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SUPPORTING INFORMATION

Stereoselective hydrofluorination of ynamides: a straightforward synthesis of novel α-fluoroenamides

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A. GENERAL METHOD

B. YNAMIDES SYNTHESIS

C. HYDROFLUORINATION REACTION

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A. 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.

^{1}H, ^{13}C and ^{19}F NMR were recorded at respectively 400 MHz 100 MHz and 376 MHz Bruker Advance DPX spectrometer using $CDCl_3$ and CD_3COCD_3 as solvent. COSY ^{1}H-^{1}H and ^{1}H-^{13}C experiments were used to confirm the NMR peaks assignments.

Melting points were determined in a capillary tube with a device Büchi melting point B-545 and were uncorrected.

Mass Spectra (MS) were performed with a Liquid Chromatography–Coupled *Tandem* Mass Spectrometry *(electronic impact).*

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

High-resolution mass-spectra were obtained on a Waters Xevo Qtof spectrometer.

All reactions for ynamide's synthesis were carried out in oven or flame-dried glassware under an argon atmosphere employing standard techniques in handling air-sensitive materials. Copper-catalyzed reactions were carried out in resealable pressure tubes.

All solvents were reagent grade. 1.4-dioxane was freshly distilled from sodium/benzophenone under argon and degassed immediately prior to use.

Copper(I) iodide (99.999% purity) was purchased from Aldrich and used as supplied. Finely powdered cesium carbonate was used for copper-mediated coupling reactions. All other reagents were used as supplied.

Unless otherwise noted, reactions were magnetically stirred and monitored by thin layer chromatography using Merck-Kiesegel $60F_{254}$ plates. Flash chromatography was performed with silica gel 60 (particle size 35-70 µm) supplied by SDS. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise noted.

Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, sext. = sextuplet, sept. = septuplet, m = multiplet, br. = broad, app. = apparent), coupling constant (*J*/Hz) and integration. Resonances that are either partially or fully obscured are denoted obscured (obs.).

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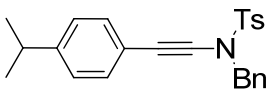
B. YNAMIDES SYNTHESIS

General procedure for the synthesis of ynamides from 1.1-dibromo-1-alkenes

A 15 mL pressure tube was charged with sulfonamide, amide or oxazolidinone (3.2 mmol), 1.1-dibromo-1-alkene (4.8 mmol), Cs_2CO_3 (4.2 g, 12.8 mmol), and copper(I) iodide (76 mg, 0.4 mmol). The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Dry and degassed 1.4-dioxane or DMF (6 mL) and *N*,*N*'-dimethylethylenediamine (60 µL, 0.6 mmol) were next added, the rubber septa was replaced by Teflon-coated screw cap and the light blue-green suspension was heated at 80°C for 1 or 2 days. The brownish suspension was cooled to rt. When the reaction was run in 1.4-dioxane, the crude reaction mixture was filtered over a plug of silica gel (washed with EtOAc), and concentrated. When the reaction was run in DMF, the crude reaction mixture was diluted with water, extracted with diethyl ether and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel.

Formation of compound 1d:

***N*-Benzyl-*N*-[(4-isopropylphenyl)ethynyl]-4-methylbenzenesulfonamide**



Reaction was run in 1.4-dioxane. The reaction crude was purified with the eluent petrolum ether/ethylacetate: 90/10, thereby obtaining ynamide (1.2 g, 93 %).

Aspect: white solid.

Mp: 75 °C

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.24 (d, $2CH_3$, *J* = 6.9 Hz), 2.47 (s, CH_3), 2.90 (sept., CH, *J* = 6.9 Hz), 4.60 (s, CH_2), 7.14 (d, 2CH, *J* = 8.0 Hz), 7.22 (d, 2CH, *J* = 7.9 Hz), 7.29-7.40 (m, 7CH), 7.83 (d, 2CH, *J* = 8.0 Hz).

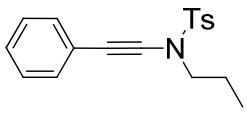
^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 21.8, 23.9, 34.1, 55.9, 71.4, 82.0, 126.4, 127.9, 128.4, 128.6, 129.0, 129.8, 131.3, 131.5, 134.6, 134.8, 144.7, 148.9.

MS (ESI, ACN): m/z 426 $[M+Na]^+$, 404 $[M+H]^+$.

HRMS (ESI, ACN): m/z 404.1687 (m/z theoretical: 404.1684) $[M+H]^+$.

Formation of compound 1k:

***N*-Propyl-*N*-(phenylethynyl)-4-methylbenzenesulfonamide**



Reaction was run in 1.4-dioxane. The reaction crude was purified with the eluent petrolum ether/ethylacetate: 90/10, thereby obtaining ynamide (946 mg, 94 %).

Aspect: yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.98 (t, CH_3, *J* = 7.4 Hz), 1.76 (app. sext., CH_2, *J* = 7.3 Hz), 2.45 (s, CH_3), 3.40 (t, CH_2, *J* = 7.3 Hz), 7.28-7.42 (m, 7CH), 7.88 (d, 2CH, *J* = 8.0 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 10.9, 21.3, 21.6, 53.2, 70.6, 82.4, 122.9, 127.6, 127.7, 128.3, 129.8, 131.3, 134.5, 144.6.

MS (ESI, ACN): m/z 336 $[M+Na]^+$, 313 $[M]^+$.

HRMS (ESI, ACN): m/z 313.1136 (m/z theoretical: 313.1137) $[M]^+$.

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All other ynamides synthesized using this method were previously reported. See: Coste, A.; Karthikeyan, G.; Couty, F.; Evano, G. *Angew. Chem. Int. Ed.* **2009**, *48*, 4381-4385.

Ynamide **1o** was prepared by copper-catalyzed cross-coupling between oxazolidinone and potassium (1-phenylethynyl) trifluoroborate and previously reported. See: Jouvin, K.; Couty, F.; Evano, G. *Org. Lett.* **2010**, *12*, 3272-3275

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C. HYDROFLUORINATION REACTION

Optimized procedures in superacidic media

General procedure A:

To a solution of HF (6 mL) maintained at -50 °C or -78°C, was added very slowly ynamide derivative. The mixture was magnetically stirred at the same temperature during 5 minutes. The reaction mixture was then neutralized with water-ice-Na_2CO_3, extracted with ethyl acetate (× 3). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Products were isolated by column chromatography over silica gel.

General procedure B:

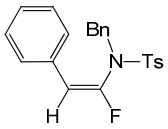
To a solution of HF (1 mL) maintained at -50 °C, was added very slowly ynamide derivative. The mixture was magnetically stirred at the same temperature during 1 minute. Then, 6 mL of a mixture of HF/Pyridine (70/30, w/w) was added. The mixture was magnetically stirred at -20°C during 5 minutes. The reaction mixture was then neutralized with water-ice-Na_2CO_3, extracted with ethyl acetate (× 3). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Products were isolated by column chromatography over silica gel.

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Formation of compound 2a and compound 3a:

Compound 2a:

(*E*)-*N*-benzyl-1-fluoro-2-phenyl-*N*-tosylethenamine



This compound was obtained from ynamide **1a** (101 mg, 0.279 mmol) following the general procedure A at -50°C. The reaction crude was purified with the eluent pentane/ethylacetate: 97/3, thereby obtaining compound **2a** (107 mg, 96 %).

Aspect: white solid.

Mp: 70-72 °C

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 2.48 (s, CH_3), 4.40 (s, CH_2), 6.17 (d, CH, *J* = 8.7 Hz), 7.08 (m, 2CH), 7.16 (m, 3CH), 7.27 (m, 3H), 7.34 (m, 4CH), 7.84 (d, 2CH, *J* = 8.1 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 21.8 (CH_3), 52.2 (CH_2), 111.5 (d, CH, *J* = 42 Hz), 128.0 (d, CH_{arom}, *J* = 1 Hz), 128.4 ($9CH_{arom}$), 129.5 ($2CH_{arom}$), 129.9 ($2CH_{arom}$), 131.2 (d, *J* = 8 Hz), 133.7 (C_{arom}), 136.0 (C_{arom}), 144.6 (C_{arom}), 147.0 (d, CF, *J* = 273 Hz).

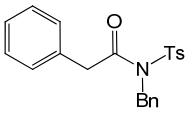
^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz, ppm) δ: -87.13.

MS (IES+, ACN): *m/z* 404 $[M+Na]^+$, 384 $[M-HF+Na]^+$.

HRMS (ESI, CH_3OH): *m/z* 404.1098 (*m/z* theoretical: 404.10965) $[M+Na]^+$.

Compound 3a:

***N*-benzyl-2-phenyl-*N*-tosylacetamide**



This compound was obtained as side product during the reaction optimization (see *Table 1*).

Aspect: white solid.

Mp: 70-72 °C

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 2.43 (s, CH_3), 3.87 (s, CH_2), 5.08 (s, CH_2), 6.99 (dd, 2CH, *J* = 7.0 Hz, *J* = 2.5 Hz), 7.25 (m, 5CH), 7.33 (m, 5CH), 7.65 (d, 2CH, *J* = 8.4 Hz).

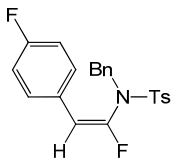
^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 21.8 (CH_3), 43.0 (CH_2), 49.8 (CH_2), 127.3, 127.9, 127.9, 128.1, 128.7, 128.8, 129.4, 129.8, (CH_{arom}), 133.3, 136.7, 136.7, 145.1 (C_{arom}), 171.4 (CO).

MS (IES+, ACN): *m/z* 380 $[M+H]^+$, 402 $[M+Na]^+$.

HRMS (ESI, CH_3OH): *m/z* 402.1136 (*m/z* theoretical: 402.11398) $[M+Na]^+$.

Formation of compound 2b:

(*E*)-*N*-benzyl-1-fluoro-2-(4-fluorophenyl)-*N*-tosylethenamine



This compound was obtained from ynamide **1b** (102 mg, 0.269 mmol) following the general procedure A at -50°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 97/3, thereby obtaining compound **2b** (105 mg, 97 %).

Aspect: white solid.

Mp: 107-109°C

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 2.46 (s, CH_3), 4.38 (s, CH_2), 6.13 (d, CH, *J* = 8.6 Hz), 6.92 (dd, 2CH, *J* = 8.8 Hz, *J* = 8.8 Hz), 7.15 (m, 5CH), 7.28 (dd, 2CH, *J* = 8.6 Hz, *J* = 5.4 Hz), 7.34 (d, 2CH, *J* = 8.0 Hz), 7.84 (d, 2CH, *J* = 7.9 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 21.7 (CH_3), 52.1 (CH_2), 110.9 (d, CH, *J* = 42 Hz), 115.3 (d, 2CH, *J* = 22 Hz), 127.2 (dd, C_{arom}, *J* = 8 Hz, *J* = 3 Hz), 128.2-128.5 ($5CH_{arom}$), 129.5 ($2CH_{arom}$), 129.9 ($2CH_{arom}$), 130.1 (dd, $2CH_{arom}$, *J* = 4 Hz, *J* = 8 Hz), 133.5 (C_{arom}), 135.7 (C_{arom}), 144.7 (C_{arom}), 146.8 (d, CF, *J* = 274 Hz), 162.4 (d, CF, *J* = 248 Hz).

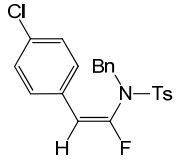
^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz, ppm) δ: -113.51 (ArF), -89.09 (CH=CF).

MS (IES+, ACN): *m/z* 402 $[M\text{-}HF+H]^+$, 422 $[M+Na]^+$.

HRMS (ESI, CH_3OH): *m/z* 400.1179 (*m/z* theoretical: 400.1183) $[M+H]^+$.

Formation of compound 2c:

(*E*)-*N*-benzyl-2-(4-chlorophenyl)-1-fluoro-*N*-tosylethenamine



This compound was obtained from ynamide **1c** (105 mg, 0.265 mmol) following the general procedure A at -78°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 99/1, thereby obtaining compound **2c** (71 mg, 65 %).

Aspect: white solid.

Mp: 127-130 °C.

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 2.47 (s, CH_3), 4.47 (s, CH_2), 6.27 (d, CH, *J* = 8.8 Hz), 7.19 (m, 5CH), 7.25 (d, 2CH, *J* = 8.5 Hz), 7.36 (d, 2CH, *J* = 8.6 Hz), 7.48 (d, 2CH, *J* = 8.2 Hz), 7.86 (d, 2CH, *J* = 8.2 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 21.5 (CH_3), 52.7 (CH_2), 111.2 (d, CH, *J* = 42 Hz), 129.0 (CH_{arom}), 129.0 (CH_{arom}), 129.2 (CH_{arom}), 130.4 ($2CH_{arom}$), 130.7 (d, $2CH_{arom}$, *J* = 4 Hz), 130.8 ($2CH_{arom}$), 131.2 (d, C_{arom}, *J* = 9 Hz), 133.9 (C_{arom}), 134.8 (C_{arom}), 136.8 (C_{arom}), 145.8 (C_{arom}), 148.3 (CF, *J* = 274 Hz).

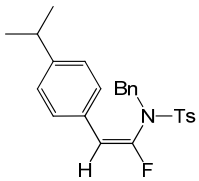
^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -87.64.

MS (IES+, ACN): *m/z* 438 $[M+Na]^+$, 418 $[M\text{-}HF+Na]^+$, 396 $[M\text{-}HF+H]^+$.

HRMS (ESI, CH_3OH): *m/z* 416.0890 (*m/z* theoretical: 416.0887) $[M+H]^+$.

Formation of compound 2d:

(*E*)-*N*-benzyl-1-fluoro-2-(4-isopropylphenyl)-*N*-tosylethenamine



This compound was obtained from ynamide **1d** (100 mg, 0.248 mmol) following the general procedure A at -50°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 96/4, thereby obtaining compound **2d** (72 mg, 69 %).

Aspect: white solid.

Mp: 77-80°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 1.23 (d, $2CH_3$, *J* = 6.9 Hz), 2.47 (s, CH_3), 2.88 (m, CH), 4.46 (s, CH_2), 6.22 (d, 1CH, *J* = 9.1 Hz), 7.16 (m, 7CH), 7.32 (d, 2CH, *J* = 8.2 Hz), 7.46 (d, 2CH, *J* = 8.6 Hz), 7.86 (d, 2CH, *J* = 8.1 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 21.5 (CH_3), 24.2 ($2CH_3$), 34.5 (CH), 52.7 (CH_2), 111.8 (d, CH_{arom}, *J* = 42 Hz), 127.0 (CH_{arom}), 129.0 (CH_{arom}), 129.0 (CH_{arom}), 129.0 (CH_{arom}), 129.2 (CH_{arom}), 129.7 (d, *J* = 8 Hz), 130.2 (CH_{arom}), 130.7 ($2CH_{arom}$), 135.0 (C_{arom}), 137.1 (C_{arom}), 145.6 (C_{arom}), 147.6 (d, CF, *J* = 272 Hz), 149.5 (C_{arom}).

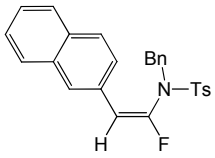
$^{19}F\{^{1}H\}$ NMR (CD_3COCD_3, 376 MHz, ppm) δ: -88.47.

MS (IES+, ACN): *m/z* 446 $[M+Na]^+$, 404 $[M-HF+H]^+$.

HRMS (ESI, CH_3OH): *m/z* 446.1267 (*m/z* theoretical: 446.12660) $[M+Na]^+$.

Formation of compound 2e:

(*E*)-*N*-benzyl-1-fluoro-2-(naphthalen-3-yl)-*N*-tosylethenamine



This compound was obtained from ynamide **1e** (107 mg, 0.260 mmol) following the general procedure A at -78°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 96/4, thereby obtaining compound **2e** (62 mg, 55 %).

Aspect: white solid.

Mp: 65-67°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 2.42 (s, CH_3), 4.54 (s, CH_2), 6.44 (d, CH_3, *J* = 9.0 Hz), 7.17 (m, 3CH), 7.23 (m, 2CH), 7.42 (d, 2CH, *J* = 8.5 Hz), 7.48 (m, 2CH), 7.59 (dd, CH, *J* = 8.6 Hz, *J* = 1.8 Hz), 7.74 (m, 3CH), 7.83 (m, CH), 7.87 (d, 2CH, *J* = 8.3 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 21.5 (CH_3), 52.7 (CH_2), 112.0 (d, CH, *J* = 43 Hz), 126.5 (d, CH, *J* = 3 Hz), 127.0 (CH_{arom}), 127.1 (CH_{arom}), 128.3 (CH_{arom}), 128.4 (CH_{arom}), 128.6 (d, CH, *J* = 5 Hz), 128.8 (CH_{arom}), 128.9 ($2CH_{arom}$), 129.1 (CH_{arom}), 129.1 ($2CH_{arom}$), 129.9 (d, C_{arom}, *J* = 9 Hz), 130.4 ($2CH_{arom}$), 130.7 ($2CH_{arom}$), 133.8 (C_{arom}), 134.1 (C_{arom}), 135.1 (C_{arom}), 137.0 (C_{arom}), 145.7 (C_{arom}), 148.3 (d, CF, *J* = 273 Hz).

$^{19}F\{^{1}H\}$ NMR (CD_3COCD_3, 376 MHz, ppm) δ: -86.93.

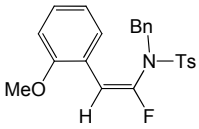
MS (IES+, ACN): *m/z* 454 $[M+Na]^+$, 434 $[M-HF+Na]^+$.

HRMS (ESI, CH_3OH): *m/z* 432.1430 (*m/z* theoretical: 432.1434) $[M+H]^+$.

Formation of compound 2f, 3f and 4:

Compound 2f:

(*E*)-*N*-benzyl-1-fluoro-2-(2-methoxyphenyl)-*N*-tosylethenamine



This compound was obtained from ynamide **1f** (109 mg, 0.279 mmol) following the general procedure A at -78°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 94/6, compound **4** (2 mg, 2%) was first eluted followed by the compound **2f** (48mg, 42 %) and the compound **3f** (33 mg, 33%).

Aspect: white solid.

Mp: 130-131 °C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 2.45 (s, CH_3), 3.69 (s, CH_3), 4.34 (s, CH_2), 6.45 (d, CH, *J* = 8.9 Hz), 6.72 (d, CH, *J* = 8.3 Hz), 6.89 (t, CH, *J* = 7.2 Hz), 7.01 (m, 2CH), 7.09 (t, 2CH, *J* = 7.3 Hz), 7.15 (m, CH), 7.20 (m, CH), 7.30 (d, 2CH, *J* = 8.0 Hz), 7.61 (dd, CH, *J* = 7.7 Hz, *J* = 1.5 Hz), 7.81 (d, 2CH, *J* = 8.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 21.8 (CH_3), 52.3 (CH_2), 55.4 (CH_3), 106.0 (d, CH, *J* = 43 Hz), 110.2 (CH_{arom}), 120.1 (d, C_{arom}, *J* = 8 Hz), 120.6 (CH_{arom}), 128.1 (CH_{arom}), 128.2 ($2CH_{arom}$), 128.3 ($2CH_{arom}$), 128.8 (CH_{arom}), 129.2 (CH_{arom}), 129.4 ($2CH_{arom}$), 129.8 ($2CH_{arom}$), 133.8 (C_{arom}), 136.1 (C_{arom}), 144.4 (C_{arom}), 147.1 (d, CF, *J* = 271 Hz), 156.8 (d, C_{arom}, *J* = 4 Hz).

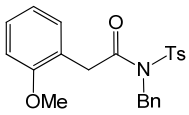
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz, ppm) *δ*: -86.47.

MS (IES+, ACN): *m/z* 434 $[M+Na]^+$, 414 $[M-HF+Na]^+$, 392 $[M-HF+H]^+$.

HRMS (ESI, CH_3OH): *m/z* 434.1204 (*m/z* theoretical: 434.12021) $[M+Na]^+$.

Compound 3f:

***N*-benzyl-2-(2-methoxyphenyl)-*N*-tosylacetamide**



Aspect: white solid.

Mp: 107-110°C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) *δ*: 2.43 (s, CH_3), 3.56 (s, CH_3), 3.85 (s, CH_2), 5.15 (s, CH_2), 6.78 (d, CH, *J* = 8.2 Hz), 6.85 (ddd, CH, *J* = 7.4 Hz, *J* = 7.4 Hz, *J* = 1.0 Hz), 6.98 (dd, CH, *J* = 7.4 Hz, *J* = 1.6 Hz), 7.22 (ddd, CH, *J* = 8.1 Hz, *J* = 8.1 Hz, *J* = 1.7 Hz), 7.27 (d, 2CH, *J* = 8.0 Hz), 7.33 (m, 3CH), 7.41 (m, 2CH), 7.69 (d, 2CH, *J* = 8.4Hz).

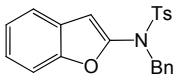
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) *δ*: 21.7 (CH_3), 38.5 (CH_2), 49.7 (CH_2), 55.1 (CH_3), 110.4 (CH_{arom}), 120.6 (CH_{arom}), 122.9 (C_{arom}), 127.8 (CH_{arom}), 128.1 ($2CH_{arom}$), 128.2 ($2CH_{arom}$), 128.7 ($2CH_{arom}$), 128.8 (CH_{arom}), 129.6 (CH_{arom}), 131.0 (CH_{arom}), 136.9 (C_{arom}), 137.0 (C_{arom}), 144.7 (C_{arom}), 157.1 (C_{arom}), 171.7 (CO).

MS (IES+, ACN): *m/z* 432 $[M+Na]^+$, 410 $[M+H]^+$.

HRMS (ESI, CH_3OH): *m/z* 410.1428 (*m/z* theoretical: 410.1426) $[M+H]^+$.

Compound 4:

***N*-benzyl-*N*-tosylbenzofuran-2-amine**



Aspect: white solid.

Mp: 109-112°C.

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) *δ*: 2.46 (s, CH_3), 4.87 (s, CH_2), 6.55 (d, CH, *J* = 0.9 Hz), 7.17-7.30 (m, $5CH_{arom}$), 7.35 (m, $3CH_{arom}$), 7.45 (d, 2CH, *J* = 8.6 Hz), 7.52 (ddd, CH, *J* = 7.6 Hz, *J* = 1.4 Hz, *J* = 0.7 Hz), 7.75 (d, 2CH, *J* = 8.4 Hz).

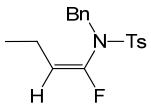
^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) *δ*: 21.5 (CH_3), 54.1 (CH_2), 103.1 (CH_{arom}), 111.7 (CH_{arom}), 122.0 (CH_{arom}), 124.0 (CH_{arom}), 125.5 (CH_{arom}), 128.6 ($2CH_{arom}$), 128.7 (CH_{arom}), 128.8 (C_{arom}), 129.2 ($2CH_{arom}$), 129.3 ($2CH_{arom}$), 130.8 ($2CH_{arom}$), 136.8 (C_{arom}), 136.9 (C_{arom}), 145.4 (C_{arom}), 149.2 (C_{arom}), 153.1 (C_{arom}).

MS (IES+, ACN): *m/z* 378 $[M+H]^+$, 400 $[M+Na]^+$.

Already reported in: Karin Dooleweerdt, Thomas Ruhland, and Troels Skrydstrup, *Org. Lett.*, **2009**, 11, 1, 221-224.

Formation of compound 2g:

(*E*)-*N*-benzyl-1-fluoro-*N*-tosylbut-1-en-1-amine



This compound was obtained from ynamide **1g** (108 mg, 0.345 mmol) following the general procedure A at -78°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 98/2, and a further purification on preparative TLC plate with the eluent petroleum ether/ethylacetate: 96/4 allowed the separation of pure compound **2g** (60 mg, 52 %).

Aspect: white solid.

Mp: 74-75°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 0.61 (td, CH_3, J = 7.5 Hz, J = 0.9 Hz), 1.78 (dqd, CH_2, J = 7.6 Hz, J = 7.6 Hz, J = 1.7 Hz), 2.47 (s, CH_3), 4.40 (s, CH_2), 5.13 (d, CH, J = 7.7 Hz), 7.34 (m, 5CH), 7.48 (d, 2CH, J = 8.0 Hz), 7.84 (d, 2CH, J = 8.3 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 13.4 (d, CH_3, J = 3 Hz), 20.1 (d, CH_2, J = 4 Hz), 21.5 (CH_3), 52.0 (CH_2), 113.6 (d, CH_2, J = 32 Hz), 128.6 ($2CH_{arom}$), 129.0 (CH_{arom}), 129.3 ($2CH_{arom}$), 130.1 ($2CH_{arom}$), 130.8 ($2CH_{arom}$), 135.9 (C_{arom}), 137.4 (C_{arom}), 145.3 (C_{arom}), 146.9 (d, CF, J = 267 Hz).

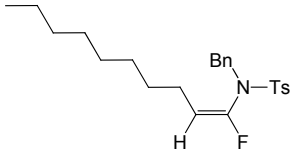
^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -99.15.

MS (IES+, ACN): *m/z* 356 $[M+Na]^+$, 336 $[M-HF+Na]^+$.

HRMS (ESI, CH_3OH): *m/z* 356.1097 (*m/z* theoretical: 356.1096) $[M+Na]^+$.

Formation of compound 2h:

(*E*)-*N*-benzyl-1-fluoro-*N*-tosyldec-1-en-1-amine



This compound was obtained from ynamide **1h** (106 mg, 0.267 mmol) following the general procedure A at -78°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 98/2, thereby obtaining compound **2h** (49 mg, 44 %).

Aspect: white solid.

Mp: 40-42°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 0.89 (t, CH_3, J = 7.1 Hz), 0.92 (m, CH_2), 1.05 (m, CH_2), 1.11-1.36 (m, $4CH_2$), 1.76 (dtd, CH_2, J = 7.9 Hz, J = 7.9 Hz, J = 1.7 Hz), 2.47 (s, CH_3), 4.41 (s, CH_2), 5.16 (dd, CH, J = 7.7 Hz, J = 7.7 Hz), 7.34 (m, 5H), 7.48 (d, 2CH, J = 8.5 Hz), 7.84 (d, 2CH, J = 8.2 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 14.4 (CH_3), 21.50 (CH_3), 23.3 ($2CH_2$), 26.8 (d, $2CH_2$, J = 3 Hz), 29.51 (d, $2CH_2$, J = 2 Hz), 30.0 ($2CH_2$), 30.1 ($2CH_2$), 32.6 ($2CH_2$), 52.0 (CH_2), 112.3 (d, CH_2, J = 32 Hz), 128.6 ($2CH_{arom}$), 129.0 (CH_{arom}), 129.3 ($2CH_{arom}$), 130.2 ($2CH_{arom}$), 130.8 ($2CH_{arom}$), 135.9 (C_{arom}), 137.4 (C_{arom}), 145.3 (C_{arom}), 147.1 (d, CF, J = 267 Hz).

^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -98.44.

MS (IES+, ACN): *m/z* 398 $[M-HF+Na]^+$, 418 $[M+H]^+$.

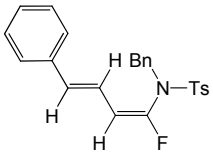
HRMS (ESI, CH_3OH): *m/z* 440.2031 (*m/z* theoretical: 440.2035) $[M+Na]^+$.

Formation of compounds 2i*E* and 2i*Z*:

These compounds were obtained from ynamide **1i** (100 mg, 0.258 mmol) following the general procedure A at -78°C. The reaction crude containing a 77/23 molar ratio of compounds **2i*E*** and **2i*Z*** was purified with the eluent petroleum ether/ethyl acetate: 95/5, thereby obtaining a mixture of the compound **2i*E*** and the compound **2i*Z*** (37 mg, 35%).

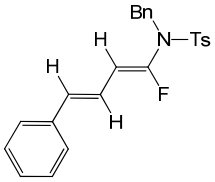
Compound 2i*E*:

(1*E*,3*E*)-*N*-benzyl-1-fluoro-4-phenyl-*N*-tosylbuta-1,3-dien-1-amine



Compound 2i*Z*:

(1*Z*,3*E*)-*N*-benzyl-1-fluoro-4-phenyl-*N*-tosylbuta-1,3-dien-1-amine



Aspect: white solid.

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) *δ*: 2.41 (s, CH_{3E}), 2.48 (s, CH_{3Z}), 4.59 (s, CH_{2Z}), 4.60 (s, CH_{2E}), 5.64 (ddd, CH_Z, J = 27.2 Hz, J = 10.9 Hz, J = 0.5 Hz), 6.04 (ddd, CH_E, J = 10.8 Hz, J = 5.1 Hz, J = 0.5 Hz), 6.32 (ddd, CH_E, J = 15.8 Hz, J = 10.8 Hz, J = 1.1 Hz), 6.50 (d, CH_E, J = 15.8 Hz), 6.62 (d, CH_Z, J = 15.9 Hz), 6.83 (ddd, CH_Z, J = 15.9 Hz, J = 10.9 Hz, J = 1.0 Hz), 7.20-7.53 (m, $12CH_{aromE}$ and $12CH_{aromZ}$), 7.85 (d, $1H_Z$, J = 8.4 Hz), 7.88 (d, CH_Z, J = 8.3 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) *δ*: 21.5 (CH_{3E}), 21.5 (CH_{3Z}), 52.6 (CH_{2Z}), 53.04 (CH_{2E}), 111.4 (d, CH_Z, J = 25 Hz), 113.0 (d, CH_E, J = 40 Hz), 120.3 (d, CH_Z, J = 1 Hz), 122.2 (d, CH_E, J = 4 Hz), 127.2 ($2CH_E$), 127.4 ($2CH_Z$), 128.6 (CH_{arom}), 128.7 (CH_{arom}), 128.9 (CH_{arom}), 129.0 (CH_{arom}), 129.1 (CH_{arom}), 129.3 (CH_{arom}), 129.4 (CH_{arom}), 129.4 (CH_{arom}), 129.5 (CH_{arom}), 129.5 (CH_{arom}), 130.1 (CH_{arom}), 130.9 ($2CH_Z$), 130.9 ($2CH_E$), 134.4 (d, CH_E, J = 11 Hz), 134.8 (d, CH_Z, J = 4 Hz), 135.9 (C_E), 136.2 (C_Z), 136.9 (C_Z), 137.3 (C_E), 137.6 (C_Z), 137.8 (C_E), 145.5 (C_Z), 145.7 (C_E), 147.7 (d, CF_Z, J = 280 Hz, C_{1Z}), 149.1 (d, CF_E, J = 276 Hz, C_{1E}).

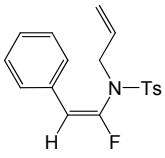
^{19}F NMR (CD_3COCD_3, 376 MHz, ppm) *δ*: -94.53 (d, F_Z, $^3J_{HF}$ = 27.3 Hz), -92.84 (d, F_E, $^3J_{HF}$ = 4.8 Hz).

MS (IES+, ACN): *m/z* 430 $[M+Na]^+$, 388 $[M-HF+H]^+$, 410 $[M-HF+Na]^+$.

HRMS (ESI, CH_3OH): *m/z* 408.1436 (*m/z* theoretical: 408.1428) $[M+H]^+$.

Formation of compound 2j:

***N*-((*E*)-1-fluoro-2-phenylvinyl)-*N*-tosylprop-2-en-1-amine**



This compound was obtained from ynamide **1j** (100 mg, 0.321 mmol) following the general procedure A at -50°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 97/3, thereby obtaining compound **2j** (82 mg, 77 %).

Aspect: white solid.

Mp: 52-53°C

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) *δ*: 2.44 (s, CH_3), 3.91 (d, CH_2, J = 6.9 Hz), 5.08 (dd, 1H, J = 10.1 Hz, J = 2.2 Hz), 5.12 (dd, 1H, J = 16.6 Hz, J = 2.3 Hz), 5.63 (tdd, CH, J = 17.0 Hz, J = 10.1 Hz, J = 6.7 Hz), 6.29 (d, CH, J = 8.5 Hz), 7.26-7.36 (m, 5CH), 7.55 (d, 2CH, J = 7.1 Hz), 7.81 (d, 2CH, J = 7.9 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 21.7 (CH_3), 51.4 (d, CH_2, J = 2 Hz), 111.3 (d, CH, J = 42 Hz), 120.6 (CH_2), 128.2 ($2CH_{arom}$), 128.3 ($2CH_{arom}$), 128.5 (d, 2CH, J = 4 Hz), 128.7 (CH_{arom}), 129.8 ($2CH_{arom}$), 130.8 (CH_{arom}), 131.4 (d, J = 8 Hz), 135.9 (C_{arom}), 144.6 (C_{arom}), 147.2 (d, CF, J = 275 Hz).

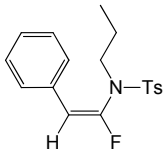
^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz, ppm) δ: -85.58.

MS (IES+, ACN): *m/z* 312 $[M\text{-}HF+H]^+$, 354 $[M+Na]^+$, 334 $[M\text{-}HF+Na]^+$.

HRMS (ESI, CH_3OH): *m/z* 354.0934 (*m/z* theoretical: 354.0940) $[M+Na]^+$.

Formation of compound 2k:

***N*-((*E*)-1-fluoro-2-phenylvinyl)-*N*-tosylpropan-1-amine**



This compound was obtained from ynamide **1k** (98 mg, 0.313 mmol) following the general procedure A at -78°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 95/5, thereby obtaining compound **2k** (52 mg, 50 %).

Aspect: light yellow oil.

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 0.76 (t, CH_3, J = 7.4 Hz), 1.48 (tq, CH_2, J = 7.6 Hz, J = 7.4 Hz), 2.45 (s, CH_3), 3.27 (td, CH_2, J = 7.6 Hz, J = 1.7 Hz), 6.44 (d, CH, J = 8.9 Hz), 7.30 (m, CH), 7.36 (m, 2CH), 7.46 (d, 2CH, J = 8.6 Hz), 7.64 (m, 2CH), 7.83 (d, 2CH, J = 8.0 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 11.4 (CH_3), 21.5 (CH_3), 21.9 (CH_2), 50.9 (CH_2), 111.8 (d, CH, J = 43 Hz), 128.9 (3CH), 129.3 ($2CH_{arom}$), 129.3 (d, 2CH, J = 4 Hz), 130.7 ($2CH_{arom}$), 132.5 (d, J = 8 Hz), 137.0 (C_{arom}), 145.5 (C_{arom}), 148.4 (d, CF, J = 273 Hz).

