar), 133.6 (s, Ar), 132.8 (s, Ar), 129.4 (s, Ar), 128.5 (s, Ar), 127.9 (s, Ar), 127.8 (s, Ar), 126.3 (s, Ar), 126.0 (s, Ar), 125.9 (s, Ar), 117.7 (s, Ar), 113.0 (s, Ar), 48.6 (s).

Synthesis of 4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**9a**)



Synthesized in accordance with general procedure 3 using phenyl acetylene (22 µL, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford the title compound as a colorless oil. Yield: 42 mg, 182 µmol, 91%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.52–7.28 (m, 6H, Ar–H and HC=C), 6.17 (d, $^{3}J_{HH}$ = 18.4 Hz, 1H, HC=C), 1.32 (s, 12H, pinacol). **^{11}B NMR** (160 MHz, $CDCl_3$, 295 K) δ/ppm: 30.1 (s). Note, the broad signal around 0 ppm is observed due to the borosilicate glass of the NMR tube. **^{13}C{^{1}H} NMR** *partial* (126 MHz, $CDCl_3$, 295 K) δ/ppm: 149.6 (s, C=C), 137.6 (s, Ar), 129.0 (s, Ar), 128.7 (s, Ar), 127.2 (s, Ar), 83.5 (s), 25.0 (s). Note, the carbon atom adjacent to the boron atom was not observed due to quadrupolar relaxation.

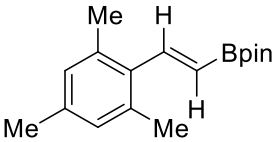
Synthesis of 2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9b**)



Synthesized in accordance with general procedure 3 using 1-ethynyl-4-methoxybenzene (26 µL, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford the title compound as a colorless oil. Yield: 45 mg, 173 µmol, 86%. Spectroscopic analyses agree with literature values.[1] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.44 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, Ar–H), 7.35 (d, $^{3}J_{HH}$ = 18.4 Hz, 1H, CH=C), 6.87 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, Ar–H), 6.01 (d, $^{3}J_{HH}$ = 18.4 Hz, 1H, CH=C), 3.81 (s, 3H, OMe), 1.31 (s, 12H, pinacol). **^{11}B NMR** (160 MHz, $CDCl_3$, 295 K) δ/ppm: 30.1 (s). Note, the broad signal around 0 ppm is observed due to the borosilicate glass of the NMR tube. **^{13}C{^{1}H} NMR** *partial* (126 MHz, $CDCl_3$, 295 K) δ/ppm: 160.4 (s, C=C), 149.2 (s, Ar), 130.4 (s, Ar), 128.6 (s, Ar),

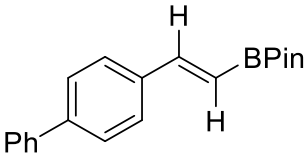
114.1 (s, Ar), 83.4 (s), 55.4 (s), 24.9 (s). Note, the carbon atom adjacent to the boron atom was not observed due to quadrupolar relaxation.

Synthesis of 2-(2,4,6-trimethylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9c**)



Synthesized in accordance with general procedure 3 using 2-ethynyl-1,3,5-trimethylbenzene (29 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford the title compound as a colorless oil. Yield: 51 mg, 187 µmol, 94%. Spectroscopic analyses agree with literature values.[6] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.44 (d, $^{3}J_{HH}$ = 18.8 Hz, 1H, CH=C), 6.86 (s, 2H, Ar–H), 5.68 (d, $^{3}J_{HH}$ = 18.8 Hz, 1H, CH=C), 2.30 (s, 6H, mesityl), 2.27 (s, 3H, mesityl), 1.33 (s, 12H, pinacol). **^{11}B NMR** (160 MHz, $CDCl_3$, 295 K) δ/ppm: 29.9 (s). Note, the broad signal around 0 ppm is observed due to the borosilicate glass of the NMR tube. **^{13}C{^{1}H} NMR** *partial* (126 MHz, $CDCl_3$, 295 K) δ/ppm: 148.6 (s, C=C), 136.9 (s, Ar), 136.0 (s, Ar), 135.2 (s, Ar), 128.8 (s, Ar), 83.4 (s), 25.0 (s), 21.1 (s), 21.1 (s). Note, the carbon atom adjacent to the boron atom was not observed due to quadrupolar relaxation.

Synthesis of 2-(2-(Biphenyl-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9d**)



Synthesized in accordance with general procedure 3 using 4-ethynyl-1,1'-biphenyl (36 mg, 200 µmol). The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford the title compound as a colorless oil. Yield: 49 mg, 136 µmol, 68%. Spectroscopic analyses agree with literature values.[7] **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.62–7.57 (m, 6H, Ar–H), 7.47–7.42 (m, 3H, Ar–H), 7.36 (m, 1H, HC=C), 6.22 (d, $^{3}J_{HH}$ = 18.4 Hz, 1H, HC=C), 1.34 (s, 12H, pinacol). **^{11}B NMR** (160 MHz, $CDCl_3$, 295 K) δ/ppm: 30.1 (s). Note, the broad signal around 0 ppm is observed due to the borosilicate glass of the NMR tube. **^{13}C{^{1}H} NMR** *partial* (126 MHz, $CDCl_3$, 295 K) δ/ppm: 149.1 (s, C=C), 141.7 (s, Ar), 140.7 (s, Ar), 136.5 (s, Ar), 128.9 (s, Ar), 127.7 (s, Ar), 127.6 (s, Ar), 127.4 (s, Ar), 127.1 (s, Ar), 83.5 (s), 25.0 (s). Note, the carbon adjacent to the boron atom was not observed due to quadrupolar relaxation.

S2 Single crystal X-ray diffraction

S2.1 Single crystal X-ray diffraction experimental

Crystallographic studies on **2**, **3**, **4**, **4·THF**, and **5** were undertaken on a single crystal mounted in paratone and studied on an Agilent SuperNova Dual Atlas three-circle diffractometer using Mo- or Cu-Kα radiation and a CCD detector. Measurements were taken at 150(2) K with temperatures maintained using an Oxford Cryostream. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on Gaussian integration over a multifaceted crystal model within CrysAlisPro.[8] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[9]

The structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers 1996144–1996147, 2022498). These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

For (Al(3,4,5-Ar^F)Me_2)$_2$ dimer, **2**, the H-atoms from the bridging methyl group could not be added using a standard HFIX command so instead were identified and added from the Fourier difference map. The restraints DFIX and DANG were used to aid the final refinement of the H-atoms, which gave a satisfactory R_1 = 5.9% and wR_2 = 13.5%.

For Al(2,3,4-Ar^F)$_3$, **4**, one of the aryl rings was disordered by a 180° rotation about the Al–C bond. This disorder was modelled by parts over two sites in an 82:18 ratio. Disordered fluorine atoms were modelled using the EADP constraint and SADI distance restraint. When applied, a final R_1 = 8.5% and wR_2 = 19.9% was achieved.

For Al(3,4,5-Ar^F)$_3$·OEt_2, **5**, the coordinated ether group was significantly disordered. This disorder was modelled by parts over two sites in a 50:50 ratio. The DFIX restraint was used for the O–C and C–C bond distances. In addition, two fluorine atoms had elongated thermal ellipsoids and so were modelled by parts. The final refinement gave R_1 = 6.9% and wR_2 = 19.0%.

For B(2,3,4-Ar^F)$_3$, **3**, during the refinement process it was found to be twinned, which prevented an acceptable completion. As a result, the twin law 1 0 0 0 −1 0 0 0 −1 generated from TwinRotMat within Platon was used,[10] along with BASF 0.48419. This gave a final satisfactory refinement of R_1 = 4.9% and wR_2 = 11.8%.

S2.2 Solid-state structures

Figure S1. Solid-state structure of *μ2-dimethyl-bis[(3,4,5-trifluorophenyl)methyl-alane]* (**2**). H-atoms omitted for clarity and thermal ellipsoids drawn at 50% probability.

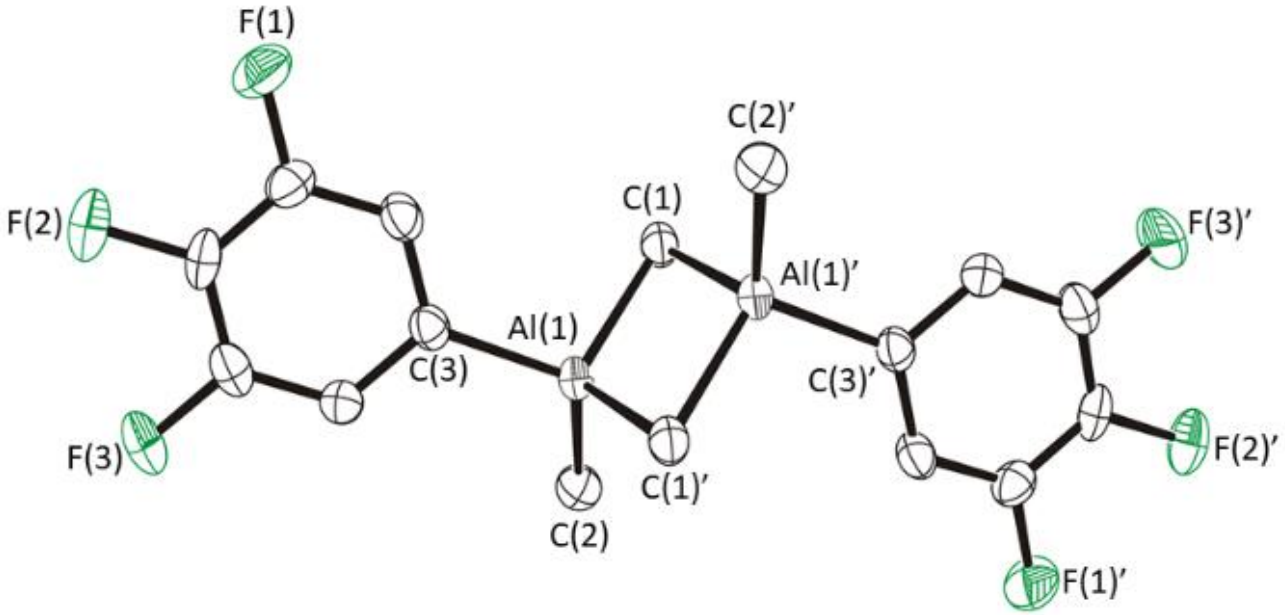


Figure S2 Solid-state structure of *tris(2,3,4-trifluorophenyl)borane* (**3**). H-atoms omitted for clarity and thermal ellipsoids drawn at 50% probability.

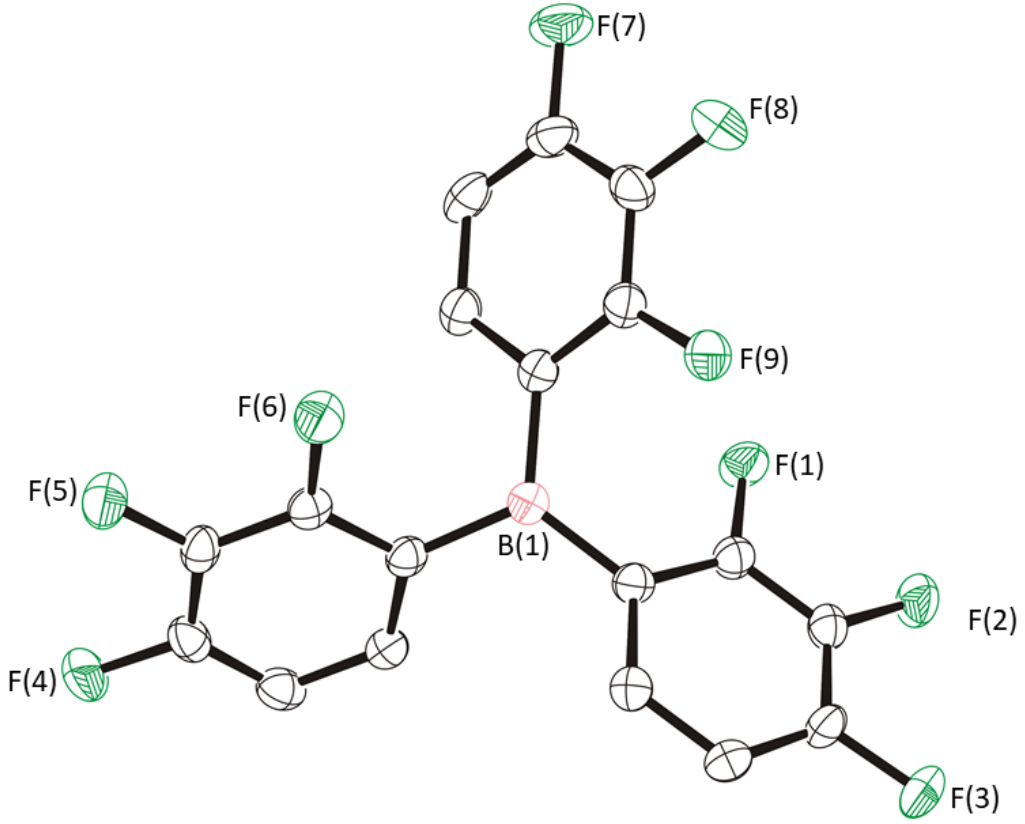


Figure S3. Solid-state structure of *tris(2,3,4-trifluorophenyl)alane* (**4**). H-atoms omitted for clarity and thermal ellipsoids drawn at 50% probability.

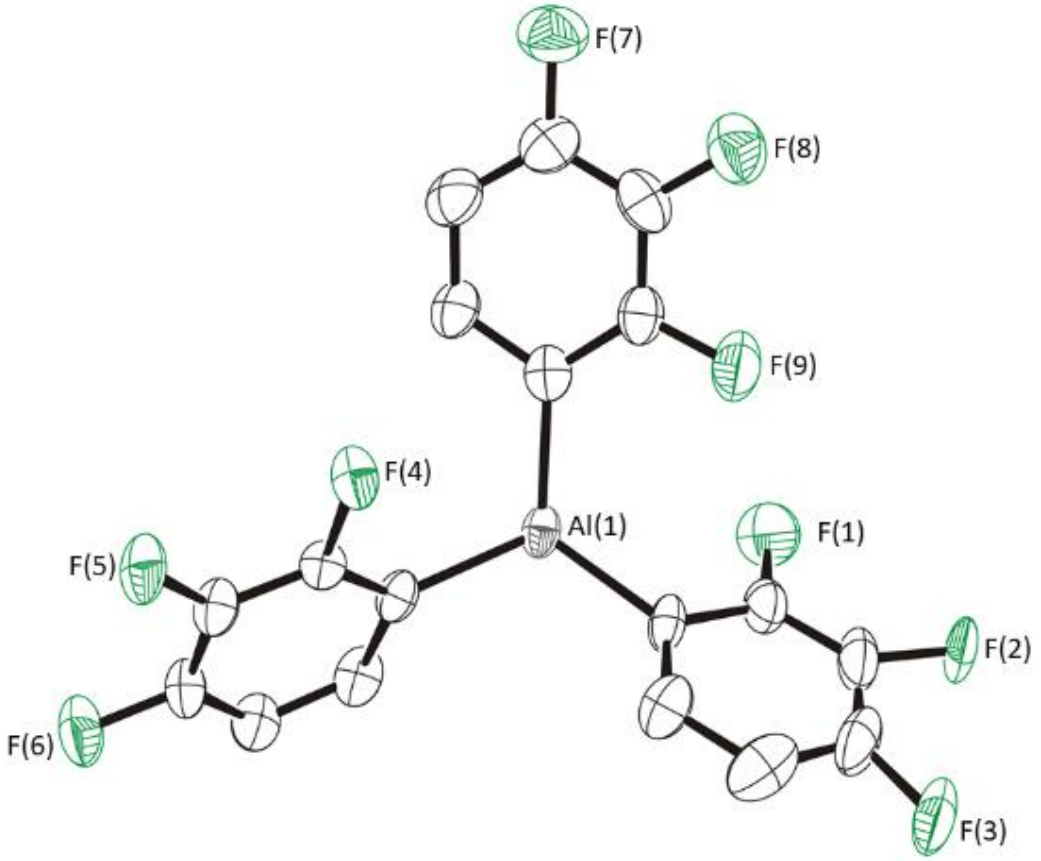


Figure S4. Solid-state structure of *tris(2,3,4-trifluorophenyl)alane tetrahydrofuran adduct* (**4·THF**). H-atoms omitted for clarity and thermal ellipsoids drawn at 50% probability.

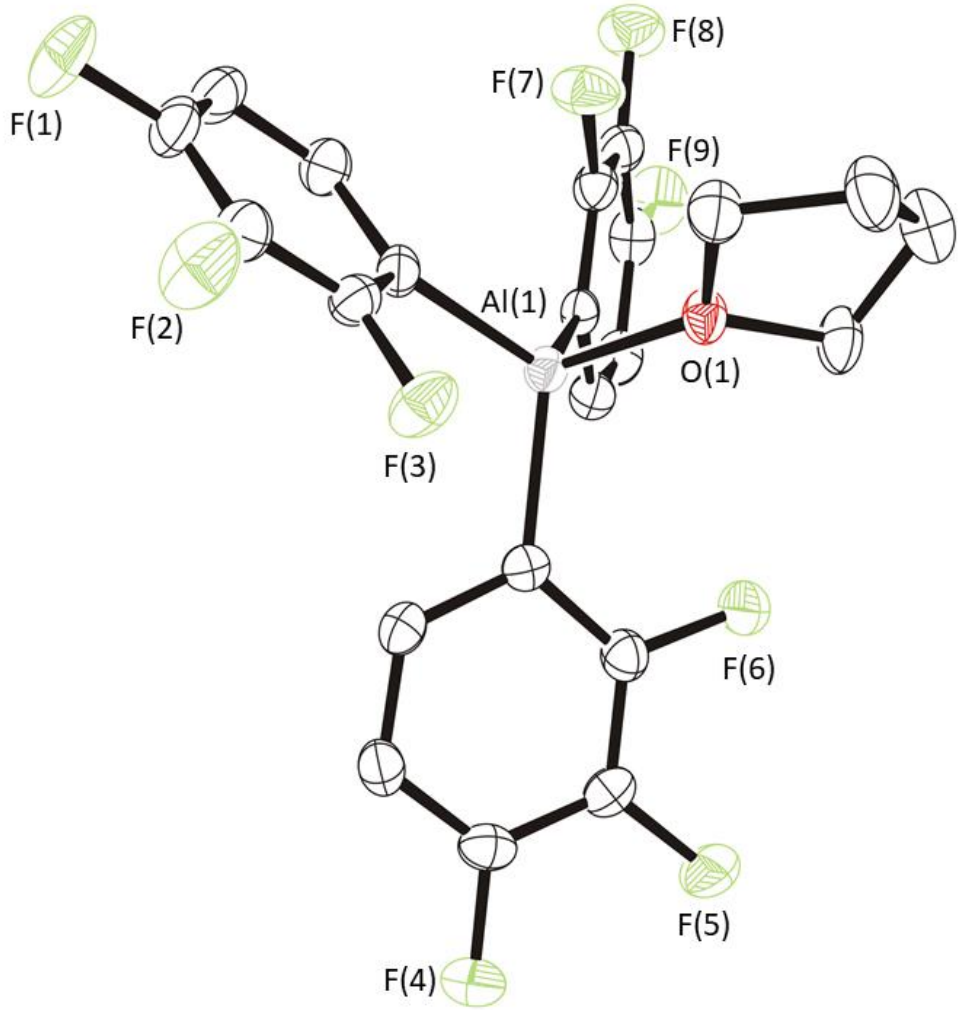
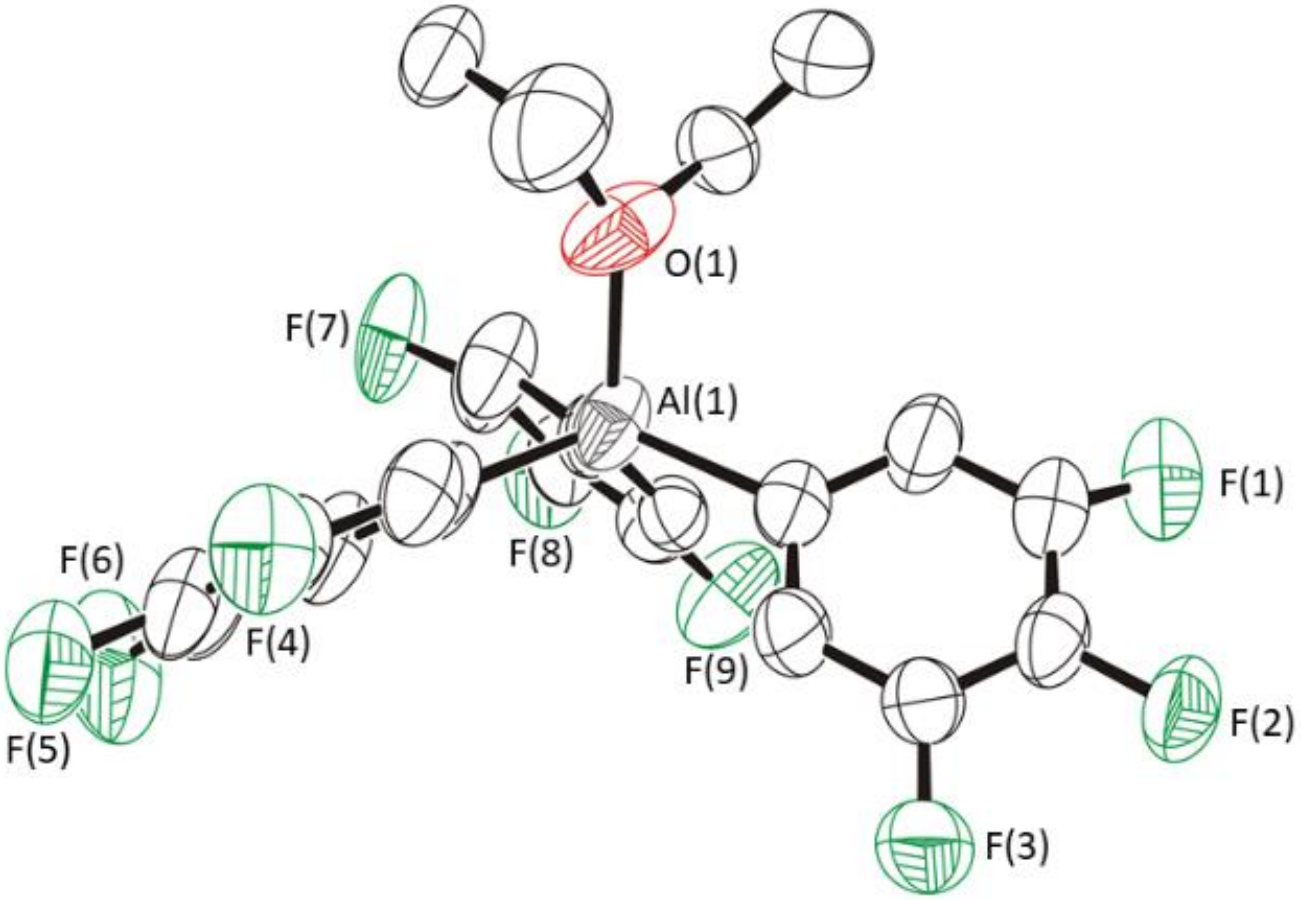


Figure S5. Solid-state structure of *tris(3,4,5-trifluorophenyl)alane etherate* (**5**). H-atoms omitted for clarity and thermal ellipsoids drawn at 50% probability.



S2.3 Refinement data

Table S1. X-ray refinement data for $(Al(3,4,5\text{-}Ar^F)Me_2)_2$, $Al(2,3,4\text{-}Ar^F)_3$ and $Al(3,4,5\text{-}Ar^F)_3{\cdot}OEt_2$.

Compound	**$(Al(3,4,5\text{-}Ar^F)Me_2)_2$**	**$Al(2,3,4\text{-}Ar^F)_3$**	**$Al(3,4,5\text{-}Ar^F)_3{\cdot}OEt_2$**
Empirical formula	$C_8H_8AlF_3$	$C_{18}H_6AlF_9$	$C_{22}H_{16}AlF_9O$
Formula Weight	188.12	420.21	494.33
Temperature/ K	150(2)	150(2)	150(2)
Wavelength /Å	0.71073	0.71073	1.54178
Crystal System	Triclinic	Orthorhombic	Triclinic
Space Group	*P*-1	*Pbca*	*P*-1
a/ Å	6.9009(10)	9.8089(7)	10.2941(10)
b/ Å	7.4059(12)	17.9147(13)	10.3687(8)
c/ Å	9.7517(11)	18.0420(19)	10.6335(7)
α/ °	68.597(13)	90	99.732(6)
β/ °	71.726(12)	90	98.186(7)
γ/ °	72.199(14)	90	90.099(7)
Volume/ Å^3	430.18(12)	3170.4(5)	1106.85(16)
Z	1	8	2
Density (calc)/ g cm^{-3}	1.452	1.761	1.483
Absorption coefficient/ mm^{-1}	0.223	0.228	1.625
F(000)	192	1664	500
Crystal size/ mm^3	0.307 × 0.219 × 0.134	0.252 × 0.240 × 0.187	0.327 × 0.176 × 0.145
θ range/ °	3.480 to 29.439	3.272 to 27.498	4.263 to 72.675
Index ranges	-9 ≤ h ≤ 9	-12 ≤ h ≤ 12	-10 ≤ h ≤ 12
	-9 ≤ k ≤ 8	-22 ≤ k ≤ 23	-12 ≤ k ≤ 12
	-12 ≤ l ≤ 12	-23 ≤ l ≤ 17	-13 ≤ l ≤ 9
Reflections collected	3077	16279	7493
Independent reflections	3077	3616	4250
R(int)	0.0476	0.0922	0.0311
Absorption Correction	Multi-scan	Semi-empirical from equivalents	Gaussian
Data / restraints / parameters	3077 / 6 / 122	3616 /12 / 266	4250 / 58 / 366
Goodness of fit, S	0.982	1.027	1.047
Final R indices [I>2σ(I)]	R_1 = 0.0585	R_1 = 0.0839	R_1 = 0.0690
	wR_2 = 0.1349	wR_2 = 0.1960	wR_2 = 0.1902
R indices (all data)	R_1 = 0.1024	R_1 = 0.1391	R_1 = 0.0946
	wR_2 = 0.1489	wR_2 = 0.2413	wR_2 = 0.2175
Max/min residual electron density/ *e*$^-$Å^{-3}	+0.305	+0.672	+0.327
	-0.345	-0.567	-0.448

Table S2. X-ray refinement data for $B(2,3,4\text{-}Ar^F)_3$ and $Al(2,3,4\text{-}Ar^F)_3\cdot THF$

Compound	**$B(2,3,4\text{-}Ar^F)_3$**	**$Al(2,3,4\text{-}Ar^F)_3\cdot THF$**
Empirical formula	$C_{18}H_6BF_9$	$C_{22}H_{14}Al\ F_9O$
Formula Weight	404.04	492.31
Temperature/ K	150(2)	150(2)
Wavelength /Å	0.71073	0.71073
Crystal System	Monoclinic	Triclinic
Space Group	$P2_1/n$	P-1
a/ Å	8.6982(5)	10.3004(5)
b/ Å	16.8822(9)	10.3101(6)
c/ Å	10.6039(5)	10.3293(6)
α/ **°**	90	71.348(5)
β/ **°**	90.014(5)	84.423(4)
γ/ **°**	90	78.631(4)
Volume/ Å^3	1557.13(15)	1018.25(10)
Z	4	2
Density (calc)/ g cm^{-3}	1.723	1.606
Absorption coefficient/ mm^{-1}	0.175	0.194
F(000)	800	496
Crystal size/ mm^3	0.479 × 0.301 × 0.199	0.445 x 0.286 x 0.210
θ range/ **°**	3.363 to 29.900	3.398 to 29.527
Index ranges	-11 ≤ h ≤ 11 -23 ≤ k ≤ 21 -14 ≤ l ≤ 14	-14 ≤ h ≤ 14, -14 ≤ k ≤ 11, -14 ≤ l ≤ 12
Reflections collected	16055	7939
Independent reflections	3966	4742
R(int)	0.0724	0.0233
Absorption Correction	Semi-empirical from equivalents	Gaussian
Data / restraints / parameters	3966 / 0 / 254	4742 / 0 / 298
Goodness of fit, S	1.117	1.024
Final R indices [I>2σ(I)]	R_1 = 0.0488 wR_2 = 0.1182	R1 = 0.0469, wR2 = 0.1008
R indices (all data)	R_1 = 0.0687 wR_2 = 0.1376	R1 = 0.0720, wR2 = 0.1158
Max/min residual electron density/ e-Å^{-3}	+0.643 -0.256	+0.437 -0.323

S3 DFT Calculations

S3.1 DFT general experimental

Density functional theory (DFT) calculations were performed using the graphical interface WebMO computational platform, which employed the Gaussian 09 package.[11] Al(2,3,4-Ar^F)$_3$, Al(3,4,5-Ar^F)$_3$, B(2,3,4-Ar^F)$_3$, B(3,4,5-Ar^F)$_3$, Al(C_6F_5)$_3$, and B(C_6F_5)$_3$ were initially geometry optimized using the meta-hybrid M06-2X functional,[12] and Dunning's correlation-consistent polarized double zeta (cc-pVDZ) basis set on all atoms.[13] After this a vibrational frequency calculation was undertaken to ensure each structure was a minimum on the potential energy landscape. Atomic coordinates are presented in Section S3.4. Natural bond orbital (NBO) analyses were then performed on the optimized geometries using the same functional and basis set described above and presented in Section S3.2.[14] Lastly, fluoride ion affinity (FIA) calculations were then performed.[15] This was done by calculating the enthalpy of the triarylalane/triarylborane, fluoride ion and triarylalane–F /triarylborane–F complex. A counterpoise correction was then performed to give a basis set superposition error (BSSE) value, which was added to the enthalpy of the reaction to give the final FIA value. Note that FIA is the negative of the reaction enthalpy plus BSSE.

S3.2 NBO analyses

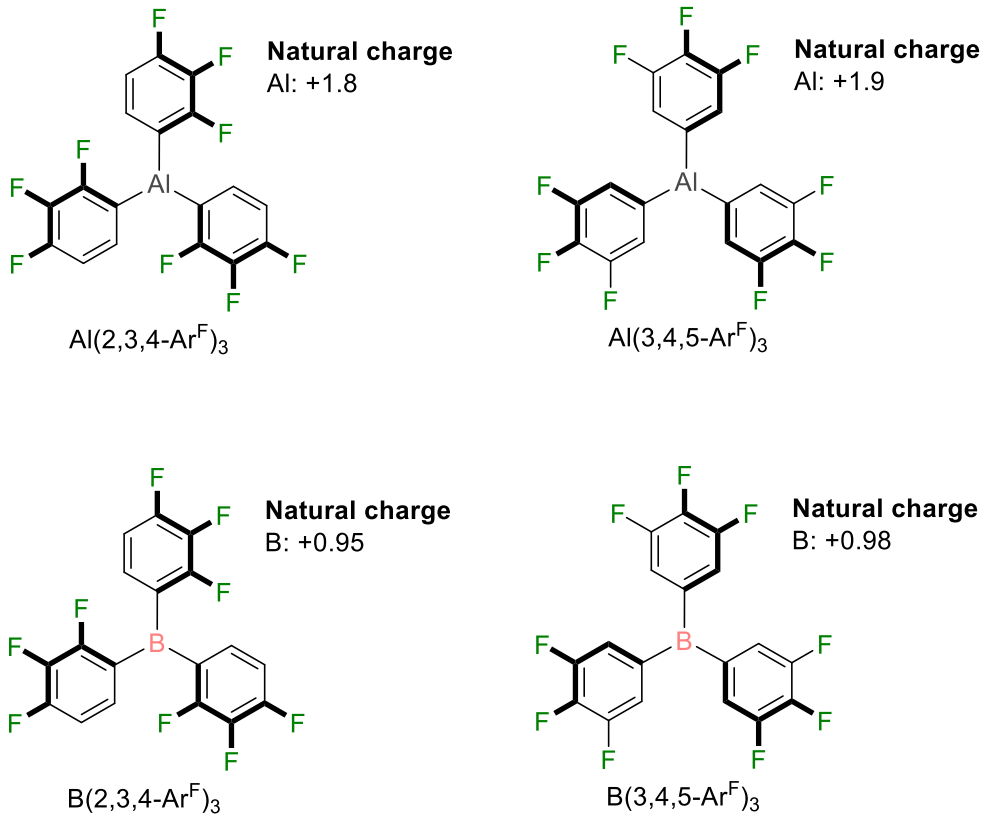


Figure S6. NBO analysis of Al(2,3,4-Ar^F)$_3$, Al(3,4,5-Ar^F)$_3$, B(2,3,4-Ar^F)$_3$ and B(3,4,5-Ar^F)$_3$.

S3.3 Fluoride ion affinity values

Table S3 Enthalpy values for determining the fluoride ion affinity. Where Ha = Hartree units.

