Supporting Information

Borane Catalysed Cyclopropenation of Arylacetylenes

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Table of Content

1. Experimental

1.1 General experimental

Except for 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, ambient temperature reactions, product recovery and sample preparation for analysis. The solvents dichloromethane, hexane, and acetonitrile were dried by employing a Grubbs-type column system (Innovative Technology) or a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. Anhydrous (with Sure/Seal) 1,2-dichloroethane (1,2-DCE) was purchased from Merck and dried over molecular sieves before use. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. All the triarylfluoroboranes were prepared as per the standard literature reports.[1] Thin-layer chromatography (TLC) was performed on pre-coated aluminum sheets of Merck silica gel 60 F254 (0.20 mm). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance II 400 or Bruker Avance 500 spectrometers. 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. 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 standard. NMR spectra were referenced to $CFCl_3$ (^{19}F).[2] The description of signals includes s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet, br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). ^{13}C NMR was measured as ^{1}H decoupled. All spectra were analysed assuming a first order approximation. IR-Spectra were measured on a Shimadzu IRAffinity-1 photo-spectrometer. Mass spectra were measured on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer. Ions were generated by the Atmospheric Solids, Analysis Probe (ASAP), GC analysis, Electrospray (ES) or Electron Ionisation (EI). The molecular ion peaks values quoted for either molecular ion (M^+), molecular ion plus hydrogen ($M+H^+$).

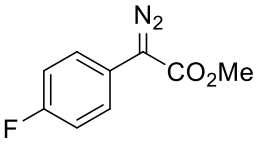
1.2 Synthesis of diazoesters

1.2.1 ***General procedure a*****:** 1,8-Diazabicyclo[5.4.0]undec-7-ene (1.5 equiv) (unless otherwise mentioned) was added dropwise to a solution of corresponding ester compound (1 equiv) and 4-acetamidobenzenesulfonyl azide (1.2 equiv) in anhydrous CH_3CN (40 mL) at 0 °C. After the complete addition, the ice bath was removed, and the reaction mixture was stirred at room

temperature overnight under a nitrogen atmosphere. Afterwards, the reaction was quenched with saturated NH_4Cl (aq.) solution (30 mL) and the organic compounds were extracted with diethyl ether (3 × 30 mL). The combined organic fractions were washed with brine solution (1 × 30 mL), dried over $MgSO_4$, and concentrated using *vacuo*. The crude compound was purified *via* column chromatography using silica gel (Merck, 60 Å, 230–400 mesh particle size) and hexane/ethyl acetate as eluent.

1.2.2 Synthesis and spectral characterisation of diazoesters

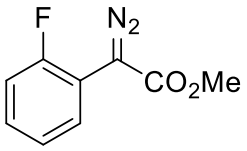
Synthesis of methyl 2-diazo-2-(4-fluorophenyl)acetate (**1a**)[3]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (4 mL, 26.7 mmol), 4-acetamidobenzenesulfonyl azide (5.14 g, 21.4 mmol), and methyl 2-(4-fluorophenyl)acetate (3.00 g, 17.8 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**1a**) was obtained as a yellow solid. Yield: 2.90 g, 14.9 mmol, 84%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.46–7.42 (m, 2H, Ar–CH), 7.11–7.07 (m, 2H, Ar–CH), 3.86 (s, 3H, COOMe); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.8 (C=O), 161.2 (d, $J_{C–F}$ = 246.3 Hz), 126.0 (d, $J_{C–F}$ = 8.0 Hz), 121.3 (d, $J_{C–F}$ = 3.2 Hz), 116.1 (d, $J_{C–F}$ = 22.0 Hz), 52.2 (COOMe); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -116.23 (Ar–F).

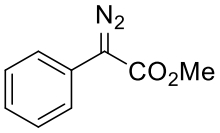
Synthesis of methyl 2-diazo-2-(2-fluorophenyl)acetate (**1b**)[3]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (2.8 mL, 17.8 mmol), 4-acetamidobenzenesulfonyl azide (4.30 g, 17.8 mmol), and methyl 2-(2-fluorophenyl)acetate (2.00 g, 11.9 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**1b**) was obtained as a yellow solid. Yield: 2.00 g, 10.4 mmol, 87%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.69 (td, J = 7.8, 1.9 Hz, 1H, Ar–CH), 7.26–7.21 (m, 1H, Ar–CH), 7.20–7.17 (m, 1H, Ar–CH), 7.10–7.06 (m, 1H, Ar–CH), 3.86 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.8 (C=O), 159.5 (d, $J_{C–F}$ = 247.4 Hz), 129.5, 128.8 (d, $J_{C–F}$ = 8.3 Hz), 124.7 (d, $J_{C–F}$ = 3.5 Hz), 115.9 (d, $J_{C–F}$ = 21.2 Hz), 113.9 (d, $J_{C–F}$ = 11.9 Hz), 52.3 (COOMe); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -114.15 (Ar–F).

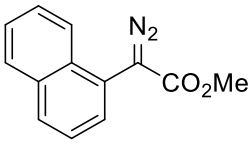
Synthesis of methyl 2-diazo-2-phenylacetate (**1c**)[3]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (4.5 mL, 29.9 mmol), 4-acetamidobenzenesulfonyl azide (5.76 g, 23.9 mmol), and methyl 2-phenylacetate (3.00 g, 19.9 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**1c**) was obtained as a red oil. Yield: 3.00 g, 17.0 mmol, 85%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.48 (d, *J* = 8.0 Hz, 1H, Ar–CH), 7.40–7.37 (m, 1H, Ar–CH), 7.20–7.17 (m, 1H, Ar–CH), 3.87 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.7 (C=O), 129.0, 125.9, 125.6, 124.1, 52.1 (COOMe).

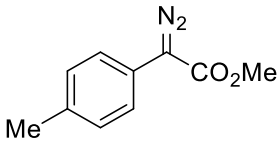
Synthesis of methyl 2-diazo-2-(naphthalen-1-yl)acetate (**1d**)[4]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (2.2 mL, 14.9 mmol), 4-acetamidobenzenesulfonyl azide (2.88 g, 11.9 mmol), and methyl 2-(naphthalen-1-yl)acetate (2.00 g, 9.9 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**1d**) was obtained as yellow oil. Yield: 1.70 g, 7.5 mmol, 75%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.02 (s, 1H, Ar–CH), 7.86 (d, *J* = 8.8 Hz, 1H, Ar–CH), 7.80 (d, *J* = 8.8 Hz, 2H, Ar–CH), 7.54 (dd, *J* = 8.7, 2.0 Hz, 1H, Ar–CH), 7.50–7.43 (m, 2H, Ar–CH), 3.91 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.9 (C=O), 133.7, 131.5, 128.8, 127.7 (d, *J* = 3.2 Hz), 126.7, 125.9, 122.7, 122.6, 121.9, 52.2 (COOMe).

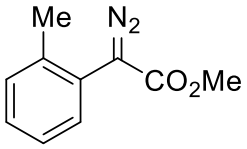
Synthesis of methyl 2-diazo-2-(p-tolyl)acetate (**1e**)[3]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (4.1 mL, 27.4 mmol), 4-acetamidobenzenesulfonyl azide (5.27 g, 21.9 mmol), and methyl 2-(*p*-tolyl)acetate (3.00 g, 18.2 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**1e**) was obtained as a red oil. Yield: 2.8 g, 14.7 mmol, 81%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.28–7.25 (m, 2H, Ar–CH), 7.11–7.09 (m, 2H, Ar–CH), 3.75 (s, 3H, COOMe), 2.24 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.9 (C=O), 135.8, 129.7, 124.2, 122.2, 51.9 (COOMe), 21.0 (Me).

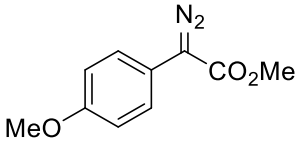
Synthesis of methyl 2-diazo-2-(o-tolyl)acetate (**1f**)[3]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (0.8 mL, 5.3 mmol), 4-acetamidobenzenesulfonyl azide (1.3 g, 5.3 mmol), and methyl 2-(*o*-tolyl)acetate (0.60 g, 3.5 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**1f**) was obtained as an orange oil. Yield: 0.32 g, 1.7 mmol, 49 %.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 7.41–7.36 (m, 1H, Ar–CH), 7.29–7.26 (m, 2H, Ar–CH), 7.20–7.16 (m, 1H, Ar–CH), 3.83 (s, 3H, COOMe), 2.31 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ: 137.8, 131.0, 130.9, 129.0, 126.57, 124.2, 52.3 (COOMe), 20.0 (Me).

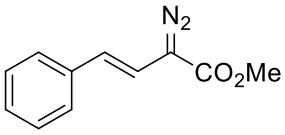
Synthesis of methyl 2-diazo-2-(4-methoxyphenyl)acetate (**1g**)[3]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (3.7 mL, 24.9 mmol), 4-acetamidobenzenesulfonyl azide (4.80 g, 19.9 mmol), and methyl 2-(4-methoxyphenyl)acetate (3.00 g, 16.6 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**1g**) was obtained as a red solid. Yield: 2.9 g, 14.0 mmol, 84%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.39–7.37 (m, 2H, Ar–CH), 6.96–6.93 (m, 2H, Ar–CH), 3.85 (s, 3H, COOMe), 3.81 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 158.2 (C=O), 126.1, 117.0, 114.7, 55.5 (OMe), 52.1 (COOMe).

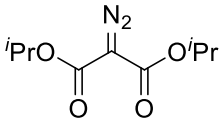
Synthesis of methyl (E)-2-diazo-4-phenylbut-3-enoate (**1h**)[5]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (2.5 mL, 17.0 mmol), 4-acetamidobenzenesulfonyl azide (4.09 g, 17.0 mmol, 1.5 equiv), and methyl (*E*)-4-phenylbut-3-enoate (2.00 g, 11.3 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**1h**) was obtained as a red oil. Yield: 1.8 g, 8.9 mmol, 78%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.25–7.17 (m, 4H, Ar–CH), 7.10–7.06 (m, 1H, Ar–CH), 6.37 (d, J = 16.3 Hz, 1H, CH_2), 6.08 (d, J = 16.3 Hz, 1H, CH_2), 3.72 (s, 3H, COOMe); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.5 (C=O), 136.8, 128.9, 127.1, 125.8, 123.1, 111.2, 52.3 (COOMe).

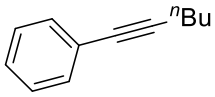
Synthesis of diisopropyl 2-diazomalonate (**1i**)[6]



Synthesised in accordance with *General Procedure a* using triethylamine (2.9 mL, 21.2 mmol, 2 equiv), 4- acetamidobenzenesulfonyl azide (3.06 g, 12.7 mmol), and diisopropyl malonate (2.0 g, 10.6 mmol). The crude compound was purified via column chromatography using hexane/ethyl acetate (80:20 v/v) as eluent. The desired product (**1i**) was obtained as a yellow liquid. Yield: 2.1 g, 9.8 mmol, 92%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 5.15 (hept, *J* = 6.2 Hz, 2H, CH), 1.29 (d, *J* = 6.3 Hz, 12H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 160.7 (C=O), 69.4 (OMe), 22.0 (Me).

1.3 Synthesis and spectral characterisation of aryl acetylenes

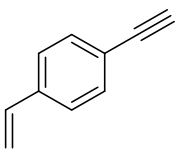
Synthesis of hex-1-ynylbenzene (**2a**)[7]



An oven-dried Schlenk flask was charged with iodobenzene (1.6 mL, 14.7 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (516 mg, 0.73 mmol, 5 mol%), and CuI (280 mg, 1.47 mmol, 10 mol%) and placed under a nitrogen atmosphere. Subsequently, NEt_3 (30 mL) and 1-hexyne (2.0 mL, 17.6 mmol, 1.2 equiv) were added into the reaction flask. The reaction mixture was stirred at room temperature until all iodobenzene was consumed. The reaction mixture was then diluted with diethyl ether (*ca.* 50 mL), washed with brine (1 × 30 mL), dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo* and the resulting residue purified *via* flash column chromatography using hexane as eluent. The desired product (**2a**) was obtained as yellow liquid. Yield: 1.9 g, 12.0 mmol, 82%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.39 (d, *J* = 7.9 Hz, 2H, Ar–CH), 7.29–7.25 (m, 3H, Ar–CH), 2.41 (t, *J* = 7.1 Hz, 2H), 1.62–1.55 (m, 2H), 1.51–1.44 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 131.6, 128.3, 127.5, 124.1, 90.5 (C≡C), 80.6 (C≡C), 30.9, 22.1, 19.2, 13.8.

Synthesis of 1-ethynyl-4-vinylbenzene (**2b**)[8]

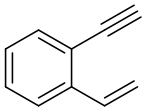


To a solution of trimethyl((4-vinylphenyl)ethynyl)silane (1.5 g, 7.4 mmol, 1.0 equiv) in dry THF (8 mL), 1.0 M THF solution of tetra-*n*-butyl ammonium fluoride (12 mL, 12 mmol, 1.6 equiv) was added dropwise and the reaction was stirred at ambient temperature for 1 h under nitrogen atmosphere. After completion, the reaction mixture was quenched with water (10 mL), and the organic layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with saturated brine solution (1 × 15 mL), dried over anhydrous MgSO4 and concentrated *in vacuo*. The crude product was

purified by flash column chromatography using hexane as eluent. The desired product (**2b**) was obtained as a colourless liquid. Yield: 790 mg, 7.5 mmol, 82%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.45 (d, *J* = 8.3 Hz, 2H, Ar–CH), 7.36 (d, *J* = 8.3 Hz, 2H, Ar–CH), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H, CH_2), 5.78 (d, *J* = 17.5 Hz, 1H, CH_2), 5.31 (d, *J* = 10.9 Hz, 1H, Me), 3.11 (s, 1H, C≡CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 138.1, 136.2, 132.4, 126.2, 121.4, 115.2, 83.7 (C≡C), 77.8 (C≡C).

Synthesis of 1-ethynyl-2-vinylbenzene (**2c**)[8]



To a solution of trimethyl((2-vinylphenyl)ethynyl)silane (1 g, 5.0 mmol, 1.0 equiv) in MeOH (10 mL), K_2CO_3 (827 mg , 6.0 mmol, 1.2 equiv) was added in one portion and the reaction was stirred at ambient temperature for 30 minutes under nitrogen atmosphere. The reaction mixture was quenched with water (15 mL), and the organic layer was extracted with hexane (3 × 15 mL). The combined organic layers were washed with saturated brine solution (1 × 15 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography using hexane as eluent. The desired product (**2c**) was obtained as a colourless liquid. Yield: 520 mg, 4.0 mmol, 81%.

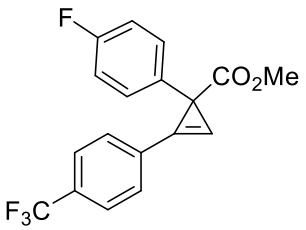
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.59–7.57 (m, 1H, Ar–CH), 7.49–7.48 (m, 1H, Ar–CH), 7.33–7.30 (m, 1H, Ar–CH), 7.26–7.19 (m, 2H, Ar–CH), 5.81 (d, *J* = 17.6 Hz, 1H, CH_2), 5.36 (d, *J* = 11.0 Hz, 1H, CH_2), 3.30 (s, 1H, C≡CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 139.8, 134.8, 133.2, 129.0, 127.5, 124.7, 120.9, 115.9, 82.0 (C≡C), 81.8 (C≡C).

2. Product Characterisation

2.1 ***General procedure b*****:** In the glove box under nitrogen atmosphere, tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] (10 mol%), arylacetylene (1 equiv) and α-aryl α-diazoester **1** (1.3 equiv) were all dissolved separately in 1,2-DCE (0.5 mL). Subsequently, the $B(C_6F_5)_3$ and arylacetylene solutions were combined and stirred for 30 seconds before α-aryl α-diazoester solution was added dropwise into the reaction mixture. The reaction tube was sealed and heated outside at 50 °C for 18–24 h. Afterwards, all volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. Note: Some of the carbocycles were found to be unstable at room temperature and decomposed quickly.

2.2 Synthesis and spectral characterisation of products

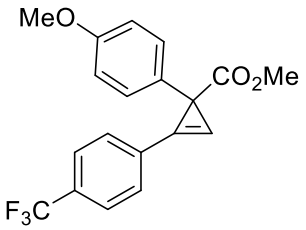
Synthesis of methyl 1-(4-fluorophenyl)-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (**3a**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (25 mg, 0.13 mmol), and 1-ethynyl-4-(trifluoromethyl)benzene (17 mg, 0.1 mmol) in 1,2-DCE to afford **3a**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3a**) was obtained as a yellow oil. Yield: 10 mg, 0.03 mmol, 30%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.72–7.68 (m, 4H, Ar–CH), 7.37 (s, 1H, C=CH), 7.33 (dd, *J* = 8.8, 5.3 Hz, 2H, Ar–CH), 6.98 (t, *J* = 8.7 Hz, 2H, Ar–CH), 3.72 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 174.5 (C=O), 161.8 (d, $J_{C–F}$ = 245.6 Hz), 136.0 (d, $J_{C–F}$ = 3.2 Hz), 132.0, 131.7, 130.1, 129.8 (d, $J_{C–F}$ = 8.0 Hz), 128.7, 126.1 (q, $J_{C–F}$ = 3.7 Hz), 124.9, 122.7, 116.7, 115.2 (d, $J_{C–F}$ = 21.4 Hz), 103.3, 52.6 (COOMe), 33.2 (quaternary C_{sp}^3); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -62.93 (s, 3F, Ar–CF_3), -115.76 (s, 1F, Ar–F); IR ν_{max} (cm^{-1}): 3056, 2957, 2923, 1718 (C=O), 1509, 1324, 1265, 1224, 1168, 1128, 1065, 1017. HRMS could not be obtained.

Synthesis of methyl 1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (**3b**)

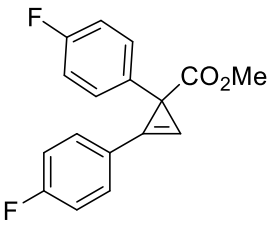


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1g** (26 mg, 0.13 mmol), and 1-ethynyl-4-(trifluoromethyl)benzene (17 mg, 0.1 mmol) in 1,2-DCE to afford **3b**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3b**) was obtained as a yellow oil. Yield: 13 mg, 0.03 mmol, 37%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.70 (q, *J* = 8.2 Hz, 4H, Ar–CH), 7.38 (s, 1H, C=CH), 7.29–7.27 (m, 2H, Ar–CH), 6.84 (d, *J* = 8.8 Hz, 2H, Ar–CH), 3.78 (s, 3H, COOMe), 3.72 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 174.9 (C=O), 158.5, 132.5, 131.8, 131.5, 130.1, 129.3, 129.1, 126.0 (q, $J_{C–F}$ = 3.8 Hz), 124.9, 122.8, 117.0, 113.8, 103.8, 55.4 (OMe),

52.5 (COOMe), 31.3 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -62.89 (Ar–F); IR ν_{max} (cm^{-1}): 3058, 2954, 2841, 1718 (C=O), 1607, 1513, 1323, 1248, 1166, 1124, 1064; HRMS (ES+) $[M+H]^+$ calculated for $[C_{19}H_{16}O_3F_3]^+$: 349.1052; found 349.1050.

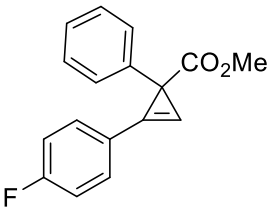
Synthesis of methyl 1,2-bis(4-fluorophenyl)cycloprop-2-ene-1-carboxylate (**3c**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (25 mg, 0.13 mmol), and 1-ethynyl-4-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3c**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3c**) was obtained as a yellow oil. Yield: 24 mg, 0.08 mmol, 84%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.61–7.57 (m, 2H, Ar–CH), 7.35–7.31 (m, 2H, Ar–CH), 7.16 (s, 1H, C=CH), 7.13 (t, J = 8.7 Hz, 2H, Ar–CH), 6.97 (t, J = 8.8 Hz, 2H, Ar–CH), 3.71 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 174.8 (C=O), 163.8 (d, $J_{C–F}$ = 251.8 Hz), 161.7 (d, $J_{C–F}$ = 245.3 Hz), 136.5 (d, $J_{C–F}$ = 3.3 Hz), 132.0 (d, $J_{C–F}$ = 8.6 Hz), 129.8 (d, $J_{C–F}$ = 8.1 Hz), 121.6 (d, $J_{C–F}$ = 3.4 Hz), 116.6, 116.4 (d, $J_{C–F}$ = 22.3 Hz), 115.1 (d, $J_{C–F}$ = 21.4 Hz), 99.72 (d, J = 2.7 Hz), 52.4 (COOMe), 33.0 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -108.87 (s, 1F, Ar–F), -116.13 (s, 1F, Ar–F); IR ν_{max} (cm^{-1}): 2953, 1716 (C=O), 1600, 1508, 1224, 1157, 1097, 1014; HRMS (ES+) $[M+H]^+$ calculated for $[C_{17}H_{13}O_2F_2]^+$: 287.0884, found: 287.0880.

Synthesis of methyl 2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylate (**3d**)[9]

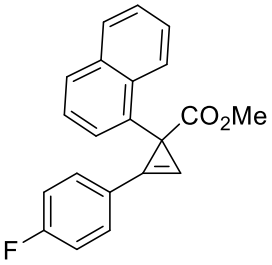


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1c** (23 mg, 0.13 mmol), and 1-ethynyl-4-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3d**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3d**) was obtained as a yellow oil. Yield: 21 mg, 0.07 mmol, 78%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.60 (dd, J = 8.8, 5.4 Hz, 2H, Ar–CH), 7.37–7.35 (m, 2H, Ar–CH), 7.31–7.28 (m, 2H, Ar–CH), 7.23–7.20 (m, 1H, Ar–CH), 7.18 (s, 1H, C=CH), 7.14–7.09 (m, 2H, Ar–CH), 3.72 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.0 (C=O), 163.7 (d, $J_{C–F}$ = 251.5 Hz), 140.7, 132.0 (d, $J_{C–F}$ = 8.7 Hz), 128.28, 128.25, 126.7,

121.8 (d, $J_{C–F}$ = 3.4 Hz), 116.6, 116.3 (d, $J_{C–F}$ = 22.2 Hz), 99.8 (d, $J_{C–F}$ = 2.7 Hz), 52.4 (COOMe), 33.7 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -109.17 (Ar–F).

Synthesis of methyl 2-(4-fluorophenyl)-1-(naphthalen-1-yl)cycloprop-2-ene-1-carboxylate (**3e**)

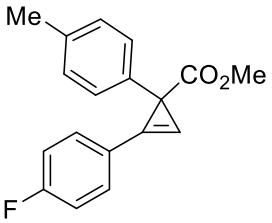


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1d** (29 mg, 0.13 mmol), and 1-ethynyl-4-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3e**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3e**) was obtained as a white solid. Yield: 20 mg, 0.06 mmol, 63%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.13 (d, *J* = 8.9 Hz, 1H, Ar–CH), 7.87 (d, *J* = 8.1 Hz, 1H, Ar–CH), 7.77 (d, *J* = 8.3 Hz, 1H, Ar–CH), 7.73 (dd, *J* = 8.8, 5.4 Hz, 2H, Ar–CH), 7.57–7.54 (m, 1H, Ar–CH), 7.52–7.49 (m, 1H, Ar–CH), 7.47 (s, 1H, C=CH), 7.43 (dd, *J* = 7.1, 1.3 Hz, 1H, Ar–CH), 7.35 (dd, *J* = 8.2, 7.0 Hz, 1H, Ar–CH), 7.18–7.15 (m, 2H, Ar–CH), 3.66 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 176.0 (C=O), 163.7 (d, $J_{C–F}$ = 251.5 Hz), 138.7, 133.9, 132.4, 131.9 (d, $J_{C–F}$ = 8.6 Hz), 128.9, 128.1, 126.3, 125.8, 125.77, 125.70, 124.5, 122.6 (d, $J_{C–F}$ = 3.3 Hz), 117.8, 116.4 (d, $J_{C–F}$ = 22.2 Hz), 103.0 (d, $J_{C–F}$ = 2.6 Hz), 52.7 (COOMe), 32.9 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -109.20 (Ar–F); IR ν_{max} (cm^{-1}): 3061, 2952, 1718 (C=O), 1599, 1502, 1434, 1265, 1221, 1155; HRMS (ES+) $[M+H]^+$ calculated for $[C_{21}H_{16}O_2F]^+$: 319.1134; found 319.1136.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ:

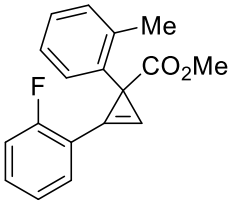
Synthesis of methyl 2-(4-fluorophenyl)-1-(p-tolyl)cycloprop-2-ene-1-carboxylate (**3f**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1e** (25 mg, 0.13 mmol), and 1-ethynyl-4-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3f**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3f**) was obtained as a yellow oil. Yield: 20 mg, 0.07 mmol, 71%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.69 (dd, *J* = 8.6, 5.5 Hz, 2H, Ar–CH), 7.35–7.33 (m, 3H, Ar–CH), 7.22–7.18 (m, 4H), 3.80 (s, 3H, COOMe), 2.40 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.2 (C=O), 163.7 (d, $J_{C–F}$ = 251.5 Hz), 137.7, 136.4, 132.0 (d, $J_{C–F}$ = 8.7 Hz), 129.0, 128.1, 121.9 (d, $J_{C–F}$ = 3.5 Hz), 116.8, 116.3 (d, $J_{C–F}$ = 22.2 Hz), 100.00 (d, *J* = 2.7 Hz), 52.3 (COOMe), 33.5 (quaternary C_{sp}^3), 21.2 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -109.30 (Ar–F); IR ν_{max} (cm^{-1}): 3134, 2951, 2922, 1716 (C=O), 1598, 1500, 1435, 1220, 1153, 1091, 1029, 1016, 1001; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_2F]^+$: 283.1134; found: 283.1136.

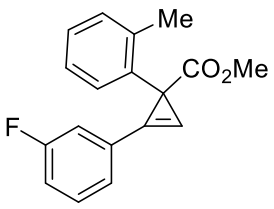
Synthesis of methyl 2-(2-fluorophenyl)-1-(o-tolyl)cycloprop-2-ene-1-carboxylate (**3g**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1f** (25 mg, 0.13 mmol), and 1-ethynyl-2-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3g**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3g**) was obtained as a colourless oil. Yield: 23 mg, 0.08 mmol, 81%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.65 (td, *J* = 7.3, 1.8 Hz, 1H, Ar–CH), 7.49 (s, 1H, C=CH), 7.45–7.39 (m, 1H, Ar–CH), 7.25–7.15 (m, 5H, Ar–CH), 7.10–7.07 (m, 1H, Ar–CH), 3.71 (s, 3H, COOMe), 2.40 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 175.5 (C=O), 161.6 (d, $J_{C–F}$ = 255.0 Hz), 140.3, 137.5, 131.9 (d, $J_{C–F}$ = 8.2 Hz,), 131.0, 130.9, 130.4, 128.5, 127.4, 126.1, 124.5 (d, $J_{C–F}$ = 3.8 Hz), 116.2 (d, $J_{C–F}$ = 20.3 Hz), 115.0, 114.9, 113.0, 106.3 (d, *J* = 4.6 Hz), 52.6 (COOMe), 32.4 (quaternary C_{sp}^3), 19.7 (Me); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -111.5 (Ar–F); IR ν_{max} (cm^{-1}): 3138, 2951, 1716 (C=O), 1608, 1577, 1485, 1450, 1433, 1265, 1219, 1022, 1001; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_2F]^+$: 283.1134; found 283.1139.

Synthesis of methyl 2-(3-fluorophenyl)-1-(o-tolyl)cycloprop-2-ene-1-carboxylate (**3h**)

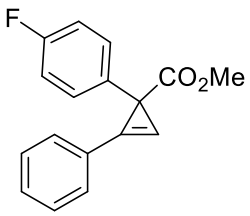


Synthetised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1f** (25 mg, 0.13 mmol), and 1-ethynyl-3-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3h**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as

eluent. The desired product (**3h**) was obtained as a colourless oil. Yield: 20 mg, 0.07 mmol, 71%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.48–7.40 (m, 3H, C=CH and Ar–CH), 7.38–7.35 (m, 1H, Ar–CH), 7.21–7.06 (m, 5H, Ar-CH), 3.71 (s, 3H, COOMe), 2.39 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 175.3 (C=O), 162.9 (d, $J_{C–F}$ = 247.5 Hz), 140.1, 137.4, 130.6 (d, $J_{C–F}$ = 8.5 Hz), 128.5, 128.3, 127.5, 126.2, 125.5 (d, $J_{C–F}$ = 3.1 Hz), 117.2, 117.0, 116.4 (d, $J_{C–F}$ = 22.4 Hz), 104.9, 52.6 (COOMe), 33.8 (quaternary C_{sp^3}), 19.8 (Me). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -112.09 (Ar–F); IR ν_{max} (cm^{-1}): 3145, 2953, 1716 (C=O), 1583, 1483, 1433, 1222, 1022; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_2F]^+$: 283.1134; found 283.1125.

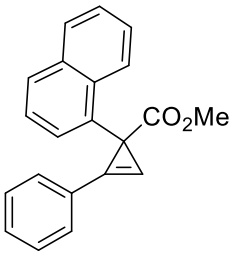
Synthesis of methyl 1-(4-fluorophenyl)-2-phenylcycloprop-2-ene-1-carboxylate (**3i**)[9]



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (25 mg, 0.13 mmol), and phenylacetylene (10 mg, 0.1 mmol) in 1,2-DCE to afford **3i**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3i**) was obtained as a yellow oil. Yield: 20 mg, 0.07 mmol, 75%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.61–7.59 (m, 2H, Ar–CH), 7.46–7.40 (m, 3H, Ar–CH), 7.37–7.34 (m, 2H, Ar–CH), 7.19 (s, 1H, C=CH), 6.97 (t, *J* = 8.8 Hz, 2H, Ar–CH), 3.71 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.0 (C=O), 161.7 (d, $J_{C–F}$ = 245.0 Hz), 136.7 (d, $J_{C–F}$ = 3.2 Hz), 130.2, 130.03, 130.01, 129.9, 129.1, 125.3, 117.4, 115.0 (d, $J_{C–F}$ = 21.4 Hz), 100.2, 52.4 (COOMe), 32.9 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.31 (Ar–F).

Synthesis of methyl 1-(naphthalen-1-yl)-2-phenylcycloprop-2-ene-1-carboxylate (**3j**)[9]

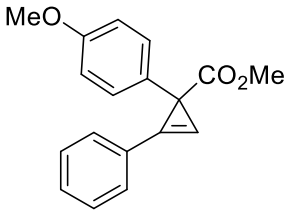


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1d** (29 mg, 0.13 mmol), and phenylacetylene (10 mg, 0.1 mmol) in 1,2-DCE to afford **3j**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3j**) was obtained as a yellow oil. Yield: 18 mg, 0.06 mmol, 60%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.15 (d, *J* = 8.4 Hz, 1H, Ar–CH), 7.88–7.86 (m, 1H, Ar–CH), 7.77–7.74 (m, 3H, Ar–CH), 7.57–7.54 (m, 1H, Ar–CH), 7.51–7.45 (m, 5H), 7.48–

7.42 (m, 1H, Ar–CH), 7.34 (dd, *J* = 8.2, 7.0 Hz, 1H, Ar–CH), 3.66 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 176.1 (C=O), 138.9, 133.9, 132.4, 130.1, 129.1, 128.9, 128.0, 126.3, 126.2, 125.9, 125.77, 125.74, 124.6, 118.6, 103.6, 52.6 (COOMe), 32.8 (quaternary C_{sp}^3).

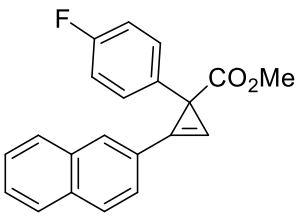
Synthesis of methyl 1-(4-methoxyphenyl)-2-phenylcycloprop-2-ene-1-carboxylate (**3k**)[9]



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1g** (27 mg, 0.13 mmol), and phenylacetylene (10 mg, 0.1 mmol) in 1,2-DCE to afford **3k**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3k**) was obtained as a colourless oil. Yield: 14 mg, 0.05 mmol, 50%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.61 (dd, *J* = 8.1, 1.6 Hz, 2H, Ar–CH), 7.44–7.37 (m, 3H, Ar–CH), 7.32–7.29 (m, 2H, Ar–CH), 7.20 (s, 1H, C=CH), 6.82 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H, OMe), 3.71 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.4 (C=O), 158.3, 133.2, 130.0, 129.4, 129.0, 125.6, 117.7, 113.6, 100.7, 55.3 (OMe), 52.3 (COOMe), 33.0 (quaternary C_{sp}^3).

Synthesis of methyl 1-(4-fluorophenyl)-2-(naphthalen-2-yl)cycloprop-2-ene-1-carboxylate (**3l**)

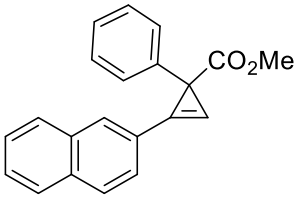


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (25 mg, 0.13 mmol), and 2-ethynylnaphthalene (15 mg, 0.1 mmol) in 1,2-DCE to afford **3l**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3l**) was obtained as a white solid. Yield: 25 mg, 0.07 mmol, 79%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.04 (s, 1H, Ar–CH), 7.91–7.84 (m, 3H, Ar–CH), 7.70 (dd, *J* = 8.4, 1.6 Hz, 1H, Ar–CH), 7.56–7.51 (m, 2H, Ar–CH), 7.43–7.40 (m, 2H, Ar–CH), 7.28 (s, 1H, C=CH), 6.98 (t, *J* = 8.8 Hz, 2H, Ar–CH), 3.73 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.0 (C=O), 161.7 (d, $J_{C–F}$ = 245.0 Hz), 148.7, 136.8 (d, $J_{C–F}$ = 3.2 Hz), 134.0, 133.2, 130.9, 130.1, 129.9 (d, *J* = 8.0 Hz), 129.0, 128.6, 128.0, 127.6, 127.5, 126.9, 126.5, 122.1, 117.3, 115.0 (d, $J_{C–F}$ = 21.3 Hz), 101.1, 52.4 (COOMe), 32.1 (quaternary C_{sp}^3);

^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.25 (Ar–F); IR ν_{max} (cm^{-1}): 3056, 2960, 1718 (C=O), 1508, 1434, 1264, 1222, 1159; HRMS (ASAP+) $[M+H]^+$ calculated for $[C_{21}H_{16}O_2F]^+$: 319.1134; found 319.1128.

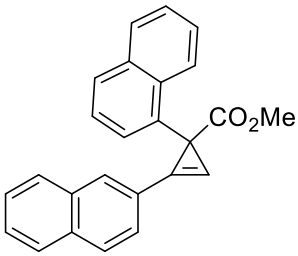
Synthesis of methyl 2-(naphthalen-2-yl)-1-phenylcycloprop-2-ene-1-carboxylate (**3m**)[9]



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1c** (23 mg, 0.13 mmol), and 2-ethynylnaphthalene (15 mg, 0.1 mmol) in 1,2-DCE to afford **3m**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3m**) was obtained as a white solid. Yield: 20 mg, 0.06 mmol, 67%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.07 (s, 1H, Ar–CH), 7.90–7.83 (m, 3H, Ar–CH), 7.72 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar–CH), 7.55–7.50 (m, 2H, Ar–CH), 7.46–7.44 (m, 2H, Ar–CH), 7.31–7.30 (m, 3H), 7.24–7.20 (m, 1H, Ar–CH), 3.74 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.1 (C=O), 141.0, 134.0, 133.2, 130.1, 128.9, 128.6, 128.3, 128.2, 128.0, 127.5, 126.9, 126.7, 126.6, 122.9, 117.2, 101.3, 52.4 (COOMe), 33.8 (quaternary C_{sp}^3).

Synthesis of methyl 1-(naphthalen-1-yl)-2-(naphthalen-2-yl)cycloprop-2-ene-1-carboxylate (**3n**)

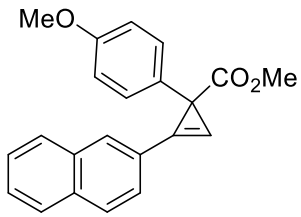


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1d** (29 mg, 0.13 mmol), and 2-ethynylnaphthalene (15 mg, 0.1 mmol) in 1,2-DCE to afford **3n**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3n**) was obtained as a white solid. Yield: 25 mg, 0.07 mmol, 71%. Single crystals of **3n** could be obtained from vapour diffusion using CH_2Cl_2/pentane.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.26 (s, 1H, Ar–CH), 8.21 (d, *J* = 7.4 Hz, 1H, Ar–CH), 7.94–7.87 (m, 4H, Ar–CH), 7.80 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar–CH), 7.77 (d, *J* = 8.2 Hz, 1H, Ar–CH), 7.60–7.50 (m, 6H, C=CH and Ar–CH), 7.34 (dd, *J* = 8.2, 7.1 Hz, 1H, Ar–CH), 3.70 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 176.1 (C=O), 138.9, 134.0, 133.9,

133.3, 132.4, 129.9, 128.98, 128.95, 128.6, 128.06, 128.04, 127.5, 126.9, 126.7, 126.2, 125.9, 125.8, 125.7, 124.6, 123.6, 118.6, 104.2, 52.7 (COOMe), 33.0 (quaternary C_{sp^3}); IR ν_{max} (cm^{-1}): 3117, 3062, 2949, 2916, 2848, 1713 (C=O), 1506, 1431, 1226; HRMS (ES+) $[M+H]^+$ calculated for $[C_{25}H_{19}O_2]^+$: 351.1385; found 351.1374.

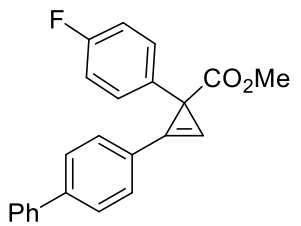
Synthesis of methyl 1-(4-methoxyphenyl)-2-(naphthalen-2-yl)cycloprop-2-ene-1-carboxylate (**3o**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1g** (26 mg, 0.13 mmol), and 2-ethynylnaphthalene (15 mg, 0.1 mmol) in 1,2-DCE to afford **3o**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3o**) was obtained as a white solid. Yield: 19 mg, 0.05 mmol, 57%. Single crystals of **3o** could be obtained from vapour diffusion using CH_2Cl_2/pentane.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.06 (s, 1H, Ar–CH), 7.89–7.83 (m, 3H, Ar–CH), 7.71 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar–CH), 7.53–7.51 (m, 2H, Ar–CH), 7.38–7.36 (m, 2H, Ar–CH), 7.30 (s, 1H, C=CH), 6.84 (d, *J* = 8.9 Hz, 2H, Ar–CH), 3.77 (s, 3H, COOMe), 3.73 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.4 (C=O), 158.4, 134.0, 133.2, 130.0, 129.4, 128.8, 128.6, 128.0, 127.4, 126.8, 126.6, 123.0, 117.5, 113.7, 101.5, 55.4 (OMe), 52.4 (COOMe), 33.2 (quaternary C_{sp^3}); IR ν_{max} (cm^{-1}): 3056, 2955, 2919, 2839, 1718 (C=O); 1510, 1264, 1249, 1176, 1031; HRMS (ES+) $[M+H]^+$ calculated for $[C_{22}H_{19}O_3]^+$: 331.1134; found 331.1332.

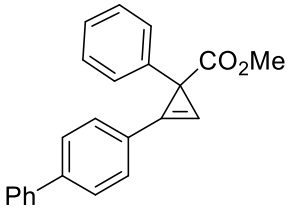
Synthesis of methyl 2-([1,1'-biphenyl]-4-yl)-1-(4-fluorophenyl)cycloprop-2-ene-1-carboxylate (**3p**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (25 mg, 0.13 mmol), and 4-ethynyl-1,1'-biphenyl (18 mg, 0.1 mmol) in 1,2-DCE to afford **3p**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3p**) was obtained as a white solid. Yield: 28 mg, 0.08 mmol, 81%.

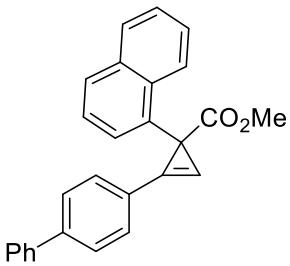
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.67 (s, 4H, Ar–CH), 7.60 (d, *J* = 7.7 Hz, 2H, Ar–CH), 7.46 (t, *J* = 7.7 Hz, 2H, Ar–CH), 7.39–7.37 (m, 3H, Ar–CH), 7.22 (s, 1H, C=CH), 6.98 (t, *J* = 8.5 Hz, 2H, Ar–CH), 3.73 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.0 (C=O), 161.7 (d, $J_{C–F}$ = 245.0 Hz), 143.1, 140.3, 136.8 (d, $J_{C–F}$ = 3.2 Hz), 130.4, 129.9 (d, $J_{C–F}$ = 8.0 Hz), 129.0, 128.0, 127.8, 127.2, 124.2, 117.1, 115.0 (d, $J_{C–F}$ = 21.4 Hz), 100.3, 52.4 (COOMe), 33.0 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.28 (Ar–F); IR ν_{max} (cm^{-1}): 3057, 3030, 2951, 1718 (C=O), 1600, 1508, 1486, 1448, 1264, 1221, 1158, 1007; HRMS (ES+) $[M+H]^+$ calculated for $[C_{23}H_{18}O_2F]^+$: 345.1291; found: 345.1285.

Synthesis of methyl 2-([1,1'-biphenyl]-4-yl)-1-phenylcycloprop-2-ene-1-carboxylate (**3q**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1c** (23 mg, 0.13 mmol), and 4-ethynyl-1,1'-biphenyl (18 mg, 0.1 mmol) in 1,2-DCE to afford **3q**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3q**) was obtained as a white solid. Yield: 26 mg, 0.08 mmol, 80%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.71–7.65 (m, 4H, Ar–CH), 7.61–7.59 (m, 2H, Ar–CH), 7.46 (t, *J* = 7.6 Hz, 2H, Ar–CH), 7.43–7.36 (m, 3H, Ar–CH), 7.30 (t, *J* = 7.6 Hz, 2H, Ar–CH), 7.24–7.20 (m, 2H), 3.74 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.1 (C=O), 143.0, 141.0, 140.3, 130.5, 129.0, 128.3, 128.2, 128.0, 127.7, 127.2, 126.6, 124.4, 117.0, 100.5, 52.3 (COOMe), 33.7 (quaternary C_{sp^3}); IR ν_{max} (cm^{-1}): 3057, 3029, 2950, 1718 (C=O), 1696, 1485, 1264, 1207, 1007; HRMS (ASAP+) $[M+H]^+$ calculated for $[C_{23}H_{19}O_2]^+$: 327.1385; found 327.1388.

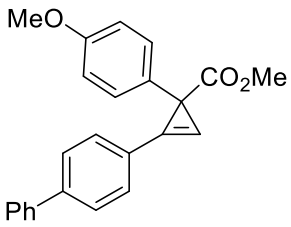
Synthesis of methyl 2-([1,1'-biphenyl]-4-yl)-1-(naphthalen-1-yl)cycloprop-2-ene-1-carboxylate (**3r**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1d** (29 mg, 0.13 mmol), and 4-ethynyl-1,1'-biphenyl (18 mg, 0.1 mmol) in 1,2-DCE to afford **3r**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3r**) was obtained as a white solid. Yield: 21 mg, 0.05 mmol, 56%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.18 (d, *J* = 7.4 Hz, 1H, Ar–CH), 7.88 (d, *J* = 8.1 Hz, 1H, Ar–CH), 7.83–7.82 (m, 2H, Ar–CH), 7.78–7.76 (m, 1H, Ar–CH), 7.72–7.70 (m, 2H, Ar–CH), 7.63 (dd, *J* = 8.4, 1.3 Hz, 2H, Ar–CH), 7.58–7.55 (m, 1H, Ar–CH), 7.53–7.46 (m, 5H), 7.41–7.35 (m, 2H, Ar–CH), 3.68 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 176.1 (C=O), 142.9, 140.3, 138.9, 133.9, 132.4, 130.4, 129.0, 128.9, 128.0, 127.8, 127.3, 126.2, 125.9, 125.79, 125.76, 125.1, 124.6, 118.3, 103.6, 52.6 (COOMe), 32.8 (quaternary C_{sp^3}); IR ν_{max} (cm^{-1}): 3125, 3063, 2955, 2917, 2848, 1714 (C=O), 1264, 1234; HRMS (ES+) $[M+H]^+$ calculated for $[C_{27}H_{21}O_2]^+$: 377.1542; found 377.1527.

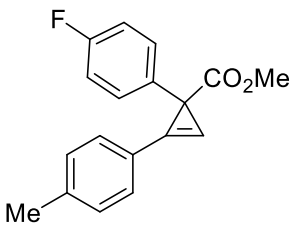
Synthesis of methyl 2-([1,1'-biphenyl]-4-yl)-1-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (**3s**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1g** (26 mg, 0.13 mmol), and 4-ethynyl-1,1'-biphenyl (18 mg, 0.1 mmol) in 1,2-DCE to afford **3s**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3s**) was obtained as a yellow solid. Yield: 18 mg, 0.05 mmol, 51%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.67 (q, *J* = 8.6 Hz, 4H, Ar–CH), 7.61–7.59 (m, 2H, Ar–CH), 7.46 (t, *J* = 7.6 Hz, 2H, Ar–CH), 7.39–7.38 (m, 1H, Ar–CH), 7.34–7.33 (m, 2H, Ar–CH), 7.23 (s, 1H, C=CH), 6.84 (d, *J* = 8.8 Hz, 2H, Ar–CH), 3.78 (s, 3H, COOMe), 3.73 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.4 (C=O), 158.4, 142.9, 140.4, 133.2, 130.4, 129.4, 129.0, 128.0, 127.7, 127.2, 124.5, 117.4, 113.7, 100.8, 55.4 (OMe), 52.3 (COOMe), 33.0 (quaternary C_{sp^3}); IR ν_{max} (cm^{-1}): 3054, 2955, 2839, 1715 (C=O), 1605, 1511, 1264, 1248, 1176, 1031; HRMS (ES+) $[M+H]^+$ calculated for $[C_{24}H_{21}O_3]^+$: 357.1491; found 357.1485.

Synthesis of methyl 1-(4-fluorophenyl)-2-(p-tolyl)cycloprop-2-ene-1-carboxylate (**3t**)

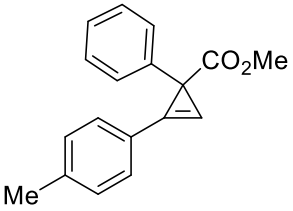


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (25 mg, 0.13 mmol), and 1-ethynyl-4-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3t**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel

and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3t**) was obtained as a yellow oil. Yield: 20 mg, 0.07 mmol, 71%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.49 (d, *J* = 8.1 Hz, 2H, Ar–CH), 7.35 (dd, *J* = 8.8, 5.3 Hz, 2H, Ar–CH), 7.24 (d, *J* = 7.7 Hz, 2H, Ar–CH), 7.11 (s, 1H, C=CH), 6.95 (t, *J* = 8.7 Hz, 2H, Ar–CH), 3.70 (s, 3H, COOMe), 2.39 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.1 (C=O), 161.6 (d, $J_{C–F}$ = 244.8 Hz), 140.7, 136.9 (d, $J_{C–F}$ = 3.2 Hz), 130.0, 129.9, 129.8, 122.5, 117.1, 114.9 (d, $J_{C–F}$ = 21.3 Hz), 99.0, 52.3 (COOMe), 32.8 (quaternary C_{sp^3}), 21.7 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.48 (Ar–F); IR ν_{max} (cm^{-1}): 2951, 2922, 1716 (C=O), 1602, 1508, 1435, 1222, 1159, 1014; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_2F]^+$: 283.1134, found: 283.1127.

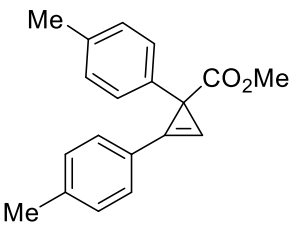
Synthesis of methyl 1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxylate (**3u**)[9]



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1c** (23 mg, 0.13 mmol), and 1-ethynyl-4-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3u**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3u**) was obtained as a colourless oil. Yield: 12 mg, 0.04 mmol, 45%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.51 (d, *J* = 8.3 Hz, 2H, Ar–CH), 7.40–7.37 (m, 3H, Ar–CH), 7.28 (d, *J* = 7.4 Hz, 1H, Ar–CH), 7.24–7.20 (m, 3H, Ar–CH), 7.13 (s, 1H, C=CH), 3.71 (s, 3H, COOMe), 2.38 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.3 (C=O), 141.2, 140.5, 130.0, 129.7, 128.3, 128.1, 126.5, 122.7, 117.1, 99.2, 52.3 (COOMe), 33.5 (quaternary C_{sp^3}), 21.7 (Me).

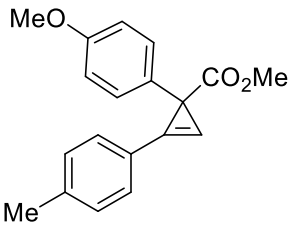
Synthesis of methyl 1,2-di-p-tolylcycloprop-2-ene-1-carboxylate (**3v**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1e** (25 mg, 0.13 mmol), and 1-ethynyl-4-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3v**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3v**) was obtained as a colourless oil. Yield: 9 mg, 0.03 mmol, 32%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.51 (d, *J* = 8.0 Hz, 2H, Ar–CH), 7.27 (s, 1H, Ar–CH), 7.23–7.19 (m, 3H, Ar–CH), 7.12 (s, 1H, C=CH), 7.09 (d, *J* = 8.2 Hz, 2H, Ar–CH), 3.70 (s, 3H, COOMe), 2.38 (s, 3H, Me), 2.30 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.5 (C=O), 140.4, 138.2, 136.1, 130.0, 129.7, 128.9, 128.2, 122.8, 117.3, 99.4, 52.3 ($COOCH_3$), 33.2 (quaternary C_{sp}^3), 21.7 (Me), 21.2 (Me); IR ν_{max} (cm^{-1}): 2951, 2924, 1717 (C=O), 1606, 1512, 1435, 1219, 1207, 1031, 1018, 1002; HRMS (ES+) $[M+H]^+$ calculated for $[C_{19}H_{19}O_2]^+$: 279.1385; found 279.1384.

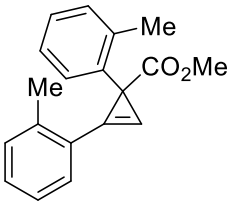
Synthesis of methyl 1-(4-methoxyphenyl)-2-(p-tolyl)cycloprop-2-ene-1-carboxylate (**3w**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1g** (26 mg, 0.13 mmol), and 1-ethynyl-4-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3w**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3w**) was obtained as a colourless oil. Yield: 14 mg, 0.04 mmol, 48%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.50 (d, *J* = 7.8 Hz, 2H, Ar–CH), 7.30 (d, *J* = 9.0 Hz, 2H, Ar–CH), 7.23 (d, *J* = 7.7 Hz, 2H, Ar–CH), 7.12 (s, 1H, C=CH), 6.82 (d, *J* = 8.9 Hz, 2H, Ar–CH), 3.77 (s, 3H, OMe), 3.70 (s, 3H, COOMe), 2.38 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.5 (C=O), 158.3, 140.4, 133.4, 130.0, 129.7, 129.4, 122.8, 117.4, 113.6, 99.4, 55.4 (OMe), 52.3 (COOMe), 32.9 (quaternary C_{sp}^3), 21.7 (CH_3); IR ν_{max} (cm^{-1}): 3132, 2951, 2837, 1716 (C=O), 1608, 1510, 1435, 1246, 1174, 1026; HRMS (ES+) $[M+H]^+$ calculated for $[C_{19}H_{19}O_3]^+$: 295.1334, found: 295.1331.

Synthesis of methyl 1,2-di-o-tolylcycloprop-2-ene-1-carboxylate (**3x**)

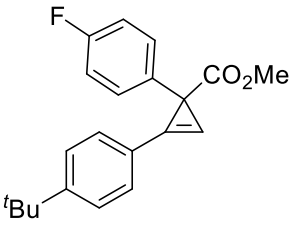


Synthetised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1f** (25 mg, 0.13 mmol), and 1-ethynyl-2-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3x**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3x**) was obtained as a yellow oil. Yield: 20 mg, 0.07 mmol, 72%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.66–7.64 (m, 1H, Ar–CH), 7.39 (s, 1H, C=CH), 7.34–7.29 (m, 3H, Ar–CH), 7.26–7.24 (m, 1H, Ar–CH), 7.18–7.14 (m, 2H, Ar–CH), 7.07–7.04 (m,

1H, Ar–CH), 3.71 (s, 3H, COOMe), 2.49 (s, 3H, Me), 2.41 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.8 (C=O), 140.8, 140.4, 137.5, 130.5, 130.3, 130.2, 130.0, 128.4, 127.3, 126.3, 126.1, 125.0, 116.9, 105.8, 52.6 (COOMe), 31.9 (quaternary C_{sp}^3), 20.3 (Me), 19.7 (Me); IR ν_{max} (cm^{-1}): 2951, 1714 (C=O), 1483, 1458, 1435, 1226, 1022, 1002; HRMS (ES+) $[M+H]^+$ calculated for $[C_{19}H_{19}O_2]^+$: 279.1385; found 279.1377.

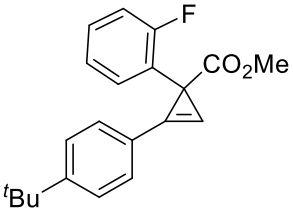
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(4-fluorophenyl)cycloprop-2-ene-1-carboxylate (**3y**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (25 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3y**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3y**) was obtained as a colourless oil. Yield: 25 mg, 0.07 mmol, 77%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.54 (d, J = 8.4 Hz, 2H, Ar–CH), 7.45 (d, J = 8.4 Hz, 2H, Ar–CH), 7.37–7.34 (m, 2H, Ar–CH), 7.12 (s, 1H, C=CH), 6.96 (t, J = 8.7 Hz, 2H, Ar–CH), 3.70 (s, 3H, COOMe), 1.33 (s, 9H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.1 (C=O), 161.6 (d, $J_{C–F}$ = 244.8 Hz), 153.7, 136.9 (d, $J_{C–F}$ = 3.3 Hz), 130.0 (d, $J_{C–F}$ = 8.0 Hz), 129.8, 126.1, 122.4, 117.2, 114.9 (d, $J_{C–F}$ = 21.4 Hz), 99.1, 52.3 (COOMe), 35.1 (quaternary C_{sp}^3), 31.3 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.50 (Ar–F); IR ν_{max} (cm^{-1}): 3138, 2962, 2868, 1716 (C=O), 1602, 1508, 1435, 1408, 1363, 1220, 1159, 1105, 1014; HRMS (ES+) $[M+H]^+$ calculated for $[C_{21}H_{22}O_2F]^+$: 325.1604; found 325.1603.

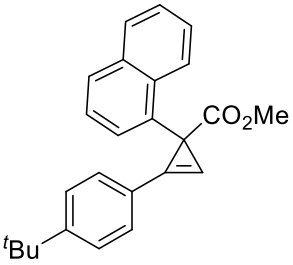
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(2-fluorophenyl)cycloprop-2-ene-1-carboxylate (**3z**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1b** (25 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3z**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3z**) was obtained as a colourless oil. Yield: 23 mg, 0.07 mmol, 71%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.63 (d, *J* = 8.4 Hz, 2H, Ar–CH), 7.46 (d, *J* = 8.4 Hz, 2H, Ar–CH), 7.24–7.17 (m, 3H, C=CH and Ar–CH), 7.06–7.01 (m, 2H, Ar–CH), 3.70 (s, 3H, COOMe), 1.32 (s, 9H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 174.9 (C=O), 161.9 (d, $J_{C–F}$ = 245.8 Hz), 153.7, 130.06, 130.01, 129.92, 129.90, 128.8 (d, $J_{C–F}$ = 8.0 Hz), 126.0, 124.1 (d, $J_{C–F}$ = 3.5 Hz), 122.4, 118.8, 115.4 (d, $J_{C–F}$ = 22.3 Hz), 98.5, 52.5 (COOMe), 35.1 (quaternary C_{sp^3}), 31.3 (Me); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -114.50 (Ar–F); IR ν_{max} (cm^{-1}): 3142, 2958, 1722 (C=O), 1608, 1489, 1435, 1259, 1228, 1205, 1105, 1091, 1020; HRMS (ES+) $[M+H]^+$ calculated for $[C_{21}H_{22}O_2F]^+$: 325.1604; found 325.1606.

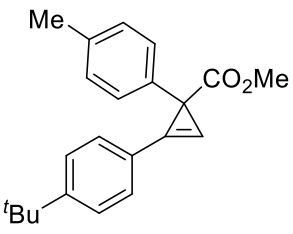
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(naphthalen-1-yl)cycloprop-2-ene-1-carboxylate (**3aa**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1d** (29 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3aa**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3aa**) was obtained as a colourless oil. Yield: 29 mg, 0.08 mmol, 81%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.16 (d, *J* = 9.0 Hz, 1H, Ar–CH), 7.87 (d, *J* = 8.1 Hz, 1H, Ar–CH), 7.75 (d, *J* = 8.4 Hz, 1H, Ar–CH), 7.70–7.68 (m, 2H, Ar–CH), 7.57–7.54 (m, 1H, Ar–CH), 7.51–7.48 (m, 4H, Ar–CH), 7.43 (s, 1H, C=CH), 7.34 (dd, *J* = 8.2, 7.1 Hz, 1H, Ar–CH), 3.66 (s, 3H, COOMe), 1.35 (s, 9H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 176.2 (C=O), 153.6, 139.1, 133.9, 132.5, 129.7, 128.9, 127.9, 126.18, 126.10, 125.9, 125.75, 125.72, 124.7, 123.3, 118.3, 102.4, 52.6 (COOMe), 35.1 (quaternary C_{sp^3}), 31.3 (Me); IR ν_{max} (cm^{-1}): 3121, 2960, 1716 (C=O), 1264, 1230; HRMS (ES+) $[M+H]^+$ calculated for $[C_{25}H_{25}O_2]^+$: 357.1855; found 357.1862.

Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(p-tolyl)cycloprop-2-ene-1-carboxylate (**3ab**)

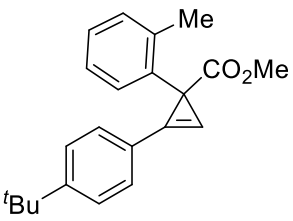


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1e** (25 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3ab**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel

and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3ab**) was obtained as a colourless oil. Yield: 17 mg, 0.05 mmol, 53%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.55 (d, *J* = 8.0 Hz, 2H, Ar–CH), 7.44 (d, *J* = 8.4 Hz, 2H, Ar–CH), 7.28 (d, *J* = 8.1 Hz, 2H, Ar–CH), 7.13 (s, 1H, C=CH), 7.09 (d, *J* = 7.8 Hz, 2H, Ar–CH), 3.70 (s, 3H, COOMe), 2.30 (s, 3H, Me), 1.32 (s, 9H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.5 (C=O), 153.5, 138.2, 136.1, 129.8, 128.9, 128.2, 126.0, 122.7, 117.3, 99.4, 52.3 (COOMe), 35.0 (quaternary C_{sp}^3), 31.3 (CH_3), 21.2 (Me); IR ν_{max} (cm^{-1}): 2962, 2868, 1716 (C=O), 1606, 1514, 1435, 1363, 1220, 1205, 1105, 1016, 1002; HRMS (ES+) $[M+H]^+$calculated for $[C_{22}H_{25}O_2]^+$: 321.1855; found 321.1850.

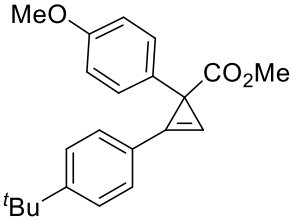
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(o-tolyl)cycloprop-2-ene-1-carboxylate (**3ac**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1f** (25 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3ac**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3ac**) was obtained as a yellow oil. Yield: 22 mg, 0.06 mmol, 69%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.62 (d, *J* = 8.4 Hz, 2H, Ar–CH), 7.48 (d, *J* = 8.3 Hz, 2H, Ar–CH), 7.27–7.25 (m, 2H, C=CH and Ar–CH), 7.16–7.13 (m, 2H, Ar–CH), 7.08–7.04 (m, 1H, Ar–CH), 3.70 (s, 3H, COOMe), 2.40 (s, 3H, Me), 1.35 (s, 9H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 175.8 (C=O), 153.5, 140.8, 137.5, 130.3, 129.6, 128.6, 127.3, 126.1, 126.0, 123.4, 118.3, 102.2, 52.5 (COOMe), 35.1 (quaternary C_{sp}^3), 31.3 (Me), 19.8 (Me); IR ν_{max} (cm^{-1}): 2964, 1712 (C=O), 1458, 1433, 1265, 1226, 1105, 1022, 1001; HRMS (ES+) $[M+H]^+$ calculated for $[C_{22}H_{25}O_2]^+$: 321.1855; found 321.1851.

Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (**3ad**)

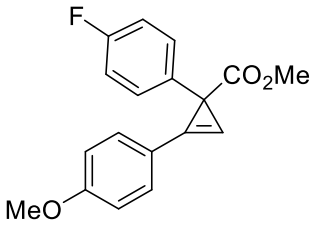


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1g** (27 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3ad**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel

and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3ad**) was obtained as a colourless oil. Yield: 22 mg, 0.06 mmol, 65%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.55 (d, *J* = 8.6 Hz, 2H, Ar–CH), 7.44 (d, *J* = 8.7 Hz, 2H, Ar–CH), 7.31 (d, *J* = 8.9 Hz, 2H, Ar–CH), 7.13 (s, 1H, C=CH), 6.82 (d, *J* = 8.9 Hz, 2H, Ar–CH), 3.77 (s, 3H, OMe), 3.70 (s, 3H, COOMe), 1.32 (s, 9H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.6 (C=O), 158.3, 153.5, 133.4, 129.8, 129.4, 126.0, 122.7, 117.5, 113.6, 99.5, 55.3 (OMe), 52.3 (COOMe), 35.0 (quaternary C_{sp}^3), 31.3 (Me); IR ν_{max} (cm^{-1}): 2960, 2904, 1714 (C=O), 1608, 1510, 1463, 1246, 1176, 1105, 1026; HRMS (ES+) $[M+H]^+$ calculated for $[C_{22}H_{25}O_3]^+$: 337.1804; found 337.1814.

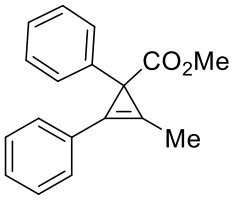
Synthesis of methyl 1-(4-fluorophenyl)-2-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (**3ae**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (25 mg, 0.13 mmol), and 1-ethynyl-4-methoxybenzene (13 mg, 0.1 mmol) in 1,2-DCE to afford **3ae**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3ae**) was obtained as a colourless oil. Yield: 15 mg, 0.05 mmol, 50%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.54 (d, *J* = 8.7 Hz, 2H, Ar–CH), 7.34 (dd, *J* = 8.8, 5.4 Hz, 2H, Ar–CH), 7.03 (s, 1H, C=CH), 6.97–6.94 (m, 4H, Ar–CH), 3.84 (s, 3H, COOMe), 3.70 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.2 (C=O), 161.6 (d, $J_{C–F}$ = 244.8 Hz), 161.2, 137.0 (d, $J_{C–F}$ = 3.3 Hz), 131.6, 129.9 (d, $J_{C–F}$ = 8.0 Hz), 117.8, 116.7, 114.9 (d, $J_{C–F}$ = 21.3 Hz), 114.6, 97.4, 55.5 (OMe), 52.3 (COOMe), 32.8 (quaternary C_{sp}^3); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.53 (Ar–F); IR ν_{max} (cm^{-1}): 2953, 2839, 1716 (C=O), 1602, 1506, 1249, 1222, 1166, 1095, 1029; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_3F]^+$: 299.1083; found 299.1078.

Synthesis of methyl 2-methyl-1,3-diphenylcycloprop-2-ene-1-carboxylate (**3af**)[9]

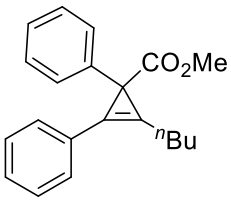


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1c** (23 mg, 0.13 mmol), and prop-1-ynylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3af**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer

chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3af**) was obtained as a yellow oil. Yield: 4 mg, 0.01 mmol, 15%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.55–7.54 (m, 2H, Ar–CH), 7.40 (t, *J* = 7.5 Hz, 2H, Ar–CH), 7.39–7.33 (m, 3H, Ar–CH), 7.28–7.26 (m, 2H, Ar–CH), 7.21–7.18 (m, 1H, Ar–CH), 3.70 (s, 3H, COOMe), 2.39 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.3 (C=O), 141.2, 129.4, 128.9, 128.3, 128.2, 126.7, 126.4, 111.4, 108.6, 52.1 (COOMe), 35.4 (quaternary C_{sp^3}), 9.8 (Me).

