Supplementary Material (ESI) for Chemical Communications

Cyclisation/Fluorination of nitrogen containing dienes in superacid HF/SbF_5: a new route to 3 and 4-fluoropiperidines.

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Supporting Information

General Method

The authors draw the reader's attention to the dangerous features of superacidic chemistry. Handling of hydrogen fluoride and antimony pentafluoride must be done by experienced chemists with all the necessary safety arrangements in place.

Reactions performed in superacid were carried out in a sealed Teflon® flask with a magnetic stirrer. No further precautions have to be taken to prevent mixture from moisture (test reaction worked out in anhydrous conditions leads to the same results as expected).

Yields refer to isolated pure products.

^1H, ^{13}C and ^{19}F NMR were recorded on a 300 MHz Brüker spectrometer using $CDCl_3$ as solvent.

Melting points were determined in a capillary tube and are uncorrected.

Mass spectra were performed with coupled gas chromatography Trace 6C Thermo Finnigan/Thermo Finnigan Automass (electronic impact).

High-resolution mass spectra were performed on a Micromass ZABSpec TOF by the Centre Regional de Mesures Physiques de l'Ouest, Université Rennes (France).

All separations were done under flash-chromatography conditions on silica gel (15-40 μm).

Crystals of dimensions, 0.30 x 0.20 x 0.06 mm (**2j**) was glued with Araldite on a glass fiber and 0.24 x 0.16 x 0.04 mm (**2e**) was mounted with Paratone-N oil (Hampton Research) coating and immediately placed in a nitrogen cold stream.

X-ray intensity data were collected on a Bruker-Nonius X8-APEX2 CCD area-detector diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Data reductions were accomplished using SAINT V7.03 [1]. The substantial redundancy (6.93 for **2j** and 5.46 for **2e**) in data allowed a semi-empirical absorption correction (SADABS V2.10)[1] to be applied, on the basis

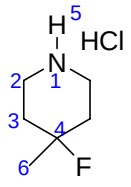
of multiple measurements of equivalent reflections. The structures were solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F^2 data using SHELXTL V6.14[2]. Hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms.

(1) APEX2 version 1.0-8; Bruker AXS: Madison, WI, 2003

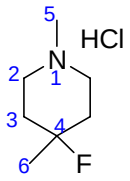
(2) SHELXTL version 6.14; Bruker AXS: Madison, WI, 2001

Optimized procedure in superacidic media

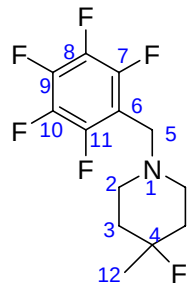
To a mixture of HF/SbF_5 (3 mL, 8/1 molar ratio) maintained at the indicated temperature was added nitrogen derivative (1 mmol). The mixture was magnetically stirred at the same temperature for reaction time. The reaction mixture was then neutralized with water-ice-Na_2CO_3, extracted with dichloromethane (× 3). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Products were isolated by column chromatography over silica gel.



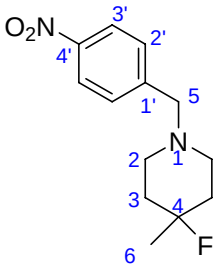
Compound 2a.HCl: 4-fluoro-4-methylpiperidine hydrochloride: Optimized procedure (0°C, 3 min reaction time) was followed, starting from 585 mg of **1a** (6.02 mmol). Addition in the crude mixture of acidified methanol (HCl) afforded 644 mg of the title compound as a colourless oil after evaporation of methanol (70%). ^{1}H NMR (300 MHz, $CDCl_3$/10% MeOD, ppm): δ 1.47 (d, $^3J_{H\text{-}F}$ = 21.6 Hz, 3H, H-6) ; 2.04 (m, 3H, H-3 a and/or b) ; 2.16 (m, 1H, H-3 a or b) ; 3.18 (m, 2H, H-2 a and/or b) ; 3.35 (m, 2H, H-2a and/or b) ; 3.49 (m, 2H, NH_2). ^{13}C NMR (75 MHz, $CDCl_3$/10% MeOD, ppm): δ 26.7 (d, $^2J_{C\text{-}F}$ = 24 Hz, CH_3, C-6) ; 32.7 (d, $^2J_{C\text{-}F}$ = 22 Hz, CH_2, C-3) ; 40.0 (d, $^3J_{C\text{-}F}$ = 2 Hz, CH_2, C-2) ; 90.0 (d, $^1J_{C\text{-}F}$ = 171 Hz, C-4). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm): -154.44. HRMS (EI): Calc for $C_6H_{12}NF$: 117.09538, found 117.0951.



Compound 2b.HCl: 4-fluoro-1,4-dimethylpiperidine hydrochloride: Optimized procedure (0°C, 3 min reaction time) was followed, starting from 300 mg of **1b** (2.70 mmol). Addition in the crude mixture acidified methanol (HCl) afforded 381 mg of the title compound as a colourless oil after evaporation of methanol (85%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.48 (d, $^{3}J_{H\text{-}F}$ = 21.6 Hz, 3H, H-6) ; 2.02 (m, 2H, H-3 a and/or b) ; 2.39 (m, 1H, H-3 a or b) ; 2.52 (m, 1H, H-3 a or b) ; 2.84 (s, 3H, H-5) ; 3.11 (m, 2H, H-2 a and/or b) ; 3.38 (m, 2H, H-2 a and/or b). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 26.2 (d, $^{2}J_{C\text{-}F}$ = 23 Hz, CH_3, C-6) ; 33.3 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, 2 CH_2, C-3) ; 42.8 (CH_3, C-5) ; 50.2 (2 CH_2, C-2) ; 89.3 (d, $^{1}J_{C\text{-}F}$ = 170 Hz, C-4). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm): -154.83. HRMS (EI): Calc for $C_7H_{13}NF$: 130.10320, found 130.1034.



Compound 2d: 4-fluoro-4-methyl-1-(pentafluorobenzyl) piperidine: Optimized procedure (0°C, 3 min reaction time) was followed, starting from 385 mg of **1d** (1.39 mmol). Purification by flash column chromatography (chloroform) afforded 279 mg of the title compound as a colourless oil (68%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.33 (d, $^{3}J_{H\text{-}F}$ = 21.4 Hz, 3H, H-12) ; 1.68 (m, 4H, H-3) ; 2.39 (m, 2H, H-2 a and/or b) ; 2.66 (m, 2H, H-2 a and/or b) ; 3.74 (s, 2H, H-5). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 27.0 (d, $^{2}J_{C\text{-}F}$ = 24 Hz, CH_3, C-12) ; 36.4 (d, $^{2}J_{C\text{-}F}$ = 21.7 Hz, 2 CH_2, C-3) ; 48.4 (2 CH_2, C-2) ; 48.7 (CH_2, C-5) ; 91.6 (d, $^{1}J_{C\text{-}F}$ = 169 Hz, C-4) ; 110.6 (m, C-6) ; 135-148 (C-7, C-8, C-9, C-10, C-11). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm): -162.61 (C-F_{arom}), -155.41 (2 C-F_{arom}) ; -152.75 (C-F); -141.60 (2 C-F_{arom}). MS (EI, 70 ev): *m/z* (relative intensity %) 297 (10), 276 (18), 181 (100), 83 (100). HRMS (ESI): Calc for $C_{13}H_{13}NF_6$: 297.0952, found 297.0946.

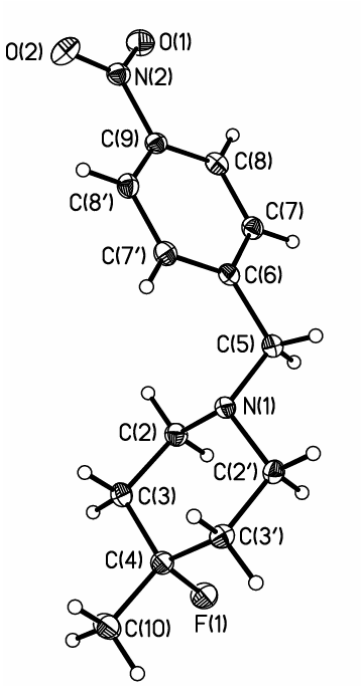


Compound 2e: 1-(4-nitrobenzyl)-4-fluoro-4-methylpiperidine: Optimized procedure (0°C, 3 min reaction time) was followed, starting from 300 mg of **1e** (1.29 mmol). Purification by flash column chromatography (99/1: dichloromethane/methanol) afforded 114 mg of the title compound as a colourless powder (35%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.36 (d, $^{3}J_{H\text{-}F}$ = 21.4 Hz, 3H, H-6) ; 1.66 and 1.79 (m, 2H, H-3 a and/or b) ; 2.37 (m, 2H, H-2 a and/or b) and 2.60 (m, 2H, H-2 a and/or b) ; 3.60 (s, 2H, H-5) ; 7.51 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.7 Hz, H-2') ; 8.17 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.1 Hz, H-3'). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 27.4 (d, $^{2}J_{C\text{-}F}$ = 24Hz, CH_3, C-6) ; 36.9 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, 2 CH_2, C-3) ; 49.9 (d, $^{3}J_{C\text{-}F}$ = 2Hz, 2 CH_2, C-2) ; 62.5 (CH_2, C-5) ; 92.4 (d, $^{1}J_{C\text{-}F}$ = 167 Hz, C-4) ; 123.9 (2 CH, C-3') ; 129.8 (2 CH, C-2') ; 147.2 (C-1') ; 147.5 (C-4'). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm): -152.31. MS (EI, 70 ev): *m/z* (relative intensity %) 252 (20), 232 (20), 132 (100), 118 (97), 91 (60). HRMS (EI): Calc for $C_{13}H_{17}N_2O_2F$: 252.12741, found 252.1279. Mp (°C): 72.

XRD: Five sets of narrow data frames (30 s per frame) were collected at different values of θ, for 4 and 1 initial values of ϕ and ω, respectively, using 0.5° increments of ϕ or ω.

Crystal structure analysis**:** C_{13} H_{17} F N_2 O_2**,** 100 K, triclinic, space group P-1; dimensions: a = 6.3802(11) Å, b 7.2136(11) Å, c = 14.245(3) Å, α = 96.205(7)° , β = 93.734(8) ° , γ = 103.868(7)°, V = 629.95(19) Å^3; Z = 2 ; total reflections collected : 26662 ; independent reflections : 3642 (2993 Fo > 4σ (Fo)) ; data were collected up to a 2Θmax value of 60.16° (98.6 % coverage). Number of variables: 164 ; R_1 = 0.0380, wR_2 = 0.1125, S = 1.075 ; highest residual electron density 0.454 e.Å $^{-3}$.

Calculated parameters:



BOND LENGTHS (Å)

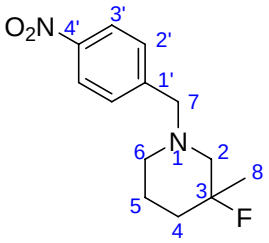
Bond	Length (Å)	Bond	Length (Å)
F(1)-C(4)	1.4358(12)	C(5)-H(5A)	0.9900
N(1)-C(5)	1.4607(13)	C(5)-H(5B)	0.9900
N(1)-C(2')	1.4693(13)	C(6)-C(7)	1.3965(14)
N(1)-C(2)	1.4713(13)	C(6)-C(7')	1.3982(15)
C(2)-C(3)	1.5263(15)	C(7)-C(8)	1.3917(15)
C(2)-H(2A)	0.9900	C(7)-H(7)	0.9500
C(2)-H(2B)	0.9900	C(8)-C(9)	1.3832(15)
C(3)-C(4)	1.5202(15)	C(8)-H(8)	0.9500
C(3)-H(3A)	0.9900	C(7')-C(8')	1.3861(15)
C(3)-H(3B)	0.9900	C(7')-H(7')	0.9500
C(2')-C(3')	1.5219(14)	C(8')-C(9)	1.3908(14)
C(2')-H(2'1)	0.9900	C(8')-H(8')	0.9500
C(2')-H(2'2)	0.9900	C(9)-N(2)	1.4699(13)
C(3')-C(4)	1.5192(14)	C(10)-H(10A)	0.9800
C(3')-H(3'1)	0.9900	C(10)-H(10B)	0.9800
C(3')-H(3'2)	0.9900	C(10)-H(10C	0.9800
C(4)-C(10)	1.5139(15)	N(2)-O(2)	1.2255(13)

ATOMIC COORDINATES (X 10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å ^2 X 10^3)

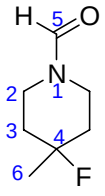
Atom	x/a	y/b	z/c	U(iso) Occ
F(1)	12681(1)	6859(1)	4807(1)	23(1)
N(1)	10191(1)	3707(1)	2768(1)	16(1)
C(2)	9705(2)	5559(1)	3077(1)	18(1)
C(3)	11778(2)	7180(2)	3204(1)	19(1)
C(2')	11633(2)	3261(1)	3511(1)	17(1)
C(3')	13785(2)	4774(2)	3640(1)	18(1)
C(4)	13501(2)	6795(2)	3892(1)	17(1)
C(5)	8196(2)	2175(2)	2568(1)	18(1)
C(6)	6896(2)	2301(1)	1659(1)	16(1)
C(7)	4648(2)	1569(2)	1564(1)	18(1)
C(8)	3416(2)	1596(1)	725(1)	17(1)
C(7')	7908(2)	3061(2)	895(1)	18(1)
C(8')	6715(2)	3092(1)	50(1)	17(1)
C(9)	4479(2)	2361(1)	-14(1)	16(1)
C(10)	15625(2)	8318(2)	3991(1)	23(1)
N(2)	3204(2)	2372(1)	-910(1)	18(1)
O(1)	1210(1)	1834(1)	-946(1)	26(1)
O(2)	4174(1)	2912(1)	-1585(1)	26(1)
H(2A)	9038	5492	3685	21
H(2B)	8657	5827	2599	21
H(3A)	12356	7328	2581	23
H(3B)	11433	8403	3442	23
H(2'1)	11882	1972	3330	20
H(2'2)	10948	3244	4115	20
H(3'1)	14739	4480	4149	21
H(3'2)	14504	4718	3046	21
H(5A)	7290	2243	3103	22
H(5B)	8567	914	2522	22
H(7)	3950	1046	2080	21
H(8)	1886	1101	662	21
H(7')	9436	3564	955	21
H(8')	7406	3598	-471	20
H(10A)	15359	9588	4164	35
H(10B)	16277	8296	3387	35
H(10C)	16615	8055	4486	35

ANGLES (DEG)

Angle	Valeur (°)	Angle	Valeur (°)
C(5)-N(1)-C(2')	110.43(8)	N(1)-C(5)-C(6)	112.79(8)
C(5)-N(1)-C(2)	110.63(8)	N(1)-C(5)-H(5A)	109.0
C(2')-N(1)-C(2)	109.18(8)	C(6)-C(5)-H(5A)	109.0
N(1)-C(2)-C(3)	110.30(8)	N(1)-C(5)-H(5B)	109.0
N(1)-C(2)-H(2A)	109.6	C(6)-C(5)-H(5B)	109.0
C(3)-C(2)-H(2A)	109.6	H(5A)-C(5)-H(5B)	107.8
N(1)-C(2)-H(2B)	109.6	C(7)-C(6)-C(7')	119.05(9)
C(3)-C(2)-H(2B)	109.6	C(7)-C(6)-C(5)	119.52(9)
H(2A)-C(2)-H(2B)	108.1	C(7')-C(6)-C(5)	121.38(9)
C(4)-C(3)-C(2)	112.02(9)	C(8)-C(7)-C(6)	120.97(10)
C(4)-C(3)-H(3A)	109.2	C(8)-C(7)-H(7)	119.5
C(2)-C(3)-H(3A)	109.2	C(6)-C(7)-H(7)	119.5
C(4)-C(3)-H(3B)	109.2	C(9)-C(8)-C(7)	118.18(9)
C(2)-C(3)-H(3B)	109.2	C(9)-C(8)-H(8)	120.9
H(3A)-C(3)-H(3B)	107.9	C(7)-C(8)-H(8)	120.9
N(1)-C(2')-C(3')	109.51(8)	C(8')-C(7')-C(6)	120.99(9)
N(1)-C(2')-H(2'1)	109.8	C(8')-C(7')-H(7')	119.5
C(3')-C(2')-H(2'1)	109.8	C(6)-C(7')-H(7')	119.5
N(1)-C(2')-H(2'2)	109.8	C(7')-C(8')-C(9)	118.21(9)
C(3')-C(2')-H(2'2)	109.8	C(7')-C(8')-H(8')	120.9
H(2'1)-C(2')-H(2'2)	108.2	C(9)-C(8')-H(8')	120.9
C(4)-C(3')-C(2')	112.23(9)	C(8)-C(9)-C(8')	122.59(9)
C(4)-C(3')-H(3'1)	109.2	C(8)-C(9)-N(2)	118.84(9)
C(2')-C(3')-H(3'1)	109.2	C(8')-C(9)-N(2)	118.56(9)
C(4)-C(3')-H(3'2)	109.2	C(4)-C(10)-H(10A)	109.5
C(2')-C(3')-H(3'2	109.2	C(4)-C(10)-H(10B)	109.5
H(3'1)-C(3')-H(3'2)	107.9	H(10A)-C(10)-H(10B)	109.5
F(1)-C(4)-C(10)	106.48(8)	C(4)-C(10)-H(10C)	109.5
F(1)-C(4)-C(3')	106.91(8)	H(10A)-C(10)-H(10C)	109.5
C(10)-C(4)-C(3')	112.64(9)	H(10B)-C(10)-H(10C)	109.5
F(1)-C(4)-C(3)	106.40(8)	O(2)-N(2)-O(1)	123.23(9)
C(10)-C(4)-C(3)	113.45(9)	O(2)-N(2)-C(9)	118.36(9)
C(3')-C(4)-C(3)	110.46(8)	O(1)-N(2)-C(9)	118.40(9)

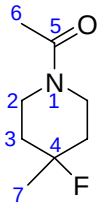


Compound 2e': 1-(4-nitrobenzyl)-3-fluoro-3-methylpiperidine: Optimized procedure (-78°C, 3 min reaction time) was followed, starting from 500 mg of **1e** (2.16 mmol). Purification by flash column chromatography (98/1/1: petroleum ether/ethyl acetate/diethylamine) afforded 285 mg of the title compound as a colourless oil (52%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.33 (d, $^{3}J_{H\text{-}F}$ = 21.6 Hz, 3H, H-8) ; 1.53 (m, 2H, H-5 and H-4) ; 1.84 (m, 2H, H-5 and H-4) ; 2.20 (m, 2H, H-6 and H-2) ; 2.55 (m, 2H, H-6 and H-2) ; 3.60 (s, 2H, H-7) ; 7.50 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.8 Hz, H-2') ; 8.14 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.7 Hz, H-3'). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 22.3 (d, $^{3}J_{C\text{-}F}$ = 4 Hz, CH_2, C-5) ; 25.3 (d, $^{2}J_{C\text{-}F}$ = 24 Hz, CH_3, C-8) ; 35.3 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, CH_2, C-4) ; 53.3 (CH_2, C-6) ; 62.1 (CH_2, C-7) ; 62.3 (d, $^{2}J_{C\text{-}F}$ = 23 Hz, CH_2, C-2) ; 92.5 (d, $^{1}J_{C\text{-}F}$ = 169 Hz, C-3) ; 123.8 (2 CH, C-2') ; 129.6 (CH, C-3') ; 146.7 (C-1') ; 147.4 (C-4'). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm): -147.44. MS (EI, 70 ev): *m/z* (relative intensity %) 252 (28), 233 (15), 132 (98), 118 (100), 91 (60). HRMS (EI): Calc for $C_{13}H_{17}N_2O_2F$: 252.12741, found 252.1277.