$E(Ar)_3 + F^- \rightarrow F - E(Ar)_3^-$			$FIA = -\Delta H$	**Definition of FIA**	
Species	$Al(3,4,5\text{-}Ar^F)_3$ (Ha)	F^- (Ha)	$^-Al(3,4,5\text{-}Ar^F)_3F$ (Ha)	BSSE (Ha)	FIA (KJ mol^{-1})
Enthalpy	-1829.83018	-99.738167	-1929.824575	0.061640431	511
Species	$Al(2,3,4\text{-}Ar^F)_3$ (Ha)	F^- (Ha)	$^-Al(2,3,4\text{-}Ar^F)_3F$ (Ha)	BSSE (Ha)	FIA (KJ mol^{-1})
Enthalpy	-1829.846028	-99.738167	-1929.837331	0.06221322	501
Species	$B(3,4,5\text{-}Ar^F)_3$ (Ha)	F^- (Ha)	$^-B(3,4,5\text{-}Ar^F)_3F$ (Ha)	BSSE (Ha)	FIA (KJ mol^{-1})
Enthalpy	-1612.267807	-99.738167	-1712.237861	0.069153069	427
Species	$B(2,3,4\text{-}Ar^F)_3$ (Ha)	F^- (Ha)	$^-B(2,3,4\text{-}Ar^F)_3F$ (Ha)	BSSE (Ha)	FIA (KJ mol^{-1})
Enthalpy	-1612.273944	-99.738167	-1712.233613	0.067797654	404
Species	$Al(C_6F_5)_3$ (Ha)	F^- (Ha)	$^-Al(C_6F_5)_3F$ (Ha)	BSSE (Ha)	FIA (KJ mol^{-1})
Enthalpy	-2425.144391	-99.738167	-2525.149834	0.061262443	541
Species	$B(C_6F_5)_3$ (Ha)	F^- (Ha)	$^-B(C_6F_5)_3F$ (Ha)	BSSE (Ha)	FIA (KJ mol^{-1})
Enthalpy	-2207.560101	-99.738167	-2307.539725	0.066692489151	459

S3.4 DFT coordinates

Coordinates for $Al(3,4,5\text{-}Ar^F)_3$

Al	-0.000000	0.000000	0.043423
C	-0.005914	1.953916	0.031770
C	-1.106856	2.687020	0.510160
C	-1.094107	4.073366	0.488820
C	0.000000	4.770604	-0.013065
C	1.090778	4.053774	-0.493193
C	1.097175	2.667362	-0.470005
H	1.984489	2.166171	-0.863412
F	2.128926	4.736186	-0.976783
F	0.002790	6.097915	-0.033038
F	-2.130378	4.776569	0.946493
H	-1.996793	2.202215	0.918284
C	1.695098	-0.971836	0.031770
C	1.761415	-2.283862	-0.470005
C	2.965282	-2.971529	-0.493193
C	4.131465	-2.385302	-0.013065
C	4.074692	-1.089158	0.488820
C	2.880456	-0.384945	0.510160
H	2.905571	0.628166	0.918284
F	5.201819	-0.543323	0.946493
F	5.279555	-3.051374	-0.033038
F	3.037194	-4.211797	-0.976783
H	0.883715	-2.801704	-0.863412
C	-1.689184	-0.982080	0.031770
C	-1.773600	-2.302076	0.510160
C	-2.980585	-2.984207	0.488820
C	-4.131465	-2.385302	-0.013065
C	-4.056060	-1.082245	-0.493193
C	-2.858590	-0.383499	-0.470005
H	-2.868204	0.635532	-0.863412
F	-5.166120	-0.524389	-0.976783
F	-5.282345	-3.046542	-0.033038
F	-3.071441	-4.233246	0.946493
H	-0.908778	-2.830381	0.918284

Coordinates for $^{-}Al(3,4,5\text{-}Ar^F)_3F$

Al	-0.024211	-0.047806	-1.158017
F	-0.128065	-0.100739	-2.880649
C	0.335778	1.821426	-0.498419
C	1.533951	2.189117	0.136808
C	1.738674	3.483824	0.592341
F	2.885338	3.834279	1.201251
C	0.763275	4.459900	0.436402
F	0.965225	5.709742	0.876980
C	-0.429712	4.110594	-0.185270
F	-1.365496	5.066304	-0.325874
C	-0.645480	2.819667	-0.640394
H	-1.608661	2.608551	-1.112123
H	2.338259	1.465546	0.293338
C	-1.807034	-0.657134	-0.459663
C	-2.731607	-1.271004	-1.322454
C	-3.966547	-1.700546	-0.859740
F	-4.855998	-2.286026	-1.681249
C	-4.328370	-1.538018	0.471816
F	-5.524486	-1.953559	0.912239
C	-3.425967	-0.930388	1.335747
F	-3.793816	-0.776220	2.619755
C	-2.189350	-0.494651	0.883327
H	-1.530231	-0.011394	1.610076
H	-2.499731	-1.416291	-2.380113
C	1.466242	-1.242363	-0.523634
C	2.755852	-1.139345	-1.077215
C	3.797003	-1.938346	-0.630099
F	5.028244	-1.843690	-1.162145
C	3.600625	-2.867444	0.384399
F	4.609564	-3.639424	0.811718
C	2.333666	-2.980537	0.942231
F	2.158917	-3.887501	1.919475
C	1.284817	-2.186305	0.501752
H	0.309665	-2.330380	0.974670
H	2.975691	-0.433727	-1.882762

Coordinates for $Al(2,3,4\text{-}Ar^F)_3$

Al	0.000000	-0.000000	-0.030175
C	-0.000000	1.954687	0.077699
C	-1.072024	2.661014	0.655674
C	-1.052258	4.044837	0.804440
C	0.055632	4.752353	0.358755
C	1.133454	4.099181	-0.227822
C	1.081781	2.716313	-0.352261
F	2.138489	2.118025	-0.928284
F	2.186799	4.787024	-0.661438
F	0.111186	6.077501	0.477069
H	-1.878468	4.596081	1.251867
H	-1.955586	2.117067	0.993854
C	1.692809	-0.977344	0.077699
C	1.811506	-2.295007	-0.352261
C	2.983267	-3.031190	-0.227822
C	4.087842	-2.424355	0.358755
C	4.029061	-1.111136	0.804440
C	2.840518	-0.402107	0.655674
H	2.811226	0.635053	0.993854
H	4.919557	-0.671239	1.251867
F	5.207678	-3.135041	0.477069
F	3.052285	-4.287336	-0.661438
F	0.765019	-2.910998	-0.928284
C	-1.692809	-0.977344	0.077699
C	-1.768494	-2.258907	0.655674
C	-2.976803	-2.933701	0.804440
C	-4.143474	-2.327998	0.358755
C	-4.116721	-1.067990	-0.227822
C	-2.893287	-0.421307	-0.352261
F	-2.903508	0.792973	-0.928284
F	-5.239084	-0.499688	-0.661438
F	-5.318864	-2.942461	0.477069
H	-3.041088	-3.924842	1.251867
H	-0.855641	-2.752120	0.993854

Coordinates for $^{-}Al(2,3,4\text{-}Ar^F)_3F$

Al	-0.185071	0.079510	-1.130864
F	-0.320721	0.151103	-2.849324
C	1.284547	1.379168	-0.688540
C	1.879397	1.453109	0.561504
F	1.454305	0.648883	1.558631
C	2.913368	2.330955	0.868910
F	3.456870	2.368326	2.094158
C	3.381531	3.179679	-0.126472
F	4.380906	4.028416	0.176504
C	2.831984	3.151169	-1.398573
C	1.795497	2.252372	-1.662307
H	1.367792	2.213450	-2.666793
H	3.229932	3.829113	-2.154112
C	-1.884836	0.752707	-0.265501
C	-3.125886	0.181805	-0.506012
F	-3.236214	-0.878917	-1.337684
C	-4.308985	0.628320	0.073454
F	-5.481657	0.034596	-0.192270
C	-4.256898	1.711192	0.941138
F	-5.403438	2.141202	1.497326
C	-3.049686	2.329705	1.224250
C	-1.888108	1.843971	0.619928
H	-0.940434	2.339748	0.845269
H	-3.042825	3.178538	1.908171
C	0.196093	-1.783671	-0.464135
C	1.496296	-2.232707	-0.272612
F	2.545575	-1.446228	-0.582648
C	1.808818	-3.490915	0.233785
F	3.082913	-3.874562	0.400107
C	0.774011	-4.353397	0.566880
F	1.084516	-5.567873	1.054735
C	-0.546081	-3.967163	0.398223
C	-0.814537	-2.694577	-0.109387
H	-1.858056	-2.402231	-0.242330
H	-1.337106	-4.667091	0.668023

Coordinates for $B(3,4,5\text{-}Ar^F)_3$

B	0.000000	0.000000	0.000000
C	0.000000	1.566743	0.000000
C	1.023604	2.288703	0.640166
C	1.008916	3.673311	0.646818
F	1.965076	4.365904	1.265129
C	0.000000	4.380270	0.000000
F	0.000000	5.706587	0.000000
C	-1.008916	3.673311	-0.646818
F	-1.965076	4.365904	-1.265129
C	-1.023604	2.288703	-0.640166
H	-1.840585	1.784762	-1.158246
H	1.840585	1.784762	1.158246
C	1.356839	-0.783372	0.000000
C	2.493877	-0.257885	-0.640166
C	3.685638	-0.962909	-0.646818
F	4.763522	-0.481147	-1.265129
C	3.793425	-2.190135	0.000000
F	4.942049	-2.853293	0.000000
C	2.676723	-2.710402	0.646818
F	2.798446	-3.884758	1.265129
C	1.470274	-2.030818	0.640166
H	0.625357	-2.486375	1.158246
H	2.465942	0.701612	-1.158246
C	-1.356839	-0.783372	0.000000
C	-1.470274	-2.030818	-0.640166
C	-2.676723	-2.710402	-0.646818
F	-2.798446	-3.884758	-1.265129
C	-3.793425	-2.190135	0.000000
F	-4.942049	-2.853293	0.000000
C	-3.685638	-0.962909	0.646818
F	-4.763522	-0.481147	1.265129
C	-2.493877	-0.257885	0.640166
H	-2.465942	0.701612	1.158246
H	-0.625357	-2.486375	-1.158246

Coordinates for $^{-}B(3,4,5\text{-}Ar^F)_3F$

B	0.000000	0.000000	0.967396
F	0.000000	0.000000	2.411169
C	0.162046	1.544913	0.459665
C	-0.207083	1.990947	-0.818067
C	-0.000000	3.308034	-1.198972
F	-0.353270	3.737973	-2.423968
C	0.566199	4.227825	-0.326670
F	0.757226	5.503099	-0.699054
C	0.922019	3.795902	0.945586
F	1.460259	4.700285	1.784436
C	0.727442	2.482095	1.337394
H	1.011645	2.181004	2.346501
H	-0.686237	1.324030	-1.538671
C	1.256911	-0.912793	0.459665
C	1.827752	-0.816135	-0.818067
C	2.864841	-1.654017	-1.198972
F	3.413815	-1.563046	-2.423968
C	3.378304	-2.604256	-0.326670
F	4.387211	-3.407327	-0.699054
C	2.826339	-2.696443	0.945586
F	3.340437	-3.614764	1.784436
C	1.785836	-1.871030	1.337394
H	1.382983	-1.966612	2.346501
H	1.489762	-0.067716	-1.538671
C	-1.418957	-0.632120	0.459665
C	-1.620669	-1.174813	-0.818067
C	-2.864841	-1.654017	-1.198972
F	-3.060545	-2.174927	-2.423968
C	-3.944504	-1.623570	-0.326670
F	-5.144437	-2.095773	-0.699054
C	-3.748357	-1.099460	0.945586
F	-4.800696	-1.085521	1.784436
C	-2.513278	-0.611065	1.337394
H	-2.394628	-0.214392	2.346501
H	-0.803525	-1.256313	-1.538671

Coordinates for $B(2,3,4\text{-}Ar^F)_3$

B	-0.168177	-0.186317	-0.040803
C	0.939258	-1.287071	0.068786
C	2.213084	-1.142534	-0.490086
F	2.529919	-0.056099	-1.197474
C	3.194548	-2.116612	-0.369883
F	4.387124	-1.949972	-0.934009
C	2.910714	-3.274321	0.347584
F	3.864442	-4.194929	0.459193
C	1.664966	-3.467680	0.926538
C	0.693754	-2.484670	0.767705
H	-0.288174	-2.636867	1.217527
H	1.479727	-4.385929	1.481984
C	0.137649	1.342006	-0.125860
C	1.279738	1.920129	0.435870
F	2.151042	1.182306	1.128066
C	1.557044	3.276000	0.329723
F	2.646256	3.792694	0.891768
C	0.676666	4.089662	-0.374948
F	0.961001	5.385315	-0.475447
C	-0.469818	3.566903	-0.956364
C	-0.731874	2.210224	-0.812704
H	-1.636038	1.798628	-1.263640
H	-1.135224	4.235556	-1.500520
C	-1.658276	-0.678495	-0.131742
C	-2.712616	-0.016781	0.504101
F	-2.482297	1.037830	1.290619
C	-4.034026	-0.427924	0.379660
F	-5.006776	0.219390	1.014616
C	-4.325096	-1.528943	-0.418537
F	-5.596547	-1.903269	-0.535963
C	-3.315955	-2.222511	-1.071111
C	-1.999912	-1.802155	-0.909008
H	-1.204005	-2.349443	-1.416015
H	-3.581965	-3.081114	-1.685983

Coordinates for $^{-}B(2,3,4\text{-}Ar^F)_3F$

B	-0.107391	-0.037728	0.842023
F	0.114420	0.045880	2.256087
C	-1.744346	0.045022	0.632491
C	-2.453720	-0.235903	-0.529511
F	-1.823747	-0.668407	-1.645936
C	-3.836403	-0.110254	-0.636764
F	-4.463001	-0.398746	-1.787445
C	-4.562499	0.314368	0.465823
F	-5.897996	0.434327	0.350743
C	-3.914520	0.602098	1.656148
C	-2.528576	0.460596	1.721652
H	-2.006482	0.673275	2.654893
H	-4.508214	0.927804	2.510779
C	0.599565	1.248432	0.088094
C	1.586977	2.023891	0.695475
F	2.044902	1.758440	1.925330
C	2.176875	3.122492	0.072131
F	3.113915	3.841981	0.709875
C	1.791739	3.472409	-1.212171
F	2.371561	4.540103	-1.794240
C	0.827369	2.729924	-1.871608
C	0.250831	1.642701	-1.214337
H	-0.505605	1.067738	-1.748394
H	0.539635	3.016008	-2.883265
C	0.519529	-1.465990	0.319768
C	1.900728	-1.649599	0.298049
F	2.732706	-0.656415	0.649117
C	2.506363	-2.848688	-0.064638
F	3.842538	-2.968550	-0.069730
C	1.709524	-3.929422	-0.415174
F	2.307862	-5.085547	-0.758331
C	0.330322	-3.812619	-0.400486
C	-0.238199	-2.591242	-0.034226
H	-1.326249	-2.515248	-0.014578
H	-0.273909	-4.677822	-0.673077

Coordinates for $Al(C_6F_5)_3$

Al	0.000000	0.000000	0.000000
C	-0.000000	1.951248	-0.000000
C	1.037867	2.680360	0.570896
F	2.054911	2.035685	1.156484
C	1.059071	4.068143	0.582009
F	2.059545	4.740318	1.140257
C	-0.000000	4.758589	-0.000000
F	-0.000000	6.082713	-0.000000
C	-1.059071	4.068143	-0.582009
F	-2.059545	4.740318	-1.140257
C	-1.037867	2.680360	-0.570896
F	-2.054911	2.035685	-1.156484
C	1.689830	-0.975624	-0.000000
C	2.840193	-0.441360	-0.570896
F	2.790411	0.761763	-1.156484
C	4.052651	-1.116889	-0.582009
F	5.135008	-0.586541	-1.140257
C	4.121059	-2.379295	-0.000000
F	5.267784	-3.041356	-0.000000
C	2.993580	-2.951254	0.582009
F	3.075463	-4.153777	1.140257
C	1.802326	-2.238999	0.570896
F	0.735500	-2.797448	1.156484
C	-1.689830	-0.975624	-0.000000
C	-1.802326	-2.238999	-0.570896
F	-0.735500	-2.797448	-1.156484
C	-2.993580	-2.951254	-0.582009
F	-3.075463	-4.153777	-1.140257
C	-4.121059	-2.379295	-0.000000
F	-5.267784	-3.041356	-0.000000
C	-4.052651	-1.116889	0.582009
F	-5.135008	-0.586541	1.140257
C	-2.840193	-0.441360	0.570896
F	-2.790411	0.761763	1.156484

Coordinates for $^{-}Al(C_6F_5)_3F$

Al	-0.048129	-0.009176	-1.166034
F	-0.114815	-0.136122	-2.869643
C	-1.591285	1.048961	-0.411646
C	-2.704549	1.510833	-1.096714
F	-2.846412	1.278615	-2.408452
C	-3.725129	2.232578	-0.481679
F	-4.785581	2.666877	-1.173959
C	-3.638616	2.507362	0.876248
F	-4.607449	3.199532	1.483438
C	-2.542455	2.061637	1.604654
F	-2.464672	2.328557	2.913371
C	-1.553224	1.346410	0.943057
F	-0.504870	0.930224	1.679072
C	-0.166572	-1.846877	-0.326031
C	-1.187127	-2.692017	-0.739348
F	-2.056074	-2.274671	-1.675428
C	-1.380465	-3.971790	-0.231159
F	-2.375844	-4.757058	-0.660272
C	-0.515972	-4.437281	0.750940
F	-0.676448	-5.663034	1.258882
C	0.512692	-3.624860	1.207983
F	1.333049	-4.078316	2.163333
C	0.661573	-2.351743	0.666171
F	1.662977	-1.609213	1.165023
C	1.698830	0.862834	-0.645782
C	2.871273	0.139320	-0.813172
F	2.814635	-1.108969	-1.310250
C	4.130081	0.626481	-0.486118
F	5.236689	-0.104196	-0.663258
C	4.234313	1.909958	0.036063
F	5.432907	2.406123	0.357394
C	3.091498	2.674698	0.221587
F	3.199150	3.911442	0.722845
C	1.854954	2.137883	-0.124787
F	0.789065	2.933870	0.068662

Coordinates for $B(C_6F_5)_3$

B	0.000000	0.000000	-0.004074
C	-0.000000	-0.000000	1.564557
C	0.413434	1.111049	2.307194
F	0.838429	2.214180	1.689229
C	0.430842	1.124862	3.693842
F	0.848919	2.193905	4.361059
C	-0.000000	-0.000000	4.387817
F	-0.000000	-0.000000	5.710499
C	-0.430842	-1.124862	3.693842
F	-0.848919	-2.193905	4.361059
C	-0.413434	-1.111049	2.307194
F	-0.838429	-2.214180	1.689229
C	-0.331543	1.318060	-0.786620
C	-1.241161	2.263605	-0.299896
F	-1.878030	2.055730	0.853339
C	-1.548637	3.432423	-0.980320
F	-2.430047	4.295836	-0.489656
C	-0.917854	3.698093	-2.190151
F	-1.191119	4.813434	-2.846089
C	0.000000	2.793002	-2.710824
F	0.604786	3.053132	-3.863814
C	0.267808	1.624682	-2.013151
F	1.157917	0.792721	-2.555694
C	0.331543	-1.318060	-0.786620
C	-0.267808	-1.624682	-2.013151
F	-1.157917	-0.792721	-2.555694
C	-0.000000	-2.793002	-2.710824
F	-0.604786	-3.053132	-3.863814
C	0.917854	-3.698093	-2.190151
F	1.191119	-4.813434	-2.846089
C	1.548637	-3.432423	-0.980320
F	2.430047	-4.295836	-0.489656
C	1.241161	-2.263605	-0.299896
F	1.878030	-2.055730	0.853339

Coordinates for $^{-}B(C_6F_5)_3F$

B	0.083655	-0.050743	-0.943225
F	0.068707	0.024887	-2.357566
C	1.627814	-0.439222	-0.508038
C	2.639572	0.470000	-0.811873
F	2.327959	1.662547	-1.338757
C	3.987474	0.232064	-0.583767
F	4.916673	1.146130	-0.888105
C	4.374977	-0.979610	-0.026418
F	5.668195	-1.233921	0.199993
C	3.409000	-1.920027	0.288642
F	3.775096	-3.093338	0.819634
C	2.066689	-1.638361	0.038739
F	1.208590	-2.620958	0.358000
C	-0.404150	1.409300	-0.330776
C	-1.561189	1.972921	-0.865881
F	-2.238466	1.328674	-1.825128
C	-2.090971	3.186182	-0.441584
F	-3.201465	3.690416	-0.994584
C	-1.459330	3.880385	0.581167
F	-1.951150	5.049176	1.006845
C	-0.318784	3.347448	1.161624
F	0.286240	4.008704	2.156336
C	0.180331	2.131417	0.703170
F	1.280791	1.684613	1.327756
C	-1.037378	-1.121846	-0.392616
C	-1.962898	-1.783527	-1.190010
F	-1.954702	-1.664357	-2.520726
C	-2.952544	-2.611792	-0.660140
F	-3.824643	-3.236397	-1.462097
C	-3.039361	-2.793117	0.710694
F	-3.984670	-3.585660	1.228885
C	-2.136399	-2.145350	1.544993
F	-2.215697	-2.319387	2.869991
C	-1.169154	-1.330817	0.976716
F	-0.310401	-0.723637	1.813777

S4 NMR spectra

S4.1 NMR spectra of borane complexes

Figure S7 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *tris(3,4,5-trifluorophenyl)borane* (**1**)

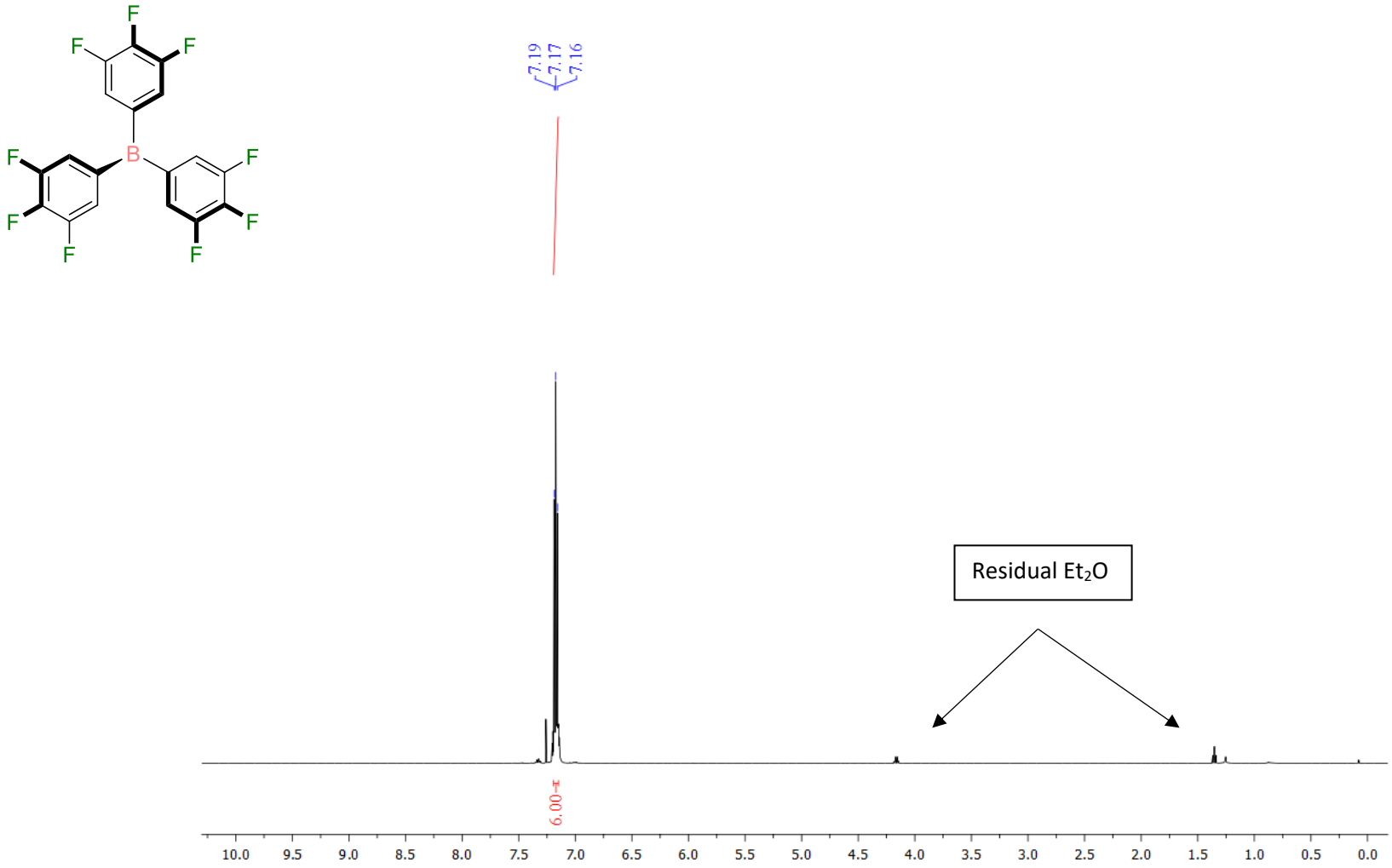


Figure S8 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *tris(3,4,5-trifluorophenyl)borane* (**1**)

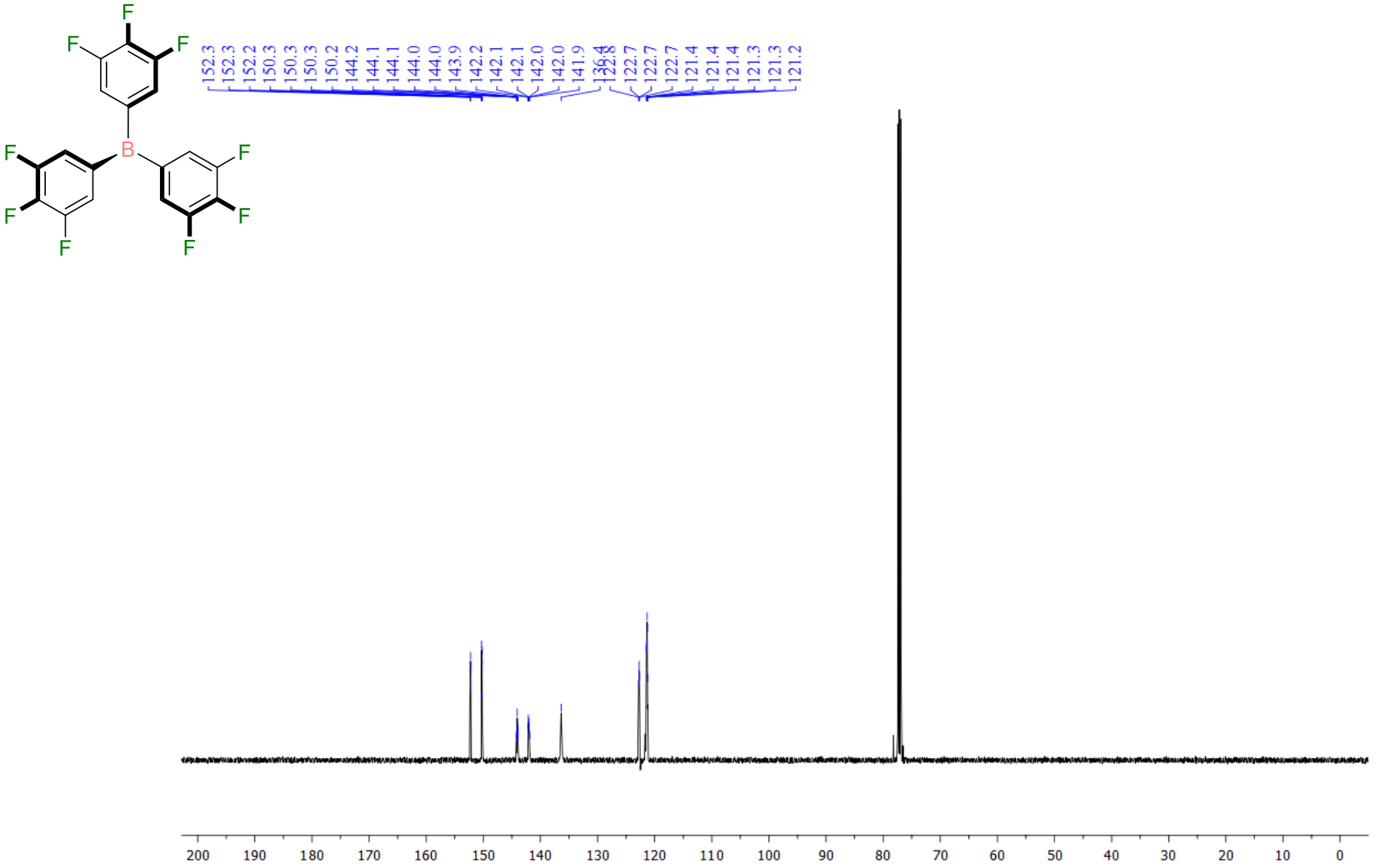
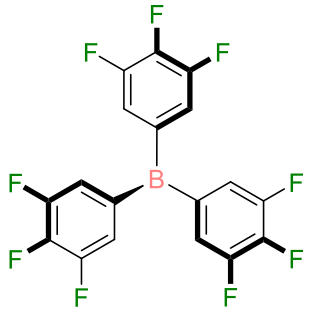


Figure S9 $^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 295 K) spectrum of *tris(3,4,5-trifluorophenyl)borane* (**1**)



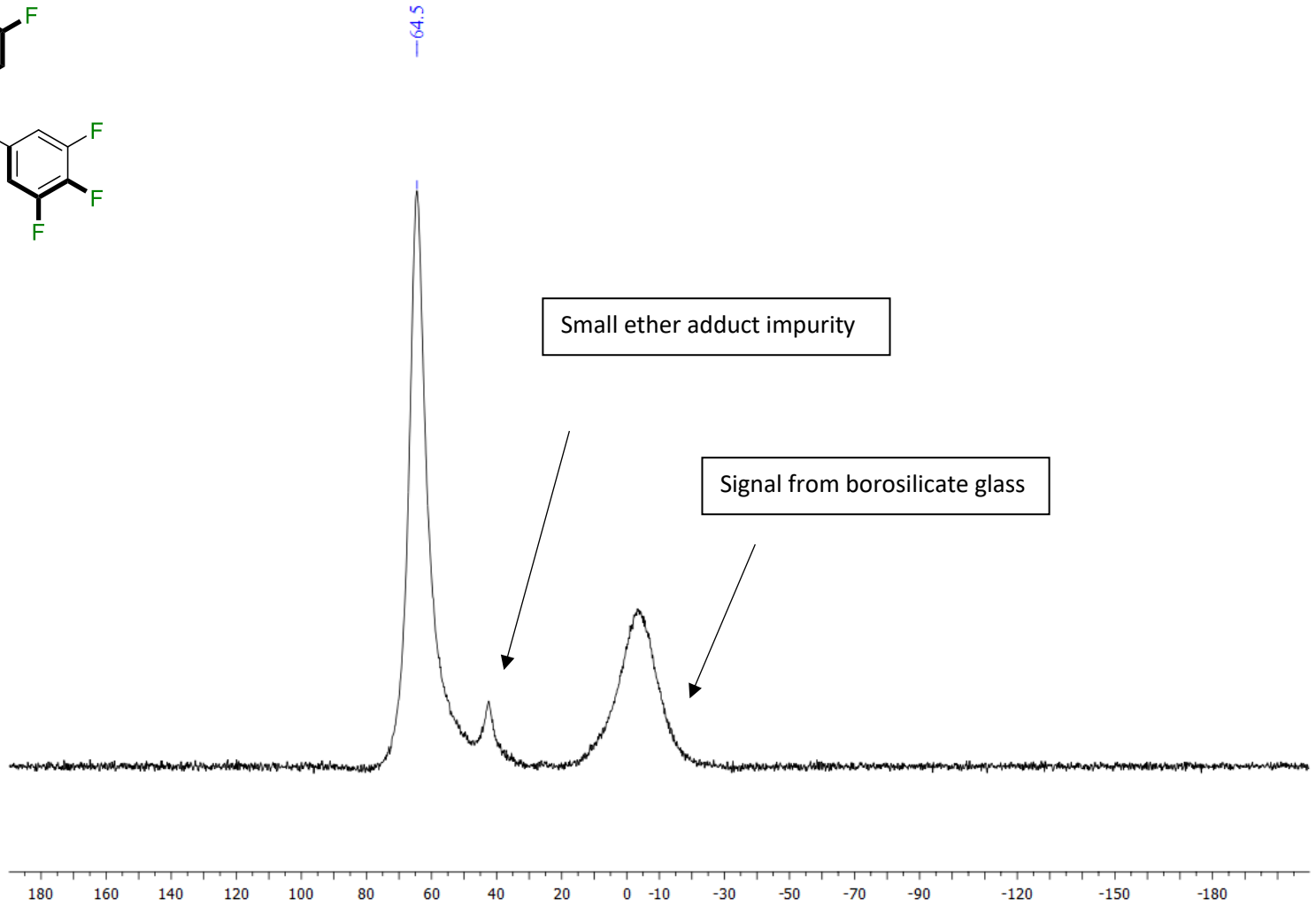


Figure S10 ^{19}F NMR (471 MHz, $CDCl_3$, 295 K) spectrum of *tris(3,4,5-trifluorophenyl)borane* (**1**)

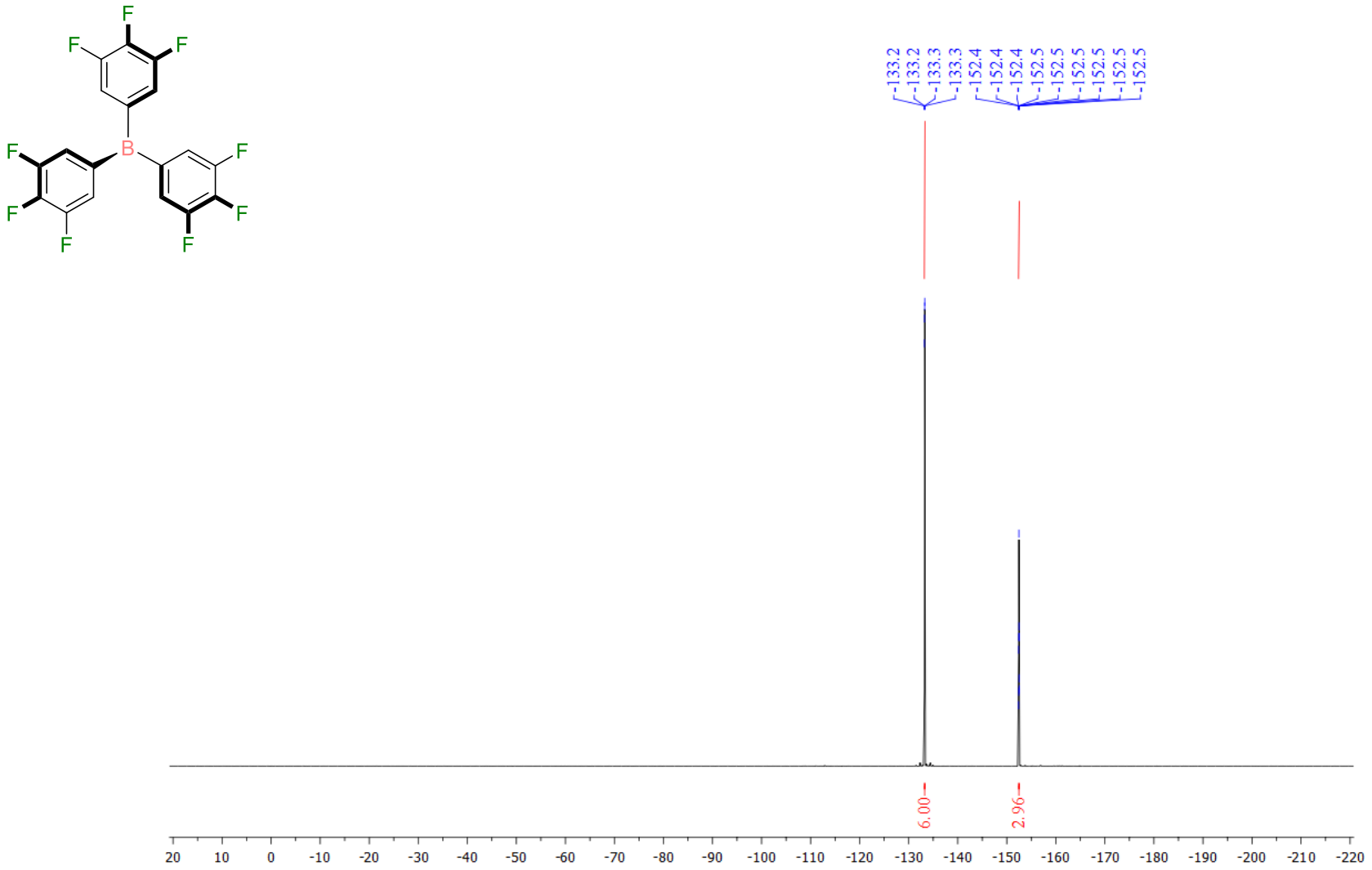
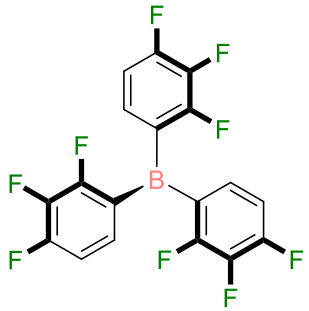


Figure S11 ^{1}H NMR (400 MHz, C_6D_6, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)borane* (**3**)



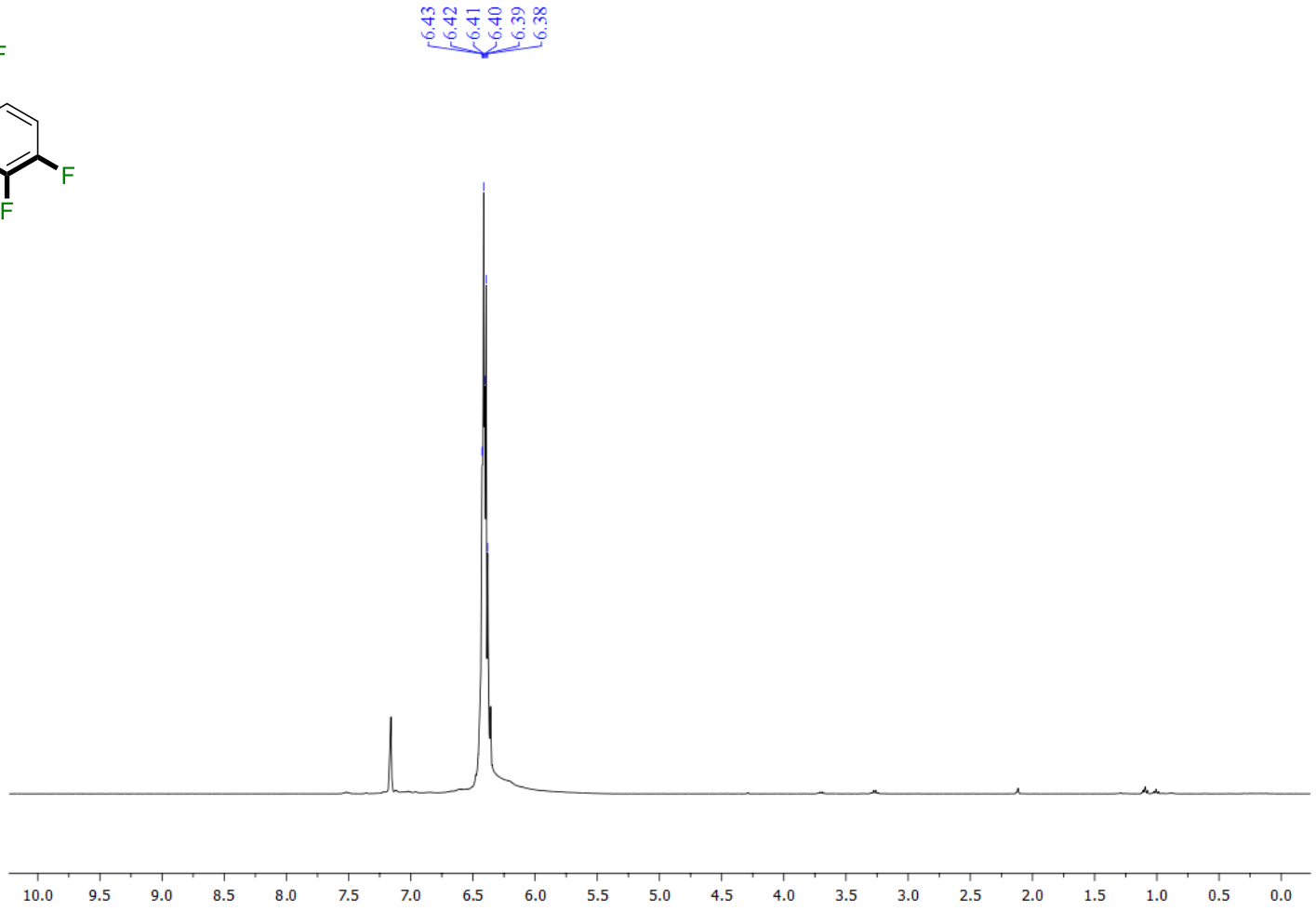


Figure S12 $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)borane* (**3**)