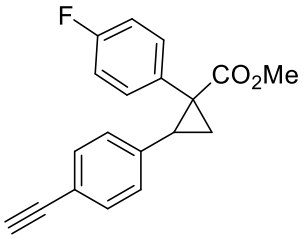
Synthesis of methyl 2-butyl-1,3-diphenylcycloprop-2-ene-1-carboxylate (**3ag**)[10]



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1c** (23 mg, 0.13 mmol), and **2a** (16 mg, 0.1 mmol) in 1,2-DCE to afford **3ag**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3ag**) was obtained as a yellow oil. Yield: 8 mg, 0.02 mmol, 26%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.54 (d, *J* = 7.0 Hz, 2H, Ar–CH), 7.42–7.39 (m, 2H, Ar–CH), 7.36–7.34 (m, 3H, Ar–CH), 7.27–7.24 (m, 2H, Ar–CH), 7.20–7.17 (m, 1H, Ar–CH), 3.69 (s, 3H, COOMe), 2.74 (t, *J* = 7.4 Hz, 2H, CH_2), 1.77–1.71 (m, 2H, CH_2), 1.45–1.40 (m, 2H, CH_2), 0.93 (t, *J* = 7.4 Hz, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.4 (C=O), 141.4, 129.4, 128.9, 128.8, 128.3, 128.1, 126.7, 126.2, 115.7, 107.8, 52.0 (COOMe), 35.4 (quaternary C_{sp^3}), 29.7, 24.7, 22.6, 13.8.

Synthesis of methyl 2-(4-ethynylphenyl)-1-(4-fluorophenyl)cyclopropane-1-carboxylate (**3ah**)

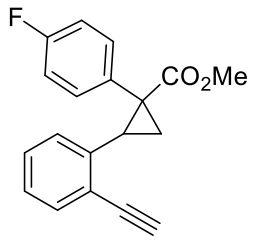


Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (45 mg, 0.23 mmol), and 1-ethynyl-4-vinylbenzene (13 mg, 0.1 mmol) in 1,2-DCE to afford **3ah**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3ah**) was obtained as a colourless oil. Yield: 25 mg, 0.08 mmol, 85%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.21 (d, *J* = 8.3 Hz, 2H, Ar–CH), 6.98–6.95 (m, 2H, Ar–CH), 6.83 (t, *J* = 8.8 Hz, 2H, Ar–CH), 6.71 (d, *J* = 8.1 Hz, 2H, Ar–CH), 3.67 (s, 3H, COOMe), 3.08 (dd, *J* = 9.3, 7.2 Hz, 1H, CH), 3.02 (s, 1H, C≡CH), 2.16 (dd, *J* = 9.3, 5.0 Hz,

1H, CH), 1.83 (dd, *J* = 7.3, 5.0 Hz, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 173.9 (C=O), 161.9 (d, $J_{C–F}$ = 246.4 Hz), 137.3, 133.5 (d, $J_{C–F}$ = 8.2 Hz), 131.7, 130.3 (d, $J_{C–F}$ = 3.3 Hz), 128.0, 120.2, 115.0 (d, $J_{C–F}$ = 21.5 Hz), 83.5 (C≡C), 77.4 (C≡C) 52.8 (COOMe), 37.1 (CH), 33.0 (CH), 20.8 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -114.62 (Ar–F); IR ν_{max} (cm^{-1}): 3300 (C≡CH), 2953, 1714 (C=O), 1512, 1257; HRMS (GC) [M] calculated for [$C_{19}H_{15}O_2F$]: 294.1050; found 294.1050.

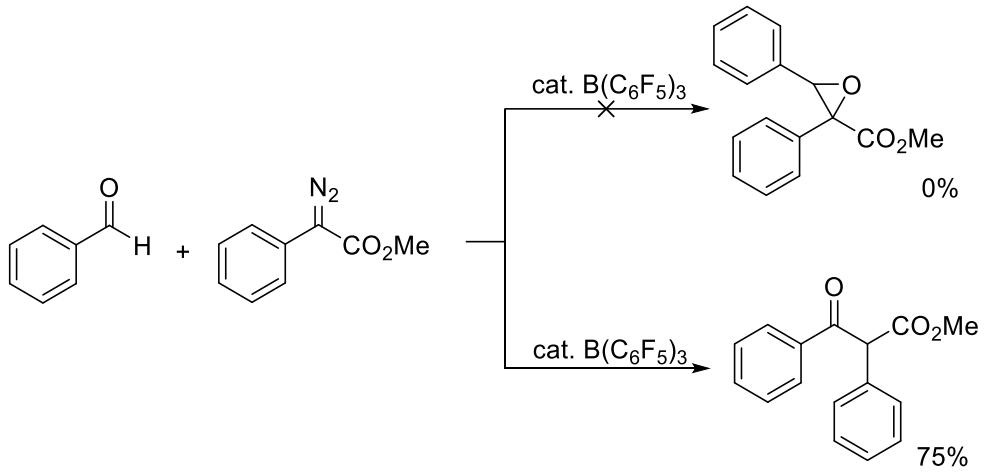
Synthesis of methyl 2-(2-ethynylphenyl)-1-(4-fluorophenyl)cyclopropane-1-carboxylate (**3ai**)



Synthesised in accordance with *General procedure b* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **1a** (45 mg, 0.23 mmol), and 1-ethynyl-2-vinylbenzene (13 mg, 0.1 mmol) in 1,2-DCE to afford **3ai**. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3ai**) was obtained as a colourless oil. Yield: 12 mg, 0.04 mmol, 41%.

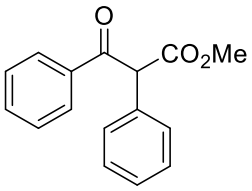
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.44 (dd, *J* = 7.7, 1.5 Hz, 1H, Ar–CH), 7.09–7.03 (m, 3H, Ar–CH), 6.96 (t, *J* = 7.7 Hz, 1H, Ar–CH), 6.77 (t, *J* = 8.7 Hz, 2H, Ar–CH), 6.42 (d, *J* = 7.4 Hz, 1H, Ar–CH), 3.69 (s, 3H, COOMe), 3.52 (dd, *J* = 9.2, 7.5 Hz, 1H, CH), 3.40 (s, 1H, C≡CH), 2.13 (dd, *J* = 9.1, 5.1 Hz, 1H, CH), 1.97 (dd, *J* = 7.5, 5.0 Hz, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 174.1 (C=O), 161.8 (d, $J_{C–F}$ = 245.9 Hz), 139.0, 133.2 (d, $J_{C–F}$ = 8.1 Hz), 132.6, 130.8 (d, $J_{C–F}$ = 3.2 Hz), 128.5, 126.5, 125.9, 123.9, 114.7 (d, $J_{C–F}$ = 21.5 Hz), 82.48 (C≡C), 82.44 (C≡C), 52.7 (COOMe), 36.1 (CH), 32.3 (CH), 19.0 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -115.15 (Ar–F); IR ν_{max} (cm^{-1}): 3298 (C≡CH), 2953, 2926, 1718 (C=O), 1513, 1260, 1221, 1160; HRMS (ES+) $[M+H]^+$ calculated for $[C_{19}H_{16}O_2F]^+$: 295.1134; found 295.1136.

3. Attempted reaction



3.1 Synthesis and spectral characterization of product

Synthesis of methyl 3-oxo-2,3-diphenylpropanoate[11]



In the glove box under nitrogen atmosphere, tris(pentafluorophenyl)borane $B(C_6F_5)_3$ (5 mg, 0.01 mmol), benzaldehyde (11 mg, 0.1 mmol, 1 equiv), and **1c** (23 mg, 0.13 mmol, 1.3 equiv) were all dissolved separately in 1,2-DCE (0.5 mL). The $B(C_6F_5)_3$ solution was mixed with the aldehyde solution, and then the **1c** solution was added dropwise into the reaction mixture. The reaction tube was sealed and was left to stir at room temperature for 3 h. Afterwards, all volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The product was obtained as yellow oil. Yield: 19 mg, 0.07 mmol, 75%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.96–7.94 (m, 2H, Ar–CH), 7.55–7.52 (m, 1H, Ar–CH), 7.44–7.34 (m, 6H, Ar–CH), 7.32–7.29 (m, 1H, Ar–CH), 5.63 (s, 1H, C–CH), 3.76 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 193.3 (C=O), 169.4 (C=O), 135.7, 133.7, 133.0, 129.7, 129.1, 129.0, 128.8, 128.3, 60.5 (C–CH), 52.9 (COOMe).

4. NMR Spectra

Figure S1: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) spectrum of **1a**.

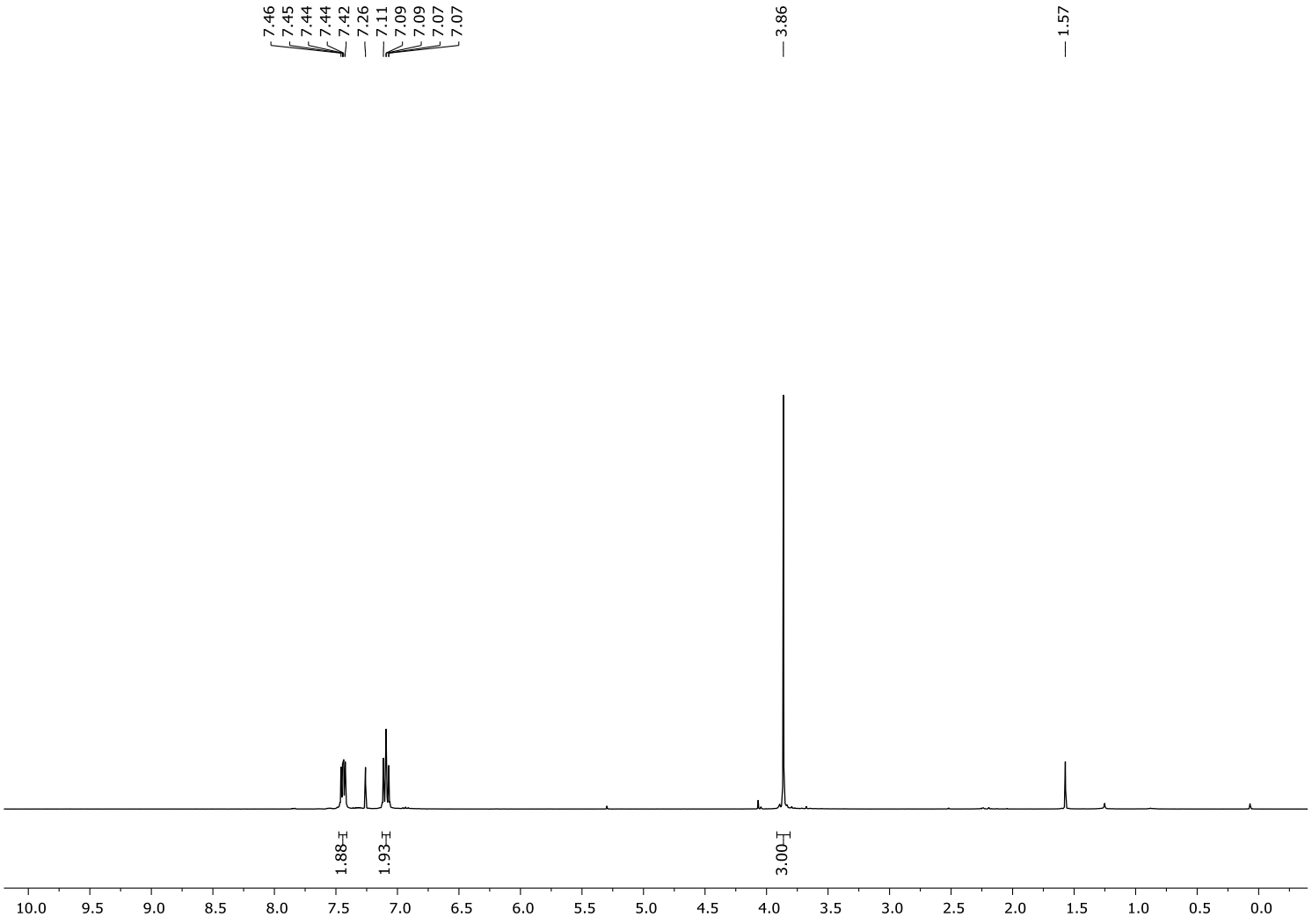


Figure S2: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **1a**.

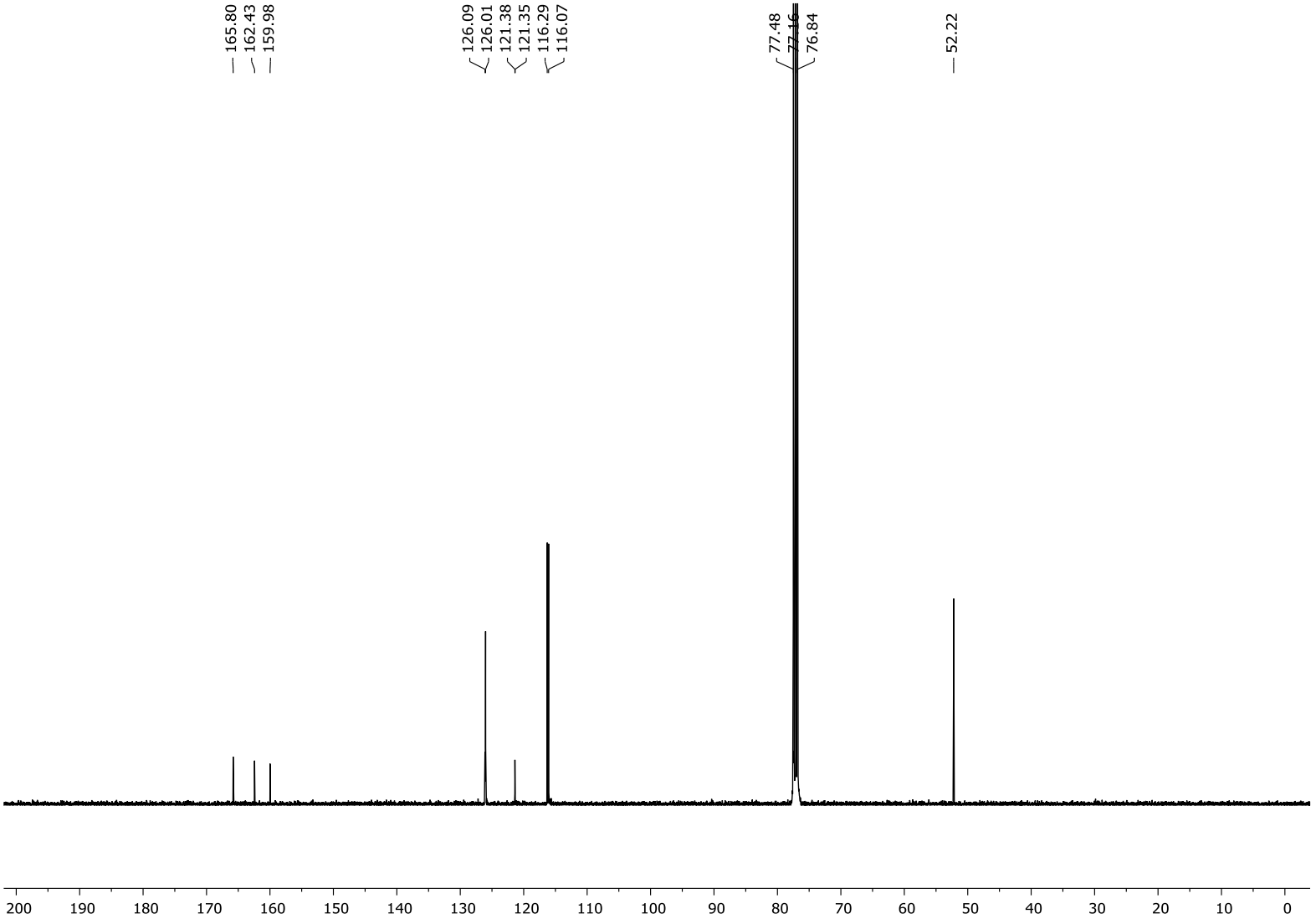


Figure S3: **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) spectrum of **1a**.

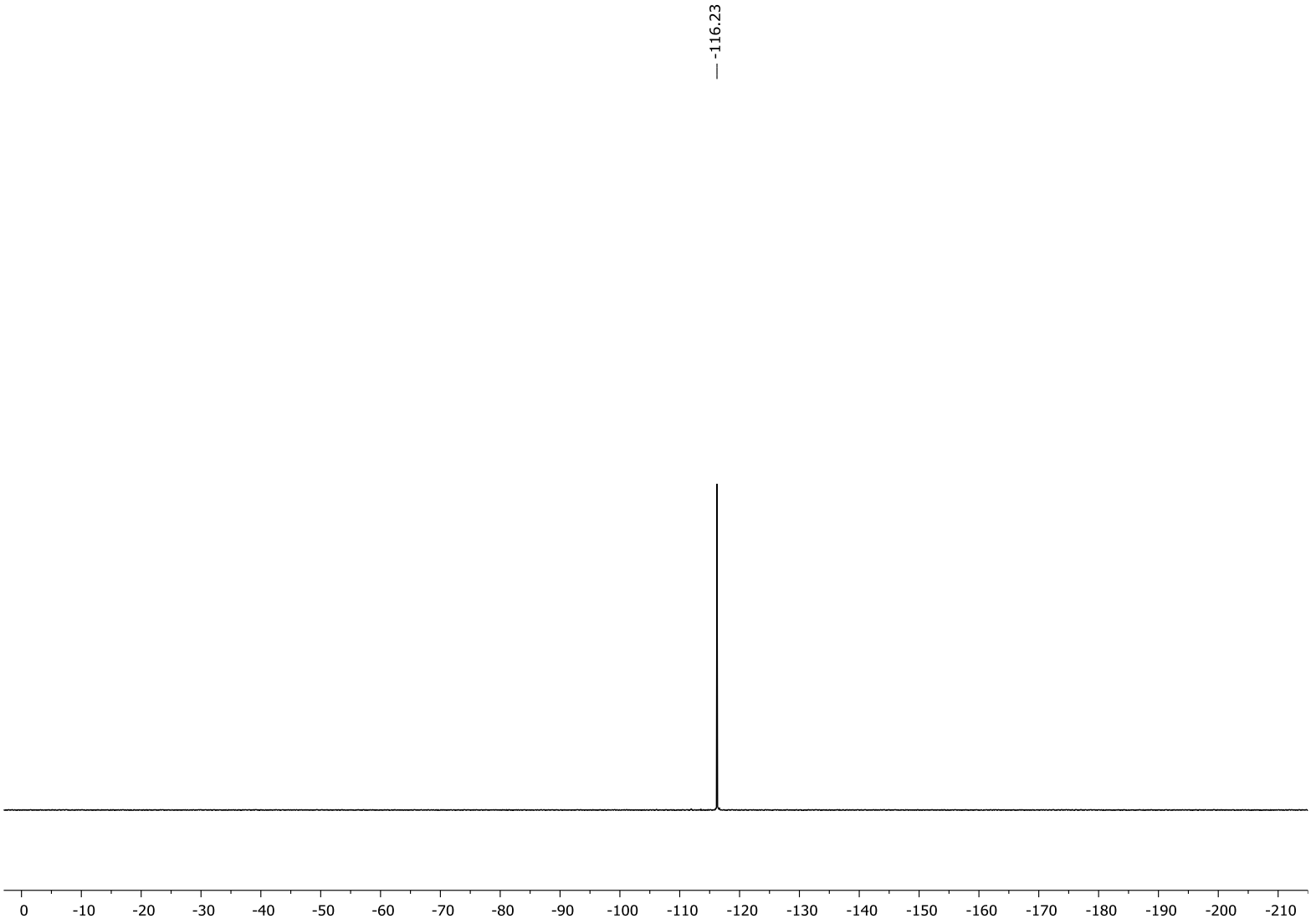


Figure S4: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1b**.

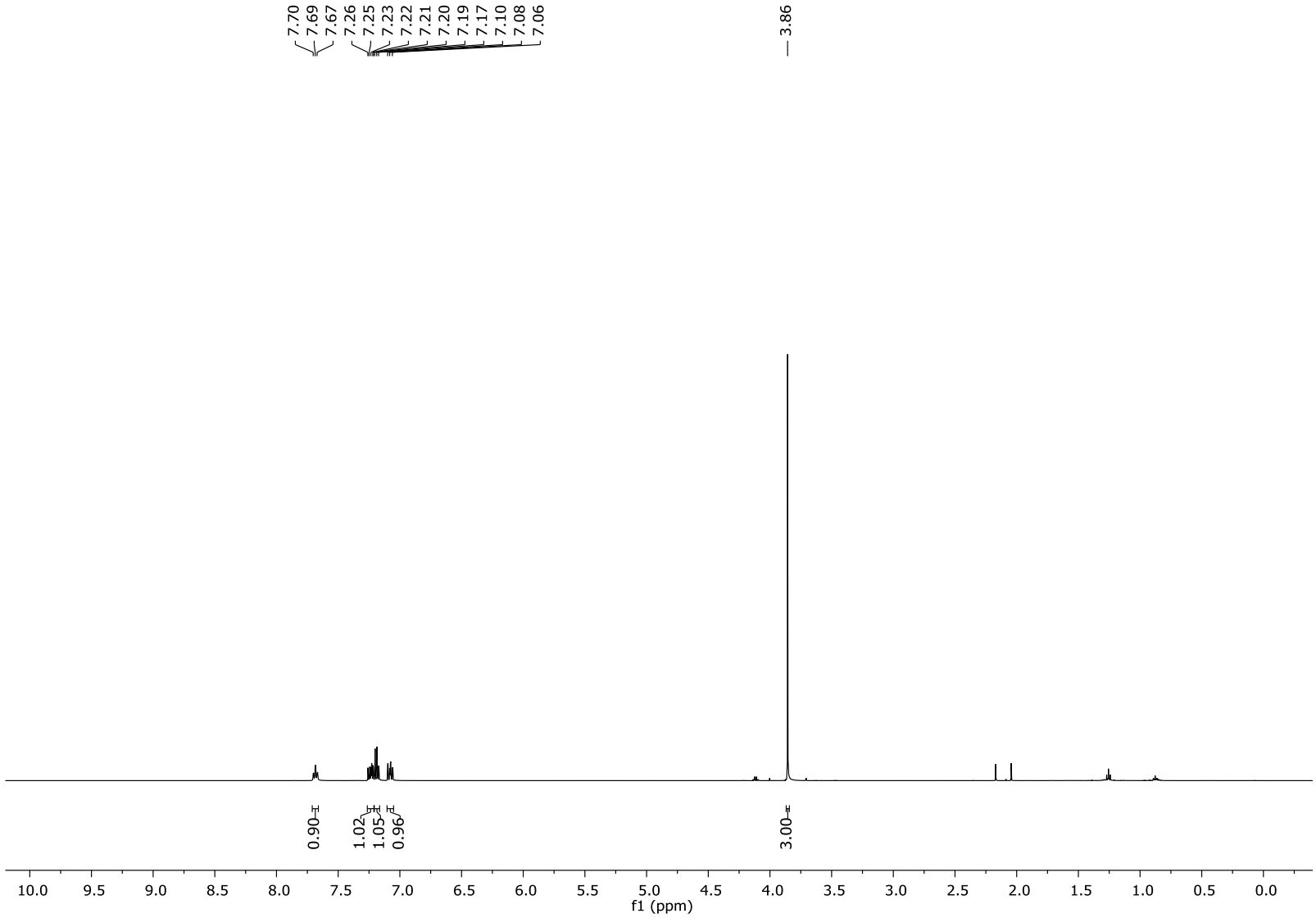


Figure S5: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1b**.

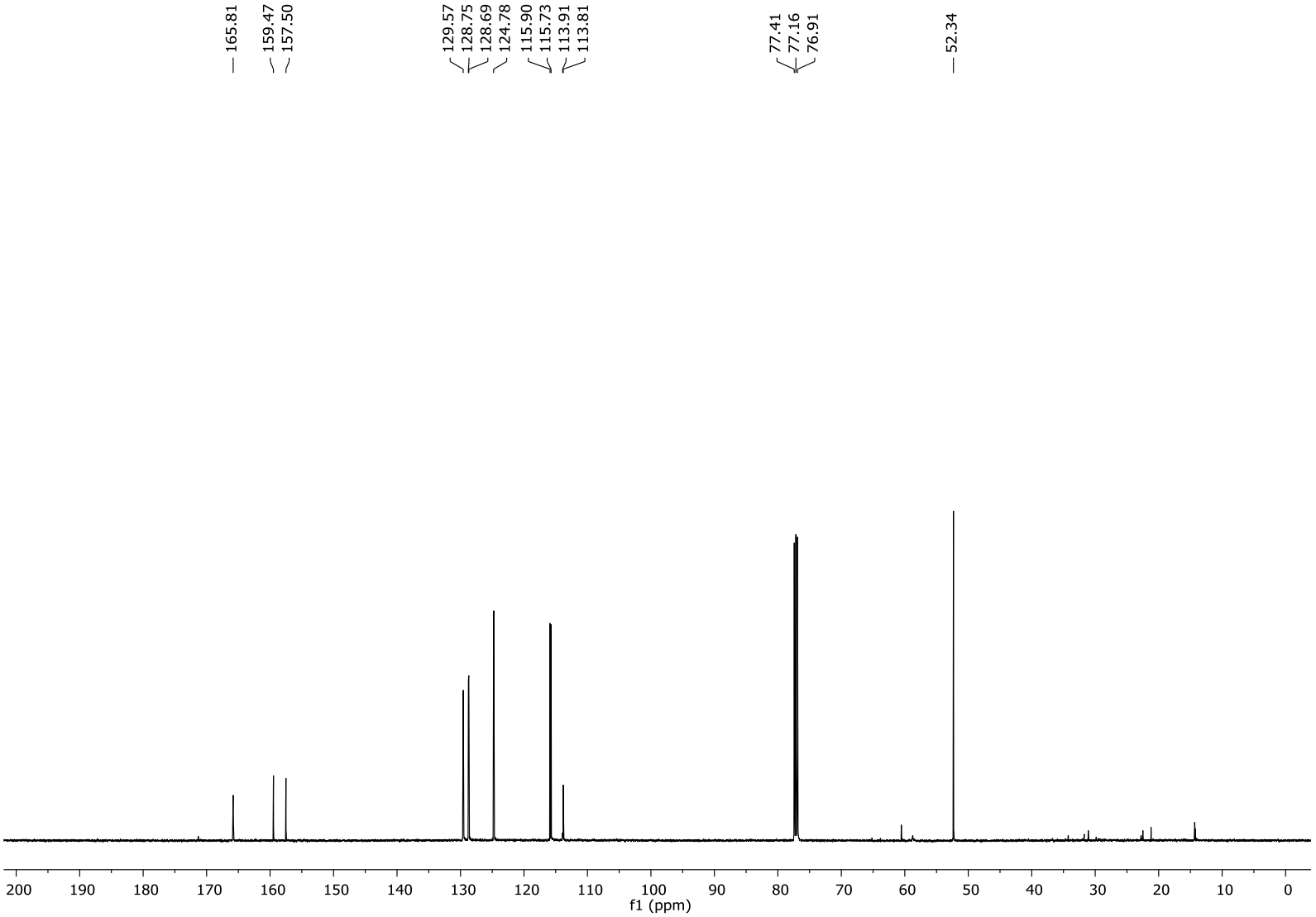


Figure S6: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **1b**.

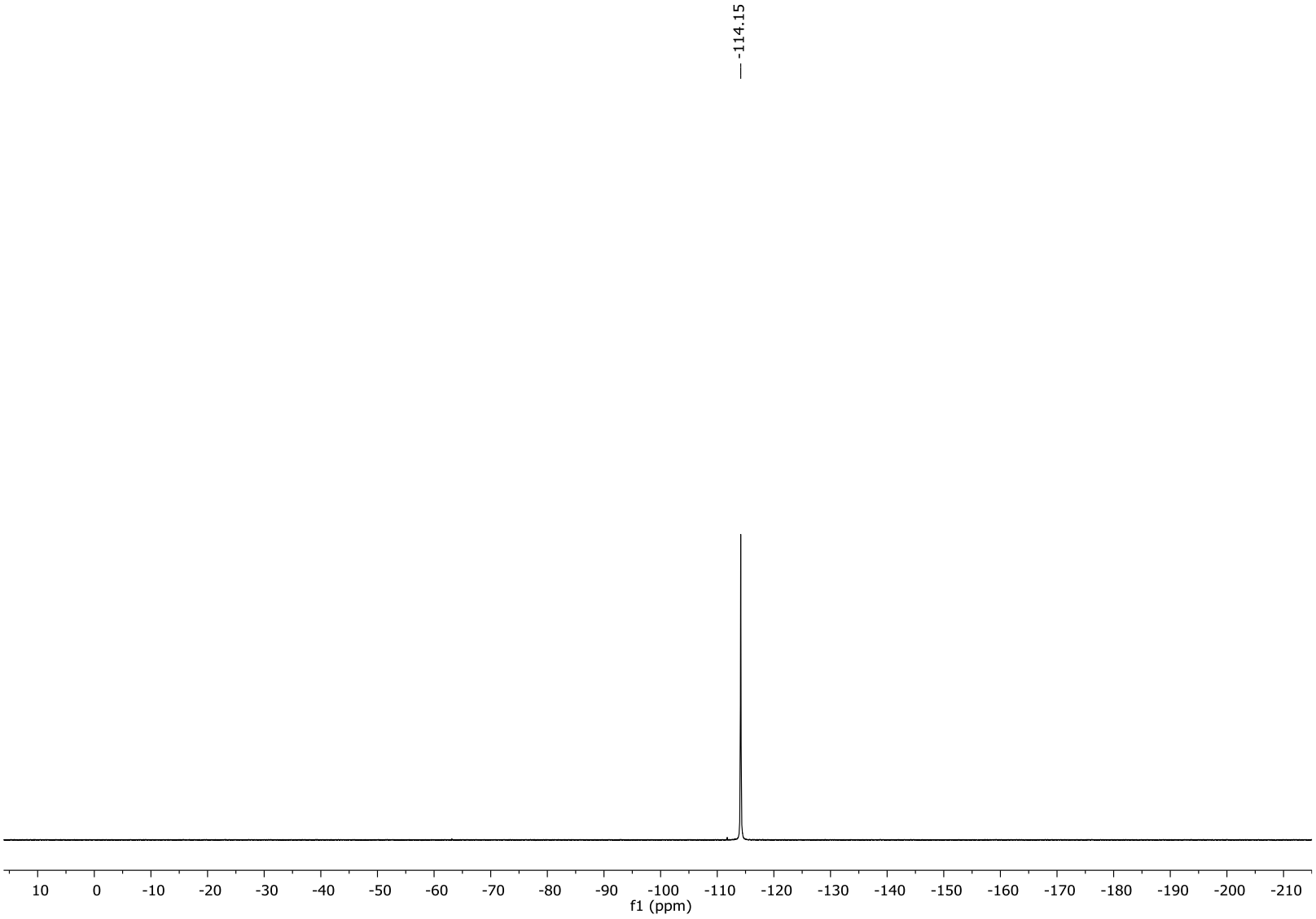


Figure S7: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1c**.

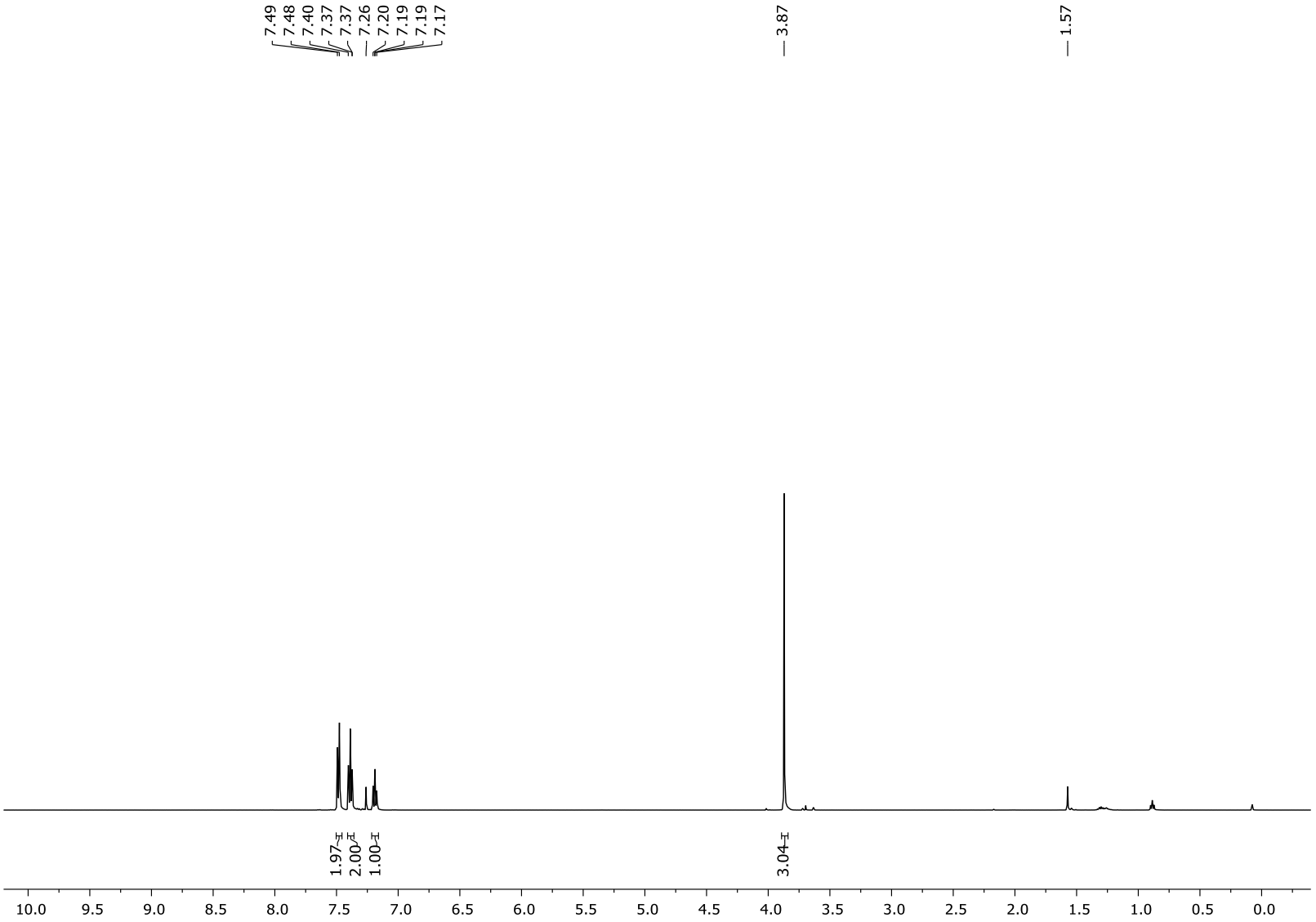


Figure S8: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1c**.

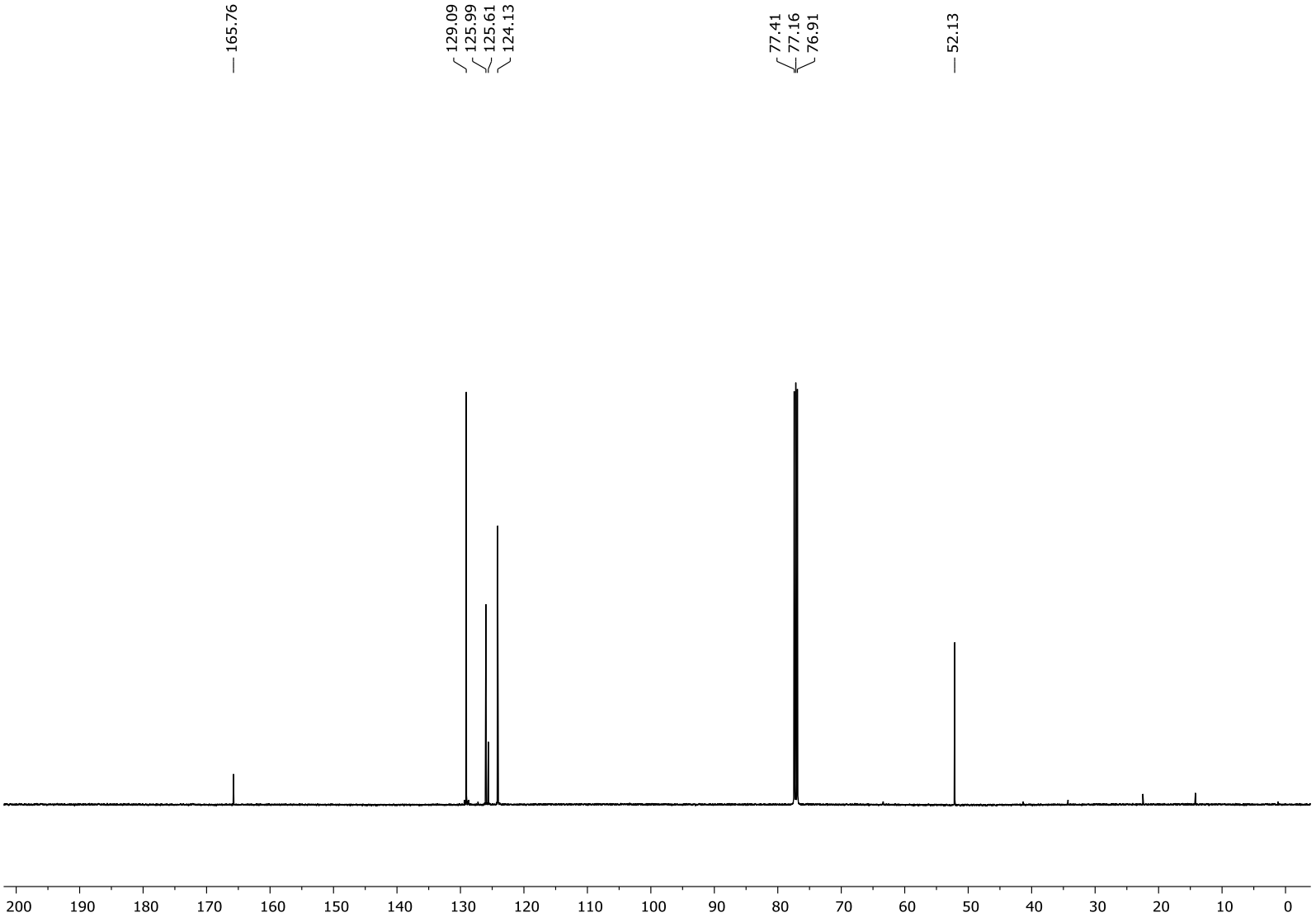


Figure S9: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1d**.

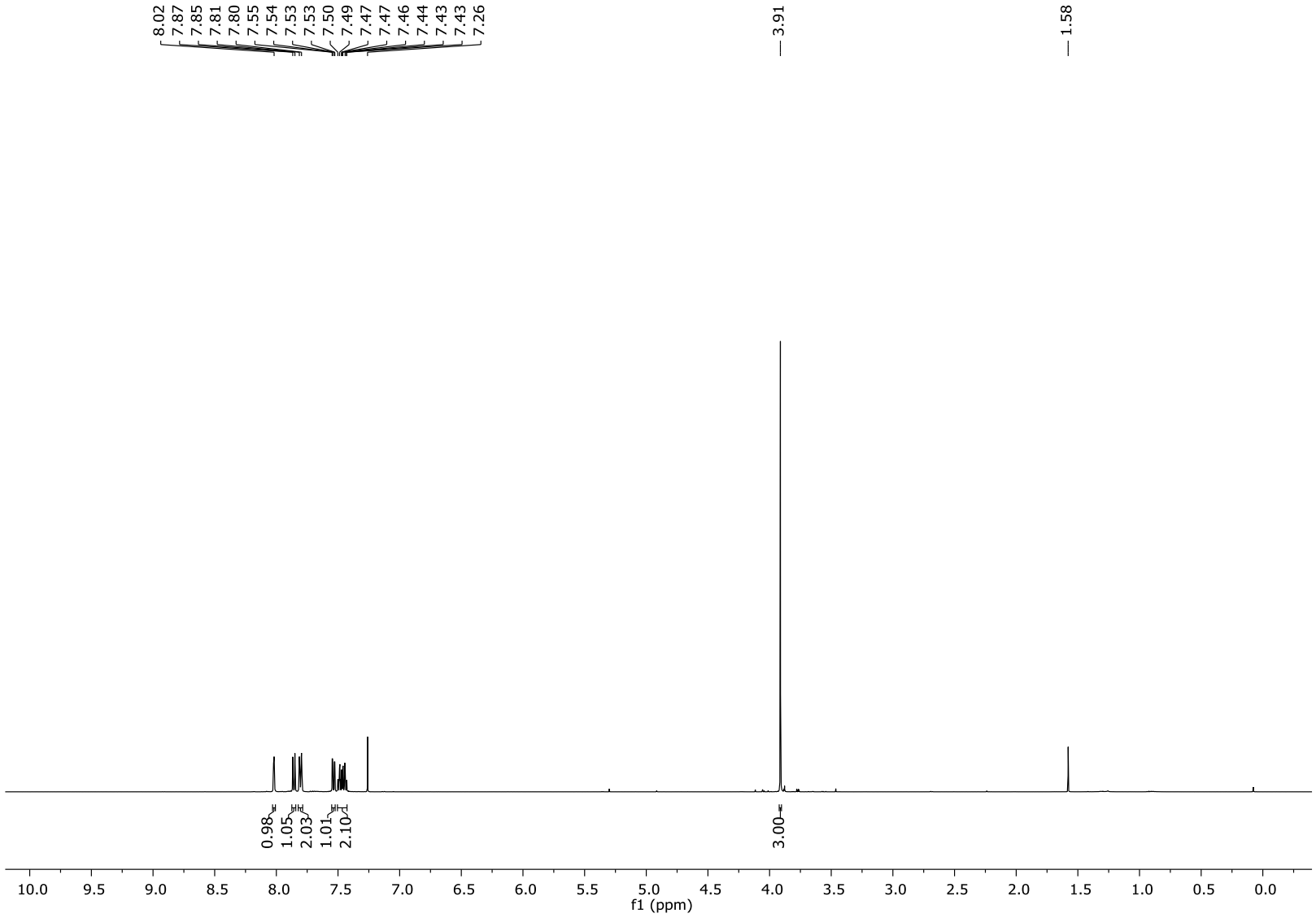


Figure S10: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1d**.

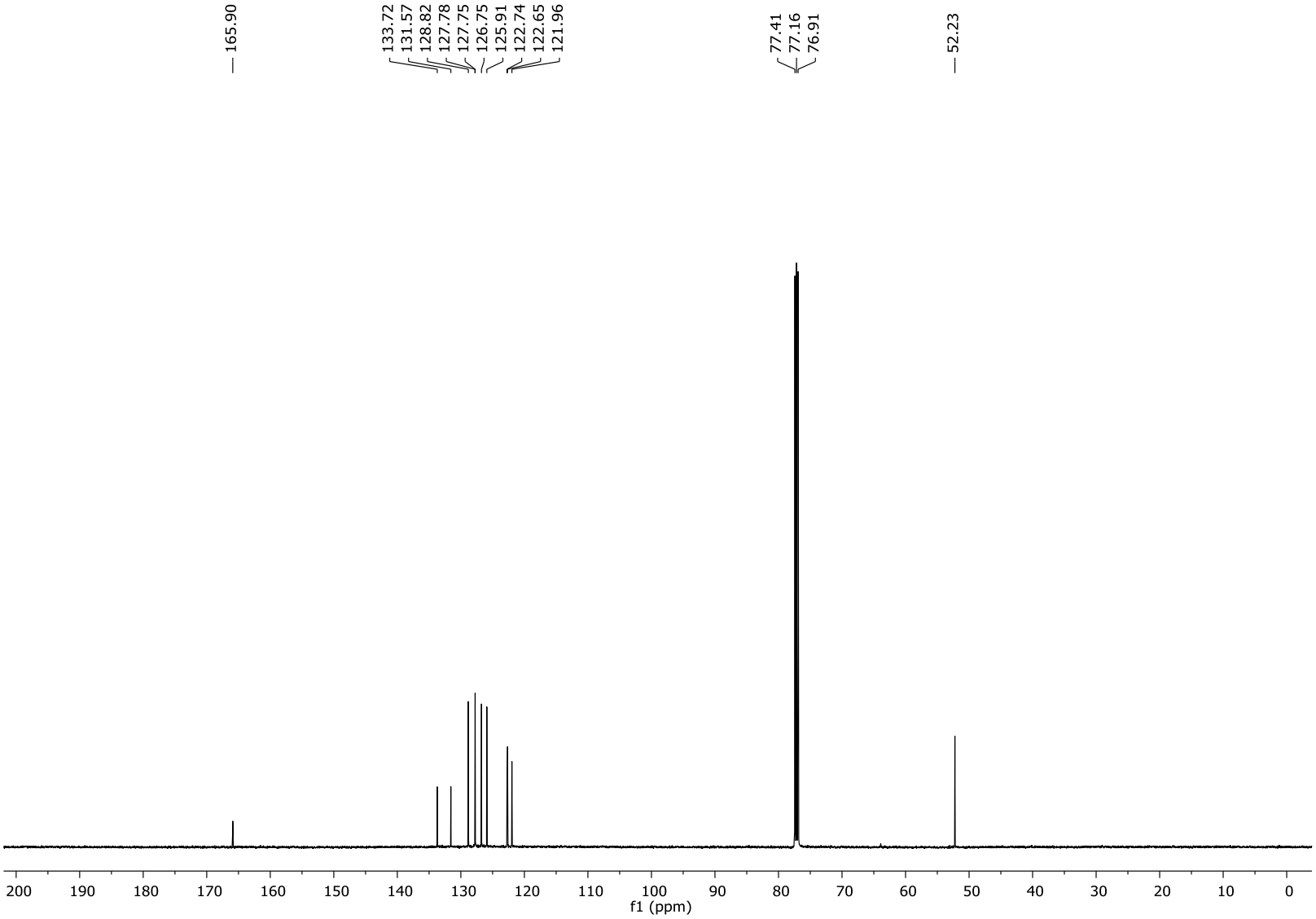


Figure S11: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) spectrum of **1e**.

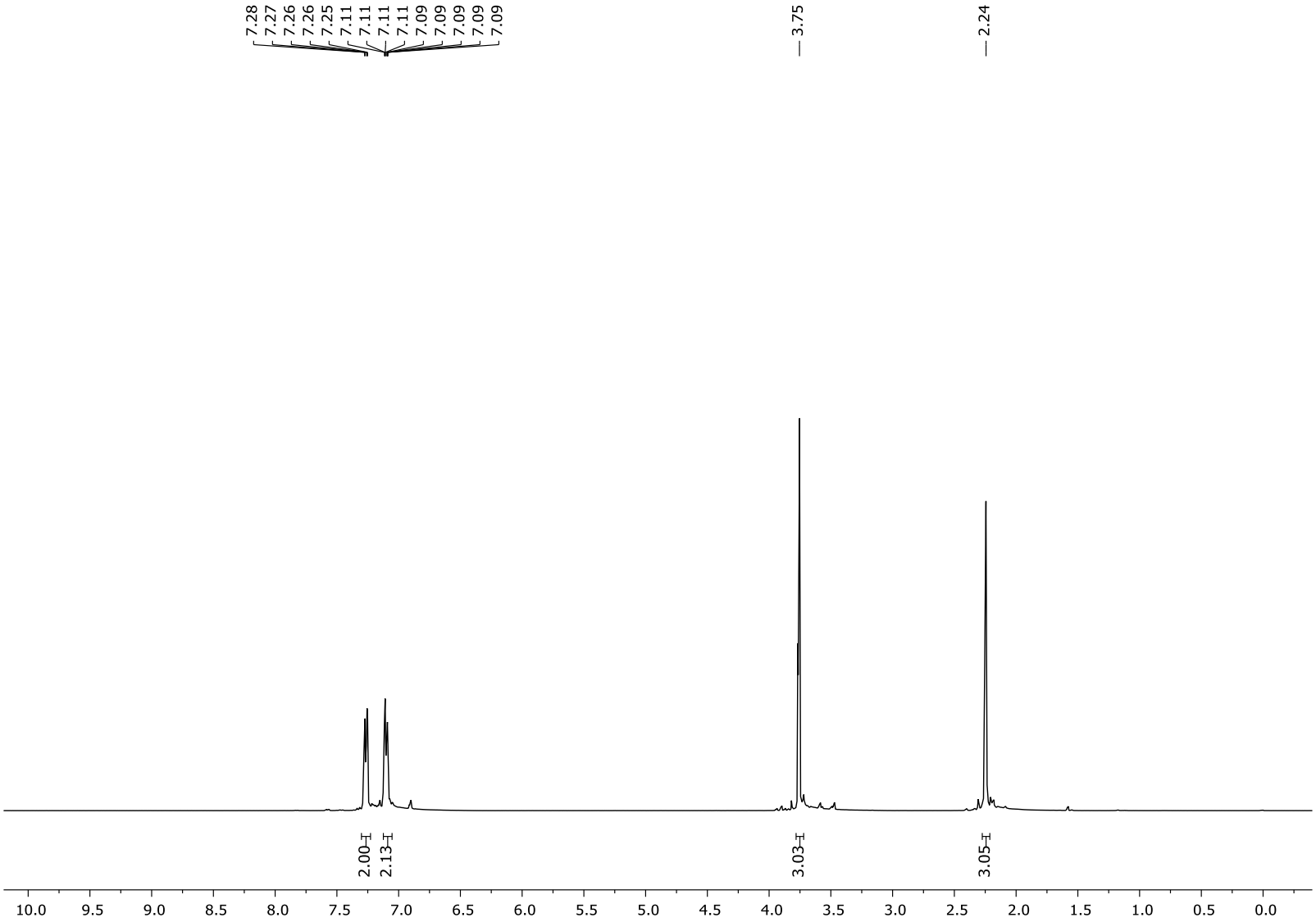


Figure S12: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **1e**.

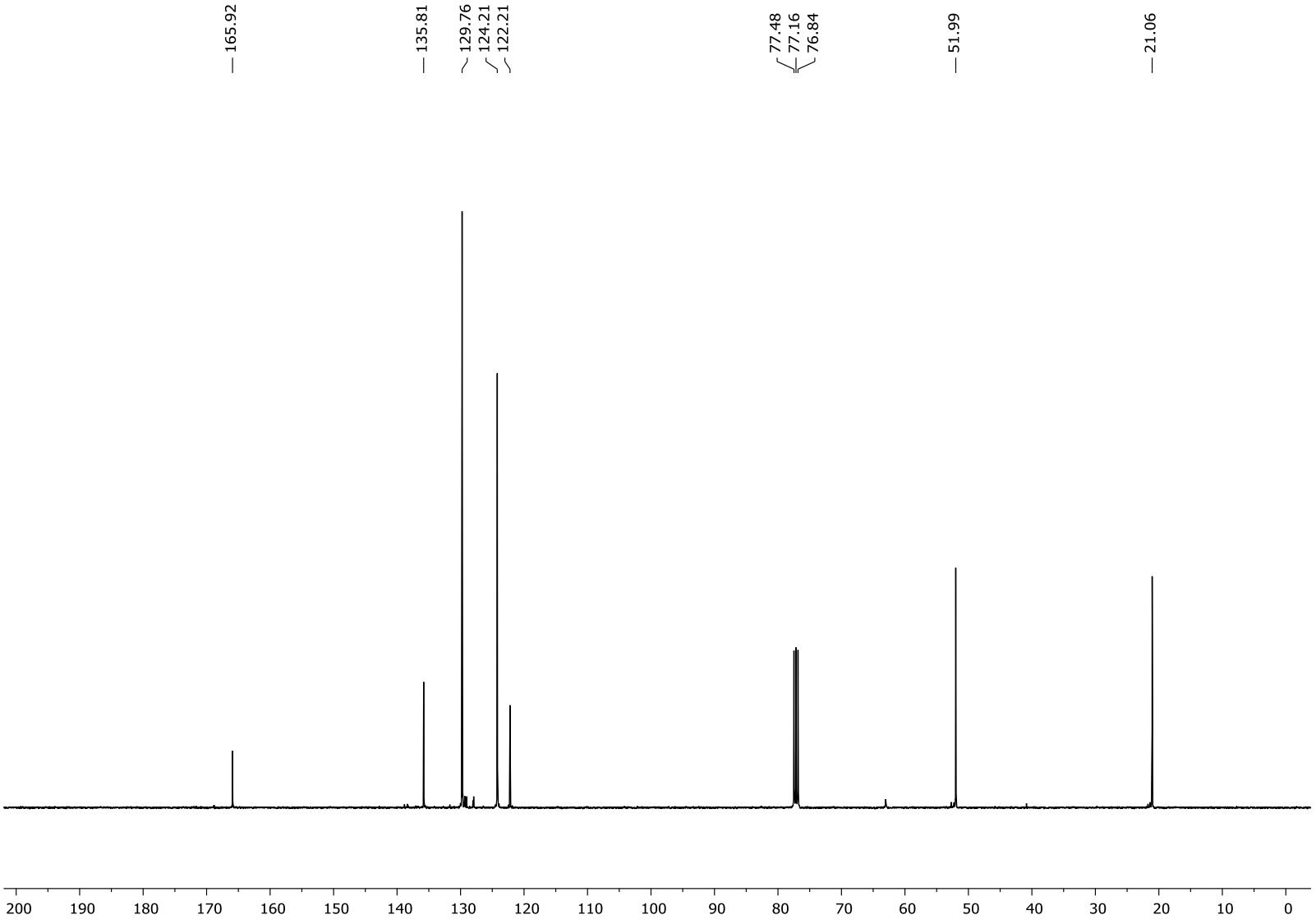


Figure S13: **^{1}H NMR** (300 MHz, $CDCl_3$, 298 K) spectrum of **1f**.

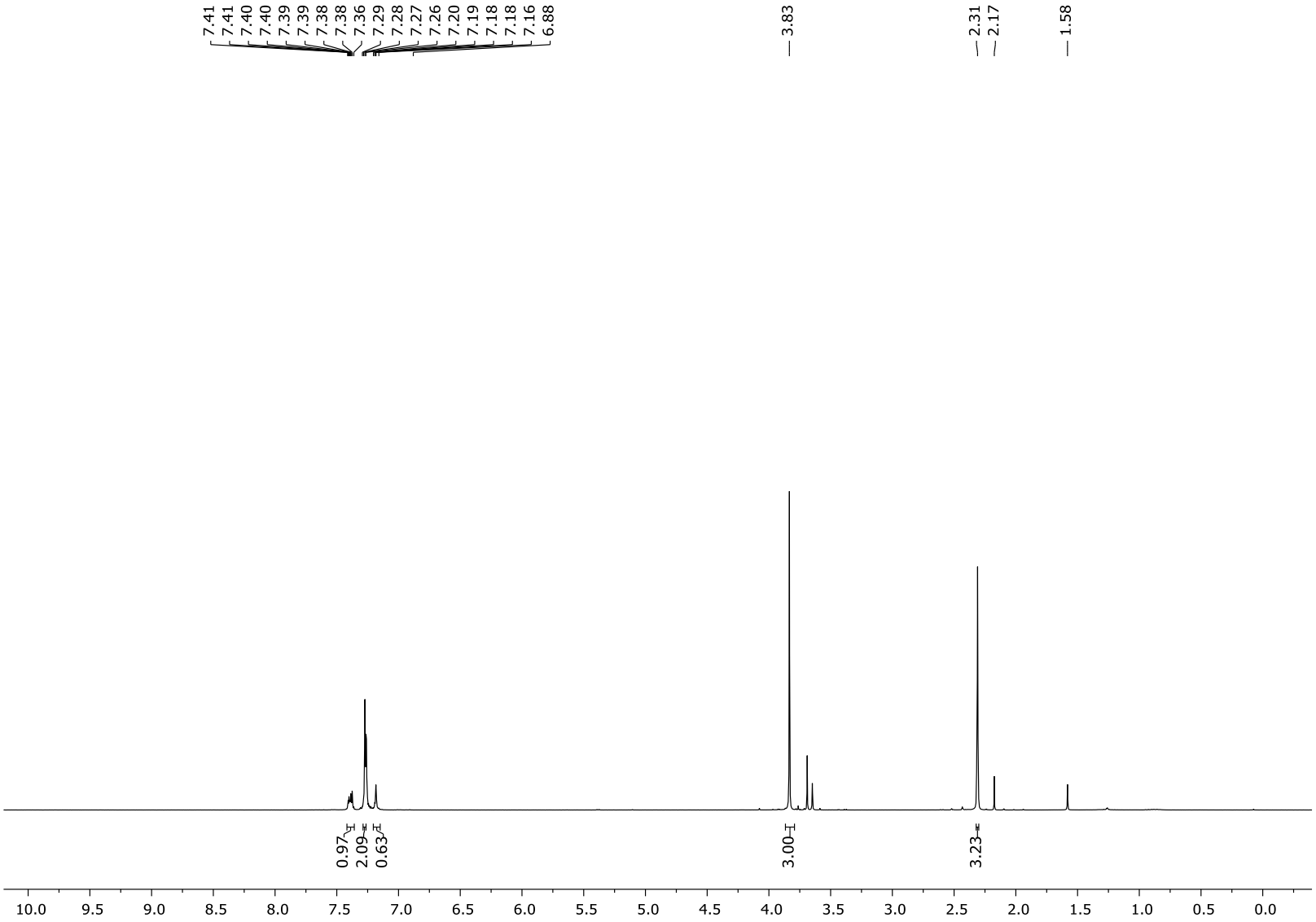


Figure S14: **^{13}C NMR** (75 MHz, $CDCl_3$, 298 K) spectrum of **1f**.

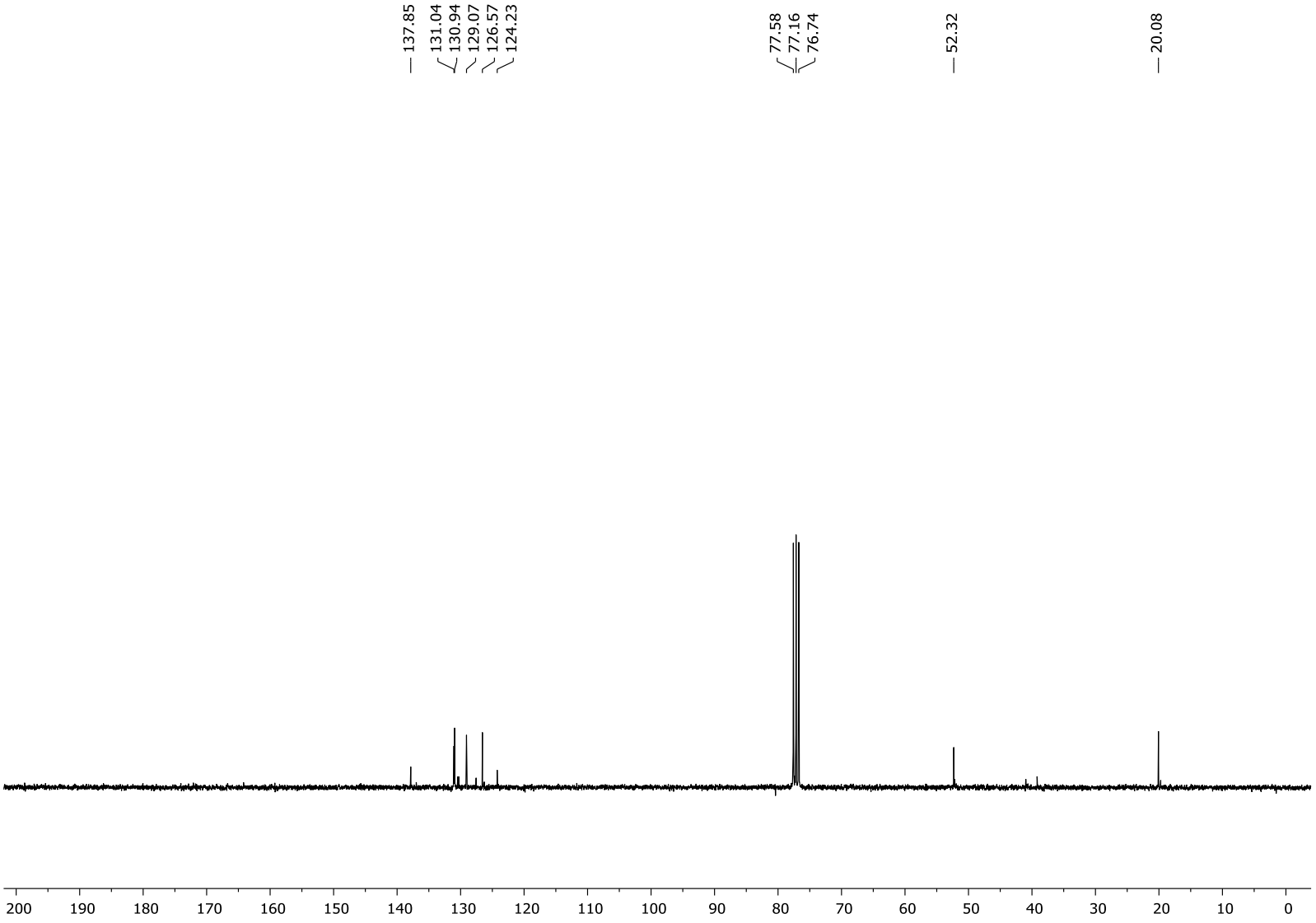


Figure S15: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) spectrum of **1g**.

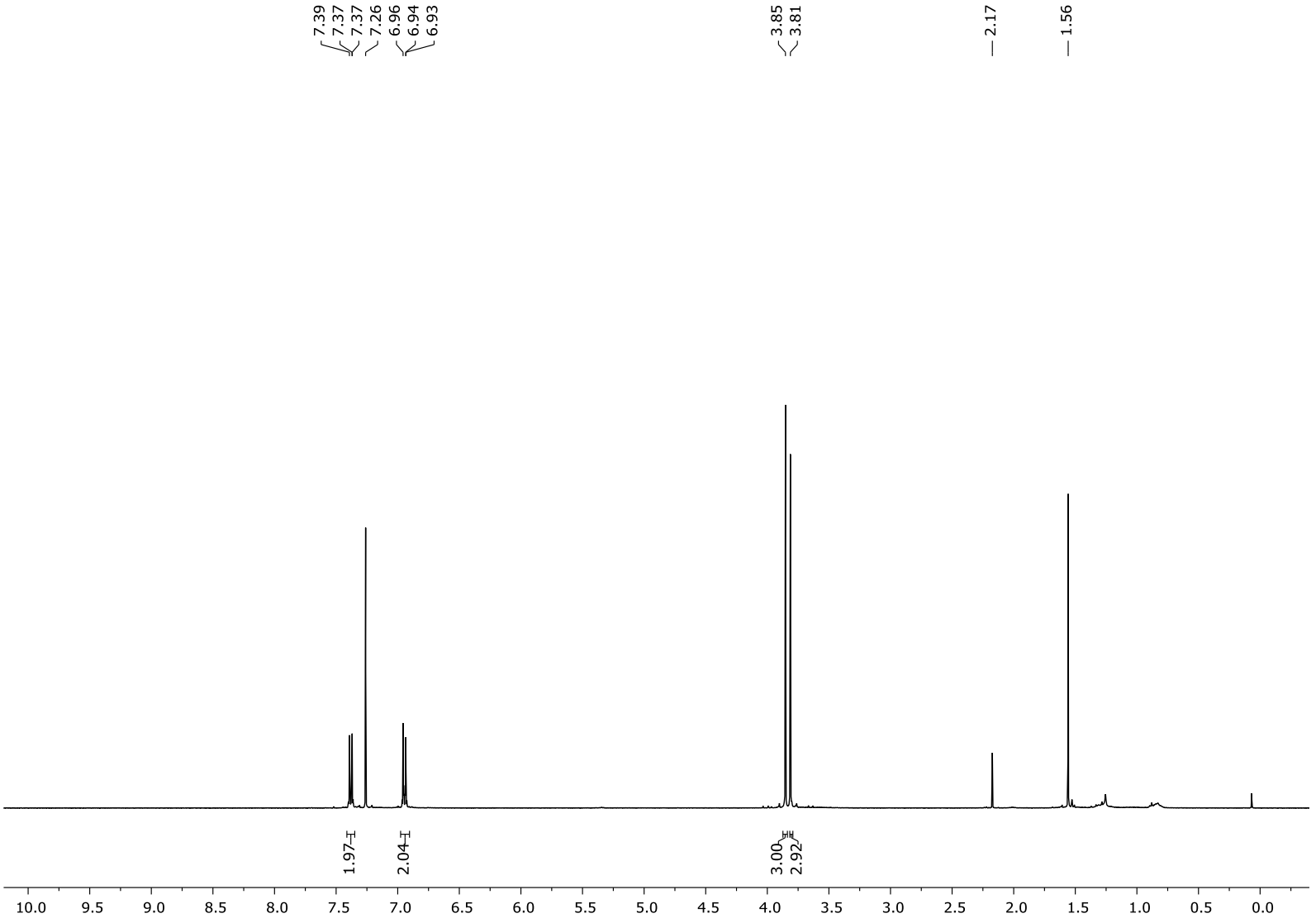


Figure S16: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **1g**.

