SUPPORTING INFORMATION

for

Gold Catalyzed Synthesis of 2-Aryl-3-Fluoropyrroles

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I. General methods

^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) and ^{19}F NMR (282MHz) spectra were run with a 300 MHz NMR spectrometer. The compounds were diluted in $CDCl_3$ with tetramethylsilane (TMS, δ=0 ppm) as a reference. ^{19}F NMR spectra were recorded using $CDCl_3$ as a lock solvent. Peak assignments were performed with the use of HSQC ^{1}H ^{13}C NMR. IR spectra were obtained from an FTIR-ATR infrared spectrometer. Mass spectra were recorded using either GC-MS (70eV) coupling or a direct inlet system. LC-MS was performed using positive or negative electronspray. Elemental analysis of selected new compounds was performed using an CHN-Elemental Analyser.

II. Synthetic procedures and spectral data

1. Synthesis of *N*-(arylmethylidene)arenesulfonamides 2

Compounds **2** were synthesized from the corresponding (dimethoxymethyl)benzenes **1** according to literature procedures in 99-100% yield.[i] Spectroscopic data of compounds **2** were in agreement with literature data.[ii]

2. Synthesis of difluoropropargyl bromides 4

Compounds **4a-c** were synthesized from acetylenes **3a-c** according to literature procedures in 55, 38 and 61% yield, respectively (Lit. yields: 82, 52, 81% yield).[iii] Spectroscopic data of compounds **4a-c** were in agreement with literature data.[iii,iv]

[i] Albrecht, R.; Kreaze, G.; Mlakar, B. *Chem. Ber.* **1964**, *97*, 483; *Chem. Abstr.* **1964**, *60*, 52474.
[ii] (a) Wang, C.-J.; Shi, M. *J. Org. Chem.* **2003**, *68*, 6229. (b) Guo, H.; Qian, R.; Liao, Y.; Ma, S.; Guo, Y. *J. Am. Chem. Soc.* **2005**, *127*, 13060. (c) Hasaninejad, A.; Zare, A. *J. Sulfur Chem.* **2007**, *28*, 357. (d) Jin, T.; Feng, G.; Yang, M.; Li, T. *Synth. Commun.* **2004**, *34*, 1277.
[iii] Hammond, G. B. *J. Fluorine Chem.* **2006**, *127*, 476.
[iv] Barlow, M. G.; Tajammal, S.; Tipping, A. E. *J. Fluorine Chem.* **1993**, *64*, 61.

3. Synthesis of *N*-(1-aryl-2,2-difluorobut-3-yn-1-yl)arylsulfonamides 11

***N*-[1-(4-Chlorophenyl)-2,2-difluoro-4-phenylbut-3-yn-1-yl]-4-methylbenzenesulfonamide 11a.** In a flame dried flask of 50 mL, 1.00 g (4.33 mmol, 1.0 equiv) of (3-bromo-3,3-difluoroprop-1-yn-1-yl)benzene **2a** and 1.27 g (4.33 mmol, 1.0 equiv) *N*-[(4-chlorophenyl)methylidene]-4-methylbenzenesulfonamide **7a** were dissolved in 25 mL of dry tetrahydrofuran and placed under N_2 atmosphere. The mixture was cooled to –78°C and 1.9 mL of *n*-butyllithium (2.5 M in hexane, 4.76 mmol, 1.1 equiv) was added dropwise. After stirring for 30 minutes at the same temperature, the reaction mixture was quenched with 15 mL of saturated aq. NH_4Cl and warmed up to room temperature. The organic layer was separated and the aqueous phase was extracted with 2 x 15 mL of dichloromethane. The combined organic phases were dried over $MgSO_4$ and after filtration, the solvent was evaporated in vacuo and 20 mL of cold diethyl ether was added to the residue. The white crystals that were formed were separated by filtration and the crystals were washed with 2 x 10 mL of cold diethyl ether and dried under high vacuum to yield 1.01 g of pure *N*-[1-(4-chlorophenyl)-2,2-difluoro-4-phenylbut-3-yn-1-yl]-4-methylbenzenesulfonamide **11a** (2.25 mmol, yield = 52%). Hexane/EtOAc 4:1, R_f = 0.20. M.p. = 169.8°C (diethyl ether). White crystals. ^{1}H NMR ($CDCl_3$): δ 2.33 (3H, s, CH_3); 4.87 (1H, q, J = 9.6 Hz, CH); 6.00 (1H, d, J = 9.6 Hz, NH); 7.09 (2H, d, J = 8.3 Hz, 2 × CH_{ar}); 7.19 (4H, s, 4 × CH_{ar}); 7.28-7.44 (5H, m, 5 × CH_{ar}); 7.59 (2H, d, J = 8.3 Hz, 2 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –89.8 (1F, dd, J = 270.6 Hz, 9.6 Hz, C$\underline{F}_aF_b$); -90.0 (1F, dd, J = 270.6 Hz, 9.6 Hz, C$F_a\underline{F}_b$). ^{13}C NMR ($CDCl_3$): δ 21.4 (CH_3); 62.4 (t, J = 28.8 Hz, CH); 78.8 (t, J = 38.8 Hz, C≡); 90.4 (t, J = 6.9 Hz, C≡); 112.7 (t, J = 240.0 Hz, CF_2); 119.2 ($\underline{C}_{ar}$C≡); 127.0 (2 × CH_{ar}); 128.4 (2 × CH_{ar}); 128.5 (2 × CH_{ar}); 129.4 (2 × CH_{ar}); 129.7 (2 × CH_{ar}); 130.3 (CH_{ar}); 131.9 (C_{ar}Cl); 132.2 (2 × CH_{ar}); 134.9 (C_{ar}); 136.9 (C_{ar}); 143.7 (C_{ar}). IR (ATR, cm^{-1}): *ν* = 3245 (NH); 2240 (C≡C); 1597; 1490; 1454; 1327; 1287; 1165; 1151; 1124; 1086; 1048; 1017; 911; 812; 773; 761; 666. MS (ES-) *m/z* (%): 444/446 ($M\text{-}H^+$, 100). Anal. Calcd. for $C_{23}H_{18}ClF_2NO_2S$: C, 61.95; H, 4.07; N, 3.14. Found: C, 61.63; H, 4.38; N, 3.14.

***N*-(2,2-Difluoro-1,4-diphenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide 11b.** Yield = 54%. M.p. = 161.8°C (diethyl ether). White crystals. ^{1}H NMR ($CDCl_3$): δ 2.28 (3H, s, CH_3); 4.90 (1H, q, J = 9.9 Hz, CH); 6.04 (1H, d, J = 9.9 Hz, NH); 7.05 (2H, d, J = 7.7 Hz, 2 × CH_{ar}); 7.22-7.27 (5H, m, 5 × CH_{ar}); 7.28-7.41 (5H, m, 5 × CH_{ar}); 7.60 (2H, d, J = 8.3 Hz, 2 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –89.7 (1F, dd, J = 270.0 Hz, 9.9 Hz, C$\underline{F}_aF_b$); -90.1 (1F, dd, J = 270.0 Hz, 9.9 Hz, C$F_a\underline{F}_b$). ^{13}C NMR ($CDCl_3$): δ 21.4 (CH_3); 63.0 (t, J = 28.8 Hz, CH); 79.2 (t,

J = 38.7 Hz, C≡); 90.1 (t, J = 6.9 Hz, C≡); 113.0 (t, J = 239.4 Hz, CF_2); 119.4 ($\underline{C}_{ar}C$≡); 127.0 (2 × CH_{ar}); 128.3 (4 × CH_{ar}); 128.4 (2 × CH_{ar}); 128.7 (CH_{ar}); 129.3 (2 × CH_{ar}); 130.1 (CH_{ar}); 132.1 (2 × CH_{ar}); 134.4 (C_{ar}); 137.1 (C_{ar}); 143.3 (C_{ar}). IR (ATR, cm^{-1}): ν = 3261 (NH); 2239 (C≡C); 1598; 1480; 1457; 1444; 1330; 1280; 1164; 1125; 1090; 1047; 910; 694; 670. MS (ES-) *m/z* (%): 410 ($M\text{-}H^+$, 100). Anal. Calcd. for $C_{23}H_{19}F_2NO_2S$: C, 67.14; H, 4.65; N, 3.40. Found: C, 66.97; H, 4.43; N, 3.34.

***N*-[2,2-Difluoro-1-(4-methylphenyl)-4-phenylbut-3-yn-1-yl]-4-methylbenzenesulfonamide 11c.** Yield = 42%. M.p. = 178.9°C (diethyl ether). White crystals. ^{1}H NMR ($CDCl_3$): δ 2.29 (3H, s, CH_3); 2.31 (3H, s, CH_3); 4.86 (1H, q, J = 9.9 Hz, CH); 5.73 (1H, d, J = 9.9 Hz, NH); 7.04 (2H, d, J = 7.7 Hz, 2 × CH_{ar}); 7.08 (2H, d, J = 8.3 Hz, 2 × CH_{ar}); 7.14 (2H, d, J = 7.7 Hz, 2 × CH_{ar}); 7.28-7.43 (5H, m, 5 × CH_{ar}); 7.60 (2H, d, J = 8.3 Hz, 2 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –89.7 (1F, dd, J = 270.3 Hz, 9.9 Hz, $C\underline{F}_aF_b$); -90.2 (1F, dd, J = 270.3 Hz, 9.9 Hz, $CF_a\underline{F}_b$). ^{13}C NMR ($CDCl_3$): δ 21.1 (CH_3); 21.4 (CH_3); 62.7 (t, J = 28.8 Hz, CH); 79.3 (t, J = 39.2 Hz, C≡); 89.9 (t, J = 6.3 Hz, C≡); 113.1 (t, J = 239.4 Hz, CF_2); 119.5 ($\underline{C}_{ar}C$≡); 127.0 (2 × CH_{ar}); 128.1 (2 × CH_{ar}); 128.4 (2 × CH_{ar}); 129.0 (2 × CH_{ar}); 129.3 (2 × CH_{ar}); 130.1 (CH_{ar}); 130.4 (C_{ar}); 132.2 (2 × CH_{ar}); 137.2 (C_{ar}); 138.7 (C_{ar}); 143.3 (C_{ar}). IR (ATR, cm^{-1}): ν = 3251 (NH); 2235 (C≡C); 1598; 1490; 1445; 1326; 1286; 1164; 1122; 1086; 1049; 914; 811; 760; 690; 670. MS (ES-) *m/z* (%): 424 ($M\text{-}H^+$, 100). Anal. Calcd. for $C_{24}H_{21}F_2NO_2S$: C, 67.75; H, 4.97; N, 3.29. Found: C, 67.49; H, 4.69; N, 3.25.

***N*-[2,2-Difluoro-1-(4-methoxyphenyl)-4-phenylbut-3-yn-1-yl]benzenesulfonamide 11d.** Yield = 36%. M.p. = 135.9°C (diethyl ether). White crystals. ^{1}H NMR ($CDCl_3$): δ 3.75 (3H, s, MeO); 4.88 (1H, q, J = 10.0 Hz, CH); 5.95 (1H, d, J = 10.0 Hz, NH); 6.73 (2H, d, J = 8.8 Hz, 2 × CH_{ar}); 7.16 (2H, d, J = 8.3 Hz, 2 × CH_{ar}); 7.25-7.33 (4H, m, 4 × CH_{ar}); 7.35-7.44 (4H, m, 4 × CH_{ar}); 7.72 (2H, d, J = 8.8 Hz, 2 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –89.6 (1F, dd, J = 269.7 Hz, 10.0 Hz, $C\underline{F}_aF_b$); -90.5 (1F, dd, J = 269.7 Hz, 10.0 Hz, $CF_a\underline{F}_b$). ^{13}C NMR ($CDCl_3$): δ 55.2 (MeO); 62.5 (t, J = 28.8 Hz, CH); 79.2 (t, J = 39.2 Hz, C≡); 90.1 (t, J = 6.9 Hz, C≡); 113.1 (t, J = 238.8 Hz, CF_2); 113.8 (2 × CH_{ar}); 119.5 ($\underline{C}_{ar}C$≡); 125.3 (C_{ar}); 126.9 (2 × CH_{ar}); 128.4 (2 × CH_{ar}); 128.7 (2 × CH_{ar}); 129.4 (2 × CH_{ar}); 130.2 (CH_{ar}); 132.2 (2 × CH_{ar}); 132.5 (CH_{ar}); 140.2 (C_{ar}); 159.8 (C_{ar}). IR (ATR, cm^{-1}): ν = 3253 (NH); 3070; 2999; 2965; 2932; 2838; 2235 (C≡C); 1612; 1586; 1516; 1490; 1450; 1325; 1310; 1285; 1249; 1165; 1120; 1082; 1051; 1035; 917; 822; 764; 724. MS (ES-) *m/z* (%): 426 ($M\text{-}H^+$, 100).

***N*-[1-(4-Chlorophenyl)-2,2-difluoro-4-trimethylsilanylbut-3-yn-1-yl]-4-methylbenzenesulfonamide 11e.** Yield = 77%. M.p. = 182.7°C (diethyl ether). White

crystals. ^{1}H NMR ($CDCl_3$): δ 0.16 (9H, s, 3 × CH_3); 2.38 (3H, s, CH_3); 4.77 (1H, t, J = 10.5 Hz, CH); 5.33 (1H, s(broad), NH); 7.11-7.22 (6H, m, 6 × CH_{ar}); 7.57 (2H, d, J = 8.3 Hz, 2 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –89.9 (1F, dd, J = 272.3 Hz, 10.5 Hz, C$\underline{F}_aF_b$); -92.2 (1F, dd, J = 272.3 Hz, 10.5 Hz, $CF_a\underline{F}_b$). ^{13}C NMR ($CDCl_3$): δ -1.1 ($Si(Me)_3$); 21.5 (CH_3); 62.1 (t, J = 28.3 Hz, CH); 93.4 (t, J = 37.5 Hz, C≡); 98.1 (t, J = 5.2 Hz, C≡); 111.5 (t, J = 240.0 Hz, CF_2); 127.0 (2 × CH_{ar}); 128.3 (2 × CH_{ar}); 129.4 (2 × CH_{ar}); 129.8 (2 × CH_{ar}); 131.8 (C_{ar}); 134.8 (C_{ar}); 137.0 (C_{ar}); 143.7 (C_{ar}). IR (ATR, cm^{-1}): *v* = 3237 (NH); 3072; 2965; 2188 (C≡C); 1601; 1496; 1446; 1329; 1254; 1213; 1168; 1107; 1089; 1074; 1016; 919; 873; 842; 811; 760; 718; 669. MS (ES-) *m/z* (%): 440/442 ($M-H^+$, 100). Anal. Calcd. for $C_{20}H_{22}ClF_2NO_2SSi$: C, 54.35; H, 5.02; N, 3.17. Found: C, 54.07; H, 4.73; N, 3.15.

***N*-[1-(4-Chlorophenyl)-2,2-difluorobut-3-yn-1-yl]-4-methylbenzenesulfonamide 11f.** A solution of 10 mg (0.023 mmol) of *N*-[1-(4-chlorophenyl)-2,2-difluoro-4-trimethylsilanylbut-3-yn-1-yl]-4-methylbenzenesulfonamide **11e** in 1 mL of diethyl ether was treated with 1 mL of 1.5 M sodium hydroxide (1.5 mmol). The two-phase system was vigorously stirred during 5 minutes at room temperature after which the organic phase was separated, washed with brine and dried ($MgSO_4$). Evaporation of the solvent in vacuo from the filtrate afforded 7.7 mg (0.021 mmol, 90%) of *N*-[1-(4-chlorophenyl)-2,2-difluorobut-3-yn-1-yl]-4-methylbenzenesulfonamide **11f**. M.p. = 160.9°C (diethyl ether). White crystals. ^{1}H NMR ($CDCl_3$): δ 2.37 (3H, s, CH_3); 2.77 (1H, t, J = 5.2 Hz, ≡CH); 4.80 (1H, q, J = 9.8 Hz, CH); 5.87 (1H, d, J = 9.8 Hz, NH); 7.11-7.21 (6H, m, 6 × CH_{ar}); 7.58 (2H, d, J = 8.8 Hz, 2 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –91.59 (1F, d, J = 9.8 Hz, C$\underline{F}_aF_b$); -91.63 (1F, d, J = 9.8 Hz, $CF_a\underline{F}_b$). ^{13}C NMR ($CDCl_3$): δ 21.5 (CH_3); 62.1 (t, J = 28.8 Hz, CH); 73.7 (t, J = 39.2 Hz, C≡); 78.9 (t, J = 6.9 Hz, HC≡); 111.6 (t, J = 240.0 Hz, CF_2); 127.0 (2 × CH_{ar}); 128.6 (2 × CH_{ar}); 129.4 (2 × CH_{ar}); 129.7 (2 × CH_{ar}); 131.3 (C_{ar}); 135.0 (C_{ar}); 136.9 (C_{ar}); 143.8 (C_{ar}). IR (ATR, cm^{-1}): *v* = 3270; 3236 (NH); 2952; 2916; 2133 (C≡C); 1598; 1494; 1441; 1327; 1308; 1162; 1118; 1086; 1066; 1014; 911; 843; 810; 796; 704. MS (ES-) *m/z* (%): 368/370 ($M-H^+$, 100). Anal. Calcd. for $C_{17}H_{14}ClF_2NO_2S$: C, 55.21; H, 3.82; N, 3.79. Found: C, 54.93; H, 3.69; N, 3.79.