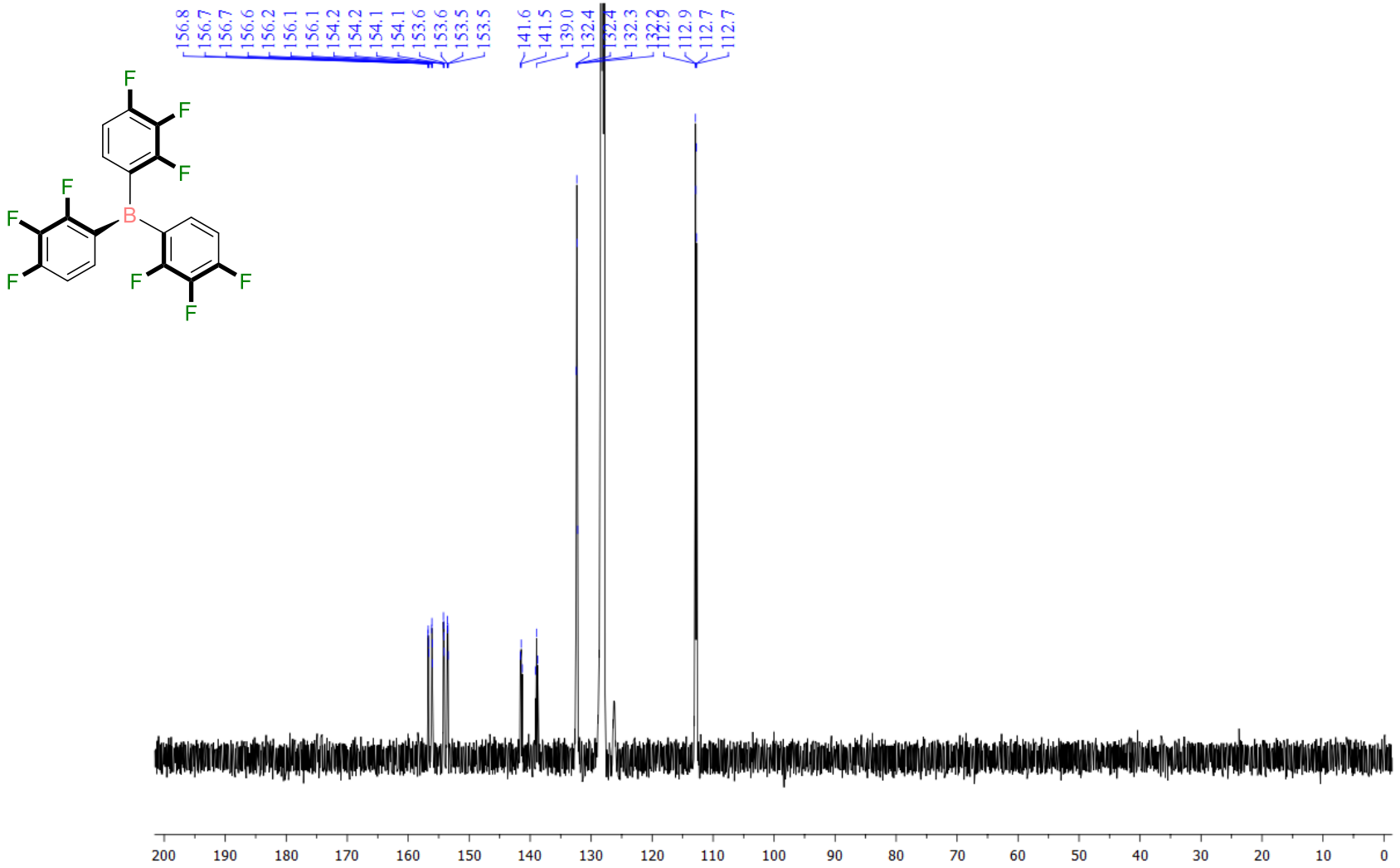


Figure S13 $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)borane* (**3**)

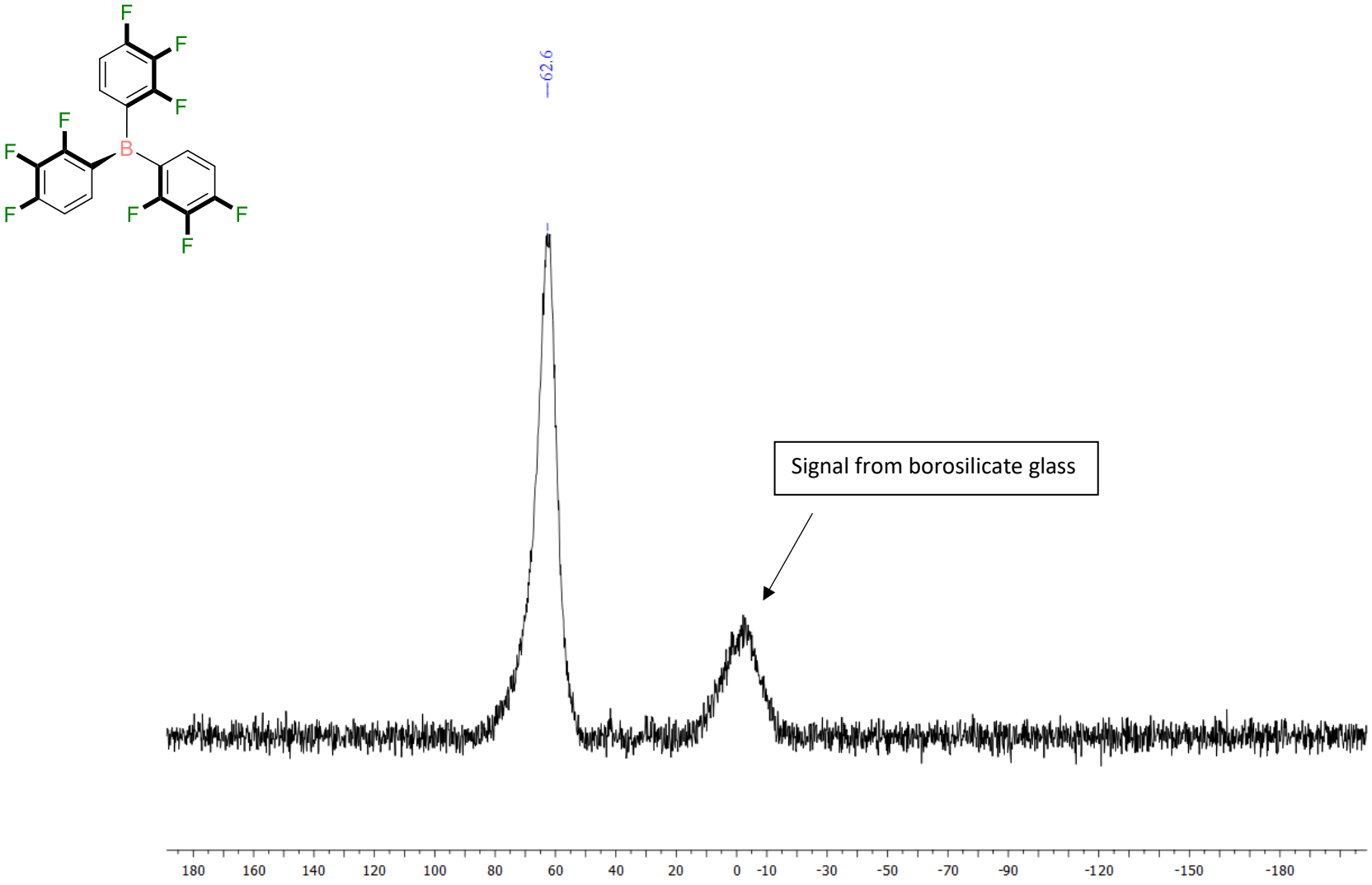
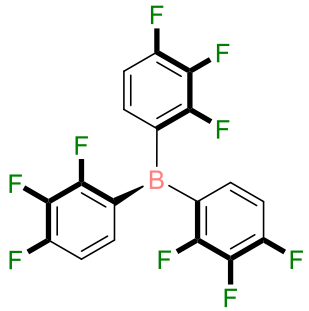
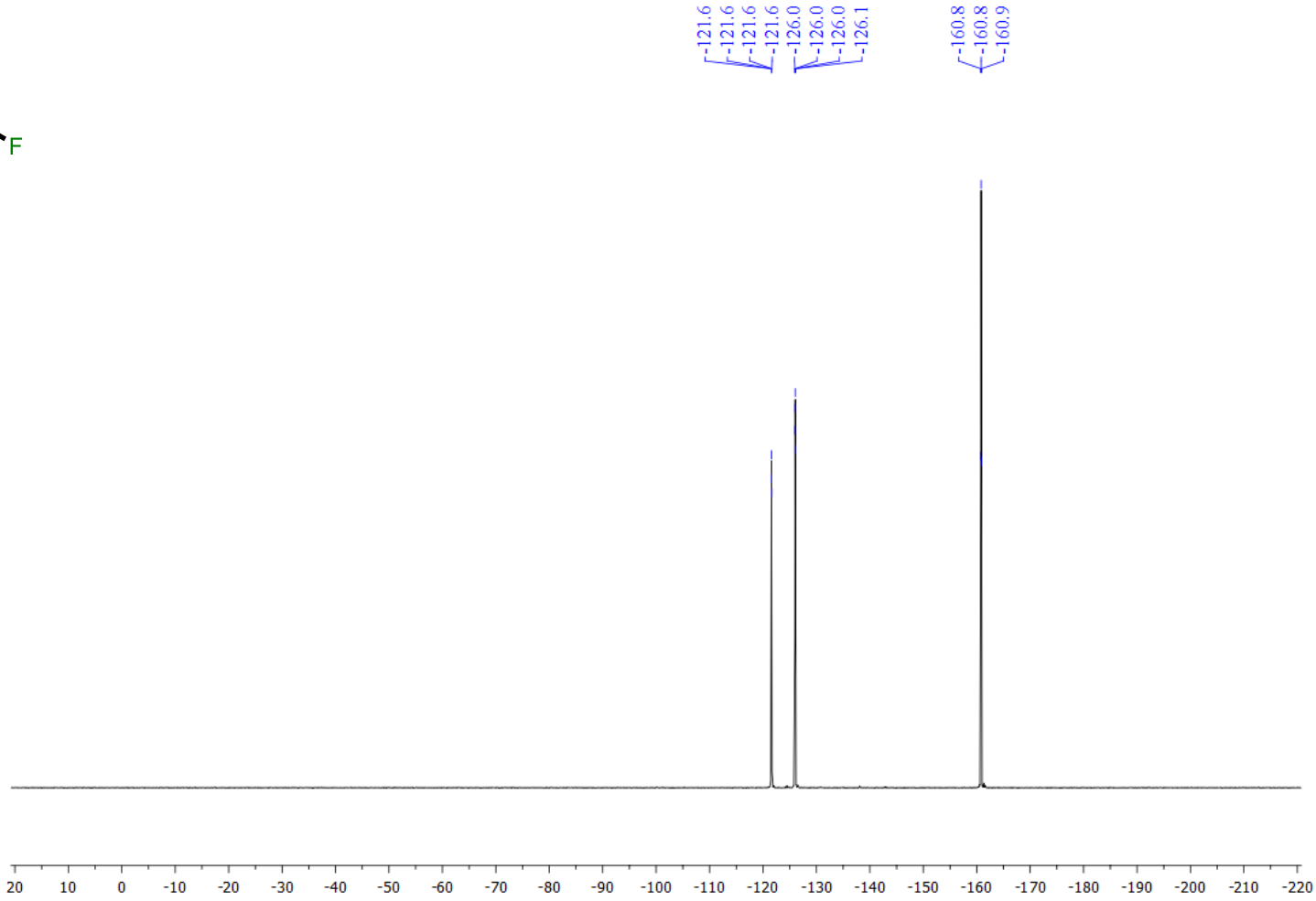


Figure S14 $^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)borane* (**3**)





S4.2 NMR spectra of alane complexes

Figure S15 ^{1}H NMR (500 MHz, C_6D_6, 295 K) spectrum of μ2-dimethyl-bis[(3,4,5-trifluorophenyl)methyl-alane] (**2**)

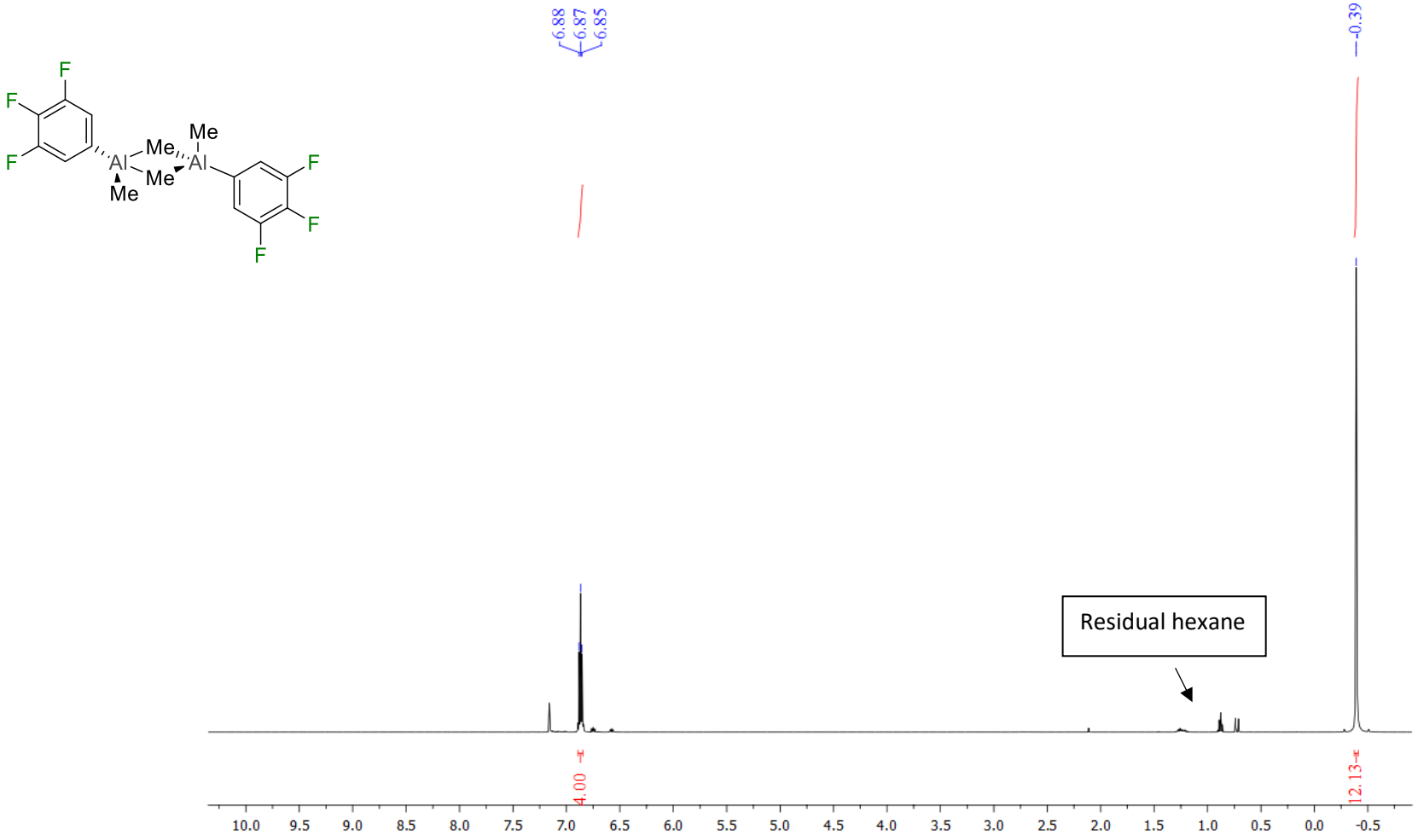


Figure S16 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 295 K) spectrum of μ2-dimethyl-bis[(3,4,5-trifluorophenyl)methyl-alane] (**2**)

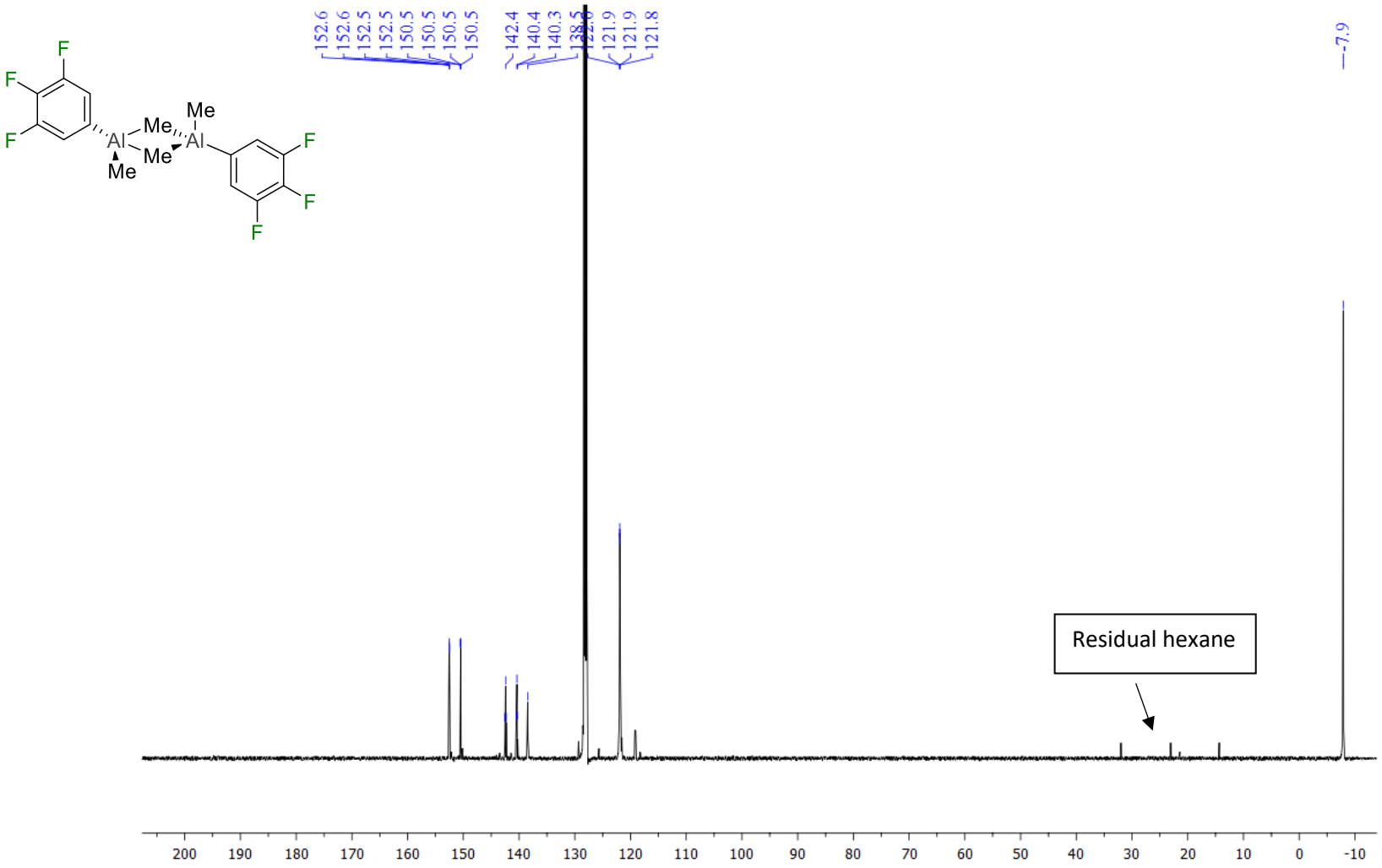


Figure S17 ^{19}F NMR (376 MHz, C_6D_6, 295 K) spectrum of μ2-dimethyl-bis[(3,4,5-trifluorophenyl)methyl-alane] (**2**)

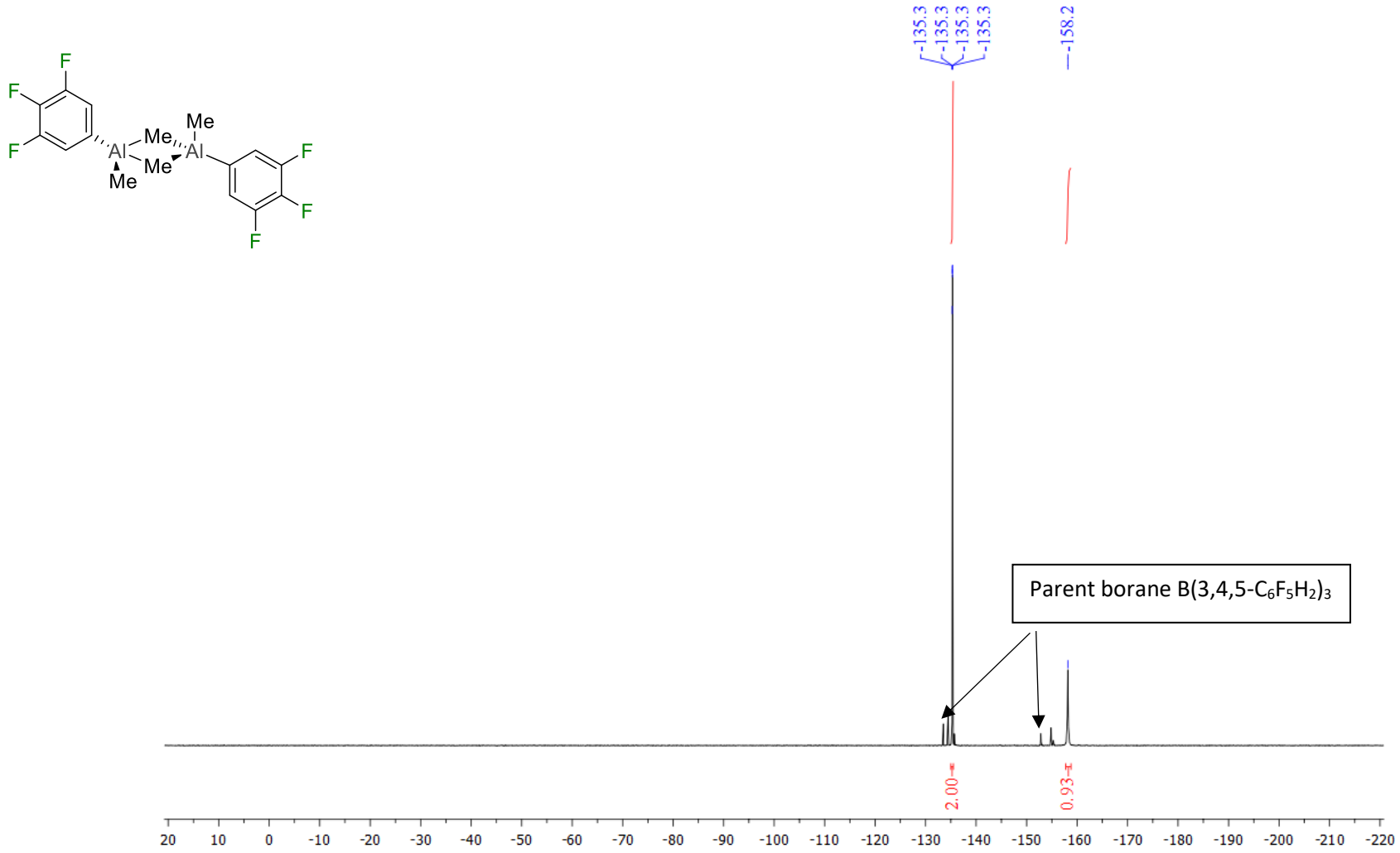


Figure S18 ^{1}H NMR (400 MHz, C_6D_6, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)alane* (**4**)

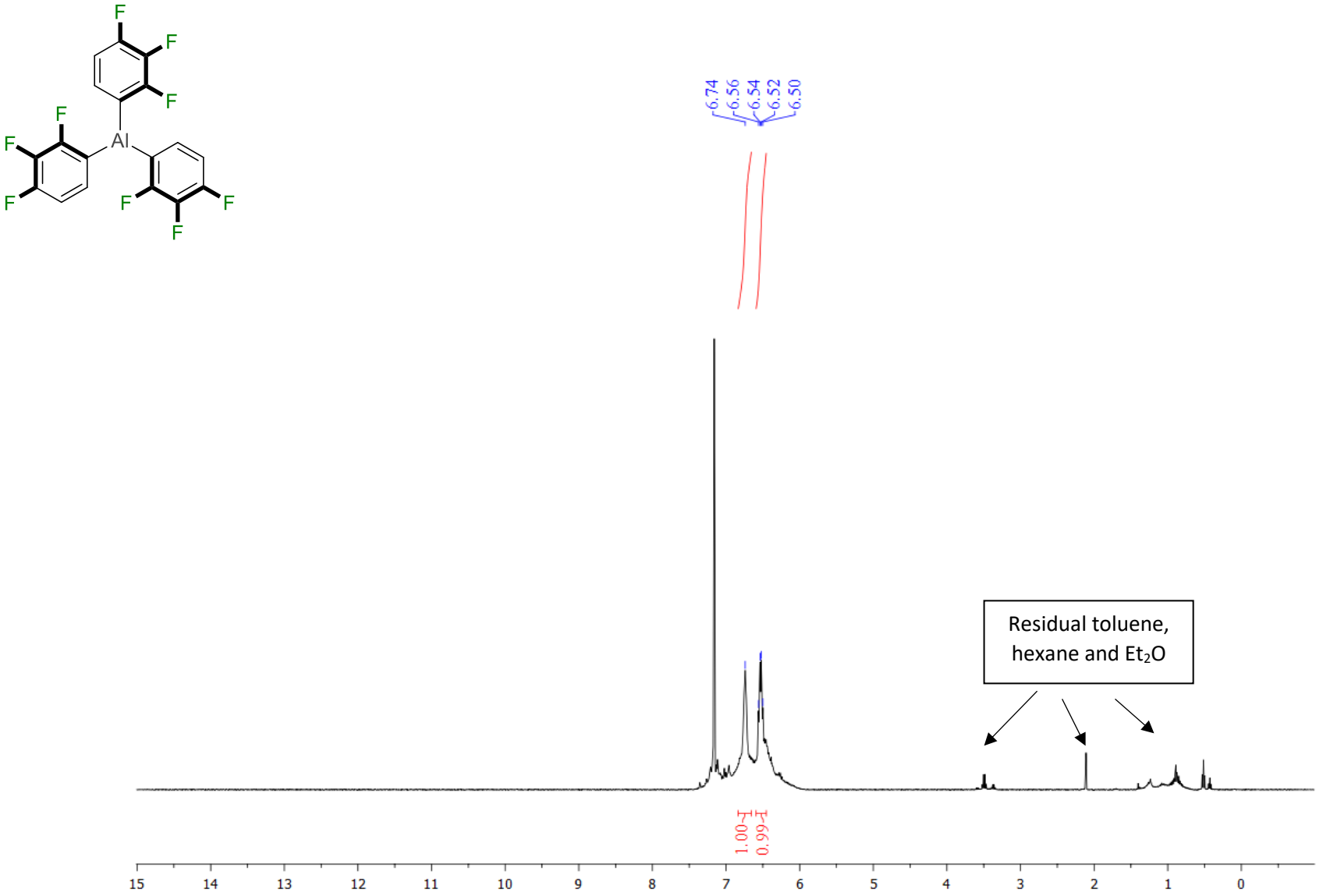


Figure S19 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)alane* (**4**)

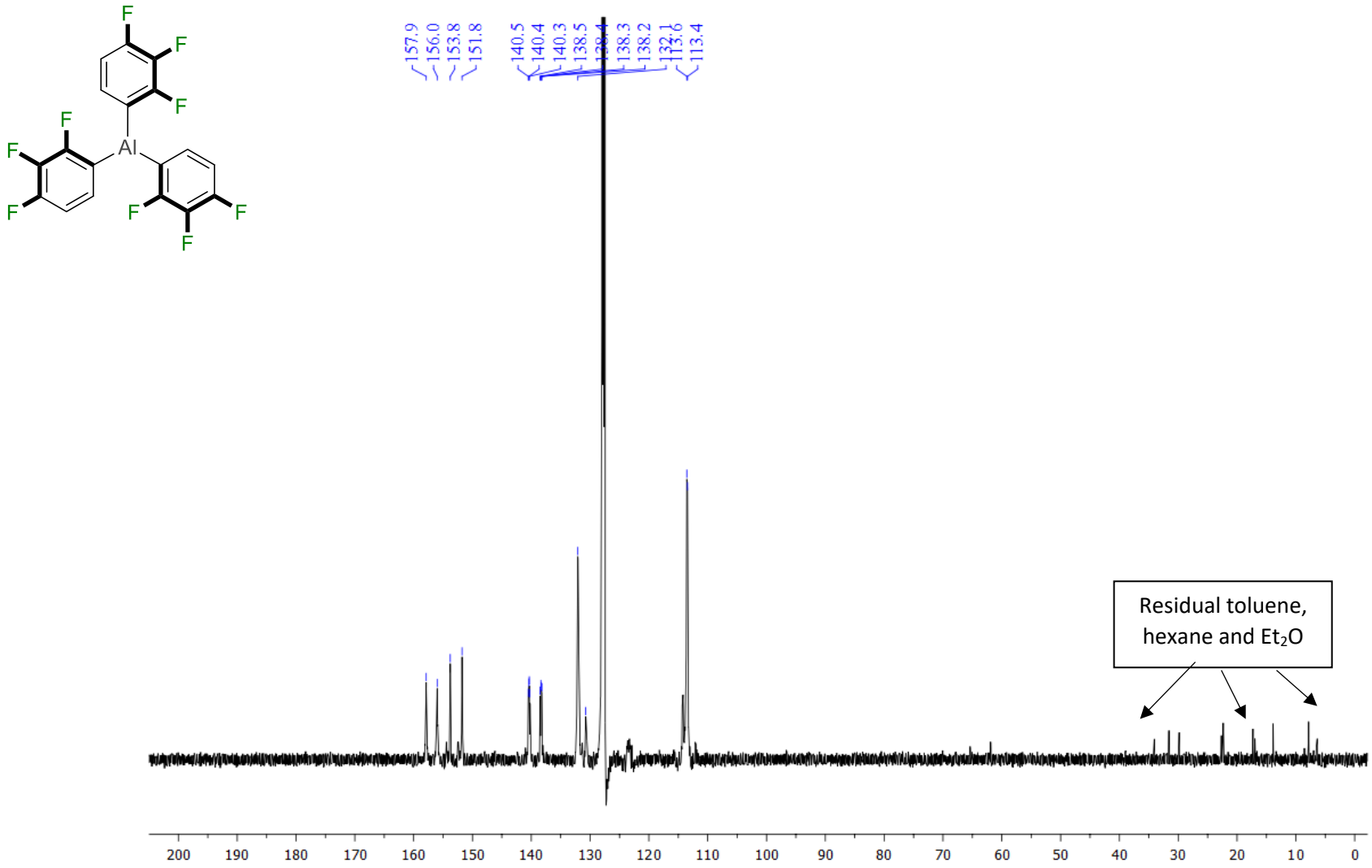


Figure S20 ^{19}F NMR (376 MHz, C_6D_6, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)alane* (**4**)

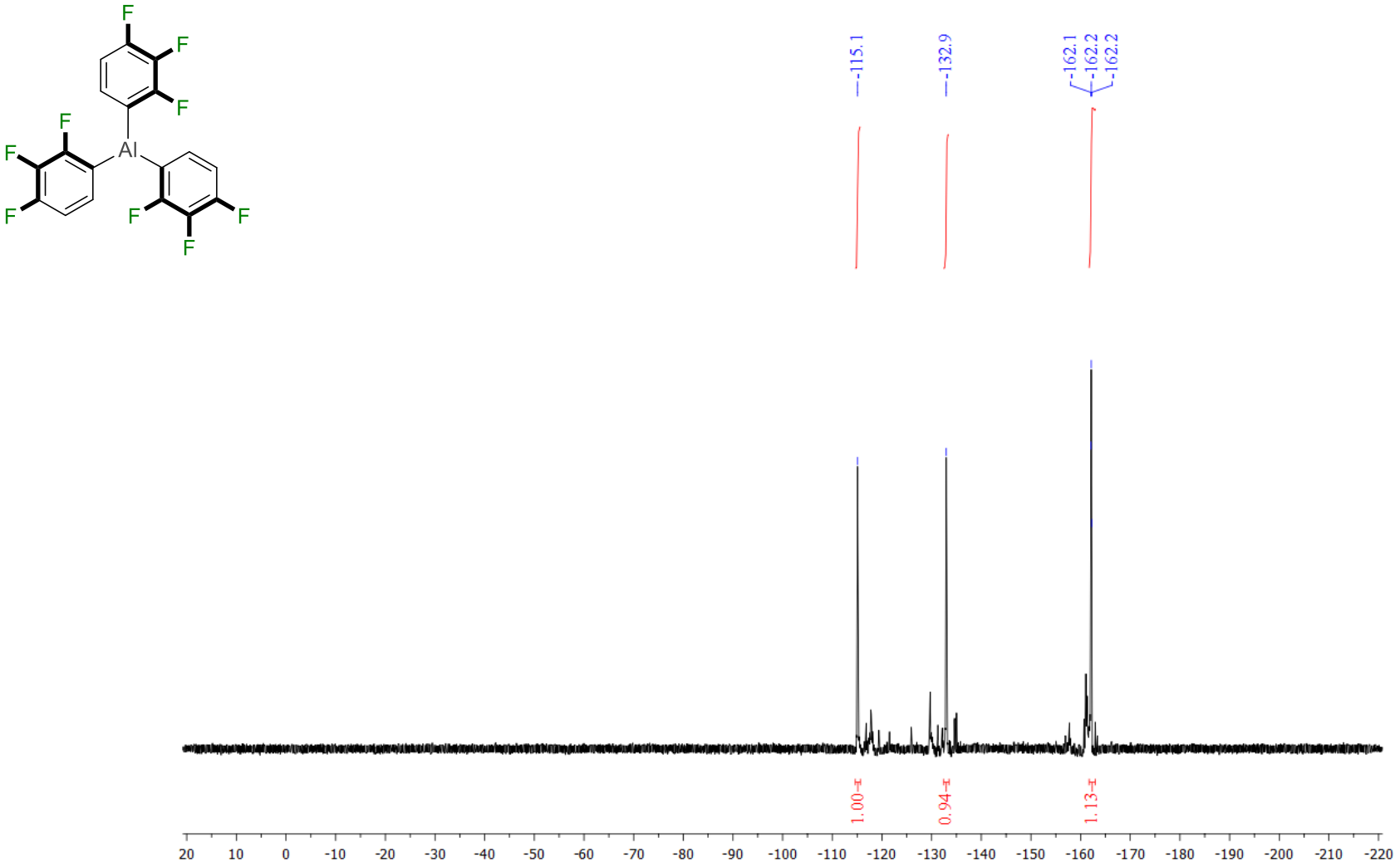


Figure S21 ^{1}H NMR (400 MHz, $CDCl_3$, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)alane·THF* (**4·THF**)

