Supplementary Information for:

Synthesis and Reactivity of *N,N*-1,4-diazabutadiene Derived Borocations

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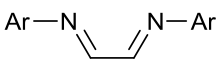
1. Experimental

1.1 General Experimental

With the exception of the starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBraun) was used to manipulate solids including the storage of starting materials, room temperature reactions, product recovery and sample preparation for analysis. All solvents (toluene, CH_2Cl_2, hexane) were dried by a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals, namely anilines and boranes, were purchased from commercial suppliers and used as received. ^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{27}Al and ^{31}P NMR spectra were recorded on a Bruker Avance II 400 spectrometer. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $CDCl_3$ (7.26/77.16 ppm) as internal standards. NMR spectra were referenced to $CFCl_3$ (^{19}F), $Al(NO_3)_3/D_2O$ (^{27}Al), $BF_3{\cdot}Et_2O/CDCl_3$ (^{11}B) and H_3PO_4 (^{31}P). The description of signals include: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet and br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). ^{13}C NMR was measured as ^{1}H decoupled. Yields are given as isolated yields. All spectra were analysed assuming a first order approximation. IR-Spectra were measured on a Shimadzu IRAffinity-1 photospectrometer. Mass spectra were measured in house on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer. Elemental analyses were performed at the London Metropolitan University.

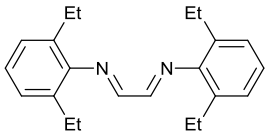
1.2 Synthesis of starting materials.

1.2.1 General synthesis 1: synthesis of 1,4-diazabutadiene precursors (1)



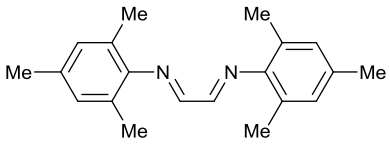
In a procedure adapted from that of Yan *et al*.[1] The aniline derivative (2 equiv.) was added to a solution of 40 wt. % aqueous solution of glyoxal (1 equiv.) in ethanol (6 ml) and stirred at ambient temperature for 1 hour, unless stated otherwise. The crude product **1** precipitated as a yellow solid which was filtered off, washed with ethanol and dried thoroughly *in vacuo* to give the pure product as a yellow-brown solid.

*Synthesis of (E,E)-N^1,N^2-bis(2,6-diethylphenyl)ethane-1,2-diimine (**1a**).*



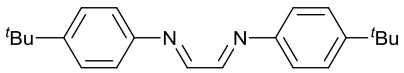
Compound **1a** was synthesised according to general synthesis 1 using 2,6-diethylaniline (1.5 ml, 9.1 mmol, 2 equiv.) and glyoxal (4.5 mmol, 1 equiv.). Analytical data agrees with the literature reported values. [1] **Yield**: 381 mg, 1.2 mmol, 26%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 8.16 (s, 2H, H-C=N), 7.16 – 7.12 (m, 6H, aryl), 2.56 (q, 8H, $^3J_{HH}$ = 7.5 Hz, CH_2), 1.21 (t, 12H, $^3J_{HH}$ = 7.5 Hz, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 163.1 (s), 149.2 (s), 132.3 (s), 126.5 (s), 124.9 (s), 24.6 (s), 14.6 (s).

*Synthesis of (E,E)-N^1,N^2-dimesitylethane-1,2-diimine (**1b**).*



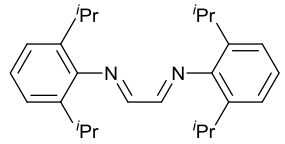
Compound **1b** was synthesised according to general synthesis 1 using 2,4,6-trimethylaniline (1.6 ml, 11 mmol, 2 equiv.) and glyoxal (5.5 mmol, 1 equiv.). Analytical data agrees with the literature reported values.[1] **Yield**: 501 mg, 1.7 mmol, 31%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 8.11 (s, 2H, H-C=N), 6.92 (s, 4H, aryl), 2.31 (s, 6H, *p*-Me), 2.17 (s, 12H, *o*-Me). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) 163.5 (s), 147.4 (s), 134.3 (s), 129.0 (s), 126.6 (s), 20.8 (s), 18.2 (s).

*Synthesis of (E,E)-N^1,N^2-bis(4-(tert-butyl)phenyl)ethane-1,2-diimine (**1c**).*



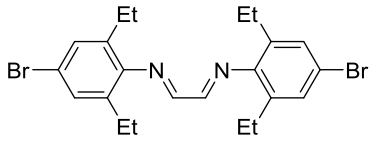
Compound **1c** was synthesised according to general synthesis 1 using 4-tert-butylaniline (1.5 ml, 9.4 mmol, 2 equiv.) and glyoxal (4.7 mmol, 1 equiv.). Analytical data agrees with the literature reported values.[1] **Yield**: 812 mg, 2.5 mmol, 53%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) 8.47 (s, 2H, H-C=N), 7.49 (d, 4H, $^3J_{HH}$ = 8.7 Hz, aryl), 7.31 (d, 4H, $^3J_{HH}$ = 8.7 Hz, aryl), 1.38 (s, 18H, ^{t}Bu). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 159.3 (s), 151.4 (s), 147.7 (s), 126.3 (s), 121.2 (s), 34.7 (s), 31.3 (s).

*Synthesis of (E,E)-N^1,N^2-bis(2,6-diisopropylphenyl)ethane-1,2-diimine (**1d**).*



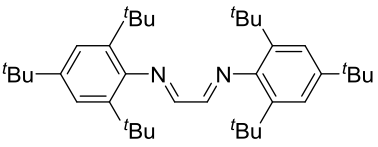
Compound **1d** was synthesised according to general synthesis 1 using 2,6-diisopropylaniline (0.94 ml, 7.4 mmol, 2 equiv.) and glyoxal (3.7 mmol, 1 equiv.). Analytical data agrees with the literature reported values.[1] **Yield**: 679 mg, 1.8 mmol, 49%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 8.10 (s, 2H, H-C=N), 7.16-7.04 (m, 6H, aryl), 2.87 (sep, 4H, $^3J_{HH}$ = 6.8 Hz, ^{i}Pr H), 1.14 (d, 24H, $^3J_{HH}$ = 6.8 Hz, ^{i}Pr Me). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 163.1 (s), 148.0 (s), 136.7 (s), 125.1 (s), 123.2 (s), 28.0 (s), 23.4 (s).

*Synthesis of (E,E)-N^1,N^2-bis(4-bromo-2,6-diethylphenyl)ethane-1,2-diimine (**1e**).*



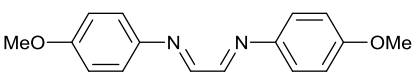
Compound **1e** was synthesised according to general synthesis 1 using 2,6-diethyl-4-bromoaniline (1.18 ml, 7.4 mmol, 2 equiv.) and glyoxal (3.7 mmol, 1 equiv.). **Yield**: 754 mg, 1.6 mmol, 43%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 8.00 (s, 2H, H-C=N), 7.16 (s, 4H, aryl), 2.40 (q, 8H, $^3J_{HH}$ = 7.6 Hz, CH_2), 1.08 (t, 12H, $^3J_{HH}$ = 7.5 Hz, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 163.1 (s), 148.0 (s), 136.7 (s), 125.1 (s), 123.2 (s), 28.0 (s), 23.4 (s). **MP**: 104-106 °C. **IR** ν_{max} (cm^{-1}): 2963, 2936, 2876, 1618, 1609, 1572, 1454, 1441, 1408, 1371, 1327, 1304, 1271, 1233, 1173, 1022, 964, 872, 860, 841, 800, 779, 756, 702, 615, 586, 552. **HRMS (ES$^+$)** $[M+H]^+$ $[C_{22}H_{27}N_2Br_2]^+$: calculated: 477.0541 found: 477.0527. **EA** (%) for $C_{22}H_{26}N_2Br_2$: Calculated C 55.25, H 5.48, N 5.86, Found C 55.14, H 5.36, N 5.95.

*Synthesis of (E,E)-N^1,N^2-bis(2,4,6-tri-tert-butylphenyl)ethane-1,2-diimine (**1f**).*



Compound **1f** was synthesised according to general synthesis 1, but was heated to reflux for 72 hours using 2,4,6-tri-tert-butylaniline (0.48 mg, 1.85 mmol, 2 equiv.) and glyoxal (0.92 mmol, 1 equiv.). Analytical data agrees with the literature reported values.[1] **Yield**: 117 mg, 0.2 mmol, 23%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 8.16 (s, 2H, H-C=N), 7.38 (s, 4H, aryl), 1.36 (s, 36H, *o*^{t}Bu), 1.35 (s, 18H, *p*^{t}Bu). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 163.4 (s), 149.3 (s), 145.0 (s), 137.4 (s), 121.9 (s), 36.0 (s), 34.8 (s), 31.5 (s).

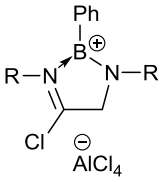
*Synthesis of (E,E)-N^1,N^2-bis(4-methoxyphenyl)ethane-1,2-diimine (**1g**).*



Compound **1c** was synthesised according to general synthesis 1 using 4-methoxyaniline (1.5 g, 12 mmol, 2 equiv.) and glyoxal (6 mmol, 1 equiv.). Analytical data agrees with the literature reported values.[1] **Yield**: 1.25 g, 4.7 mmol, 76%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 8.43 (s, 2H, H-C=N), 7.35 (d, $^3J_{HH}$ = 8.5 Hz, 4H, aryl), 6.97 (d, $^3J_{HH}$ = 8.5 Hz, 4H, aryl), 3.86 (s, 6H, OMe). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 159.8 (s), 157.6 (s), 142.9 (s), 123.1 (s), 114.6 (s), 55.6 (s).

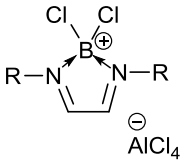
1.3 Synthesis of products

1.3.1 General synthesis 2: synthesis of borenium cations (**3**)



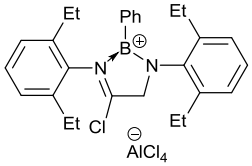
Diazabutadiene **1** (0.1 mmol, 1 equiv.) was dissolved in $CDCl_3$ (*ca.* 0.6 ml), to which $PhBCl_2$ (16 mg, 0.1 mmol, 1 equiv.) was added. Formation of the intermediate **2** was complete within 10 minutes, as monitored by *in situ* multinuclear NMR spectroscopy. Upon completion, $AlCl_3$ (13 mg, 0.1 mmol, 1 equiv.) was added to give a dark red/brown coloured solution. The solvent was reduced and layered with hexane and stored at -40 °C to yield either a solid precipitate or a crop of red/brown coloured crystals suitable for X-ray diffraction. The solvent was then removed and the crystals were subsequently washed with cold hexane (3 × 2 ml) then dried *in vacuo* to give the pure product **3**.

1.3.2 General synthesis 3: synthesis of boronium cations (**4**)



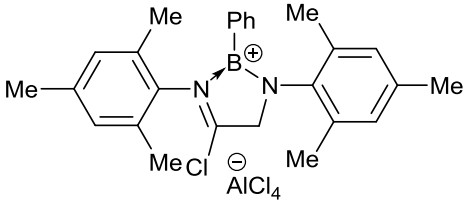
Diazabutadiene **1** (0.1 mmol, 1 equiv.) was dissolved in $CDCl_3$ (*ca.* 0.6 ml), to which BCl_3 (0.2 ml, 1M in DCM, 0.2 mmol, 2 equiv.) was added, instantly forming a dark red solution. Monitoring by *in situ* multinuclear NMR spectroscopy showed that the reaction was complete within 10 minutes. Upon completion, $AlCl_3$ (13 mg, 0.1 mmol, 1 equiv.) was added to give a deep red coloured solution. The solvent was reduced and layered with hexane and stored at -40 °C to yield a crop of red coloured crystals suitable for X-ray diffraction. The remaining solvent was removed and the crystals were subsequently washed with cold hexane (3 × 2 ml) then dried *in vacuo* to give the pure product.

*Synthesis of 4-chloro-1,3-bis(2,6-diethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3a**).*



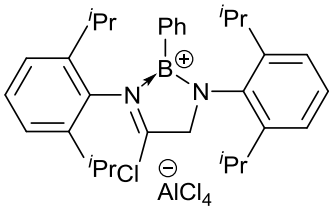
Compound **3a** was synthesised using general synthesis 2 using diazabutadiene **1a** (32 mg, 0.1 mmol). Yield: 56 mg, 0.09 mmol, 91%. After multiple EA attempts satisfactory results could not be obtained. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 7.67 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, *p*-aryl), 7.45 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H), 7.40 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H), 7.32 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H), 7.10 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H), 6.83 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H), 5.60 (s, 2H, N-CH_2), 2.74-2.36 (m, 8H, CH_2), 1.23-1.17 (m, 12H, CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K): 34.4 (s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 140.1 (s), 137.2 (s), 134.4 (s), 133.7 (s), 133.6 (s), 133.2 (s), 132.2 (s), 129.9 (s), 128.8 (s), 128.1 (s), 127.5 (s), 65.8 (s), 24.6 (s), 24.2 (s), 14.3 (s), 13.7 (s). **^{27}Al NMR** (104 MHz, $CDCl_3$, 298 K): 103.92 (s).

*Synthesis of 4-chloro-1,3-bis(2,4,6-trimethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3b**).*



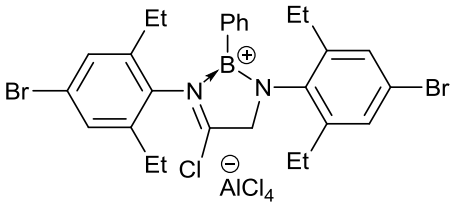
Compound **3b** was synthesised using general synthesis 2 using diazabutadiene **1b** (30 mg, 0.1 mmol). Yield: 55 mg, 0.1 mmol, 95%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 7.44 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, *p*-aryl), 7.18-7.15 (m, 6H), 6.91 (d, $^{3}J_{HH}$ = 7.1 Hz, 2H, *o*-aryl), 5.54 (s, 2H, N-CH_2), 2.46 (s, 3H, *p*-Me), 2.36 (s, 3H, *p*-Me), 2.25 (s, 6H, *o*-Me), 2.20 (s, 6H, *o*-Me). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K): 33.9 (br s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 191.0 (s), 142.3 (s). 139.3 (s), 134.1 (s), 133.5 (s), 133.1 (s), 132.8 (s), 131.6 (s), 131.4 (s), 130.9 (s), 130.5 (s), 128,9 (s), 64.8 (s), 21.3 (s), 21.1 (s), 18.2 (s), 18.0 (s). **^{27}Al NMR** (104 MHz, $CDCl_3$, 298 K): 103.96 (s).

*Synthesis of 4-chloro-1,3-bis(2,6-diisopropylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3d**).*



Compound **3d** was synthesised using general synthesis 2 using diazabutadiene **1d** (33 mg, 0.1 mmol). Yield: 62 mg, 0.09 mmol, 92%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 7.73 (t, $^{3}J_{HH}$ = 7.9 Hz, 1H, *p*-aryl), 7.53-7.48 (m, 3H), 7.38 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, *p*-aryl), 7.33 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, aryl), 7.08 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H, *m*-aryl), 6.78 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H, *o*-aryl), 5.64 (s, 2H, N-CH_2), 2.94 (sep, $^{3}J_{HH}$ = 6.7 Hz, 2H, ^{i}Pr H), 2.61 (sep, $^{3}J_{HH}$ = 6.7 Hz, 2H, ^{i}Pr H), 1.36 (2d (overlapped), $^{3}J_{HH}$ = 6.5 Hz, 12H, ^{i}Pr Me), 0.98 (d, $^{3}J_{HH}$ = 6.7 Hz, 12H, ^{i}Pr Me). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K): 31.8 (s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 190.7 (s), 145.2 (s), 142.3 (s), 134.6 (s), 133.7 (s), 132.7 (s), 131.4 (s), 130.3 (s), 128.5 (s), 126.1 (s), 125.4 (s), 66.9 (s), 30.1 (s), 29.0 (s), 25.2 (s), 24.3 (s), 23.9 (s), 23.3 (s). **^{27}Al NMR** (104 MHz, $CDCl_3$, 298 K): 103.97 (s). **EA** (%) for $C_{32}H_{41}N_2AlBCl_5$: Calculated C 57.47, H 6.18, N 4.19, Found C 57.63, H 6.33, 4.27.

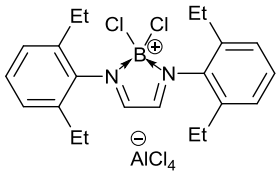
*Synthesis of 4-chloro-1,3-bis(2,6-diethyl-4-bromophenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3e**).*



Compound **3e** was synthesised using general synthesis 2 using diazabutadiene **1e** (48 mg, 0.1 mmol). Yield: 64 mg, 0.08 mmol, 83%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 7.61 (s, 2H, *m*-aryl), 7.48 (t, 1H, *p*-aryl), 7.45 (s, 2H, *m*-aryl), 7.20 (t, 2H, *m*-aryl), 6.86 (d, 2H, *o*-aryl), 5.52 (s, 2H, N-CH_2), 2.68-2.32 (m, 8H, CH_2), 1.22-1.17 (m, 12H, CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K): 33.4 (s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 191.6 (s), 142.1 (s), 139.2 (s), 133.5 (s), 131.4 (s), 130.7 (s), 129.2 (s), 126.9 (s), 124.3 (s), 65.6 (s), 24.5 (s), 24.1 (s), 14.0 (s), 13.4 (s). **^{27}Al NMR** (104 MHz, $CDCl_3$, 298 K): 103.82

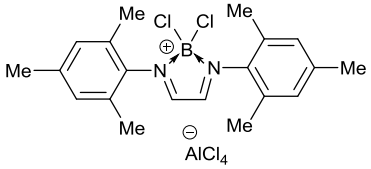
(s). **EA** (%) for $C_{28}H_{31}N_2AlBCl_5Br_2$: Calculated C 43.65, H 4.06, N 3.64, Found C 43.57, H 4.14, N 3.72.

*Synthesis of 2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium (**4a**).*



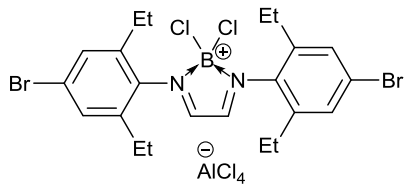
Compound **4a** was synthesised using general synthesis 3 using diazabutadiene **1a** (32 mg, 0.1 mmol). Yield: 56 mg, 0.1 mmol, 98%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 9.53 (s, 2H, N=C–H), 7.52 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *p*-aryl), 7.38 (d, 4H, $^3J_{HH}$ = 7.7 Hz, *m*-aryl), 2.79-2.62 (m, 8H, CH_2), 1.31 (t, 12H, $^3J_{HH}$ = 7.6 Hz, CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K): 10.6 (s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 165.0 (s), 138.2 (s), 133.7 (s), 131.2 (s), 127.4 (s), 24.9 (s), 15.2 (s). **^{27}Al NMR** (104 MHz, $CDCl_3$, 298 K): 103.98 (s).

*Synthesis of 2,2-dichloro-1,3-dimesityl-2H-1,3l4,2l4-diazaborol-1-ium (**4b**).*



Compound **4b** was synthesised using General synthesis 3 using diazabutadiene **1b** (30 mg, 0.1 mmol). Yield: 53 mg, 0.1 mmol, 98%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 9.48 (s, 2H, N=C–H), 7.08 (s, 4H, Ar-H), 2.41 (s, 12H, *o*-Me), 2.37 (s, 6H, *p*-Me). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K): 10.6 (br. s). **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K): 165.2 (s), 141.2 (s), 133.2 (s), 132.2 (s), 130.9 (s), 20.8 (s), 19.4 (s). **^{27}Al NMR** (104 MHz, $CDCl_3$, 298 K): 103.81 (s).

*Synthesis of 2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium (**4e**).*

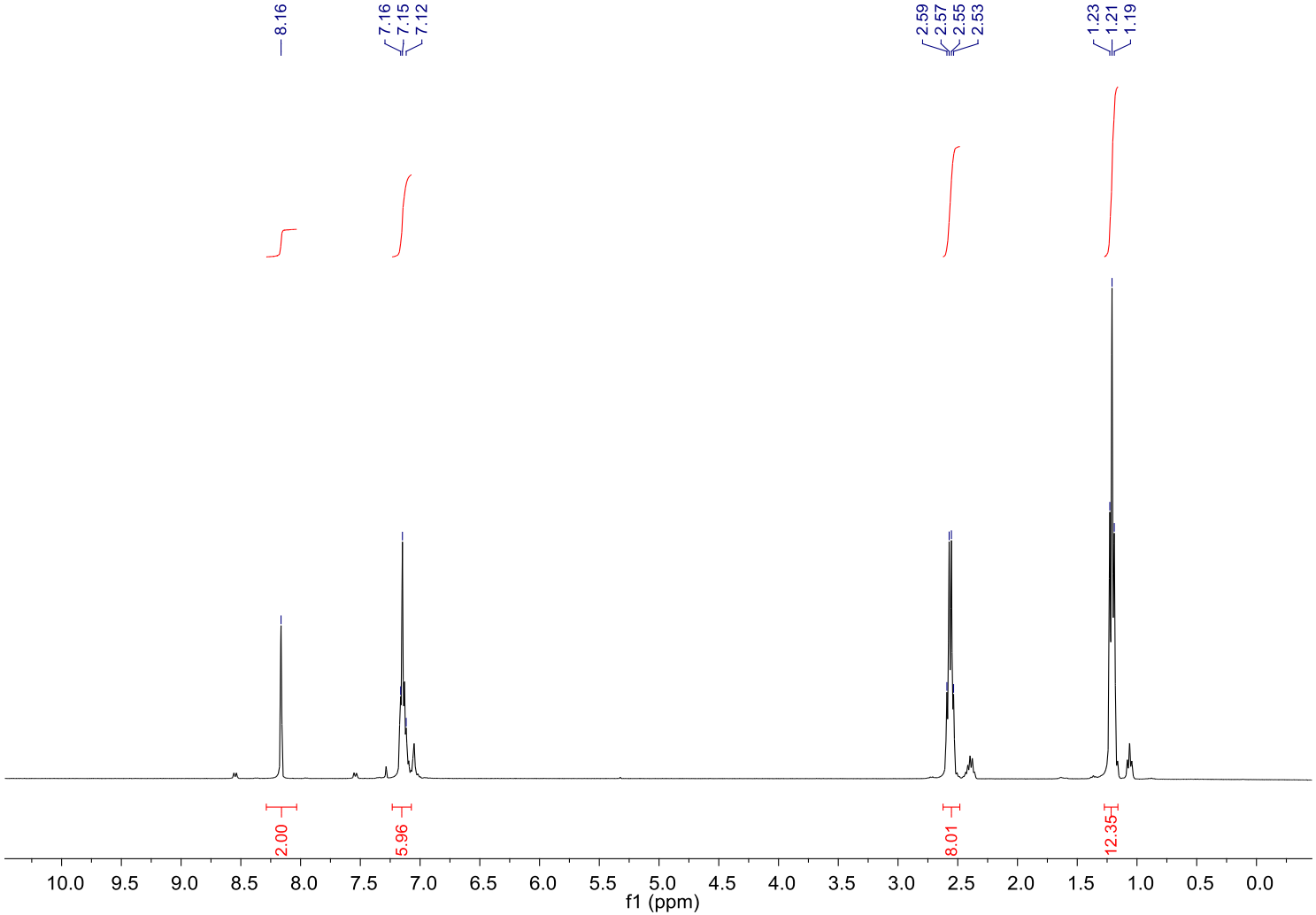


Compound **4d** was synthesised using general synthesis 3 using diazabutadiene **1e** (48 mg, 0.1 mmol). Yield: 46 mg, 0.06 mmol, 63%. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 9.43 (s, 2H), 7.51 (s, 4H), 2.75-2.55 (m, 8H, CH_2), 1.31 (t, 12H, $^3J_{HH}$ = 7.4 Hz, CH_3). **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K): 10.5. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): 165.0 (s), 140.6 (s), 132.4 (s), 130.8 (s), 126.2 (s), 25.1 (s), 15.4 (s). **^{27}Al NMR** (104 MHz, $CDCl_3$, 298 K): 103.81 (s).

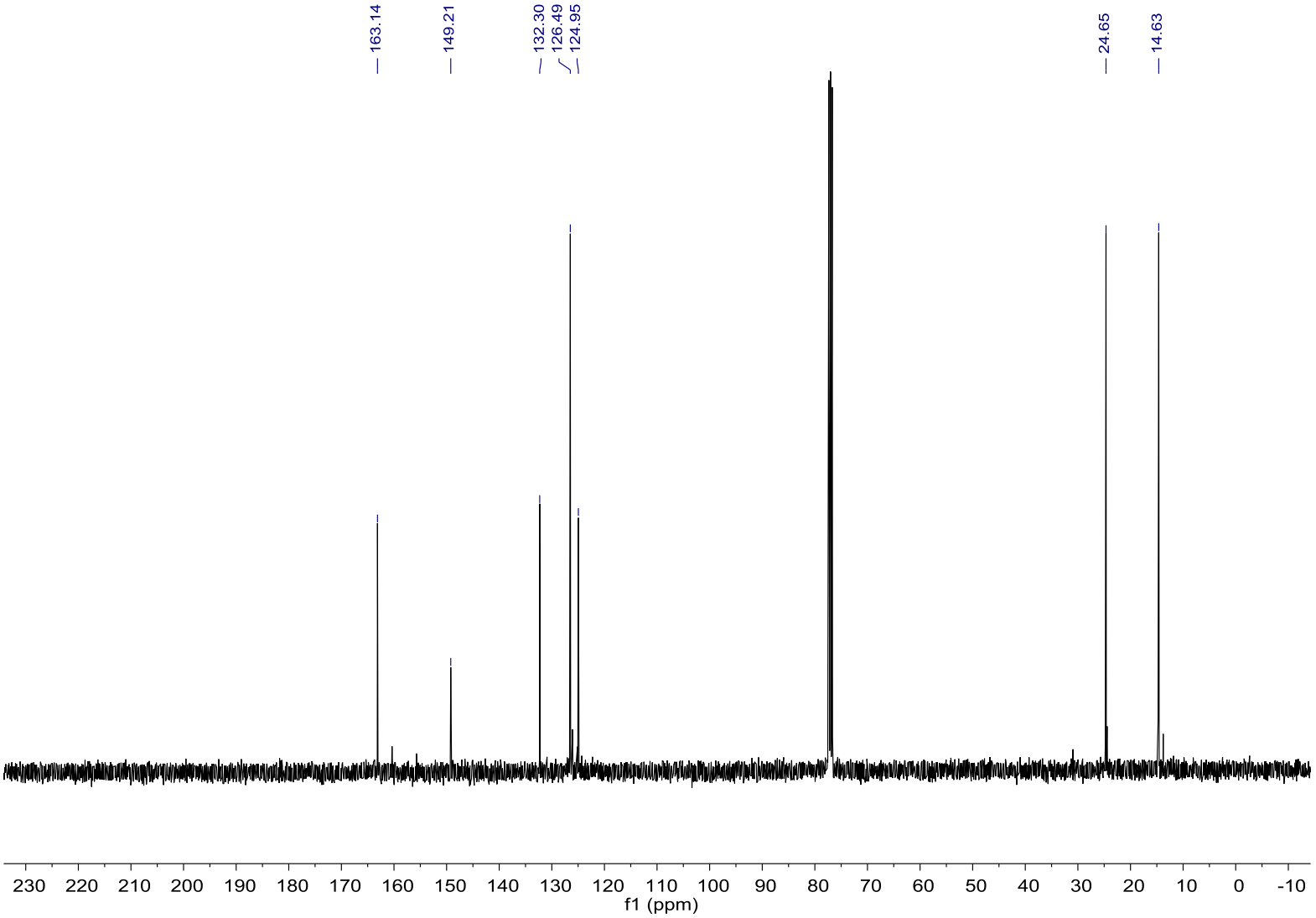
2. Experimental: NMR spectra

2.1 NMR spectra of starting materials.

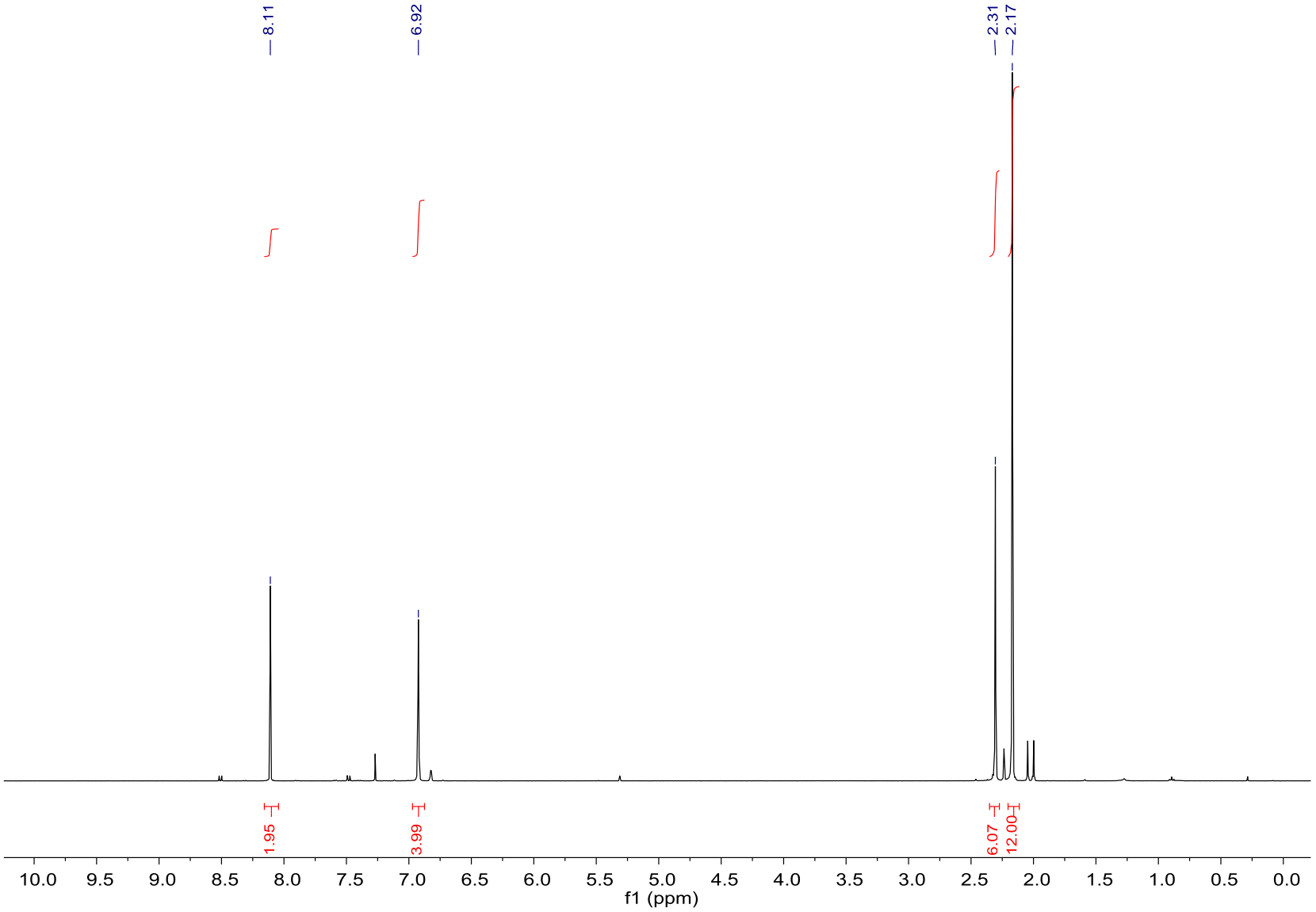
S1 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(2,6-diethylphenyl)ethane-1,2-diimine* (**1a**).



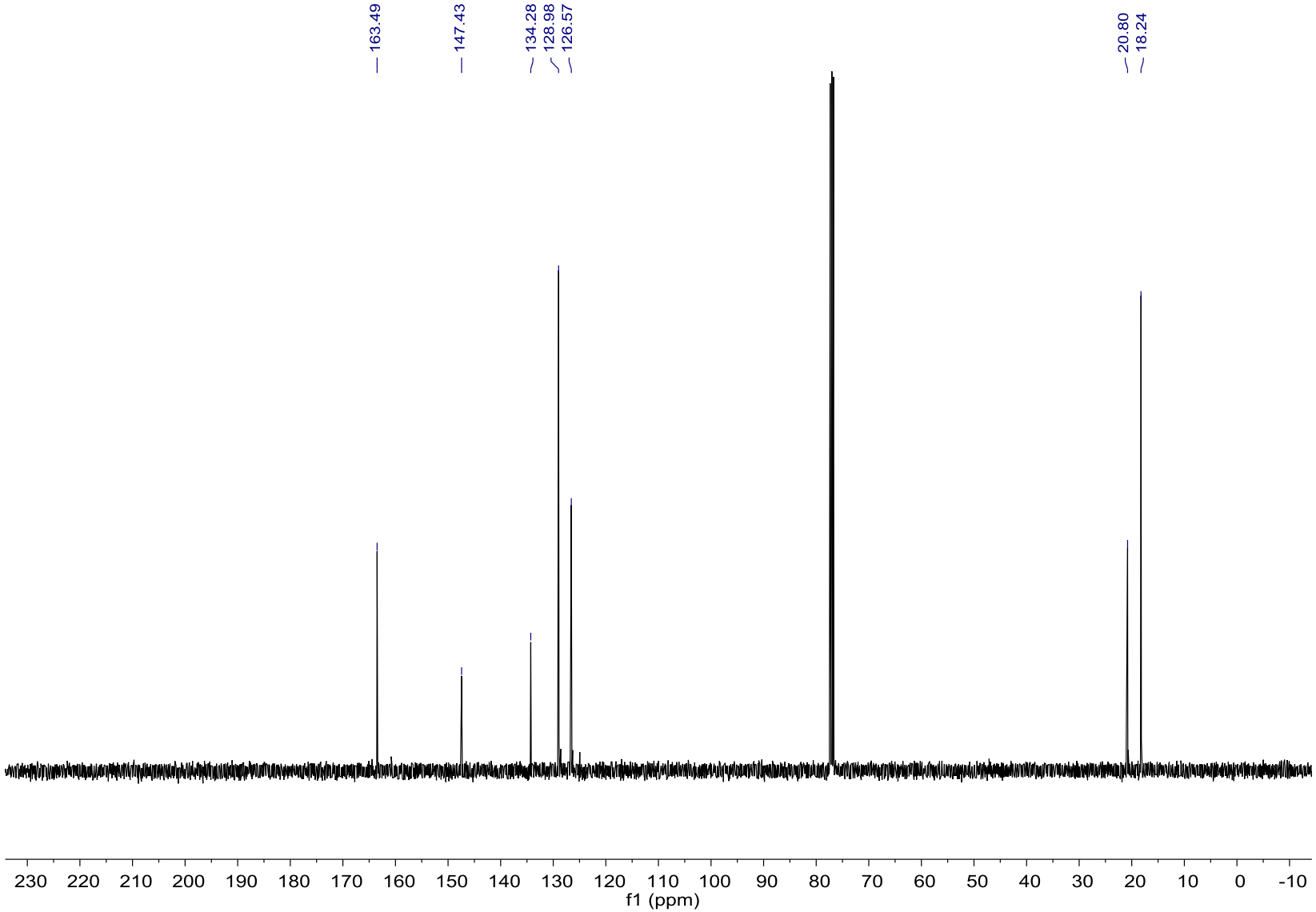
S2 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(2,6-diethylphenyl)ethane-1,2-diimine* (**1a**).