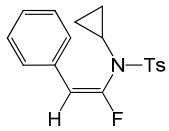
^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -86.35.

MS (IES+, ACN): *m/z* 356 $[M+Na]^+$, 314 $[M\text{-}HF+H]^+$.

HRMS (ESI, CH_3OH): *m/z* 356.1092 (*m/z* theoretical: 356.10965) $[M+Na]^+$.

Formation of compound 1l:

***N*-((*E*)-1-fluoro-2-phenylvinyl)-*N*-tosylcyclopropanamine**



This compound was obtained from ynamide **1l** (101 mg, 0.325 mmol) following the general procedure A at -78°C. The reaction crude was purified with the eluent petroleum ether/ethylacetate: 95/5, thereby obtaining compound **2l** (61 mg, 57 %).

Aspect: white solid.

Mp: 95-98°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 0.29-1.21 (m, 4H), 2.46 (s, CH_3), 2.51 (m, CH), 6.37 (d, CH, J = 8.7 Hz), 7.29 (m, 1H), 7.35 (m, 2CH), 7.48 (d, 2CH, J = 8.6 Hz), 7.55 (m, 2CH), 7.86 (d, 2CH, J = 8.0 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 4.8-10.4 (m, $2CH_2$), 21.5 (CH_3), 30.9 (d, CH, J = 1 Hz), 110.6 (d, CH, J = 42 Hz), 128.8 (CH_{arom}), 129.0 (d, 2CH, J = 4 Hz), 129.3 (d, 2CH, J = 1 Hz), 129.3 ($2CH_{arom}$), 130.6 ($2CH_{arom}$), 132.7 (d, C_{arom}, J = 8 Hz), 136.2 (C_{arom}), 145.8 (C_{arom}), 149.7 (d, CF, J = 275 Hz).

^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -87.32.

MS (IES+, ACN): *m/z* 354 $[M+Na]^+$, 312 $[M\text{-}HF+H]^+$.

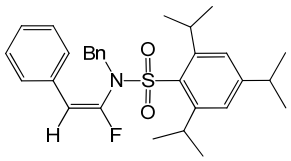
HRMS (ESI, CH_3OH): *m/z* 354.0939 (*m/z* theoretical: 354.09400) $[M+Na]^+$.

Formation of compounds 2m*E* and 2m*Z*:

These compounds were obtained from ynamide **1m** (108 mg, 0.228 mmol) following the general procedure A at -78°C. The reaction crude was purified with the eluent petroleum ether/ethyl acetate: 99.5/0.5, thereby obtaining a mixture of the compound **2m*E*** and the compound **2m*Z*** (59 mg, 53%) with a NMR ratio 3b/3c: 92/8.

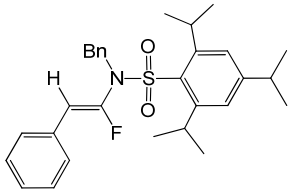
Compound 2m*E*:

***N*-benzyl-*N*-((*E*)-1-fluoro-2-(phenyl)vinyl)-2,4,6-triisopropylbenzenesulfonamide**



Compound 2m*Z*:

***N*-benzyl-*N*-((*Z*)-1-fluoro-2-(phenyl)vinyl)-2,4,6-triisopropylbenzenesulfonamide**



Aspect: white solid.

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) *δ*: 1.21 (d, $6CH_{3Z}$, *J* = 6.8 Hz), 1.26 (d, $6CH_{3E}$, *J* = 6.8 Hz, *J* = 1.0 Hz), 2.98 (m, CH_E and CH_Z), 4.20 (m, $2CH_E$ and $2CH_Z$), 4.68 (s, CH_{2E}), 4.82 (s, CH_{2Z}), 5.58 (d, CH_Z, *J* = 30.3 Hz), 6.29 (d, CH_E, *J* = 10.1 Hz), 7.16-7.35 (m, $10CH_E$ and $10CH_Z$), 7.36 (s, $2CH_Z$), 7.37 (s, $2CH_E$).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) *δ*: 23.8 ($2CH_{3E}$), 24.6 ($2CH_{3Z}$), 25.02 ($4CH_{3Z}$), 25.2 ($4CH_{3E}$), 30.6 (CH_{aromZ}), 31.18 (CH_{aromE}), 34.8 ($2CH_{aromE}$), 35.0 ($2CH_{aromZ}$), 51.1 (CH_{2Z}), 51.7 (CH_{2E}), 111.4 (d, CH_Z, *J* = 21 Hz), 112.3 (d, CH_E, *J* = 43 Hz), 125.1 ($2CH_{aromZ}$), 125.3 ($2CH_{aromE}$), 128.7 (d, $2CH_E$, *J* = 2 Hz), 128.9 ($2CH_{aromE}$), 128.9 (CH_{aromZ}), 129.1 (CH_{aromE}), 129.2 (CH_{aromE}).129.2 ($2CH_{aromE}$), 129.3 (CH_{aromZ}), 129.4 (CH_{aromZ}), 129.4 (CH_{aromZ}), 129.5 (CH_{aromZ}), 129.9 (CH_{aromZ}), 130.4 ($2CH_{aromE}$), 132.0 (d, C_{aromE}, *J* = 8 Hz), 132.2 (C_{aromZ}), 132.8 (d, C_{aromZ}, *J* = 7 Hz), 133.8 (C_{aromE}), 135.4 (C_{aromE}), 136.2 (C_{aromZ}), 147.5 (d, CF_E, *J* = 270 Hz), 150.2 (d, CF_Z, *J* = 276 Hz), 152.3 (C_{aromE}), 152.6 (C_{aromZ}), 154.8 (C_{aromE}), 155.1 (C_{aromZ}).

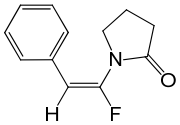
^{19}F NMR (CD_3COCD_3, 376 MHz, ppm) *δ*: -89.22 (d, F_Z, $^{3}J_{HF}$ = 29.9 Hz), -83.86 (d, F_E, $^{3}J_{HF}$ = 10.0 Hz).

MS (IES+, ACN): *m/z* 516 $[M+Na]^+$, 496 $[M-HF+Na]^+$, 474 $[M-HF+H]^+$.

HRMS (ESI, CH_3OH): *m/z* 494.2527 (*m/z* theoretical: 494.25235) $[M+H]^+$.

Formation of compound 2n:

1-((*E*)-1-fluoro-2-phenylvinyl)pyrrolidin-2-one



This compound was obtained from ynamide **1n** (49 mg, 0.265 mmol) following the general procedure B. The reaction crude was purified on prepartive TLC plate with the eluent petroleum ether/dichloromethane: 10/90, thereby obtaining compound **2n** (35 mg, 65%).

Aspect: white solid.

Mp: 29-31°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) *δ*: 2.20 (m, CH_2), 2.40 (t, CH_2, *J* = 8.3 Hz), 3.68 (dt, CH_2, *J* = 7.0 Hz, *J* = 2.2 Hz), 6.26 (d, CH, *J* = 9.1 Hz), 7.23 (m, CH), 7.30 (m, 4CH).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 19.8 (CH_2), 31.1 (CH_2), 47.3 (d, CH_2, J = 3 Hz), 106.5 (d, 2CH, J = 40 Hz), 128.2 (d, 2CH, J = 1 Hz), 128.5 (d, 2CH, J = 4 Hz), 129.4 (CH_{arom}), 133.1 (d, J = 9 Hz), 148.5 (d, CF, J = 262 Hz), 174.8 (d, CO, J = 3.7 Hz).

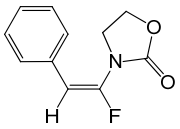
^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -90.19.

MS (IES+, ACN): *m/z* 206 $[M+H]^+$, 228 $[M+Na]^+$.

HRMS (ESI, CH_3OH): *m/z* 206.0983 (*m/z* theoretical: 206.0981) $[M+H]^+$.

Formation of compound 2o:

3-((*E*)-1-fluoro-2-phenylvinyl)oxazolidin-2-one



This compound was obtained from ynamide **1o** (93 mg, 0.534 mmol) following the general procedure B. The reaction crude was purified with the eluent petroleum ether/ethyl acetate: 85/15, thereby obtaining compound **2o** (75 mg, 73%).

Aspect: white solid.

Mp: 57-59°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 3.97 (ddd, CH_2, J = 9.4 Hz, J = 7.2 Hz, J = 2.7 Hz), 4.57 (dd, CH_2, J = 8.6 Hz, J = 7.2 Hz), 6.34 (d, CH, J = 8.6 Hz), 7.27 (t, CH, J = 6.9 Hz), 7.37 (m, 4CH).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 44.7 (d, CH_2, J = 2 Hz), 64.1 (CH_2), 107.5 (d, CH, J = 40 Hz), 128.5 (d, $2CH_{arom}$, J = 1 Hz), 128.8 (d, $2CH_{arom}$, J = 4 Hz), 129.5 (CH_{arom}), 132.6 (d, C_{arom}, J = 8 Hz), 147.5 (d, CF, J = 263 Hz), 155.5 (d, CO, J = 3 Hz).

^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -92.38.

MS (IES+, ACN): *m/z* 208 $[M+H]^+$, 230 $[M+Na]^+$.

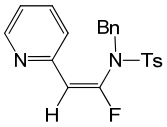
HRMS (ESI, CH_3OH): *m/z* 208.0779 (*m/z* theoretical: 208.0774) $[M+H]^+$.

Formation of compound 2p and 3p':

These compounds were obtained from ynamide **1p** (105 mg, 0.290 mmol) following the general procedure A at -50°C. The reaction crude was purified with the eluent petroleum ether/ethyl acetate: 80/20, thereby obtaining compound **2p'** (59 mg, 54 %) and compound **2p** (29 mg, 26 %).

Compound 2p:

(*E*)-*N*-benzyl-1-fluoro-2-(pyridin-2-yl)-*N*-tosylethenamine



Aspect: beige solid

Mp: 73-76°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 2.44 (s, CH_3), 4.67 (d, CH_2, J = 1.9 Hz), 6.30 (d, CH, J = 8.4 Hz), 7.15 (ddd, CH, J = 7.4 Hz, J = 4.8 Hz, J = 0.9 Hz), 7.23 (m, 5CH), 7.40 (d, 2CH, J = 8.5 Hz), 7.53 (d, CH, J = 8.0 Hz), 7.64 (ddd, CH, J = 7.8 Hz, J = 7.8 Hz, J = 1.8 Hz), 7.83 (d, 2CH, J = 8.3 Hz), 8.34 (ddd, 1H, J = 4.8 Hz, J = 1.7 Hz, J = 0.9 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 21.5 (CH_3), 53.5 (CH_2), 112.1 (d, CH, J = 43 Hz), 123.0 (d, CH, J = 1 Hz), 124.0 (d, CH_{arom}, J = 4 Hz), 128.9 (CH_{arom}), 129.0 (CH_{arom}), 129.1 (CH_{arom}), 130.1 ($2CH_{arom}$), 130.6 ($2CH_{arom}$), 135.6 (d, J = 1.0 Hz, C_{arom}), 136.8 (CH_{arom}), 137.4 (C_{arom}), 145.4 (C_{arom}), 150.0 (CH_{arom}), 150.7 (d, CF, J = 274 Hz), 152.1 (d, C_{arom}, J = 12 Hz).

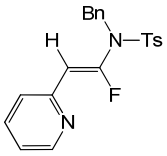
^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -78.64.

MS (IES+, ACN): *m/z* 383 $[M+H]^+$, 363 $[M-HF+H]^+$.

HRMS (ESI, CH_3OH): *m/z* 383.1233 (*m/z* theoretical: 383.1230) $[M+H]^+$.

Compound 2p':

(*Z*)-*N*-benzyl-1-fluoro-2-(pyridin-2-yl)-*N*-tosylethenamine



Aspect: brown solid

Mp: 118-121°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 2.47 (s, CH_3), 4.69 (s, CH_2), 5.87 (d, CH, *J* = 29.9 Hz), 7.20 (dd, CH, *J* = 7.5 Hz, *J* = 4.8 Hz), 7.28 (m, CH), 7.34 (m, 2CH), 7.39 (m, 2CH), 7.50 (d, 2CH, *J* = 8.5 Hz), 7.54 (d, CH, *J* = 8.0 Hz), 7.71 (ddd, CH, *J* = 7.8 Hz, *J* = 7.8 Hz, *J* = 1.8 Hz), 7.88 (d, 2CH, *J* = 8.4 Hz), 8.50 (ddd, CH, *J* = 4.8 Hz, *J* = 1.8 Hz, *J* = 1.0 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 21.5 (CH_3), 52.9 (CH_2), 111.6 (d, CH, *J* = 20 Hz), 123.3 (CH_{arom}), 124.3 (d, CH_{arom}, *J* = 13 Hz), 128.6 ($2CH_{arom}$), 128.9 (CH_{arom}), 129.4 ($2CH_{arom}$), 129.5 ($2CH_{arom}$), 130.9 ($2CH_{arom}$), 136.1 (C_{arom}), 136.7 (C_{arom}), 137.2 (CH_{arom}), 145.7 (C_{arom}), 149.8 (d, CF, *J* = 285 Hz), 150.4 (CH_{arom}), 152.5 (d, C_{arom}, *J* = 8.2 Hz).

^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -84.70.

MS (IES+, ACN): *m/z* 383 $[M+H]^+$, 363 $[M-HF+H]^+$.

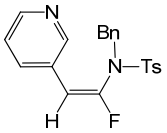
HRMS (ESI, CH_3OH): *m/z* 383.1232 (*m/z* theoretical: 383.1230) $[M+H]^+$, 363.1166 (*m/z* theoretical: 363.11672) $[M-HF+H]^+$.

Formation of compound 2q and 2q':

These compounds were obtained from ynamide **1q** (101 mg, 0.279 mmol) following the general procedure A at -50°C. The reaction crude was purified on TLC plate with the eluent petroleum ether/CH_2Cl_2/MeOH: 50/48/2, compound **2q'** (8 mg, 7 %) first eluted followed by compound **2q** (81 mg, 79 %).

Compound 2q:

(*E*)-*N*-benzyl-1-fluoro-2-(pyridin-3-yl)-*N*-tosylethenamine



Aspect: light brown solid.

Mp: 89-92°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) δ: 2.47 (s, CH_3), 4.48 (s, CH_2), 6.31 (d, CH, *J* = 8.3 Hz), 7.18 (m, 6CH), 7.49 (d, 2CH, *J* = 8.6 Hz), 7.79 (ddd, CH, *J* = 8.0 Hz, *J* = 1.7 Hz, *J* = 0.5 Hz), 7.88 (d, 2CH, *J* = 8.0 Hz), 8.40 (dd, CH, *J* = 4.8 Hz, *J* = 1.6 Hz), 8.48 (d, CH, *J* = 2.1 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) δ: 21.5 (CH_3), 52.7 (CH_2), 109.5 (d, CH, *J* = 44 Hz), 123.8 (CH_{arom}), 128.4 (d, C_{arom}, *J* = 8 Hz), 129.0 ($2CH_{arom}$), 129.1 ($2CH_{arom}$), 129.2 (CH_{arom}), 130.4 ($2CH_{arom}$), 130.9 ($2CH_{arom}$), 134.6 (C_{arom}), 135.2 (d, CH_{arom}, *J* = 3 Hz), 136.6 (C_{arom}), 145.9 (C_{arom}), 148.9 (d, CF, *J* = 276 Hz), 149.6 (CH_{arom}), 150.4 (d, CH_{arom}, *J* = 4 Hz).

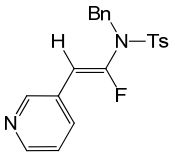
^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) δ: -87.08.

MS (IES+, ACN): *m/z* 383 $[M+H]^+$.

HRMS (ESI, CH_3OH): *m/z* 383.1229 (*m/z* theoretical: 383.12295) $[M+H]^+$.

Compound 2q':

(*Z*)-*N*-benzyl-1-fluoro-2-(pyridin-3-yl)-*N*-tosylethenamine



Aspect: white solid.

Mp: 135-137°C

^{1}H NMR (CD_3COCD_3, 400 MHz, ppm) *δ*: 2.49 (s, CH_3), 4.64 (d, CH_2, *J* = 0.8 Hz), 5.82 (d, CH, *J* = 30.3 Hz), 7.33 (m, 6CH), 7.52 (d, 2CH, *J* = 8.6 Hz), 7.77 (d, CH, *J* = 8.0 Hz, *J* = 1.8 Hz), 7.88 (d, 2CH, *J* = 8.3 Hz), 8.44 (dd, CH, *J* = 4.8 Hz, *J* = 1.5 Hz), 8.52 (d, CH, *J* = 2.0 Hz).

^{13}C NMR (CD_3COCD_3, 100 MHz, ppm) *δ*: 21.5 (CH_3), 52.9 (CH_2), 107.6 (d, CH, *J* = 22 Hz), 124.4 (CH_{arom}), 128.7 ($2CH_{arom}$), 129.0 (CH_{arom}), 129.1 (d, *J* = 5 Hz), 129.4 ($2CH_{arom}$), 129.6 ($2CH_{arom}$), 131.0 (CH_{arom}), 135.9 (d, CH_{arom}, *J* = 9 Hz), 136.1 (d, C_{arom}, *J* = 1 Hz), 136.7 (C_{arom}), 145.7 (C_{arom}), 149.1 (d, CF, *J* = 282 Hz), 149.7 (CH_{arom}), 150.5 (d, CH_{arom}, *J* = 7 Hz).

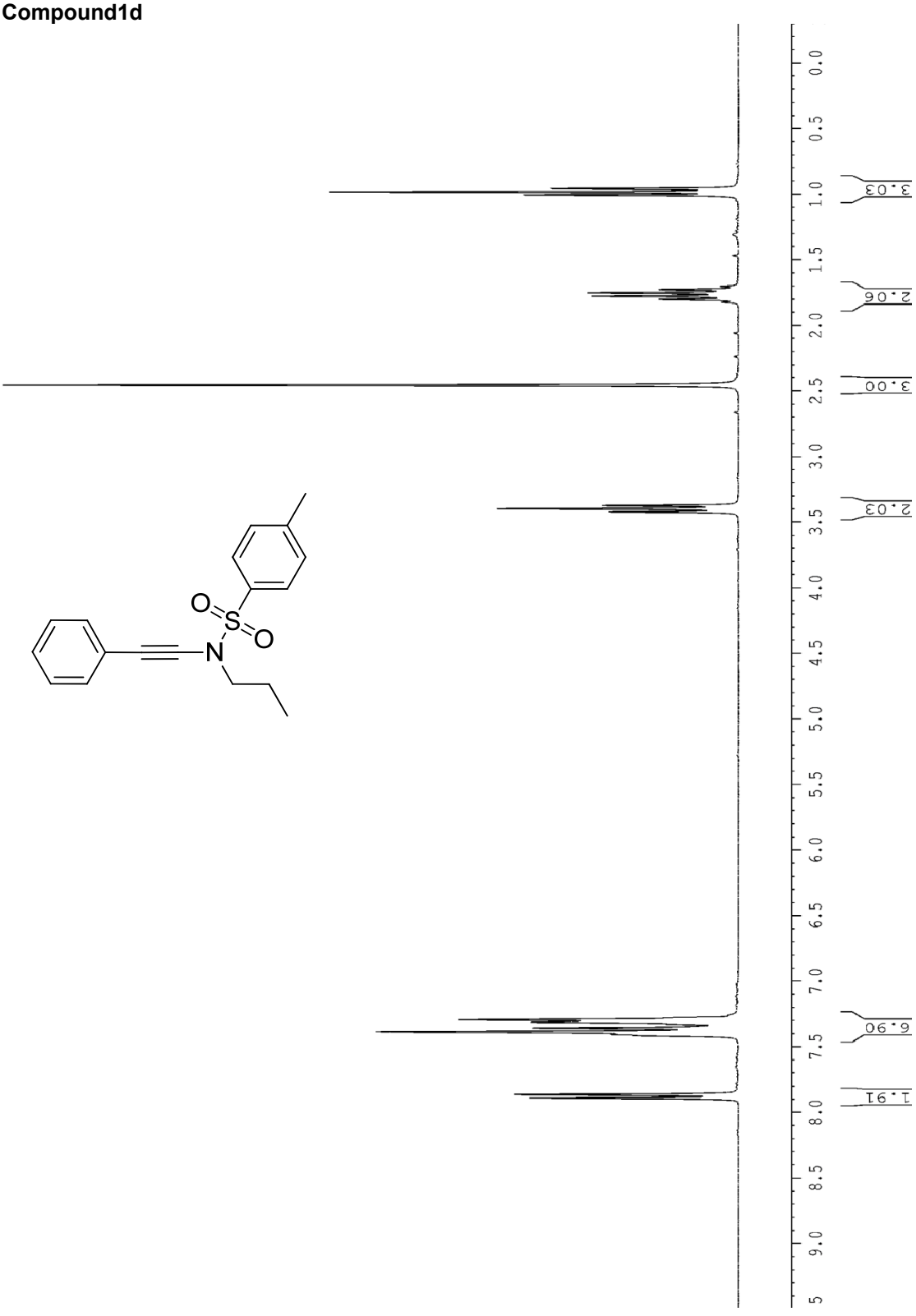
^{19}F{^{1}H} NMR (CD_3COCD_3, 376 MHz, ppm) *δ*: -87.09.

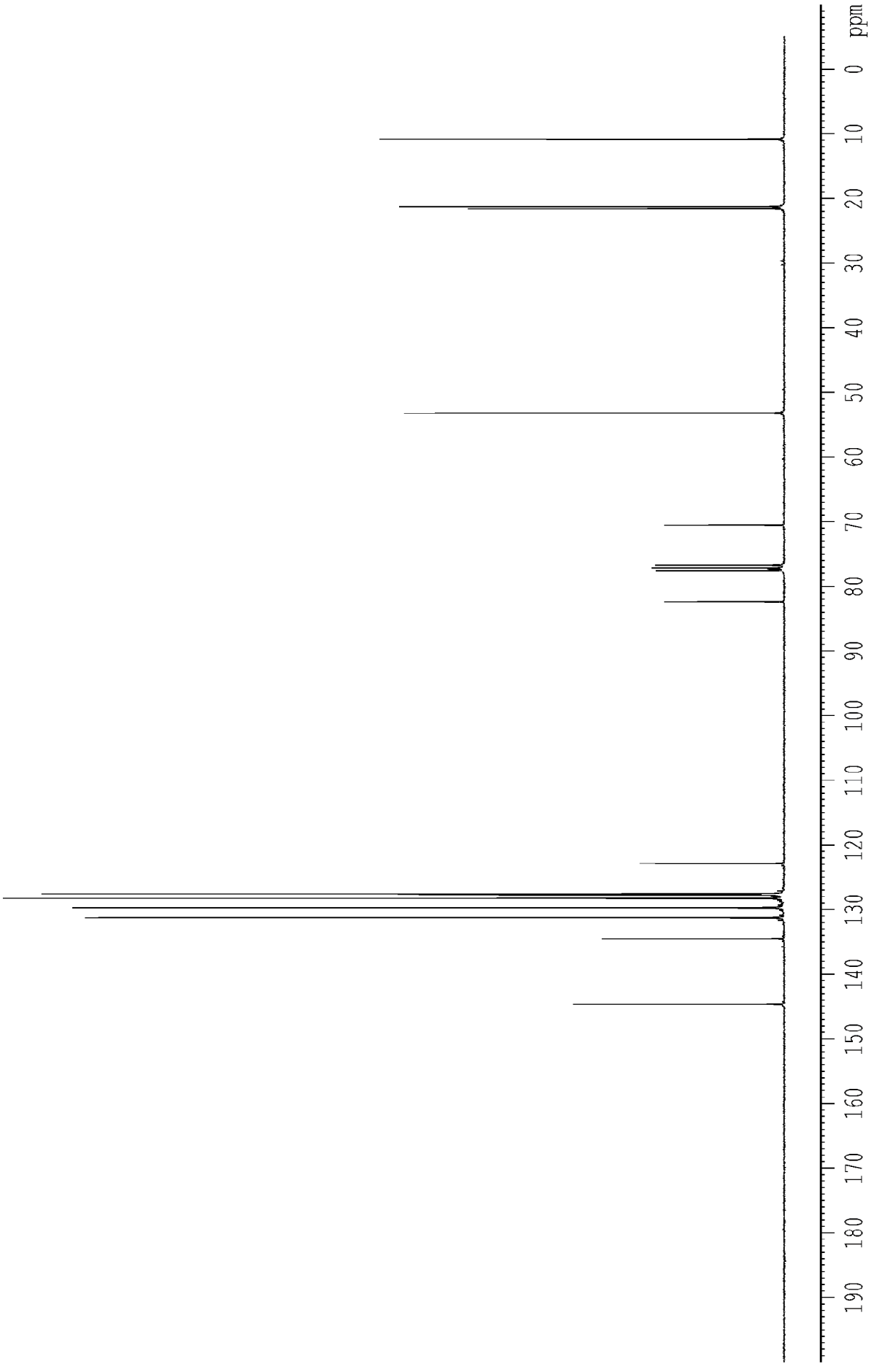
MS (IES+, ACN): *m/z* 383 $[M+H]^+$, 403 $[M+Na]^+$.

HRMS (ESI, CH_3OH): *m/z* 383.1229 (*m/z* theoretical: 383.12295) $[M+H]^+$.

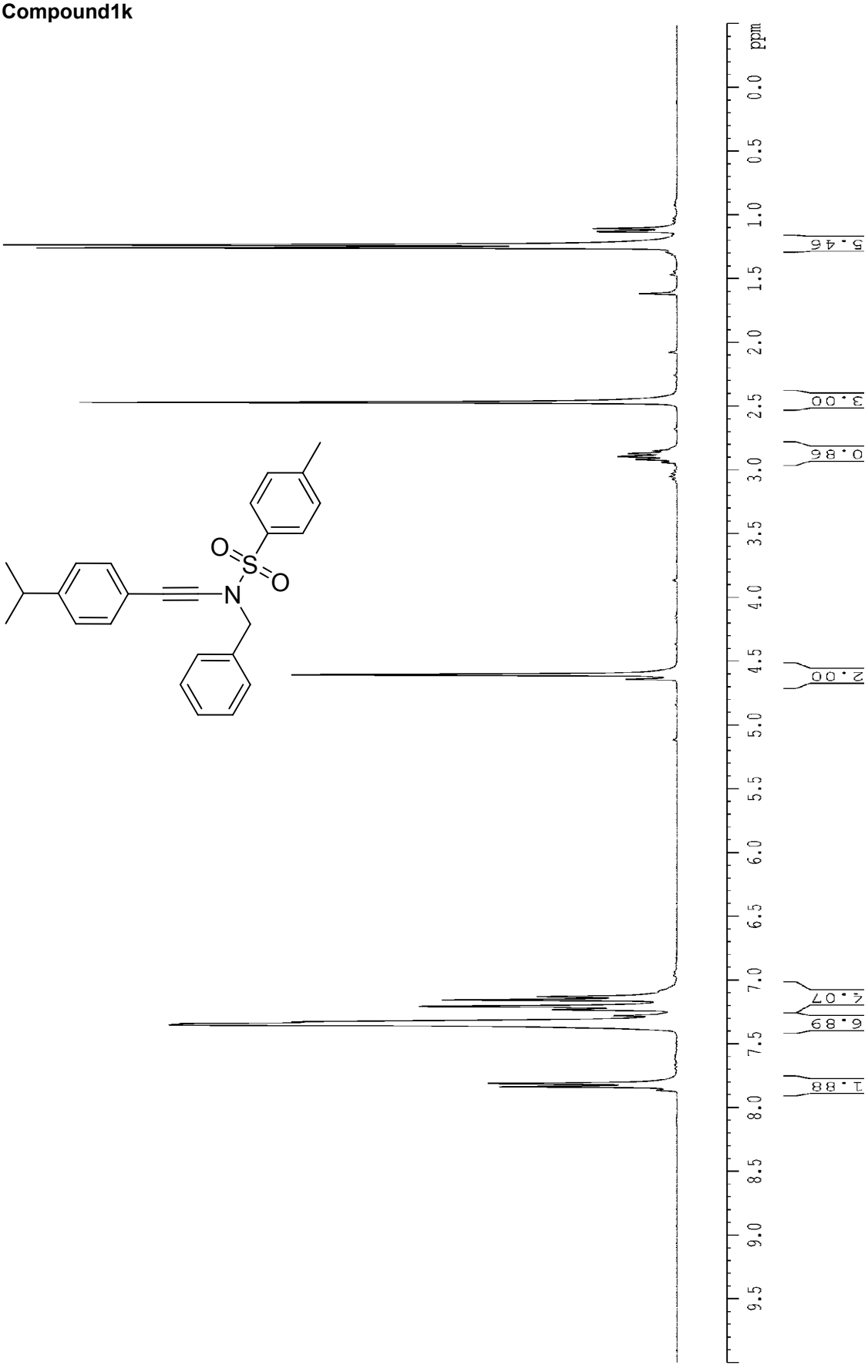
D. NMR SPECTRA

Compound1d

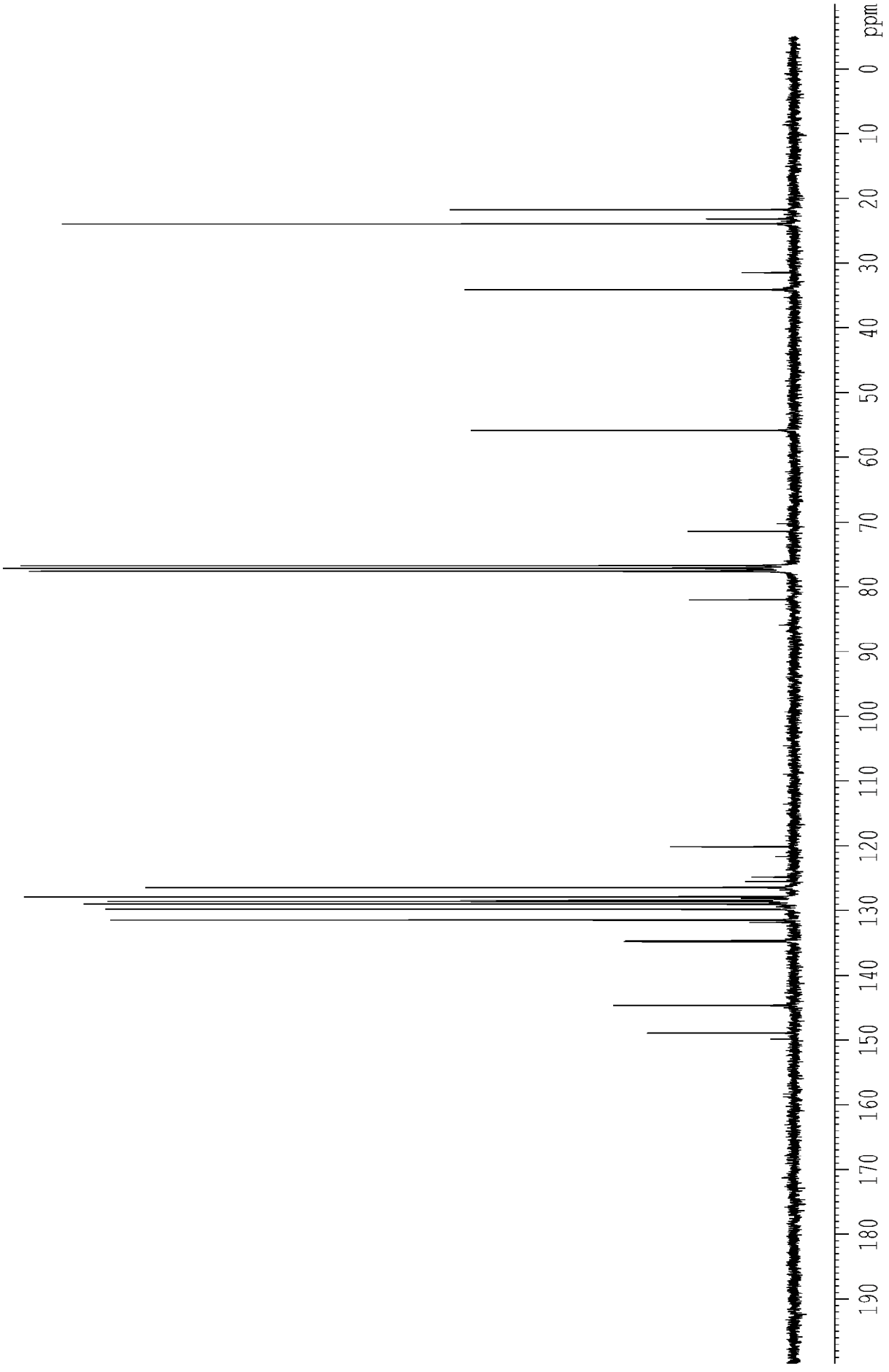



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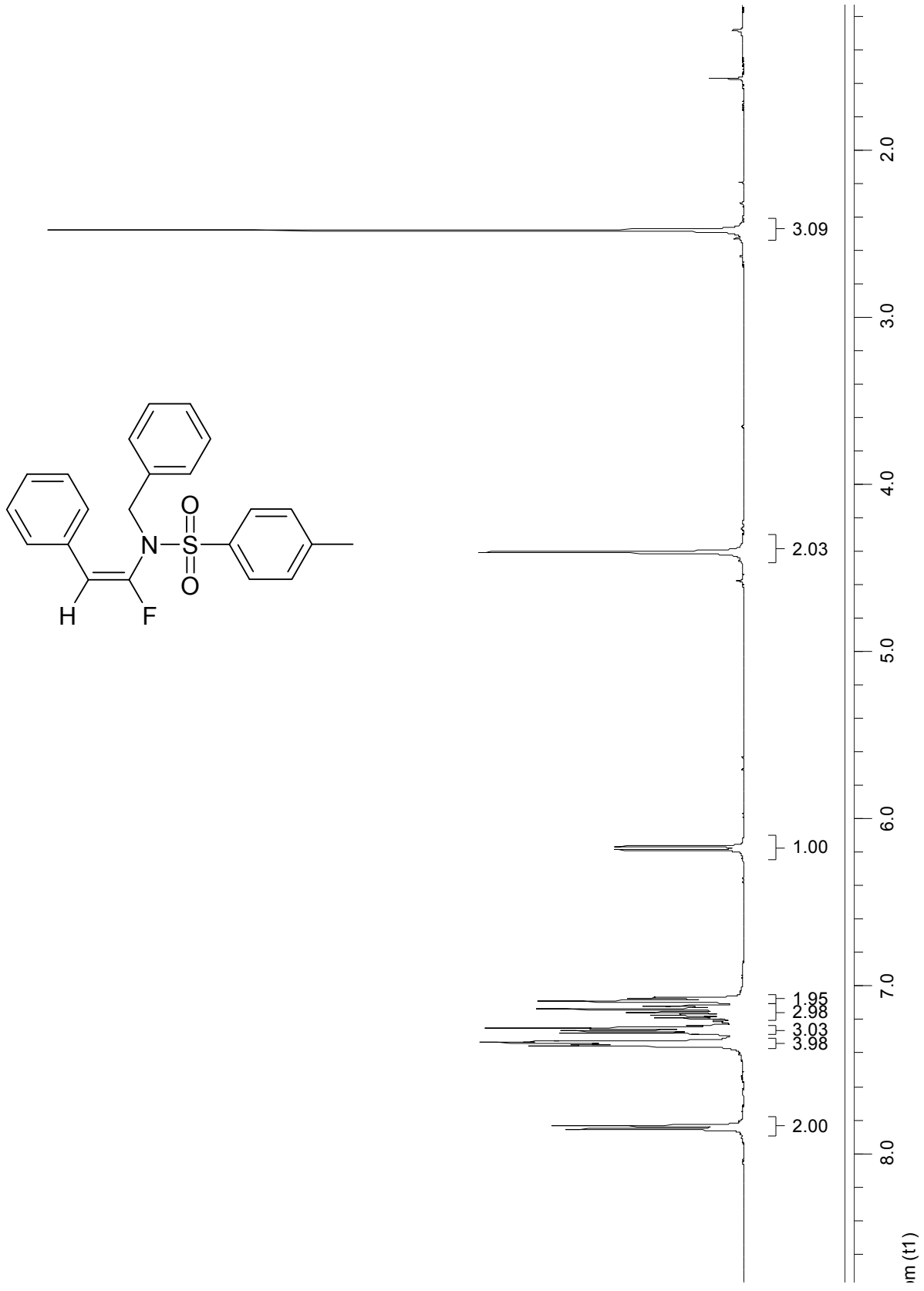
Compound1k