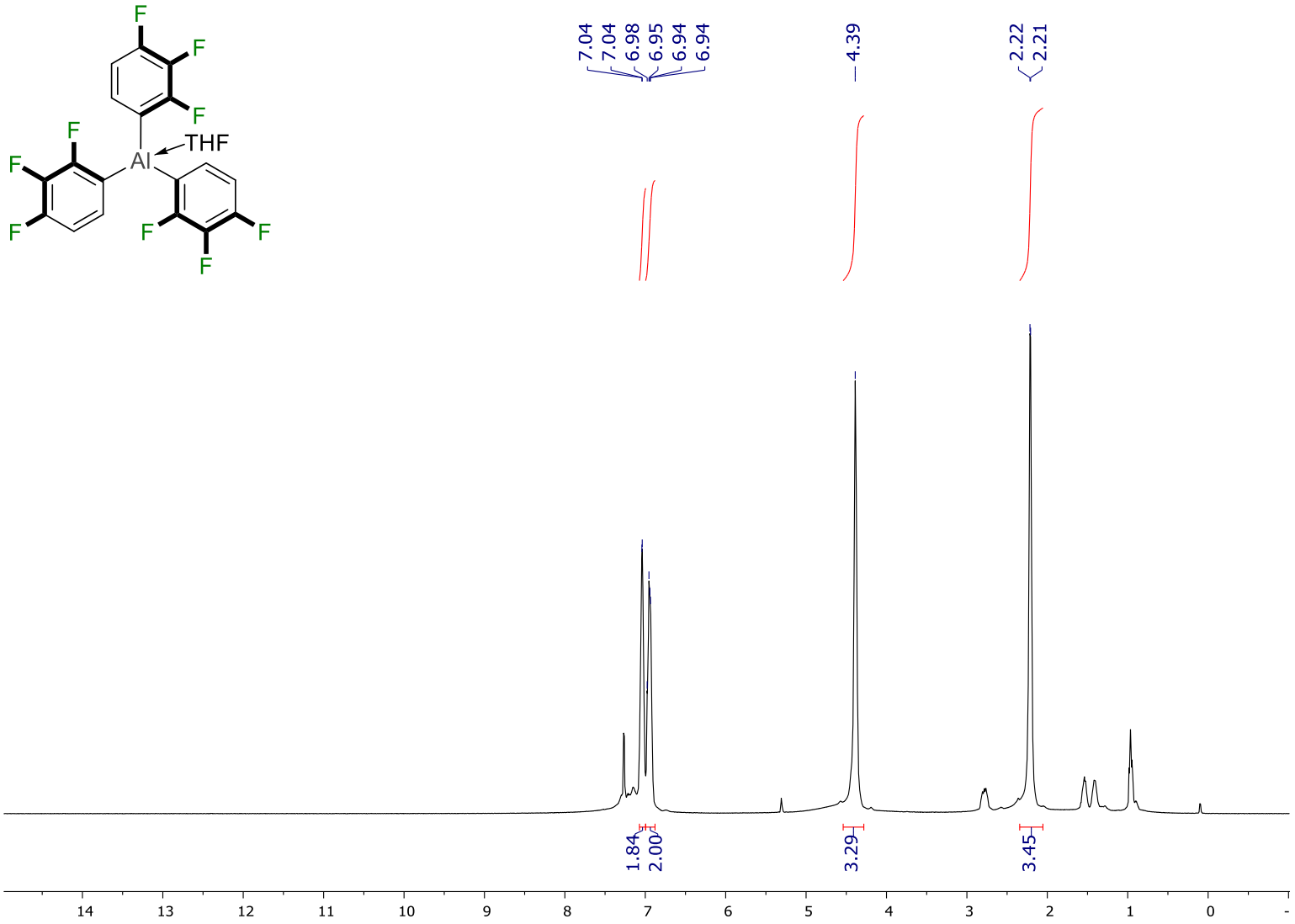


Figure S22 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)alane·THF* (**4·THF**)

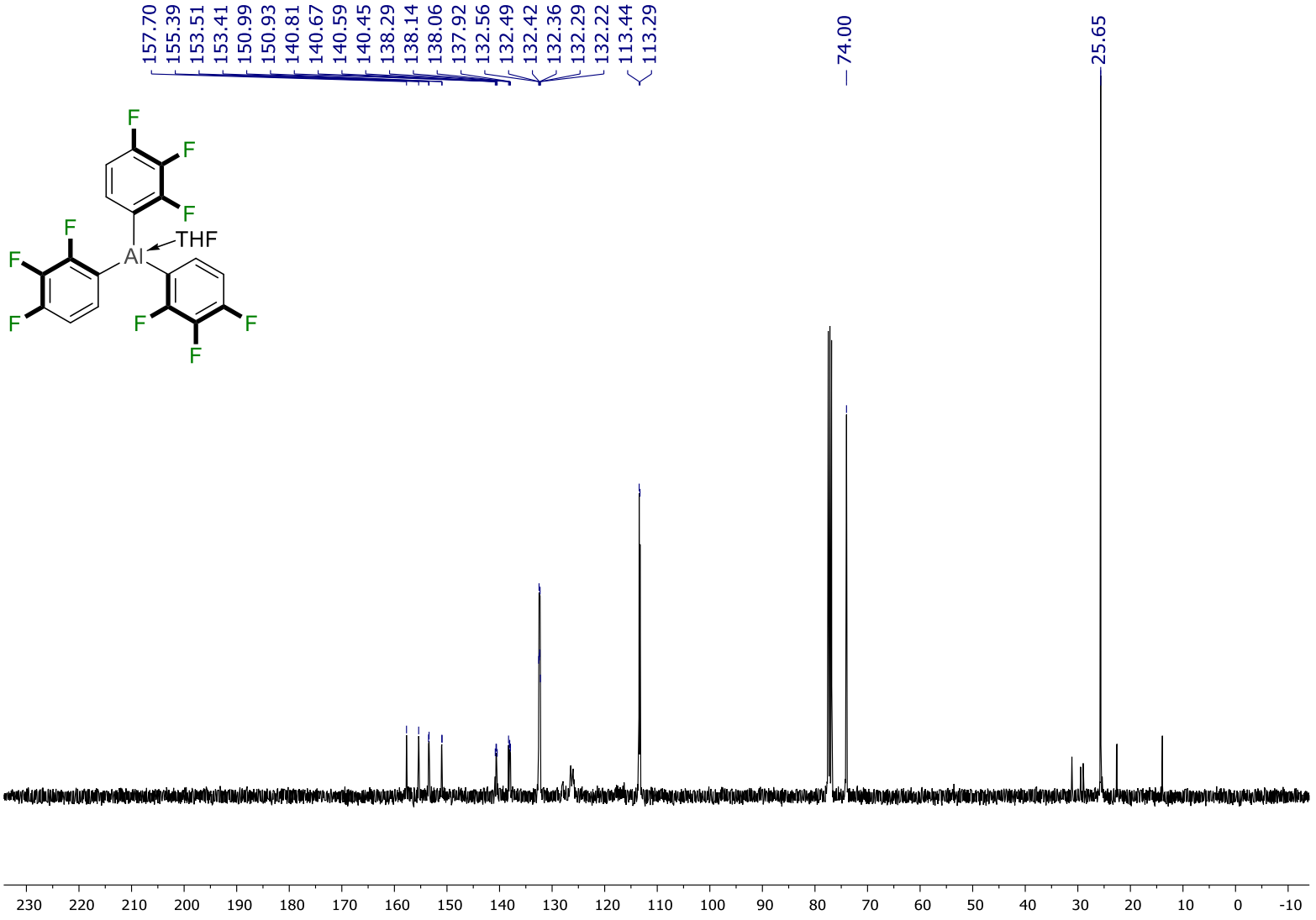


Figure S23 ^{19}F NMR (376 MHz, $CDCl_3$, 295 K) spectrum of *tris(2,3,4-trifluorophenyl)alane·THF* (**4·THF**)

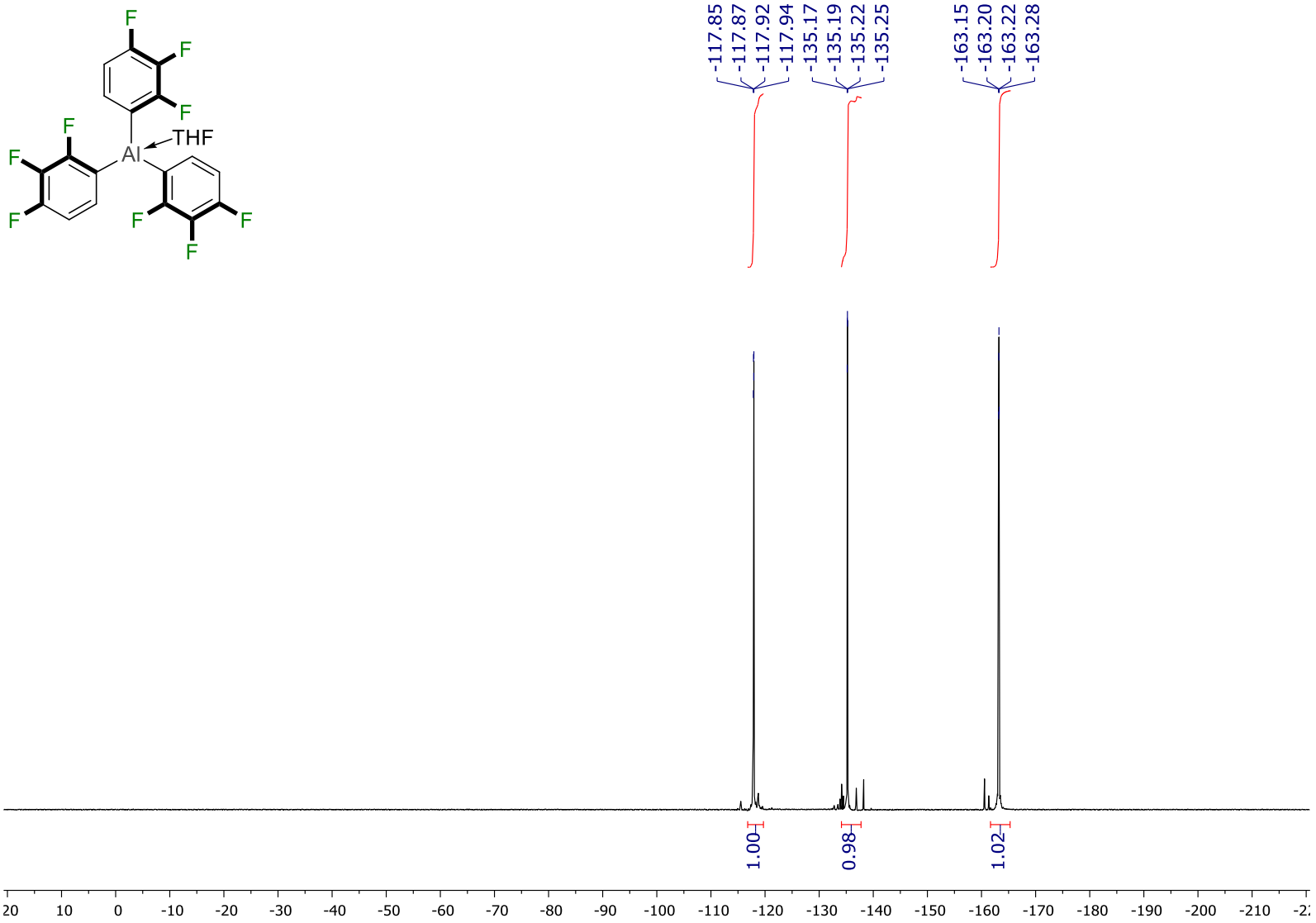
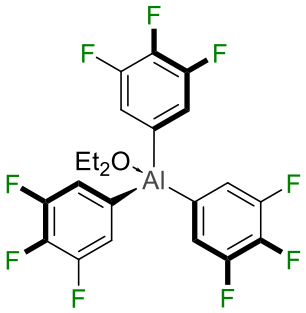


Figure S24 ^{1}H NMR (400 MHz, C_6D_6, 295 K) spectrum of *tris(3,4,5-trifluorophenyl)alane etherate* (**5**)



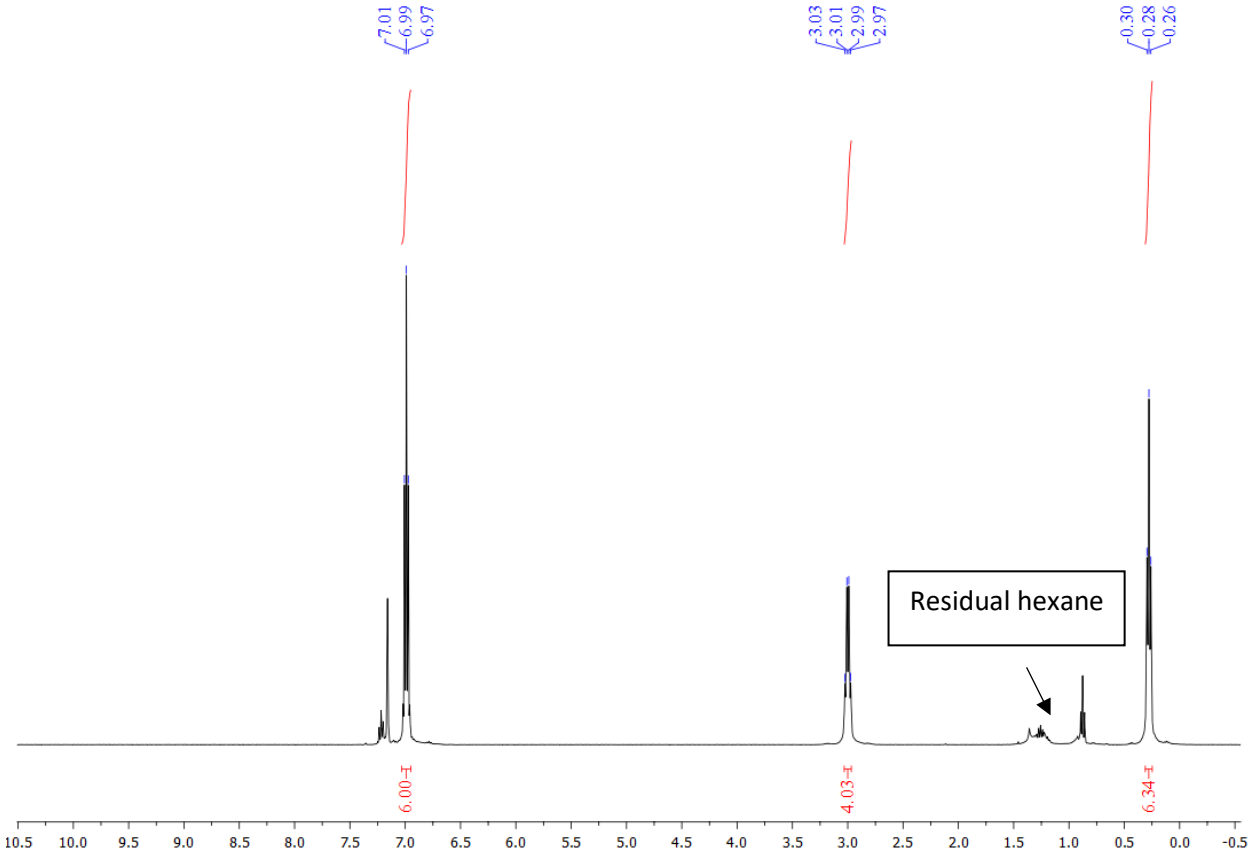


Figure S25 $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 295 K) spectrum of *tris(3,4,5-trifluorophenyl)alane etherate* (**5**)

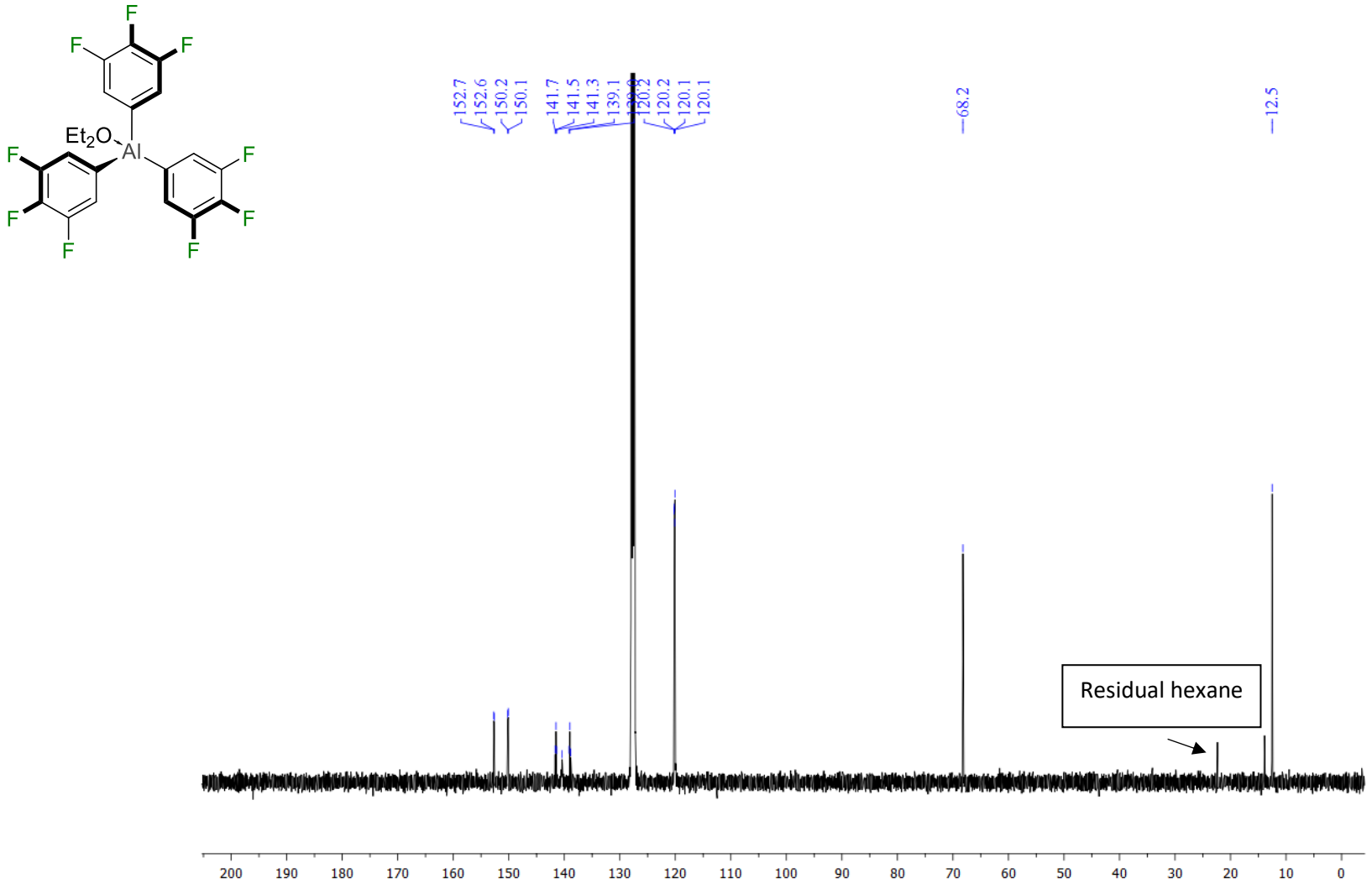
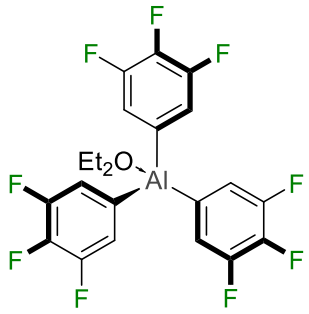
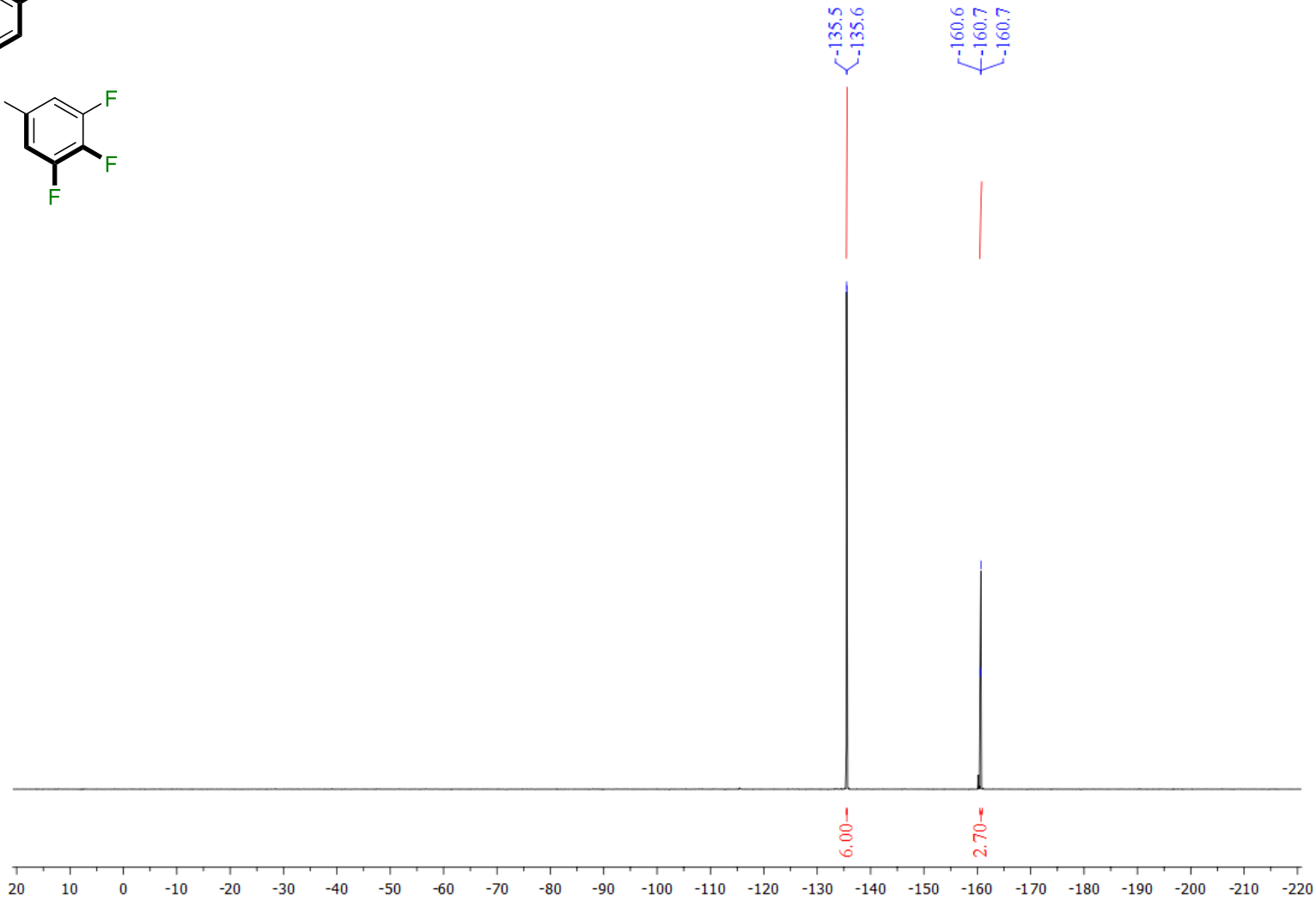


Figure S26 ^{19}F NMR (376 MHz, C_6D_6, 295 K) spectrum of *tris(3,4,5-trifluorophenyl)alane etherate* (**5**)





S4.3 NMR spectra of imine starting materials

Figure S27 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *(E)-N,1-diphenylmethanimine*

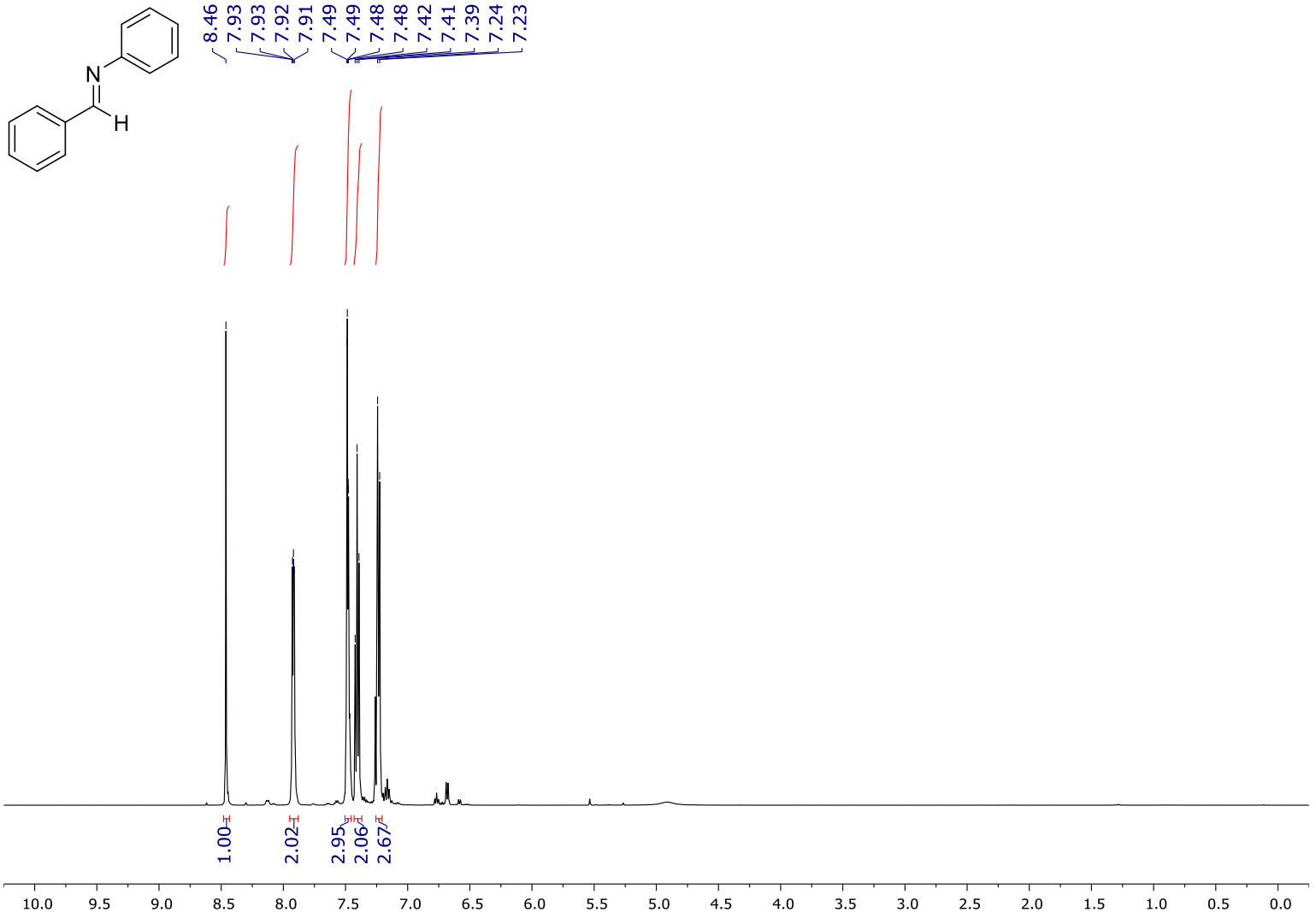


Figure S28 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *(E)-1-(4-methoxyphenyl)-N-phenylmethanimine*

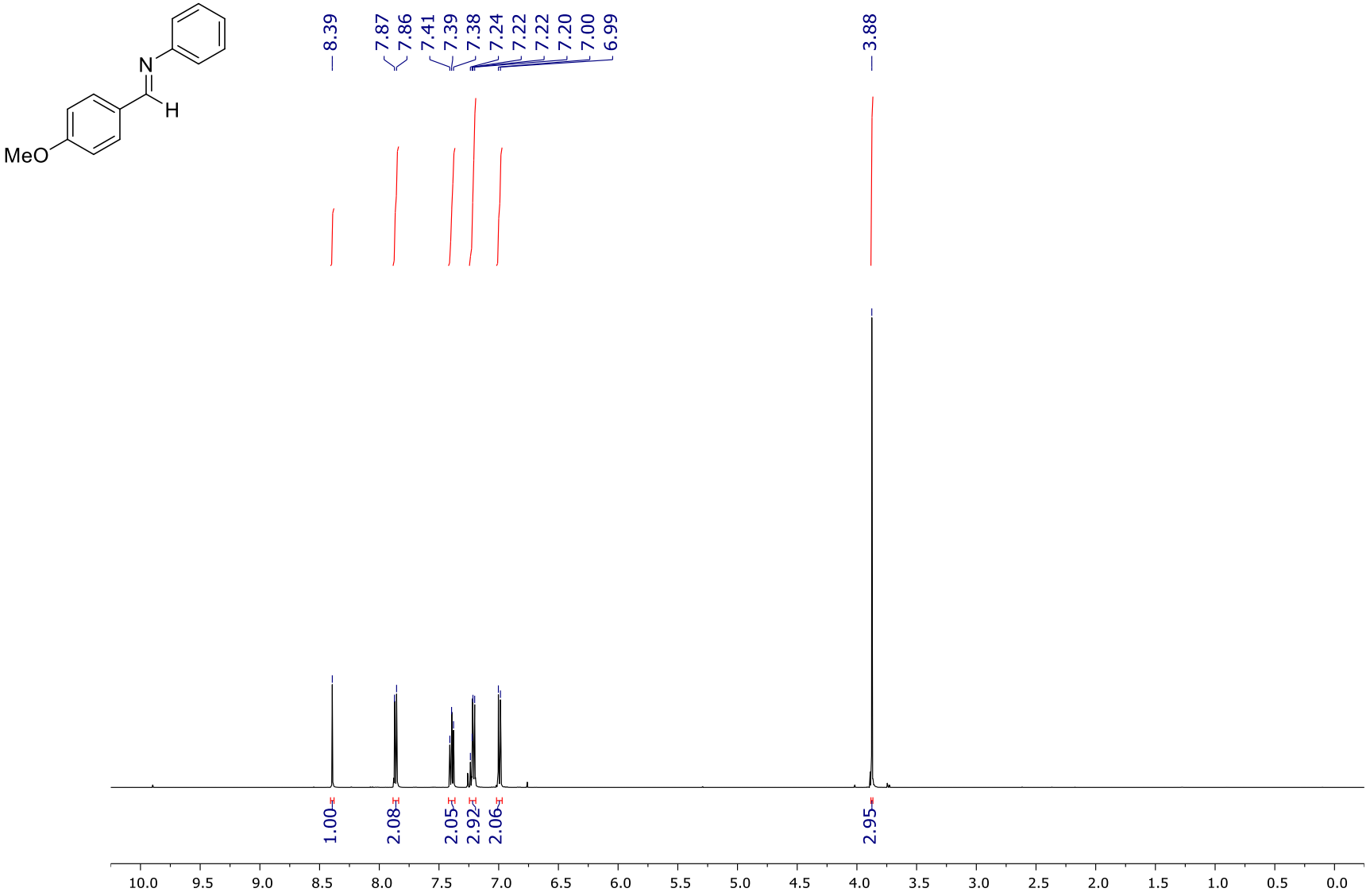


Figure S29 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *(E)-1-(4-nitrophenyl)-N-phenylmethanimine*

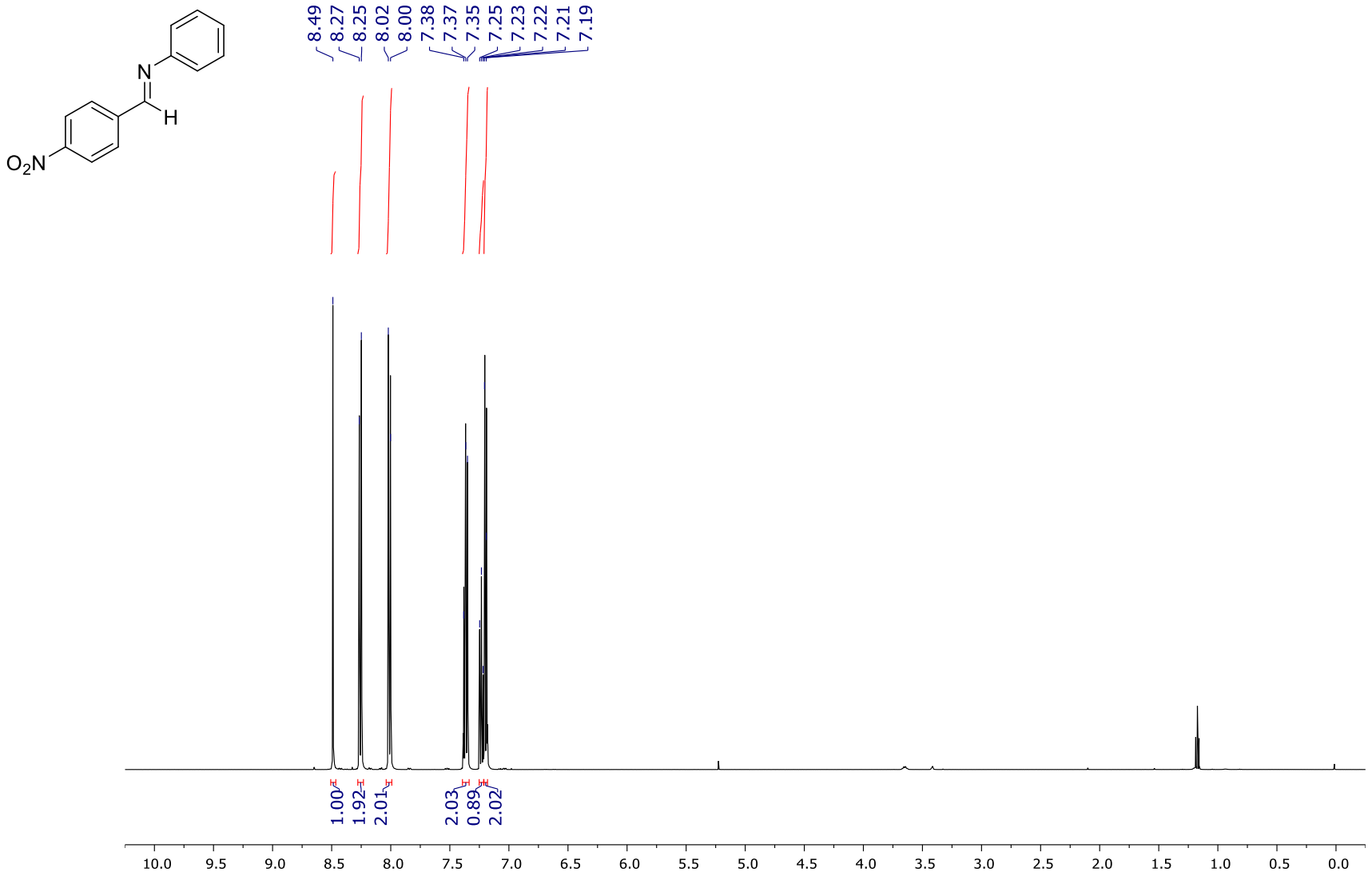
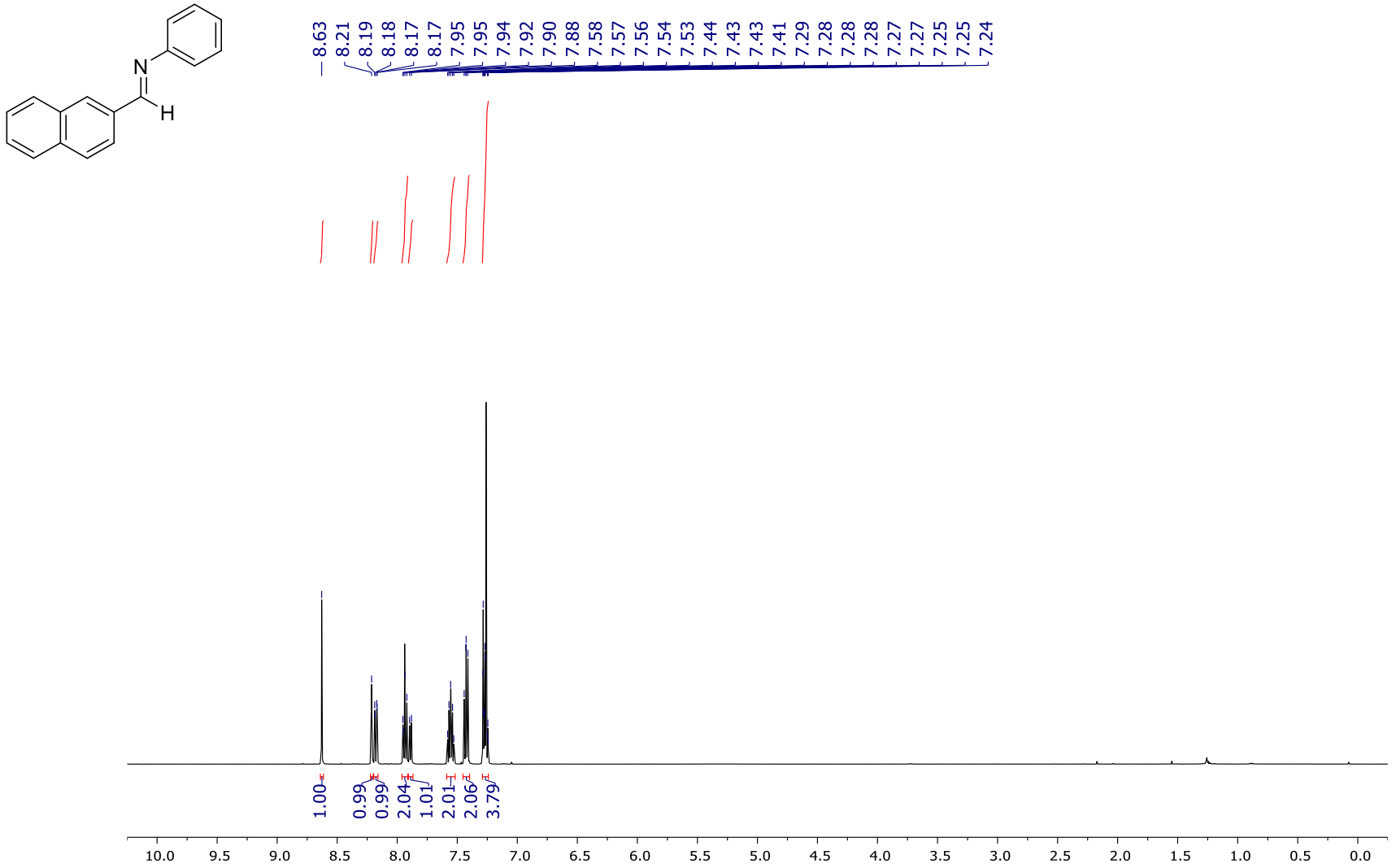


