Supplementary Information for:

Asymmetric Hydroboration of Ketones Catalyzed by Alkali Metal Complexes Derived from BINOL Ligands

Darren Willcox, Jamie L. Carden, Adam J. Ruddy, Paul D. Newman* and Rebecca L. Melen*

Contents

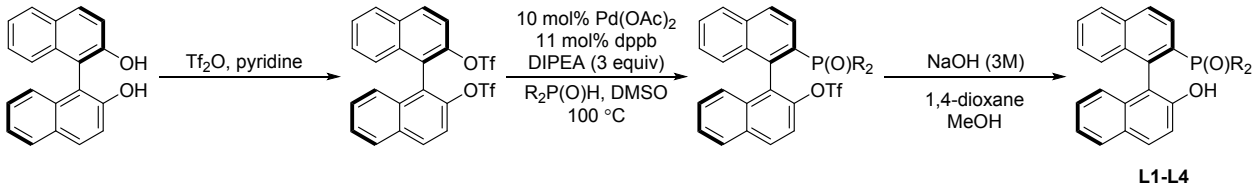
General experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk and glove box techniques. With the exception of THF, all solvents used were dried by passing through an alumina column incorporated into an MB SPS-800 solvent purification system, degassed and stored in an ampoule fitted with a Teflon valve under a nitrogen atmosphere. THF was dried over molten potassium for three days and distilled over argon. Acetone was dried by stirring over magnesium sulphate under a nitrogen atmosphere for 18 hours. Anhydrous DMSO was purchased from Sigma Aldrich and used as received. Deuterated solvents were distilled and/or dried over molecular sieves and stored in a glove box before use. Pinacolborane and *R*-BINOL were purchased from Fluorochem and used as received. ^{1}H, $^{13}C\{^{1}H\}$, ^{11}B and ^{31}P NMR spectra were recorded on a Bruker Avance 300, 400 or 500 MHz spectrometer. Chemical shifts are expressed as parts per million (ppm, δ) and are referenced to $CDCl_3$ (7.26/77.16 ppm) or DMSO (2.50/39.51 ppm). Multinuclear NMR spectra were referenced to $BF_3{\cdot}Et_2O$ (^{11}B), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P). The description of signals includes s = singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet. All coupling constants are absolute values and are expressed in Hertz (Hz).

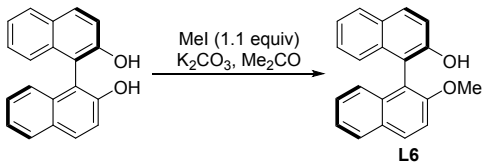
HPLC analyses was performed using an Aglient Technologies 1260 infinity system fitted with a LUX® 5 μm Cellulose-1 column of dimensions 250 x 4.6 mm. Hexane/isopropanol was used as the mobile phase in 90:10 (unless otherwise stated) at a flow rate of 1 mL/min and the products were analysed at 254 nm.

Ligand synthesis

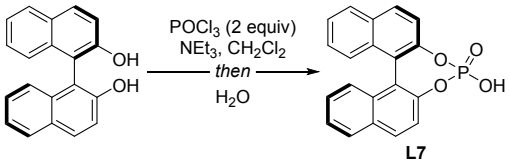
Ligand **L1**, **L2**, **L3** and **L4** were prepared according to the literature method.[1] Ligand **L5** is commercially available, purchased from fluorochem and used as received. Ligand **L6**[2] and **L7**[3] were prepared in accordance with literature procedures. The synthetic routes are depicted in scheme S1-3



Scheme S1 – Synthesis of ligands **L1**-**L4**



Scheme S2 – Synthesis of ligand **L6**



Scheme S3 – Synthesis of ligand **L7**

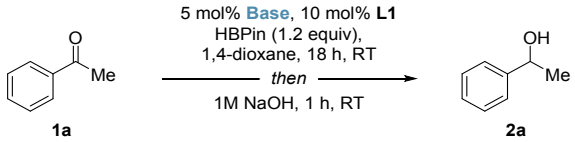
General experimental for hydroboration of ketones using optimised procedure

A flame dried 5 mL microwave vial containing a magnetic stirring bar was charged with **L1** (11.7 mg, 0.025 mmol) and LDA (1.3 mg, 0.0125 mmol) in 1,4-dioxane (0.5 mL) This mixture was stirred at room temperature for 5 minutes. To this bright yellow solution was added pinacolborane (40 μL, 0.275 mmol) followed by the ketone (0.25 mmol). The reaction mixture was then allowed to stir under a nitrogen atmosphere for 18 hours. After 18 hours the reaction was quenched with 1M NaOH (1M, 1 mL) and allowed to stir for 1 hour. The mixture was extracted with ether (3 x 5 mL) and the organic layer was dried (Na_2SO_4) and purified by flash column chromatography using 2:1 hexane/diethyl ether as the eluent.

Optimization tables for ketone hydroboration

All reactions were performed according to the general procedure above.

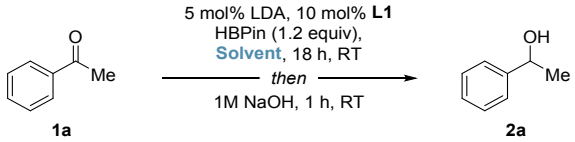
Table S1 – Base Screen:



Entry	Base	Yield (%)[a]	e.r (%)[b]
1	NaO^{t}Bu	94	70:30
2	LiO^{t}Bu	99	70.30
3	KO^{t}Bu	95	53:47
4	n-BuLi	95	71:29
5	LiHMDS	99	55:45
6	LiH	70	68:32
7	LDA	94	79:21
8	$LiNH_2$	99	66:34

a) NMR yield using 1,1,2,2-tetrachloroethane as internal standard; b) measured using chiral HPLC

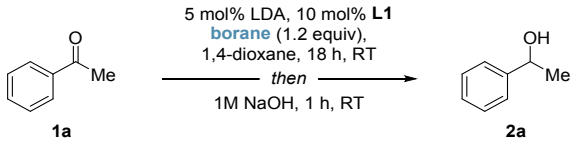
Table S2 – Solvent Screen:



Entry	Solvent	Yield (%)[a]	e.r (%)[b]
1	1,4-dioxane	94	79:21
2	^{t}BuOMe	>99	65:35
3	Et_2O	99	65:35
4	THF	98	65:35
5	PhMe	96	50:50
6	CH_2Cl_2	98	56:44

a) NMR yield using 1,1,2,2-tetrachloroethane as internal standard; b) measured using chiral HPLC

Table S3 – Borane screen:

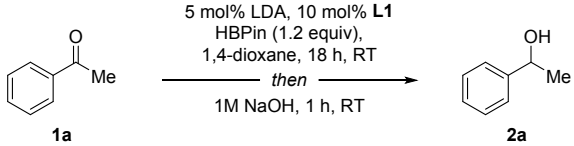


1a 2a

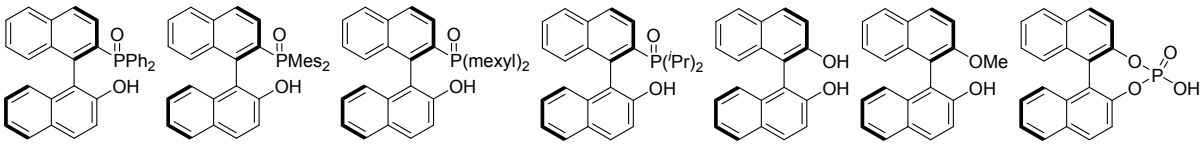
Entry	Base	Yield (%)[a]	e.r (%)[b]
1	HBPin	94	79:21
2	HBCat	98	56:44
3	$BH_3.HNMe_2$	54	53:47
4	$HBCl_2.SMe_2$	6	N.D.

a) NMR yield using 1,1,2,2-tetrachloroethane as internal standard; b) measured using chiral HPLC

Scheme S4 – Ligand screen:



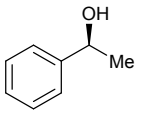
1a 2a



L1 94% (79:21 e.r) **L2** 99% (58:42 e.r) **L3** 96% (57.5:42.5 e.r) **L4** 97% (53:47 e.r) **L5** 81% (52:48 e.r) **L6** 97% (51:49 e.r) **L7** 55% (50:50 e.r)

Product characterization

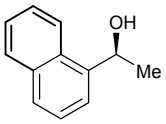
(*S*)-1-Phenylethanol (**2a**)[4]



Prepared according to the general procedure using acetophenone (30 μL, 0.25 mmol) to afford the title compound as a colorless oil (29 mg, 95%). Spectroscopic data agrees with the literature.

R*f* = 0.19 (hexane/ether 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.41–7.32 (3H, m), 7.31–7.23 (2H, m), 4.91 (1H, q, *J* = 6.1 Hz), 1.79 (1H, s), 1.51 (3H, d, *J* = 6.5 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ_C: 145.9, 128.6, 127.6, 125.5, 70.6, 25.3. **HPLC**: eluent 90:10 hexane/isopropanol: (*R*)-enantiomer: t_R = 6.69 min; (*S*)-enantiomer: t_R = 7.75 min. $[\alpha_d^{20}]$ = −0.04° (c = 1, $CHCl_3$).

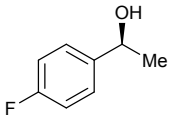
(*S*)-1-(Naphthalen-1-yl)ethan-1-ol (**2b**)[5]



Prepared according to the general procedure using 1-acetylnaphthalene (38 μL, 0.25 mmol) to afford the title compound as a colorless oil (33 mg, 77%). Spectroscopic data agrees with the literature.

R*f* = 0.18 (hexane/ether 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 8.14–8.12 (1H, m), 7.91–7.86 (1H, m), 7.80–7.78 (1H, m), 7.70–7.67 (1H, m), 7.56–7.46 (3H, m), 5.70 (1H, q, *J* = 6.5 Hz), 1.90 (1H, s), 1.69 (3H, d, *J* = 6.5 Hz); **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ_C: 141.5, 134.0, 130.4, 129.1, 128.1, 126.2, 125.7, 125.7, 123.3, 122.1, 67.3, 24.5; **HPLC**: eluent 80:20 hexane/isopropanol: (*S*)-enantiomer: t_R = 7.43 min; (*R*)-enantiomer: t_R = 12.53 min. $[\alpha_d^{20}]$ = −0.06° (c = 1, $CHCl_3$).

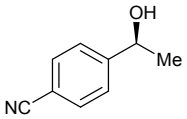
(*S*)-1-(4-Fluorophenyl)ethan-1-ol (**2c**)[4]



Prepared according to the general procedure using 4-fluoroacetophenone (31 μL, 0.25 mmol) to afford the title compound as a colorless oil (31 mg, 88%). Spectroscopic data agrees with the literature.

R*f* = 0.20 (hexane/ether 2:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H: 7.35–7.23 (2H, m), 6.98–6.90 (2H, m), 4.80 (1H, q, *J* = 6.5 Hz), 1.93 (1H, s), 1.39 (3H, d, *J* = 6.5 Hz); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ_C: 162.2 (d, *J* = 245.1 Hz), 141.6 (d, *J* = 3.1 Hz), 127.2 (d, *J* = 8.1 Hz), 115.4 (d, *J* = 21.3 Hz), 69.9, 25.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ_F: −115.35 (s). **HPLC**: eluent 90:10 hexane/isopropanol: (*S*)-enantiomer: t_R = 8.26 min; (*R*)-enantiomer: t_R = 8.63 min. $[\alpha_d^{20}]$ = −0.05° (c = 1, $CHCl_3$).

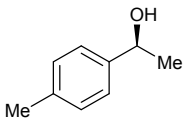
(*S*)-4-(1-Hydroxyethyl)benzonitrile (**2d**)[6]



Prepared according to the general procedure using 4-acetylbenzonitrile (36 mg, 0.25 mmol) to afford the title compound as a colorless oil (35 mg, 95%). Spectroscopic data agrees with the literature.

R*f* = 0.13 (hexane/ether 1:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H: 7.68–7.61 (2H, m), 7.51–7.46 (2H, m), 4.97 (1H, q, *J* = 6.5 Hz), 1.93 (1H, s), 1.50 (3H, d, *J* = 6.5 Hz); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ_C: 151.2, 132.5, 126.2, 119.0, 111.3, 69.8, 25.6; **HPLC**: eluent 95:5 hexane/isopropanol: (*S*)-enantiomer: t_R = 18.75 min; (*R*)-enantiomer: t_R = 20.36 min. $[\alpha_d^{20}]$ = −0.12° (c = 1, $CHCl_3$).

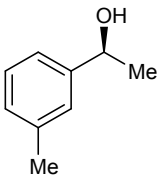
(*S*)-1-(*p*-Tolyl)ethan-1-ol (**2e**)[4]



Prepared according to the general procedure using 4-acetyltoluene (34 μL, 0.25 mmol) to afford the title compound as a colorless oil (30.6 mg, 90%). Spectroscopic data agrees with the literature.

R*f* = 0.16 (hexane/ether 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.29–7.25 (2H, m), 7.19–7.15 (1H, m), 4.86 (1H, q, *J* = 6.2 Hz), 2.35 (3H, s), 1.92 (1H, s), 1.49 (3H, d, *J* = 6.5 Hz); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ_C: 143.9, 137.3, 129.3, 125.5, 70.4, 25.2, 21.2; **HPLC**: eluent 90:10 hexane/isopropanol: (*S*)-enantiomer: t_R = 6.65 min; (*R*)-enantiomer: t_R = 7.09 min. $[\alpha_d^{20}]$ = −0.03° (c = 1, $CHCl_3$).

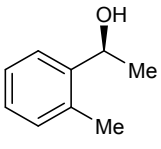
(*S*)-1-(*m*-Tolyl)ethan-1-ol (**2f**)[7]



Prepared according to the general procedure using 3-methylacetophenone (34 μL, 0.25 mmol) to afford the title compound as a colorless oil (32 mg, 95%). Spectroscopic data agrees with the literature.

R*f* = 0.22 (hexane/ether 2:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H: 7.24 (1H, d, *J* = 7.5 Hz), 7.20–7.19 (1H, m), 7.18–7.16 (1H, m), 7.11–7.08 (1H, m), 4.87 (1H, q, *J* = 6.5 Hz), 2.36 (3H, s), 1.78 (1H, s), 1.49 (3H, d, *J* = 6.5 Hz); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ_C: 145.9, 138.3, 128.6, 128.4, 126.2, 122.6, 70.6, 25.3, 21.6; **HPLC**: eluent 90:10 hexane/isopropanol: (*R*)-enantiomer: t_R = 6.32 min; (*S*)-enantiomer: t_R = 7.21 min. $[\alpha_d^{20}]$ = −0.07° (c = 1, $CHCl_3$).

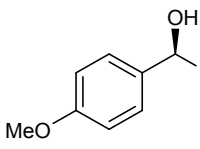
(*S*)-1-(*o*-Tolyl)ethan-1-ol (**2g**)[4]



Prepared according to the general procedure using 2-methylacetophenone (34 μL, 0.25 mmol) to afford the title compound as a colorless oil (16 mg, 47%). Spectroscopic data agrees with the literature.

R*f* = 0.32 (hexane/ether 2:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H: 7.53–7.51 (1H, m), 7.28–7.21 (1H, m), 7.21–7.10 (2H, m), 5.14 (1H, q, *J* = 6.4 Hz), 2.35 (3H, s), 1.68 (1H, s), 1.47 (3H, d, *J* = 6.4 Hz); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ_C: 144.0, 134.4, 130.5, 127.3, 126.5, 124.6, 67.0, 24.1, 19.1.; **HPLC**: eluent 90:10 hexane/isopropanol: (*R*)-enantiomer: t_R = 6.29 min; (*S*)-enantiomer: t_R = 7.17 min. $[\alpha_d^{20}]$ = −0.05° (c = 1, $CHCl_3$).

(*S*)-1-(4-Methoxyphenyl)ethan-1-ol (**2h**)[6]

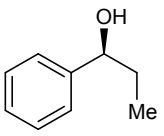


Prepared according to the general procedure using 4-methoxyacetophenone (37.5 mg, 0.25 mmol) to afford the title compound as a colorless oil (23 mg, 60%). Spectroscopic data agrees with the literature.

R*f* = 0.10 (hexane/ether 2:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H: 7.33–7.28 (2H, m), 6.92–6.85 (2H, m), 4.86 (1H, q, *J* = 6.4 Hz), 3.81 (3H, s), 1.74 (1H, s), 1.48 (3H, d, *J* = 6.4 Hz); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ_C: 159.0, 138.0, 126.7, 113.9, 70.0, 55.3, 25.0; **HPLC**: eluent

90:10 hexane/isopropanol: (*R*)-enantiomer: t_R = 7.10 min; (S)-enantiomer: t_R = 7.99 min. $[\alpha_d^{20}]$ = −0.03° (c = 1, $CHCl_3$).

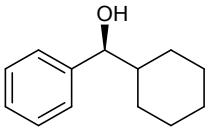
(*S*)-1-Phenylpropan-1-ol (**2i**)[8]



Prepared according to the general procedure using propiophenone (33 μL, 0.25 mmol) to afford the title compound as a colorless oil (32 mg, 94%). Spectroscopic data agrees with the literature.

R*f* = 0.21 (hexane/ether 2:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H: 7.36–7.33 (4H, m), 7.31–7.26 (1H, m), 4.60 (1H, dd, *J* = 7.1, 6.1 Hz), 1.87–1.72 (2H, m), 0.92 (3H, t, *J* = 7.4 Hz); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ_C: 144.7, 128.6, 127.7, 126.1, 76.2, 32.0, 10.3; **HPLC**: eluent 97.5:2.5 hexane/isopropanol: (*R*)-enantiomer: t_R = 14.22 min; (S)-enantiomer: t_R = 15.22 min. $[\alpha_d^{20}]$ = −0.04° (c = 1, $CHCl_3$).

