Supporting Information

Chemo- and Regio-Selective Amidation of Indoles with Isocyanates Using Borane Lewis Acids

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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. All solvents (toluene, dichloromethane, hexane, 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-$C_2H_4Cl_2$) and α,α,α-trifluorotoluene ($C_6H_5CF_3$) were 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 report.[1] Thin-layer chromatography (TLC) was performed on pre-coated aluminium sheets of Merck silica gel 60 F254 (0.20 mm). ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on a Bruker Avance II 400 or Bruker Avance 500 spectrometer. 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. 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). 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), Electrospray (ES), or Electron Ionisation (EI). The molecular ion peaks values quoted for either molecular ion (M^+), molecular ion plus or minus hydrogen ($M+H^+$, $M-H^-$), molecular ion plus sodium ($M+Na^+$).

2. Synthesis and Characterisation

2.1 General Procedures

General Procedure a

In the glovebox, three glass microwave vials were charged separately with protected indole (1 equiv), aryl isocyanate (1.5 equiv), and $B(C_6F_5)_3$ (30 mol %), and then capped with a septum. The three vials were taken outside the glovebox and 0.5 mL of α,α,α-trifluorotoluene (TFT) were added to each vial using a syringe. Ar-NCO solution was added to the $B(C_6F_5)_3$ solution and the resulting solution was added to the indole solution dropwise with vigorus strirring at room temperature. All the reactions were carried out at an optimum temperature 80 °C for 22–24 h. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent.

General Procedure b

In the glovebox, three glass microwave vials were charged separately with uprotected indole (1 equiv), aryl isocyanate (1.5 equiv), and BCl_3 [1M solution in hexane] (5 mol %), and then capped with a septum. The three vials were brought outside the glovebox and 0.5 mL of 1,2 dichloroethane (1,2-$C_2H_4Cl_2$) were added to each vial using a syringe. Ar-NCO solution was added to the BCl_3 solution and the resulting solution was added to the indole solution dropwise with vigorus strirring at room temperature. All the reactions were carried out at an optimum temperature 60 °C for 16–24 h. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent.

General Procedure c

In the glovebox, three glass microwave vial were charged separately with alkyne derivatives (1 equiv), aryl isocyanate (1.5 equiv), and BCl_3 [1M solution in hexane] (5 mol%), and then capped with a septum. The three vials were brought outside the glovebox and 0.5 mL of 1,2-$C_2H_4Cl_2$ were added to each vial using a syringe. Ar-NCO solution was added to the BCl_3 solution and the resulting solution was added to the indole solution dropwise with vigorus strirring at room temperature. All the reactions were carried out at an optimum temperature 60 °C for 22–24 h. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent.

For 0.1 mmol scale reaction, 5% catalyst loading require 5 μL of the BCl_3-hexane (1M) solution (a micropipette was used to make a quick transfer the catalyst into the reaction vial and then closed with a cap with septum immediately using a crimper.

2.2 Table S1: Optimisation of the reaction conditions for the C3 C–H amidation of 1-methylindole using phenyl isocyanate.

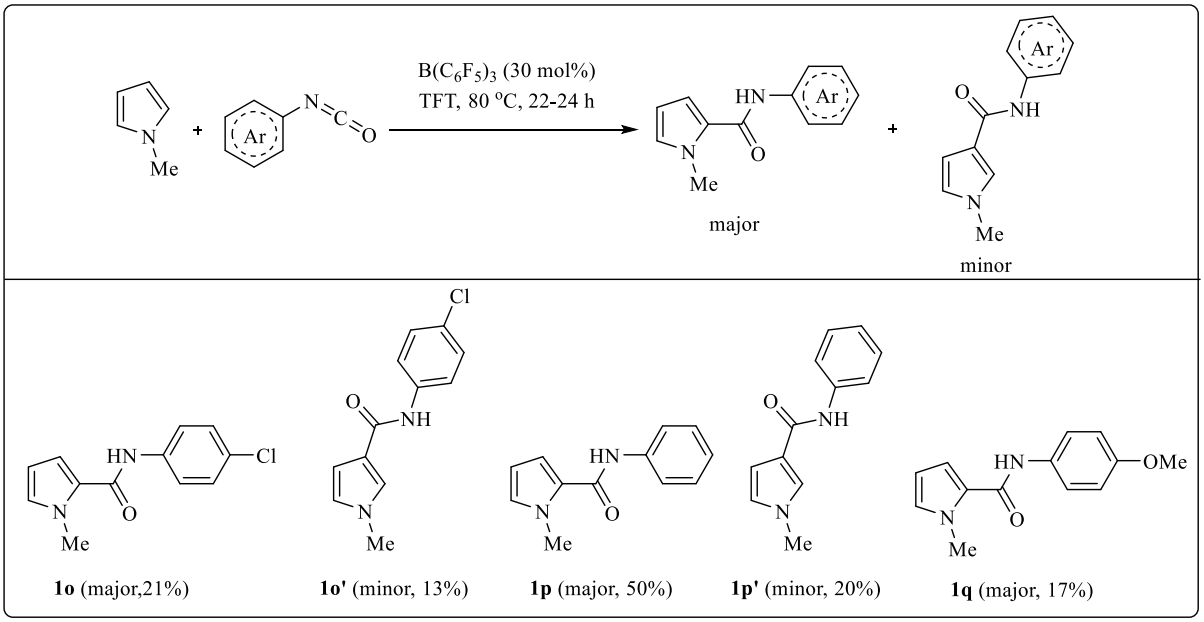
All reactions were carried out on a 0.1 mmol scale using 10 mol% catalyst unless stated otherwise; yields reported are isolated; [a] 20 mol%, [b] 30 mol% [c] 5 mol% $B(C_6F_5)_3$.

Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)
1	None	1,2-$C_2H_4Cl_2$	rt	24	-
2	None	1,2-$C_2H_4Cl_2$	60	24	-
3	None	1,2-$C_2H_4Cl_2$	80	24	-
4	$BF_3{\cdot}OEt_2$	1,2-$C_2H_4Cl_2$	80	24	-
5	2,4,6-BAr^F	1,2-$C_2H_4Cl_2$	80	24	18
6	3,4,5-BAr^F	1,2-$C_2H_4Cl_2$	80	24	23
7	$B(C_6F_5)_3$	1,2-$C_2H_4Cl_2$	80	24	18
8	BCl_3	1,2-$C_2H_4Cl_2$	80	24	10
9	$B(C_6F_5)_3$	Et_2O	80	24	-
10	$B(C_6F_5)_3$	THF	80	24	-
11	$B(C_6F_5)_3$	CH_3CN	80	24	-
12	$B(C_6F_5)_3$	TFT	80	24	35
13	$B(C_6F_5)_3$[a]	TFT	80	24	44
14	$B(C_6F_5)_3$[b]	TFT	80	24	58
15	$B(C_6F_5)_3$[c]	TFT	80	48	14

Reported yields are isolated yields.

2.3 Substrate scope for the $B(C_6F_5)_3$ catalysed amidation of 1-methylpyrrole using aryl isocyanates

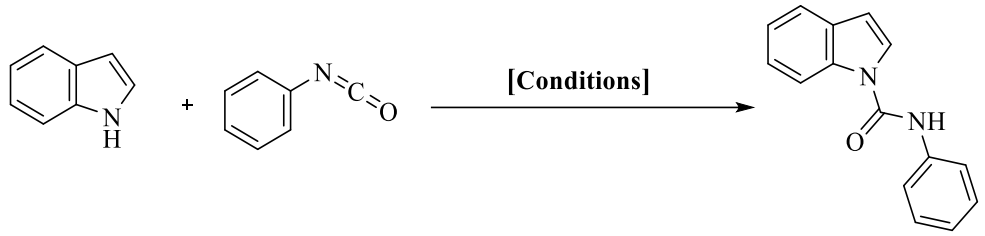
Scheme S1. Substrate scope for the amidation of 1-methylpyrrole using aryl isocyanates using 30 mol% $B(C_6F_5)_3$.



Reported yields are isolated yields.

2.4 Optimisation for the N–H Amidation of 1*H*-Indole

Table S2. Optimisation for the N–H insertion of 1*H*-Indole.

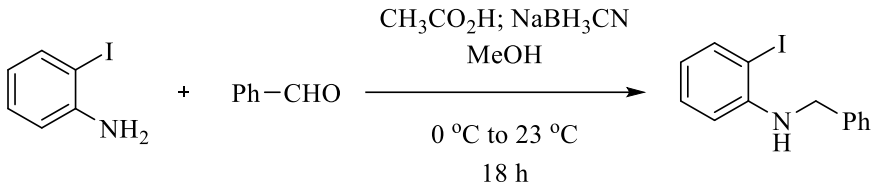


Entry	Catalyst (mol%)	Solvent	Temp (°C)	Time (h)	Yield of **5a** (%)
1	$B(C_6F_5)_3$ (30)	TFT	80	24	17
2	$B(C_6F_5)_3$ (30)	TFT	80	72	23
3	$B(C_6F_5)_3$ (30)	1,2-$C_2H_4Cl_2$	80	96	38
4	$B(C_6F_5)_3$ (10)	TFT	80	24	10
5	$B(C_6F_5)_3$ (20)	TFT	80	24	14
6	$B(C_6F_5)_3$ (30)	TFT	25	24	12
7	$B(C_6F_5)_3$ (30)	TFT	110	24	24
8	-	TFT	80	24	0
9	$BF_3{\cdot}OEt_2$ (20)	1,2-$C_2H_4Cl_2$	87	24	46
10	BCl_3 (20)	1,2-$C_2H_4Cl_2$	87	24	93
11	BCl_3 (10)	1,2-$C_2H_4Cl_2$	87	24	87
12	BCl_3 (5)	1,2-$C_2H_4Cl_2$	87	18	93
13	BCl_3 (5)	1,2-$C_2H_4Cl_2$	60	18	93
14	BCl_3 (1)	1,2-$C_2H_4Cl_2$	60	24	0
15	BCl_3 (5)	1,2-$C_2H_4Cl_2$	25	18	20
16	BCl_3 (5)	1,2-$C_2H_4Cl_2$	45	18	52
17	H_3BO_3 (5)	1,2-$C_2H_4Cl_2$	60	24	0

Reported yields are isolated yields.

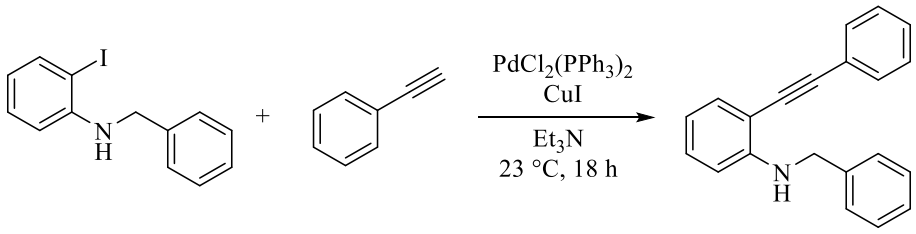
2.5 Synthesis and characterisation of starting materials

Synthesis of N-Benzyl o-iodoaniline



Synthesised in accordance with the procedure illustrated by Wang and co-workers,[2] the following procedure was performed under a moisture and oxygen free N_2 atmosphere. A two-necked round bottom flask was charged with *o*-iodoaniline (10 g, 45.7 mmol, 1 equiv) and benzaldehyde (11.1 mL, 109.6 mmol, 2.4 equiv) and dissolved in methanol (MeOH) (180 mL). The solution was cooled to 0 °C then acetic acid (CH_3CO_2H) (10.5 ml, 182.8 mmol, 4 equiv) was added dropwise under vigorous stirring. Sequentially, sodium cyanoborohydride ($NaBH_3CN$) (5.74 g, 91,4 mmol, 2 equiv) was added portionwise letting the evolution of gas cease before adding a new portion. The reaction mixture was left to react overnight (ca. 18 h) and was then quenched with cold water, leading to the immediate formation of a white precipate. The organic solvent was removed *in vacuo* and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The organic phases were collected, washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*, leaving a yellow oil which was used in the next step without further purification.

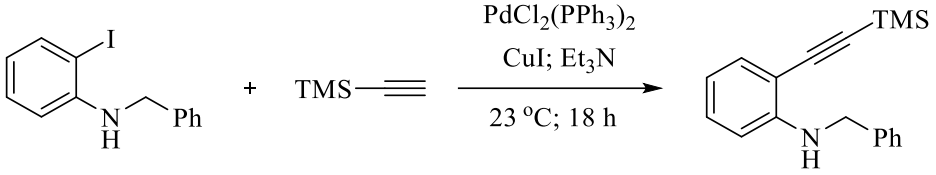
Synthesis of N-benzyl-2-(phenylethynyl)aniline



Synthesised in accordance with the procedure by Wang and co-workers.[2] The following procedure was performed under a moisture and oxygen free N_2 atmosphere. A one necked Schlenk round bottom flask was charged with N-Benzyl *o*-iodoaniline (2 g, 6.5 mmol, 1 equiv), dissolved in triethylamine (Et_3N) (26 mL). To this solution, phenylacetylene (1.4 mL, 13 mmol, 2 equiv) was added dropwise. Sequentially, $PdCl_2(PPh_3)_2$ (2.2 mg, 3 µmol, 0.02 equiv) was added and the reaction mixture was stirred for 5 minutes before adding CuI (1.5 mg, 8 µmol, 0.05 equiv). The reaction was left to stir at room temperature until completion (24 h). After

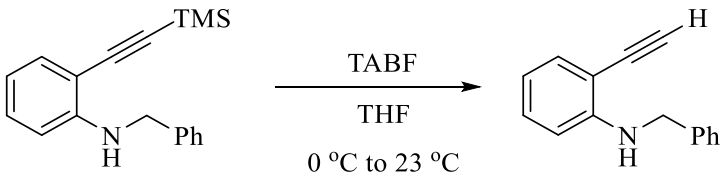
consumption of the starting material, checked by TLC, the solvent was removed under vacuum leading to a dark oil which was passed through a silica plug. The crude reaction mixture was purified by column chromatography using hexane/ethyl acetate (100:0 to 100:10 v/v) as the eluent to afford the desired product as a yellow solid (1.60 g, 87% yield). The spectroscopic data are in agreement with the literature.[2]

Synthesis of N-benzyl-2-((trimethylsilyl)ethynyl)aniline



Synthesised in accordance with the procedure illustrated by Wang and co-workers.[2] The following procedure was performed under a moisture and oxygen free N_2 atmosphere. A one necked round bottomed Schlenk flask was charged with N-Benzyl *o*-iodoaniline (2 g, 6.5 mmol, 1 equiv) and dissolved in Et_3N (26 mL). To this solution, trimethylsilylacetylene (1.9 mL, 13 mmol, 2 equiv) was added dropwise. Sequentially, $PdCl_2(PPh_3)_2$ (2 mg, 3 µmol, 0.02 equiv) was added and the reaction mixture was stirred for 5 minutes before adding CuI (2 mg, 8 µmol, 0.05 equiv). The reaction was left to stir at room temperature until completion (18 h). After consumption of the starting material, checked by TLC, the solvent was removed *in vacuo* leading to a dark oil which was passed through a silica plug. The crude reaction mixture was purified by column chromatography using hexane/ethyl acetate (100:0 to 100:5) as the eluent to afford the desired product as a yellow oil (1.6 g, 86% yield). The spectroscopic data are in agreement with the literature.[2]

Synthesis of N-benzyl-2-ethynylaniline



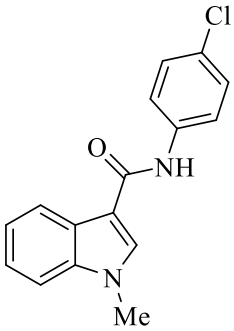
Synthesised in accordance with the procedure illustrated by Wang and co-workers.[2] The following procedure was performed under a moisture and oxygen free N_2 atmosphere. A one necked round bottomed Schlenk flask was charged with N-benzyl-2-((trimethylsilyl)ethynyl)aniline (0.7 g, 2.5 mmol, 1 equiv) dissolved in THF (20 mL) and

cooled to 0 °C. To this solution, tetra-*n*-butylammonium fluoride (3 mL, 3 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred until completion (18 h). After consumption of the starting material, checked by TLC, water was added to the reaction mixture, leading to the formation of a white precipitate. The ethereal solvent was removed *in vacuo* and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic phases were then collected, washed with brine, dried over Na_2SO_4 and concentrated *in vacuo* to give a golden yellow oil which was purified by column chromatography using hexane:ethyl acetate (100:0 to 100:5 v/v) as the eluent affording the desired product as a yellow oil (0.33 g, 63% yield). The spectroscopic data are in agreement with the literature.[2]

2.5 Synthesis and spectral characterisation of C3 C–H amidated products

Synthesis of N-(4-chlorophenyl)-1-methyl-1H-indole-3-carboxamide (**1a**)[3]

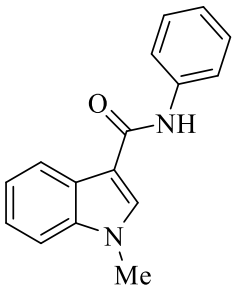
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-chlorophenyl isocyanate (23 mg, 0.15 mmol), and *N*-methylindole (13 µL, 0.1 mmol) in TFT to afford **1a**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1a** was obtained as a white solid. Yield: 11 mg, 0.04 mmol, 39%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.92 (d, *J* = 7.8 Hz, 1H, Ar–CH), 7.71 (br., s, 1H, NH), 7.67 (s, 1H, CH), 7.54–7.46 (m, 2H, Ar–CH), 7.40–7.27 (m, 3H, Ar–CH), 7.25–7.20 (m, 2H, Ar–CH), 3.73 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 163.7, 137.4, 136.7, 133.3, 129.13, 129.10, 125.0, 123.1, 122.1, 121.5, 119.7, 110.6, 110.3, 33.39. Data agrees with literature values.[3]

Synthesis of Synthesis of 1-methyl-N-phenyl-1H-indole-3-carboxamide (**1b**)[3]

Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), phenyl isocyanate (16 µL, 0.15 mmol), and *N*-methylindole (13 µL, 0.1 mmol) in TFT to afford **1b**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1b** was obtained as a white solid. Yield: 15 mg, 0.06 mmol, 58%.

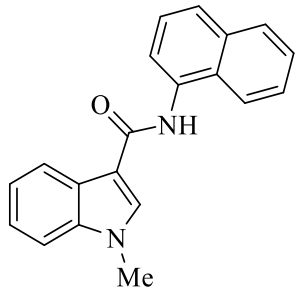


^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.06–8.04 (m, 1H, Ar–CH), 7.76 (br., s, 1H, NH), 7.73 (s, 1H, CH), 7.68–7.64 (m, 2H, Ar–CH), 7.40–7.29 (m, 5H, Ar–CH), 7.12 (t, *J* = 7.4 Hz, 1H, Ar–CH), 3.79 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ:

163.3, 138.6, 137.5, 132.8, 129.2, 125.5, 124.1, 123.0, 121.9, 120.19, 120.16, 111.2, 110.4, 33.5. Data agrees with literature values.[3]

Synthesis of 1-methyl-N-(naphthalen-1-yl)-1H-indole-3-carboxamide (**1c**)

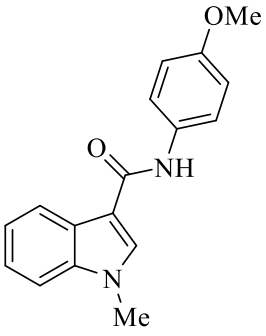
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 1-naphthyl isocyanate (22 µL, 0.15 mmol), and *N*-methylindole (13 µL, 0.1 mmol) in TFT to afford **1c**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1c** was obtained as a white solid. Yield: 14 mg, 0.05 mmol, 47%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.17–8.03 (m, 3H, Ar–CH), 7.99 (d, *J* = 7.4 Hz, 1H, Ar–CH), 7.90 (d, *J* = 7.5 Hz, 1H, Ar–CH), 7.82 (s, 1H, CH), 7.73 (d, *J* = 8.1 Hz, 1H, Ar–CH), 7.59–7.48 (m, overlapped Ar–CH and NH, 3H), 7.44 (d, *J* = 7.6 Hz, 1H, Ar–CH), 7.40–7.30 (m, 2H, Ar–CH), 3.87 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.0, 137.6, 134.4, 133.12, 133.05, 129.0, 127.6, 126.5, 126.09, 126.06, 125.6, 125.59, 123.0, 122.1, 121.1, 121.0, 120.3, 111.2, 110.5, 33.6; IR ν_{max} (cm^{-1}): 3292, 3049, 1635 (C=O); 1524, 1496, 1462, 1227, 1111, 744. HRMS (ES+) $[M+H]^+$ $[C_{20}H_{17}N_2O]^+$: calculated 301.1341, found 301.1342.

Synthesis of N-(4-methoxyphenyl)-1-methyl-1H-indole-3-carboxamide (**1d**)[3]

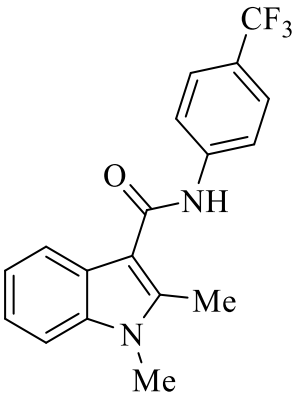
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-methoxyphenyl isocyanate (19 µL, 0.15 mmol), *N*-methylindole (13 µL, 0.1 mmol) in TFT to afford **1d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1d** was obtained as a white solid. Yield: 11 mg, 0.04 mmol, 39%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.82 (d, *J* = 7.9 Hz, 1H, Ar–CH), 7.64 (s, 1H, CH), 7.55 (br., s, 1H, NH), 7.38–7.24 (m, 5H, Ar–CH), 6.76 (d, *J* = 8.9 Hz, 2H, Ar–CH), 3.68 (s, 3H, OMe), 3.65 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.4, 157.0, 137.4, 133.4, 130.3, 124.8, 123.1, 123.0, 122.1, 119.3, 114.4, 110.7, 110.1, 55.5, 33.2. Data agrees with literature values.[3]

Synthesis of 1,2-dimethyl-N-(4-(trifluoromethyl)phenyl)-1H-indole-3-carboxamide (**1e**)

Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-

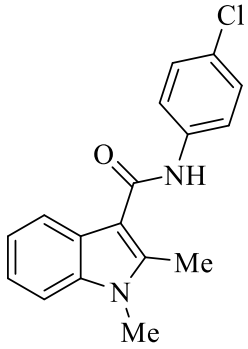


(trifluoromethyl)phenyl isocyanate (21 µL, 0.15 mmol), and 1,2-dimethylindole (15 mg, 0.1 mmol) in TFT to afford **1e**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1e** was obtained as a white solid. Yield: 11 mg, 0.03 mmol, 33%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.90 (br., s, 1H, NH), 7.81–7.72 (m, 3H, Ar–CH), 7.62 (d, J = 8.5 Hz, 2H, Ar–CH), 7.39–7.37 (m, 1H, Ar–CH), 7.32–7.27 (m, 2H, Ar–CH), 3.70 (s, 3H, NMe), 2.75 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.7, 143.9, 141.8, 136.7, 126.5, 126.5 (q, $J_{C–F}$ = 3.7 Hz), 125.6 (q, $J_{C–F}$ = 32.5 Hz),124.7, 124.3 (q, $J_{C–F}$ = 272.7 Hz), 122.3, 121.9, 119.4, 118.3, 118.2, 110.2, 107.4, 29.8, 11.8 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -61.91; IR ν_{max} (cm^{-1}): 3292, 1643 (C=O), 1599, 1522, 1406, 1319, 1111, 1067. HRMS (CI) $[M+H]^+$ $[C_{18}H_{16}F_3N_2O]^+$: calculated 333.1209, found 333.1208.

Synthesis of N-(4-chlorophenyl)-1,2-dimethyl-1H-indole-3-carboxamide (**1f**)

Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-

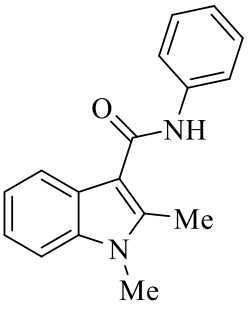


chlorophenyl isocyanate (23 mg, 0.15 mmol), and 1,2-dimethylindole (15 mg, 0.1 mmol) in TFT to afford **1f**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1f** was obtained as a white solid. Yield: 13 mg, 0.04 mmol, 43%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.77–7.74 (m, 1H, Ar–CH), 7.71 (br., s, 1H, NH), 7.60 (d, J = 8.8 Hz, 2H, Ar–CH), 7.40–7.36 (m, 1H, Ar–CH), 7.33 (d, J = 8.8 Hz, 2H, Ar–CH), 7.30–7.24 (m, 2H, Ar–CH), 3.72 (s, 3H, NMe), 2.76 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.5, 143.5, 137.4, 136.7, 129.1, 128.7, 124.9, 122.1, 121.7, 121.1, 118.3, 110.0, 107.6, 29.7, 11.7; IR ν_{max} (cm^{-1}): 3287, 1634 (C=O), 1591, 1491, 1404. HRMS (EI) [M] $[C_{17}H_{15}Cl^{35}N_2O]$: calculated 298.0867, found 298.0865.

Synthesis of 1,2-dimethyl-N-phenyl-1H-indole-3-carboxamide (**1g**)

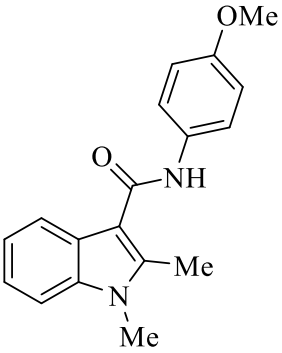
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), phenyl isocyanate (16 µL, 0.15 mmol), and 1,2-dimethylindole (15 mg, 0.1 mmol) in TFT to afford **1g**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1g** was obtained as a white solid. Yield: 13 mg, 0.05 mmol, 49%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.82–7.77 (m, 1H, Ar–CH), 7.72 (br., s, 1H, NH), 7.65 (d, *J* = 7.5 Hz, 2H, Ar–CH), 7.42–7.34 (m, 3H, Ar–CH), 7.31–7.26 (m, 2H, Ar–CH), 7.13 (t, *J* = 7.4 Hz, 1H, Ar–CH), 3.72 (s, 3H, NMe), 2.77 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.7 (C=O), 143.3, 138.6, 136.6, 129.2, 124.9, 124.1, 122.1, 121.6, 120.1, 118.3, 110.0, 107.8, 29.7, 11.7; IR ν_{max} (cm^{-1}): 3285, 1638 (C=O), 1595, 1535, 1499, 1437, 1312. HRMS (EI) [M] [$C_{17}H_{16}N_2O$]: calculated 264.1257, found 264.1255.

Synthesis of N-(4-methoxyphenyl)-1,2-dimethyl-1H-indole-3-carboxamide (**1h**)

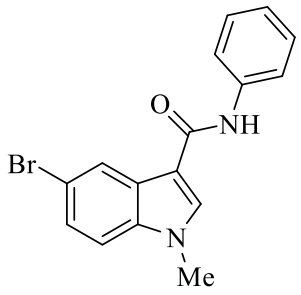
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-methoxyphenyl isocyanate (19 µL, 0.15 mmol), and 1,2-dimethylindole (15 mg, 0.1 mmol) in TFT to afford **1h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1h** was obtained as a white solid. Yield: 7 mg, 0.02 mmol, 24%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.81–7.77 (m, 1H, Ar–CH), 7.63 (br., s, 1H, NH), 7.55 (d, *J* = 9.0 Hz, 2H, Ar–CH), 7.39–7.34 (m, 1H, Ar–CH), 7.30–7.23 (m, 2H, Ar–CH), 6.92 (d, *J* = 9.0 Hz, 2H, Ar–CH), 3.82 (s, 3H, OMe), 3.72 (s, 3H, NMe), 2.76 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.5, 156.3, 143.1, 136.6, 131.7, 125.0, 122.0, 121.9, 121.5, 118.4, 114.3, 109.9, 107.8, 55.7, 29.7, 11.7; IR ν_{max} (cm^{-1}): 3277, 1633 (C=O), 1508, 1408, 1233, 1161, 1105, 1032. HRMS (CI) $[M+H]^+$ $[C_{18}H_{19}N_2O_2]^+$: calculated 295.1441, found 295.1443.

Synthesis of 5-bromo-1-methyl-N-phenyl-1H-indole-3-carboxamide (**1i**)

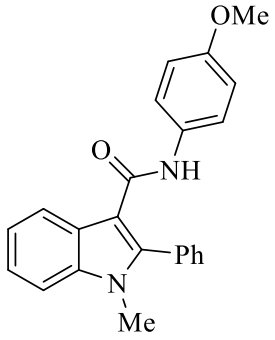
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), phenyl isocyanate (16 µL, 0.15 mmol), and 5-bromo-1-methylindole (21 mg, 0.1 mmol) in TFT to afford **1i**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1i** was obtained as a white solid. Yield: 11 mg, 0.03 mmol, 33%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.27 (d, *J* = 1.8 Hz, 1H), 7.68 (s, 1H, CH), 7.64 (d, *J* = 7.6 Hz, 2H, Ar–CH), 7.55 (br., s, 1H, NH), 7.44–7.36 (m, 3H, Ar–CH), 7.28–7.23 (m, 1H, Ar–CH), 7.14 (t, *J* = 7.4 Hz, 1H), 3.83 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 162.8, 138.3, 136.1, 132.7, 129.2, 127.4, 126.1, 124.3, 123.4, 120.9, 120.3, 115.6, 111.7, 33.7; IR ν_{max} (cm^{-1}): 3298, 1636 (C=O), 1597, 1528, 1466, 1240, 1111. HRMS (ES+) $[M+H]^+$ $[C_{16}H_{14}BrN_2O]^+$: calculated 329.0290, found 329.0290.

Synthesis of N-(4-methoxyphenyl)-1-methyl-2-phenyl-1H-indole-3-carboxamide (**1j**)

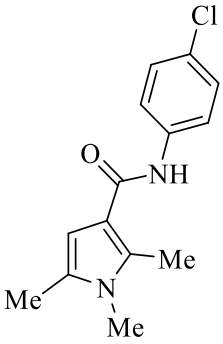
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-methoxyphenyl isocyanate (19 µL, 0.15 mmol), and 1-methyl-2-phenylindole (21 mg, 0.1 mmol) in TFT to afford **1j**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1j** was obtained as a white solid. Yield: 13 mg, 0.04 mmol, 36%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.50–8.46 (m, 1H, Ar–CH), 7.68–7.61 (m, 3H, Ar–CH), 7.58–7.54 (m, 2H, Ar–CH), 7.41–7.31 (m, 3H, Ar–CH), 7.09 (d, *J* = 9.0 Hz, 2H, Ar–CH), 6.91 (br., s, 1H, NH), 6.76 (d, *J* = 9.0 Hz, 2H, Ar–CH), 3.75 (s, 3H, OMe), 3.58 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 163.1, 155.8, 141.1, 137.0, 131.9, 131.1, 131.0, 130.4, 129.7, 127.3, 123.3, 122.4, 122.2, 120.9, 114.1, 109.7, 109.4, 55.6, 31.0; IR ν_{max} (cm^{-1}): 3292, 3265, 3118, 3048, 2814, 1635 (C=O), 1523, 1496, 1396, 1375, 1335, 1247, 1155, 1128, 1084, 1010. HRMS (ES+) $[M+H]^+$ $[C_{23}H_{21}N_2O_2]^+$: calculated 357.1609, found 357.1603.

Synthesis of N-(4-chlorophenyl)-1,2,5-trimethyl-1H-pyrrole-3-carboxamide (**1k**)

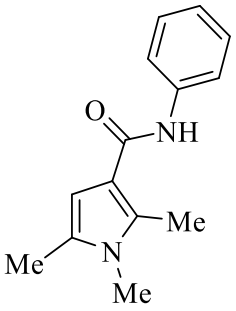
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-chlorophenyl isocyanate (23 mg, 0.15 mmol), and 1,2,5-trimethylpyrrole (14 µL, 0.1 mmol) in TFT to afford **1k**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1k** was obtained as a white solid. Yield: 13 mg, 0.05 mmol, 50%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.55–7.50 (m, 2H, Ar–CH), 7.45 (br., s, 1H, NH), 7.28–7.22 (m, 2H, Ar–CH), 6.05 (s, 1H, CH), 3.39 (s, 3H, NMe), 2.54 (s, 3H, Me), 2.20 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.2, 137.5, 134.8, 128.9, 128.3, 128.2, 121.1, 113.2, 103.7, 30.3, 12.5, 11.4; IR ν_{max} (cm^{-1}): 3294, 2910, 1636 (C=O), 1589, 1530, 1508, 1301, 1242, 826. HRMS (ES+) $[M+H]^+$ $[C_{14}H_{16}ClN_2O]^+$: calculated 263.0951, found 263.0950.

Synthesis of 1,2,5-trimethyl-N-phenyl-1H-pyrrole-3-carboxamide (**1l**)

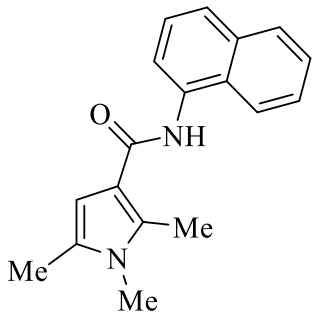
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), phenyl isocyanate (16 µL, 0.15 mmol), and 1,2,5-trimethylpyrrole (14 µL, 0.1 mmol) in TFT to afford **1l**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1l** was obtained as a white solid. Yield: 8 mg, 0.04 mmol, 35%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.60–7.55 (m, 2H, Ar–CH), 7.42 (br, s, 1H, NH), 7.34–7.29 (m, 2H, Ar–CH), 7.09–7.04 (m, 1H, Ar–CH), 6.07 (s, 1H, CH), 3.40 (s, 3H, NMe), 2.56 (s, 3H, Me), 2.22 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.4 (C=O), 138.8, 134.6, 129.0, 128.2, 123.6, 120.0, 113.6, 103.8, 30.3 (NMe), 12.5 (Me), 11.5 (Me); IR ν_{max} (cm^{-1}): 3337, 2911, 1634 (C=O), 1595, 1533, 1497, 1305, 1244. HRMS (ES+) $[M+H]^+$ $[C_{14}H_{17}N_2O]^+$: calculated 229.1341, found 229.1338.

Synthesis of 1,2,5-trimethyl-N-(naphthalen-1-yl)-1H-pyrrole-3-carboxamide (**1m**)

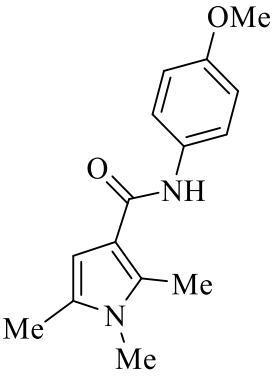
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 1-naphthyl isocyanate (22 µL, 0.15 mmol), and 1,2,5-trimethylpyrrole (14 µL, 0.1 mmol) in TFT to afford **1m**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1m** was obtained as a white solid. Yield: 15 mg, 0.05 mmol, 52%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.07 (d, *J* = 7.5 Hz, 1H, Ar–CH), 7.91 (d, *J* = 8.0 Hz, 1H, Ar–CH), 7.88–7.85 (m, 1H, Ar–CH), 7.83 (br., s, 1H, NH), 7.67 (d, *J* = 8.2 Hz, 1H, Ar–CH), 7.56–7.44 (m, 3H, Ar–CH), 6.22 (s, 1H, CH), 3.44 (s, 3H, NMe), 2.61 (s, 3H, Me), 2.27 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.6, 134.8, 134.3, 133.3, 128.9, 128.3, 127.4, 126.2, 126.1, 125.9, 125.0, 120.9, 120.5, 113.6, 103.8, 30.4, 12.6, 11.5; IR ν_{max} (cm^{-1}): 3277, 3051, 3916, 1637 (C=O), 1521, 1487, 1396, 1250, 769. HRMS (CI) [M] [$C_{18}H_{18}N_2O$]: calculated 278.1414, found 278.1416.

Synthesis of N-(4-methoxyphenyl)-1,2,5-trimethyl-1H-pyrrole-3-carboxamide (**1n**)

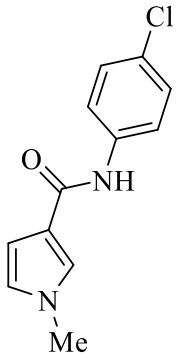
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-methoxyphenyl isocyanate (19 µl, 0.15 mmol), and 1,2,5-trimethylpyrrole (14 µL, 0.1 mmol) in TFT to afford **1n**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1n** was obtained as a white solid. Yield: 11 mg, 0.04 mmol, 42%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.42–7.36 (m, 2H, Ar–CH), 7.32 (br., s, 1H, NH), 6.86–6.80 (m, 2H, Ar–CH), 6.03 (s, 1H, CH), 3.76 (s, 3H, OMe), 3.39 (s, 3H, NMe), 2.50 (s, 3H, Me), 2.21 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.6, 156.2, 134.2, 131.6, 128.2, 122.3, 114.2, 113.4, 103.8, 55.6, 30.3, 12.5, 11.4; IR ν_{max} (cm^{-1}): 3331, 2934, 1638 (C=O), 1508, 1460, 1410, 1233. HRMS (ES+) $[M+H]^+$ $[C_{15}H_{19}N_2O_2]^+$: calculated 259.1447, found 259.1441.

Synthesis of N-(4-chlorophenyl)-1-methyl-1H-pyrrole-3-carboxamide (**1o'**)

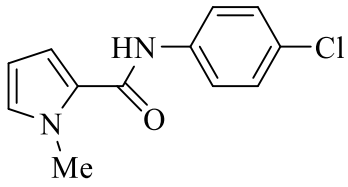
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-chlorophenyl isocyanate (23 mg, 0.15 mmol), and *N*-methylpyrrole (9 µL, 0.1 mmol) in TFT to afford **1o'**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1o'** was obtained as a white solid. Yield: 3 mg, 0.01 mmol, 13%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.57–7.51 (m, 2H, Ar–CH), 7.44 (br., s, 1H, NH), 7.30–7.25 (m, overlapped, Ar–CH and pyrrole CH, 3H), 6.61 (t, *J* = 2.5 Hz, 1H, pyrrole CH), 6.45–6.40 (m, 1H, pyrrole CH), 3.69 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 162.8, 137.1, 129.1, 128.8, 125.5, 123.2, 121.2, 119.8, 107.2, 36.8; IR ν_{max} (cm^{-1}): 3296, 3121, 2924, 1643, 1591, 1537, 1510, 1491, 1464, 1400, 1090. HRMS (APCI) $[M+H]^+$ $[C_{12}H_{12}ClN_2O]^+$: calculated 235.0638, found 235.0641.

Synthesis of N-(4-chlorophenyl)-1-methyl-1H-pyrrole-2-carboxamide (**1o**)[4]

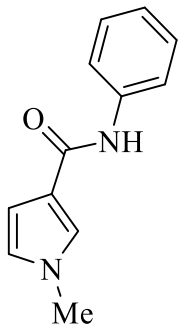
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-chlorophenyl isocyanate (23 mg, 0.15 mmol), and *N*-methylpyrrole (9 µL, 0.1 mmol) in TFT to afford **1o**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1o** was obtained as a light-yellow solid. Yield: 5 mg, 0.02 mmol, 21%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.59 (br., s, 1H, NH), 7.53–7.48 (m, 2H, Ar–CH), 7.32–7.27 (m, 2H, Ar–CH), 6.80–6.78 (m, 1H, pyrrole CH), 6.69 (dd, *J* = 4.0, 1.7 Hz, 1H, pyrrole CH), 6.14 (dd, *J* = 4.0, 2.6 Hz, 1H, pyrrole CH), 3.97 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 159.9, 136.8, 129.22, 129.15, 129.0, 125.5, 121.3, 112.5, 107.7, 37.0. Data agrees with literature values.[4]

Synthesis of 1-methyl-N-phenyl-1H-pyrrole-3-carboxamide (**1p'**)[5]

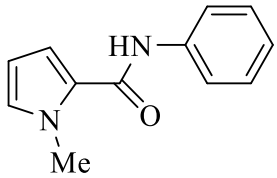
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), phenyl isocyanate (16 µL, 0.15 mmol), and *N*-methylpyrrole (9 µL, 0.1 mmol) in TFT to afford **1p'**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1p'** was obtained as a light-yellow solid. Yield: 4 mg, 0.02 mmol, 20%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.60 (d, *J* = 7.8 Hz, 2H, Ar–CH), 7.44 (br., s, 1H, NH), 7.36–7.30 (m, 2H, Ar–CH), 7.29–7.27 (m, 1H, Ar–CH), 7.09 (t, *J* = 7.4 Hz, 1H, pyrrole CH), 6.61 (t, *J* = 2.5 Hz, 1H, pyrrole CH), 6.44 (t, *J* = 2.2 Hz, 1H, pyrrole CH), 3.70 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 162.8, 138.5, 129.3, 129.1, 125.4, 123.9, 123.1, 120.0, 107.2, 36.8. Data agrees with literature values.[5]

Synthesis of 1-methyl-N-phenyl-1H-pyrrole-2-carboxamide (**1p**)[6]

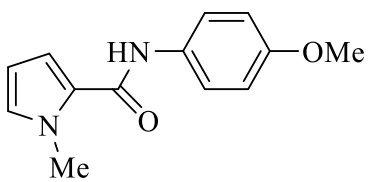
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), phenyl isocyanate (16 µL, 0.15 mmol), and *N*-methylpyrrole (9 µL, 0.1 mmol) in TFT to afford **1p**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1p** was obtained as a white solid. Yield: 10 mg, 0.05 mmol, 50%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.58 (br., s, 1H, NH), 7.57–7.53 (m, 2H, Ar–CH), 7.37–7.31 (m, 2H, Ar–CH), 7.13–7.09 (m, 1H, Ar–CH), 6.79 (t, *J* = 2.1, 1H, pyrrole CH), 6.70 (dd, *J* = 4.0, 1.7 Hz, 1H, pyrrole CH), 6.15 (dd, *J* = 3.8, 2.6 Hz, 1H, pyrrole CH), 3.98 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 160.0, 138.2, 129.2, 129.0, 125.9, 124.2, 120.1, 112.3, 107.6, 37.0. Data agrees with literature values.[6]

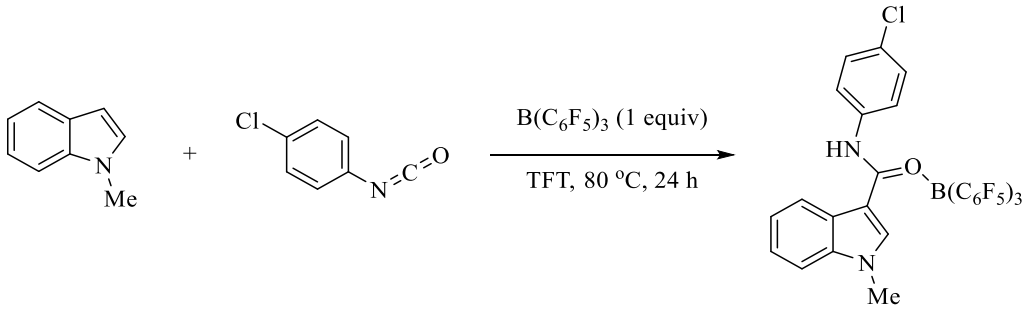
Synthesis of N-(4-methoxyphenyl)-1-methyl-1H-pyrrole-2-carboxamide (**1q**)[4]

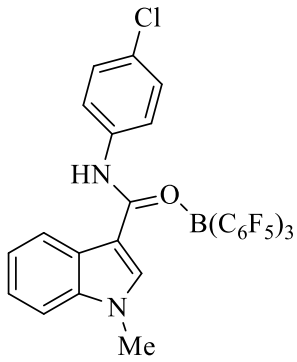
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (15 mg, 0.03 mmol), 4-methoxyphenyl isocyanate (19 µL, 0.15 mmol), and *N*-methylpyrrole (9 µL, 0.1 mmol) in TFT to afford **1q**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **1q** was obtained as a pale-yellow solid. Yield: 4 mg, 0.02 mmol, 17%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.49 (br., s, 1H, NH), 7.47–7.42 (m, 2H, Ar–CH), 6.92–6.86 (m, 2H, Ar–CH), 6.77 (t, *J* = 2.1, 1H, pyrrole CH), 6.67 (dd, *J* = 4.0, 1.7 Hz, 1H, pyrrole CH), 6.13 (dd, *J* = 3.9, 2.6 Hz, 1H, pyrrole CH), 3.97 (s, 3H, NMe), 3.80 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 160.1, 156.5, 131.2, 128.7, 126.0, 122.2, 114.4, 112.0, 107.6, 55.7, 37.0. Data agrees with literature values.[4]

Synthesis of N-(4-chlorophenyl)-1-methyl-1H-indole-3-carboxamide-B(C_6F_5)$_3$ adduct. (**1a**·B(C_6F_5)$_3$)

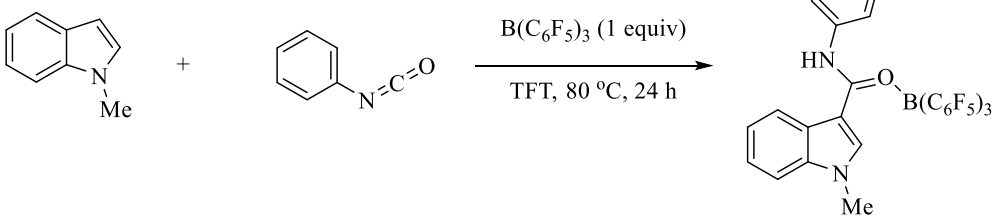




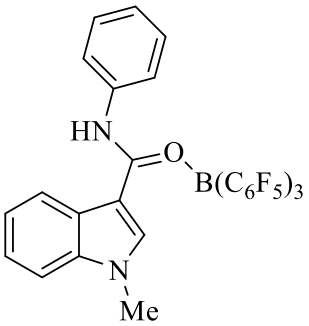
Synthesised in accordance with *General Procedure a* using B(C_6F_5)$_3$ (1 equiv, 51 mg, 0.1 mmol), 4-chlorophenyl isocyanate (2 equiv, 31 mg, 0.20 mmol), and *N*-methylindole (1 equiv, 12 µL, 0.1 mmol,) in TFT to afford **1a**·B(C_6F_5)$_3$. The rection mixture was kept inside the glovebox for crystallisation. After several days, light pink crystals formed. The crystals were collected and washed with pentane. Yield: 36 mg, 0.05 mmol, 45%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.78 (br., s, 1H, NH), 7.72 (d, *J*=7.9 Hz, 1H, Ar–CH), 7.66 (s, 1H, CH), 7.46–7.32 (m, 7H, Ar–CH), 3.84 (s, 3H, NMe); ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -1.67; ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -135.15 (d, *J* = 20.0 Hz, 2F), -157.06 (t, *J* = 19.8 Hz, 1F), -163.72 (t, *J* = 18.4 Hz, 2F).

Synthesis of 1-methyl-N-phenyl-1H-indole-3-carboxamide-B(C_6F_5)$_3$ adduct (**1b**·B(C_6F_5)$_3$).



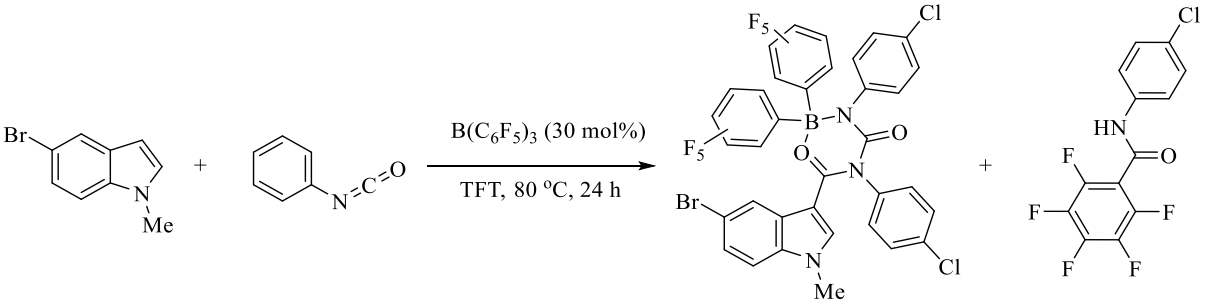
Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (1 equiv, 51 mg, 0.1 mmol,), phenyl isocyanate (2 equiv, 22 µL, 0.2 mmol,), and *N*-methylindole (1 equiv, 13 µL, 0.1 mmol,) in TFT to afford **1b**·$B(C_6F_5)_3$. The reaction mixture was kept inside the glovebox for crystallisation. After several days, light pink crystals formed. The crystals were collected and washed with pentane. Yield: 18 mg, 0.02 mmol, 24%.

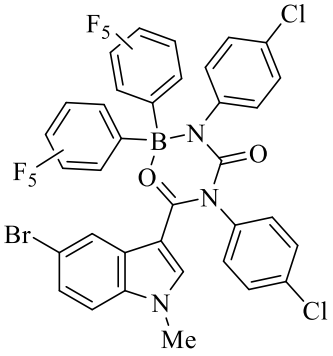


^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.86 (br., s, 1H, NH), 7.68 (d, *J* = 7.9 Hz, 1H, Ar–CH), 7.64 (s, 1H, CH), 7.47–7.31 (m, 8H, Ar–CH), 3.82 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.2, 137.5, 135.9, 134.8, 129.5, 126.7, 124.4, 124.1, 123.2, 122.1, 118.7, 111.2, 107.4, 33.7 (NMe);* ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -2.01; ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -135.05 (br., 2F), -157.45 (br., 1F), -163.96 (br., 2F).

*The C_6F_5 carbon atoms could not be detected in ^{13}C NMR in sufficient intensity to assign them.

*Synthesis of **2** and **3***



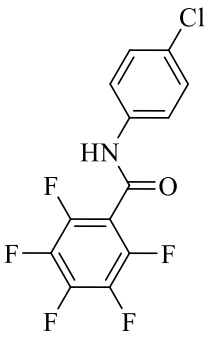


Complex **2** was synthesized by *General Procedure a* using $B(C_6F_5)_3$ (0.3 equiv, 15 mg, 0.03 mmol), 4-chlorophenyl isocyanate (1.5 equiv, 23 mg, 0.15 mmol,), and 5-bromo-1-methylindole (1 equiv, 21 mg, 0.1 mmol,) in TFT to afford **2** and **3**. The crude reaction mixture was purified via preparative thin layer chromatography using hexane/ethyl acetate as eluent. Compound **2** was obtained as a light pink solid. Yield: 10 mg, 0.01 mmol, 39%.**

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.19 (s, 1H, Ar–CH), 7.62 (d, *J* = 8.5 Hz, 2H, Ar–CH), 7.52–7.39 (m, 3H, Ar–CH), 7.20 (m, 5H, Ar–CH), 5.94 (s, 1H, indole C2), 3.66 (s, 3H, NMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 167.5, 152.7, 137.6, 136.6, 135.4, 135.3, 135.1, 132.0, 130.5, 129.9, 129.2, 126.9, 125.5, 121.7, 116.8, 111.3, 108.3, 33.9;* ^{11}B NMR (128 MHz,

$CDCl_3$) δ: 3.7; ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -136.72 (td, *J* = 22.6, 9.4 Hz, 2F), -155.10 (t, *J* = 20.2 Hz, 1F), -162.85 (td, *J* = 23.9, 9.9 Hz, 2F). HRMS (ES+) $[M+H]^+$ $[C_{35}H_{16}BBrCl_2F_{10}N_3O_2]^+$: calculated 861.9716, found 861.9739.

Compound **3** was obtained as a pinkish-white solid. Yield: 4 mg, 0.0124 mmol, 41%.**

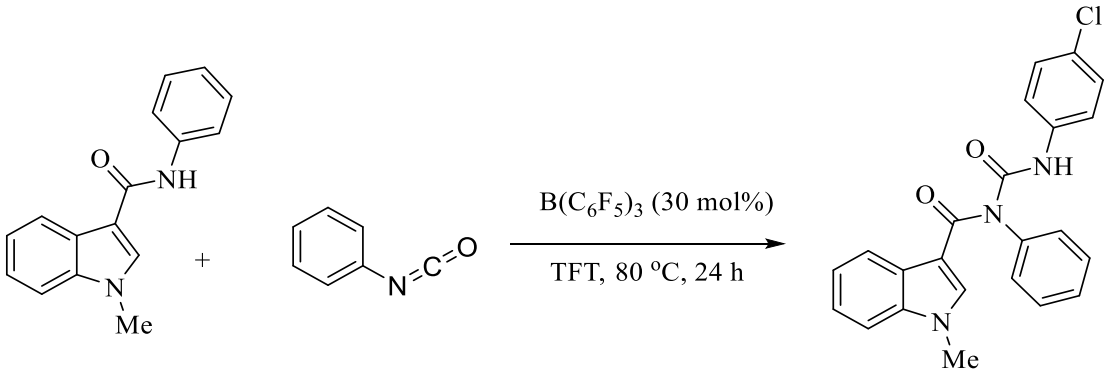


^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.74 (br., s, 1H, NH), 7.57–7.49 (m, 2H, Ar–CH), 7.39–7.31 (m, 2H, Ar–CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 155.4 (C=O), 135.3, 131.1, 129.5, 121.8;* ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -139.74–139.96 (m, 2F), -149.06 (tt, *J* = 20.9, 3.5 Hz, 1F), -159.19 (tt, *J* = 20.9, 5.9 Hz, 2F); IR ν_{max} (cm^{-1}): 3255, 3188, 1672 (C=O), 1521, 1502. HRMS (ES-) $[M-H]^-$ $[C_{13}H_4ClF_5NO]^-$: calculated 319.9902, found 319.9908.

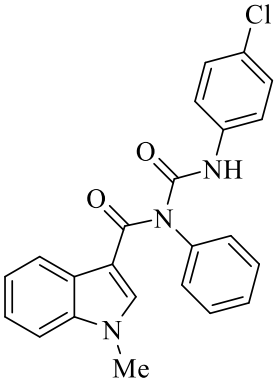
*The C_6F_5 carbons could not be detected in ^{13}C NMR in sufficient intensity to assign them.

**Yields are calculated based on the amount of $B(C_6F_5)_3$ used.

Synthesis of N-((4-chlorophenyl)carbamoyl)-1-methyl-N-phenyl-1H-indole-3-carboxamide, (**4**).



Synthesised in accordance with *General Procedure a* using $B(C_6F_5)_3$ (0.3 equiv, 15 mg, 0.03 mmol), 4-chlorophenyl isocyanate (0.15 equiv, 23 mg, 0.15 mmol,), and **1b** (1 equiv, 25 mg, 0.1 mmol) in TFT to afford **4**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. Compound **4** was obtained as a white solid. Yield: 10 mg, 0.02 mmol, 21%.

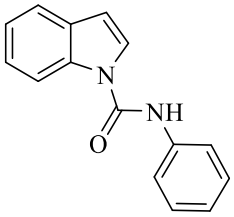


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 12.16 (br., s, 1H, NH), 8.49–8.46 (m, 1H, Ar–CH), 7.63–7.59 (m, 2H, Ar–CH), 7.54–7.49 (m, 3H Ar–CH), 7.43–7.39 (m, 2H, Ar–CH), 7.36 –7.27 (m, 5H, Ar–CH), 5.49 (s, 1H, CH), 3.49 (s, 3H, NMe); ^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ: 168.4, 153.2, 139.4, 137.0, 136.3, 135.0, 130.8, 129.6, 129.5, 129.2, 129.1, 128.9, 123.6, 122.84, 122.80, 121.6, 109.7, 108.8, 33.5; IR ν_{max} (cm^{-1}): 2924, 2853, 2349, 1709 (C=O), 1581, 1515 (C=O), 1490, 1359, 1234, 1151, 1109, 748. HRMS (ES+) $[M+H]^+$ $[C_{23}H_{19}ClN_3O_2]^+$: calculated 404.1166, found 404.1164.

2.6 Synthesis and spectral characterisation of *N*–carboxamidated products

Synthesis of N-phenyl-1H-indole-1-carboxamide (**5a**)[7]

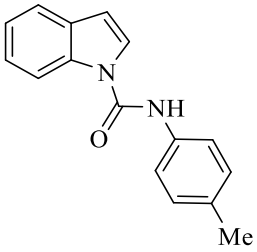
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), indole (12 mg, 0.10 mmol), and phenylisocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5a**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5a** was obtained as a white solid. Yield: 22 mg, 0.09 mmol, 93%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.11 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar–CH), 7.64 (dt, *J* = 7.8, 1.3, 0.8 Hz, 1H, Ar–CH), 7.56 (d, *J* = 3.7 Hz, 1H, indole C2), 7.57–7.50 (m, 2H, Ar–CH), 7.43–7.32 (m, 4H, Ar–CH), 7.29–7.25 (m, 1H, Ar–CH), 7.21–7.17 (m, 1H, Ar–CH), 6.69 (dd, *J* = 3.7, 0.8 Hz, 1H, indole C3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 149.6, 137.2, 135.2, 130.6, 129.5, 125.0, 124.7, 124.2, 122.8, 121.6, 120.5, 114.1, 107.9. Data agrees with literature values.[7]

Synthesis of N-(p-tolyl)-1H-indole-1-carboxamide (**5b**)[8]

Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), indole (12 mg, 0.10 mmol), and *p*-tolyl isocyanate (19 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5b**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5b** was obtained as a brown solid. Yield: 25 mg, 0.07 mmol, 72%.

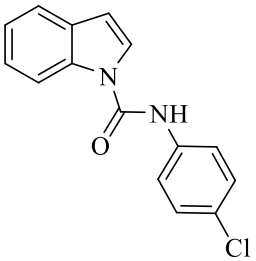


^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.02 (d, *J* = 9.2 Hz, 1H, Ar–CH), 7.53 (dd, *J* = 7.8, 1.0 Hz, 1H, Ar–CH), 7.44 (d, *J* = 3.6 Hz, 1H, indole C2), 7.33 (br, s, 1H, NH), 7.30 (d, *J* = 8.4 Hz, 2H, Ar–CH), 7.24 (t, *J* = 8.4 Hz, 1H, Ar–CH), 7.19–7.14 (m, 1H, Ar–CH), 7.07 (d, *J* = 8.1 Hz,

2H, Ar–CH), 6.55 (d, *J* = 3.6 Hz, 1H, indole C3), 2.25 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 149.9, 135.2, 134.7, 134.5, 130.4, 129.8, 124.5, 124.3, 122.7, 121.5, 120.8, 114.2, 107.7, 21.0. Data agrees with literature values.[8]

Synthesis of N-(4-chlorophenyl)-1H-indole-1-carboxamide (**5c**)[8]

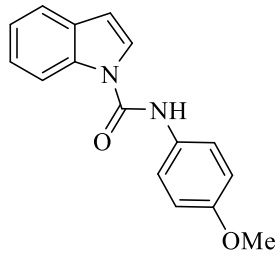
Synthesised in accordance with *General Procedure a* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), indole (12 mg, 0.10 mmol), and 4-chlorophenyl isocyanate (23 mg, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5c**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent The desired compound **5c** was obtained as an off-white solid. Yield: 25 mg, 0.09 mmol, 93%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.99 (d, *J* = 9.3 Hz, 1H, Ar–CH), 7.52 (d, *J* = 8.8 Hz, 1H, indole C3), 7.40 (d, *J* = 3.7 Hz, 1H, Ar–CH), 7.39 (br., s, 1H, NH), 7.37–7.33 (m, 2H, Ar–CH), 7.27–7.19 (m, 3H, Ar–CH), 7.18–7.13 (m, 1H, Ar–CH), 6.55 (d, *J* = 3.7 Hz, 1H, indole C2); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 149.7, 135.7, 135.2, 130.5, 130.1, 129.4, 124.7, 124.0, 123.0, 121.9, 121.6, 114.2, 108.2. Data agrees with literature values.[8]

Synthesis of N-(4-methoxyphenyl)-1H-indole-1-carboxamide (**5d**)[9]

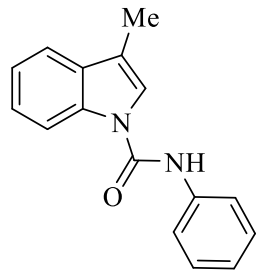
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), indole (12 mg, 0.10 mmol), and 4-methoxy phenyl isocyanate (19 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5d** was obtained as an off-white solid. Yield: 25 mg, 0.09 mmol, 94%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.01 (d, *J* = 8.1 Hz, 1H, Ar–CH), 7.51 (d, *J* = 7.8 Hz, 1H, Ar–CH), 7.42 (d, *J* = 3.7 Hz, 1H, indole C2), 7.33 (br., s, 1H, NH), 7.27 (d, *J* = 9.0 Hz, 2H, Ar–CH), 7.22 (t, *J* = 8.4 Hz, 1H, Ar-CH), 7.16–7.12 (m, 1H, Ar–CH), 6.76 (d, *J* = 9.0 Hz, 2H, Ar–CH), 6.52 (d, *J* = 3.7 Hz, 1H, indole C3), 3.68 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 157.1, 150.2, 135.3, 130.4, 129.9, 124.5, 124.2, 122.9, 122.7, 121.5, 114.5, 114.2, 107.7, 55.7. Data agrees with literature values.[9]

Synthesis of 3-methyl-N-phenyl-1H-indole-1-carboxamide (**5e**)

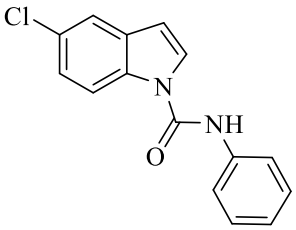
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), 3-methylindole (13 mg, 0.10 mmol), and methoxy-phenylisocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5e**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5e** was obtained as an off-white solid. Yield: 21 mg, 0.08 mmol, 84%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.04 (dt, *J* = 8.3, 0.9 Hz, 1H, Ar–CH), 7.48–7.44 (m, 1H, Ar–CH), 7.43 (dd, *J* = 8.6, 1.1 Hz, 2H, Ar–CH), 7.31–7.28 (m, 1H, Ar–CH), 7.29–7.23 (m, 3H, Ar–CH), 7.20 (s, 1H, indole C2), 7.18-7.17 (m, 1H, Ar–CH), 7.09–7.04 (m, 1H, Ar–CH), 2.20 (d, *J* = 1.3 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 149.8, 137.3, 135.7, 131.2, 129.3, 124.72, 124.67, 122.4, 121.0, 120.5, 119.5, 117.3, 114.4, 9.8; IR ν_{max} (cm^{-1}): 3246, 3107, 3048, 2965, 2916, 2857, 1670 (C=O), 1597, 1528, 1447, 1343, 1215, 1088. HRMS (EI) [M] [$C_{16}H_{14}ON_2$]: calculated. 250.1101, found: 250.1102.

Synthesis of 5-chloro-N-phenyl-1H-indole-1-carboxamide (**5f**)

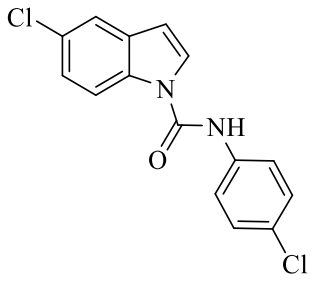
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), 5-chloro-indole (15 mg, 0.10 mmol), phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5f**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5f** was obtained as a green solid. Yield: 23 mg, 0.09 mmol, 85%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.09 (d, *J* = 8.8 Hz, 1H, Ar–CH), 7.58 (d, *J* = 2.7 Hz, 1H, Ar–CH), 7.53 (d, *J* = 3.7 Hz, 1H, Indole C2), 7.52–7.49 (m, 2H, Ar–CH), 7.41–7.36 (m, 2H, Ar–CH), 7.34 (br., s, 1H, NH), 7.29 (dd, *J* = 8.8, 2.1 Hz, 1H, Ar–CH), 7.21–7.17 (m, 1H, Ar–CH), 6.61 (dd, *J* = 3.7, 0.8 Hz, 1H, Indole C3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 149.4, 136.9, 133.9, 131.4, 129.5, 128.5, 125.2, 125.0, 124.9, 121.0, 120.7, 115.6, 107.4; IR ν_{max} (cm^{-1}): 3294, 3138, 3063, 1678 (C=O), 1599, 1574, 1526, 1445, 1364, 1333, 1266, 1248, 1200, 1092, 1067, 1032. HRMS (EI) [M] [$C_{15}H_{11}ON_2{}^{35}Cl$]: calculated. 270.0554, found: 270.0552.

Synthesis of 5-chloro-N-(4-chlorophenyl)-1H-indole-1-carboxamide (**5g**)

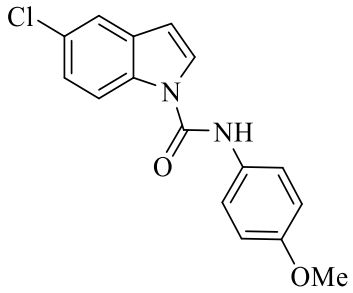
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), 5-chloro-indole (15 mg, 0.10 mmol), and 4-chloro-phenylisocyanate (23 mg, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5g**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5g** was obtained as an off-white solid. Yield: 30 mg, 0.10 mmol, 98%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.06 (d, *J* = 8.9 Hz, 1H, Ar–CH), 7.57 (d, *J* = 2.1 Hz, 1H, Ar–CH), 7.49 (d, *J* = 3.7 Hz, 1H, Indole C2), 7.46–7.42 (m, 2H, Ar–CH), 7.36 (br., s, 1H, NH), 7.35–7.31 (m, 2H, Ar–CH), 7.29 (dd, *J* = 8.9, 2.1 Hz, 1H, Ar–CH), 6.60 (d, *J* = 3.8 Hz, 1H, Indole C3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 149.3, 135.5, 133.9, 131.4, 130.4, 129.4, 128.6, 125.0, 124.8, 122.0, 121.0, 115.6, 107.7; IR ν_{max} (cm^{-1}): 330, 1676 (C=O), 1593, 1518, 1493, 1449, 1400, 1329, 1285, 1244, 1200, 1090, 1067, 1015. HRMS (EI) [M] [$C_{15}H_{10}ON_2{}^{35}Cl_2$]: calculated. 304.0165, found: 304.0169.

Synthesis of 5-chloro-N-(4-methoxyphenyl)-1H-indole-1-carboxamide (**5h**)

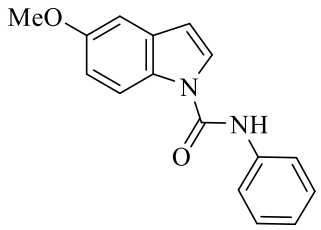
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), 5-chloro-indole (15 mg, 0.10 mmol), and 4-methoxy-phenyl isocyanate (19 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5h** was obtained as a off-white solid. Yield: 16 mg, 0.05 mmol, 53%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.10 (d, *J* = 8.9 Hz, 1H, Ar–CH), 7.58 (d, *J* = 2.1 Hz, 1H, Ar–CH), 7.52 (d, *J* = 3.7 Hz, 1H, Indole C2), 7.43–7.36 (m, 2H, Ar–CH), 7.29 (dd, *J* = 8.9, 2.1 Hz, 1H, Ar–CH), 7.25 (br., s, 1H, NH), 6.96–6.87 (m, 2H, Ar–CH), 6.61 (dd, *J* = 3.7, 0.8 Hz, 1H, Indole C3), 3.81 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 157.2, 149.8, 133.9, 131.3, 129.6, 128.3, 124.9, 124.8, 123.0, 120.9, 115.6, 114.6, 107.3, 55.7; IR ν_{max} (cm^{-1}): 3320, 2924, 2853, 1937, 1881, 1709, 1678 (C=O), 1601, 1572, 1514, 1474, 1441, 1414, 1360, 1333, 1302, 1265, 1244, 1198, 1173, 1109, 1090, 1063, 1032. HRMS (ES+) [M+H] [$C_{16}H_{14}O_2N_2{}^{35}Cl$]$^+$: calculated. 301.0744, found: 301.0735.

Synthesis of 5-methoxy-N-phenyl-1H-indole-1-carboxamide (**5i**)

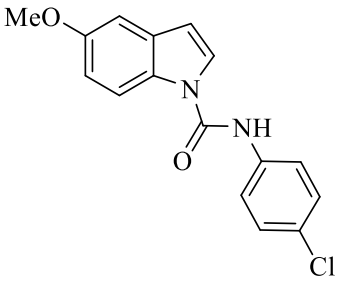
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), 5-methoxy indole (15 mg, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5i**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5i** was obtained as an off-white solid. Yield: 19 mg, 0.07 mmol, 71%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.01 (d, *J* = 9.8 Hz, 1H, Ar–CH), 7.53–7.48 (m, 3H, Ar–CH and Indole C2), 7.43 (br., s, 1H, NH), 7.37 (t, *J* = 8.1 Hz, 2H, Ar–CH), 7.20–7.14 (m, 1H, Ar–CH), 7.07 (d, *J* = 2.4 Hz, 1H, Ar–CH), 6.96 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar–CH), 6.58 (d, *J* = 3.5 Hz, 1H, Indole C3), 3.86 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 155.9, 149.7, 137.2, 131.3, 130.2, 129.4, 124.9, 124.6, 120.6, 115.1, 113.6, 107.7, 103.8, 55.8; IR ν_{max} (cm^{-1}): 3245, 3066, 1671 (C=O), 1594, 1542, 1471, 1438, 1308, 1263, 1202, 1148, 1115, 1021. HRMS (EI) [M] [$C_{16}H_{14}O_2N_2$]: calculated. 266.1050, found: 266.1049.

Synthesis of N-(4-chlorophenyl)-5-methoxy-1H-indole-1-carboxamide (**5j**)

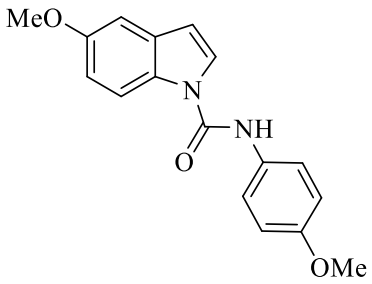
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), 5-methoxy indole (15 mg, 0.10 mmol), and 4-chloro phenyl isocyanate (23 mg, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5j**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5j** was obtained as an off-white solid. Yield: 10 mg, 0.03 mmol, 33%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.00 (d, *J* = 9.0 Hz, 1H, Ar–CH), 7.50 (d, *J* = 3.7 Hz, 1H, Indole C2), 7.49–7.45 (m, 2H, Ar–CH), 7.37–7.33 (m, 2H, Ar–CH), 7.30 (br., s, 1H, NH), 7.08 (d, *J* = 2.5 Hz, 1H, Ar–CH), 6.98 (dd, *J* = 9.0, 2.6 Hz, 1H, Ar–CH), 6.62 (dd, *J* = 3.6, 0.8 Hz, 1H, Ar–CH), 3.87 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 156.1, 149.5, 135.8, 131.3, 130.1, 130.0, 129.4, 124.4, 121.7, 115.0, 113.8, 108.1, 103.9, 55.9; IR ν_{max} (cm^{-1}): 2833, 2351, 1715, 1668 (C=O), 1645, 1634, 1622, 1614, 1595, 1568, 1506, 1495, 1472, 1457, 1445, 1402, 1368, 1337, 1310, 1290, 1263, 1209, 1182, 1152, 1121, 1106, 1094, 1020, 1013. HRMS (EI) [M] [$C_{16}H_{13}O_2N_2{}^{35}Cl$]: calculated. 300.0660, found: 300.0663.

Synthesis of 5-methoxy-N-(4-methoxyphenyl)-1H-indole-1-carboxamide (**5k**)

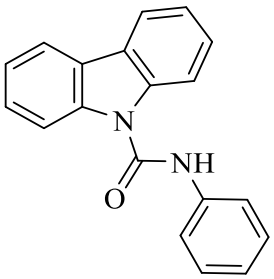
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), 5-methoxy-indole (15 mg, 0.10 mmol), and 4-methoxy-phenylisocyanate (19 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5k**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5k** was obtained as an off-white solid. Yield: 17 mg, 0.06 mmol, 57%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.02 (d, *J* = 9.0 Hz, 1H, Ar–CH), 7.51 (d, *J* = 3.6 Hz, 1H, Indole C2), 7.43–7.37 (m, 2H, Ar–CH), 7.22 (br., s, 1H, NH), 7.08 (d, *J* = 2.6 Hz, 1H, Ar–CH), 6.97 (dd, *J* = 9.0, 3.0 Hz, 1H, Ar–CH), 6.94–6.87 (m, 2H, Ar–CH), 6.60 (dd, *J* = 3.6, 0.8 Hz, 1H, Indole C3), 3.86 (s, 3H, OMe), 3.81 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 157.1, 155.9, 150.1, 131.3, 130.2, 130.0, 124.6, 122.9, 115.1, 114.6, 113.7, 107.6, 103.7, 55.8, 55.7; IR ν_{max} (cm^{-1}): 3310, 3138, 2999, 2936, 2833, 1672 (C=O), 1613, 1601, 1512, 1474, 1414, 1368, 1335, 1298, 1254, 1211, 1198, 1150, 1121, 1032. HRMS (EI) [M] [$C_{17}H_{16}O_3N_2$]: calculated. 296.1055, found: 296.1056.

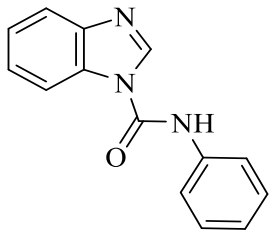
Synthesis of N-phenyl-9H-carbazole-9-carboxamide (**5l**)

Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), carbazole (16 mg, 0.10 mmol), and phenylisocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5l**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5l** was obtained as a white solid. Yield: 24 mg, 0.08 mmol, 84%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.04 (d, *J* = 10.8 Hz, 4H, Ar–CH), 7.62–7.58 (m, 2H, Ar–CH), 7.53 (br., s, 1H, NH), 7.52–7.47 (m, 2H, Ar–CH), 7.47–7.41 (m, 2H, Ar–CH), 7.40–7.34 (m, 2H, Ar–CH), 7.23–7.19 (m, 1H, Ar–CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 150.2, 138.3, 137.3, 129.5, 127.3, 125.4, 124.9, 122.8, 120.5, 120.1, 113.6; IR ν_{max} (cm^{-1}): 3260, 1668 (C=O), 1599, 1526, 1445, 1352, 1327, 1310, 1256, 1236, 1219, 1200, 1120, 1078, 1028. HRMS (ES+) [M+H] $[C_{19}H_{15}ON_2]^+$: calculated. 287.1184, found: 287.1186.

Synthesis of N-phenyl-1H-benzo[d]imidazole-1-carboxamide (**5m**)

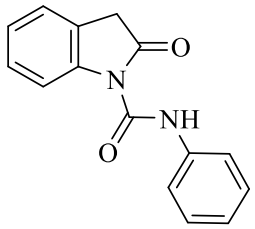


Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), benzoimidazole (12 mg, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5m**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5m** was obtained as a white solid. Yield: 23 mg, 0.10 mmol, 97%.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 9.11 (br., s, 1H, NH), 8.48 (dd, *J* = 8.5, 0.9 Hz, 1H, Ar–CH), 8.12 (s, 1H, C2), 7.76 (dt, *J* = 8.0, 1.0 Hz, 1H, Ar–CH), 7.71–7.64 (m, 2H, Ar–CH), 7.62 –7.53 (m, 1H, Ar–CH), 7.44–7.36 (m, 2H, Ar–CH), 7.37–7.30 (m, 1H, Ar–CH), 7.17 (tt, *J* = 7.4, 1.1 Hz, 1H, Ar–CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 148.9, 139.3, 137.9, 137.3, 129.4, 129.3, 126.0, 124.5, 123.7, 121.2, 119.8, 115.0; IR ν_{max} (cm^{-1}): 3358, 1722 (C=O), 1591, 1522, 1497, 1466, 1441, 1427, 1416, 1368, 1352, 1325, 1310, 1297, 1269, 1229, 1217, 1175, 1156, 1142, 1113, 1080, 1034, 1020, 1009. HRMS (EI) [M] [$C_{14}H_{11}ON_3$]: calculated. 237.0897, found: 237.0895.

Synthesis of 2-oxo-N-phenylindoline-1-carboxamide (**5n**)[10]

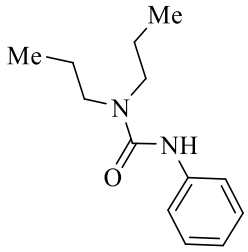
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), oxindole (13 mg, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5n**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5n** was obtained as an off-white solid. Yield: 12 mg, 0.05 mmol, 48%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 10.69 (br., s, 1H, NH), 8.32 (d, *J* = 8.2 Hz, 1H, Ar–CH), 7.64–7.53 (m, 2H, Ar–CH), 7.40–7.33 (m, 3H, Ar–CH), 7.29 (d, *J* = 8.9 Hz, 1H, Ar–CH), 7.19 (t, *J* = 8.0 Hz, 1H, Ar–CH), 7.15 (tt, *J* = 7.4, 1.2 Hz, 1H, Ar–CH), 3.81 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 177.8, 149.6, 141.7, 137.2, 129.2, 128.6, 124.9, 124.7, 124.1, 123.0, 120.7, 116.9, 37.2. Data agrees with literature values.[10]

Synthesis of 3-phenyl-1,1-dipropylurea (**5o**)[10]

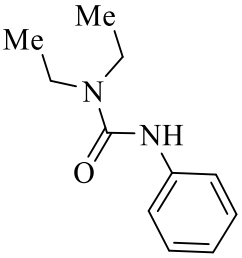
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), dipropylamine (14 µL, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5o**. The crude reaction mixture was purified *via* silica-plug using hexane/ethyl acetate as eluent. The desired compound **2o** was obtained as a white solid. Yield: 21 mg, 0.10 mmol, 96%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.33–7.28 (m, 2H, Ar–CH), 7.23–7.17 (m, 2H, Ar–CH), 6.94 (tt, *J* = 7.4, 1.2 Hz, 1H, Ar–CH), 6.25 (br., s, 1H, NH), 3.19 (t, *J* = 7.8 Hz, 4H, α-CH_2), 1.57 (m, *J* = 7.4 Hz, 4H, *β*-CH_2), 0.87 (t, *J* = 7.4 Hz, 6H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 155.0, 139.4, 128.9, 122.8, 119.8, 49.5, 22.0, 11.5. Data agrees with literature values.[10]

Synthesis of 1,1-diethyl-3-phenylurea (**5p**)[11]

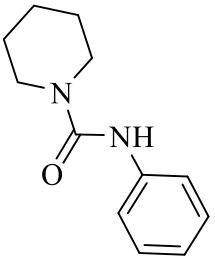
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), diethylamine (14 µL, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5p**. The crude reaction mixture was purified *via* silica-plug using hexane/ethyl acetate as eluent. The desired compound **5p** was obtained as a white solid. Yield: 19 mg, 0.10 mmol, 99%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.35–7.29 (m, 2H, Ar–CH), 7.24–7.17 (m, 2H, Ar–CH), 6.94 (tt, *J* = 7.3, 1.2 Hz, 1H, Ar–CH), 6.25 (br., s, 1H, NH), 3.30 (q, *J* = 7.1 Hz, 4H, *α*-CH_2), 1.15 (t, *J* = 7.2 Hz, 6H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 154.7, 139.4, 128.9, 122.9, 119.9, 41.7, 14.1. Data agrees with literature values.[11]

Synthesis of N-phenylpiperidine-1-carboxamide (**5q**)[11]

Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), piperidine (10 µL, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5q**. The crude reaction mixture was purified *via* silica-plug using hexane/ethyl acetate as eluent. The desired compound **5q** was obtained as a white solid. Yield: 16 mg, 0.08 mmol, 78%.

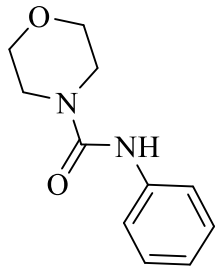


^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.31–7.25 (m, 2H, Ar–CH), 7.23–7.16 (m, 2H, Ar–CH), 6.93 (tt, *J* = 7.3, 1.1 Hz, 1H, Ar–CH), 6.39 (br., s, 1H, NH), 3.37–3.35

(m, 4H, CH_2), 1.55–1.51 (m, 6H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 155.1, 139.4, 128.9, 122.9, 119.9, 45.3, 25.8, 24.5. Data agrees with literature values.[11]

Synthesis of N-phenylmorpholine-4-carboxamide (**5r**)[11]

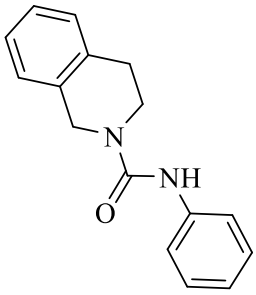
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), morpholine (9 µL, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5r**. The crude reaction mixture was purified *via* silica-plug using hexane/ethyl acetate as eluent. The desired compound **5r** was obtained as a white solid. Yield: 16 mg, 0.078 mmol, 78%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.28–7.23 (m, 2H, Ar–CH), 7.23–7.18 (m, 2H, Ar–CH), 6.98 (tt, *J* = 7.3, 1.3 Hz, 1H, Ar–CH), 6.49 (br., s, 1H, NH), 3.63 (t, *J* = 4.6 Hz, 4H, N–CH_2), 3.38 (t, *J* = 5.2 Hz, 4H, OCH_2); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 155.3, 138.8, 129.0, 123.5, 120.3, 66.6, 44.3. Data agrees with literature values.[11]

Synthesis of N-phenyl-3,4-dihydroisoquinoline-2(1H)-carboxamide (**5s**)[11]

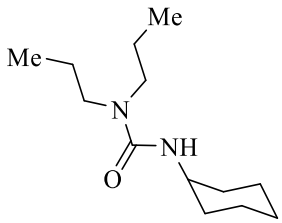
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), tetrahydroisoquinoline (13 µL, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5s**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **5s** was obtained as an off-white solid. Yield: 23 mg, 0.09 mmol, 91%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.42–7.38 (m, 2H, Ar–CH), 7.31–7.27 (m, 2H, Ar–CH), 7.23–7.16 (m, 3H, Ar–CH), 7.15–7.12 (m, 1H, Ar–CH), 7.04 (tt, *J* = 7.3, 1.2 Hz, 1H, Ar–CH), 6.56 (br., s, 1H, NH), 4.66 (s, 2H, α-N benzylic CH_2), 3.72 (t, *J* = 5.9 Hz, 2H), 2.92 (t, *J* = 5.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 155.1, 139.1, 135.1, 133.2, 129.0, 128.5, 126.9, 126.6, 126.5, 123.2, 120.2, 45.8, 41.7, 29.1. Data agrees with literature values.[11]

Synthesis of 3-cyclohexyl-1,1-dipropylurea (**5t**)[12]

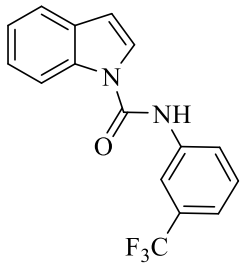
Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), di-propylamine (14 µL, 0.10 mmol), and cyclohexyl isocyanate (19 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **2t**. The crude reaction mixture was purified *via* silica-plug using hexane/ethyl acetate as eluent. The desired compound **2t** was obtained as a white solid. Yield: 15 mg, 0.07 mmol, 66%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 4.11 (br., s, 1H, NH), 3.63 (m, 1H, CH), 3.11 (t, *J* = 8.2 Hz, 4H, α-N-CH_2), 1.97–1.89 (m, 2H, CH_2), 1.69–1.62 (m, 2H, Cy-CH_2), 1.54 (m, *J* = 7.4 Hz, 4H, β-N-CH_2), 1.41–1.28 (m, 2H, Cy-CH_2), 1.24 (s, 1H, Cy-CH_2), 1.19–1.02 (m, 3H, Cy-CH_2), 0.88 (t, *J* = 7.4 Hz, 6H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 157.2, 49.3, 49.1, 34.2, 25.9, 25.2, 21.9, 11.5. Data agrees with literature values.[12]

Synthesis of N-(3-(trifluoromethyl)phenyl)-1H-indole-1-carboxamide (**5u**)[8]

Synthesised in accordance with *General Procedure b* using BCl_3 (1 M in hexane, 0.85 ml, 0.85 mmol), indole (1 g, 8.5 mmol), and 3-trifluoromethyl-phenyl isocyanate (1.8 mL, 12.8 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5u**. The crude reaction mixture was purified *via* coloumn chromatography using hexane/ethyl acetate as eluent. The desired compound **5u** was obtained as an off-white solid. Yield: 2.0 g, 6.97 mmol, 82%.

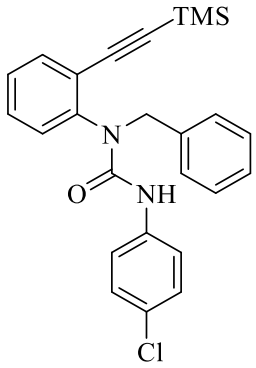


^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.05 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar–CH), 7.77 (br., s, 1H, NH), 7.70–7.64 (m, 1H, Ar–CH), 7.57 (dt, *J* = 7.8, 1.0 Hz, 1H, indole C2), 7.46 (d, *J* = 3.6 Hz, 2H, Ar-CH), 7.43 (t, *J* = 8.0 Hz, 1H, Ar–CH), 7.36 (m, 1H, Ar–CH), 7.30 (m, 1H, Ar-CH), 7.25–7.18 (m, 1H, Ar–CH), 6.63 (dd, *J* = 3.7, 0.8 Hz, 1H, Indole C3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 149.6, 137.8, 135.3, 131.9 (q, $J_{C–F}$ = 32.7 Hz), 130.5, 130.0, 124.9, 123.9, (q, $J_{C–F}$ = 272.4 Hz), 123.6, 123.5, 123.1, 122.8, 121.7, 121.54-121.45 (q, $J_{C–F}$ = 3.8 Hz), 117.2 (q, *J* = 4.0 Hz), 114.2, 108.5. Data agrees with literature values.[8]

2.7 Synthesis and spectral characterisation of *N*–carboxamidated 2-alkynyl products

Synthesis of 1-benzyl-3-(4-chlorophenyl)-1-(2-((trimethylsilyl)ethynyl)phenyl)urea (**6a**)

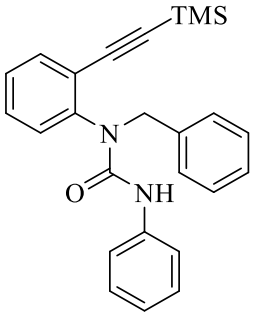
Synthesised in accordance with *General Procedure c* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), *N*-benzyl-2-((trimethylsilyl)ethynyl)aniline (28 mg, 0.10 mmol), and 4-chlorophenyl isocyanate (23 mg, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **6a**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **6a** was obtained as an off-white solid. Yield: 26 mg, 0.06 mmol, 61%.