4. Synthesis of *N*-[1-(4-chlorophenyl)-2-fluoro-4-phenylbut-1-en-3-yn-1-yl]-4-methylbenzenesulfonamide 12. To a solution containing 0.18 g (0.40 mmol, 1 equiv) of *N*-[1-(4-chlorophenyl)-2,2-difluoro-4-phenylbut-3-yn-1-yl]-4-methylbenzenesulfonamide **11a** in 10 mL of dry THF was added 0.18 g (1.20 mmol, 3 equiv) of DBU. The resulting mixture was

stirred at reflux temperature under a N_2-atmosphere for 15 hours. The reaction mixture was cooled to room temperature and poured in 25 mL of water and extracted with 3 x 25 mL of ethyl acetate. The organic phase was dried over $MgSO_4$ and after filtration the solvent was evaporated in vacuo. The crude product was purified by silica gel chromatography (hexane/EtOAc 4:1, R_f = 0.08). After recrystallization in cold diethyl ether, 0.15 g of pure (*E*)-*N*-[1-(4-chlorophenyl)-2-fluoro-4-phenylbut-1-en-3-yn-1-yl]-4-methylbenzenesulfonamide **12** (0.36 mmol, yield = 88%) was obtained as white crystals. Because of steric reasons, compound 12 is believed to occur as the *E*-isomer. M.p. = 145.3°C (diethyl ether). ^{1}H NMR ($CDCl_3$): δ 2.38 (3H, s, CH_3); 7.23 (2H, d, J = 8.3 Hz, 2 × CH_{ar}); 7.35 (2H, d, J = 8.8 Hz, 2 × CH_{ar}); 7.40-7.45 (5H, m, 5 × CH_{ar}); 7.49-7.53 (2H, m, 2 × CH_{ar}); 7.69 (2H, d, J = 8.3 Hz, 2 × CH_{ar}); 8.44 (1H, s(broad), NH). ^{19}F NMR ($CDCl_3$): δ –156.6 (1F, s, CF). ^{13}C NMR (acetone-d6): δ 20.7 (CH_3); 111.6 (d, J = 11.5 Hz, C≡); 114.9 (d, J = 17.3 Hz, C≡); 126.5 (d, J = 4.6 Hz, 2 × CH_{ar}); 126.8 (2 × CH_{ar}); 127.8 (d, J = 4.6 Hz, C_q); 127.9 (2 × CH_{ar}); 129.1 (2 × CH_{ar}); 129.2 (CH_{ar}); 129.8 (2 × CH_{ar}); 130.2 (C_{ar}); 130.5 (2 × CH_{ar}); 132.3 (C_{ar}); 132.9 (C_{ar}); 141.3 (C_{ar}); 143.9 (C_{ar}); 145.6 (d, J = 252.7 Hz, CF). IR (ATR, cm^{-1}): *v* = 3248 (NH); 3098; 2974; 2926; 2872; 2163 (C≡C); 1617; 1594; 1496; 1454; 1400; 1312; 1304; 1222; 1139; 1120; 1090; 1055; 1013; 813; 684. MS (ES-) *m/z* (%): 425/427 ($M-H^+$, 100).

5. Synthesis of 2-aryl-1-(arylsulfonyl)-3-fluoro-1*H*-pyrroles 15

2-(4-Chlorophenyl)-3-fluoro-1-[(4-methylphenyl)sulfonyl]-5-phenyl-1*H*-pyrrole

15a. To a solution containing 0.30 g (0.67 mmol, 1 equiv) of *N*-[1-(4-chlorophenyl)-2,2-difluoro-4-phenylbut-3-yn-1-yl]-4-methylbenzenesulfonamide **11a** in 6 mL of dry acetonitrile was added 0.020 g (0.067 mmol, 0.1 equiv) of $AuCl_3$. The mixture was stirred at room temperature under a N_2-atmosphere for 15 hours. Afterwards, 0.5 mL of Et_3N was added and the reaction mixture was filtered over a short plug of silica gel eluting with 50 mL of ethyl acetate. After evaporation of the solvent, the crude product was purified by silica gel chromatography (hexane/EtOAc 9:1, R_f = 0.24). After recrystallization in cold diethyl ether, 0.20 g of pure 2-(4-chlorophenyl)-3-fluoro-1-[(4-methylphenyl)sulfonyl]-5-phenyl-1*H*-pyrrole **15a** (0.46 mmol, yield = 69%) was obtained as white crystals. M.p. = 167.6°C. ^{1}H NMR ($CDCl_3$): δ 2.38 (3H, s, CH_3); 6.15 (1H, s, $CH_{pyrrole}$); 7.04 (2H, d, J = 8.3 Hz, 2 × CH_{ar}); 7.12 (2H, d, J = 8.3 Hz, 2 × CH_{ar}); 7.39-7.51 (9H, m, 9 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –152.8 (1F, s, CF). ^{13}C NMR ($CDCl_3$): δ 21.6 (CH_3); 109.2 (d, J = 20.8 Hz, $CH_{pyrrole}$); 121.1 (d, J =

20.8 Hz, N$\underline{C}_q$CF); 127.1 (2 × CH_{ar}); 127.7 (2 × CH_{ar}); 127.8 (C_{ar}); 128.0 (2 × CH_{ar}); 128.7 (CH_{ar}); 129.0 (2 × CH_{ar}); 129.6 (2 × CH_{ar}); 131.0 (2 × CH_{ar}); 132.2 (C_{ar}); 133.4 (C_{ar}); 134.0 (C_{ar}); 139.8 (d, J = 5.8 Hz, N$\underline{C}_q$CH); 145.0 (C_{ar}); 152.7 (d, J = 258.5 Hz, CF). IR (ATR, cm^{-1}): ν = 3061; 3033; 2921; 1616; 1595; 1490; 1417; 1398; 1380; 1192; 1176; 1168; 1140; 1089; 1059; 810; 760; 691. MS (ES+) *m/z* (%): 426/428 ($M+H^+$, 100). Anal. Calcd. for $C_{23}H_{17}ClFNO_2S$: C, 64.86; H, 4.02; N, 3.29. Found: C, 64.72; H, 3.87; N, 3.26.

3-Fluoro-1-[(4-methylphenyl)sulfonyl]-2,5-diphenyl-1*H*-pyrrole 15b. Flash chromatography (hexane/EtOAc 9:1, R_f = 0.20). Yield = 57%. M.p. = 164.3°C (diethyl ether). White crystals. ^{1}H NMR ($CDCl_3$): δ 2.35 (3H, s, CH_3); 6.14 (1H, s, $CH_{pyrrole}$); 7.08 (4H, s, 4 × CH_{ar}); 7.34-7.55 (10H, m, 10 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –153.4 (1F, s, CF). ^{13}C NMR ($CDCl_3$): δ 21.6 (CH_3); 109.2 (d, J = 21.9 Hz, $CH_{pyrrole}$); 122.2 (d, J = 20.8 Hz, N$\underline{C}_q$CF); 127.2 (2 × CH_{ar}); 127.7 (4 × CH_{ar}); 128.0 (CH_{ar}); 128.6 (CH_{ar}); 128.9 (2 × CH_{ar}); 129.3 (d, J = 3.5 Hz, C_{ar}); 129.6 (2 × CH_{ar}); 129.9 (2 × CH_{ar}); 132.4 (C_{ar}); 133.5 (C_{ar}); 139.3 (d, J = 6.9 Hz, N$\underline{C}_q$CH); 144.8 (C_{ar}); 152.5 (d, J = 257.3 Hz, CF). IR (ATR, cm^{-1}): ν = 3113; 3057; 1625; 1597; 1494; 1446; 1414; 1372; 1169; 1137; 1090; 1056; 754. MS (ES+) *m/z* (%): 392 ($M+H^+$, 100). Anal. Calcd. for $C_{23}H_{18}FNO_2S$: C, 70.57; H, 4.63; N, 3.58. Found: C, 70.23; H, 4.36; N, 3.58.

3-Fluoro-2-(4-methylphenyl)-1-[(4-methylphenyl)sulfonyl]-5-phenyl-1*H*-pyrrole 15c. Flash chromatography (hexane/EtOAc 9:1, R_f = 0.21). Yield = 50%. M.p. = 154.5°C (diethyl ether). White crystals. ^{1}H NMR ($CDCl_3$): δ 2.38 (3H, s, CH_3); 2.43 (3H, s, CH_3); 6.14 (1H, d, J = 1.1 Hz, $CH_{pyrrole}$); 7.09 (2H, d, J = 8.8 Hz, 2 × CH_{ar}); 7.11 (2H, d, J = 8.8 Hz, 2 × CH_{ar}); 7.27 (2H, d, J = 7.2 Hz, 2 × CH_{ar}); 7.39-7.44 (5H, m, 5 × CH_{ar}); 7.47-7.52 (2H, m, 2 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –153.9 (1F, s, CF). ^{13}C NMR ($CDCl_3$): δ 21.4 (CH_3); 21.6 (CH_3); 109.3 (d, J = 20.8 Hz, $CH_{pyrrole}$); 122.4 (d, J = 20.8 Hz, N$\underline{C}_q$CF); 126.4 (d, J = 3.5 Hz, C_{ar}); 127.2 (2 × CH_{ar}); 127.7 (2 × CH_{ar}); 128.5 (3 × CH_{ar}); 128.9 (2 × CH_{ar}); 129.6 (2 × CH_{ar}); 129.8 (2 × CH_{ar}); 132.5 (C_{ar}); 133.6 (C_{ar}); 138.0 (C_{ar}); 139.0 (d, J = 5.8 Hz, N$\underline{C}_q$CH); 144.7 (C_{ar}); 152.3 (d, J = 256.1 Hz, CF). IR (ATR, cm^{-1}): ν = 3115; 3052; 3032; 2965; 2923; 2864; 1623; 1597; 1507; 1493; 1482; 1447; 1417; 1404; 1375; 1261; 1191; 1171; 1139; 1090; 1062; 1023; 812; 760; 697. MS (ES+) *m/z* (%): 406 ($M+H^+$, 100). Anal. Calcd. for $C_{24}H_{20}FNO_2S$: C, 71.09; H, 4.97; N, 3.45. Found: C, 70.74; H, 4.77; N, 3.33.

3-Fluoro-2-(4-methoxyphenyl)-5-phenyl-1-(phenylsulfonyl)-1*H*-pyrrole 15d. Flash chromatography (hexane/EtOAc 9:1, R_f = 0.13). Yield = 55%. Yellow viscous oil. ^{1}H NMR ($CDCl_3$): δ 3.88 (3H, s, MeO); 6.16 (1H, s, $CH_{pyrrole}$); 6.98 (2H, d, J = 8.8 Hz, 2 × CH_{ar}); 7.20

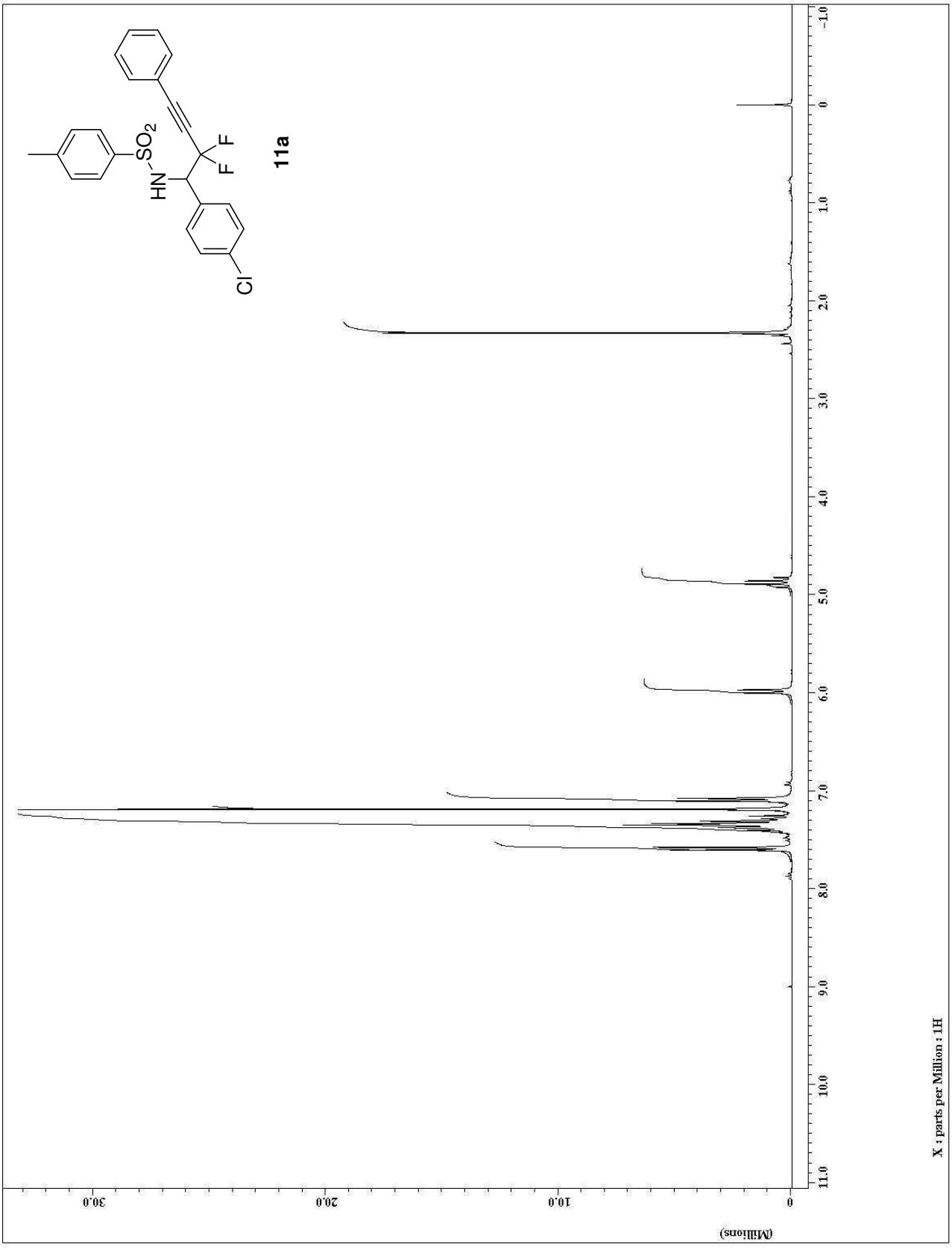
(2H, d, J = 7.7 Hz, 2 × CH_{ar}); 7.33 (2H, t, J = 7.7 Hz, 2 × CH_{ar}); 7.39-7.44 (5H, m, 5 × CH_{ar}); 7.48-7.54 (3H, m, 3 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –154.6 (1F, s, CF). ^{13}C NMR ($CDCl_3$): δ 55.3 (MeO); 109.3 (d, J = 20.8 Hz, $CH_{pyrrole}$); 113.2 (2 × CH_{ar}); 121.5 (d, J = 3.5 Hz, C_{ar}); 122.1 (d, J = 20.8 Hz, N$\underline{C}_q$CF); 127.1 (2 × CH_{ar}); 127.7 (2 × CH_{ar}); 128.3 (2 × CH_{ar}); 128.5 (CH_{ar}); 129.4 (2 × CH_{ar}); 131.3 (2 × CH_{ar}); 132.6 (C_{ar}); 133.7 (CH_{ar}); 136.5 (C_{ar}); 138.5 (d, J = 6.9 Hz, N$\underline{C}_q$CH); 152.0 (d, J = 255.0 Hz, CF); 159.5 (C_{ar}). IR (ATR, cm^{-1}): ν = 2930; 1604; 1508; 1448; 1409; 1376; 1294; 1251; 1176; 1146; 1090; 1028; 911; 834; 758; 732; 687. MS (ES+) *m/z* (%): 408 ($M+H^+$, 100).