(*S*)-Cyclohexyl(phenyl)methanol (**2j**)[7]



Prepared according to the general procedure using cyclohexyl phenyl Ketone (47 mg, 0.25 mmol) to afford the title compound as a colorless oil (34 mg, 71%). Spectroscopic data agrees with the literature.

R*f* = 0.33 (hexane/ether 2:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H: 7.54–6.99 (5H, m), 4.37 (1H, dd, *J* = 7.2, 2.9 Hz), 2.02–1.96 (1H, m), 1.82 (1H, d, *J* = 3.1 Hz), 1.79–1.75 (1H, m), 1.71–1.58 (3H, m), 1.38 (1H, m), 1.29–0.85 (5H, m); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ_C: 143.8, 128.3, 127.6, 126.8, 79.5, 45.1, 29.5, 29.0, 26.6, 26.2, 26.1; **HPLC**: eluent 90:10 hexane/isopropanol: (S)-enantiomer: t_R = 6.15 min; (*R*)-enantiomer: t_R = 7.63 min. $[\alpha_d^{20}]$ = −0.02° (c = 1, $CHCl_3$).

Preliminary mechanistic investigations

Addition of LDA to ligand. In 1,4-dioxane with benzene-d_6 lock. To a 5 mL microwave vial was added (*R*)-**L1** (0.024 g, 0.10 mmol) and lithium diisopropylamide (0.036 mg, 0.10 mmol) in 1,4-dioxane (1.0 mL) and benzene-d_6 (0.25 mL). After 0.5 h, the resulting reaction mixture was examined by ^{1}H NMR spectroscopy using a presaturation method.

Figure S1 – (*R*)-**L1**

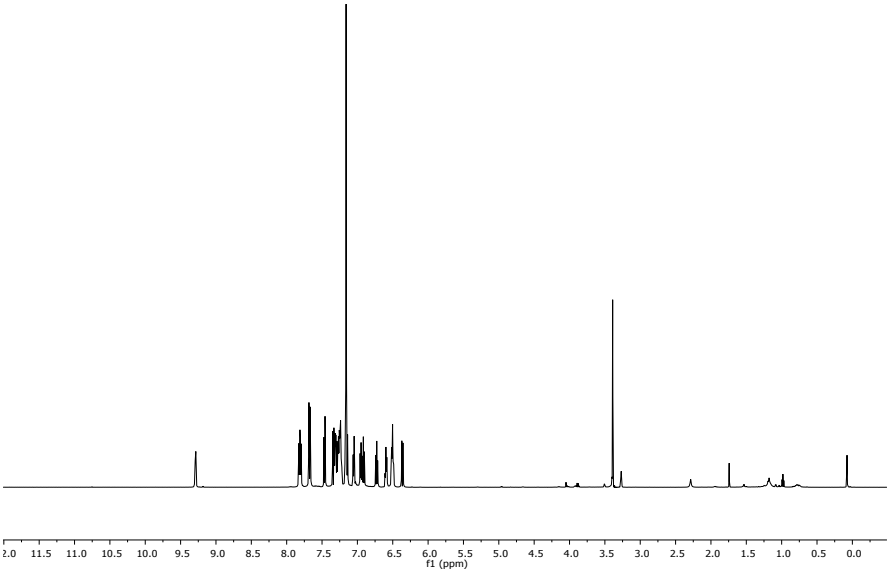
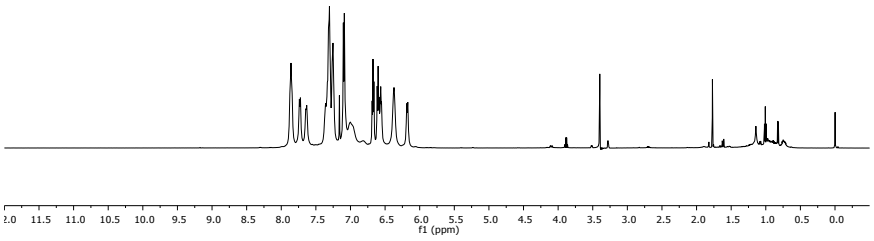


Figure S2 – (R)-**L1** + LDA



Addition of Li-alkoxide to pinacolborane. In 1,4-dioxane with benzene-d_6 lock. To a 5 mL microwave vial was added (*R*)-**L1** (0.024 g, 0.10 mmol) and lithium diisopropylamide (0.036 mg, 0.10 mmol) in 1,4-dioxane (1.0 mL) and benzene-d_6 (0.25 mL). After 0.5 h, pinacolborane (0.10 mmol) was added and the mixture stirred for a further 0.5 h. The resulting reaction mixture was examined by ^{11}B NMR spectroscopy.

Figure S3 – *HBPin*

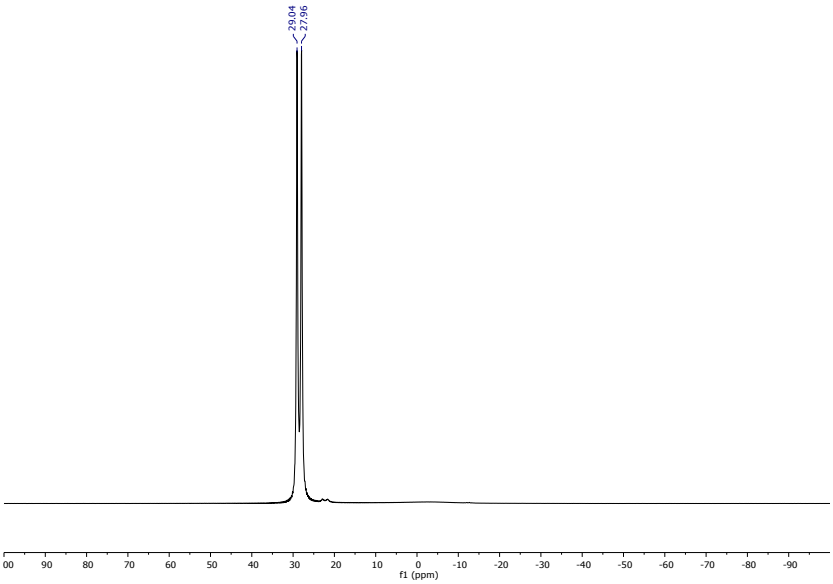
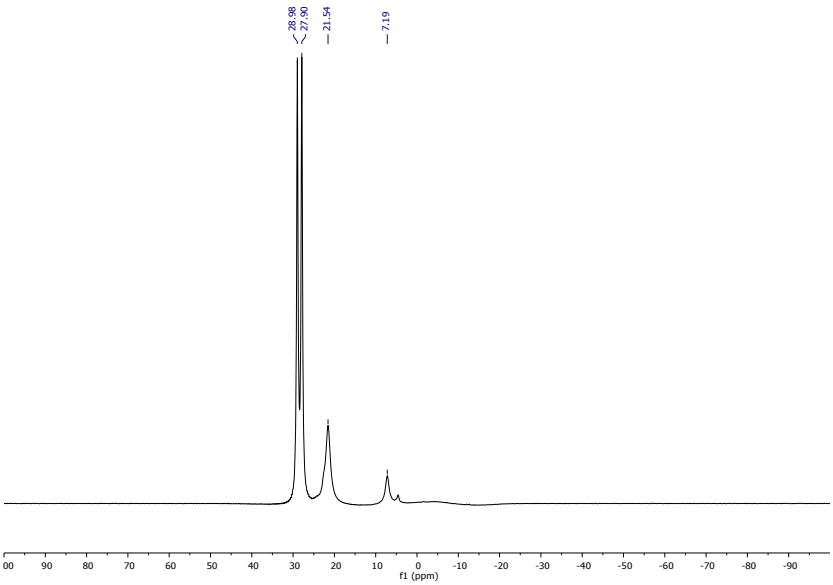