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.56–7.52 (m, 1H, Ar–CH), 7.29–7.19 (m, 9H, Ar–CH), 7.15 (s, 2H, Ar–CH), 7.00–6.95 (m, 1H, Ar–CH), 6.01 (br, s, 1H, NH), 5.28 (br., s, 1H, benzyl CH)*, 4.53 (br., s, 1H, benzyl CH), 0.13 (s, 9H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ: 154.1, 142.5, 138.0, 137.8, 134.2, 130.1, 130.0, 129.11, 129.08, 128.8, 128.5, 128.0, 127.5, 123.6, 121.0, 101.8, 100.3, 52.5, -0.2;[13] IR ν_{max} (cm^{-1}): 3320, 2957, 2158, 1661 (C=O), 1591, 1559, 1506, 1493, 1481, 1458, 1447, 1427, 1398, 1364, 1321, 1300, 1283, 1271, 1262, 1242, 1219, 1198, 1173, 1113, 1090, 1076, 1040, 1030, 1013. HRMS (ES+) [M+H] $[C_{25}H_{26}OSiCl]^+$: calculated. 433.1503, found: 433.1495.

Synthesis of 1-benzyl-3-phenyl-1-(2-((trimethylsilyl)ethynyl)phenyl)urea (**6b**)

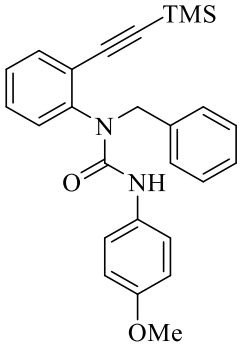
Synthesised in accordance with *General Procedure c* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), *N*-benzyl-2-((trimethylsilyl)ethynyl)aniline (28 mg, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **6b**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **6b** was obtained as a white solid. Yield: 19 mg, 0.05 mmol, 48%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.60–7.53 (m, 1H, Ar–CH), 7.32–7.19 (m, 11H, Ar–CH), 7.03–6.94 (m, 2H, Ar–CH), 6.03 (br., s, 1H, NH), 5.34 (br., s, 1H, benzyl CH), 4.62 (br s, 1H, benzyl CH), 0.16 (s, 9H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 154.3, 142.7, 139.2, 138.2, 134.2, 130.1, 130.0, 129.1, 128.8, 128.4, 128.3, 127.4, 123.6, 123.1, 119.8, 101.6, 100.5, 52.4, -0.2;[13] IR ν_{max} (cm^{-1}): 3428, 3061, 3030, 2957, 2160, 1674 (C=O), 1595, 1518, 1501, 1483, 1439, 1400, 1364, 1310, 1269, 1248, 1219, 1196, 1155, 1109, 1078, 1044, 1030. HRMS (ES+) [M+H] $[C_{25}H_{27}N_2OSi]^+$: calculated. 399.1893, found: 399.1886.

Synthesis of 1-benzyl-3-(4-methoxyphenyl)-1-(2-((trimethylsilyl)ethynyl)phenyl)urea (**6c**)

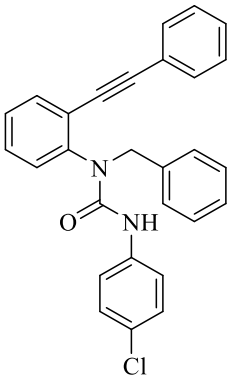
Synthesised in accordance with *General Procedure c* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), *N*-benzyl-2-((trimethylsilyl)ethynyl)aniline (28 mg, 0.10 mmol), and 4-methoxyphenyl isocyanate (19 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **6c**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **6c** was obtained as a light brown solid. Yield: 25 mg, 0.06 mmol, 58%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.56–7.52 (m, 1H, Ar–CH), 7.29–7.16 (m, 10H, Ar–CH), 7.02–6.96 (m, 1H, Ar–CH), 6.77 (d, J = 8.9 Hz, 2H, Ar–CH), 5.88 (br., s, 1H, NH), 5.32 (br., s, 1H, benzyl CH), 4.58 (br., s, 1H, benzyl CH) 3.74 (s, 3H, OMe), 0.17 (s, 9H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 155.9, 154.8, 142.9, 138.3, 134.2, 132.3, 130.2, 130.0, 129.1, 128.4, 128.2, 127.3, 123.6, 122.2, 114.1, 101.5, 100.6, 55.6, 52.4, -0.1;[13] IR ν_{max} (cm^{-1}): 3429, 2955, 2160, 1670. (C=O), 1595, 1510, 1483, 1464, 1447, 1410, 1356, 1296, 1219, 1196, 1179, 1109, 1074, 1032. HRMS (ES+) [M+H] $[C_{26}H_{29}N_2O_2Si]^+$: calculated. 429.1998, found: 429.1984.

Synthesis of 1-benzyl-3-(4-chlorophenyl)-1-(2-(phenylethynyl)phenyl)urea (**6d**)

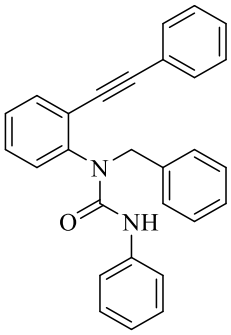
Synthesised in accordance with *General Procedure c* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), *N*-benzyl-2-(phenylethynyl)aniline (28 mg, 0.10 mmol), and 4-chlorophenyl isocyanate (23 mg, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **6d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **6d** was obtained as an off-white solid. Yield: 27 mg, 0.06 mmol, 62%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.63 (dd, *J* = 7.6, 1.7 Hz, 1H, Ar–CH), 7.44 (m, 2H, Ar–CH), 7.38–7.26 (m, 7H, Ar–CH), 7.26–7.18 (m, 5H, Ar–CH), 7.15 (d, *J* = 8.8 Hz, 2H, Ar–CH), 7.05 (d, *J* = 9.2 Hz, 1H, Ar–CH), 6.09 (br., s, 1H, NH), 5.37 (br., s, 1H, benzyl CH), 4.60 (br., s, 1H, benzyl CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 154.4, 141.9, 137.9, 137.6, 133.8, 131.9, 130.2, 129.8, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4, 128.0, 127.5, 123.8, 122.4, 121.1, 95.8, 85.0, 52.7;[13] IR ν_{max} (cm^{-1}): 3422, 3318, 3061, 3030, 2922, 2853, 1667 (C=O), 1591, 1508, 1491, 1447, 1398, 1358, 1304, 1285, 1234, 1200, 1177, 1159, 1090, 1070, 1042, 1026, 1011. HRMS (ES+) [M+H] $[C_{28}H_{22}N_2OCl]^+$: calculated. 437.1421, found: 429.1415.

Synthesis of 1-benzyl-3-phenyl-1-(2-(phenylethynyl)phenyl)urea (**6e**)

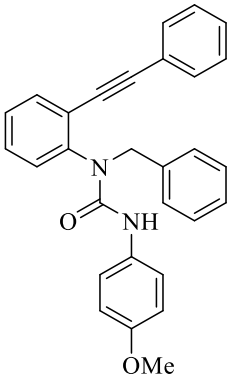
Synthesised in accordance with *General Procedure c* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), *N*-benzyl-2-(phenylethynyl)aniline (28 mg, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **6e**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **6e** was obtained as a yellow solid. Yield: 18 mg, 0.04 mmol, 45%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.65 (d, *J* = 7.7 Hz, 1H, Ar–CH), 7.48 (d, *J* = 1.6 Hz, 2H, Ar–CH), 7.33 (m, 9H, Ar–CH), 7.25–7.17 (m, 5H, Ar–CH), 7.06 (d, *J* = 7.7 Hz, 1H, Ar–CH), 7.01–6.95 (m, 1H, Ar–CH), 6.10 (br., s, 1H, NH), 5.35 (br., s, 1H, Benzyl CH), 4.65 (br., s, 1H, Benzyl CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 154.6, 142.2, 139.1, 138.2, 133.8, 132.0, 130.3, 129.8, 129.1, 128.93, 128.89, 128.6, 128.5, 128.4, 127.4, 124.0, 123.2, 122.6, 120.0, 95.8, 85.2, 52.6;[13] IR ν_{max} (cm^{-1}): 3426, 3321, 3061, 3030, 2959, 2924, 1674 (C=O), 1595, 1520, 1495, 1479, 1439, 1362, 1312, 1261, 1238, 1200, 1179, 1157, 1101, 1028. HRMS (ES+) [M+H] $[C_{28}H_{23}N_2O]^+$: calculated. 403.1810, found: 403.1802.

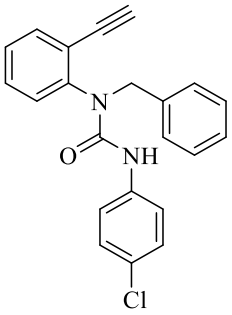
Synthesis of 1-benzyl-3-(4-methoxyphenyl)-1-(2-(phenylethynyl)phenyl)urea (**6f**)

Synthesised in accordance with *General Procedure c* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), *N*-benzyl-2-(phenylethynyl)aniline (28 mg, 0.10 mmol), and 4-methoxyphenyl isocyanate (19 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **6f**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **6f** was obtained as a brown oil. Yield: 21 mg, 0.05 mmol, 49%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.64 (dd, *J* = 7.6, 1.7 Hz, 1H, Ar–CH), 7.51–7.47 (m, 2H, Ar–CH), 7.37–7.28 (m, 7H, Ar–CH), 7.26–7.17 (m, 5H, Ar–CH), 7.07 (dd, *J* = 7.8, 1.5 Hz, 1H, Ar–CH), 6.76 (d, *J* = 9.0 Hz, 2H, Ar–CH), 5.98 (br., s, 1H, NH), 5.38 (br., s, 1H, benzyl CH), 4.66 (br., s, 1H, benzyl CH), 3.74 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 156.0, 155.1, 142.4, 138.3, 133.8, 132.1, 132.0, 130.3, 129.7, 129.1, 128.9, 128.52, 128.46, 128.4, 127.4, 123.9, 122.7, 122.5, 114.1, 95.6, 85.3, 55.6, 52.6;[13] IR ν_{max} (cm^{-1}): 3426, 3323, 3061, 3030, 2928, 2833, 2218, 1665(C=O), 1595, 1508, 1495, 1479, 1464, 1410, 1356, 1296, 1231, 1207, 1179, 1107, 1071, 1028. HRMS (ES+) [M+H] $[C_{29}H_{25}N_2O_2]^+$: calculated. 433.1916, found: 433.1909.



Synthesis of 1-benzyl-3-(4-chlorophenyl)-1-(2-ethynylphenyl)urea (**6g**)

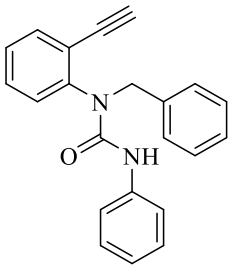
Synthesised in accordance with *General Procedure c* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), *N*-benzyl-2-ethynylaniline (21 mg, 0.10 mmol), and 4-chlorophenyl isocyanate (23 mg, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **6g**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **6g** was obtained as an off-white solid. Yield: 14 mg, 0.04 mmol, 39%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.58 (dd, *J* = 7.3, 2.0 Hz, 1H, Ar–CH), 7.28 (m, 2H, Ar–CH), 7.23–7.18 (m, 8H, Ar–CH), 7.16–7.13 (m, 2H, Ar–CH), 6.93 (dd, *J* = 7.3, 1.9 Hz, 1H, Ar–CH), 5.95 (br., s, 1H, NH), 5.35 (br., s, 1H, benzyl CH), 4.41 (br., s, 1H, benzyl CH), 3.25 (s, 1H, alkyne CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 154.2, 142.5, 137.8, 137.6, 134.8, 130.44, 130.36, 129.1, 128.9, 128.7, 128.5, 128.2, 127.6, 122.7, 121.1, 83.6, 79.2, 52.5;[13] IR ν_{max} (cm^{-1}): 3271, 2922, 2853, 1655, 1589, 1571, 1514, 1487, 1435, 1424, 1400, 1372, 1360, 1312, 1287, 1262, 1238, 1225, 1188, 1177, 1090, 1076, 1049, 1026, 1011. HRMS (ES+) [M+H] $[C_{22}H_{18}N_2OCl]^+$: calculated. 361.1108, found: 361.1104.

Synthesis of 1-benzyl-1-(2-ethynylphenyl)-3-phenylurea (**6h**)

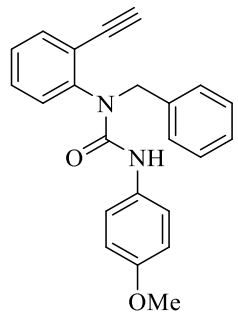
Synthesised in accordance with *General Procedure c* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), *N*-benzyl-2-ethynylaniline (21 mg, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **6h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **6h** was obtained as an off-white solid. Yield: 13 mg, 0.04 mmol, 40%.



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.63 (dd, *J* = 7.3, 2.0 Hz, 1H, Ar–CH), 7.37–7.27 (m, 8H, Ar–CH), 7.24 (m, 3H, Ar–CH), 7.04–6.97 (m, 2H, Ar–CH), 6.00 (br., s, 1H, NH), 5.00 (br., s, 2H, benzyl CH_2), 3.30 (s, 1H, alkyne CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 154.4, 142.7, 139.0, 138.1, 134.7, 130.5, 130.4, 129.1, 128.9, 128.6, 128.5, 127.5, 123.2, 122.8, 119.9, 83.5, 79.3, 52.4.[13] IR ν_{max} (cm^{-1}): 3291, 3260, 3061, 3030, 2924, 2853, 1655 (C=O), 1616, 1595, 1568, 1559, 1522, 1503, 1486, 1439, 1368, 1312, 1242, 1211, 1188, 1157, 1078, 1044, 1028. HRMS (ES+) [M+H] $[C_{22}H_{19}N_2O]^+$: calculated. 327.1497, found: 327.1490.

Synthesis of 1-benzyl-1-(2-ethynylphenyl)-3-(4-methoxyphenyl)urea (**6i**)

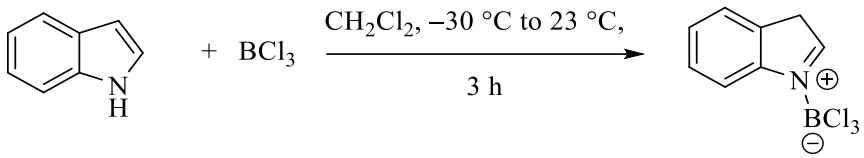
Synthesised in accordance with *General Procedure c* using BCl_3 (1 M in hexane, 5 µL, 0.005 mmol), *N*-benzyl-2-ethynylaniline (21 mg, 0.10 mmol), and 4-methoxyphenyl isocyanate (19 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **6i**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. The desired compound **6i** was obtained as a pale-yellow solid. Yield: 15 mg, 0.04 mmol, 42%.



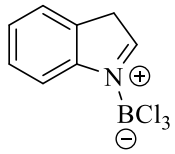
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.62–7.55 (m, 1H, Ar–CH), 7.31–7.14 (m, 11H, Ar–CH), 6.97–6.93 (m, 1H, Ar–CH), 6.79–6.73 (m, 2H, Ar–CH), 5.83 (br., s, 1H, NH), 5.36 (br., s, 1H, benzyl CH), 4.50 (br., s, 1H, benzyl CH), 3.72 (s, 3H, OMe), 3.27 (s, 1H, alkyne CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 156.0, 154.9, 142.9, 138.2, 134.7, 132.0, 130.5, 130.3, 129.1, 128.5, 128.4, 127.4, 122.8, 122.3, 114.2, 83.4, 79.4, 55.7, 52.4;[13] IR ν_{max} (cm^{-1}): 3426, 3283, 3063, 3030, 3001, 2930, 2833, 1663(C=O), 1595, 1510, 1483, 1464, 1447, 1412, 1356, 1314, 1296, 1233, 1211, 1179, 1107, 1074, 1030. HRMS (ES+) [M+H] $[C_{23}H_{21}N_2O_2]^+$: calculated. 357.1603, found: 357.1593.

2.8 Experiments to support proposed mechanism

Synthesis of **10**·BCl_3[14]

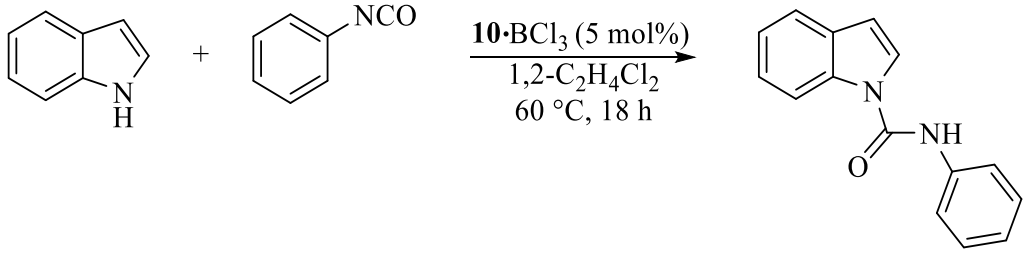


In the glovebox, indole (1 equiv, 0.6 g, 4.78 mmol) was dissolved in CH_2Cl_2 (3 mL) and cooled to -30 °C. To this solution, BCl_3 was added dropwise (1M in CH_2Cl_2, 4.78 mL, 4.78 mmol) and the reaction mixture was stirred at 23 °C for 3 h. Next, the solution was decanted and the pink solid obtained was washed several times with pentane. Compound **10**·BCl_3 was obtained as pink solid. Yield: 0.8 g, 3.23 mmol, 68%.



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ: 9.38 (d, *J* = 3.0 Hz, 1H, indole C2), 8.30 (d, *J* = 7.3 Hz, 1H, Ar–CH), 7.61 (d, *J* = 7.1 Hz, 2H, Ar–CH), 7.52 (m, 2H, Ar–CH), 4.18 (s, 2H, indole C3); ^{13}C NMR (101 MHz, CD_2Cl_2, 298 K) δ: 175.5, 129.6, 128.9, 125.1, 122.2, 41.7. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) δ: 5.8.

*Synthesis of N-phenyl-1H-indole-1-carboxamide (**5a**) using 0.05 equiv of* **10**·BCl_3 *as the catalyst.*



Synthesised in accordance with *General Procedure b* using **10**·BCl_3 (1 mg, 0.005 mmol), indole (12 mg, 0.10 mmol), and phenyl isocyanate (16 µL, 0.15 mmol) in 1,2-$C_2H_4Cl_2$ to afford **5a**. The solvent was removed under vacuum to afford a yellow oil which revealed formation of the product **5a** (See Figure S121 and Figure S122 for comparison of the crude ^{1}H NMR spectrum with that of compound **5a**).

3. NMR Spectra

Figure S1: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1a**.

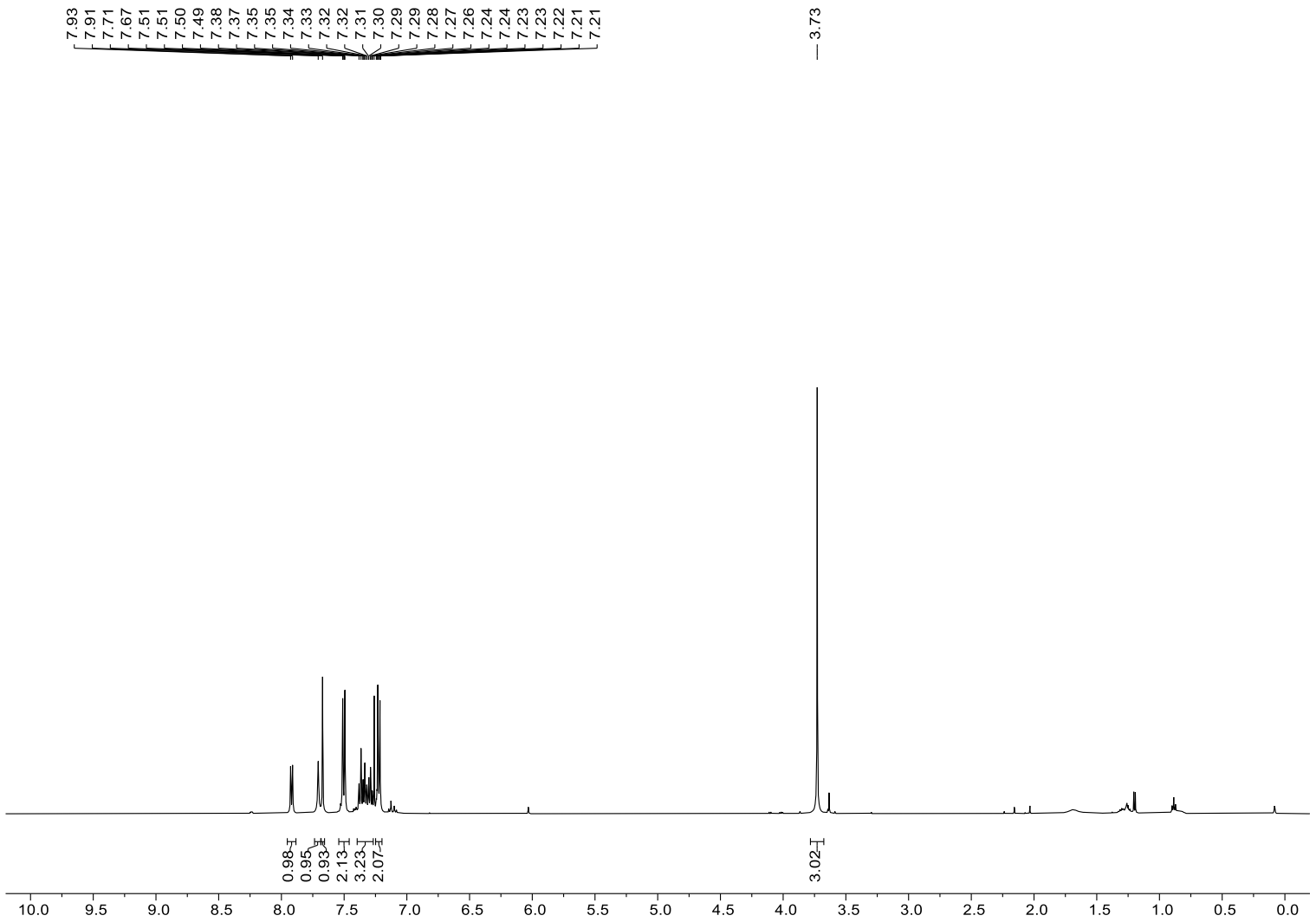


Figure S2: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1a**.

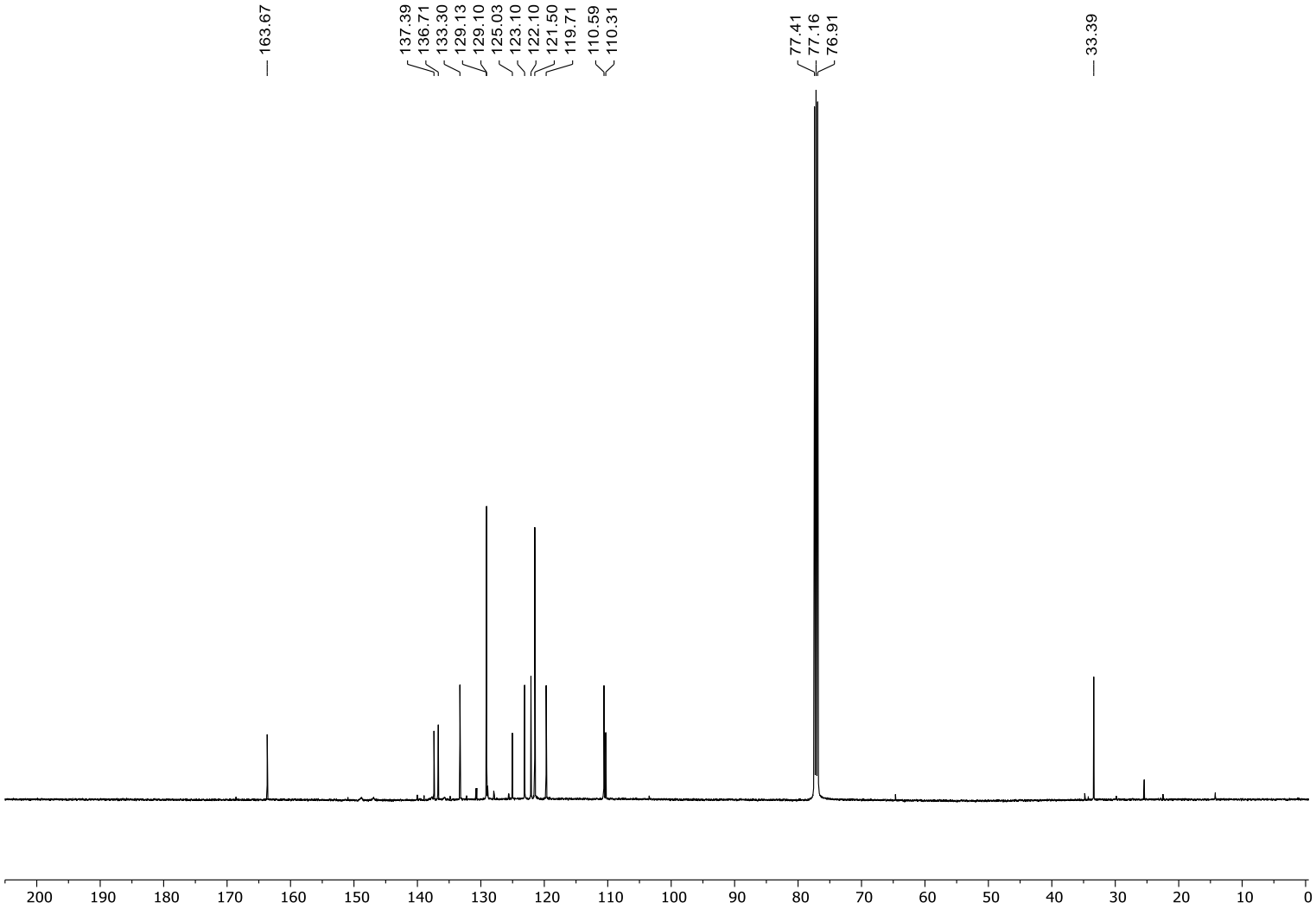


Figure S3: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1b**.

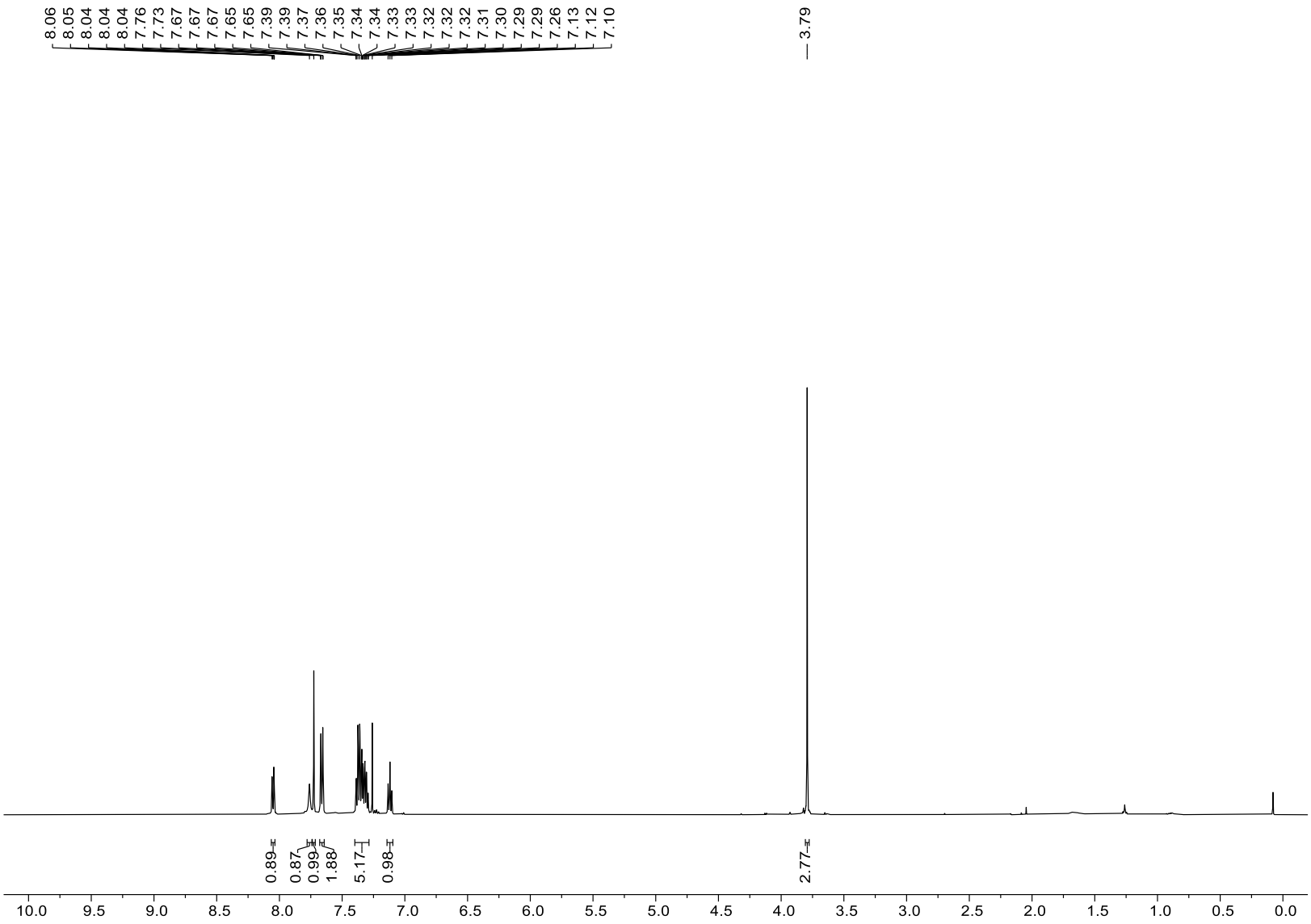


Figure S4: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1b**.

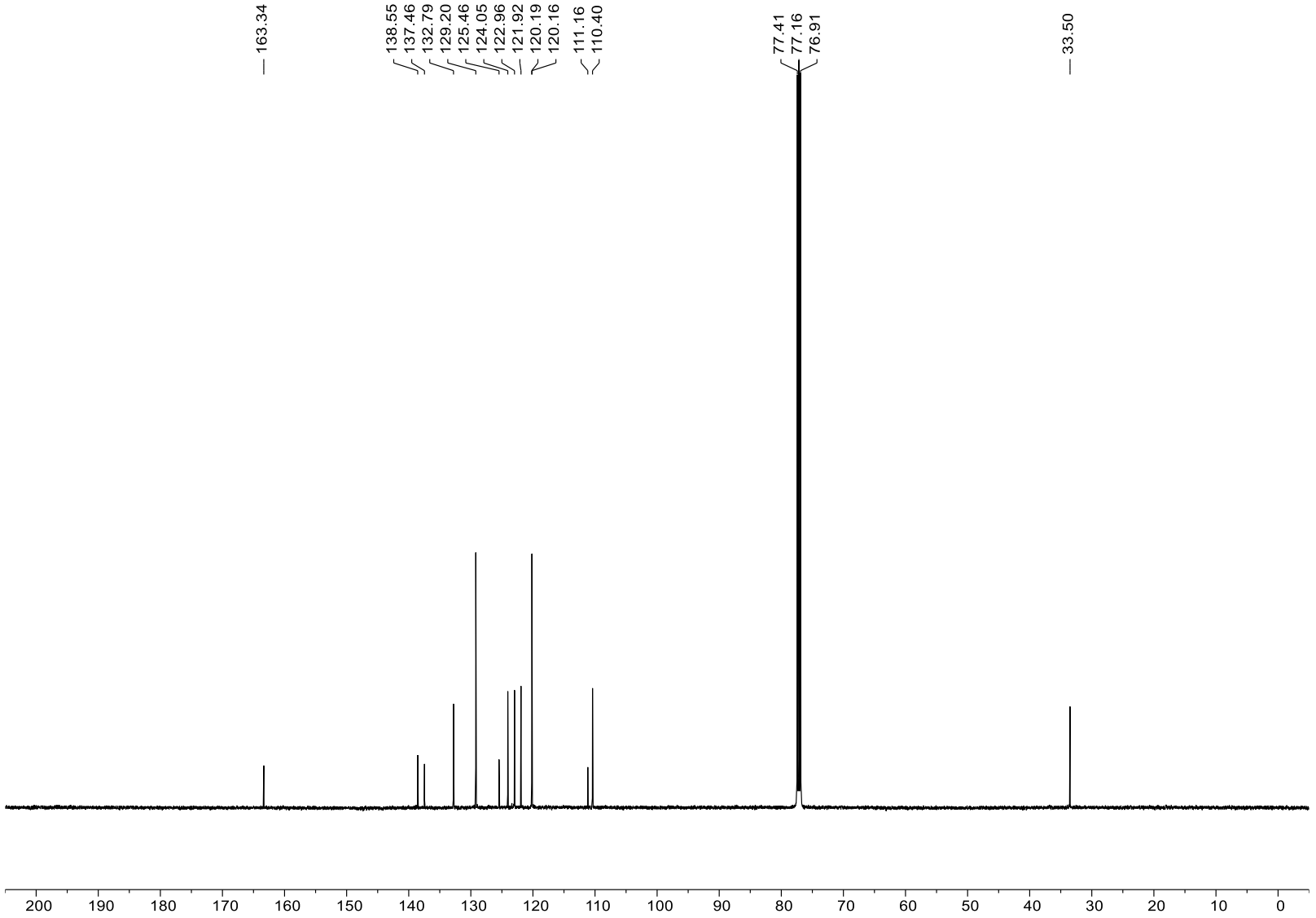


Figure S5: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1c**.

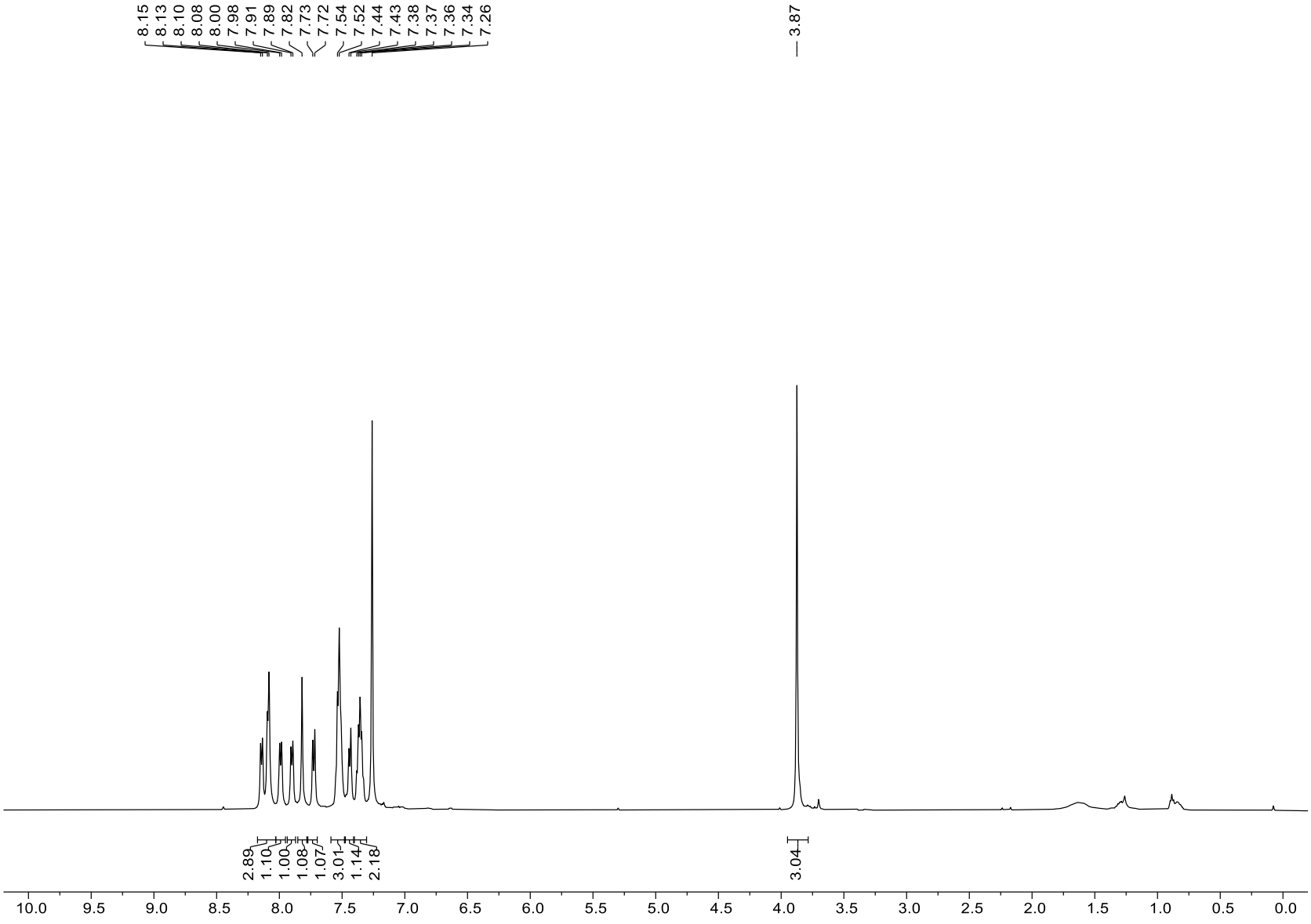


Figure S6: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1c**.

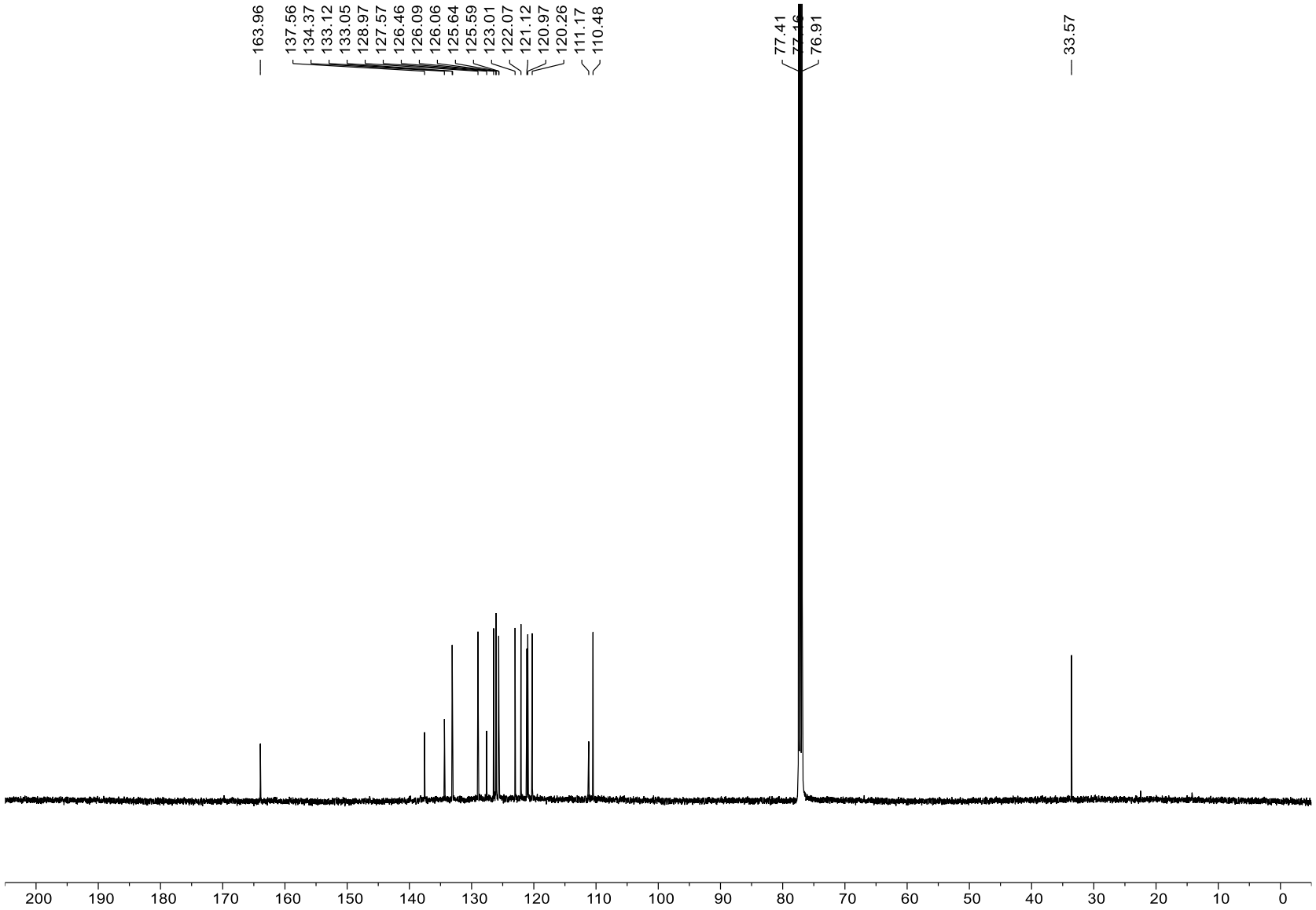


Figure S7: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1d**.

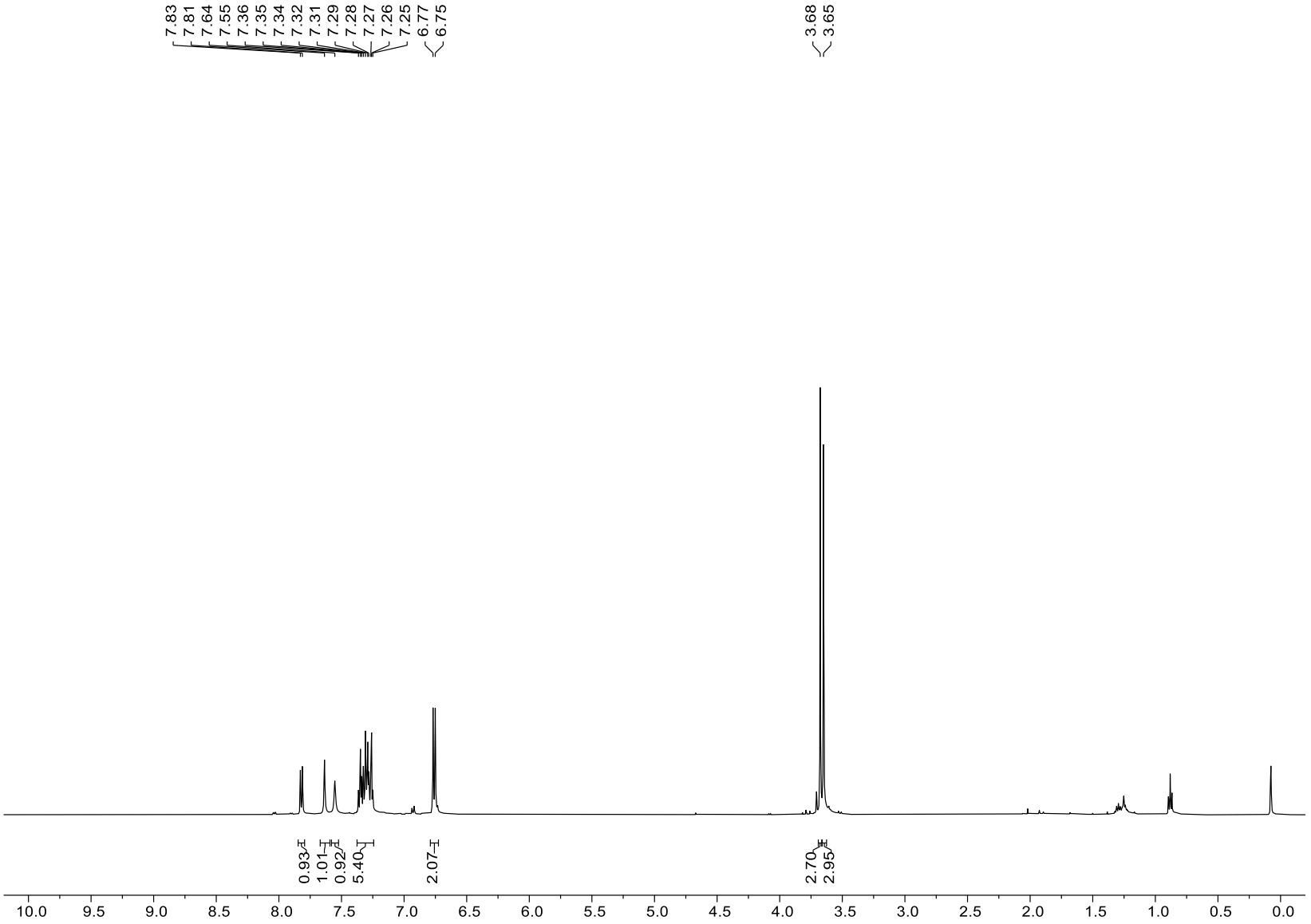


Figure S8: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1d**.

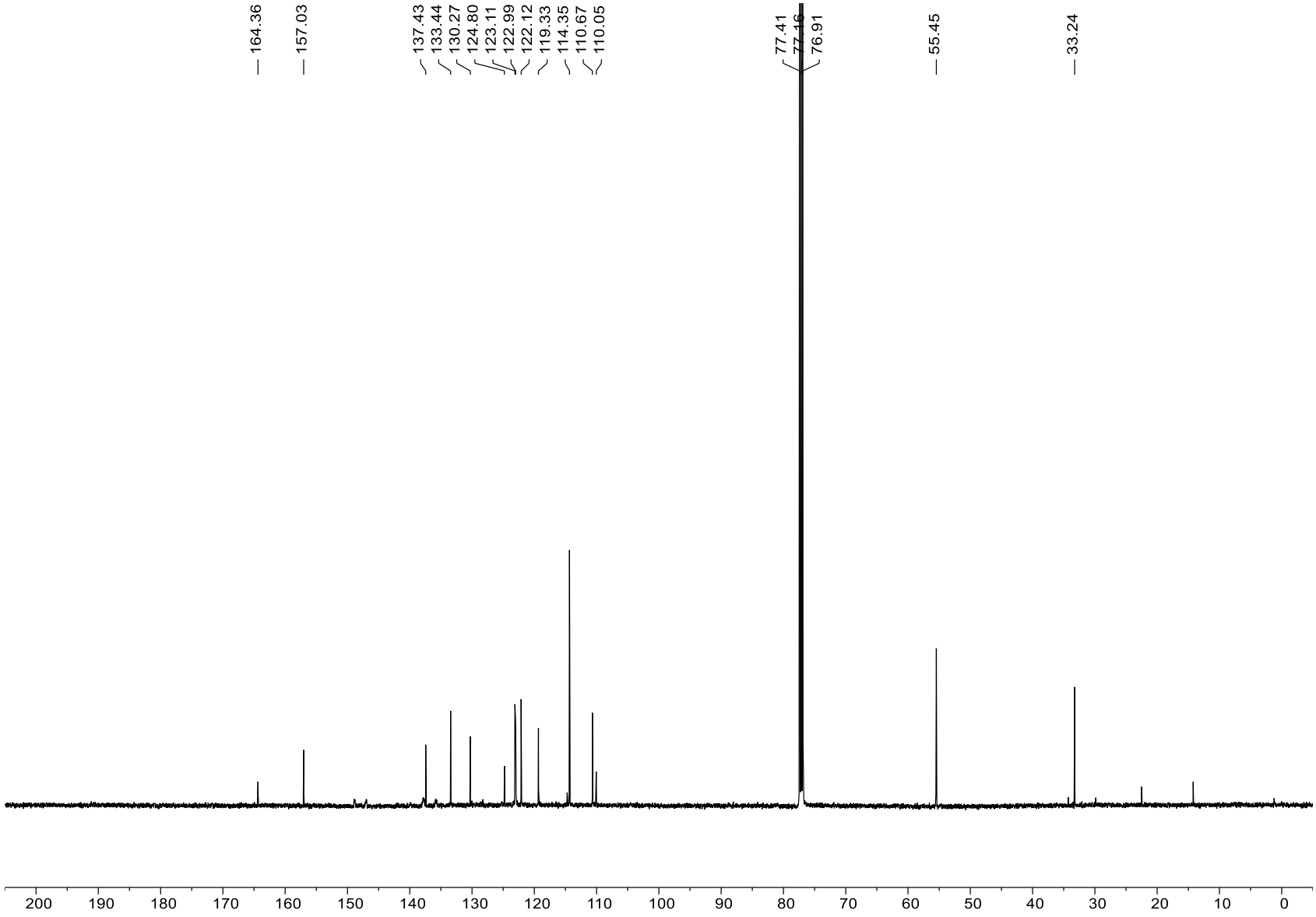


Figure S9: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1e**.

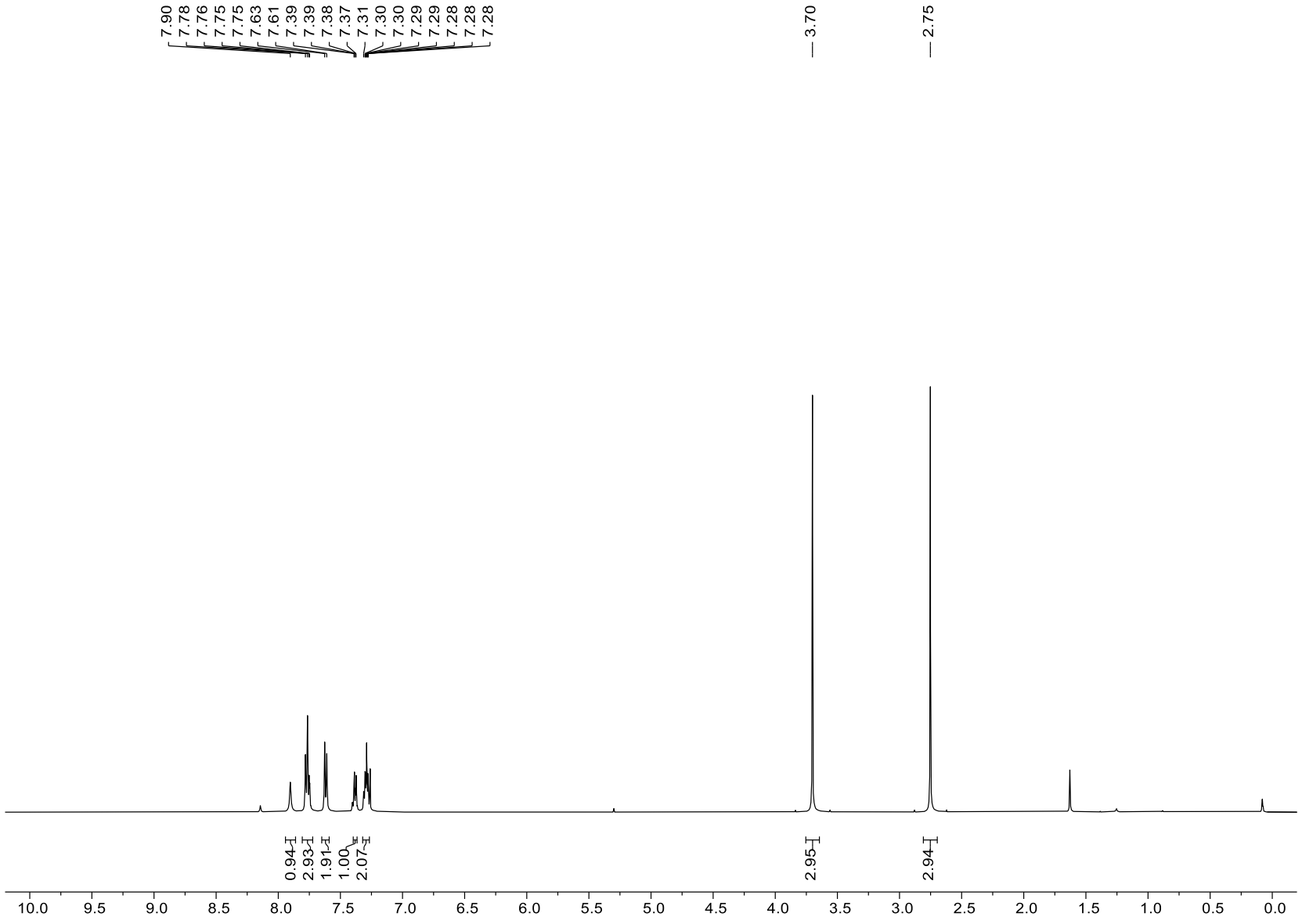


Figure S10: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1e**.

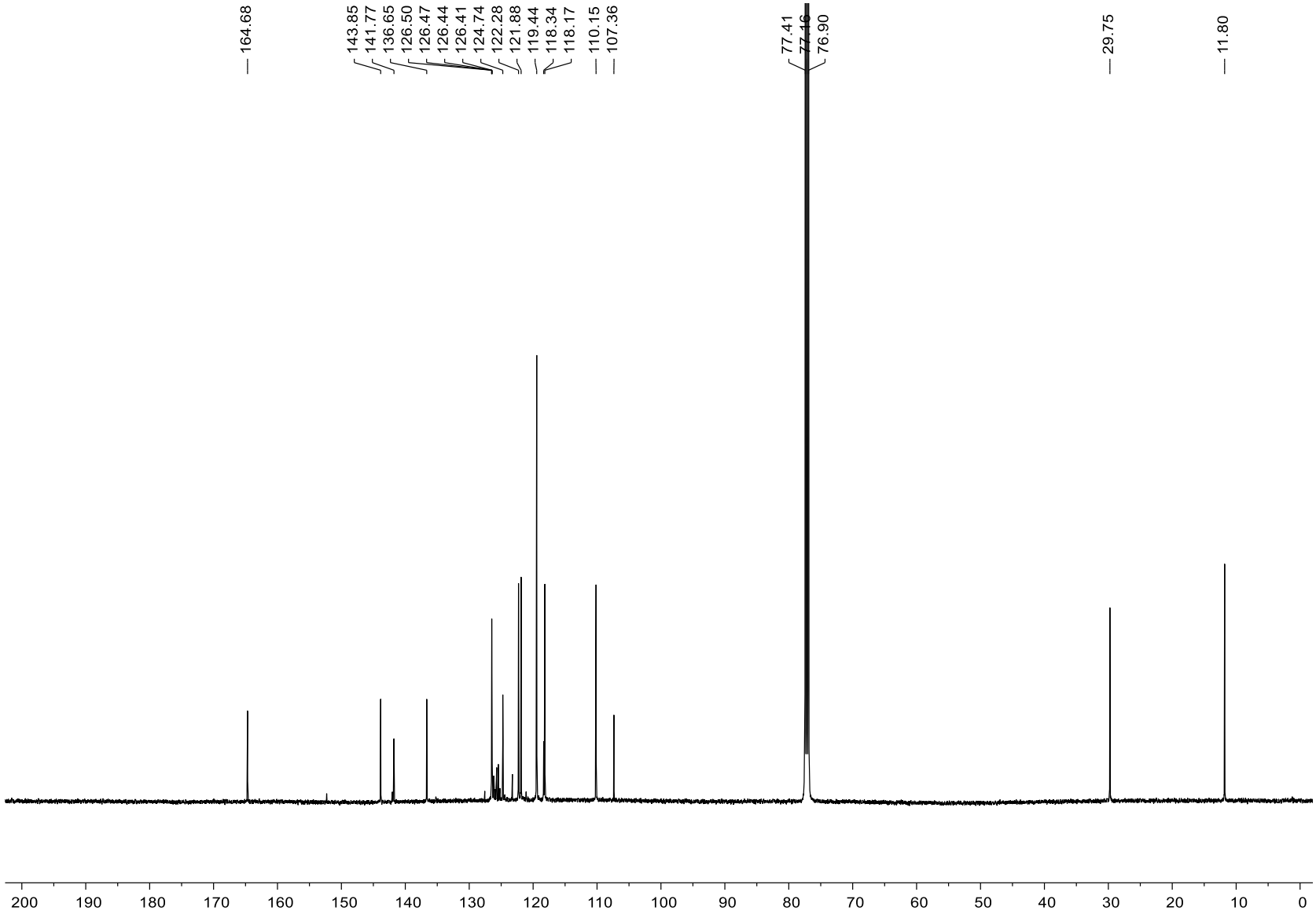


Figure S11: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **1e**.

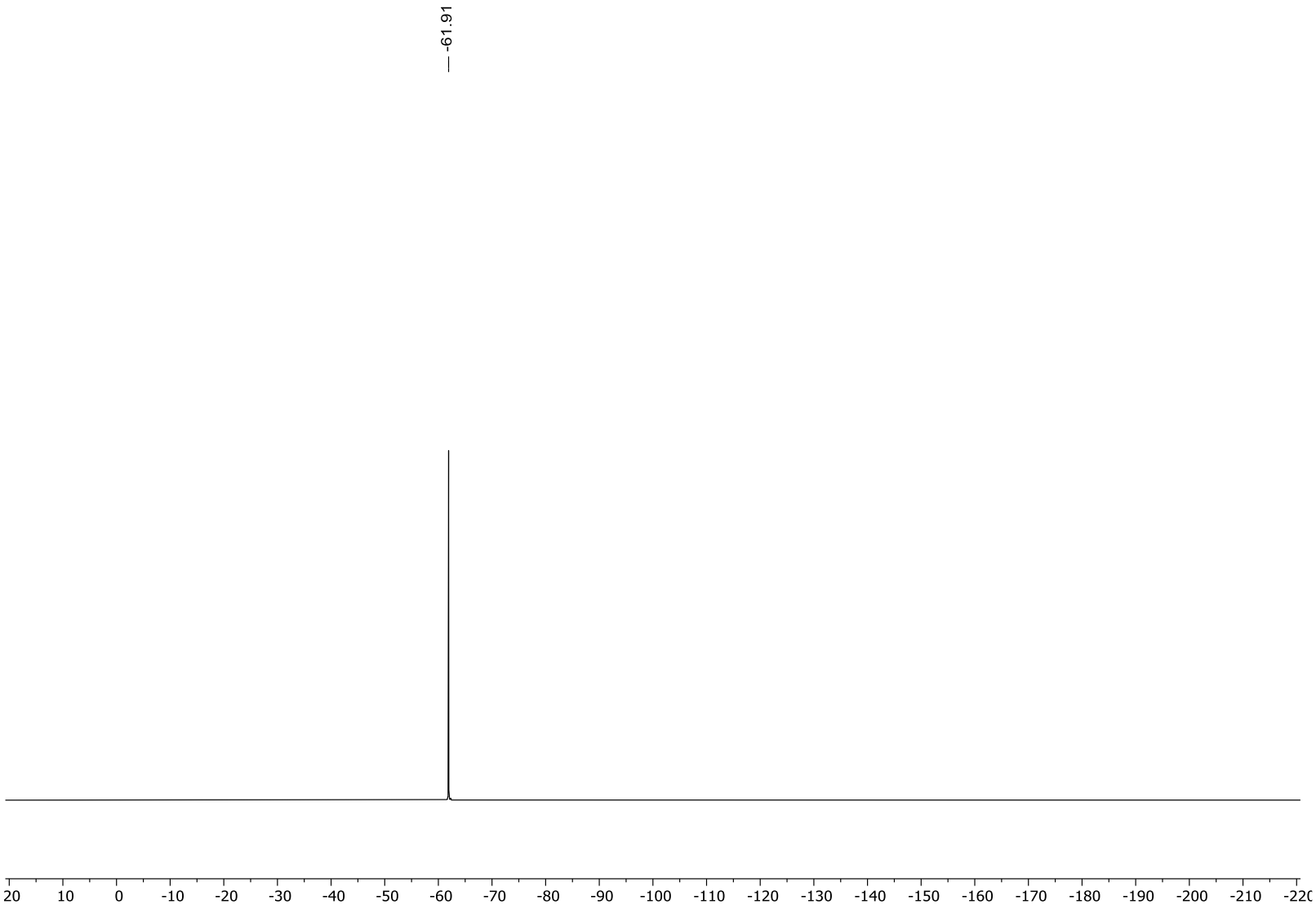


Figure S12: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1f**.

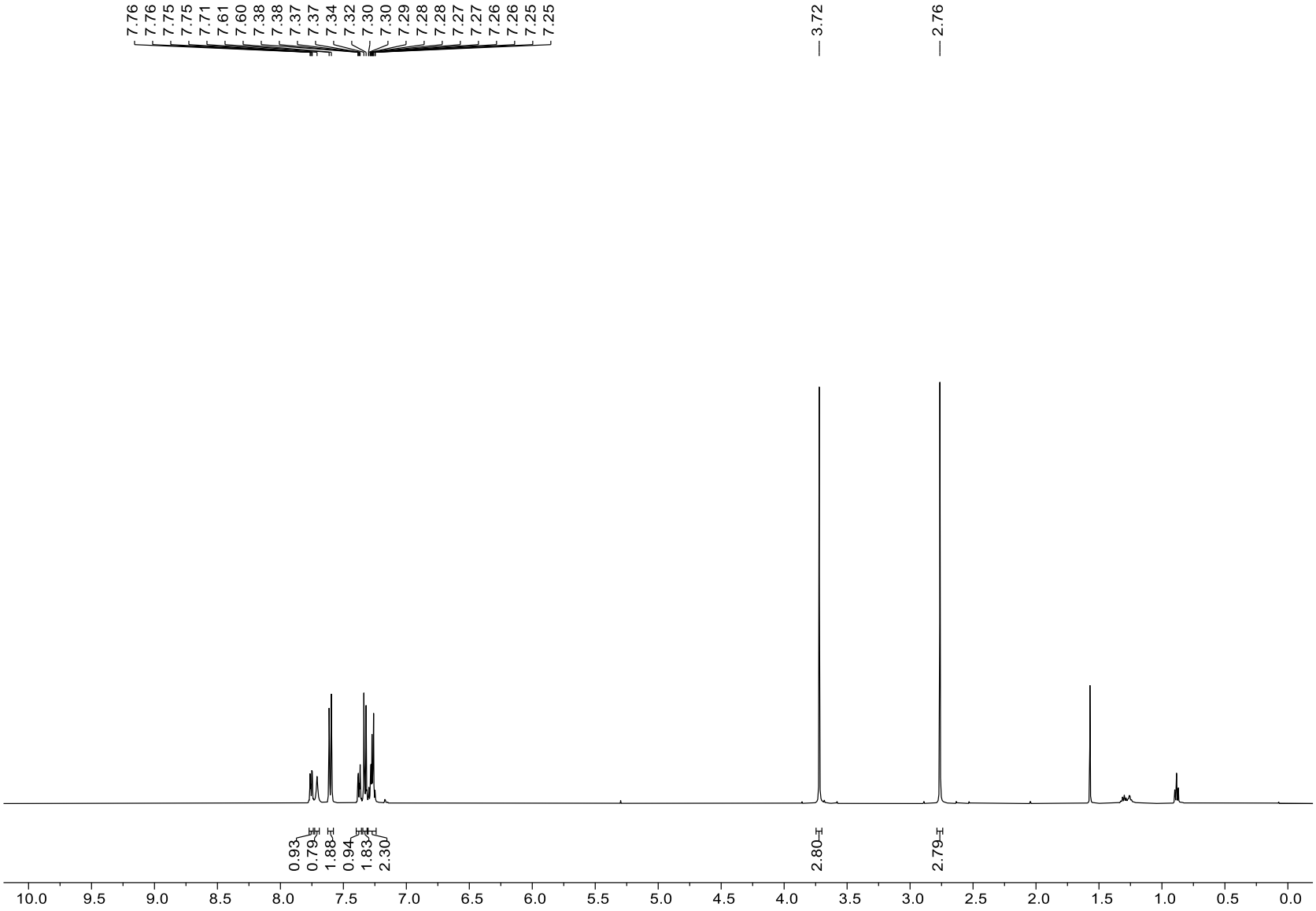


Figure S13: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1f**.

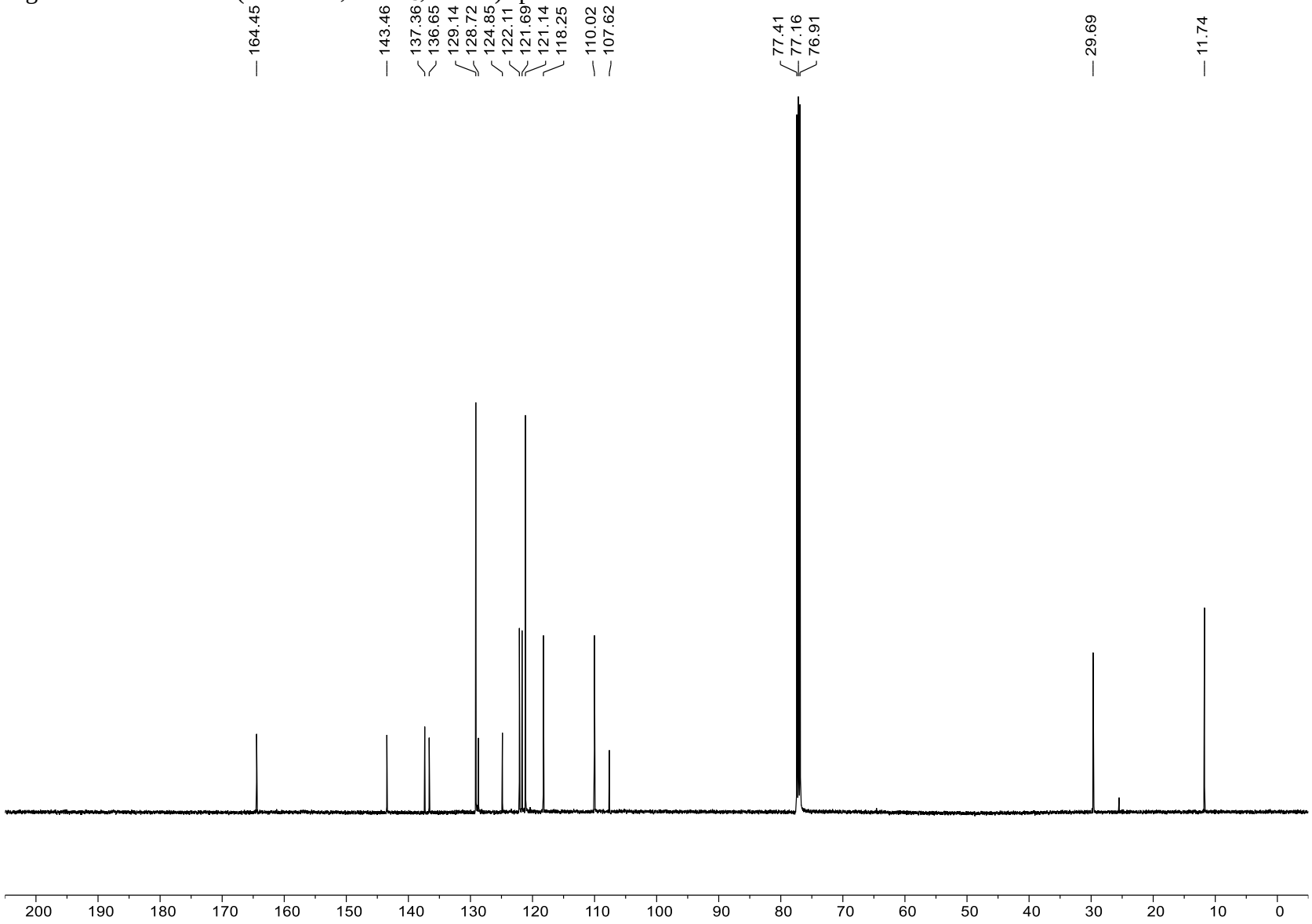


Figure S14: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1g**.

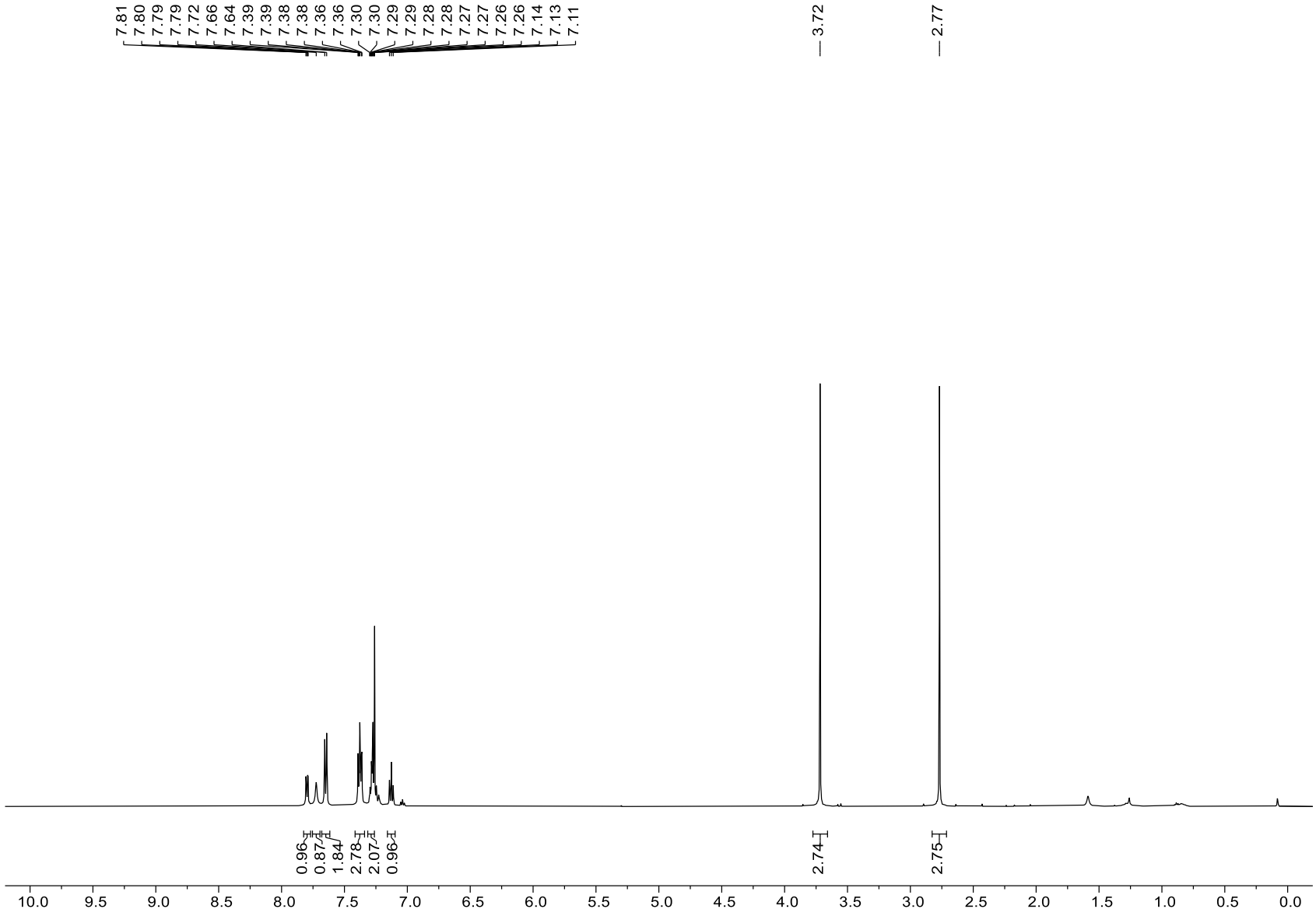


Figure S15: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1g**.

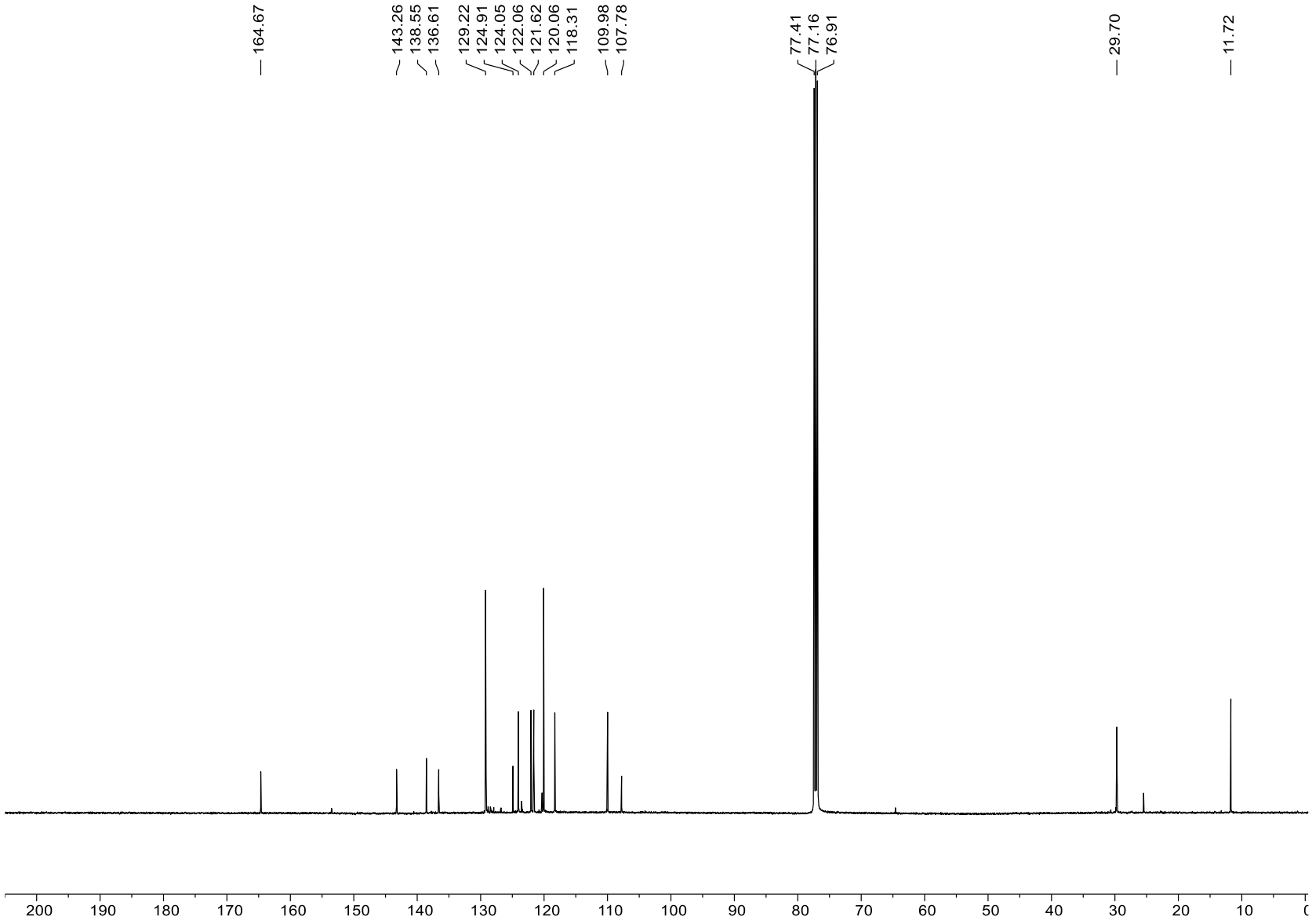


Figure S16: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1h**.

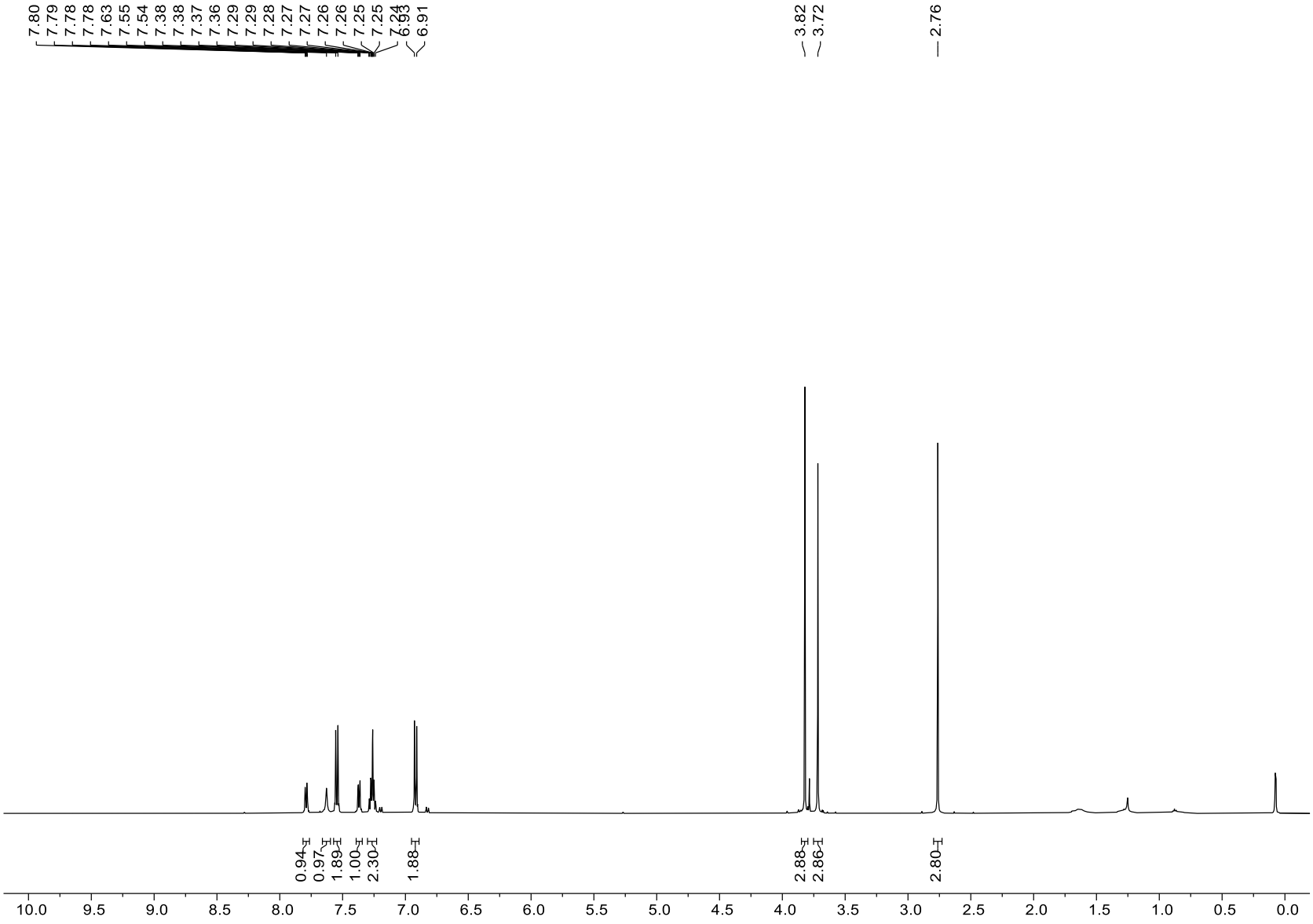


Figure S17: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1h**.

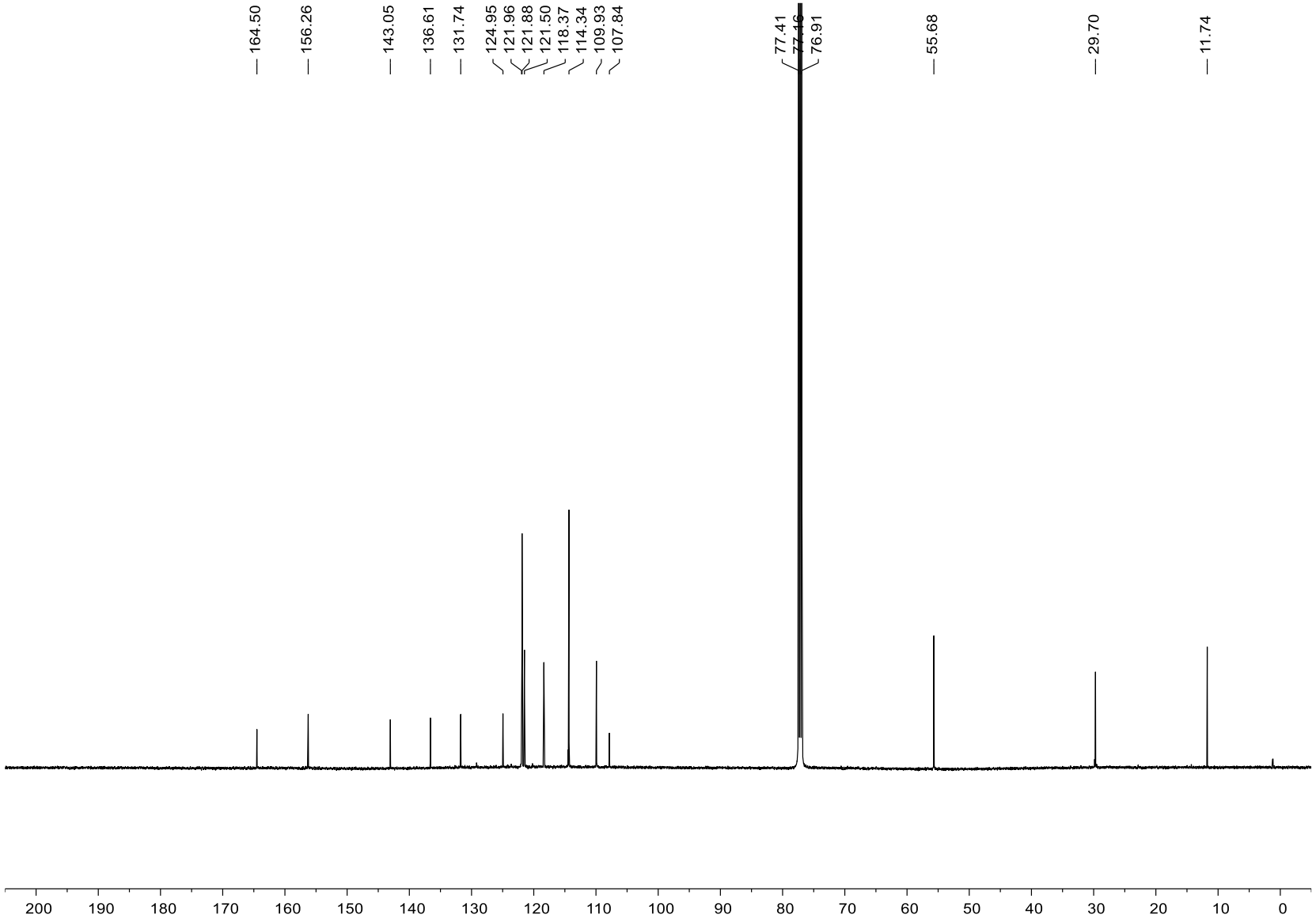


Figure S18: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1i**.

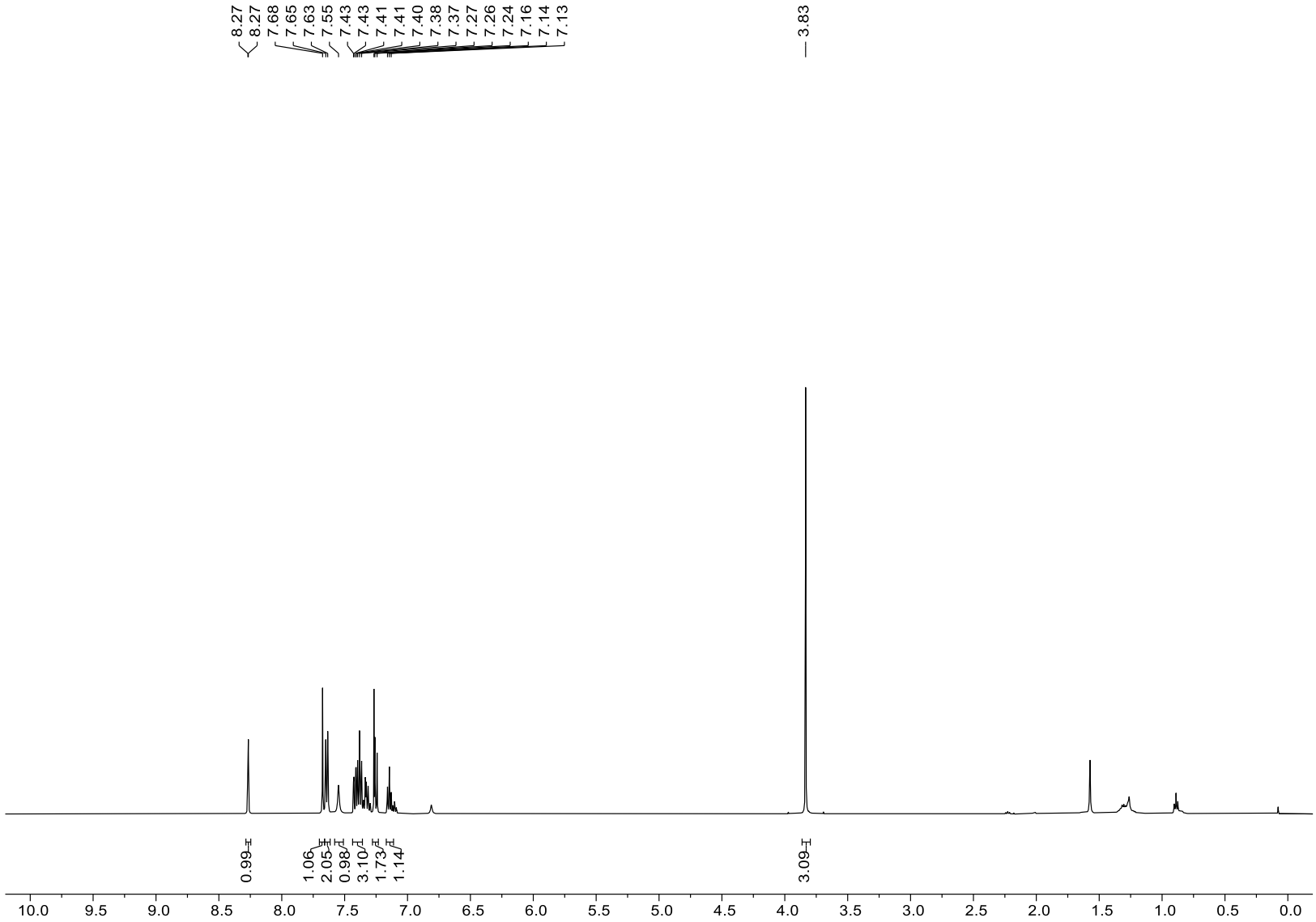


Figure S19: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1i**.