Figure S30 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *(E)-1-(naphthalen-2-yl)-N-phenylmethanimine*



S4.4 NMR spectra of reduction products

Figure S31 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *phenylmethanol* (**6a**)

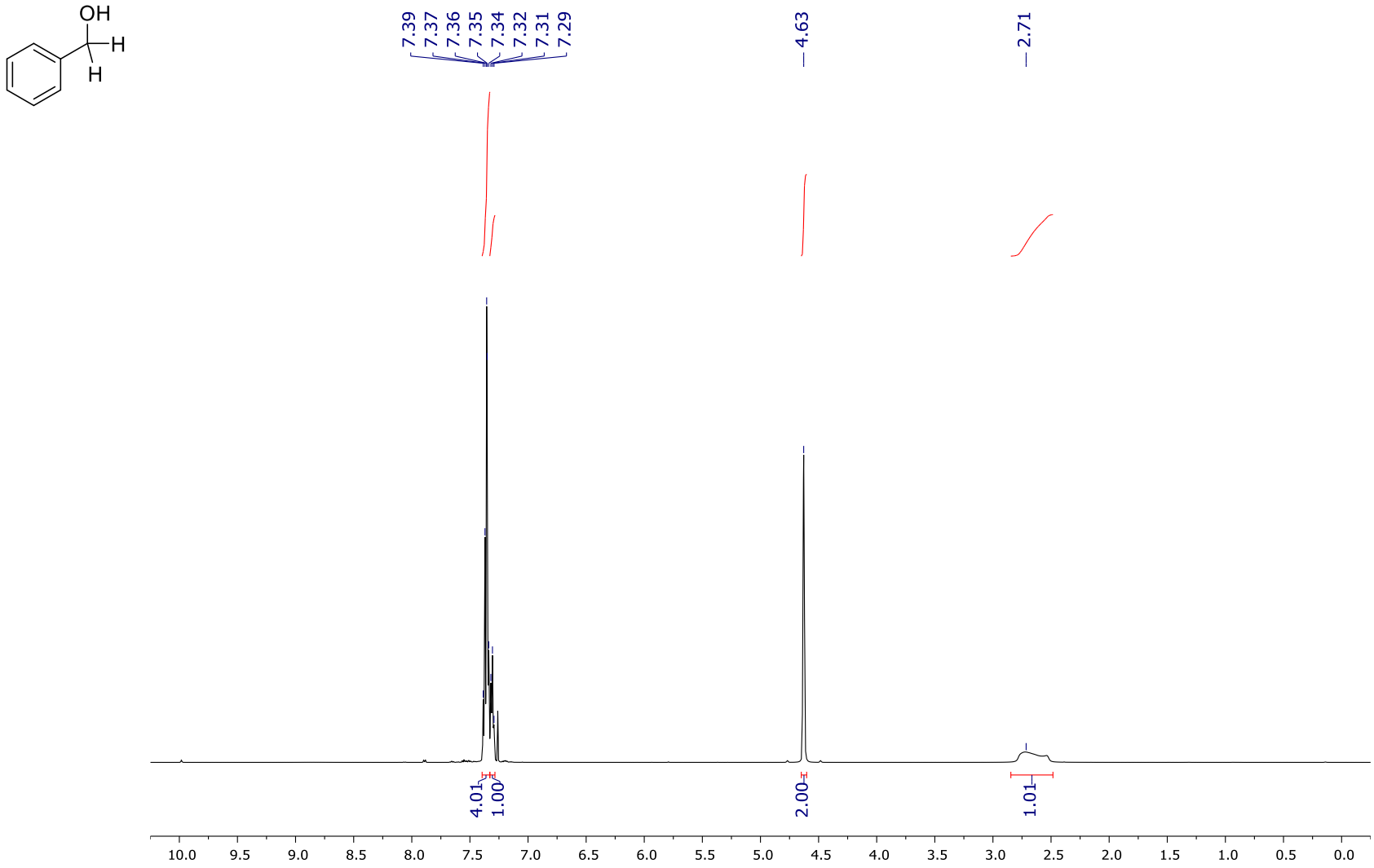


Figure S32 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *phenylmethanol* (**6a**)

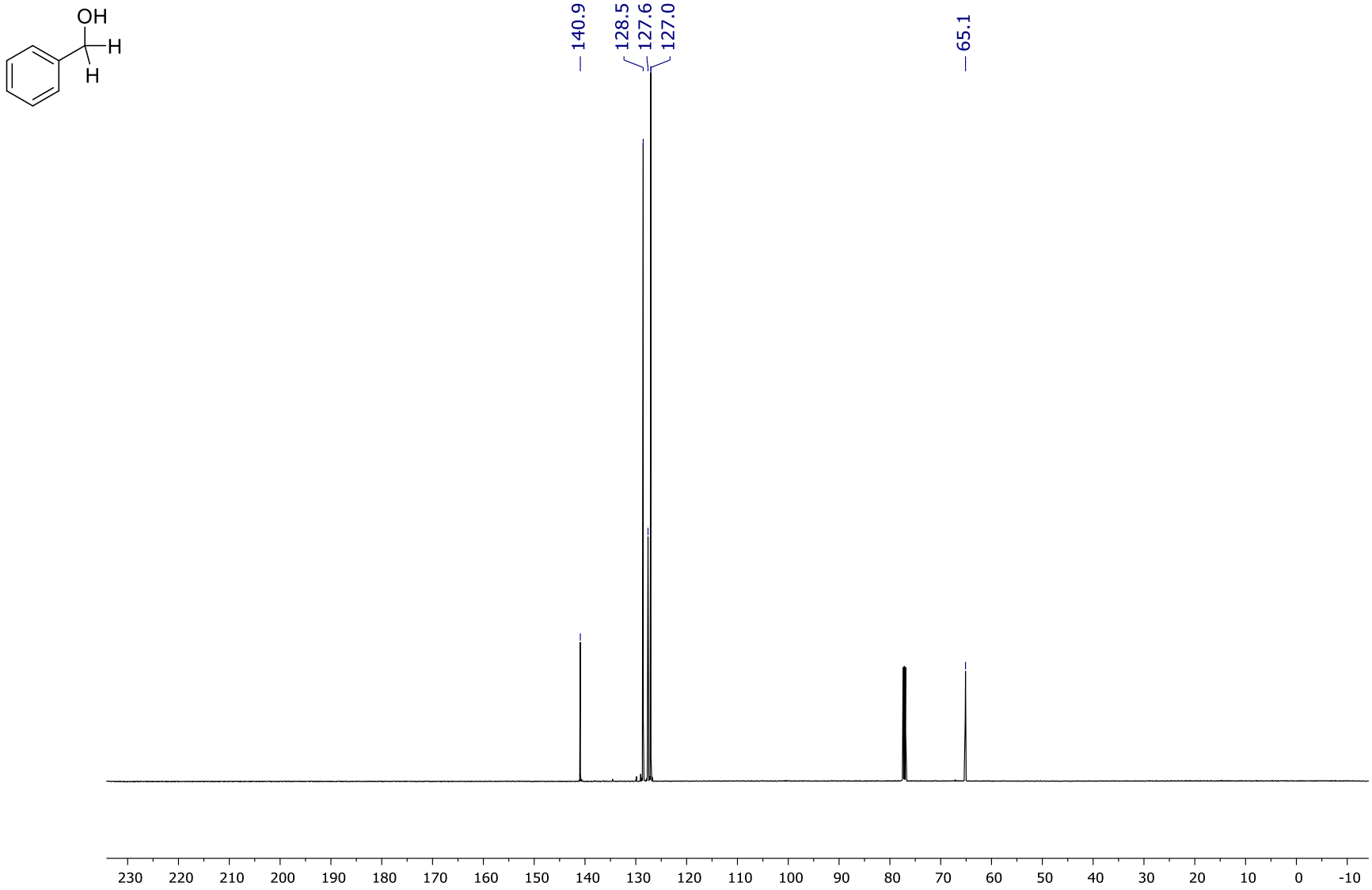


Figure S33 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *(4-methoxyphenyl)methanol* (**6b**)

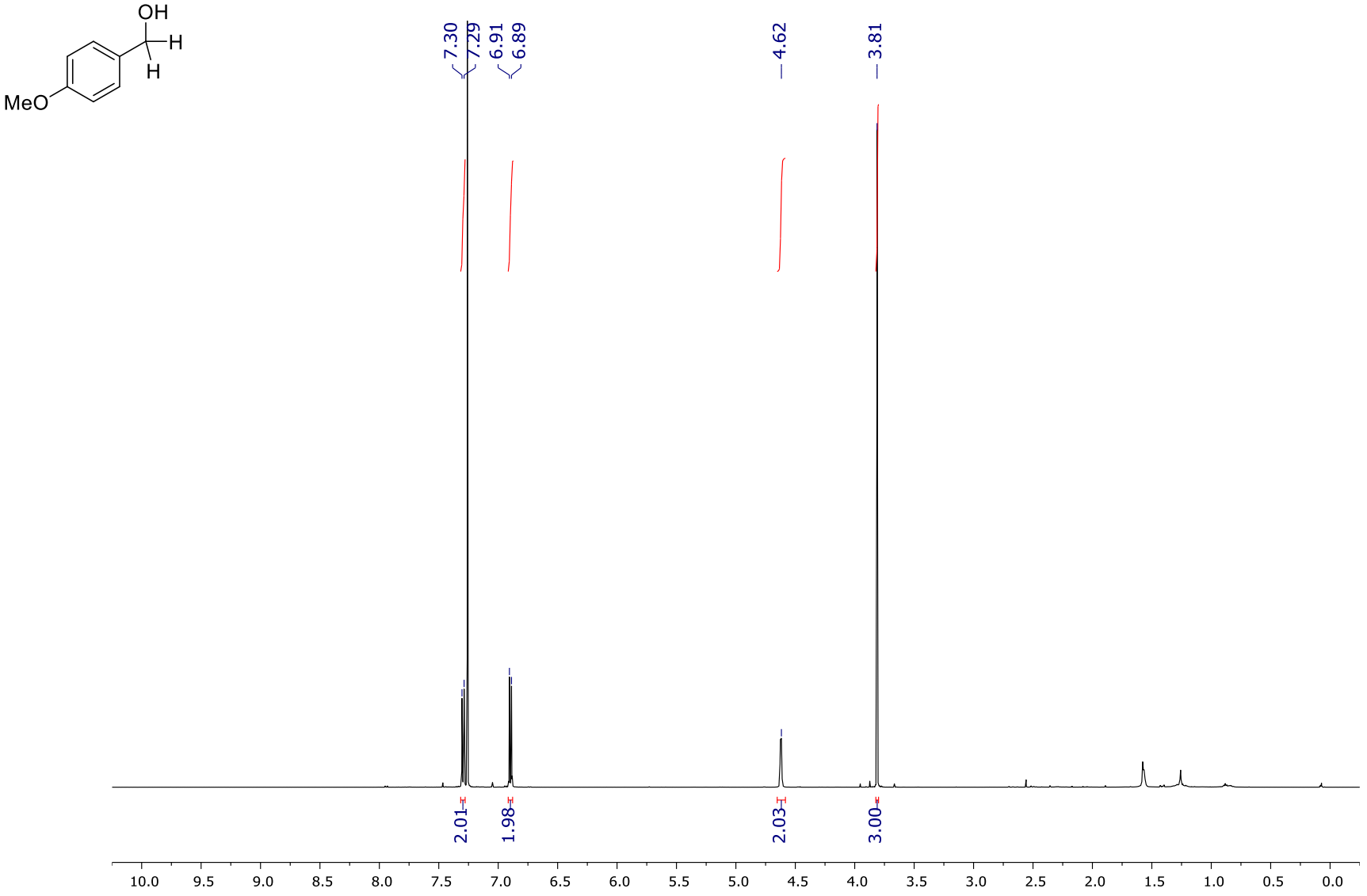


Figure S34 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of (*4-methoxyphenyl)methanol* (**6b**)

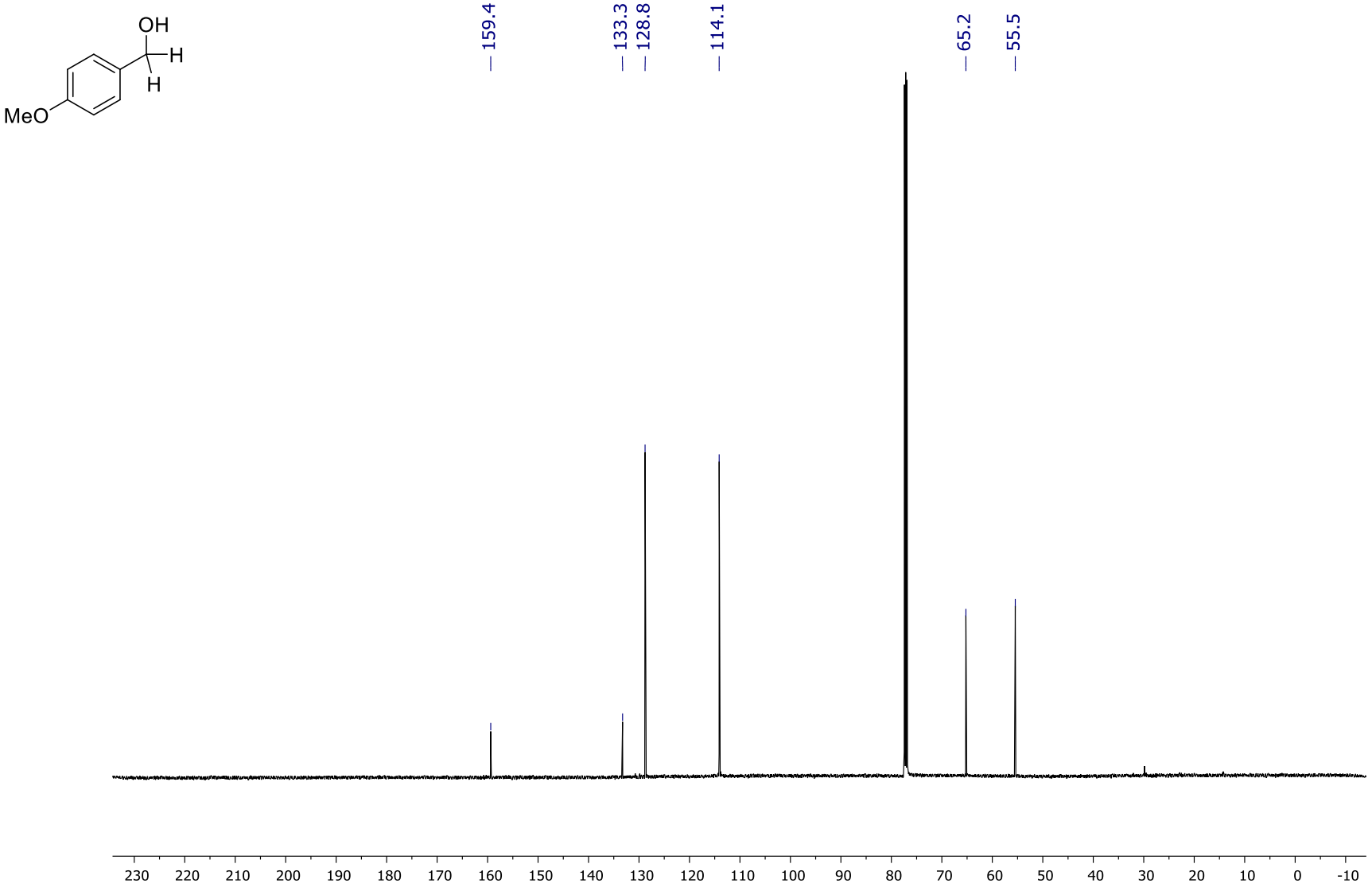


Figure S35 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of (*4-nitrophenyl)methanol* (**6c**)

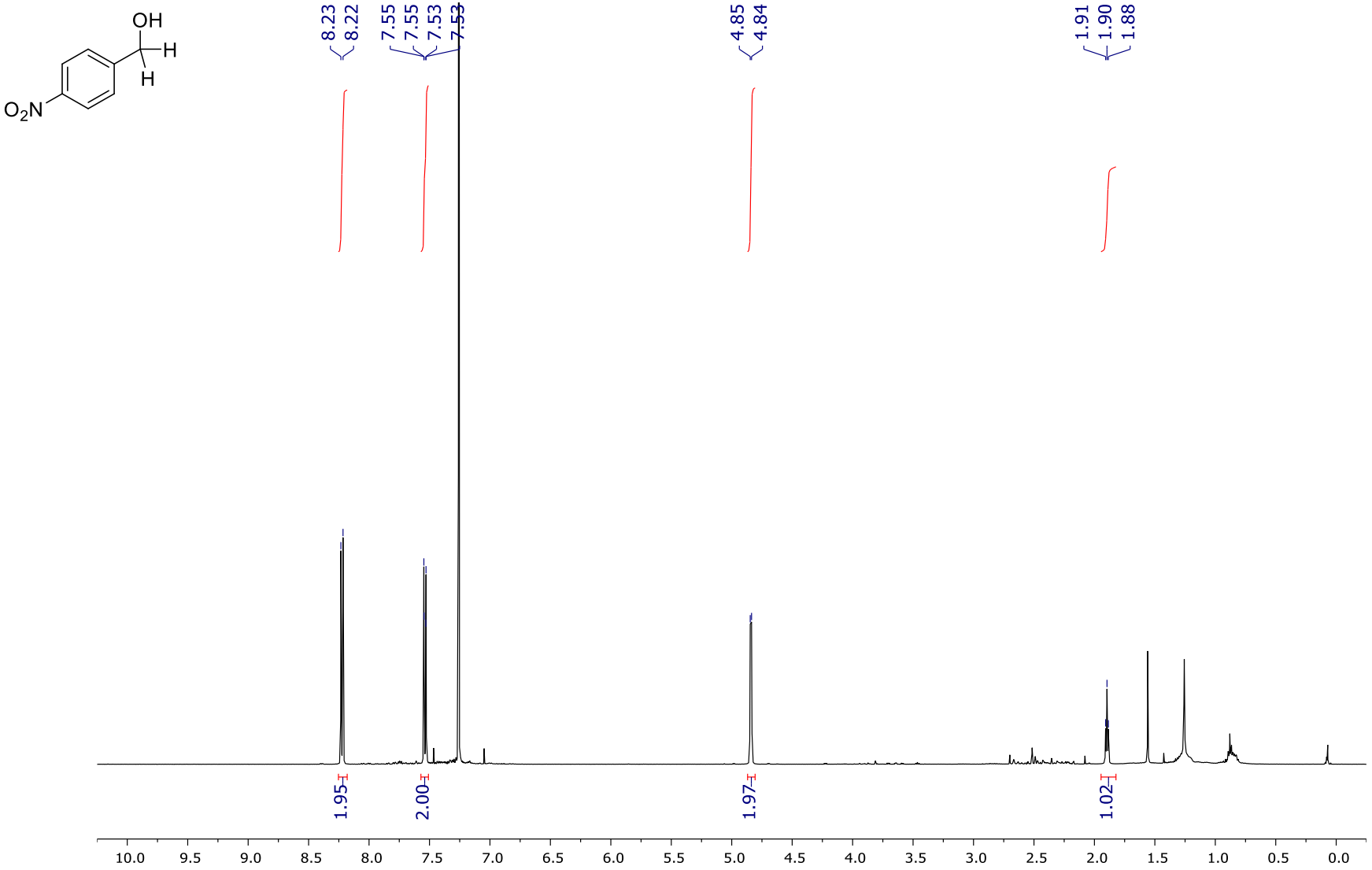


Figure S36 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of (*4-nitrophenyl)methanol* (**6c**)

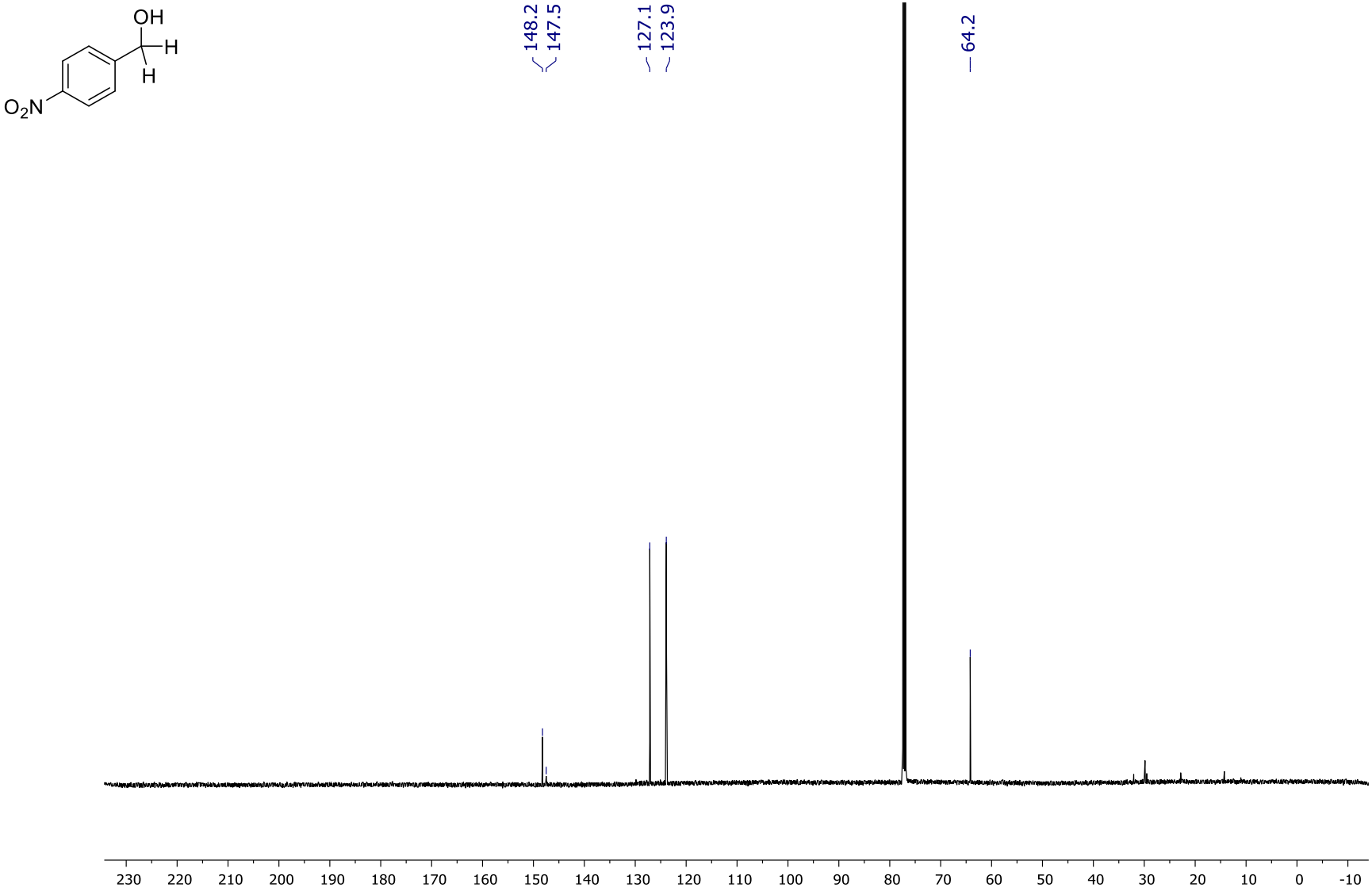


Figure S37 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *napthalen-2-ylmethanol* (**6d**)

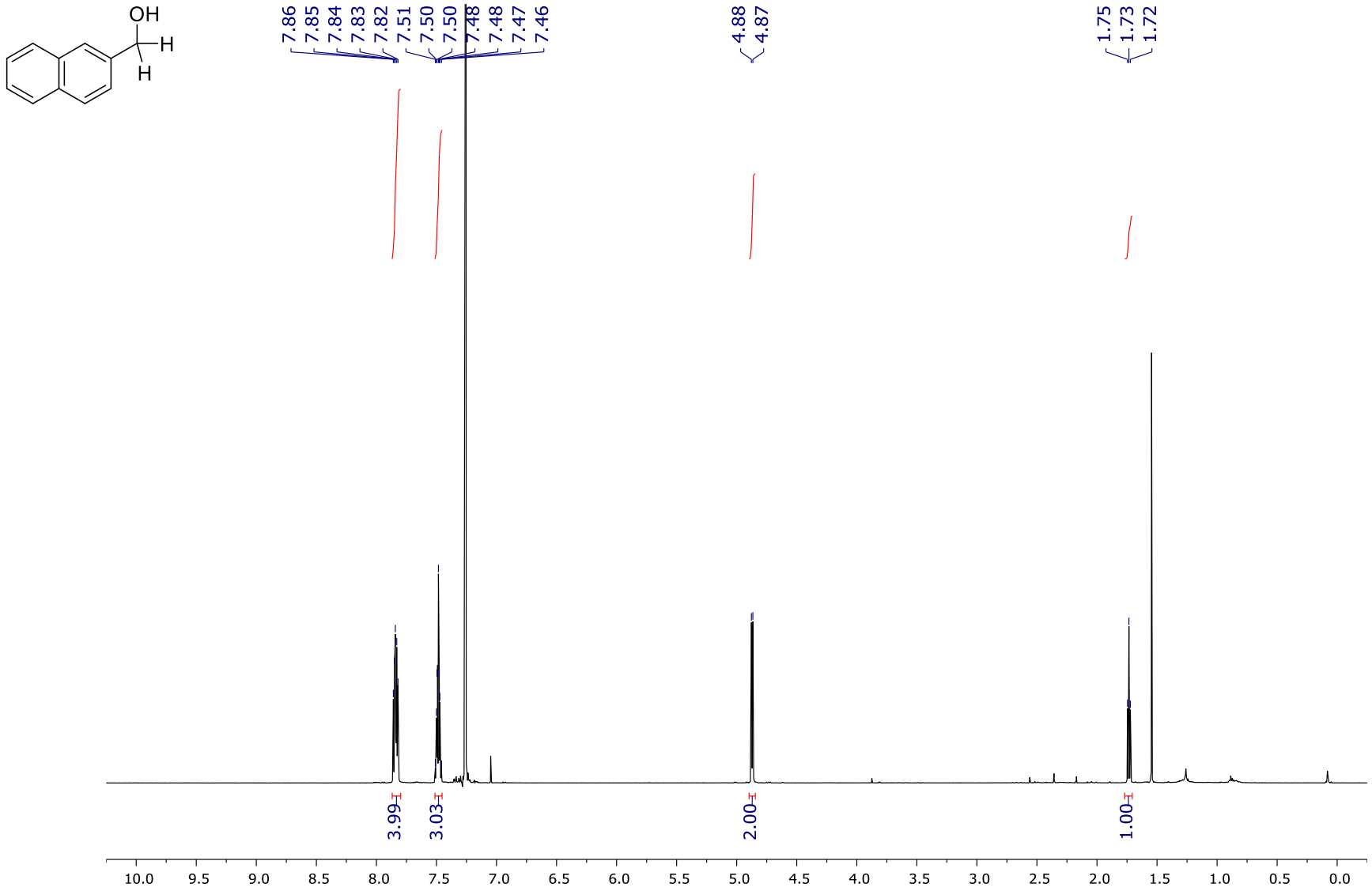


Figure S38 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *napthalen-2-ylmethanol* (**6d**)

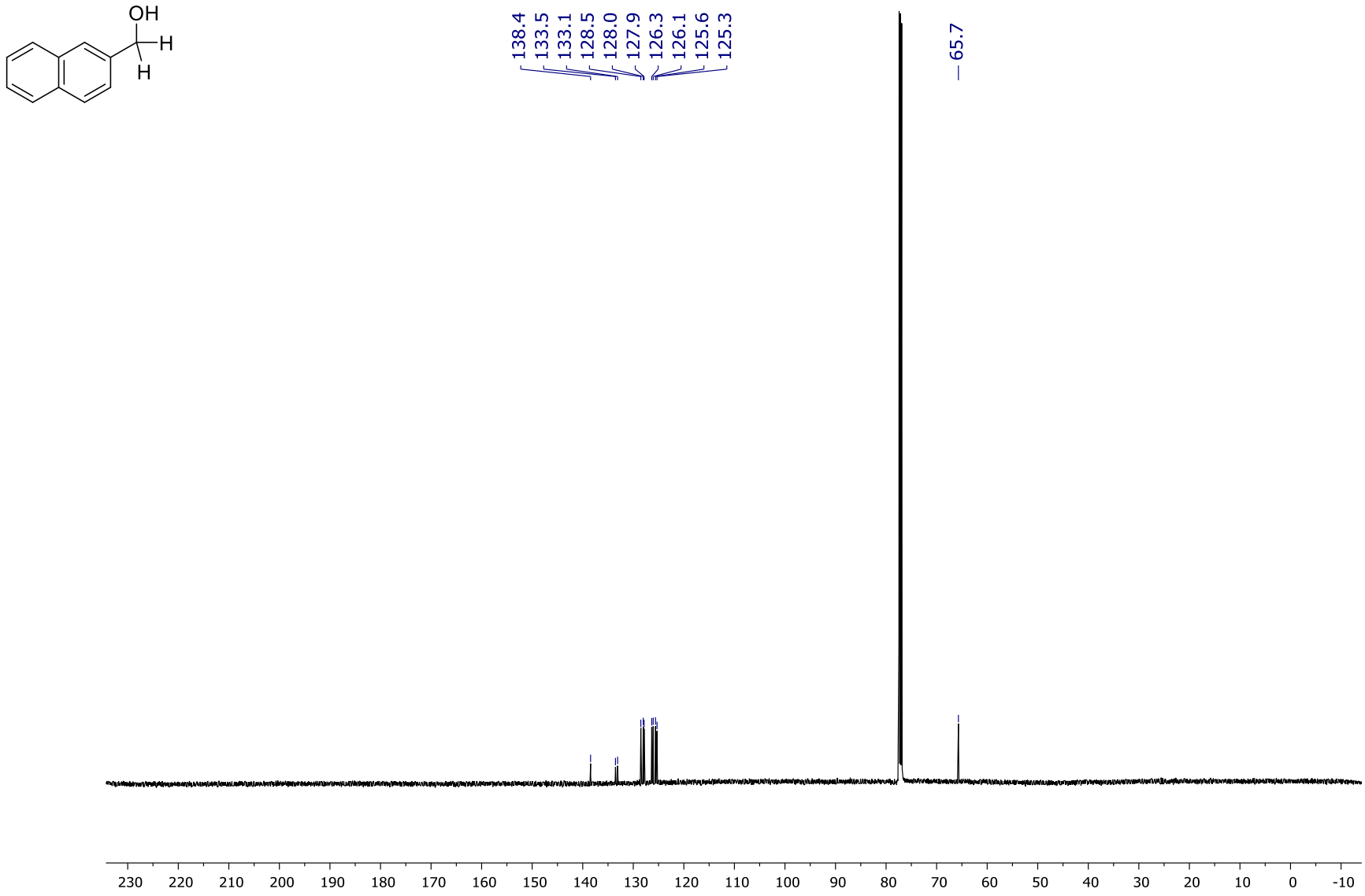


Figure S39 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *1-phenylethanol* (**7a**)

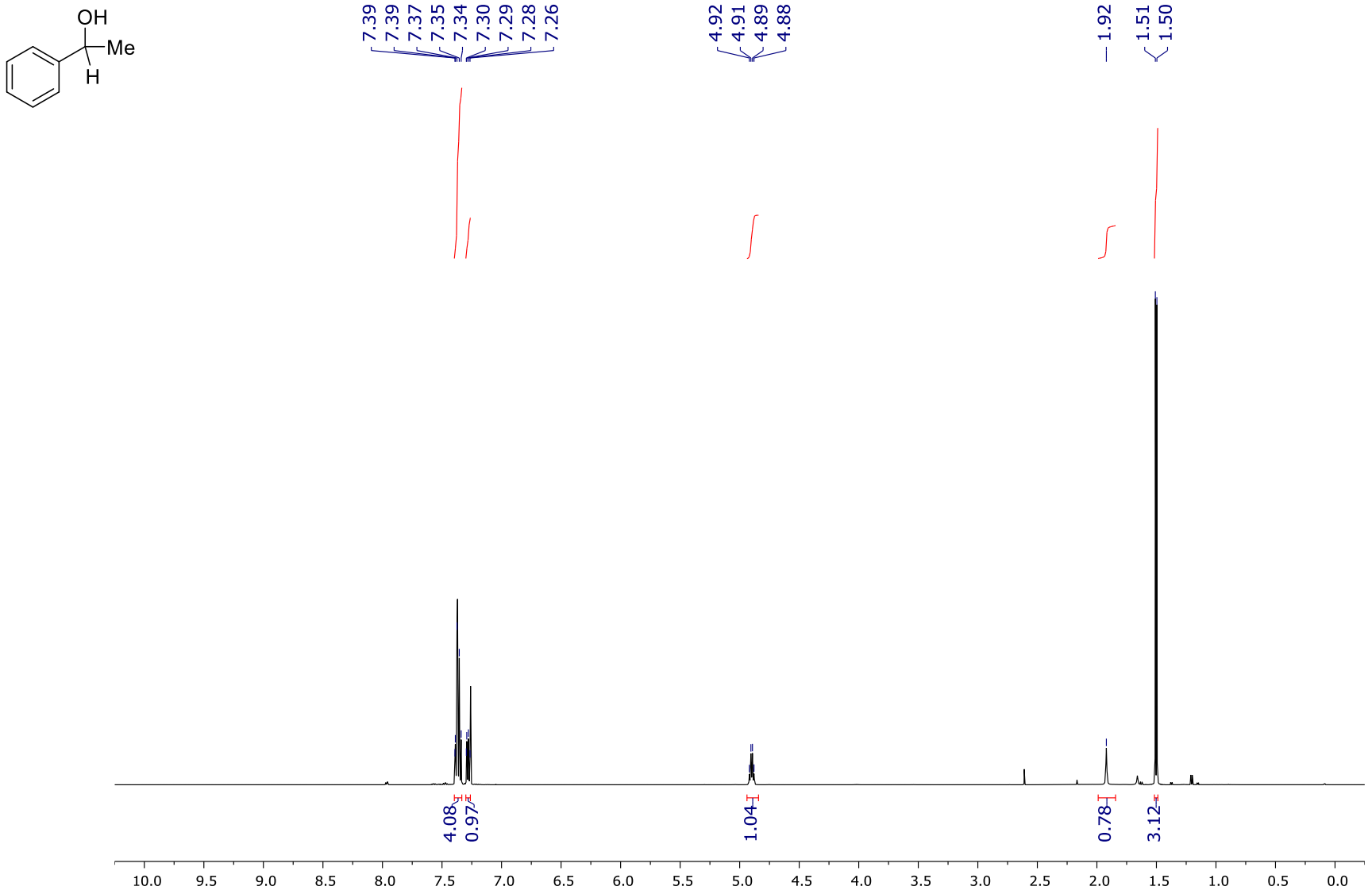


Figure S40 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *1-phenylethanol* (**7a**)