Figure S4 – *HBPin + **L1** + LDA*



NMR spectra

Figure S5 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2a**

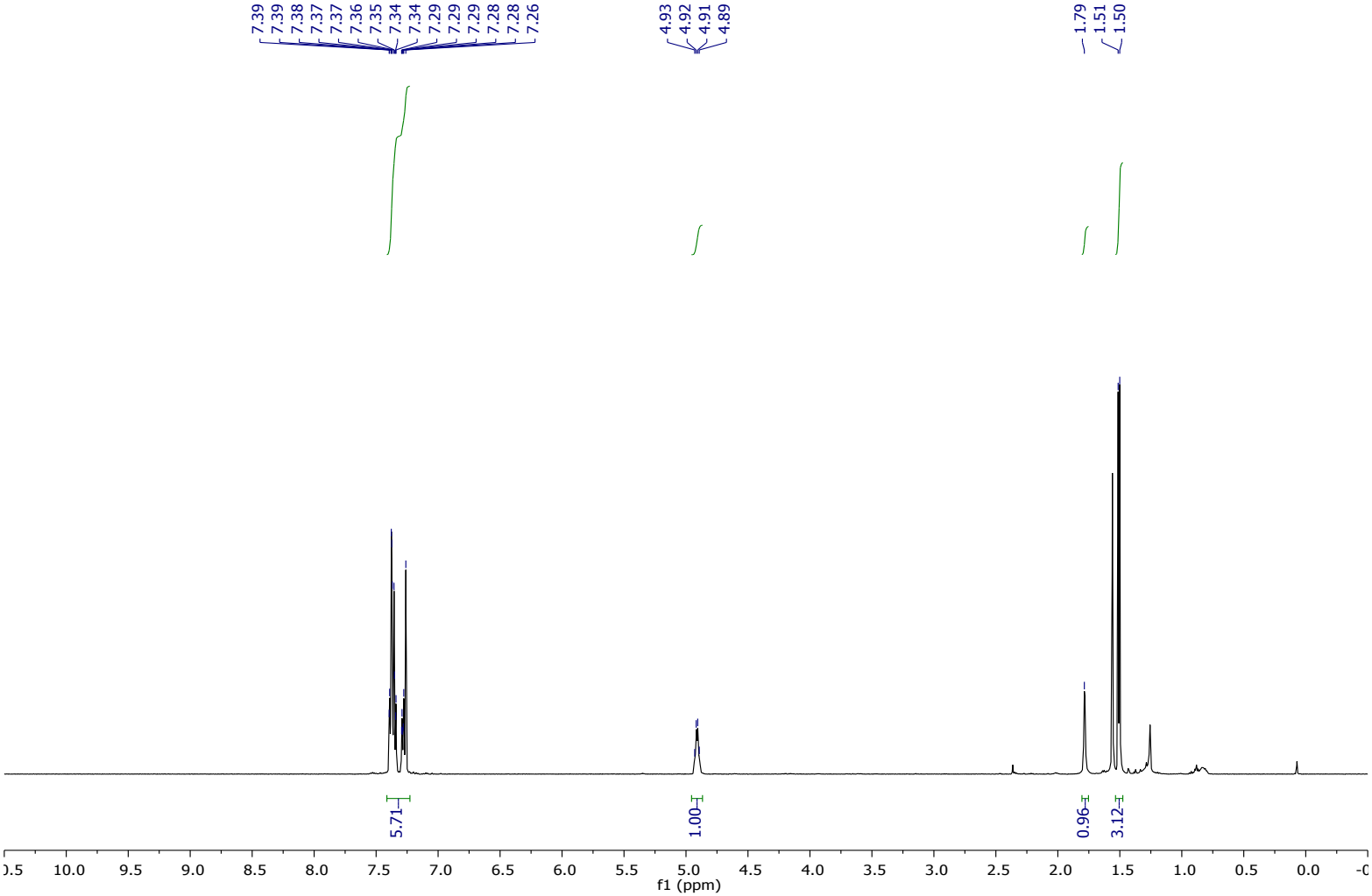


Figure S6 – $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2a**

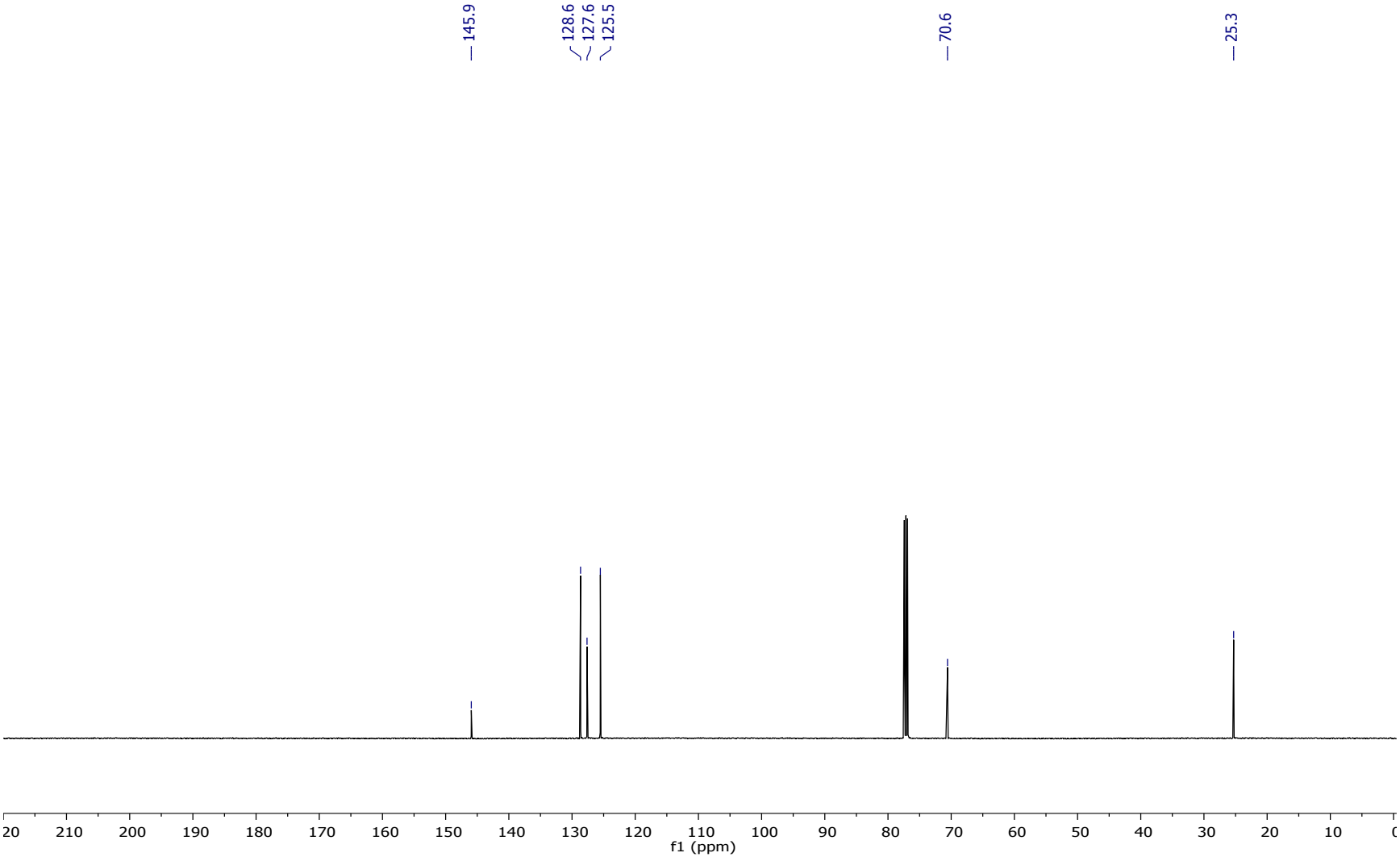


Figure S7 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2b**

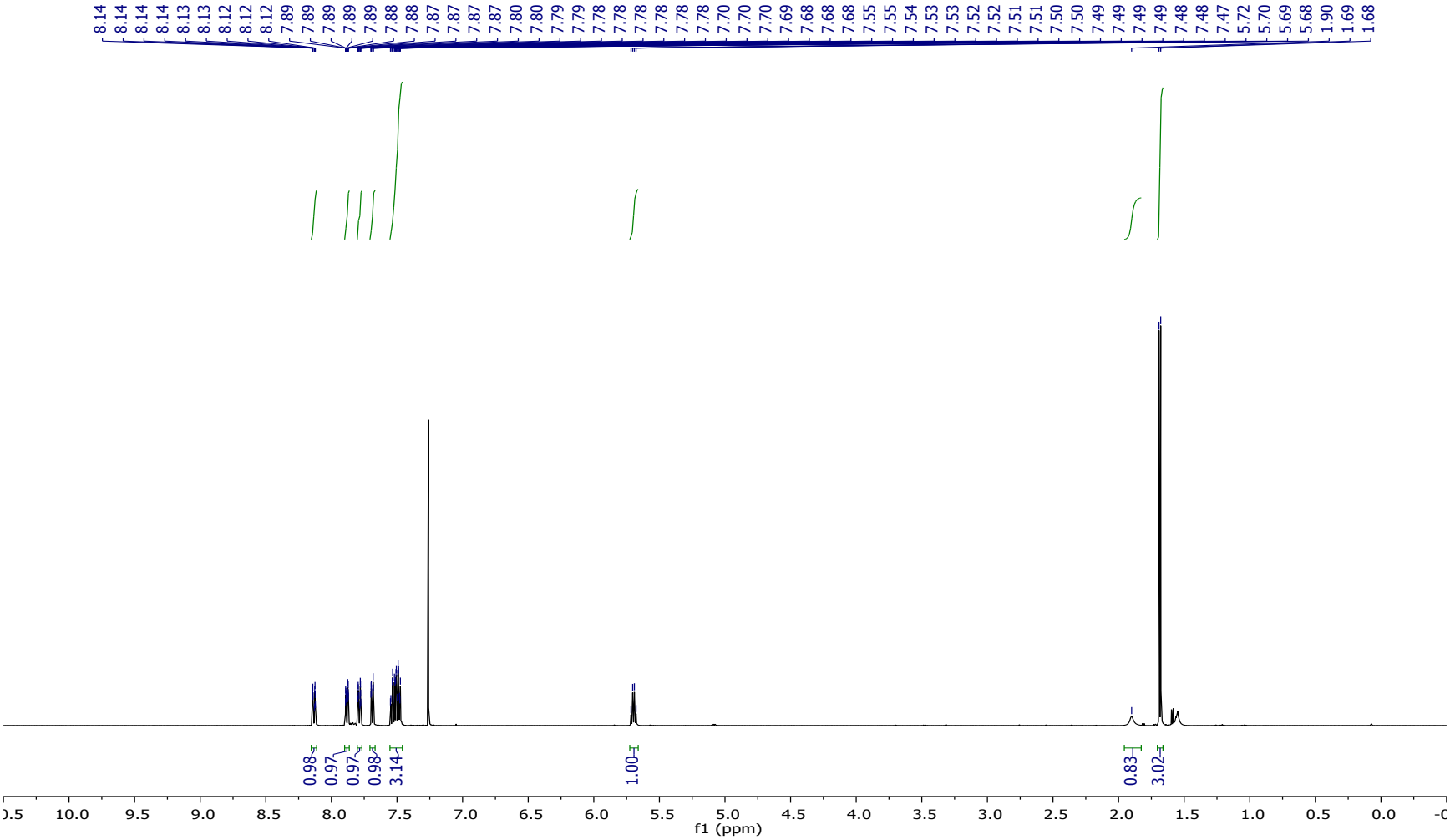


Figure S8 – $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2b**

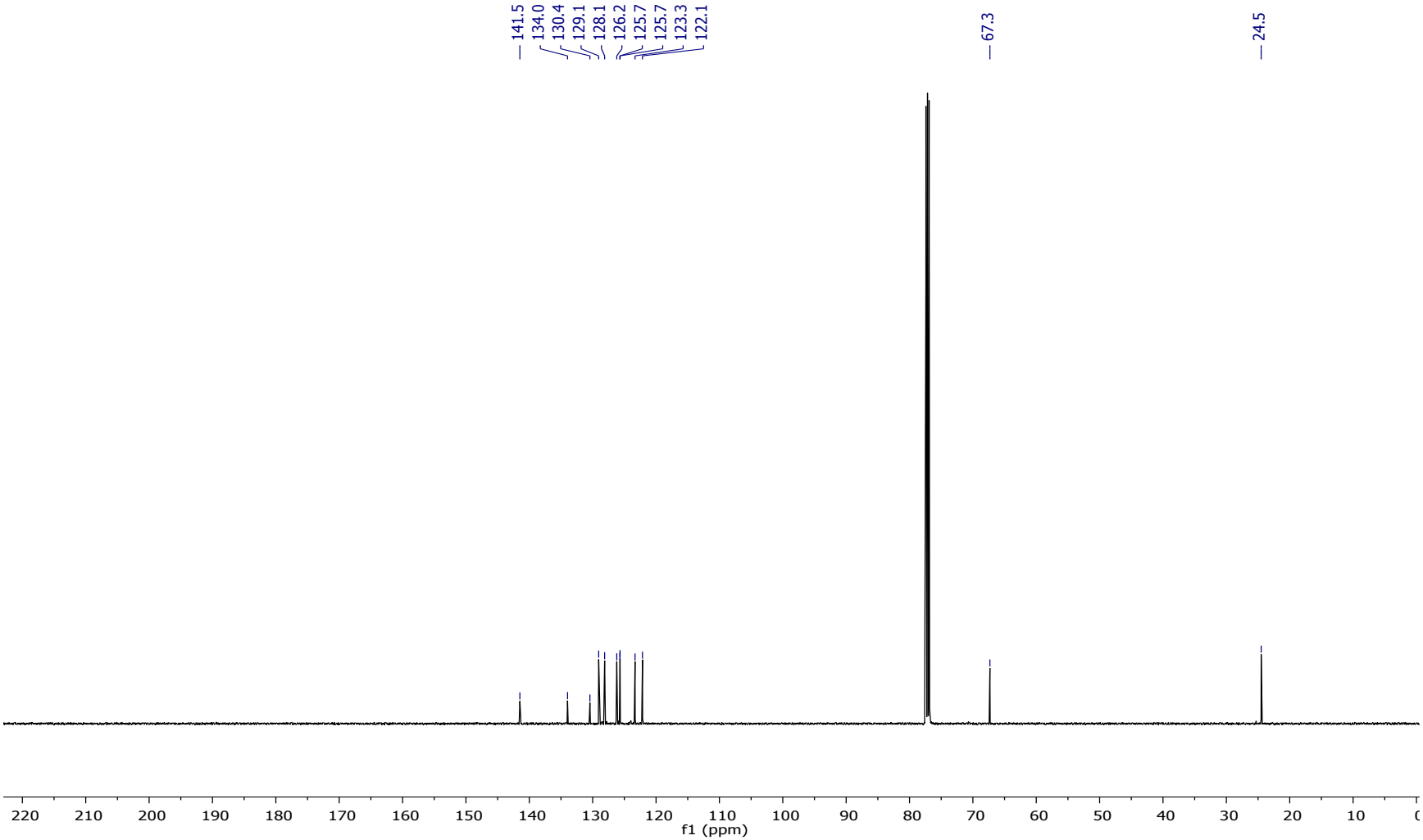


Figure S9 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2c**

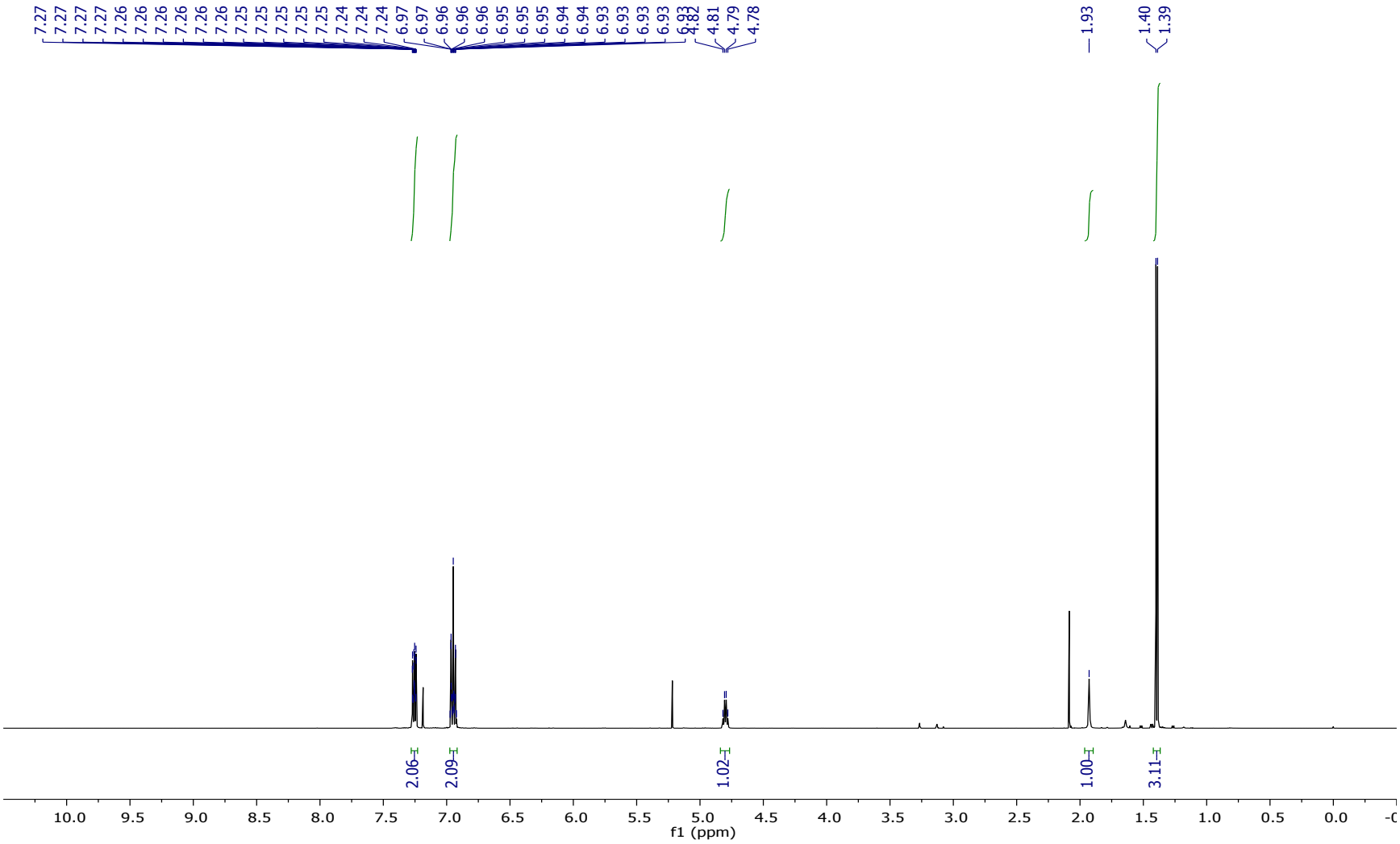


Figure S10 – $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2c**