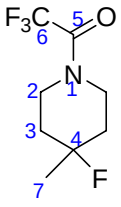


Compound 2f: 1-formamide-4-fluoro-4-methylpiperidine: Optimized procedure (0°C, 60 min reaction time) was followed, starting from 300 mg of **1f** (2.40 mmol). Purification by flash column chromatography (99/1: diethyl ether/methanol) afforded 118 mg of the title compound as a colourless oil (34%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.34 (d, $^{3}J_{H\text{-}F}$ = 21.5 Hz, 3H, H-6) ; 1.46 (m, 2H) and 1.86 (m, 2H), H-3 ; 2.95 (m, 1H) and 3.38 (m, 2H) and 4.17 (m, 1H), H-2 ; 7.98 (s, 1H, H-5). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 26.9 (d, $^{2}J_{C\text{-}F}$ = 24 Hz, CH_3, C-6) ; 35.3 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, CH_2) and 36.7 (d, $^{2}J_{C\text{-}F}$ = 23 Hz, CH_2), C-3 ; 35.5 (d, $^{3}J_{C\text{-}F}$ = 3 Hz, CH_2) and 41.7 (d, $^{3}J_{C\text{-}F}$ = 2 Hz, CH_2), C-2 ; 92.5 (d, $^{1}J_{C\text{-}F}$ = 169 Hz, C-4) ; 160.6 (CH, C-5). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm): -155.25. MS (EI, 70 ev): *m/z* (relative intensity %) 147 (100), 146 (54), 132 (27), 126

(10), 112 (35), 98 (38), 87 (75), 58 (74). HRMS (EI): Calc for $C_7H_{12}NOF$: 145.09029, found 145.0897.

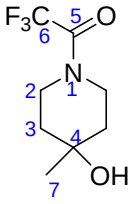


Compound 2g: 1-acetyl-4-fluoro-4-methylpiperidine: Optimized procedure (-30°C, 5 min reaction time) was followed, starting from 400 mg of **1g** (2.88 mmol). Purification by flash column chromatography (98/2: diethyl ether/methanol) afforded 137 mg of the title compound as a colourless oil (30%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.39 (d, $^3J_{H-F}$ = 21.4 Hz, 3H, H-7) ; 1,58 (m, 2H) and 1.84 (m, 2H), H-3 ; 2.11 (s, 3H, H-6) ; 2.98 (m, 1H, H-2 a or b) and 3.44 (m, 1H, H-2 a or b) ; 3.63 (m, 1H, H-2 a or b) and 4.43 (m, 1H, H-2 a or b). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 21.4 (CH_3, C-6) ; 27.4 (d, $^2J_{C-F}$ = 24 Hz, CH_3, C-1) ; 36.3 (d, $^2J_{C-F}$ = 22 Hz, CH_2) and 37.2 (d, $^2J_{C-F}$ = 22 Hz, CH_2), C-3 ; 37.9 and 42.9 (2 CH_2, C-2) ; 92.1 (d, $^1J_{C-F}$ = 168 Hz, C, C-4) ; 168.8 (C-5). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm): δ – 154.56. MS (EI, 70 ev): *m/z* (relative intensity %) (16), 159 (100), 139 (72), 116 (60), 96 (80), 82 (68), 57 (32). HRMS (ESI): Calc for $C_8H_{14}NOF$: 159.1059, found 159.1052.

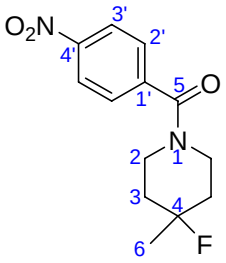


Compound 2h: 4-fluoro-4-methyl-1-(trifluoroacetyl) piperidine: Optimized procedure (-30°C, 5 min reaction time) was followed, starting from 500 mg of **1h** (2.58 mmol). Purification by flash column chromatography (90/10: petroleum ether/ethyl acetate) afforded 378 mg of the title compound as a colourless oil (69%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.42 (d, $^3J_{H-F}$ = 21.4 Hz, 3H, H-7) ; 1.71 (m, 2H, H-3 a and/or b) ; 1.95 (m, 2H, H-3 a and/or b) ; 3.12 (m, 1H, H-2 a or b) ; 3.47 (m, 1H, H-2 a or b) ; 3.86 (m, 1H, H-2 a or b) ; 4.40 (m, 1H, H-2 a or b). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 26.9 (d, $^2J_{C-F}$ = 23 Hz, CH_3, C-7) ; 35.8 and 36.8 (d, $^2J_{C-F}$ = 22 Hz, 2 CH_2, C-3) ; 39.7 and 41.8 (2 CH_2, C-2) ; 91.6 (d, $^1J_{C-F}$ = 168 Hz, C-4) ; 116.5 (q, $^1J_{C-F}$ = 286 Hz, C-6) ; 155.2 (q, $^2J_{C-F}$ = 36 Hz, C-5). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm): δ -70 (CF_3) ; -154.81 (F). MS

(EI, 70 ev): *m/z* (relative intensity %) 213 (100), 178 (99), 152 (38), 144 (96), 81 (60). HRMS (EI): Calc for $C_8H_{11}NOF_4$: 213.07768, found 213.0770.



Compound 2h': 4-hydroxy-4-methyl-1-(trifluoroacetyl) piperidine: Optimized procedure (-30°C, 60 min reaction time) was followed, starting from 388 mg of **1h** (2.01 mmol). Purification by flash column chromatography (90/10: petroleum ether/ethyl acetate) afforded 119 mg of compound **2h** (28%). The title compound **2h'** (131 mg, 31%) was then eluted (80/20: petroleum ether/ethyl acetate) as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.28 (s, 3H, H-7) ; 1.67 (m, 4H, H-3 a and b) ; 3.25 (m, 1H, H-2 a or b) ; 3.56 (m, 1H, H-2 a or b) ; 3,76 (m, 1H, H-2 a or b) ; 4.26 (m, 1H, H-2 a or b). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 30.9 (CH_3, C-7) ; 37.4 and 38.2 (2 CH_2, C-3) ; 39.1 and 41.0 (2 CH_2, C-2) ; 68.5 (C-4) ; 117.5 (q, $^1J_{C\text{-}F}$ = 284 Hz, C-6) ; 154.3 (q, $^2J_{C\text{-}F}$ = 35 Hz, C-5). MS (EI, 70 ev): *m/z* (relative intensity %) 211 (14), 193 (100), 178 (88), 140 (40). HRMS (EI): Calc for $C_8H_{12}NO_2F_3$: 211.08201, found 211.0827. Mp (°C): 70.



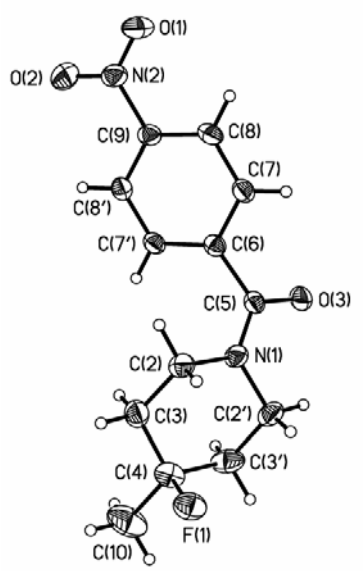
Compound 2j: 4-fluoro-4-methyl-1-(4-nitrobenzoyl) piperidine: Optimized procedure (-30°C, 5 min reaction time) was followed, starting from 500 mg of **1j** (2.03 mmol). Purification by flash column chromatography (70/30: petroleum ether/ethyl acetate) afforded 296 mg of the title compound as a colourless powder (55%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.43 (d, $^3J_{H\text{-}F}$ = 21.4 Hz, 3H, H-6) ; 1.79 (m, 4H, H-") ; 3.19 (m, 1H) and 4.55 (m, 1H), H-2 a and/or b ; 3.36 (m, 2H, H-2 a and/or b) ; 7.58 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, H-2') ; 8.28 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 2H, H-3'). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 27.0 (d, $^2J_{C\text{-}F}$ = 24 Hz, CH_3, C-6) ; 35.9 (d, $^2J_{C\text{-}F}$ = 22 Hz, CH_2) and 36.8 (d, $^2J_{C\text{-}F}$ = 23,3 Hz, CH_2), C-3 ; 38.8 and 43.6 (2 CH_2, C-2) ; 92.0 (d, $^1J_{C\text{-}F}$ = 168 Hz, C-4) ; 123.9 (2 CH, C-3') ; 127.9 (2 CH, C-

2') ; 142.5 (C-1') ; 148.3 (C-4') ; 170.0 (C-5). $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm) ppm): -154.72. MS (EI, 70 ev): *m/z* (relative intensity %) 266 (6), 247 (28), 150 (100), 104 (78), 83 (80). HRMS (ESI): Calc for $C_{13}H_{14}N_2O_3F$: 265.09885, found 265.0987. Mp (°C): 145.

XRD: Seven sets of narrow data frames (30 s per frame) were collected at different values of θ, for 2 and 5 initial values of ϕ and ω, respectively, using 0.5° increments of ϕ or ω.

Crystal structure analysis: C_{13} H_{15} F N_2 O_3, room temperature, triclinic, space group P-1 ; dimensions: a = 6.6927(3) Å, b = 8.2566(3) Å, c = 12.1565(5) Å, α = 79.479(2)° , β = 80.510(2) ° , γ = 78.922(2)°, V = 642.26(5)$Å^3$; Z = 2; total reflections collected: 13438 ; independent reflections: 2260 (1917 Fo > 4σ (Fo)) ; data were collected up to a 2Θmax value of 50° (100 % coverage). Number of variables: 173; R_1 = 0.0366, wR_2 = 0.1177, S = 1.136 ; highest residual electron density 0.163 e.$Å^{-3}$.

Calculated parameters:



BOND LENGTHS (Å)

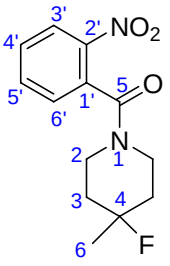
Bond	Length (Å)	Bond	Length (Å)
C(1)-C(2)	1.381(2)	C(9)-H(9A)	0.9700
C(1)-C(6)	1.387(2)	C(9)-H(9B)	0.9700
C(1)-H(1)	0.9300	C(10)-C(11)	1.513(2)
C(2)-C(3)	1.375(2)	C(10)-H(10A)	0.9700
C(2)-H(2)	0.9300	C(10)-H(10B)	0.9700
C(3)-C(4)	1.378(2)	C(11)-F(18)	1.4301(19)
C(3)-N(14)	1.469(2)	C(11)-C(12)	1.503(3)
C(4)-C(5)	1.380(2)	C(11)-C(19)	1.508(3)
C(4)-H(4)	0.9300	C(12)-C(13)	1.505(3)
C(5)-C(6)	1.392(2)	C(12)-H(12A)	0.9700
C(5)-H(5)	0.9300	C(12)-H(12B)	0.9700
C(6)-C(7)	1.504(2)	C(13)-H(13A)	0.9700
C(7)-O(17)	1.2266(17)	C(13)-H(13B)	0.9700
C(7)-N(8)	1.3451(19)	N(14)-O(16)	1.2167(19)
N(8)-C(9)	1.4603(19)	N(14)-O(15)	1.2172(19)
N(8)-C(13)	1.4632(19)	C(19)-H(19A)	0.9600
C(9)-C(10)	1.507(2)	C(19)-H(19B)	0.9600
		C(19)-H(19C)	0.9600

ATOMIC COORDINATES (X 10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å ^2 X 10^3)

Atom	x/a	y/b	z/c	U(iso) Occ
C(1)	1627(2)	2802(2)	2598(1)	43(1)
C(2)	3117(2)	2943(2)	1670(1)	45(1)
C(3)	4920(2)	3413(2)	1794(1)	40(1)
C(4)	5286(2)	3752(2)	2804(1)	41(1)
C(5)	3797(2)	3583(2)	3730(1)	40(1)
C(6)	1959(2)	3099(2)	3635(1)	37(1)
C(7)	211(2)	3030(2)	4586(1)	38(1)
N(8)	527(2)	2003(2)	5559(1)	44(1)
C(9)	2379(2)	798(2)	5774(1)	47(1)
C(10)	3257(3)	1141(2)	6757(2)	54(1)
C(11)	1685(3)	1225(2)	7802(1)	54(1)
C(12)	-272(3)	2366(2)	7537(2)	65(1)
C(13)	-1074(2)	2005(2)	6537(1)	54(1)
N(14)	6512(2)	3555(2)	809(1)	51(1)
O(15)	8022(2)	4122(2)	889(1)	71(1)
O(16)	6237(2)	3103(2)	-45(1)	72(1)
O(17)	-1454(2)	3902(2)	4437(1)	52(1)
F(18)	1182(2)	-418(1)	8123(1)	63(1)
C(19)	2513(5)	1558(3)	8805(2)	95(1)
H(1)	389	2504	2528	51
H(2)	2906	2726	978	55
H(4)	6510	4086	2862	50
H(5)	4023	3794	4421	48
H(9A)	3395	864	5106	56
H(9B)	2051	-323	5936	56
H(10A)	3771	2191	6548	65
H(10B)	4406	265	6927	65
H(12A)	-31	3513	7388	78
H(12B)	-1310	2258	8192	78
H(13A)	-1520	925	6720	65
H(13B)	-2250	2848	6357	65
H(19A)	1489	1474	9457	143
H(19B)	2858	2661	8651	143
H(19C)	3719	752	8945	143

ANGLES (DEG)

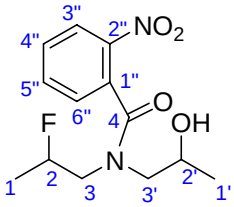
Angle	Valeur (°)	Angle	Valeur (°)
C(2)-C(1)-C(6)	120.71(14)	C(9)-C(10)-H(10A)	109.1
C(2)-C(1)-H(1)	119.6	C(11)-C(10)-H(10A)	109.1
C(6)-C(1)-H(1)	119.6	C(9)-C(10)-H(10B)	109.1
C(3)-C(2)-C(1)	118.41(13)	C(11)-C(10)-H(10B)	109.1
C(3)-C(2)-H(2)	120.8	H(10A)-C(10)-H(10B)	107.9
C(1)-C(2)-H(2)	120.8	F(18)-C(11)-C(12)	106.29(15)
C(2)-C(3)-C(4)	122.48(14)	F(18)-C(11)-C(19)	105.05(15)
C(2)-C(3)-N(14)	118.48(13)	C(12)-C(11)-C(19)	114.17(17)
C(4)-C(3)-N(14)	119.04(14)	F(18)-C(11)-C(10)	105.46(13)
C(3)-C(4)-C(5)	118.55(13)	C(12)-C(11)-C(19)	111.19(14)
C(3)-C(4)-H(4)	120.7	F(18)-C(11)-C(19)	113.79(18)
C(5)-C(4)-H(4)	120.7	C(12)-C(11)-C(10)	113.20(14)
C(4)-C(5)-C(6)	120.42(13)	C(19)-C(11)-C(10)	108.9
C(4)-C(5)-H(5)	119.8	C(11)-C(12)-C(13)	108.9
C(6)-C(5)-H(5)	119.8	C(11)-C(12)-H(12A)	108.9
C(1)-C(6)-C(5)	119.41(13)	C(13)-C(12)-H(12A)	108.9
C(1)-C(6)-C(7)	117.48(13)	C(11)-C(12)-H(12B)	107.8
C(5)-C(6)-C(7)	122.88(12)	C(13)-C(12)-H(12B)	110.32(14)
O(17)-C(7)-N(8)	122.64(13)	H(12A)-C(12)-H(12B)	109.6
O(17)-C(7)-C(6)	118.47(13)	N(8)-C(13)-C(12)	109.6
N(8)-C(7)-C(6)	118.89(12)	N(8)-C(13)-H(13A)	109.6
C(7)-N(8)-C(9)	126.47(12)	C(12)-C(13)-H(13A)	109.6
C(7)-N(8)-C(13)	120.59(12)	H(13A)-C(13)-H(13B)	108.1
C(9)-N(8)-C(13)	112.94(12)	O(16)-N(14)-O(15)	123.68(14)
N(8)-C(9)-C(10)	110.77(13)	O(16)-N(14)-C(3)	117.91(14)
N(8)-C(9)-H(9A)	109.5	O(15)-N(14)-C(3)	118.41(14)
C(10)-C(9)-H(9A)	109.5	C(11)-C(19)-H(19A)	109.5
N(8)-C(9)-H(9B)	109.5	C(11)-C(19)-H(19B)	109.5
C(10)-C(9)-H(9B)	109.5	H(19A)-C(19)-H(19B)	109.5
H(9A)-C(9)-H(9B)	108.1	C(11)-C(19)-H(19C)	109.5
C(9)-C(10)-C(11)	112.34(14)	H(19A)-C(19)-H(19C)	109.5
		H(19B)-C(19)-H(19C)	109.5



Compound 2k: 4-fluoro-4-methyl-1-(2-nitrobenzoyl) piperidine: Optimized procedure (-30°C, 5 min reaction time) was followed, starting from 500 mg of **1k** (2.03 mmol). Purification by flash column chromatography (99/1: dichloromethane/NH_3aq) afforded 284 mg of the title compound as a colourless oil (53%). The second compound *N*-(2-fluoropropyl)-*N*-(2-hydroxypropyl)-2-nitrobenzamide **2k'** (95 mg, 17 %) was then eluted (98/1/1: dichloromethane/methanol/NH_3aq) as a colourless oil.