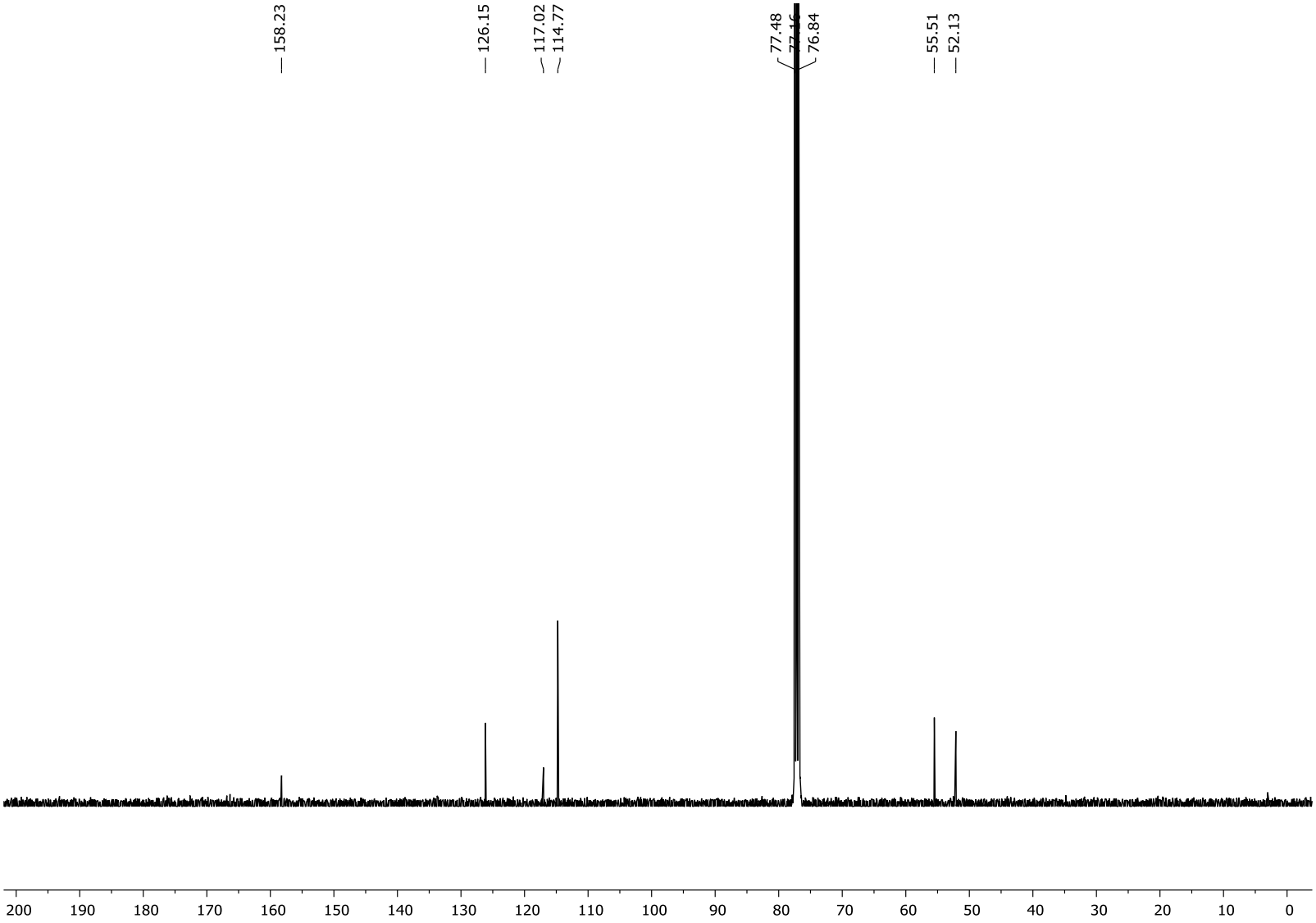


Figure S17: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) spectrum of **1h**.

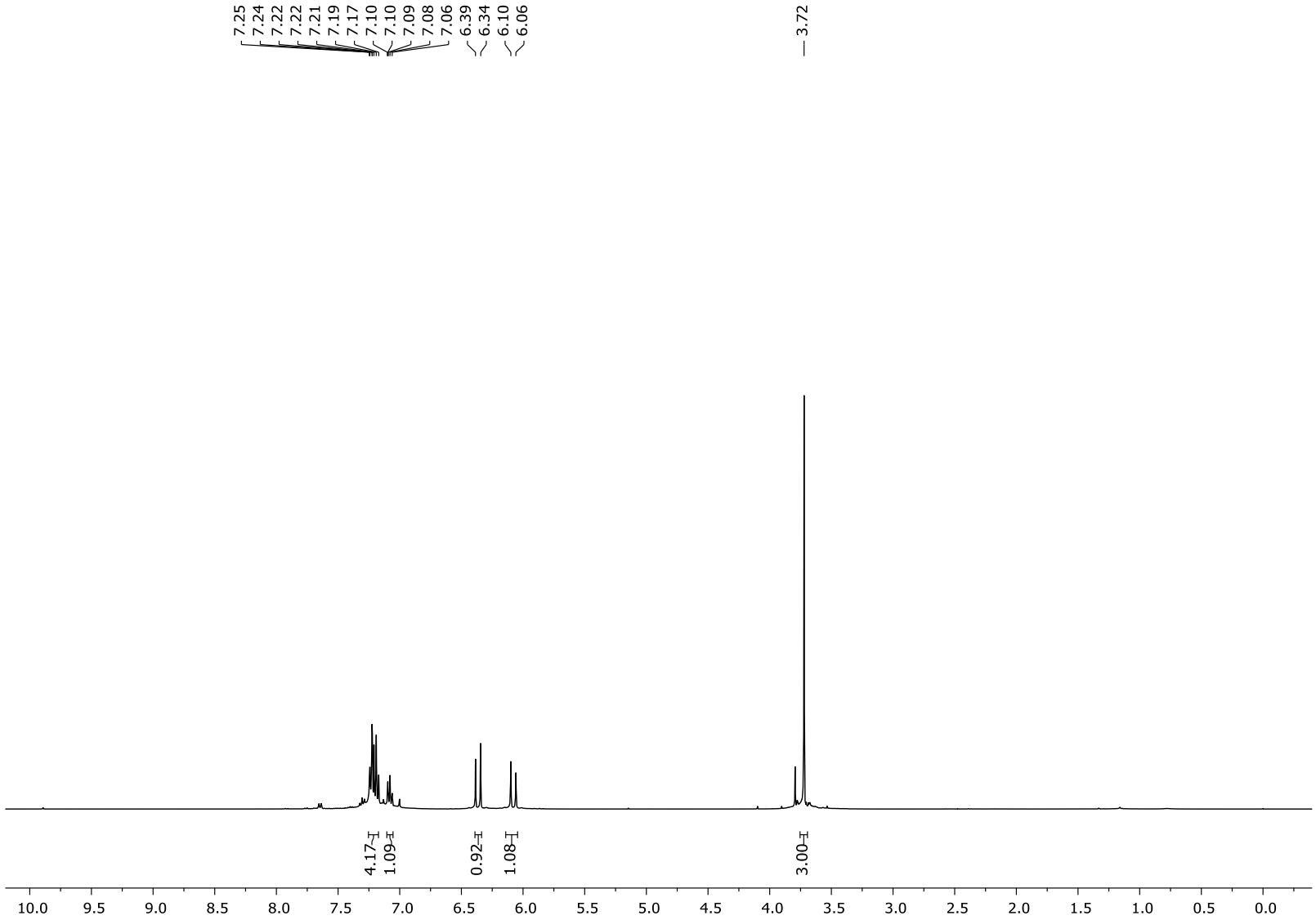


Figure S18: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **1h**.

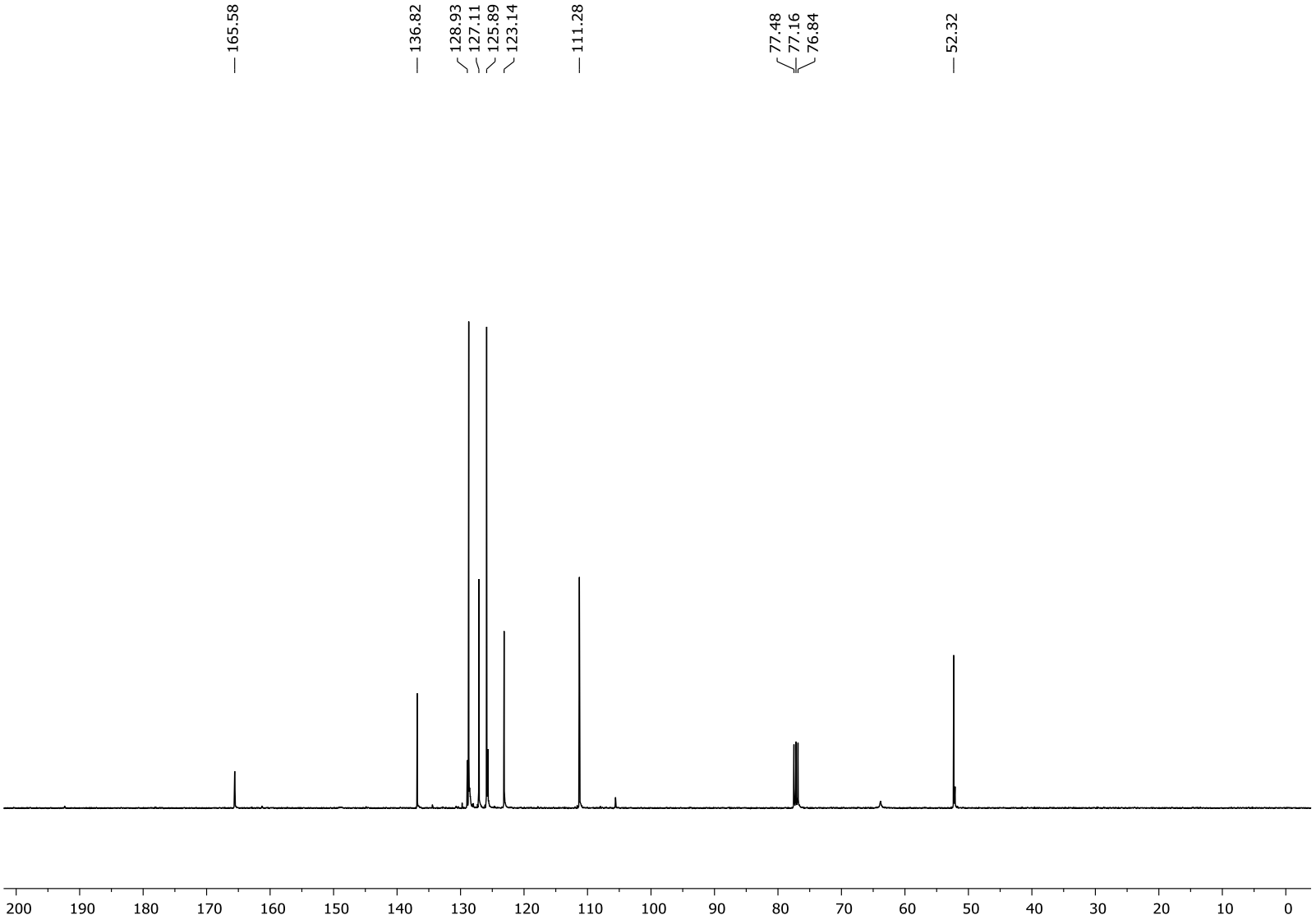


Figure S19: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) spectrum of **1i**.

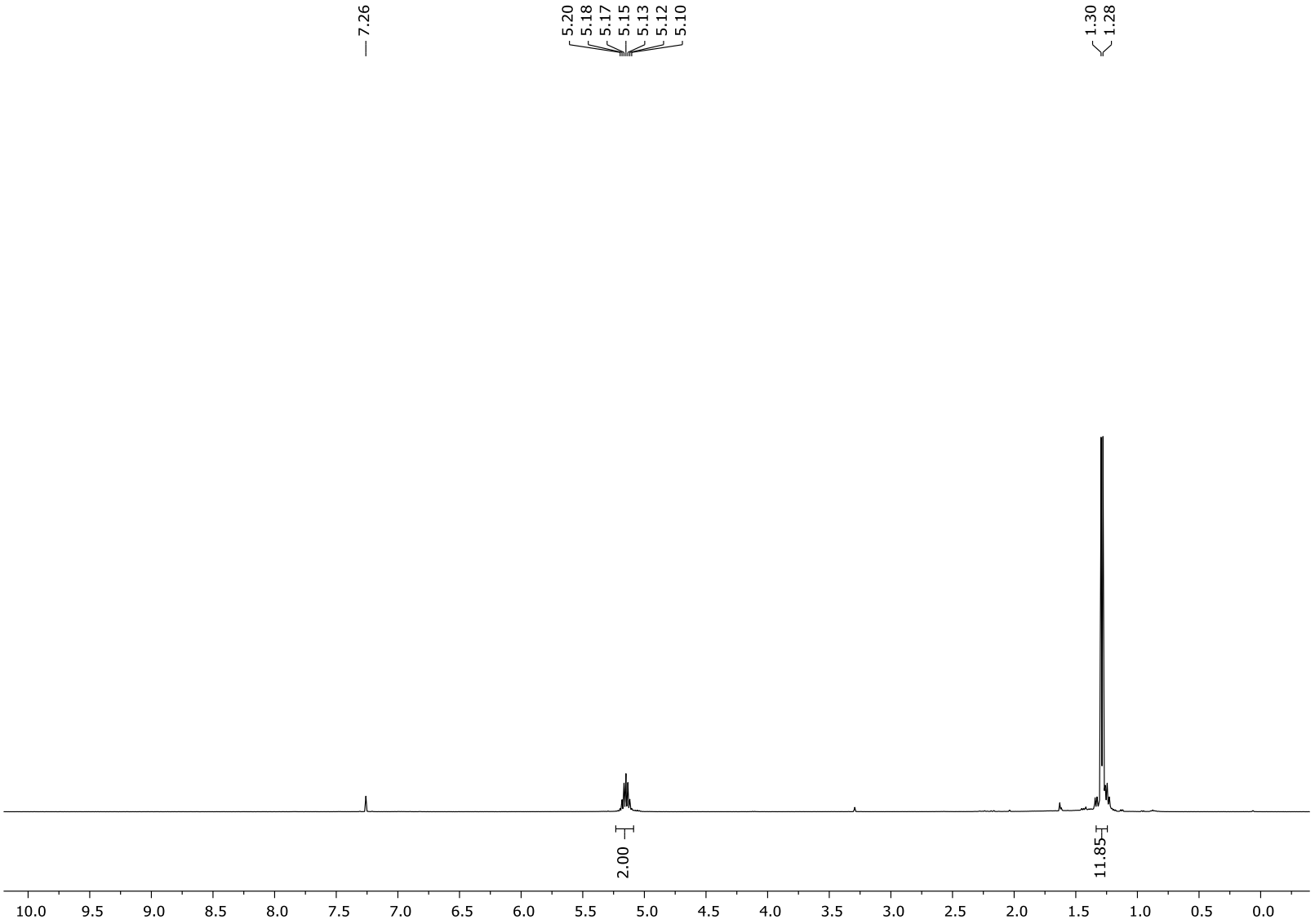


Figure S20: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **1i**.

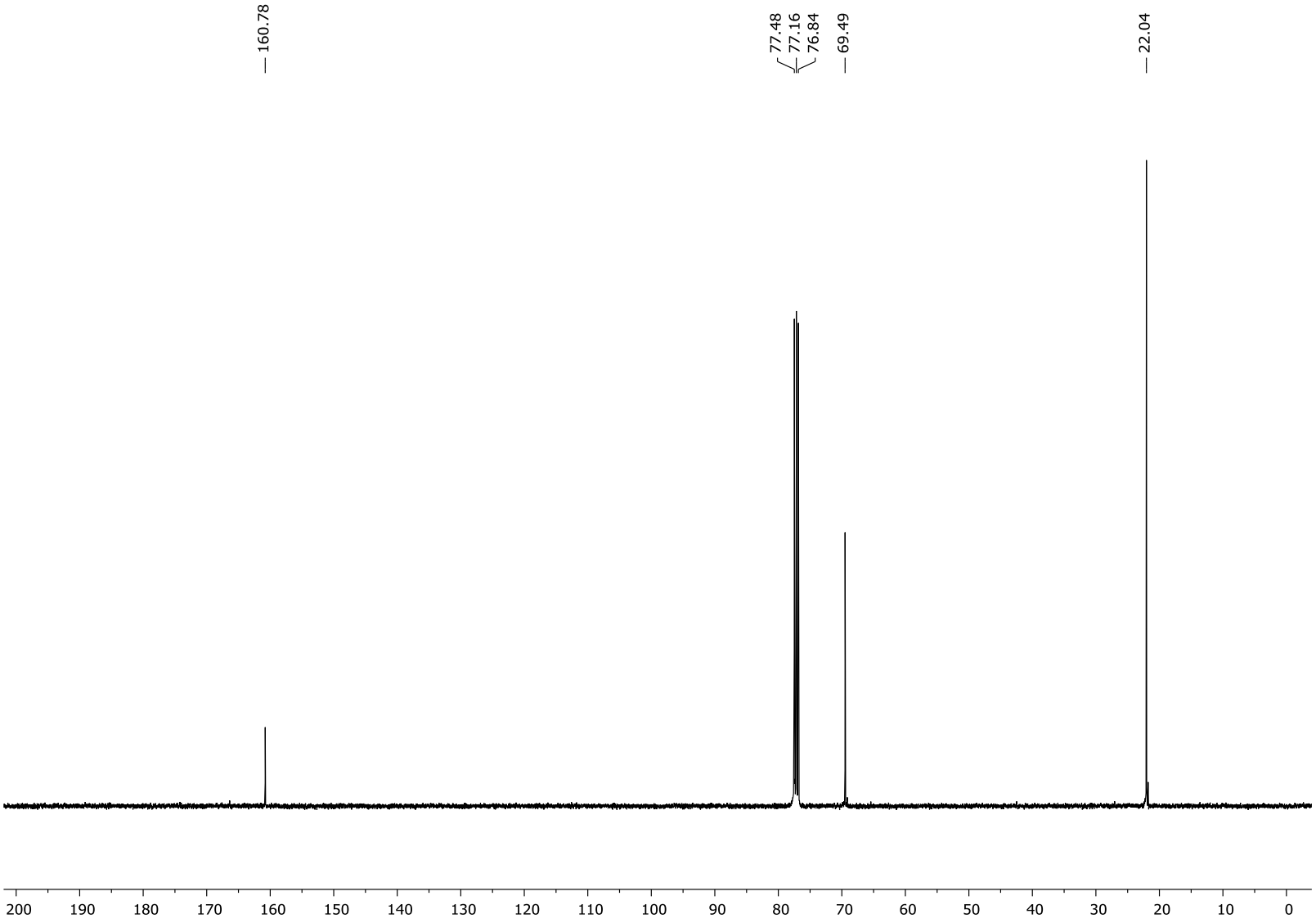


Figure S21: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

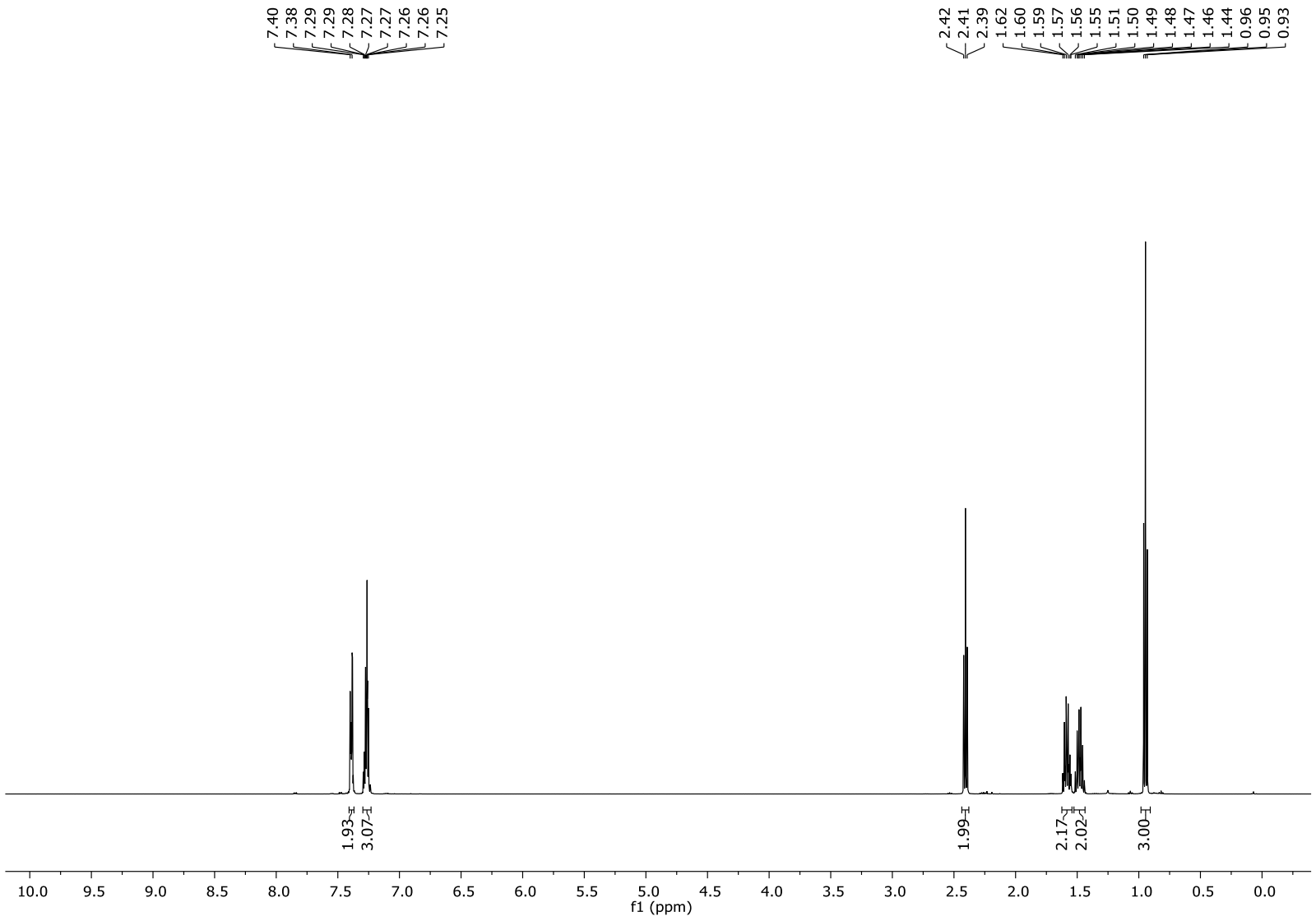


Figure S22: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

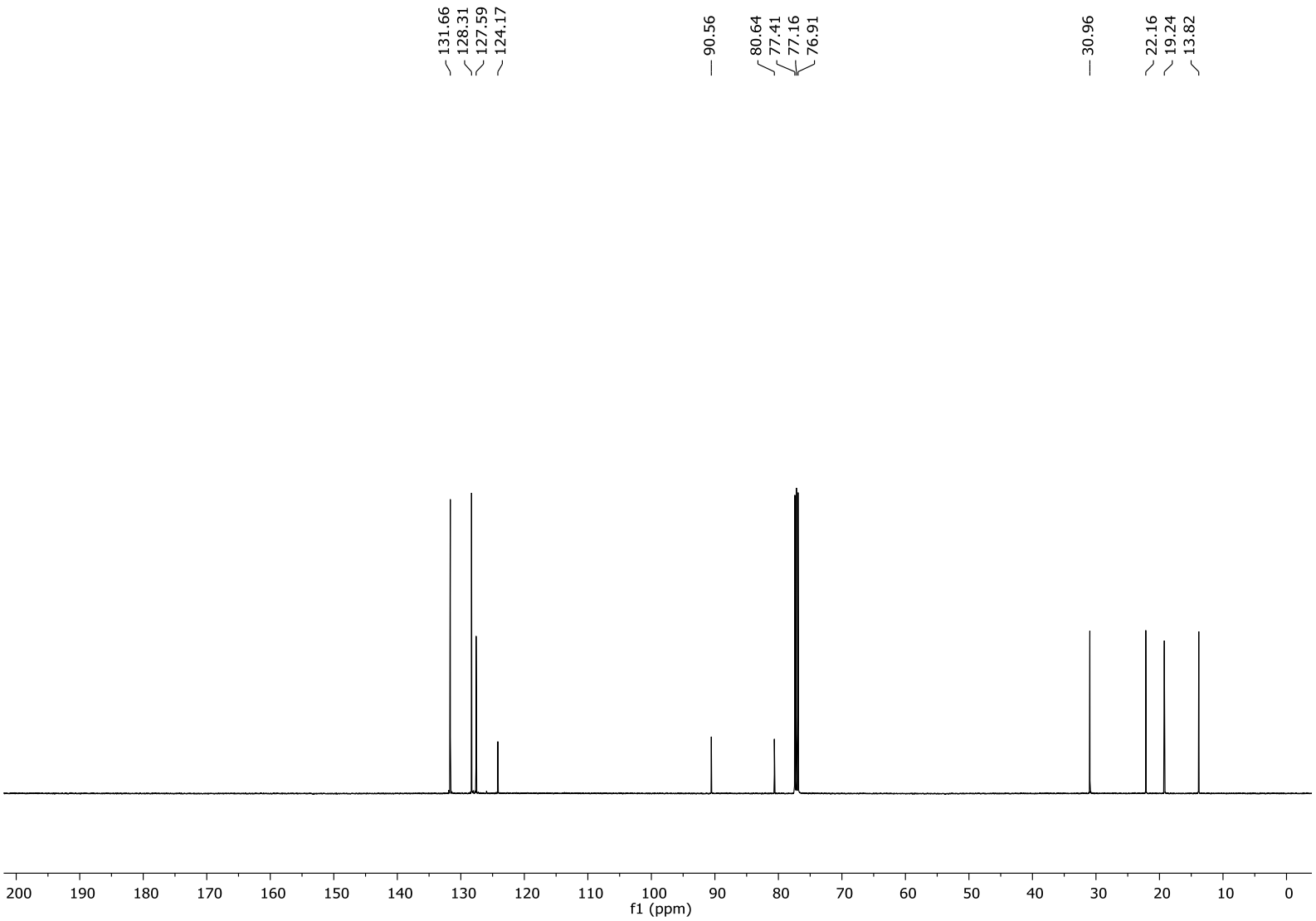


Figure S23: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

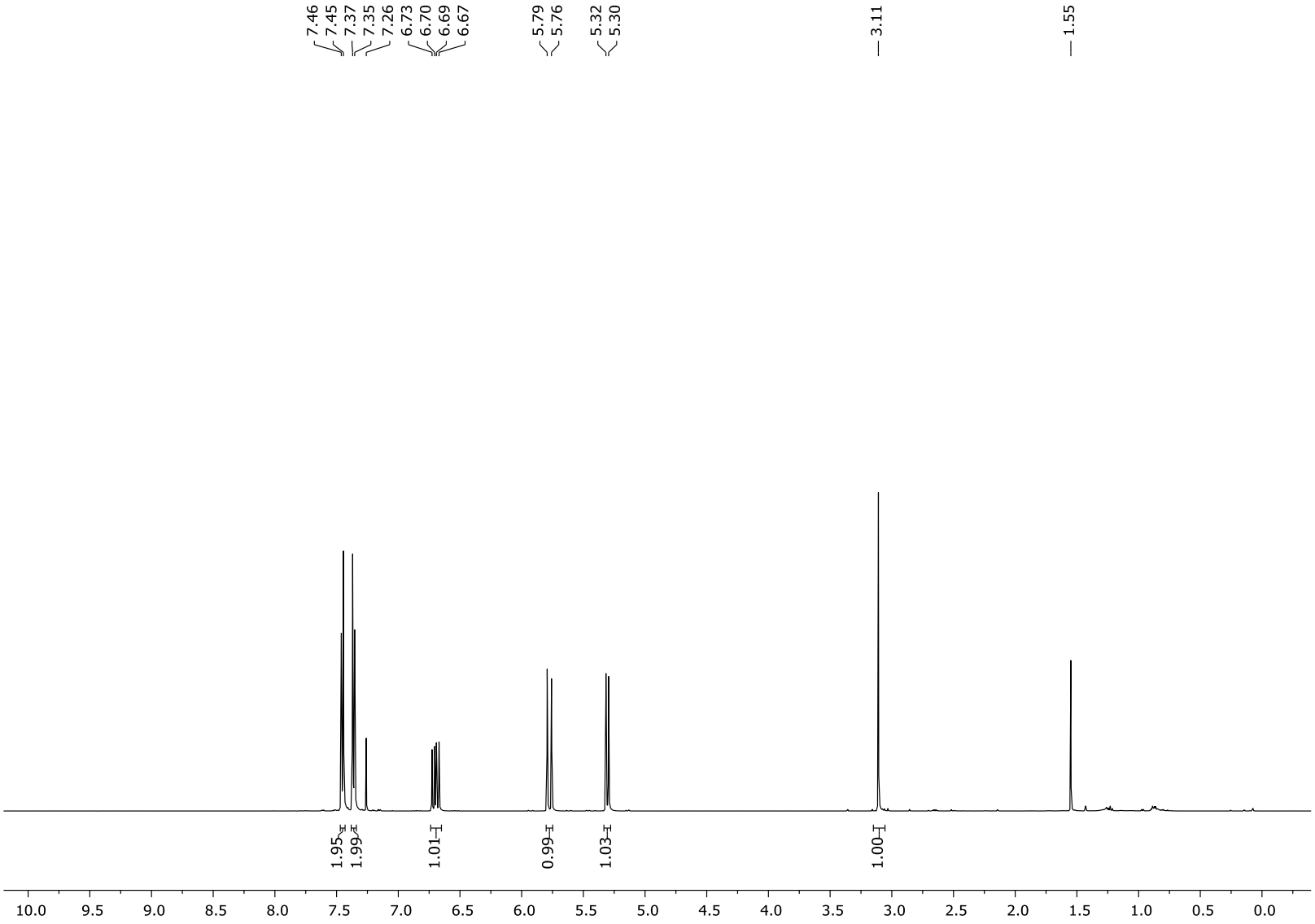


Figure S24: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

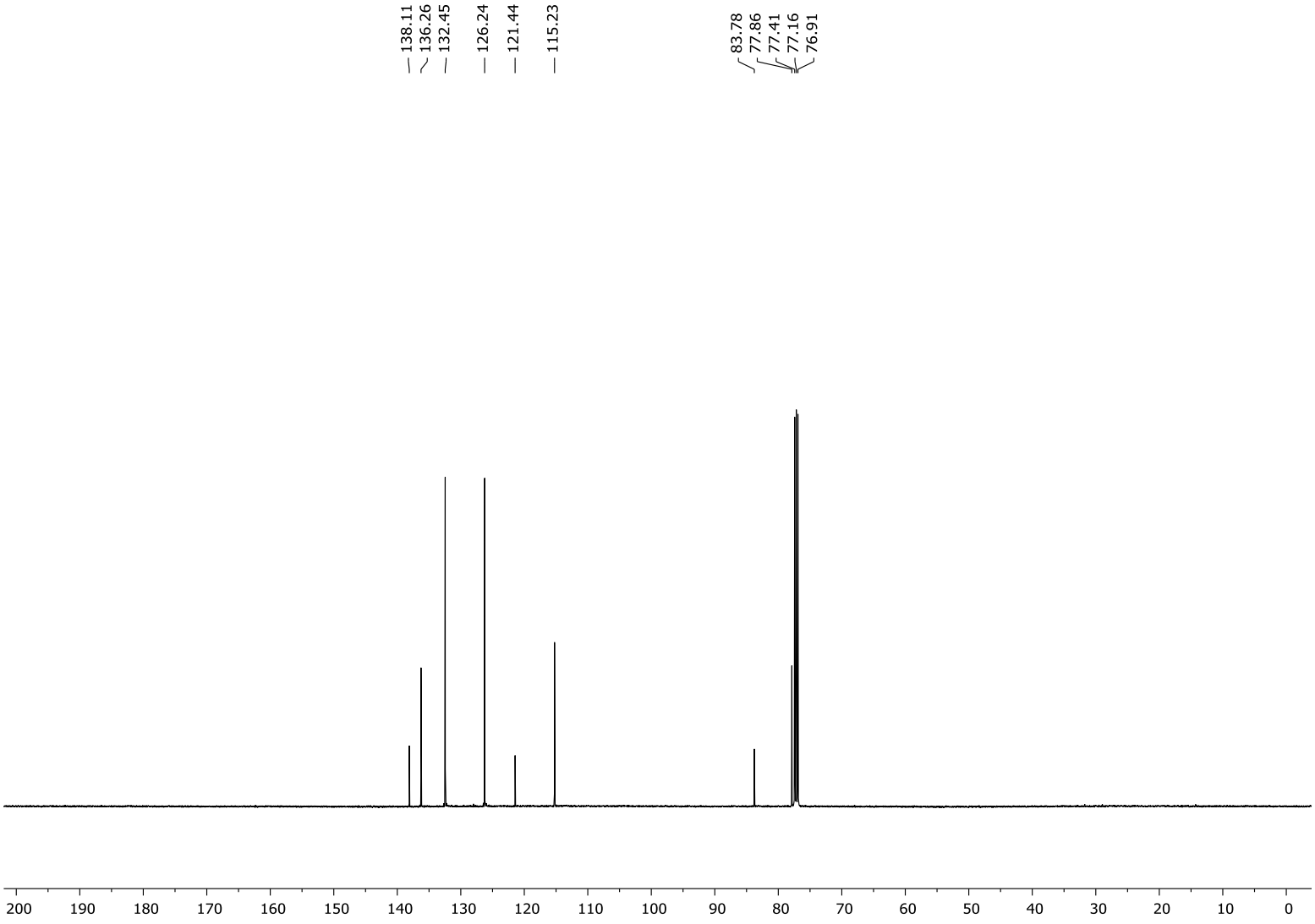


Figure S25: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

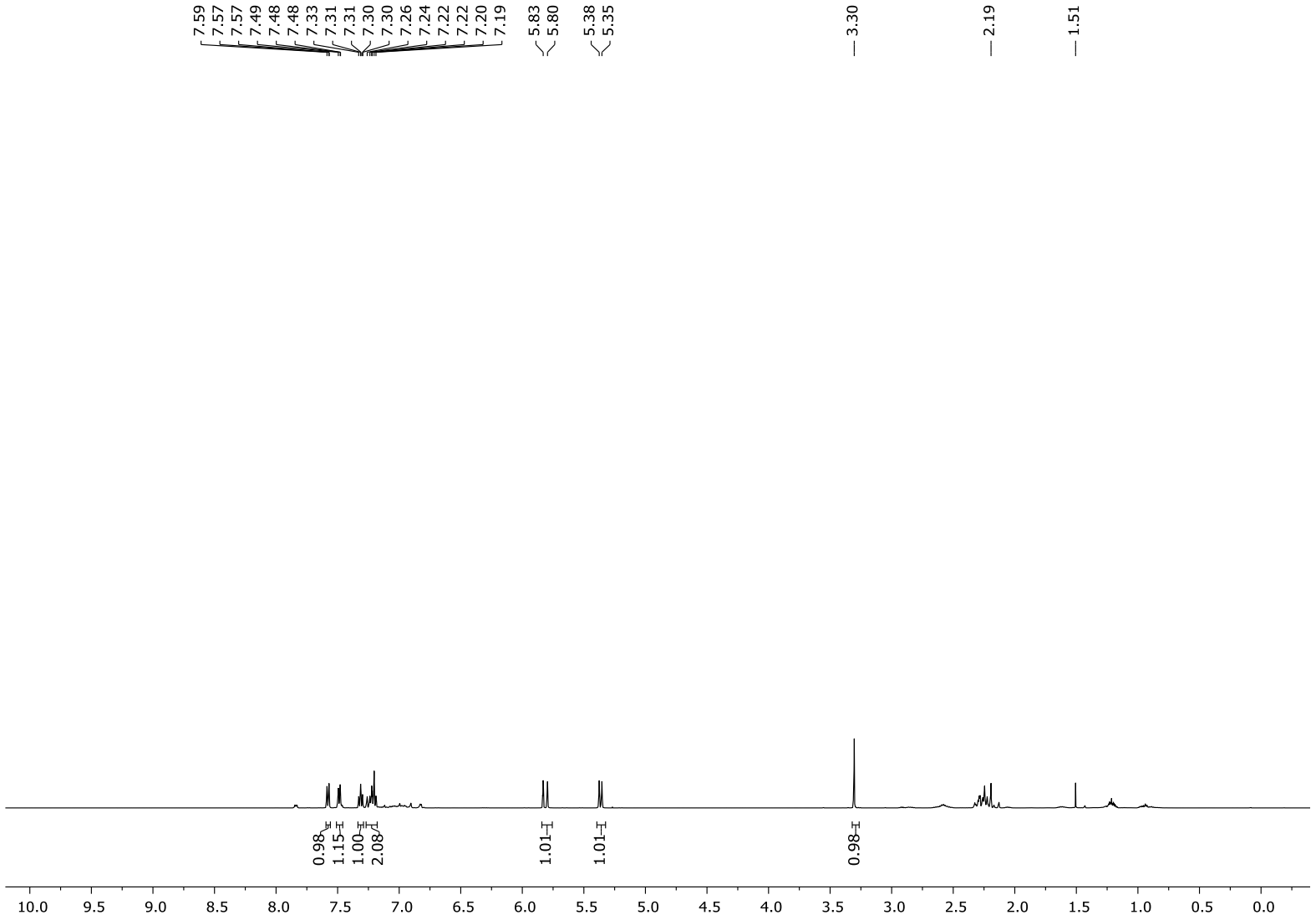


Figure S26: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

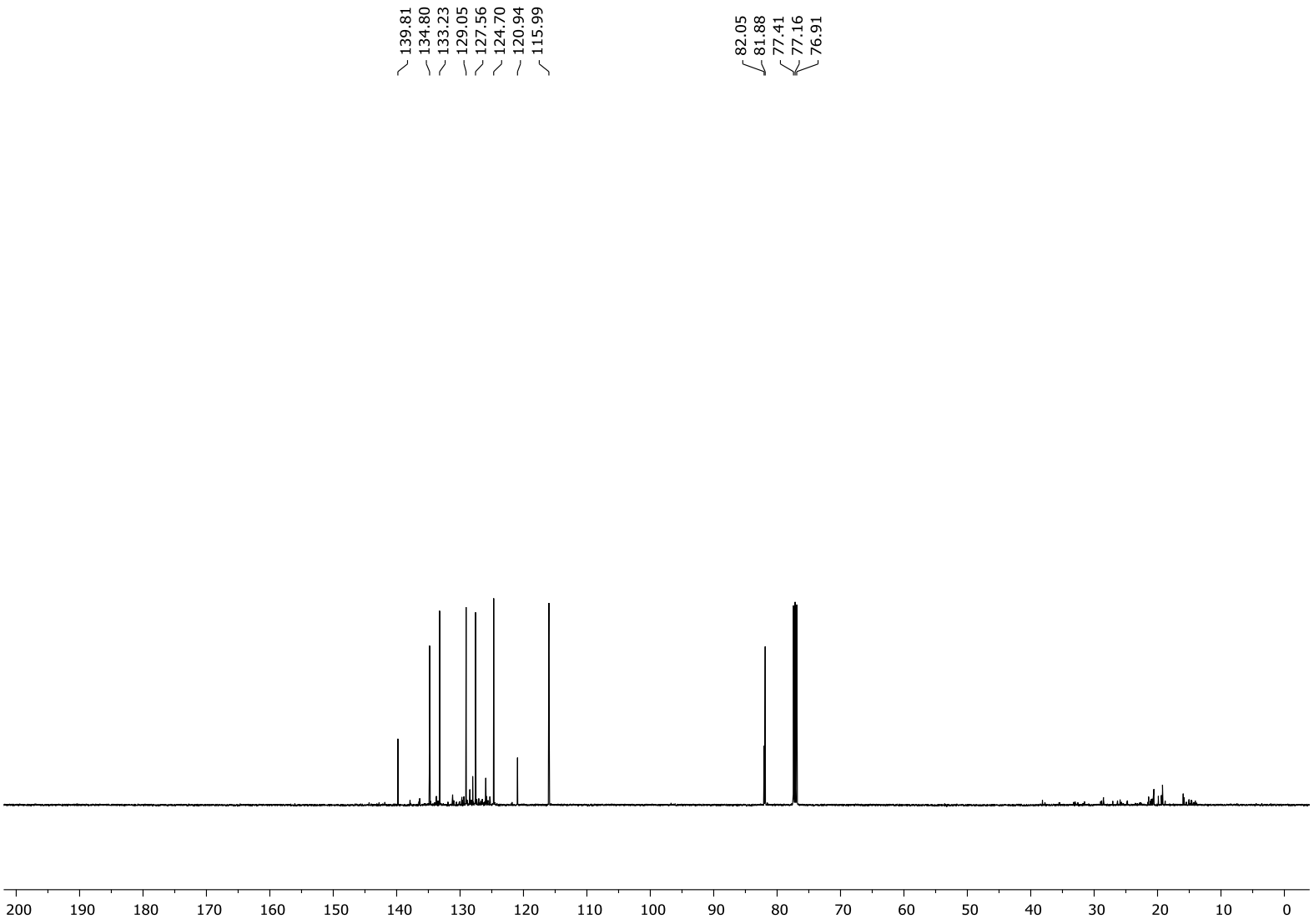


Figure S27: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

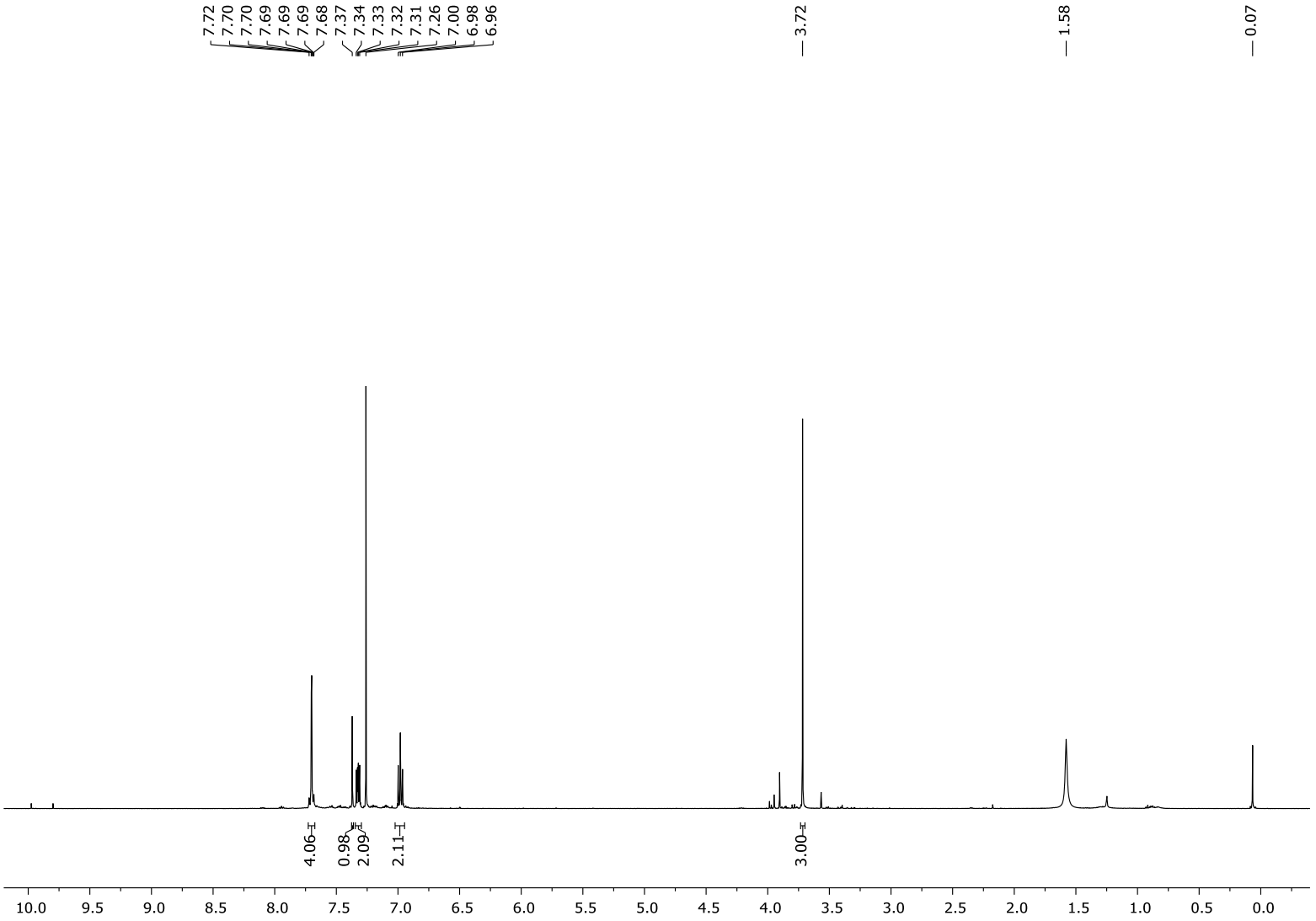


Figure S28: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

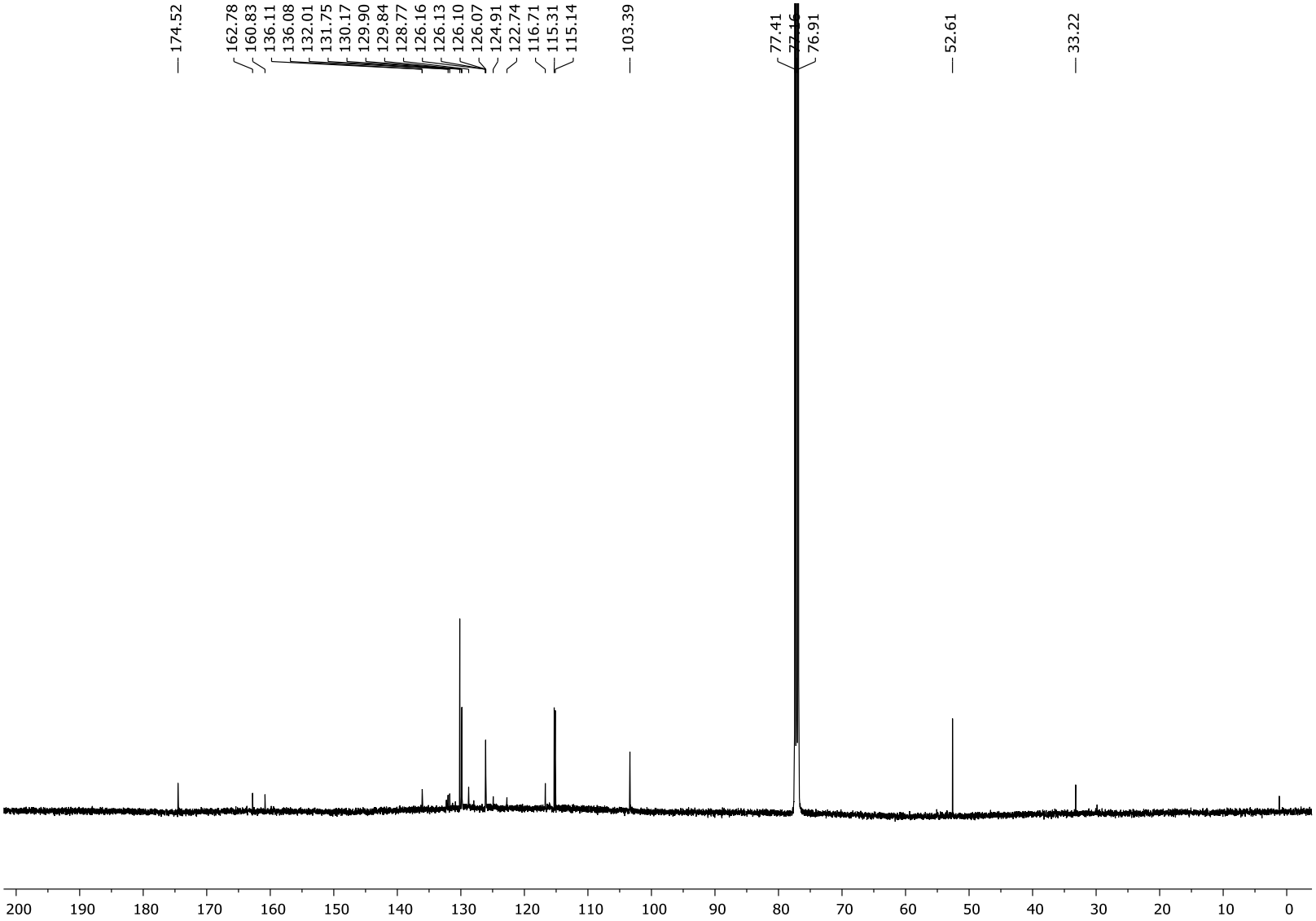


Figure S29: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

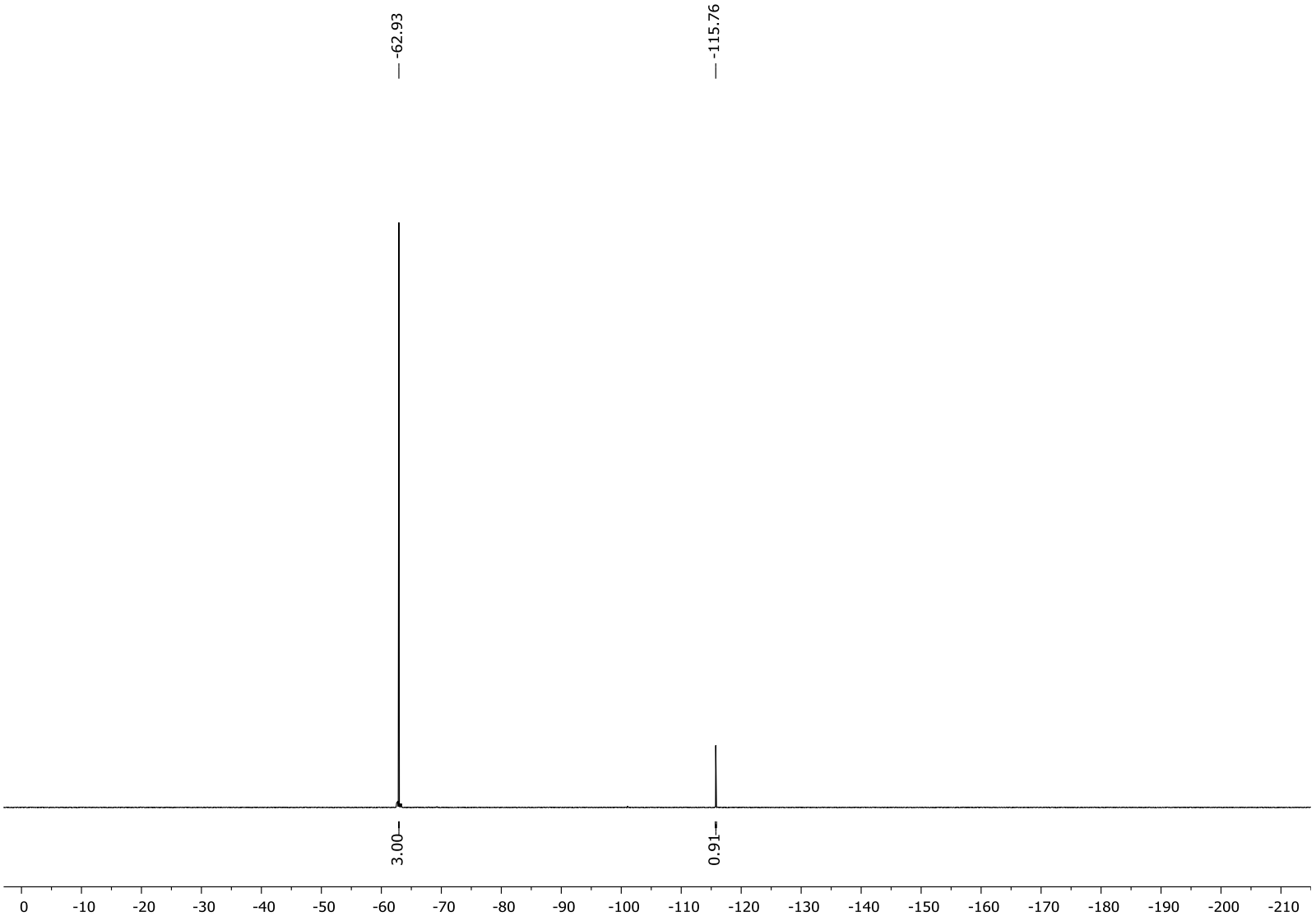


Figure S30: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

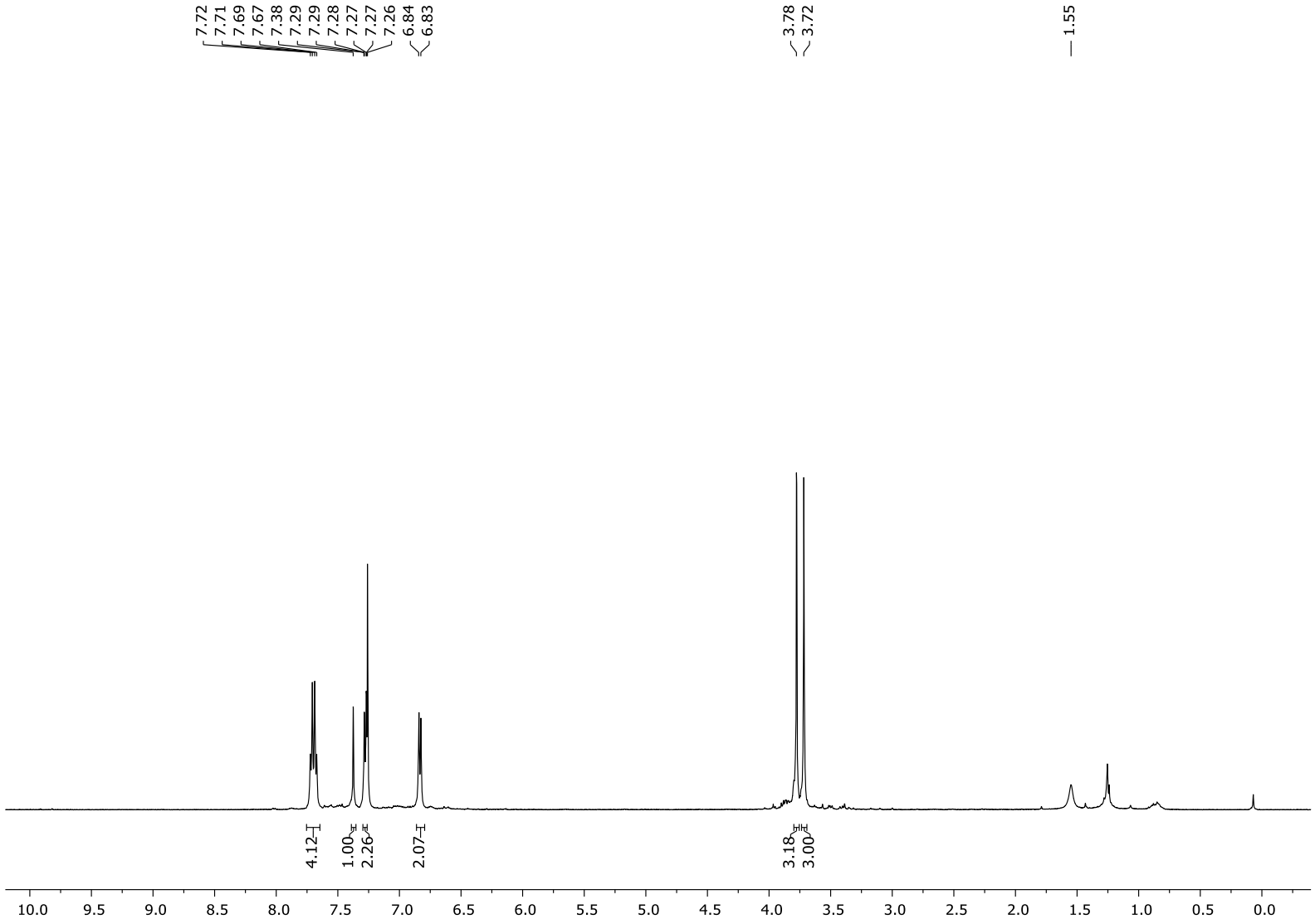


Figure S31: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

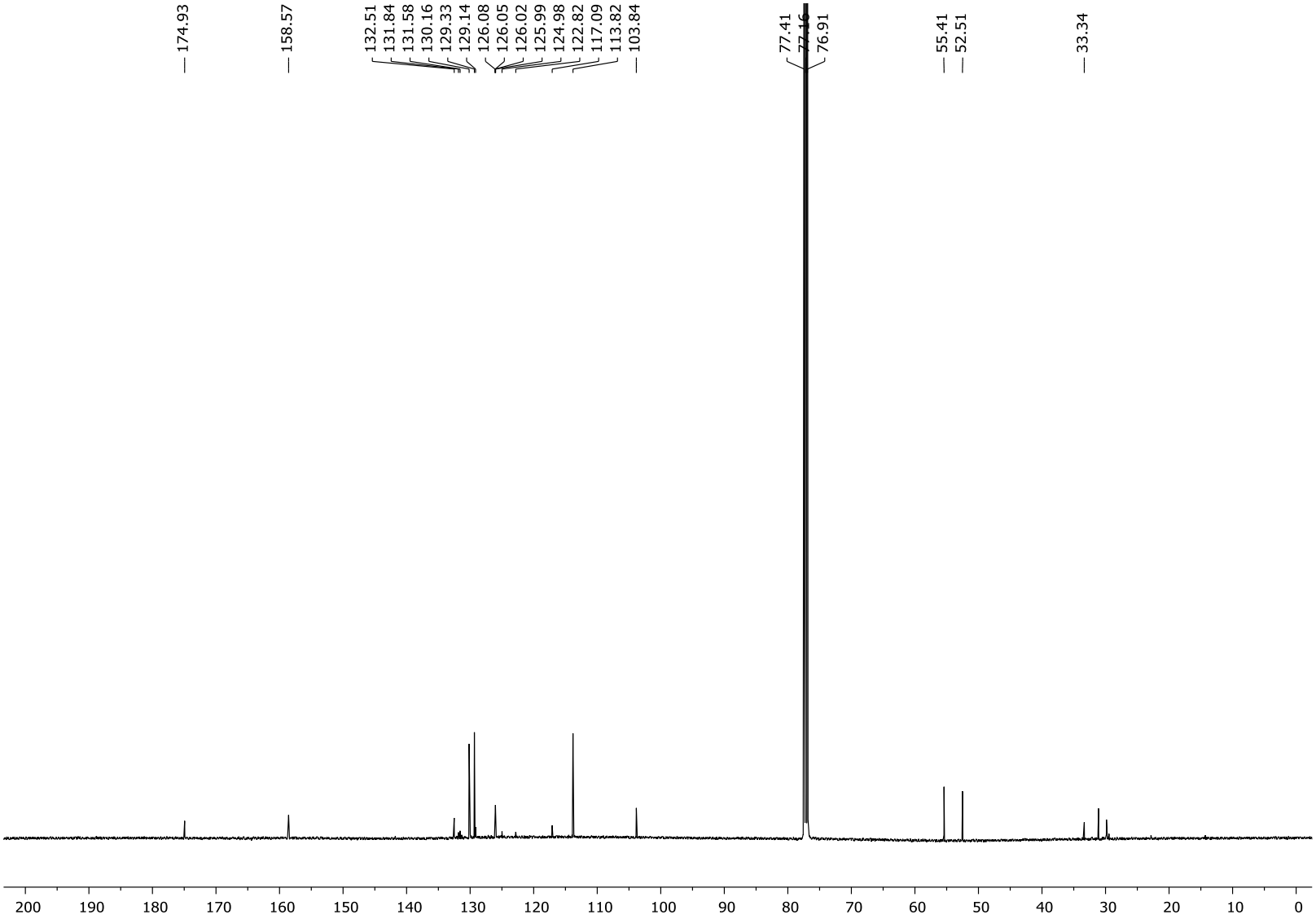


Figure S32: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

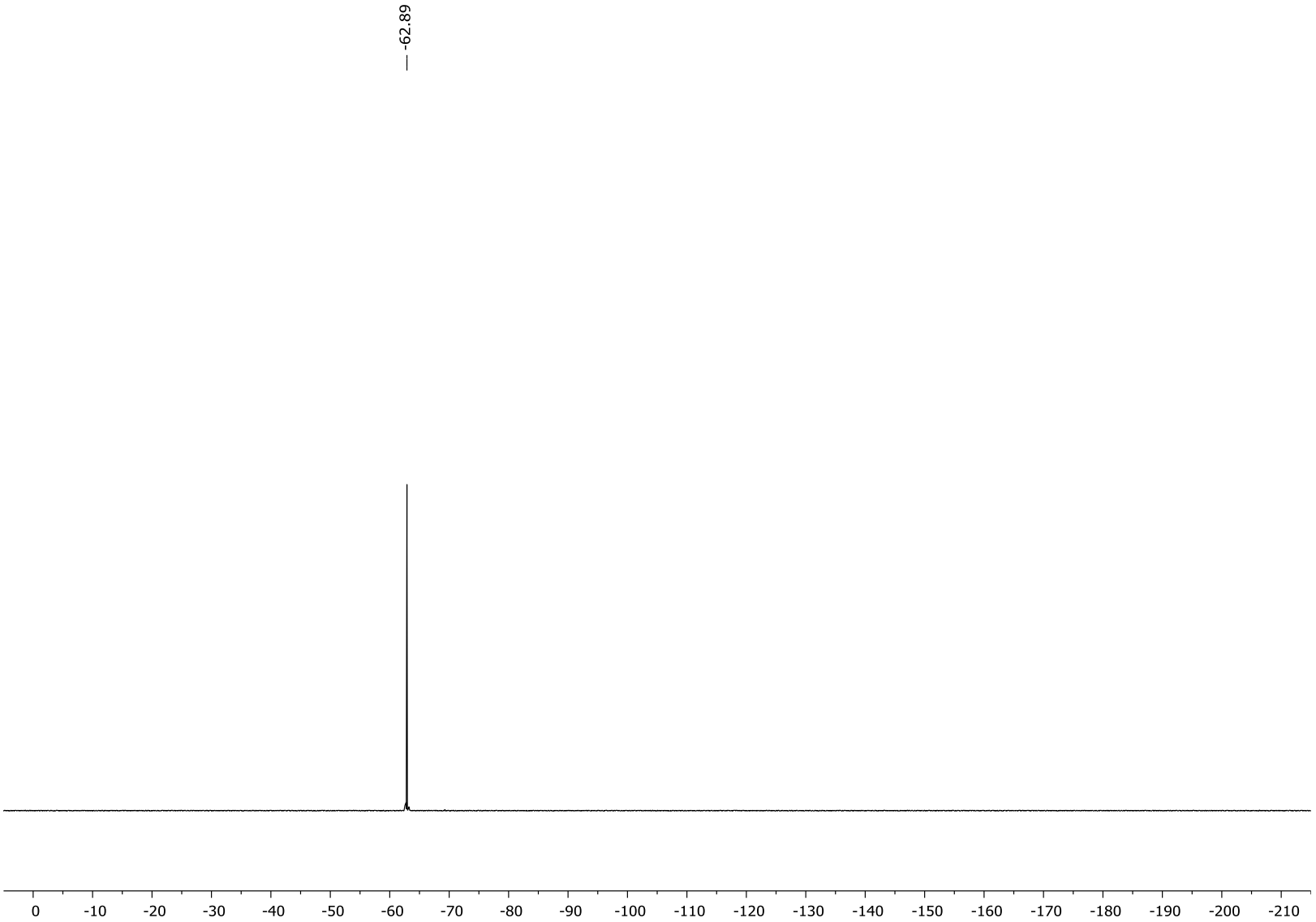


Figure S33: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3c**.