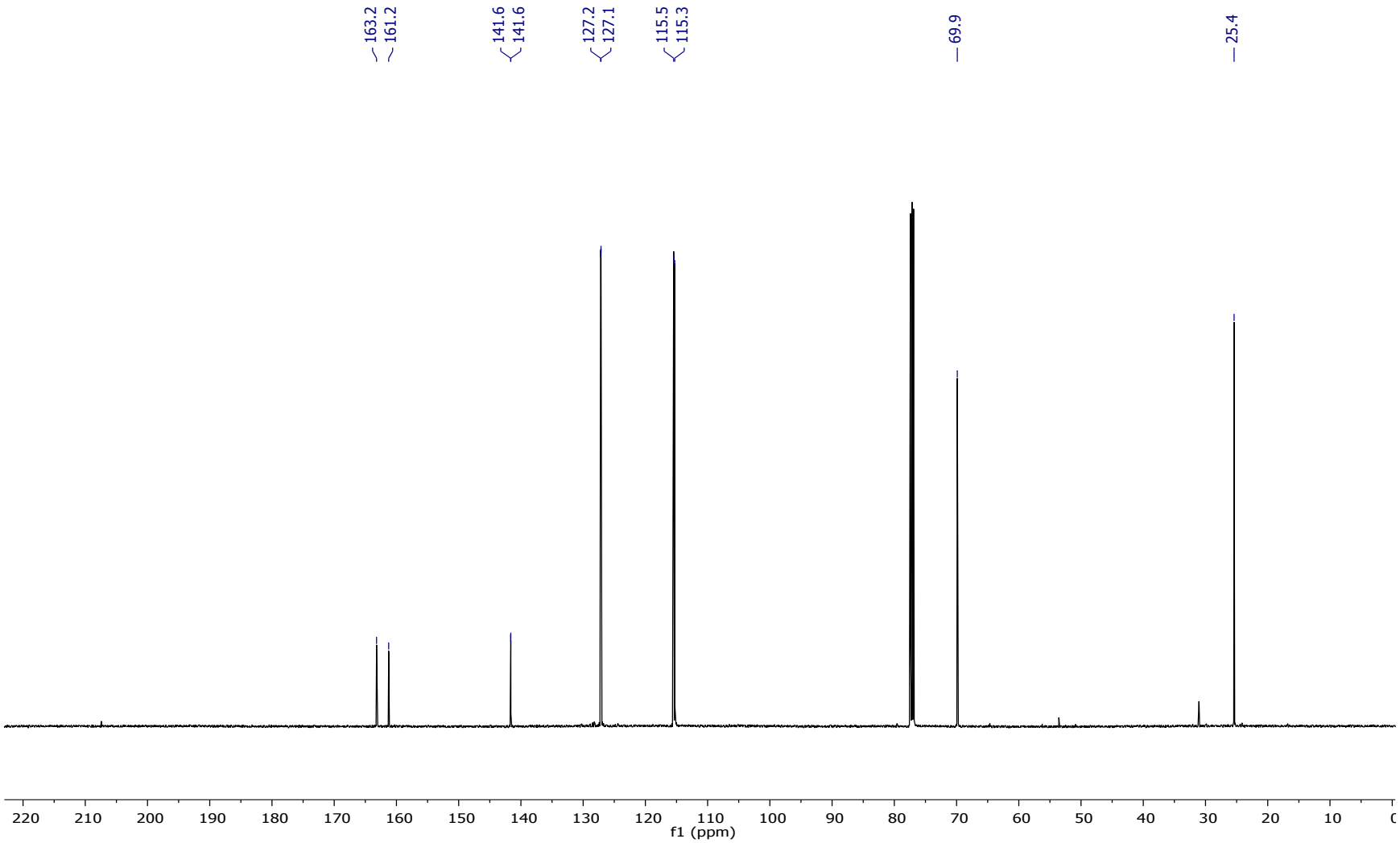


Figure S11 – $^{19}F\{^{1}H\}$ (471 MHz, $CDCl_3$, 298 K) NMR spectrum of **2c**

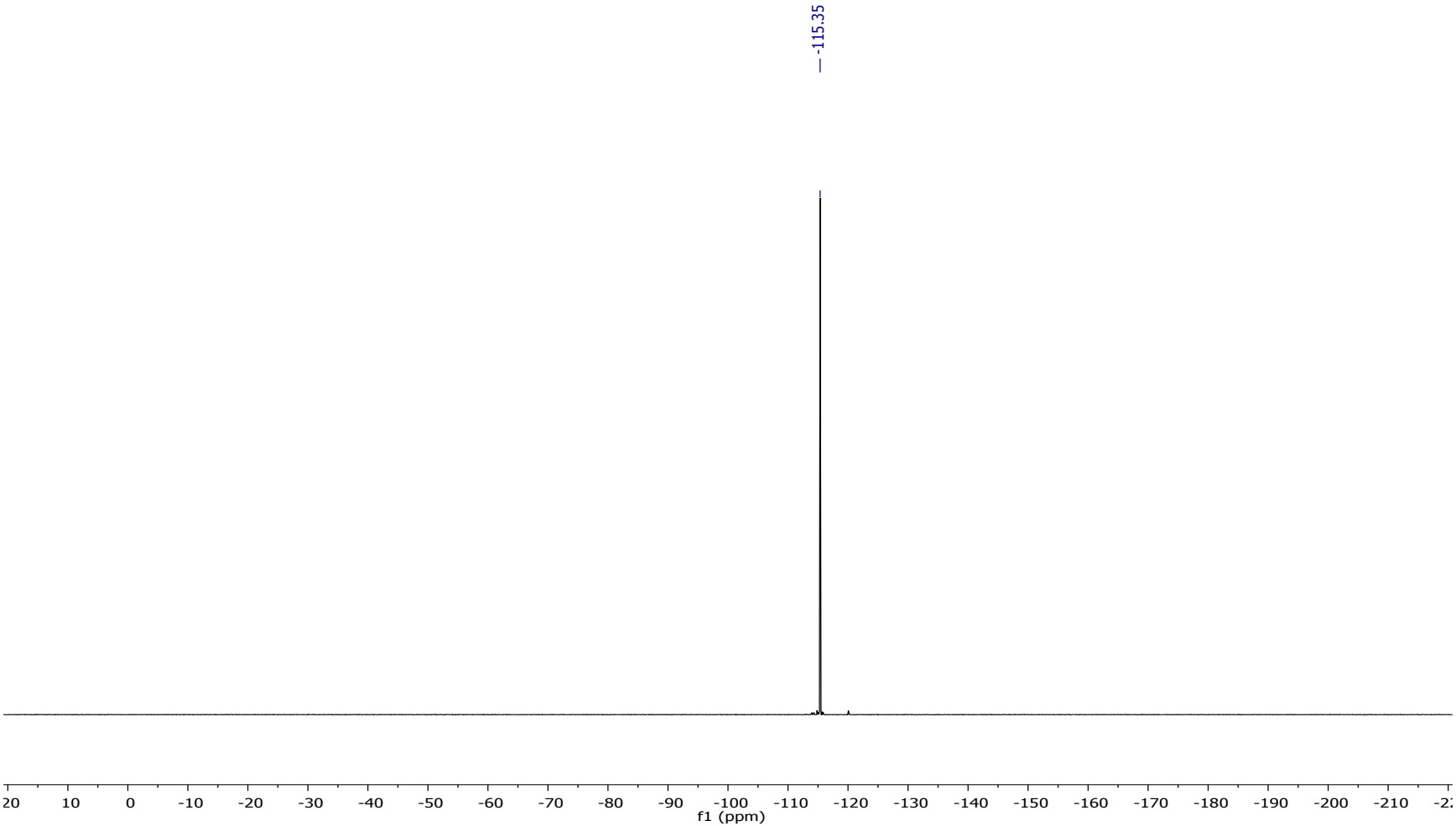


Figure S12 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2d**

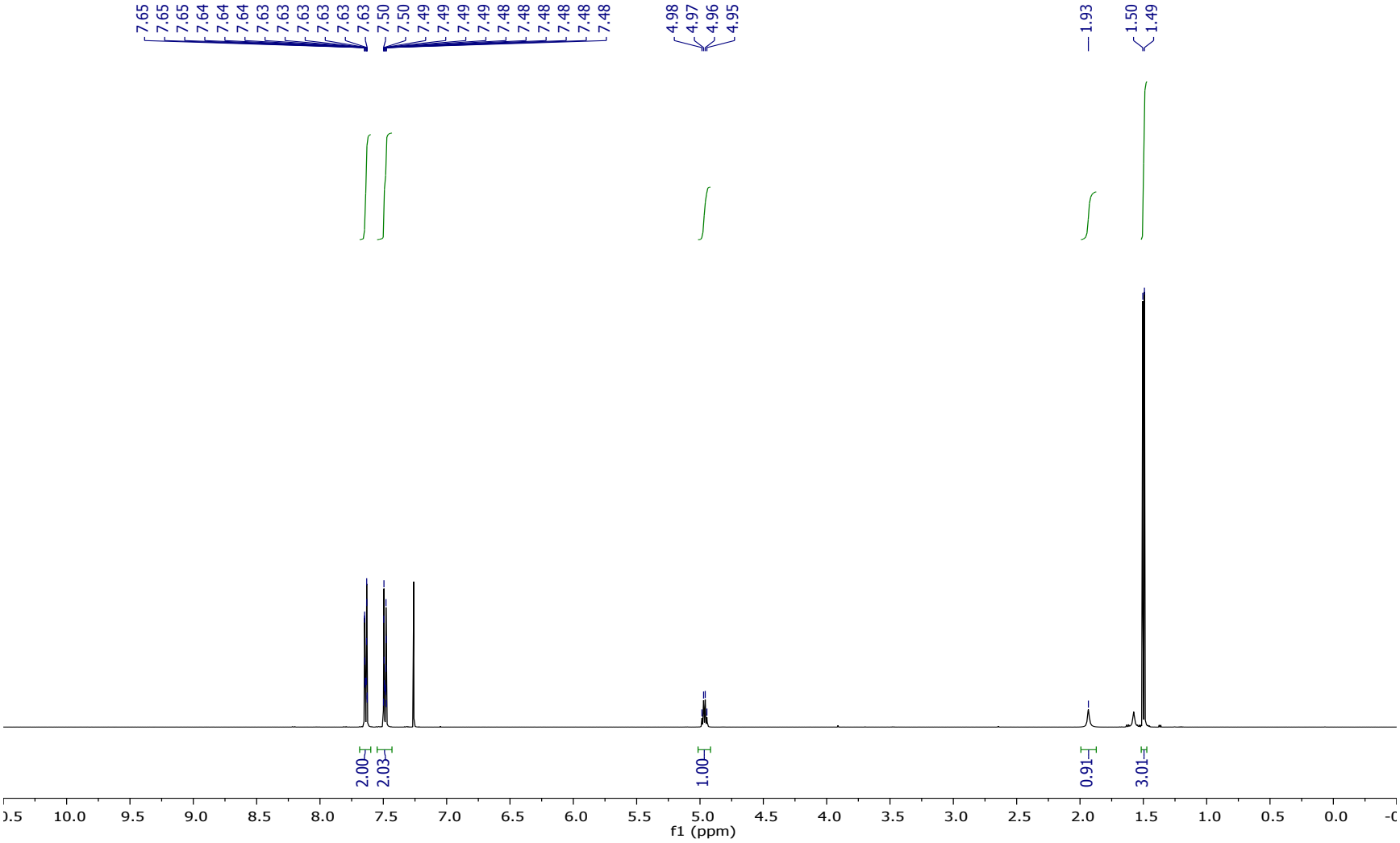


Figure S13 – $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2d**

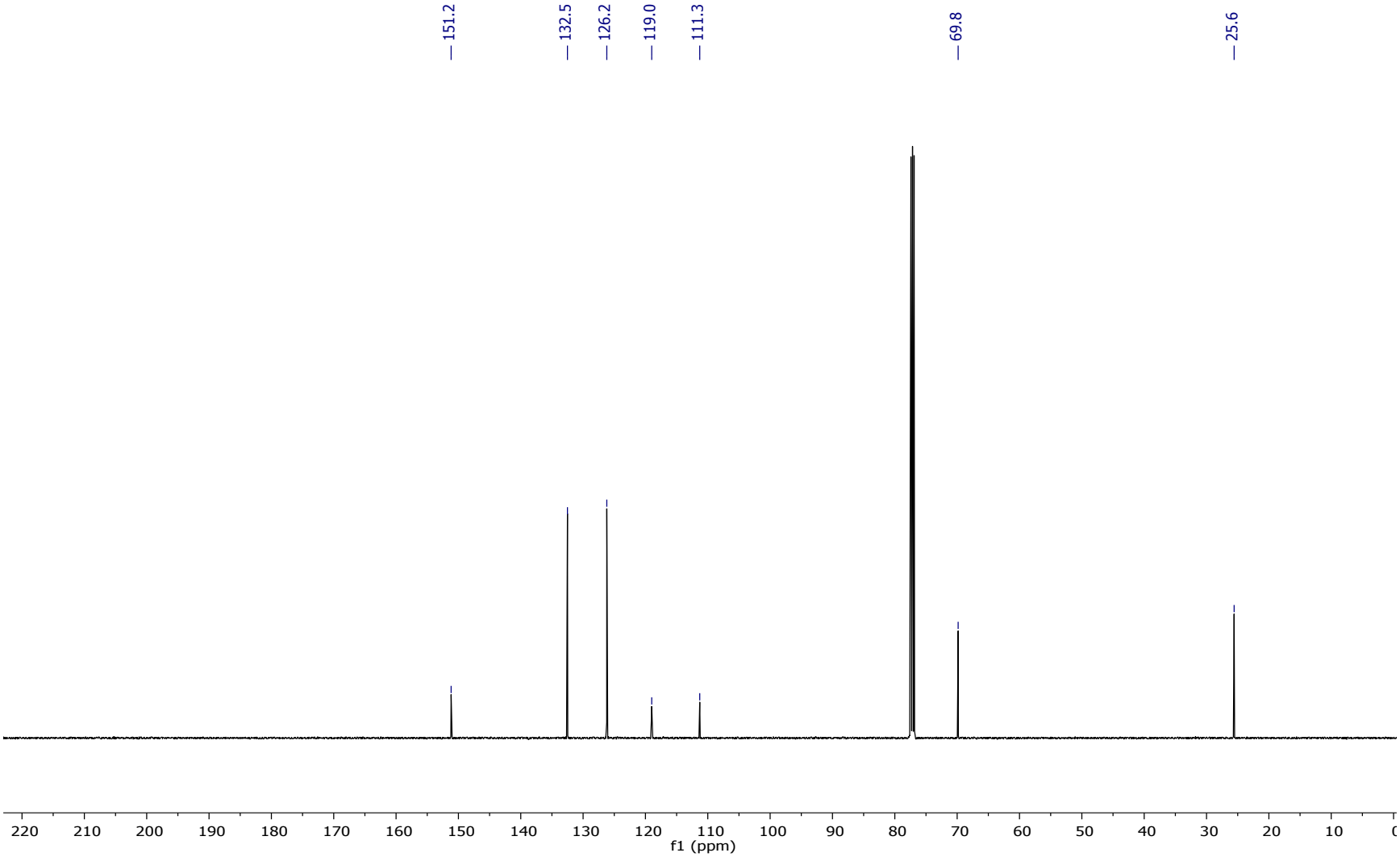


Figure S14 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2e**

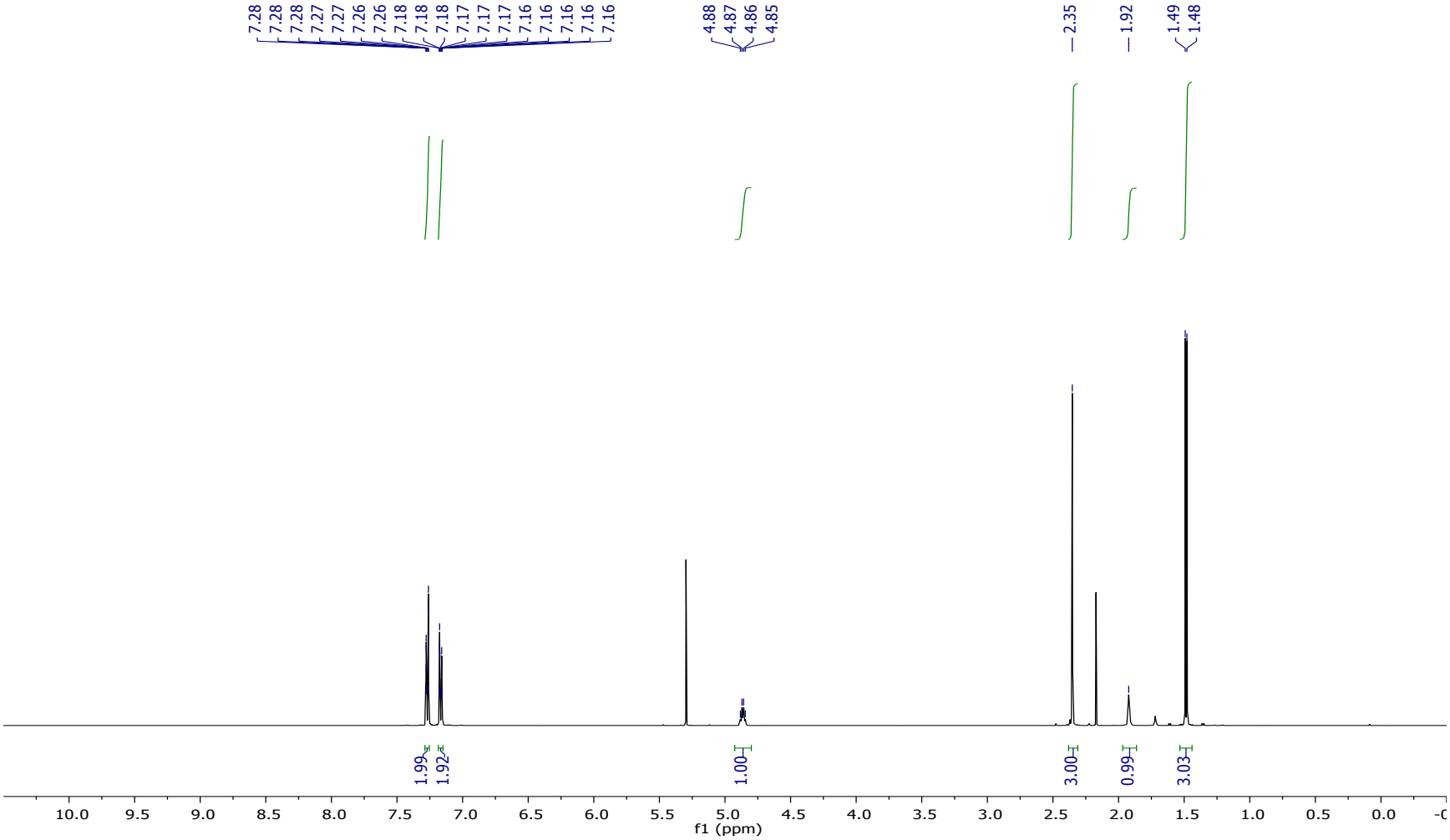


Figure S15 – $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2e**

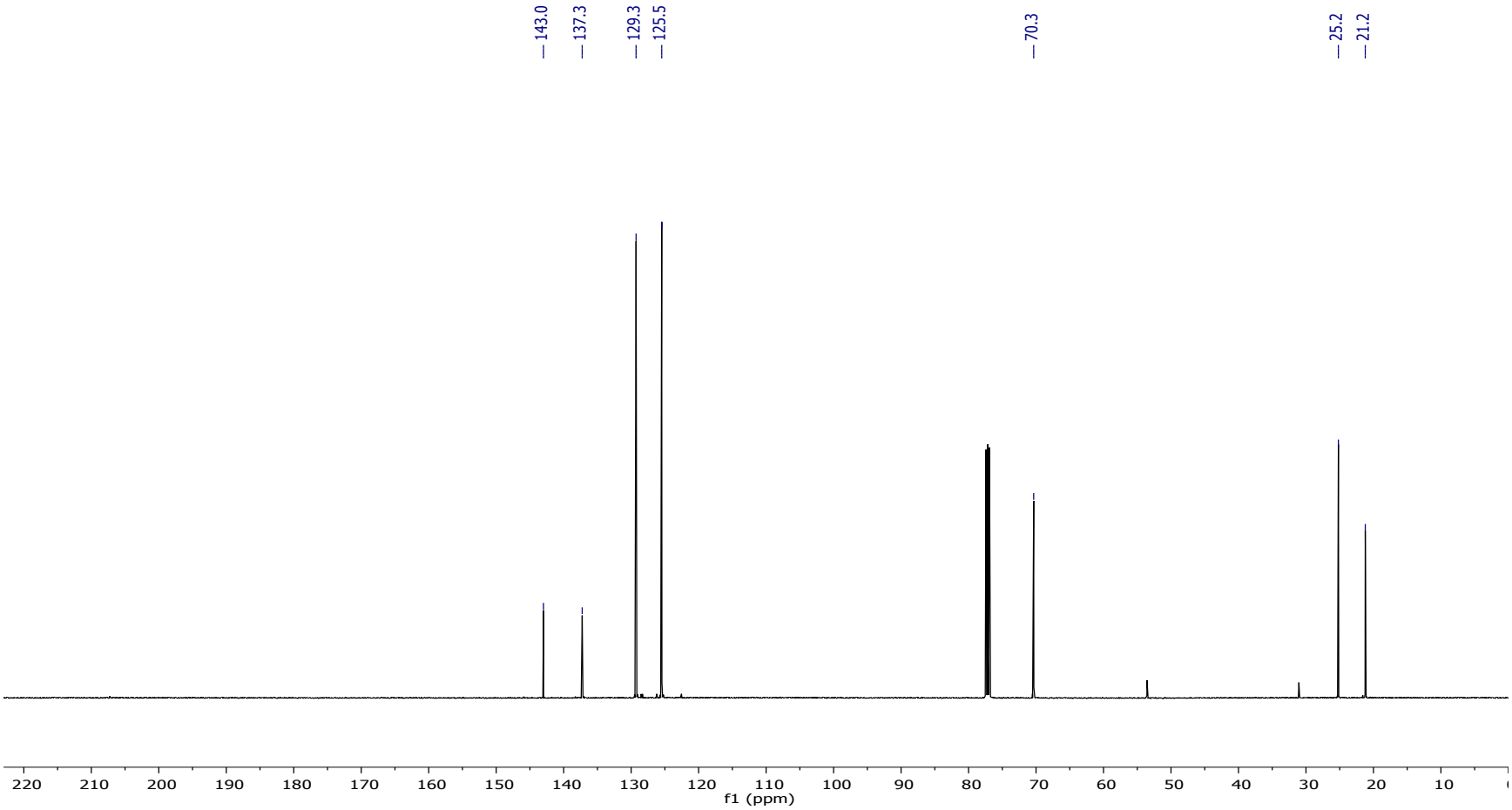


Figure S16 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2f**