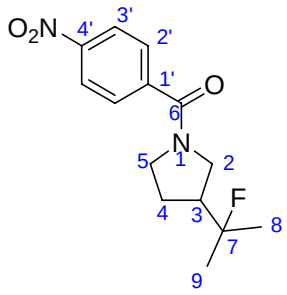
Compound 2k: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.39 (d, $^{3}J_{H\text{-}F}$ = 21.5 Hz, 3H, H-6) ; 1.77 (m, 4H, H-2) ; 3.25 (m, 3H) and 4.58 (m, 1H), H-3 a and/or b) ; 7.36 (d, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 1H, H-6') ; 7.54 (d, $^{3}J_{H\text{-}H}$ = 7.9 Hz, 1H, H-5') ; 7.68 (d, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 1H, H-4') ; 8.15 (d, $^{3}J_{H\text{-}H}$ = 8.1 Hz, 1H, H-3'). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 27.3 (d, $^{2}J_{C\text{-}F}$ = 24 Hz, CH_3, C-6) ; 36.4 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, 2 CH_2, C-3) ; 38.1 (d, $^{3}J_{C\text{-}F}$ = 2 Hz, 2 CH_2, C-2) ; 92.4 (d, $^{1}J_{C\text{-}F}$ = 169 Hz, C-4) ; 125.1 (CH, C-3') ; 128.3 (CH, C-6') ; 130.1 (CH, C-4') ; 133.3 (C-1') ; 134.8 (CH, C-5') ; 145.6 (C-2') ; 166.4 (C-5). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm):-155.26 . MS (EI, 70 ev): *m/z* (relative intensity %) 252 (26), 232 (51), 132 (65), 112 (100), 91 (73). HRMS (EI): Calc for $C_{13}H_{15}N_2O_3F$: 266.10667, found 266.1058.

It should be pointed out that in ^{13}C NMR spectrum of compound **2k'**, peaks are doubled due to the presence of rotamers.



Compound 2k': *N*-(2-fluoropropyl)-*N*-(2-hydroxypropyl)-2-nitrobenzamide: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.30 (dd, $^{3}J_{H\text{-}F}$ = 23.5 Hz, $^{4}J_{H\text{-}F}$ = 6.4 Hz, 3H, H-1) ; 1.34 (d, $^{3}J_{H\text{-}H}$ = 6.4 Hz, 3H, H-1') ; 2.71 (sl, 1H, OH) ; 2.80 (m, 4H, H-3 and H-3') ; 4.76 (dm, $^{1}J_{H\text{-}F}$ = 48.6 Hz, H-2) ; 5.28 (m, 1H, H-2') ; 7.72 (dd, 1H, $^{4}J_{H\text{-}H}$ = 1.5 Hz, $^{3}J_{H\text{-}H}$ = 7.4 Hz, H-5" or H-6") ; 7.59 (dd, 1H, $^{4}J_{H\text{-}H}$ = 1.9 Hz, $^{3}J_{H\text{-}H}$ = 7.6 Hz, H-5" or H-6") ; 7.63 (t, 1H, $^{4}J_{H\text{-}H}$ = 1.9 Hz, H-4") ; 7.88 (d, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 1H, H-3"). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ.17.6 and 17.7 (CH_3, C-1') ; 18.6 and 18.7 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, CH_3, C-1) ; 54.1 and 54.2 (CH_2, C-3') ; 54.7 and 54.8 (d, $^{2}J_{C\text{-}F}$ = 21 Hz, CH_2, C-3) ; 73.0 and 73.1 (CH, C-2') ;

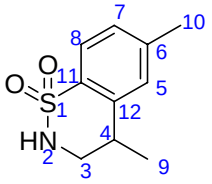
90.7 and 90.8 (d, $^{1}J_{C\text{-}F}$ = 165 Hz, C-2) ; 124.1 (CH, C-3") ; 128.3 (C-1") ; 130.2 (CH, C-6") ; 131.9 (CH, C-4") ; 133.3 (CH, C-5") ; 148.3 (C-2") ; 165.4 (C-4). $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm): -179.27 and -179.24. MS (EI, 70 ev): *m/z* (relative intensity %) 250 (15), 193 (26), 119 (39), 106 (70), 72 (100), 60 (69). HRMS (EI): Calc for $C_{11}H_{12}N_2O_3F$: 239.08320, found 239.0840 and for $C_{11}H_{13}N_2O_4$: 237.08753, found 237.0883.



Compound 2l: (3-(2-fluoropropan-2-yl) pyrrolidin-1-yl) (4-nitrophenyl) methanone:

Optimized procedure (0°C, 3 min reaction time) was followed, starting from 300 mg of **1m** (1.15 mmol). Purification by flash column chromatography (99/1: dichloromethane/methanol) afforded 240 mg of the title compound as a colourless powder (86%).

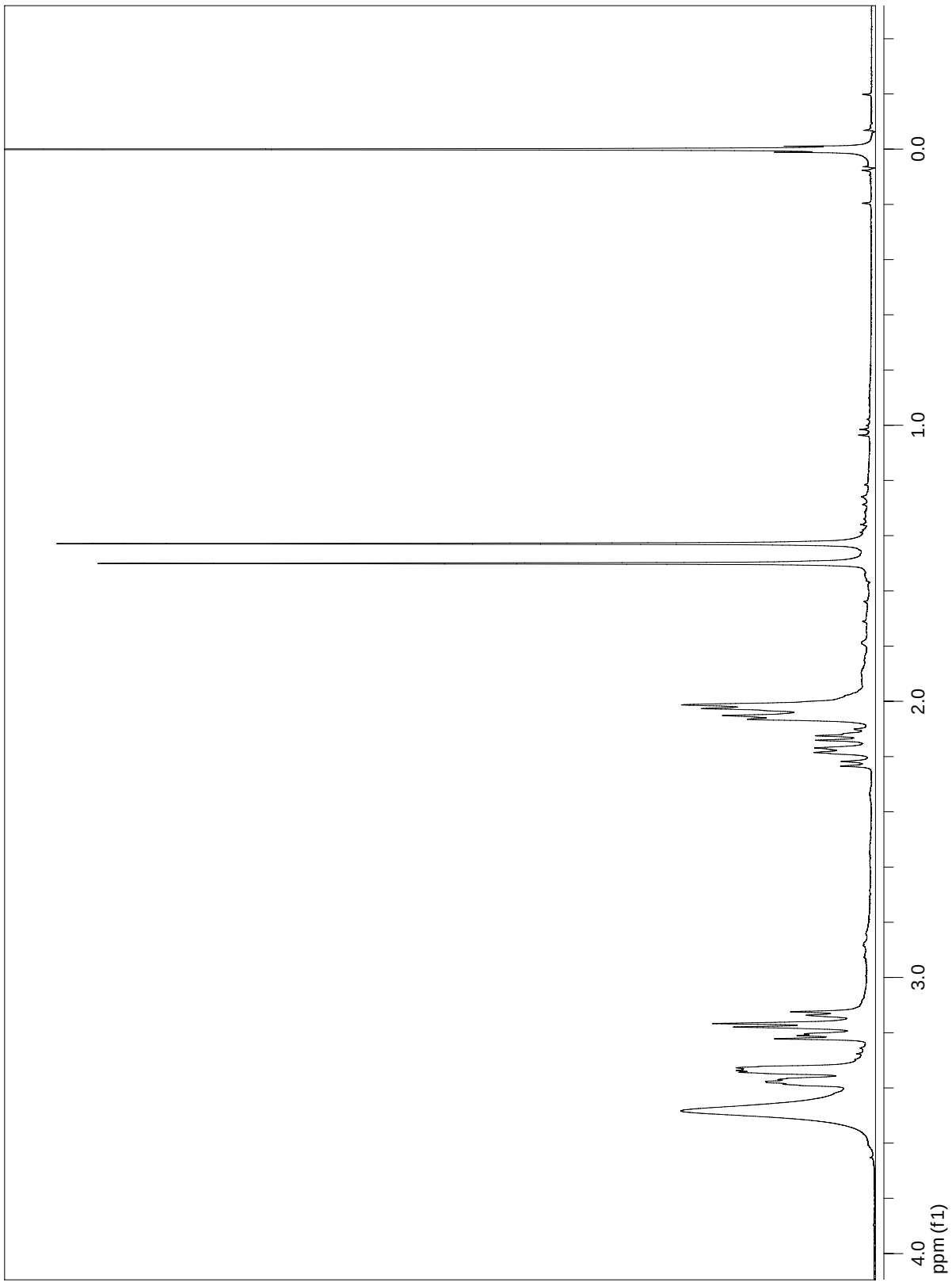
^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.28 (d, $^{3}J_{H\text{-}F}$ = 20.8 Hz, 3H, H-8 or H-9) ; 1.40 (d, $^{3}J_{H\text{-}F}$ = 21.4 Hz) and 1.41 (d, $^{3}J_{H\text{-}F}$ = 21.3 Hz), 3H, H-9 or H-8 ; 1.96 (m, 2H, H-4) ; 2.39 (m, 1H, H-3) ; 3.47 (m, 3H, H-5 and H-2 a or b) ; 3.82 (m, 1H, H-2 a or b) ; 7.65 (d, $^{3}J_{H\text{-}H}$ = 8.8 Hz) and 7.67 (d, $^{3}J_{H\text{-}H}$ = 8.8 Hz), 2H, H-2' ; 8.25 (d, $^{3}J_{H\text{-}H}$ = 8.8 Hz) and 8.27 (d, $^{3}J_{H\text{-}H}$ = 8.8 Hz), 2H, H-3'. ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 25.3 and 27.2 (d, CH_2, $^{3}J_{C\text{-}F}$ = 4 Hz, C-4) ; 25.6 (d, CH_3, $^{2}J_{C\text{-}F}$ = 24.6 Hz) and 25.8 (d, CH_3, $^{2}J_{C\text{-}F}$ = 24.7 Hz) and 26.3 (d, CH_3, $^{2}J_{C\text{-}F}$ = 26.2 Hz) and 26.7 (d, CH_3, $^{2}J_{C\text{-}F}$ = 24.8 Hz), C-8 and C-9 ; 46.7 and 49.8 (CH_2, C-5) ; 47.2 (d, CH, $^{2}J_{C\text{-}F}$ = 22.7 Hz) and 49.0 (d, CH, $^{2}J_{C\text{-}F}$ = 22.2 Hz), C-3 ; 47,3 and 49.9 (d, 2 CH_2, $^{3}J_{C\text{-}F}$ = 4.8 Hz, C-2) ; 94.0 (d, $^{1}J_{C\text{-}F}$ = 168.9 Hz) and 94.2 (d, $^{1}J_{C\text{-}F}$ = 168.3 Hz), C-7 ; 123.6 and 123.7 (2 CH, C-3') ; 128.1 (2 CH, C-2') ; 142.5 and 142.7 (C-1') ; 148.4 (C-4') ; 167.3 and 167.4 (C-6). $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$, external standard C_6F_6 (δ_F -162.90 ppm), ppm):-151.41 and -151.31. MS (EI, 70 ev): *m/z* (relative intensity %) 168 (35), 150 (61), 73 (88), 59 (100). HRMS (EI): Calc for $C_{14}H_{17}N_2O_3F$: 280.12232, found 280.1220. Mp (°C): 69.



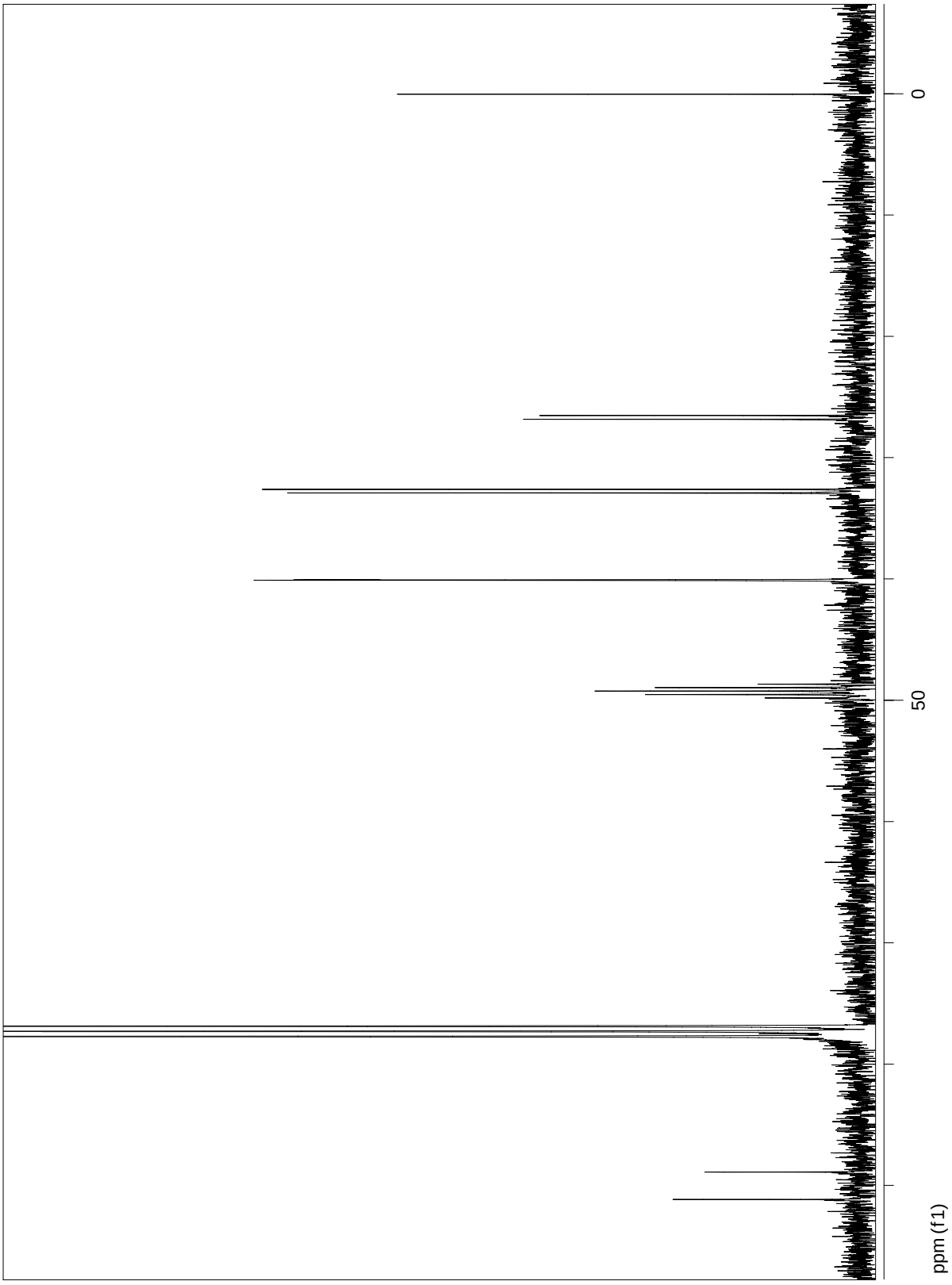
Compound 2p: 4,6-dimethyl-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-dioxide: Optimized procedure (0°C, 3 min reaction time) was followed, starting from 507 mg of **1p** (1.98 mmol). Purification by flash column chromatography (95/5: petroleum ether/ethyl acetate) afforded 340 mg of the title compound as a white power (81%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.34 (d, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 3H, H-9) ; 2.37 (s, 3H, H-10) ; 2.99 (m, 1H, H-12) ; 3.43 (m, 1H, H-3 or H-3') ; 3.83 (m, 1H, H-3 or H-3') ; 5.00 (t, $^{3}J_{H\text{-}H}$ = 7.7 Hz, 1H, H-2) ; 7.13 (s, 1H, H-5) ; 7.17 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 1H, H-7) ; 7.90 (d, $^{3}J_{H\text{-}H}$ = 9.6 Hz, 1H, H-8). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 20.2 (CH_3, C-9) ; 22.0 (CH_3, C-10) ; 31.6 (CH, C-4) ; 48.2 (CH_2, C-3) ; 123.2 (CH, C-8) ; 128.2 (CH, C-7) ; 129.0 (CH, C-5) ; 134.3 (C-11) ; 140.2 (C-6) ; 143.3 (C-12). MS (EI, 70 ev): *m/z* (relative intensity %) (38), 132 (64), 117 (100), 85 (52), 83 (74). HRMS (ESI): Calc for $C_{10}H_{13}NO_2S$: 211.06670, found 211.0664. Mp (°C): 84.