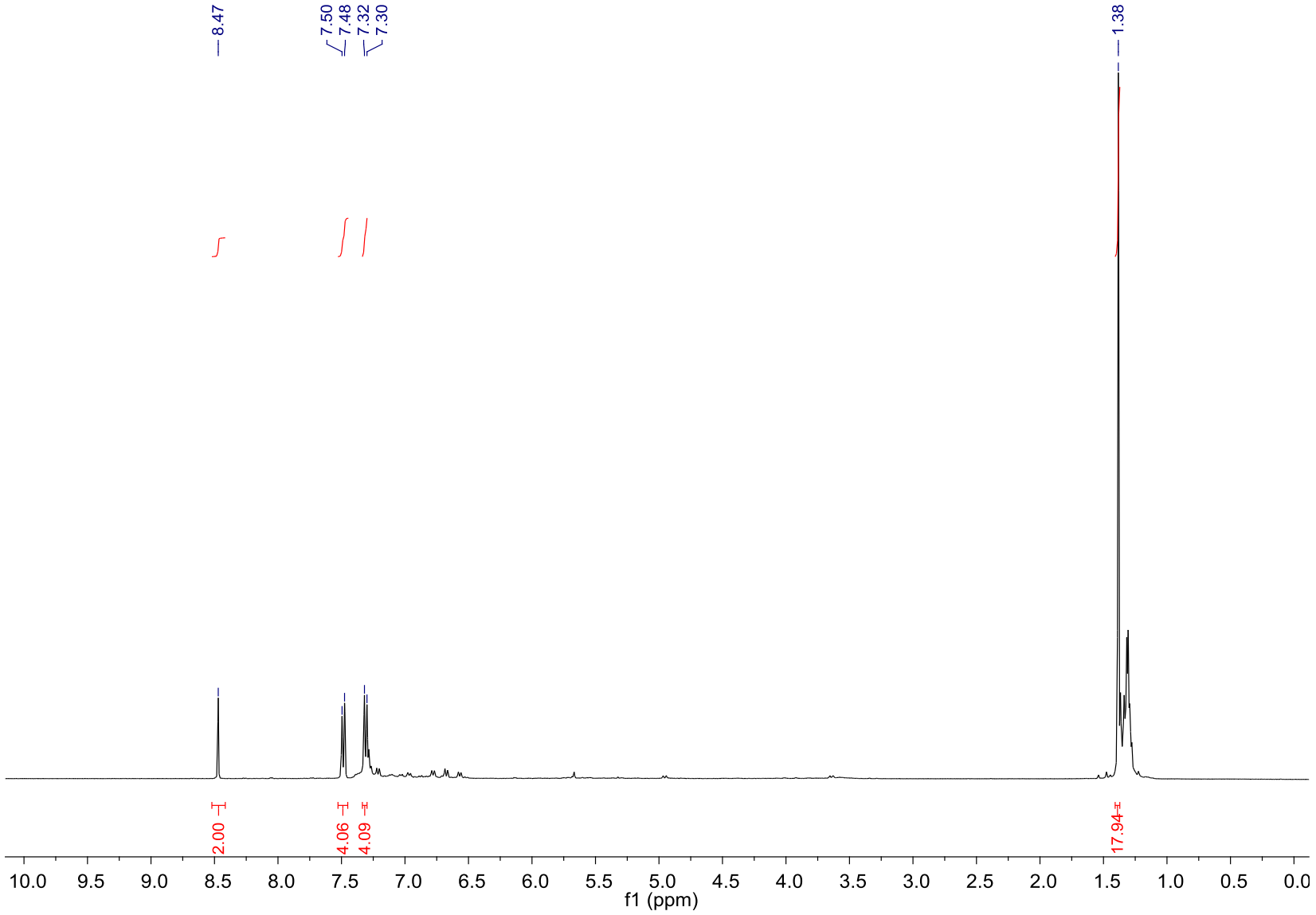
S3 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-dimesitylethane-1,2-diimine* (***1b***).



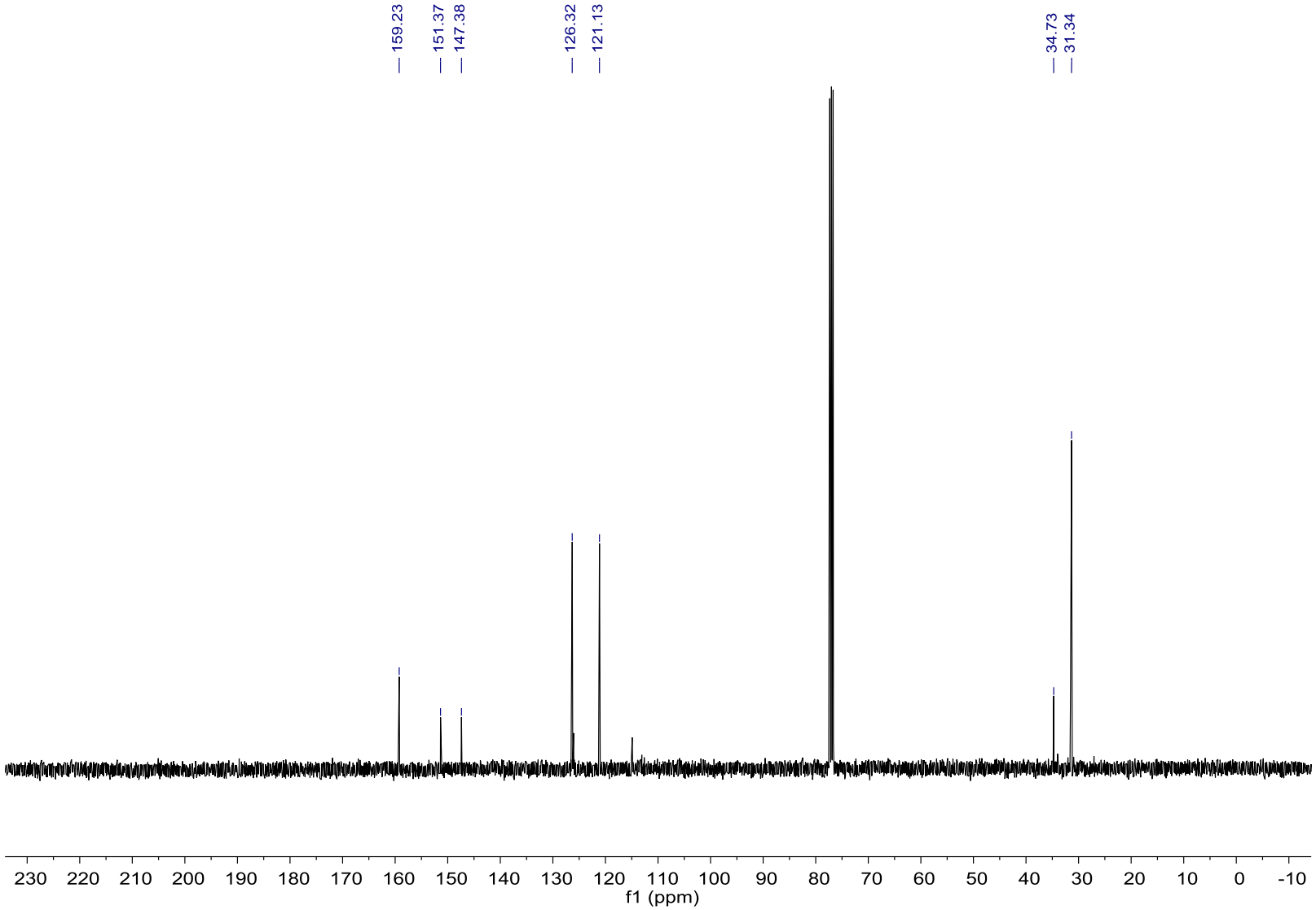
S4 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum *(E,E)-N^1,N^2-dimesitylethane-1,2-diimine (**1b**)*.



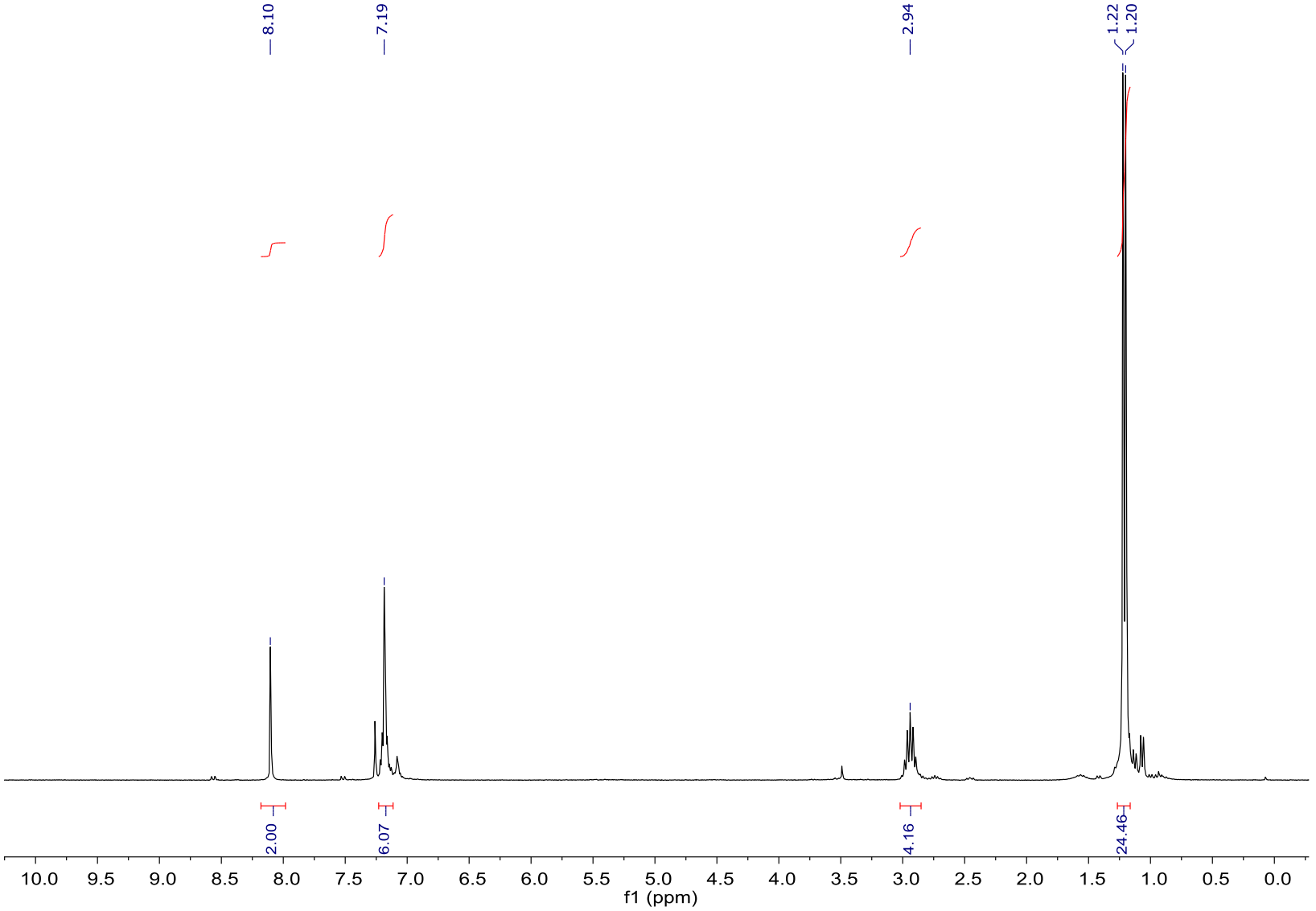
S5 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(4-(tert-butyl)phenyl)ethane-1,2-diimine (**1c**).*



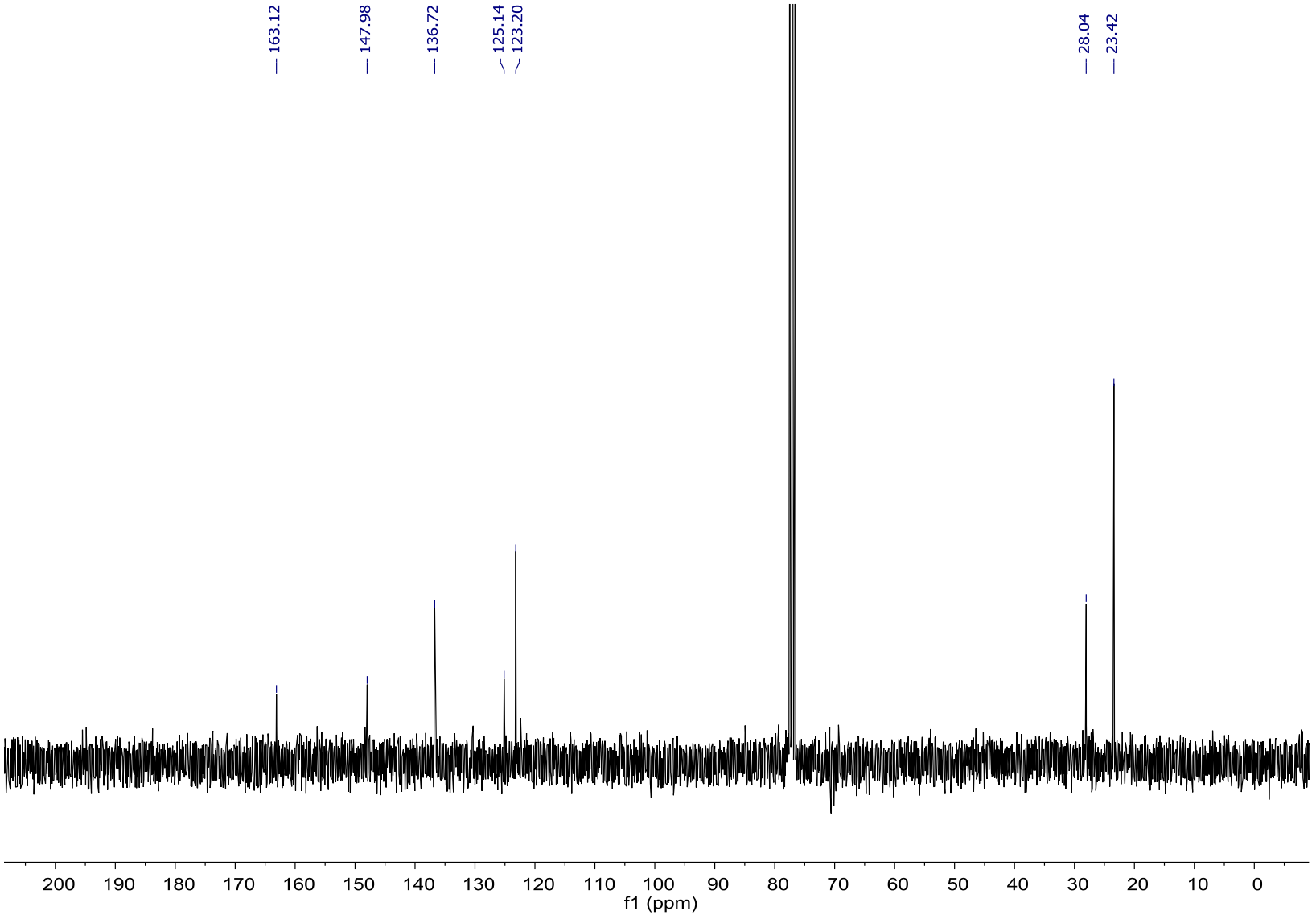
S6 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum *(E,E)-N^1,N^2-bis(4-(tert-butyl)phenyl)ethane-1,2-diimine (**1c**).*



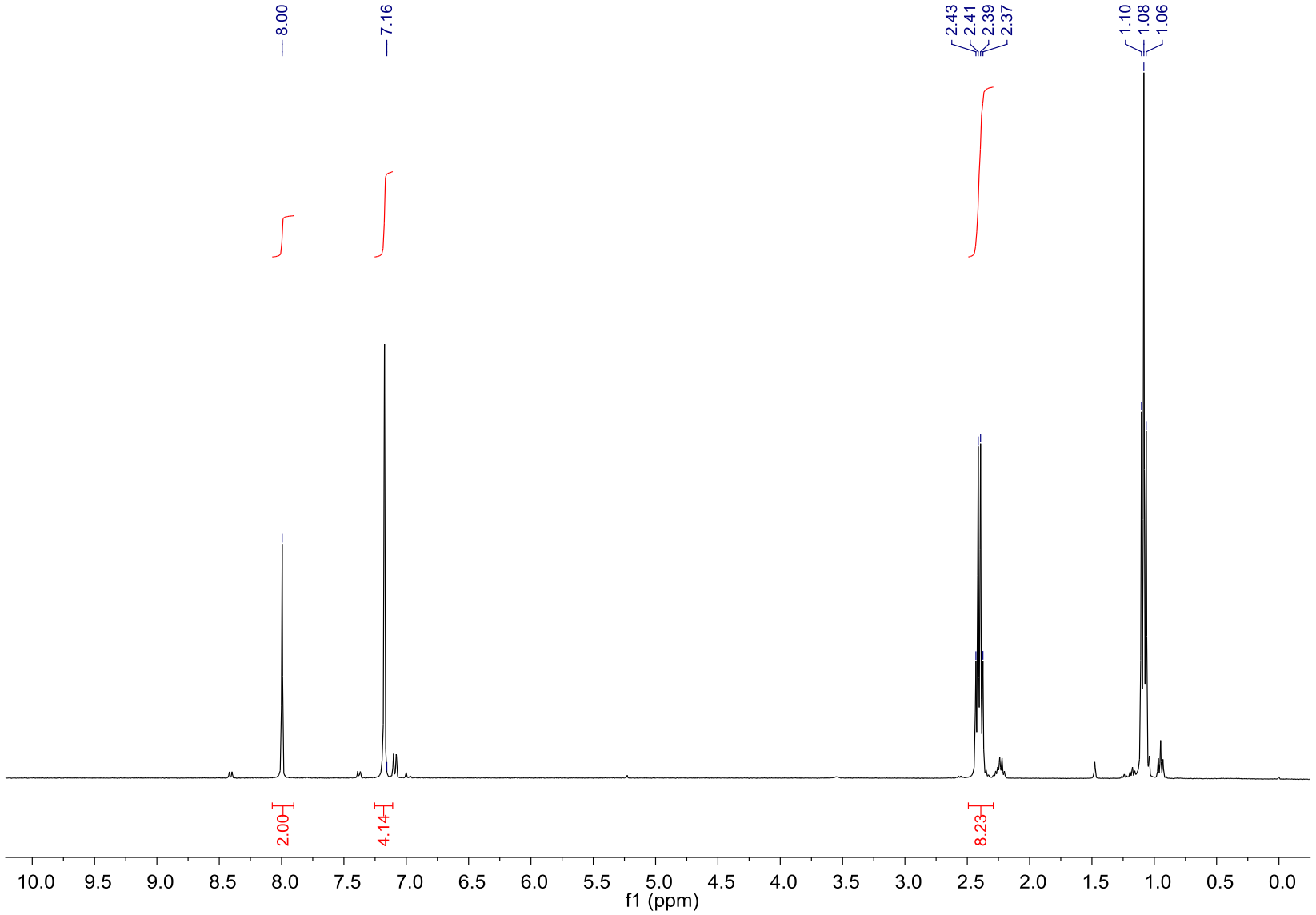
S7 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(2,6-diisopropylphenyl)ethane-1,2-diimine* (**1d**).



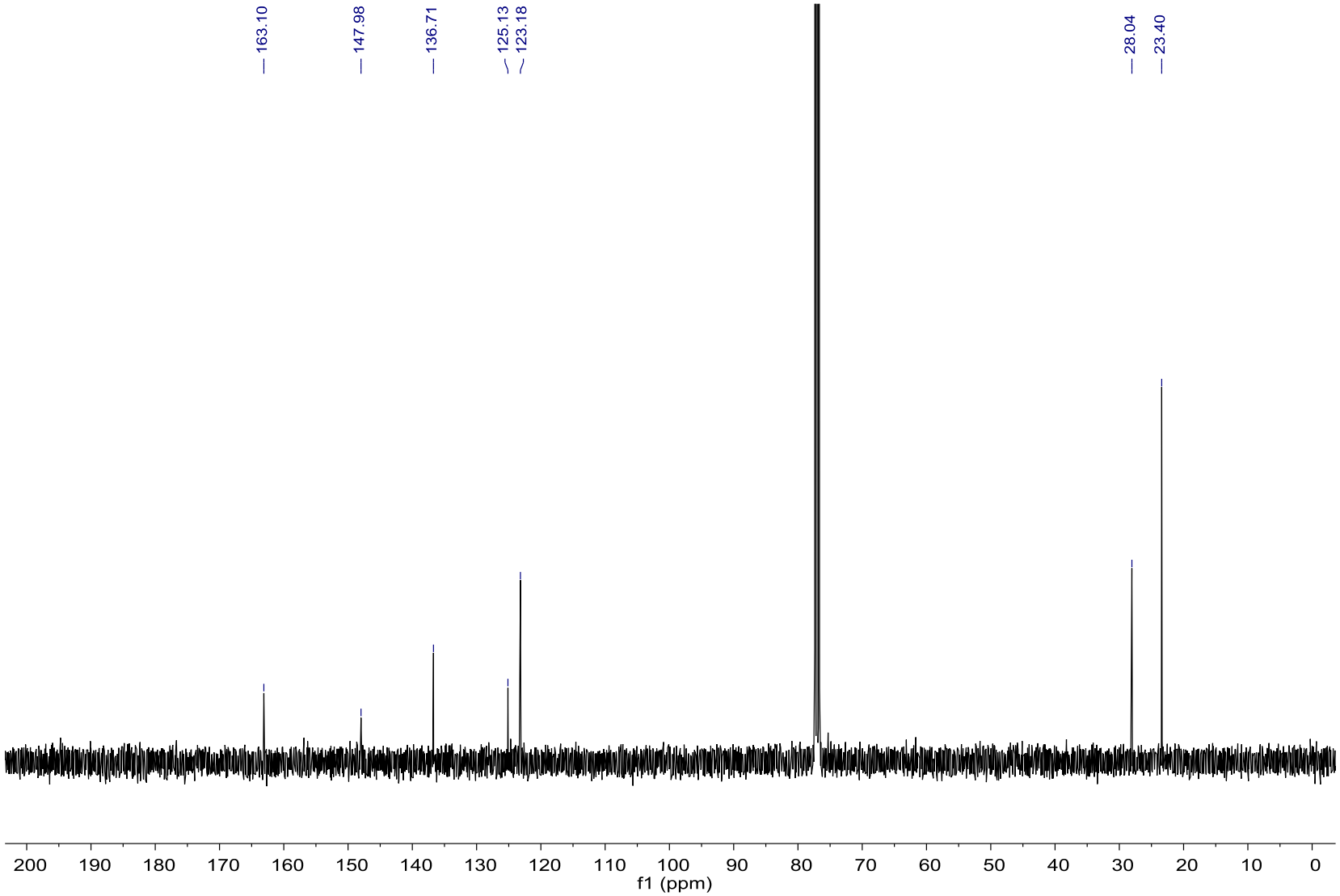
S8 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(2,6-diisopropylphenyl)ethane-1,2-diimine* (**1d**).



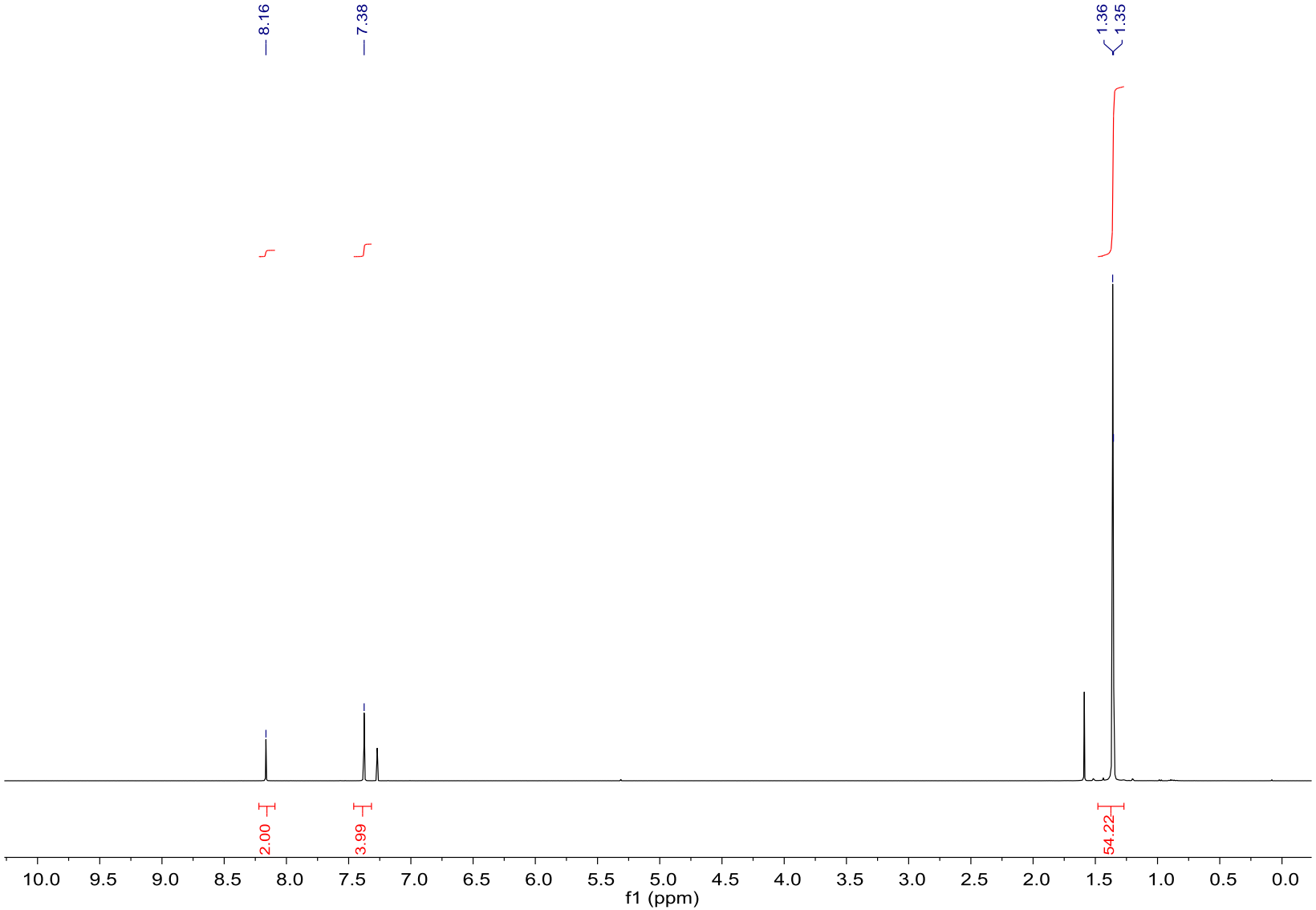
S9 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(4-bromo-2,6-diethylphenyl)ethane-1,2-diimine* (**1e**).



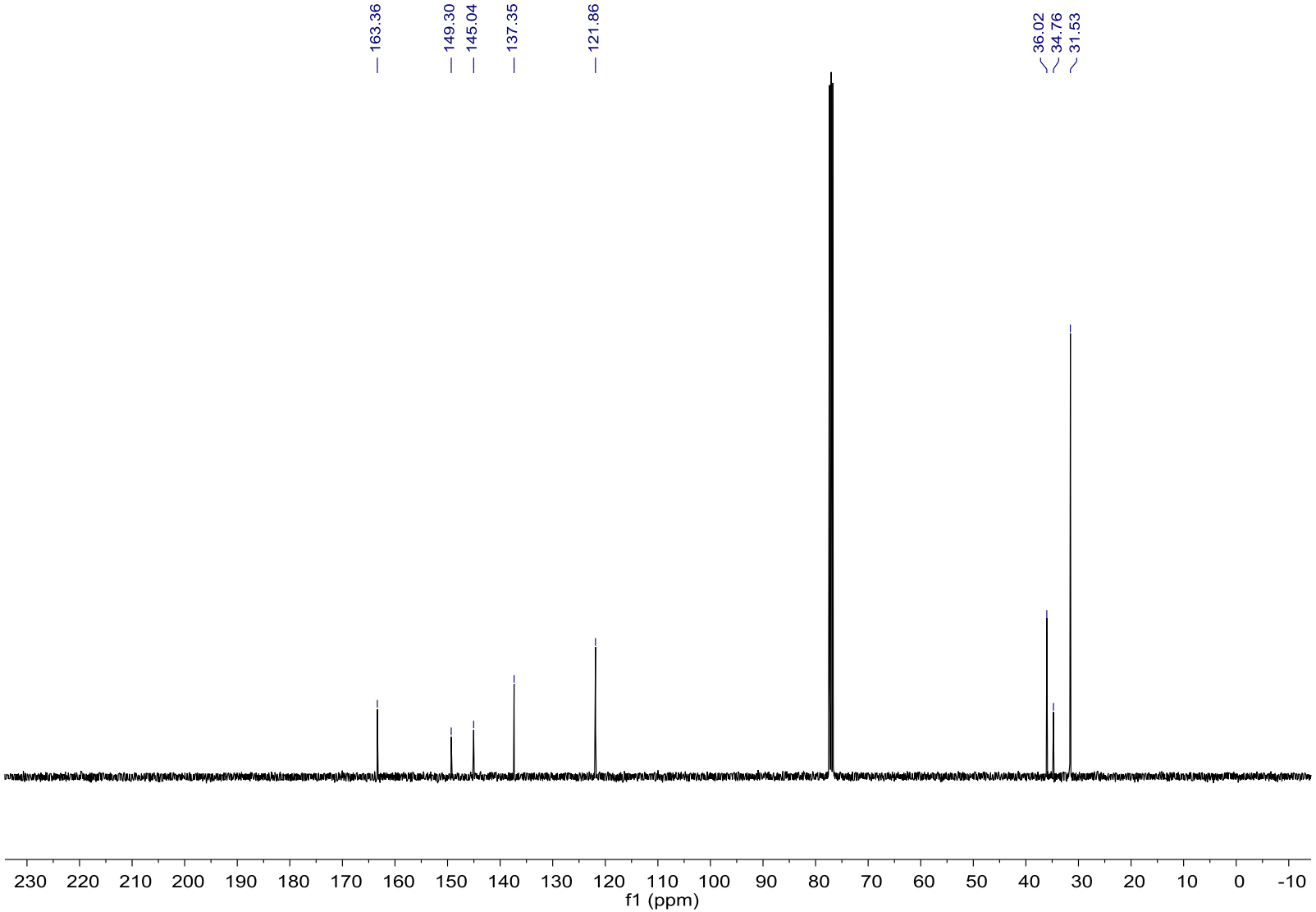
S10 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(4-bromo-2,6-diethylphenyl)ethane-1,2-diimine* (**1e**).



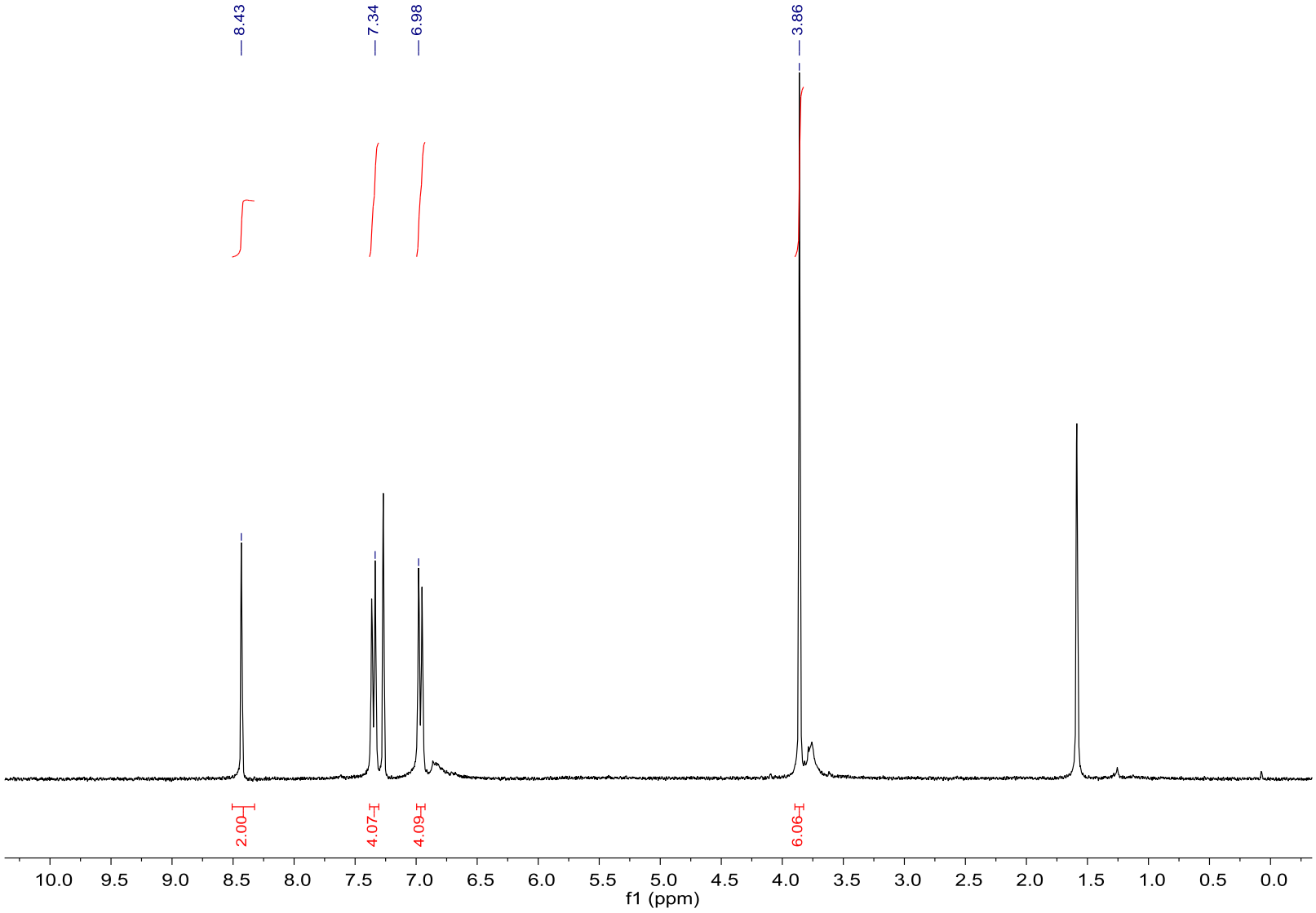
S11 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(2,4,6-tri-tert-butylphenyl)ethane-1,2-diimine (**1f**).*



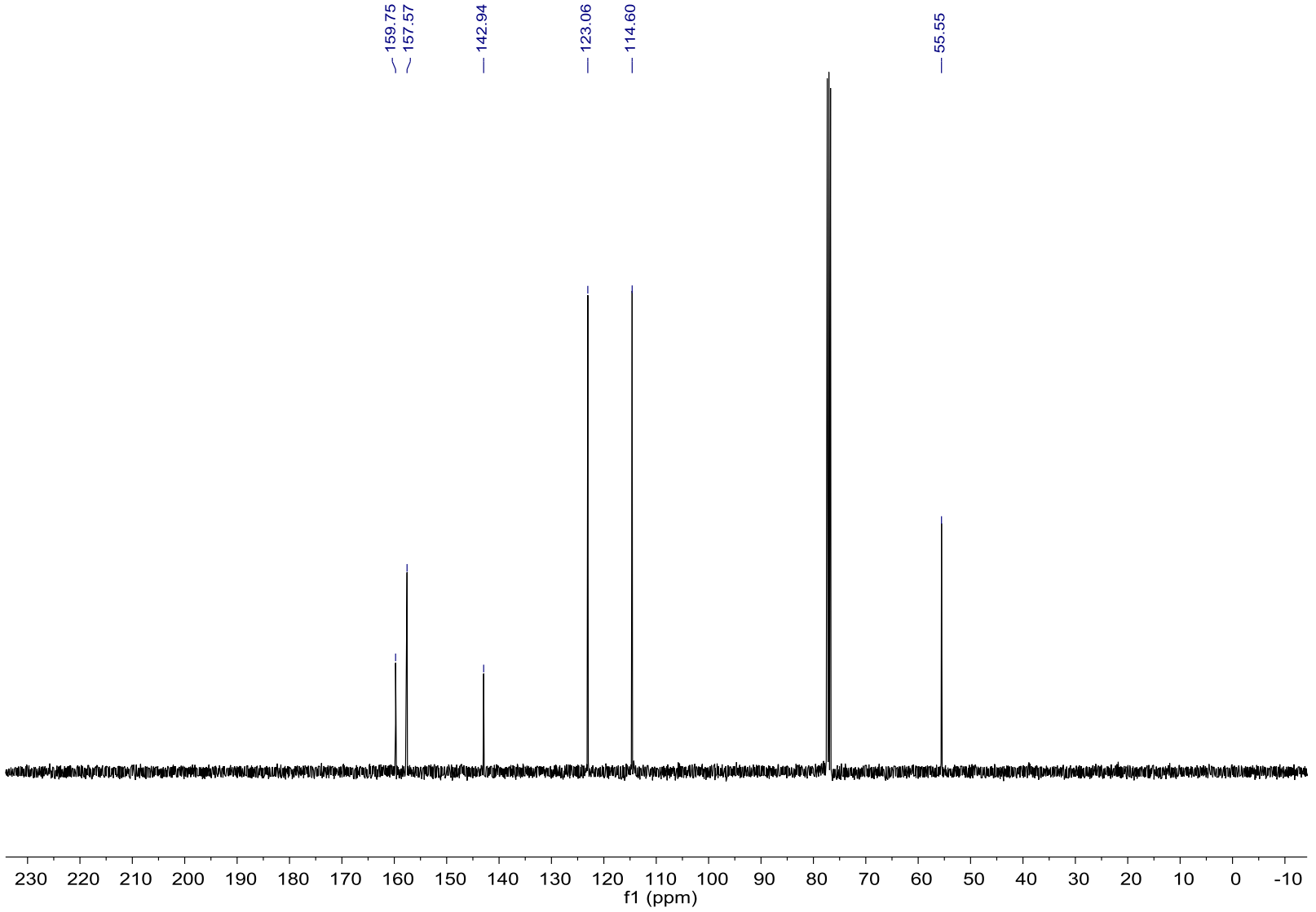
S12 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(2,4,6-tri-tert-butylphenyl)ethane-1,2-diimine* (***1f***).