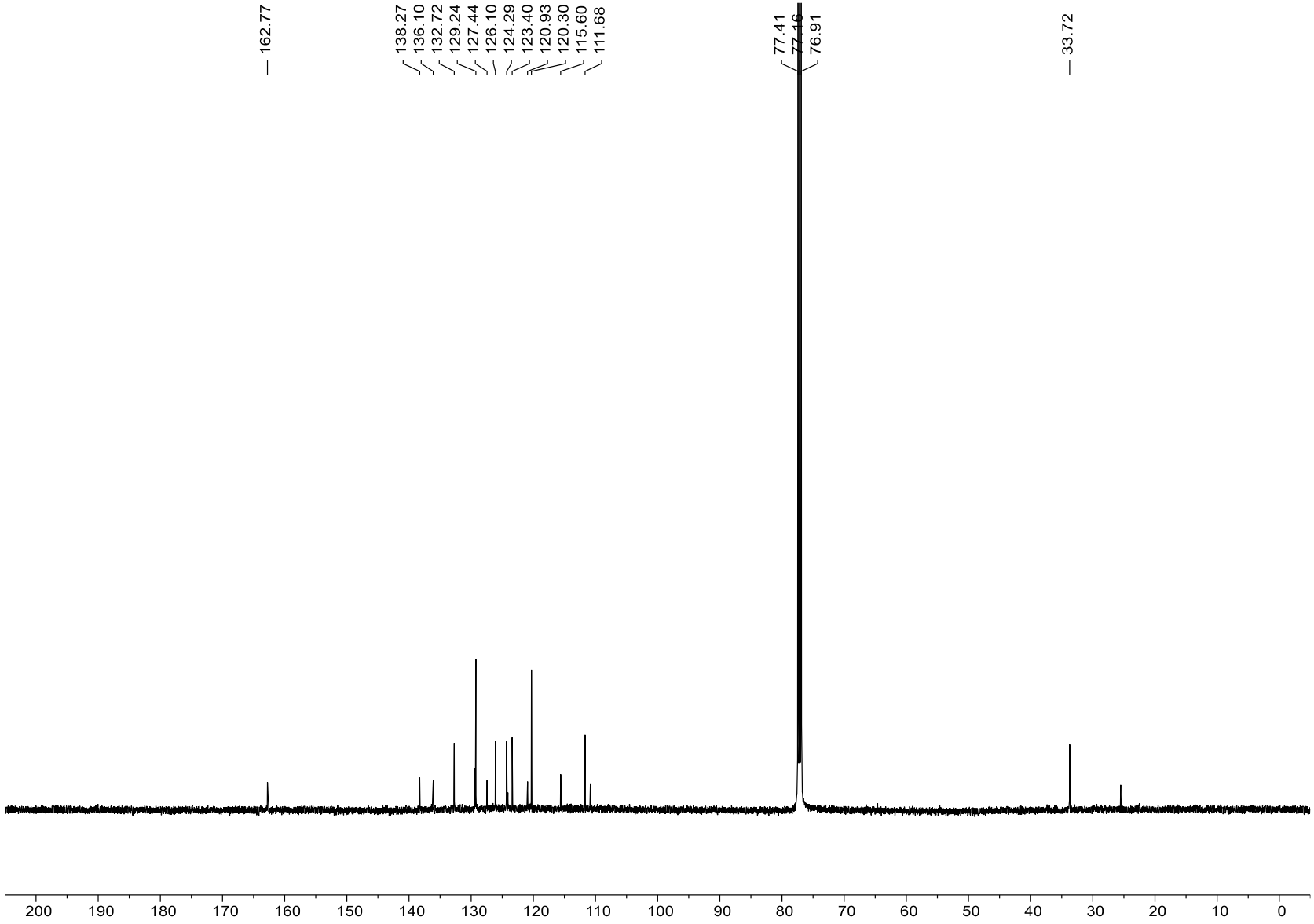


Figure S20: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1j**.

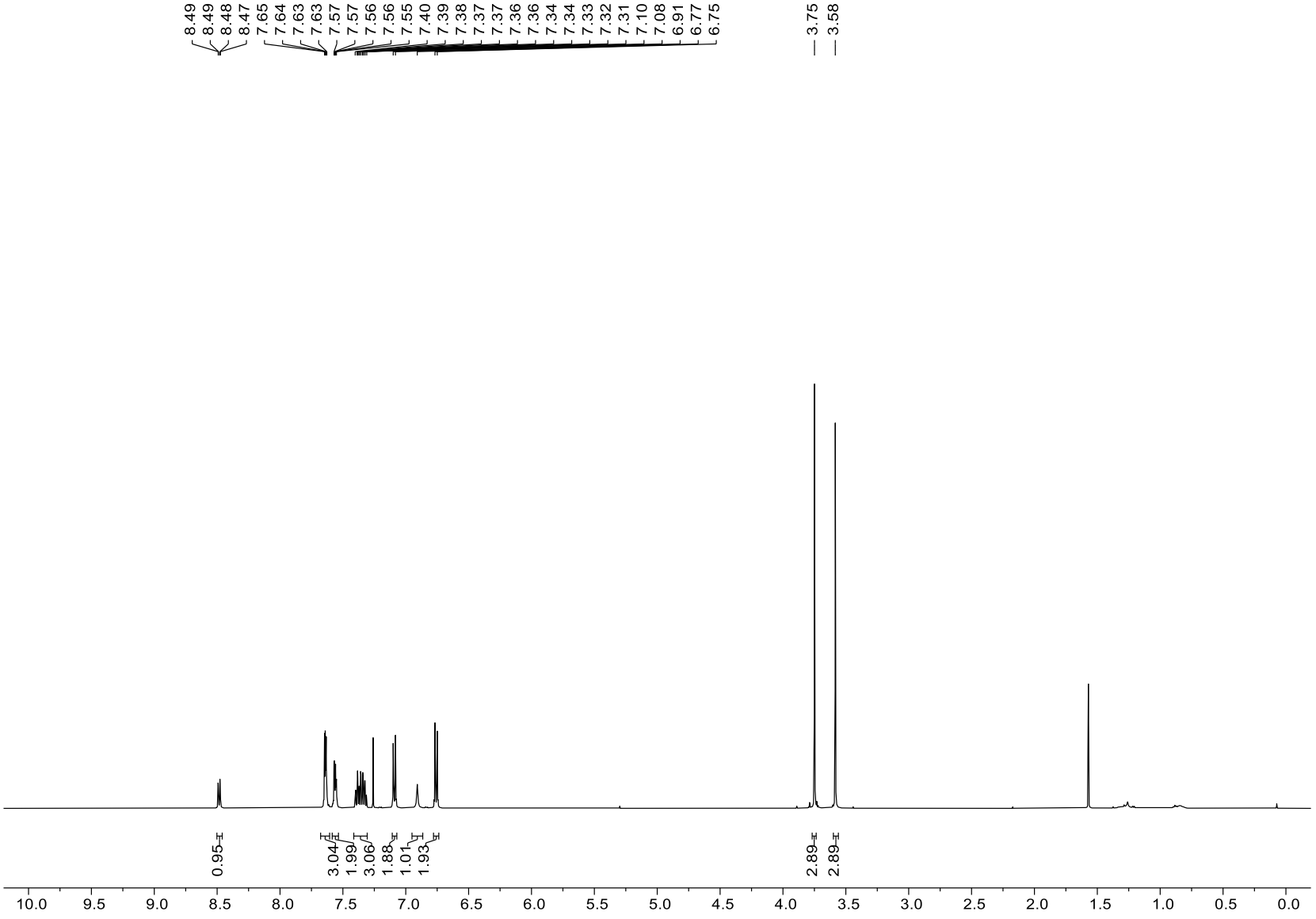


Figure S21: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1j**.

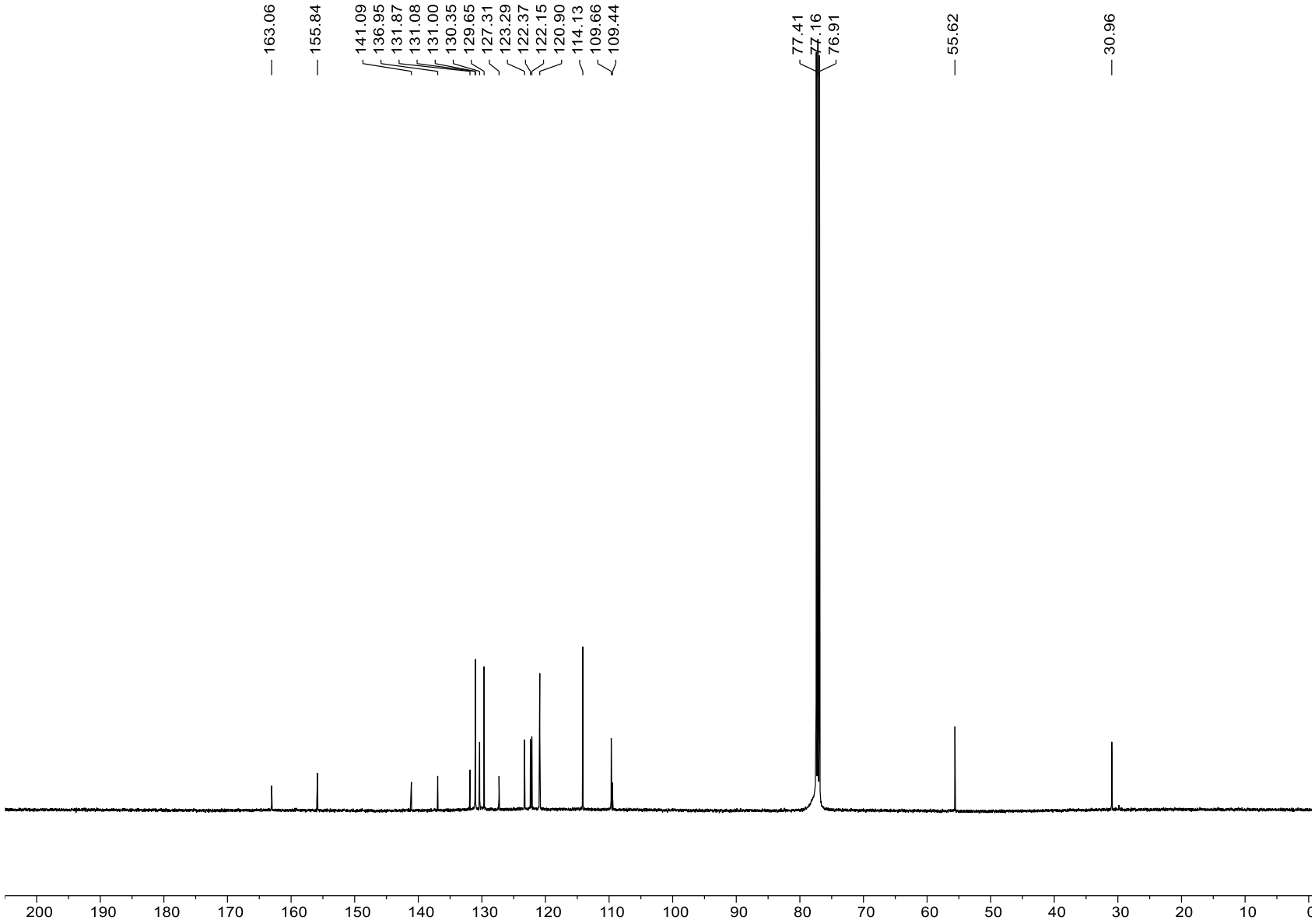


Figure S22: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1k**.

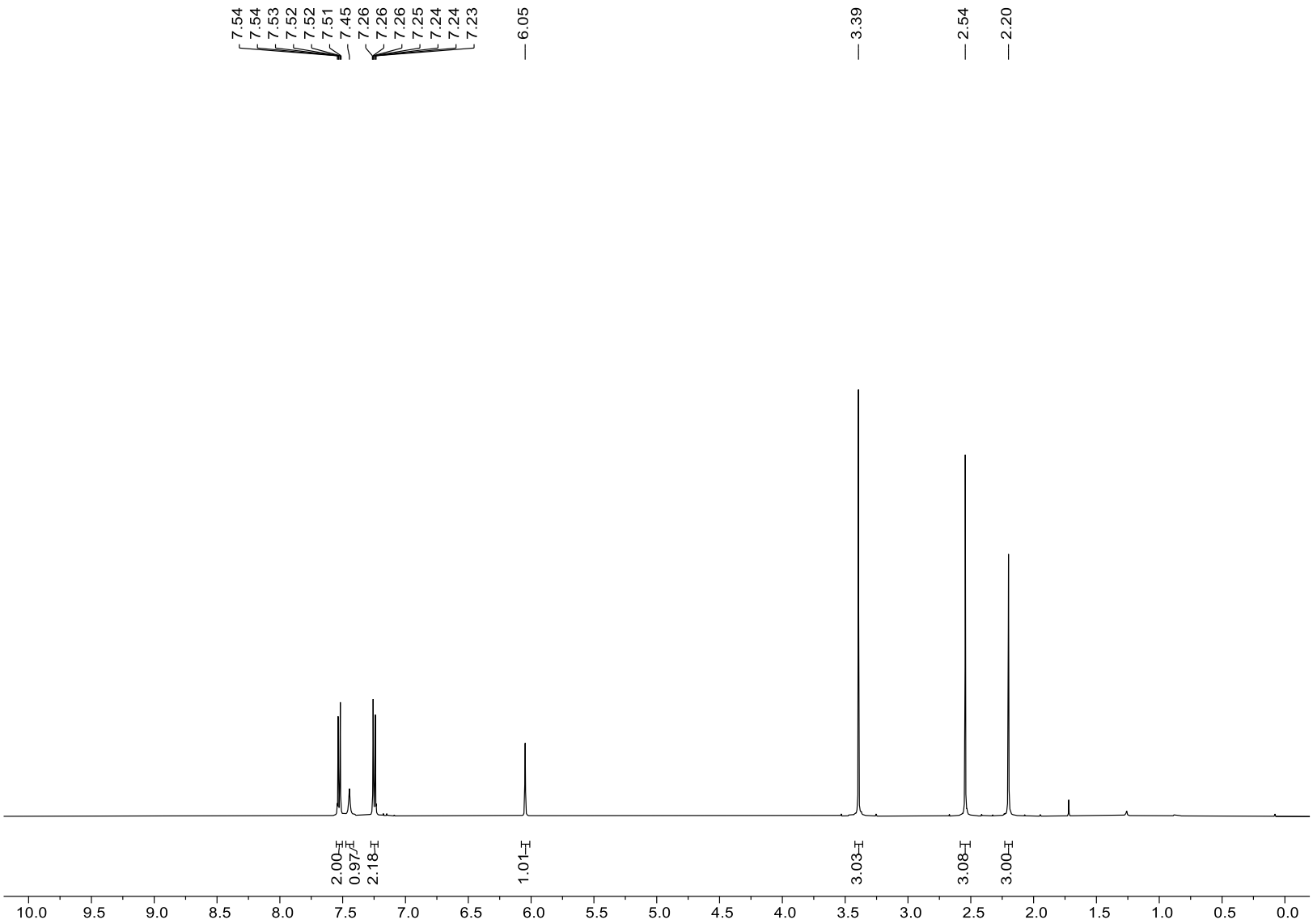


Figure S23: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1k**.

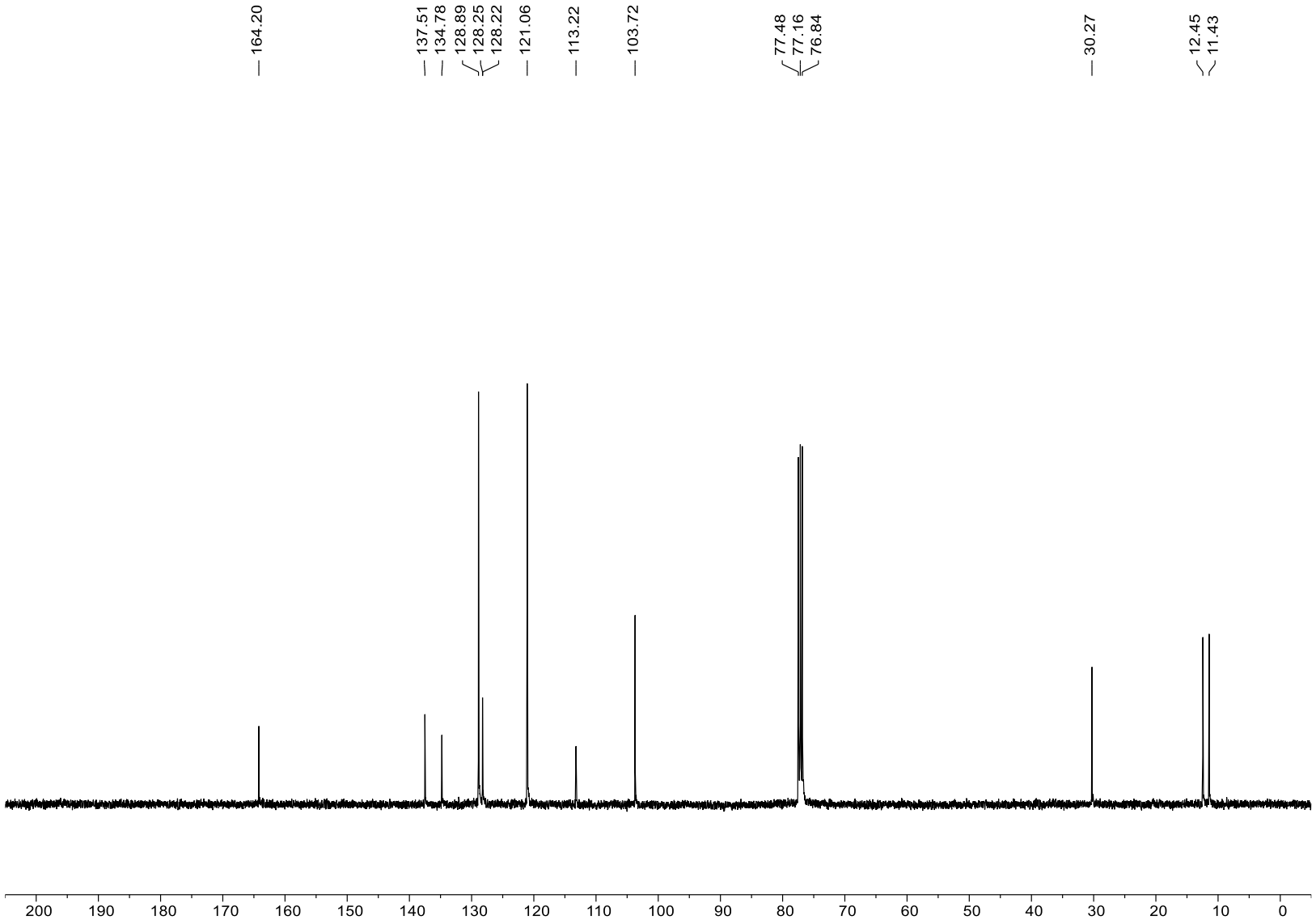


Figure S24: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1l**.

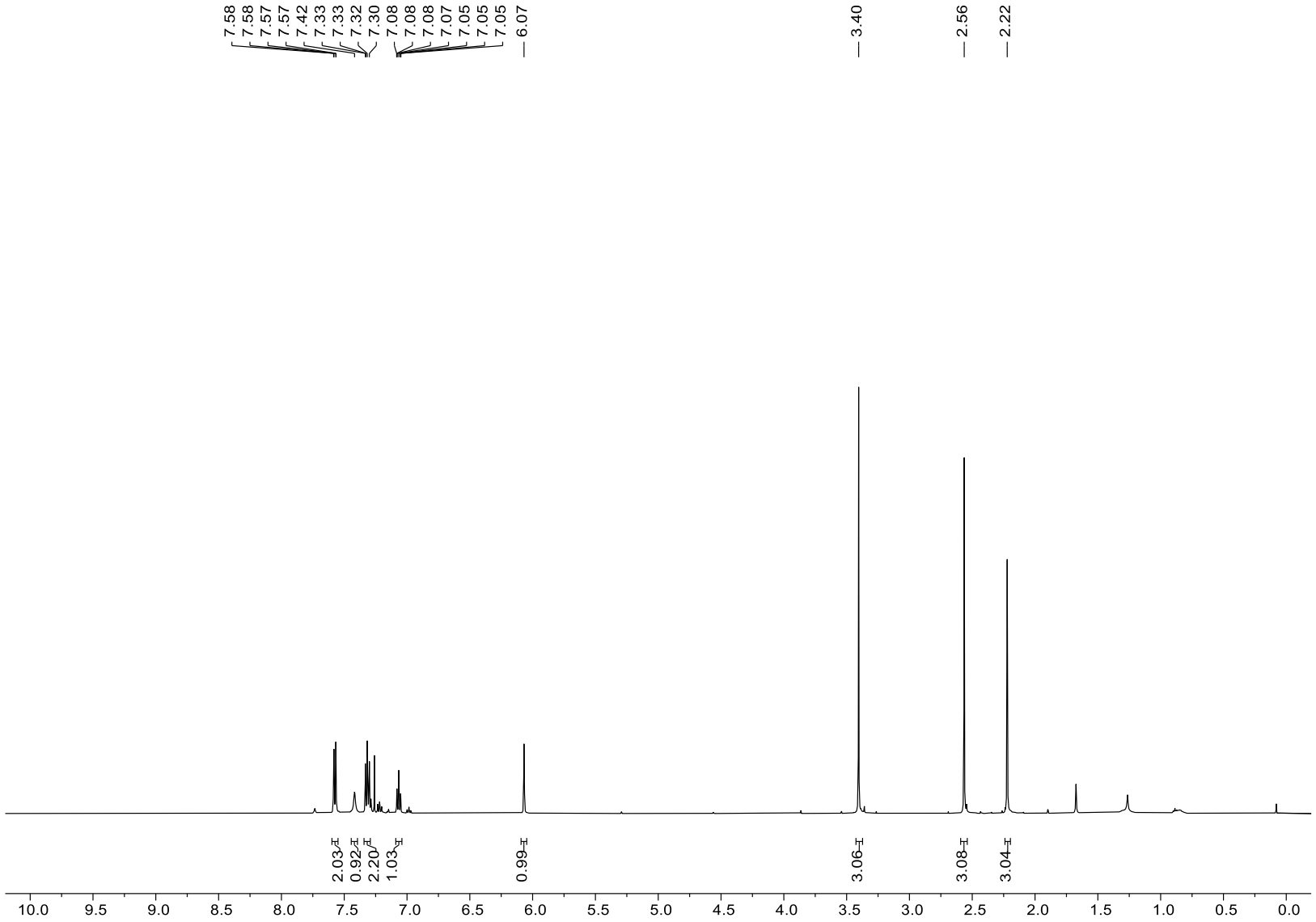


Figure S25: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1l**.

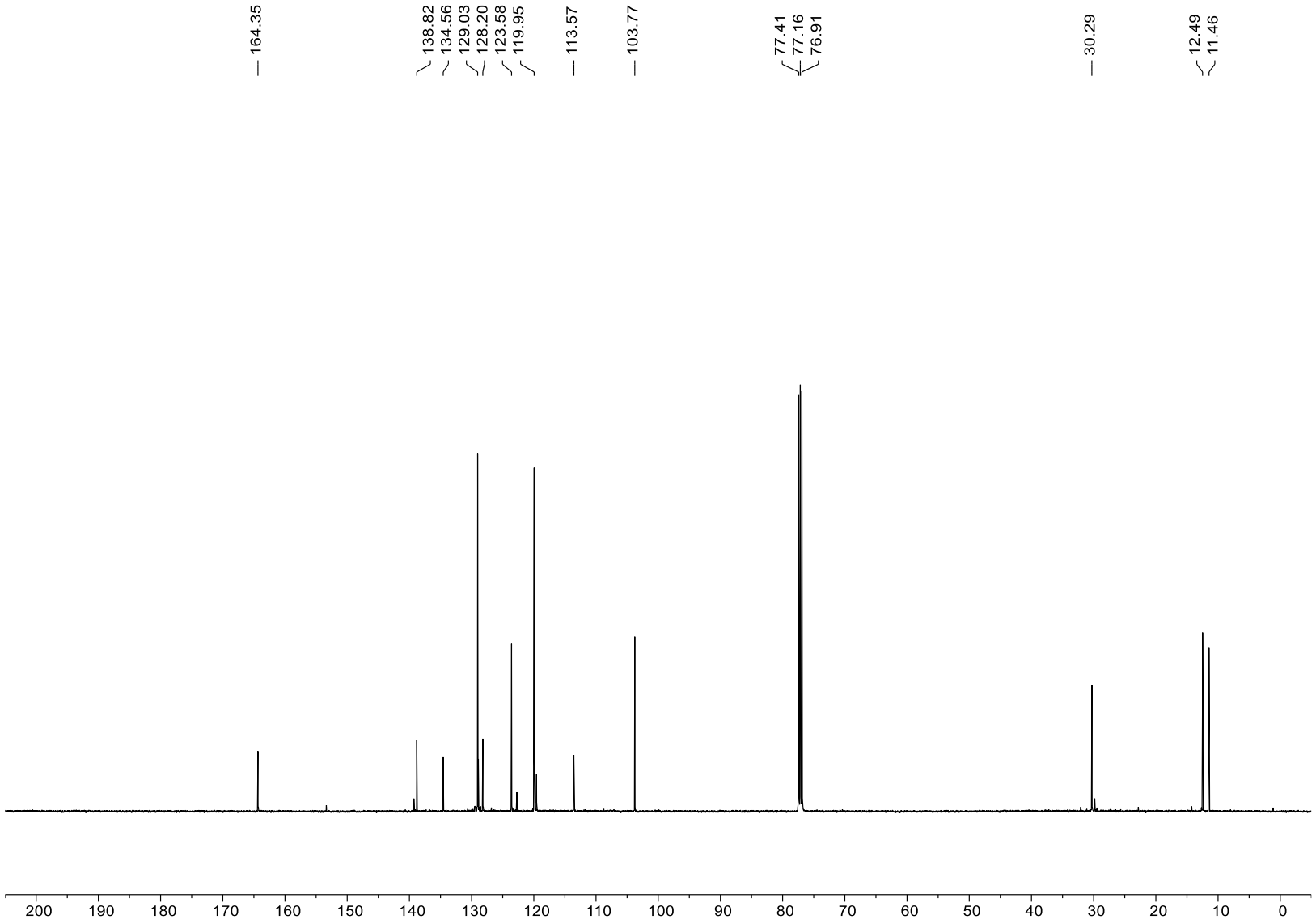


Figure S26: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1m**.

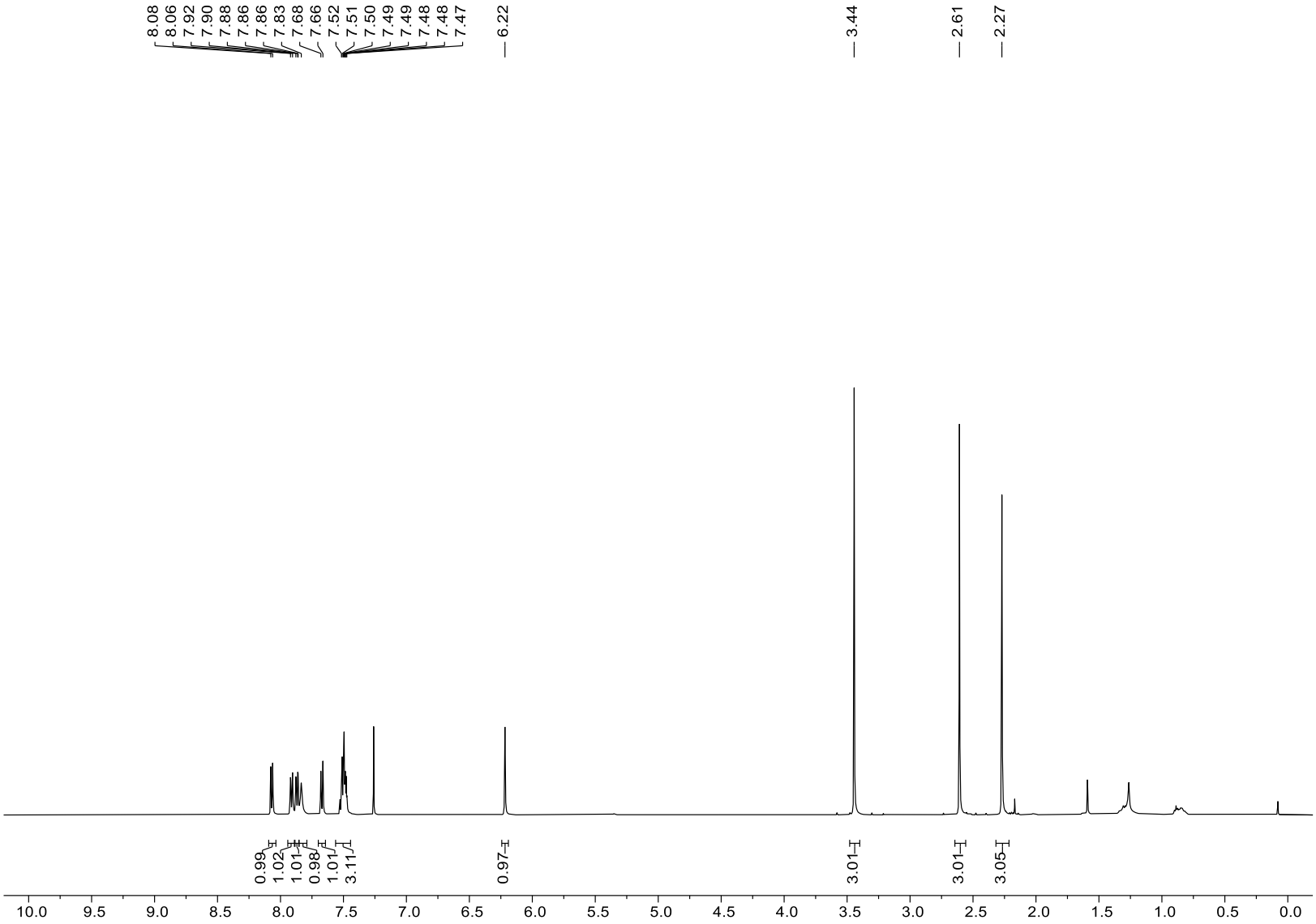


Figure S27: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1m**.

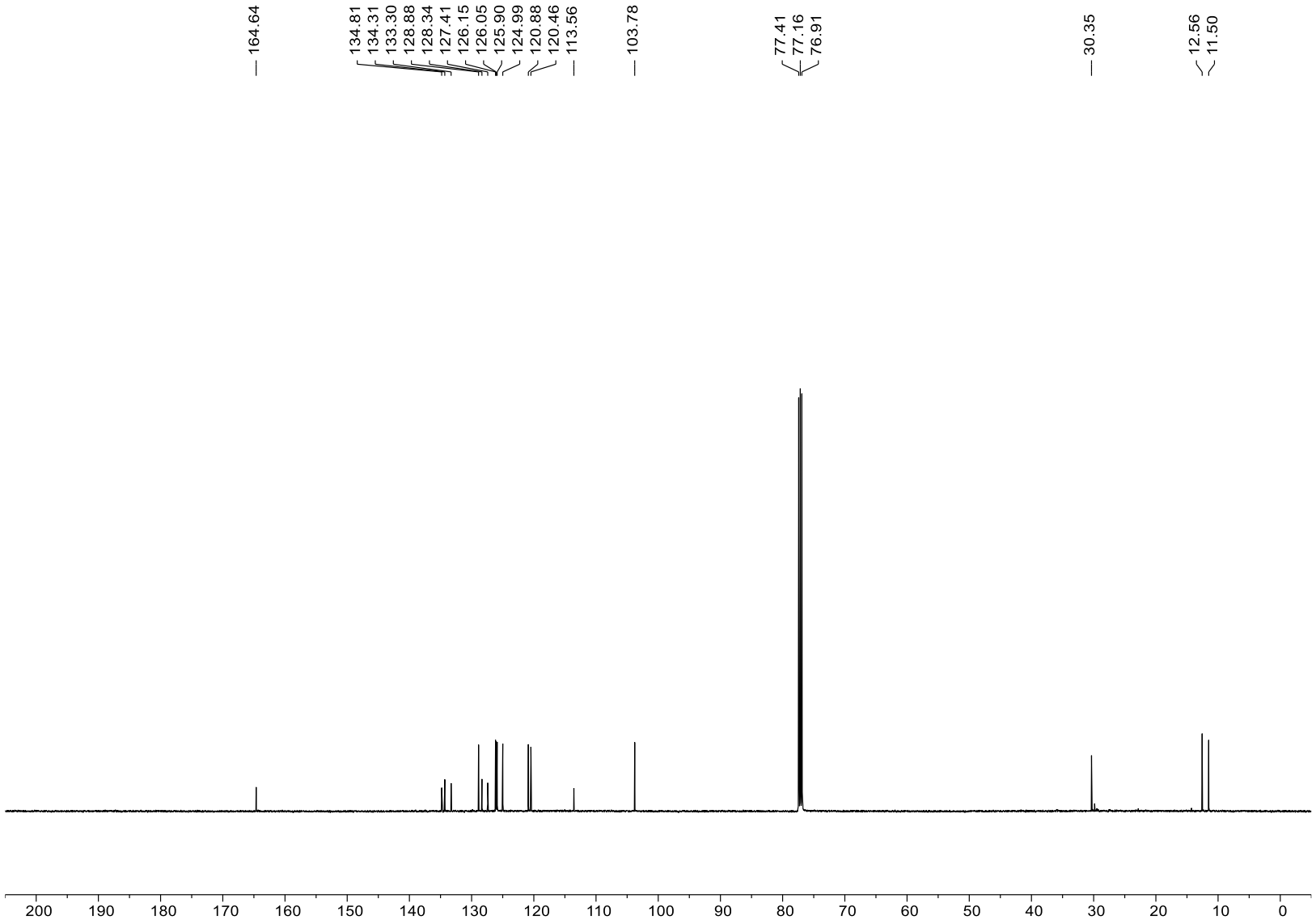


Figure S28: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1n**.

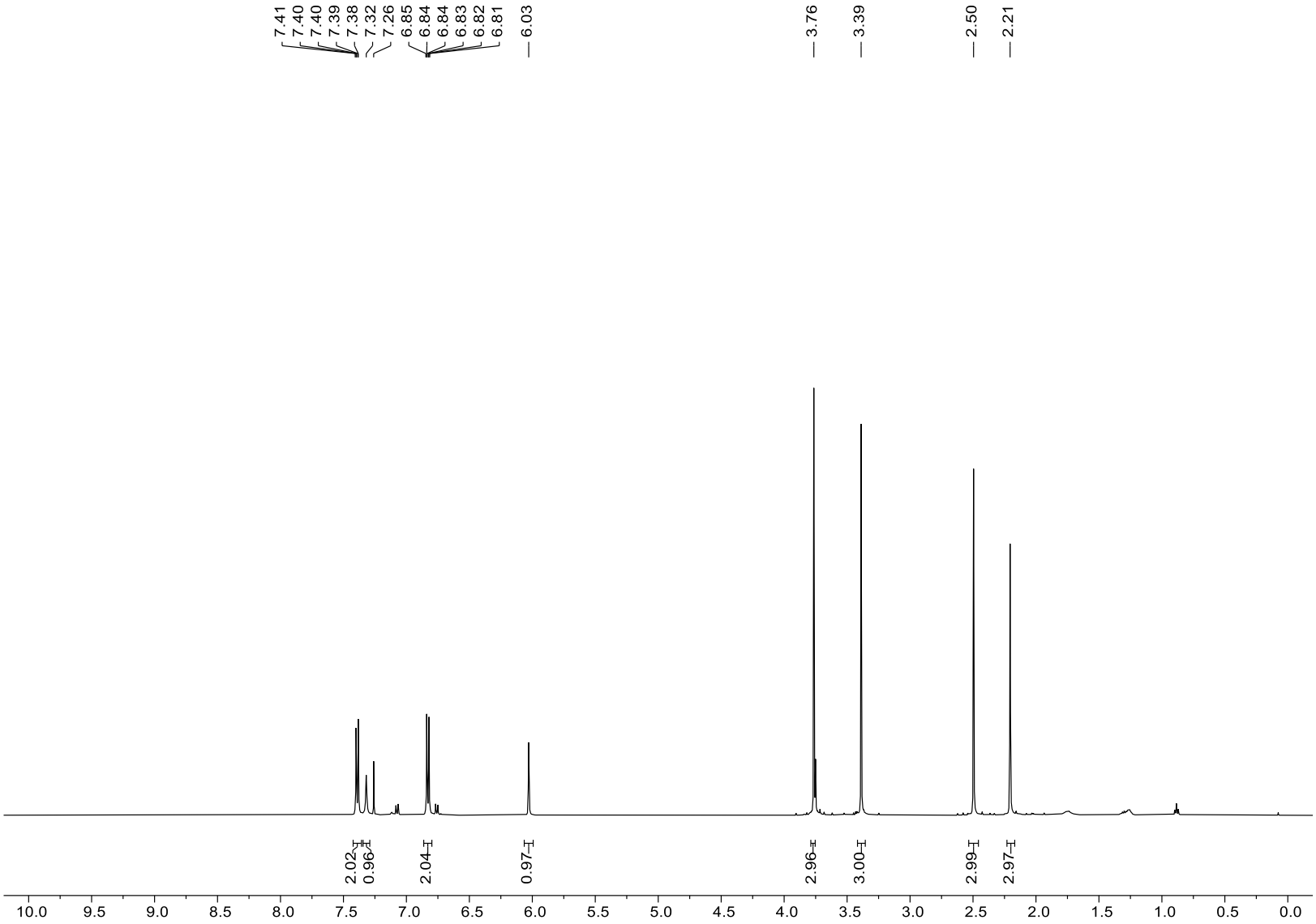


Figure S29: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1n**.

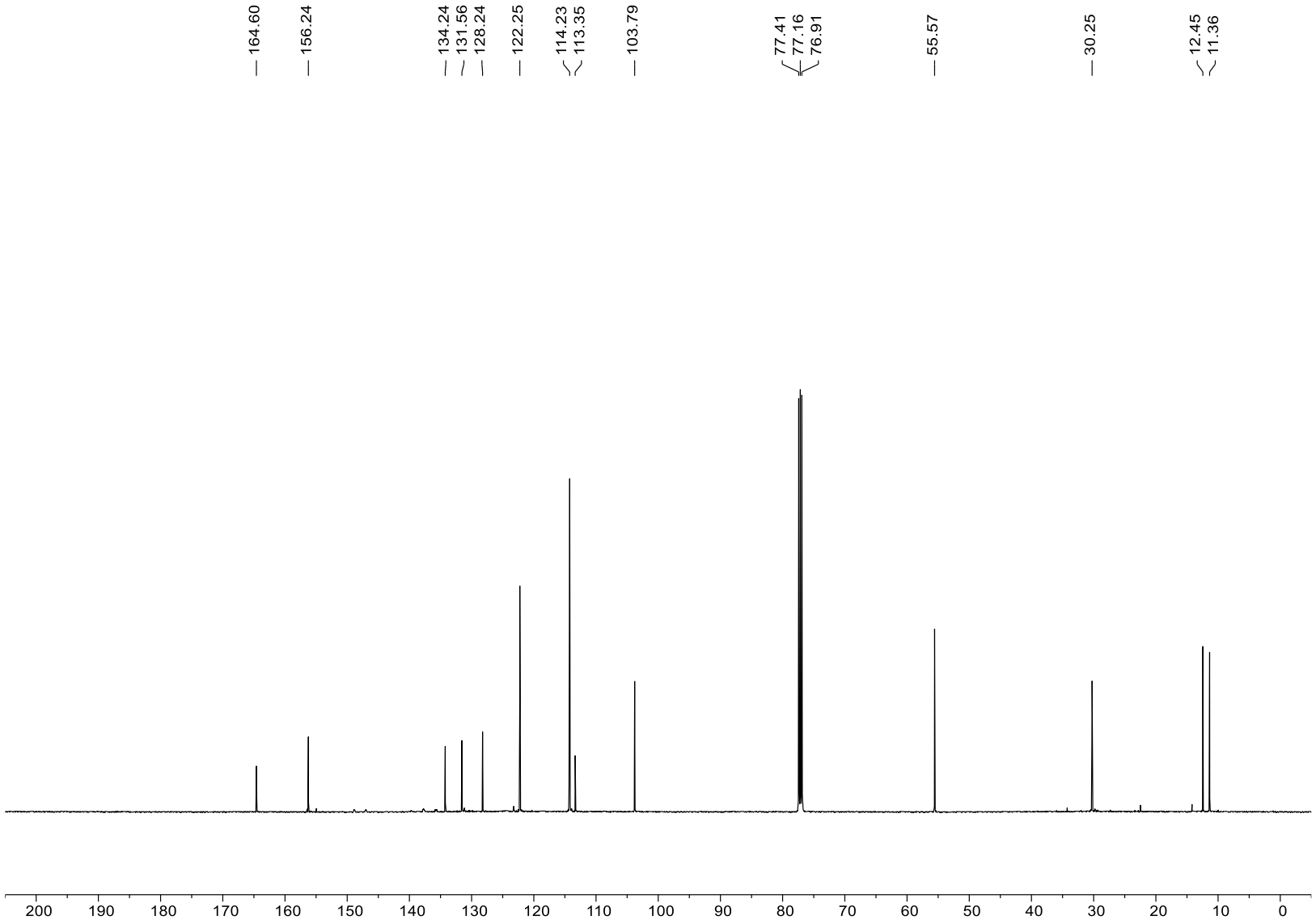


Figure S30: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1o'**.

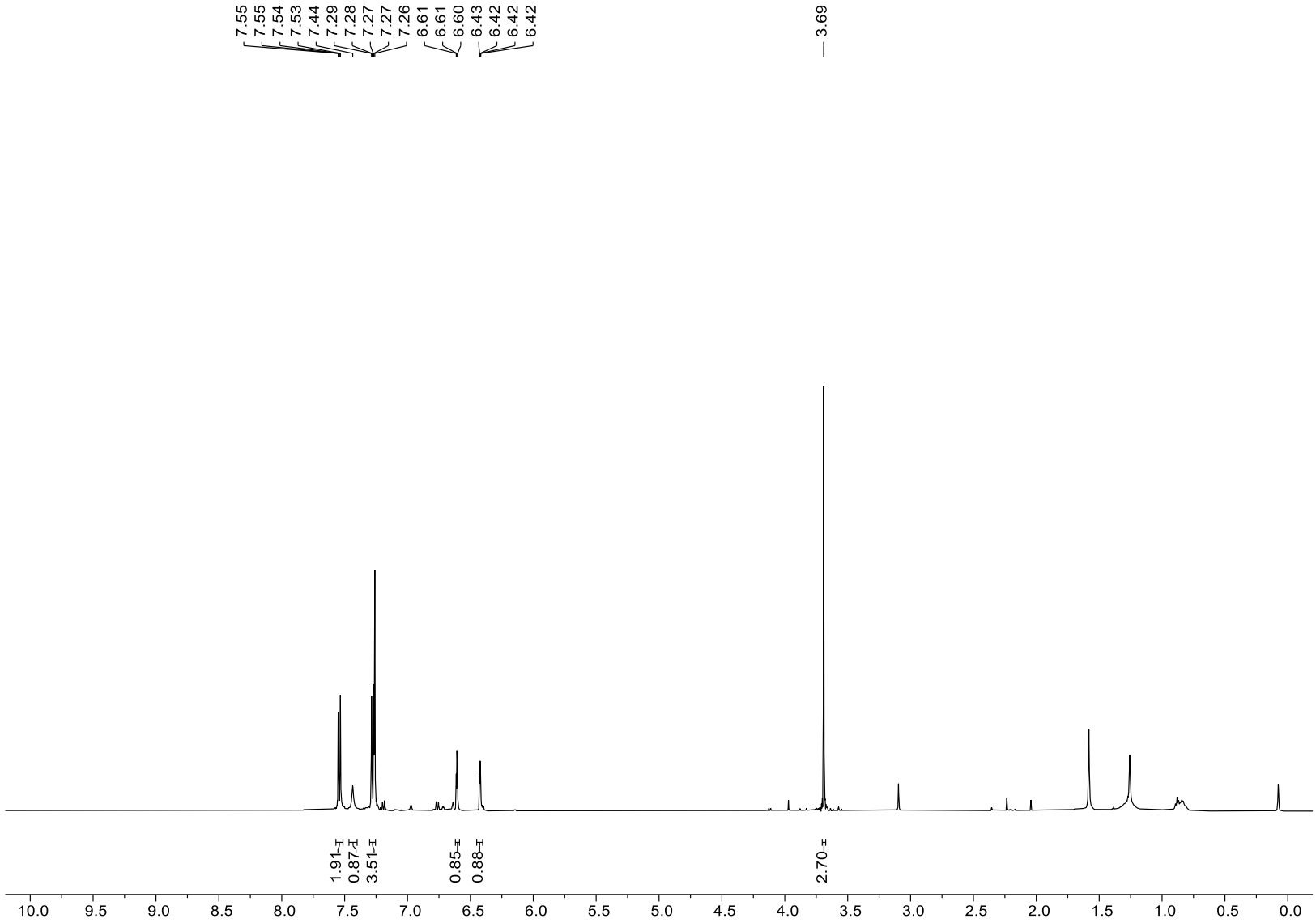


Figure S31: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1o'**.

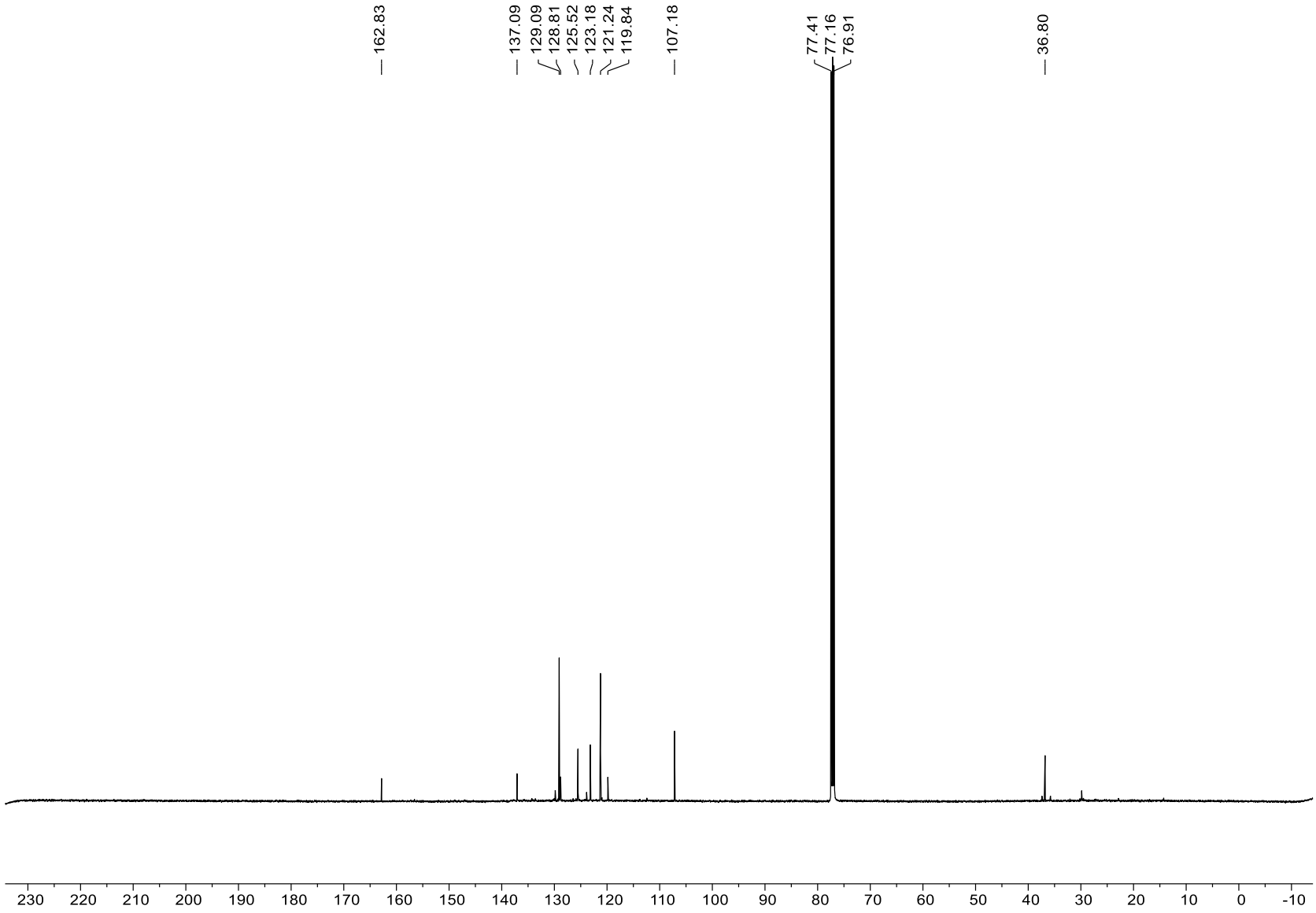


Figure S32: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1o**.

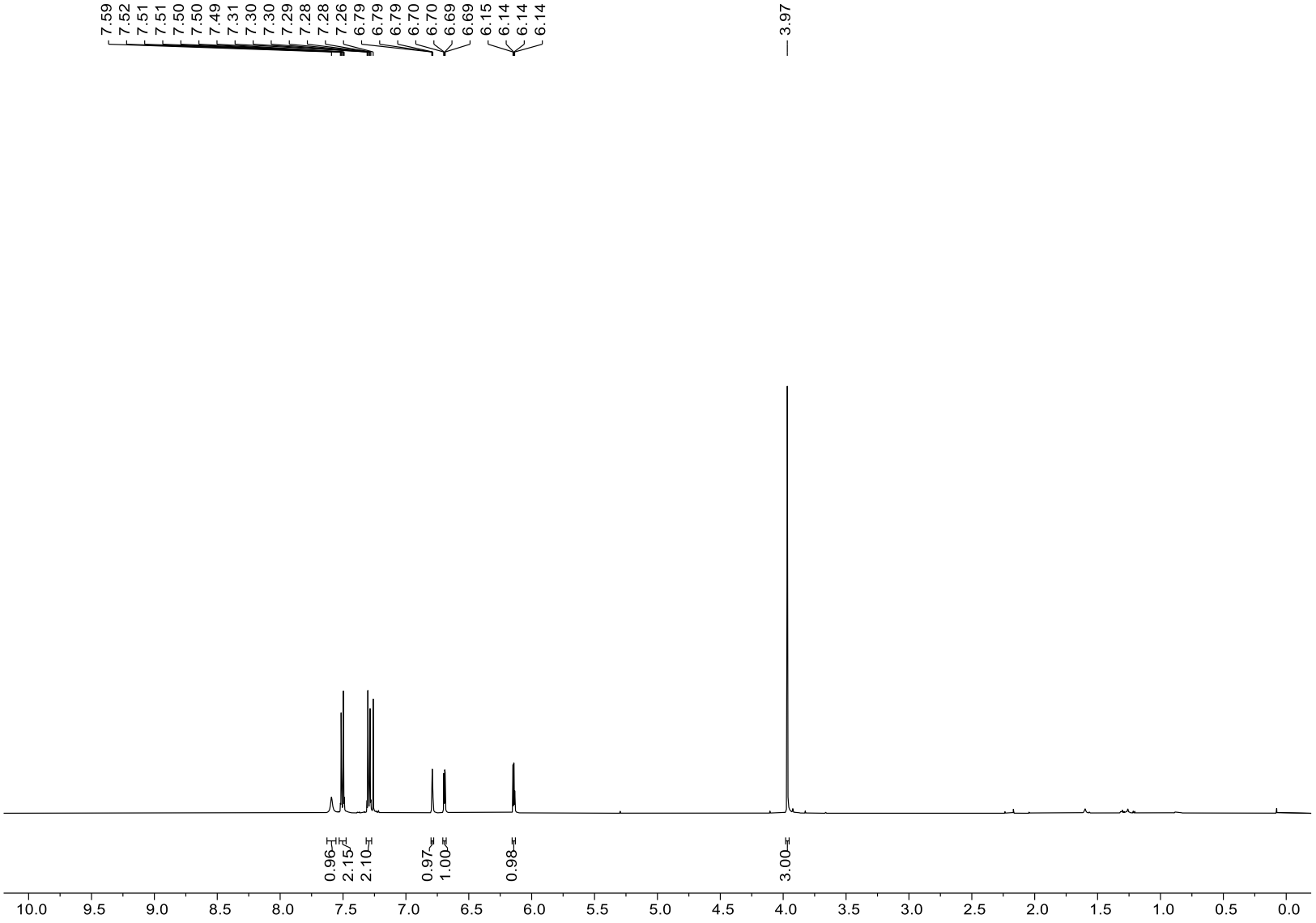


Figure S33: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1o**.

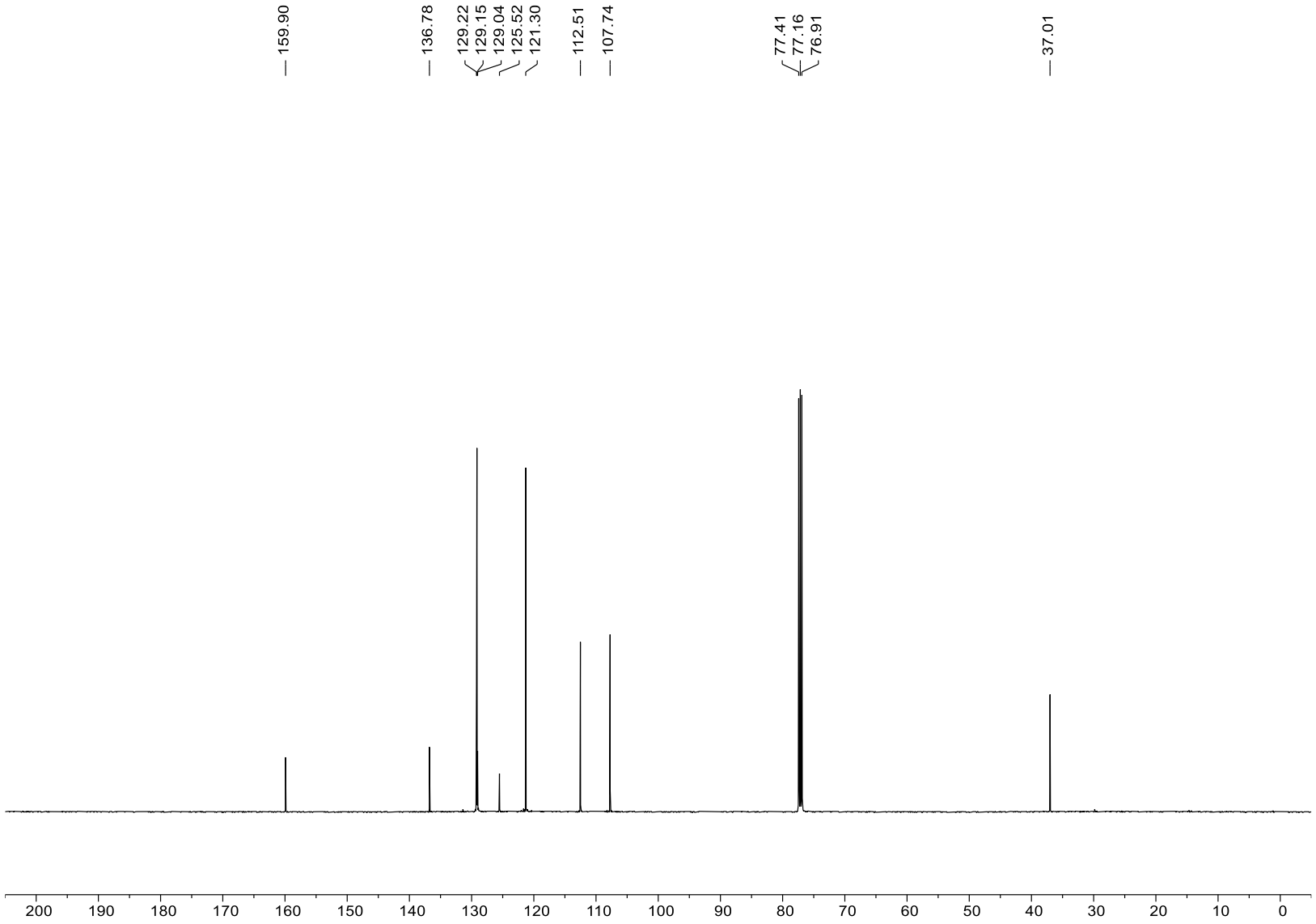


Figure S34: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1p'**.

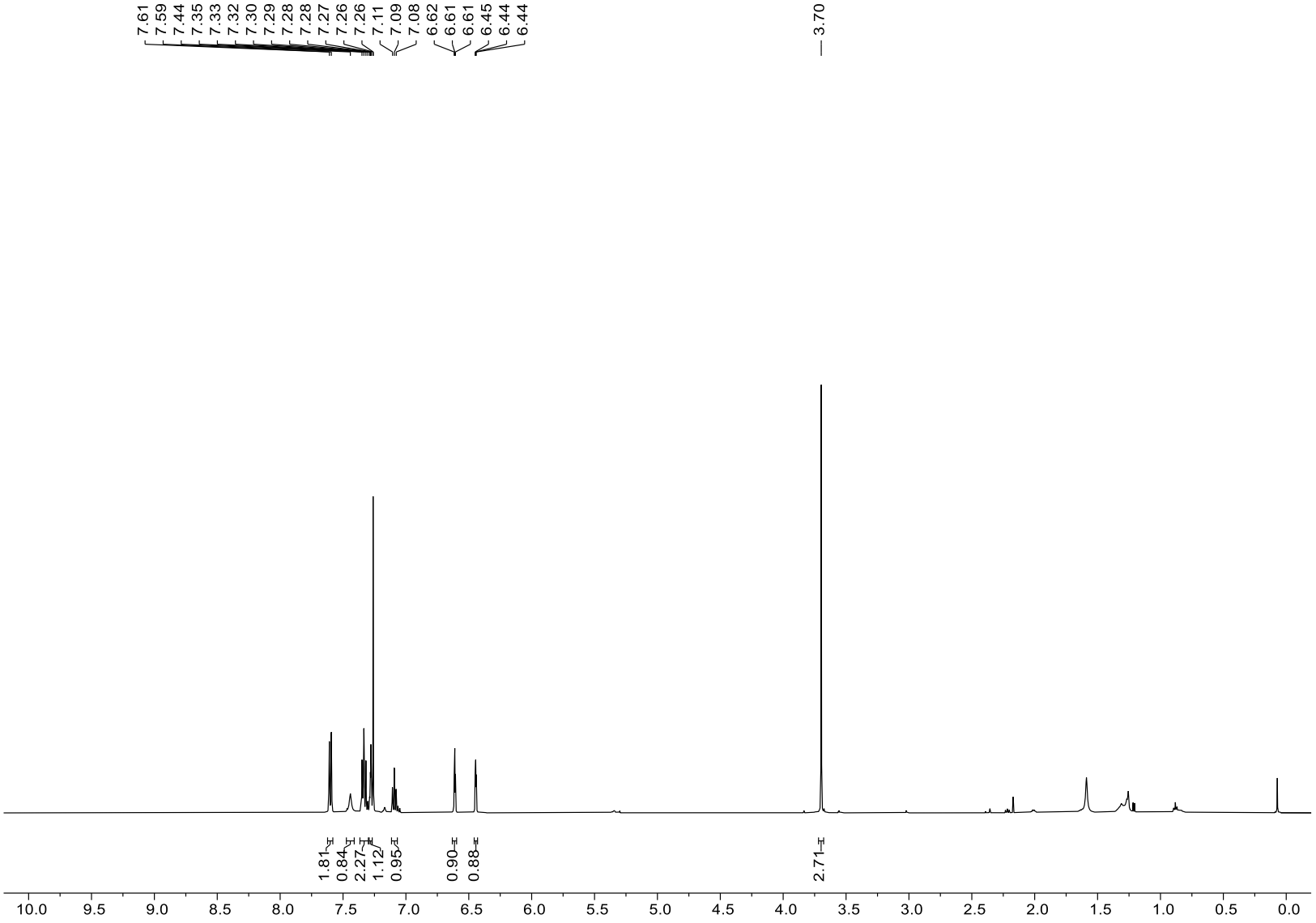


Figure S35: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1p'**.

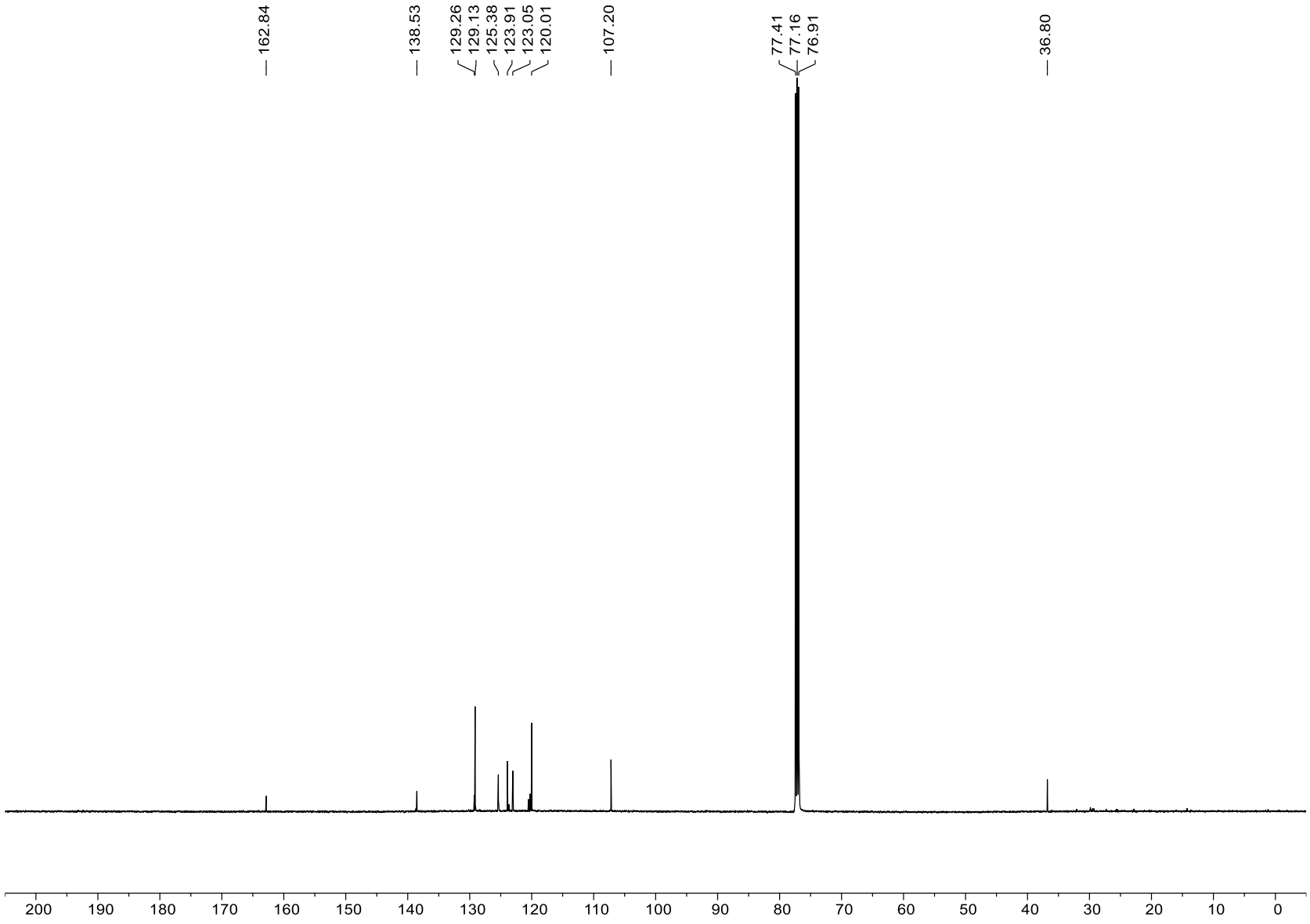


Figure S36: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1p**.

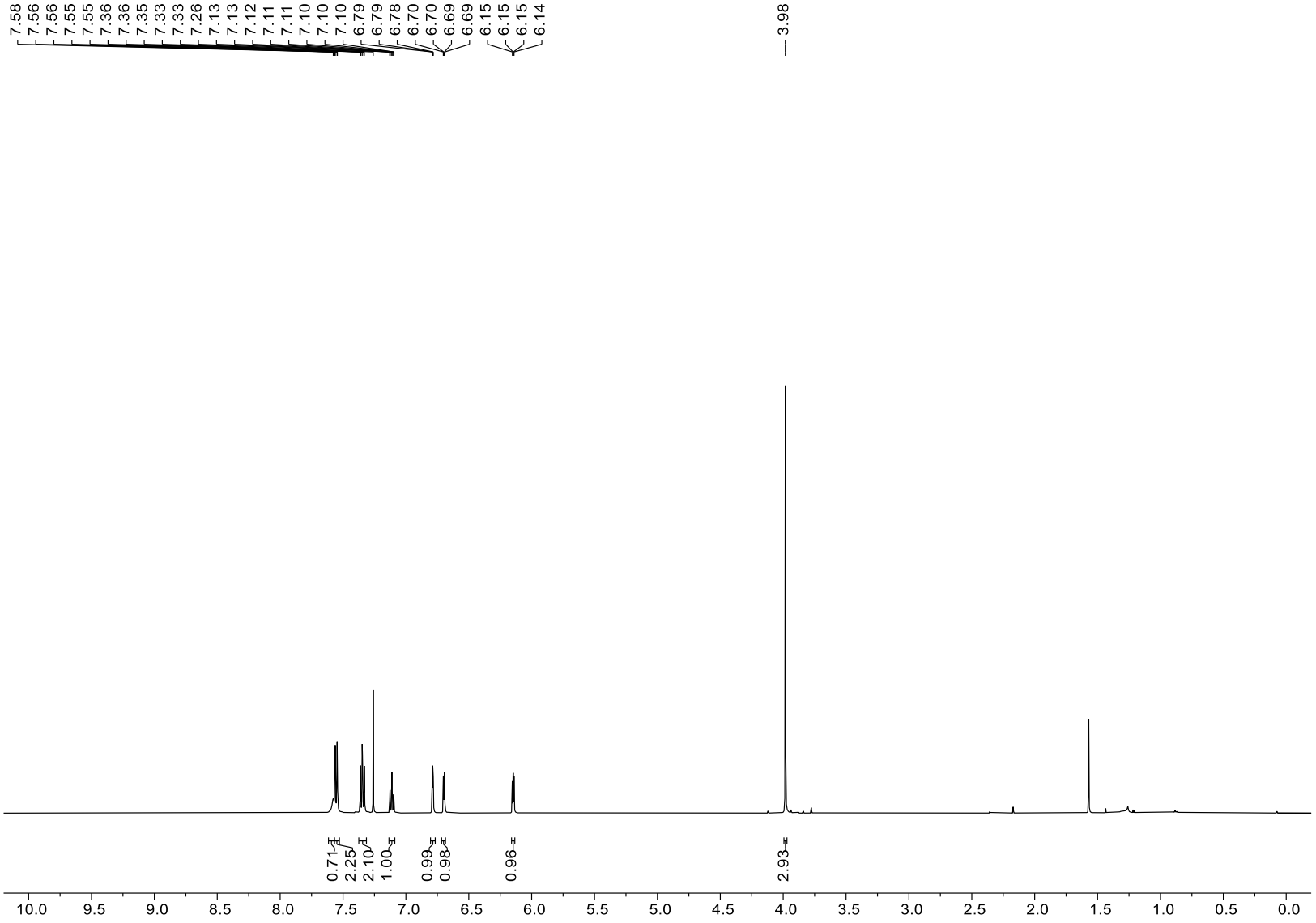


Figure S37: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1p**.

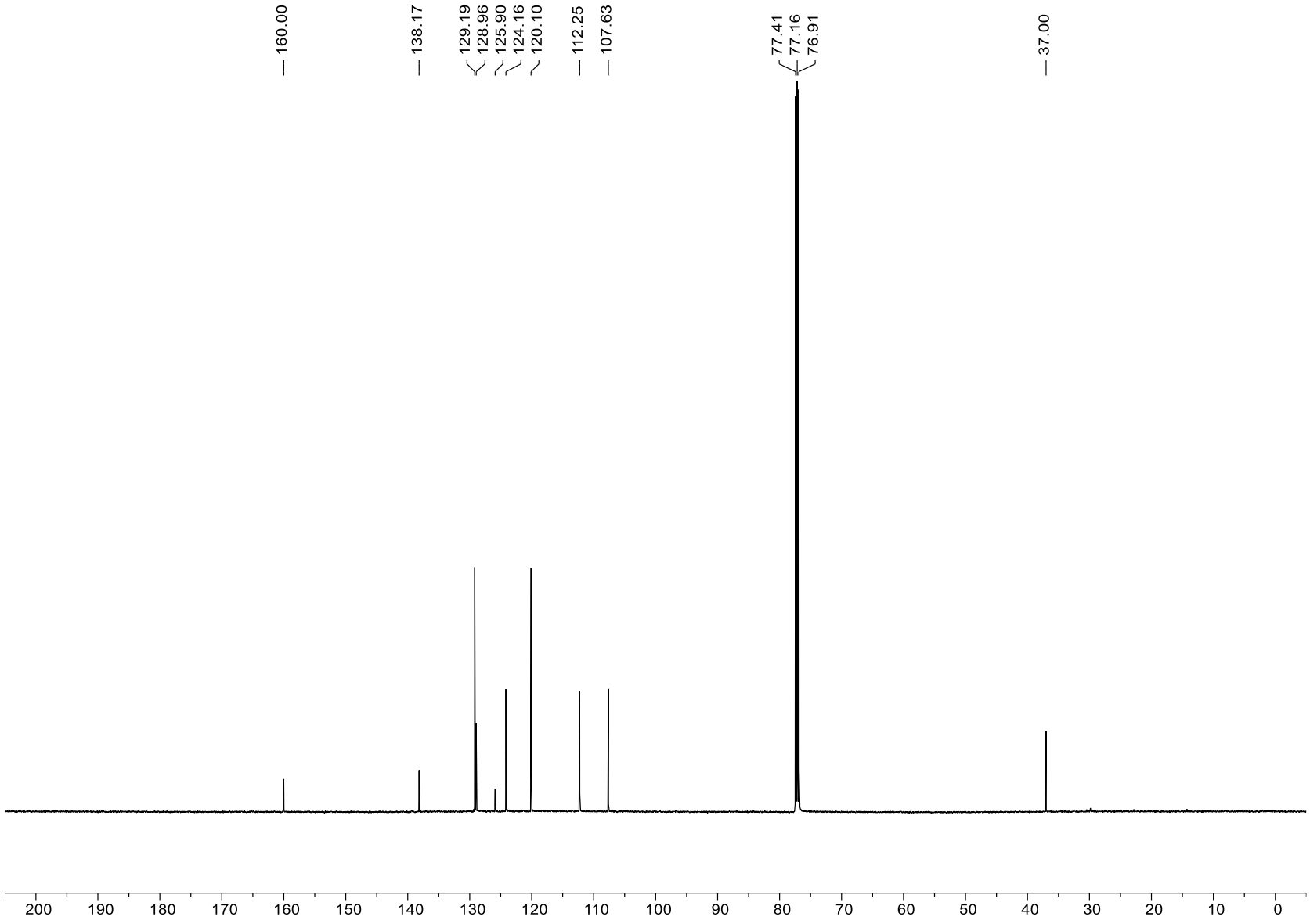


Figure S38: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1q**.

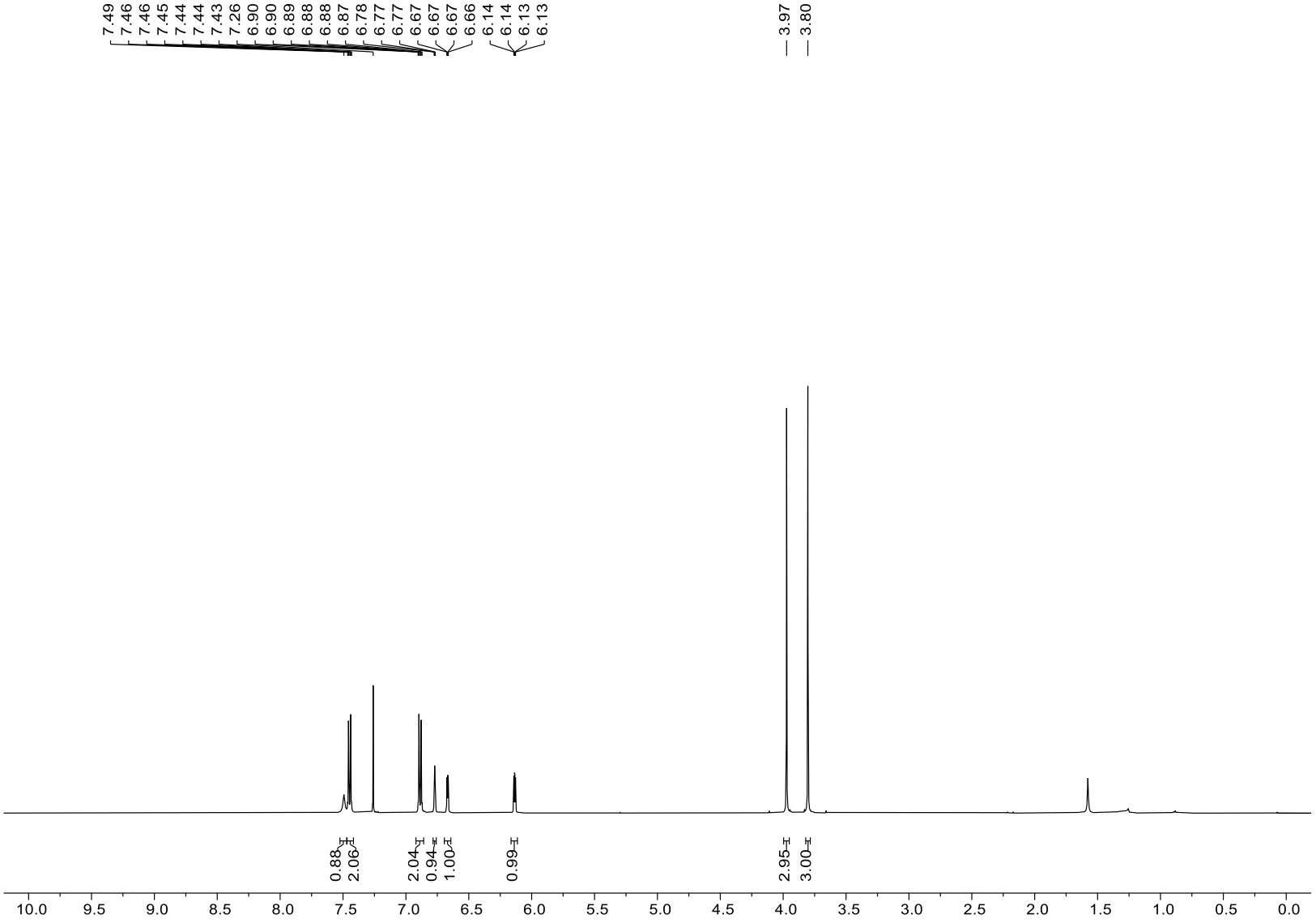


Figure S39: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1q**.

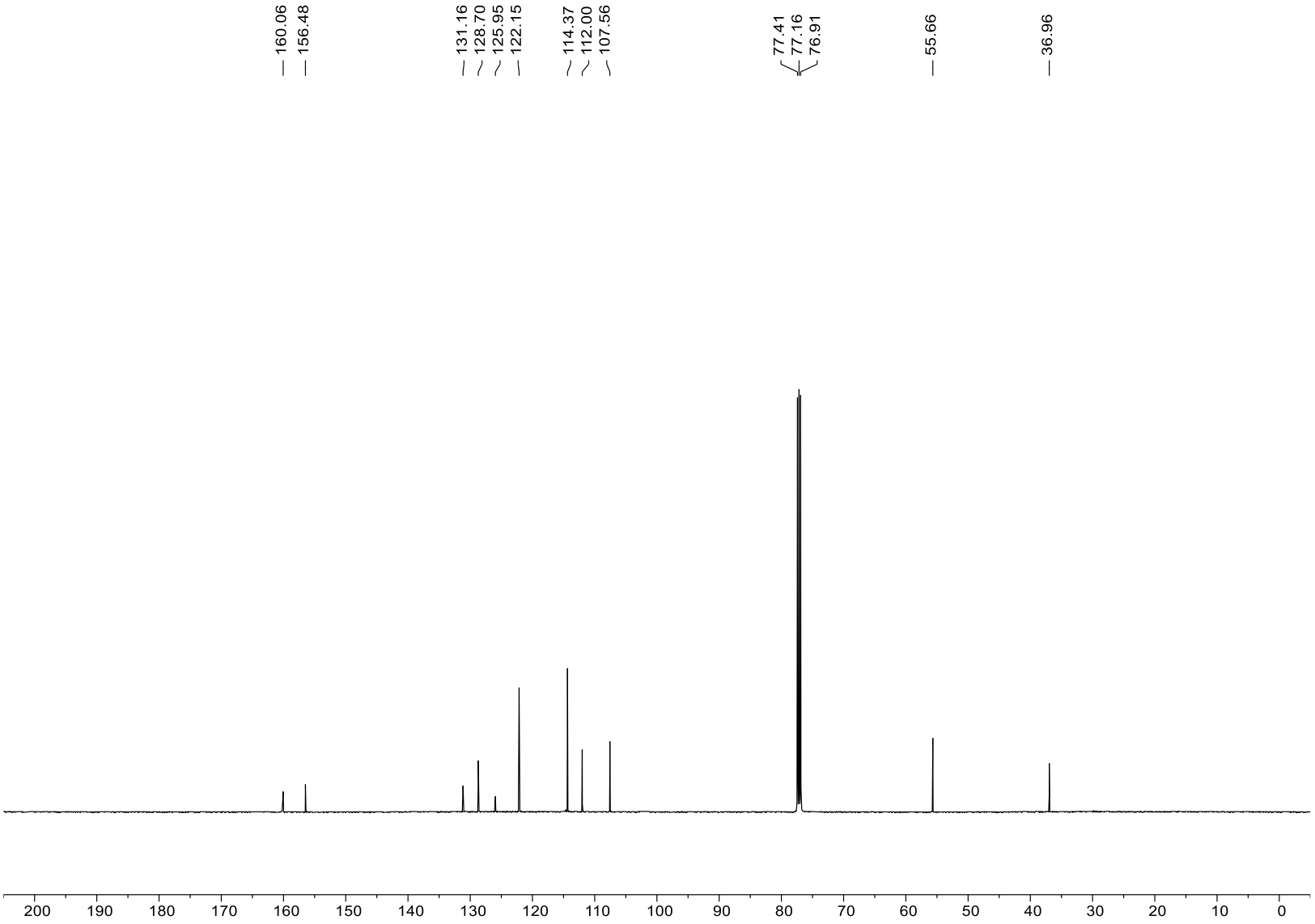


Figure S40: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1a·B(C_6F_5)$_3$**.

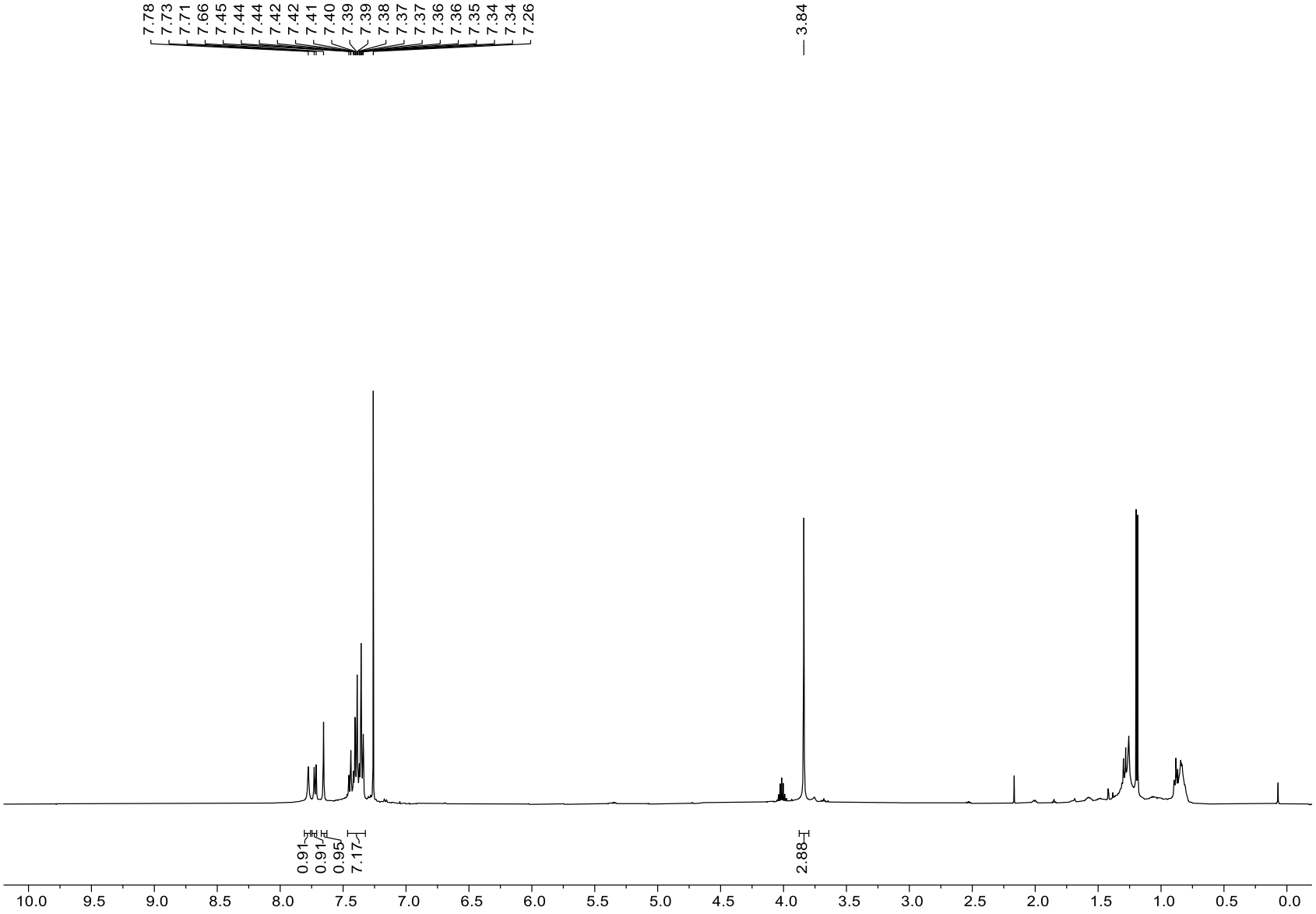


Figure S41: **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) spectrum of **1a·B(C_6F_5)$_3$**.

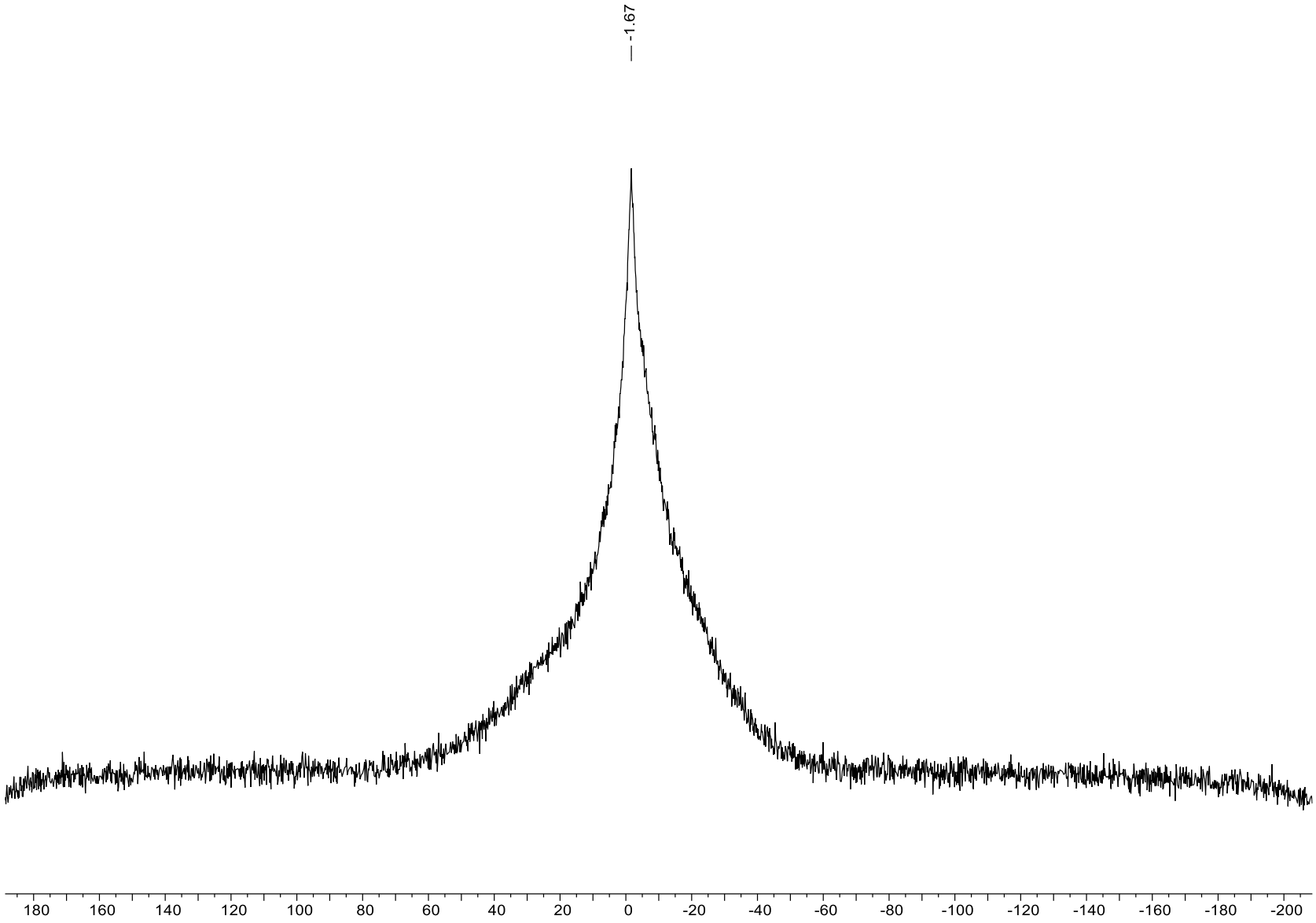


Figure S42: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) of **1a·B(C_6F_5)$_3$**.