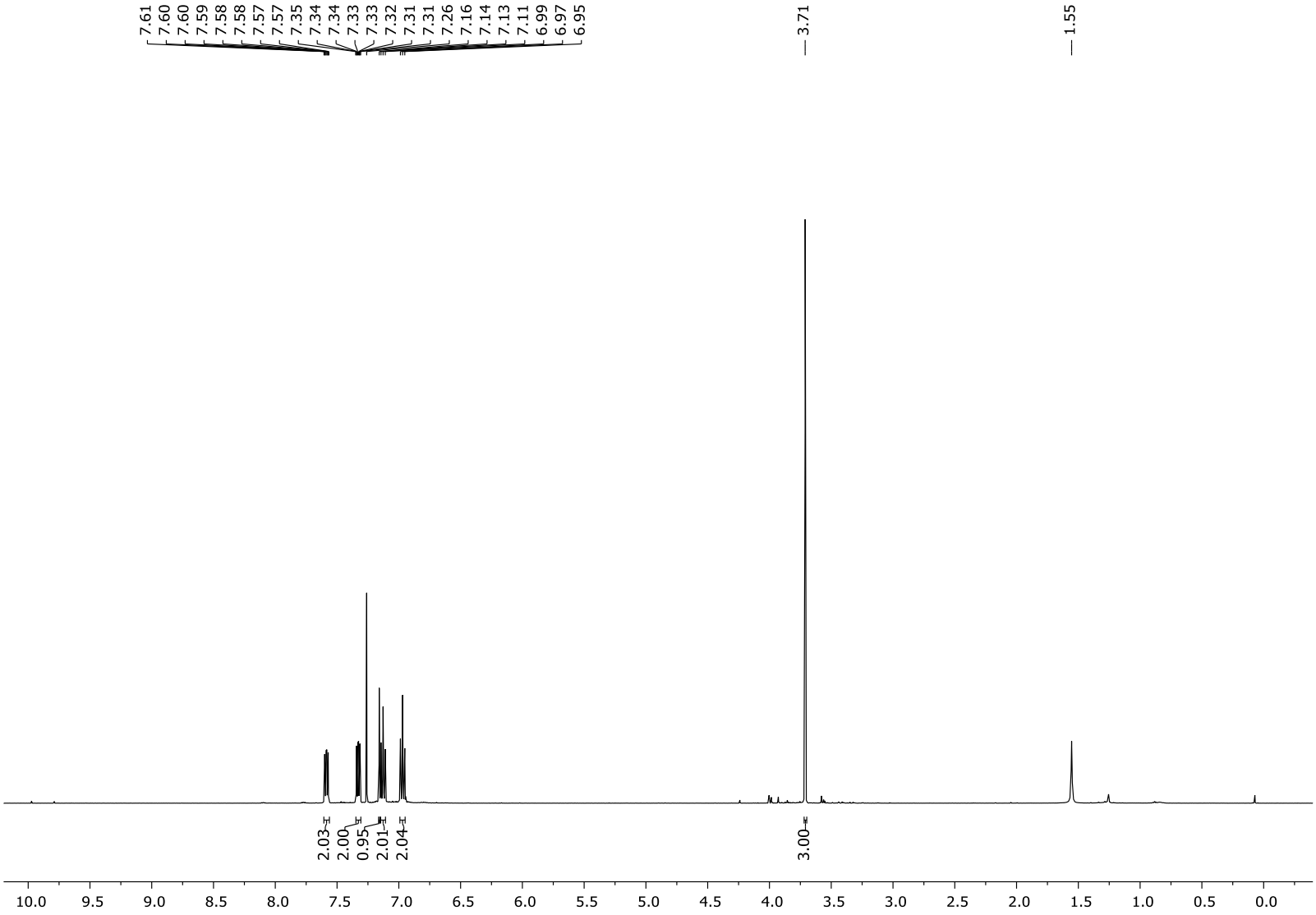


Figure S34: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3c**.

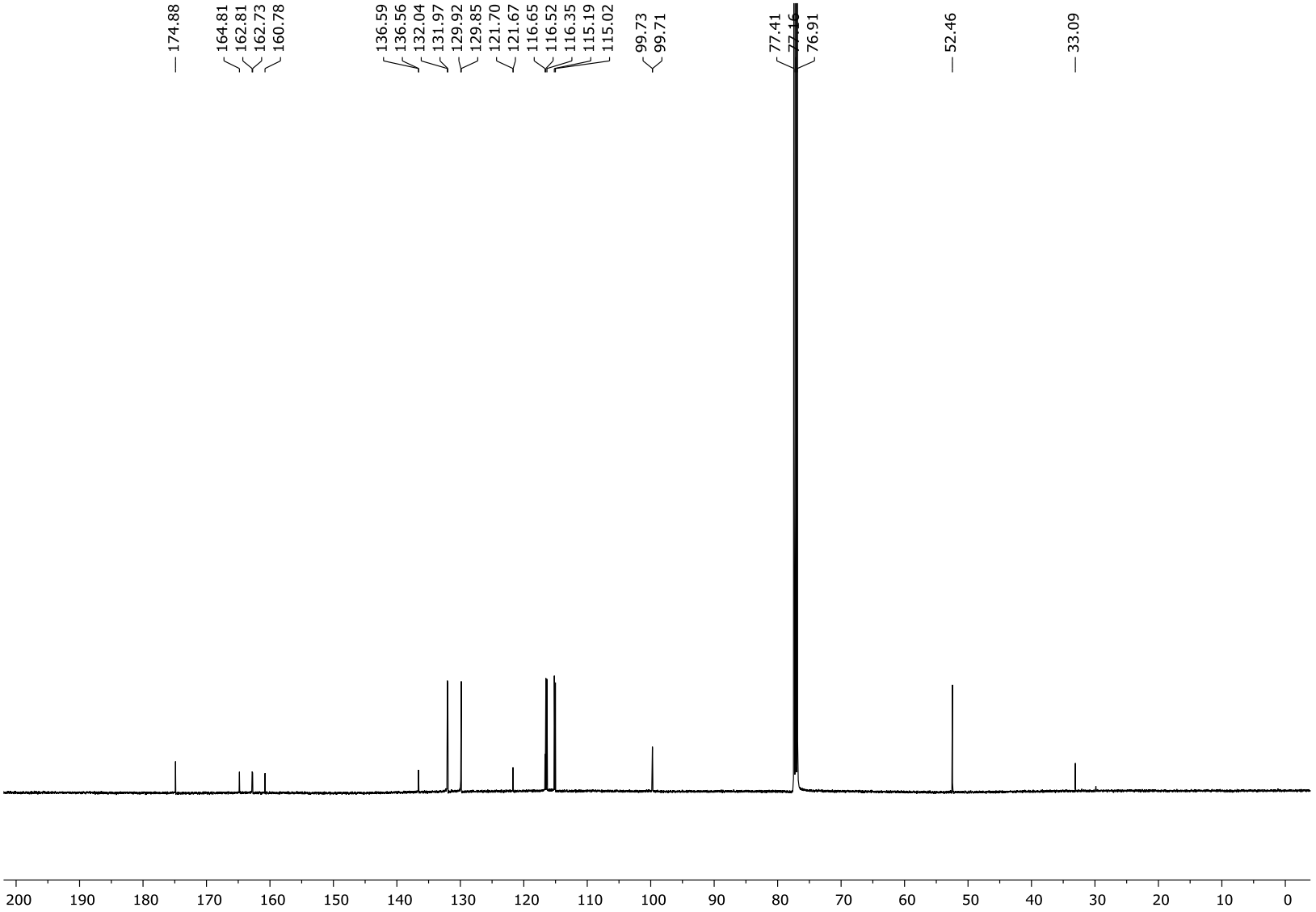


Figure S35: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3c**.

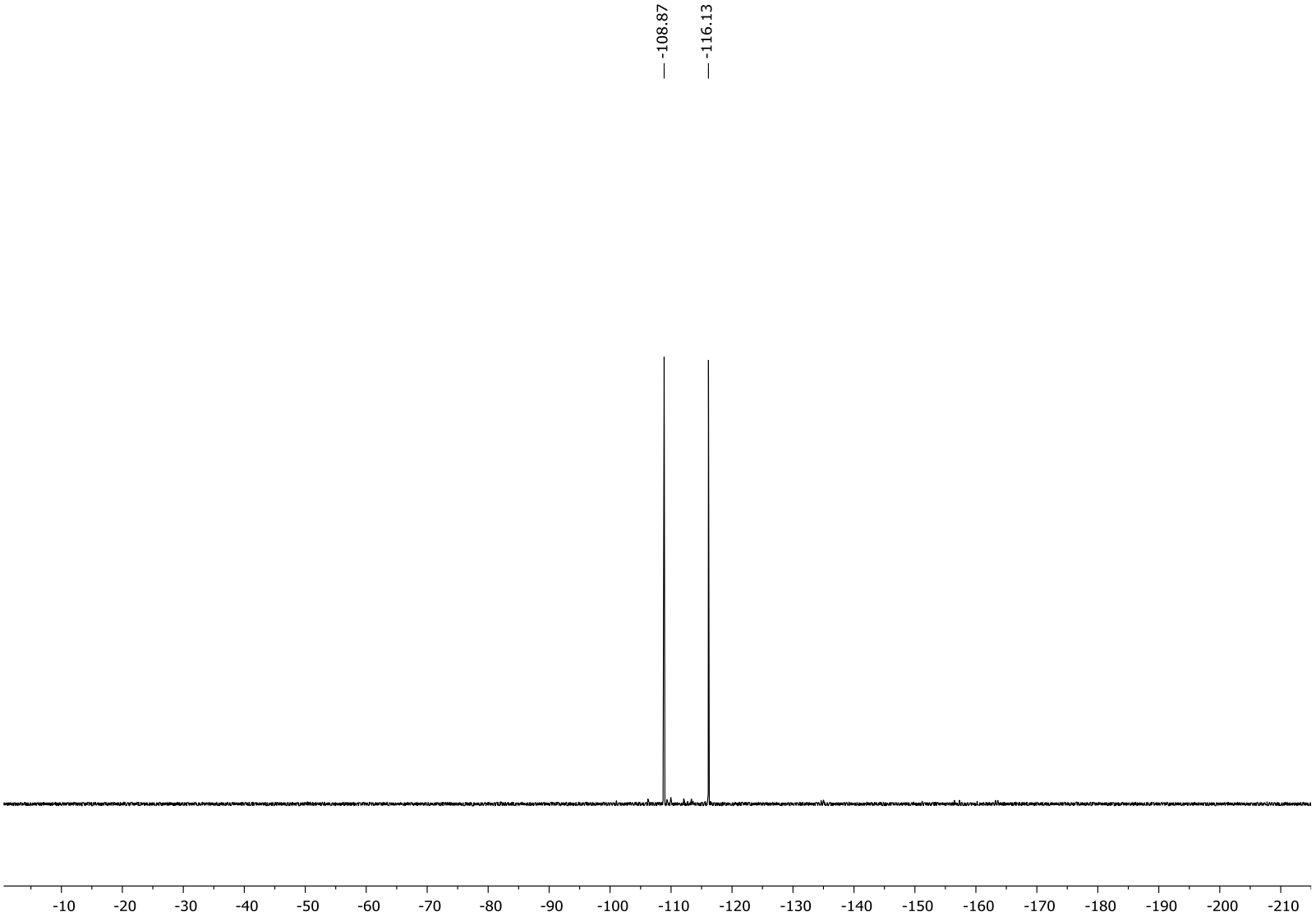


Figure S36: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

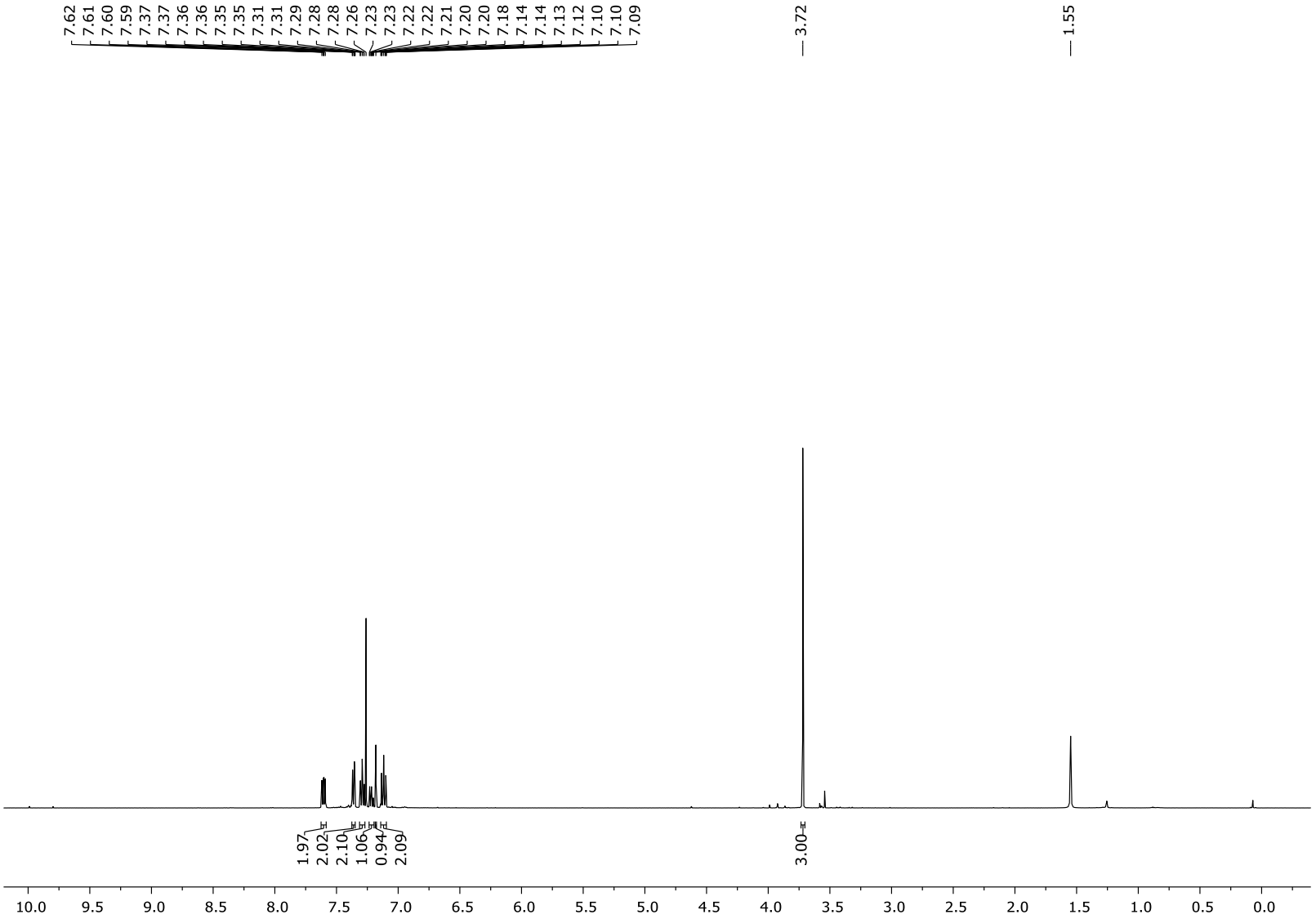


Figure S37: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

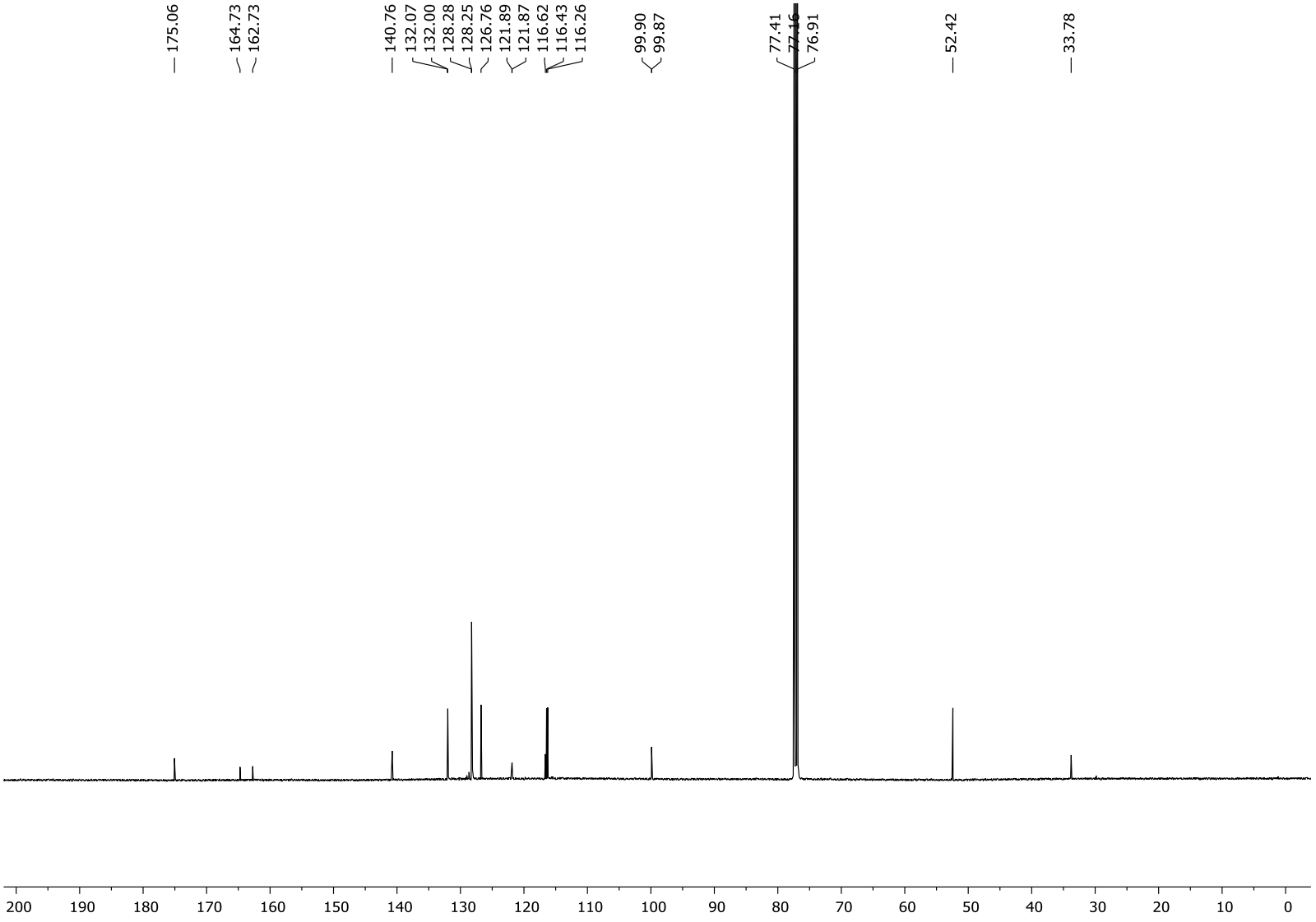


Figure S38: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

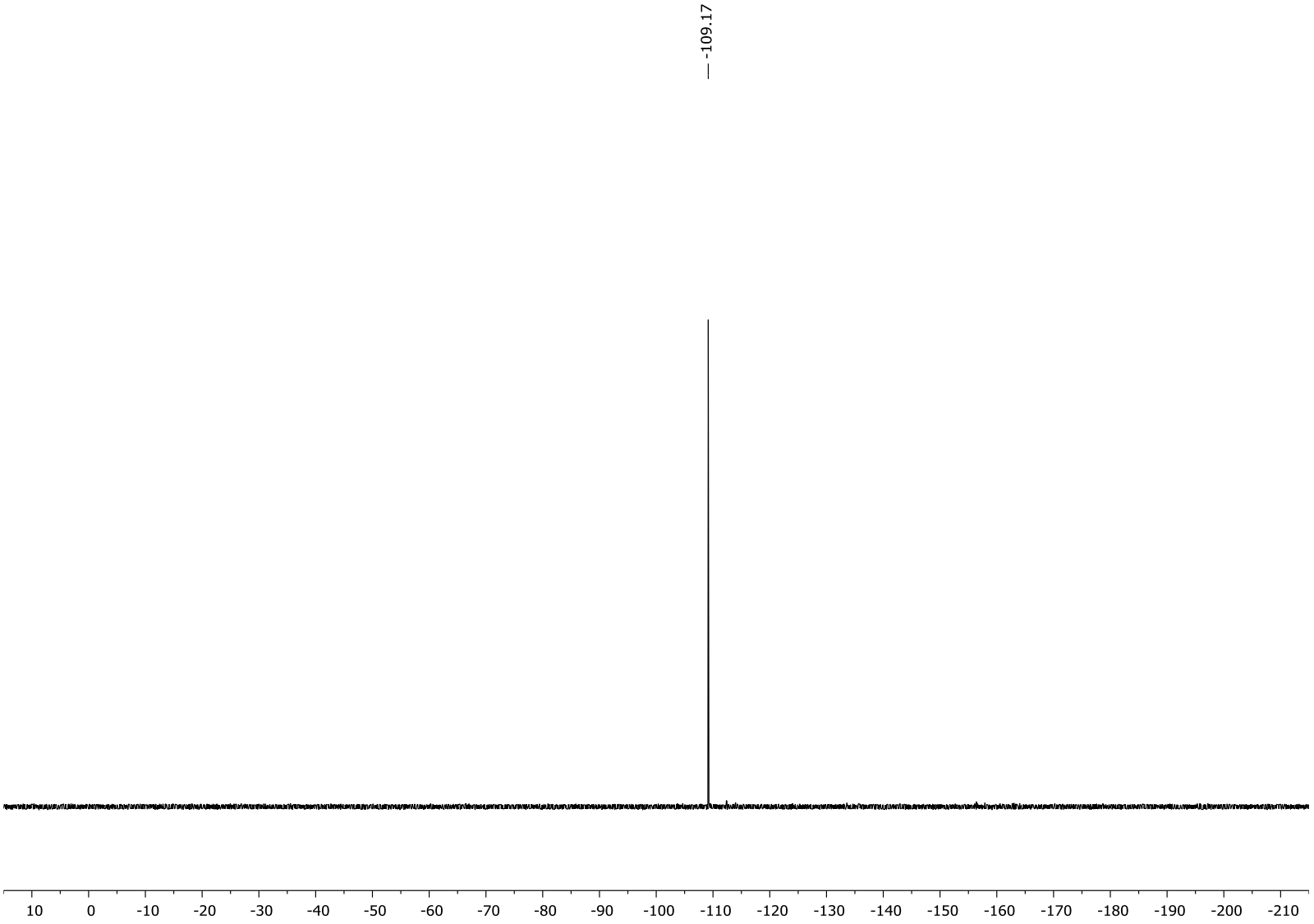


Figure S39: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3e**.

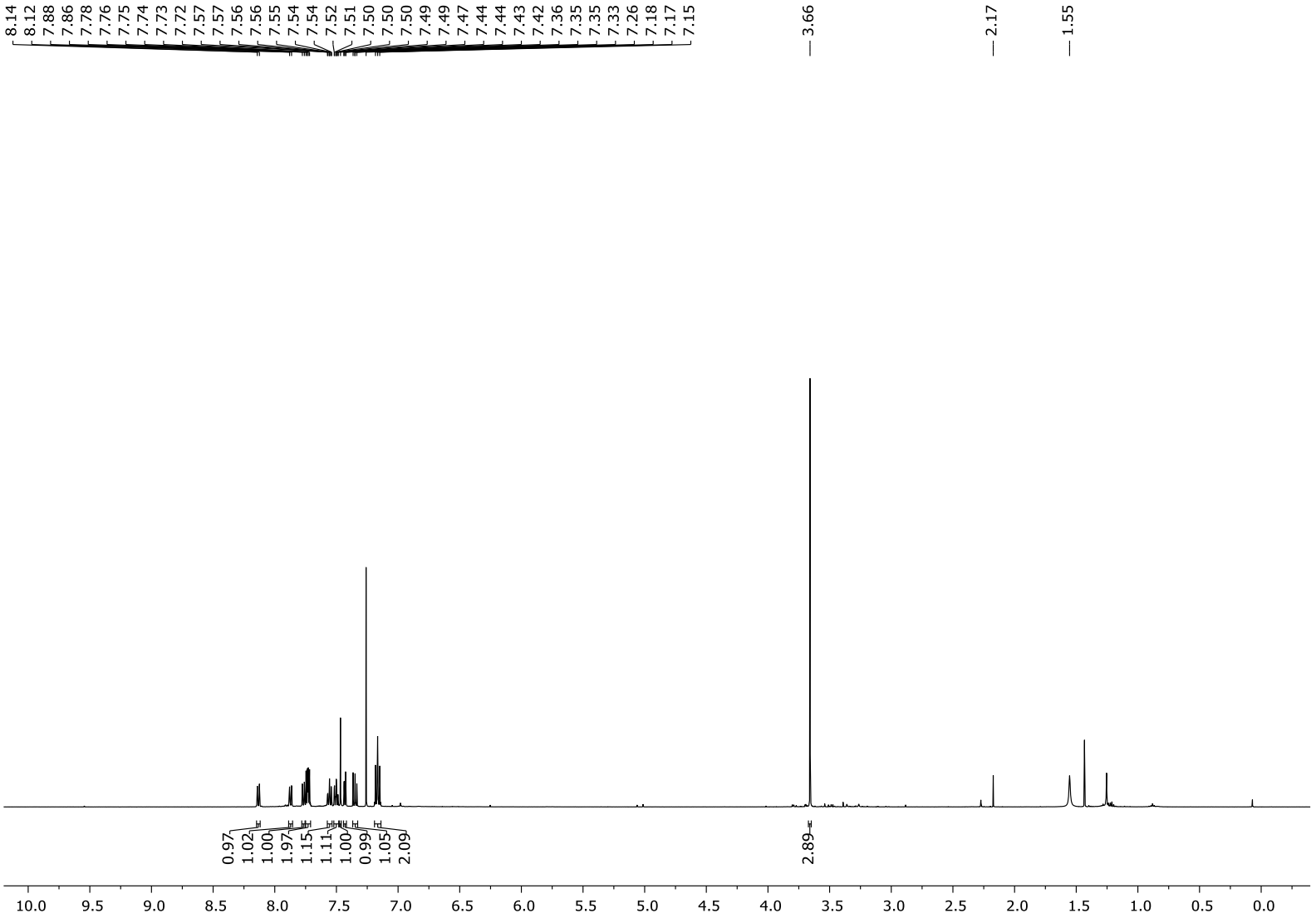


Figure S40: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3e**.

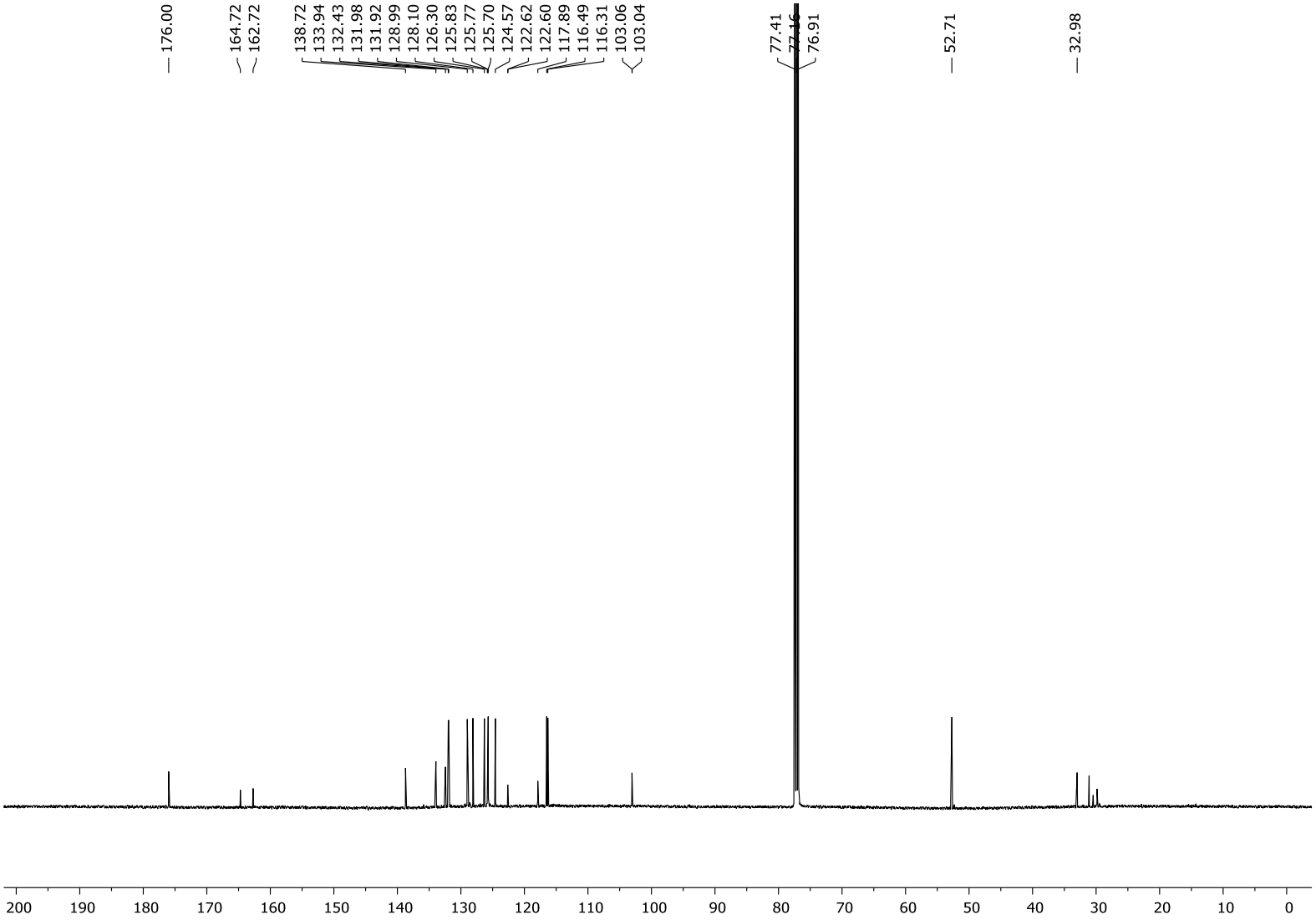


Figure S41: **^{19}F NMR** (471MHz, $CDCl_3$, 298 K) spectrum of **3e**.

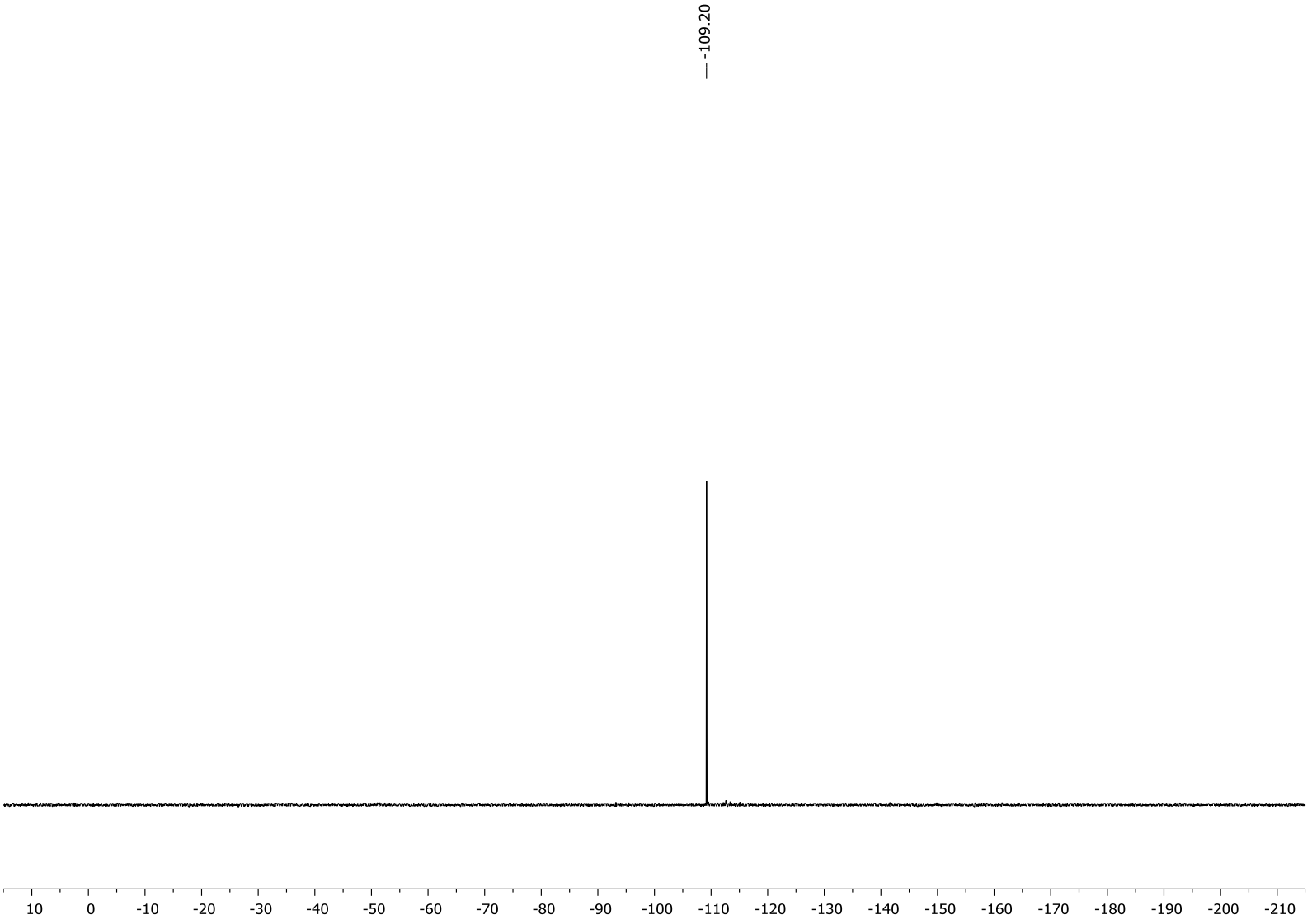


Figure S42: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

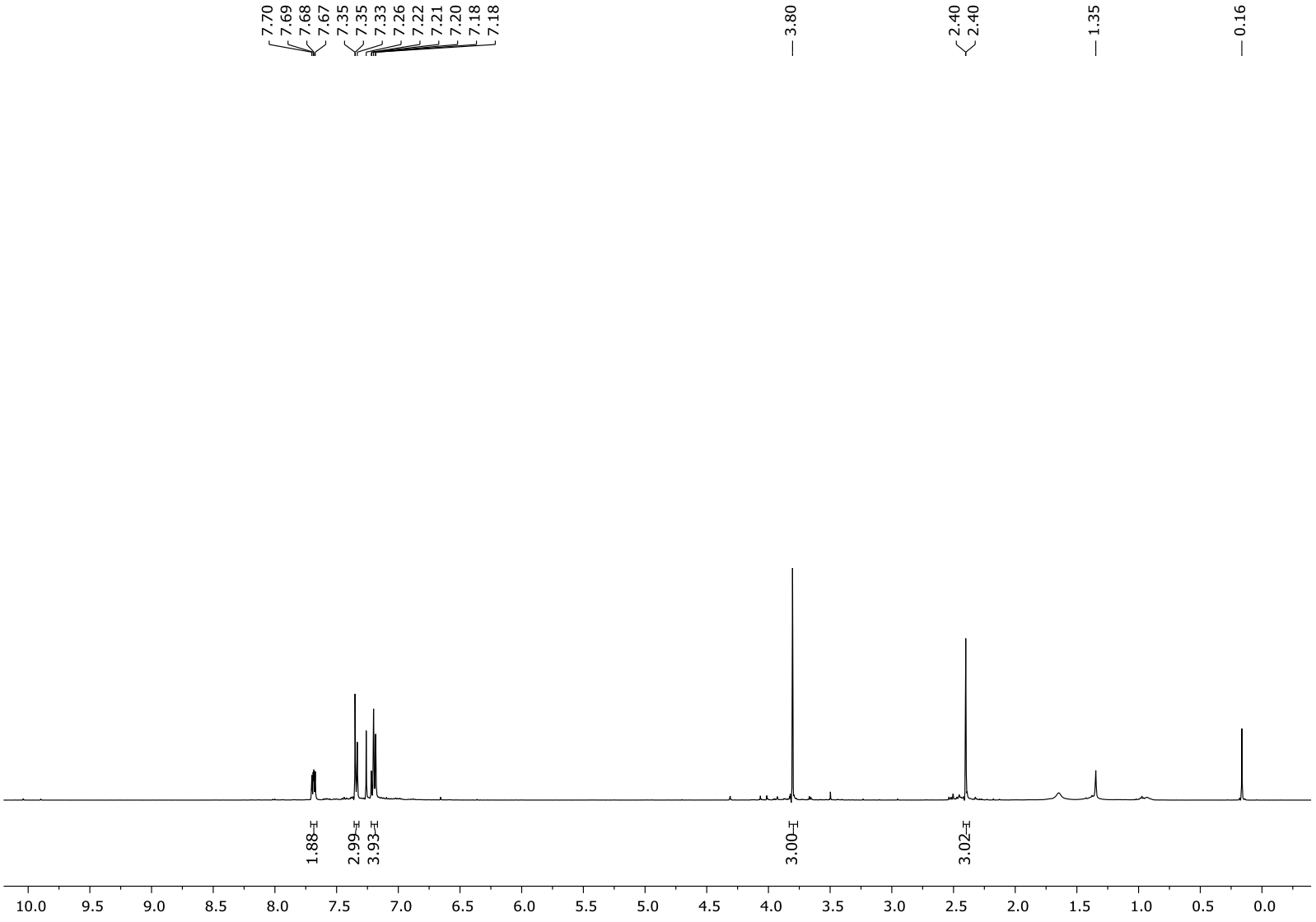


Figure S43: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

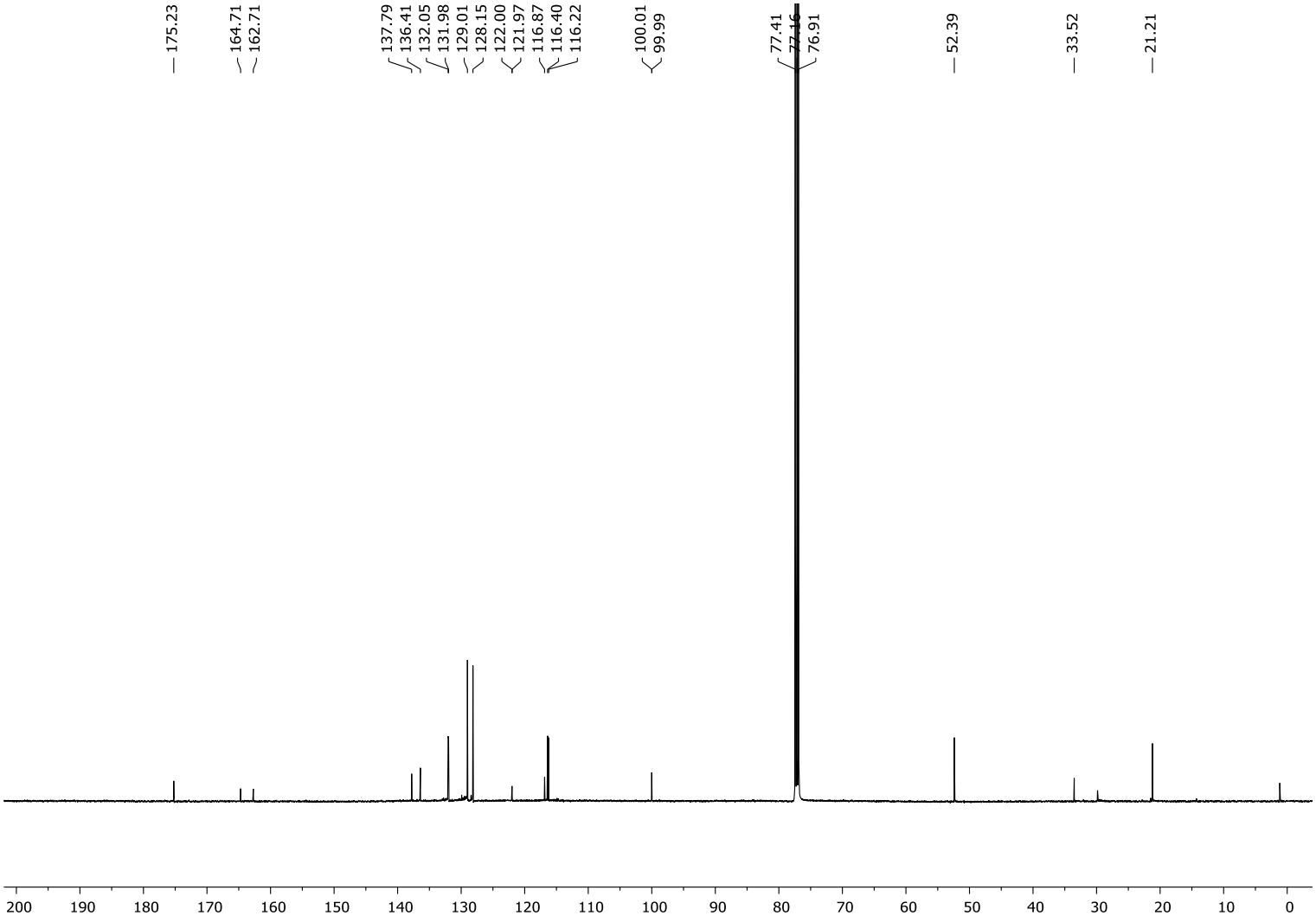


Figure S44: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

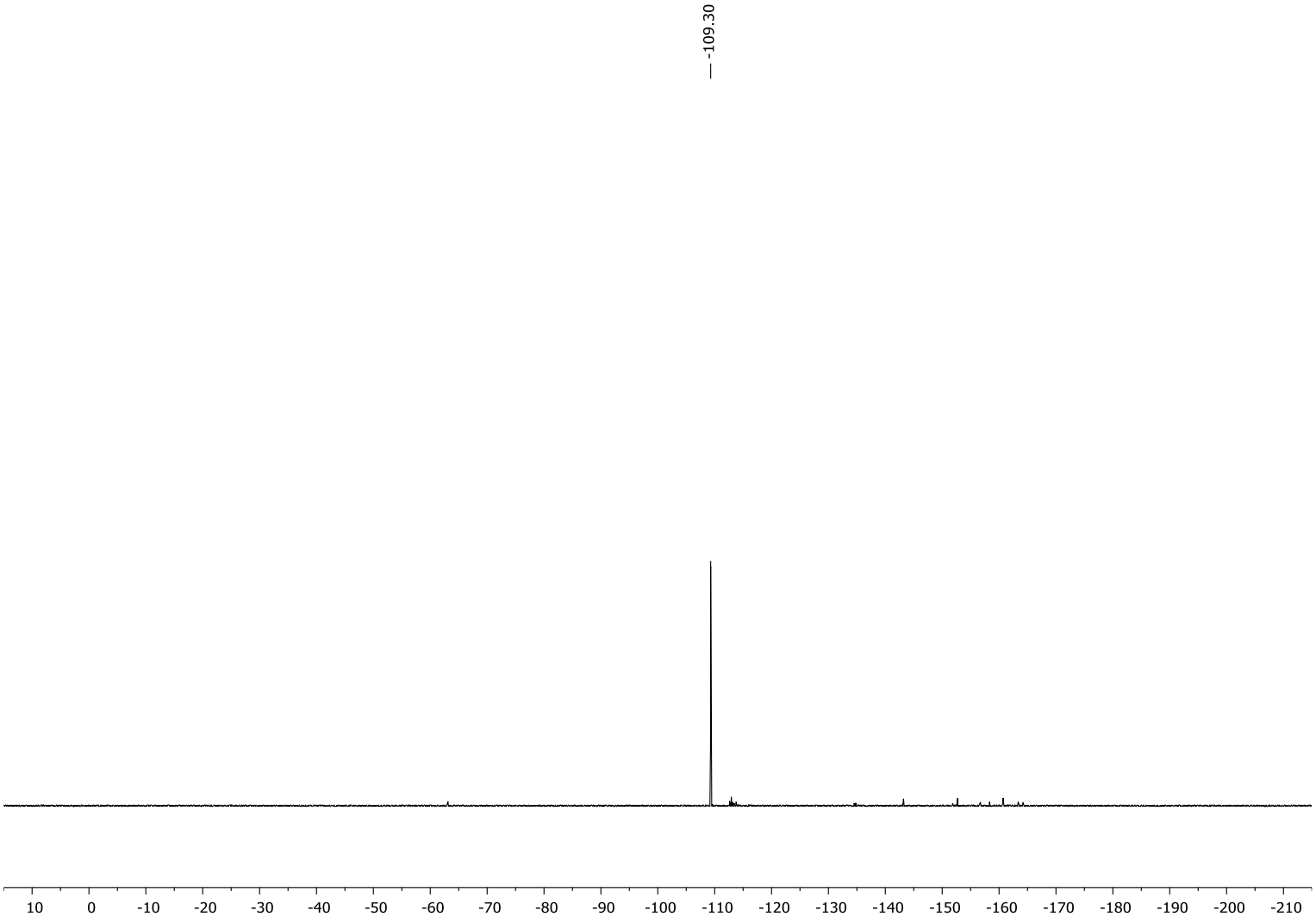


Figure S45: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) spectrum of **3g**.

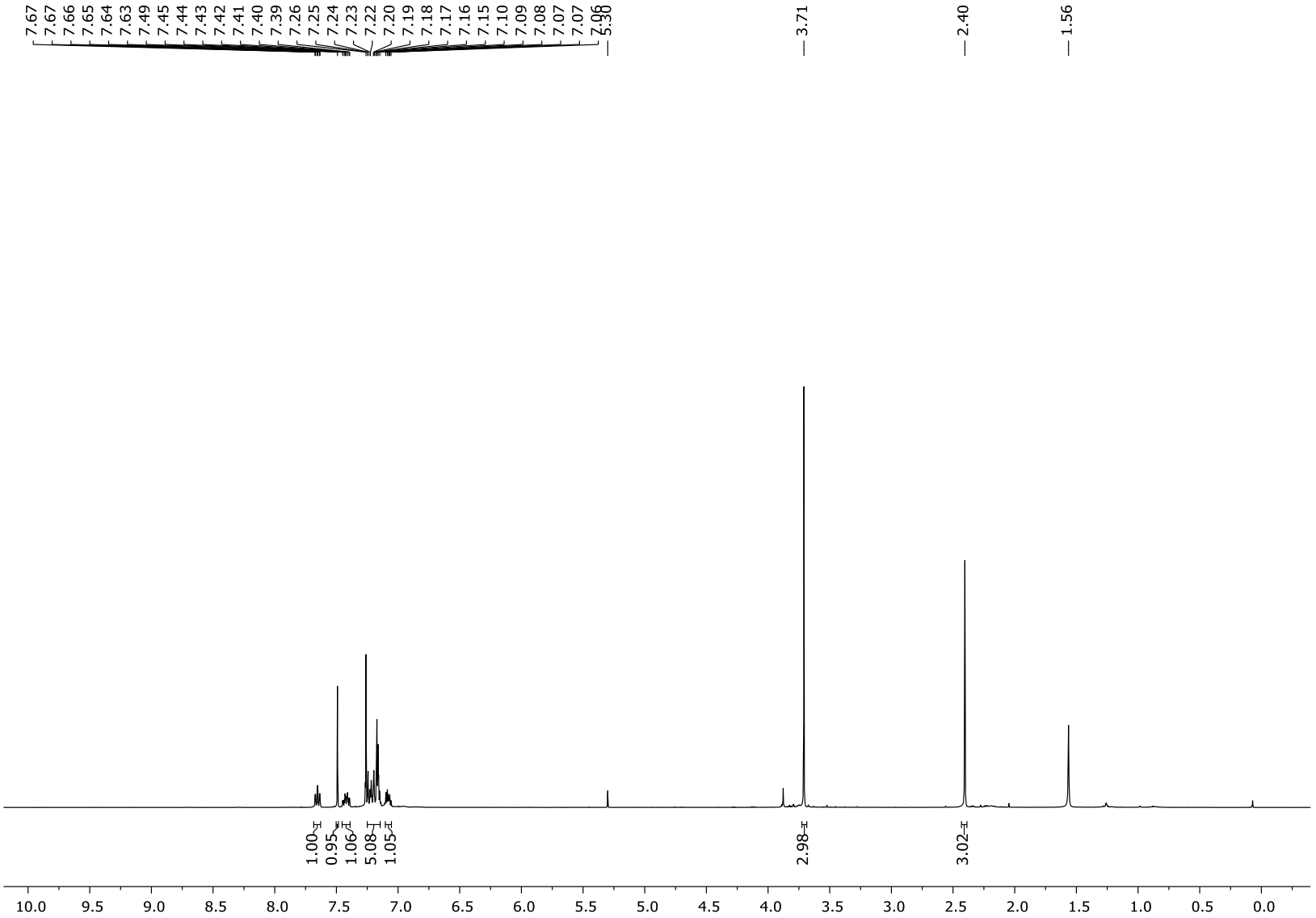


Figure S46: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **3g**.

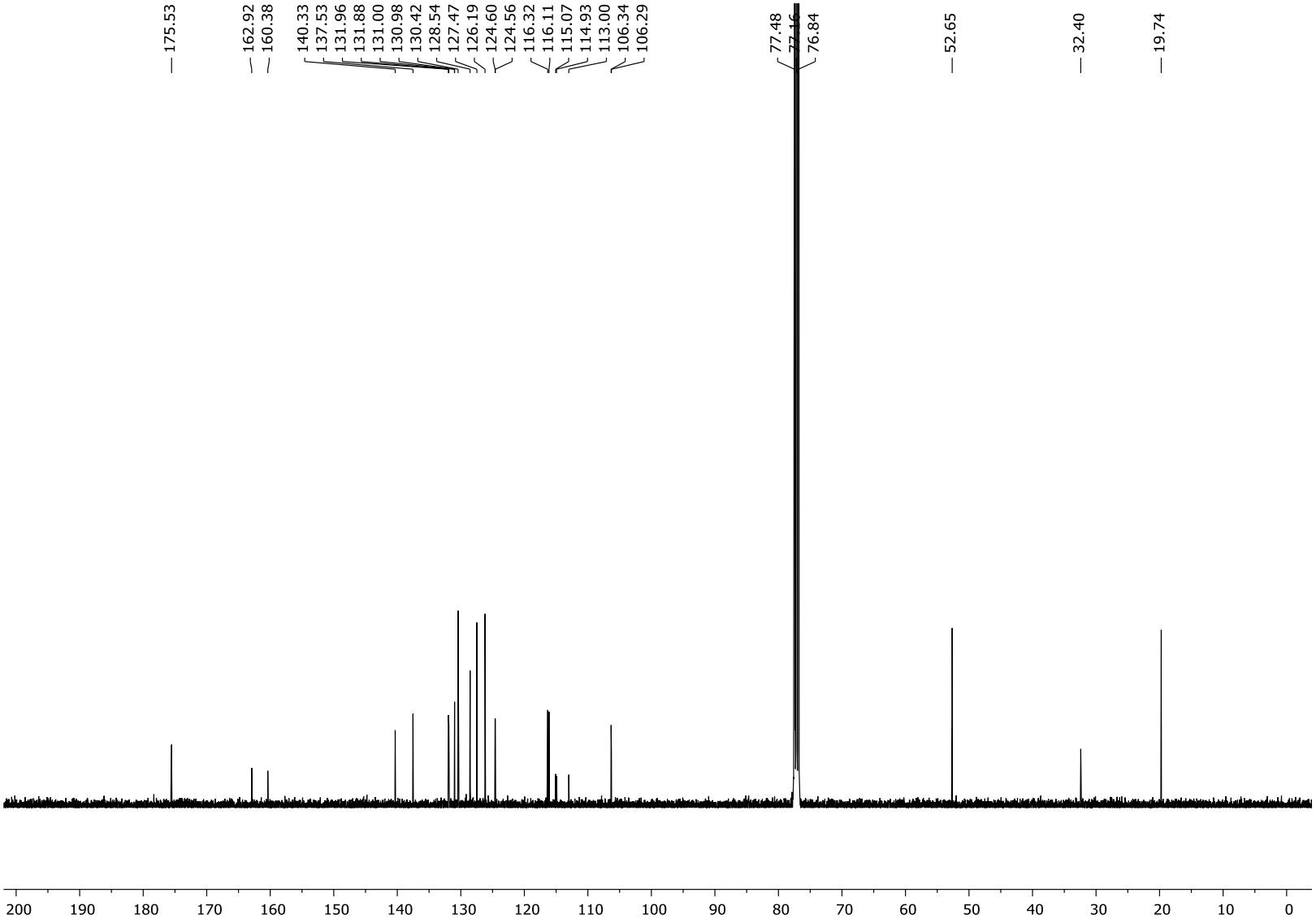


Figure S47: **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) spectrum of **3g**.

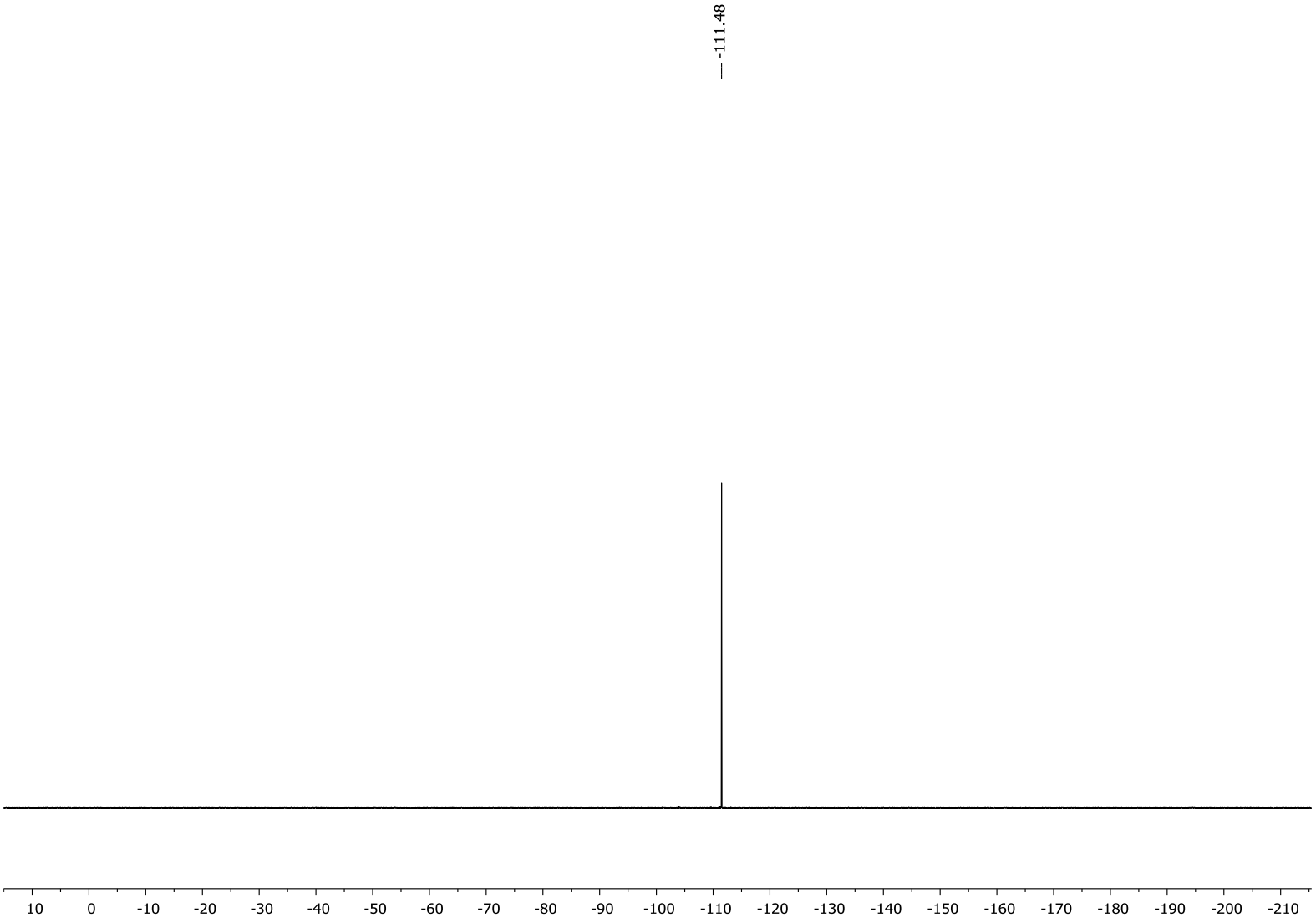


Figure S48: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) spectrum of **3h**.

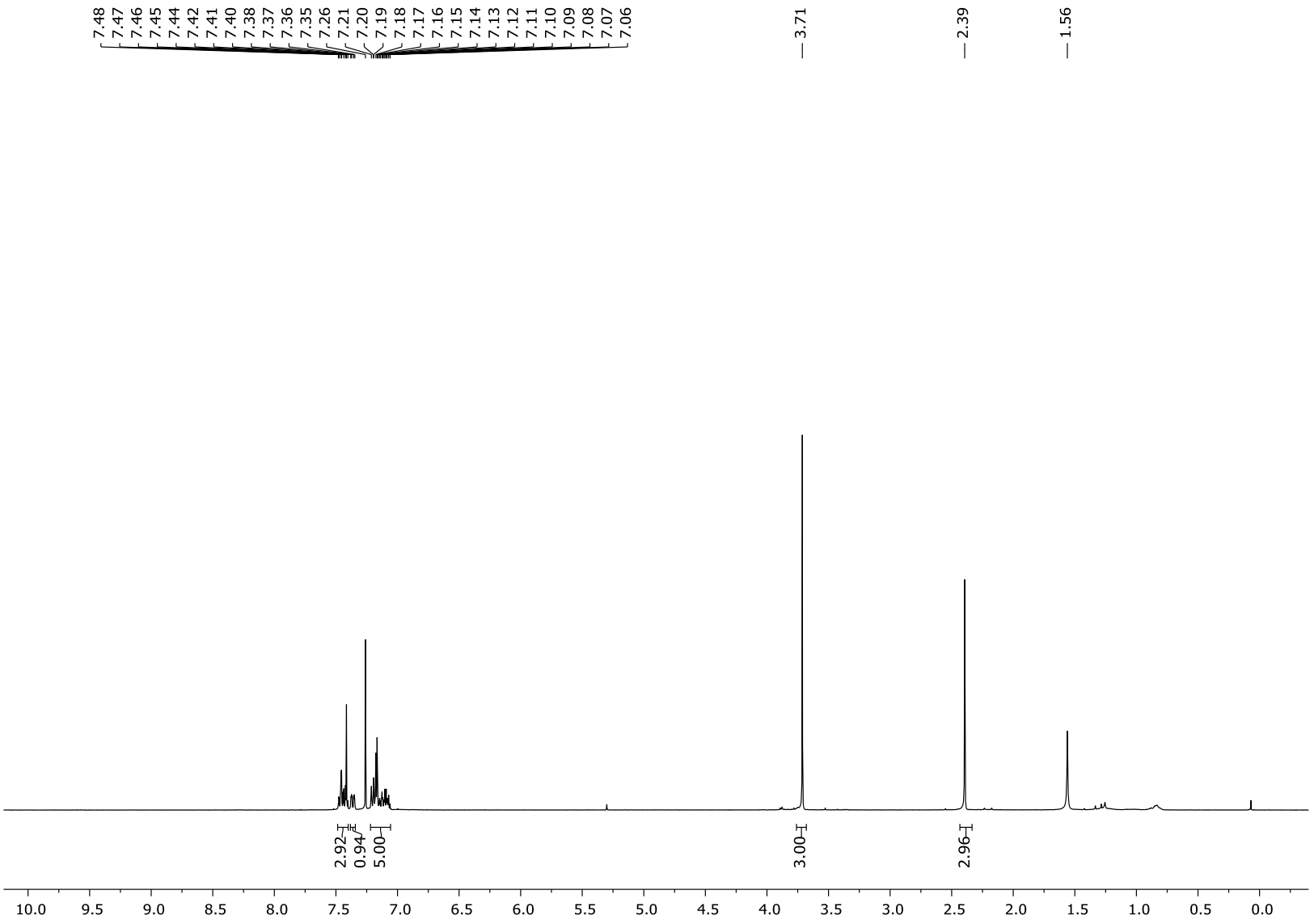


Figure S49: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **3h**.

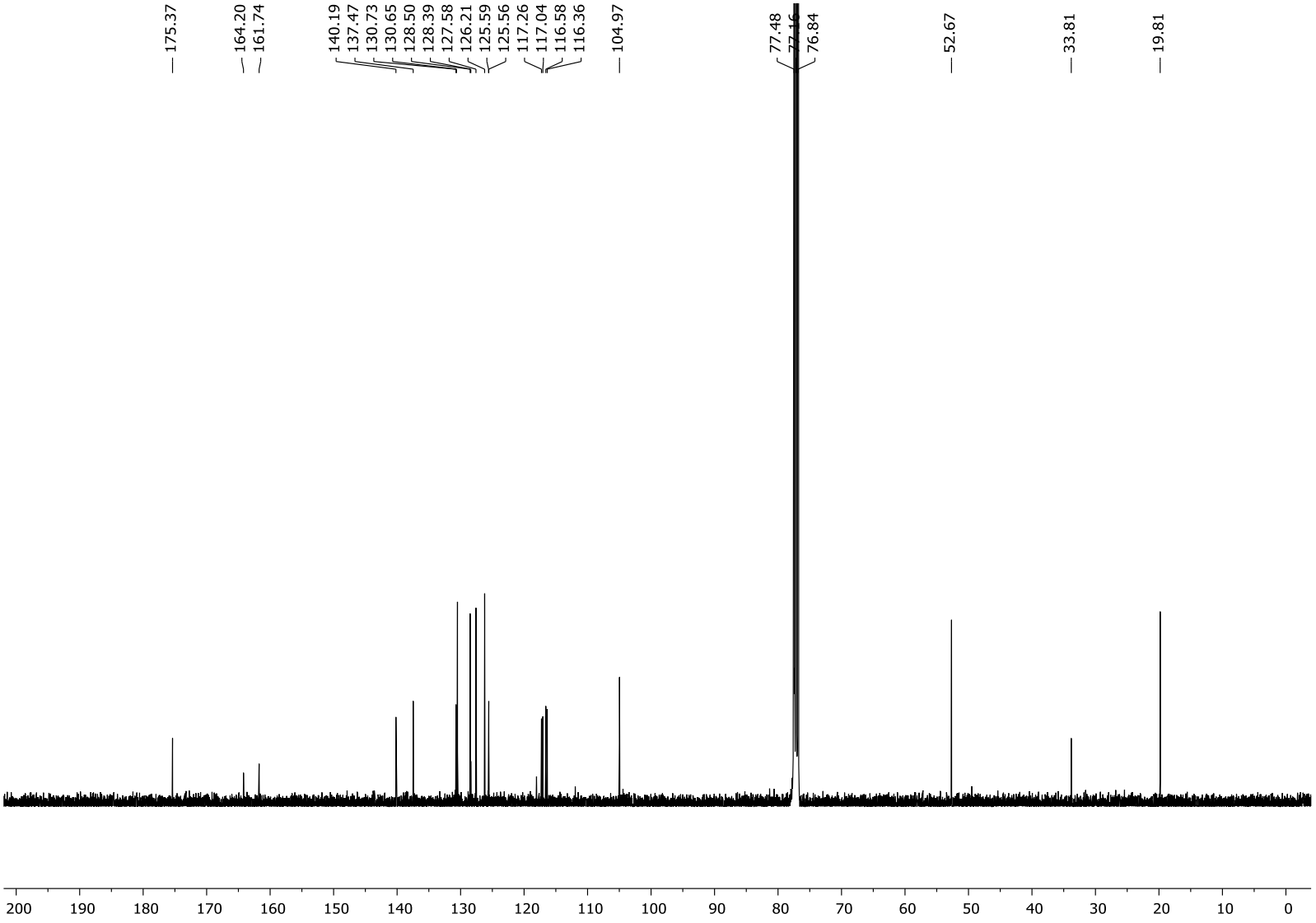


Figure S50: **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) spectrum of **3h**.