S13 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(4-methoxyphenyl)ethane-1,2-diimine* (**1g**).

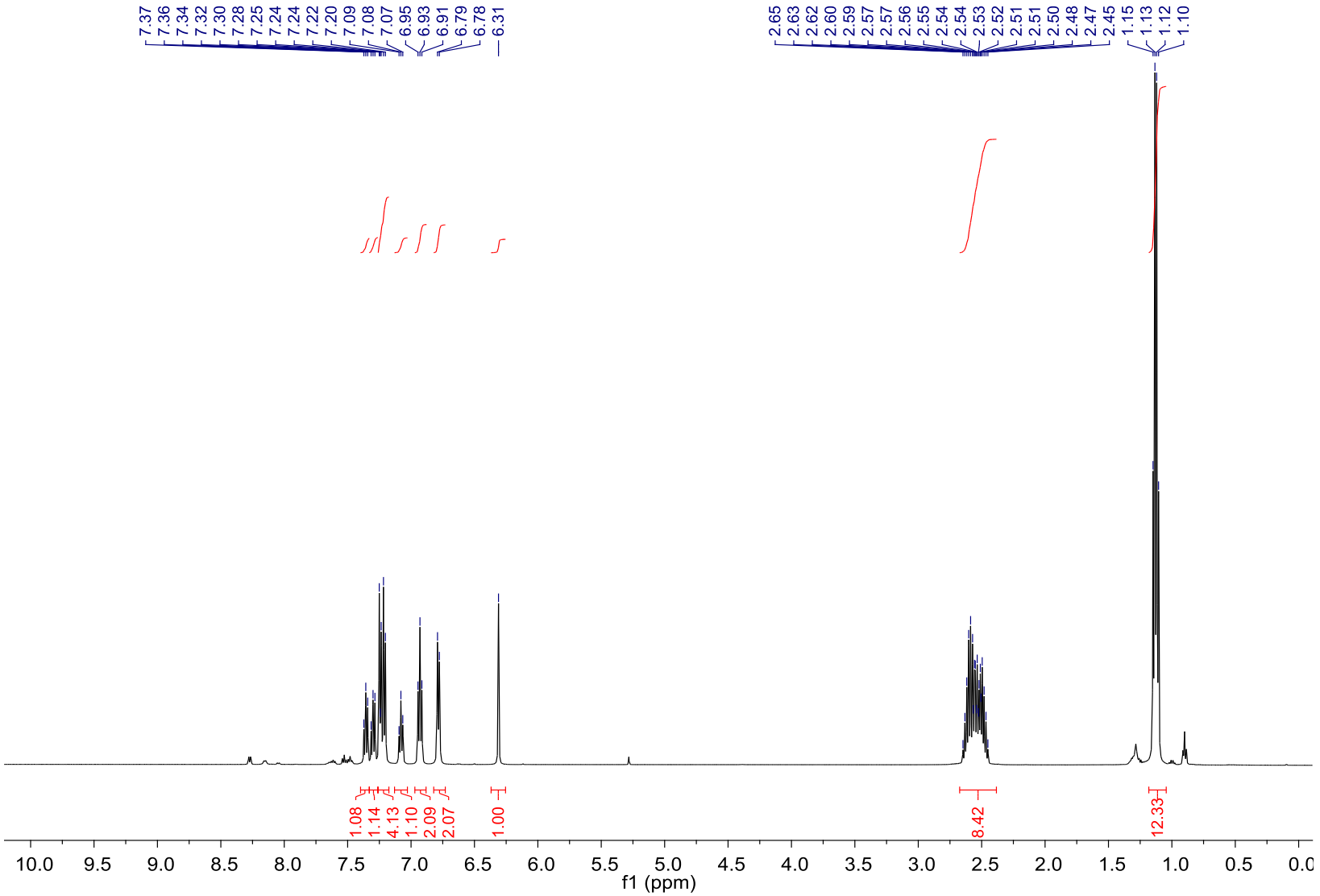


S14 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *(E,E)-N^1,N^2-bis(4-methoxyphenyl)ethane-1,2-diimine* (**1g**).

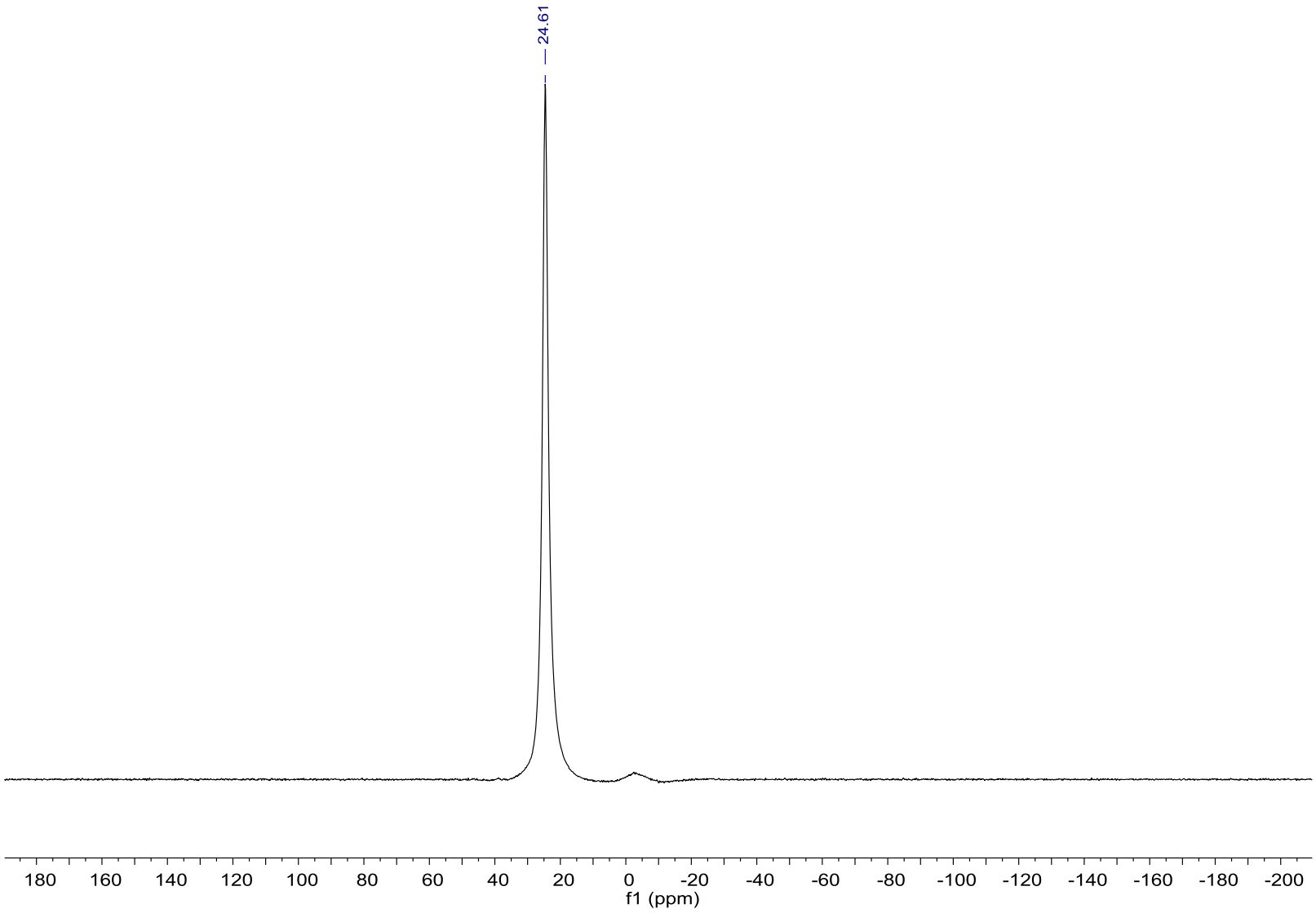


2.2 NMR spectra of products.

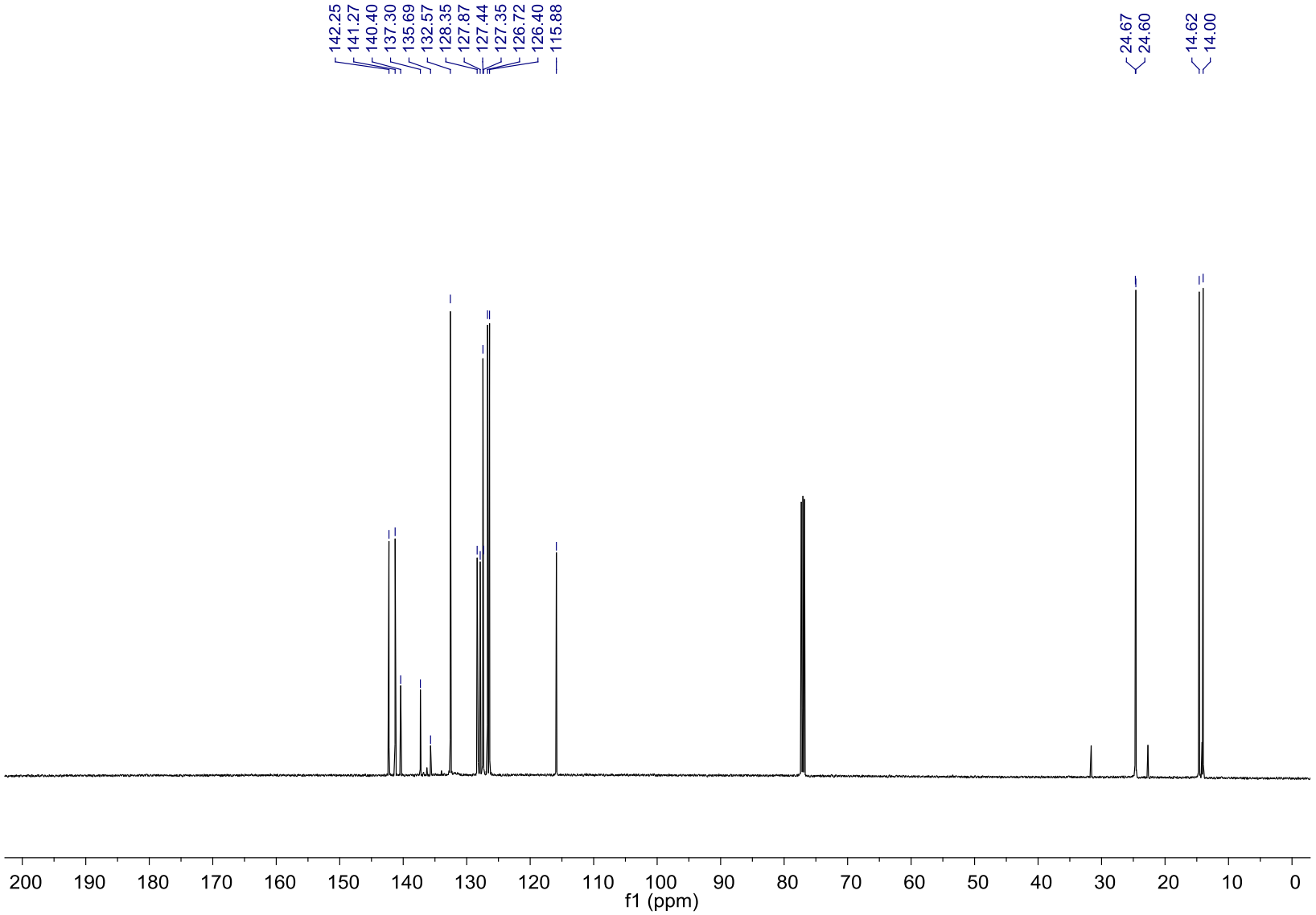
S15 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethylphenyl)-2-phenyl-2,3-dihydro-1H-1,3,2-diazaborole* ***(2a).***



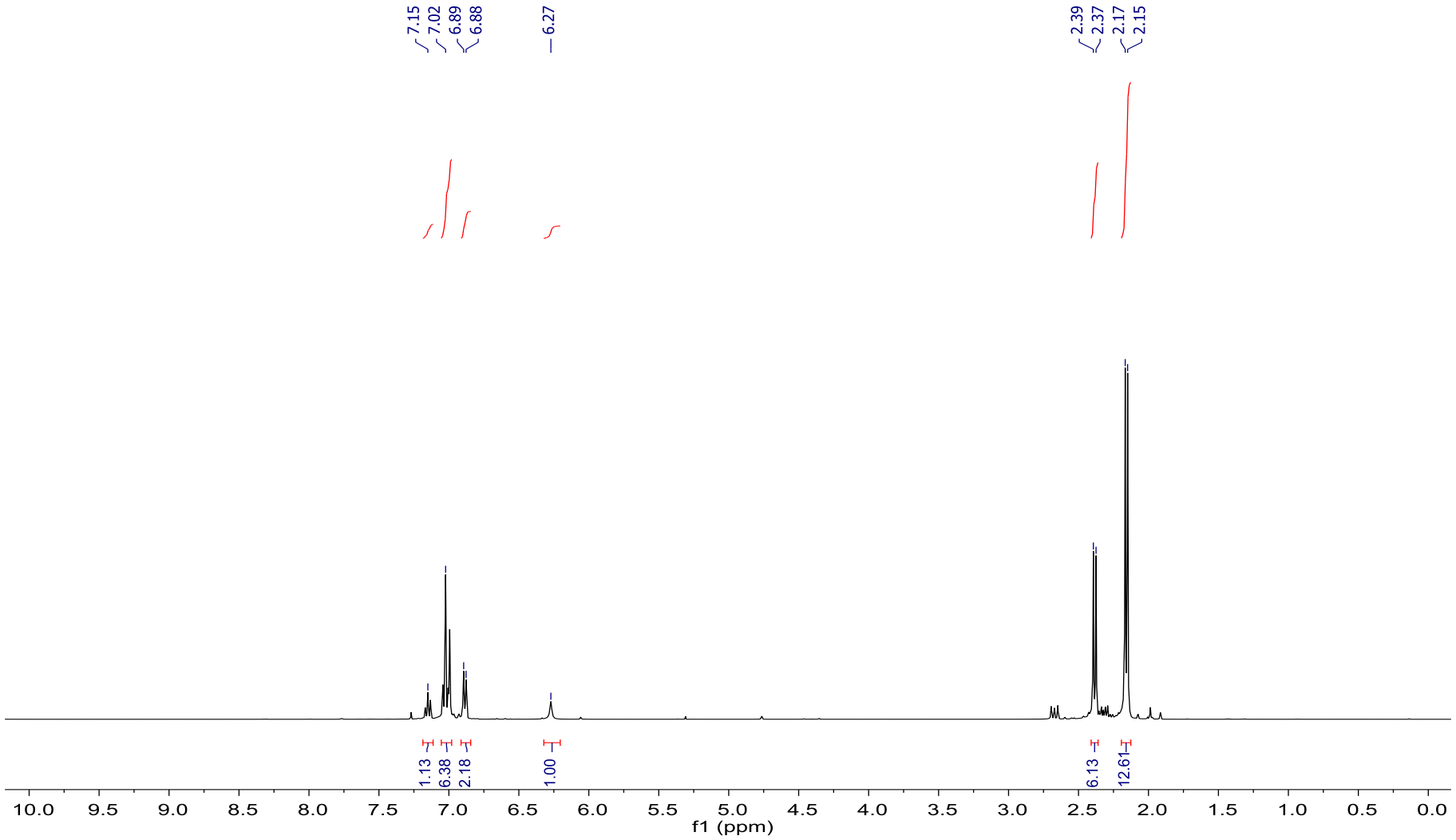
S16 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethylphenyl)-2-phenyl-2,3-dihydro-1H-1,3,2-diazaborole* ***(2a)***.



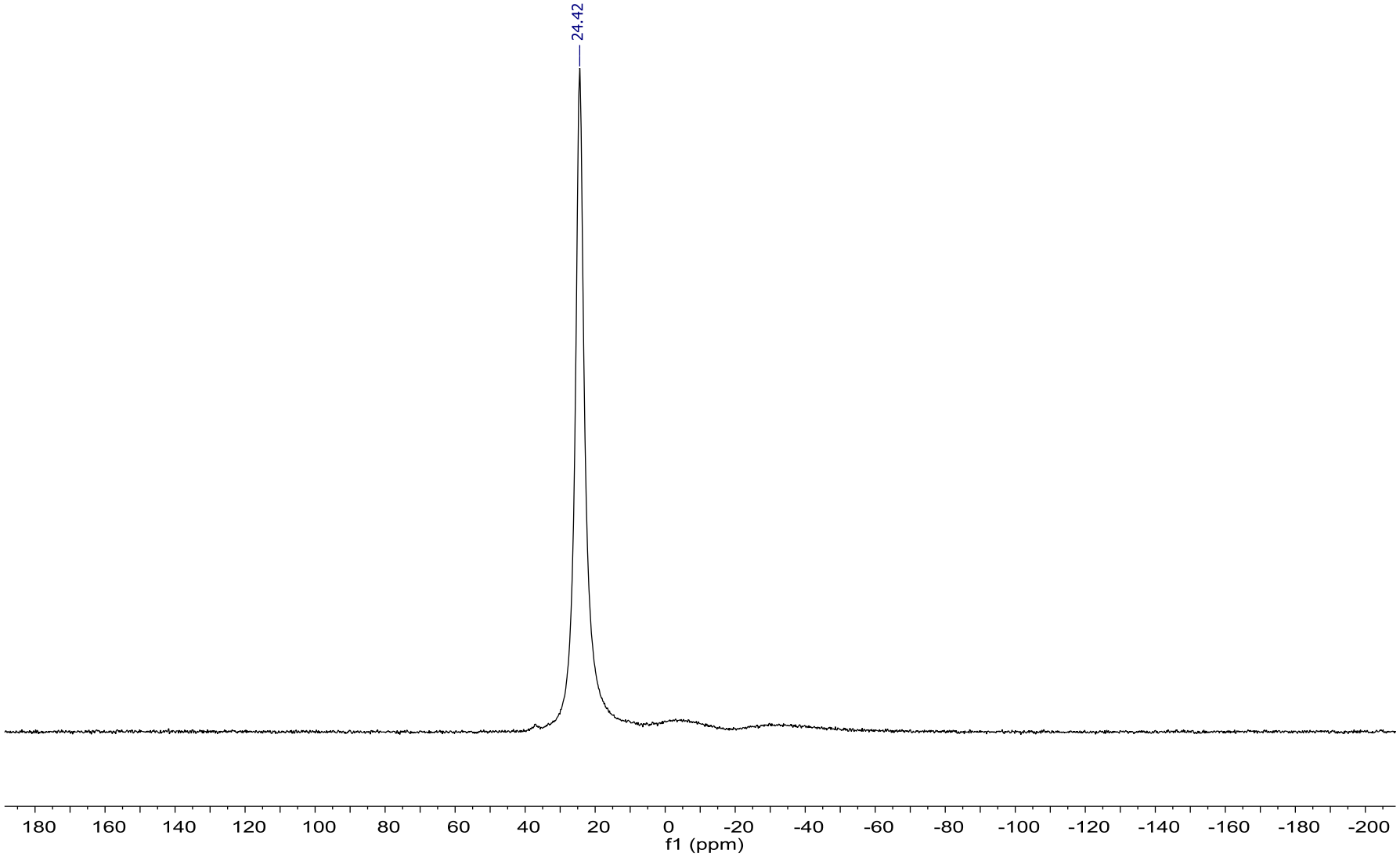
S17 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethylphenyl)-2-phenyl-2,3-dihydro-1H-1,3,2-diazaborole* ***(2a)***.



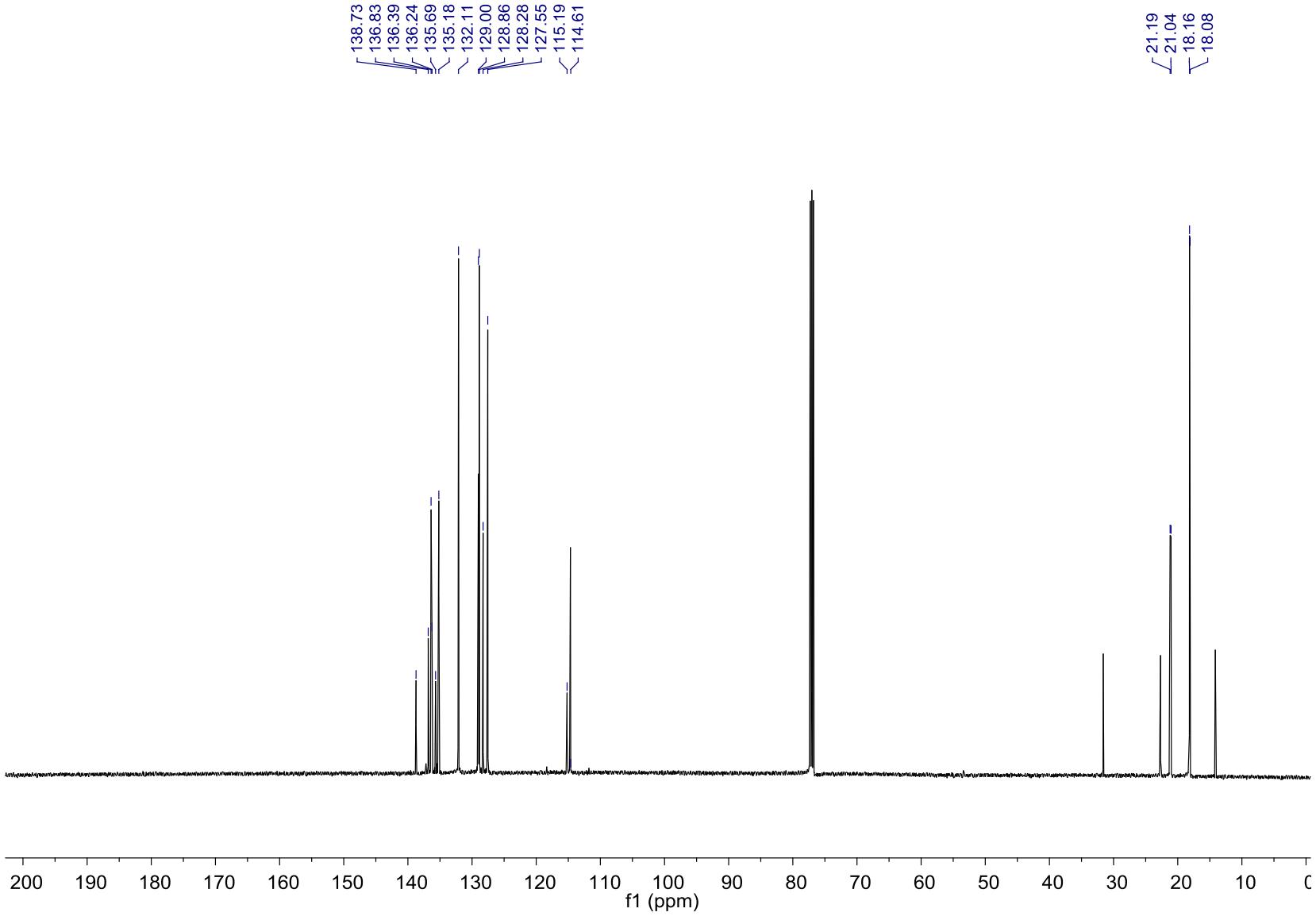
S18 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,4,6-trimethylphenyl)-2-phenyl-2,3-dihydro-1H-1,3,2-diazaborole (**2b**)*.



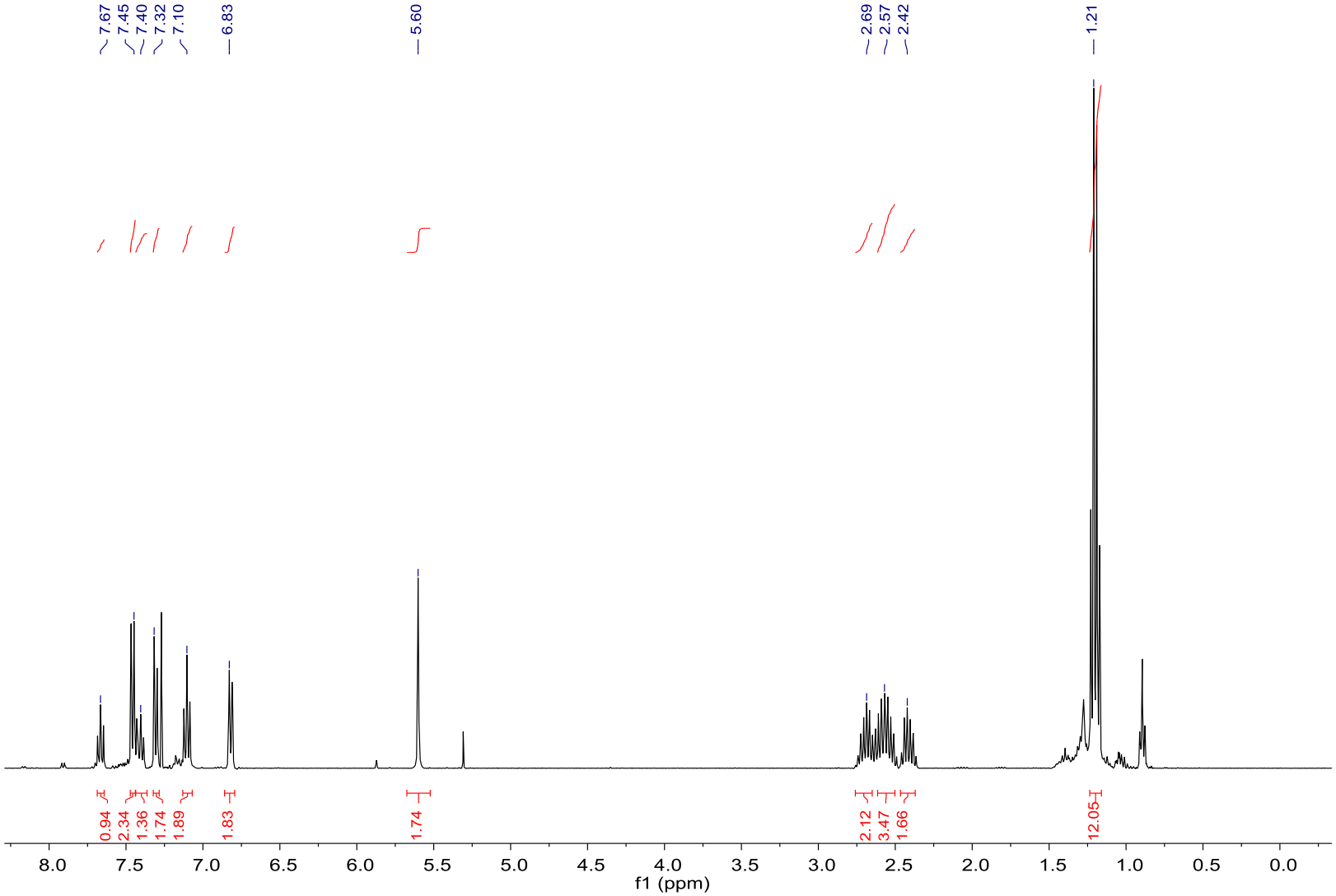
S19 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,4,6-trimethylphenyl)-2-phenyl-2,3-dihydro-1H-1,3,2-diazaborole (**2b**)*.



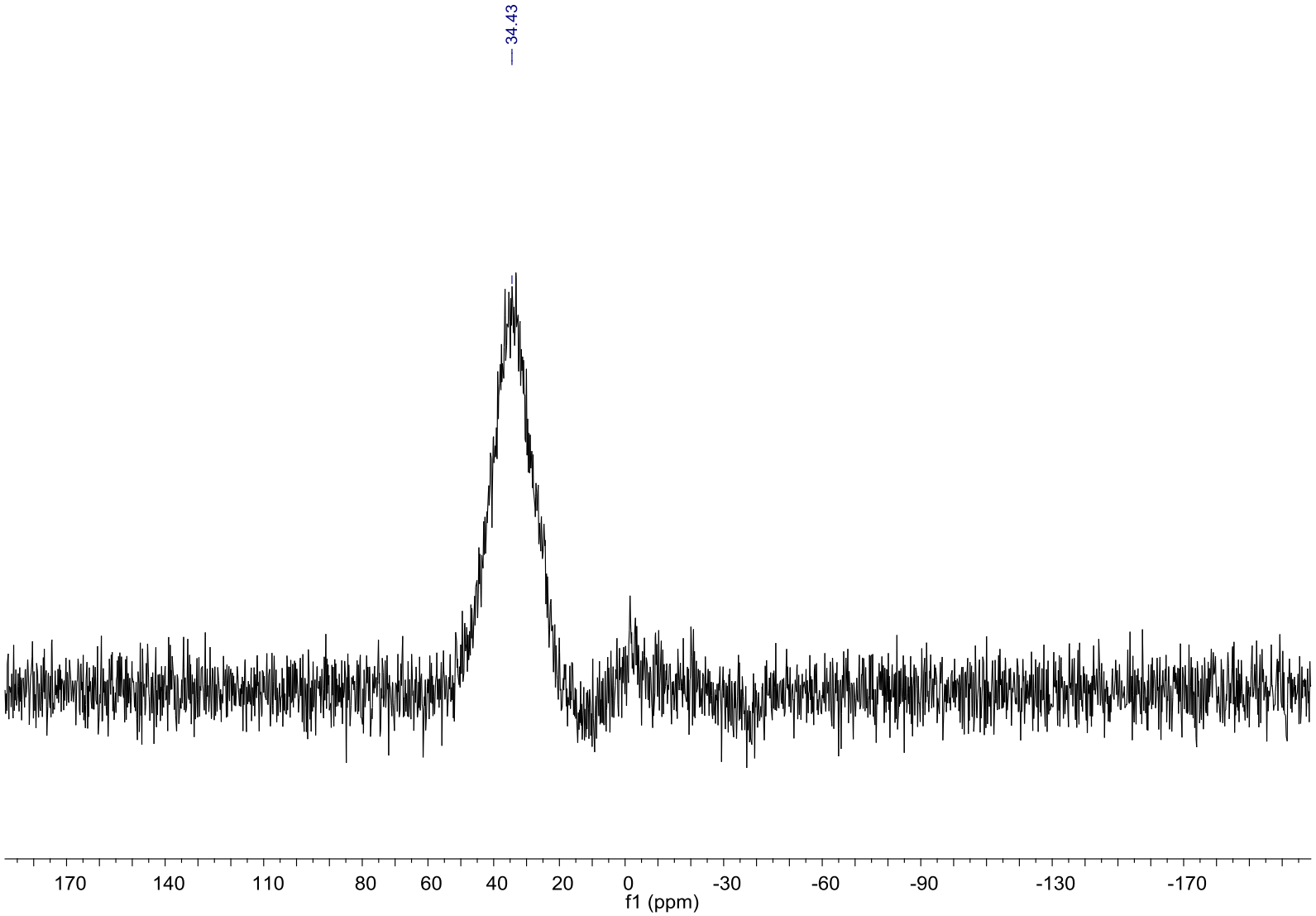
S20 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,4,6-trimethylphenyl)-2-phenyl-2,3-dihydro-1H-1,3,2-diazaborole (**2b**)*.