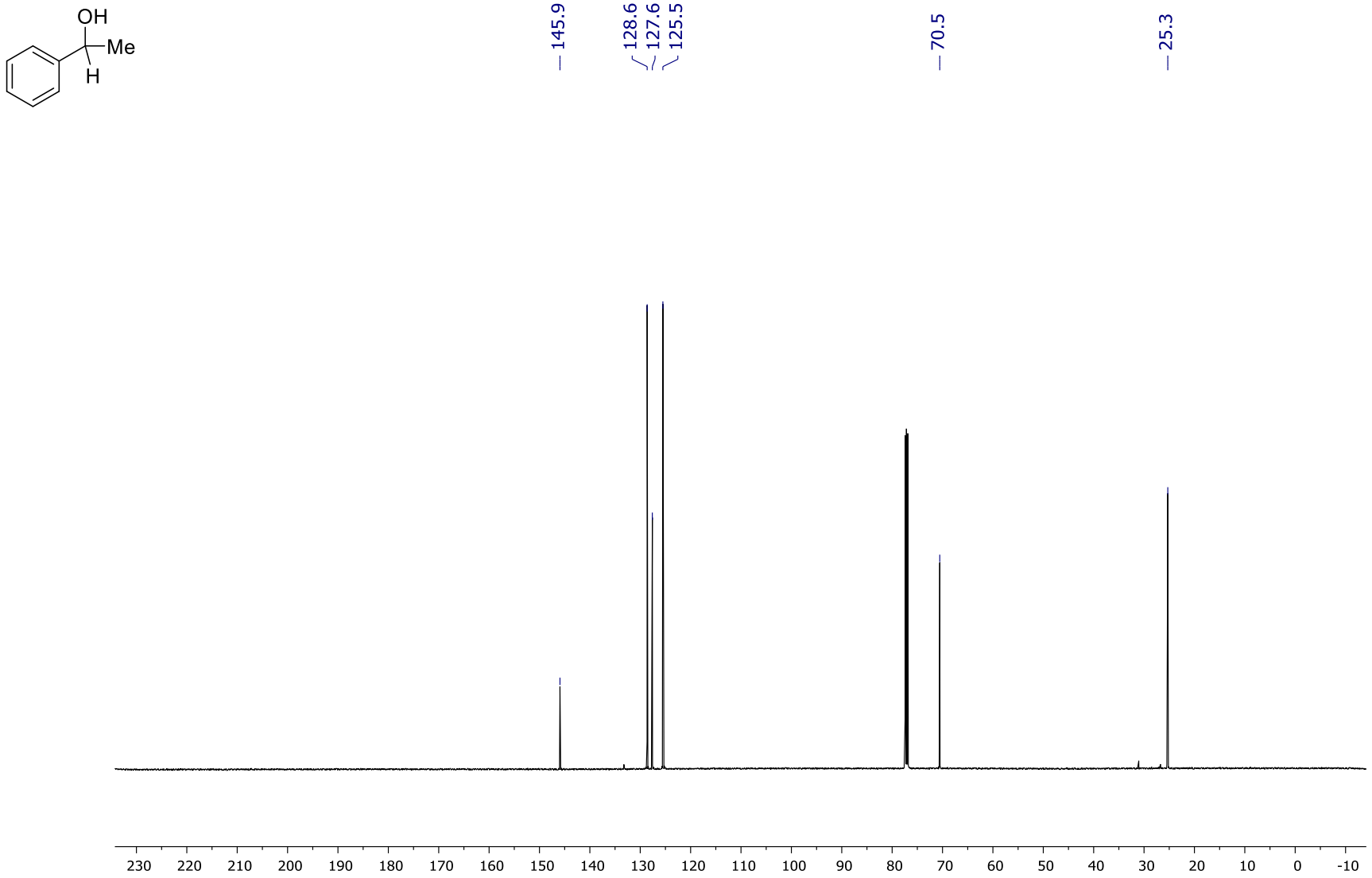


Figure S41 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *1-(4-methoxyphenyl)ethanol* (**7b**)

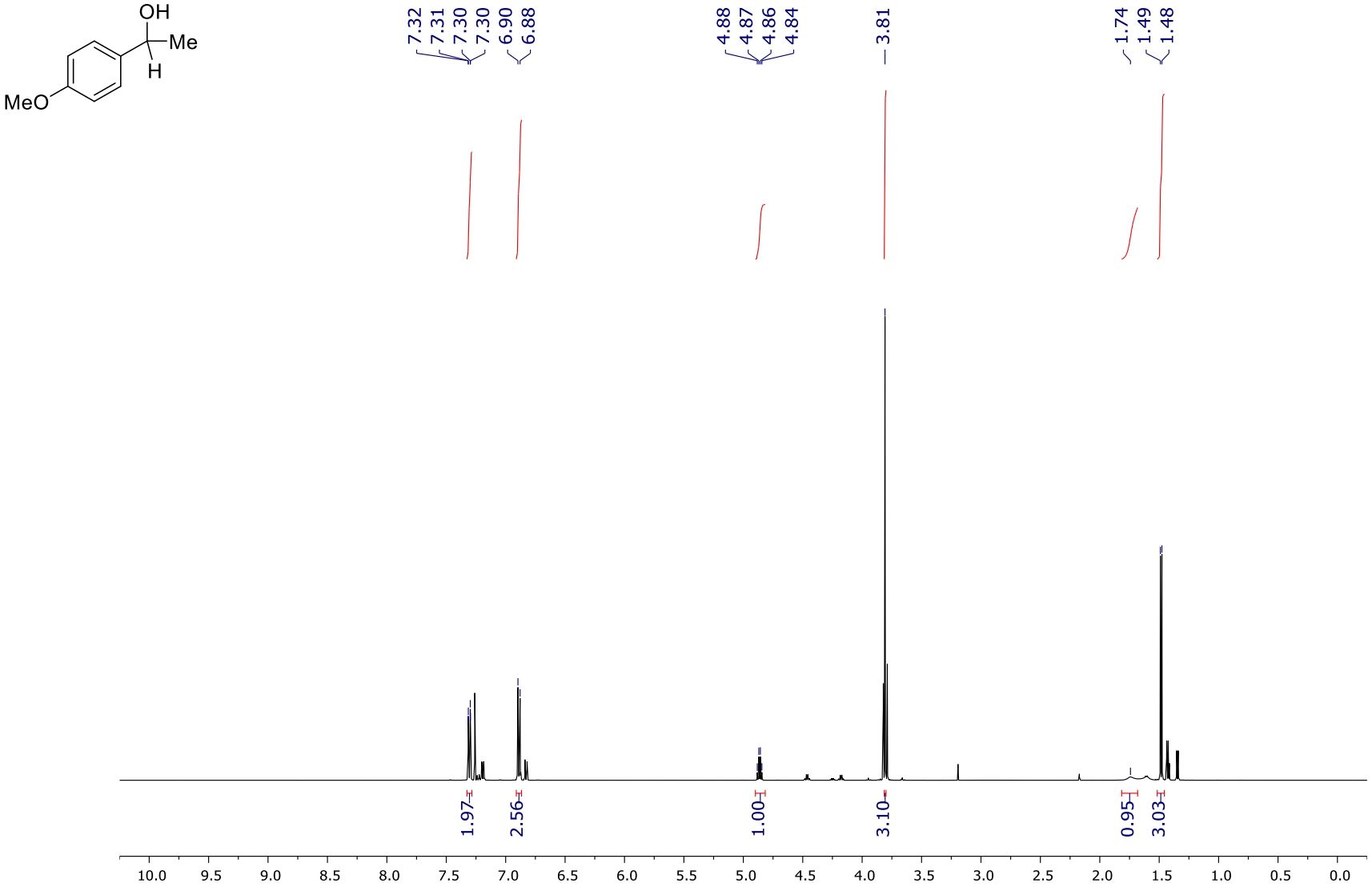


Figure S42 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *1-(4-methoxyphenyl)ethanol* (**7b**)

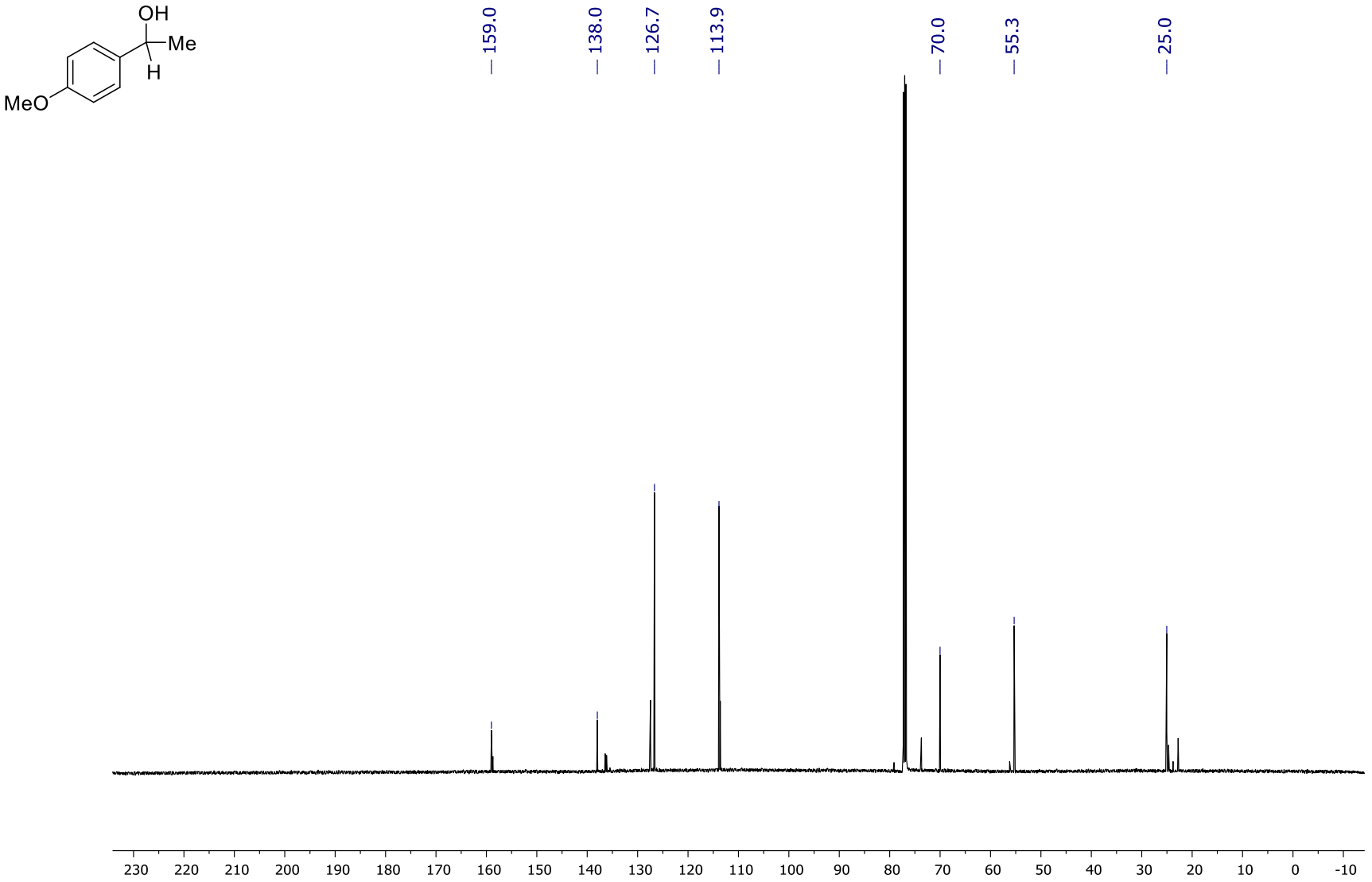


Figure S43 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *1-(4-nitrophenyl)ethanol* (**7c**)

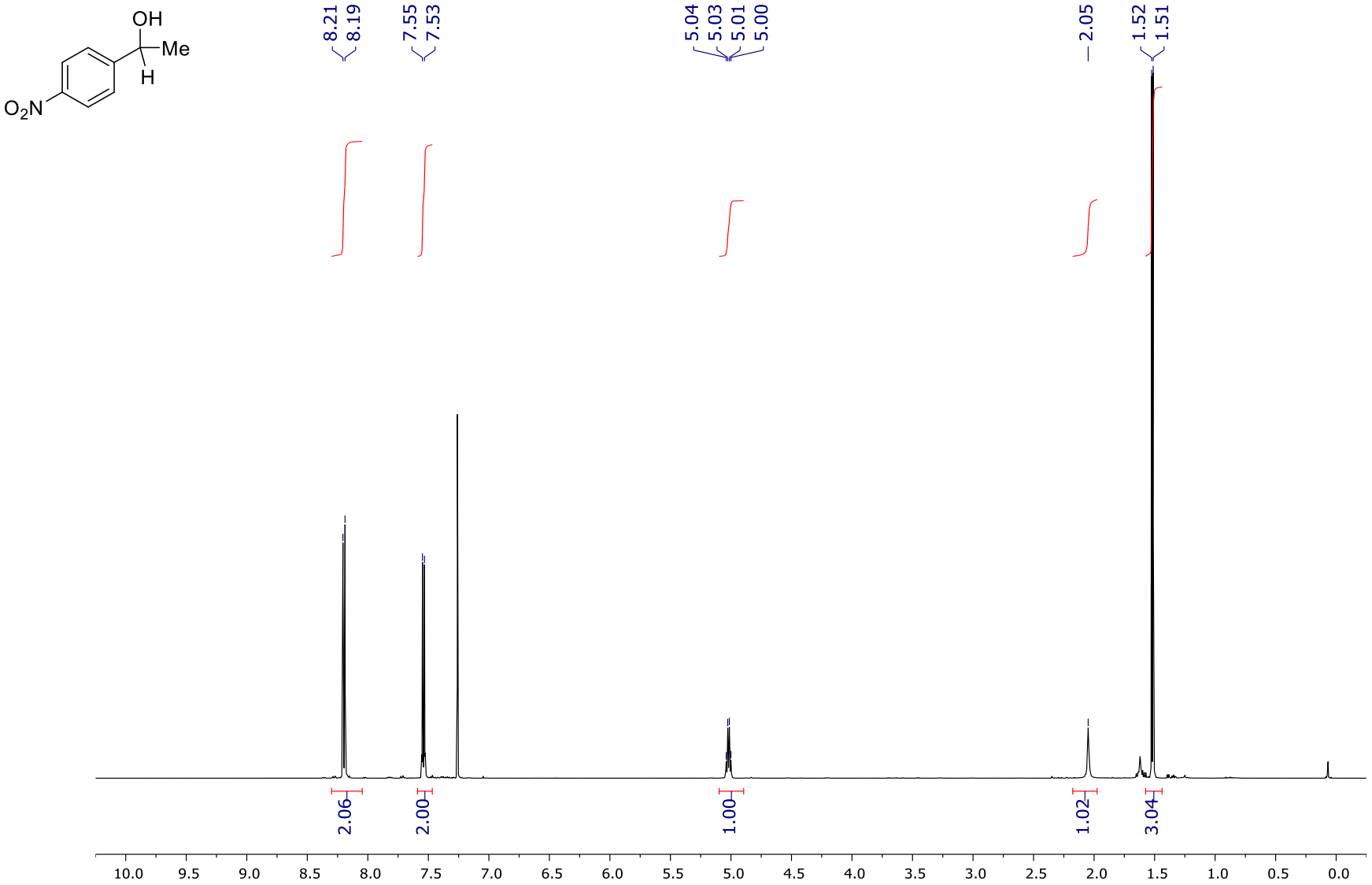


Figure S44 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *1-(4-nitrophenyl)ethanol* (**7c**)

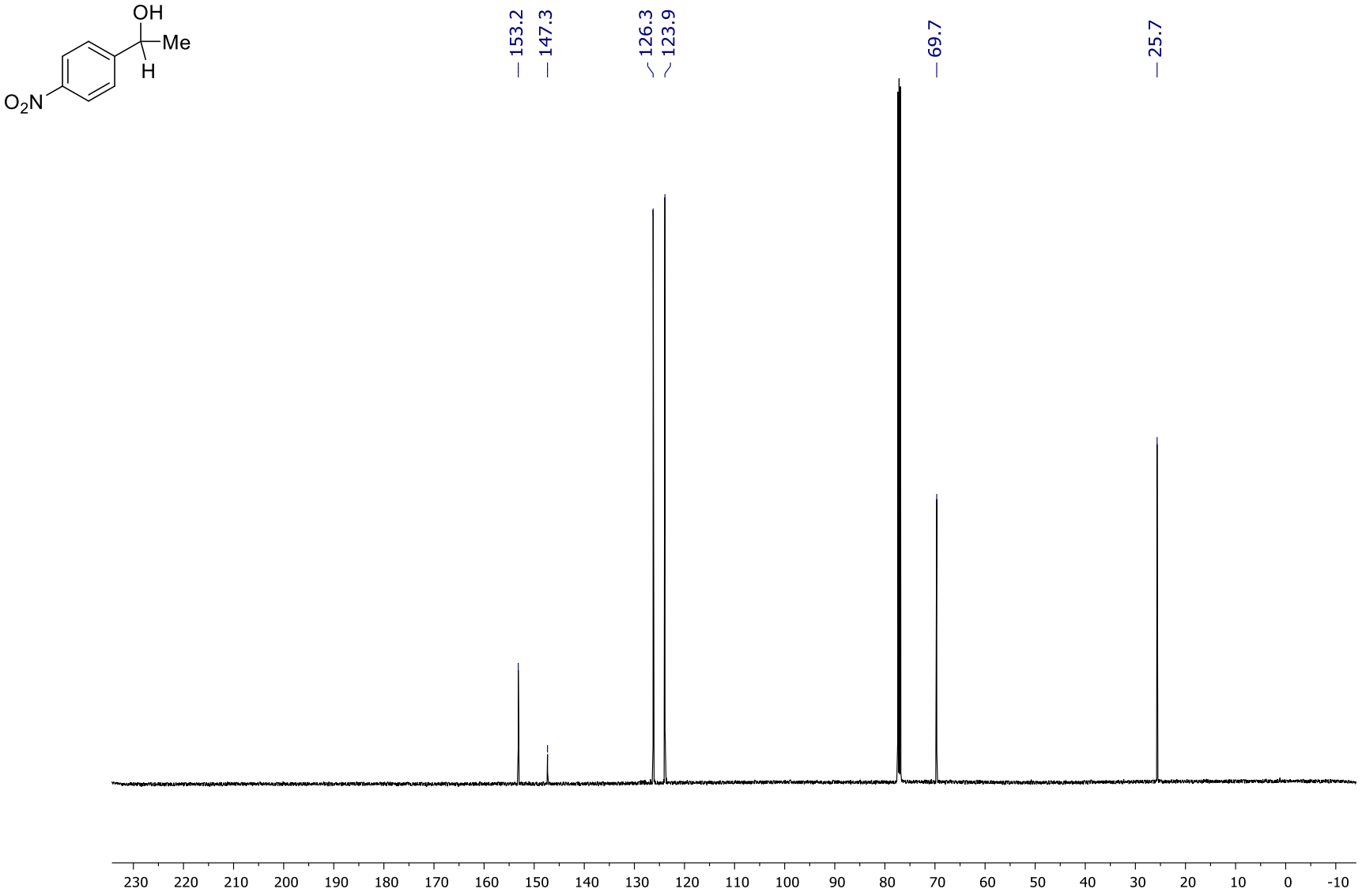


Figure S45 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *1-(napthalen-2-yl)ethanol* (**7d**)

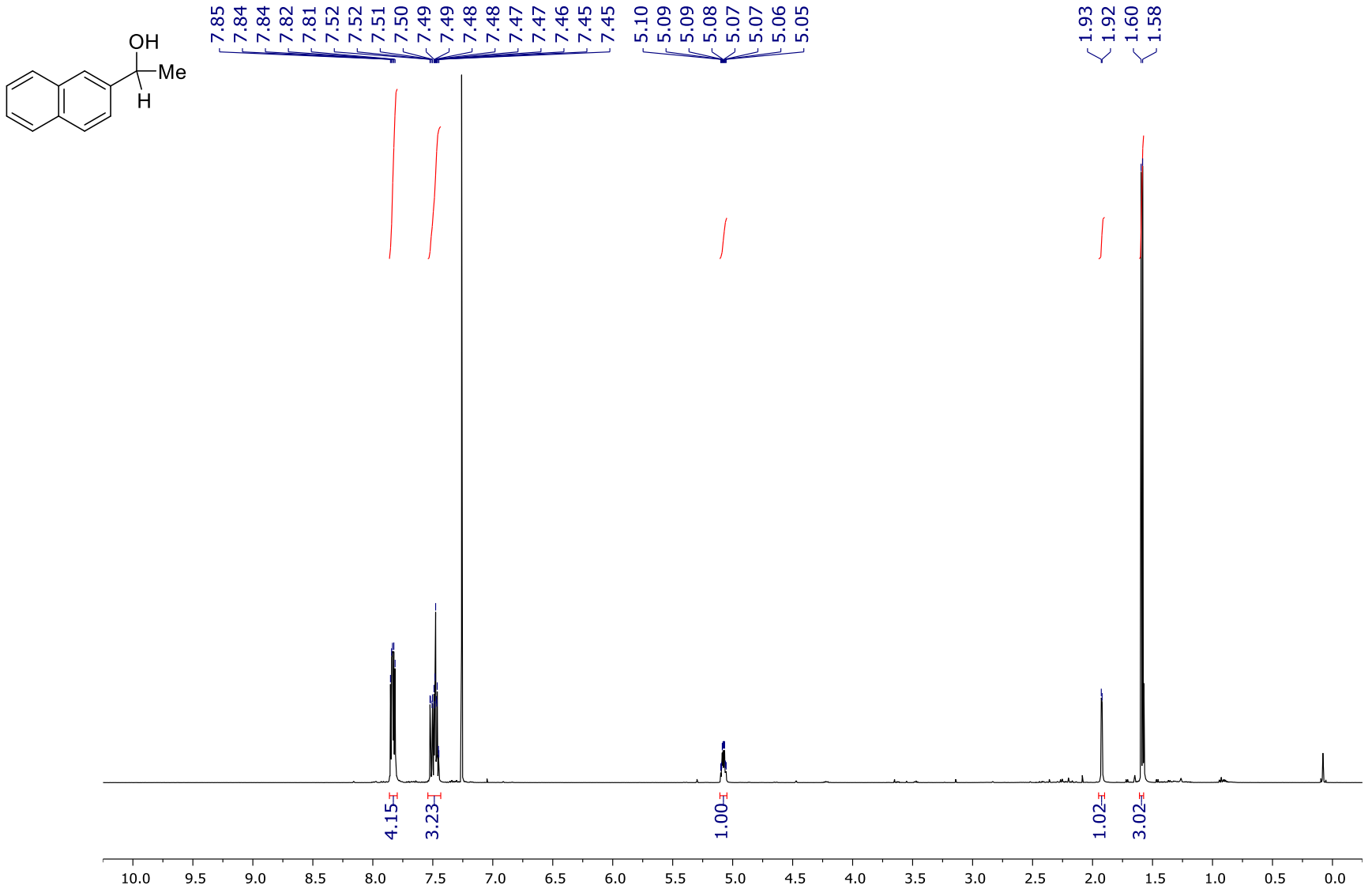


Figure S46 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *1-(napthalen-2-yl)ethanol* (**7d**)

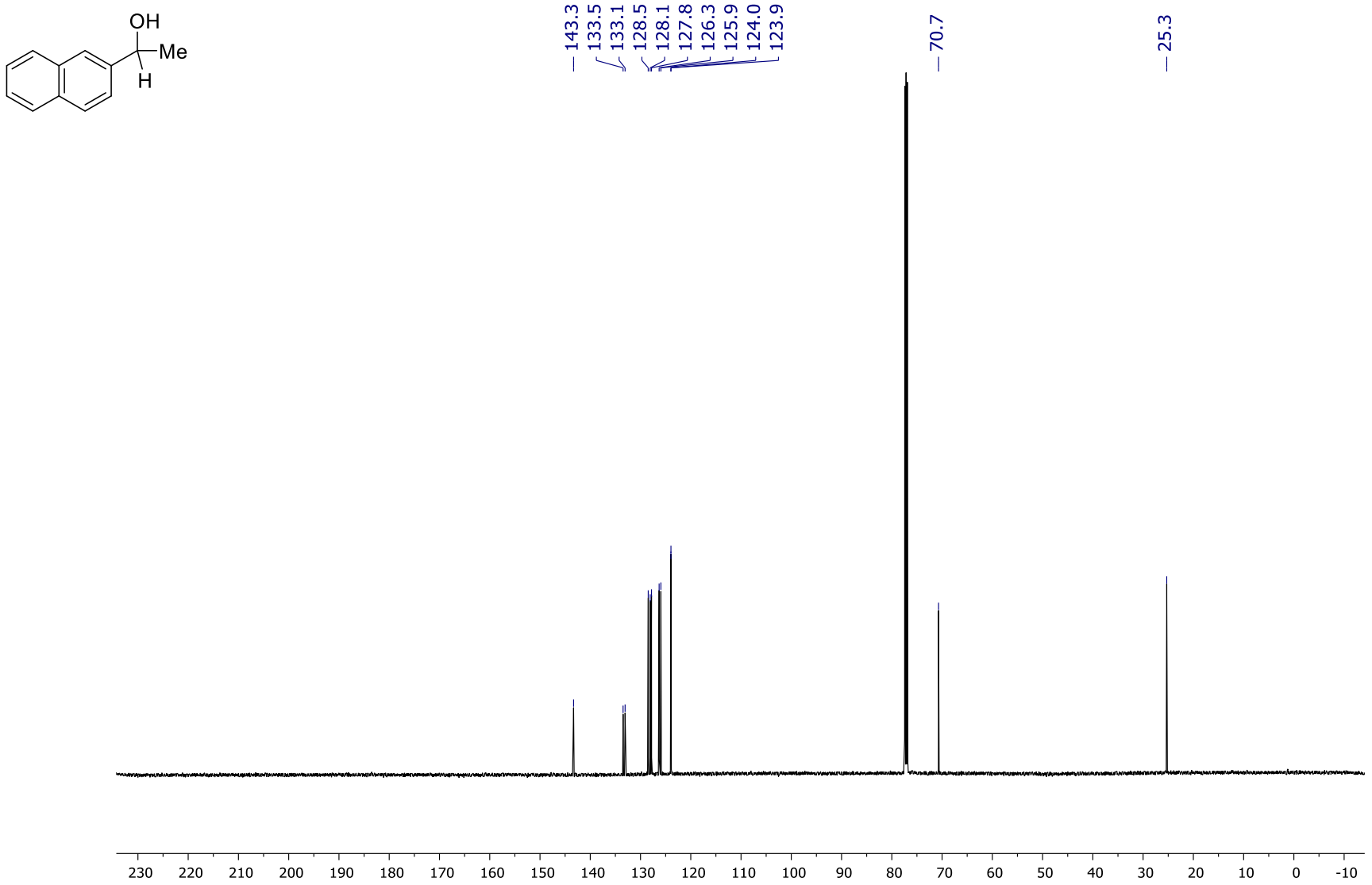


Figure S47 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *N-benzylaniline* (**8a**)

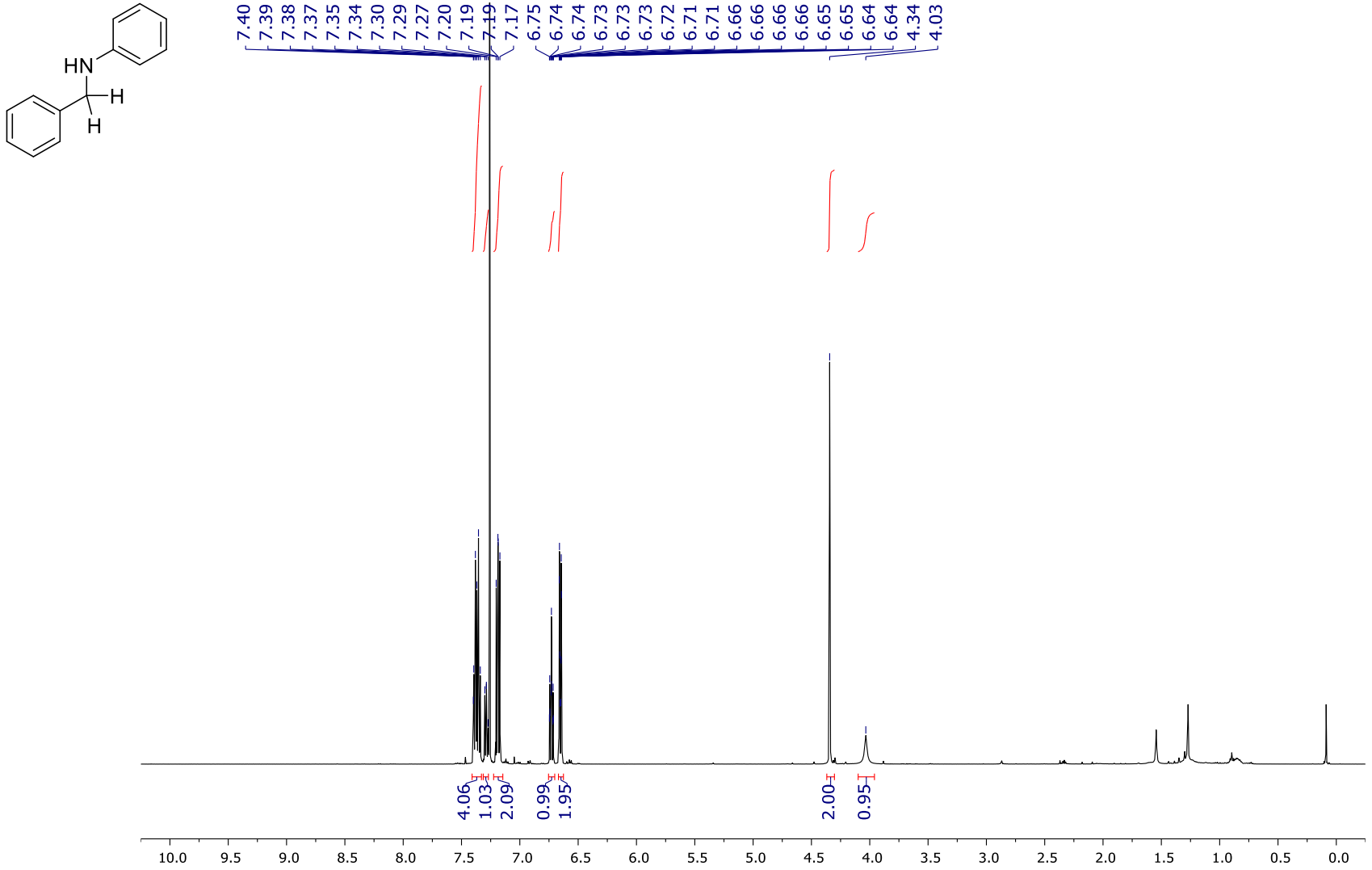


Figure S48 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *N-benzylaniline* (**8a**)

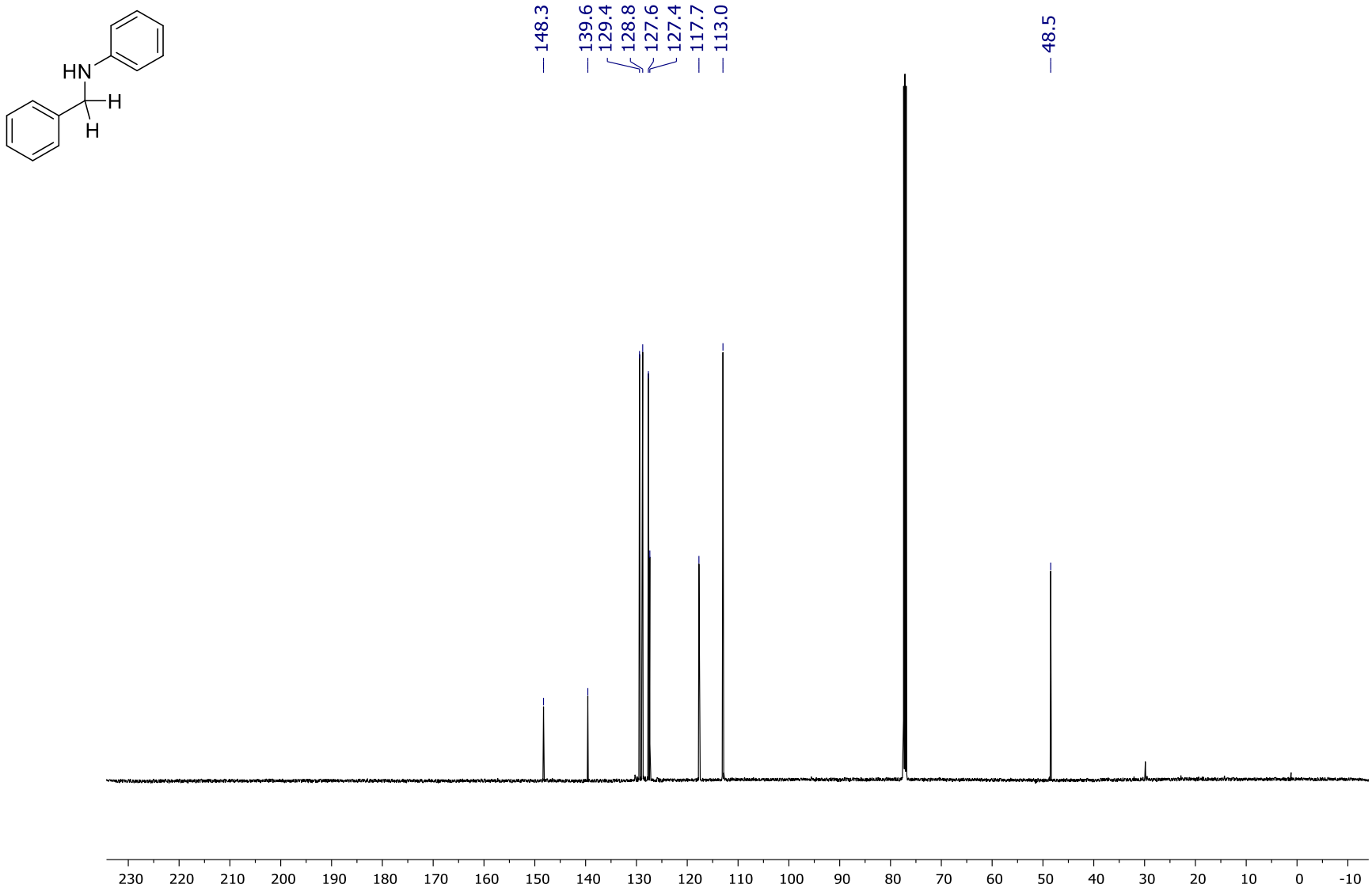


Figure S49 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *N-(4-methoxybenzyl)aniline* (**8b**)