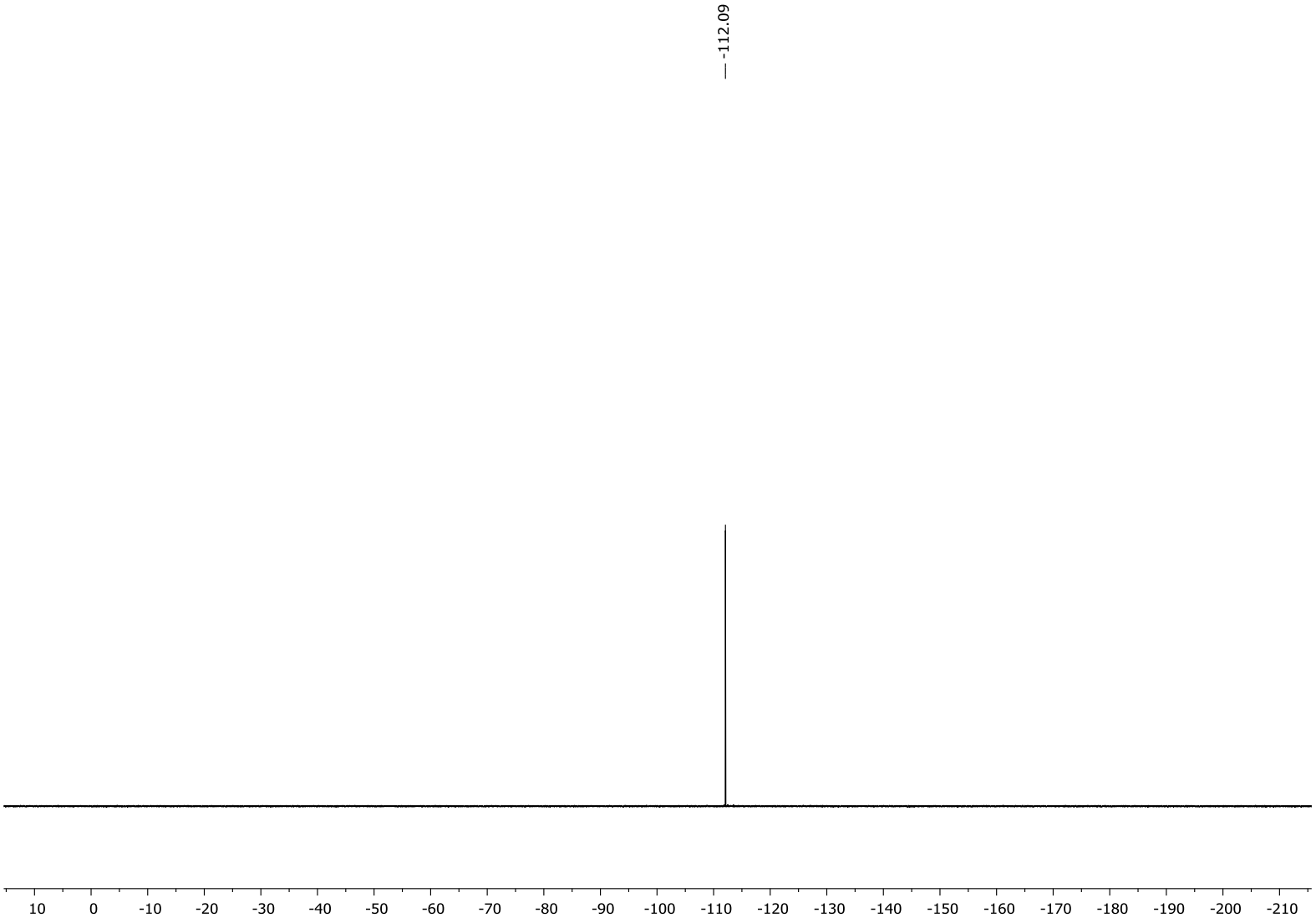


Figure S51: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3i**.

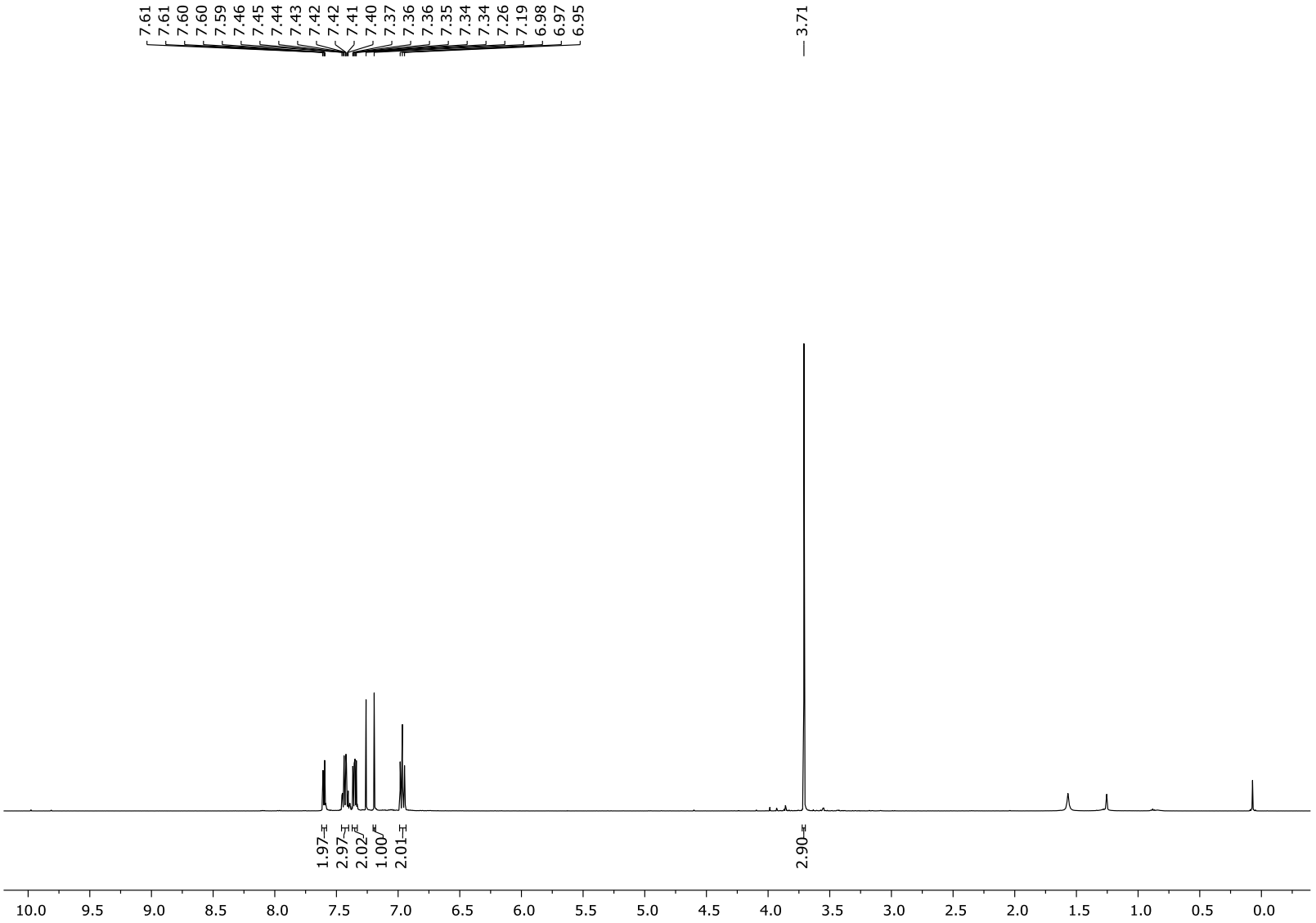


Figure S52: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3i**.

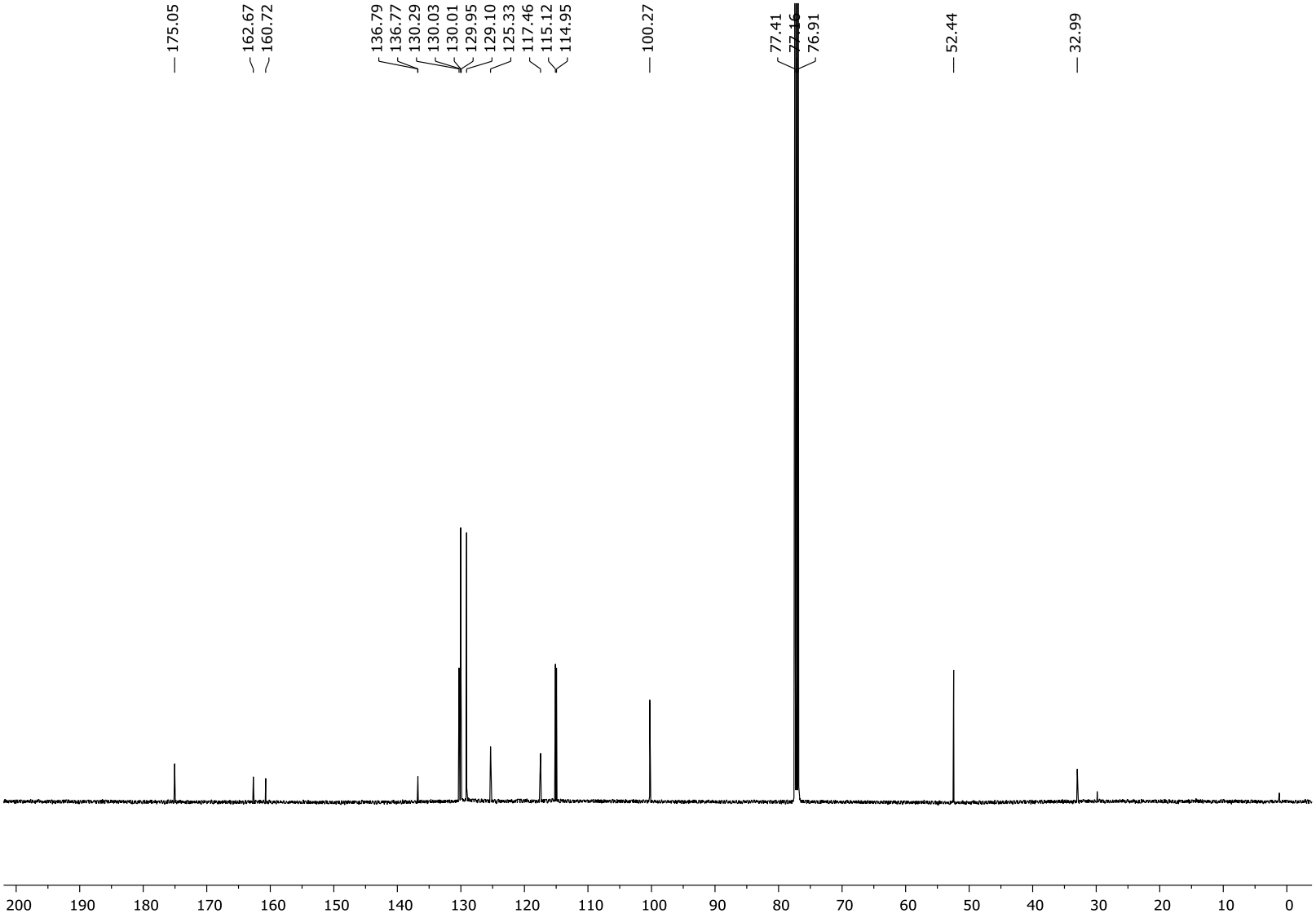


Figure S53: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3i**.

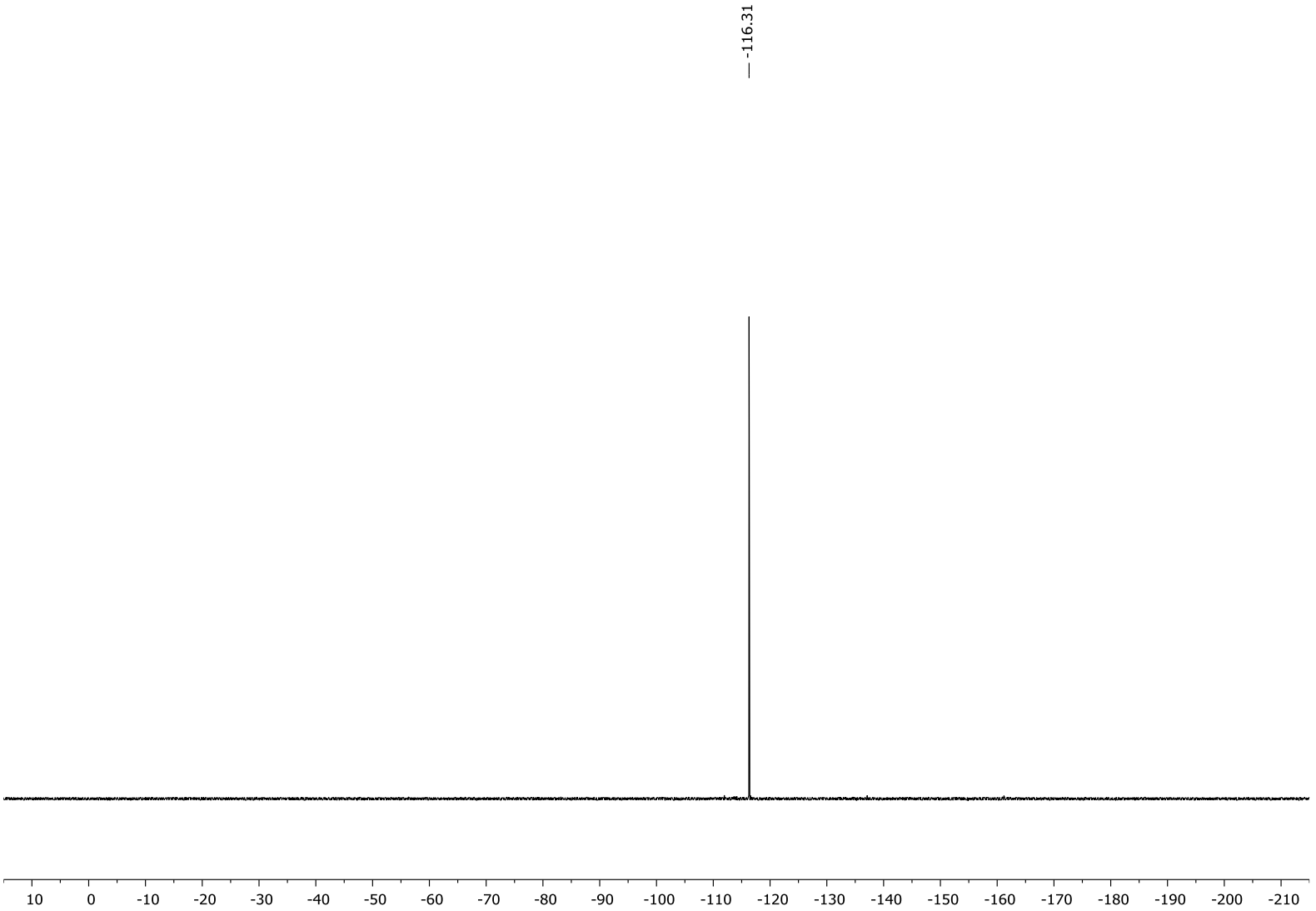


Figure S54: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3j**.

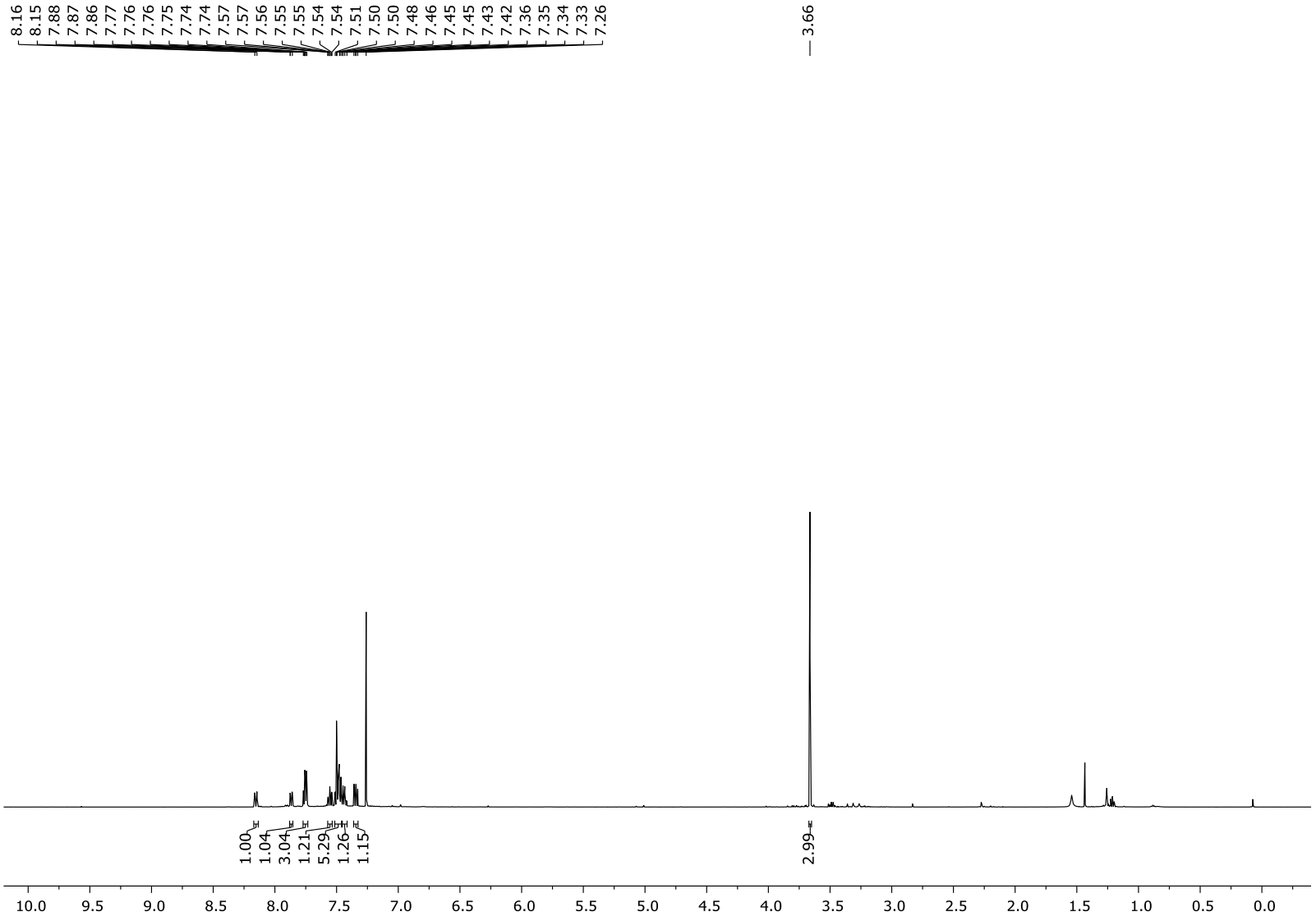


Figure S55: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3j**.

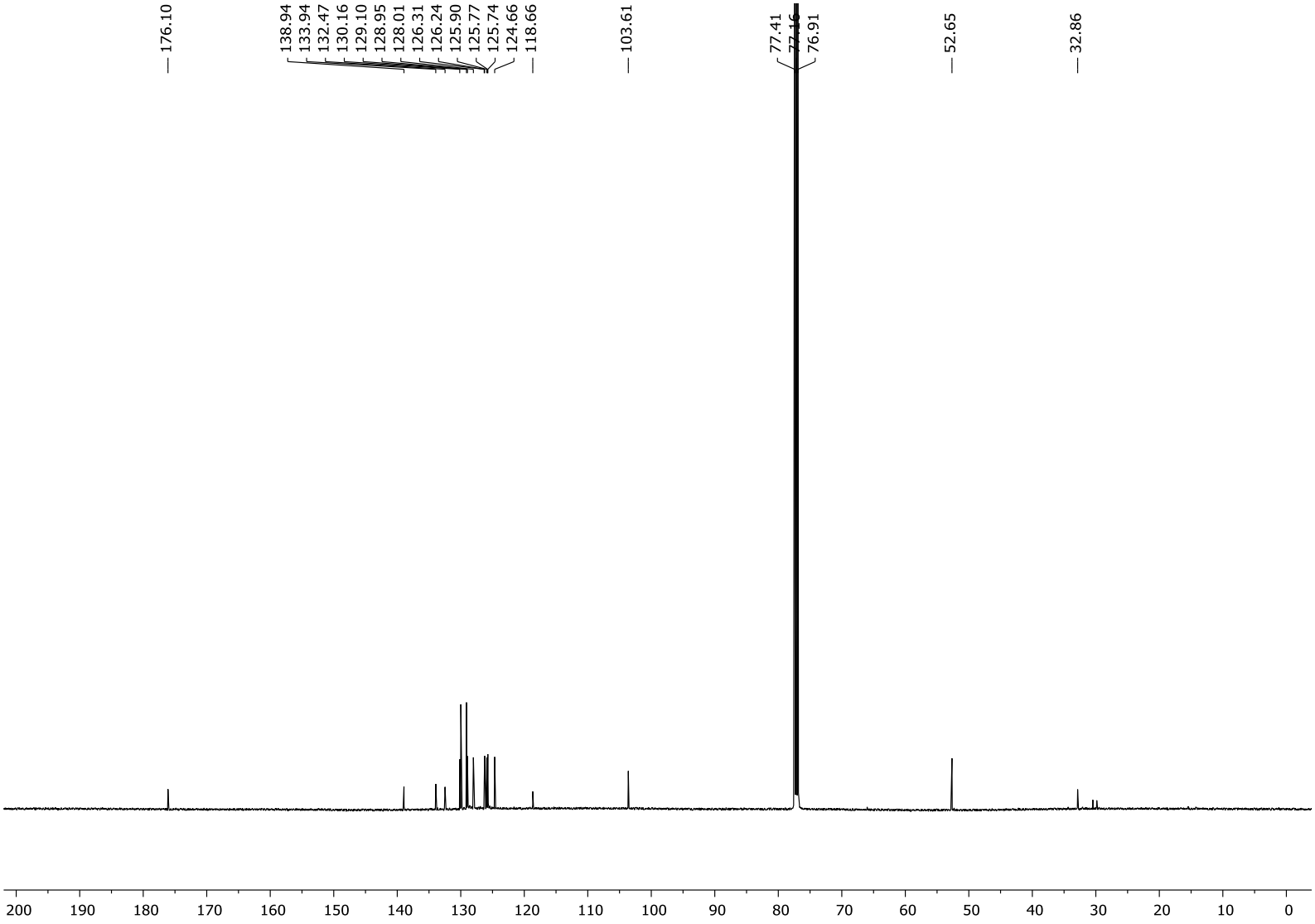


Figure S56: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3k**.

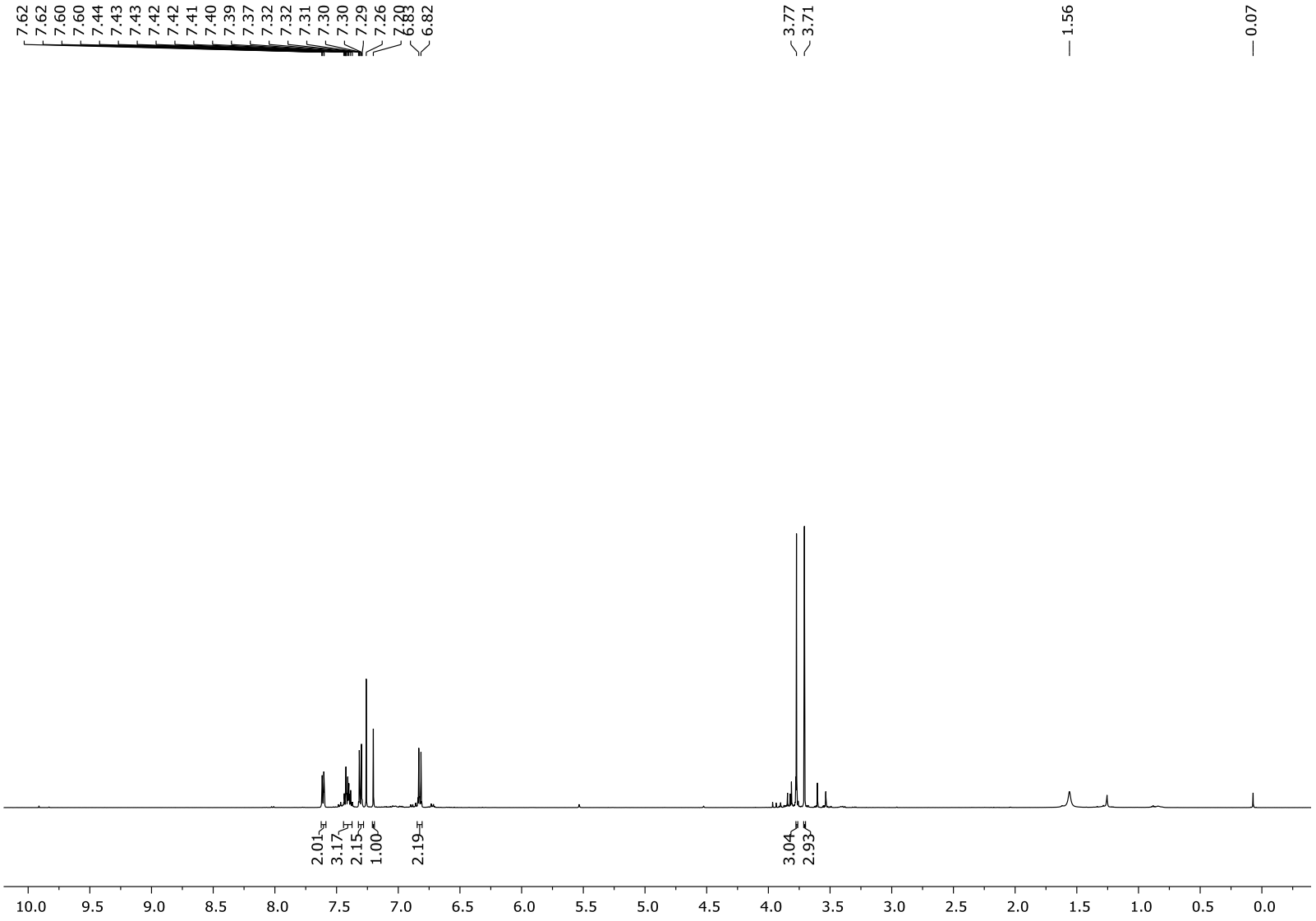


Figure S57: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3k**.

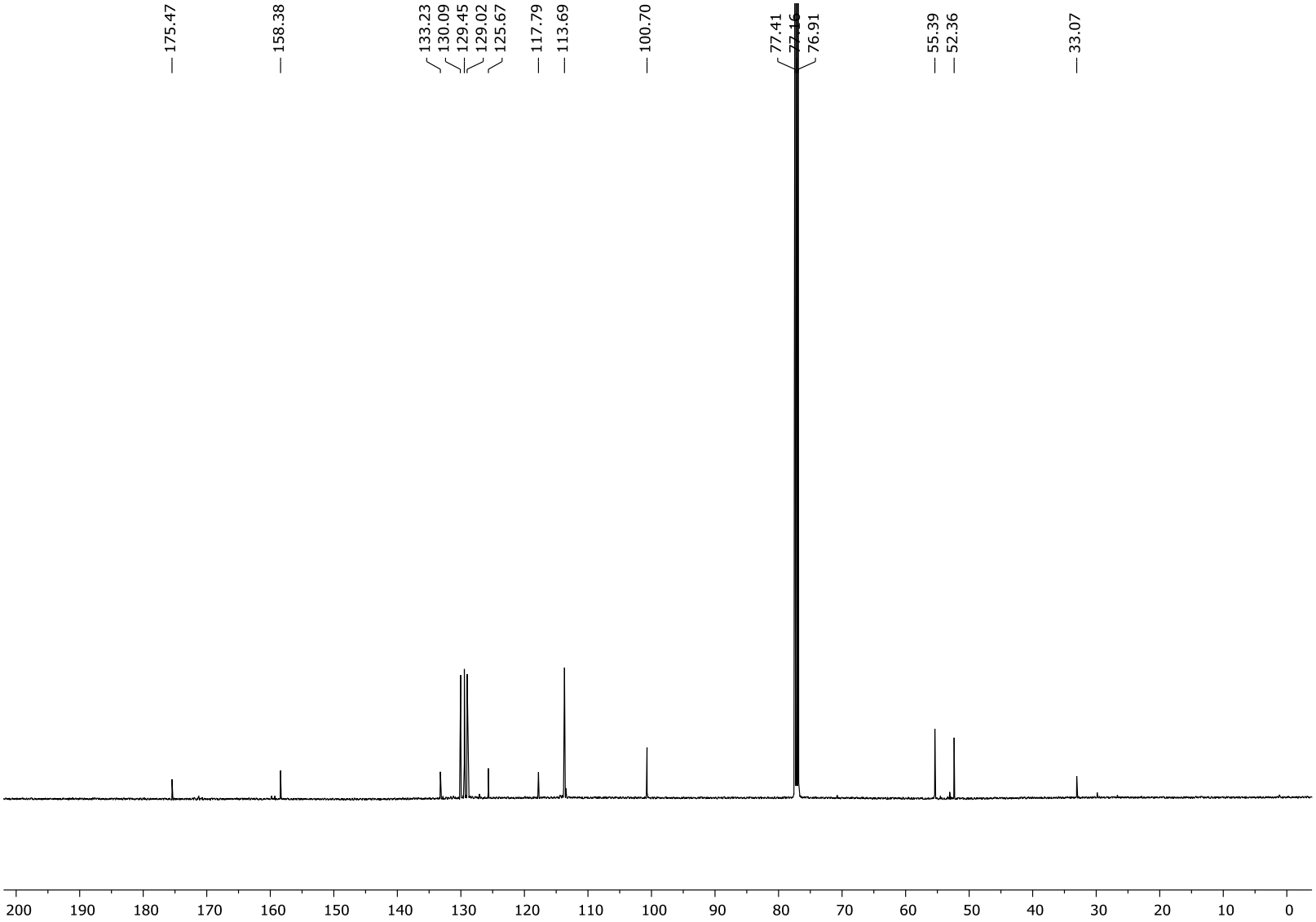


Figure S58: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3l**.

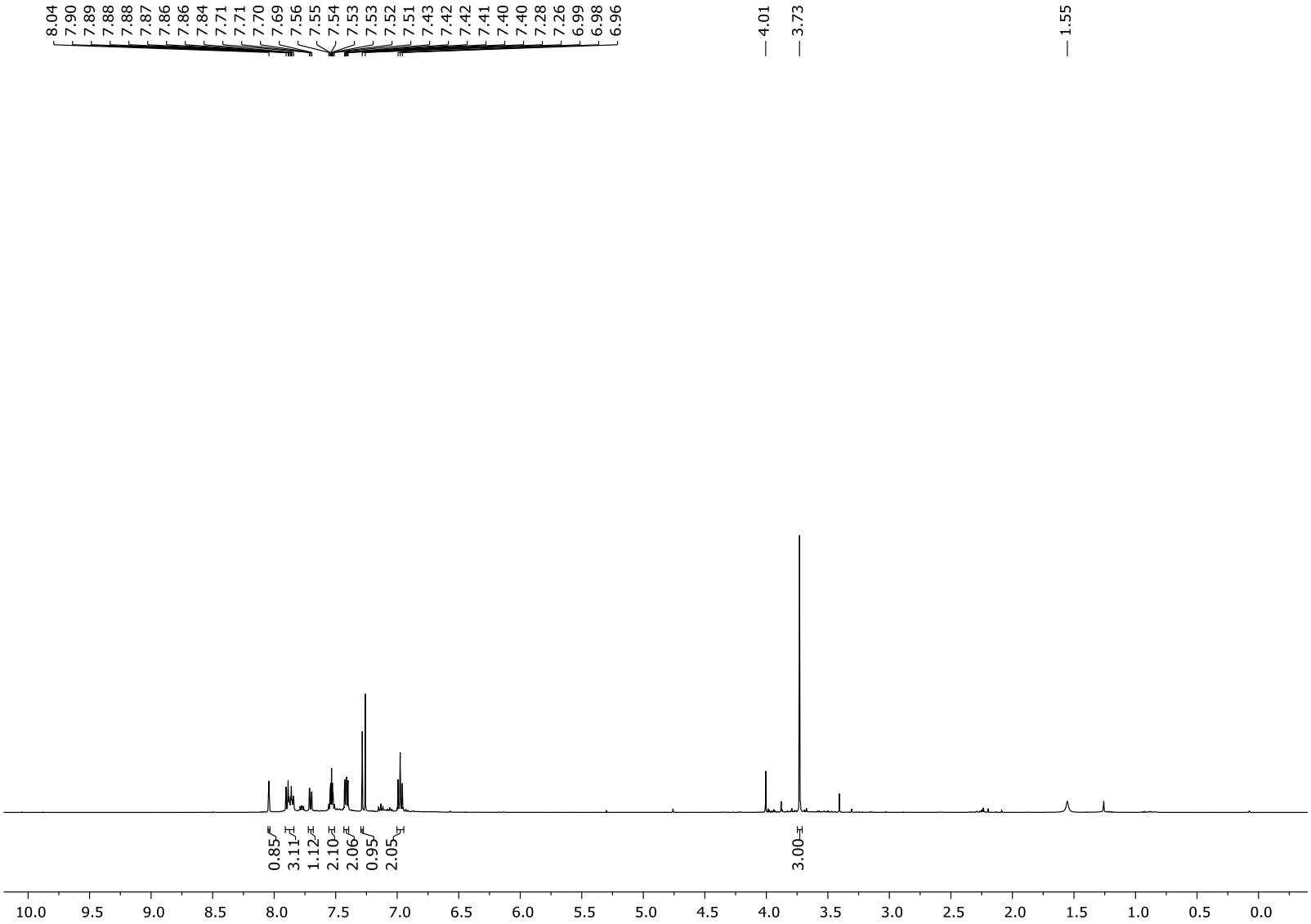


Figure S59: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3l**.

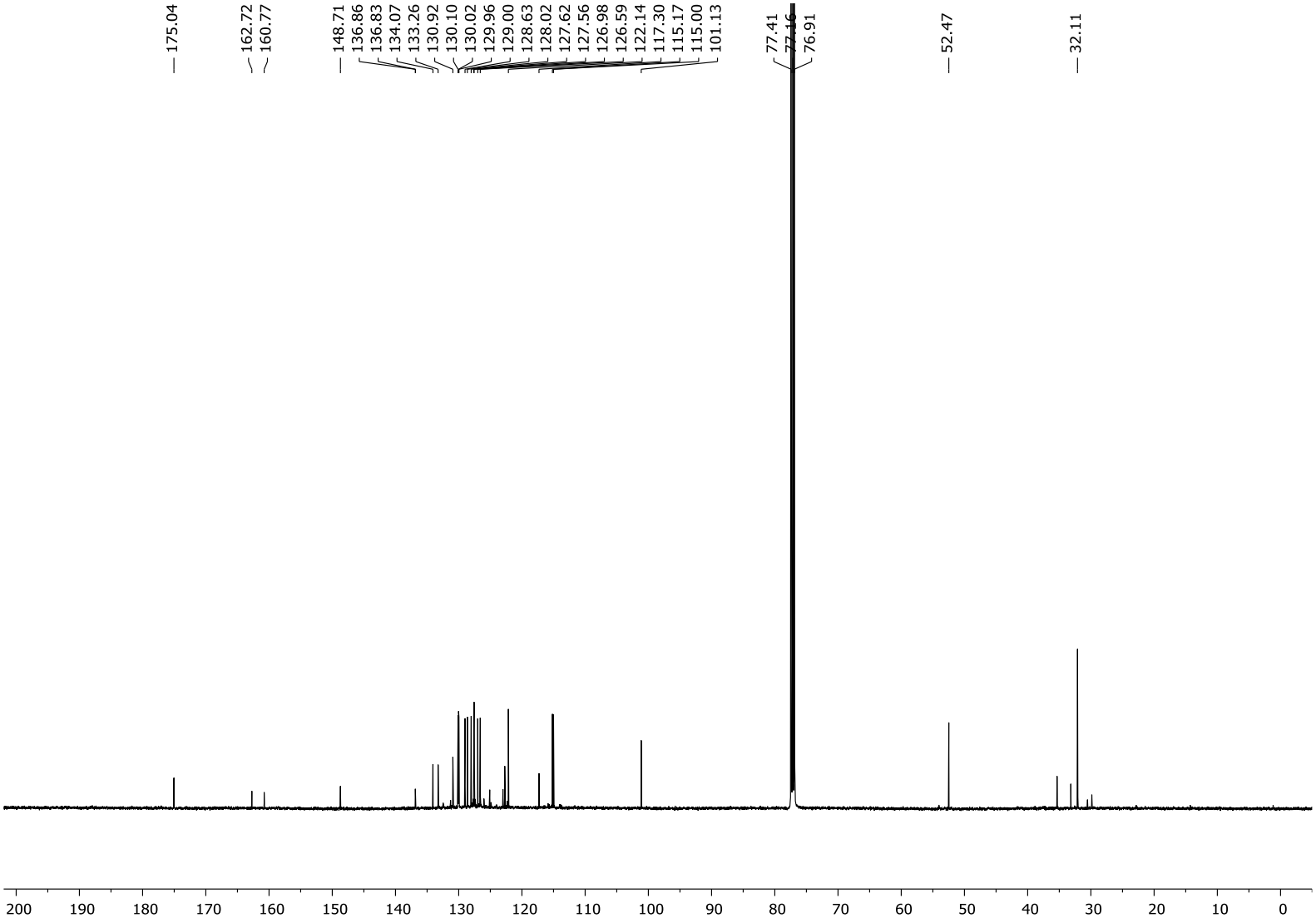


Figure S60: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3l**.

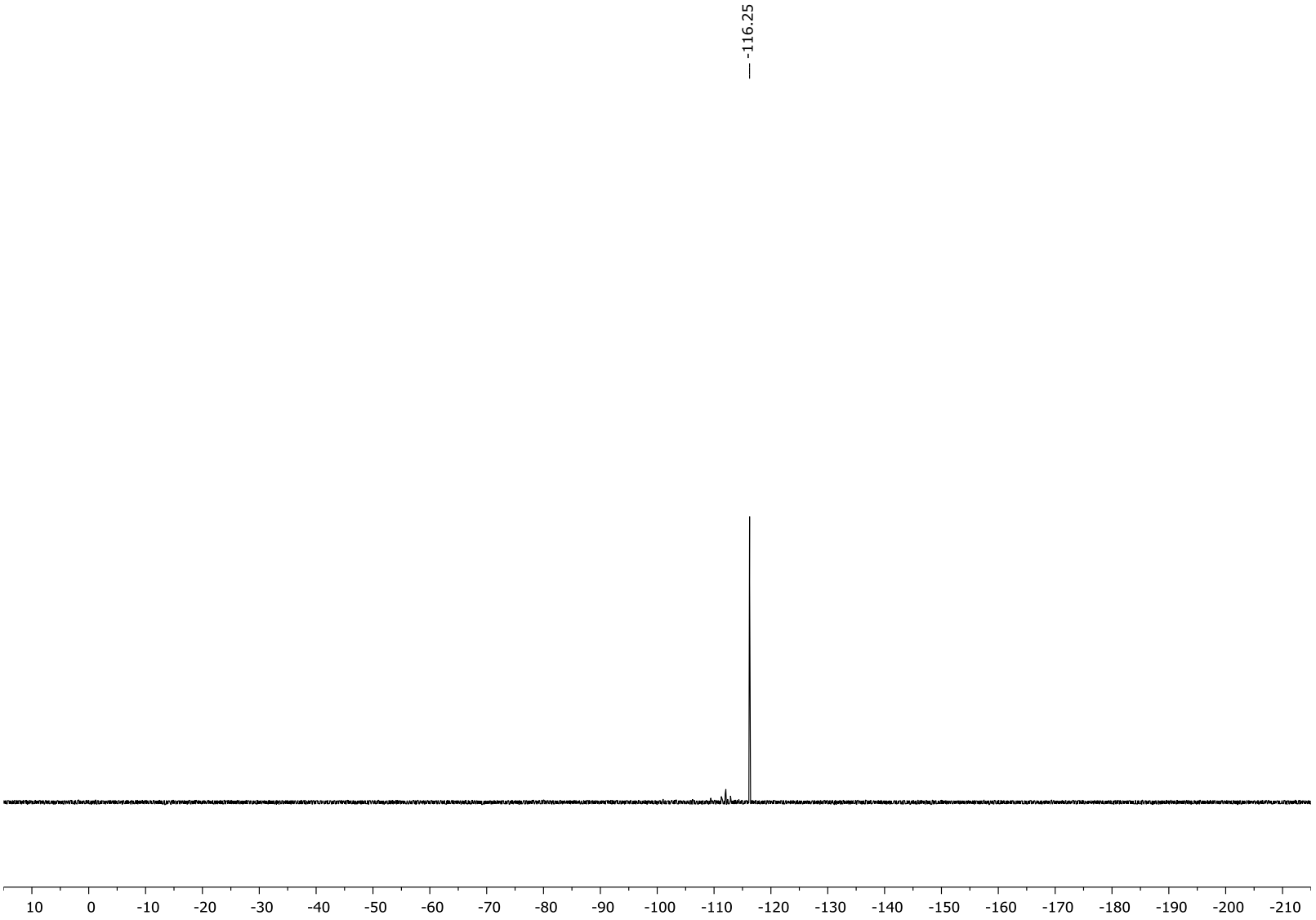


Figure S61: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3m**.

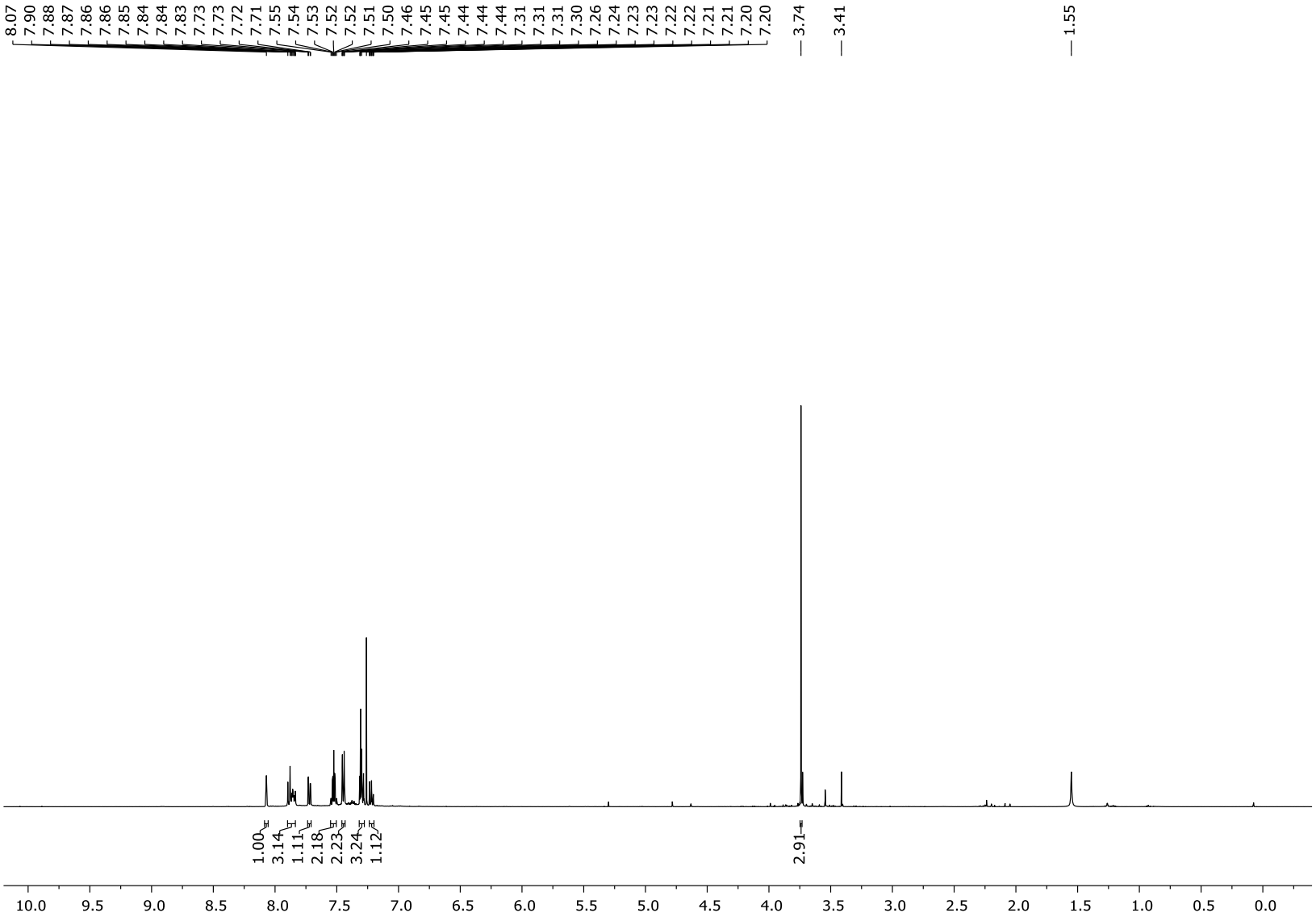


Figure S62: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3m**.

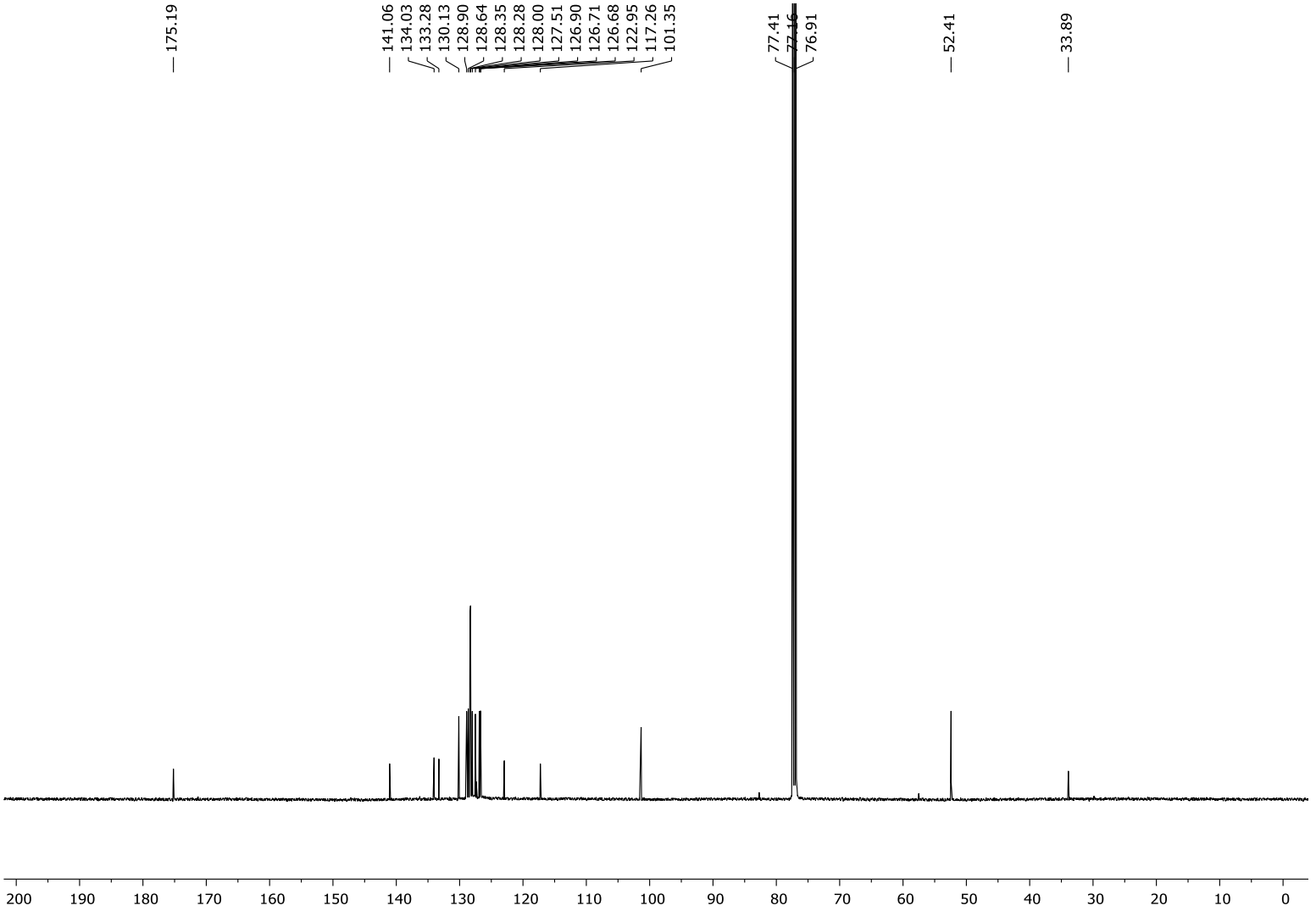


Figure S63: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3n**.

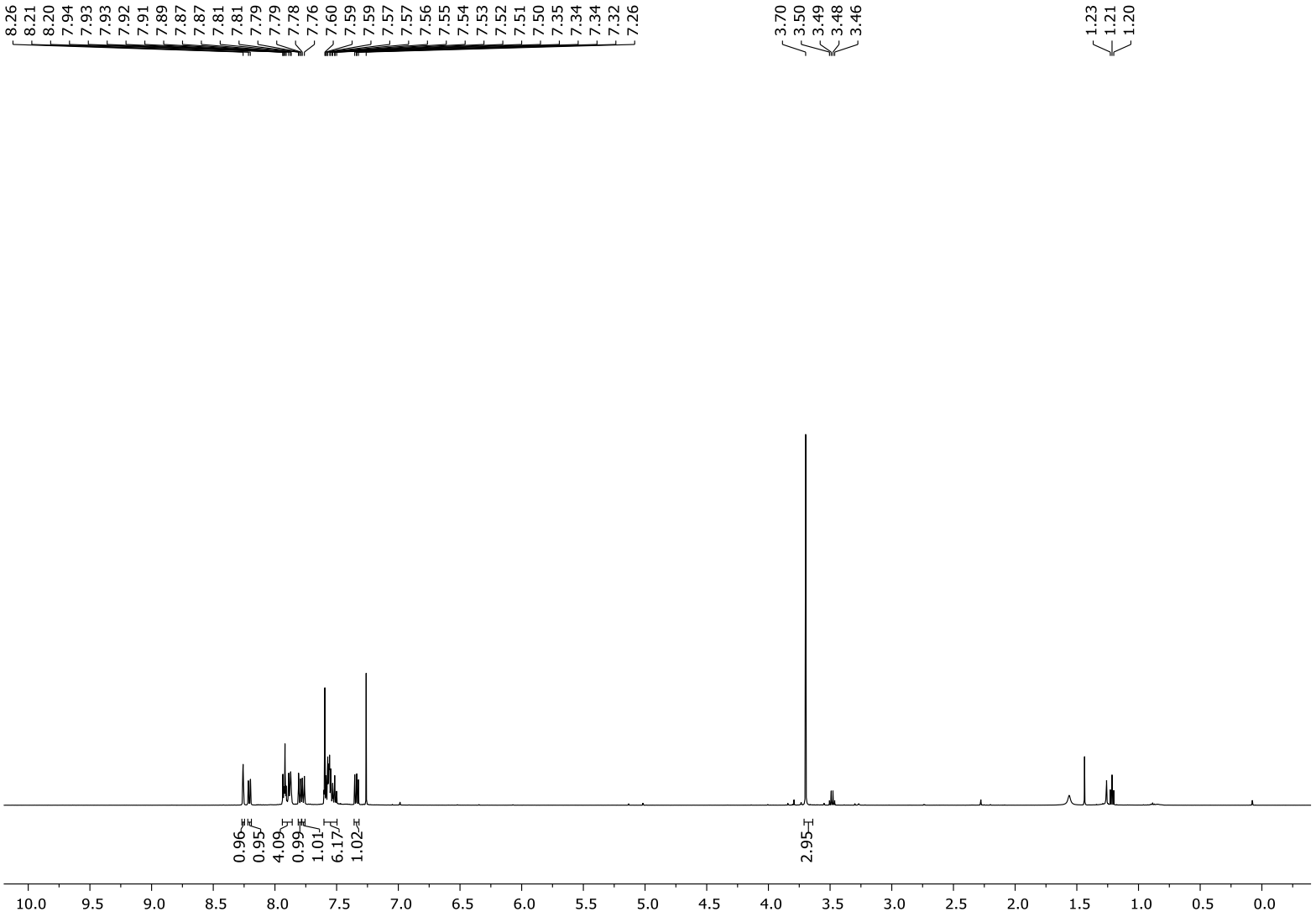


Figure S64: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3n**.

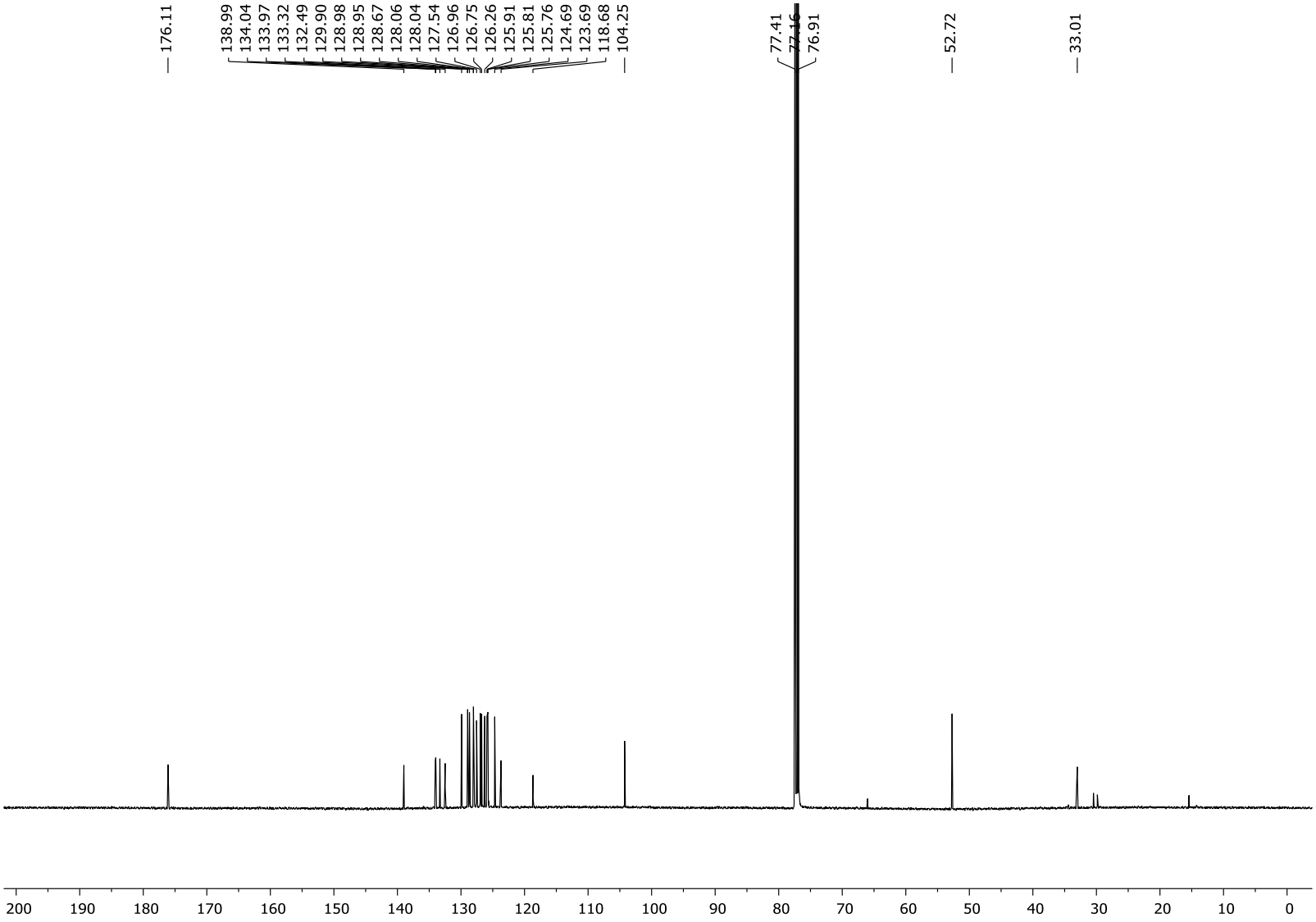


Figure S65: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3o**.

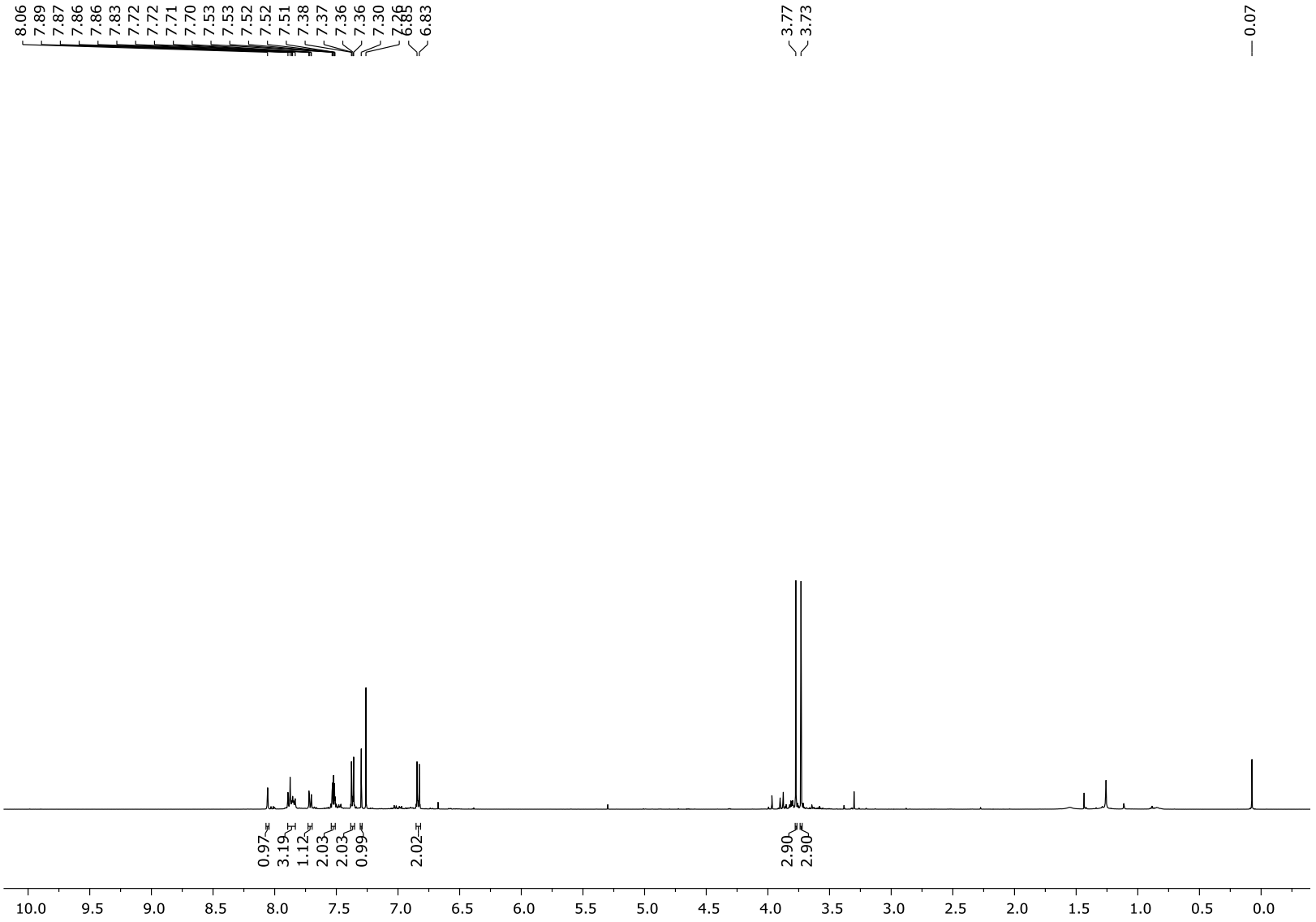


Figure S66: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3o**.

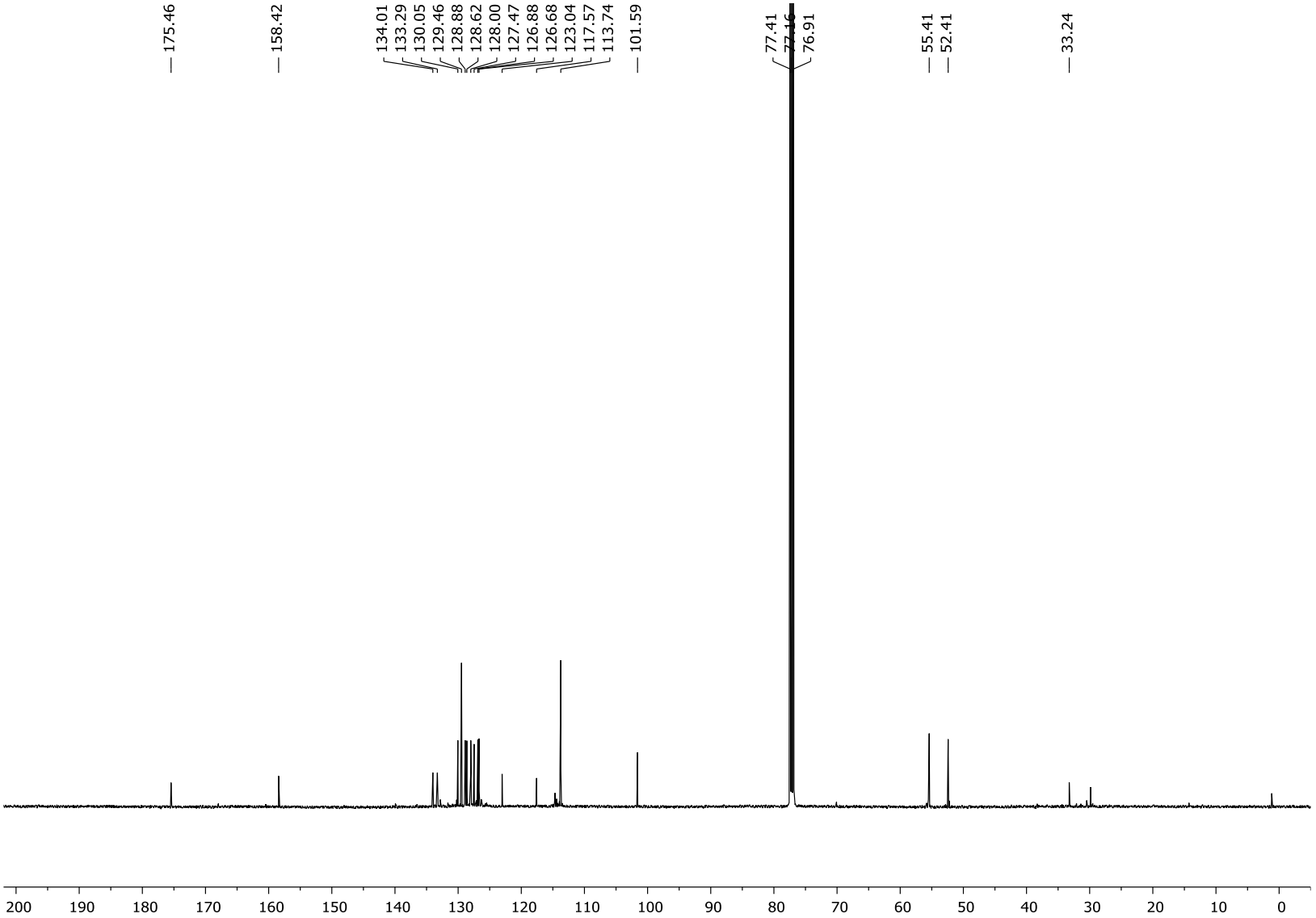


Figure S67: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3p**.