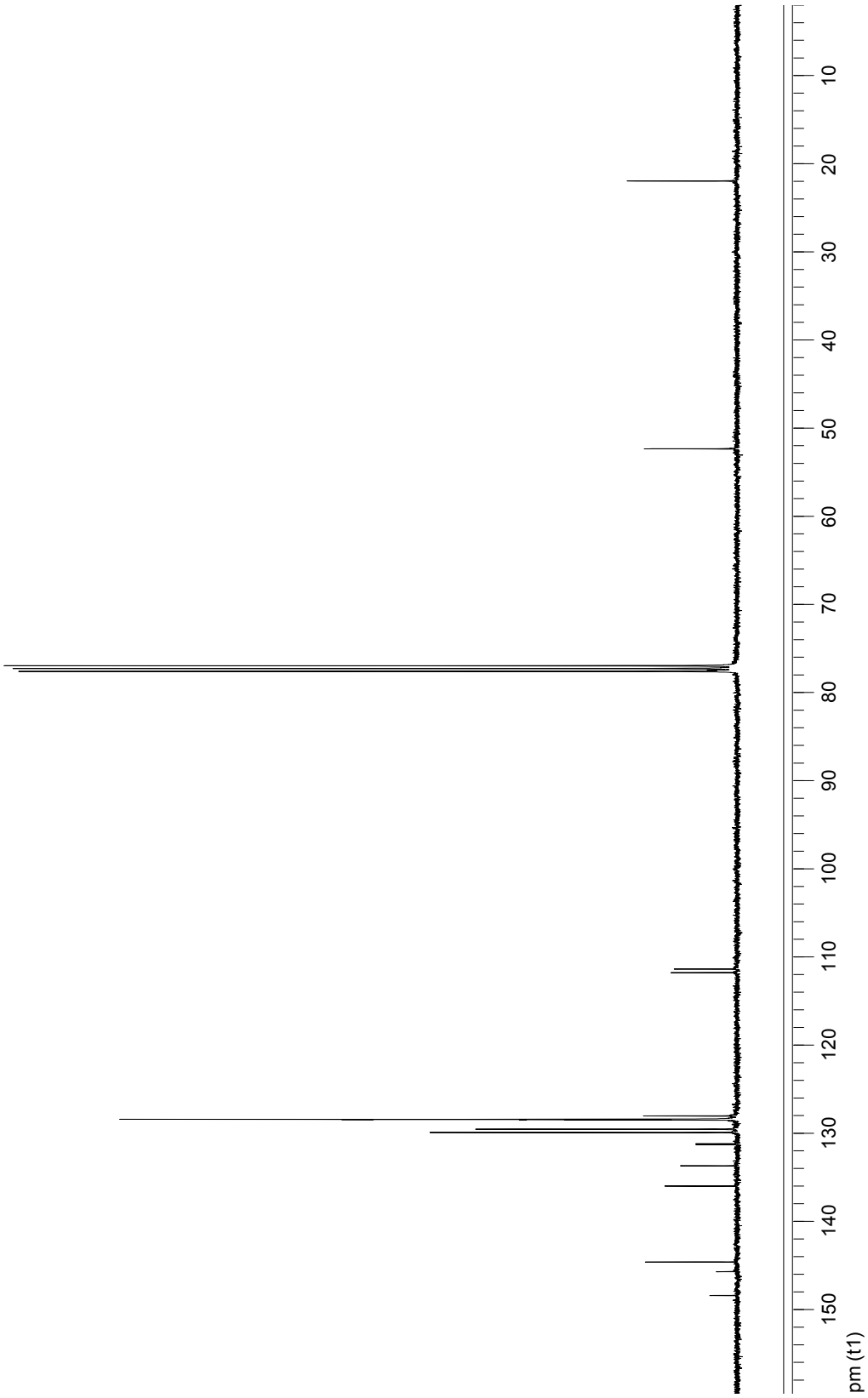

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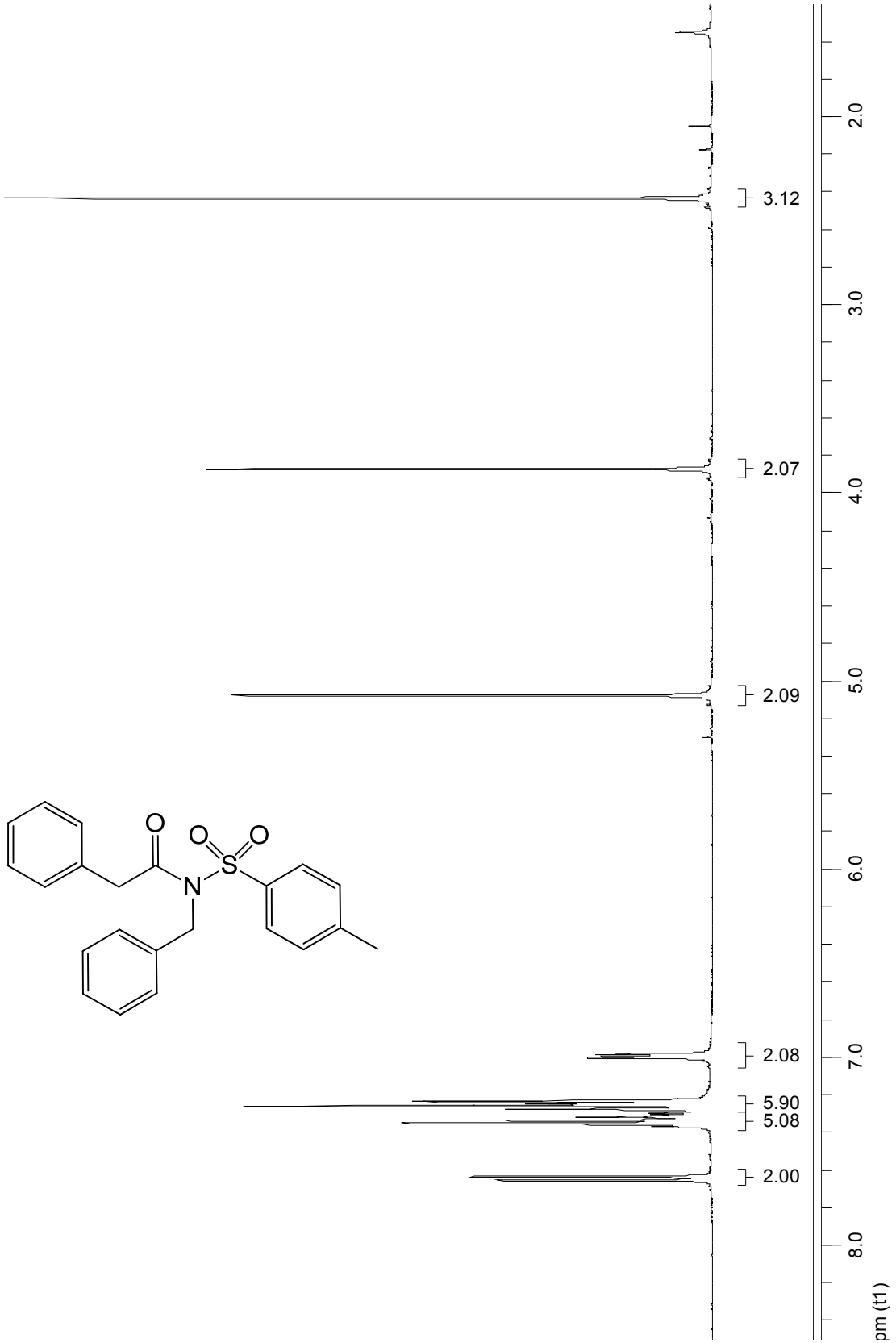


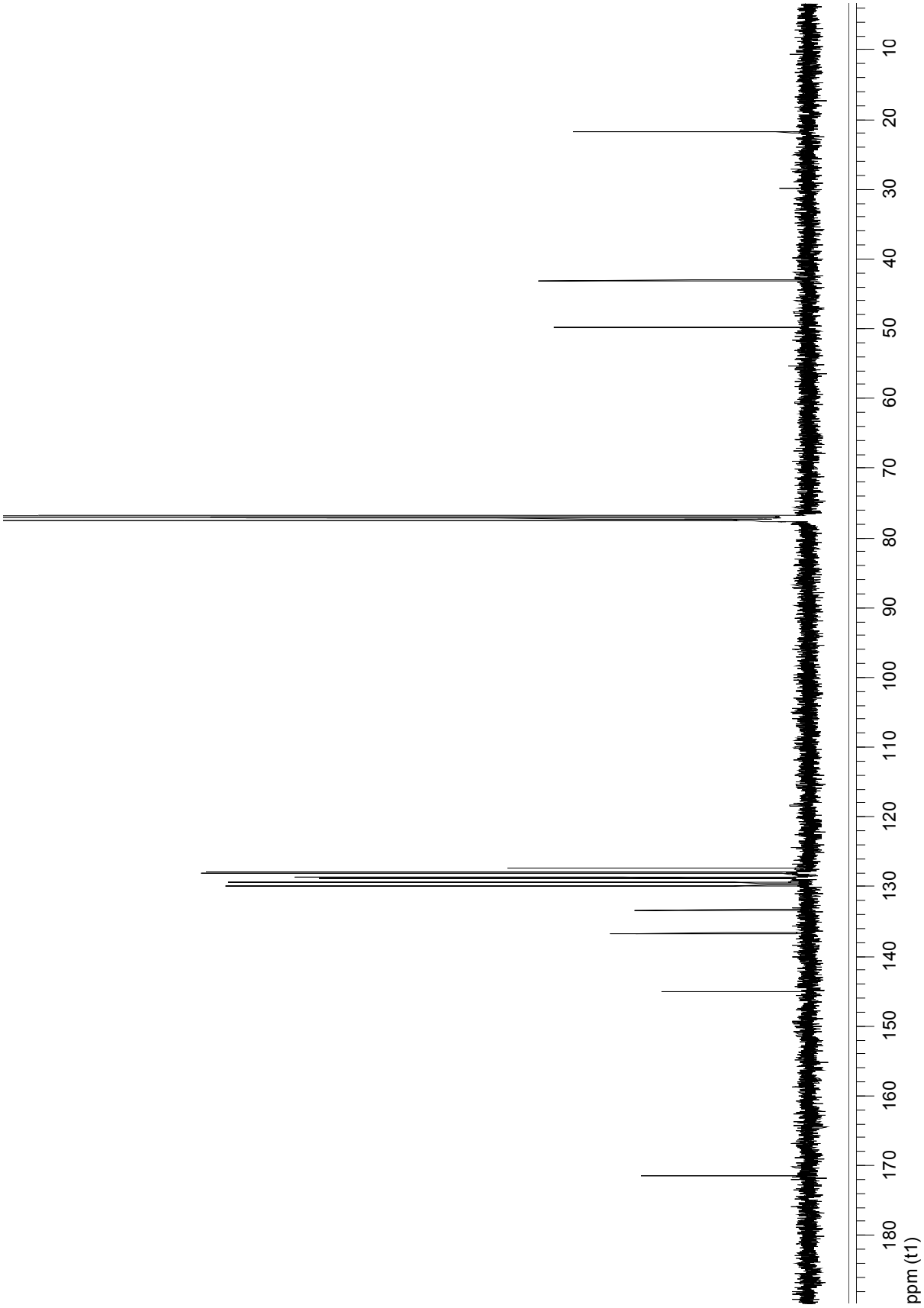
Compound 2a



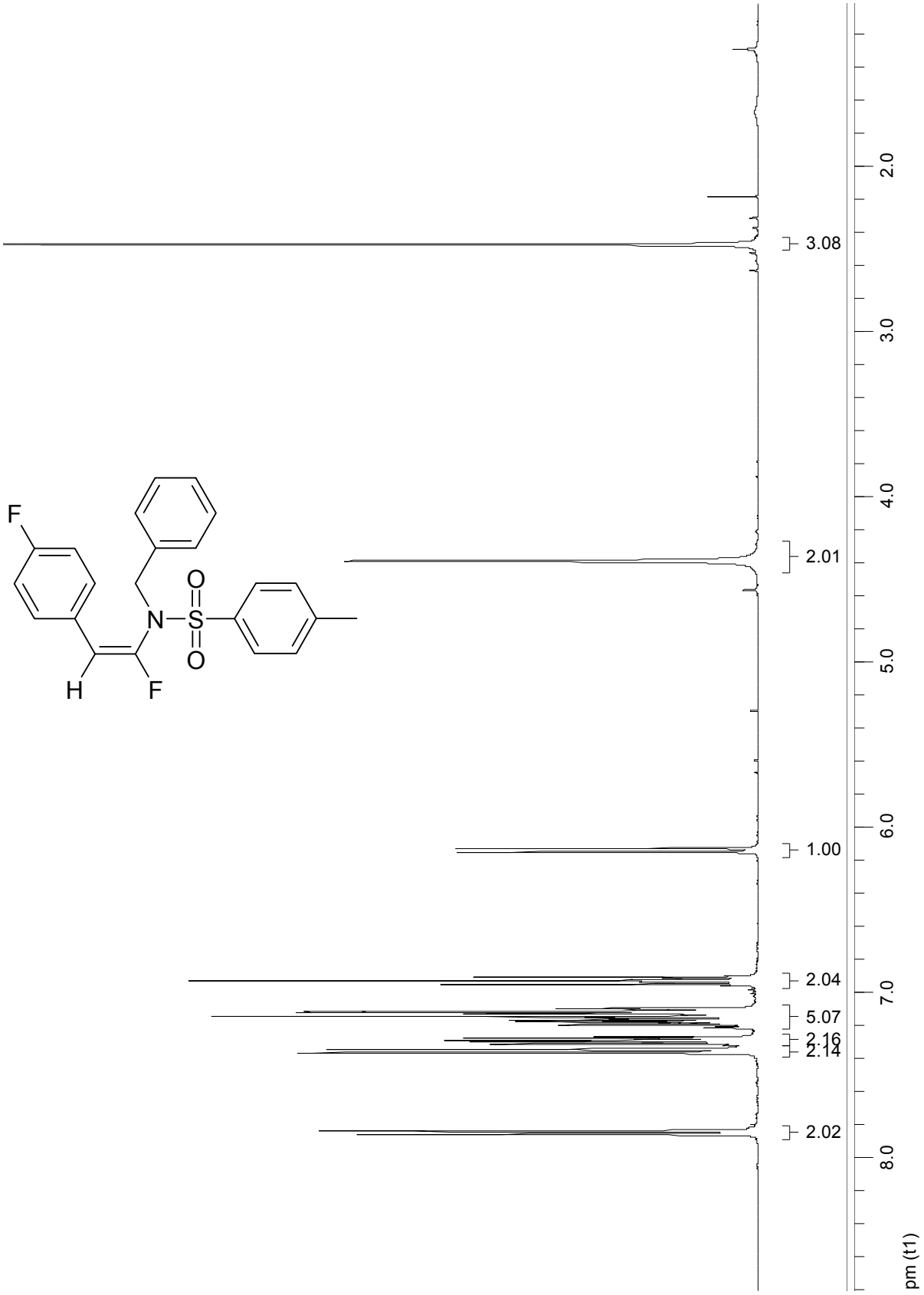

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pm (t1)

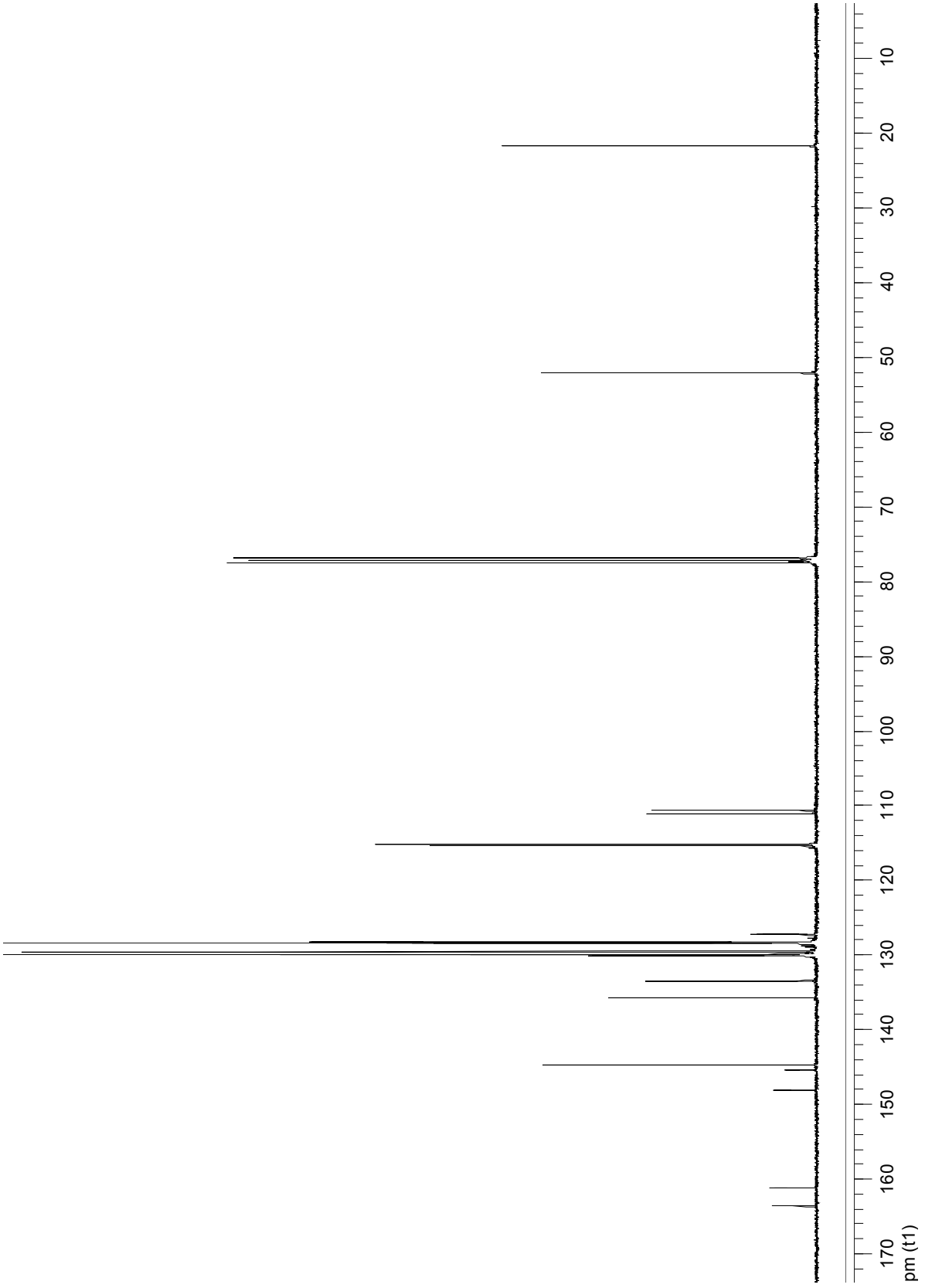
Compound 3a:



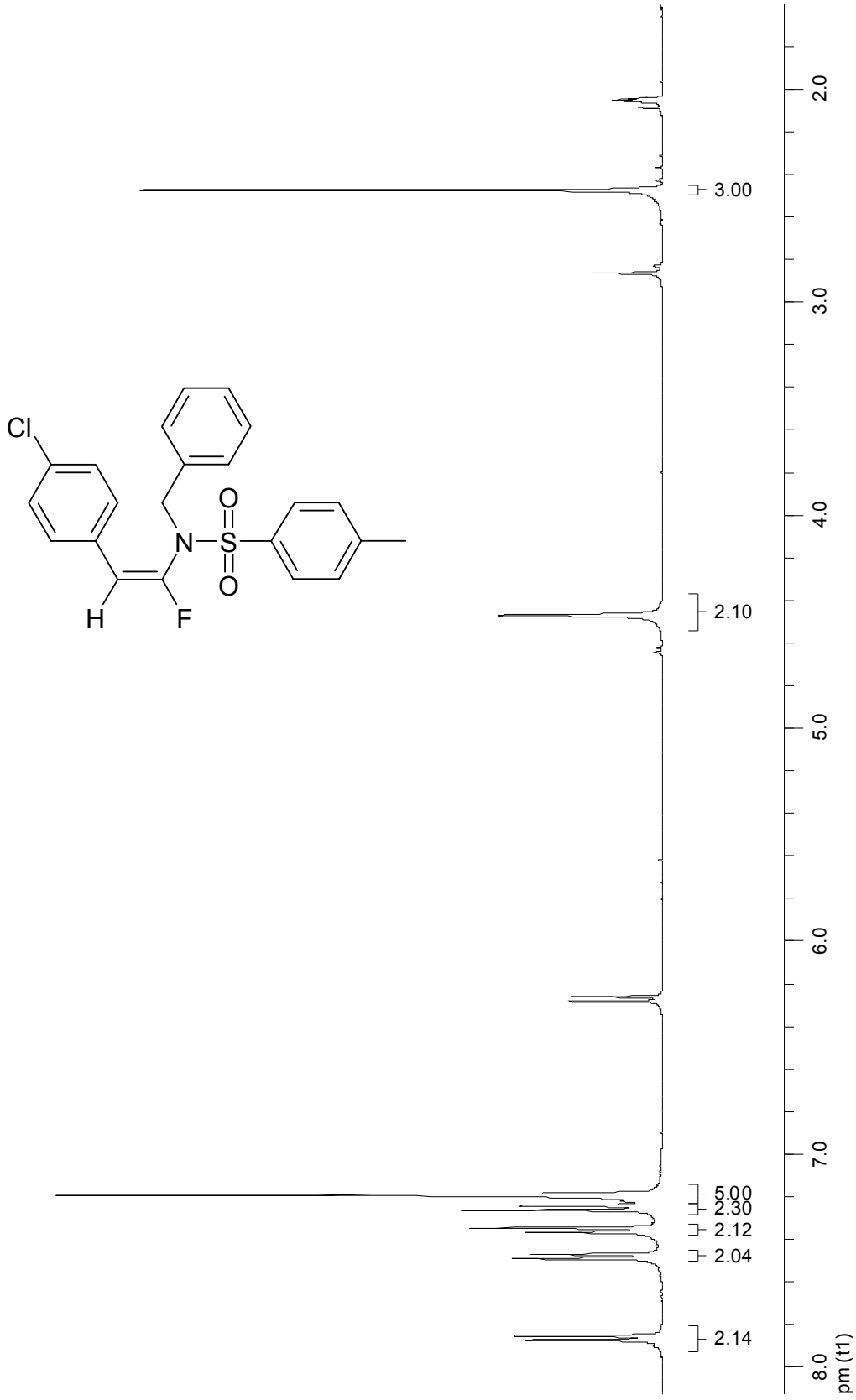

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ppm (t1)

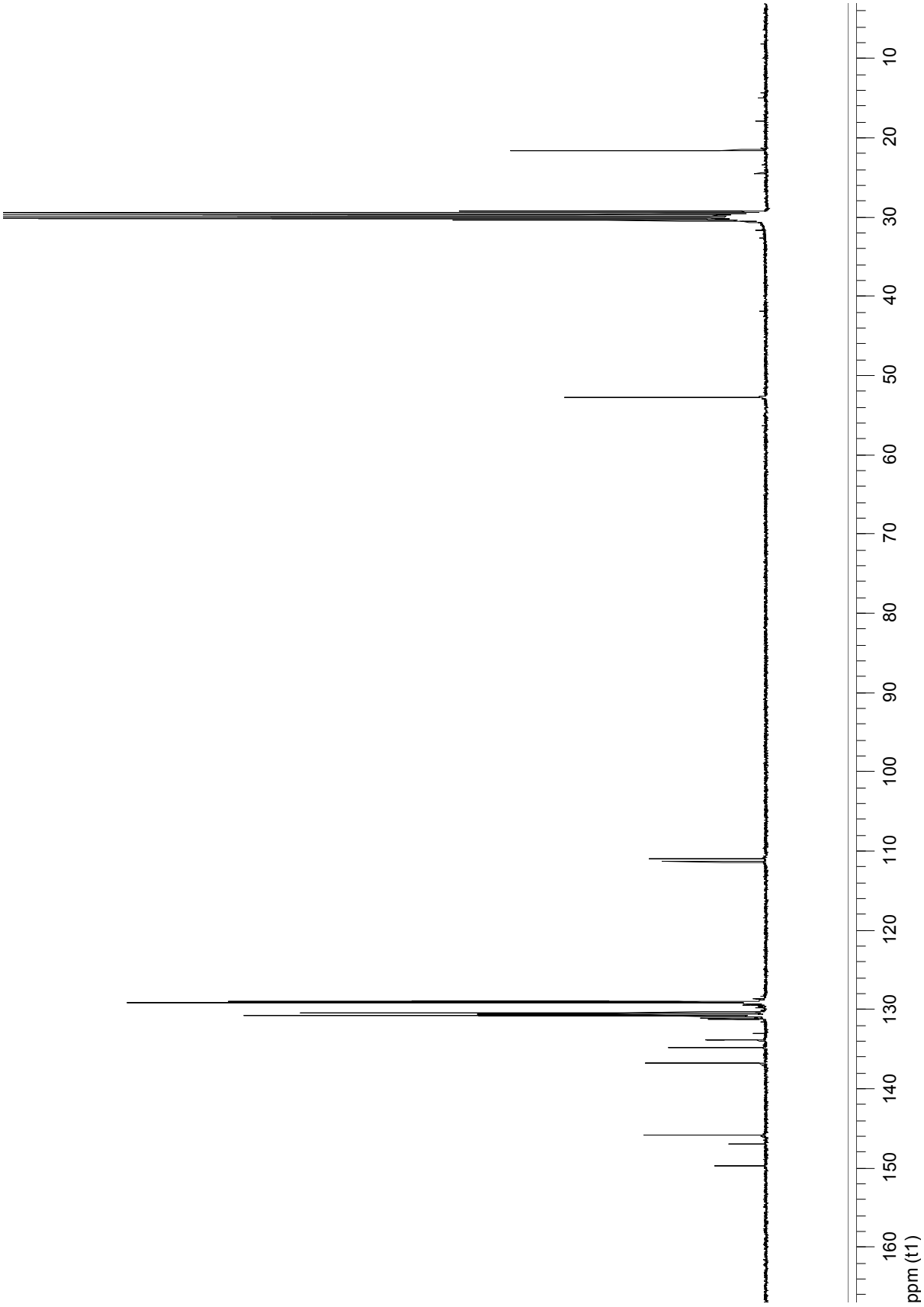
Compound 2b:



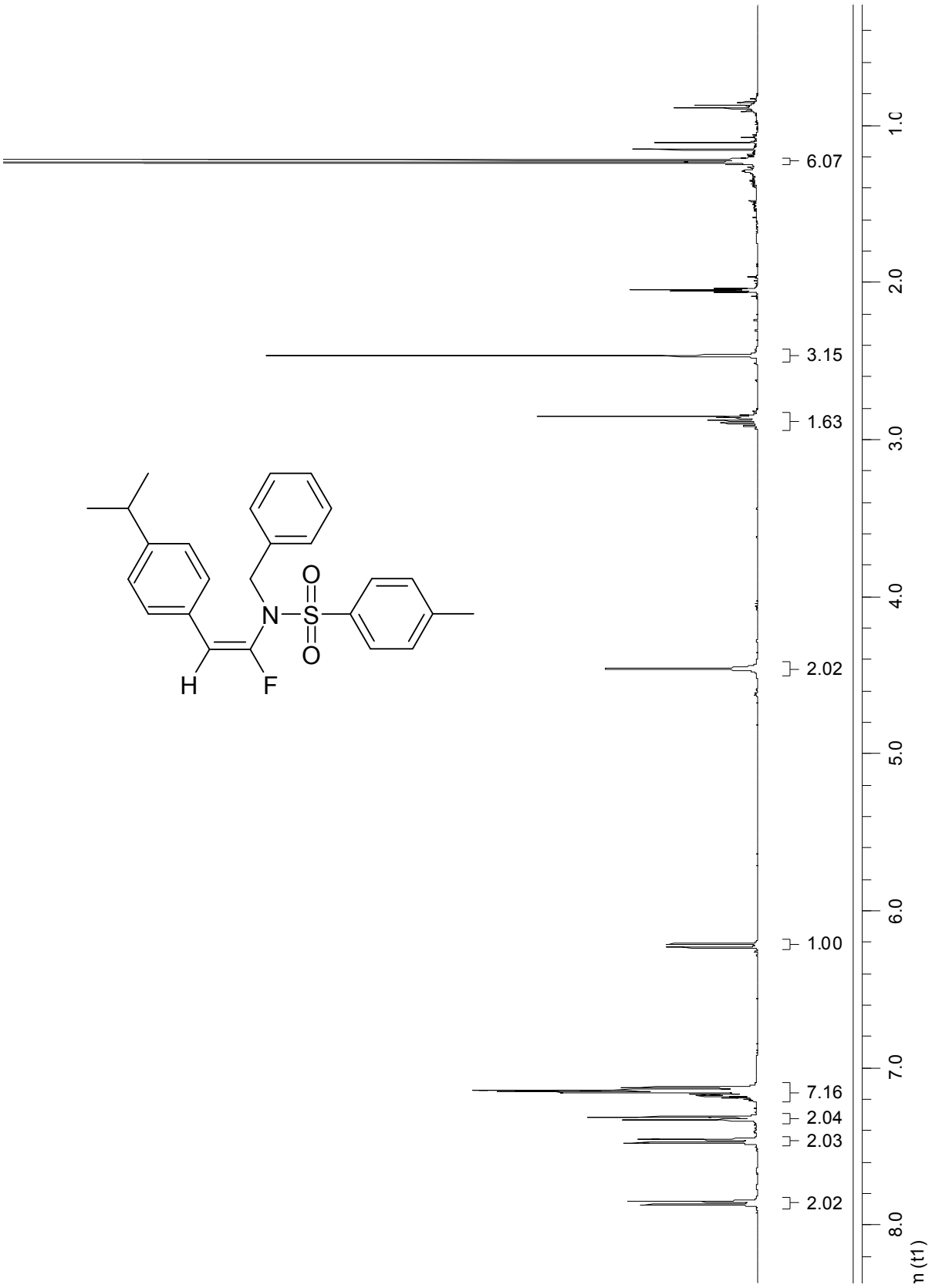

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pm (t1)