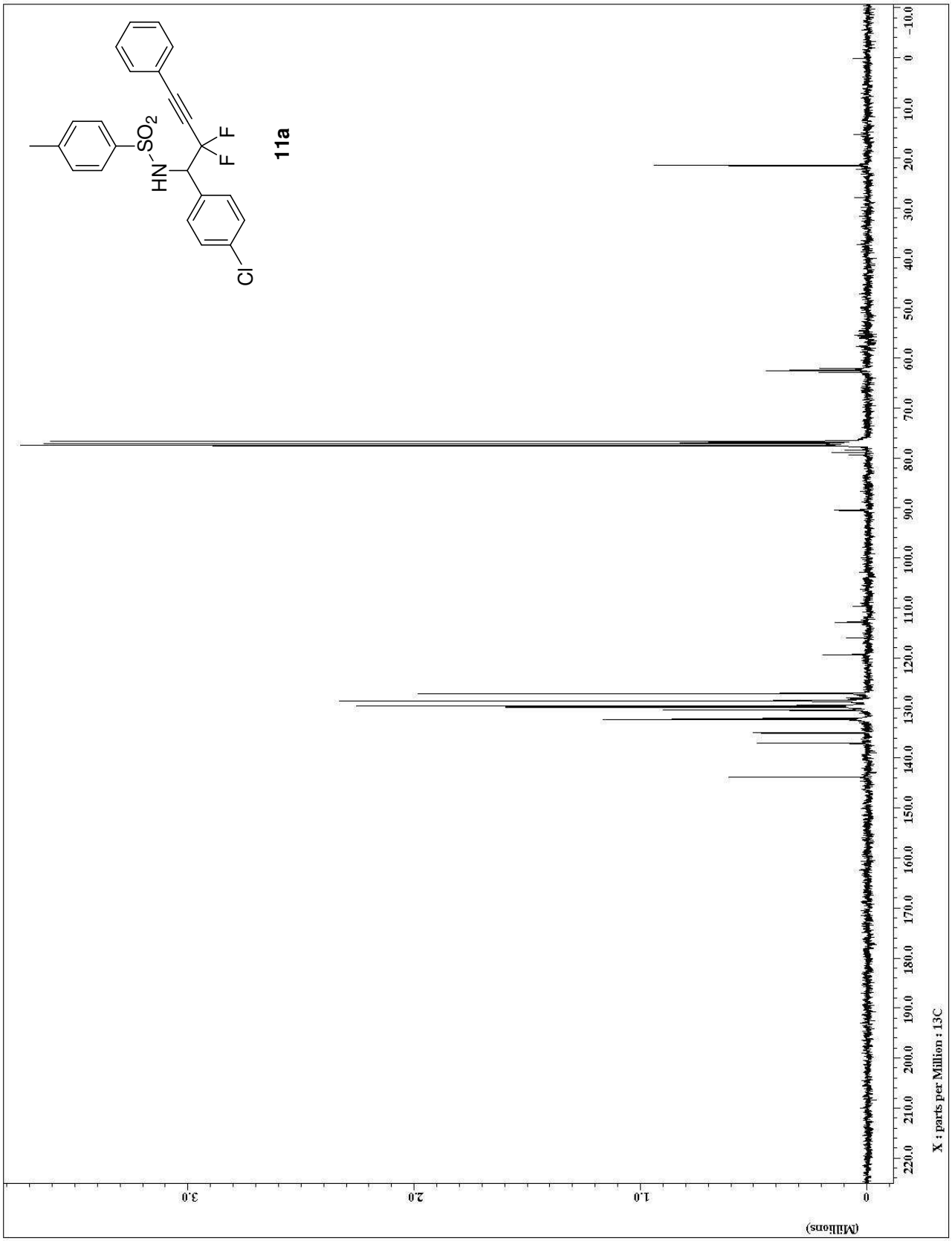
2-(4-Chlorophenyl)-3-fluoro-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrrole 15e. Compound **15e** was prepared analogously from amine **11e** respecting a longer reaction time of 3 days. Flash chromatography (hexane/EtOAc 9:1, R_f = 0.22). Yield = 63%. M.p. = 116.9°C (hexane). White crystals. ^1H NMR ($CDCl_3$): δ 2.38 (3H, s, CH_3); 6.22 (1H, dd, J = 3.9 Hz, 1.1 Hz, CFC$\underline{H}_{pyrrole}$); 7.14 (2H, d, J = 8.3 Hz, 2 × CH_{ar}); 7.19 (2H, d, J = 8.3 Hz, 2 × CH_{ar}); 7.25 (2H, d, J = 8.8 Hz, 2 × CH_{ar}); 7.28 (1H, dd, J = 5.5 Hz, 3.9 Hz, NCH); 7.35 (2H, d, J = 8.8 Hz, 2 × CH_{ar}). ^{19}F NMR ($CDCl_3$): δ –155.5 (1F, d, J = 5.5 Hz, CF). ^{13}C NMR ($CDCl_3$): δ 21.6 (CH_3); 103.6 (d, J = 19.6 Hz, CFC$H_{pyrrole}$); 117.2 (d, J = 24.2 Hz, N$\underline{C}_q$CF); 121.3 (d, J = 4.6 Hz, N$CH_{pyrrole}$); 125.6 (d, J = 3.5 Hz, C_{ar}); 127.0 (2 × CH_{ar}); 127.9 (2 × CH_{ar}); 129.5 (2 × CH_{ar}); 132.4 (2 × CH_{ar}); 134.6 (C_{ar}); 134.7 (C_{ar}); 145.2 (C_{ar}); 151.4 (d, J = 253.8 Hz, CF). IR (ATR, cm^{-1}): ν = 3148; 1615; 1495; 1374; 1167; 1117; 834. MS (ES+) *m/z* (%): 350/352 ($M+H^+$, 100). Anal. Calcd. for $C_{17}H_{13}ClFNO_2S$: C, 58.37; H, 3.75; N, 4.00. Found: C, 58.61; H, 3.83; N, 4.23.

6. Synthesis of 2-(4-chlorophenyl)-3-fluoro-5-phenyl-1*H*-pyrrole 16. In a flask of 25 mL, 0.13 g (0.31 mmol, 1 equiv) of 2-(4-chlorophenyl)-3-fluoro-1-[(4-methylphenyl)sulfonyl]-5-phenyl-1*H*-pyrrole **15a** was added to a solution of 0.39 g (9.75 mmol, 32 equiv) NaOH in 10 mL of EtOH and stirred at reflux temperature for 3 hours. The solution was concentrated in vacuo and the residue was dissolved in 10 mL of dichloromethane and washed with 10 mL of water. The organic layer was dried ($MgSO_4$) and concentrated in vacuo to give 0.06 g of 2-(4-chlorophenyl)-3-fluoro-5-phenyl-1*H*-pyrrole **16** (0.22 mmol, yield = 75%) after flash chromatography (hexane/EtOAc 9:1, R_f = 0.30). Red viscous oil. ^1H NMR ($CDCl_3$): δ 6.36 (1H, d, J = 2.8 Hz, $CH_{pyrrole}$); 7.23-7.30 (1H, m, CH_{ar}); 7.34-7.43 (4H, m, 4 × CH_{ar}); 7.45-7.51 (4H, m, 4 × CH_{ar}); 8.06 (1H, s(broad), NH). ^{19}F NMR ($CDCl_3$): δ –159.1 (1F, s, CF). ^{13}C NMR ($CDCl_3$): δ 96.7 (d, J = 16.2 Hz, $CH_{pyrrole}$); 114.5 (d, J = 19.6 Hz, N$\underline{C}_q$CF); 123.8 (2 ×

CH_{ar}); 125.1 (2 × CH_{ar}); 127.3 (CH_{ar}); 128.6 (d, J = 4.6 Hz, C_{ar}); 129.2 (2 × CH_{ar}); 129.3 (2 × CH_{ar}); 129.3 (C_{ar}); 129.4 (C_{ar}); 131.6 (d, J = 9.2 Hz, N$\underline{C}_q$CH); 150.5 (d, J = 245.8 Hz, CF). IR (ATR, cm^{-1}): ν = 3444; 3064; 1647; 1614; 1523; 1493; 1458; 1400; 1291; 1188; 1092; 1013; 907; 827; 754; 732; 692. MS (ES-) *m*/*z* (%): 270/272 ($M\text{-}H^+$, 100).