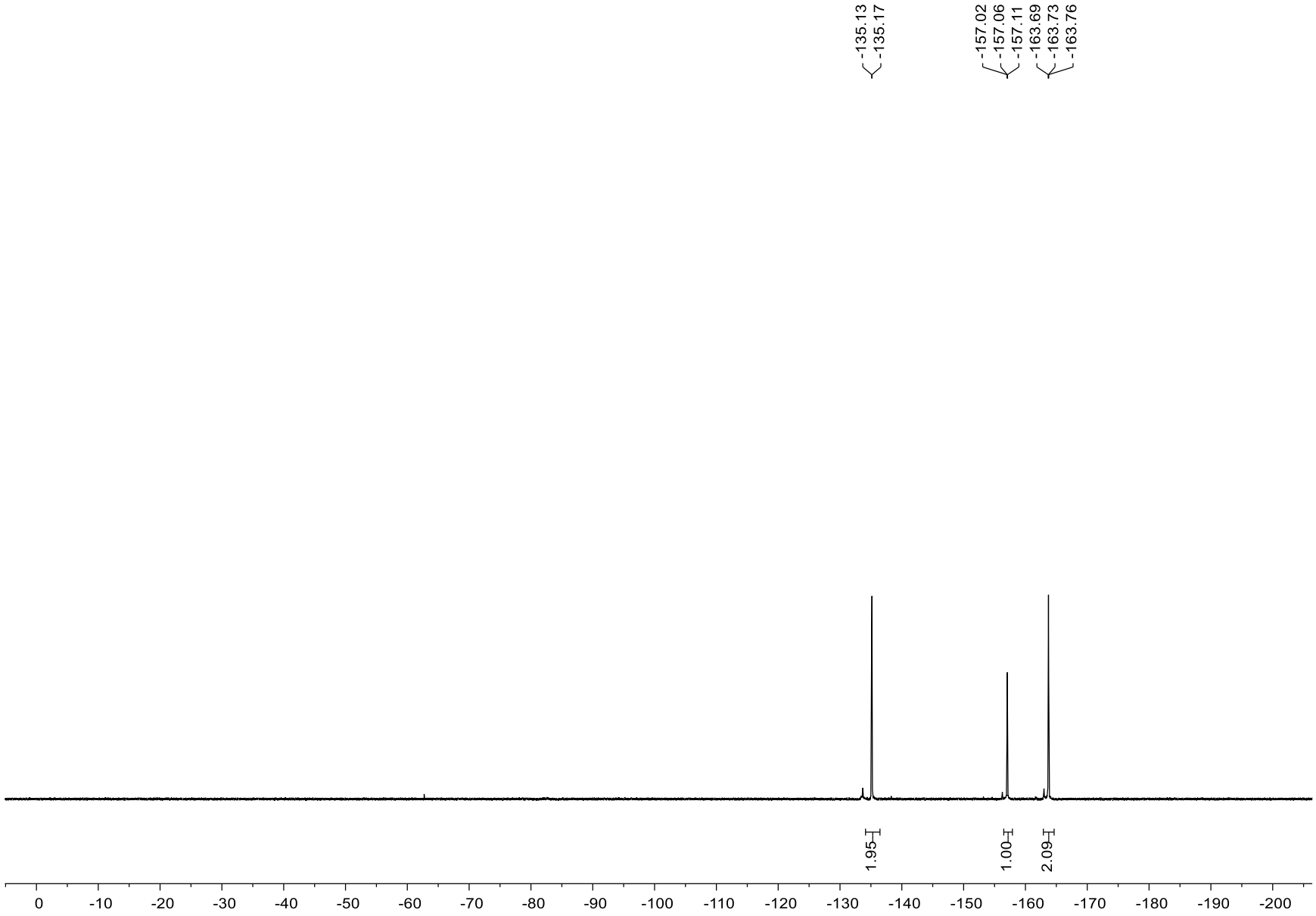


Figure S43: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **1b·B(C_6F_5)$_3$**.

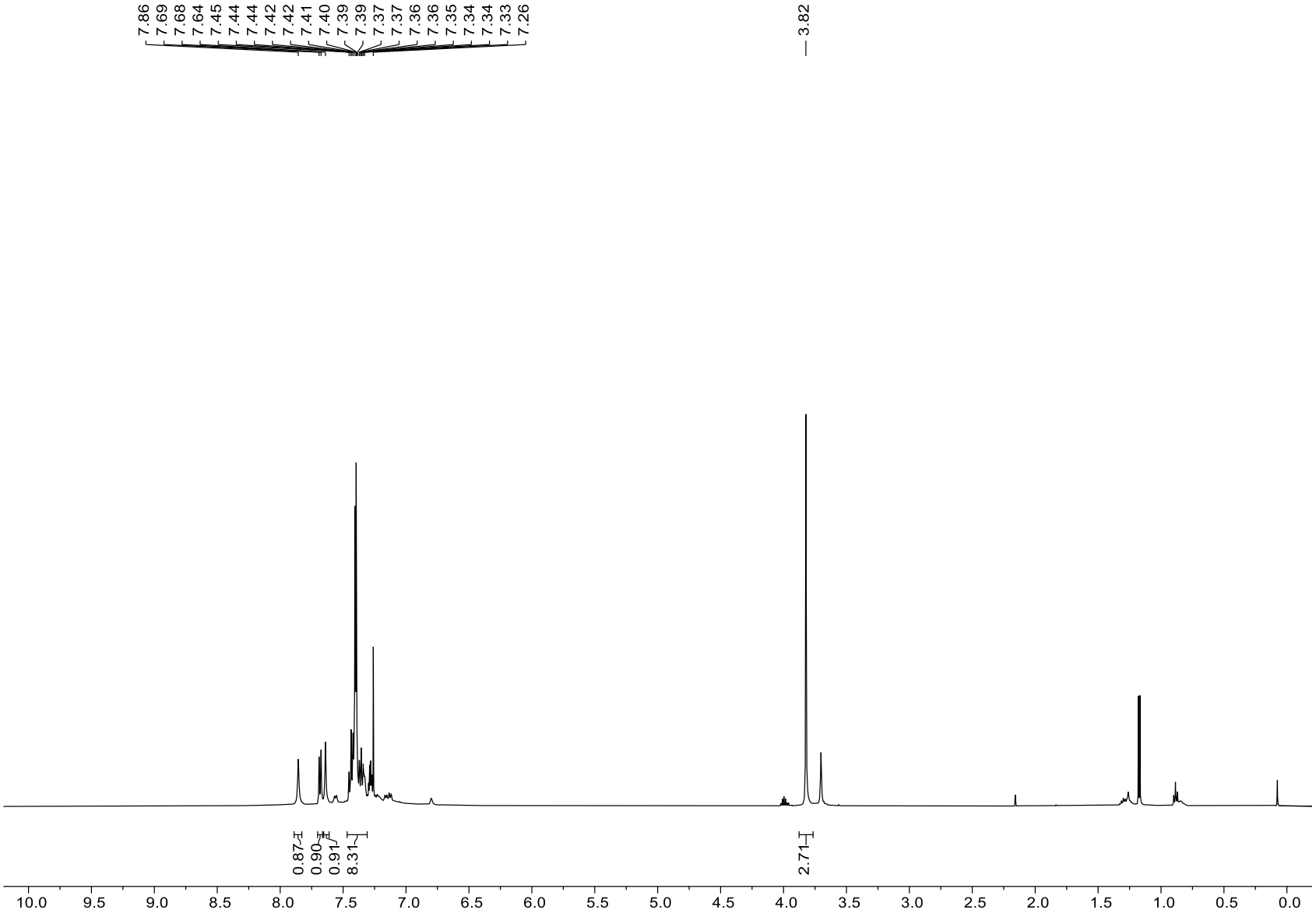


Figure S44: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **1b·B(C_6F_5)$_3$**.

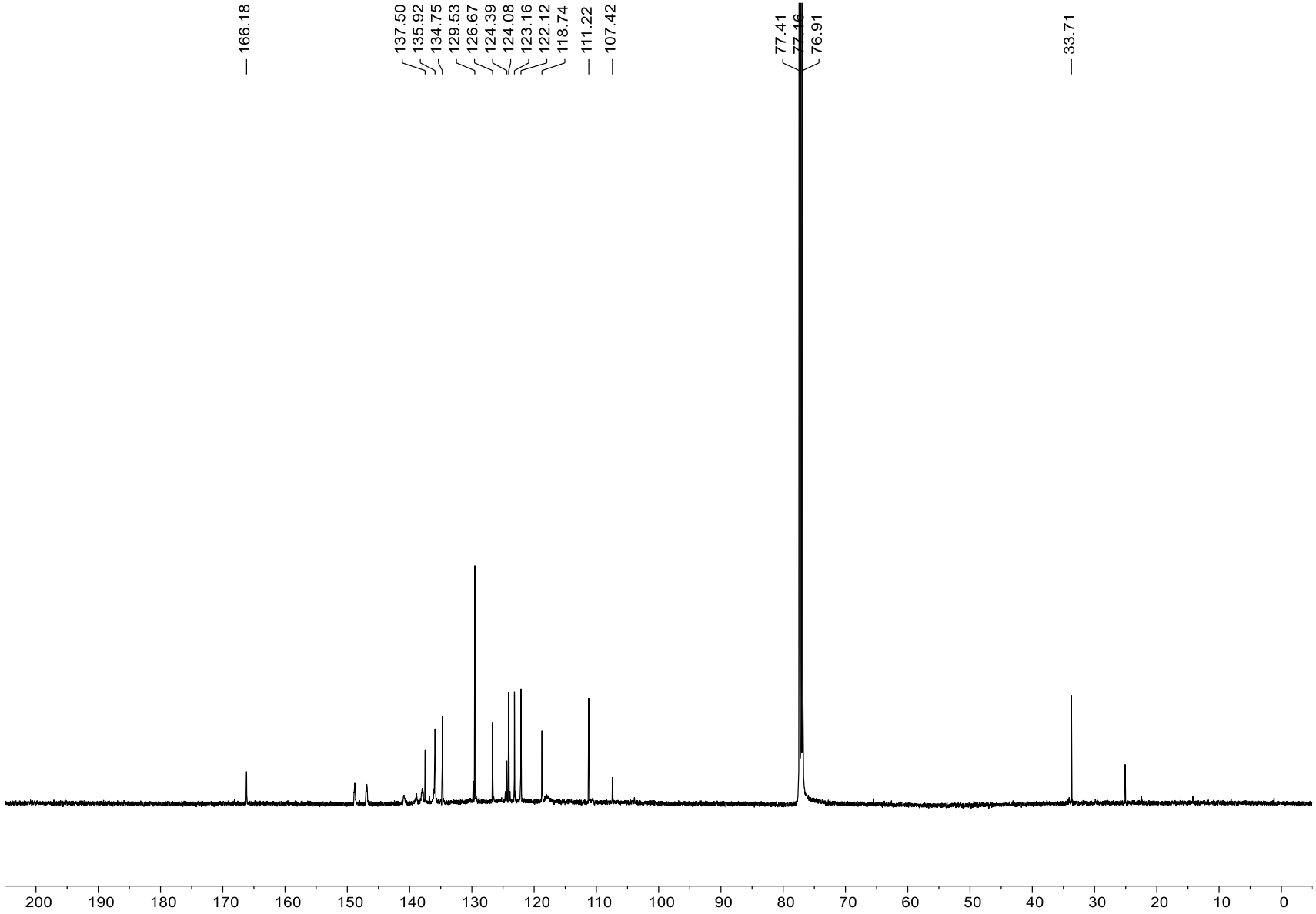


Figure S45: **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) spectrum of **1b·B(C_6F_5)$_3$**.

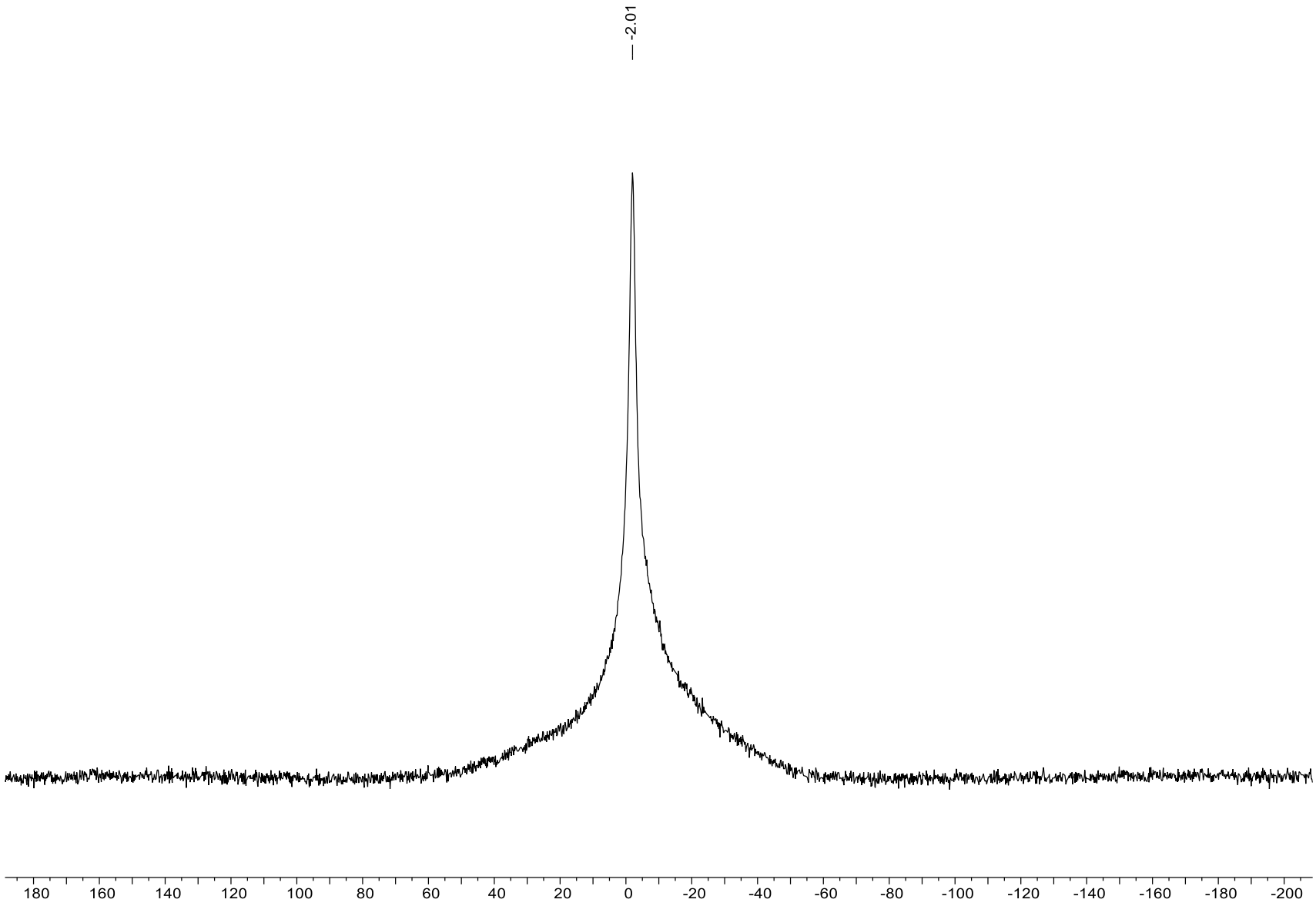


Figure S46: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) of **1b·B(C_6F_5)$_3$**.

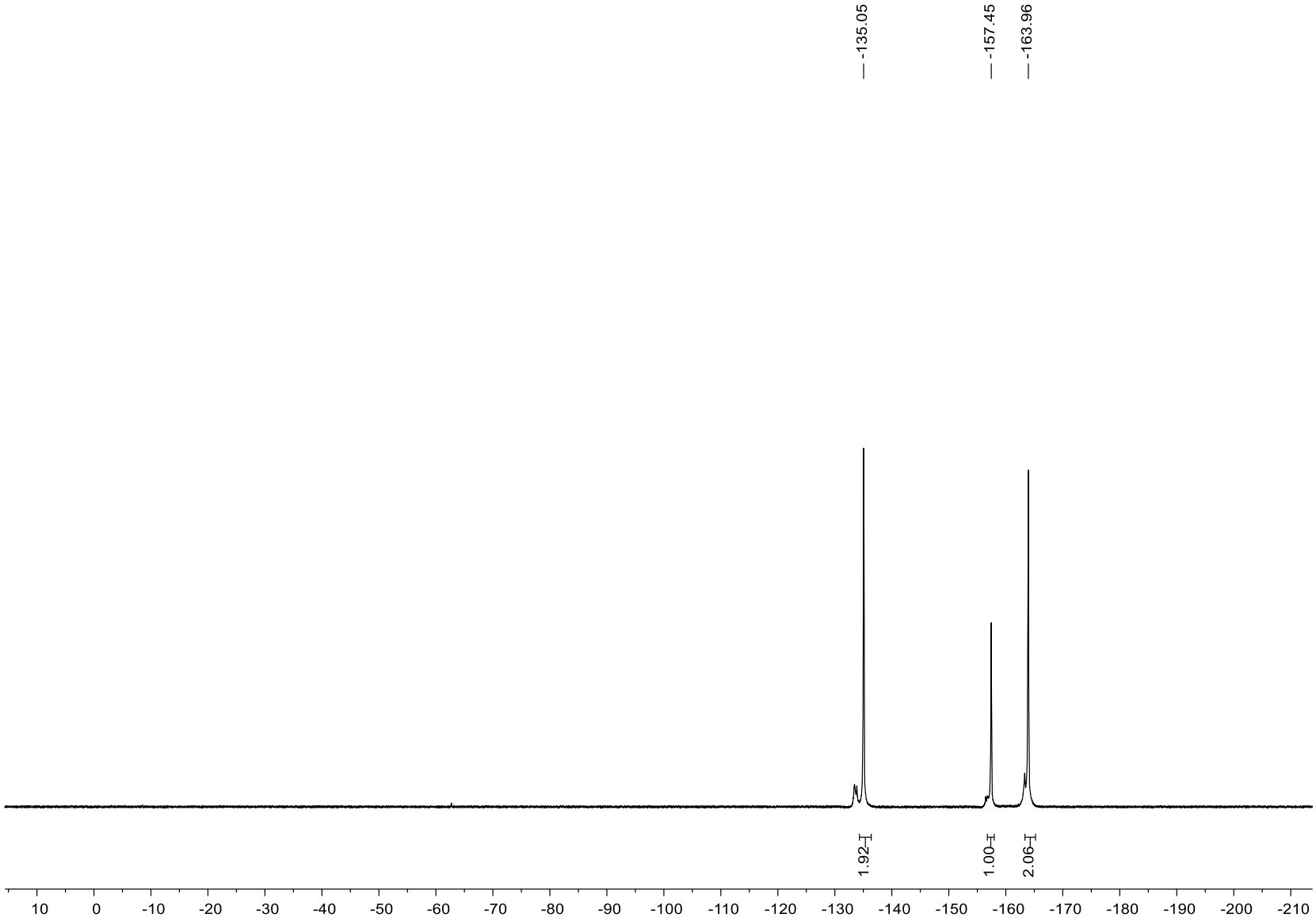


Figure S47: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **2**.

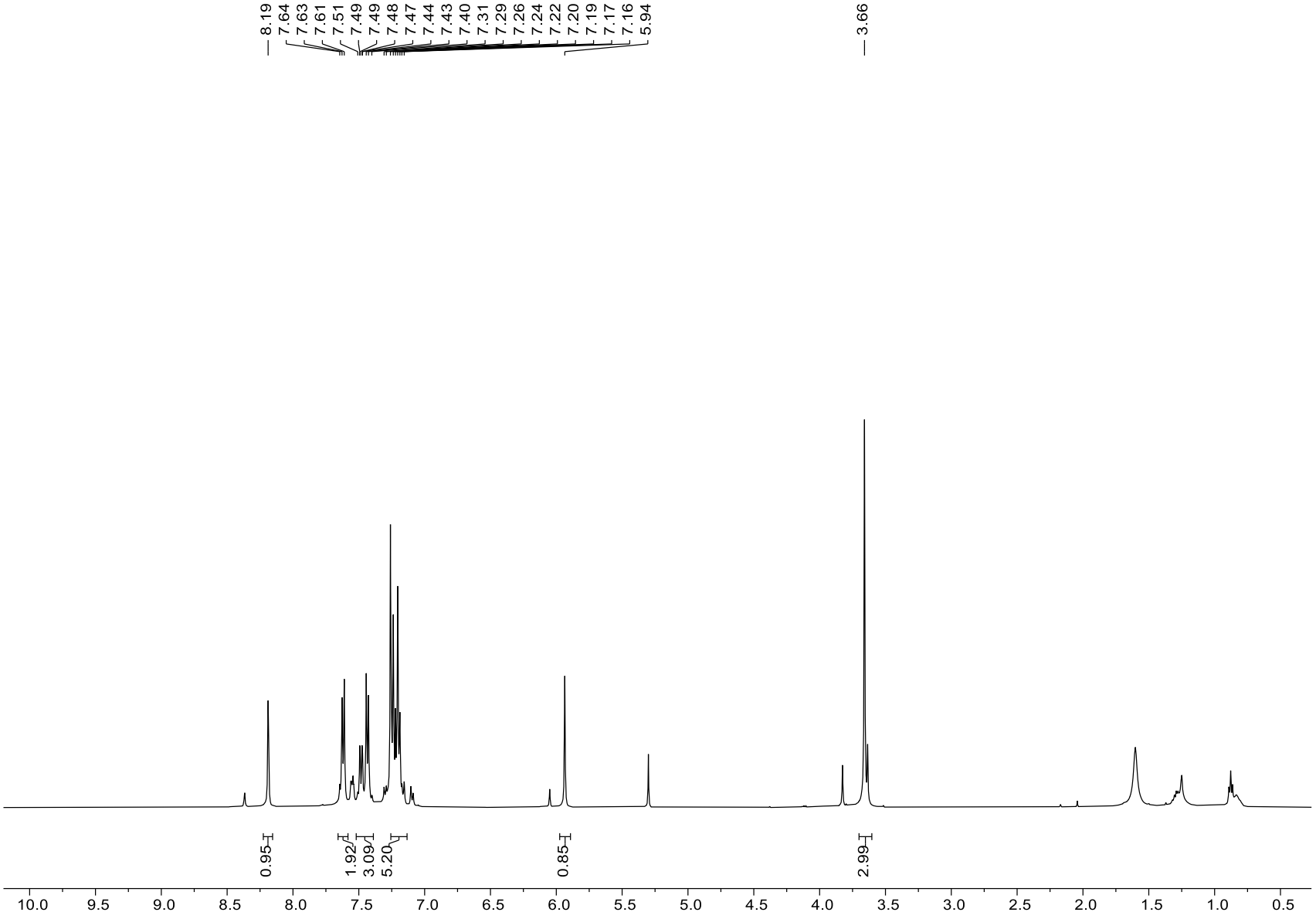


Figure S48: **^{13}C NMR** (126 MHz, $CDCl_3$, 298K) spectrum of **2**.

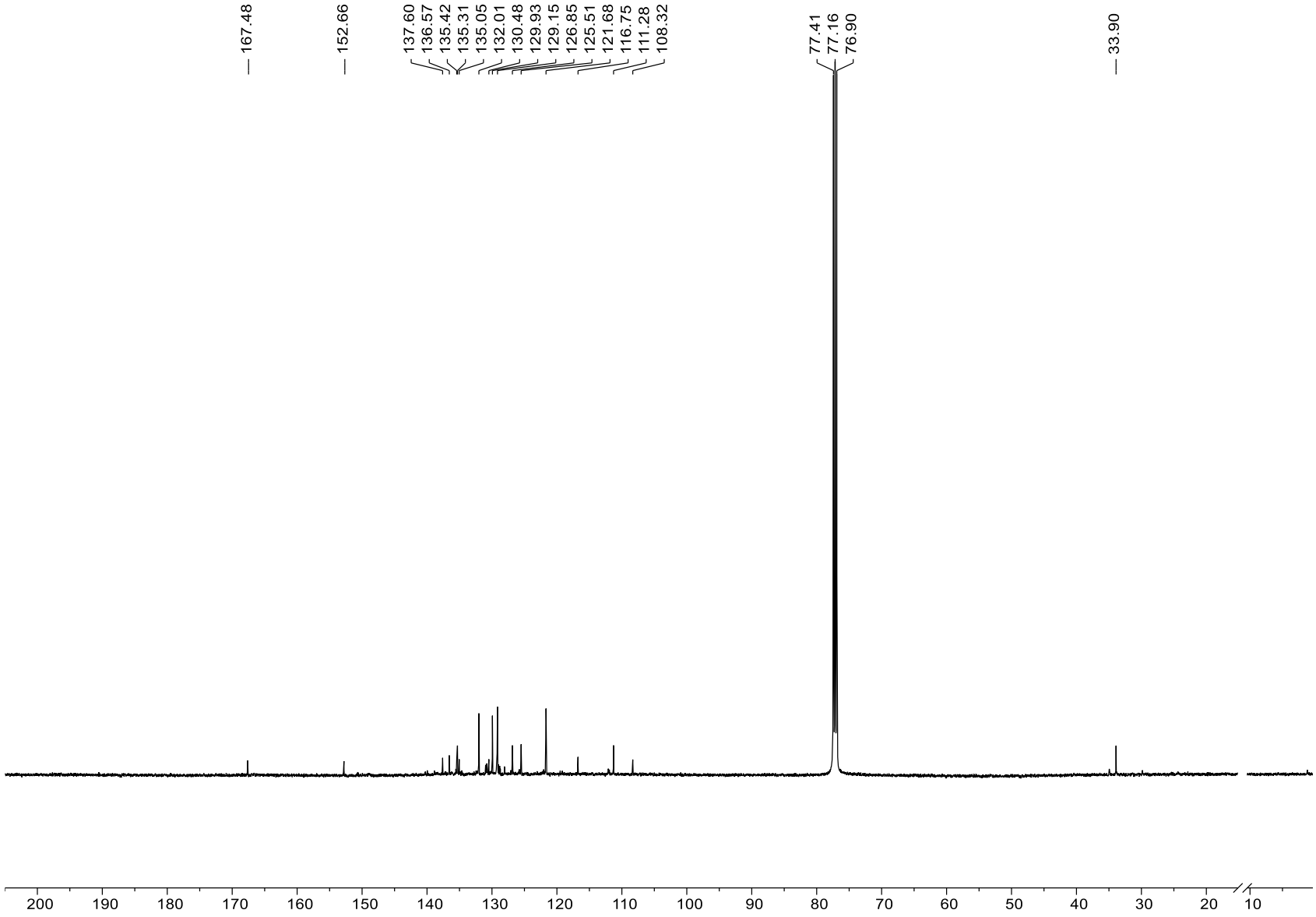


Figure S49: **^{11}B NMR** (128 MHz, $CDCl_3$, 298 K) spectrum of **2**.

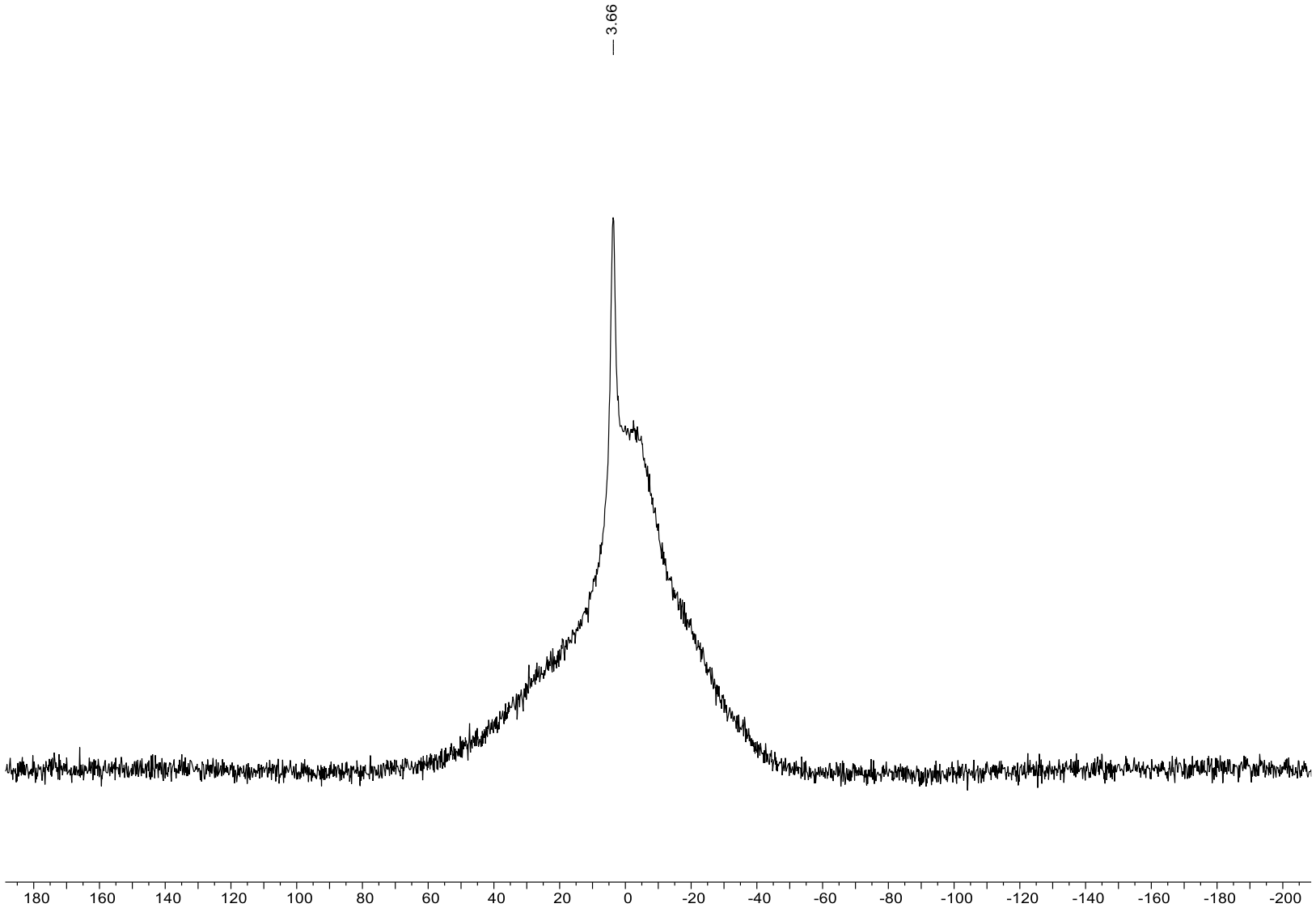


Figure S50: **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K) spectrum of **2**.

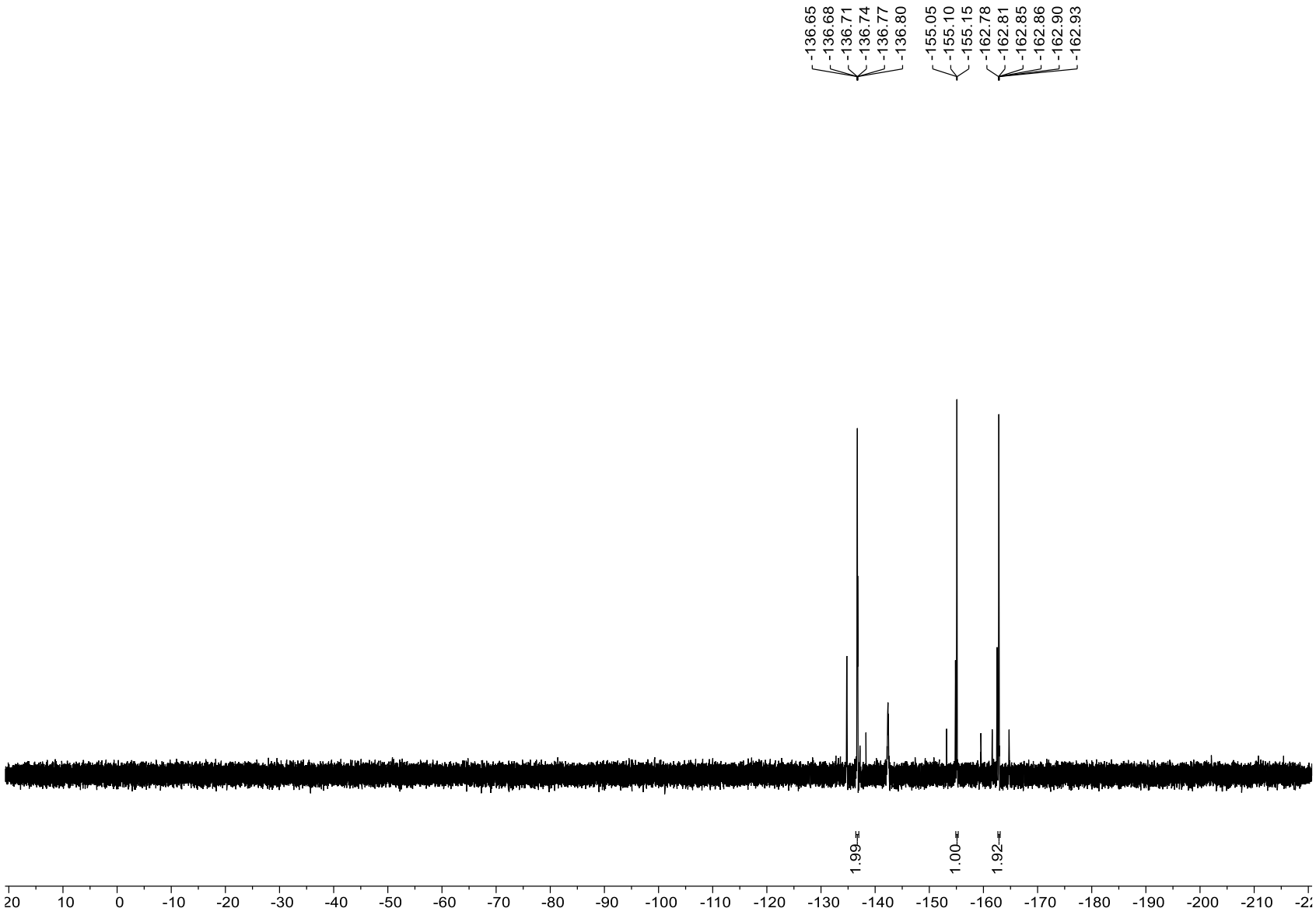


Figure S51: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **3**.

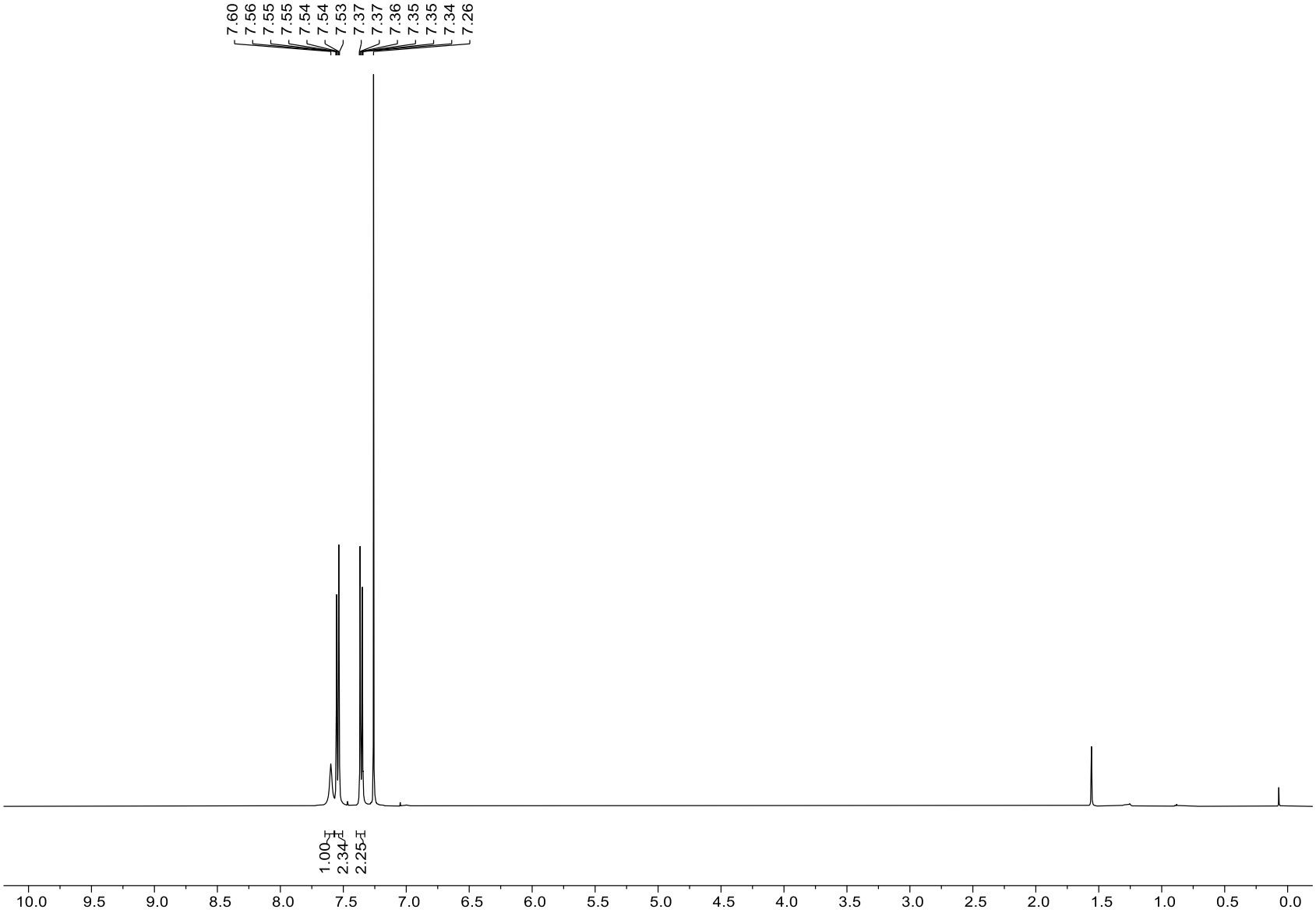


Figure S52: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **3**.

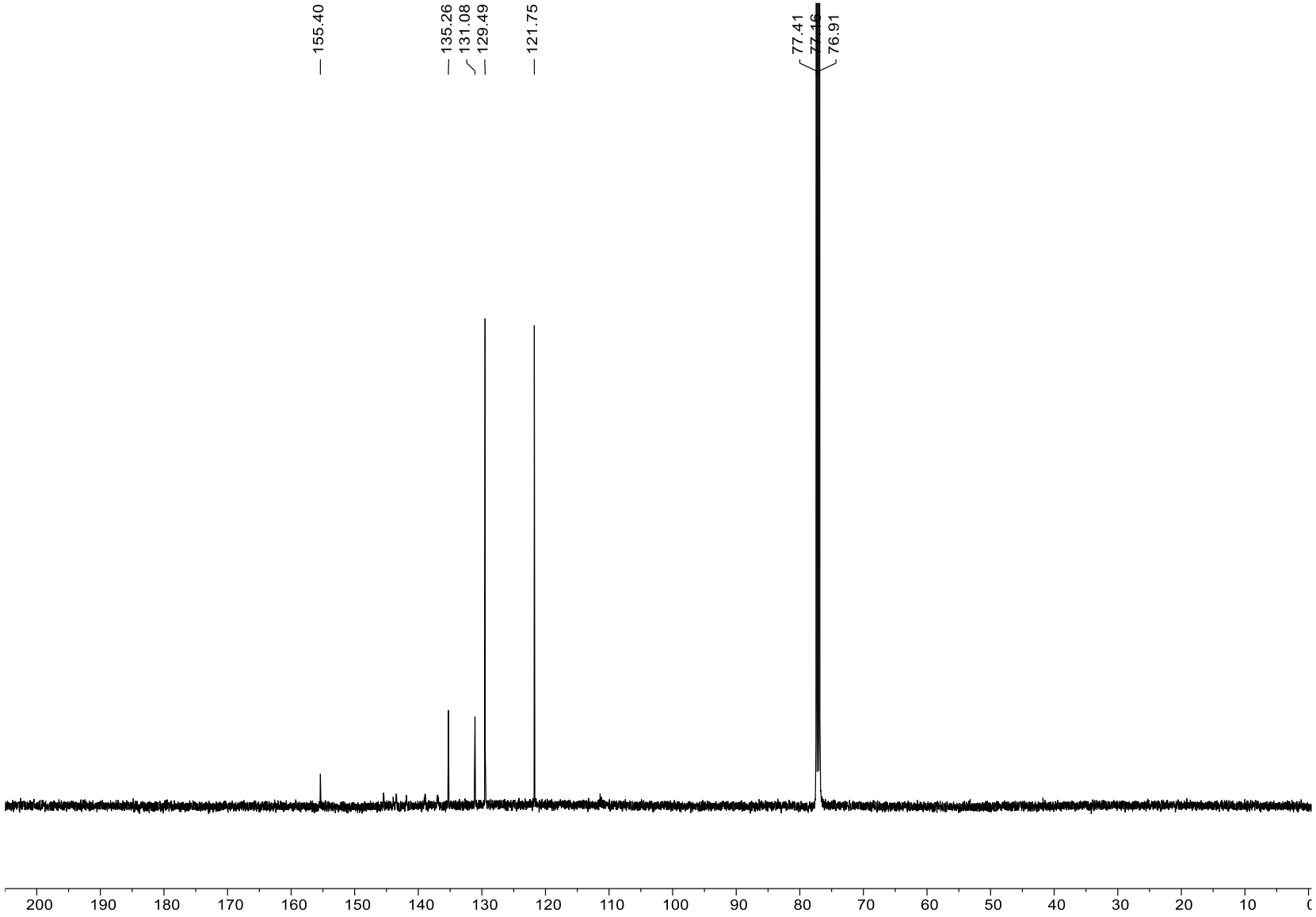


Figure S53: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) of **3**.

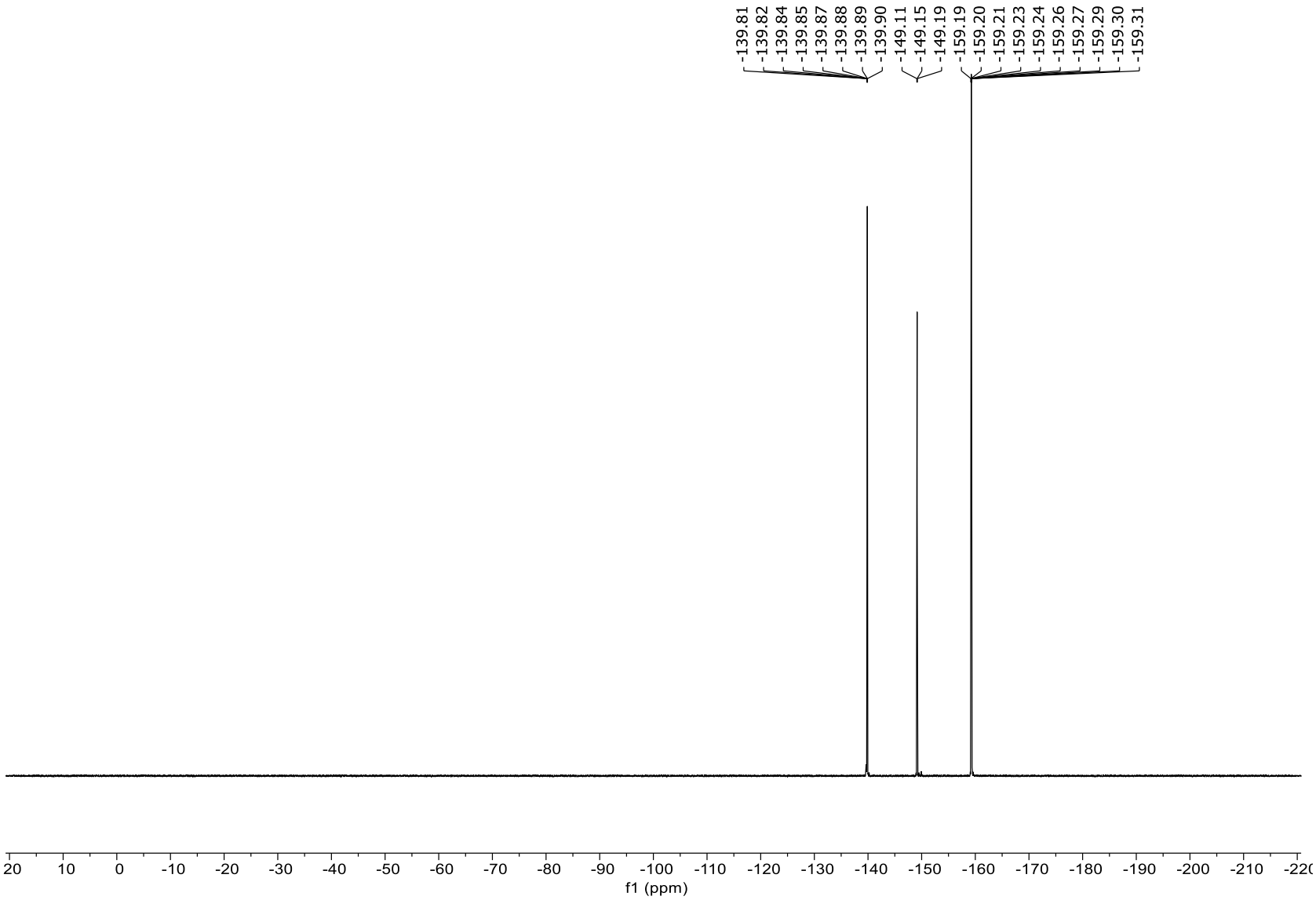


Figure S54: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **4**.

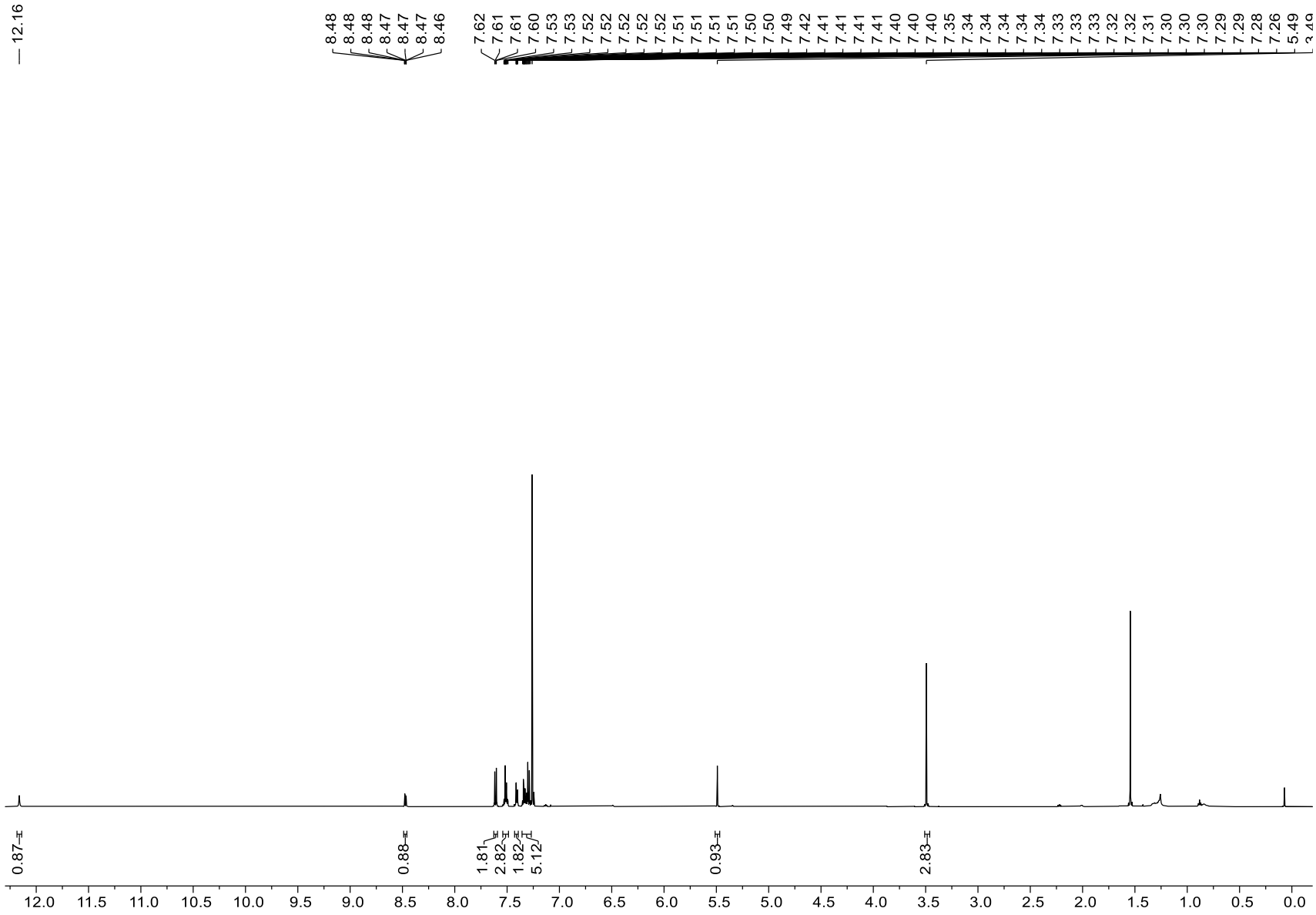


Figure S55: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **4**.

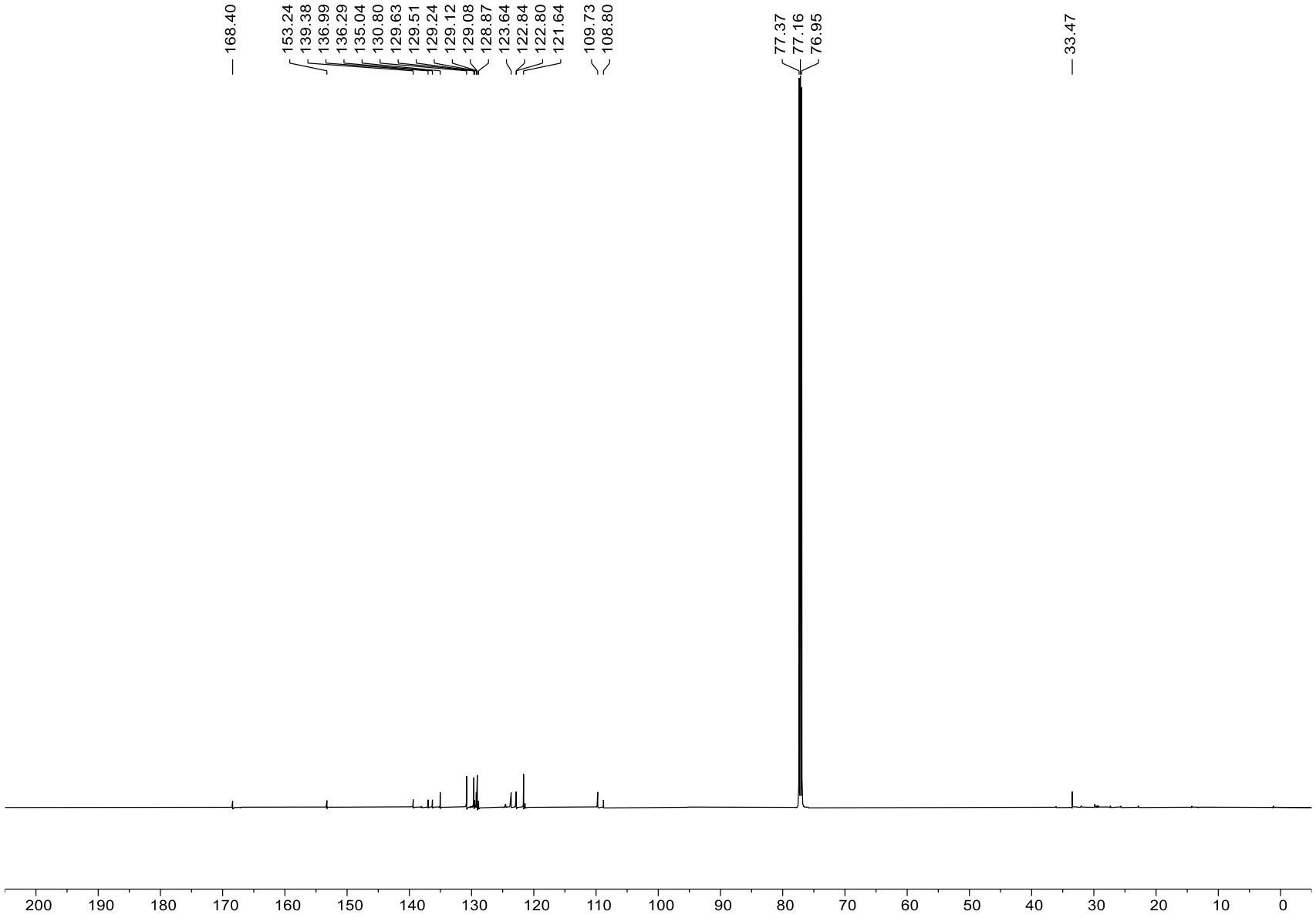


Figure S58: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5a**.

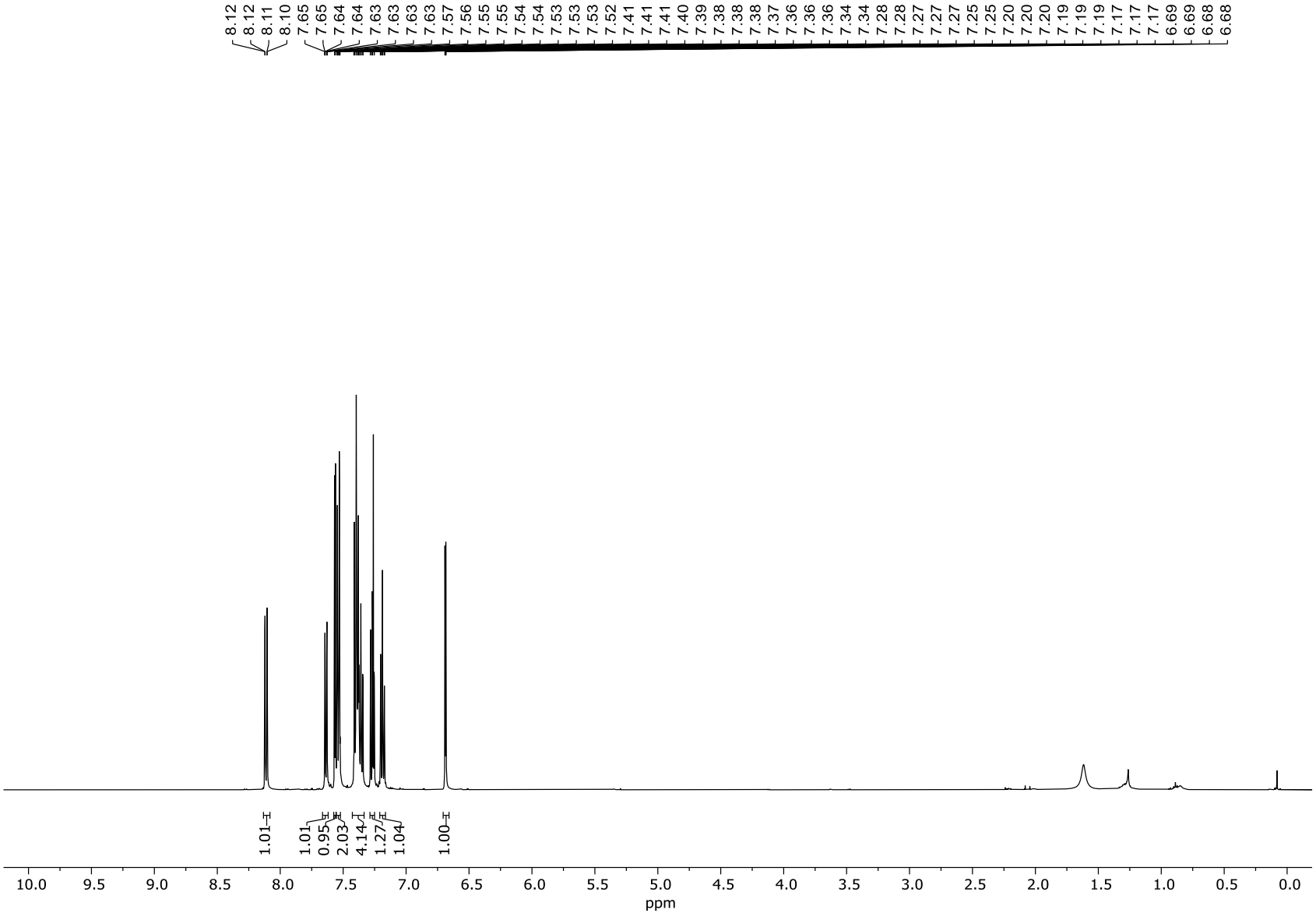


Figure S59: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5a**.

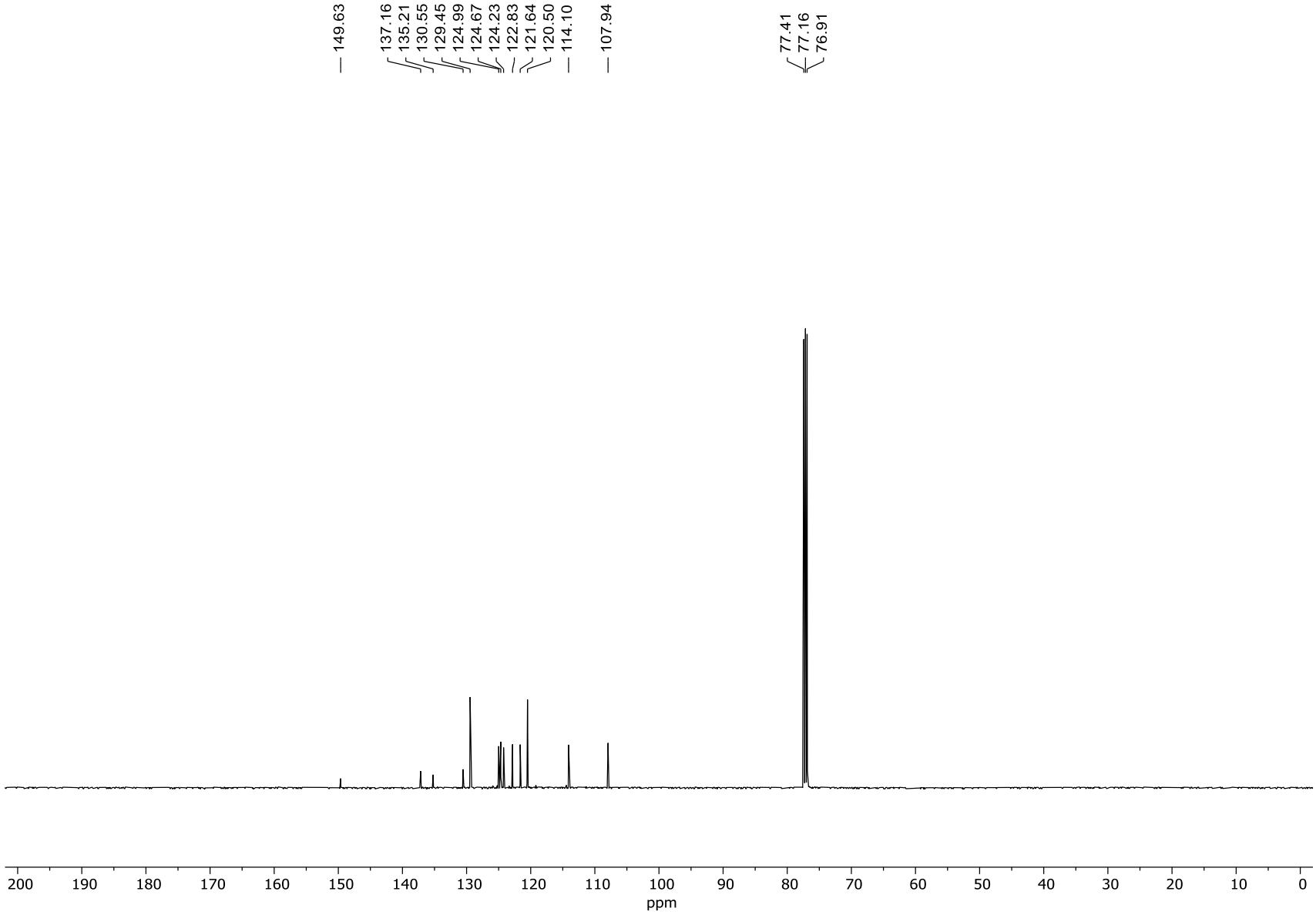


Figure S60: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5b**.

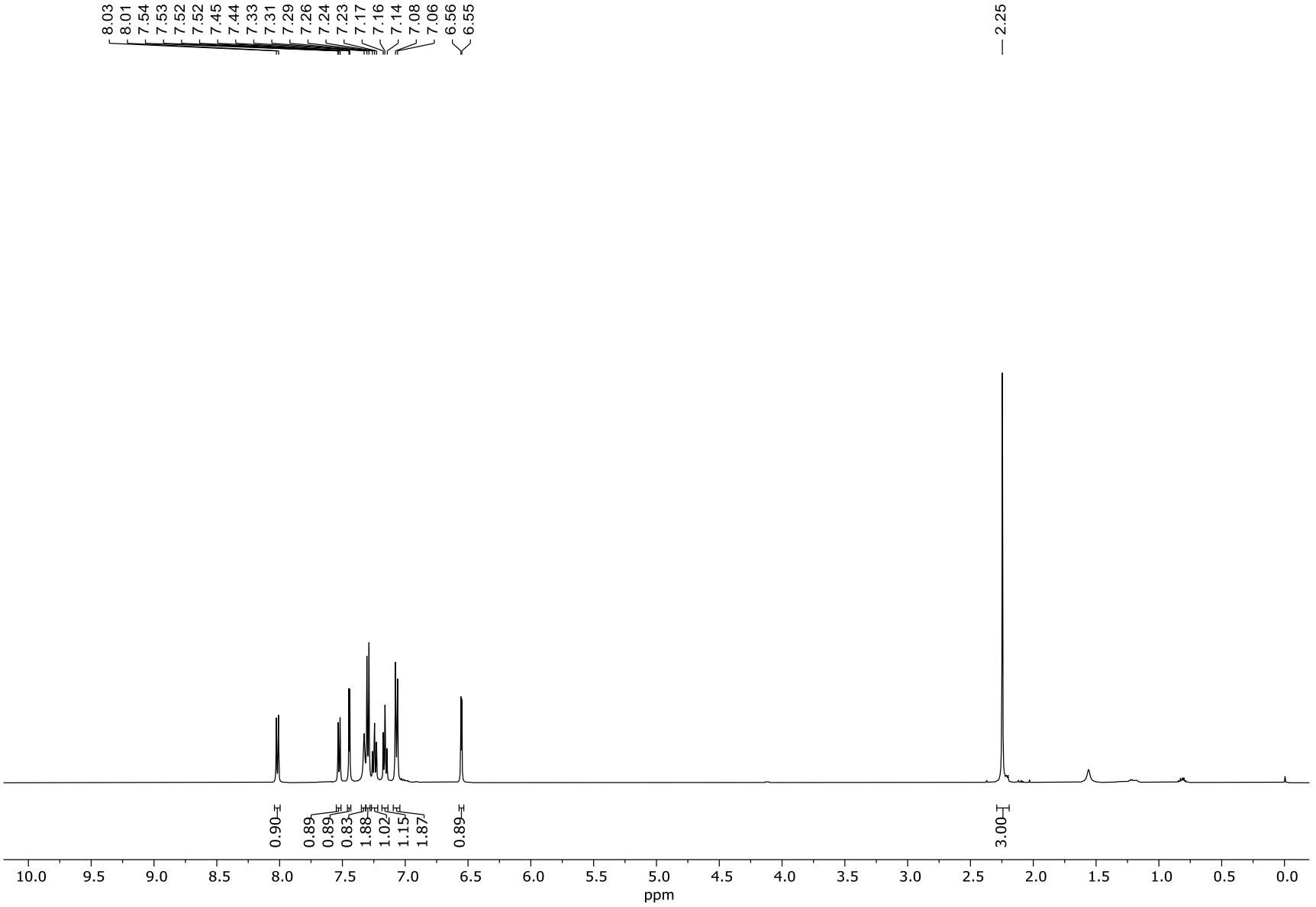


Figure S61: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5b**.

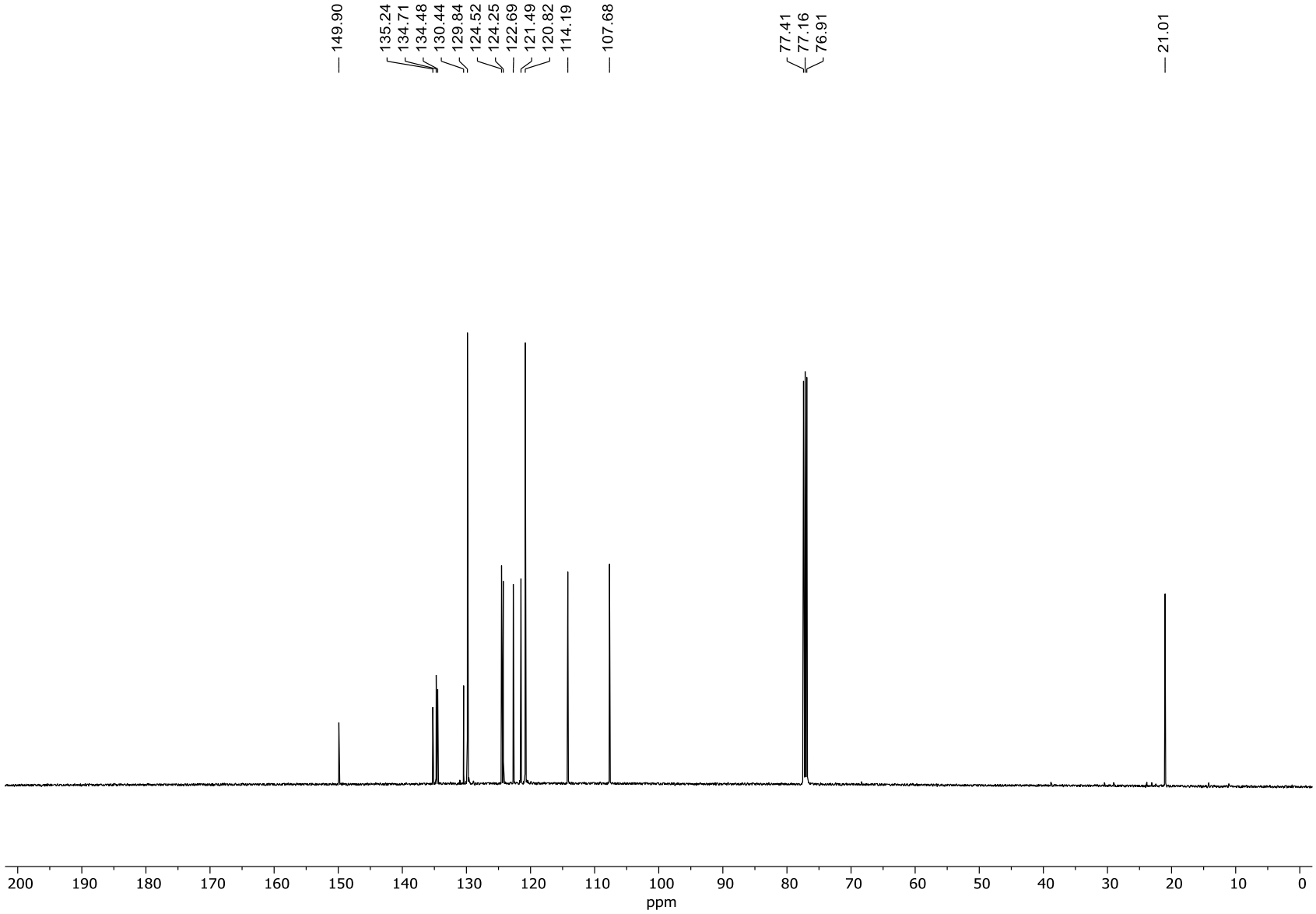


Figure S56: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5c**.

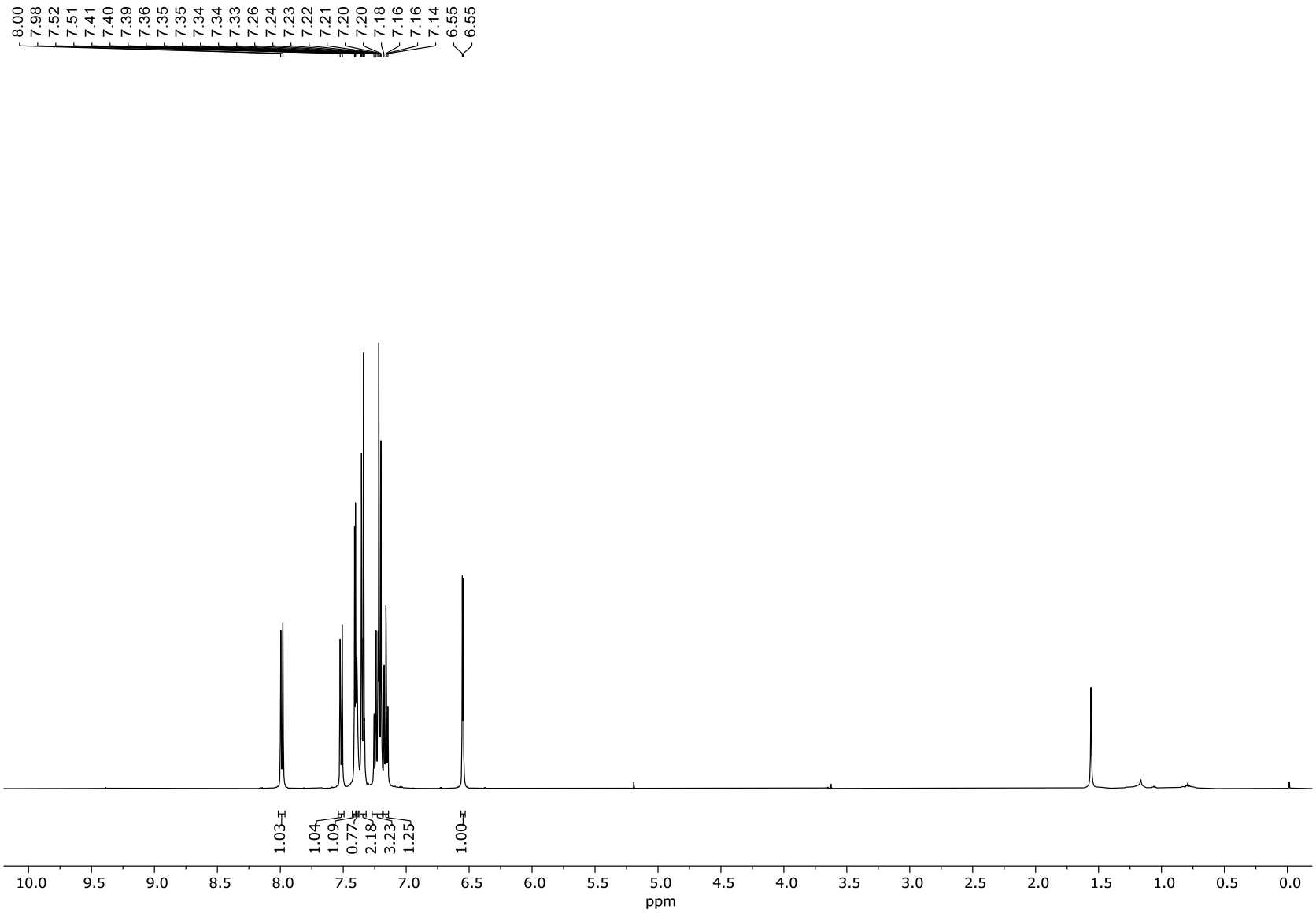


Figure S57: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5c**.

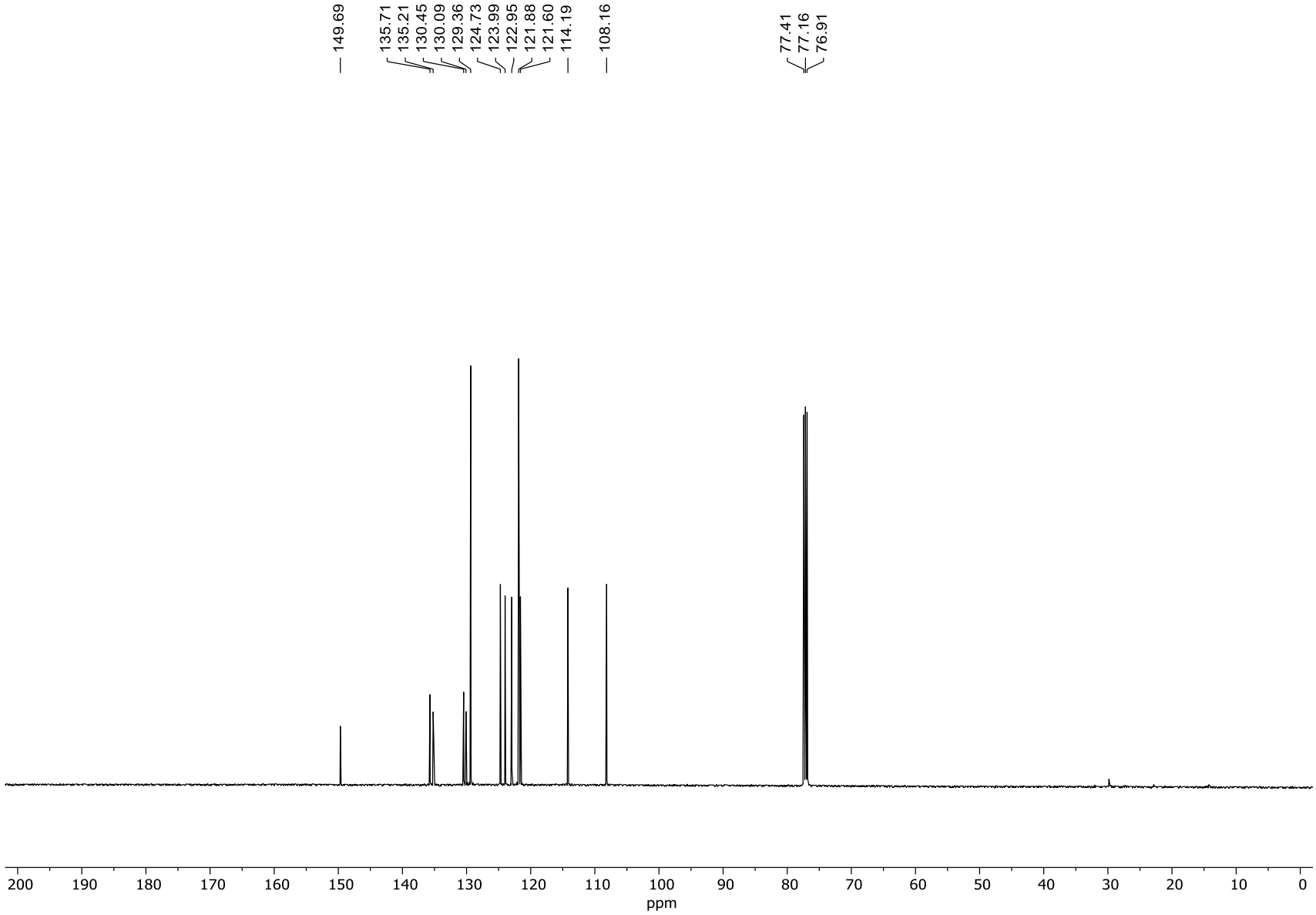


Figure S62: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5d**.

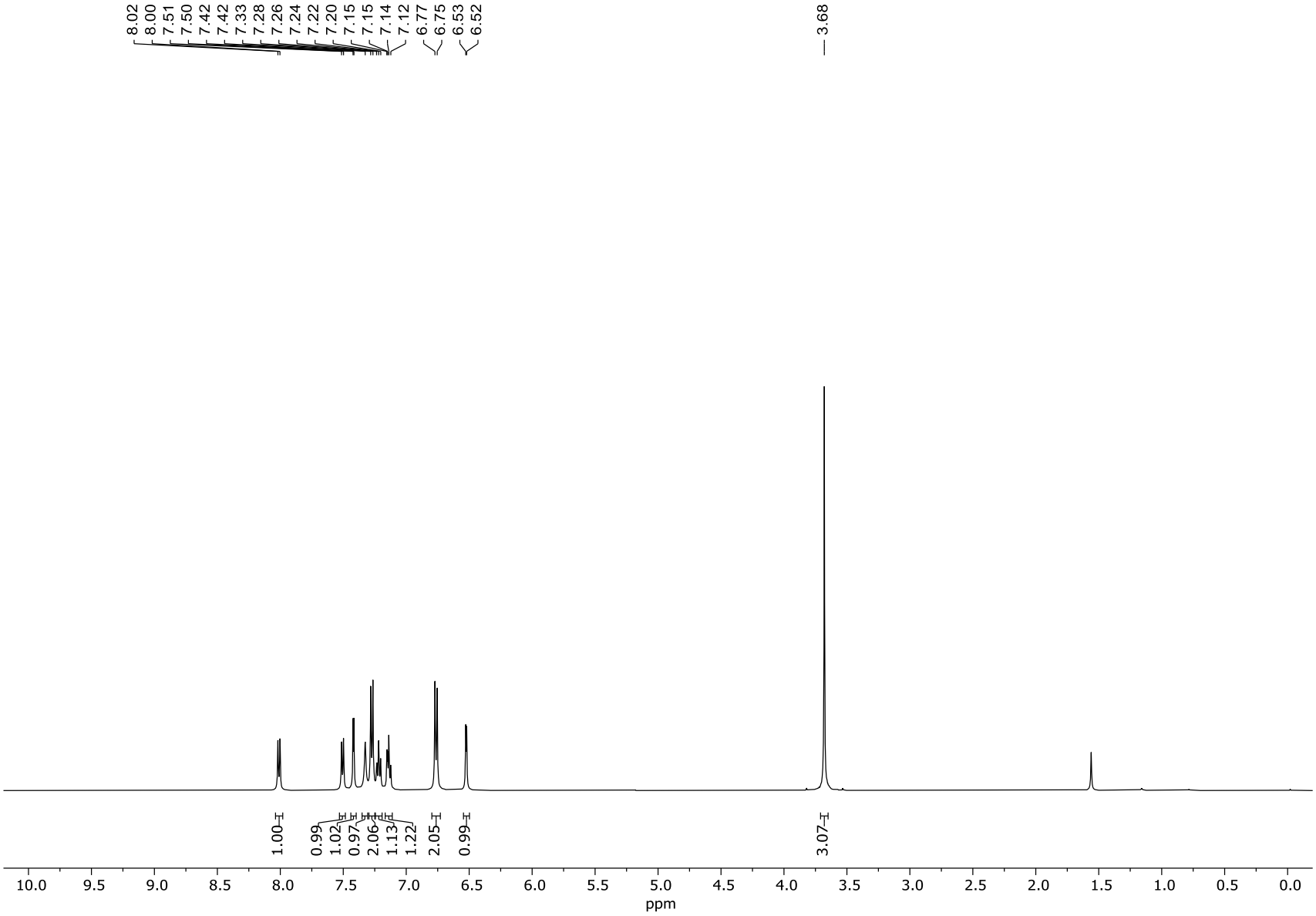


Figure S63: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5d**.

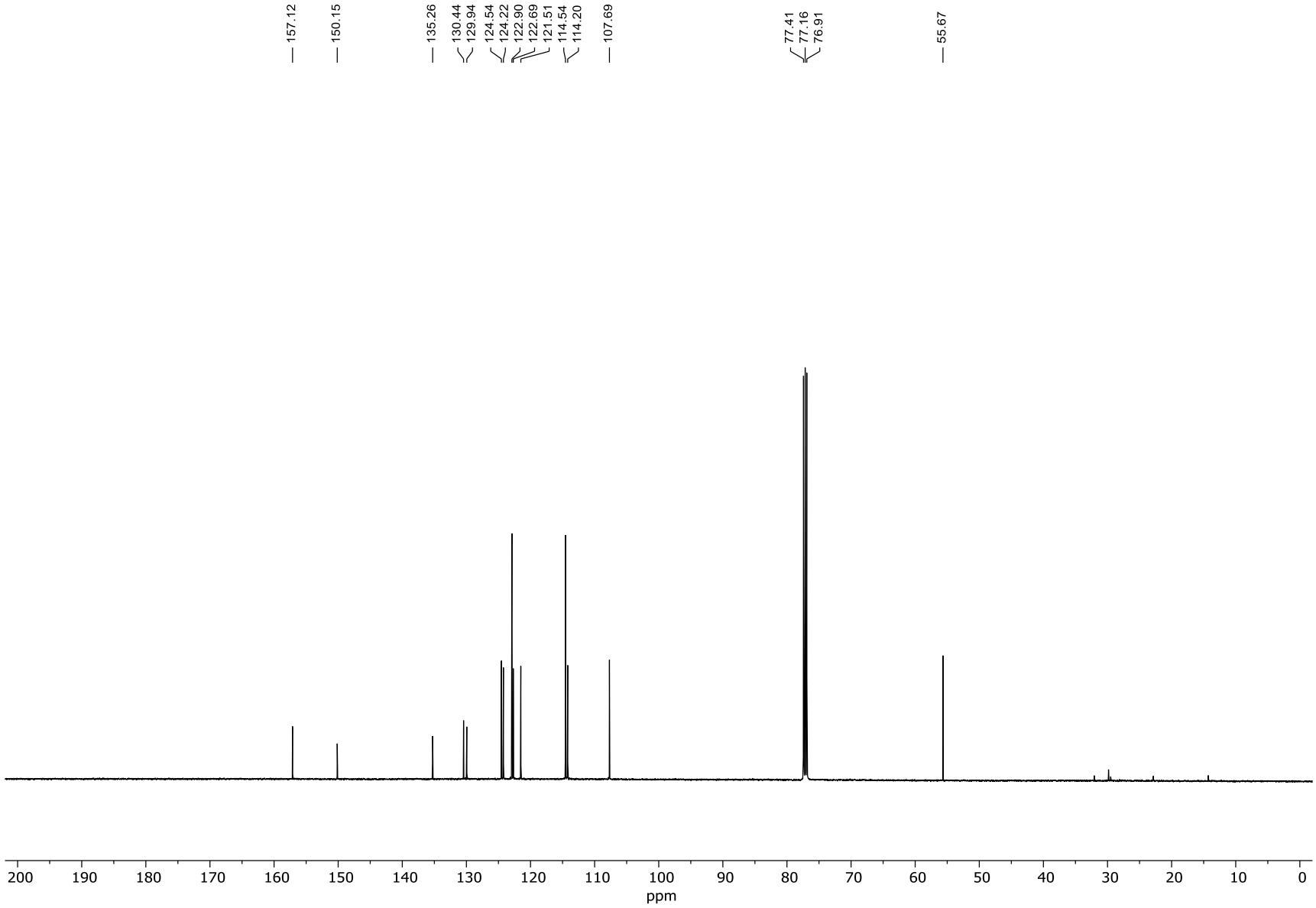


Figure S64: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5e**.

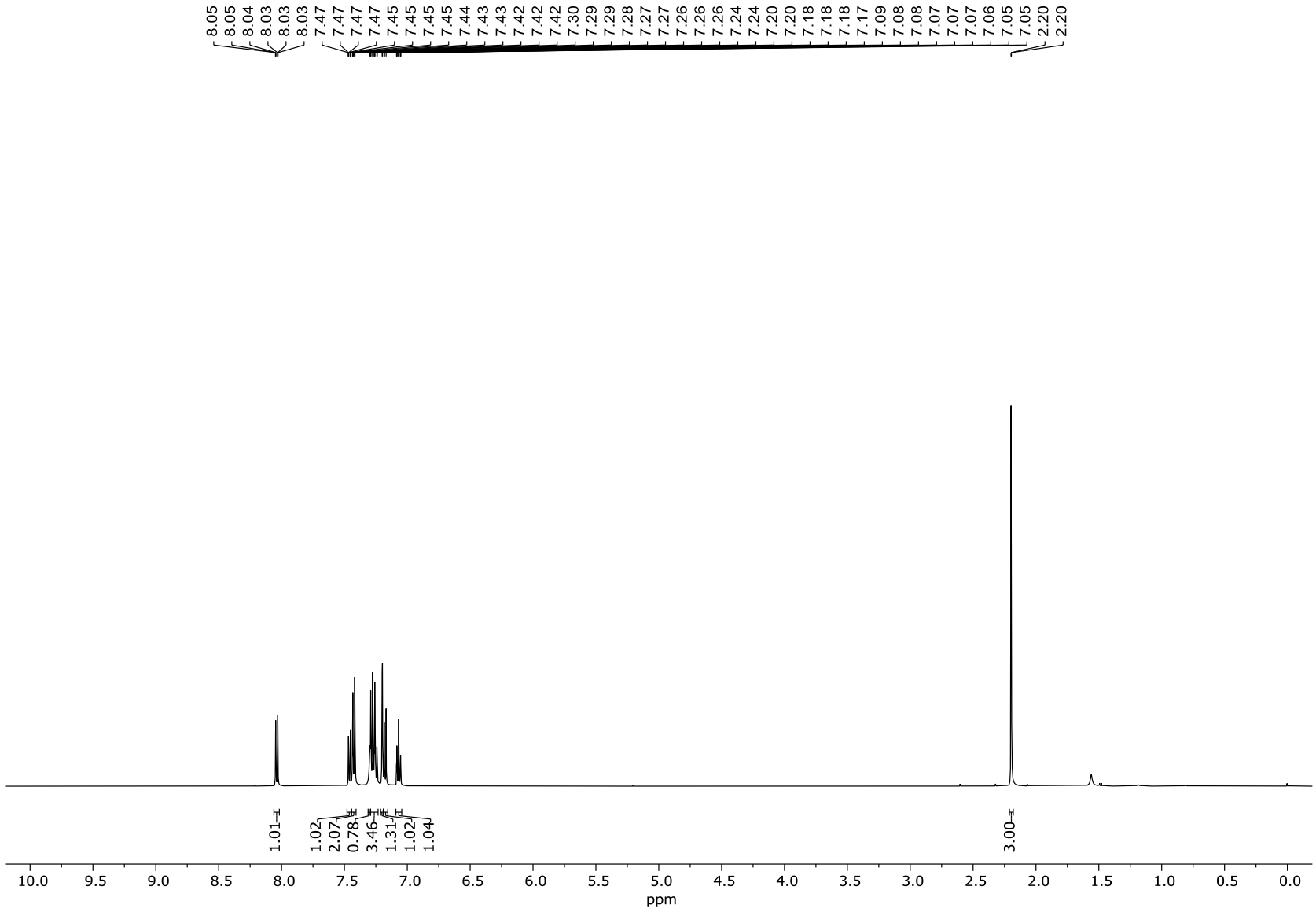


Figure S65: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5e**.