Supplementary Material (ESI) for Chemical Communications

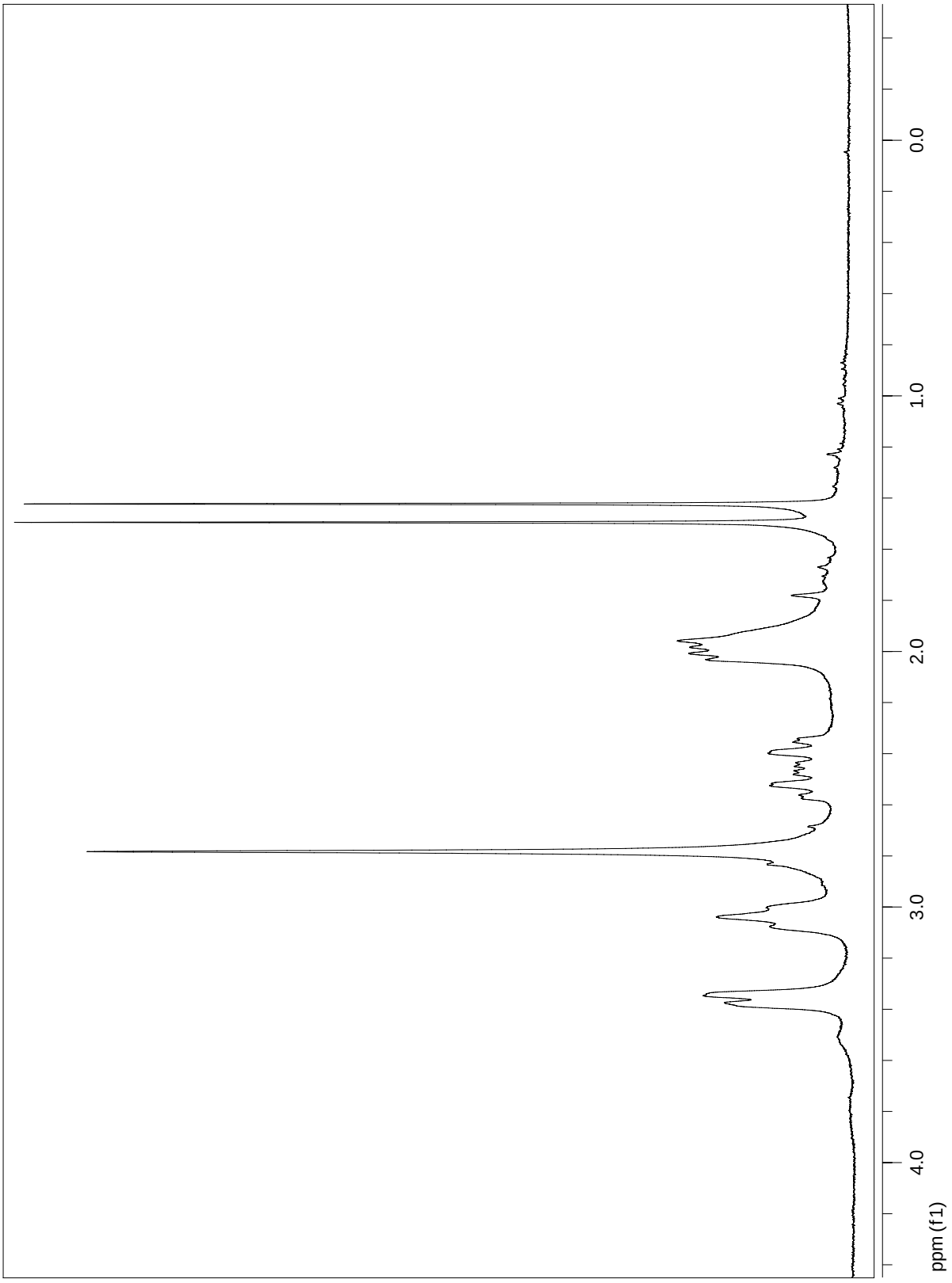
^{1}H NMR of compound **2a.HCl**:



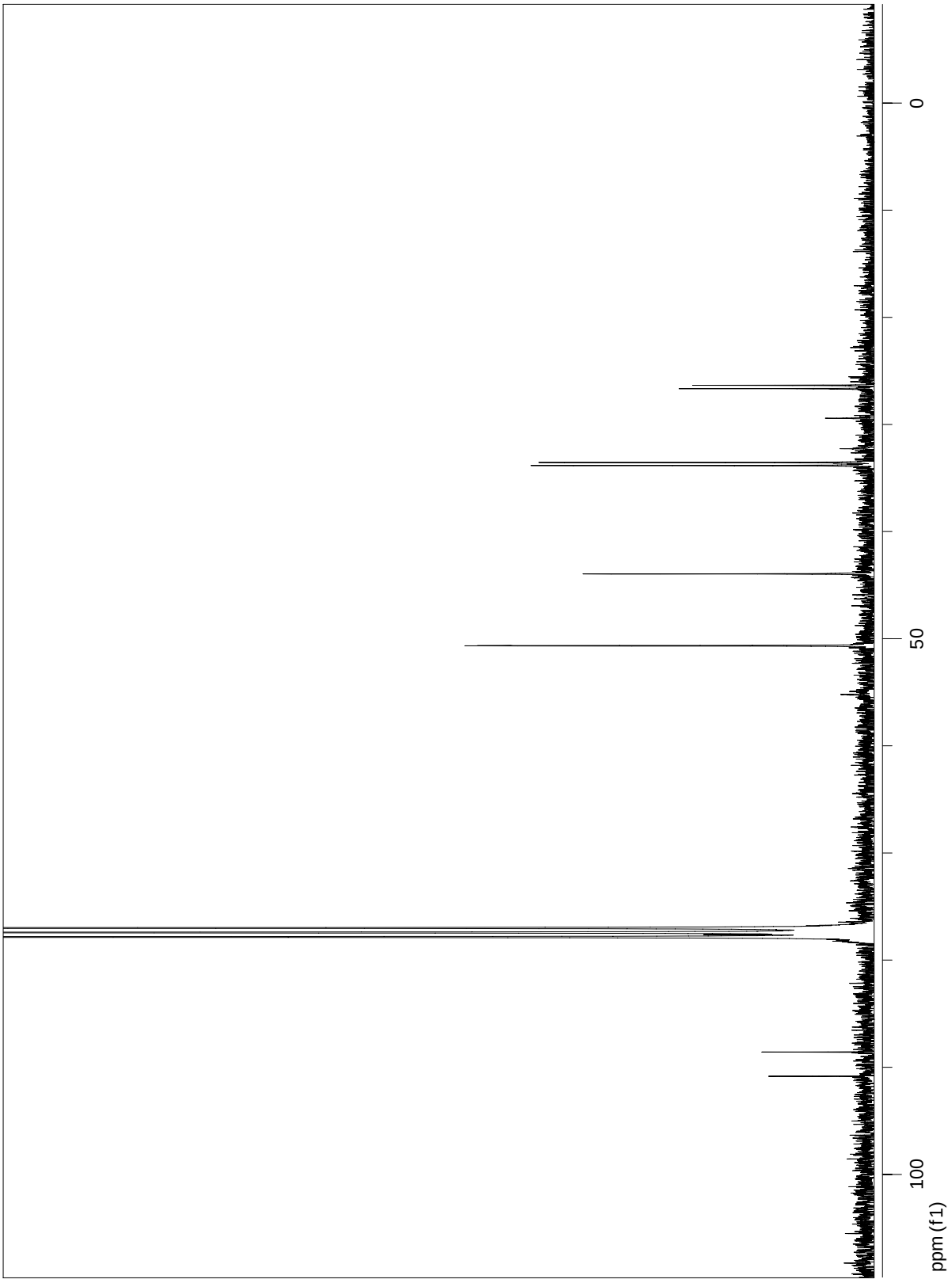
^{13}C NMR of compound **2a.HCl**:



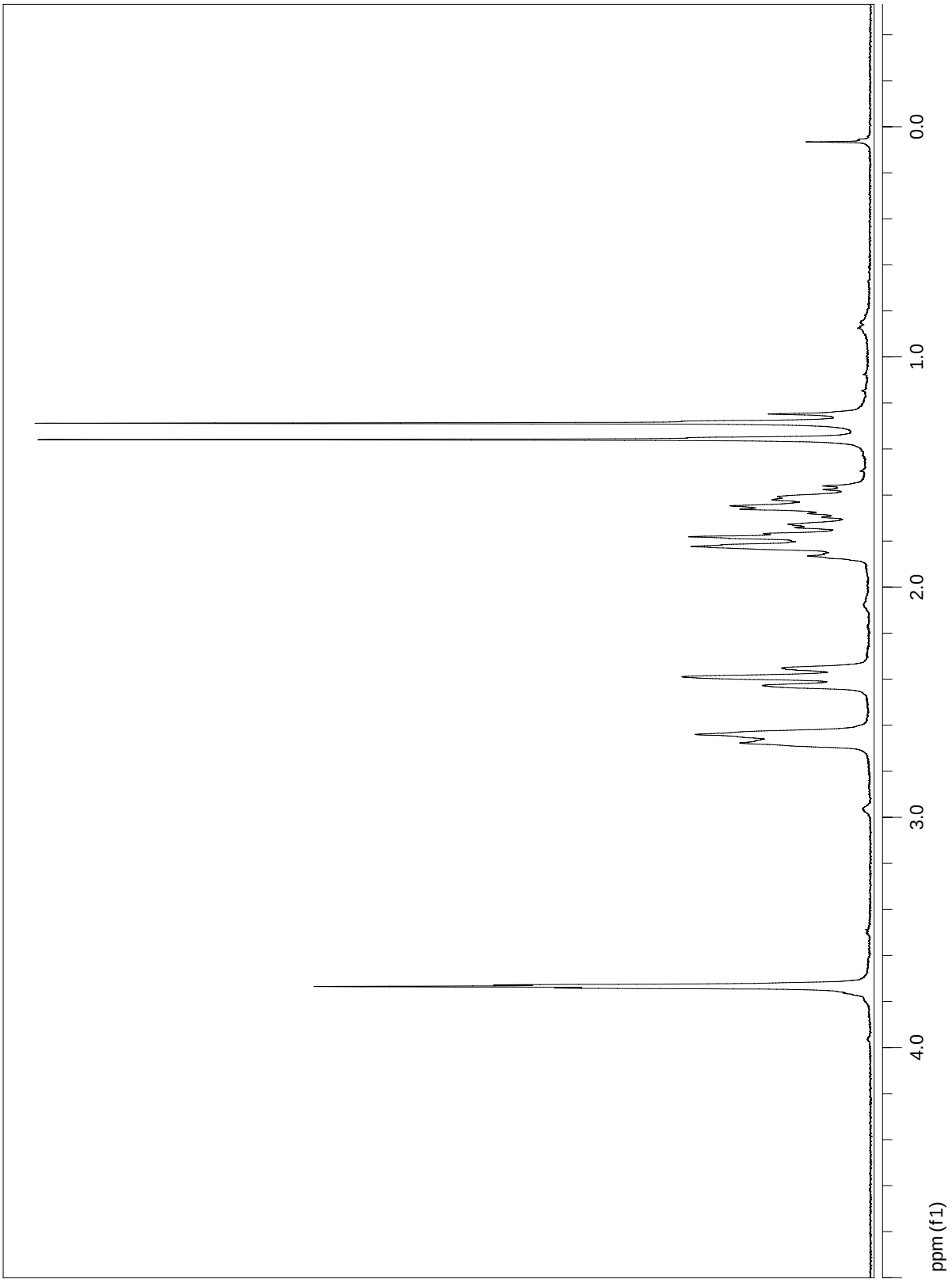
^{1}H NMR of compound **2b.HCl**:



^{13}C NMR of compound **2b.HCl**:



^{1}H NMR of compound **2d**:



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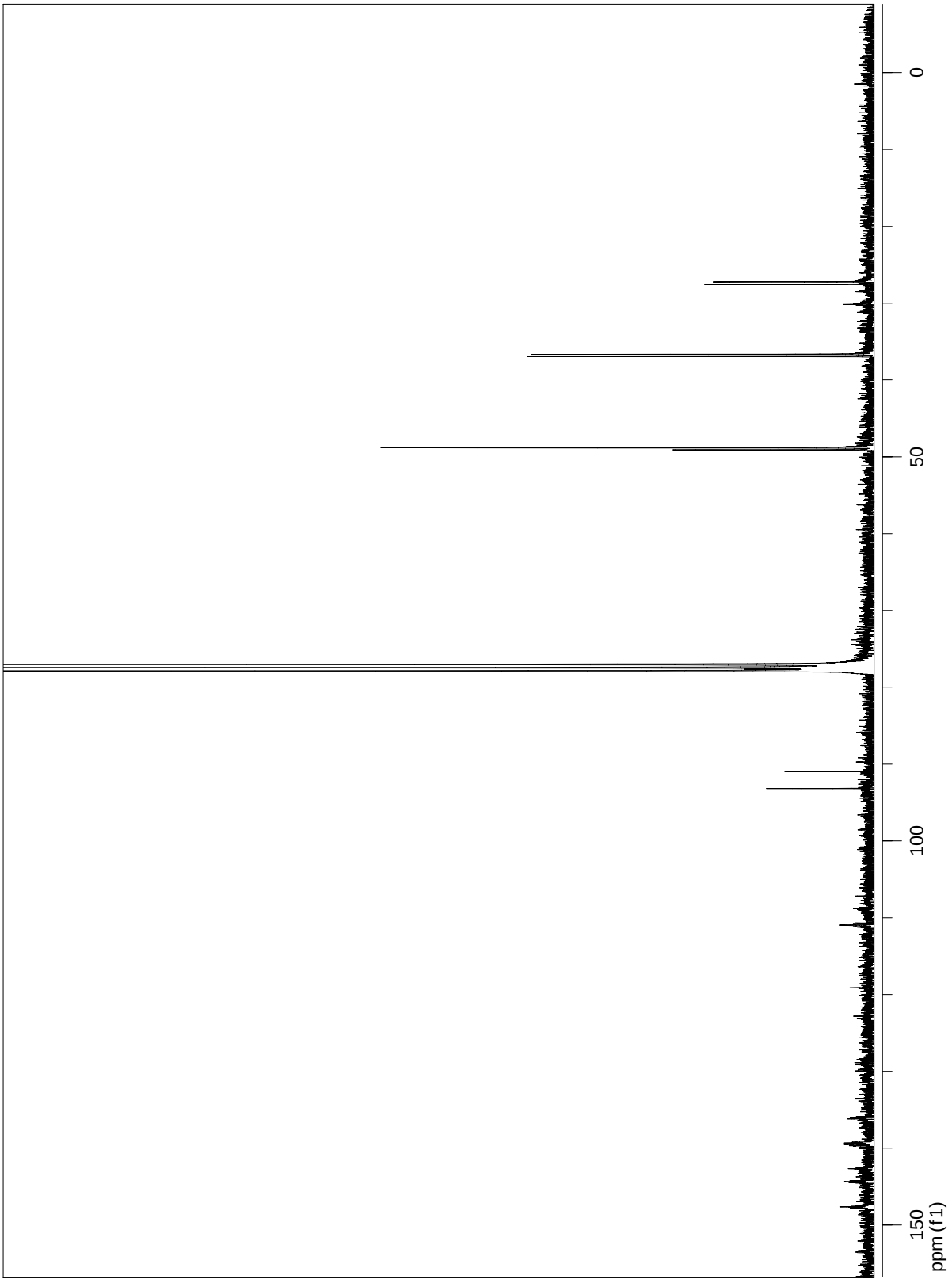

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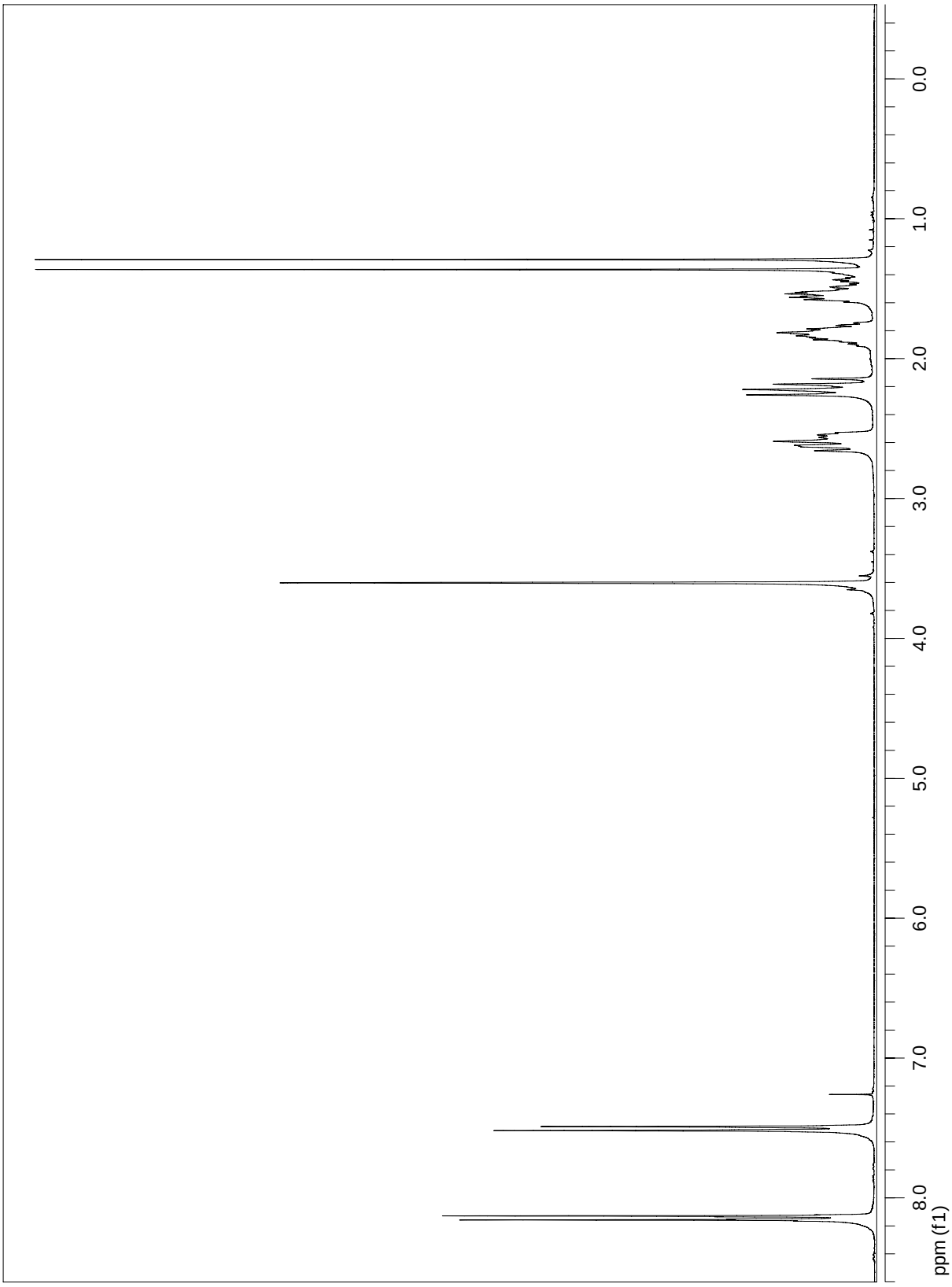
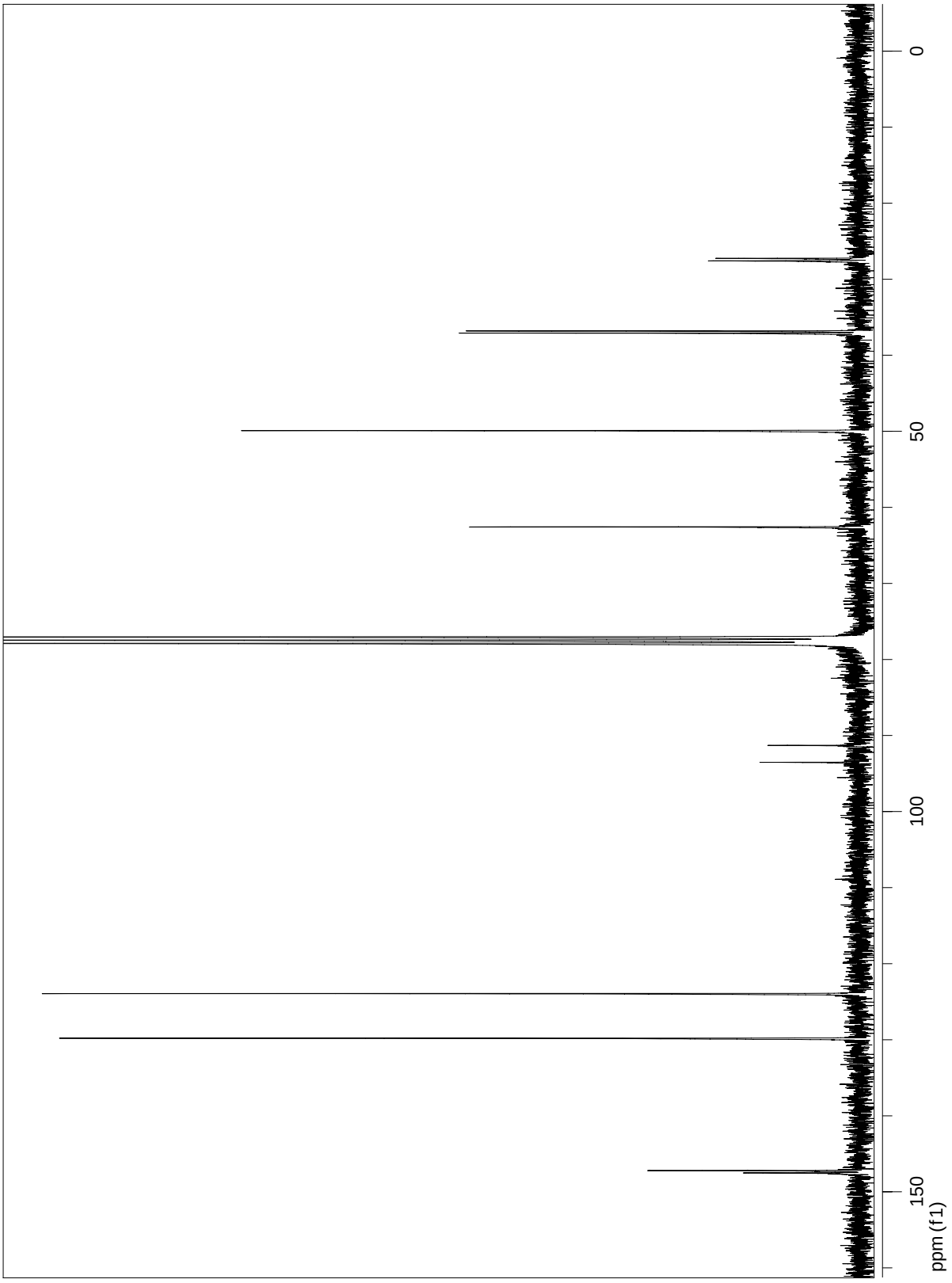