III. Copies of ^{1}H NMR and ^{13}C NMR spectra

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F F
Cl
(Millions)
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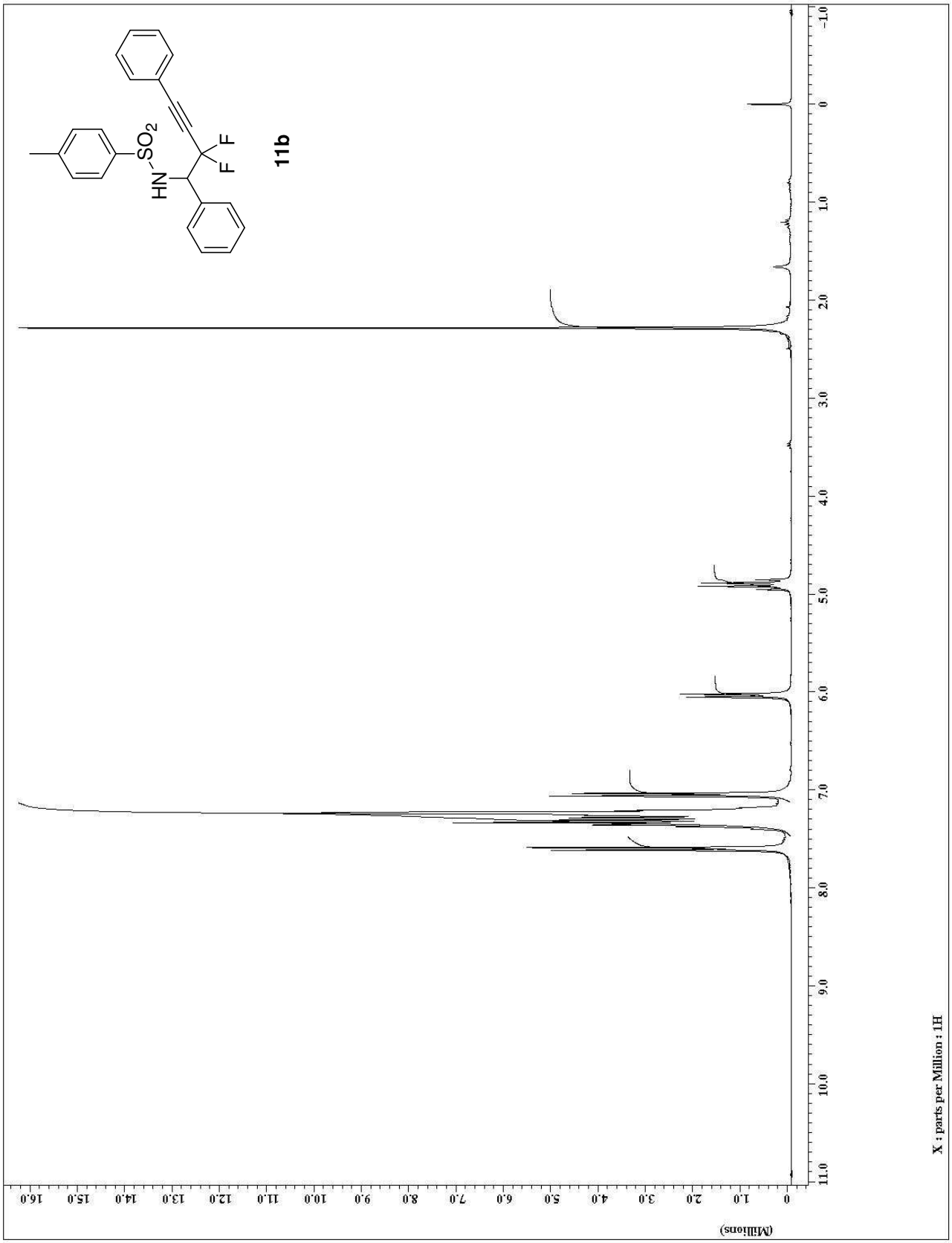
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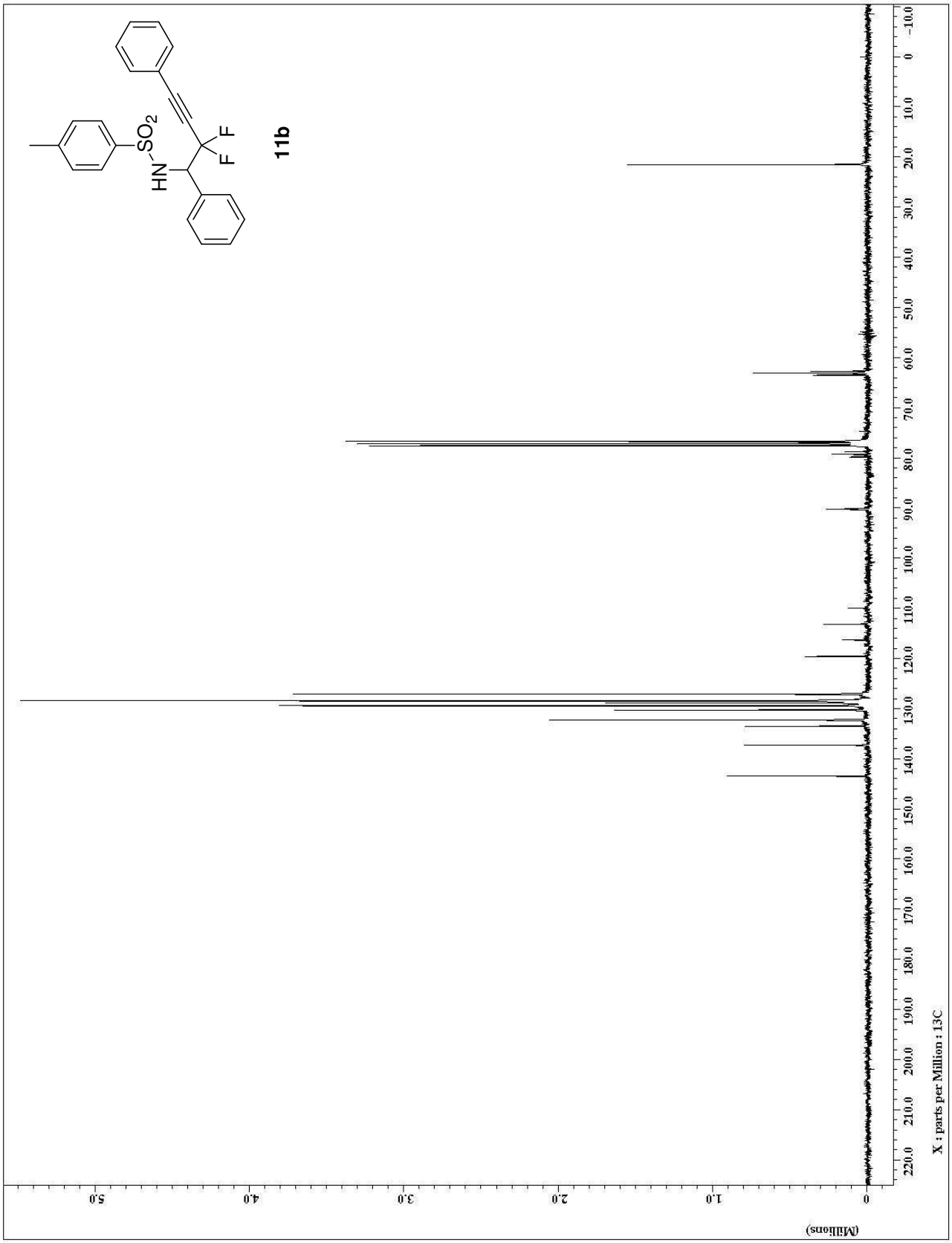
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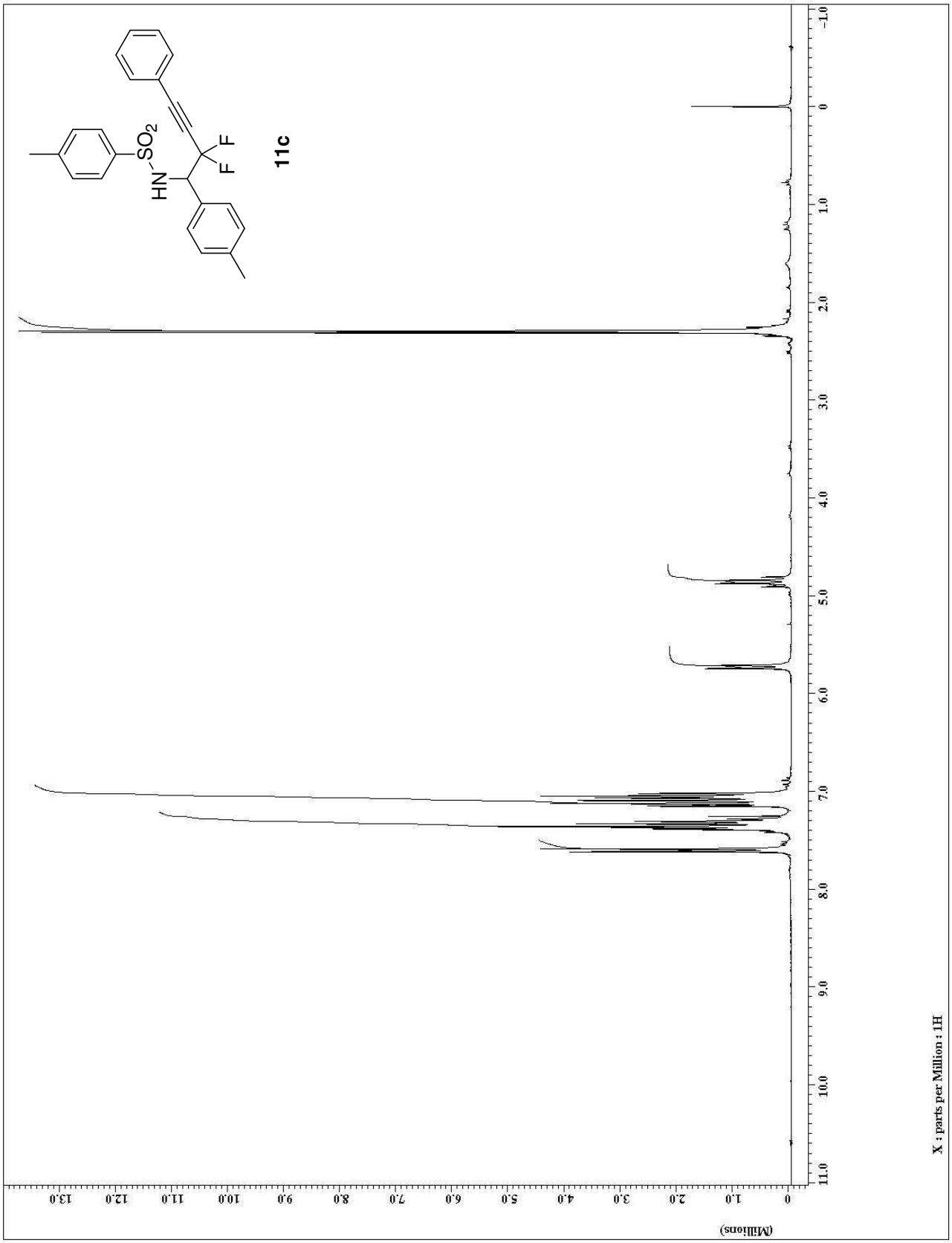
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SO2
F
F
(Millions)
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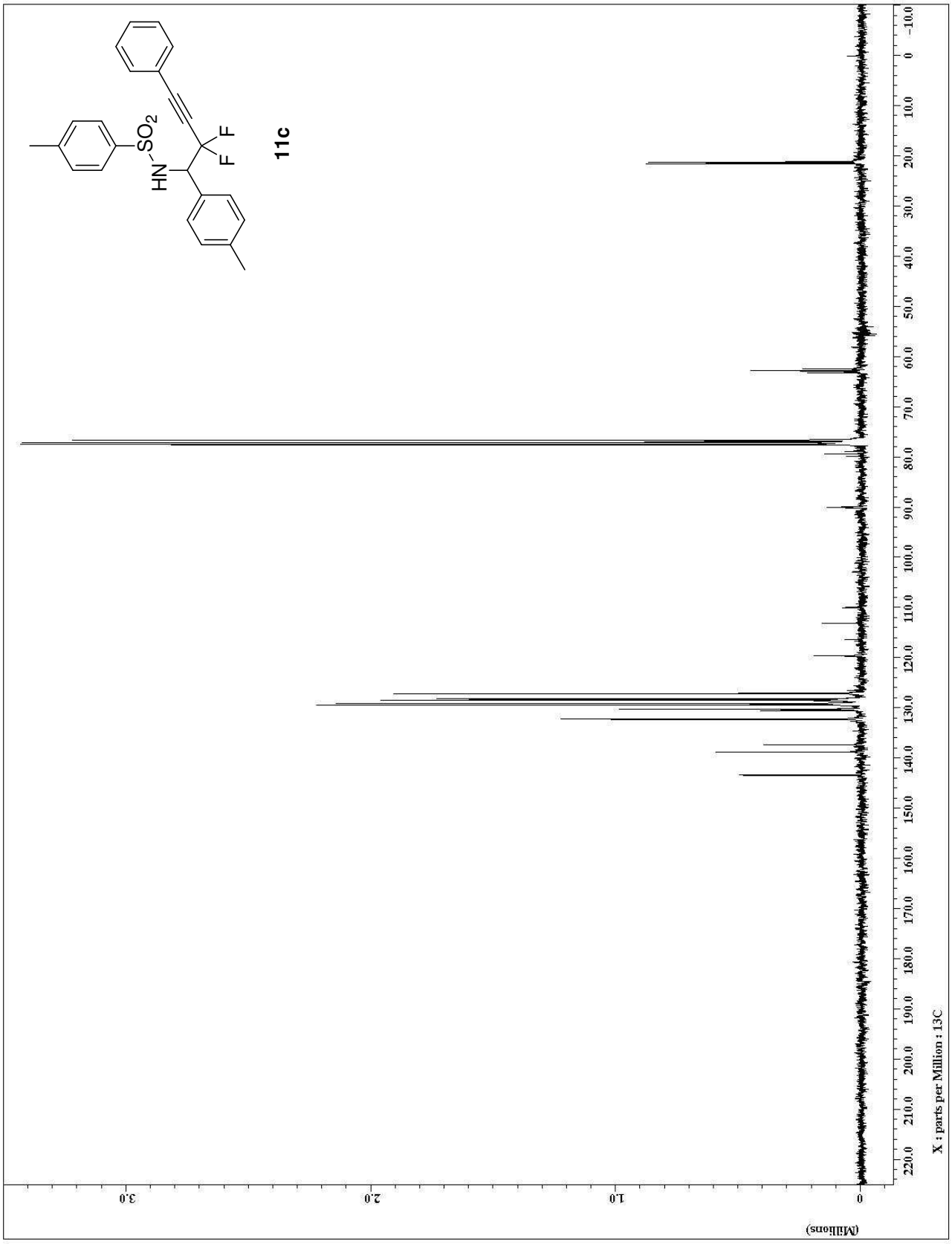
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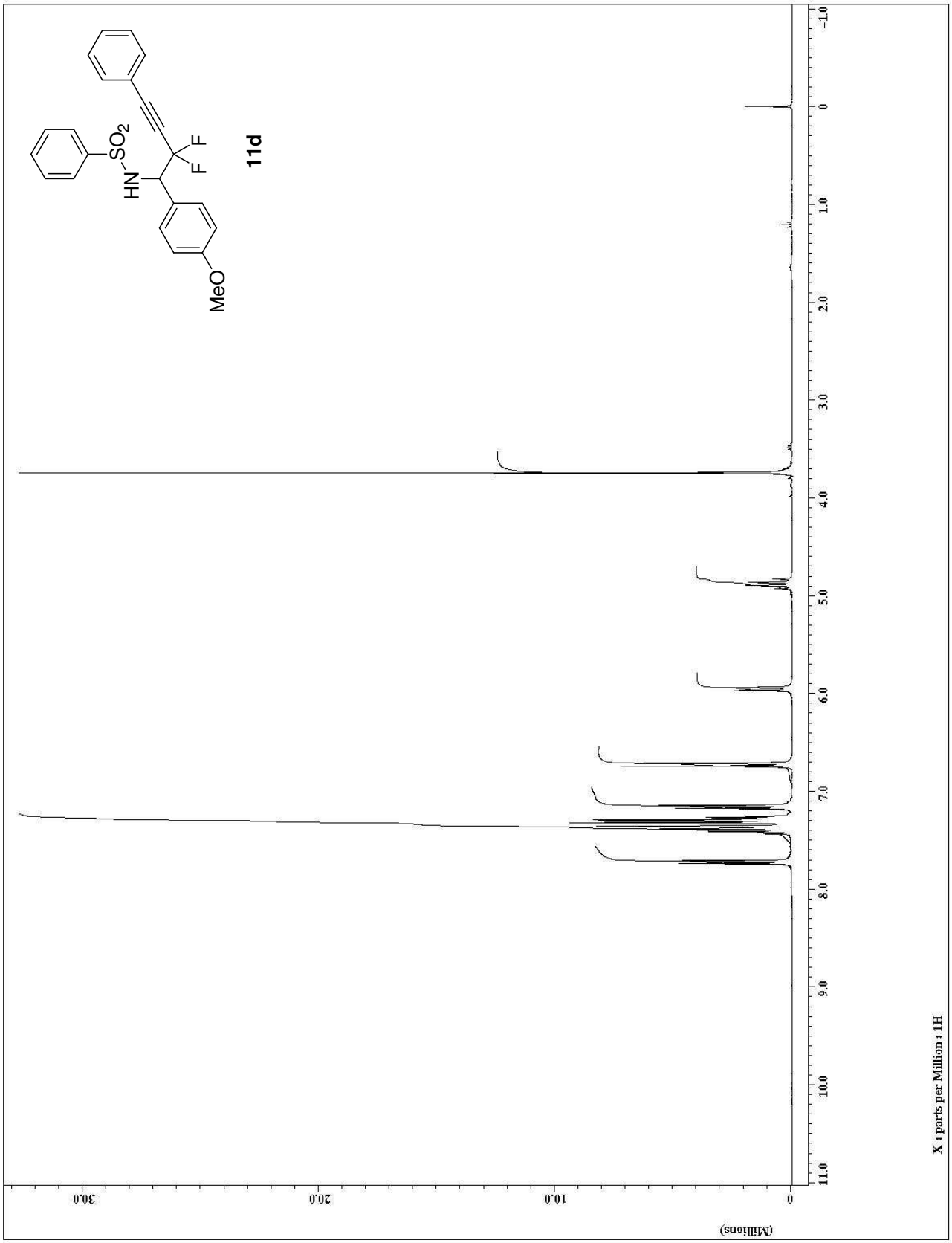
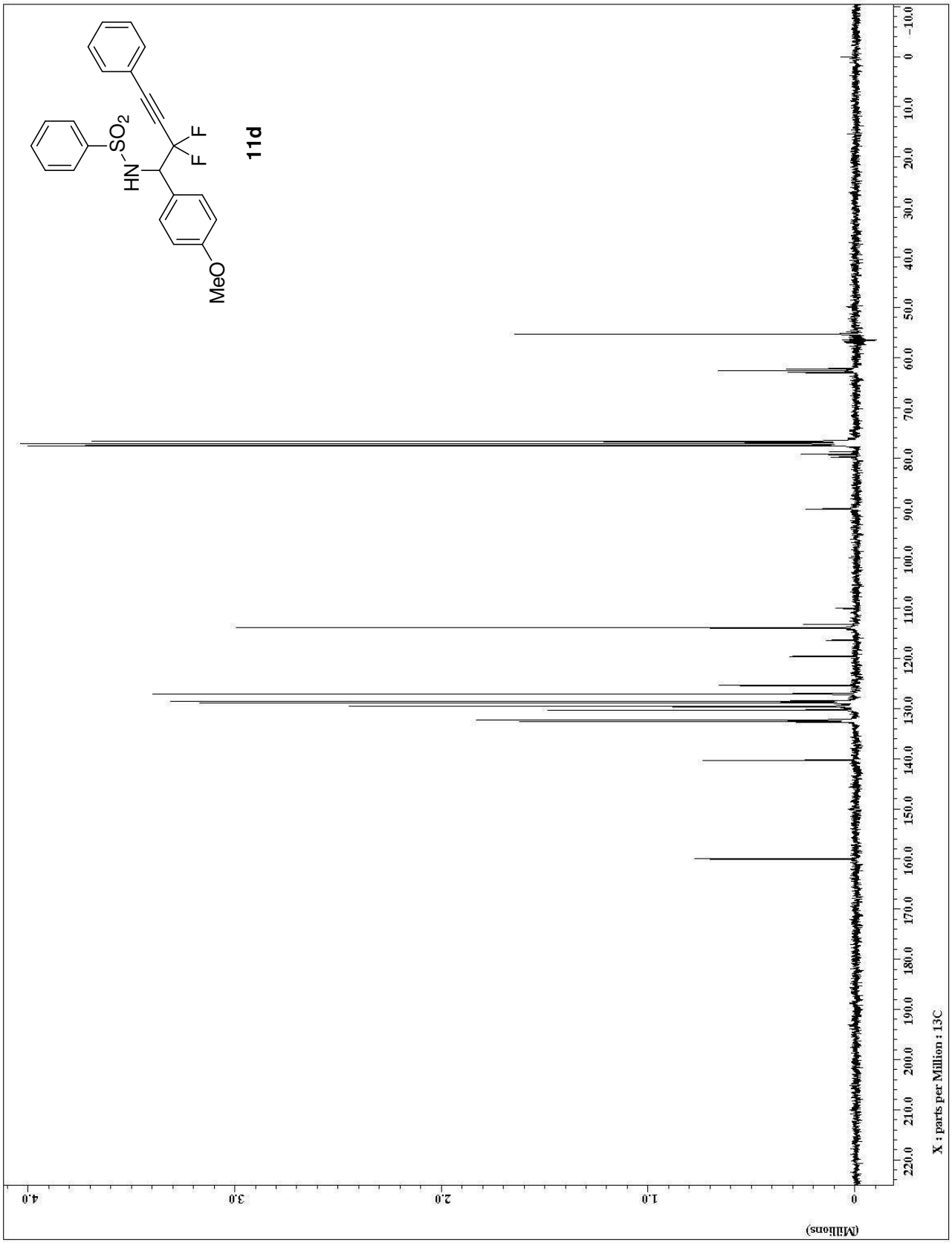
SO2
(Millions)
X : parts per Million : 13C