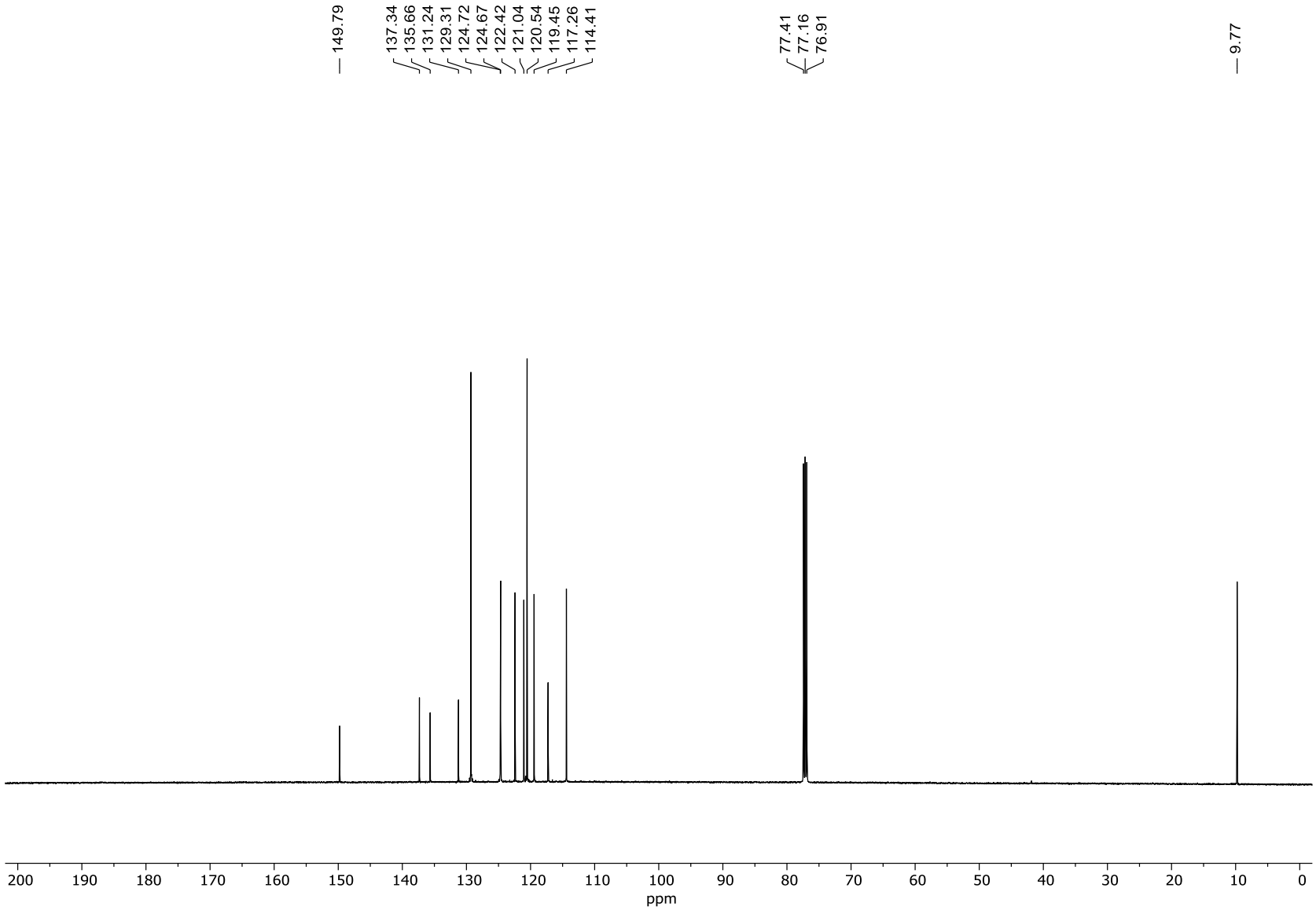


Figure S66: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5f**.

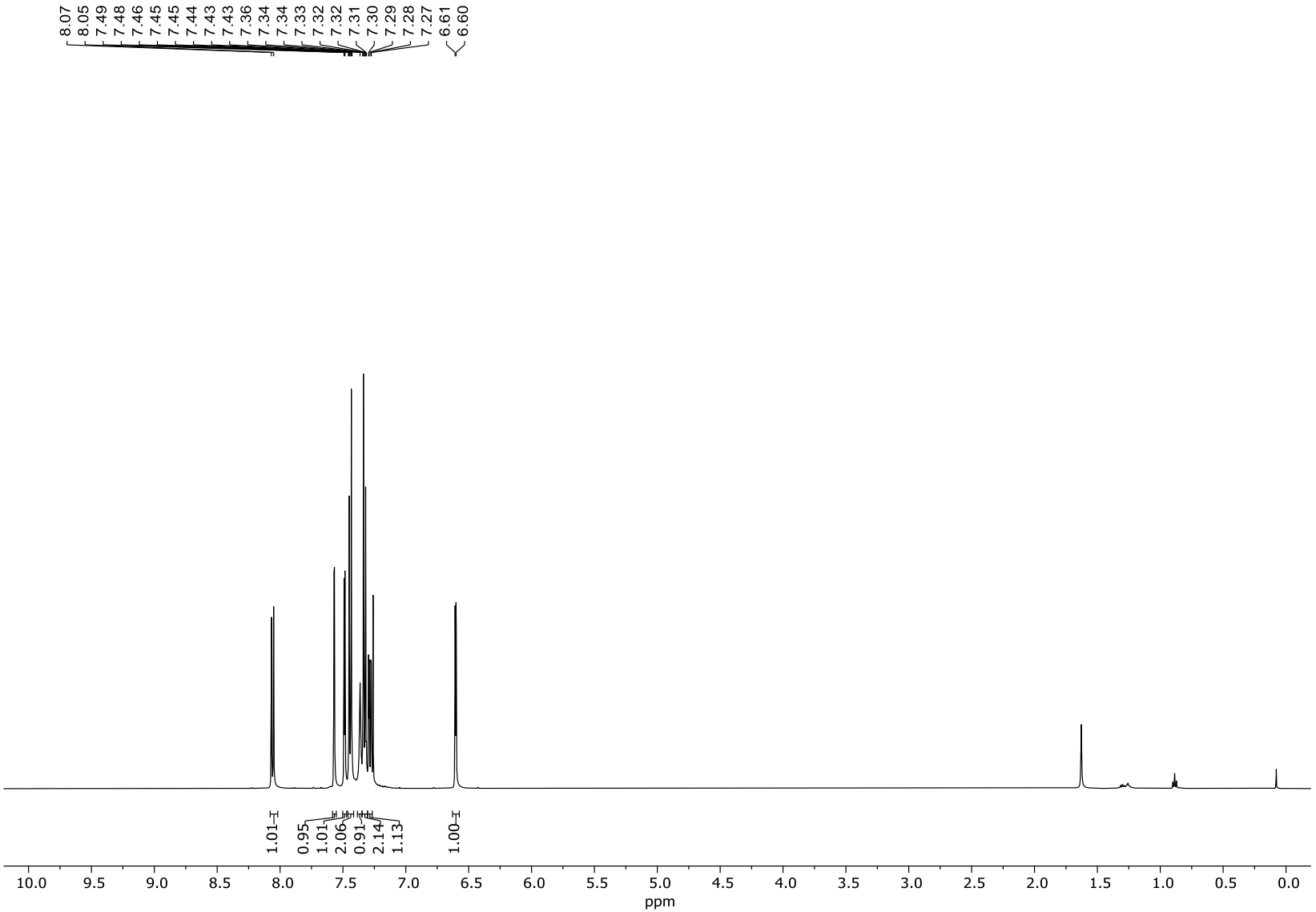


Figure S67: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5f**.

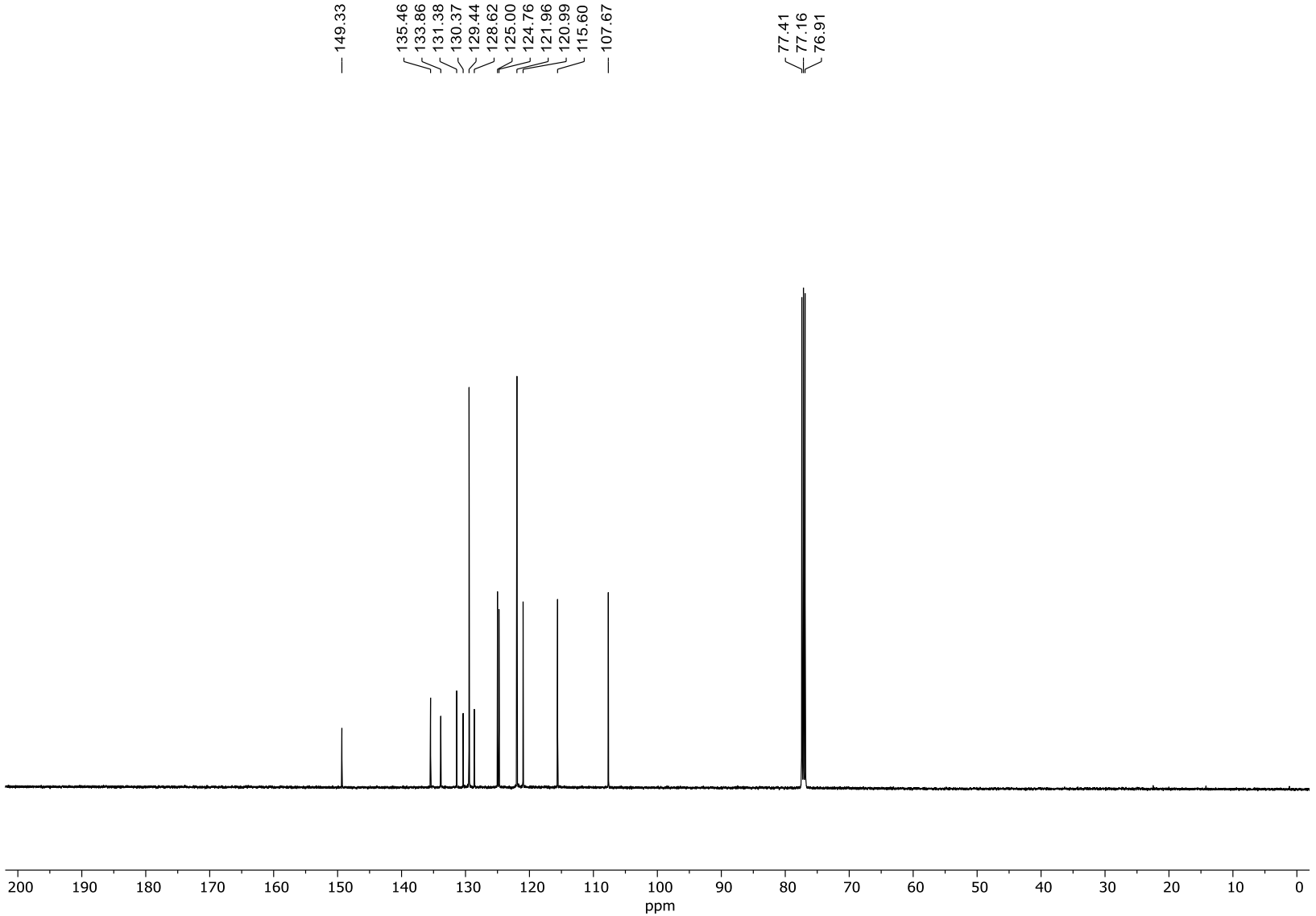


Figure S68: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5g**.

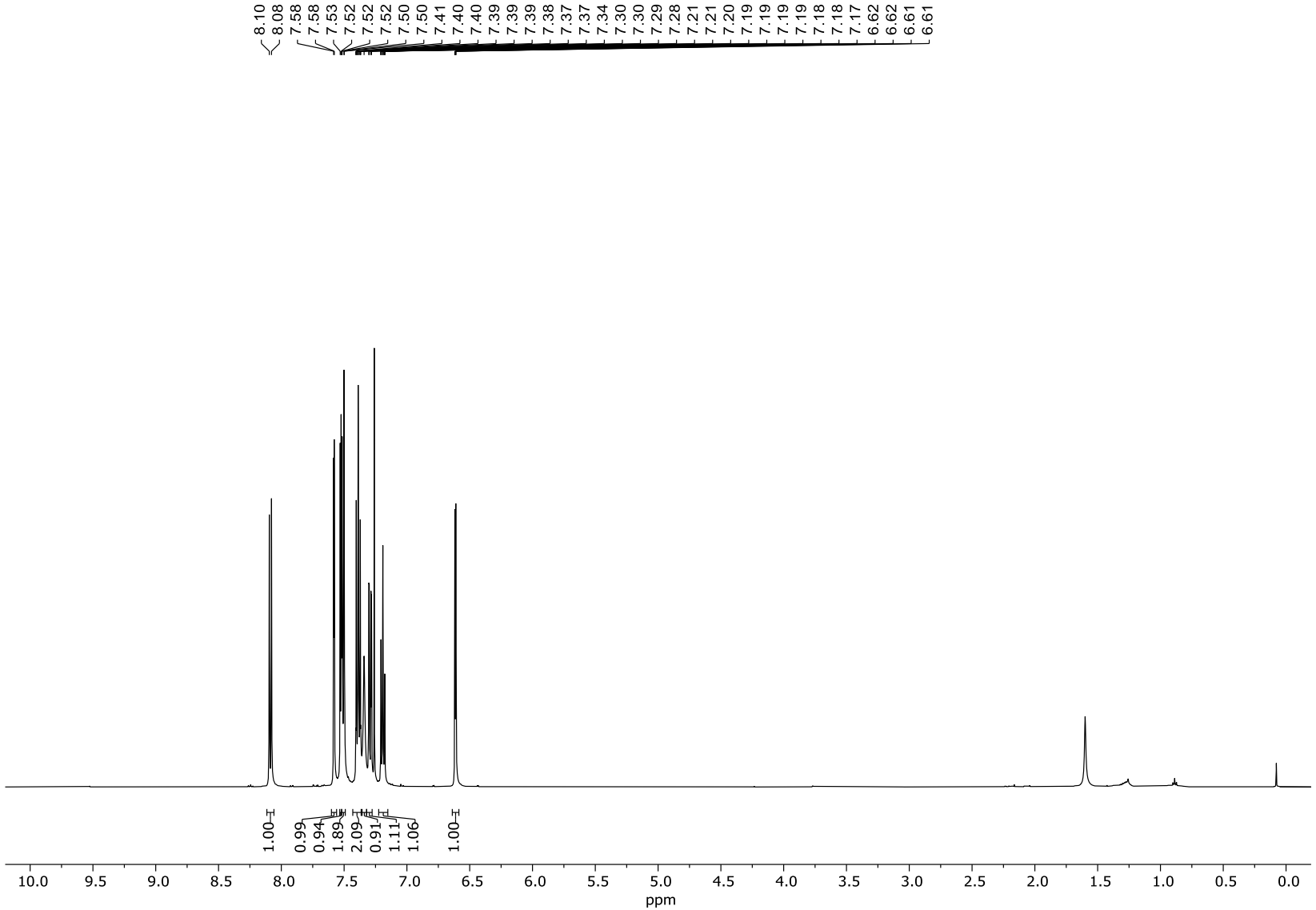


Figure S69: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5g**.

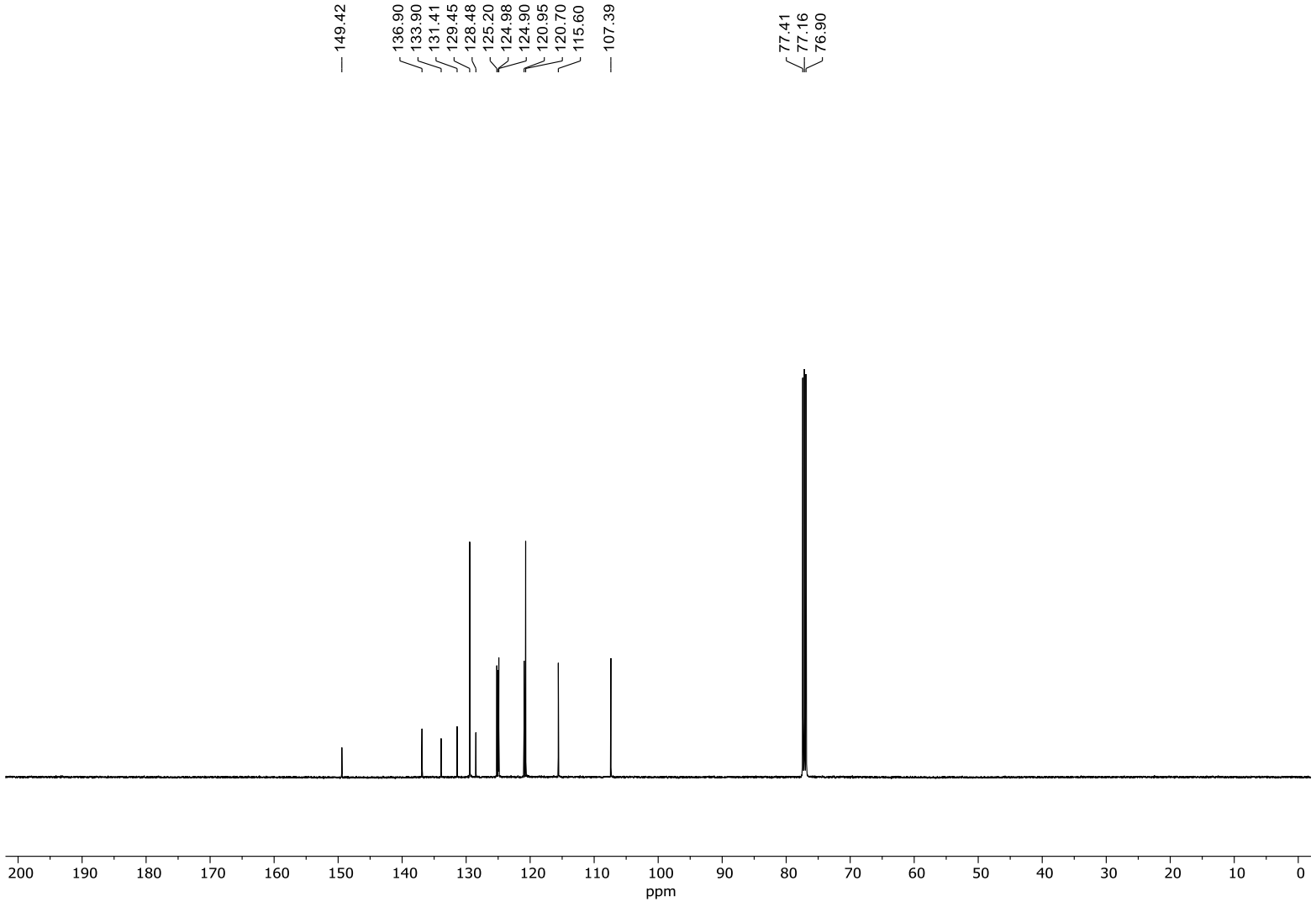


Figure S70: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5h**.

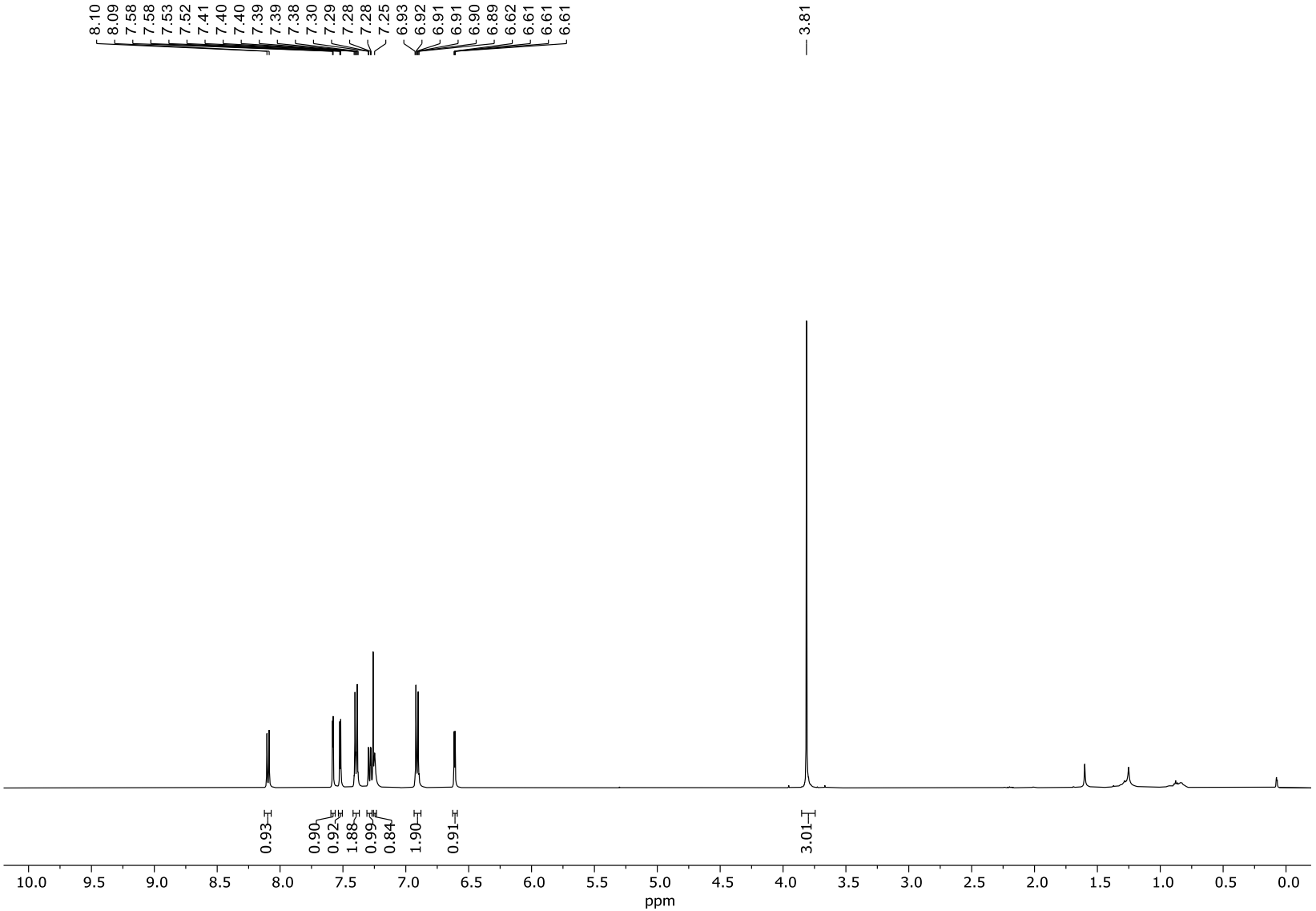


Figure S71: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5h**.

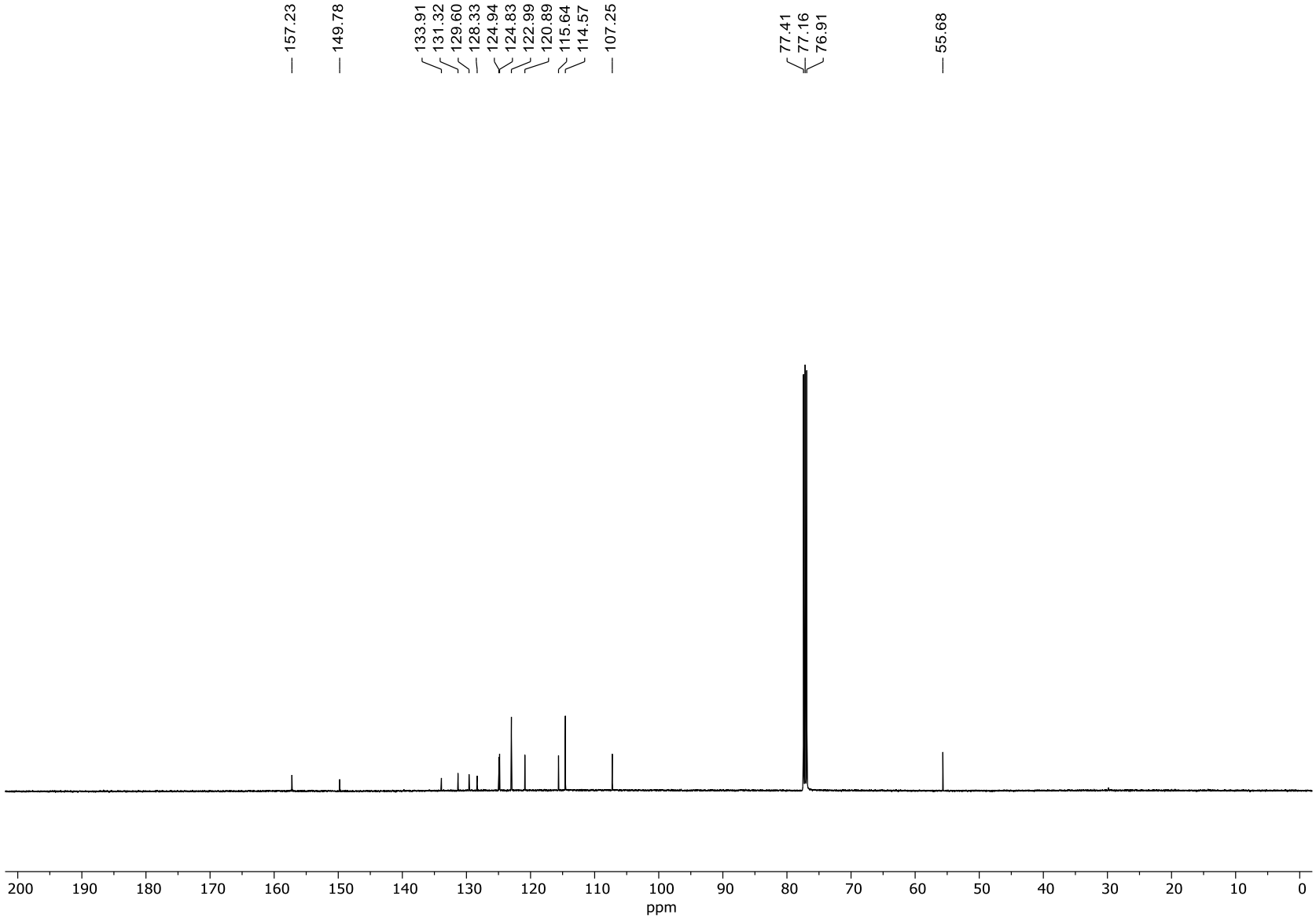


Figure S72: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5i**.

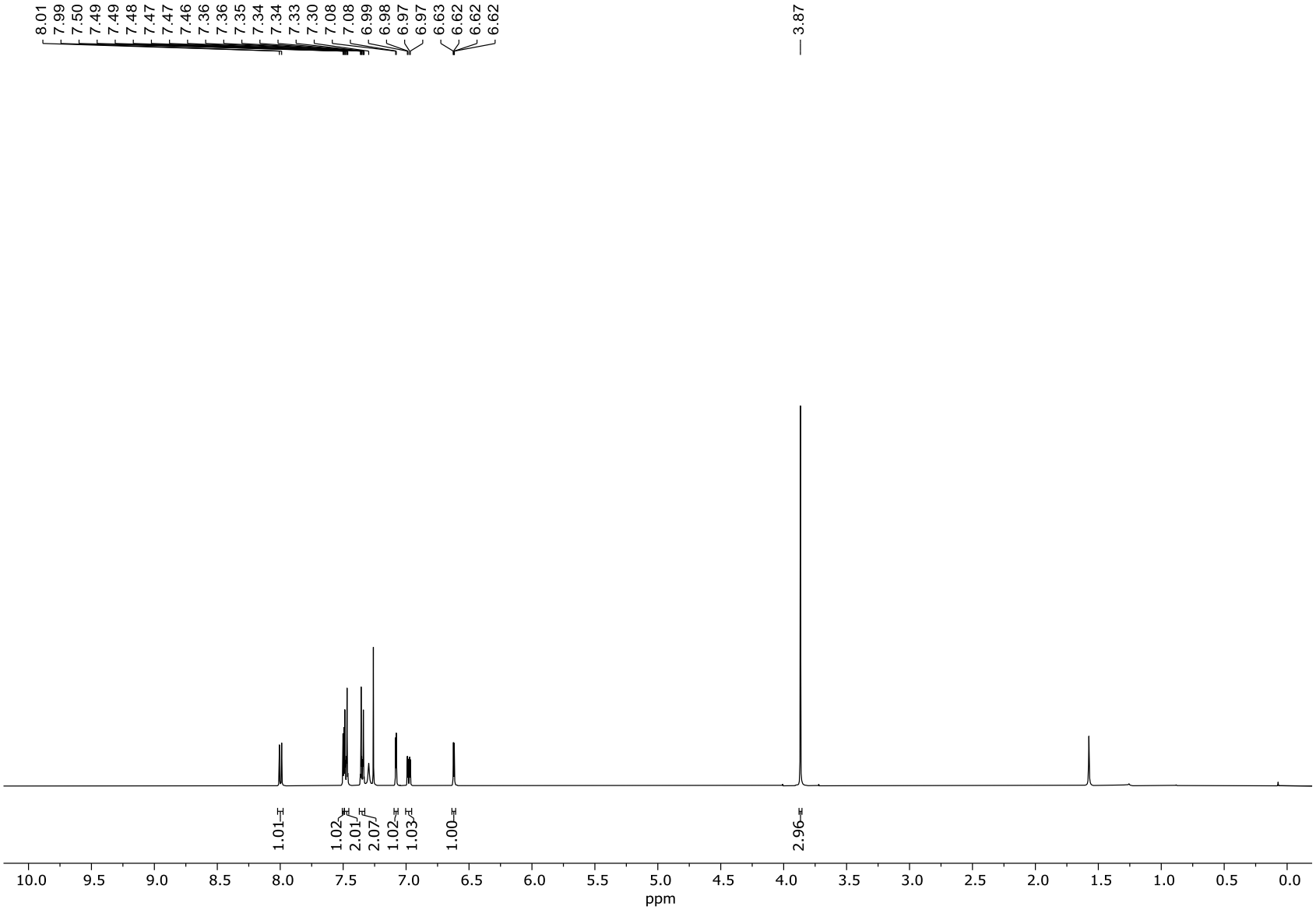


Figure S73: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5i**.

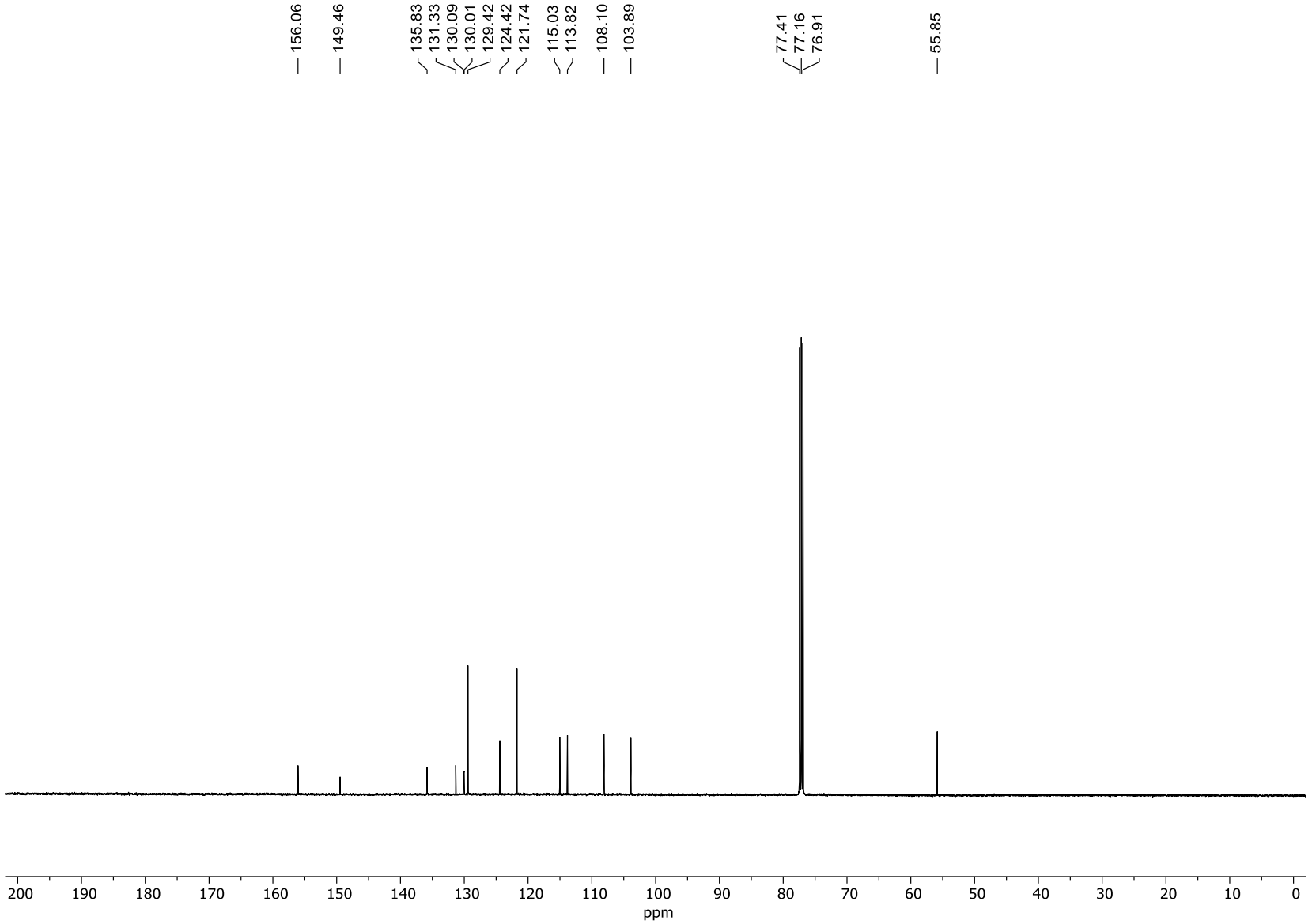


Figure S74: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5j**.

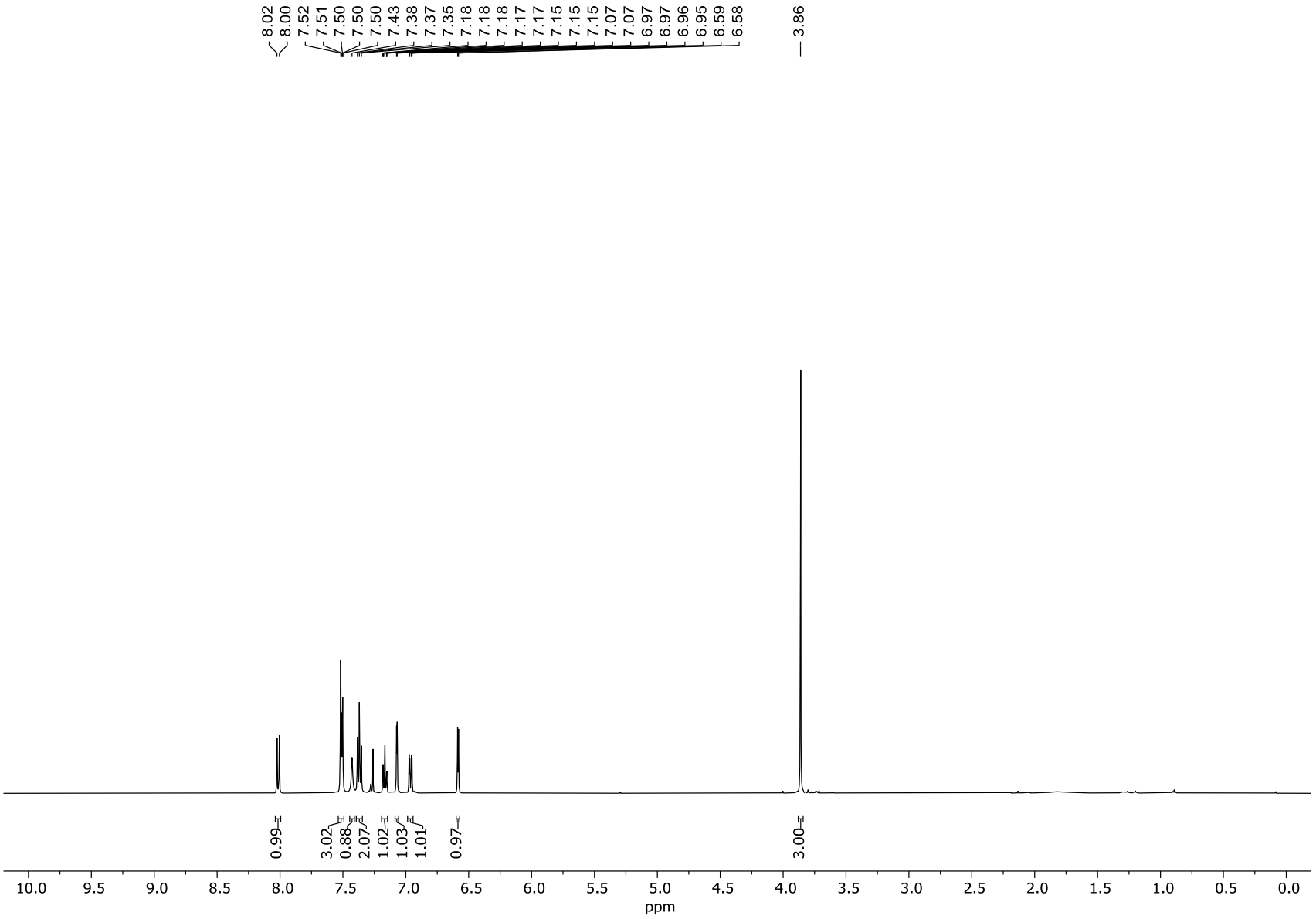


Figure S75: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5j**.

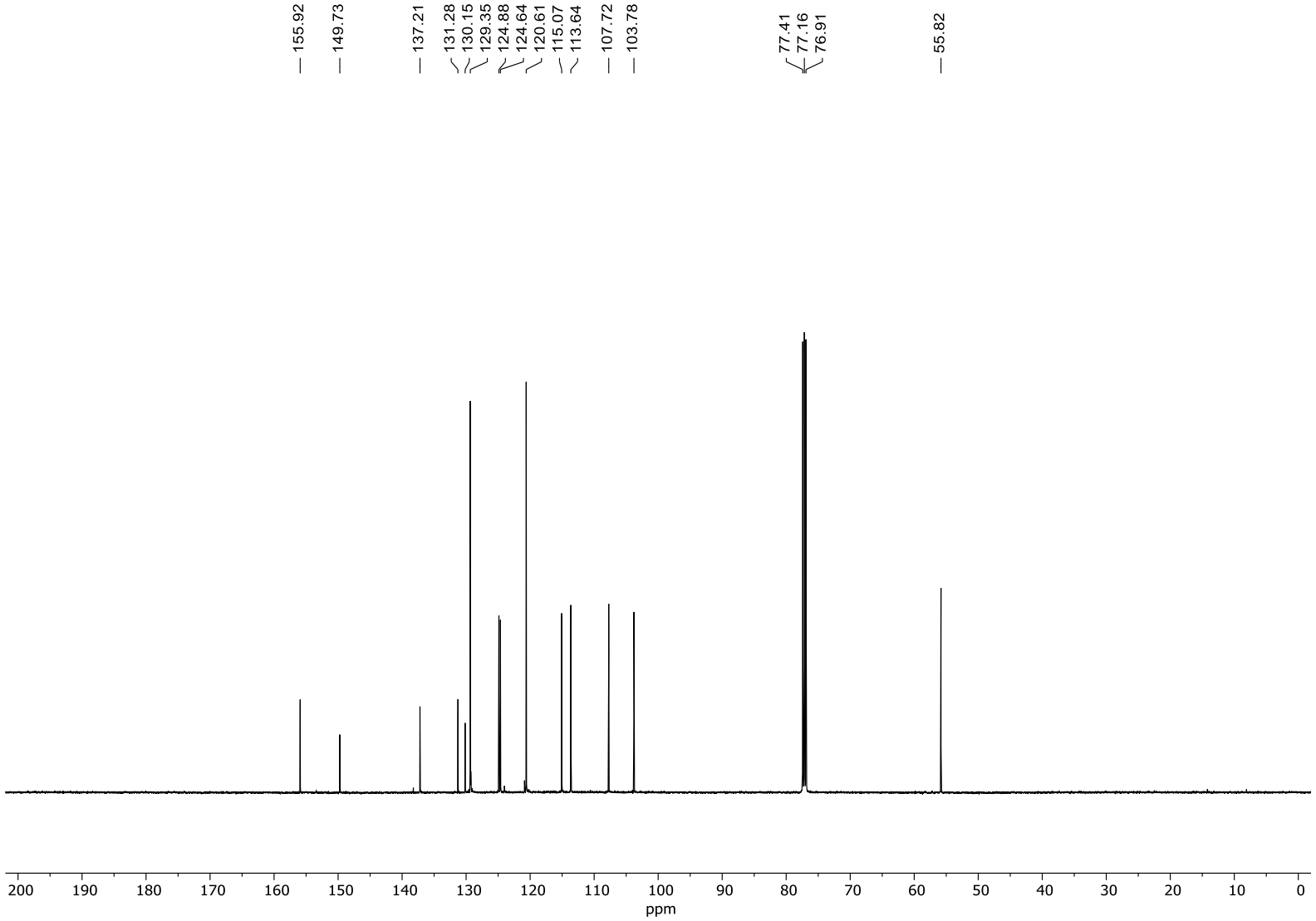


Figure S76: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5k**.

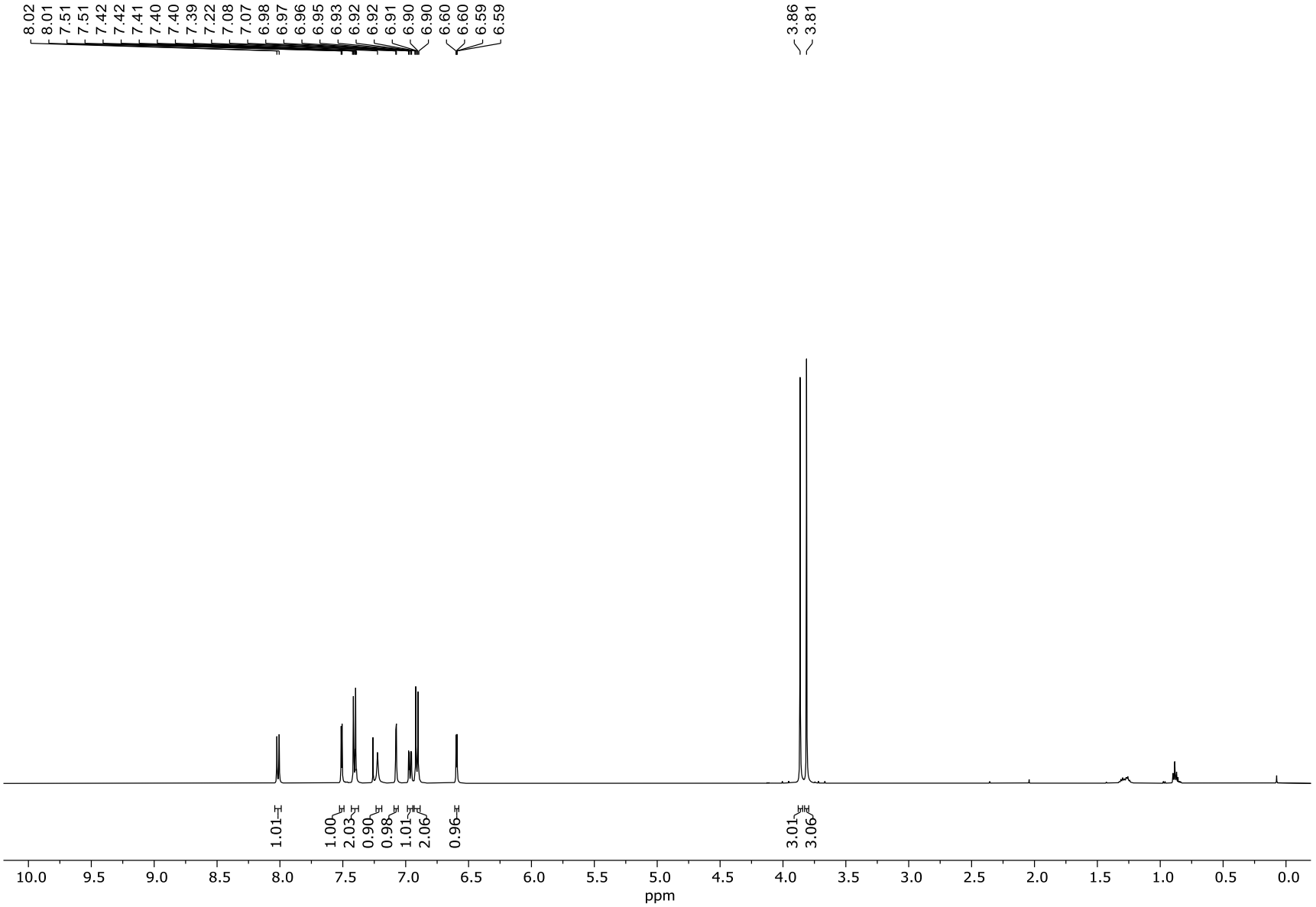


Figure S77: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5k**.

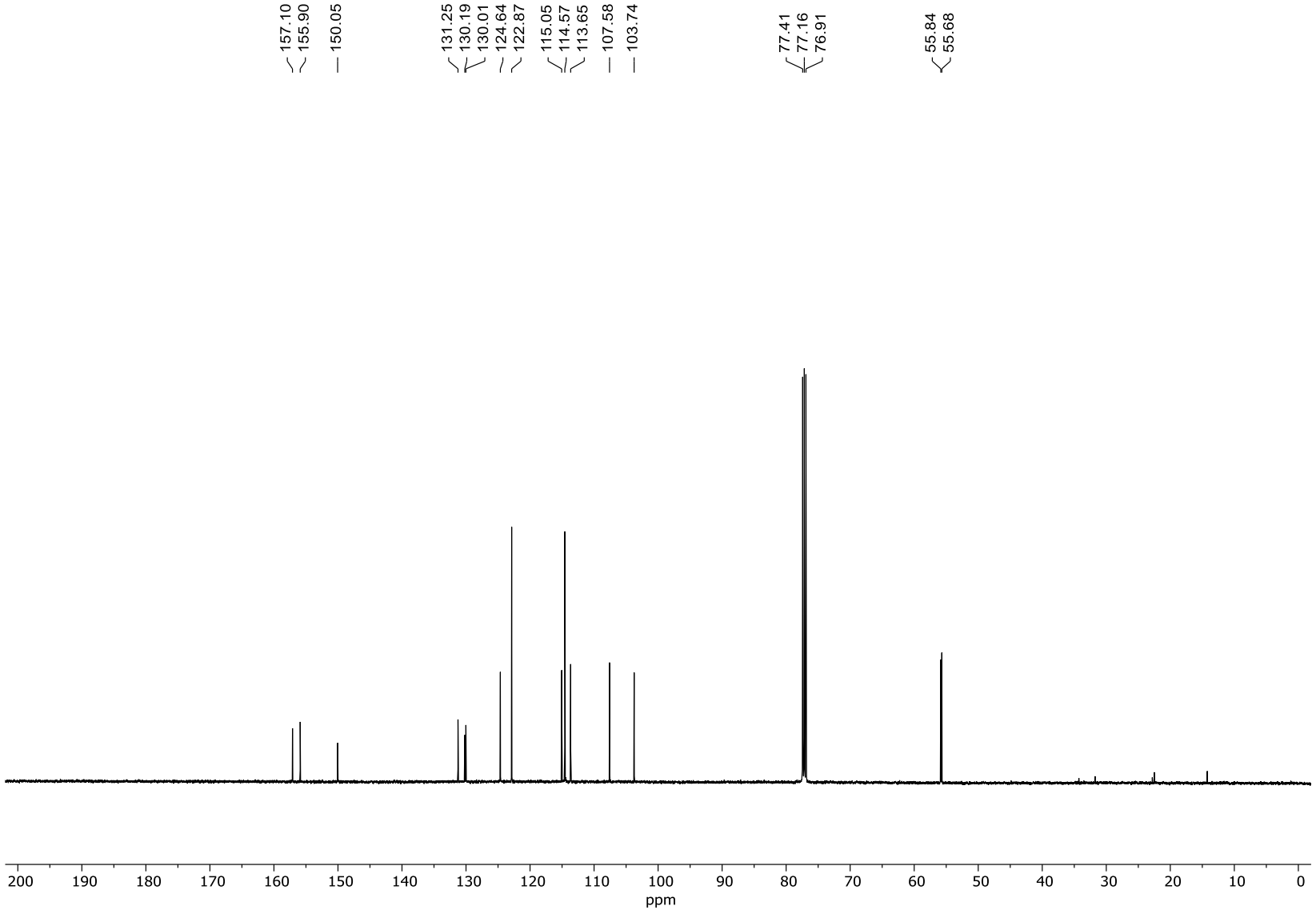


Figure S78: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5l**.

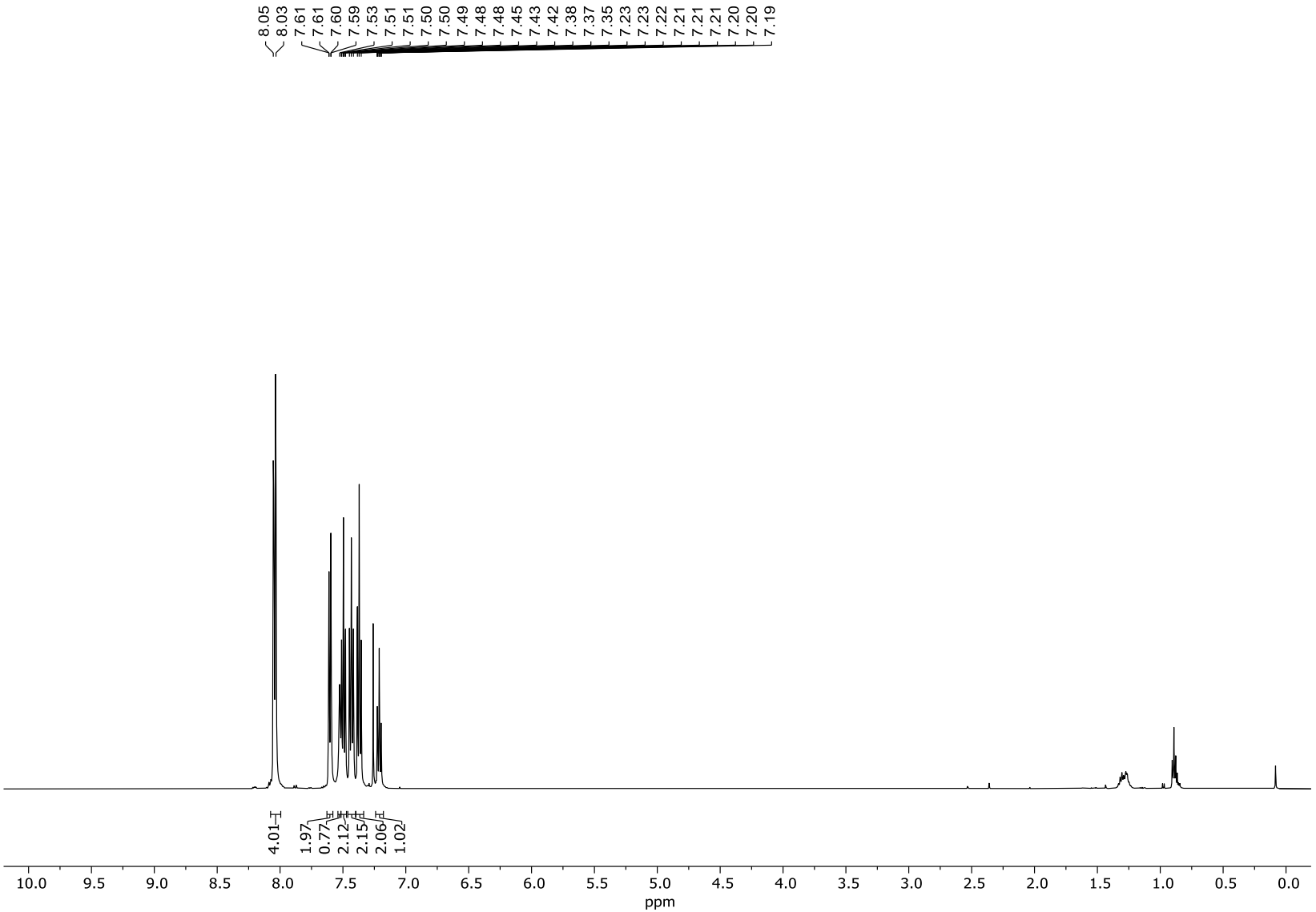


Figure S79: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5l**.

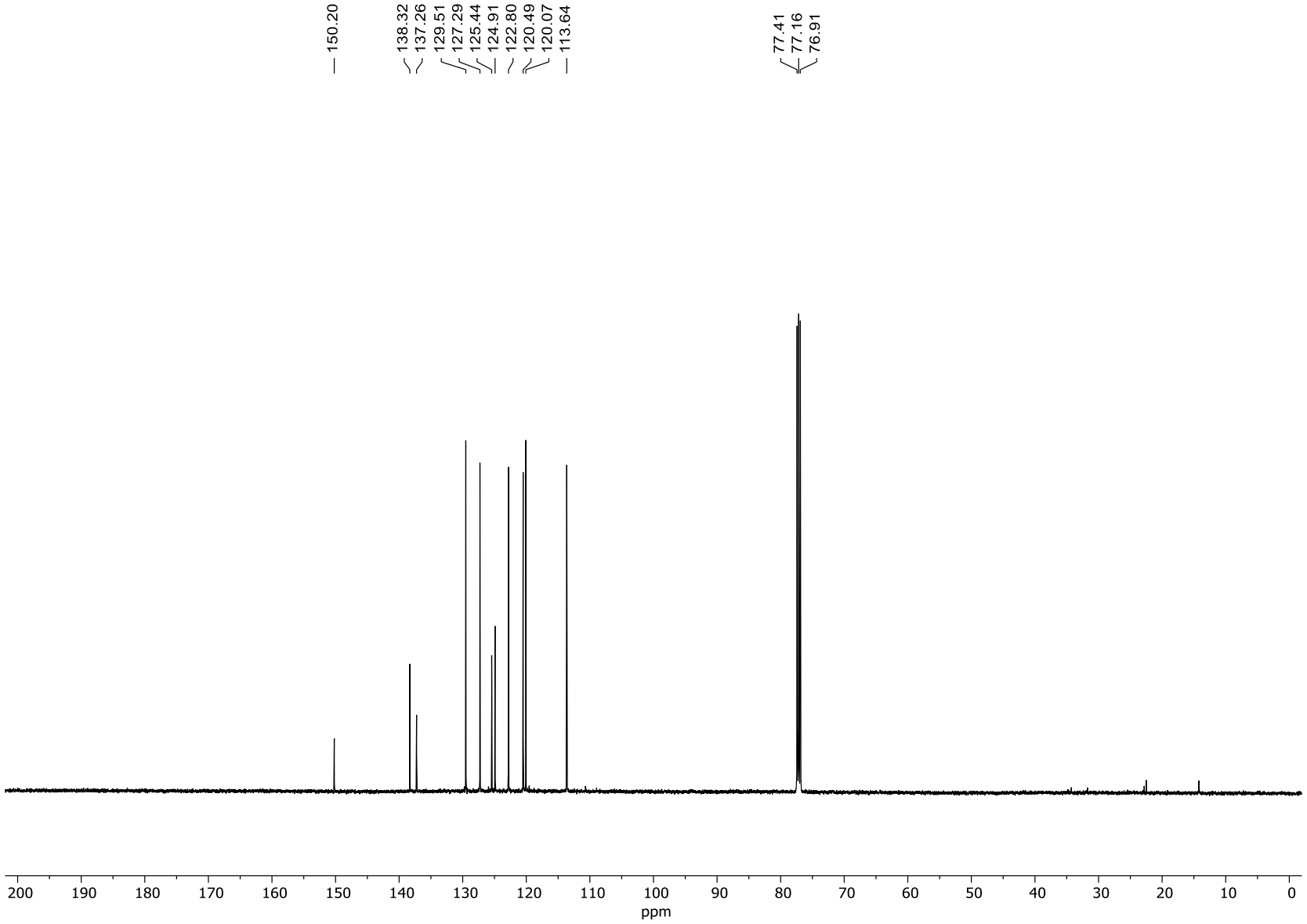


Figure S80: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5m**.

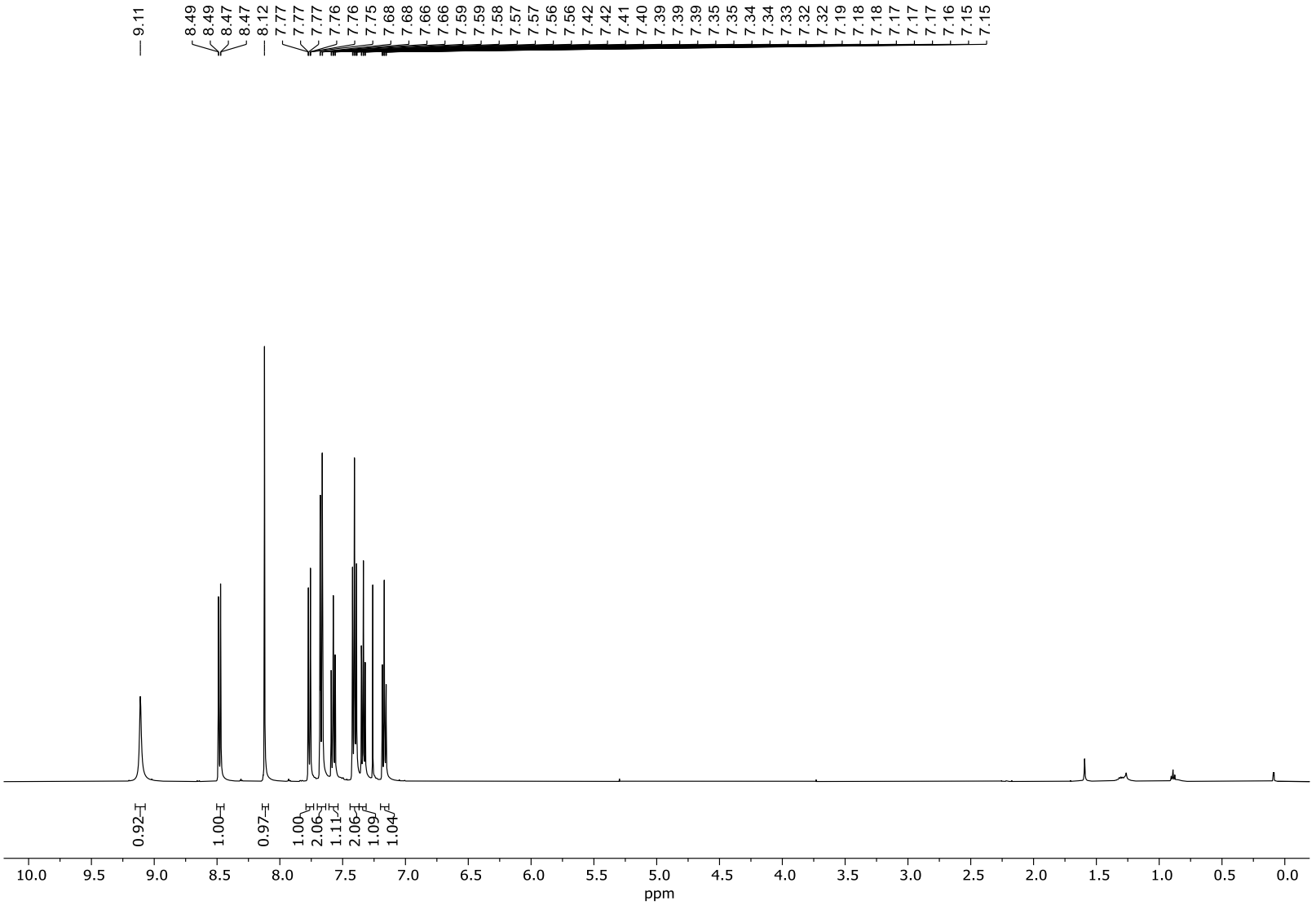


Figure S81: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5m**.

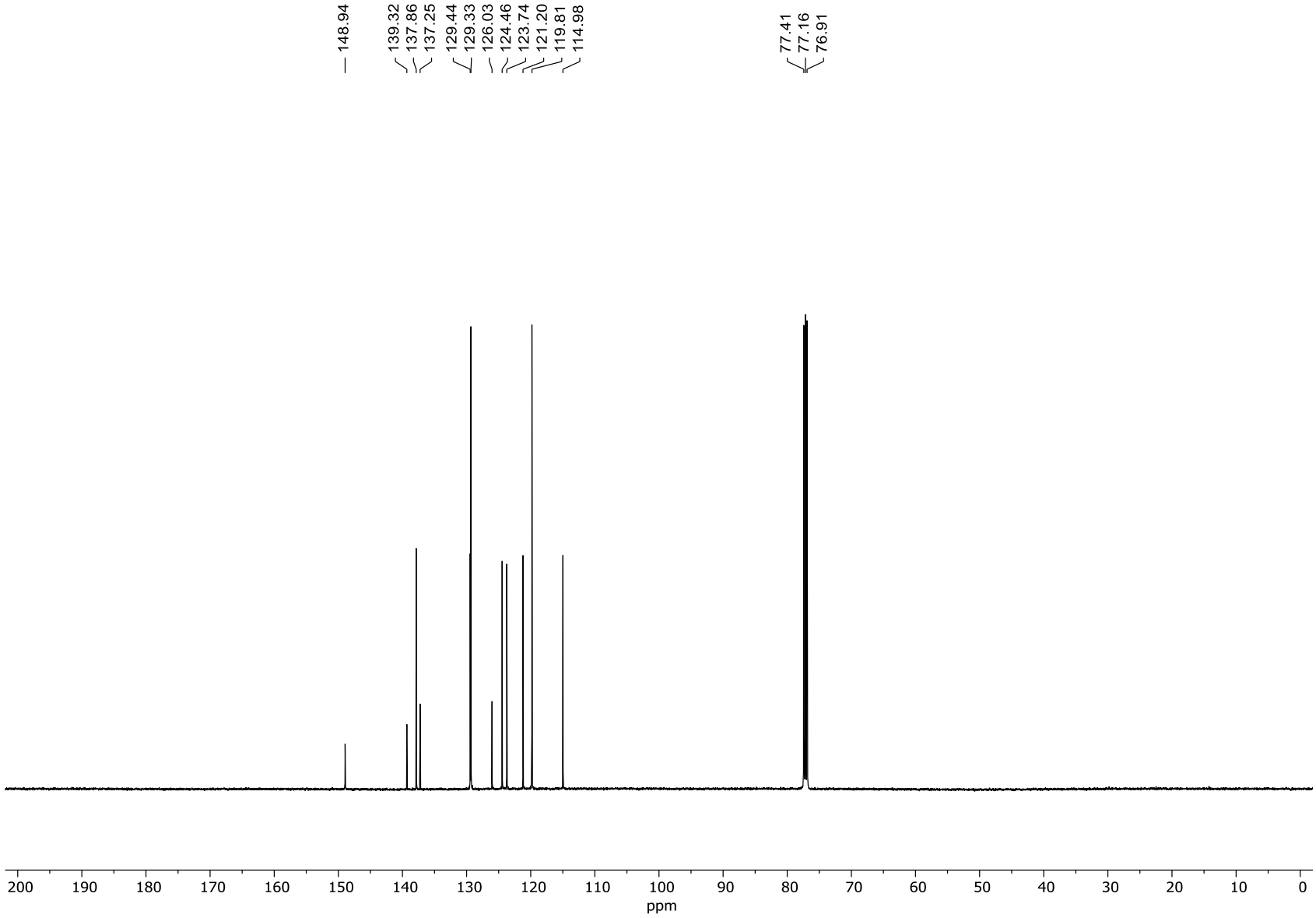


Figure S82: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5n**.

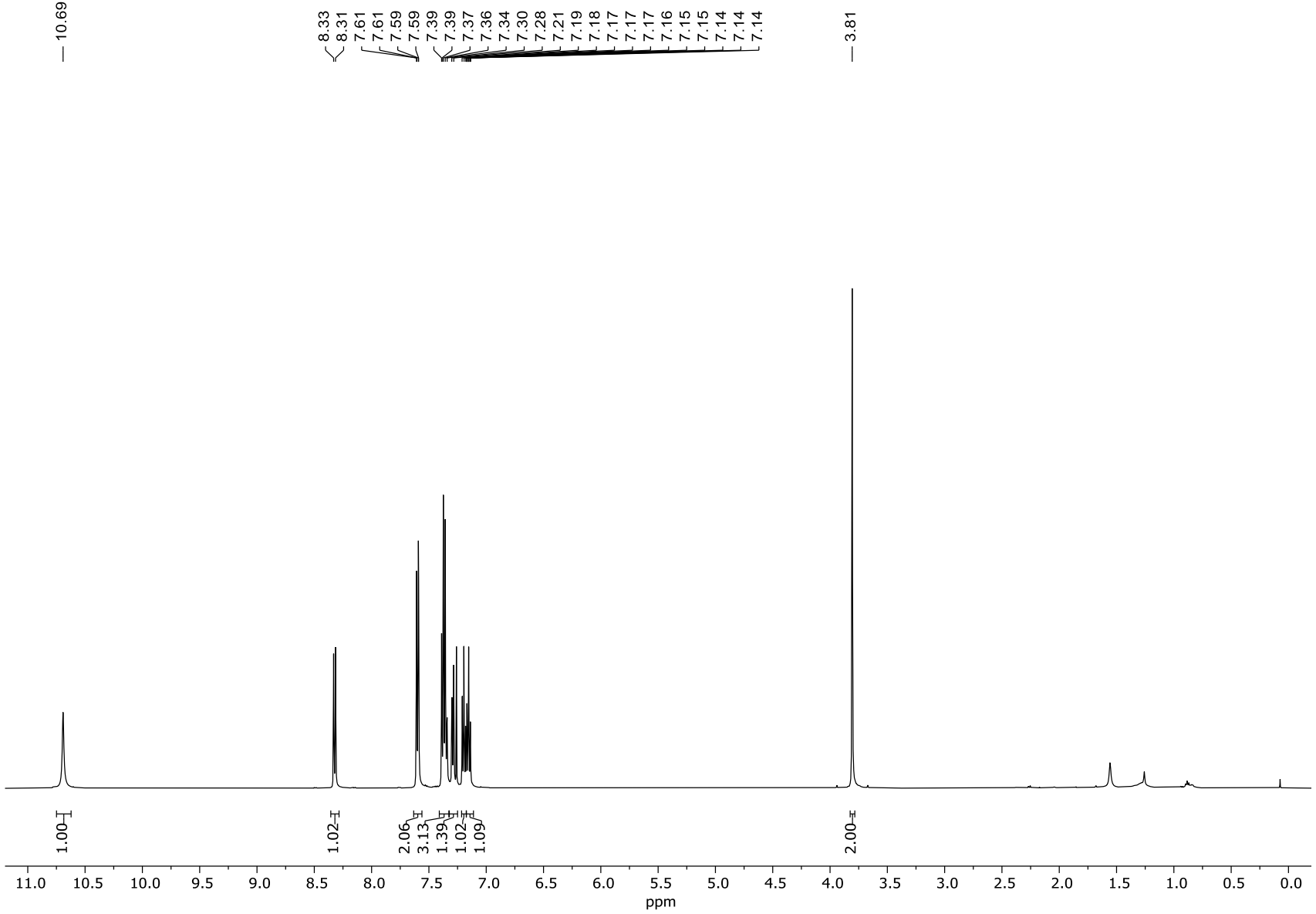


Figure S83: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5n**.

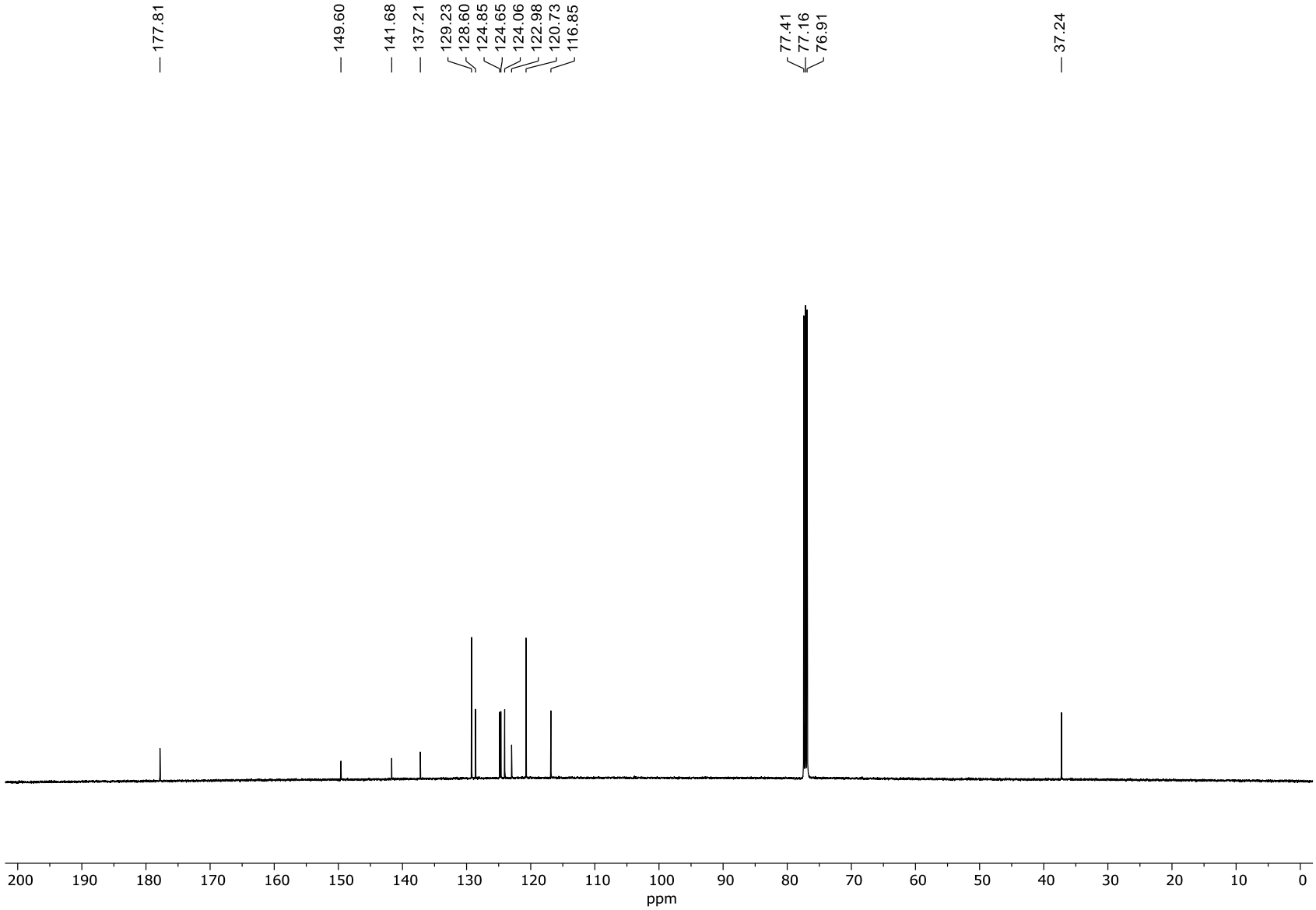


Figure S84: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5o**.

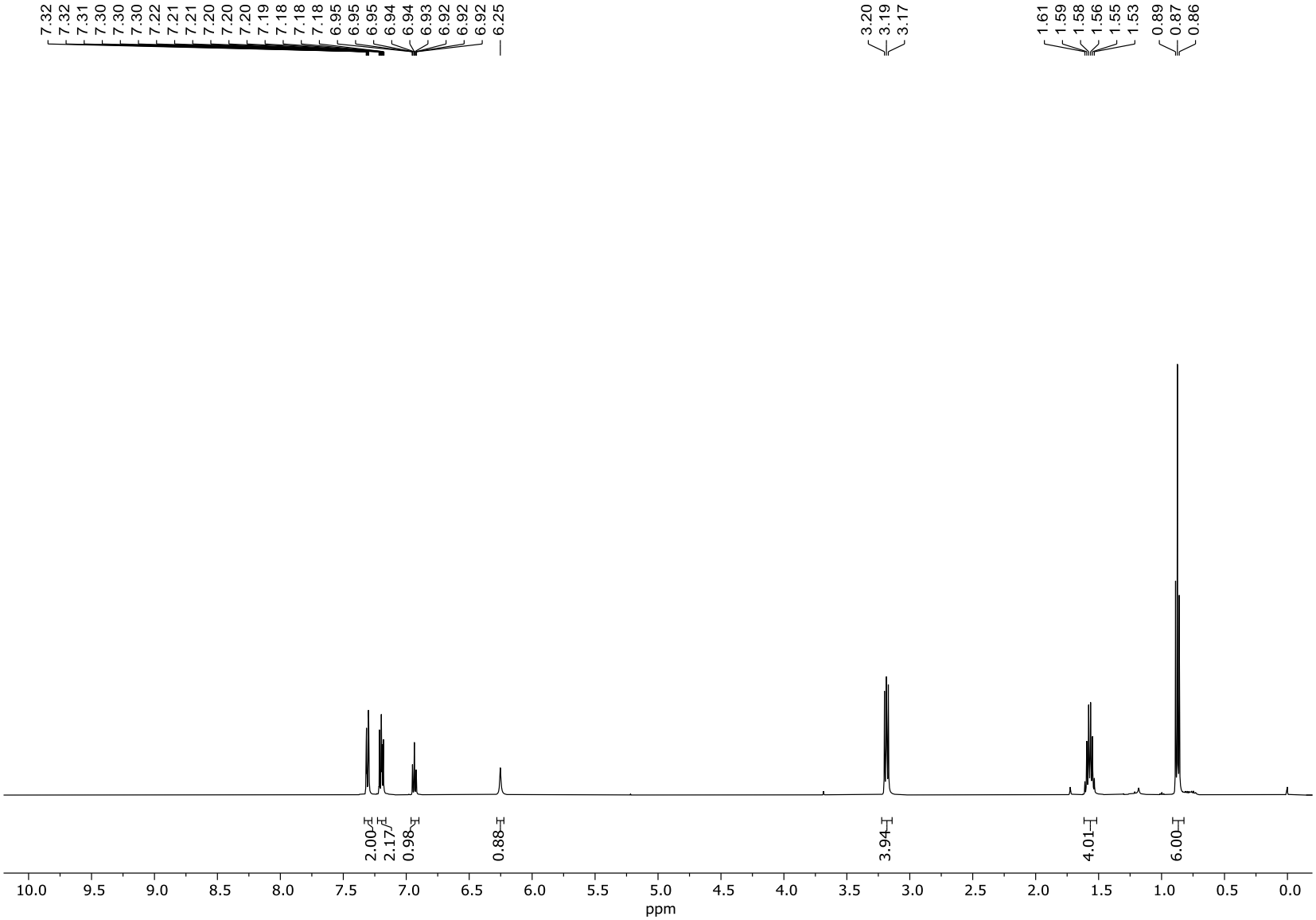


Figure S85: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **5o**.

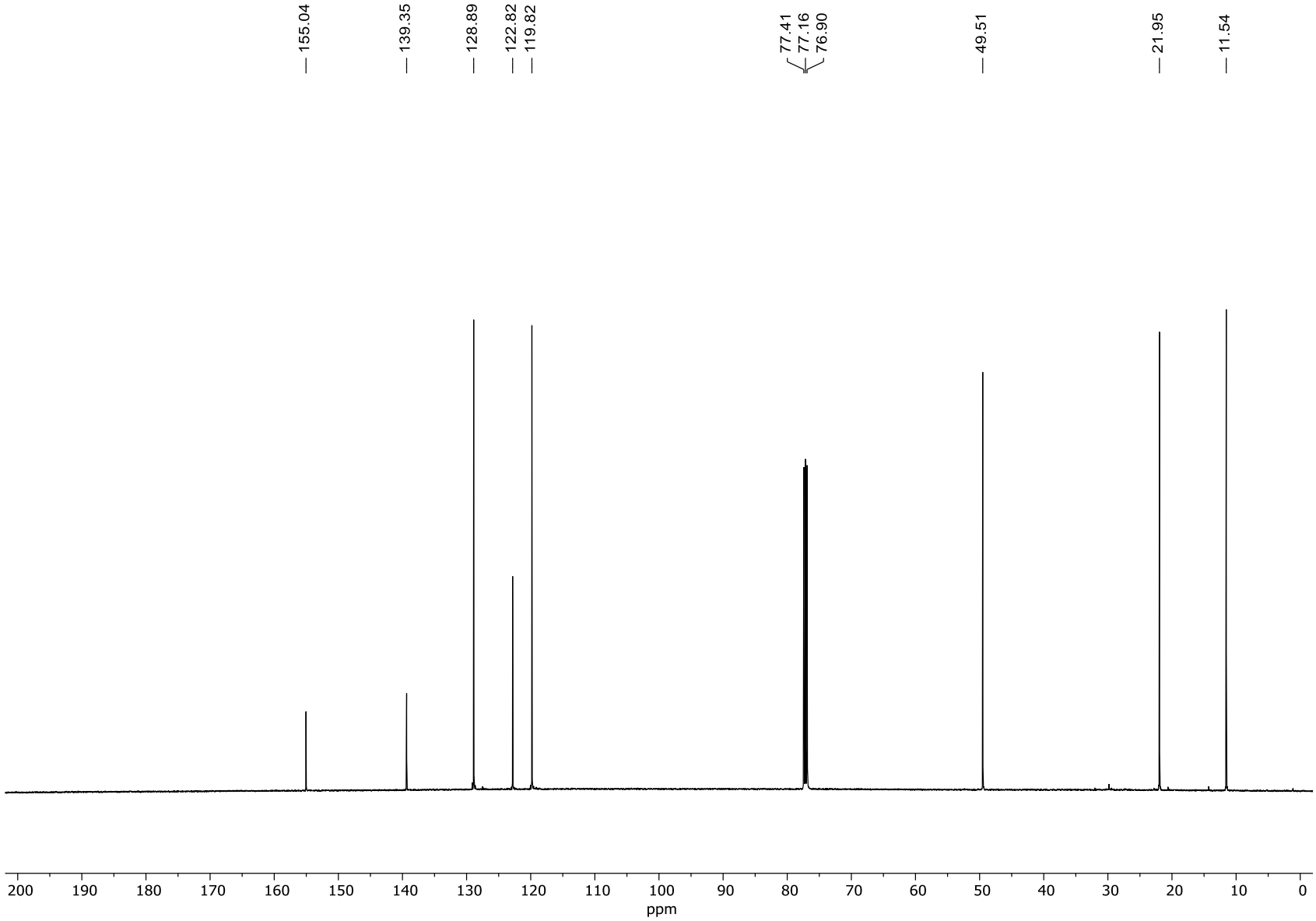


Figure S86: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5p**.

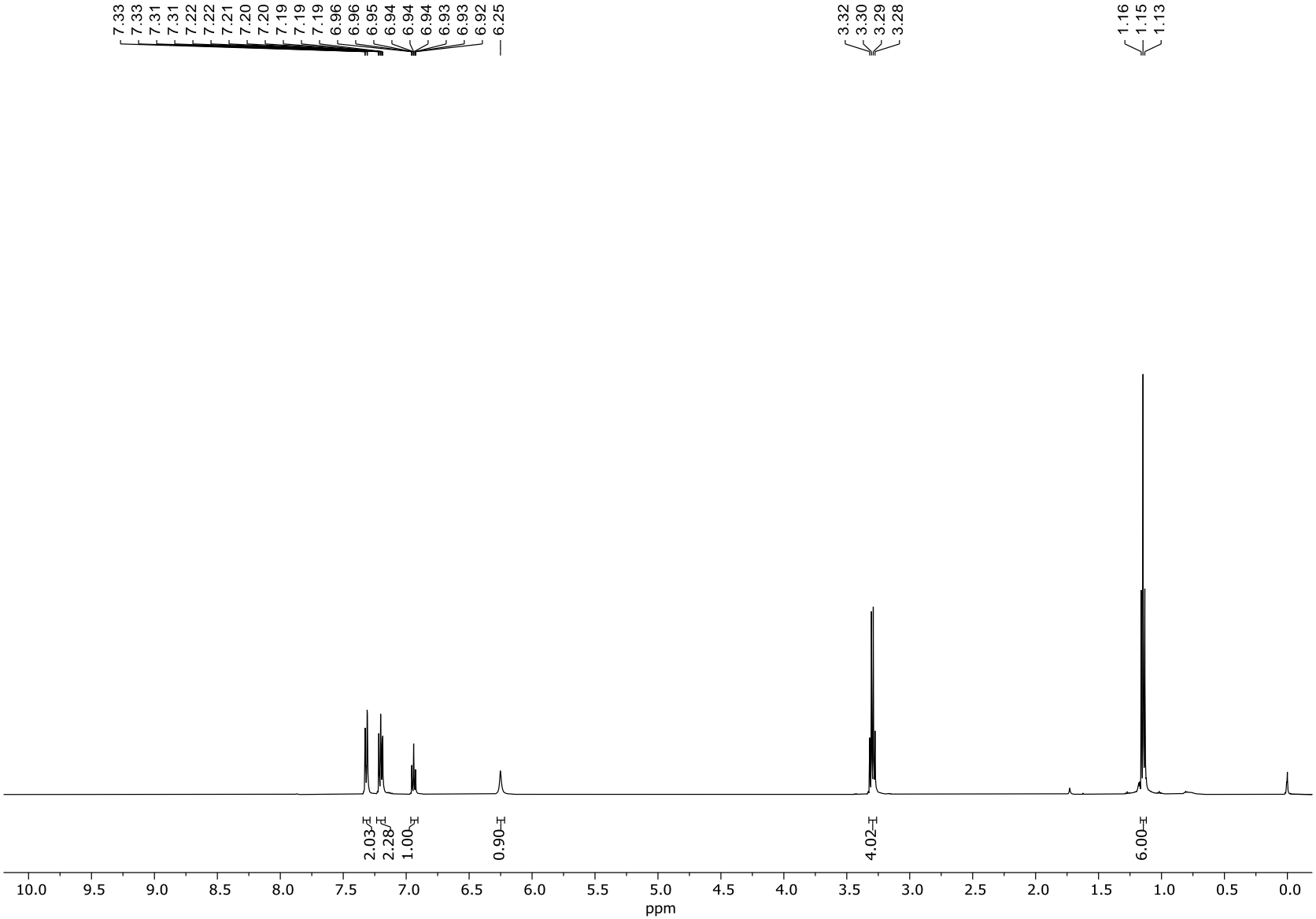


Figure S87: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **5p**.