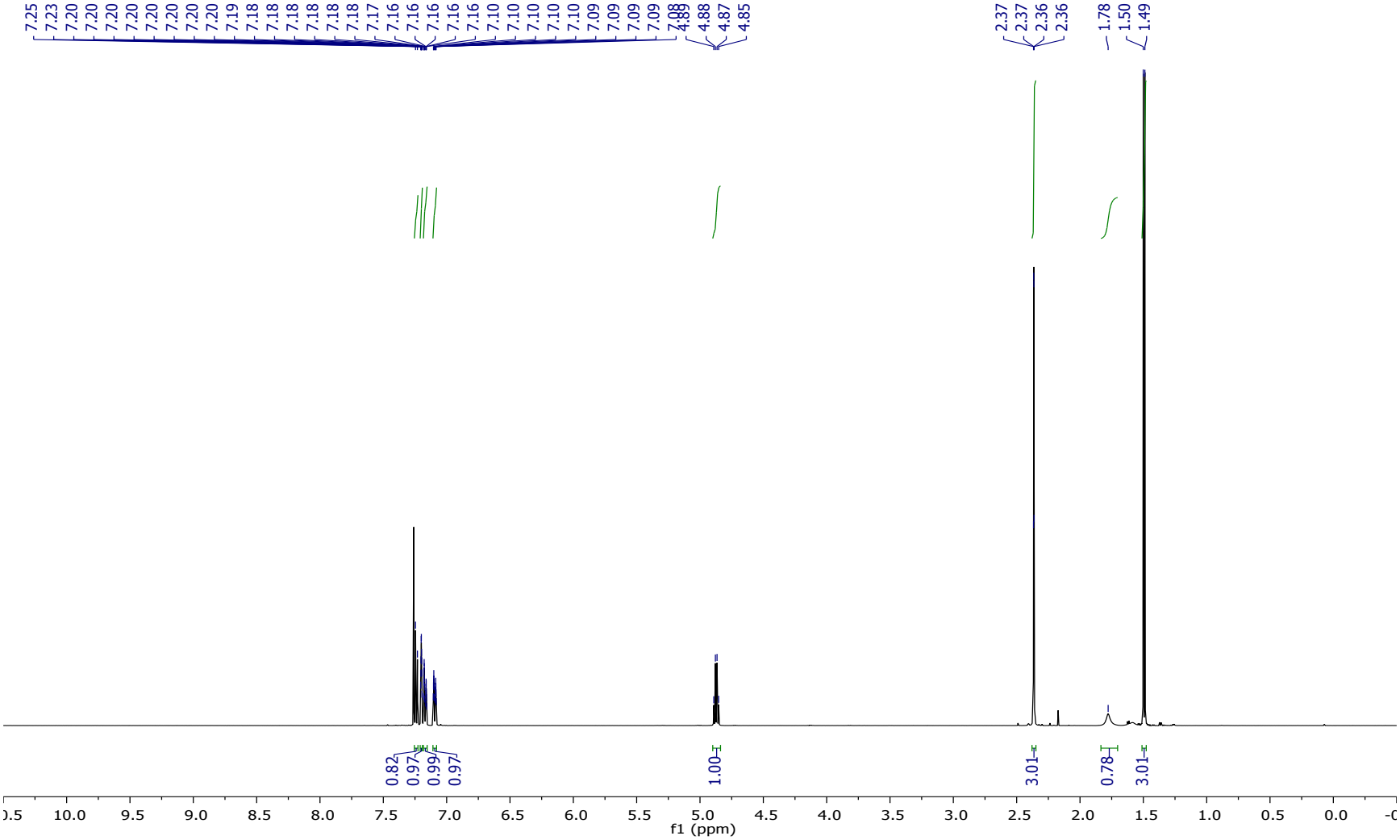


Figure S17 – $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2f**

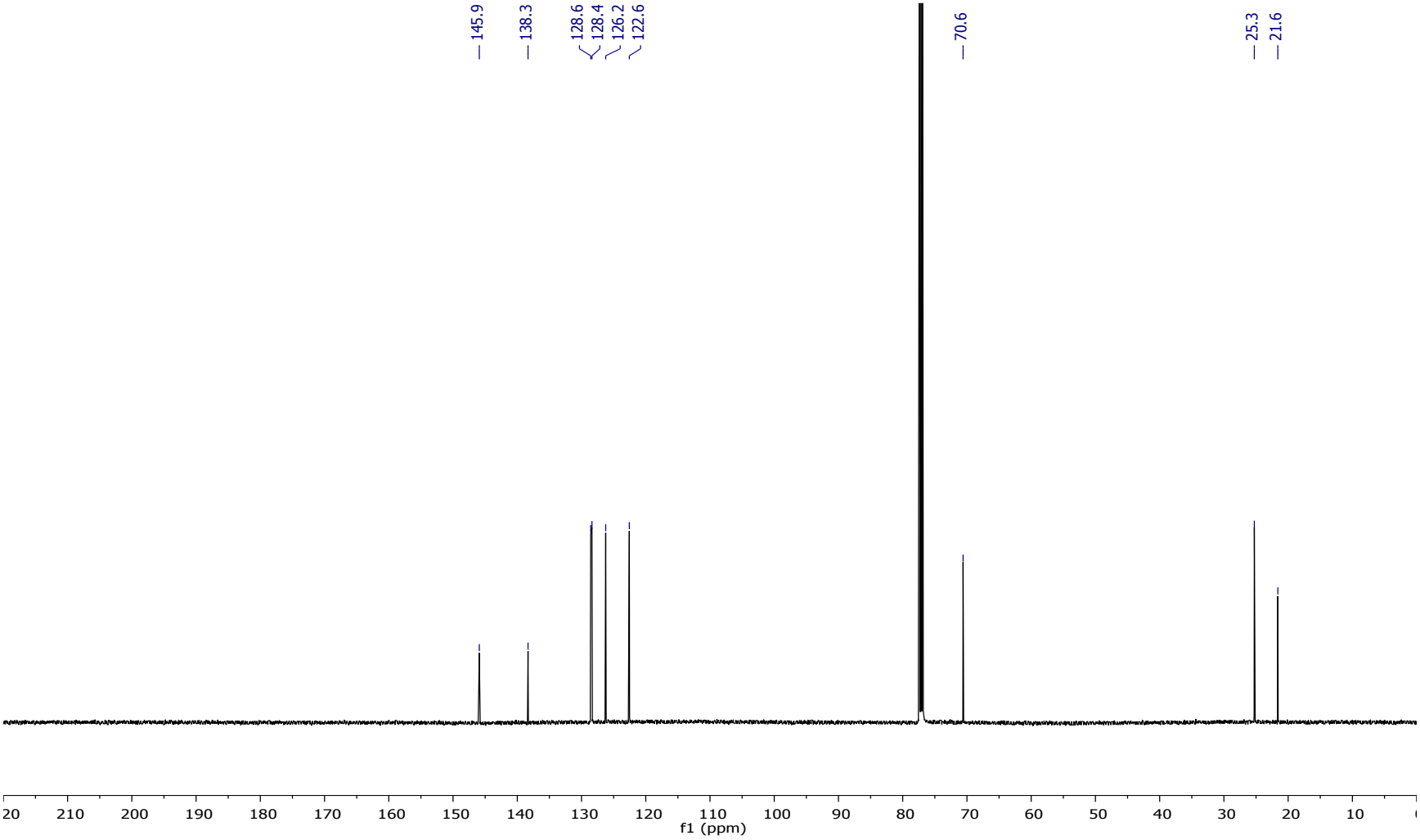


Figure S18 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2g**

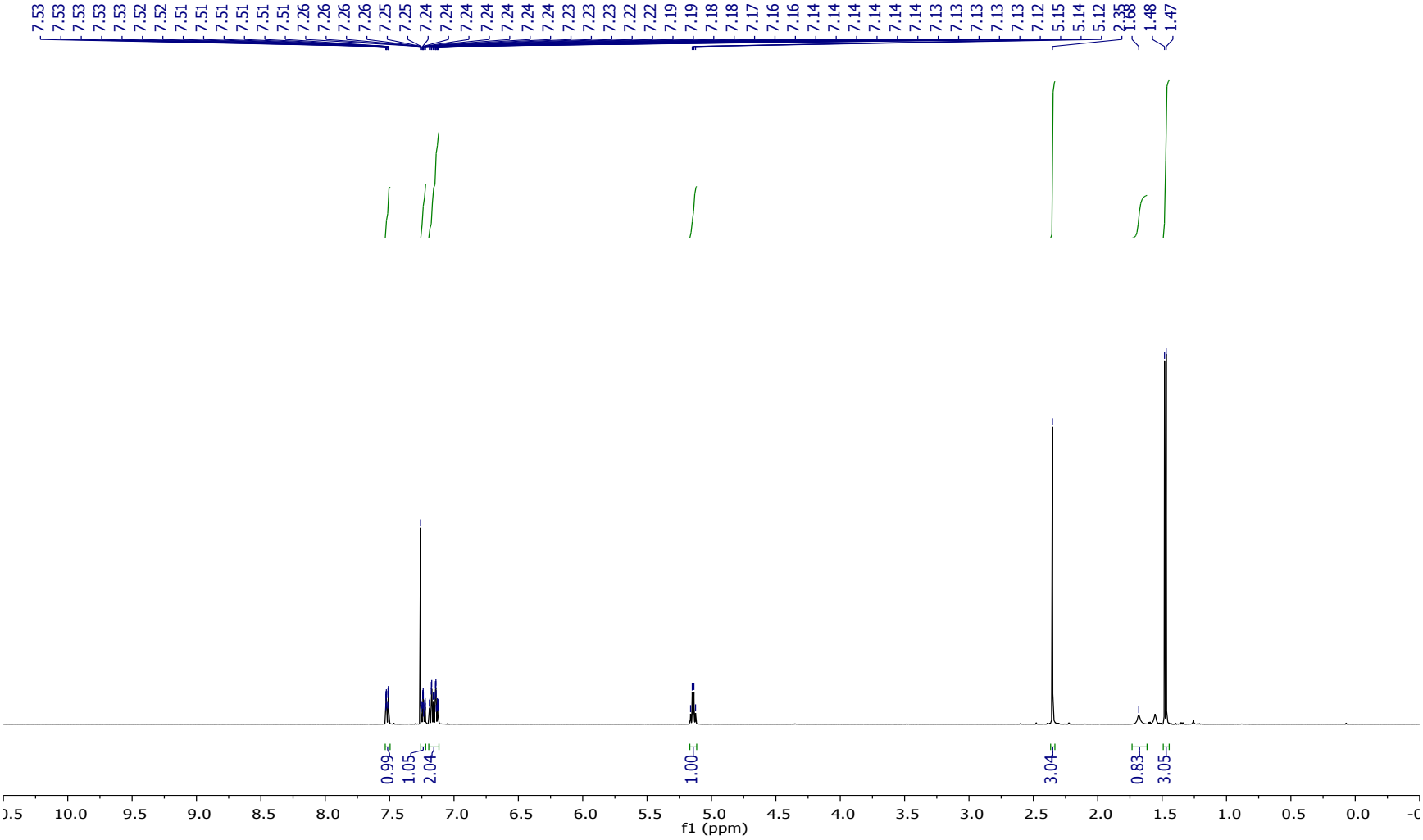


Figure S19 – ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2g**

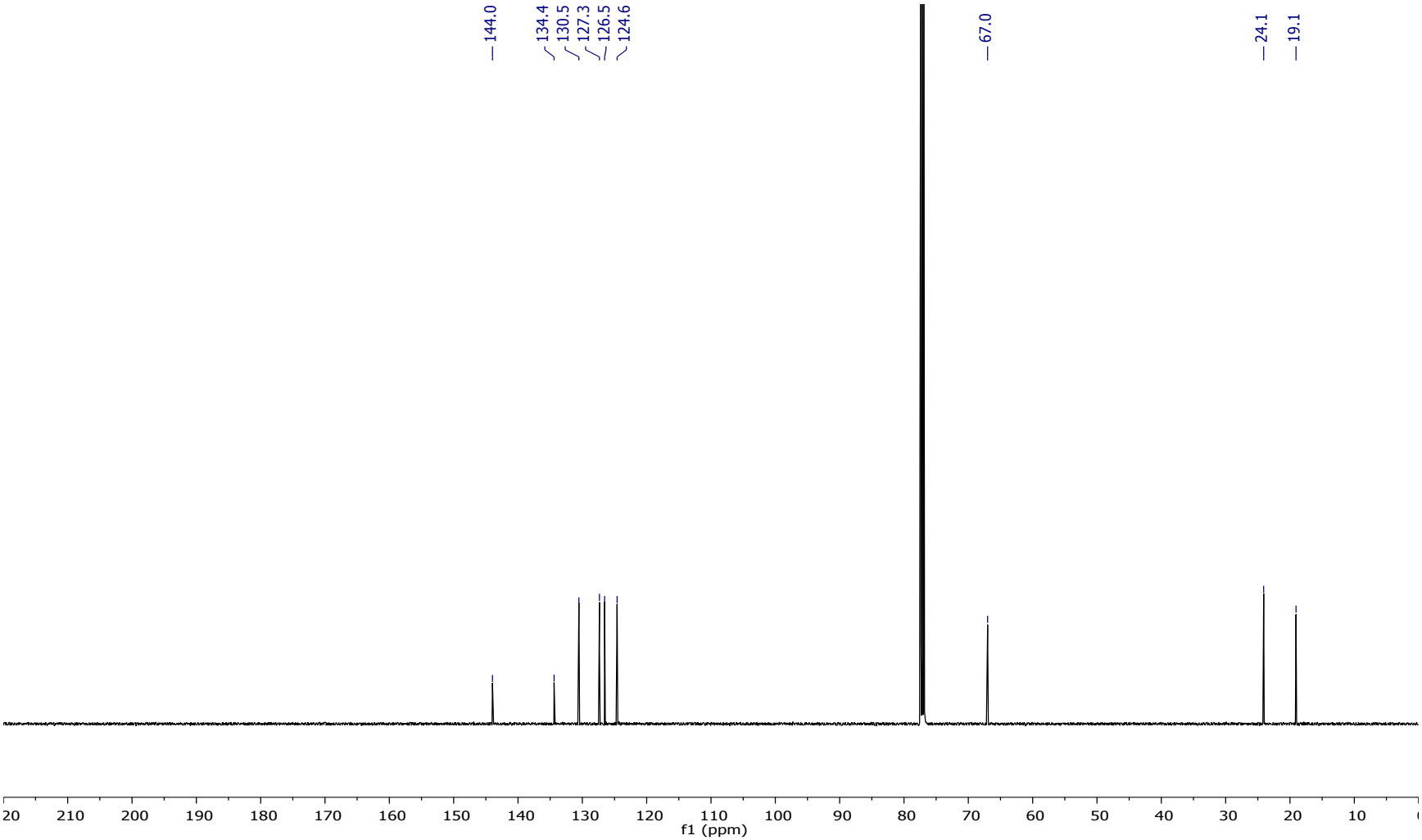


Figure S20 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2h**

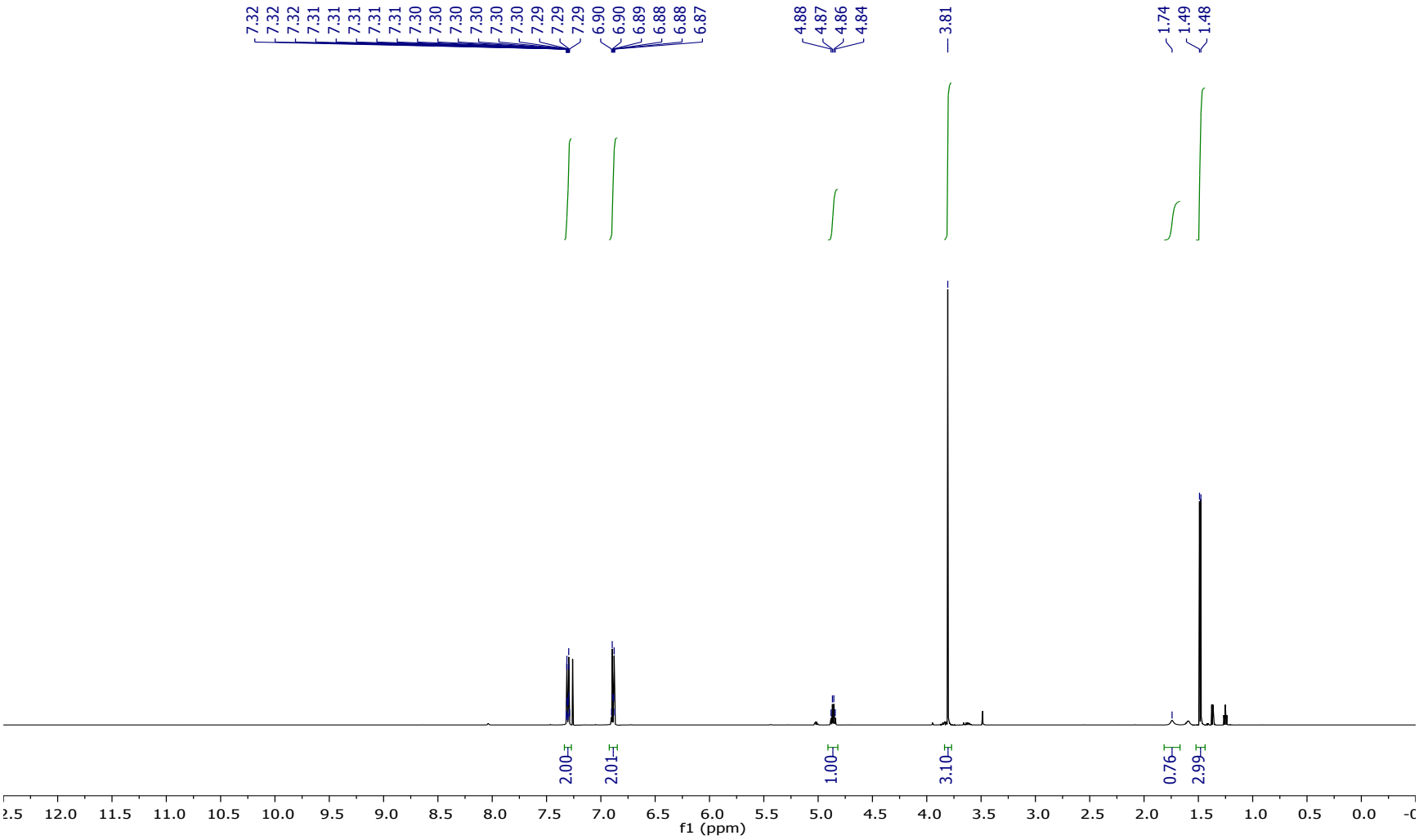

7.32
7.32
7.32
7.31
7.31
7.31
7.31
7.30
7.30
7.30
7.30
7.30
7.29
7.29
6.90
6.90
6.89
6.88
6.88
6.87
4.88
4.87
4.86
4.84
3.81
1.74
1.49
1.48
2.00
2.01
1.00
3.10
0.76
2.99
f1 (ppm)