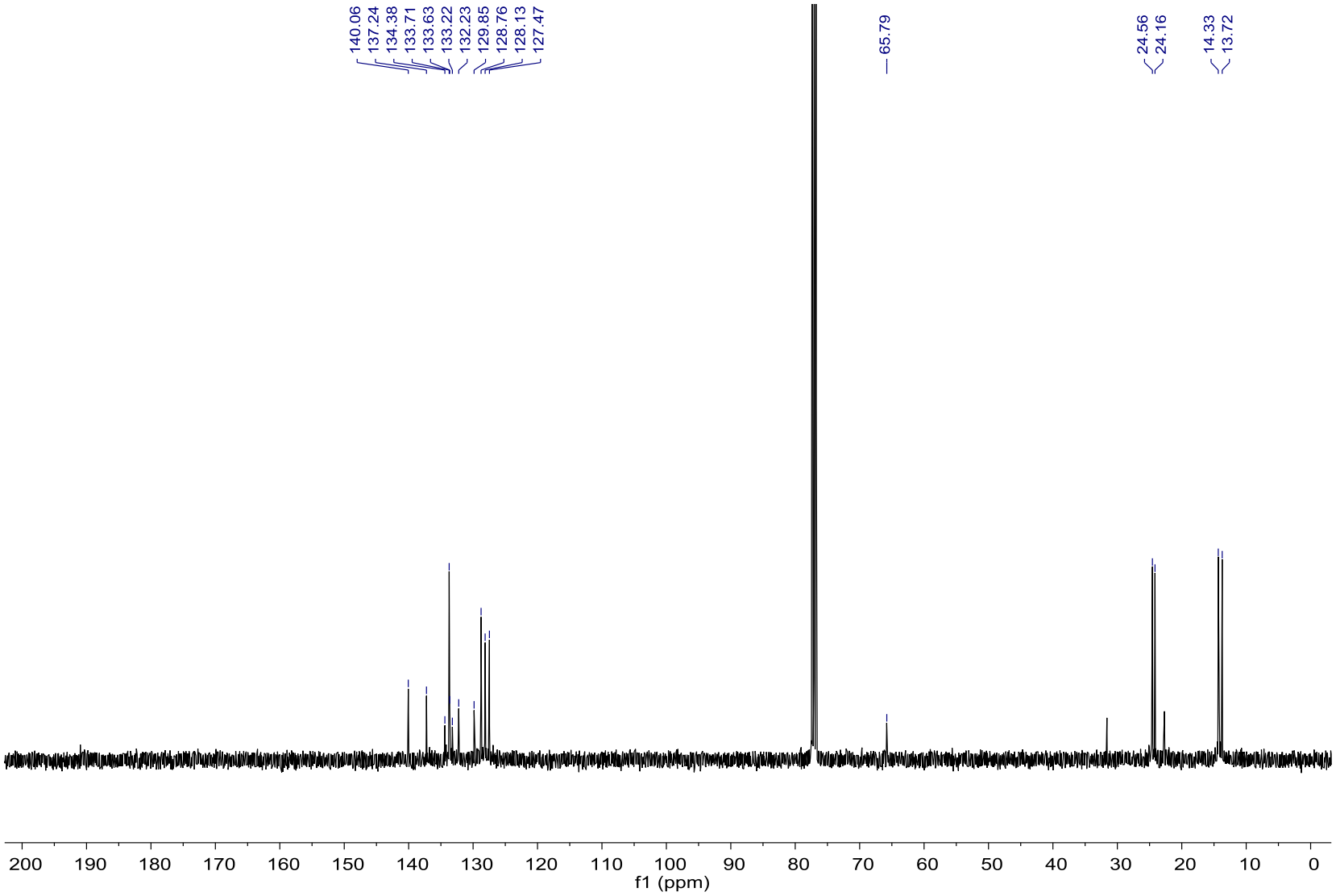
S21 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate* ***(3a).***



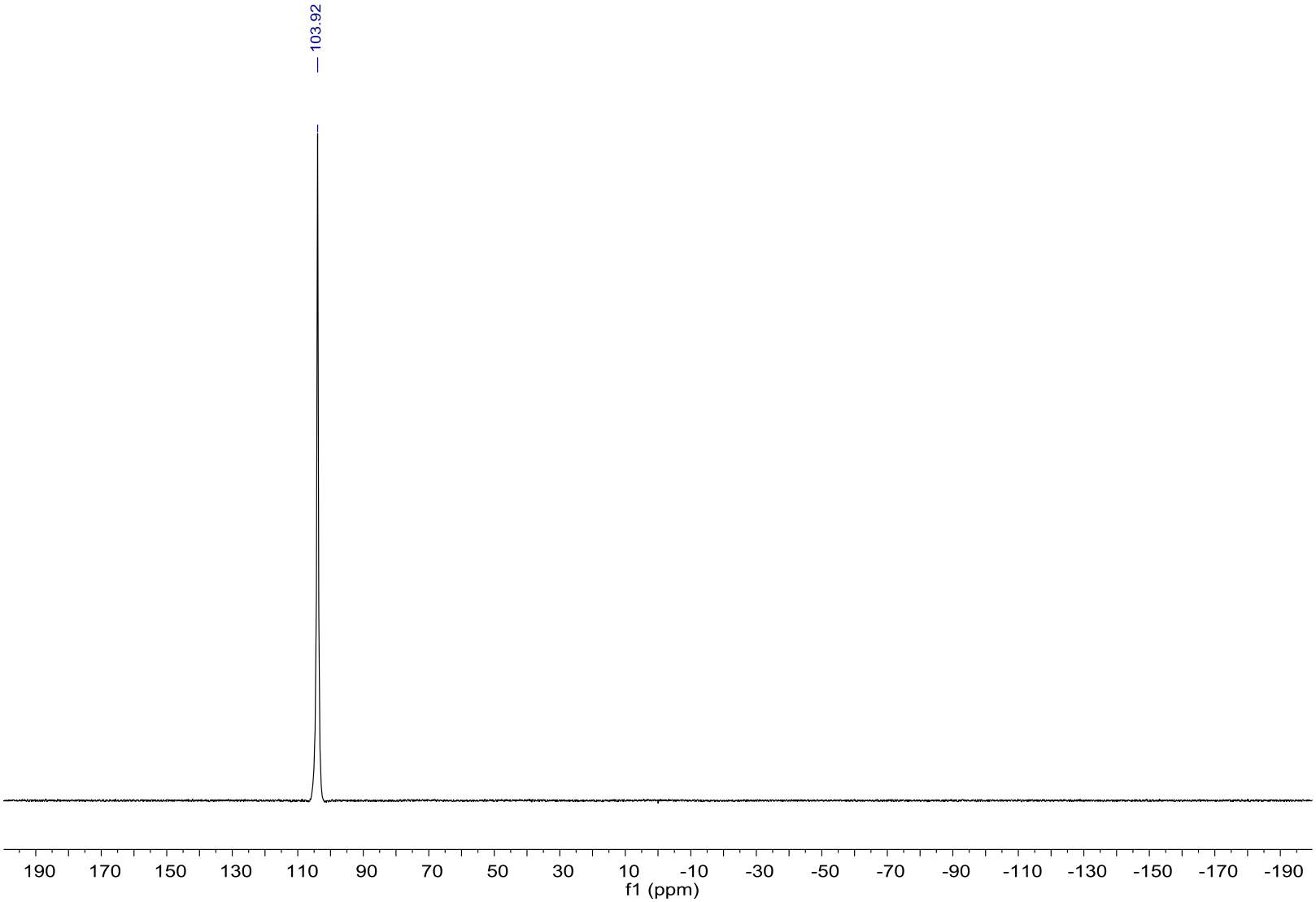
S22 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate* (**3a**).



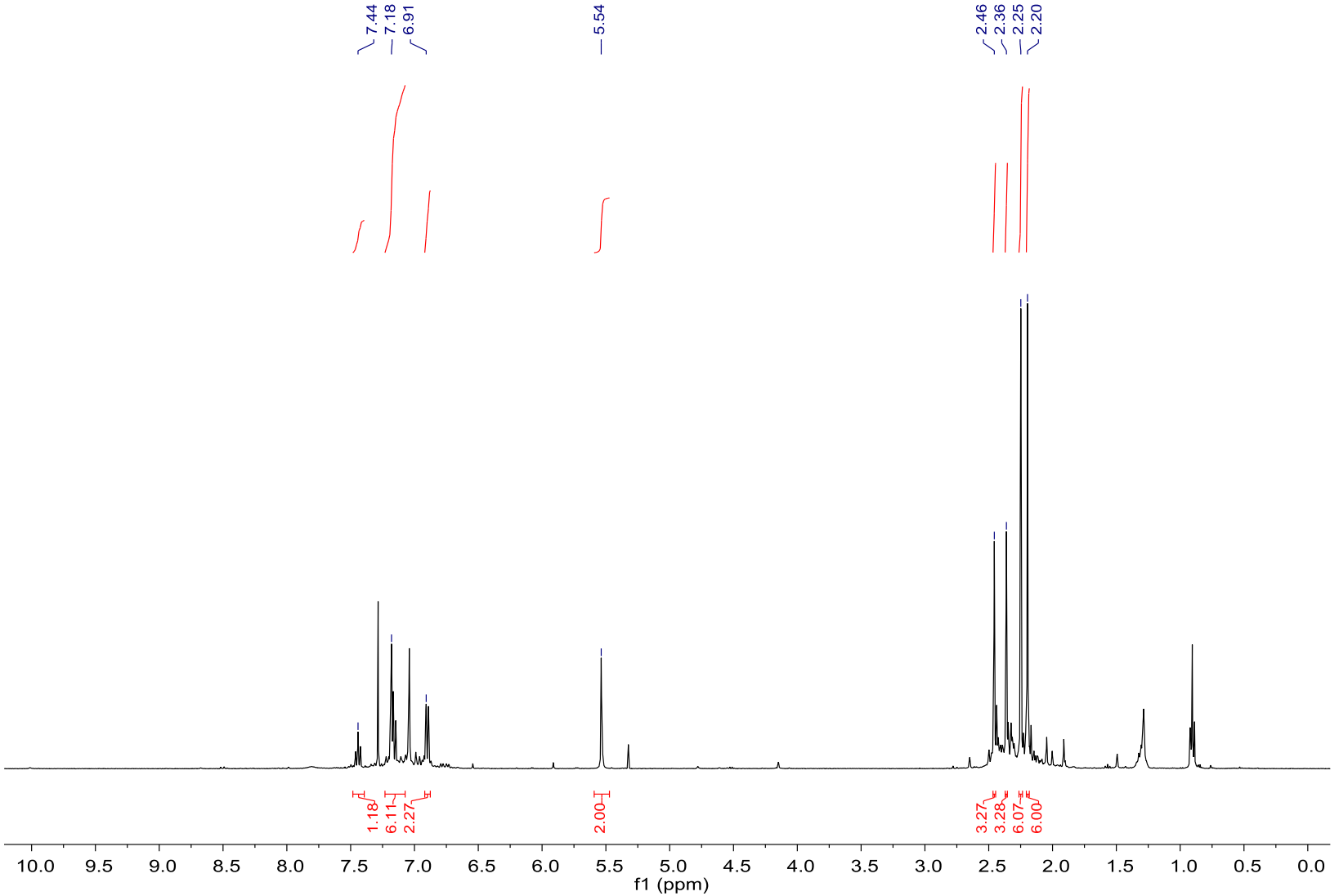
S23 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of*4-chloro-1,3-bis(2,6-diethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate* (**3a**).



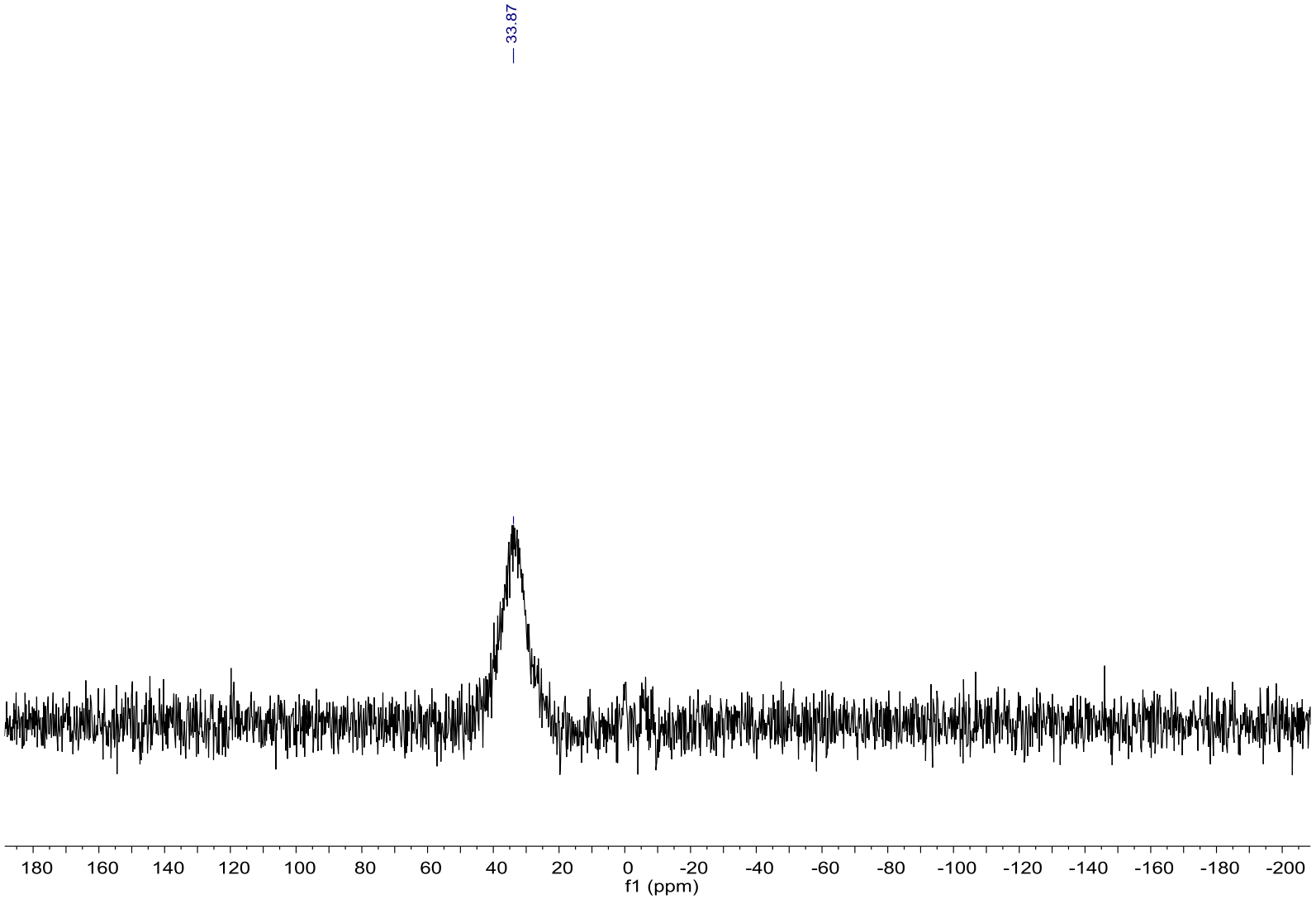
S24 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate* (**3a**).



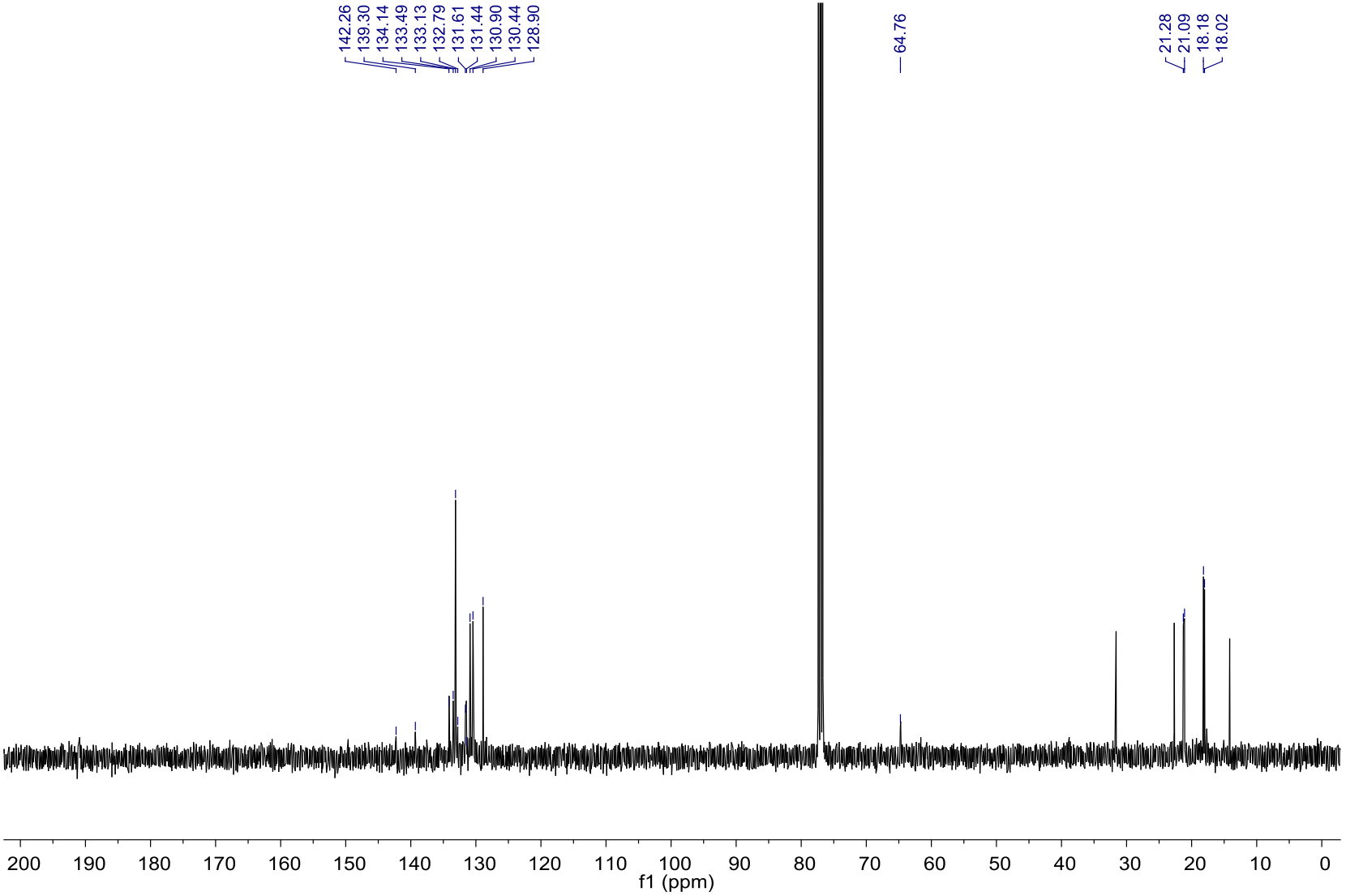
S25 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,4,6-trimethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3b**).*



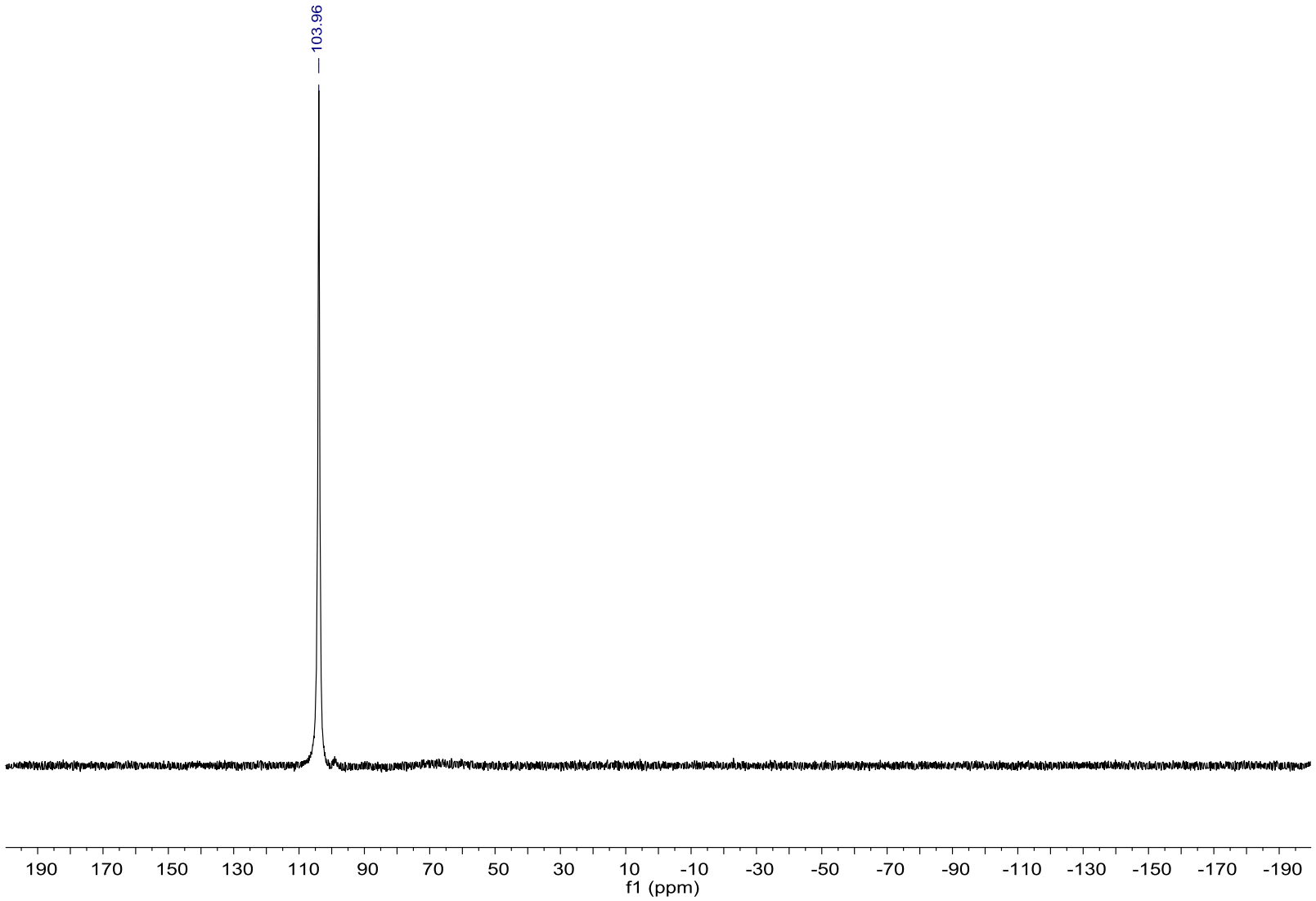
S26 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,4,6-trimethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3b**).*



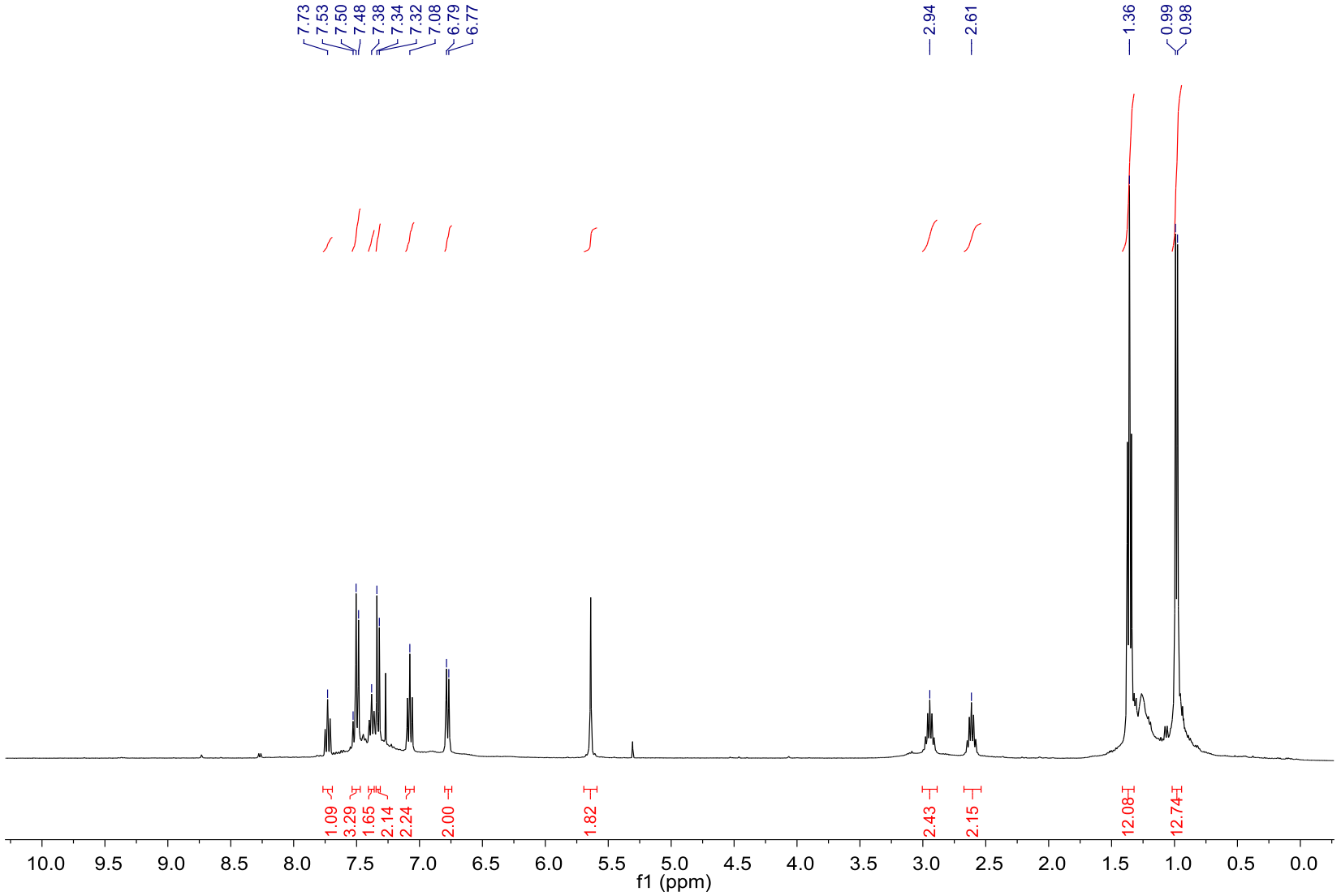
S27 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,4,6-trimethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3b**).*



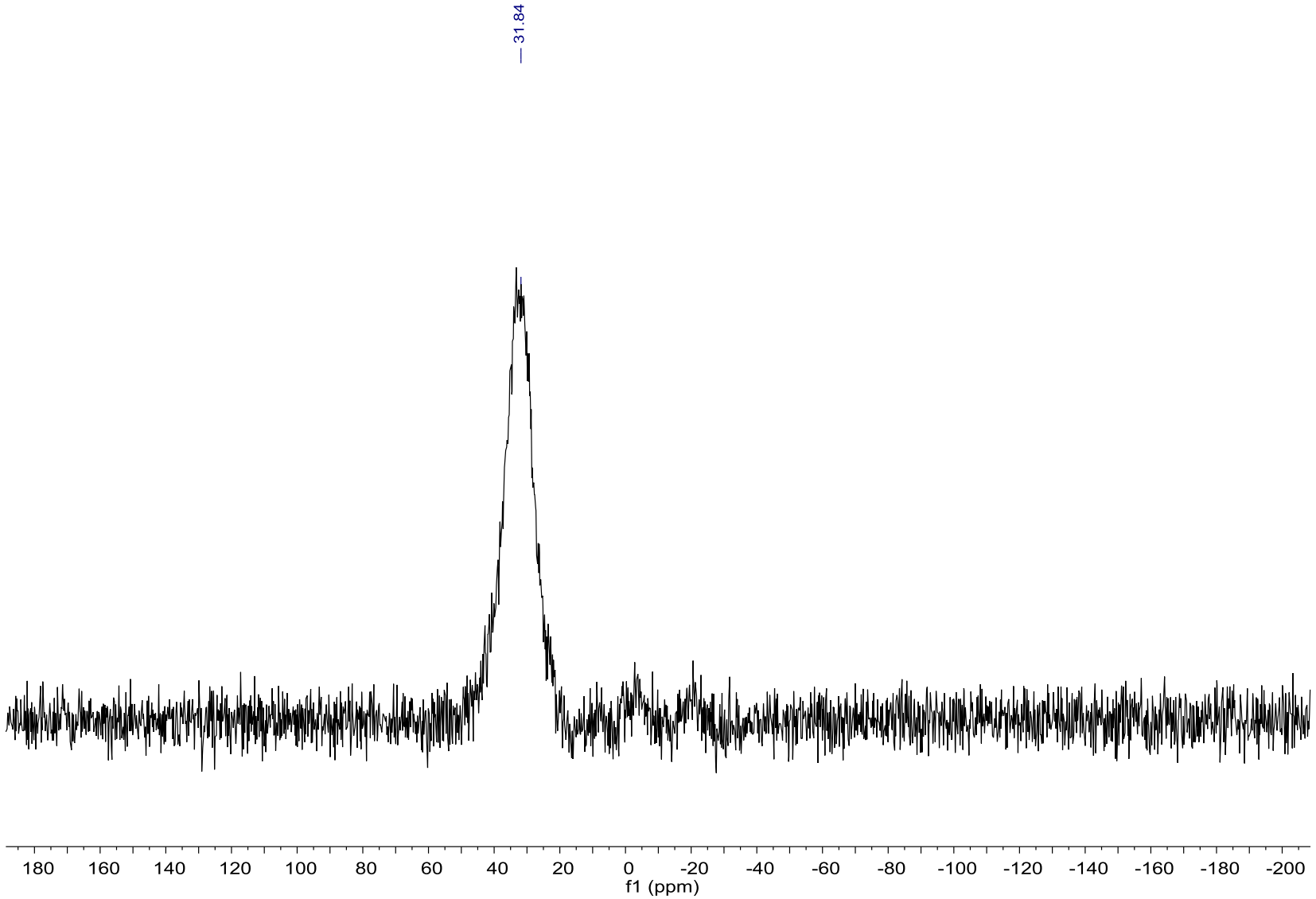
S28 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,4,6-trimethylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3b**).*



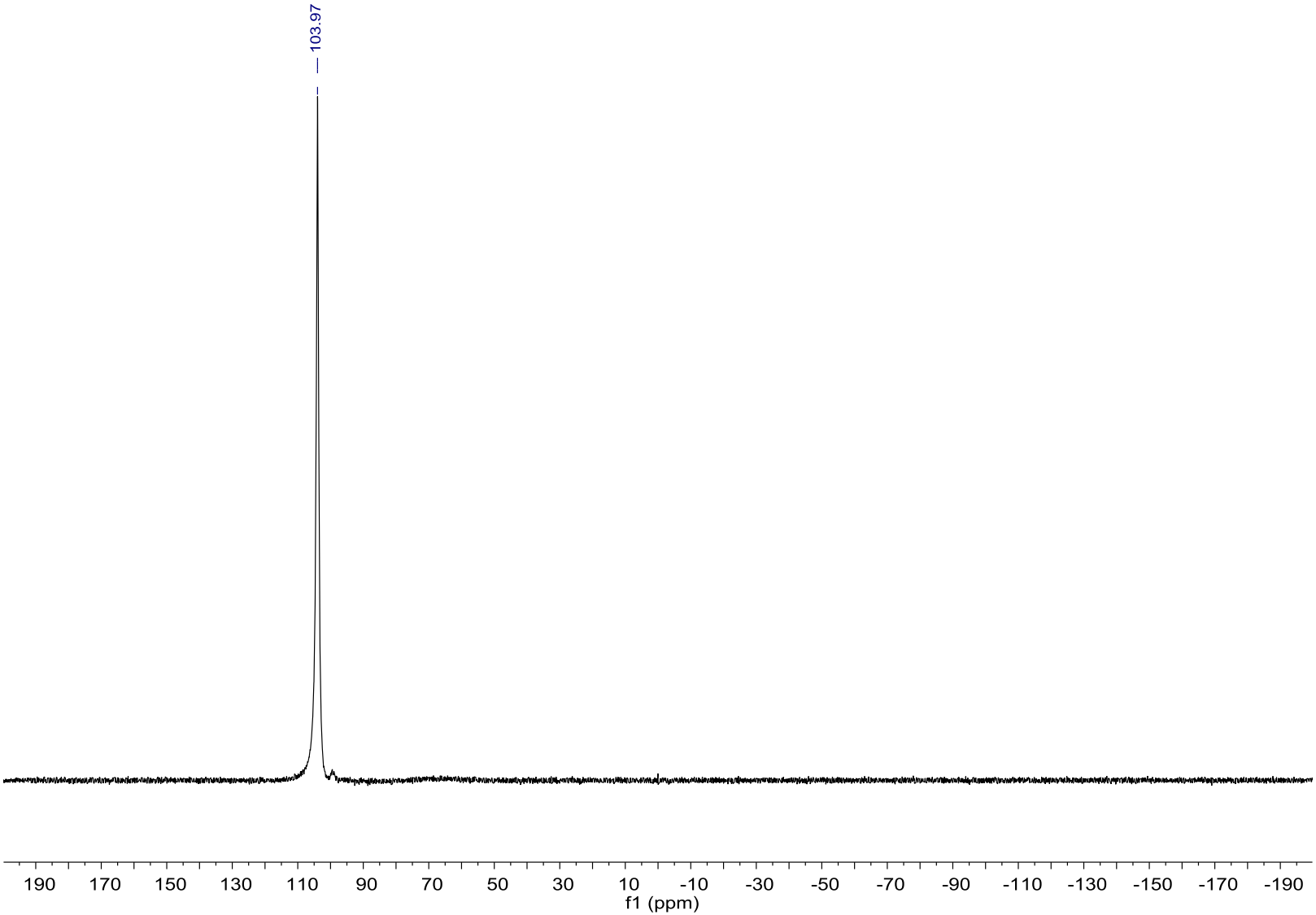
S29 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diisopropylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3d**).*



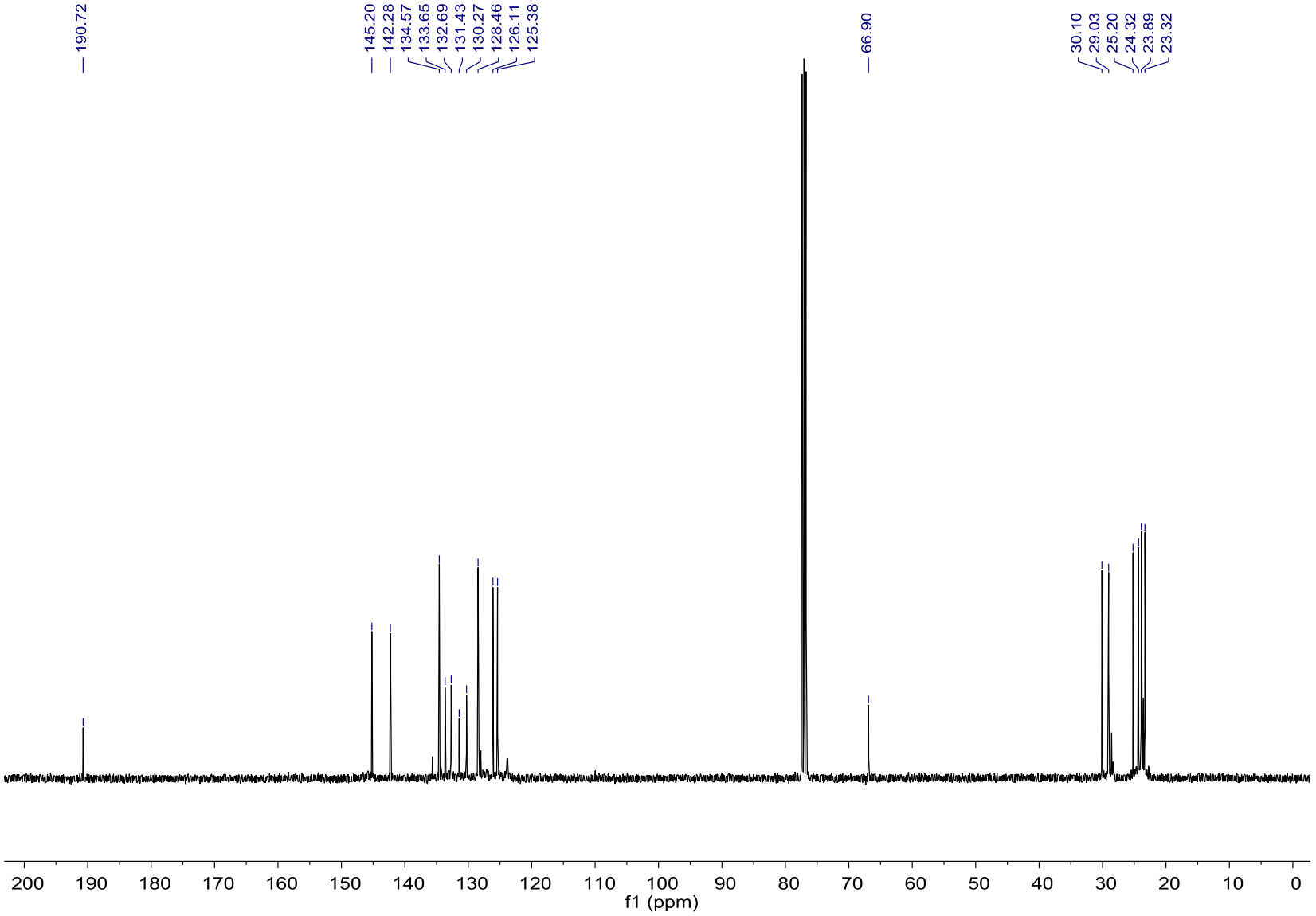
S30 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diisopropylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3d**)*.