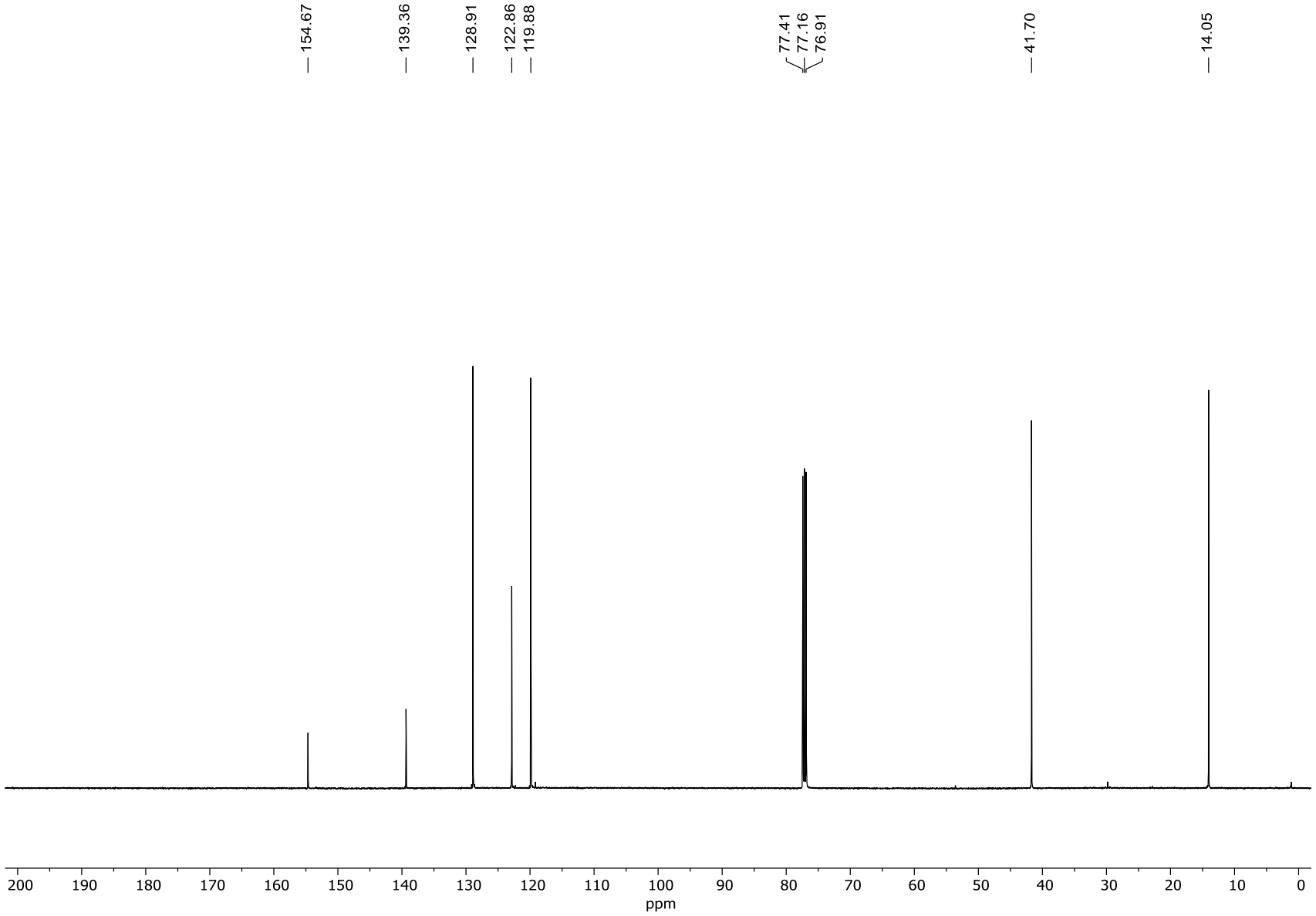


Figure S88: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5q**.

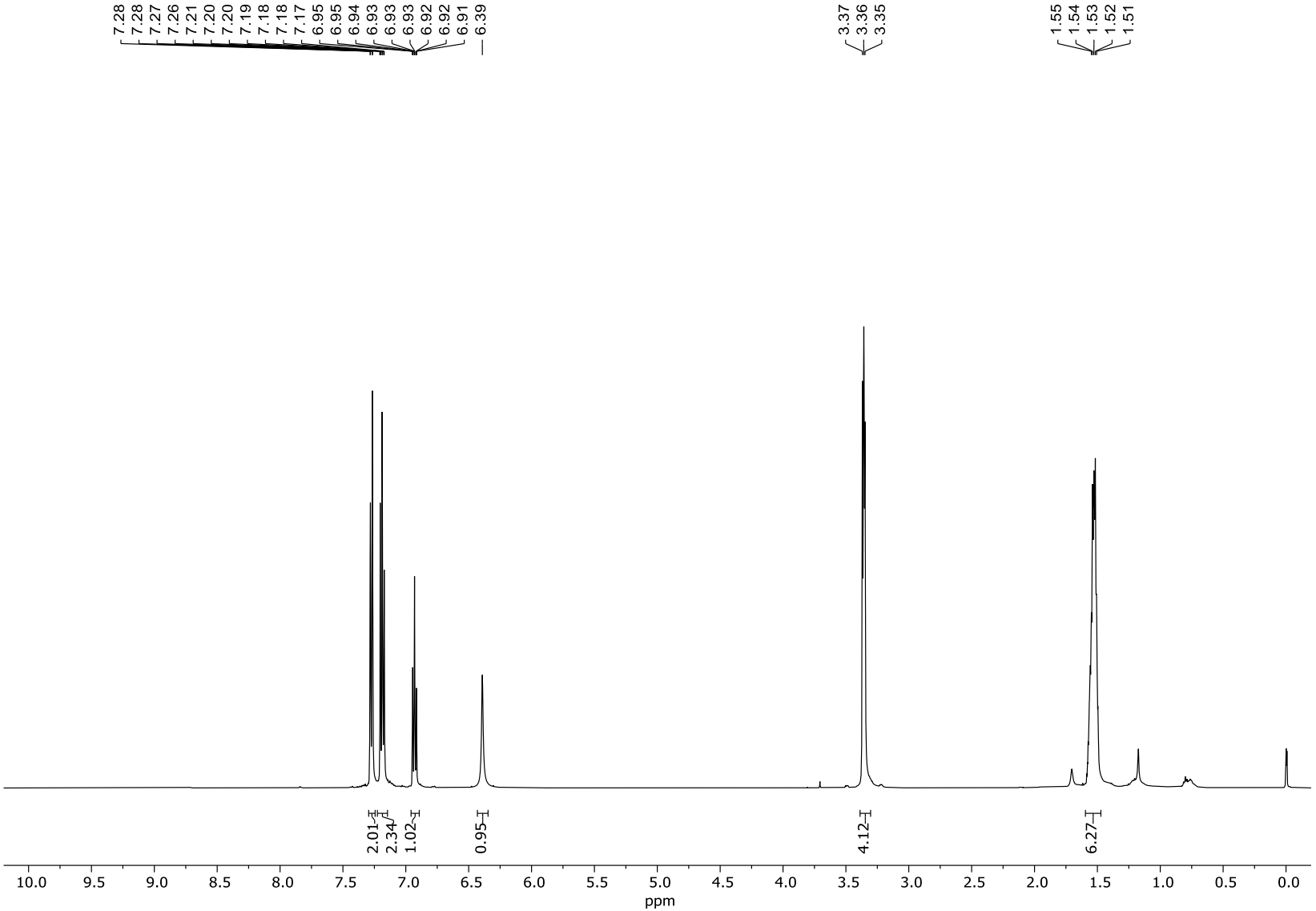


Figure S89: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **5q**.

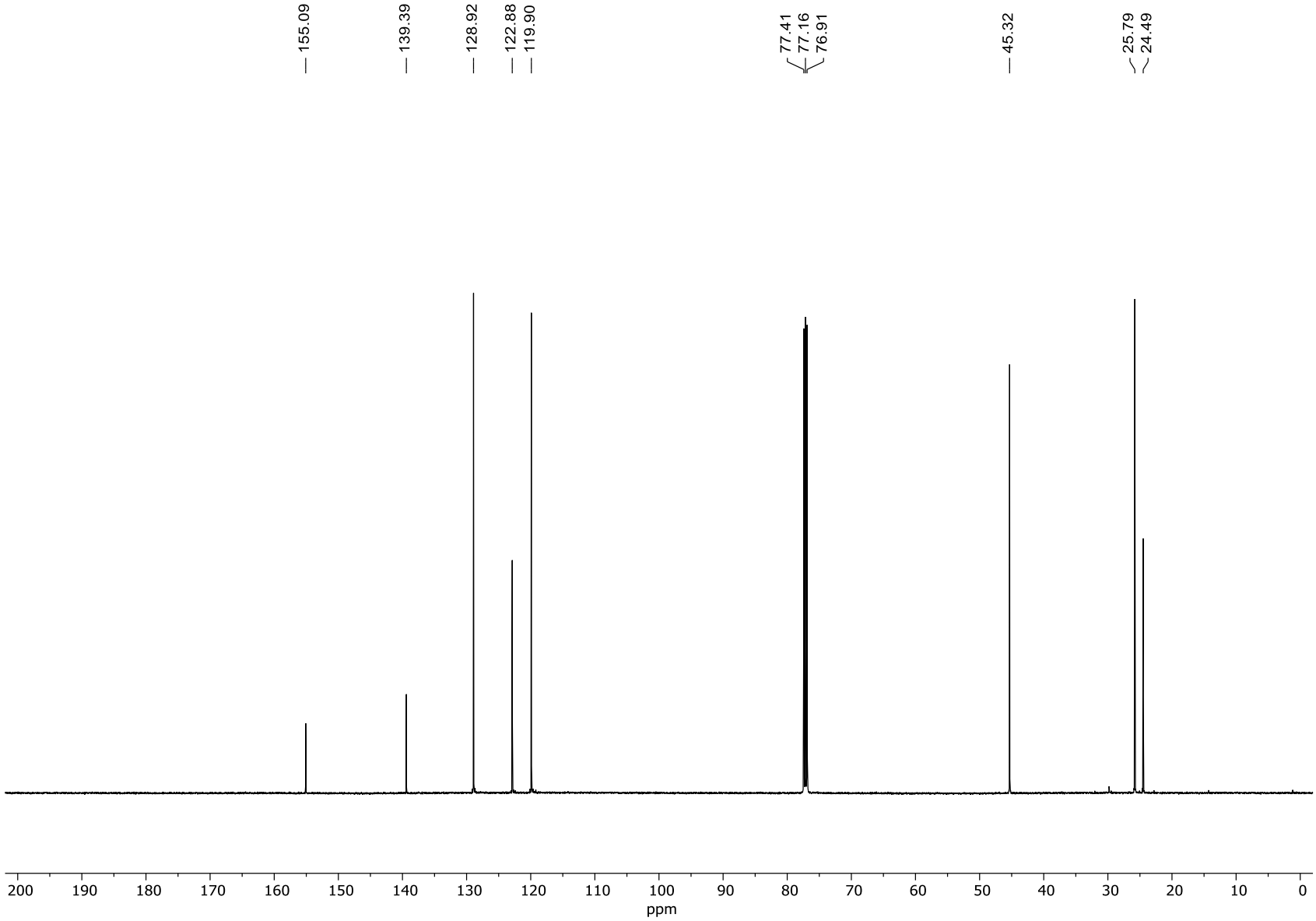


Figure S90: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5r**.

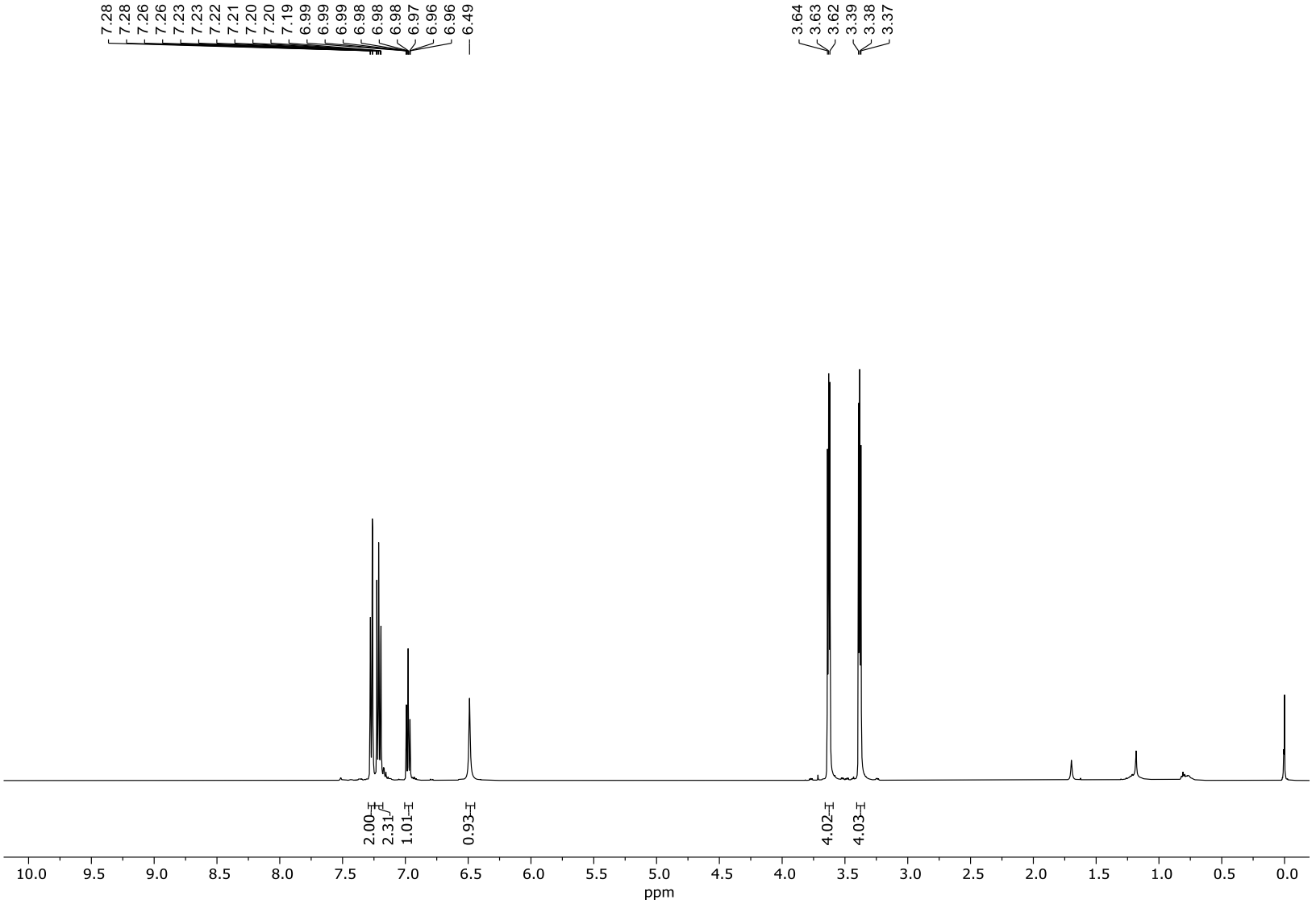


Figure S91: **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K) spectrum of **5r**.

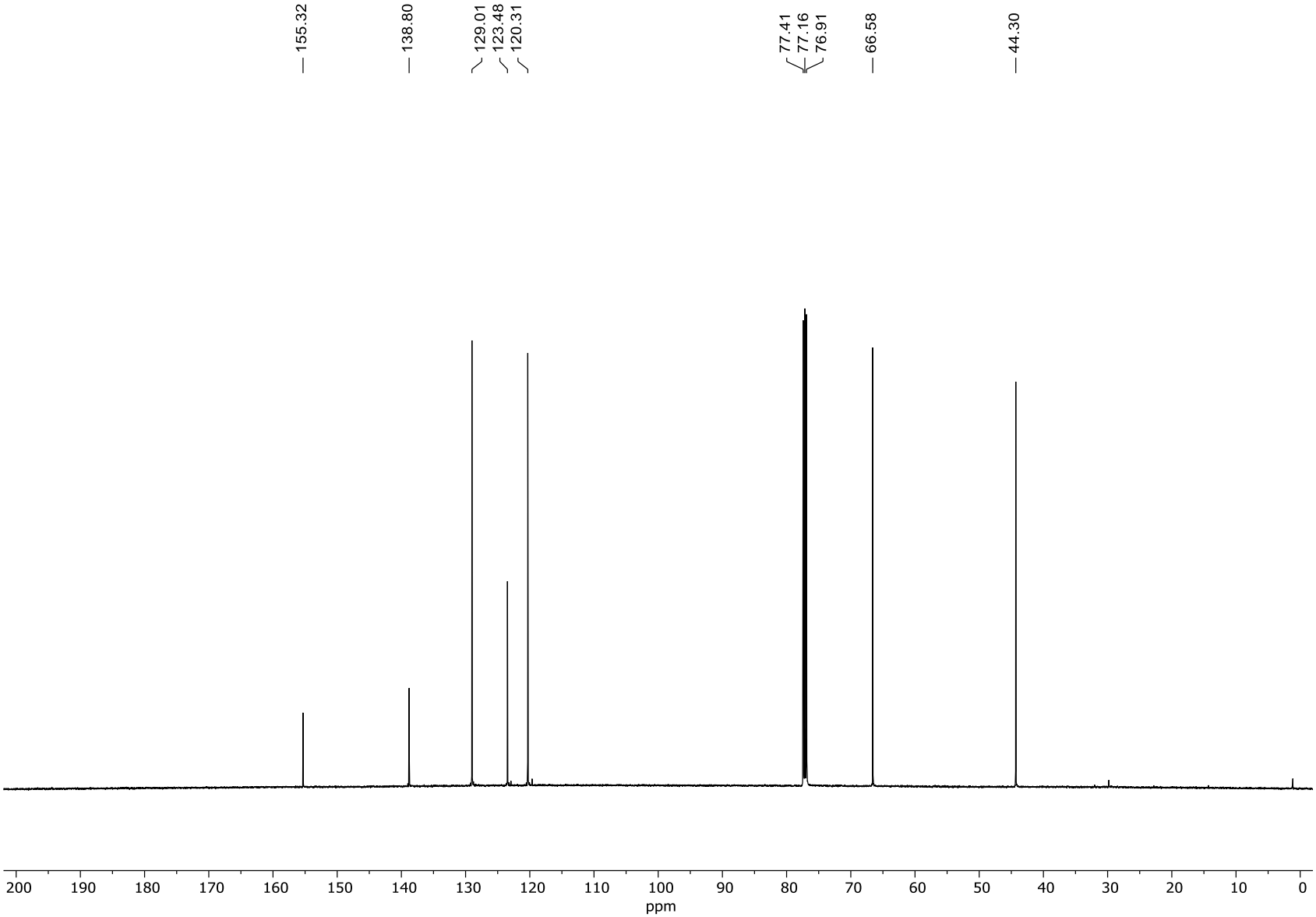


Figure S92: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5s**.

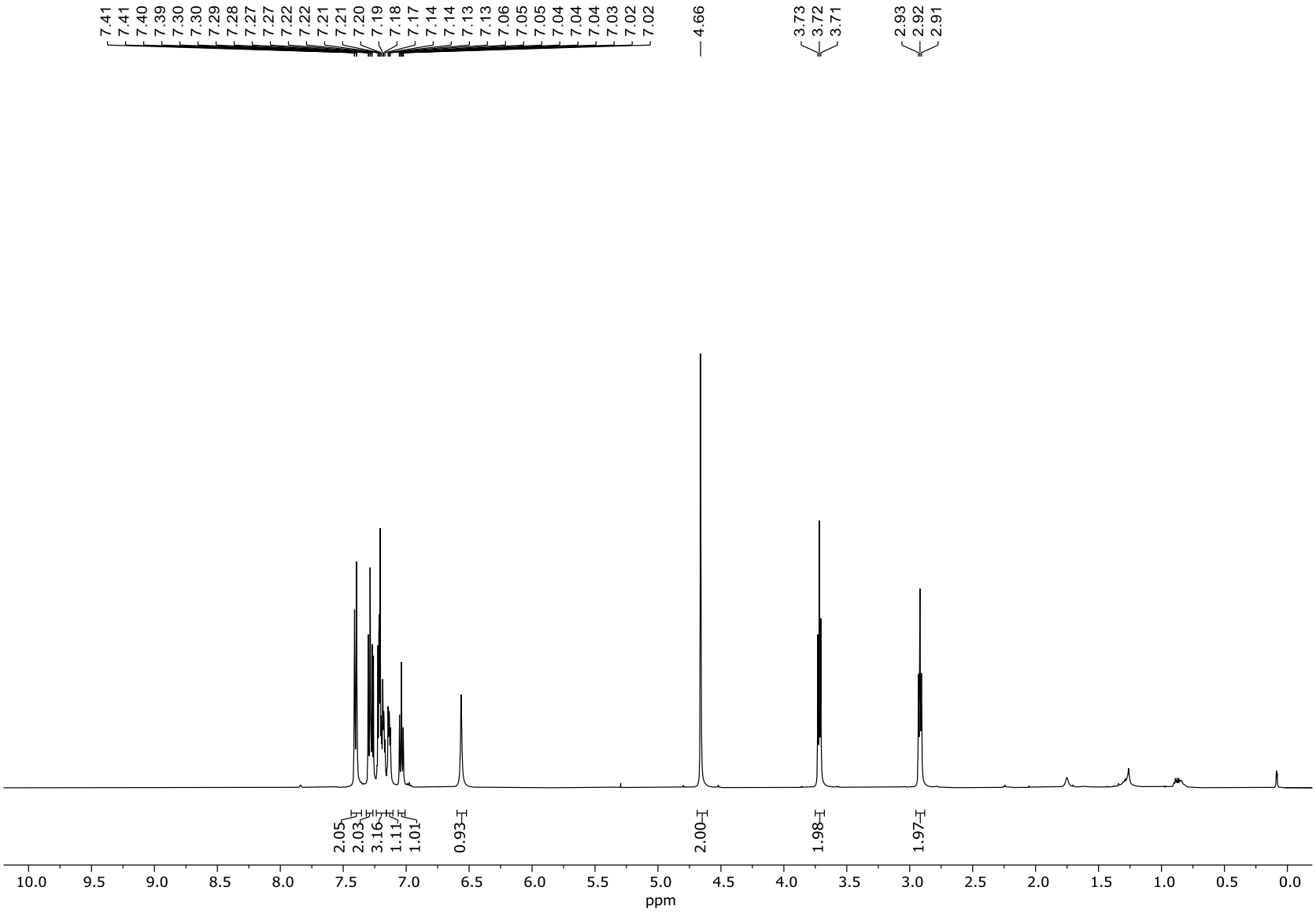


Figure S93: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5s**.

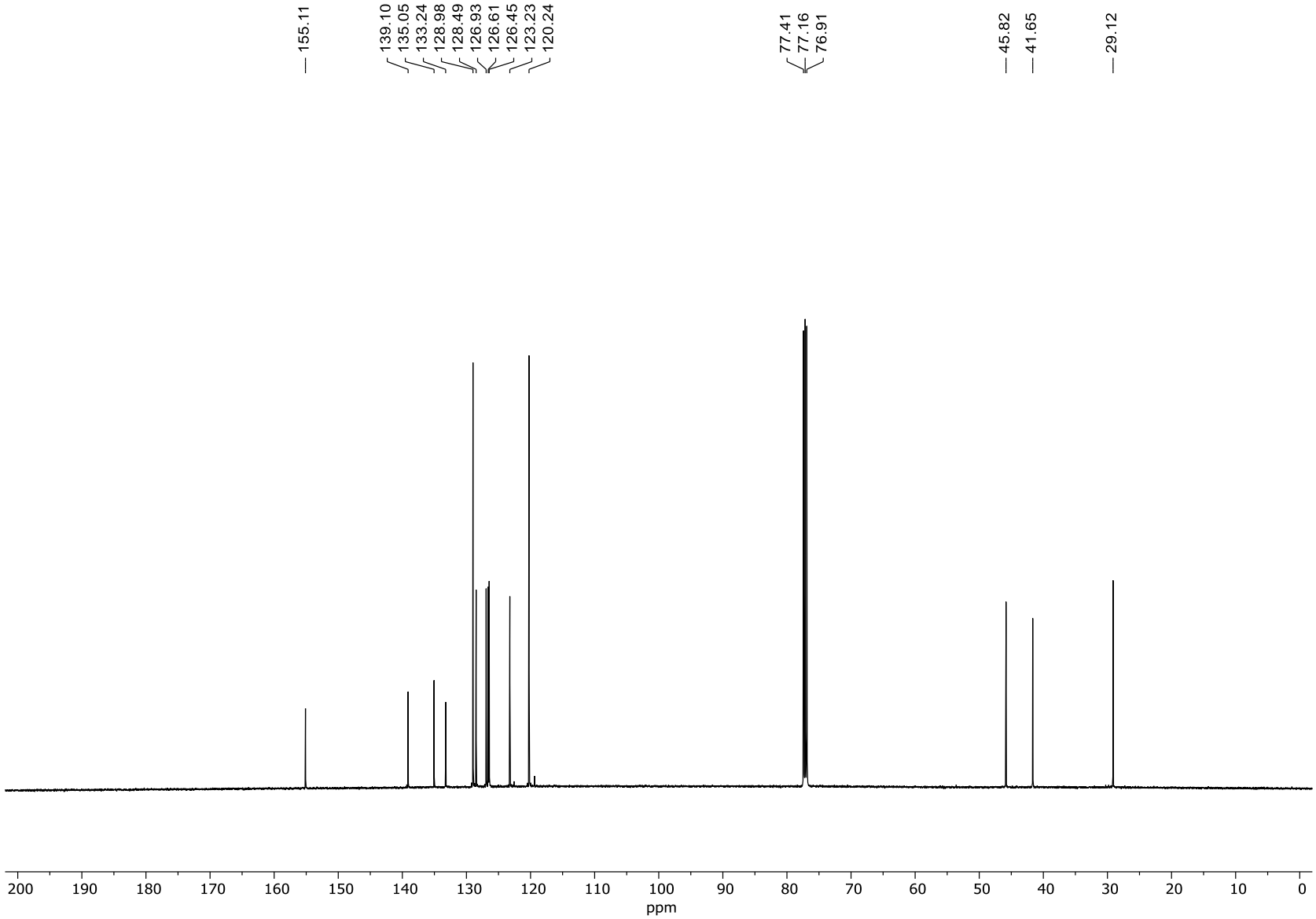


Figure S94: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5t**.

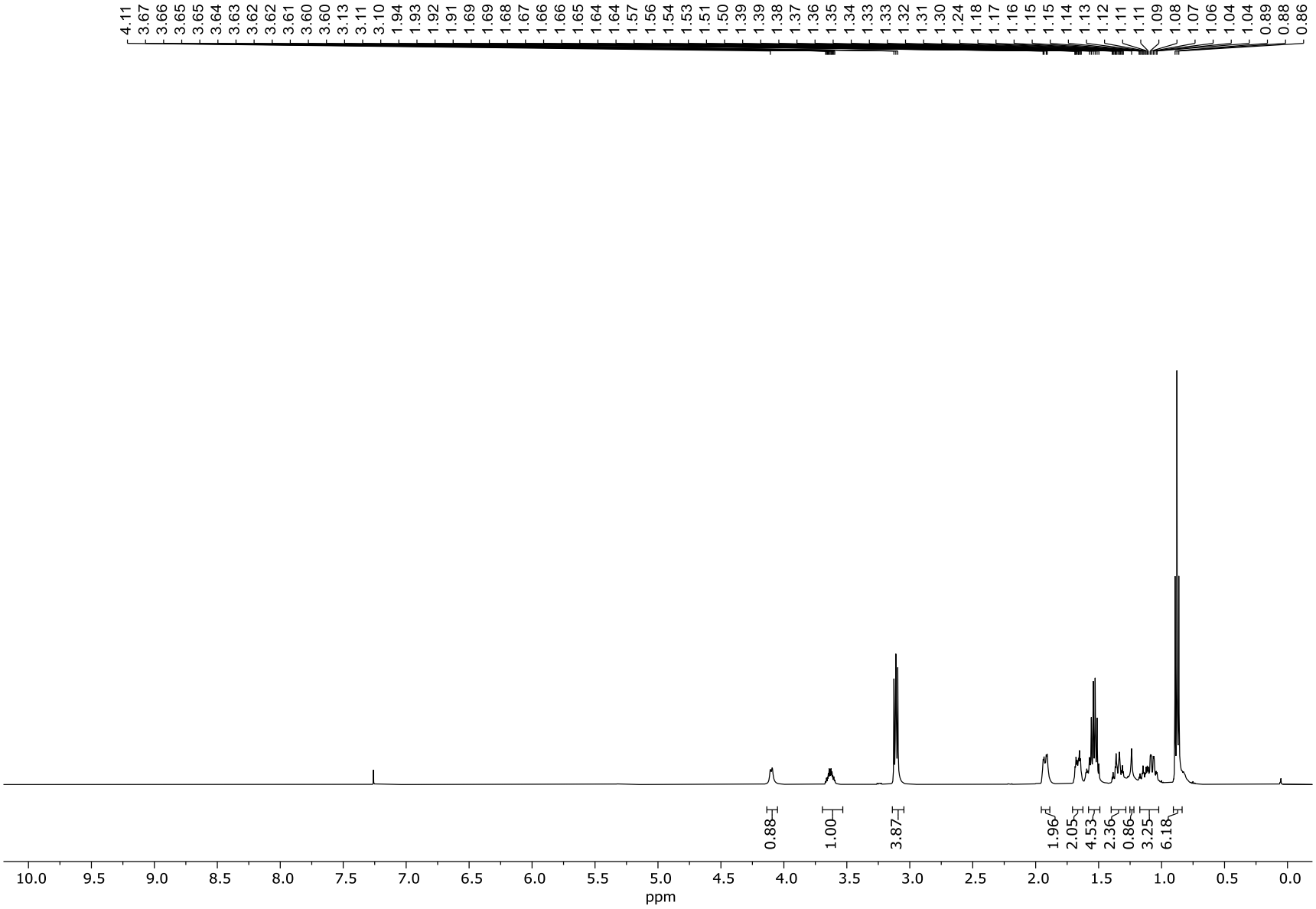


Figure S95: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5t**.

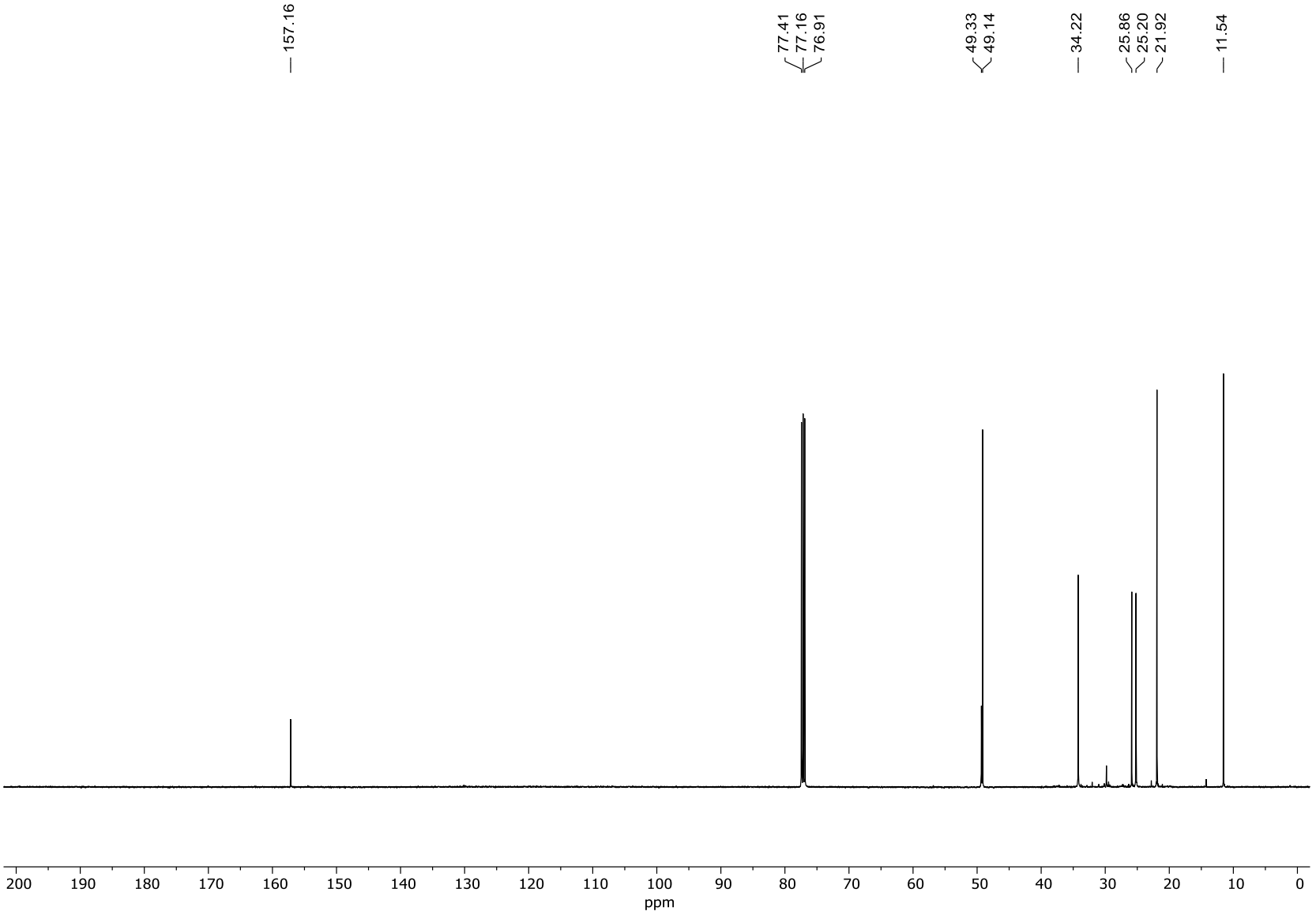
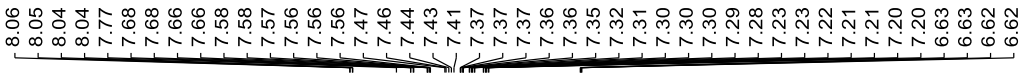


Figure S96: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **5u**.



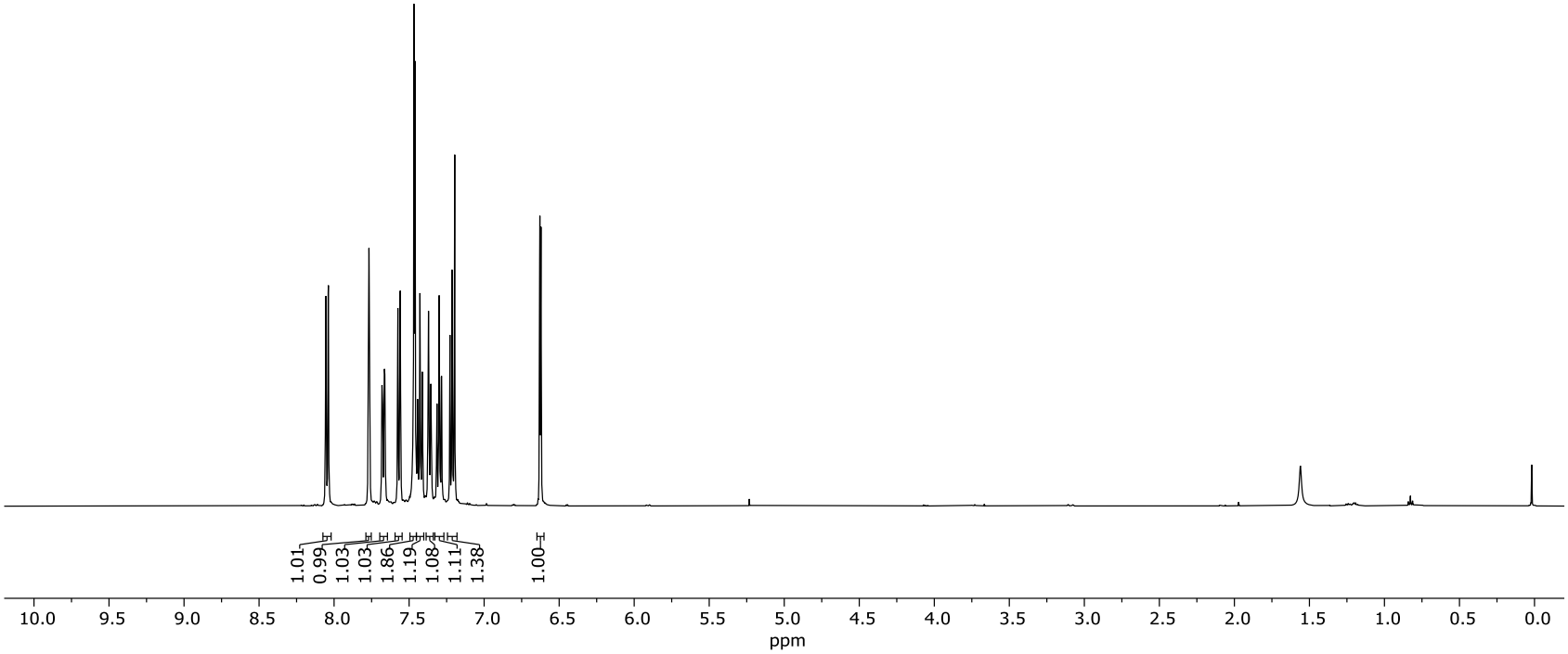


Figure S97: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **5u**.

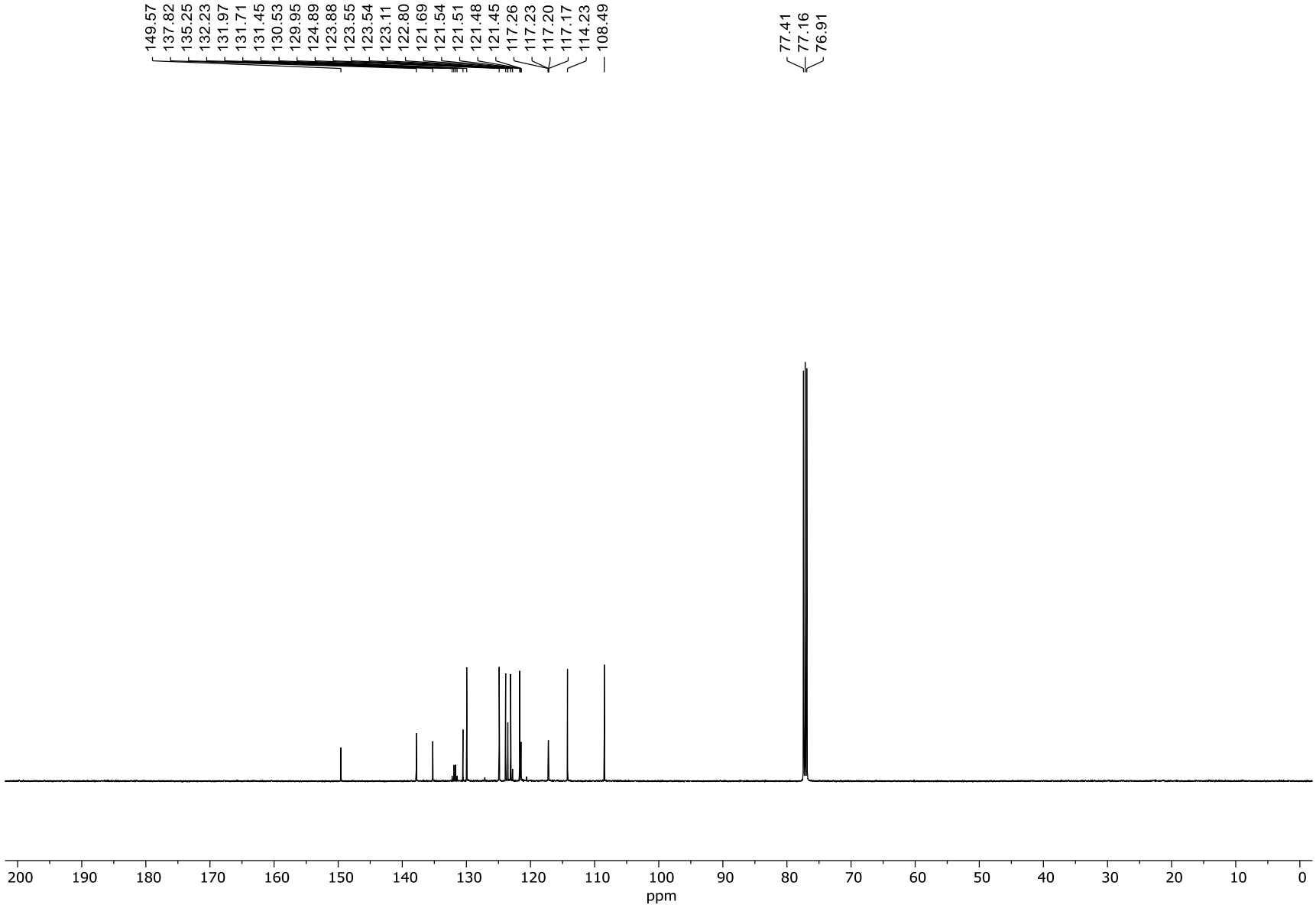


Figure S98: **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) spectrum of **5u**.

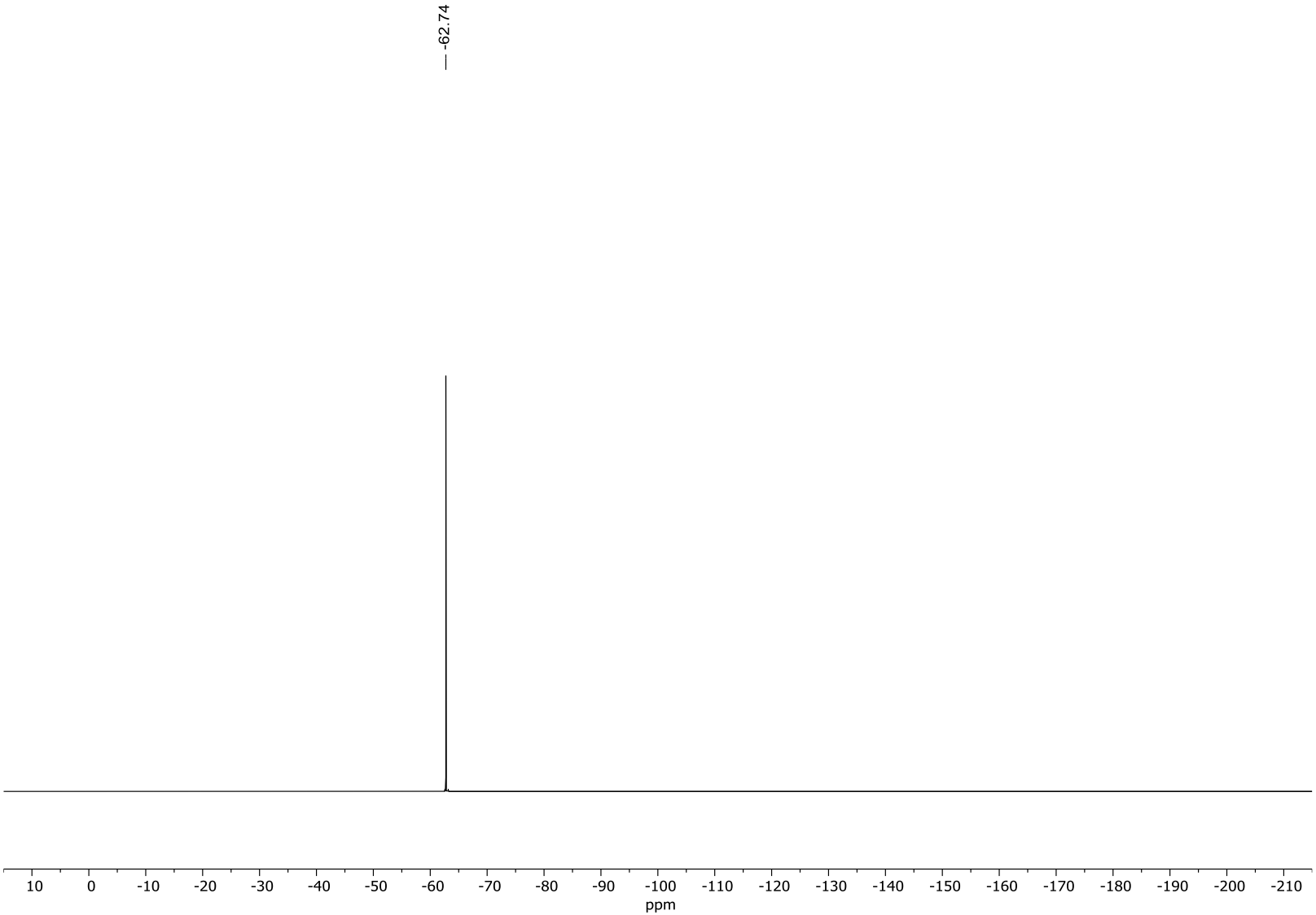


Figure S99: **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K) spectrum of **6a**.

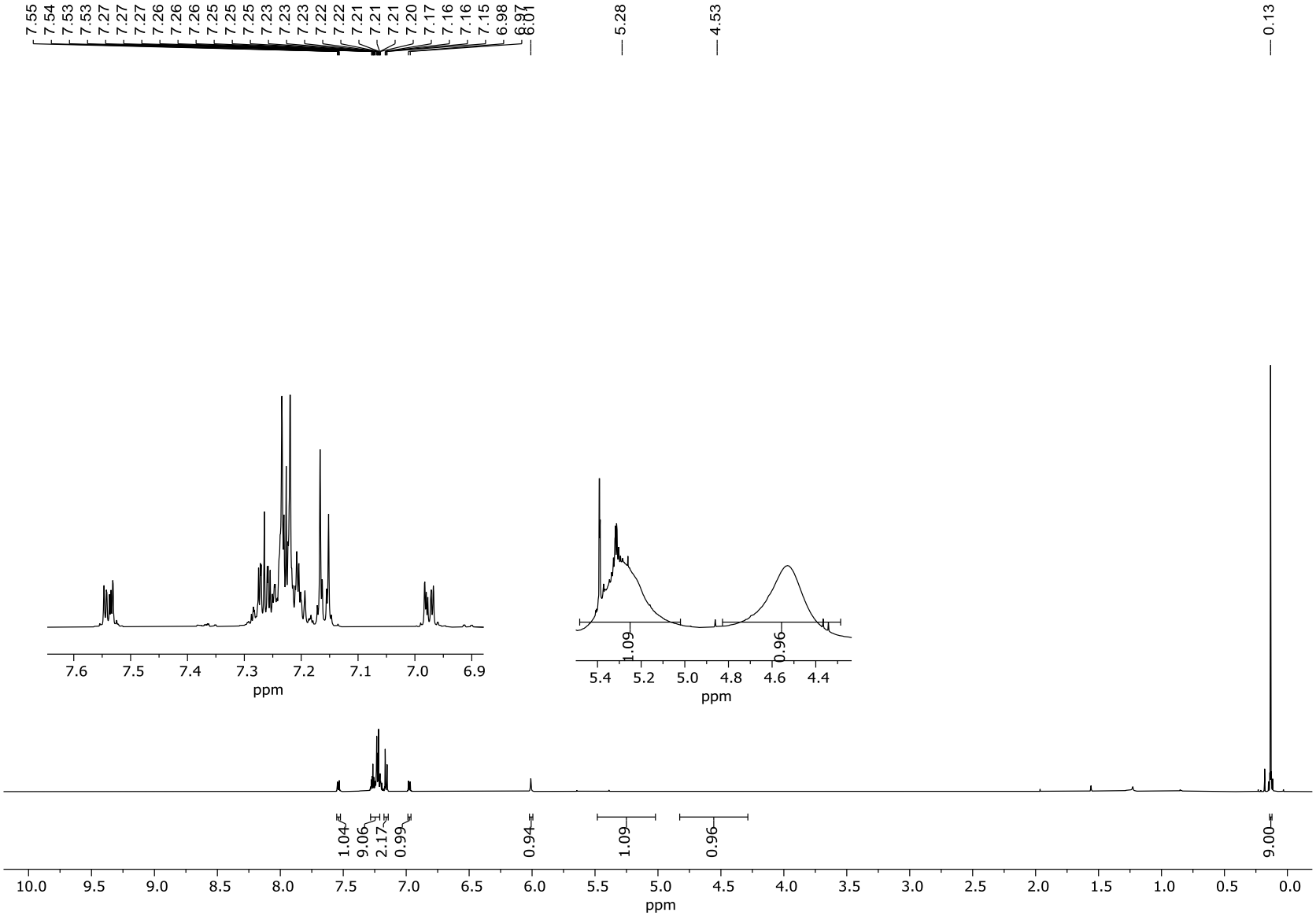


Figure S100: **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K) spectrum of **6a**.

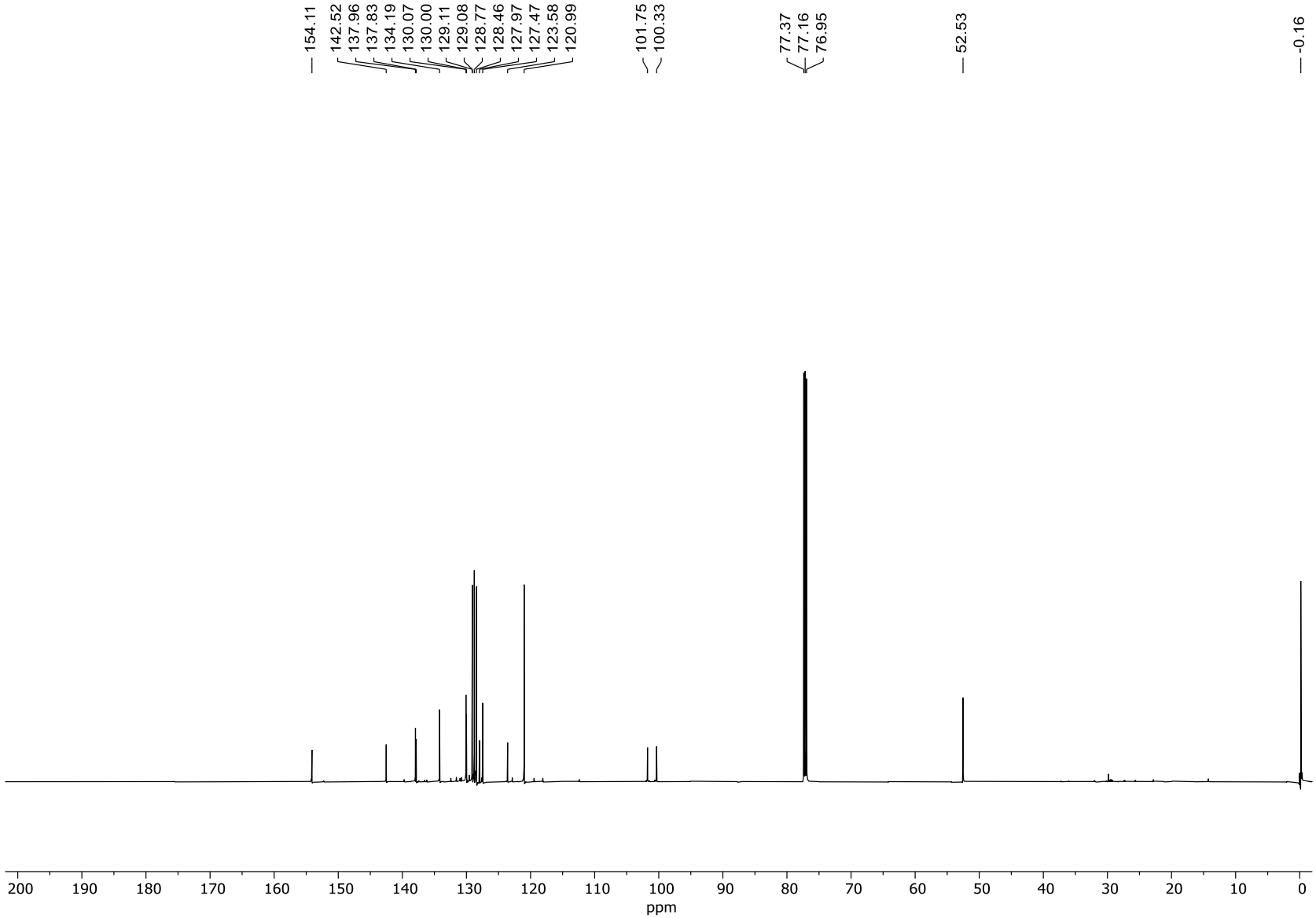


Figure S101: **HSQC NMR** (600 MHz, $CDCl_3$, 298 K) spectrum of **6a**.

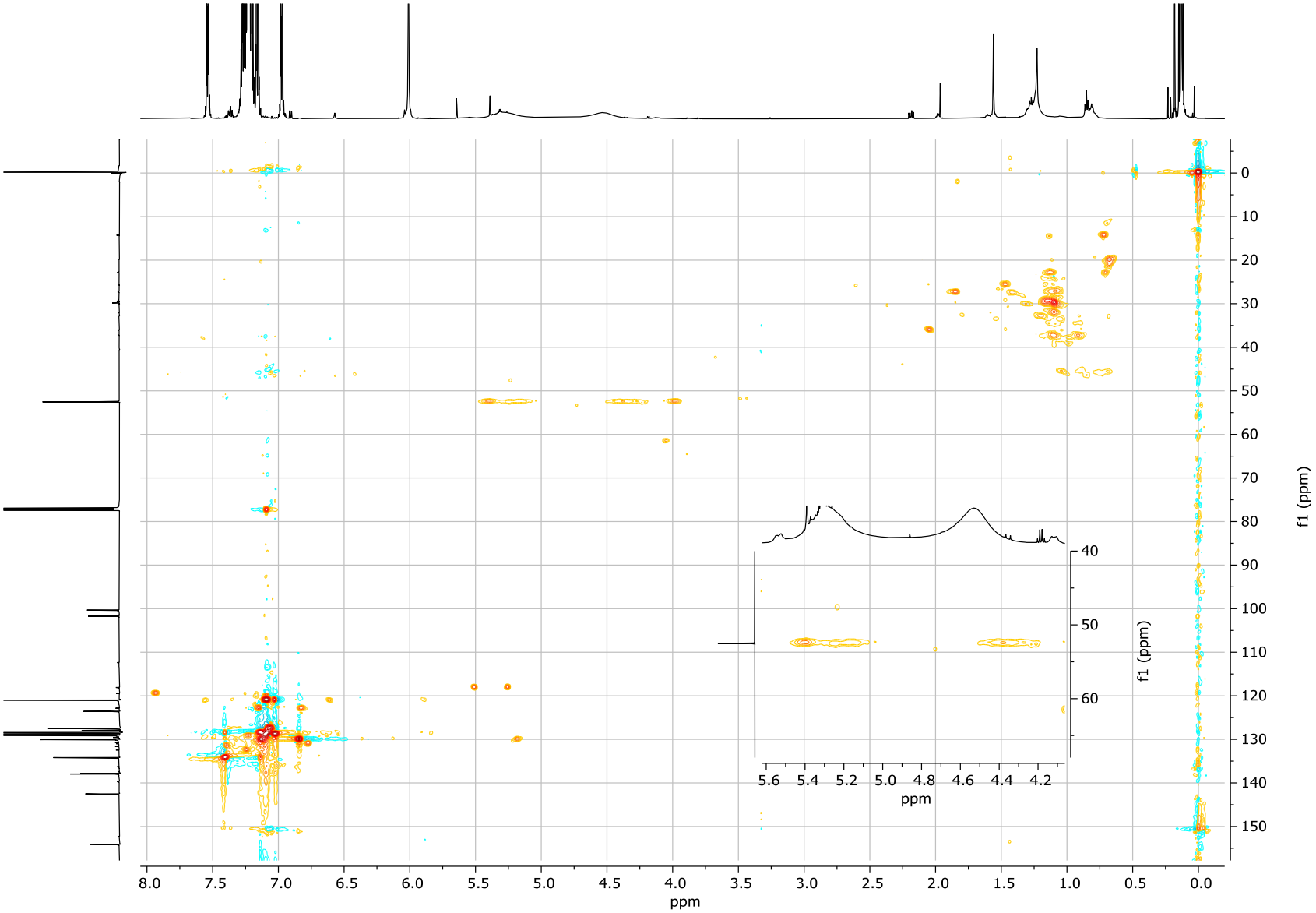


Figure S102: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **6b**.

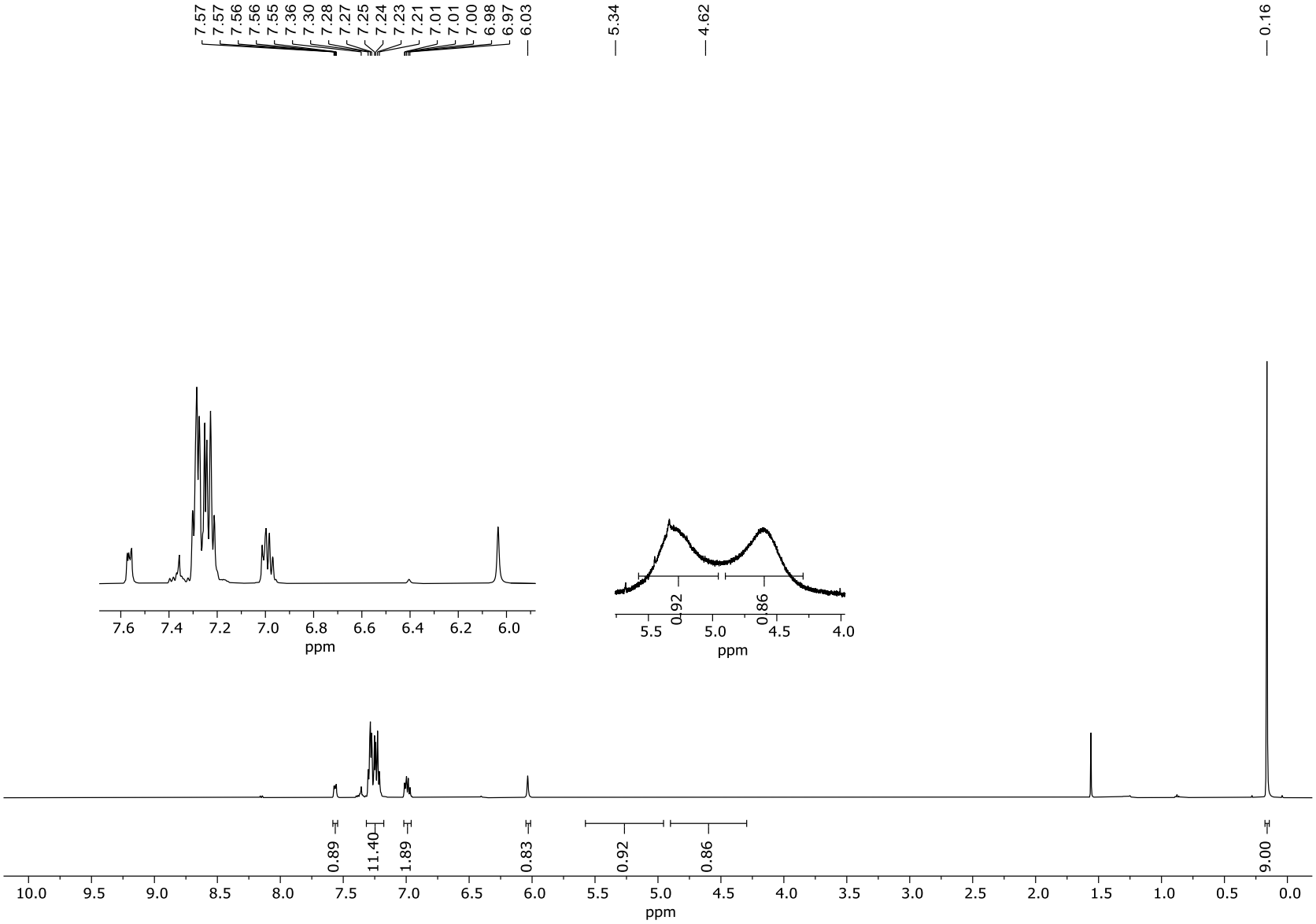


Figure S103: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **6b**.

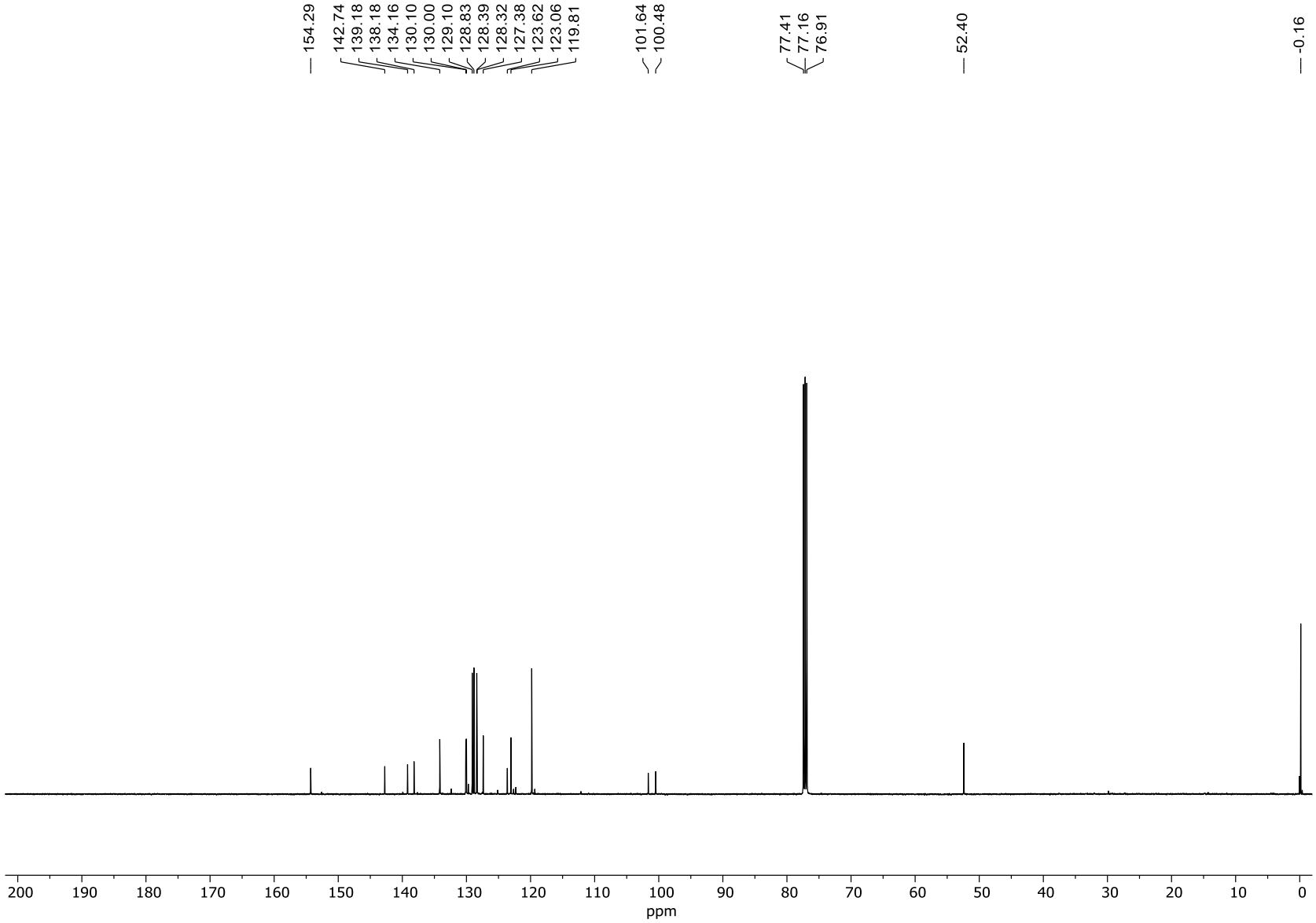


Figure S104: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **6c**.

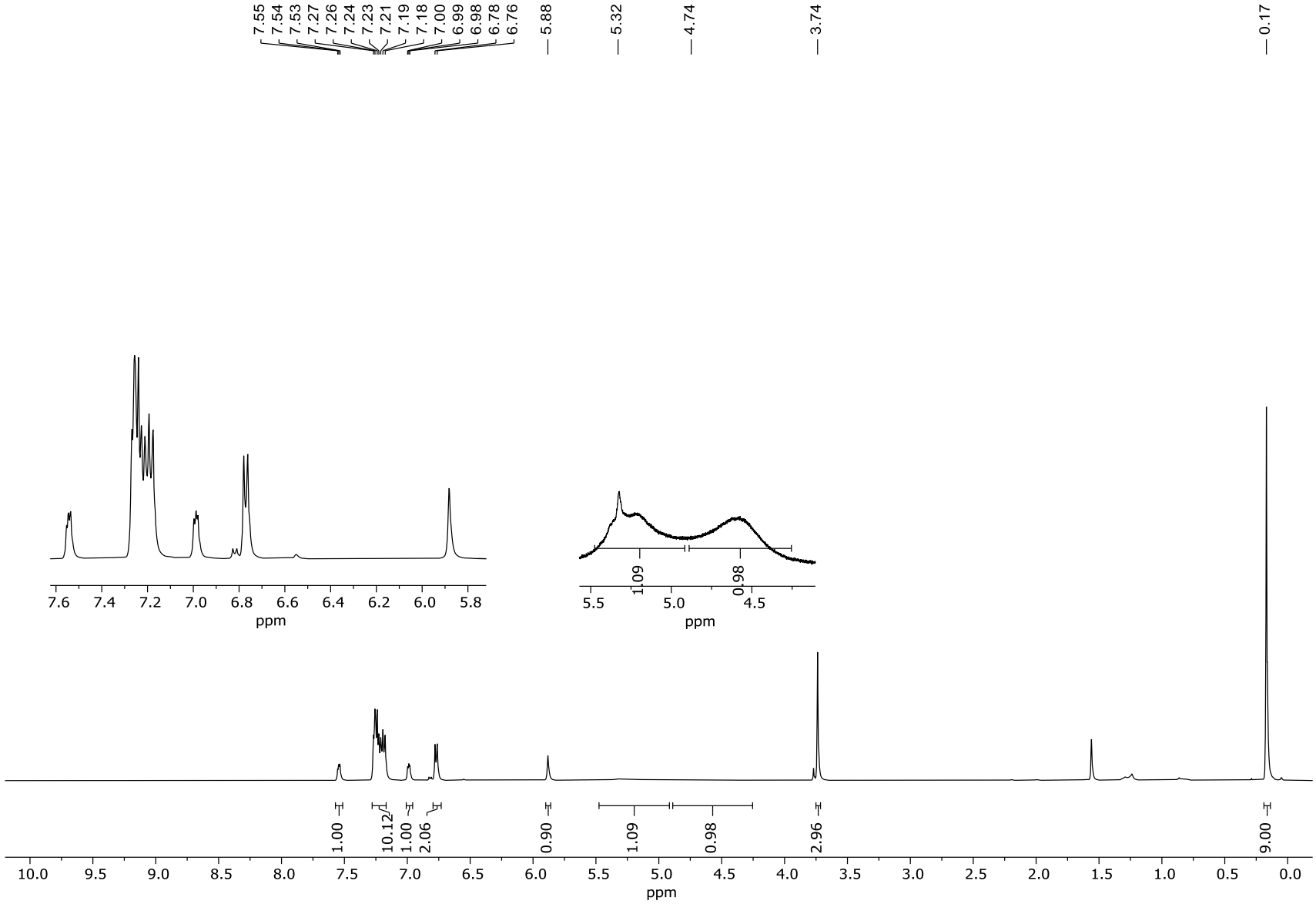


Figure S105: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **6c**.

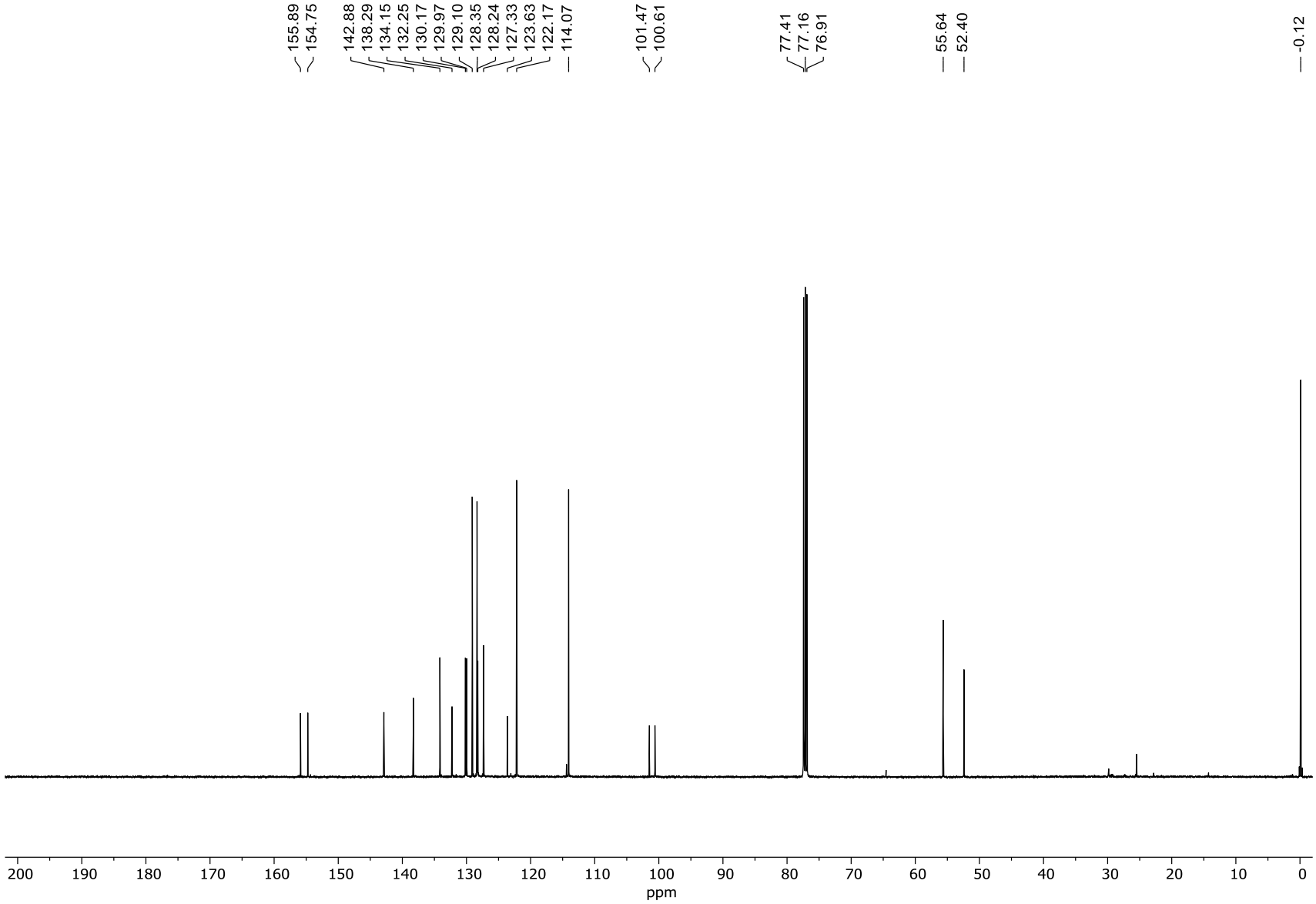


Figure S106: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **6d**.

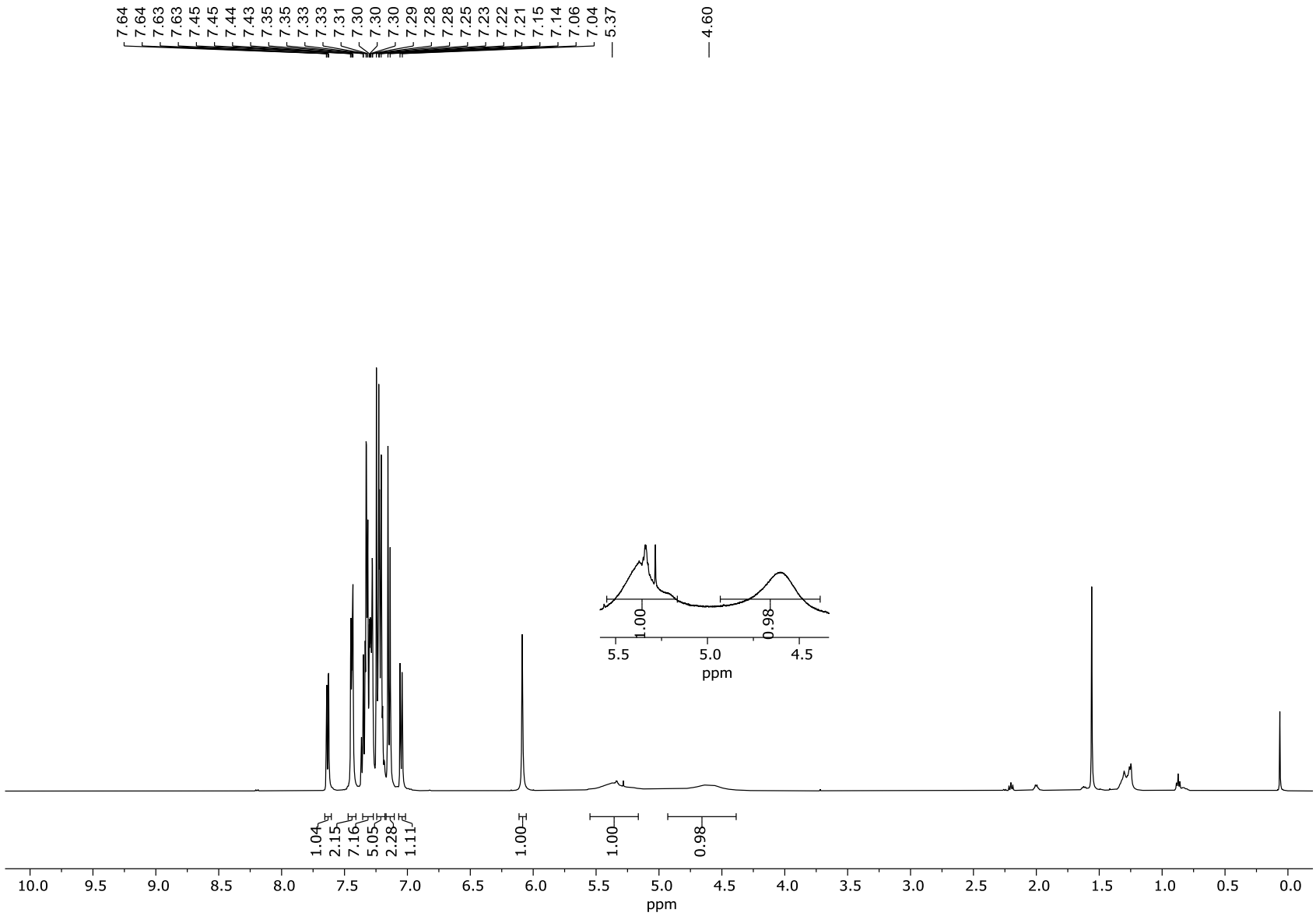


Figure S107: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **6d**.

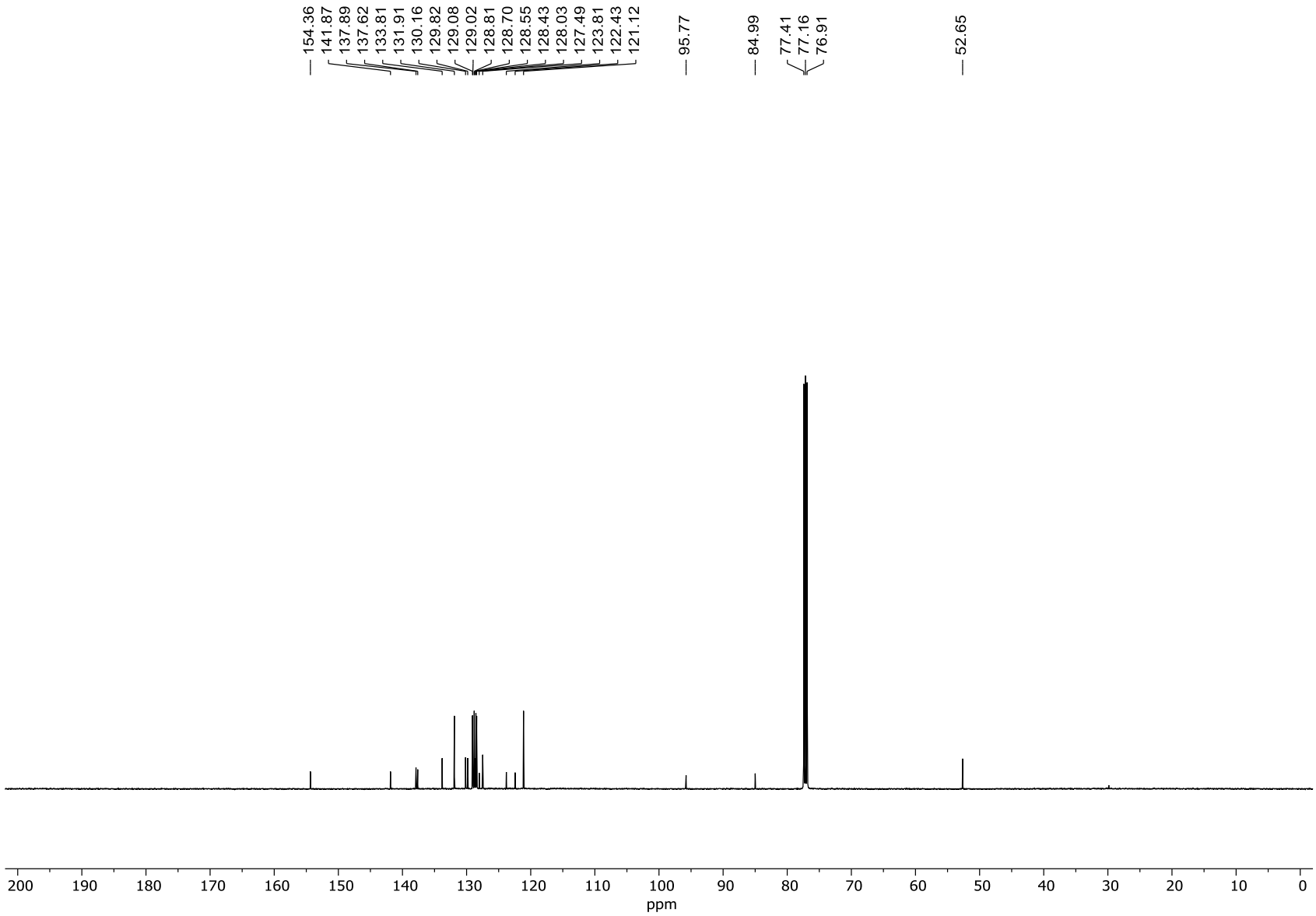


Figure S108: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **6e**.

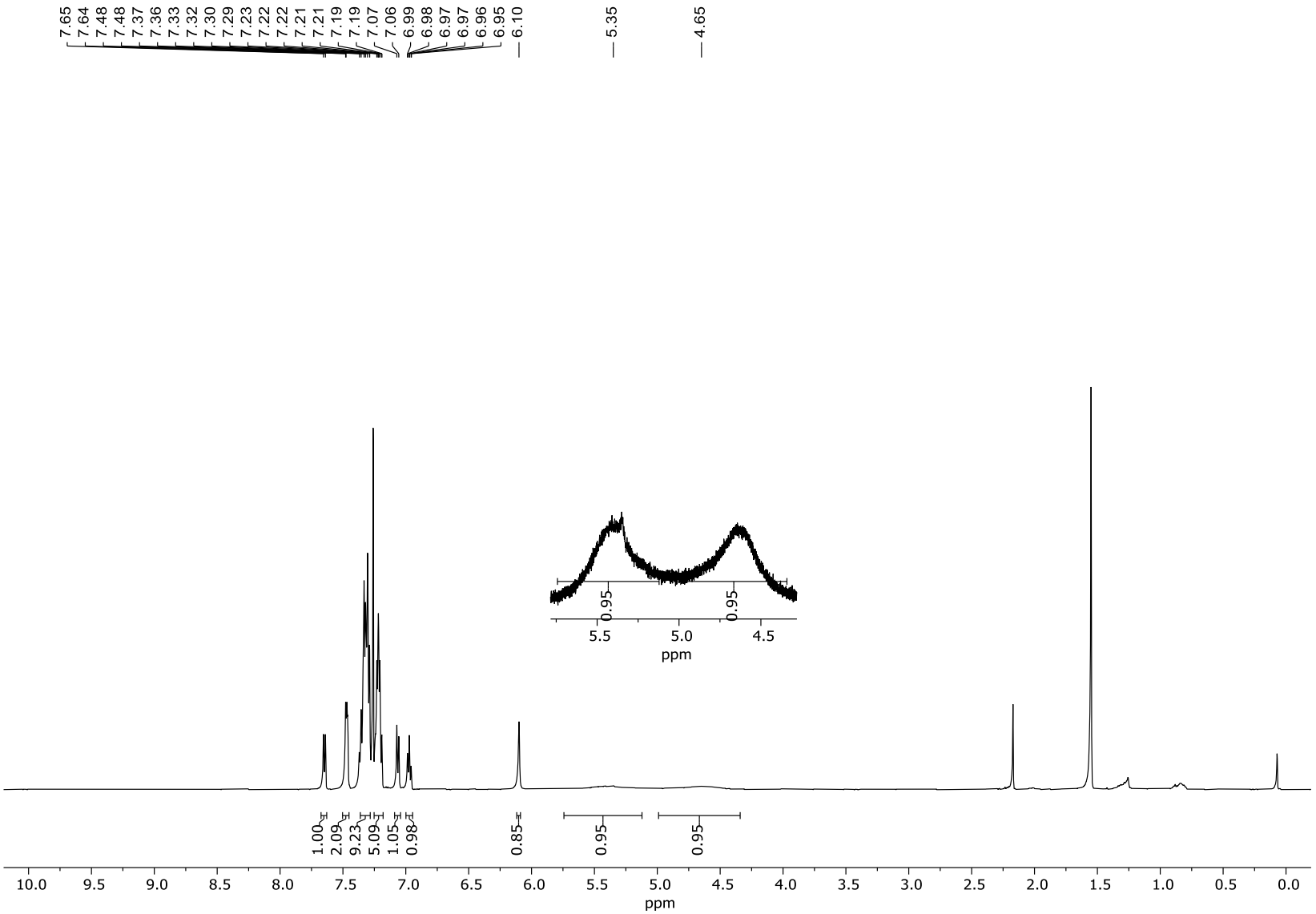


Figure S109: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **6e**.

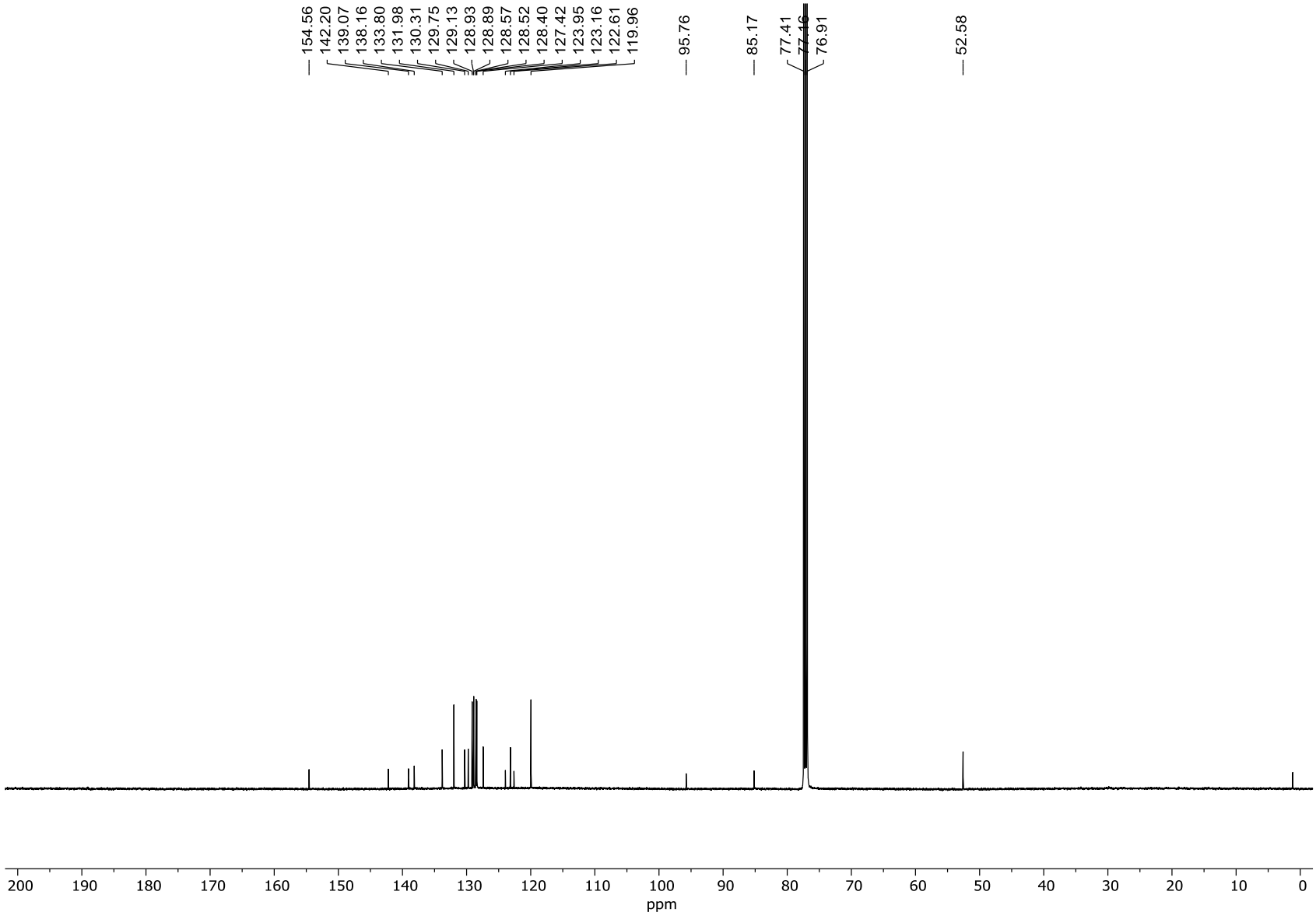


Figure S110: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **6f**.