11d
HN
SO2
F
F
MeO
(Millions)
X : parts per Million : 1H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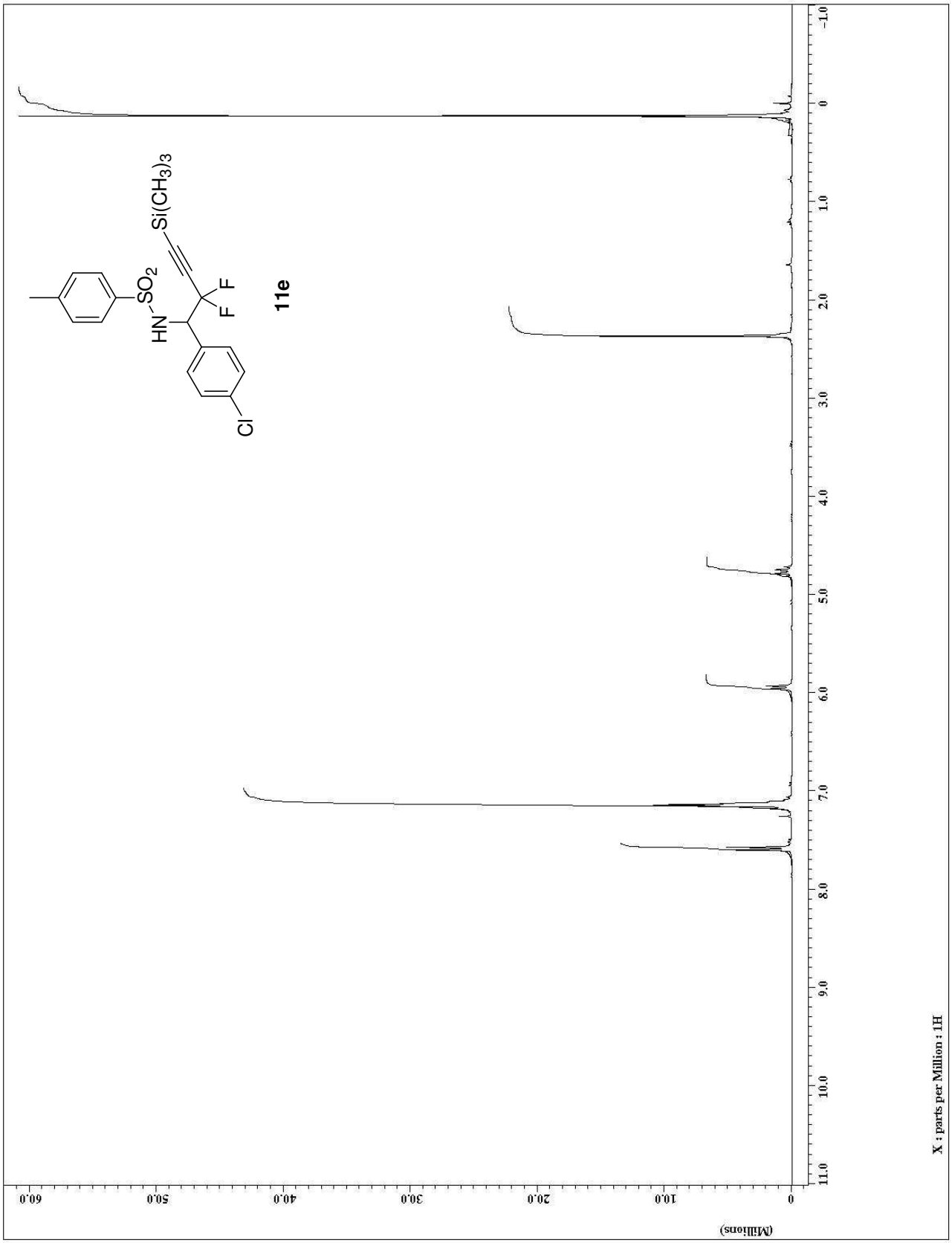
HN
SO2
F
F
MeO
(Millions)
X : parts per Million : 13C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HN
F F
Cl
11e
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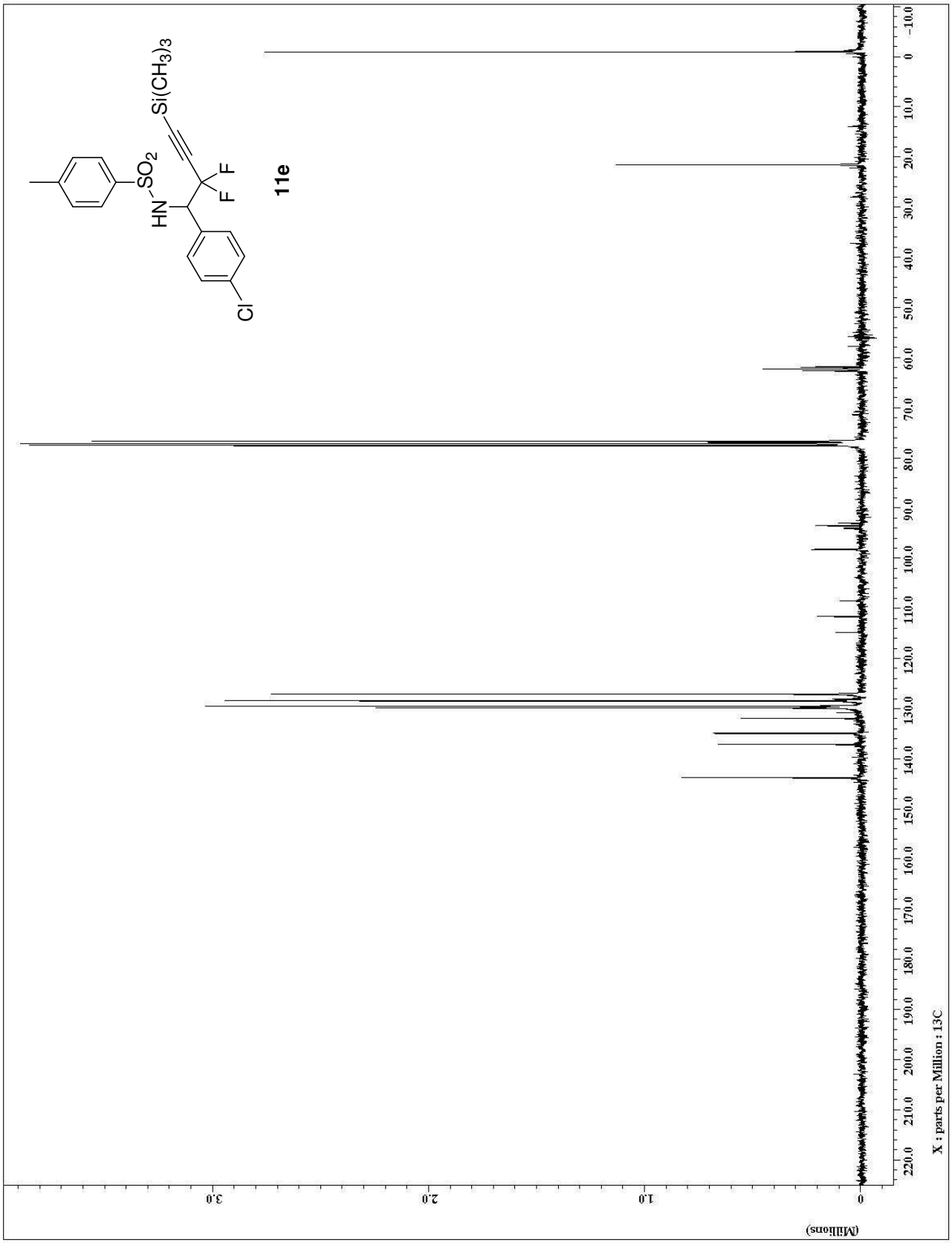
X : parts per Million : 1H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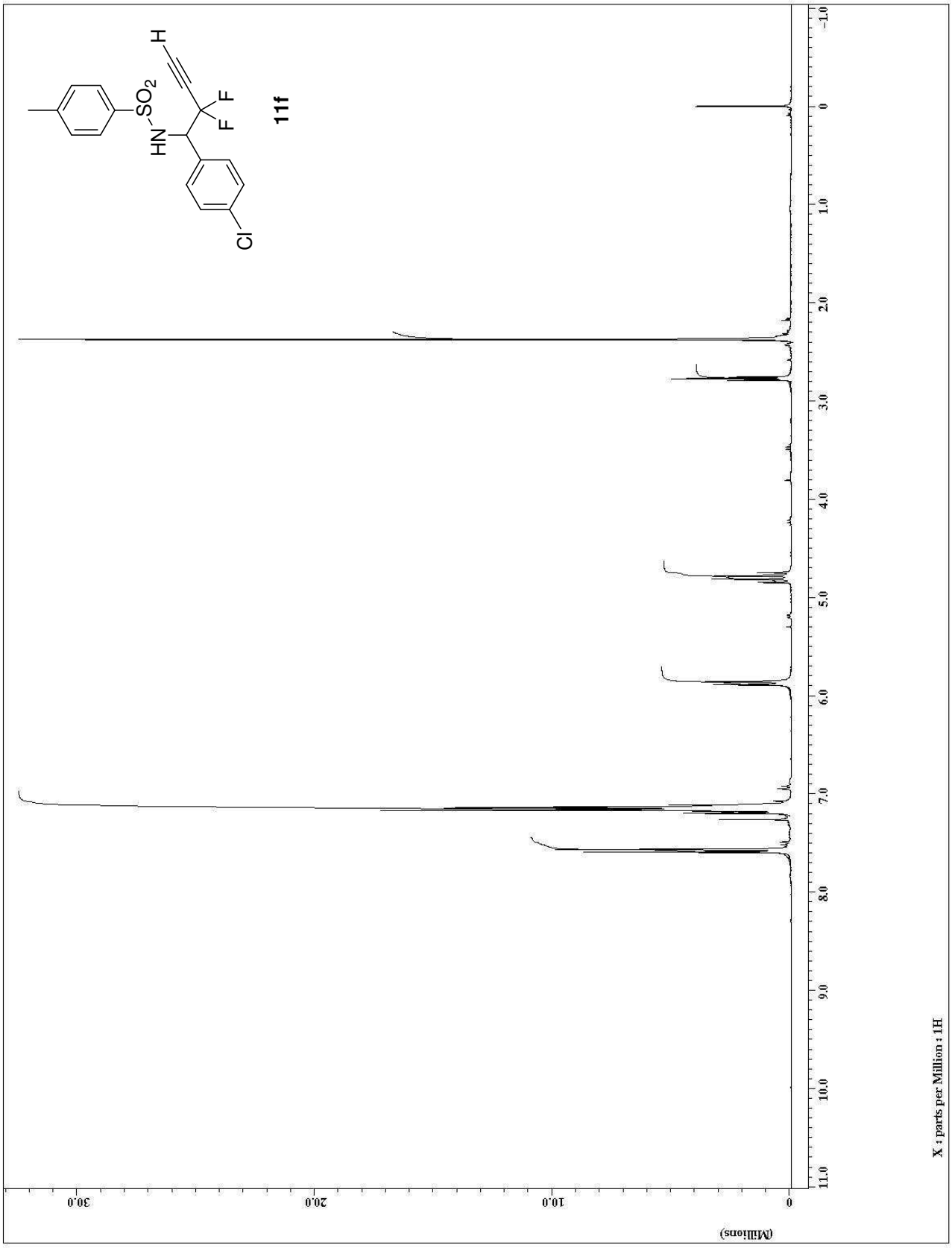
SO2
HN
F F
Cl
11e
(Millions)