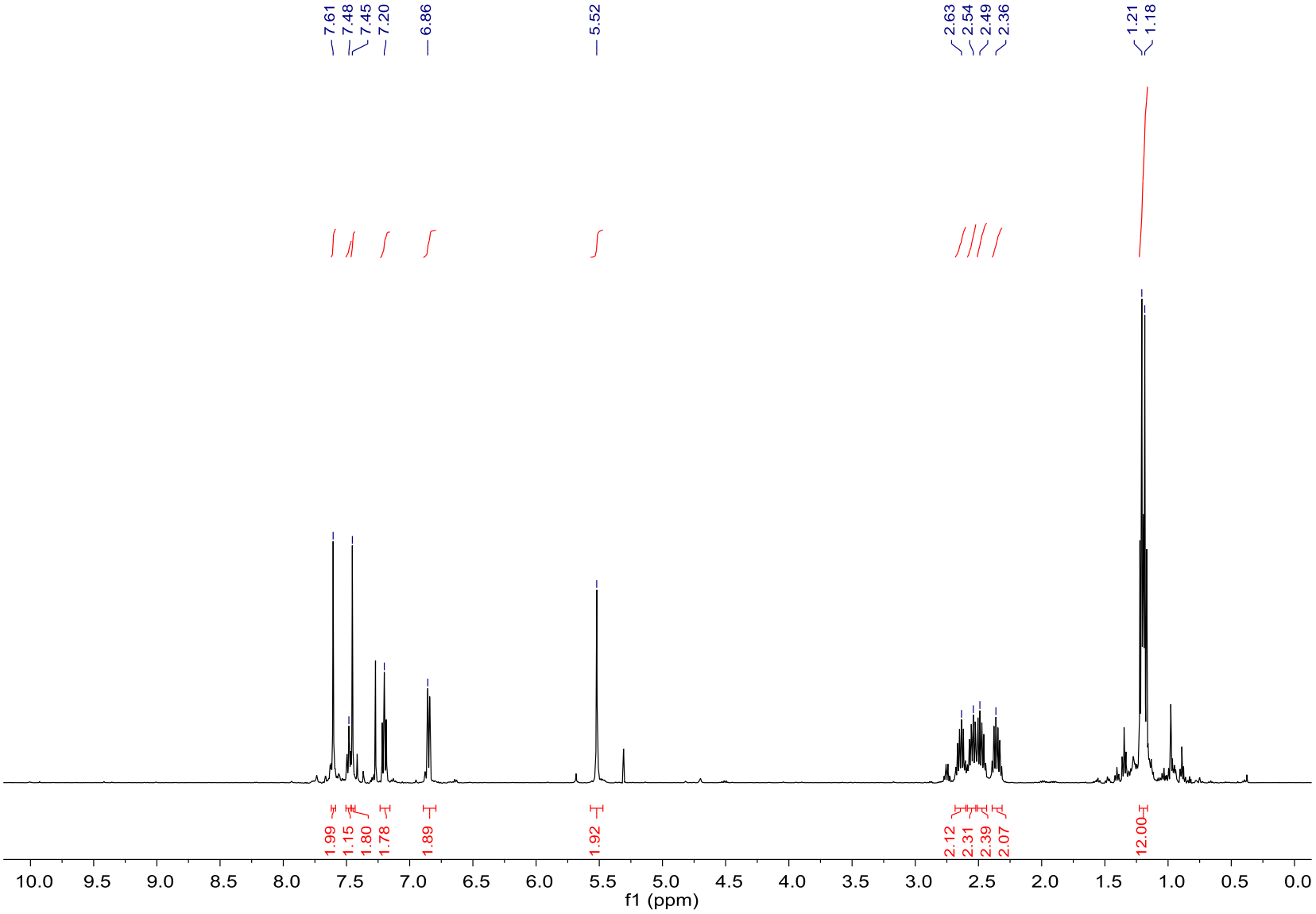
S31 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diisopropylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3d**).*



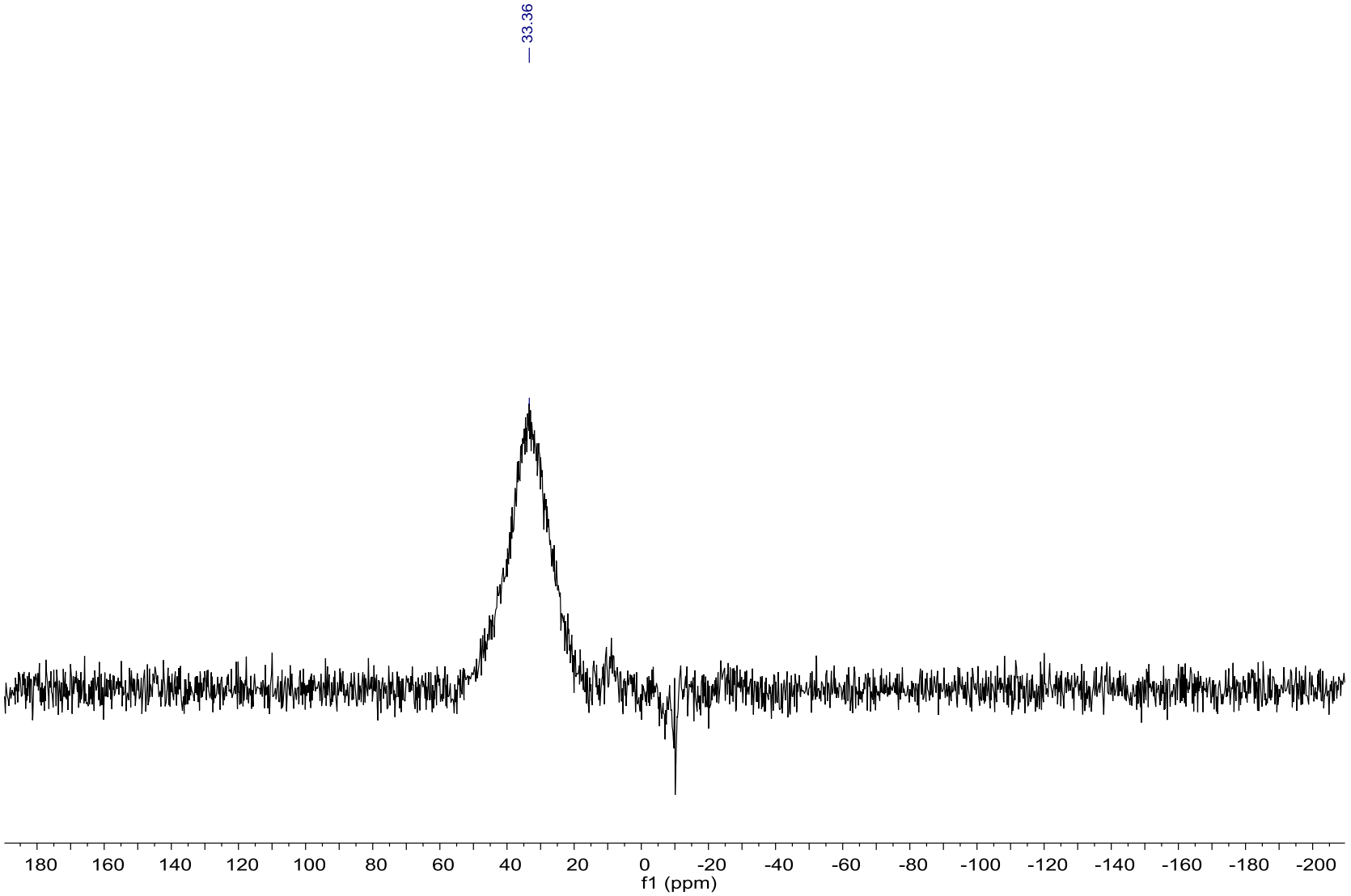
S32 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diisopropylphenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate (**3d**).*



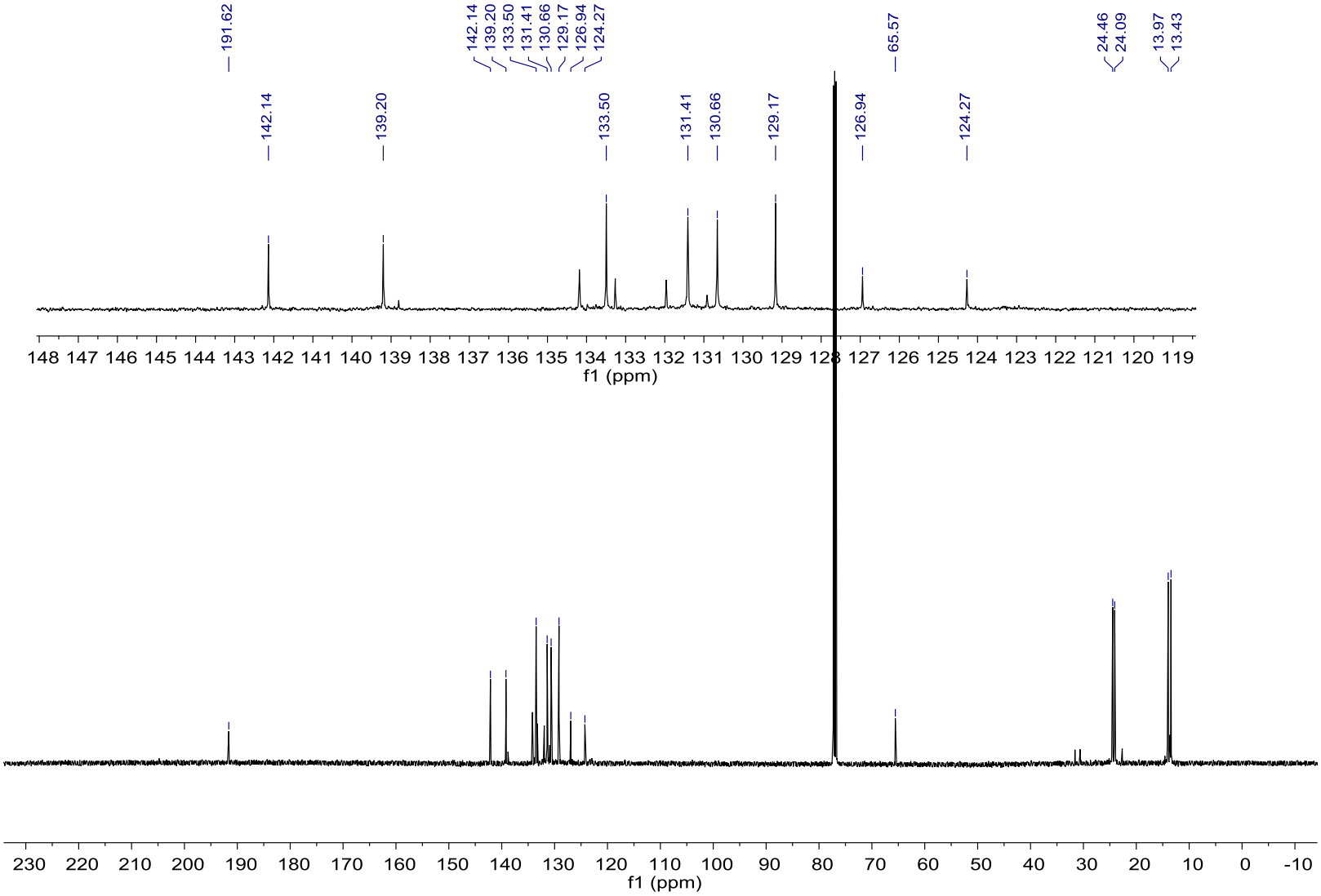
S33 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethyl-4-bromophenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate* ***(3e).***



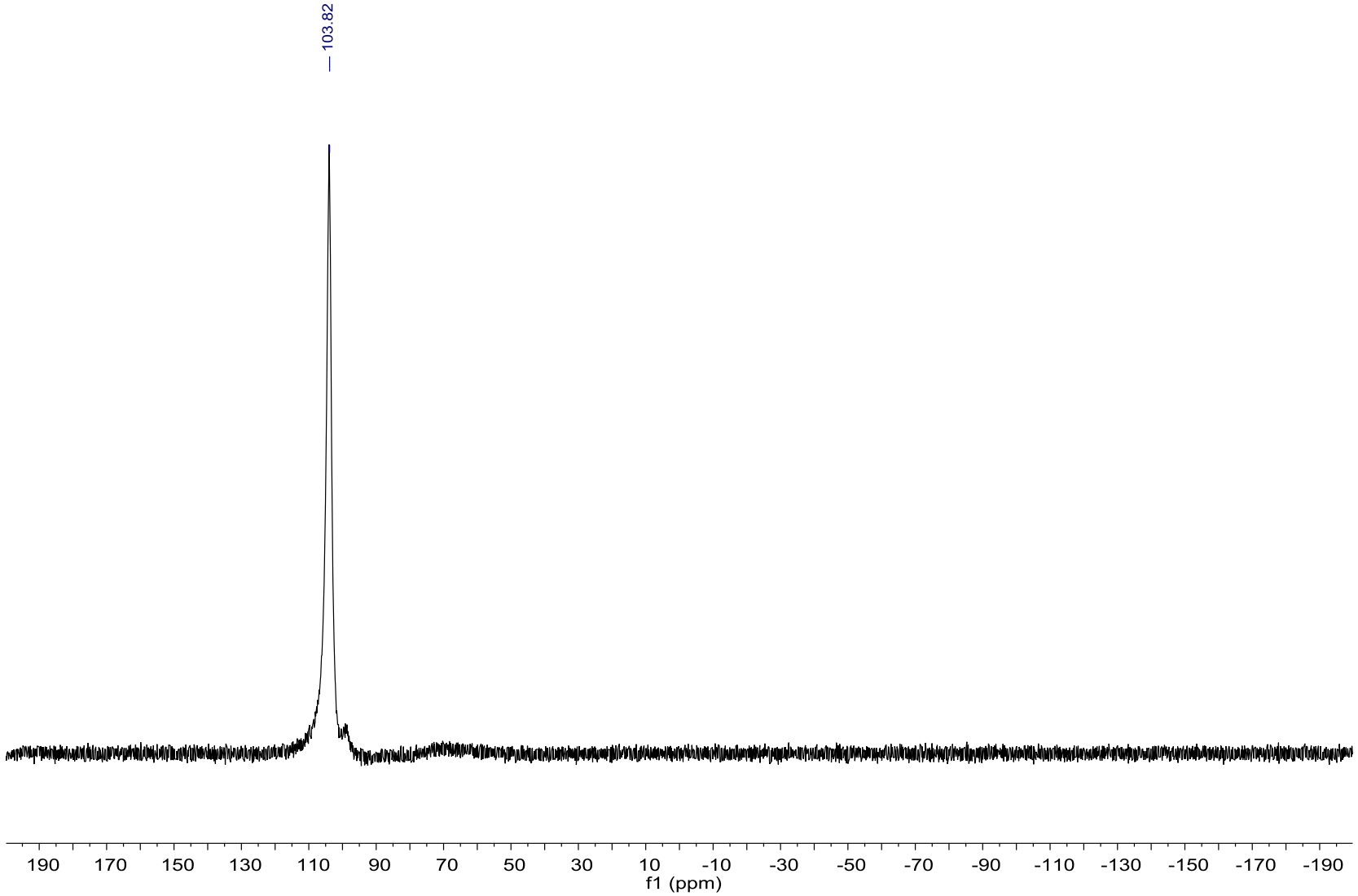
S34 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethyl-4-bromophenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate* ***(3e).***



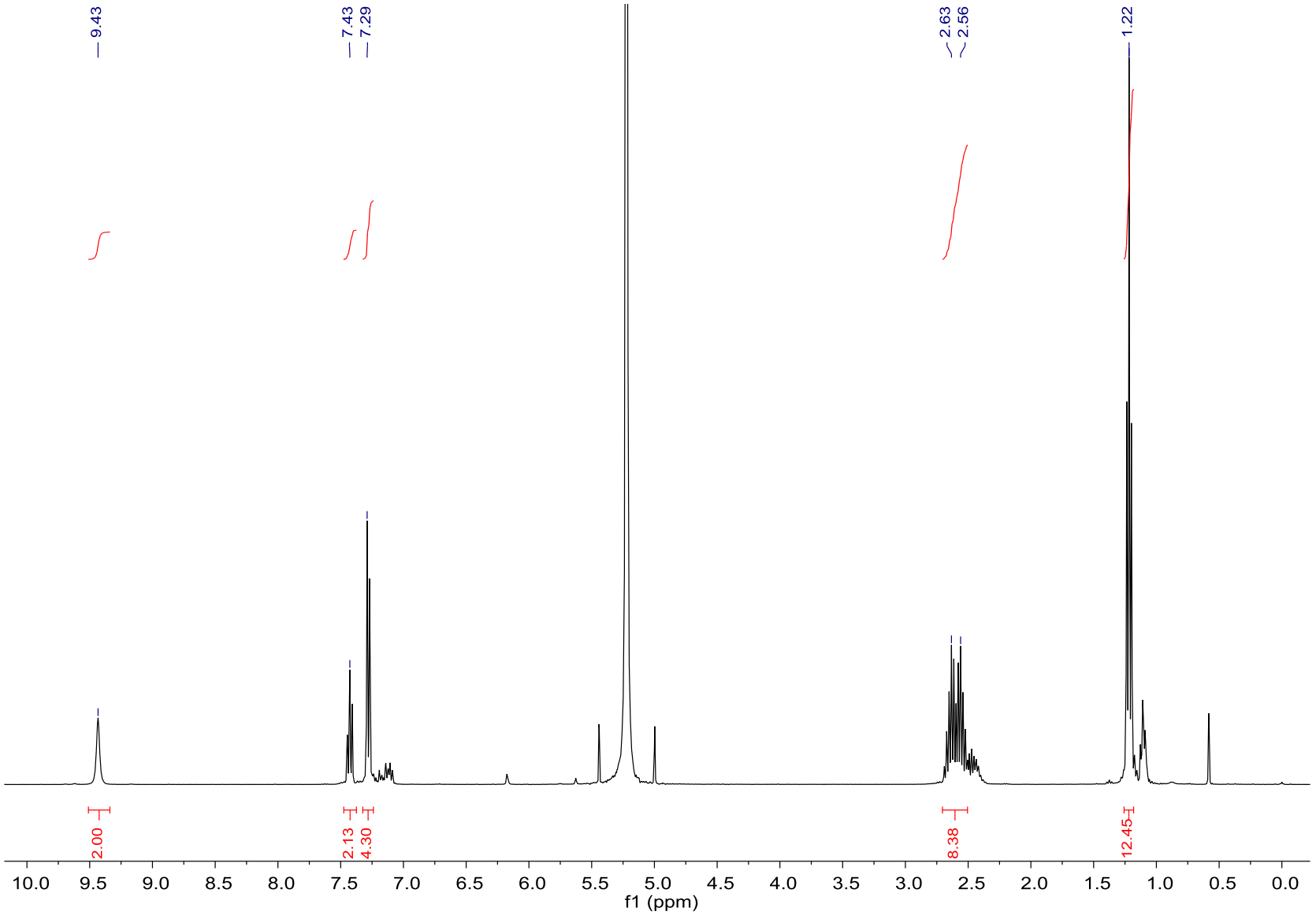
S35 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethyl-4-bromophenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate* ***(3e).***



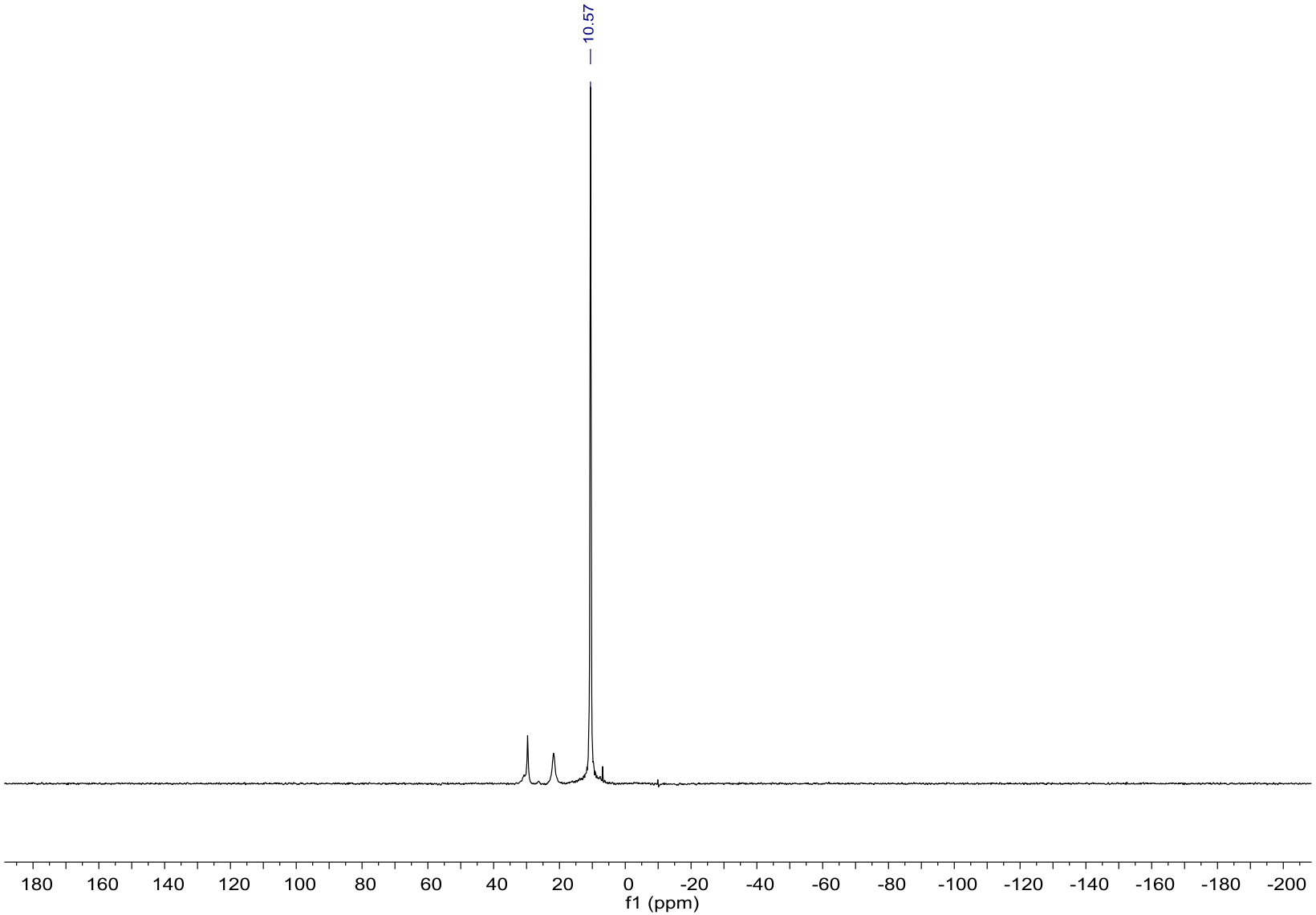
S36 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of *4-chloro-1,3-bis(2,6-diethyl-4-bromophenyl)-2-phenyl-2,5-dihydro-1H-1,3,2-diazaborol-3-ium tetrachloroaluminate* ***(3e).***



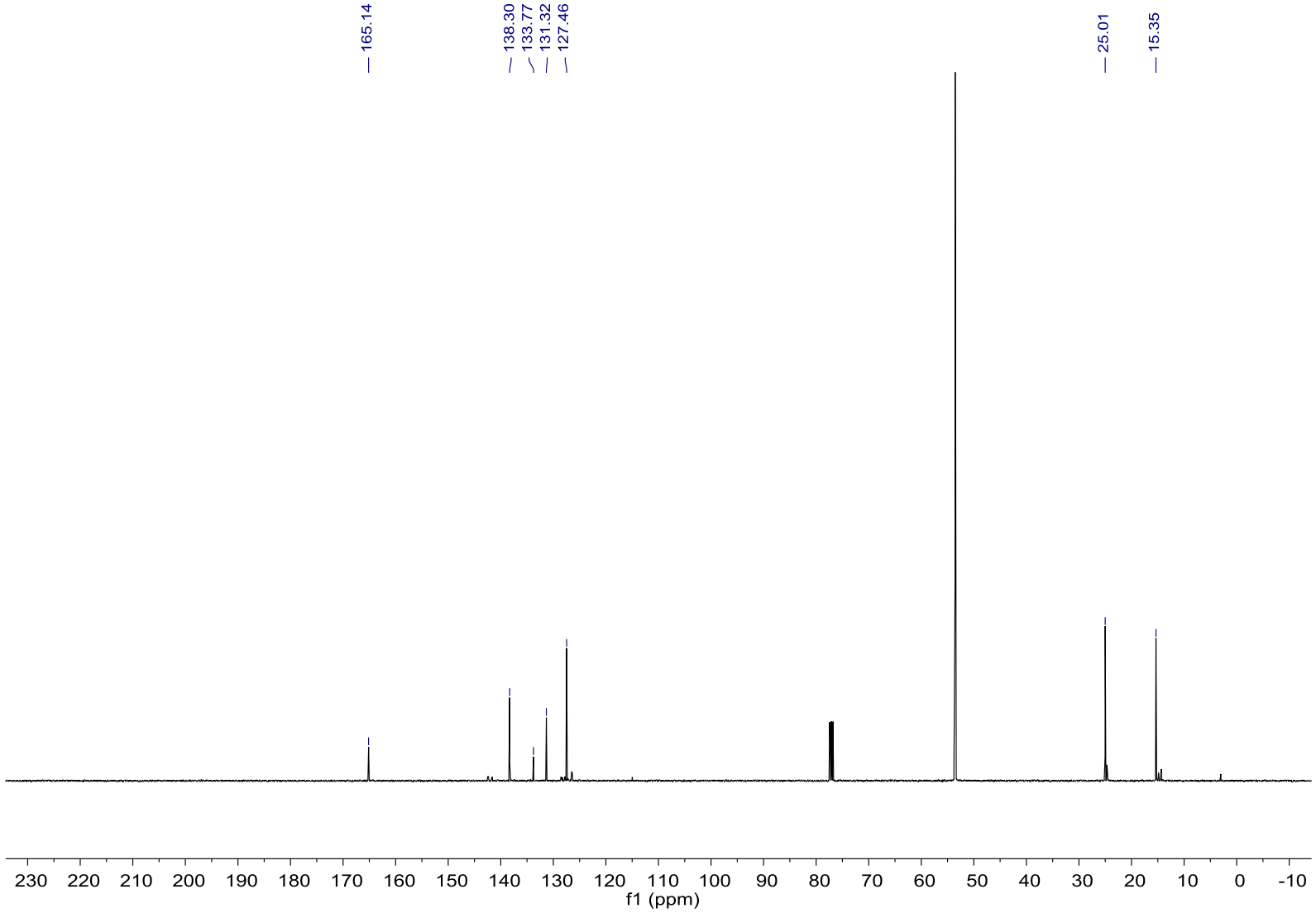
S37 *in situ* ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium* (***4a***).



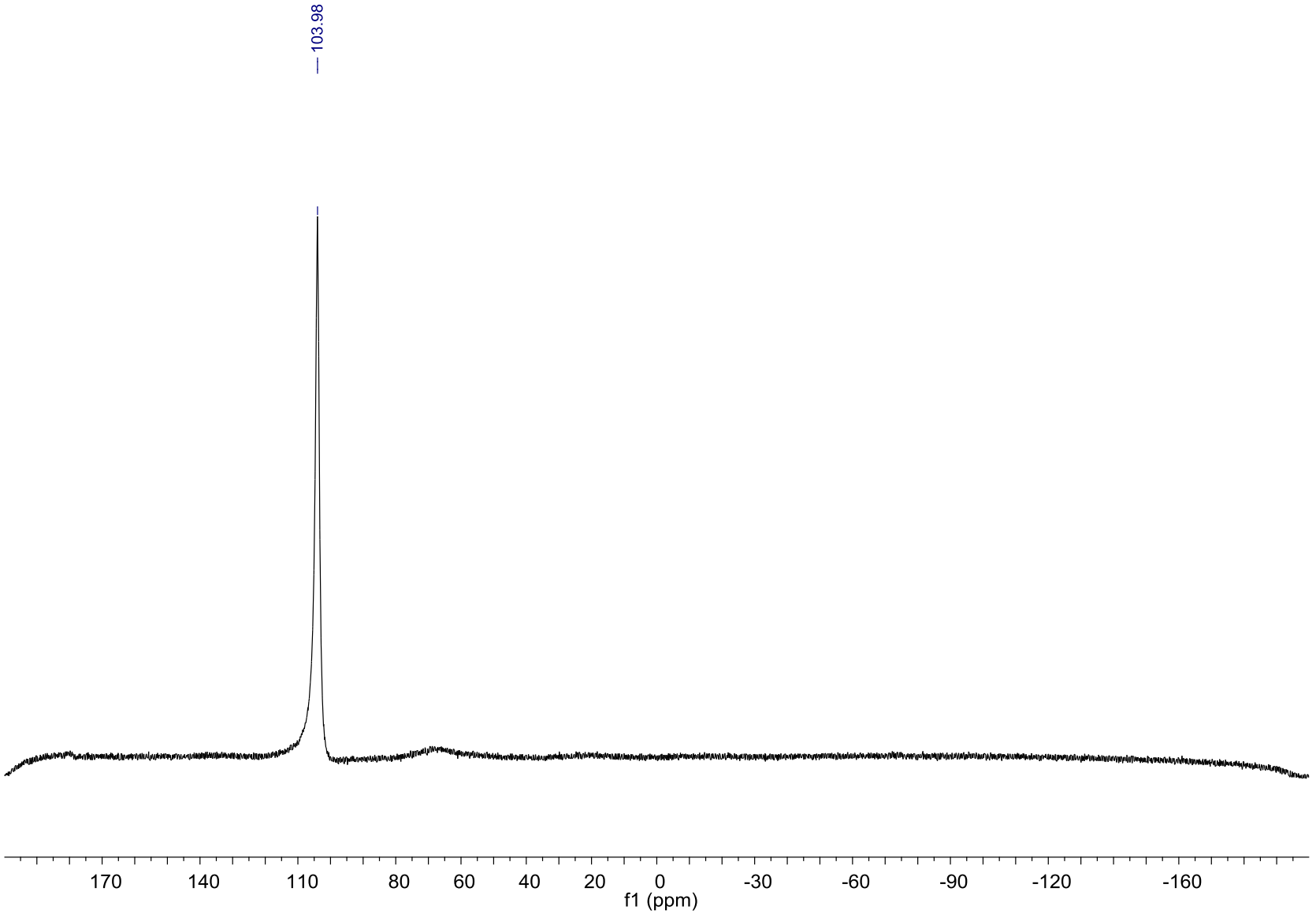
S38 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium (**4a**).*



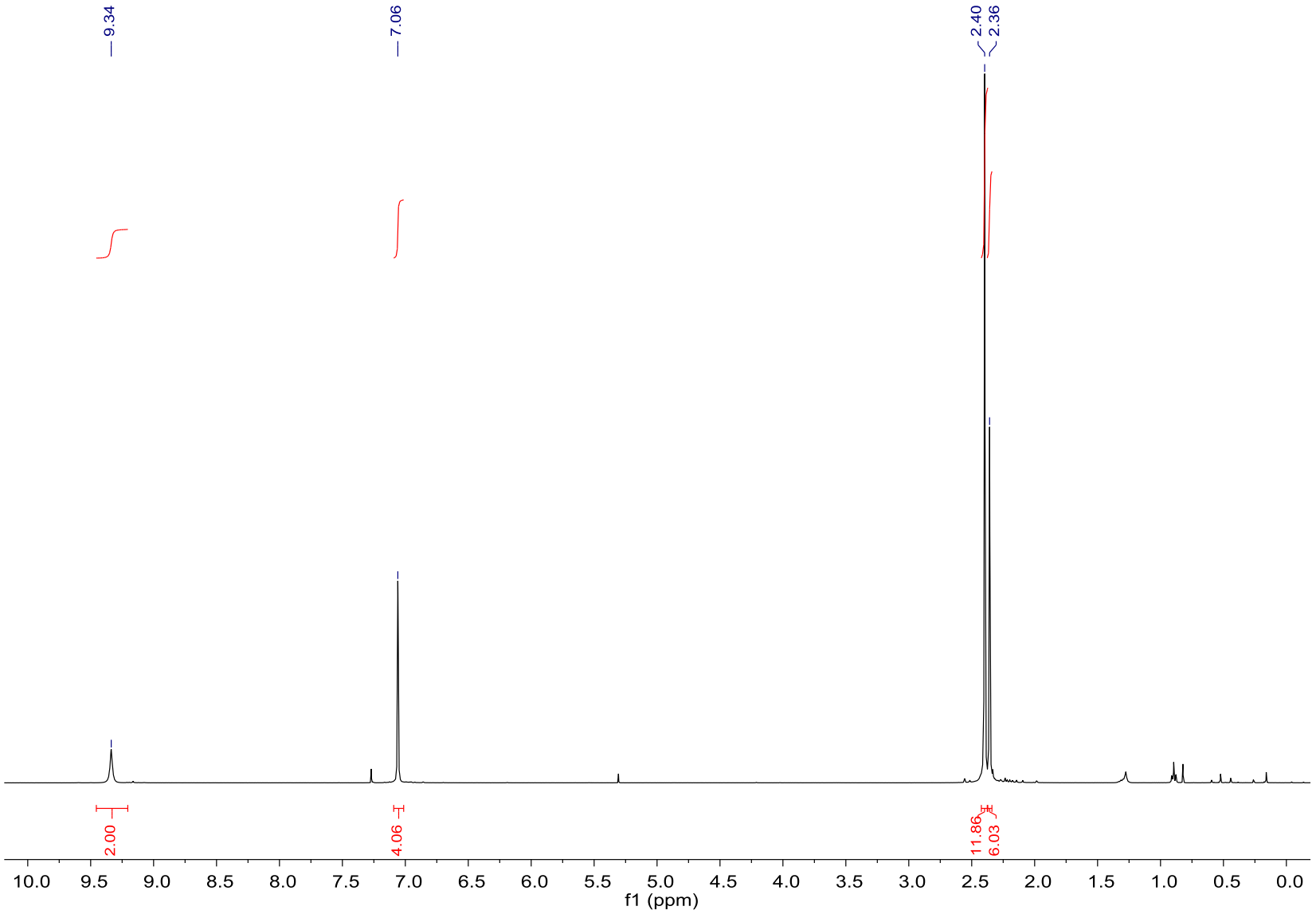
S39 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium (**4a**).*



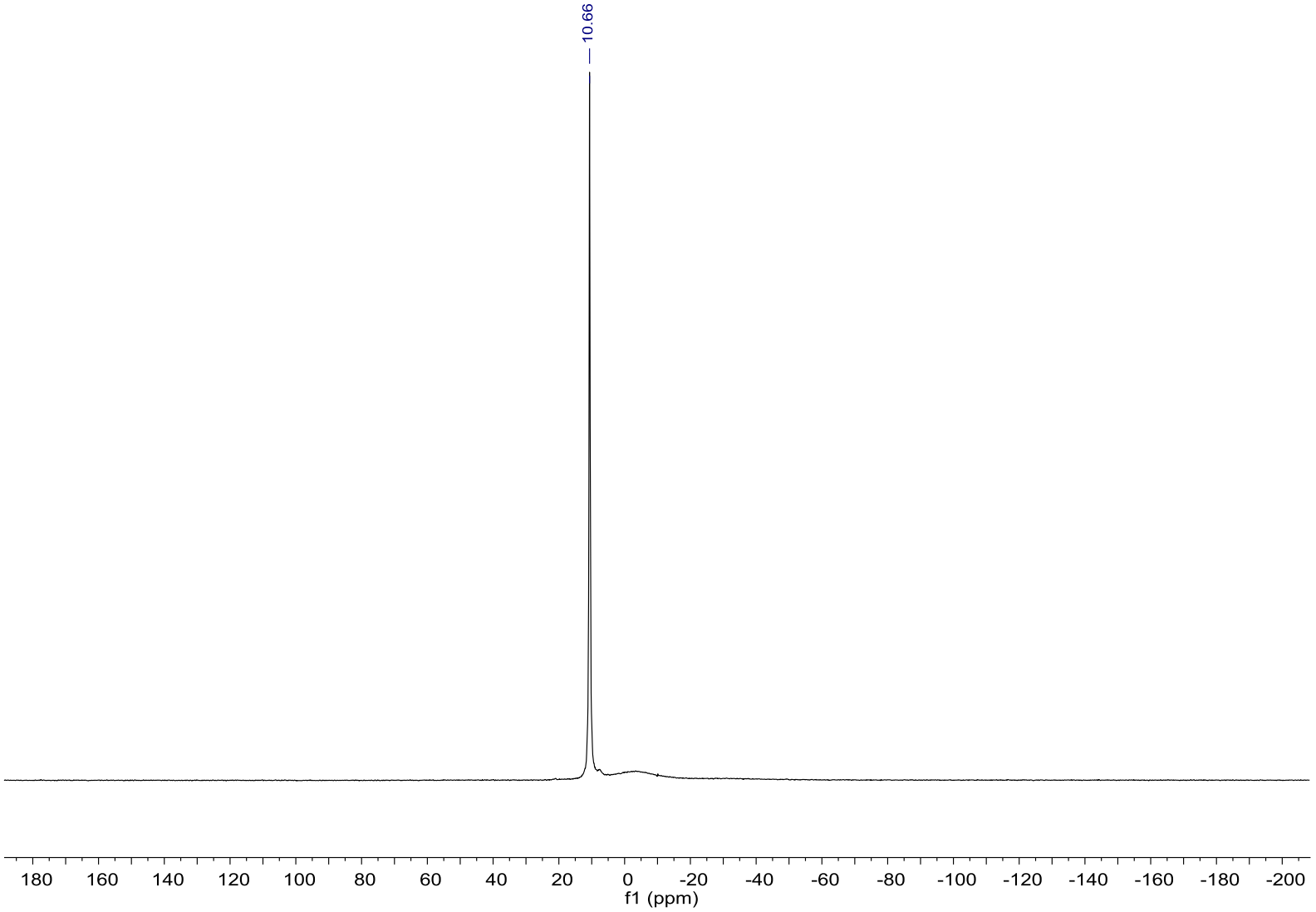
S40 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium* (***4a***).