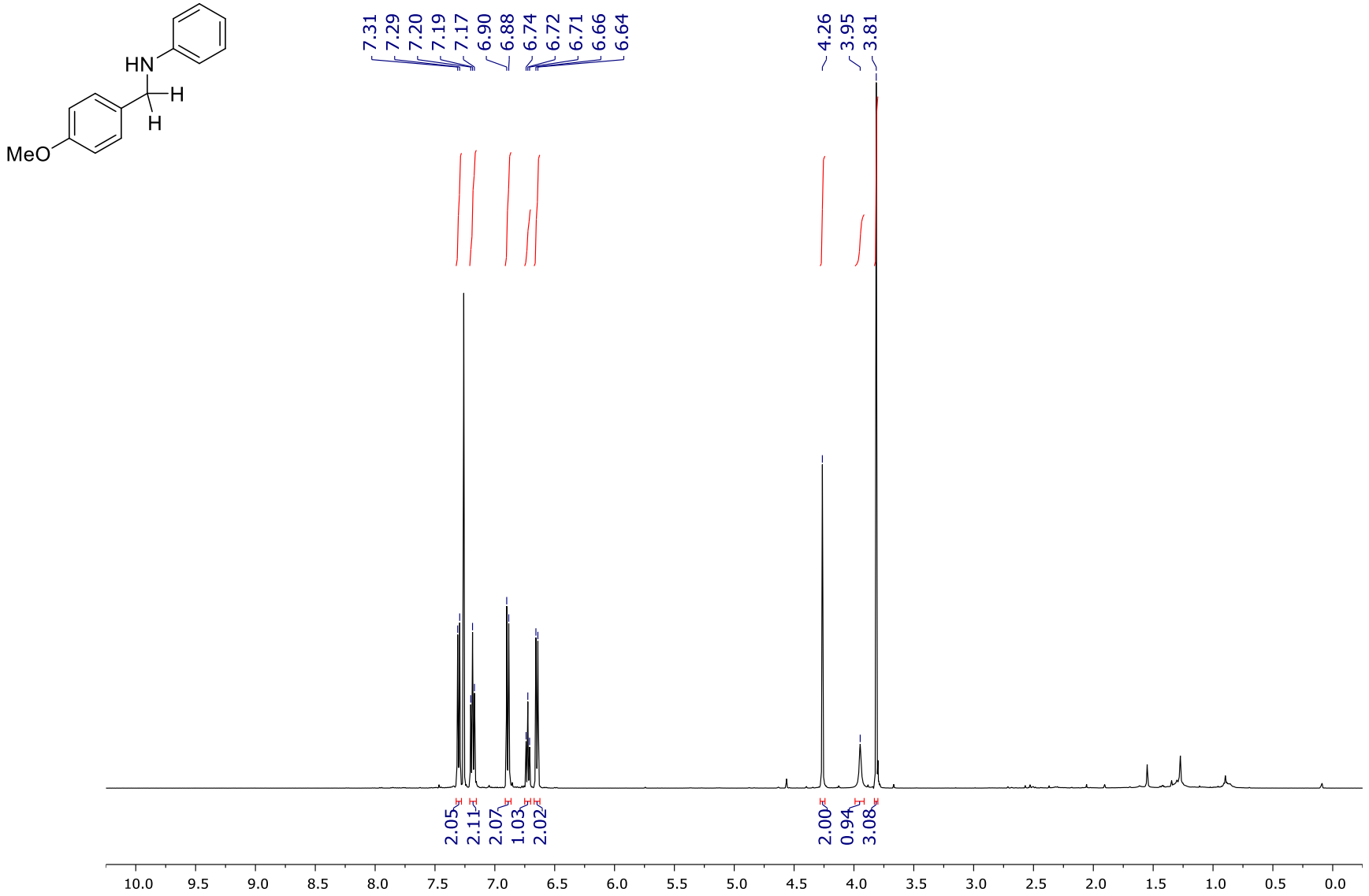


Figure S50 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *N-(4-methoxybenzyl)aniline* (**8b**)

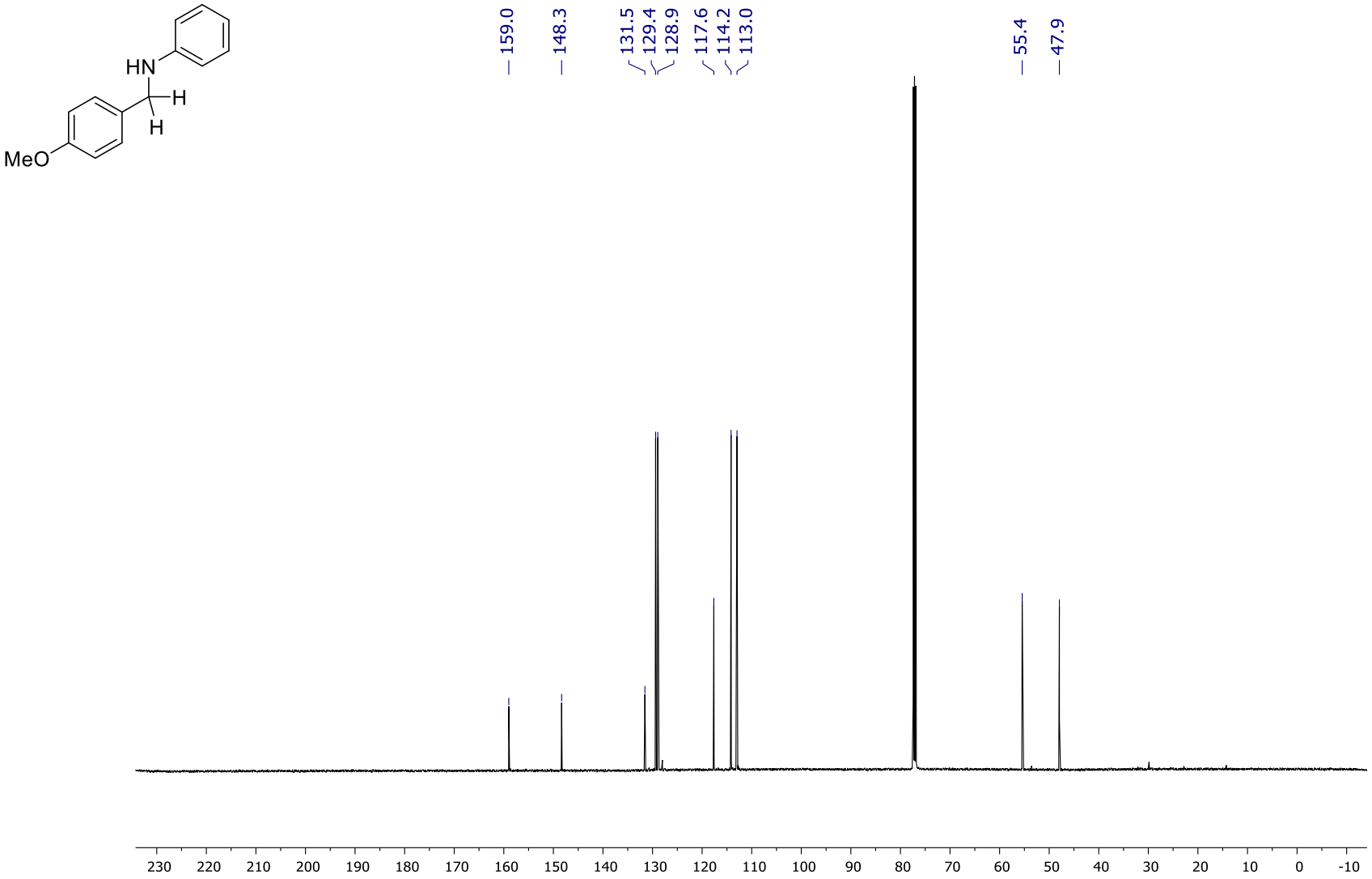


Figure S51 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *N-(4-nitrobenzyl)aniline* (**8c**)

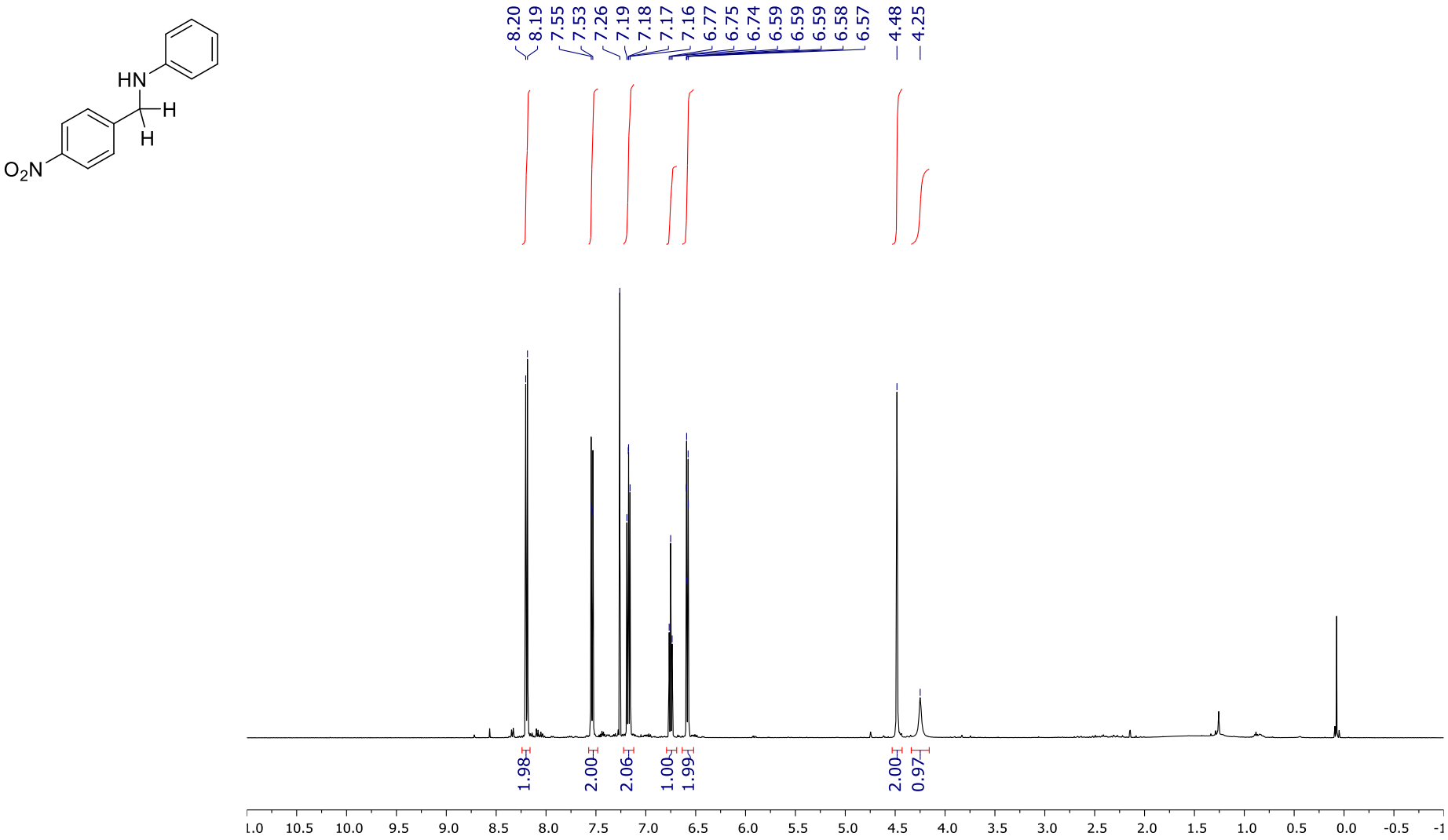


Figure S52 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *N-(4-nitrobenzyl)aniline* (**8c**)

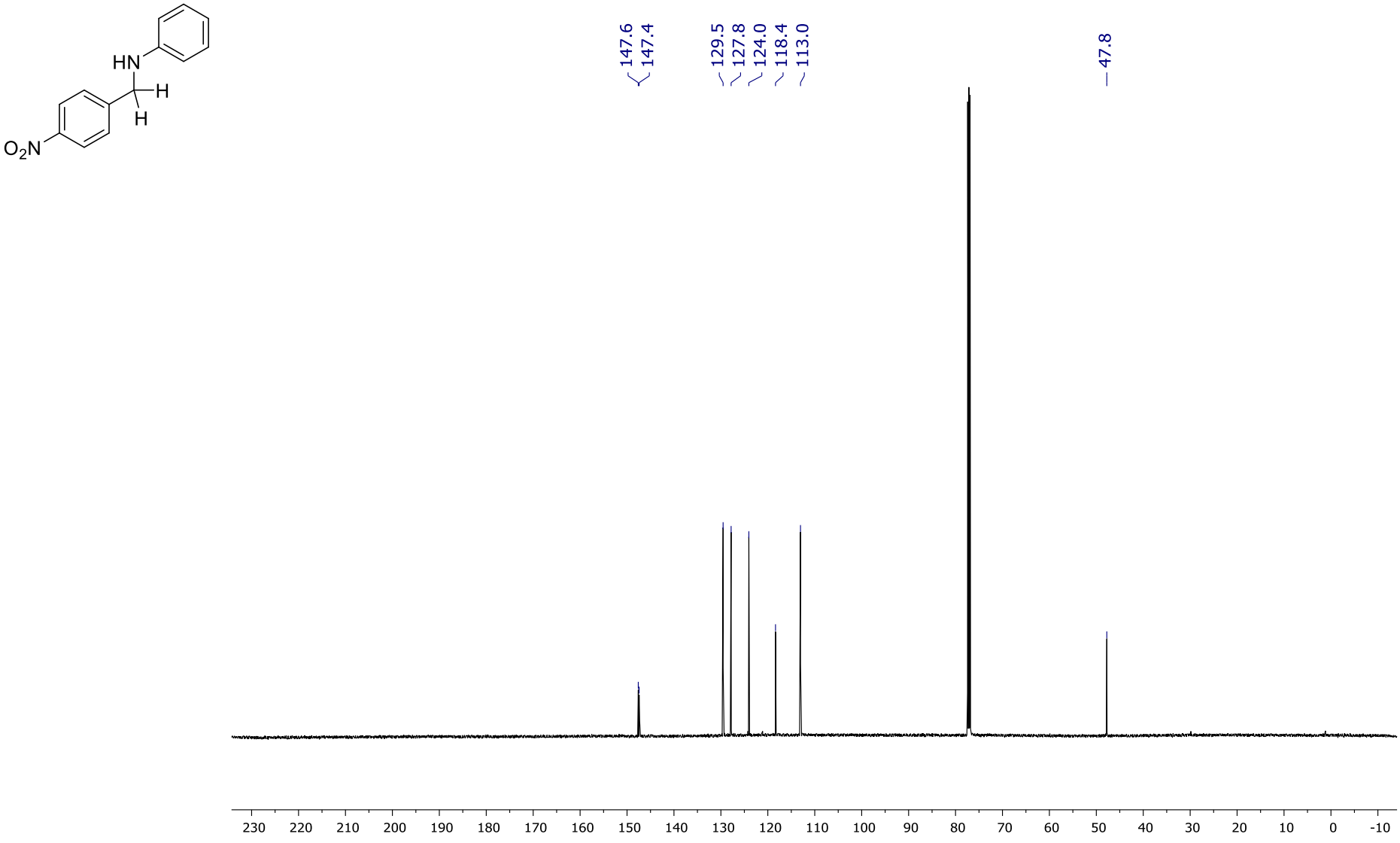


Figure S53 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *N-(napthalen-2-ylmethyl)aniline* (**8d**)

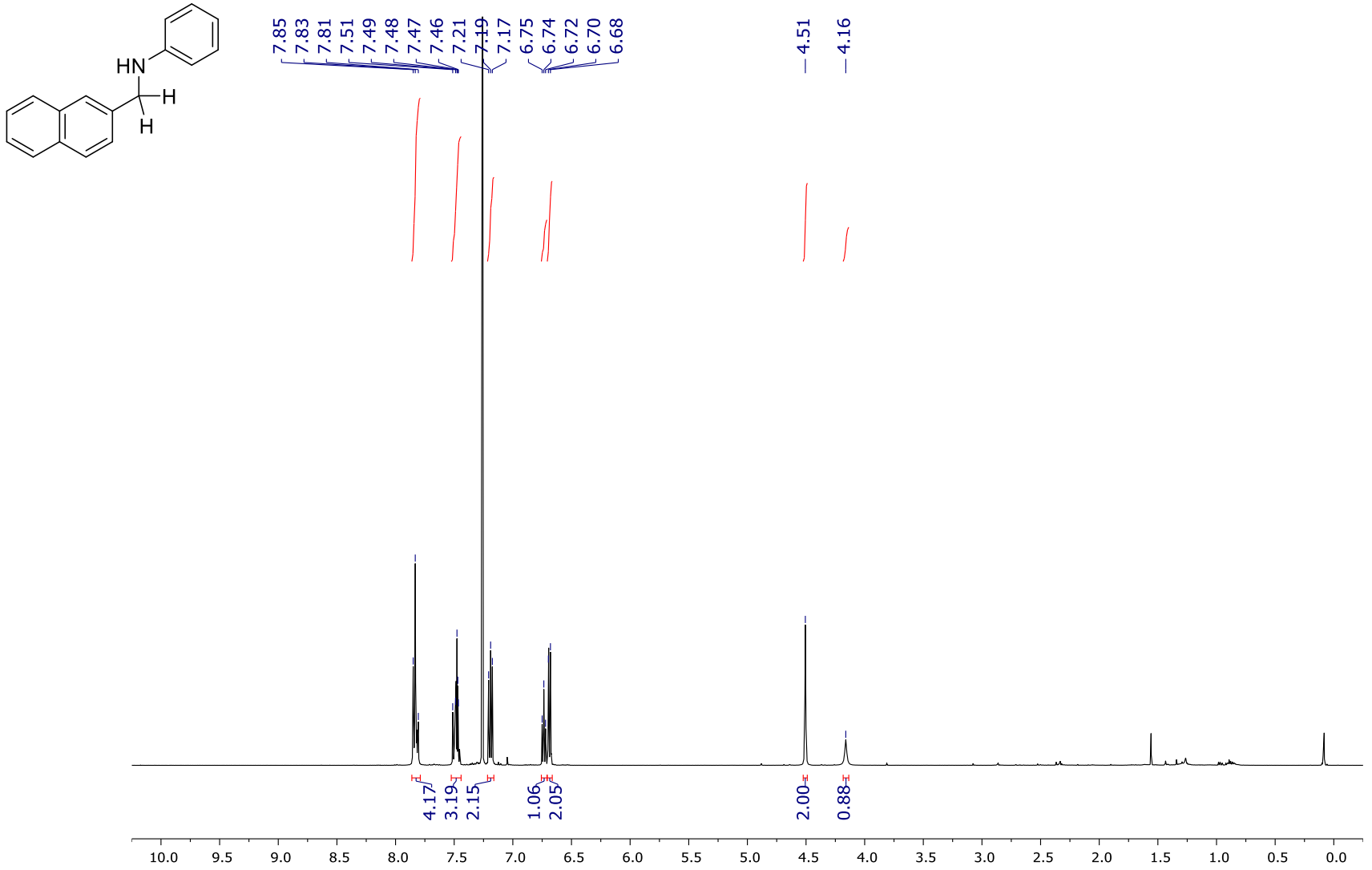


Figure S54 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *N-(napthalen-2-ylmethyl)aniline* (**8d**)

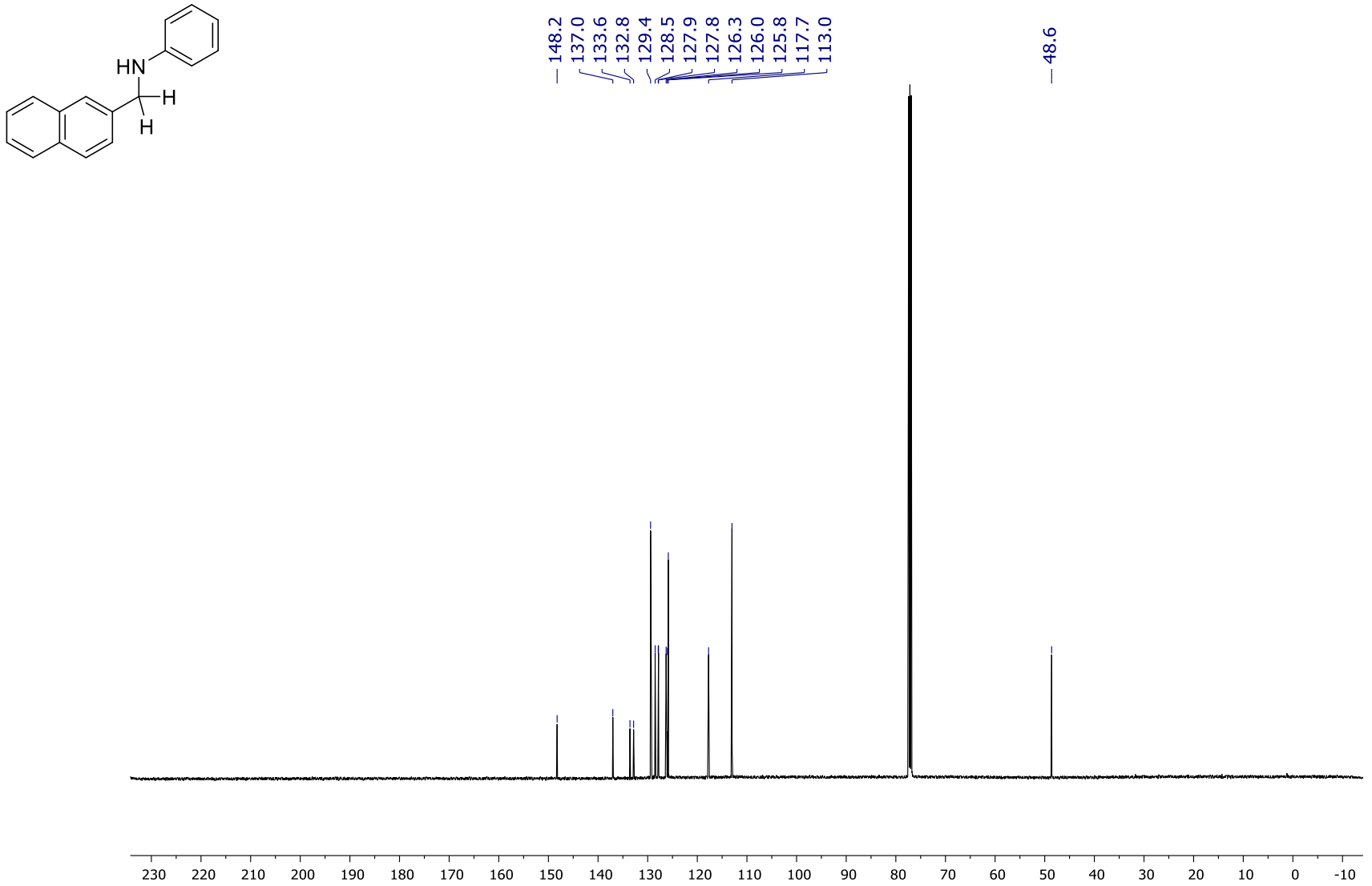


Figure S55 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane* (**9a**)

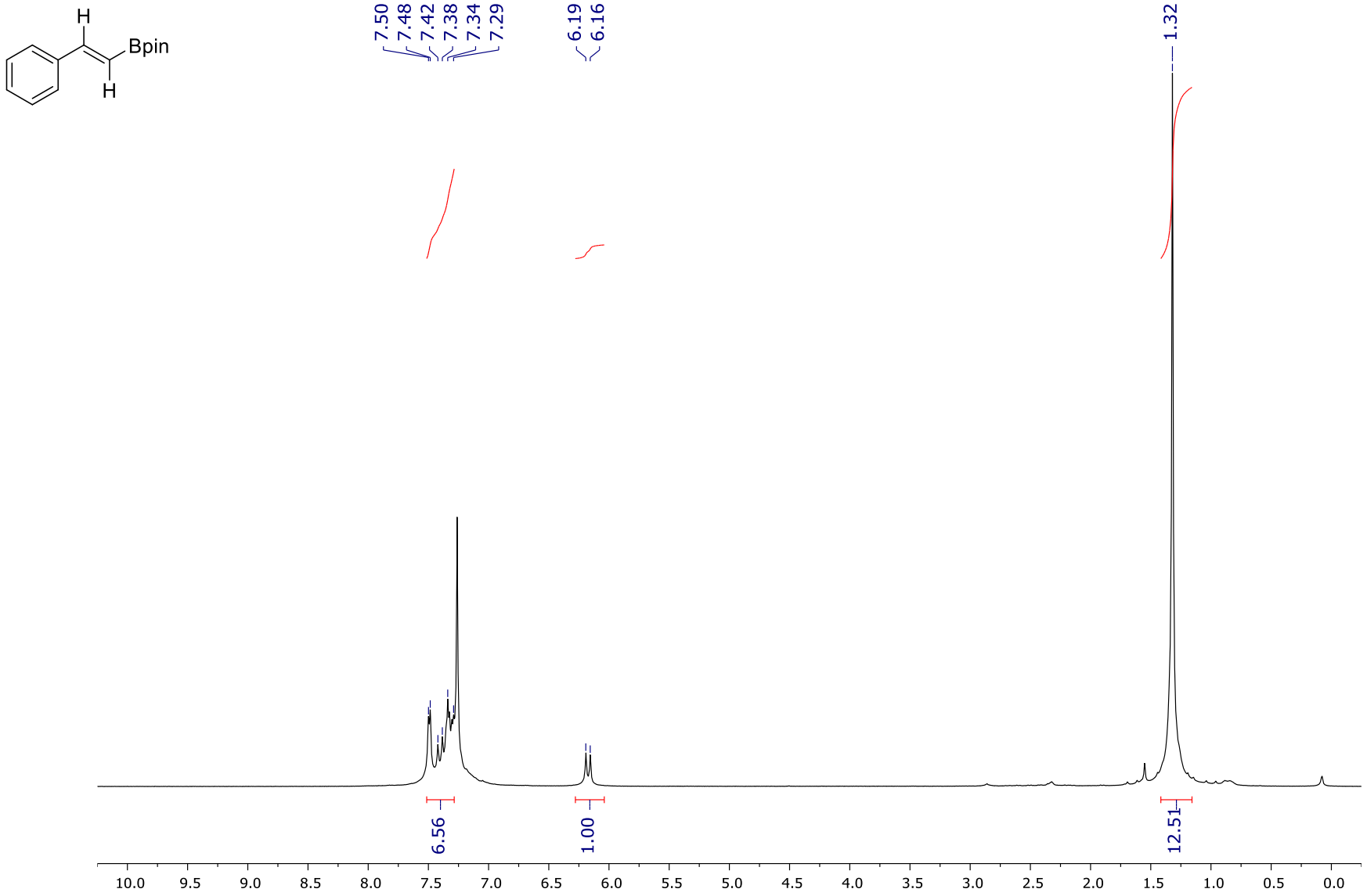
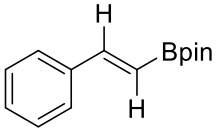


Figure S56 ^{11}B NMR (160 MHz, $CDCl_3$, 295 K) spectrum of *4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane* (**9a**)



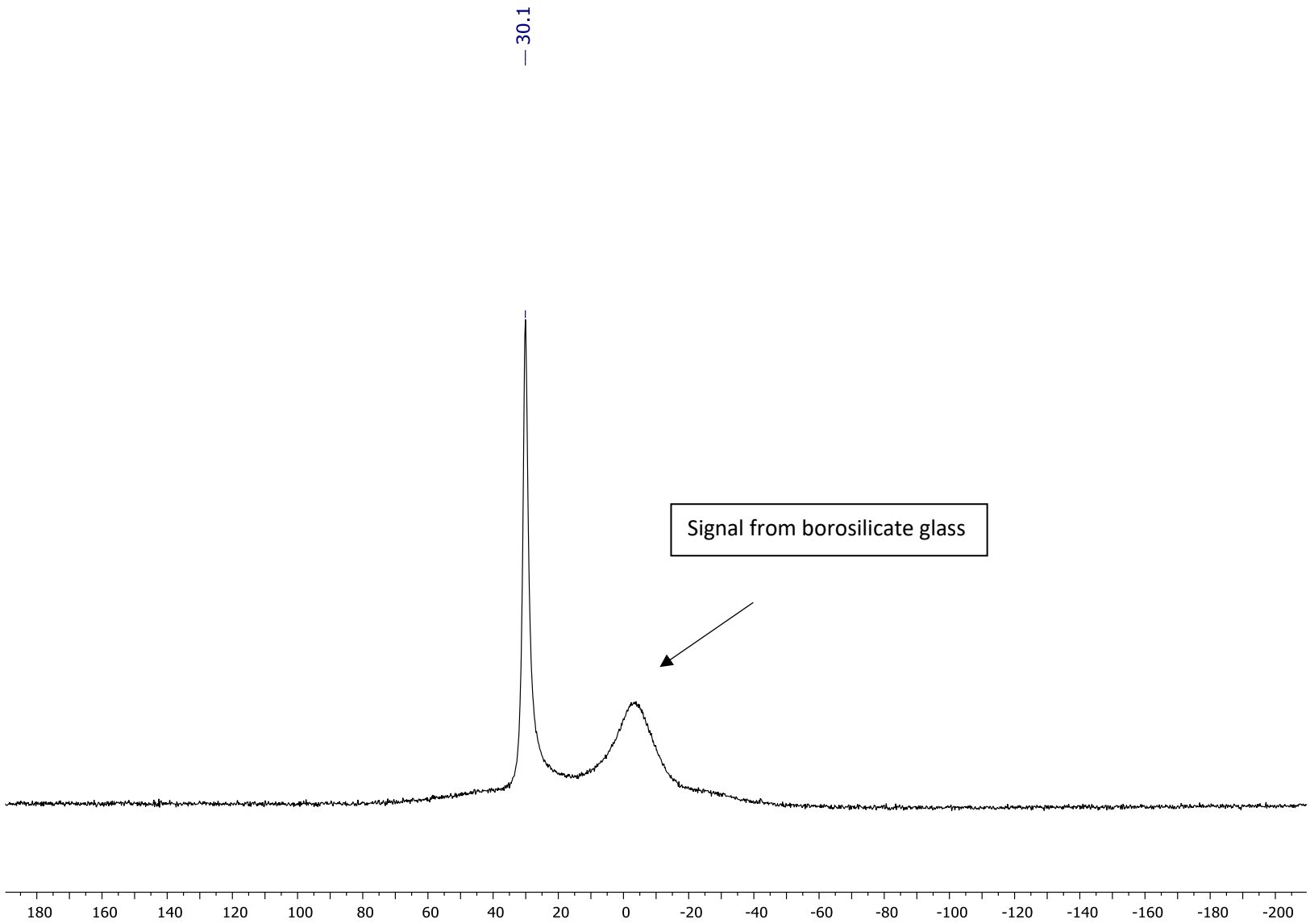
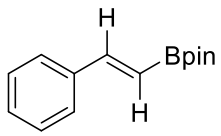


Figure S57 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane* (**9a**)



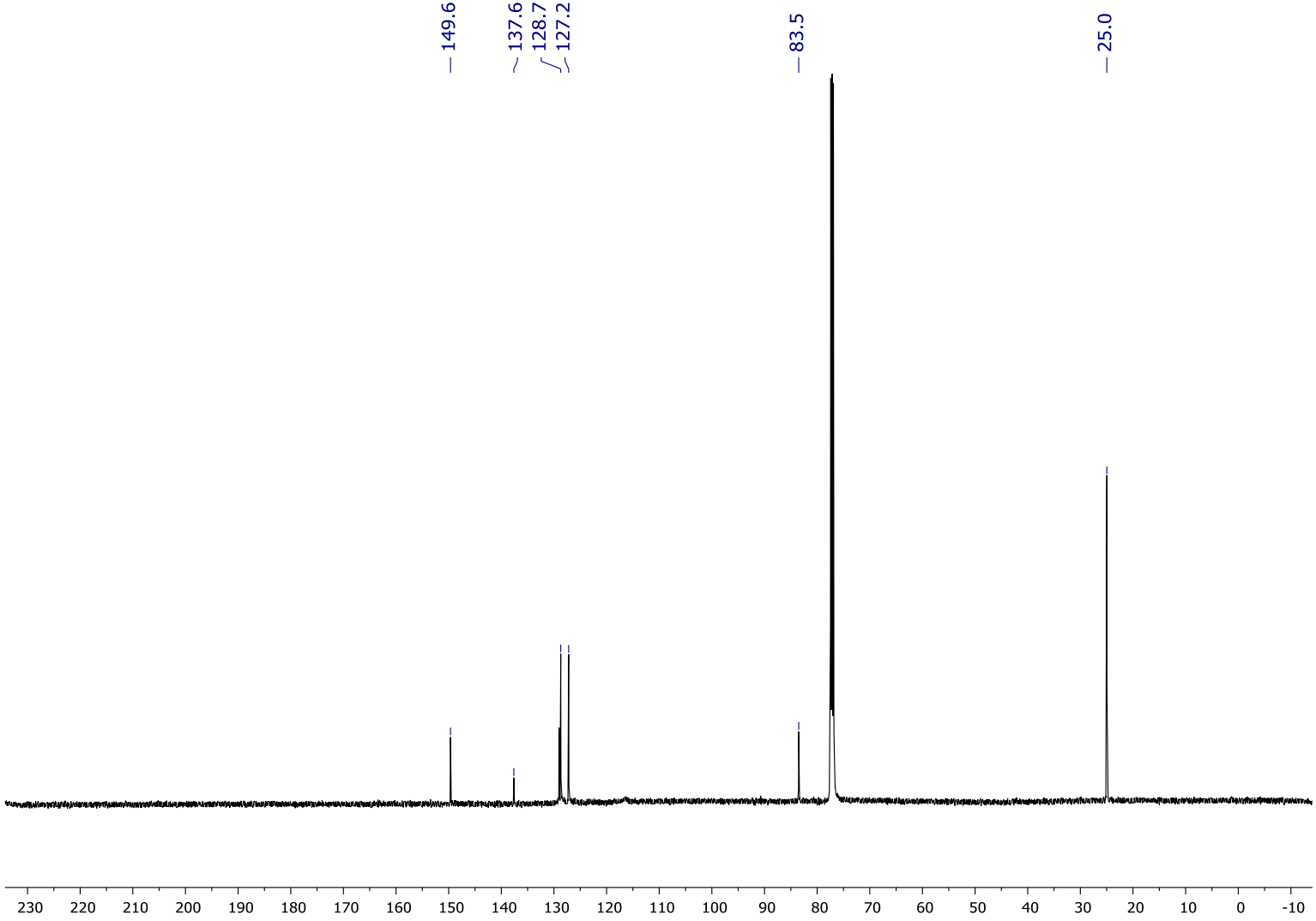


Figure S58 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9b**)

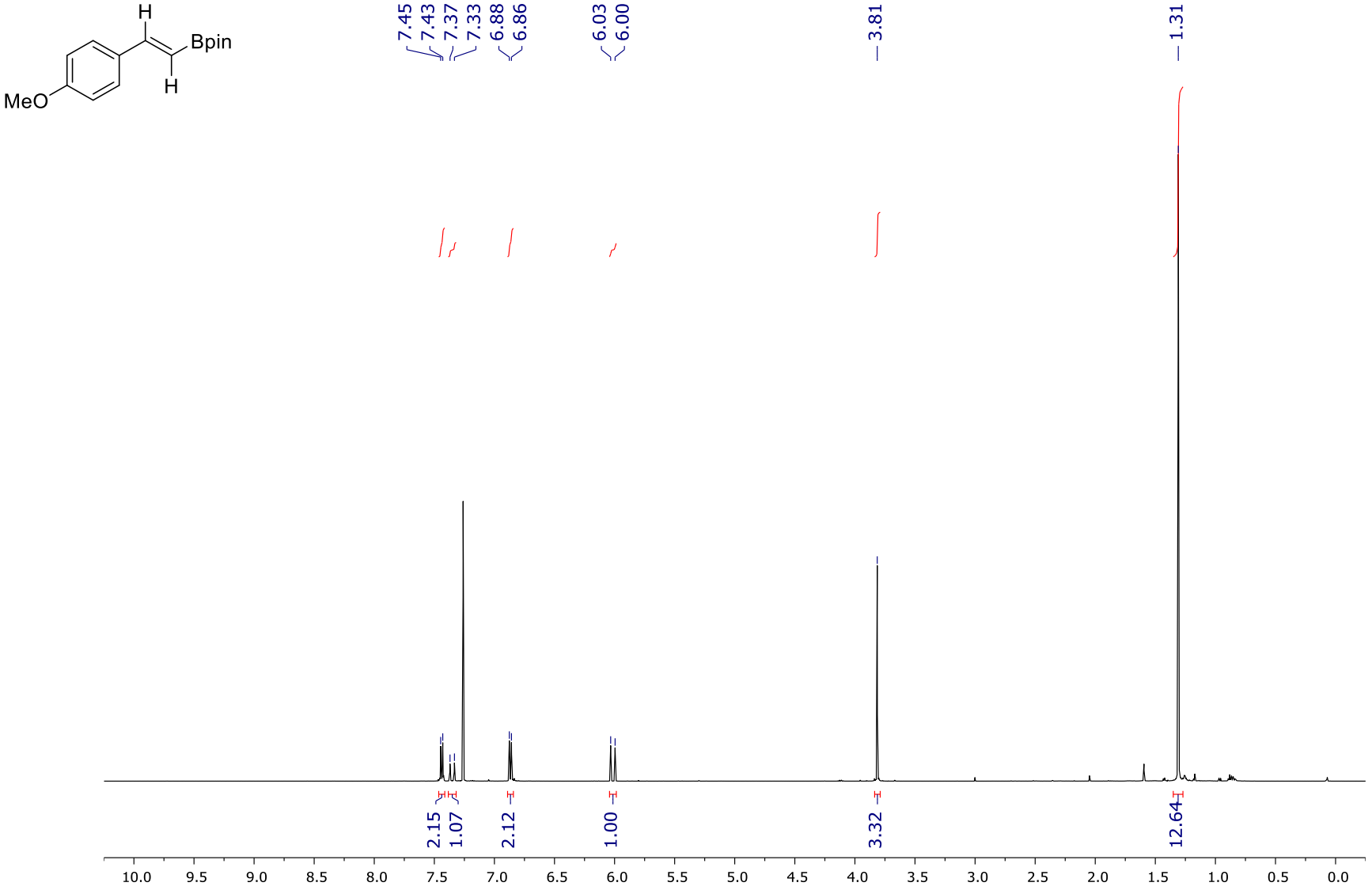


Figure S59 ^{11}B NMR (160 MHz, $CDCl_3$, 295 K) spectrum of *2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9b**)