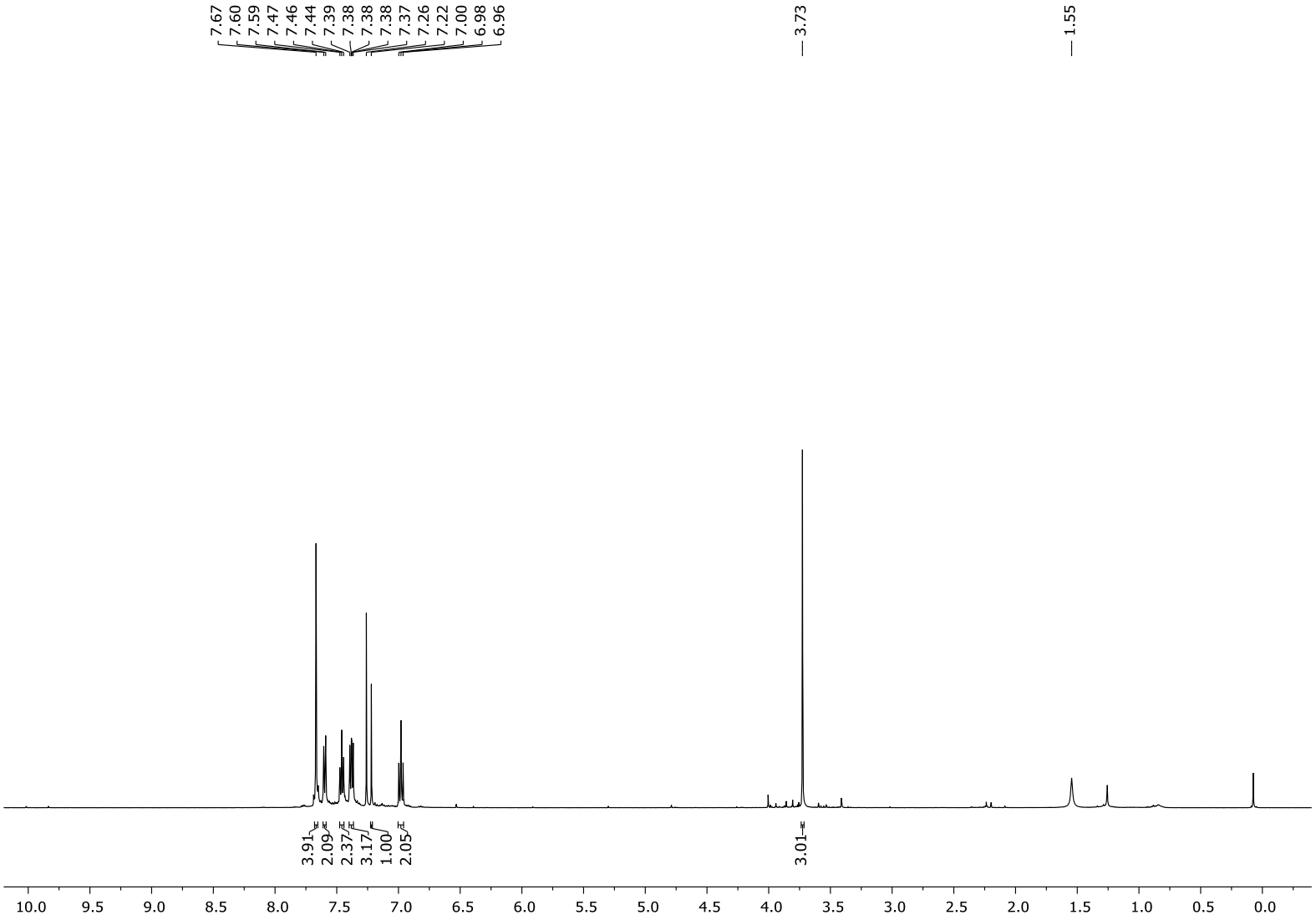


Figure S68: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3p**.

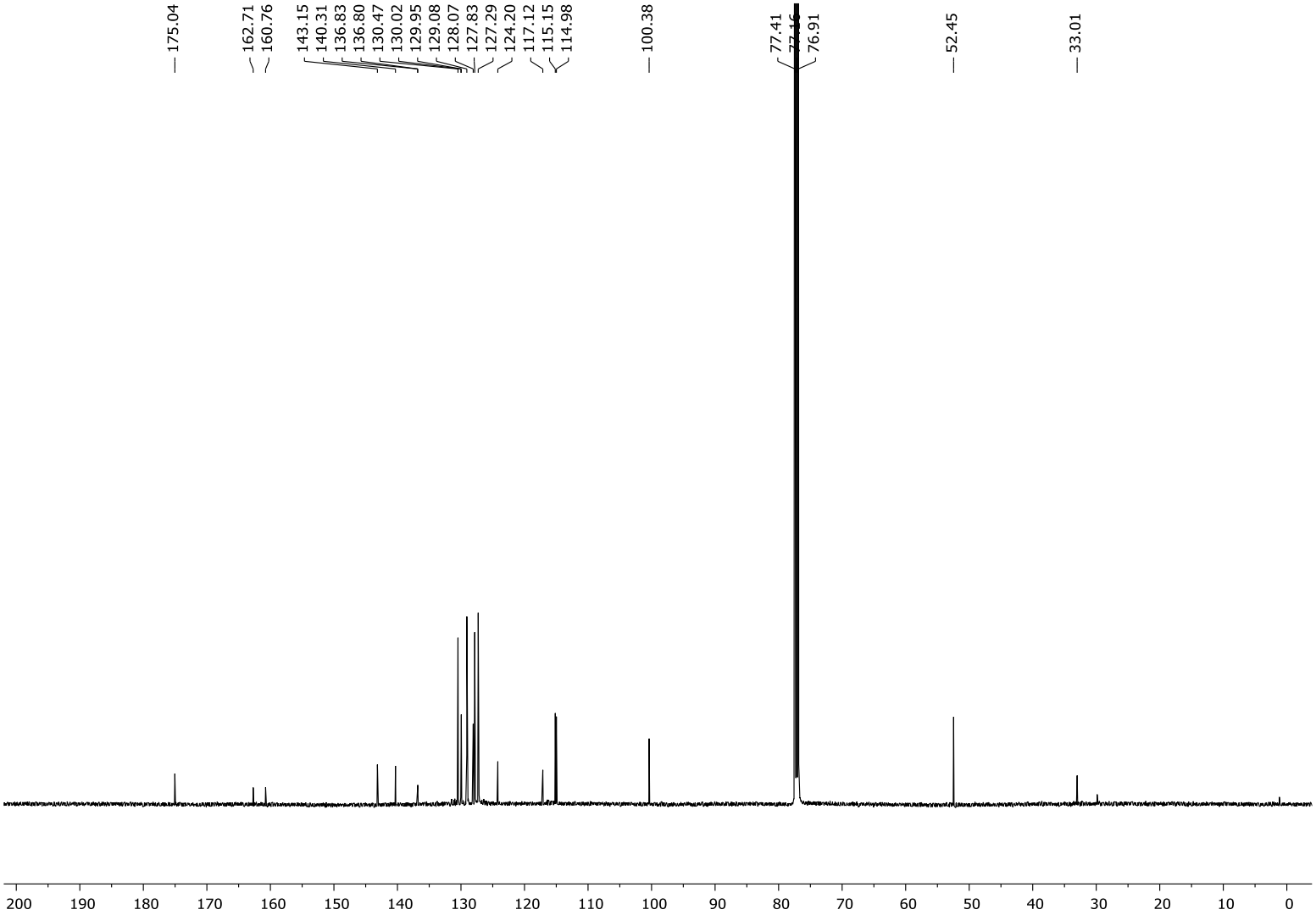


Figure S69: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3p**.

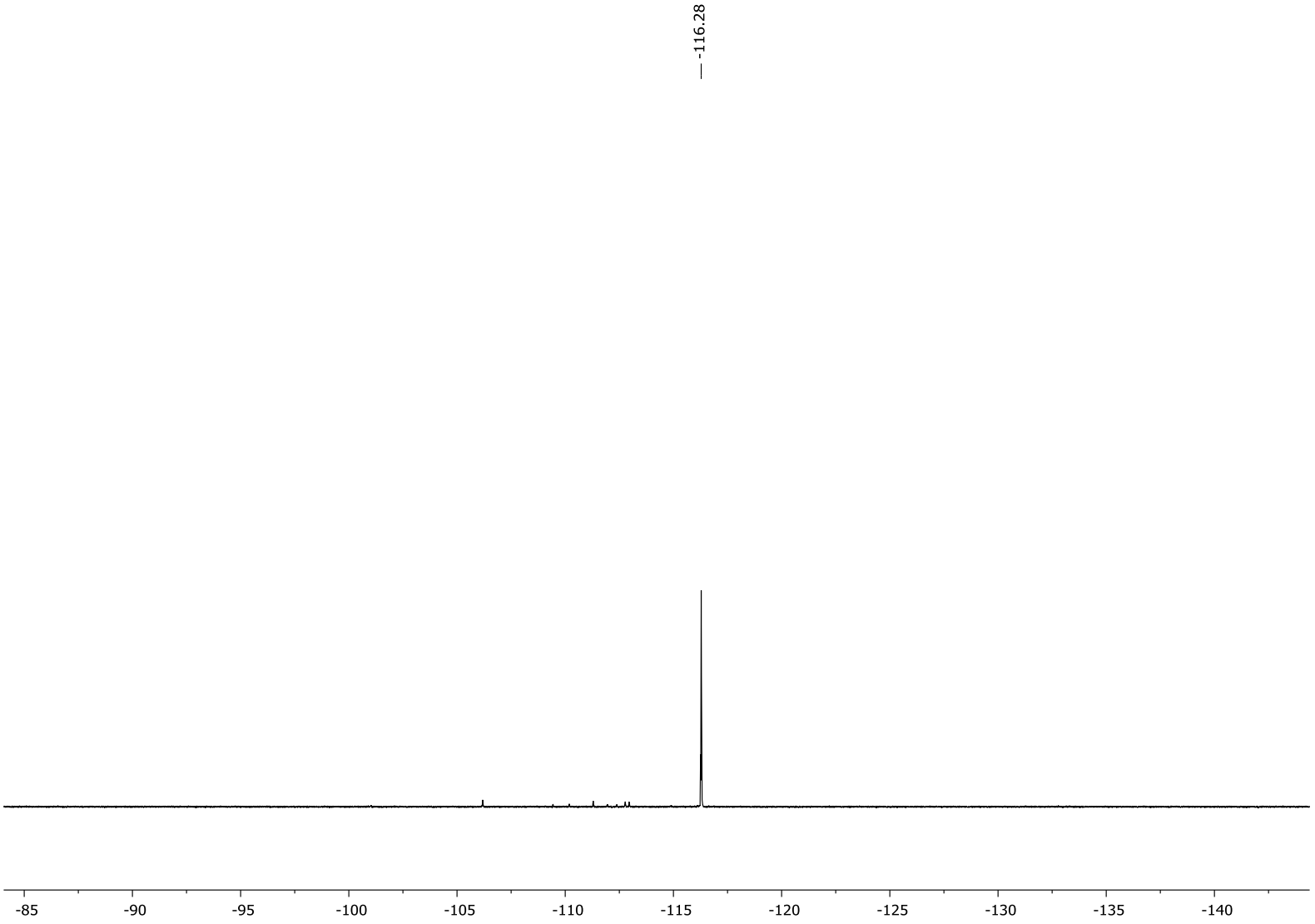


Figure S70: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3q**.

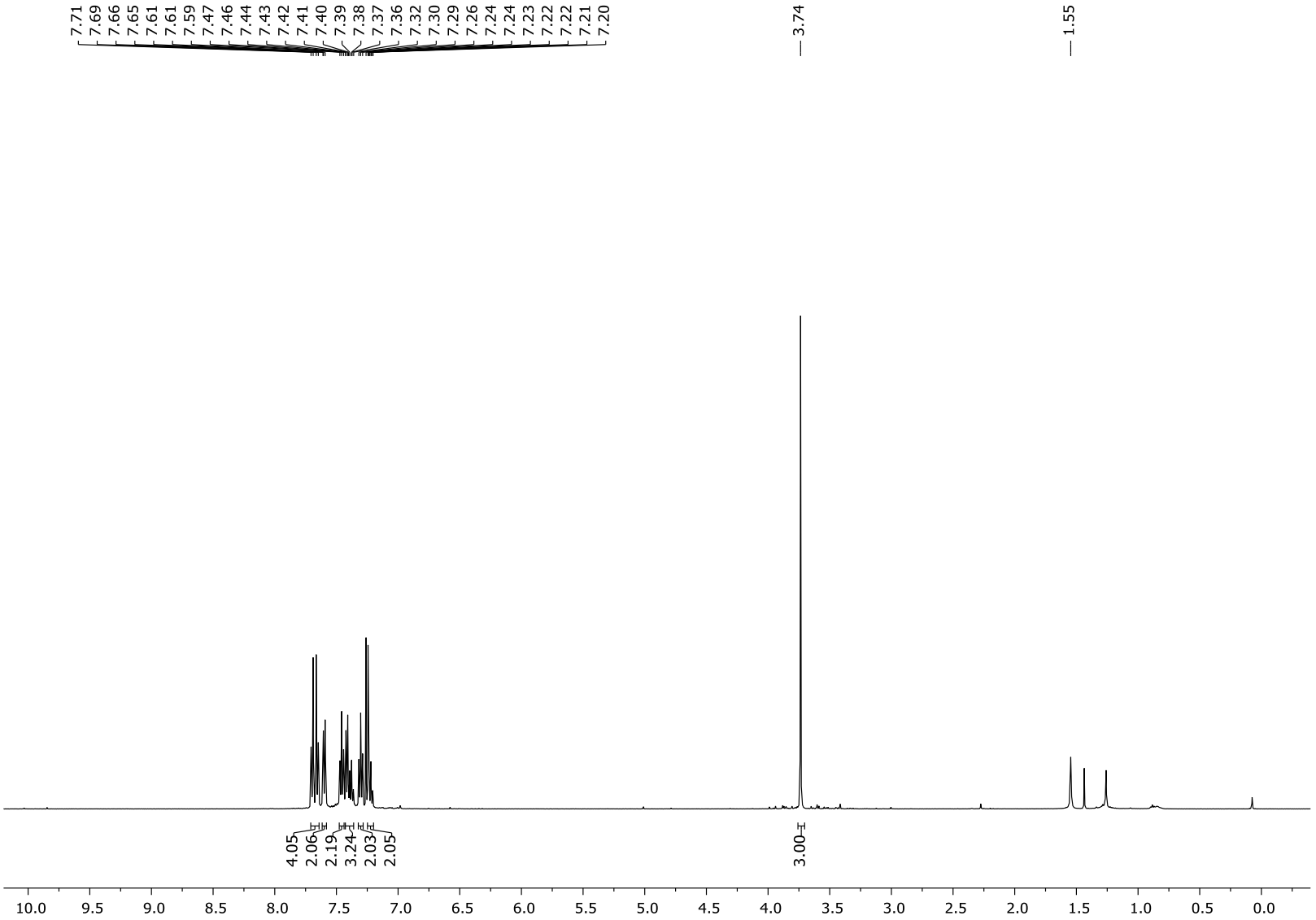


Figure S71: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3q**.

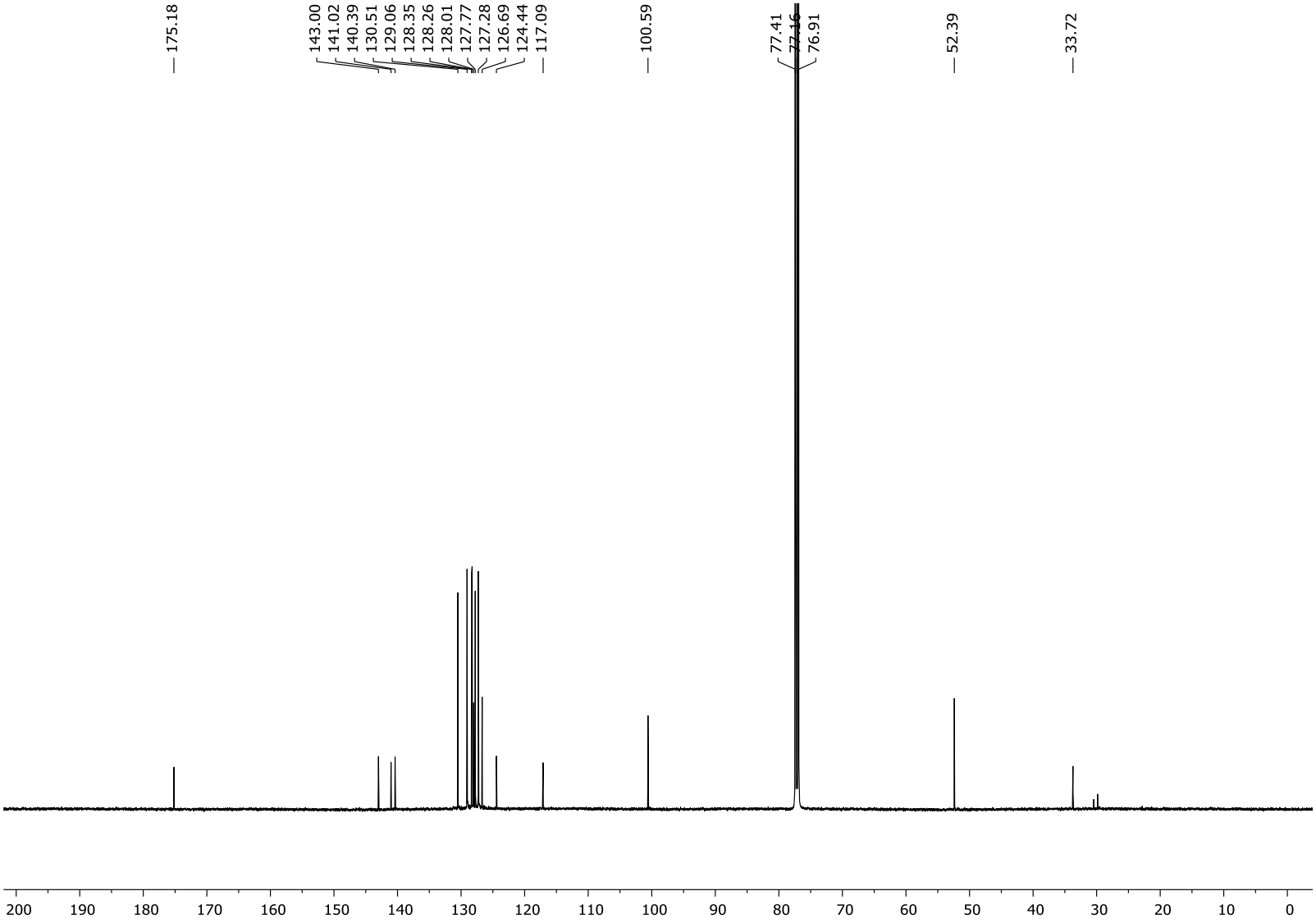


Figure S72: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3r**.

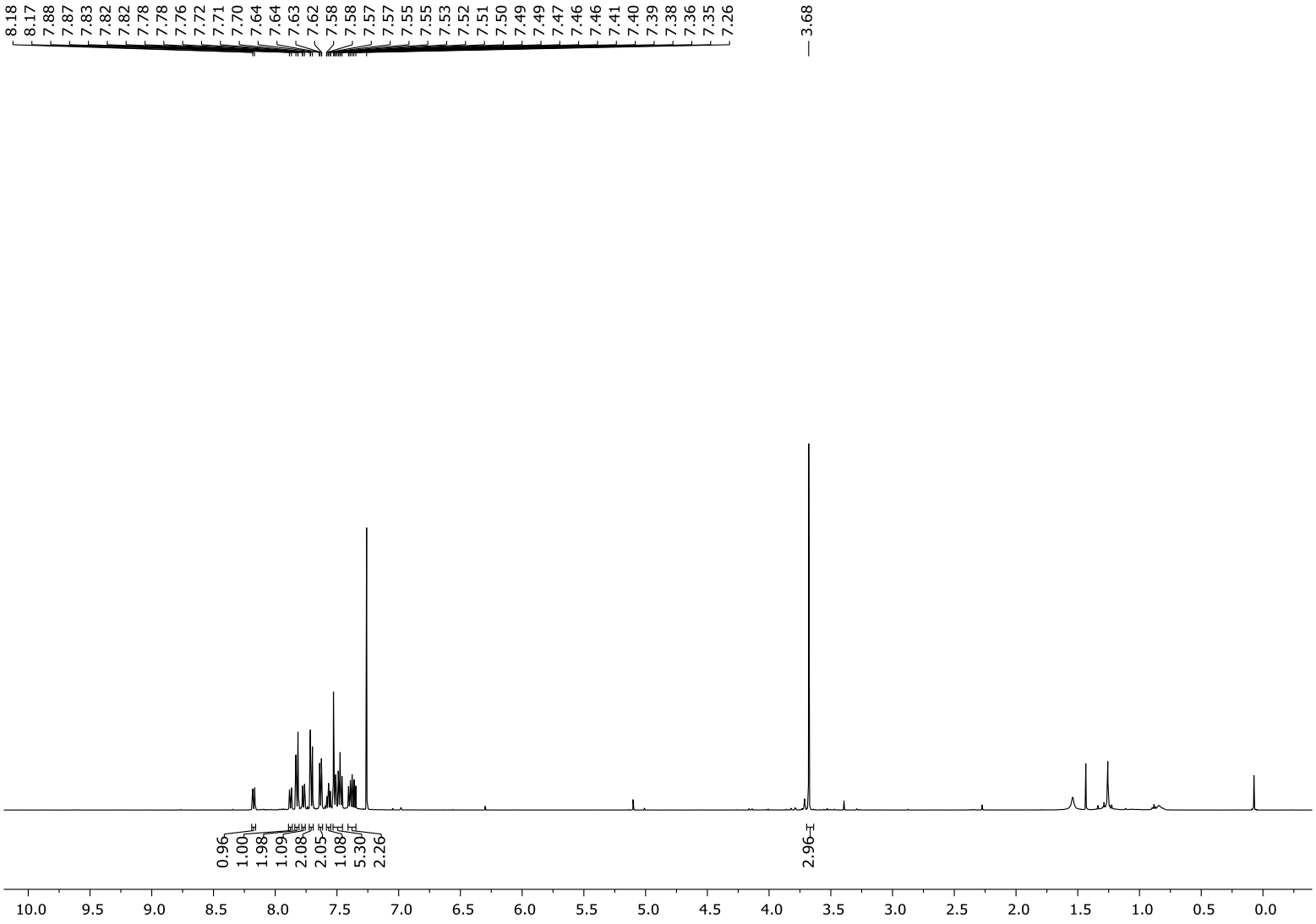


Figure S73: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3r**.

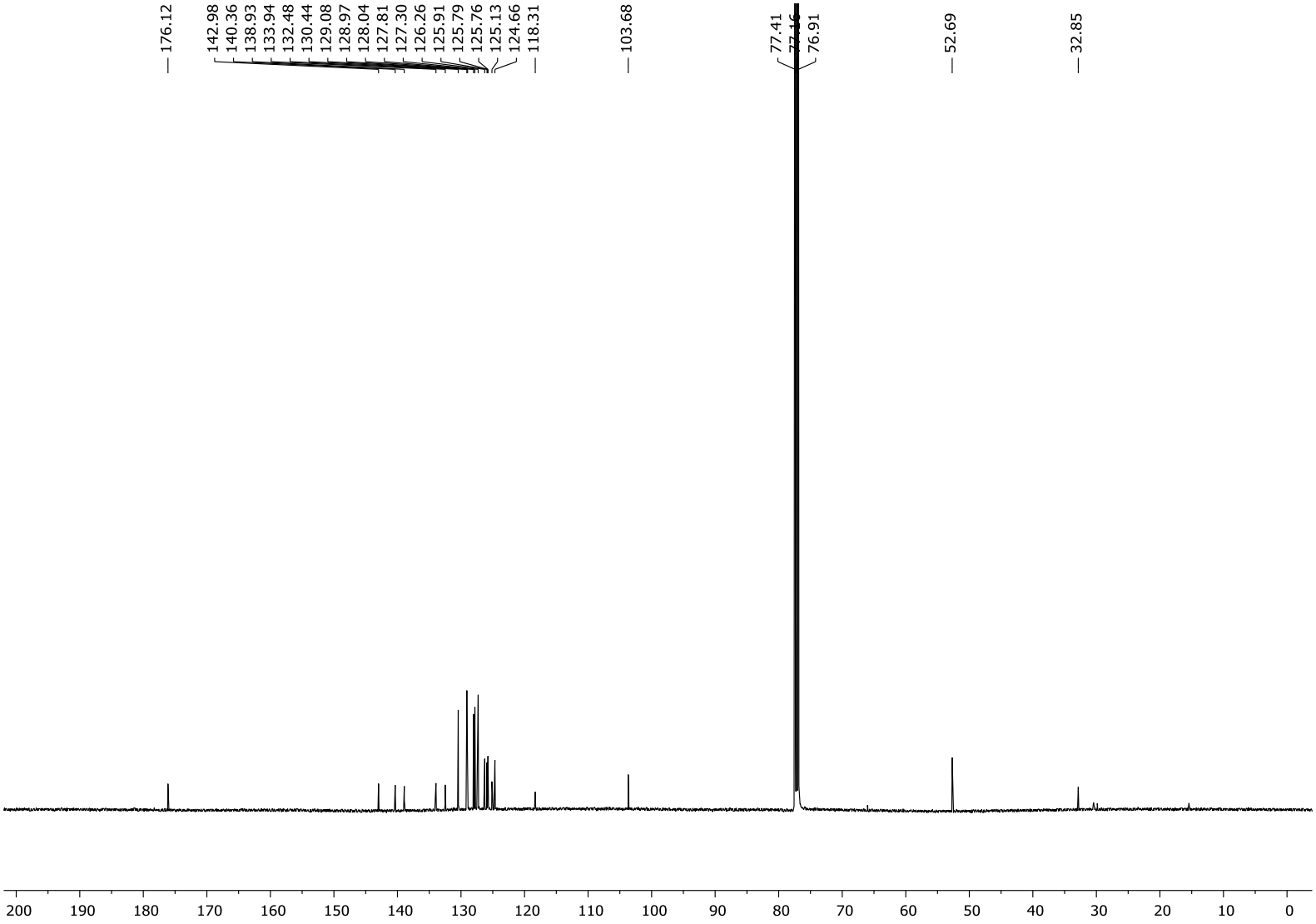


Figure S74: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3s**.

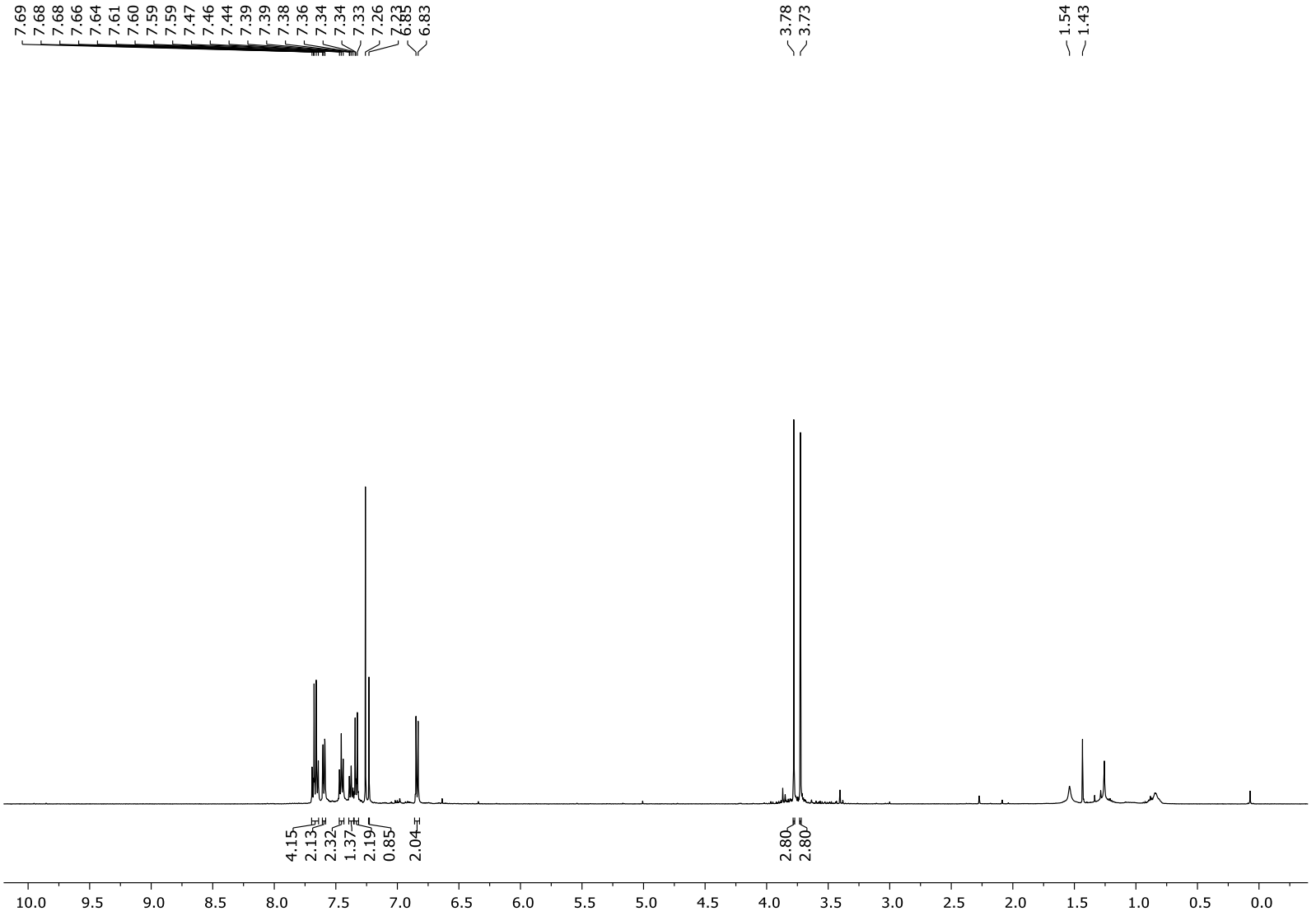


Figure S75: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3s**.

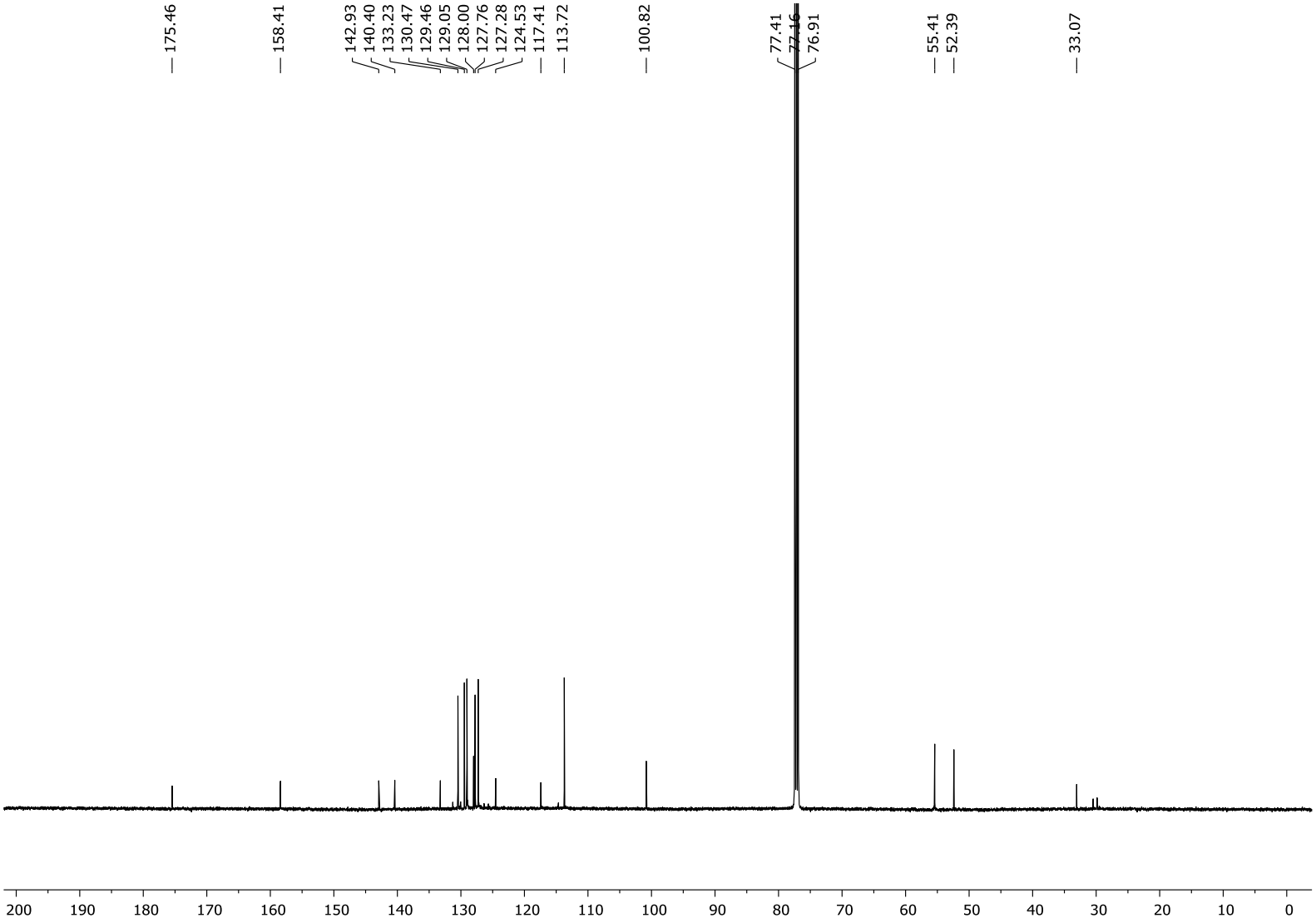


Figure S76: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3t**.

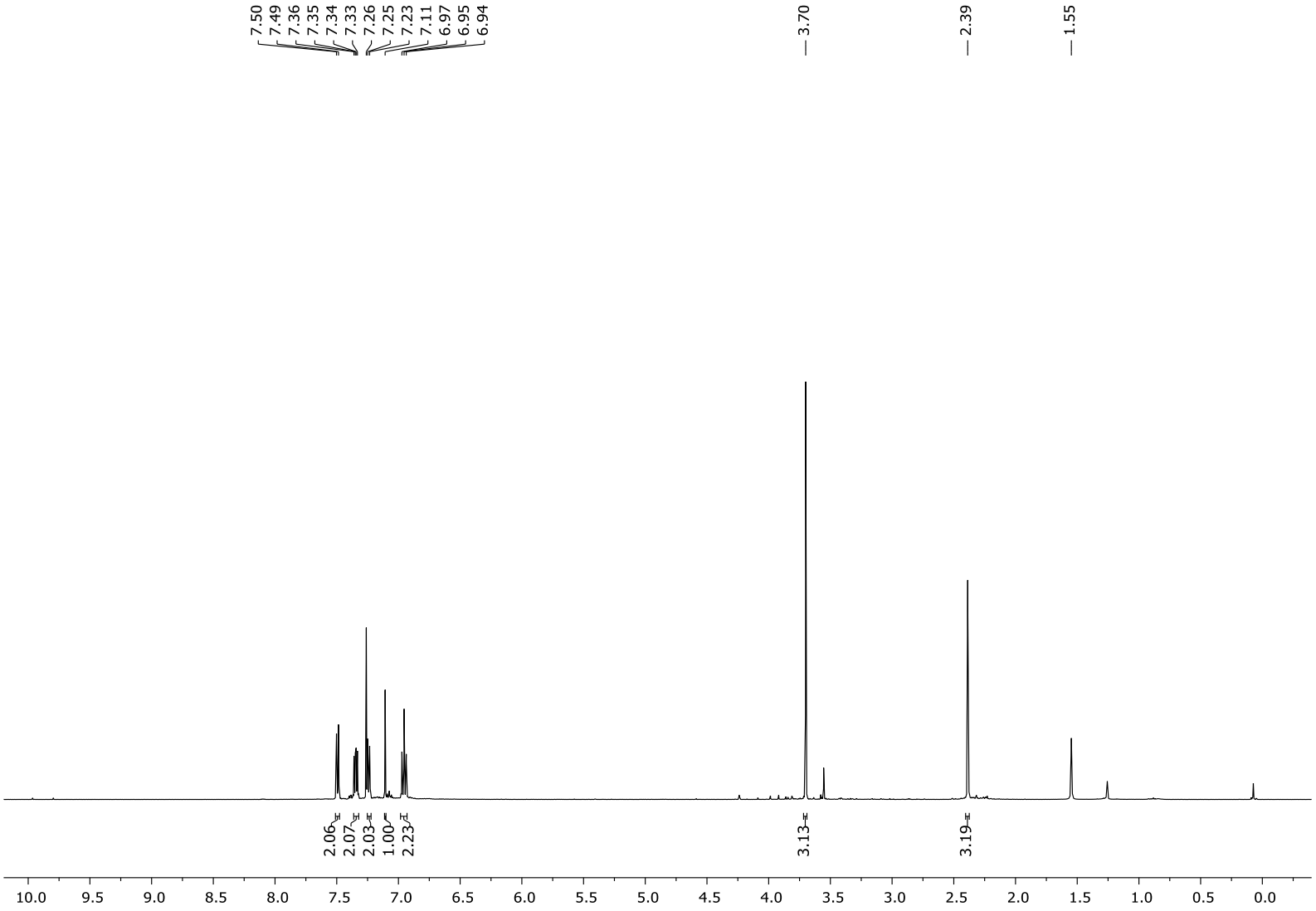


Figure S77: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3t**.

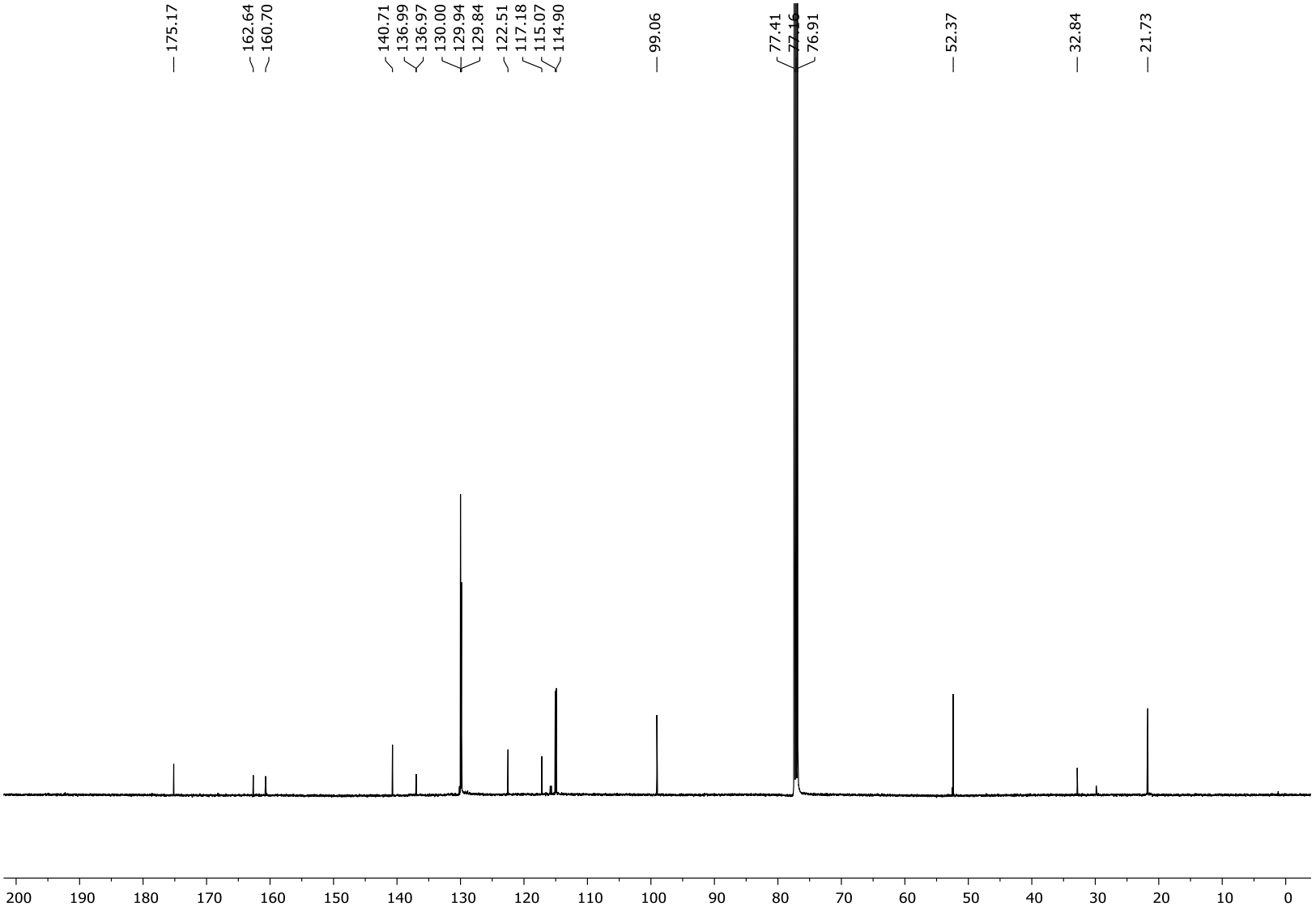


Figure S78: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3t**.

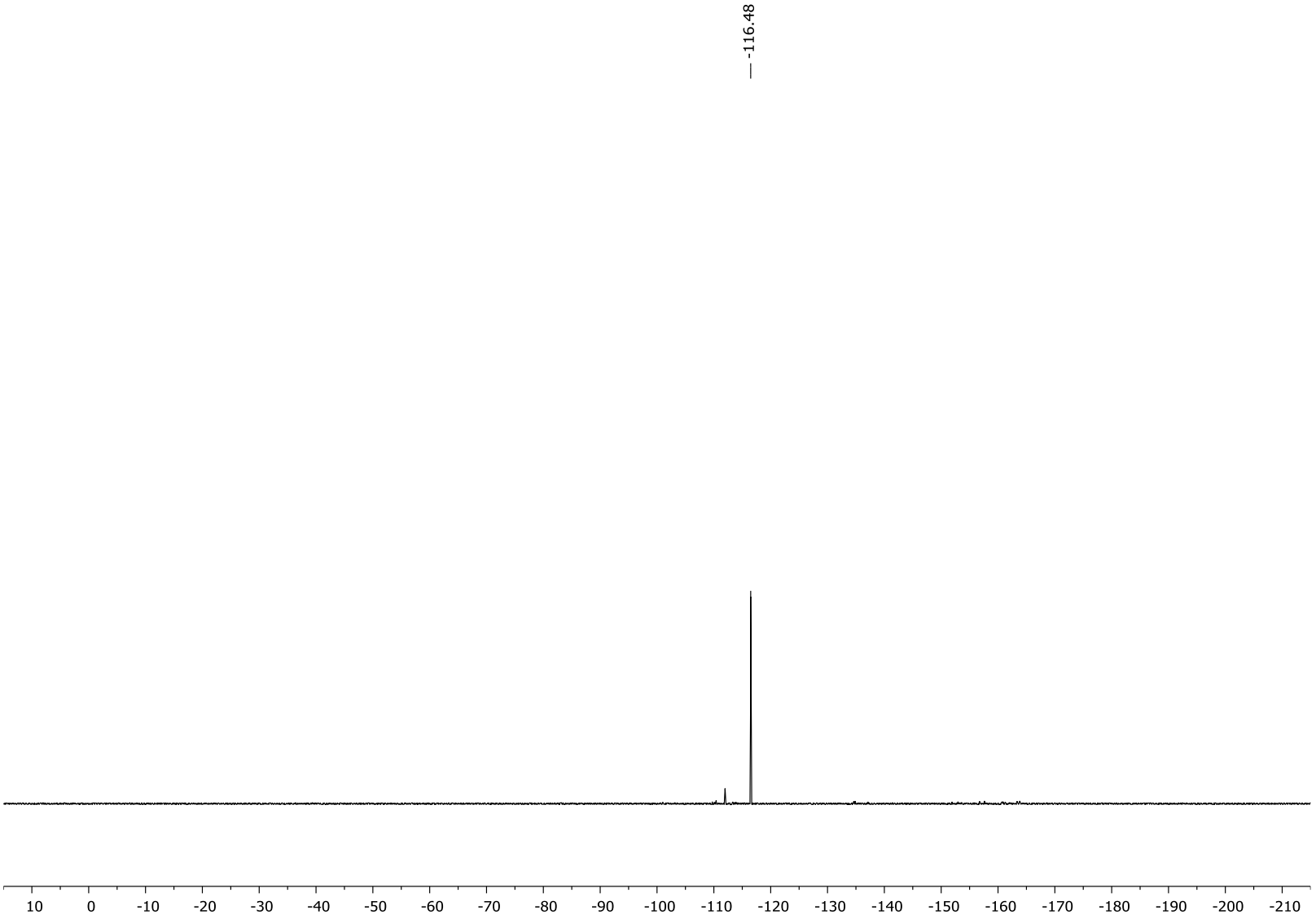


Figure S79: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3u**.

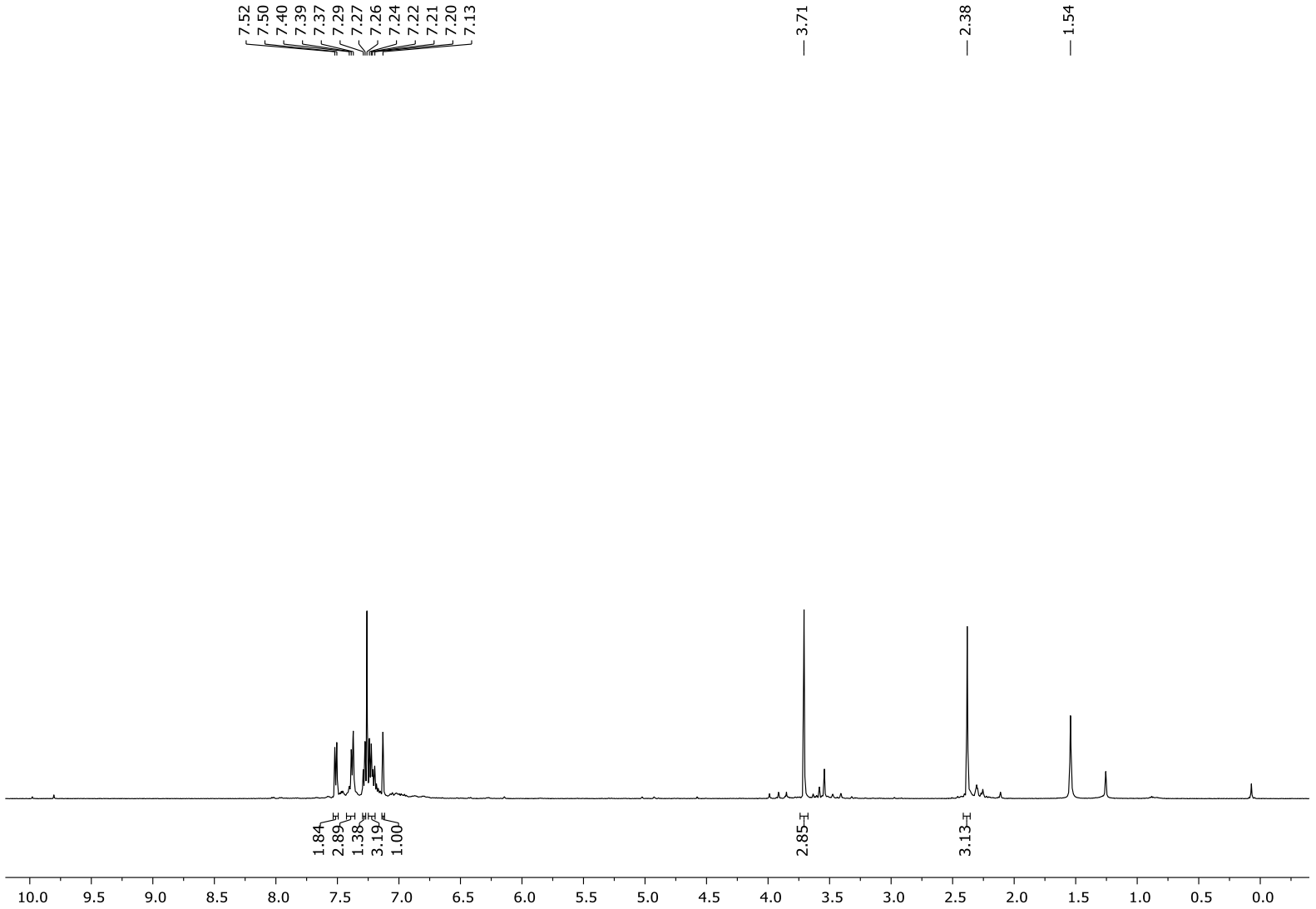


Figure S80: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3u**.

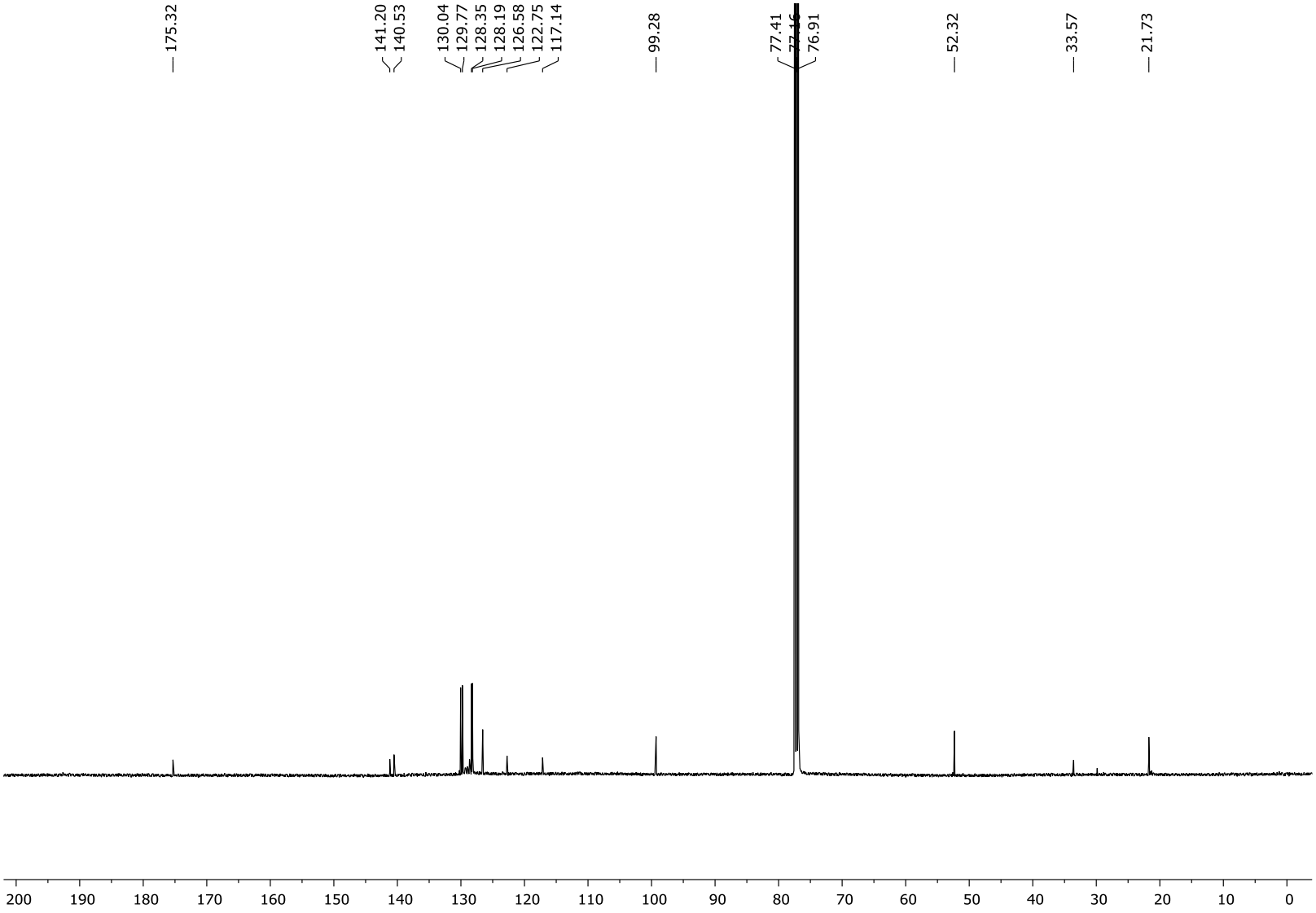


Figure S81: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3v**.

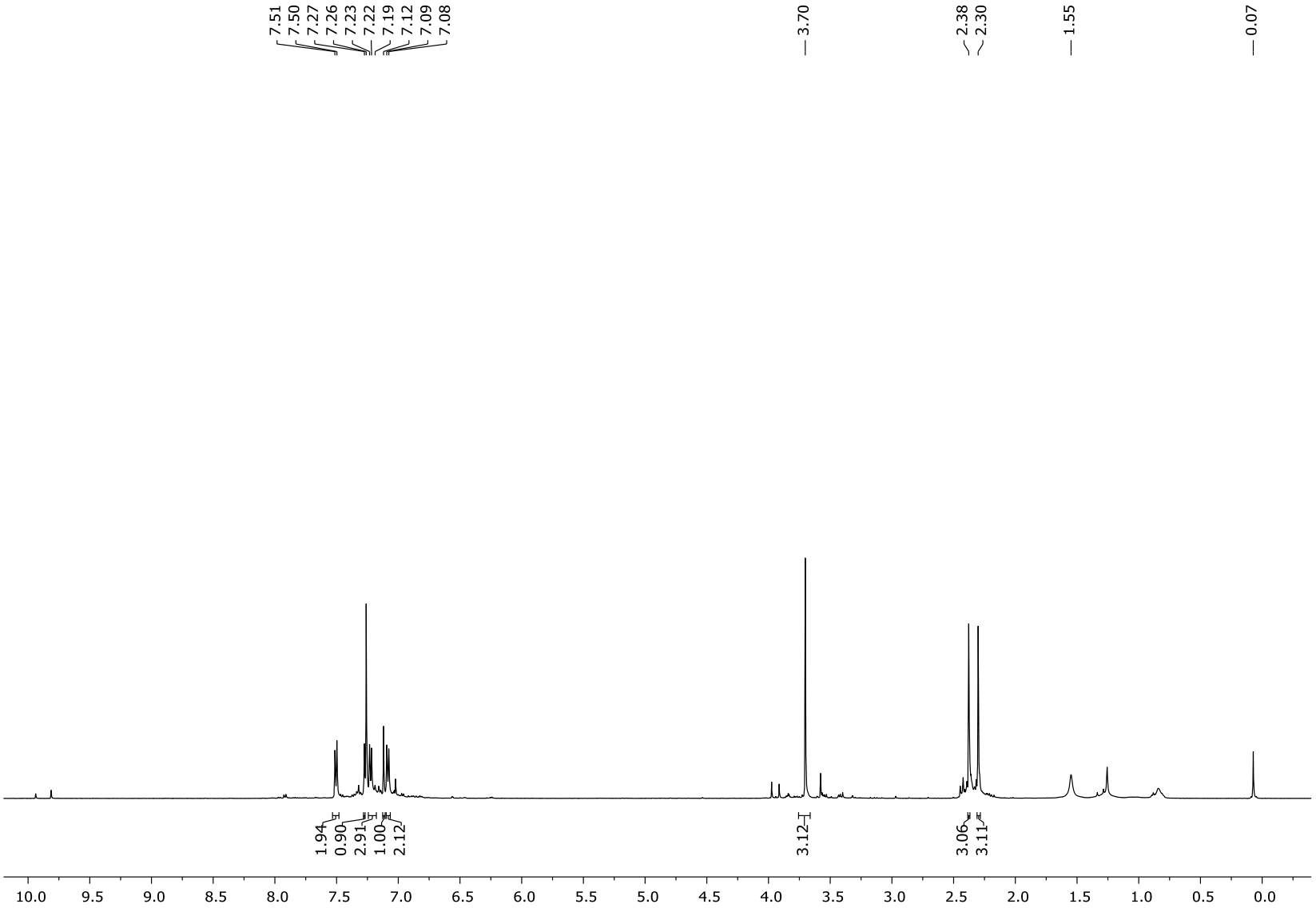


Figure S82: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3v**.

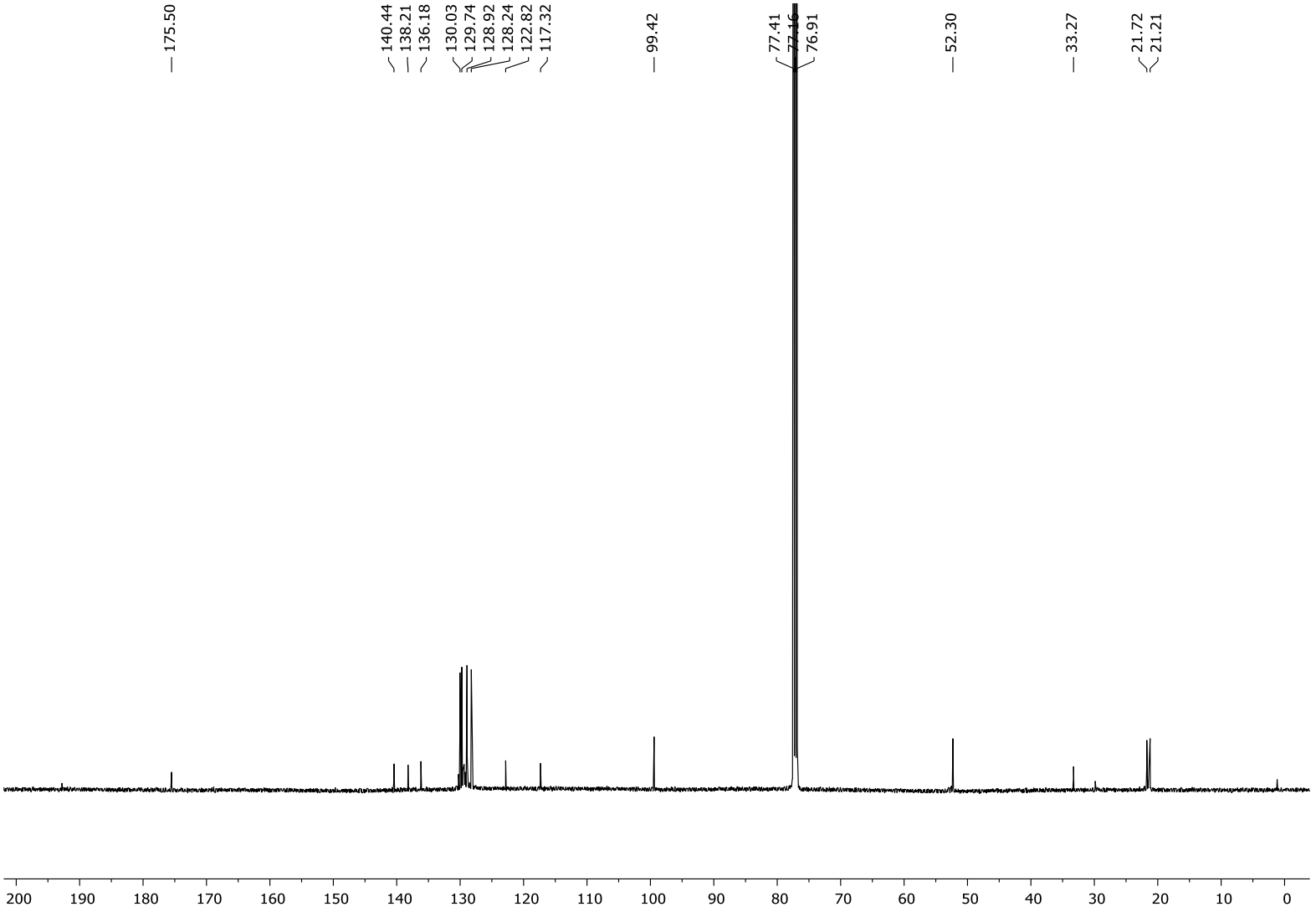


Figure S83: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3w**.

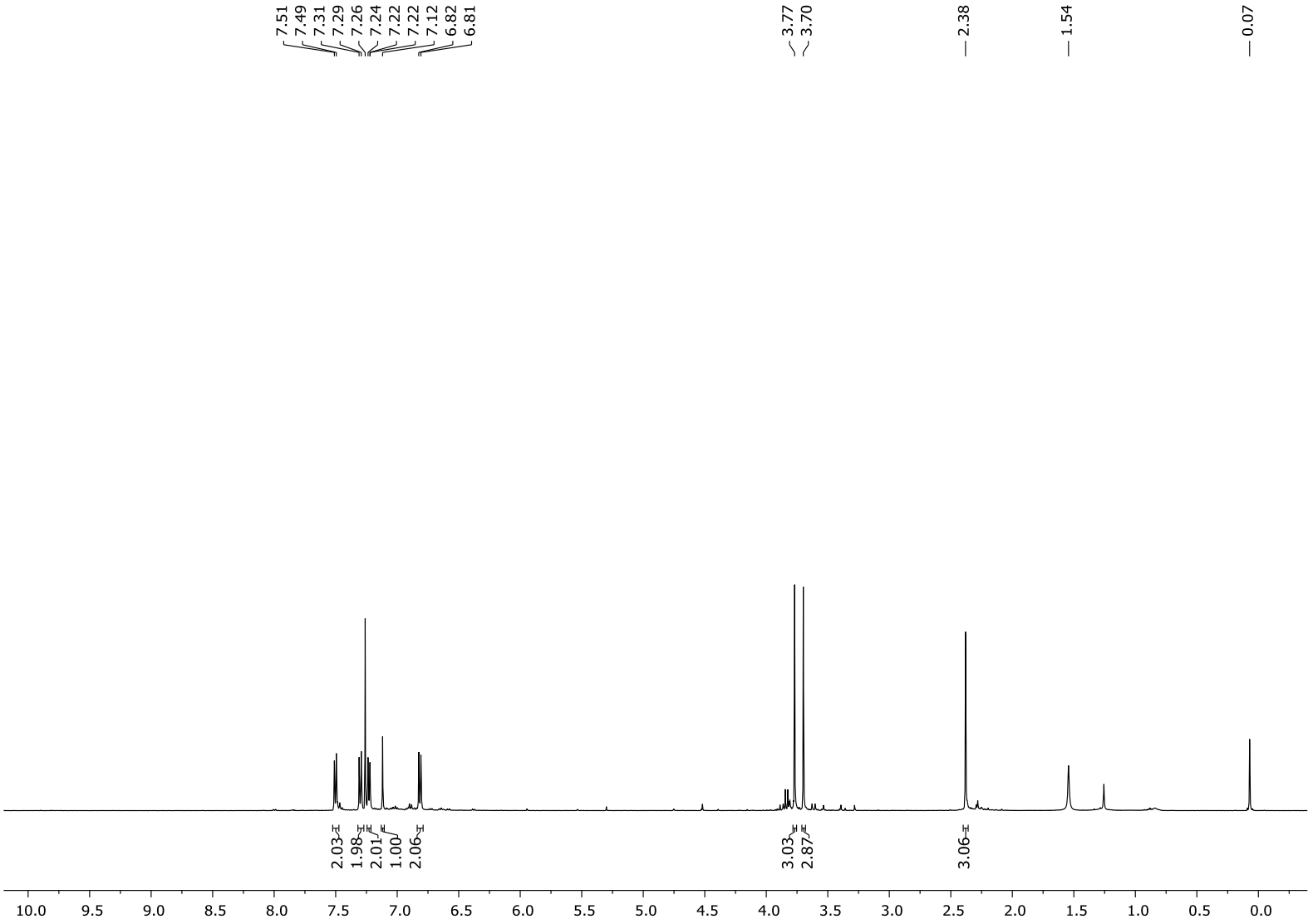


Figure S84: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3w**.