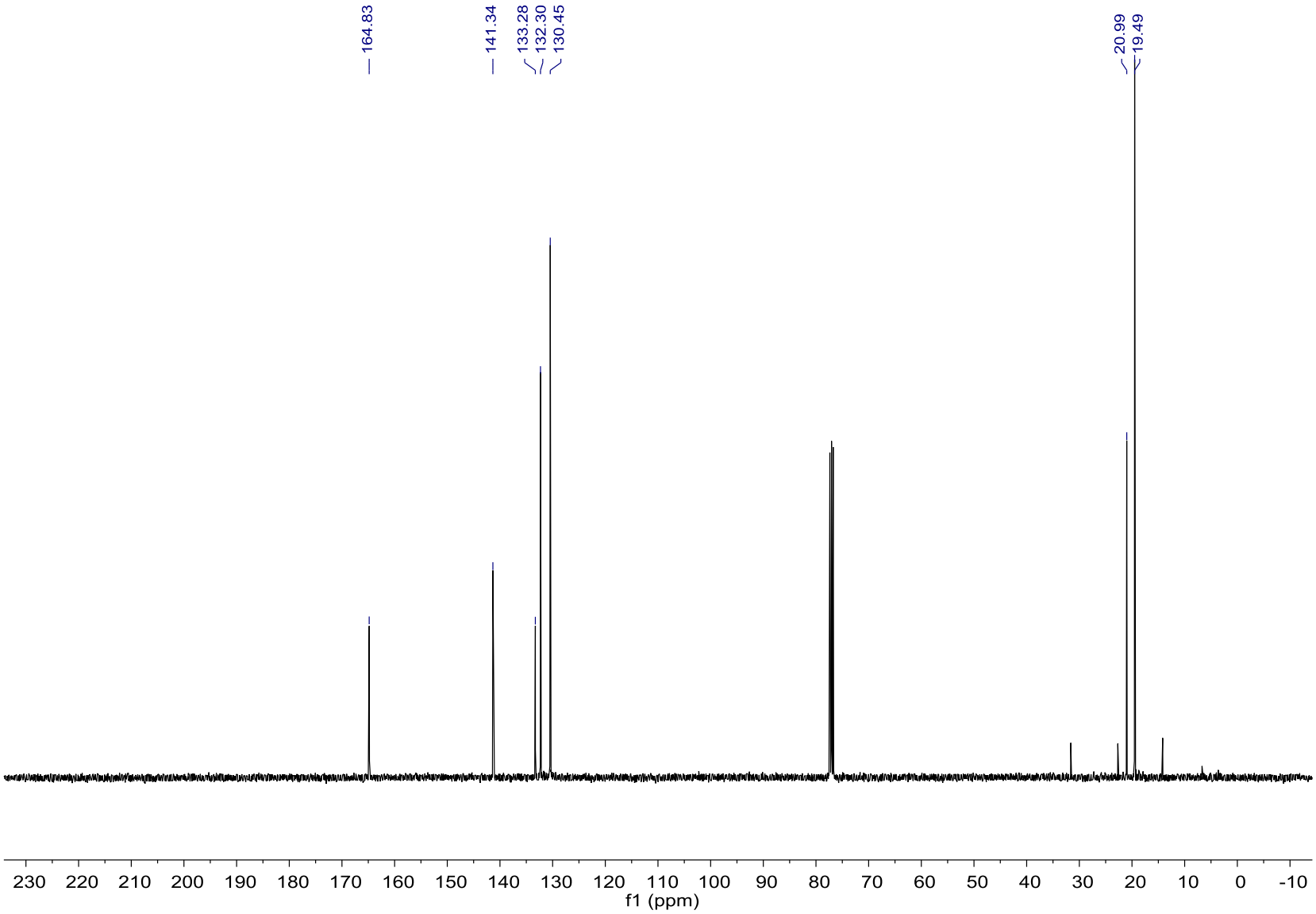
S41 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-dimesityl-2H-1,3l4,2l4-diazaborol-1-ium* (***4b***).



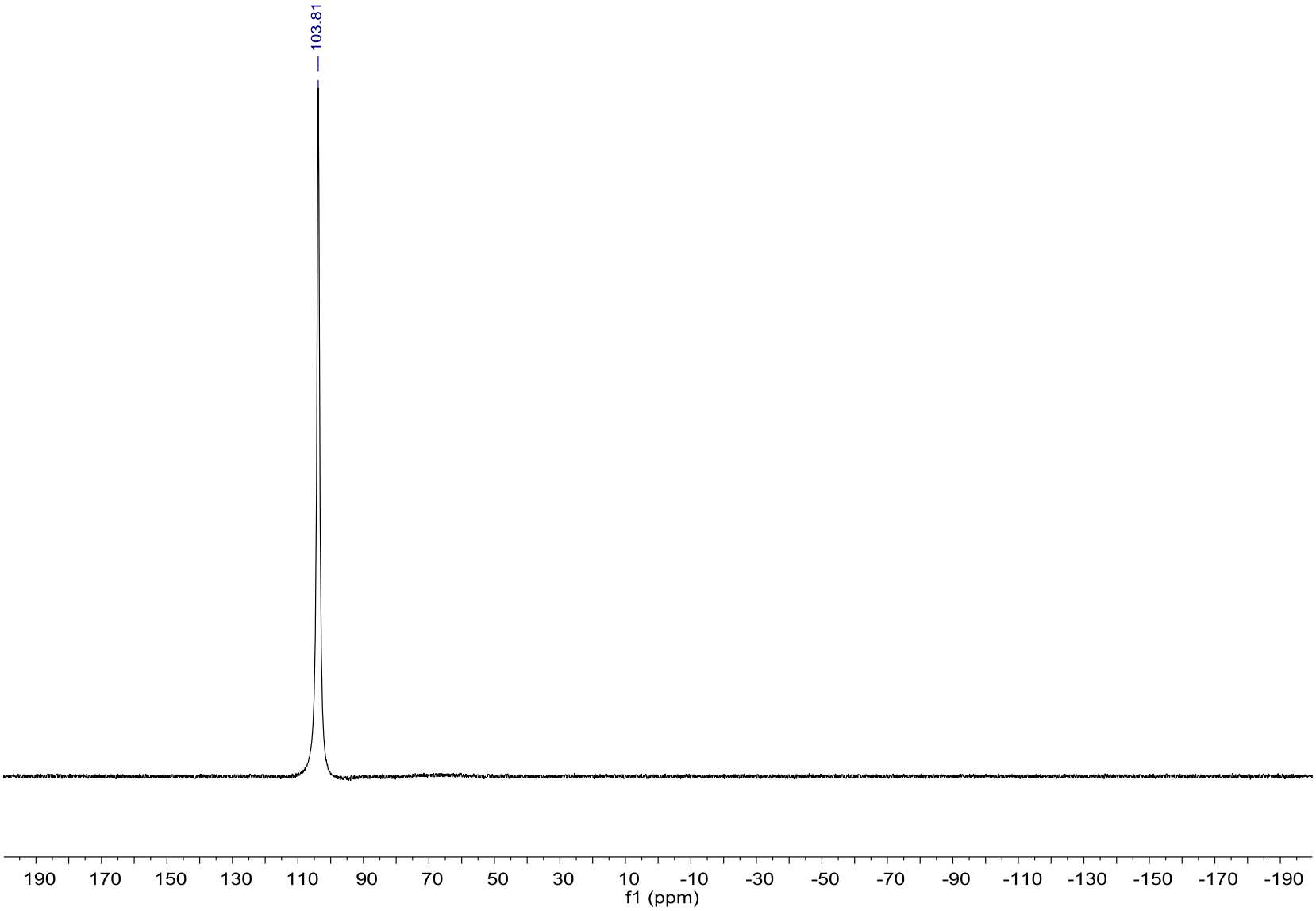
S42 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-dimesityl-2H-1,3l4,2l4-diazaborol-1-ium* (***4b***).



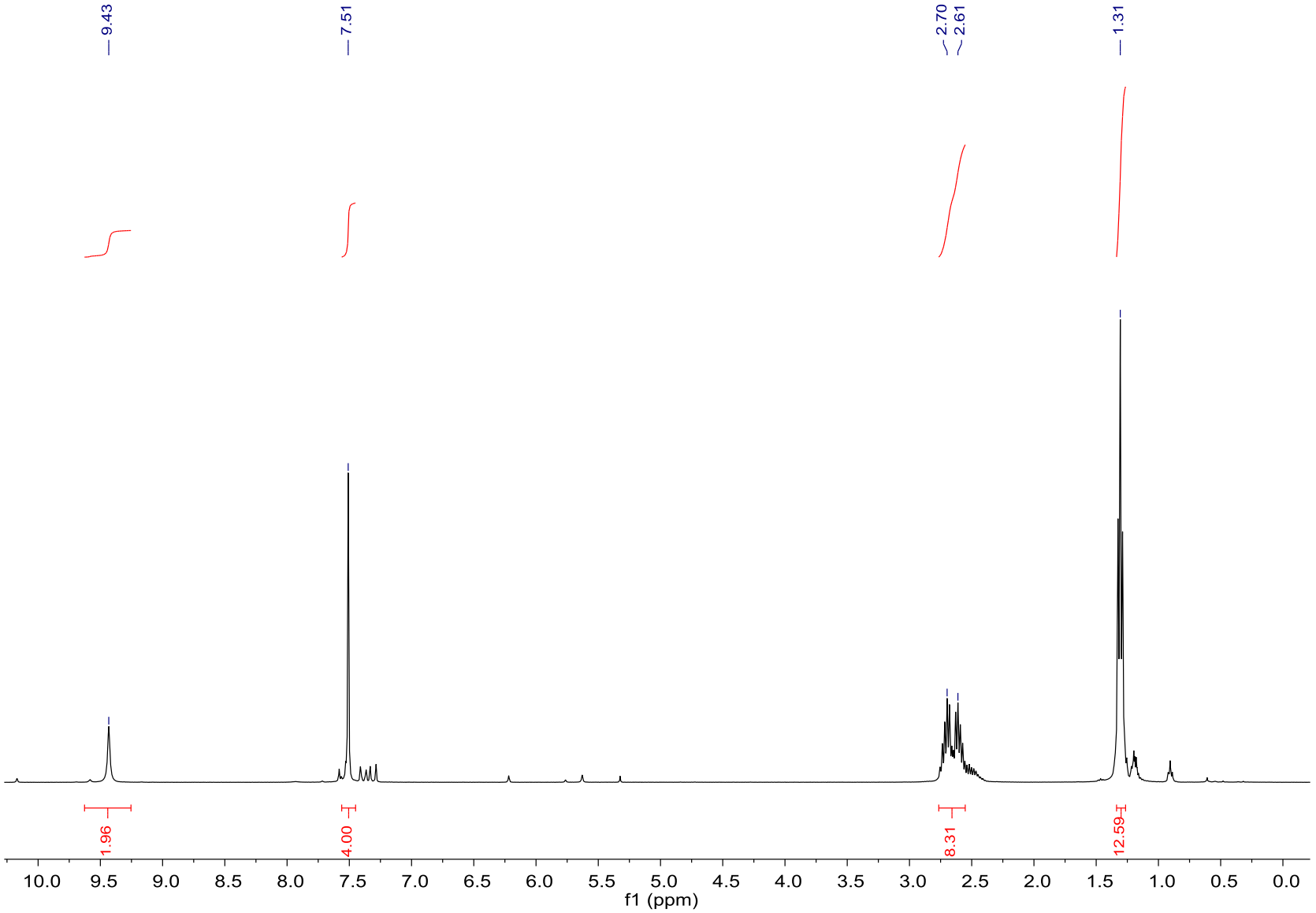
S43 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-dimesityl-2H-1,3l4,2l4-diazaborol-1-ium* (***4b***).



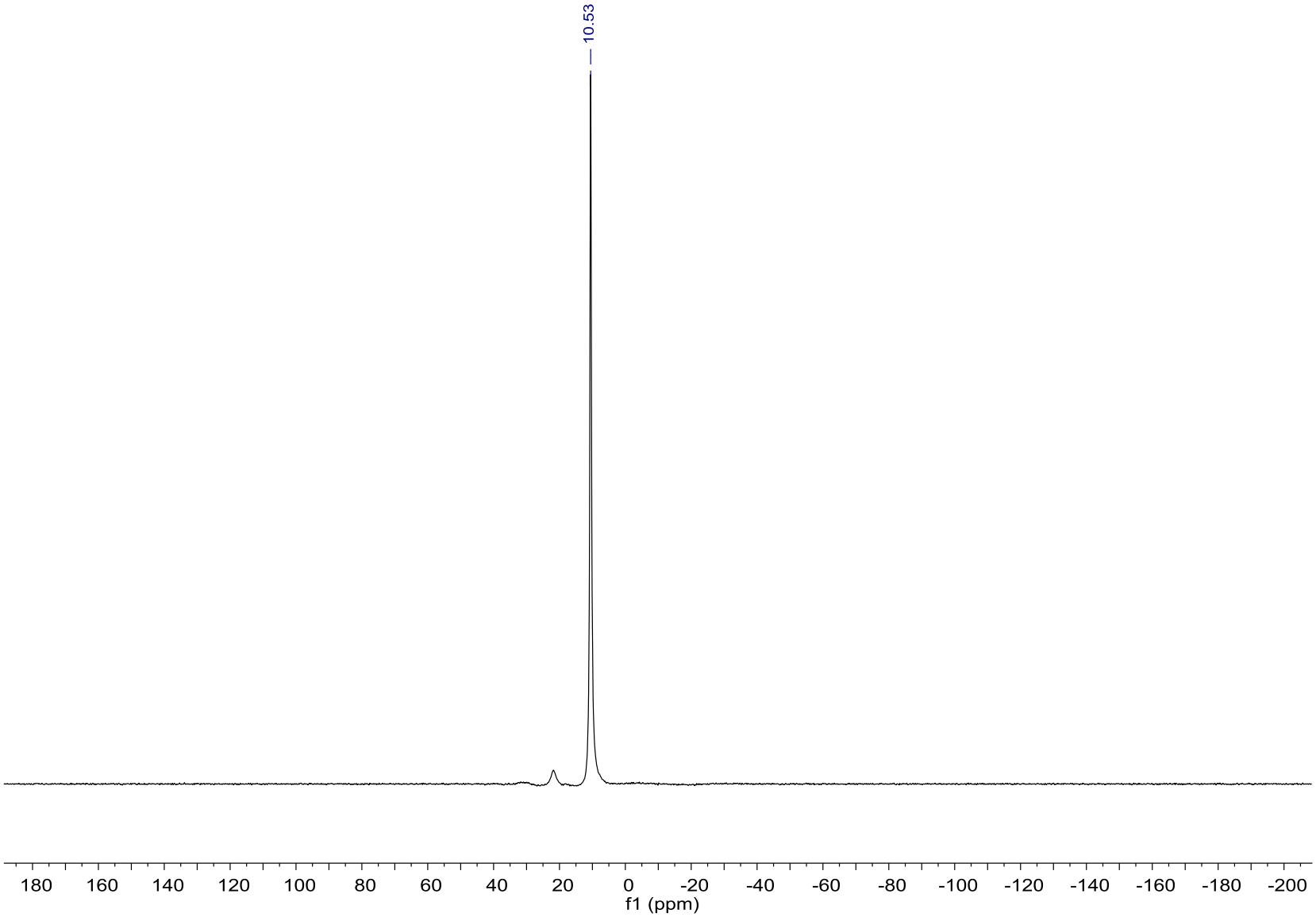
S44 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-dimesityl-2H-1,3l4,2l4-diazaborol-1-ium* (***4b***).



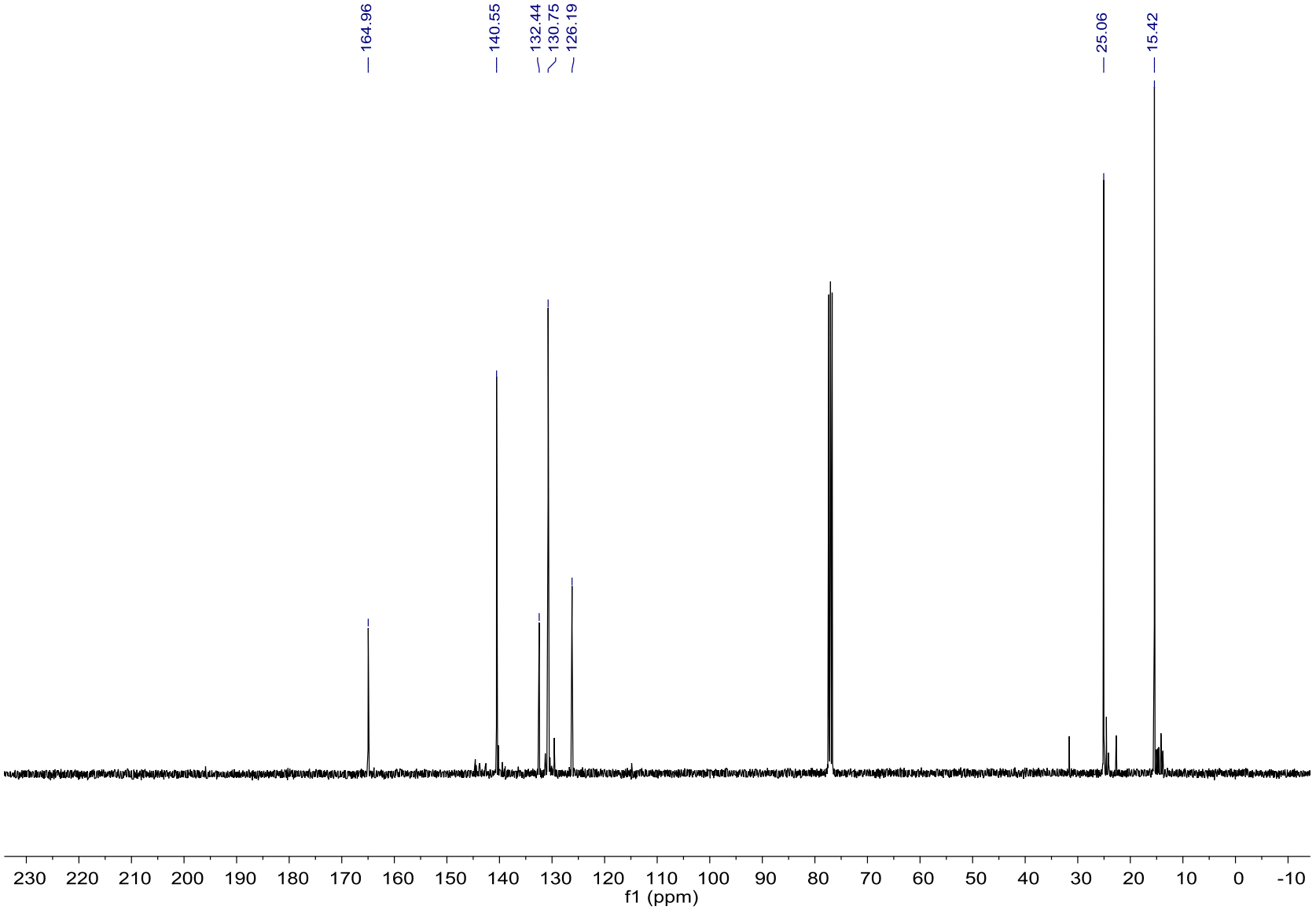
S45 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium* (***4e***).



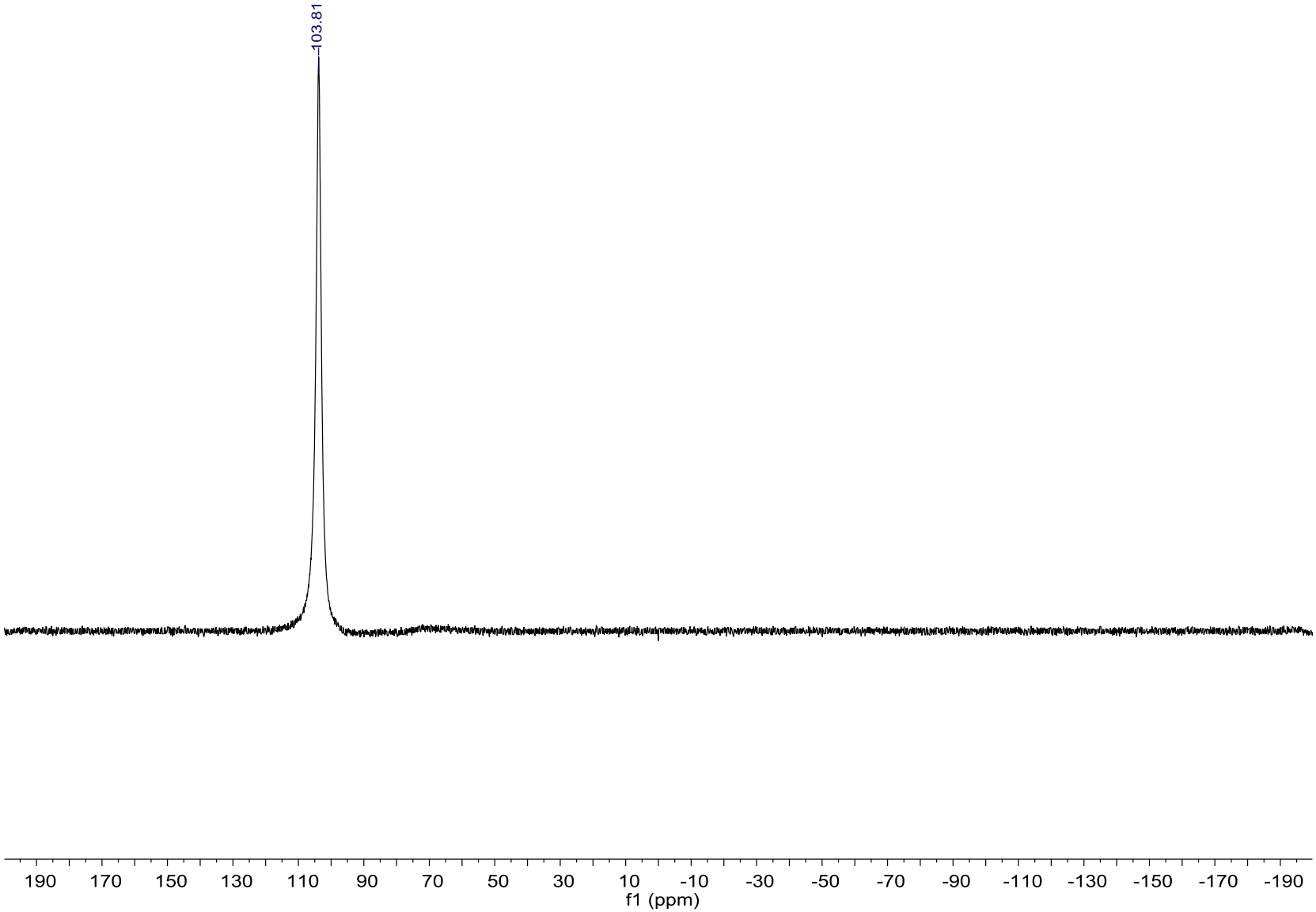
S46 ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium (**4e**).*



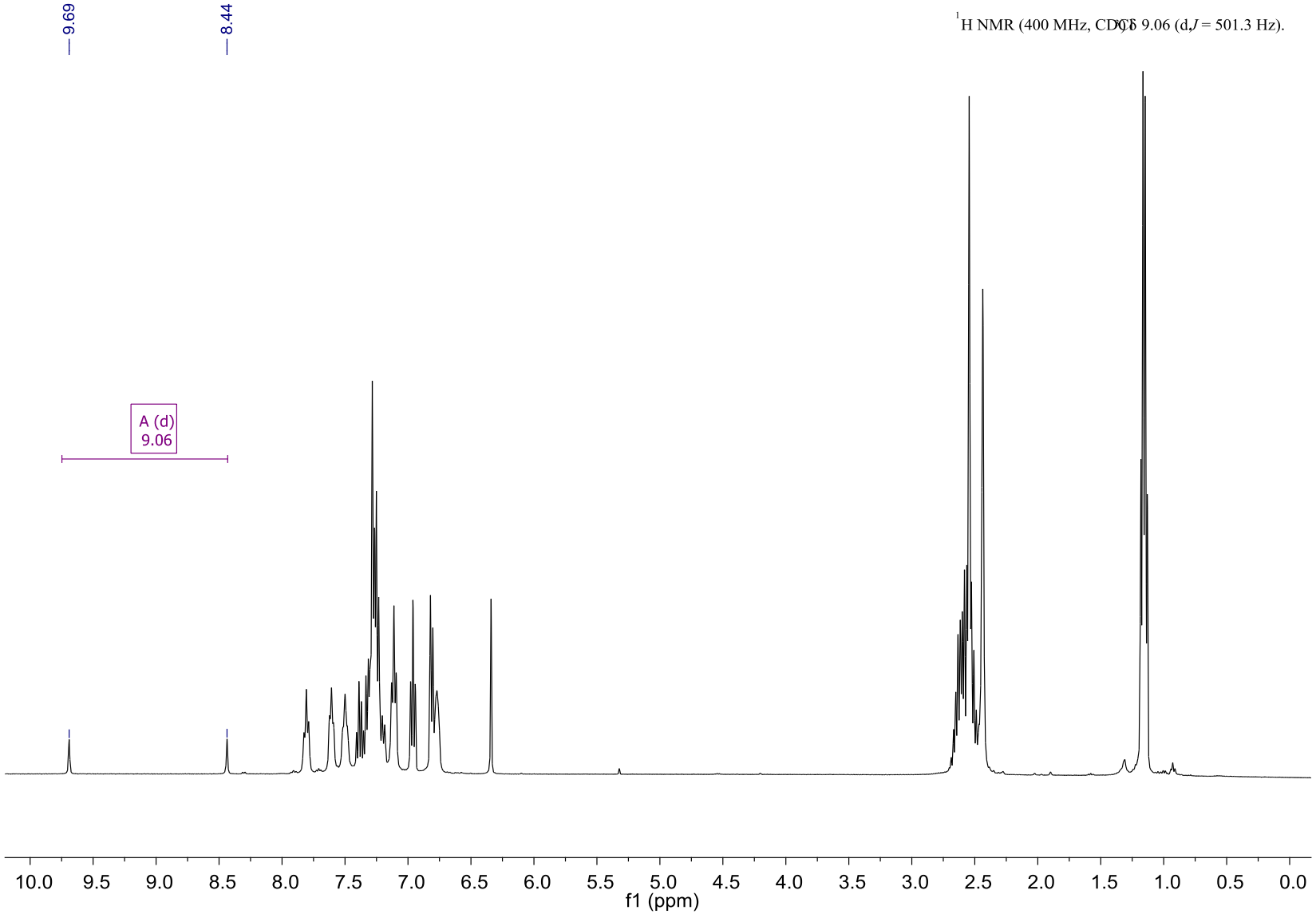
S47 ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium (**4e**).*



S48 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of *2,2-dichloro-1,3-bis(2,6-diethylphenyl)-2H-1,3l4,2l4-diazaborol-1-ium* (***4e***).

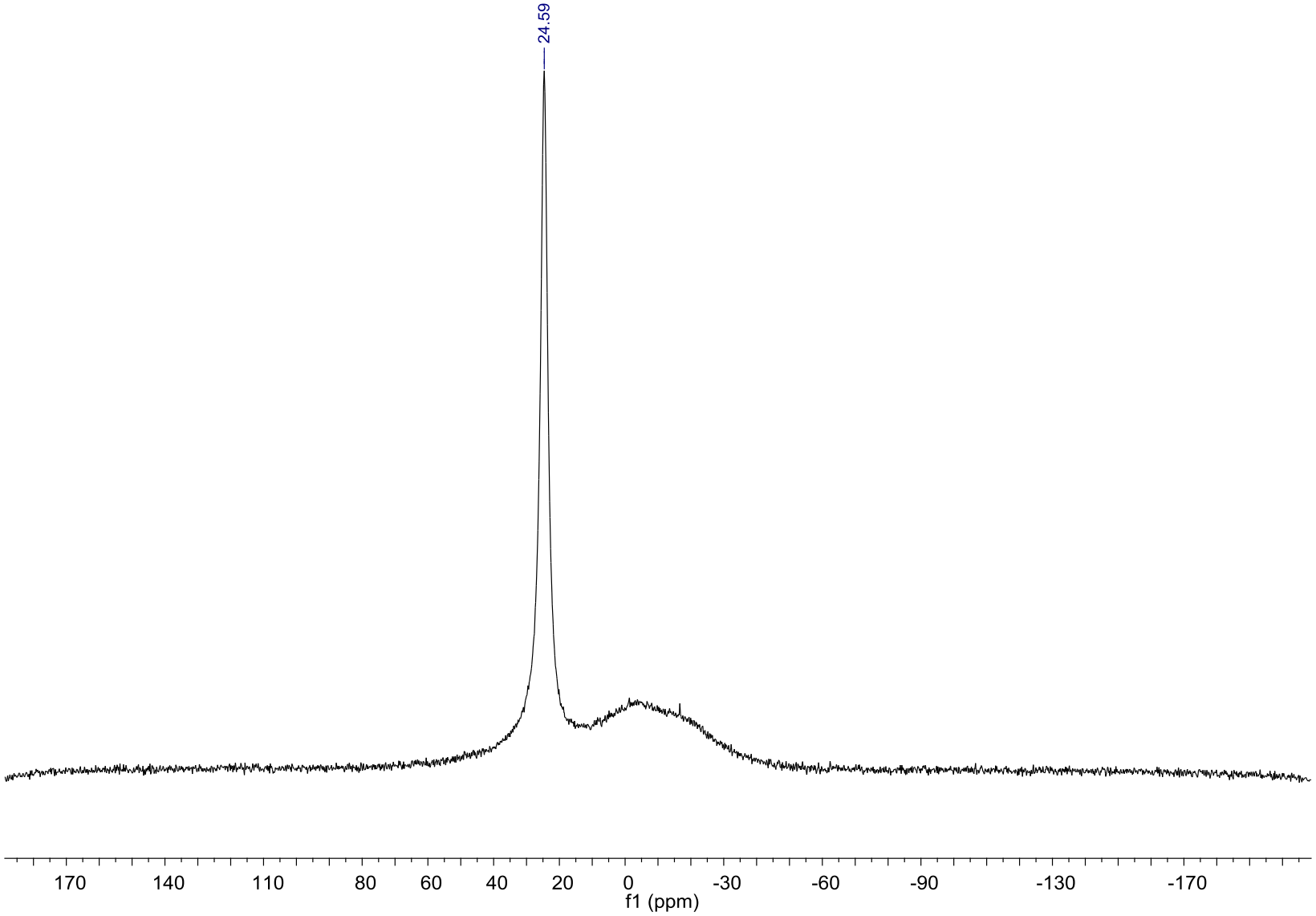


S49 *in situ* ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of the reaction of **3a** with tri(*o*-tolyl)phosphine.