X : parts per Million : 13C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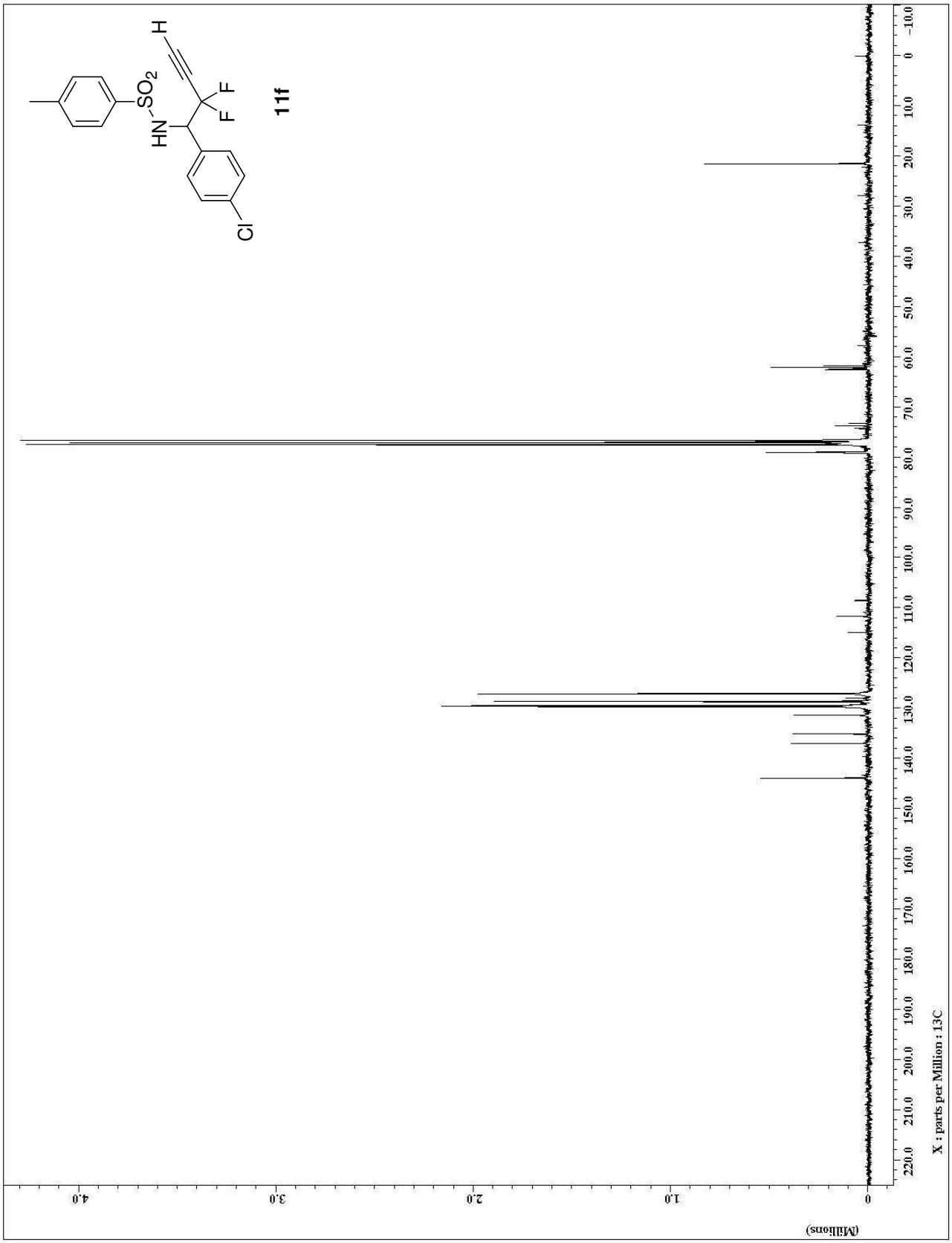
(Millions)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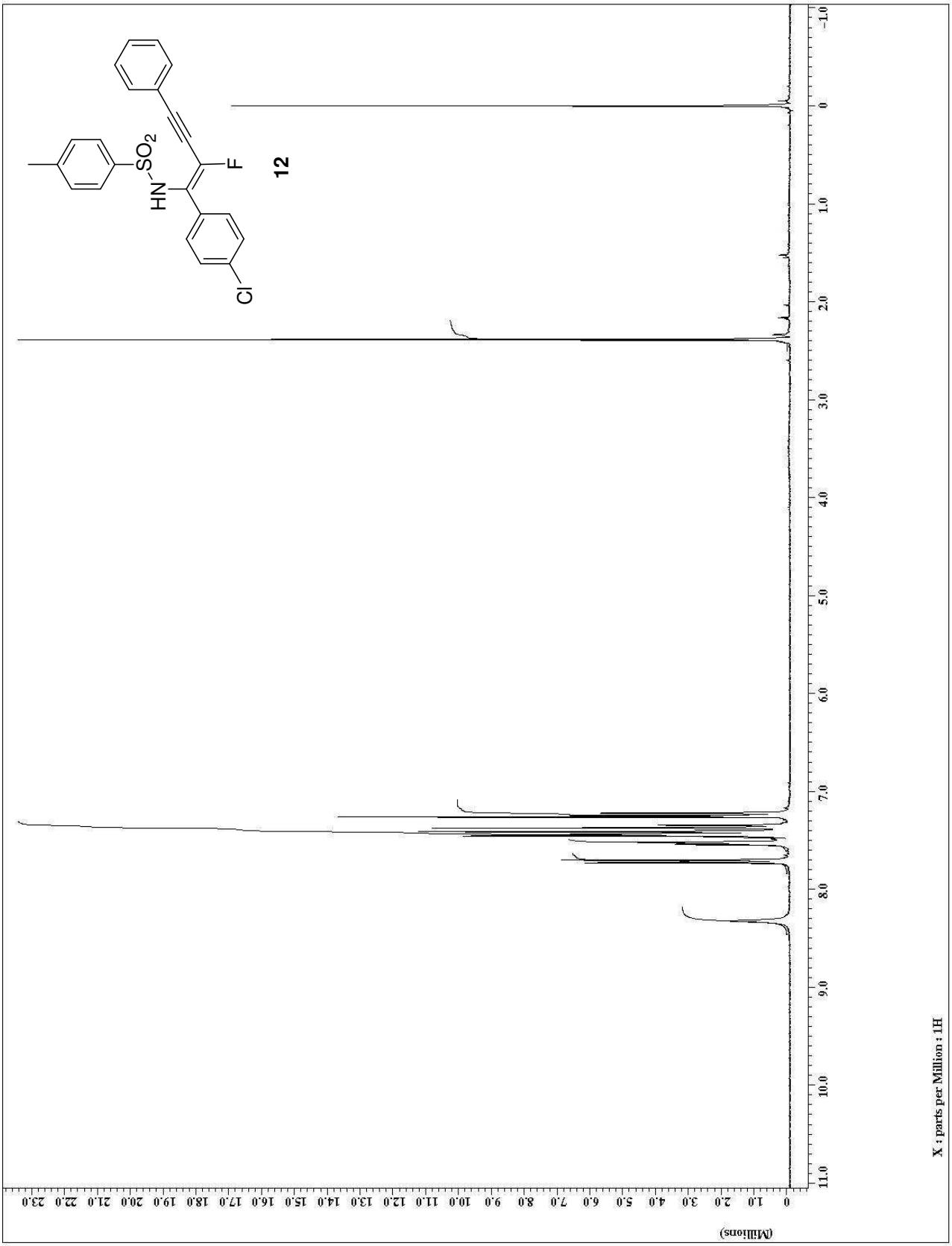
H
SO2
HN
F
F
Cl
(Millions)
X : parts per Million : 13C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SO2
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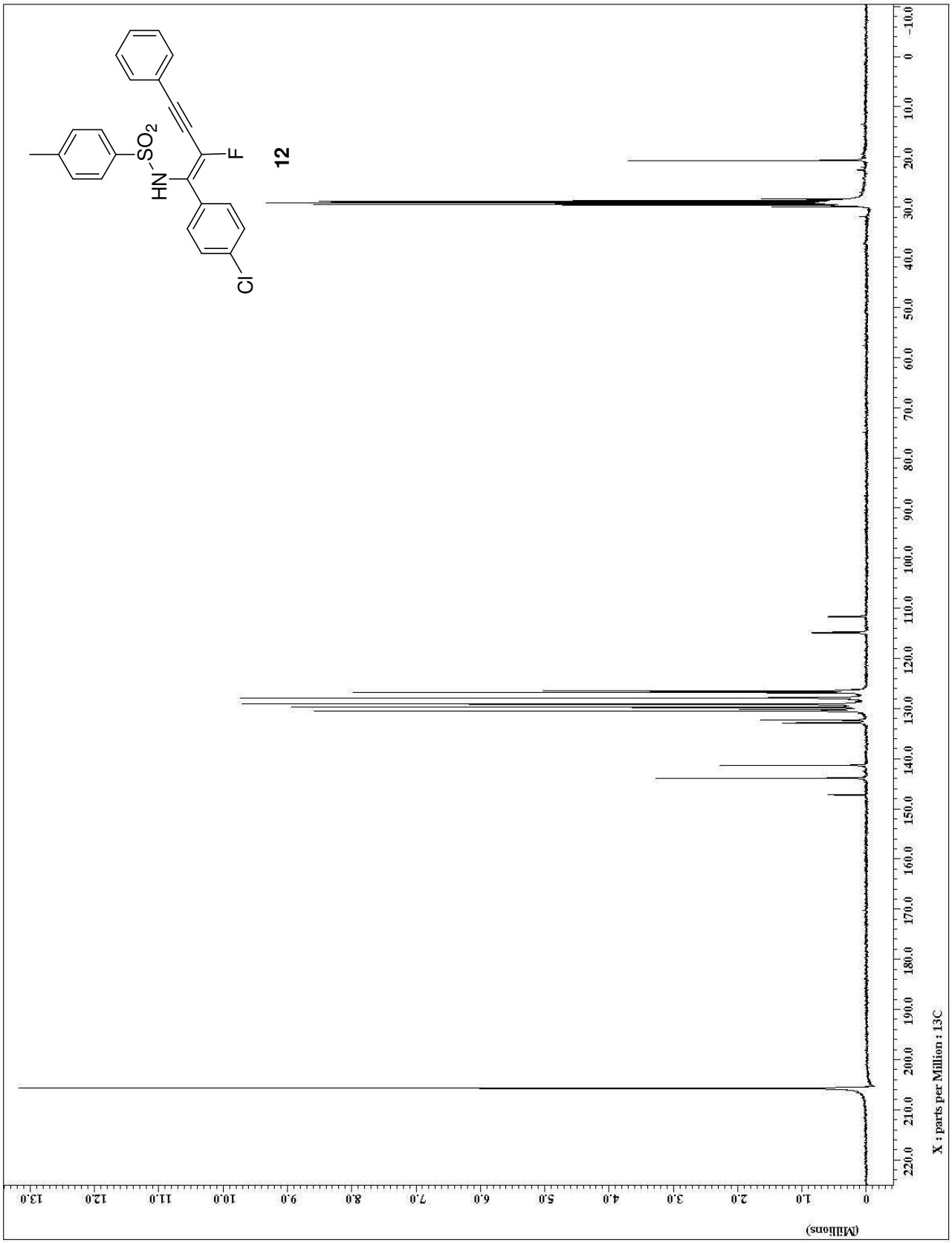
(Millions)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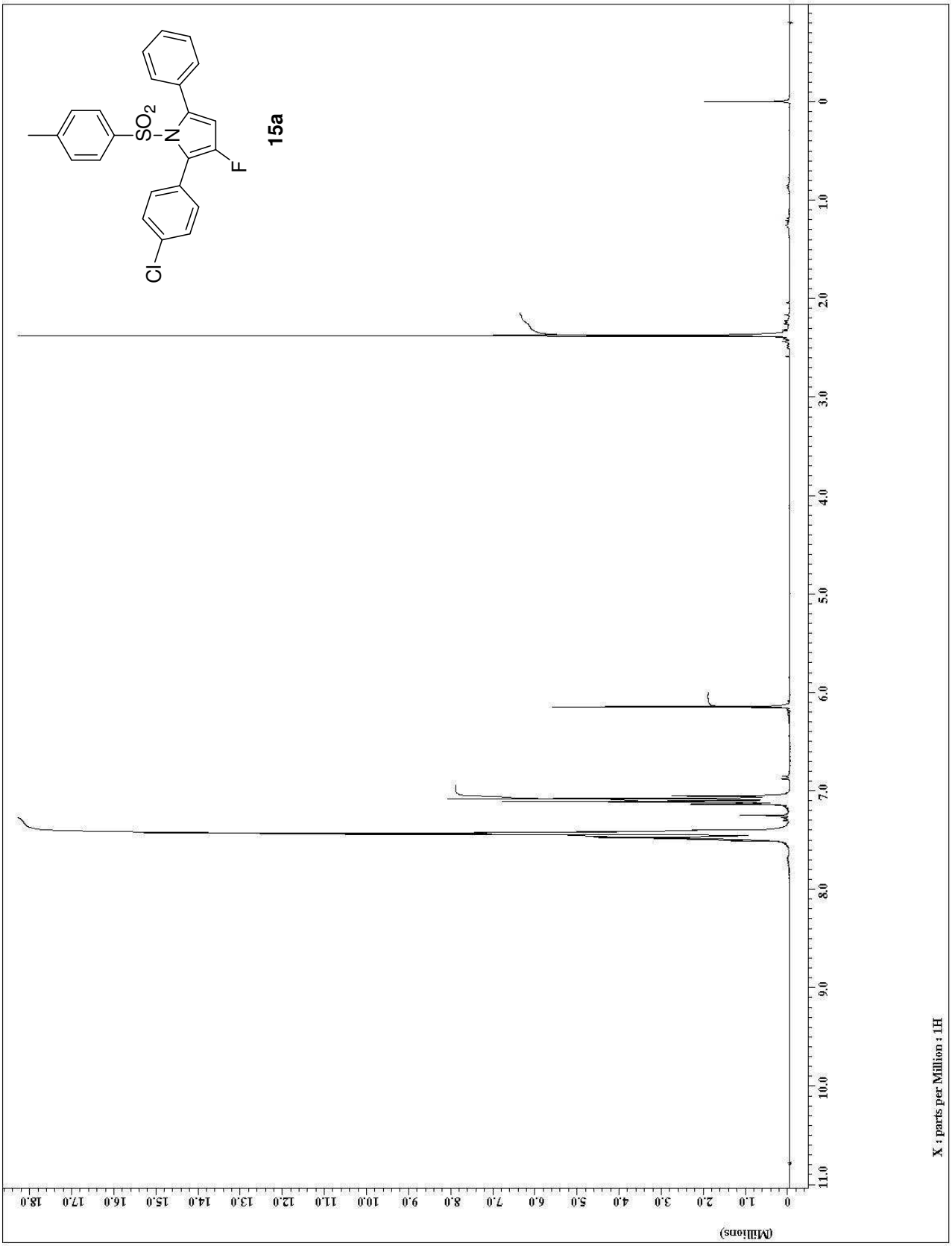
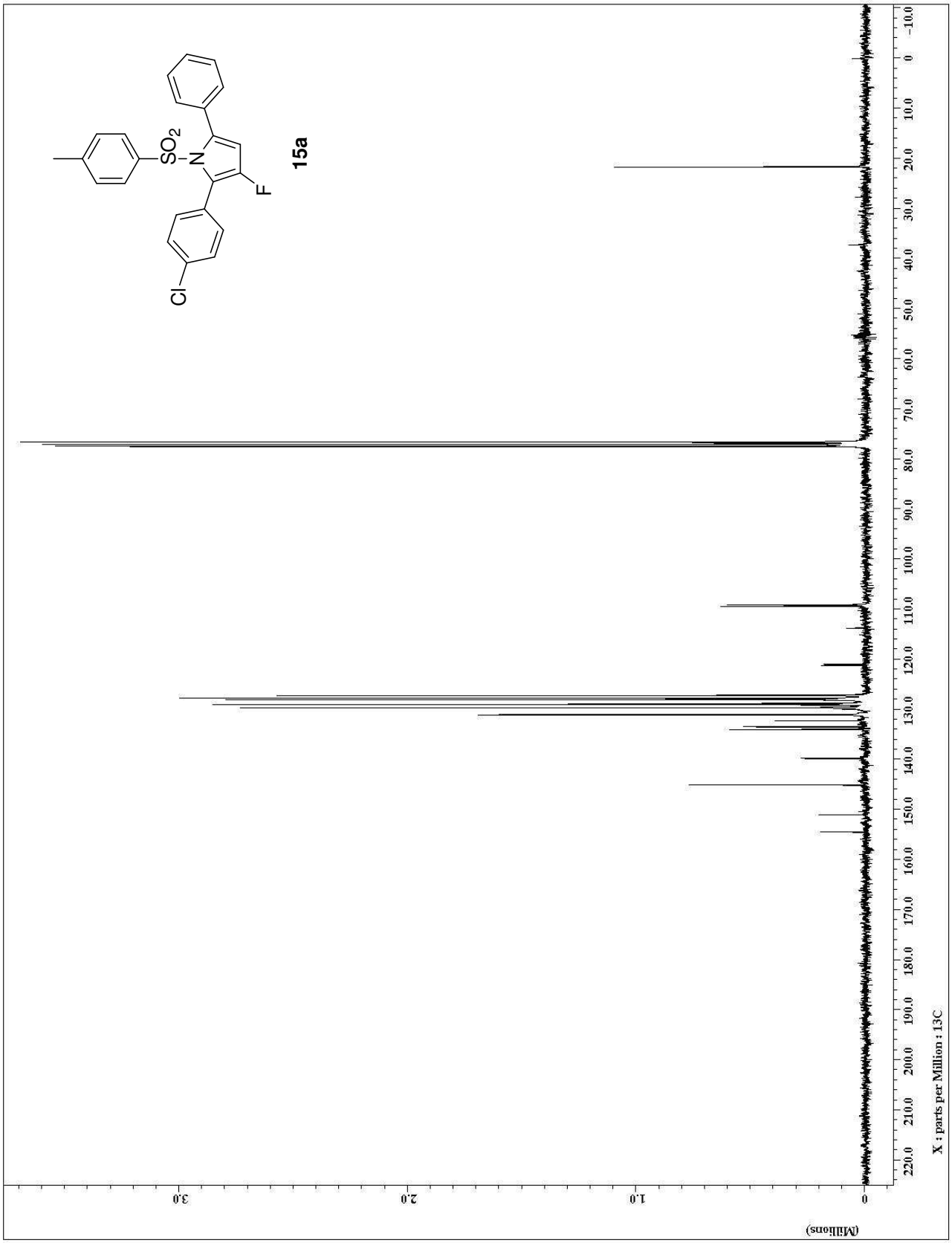
SO2
F
Cl
(Millions)
X : parts per Million : 13C


15a
X : parts per Million : 1H
(Millions)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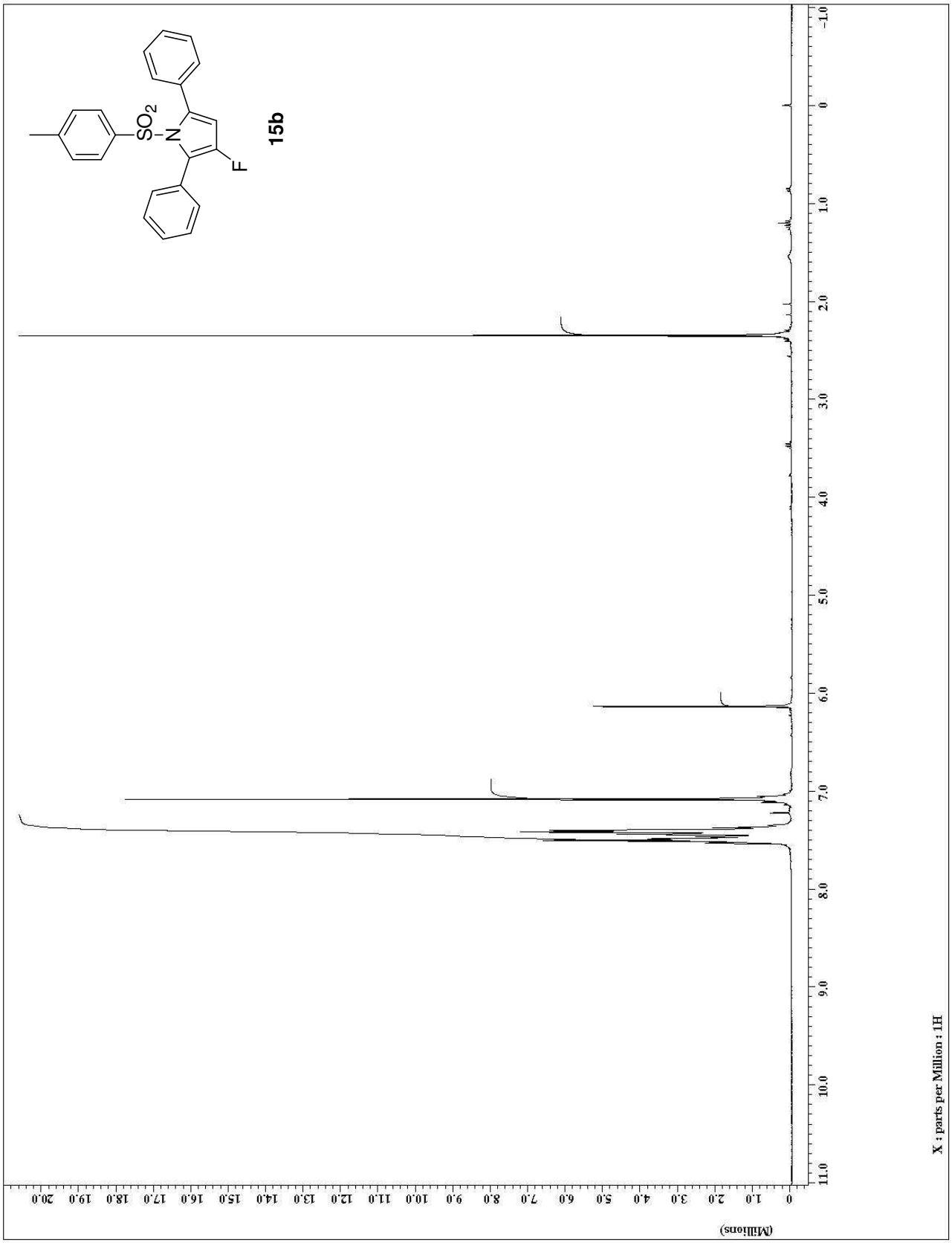
N
F
Cl
(Millions)
X : parts per Million : 13C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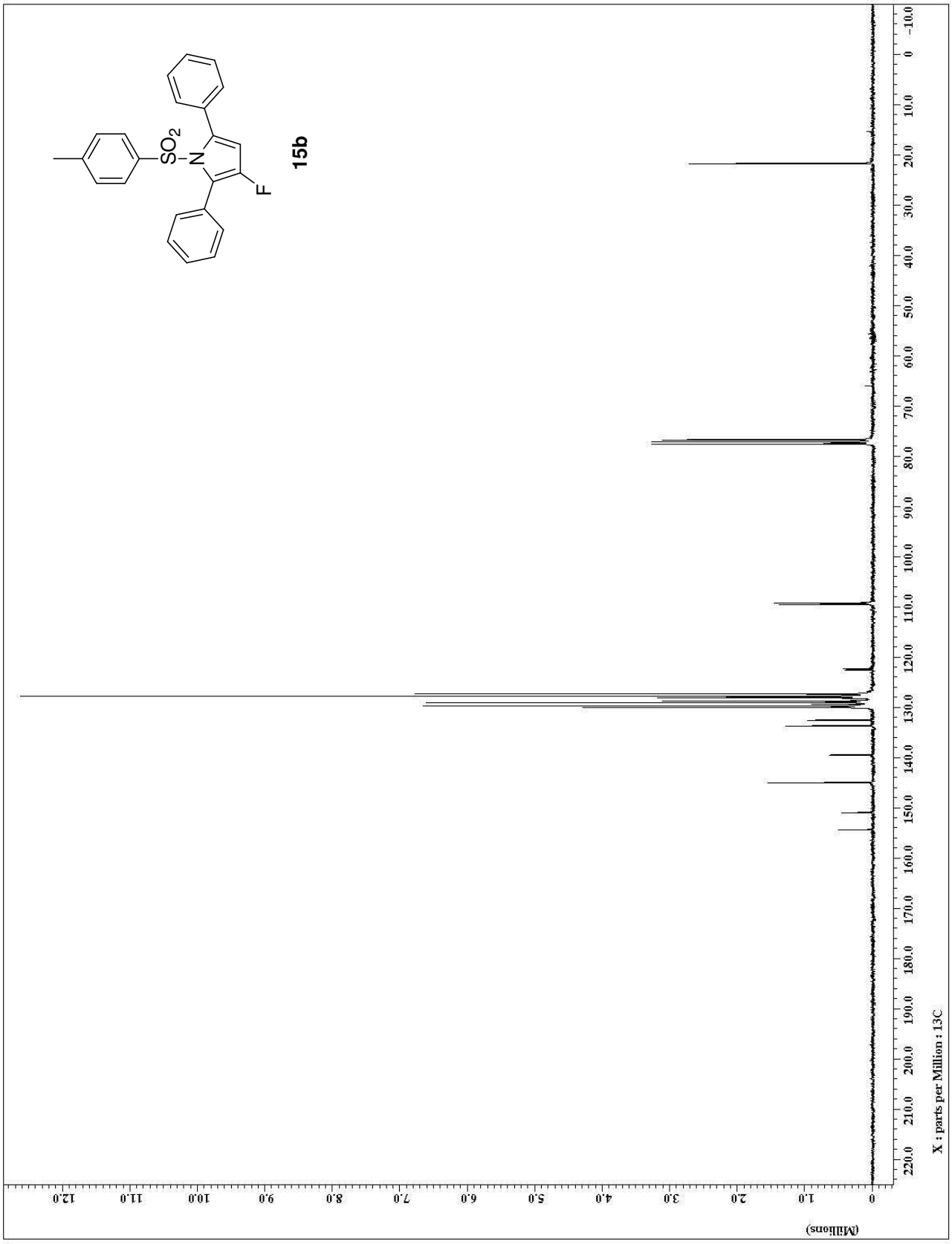
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(Millions)
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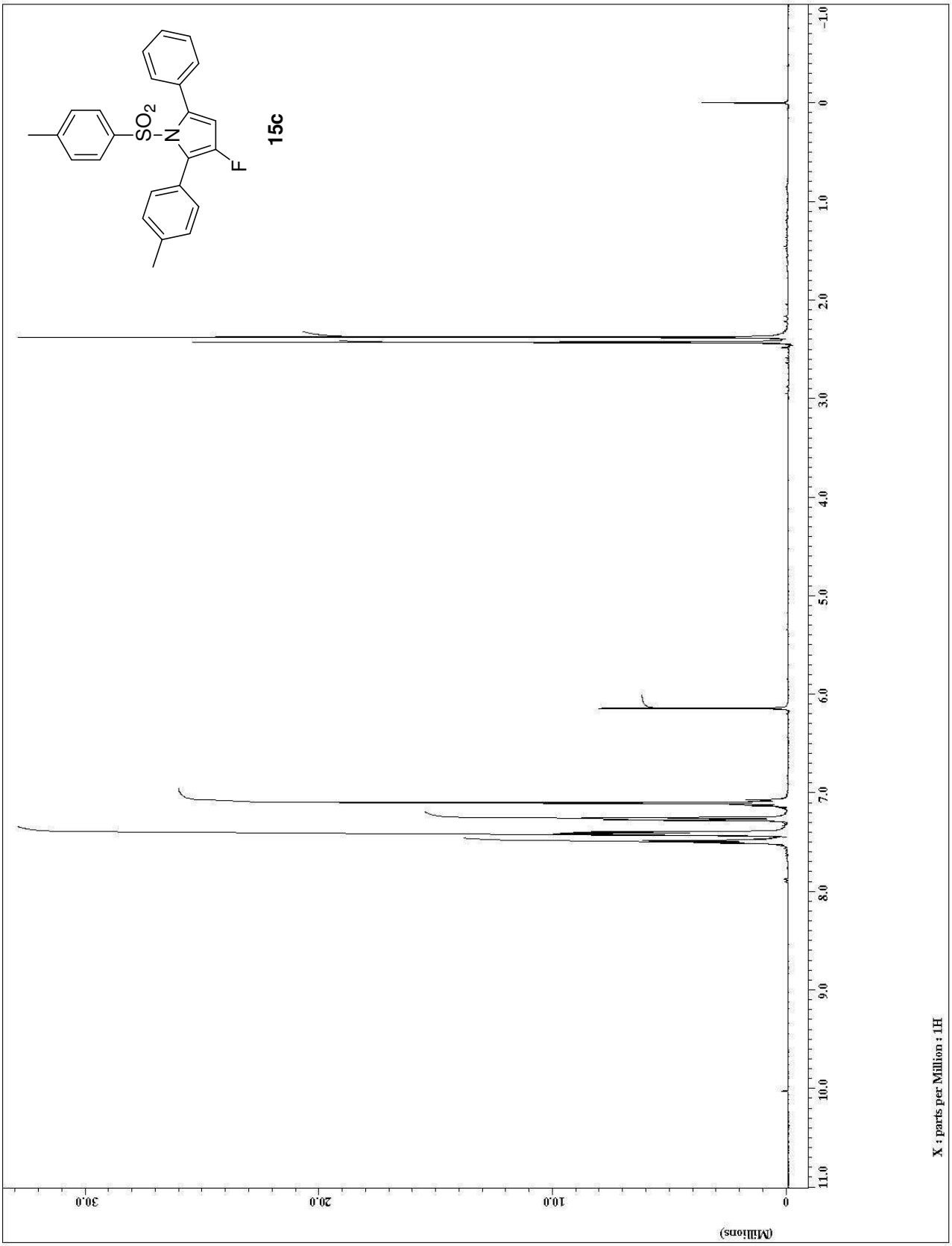
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F
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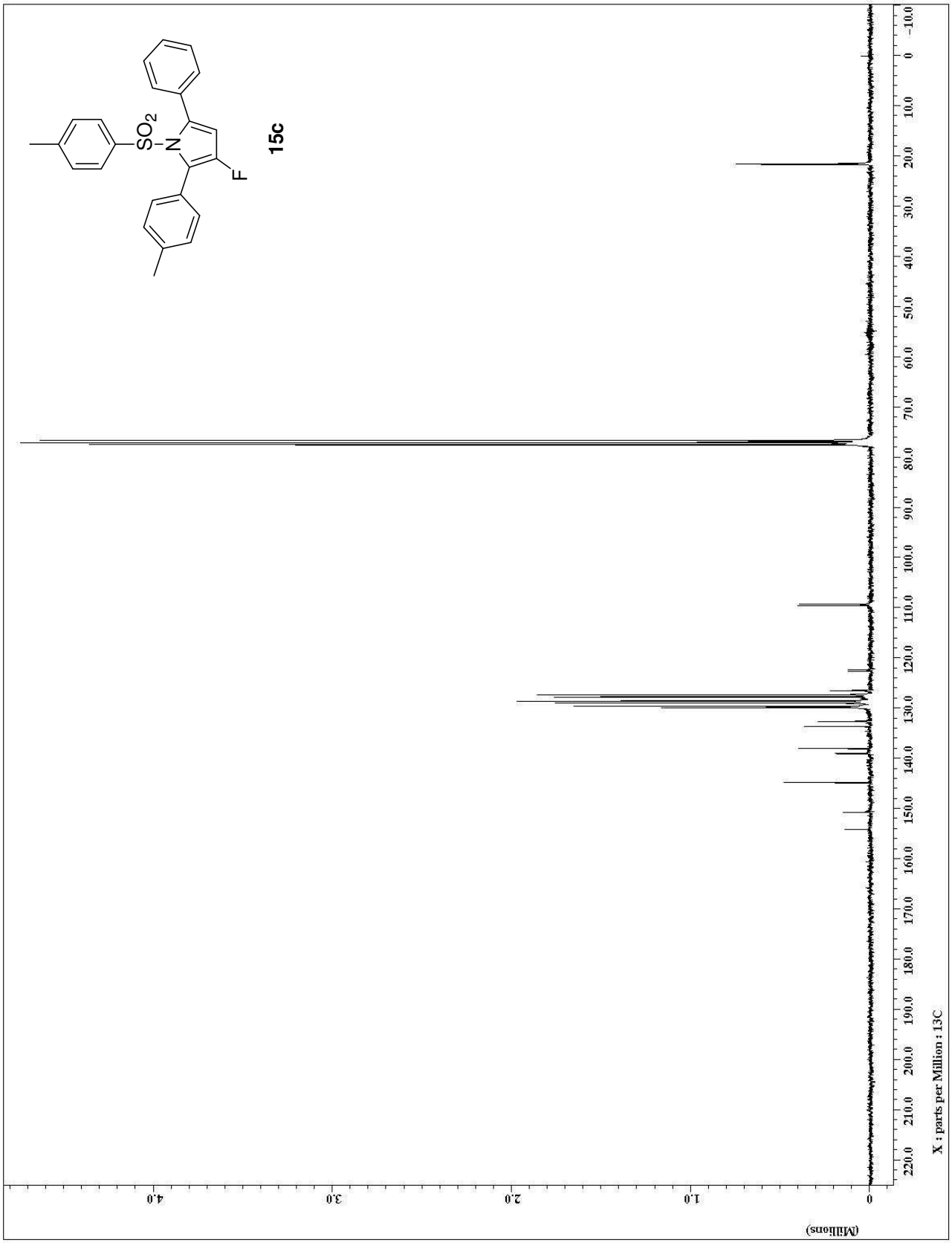
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F
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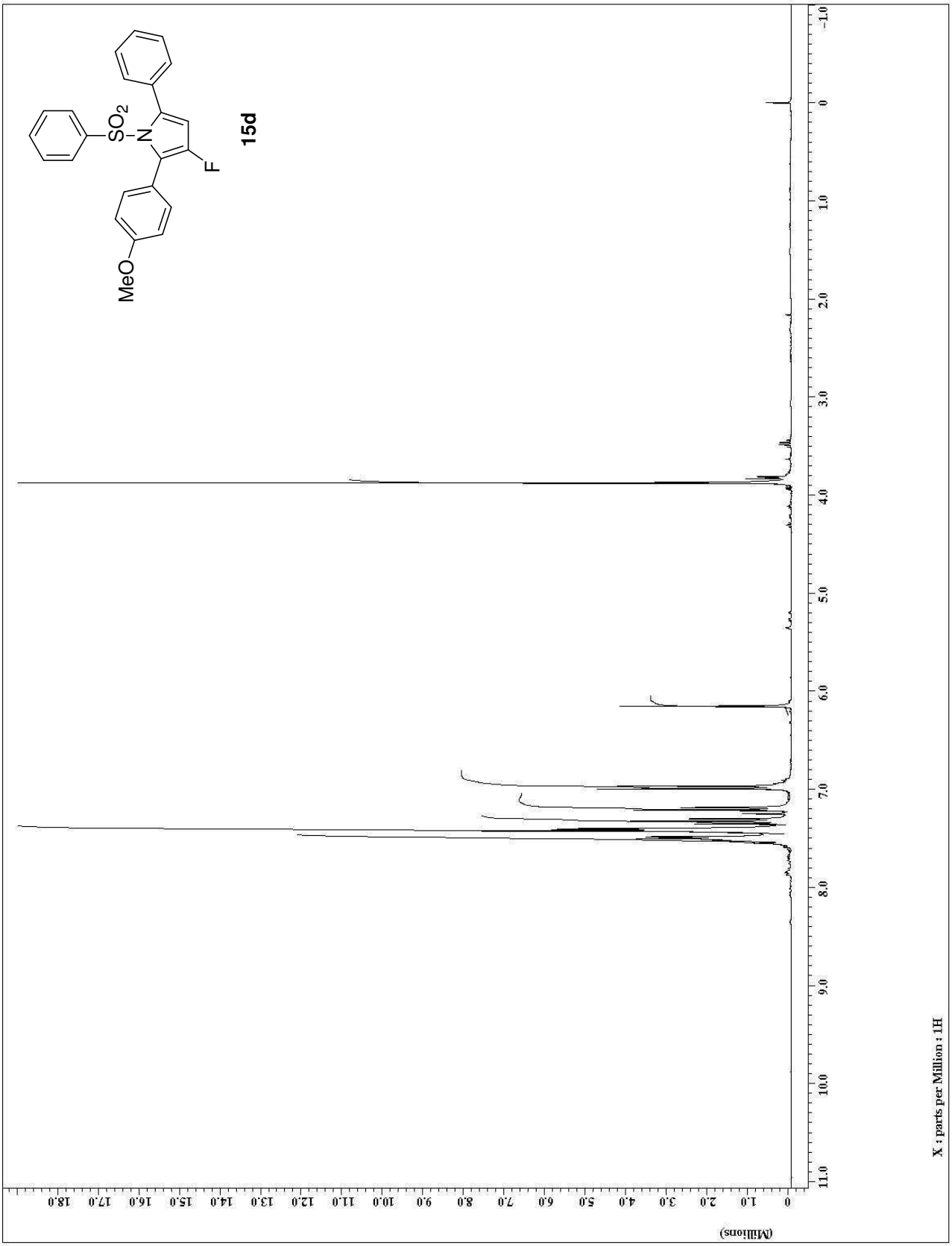
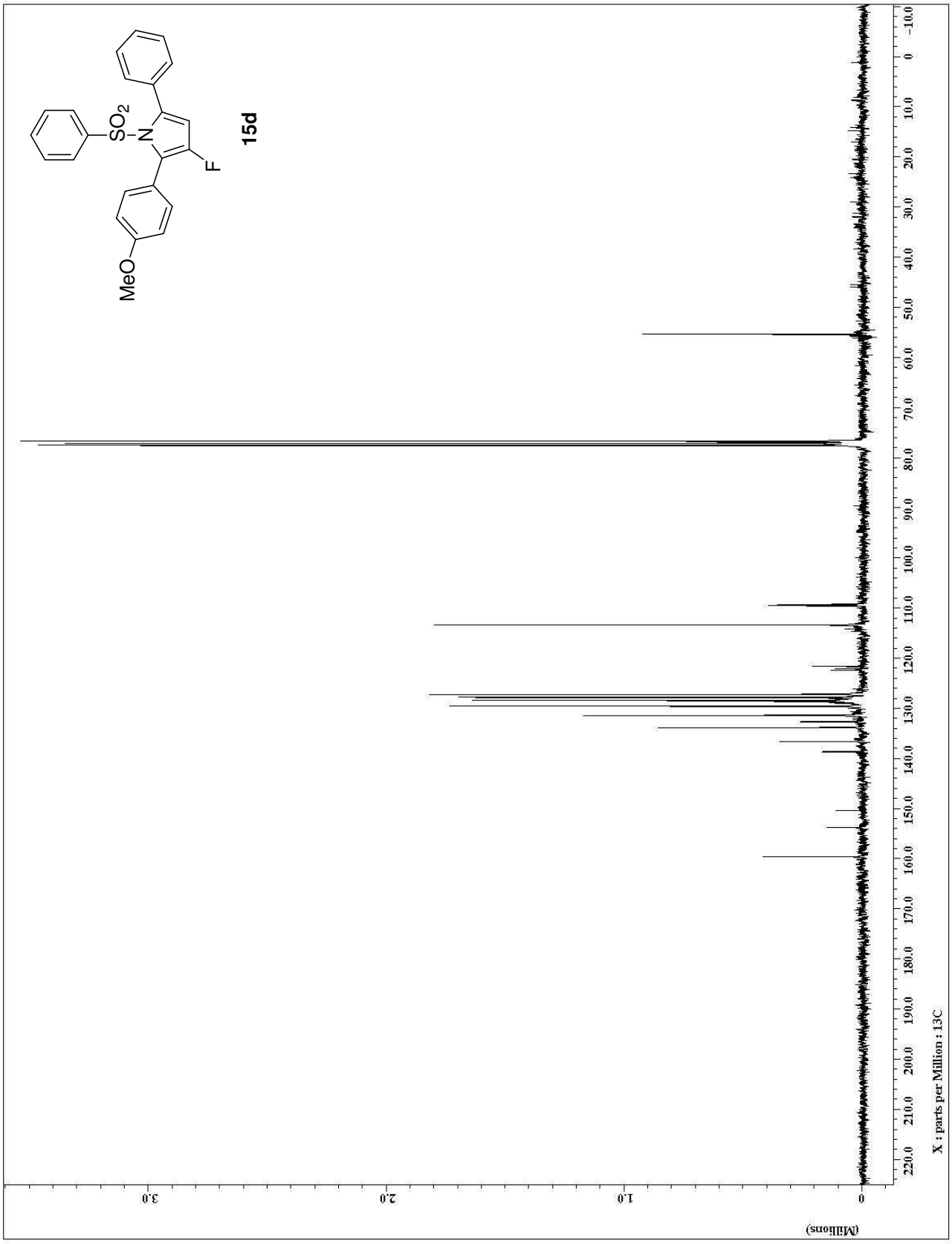
(Millions)