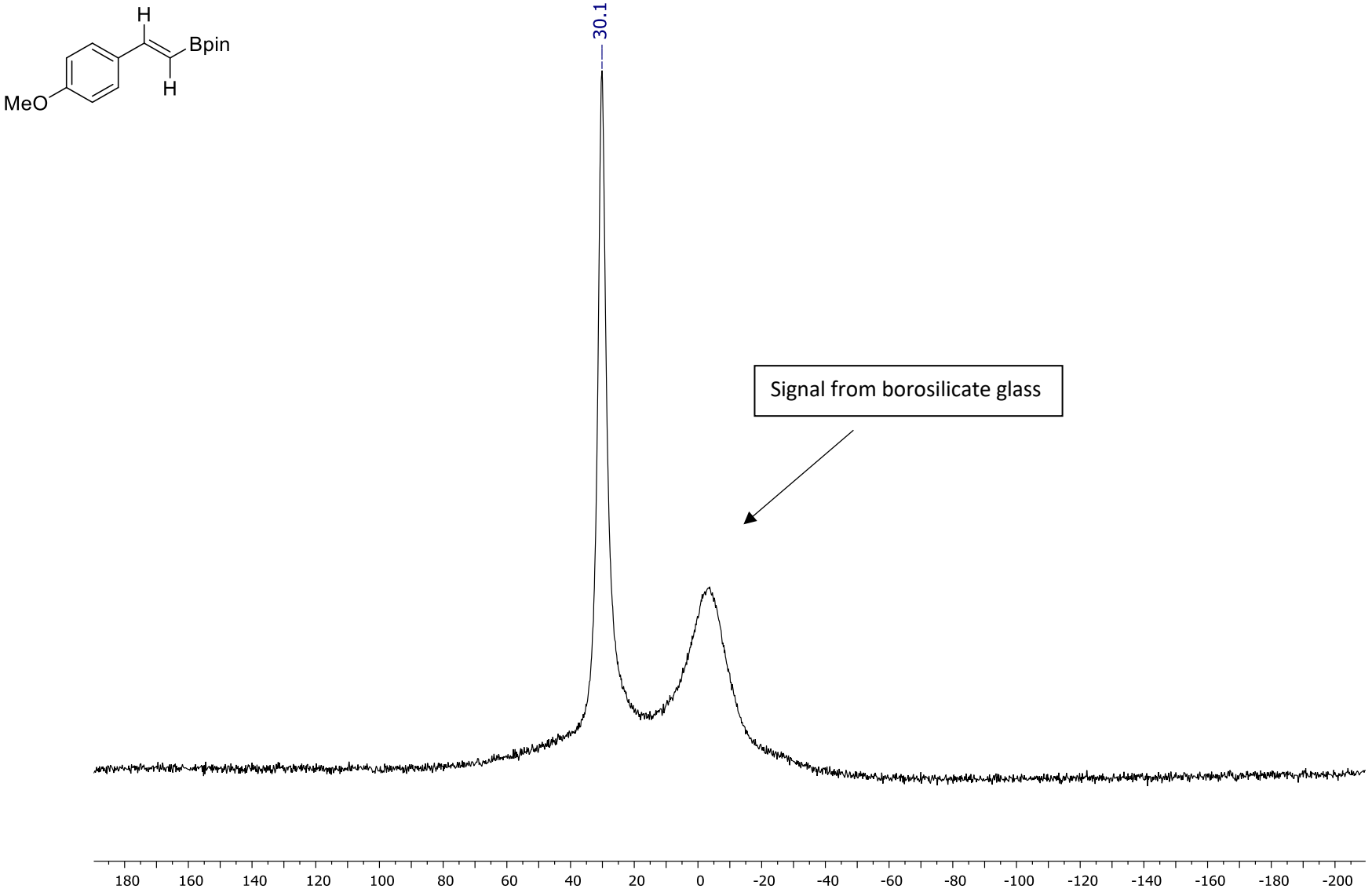


Figure S60 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9b**)

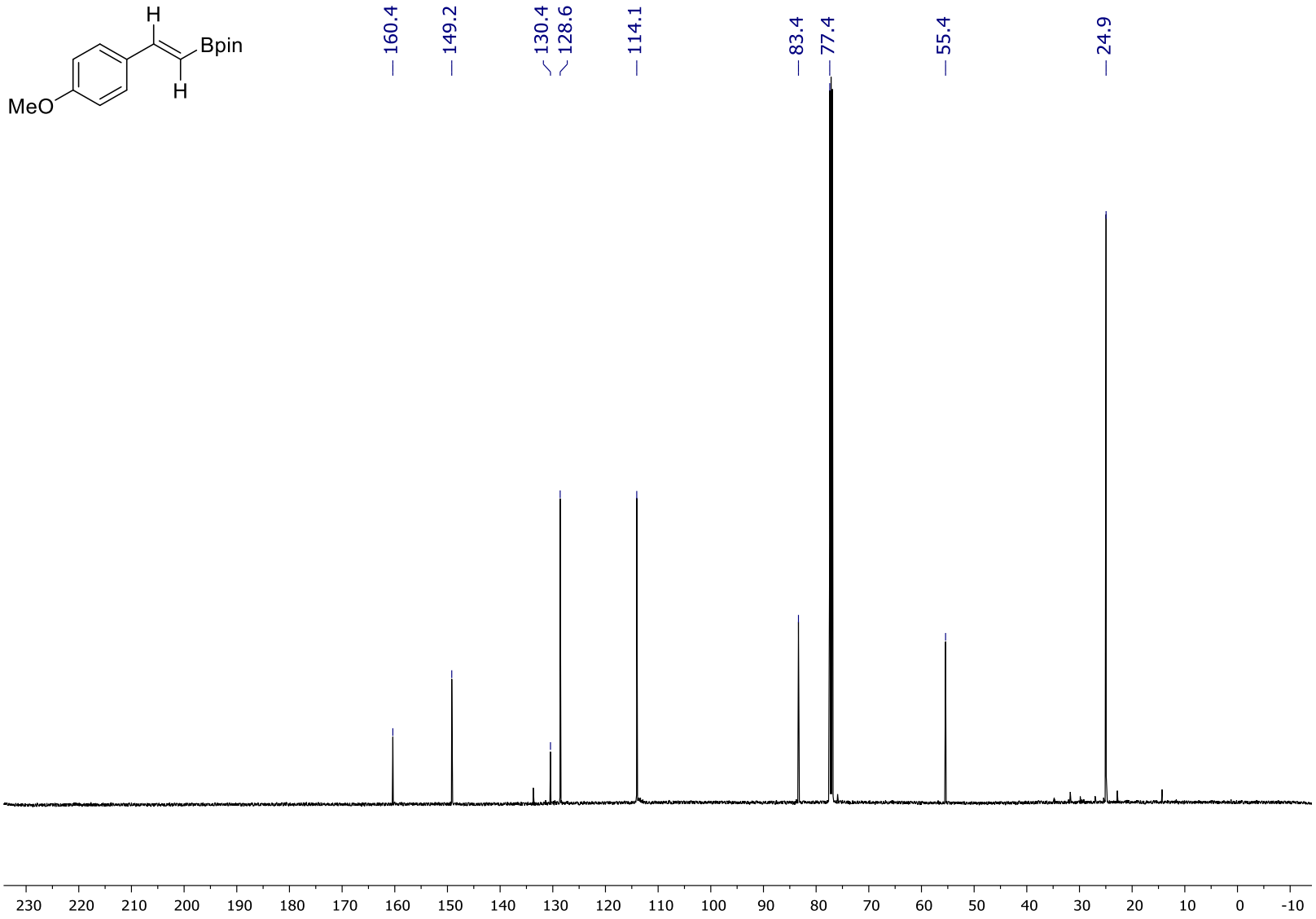


Figure S61 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *2-(2,4,6-trimethylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9c**)

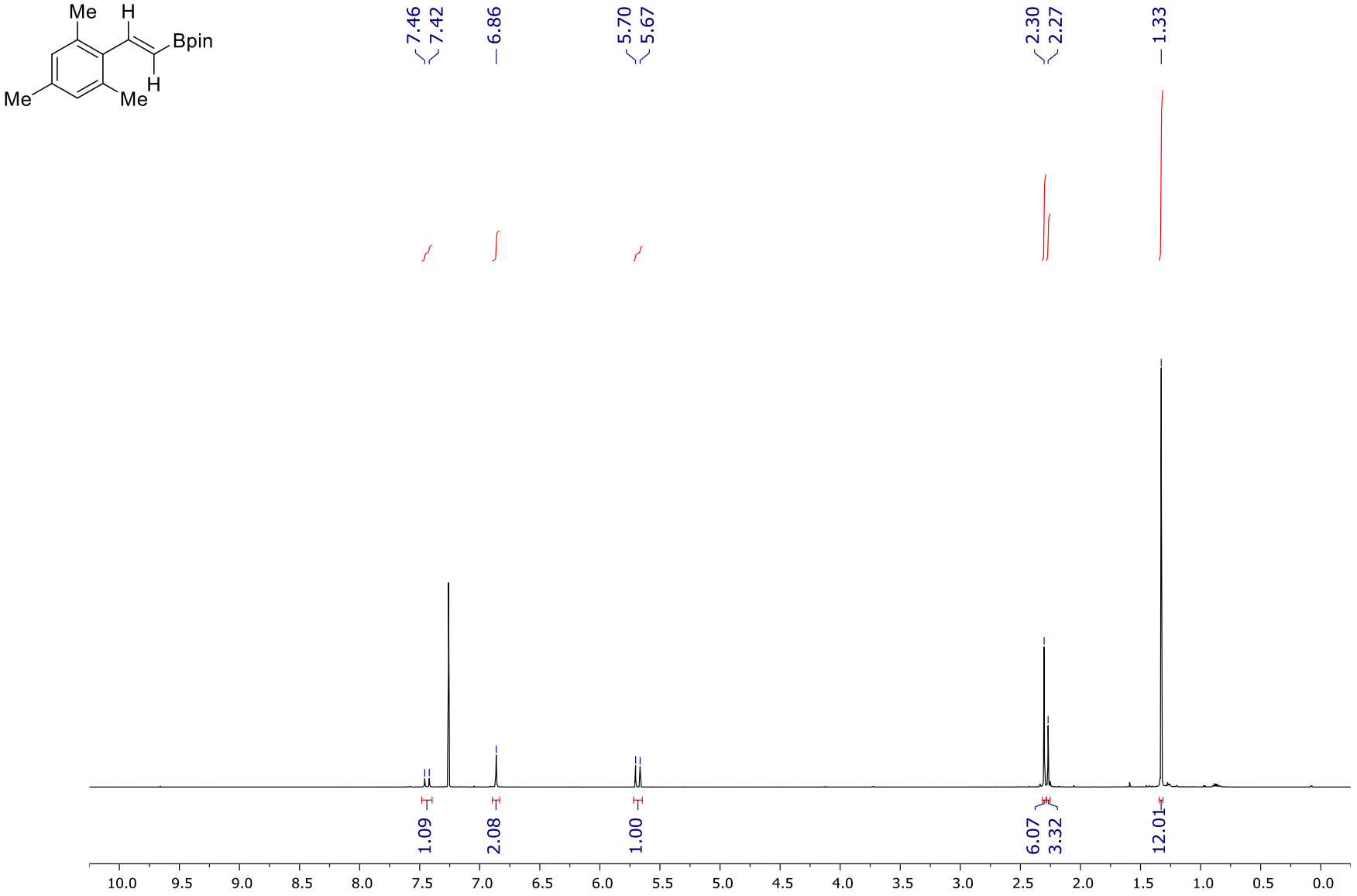


Figure S62 ^{11}B NMR (160 MHz, $CDCl_3$, 295 K) spectrum of *2-(2,4,6-trimethylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9c**)

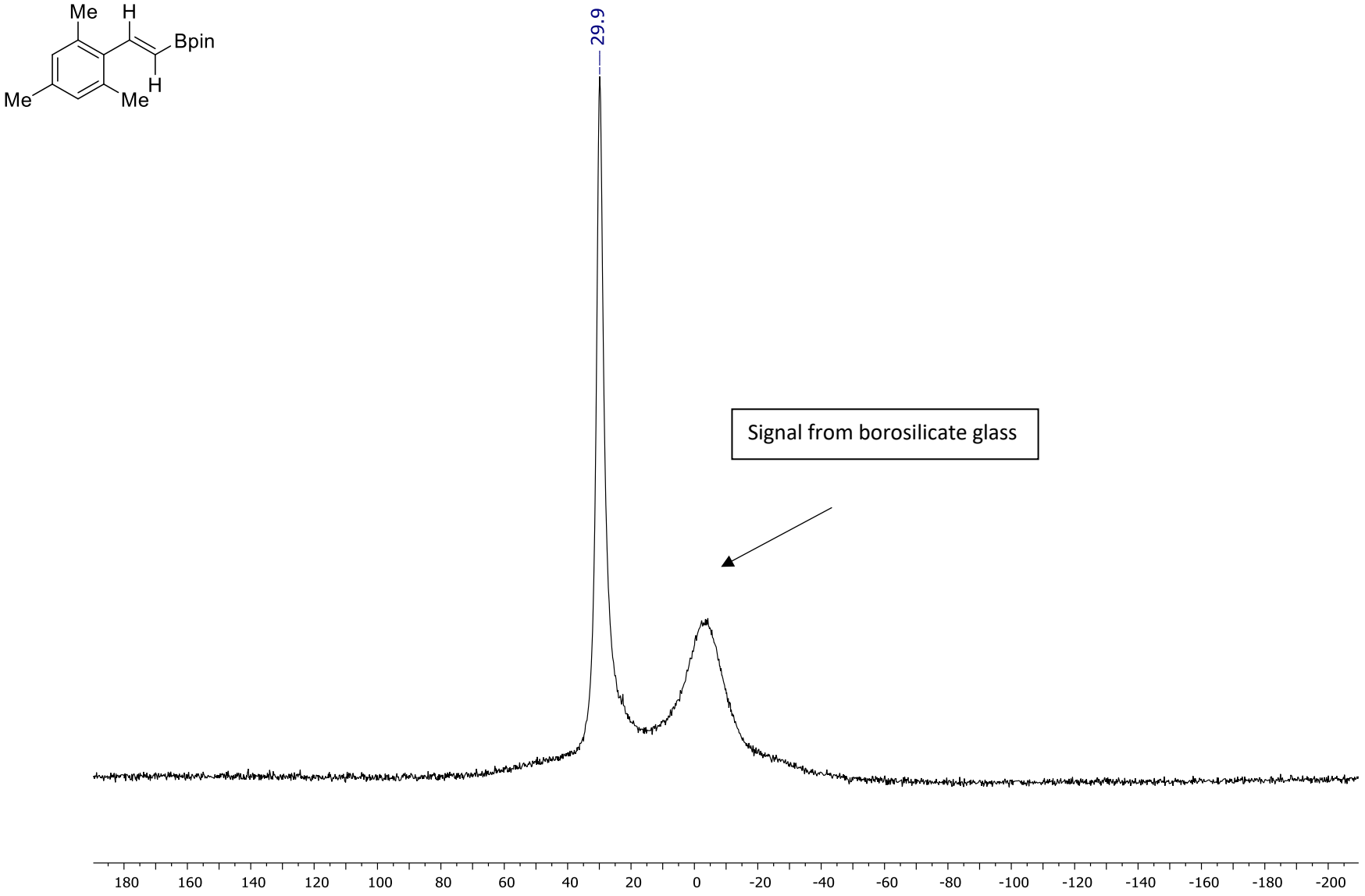


Figure S63 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *2-(2,4,6-trimethylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9c**)

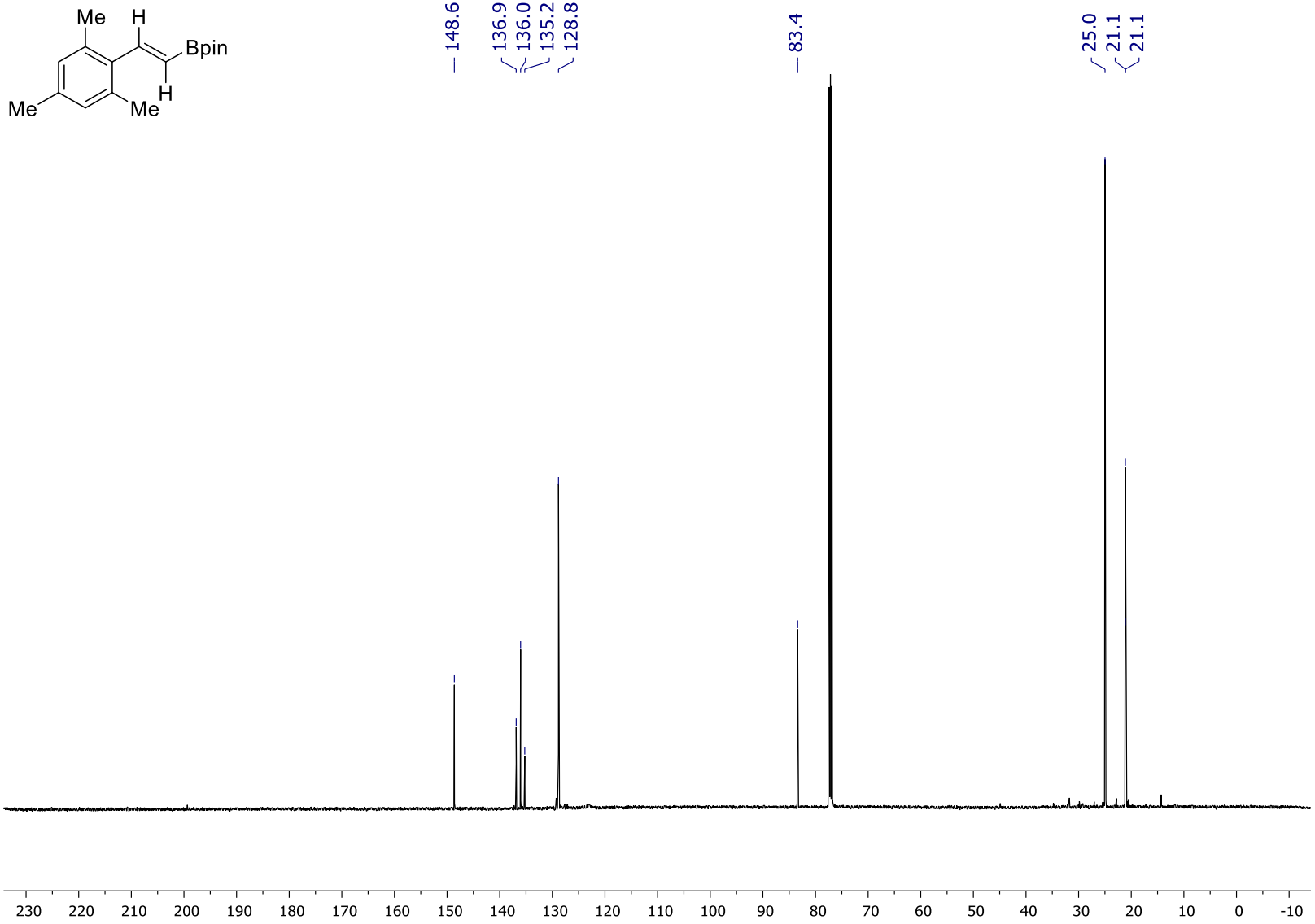


Figure S64 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of *2-(2-(biphenyl-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9d**)

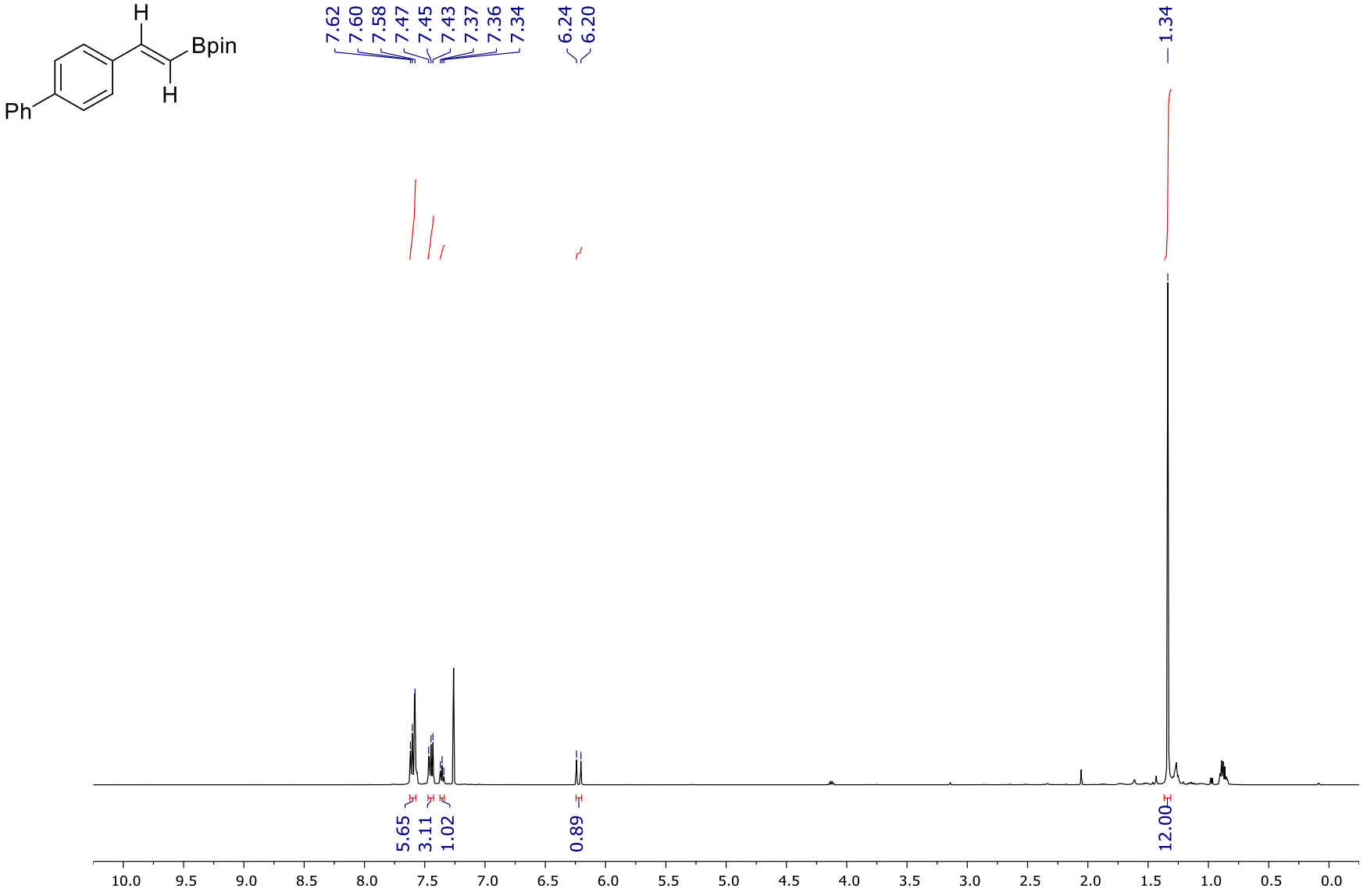


Figure S65 ^{11}B NMR (160 MHz, $CDCl_3$, 295 K) spectrum of *2-(2-(biphenyl-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9d**)

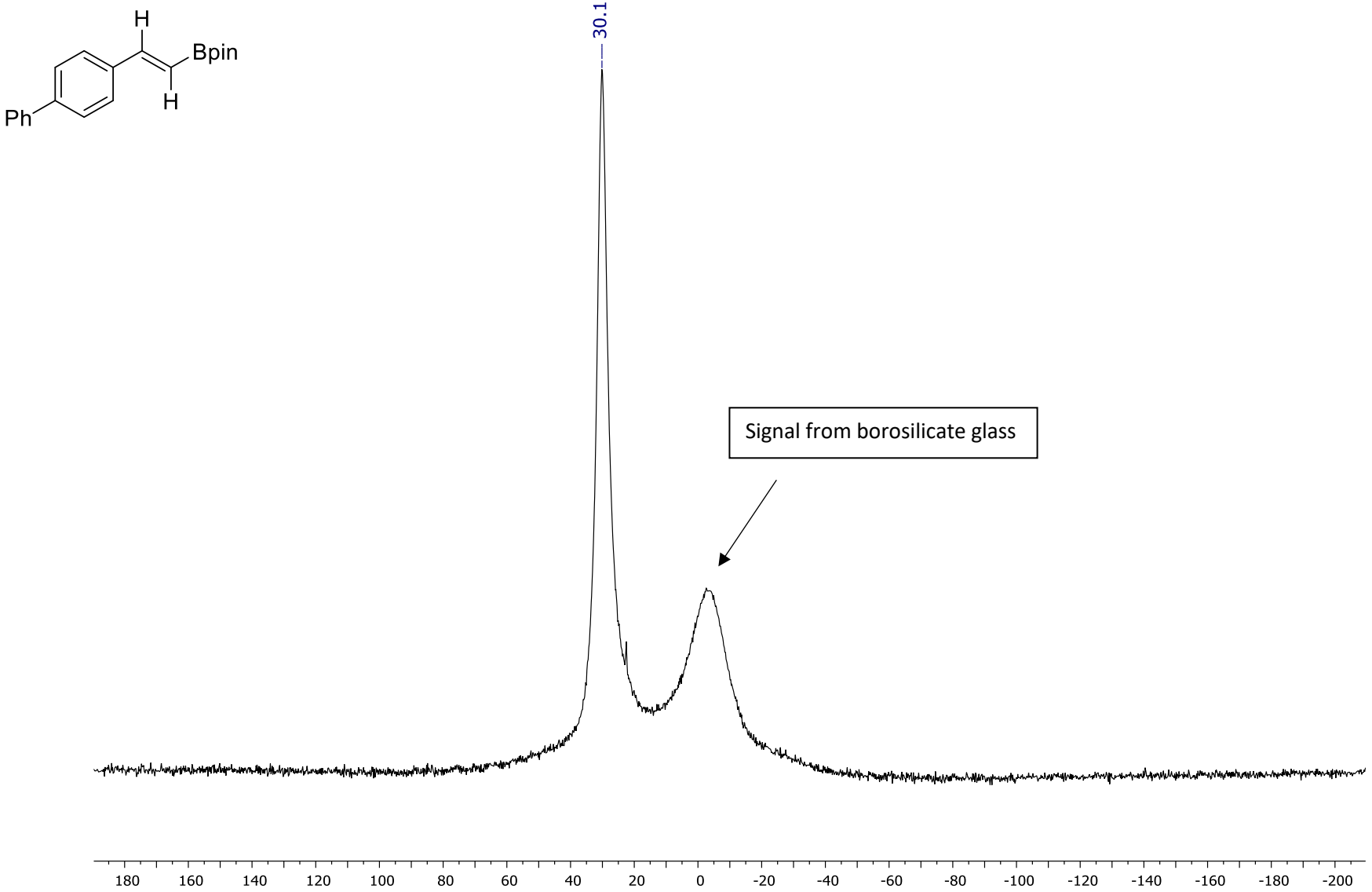
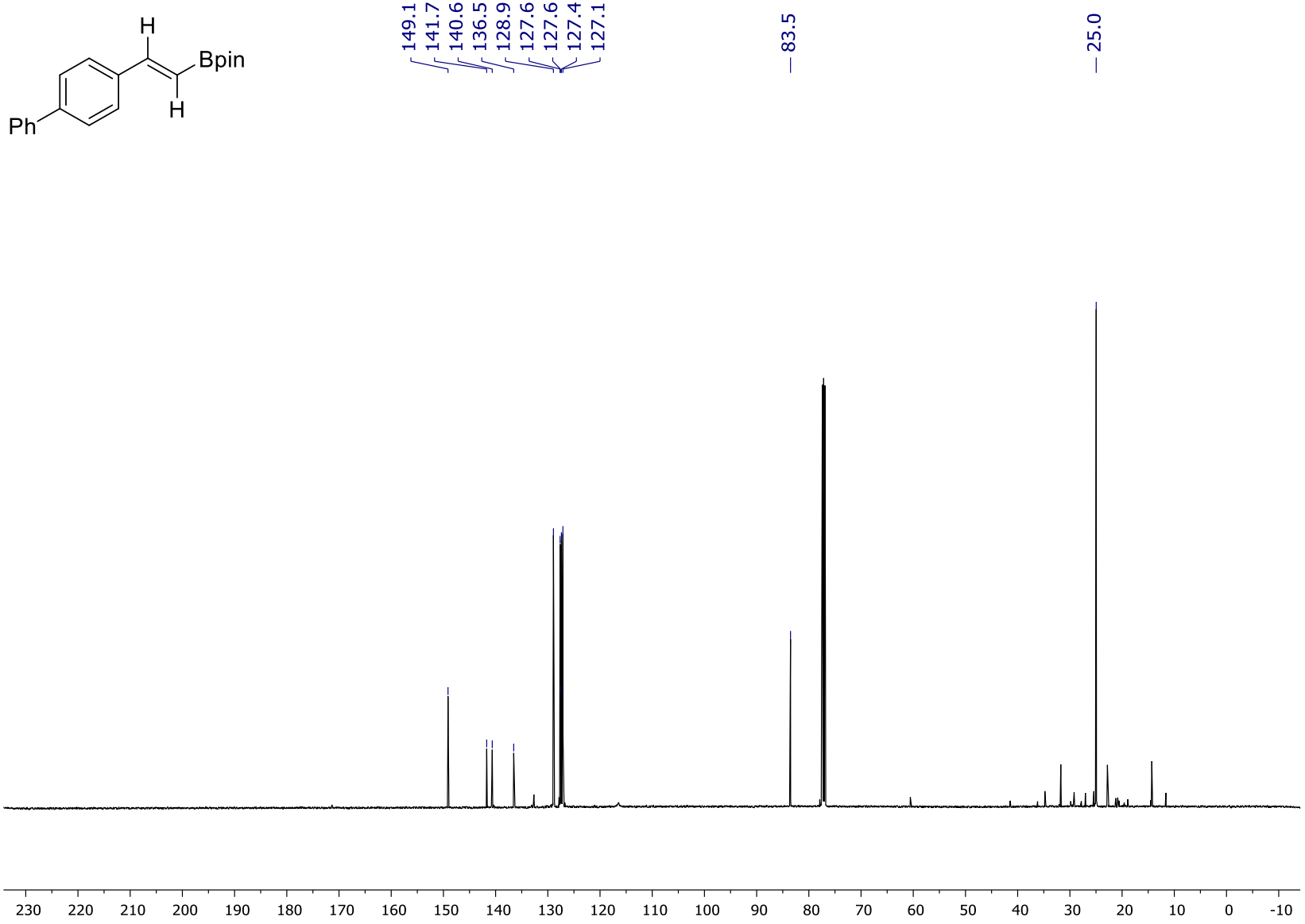
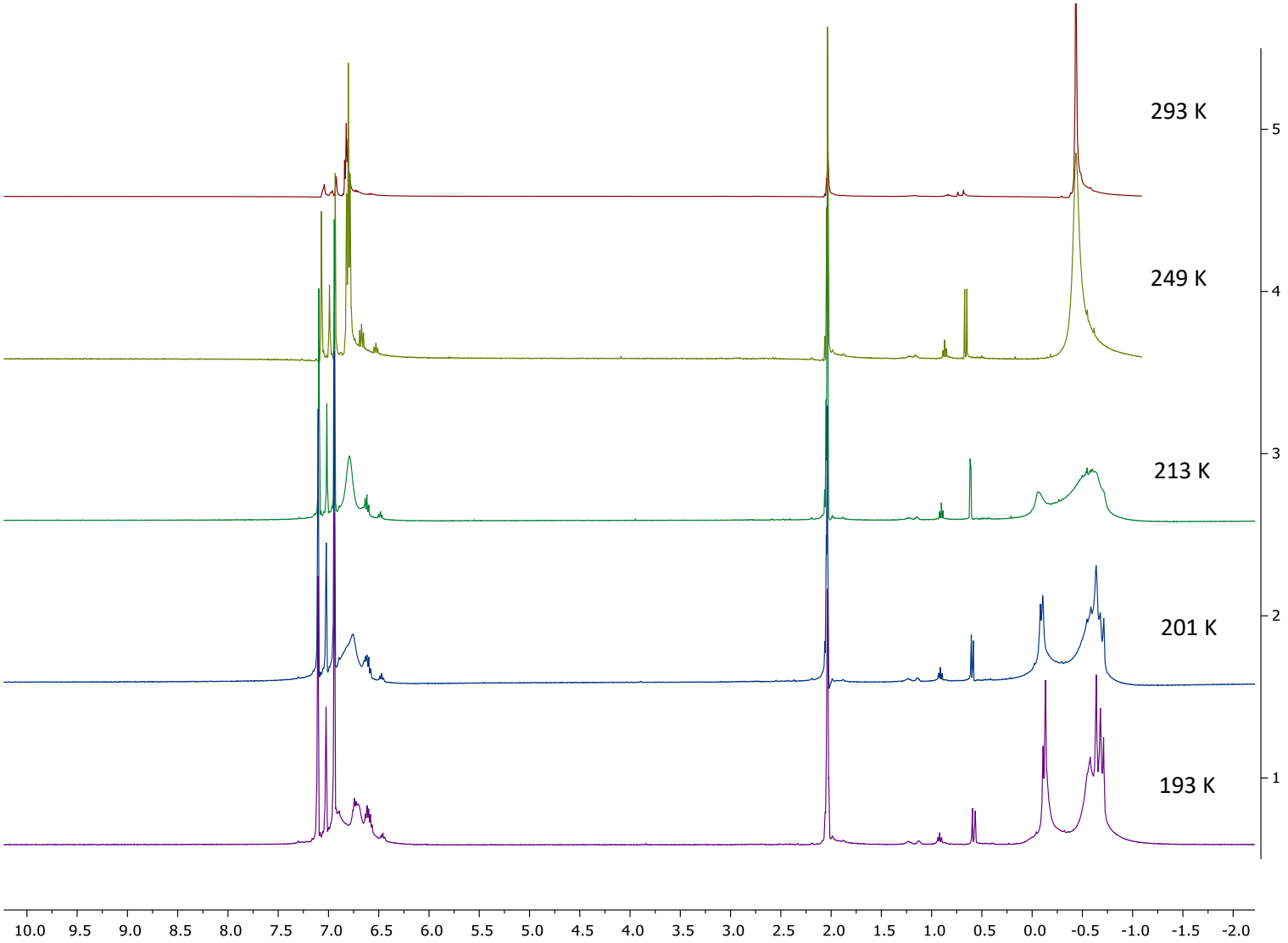


Figure S66 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of *2-(2-(biphenyl-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9d**)



S4.5 VT NMR

Figure S67 VT ^{1}H NMR (400 MHz, toluene-d^{8}, variable temperature) spectrum of *μ2-dimethyl-bis[(3,4,5-trifluorophenyl)methyl-alane]* (**2**)



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