^{13}C NMR of compound **2e**:



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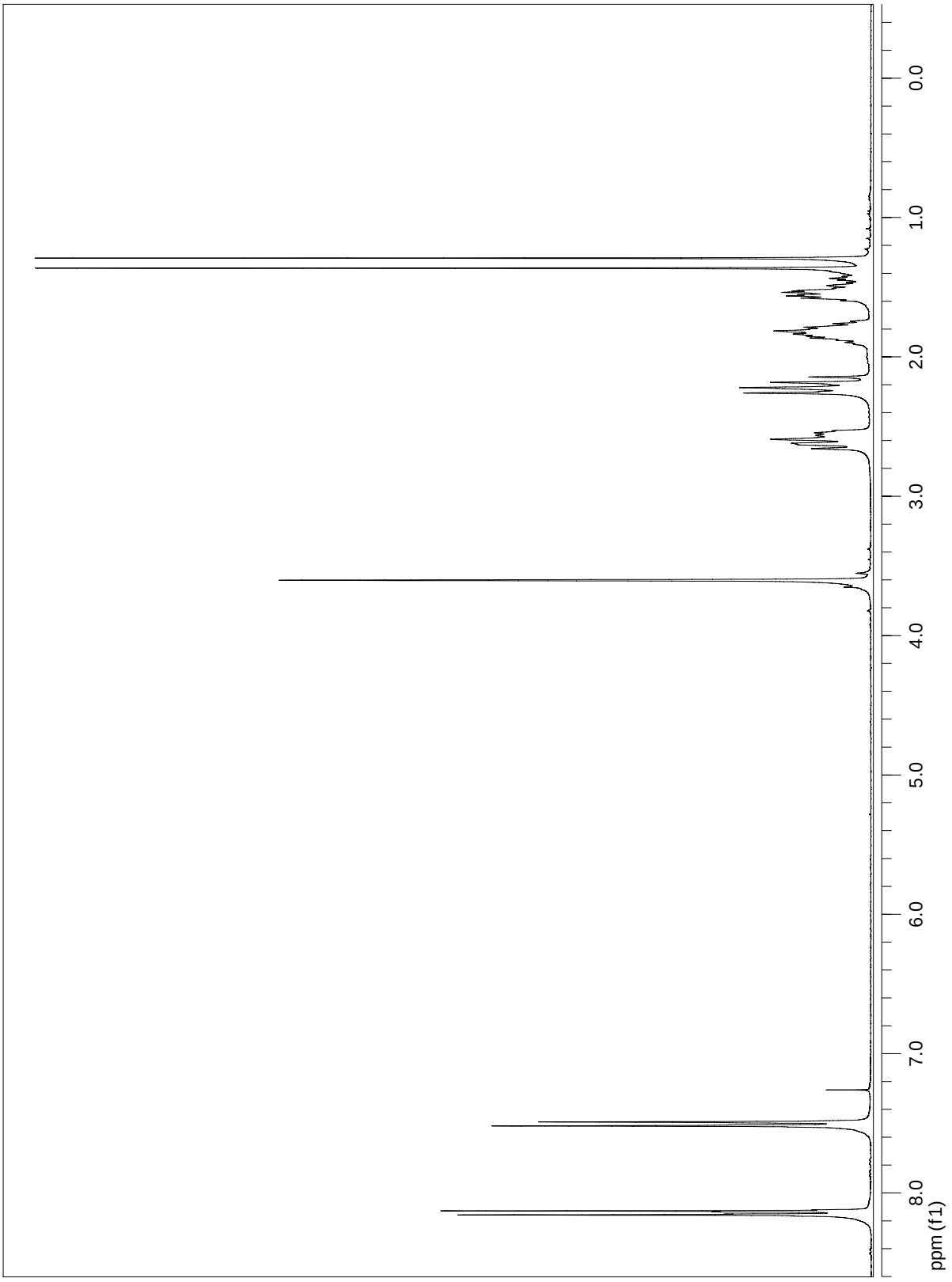

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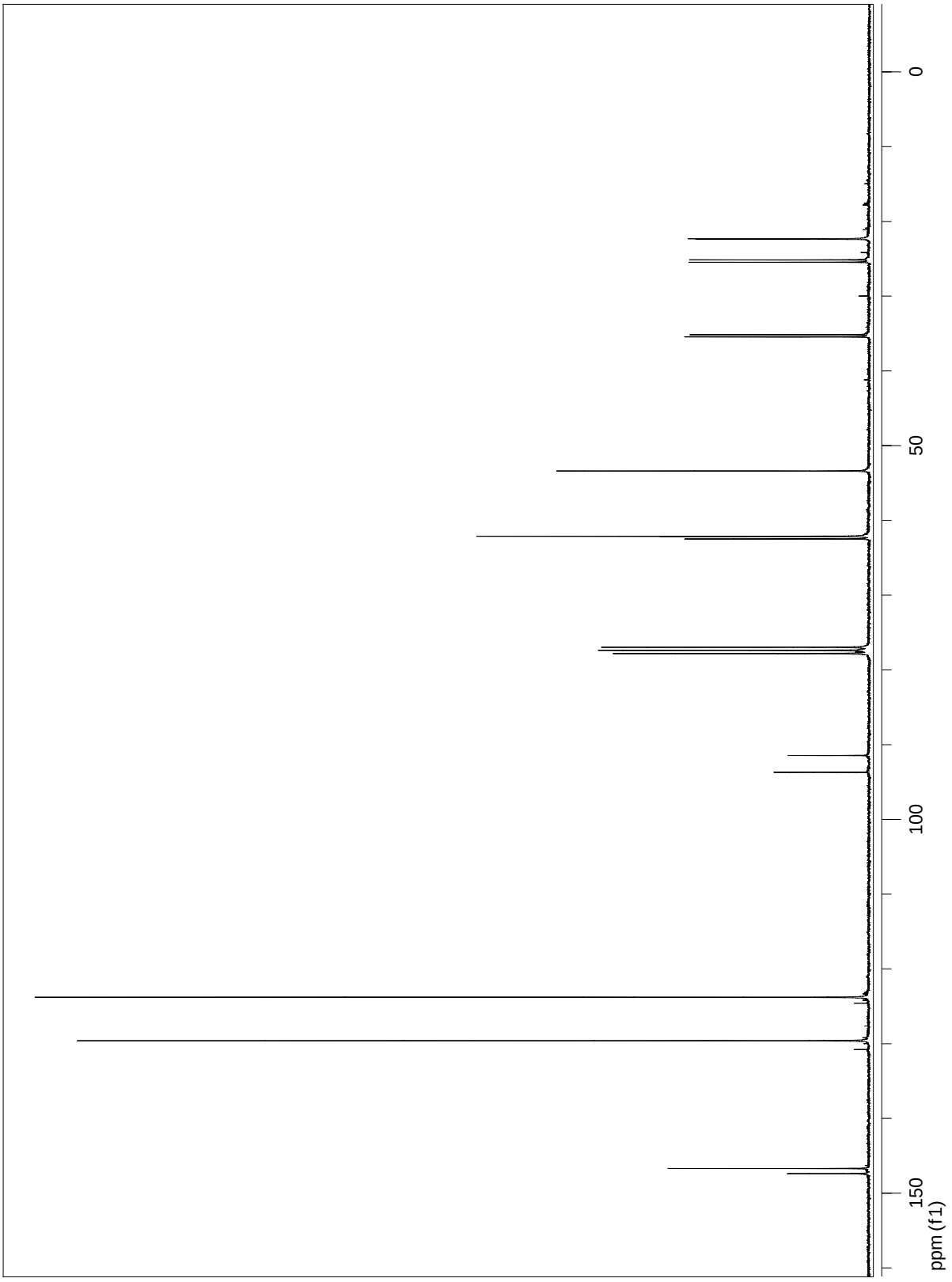
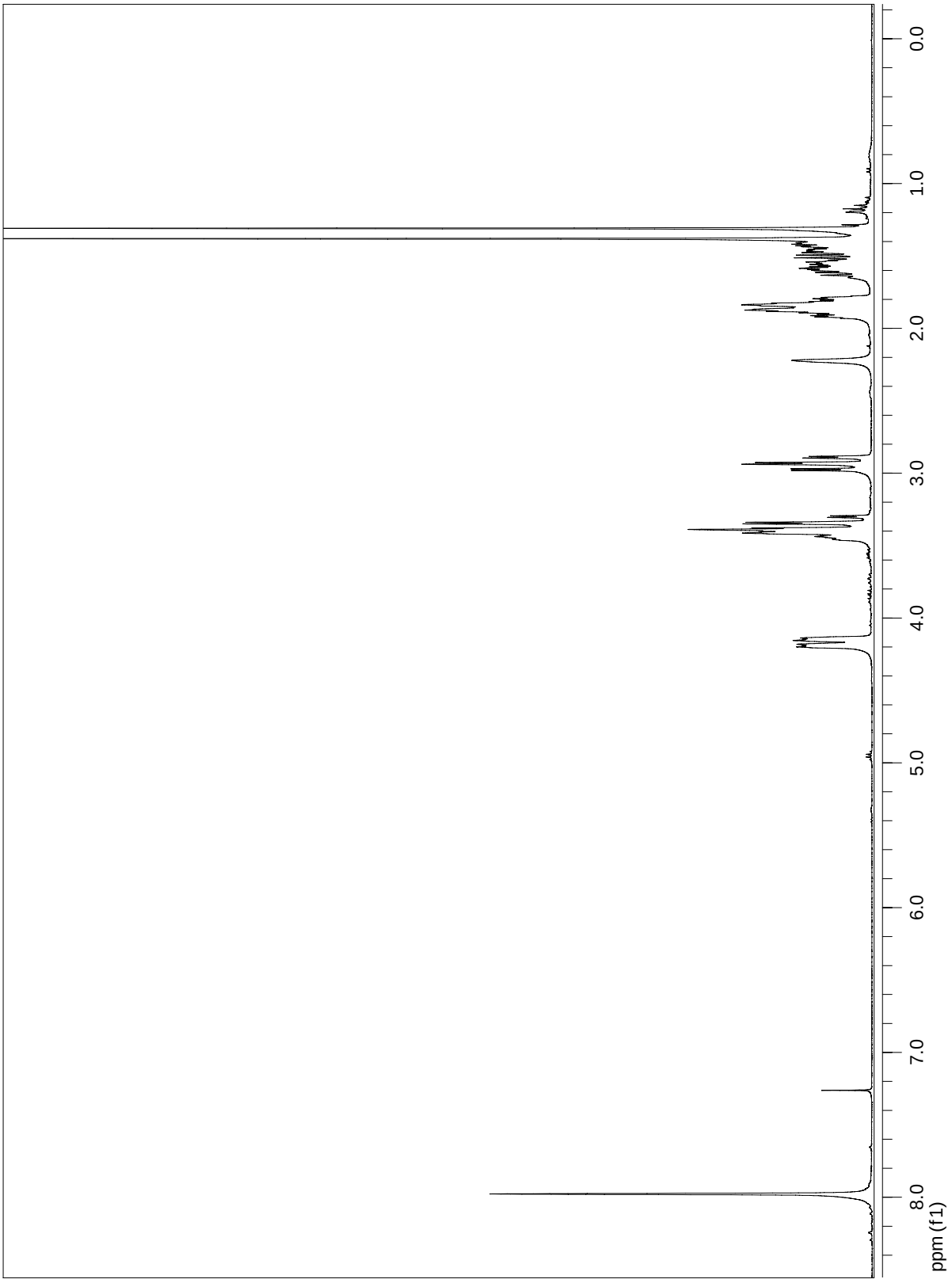
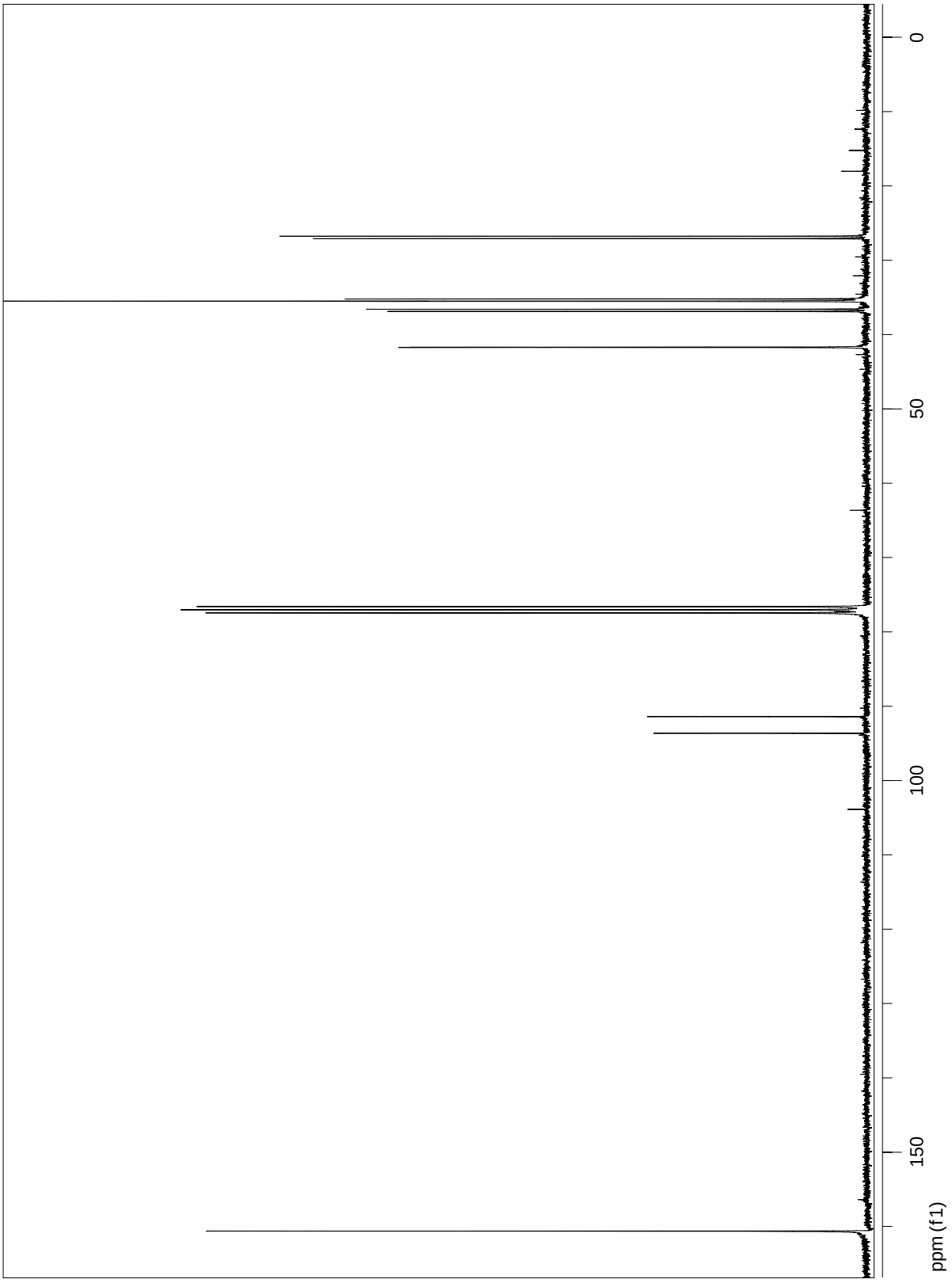