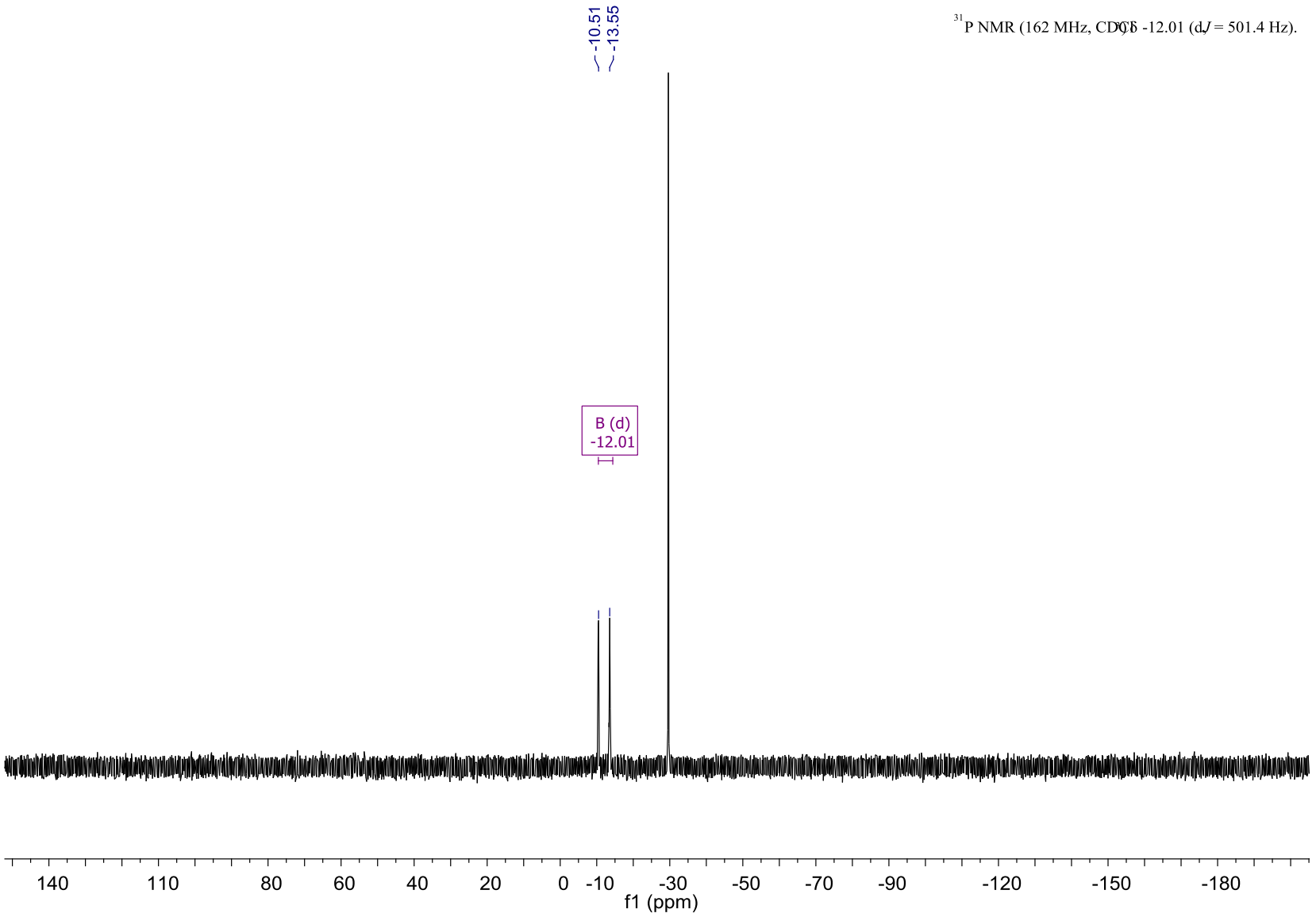


^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 501.3 Hz).

S50 *in situ* ^{11}B NMR (400 MHz, $CDCl_3$, 298 K) spectrum of the reaction of **3a** with tri(*o*-tolyl)phosphine.

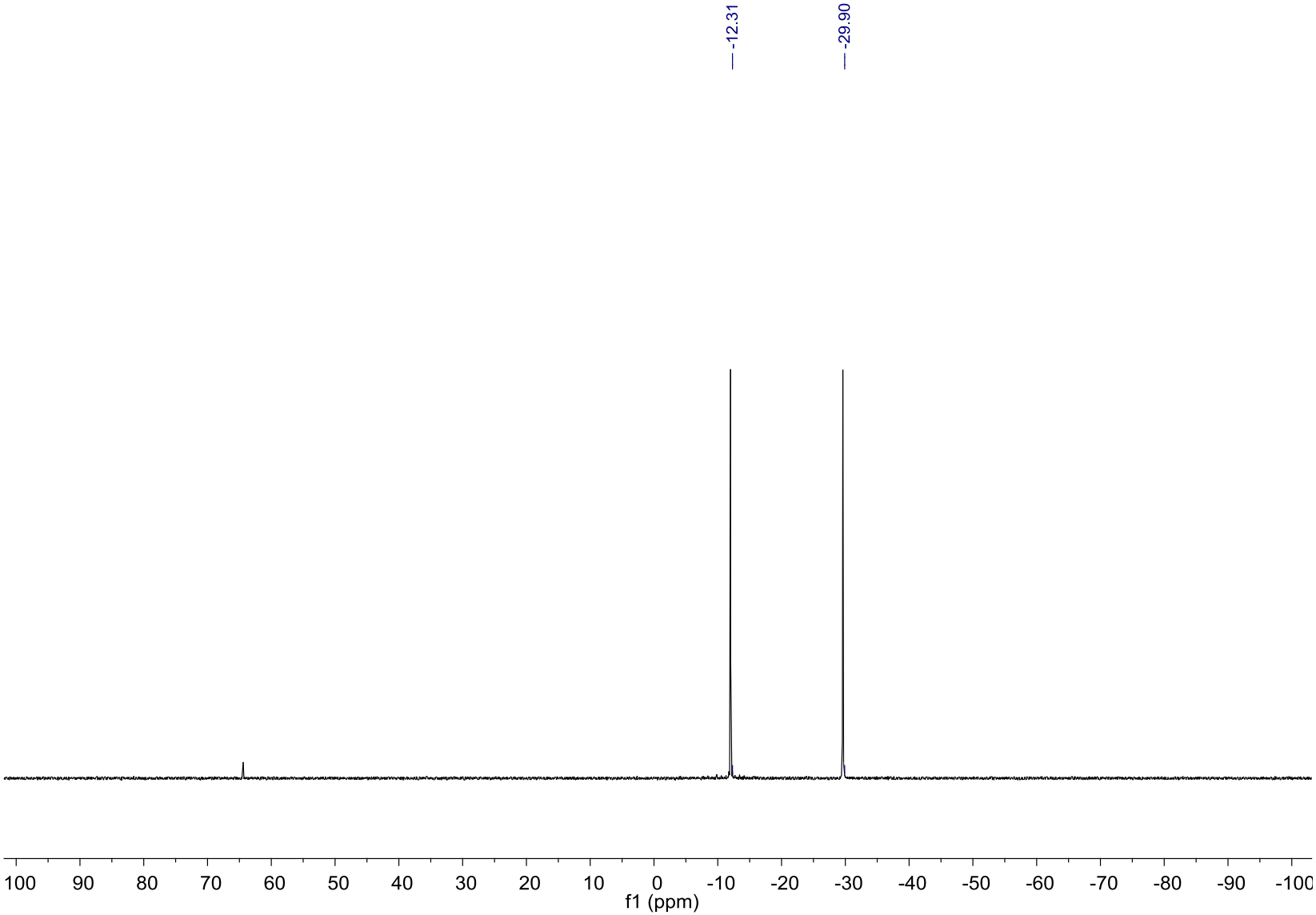


S51 *in situ* ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of the reaction of **3a** with tri(*o*-tolyl)phosphine.

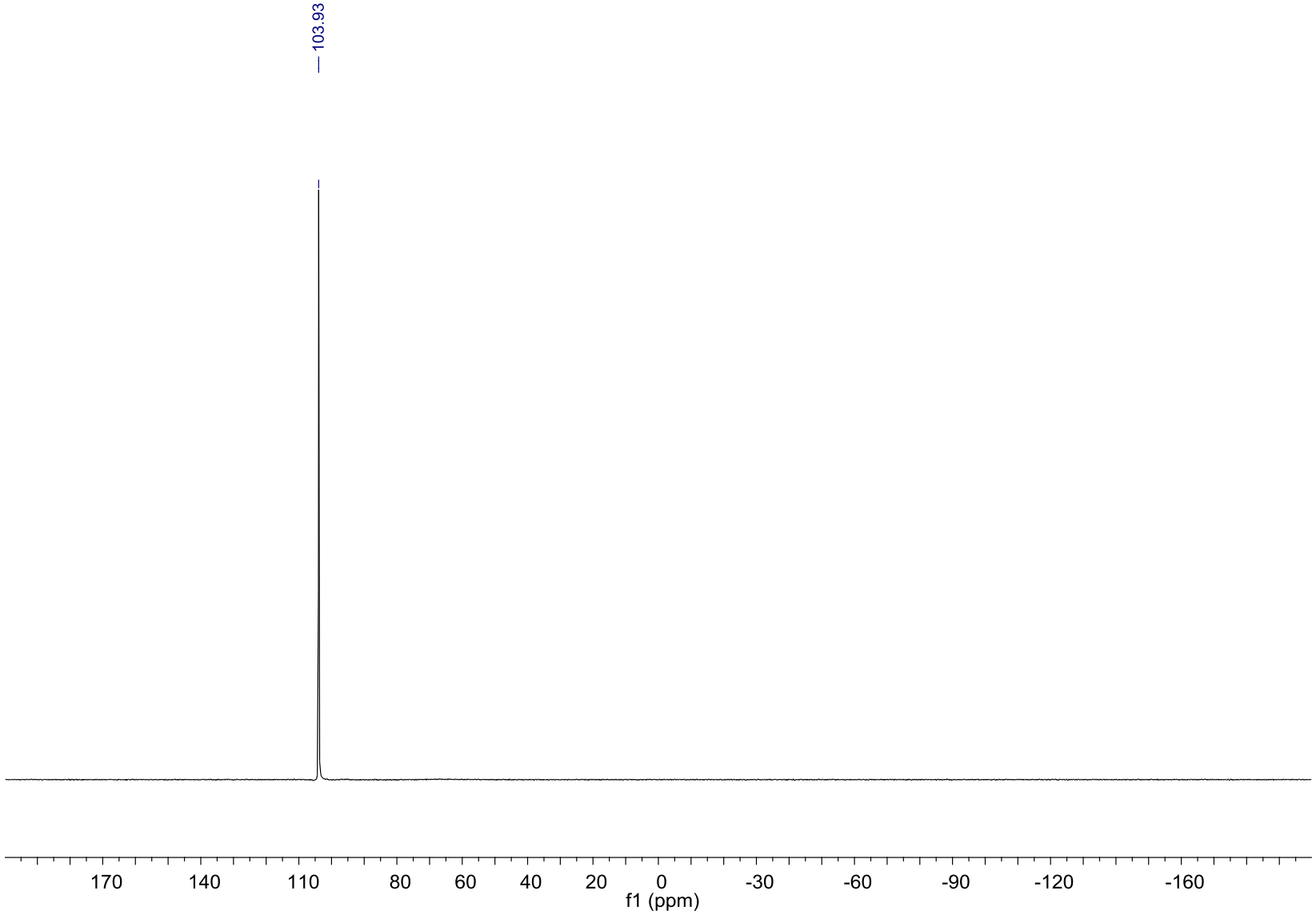


^{31}P NMR (162 MHz, $CDCl_3$) δ -12.01 (d, *J* = 501.4 Hz).

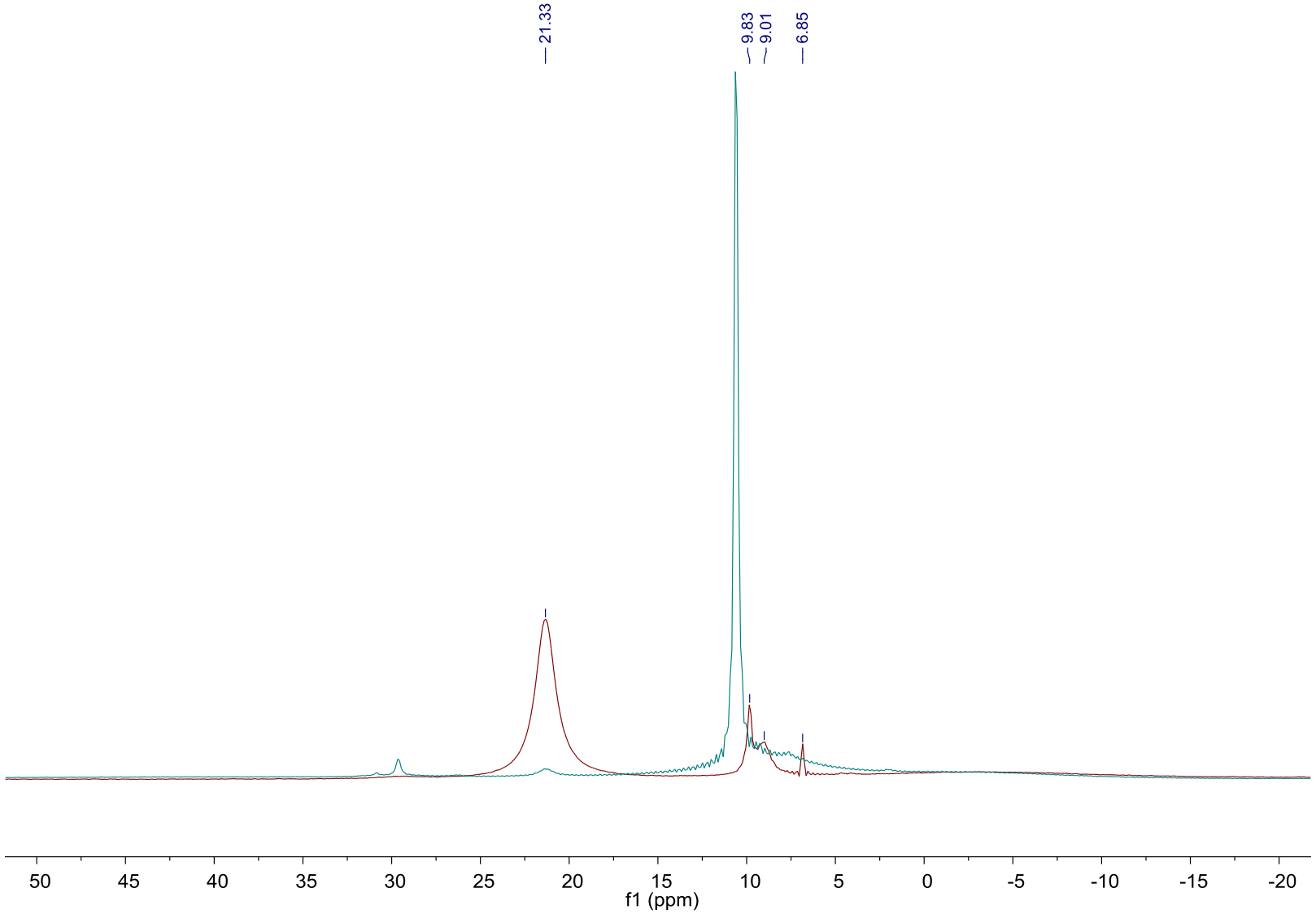
S52 *in situ* $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of the reaction of **3a** with tri(*o*-tolyl)phosphine.



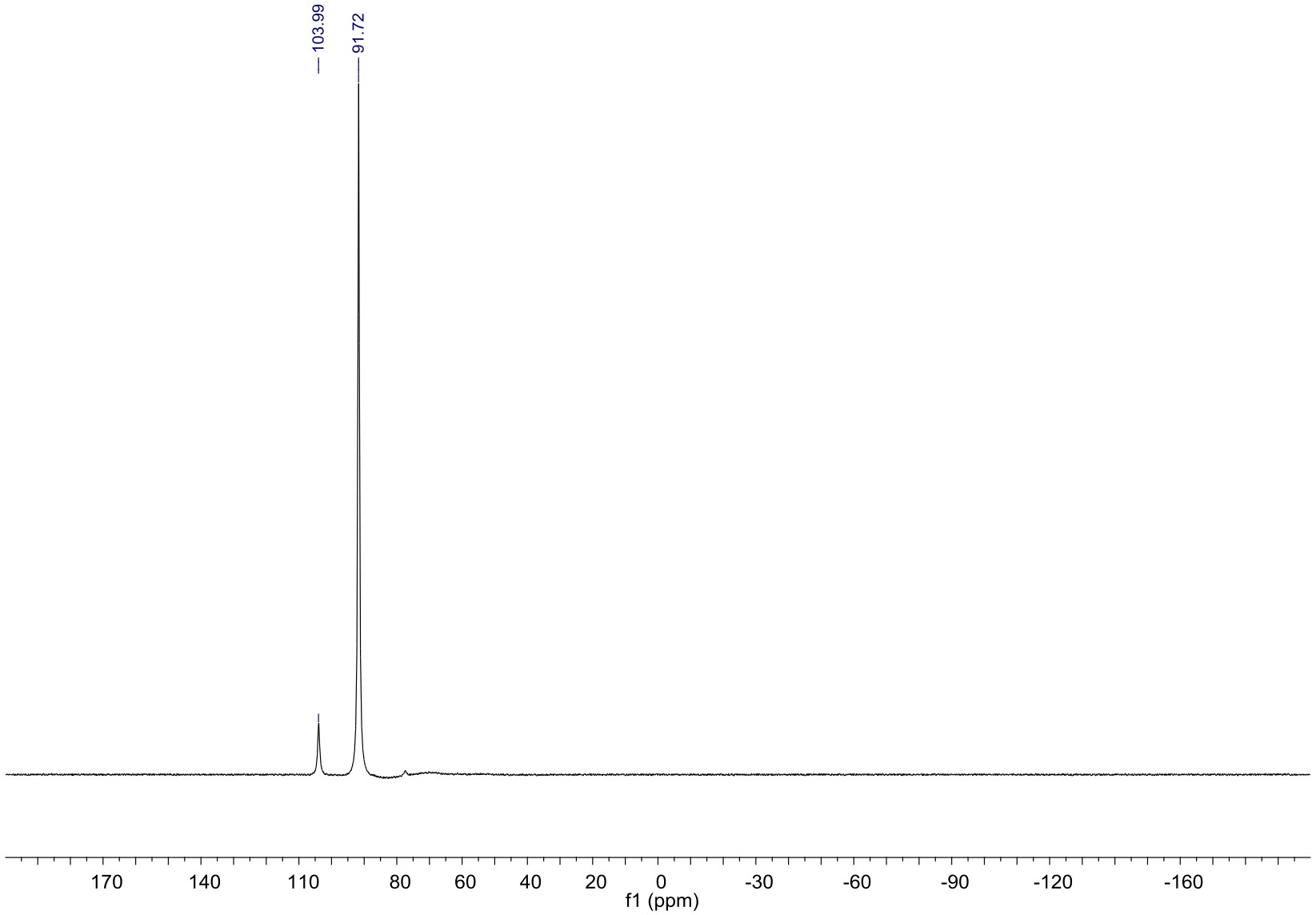
S53 *in situ* ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of the reaction of **3a** with tri(*o*-tolyl)phosphine.



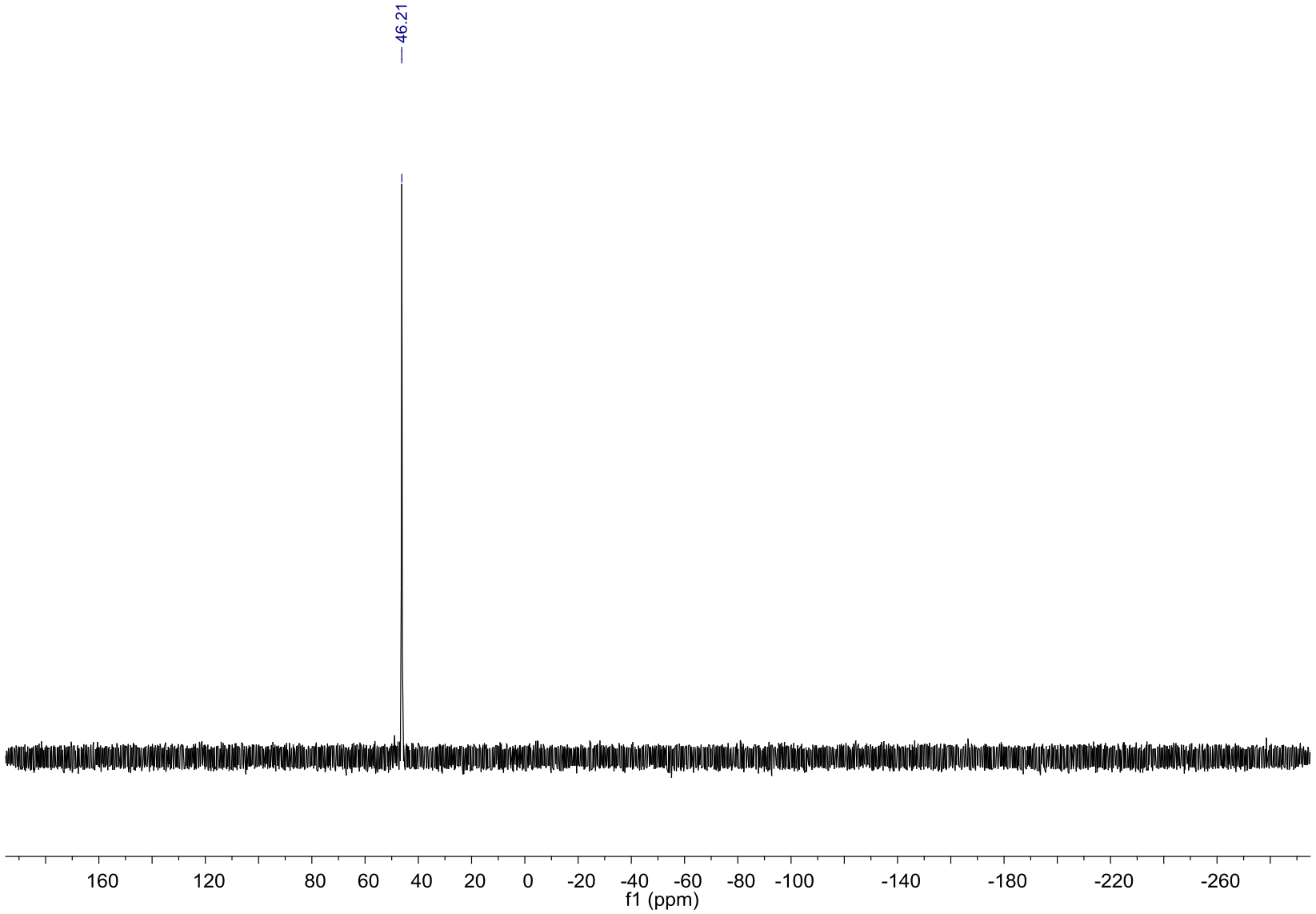
S54 *in situ overlay* ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of the reaction of **1b** with 1 equiv. BCl_3 (red) and 2 equiv. BCl_3 (blue).



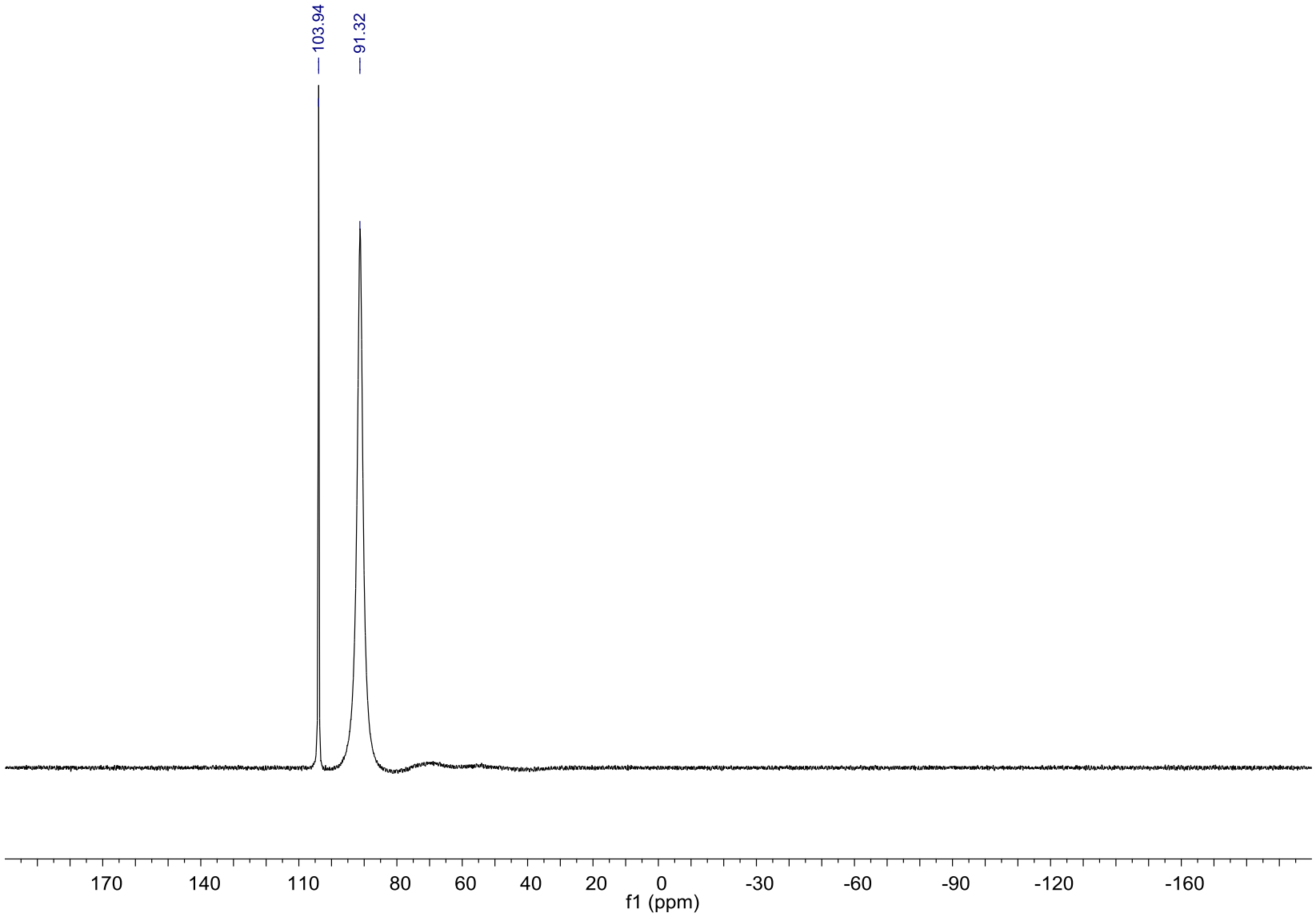
S55 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of **3a** + Ph_3PO



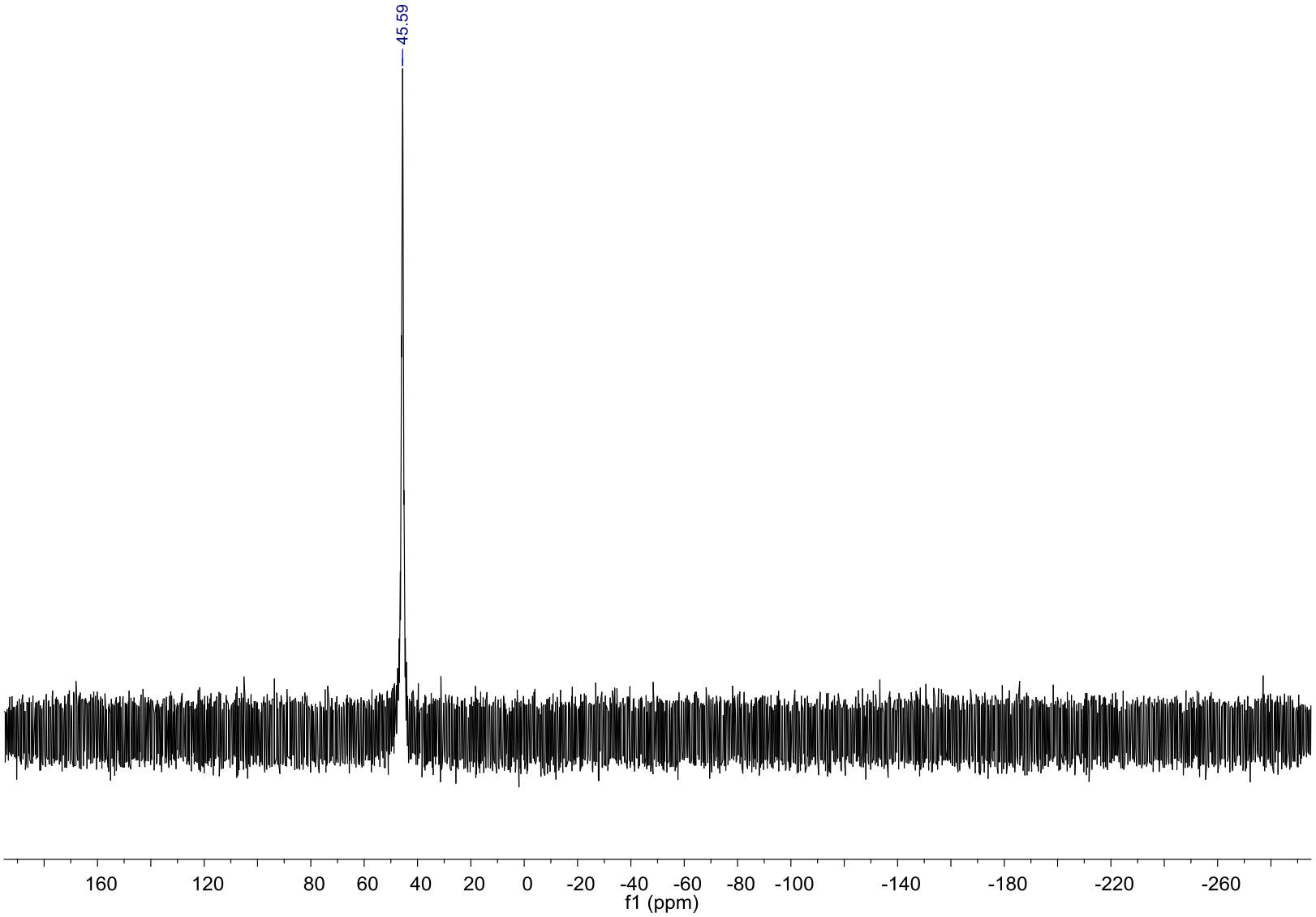
S56 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **3a** + Ph_3PO



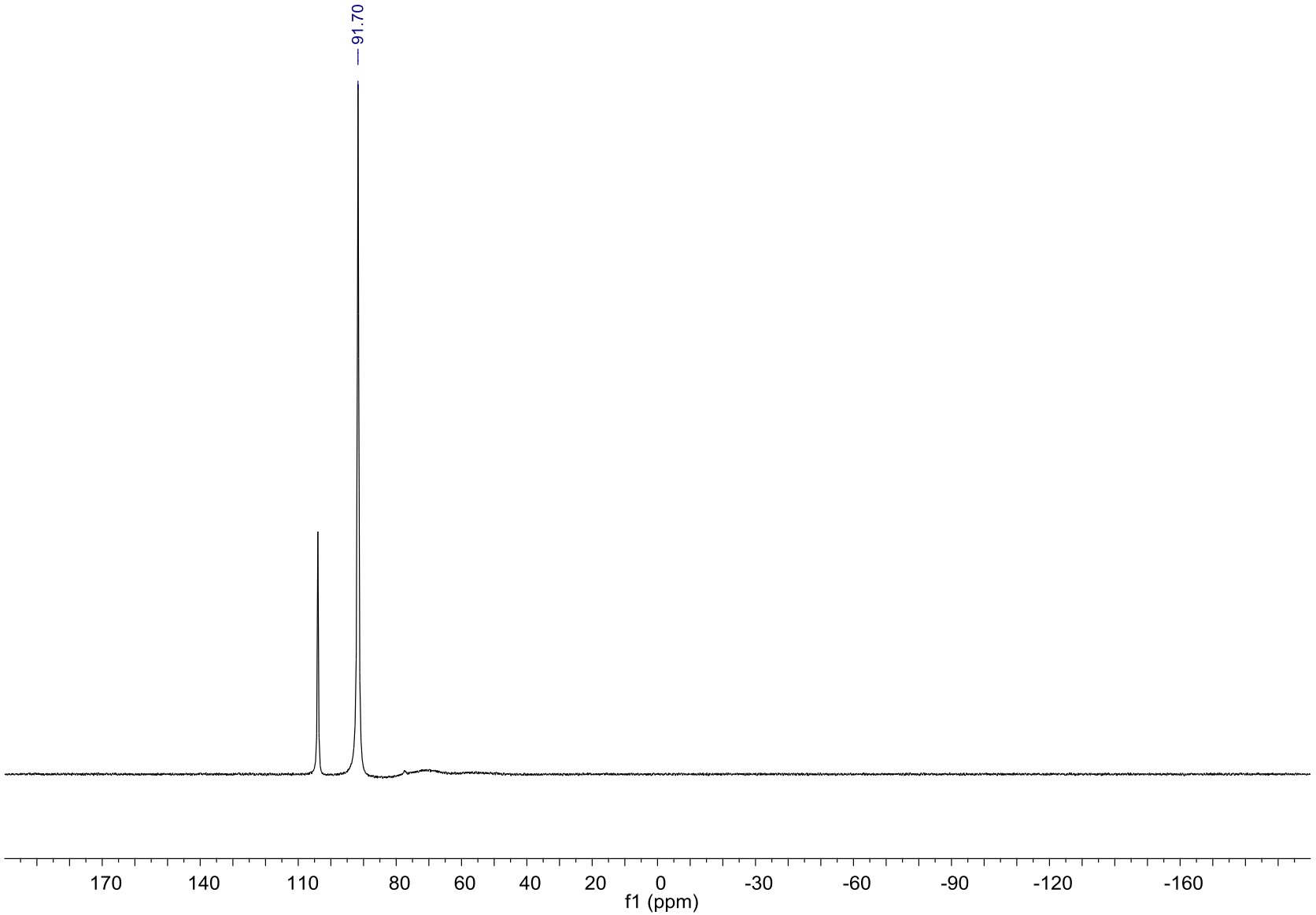
S57 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of **3b** + Ph_3PO



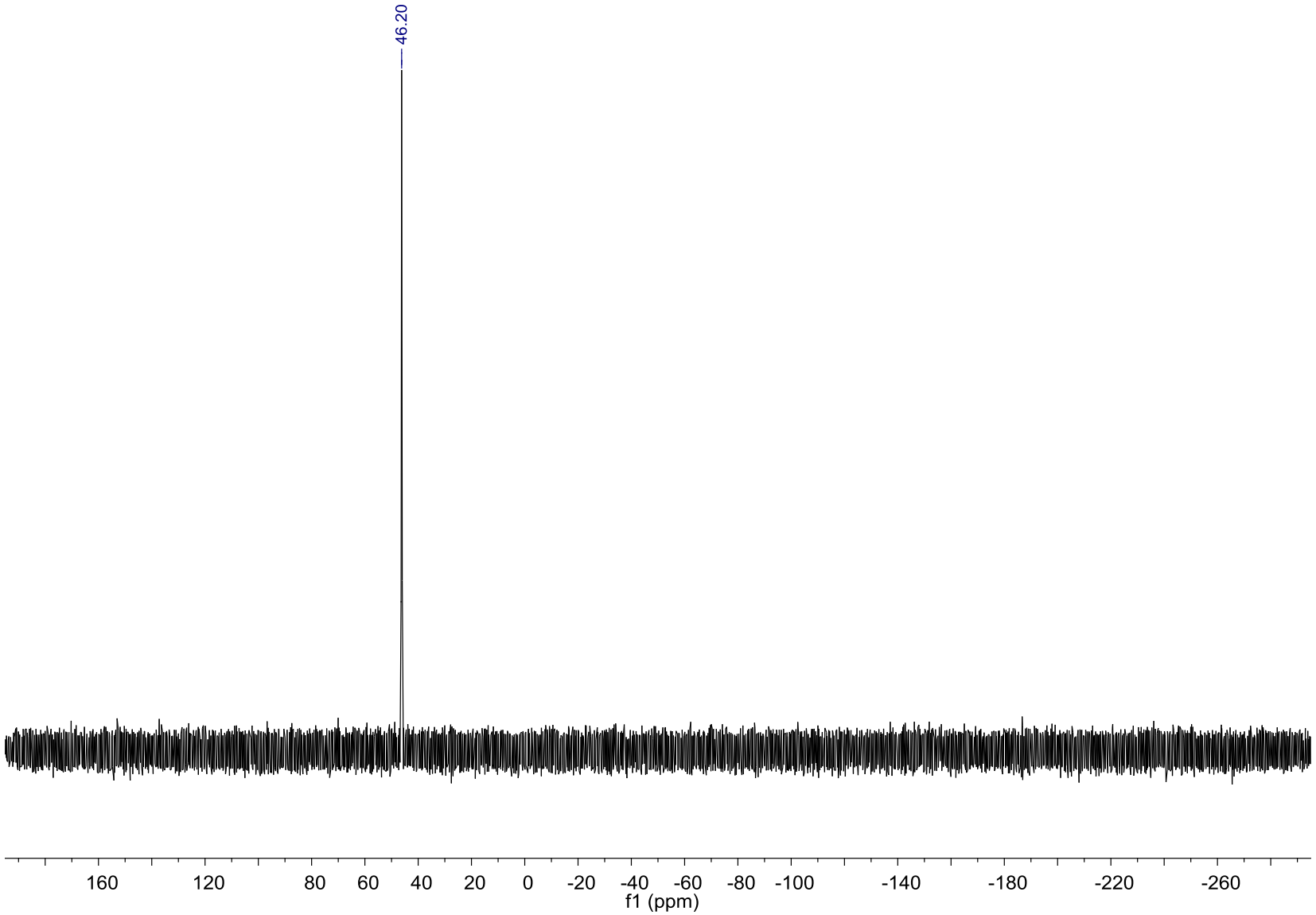
S58 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **3b** + Ph_3PO



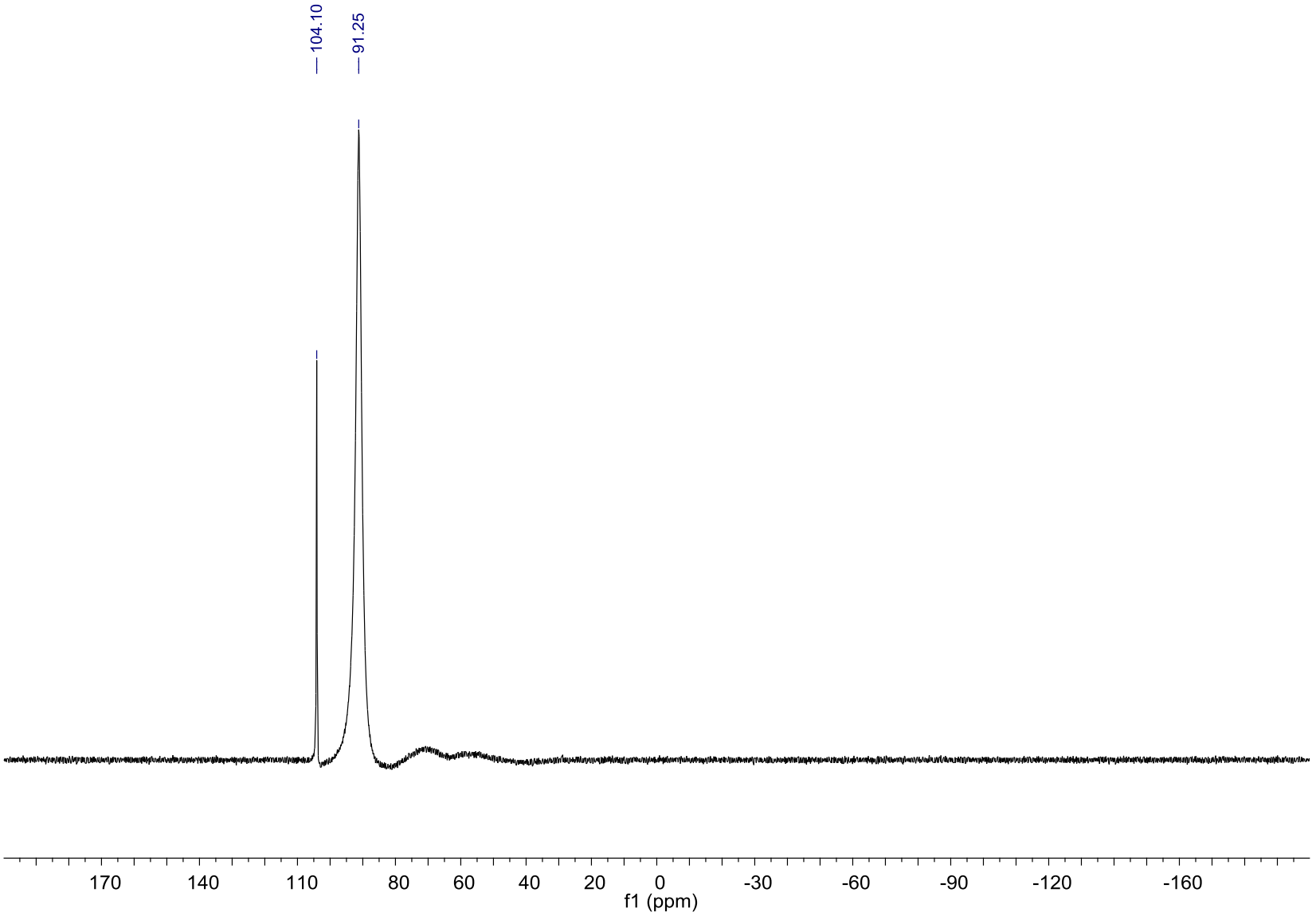
S59 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of **3d** + Ph_3PO



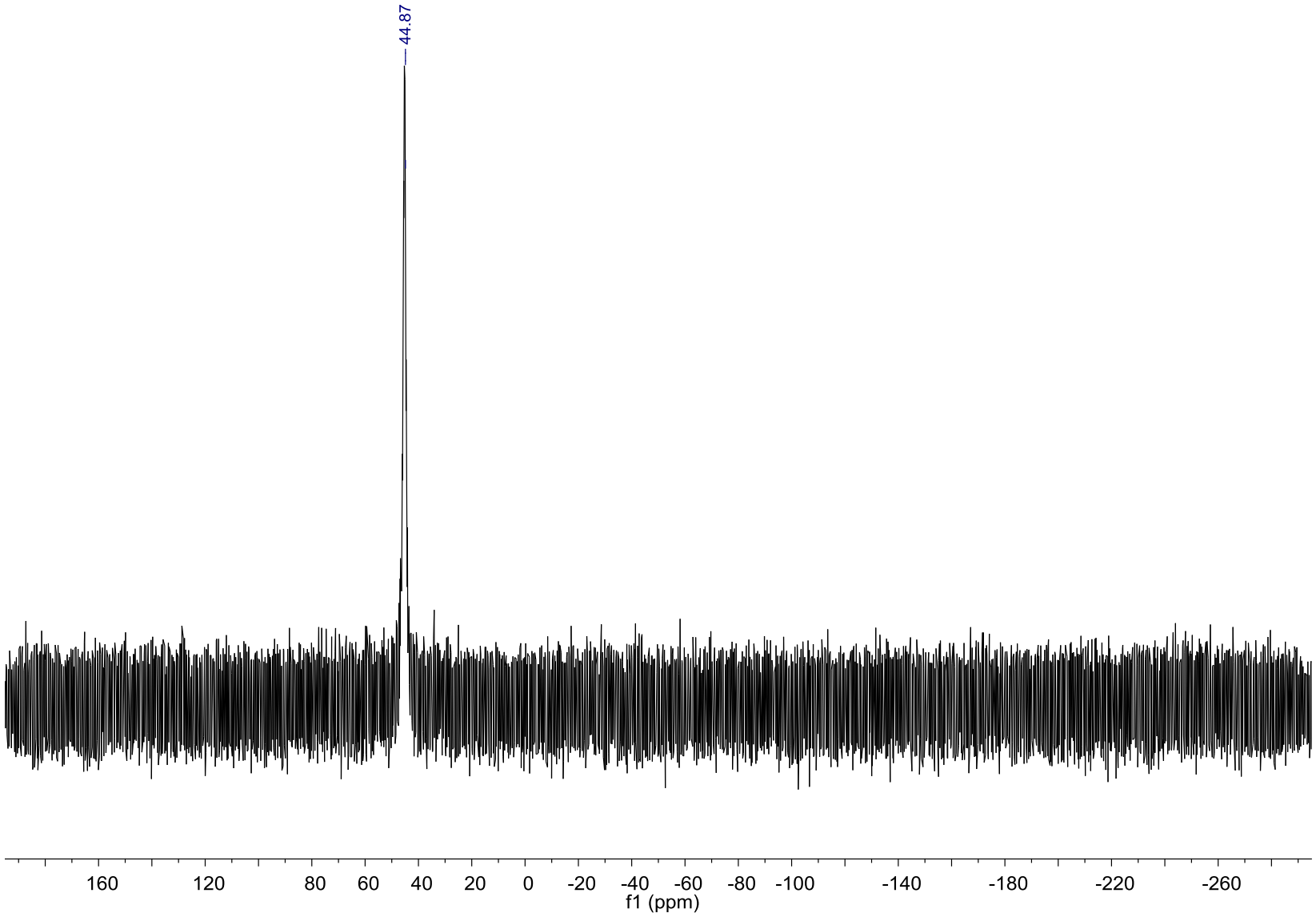
S60 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **3d** + Ph_3PO



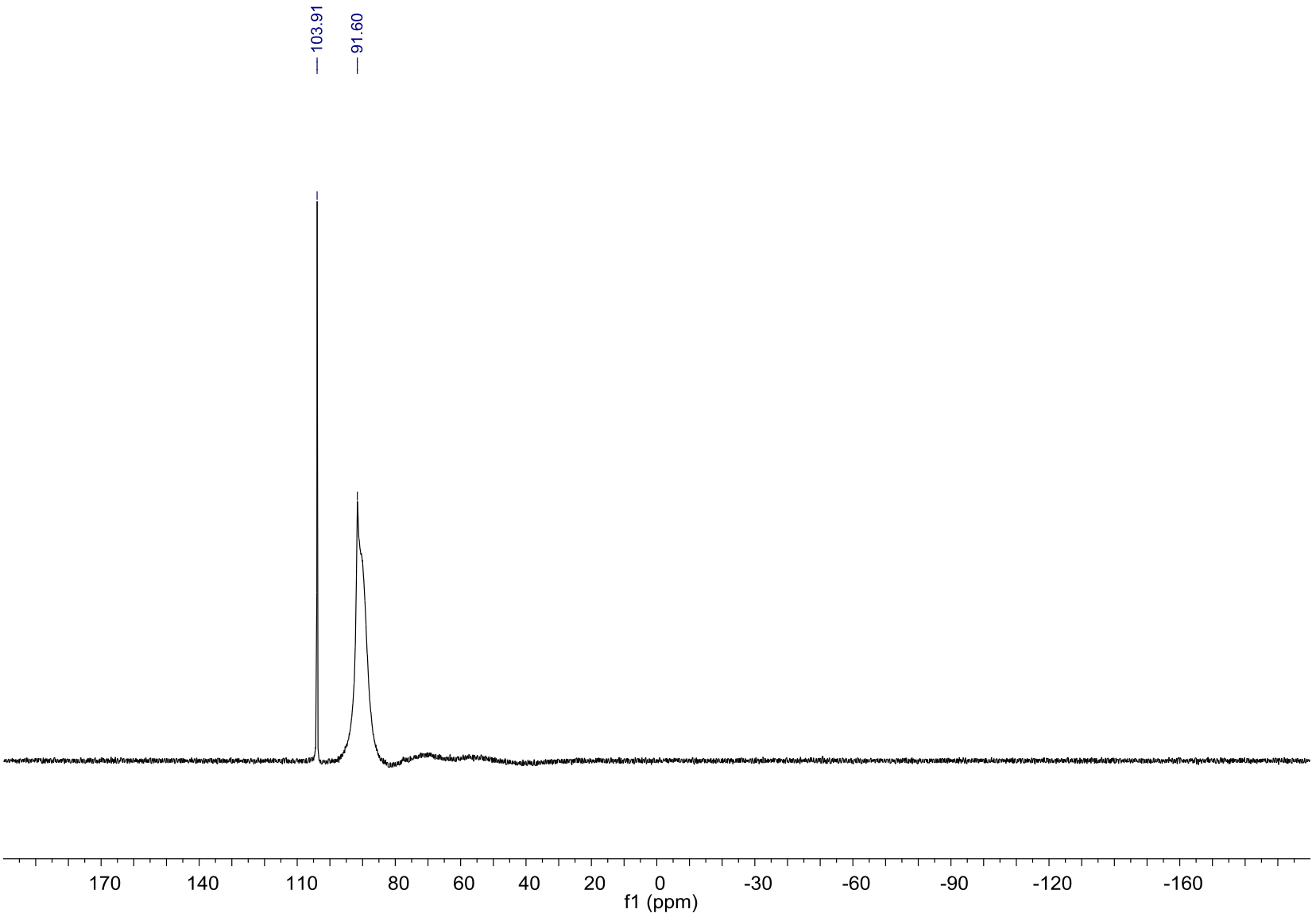
S61 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of **3e** + Ph_3PO



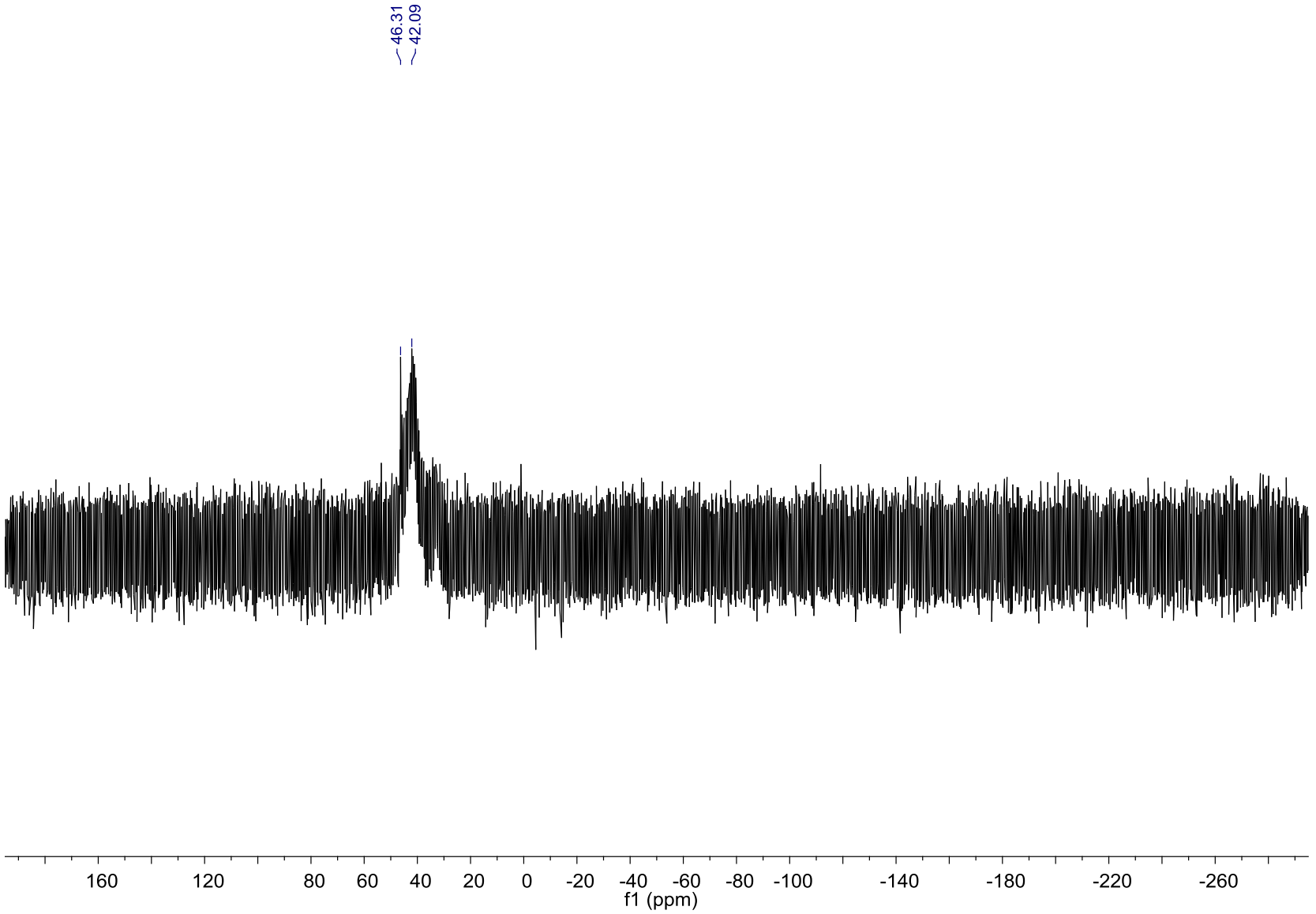
S62 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **3e** + Ph_3PO



S63 ^{27}Al NMR (104 MHz, $CDCl_3$, 298 K) spectrum of $AlCl_3$ + Ph_3PO



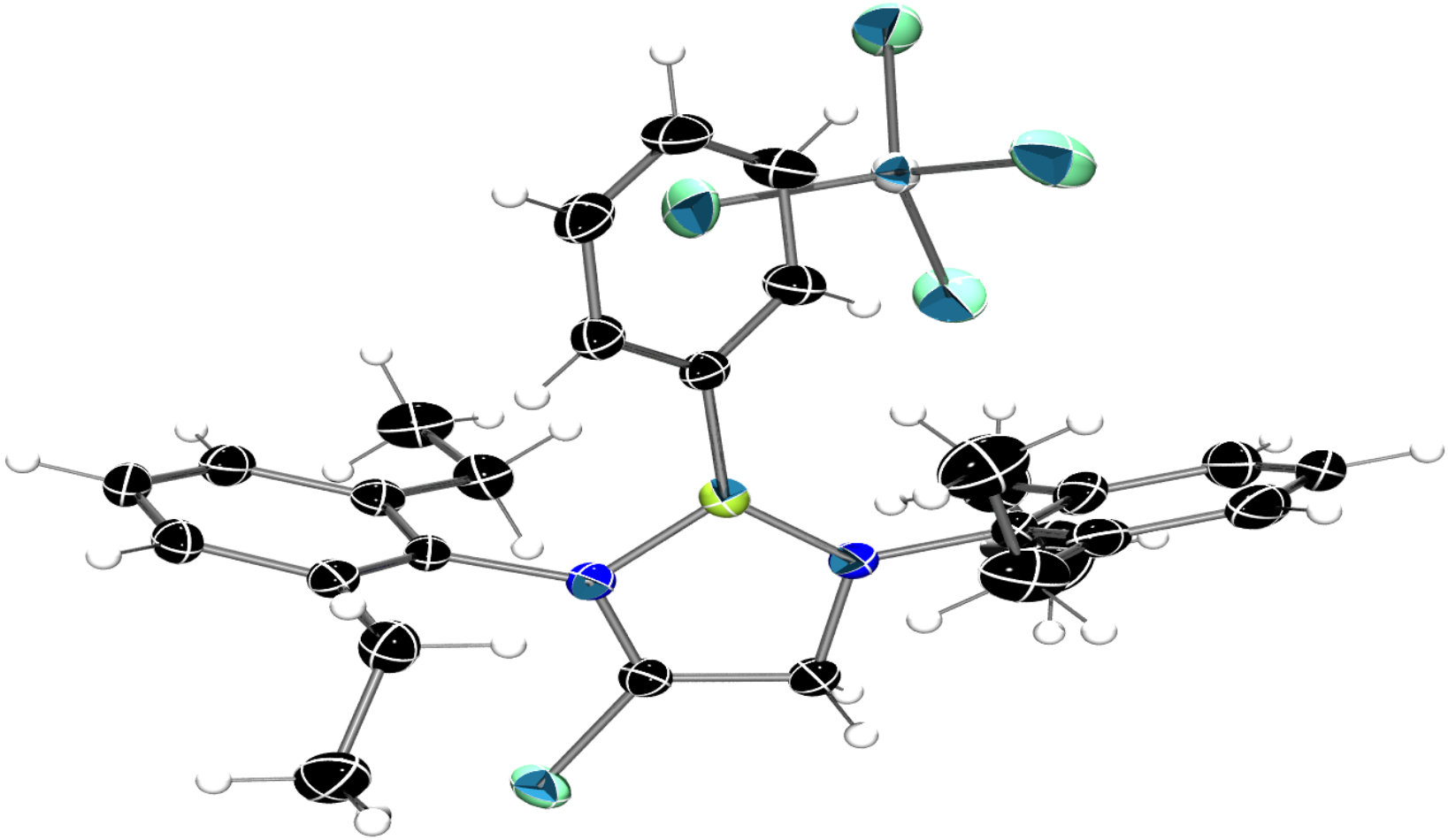
S64 ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of $AlCl_3$ + Ph_3PO



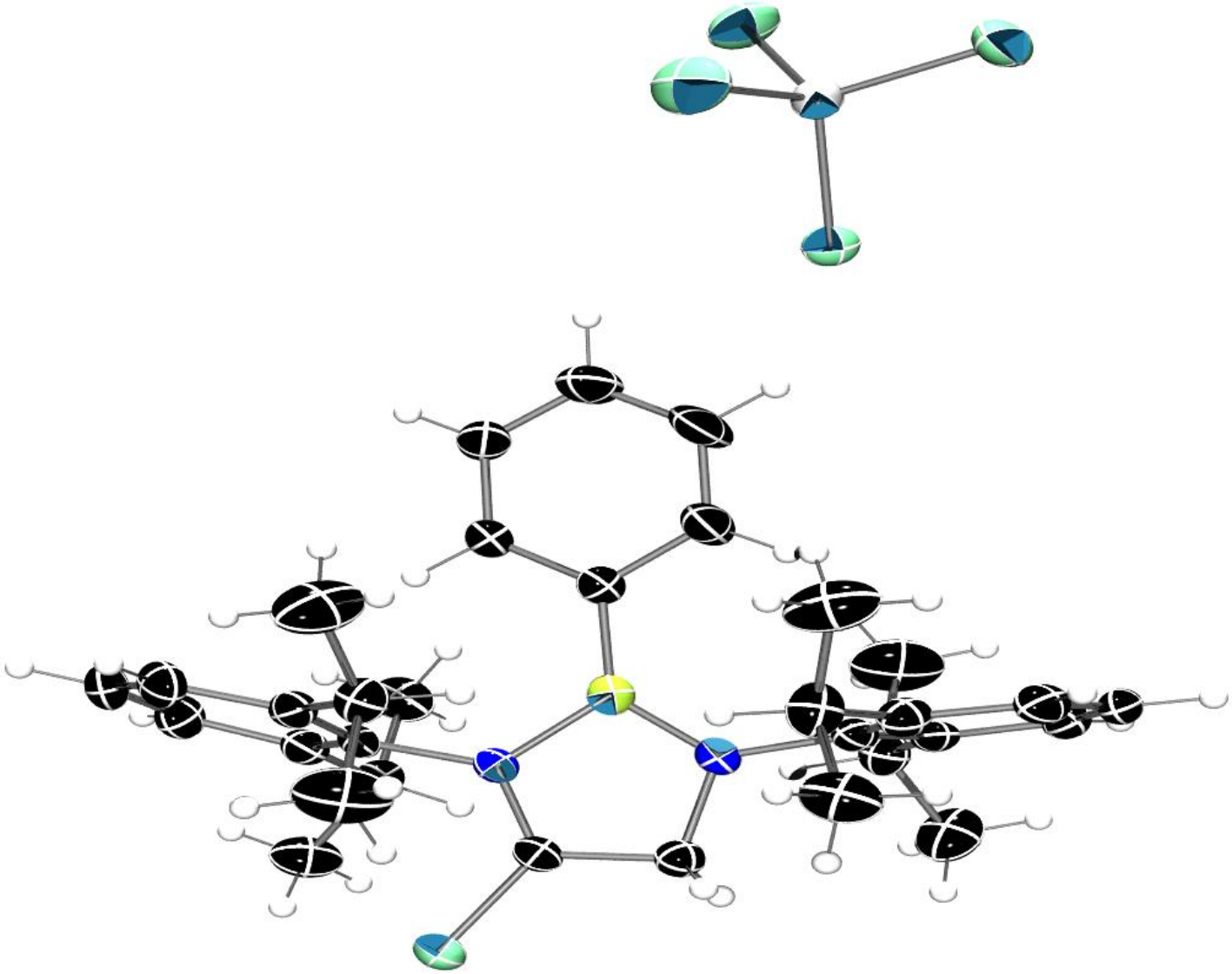
3. Crystallographic studies.

3.1 Thermal ellipsoid plots

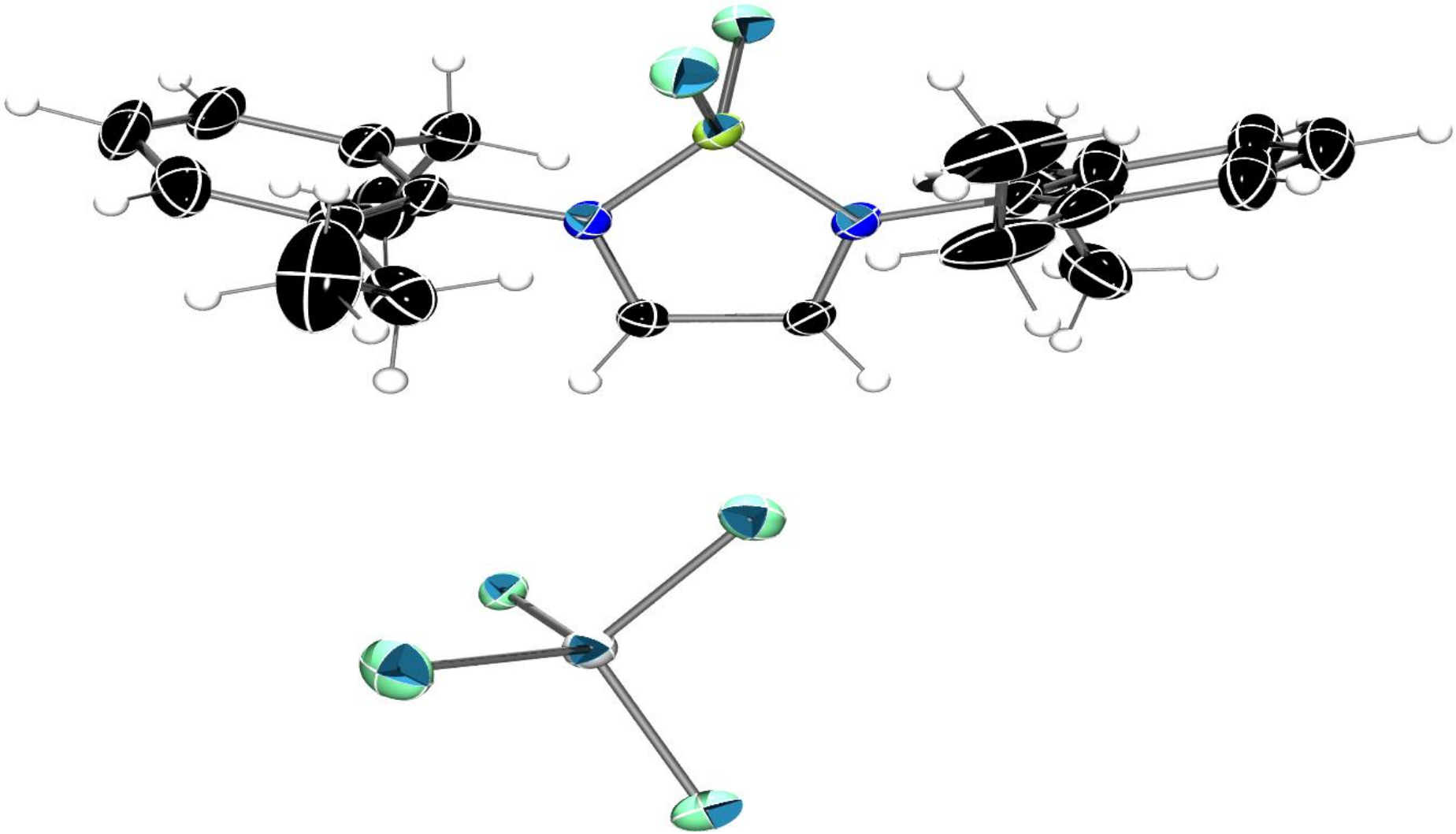
S65 Thermal ellipsoid of 3**a** (ellipsoid probability 50 %). C: black, N: blue, B: yellow-green, H: white, Al: grey, Cl: aquamarine.



S66 Thermal ellipsoid of **3d** (ellipsoid probability 50 %). C: black, N: blue, B: yellow-green, H: white, Al: grey, Cl: aquamarine.



S67 Thermal ellipsoid of **4a** (ellipsoid probability 50 %). C: black, N: blue, B: yellow-green, H: white, Al: grey, Cl: aquamarine.



3.2 Refinement data

Single crystals of **3a** and **3d** were grown under an inert atmosphere. Crystallographic studies were undertaken of a single crystal mounted in paratone and studied on an Agilent SuperNova Dual Atlas three-circle diffractometer using Cu-Kα or Mo-Kα radiation and a CCD detector. Measurements were carried out at 150(2) K or 100(2) K (**3d**) with temperatures maintained using an Oxford cryostream unless otherwise stated. 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.[2] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[3] A summary of crystallographic data are available as ESI and the structures deposited with the Cambridge Structural Database (CCDC deposition numbers 1499077 (**3a**), 1499078 (**3d**), 1499079 (**4a**)). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S1. Crystallographic data for **3a** and **3d**.

Compound	**3a**	**3d**
Empirical Formula	$C_{28}H_{33}AlBCl_5N_2$	$C_{32}H_{41}AlBCl_5N_2$
Crystal System	Triclinic	Orthorhombic
Space Group	*P-1*	$P2_12_12$
a/Å	9.7882(4)	18.9942(4)
b/Å	11.2460(5)	18.2174(4)
c/Å	14.7984(6)	10.5733(2)
α/°	88.786(4)	90
β/°	79.559(4)	90
γ/°	74.904(4)	90
V/Å^3	1546.35(12)	3658.63(15)
Z	2	4
T /K	150(2)	100(2)
D_c/g.cm^{-3}	1.316	1.214
Crystal size/mm	0.354 x 0.252 x 0.236	0.070 x 0.050 x 0.040
Total data	12778	41108
Unique data	7336	6461
R_{int}	0.0373	0.0573
$R_1[F^2>2\ \sigma(F^2)]$	0.0451	0.0350
wR2 (all data)	0.1168	0.0843
GoF	1.006	1.023
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.631/0.656	-0300/0.333
CCDC code	1499077	1499078

4. Computational studies.

All geometry optimisations were undertaken using the B3LYP functional[4] and 6-31G* basis set[5] within Gaussian 09.[6] Subsequent single point calculations were undertaken using the B3LYP functional and larger 6-311G* basis set. In addition, partial charges were determined using an NBO analysis.[7]

Figure S68. Overlay of geometry optimised structure and experimental solid-state crystal structure of **3a** (left) and **4a** (right)**.**

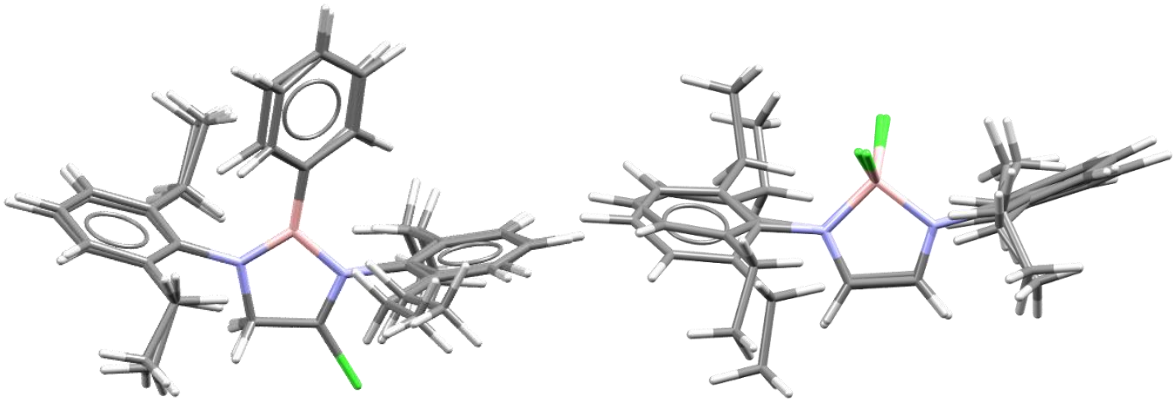
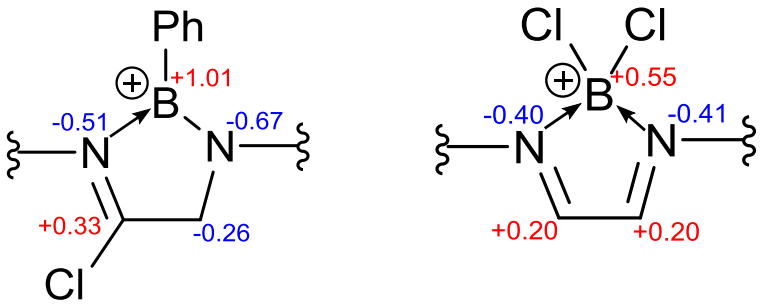


Figure S69. Key NBO charge distributions for **3a** (left) and **4a** (right)



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