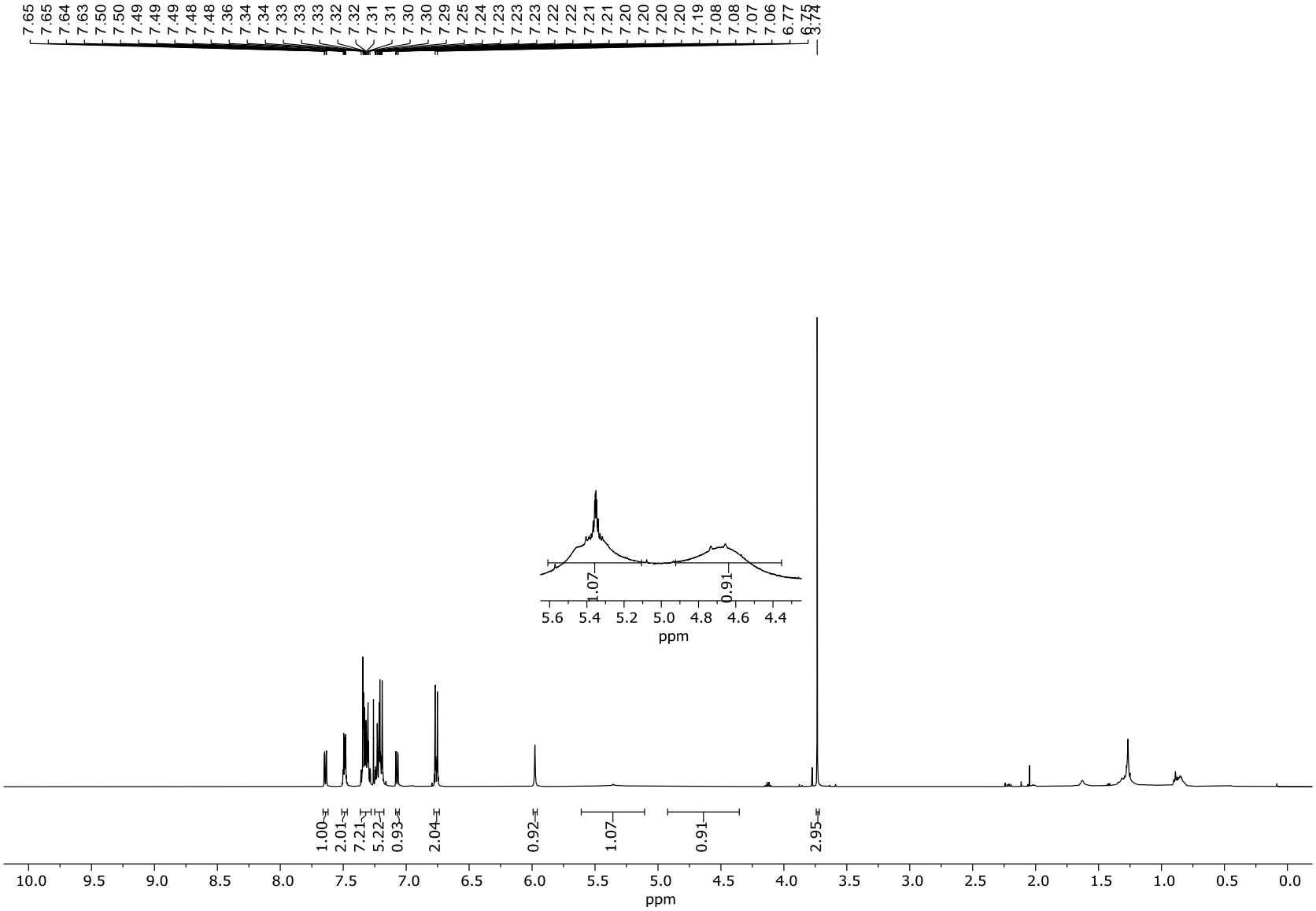


Figure S111: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **6f**.

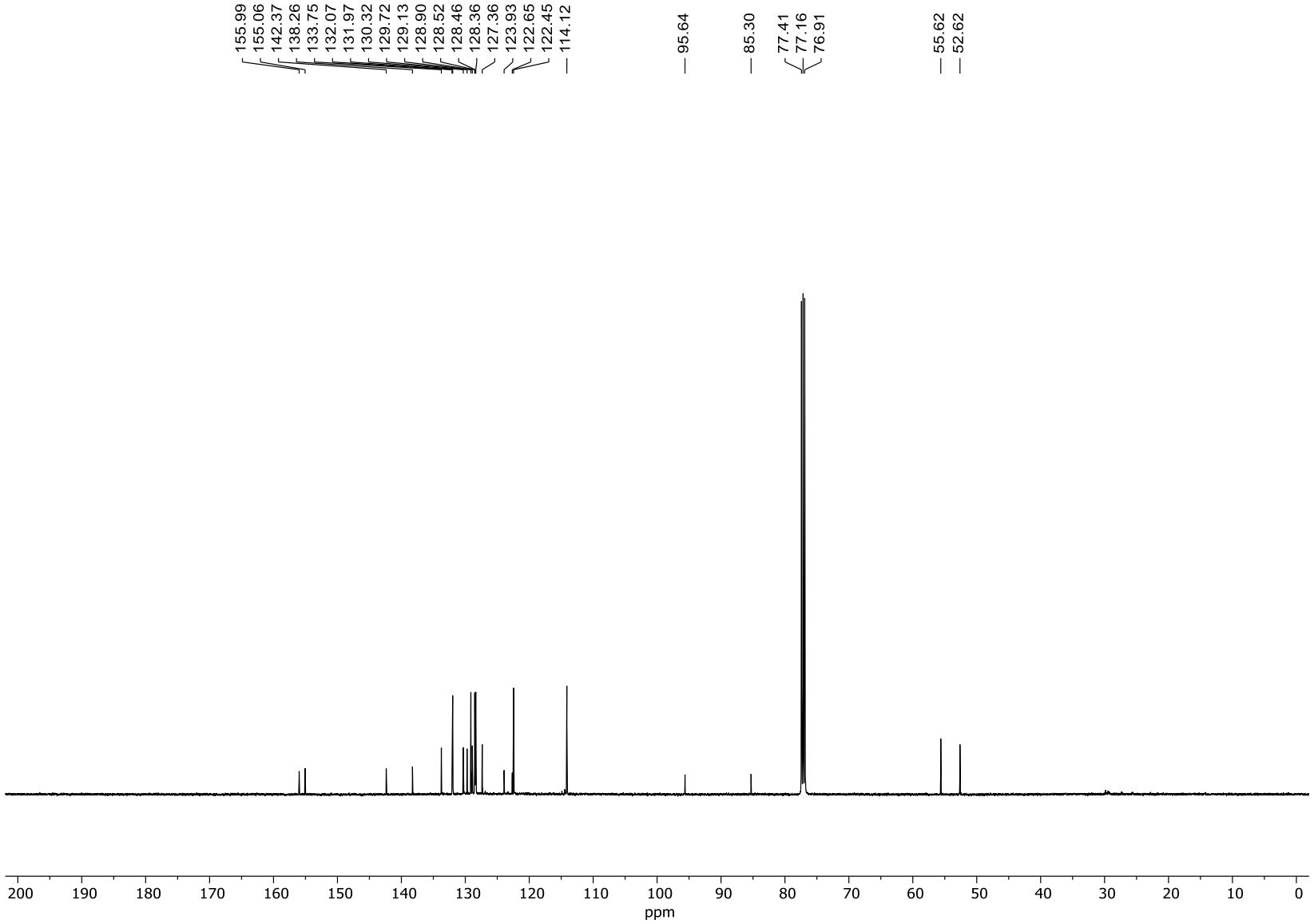


Figure S112: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **6g**.

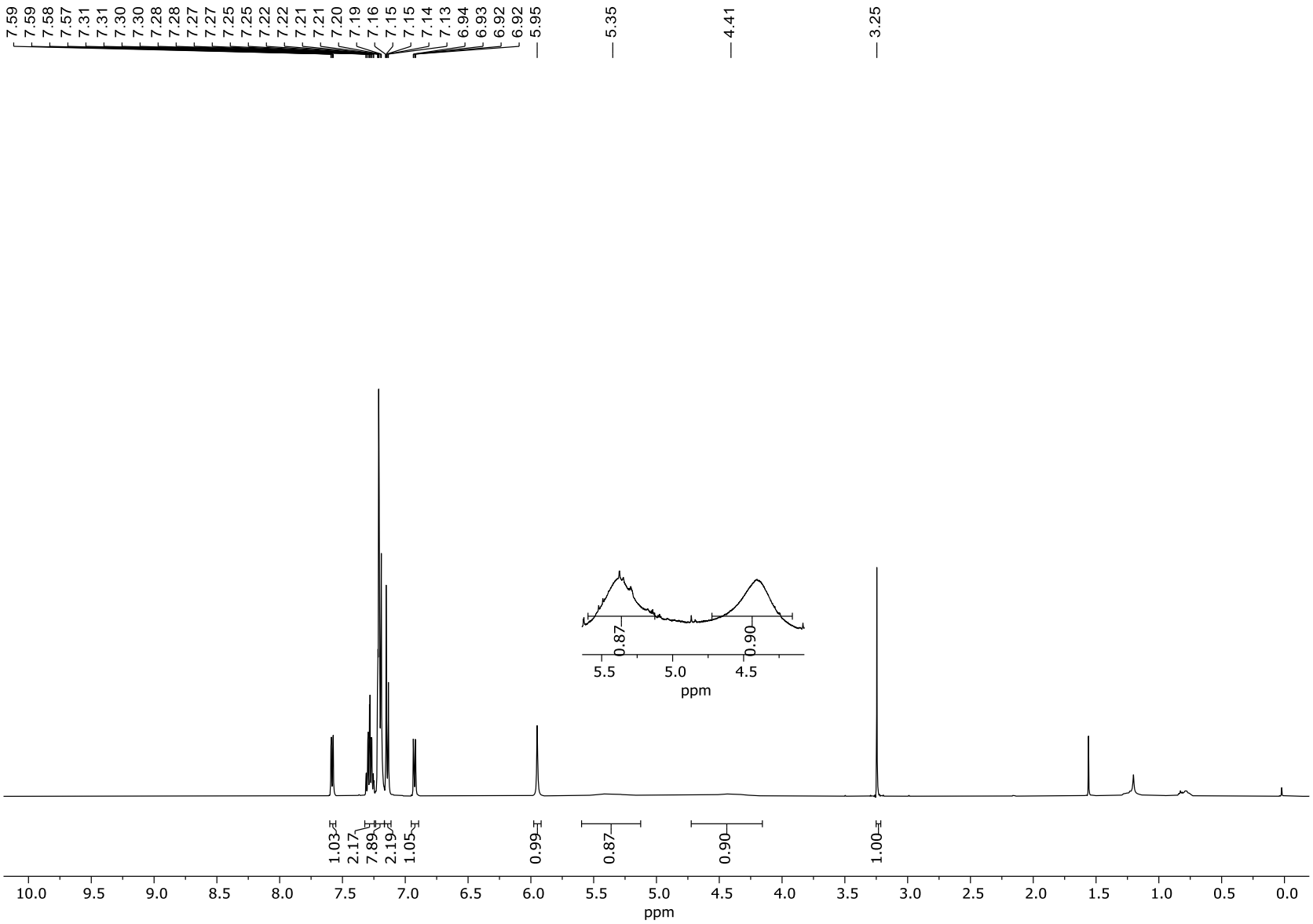


Figure S113: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **6g**.

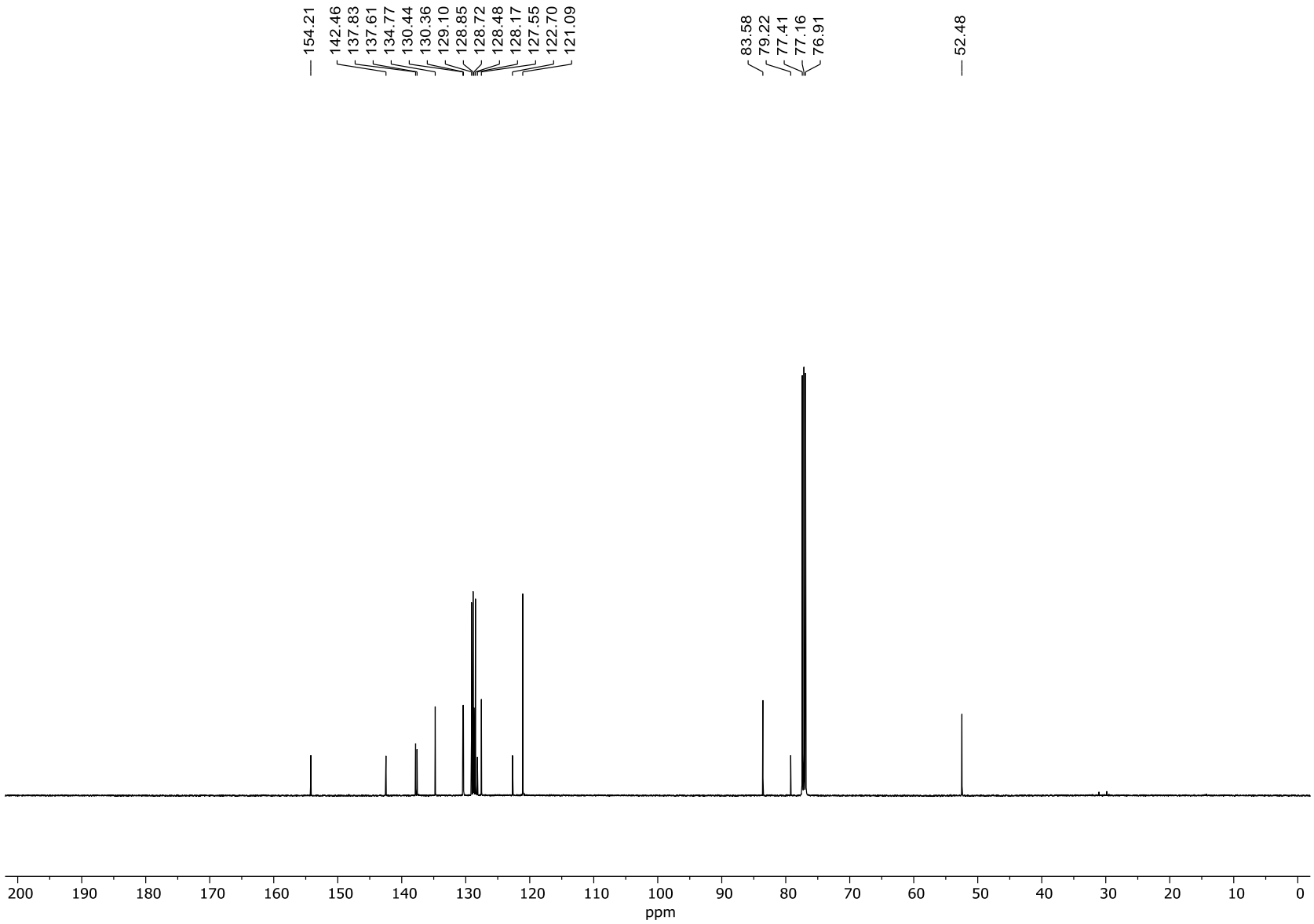


Figure S114: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **6h**.

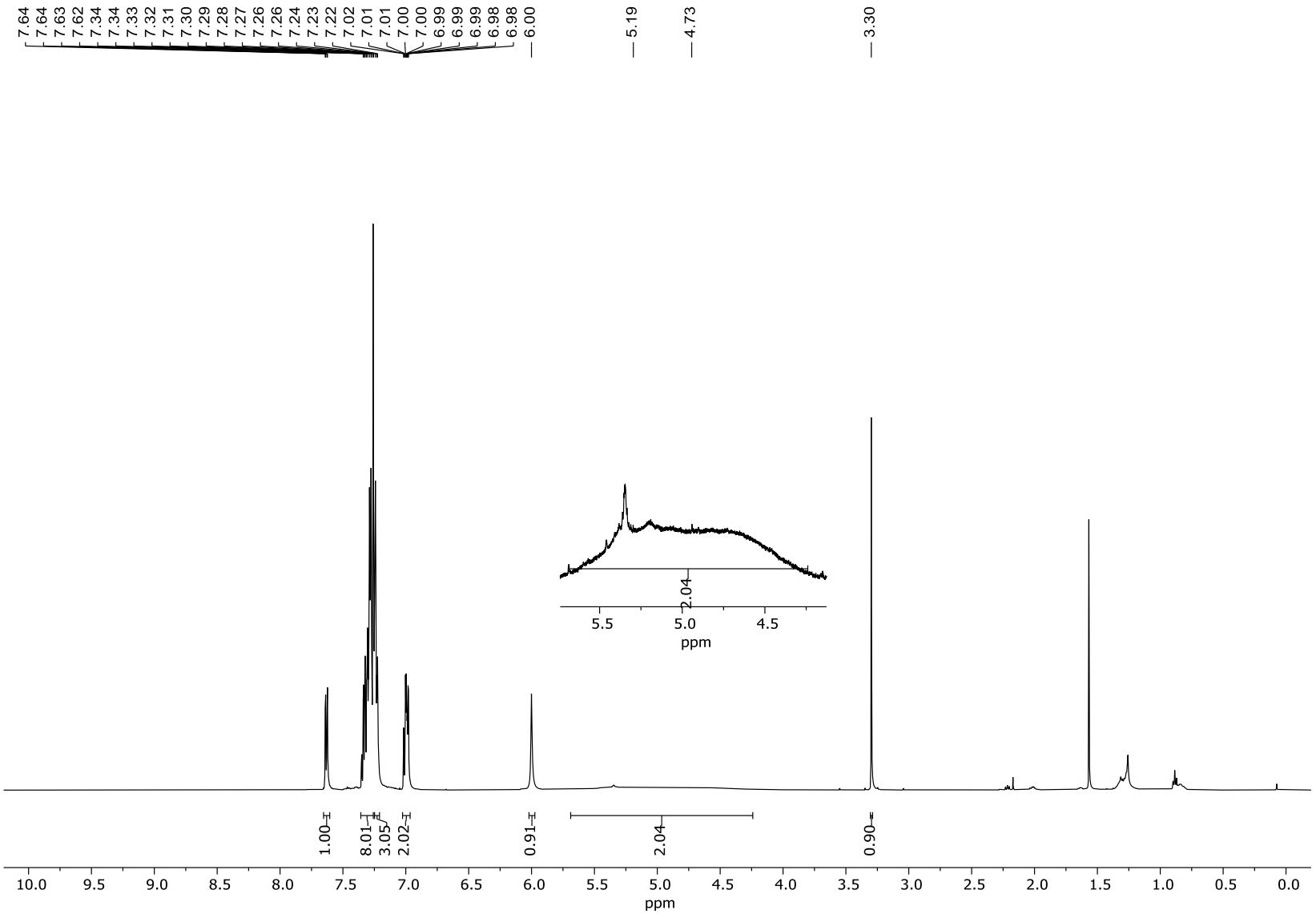


Figure S115: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **6h**.

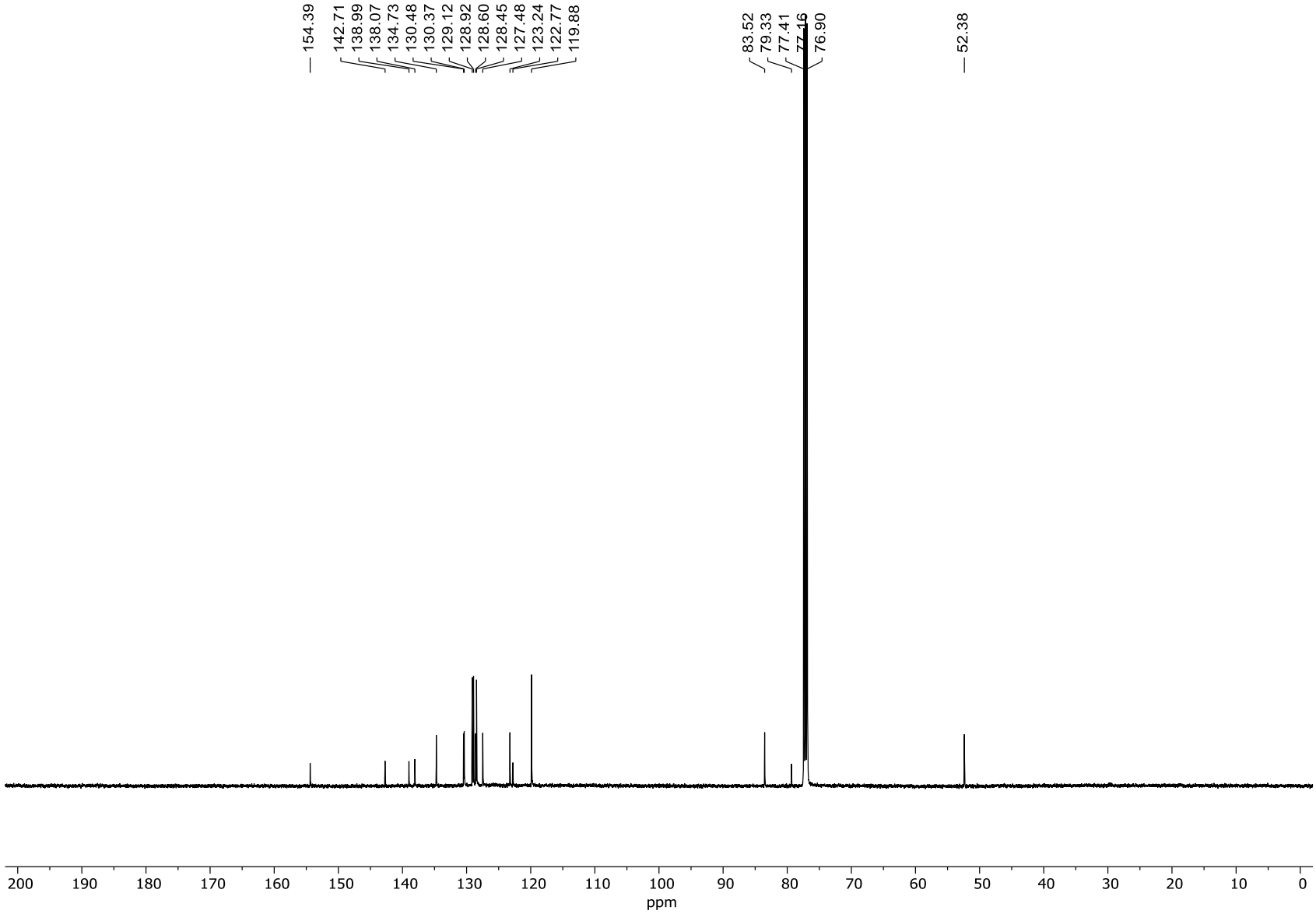


Figure S116: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) spectrum of **6i**.

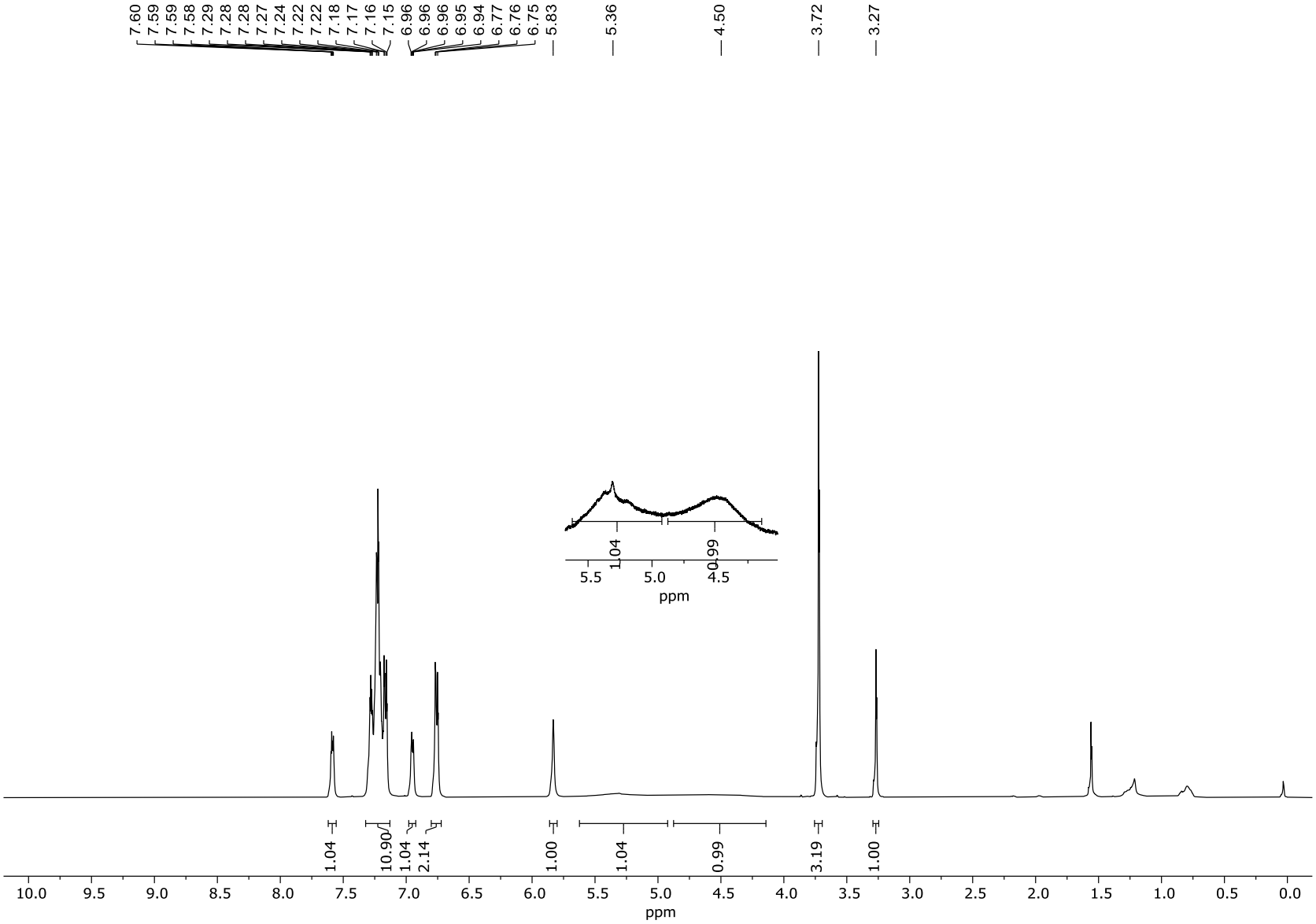


Figure S117: **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) spectrum of **6i**.

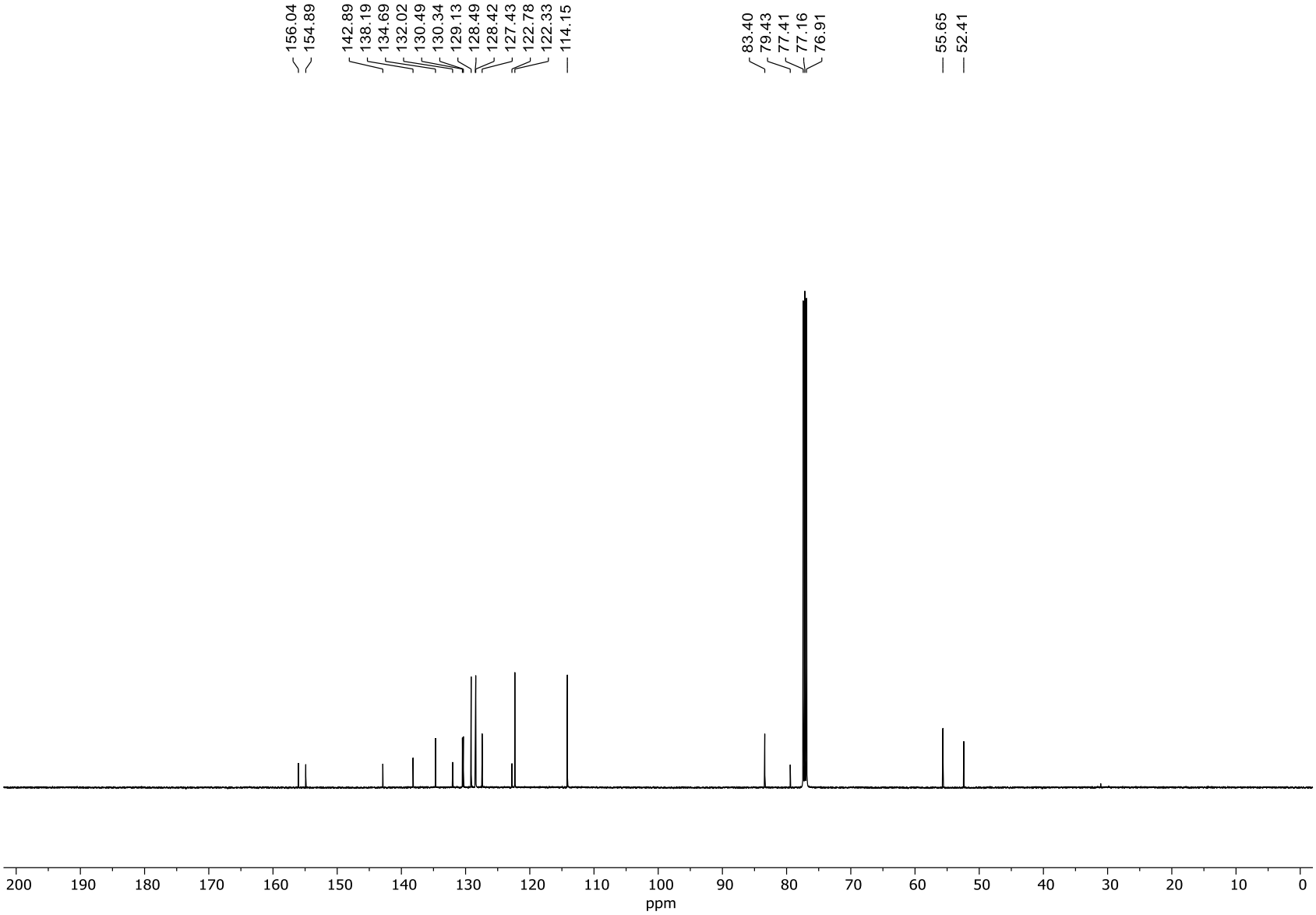


Figure S118: **^{1}H NMR** (400 MHz, CD_2Cl_2, 298 K) spectrum of **10**·BCl_3.

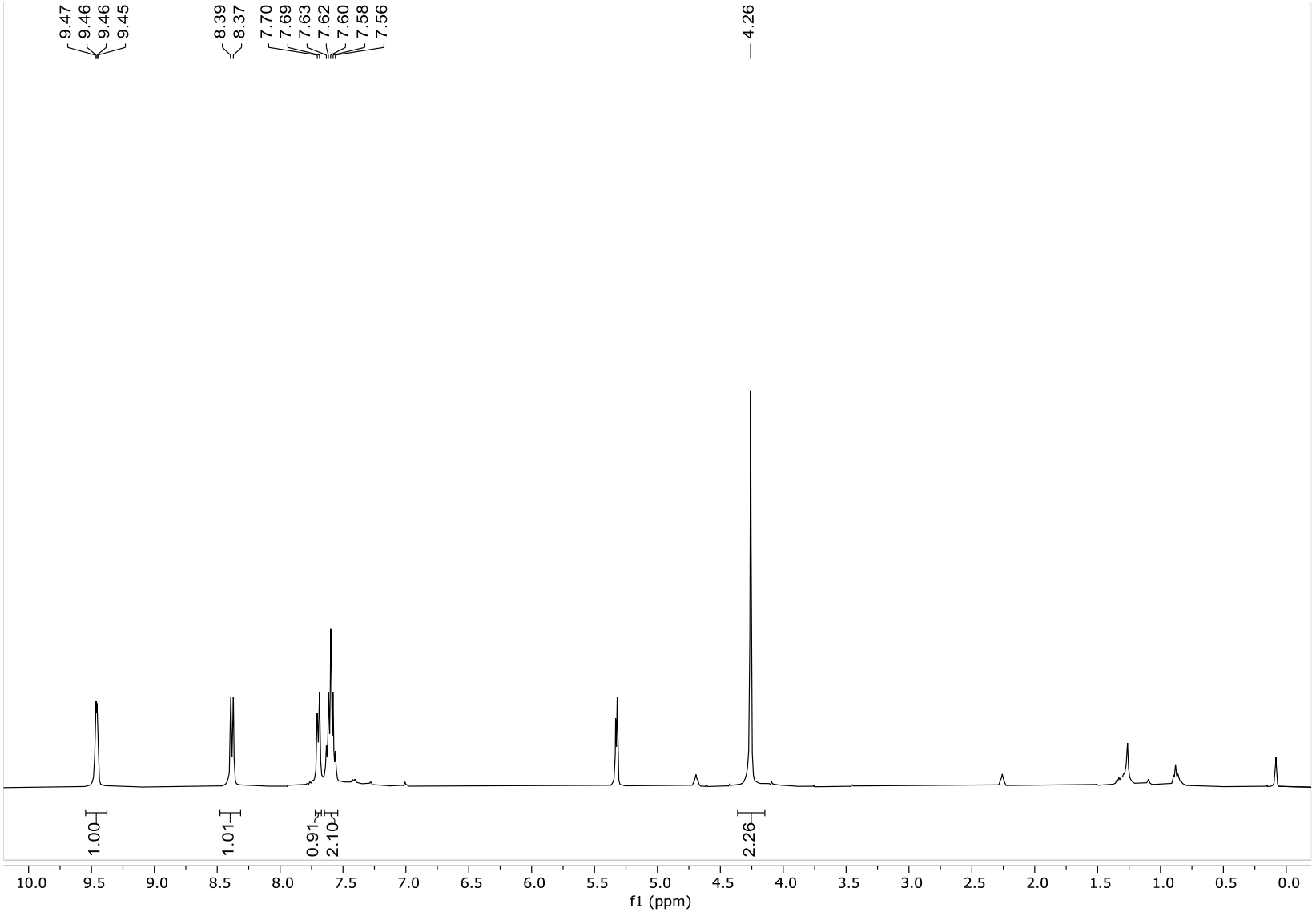


Figure S119: **^{13}C NMR** (101 MHz, CD_2Cl_2, 298 K) spectrum of **10**·BCl_3.

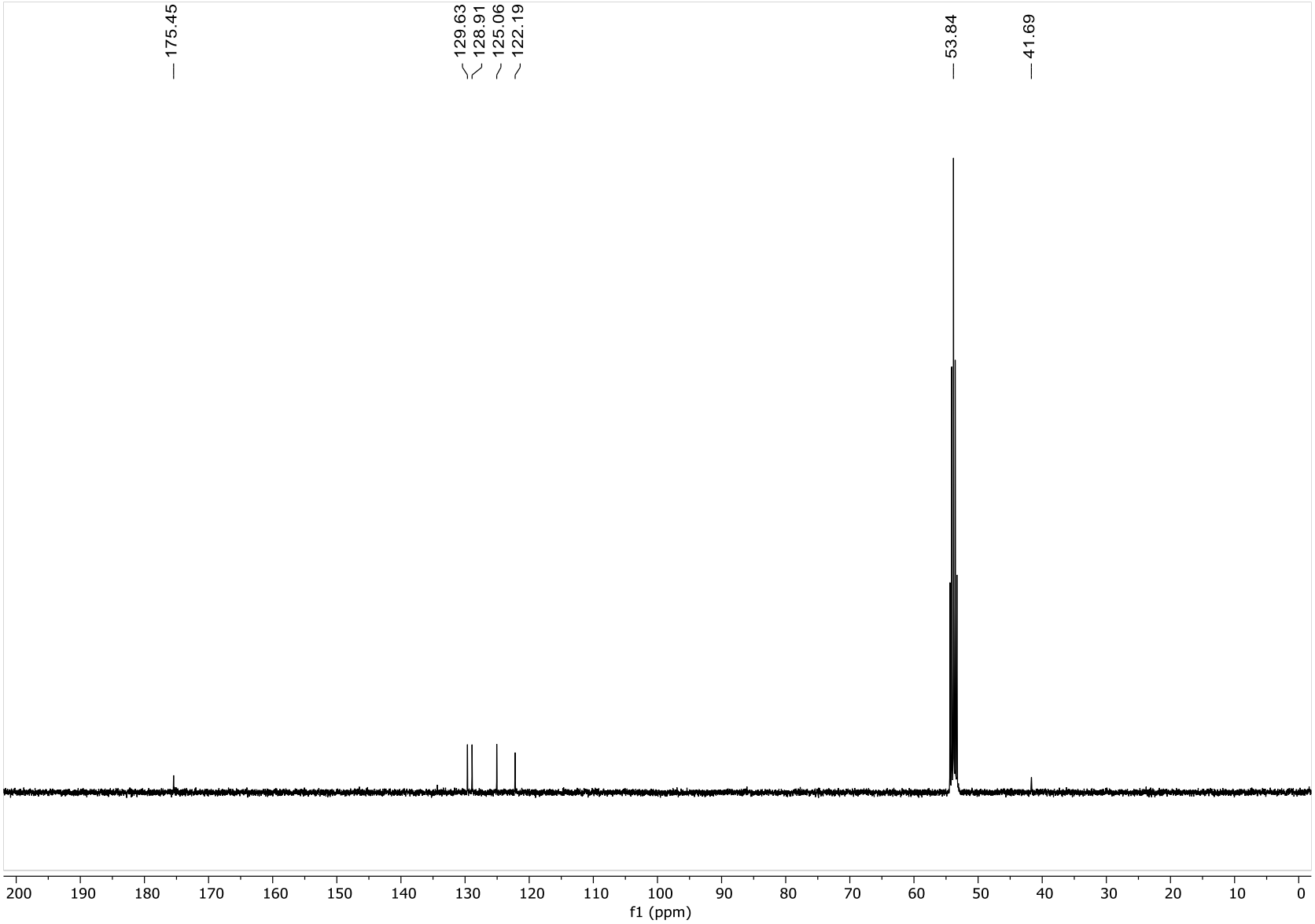


Figure S120: **^{11}B NMR** (128 MHz, CD_2Cl_2, 298 K) spectrum of **10**·BCl_3.

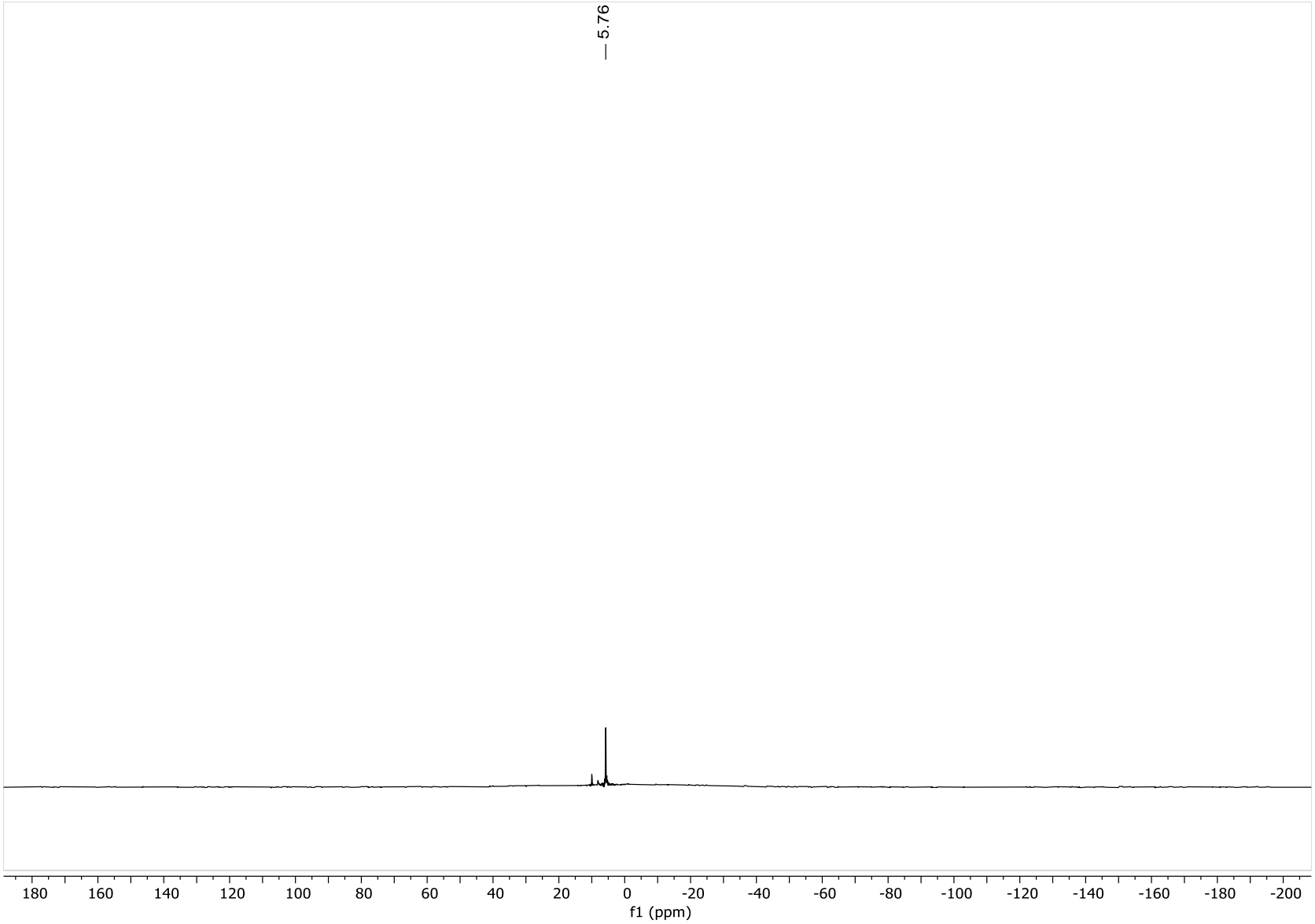


Figure S121: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) of the reaction to afford **5a** using 0.05 equiv of **10**·BCl_3 (0.1 mmol toluene used as internal standard).

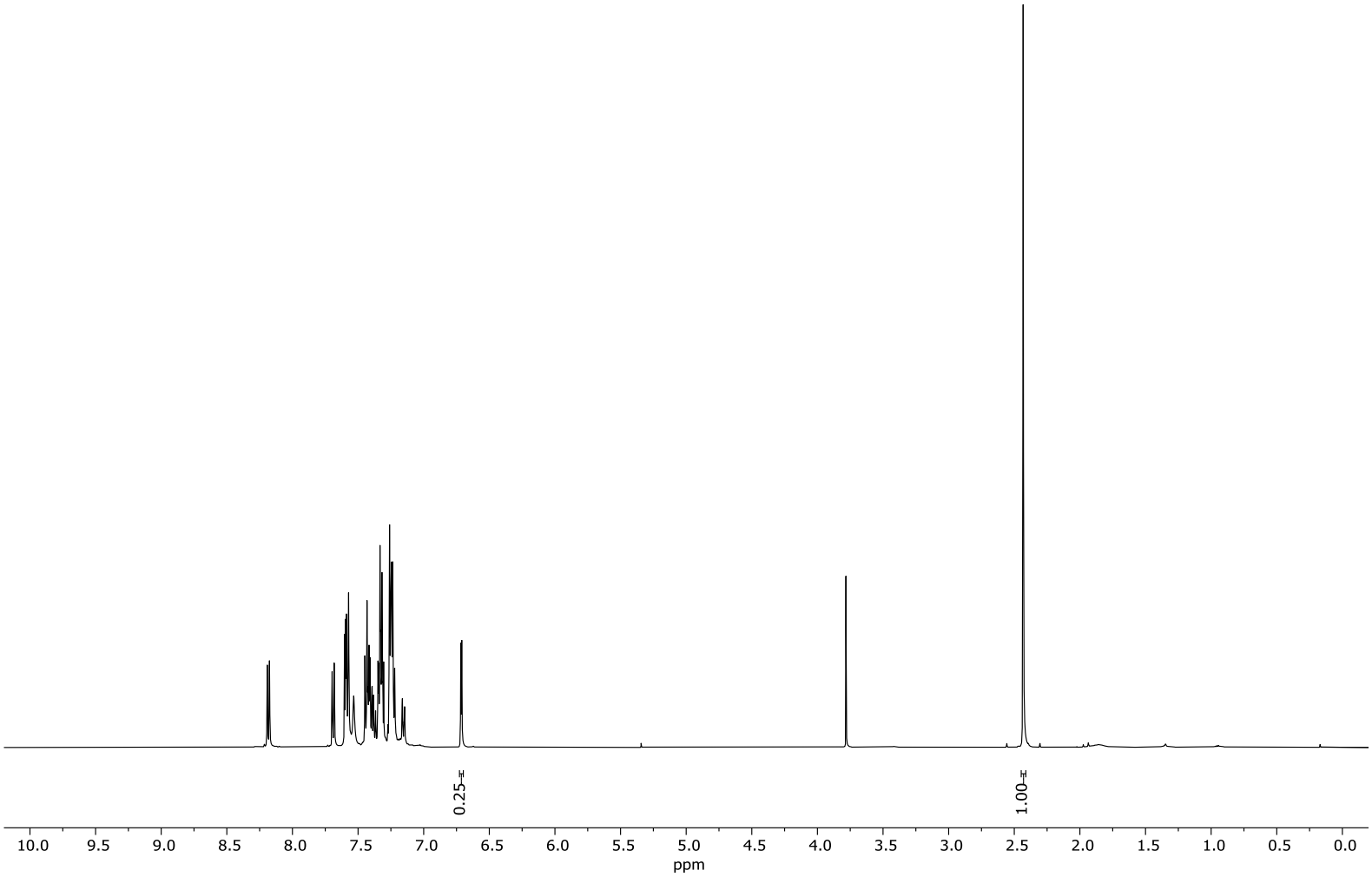
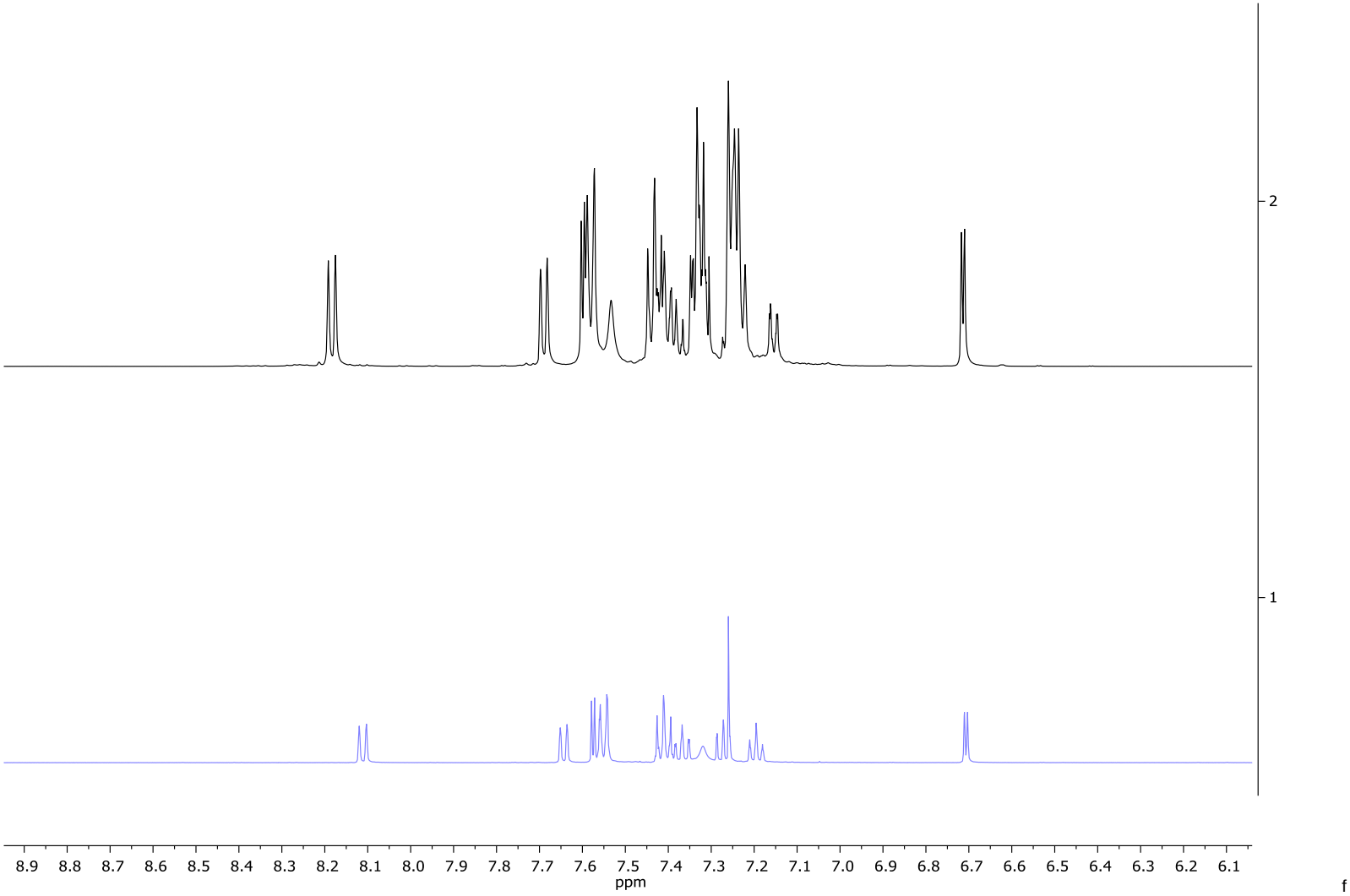


Figure S122: Stacked **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) of the crude reaction mixture (top) and **5a** (bottom).



4. Crystallographic data

4.1 Single crystal X-ray diffraction experimental

Single crystals of **1b**, **2**, **3**, **4**, **5a**, **5i**, **5t**, and **6a** were grown in a fume hood by slow evaporation or vapor diffusion, **1a·B(C$_6$F$_5$)$_3$**, **1b·B(C$_6$F$_5$)$_3$** and **10·**BCl_3 were grown in a glovebox under a nitrogen atmosphere by slow evaporation at room temperature (23 ^{o}C). Crystallographic studies were undertaken on a single crystal mounted in Fomblin®Y and studied on an Agilent SuperNova Dual Atlas three-circle diffractometer using Mo- or Cu-Kα radiation and a CCD detector. Measurements were taken at 298(1) K for **1b**, **4**, **5i** and **5t**; 200(1) K for **2** and **6a**; 180(1) K for **1a·B(C$_6$F$_5$)$_3$**, **1b·B(C$_6$F$_5$)$_3$**, **3**, **5a** and **10·**BCl_3 with temperatures maintained using an Oxford cryostream. Data were collected, integrated and corrected for absorption within CrysAlisPro.[14] The absorption correction implemented a numerical absorption correction based on Gaussian integration over a multifaceted crystal model. The structure was solved by intrinsic phasing and refined against F^2 within SHELXL-2013.[15] The structure has been deposited with the Cambridge Structural Database [CCDC deposition numbers 2125082 (**1b**), 2125086, (**1a·B(C$_6$F$_5$)$_3$**), 2125087 (**1b·B(C$_6$F$_5$)$_3$**), 2125085 (**2**), 2163367 (**3**), 2167662 (**4**), 2143129 (**5a**), 2125083 (**5i**), 2163369 (**5t**), 2163272 (**6a**), 2163368 (**10·**BCl_3)]. This can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In the refinement of crystal **1b**, weak high angle data (> 50^{o}) with negative intensities (I/s > 3) were omitted in the latter stages of refinement (OMIT -3 50) while maintaining sufficient data to provide a data:parameter ratio of approximately 10:1.

The structure of **2** contained two CH_2Cl_2 molecules in the asymmetric unit, one of which was found to be disordered and modelled over two positions. The relative sof's were initially refined using a common U_{iso} for the Cl atoms and then the sof fixed with an occupancy of 46:54% and the Uij refined freely for the Cl atoms. To add H atoms the CH_2Cl_2 unit was modelled over two sites with common fractional atomic coordinates (EXYZ) and U_{ij} (EADP) for the two components of C atom disorder and the two components of Cl atom disorder modelled anisotropically with a common C–Cl bond distance (SADI). This reduced the residual electron density and improved the final R_1 and wR_2 values.

In the refinement of crystal **5a**, nine particularly disagreeable reflections with computed intensity errors $F_o^2 - F_c^2$ >7s were omitted (OMIT) in latter stages of refinement as these were obscured by the beamstop. Residual electron density (>0.75 e Å^{-3}) was located around C27–H27 during the refinement with H27 added at the calculated position (HFIX 43). Alternatively, this H atom was

located in the difmap and refined with a DFIX instruction (DFIX 0.954 H27 C27) which reduced the residual electron density to < 0.55 e $Å^{-3.}$

Crystal **5i** was small and weakly diffracting but was the best of nine crystals screened. Much of the high angle data were weak despite selecting a data collection strategy with long exposure times and were omitted in the latter stages of refinement (OMIT -3 45). Despite omitting these high angle reflections, sufficient data were maintained to provide a data:parameter ratio of approximately 10:1.

The structure of **5t** displayed positional disorder on two n-propyl groups, both of which were modelled over two positions. The relative sof's were refined using a common U_{iso} for the C atoms and the sof was fixed with occupancies at 80:20% for the first n-propyl group, C14/C15/C16, and 59:41% for the second group, C31/C32/C33. In the C14-C16 chain a common U_{ij} was applied to the two components of C atom disorder (EADP) and the C atoms were modelled anisotropically with common N–C and C–C distances (SADI). H atoms were added to both components in the latter stages of refinement. In the C31-C33 chain, the C31 atom position and U_{ij} was fixed with EADP and EXYZ instructions, the two components of C atom disorder (C32 and C33) were further addressed with EADP and modelled anisotropically with common C–C distances (SADI) prior to addition of the H atoms. This reduced the residual electron density and improved the final R_1 and wR_2 values.

The structure of **6a** displayed rotational disorder on one TMS group in the asymmetric unit and this was modelled over two positions. The relative sof's were refined using a common U_{iso} for the C atoms and the sof was then fixed with occupancies at 74:26%. To add the H atoms, the TMS group was modelled over two sites with common U_{ij} (EADP) for the two components of C atom disorder, and the C atoms were modelled anisotropically with a common Si–C and C–C bond distance (SADI). DELU instructions were later used to improve the thermal ellipsoids of the C atoms (DELU 0.01 0.01 C78A C78B C79A C79B C80A C80B). This reduced the residual electron density and improved the R_1 and wR_2 values. Additionally, three particularly disagreeable reflections ($Fo^2 – Fc^2 > 7s$) were omitted (OMIT) in latter stages of refinement.

4.2 Crystal Structures

Figure S123. Crystal structure of **1b**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue.

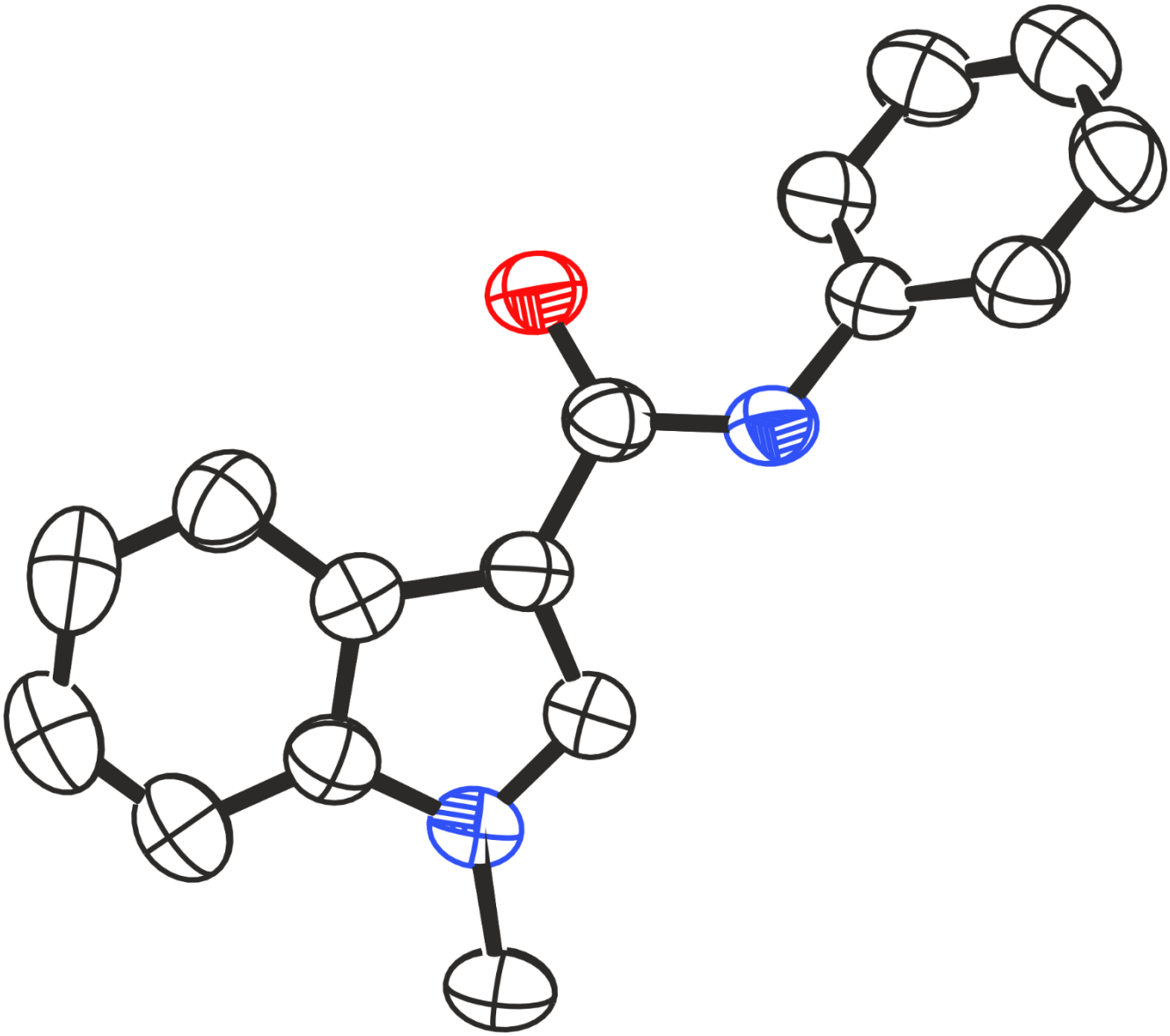


Figure S124. Crystal structure of **1a·B(C_6F_5)$_3$**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue, Cl in bright green, F in light green, B in pink.

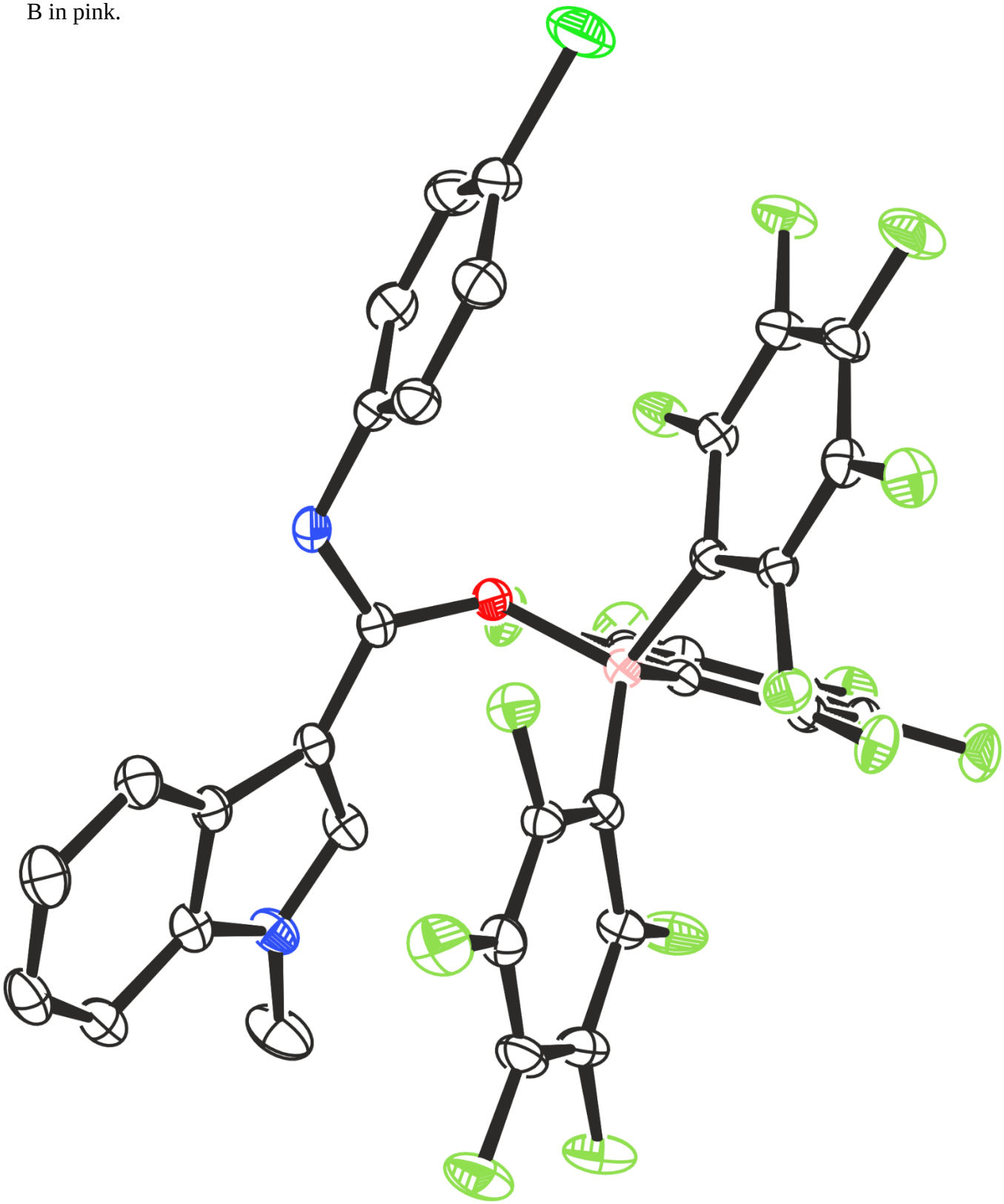


Figure S125. Crystal structure of **1b·B(C_6F_5)$_3$**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue, Cl in bright green, F in light green, B in pink.

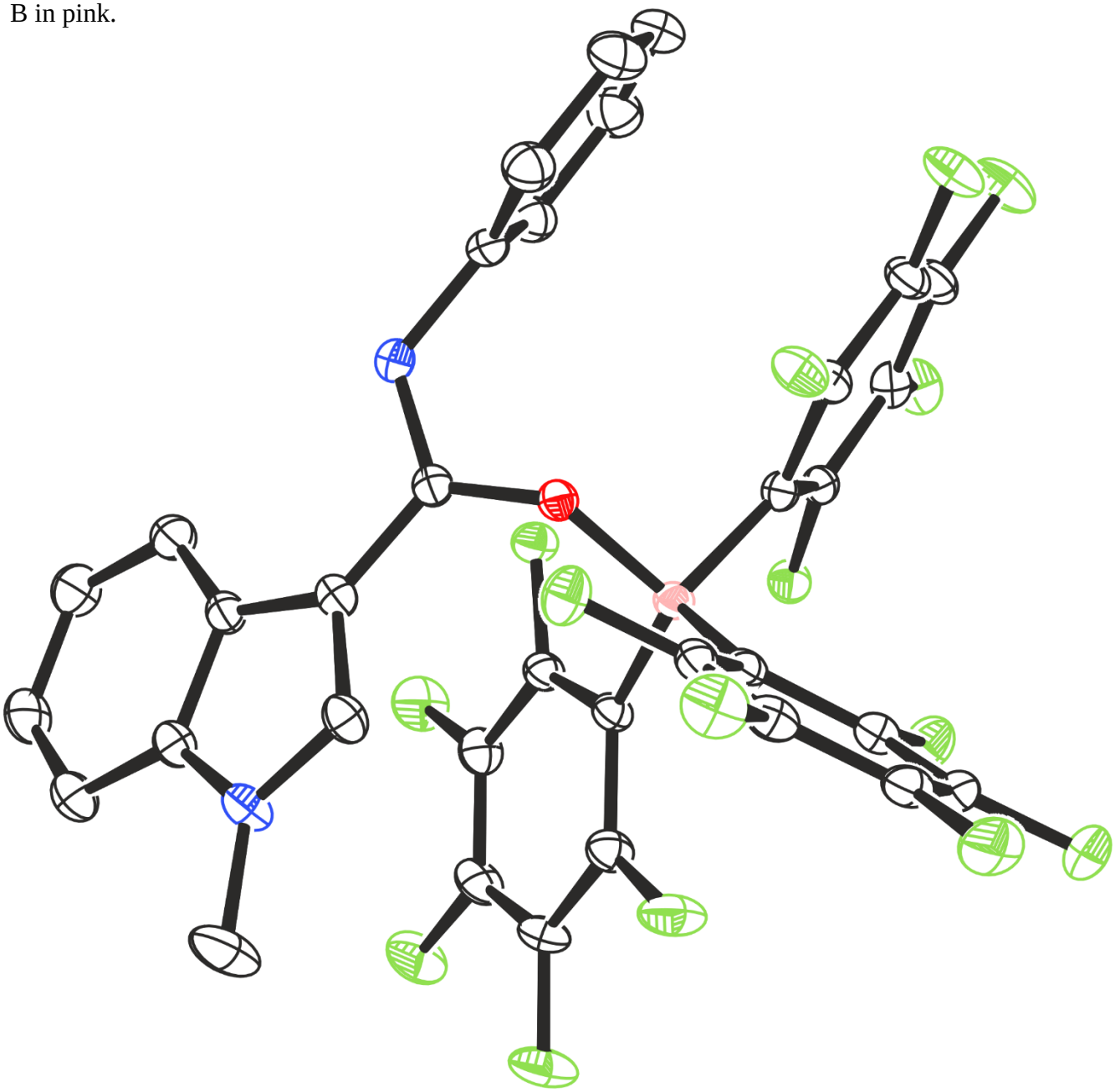


Figure S126. Crystal structure of **2**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue, Cl in bright green, F in light green, B in pink, Br in maroon.

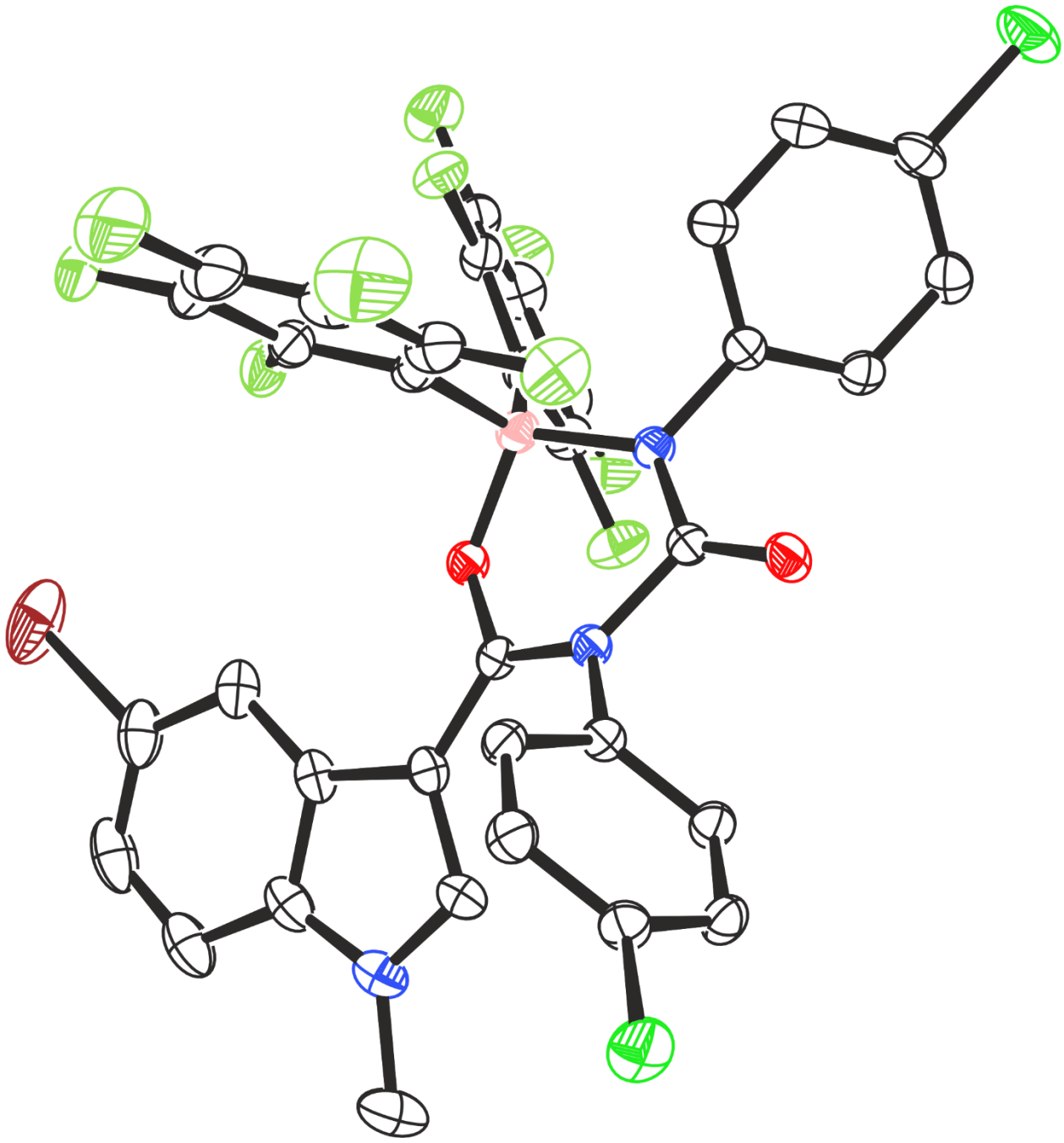


Figure S127. Crystal structure of **3**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue, Cl in bright green, F in light green.

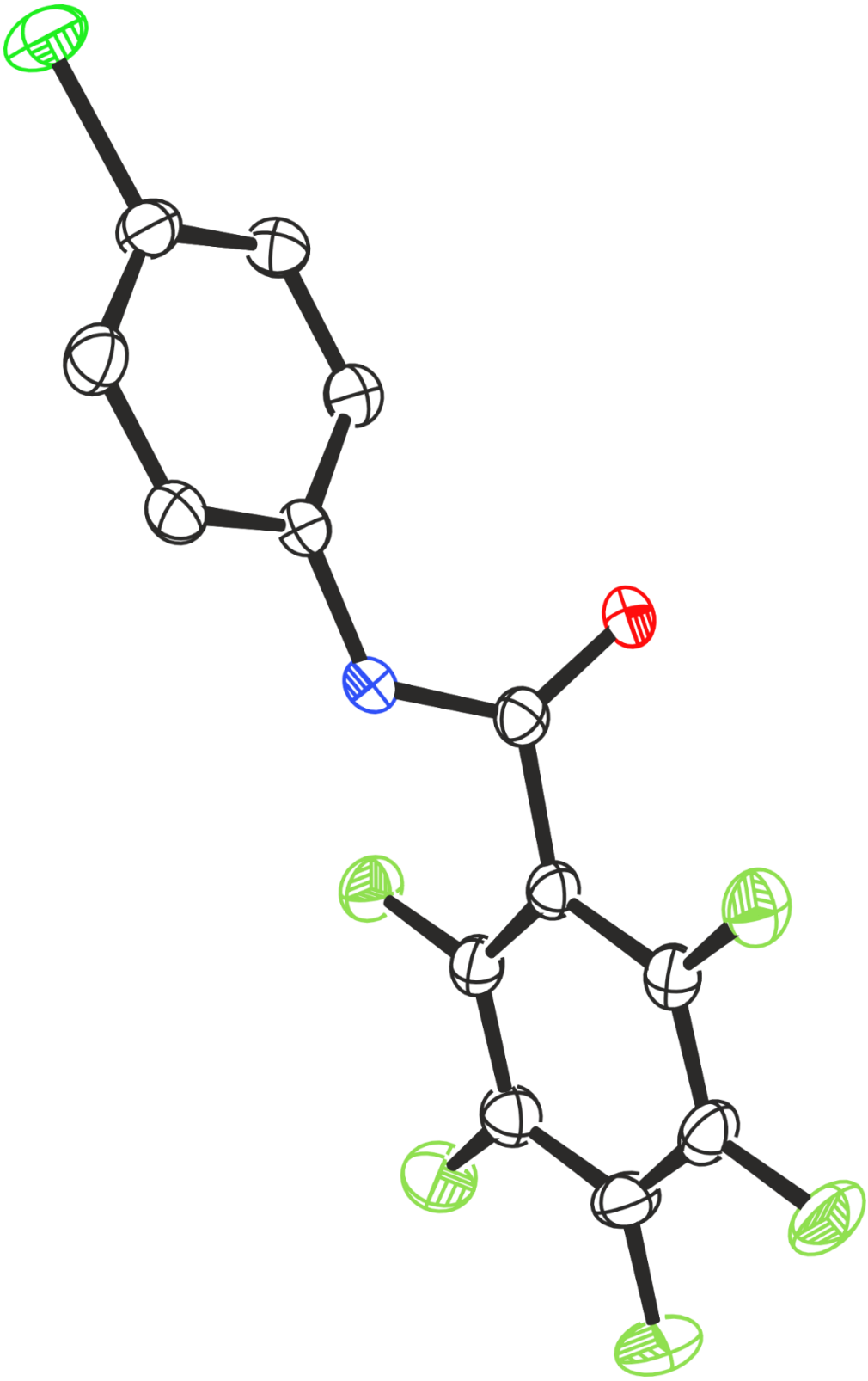


Figure S128. Crystal structure of **4**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue, Cl in green.

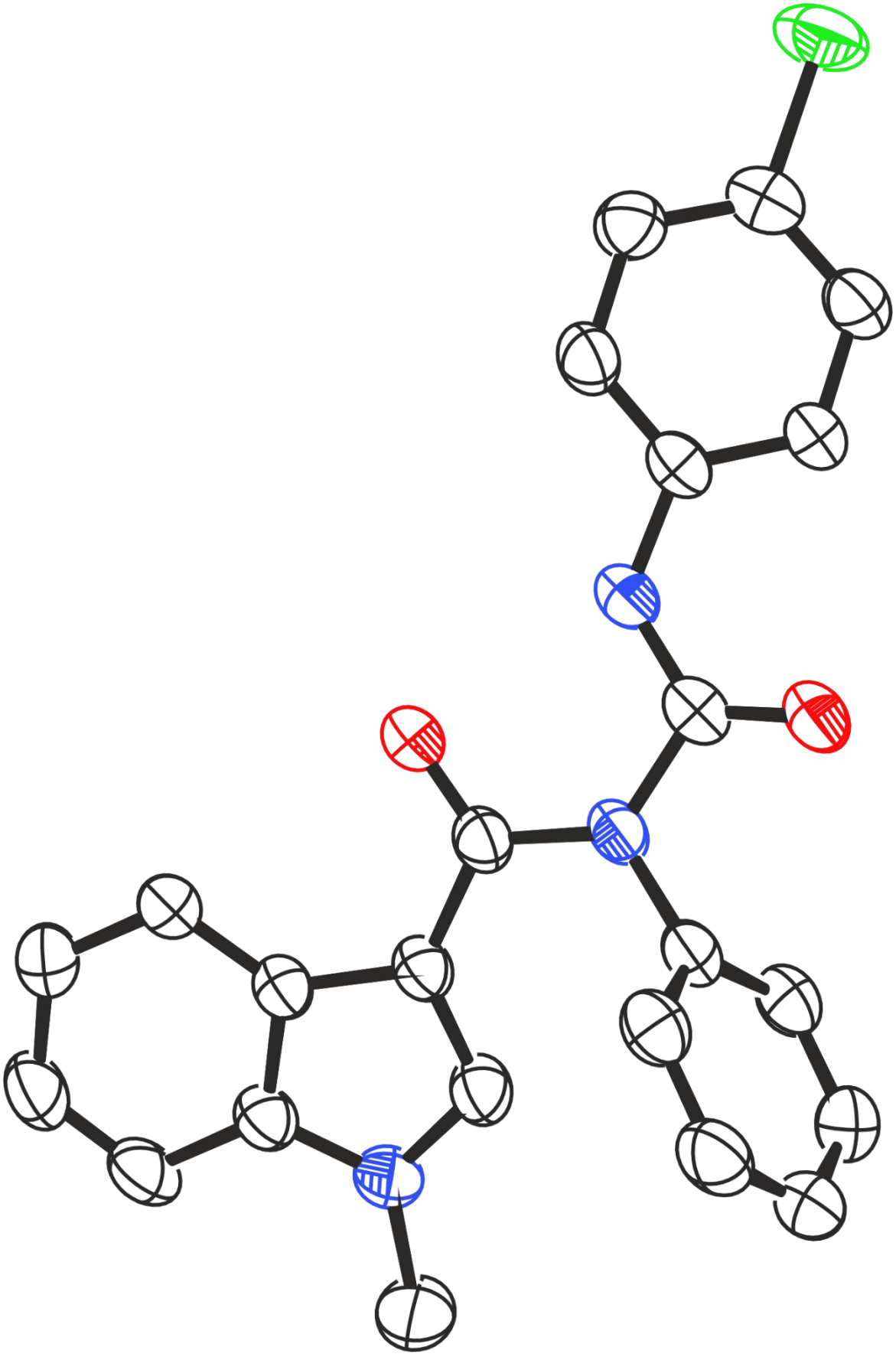


Figure S129. Crystal structure of **5a**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue.

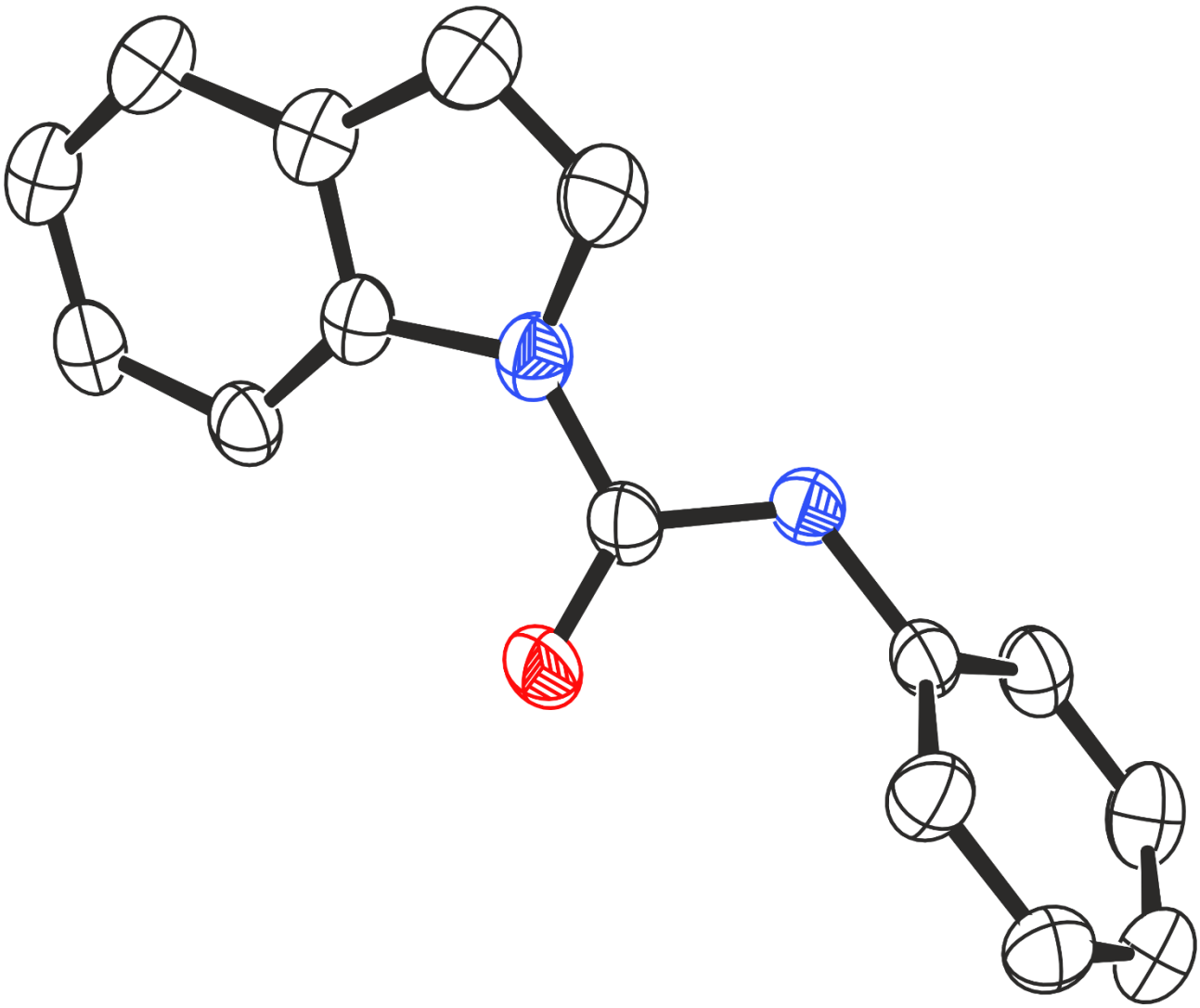


Figure S130. Crystal structure of **5i**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue.

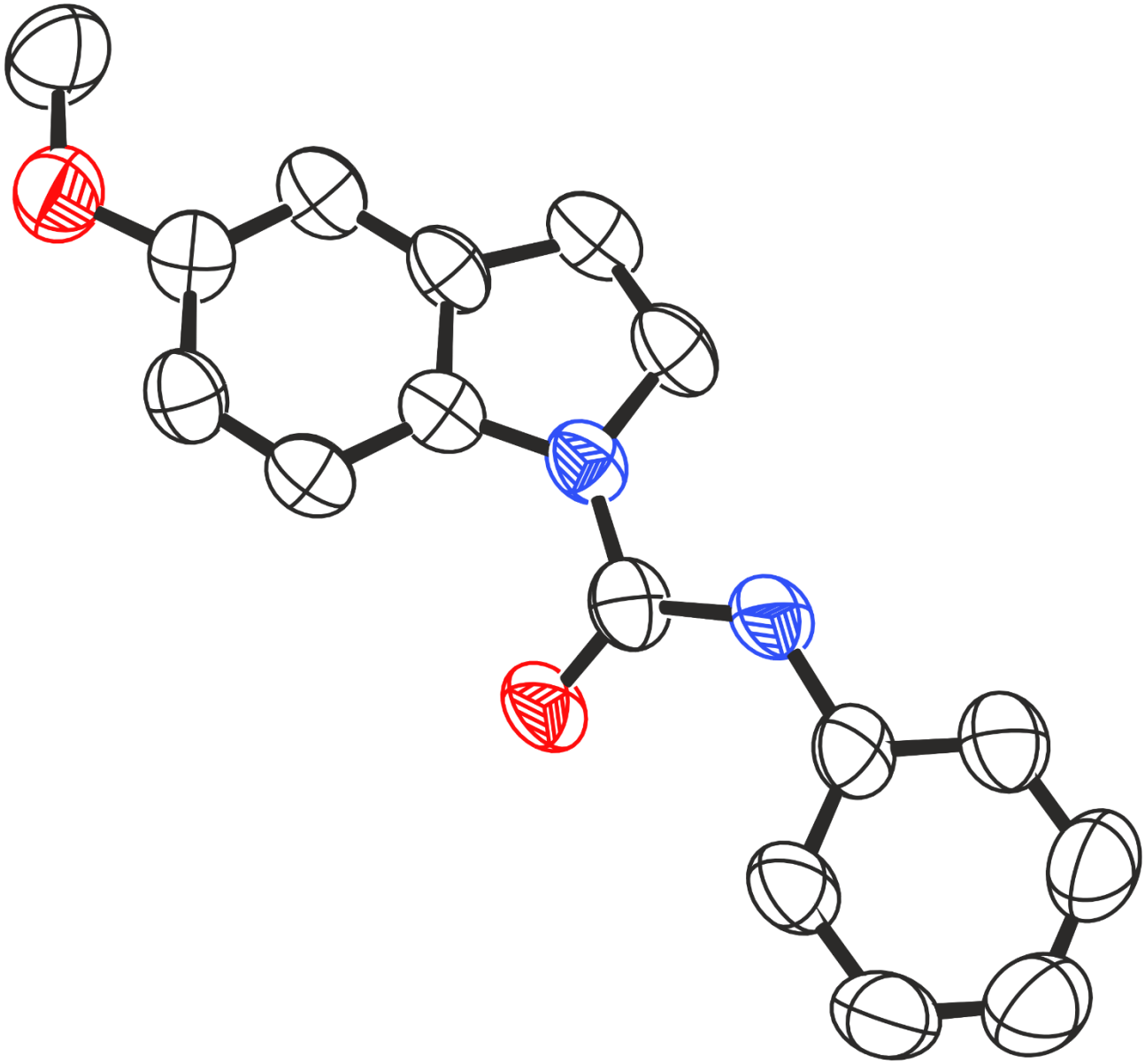


Figure S131. Crystal structure of **5t**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue.

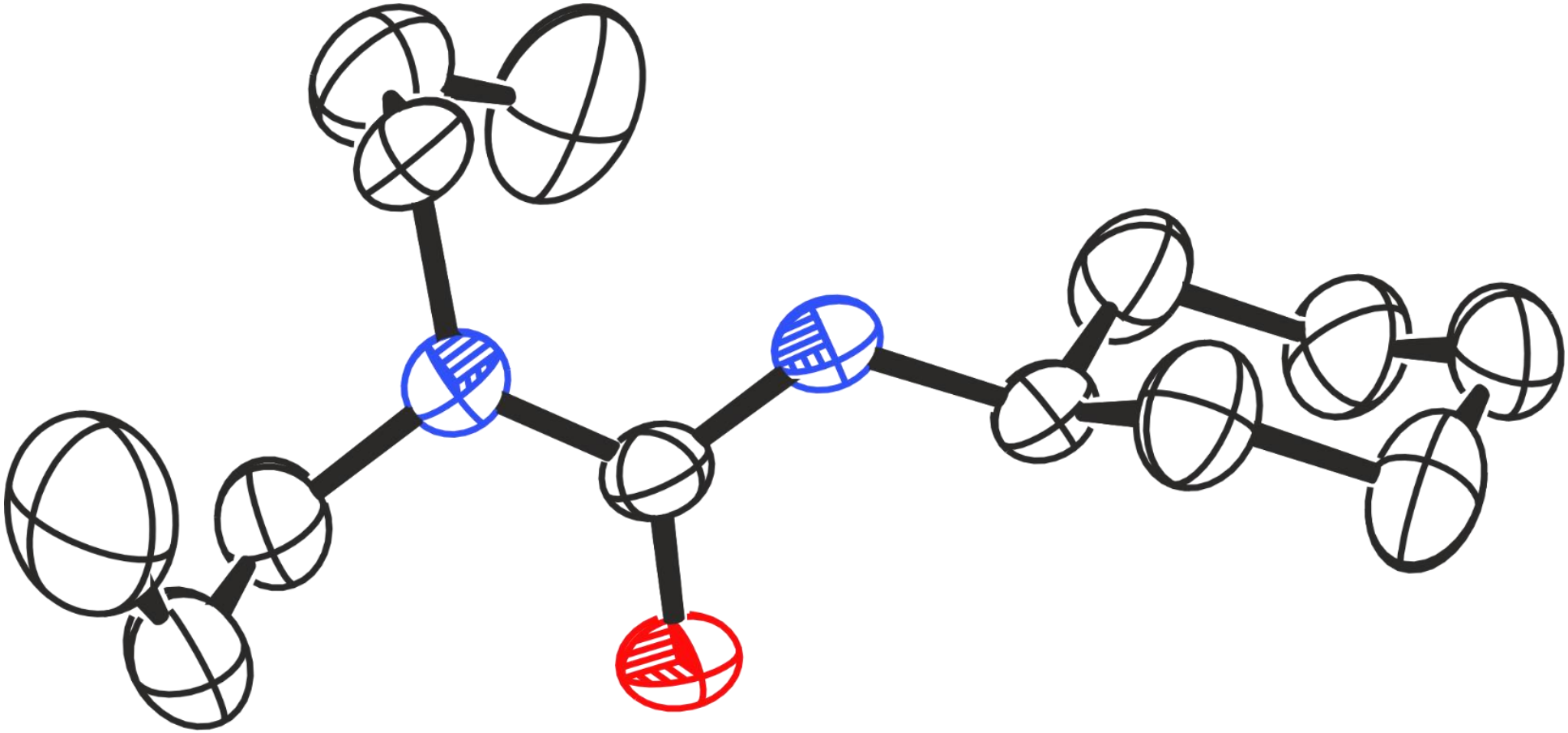


Figure S132. Crystal structure of **6a**, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, O in red, N in blue, Cl in bright green, Si in beige.