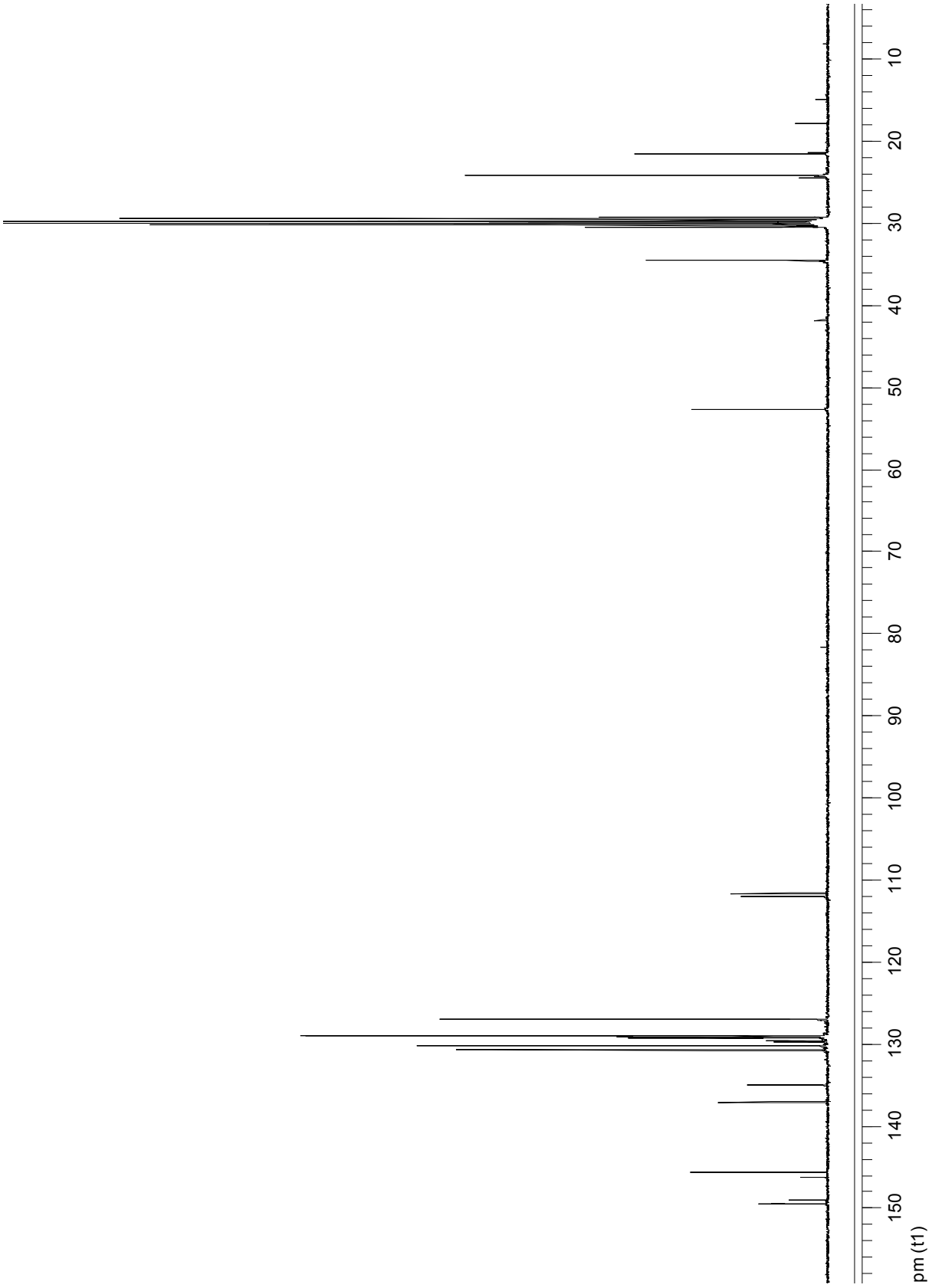
Compound 2C:



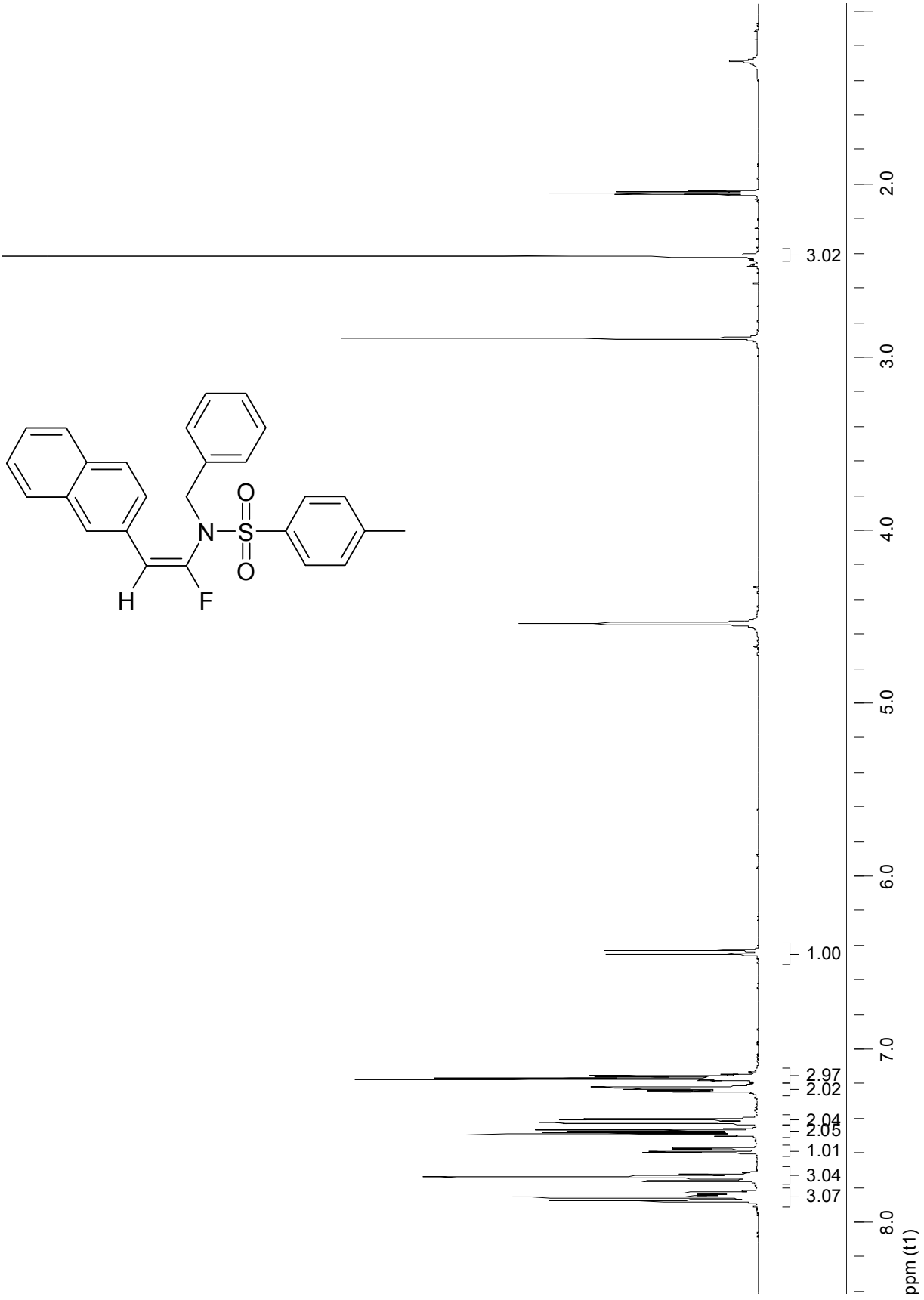

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ppm (t1)

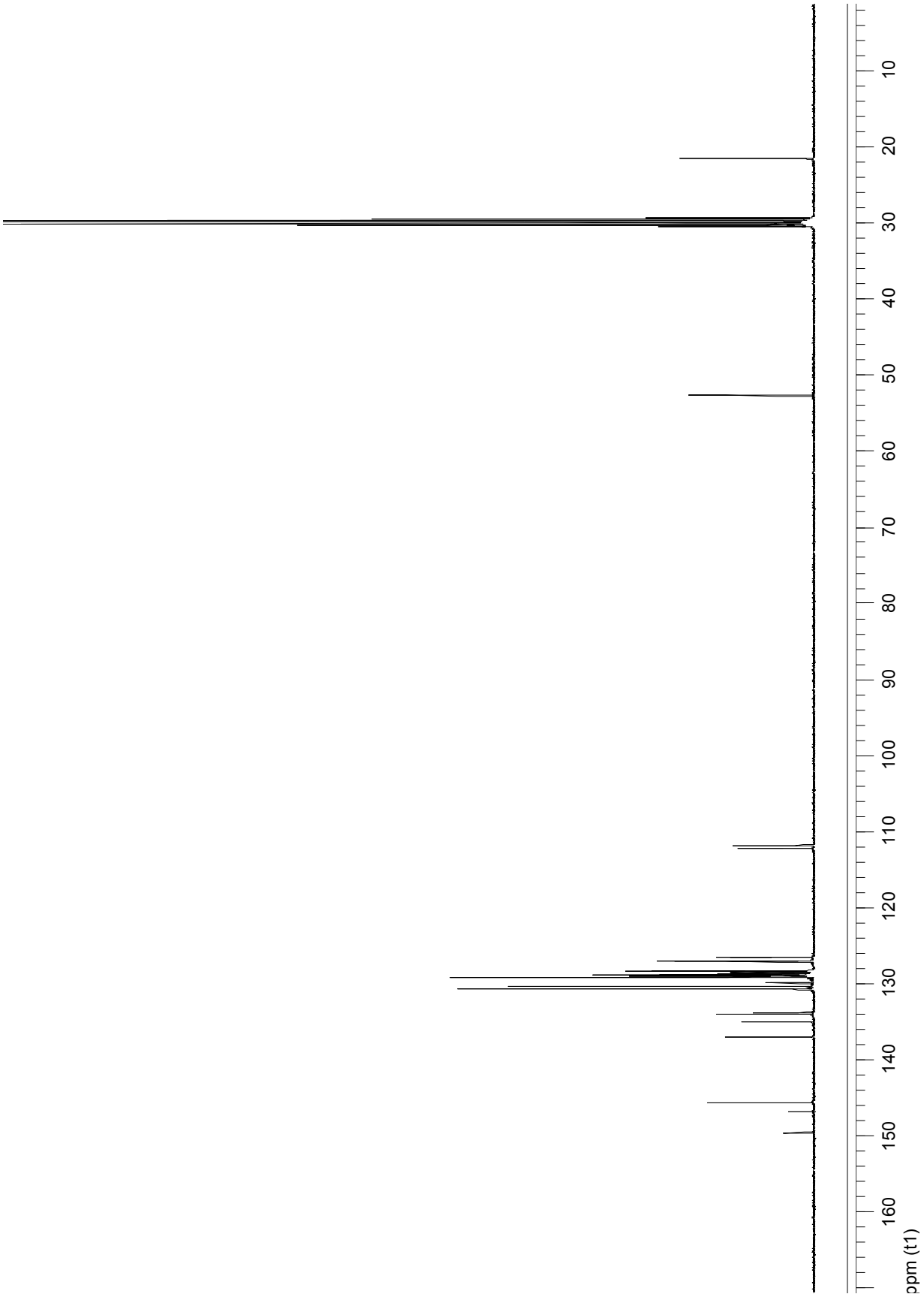
Compound 2d:


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7.16
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2.03
2.02
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n (t1)
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N
S
O
H
F

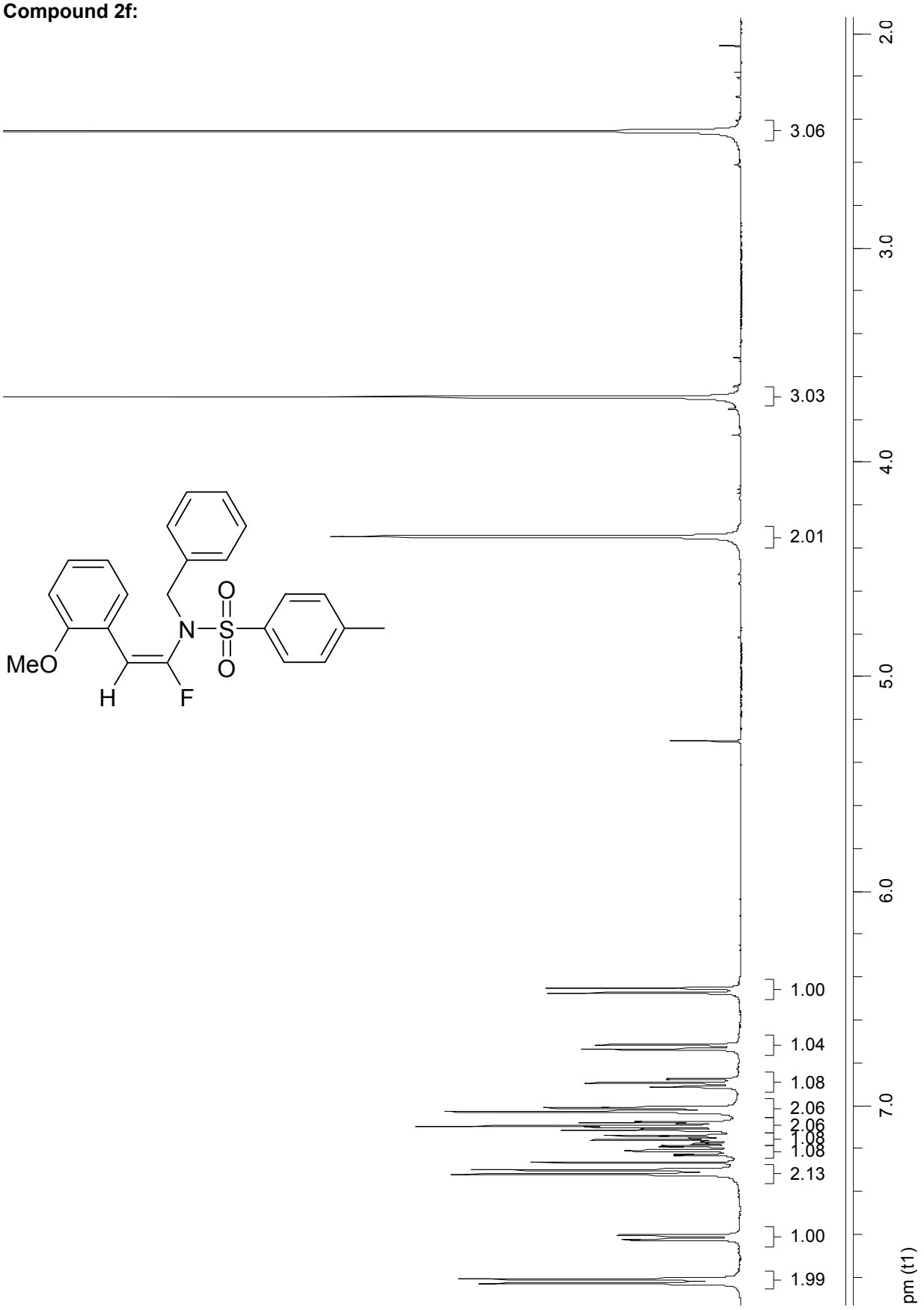

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140
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pm (t1)

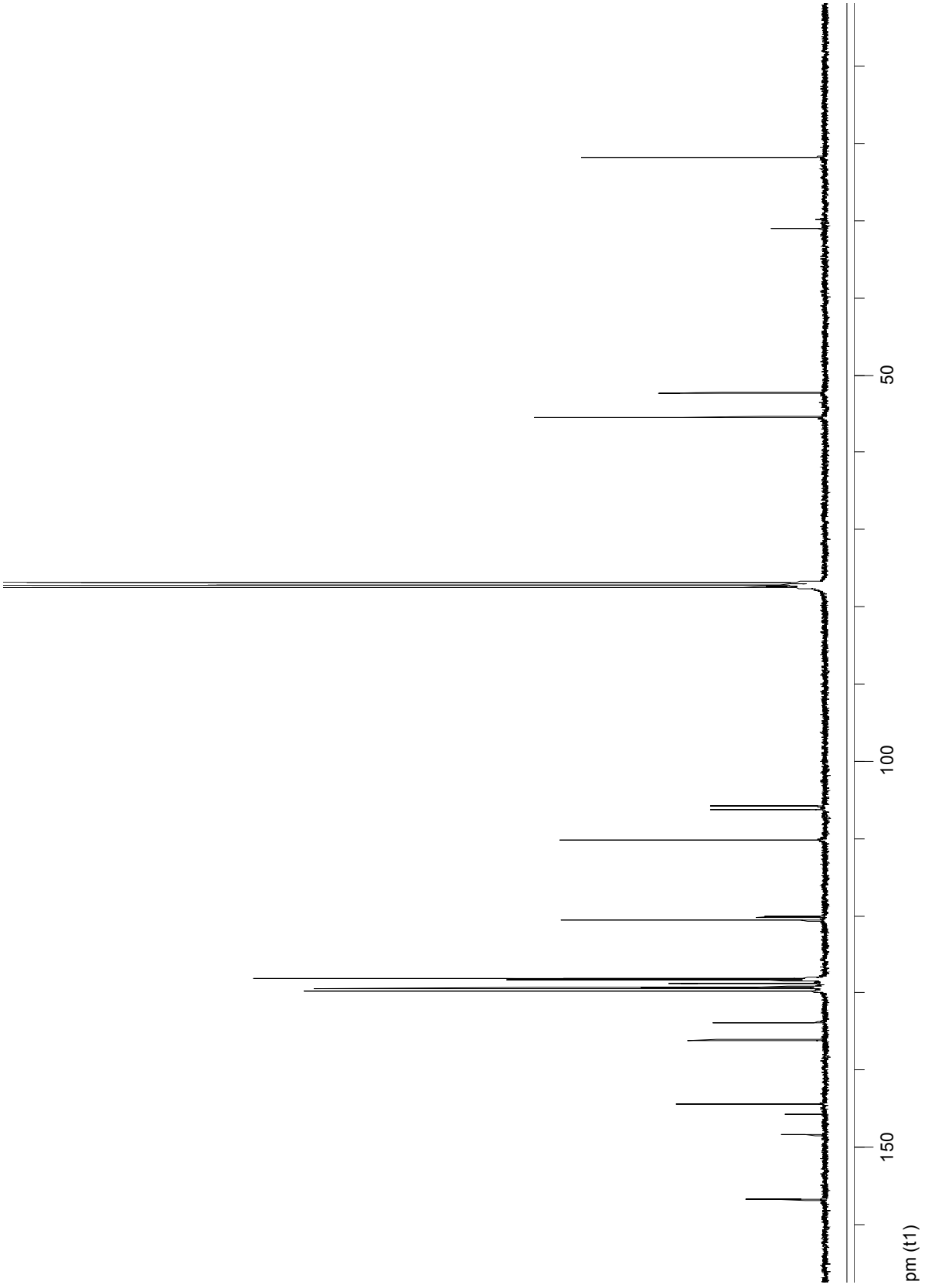
Compound 2e:


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S
O
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F
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2.97
2.02
2.04
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ppm (t1)

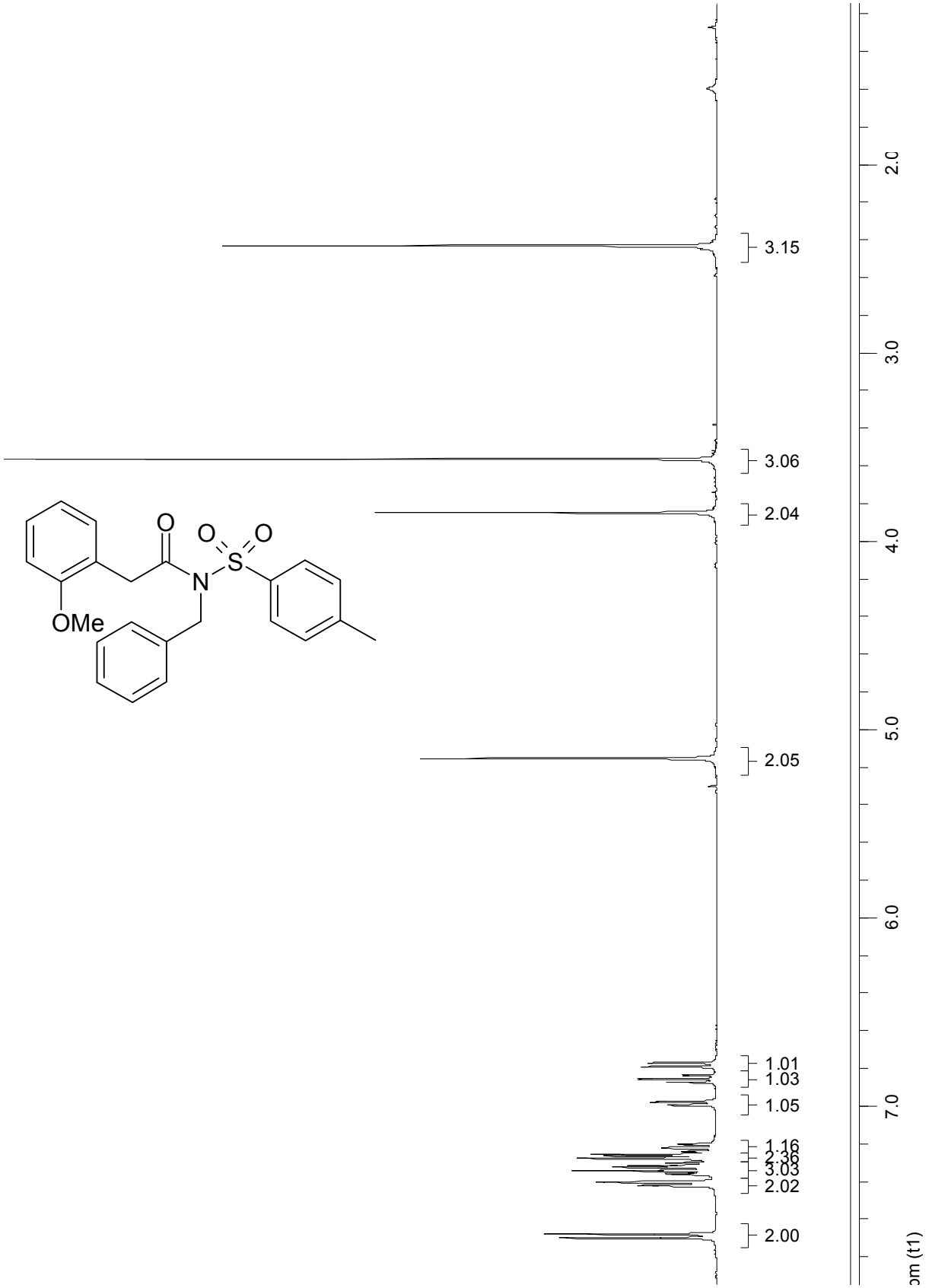

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ppm (t1)

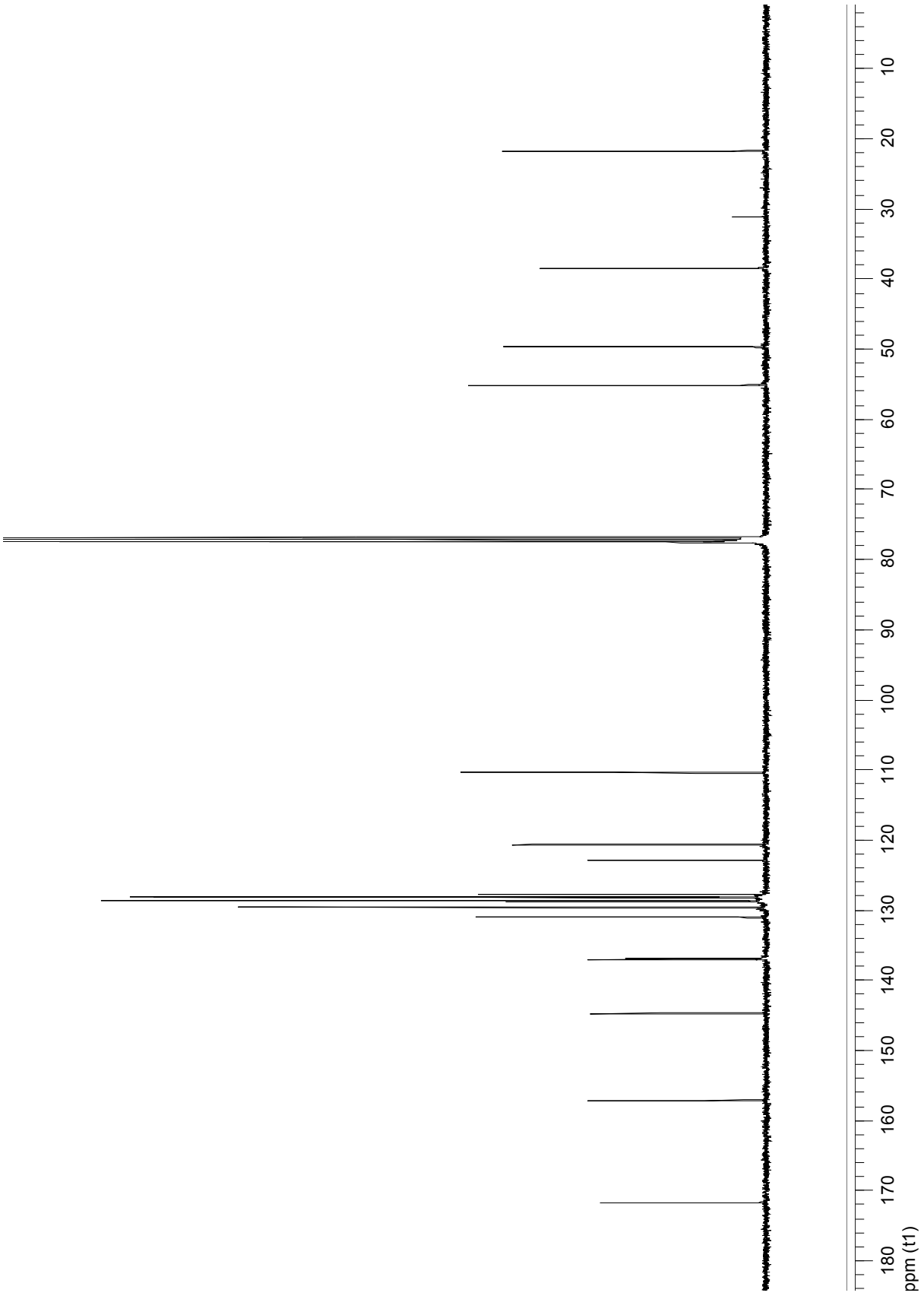
Compound 2f:


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H
F
N
S
O
O
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3.03
2.01
1.00
1.04
1.08
2.06
2.06
1.08
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pm (t1)

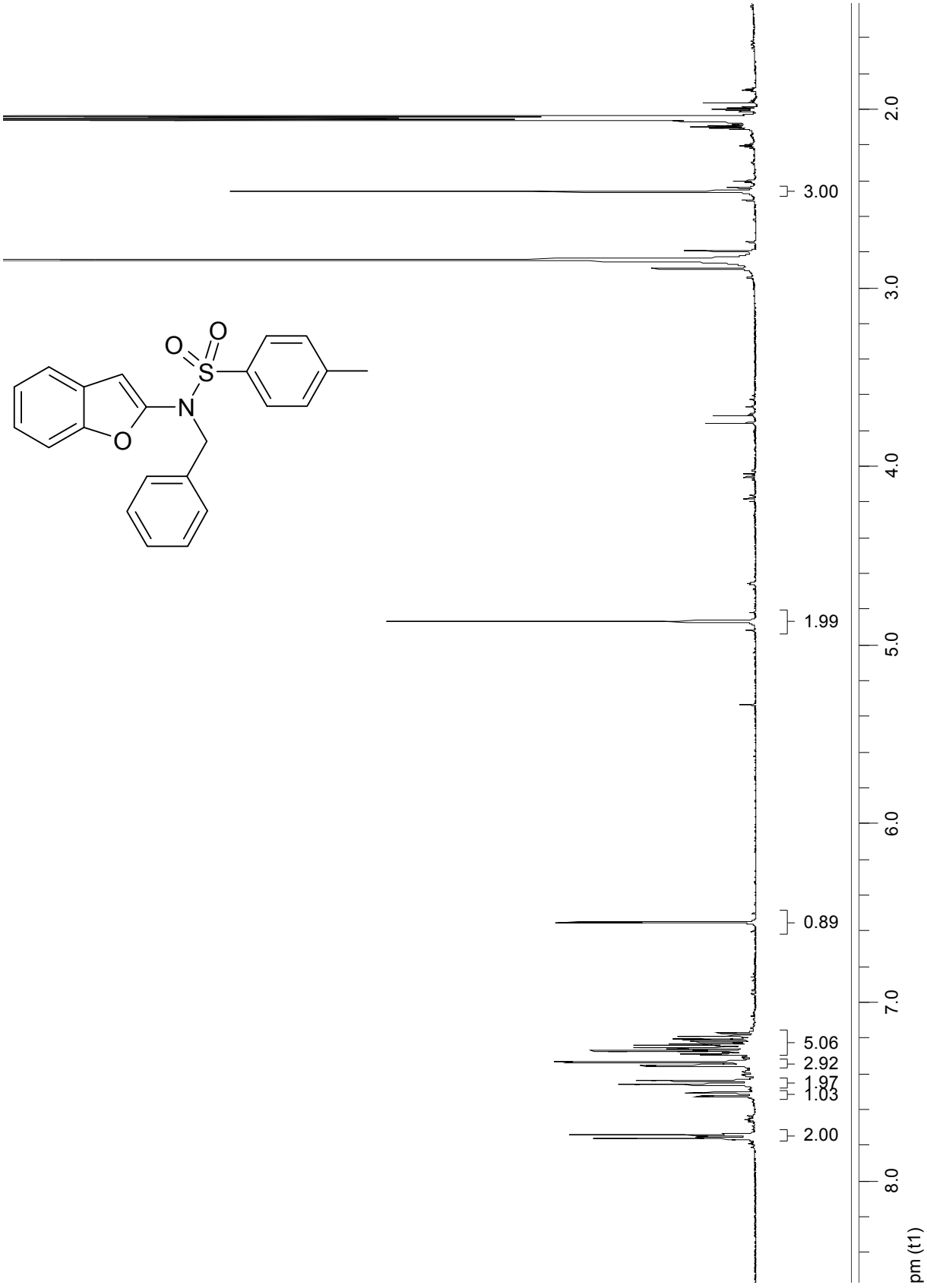

50
100
150
pm (t1)

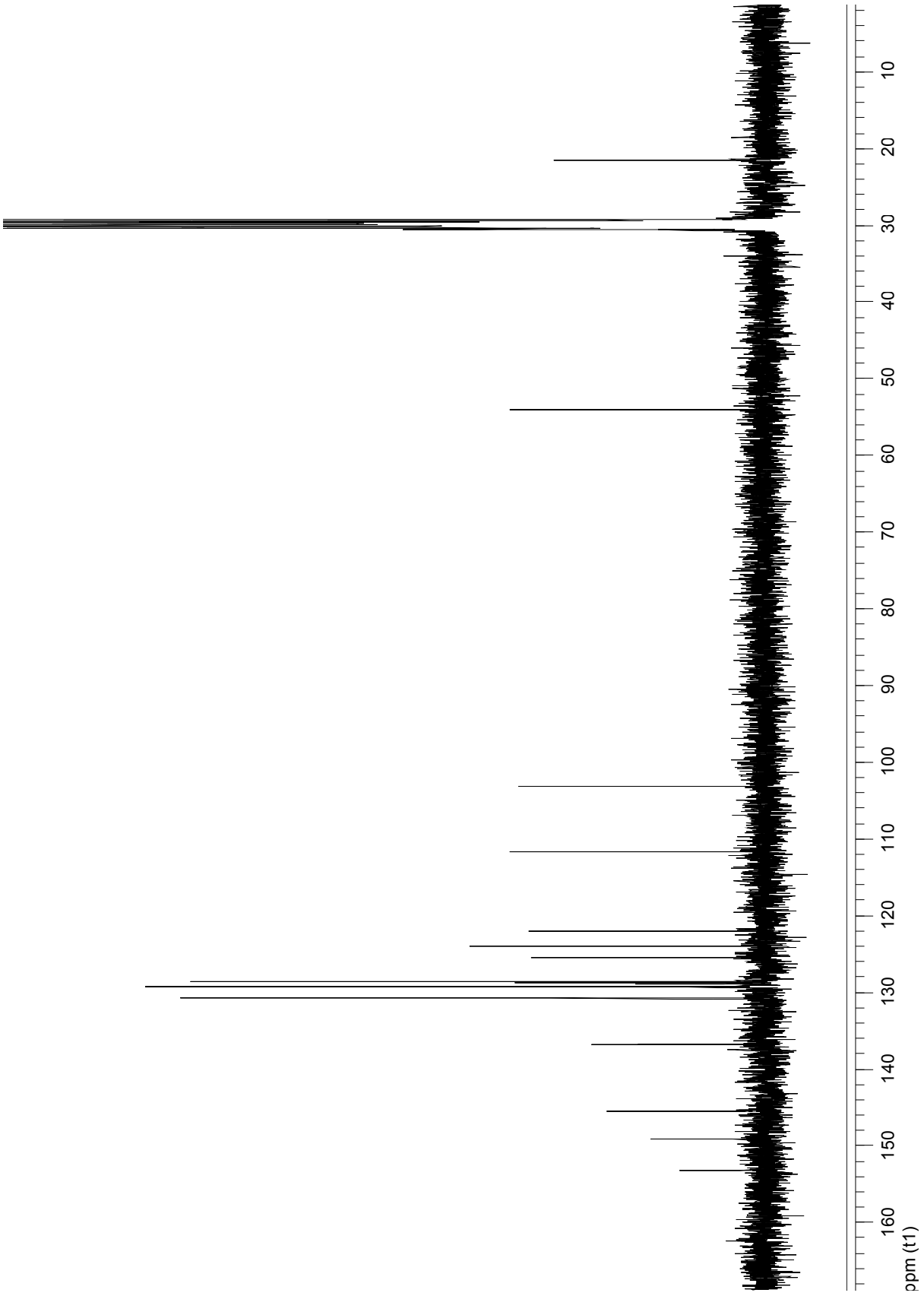
Compound 3f:


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O
S
N
OMe
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2.04
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7.0
om (t1)