Figure S21 – $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2h**

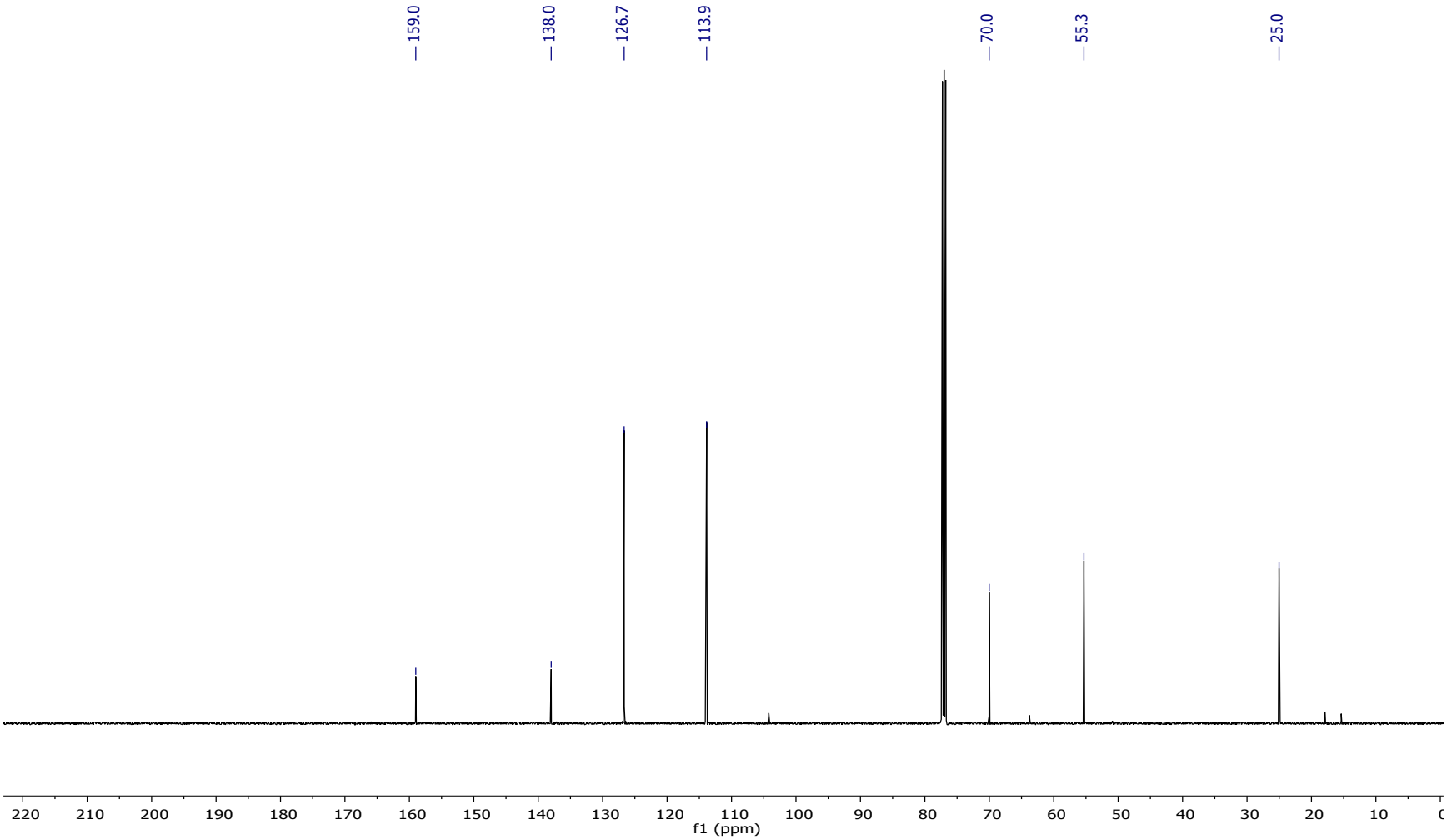


Figure S22 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2i**

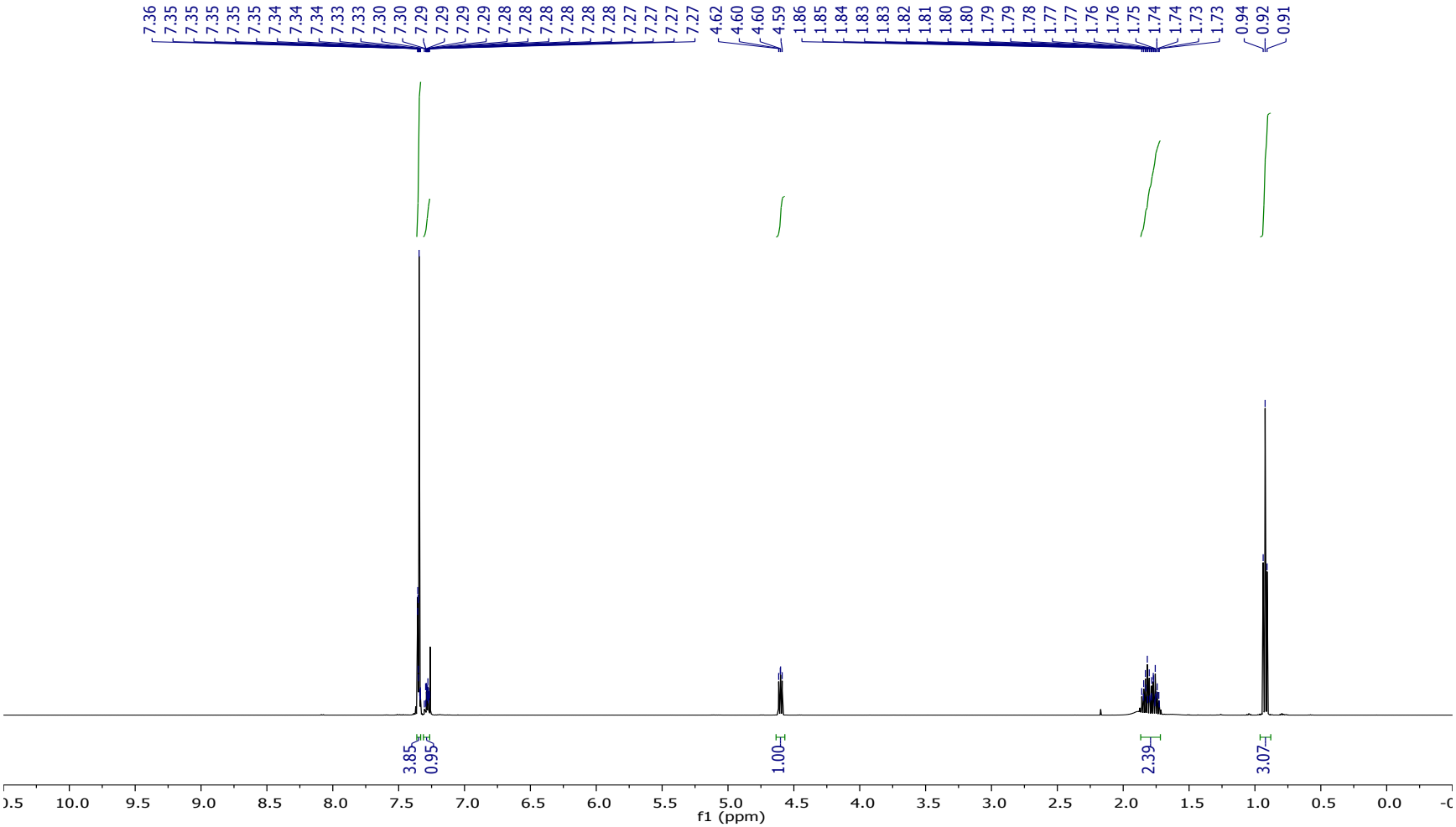


Figure S23 – $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2i**

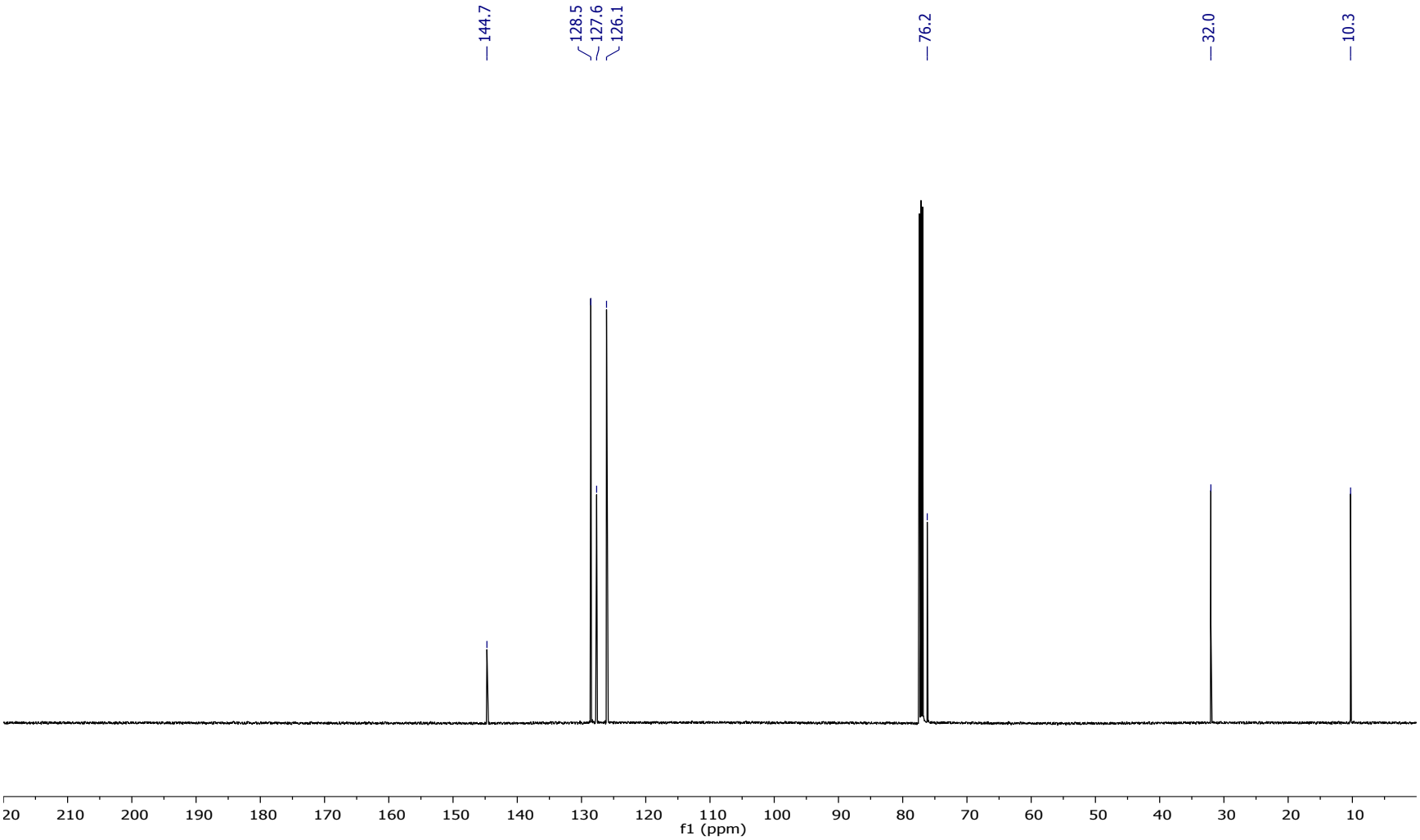


Figure S24 – ^{1}H (500 MHz, $CDCl_3$, 298 K) NMR spectrum of **2j**

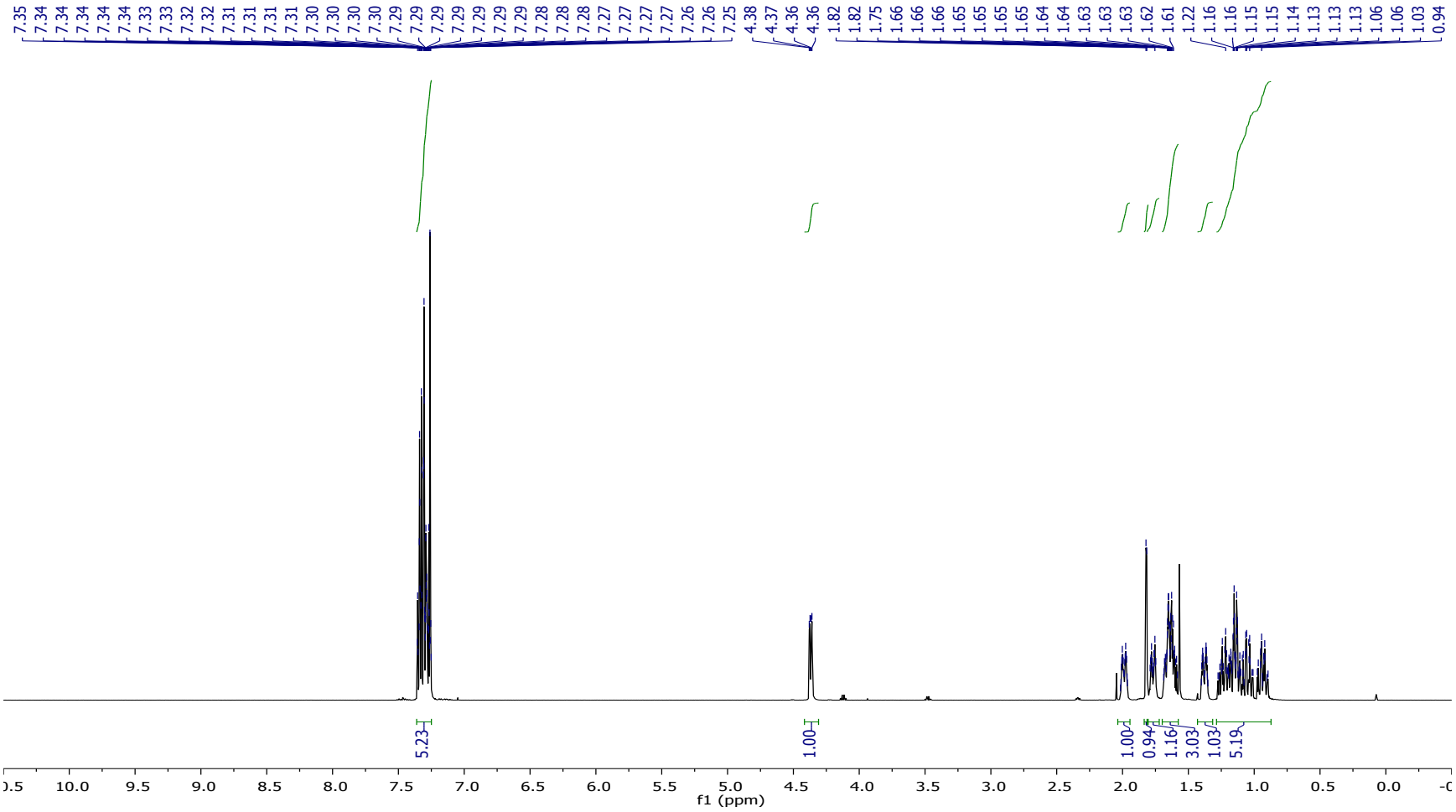
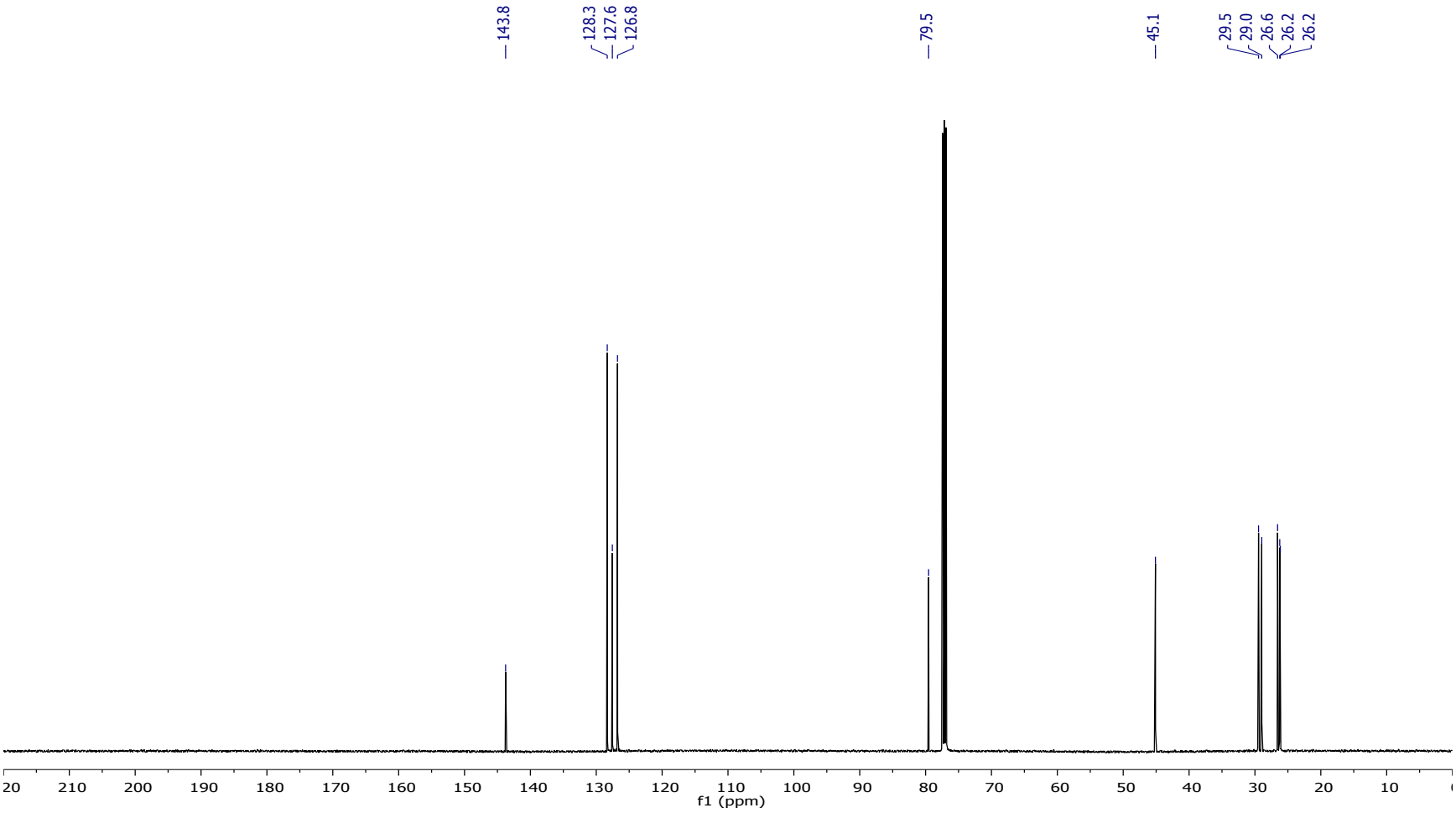
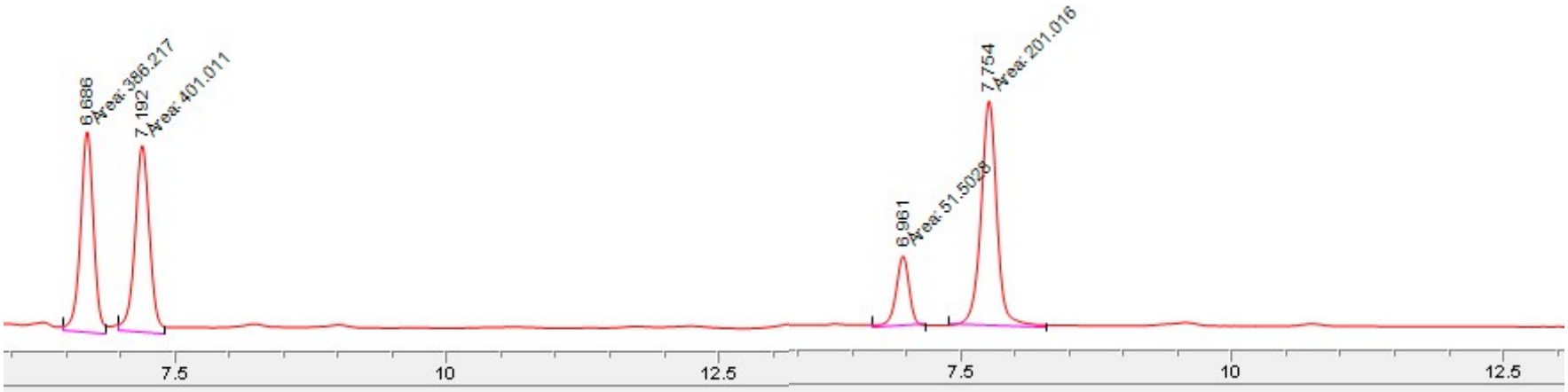


Figure S25 – $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$, 298 K) NMR spectrum of **2j**



Chiral HPLC chromatographs

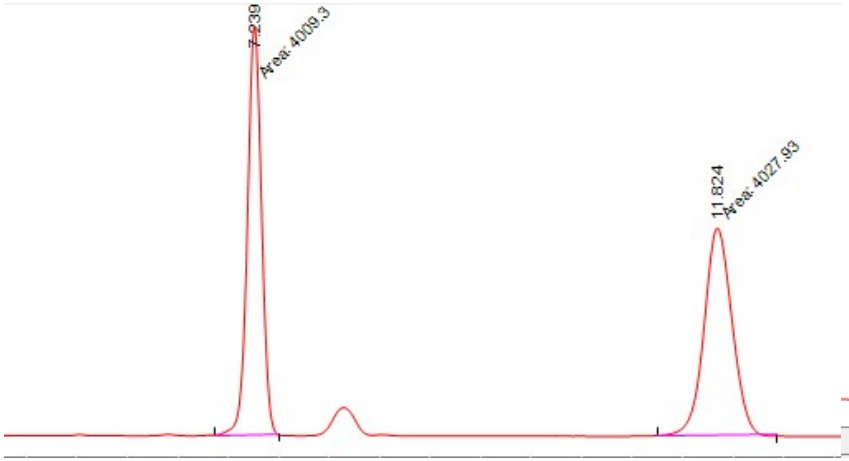
Figure S26 – HPLC chromatograph of **2a**

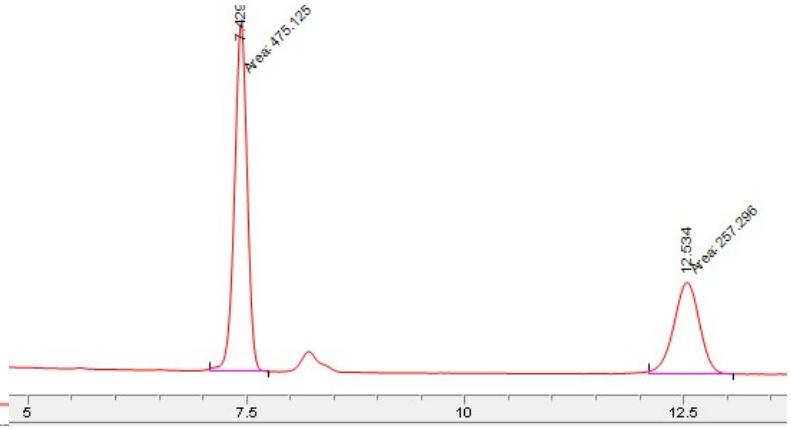


#	Time	Area	Height	Width	Area%	Symmetry
1	6.686	386.2	46	0.1398	49.060	1.024
2	7.192	401	42.9	0.1558	50.940	0.968

#	Time	Area	Height	Width	Area%	Symmetry
1	6.961	51.5	6.1	0.1418	20.396	1.139
2	7.754	201	19.4	0.1726	79.604	0.992

Figure S27 – HPLC chromatograph of **2b**

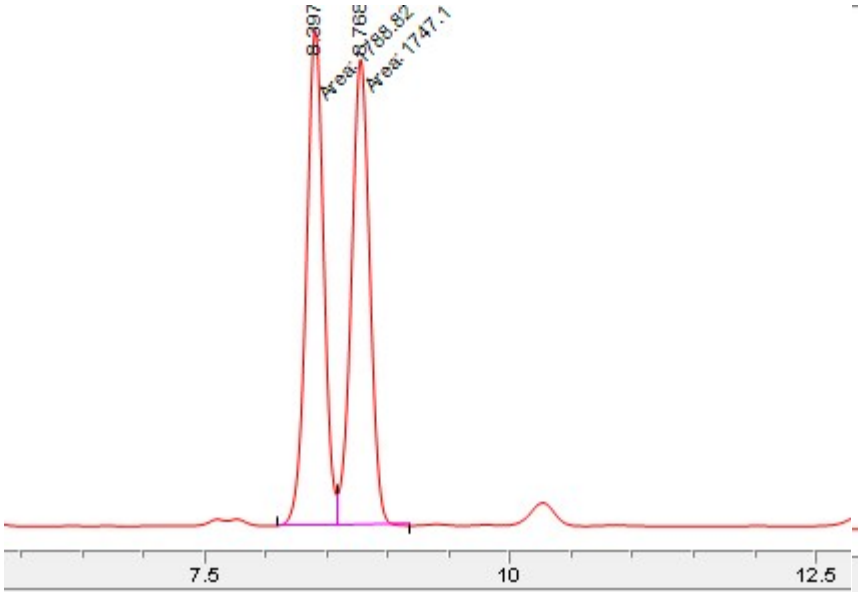


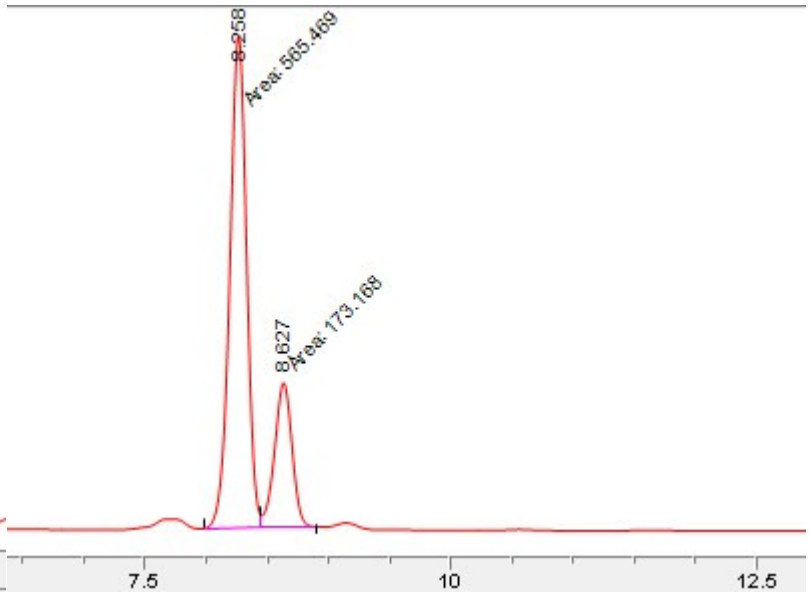


#	Time	Area	Height	Width	Area%	Symmetry
1	7.239	4009.3	407.6	0.164	49.884	0.997
2	11.824	4027.9	207.1	0.3242	50.116	0.91

#	Time	Area	Height	Width	Area%	Symmetry
1	7.429	475.1	46.4	0.1706	64.871	1.069
2	12.534	257.3	12.3	0.3481	35.129	1.038

Figure S28 – HPLC chromatograph of **2c**

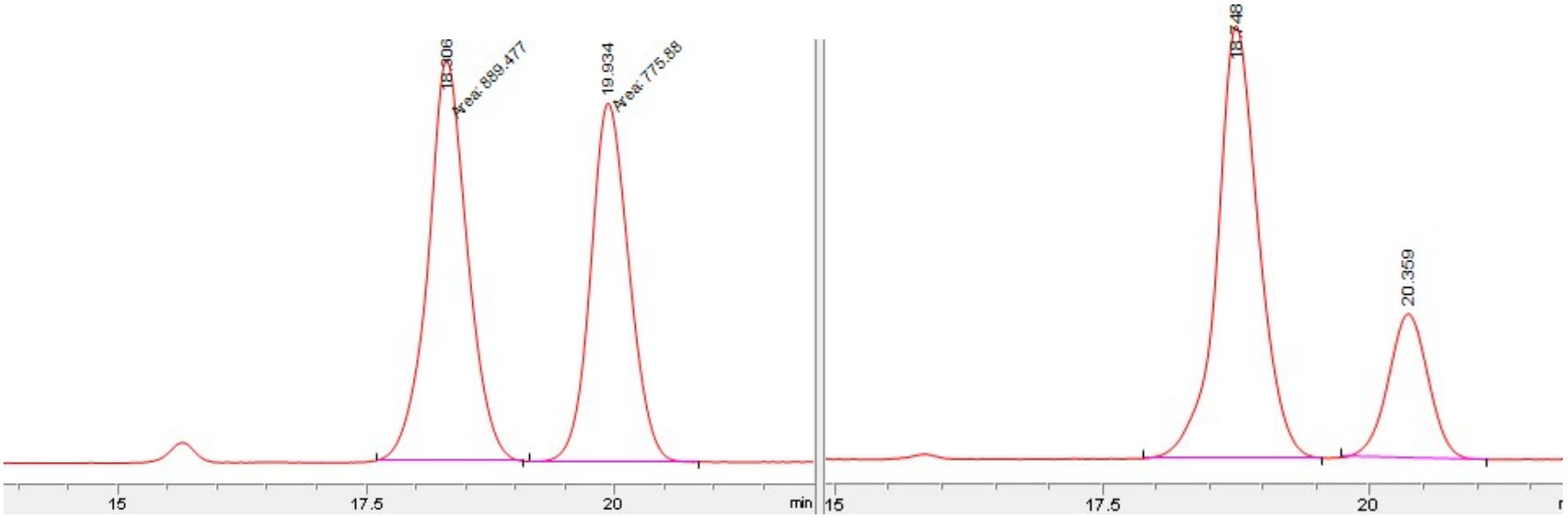




#	Time	Area	Height	Width	Area%	Symmetry
1	8.397	1788.8	179.9	0.1657	50.590	1.018
2	8.768	1747.1	168.8	0.1725	49.410	0.986

#	Time	Area	Height	Width	Area%	Symmetry
1	8.258	565.5	59.2	0.1593	76.556	1.061
2	8.627	173.2	17.4	0.1659	23.444	1.046

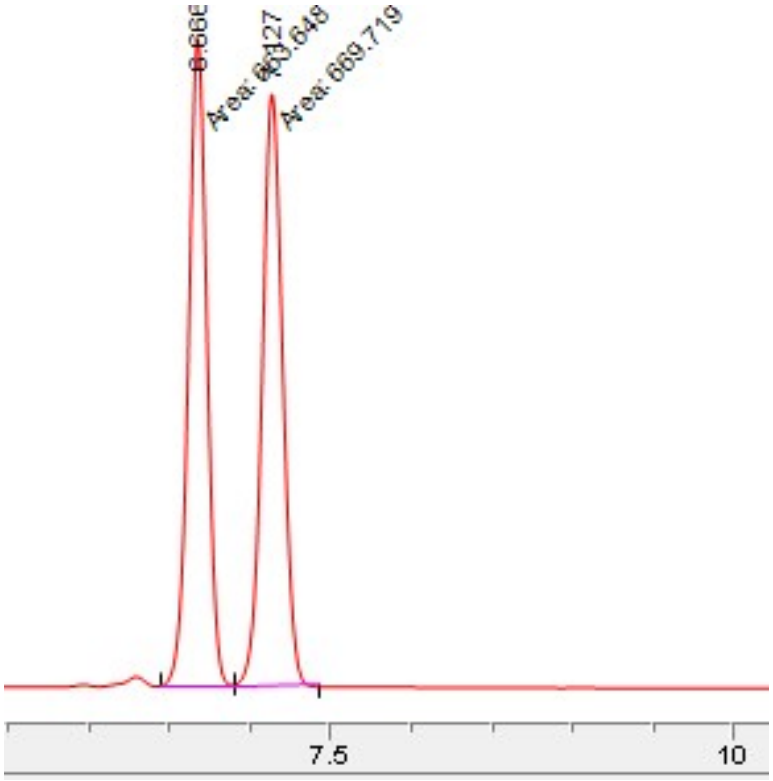
Figure S29 – HPLC chromatograph of **2d**

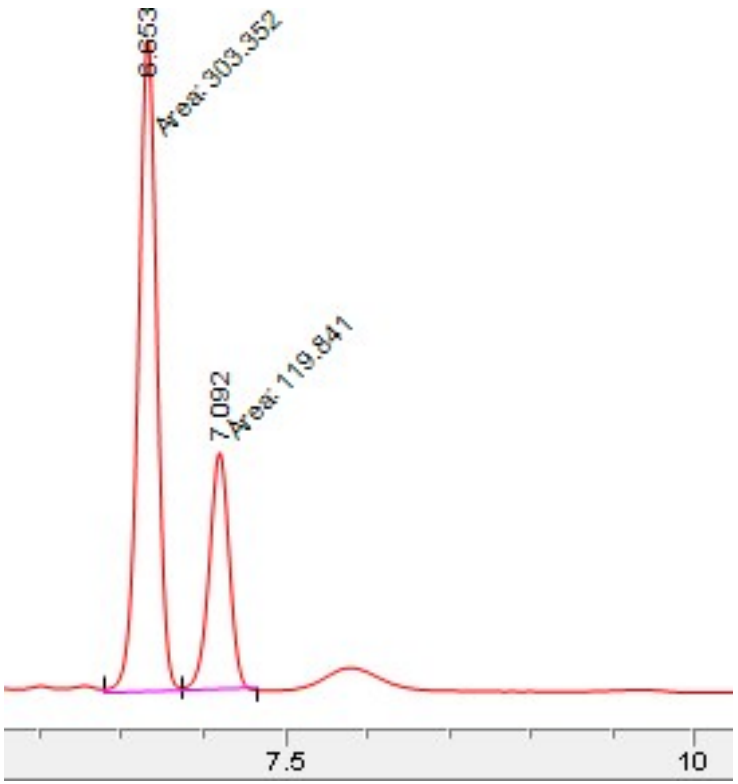


#	Time	Area	Height	Width	Area%	Symmetry
1	18.306	889.5	32.1	0.4616	53.411	0.883
2	19.934	775.9	28.8	0.4497	46.589	0.841

#	Time	Area	Height	Width	Area%	Symmetry
1	18.748	429.8	15.9	0.3989	75.567	0.854
2	20.359	139	5.3	0.3889	24.433	1.003

Figure S30 – HPLC chromatograph of **2e**

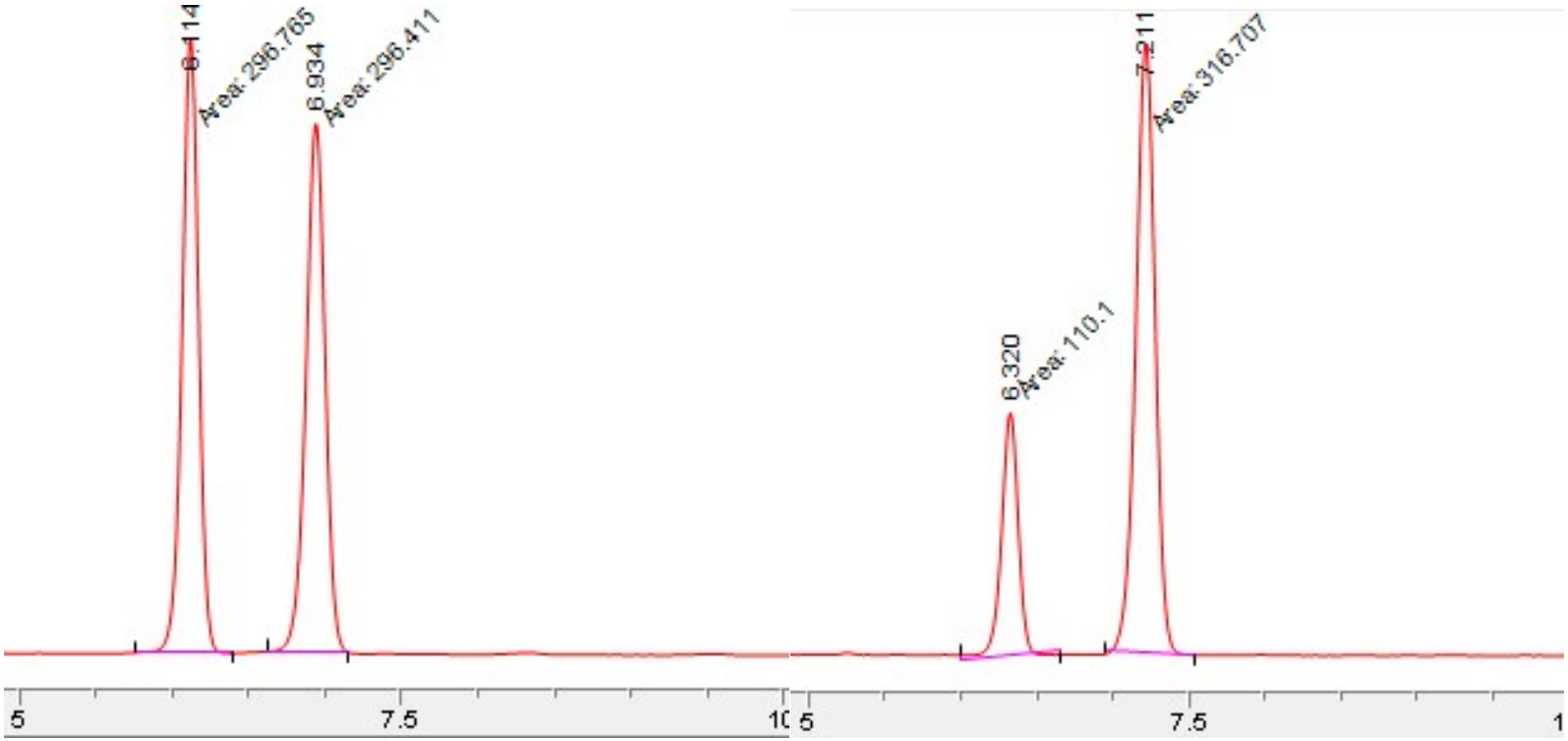




#	Time	Area	Height	Width	Area%	Symmetry
1	6.666	663.6	82.8	0.1335	49.772	0
2	7.127	669.7	75.7	0.1475	50.228	0.916

#	Time	Area	Height	Width	Area%	Symmetry
1	6.653	303.4	38.3	0.132	71.682	1.037
2	7.092	119.8	14	0.1431	28.318	1.064

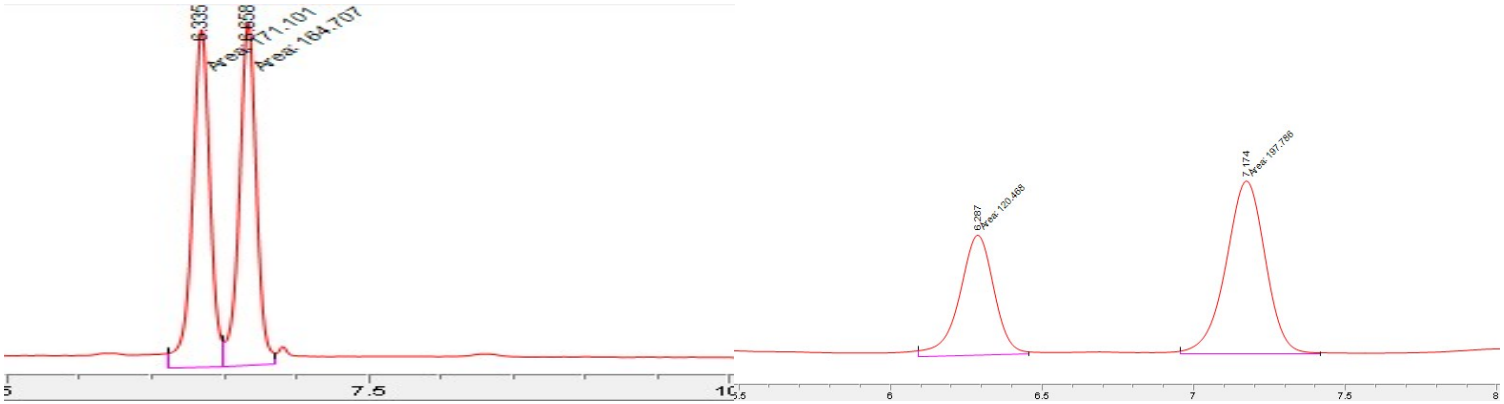
Figure S31 – HPLC chromatographs of **2f**



#	Time	Area	Height	Width	Area%	Symmetry
1	6.114	296.8	39.1	0.1264	50.030	1.056
2	6.934	296.4	33.8	0.1463	49.970	1.054

#	Time	Area	Height	Width	Area%	Symmetry
1	6.32	110.1	14.2	0.1294	25.796	1.14
2	7.211	316.7	35.5	0.1486	74.204	1.052

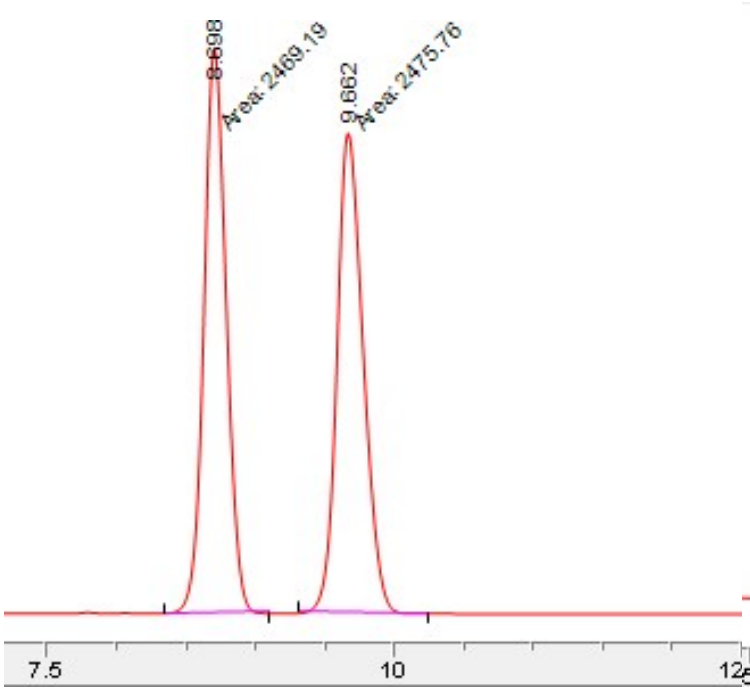
Figure S32 – HPLC chromatograph of **2g**

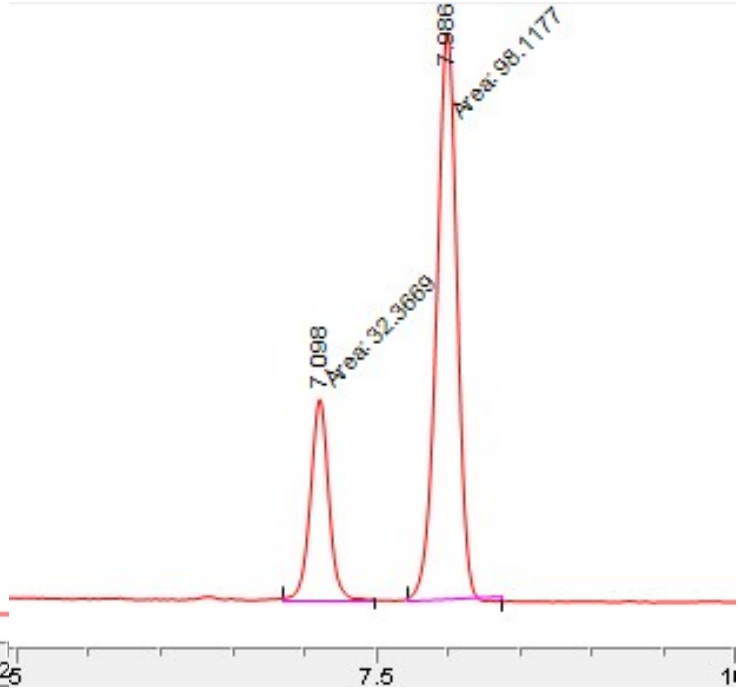


#	Time	Area	Height	Width	Area%	Symmetry
1	6.335	171.1	20	0.1428	50.952	1.061
2	6.658	164.7	20.2	0.1356	49.048	1.019

#	Time	Area	Height	Width	Area%	Symmetry
1	6.287	120.5	15.2	0.1318	37.853	1.117
2	7.174	197.8	21.9	0.1503	62.147	1.064

Figure S33 – HPLC chromatographs of **2h**

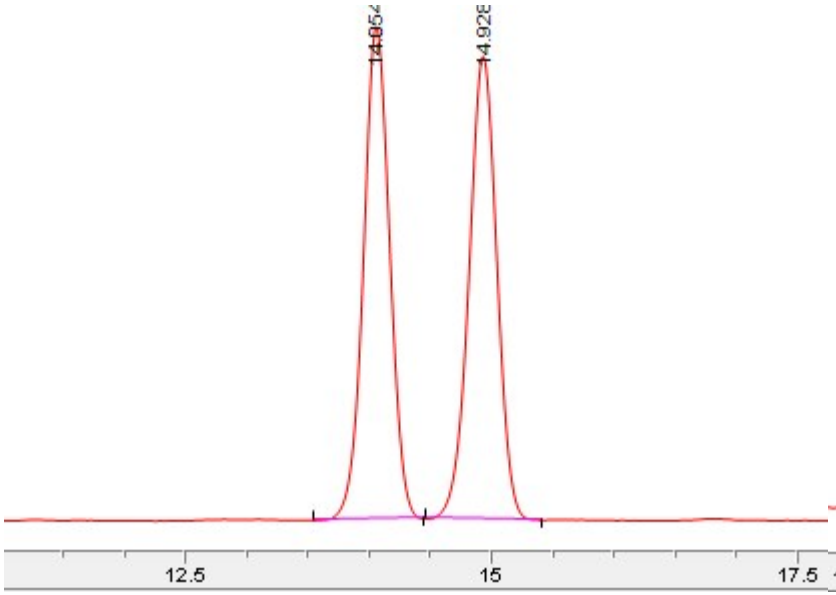




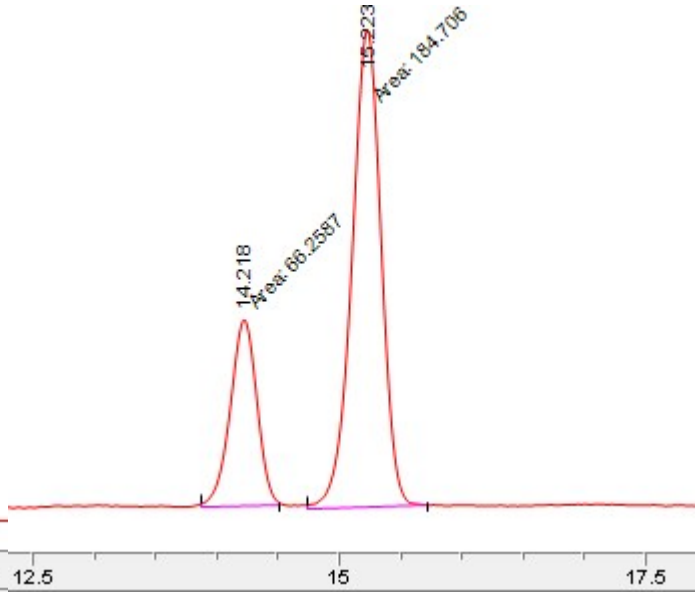
#	Time	Area	Height	Width	Area%	Symmetry
1	8.698	2469.2	220.2	0.1869	49.934	0.858
2	9.662	2475.8	187.3	0.2203	50.066	0.726

#	Time	Area	Height	Width	Area%	Symmetry
1	7.098	32.4	3.5	0.1524	24.805	0.998
2	7.986	98.1	9.9	0.1649	75.195	1.096

Figure S34 – HPLC chromatographs of **2i**

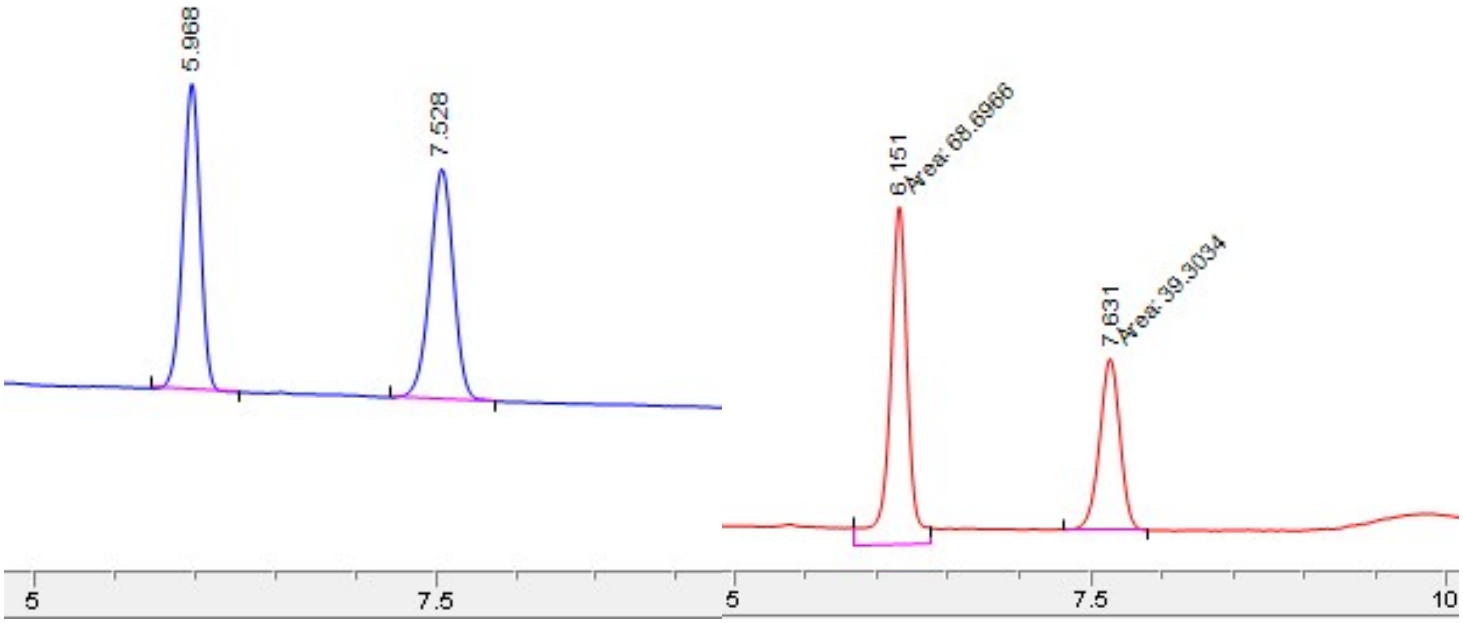


#	Time	Area	Height	Width	Area%	Symmetry
1	14.054	382	25.6	0.2298	50.000	0.942
2	14.928	382	24.1	0.2451	50.000	1.019



#	Time	Area	Height	Width	Area%	Symmetry
1	14.218	66.3	4.3	0.2545	26.402	1.086
2	15.223	184.7	11.1	0.2775	73.598	1.083

Figure S35 – HPLC chromatographs of **2j**



#	Time	Area	Height	Width	Area%	Symmetry
1	5.968	61.1	8.1	0.1158	49.534	1.068
2	7.528	62.2	6.1	0.159	50.466	1.042

#	Time	Area	Height	Width	Area%	Symmetry
1	6.151	68.7	7.8	0.1466	63.608	1.125
2	7.631	39.3	4	0.1657	36.392	1.049

References

1. a) Y. Uozumi, A. Tanahashi, S.-Y. Lee, T. Hayashi, *J. Org. Chem*., 1993, **58**, 1945; b) T. V. RajanBabu, N. Nomura, J. Jin, M. Nandi, H. Park, X. Sun, *J. Org. Chem*., 2003, **68**, 8431.
2. Y. Zhou, D. Zhang, L. Zhu, Z. Shuai and D. Zhu, *J. Org. Chem.*, 2006, **71**, 2123.
3. R. Hrdina, L. Guénée, D. Moraleda and J. Lacour, *Organometallics*, 2013, **32**, 473.
4. S. R. Tamang and M. Findlater, *J. Org. Chem.*, 2017, **82**, 12857.
5. V. K. Jakhar, M. K. Barman and Sharanappa Nembenna, *Org. Lett.*, 2016, **18**, 4710.
6. I. D. Alshakova and G. I. Nikonov, *Synthesis*, 2019, **51**, 3305.
7. L. Weidner, C. J. Barger, M. Delferro, T. L. Lohr and T. J. Marks, *ACS Catal.*, 2017, **7**, 1244.
8. K. Kuciński and G. Hreczycho, *Green Chem.*, 2019, **21**, 1912.