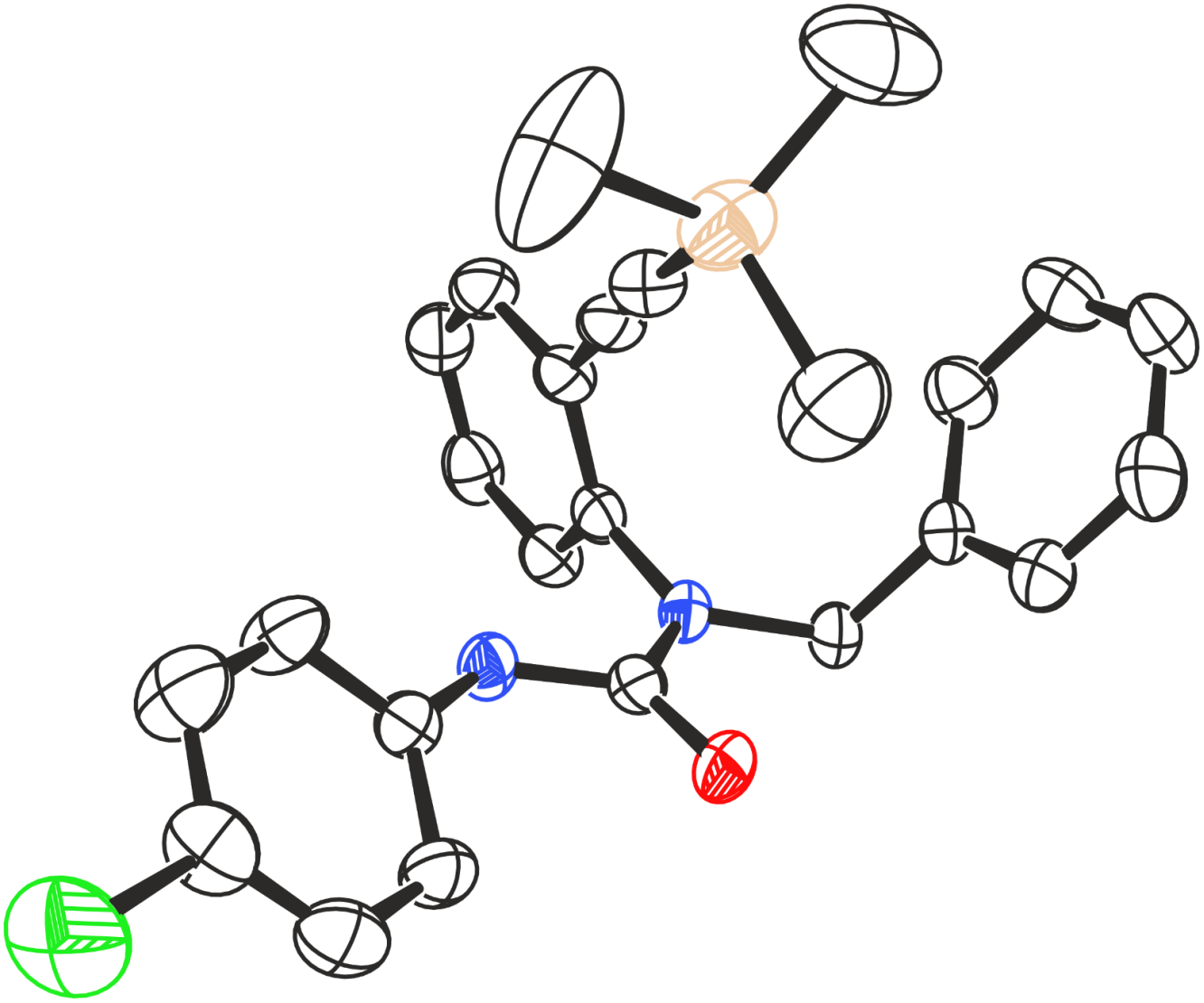
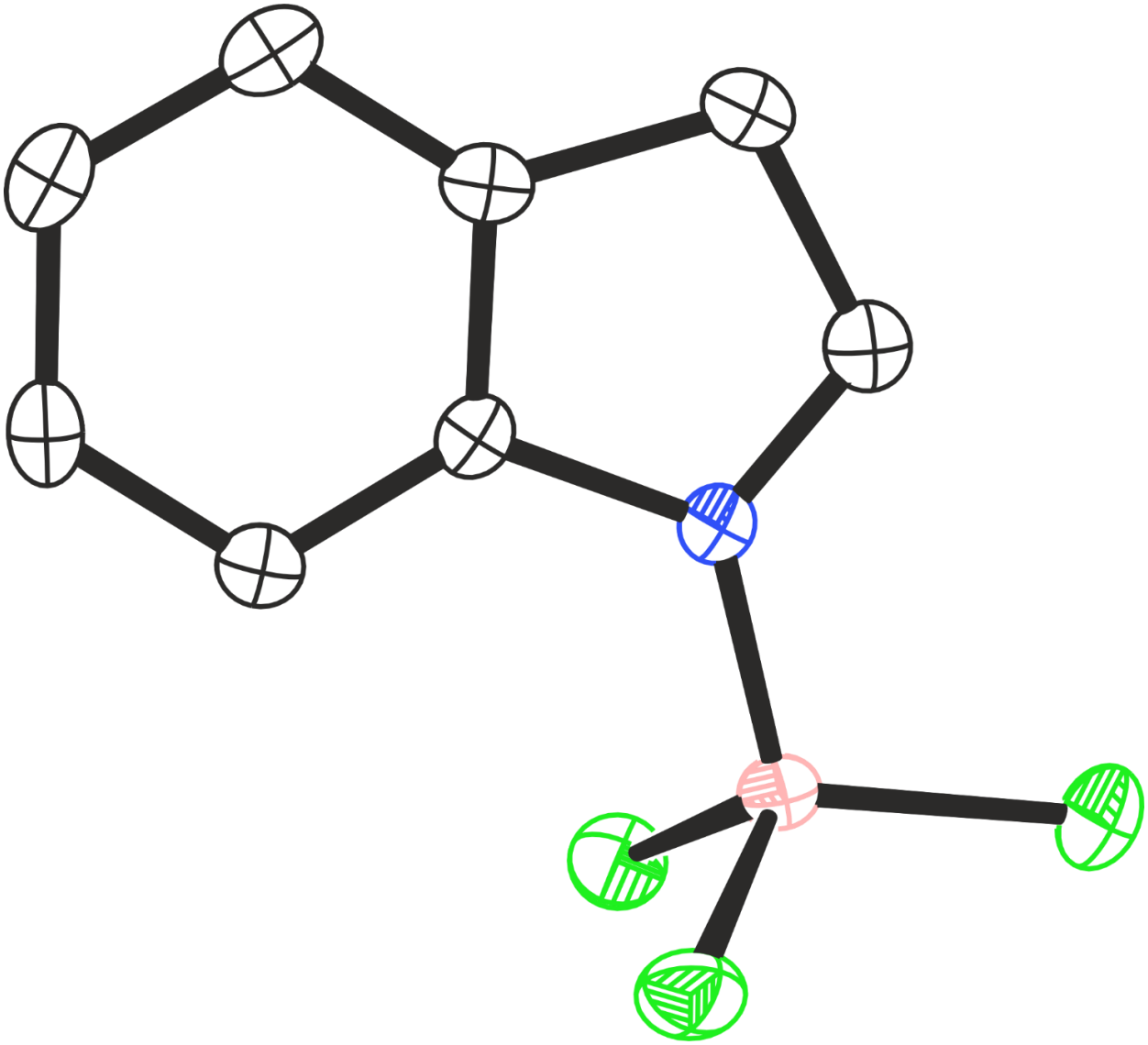


Figure S133. Crystal structure of **10**·BCl_3, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity, C atoms in black, N in blue, B in pink, Cl in bright green.



4.3 Crystal Structure Data:

Table S2: Crystal data and structure refinement for compound **1b**.

Compound	**1b**
Empirical formula	$C_{16}H_{14}N_2O$
M_r	250.29
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature (K)	298
a, *b*, *c* (Å)	22.5646 (17), 13.0075 (10), 8.9569 (10)
α, β, γ (°)	90, 95.530 (8), 90
Volume, V (Å^3)	2616.7 (4)
Z	8
Density, calc (g cm^{-3})	1.271
Absorption coefficient, μ (mm^{-1})	0.08
Crystal size (mm)	0.29 × 0.07 × 0.05
Radiation type	Mo K\a
Wavelength (Å)	0.71073
θ range (°)	3.7–21.8
Index ranges	–26≤ h ≤ 26
	-15≤ k ≤15
	-8 ≤ l ≤ 10
Reflections collected	21848
Independent reflections	4601
R(int)	0.086
Absorption correction	Gaussian
Data / restraints / parameters	4601 / 1 / 359
Goodness of fit, S	1.072
Final R indices [I>2σ(I)]	R_1 = 0.0650
	wR_2 = 0.1463
R indices (all data)	R_1 = 0.1563
	wR_2 = 0.1930
Min/Max residual electron density (e^-Å^{-3})	0.16, -0.21

Table S3: Crystal data and structure refinement for compound **1a·B(C$_6$F$_5$)$_3$**.

Compound	**1a·B(C$_6$F$_5$)$_3$**
Empirical formula	$C_{34}H_{13}BClF_{15}N_2O$
M_r	796.72
Crystal system	Triclinic
Space group	*P -1*
Temperature (K)	180
a, *b*, *c* (Å)	8.0666 (6)), 12.7868 (8), 15.6641 (11)
α, β, γ (°)	77.581 (6), 87.401 (6), 78.419 (6)
Volume, V (Å^3)	1545.76 (19)
Z	2
Density, calc (g cm^{-3})	1.712
Absorption coefficient, μ (mm^{-1})	0.25
Crystal size (mm)	0.44 × 0.28 × 0.20
Radiation type	Mo K\a
Wavelength (Å)	0.71073
θ range (°)	3.7–29.5
Index ranges	–11 ≤ h ≤ 10
	-17 ≤ k ≤17
	-20 ≤ l ≤ 21
Reflections collected	15105
Independent reflections	7363
R(int)	0.025
Absorption correction	Gaussian
Data / restraints / parameters	7363 / 0 / 492
Goodness of fit, S	0.969
Final R indices [I>2σ(I)]	R_1 = 0.0451
	wR_2 = 0.0940
R indices (all data)	R_1 = 0.1125
	wR_2 = 0.0703
Max/Min residual electron density (e^-Å^{-3})	0.33, -0.45

Table S4: Crystal data and structure refinement for compound **1b·B(C_6F_5)$_3$**.

Compound	**1b·B(C_6F_5)$_3$**
Empirical formula	$C_{34}H_{14}BF_{15}N_2O$
M_r	762.28
Crystal system	Triclinic
Space group	*P -1*
Temperature (K)	180
a, *b*, *c* (Å)	7.9694 (4) , 12.4723 (8), 15.5816 (8)
α, β, γ (°)	78.311 (5), 86.618 (4), 79.065 (4)
Volume, V (Å^3)	1488.76 (15)
Z	2
Density, calc (g cm^{-3})	1.700
Absorption coefficient, μ (mm^{-1})	0.17
Crystal size (mm)	0.60 × 0.24 × 0.17
Radiation type	Mo K\a
Wavelength (Å)	0.71073
θ range (°)	3.8–28.6
Index ranges	–10 ≤ h ≤ 10
	-13 ≤ k ≤16
	-20 ≤ l ≤ 21
Reflections collected	13554
Independent reflections	7125
R(int)	0.022
Absorption correction	Gaussian
Data / restraints / parameters	7125 / 0 / 483
Goodness of fit, S	1.062
Final R indices [I>2σ(I)]	R_1 = 0.0443
	wR_2 = 0.0878
R indices (all data)	R_1 = 0.0718
	wR_2 = 0.1047
Max/Min residual electron density (e^-Å^{-3})	0.30, -0.25

Table S5: Crystal data and structure refinement for compound **2**.

Compound	**2**
Empirical formula	$C_{35}H_{16}BBrCl_2F_{10}N_3O_2 \cdot CH_2Cl_2$
M_r	946.04
Crystal system	Triclinic
Space group	*P -1*
Temperature (K)	200
a, *b*, *c* (Å)	12.7275 (4), 16.2624 (4), 19.5564 (6)
α, β, γ (°)	69.141 (3), 77.001 (3), 87.734 (2)
Volume, V (Å^3)	3681.9 (2)
Z	4
Density, calc (g cm^{-3})	1.707
Absorption coefficient, μ (mm^{-1})	5.01
Crystal size (mm)	0.33 × 0.16 × 0.05
Radiation type	Cu K\a
Wavelength (Å)	1.54178
θ range (°)	3.8–73.0
Index ranges	–15 ≤ h ≤ 12
	-14 ≤ k ≤20
	-24 ≤ l ≤ 23
Reflections collected	26747
Independent reflections	14256
R(int)	0.034
Absorption correction	Gaussian
Data / restraints / parameters	14256 / 3 / 1047
Goodness of fit, S	1.040
Final R indices [I>2σ(I)]	R_1 = 0.0584
	wR_2 = 0.1632
R indices (all data)	R_1 = 0.0699
	wR_2 = 0.1792
Max/Min residual electron density (e^-Å^{-3})	1.39, -1.45

Table S6: Crystal data and structure refinement for compound **3**.

Compound	**3**
Empirical formula	$C_{13}H_5ClF_5NO$
M_r	321.63
Crystal system	Monoclinic
Space group	$P2_1/n$
Temperature (K)	180
a, *b*, *c* (Å)	5.6086 (2), 9.3087 (3), 23.8205 (7)
α, β, γ (°)	90, 90.950 (3), 90
Volume, V (Å^3)	1243.47 (7)
Z	4
Density, calc (g cm^{-3})	1.718
Absorption coefficient, μ (mm^{-1})	3.34
Crystal size (mm)	0.55 × 0.47 × 0.10
Radiation type	Cu K\a
Wavelength (Å)	1.54178
θ range (°)	3.7–72.7
Index ranges	$-6 \leq h \leq 6$
	$-6 \leq k \leq 11$
	$-29 \leq l \leq 29$
Reflections collected	4597
Independent reflections	2393
R(int)	0.025
Absorption correction	Gaussian
Data / restraints / parameters	4597 / 0 / 190
Goodness of fit, S	1.043
Final R indices [I>2σ(I)]	R_1 = 0.0377
	wR_2 = 0.0997
R indices (all data)	R_1 = 0.0431
	wR_2 = 0.1053
Max/Min residual electron density (e^-Å^{-3})	0.26, -0.40

Table S7: Crystal data and structure refinement for compound **4**.

Compound	**4**
Empirical formula	$C_{23}H_{18}ClN_3O_2$
M_r	403.85
Crystal system	Orthorhombic
Space group	*P 21 21 21*
Temperature (K)	298
a, *b*, *c* (Å)	5.7822(3), 12.3852(6), 27.1093(14)
α, β, γ (°)	90, 90, 90
Volume, V (Å^3)	1941.40 (17)
Z	4
Density, calc (g cm^{-3})	1.382
Absorption coefficient, μ (mm^{-1})	1.95
Crystal size (mm)	0.66 × 0.06 × 0.04
Radiation type	Cu K\a
Wavelength (Å)	1.54178
θ range (°)	3.9–72.8
Index ranges	–6 ≤ h ≤ 6
	-10 ≤ k ≤15
	-33 ≤ l ≤ 28
Reflections collected	7005
Independent reflections	3727
R(int)	0.058
Absorption correction	Gaussian
Data / restraints / parameters	3727 / 0 / 263
Goodness of fit, S	1.027
Final R indices [I>2σ(I)]	R_1 = 0.0667
	wR_2 = 0.1709
R indices (all data)	R_1 = 0.0764
	wR_2 = 0.1829
Max/Min residual electron density (*e*$^-$Å^{-3})	0.42, -0.38

Table S8: Crystal data and structure refinement for compound **5a**.

Compound	**5a**
Empirical formula	$C_{15}H_{12}N_2O$
M_r	236.27
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature (K)	180
a, *b*, *c* (Å)	5.5956 (4), 23.7388 (13), 9.2195 (6)
α, β, γ (°)	90, 99.725 (7), 90
Volume, V (Å^3)	1207.05 (14)
Z	4
Density, calc (g cm^{-3})	1.300
Absorption coefficient, μ (mm^{-1})	0.08
Crystal size (mm)	0.30 × 0.20 × 0.08
Radiation type	Mo K\a
Wavelength (Å)	0.71073
θ range (°)	4.1–28.3
Index ranges	$-7 \leq h \leq 6$
	$-32 \leq k \leq 29$
	$-12 \leq l \leq 9$
Reflections collected	6033
Independent reflections	2867
R(int)	0.025
Absorption correction	Gaussian
Data / restraints / parameters	2867 / 1 / 173
Goodness of fit, S	1.08
Final R indices [I>2σ(I)]	$R_1 = 0.0519$
	$wR_2 = 0.1231$
R indices (all data)	$R_1 = 0.0725$
	$wR_2 = 0.1371$
Max/Min residual electron density (e^-Å^{-3})	0.53, -0.19

Table S9: Crystal data and structure refinement for compound **5i**.

Compound	**5i**
Empirical formula	$C_{16}H_{14}N_2O_2$
M_r	266.29
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature (K)	293
a, *b*, *c* (Å)	26.505 (6), 5.5966 (7), 9.4104 (11)
α, β, γ (°)	90, 98.519 (15), 90
Volume, V (Å^3)	1380.5 (4)
Z	4
Density, calc (g cm^{-3})	1.281
Absorption coefficient, μ (mm^{-1})	0.09
Crystal size (mm)	0.21 × 0.10 × 0.06
Radiation type	Mo K\a
Wavelength (Å)	0.71073
θ range (°)	3.9–20.1
Index ranges	-28 ≤ h ≤ 19
	-6 ≤ k ≤ 6
	-10 ≤ l ≤ 10
Reflections collected	7061
Independent reflections	1786
R(int)	0.068
Absorption correction	Gaussian
Data / restraints / parameters	1786 / 1 / 185
Goodness of fit, S	1.07
Final R indices [I>2σ(I)]	R_1 = 0.0726
	wR_2 = 0.1669
R indices (all data)	R_1 = 0.1258
	wR_2 = 0.2072
Max/Min residual electron density (e^-Å^{-3})	0.21, -0.18

Table S10: Crystal data and structure refinement for compound **5t**.

Compound	**5t**
Empirical formula	$C_{13}H_{26}N_2O$
M_r	226.36
Crystal system	Monoclinic
Space group	*C*2/*c*
Temperature (K)	293
a, *b*, *c* (Å)	16.5207 (4), 9.9632 (2), 34.8180 (9)
α, β, γ (°)	90, 91.771 (2), 90
Volume, V (Å^3)	5728.3 (2)
Z	16
Density, calc (g cm^{-3})	1.050
Absorption coefficient, μ (mm^{-1})	0.51
Crystal size (mm)	0.59 × 0.11 × 0.05
Radiation type	Cu K\a
Wavelength (Å)	1.54178
θ range (°)	5.1–72.7
Index ranges	-20 ≤ h ≤ 18
	-11 ≤ k ≤ 7
	-42 ≤ l ≤ 40
Reflections collected	10376
Independent reflections	5488
R(int)	0.017
Absorption correction	Gaussian
Data / restraints / parameters	5488 / 13 / 319
Goodness of fit, S	1.05
Final R indices [I>2σ(I)]	R_1 = 0.0559
	wR_2 = 0.1658
R indices (all data)	R_1 = 0.0721
	wR_2 = 0.1717
Max/Min residual electron density (e^-Å^{-3})	0.16, -0.17

Table S11: Crystal data and structure refinement for compound **6a**.

Compound	**6a**
Empirical formula	$C_{25}H_{25}ClN_2OSi$
M_r	433.01
Crystal system	Triclinic
Space group	P-*1*
Temperature (K)	200
a, *b*, *c* (Å)	10.0506 (6), 12.4111 (9), 19.1784 (12)
α, β, γ (°)	99.504 (5), 93.559 (5), 90.568 (5)
Volume, V (Å^3)	2354.4 (3)
Z	4
Density, calc (g cm^{-3})	1.222
Absorption coefficient, μ (mm^{-1})	2.06
Crystal size (mm)	0.18 × 0.13 × 0.03
Radiation type	Cu K\a
Wavelength (Å)	1.54178
θ range (°)	3.9–72.0
Index ranges	-10 ≤ h ≤ 12
	-15 ≤ k ≤ 15
	-23 ≤ l ≤ 19
Reflections collected	17234
Independent reflections	9111
R(int)	0.069
Absorption correction	Gaussian
Data / restraints / parameters	9111 / 30 / 578
Goodness of fit, S	0.97
Final R indices [I>2σ(I)]	R_1 = 0.0588
	wR_2 = 0.1384
R indices (all data)	R_1 = 0.1023
	wR_2 = 0.1677
Max/Min residual electron density (e^-Å^{-3})	0.28, -0.41

Table S12: Crystal data and structure refinement for compound **10**·BCl_3.

Compound	**10**·BCl_3
Empirical formula	$C_8H_7BCl_3N$
M_r	243.31
Crystal system	Monoclinic
Space group	*C*2/*m*
Temperature (K)	180
a, *b*, *c* (Å)	15.121 (2), 6.9264 (7), 9.8879 (13)
α, β, γ (°)	90, 109.906 (14), 90
Volume, V (Å^3)	973.7 (2)
Z	4
Density, calc (g cm^{-3})	1.598
Absorption coefficient, μ (mm^{-1})	0.89
Crystal size (mm)	0.64 × 0.27 × 0.15
Radiation type	Mo K\a
Wavelength (Å)	0.71073
θ range (°)	4.1 – 28.4
Index ranges	-20 ≤ h ≤ 20
	-9 ≤ k ≤ 7
	-13 ≤ l ≤ 12
Reflections collected	2544
Independent reflections	1257
R(int)	0.024
Absorption correction	Gaussian
Data / restraints / parameters	1257 / 0 / 76
Goodness of fit, S	1.12
Final R indices [I>2σ(I)]	R_1 = 0.0378
	wR_2 = 0.0754
R indices (all data)	R_1 = 0.0518
	wR_2 = 0.0830
Max/Min residual electron density (e^-Å^{-3})	0.34, -0.24

5. Computational Data

5.1 Computational details

Gaussian 16[16] was used to fully optimise all the structures reported in this paper at the M06-2X level of theory.[17] For all the calculations, solvent effects were considered using the SMD solvation model[18] with dichloroethane as the solvent. The 6-31G(d) basis set[19] was used for all atoms. This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory as those for the structural optimisation. Transition structures were located using the Berny algorithm. Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structures and minima.[20] To further refine the energies obtained from the SMD/M06-2X/6-31G(d) calculations, we carried out single-point energy calculations using the M06-2X functional method for all of the structures with a larger basis set (BS2). BS2 utilises the def2-TZVP basis set[21] on all atoms. Tight convergence criterion and ultrafine integral grid were also employed to increase the accuracy of the calculations. In this work, the free energy for each species in solution was calculated using the following formula:

$$G = E(BS2) + G(BS1) - E(BS1) + \Delta G^{1atm \rightarrow 1M} \quad (1)$$

where $\Delta G^{1atm \rightarrow 1M}$ = 1.89 kcal/mol is the free-energy change for compression of 1 mol of an ideal gas from 1 atm to the 1 M solution phase standard state.

To validate the accuracy of the results obtained at the SMD/M06-2X/def2-TZVP/ SMD/M06-2X/6-31G(d) level of theory, some of the key structures were re-optimized using the SMD/M06-2X/def2-TZVP calculations. The results show that this change in methodology has a negligible effect on the relative free energy of the structures. Using the SMD/M06-2X/def2-TZVP/ SMD/M06-2X/6-31G(d) calculations, the relative free energies of **TS$_{16\text{-}17}$**, **TS$_{18}$**, **10·BCl$_3$**, **TS$_{10\text{-}12}$**, **5a·BCl$_3$**, and **5** are 23.2, 29.6, -11.1, 21.9, -11.0, and -3.8 kcal/mol, respectively. Using the SMD/M06-2X/def2-TZVP calculations, the relative free energies are 23.7, 29.7, -11.0, 21.7, -10.7, and -3.8 kcal/mol, respectively.

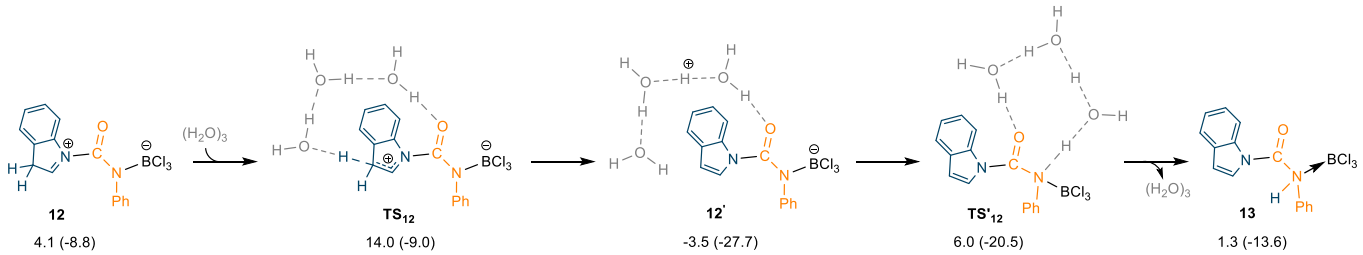


Figure S2. Calculated mechanism for proton transfer converting **12** to **13** mediated by model water cluster $(H_2O)_3$.

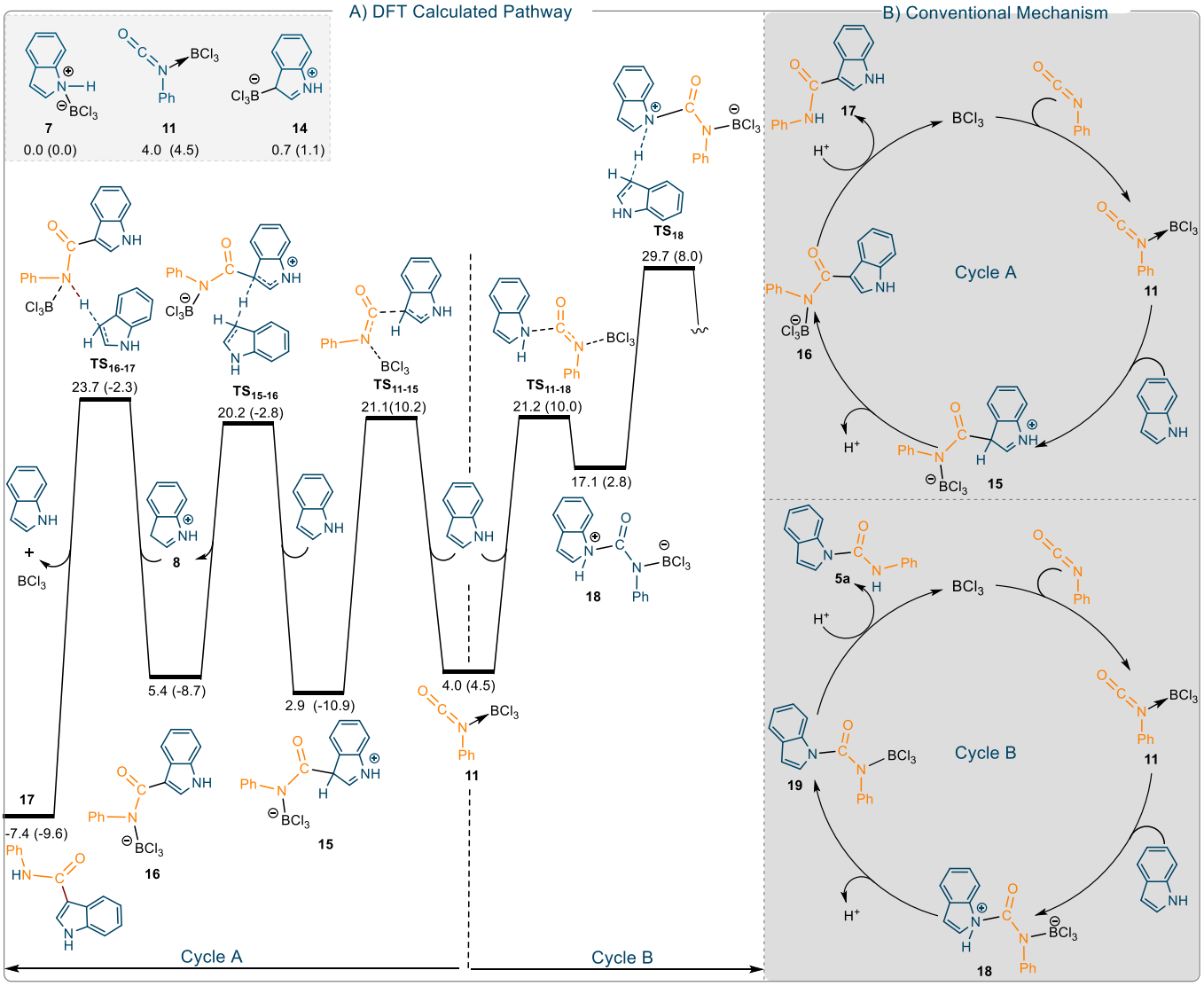


Figure S134. DFT calculated reaction pathway at the SMD/M06-2X-D3/def2-TZVP//SMD/M06-2X/6-31G(d) level of theory in CH_2Cl_2 for the amidation of 1*H*-indole using phenyl isocyanate and BCl_3 as a catalyst. Free energies (potential energies) are given in kcal/mol (A). DFT proposed catalytic cycle for the C3 amidation and *N*-carboxamidation of 1*H*-indole with phenyl isocyanate and catalytic BCl_3 (B).

5.2 Cartesian Coordinates and Total Energies for the Calculated Structures

Total potential (E), enthalpy (H) and Gibbs free energies (G) of all structures optimized at the SMD/M06-2X/BS1 level of theory along with the total potential energies calculated by SMD/ M06-2X/BS2//SMD/M06-2X/BS1 and cartesian coordinates for all of the calculated structures.

BCl_3

E (SMD/M06-2X/BS1) = -1405.4610358 au

G (SMD/M06-2X/BS1) = -1405.480883 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -1405.57478984 au

B	0.00000000	0.00000000	0.00000000
Cl	0.00000000	1.74493100	0.00000000
Cl	-1.51115400	-0.87246500	0.00000000
Cl	1.51115400	-0.87246500	0.00000000

phenyl isocyanate

E (SMD/M06-2X/BS1) = -399.573059777 au

G (SMD/M06-2X/BS1) = -399.50079 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -399.731207695 au

C	2.53077800	-0.07655500	-0.00010600
O	3.64198800	0.30079900	-0.00093300
N	1.44573300	-0.59461800	0.00103100
C	0.08652000	-0.25808400	0.00047800
C	-0.84931800	-1.29255900	0.00008900
C	-0.32905100	1.07647100	0.00056700
C	-2.20716000	-0.98710900	-0.00042500
H	-0.50290700	-2.32082900	0.00017300
C	-1.68863400	1.36790300	0.00002600
H	0.41323900	1.86909200	0.00111700
C	-2.63134600	0.34020900	-0.00051800
H	-2.93503100	-1.79253500	-0.00076700
H	-2.01085400	2.40459200	0.00002900
H	-3.69120700	0.57395000	-0.00097100

1*H*-Indole

E (SMD/M06-2X/BS1) = -363.676769872 au

G (SMD/M06-2X/BS1) = -363.575437 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -363.814825175 au

C	-0.24969900	0.75173700	-0.00000100
C	-0.25014000	-0.66738700	0.00000000
C	0.93219500	-1.41775900	-0.00000100
C	2.12867300	-0.72101600	-0.00000100
C	2.15500200	0.68998600	0.00000200
C	0.98384700	1.42775800	0.00000000

C	-1.62501200	1.16681200	-0.00000100
C	-2.38155600	0.02666300	-0.00000100
H	0.90638700	-2.50341800	-0.00000300
H	3.06522400	-1.27052400	-0.00000300
H	3.11302200	1.20114400	0.00000500
H	1.01312300	2.51401400	0.00000300
H	-1.99980700	2.18074800	-0.00000200
H	-3.45537800	-0.09781500	-0.00000100
N	-1.56096100	-1.07550200	0.00000200
H	-1.87570400	-2.03640600	0.00000400

5a·BCl_3

E (SMD/M06-2X/BS1) = -2168.78558766 au

G (SMD/M06-2X/BS1) = -2168.584412 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.18159618 au

C	3.46377300	-1.46295300	0.17582900
C	2.43341900	-0.64040900	-0.31344800
C	2.67258000	0.41527100	-1.19110700
C	3.99433100	0.64245500	-1.55369800
C	5.04130000	-0.15348600	-1.06216100
C	4.78750100	-1.20920000	-0.19954900
C	2.85866600	-2.47849600	1.01203200
C	1.52467400	-2.28410200	1.00185500
H	1.87485400	1.04288600	-1.56869900
H	4.21824200	1.46167800	-2.22937200
H	6.06099600	0.06121800	-1.36564800
H	5.59210100	-1.83453700	0.17472700
H	0.73937100	-2.79356000	1.54228200
N	1.22161600	-1.15587500	0.20899500
C	-0.02755200	-0.73257100	-0.11932800
O	-0.20860500	0.49449200	-0.49034700
N	-1.02787400	-1.58959300	-0.12342700
H	-0.80719700	-2.56637800	0.06091500
C	-2.41236500	-1.31389100	-0.36763600
C	-3.33567900	-2.04325100	0.37768700
C	-2.82207800	-0.39943300	-1.33592200
C	-4.69485200	-1.83806000	0.16592400
H	-2.98774500	-2.75316500	1.12263400
C	-4.18555000	-0.19975500	-1.52999100
H	-2.09601700	0.14659200	-1.92557800
C	-5.12207900	-0.91145900	-0.78289500
H	-5.41776100	-2.40023900	0.74811700
H	-4.51363800	0.51526600	-2.27746700
H	-6.18282200	-0.74732500	-0.94339200

H	3.37889900	-3.24622700	1.56785000
B	-0.36905200	1.65690700	0.44455400
Cl	-1.75958300	1.29291500	1.62949300
Cl	-0.76544000	3.08472100	-0.65551900
Cl	1.18632300	1.96046000	1.41009100

5a

E (SMD/M06-2X/BS1) = -763.287676171 au

G (SMD/M06-2X/BS1) = -763.088521 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -763.576904733 au

C	-3.24104700	0.86936900	-0.11672600
C	-2.26574700	-0.14639500	-0.00354600
C	-2.60700400	-1.47185000	0.28518700
C	-3.95476400	-1.75777600	0.45042700
C	-4.94143000	-0.76188800	0.33441000
C	-4.59570400	0.54983100	0.05334600
C	-2.54676800	2.09969900	-0.40505700
C	-1.22173700	1.81562600	-0.44602300
H	-1.85092700	-2.24139100	0.36695200
H	-4.25230500	-2.77822800	0.67189600
H	-5.98543000	-1.02807900	0.46831400
H	-5.35480000	1.32184200	-0.03325500
H	-0.38845700	2.46156600	-0.68367800
N	-1.01878600	0.45558600	-0.19603700
C	0.21018900	-0.23229500	-0.16643400
O	0.26243300	-1.43720100	-0.32451300
N	1.28156600	0.58304000	0.05494000
H	1.09503500	1.50824700	0.42364300
C	2.63948300	0.20310300	0.05892500
C	3.54333300	1.09614800	0.64698100
C	3.11103600	-0.97952100	-0.52091600
C	4.90271500	0.80993700	0.66055000
H	3.17116700	2.01479800	1.09385800
C	4.47689100	-1.25293100	-0.49554300
H	2.42185700	-1.67444300	-0.98005300
C	5.37935500	-0.36945300	0.09065000
H	5.58975200	1.51336100	1.12108500
H	4.83416900	-2.17373700	-0.94697700
H	6.44069000	-0.59569500	0.10312400
H	-2.99247800	3.06935800	-0.57850400

7

E (SMD/M06-2X/BS1) = -1769.16673172 au

G (SMD/M06-2X/BS1) = -1769.063037 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -1769.41132742 au

C	1.90574200	1.01755300	-0.12366300
C	1.11232500	-0.07341800	-0.48556700
C	1.59185300	-1.37018400	-0.52467300
C	2.92419700	-1.55766400	-0.15001000
C	3.72877900	-0.48394400	0.23899500
C	3.23120400	0.81695400	0.25156000
C	1.09981500	2.22518500	-0.27477600
C	-0.11538600	1.88226600	-0.70240900
H	0.97734400	-2.20583300	-0.83364800
H	3.33739000	-2.56077800	-0.16536500
H	4.75955900	-0.66633700	0.52555000
H	3.85794500	1.65580600	0.53620500
H	1.43549300	3.23647100	-0.08588900
H	-0.98401700	2.47807500	-0.93639000
N	-0.23415800	0.41791900	-0.82012500
H	-0.46010400	0.17567200	-1.79737900
B	-1.46680800	-0.17354300	0.08510600
Cl	-1.06577000	0.13772800	1.84702400
Cl	-2.99310800	0.72129100	-0.45644600
Cl	-1.63651300	-1.97144700	-0.29084200

8

E (SMD/M06-2X/BS1) = -364.104913286 au

G (SMD/M06-2X/BS1) = -363.991370 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -364.237747309 au

H	1.93174700	1.75946000	0.88044000
C	0.20544300	0.73208100	0.00005000
C	0.17894800	-0.66263200	0.00016200
C	-0.97871300	-1.42184600	0.00037500
C	-2.17464000	-0.70647400	0.00002900
C	-2.18078200	0.69263100	-0.00008100
C	-0.99430900	1.42851800	-0.00016200
C	1.64280900	1.17041200	0.00024700
C	2.36738000	-0.12526300	0.00006400
H	-0.95308800	-2.50617700	0.00020300
H	-3.11564400	-1.24607500	-0.00011400
H	-3.13038000	1.21764700	-0.00017400
H	-1.01095200	2.51351400	-0.00026200
H	1.93123400	1.76001000	-0.88035500
H	3.43787400	-0.29195200	0.00073700
N	1.52989100	-1.10831300	-0.00058400
H	1.80315100	-2.09280100	-0.00049300

9

E (SMD/M06-2X/BS1) = -1768.74038238 au
G (SMD/M06-2X/BS1) = -1768.649892 au
E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -1768.98654441 au

C	2.11114100	1.05893500	-0.00274800
C	1.11944000	0.04320100	-0.00579300
C	1.46835200	-1.31526400	-0.00352400
C	2.81628500	-1.63891300	-0.00094100
C	3.81160900	-0.64119800	0.00048500
C	3.46993000	0.70066000	0.00009500
C	1.41094800	2.31070500	-0.00298700
C	0.07858900	2.01097900	-0.00625700
H	0.70884100	-2.08941300	-0.00390000
H	3.11012400	-2.68455300	0.00010200
H	4.85805500	-0.93239700	0.00235500
H	4.23841900	1.46935600	0.00216300
H	1.84260500	3.30227600	-0.00107500
H	-0.76804800	2.68132500	-0.00681900
N	-0.13025400	0.64439700	-0.00929300
B	-1.45519000	-0.08543400	-0.00077300
Cl	-1.60407600	-1.15822300	1.54572800
Cl	-2.88158600	1.12670400	-0.02022700
Cl	-1.60375200	-1.20406000	-1.51337700

10·BCl_3
E (SMD/M06-2X/BS1) = -1769.18619985 au
G (SMD/M06-2X/BS1) = -1769.083648 au
E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -1769.42770120 au

C	2.11089300	1.01412900	0.00004600
C	1.13375200	0.01794900	0.00000900
C	1.44052200	-1.33627900	-0.00005800
C	2.79385500	-1.66995200	-0.00002500
C	3.78622200	-0.68590700	0.00007100
C	3.45451000	0.66864800	0.00009000
C	1.41706400	2.34119900	-0.00004200
C	-0.00995800	1.93525200	-0.00014100
H	0.67535200	-2.10283400	-0.00014500
H	3.07733700	-2.71726400	-0.00007700
H	4.83053100	-0.98123800	0.00011500
H	4.22527900	1.43287200	0.00012500
H	1.63221100	2.95996800	-0.88107000
H	-0.86148300	2.60440500	-0.00026200
N	-0.16156000	0.65056300	-0.00007400
H	1.63198000	2.95993300	0.88107700
B	-1.52989700	-0.13562400	-0.00003900

Cl	-2.93623400	1.06585100	0.00041800
Cl	-1.56679400	-1.17263900	1.53417900
Cl	-1.56708800	-1.17214700	-1.53452400

10

E (SMD/M06-2X/BS1) = -363.660971275 au

G (SMD/M06-2X/BS1) = -363.560821 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -363.795130470 au

C	-0.24541500	0.70909200	0.00003200
C	-0.23027900	-0.69348300	-0.00004500
C	0.95865800	-1.41175500	-0.00004600
C	2.15297300	-0.68936200	0.00003100
C	2.14662400	0.70788700	0.00010800
C	0.94418100	1.42192600	0.00010900
C	-1.68955500	1.11996100	0.00001000
C	-2.35052600	-0.23414800	-0.00009000
H	0.95032500	-2.49744800	-0.00010700
H	3.10026200	-1.22008000	0.00003200
H	3.08916200	1.24695900	0.00016800
H	0.94834400	2.50835100	0.00016800
H	-1.97989300	1.70411200	-0.88199400
H	-3.42833200	-0.37729500	-0.00013600
N	-1.54569900	-1.23561300	-0.00012400
H	-1.97994200	1.70398600	0.88208200

10'

E (SMD/M06-2X/BS1) = -2168.72782513 au

G (SMD/M06-2X/BS1) = -2168.533642 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.12427751 au

C	-1.05853000	0.00482300	1.74366800
O	-1.04434600	-0.19279400	2.86959600
N	-1.19209400	0.20492600	0.50479100
C	-0.45649500	1.32480200	-0.08644000
C	-0.67304300	2.59903200	0.42349400
C	0.43804200	1.07608500	-1.12030700
C	0.04992500	3.66246000	-0.11070400
H	-1.39328300	2.75132000	1.22228900
C	1.14469700	2.15294200	-1.64951100
H	0.59540400	0.06749300	-1.48400400
C	0.95812400	3.43935100	-1.14356000
H	-0.10271600	4.66304100	0.28013100
H	1.85208000	1.97867800	-2.45412900
H	1.51971800	4.27017700	-1.55873500
B	-2.39079400	-0.56597700	-0.28055600

Cl	-3.55805300	0.73769600	-0.83977200
Cl	-1.66050300	-1.48895400	-1.68834700
Cl	-3.16754300	-1.71591200	0.93966300
C	3.29941400	-0.48446000	0.10880900
C	2.11025400	-0.88524300	0.73413000
C	1.47618800	-2.07914300	0.41587400
C	2.06402200	-2.88049300	-0.56461100
C	3.24770800	-2.48904800	-1.19554300
C	3.87937600	-1.28592900	-0.86306200
C	3.65865200	0.85244600	0.69001900
C	2.50610900	1.05226800	1.63781900
H	0.55415900	-2.37403900	0.91051200
H	1.59244400	-3.81794000	-0.84334100
H	3.68317000	-3.12861200	-1.95721400
H	4.79772200	-0.98978300	-1.36205600
H	3.69288600	1.65883200	-0.05375200
H	2.37433500	1.93888100	2.25320000
N	1.65214500	0.09160900	1.66049200
H	4.61947200	0.86096100	1.21943900

11

E (SMD/M06-2X/BS1) = -1805.05429067 au

G (SMD/M06-2X/BS1) = -1804.980448 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -1805.32100188 au

C	0.49460200	1.91746800	0.05078300
O	0.74279900	3.03433800	0.07411200
N	0.20359400	0.69659300	0.02581100
C	-1.22998500	0.36982500	0.01588900
C	-1.87150700	0.15907400	1.22959600
C	-1.87632900	0.26515300	-1.20929200
C	-3.22145400	-0.18167700	1.20650200
H	-1.32650000	0.25973600	2.16204400
C	-3.22627500	-0.07515500	-1.21149000
H	-1.33381900	0.44603700	-2.13122800
C	-3.89410400	-0.29953400	-0.00858600
H	-3.74478600	-0.35252900	2.14131900
H	-3.75332400	-0.16312700	-2.15564900
H	-4.94641400	-0.56493800	-0.01821600
B	1.37426100	-0.42513200	-0.01101300
Cl	1.15682200	-1.47621500	1.47470700
Cl	2.96377200	0.51699100	0.02555300
Cl	1.16271800	-1.36908700	-1.56832900

12

E (SMD/M06-2X/BS1) = -2168.76296011 au

G (SMD/M06-2X/BS1) = -2168.563514 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.15625420 au

C	0.33971100	-1.19603400	-0.73456600
O	0.74751700	-2.26809300	-1.09399700
N	0.97428100	-0.17983600	-0.12536600
C	0.37028400	1.12988200	-0.12859400
C	0.22090400	1.81066900	-1.33578300
C	-0.05040100	1.71080200	1.06654500
C	-0.37398700	3.07035400	-1.35003700
H	0.57513100	1.35100700	-2.25506000
C	-0.63653200	2.97281600	1.04748200
H	0.08897000	1.17462400	1.99995900
C	-0.80398200	3.65145800	-0.15918500
H	-0.49216600	3.59836400	-2.29110900
H	-0.96434200	3.42544600	1.97797900
H	-1.26419700	4.63462300	-0.16955400
B	2.47400900	-0.38734600	0.24164200
Cl	3.47789700	-0.62047800	-1.32595100
Cl	3.12439300	1.10729200	1.14113200
Cl	2.64761100	-1.87777400	1.35580200
C	-3.34581500	-0.67746200	-0.52376900
C	-2.10322900	-0.84609800	0.08409900
C	-1.91027500	-0.94058400	1.45244500
C	-3.05696300	-0.83512700	2.23666700
C	-4.31642200	-0.64884100	1.65651700
C	-4.47756900	-0.57175600	0.27238900
C	-3.14136000	-0.67328800	-2.01121900
C	-1.67470000	-0.87099100	-2.12499800
H	-0.92754600	-1.09224200	1.88784000
H	-2.96814400	-0.90129500	3.31574900
H	-5.18815600	-0.57021000	2.29797200
H	-5.46013800	-0.43898100	-0.16844300
H	-3.42316100	0.26937200	-2.50032800
H	-1.08223800	-0.94230400	-3.03113900
N	-1.12518700	-0.93739400	-0.95683300
H	-3.67414600	-1.47479900	-2.53937700

12'

E (SMD/M06-2X/BS1) = -2397.93855741 au

G (SMD/M06-2X/BS1) = -2397.678588 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2398.47320820 au

C	-0.15843900	-0.55838100	0.11006500

O	0.14773200	-1.67870600	0.54514600
N	-1.43221800	-0.17375200	-0.09600400
C	-1.74905400	1.23307100	-0.03892100
C	-1.51359100	1.93474900	1.14156800
C	-2.28749800	1.88220300	-1.14926400
C	-1.80499600	3.29605000	1.20584400
H	-1.10020800	1.41440300	2.00135300
C	-2.58415100	3.23916300	-1.07665400
H	-2.46425600	1.31975800	-2.06084700
C	-2.34142300	3.94925900	0.09932700
H	-1.61555900	3.84171000	2.12498400
H	-3.00248000	3.74334900	-1.94229600
H	-2.57101700	5.00904900	0.15150600
B	-2.55758400	-1.23995300	0.06110200
Cl	-2.69844900	-1.75894900	1.85975100
Cl	-4.20297300	-0.53135800	-0.46141900
Cl	-2.20509400	-2.72220600	-1.02811600
C	2.89079300	1.38330800	-0.09681700
C	2.07724900	0.42432800	0.54270400
C	2.47757800	-0.23346000	1.71029500
C	3.73599000	0.07202100	2.20671500
C	4.57178100	1.00803200	1.57166600
C	4.15866600	1.67079000	0.42772000
C	2.14785500	1.88366600	-1.22983500
C	0.94630400	1.24586700	-1.24294100
H	1.83416200	-0.94626300	2.21396600
H	4.07890000	-0.42216300	3.11043200
H	5.54995400	1.21874200	1.99275700
H	4.79606500	2.40726400	-0.05276100
H	2.66343700	0.23978100	-2.69146600
H	0.12653400	1.32098800	-1.94151500
N	0.87678700	0.35382600	-0.17413400
H	2.47273700	2.63307200	-1.93945700
O	3.19463500	-0.53121100	-2.96525200
H	3.87166200	-0.17285800	-3.56388300
H	3.83258900	-1.20056000	-1.63955400
O	4.13107300	-1.66942800	-0.80116400
H	3.13512400	-2.33768700	-0.27637500
H	4.86343200	-2.26181400	-1.04991500
O	2.29277700	-2.90103000	0.19633700
H	2.05438600	-3.67339100	-0.35374500
H	1.42910900	-2.32241300	0.31923300

13

E (SMD/M06-2X/BS1) = -2168.76817347 au

G (SMD/M06-2X/BS1) = -2168.565459 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.16392264 au

C	-3.68606700	-0.17468600	-0.97368600
C	-2.80081100	-0.36533900	0.10332000
C	-3.24250000	-0.74543800	1.37002600
C	-4.61226200	-0.92941900	1.52912200
C	-5.51079200	-0.74181000	0.46897100
C	-5.05808200	-0.36430200	-0.78755700
C	-2.89685900	0.20409200	-2.12581000
C	-1.60333400	0.23491300	-1.75115100
H	-2.55916600	-0.89145800	2.19463000
H	-4.98995800	-1.22574500	2.50259600
H	-6.57232300	-0.89483700	0.63595700
H	-5.74856200	-0.21787800	-1.61236200
H	-0.74204900	0.48780000	-2.35232700
N	-1.49521900	-0.11095200	-0.38351600
C	-0.38487000	-0.17869100	0.41149100
O	-0.37980600	-0.44609500	1.57997500
N	0.90806500	0.10500100	-0.27505800
C	1.83216500	-1.05557800	-0.21346700
C	2.29895500	-1.54782100	-1.42772800
C	2.22048100	-1.61224800	0.99993400
C	3.18099400	-2.62327700	-1.42990400
H	1.98240100	-1.09670400	-2.36384200
C	3.09966800	-2.69323200	0.97914500
H	1.84299900	-1.22479000	1.93632400
C	3.58205800	-3.19719700	-0.22602500
H	3.54928600	-3.00874600	-2.37477300
H	3.40739100	-3.13951900	1.91901300
H	4.26861700	-4.03773600	-0.22760700
H	-3.26871000	0.42811700	-3.11593200
H	0.72802800	0.24368300	-1.27373000
B	1.55365400	1.57425400	0.17066700
Cl	2.08533200	1.54940600	1.91288100
Cl	2.95839500	1.84221000	-0.98689800
Cl	0.18979300	2.78821700	-0.12075600

14

E (SMD/M06-2X/BS1) = -1769.16605901 au

G (SMD/M06-2X/BS1) = -1769.063062 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -1769.40950483 au

C	-1.11243700	0.15119500	-0.61622300

C	-1.85794100	-0.93738400	-0.15411300
C	-3.15540200	-0.84978600	0.32702500
C	-3.72427300	0.42023100	0.32452300
C	-3.00853100	1.53008900	-0.14212400
C	-1.70106600	1.41224800	-0.61126400
C	0.24852500	-0.34617400	-0.98729300
C	0.11202600	-1.79229400	-0.80849500
H	-3.69307800	-1.72296000	0.68089700
H	-4.73869000	0.55032500	0.68683400
H	-3.48336900	2.50604600	-0.13647700
H	-1.15773700	2.28155100	-0.96465800
H	0.61428800	-0.07247800	-1.98226700
H	0.85515300	-2.55903400	-0.99198500
N	-1.04663600	-2.08735300	-0.29763800
H	-1.33237400	-3.02802900	-0.02717400
B	1.47016400	0.17293900	0.04503000
Cl	1.64342200	2.01763100	-0.12141700
Cl	3.06381900	-0.66008000	-0.47638700
Cl	1.06370200	-0.28327900	1.80962300

15

E (SMD/M06-2X/BS1) = -2168.76410526 au

G (SMD/M06-2X/BS1) = -2168.562723 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.16008849 au

C	0.21690000	0.47507600	-0.58684500
O	0.38479400	1.63099800	-0.94694700
N	-0.95973700	-0.02916100	-0.13258700
C	-2.01834900	0.95035700	-0.07500800
C	-2.22455200	1.66847900	1.09882800
C	-2.82319800	1.16722800	-1.18989100
C	-3.25409500	2.60471100	1.16049400
H	-1.58396400	1.48071100	1.95607900
C	-3.85090500	2.10443800	-1.12431700
H	-2.64446600	0.59328000	-2.09491800
C	-4.06828600	2.82327000	0.05048200
H	-3.42047500	3.16228300	2.07724800
H	-4.48330700	2.27179500	-1.99097500
H	-4.87160200	3.55204100	0.10082700
B	-1.24472200	-1.49273800	0.22545500
Cl	-0.13716600	-2.06748700	1.64762900
Cl	-3.01035800	-1.72819500	0.74251800
Cl	-0.91781000	-2.60539800	-1.27750600
C	2.59968800	0.10013100	0.17472800
C	3.63745700	0.45057100	-0.68655500

C	4.84190100	0.99146000	-0.27424200
C	4.98142600	1.18957400	1.09910200
C	3.95382000	0.85491200	1.98610500
C	2.74926100	0.30744700	1.53706400
C	1.46335000	-0.44825500	-0.65243200
C	2.02212400	-0.35715500	-2.03154200
H	5.62662300	1.24691500	-0.97786200
H	5.90351800	1.61281400	1.48297400
H	4.09466300	1.02602000	3.04838700
H	1.95397800	0.05476500	2.23069100
H	1.24685100	-1.49589000	-0.42631200
H	1.53651500	-0.64738700	-2.95664800
N	3.21071000	0.14136600	-2.00887100
H	3.78152200	0.29780300	-2.84170100

16

E (SMD/M06-2X/BS1) = -2168.33243985 au

G (SMD/M06-2X/BS1) = -2168.144391 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2168.73204641 au

C	0.22371900	-0.80598300	0.00898000
O	0.23135500	-2.01922700	0.20415600
N	-0.96612600	-0.08115700	0.04207400
C	-2.13438600	-0.89962600	-0.16103400
C	-2.79239500	-0.85046500	-1.38730000
C	-2.61094300	-1.73577100	0.84988600
C	-3.93487600	-1.62327700	-1.59939800
H	-2.40669200	-0.20175200	-2.16777700
C	-3.74505400	-2.51062400	0.63424900
H	-2.08768200	-1.76353200	1.80020900
C	-4.41301800	-2.45433700	-0.59072500
H	-4.44610900	-1.57552200	-2.55649600
H	-4.11252100	-3.15846400	1.42488900
H	-5.30113700	-3.05744100	-0.75505200
B	-1.20382800	1.37818400	0.38161800
Cl	-1.43116600	2.45559700	-1.18764300
Cl	-2.80887800	1.57164700	1.36672600
Cl	0.14836900	2.13863700	1.43387000
C	2.79680100	-0.65554100	-0.02090700
C	3.73781400	0.20749900	-0.63048900
C	5.11889800	0.02480700	-0.50898900
C	5.55162000	-1.05399900	0.24497600
C	4.63289900	-1.92892100	0.86052100
C	3.26566400	-1.74341200	0.73477600
C	1.48848100	-0.14245700	-0.35112400

C	1.69084000	0.96162900	-1.14564300
H	5.81856000	0.70361700	-0.98736500
H	6.61673900	-1.22982800	0.36247100
H	5.00848800	-2.76603000	1.44165400
H	2.55917800	-2.42218200	1.20004500
H	0.96861700	1.61792400	-1.61006800
N	3.02659100	1.17227300	-1.31091600
H	3.42968700	1.92118900	-1.85882800

17

E (SMD/M06-2X/BS1) = -763.291664655 au

G (SMD/M06-2X/BS1) = -763.092760 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -763.582422909 au

C	2.30629900	-0.19095800	-0.00987900
C	3.27845800	0.83284400	0.06818500
C	4.65073400	0.57968100	-0.02778700
C	5.03860900	-0.73748600	-0.20509400
C	4.08696400	-1.77554500	-0.28563300
C	2.72952400	-1.51923500	-0.19003200
C	1.02078000	0.45185800	0.11805400
C	1.26807900	1.79872000	0.27787800
H	5.37571500	1.38533100	0.03531700
H	6.09493700	-0.97611100	-0.28292500
H	4.43013300	-2.79650200	-0.42320800
H	1.99839400	-2.31782800	-0.24669800
H	0.58499000	2.62268000	0.43761000
N	2.60894100	2.02485700	0.24518900
H	3.04511300	2.93174200	0.35412600
C	-0.27269800	-0.25137300	0.11231700
O	-0.34196000	-1.46788900	0.25413500
N	-1.37414800	0.55080200	-0.06387600
H	-1.19763100	1.52022200	-0.30027500
C	-2.73071800	0.18753100	-0.05196600
C	-3.65615800	1.19280300	-0.36882600
C	-3.19516000	-1.09470200	0.27049000
C	-5.01852400	0.92484400	-0.36685100
H	-3.29520000	2.18823900	-0.61609300
C	-4.56604200	-1.34584200	0.26834000
H	-2.49193100	-1.87759600	0.51411100
C	-5.48551100	-0.34976100	-0.04792600
H	-5.71681400	1.71831800	-0.61596900
H	-4.91343700	-2.34370200	0.52037600
H	-6.54995000	-0.56157000	-0.04625400

18

E (SMD/M06-2X/BS1) = -2168.74353481 au

G (SMD/M06-2X/BS1) = -2168.541370 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.13823683 au

C	-0.44464500	-0.98405300	1.10411000
O	-0.89482800	-2.02732100	1.49187600
N	-0.97292300	-0.04780200	0.31864900
C	-0.24782600	1.14559600	-0.03044900
C	-0.45609200	2.30818400	0.71188800
C	0.62186800	1.13444700	-1.11592300
C	0.26305800	3.45594100	0.39979400
H	-1.16967900	2.29452000	1.53110900
C	1.34871700	2.28498800	-1.41582000
H	0.73639100	0.22818400	-1.70431400
C	1.17883600	3.43906000	-0.65330200
H	0.11301700	4.36133000	0.97936200
H	2.04579300	2.27734200	-2.24813000
H	1.74726900	4.33309800	-0.89081600
B	-2.40197400	-0.32867300	-0.25738900
Cl	-3.62830100	-0.49883600	1.14155900
Cl	-2.92118900	1.08709000	-1.34471300
Cl	-2.35393100	-1.89154700	-1.28574300
C	3.03052500	-0.19964000	0.49563400
C	2.01269000	-1.15032400	0.51489600
C	1.93520500	-2.23631000	-0.33150800
C	2.96703000	-2.35276000	-1.26619900
C	4.00477800	-1.41666900	-1.31585800
C	4.05348700	-0.33302500	-0.43879500
C	2.72568400	0.80587200	1.51339500
C	1.56752900	0.49899700	2.10303000
H	1.11891000	-2.95026200	-0.28297900
H	2.95798800	-3.18327500	-1.96389900
H	4.78873700	-1.53560800	-2.05681600
H	4.85984700	0.39130200	-0.48760400
H	3.33281300	1.67071400	1.74744000
H	1.00623100	0.96268800	2.90066700
N	1.04776600	-0.77493500	1.56257300
H	1.10038100	-1.47477900	2.32124500

TS$_{7\text{-}9}$

E (SMD/M06-2X/BS1) = -2132.83905148 au

G (SMD/M06-2X/BS1) = -2132.619475 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2133.21617916 au

C	0.47205600	1.82370800	-1.01068100

C	-0.39927400	1.36840900	-0.00466700
C	-0.65253500	2.12312000	1.13791700
C	-0.01497800	3.35721800	1.24678300
C	0.85933000	3.81968500	0.25396500
C	1.11170100	3.05823100	-0.88061600
C	0.55168900	0.78134200	-2.01250500
C	-0.23078700	-0.23508300	-1.60547400
H	-1.31910300	1.77637300	1.91714700
H	-0.20101900	3.96955600	2.12361900
H	1.34441500	4.78328500	0.37599400
H	1.79532400	3.40707700	-1.64879300
H	1.14444800	0.80524500	-2.91726000
H	-0.43295500	-1.18314400	-2.08118900
N	-0.82908700	0.03827700	-0.33190800
H	-0.10703200	-0.73079100	0.56407600
B	-2.30564000	-0.42820200	-0.12056400
Cl	-3.45565900	0.67638300	-1.07263000
Cl	-2.44475700	-2.19593400	-0.72018400
Cl	-2.72552600	-0.40930000	1.69722900
C	2.01704300	-0.81146600	0.91122700
C	2.49425500	-1.81603900	0.05148300
C	3.63245600	-1.66481000	-0.73856000
C	4.30999700	-0.45906200	-0.62588100
C	3.86124400	0.55541800	0.24001800
C	2.71421100	0.39762300	1.00465300
C	0.74875500	-1.29547700	1.46583100
C	0.63169000	-2.62825200	1.00437800
H	3.96806600	-2.45185500	-1.40586600
H	5.20527100	-0.29557500	-1.21725700
H	4.41945500	1.48454600	0.30020300
H	2.35541800	1.19516300	1.64955300
H	0.30412800	-0.95595100	2.39664600
H	-0.14227800	-3.35483900	1.21283100
N	1.61451100	-2.89634800	0.14816800
H	1.69600600	-3.75850400	-0.38298300

$TS_{10\text{-}12}$

E (SMD/M06-2X/BS1) = -2168.72699749 au

G (SMD/M06-2X/BS1) = -2168.533100 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.12260166 au

C	-0.76925800	-0.44592200	1.56966500
O	-0.65418900	-0.93142300	2.60212900
N	-1.19499200	-0.02548900	0.45061800
C	-0.67421500	1.22585400	-0.09133100

C	-0.97269600	2.40855600	0.57343100
C	0.11132600	1.19576100	-1.23667900
C	-0.45365600	3.60241500	0.07810100
H	-1.59481900	2.38942800	1.46327300
C	0.62064400	2.39725700	-1.72135400
H	0.34044300	0.25209700	-1.71830900
C	0.34245100	3.59608600	-1.06549700
H	-0.67430500	4.53444800	0.58815400
H	1.24290300	2.39211600	-2.61035000
H	0.74658200	4.52797600	-1.44807400
B	-2.52081700	-0.71607300	-0.18127100
Cl	-3.88424600	0.51401200	-0.02998600
Cl	-2.15427600	-1.11143000	-1.94014000
Cl	-2.87771400	-2.25045000	0.77997700
C	3.64870200	-0.18973400	0.28379300
C	2.34619500	-0.69046100	0.40635300
C	1.92598700	-1.83610000	-0.25733500
C	2.85944400	-2.48767500	-1.06466900
C	4.16271600	-1.99934000	-1.19265400
C	4.57121500	-0.84432400	-0.51889600
C	3.71784900	1.04782900	1.13176600
C	2.31492800	1.08799600	1.67226500
H	0.90977400	-2.20806700	-0.15043300
H	2.56925900	-3.38621900	-1.60026400
H	4.86939500	-2.52559900	-1.82694700
H	5.58620200	-0.47282100	-0.62599500
H	3.93678300	1.95823500	0.55932000
H	1.93626100	1.85996800	2.33697500
N	1.56335600	0.12902300	1.26545500
H	4.45678600	0.99001500	1.94023600

$TS_{16\text{-}17}$

E (SMD/M06-2X/BS1) = -2532.42743211 au

G (SMD/M06-2X/BS1) = -2532.106436 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2532.95695140 au

C	0.10191400	-0.65858300	-0.71805600
O	0.02377000	-1.04041000	-1.86678700
N	-1.14772700	-0.30036600	-0.04142000
C	-2.27104100	-1.00016000	-0.68077600
C	-3.37846500	-0.29793600	-1.14345000
C	-2.24536200	-2.39320100	-0.76174800
C	-4.45427500	-0.98822700	-1.70134600
H	-3.43530100	0.77954700	-1.04052300
C	-3.32121500	-3.07643000	-1.31607000

H	-1.38299100	-2.93872000	-0.39102000
C	-4.42902000	-2.37573300	-1.79232000
H	-5.31684100	-0.43216200	-2.05529100
H	-3.29313000	-4.16010700	-1.37378700
H	-5.26871800	-2.91037400	-2.22531300
B	-1.26356100	-0.27163200	1.53762200
Cl	-0.42754300	1.25528100	2.22296200
Cl	-3.05672300	-0.14663900	2.04710100
Cl	-0.53112500	-1.81711400	2.27736700
C	2.37975600	-1.65731900	-0.24687600
C	3.58323300	-1.23165200	0.35739300
C	4.72540800	-2.03727200	0.40546900
C	4.64027800	-3.29176900	-0.17536200
C	3.44936300	-3.73552600	-0.78643500
C	2.32053800	-2.93416100	-0.82751800
C	1.42267200	-0.58821400	-0.06796200
C	2.08761600	0.42591100	0.58188900
H	5.63755400	-1.68864200	0.87980500
H	5.50674200	-3.94583000	-0.16049600
H	3.42082700	-4.72450000	-1.23358700
H	1.40862400	-3.27771300	-1.30683800
H	-1.23230400	1.03068600	-0.49199600
H	1.75888300	1.41920200	0.84422700
N	3.36974700	0.04305900	0.83371200
H	4.06216700	0.62408000	1.28878100
C	0.16499700	2.65111500	-1.26194500
C	0.31344600	3.64483300	-0.27960700
C	1.53257000	4.25325800	0.01247900
C	2.62344000	3.85360500	-0.74875700
C	2.49422700	2.88326200	-1.75828500
C	1.27650400	2.26869500	-2.01866300
C	-1.23018700	2.20041100	-1.20879000
C	-1.85138200	3.06709800	-0.27179500
H	1.61919200	5.00642100	0.78890200
H	3.59337400	4.30471100	-0.56467700
H	3.36866300	2.60205400	-2.33667400
H	1.18906500	1.49955300	-2.78027000
H	-1.76231100	1.82208200	-2.07912500
H	-2.88576700	3.09521400	0.04732600
N	-0.94717600	3.86292200	0.28209300
H	-1.13242700	4.48860300	1.06092100

TS_{12}

E (SMD/M06-2X/BS1) = -2397.93855741 au

G (SMD/M06-2X/BS1) = -2397.678588 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2398.47320820 au

C	-0.26491100	-0.70039100	-0.05023800
O	0.04526100	-1.84876500	0.20678600
N	-1.50528000	-0.19353000	-0.13912300
C	-1.69422300	1.23400900	-0.04765500
C	-1.41388800	1.88349000	1.15226000
C	-2.15397700	1.95023400	-1.15111900
C	-1.58449000	3.26356500	1.24388500
H	-1.06360500	1.30646000	2.00413100
C	-2.32735300	3.32731000	-1.05181400
H	-2.37401500	1.42229000	-2.07450600
C	-2.04128900	3.98585800	0.14413600
H	-1.36281800	3.77070300	2.17771300
H	-2.68589700	3.88632500	-1.91051600
H	-2.17673000	5.06043000	0.21784500
B	-2.70591500	-1.17488000	0.02258000
Cl	-2.69948000	-1.90005900	1.75274800
Cl	-4.31422500	-0.26628400	-0.22243300
Cl	-2.59282800	-2.53108800	-1.25979900
C	2.84757800	1.24192000	-0.03614600
C	1.96002600	0.33461800	0.55741300
C	2.20808500	-0.29968500	1.77245000
C	3.40409400	0.02230300	2.40005500
C	4.30657900	0.93486900	1.83032400
C	4.04625800	1.54458600	0.60993600
C	2.27887600	1.61024100	-1.34426500
C	0.98821100	1.01409200	-1.35468300
H	1.50849500	-1.00767400	2.20345700
H	3.64343100	-0.44233300	3.35096700
H	5.22839200	1.16378900	2.35577300
H	4.75170900	2.24301200	0.17103700
H	2.85870500	0.75675200	-2.12330100
H	0.23175100	1.05589700	-2.12944200
N	0.82869500	0.24147900	-0.28607000
H	2.45946900	2.55808100	-1.84585900
O	3.55646800	-0.22683800	-2.80890300
H	4.29321800	0.19330900	-3.28797900
H	3.97613900	-0.78921800	-2.07072800
O	4.53565600	-1.53665400	-0.81470200
H	3.81230300	-2.06372300	-0.38196000
H	5.21351200	-2.18812900	-1.05695500
O	2.57968800	-3.03382000	0.24914400
H	2.46102800	-3.85321300	-0.25750800

H	1.70758800	-2.59118800	0.21667000

TS'$_{12}$

E (SMD/M06-2X/BS1) = -2397.95938490 au

G (SMD/M06-2X/BS1) = -2397.693891 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2398.49146483 au

C	-0.23604600	-0.17533000	-0.52997100
O	-0.43630100	-0.91714000	-1.46515600
N	1.06361700	-0.06322900	0.11355800
C	1.63864200	1.27568900	-0.06472300
C	1.51463200	1.92063300	-1.29274900
C	2.30071800	1.88737300	0.99813300
C	2.05378400	3.19458800	-1.45398600
H	1.00384200	1.43159300	-2.11765400
C	2.84244900	3.15757400	0.82471500
H	2.39525300	1.37550000	1.95110500
C	2.71960600	3.81327600	-0.39904100
H	1.95389200	3.69841100	-2.40994500
H	3.35895400	3.63430300	1.65155700
H	3.14054000	4.80523000	-0.52861600
B	2.07100300	-1.25905900	-0.23525800
Cl	2.61240300	-1.22372300	-1.99942900
Cl	3.54671800	-1.08220400	0.88209200
Cl	1.20496300	-2.85979400	0.19119600
C	-3.33697300	1.31736500	0.51470600
C	-2.60138800	0.49013000	-0.35715000
C	-3.21874600	-0.22731600	-1.38297400
C	-4.59877300	-0.09946400	-1.50524200
C	-5.34559600	0.71370500	-0.64139900
C	-4.72250400	1.42886100	0.37156900
C	-2.40050700	1.92399300	1.43363000
C	-1.16902100	1.47009700	1.12635700
H	-2.65988000	-0.84851200	-2.06787700
H	-5.10478100	-0.64415600	-2.29612200
H	-6.42087000	0.78584300	-0.77118400
H	-5.29231200	2.06546500	1.04163700
H	0.81237500	-0.32853900	1.38612000
H	-0.21926800	1.74440700	1.55651600
N	-1.24490800	0.57565500	0.03710200
H	-2.63386100	2.63119700	2.21753900
O	0.48750700	-0.71935300	2.46819300
H	0.36596700	0.02468400	3.08916700
H	-0.44714700	-1.17463500	2.34178500
O	-1.79829300	-1.66993500	2.04260400

H	-1.88600300	-2.17269500	1.18584800
H	-2.12202800	-2.26962000	2.73607800
O	-2.01923900	-2.99339200	-0.28059600
H	-1.60137400	-3.86514700	-0.17894900
H	-1.42974100	-2.51624100	-0.89252300

TS$_{11\text{-}15}$

E (SMD/M06-2X/BS1) = -2168.72854766 au

G (SMD/M06-2X/BS1) = -2168.531881 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.12640697 au

C	0.12485300	0.49421200	0.49695100
O	0.73969000	1.22995600	1.14929600
N	-1.00116400	-0.07778400	0.20668100
C	-2.12547400	0.85529500	0.22000700
C	-2.55181400	1.38738400	1.43220700
C	-2.74075700	1.17557200	-0.98476800
C	-3.63281200	2.26405900	1.43344000
H	-2.05025300	1.10833300	2.35421200
C	-3.82855500	2.04576200	-0.96655000
H	-2.37792900	0.74504600	-1.91232300
C	-4.27167100	2.58970400	0.23741700
H	-3.97983400	2.68505700	2.37143600
H	-4.32497700	2.30081500	-1.89727900
H	-5.11754000	3.26990100	0.24447800
B	-1.19076400	-1.62214900	-0.01544700
Cl	0.27056700	-2.47681800	0.75184800
Cl	-2.75071000	-2.11511300	0.84119000
Cl	-1.31301600	-1.99915400	-1.83348900
C	2.87465600	-0.08435100	-0.44086000
C	3.27980400	1.26714500	-0.43927900
C	4.42529000	1.71293100	0.22435200
C	5.17396600	0.75677300	0.89123200
C	4.79274300	-0.60034100	0.90047700
C	3.64996600	-1.03057400	0.24665300
C	1.63555200	-0.14348000	-1.17871600
C	1.40125000	1.14632200	-1.65479500
H	4.71207400	2.75956200	0.21396300
H	6.07396600	1.05858900	1.41796700
H	5.40846900	-1.31854400	1.43280300
H	3.35919300	-2.07638300	0.25900800
H	1.12378800	-1.03070700	-1.52099800
H	0.59580900	1.51482900	-2.27691900
N	2.35522800	1.97843800	-1.18938600
H	2.37681800	2.97999300	-1.34348200

$TS_{11\text{-}18}$

E (SMD/M06-2X/BS1) = -2168.72946445 au

G (SMD/M06-2X/BS1) = -2168.532263 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.12671088 au

C	-0.80048500	-0.57226600	1.47477700
O	-1.14938700	-1.17562900	2.39808600
N	-0.97150800	-0.00163100	0.34283400
C	-0.16995100	1.14390400	-0.04668300
C	-0.28184800	2.31960700	0.68973200
C	0.65354500	1.04651500	-1.16062300
C	0.47090000	3.42571700	0.30604000
H	-0.94801000	2.36089800	1.54685800
C	1.39960000	2.16091700	-1.53451200
H	0.71871000	0.11156900	-1.70875400
C	1.31138400	3.34462900	-0.80295600
H	0.39746600	4.34803400	0.87295700
H	2.05667700	2.09795600	-2.39617400
H	1.89682200	4.20877300	-1.10137500
B	-2.41185800	-0.31245200	-0.34437500
Cl	-3.67421400	0.67204000	0.58799900
Cl	-2.32690500	0.19464500	-2.10266700
Cl	-2.72576500	-2.12777500	-0.18975000
C	3.04633100	-0.35157300	0.25711000
C	2.01620900	-1.19823800	0.69681200
C	1.65461200	-2.36122500	0.02868600
C	2.37080800	-2.67639400	-1.12277600
C	3.40112900	-1.84252200	-1.58471200
C	3.74709400	-0.67791400	-0.90723000
C	3.09328700	0.77023400	1.18097700
C	2.13082900	0.57665500	2.10631100
H	0.84324500	-2.98978000	0.38563400
H	2.12272900	-3.57696700	-1.67532800
H	3.93382800	-2.11207400	-2.49150700
H	4.53784400	-0.03237400	-1.27775300
H	3.76625400	1.61563600	1.12848600
H	1.85411200	1.17153200	2.96574300
N	1.39245100	-0.60293700	1.82207500
H	1.22448400	-1.21371200	2.62341300

$TS_{15\text{-}16}$

E (SMD/M06-2X/BS1) = -2532.42831649 au

G (SMD/M06-2X/BS1) = -2532.109677 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2532.95775850 au

C	0.79968000	0.35376000	-0.83321100
O	0.84070100	0.21912500	-2.05361400
N	1.92157900	0.26803600	-0.04497100
C	3.05563200	-0.30219300	-0.73434800
C	3.41940000	-1.61889600	-0.46809100
C	3.78071300	0.45428200	-1.65383600
C	4.51984200	-2.17993100	-1.11679100
H	2.84626400	-2.19266800	0.25435600
C	4.87354200	-0.10960700	-2.30280000
H	3.48324700	1.48034100	-1.84679300
C	5.24715700	-1.42768200	-2.03462400
H	4.80539600	-3.20544000	-0.90215500
H	5.43801200	0.48116400	-3.01807500
H	6.10333200	-1.86400300	-2.54021800
B	2.14254500	0.74342600	1.39012200
Cl	1.78979500	-0.66034500	2.63693700
Cl	3.92671000	1.25280300	1.64709100
Cl	1.08502000	2.23039200	1.83150300
C	-1.52481500	1.50266800	-0.77075400
C	-2.54258600	1.63704600	0.18805500
C	-3.67761000	2.42007500	-0.01388300
C	-3.76101100	3.09449700	-1.22351900
C	-2.75110800	2.97736400	-2.19631000
C	-1.63422800	2.17887200	-1.98930500
C	-0.56380100	0.53229000	-0.23496700
C	-1.03632300	0.22381600	1.06328700
H	-4.45473900	2.49312000	0.74010600
H	-4.62359600	3.72165800	-1.42496100
H	-2.85287400	3.52018700	-3.13081800
H	-0.86211500	2.07339200	-2.74382700
H	-1.10553300	-0.62833900	-0.88538500
H	-0.60387700	-0.43336000	1.80558000
N	-2.20124800	0.83379100	1.27343800
H	-2.77912400	0.69572500	2.09706500
C	-2.92756900	-1.70002100	-0.80381700
C	-2.67284200	-2.45840200	0.35413500
C	-3.58326400	-2.56689500	1.40589800
C	-4.78779900	-1.89599600	1.25606700
C	-5.07166100	-1.14345200	0.09889100
C	-4.14985500	-1.02786200	-0.92985200
C	-1.69482400	-1.70948000	-1.58416500
C	-0.84017200	-2.61949500	-0.93237200
H	-3.35550000	-3.14730600	2.29406100
H	-5.53056800	-1.95684900	2.04528400

H	-6.02870100	-0.63733500	0.01939200
H	-4.36082400	-0.42552600	-1.80863600
H	-1.58217100	-1.40154400	-2.61686000
H	0.16138700	-2.92758200	-1.20296800
N	-1.38974400	-2.98964300	0.22820900
H	-0.93537100	-3.57806100	0.92025800

TS_{18}

E (SMD/M06-2X/BS1) = -2532.41671109 au

G (SMD/M06-2X/BS1) = -2532.098486 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2532.94472985 au

C	0.83421400	-0.05000800	-0.84757100
O	0.77112900	-0.50398800	-1.96925000
N	1.94403300	0.09623500	-0.08142200
C	3.01580200	-0.80279100	-0.45668400
C	3.34809200	-1.82687400	0.42513800
C	3.70279500	-0.65214400	-1.66004800
C	4.38234200	-2.70569500	0.10403700
H	2.80073900	-1.92563400	1.35762000
C	4.72714900	-1.53743400	-1.97885000
H	3.43398300	0.15667500	-2.33114600
C	5.07076000	-2.56339500	-1.09744300
H	4.64444600	-3.50197000	0.79393500
H	5.26320200	-1.42213200	-2.91594200
H	5.87468800	-3.24853700	-1.34856100
B	2.29392600	1.26401900	0.87206300
Cl	2.20425000	0.73288600	2.67852900
Cl	4.05028000	1.83181900	0.54519700
Cl	1.16874000	2.72013100	0.56929900
C	-1.37650800	1.18902200	-0.79126400
C	-2.18769700	1.67502900	0.24111100
C	-3.21113500	2.57199900	-0.06543200
C	-3.37760000	2.95627700	-1.39292300
C	-2.54717200	2.45534200	-2.40400200
C	-1.53036500	1.54352700	-2.12112300
C	-0.71993000	0.23497700	1.20488700
H	-3.86235400	2.95463400	0.71412900
H	-4.16535800	3.65659600	-1.65201500
H	-2.69902600	2.77610800	-3.42954600
H	-0.89162000	1.13782100	-2.89730400
H	-1.06659500	-0.88428300	-0.56652400
H	-0.12462700	-0.40965400	1.83427000
C	-3.15457400	-1.63718900	-0.49811400
C	-3.24948400	-2.29198300	0.74555400

C	-4.31820300	-2.10226900	1.62340000
C	-5.32125300	-1.24123800	1.20656000
C	-5.25771700	-0.58989500	-0.04126500
C	-4.18241300	-0.77187400	-0.89607000
C	-1.86322000	-2.00505700	-1.06860200
C	-1.31529700	-2.94572400	-0.18212800
H	-4.35720400	-2.60660400	2.58343300
H	-6.17402000	-1.06535600	1.85459000
H	-6.06423000	0.07641600	-0.33135200
H	-4.12549500	-0.24585800	-1.84505800
H	-1.57102800	-1.91161600	-2.10923100
H	-0.37946800	-3.48514700	-0.25049100
N	-2.10981800	-3.07472700	0.88897700
H	-1.89112100	-3.63738700	1.70486600
N	-0.48629300	0.20422600	-0.21837000
C	-1.75557300	1.04371700	1.47851300
H	-2.19270600	1.19746000	2.45620500

$TS_{9\text{-}10}$

E (SMD/M06-2X/BS1) = -2133.21948180 au

G (SMD/M06-2X/BS1) = -2132.622128 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2133.22251296 au

C	-0.54580500	0.72548500	-1.50001900
C	0.45412400	0.94298800	-0.53364400
C	0.33648900	1.94462300	0.43431400
C	-0.80235400	2.73753800	0.39154200
C	-1.79971400	2.54244900	-0.58031800
C	-1.68789800	1.53204800	-1.52389600
C	-0.14317200	-0.46477300	-2.24075400
C	1.15592000	-0.75911800	-1.78651300
H	1.10434100	2.10788500	1.18132300
H	-0.92036700	3.53118600	1.12288800
H	-2.67373000	3.18663000	-0.58335400
H	-2.46638100	1.36547300	-2.26239300
H	-0.53908200	-0.78730100	-3.19671900
H	1.81141100	-1.55012600	-2.12327500
N	1.48016700	-0.00261200	-0.72888500
B	2.76561100	-0.09043700	0.12266000
Cl	2.29559800	-0.34054700	1.92548700
Cl	3.80275000	-1.52653500	-0.43360600
Cl	3.72019000	1.49859600	-0.05763600
H	-0.73112400	-1.39037800	-1.30997600
C	-2.63589800	-1.41158000	-0.08050800
C	-2.40122900	-0.64091700	1.07429200

C	-3.31493300	0.28998900	1.56522100
C	-4.50508000	0.42593400	0.86469400
C	-4.76782900	-0.34083300	-0.28555900
C	-3.84290500	-1.25507500	-0.77076200
C	-1.41896700	-2.18016500	-0.33209500
C	-0.57577300	-1.90370900	0.76720200
H	-3.09765200	0.88253900	2.44820400
H	-5.24852900	1.13653900	1.21182300
H	-5.71321300	-0.21020000	-0.80297400
H	-4.04898500	-1.83601800	-1.66476300
H	-1.37018400	-3.11118400	-0.88857500
H	0.40646800	-2.29943300	0.99110700
N	-1.13892300	-0.98068200	1.55229100
H	-0.67472100	-0.53541400	2.33818600

$TS_{10\text{-}11}$

E (SMD/M06-2X/BS1) = -2168.72699749 au

G (SMD/M06-2X/BS1) = -2168.533100 au

E (SMD/M06-2X/BS2//SMD/M06-2X/BS1) = -2169.12260166 au

C	-0.76925800	-0.44592200	1.56966500
O	-0.65418900	-0.93142300	2.60212900
N	-1.19499200	-0.02548900	0.45061800
C	-0.67421500	1.22585400	-0.09133100
C	-0.97269600	2.40855600	0.57343100
C	0.11132600	1.19576100	-1.23667900
C	-0.45365600	3.60241500	0.07810100
H	-1.59481900	2.38942800	1.46327300
C	0.62064400	2.39725700	-1.72135400
H	0.34044300	0.25209700	-1.71830900
C	0.34245100	3.59608600	-1.06549700
H	-0.67430500	4.53444800	0.58815400
H	1.24290300	2.39211600	-2.61035000
H	0.74658200	4.52797600	-1.44807400
B	-2.52081700	-0.71607300	-0.18127100
Cl	-3.88424600	0.51401200	-0.02998600
Cl	-2.15427600	-1.11143000	-1.94014000
Cl	-2.87771400	-2.25045000	0.77997700
C	3.64870200	-0.18973400	0.28379300
C	2.34619500	-0.69046100	0.40635300
C	1.92598700	-1.83610000	-0.25733500
C	2.85944400	-2.48767500	-1.06466900
C	4.16271600	-1.99934000	-1.19265400
C	4.57121500	-0.84432400	-0.51889600
C	3.71784900	1.04782900	1.13176600

C	2.31492800	1.08799600	1.67226500
H	0.90977400	-2.20806700	-0.15043300
H	2.56925900	-3.38621900	-1.60026400
H	4.86939500	-2.52559900	-1.82694700
H	5.58620200	-0.47282100	-0.62599500
H	3.93678300	1.95823500	0.55932000
H	1.93626100	1.85996800	2.33697500
N	1.56335600	0.12902300	1.26545500
H	4.45678600	0.99001500	1.94023600

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[* the benzylic protons (CH_2) in **6a-6i** compounds, appeared as very weak broad singlets in the region between 4.5–5.5 ppm, as evidenced from the HSQC for this compound (Figure S101). This is also supported by this literature report.]

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