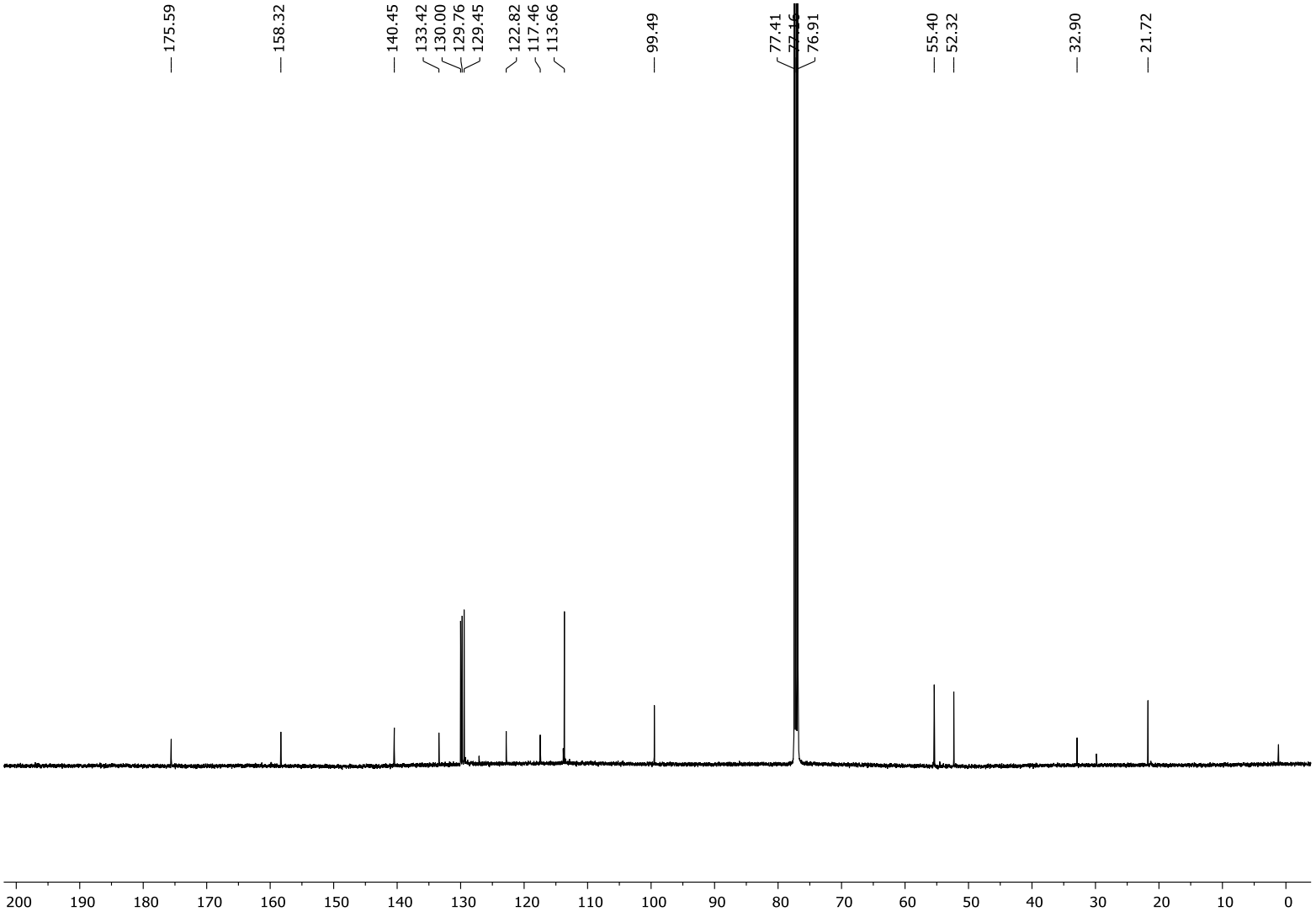


Figure S85: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3x**.

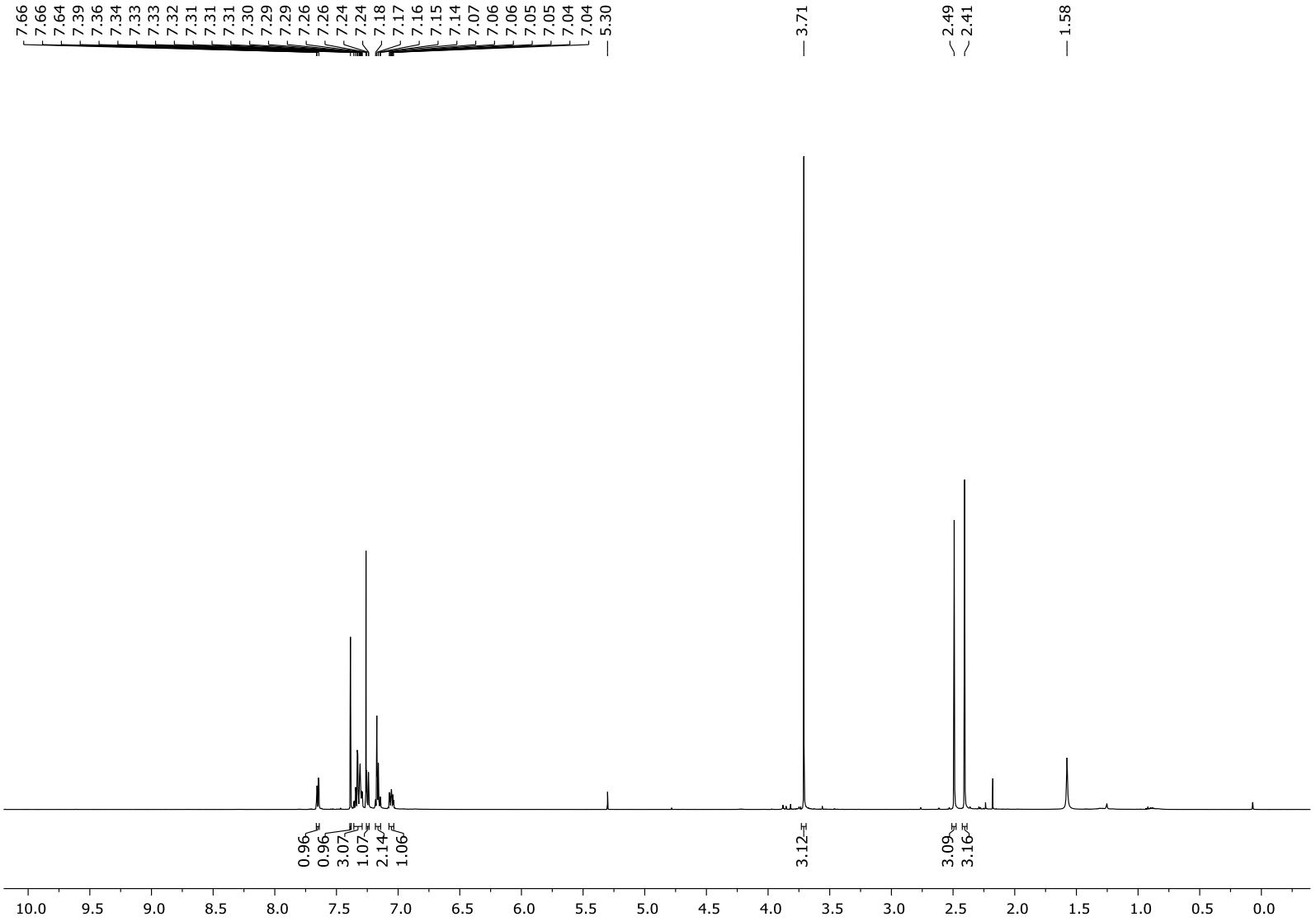


Figure S86: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3x**.

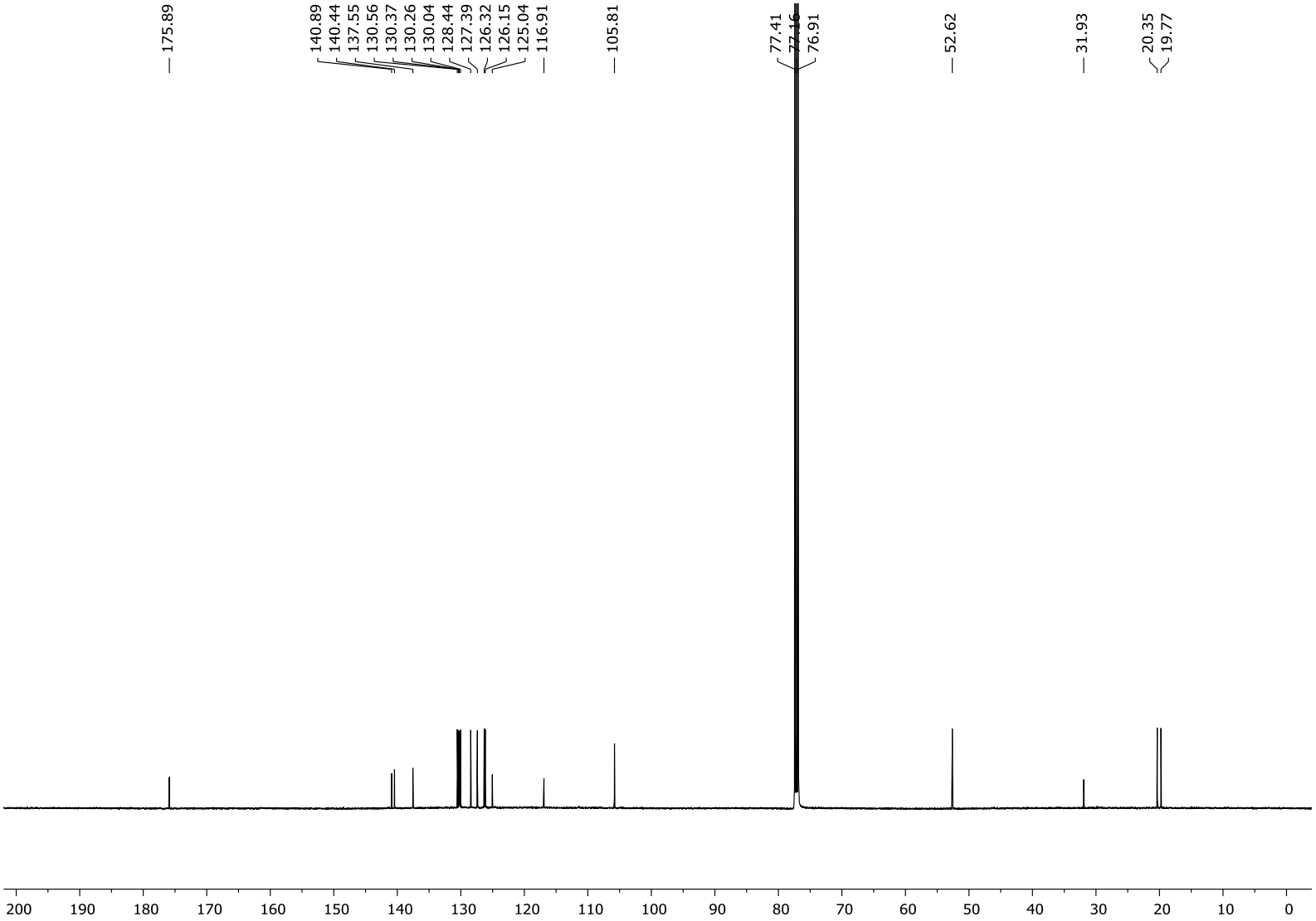


Figure S87: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3y**.

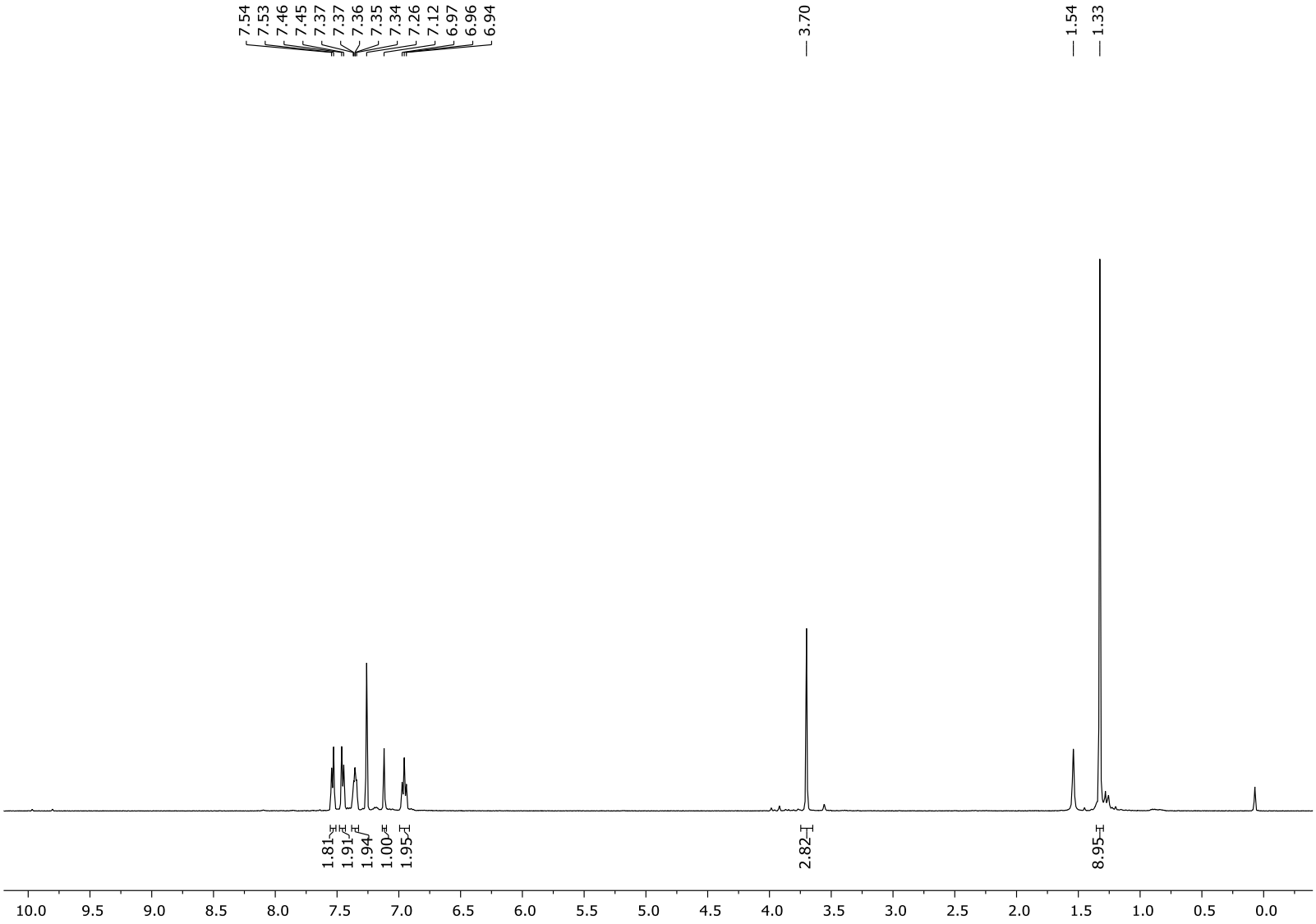


Figure S88: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3y**.

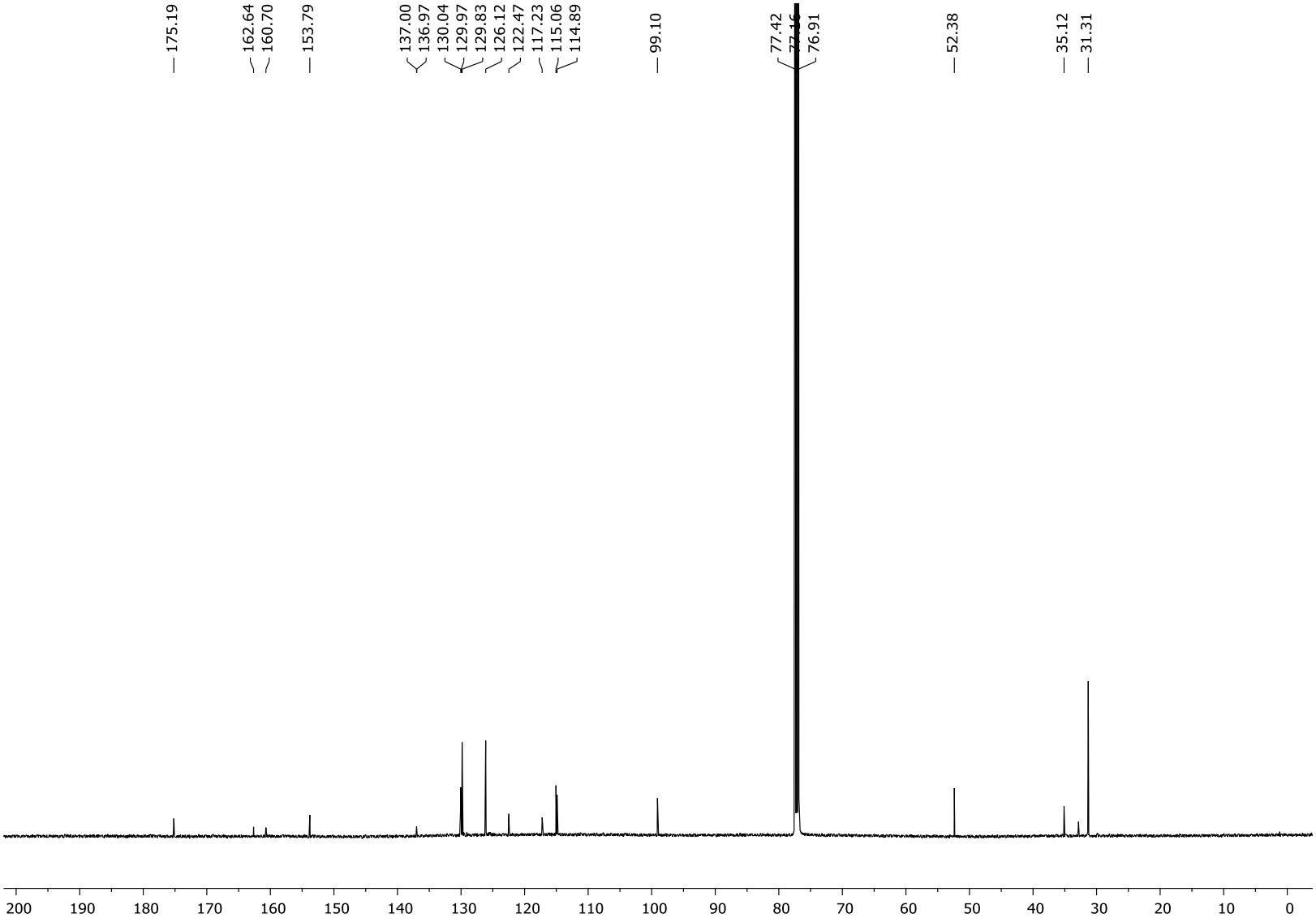


Figure S89: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3y**.

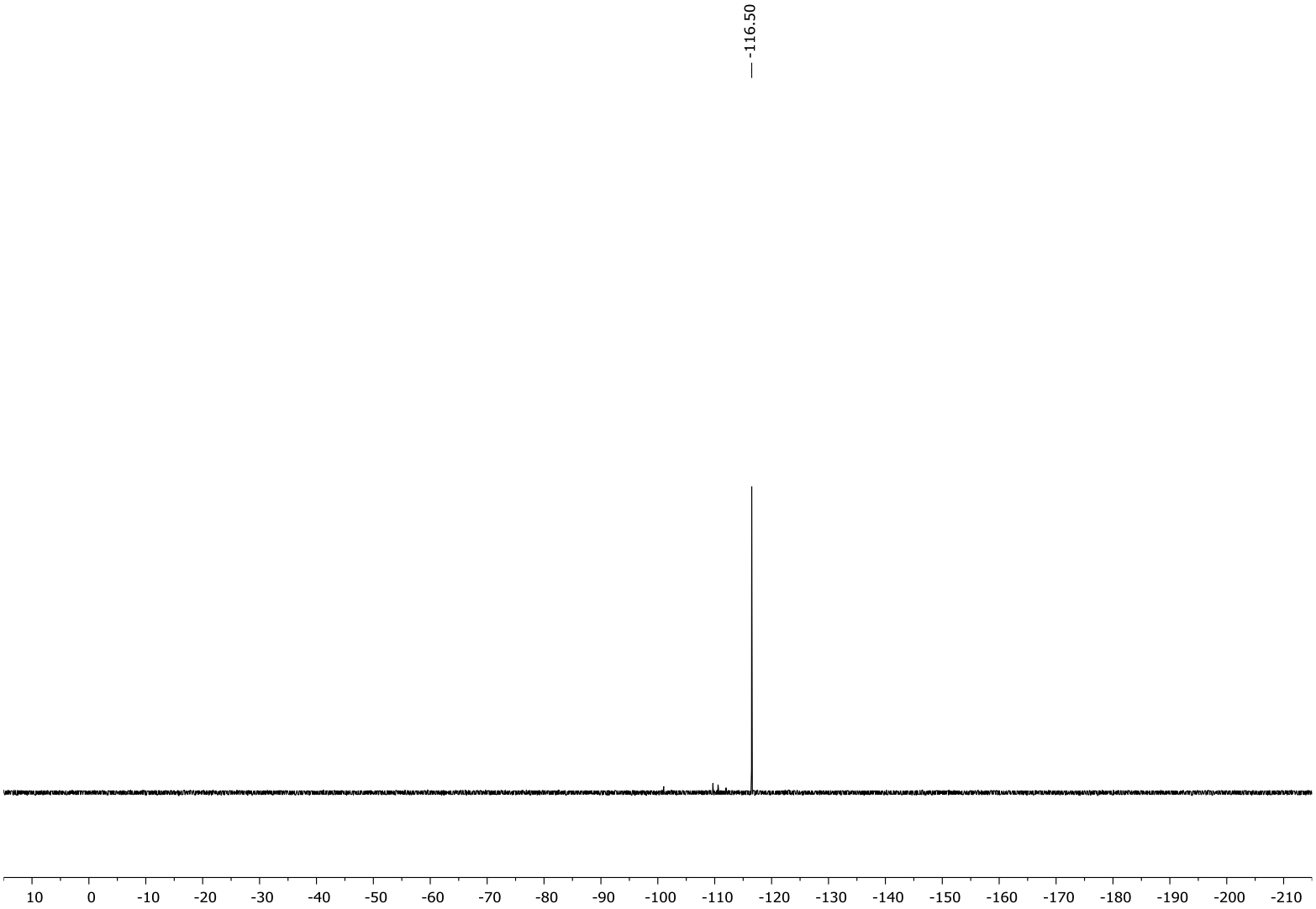


Figure S90: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) spectrum of **3z**.

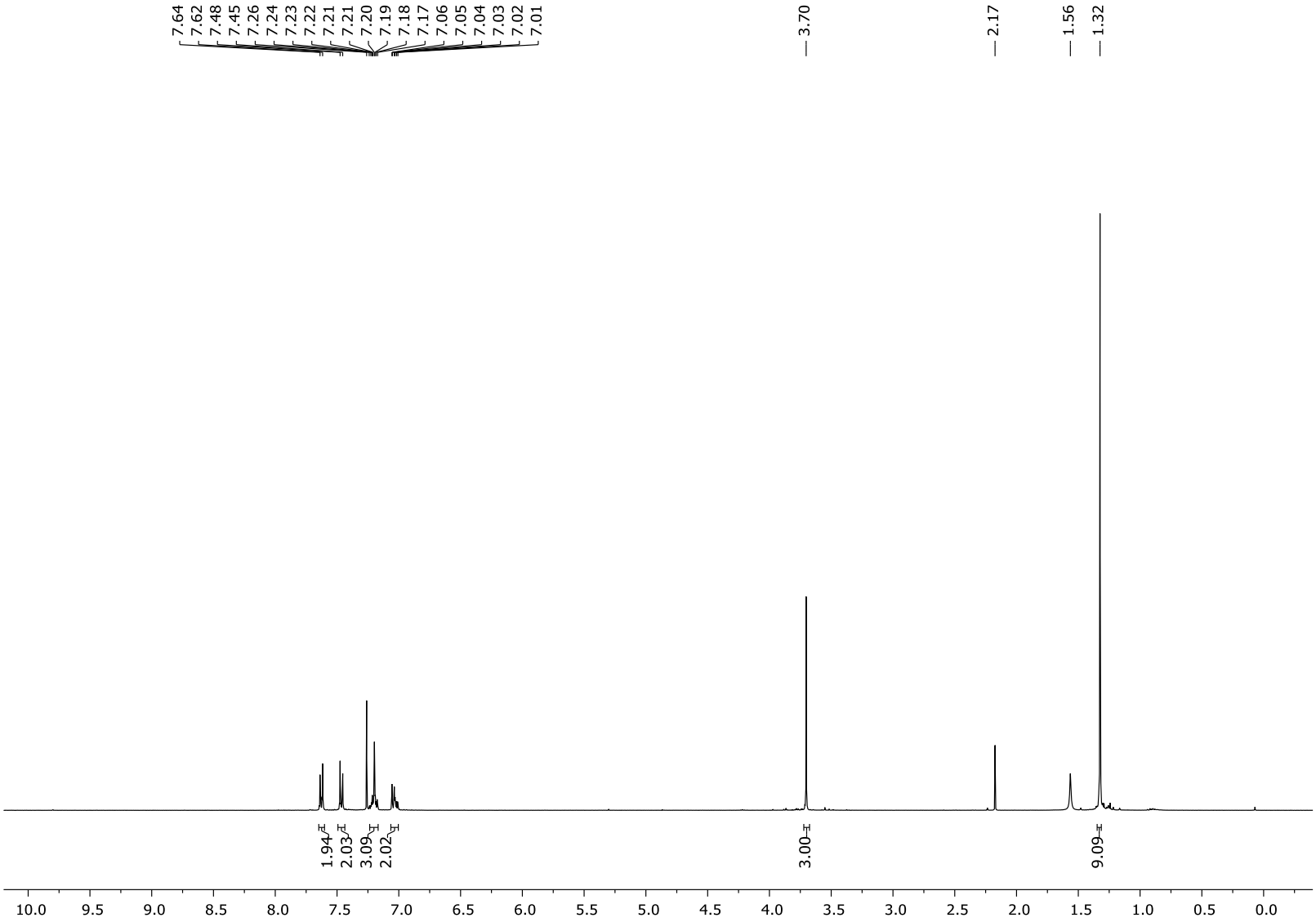


Figure S91: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **3z**.

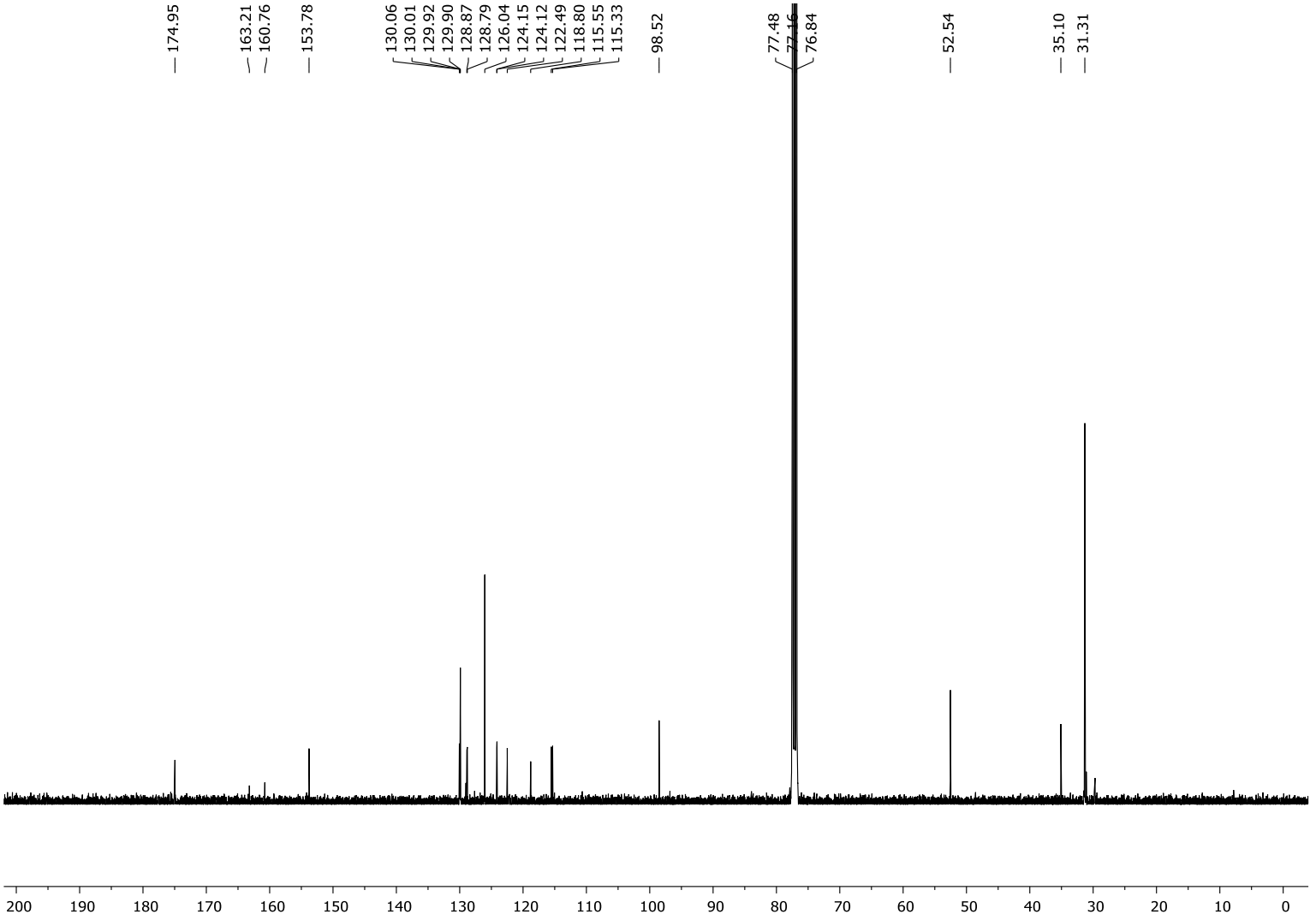


Figure S92: **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) spectrum of **3z**.

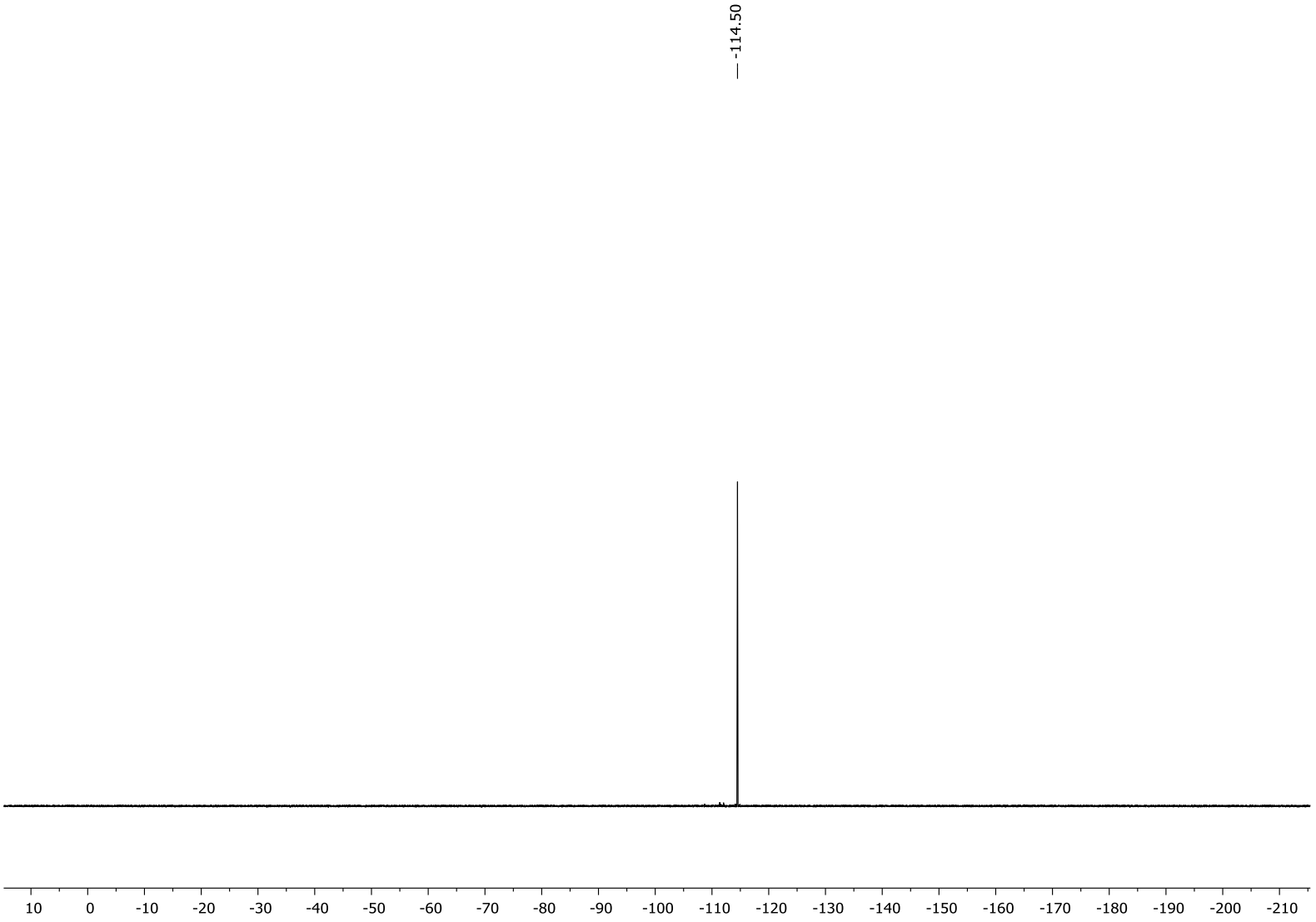


Figure S93: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3aa**.

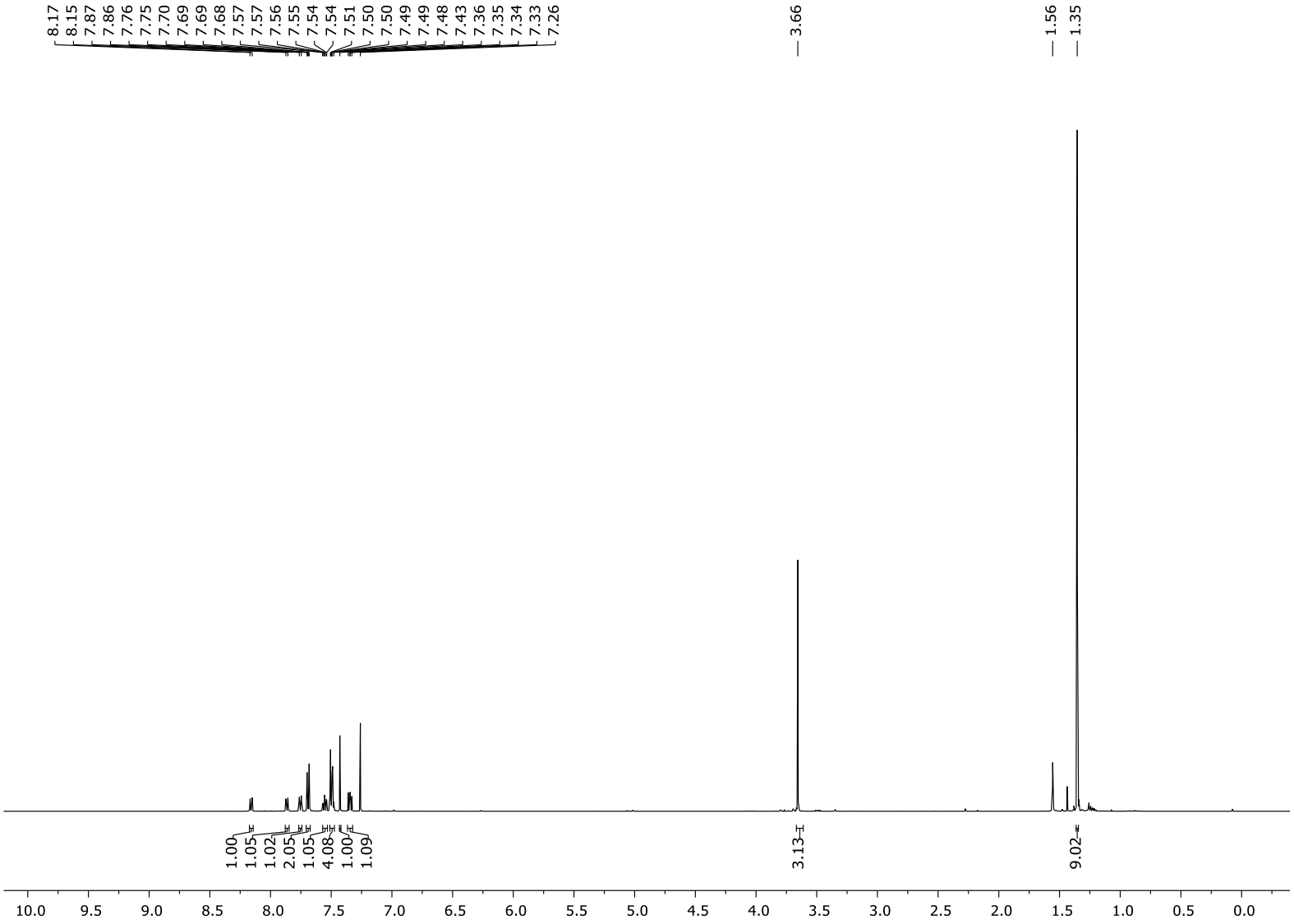


Figure S94: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3aa**.

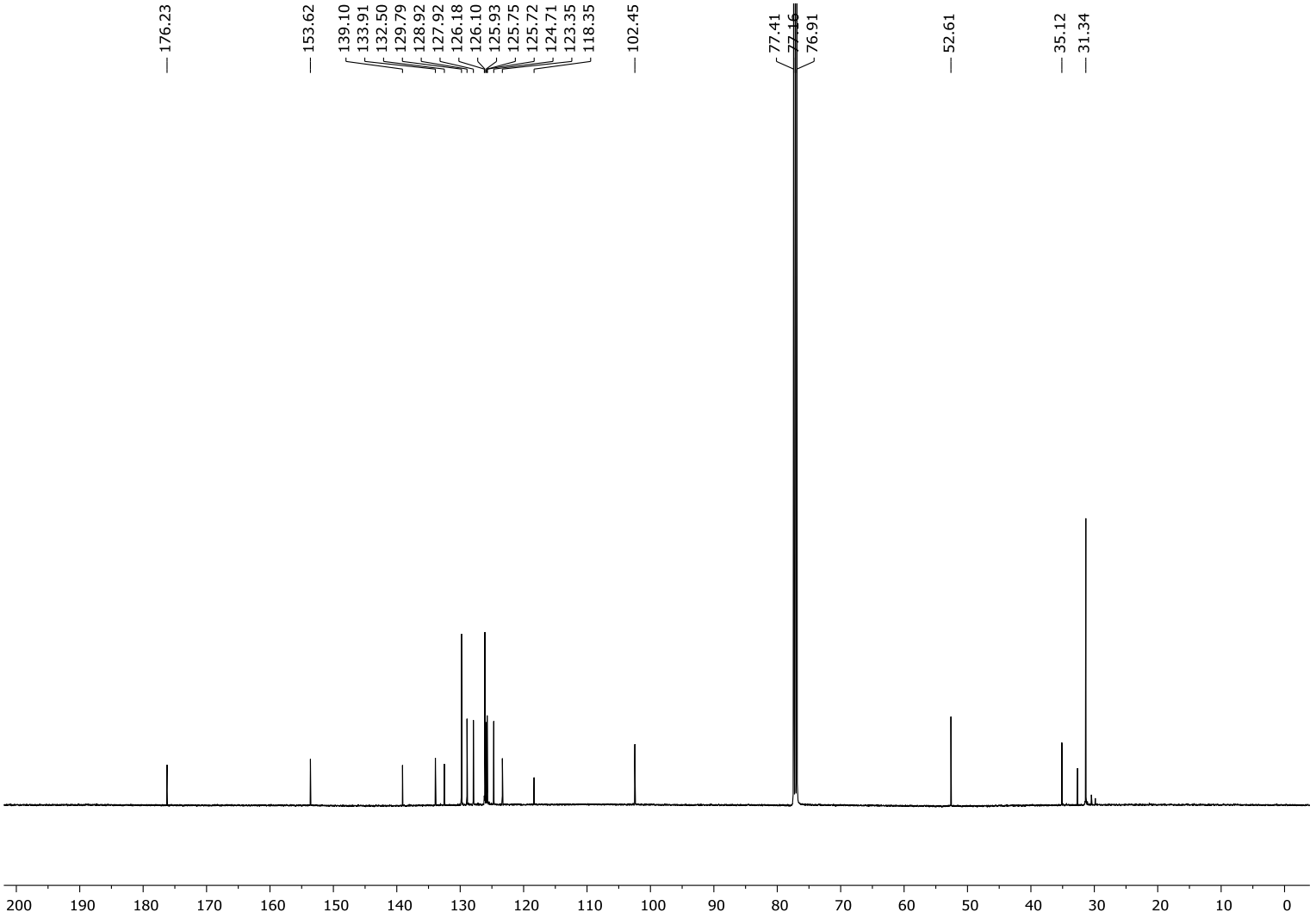


Figure S95: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3ab**.

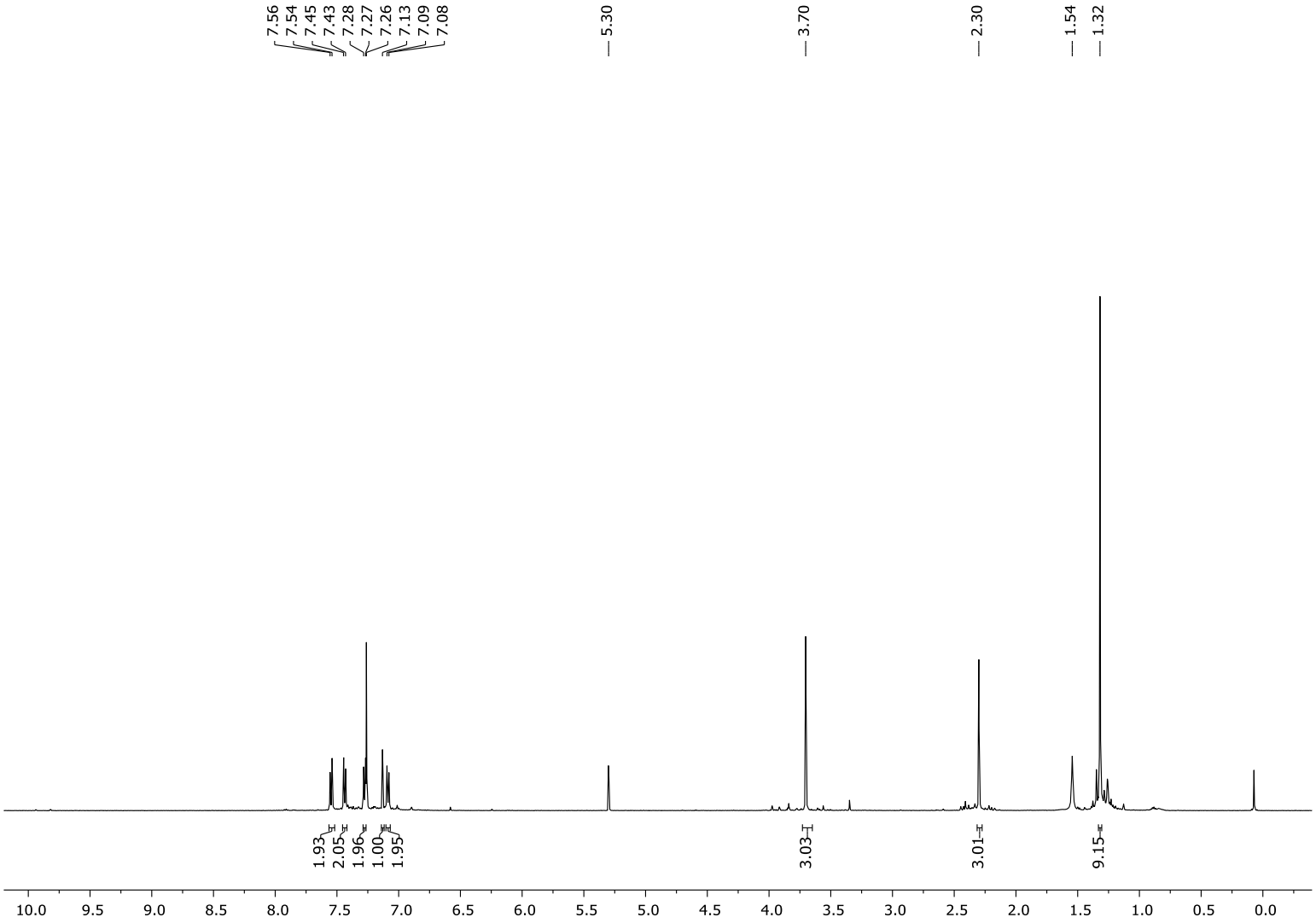


Figure S96: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3ab**.

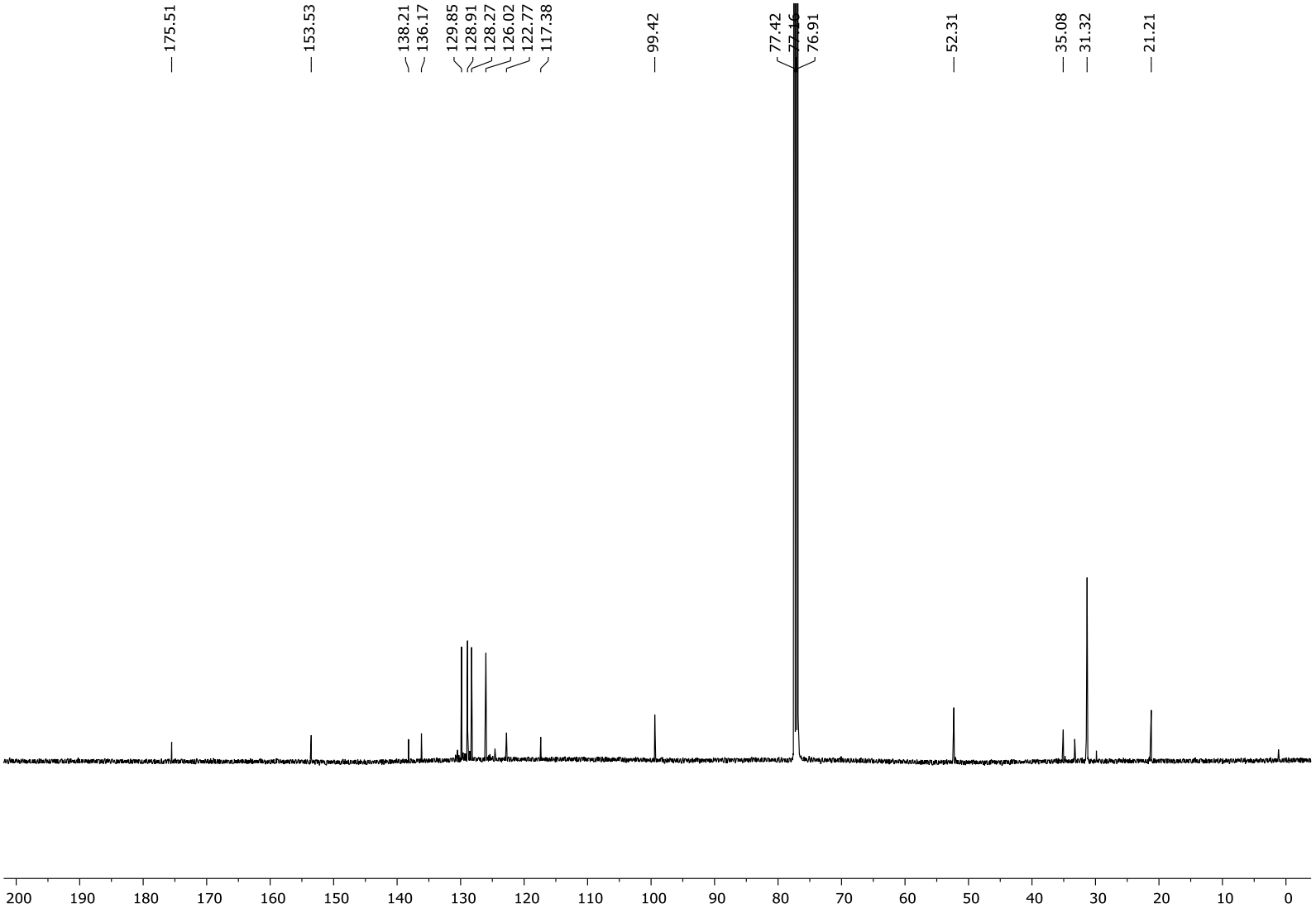


Figure S97: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) spectrum of **3ac**.

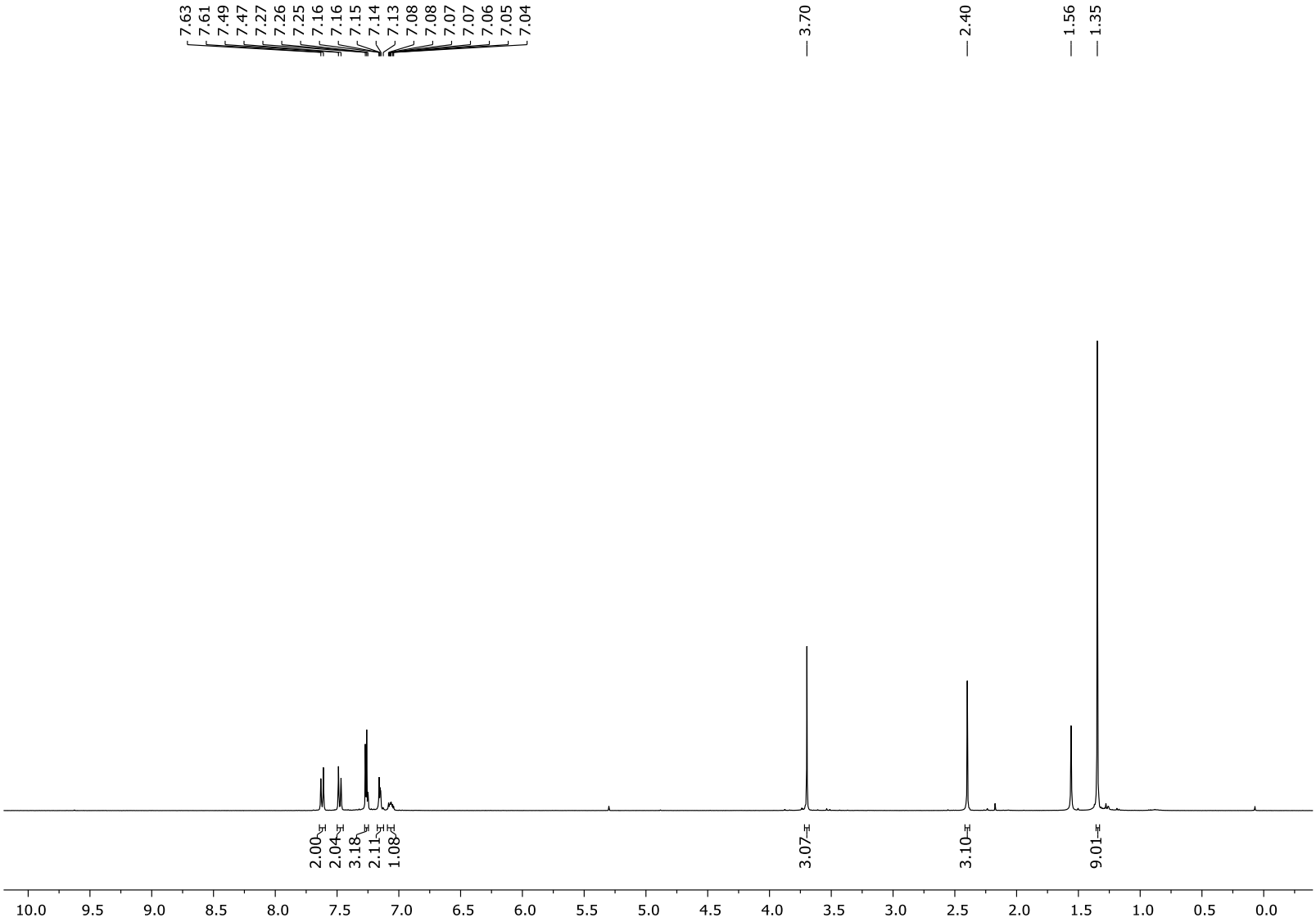


Figure S98: **^{13}C NMR** ($CDCl_3$, 298 K) spectrum of **3ac**.

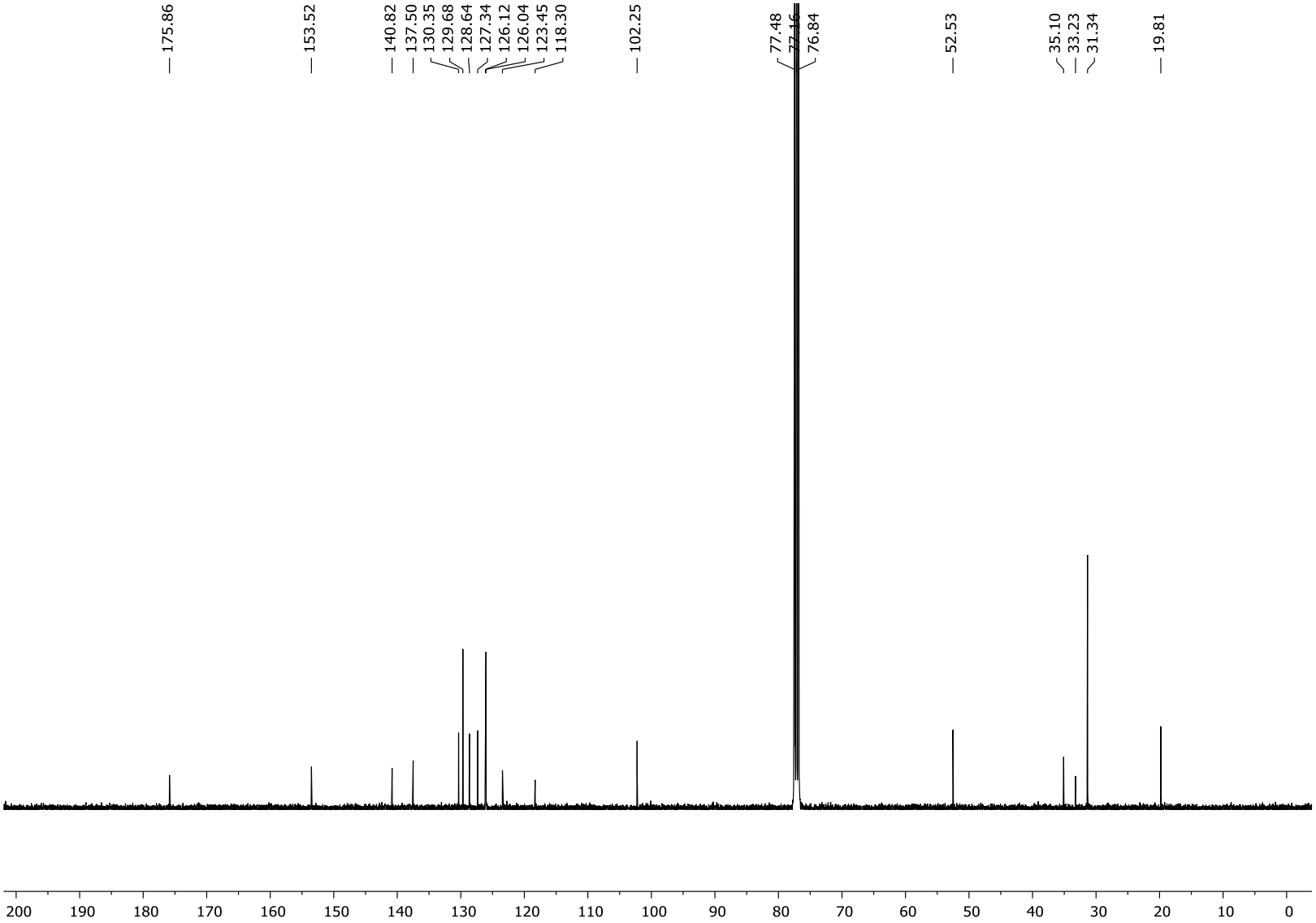


Figure S99: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3ad**.

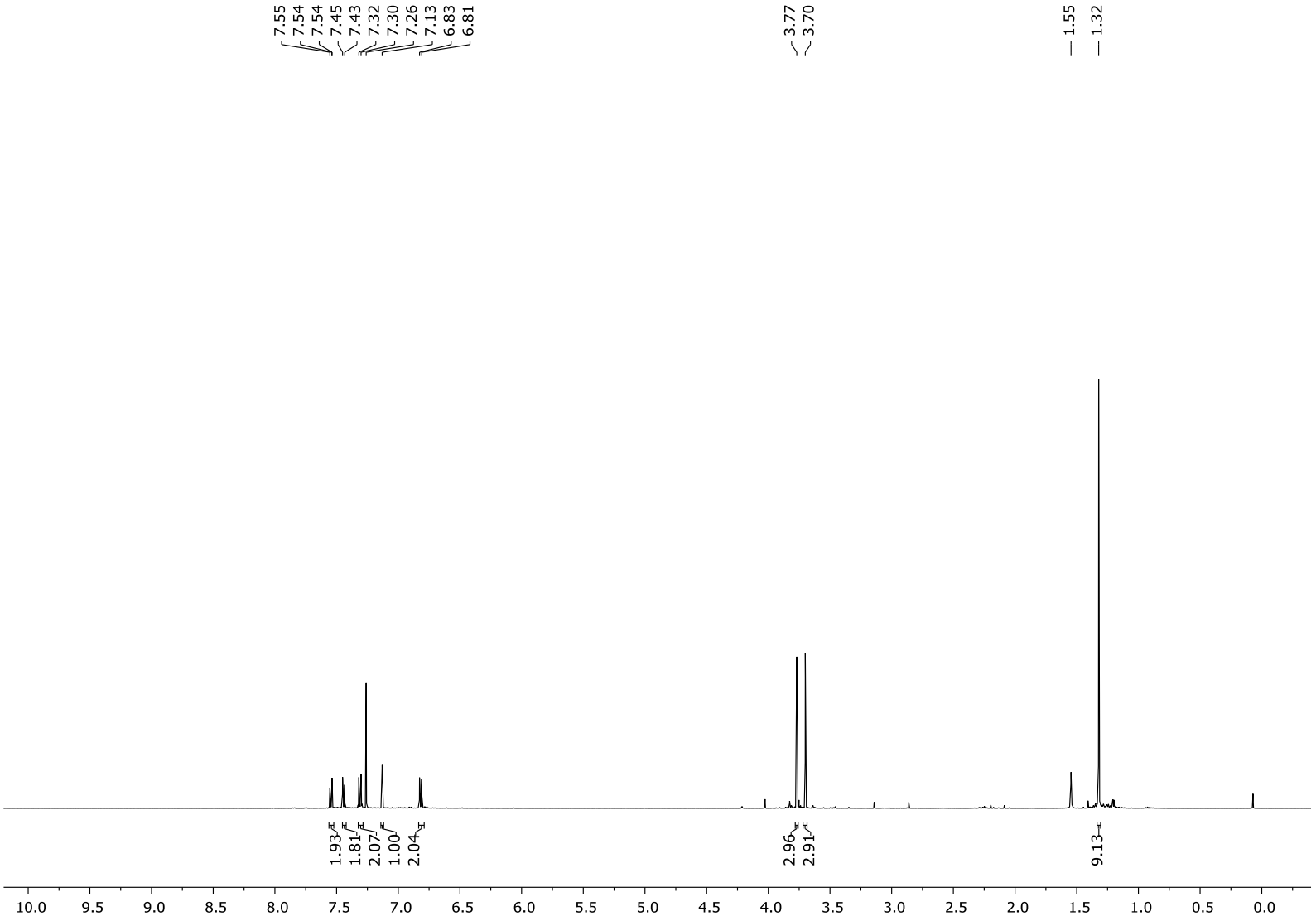


Figure S100: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3ad**.

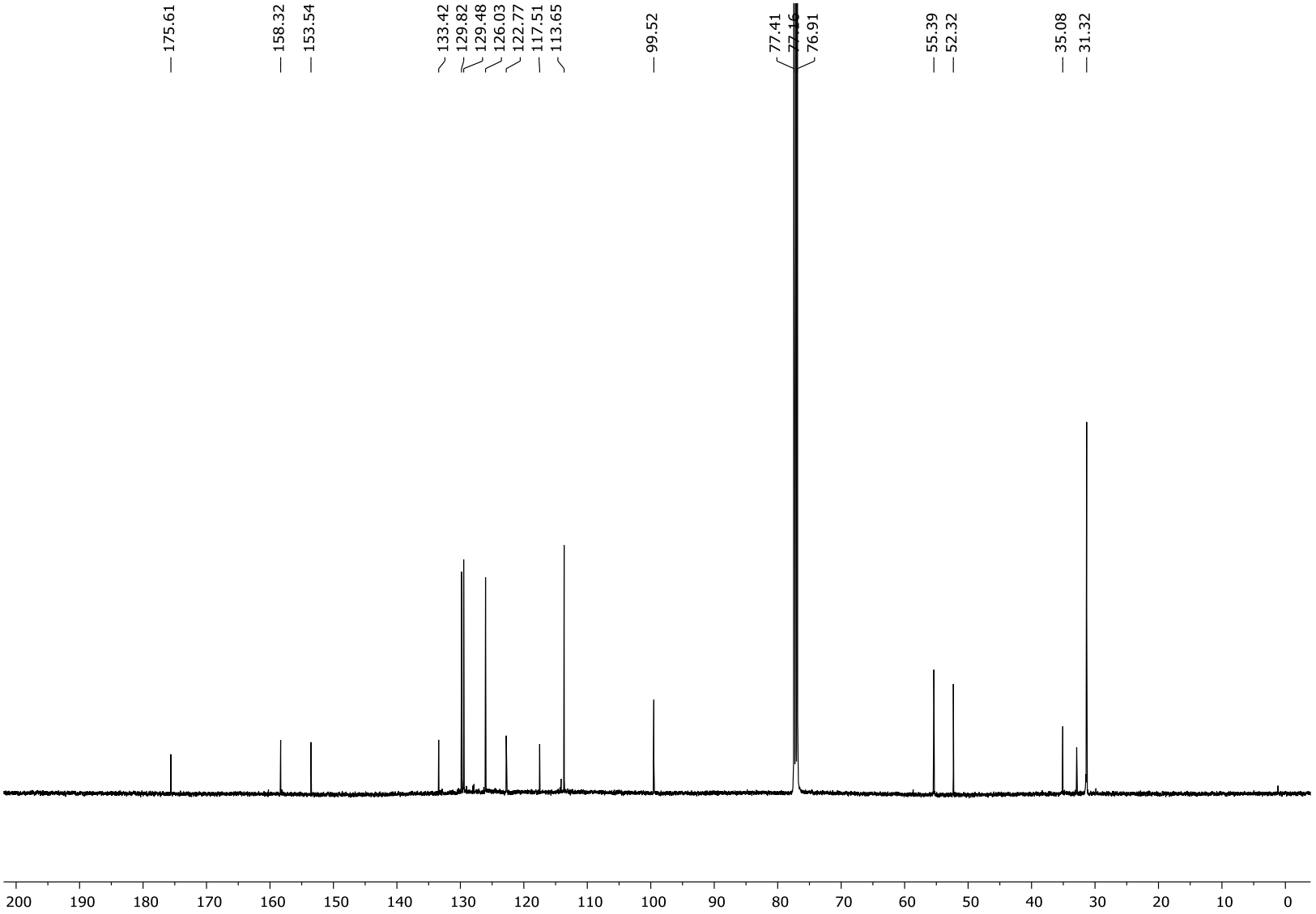


Figure S101: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3ae**.