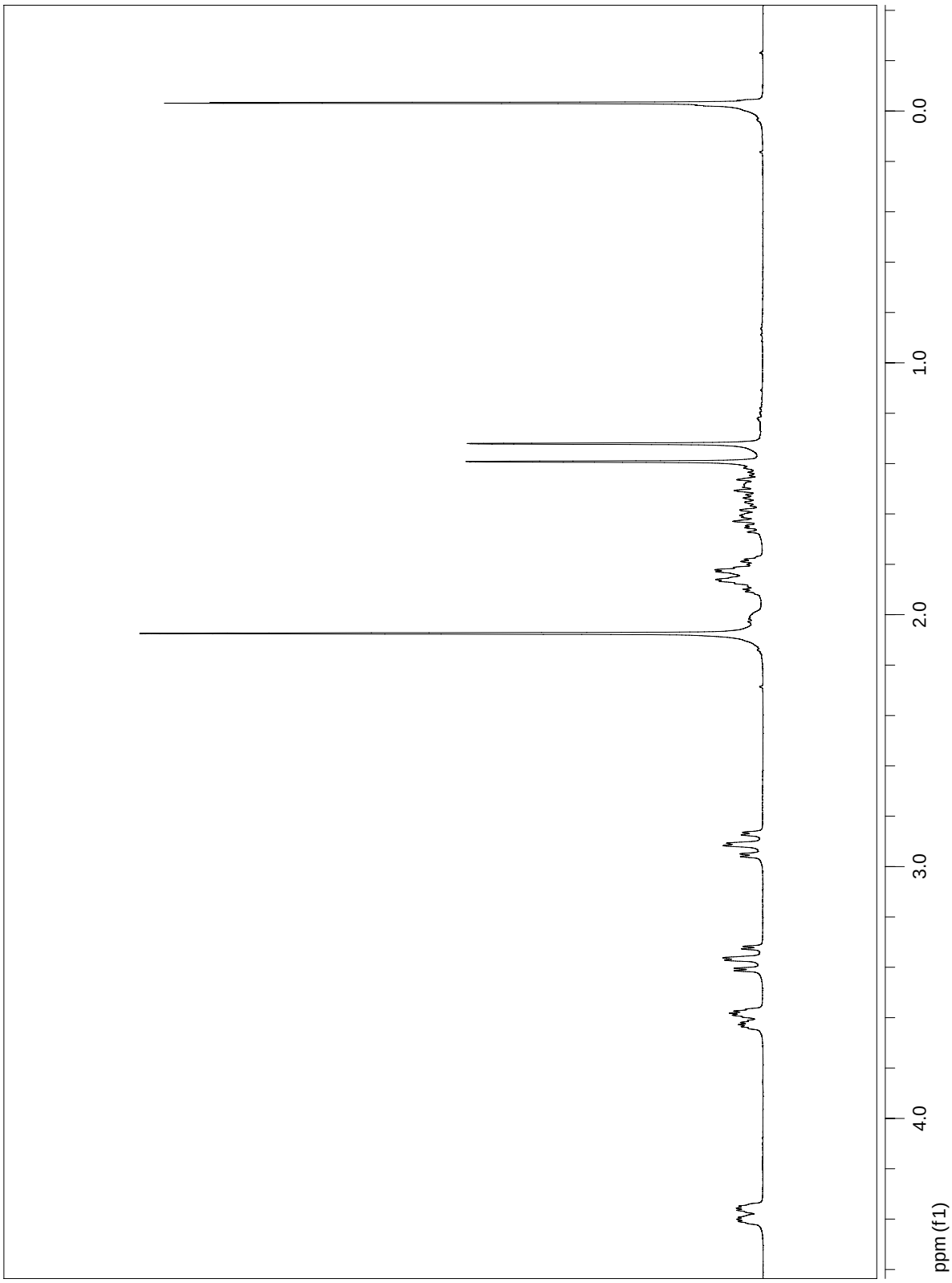
^{1}H NMR of compound **2f**:



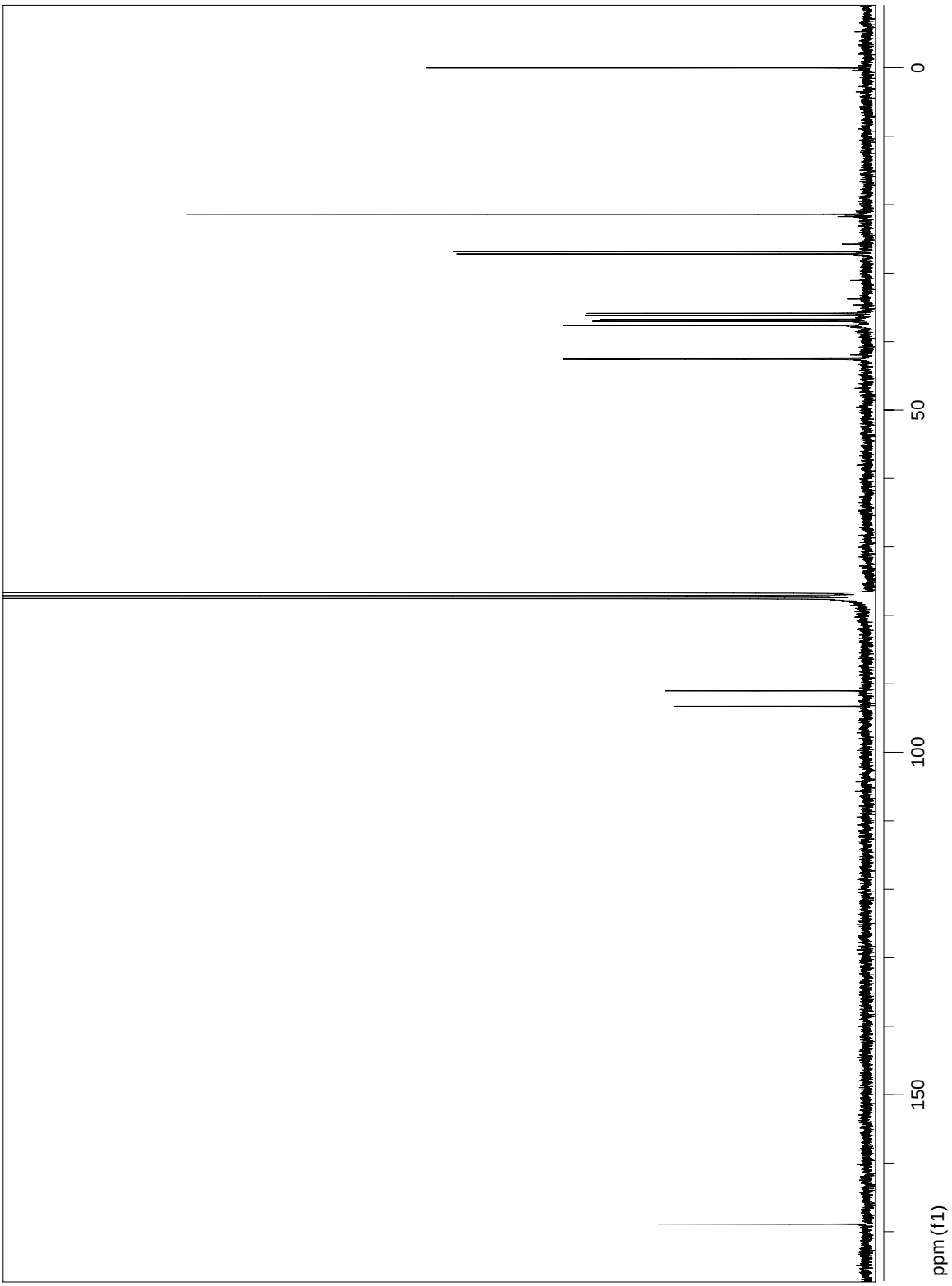
^{13}C NMR of compound **2f**:



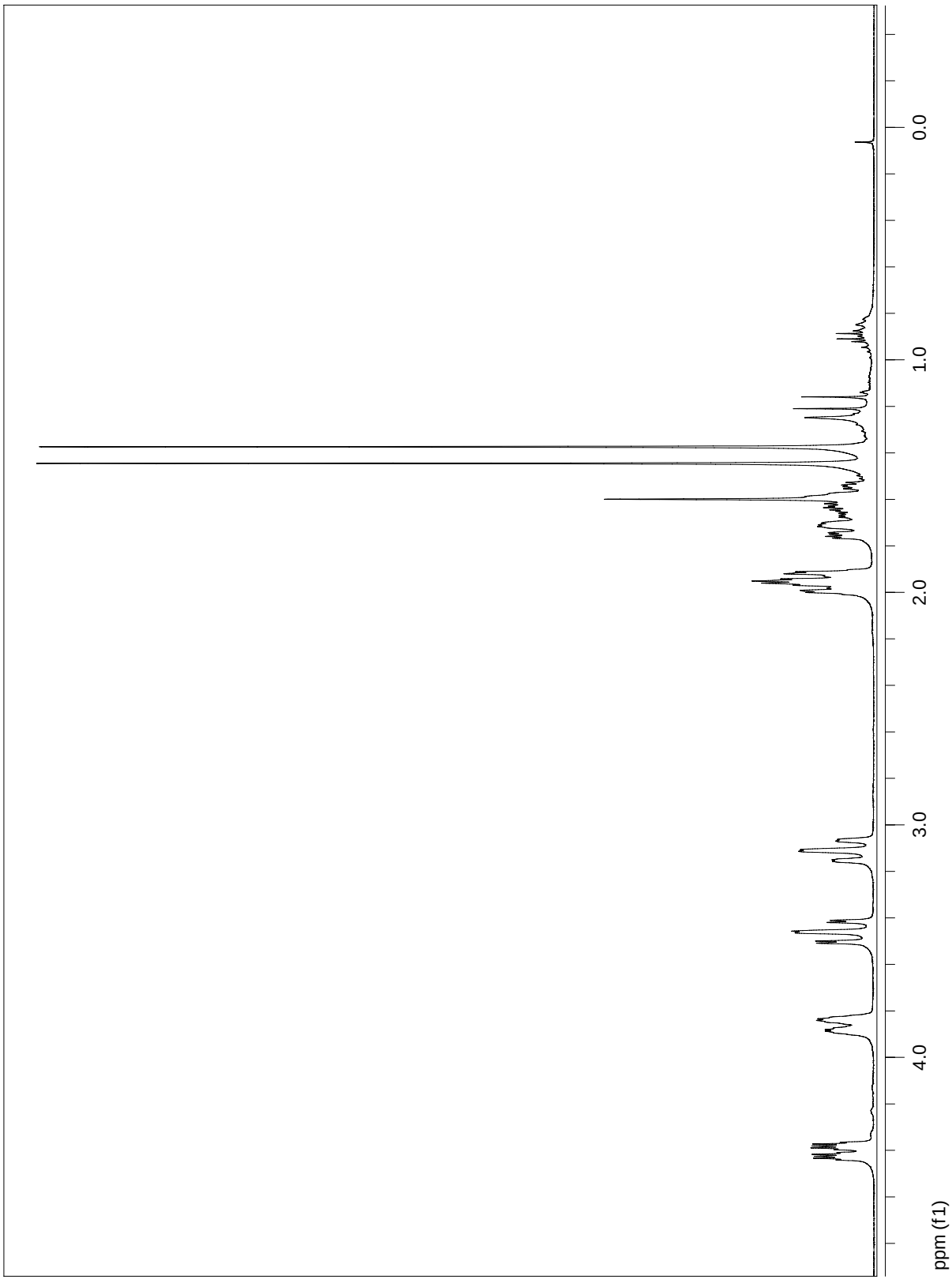
^{1}H NMR of compound **2g**:



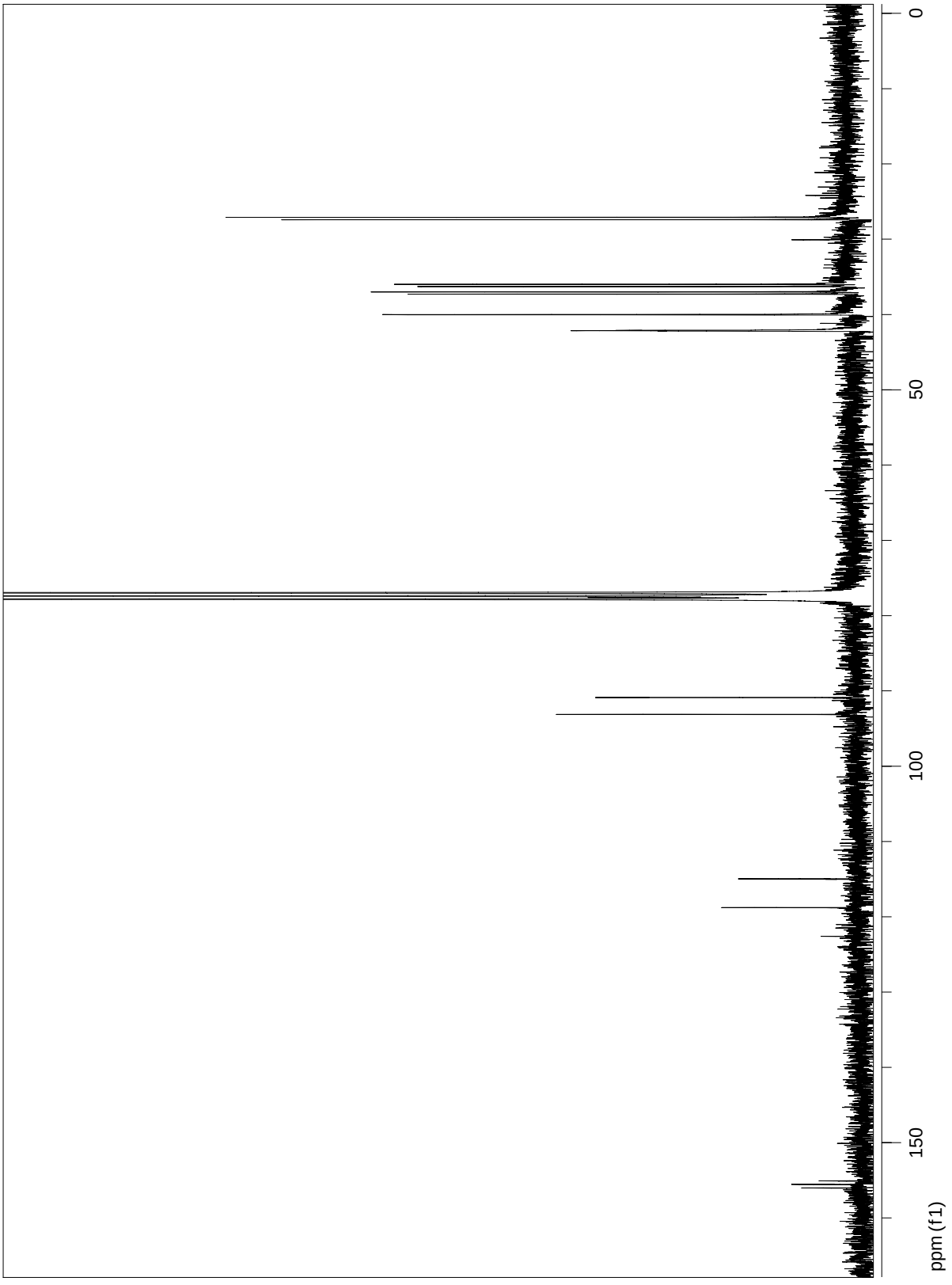
^{13}C NMR of compound **2g**:



^{1}H NMR of compound **2h**:



^{13}C NMR of compound **2h**:



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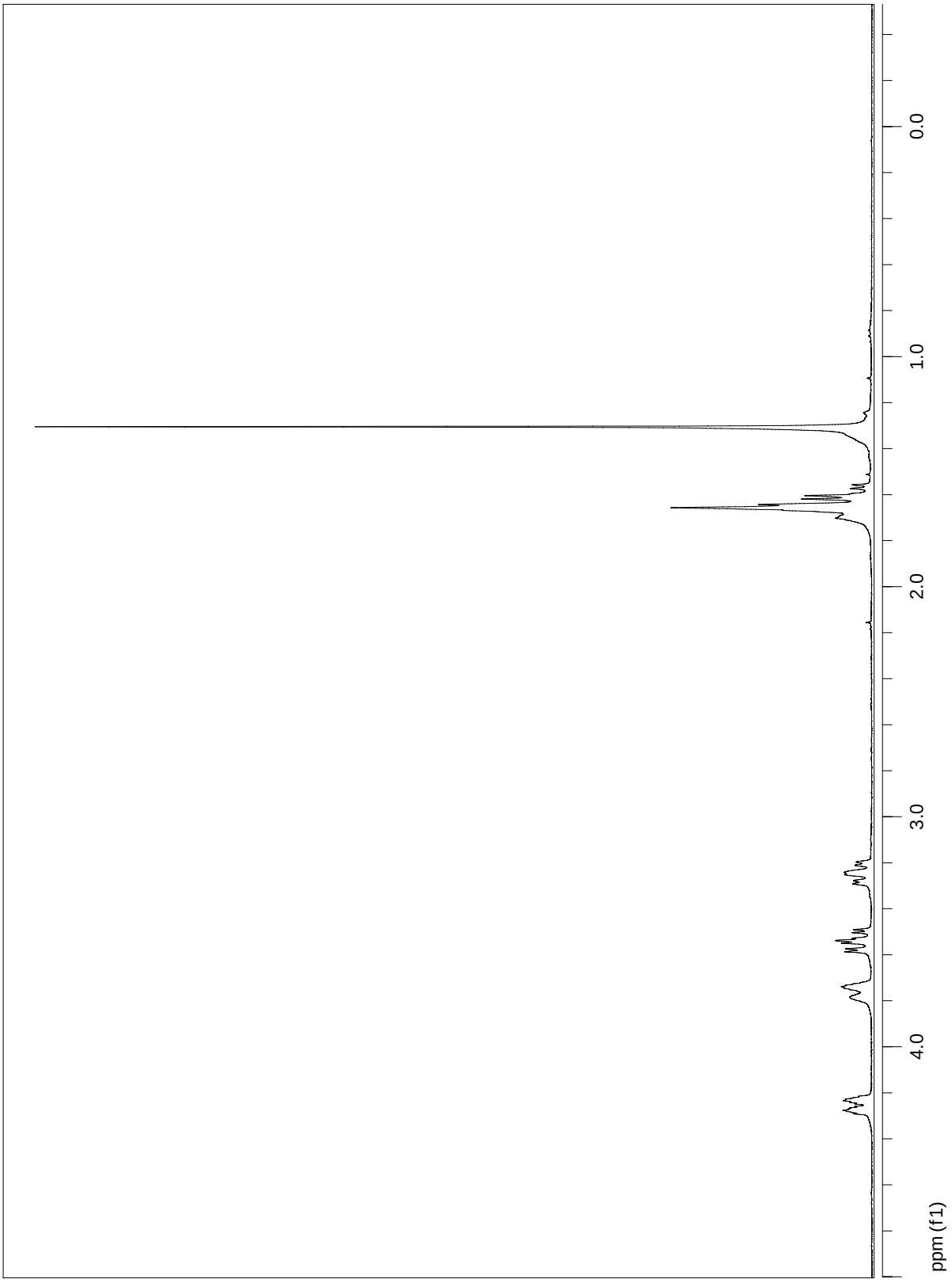
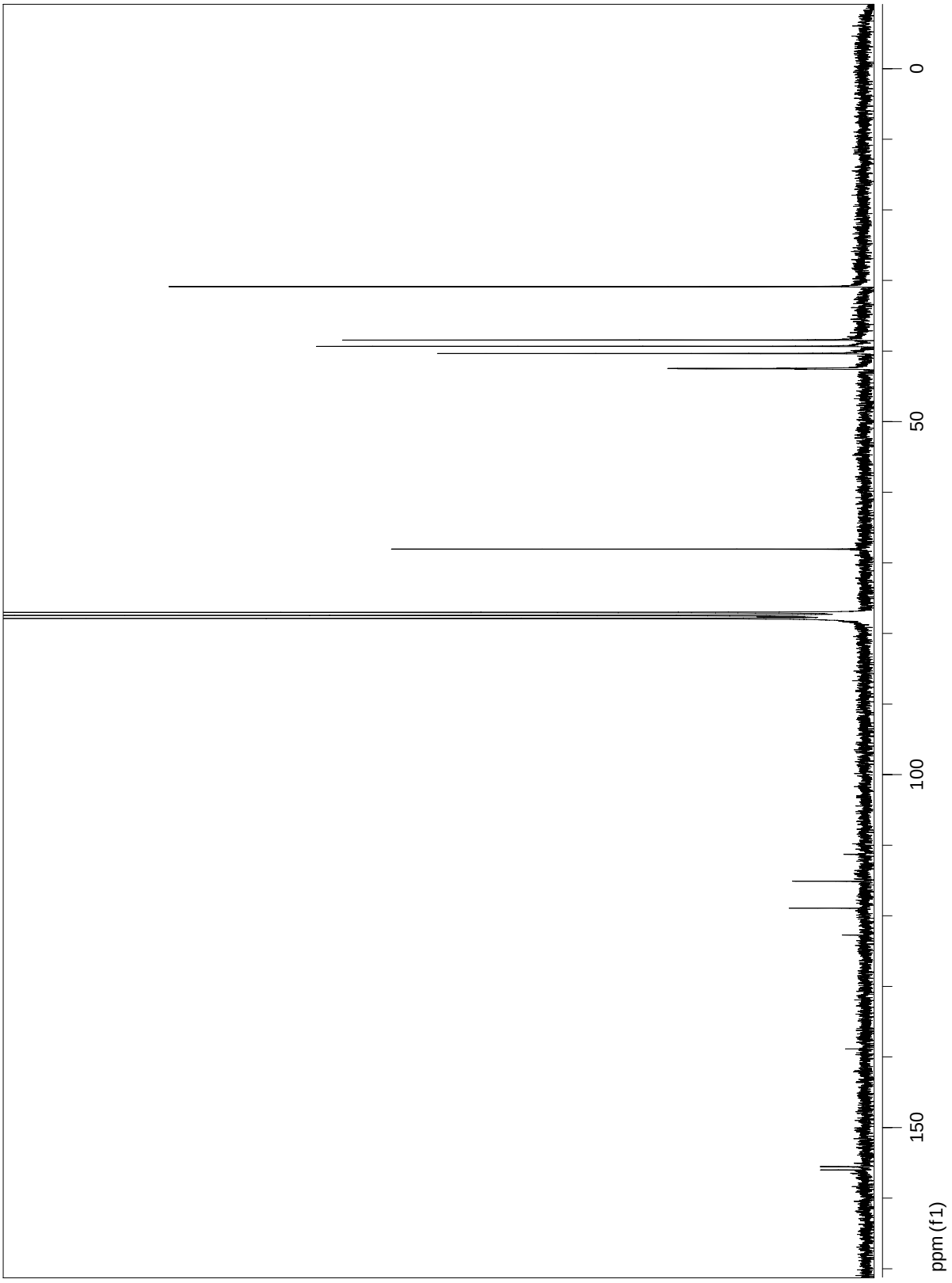
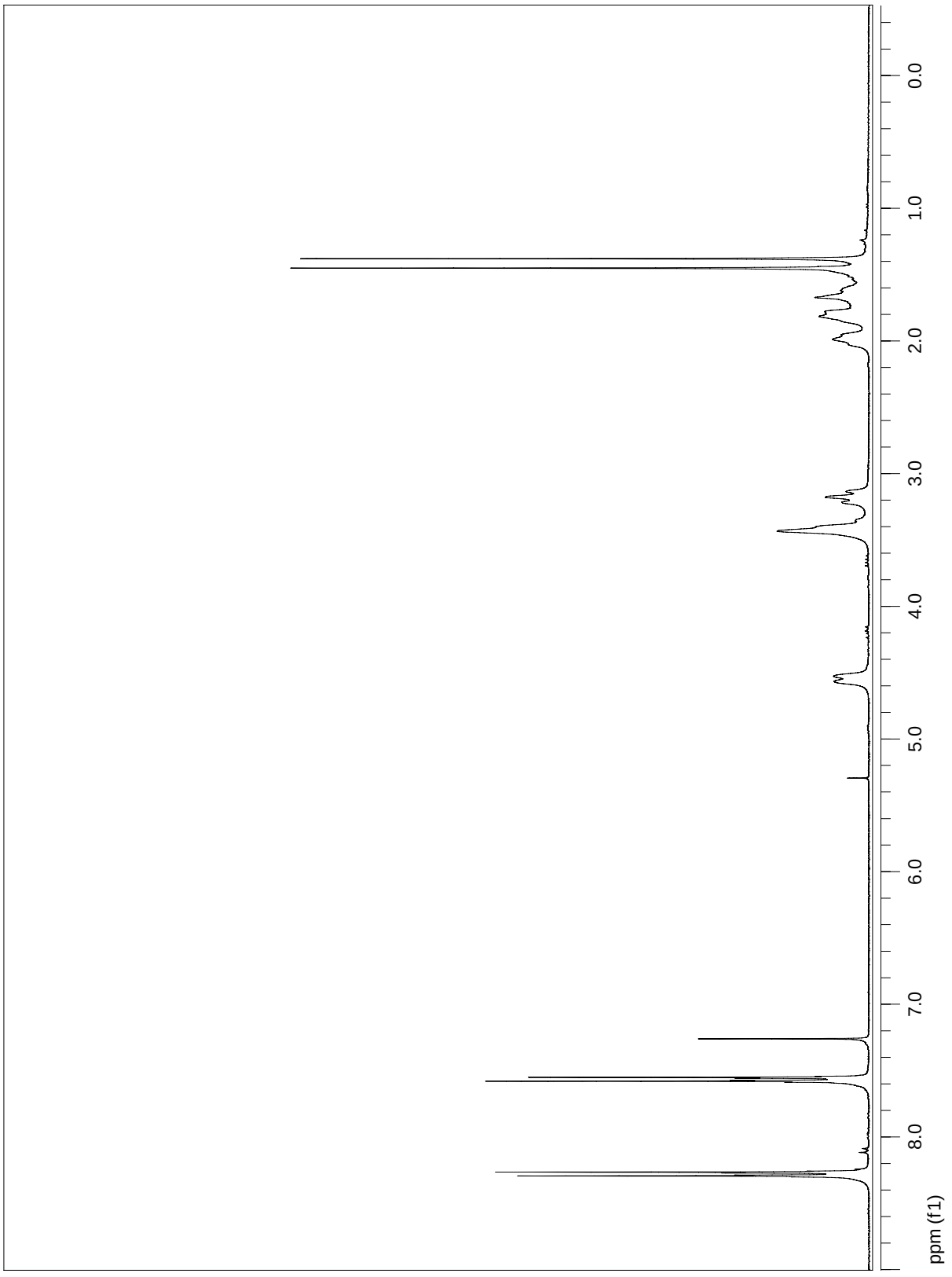


^{13}C NMR of compound **2h'**:



^{1}H NMR of compound **2j**:



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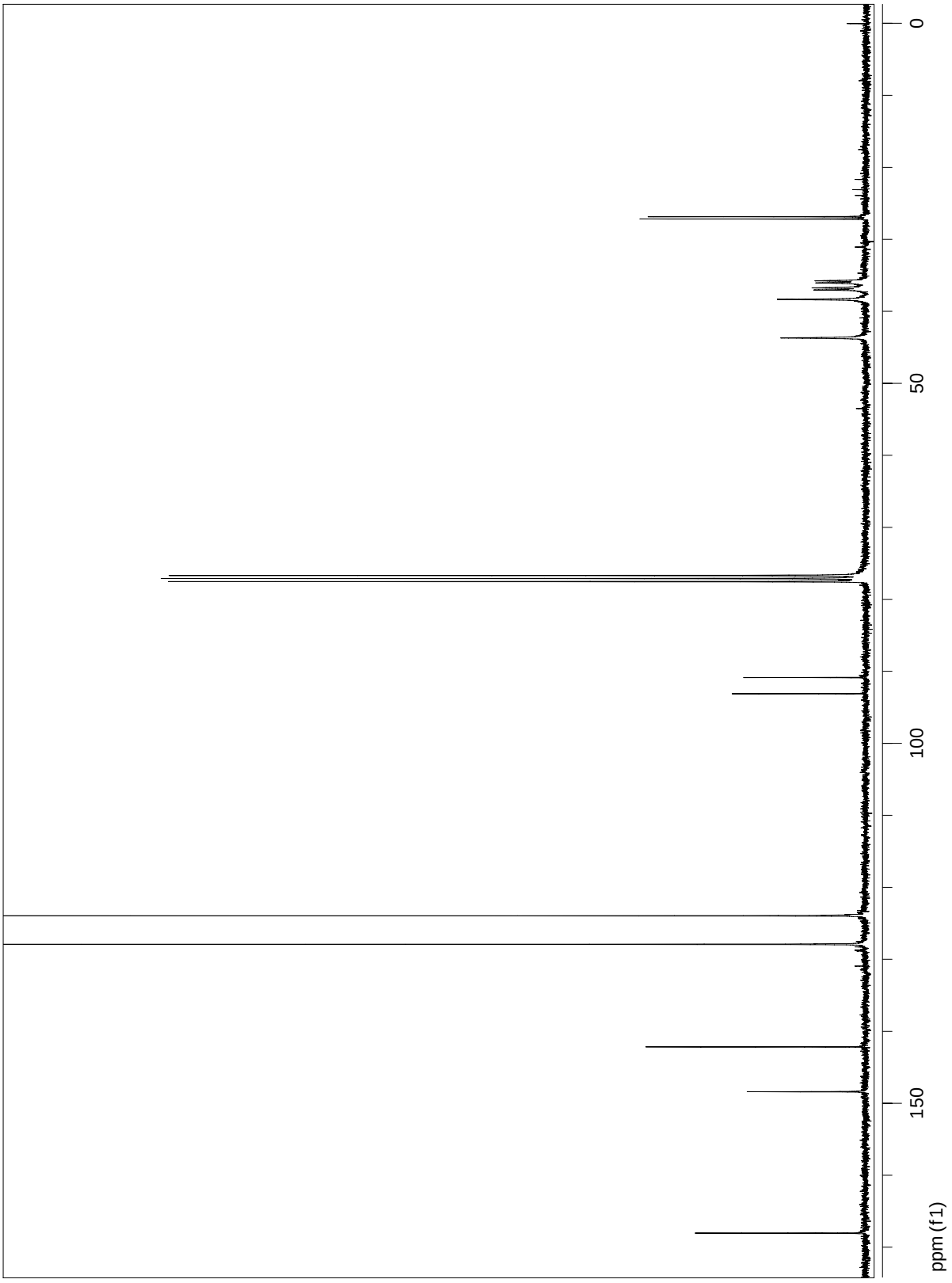
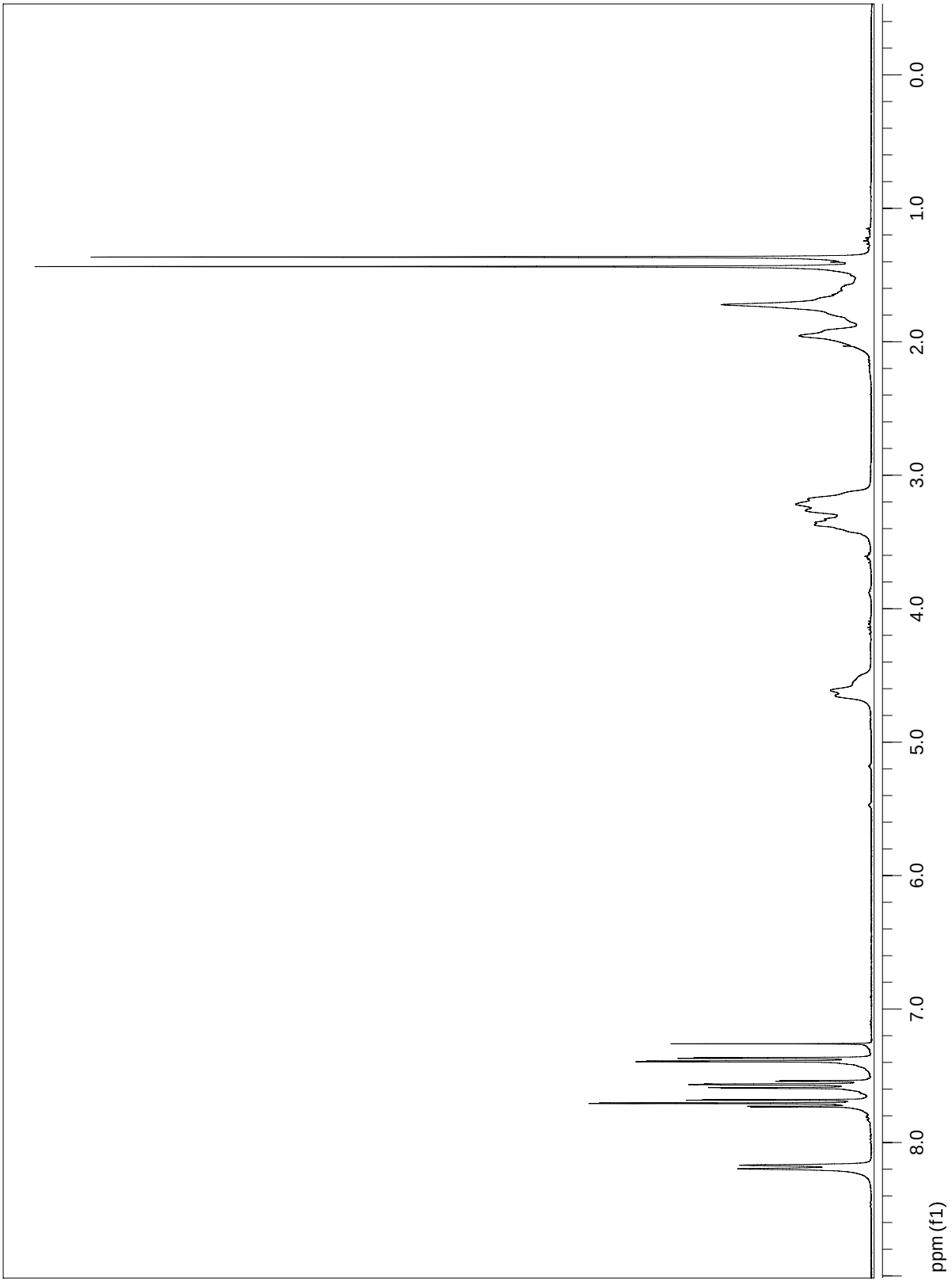


^{1}H NMR of compound **2k**:



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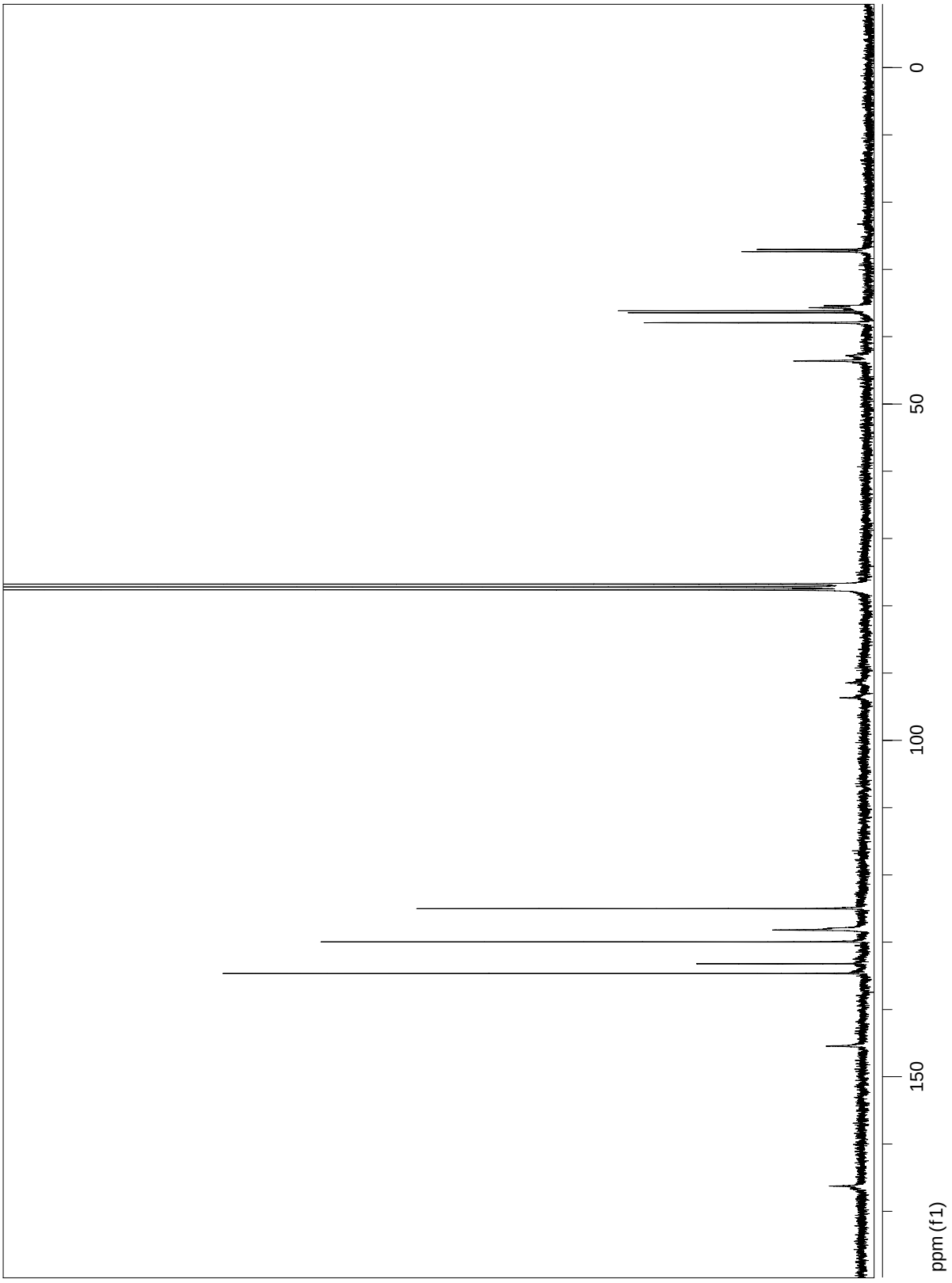