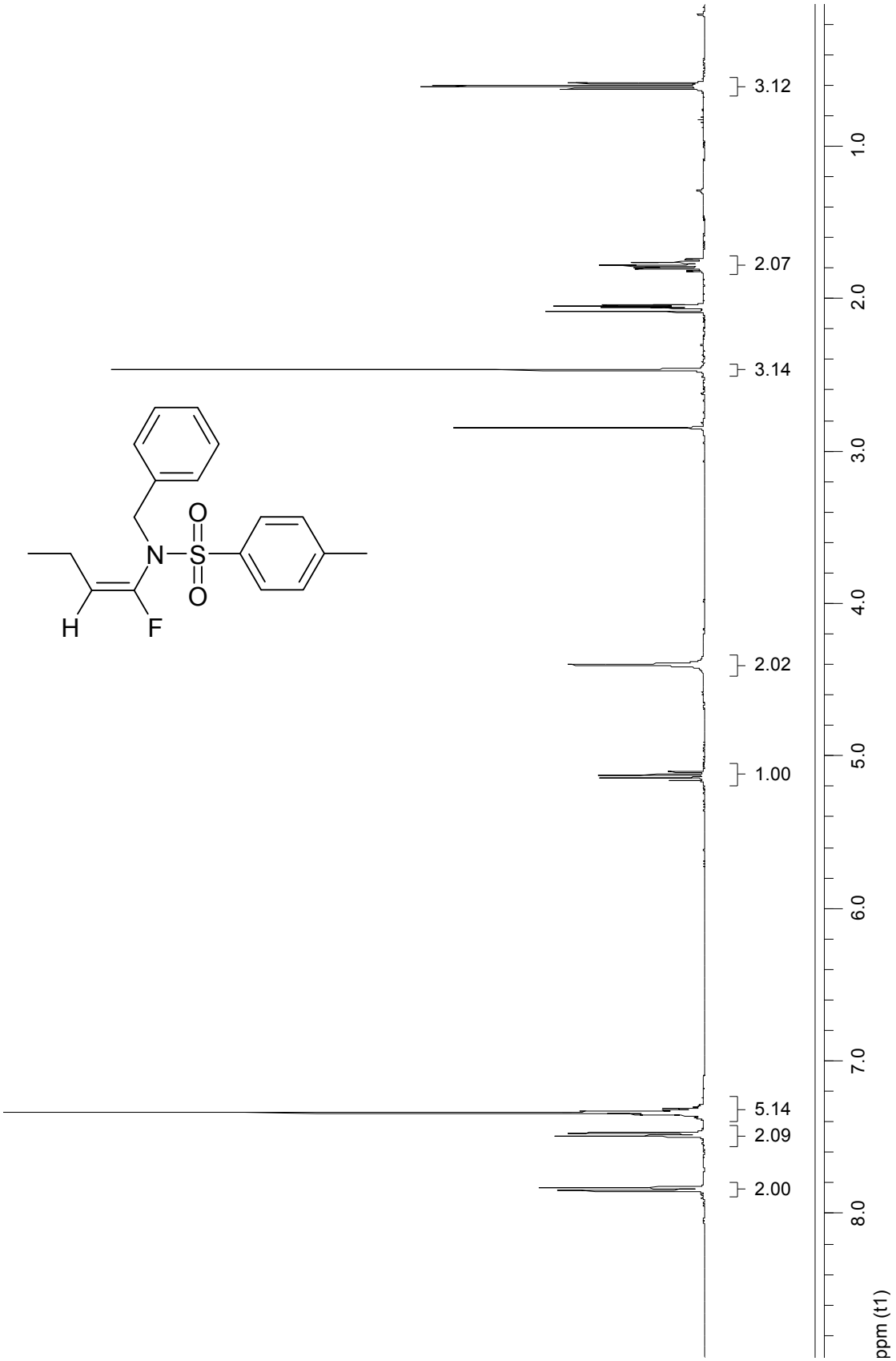

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ppm (t1)

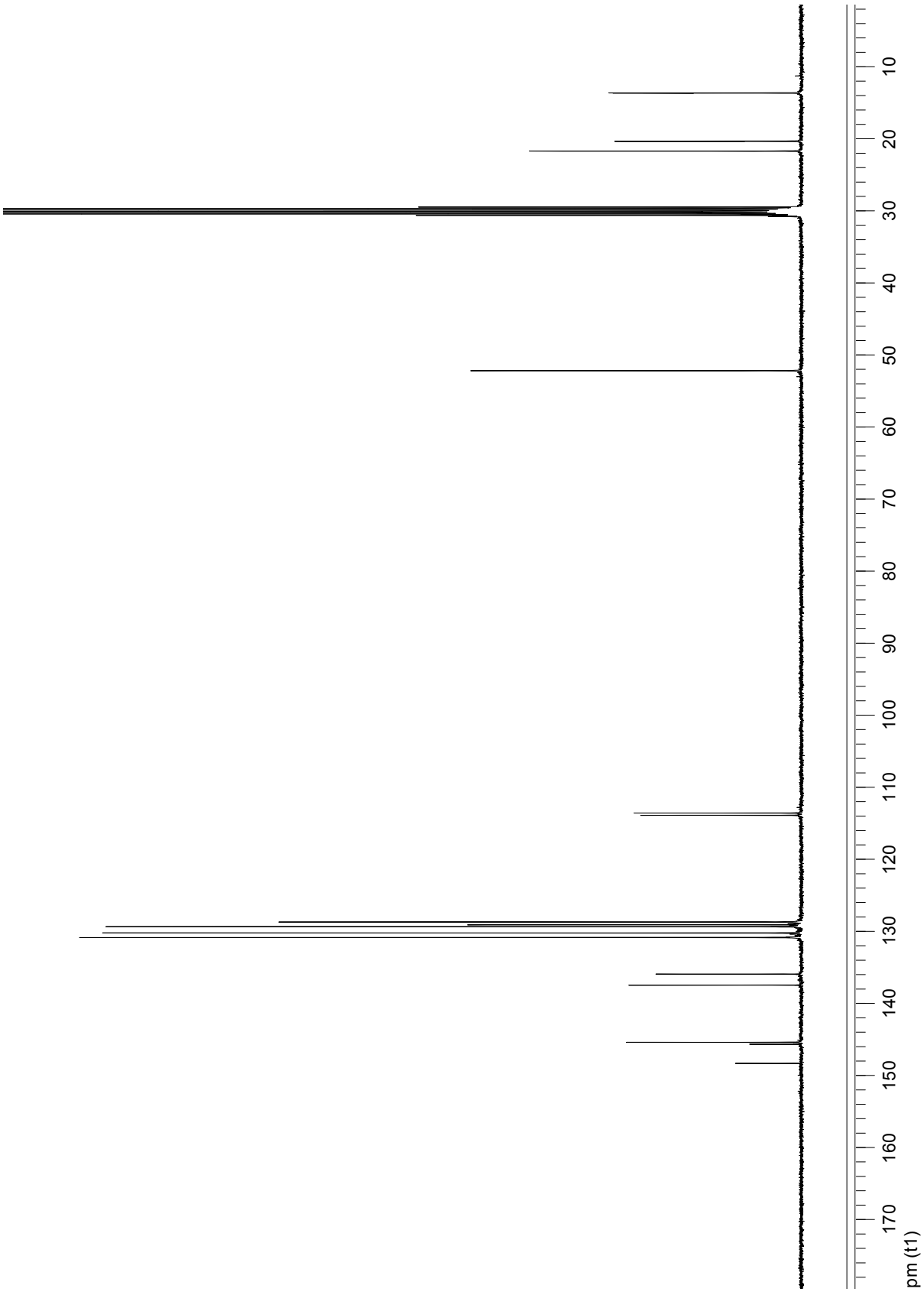
Compound 4:



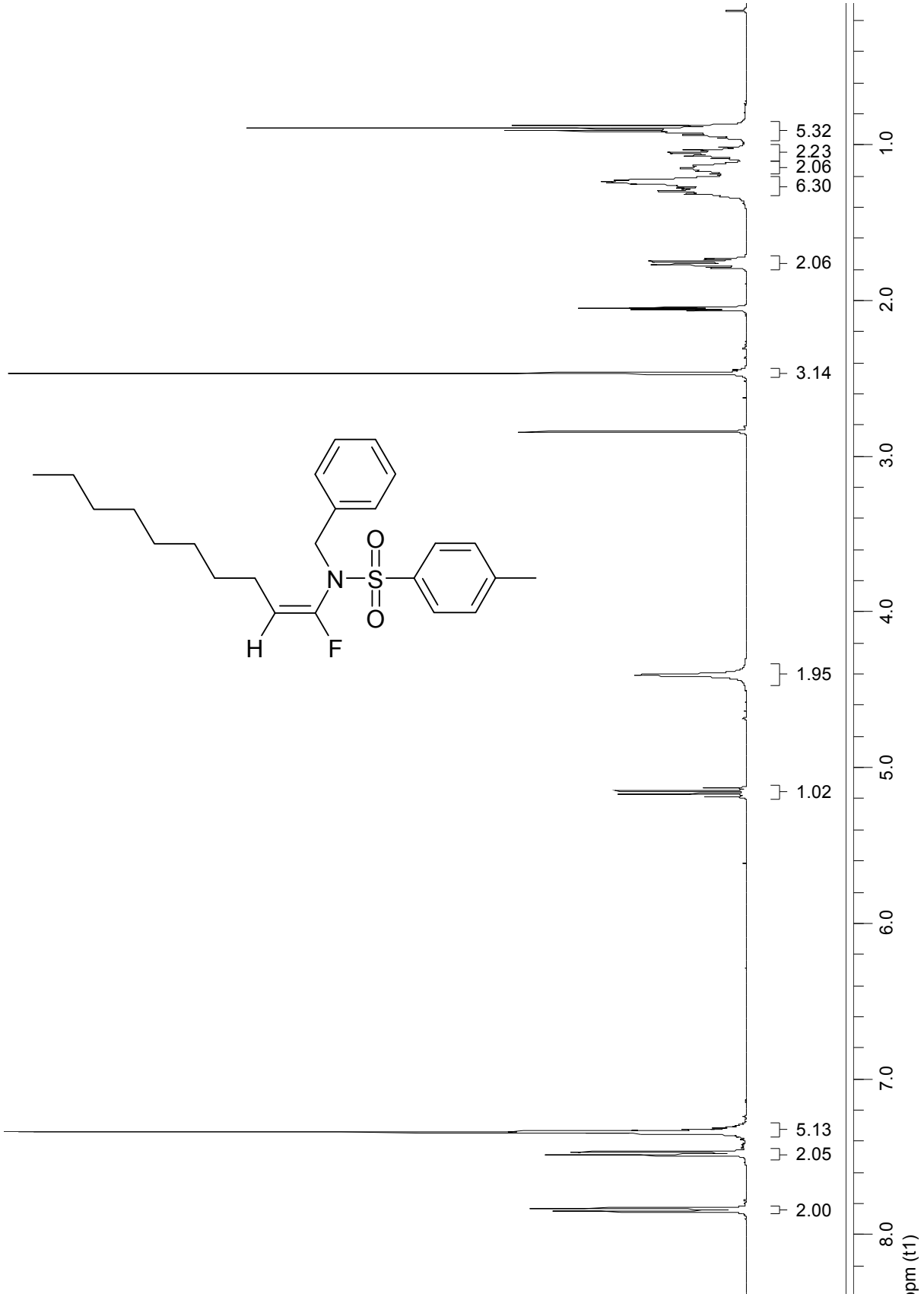

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120
130
140
150
160
ppm (t1)

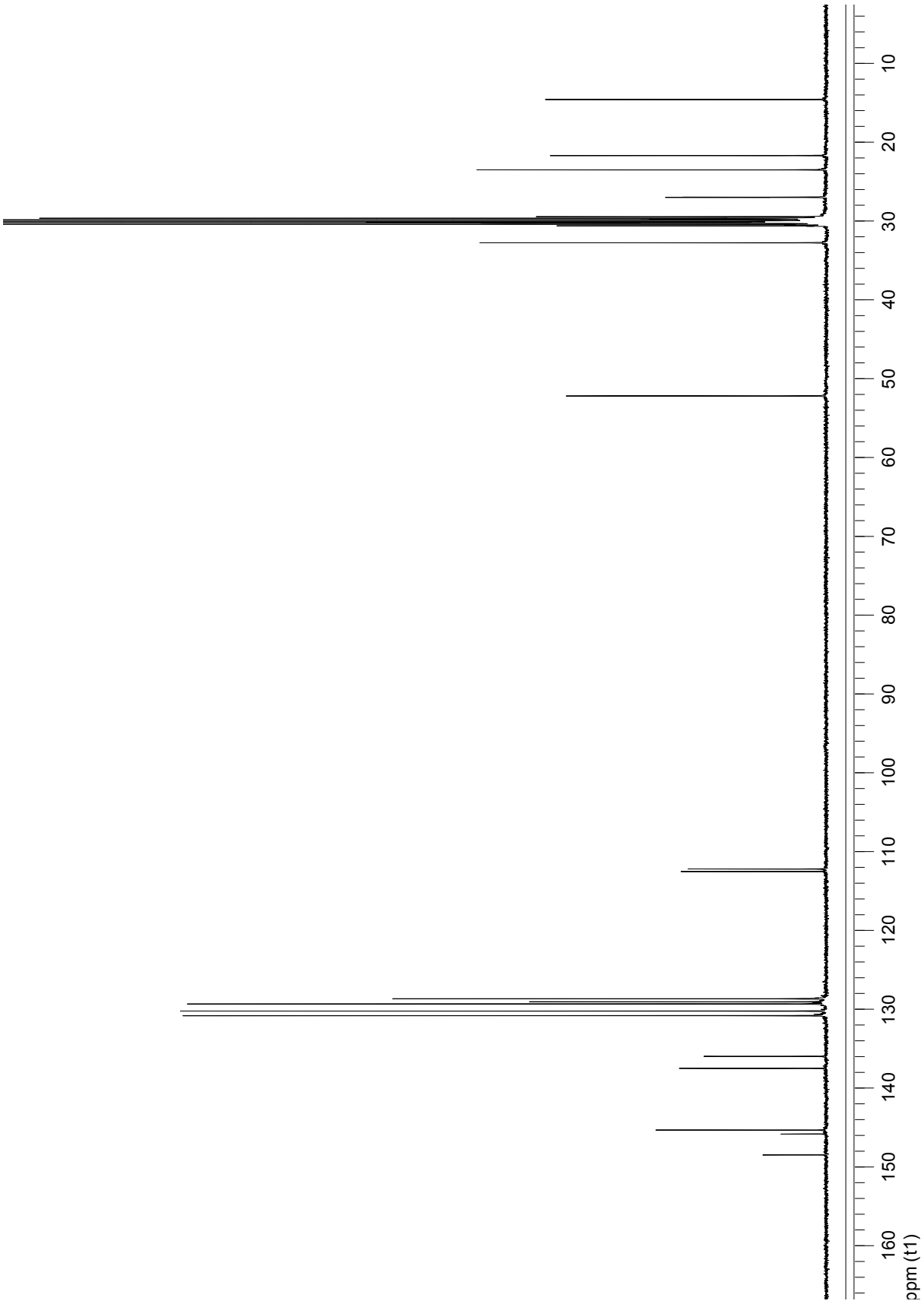
Compound 2g:


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2.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)
O
N
S
O
H
F

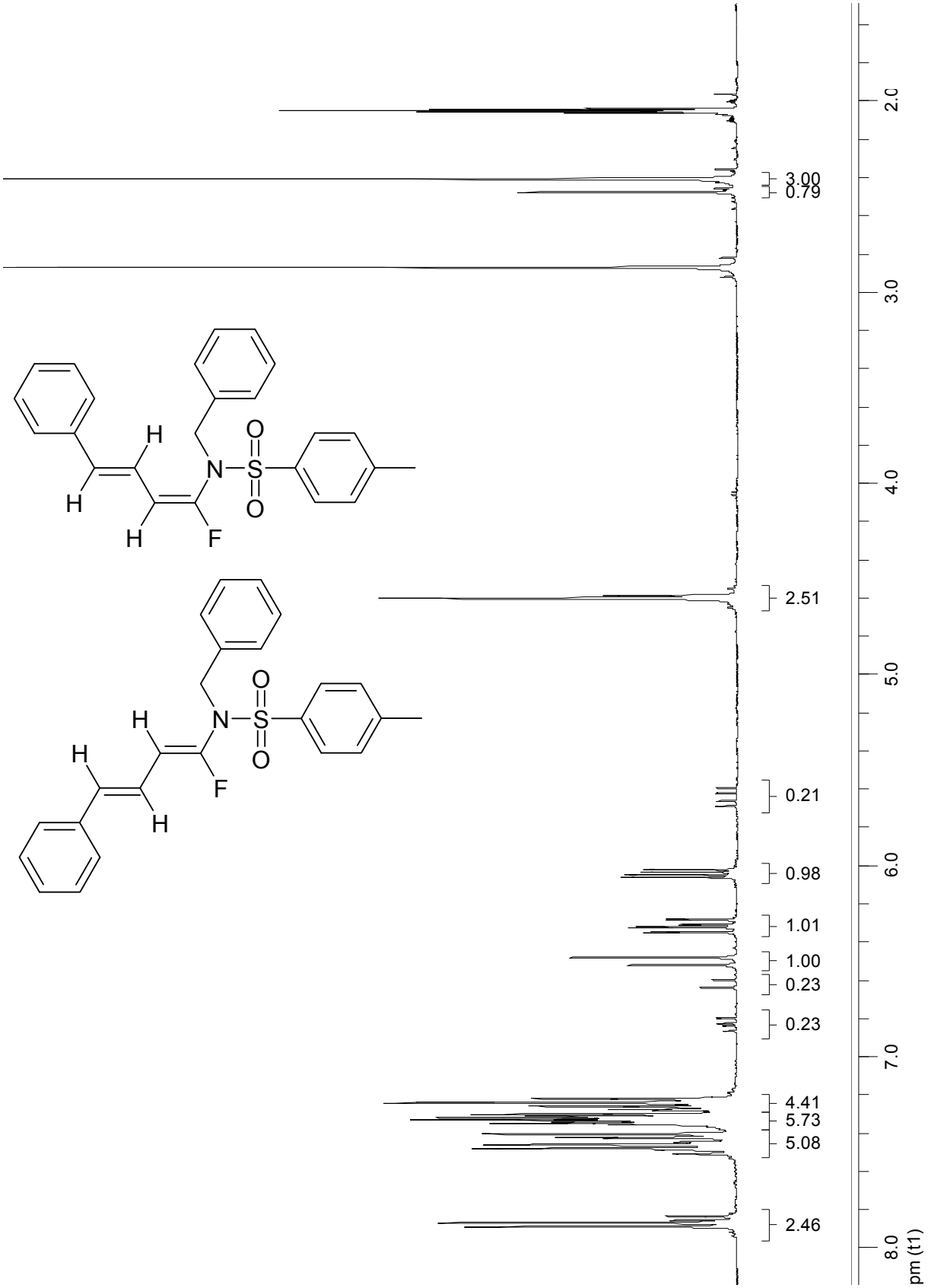

10
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100
110
120
130
140
150
160
170
pm (t1)

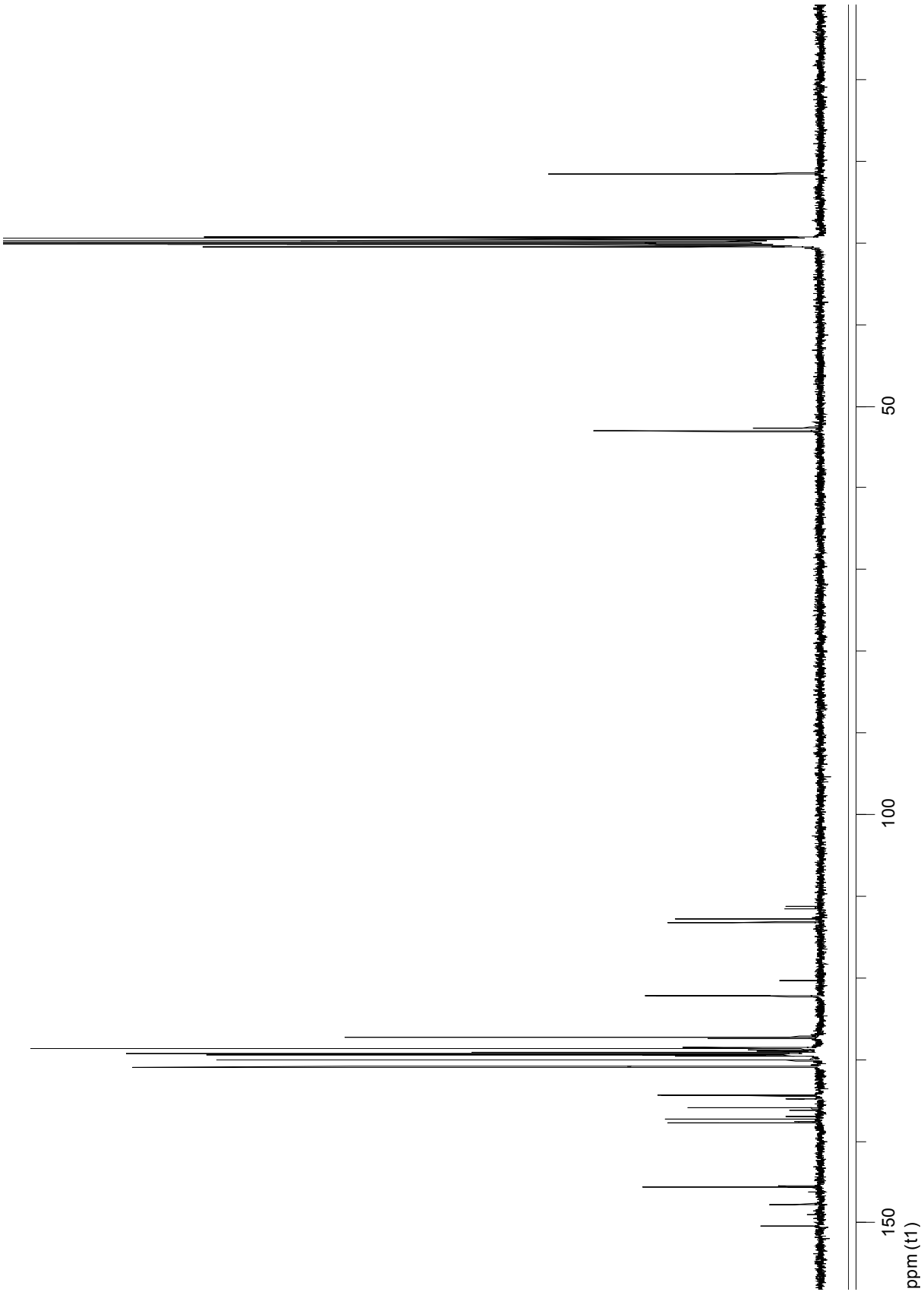
Compound 2h:


5.32
2.23
2.06
6.30
2.06
3.14
1.95
1.02
5.13
2.05
2.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)
N
S
O
O
H
F

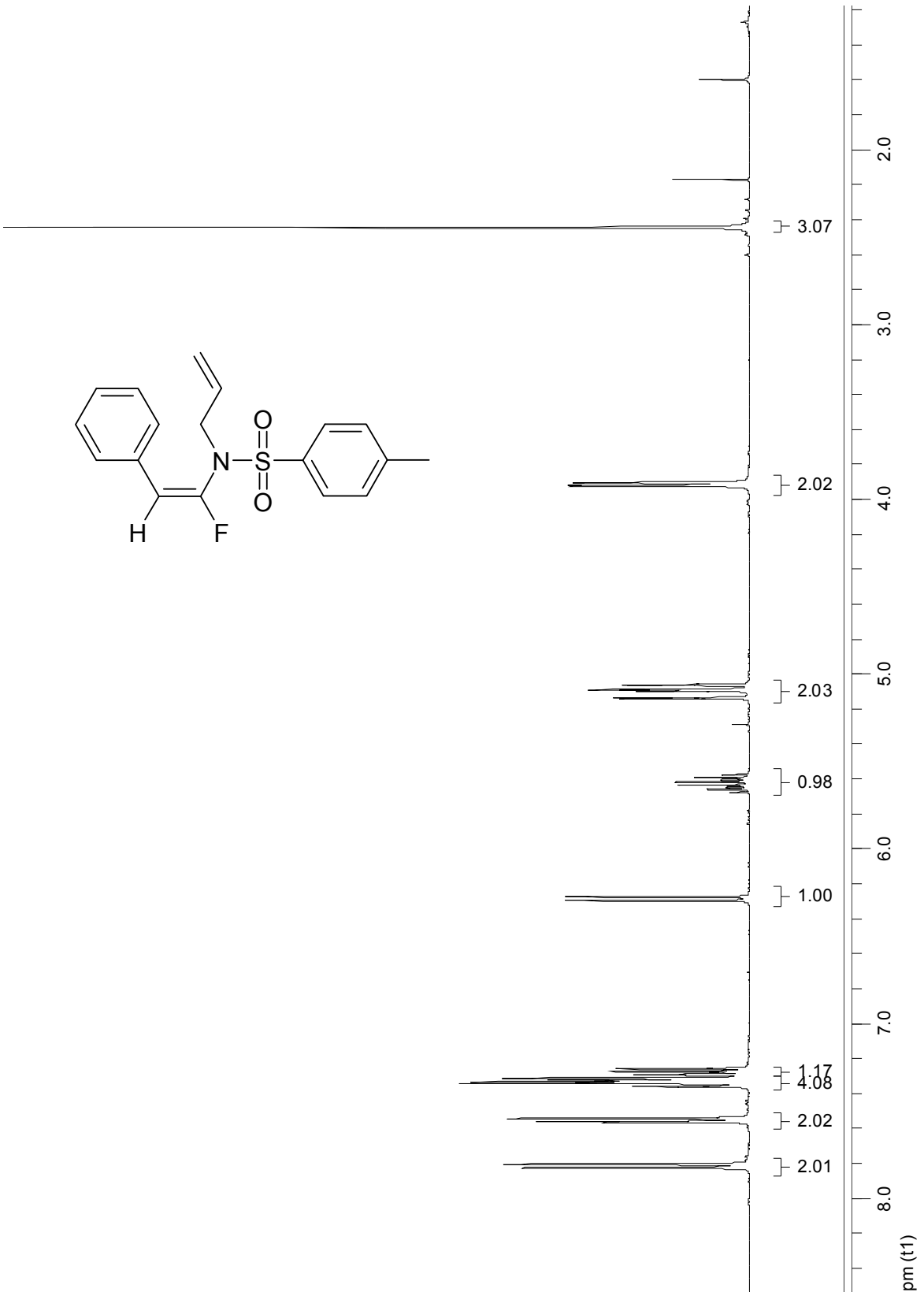

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50
60
70
80
90
100
110
120
130
140
150
160
ppm (t1)

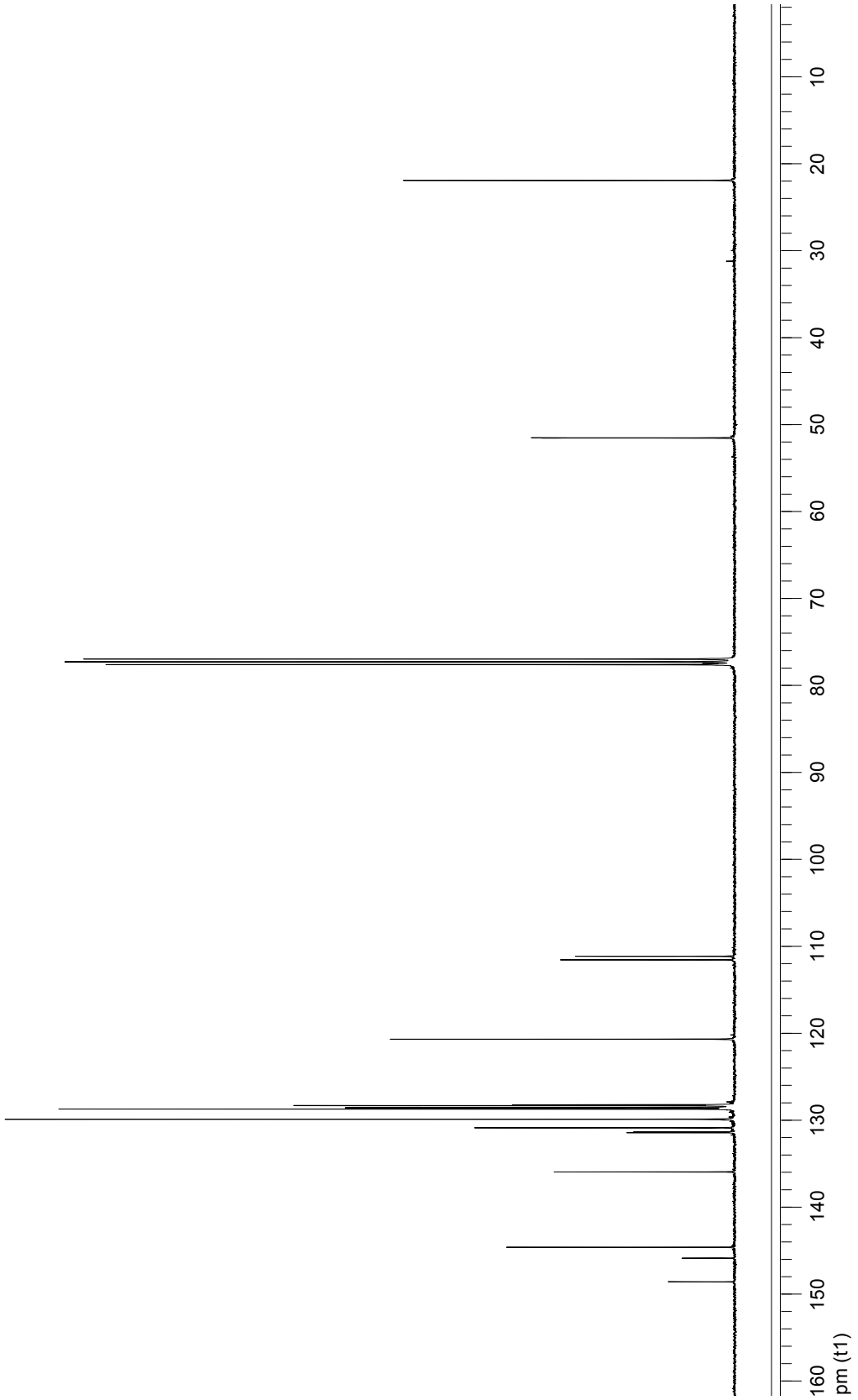
Compound 2i:


3.00
0.79
2.51
0.21
0.98
1.01
1.00
0.23
0.23
4.41
5.73
5.08
2.46
2.0
3.0
4.0
5.0
6.0
7.0
8.0
pm (t1)

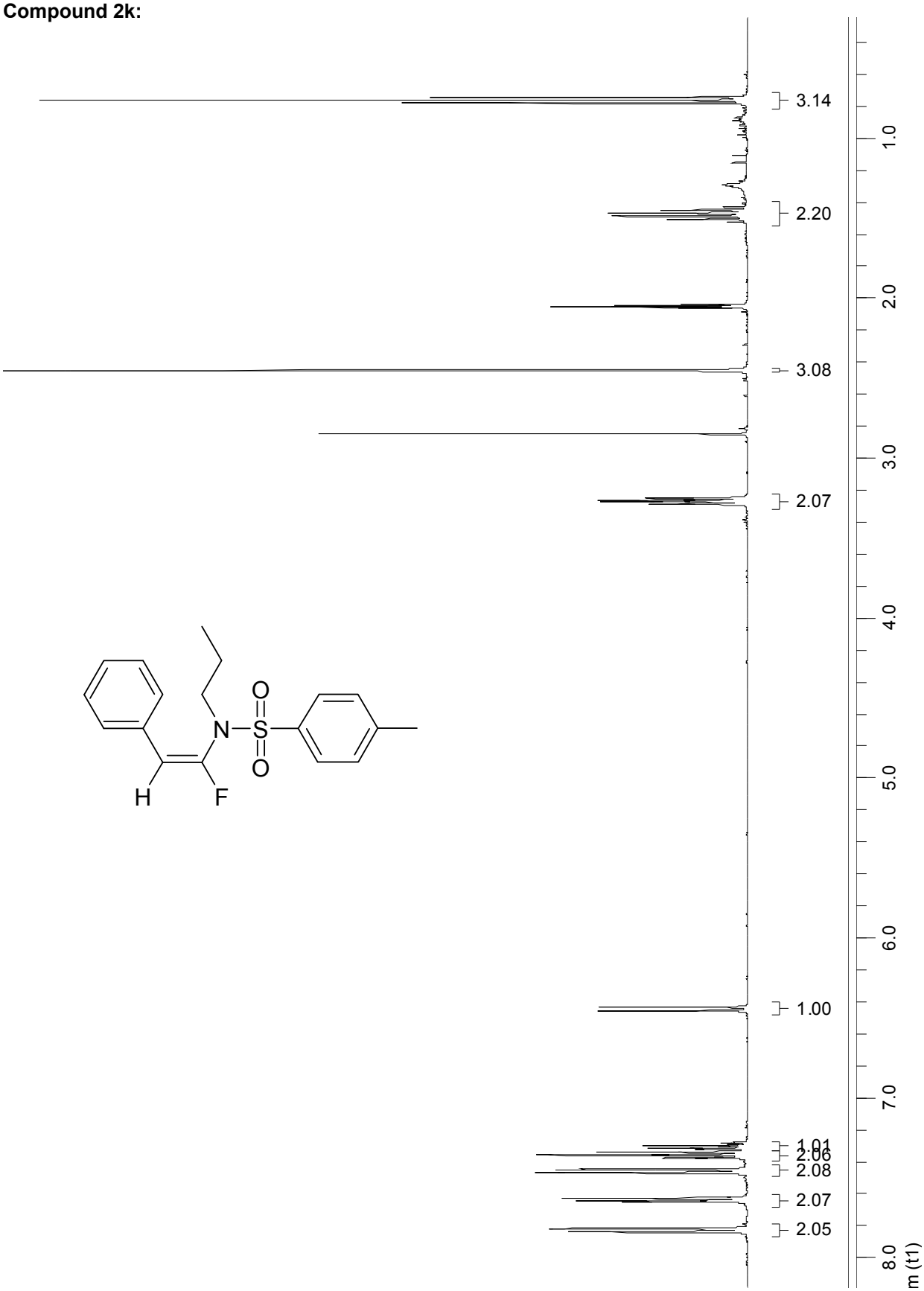

50
100
150
ppm (t1)

Comound 2j:

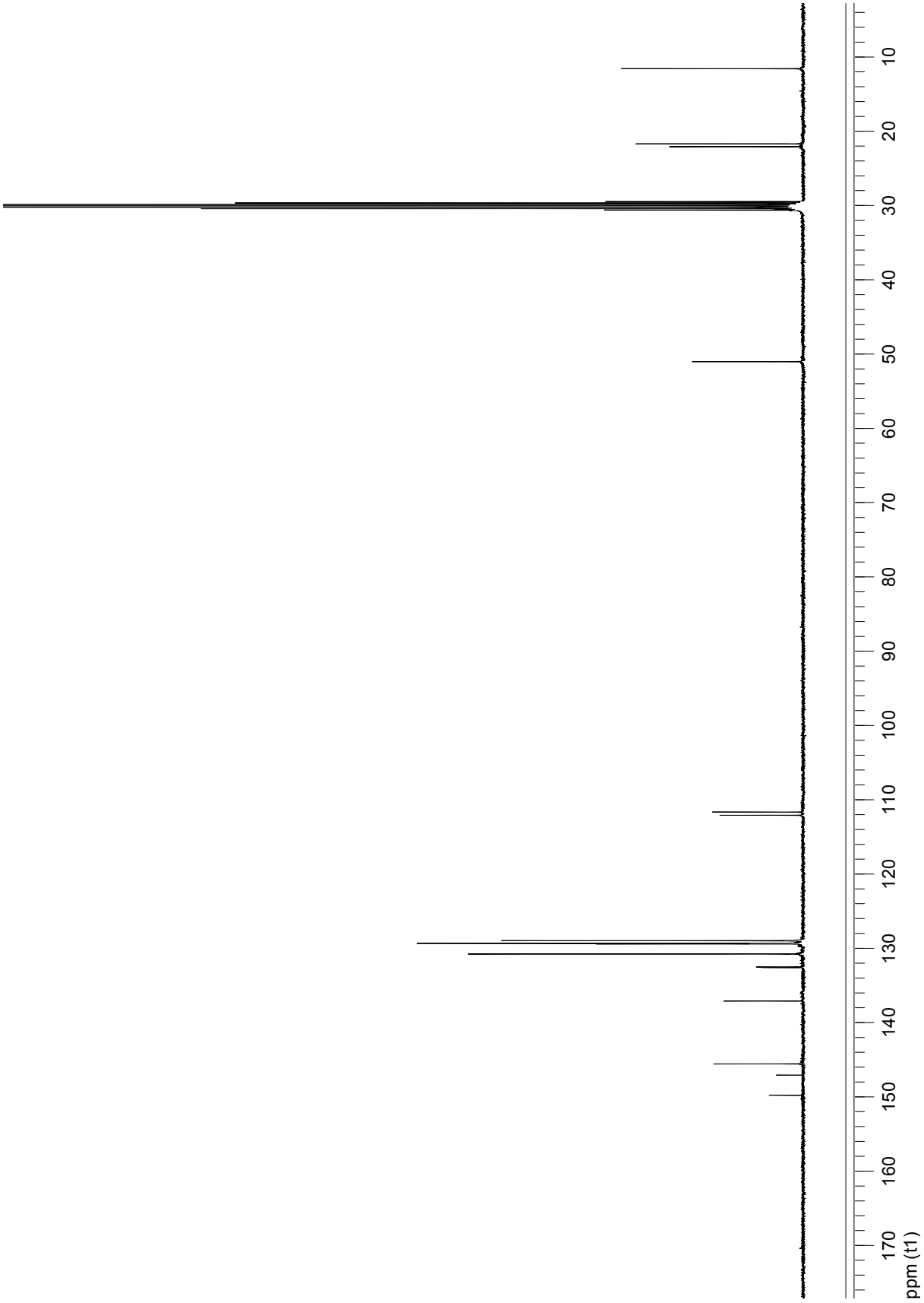

O
N
S
O
H
F
3.07
2.02
2.03
0.98
1.00
1.17
4.08
2.02
2.01
2.0
3.0
4.0
5.0
6.0
7.0
8.0
pm (t1)


10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
pm (t1)

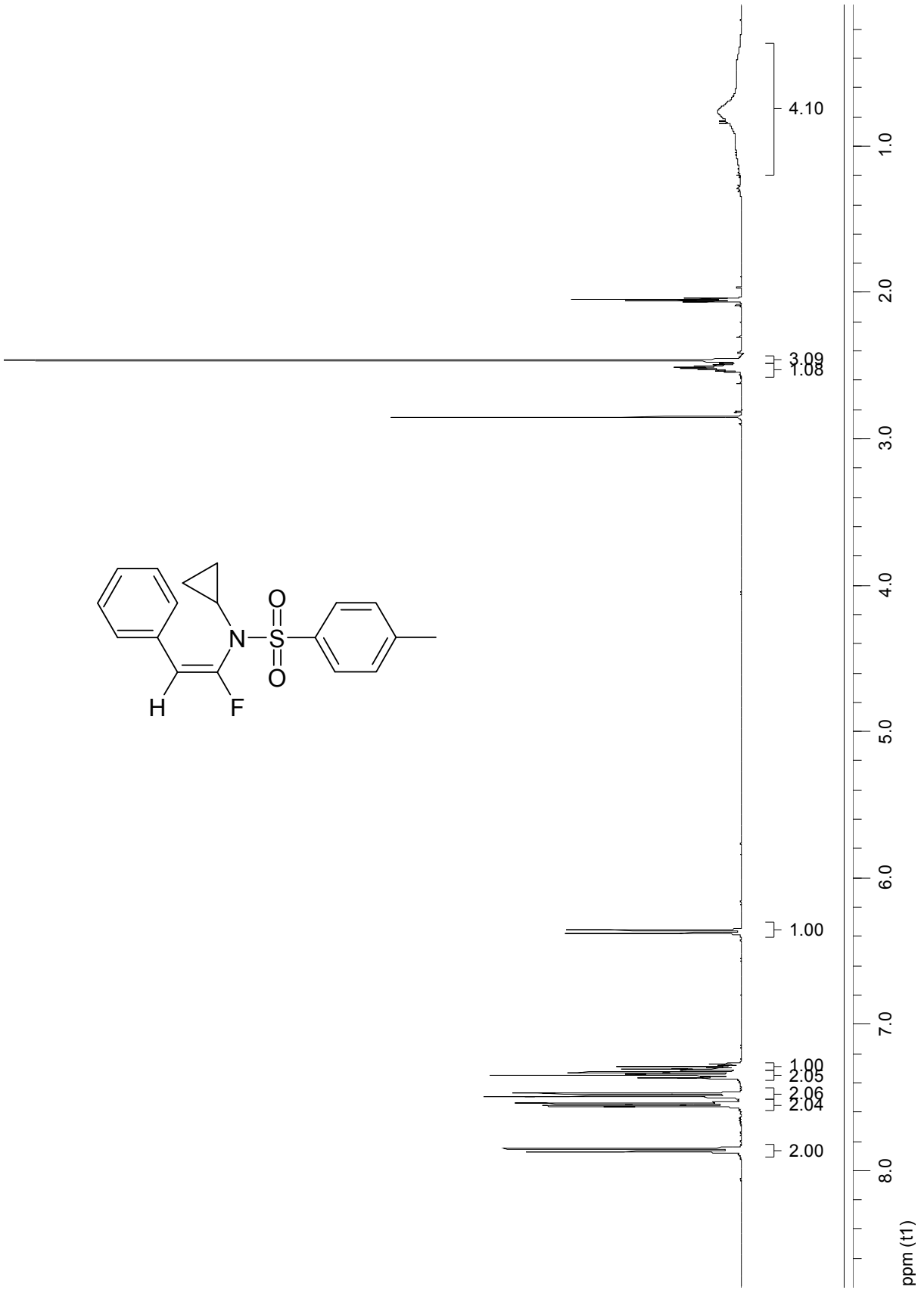
Compound 2k:

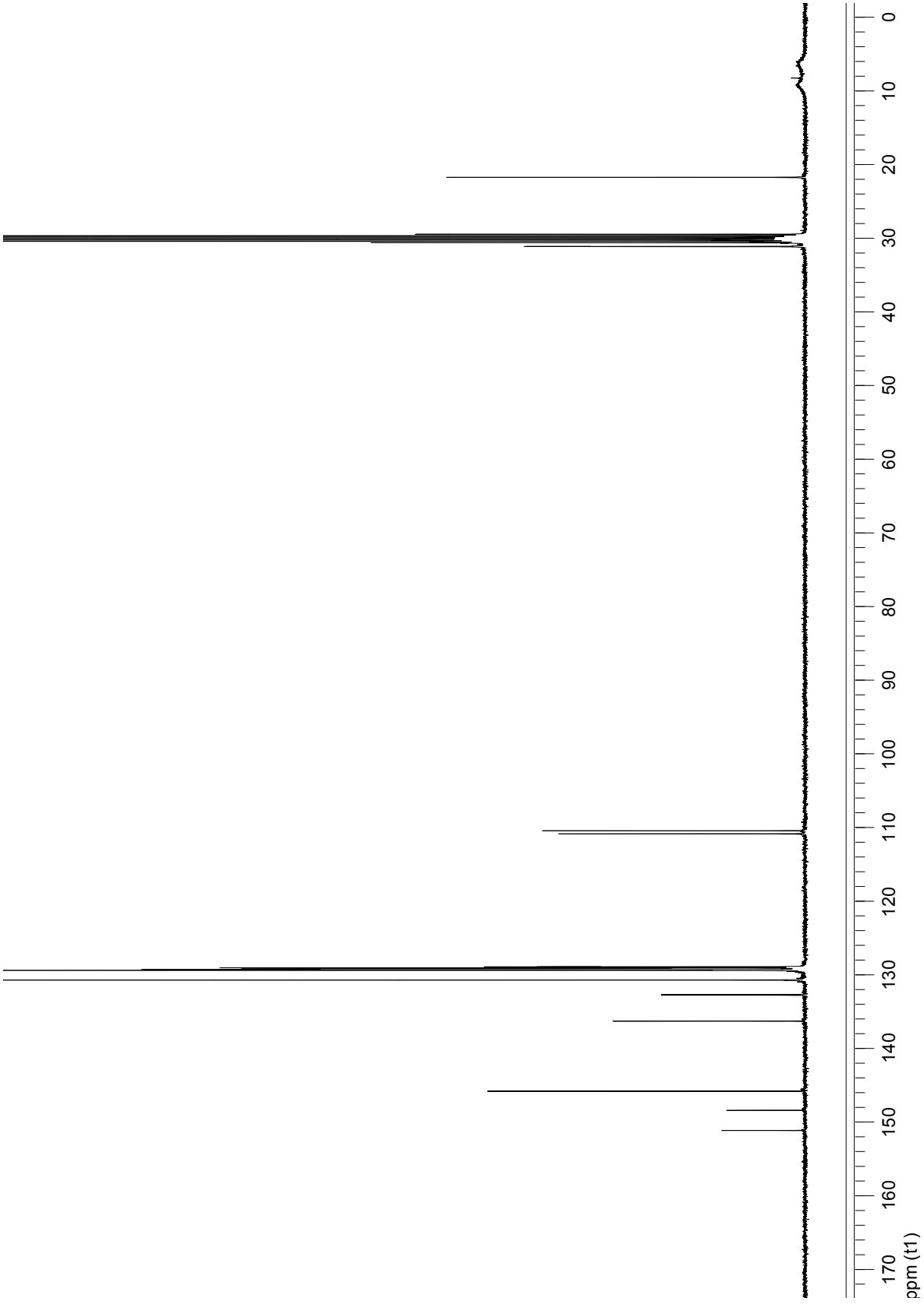

3.14
2.20
3.08
2.07
1.00
1.01
2.06
2.08
2.07
2.05
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
m (t1)
O
N
S
O
H
F

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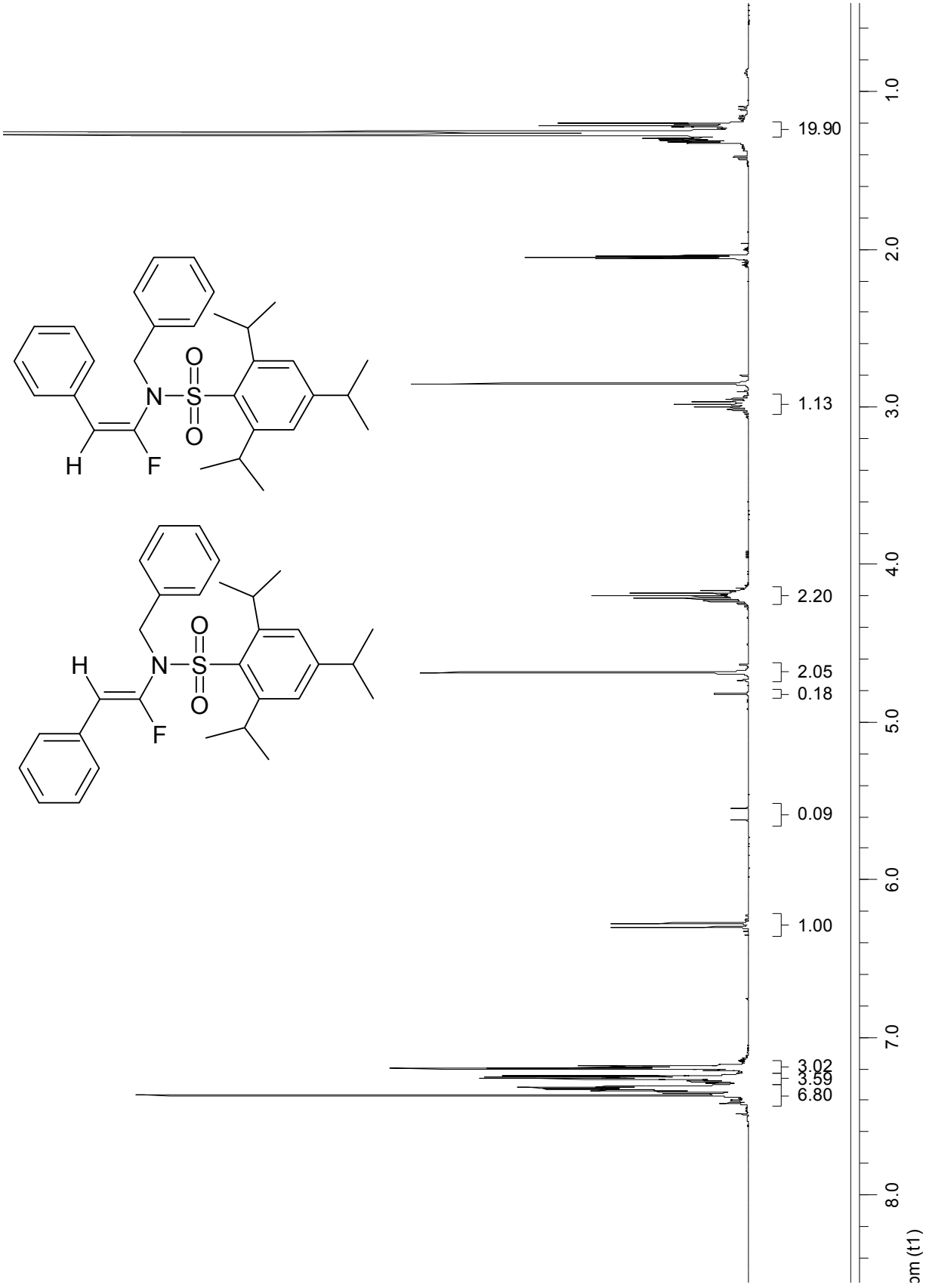


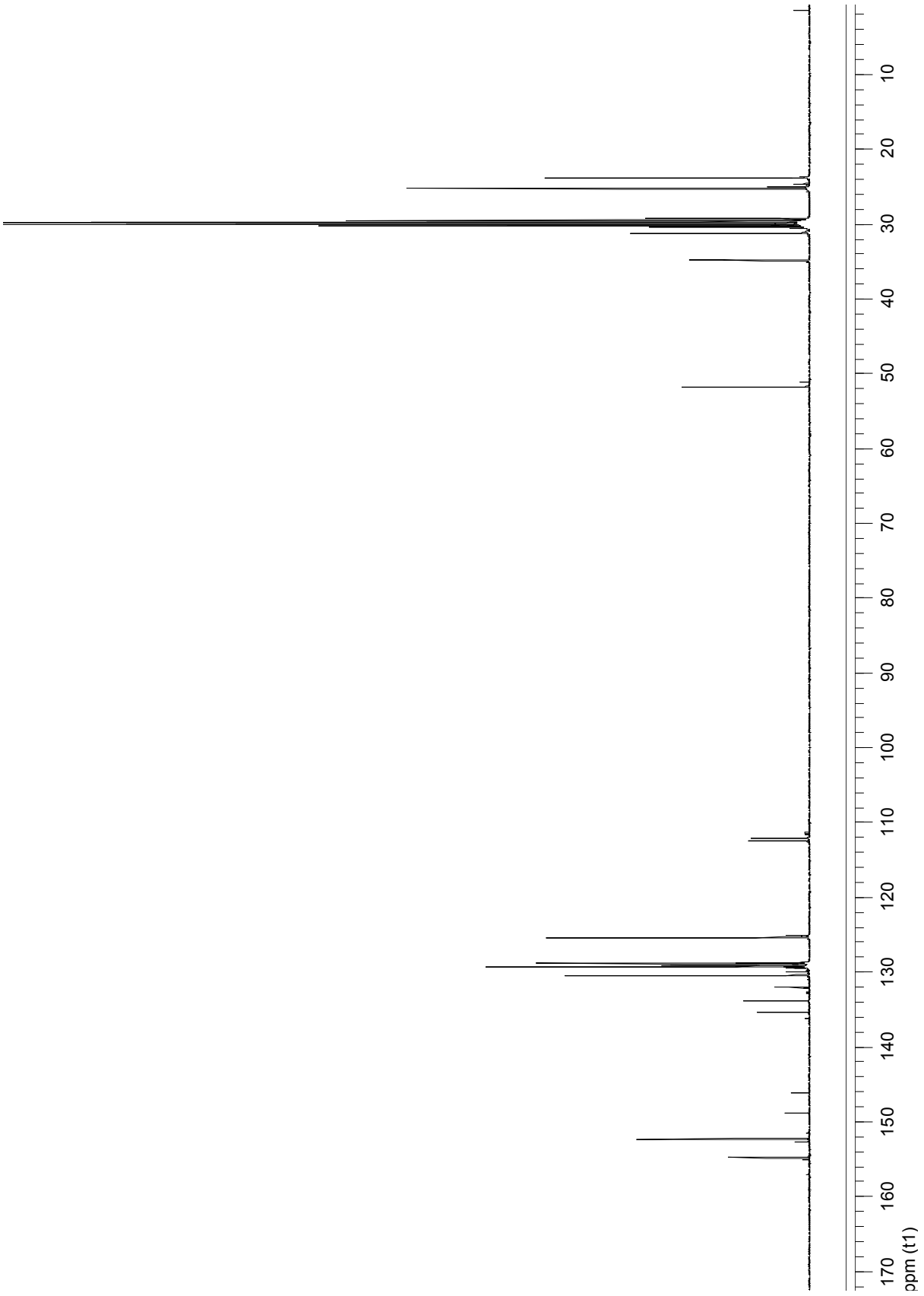
Compound 2l:


4.10
3.09
1.08
1.00
1.00
2.05
2.06
2.04
2.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)
O
N
S
O
H
F

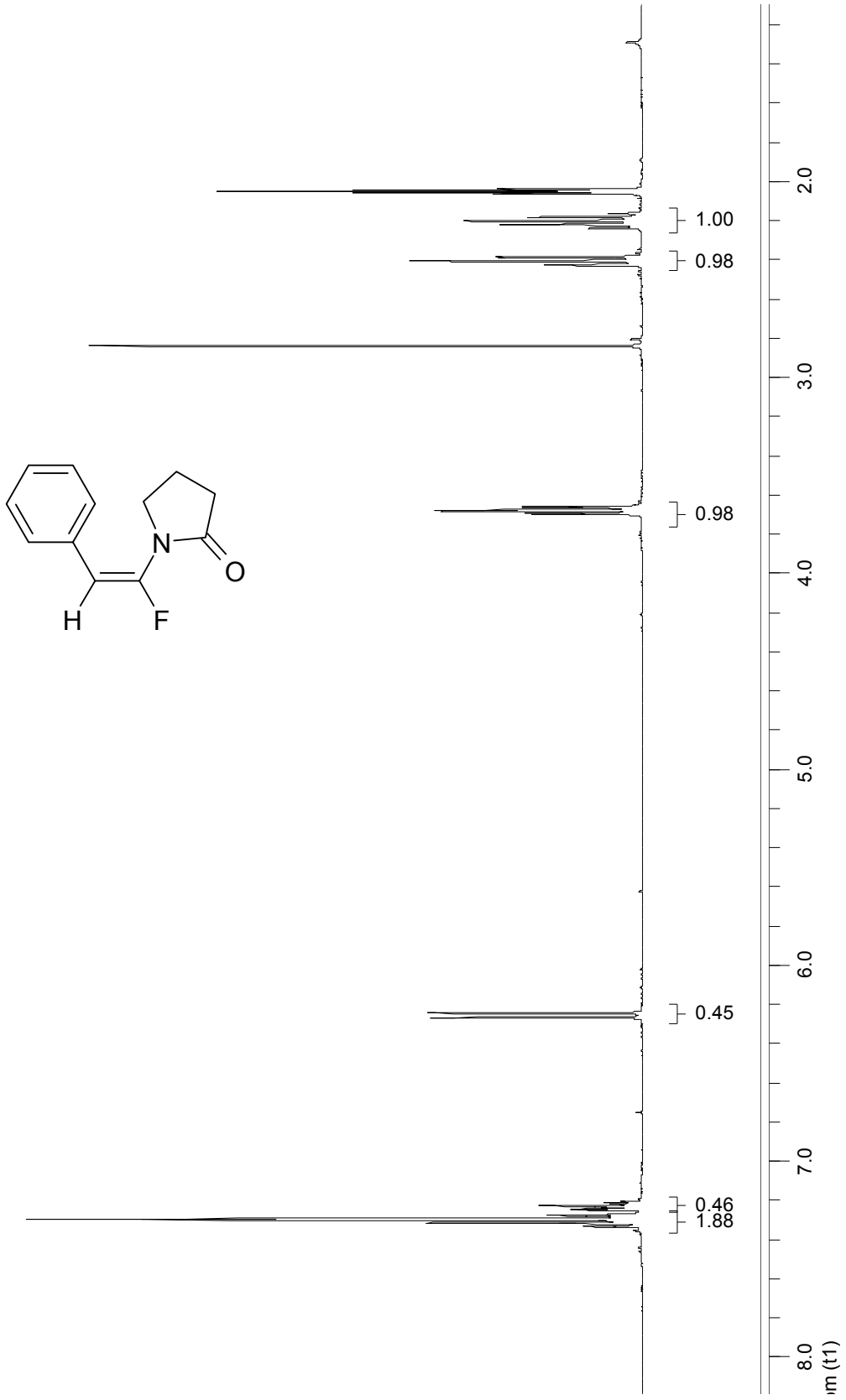

0
10
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40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm (t1)

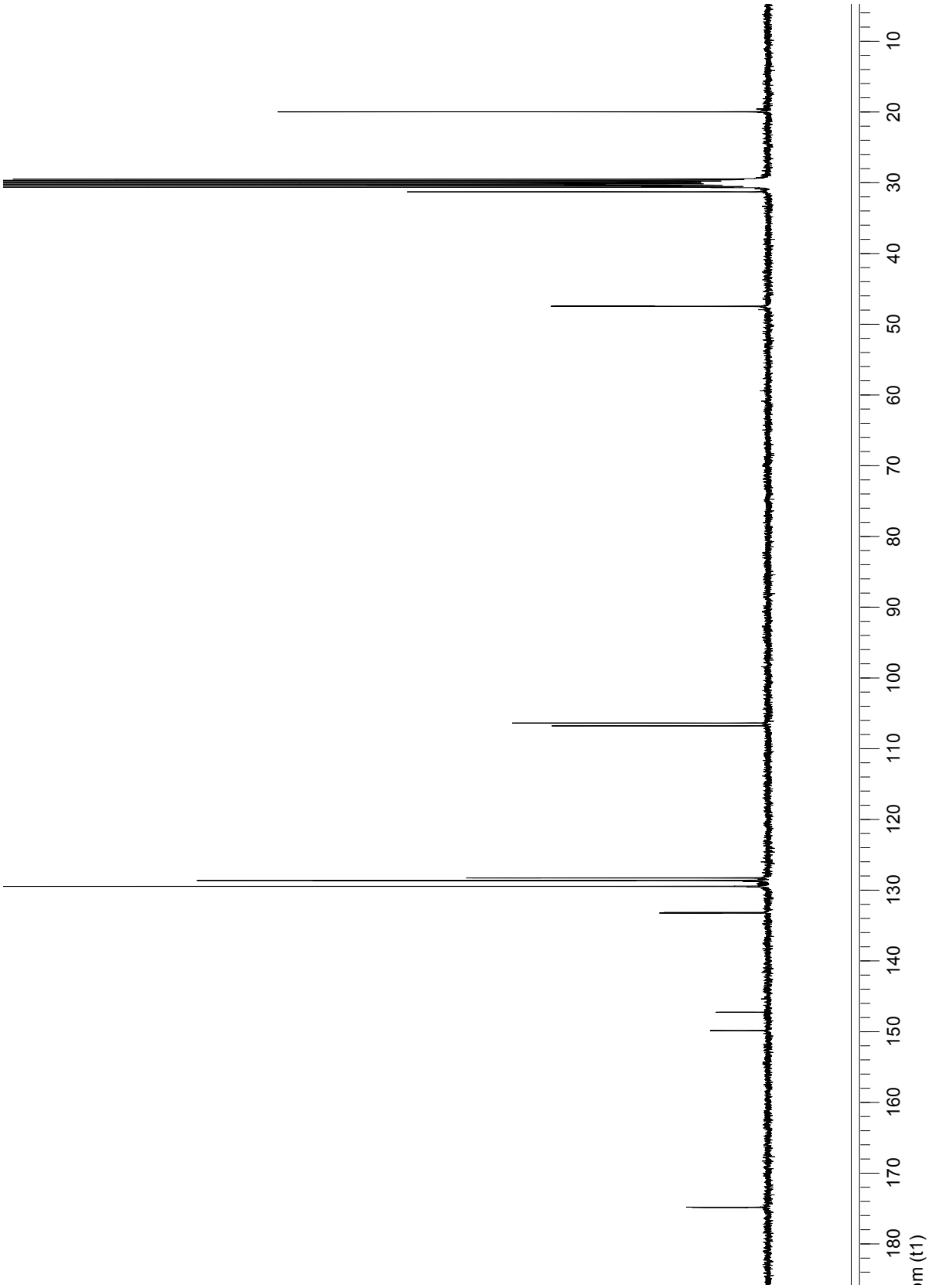
Compound 2m:


19.90
1.13
2.20
2.05
0.18
0.09
1.00
3.02
3.59
6.80
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
H
N
S
O
O
F
H
F

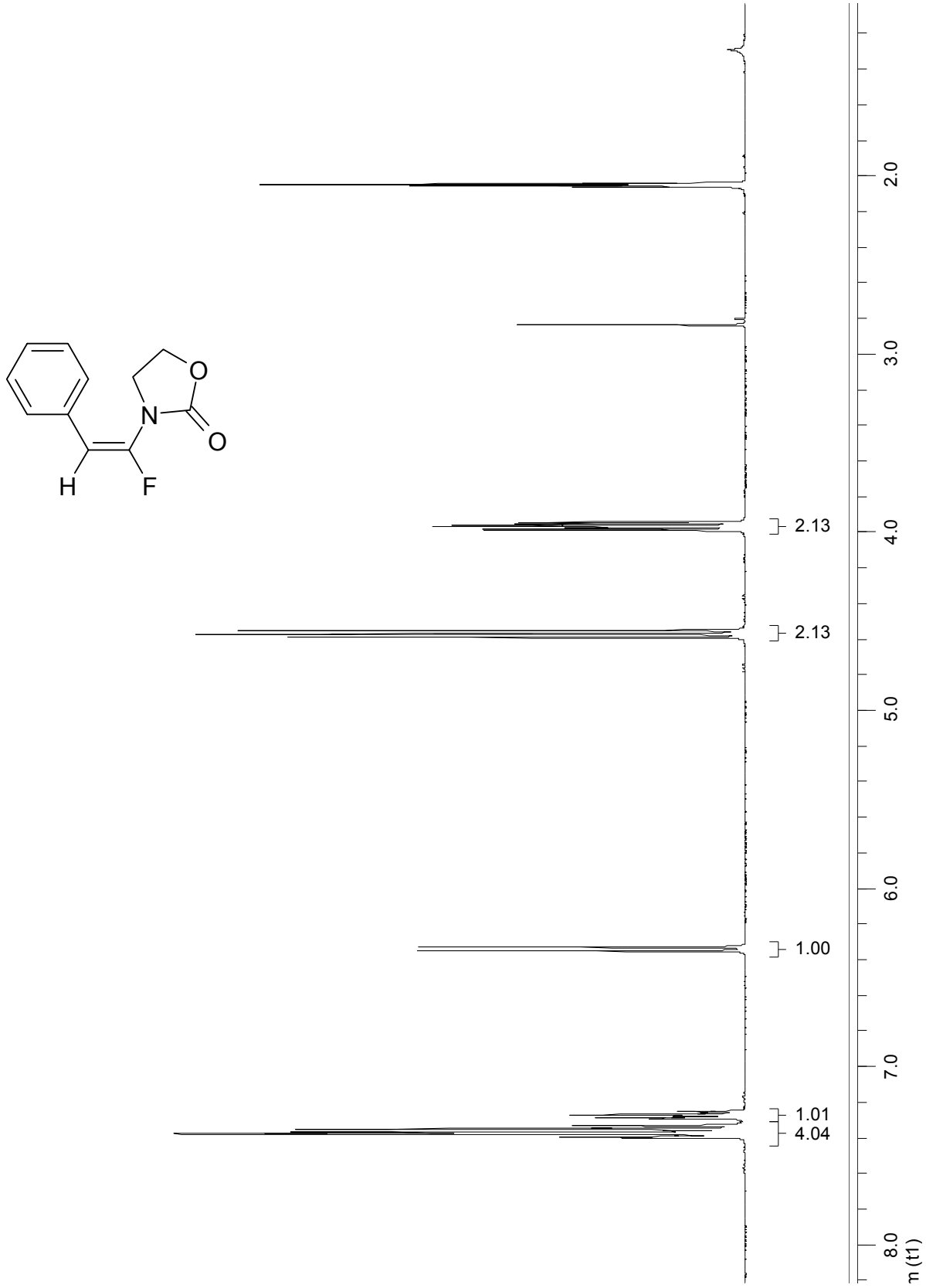

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70
80
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100
110
120
130
140
150
160
170
ppm (t1)

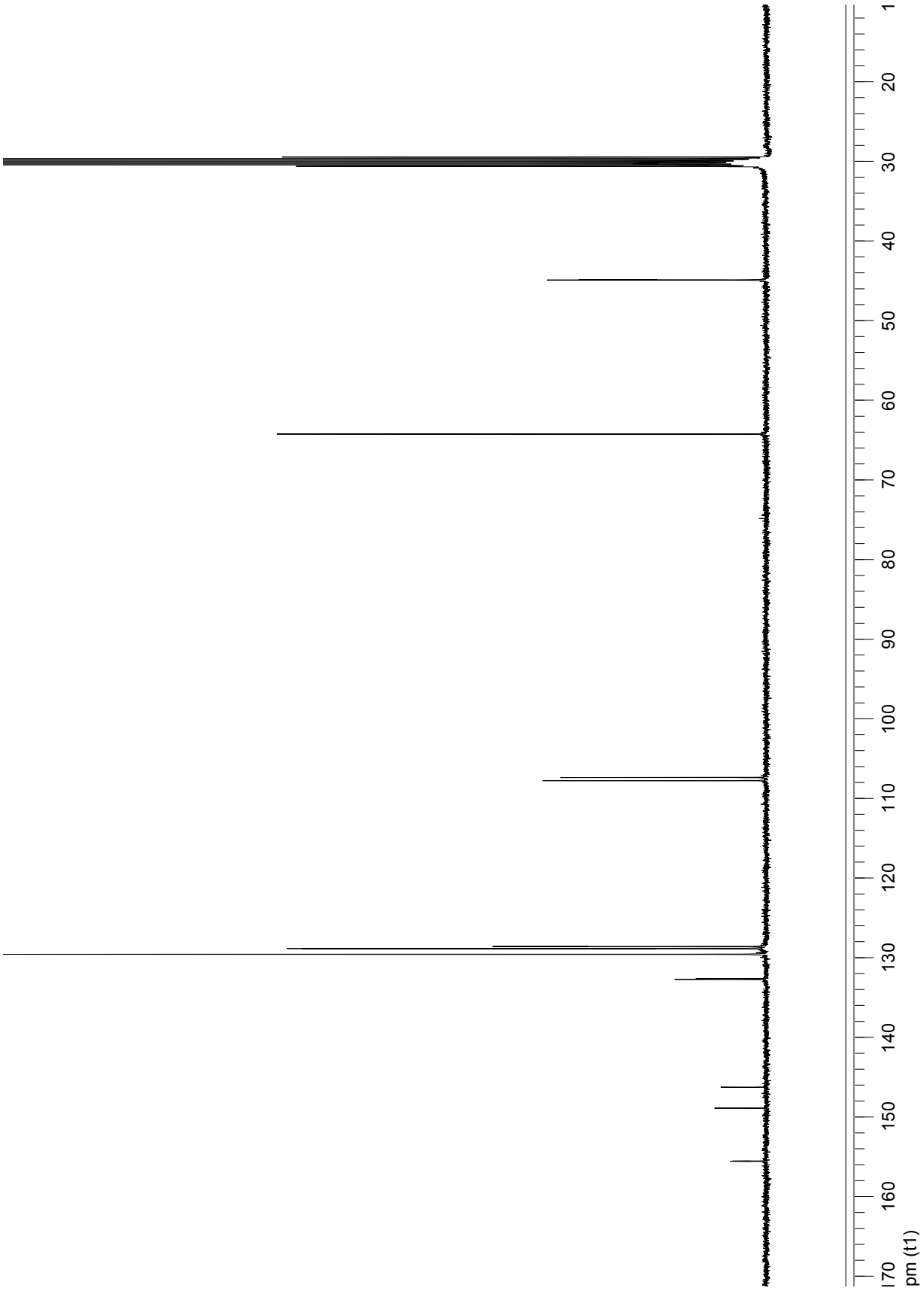
Compound 2n:



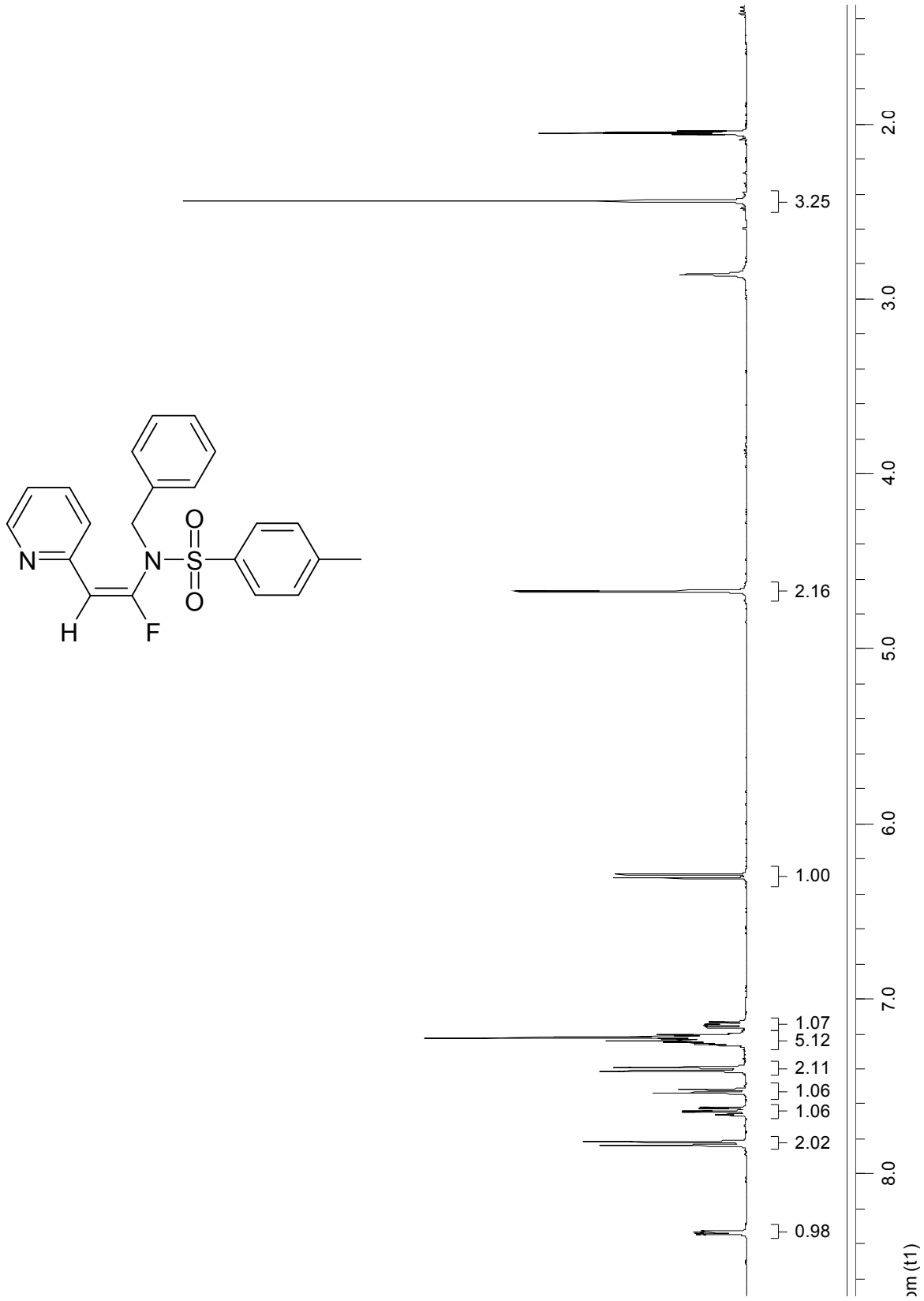

10
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50
60
70
80
90
100
110
120
130
140
150
160
170
180
m (t1)

Compound 2o:

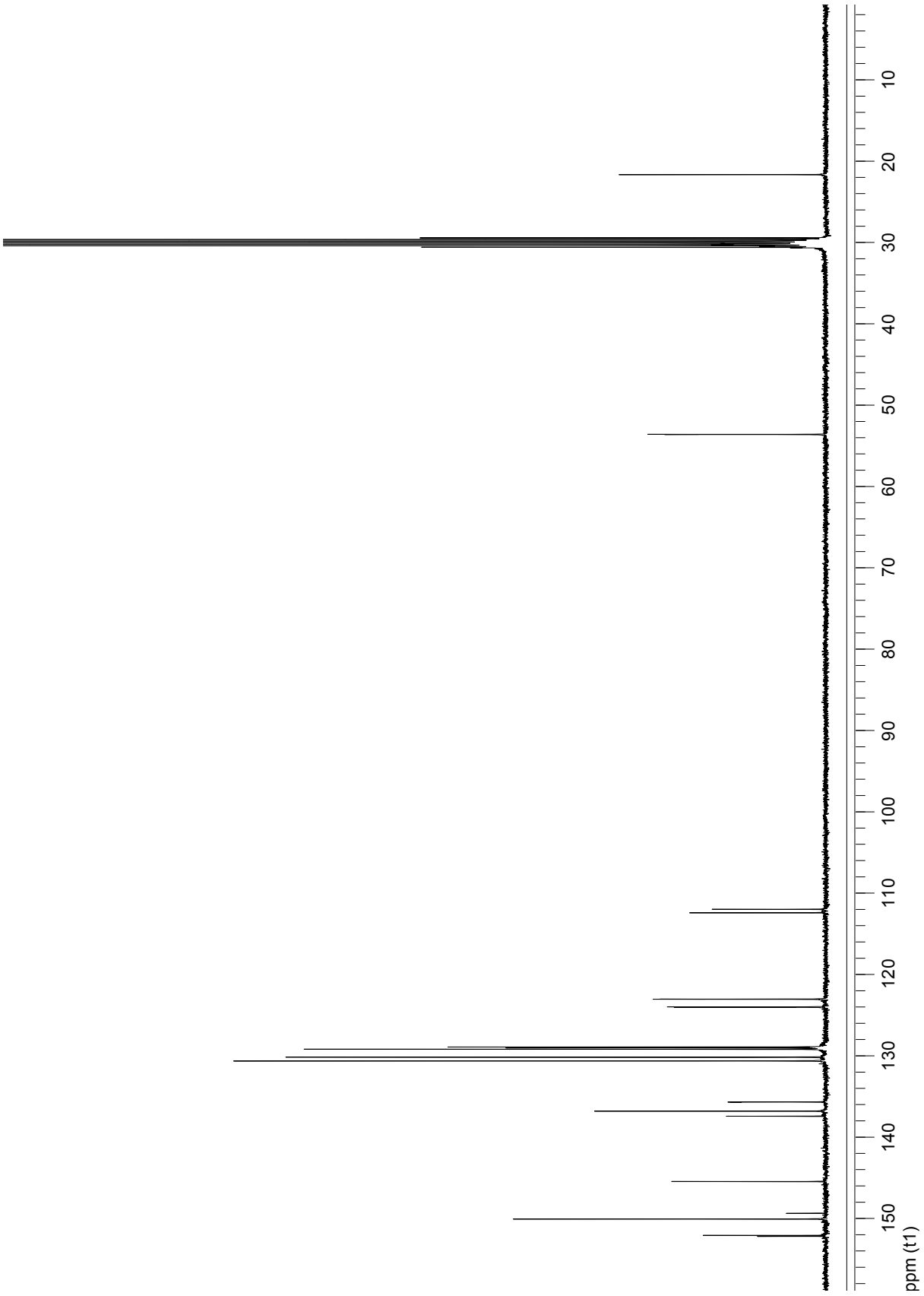



1
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50
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70
80
90
100
110
120
130
140
150
160
170
ppm (t1)

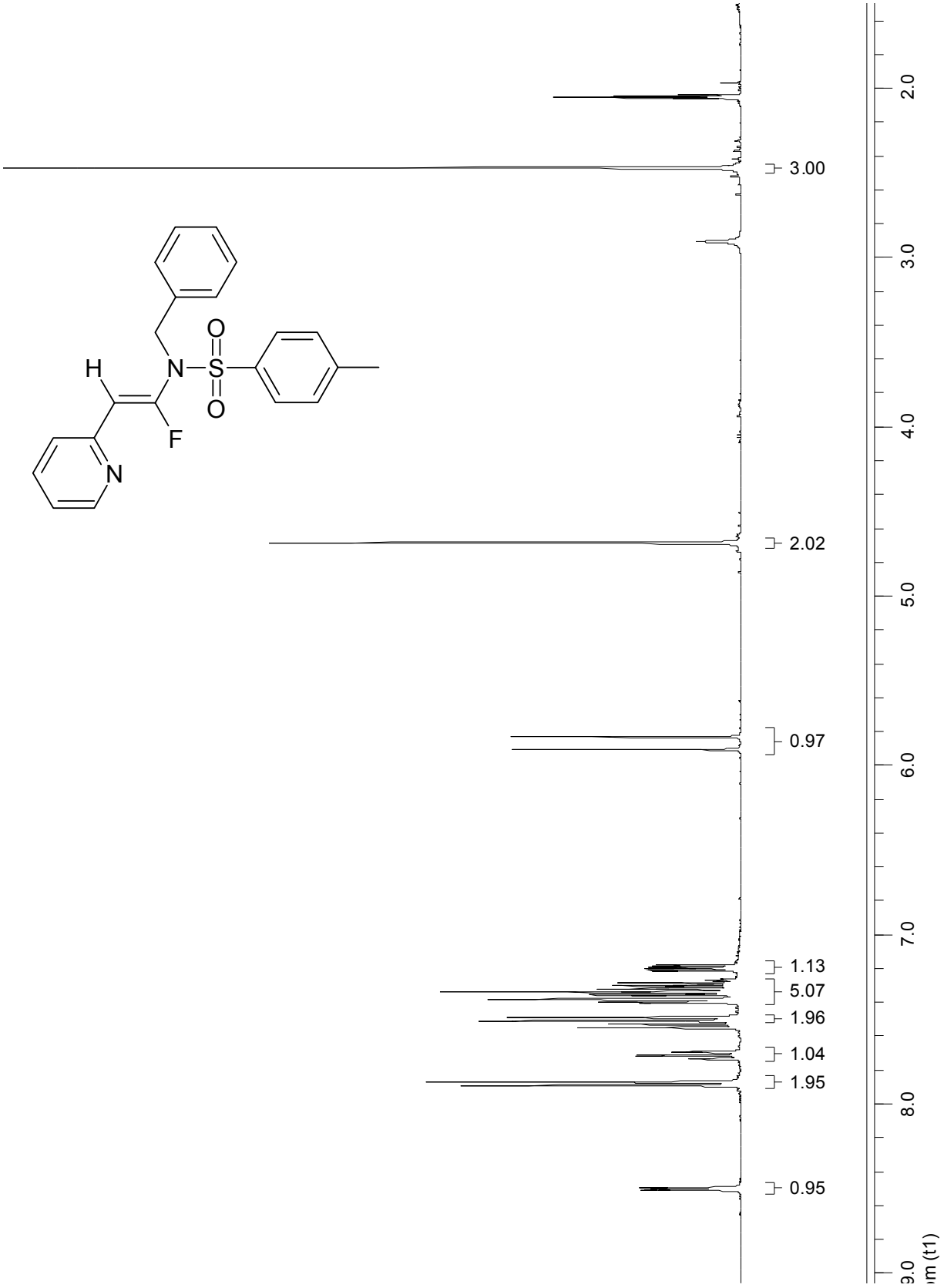
Compound 2p:

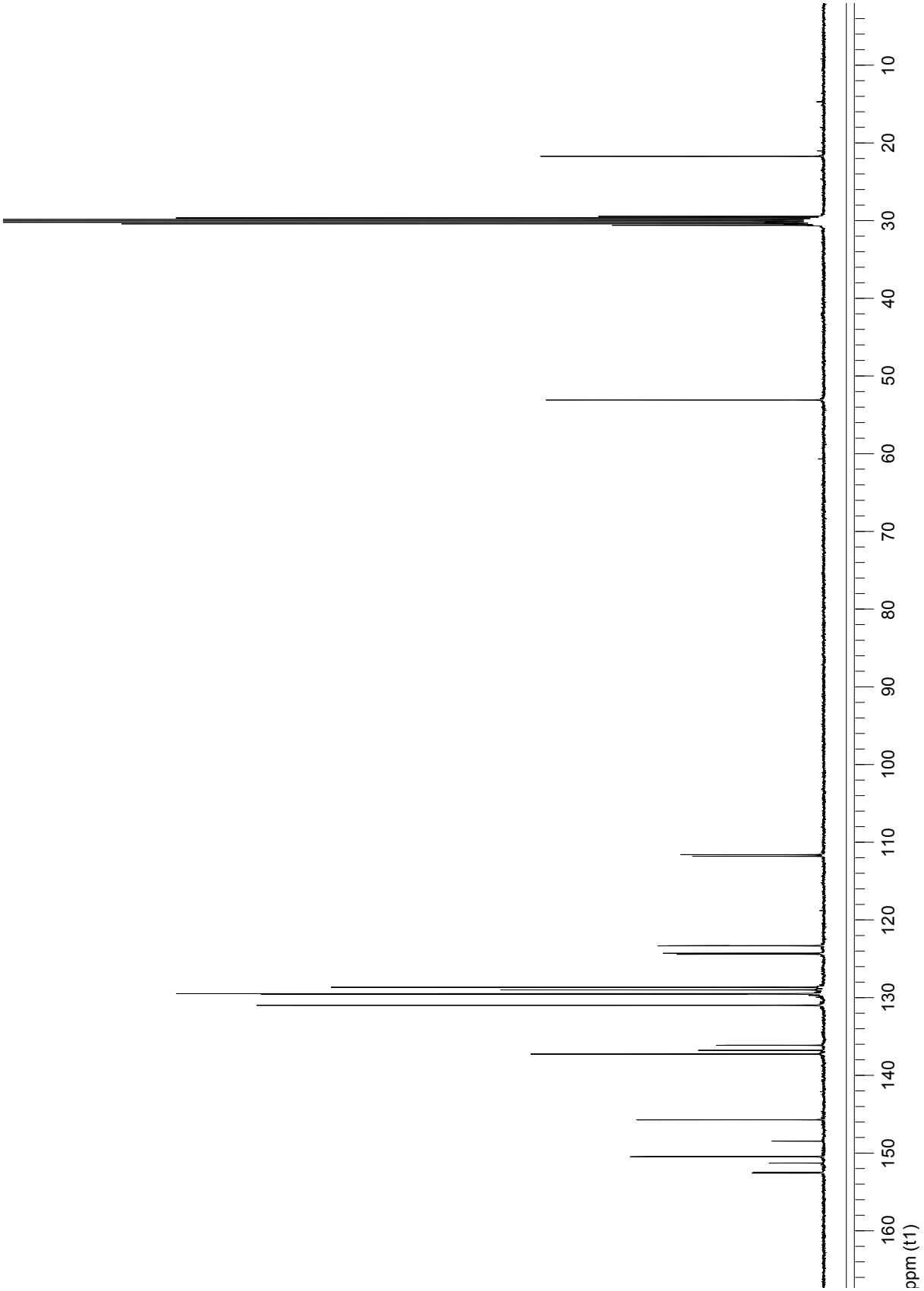

N
N
S
O
O
H
F
3.25
2.16
1.00
1.07
5.12
2.11
1.06
1.06
2.02
0.98
2.0
3.0
4.0
5.0
6.0
7.0
8.0
(t1)

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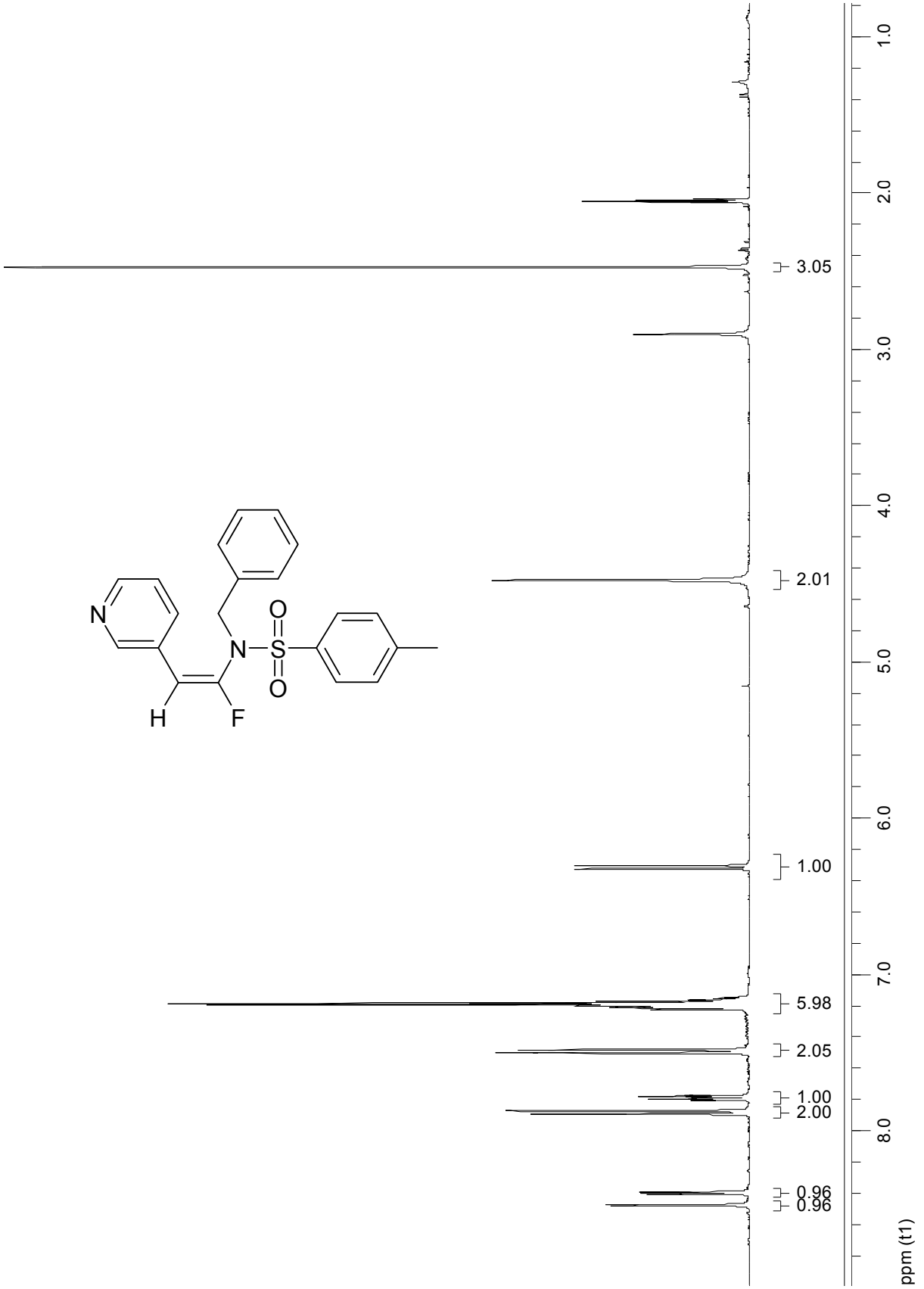


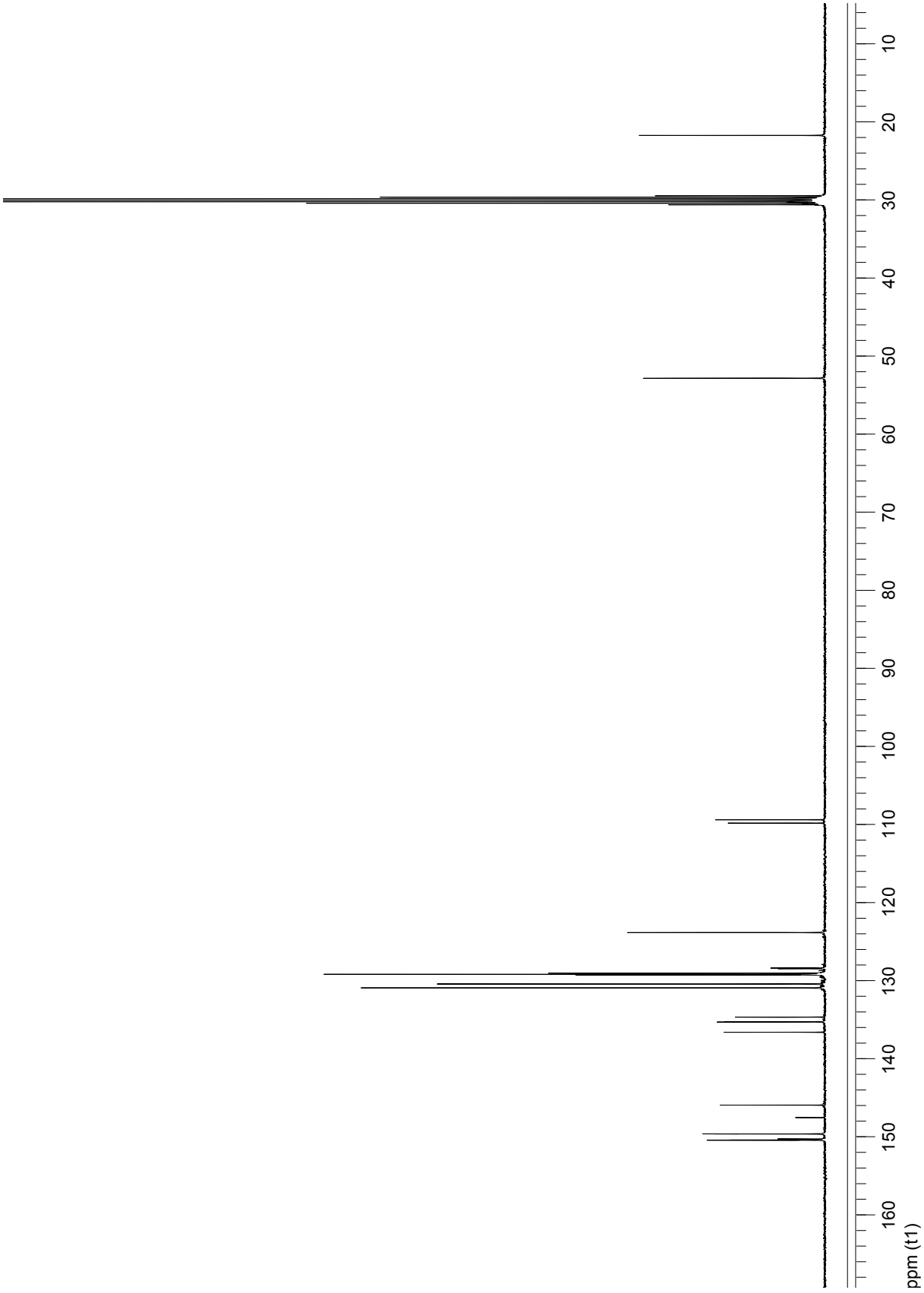
Compound 2p':


H
N
S
O
O
F
N
3.00
2.02
0.97
1.13
5.07
1.96
1.04
1.95
0.95
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
m (t1)

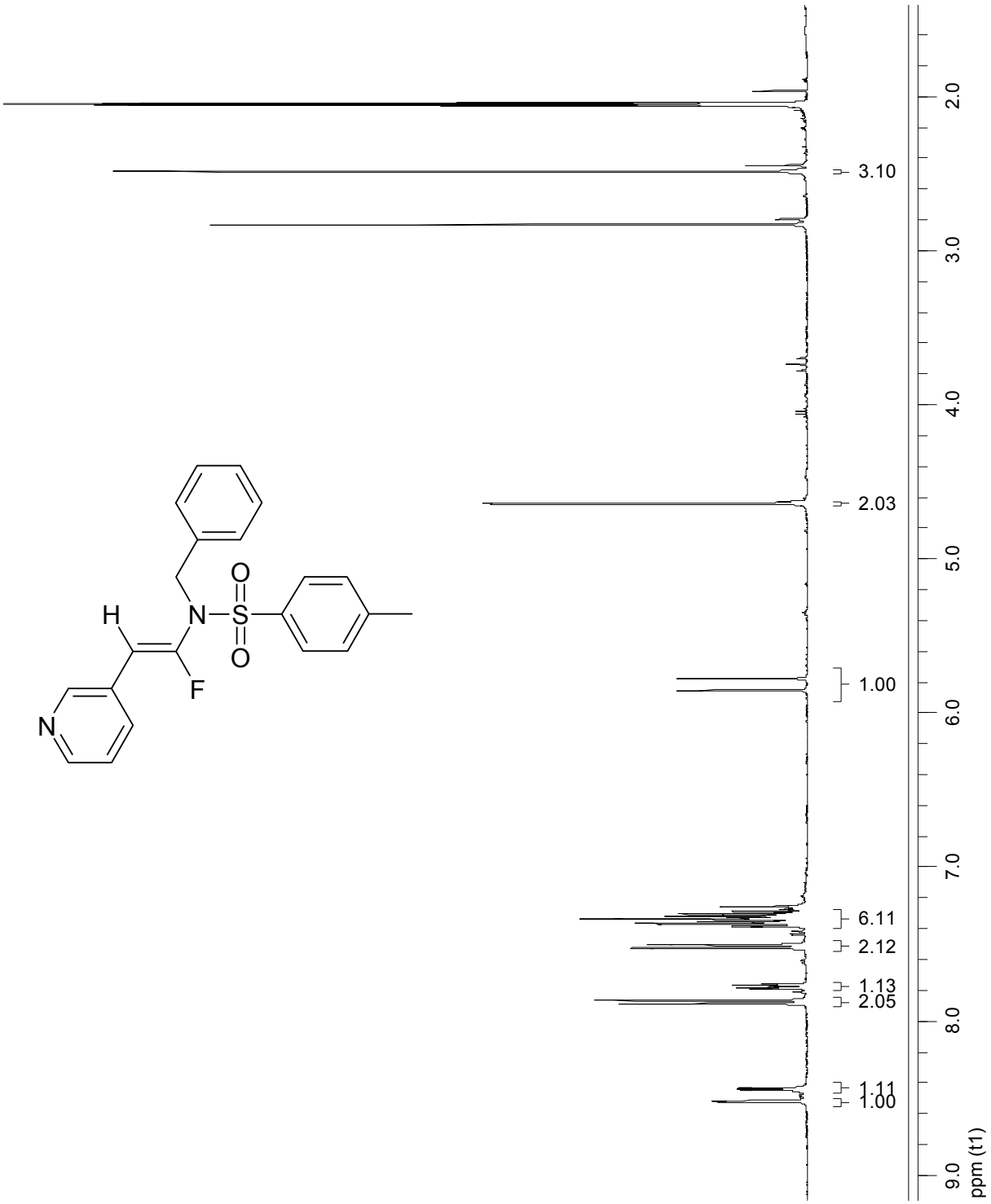

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80
90
100
110
120
130
140
150
160
ppm (t1)

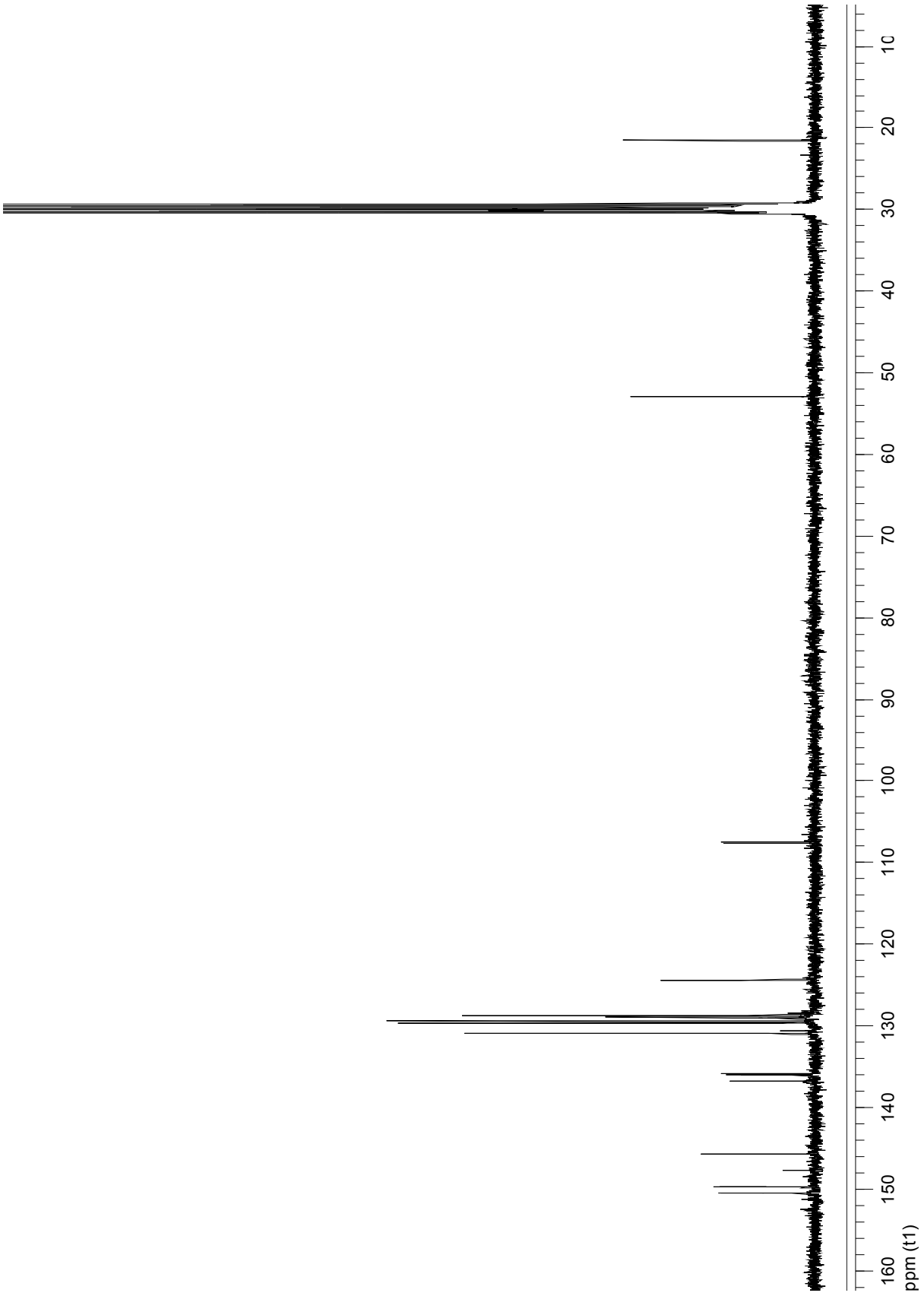
Compound 2q:


N
O
N
S
O
H
F
3.05
2.01
1.00
5.98
2.05
1.00
2.00
0.96
0.96
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)


10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm (t1)

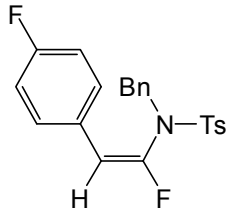
Compound 2q':

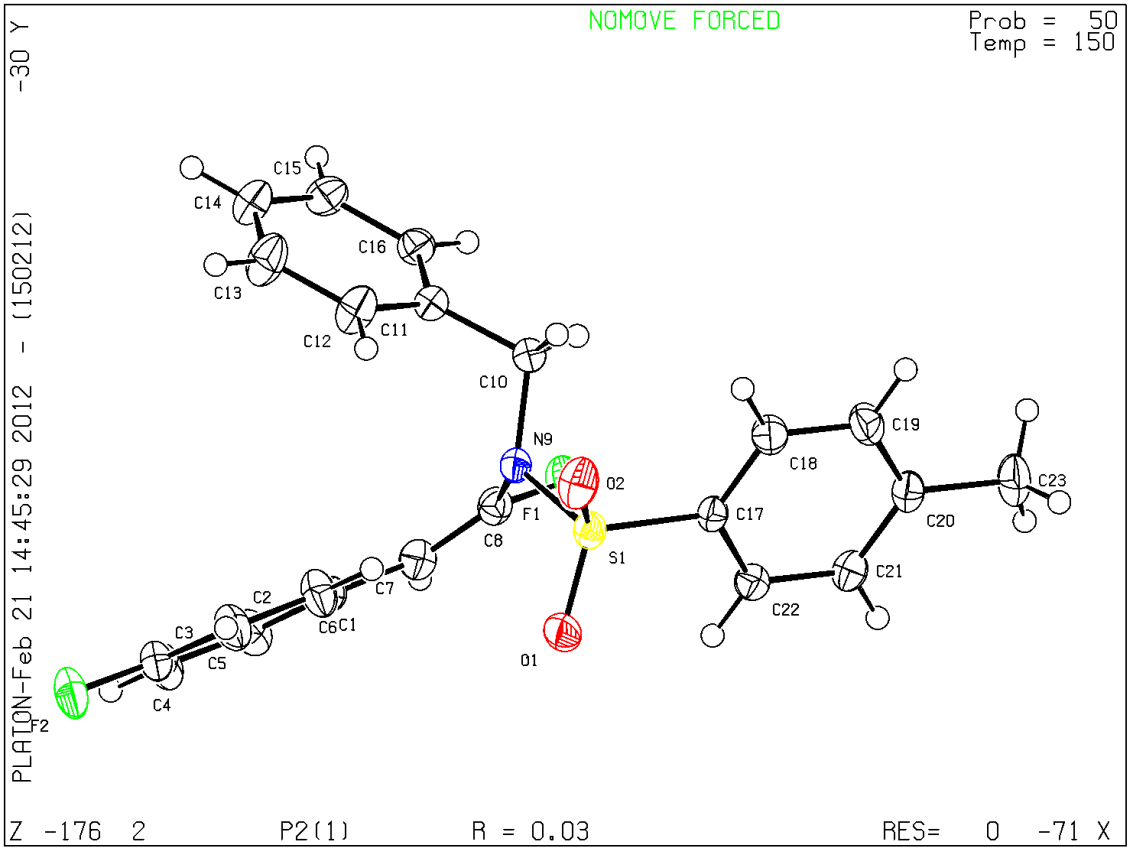

H
N
S
O
O
F
N
3.10
2.03
1.00
6.11
2.12
1.13
2.05
1.11
1.00
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)


10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm (t1)

E. X-RAY ANALYSIS DATA

X-RAY ANALYSIS DATA for compound 2b (CCDC 868336)





Crystal data

C22H19F2NO2S *F*(000) = 416
Mr = 399.44 *D*x = 1.356 Mg m−3
Monoclinic, *P*21 Mo *K*α radiation, λ = 0.71073 Å
a = 9.0138 (8) Å Cell parameters from 9603 reflections
b = 12.0813 (10) Å θ = 2.4–30.0°
c = 9.5129 (9) Å μ = 0.20 mm−1
β = 109.254 (4)° *T* = 150 K
V = 978.00 (15) Å3 Parallelepiped, Colorless
Z = 2 0.25 × 0.15 × 0.10 mm

Data collection

Bruker APEX-II CCD
diffractometer 5702 independent reflections
Radiation source: fine-focus sealed tube 5542 reflections with $I > 2\sigma(I)$
Graphite monochromator *R*int = 0.027

Detector resolution: 512x512 pixels mm-1 θmax = 30.0°, θmin = 2.3°
φ and ω scans *h* = −12→12
Absorption correction: Multi-scan
SADABS (Sheldrick, V2.10) *k* = −16→16
*T*min = 0.951, *T*max = 0.980 *l* = −13→13
86545 measured reflections

Refinement

Refinement on *F*2 Secondary atom site location: Difference Fourier map
Least-squares matrix: Full Hydrogen site location: Inferred from neighbouring sites
R[*F*2 > 2σ(*F*2)] = 0.028 H-atom parameters constrained
wR(*F*2) = 0.079 *w* = 1/[σ2(*F*o
2) + (0.0531*P*)2 + 0.0956*P*]
where *P* = (*F*o
2 + 2*F*c
2)/3
S = 1.08 (Δ/σ)max < 0.001
5702 reflections Δρmax = 0.41 e Å−3
254 parameters Δρmin = −0.17 e Å−3
1 restraint Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
Primary atom site location: Structure-invariant direct methods Flack parameter: −0.01 (4)

Special details

Experimental. 'Blessing, Acta Cryst. (1995) A51, 33-38'
Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. Refinement of F2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F2, conventional Rfactors R are based on F, with F set to zero for negative F2. The threshold expression of F2 > 2sigma(F2) is used only for calculating Rfactors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

*x y z U*iso*/*U*eq

S1	0.17294 (3)	0.25214 (2)	0.26877 (3)	0.02330 (6)
F1	0.37828 (10)	0.03262 (6)	0.23921 (10)	0.03664 (18)
F2	0.78144 (10)	0.58138 (8)	0.11387 (11)	0.0446 (2)
O1	0.15830 (11)	0.28928 (8)	0.12167 (11)	0.03319 (19)
O2	0.15727 (11)	0.32894 (8)	0.37818 (12)	0.0344 (2)
C1	0.52484 (16)	0.38457 (11)	0.20383 (15)	0.0322 (2)
H1	0.4439	0.3835	0.2472	0.039*
C2	0.59324 (17)	0.48462 (11)	0.18828 (15)	0.0335 (3)
H2	0.5591	0.5521	0.2188	0.040*
C3	0.71320 (15)	0.48322 (11)	0.12672 (15)	0.0323 (2)
C4	0.76177 (15)	0.38895 (13)	0.07579 (18)	0.0391 (3)
H4	0.8424	0.3912	0.0319	0.047*

C5 0.69011 (15) 0.28958 (12) 0.08981 (16) 0.0340 (3)
H5 0.7212 0.2234 0.0533 0.041*
C6 0.57298 (13) 0.28503 (10) 0.15668 (12) 0.0249 (2)
C7 0.50804 (13) 0.17556 (10) 0.16811 (13) 0.0271 (2)
H7 0.5354 0.1191 0.1115 0.033*
C8 0.41680 (13) 0.14269 (9) 0.24524 (13) 0.0249 (2)
N9 0.35567 (11) 0.20251 (8) 0.33997 (10) 0.02284 (17)
C10 0.40053 (13) 0.15908 (10) 0.49511 (13) 0.0264 (2)
H10A 0.3794 0.0786 0.4926 0.032*
H10B 0.3361 0.1956 0.5482 0.032*
C11 0.57245 (13) 0.18007 (10) 0.57756 (12) 0.02406 (19)
C12 0.62612 (15) 0.28787 (11) 0.61069 (16) 0.0343 (3)
H12 0.5551 0.3481 0.5788 0.041*
C13 0.78325 (17) 0.30812 (11) 0.69035 (19) 0.0398 (3)
H13 0.8196 0.3820 0.7121 0.048*
C14 0.88688 (15) 0.22046 (12) 0.73798 (15) 0.0342 (3)
H14 0.9940 0.2343 0.7935 0.041*
C15 0.83450 (14) 0.11259 (11) 0.70480 (14) 0.0311 (2)
H15 0.9057 0.0525 0.7367 0.037*
C16 0.67668 (14) 0.09269 (9) 0.62434 (12) 0.0259 (2)
H16 0.6406 0.0188 0.6016 0.031*
C17 0.04224 (12) 0.14193 (9) 0.25472 (12) 0.02102 (18)
C18 −0.00975 (15) 0.11589 (11) 0.37343 (13) 0.0293 (2)
H18 0.0247 0.1577 0.4630 0.035*
C19 −0.11286 (16) 0.02772 (12) 0.35843 (14) 0.0328 (2)
H19 −0.1471 0.0085 0.4396 0.039*
C20 −0.16689 (13) −0.03289 (10) 0.22703 (13) 0.0262 (2)
C21 −0.11434 (13) −0.00448 (9) 0.10897 (13) 0.0257 (2)
H21 −0.1512 −0.0449 0.0184 0.031*
C22 −0.00903 (13) 0.08188 (9) 0.12225 (12) 0.02334 (19)
H22 0.0276 0.0998 0.0422 0.028*
C23 −0.28116 (16) −0.12651 (12) 0.21144 (18) 0.0386 (3)
H23A −0.2487 −0.1714 0.3024 0.058*
H23B −0.2828 −0.1727 0.1263 0.058*
H23C −0.3864 −0.0964 0.1955 0.058*

Atomic displacement parameters (Å2)

*U*11 *U*22 *U*33 *U*12 *U*13 *U*23
S1 0.02090 (11) 0.01799 (10) 0.02952 (12) −0.00061 (9) 0.00629 (8) 0.00189 (9)
F1 0.0416 (4) 0.0207 (3) 0.0514 (5) −0.0046 (3) 0.0205 (4) −0.0026 (3)
F2 0.0361 (4) 0.0442 (5) 0.0553 (5) −0.0156 (4) 0.0176 (4) 0.0084 (4)
O1 0.0290 (4) 0.0303 (4) 0.0368 (4) −0.0015 (3) 0.0063 (3) 0.0141 (3)
O2 0.0313 (4) 0.0227 (4) 0.0478 (5) −0.0015 (3) 0.0113 (4) −0.0095 (4)
C1 0.0357 (6) 0.0304 (6) 0.0382 (6) −0.0087 (5) 0.0225 (5) −0.0077 (5)
C2 0.0397 (7) 0.0301 (6) 0.0359 (6) −0.0112 (5) 0.0193 (5) −0.0064 (5)
C3 0.0242 (5) 0.0372 (6) 0.0345 (6) −0.0077 (5) 0.0083 (5) 0.0076 (5)
C4 0.0251 (5) 0.0448 (8) 0.0539 (8) 0.0056 (5) 0.0219 (5) 0.0154 (6)
C5 0.0265 (5) 0.0349 (6) 0.0462 (7) 0.0087 (5) 0.0196 (5) 0.0091 (5)
C6 0.0197 (4) 0.0298 (5) 0.0253 (5) 0.0002 (4) 0.0073 (4) 0.0016 (4)
C7 0.0255 (5) 0.0268 (5) 0.0298 (5) 0.0003 (4) 0.0100 (4) −0.0027 (4)
C8 0.0228 (5) 0.0217 (5) 0.0285 (5) −0.0010 (4) 0.0062 (4) 0.0001 (4)
N9 0.0186 (4) 0.0242 (4) 0.0247 (4) −0.0020 (3) 0.0058 (3) 0.0026 (3)
C10 0.0220 (5) 0.0307 (5) 0.0249 (5) −0.0036 (4) 0.0055 (4) 0.0056 (4)
C11 0.0223 (5) 0.0255 (5) 0.0234 (4) −0.0011 (4) 0.0063 (4) 0.0007 (4)
C12 0.0268 (6) 0.0236 (5) 0.0454 (7) 0.0026 (4) 0.0024 (5) −0.0039 (5)
C13 0.0316 (6) 0.0265 (6) 0.0524 (8) −0.0040 (5) 0.0017 (6) −0.0079 (5)
C14 0.0236 (5) 0.0375 (6) 0.0358 (6) −0.0015 (4) 0.0022 (4) −0.0043 (5)
C15 0.0268 (6) 0.0318 (6) 0.0314 (5) 0.0056 (4) 0.0053 (4) 0.0027 (5)
C16 0.0278 (5) 0.0220 (5) 0.0263 (5) 0.0000 (4) 0.0067 (4) 0.0010 (4)

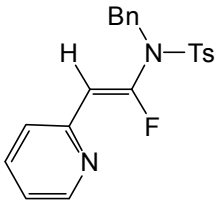
C17 0.0172 (4) 0.0206 (4) 0.0248 (4) −0.0006 (3) 0.0062 (3) −0.0001 (3)
C18 0.0301 (5) 0.0350 (6) 0.0249 (5) −0.0081 (5) 0.0119 (4) −0.0063 (4)
C19 0.0320 (6) 0.0411 (6) 0.0300 (5) −0.0109 (5) 0.0163 (5) −0.0033 (5)
C20 0.0202 (5) 0.0243 (5) 0.0336 (6) −0.0018 (4) 0.0081 (4) 0.0001 (4)
C21 0.0237 (5) 0.0236 (5) 0.0291 (5) −0.0007 (4) 0.0079 (4) −0.0054 (4)
C22 0.0223 (5) 0.0244 (5) 0.0245 (4) 0.0010 (4) 0.0093 (4) −0.0015 (4)
C23 0.0312 (6) 0.0324 (6) 0.0527 (8) −0.0119 (5) 0.0145 (6) −0.0016 (5)

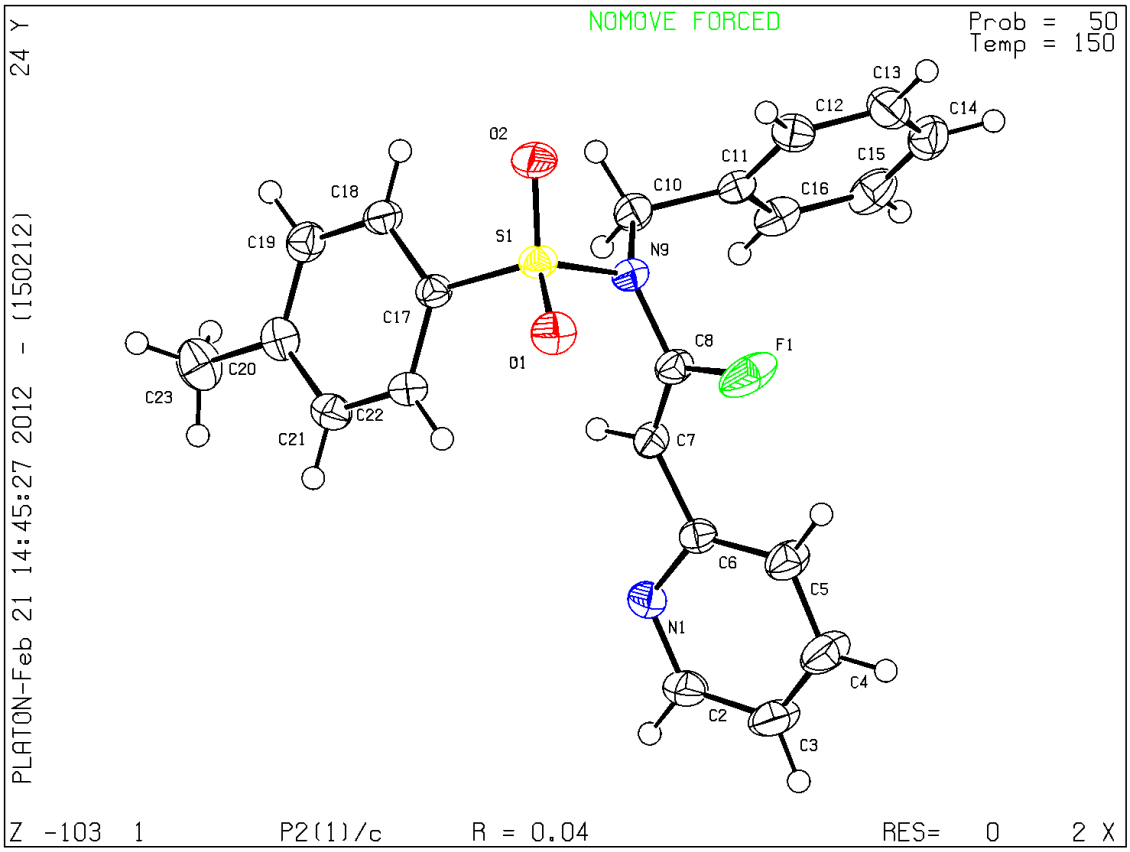
Geometric parameters (Å, º)

S1—O1 1.4336 (10) C11—C12 1.3888 (17)
S1—O2 1.4356 (10) C12—C13 1.3901 (18)
S1—N9 1.6720 (10) C12—H12 0.9500
S1—C17 1.7535 (11) C13—C14 1.3857 (19)
F1—C8 1.3708 (13) C13—H13 0.9500
F2—C3 1.3599 (14) C14—C15 1.3866 (19)
C1—C2 1.3867 (17) C14—H14 0.9500
C1—C6 1.4014 (17) C15—C16 1.3962 (16)
C1—H1 0.9500 C15—H15 0.9500
C2—C3 1.3892 (18) C16—H16 0.9500
C2—H2 0.9500 C17—C18 1.3939 (15)
C3—C4 1.365 (2) C17—C22 1.3942 (15)
C4—C5 1.390 (2) C18—C19 1.3897 (17)
C4—H4 0.9500 C18—H18 0.9500
C5—C6 1.4019 (16) C19—C20 1.3907 (17)
C5—H5 0.9500 C19—H19 0.9500
C6—C7 1.4648 (16) C20—C21 1.3980 (16)
C7—C8 1.3306 (17) C20—C23 1.5038 (16)
C7—H7 0.9500 C21—C22 1.3879 (15)
C8—N9 1.4019 (15) C21—H21 0.9500
N9—C10 1.4911 (14) C22—H22 0.9500
C10—C11 1.5097 (15) C23—H23A 0.9800
C10—H10A 0.9900 C23—H23B 0.9800
C10—H10B 0.9900 C23—H23C 0.9800
C11—C16 1.3854 (16)
O1—S1—O2 120.39 (6) C12—C11—C10 119.77 (11)
O1—S1—N9 105.60 (5) C11—C12—C13 120.31 (11)
O2—S1—N9 104.92 (5) C11—C12—H12 119.8
O1—S1—C17 108.66 (5) C13—C12—H12 119.8
O2—S1—C17 108.78 (5) C14—C13—C12 119.97 (12)
N9—S1—C17 107.81 (5) C14—C13—H13 120.0
C2—C1—C6 121.22 (11) C12—C13—H13 120.0
C2—C1—H1 119.4 C13—C14—C15 120.11 (12)
C6—C1—H1 119.4 C13—C14—H14 119.9
C1—C2—C3 118.01 (12) C15—C14—H14 119.9
C1—C2—H2 121.0 C14—C15—C16 119.70 (11)
C3—C2—H2 121.0 C14—C15—H15 120.1
F2—C3—C4 119.22 (11) C16—C15—H15 120.1
F2—C3—C2 117.73 (12) C11—C16—C15 120.35 (11)
C4—C3—C2 123.03 (12) C11—C16—H16 119.8
C3—C4—C5 118.22 (11) C15—C16—H16 119.8
C3—C4—H4 120.9 C18—C17—C22 121.00 (10)
C5—C4—H4 120.9 C18—C17—S1 120.43 (8)
C4—C5—C6 121.37 (13) C22—C17—S1 118.57 (8)
C4—C5—H5 119.3 C19—C18—C17 118.81 (10)
C6—C5—H5 119.3 C19—C18—H18 120.6
C1—C6—C5 118.07 (11) C17—C18—H18 120.6
C1—C6—C7 125.28 (10) C18—C19—C20 121.33 (11)
C5—C6—C7 116.63 (11) C18—C19—H19 119.3
C8—C7—C6 130.18 (11) C20—C19—H19 119.3

C8—C7—H7 114.9 C19—C20—C21 118.80 (10)
C6—C7—H7 114.9 C19—C20—C23 120.67 (11)
C7—C8—F1 117.42 (10) C21—C20—C23 120.52 (11)
C7—C8—N9 130.25 (11) C22—C21—C20 120.94 (10)
F1—C8—N9 112.28 (10) C22—C21—H21 119.5
C8—N9—C10 114.77 (9) C20—C21—H21 119.5
C8—N9—S1 117.90 (8) C21—C22—C17 119.10 (10)
C10—N9—S1 115.88 (7) C21—C22—H22 120.4
N9—C10—C11 110.61 (9) C17—C22—H22 120.4
N9—C10—H10A 109.5 C20—C23—H23A 109.5
C11—C10—H10A 109.5 C20—C23—H23B 109.5
N9—C10—H10B 109.5 H23A—C23—H23B 109.5
C11—C10—H10B 109.5 C20—C23—H23C 109.5
H10A—C10—H10B 108.1 H23A—C23—H23C 109.5
C16—C11—C12 119.55 (10) H23B—C23—H23C 109.5
C16—C11—C10 120.66 (11)

X-RAY ANALYSIS DATA for compound 2p' (CCDC 868335)





Crystal data

C21H19FN2O2S *F*(000) = 800
Mr = 382.44 *D*x = 1.337 Mg m−3
Monoclinic, *P*21/*c* Mo *K*α radiation, λ = 0.71073 Å
a = 11.4189 (10) Å Cell parameters from 9411 reflections
b = 14.9794 (13) Å θ = 2.4–29.9°
c = 12.4070 (9) Å μ = 0.20 mm−1
β = 116.424 (3)° *T* = 150 K
V = 1900.5 (3) Å3 Parallelepiped, Colorless
Z = 4 0.28 × 0.20 × 0.10 mm

Data collection

Bruker APEX-II CCD
diffractometer 5522 independent reflections
Radiation source: fine-focus sealed tube 5005 reflections with $I > 2\sigma(I)$

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Graphite monochromator *R*int = 0.027
Detector resolution: 512x512 pixels mm-1 θmax = 30.0°, θmin = 2.0°
φ and ω scans *h* = −16→16
Absorption correction: Multi-scan
SADABS (Sheldrick, V2.10) *k* = −21→21
*T*min = 0.947, *T*max = 0.981 *l* = −17→17
175446 measured reflections

Refinement

Refinement on *F*2 Primary atom site location: Structure-invariant direct
methods
Least-squares matrix: Full Secondary atom site location: Difference Fourier map
R[*F*2 > 2σ(*F*2)] = 0.038 Hydrogen site location: Inferred from neighbouring
sites
wR(*F*2) = 0.122 H-atom parameters constrained
S = 1.06 *w* = 1/[σ2(*F*o
2) + (0.0726*P*)2 + 0.5579*P*]
where *P* = (*F*o
2 + 2*F*c
2)/3
5522 reflections (Δ/σ)max = 0.001
245 parameters Δρmax = 0.72 e Å−3
0 restraints Δρmin = −0.64 e Å−3

Special details

Experimental. 'Blessing, Acta Cryst. (1995) A51, 33-38'
Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell
esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell
parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for
estimating esds involving l.s. planes.
Refinement. Refinement of F2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F2, conventional Rfactors
R are based on F, with F set to zero for negative F2. The threshold expression of F2 > 2sigma(F2) is used only for calculating Rfactors(
gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F2 are statistically about twice as large as
those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

*x y z U*iso*/*U*eq
S1 0.46980 (3) 0.290687 (18) 0.52467 (2) 0.02636 (9)
O1 0.48519 (9) 0.28876 (6) 0.64581 (8) 0.0347 (2)
O2 0.57876 (8) 0.27408 (7) 0.50001 (9) 0.0370 (2)
F1 0.31535 (8) 0.12487 (7) 0.57826 (9) 0.0567 (3)
N1 −0.04275 (10) 0.26277 (7) 0.47442 (9) 0.0301 (2)
C2 −0.13767 (13) 0.24572 (9) 0.50654 (12) 0.0362 (3)
H2 −0.2075 0.2873 0.4835 0.043*
C3 −0.14057 (14) 0.17128 (11) 0.57128 (14) 0.0434 (3)
H3 −0.2110 0.1615 0.5909 0.052*
C4 −0.03799 (14) 0.11148 (11) 0.60659 (14) 0.0455 (3)
H4 −0.0361 0.0600 0.6521 0.055*
C5 0.06218 (12) 0.12740 (9) 0.57482 (12) 0.0359 (3)
H5 0.1336 0.0871 0.5982 0.043*
C6 0.05644 (11) 0.20356 (7) 0.50796 (10) 0.0251 (2)

C7 0.15378 (10) 0.22692 (7) 0.46542 (9) 0.0253 (2)
H7 0.1301 0.2741 0.4084 0.030*
C8 0.27016 (11) 0.19088 (8) 0.49612 (10) 0.0271 (2)
N9 0.35973 (10) 0.21243 (6) 0.45169 (9) 0.02627 (19)
C10 0.31896 (13) 0.19997 (8) 0.32091 (10) 0.0307 (2)
H10A 0.3891 0.2214 0.3011 0.037*
H10B 0.2393 0.2356 0.2739 0.037*
C11 0.29172 (11) 0.10295 (8) 0.28741 (9) 0.0260 (2)
C12 0.39195 (11) 0.04046 (8) 0.33697 (11) 0.0315 (2)
H12 0.4770 0.0592 0.3927 0.038*
C13 0.36837 (14) −0.04910 (9) 0.30554 (12) 0.0381 (3)
H13 0.4373 −0.0914 0.3397 0.046*
C14 0.24420 (15) −0.07685 (9) 0.22425 (12) 0.0398 (3)
H14 0.2280 −0.1381 0.2028 0.048*
C15 0.14446 (13) −0.01532 (10) 0.17469 (11) 0.0403 (3)
H15 0.0595 −0.0343 0.1189 0.048*
C16 0.16768 (12) 0.07441 (9) 0.20602 (11) 0.0334 (2)
H16 0.0985 0.1164 0.1717 0.040*
C17 0.39602 (10) 0.39119 (7) 0.45470 (9) 0.0242 (2)
C18 0.41867 (11) 0.42393 (8) 0.36087 (10) 0.0280 (2)
H18 0.4796 0.3954 0.3394 0.034*
C19 0.35073 (12) 0.49897 (8) 0.29902 (10) 0.0306 (2)
H19 0.3664 0.5221 0.2353 0.037*
C20 0.26010 (11) 0.54097 (8) 0.32849 (10) 0.0297 (2)
C21 0.24119 (11) 0.50803 (8) 0.42476 (10) 0.0303 (2)
H21 0.1811 0.5371 0.4469 0.036*
C22 0.30863 (11) 0.43350 (8) 0.48882 (10) 0.0275 (2)
H22 0.2956 0.4117 0.5546 0.033*
C23 0.18343 (15) 0.61993 (10) 0.25683 (12) 0.0424 (3)
H23A 0.2422 0.6711 0.2718 0.064*
H23B 0.1150 0.6350 0.2811 0.064*
H23C 0.1432 0.6052 0.1709 0.064*

Atomic displacement parameters (Å2)

*U*11 *U*22 *U*33 *U*12 *U*13 *U*23
S1 0.02201 (14) 0.02961 (15) 0.02923 (15) 0.00276 (9) 0.01300 (11) 0.00224 (9)
O1 0.0336 (4) 0.0403 (5) 0.0274 (4) 0.0028 (3) 0.0111 (3) 0.0033 (3)
O2 0.0249 (4) 0.0404 (5) 0.0512 (5) 0.0058 (3) 0.0220 (4) 0.0041 (4)
F1 0.0391 (4) 0.0729 (6) 0.0706 (6) 0.0259 (4) 0.0355 (4) 0.0506 (5)
N1 0.0279 (4) 0.0284 (5) 0.0364 (5) 0.0020 (4) 0.0165 (4) −0.0002 (4)
C2 0.0324 (6) 0.0385 (6) 0.0444 (7) 0.0064 (5) 0.0231 (5) 0.0024 (5)
C3 0.0374 (6) 0.0547 (8) 0.0502 (7) 0.0059 (6) 0.0303 (6) 0.0117 (6)
C4 0.0397 (7) 0.0532 (8) 0.0529 (8) 0.0080 (6) 0.0289 (6) 0.0234 (7)
C5 0.0286 (5) 0.0411 (6) 0.0411 (6) 0.0065 (5) 0.0182 (5) 0.0147 (5)
C6 0.0223 (4) 0.0284 (5) 0.0246 (5) −0.0007 (4) 0.0104 (4) −0.0006 (4)
C7 0.0249 (5) 0.0254 (5) 0.0259 (5) −0.0008 (4) 0.0116 (4) 0.0022 (4)
C8 0.0274 (5) 0.0301 (5) 0.0266 (5) 0.0025 (4) 0.0144 (4) 0.0063 (4)
N9 0.0287 (4) 0.0278 (4) 0.0278 (4) −0.0015 (3) 0.0175 (4) 0.0000 (3)
C10 0.0403 (6) 0.0293 (5) 0.0277 (5) 0.0002 (4) 0.0197 (5) 0.0026 (4)
C11 0.0281 (5) 0.0302 (5) 0.0236 (4) −0.0007 (4) 0.0151 (4) 0.0017 (4)
C12 0.0272 (5) 0.0359 (6) 0.0306 (5) 0.0019 (4) 0.0121 (4) −0.0009 (4)
C13 0.0451 (7) 0.0339 (6) 0.0390 (6) 0.0074 (5) 0.0221 (5) 0.0016 (5)
C14 0.0563 (8) 0.0346 (6) 0.0366 (6) −0.0107 (6) 0.0280 (6) −0.0056 (5)
C15 0.0367 (6) 0.0524 (8) 0.0314 (6) −0.0167 (6) 0.0150 (5) −0.0035 (5)
C16 0.0262 (5) 0.0449 (7) 0.0290 (5) −0.0002 (5) 0.0123 (4) 0.0060 (4)
C17 0.0215 (4) 0.0261 (5) 0.0258 (4) −0.0011 (4) 0.0114 (4) −0.0014 (4)
C18 0.0288 (5) 0.0306 (5) 0.0293 (5) −0.0027 (4) 0.0171 (4) −0.0026 (4)
C19 0.0365 (6) 0.0312 (5) 0.0256 (5) −0.0036 (4) 0.0150 (4) −0.0005 (4)
C20 0.0289 (5) 0.0288 (5) 0.0254 (5) −0.0010 (4) 0.0066 (4) −0.0018 (4)

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C21 0.0276 (5) 0.0317 (5) 0.0328 (5) 0.0028 (4) 0.0144 (4) −0.0023 (4)
C22 0.0270 (5) 0.0306 (5) 0.0288 (5) 0.0007 (4) 0.0158 (4) −0.0005 (4)
C23 0.0444 (7) 0.0379 (7) 0.0357 (6) 0.0090 (5) 0.0094 (5) 0.0059 (5)

Geometric parameters (Å, º)

S1—O2 1.4291 (9) C11—C12 1.3921 (16)
S1—O1 1.4337 (9) C12—C13 1.3895 (18)
S1—N9 1.6616 (10) C12—H12 0.9500
S1—C17 1.7547 (11) C13—C14 1.388 (2)
F1—C8 1.3471 (13) C13—H13 0.9500
N1—C2 1.3354 (16) C14—C15 1.379 (2)
N1—C6 1.3502 (14) C14—H14 0.9500
C2—C3 1.3833 (19) C15—C16 1.392 (2)
C2—H2 0.9500 C15—H15 0.9500
C3—C4 1.382 (2) C16—H16 0.9500
C3—H3 0.9500 C17—C18 1.3895 (15)
C4—C5 1.3863 (17) C17—C22 1.3974 (14)
C4—H4 0.9500 C18—C19 1.3872 (16)
C5—C6 1.3948 (16) C18—H18 0.9500
C5—H5 0.9500 C19—C20 1.3919 (17)
C6—C7 1.4692 (15) C19—H19 0.9500
C7—C8 1.3236 (15) C20—C21 1.3952 (17)
C7—H7 0.9500 C20—C23 1.5044 (17)
C8—N9 1.3986 (13) C21—C22 1.3879 (16)
N9—C10 1.4872 (14) C21—H21 0.9500
C10—C11 1.5055 (16) C22—H22 0.9500
C10—H10A 0.9900 C23—H23A 0.9800
C10—H10B 0.9900 C23—H23B 0.9800
C11—C16 1.3913 (16) C23—H23C 0.9800
O2—S1—O1 120.58 (6) C13—C12—C11 120.45 (11)
O2—S1—N9 106.26 (6) C13—C12—H12 119.8
O1—S1—N9 105.50 (5) C11—C12—H12 119.8
O2—S1—C17 108.39 (5) C14—C13—C12 120.04 (12)
O1—S1—C17 110.11 (5) C14—C13—H13 120.0
N9—S1—C17 104.80 (5) C12—C13—H13 120.0
C2—N1—C6 117.61 (11) C15—C14—C13 119.84 (12)
N1—C2—C3 124.04 (12) C15—C14—H14 120.1
N1—C2—H2 118.0 C13—C14—H14 120.1
C3—C2—H2 118.0 C14—C15—C16 120.28 (12)
C4—C3—C2 118.08 (12) C14—C15—H15 119.9
C4—C3—H3 121.0 C16—C15—H15 119.9
C2—C3—H3 121.0 C11—C16—C15 120.36 (12)
C3—C4—C5 119.25 (12) C11—C16—H16 119.8
C3—C4—H4 120.4 C15—C16—H16 119.8
C5—C4—H4 120.4 C18—C17—C22 121.20 (10)
C4—C5—C6 118.91 (12) C18—C17—S1 119.34 (8)
C4—C5—H5 120.5 C22—C17—S1 119.32 (8)
C6—C5—H5 120.5 C19—C18—C17 118.86 (10)
N1—C6—C5 122.10 (11) C19—C18—H18 120.6
N1—C6—C7 113.45 (10) C17—C18—H18 120.6
C5—C6—C7 124.44 (10) C18—C19—C20 121.27 (10)
C8—C7—C6 128.52 (10) C18—C19—H19 119.4
C8—C7—H7 115.7 C20—C19—H19 119.4
C6—C7—H7 115.7 C19—C20—C21 118.78 (11)
C7—C8—F1 120.97 (10) C19—C20—C23 120.35 (11)
C7—C8—N9 127.53 (10) C21—C20—C23 120.86 (11)
F1—C8—N9 111.50 (9) C22—C21—C20 121.12 (11)
C8—N9—C10 118.18 (10) C22—C21—H21 119.4
C8—N9—S1 117.17 (8) C20—C21—H21 119.4

C10—N9—S1 118.47 (7) C21—C22—C17 118.71 (10)
N9—C10—C11 110.38 (9) C21—C22—H22 120.6
N9—C10—H10A 109.6 C17—C22—H22 120.6
C11—C10—H10A 109.6 C20—C23—H23A 109.5
N9—C10—H10B 109.6 C20—C23—H23B 109.5
C11—C10—H10B 109.6 H23A—C23—H23B 109.5
H10A—C10—H10B 108.1 C20—C23—H23C 109.5
C16—C11—C12 119.03 (11) H23A—C23—H23C 109.5
C16—C11—C10 121.03 (11) H23B—C23—H23C 109.5
C12—C11—C10 119.94 (10)