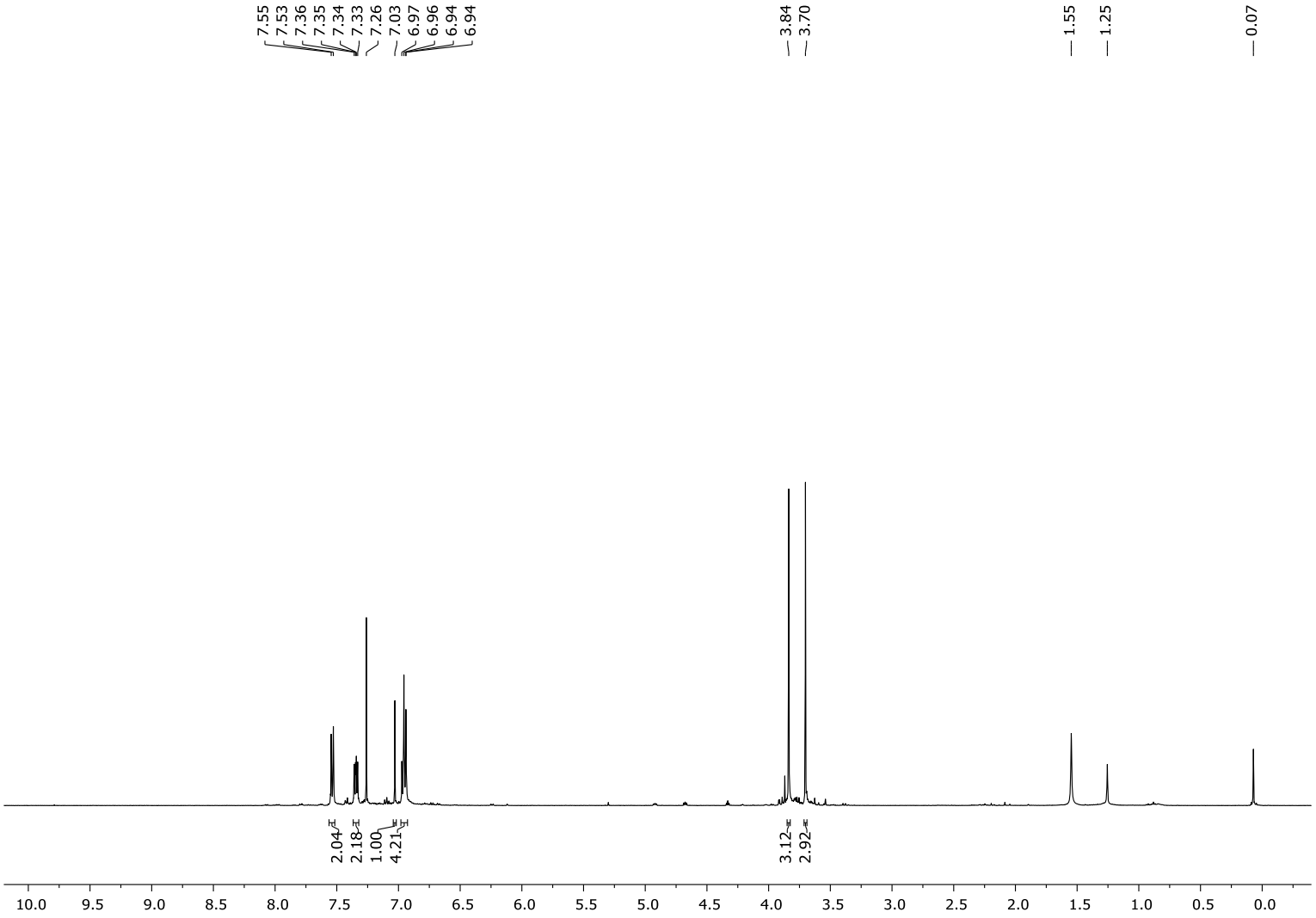


Figure S102: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3ae**.

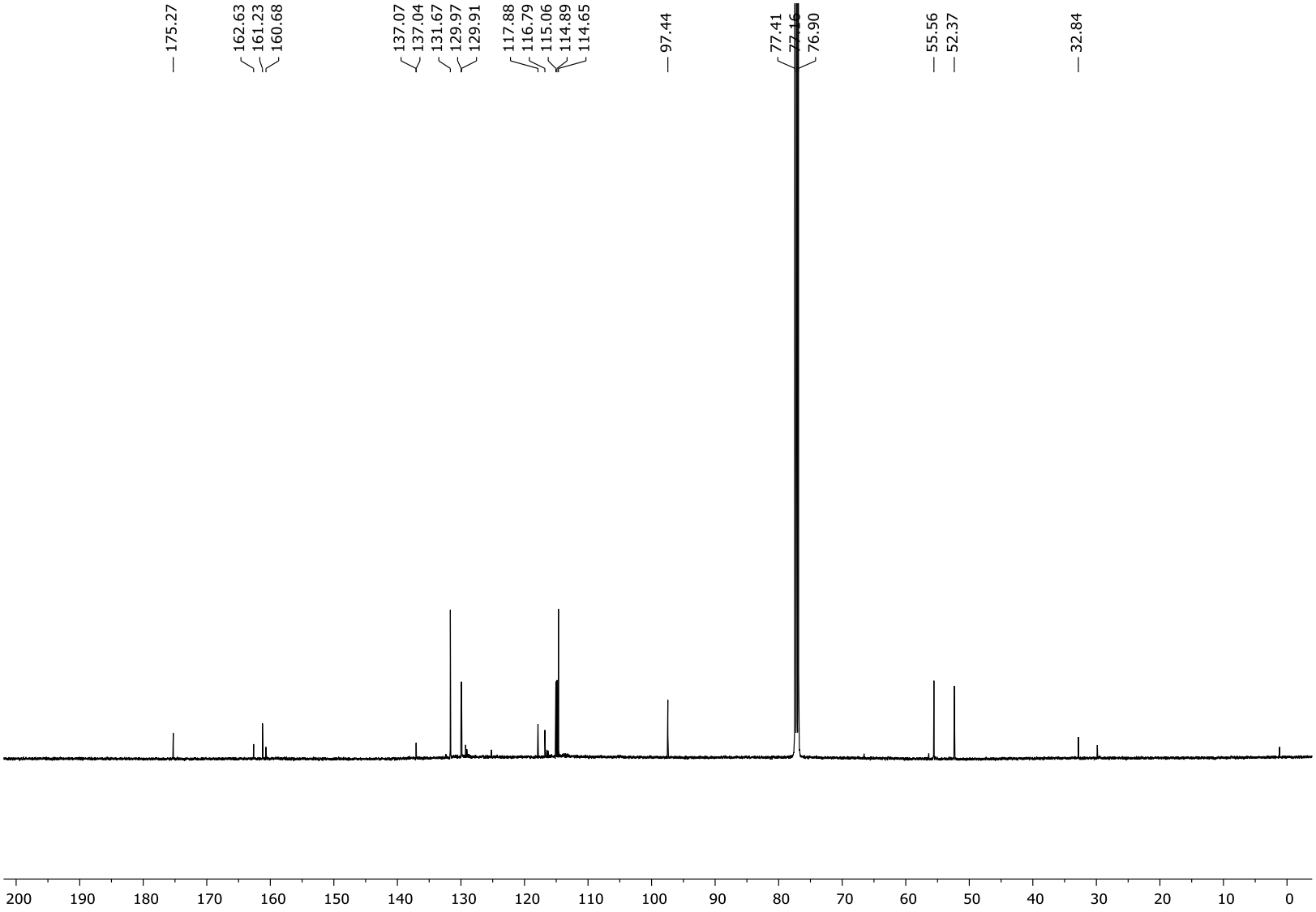


Figure S103: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3ae**.

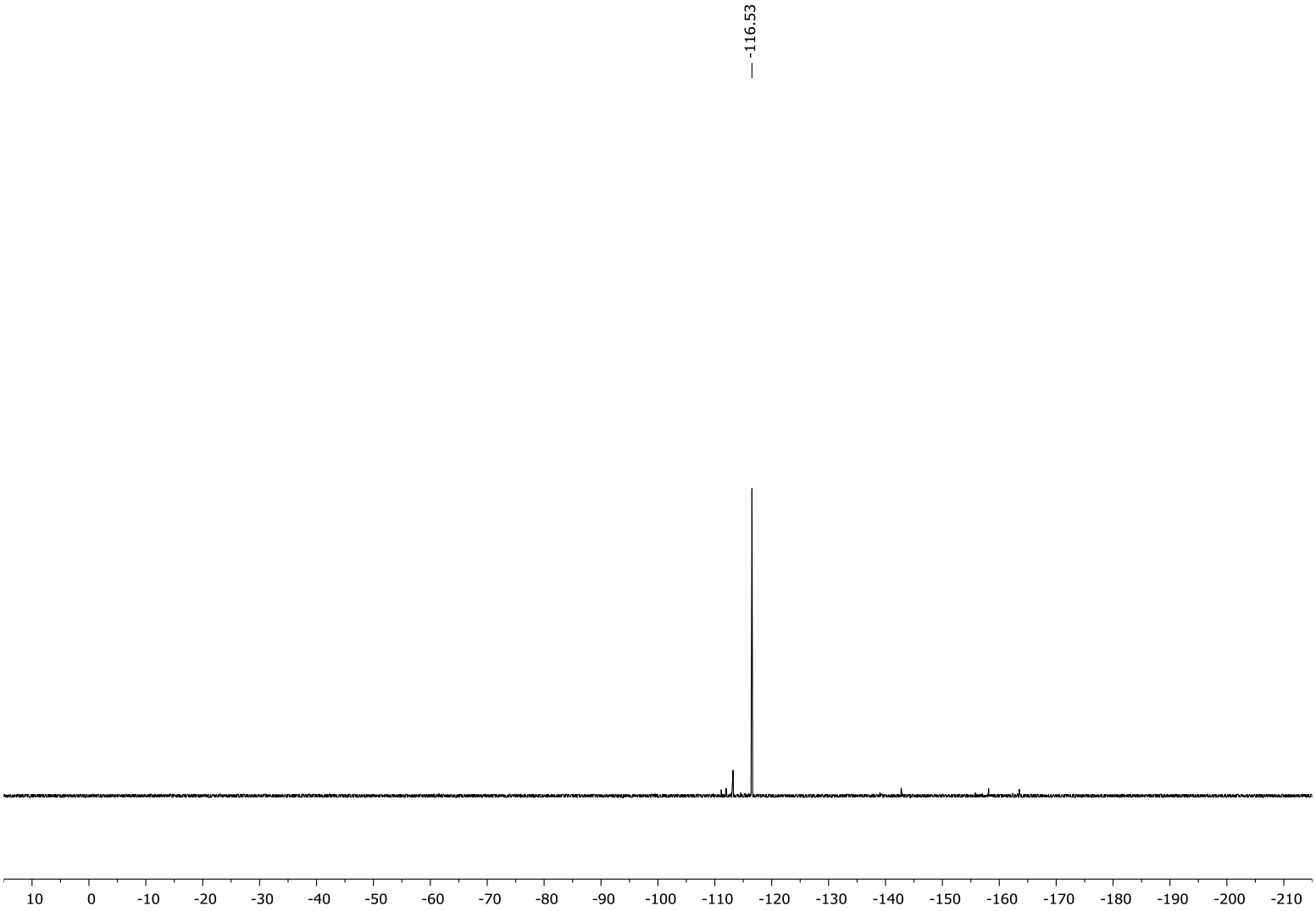


Figure S104: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3af**.

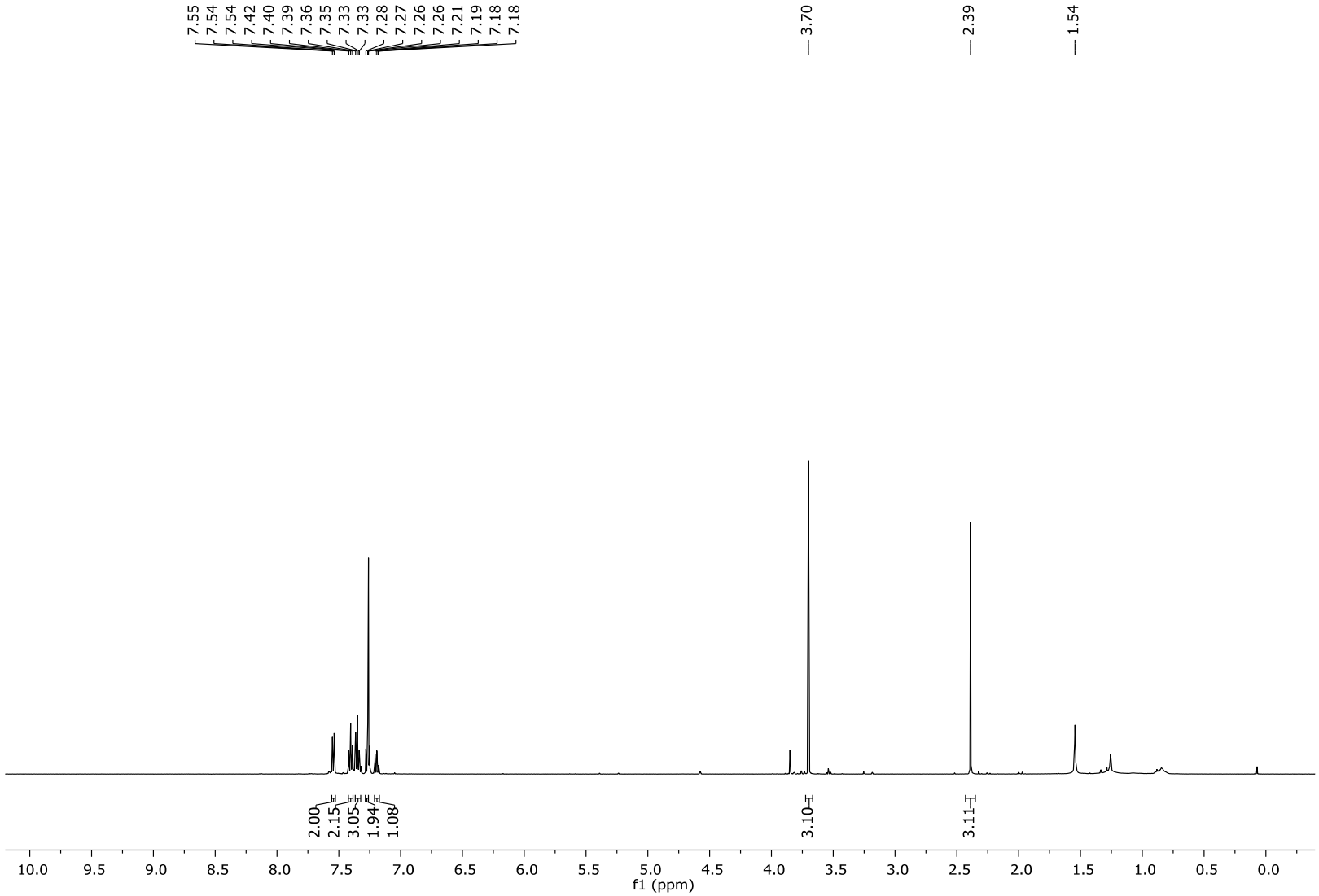


Figure S105: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3af**.

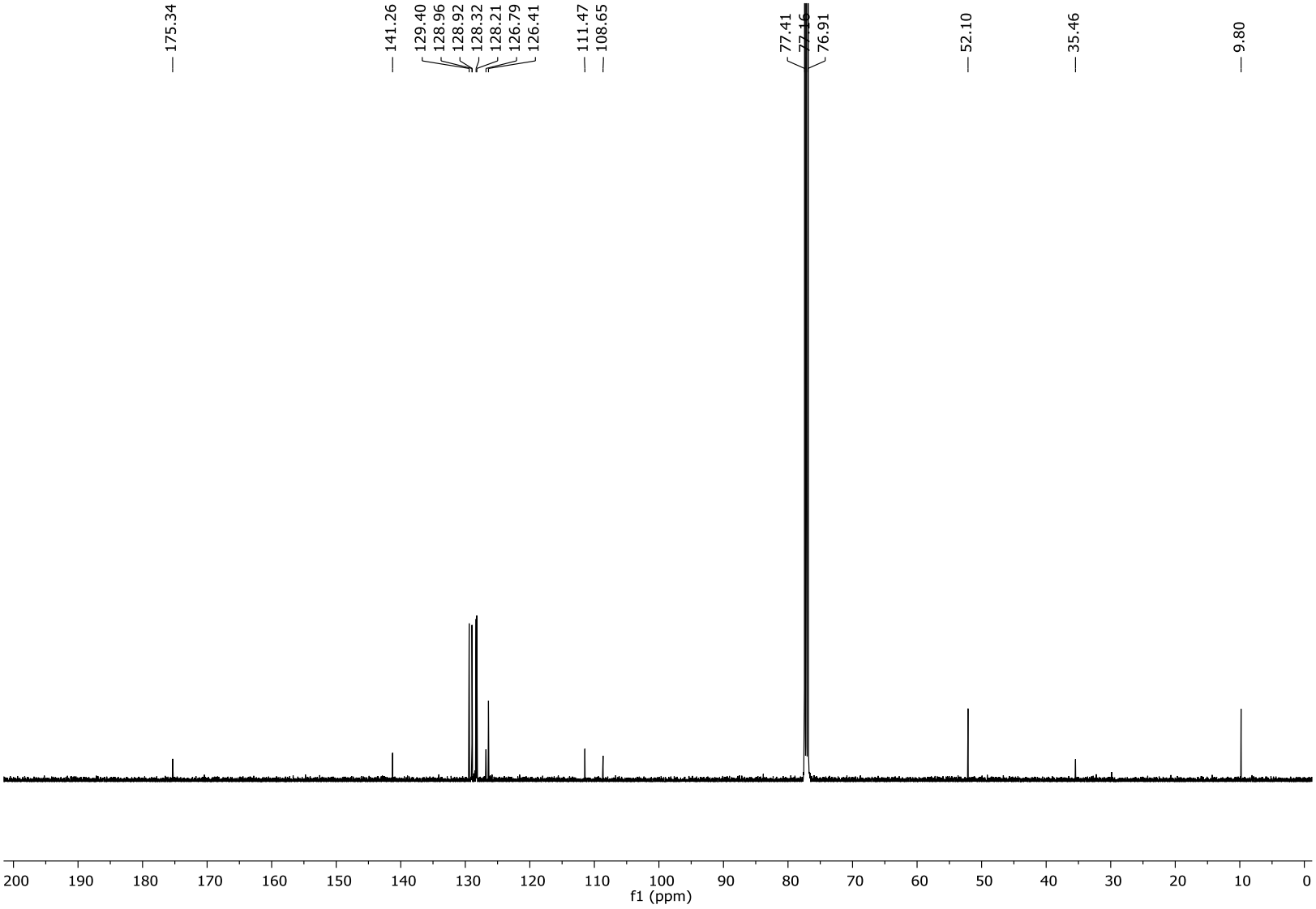


Figure S106: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3ag**.

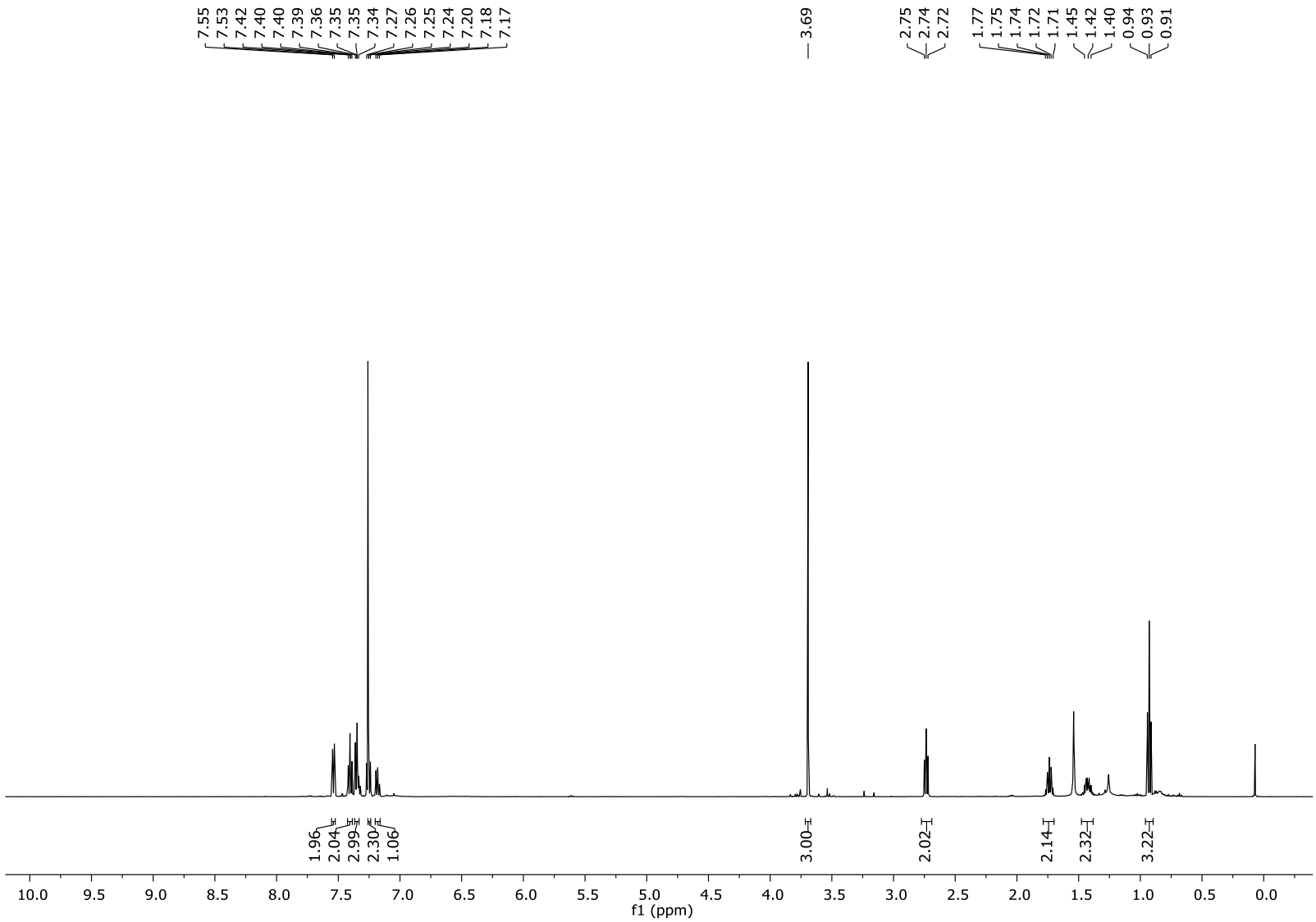


Figure S107: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3ag**.

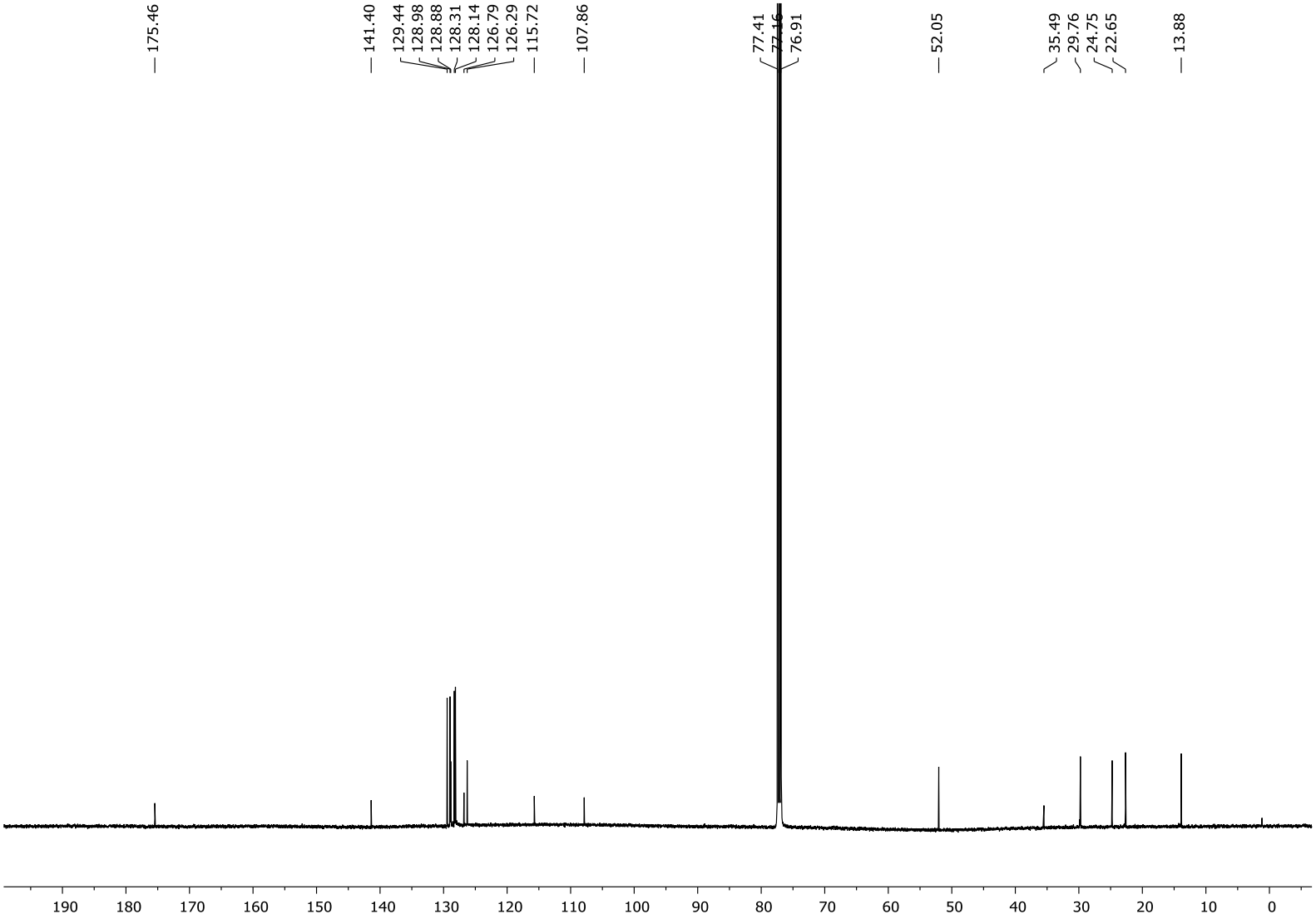


Figure S108: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3ah**.

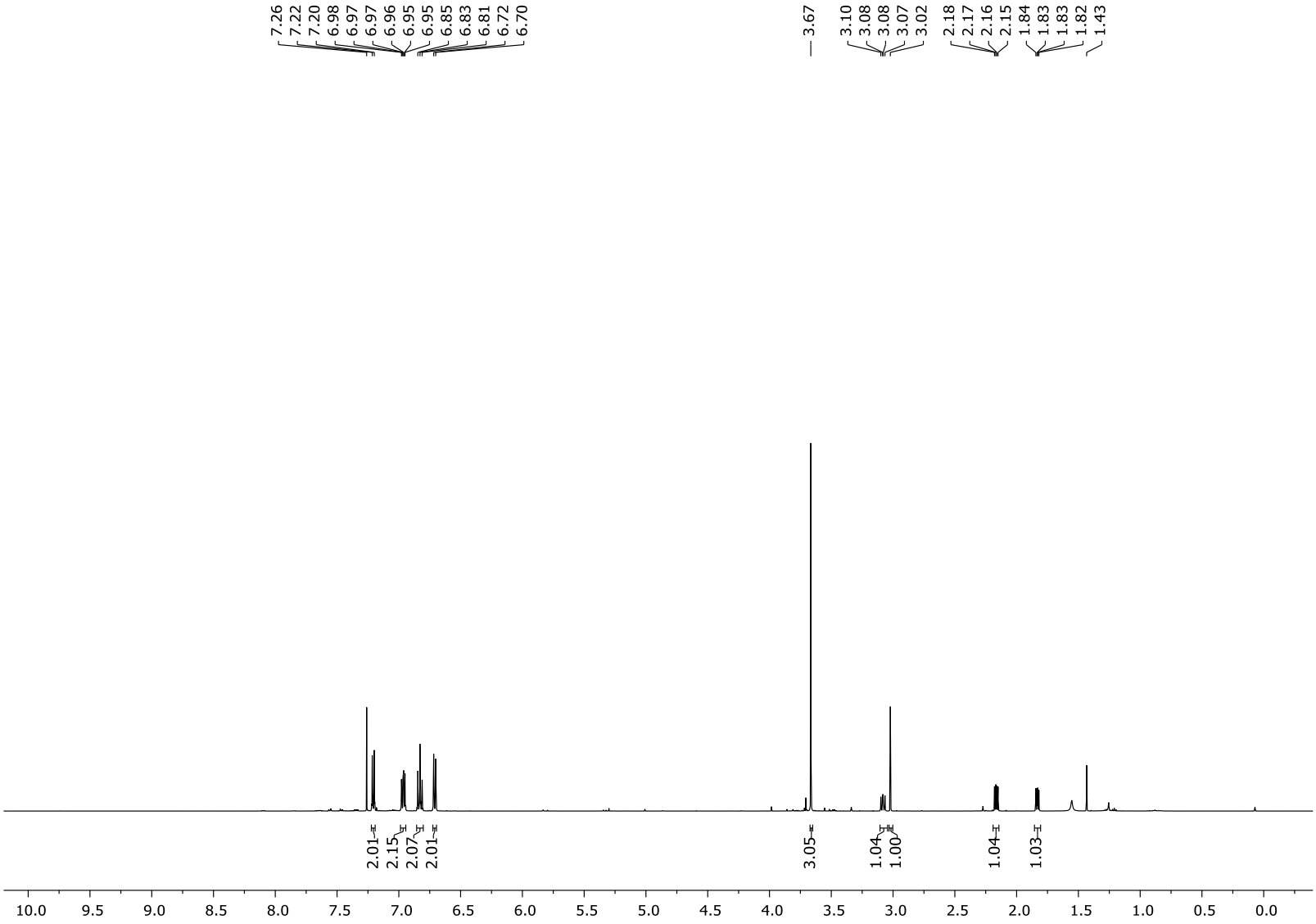


Figure S109: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3ah**.

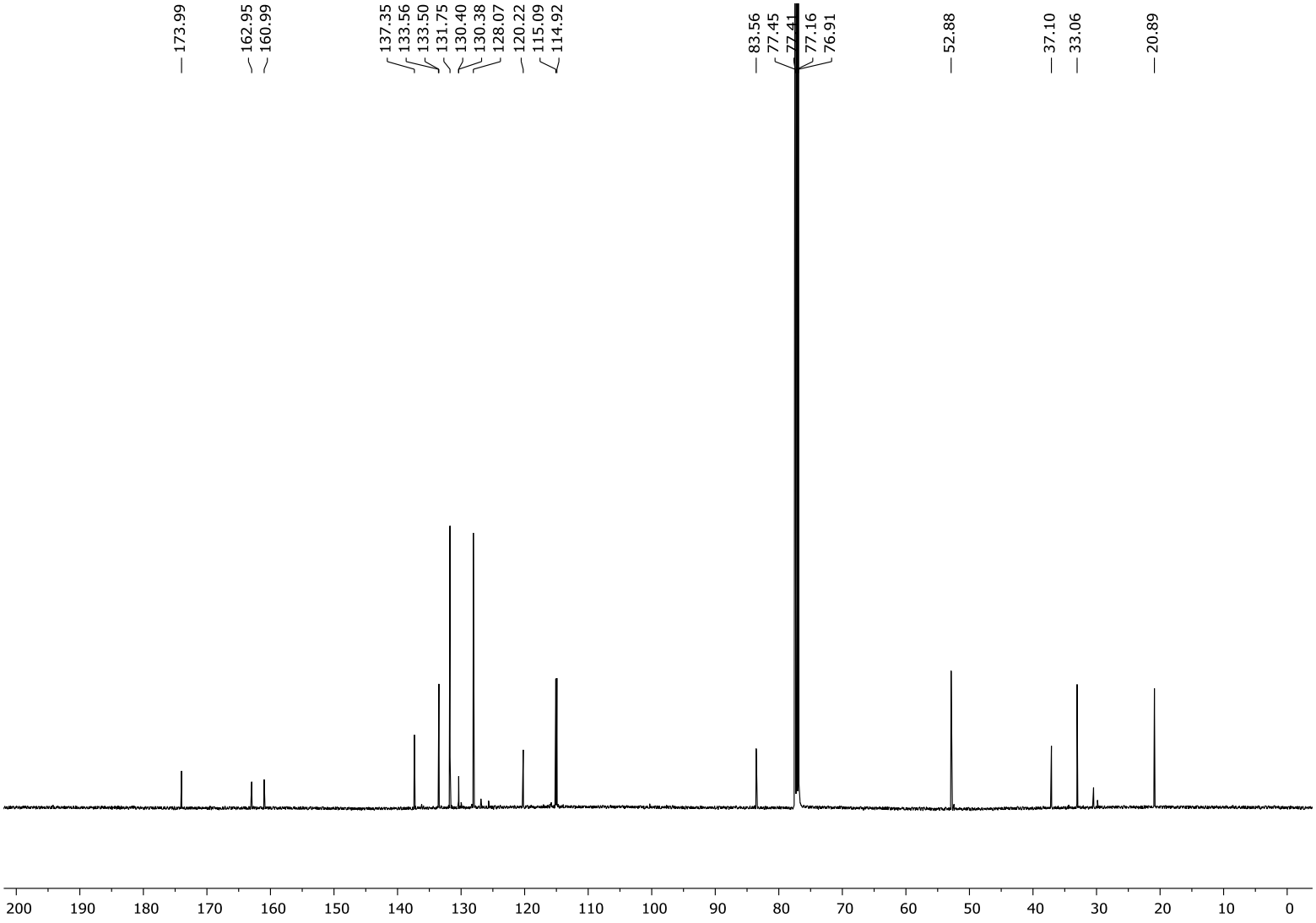


Figure S110: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3ah**.

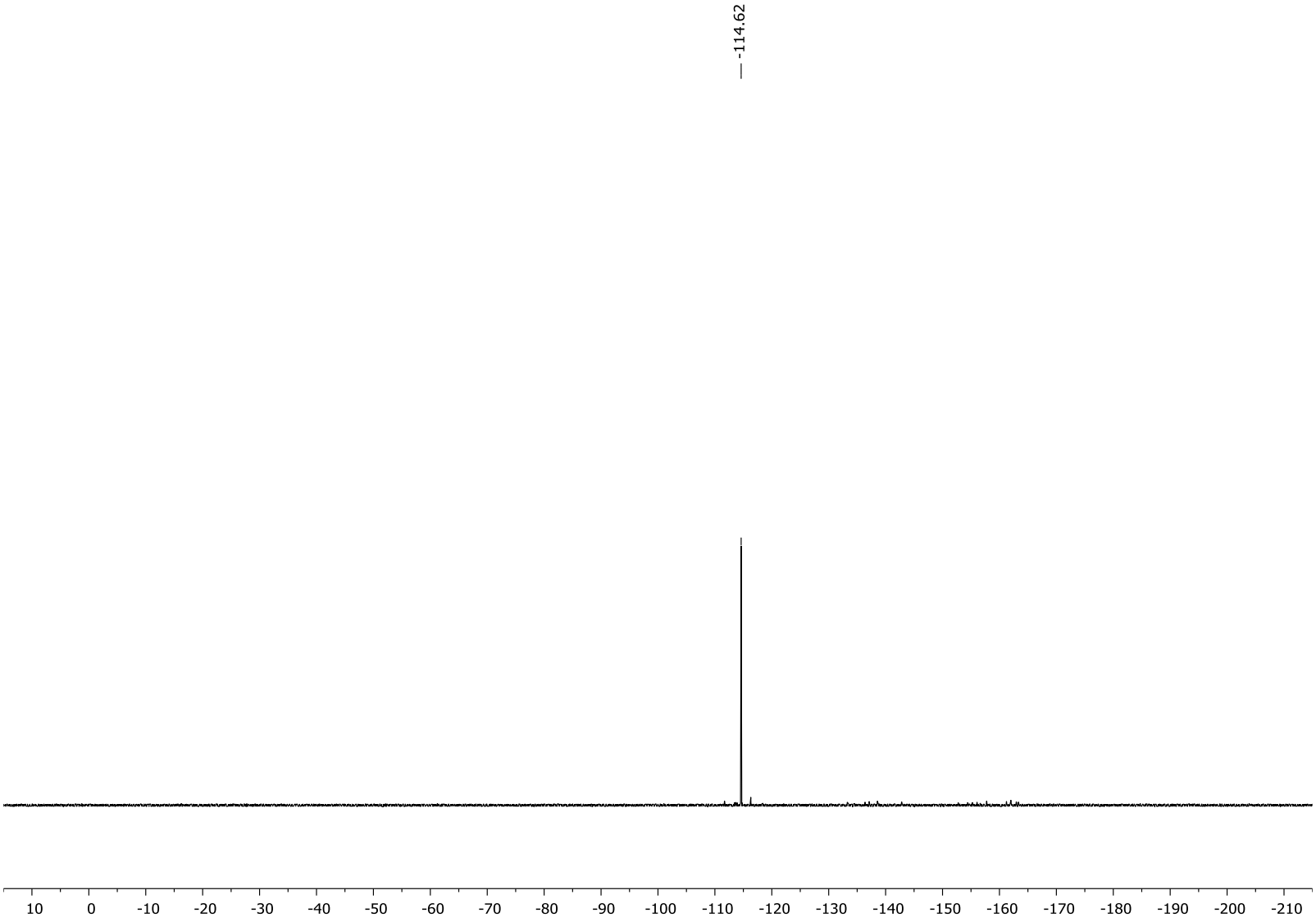


Figure S111: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3ai**.

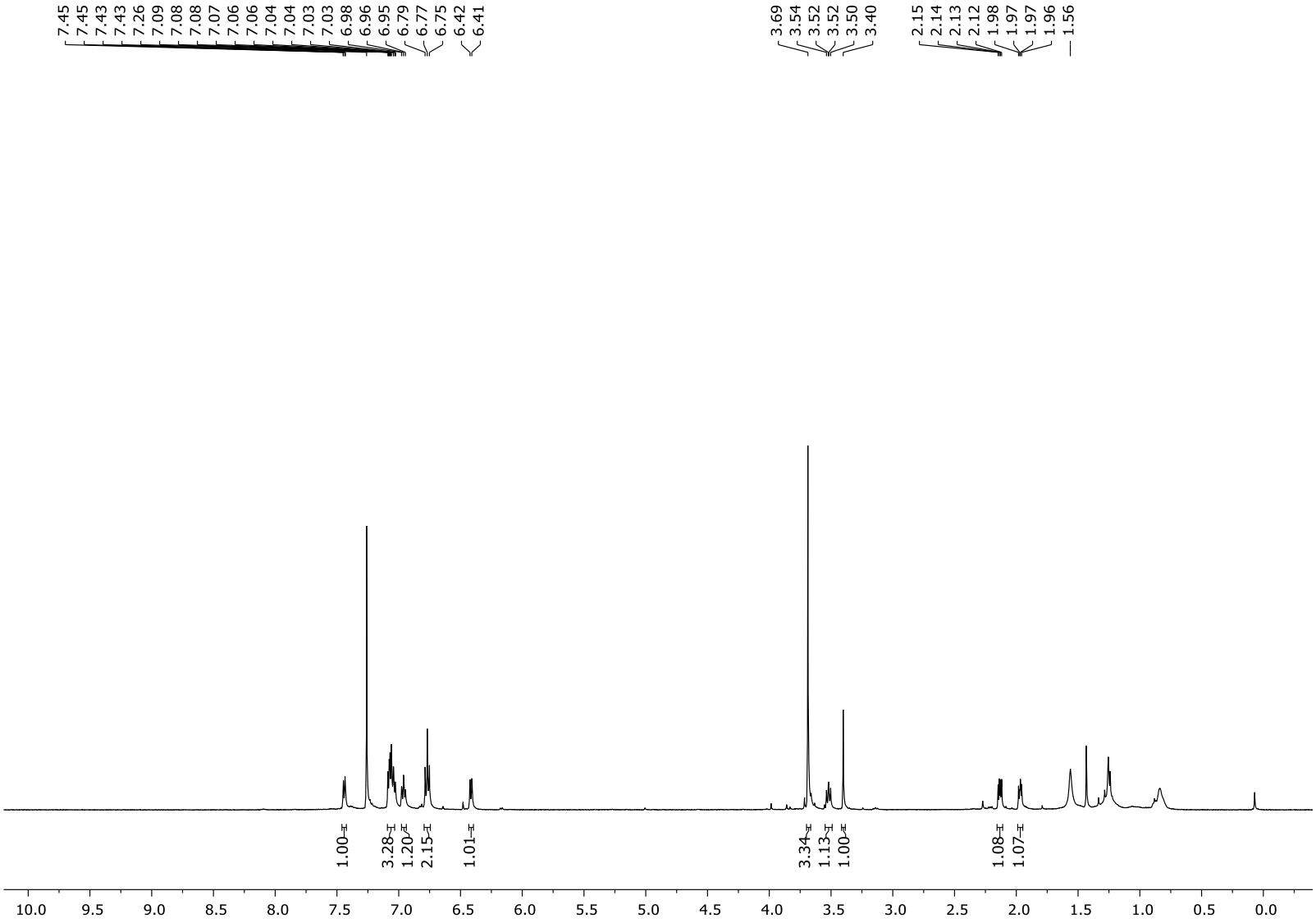


Figure S112: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3ai**.

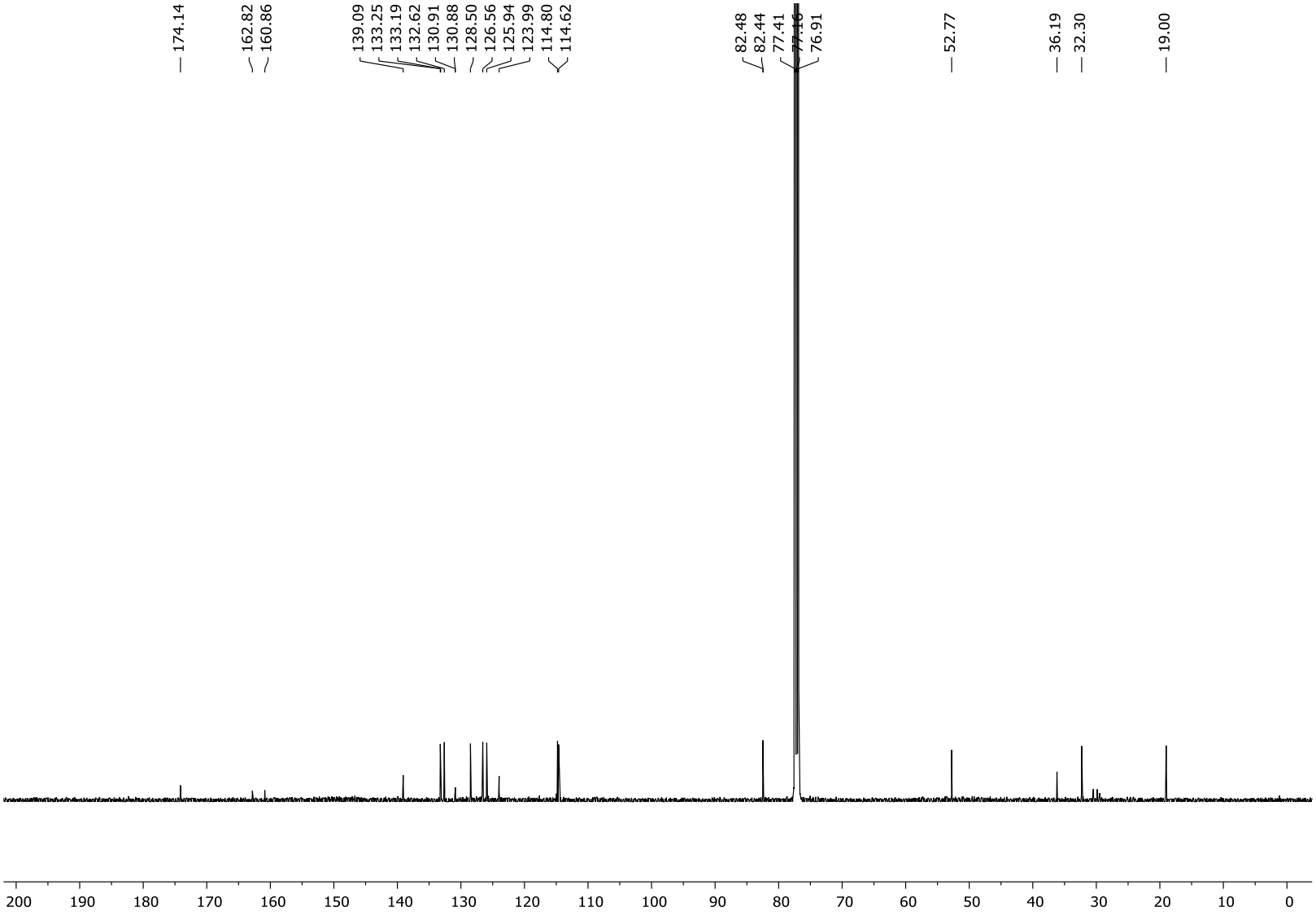


Figure S113: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **3ai**.

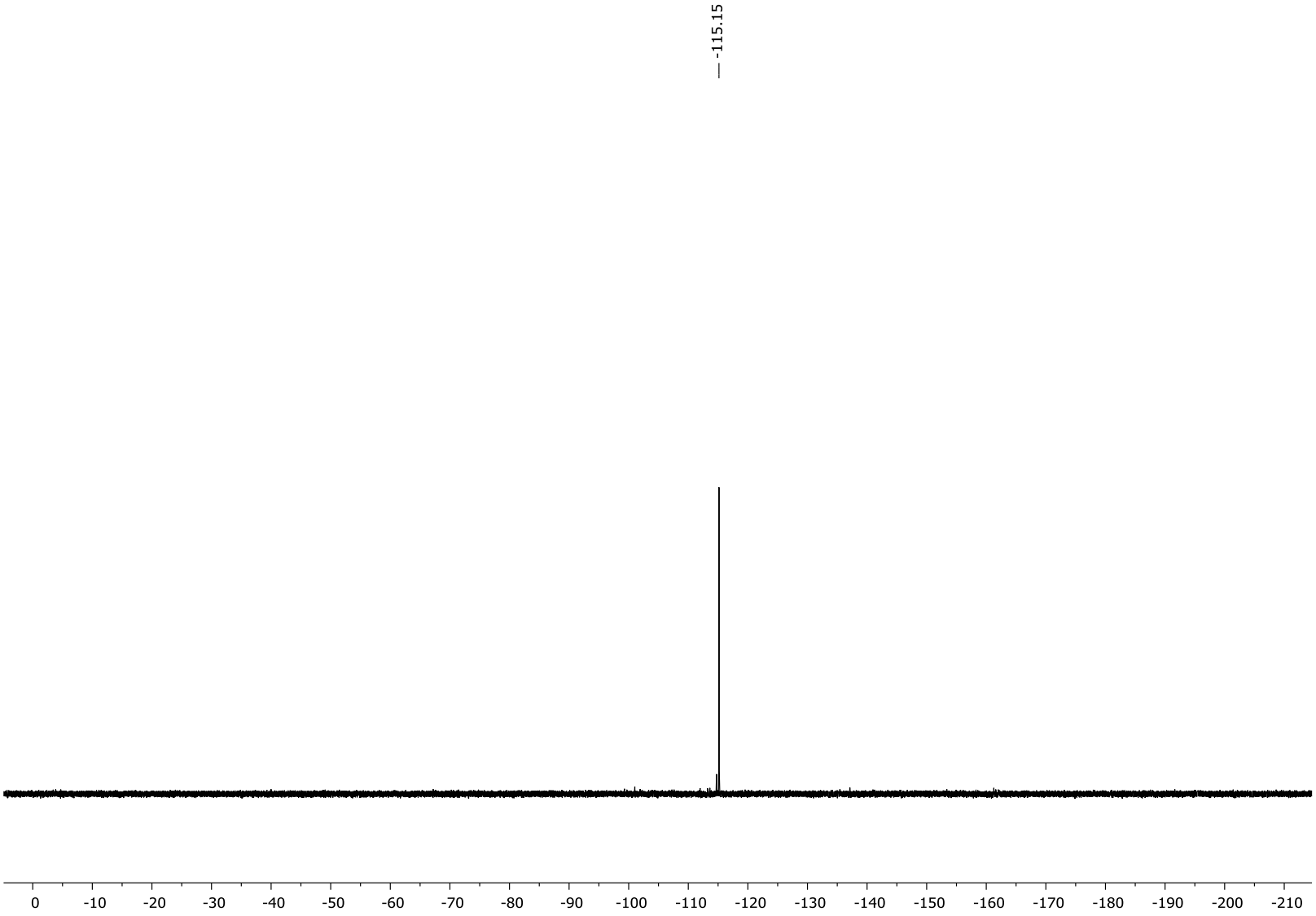


Figure S114: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of methyl 3-oxo-2,3-diphenylpropanoate.

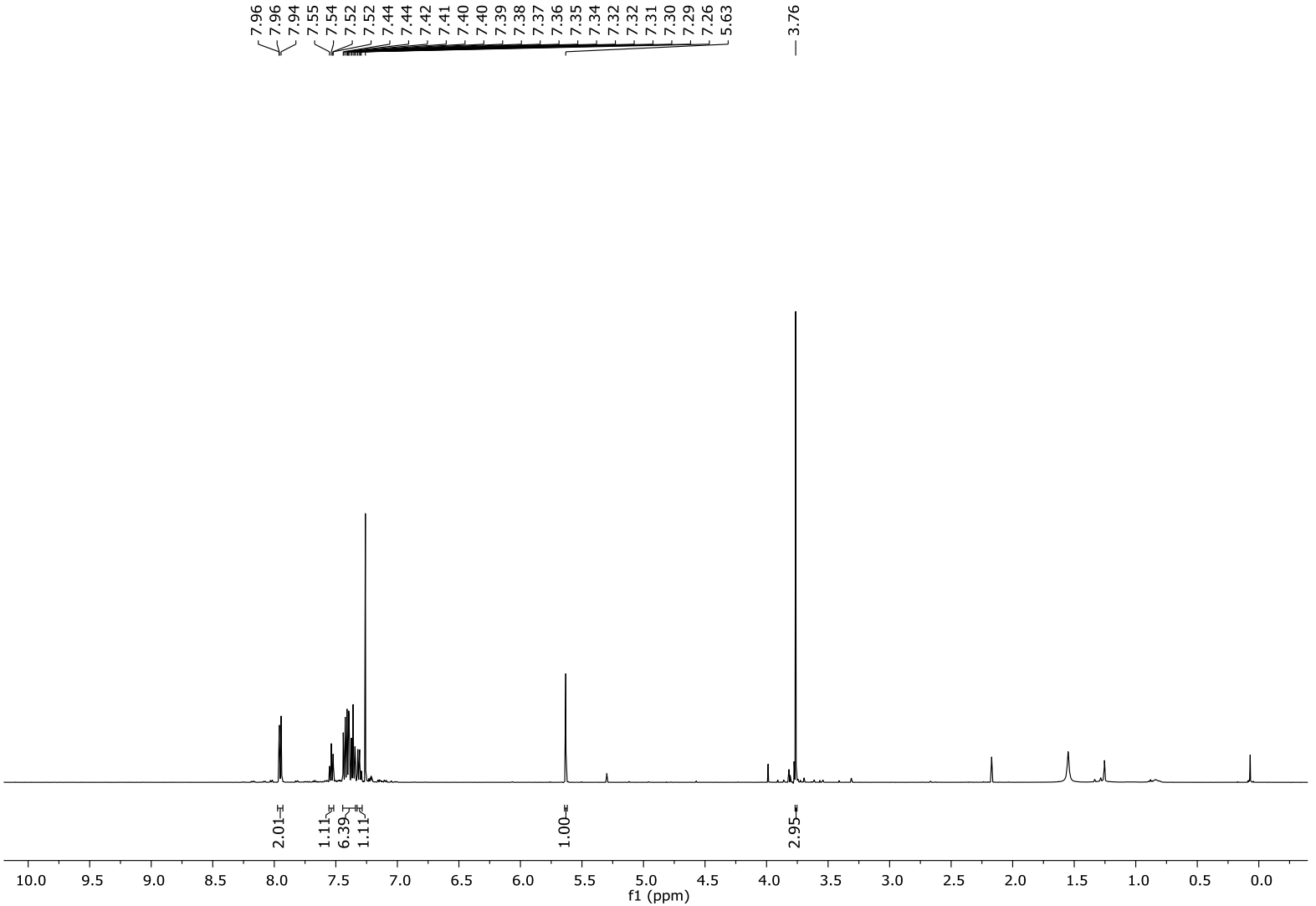
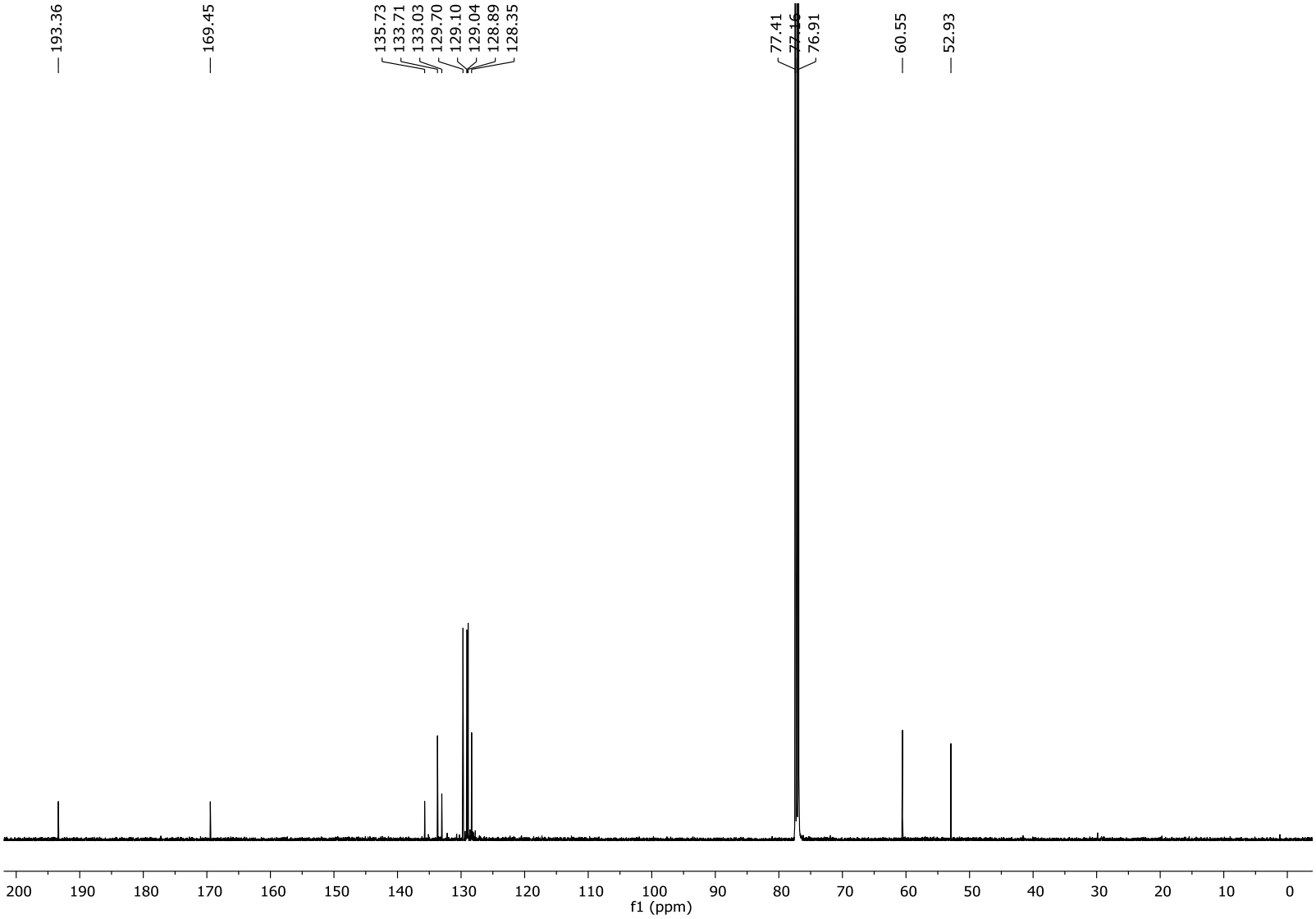


Figure S115: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of methyl 3-oxo-2,3-diphenylpropanoate.



5. Crystallographic Data

5.1 Single crystal X-ray diffraction experimental

Single crystals of **3n** and **3o** were grown in a freezer (3 °C) by vapour diffusion using CH_2Cl_2/pentane. Crystallographic studies were undertaken on single crystal mounted in paratone and studied on an Agilent SuperNova Dual Atlas three-circle diffractometer using Cu-Kα radiation and a CCD detector. Measurements were taken at 150 (2) K (**3n**, **3o**) 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.[12] The structures were solved by direct methods and refined against F2 within SHELXL-2013.[13] The structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers **2072873**, **2072872**). These can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

5.2 Solid-state structures

Figure S116. Solid-state structure of compound **3n**, Thermal ellipsoids drawn at 50% probability. Carbon: black; oxygen: red. H atoms omitted for clarity.

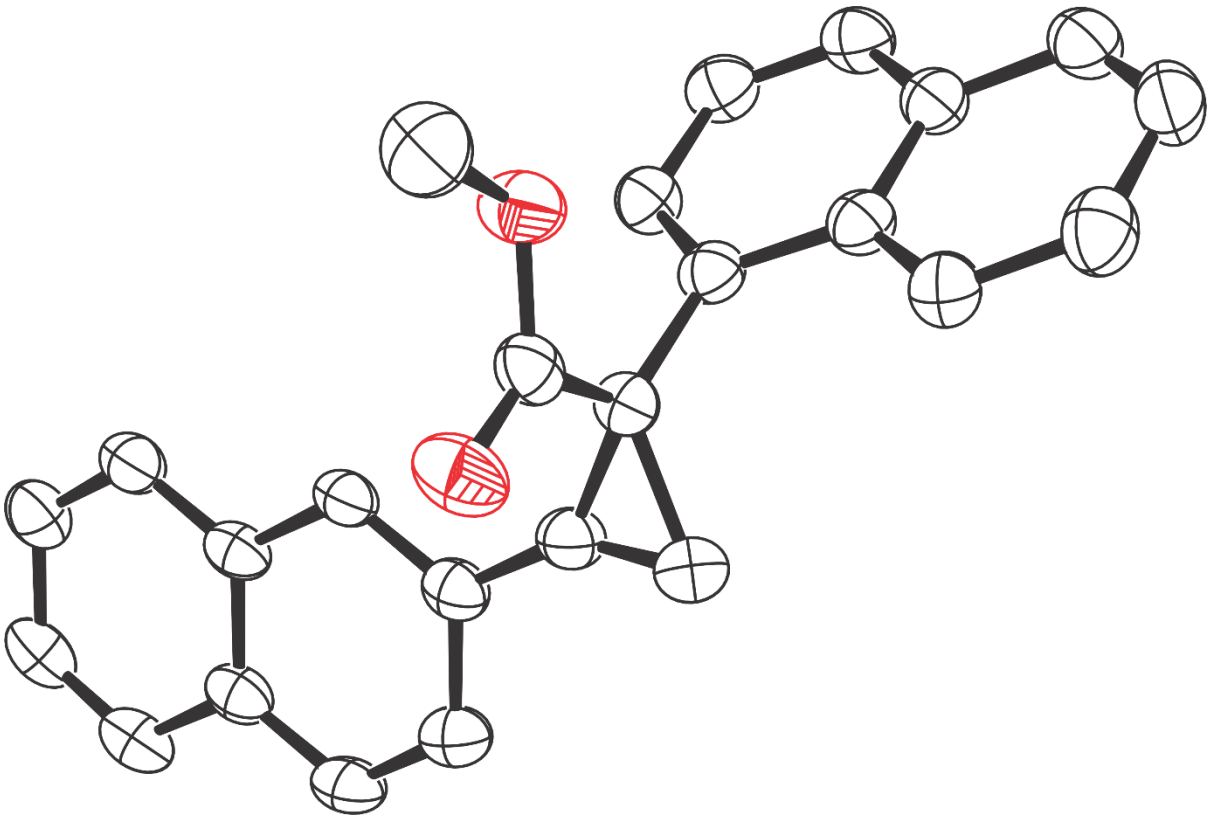
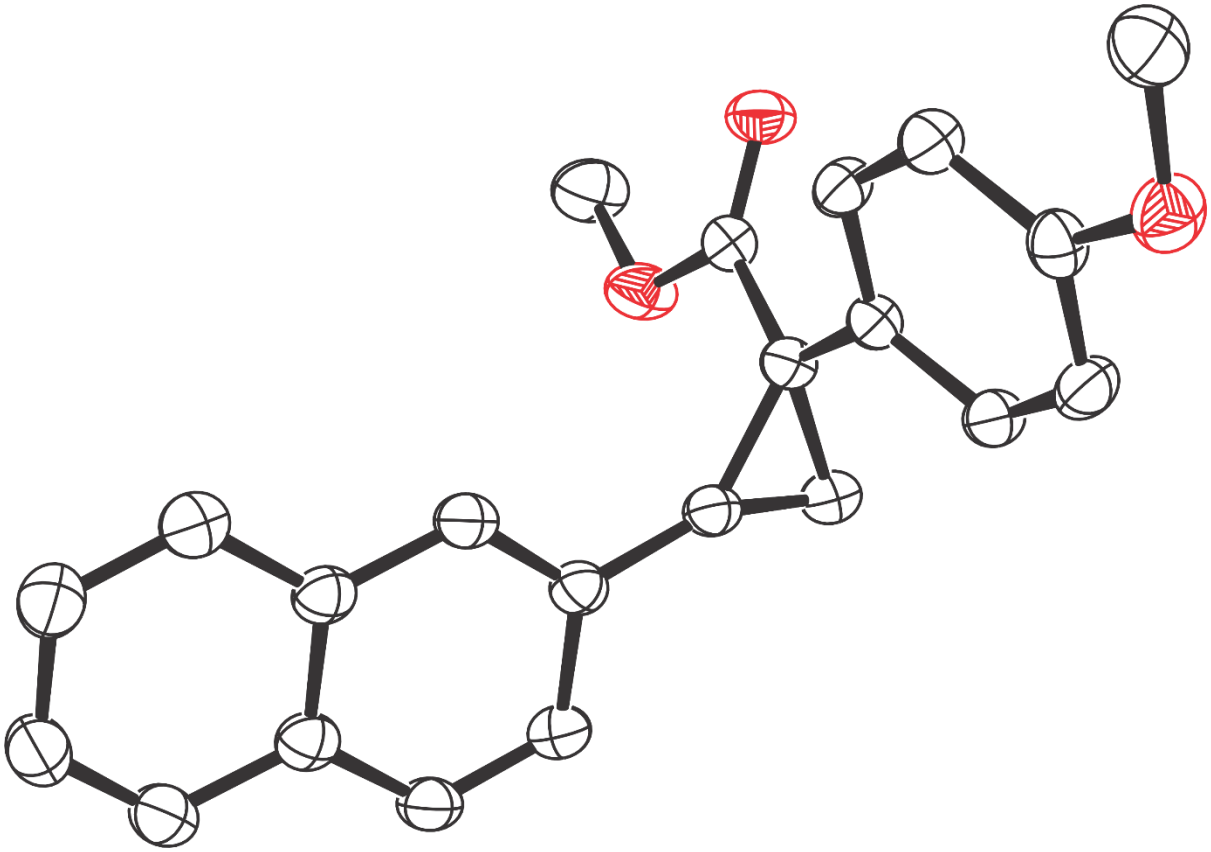


Figure S117. Solid-state structure of compound **3o**, Thermal ellipsoids drawn at 50% probability. Carbon: black; oxygen: red. H atoms omitted for clarity.



5.3 X-ray refinement data

Table S1. Crystal data and structure refinement for compound **3n**. [CCDC: 2072873]

Empirical formula	$C_{25}H_{18}O_2$
Formula weight	350.39
Temperature/K	150 (2)
Crystal system	Orthorhombic
Space group	Pca21
a/Å	26.0464 (11)
b/Å	18.2137 (8)
c/Å	7.6051 (4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3607.9 (3)
Z	8
Density (ρ_{calc}g/cm^3)	1.290
Absorption coefficient (μ/mm^{-1})	0.636
F(000)	1472.0
Crystal size/mm^3	0.199 × 0.063 × 0.040
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.260 to 151.604
Index ranges	$-25 \leq h \leq 32$, $-22 \leq k \leq 19$, $-9 \leq l \leq 9$
Reflections collected	34640
Independent reflections	7272 [R_{int} = 0.0785, R_{sigma} = 0.0584]
Data/restraints/parameters	7272/1/489
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.052, wR_2 = 0.117
Final R indexes [all data]	R_1 = 0.080, wR_2 = 0. 0.141
Largest diff. peak/hole / e Å^{-3}	0.23/-0.21

Table S2. Crystal data and structure refinement for compound **3o**. [CCDC: 2072872]

Empirical formula	$C_{22}H_{18}O_3$
Formula weight	330.36
Temperature/K	150 (2)
Crystal system	Monoclinic
Space group	C2/c
a/Å	29.133 (2)
b/Å	5.3113 (3)
c/Å	22.5850 (13)
α/°	90
β/°	107.704 (8)
γ/°	90
Volume/$Å^3$	3329.1 (4)
Z	8
Density ($\rho_{calc}g/cm^3$)	1.318
Absorption coefficient (μ/mm^{-1})	0.697
F(000)	1392.0
Crystal size/mm^3	0.225 × 0.120 × 0.100
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.200 to 147.944
Index ranges	$-36 \leq h \leq 36$, $-6 \leq k \leq 6$, $-28 \leq l \leq 21$
Reflections collected	14074
Independent reflections	3476 [R_{int} = 0.0936, R_{sigma} = 0.0763]
Data/restraints/parameters	3476/0/228
Goodness-of-fit on F^2	0.868
Final R indexes [I>=2σ (I)]	R_1 = 0.047, wR_2 = 0.098
Final R indexes [all data]	R_1 = 0.0798, wR_2 = 0.107
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.23

6. References

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