15d
SO2
N
F
MeO
(Millions)
X : parts per Million : 1H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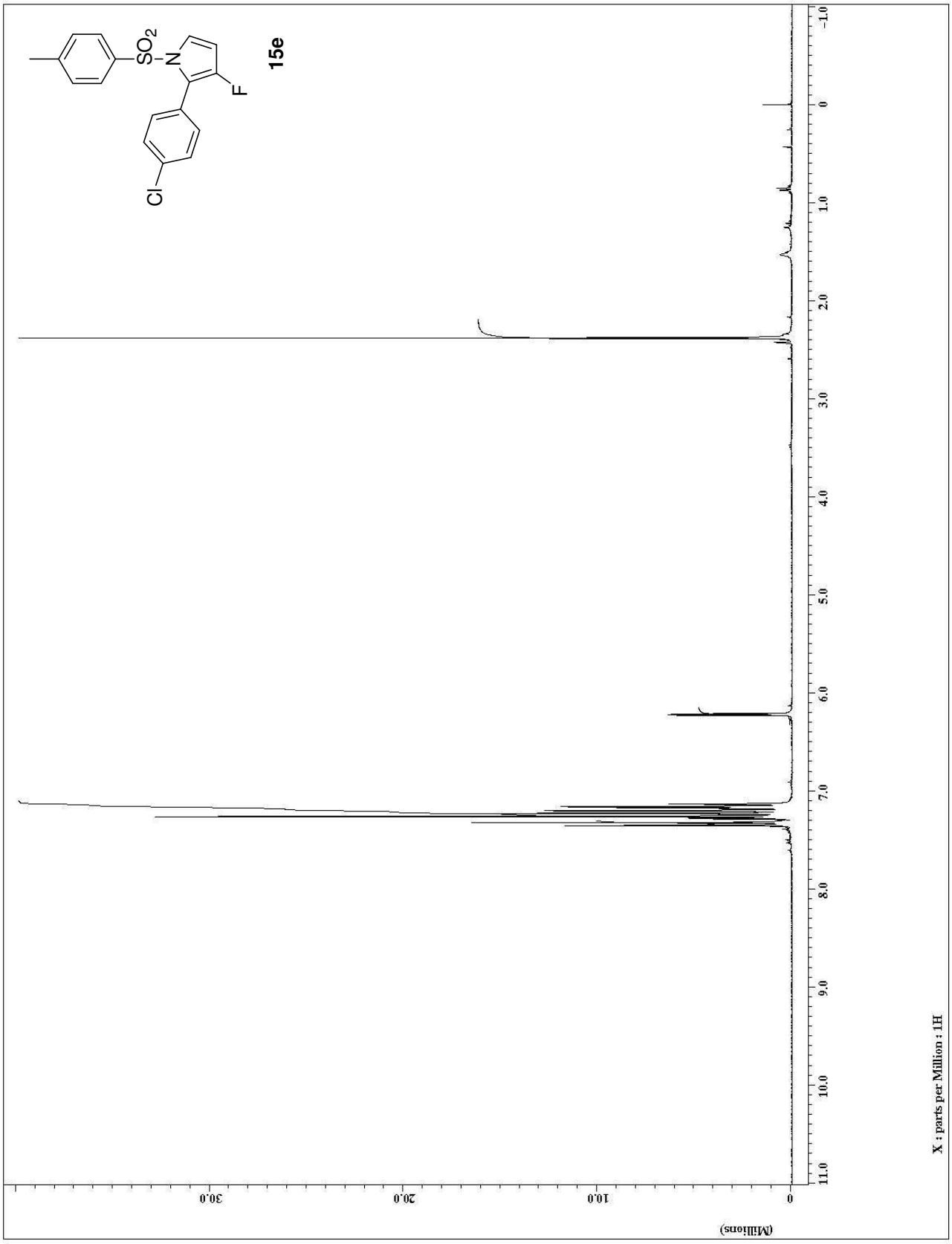
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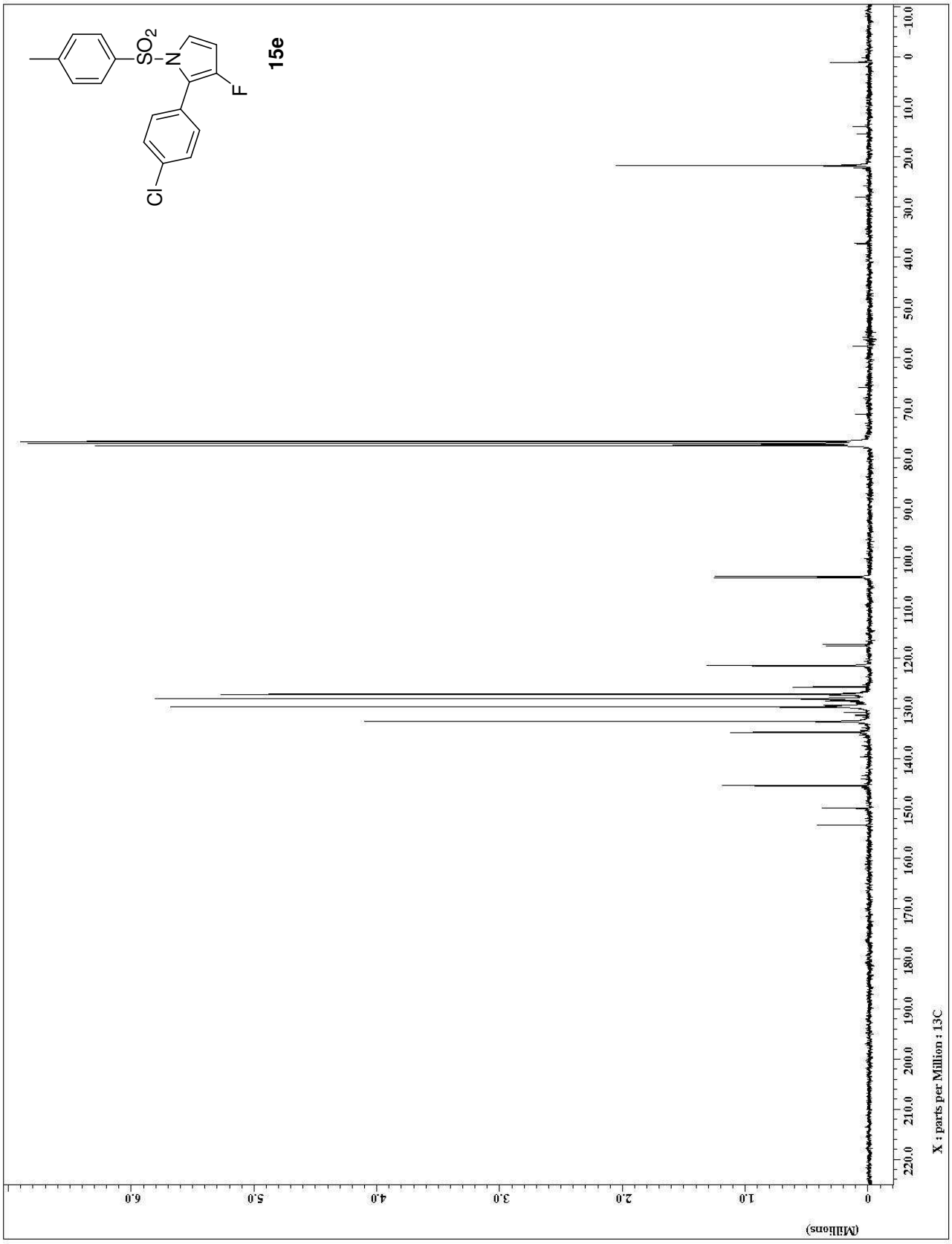
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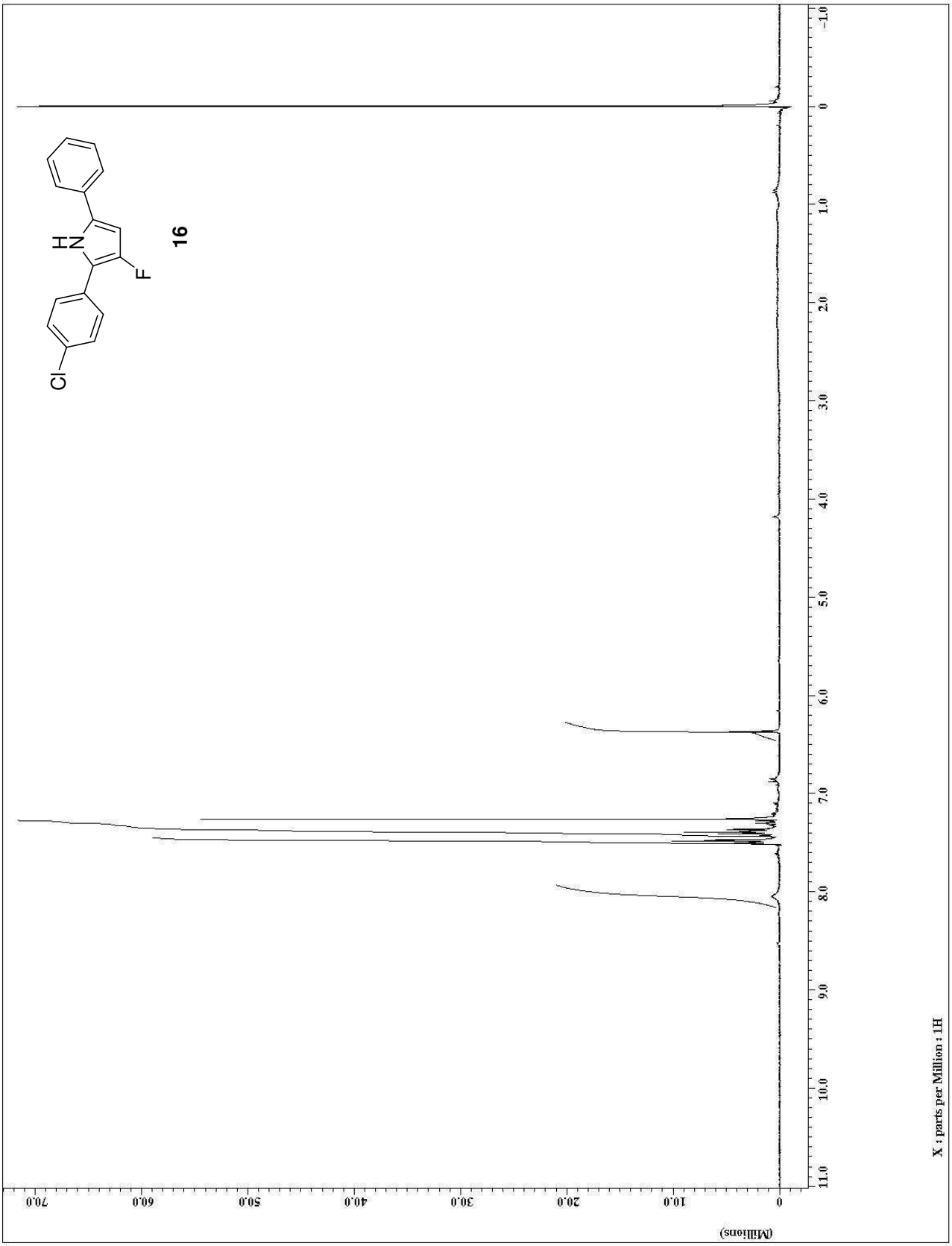
16
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N
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Cl
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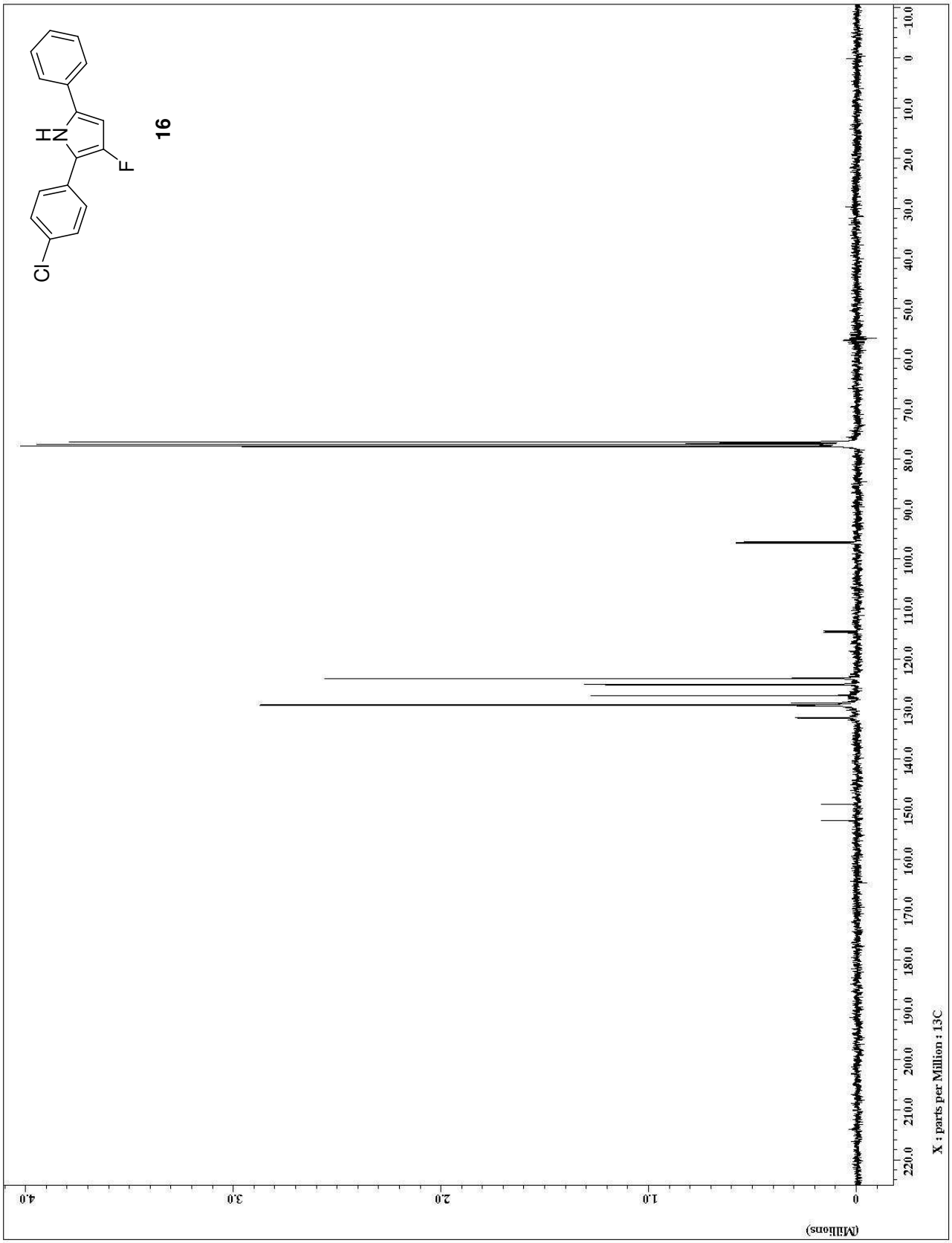
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Cl
(Millions)
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
X : parts per Million : 13C