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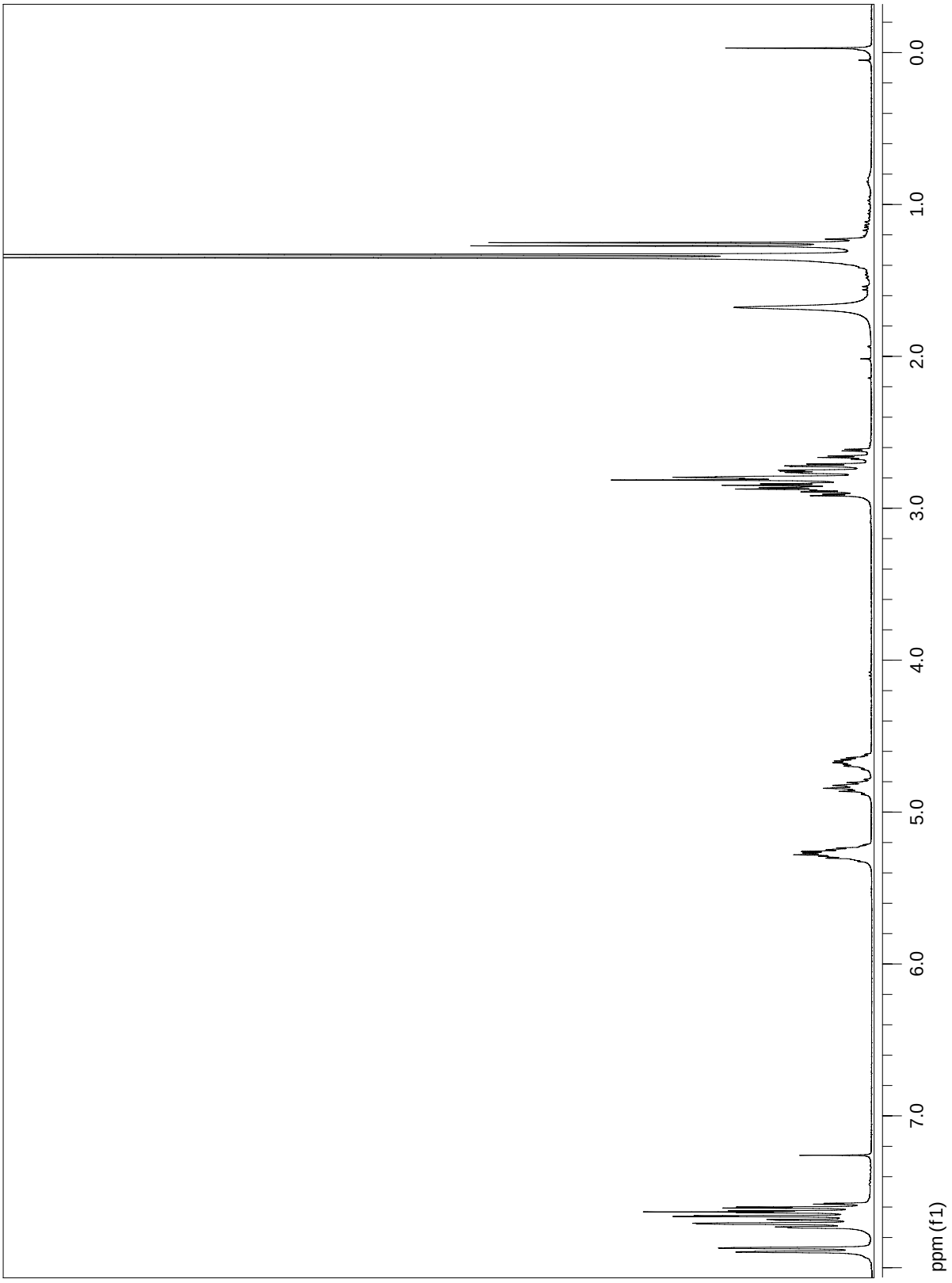

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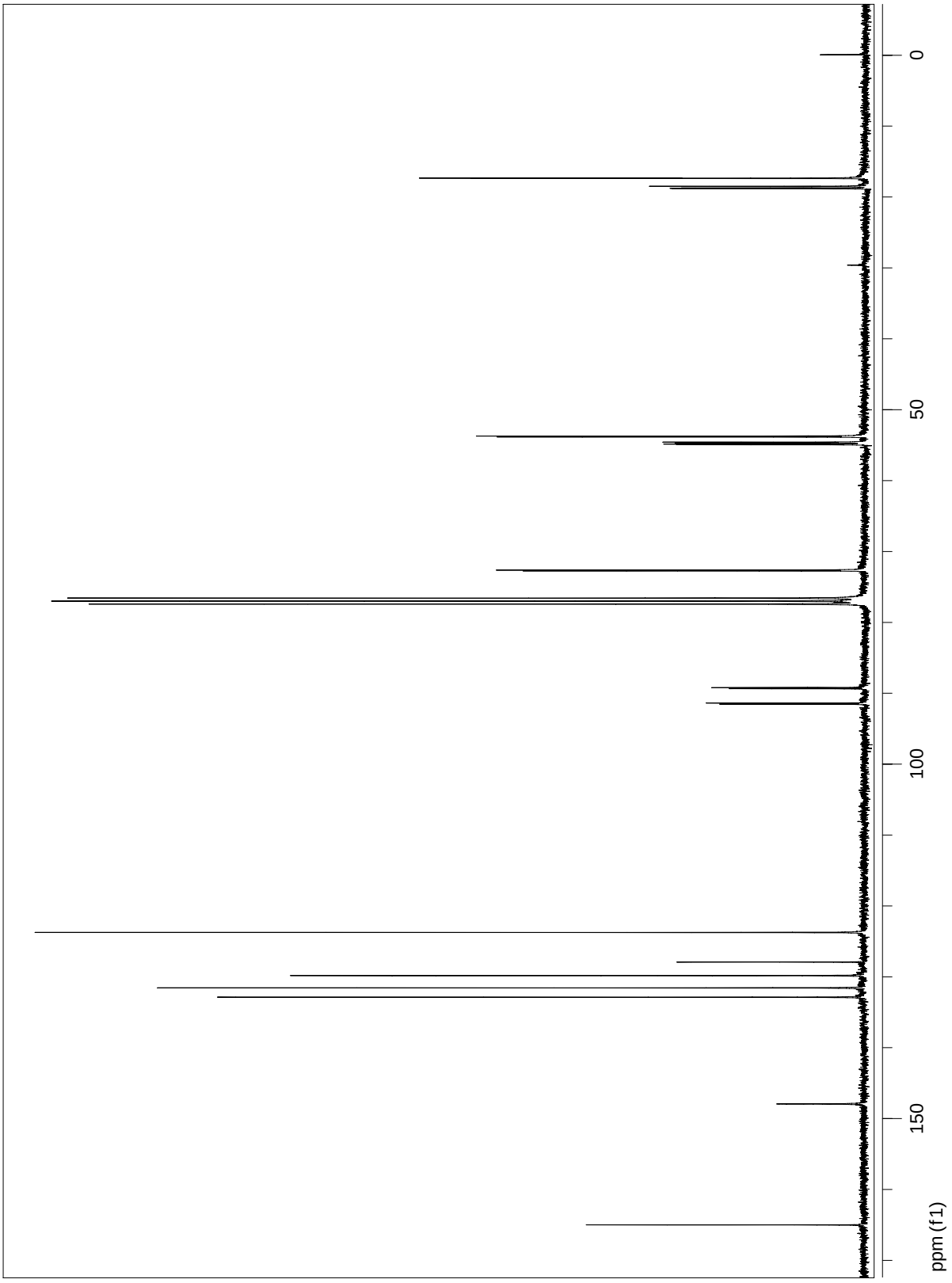
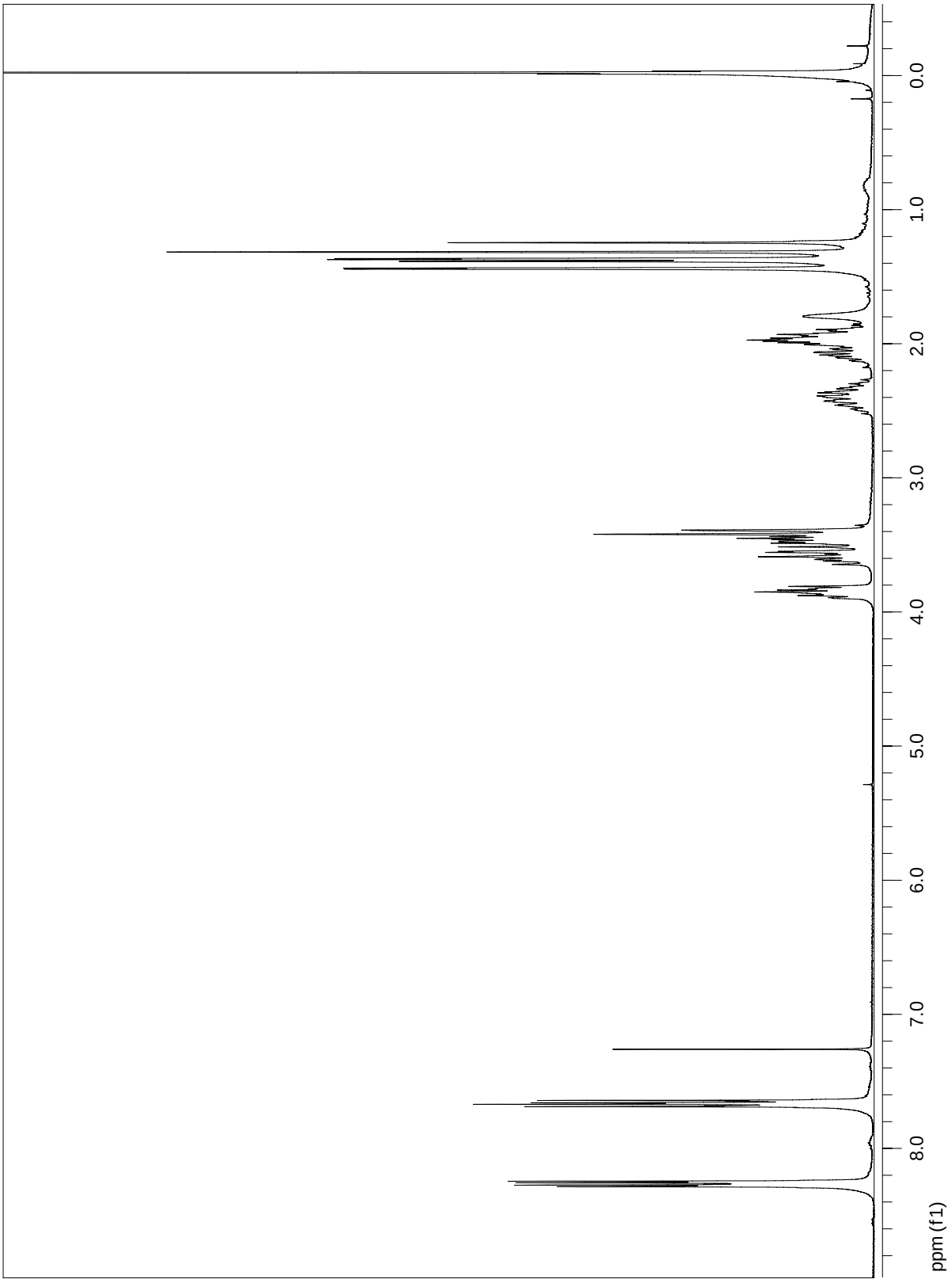


^{1}H NMR of compound **2l**:



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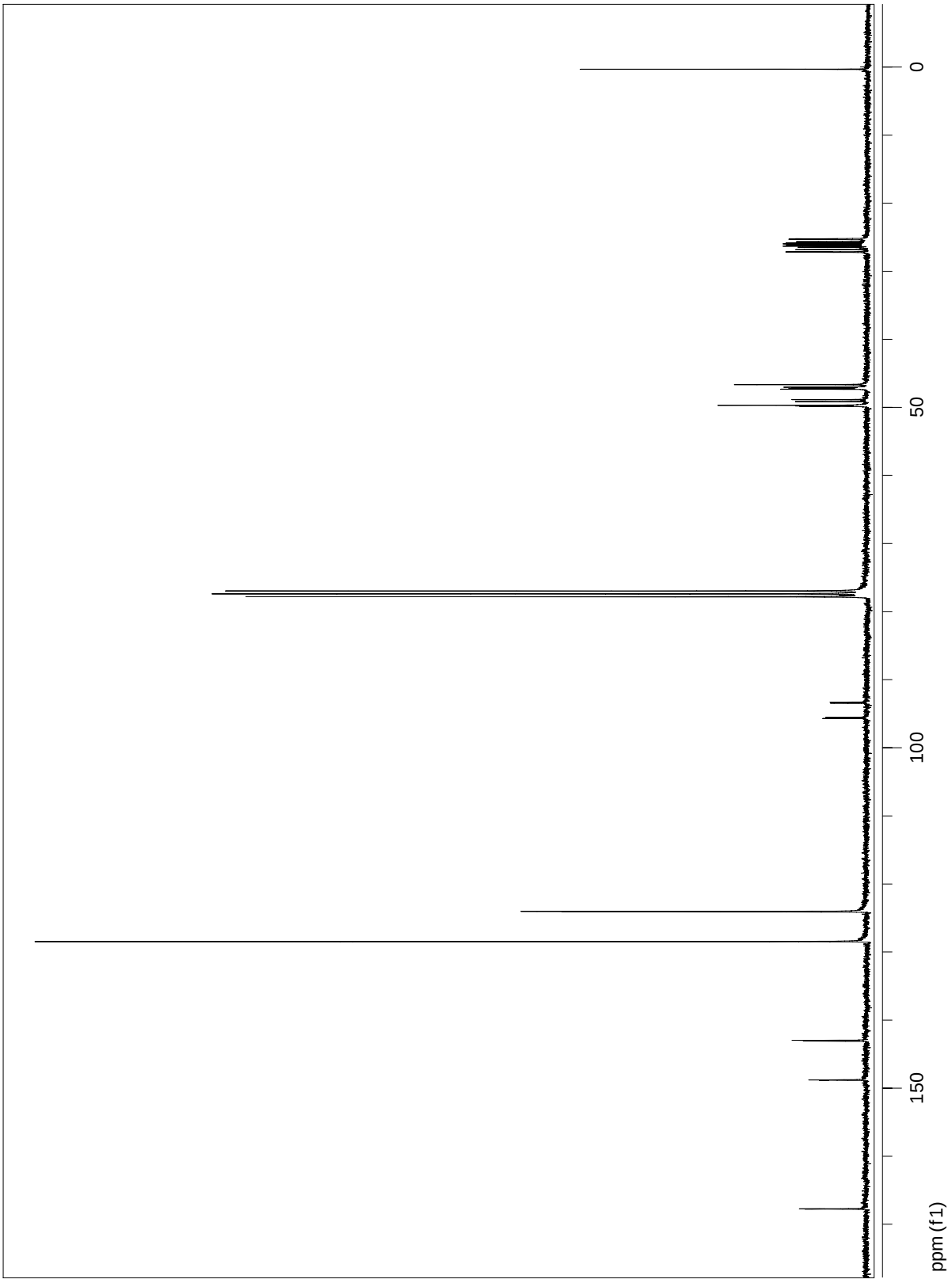
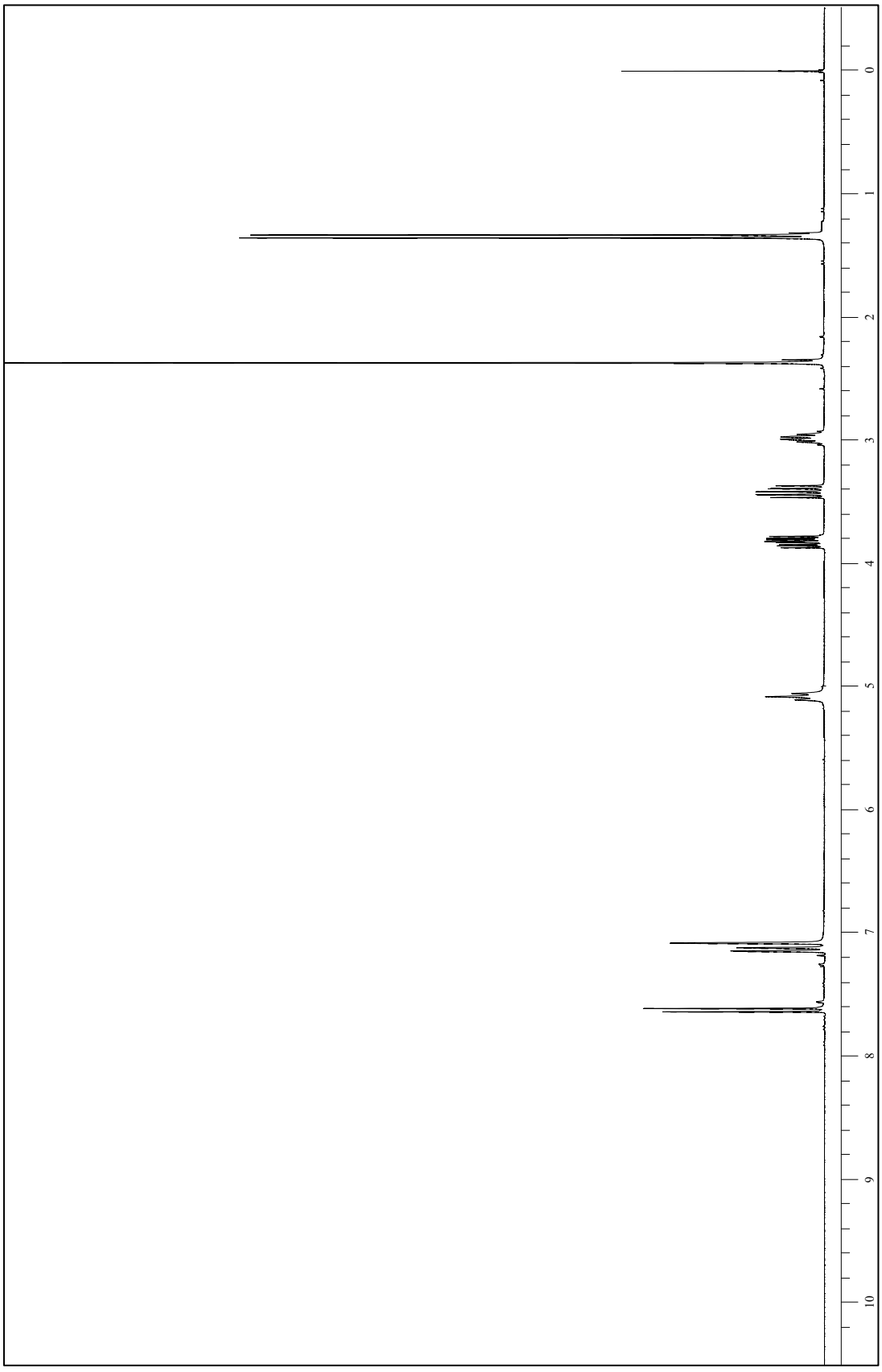


^{1}H NMR of compound **2p**:



^{13}C NMR of compound **2p**: