Supporting Information
for

Polysubstituted 3-trifluoromethylpyrazoles: regioselective (3+2)-cycloaddition of trifluoroacetonitrile imines with enol ethers and functional group transformations

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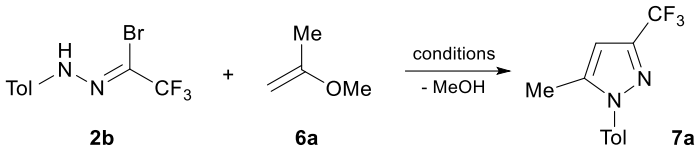
1. Synthetic details

General information: Reagents and solvents were purchased (Sigma-Aldrich, Acros) and used as received without further purification. Tetrahydrofuran was dried over sodium metal in the presence of 1,4-benzoquinone and distilled just before usage. If not stated otherwise, reactions were carried out under argon in a flame-dried flask with addition of the reactants by using syringe; subsequent manipulations were conducted in air. Products were purified by flash chromatography on silicagel LC60A (70–200 micron, Fluorochem). Unless stated otherwise, reported yields refer to analytically pure samples. NMR spectra were measured with a Bruker AVIII 600 [^{1}H NMR (600 MHz); ^{13}C NMR (151 MHz)] or with a Varian Gemini 2000 BB 200 MHz [^{19}F NMR (188 MHz)] instruments. Chemical shifts are reported relative to solvent residual peaks (^{1}H NMR: δ = 7.26 ppm [$CDCl_3$]; δ = 2.50 ppm [DMSO-d_6]; ^{13}C NMR: δ = 77.00 ppm [$CDCl_3$]; δ = 39.52 ppm [DMSO-d_6]) or to $CFCl_3$ (δ = 0.00 ppm) used as an external standard in ^{19}F NMR measurements. All ^{13}C-NMR spectra are proton-decoupled; substitution patterns of the carbon atoms were determined by 2D NMR spectroscopy (COSY, HMQC, HMBC) and are indicated as ^{13}C NMR peak multiplicity; coupling constants *J* are given in Hz. IR spectra were measured with a FTIR NEXUS spectrometer (as KBr pellets or thin films). MS spectra were performed with a Varian 500-MS LC Ion Trap or with a Waters SYNAPT G2-S HDMS instrument. Melting points were measured in capillaries with a Mel-Temp II apparatus (Aldrich) and are uncorrected. Elemental analyses were obtained with a Vario EL III (Elementar Analysensysteme GmbH) instrument. Single-crystal X-ray data were collected with a Rigaku Oxford Diffraction XtaLAB Synergy, Pilatus 300K diffractometer (Cu Kα radiation, λ = 1.54178 Å, PhotonJet (Cu) X-ray Source with mirror); the structure solution and refinement was performed by using SHELXS-97[1] and SHELXL-2014.[2] Crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-1531330 (*p*-nitrobenzoate **9**) and CCDC-1531331 (adduct **8g**). These data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223 336 033; email: deposit@ccdc.cam.ac.uk (or via http://www.ccdc.cam.ac.uk/conts/retrieving.html).

Hydrazonoyl bromides **2a-h** were prepared by treatment of the corresponding fluoral arylhydrazones **5** with slide excess NBS, in dry DMF, as reported previously.[3] Hydrazones **5** were obtained by heating methanolic solutions of the appropriate hydrazine **3** with three-fold excess fluoral hydrate (**4**) in a closed ampoule at 75 °C overnight in the presence of molecular sieves 4Å according to literature protocols.[4,5] All NMR spectra of hydrazones **5** and bromides **2** were in accordance with those reported.[3,5] Enol ethers **6a-c**,**f-h** are commercially available (Sigma-Aldrich). Enol ethers **6d** and **6e** were prepared by silylation of the respective ketones as described,[6] and were used for the next step without further purification.

Table S1. Optimization reactions of bromide **2b** with enol ether **6a** leading to pyrazole **7a**.[a]

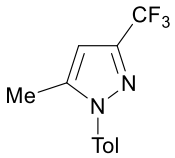


2b **6a** **7a**

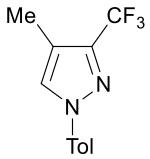
	Reaction conditions					
entry	**6a** (equiv.)	Et_3N (equiv.)	solvent	temp.	time	yield of **7a** (%) [b]
1	1.0	2.0	THF	rt	4d	58
2	1.0	5.0	THF	rt	2d	63
3	1.0	10.0	THF	rt	1d	72
4	0.5	10.0	THF	rt	1d	70
5	2.1	10.0	THF	rt	1d	61
6	1.0	10.0	CH_2Cl_2	rt	2d	22
7	1.0	10.0	MeOH	rt	2d	49
8	1.0	10.0	toluene	rt	1d	74
9	1.0	10.0	THF	0 °C	2d	71
10	1.0	10.0	THF	50 °C	1d	63 [c]

[a] reactions performed using 1.05 equiv. of bromide **2b**; [b] isolated yield; [c] reaction carried out in a closed ampoule.

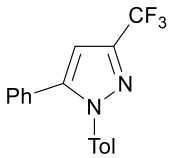
Synthesis of pyrazoles 7a-7n; General Procedure 1 (GP1): To a mixture of bromide **2** (1.05 mmol) and enol ether **6** (1.0 mmol) in dry THF (5.0 mL) was added dropwise Et_3N (1.5 mL) and the resulting mixture was stirred at room temperature for 24 hrs. The precipitate trimethylamine hydrochloride was filtered off, and the solvents were removed under reduced pressure. The resulting products **7a-7e** were purified by column chromatography (CC). In the case of cyclic enol ethers (**6f-6h**), crude product was dissolved in $CHCl_3$ (15 mL) followed by addition of 10% aq. HCl (1.0 mL), and the mixture was stirred at rt until the respective adduct of type **8** was fully consumed (typically 3-5 h, TLC monitoring: petroleum ether/CH_2Cl_2 1:1). The organic layer was washed with 10% aq. $NaHCO_3$ (10 mL), then with H_2O (2 × 10 mL), dried (Na_2SO_4), filtered, and solvents were removed in vacuo. Resulting 4-(ω-hydroxylkyl)pyrazole (**7f-7n**) was purified by column chromatography.



5-Methyl-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (7a): CC (SiO_2, petroleum ether/EtOAc 9:1); pale yellow oil, yield: 173 mg (72%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.32 (s, 3 H, 5-CH_3), 2.42 (s, 3 H, CH_3, Tol), 6.44 (s, 1 H, 4-H), 7.28, 7.32 (2 d_{br}, J ≈ 8.5 Hz, 2 × 2 H, Tol) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 12.2 (q, 5-CH_3), 21.1 (q, CH_3, Tol), 104.6 (q, $^3J_{C\text{-}F}$ = 2.2 Hz, C-4), 121.5 (q, $^1J_{C\text{-}F}$ = 268.6 Hz, CF_3), 125.2, 129.8 (2 d, 2 × 2 CH, Tol), 136.5, 138.8 (2 s, 2 *i*-C, Tol), 140.6 (s, *i*-C, C-5), 142.5 (q, $^2J_{C\text{-}F}$ = 38.0 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –62.7 (s, CF_3) ppm. IR (film): ν = 1519, 1489, 1248, 1174, 1140 cm^{-1}. ESI-MS (*m*/*z*): 241.1 (100, $[M+H]^+$). Anal. Calcd for $C_{12}H_{11}F_3N_2$: C, 60.00; H, 4.62; N, 11.66. Found: C, 59.88; H, 4.58; N, 11.66.

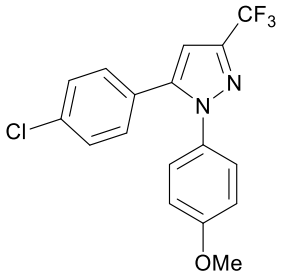


4-Methyl-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (7b): CC (SiO_2, petroleum ether/CH_2Cl_2 3:1); colorless oil, yield: 190 mg (79%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.23 (s_{br}, 3 H, 4-CH_3), 2.39 (s, 3 H, CH_3, Tol), 7.25, 7.53 (2 d_{br}, J ≈ 8.3 Hz, 2 × 2 H, Tol), 7.69 (s, 1 H, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 8.2 (q, 4-CH_3), 20.9 (q, CH_3, Tol), 116.9 (q, $^3J_{C\text{-}F}$ = 1.4 Hz, C-4), 119.5 (d, 2 CH, Tol), 121.9 (q, $^1J_{C\text{-}F}$ = 269.3 Hz, CF_3), 127.6 (d, C-5), 130.0 (d, 2 CH, Tol), 137.2, 137.3 (2 s, 2 *i*-C, Tol), 141.8 (q, $^2J_{C\text{-}F}$ = 36.3 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –62.0 (s, CF_3) ppm. IR (film): ν = 1523, 1278, 1174, 1123, 1074, 1059, 814 cm^{-1}. ESI-MS (*m*/*z*): 241.1 (100, $[M+H]^+$). Anal. Calcd for $C_{12}H_{11}F_3N_2$: C, 60.00; H, 4.62; N, 11.66. Found: C, 59.98; H, 4.84; N, 11.88.

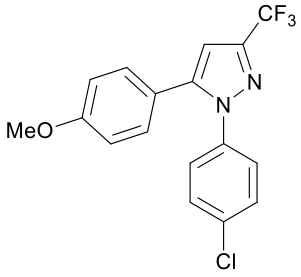


5-Phenyl-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (7c): CC (SiO_2, petroleum ether/EtOAc 9:1); pale yellow solid, yield: 154 mg (51%), mp 78-79 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.37 (s, 3 H, CH_3, Tol), 6.73 (s, 1 H, 4-H), 7.15, 7.19 (2 d_{br}, J ≈ 8.4 Hz, 2 × 2 H, Tol), 7.21-7.24, 7.30-7.35 (2 m, 2 H, 3 H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 21.1 (q, CH_3, Tol), 105.4 (q, $^3J_{C\text{-}F}$ = 1.9 Hz, C-4), 121.4 (q, $^1J_{C\text{-}F}$ = 268.7 Hz, CF_3), 125.3, 128.6, 128.8, 128.9, 129.6 (5 d, 9 CH, Tol, Ph), 129.4, 136.9, 138.5, 144.6 (4 s, 4 *i*-C, Tol, Ph, C-5), 143.0 (q, $^2J_{C\text{-}F}$ = 38.3 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –62.7 (s, CF_3) ppm.

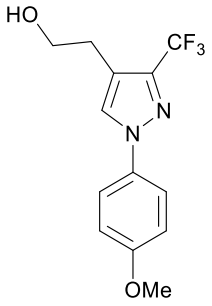
IR (KBr): v = 1474, 1453, 1231, 1150, 981 cm^{-1}. ESI-MS (m/z): 303.2 (100, $[M+H]^+$). Anal. Calcd for $C_{17}H_{13}F_3N_2$: C, 67.54; H, 4.33; N, 9.27. Found: C, 67.46; H, 4.31; N, 9.48.



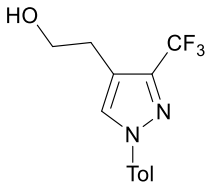
5-(4'-Chlorophenyl)-1-(4'-methoxyphenyl)-3-trifluoromethyl-1*H*-pyrazole[7] **(*SC-560*, 7d)**: CC (SiO_2, petroleum ether/CH_2Cl_2 4:1 gradient 2:1); yellow oil, yield: 159 mg (45%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.82 (s, 3 H, OCH_3), 6.73 (s, 1 H, 4-H), 6.88 (d_{br}, J ≈ 8.8 Hz, 2 H), 7.15 (d_{br}, J ≈ 8.4 Hz, 2 H), 7.21 (d_{br}, J ≈ 8.8 Hz, 2 H), 7.29 (d_{br}, J ≈ 8.4 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 55.5 (q, OCH_3), 105.2 (q, $^3J_{C\text{-}F}$ = 2.1 Hz, C-4), 114.3 (d, 2 CH), 121.2 (q, $^1J_{C\text{-}F}$ = 268.9 Hz, CF_3), 126.9 (d, 2 CH), 127.7 (s, *i*-C), 128.9, 130.0 (2 d, 2 × 2 CH), 132.1, 135.1 (2 s, 2 *i*-C), 142.9 (q, $^2J_{C\text{-}F}$ = 38.4 Hz, C-3), 143.4, 159.7 (2 s, i-C, C-5) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –62.2 (s, CF_3) ppm. ESI-MS (m/z): 353.1 (100, $[M+H]^+$).



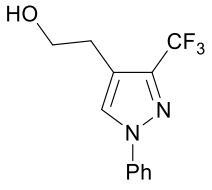
1-(4'-Chlorophenyl)-5-(4'-methoxyphenyl)-3-trifluoromethyl-1*H*-pyrazole[7] **(7e)**: CC (SiO_2, petroleum ether/CH_2Cl_2 4:1 gradient 2:1); thick yellow oil; yield: 218 mg (62%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.82 (s, 3 H, OCH_3), 6.69 (s, 1 H, 4-H), 6.87, 7.14 (2 d_{br}, J ≈ 8.8 Hz, 2 × 2 H), 7.26, 7.33 (2 d_{br}, J ≈ 8.8 Hz, 2 × 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 55.3 (q, OCH_3), 105.3 (q, $^3J_{C\text{-}F}$ = 1.8 Hz, C-4), 114.4 (d, 2 CH), 121.2 (s, *i*-C), 121.2 (q, $^1J_{C\text{-}F}$ = 269.0 Hz, CF_3), 126.6, 129.2, 130.1 (3 d, 6 CH), 134.1, 137.9 (2 s, 2 *i*-C), 143.4 (q, $^2J_{C\text{-}F}$ = 38.4 Hz, C-3), 144.7, 160.3 (2 s, 2 *i*-C) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –62.9 (s, CF_3) ppm. ESI-MS (m/z): 353.2 (100, $[M+H]^+$).



4-(2'-Hydroxyethyl)-1-(4'-methoxyphenyl)-3-trifluoromethyl-1*H*-pyrazole (7f): CC (SiO_2, CH_2Cl_2); pale yellow oil, yield: 140 mg (49%). ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 2.71 (t, J = 7.0 Hz, 2 H, 4-CH_2), 3.62 (t, J = 7.0 Hz, 2 H, CH_2), 3.81 (s, 3 H, OCH_3), 4.76 (s_{br}, 1 H, OH), 7.07, 7.73 (2 d_{br}, $J \approx$ 9.0 Hz, 2 × 2 H), 8.42 (s, 1 H, 5-H) ppm; ^{13}C NMR (DMSO-d_6, 151 MHz): δ = 26.7 (t, 4-CH_2), 55.4 (q, OCH_3), 60.7 (t, CH_2), 114.6 (d, 2 CH), 118.5 (q, $^3J_{C\text{-}F}$ = 1.9 Hz, C-4), 120.6 (d, 2 CH), 122.0 (q, $^1J_{C\text{-}F}$ = 269.2 Hz, CF_3), 129.3 (d, C-5), 132.4 (s, *i*-C), 139.6 (q, $^2J_{C\text{-}F}$ = 35.7 Hz, C-3), 159.4 (s, *i*-C) ppm; ^{19}F NMR (DMSO-d_6, 188 MHz): δ = –60.4 (s, CF_3) ppm. IR (film): ν = 3422 (O-H), 1520, 1497, 1252, 1167, 1124, 1063, 833 cm^{-1}. ESI-MS (*m*/*z*): 287.1 (100, $[M+H]^+$). Anal. Calcd for $C_{13}H_{13}F_3N_2O_2$: C, 54.55; H, 4.58; N, 9.79. Found: C, 54.58; H, 4.70; N, 9.82.

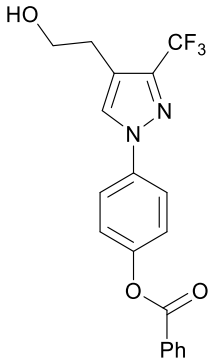


4-(2'-Hydroxyethyl)-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (7g): CC (SiO_2, CH_2Cl_2); pale brown solid; yield: 205 mg (76%); mp 38-39 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.39 (s, 3 H, CH_3), 2.88, 3.86 (2 t, J = 6.3 Hz, 2 × 2 H, 2 CH_2), 7.25, 7.55 (2 d_{br}, $J \approx$ 8.5 Hz, 2 × 2 H), 7.86 (s, 1 H, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 20.9 (q, CH_3), 26.8, 62.3 (2 t, 2 CH_2), 118.2 (q, $^3J_{C\text{-}F}$ = 0.8 Hz, C-4), 119.5 (d, 2 CH, Tol), 121.8 (q, $^1J_{C\text{-}F}$ = 269.5 Hz, CF_3), 128.1 (d, C-5), 130.0 (d, 2 CH, Tol), 137.1, 137.5 (2 s, 2 *i*-C), 141.4 (q, $^2J_{C\text{-}F}$ = 36.4 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.3 (s, CF_3) ppm. IR (KBr): ν = 3451 (O-H), 1497, 1287, 1159, 1128, 1064, 812 cm^{-1}. ESI-MS (*m*/*z*): 293.1 (98, $[M+Na]^+$), 271.1 (100, $[M+H]^+$). Anal. Calcd for $C_{13}H_{13}F_3N_2O$: C, 57.78; H, 4.85; N, 10.37. Found: C, 57.65; H, 4.89; N, 10.31.

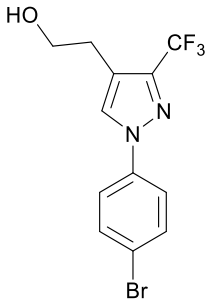


4-(2'-Hydroxyethyl)-1-phenyl-3-trifluoromethyl-1*H*-pyrazole (7h): CC (SiO_2, CH_2Cl_2); light pink oil, yield: 167 mg (65%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.88 (t, J = 6.4 Hz, 2 H, 4-CH_2), 3.85 (t, J = 6.4 Hz, 2 H, CH_2O), 7.32-7.34, 7.44-7.47, 7.66-7.68 (3 m, 1 H, 2 H, 2 H, Ph), 7.89 (s, 1 H, 5-H)

ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 26.7, 62.2 (2 t, 2 CH_2), 118.5 (q, $^3J_{C\text{-}F}$ = 0.9 Hz, C-4), 119.6 (d, 2 CH, Ph), 121.8 (q, $^1J_{C\text{-}F}$ = 269.6 Hz, CF_3), 127.5 (d, C-5), 128.2, 129.5 (2 d, 3 H, Ph), 139.3 (s, *i*-C, Ph), 141.8 (q, $^2J_{C\text{-}F}$ = 36.4 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.9 (s, CF_3) ppm. IR (KBr): *v* = 3381 (O-H), 1494, 1287, 1170, 1126, 1081, 1063, 758 cm^{-1}. ESI-MS (*m*/*z*): 279.1 (60, $[M+Na]^+$), 257.1 (100, $[M+H]^+$). Anal. Calcd for $C_{12}H_{11}F_3N_2O$: C, 56.25; H, 4.33; N, 10.93. Found: C, 56.37; H, 4.45; N, 10.73.

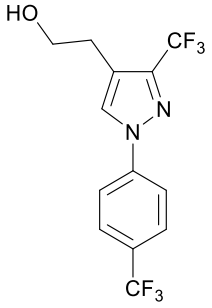


1-(4'-Benzoyloxyphenyl)-4-(2'-hydroxyethyl)-3-trifluoromethyl-1*H*-pyrazole (7i): CC (SiO_2, CH_2Cl_2); colorless solid, yield: 256 mg (68%), mp 74-75 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.90 (t, *J* = 6.3 Hz, 2 H, 4-CH_2), 3.89 (t, *J* = 6.3 Hz, 2 H, CH_2), 7.35 (d_{br}, *J* ≈ 8.9 Hz, 2 H), 7.52-7.55, 7.65-7.68 (2 m, 2 H, 1 H, Bz), 7.75 (d_{br}, *J* ≈ 8.9 Hz, 2 H), 7.91 (s, 1 H, 5-H), 8.20-8.22 (m, 2 H, Bz) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 26.7, 62.2 (2 t, 2 CH_2), 118.7 (q, $^3J_{C\text{-}F}$ = 0.8 Hz, C-4), 120.7 (d, 2 CH), 121.7 (q, $^1J_{C\text{-}F}$ = 269.6 Hz, CF_3), 122.8 (d, 2 CH), 128.3 (d, C-5), 128.7 (d, 2 CH, Bz), 129.2 (s, *i*-C, Bz), 130.2, 133.8 (2 d, 2 CH, 1 CH, Bz), 137.0 (s, *i*-C), 141.9 (q, $^2J_{C\text{-}F}$ = 36.4 Hz, C-3), 150 (s, *i*-C), 164.9 (s, C=O) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.4 (s, CF_3) ppm. IR (KBr): *v* = 3385 (O-H), 1734 (C=O), 1517, 1495, 1277, 1220, 1168, 1124, 1062, 1047, 711 cm^{-1}. ESI-MS (*m*/*z*): 399.2 (13, $[M+Na]^+$), 377.2 (100, $[M+H]^+$). Anal. Calcd for $C_{19}H_{15}F_3N_2O_3$: C, 60.64; H, 4.02; N, 7.44. Found: C, 60.50; H, 4.11; N, 7.34.

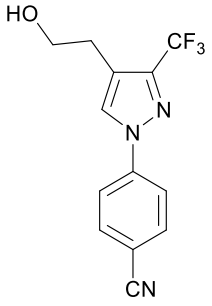


1-(4'-Bromophenyl)-4-(2'-hydroxyethyl)-3-trifluoromethyl-1*H*-pyrazole (7j): CC (SiO_2, CH_2Cl_2); yellow solid; yield: 224 mg (67%), mp 53-54 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.89 (t, *J* = 6.2 Hz, 2 H, 4-CH_2), 3.88 (t, *J* = 6.2 Hz, 2 H, CH_2), 7.58 (s_{br}, 4 H), 7.90 (s, 1 H, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 26.7, 62.1 (2 t, 2 CH_2), 119.0 (q, $^3J_{C\text{-}F}$ = 0.8 Hz, C-4), 120.90 (s, *i*-C), 120.92 (d, 2 CH), 121.6

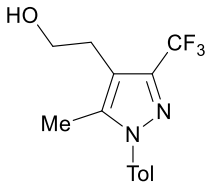
(q, $^{1}J_{C\text{-}F}$ = 269.7 Hz, CF_3), 128.0 (d, C-5), 132.6 (d, 2 CH), 138.3 (s, *i*-C), 142.1 (q, $^{2}J_{C\text{-}F}$ = 36.5 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.5 (s, CF_3) ppm. IR (KBr): *v* = 3301 (O-H), 1493, 1168, 1117, 1075, 1061 cm^{-1}. ESI-MS (*m*/*z*): 337.0 (94, [M{^{81}Br}+H]$^{+}$), 335.1 (100, [M{^{79}Br}+H]$^{+}$). Anal. Calcd for $C_{12}H_{10}BrF_3N_2O$: C, 43.01; H, 3.01; N, 8.36. Found: C, 42.95; H, 3.05; N, 8.37.



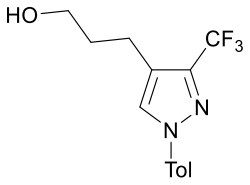
4-(2'-Hydroxyethyl)-1-(4'-trifluromethylphenyl)-3-trifluoromethyl-1*H*-pyrazole (7k): CC (SiO_2, CH_2Cl_2); colorless oil; yield: 217 mg (67%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.88 (t, *J* = 6.3 Hz, 2 H, 4-CH_2), 3.87 (t, *J* = 6.3 Hz, 2 H, CH_2), 7.71, 7.81 (2 d_{br}, *J* ≈ 8.7 Hz, 2 × 2 H), 7.98 (s, 1 H, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 26.6, 62.0 (2 t, 2 CH_2), 119.2 (d, 2 CH), 119.4 (q, $^{3}J_{C\text{-}F}$ = 0.8 Hz, C-4), 121.5 (q, $^{1}J_{C\text{-}F}$ = 269.7 Hz, CF_3), 123.7 (q, $^{1}J_{C\text{-}F}$ = 272.0 Hz, CF_3), 126.8 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, 2 CH), 128.2 (d, C-5), 129.4 (q, $^{2}J_{C\text{-}F}$ = 33.1 Hz, *i*-C), 141.6 (s, *i*-C), 142.7 (q, $^{2}J_{C\text{-}F}$ = 36.6 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.8, –63.1 (2 s, 2 CF_3) ppm. IR (film): *v* = 3384 (O-H), 1620, 1498, 1329, 1288, 1170, 1128, 1057 cm^{-1}. ESI-MS (*m*/*z*): 325.1 (100, [M+H]$^{+}$). Anal. Calcd for $C_{13}H_{10}F_6N_2O$: C, 48.16; H, 3.11; N, 8.64. Found: C, 48.22; H, 3.14; N, 8.73.



1-(4'-Cyanophenyl)-4-(2'-hydroxyethyl)-3-trifluoromethyl-1*H*-pyrazole (7l): CC (SiO_2, CH_2Cl_2); colorless solid, yield: 174 mg (62%), mp 134-135 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.90 (t, *J* = 6.1 Hz, 2 H, 4-CH_2), 3.90 (t, *J* = 6.1 Hz, 2 H, CH_2), 7.77, 7.85 (2 d_{br}, *J* ≈ 8.8 Hz, 2 × 2 H), 8.01 (s, 1 H, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 26.6, 61.9 (2 t, 2 CH_2), 110.9 (s, CN), 118 (s, *i*-C), 119.4 (d, 2 CH), 120.0 (s_{br}, C-4), 121.4 (q, $^{1}J_{C\text{-}F}$ = 269.9 Hz, CF_3), 128.1 (d, C-5), 133.7 (d, 2 CH), 142.1 (s, *i*-C), 143.2 (q, $^{2}J_{C\text{-}F}$ = 36.5 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.9 (s, CF_3) ppm. IR (KBr): *v* = 3497 (O-H), 2232 (CN), 1520, 1495, 1281, 1169, 1126, 1060 cm^{-1}. ESI-MS (*m*/*z*): 282.2 (100, [M+H]$^{+}$). Anal. Calcd for $C_{13}H_{10}F_3N_3O$: C, 55.52; H, 3.58; N, 14.94. Found: C, 55.77; H, 3.73; N, 14.76.



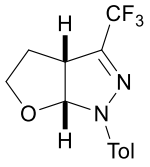
4-(2'-Hydroxyethyl)-5-methyl-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (7m): flash CC (SiO_2, petroleum ether/acetone 95:5); colorless oil, yield: 162 mg (57%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.52 (t_{br}, J ≈ 5.5 Hz, 1 H, OH), 2.27 (s, 3 H, 5-CH_3), 2.41 (s, 3 H, CH_3, Tol), 2.83 (t, J = 6.7 Hz, 2 H, 4-CH_2), 3.79 (dt_{br}, J ≈ 5.5, 6.7 Hz, 2 H, CH_2), 7.27, 7.30 (2 d_{br}, J ≈ 8.6 Hz, 2 × 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 10.8, 21.1 (2 q, 2 CH_3), 26.8, 62.8 (2 t, 2 CH_2), 114.2 (q, $^3J_{C\text{-}F}$ = 0.7 Hz, C-4), 122.1 (q, $^1J_{C\text{-}F}$ = 269.5 Hz, CF_3), 125.2, 129.8 (2 d, 2 × 2 CH), 136.6, 138.7, 139.6 (3 s, 3 *i*-C), 140.8 (q, $^2J_{C\text{-}F}$ = 36.0 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.5 (s, CF_3) ppm. IR (film): v = 3384 (O-H), 1520, 1464, 1383, 1282, 1128, 1055, 825 cm^{-1}. ESI-MS (*m*/*z*): 285.2 (100, $[M+H]^+$). Anal. Calcd for $C_{14}H_{15}F_3N_2O$: C, 59.15; H, 5.32; N, 9.85. Found: C, 59.02; H, 5.47; N, 9.92.



4-(3'-Hydroxypropyl)-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (7n): CC (SiO_2, CH_2Cl_2); colorless solid, yield: 111 mg (39%); mp 40-41 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 1.73-1.78 (m, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 2.60 (t, J = 7.9 Hz, 2 H, 4-CH_2), 3.47 (td, J = 5.1, 6.2 Hz, 2 H, CH_2OH), 4.51 (t, J = 5.1 Hz, 1 H, OH), 7.33, 7.72 (2 d_{br}, J ≈ 8.3 Hz, 2 × 2 H), 8.49 (s, 1 H, 5-H) ppm; ^{13}C NMR (DMSO-d_6, 151 MHz): δ = 19.4 (t, CH_2), 20.4 (q, CH_3), 32.8, 59.9 (2 t, 2 CH_2), 118.8 (d, 2 CH, Tol), 121.6 (q, $^3J_{C\text{-}F}$ = 1.0 Hz, C-4), 121.9 (q, $^1J_{C\text{-}F}$ = 269.0 Hz, CF_3), 128.7 (d, C-5), 130.0 (d, 2 CH, Tol), 136.6, 136.8 (2 s, 2 *i*-C, Tol), 139.5 (q, $^2J_{C\text{-}F}$ = 35.7 Hz, C-3) ppm; ^{19}F NMR (DMSO-d_6, 188 MHz): δ = –60.4 (s, CF_3) ppm. IR (KBr): v = 3263 (O-H), 1523, 1496, 1300, 1164, 1116, 1081, 1067 cm^{-1}. ESI-MS (*m*/*z*): 307.2 (31, $[M+Na]^+$), 285.2 (100, $[M+H]^+$). Anal. Calcd for $C_{14}H_{15}F_3N_2O$: C, 59.15; H, 5.32; N, 9.85. Found: C, 59.09; H, 5.33; N, 9.84.

Synthesis of cis-1-Tolyl-3-trifluoromethyl-3a,4,5,6a-tetrahydro-1H-furo[2,3-c]pyrazole (8g): Following general procedure 1 (**GP1**) to a mixture of bromide **2b** (294 mg, 1.05 mmol) and 2,3-dihydrofuran **6f** (76 µL, 70 mg, 1.0 mmol) in dry THF (5.0 mL) was added dropwise Et_3N (1.5 mL) and the resulting mixture was stirred at room temperature overnight. The resulting mixture was washed with H_2O (3 × 10 mL), the organic layer was dried (Na_2SO_4), filtered, and the solvents were removed

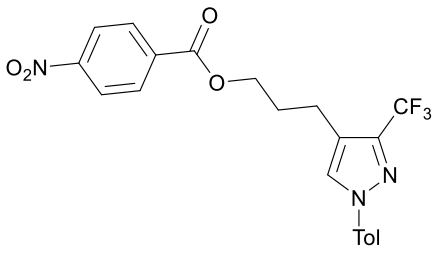
under reduced pressure (cold bath). Crude product was purified by column chromatography (SiO_2 was deactivated with 2% Et_3N in petroleum ether before usage; petroleum ether/CH_2Cl_2 3:1) to give (3+2)-cycloadduct **8g** (221 mg, 82%) as a colorless solid.



Mp 94-96 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ = 2.12-2.18, 2.18-2.23 (2 m, 2 × 1 H, 4-H_2), 2.25 (s, 3 H, CH_3), 3.31 (ddd, J = 5.3, 9.0, 11.4 Hz, 1 H, 5-H), 4.05 (ddd, J = 1.5, 7.1, 9.0 Hz, 1 H, 5-H), 4.19 (ddd, J = 1.8, 7.8, 9.3 Hz, 1 H, 3a-H), 6.28 (d, J = 7.8 Hz, 1 H, 6a-H), 7.09, 7.13 (2 d_{br}, $J \approx$ 8.6 Hz, 2 × 2 H) ppm; ^{13}C NMR (DMSO-d_6, 151 MHz): δ = 20.1 (q, CH_3), 30.1 (t, C-4), 48.0 (d, C-3a), 65.8 (t, C-5), 94.8 (d, C-6a), 113.7 (d, 2 CH, Tol), 121.1 (q, $^1J_{C\text{-}F}$ = 269.3 Hz, CF_3), 129.5 (d, 2 CH, Tol), 130.2 (s, *i*-C), 137.5 (q, $^2J_{C\text{-}F}$ = 35.7 Hz, C-3), 139.3 (s, *i*-C) ppm; ^{19}F NMR (DMSO-d_6, 188 MHz): δ = –63.8 (s, CF_3) ppm. IR (KBr): ν = 1523, 1350, 1301, 1268, 1180, 1143, 1112, 1046, 812 cm^{-1}. ESI-MS (*m*/*z*): 271.1 (100, $[M+H]^+$). Anal. Calcd for $C_{13}H_{13}F_3N_2O$: C, 57.78; H, 4.85; N, 10.37. Found: C, 57.77; H, 4.87; N, 10.54.

Suitable crystals for an X-ray crystal structure determination were obtained from hexanes/CH_2Cl_2 solution by slow evaporation of the solvents.

Synthesis of 3-(1'-tolyl-3'-trifluoromethyl-1H-pyrazol-4'-yl)propyl p-nitrobenzoate (9): To a solution of pyrazole **7n** (71 mg, 0.25 mmol) in dry CH_2Cl_2 (2 mL) was added Et_3N (70 µL, 0.5 mmol), followed by solution of *p*-nitrobenzoyl chloride (51 mg, 0.275 mmol) in CH_2Cl_2 (1 mL). The resulting mixture was stirred at room temeprature for 30 min, then H_2O (10 mL) was added, the organic layer was separated, dried over Na_2SO_4, and the solvents were removed under reduced pressure. Crude product was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 2:1) to give ester **9** (87 mg, 80%) as a colorless solid.

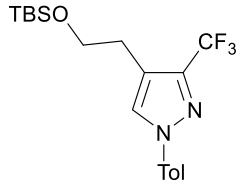


Mp 104-106 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.13-2.17 (m, 2 H, CH_2), 2.39 (s, 3 H, CH_3), 2.82 (t, J = 7.5 Hz, 2 H, 4-CH_2), 4.46 (t, J = 6.3 Hz, 2 H, CH_2), 7.24, 7.51 (2 d_{br}, $J \approx$ 8.5 Hz, 2 × 2 H), 7.76 (s, 1 H, 5-H), 8.17, 8.26 (2 d_{br}, $J \approx$ 8.9 Hz, 2 × 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 20.1 (t, CH_2), 20.9 (q, CH_3), 29.3, 65.0 (2 t, 2 CH_2), 119.4 (d, 2 CH, Tol), 120.7 (q, $^3J_{C\text{-}F}$ = 1.2 Hz, C-4'), 121.8 (q, $^1J_{C\text{-}F}$ = 269.5 Hz, CF_3), 123.6 (d, 2 CH, Tol), 127.1 (d, C-5'), 130.0, 130.6 (2 d, 2 × 2 CH),

135.5, 137.0, 137.6 (3 s, 3 *i*-C), 141.2 (q, $^{2}J_{C\text{-}F}$ = 36.6 Hz, C-3'), 150.6 (s, *i*-C), 164.7 (s, C=O) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.6 (s, CF_3) ppm. IR (KBr): *v* = 1716 (C=O), 1527, 1288, 1167, 1119, 1062 cm^{-1}. ESI-MS (*m*/*z*): 456.2 (54, $[M+Na]^+$), 434.2 (100, $[M+H]^+$). Anal. Calcd for $C_{21}H_{18}F_3N_3O_4$: C, 58.20; H, 4.19; N, 9.70. Found: C, 58.32; H, 4.14; N, 9.73.

Suitable crystals for an X-ray crystal structure determination were obtained from hexanes/CH_2Cl_2 solution by slow evaporation of the solvents.

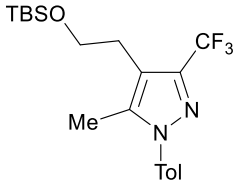
Synthesis of 4-[2'-(tert-Butyldimethylsiloxy)ethyl]-1-tolyl-3-trifluoromethyl-1H-pyrazole (10): To a solution of alcohol **7g** (951 mg, 3.5 mmol) in dry CH_2Cl_2 (20 mL) were added at 0 °C imidazole (334 mg, 4.9 mmol) and DMAP (18 mg, 0.15 mmol) followed by solution of TBSCl (723 mg, 4.8 mmol) in CH_2Cl_2 (8 mL). The mixture was allowed to reach room temperature, and stirred for 30 min. Then, H_2O (30 mL) was added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL), the combined organics were washed with brine, dried (Na_2SO_4), filtered, and the solvents were removed in vacuo. Purification by flash column chromatography provided **10** (1.22 g, 90%) as a colorless oil.



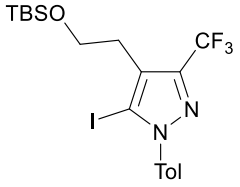
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.00, 0.86 (2 s, 6 H, 9 H, TBS), 2.34 (s, 3 H, CH_3, Tol), 2.79 (t, *J* = 6.5 Hz, 2 H, 4-CH_2), 3.78 (t, *J* = 6.5 Hz, 2 H, CH_2O), 7.20, 7.50 (2 d_{br}, *J* ≈ 8.4 Hz, 2 × 2 H), 7.78 (s, 1 H, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4, 18.2 (q, s, TBS), 20.9 (q, CH_3, Tol), 25.9 (q, TBS), 26.9, 62.8 (2 t, 2 CH_2), 118.8 (q, $^{3}J_{C\text{-}F}$ = 0.7 Hz, C-4), 119.2 (d, 2 CH, Tol), 121.9 (q, $^{1}J_{C\text{-}F}$ = 269.5 Hz, CF_3), 128.2 (d, C-5), 130.0 (d, 2 CH, Tol), 137.3* (s, 2 *i*-C, Tol), 141.4 (q, $^{2}J_{C\text{-}F}$ = 36.2 Hz, C-3) ppm, *higher intensity; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.3 (s, CF_3) ppm. IR (film): *v* = 2954-2858, 1522, 1496, 1288, 1255, 1126, 1061 cm^{-1}. ESI-MS (*m*/*z*): 385.3 (100, $[M+H]^+$). Anal. Calcd for $C_{19}H_{27}F_3N_2OSi$: C, 59.35; H, 7.08; N, 7.29. Found: C, 59.53; H, 7.25; N, 7.33.

Synthesis of pyrazoles 12a-12h; General Procedure 2 (GP2): Lithiated pyrazole **11** was generated under dry argon by treating a solution of pyrazole **10** (192 mg, 0.50 mmol) in anhydrous THF (3 mL) with *n*-BuLi (2.5M in hexane, 0.22 mL, 0.55 mmol) at –78 °C. After 30 min, excess electrophile was added slowly at –78 °C. The mixture was stirred at this temperature for 10 min, then quenched by addition of sat. aq. NH_4Cl solution (5 mL). The mixture was warmed to room temperature, H_2O was added (10 mL) and extracted with Et_2O (3 × 10 mL). Combined organic layers were dried (Na_2SO_4),

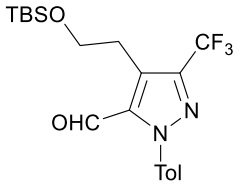
filtered, and the solvents were removed under reduced pressure. Crude product **12** was purified by flash column chromatography.



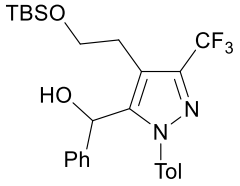
4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-methyl-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (12a): following *GP2*, lithiated pyrazole **11** was treated with MeI (284 mg, 2.0 mmol). CC (SiO_2, petroleum ether/CH_2Cl_2 1:1); colorless oil, yield: 181 mg (91%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.00, 0.87 (2 s, 6 H, 9 H, TBS), 2.25 (s, 3 H, 5-CH_3), 2.42 (s, 3 H, CH_3, Tol), 2.78 (t, *J* = 6.8 Hz, 2 H, 4-CH_2), 3.75 (t, *J* = 6.8 Hz, 2 H, CH_2O), 7.27 (s_{br}, 4 H, Tol) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4 (q, 2 CH_3, TBS), 10.9 (q, 5-CH_3), 18.3 (s, TBS), 21.1 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 26.9, 63.4 (2 t, 2 CH_2), 114.8 (q, $^3J_{C\text{-}F}$ = 0.7 Hz, C-4), 122.1 (q, $^1J_{C\text{-}F}$ = 269.4 Hz, CF_3), 125.3, 129.7 (2 d, 2 × 2 CH, Tol), 136.7, 138.6 (2 s, 2 *i*-C, Tol), 139.6 (s, C-5), 140.6 (q, $^2J_{C\text{-}F}$ = 35.9 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.3 (s, CF_3) ppm. IR (film): *v* = 2956-2857, 1522, 1385, 1284, 1174, 1128, 1063 cm^{-1}. ESI-MS (*m*/*z*): 421.2 (36, $[M+Na]^+$), 399.2 (100, $[M+H]^+$). Anal. Calcd for $C_{20}H_{29}F_3N_2OSi$: C, 60.27; H, 7.33; N, 7.03. Found: C, 60.27; H, 7.34; N, 7.10.



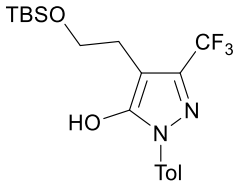
4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-iodo-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (12b): following *GP2*, lithiated pyrazole **11** was treated with a solution of I_2 (508 mg, 2.0 mmol) in dry THF (1 mL). CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); colorless solid, yield: 250 mg (98%), 47-48 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.05, 0.89 (2 s, 6 H, 9 H, TBS), 2.43 (s, 3 H, CH_3), 2.85 (t, *J* = 7.2 Hz, 2 H, 4-CH_2), 3.78 (t, *J* = 7.2 Hz, 2 H, CH_2O), 7.29, 7.34 (2 d_{br}, *J* ≈ 8.2 Hz, 2 × 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.3, 18.4 (q, s, TBS), 21.2 (q, CH_3, Tol), 26.0 (q, ^{t}Bu, TBS), 29.1, 62.6 (2 t, 2 CH_2), 88.8 (s, C-5), 121.3 (q, $^1J_{C\text{-}F}$ = 270.1 Hz, CF_3), 123.1 (s_{br}, C-4), 126.4, 129.6 (2 d, 2 × 2 CH), 142.3 (q, $^2J_{C\text{-}F}$ = 36.8 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.2 (s, CF_3) ppm. IR (KBr): *v* = 2959-2859, 1268, 1176, 1125, 1082, 1052, 837 cm^{-1}. ESI-MS (*m*/*z*): 533.0 (37, $[M+Na]^+$), 511.1 (100, $[M+H]^+$). Anal. Calcd for $C_{19}H_{26}F_3IN_2OSi$: C, 44.71; H, 5.13; N, 5.49. Found: C, 44.86; H, 5.28; N, 5.46.



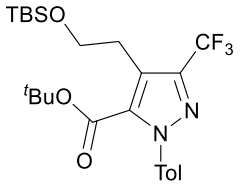
4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-formyl-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (12c): following *GP2*, lithiated pyrazole **11** was treated with dry DMF (365 mg, 0.38 mL, 5.0 mmol). CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); colorless oil, yield: 177 mg (86%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.00, 0.85 (2 s, 6 H, 9 H, TBS), 2.44 (s, 3 H, CH_3), 3.14 (t, J = 6.5 Hz, 2 H, 4-CH_2), 3.84 (t, J = 6.5 Hz, 2 H, CH_2O), 7.32, 7.34 (2 d_{br}, $J \approx$ 8.7 Hz, 2 × 2 H), 9.89 (s, 1 H, CHO) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.5, 18.3 (q, s, TBS), 21.2 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 26.2, 62.6 (2 t, 2 CH_2), 121.3 (q, $^1J_{C\text{-}F}$ = 270.1 Hz, CF_3), 124.3 (q, $^3J_{C\text{-}F}$ = 0.9 Hz, C-4), 125.6, 129.9 (2 d, 2 × 2 CH), 135.8 (s, *i*-C), 138.2 (s, C-5), 140.1 (s, *i*-C), 141.6 (q, $^2J_{C\text{-}F}$ = 36.8 Hz, C-3), 180.5 (s, C=O) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.0 (s, CF_3) ppm. IR (film): v = 2955-2858, 1697 (C=O), 1269, 1132, 1103, 1064 cm^{-1}. ESI-MS (m/z): 413.2 (100, $[M+H]^+$). Anal. Calcd for $C_{20}H_{27}F_3N_2O_2Si$: C, 58.23; H, 6.60; N, 6.79. Found: C, 58.33; H, 6.86; N, 6.98.



***rac*-4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-[hydroxy(phenyl)-methyl]-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (12d)**: following *GP2*, lithiated pyrazole **11** was treated with a solution of benzaldehyde (133 mg, 1.25 mmol) in dry THF (0.5 mL). CC (SiO_2, petroleum ether/EtOAc 7:1); colorless oil, yield: 233 mg (95%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.08, 0.10, 0.88 (3 s, 3 H, 3 H, 9 H, TBS), 2.40 (s, 3 H, CH_3), 2.58 (ddd, J = 4.4, 11.1, 15.2 Hz, 1 H, 4-CH_2), 2.65 (ddd, J = 2.8, 3.2, 15.2 Hz, 1 H, 4-CH_2), 3.72 (ddd, J = 2.8, 9.6, 11.1 Hz, 1 H, CH_2O), 3.86 (ddd, J = 3.2, 4.4, 9.6 Hz, 1 H, CH_2O), 5.09 (d, J = 7.8 Hz, OH), 5.84 (d, J = 7.8 Hz, C*H*(OH)), 7.21-7.26, 7.27-7.30, 7.32-7.34 (3 m, 5 H, 2 H, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.6, –5.4, 18.7 (2 q, s, TBS), 21.2 (q, CH_3, Tol), 25.3 (t, 4-CH_2), 26.0 (q, ^{t}Bu, TBS), 63.7 (t, CH_2O), 66.9 (d, CH(OH)), 115.3 (s_{br}, C-4), 121.9 (q, $^1J_{C\text{-}F}$ = 269.8 Hz, CF_3), 125.8, 126.0, 127.3, 128.2, 129.8 (5 d, 9 CH), 136.2, 139.3 (2 s, 2 *i*-C), 140.8 (q, $^2J_{C\text{-}F}$ = 36.1 Hz, C-3), 141.6 (s, *i*-C), 146.2 (s, C-5) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.1 (s, CF_3) ppm. IR (film): v = 3379 (O-H), 2956-2858, 1520, 1496, 1284, 1171, 1122, 1088, 1059, 839 cm^{-1}. ESI-MS (m/z): 491.3 (100, $[M+H]^+$). Anal. Calcd for $C_{26}H_{33}F_3N_2O_2Si$: C, 63.65; H, 6.78; N, 5.71. Found: C, 63.83; H, 7.01; N, 5.69.

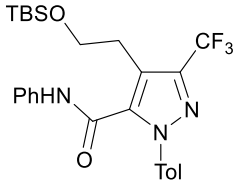


4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-hydroxy-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (12e): following *GP2*, lithiated pyrazole **11** was reacted with trimethyl borate (104 mg, 111 µL, 1.0 mmol). After standard aqueous workup, crude boronic acid was dissolved in THF (10 mL) and the mixture was cooled to –10 °C. Then, a solution of aq. NaOH (2M, 12 mL) followed by H_2O_2 (30%, 4.1 mL) were added at this temperature. The resulting mixture was warmed to room temperature and stirred for 4 h, then satd. aq. $Na_2S_2O_3$ (5 mL) solution was added and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 10 mL), the combined organic layers were dried ($MgSO_4$), filtered, and the solvents were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 1:2) to give **12e** (164 mg, 82%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.19, 0.96 (2 s, 6 H, 9 H, TBS), 2.38 (s, 3 H, CH_3), 2.82 (t, *J* = 6.6 Hz, 2 H, 4-CH_2), 4.03 (t, *J* = 6.6 Hz, 2 H, CH_2O), 7.24, 7.63 (2 d_{br}, *J* ≈ 8.3 Hz, 2 × 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.5, 18.3 (q, s, TBS), 21.0 (q, CH_3, Tol), 25.7 (t, 4-CH_2), 25.8 (q, ^{t}Bu, TBS), 65.1 (t, CH_2O), 97.3 (s_{br}, C-4), 121.8 (q, $^1J_{C\text{-}F}$ = 269.6 Hz, CF_3), 122.3, 129.4 (2 d, 2 × 2 CH), 135.8, 136.8 (2 s, 2 *i*-C), 139.3 (q, $^2J_{C\text{-}F}$ = 35.9 Hz, C-3), 151.6 (s, C-5) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.9 (s, CF_3) ppm. IR (film): *v* = 3413 (O-H), 3184-2772, 1600, 1494, 1471, 1292, 1174, 1148, 1115, 1043 cm^{-1}. ESI-MS (*m*/*z*): 423.2 (70, $[M+Na]^+$), 401.3 (100, $[M+H]^+$). Anal. Calcd for $C_{19}H_{27}F_3N_2O_2Si$: C, 56.98; H, 6.80; N, 6.99. Found: C, 56.99; H, 6.77; N, 6.82.

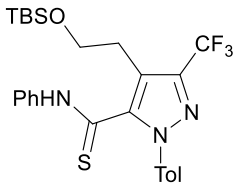


5-(*tert*-Butoxycarbonyl)-4-[2'-(*tert*-butyldimethylsiloxy)ethyl]-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (12f): following *GP2*, lithiated pyrazole **11** was treated with a solution of Boc_2O (131 mg, 0.6 mmol) in THF (0.5 mL). CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); colorless solid, yield: 208 mg (86%), mp 72-73 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.02, 0.87 (2 s, 6 H, 9 H, TBS), 1.37 (s, 9 H, Boc), 2.41 (s, 3 H, CH_3), 3.08 (t, *J* = 7.3 Hz, 2 H, 4-CH_2), 3.81 (t, *J* = 7.3 Hz, 2 H, CH_2O), 7.23, 7.25 (2 d_{br}, *J* ≈ 8.6 Hz, 2 × 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4, 18.4 (q, s, TBS), 21.2 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 27.4 (t, 4-CH_2), 27.8 (q, ^{t}Bu, Boc), 63.2 (t, CH_2O), 83.2 (s, ^{t}Bu, Boc), 121.5 (q, $^1J_{C\text{-}F}$ = 270.1 Hz, CF_3), 121.8 (q, $^3J_{C\text{-}F}$ = 0.9 Hz, C-4), 125.5, 129.3 (2 d, 2 × 2 CH), 134.7 (s, C-5), 138.0, 139.1 (2 s, 2 *i*-C), 141.5 (q, $^2J_{C\text{-}F}$ = 36.4 Hz, C-3), 158.1 (s, C=O) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.6 (s, CF_3) ppm. IR

(KBr): *v* = 3046-2861, 1716 (C=O), 1252, 1174, 1156, 1123, 1097, 1064 cm^{-1}. ESI-MS (*m*/*z*): 507.2 (100, $[M+Na]^+$), 485.1 (53, $[M+H]^+$). Anal. Calcd for $C_{24}H_{35}F_3N_2O_3Si$: C, 59.48; H, 7.28; N, 5.78. Found: C, 59.67; H, 7.34; N, 5.66.



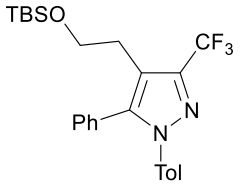
***N*-Phenyl-4-[2'-(*tert*-butyldimethylsiloxy)ethyl]-1-tolyl-3-trifluoromethyl-5-pyrazolecarboxamide (12g)**: following *GP2*, lithiated pyrazole **11** was treated with a solution of phenyl isocyanate (83 mg, 0.7 mmol) in THF (0.5 mL). CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); colorless solid, yield: 216 mg (86%), mp 83-84 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.06, 0.88 (2 s, 6 H, 9 H, TBS), 2.41 (s, 3 H, CH_3), 3.11 (t, *J* = 7.2 Hz, 2 H, 4-CH_2), 4.12 (t, *J* = 7.2 Hz, 2 H, CH_2O), 7.14-7.17, 7.26-7.38, 7.66-7.68 (3 m, 1 H, 6 H, 2 H, Ph, Tol), 10.3 (s_{br}, 1 H, NH) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4, 18.7 (q, s, TBS), 21.1 (q, CH_3, Tol), 25.6 (t, 4-CH_2), 25.9 (q, ^{t}Bu, TBS), 64.1 (t, CH_2O), 117.6 (s_{br}, C-4), 120.0 (d, 2 CH), 121.6 (q, $^1J_{C\text{-}F}$ = 269.8 Hz, CF_3), 124.4, 124.8, 129.0, 129.6 (4 d, 7 CH), 137.2, 137.7, 138.9, 139.0 (4 s, 3 *i*-C, C-5), 140.1 (q, $^2J_{C\text{-}F}$ = 36.8 Hz, C-3), 156.6 (s, C=O) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.6 (s, CF_3) ppm. IR (KBr): *v* = 3267 (N-H), 1685 (C=O), 1551, 1497, 1252, 1162, 1125, 1091, 1057 cm^{-1}. ESI-MS (*m*/*z*): 504.2 (100, $[M+H]^+$). Anal. Calcd for $C_{26}H_{32}F_3N_3O_2Si$: C, 62.01; H, 6.40; N, 8.34. Found: C, 62.14; H, 6.56; N, 8.27.



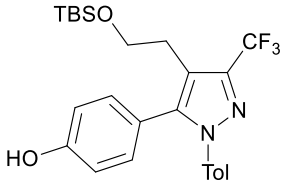
***N*-Phenyl-4-[2'-(*tert*-butyldimethylsiloxy)ethyl]-1-tolyl-3-trifluoromethyl-5-pyrazolecarbothioamide (12h)**: following *GP2*, lithiated pyrazole **11** was treated with a solution of phenyl isothiocyanate (94 mg, 0.7 mmol) in THF (0.5 mL). CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); yellow oil, yield: 210 mg (81%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.02, 0.83 (2 s, 6 H, 9 H, TBS), 2.41 (s, 3 H, CH_3), 3.07 (t, *J* = 7.2 Hz, 2 H, 4-CH_2), 4.11 (t, *J* = 7.2 Hz, 2 H, CH_2O), 7.25-7.36, 7.42-7.45, 7.81-7.83 (3 m, 5 H, 2 H, 2 H, Ph, Tol), 11.6 (s_{br}, 1 H, NH) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.5, 18.5 (q, s, TBS), 21.1 (q, CH_3, Tol), 25.5 (t, 4-CH_2), 25.8 (q, ^{t}Bu, TBS), 63.8 (t, CH_2O), 113.7 (s_{br}, C-4), 121.7 (q, $^1J_{C\text{-}F}$ = 269.8 Hz, CF_3), 123.5, 124.9, 127.2, 128.9, 129.5 (5 d, 9 CH), 137.1, 138.3, 138.6 (3 s, 3 i-C), 139.7 (q, $^2J_{C\text{-}F}$ = 36.9 Hz, C-3), 144.9 (s, C-5), 183.0 (s, C=S) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.6 (s, CF_3) ppm. IR (film): *v* = 3195, 3132-2858, 1498, 1365, 1284, 1154, 1125, 1060 cm^{-1}. ESI-MS (*m*/*z*): 542.2 (90, $[M+Na]^+$),

520.1 (100, $[M+H]^+$). Anal. Calcd for $C_{26}H_{32}F_3N_3OSSi$: C, 60.09; H, 6.21; N, 8.09; S, 6.17. Found: C, 60.09; H, 6.26; N, 7.89; S, 6.35.

Synthesis of 5-arylpyrazoles 13a-13e; General Procedure 3 (GP3): A solution of 5-iodopyrazole derivative **12b** (102 mg, 0.2 mmol), K_2CO_3 (110 mg, 0.8 mmol), and appropriate arylboronic acid (0.24 mmol) in THF/H_2O (4:1 mixture, 10 mL) was degassed by a repeated procedure of freeze-pump-thaw and $Pd(PPh_3)_4$ (23 mg, 10 mol% with respect to iodopyrazole) was added. The mixture was refluxed for 48 h, cooled to room temp., H_2O (10 mL) was added and extracted with CH_2Cl_2 (3 × 15mL). Combined organic layers were dried over Na_2SO_4, filtered, and the solvents were removed under reduced pressure. Crude product **13** was purified by column chromatography.

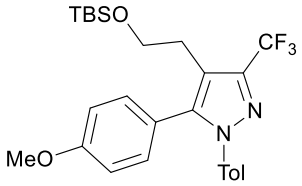


4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-phenyl-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (13a): CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); colorless oil, yield: 81 mg (88%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = –0.04, 0.83 (2 s, 6 H, 9 H, TBS), 2.30 (s, 3 H, CH_3), 2.80 (t, J = 7.3 Hz, 2 H, 4-CH_2), 3.71 (t, J = 7.3 Hz, 2 H, CH_2O), 7.06, 7.08 (2 d_{br}, $J \approx$ 8.6 Hz, 2 × 2H, Tol), 7.25-7.27, 7.32-7.37 (2 m, 2 H, 3 H, Ph) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.5, 18.3 (q, s, TBS), 21.0 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 26.7, 63.3 (2 t, 2 CH_2), 115.9 (q, $^3J_{C\text{-}F}$ = 0.8 Hz, C-4), 122.1 (q, $^1J_{C\text{-}F}$ = 269.7 Hz, CF_3), 124.9, 128.6, 128.8 (3 d, 5 CH), 129.2 (s, *i*-C), 129.4, 130.2 (2 d, 4 CH), 136.9, 137.8 (2 s, 2 *i*-C), 141.2 (q, $^2J_{C\text{-}F}$ = 36.2 Hz, C-3), 143.2 (s, C-5) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.6 (s, CF_3) ppm. IR (film): ν = 2927-2856, 1520, 1269, 1163, 1126, 1064 cm^{-1}. ESI-MS (*m*/*z*): 483.2 (35, $[M+Na]^+$), 461.1 (100, $[M+H]^+$). Anal. Calcd for $C_{25}H_{31}F_3N_2OSi$: C, 65.19; H, 6.78; N, 6.08. Found: C, 65.28; H, 6.97; N, 5.84.

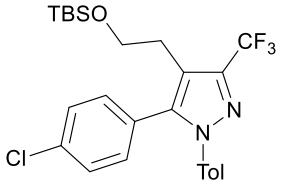


4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-(4'-hydroxyphenyl)-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (13b): CC (SiO_2, petroleum ether/CH_2Cl_2 1:4); thick colorless oil, yield: 74 mg (78%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = –0.01, 0.85 (2 s, 6 H, 9 H, TBS), 2.31 (s, 3 H, CH_3), 2.79 (t, J = 7.4 Hz, 2 H, 4-CH_2), 3.73 (t, J = 7.4 Hz, 2 H, CH_2O), 6.74-6.77, 7.06-7.09 (2 m, 2 H, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4, 18.3 (q, s, TBS), 21.0 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 26.7, 63.4 (2 t, 2 CH_2),

115.5 (s_{br}, C-4), 115.7 (d, 2 CH), 121.0 (s, *i*-C), 122.0 (q, $^1J_{C\text{-}F}$ = 269.7 Hz, CF_3), 124.9, 129.4, 131.6 (3 d, 3 × 2 CH), 136.9, 137.8 (2 s, 2 *i*-C), 141.1 (q, $^2J_{C\text{-}F}$ = 36.1 Hz, C-3), 143.3 (s, C-5), 156.4 (s, *i*-C) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.7 (s, CF_3) ppm. IR (film): *v* = 3374 (OH), 3067-2857, 1519, 1270, 1163, 1126, 1100, 1065, 838 cm^{-1}. ESI-MS (*m*/*z*): 477.3 (100, $[M+H]^+$). Anal. Calcd for $C_{25}H_{31}F_3N_2O_2Si$: C, 63.00; H, 6.56; N, 5.88. Found: C, 63.02; H, 6.71; N, 5.76.

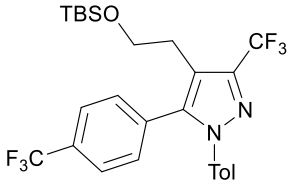


4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-(4'-methoxyphenyl)-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (13c): CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); pale yellow oil, yield: 92 mg (93%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = –0.02, 0.85 (2 s, 6 H, 9 H, TBS), 2.32 (s, 3 H, CH_3), 2.79 (t, *J* = 7.4 Hz, 2 H, 4-CH_2), 3.72 (t, *J* = 7.4 Hz, 2 H, CH_2O), 3.82 (s, 3 H, OCH_3), 6.87 (d_{br}, *J* ≈ 8.8 Hz, 2 H), 7.08. 7.10 (2 d_{br}, *J* ≈ 8.6 Hz, 2 × 2 H), 7.18 (d_{br}, *J* ≈ 8.8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4, 18.3 (q, s, TBS), 21.0 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 26.8 (t, 4-CH_2), 55.2 (q, OCH_3), 63.3 (t, CH_2O), 114.1 (d, 2 CH), 115.7 (s_{br}, C-4), 121.3 (s, *i*-C), 122.1 (q, $^1J_{C\text{-}F}$ = 269.7 Hz, CF_3), 124.9, 129.4, 131.5 (3 d, 3 × 2 CH), 137.0, 137.7 (2 s, 2 *i*-C), 141.1 (q, $^2J_{C\text{-}F}$ = 36.1 Hz, C-3), 143.1 (s, C-5), 160.0 (s, *i*-C) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.6 (s, CF_3) ppm. IR (film): *v* = 2958-2855, 1452, 1252, 1162, 1119, 1083, 1067, 839 cm^{-1}. ESI-MS (*m*/*z*): 491.3 (100, $[M+H]^+$). HRMS (ESI-TOF): *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{34}F_3N_2O_2Si$: 491.2342; found: 491.2338.



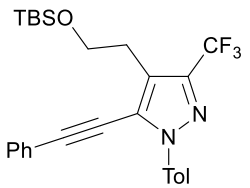
4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-(4'-chlorophenyl)-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (13d): CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); colorless oil, yield: 91 mg (92%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = –0.02, 0.84 (2 s, 6 H, 9 H, TBS), 2.33 (s, 3 H, CH_3), 2.78 (t, *J* = 7.0 Hz, 2 H, 4-CH_2), 3.75 (t, *J* = 7.0 Hz, 2 H, CH_2O), 7.07, 7.10 (2 d_{br}, *J* ≈ 8.5 Hz, 2 × 2 H), 7.24, 7.33 (2 d_{br}, *J* ≈ 8.6 Hz, 2 × 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.5, 18.3 (q, s, TBS), 21.0 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 26.6, 63.2 (2 t, 2 CH_2), 116.3 (s_{br}, C-4), 122.0 (q, $^1J_{C\text{-}F}$ = 269.8 Hz, CF_3), 125.0 (d, 2 CH), 127.6 (s, *i*-C), 128.9, 129.6, 131.6 (3 d, 3 × 2 CH), 135.1, 136.7, 138.2 (3 s, 3 *i*-C), 141.3 (q, $^2J_{C\text{-}F}$ = 36.3 Hz, C-3), 142.1 (s, C-5) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.7 (s, CF_3) ppm. IR (film): *v* = 2954-2858, 1520,

1269, 1161, 1126, 1095, 1064, 837 cm^{-1}. ESI-MS (*m*/*z*): 517 (100, $[M+Na]^+$), 495.2 (34, $[M+H]^+$). Anal. Calcd for $C_{25}H_{30}ClF_3N_2OSi$: C, 60.65; H, 6.11; N, 5.66. Found: C, 60.84; H, 6.22; N, 5.87.



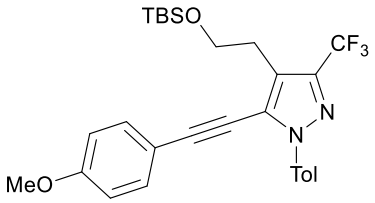
4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-1-tolyl-5-(4'-trifluoromethyl-phenyl)-3-trifluoromethyl-1*H*-pyrazole (13e): CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); colorless oil, yield: 91 mg (86%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = –0.03, 0.83 (2 s, 6 H, 9 H, TBS), 2.34 (s, 3 H, CH_3), 2.80 (t, *J* = 6.9 Hz, 2 H, 4-CH_2), 3.77 (t, *J* = 6.9 Hz, 2 H, CH_2O), 7.07, 7.11 (2 d_{br}, *J* ≈ 8.4 Hz, 2 × 2 H), 7.45, 7.61 (2 d_{br}, *J* ≈ 8.1 Hz, 2 × 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.5, 18.3 (q, s, TBS), 21.0 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 26.5, 63.2 (2 t, 2 CH_2), 116.8 (s_{br}, C-4), 121.9 (q, $^1J_{C\text{-}F}$ = 269.8 Hz, CF_3), 123.8 (q, $^1J_{C\text{-}F}$ = 272.3 Hz, CF_3), 125.0 (d, 2 CH), 125.5 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, 2 CH), 129.7, 130.7 (2 d, 2 × 2 CH), 130.9 (q, $^2J_{C\text{-}F}$ = 32.8 Hz, *i*-C), 132.9, 136.6, 138.4 (3 s, 3 *i*-C), 141.4 (q, $^2J_{C\text{-}F}$ = 36.4 Hz, C-3), 141.8 (s, C-5) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.7, –62.8 (2 s, 2 CF_3) ppm. IR (film): *v* = 3043-2857, 1325, 1165, 1128, 1064, 1018, 837, 779 cm^{-1}. ESI-MS (*m*/*z*): 551.1 (27, $[M+Na]^+$), 529.2 (100, $[M+H]^+$). Anal. Calcd for $C_{26}H_{30}F_6N_2OSi$: C, 59.08; H, 5.72; N, 5.30. Found: C, 59.36; H, 5.92; N, 5.43.

Synthesis of 5-alkynylpyrazoles 14a-14d; General Procedure 4 (GP4): A solution of 5-iodopyrazole **12b** (102 mg, 0.2 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol% with respect to **12b**), and CuI (3.8 mg, 0.02 mmol) in a mixture of dry Et_3N (1.45 mL) and dry THF (2.0 mL) was degassed by a repeated procedure of freeze-pump-thaw. Meanwile, the corresponding alkyne (0.24 mmol) was dissolved in dry THF (2.0 mL) in separate flask under argon, and the resulting mixture was added dropwise to the first reaction flask over 30 min. The mixture was heated at 65 °C for 24 h, then cooled to room temp. H_2O (10 mL) was added, and extracted with CH_2Cl_2 (3 × 15 mL). the combined organic layers were dried (Na_2SO_4), filtered, and the solvents were removed in vacuo. Crude product **14** was purified by column chromatography.

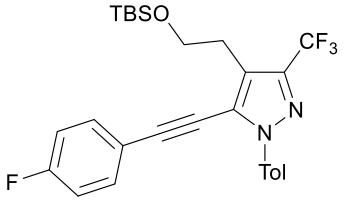


4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-(phenylethynyl)-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (14a): CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); colorless oil, yield:

81 mg (84%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.05, 0.89 (2 s, 6 H, 9 H, TBS), 2.43 (s, 3 H, CH_3), 3.01 (t, J = 7.3 Hz, 2 H, 4-CH_2), 3.89 (t, J = 7.3 Hz, 2 H, CH_2O), 7.30 (d_{br}, J ≈ 8.3 Hz, 2 H, Tol), 7.35-7.41, 7.45-7.47 (2 m, 3 H, 2 H, Ph), 7.69 (d_{br}, J ≈ 8.3 Hz, 2 H, Tol) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4, 18.3 (q, s, TBS), 21.1 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 27.5, 62.8 (2 t, 2 CH_2), 77.0, 99.1 (2 s, 2 × ≡C-), 121.6 (q, $^1J_{C\text{-}F}$ = 269.7 Hz, CF_3), 121.8 (s, *i*-C), 122.0 (q, $^3J_{C\text{-}F}$ = 1.0 Hz, C-4), 123.5 (d, 2 CH), 126.5 (s, C-5), 128.5, 129.3, 129.5, 131.5 (4 d, 7 CH), 136.9, 138.4 (2 s, 2 *i*-C), 141.1 (q, $^2J_{C\text{-}F}$ = 36.8 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.8 (s, CF_3) ppm. IR (film): ν = 2956-2855, 2220 (C≡C), 1519, 1490, 1372, 1274, 1172, 1134, 1063, 838 cm^{-1}. ESI-MS (*m*/*z*): 507.2 (21, $[M+Na]^+$), 485.2 (100, $[M+H]^+$). Anal. Calcd for $C_{27}H_{31}F_3N_2OSi$: C, 66.91; H, 6.45; N, 5.78. Found: C, 66.98; H, 6.44; N, 5.74.

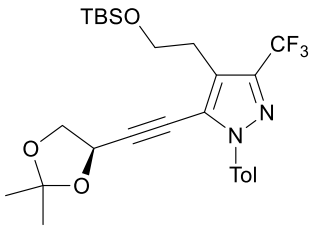


4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-(4'-methoxyphenylethynyl)-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (14b): CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); colorless oil, yield: 80 mg (78%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.04, 0.89 (2 s, 6 H, 9 H, TBS), 2.42 (s, 3 H, CH_3), 2.98 (t, J = 7.3 Hz, 2 H, 4-CH_2), 3.83 (s, 3 H, OCH_3), 3.87 (t, J = 7.3 Hz, 2 H, CH_2O), 6.88 (d_{br}, J ≈ 8.8 Hz, 2 H), 7.29 (d_{br}, J ≈ 8.3 Hz, 2 H), 7.39 (d_{br}, J ≈ 8.8 Hz, 2 H), 7.68 (d_{br}, J ≈ 8.3 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4, 18.3 (q, s, TBS), 21.1 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 27.5 (t, 4-CH_2), 55.3 (q, OCH_3), 62.8 (t, CH_2), 75.8, 99.3 (2 s, 2 × ≡C-), 113.8 (s, *i*-C), 114.2 (d, 2 CH), 121.5 (q, $^3J_{C\text{-}F}$ = 0.9 Hz, C-4), 121.6 (q, $^1J_{C\text{-}F}$ = 269.8 Hz, CF_3), 123.5 (d, 2 CH), 126.8 (s, C-5), 129.5, 133.1 (2 d, 2 × 2 CH), 137.0, 138.3 (2 s, 2 *i*-C), 141.0 (q, $^2J_{C\text{-}F}$ = 36.7 Hz, C-3), 160.5 (s, *i*-C) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.8 (s, CF_3) ppm. IR (film): ν = 3000-2856, 2216 (C≡C), 1504, 1273, 1251, 1179, 1134, 1063 cm^{-1}. ESI-MS (*m*/*z*): 537.1 (45, $[M+Na]^+$), 515.2 (100, $[M+H]^+$). HRMS (ESI-TOF): *m*/*z* $[M+H]^+$ calcd for $C_{28}H_{34}F_3N_2O_2Si$: 515.2342; found: 515.2335.



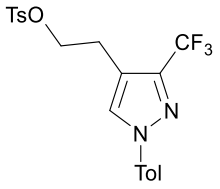
4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-(4'-fluorophenylethynyl)-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (14c): CC (SiO_2, petroleum ether/CH_2Cl_2 3:2); yellow oil, yield: 79 mg (79%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.03, 0.88 (2 s, 6 H, 9 H, TBS), 2.43 (s, 3 H, CH_3), 2.98, 3.86 (2 t, J = 7.2 Hz, 2 × 2 H, 2 CH_2), 7.05-7.08 (m, 2 H), 7.29 (d_{br}, J ≈ 8.3 Hz, 2 H, Tol), 7.42-7.44

(m, 2 H), 7.66 (d_{br}, J ≈ 8.3 Hz, 2 H, Tol) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4, 18.3 (q, s, TBS), 21.1 (q, CH_3, Tol), 25.9 (q, ^{t}Bu, TBS), 27.5, 62.8 (2 t, 2 CH_2), 76.8, 98.0 (2 s, 2 × ≡C-), 115.9 (d, $^2J_{C\text{-}F}$ = 22.1 Hz, 2 × CH), 117.9 (d, $^4J_{C\text{-}F}$ = 3.5 Hz, *i*-C), 121.5 (q, $^1J_{C\text{-}F}$ = 269.8 Hz, CF_3), 122.1 (s_{br}, C-4), 123.5 (d, 2 CH, Tol), 126.4 (s, C-5), 129.5 (d, 2 CH, Tol), 133.5 (d, $^3J_{C\text{-}F}$ = 8.7 Hz, 2 × CH), 136.9, 138.5 (2 s, 2 *i*-C), 141.1 (q, $^2J_{C\text{-}F}$ = 36.8 Hz, C-3), 163.1 (d, $^1J_{C\text{-}F}$ = 251.5 Hz, *i*-C) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.8 (s, CF_3), –108.8 (m_c, Ar-F) ppm. IR (film): ν = 2954-28568, 2219 (C≡C), 1506, 1284, 1236, 1173, 1134, 1063, 835 cm^{-1}. ESI-MS (*m*/*z*): 525.0 (48, $[M+Na]^+$), 503.1 (100, $[M+H]^+$). Anal. Calcd for $C_{27}H_{30}F_4N_2OSi$: C, 64.52; H, 6.02; N, 5.57. Found: C, 64.52; H, 5.90; N, 5.39.



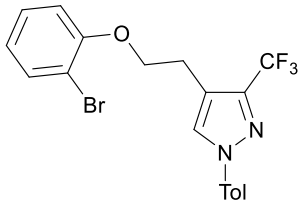
(*R*)-4-[2'-(*tert*-Butyldimethylsiloxy)ethyl]-5-[2',2'-dimethyl-1',3'-dioxolan-4'-yl)ethynyl]-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (14d): CC (SiO_2, petroleum ether/CH_2Cl_2 3:2 gradient CH_2Cl_2); colorless oil, yield: 42 mg (41%). $[\alpha]_D^{20}$ = + 24.2 (*c* 0.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.02, 0.87 (2 s, 6 H, 9 H, TBS), 1.39, 1.43 (2 s, 2 × 3 H, 2'-Me_2), 2.40 (s, 3 H, CH_3), 2.89, 3.79 (2 t, J = 7.2 Hz, 2 × 2 H, 2 CH_2), 3.95 (dd, J = 5.8, 7.9 Hz, 1 H, 5'-H), 4.19 (t_{br}, J ≈ 7.7 Hz, 1 H, 5'-H), 4.91 (t_{br}, J ≈ 6.3 Hz, 1 H, 4'-H), 7.25, 7.56 (2 d_{br}, J ≈ 8.3 Hz, 2 × 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = –5.4, 18.3 (q, s, TBS), 21.1 (q, CH_3, Tol), 25.86 (q, 2'-CH_3), 25.88 (q, ^{t}Bu, TBS), 26.0 (q, 2'-CH_3), 27.3, 62.6 (2 t, 2 CH_2), 65.8 (d, C-4'), 70.0 (t, C-5'), 73.3, 97.4 (2 s, 2 × ≡C-), 110.8 (s, C-2'), 121.5 (q, $^1J_{C\text{-}F}$ = 269.9 Hz, CF_3), 122.8 (s_{br}, C-4), 123.6 (d, 2 CH, Tol), 125.7 (s, C-5), 129.5 (d, 2 CH, Tol), 136.7, 138.6 (2 s, 2 *i*-C), 141.0 (q, $^2J_{C\text{-}F}$ = 37.1 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –60.9 (s, CF_3) ppm. IR (film): ν = 2929-2858, 1520, 1373, 1132, 1101, 1064, 837 cm^{-1}. ESI-MS (*m*/*z*): 531.2 (100, $[M+Na]^+$), 509.4 (41, $[M+H]^+$). HRMS (ESI-TOF): *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{36}F_3N_2O_3Si$: 509.2447; found: 509.2443.

Synthesis of 2-(1-tolyl-3-trifluoromethyl-1H-pyrazol-4-yl)ethyl p-toluenesulfonate (15): To a solution of pyrazole derivative **7g** (1.08 g, 4.0 mmol) in dry CH_2Cl_2 (30 mL) and Et_3N (2.0 mL), a solution of *p*-toluenesulfonyl chloride (840 mg, 4.4 mmol) in CH_2Cl_2 (15 mL) was added dropwise at 0 °C. The resulting mixture was stirred at room temperature overnight, then was washed with H_2O (2 × 80 mL), the organic layer was dried over Na_2SO_4, filtered, and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 4:1 gradient CH_2Cl_2) to afford **15** (1.61 g, 95%) as a colorless solid.



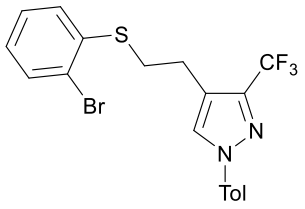
Mp 86-87 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.38, 2.40 (2 s, 2 × 3 H, 2 CH_3), 2.97, 4.22 (2 t, J = 6.3 Hz, 2 × 2 H, 2 CH_2), 7.26-7.27 (m, 4 H), 7.51 (d_{br}, J ≈ 8.5 Hz, 2 H), 7.71 (d_{br}, J ≈ 8.3 Hz, 2 H), 7.75 (s_{br}, 1 H, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 20.9, 21.5 (2 q, 2 CH_3), 23.4, 69.3 (2 t, 2 CH_2), 116.1 (q, $^{3}J_{C\text{-}F}$ = 0.9 Hz, C-4), 119.4 (d, 2 CH), 121.6 (q, $^{1}J_{C\text{-}F}$ = 269.6 Hz, CF_3), 127.7 (d, 2 CH), 128.2 (d, C-5), 129.8, 130.1 (2 d, 2 × 2 CH), 132.8, 136.9, 137.6 (3 s, 3 *i*-C), 141.1 (q, $^{2}J_{C\text{-}F}$ = 36.6 Hz, C-3), 145.0 (s, *i*-C) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.4 (s, CF_3) ppm. IR (KBr): ν = 1499, 1356, 1195, 1168, 1123, 912 cm^{-1}. ESI-MS (*m*/*z*): 447.1 (100, $[M+Na]^+$). Anal. Calcd for $C_{20}H_{19}F_3N_2O_3S$: C, 56.60; H, 4.51; N, 6.60; S, 7.55. Found: C, 56.60; H, 4.49; N, 6.57; S, 7.66.

Synthesis of pyrazoles 16a-16c; General Procedure 5 (GP5): To a suspension of NaH (60% in mineral oil, 44 mg, 1.1 mmol) in anhydrous DMF (5.0 mL) was added dropwise corresponding arylbromide (1.1 mmol) at 0 °C, and the mixture was stirred at this temperature for further 15 min. Then, a solution of pyrazole **15** (424 mg, 1.0 mmol) in dry DMF (5.0 mL) was added dropwise at 0 °C, and the resulting mixture was stirred overnight. After H_2O (15 mL) was added, the mixture was extracted with Et_2O (3 × 15 mL), the combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. Crude product **16** was purified by column chromatography.

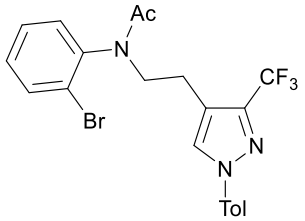


4-[2'-(*o*-Bromophenoxy)ethyl]-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (16a): CC (SiO_2, petroleum ether/CH_2Cl_2 1:1); colorless solid, yield: 318 mg (75%), mp 133-134 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.39 (s, 3 H, CH_3), 3.17, 4.21 (2 t, J = 5.9 Hz, 2 × 2 H, 2 CH_2), 6.85 (td, J ≈ 1.2, 7.9 Hz, 1 H), 6.89 (dd, J = 1.2, 8.3 Hz, 1 H), 7.25 (d_{br}, J ≈ 8.5 Hz, 2 H), 7.26 (dd_{br}, J ≈ 1.6, 8.3 Hz, 1 H), 7.55 (dd, J = 1.6, 7.9 Hz, 1 H), 7.58 (d_{br}, J ≈ 8.5 Hz, 2 H), 8.20 (s, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 20.9 (q, CH_3), 23.4, 68.1 (2 t, 2 CH_2), 111.9 (s, *i*-C), 112.9 (d, CH), 117.7 (q, $^{3}J_{C\text{-}F}$ = 0.8 Hz, C-4), 119.5 (d, 2 CH), 121.9 (q, $^{1}J_{C\text{-}F}$ = 269.5 Hz, CF_3), 122.1, 128.6 (2 d, 2 × CH), 129.5 (d, C-5), 130.0 (d, 2 CH), 133.4 (d, CH), 137.2, 137.3 (2 s, 2 *i*-C), 141.1 (q, $^{2}J_{C\text{-}F}$ = 36.2 Hz, C-3), 154.9 (s, *i*-C) ppm; ^{19}F NMR ($CDCl_3$, 188

MHz): δ = –61.1 (s, CF_3) ppm. IR (KBr): *v* = 1500, 1465, 1292, 1156, 1113, 1063, 749 cm^{-1}. ESI-MS (*m*/*z*): 427.1 (100, [M{^{81}Br}+H]$^+$), 425.2 (99, [M{^{79}Br}+H]$^+$). Anal. Calcd for $C_{19}H_{16}BrF_3N_2O$: C, 53.66; H, 3.79; N, 6.59. Found: C, 53.73; H, 3.81; N, 6.62.



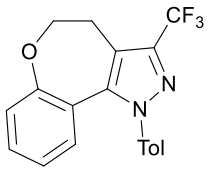
4-[2'-(*o*-Bromophenylsulfanyl)ethyl]-1-tolyl-3-trifluoromethyl-1*H*-pyrazole (16b): CC (SiO_2, petroleum ether/CH_2Cl_2 7:3); colorless solid, yield: 405 mg (92%), mp 57-58 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.39 (s, 3 H, CH_3), 3.00, 3.19 (2 t, *J* = 7.4 Hz, 2 × 2 H, 2 CH_2), 7.03-7.05, 7.25-7.31, 7.53-7.56 (3 m, 1 H, 4 H, 3 H), 7.83 (s, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 20.9 (q, CH_3), 23.0 (t, 4-CH_2), 33.5 (t, 2 CH_2S), 119.4 (q, $^3J_{C\text{-}F}$ = 0.7 Hz, C-4), 119.5 (d, 2 CH), 121.8 (q, $^1J_{C\text{-}F}$ = 269.6 Hz, CF_3), 124.1 (s, *i*-C), 127.0, 127.8 (2 d, 2 × CH), 127.9 (d, C-5), 128.7, 130.0, 133.1 (3 d, CH, 2 CH, CH), 137.0, 137.1, 137.5 (3 s, 3 *i*-C), 141.0 (q, $^2J_{C\text{-}F}$ = 36.5 Hz, C-3) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.3 (s, CF_3) ppm. IR (KBr): *v* = 1498, 1446, 1261, 1248, 1208, 1164, 1114, 1062, 809 cm^{-1}. ESI-MS (*m*/*z*): 443.0 (100, [M{^{81}Br}+H]$^+$), 441.1 (98, [M{^{79}Br}+H]$^+$). Anal. Calcd for $C_{19}H_{16}BrF_3N_2S$: C, 51.71; H, 3.65; N, 6.35; S, 7.27. Found: C, 51.82; H, 3.65; N, 6.39; S, 7.23.



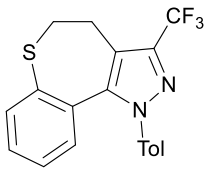
***N*-(2'-Bromophenyl)-*N*-[2'-(1''-tolyl-3''-trifluoromethyl-1''*H*-pyrazol-4''-yl)ethyl]acetamide (16c)**: CC (SiO_2, petroleum ether/EtOAc 4:1); colorless solid, yield: 302 mg (65%), mp 126-127 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.81, 2.39 (2 s, 2 × 3 H, 2 CH_3), 2.86-2.95 (m, 2 H, 4-CH_2), 3.49 (ddd, *J* = 5.9, 8.6, 14.1 Hz, 1 H, CH_2N), 4.42 (ddd, *J* = 7.1, 8.6, 13.7 Hz, 1 H, CH_2N), 7.11 (dd, *J* = 1.7, 7.9 Hz, 1 H), 7.25-7.28, 7.36-7.38 (2 m, 3 H, 1 H), 7.55 (d_{br}, *J* ≈ 8.4 Hz, 2 H), 7.71 (dd, *J* = 1.5, 7.9 Hz, 1 H), 7.94 (s, 5-H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 20.9 (q, CH_3, Tol), 21.7 (t, 4-CH_2), 22.5 (q, CH_3, Ac), 47.5 (t, 2 CH_2N), 118.4 (q, $^3J_{C\text{-}F}$ = 1.0 Hz, C-4), 119.4 (d, 2 CH), 121.7 (q, $^1J_{C\text{-}F}$ = 269.6 Hz, CF_3), 123.7 (s, *i*-C), 127.6 (d, C-5), 128.8, 129.9 (2 d, 2 CH), 130.0 (d, 2 CH), 130.6, 134.1 (2 d, 2 CH), 137.1, 137.4, 141.3 (3 s, 3 *i*-C), 141.3 (q, $^2J_{C\text{-}F}$ = 36.4 Hz, C-3), 170.6 (s, C=O) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.7 (s, CF_3) ppm. IR (KBr): *v* = 1654 (C=O), 1475, 1400, 1238, 1159, 1127, 1062 cm^{-1}. ESI-MS (*m*/*z*):

468.1 (93, [M{^{81}Br}+H]$^+$), 466.2 (100, [M{^{79}Br}+H]$^+$). Anal. Calcd for $C_{21}H_{19}BrF_3N_3O$: C, 54.09; H, 4.11; N, 9.01. Found: C, 54.15; H, 4.25; N, 8.96.

Synthesis of tricyclic pyrazoles 17a-17c; General Procedure 6 (GP6): To a three-necked round bottom flask palladium(II) acetate (5.5 mg, 0.025 mmol, 5 mol% with respect to bromide **16**), PPh_3 (8 mg, 0.025 mmol), pivalic acid (15 mg, 0.15 mmol) and K_2CO_3 (208 mg, 1.5 mmol) were added. The flask was three times was backfilled with argon, and a solution of bromide **16** (0.5 mmol) in dry DMA (2.5 mL) was added. The resulting mixture was stirred at 70 °C for 16 h (in the case of *S*-containing substrate **16b**, another portion of Pd-catalyst (5.5 mg) was added after 8h and heating was continued for further 8 h). The mixture was cooled to room temperature, H_2O (10 mL) was added and extracted with Et_2O (3 × 10 mL). Combined organic layers were dried over Na_2SO_4, filtered, and the solvents were removed. Crude product was purified by column chromatography.

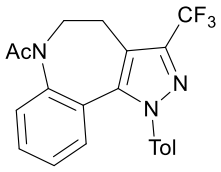


1-Tolyl-3-trifluoromethyl-4,5-dihydro-1*H*-[1]benzoxepino[5,4-*c*]pyrazole (17a): CC (SiO_2, petroleum ether/CH_2Cl_2 1:1); colorless solid, yield: 120 mg (70%), mp 117-118 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.40 (s, 3 H, CH_3), 3.12 (t, *J* = 6.2 Hz, 2 H, 4-H_2), 4.43 (t, *J* = 6.2 Hz, 2 H, 5-H_2), 6.83 (dd, *J* = 2.0, 7.9 Hz, 1 H), 6.86 (ddd, *J* = 1.3, 6.8, 7.9 Hz, 1 H), 7.16 (dd, *J* = 1.3, 8.1 Hz, 1 H), 7.20-7.24 (m, 5 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 21.1 (q, CH_3), 25.0 (t, C-4), 73.6 (t, C-5), 116.5 (q, $^3J_{C\text{-}F}$ = 0.8 Hz, C-3a), 121.9 (q, $^1J_{C\text{-}F}$ = 269.6 Hz, CF_3), 121.9 (s, C-10b), 122.4, 123.3 (2 d, 2 CH), 125.7 (d, 2 CH, Tol), 129.6, 129.7 (2 d, 2 CH), 129.9 (d, 2 CH, Tol), 137.8, 138.6 (2 s, 2 *i*-C, Tol), 138.7 (s, C-10a), 140.6 (q, $^2J_{C\text{-}F}$ = 36.5 Hz, C-3), 158.2 (s, C-6a) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –62.1 (s, CF_3) ppm. IR (KBr): *v* = 1519, 1450, 1285, 1211, 1191, 1167, 1128, 1108, 1065, 1054, 981, 823 cm^{-1}. ESI-MS (*m*/*z*): 345.2 (100, [M+H]$^+$). Anal. Calcd for $C_{19}H_{15}F_3N_2O$: C, 66.27; H, 4.39; N, 8.14. Found: C, 66.25; H, 4.50; N, 8.14.



1-Tolyl-3-trifluoromethyl-4,5-dihydro-1*H*-[1]benzothiepino[5,4-*c*]pyrazole (17b): CC (SiO_2, petroleum ether/CH_2Cl_2 7:3); colorless solid, yield: 76 mg (42%), mp 105-107 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.36 (s, 3 H, CH_3), 2.94 (t, *J* = 6.2 Hz, 2 H, 4-H_2), 3.41 (t, *J* = 6.2 Hz, 2 H, 5-H_2), 6.85

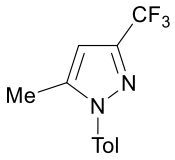
(dd, *J* = 1.6, 7.8 Hz, 1 H), 7.12-7.17, 7.23-7.26 (2 m, 5 H, 1 H), 7.73 (dd, *J* = 1.6, 7.8 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 21.1 (q, CH_3), 22.5 (t, C-4), 40.6 (t, C-5), 119.1 (q, $^3J_{C\text{-}F}$ = 0.7 Hz, C-3a), 121.9 (q, $^1J_{C\text{-}F}$ = 269.7 Hz, CF_3), 125.1 (d, 2 CH, Tol), 128.0, 128.8 (2 d, 2 CH), 129.6 (d, 2 CH, Tol), 130.6 (d, CH), 134.1, 134.6 (2 s, C-10a, C-6a), 135.3 (d, CH), 136.7, 138.3 (2 s, 2 *i*-C, Tol), 140.2 (q, $^2J_{C\text{-}F}$ = 36.5 Hz, C-3), 140.9 (s, C-10b) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –61.5 (s, CF_3) ppm. IR (KBr): *v* = 1518, 1438, 1299, 1264, 1159, 1131, 1110, 1049 cm^{-1}. ESI-MS (*m*/*z*): 361.1 (100, $[M+H]^+$). Anal. Calcd for $C_{19}H_{15}F_3N_2S$: C, 63.32; H, 4.20; N, 7.77; S, 8.90. Found: C, 63.43; H, 4.45; N, 7.73; S, 9.12.



6-Acetyl-1-tolyl-3-trifluoromethyl-1,4,5,6-tetrahydropyrazolo-[4,3-*d*][1]benzazepine (17c): CC (SiO_2, petroleum ether/EtOAc 1:1); colorless solid, yield: 183 mg (95%), mp 215-216 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.98, 2.40 (2 s, 2 × 3 H, 2 CH_3), 2.80 (ddd, *J* = 5.3, 5.5, 16.5, 1 H, 4-H), 3.15 (ddd, *J* = 5.5, 9.3, 13.4 Hz, 1 H, 5-H), 3.41 (ddd, *J* = 6.9, 9.3, 16.5 Hz, 1 H, 4-H), 4.88 (ddd, *J* = 5.3, 6.9, 13.4 Hz, 1 H, 5-H), 6.93 (dd, *J* = 1.0, 7.9 Hz, 1 H), 7.10-7.13 (m, 1 H), 7.14, 7.21 (2 d_{br}, *J* ≈ 8.2 Hz, 2 × 2 H), 7.29-7.35 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 21.1 (q, CH_3, Tol), 22.5 (t, C-4), 22.9 (q, CH_3, Ac), 47.4 (t, C-5), 117.6 (s_{br}, C-3a), 121.7 (q, $^1J_{C\text{-}F}$ = 269.8 Hz, CF_3), 125.5 (d, 2 CH, Tol), 126.6 (s, C-10a), 127.4, 128.6, 129.4 (3 d, 3 CH), 130. (d, 2 CH, Tol), 130.4 (d, CH), 137.4 (s, *i*-C, Tol), 137.9 (s, C-10b), 138.8 (s, *i*-C, Tol), 141.2 (q, $^2J_{C\text{-}F}$ = 36.7 Hz, C-3), 141.9 (s, C-6a), 169.2 (s, C=O) ppm; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –62.6 (s, CF_3) ppm. IR (KBr): *v* = 1660 (C=O), 1520, 1453, 1378, 1164, 1132, 1066 cm^{-1}. ESI-MS (*m*/*z*): 408.2 (100, $[M+Na]^+$), 386.1 (19, $[M+H]^+$). Anal. Calcd for $C_{21}H_{18}F_3N_3O$: C, 65.45; H, 4.71; N, 10.90. Found: C, 65.50; H, 4.70; N, 10.98.

2. NMR spectra

Copies of ^{1}H and ^{13}C NMR spectra for compounds **7-10,12-17** are shown in Figures S1-S82.



5-Methyl-1-tolyl-3-trifluoromethylpyrazole (7a)

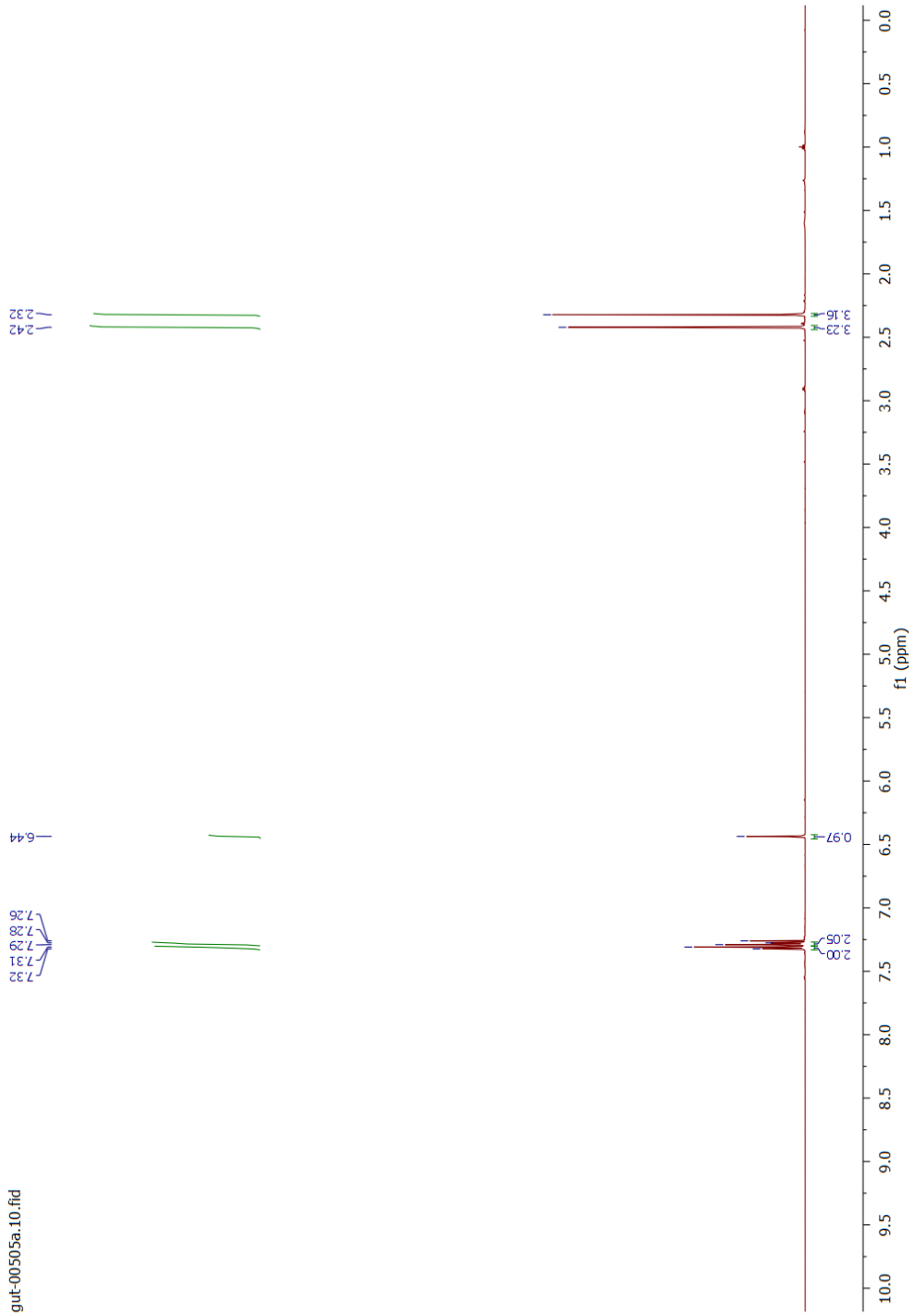


Figure S1. ^{1}H NMR of **7a** ($CDCl_3$, 600 MHz).

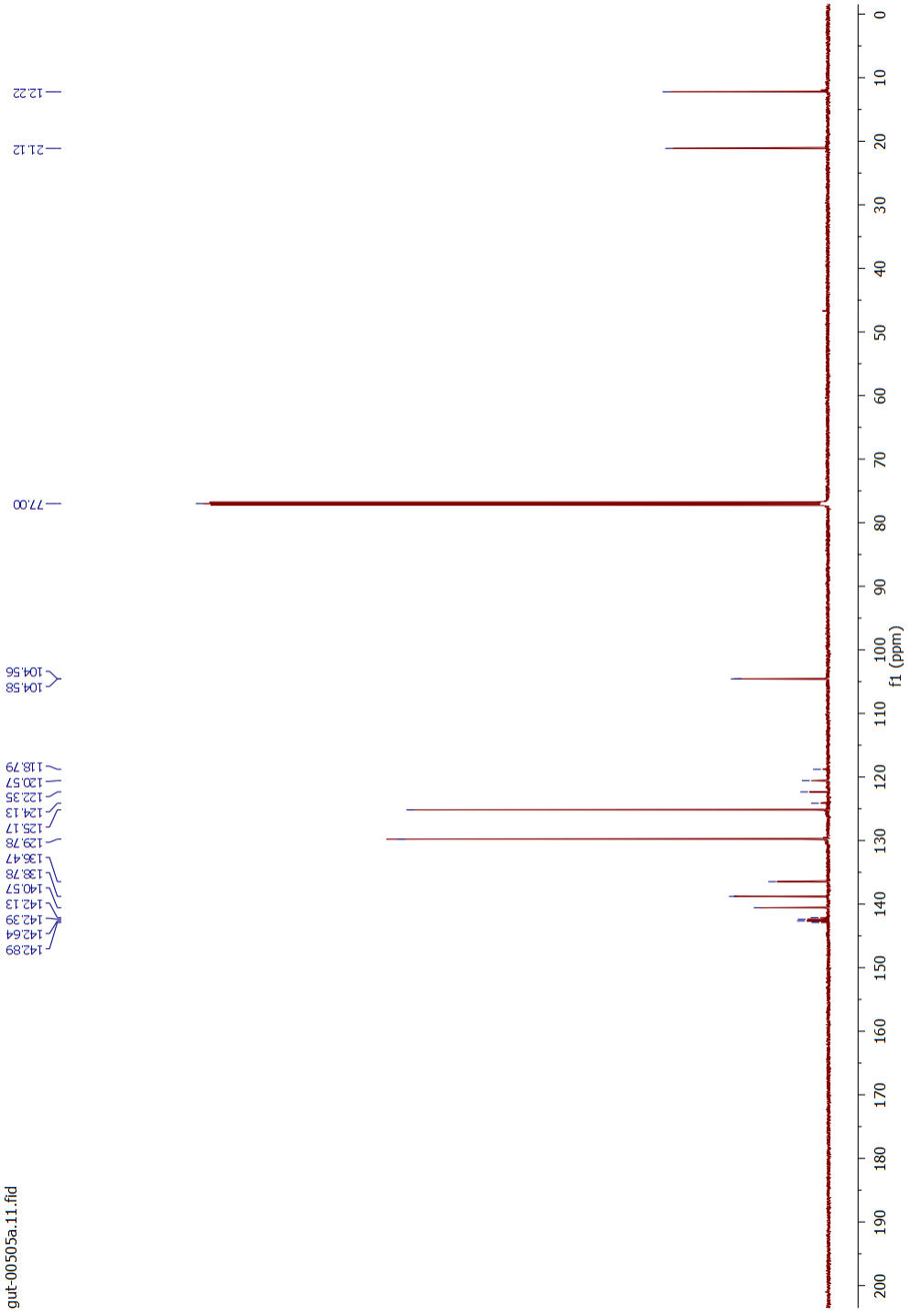
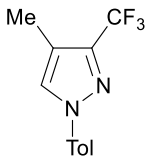


Figure S2. ^{13}C NMR of **7a** ($CDCl_3$, 151 MHz).



4-Methyl-1-tolyl-3-trifluoromethylpyrazole (7b)

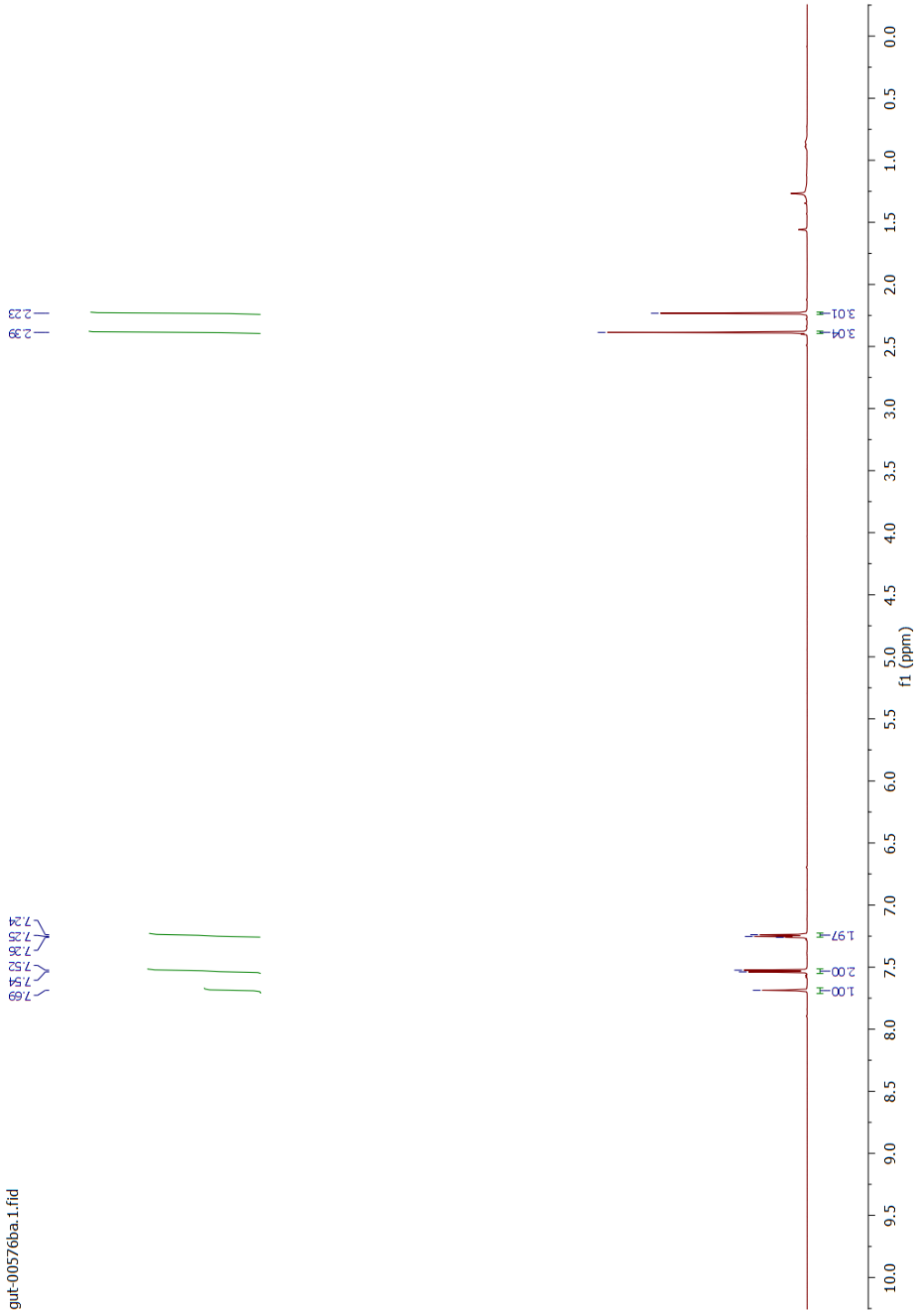


Figure S3. ^{1}H NMR of **7b** ($CDCl_3$, 600 MHz).

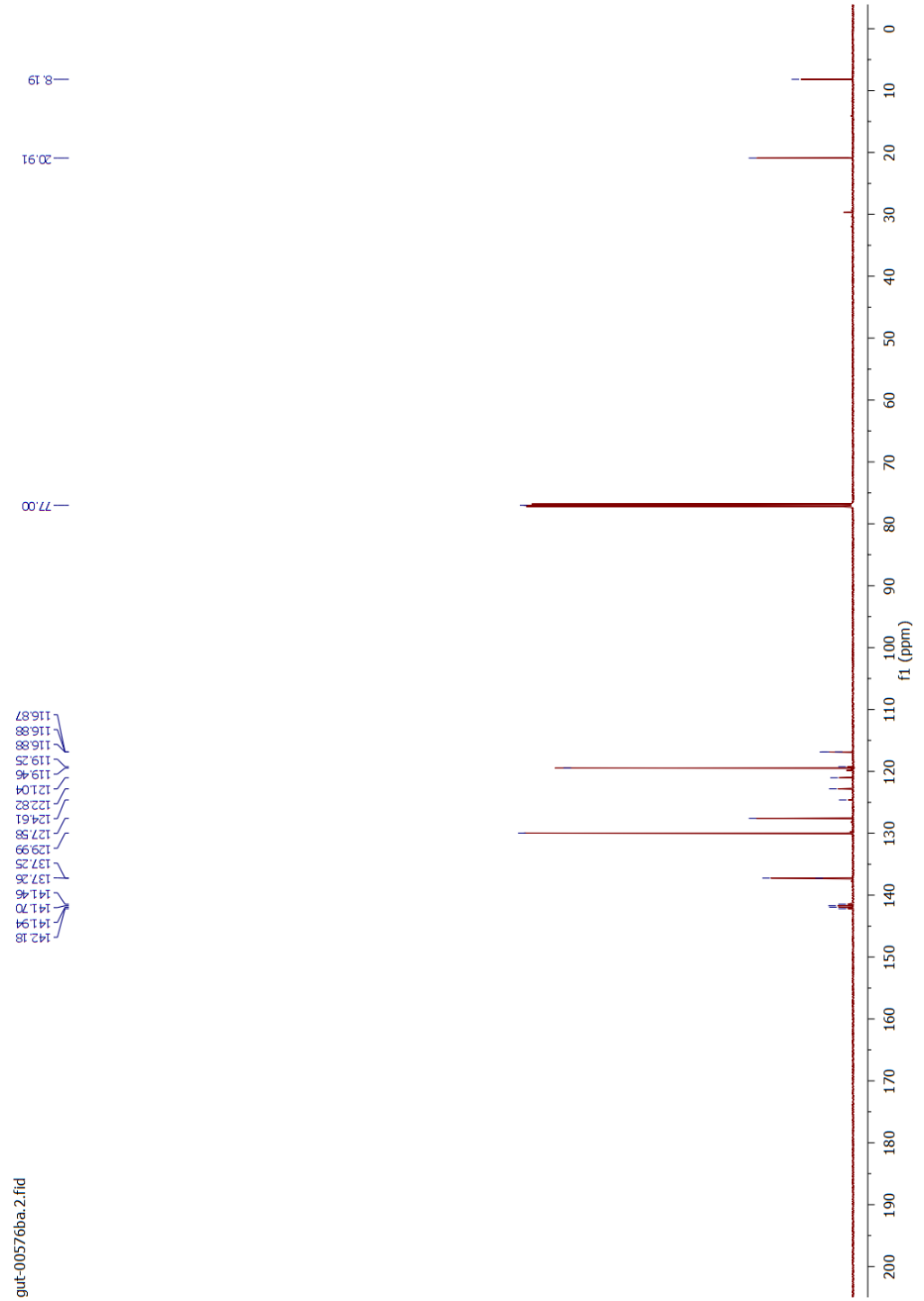
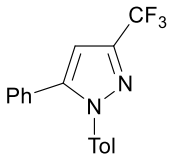


Figure S4. ^{13}C NMR of **7b** ($CDCl_3$, 151 MHz).



5-Phenyl-1-tolyl-3-trifluoromethylpyrazole (7c)

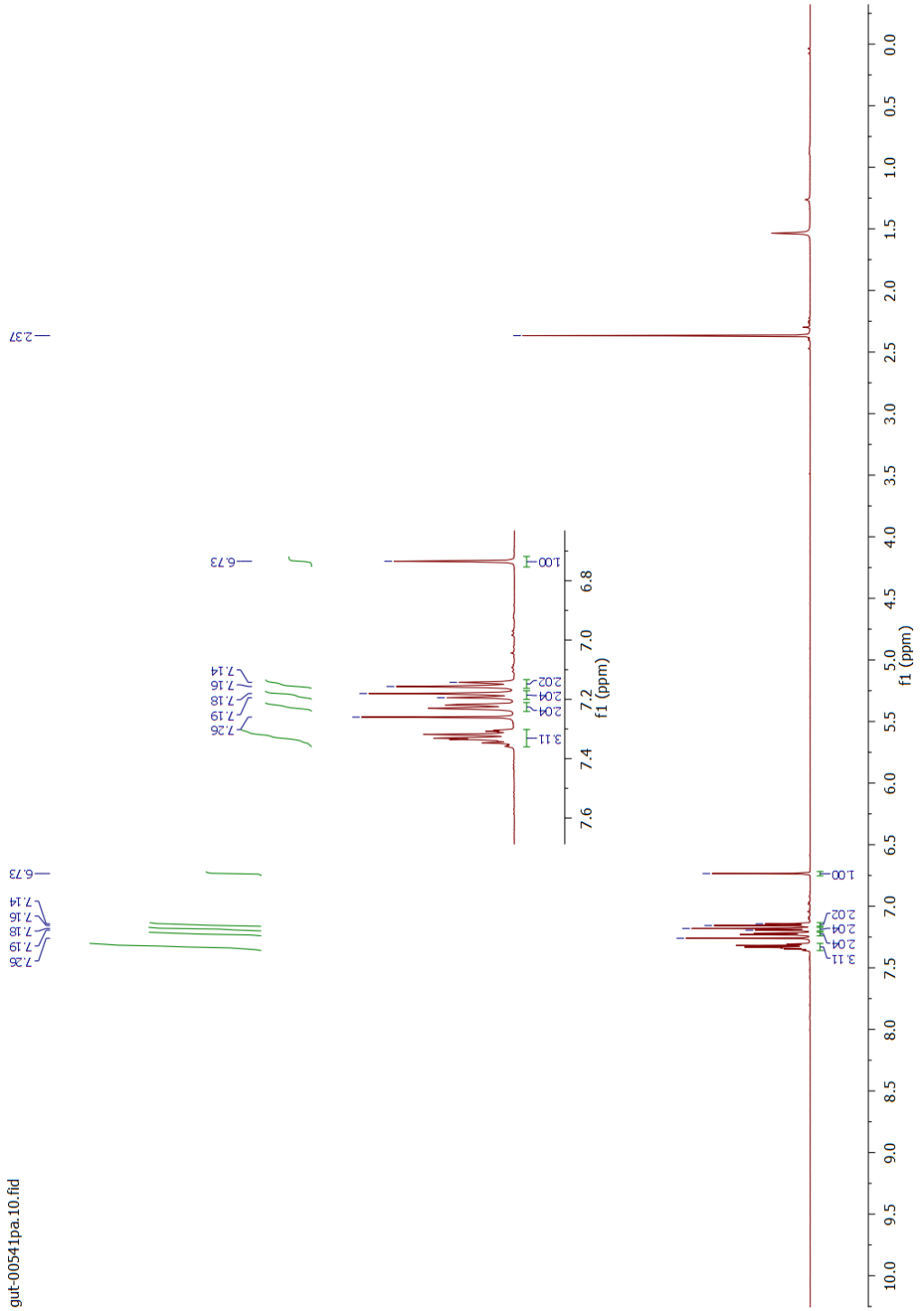


Figure S5. ^{1}H NMR of **7c** ($CDCl_3$, 600 MHz).

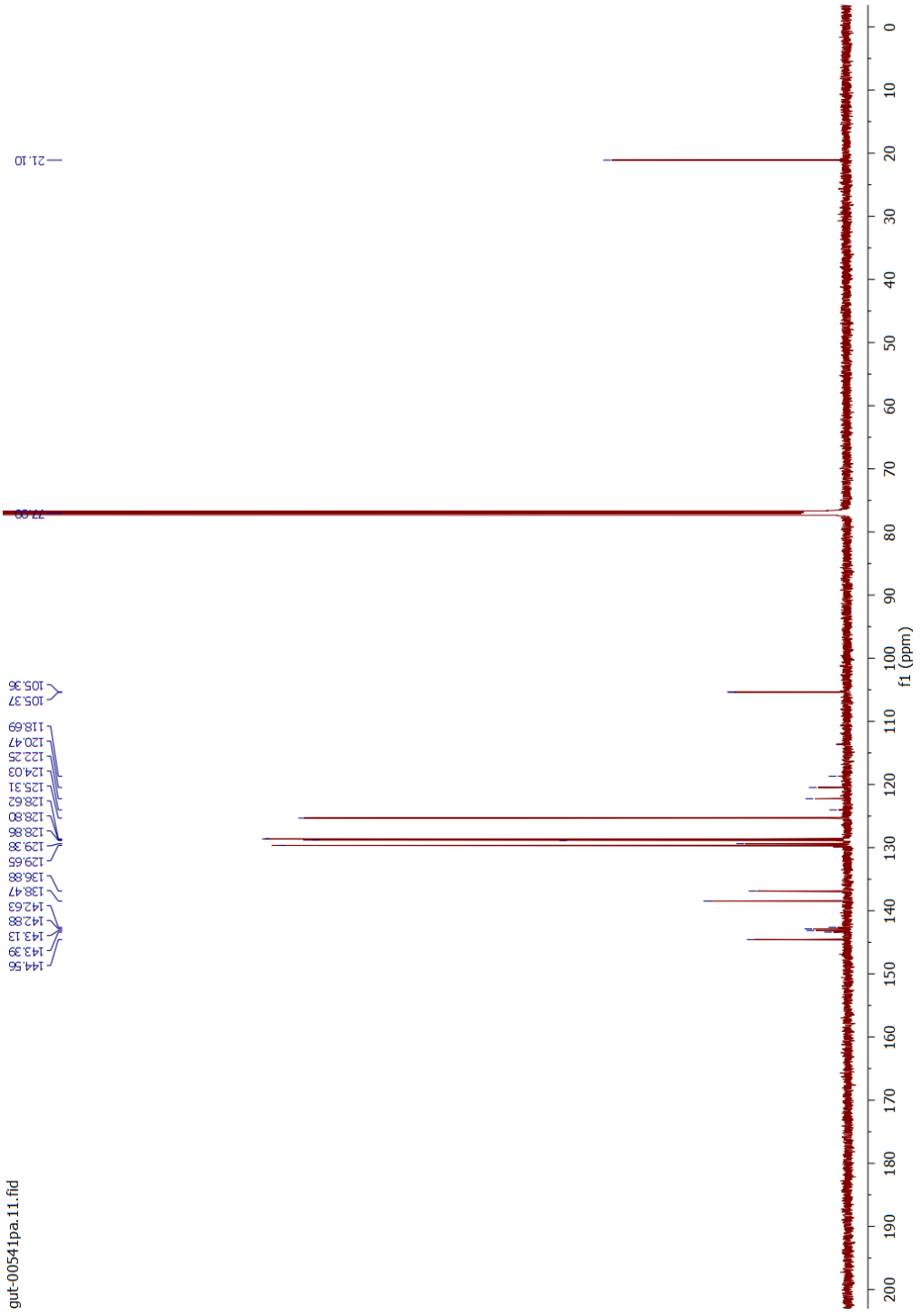
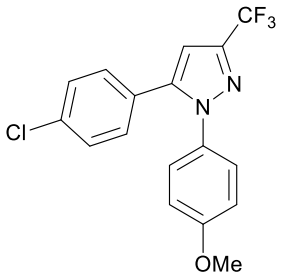


Figure S6. ^{13}C NMR of **7c** ($CDCl_3$, 151 MHz).



5-(4'-Chlorophenyl)-1-(4'-methoxyphenyl)-3-trifluoromethyl-1H-pyrazole (7d)

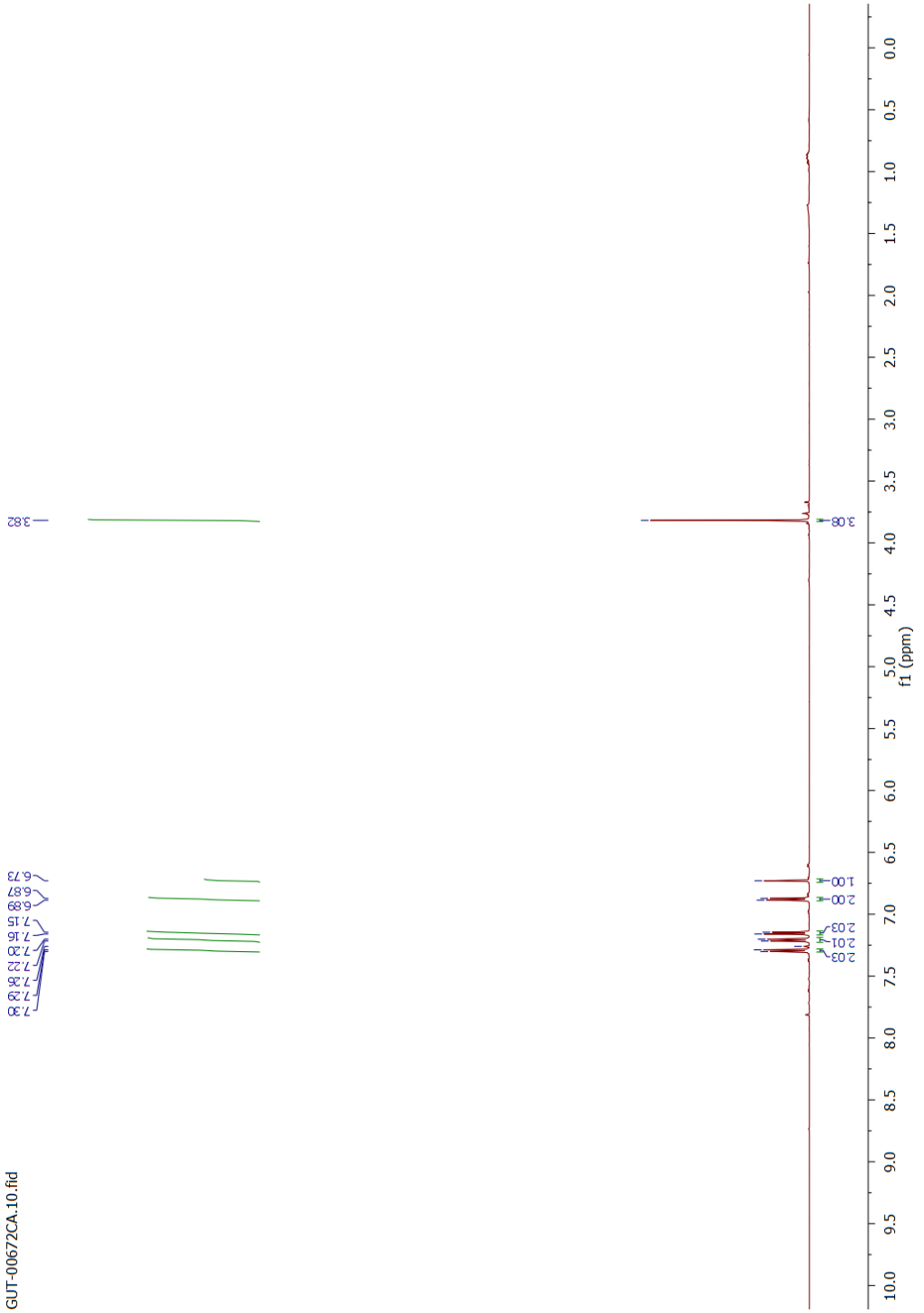


Figure S7. ^{1}H NMR of **7d** ($CDCl_3$, 600 MHz).

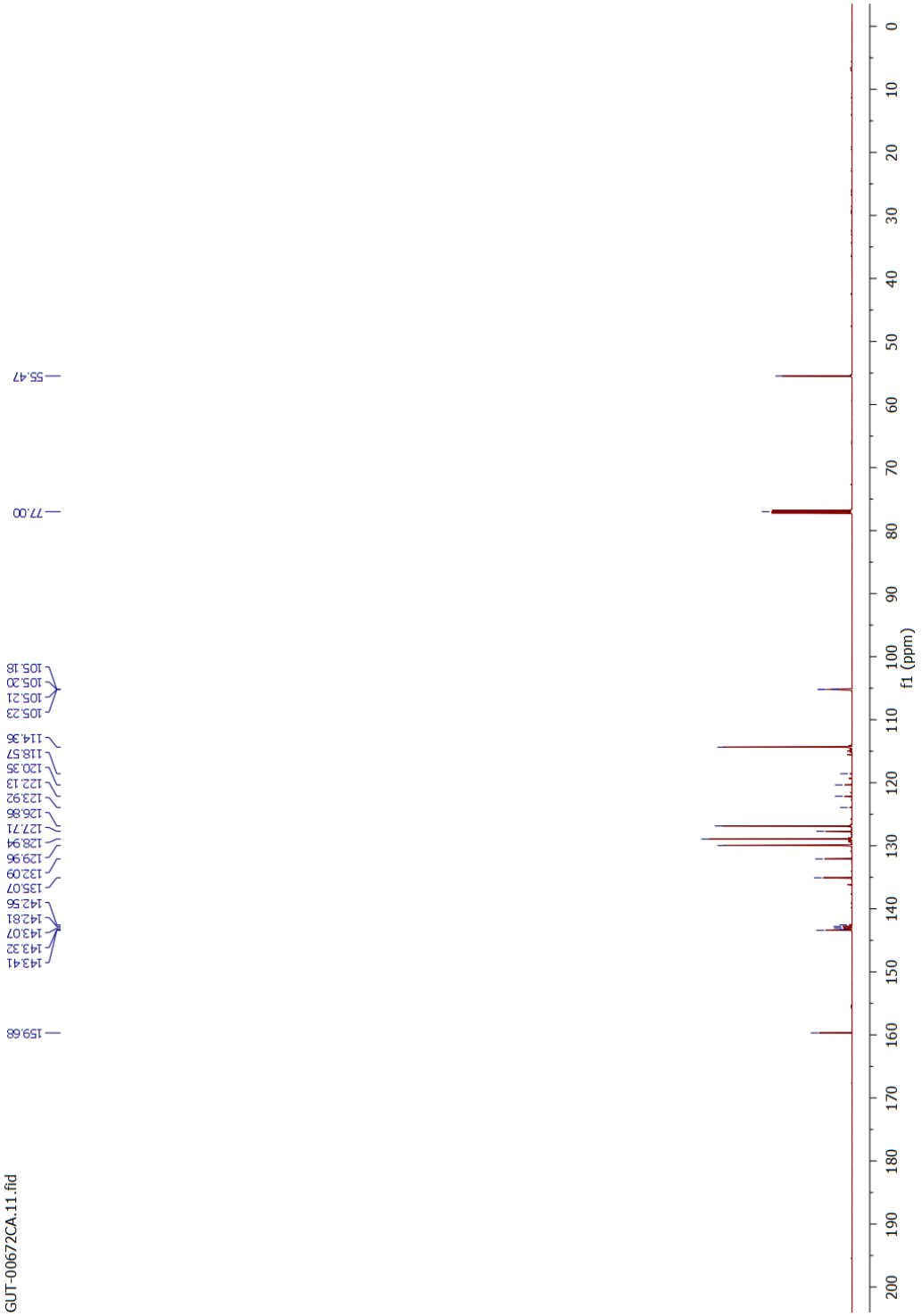
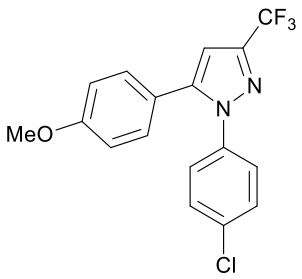


Figure S8. ^{13}C NMR of **7d** ($CDCl_3$, 151 MHz).



1-(4'-Chlorophenyl)-5-(4'-methoxyphenyl)-3-trifluoromethyl-1H-pyrazole (7e)

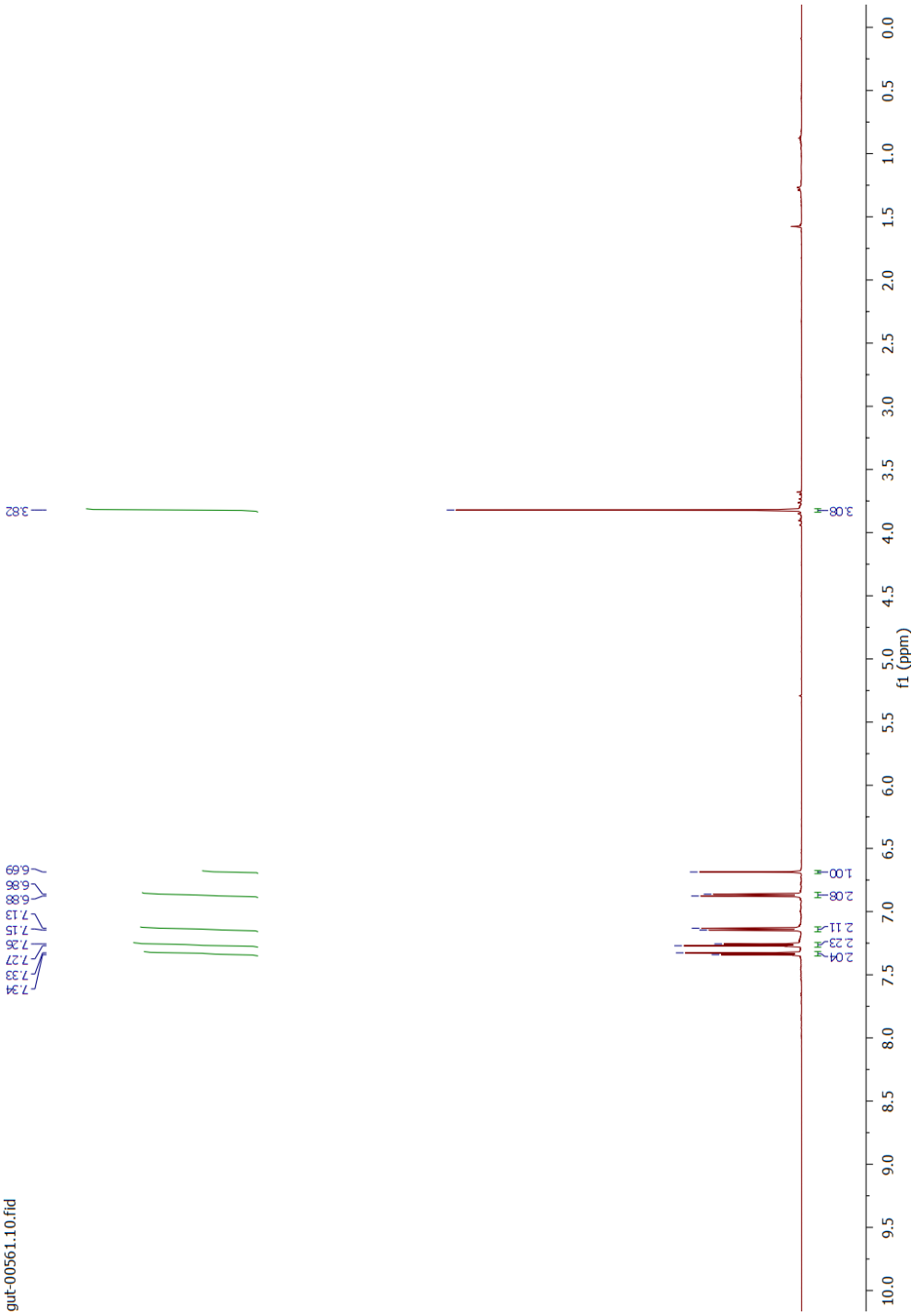


Figure S9. ^{1}H NMR of **7e** ($CDCl_3$, 600 MHz).

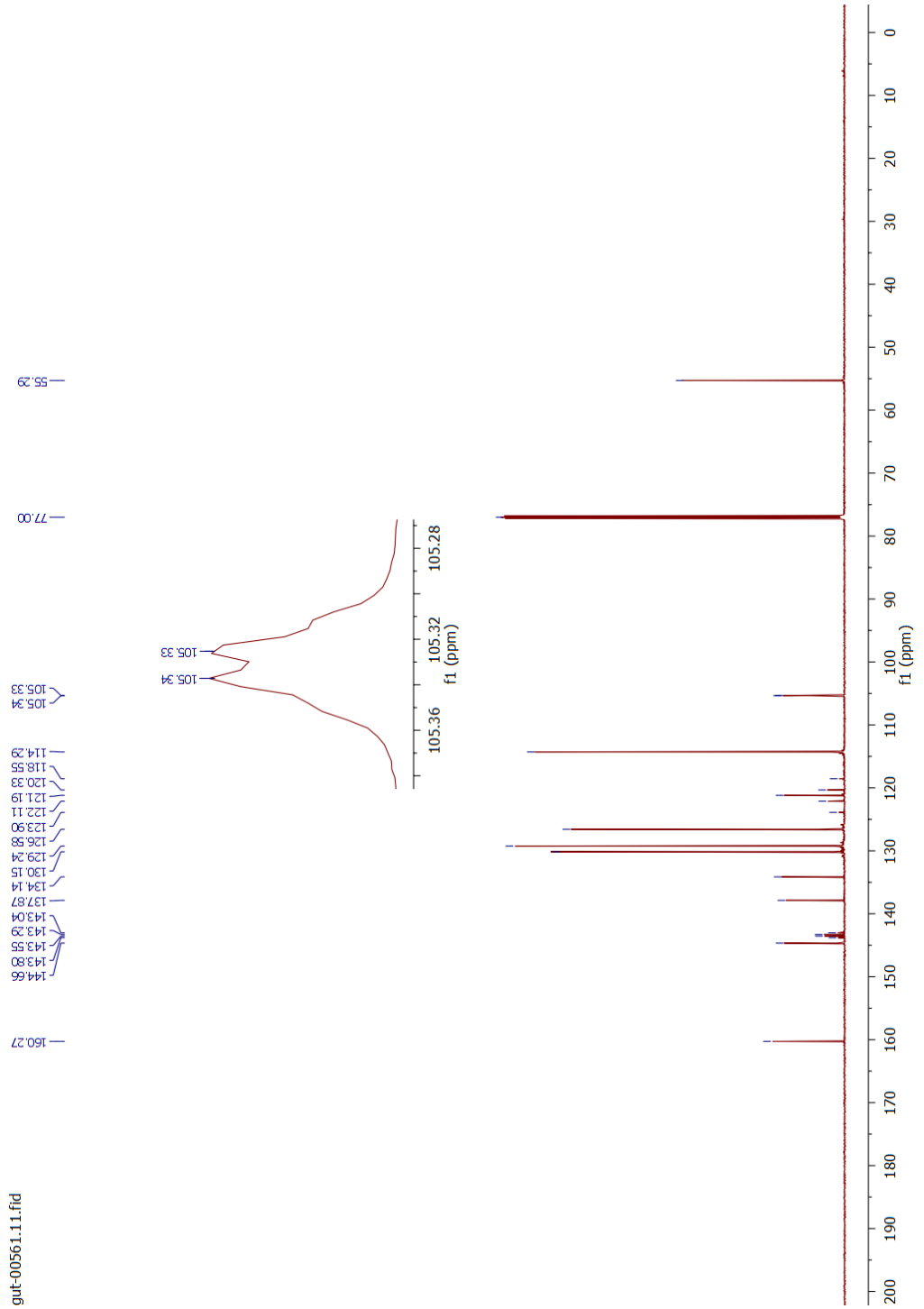
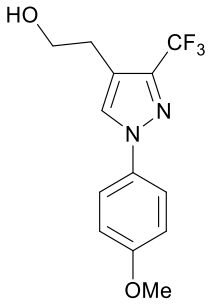


Figure S10. ^{13}C NMR of **7e** ($CDCl_3$, 151 MHz).



4-(2'-Hydroxyethyl)-1-(4'-methoxyphenyl)-3-trifluoromethyl-1H-pyrazole (7f)

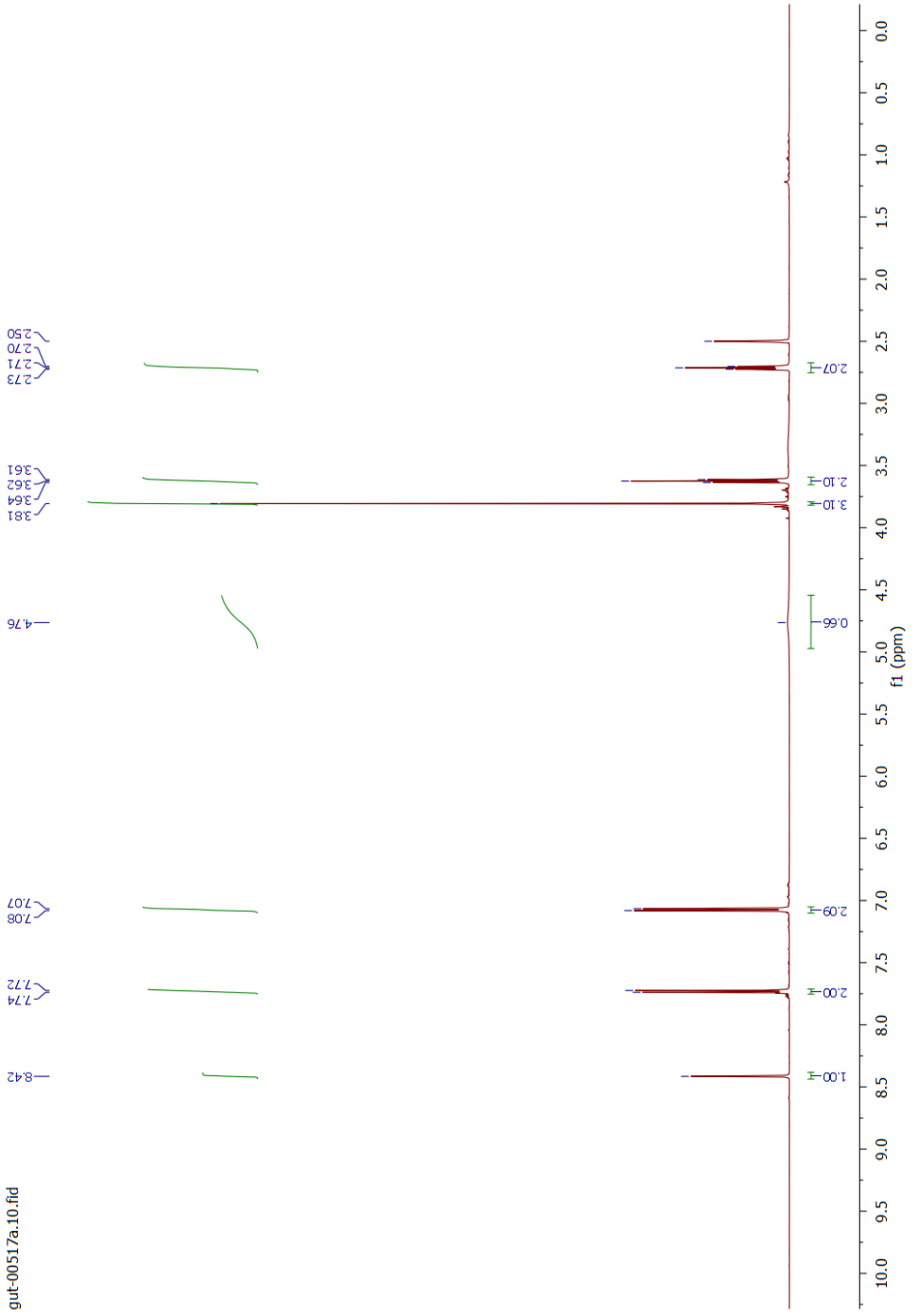


Figure S11. ^{1}H NMR of **7f** (DMSO-d_6, 600 MHz).

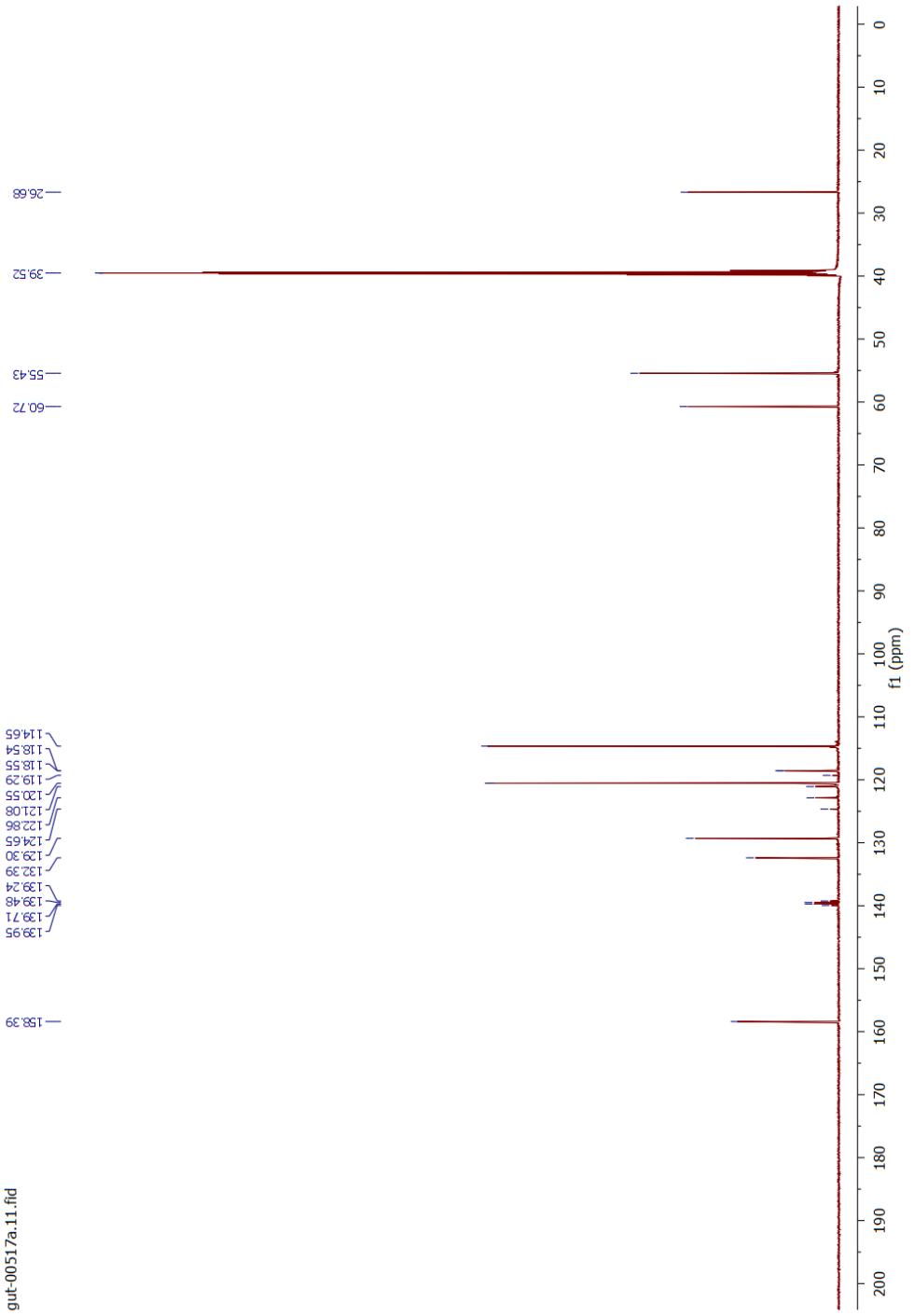
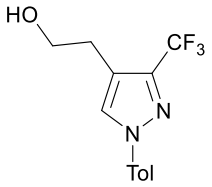


Figure S12. ^{13}C NMR of **7f** (DMSO-d_6, 151 MHz).



4-(2'-Hydroxyethyl)-1-tolyl-3-trifluoromethyl-1H-pyrazole (7g)

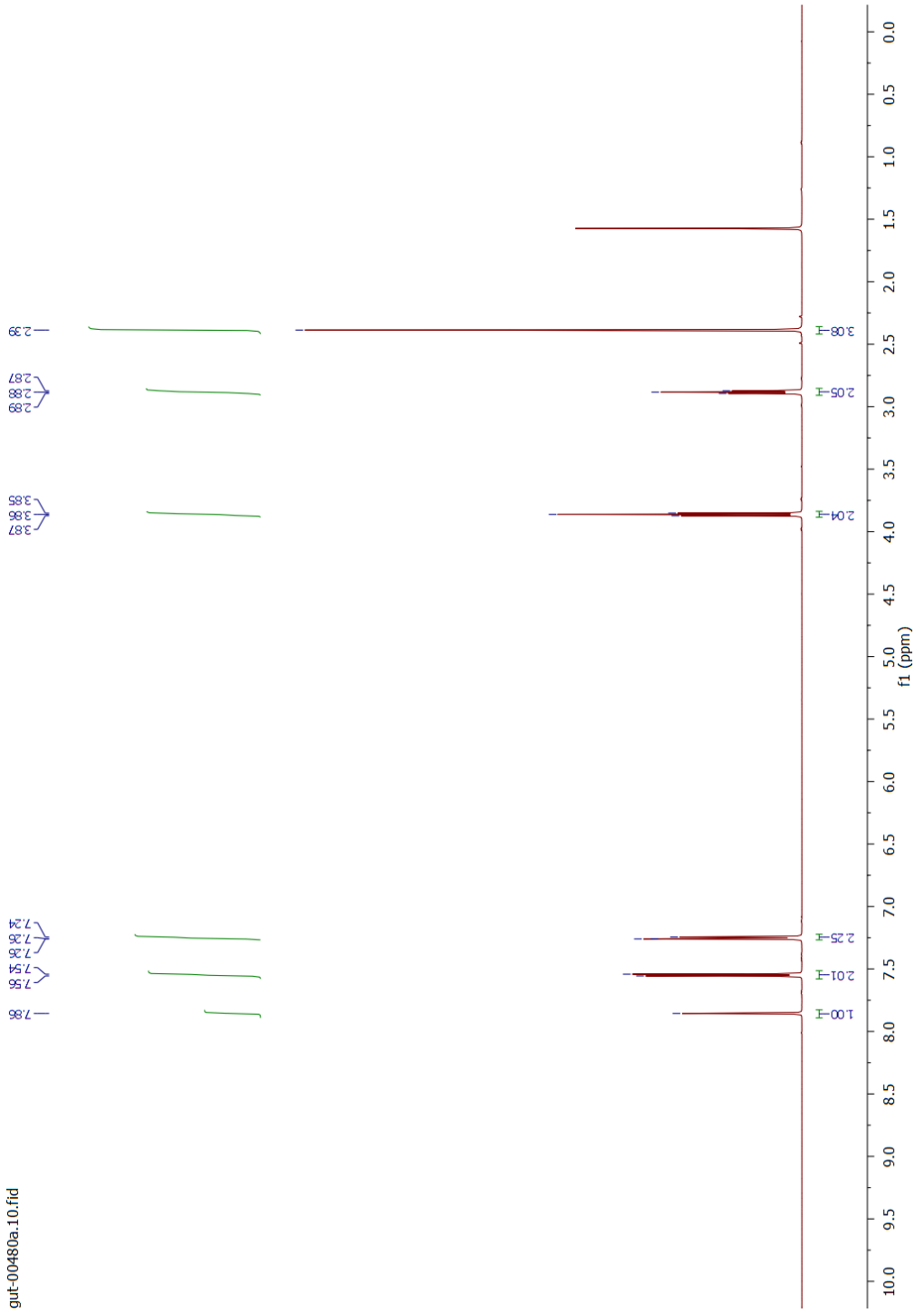


Figure S13. ^{1}H NMR of **7g** ($CDCl_3$, 600 MHz).

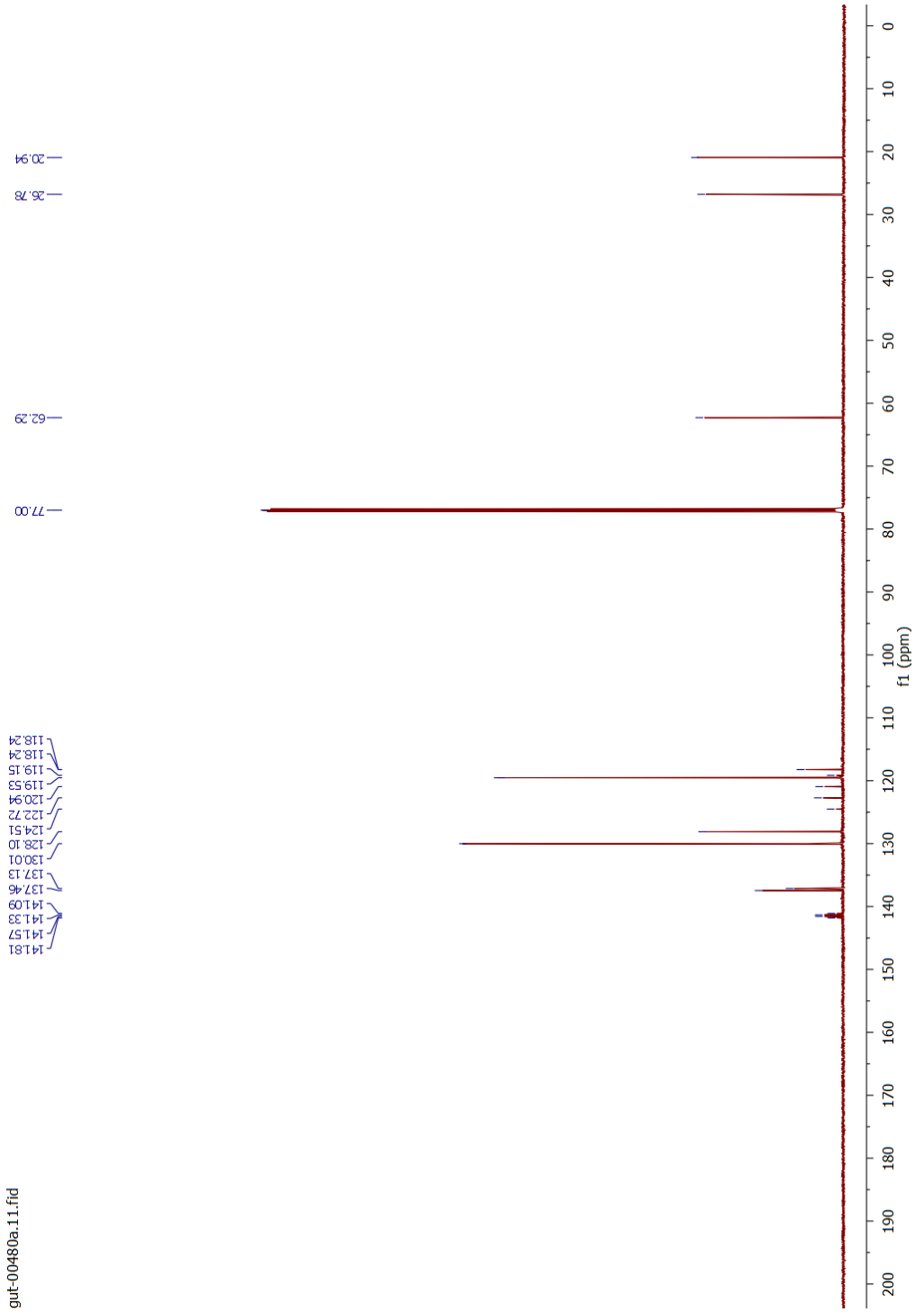
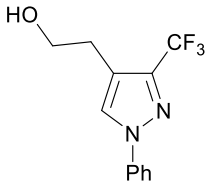


Figure S14. ^{13}C NMR of **7g** ($CDCl_3$, 151 MHz).



4-(2'-Hydroxyethyl)-1-phenyl-3-trifluoromethyl-1H-pyrazole (7h)

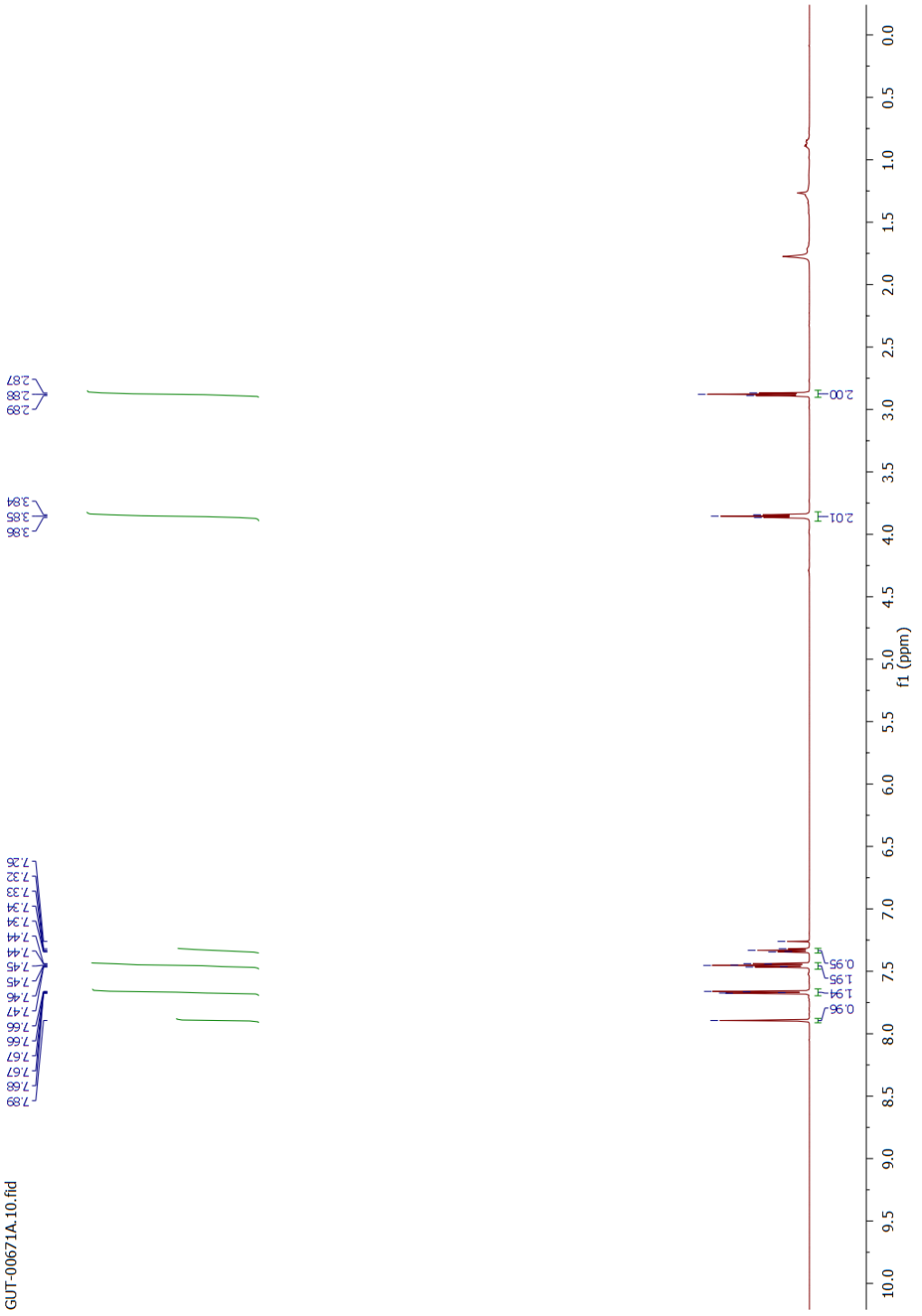


Figure S15. ^{1}H NMR of **7h** ($CDCl_3$, 600 MHz).

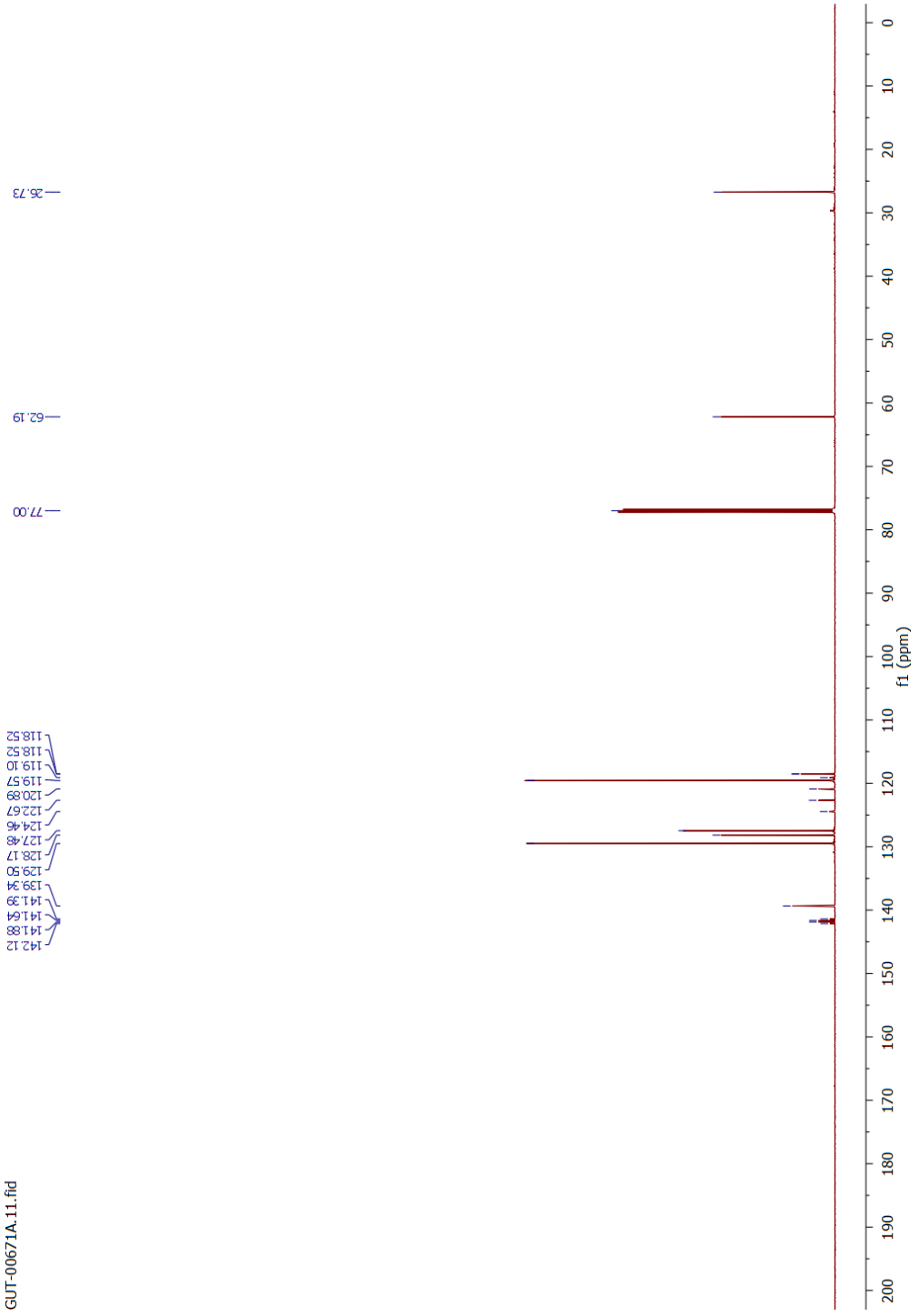
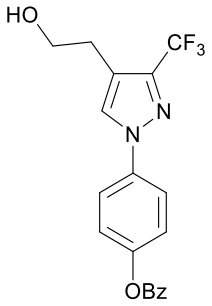


Figure S16. ^{13}C NMR of **7h** ($CDCl_3$, 151 MHz).



1-(4'-Benzoyloxyphenyl)-4-(2'-hydroxyethyl)-3-trifluoromethyl-1H-pyrazole (7i)

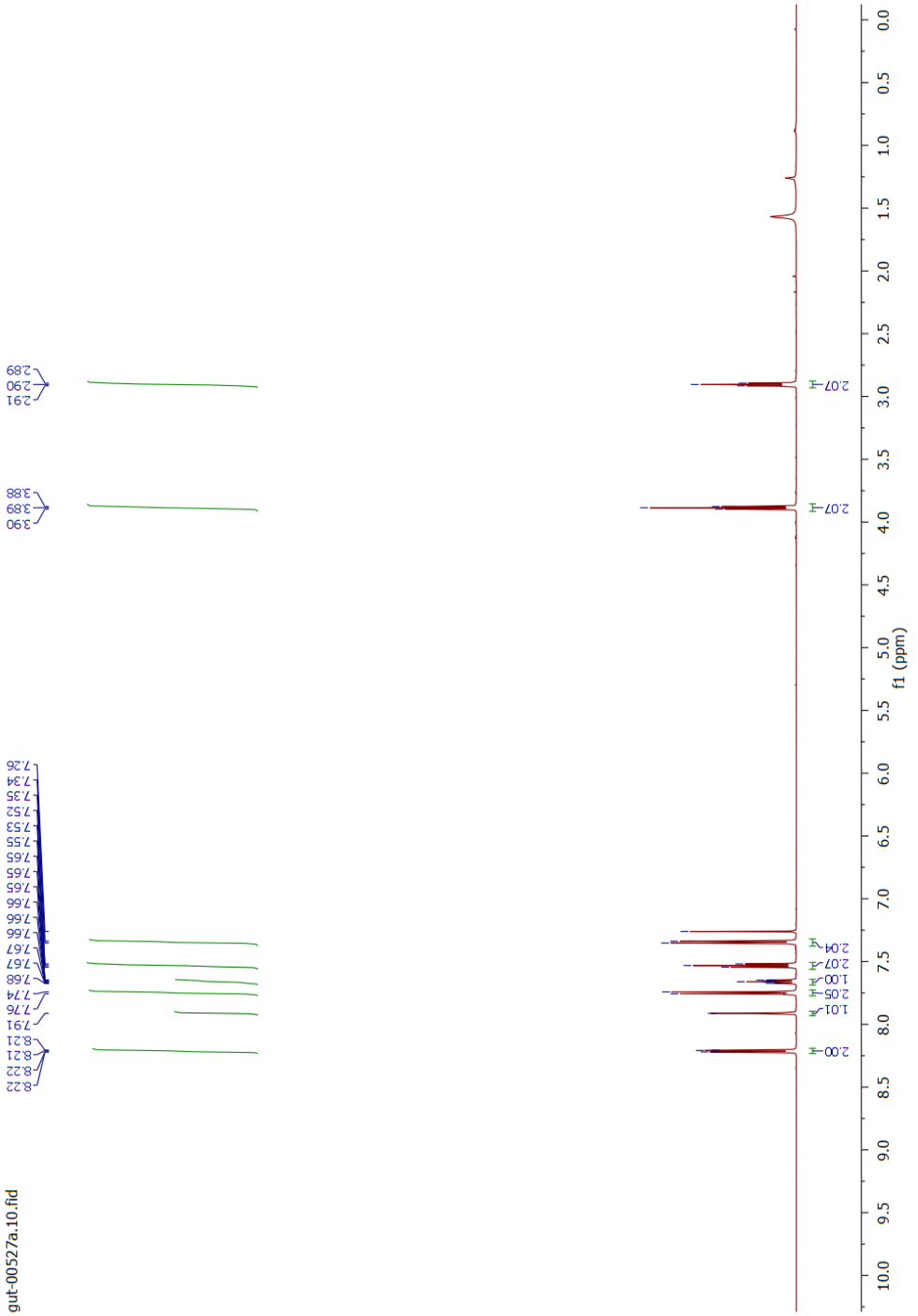


Figure S17. ^{1}H NMR of **7i** ($CDCl_3$, 600 MHz).

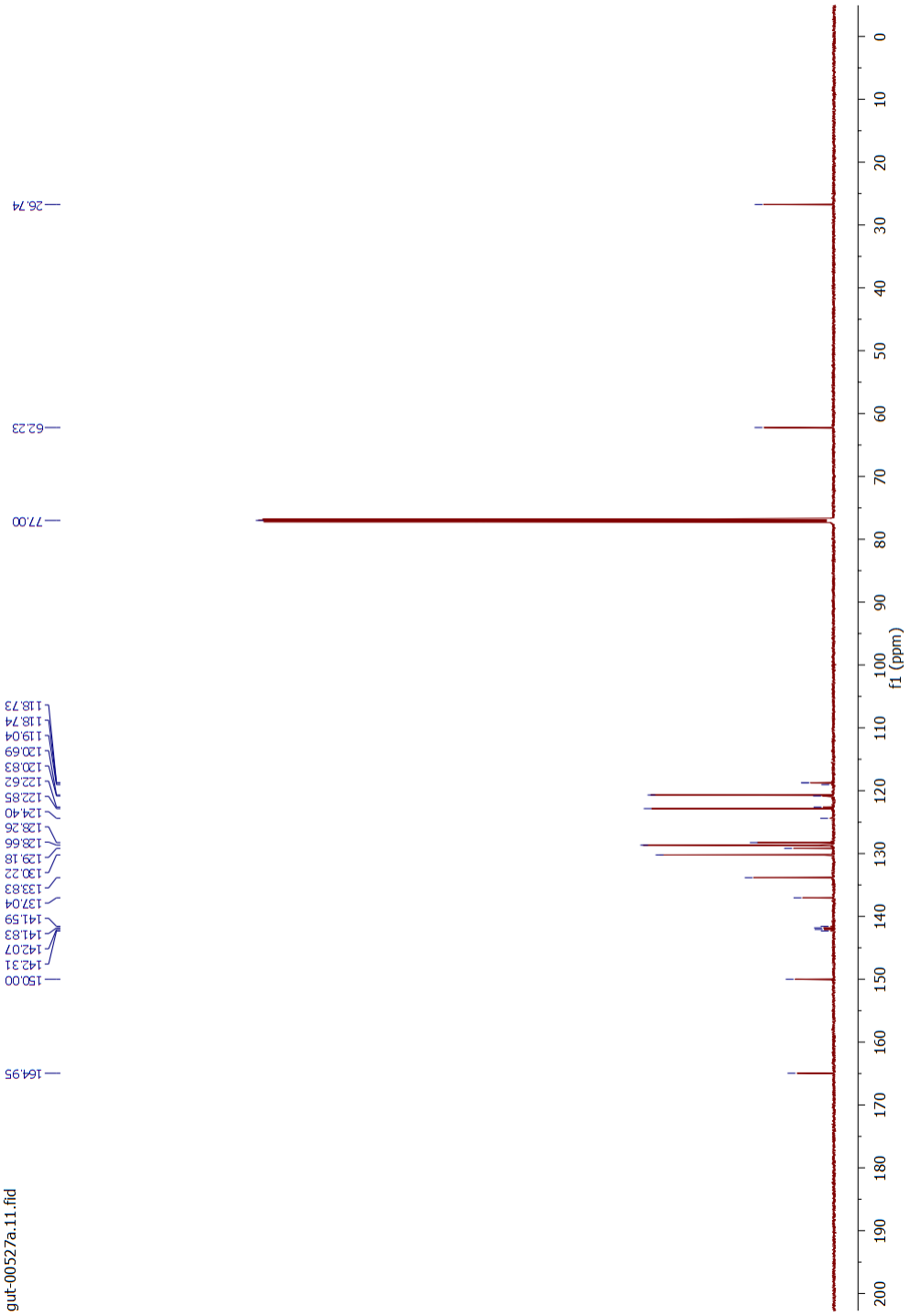
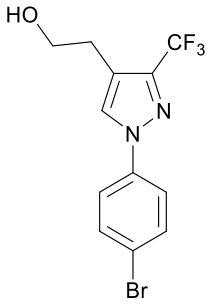


Figure S18. ^{13}C NMR of **7i** ($CDCl_3$, 151 MHz).



1-(4'-Bromophenyl)-4-(2'-hydroxyethyl)-3-trifluoromethyl-1H-pyrazole (7j)

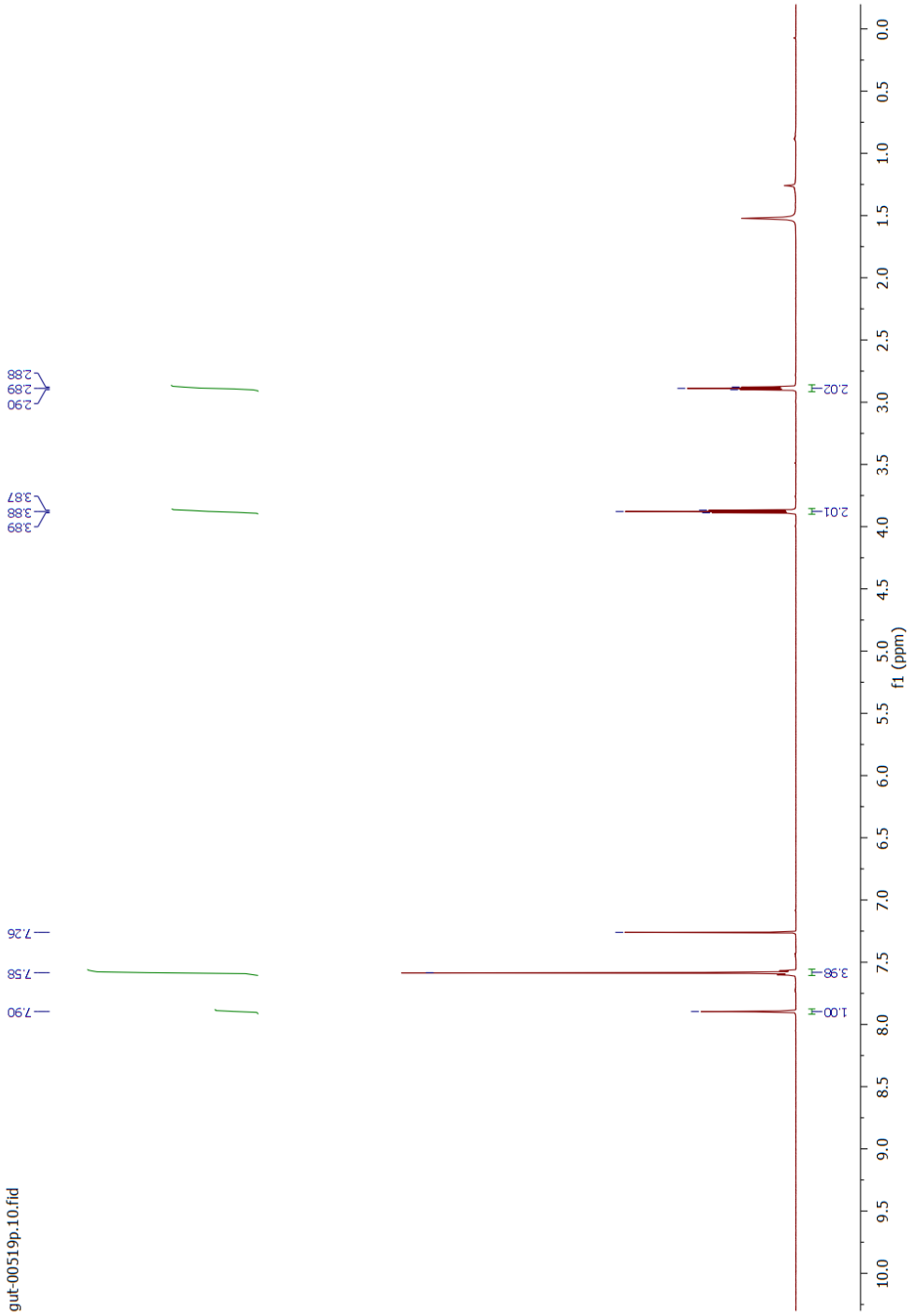


Figure S19. ^{1}H NMR of **7j** ($CDCl_3$, 600 MHz).

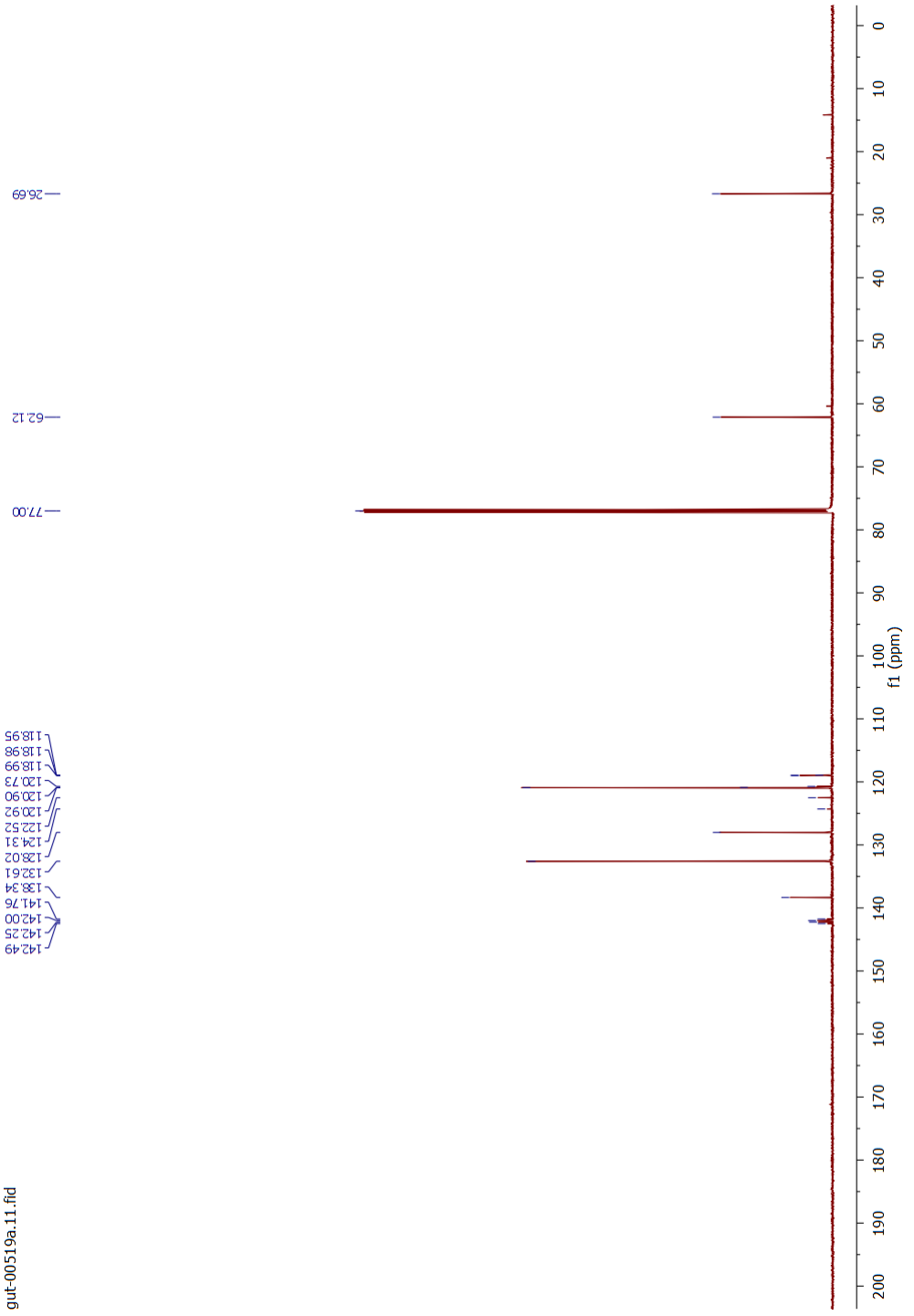
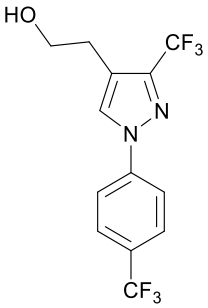


Figure S20. ^{13}C NMR of **7j** ($CDCl_3$, 151 MHz).



4-(2'-Hydroxyethyl)-1-(4'-trifluromethylphenyl)-3-trifluoromethyl-1H-pyrazole (7k)

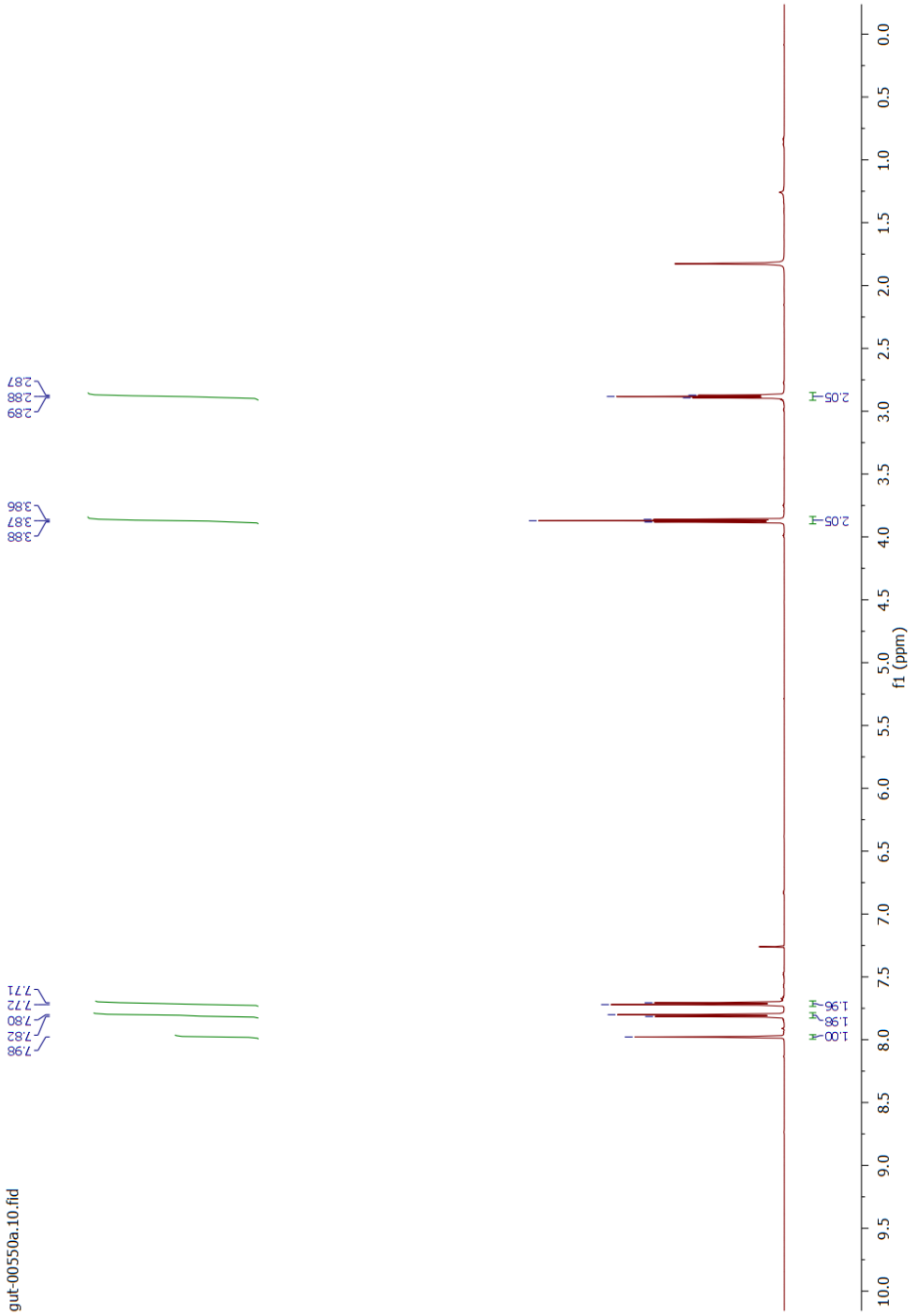


Figure S21. ^{1}H NMR of **7k** ($CDCl_3$, 600 MHz).

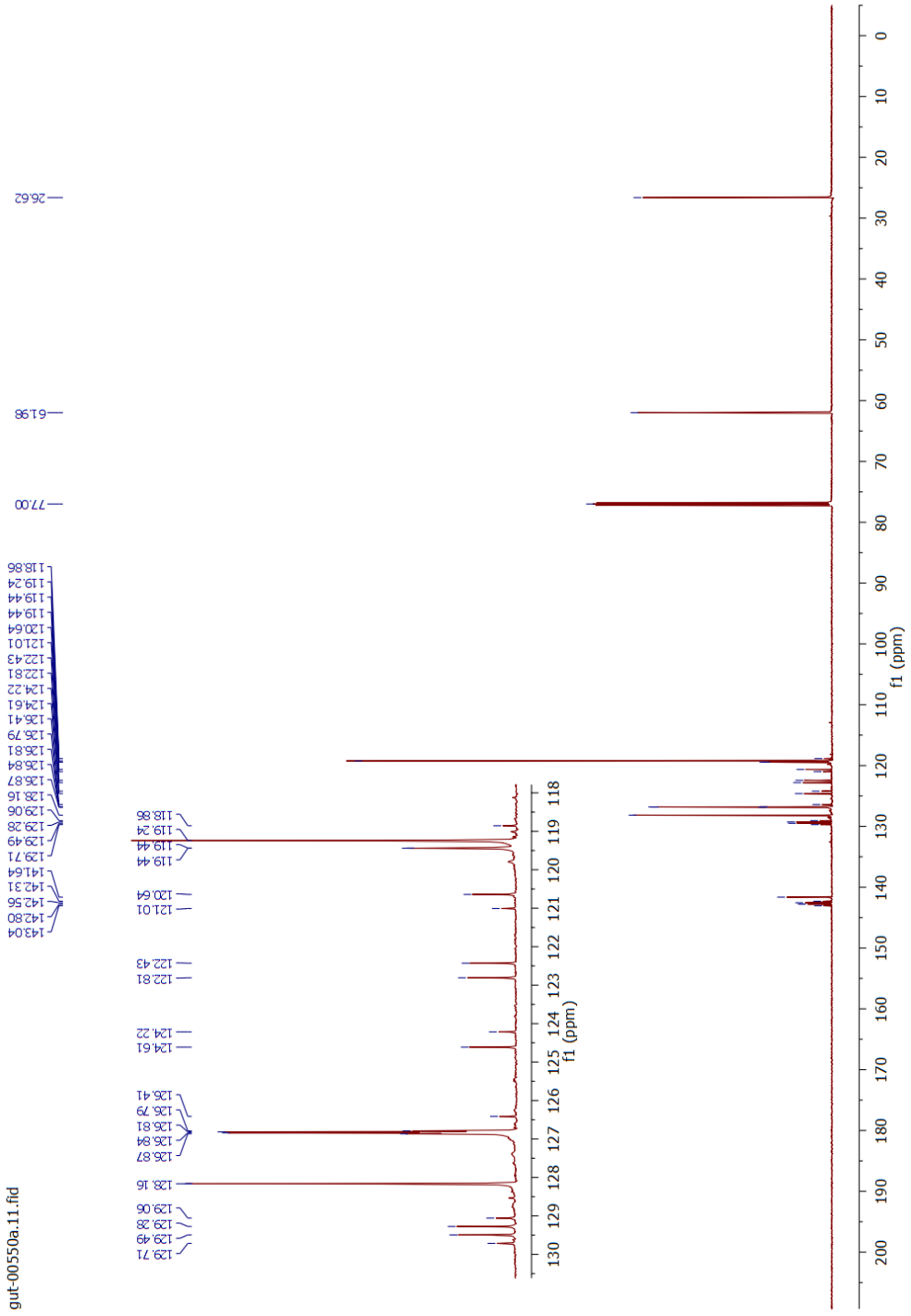
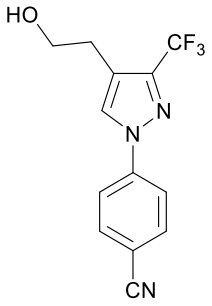


Figure S22. ^{13}C NMR of **7k** ($CDCl_3$, 151 MHz).



1-(4'-Cyanophenyl)-4-(2'-hydroxyethyl)-3-trifluoromethyl-1H-pyrazole (7l)

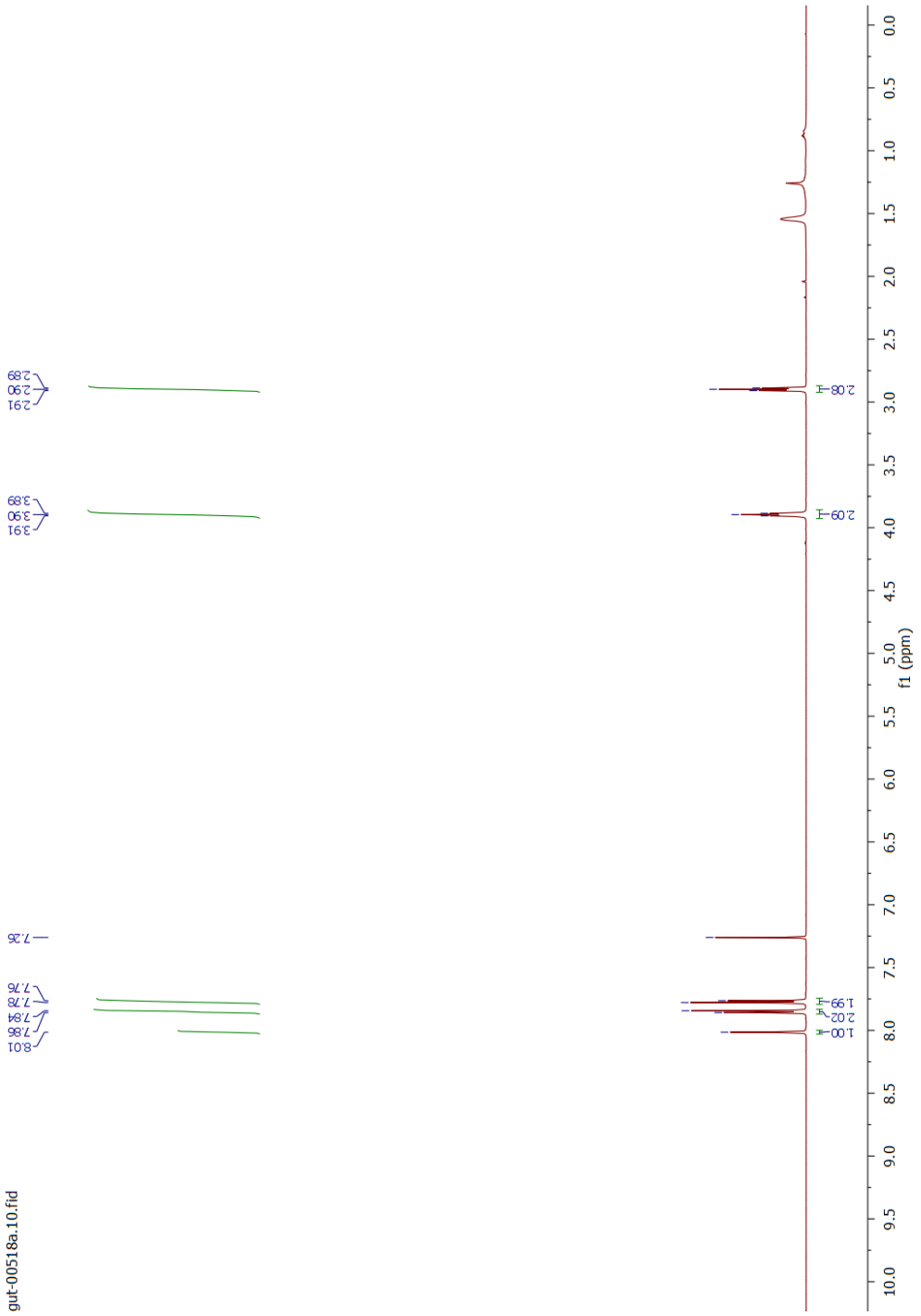


Figure S23. ^{1}H NMR of **7l** ($CDCl_3$, 600 MHz).

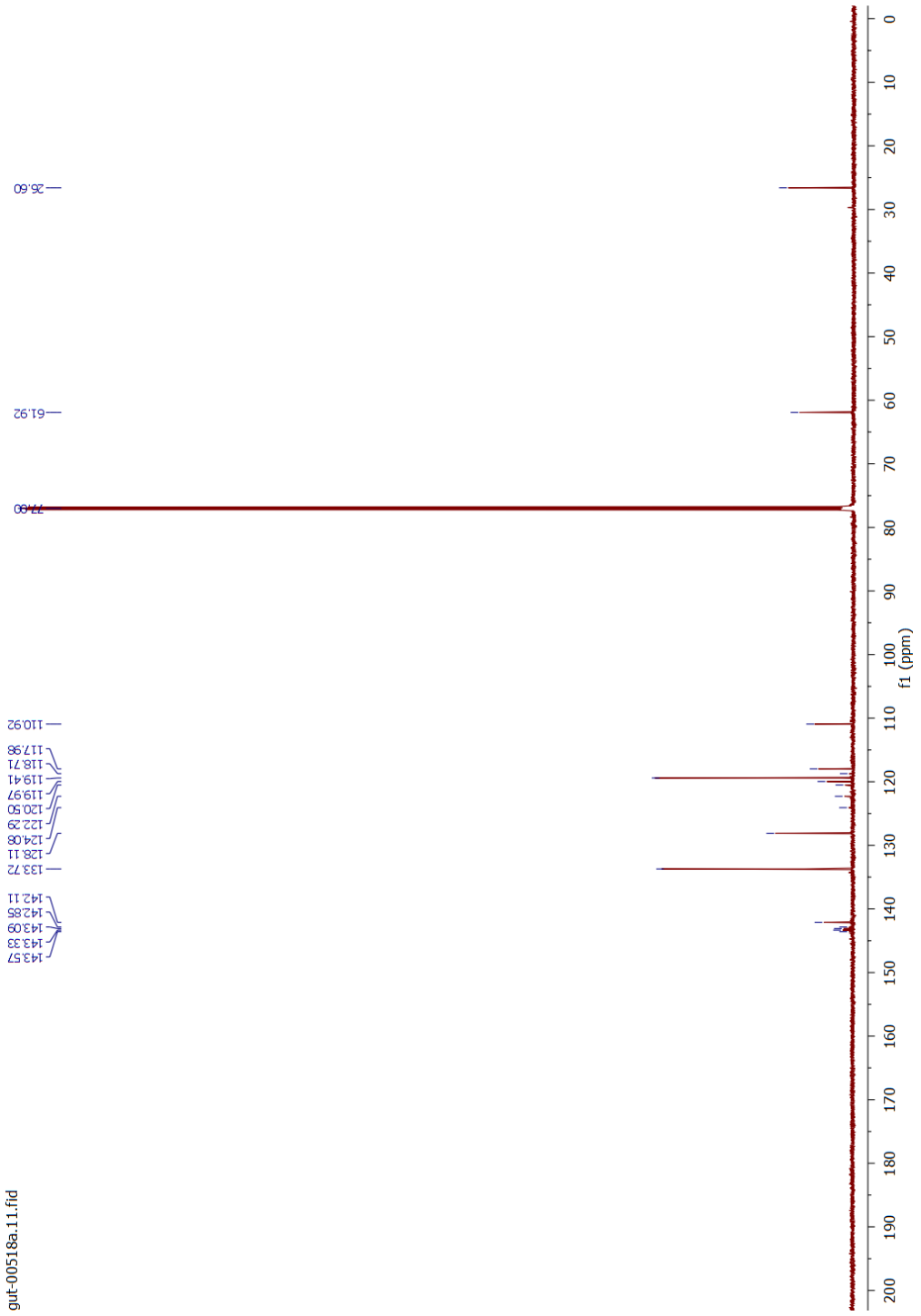
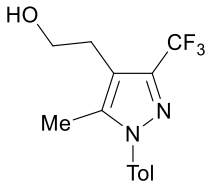


Figure S24. ^{13}C NMR of **7l** ($CDCl_3$, 151 MHz).



4-(2'-Hydroxyethyl)-5-methyl-1-tolyl-3-trifluoromethyl-1H-pyrazole (7m)

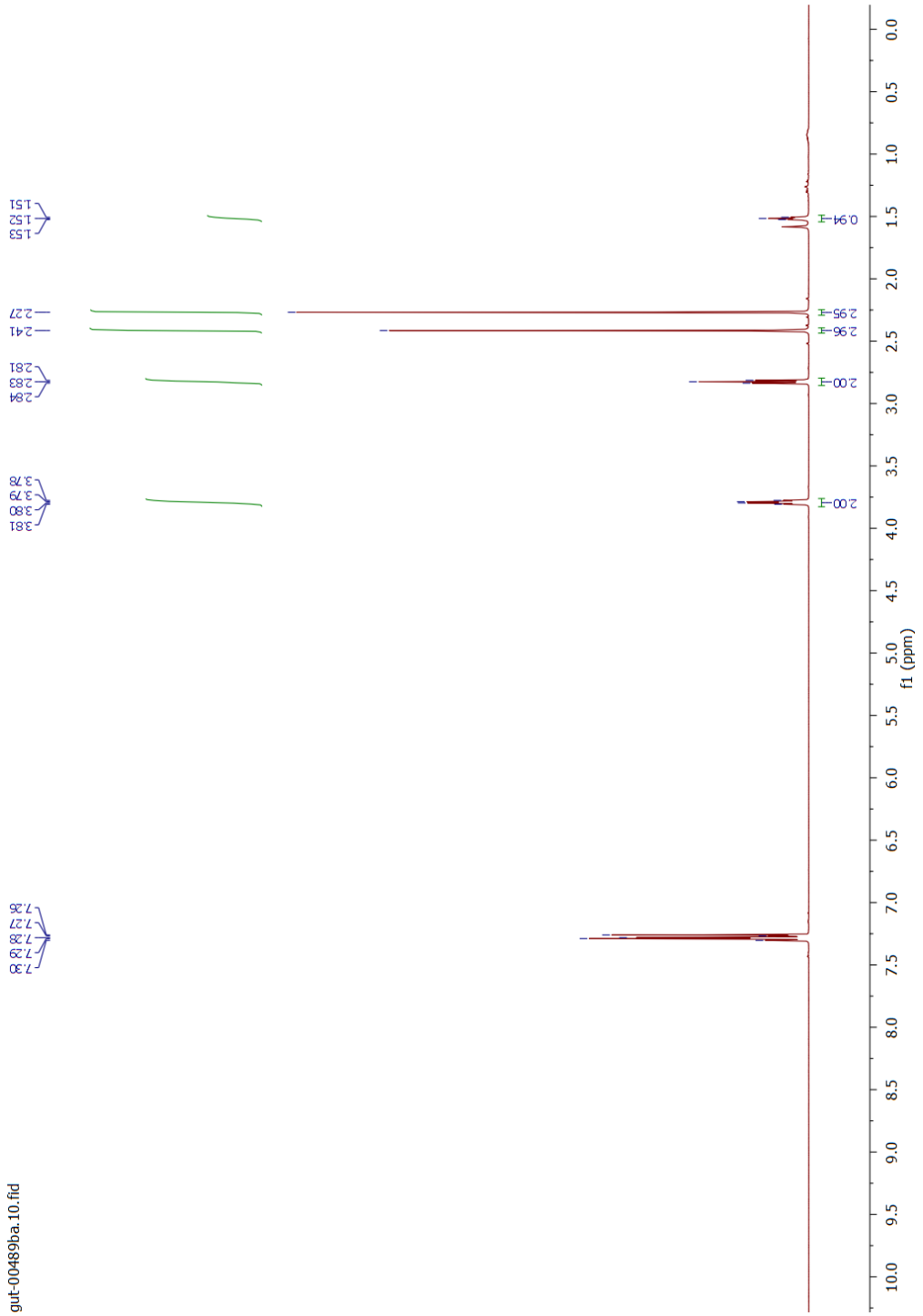


Figure S25. ^{1}H NMR of **7m** ($CDCl_3$, 600 MHz).

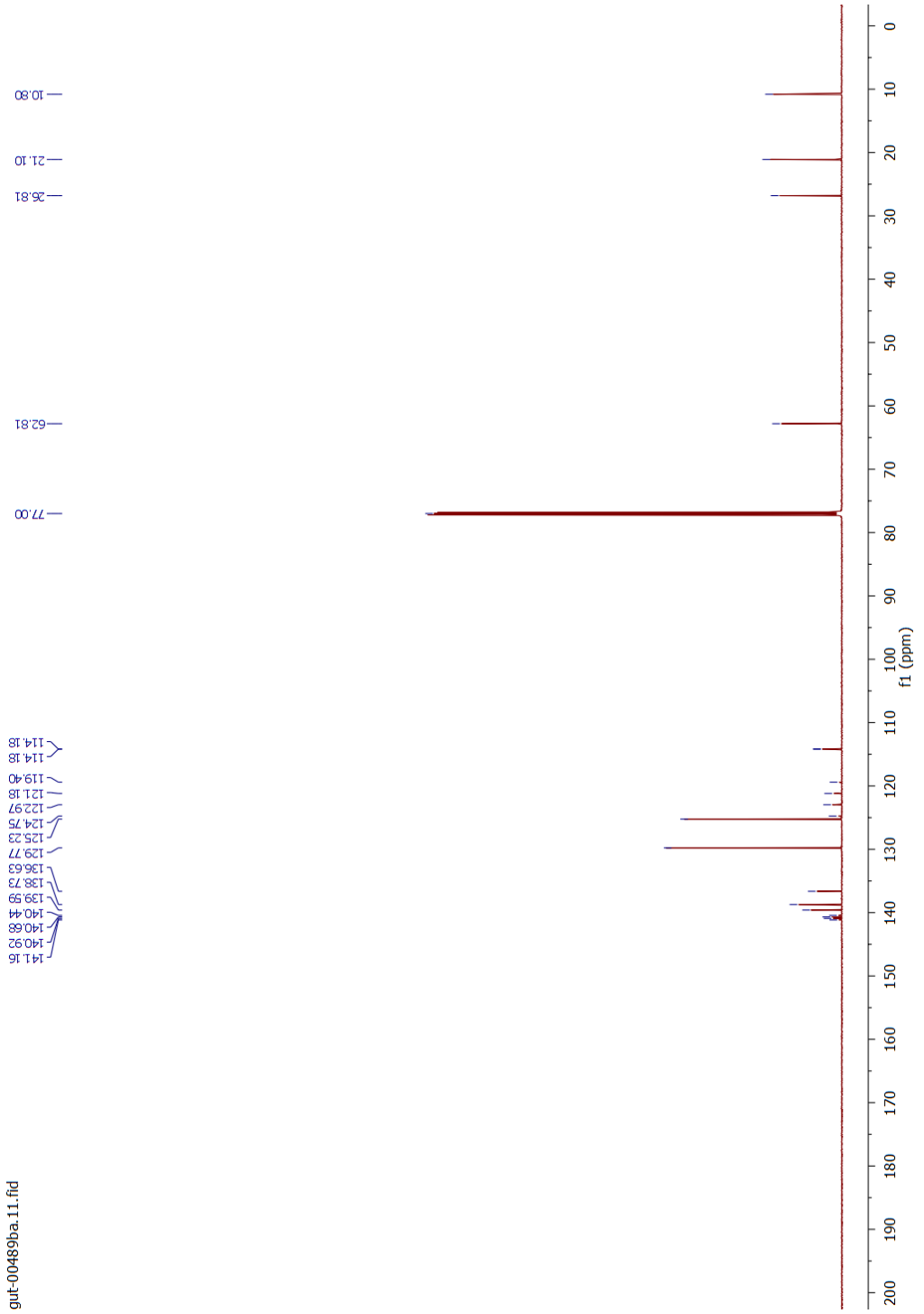
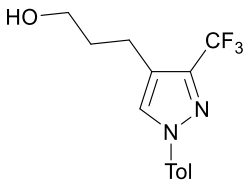


Figure S26. ^{13}C NMR of **7m** ($CDCl_3$, 151 MHz).



4-(3'-Hydroxypropyl)-1-tolyl-3-trifluoromethyl-1H-pyrazole (7n)

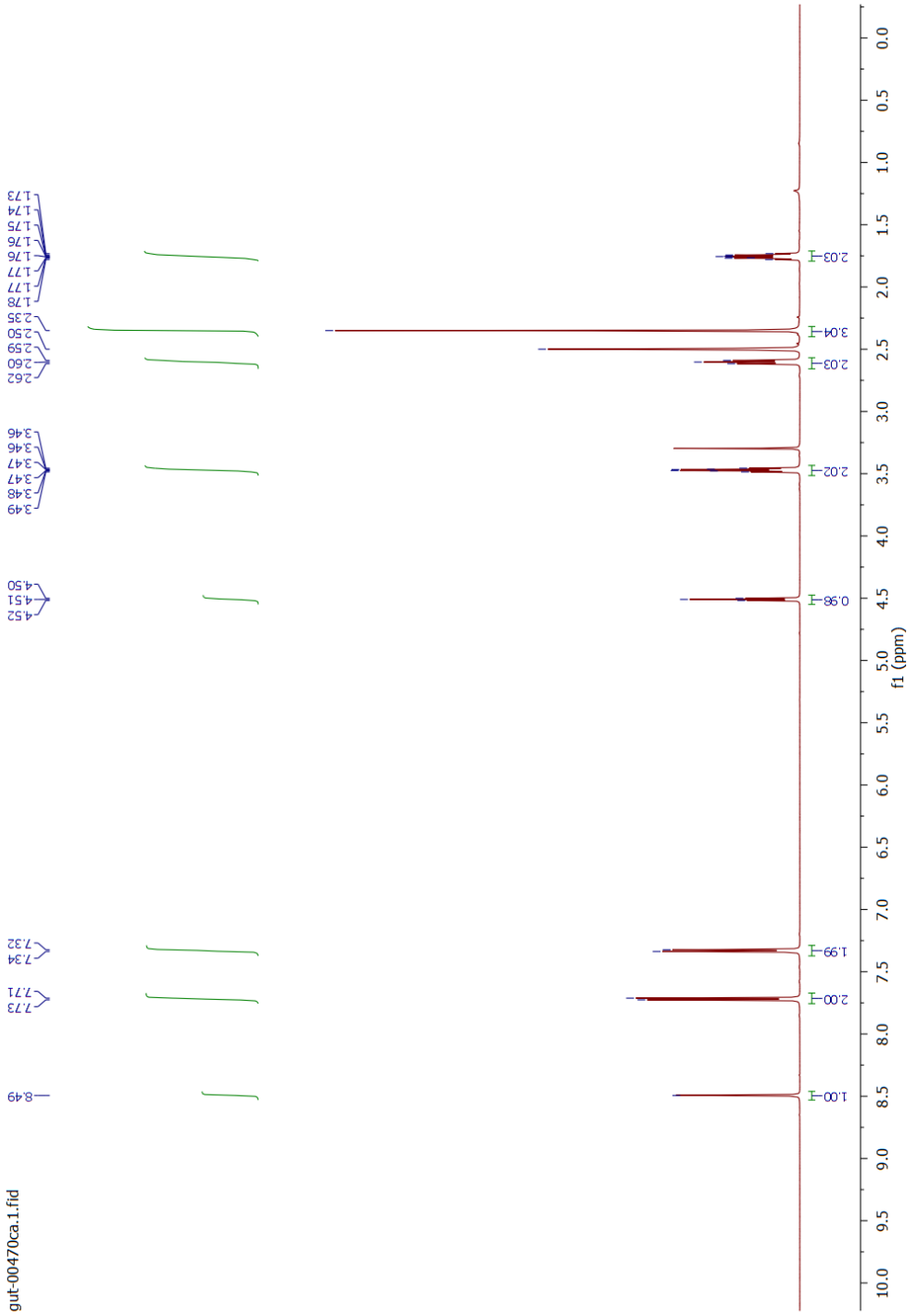


Figure S27. ^{1}H NMR of **7n** (DMSO-d_6, 600 MHz).

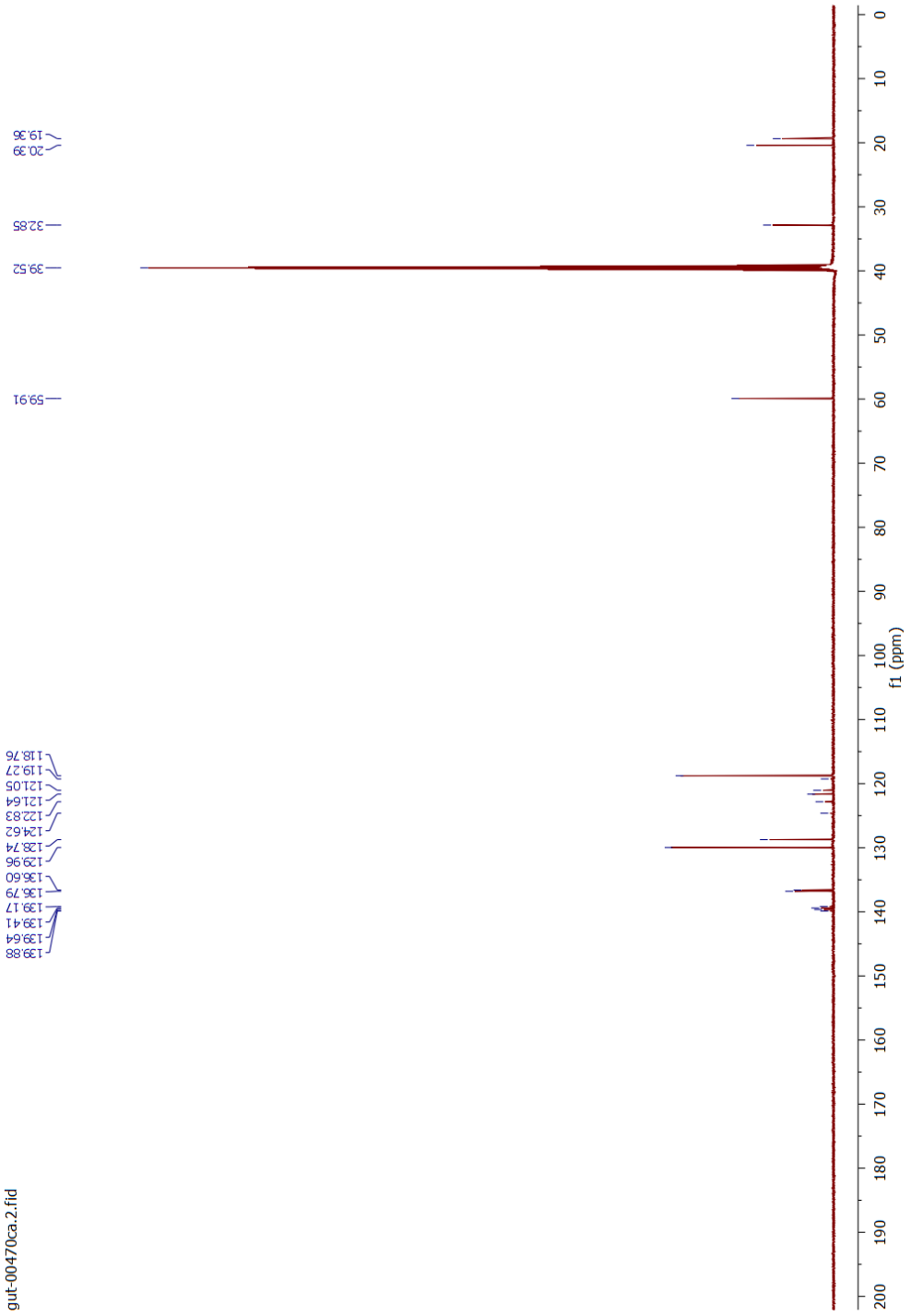
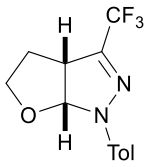


Figure S28. ^{13}C NMR of **7n** (DMSO-d_6, 151 MHz).



cis-1-Tolyl-3-trifluoromethyl-3a,4,5,6a-tetrahydro-1H-furo[2,3-c]pyrazole (8g)

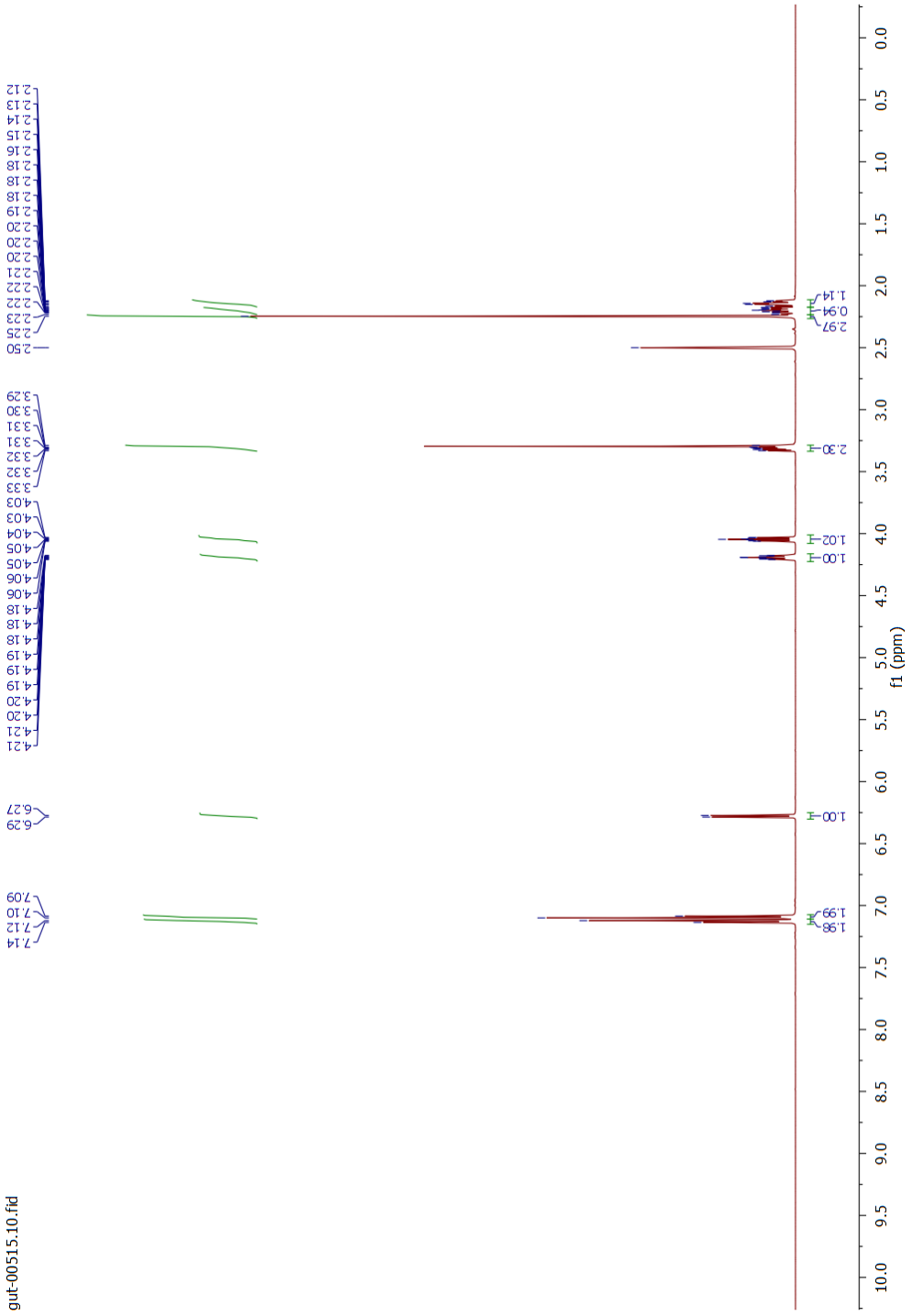


Figure S29. ^{1}H NMR of **8g** (DMSO-d_6, 600 MHz).

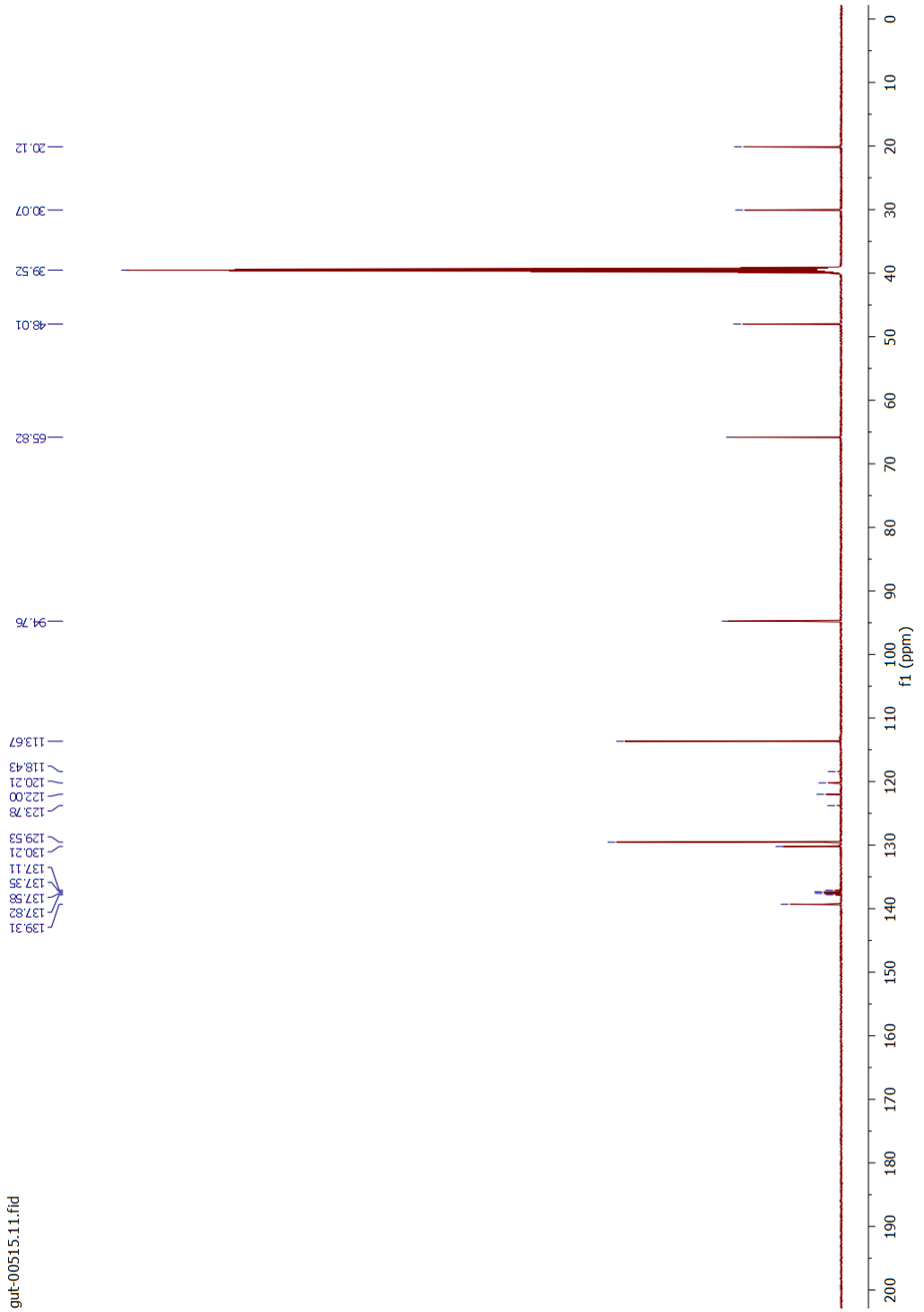
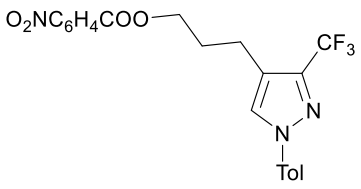


Figure S30. ^{13}C NMR of **8g** (DMSO-d_6, 151 MHz).



3-(1'-tolyl-3'-trifluoromethyl-1H-pyrazol-4'-yl)propyl p-nitrobenzoate (9)

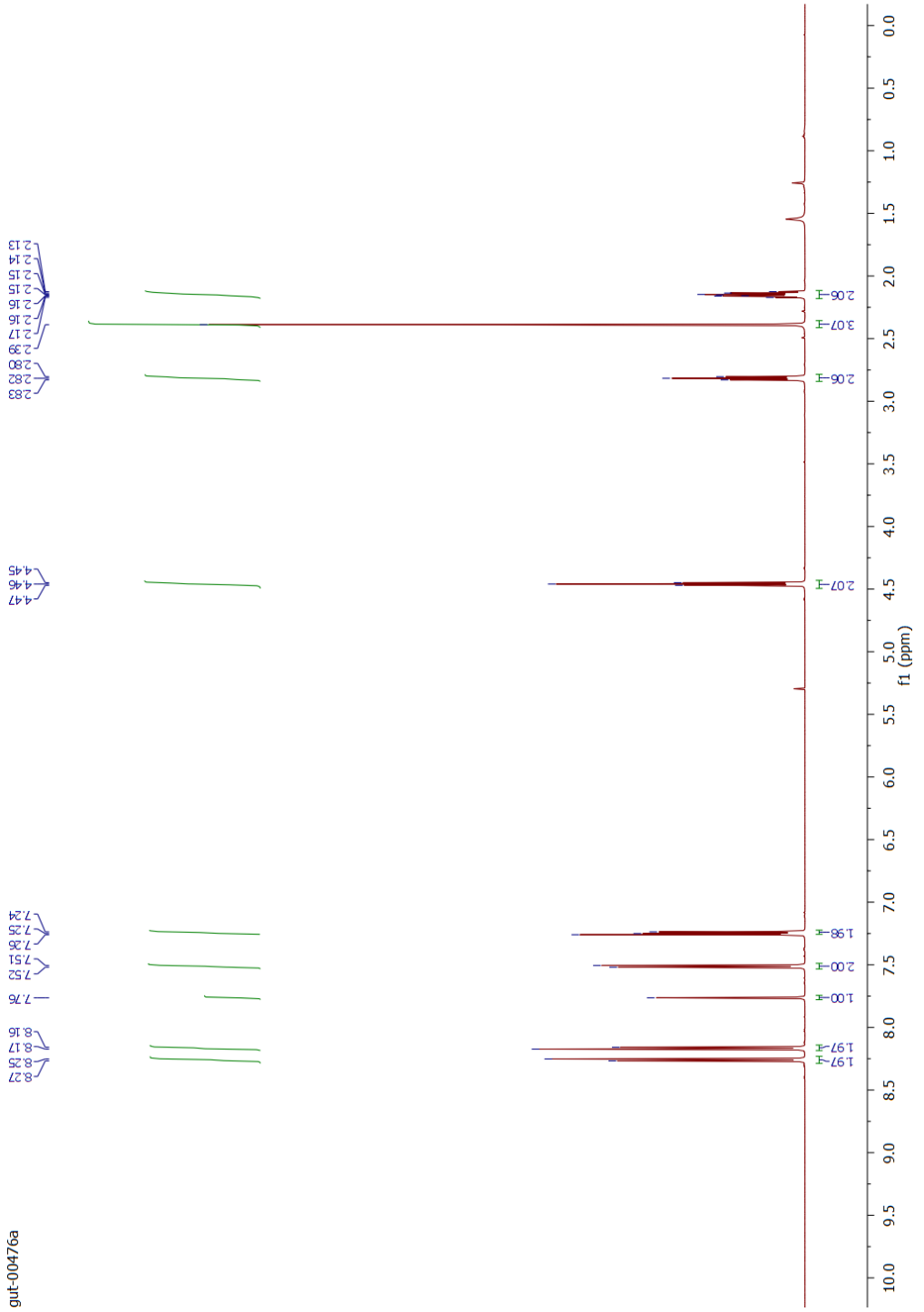


Figure S31. ^{1}H NMR of **9** ($CDCl_3$, 600 MHz).

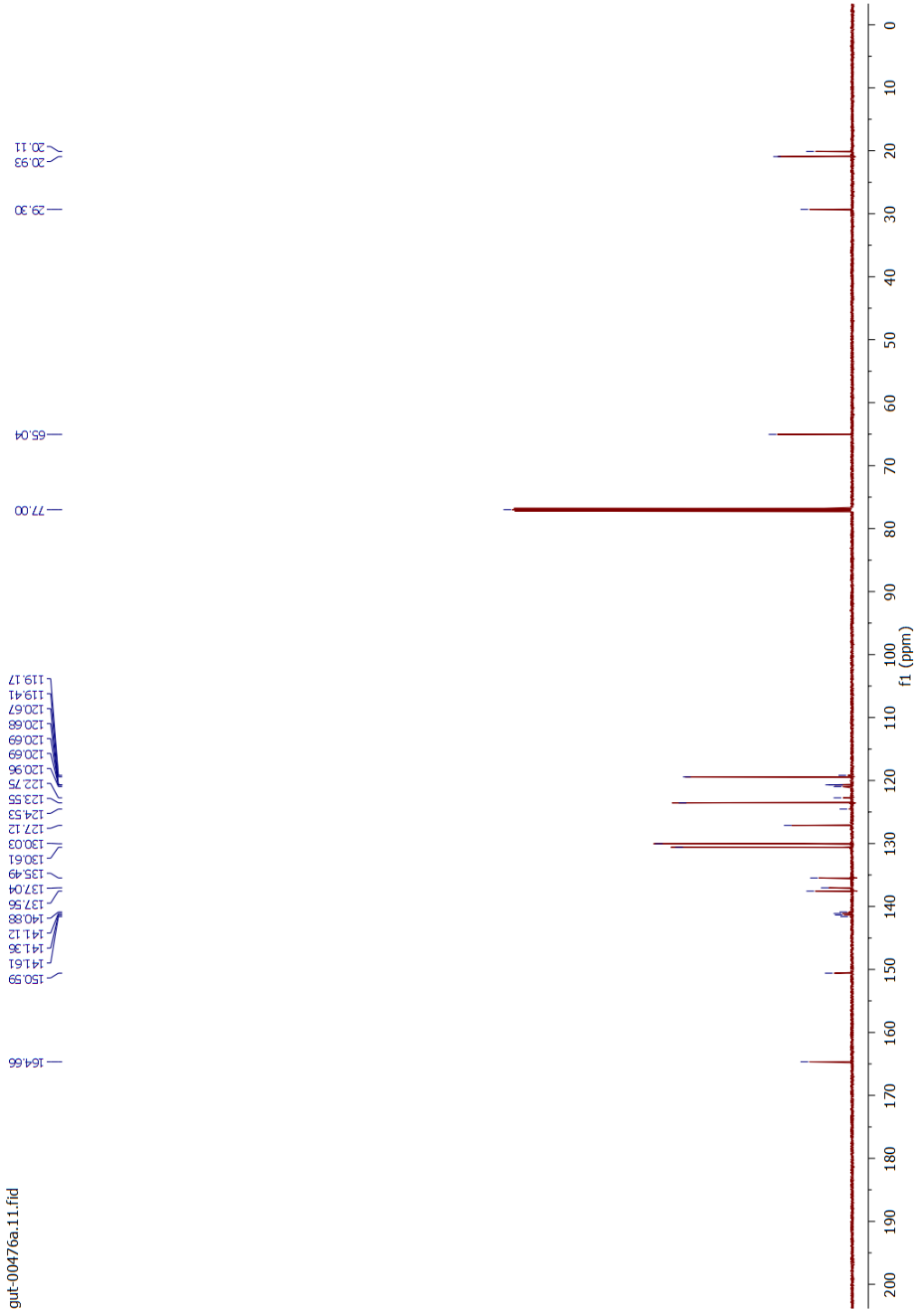
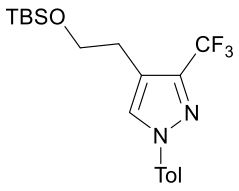


Figure S32. ^{13}C NMR of **9** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-1-tolyl-3-trifluoromethyl-1H-pyrazole (10)

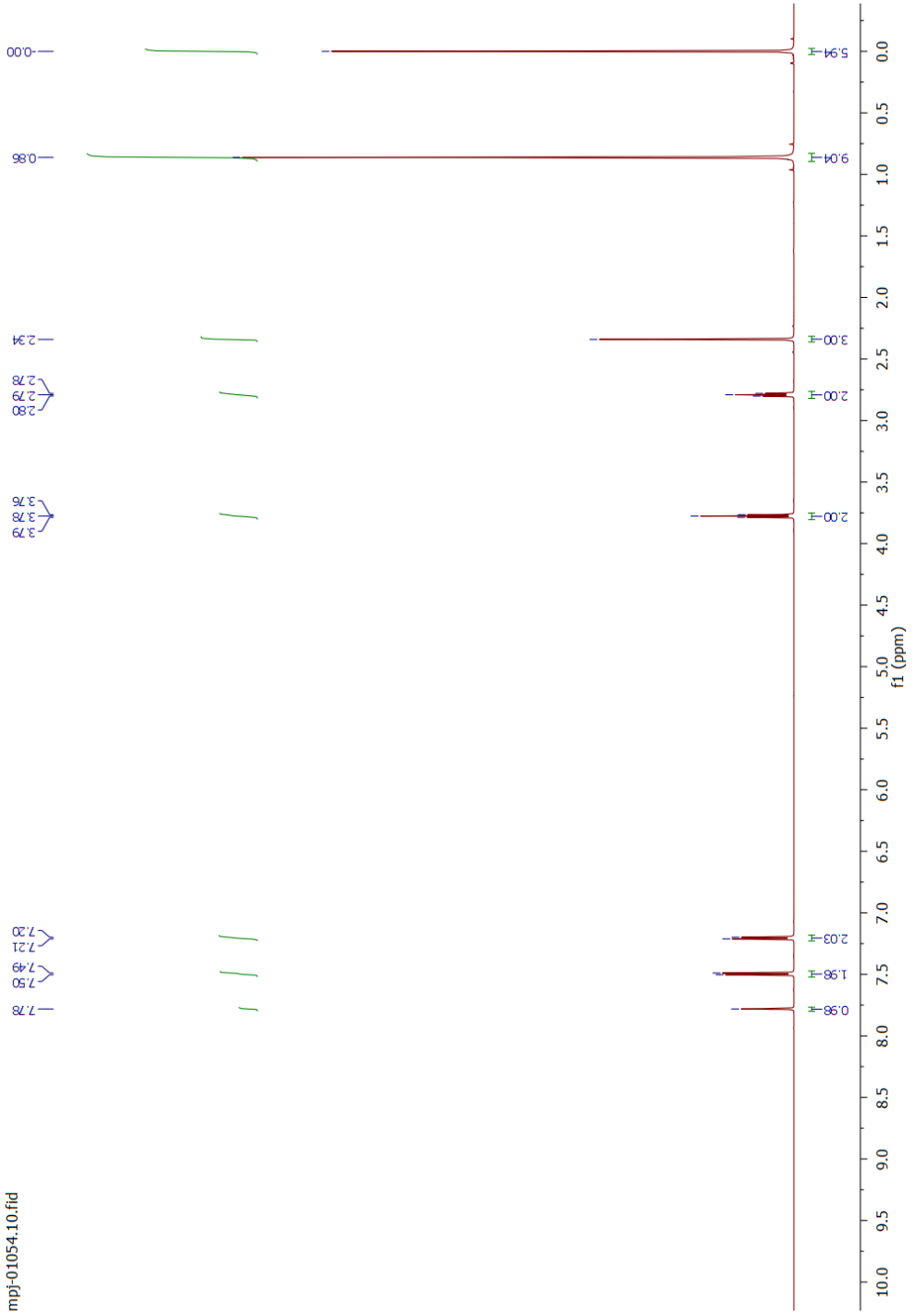


Figure S33. ^{1}H NMR of **10** ($CDCl_3$, 600 MHz).

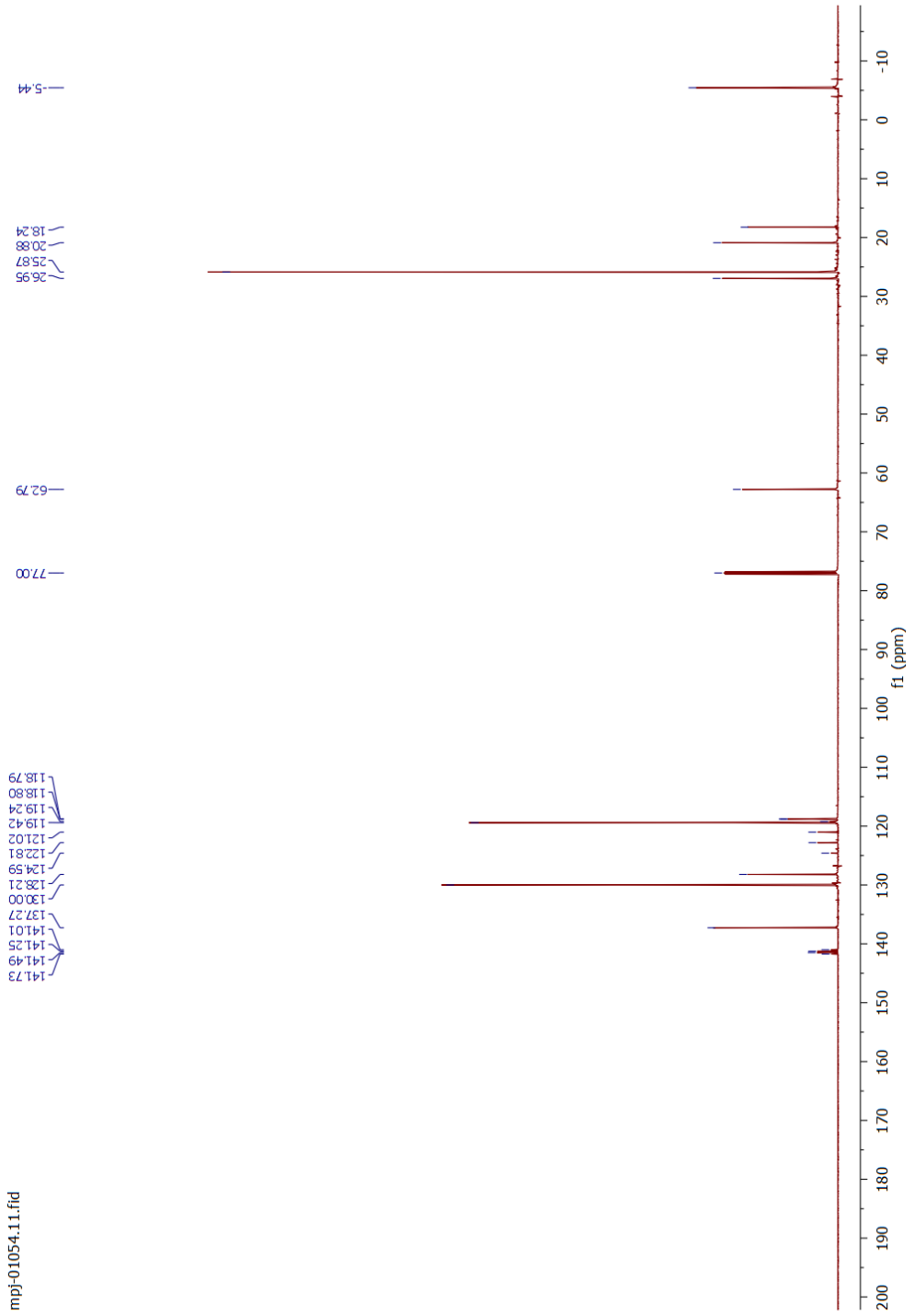
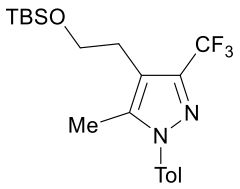


Figure S34. ^{13}C NMR of **10** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-methyl-1-tolyl-3-trifluoromethyl-1H-pyrazole (12a)

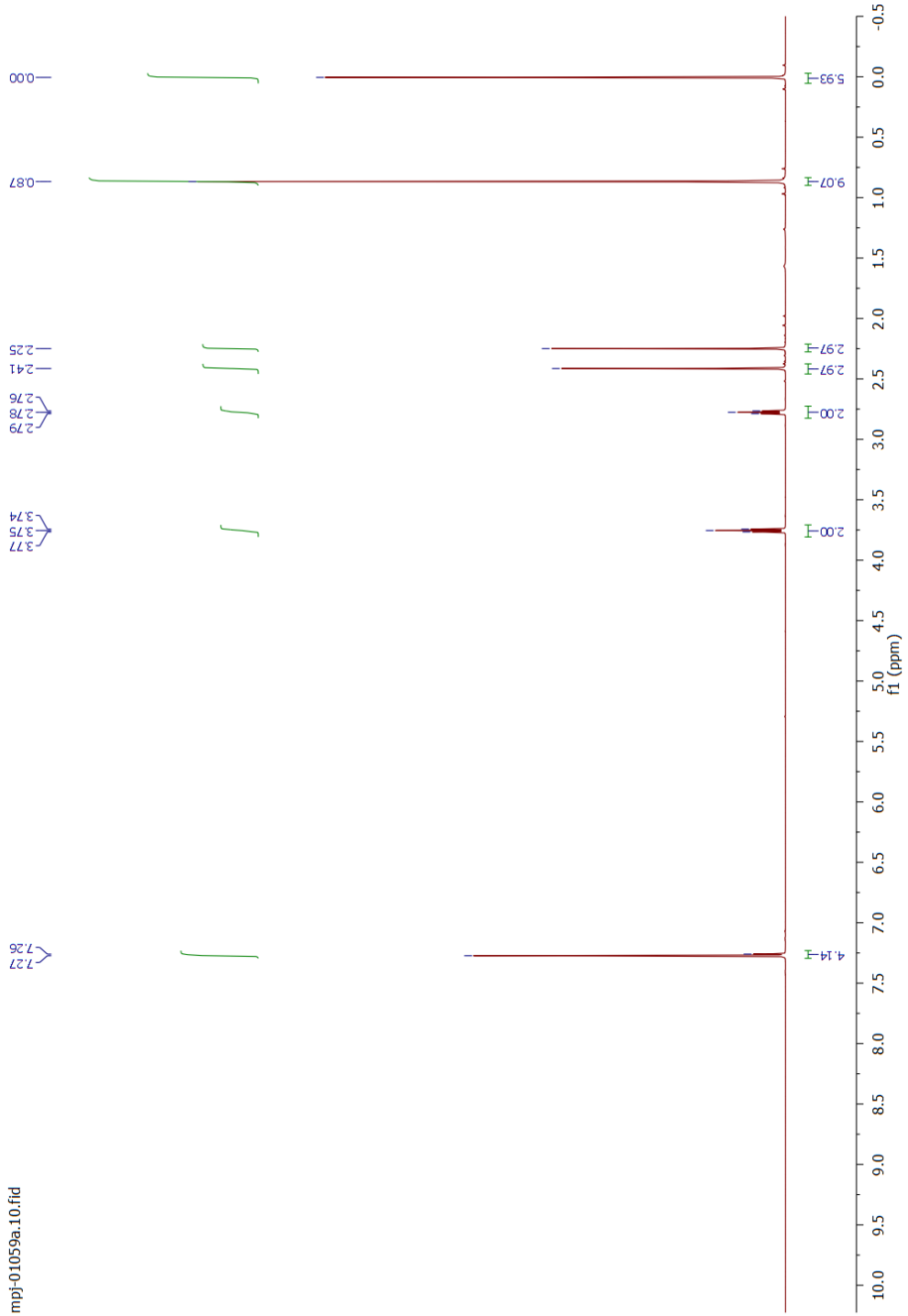


Figure S35. ^{1}H NMR of **12a** ($CDCl_3$, 600 MHz).

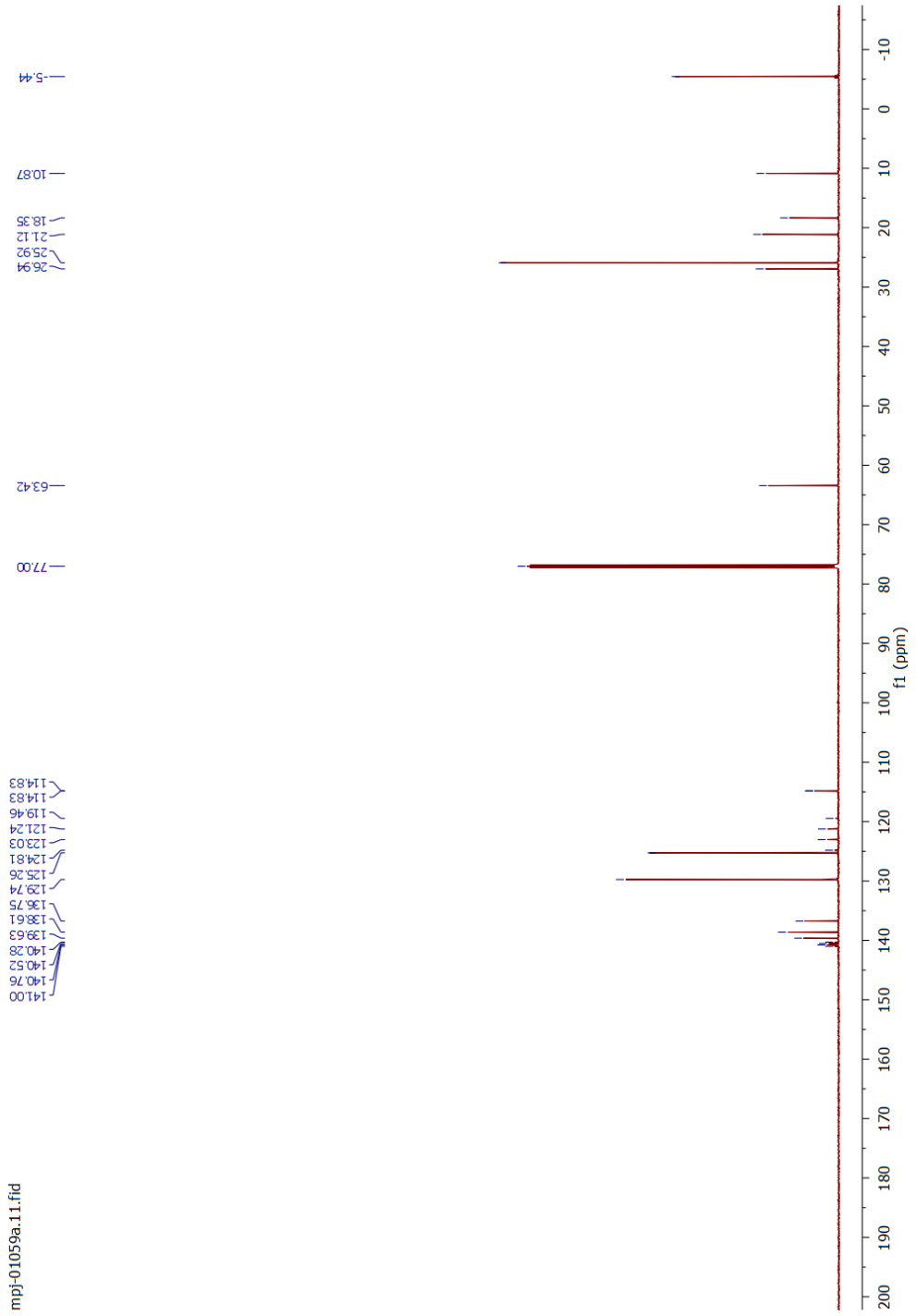
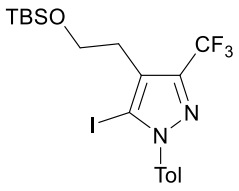


Figure S36. ^{13}C NMR of **12a** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-iodo-1-tolyl-3-trifluoromethyl-1H-pyrazole (12b)

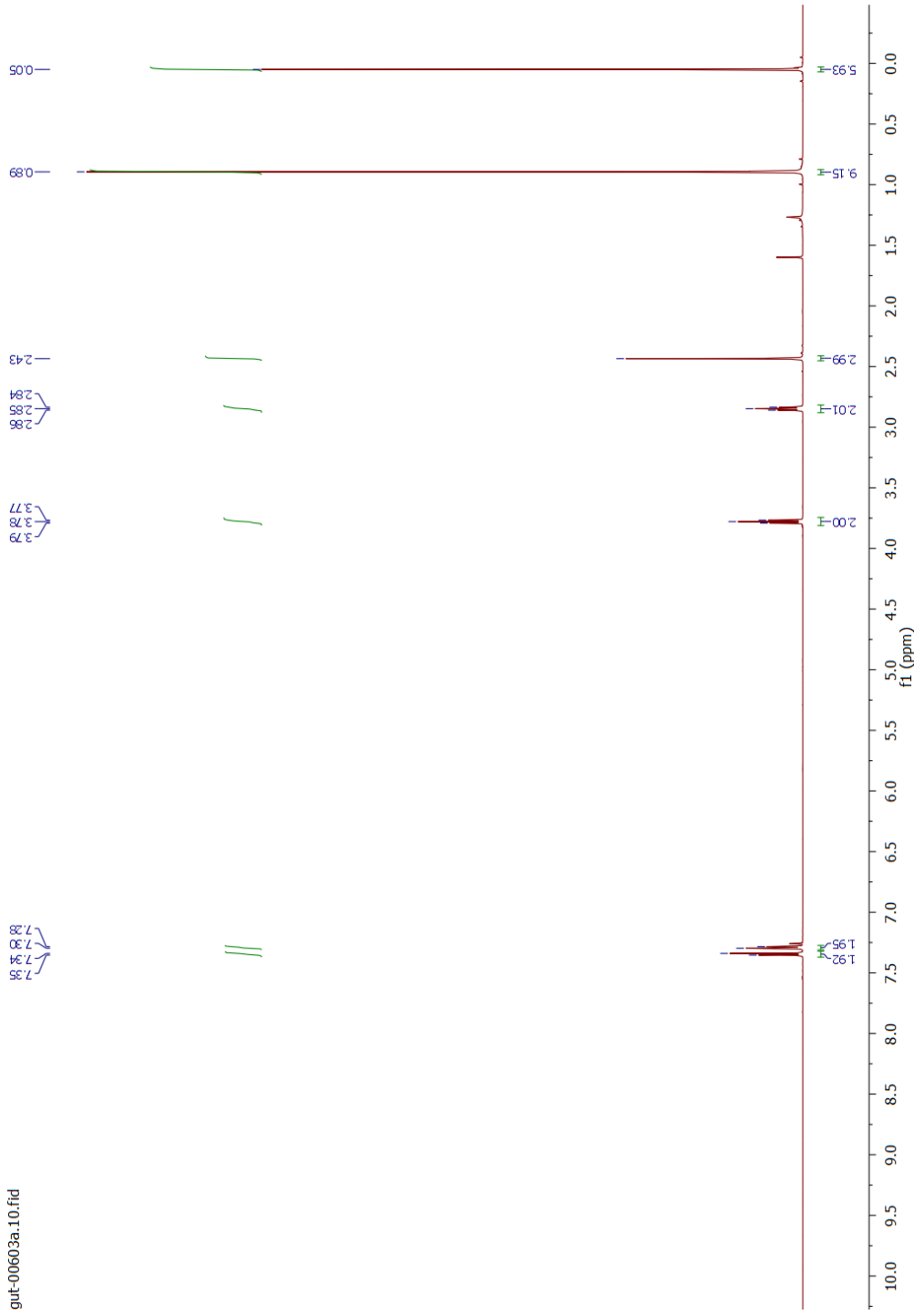


Figure S37. ^{1}H NMR of **12b** ($CDCl_3$, 600 MHz).

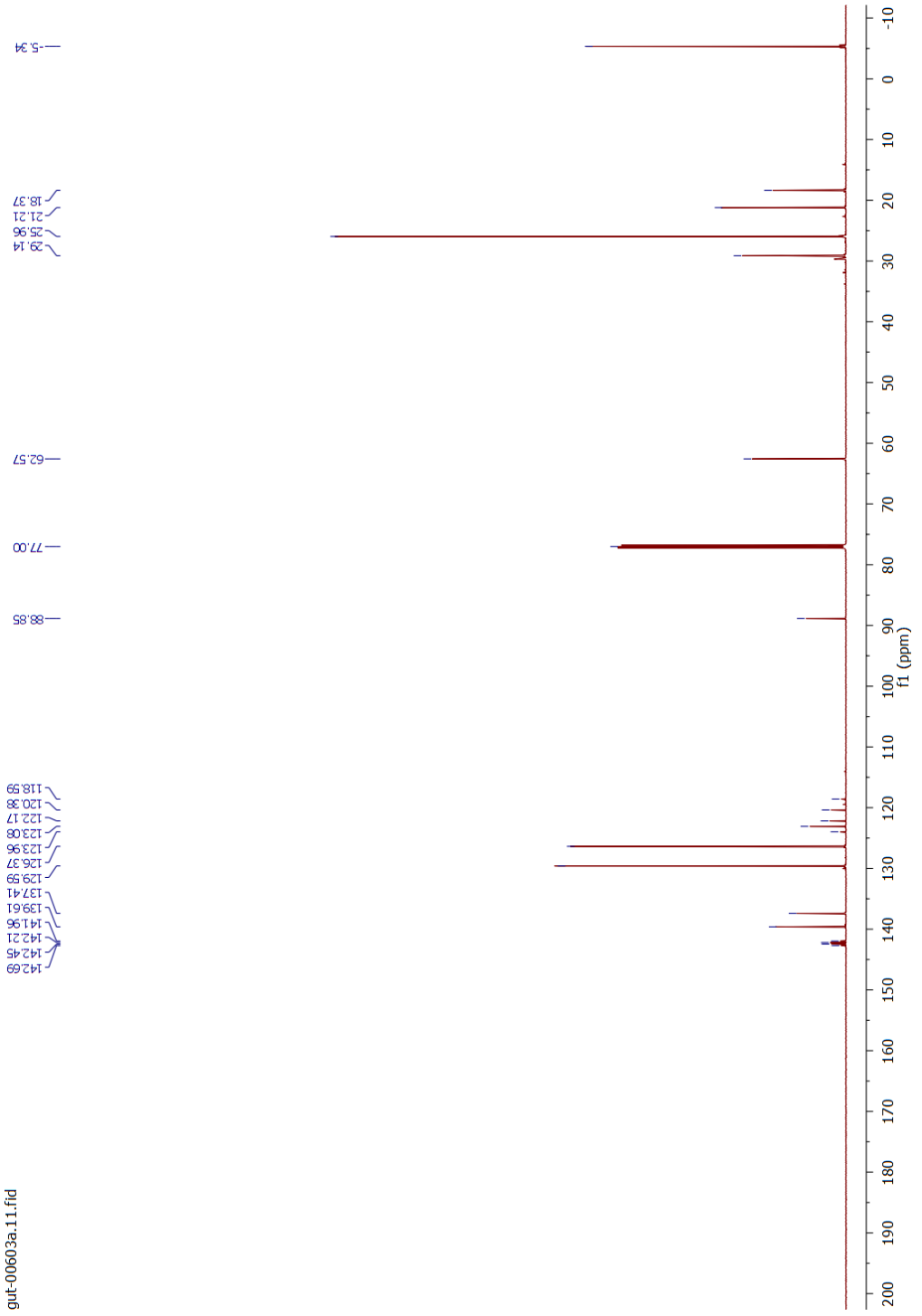
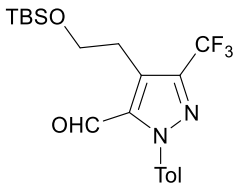


Figure S38. ^{13}C NMR of **12b** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-formyl-1-tolyl-3-trifluoromethyl-1H-pyrazole (12c)

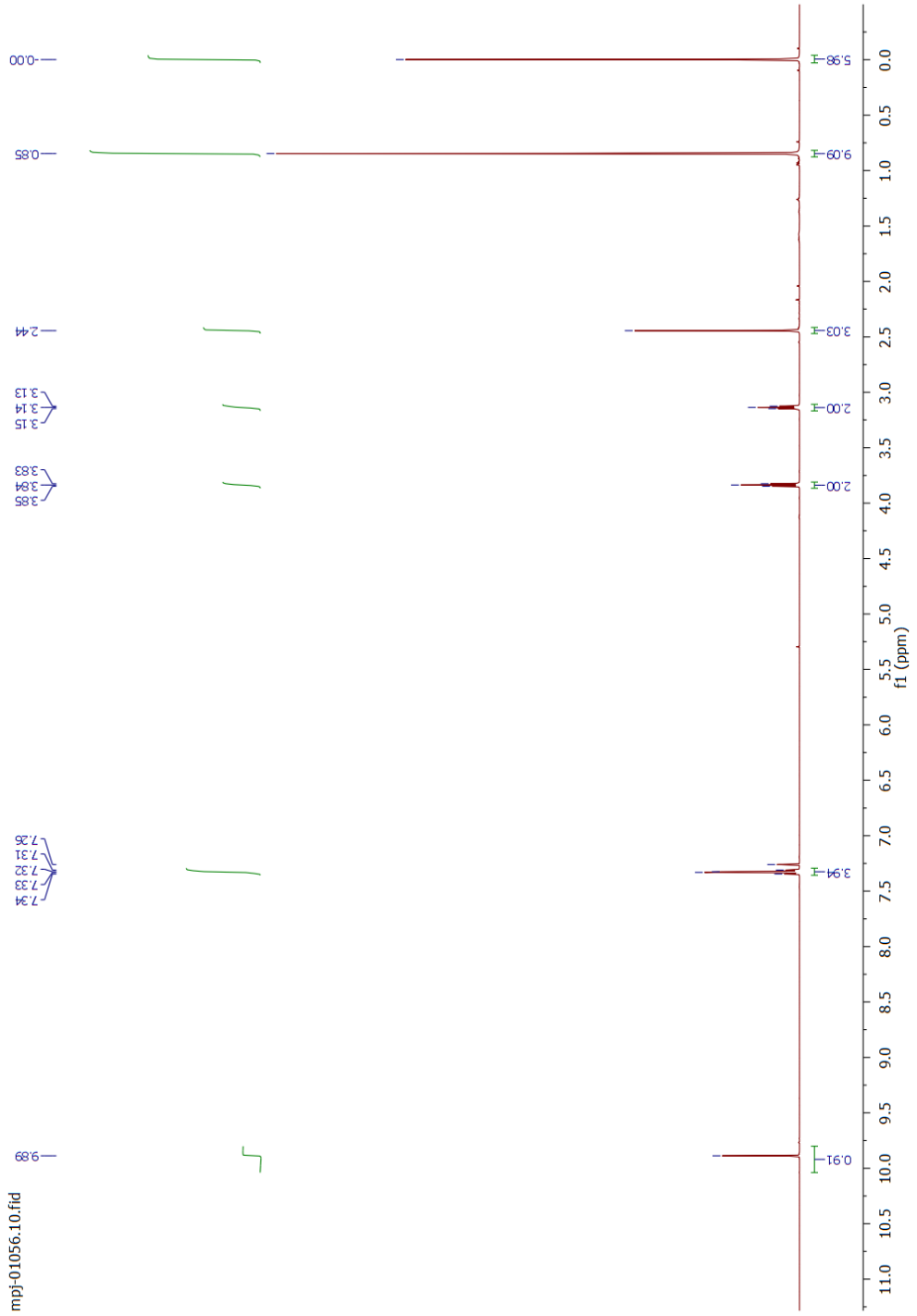


Figure S39. ^{1}H NMR of **12c** ($CDCl_3$, 600 MHz).

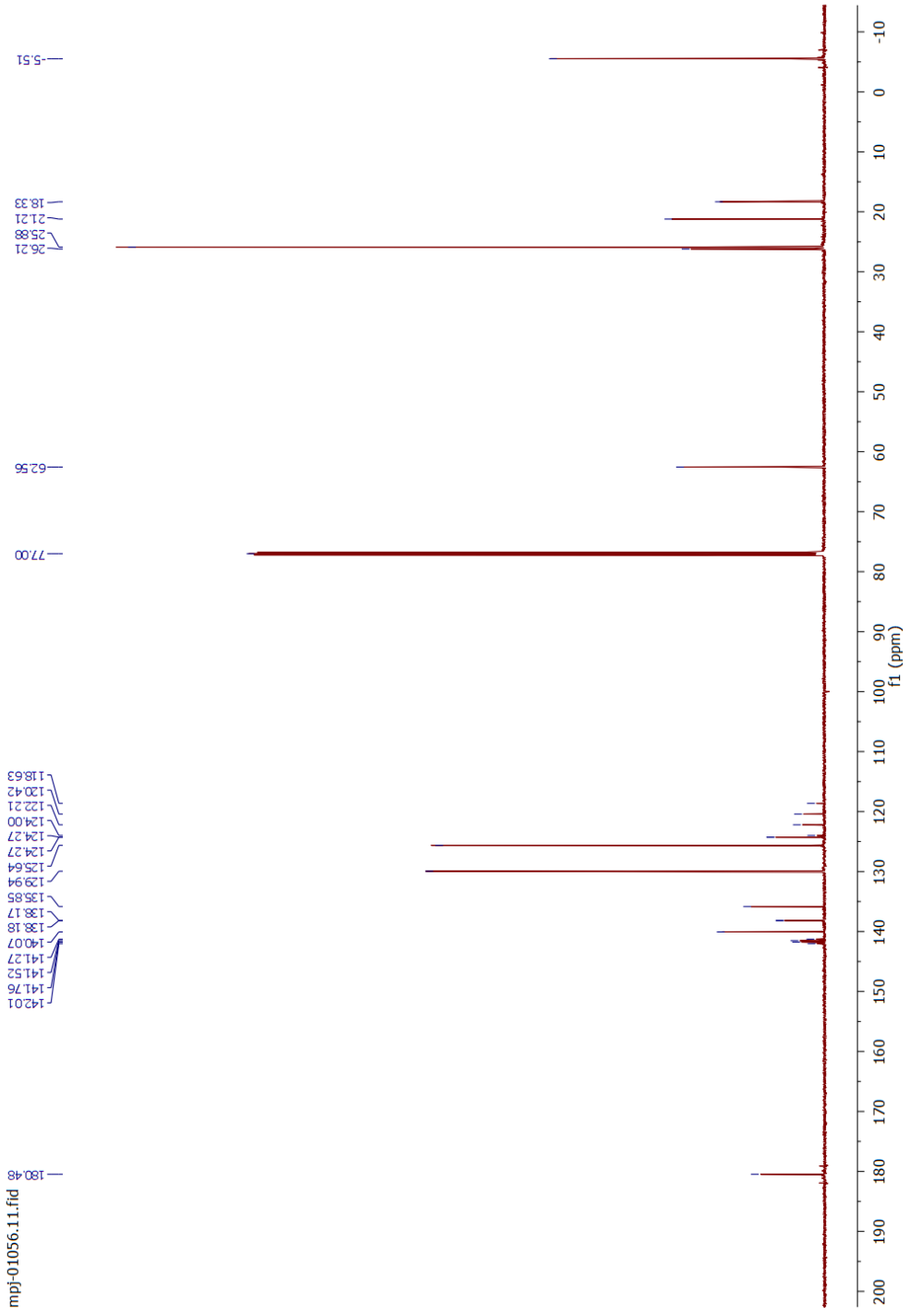
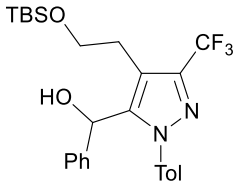


Figure S40. ^{13}C NMR of **12c** ($CDCl_3$, 151 MHz).



rac-4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-[hydroxy(phenyl)-methyl]-1-tolyl-3-trifluoromethyl-1H-pyrazole (12d)

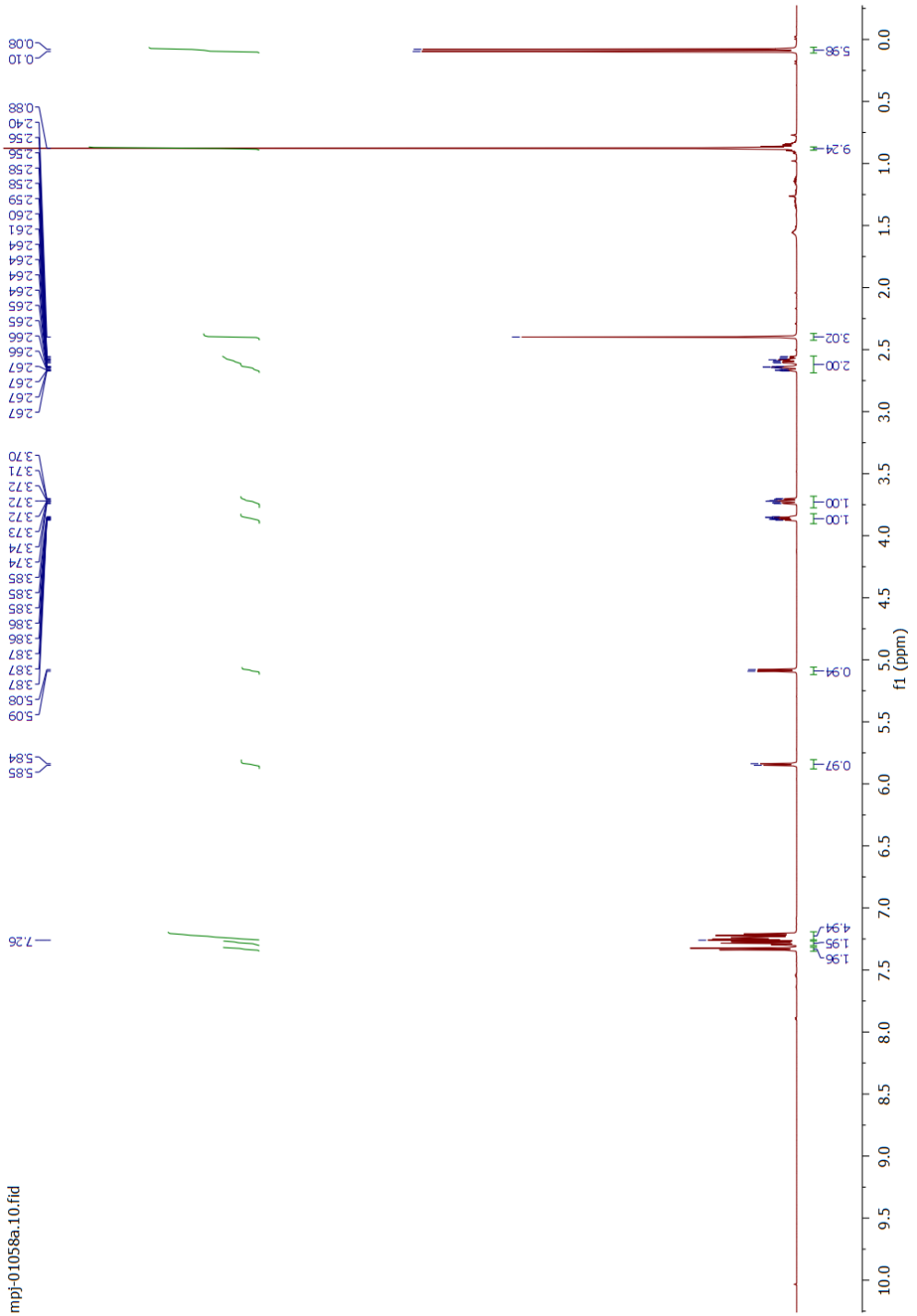


Figure S41. ^{1}H NMR of **12d** ($CDCl_3$, 600 MHz).

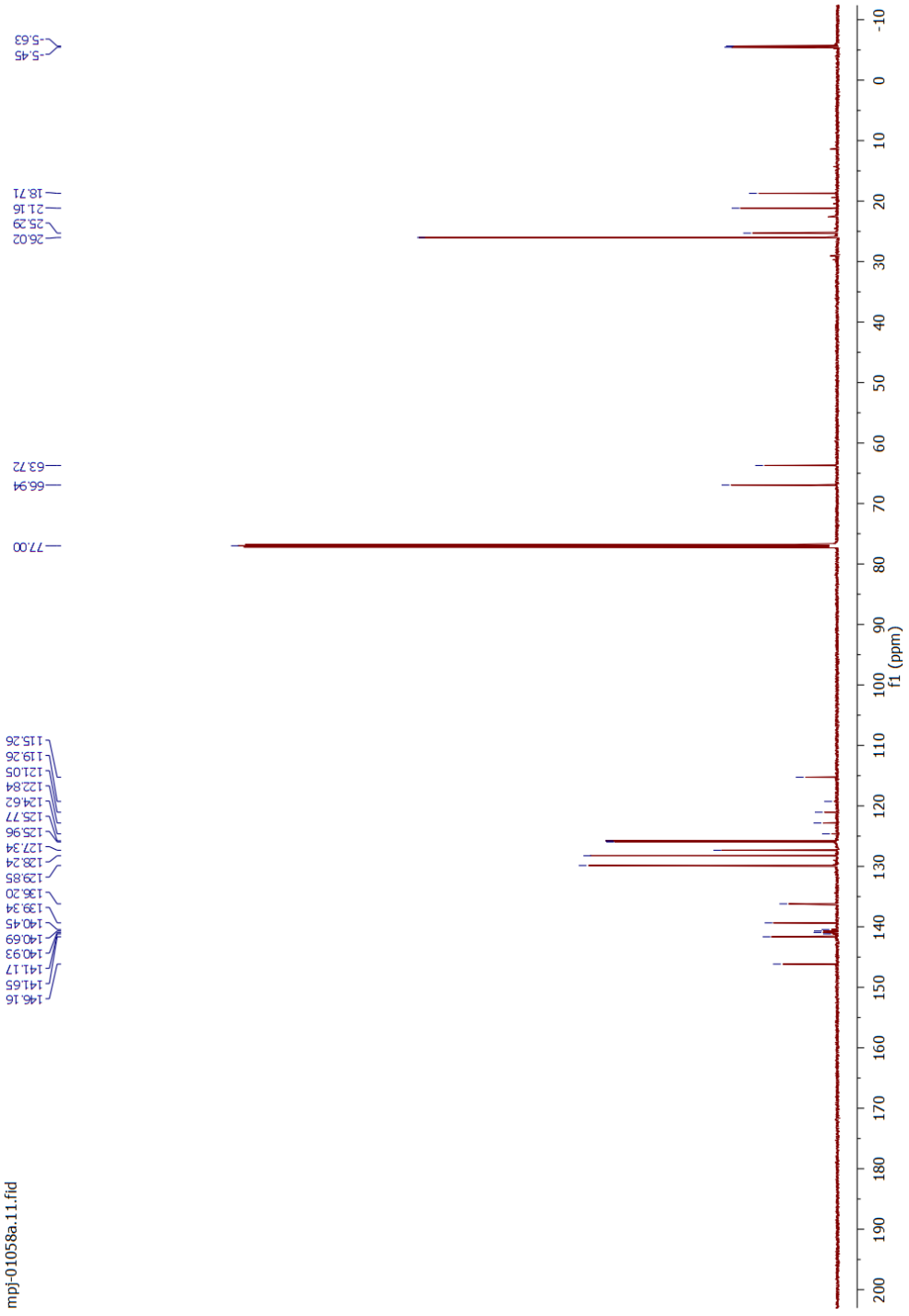
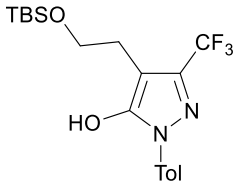


Figure S42. ^{13}C NMR of **12d** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-hydroxy-1-tolyl-3-trifluoromethyl-1H-pyrazole (12e)

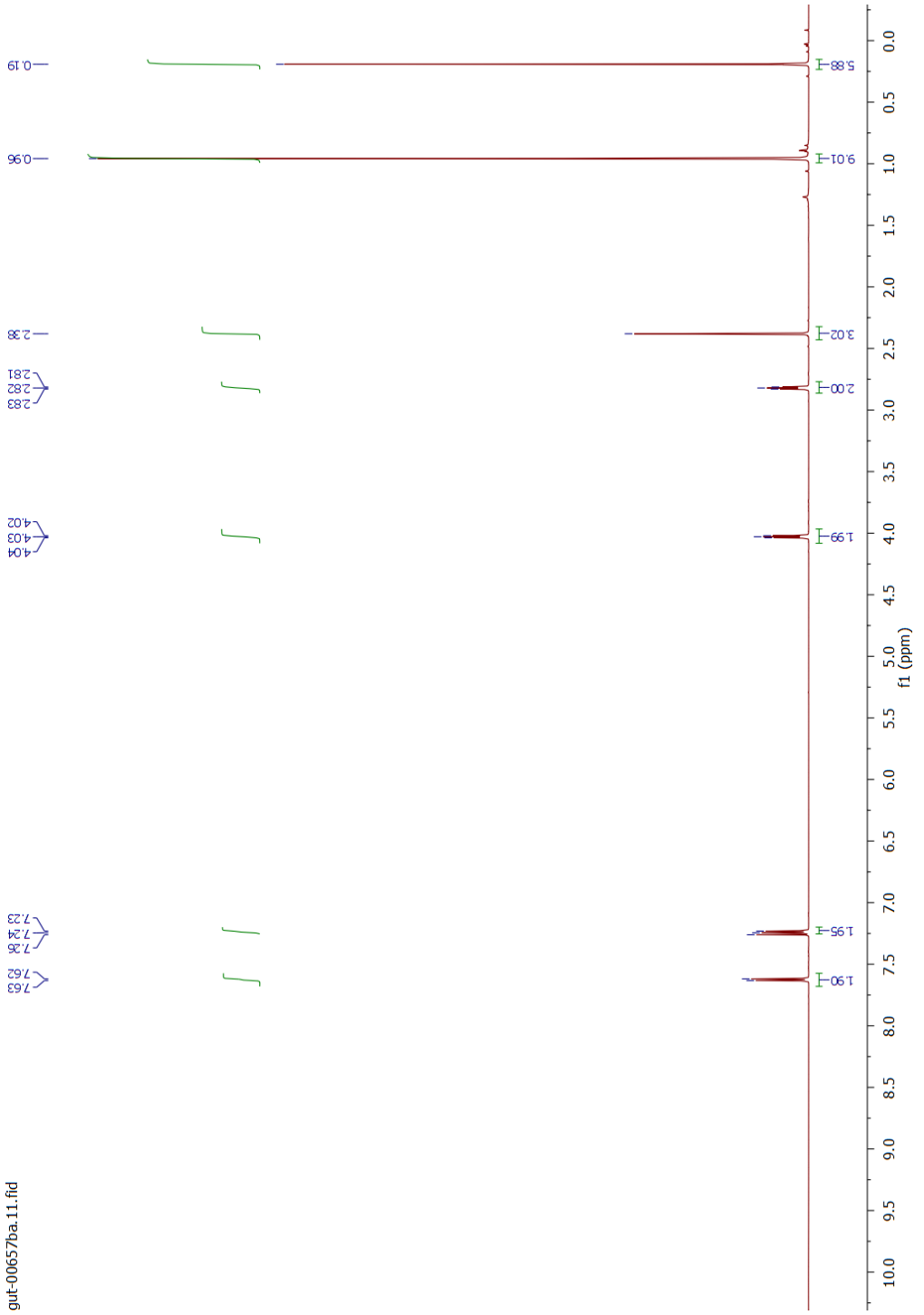


Figure S43. ^{1}H NMR of **12e** ($CDCl_3$, 600 MHz).

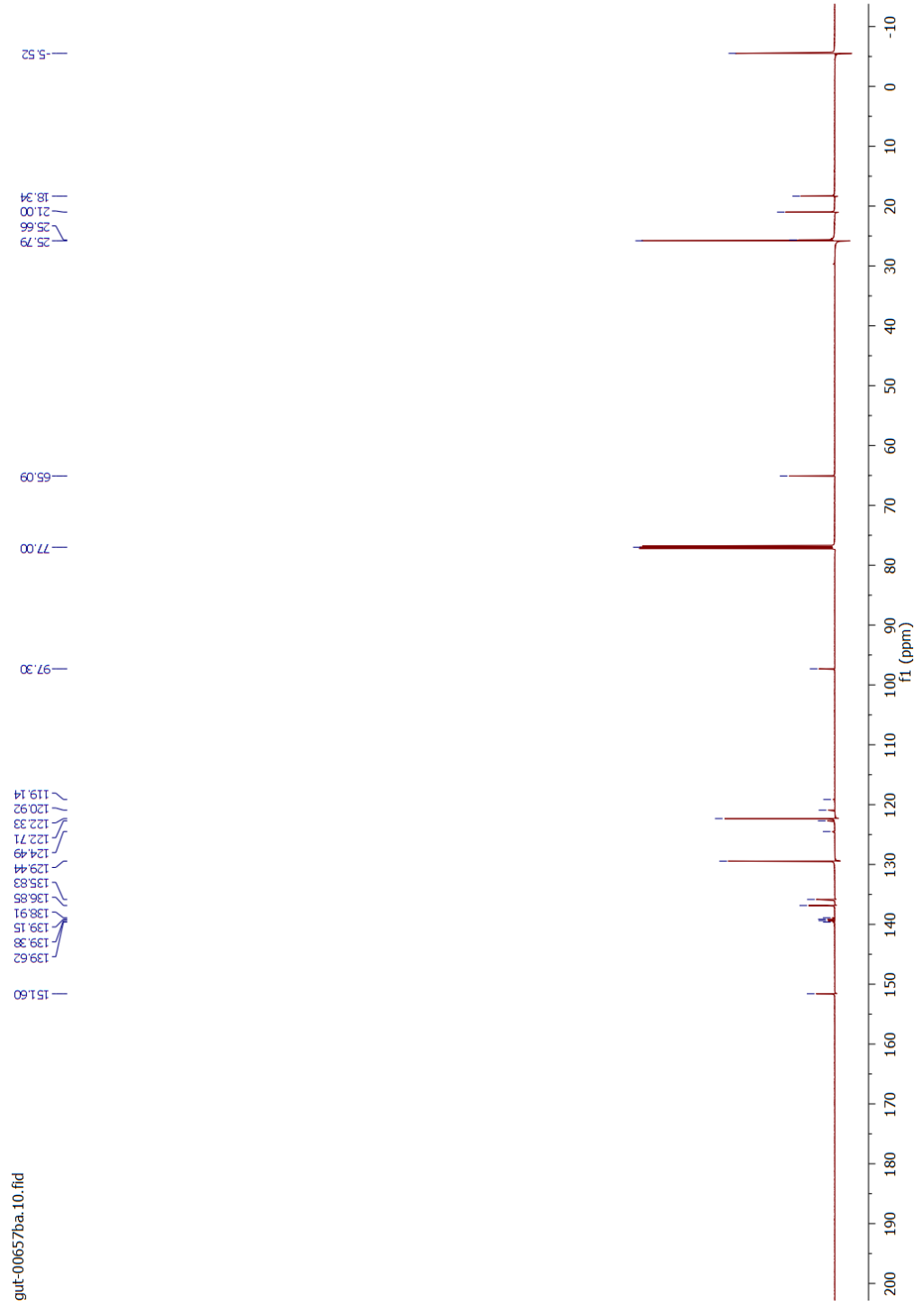
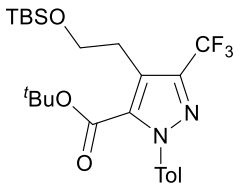


Figure S44. ^{13}C NMR of **12e** ($CDCl_3$, 151 MHz).



5-(tert-Butoxycarbonyl)-4-[2'-(tert-butyldimethylsiloxy)ethyl]-1-tolyl-3-trifluoromethyl-1H-pyrazole (12f)

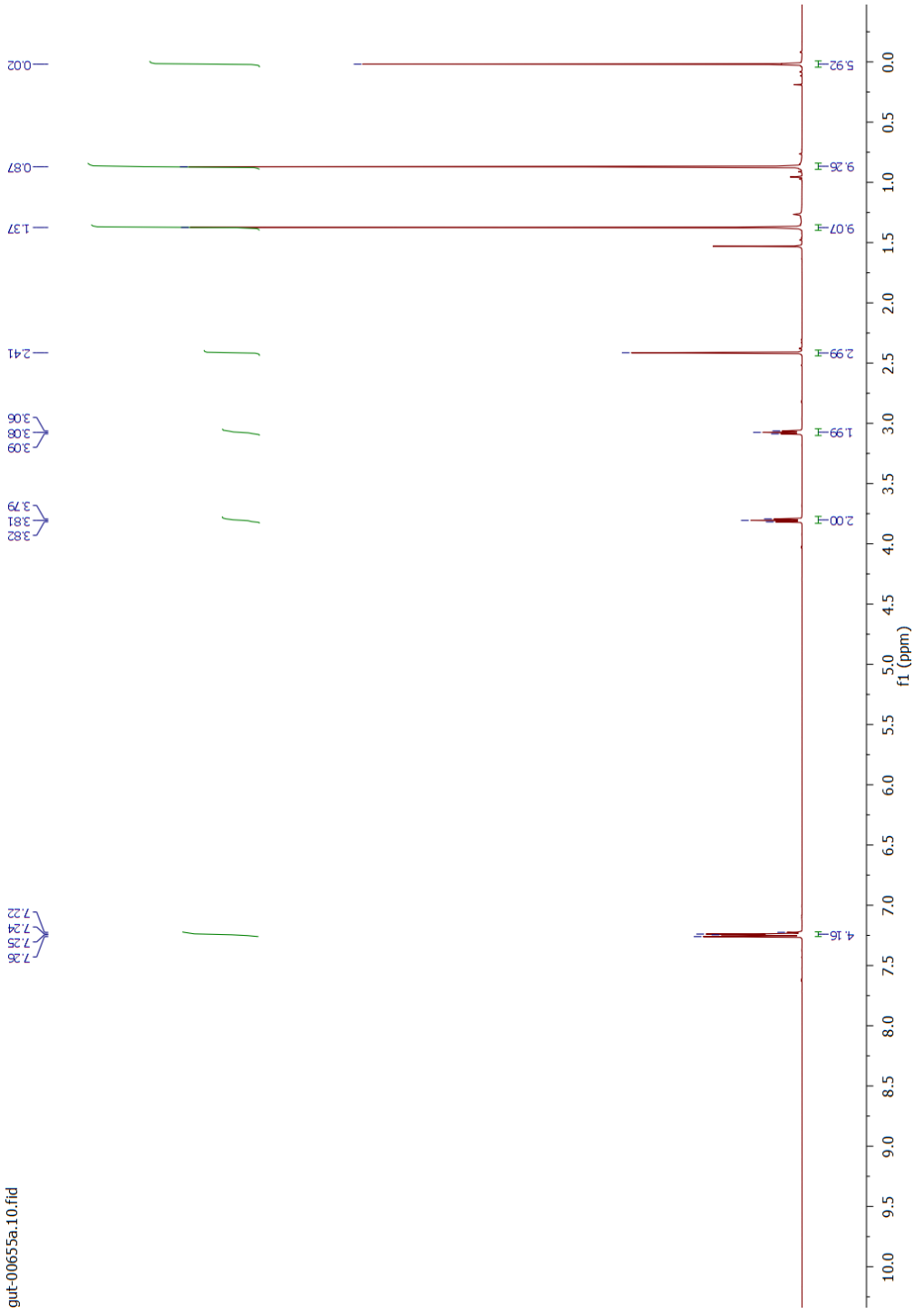


Figure S45. ^{1}H NMR of **12f** ($CDCl_3$, 600 MHz).

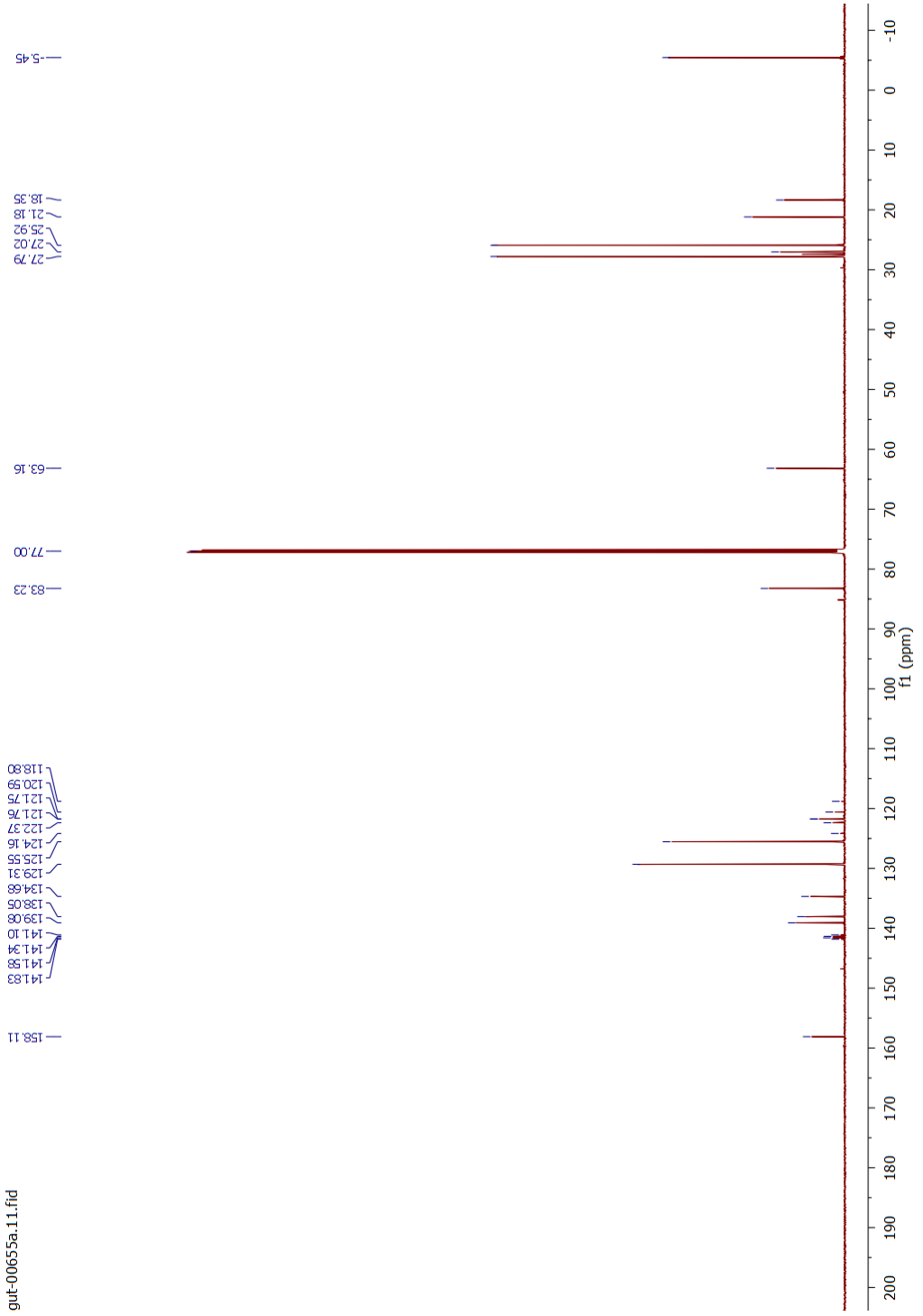
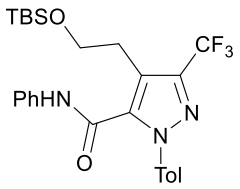


Figure S46. ^{13}C NMR of **12f** ($CDCl_3$, 151 MHz).



N-Phenyl-4-[2'-(tert-butyldimethylsiloxy)ethyl]-1-tolyl-3-trifluoromethyl-5-pyrazolecarboxamide (12g)

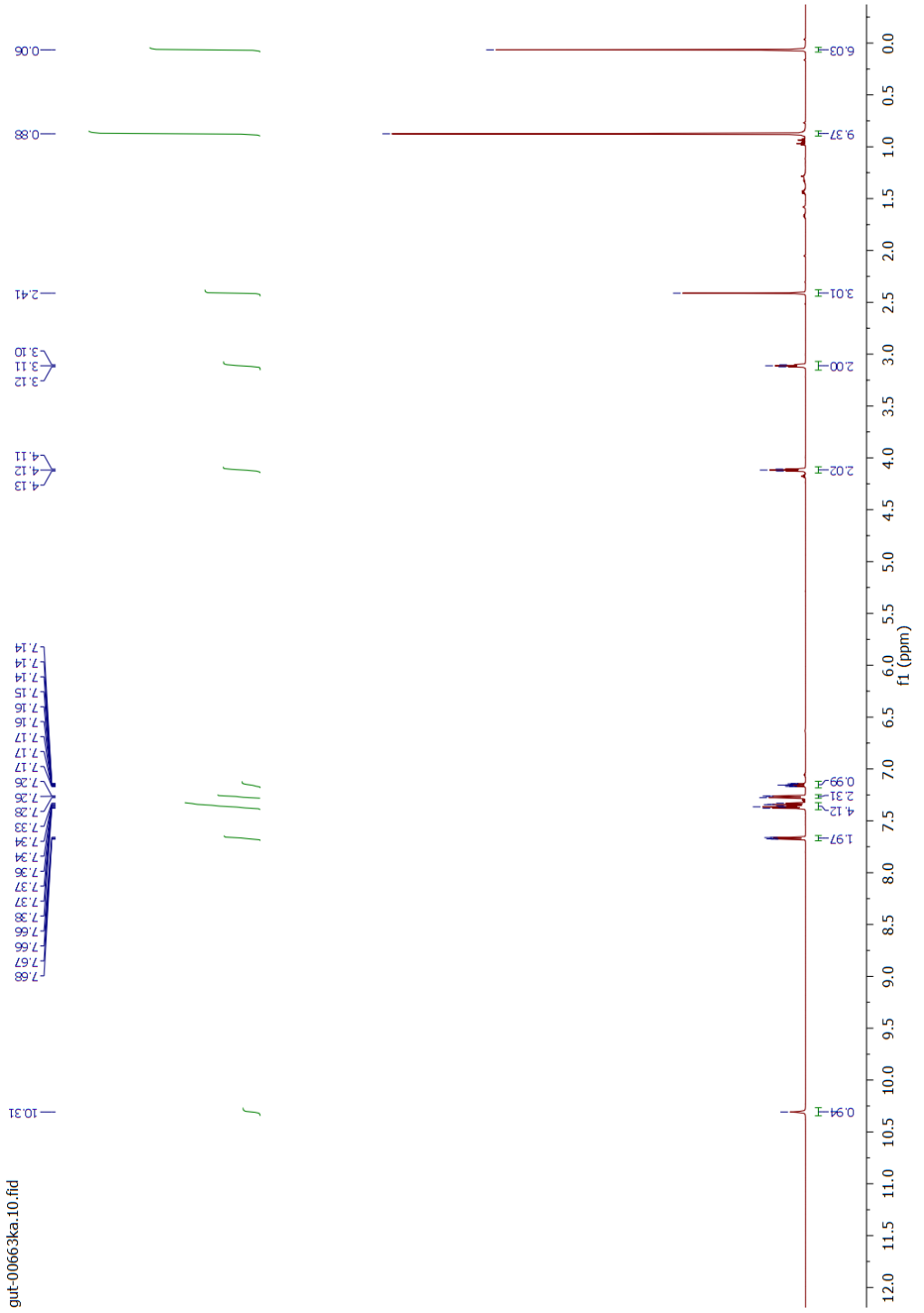


Figure S47. ^{1}H NMR of **12g** ($CDCl_3$, 600 MHz).

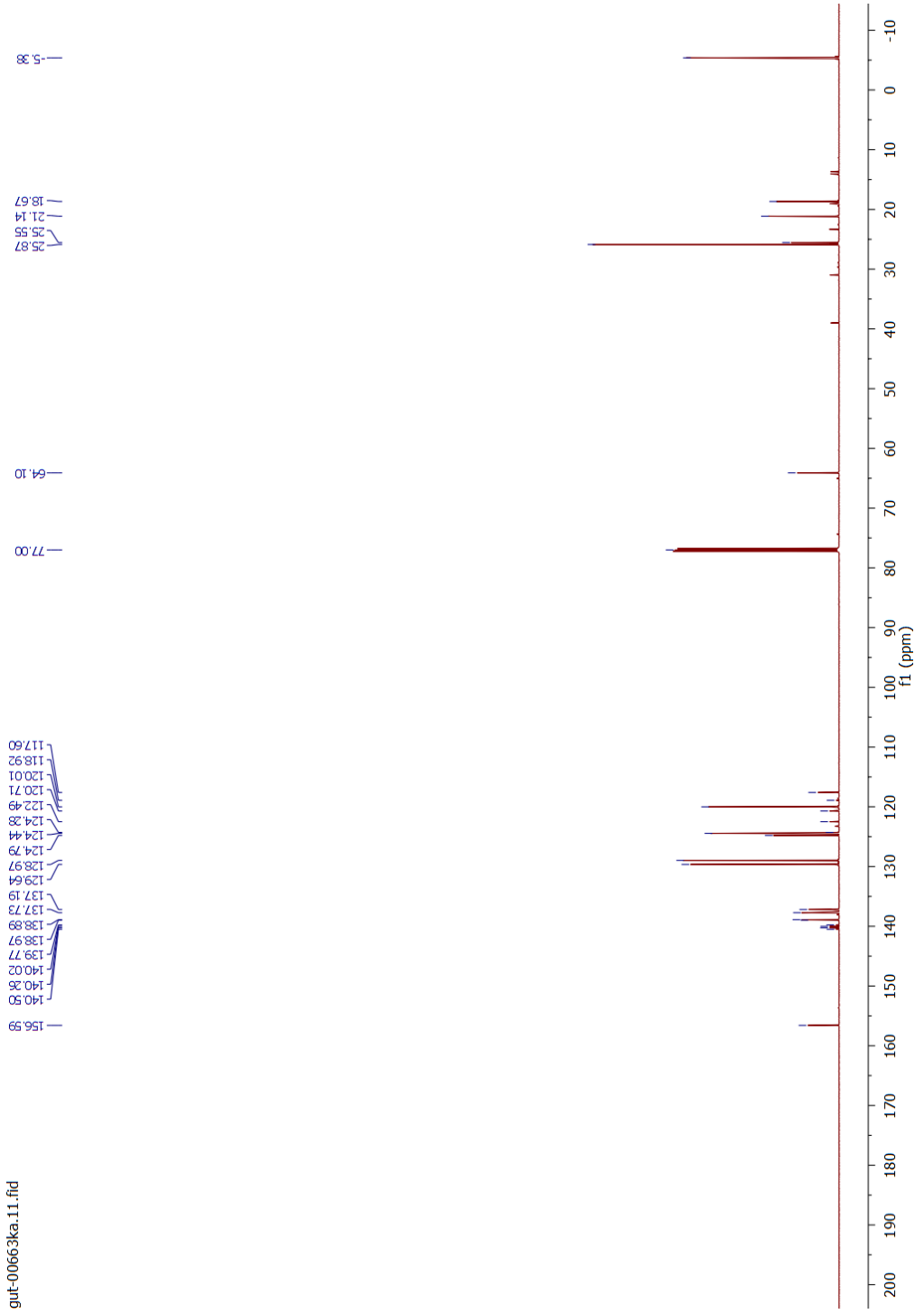
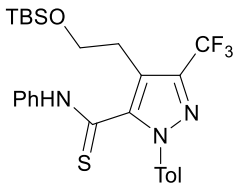


Figure S48. ^{13}C NMR of **12g** ($CDCl_3$, 151 MHz).



N-Phenyl-4-[2'-(tert-butyldimethylsiloxy)ethyl]-1-tolyl-3-trifluoromethyl-5-pyrazolecarbothioamide (12h)

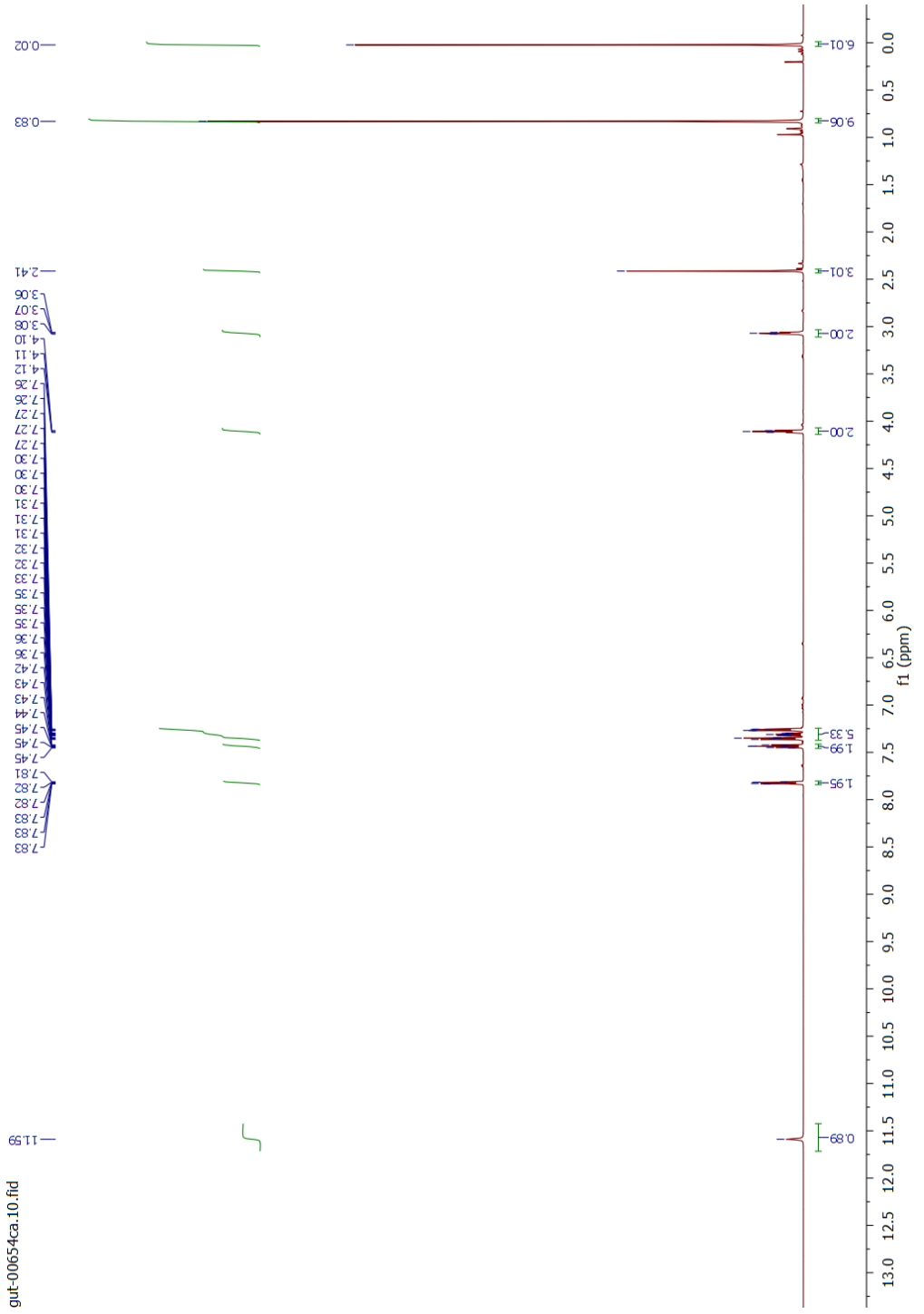


Figure S49. ^{1}H NMR of **12h** ($CDCl_3$, 600 MHz).

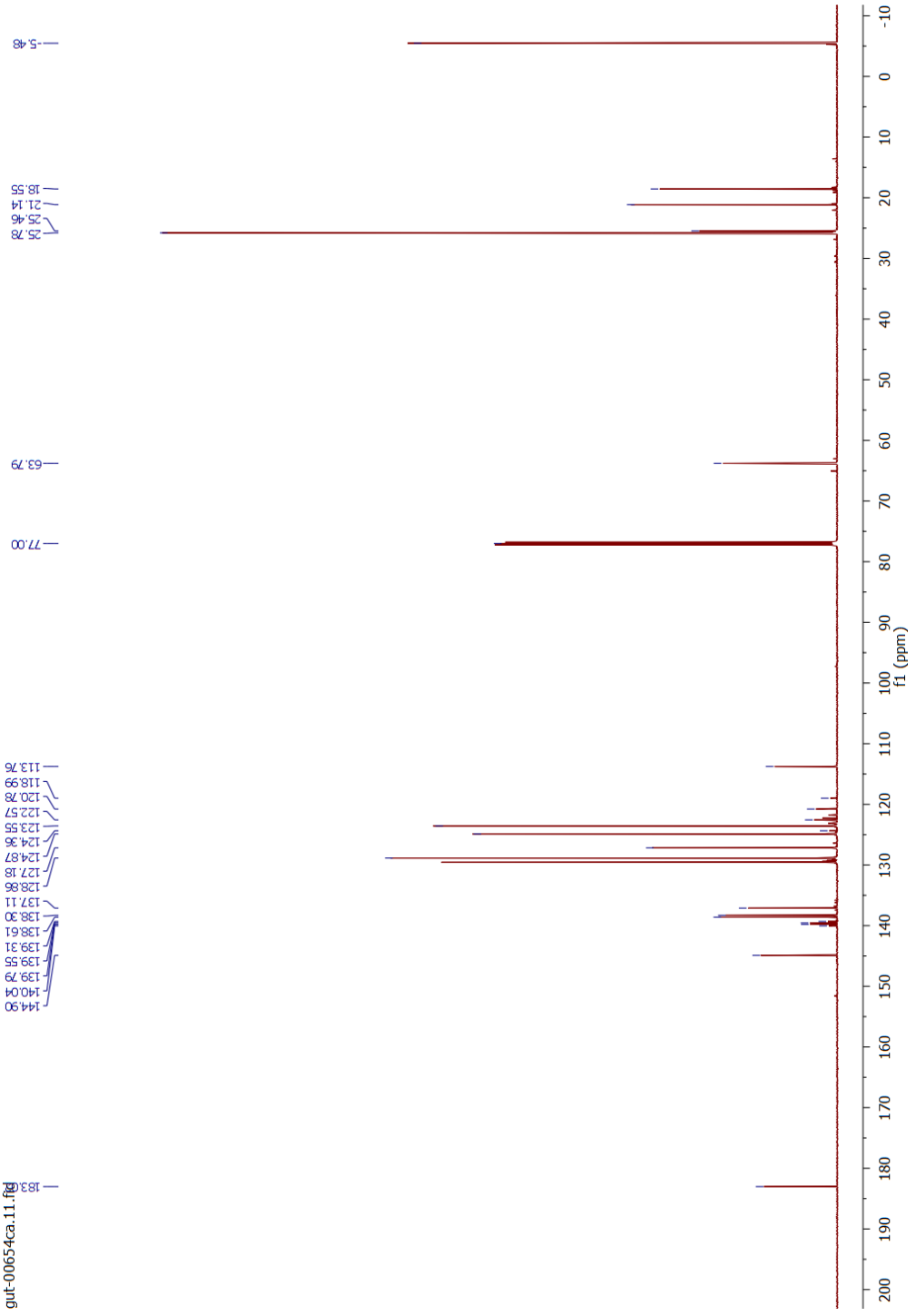
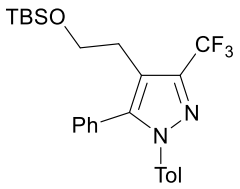


Figure S50. ^{13}C NMR of **12h** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-phenyl-1-tolyl-3-trifluoromethyl-1H-pyrazole (13a)

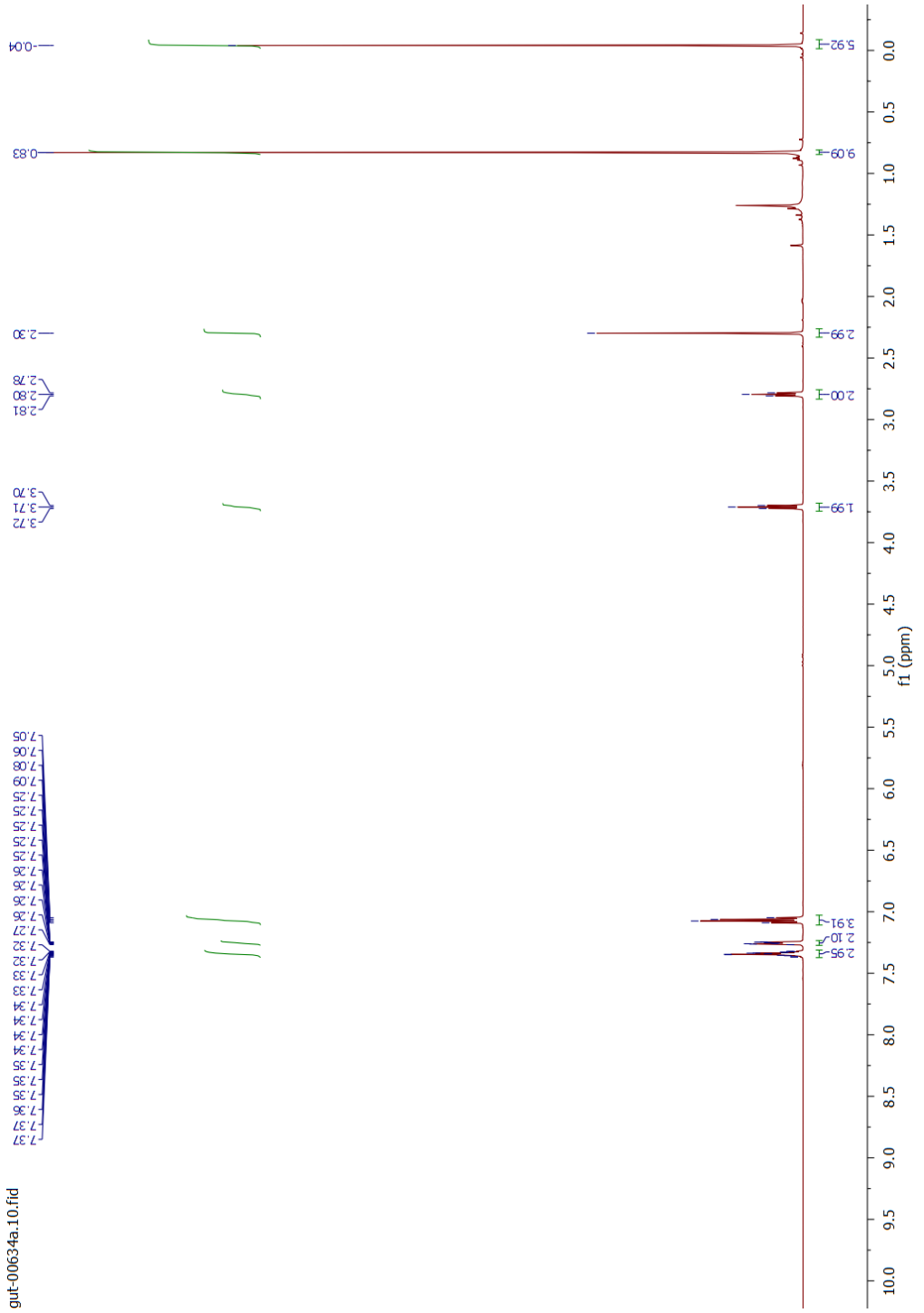


Figure S51. ^{1}H NMR of **13a** ($CDCl_3$, 600 MHz).

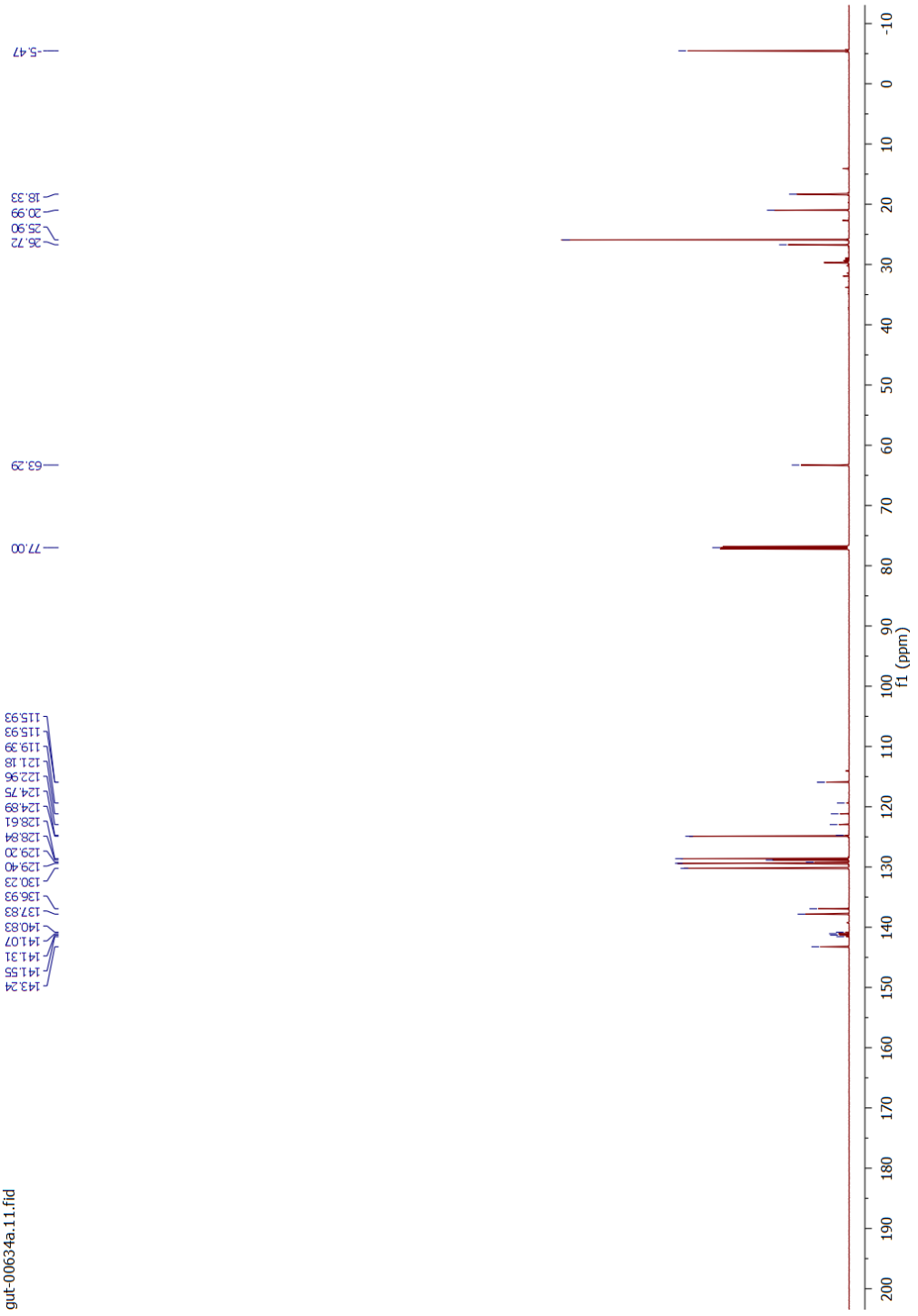
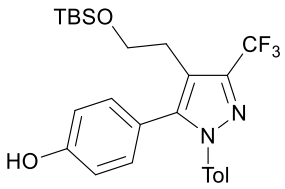


Figure S52. ^{13}C NMR of **13a** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-(4'-hydroxyphenyl)-1-tolyl-3-trifluoromethyl-1H-pyrazole (13b)

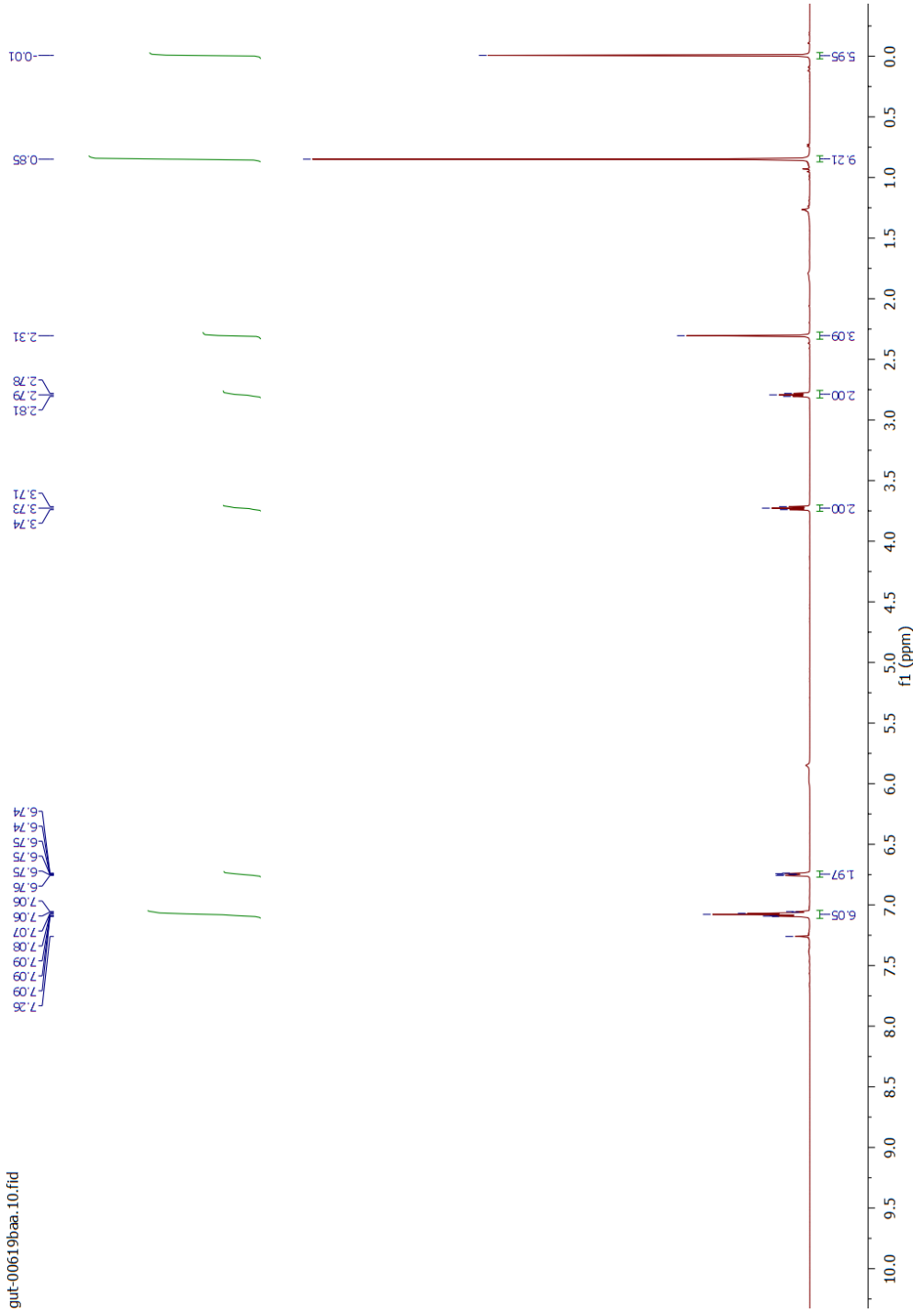


Figure S53. ^{1}H NMR of **13b** ($CDCl_3$, 600 MHz).

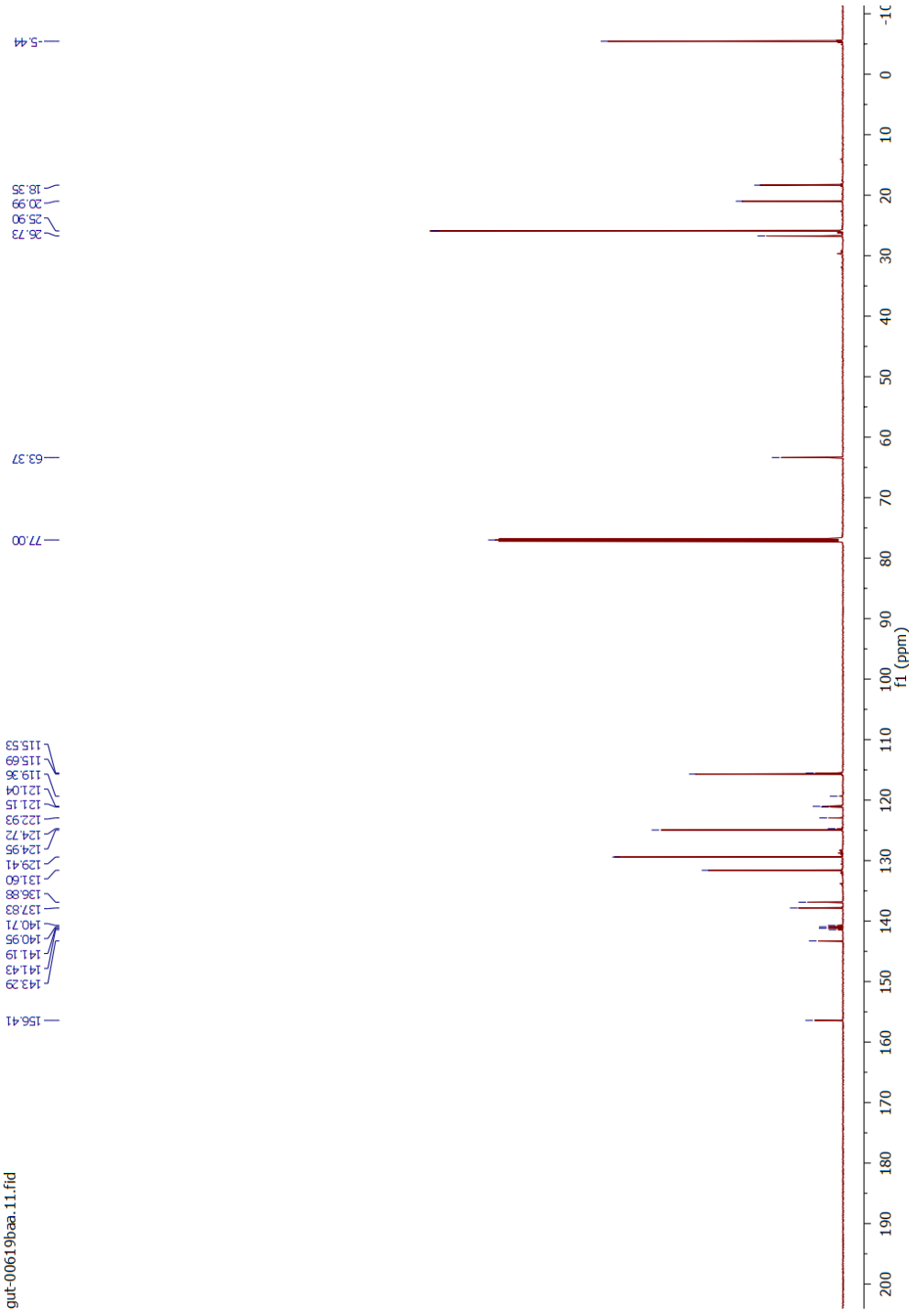
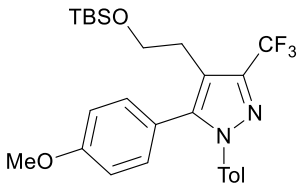


Figure S54. ^{13}C NMR of **13b** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-(4'-methoxyphenyl)-1-tolyl-3-trifluoromethyl-1H-pyrazole (13c)

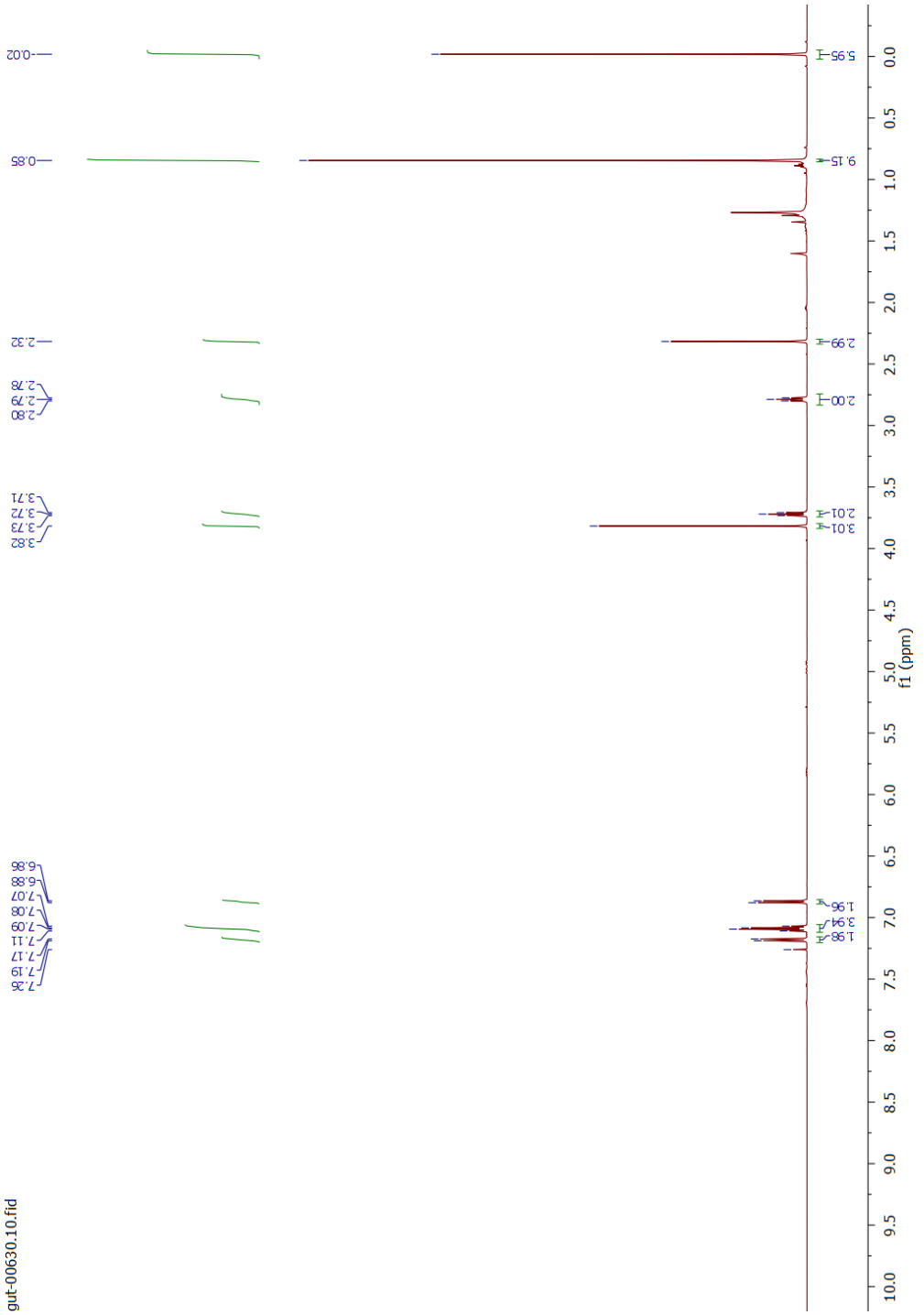


Figure S55. ^{1}H NMR of **13c** ($CDCl_3$, 600 MHz).

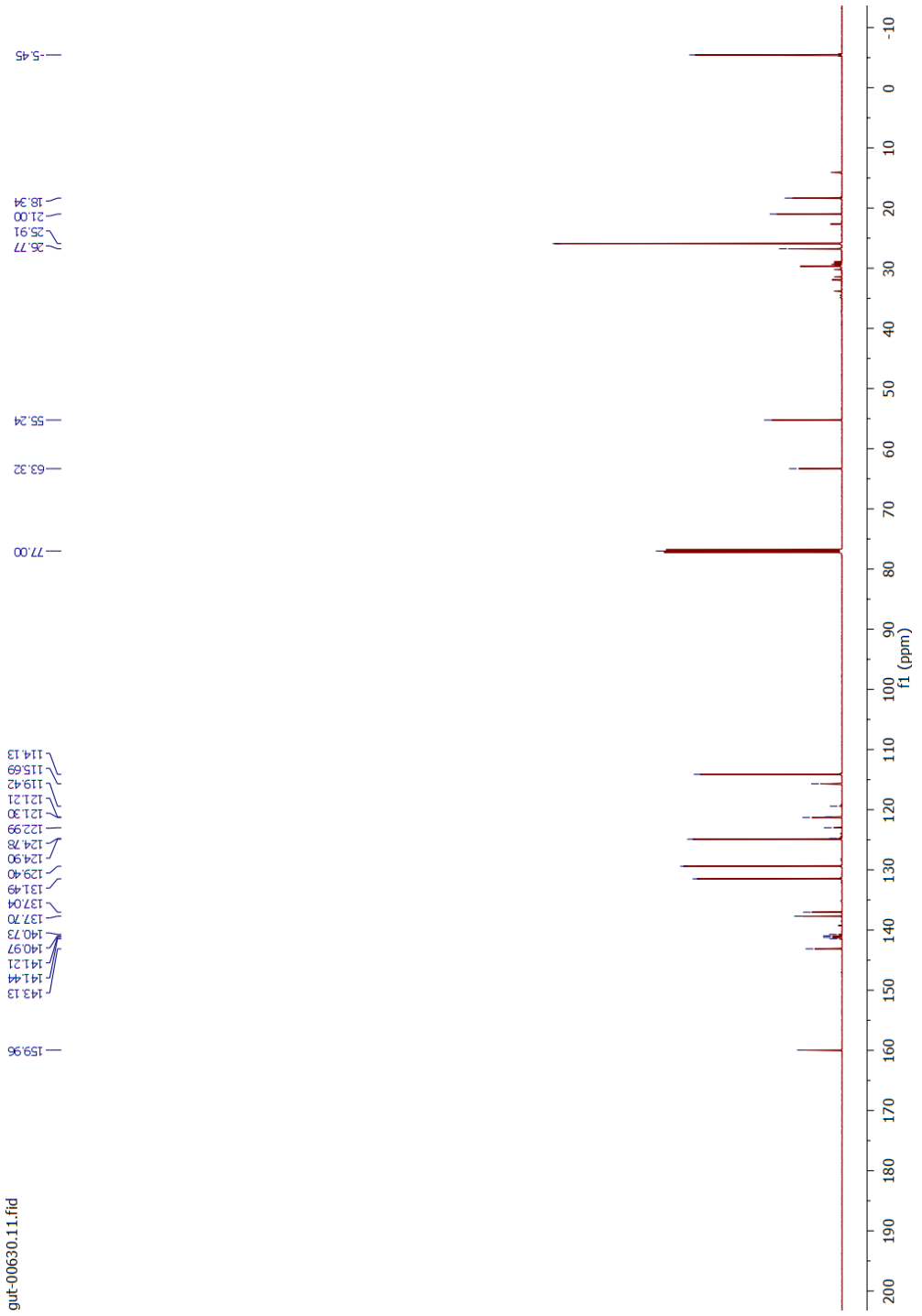
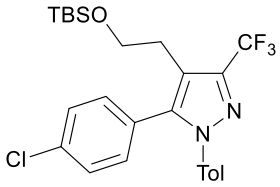


Figure S56. ^{13}C NMR of **13c** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-(4'-chlorophenyl)-1-tolyl-3-trifluoromethyl-1H-pyrazole (13d)

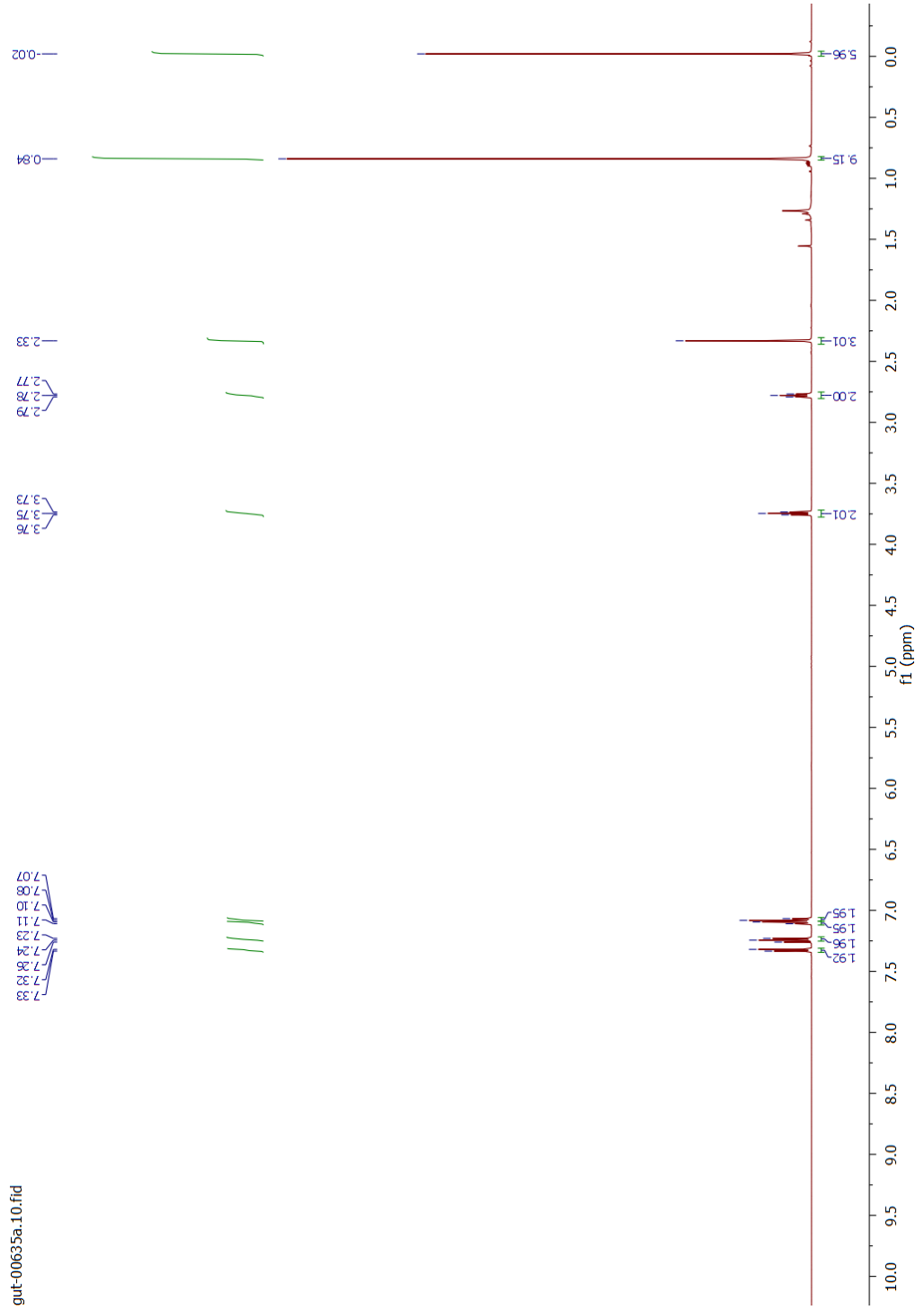


Figure S57. ^{1}H NMR of **13d** ($CDCl_3$, 600 MHz).

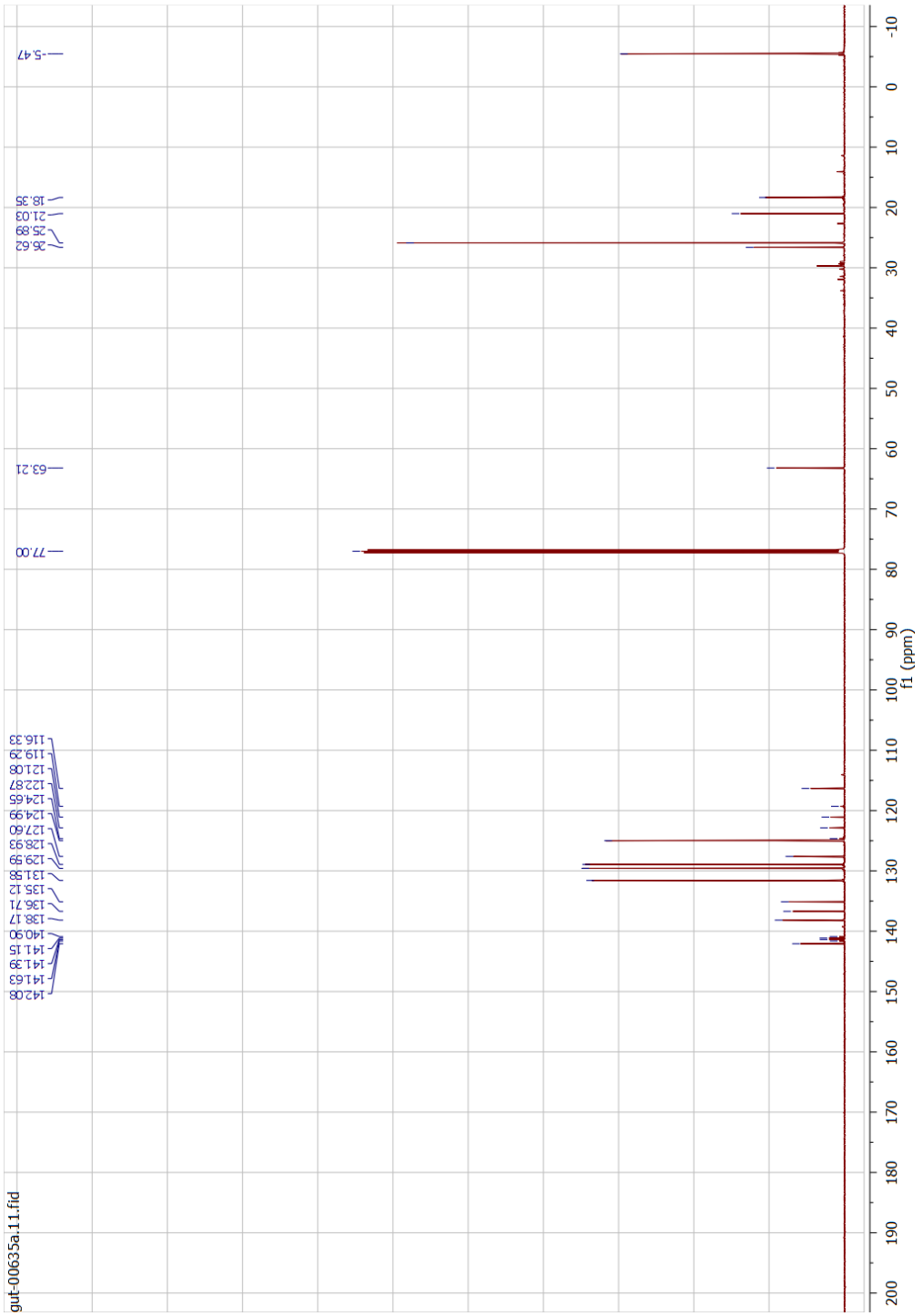
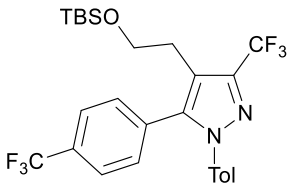


Figure S58. ^{13}C NMR of **13d** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-1-tolyl-5-(4'-trifluoromethylphenyl)-3-trifluoromethyl-1H-pyrazole (13e)

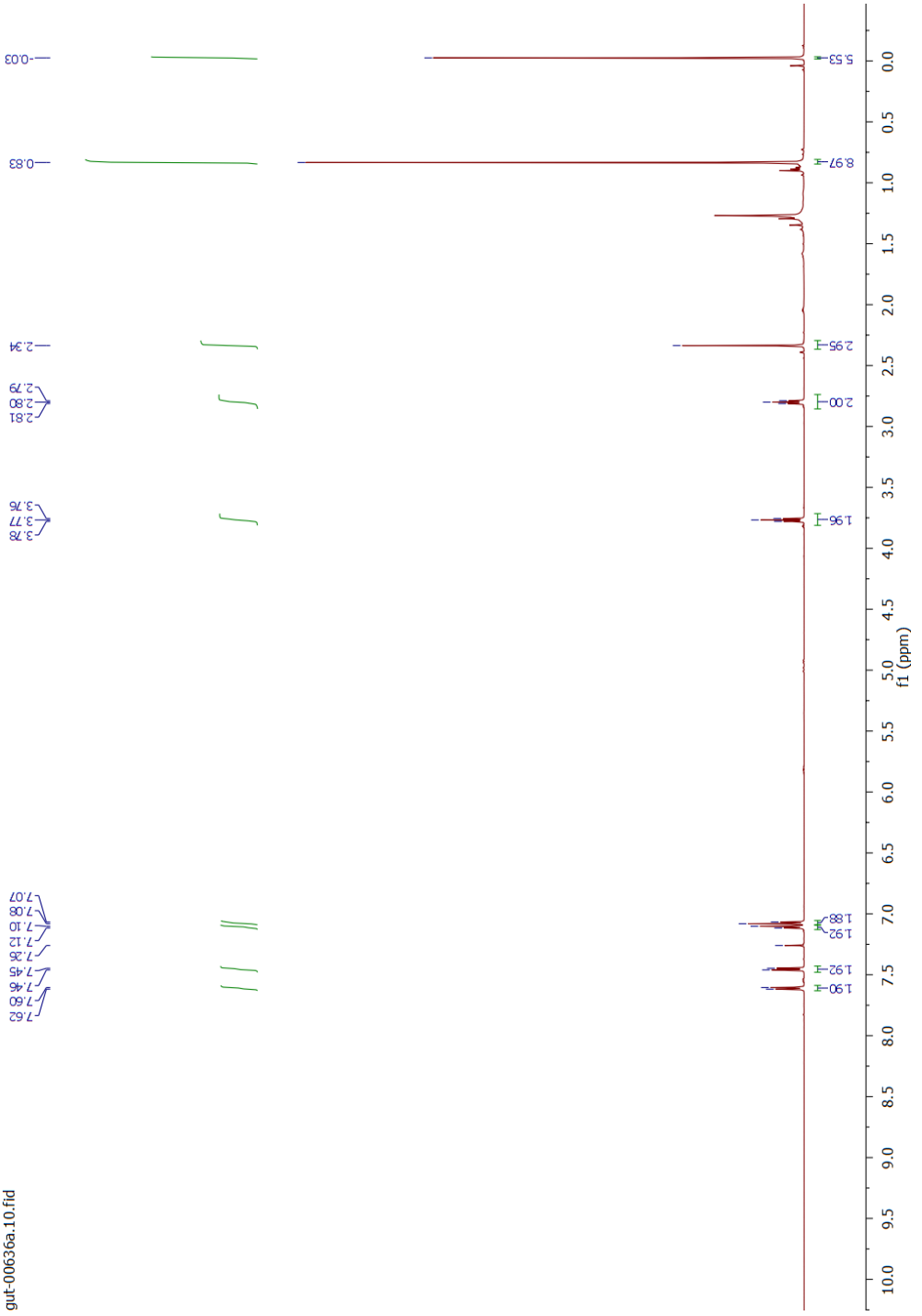


Figure S59. ^{1}H NMR of **13e** ($CDCl_3$, 600 MHz).

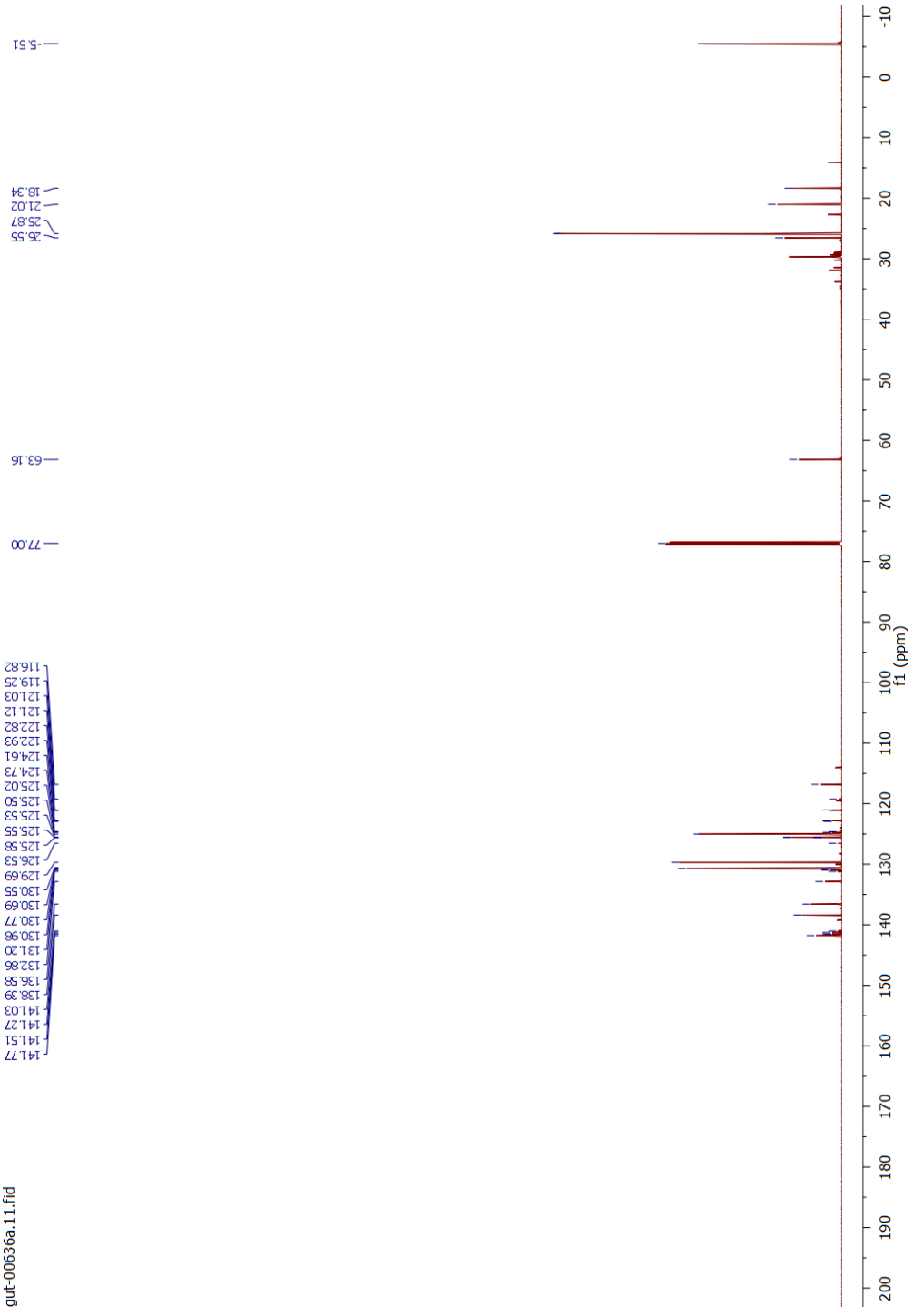
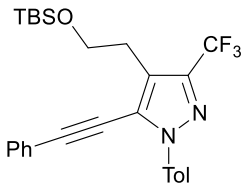


Figure S60. ^{13}C NMR of **13e** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-(phenylethynyl)-1-tolyl-3-trifluoromethyl-1H-pyrazole (14a)

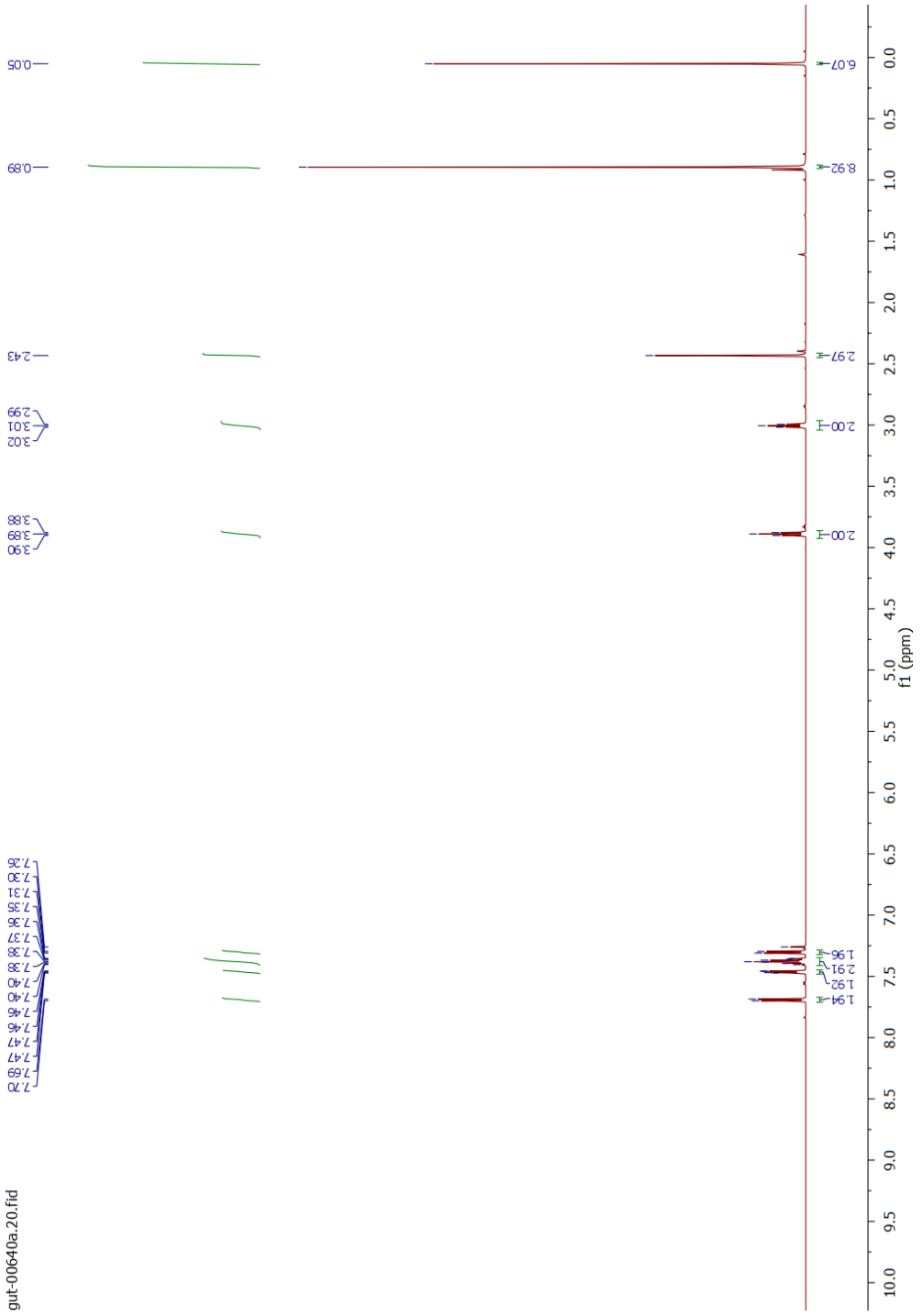


Figure S61. ^{1}H NMR of **14a** ($CDCl_3$, 600 MHz).

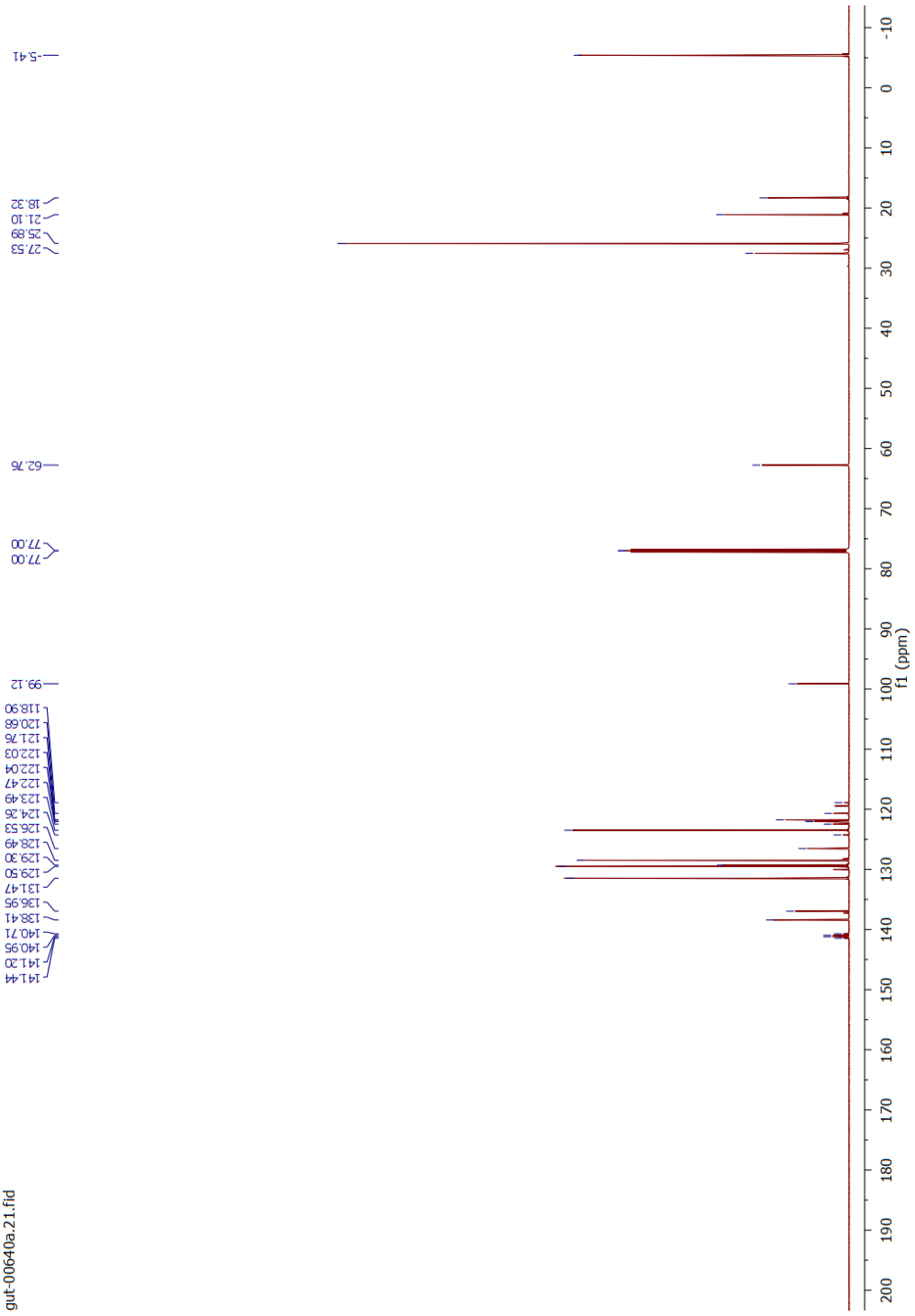
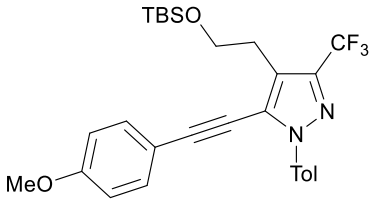


Figure S62. ^{13}C NMR of **14a** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-(4'-methoxyphenylethynyl)-1-tolyl-3-trifluoromethyl-1H-pyrazole (14b)

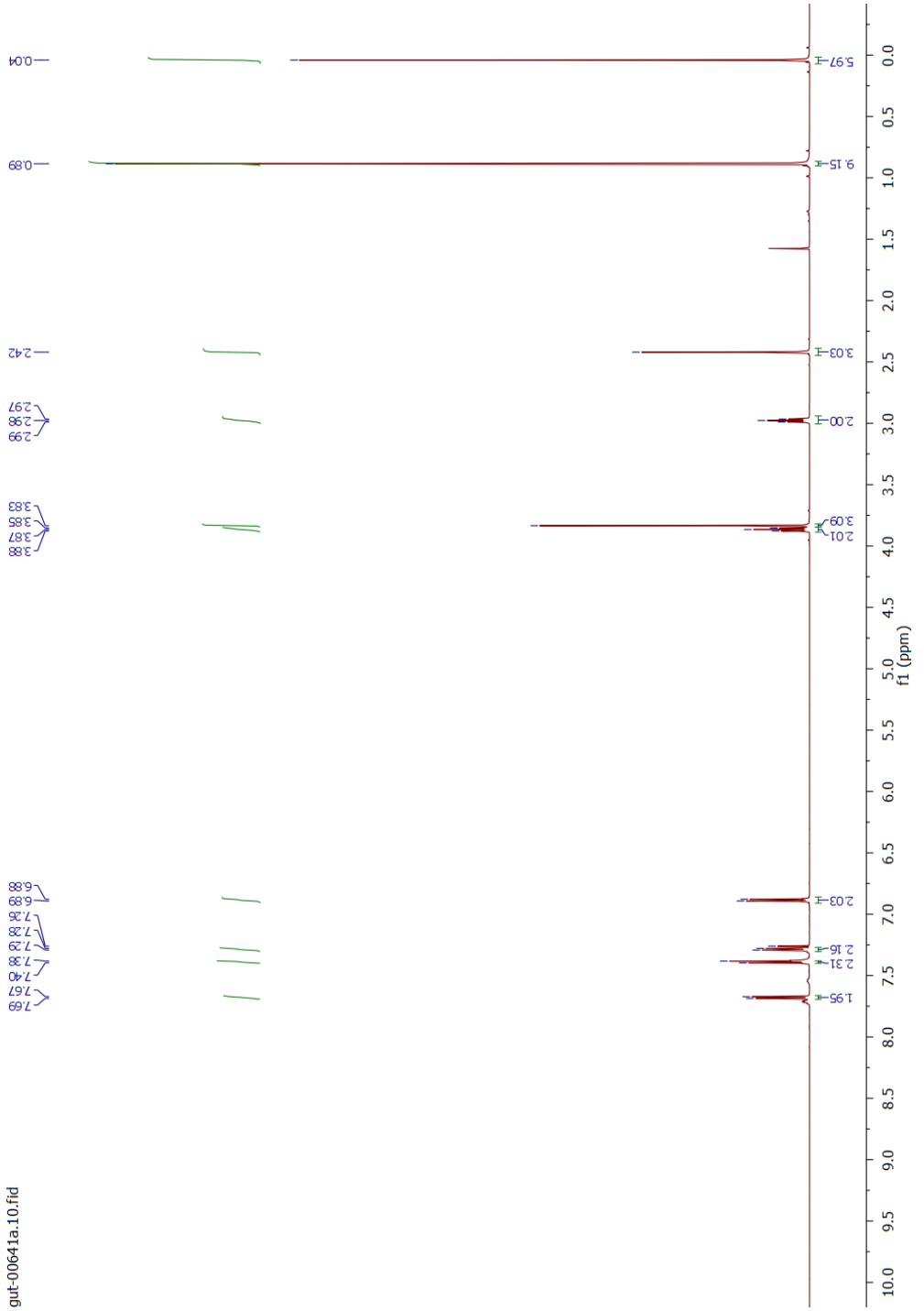


Figure S63. ^{1}H NMR of **14b** ($CDCl_3$, 600 MHz).

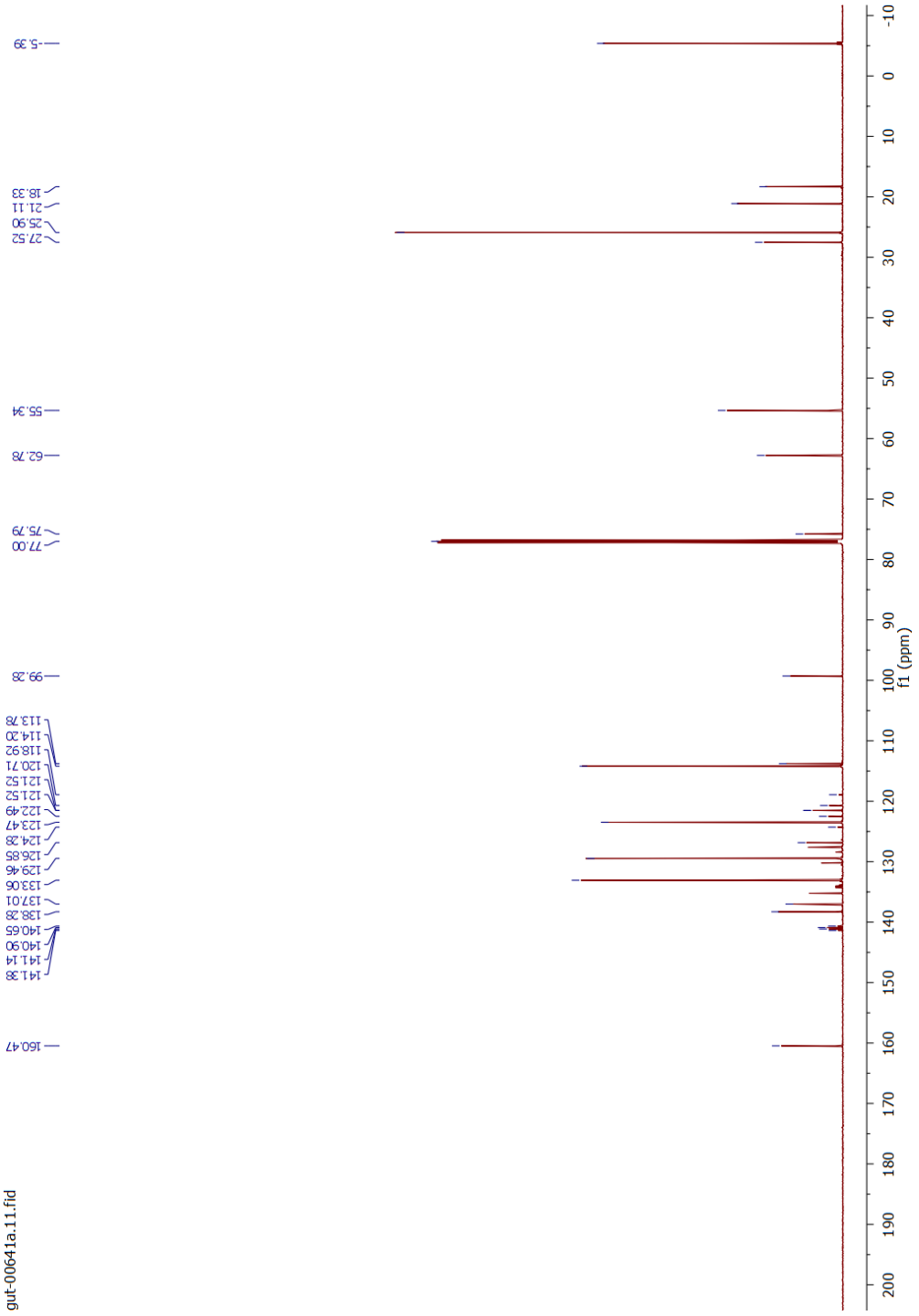
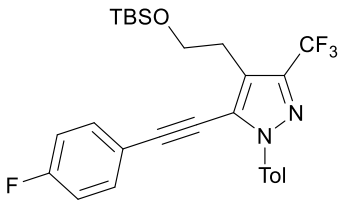


Figure S64. ^{13}C NMR of **14b** ($CDCl_3$, 151 MHz).



4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-(4'-fluorophenyl-ethynyl)-1-tolyl-3-trifluoromethyl-1H-pyrazole (14c)

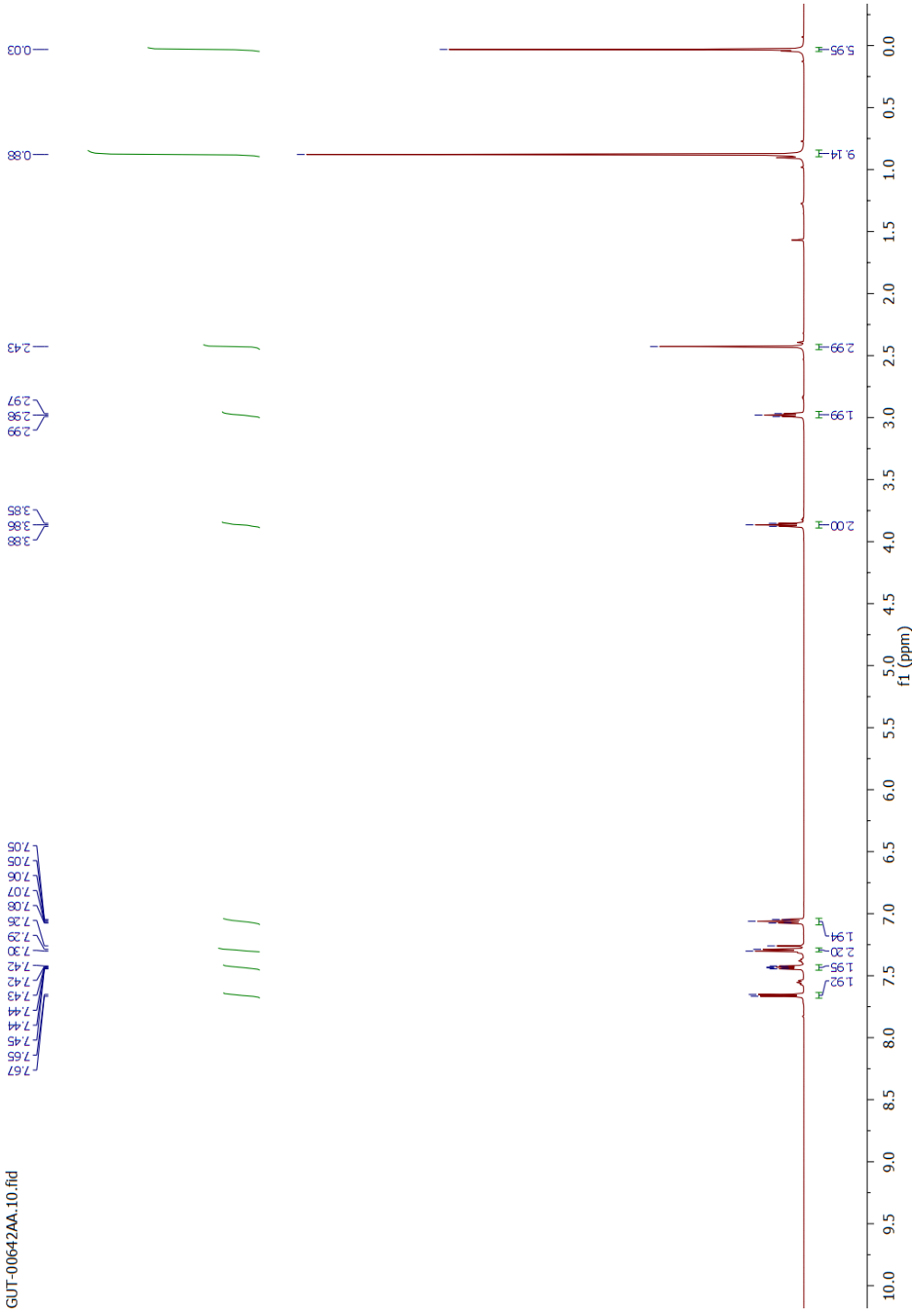


Figure S65. ^{1}H NMR of **14c** ($CDCl_3$, 600 MHz).

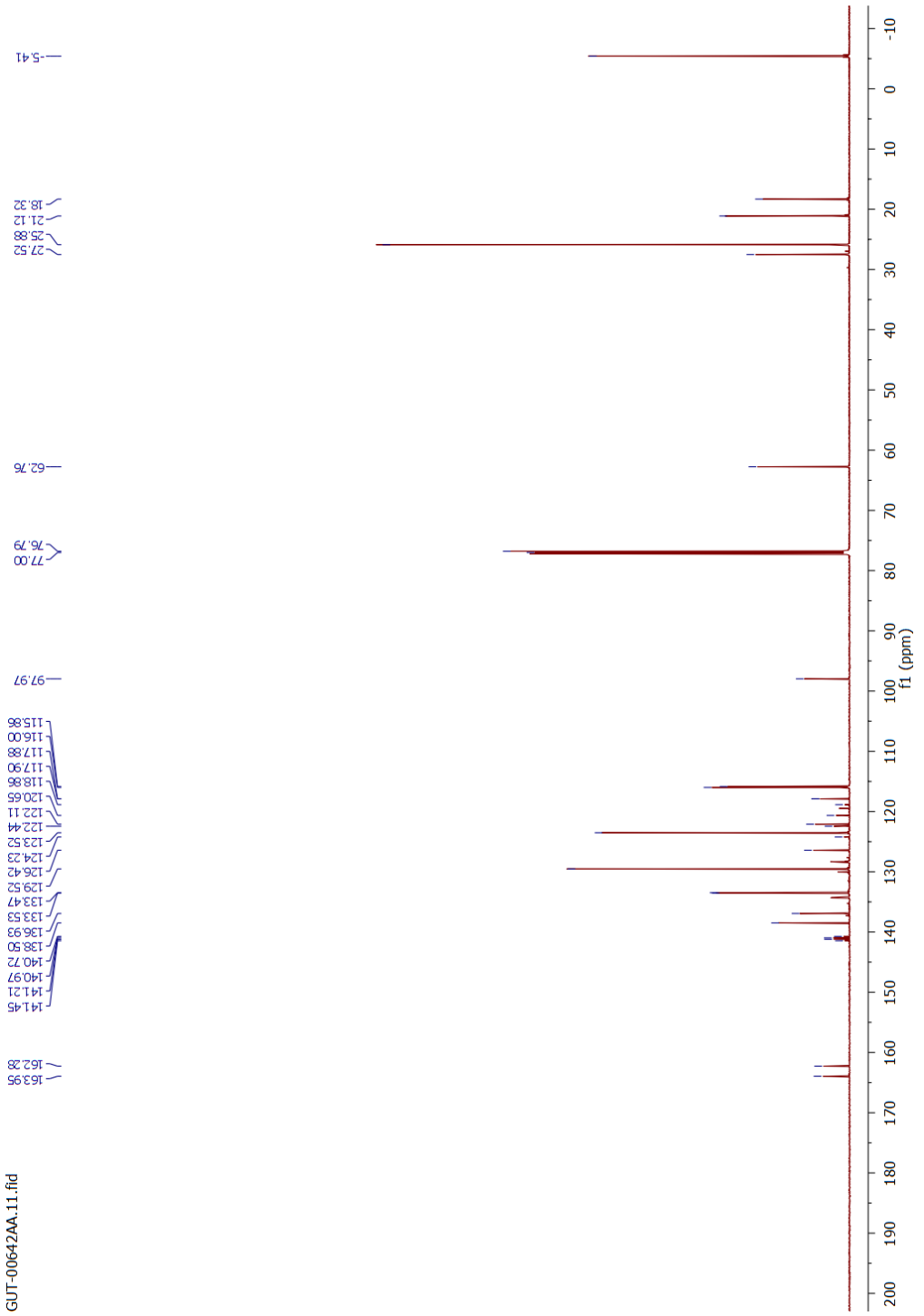
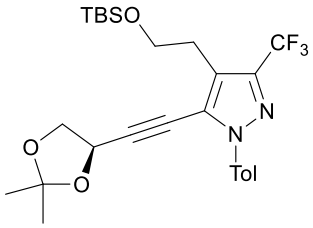


Figure S66. ^{13}C NMR of **14c** ($CDCl_3$, 151 MHz).



(R)-4-[2'-(tert-Butyldimethylsiloxy)ethyl]-5-[2',2'-dimethyl-1',3'-dioxolan-4'-yl)ethynyl]-1-tolyl-3-trifluoromethyl-1H-pyrazole (14d)

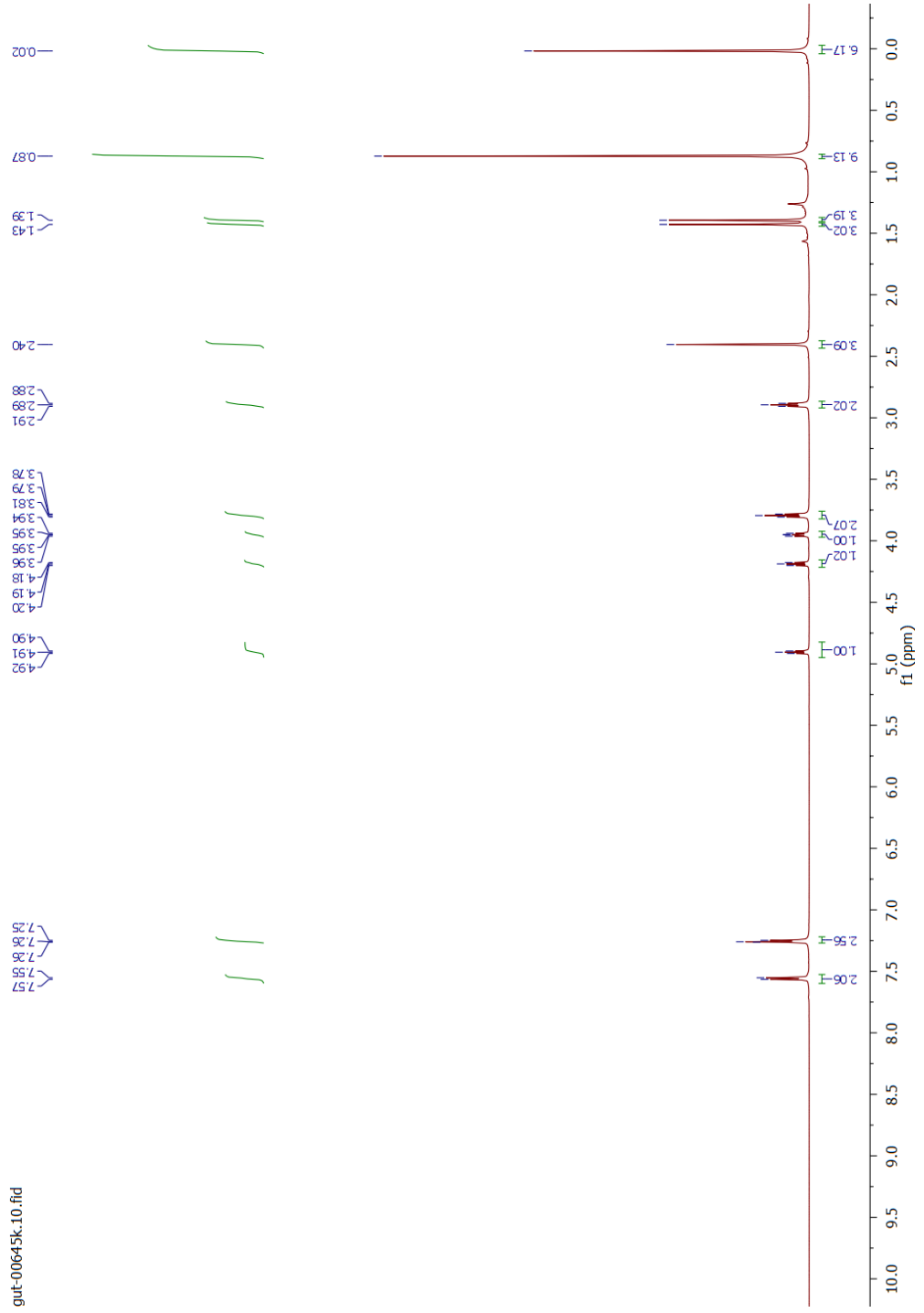


Figure S67. ^{1}H NMR of **14d** ($CDCl_3$, 600 MHz).

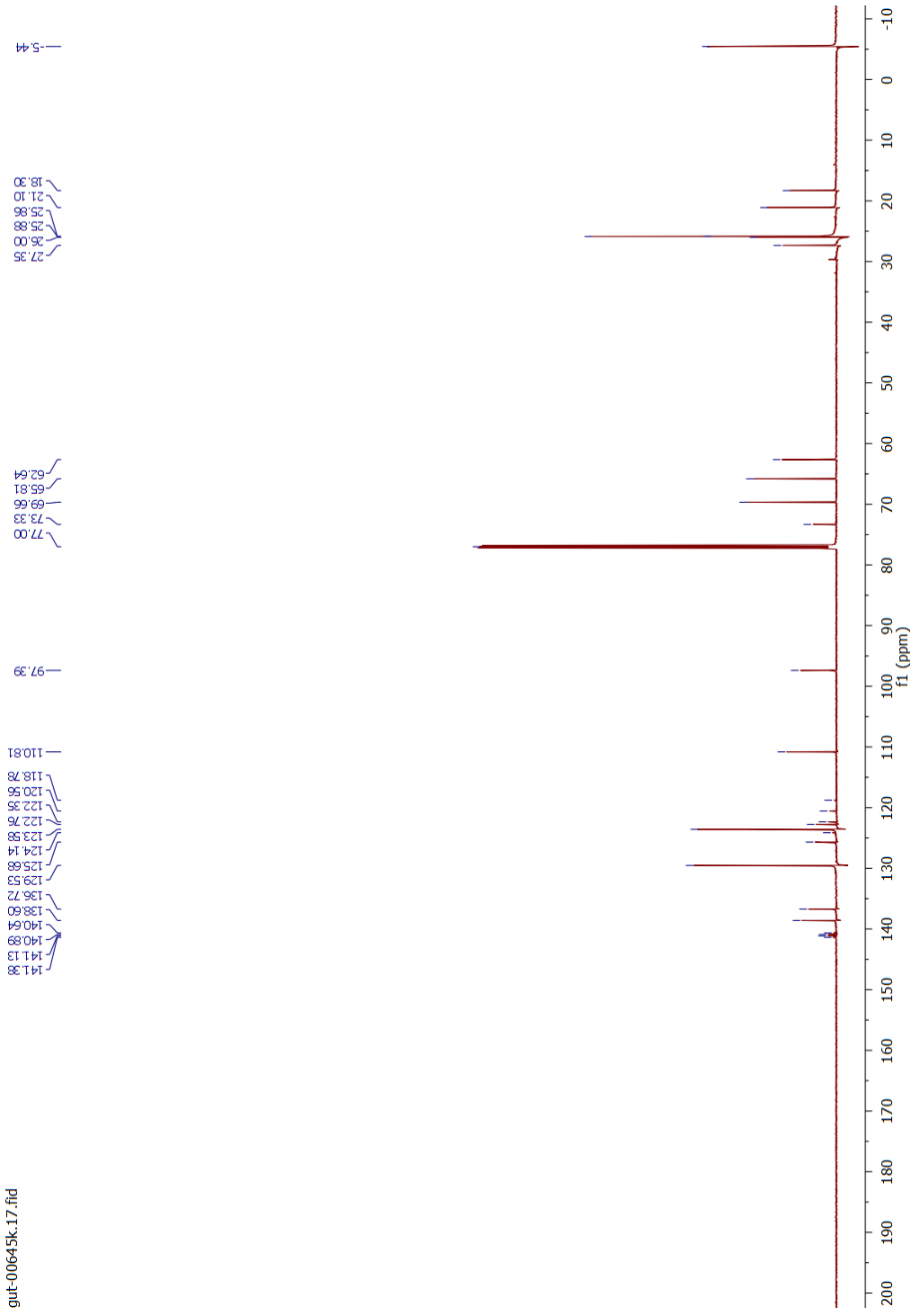
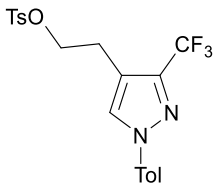


Figure S68. ^{13}C NMR of **14d** ($CDCl_3$, 151 MHz).



2-(1-tolyl-3-trifluoromethyl-1H-pyrazol-4-yl)ethyl p-toluenesulfonate (15)

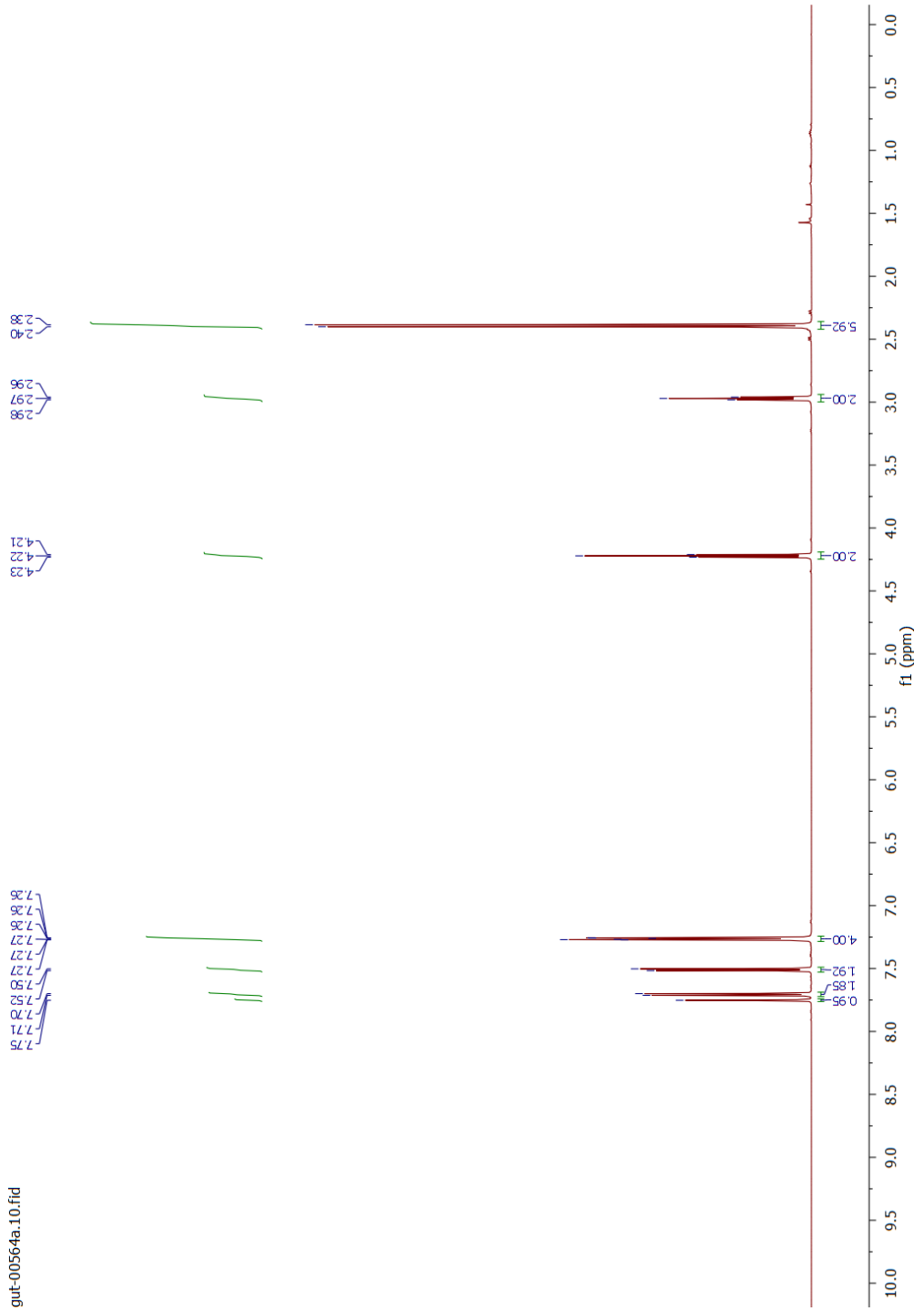


Figure S69. ^{1}H NMR of **15** ($CDCl_3$, 600 MHz).

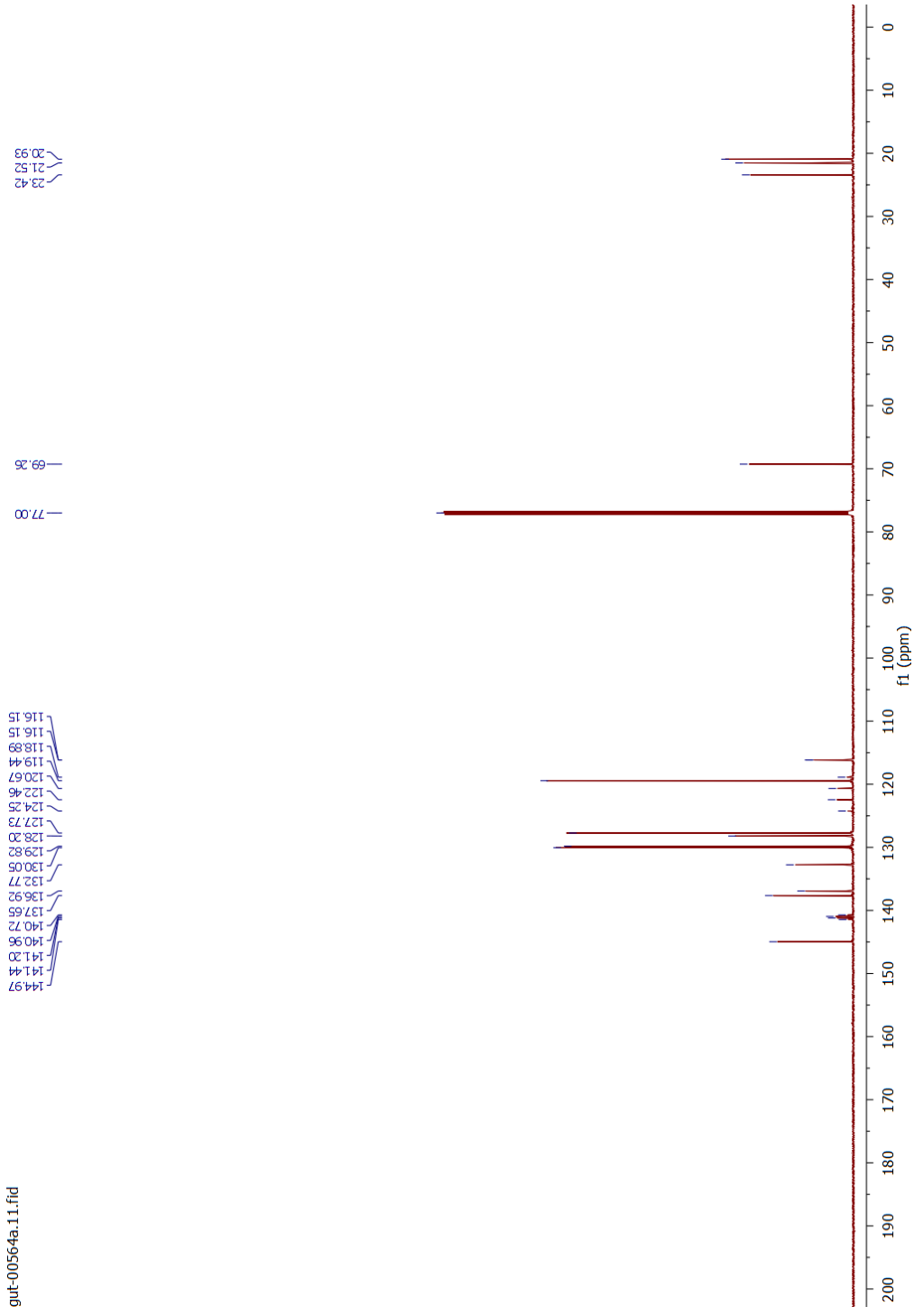
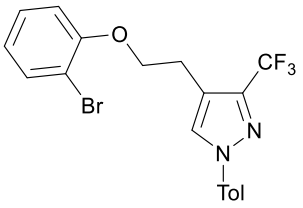


Figure S70. ^{13}C NMR of **15** ($CDCl_3$, 151 MHz).



4-[2'-(o-Bromophenoxy)ethyl]-1-tolyl-3-trifluoromethyl-1H-pyrazole (16a)

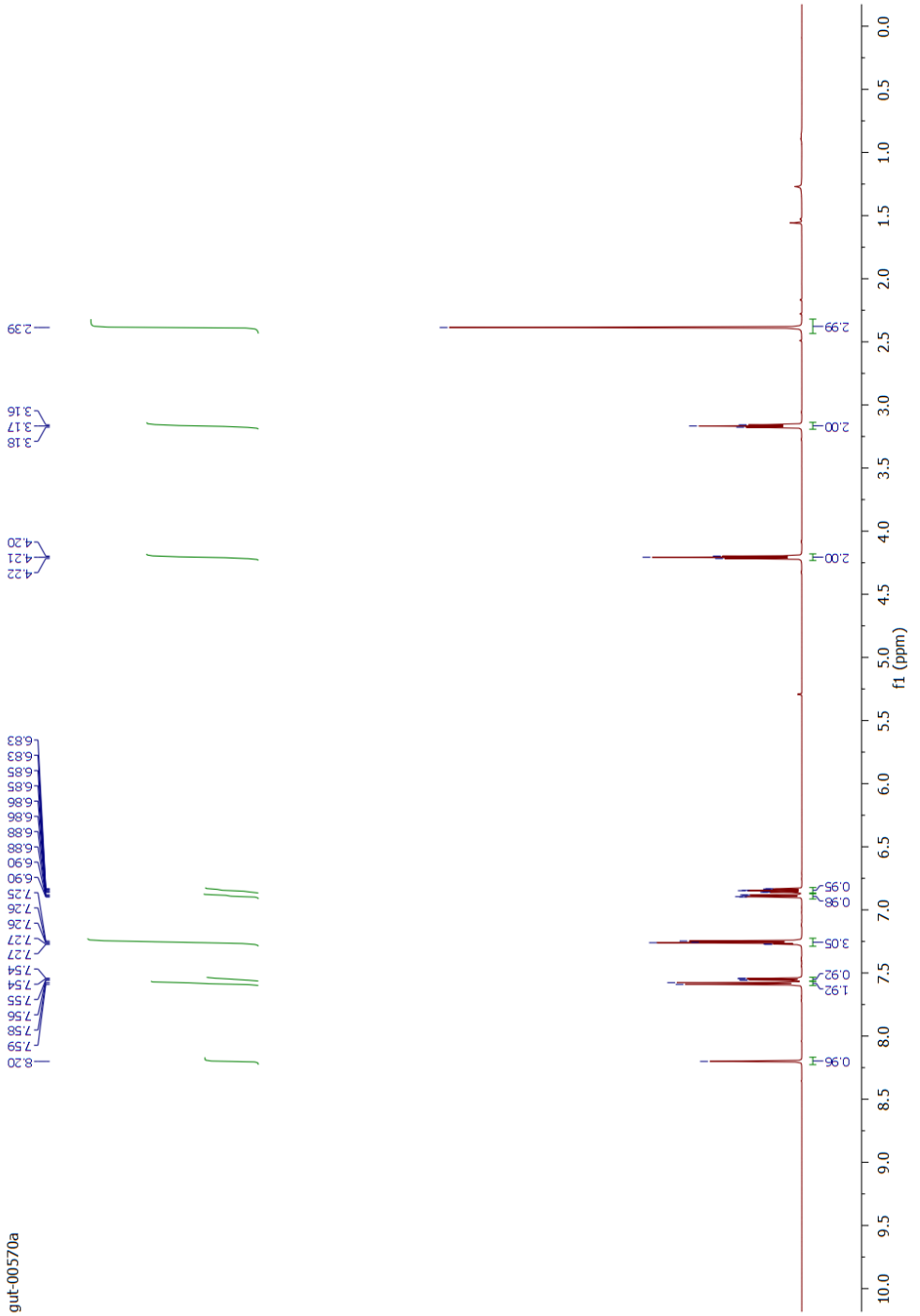


Figure S71. ^{1}H NMR of **16a** ($CDCl_3$, 600 MHz).

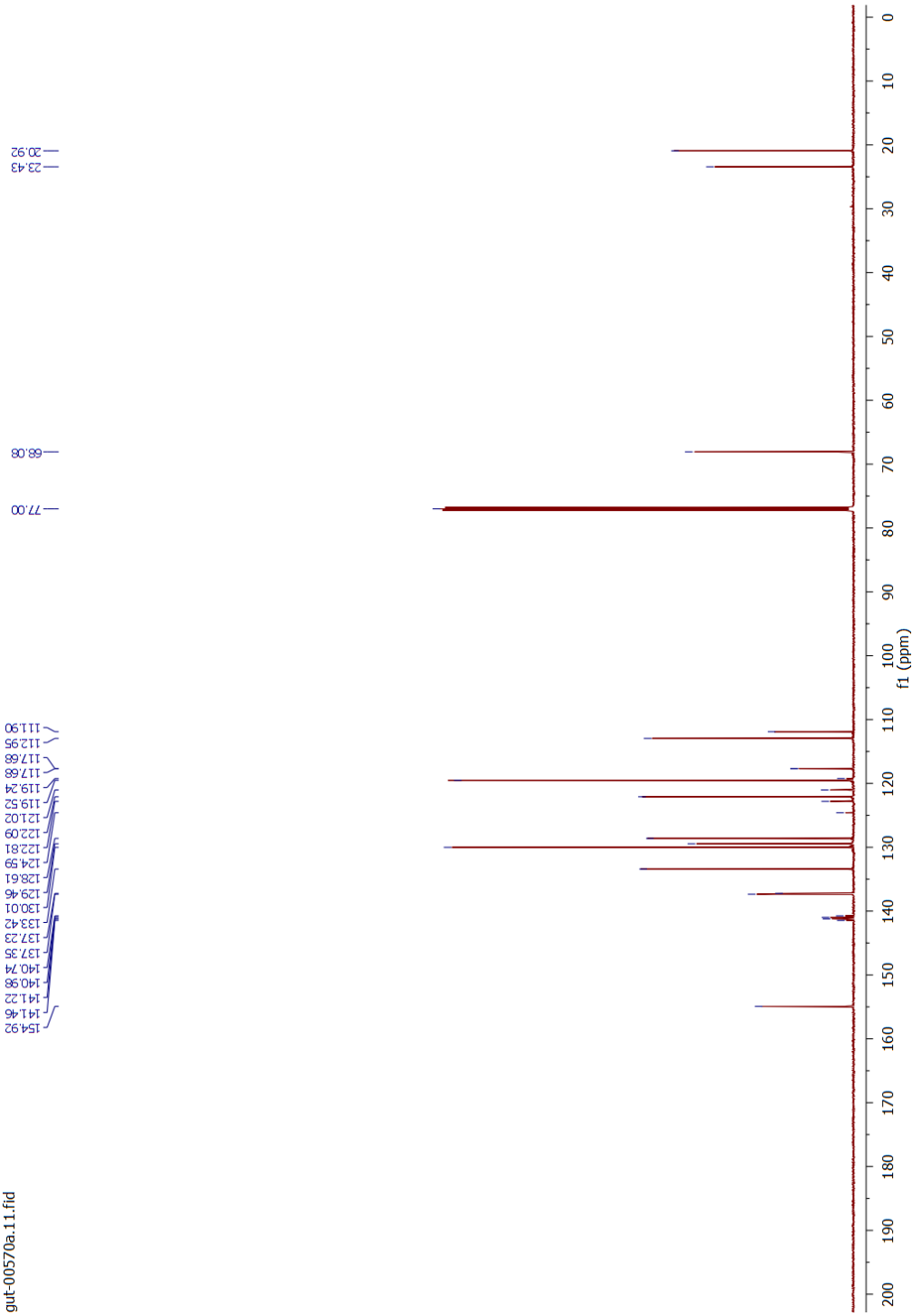
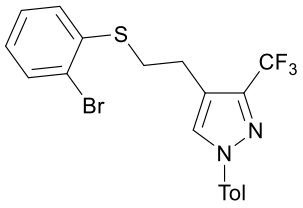


Figure S72. ^{13}C NMR of **16a** ($CDCl_3$, 151 MHz).



4-[2'-(o-Bromophenylsulfanyl)ethyl]-1-tolyl-3-trifluoromethyl-1H-pyrazole (16b)

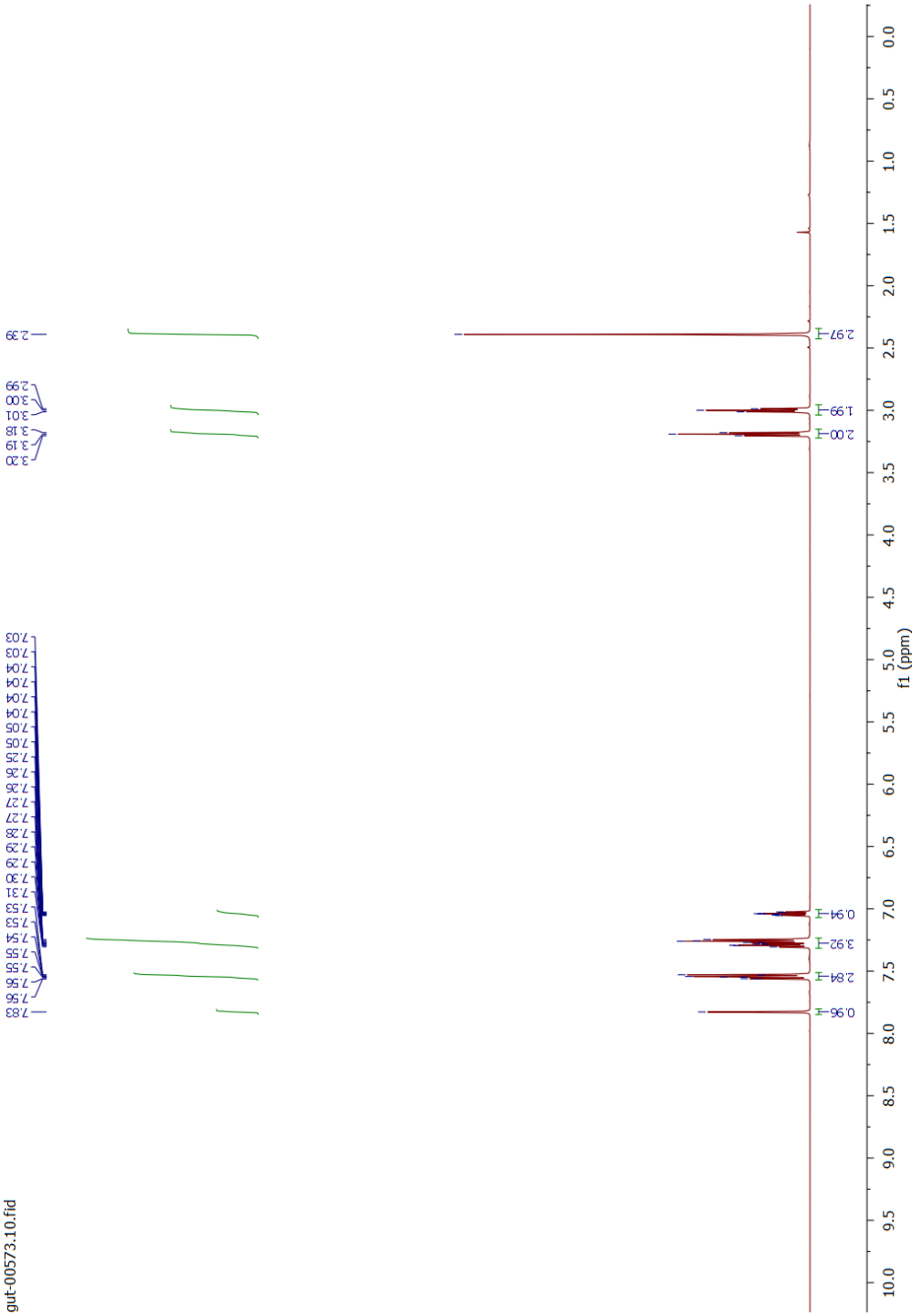


Figure S73. ^{1}H NMR of **16b** ($CDCl_3$, 600 MHz).

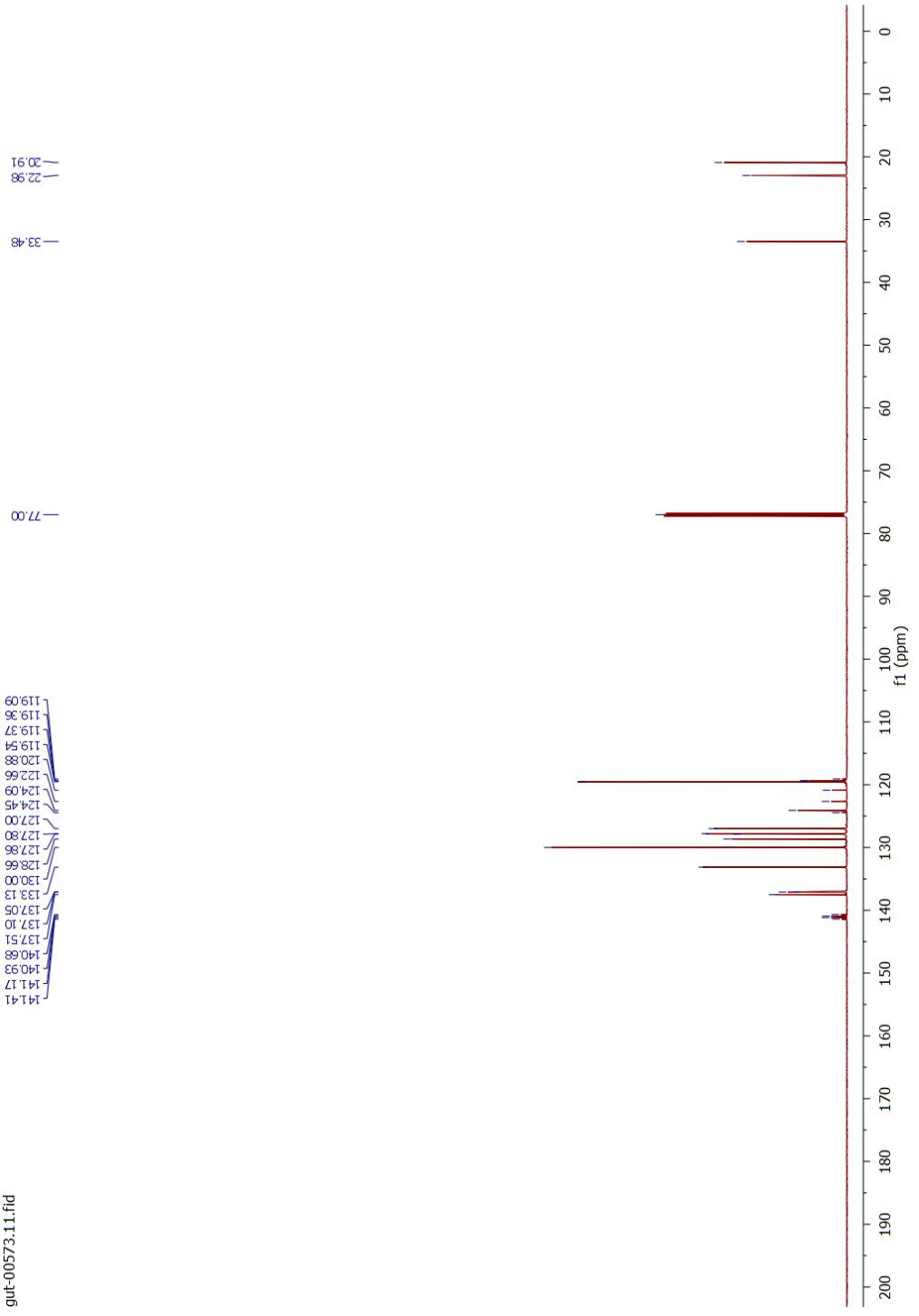
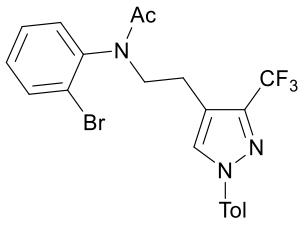


Figure S74. ^{13}C NMR of **16b** ($CDCl_3$, 151 MHz).



N-(2'-Bromophenyl)-N-[2'-(1''-tolyl-3''-trifluoromethyl-1''H-pyrazol-4''-yl)ethyl]acetamide (16c)

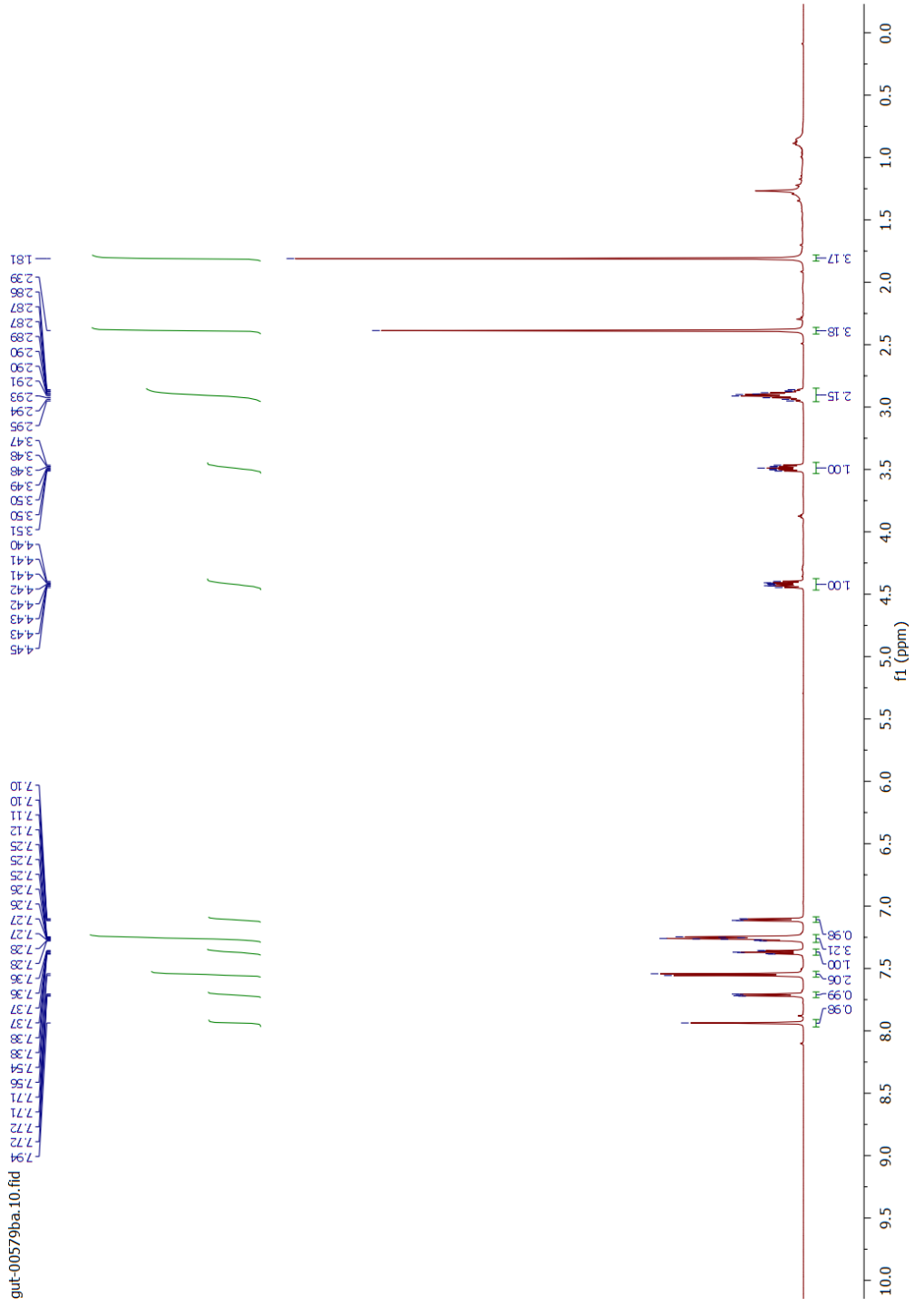


Figure S75. ^{1}H NMR of **16c** ($CDCl_3$, 600 MHz).

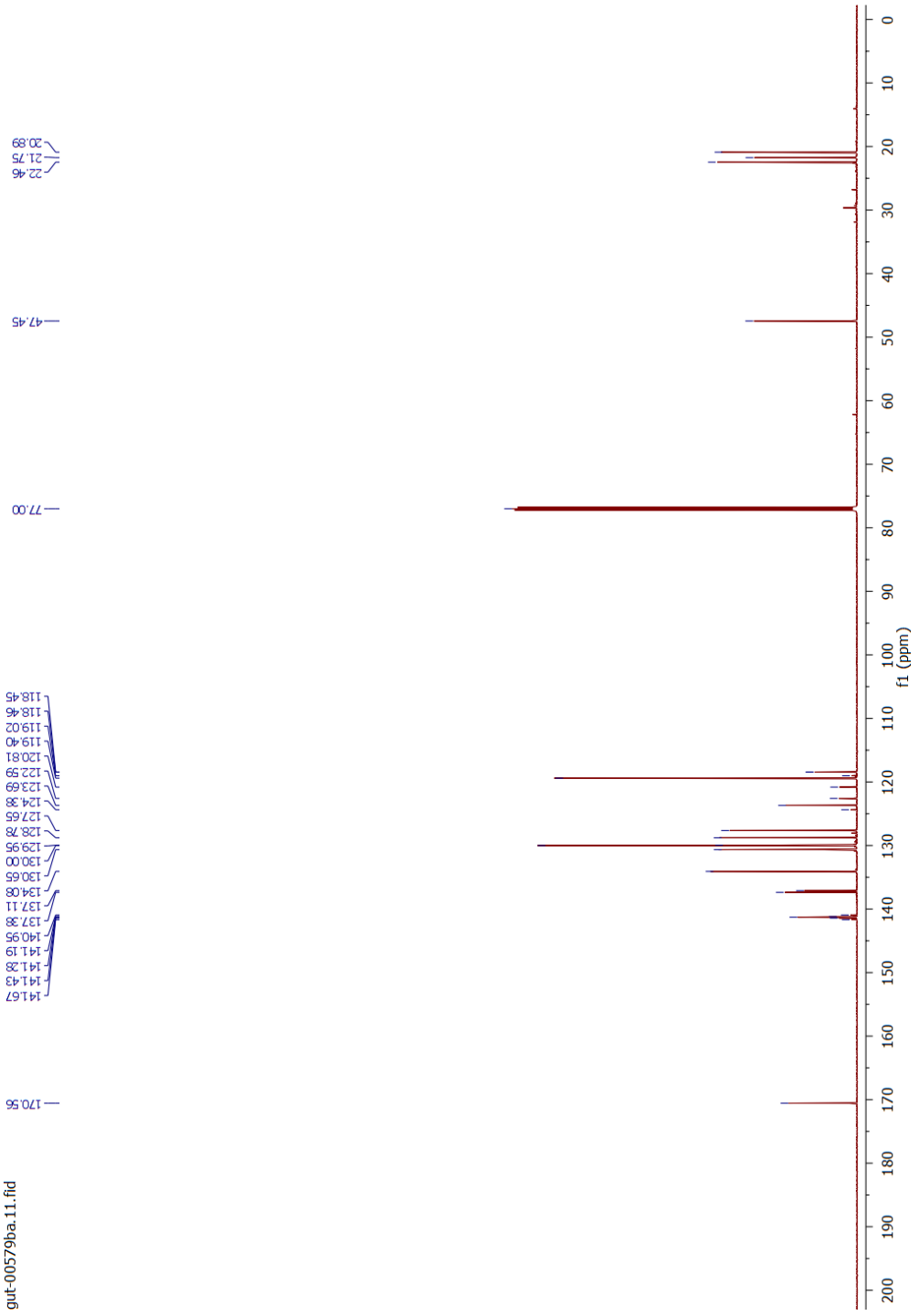
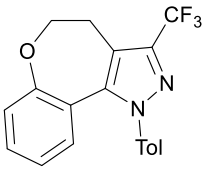


Figure S76. ^{13}C NMR of **16c** ($CDCl_3$, 151 MHz).



1-Tolyl-3-trifluoromethyl-4,5-dihydro-1H-[1]benzoxepino[5,4-c]pyrazole (17a)

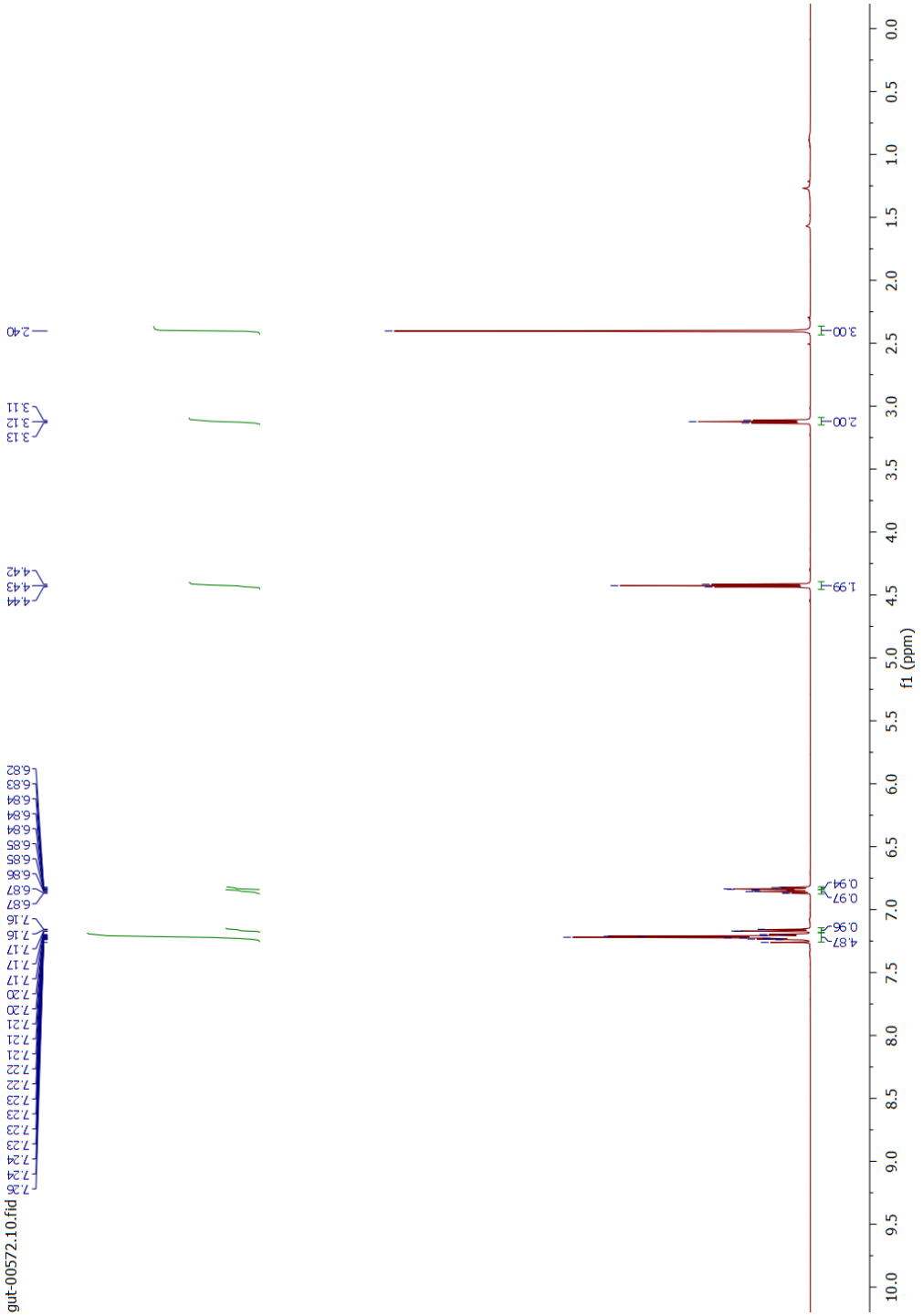


Figure S77. ^{1}H NMR of **17a** ($CDCl_3$, 600 MHz).

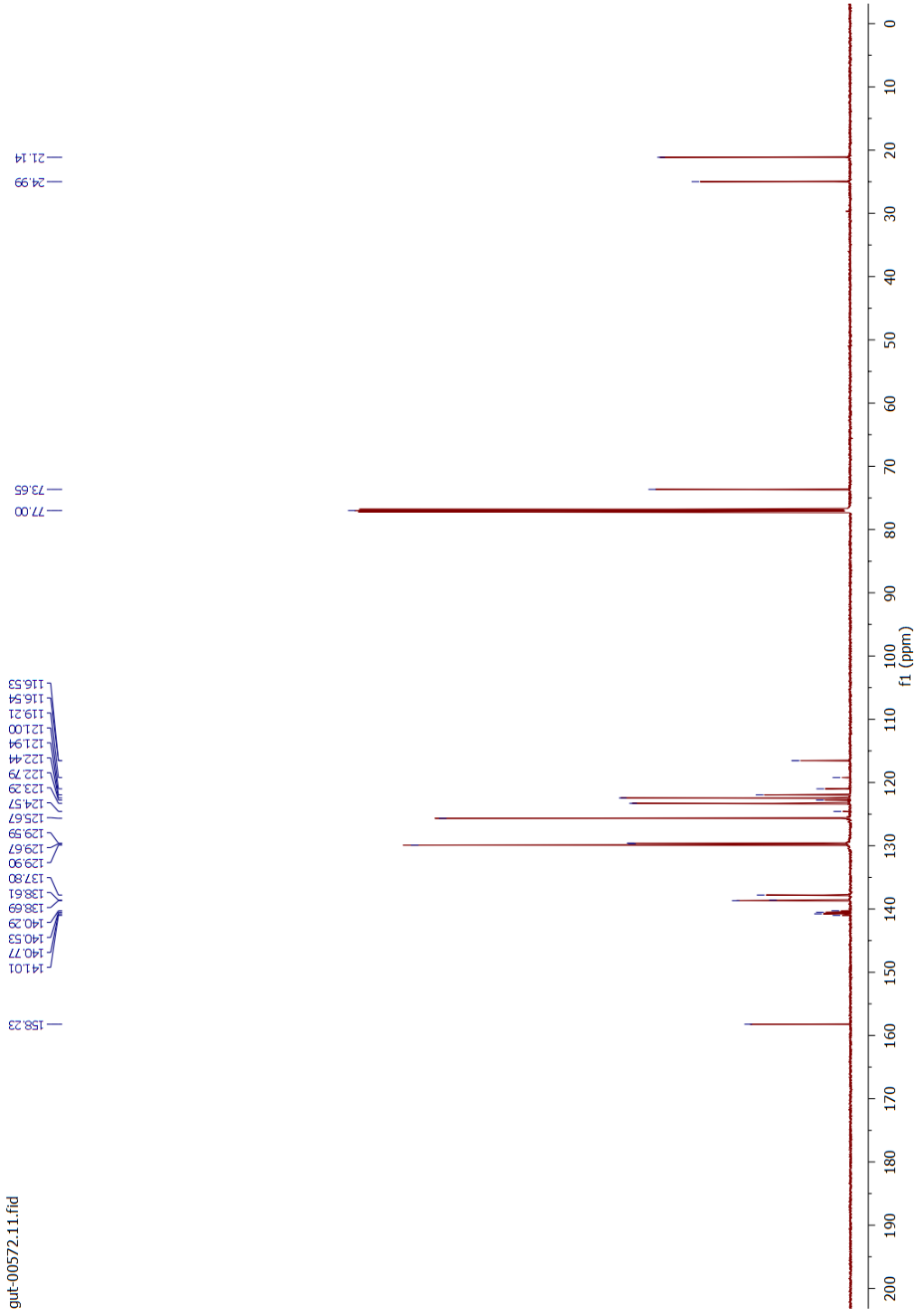
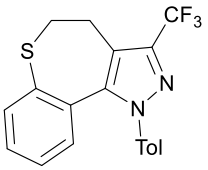


Figure S78. ^{13}C NMR of **17a** ($CDCl_3$, 151 MHz).



1-Tolyl-3-trifluoromethyl-4,5-dihydro-1H-[1]benzothiepino[5,4-c]pyrazole (17b)

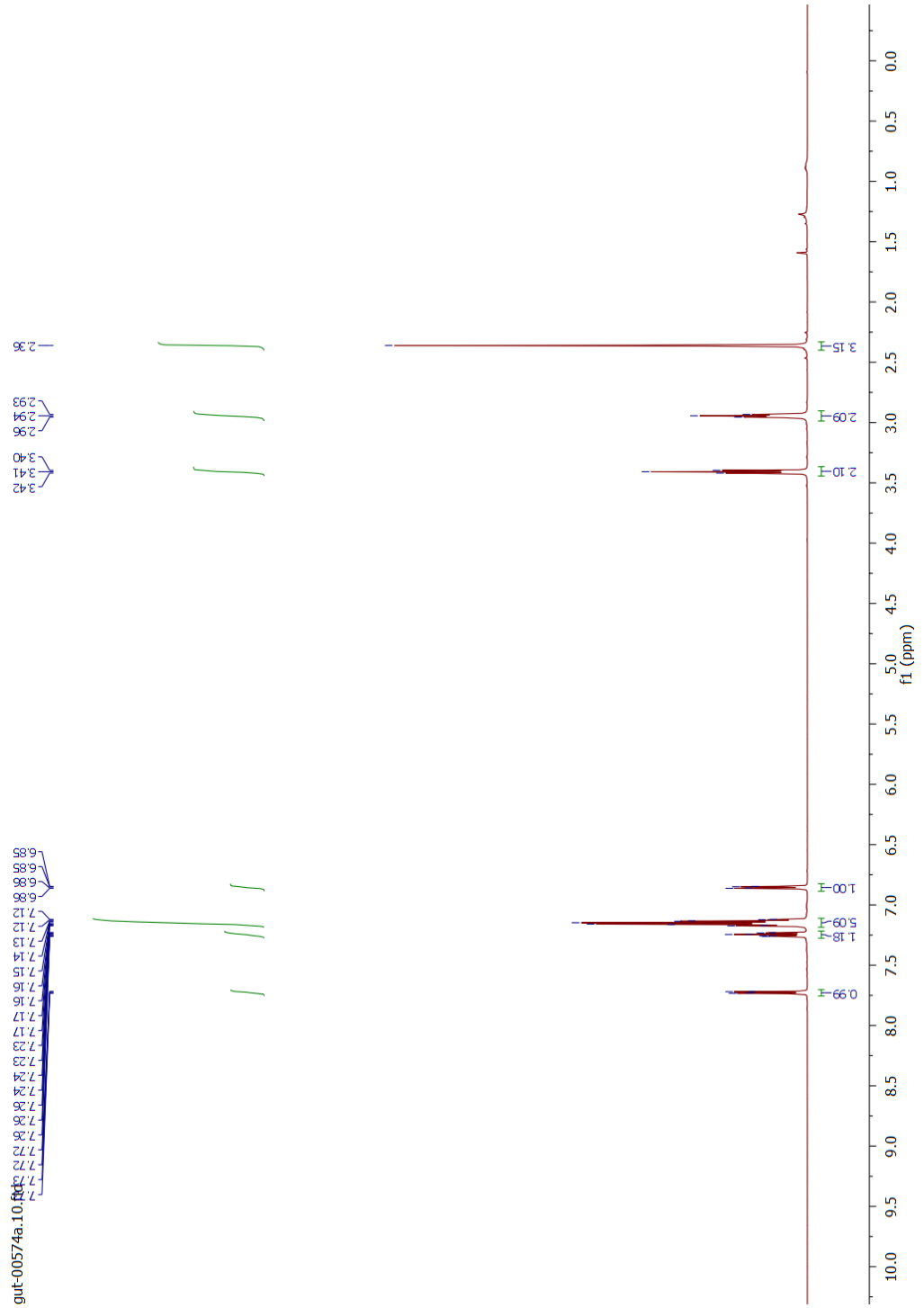


Figure S79. ^{1}H NMR of **17b** ($CDCl_3$, 600 MHz).

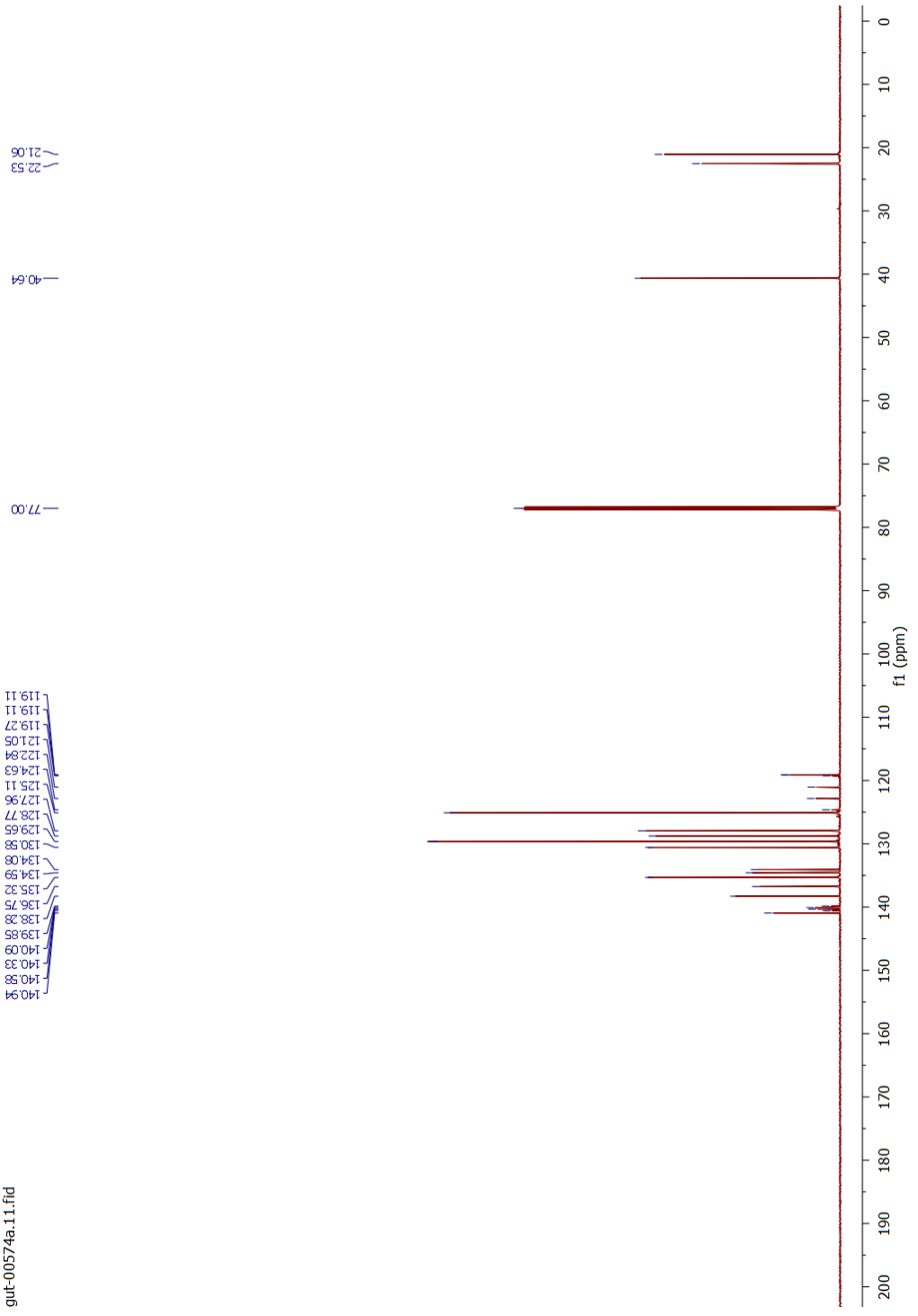
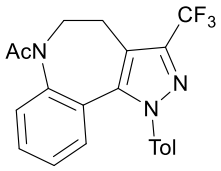


Figure S80. ^{13}C NMR of **17b** ($CDCl_3$, 151 MHz).



6-Acetyl-1-tolyl-3-trifluoromethyl-1,4,5,6-tetrahydropyrazolo-[4,3-d][1]benzazepine (17c)

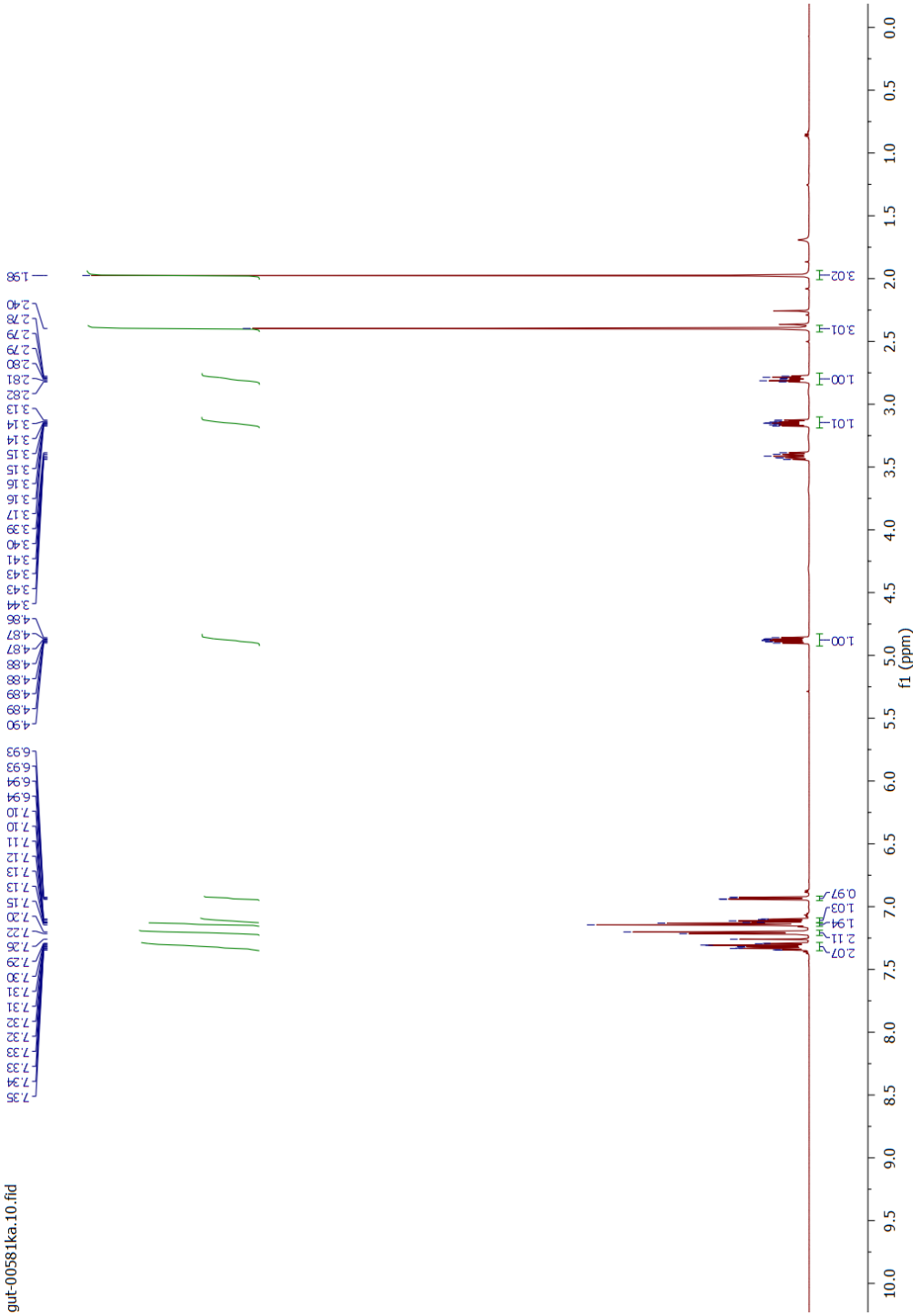


Figure S81. ^{1}H NMR of **17c** ($CDCl_3$, 600 MHz).

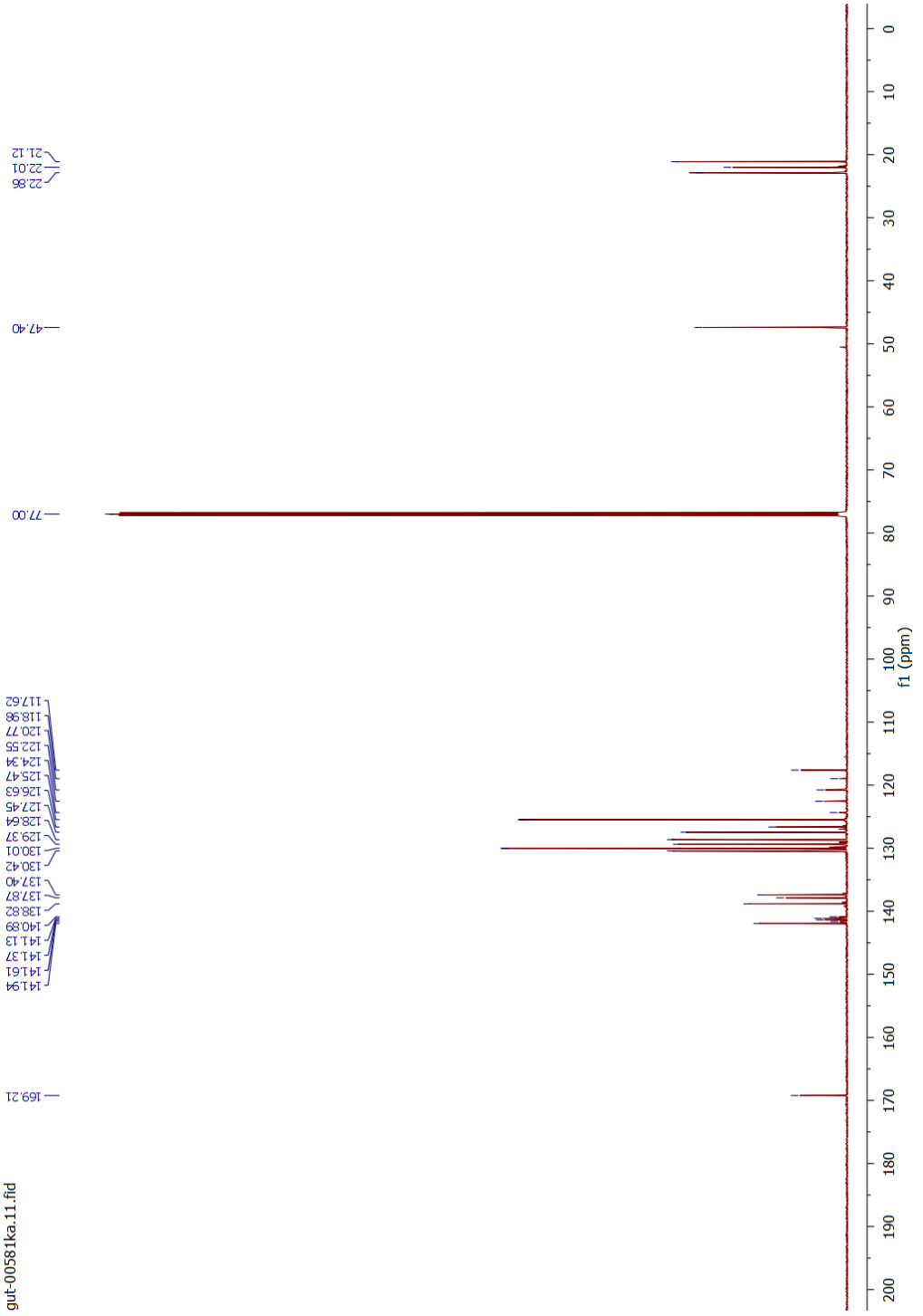


Figure S82. ^{13}C NMR of **17c** ($CDCl_3$, 151 MHz).

3. X-ray data

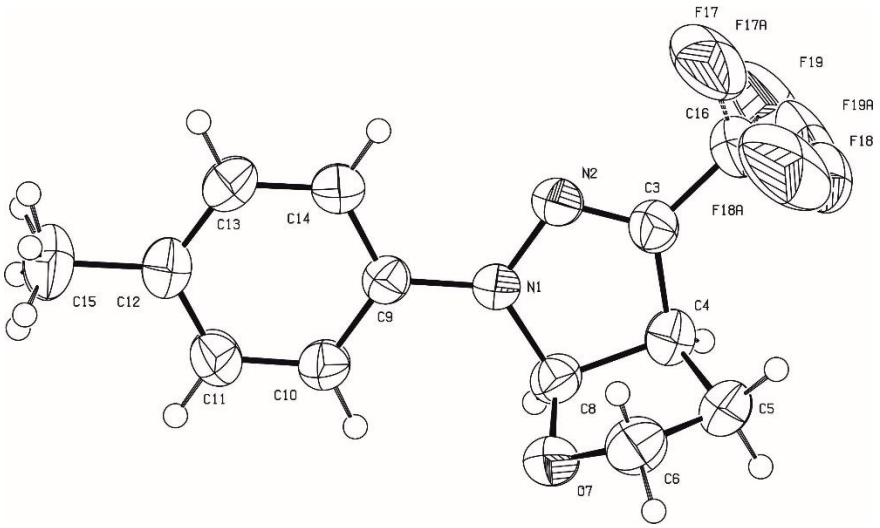


Figure S83. A view of the molecular structure of compound **8g**. Displacement ellipsoids are drawn at the 50% probability level. X-ray data collected at the ambient temperature 293 K.

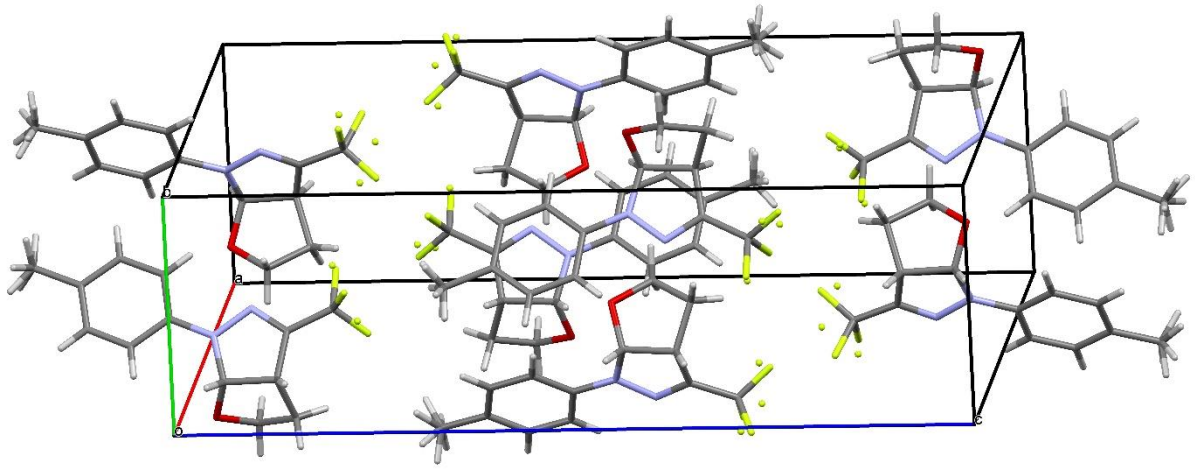


Figure S84. A view of the molecular packing in crystal of **8g**.

Table S2. Crystal data and structure refinement details for **8g**.

Empirical formula	$C_{13}H_{13}F_3N_2O$
Formula weight	270.25
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.5438(3)
b/Å	7.15478(11)
c/Å	23.2224(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2582.62(8)
Z	8
ρcalcg/cm^3	1.390
μ/mm^{-1}	1.029
F(000)	1120.0
Crystal size/mm^3	0.853 × 0.422 × 0.129
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.508 to 136.486
Index ranges	-18 ≤ h ≤ 18, -5 ≤ k ≤ 8, -27 ≤ l ≤ 27
Reflections collected	11966
Independent reflections	2371 [R_{int} = 0.0343, R_{sigma} = 0.0294]
Data/restraints/parameters	2371/30/201
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0390, wR_2 = 0.1010
Final R indexes [all data]	R_1 = 0.0454, wR_2 = 0.1049
Largest diff. peak/hole / e Å^{-3}	0.18/-0.15

Computer programs: *CrysAlis PRO* [Rigaku Oxford Diffraction (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England]; SHELXS972014 [Sheldrick, G. M. Acta Cryst., Sect. A 2008, 64, 112]; SHELXL2014 [Sheldrick, G. M. Acta Cryst., Sect. C 2015, 71, 3.]; *OLEX2 [Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst.* **42***, 339–341]* and Mercury [Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. J. Appl. Cryst. 2008, 41, 466]

Table S3. Bond distances for **8g** (Å).

F17	-C16	1.321(8)	C11	-C12	1.377(2)
F17A	-C16	1.243(6)	C12	-C13	1.381(2)
F18	-C16	1.278(5)	C12	-C15	1.511(2)
F18A	-C16	1.321(9)	C13	-C14	1.380(2)
F19	-C16	1.347(7)	F19A	-C16	1.295(7)
O7	-C6	1.4377(19)	O7	-C8	1.4038(15)
N1	-N2	1.3560(15)	N1	-C9	1.4040(15)
N1	-C8	1.4566(17)	N2	-C3	1.2837(18)
C3	-C16	1.480(2)	C3	-C4	1.4928(19)
C4	-C5	1.533(2)	C4	-C8	1.5460(18)
C5	-C6	1.495(2)	C9	-C10	1.3847(18)
C9	-C14	1.3855(18)	C10	-C11	1.382(2)

Table S4. Bond angles for **8g** (°).

C6	-O7	-C8	107.10(10)	F17A	-C16	-C3	115.0(3)
N2	-N1	-C8	113.38(9)	F18A	-C16	-F19A	103.7(6)
N2	-N1	-C9	120.53(11)	F18A	-C16	-C3	108.1(4)
C8	-N1	-C9	126.05(10)	F19A	-C16	-C3	111.5(4)
N1	-N2	-C3	108.39(11)	F17	-C16	-C3	115.2(3)
N2	-C3	-C4	114.91(12)	F18	-C16	-C3	117.3(3)
N2	-C3	-C16	119.33(13)	F19	-C16	-C3	110.9(3)
C4	-C3	-C16	125.76(12)	F17	-C16	-F18	106.3(6)
C3	-C4	-C5	114.93(12)	F17	-C16	-F19	101.3(5)
C3	-C4	-C8	100.84(11)	F18	-C16	-F19	104.1(5)
C5	-C4	-C8	103.19(10)	C4	-C5	-C6	102.38(11)
O7	-C6	-C5	104.44(13)	O7	-C8	-N1	112.72(10)
O7	-C8	-C4	107.31(10)	N1	-C8	-C4	102.44(9)
N1	-C9	-C10	120.12(11)	N1	-C9	-C14	121.02(11)
C10	-C9	-C14	118.86(12)	C9	-C10	-C11	119.89(12)
C10	-C11	-C12	122.14(13)	C11	-C12	-C13	117.12(13)
C11	-C12	-C15	121.45(14)	C13	-C12	-C15	121.42(14)
C12	-C13	-C14	122.08(13)	C9	-C14	-C13	119.92(13)
F17A	-C16	-F18A	106.1(6)	F17A	-C16	-F19A	111.7(8)

Table S5. Torsion angles for **8g** (°).

C8	-O7	-C6	-C5	-38.97(14)	N2	-C3	-C16	-F19A	-144.7(6)
C6	-O7	-C8	-N1	-88.83(12)	C4	-C3	-C16	-F17A	164.4(6)
C6	-O7	-C8	-C4	23.20(14)	C4	-C3	-C16	-F18A	-77.4(5)
C8	-N1	-N2	-C3	1.81(15)	C4	-C3	-C16	-F19A	35.9(7)
C9	-N1	-N2	-C3	-176.11(12)	C3	-C4	-C5	-C6	85.54(15)
N2	-N1	-C8	-O7	113.41(12)	C8	-C4	-C5	-C6	-23.25(15)
N2	-N1	-C8	-C4	-1.59(14)	C3	-C4	-C8	-O7	-118.11(11)
C9	-N1	-C8	-O7	-68.80(16)	C3	-C4	-C8	-N1	0.78(12)
C9	-N1	-C8	-C4	176.19(12)	C5	-C4	-C8	-O7	0.95(14)
N2	-N1	-C9	-C10	176.13(12)	C5	-C4	-C8	-N1	119.83(12)
N2	-N1	-C9	-C14	-3.95(19)	C4	-C5	-C6	-O7	37.88(14)
C8	-N1	-C9	-C10	-1.50(19)	N1	-C9	-C10	-C11	179.79(12)
C8	-N1	-C9	-C14	178.41(12)	C14	-C9	-C10	-C11	-0.1(2)
N1	-N2	-C3	-C4	-1.22(16)	N1	-C9	-C14	-C13	-179.93(12)
N1	-N2	-C3	-C16	179.31(13)	C10	-C9	-C14	-C13	0.0(2)
N2	-C3	-C4	-C5	-109.98(14)	C9	-C10	-C11	-C12	0.0(2)
N2	-C3	-C4	-C8	0.22(15)	C10	-C11	-C12	-C13	0.3(2)
C16	-C3	-C4	-C5	69.46(18)	C10	-C11	-C12	-C15	-178.82(14)
C16	-C3	-C4	-C8	179.66(14)	C11	-C12	-C13	-C14	-0.4(2)
N2	-C3	-C16	-F17A	-16.2(6)	C15	-C12	-C13	-C14	178.66(15)
N2	-C3	-C16	-F18A	102.0(5)	C12	-C13	-C14	-C9	0.3(2)

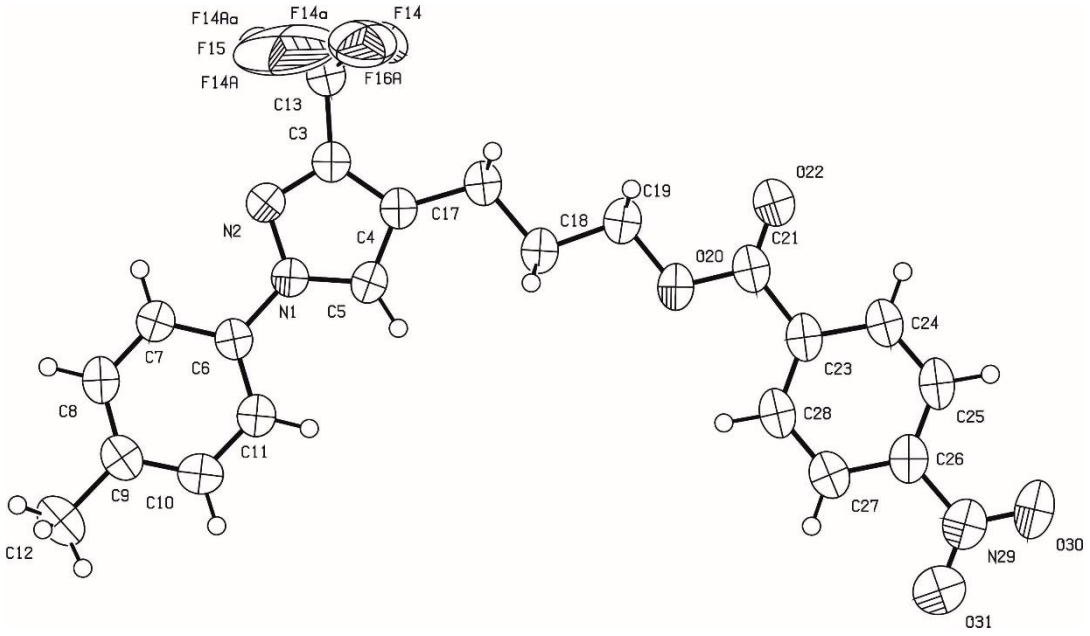


Figure S85. A view of the molecular structure of compound **9**. Displacement ellipsoids are drawn at the 50% probability level. X-ray data collected at the ambient temperature 293 K.

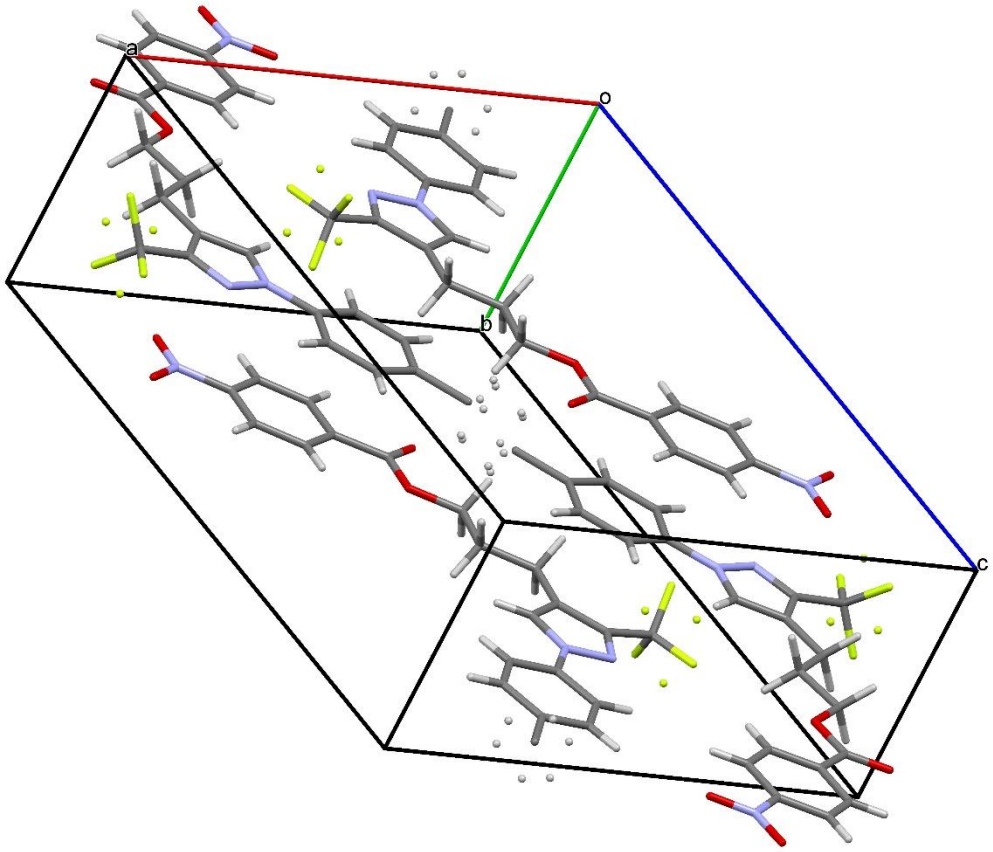


Figure S86. A view of the molecular packing in crystal of **9**.

Table S6. Crystal data and structure refinement details for pyrazole **9**.

Empirical formula	$C_{21}H_{18}N_3O_4F_3$
Formula weight	433.38
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pnma
a/Å	14.9764(4)
b/Å	6.8786(2)
c/Å	19.4161(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2000.18(9)
Z	4
ρcalcg/cm^3	1.439
μ/mm^{-1}	1.026
F(000)	896.0
Crystal size/mm^3	0.931 × 0.28 × 0.151
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.11 to 136.49
Index ranges	-17 ≤ h ≤ 15, -4 ≤ k ≤ 8, -23 ≤ l ≤ 23
Reflections collected	9487
Independent reflections	1989 [R_{int} = 0.0252, R_{sigma} = 0.0199]
Data/restraints/parameters	1989/0/202
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.1106
Final R indexes [all data]	R_1 = 0.0468, wR_2 = 0.1151
Largest diff. peak/hole / e Å^{-3}	0.17/-0.14

Computer programs: *CrysAlis PRO* [Rigaku Oxford Diffraction (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England]; SHELXS972014 [Sheldrick, G. M. Acta Cryst., Sect. A 2008, 64, 112]; SHELXL2014 [Sheldrick, G. M. Acta Cryst., Sect. C 2015, 71, 3.]; *OLEX2 [Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst.* **42***, 339–341]* and Mercury [Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. J. Appl. Cryst. 2008, 41, 466]

Table S7. Bond distances for **9** (Å).

F14	-C13	1.326(3)	C23	-C28	1.378(3)
F14A	-C13	1.255(13)	C23	-C24	1.395(3)
F15	-C13	1.286(3)	C24	-C25	1.374(3)
F16A	-C13	1.150(12)	C25	-C26	1.372(3)
O20	-C19	1.450(3)	C26	-C27	1.385(3)
O20	-C21	1.328(2)	C27	-C28	1.382(3)
O22	-C21	1.198(3)	O30	-N29	1.218(3)
O31	-N29	1.211(3)	N1	-C6	1.429(2)
N1	-N2	1.347(2)	N1	-C5	1.358(2)
N2	-C3	1.322(2)	N29	-C26	1.472(3)
C3	-C13	1.484(3)	C3	-C4	1.400(3)
C4	-C5	1.363(3)	C4	-C17	1.504(3)
C6	-C7	1.370(3)	C6	-C11	1.366(3)
C7	-C8	1.377(3)	C8	-C9	1.378(3)
C9	-C12	1.505(3)	C9	-C10	1.374(3)
C10	-C11	1.382(3)	C17	-C18	1.508(3)
C18	-C19	1.502(3)	C21	-C23	1.483(3)

Table S8. Bond angles for **9** (°).

C5	-N1	-C6	128.77(16)	F16A	-C13	-C3	115.8(6)
N1	-N2	-C3	103.91(15)	F14_a	-C13	-C3	112.16(15)
O30	-N29	-O31	123.0(2)	F14A_a	-C13	-C3	112.1(4)
O30	-N29	-C26	118.5(2)	F14A	-C13	-F16A	107.6(7)
O31	-N29	-C26	118.51(19)	F14A	-C13	-F14A_a	100.2(9)
N2	-C3	-C4	113.46(17)	F14A_a	-C13	-F16A	107.6(7)
N2	-C3	-C13	118.34(17)	C4	-C17	-C18	113.67(18)
C4	-C3	-C13	128.20(18)	C17	-C18	-C19	110.38(18)
C3	-C4	-C5	102.99(17)	O20	-C19	-C18	109.15(17)
C3	-C4	-C17	128.82(18)	O20	-C21	-O22	122.5(2)
C5	-C4	-C17	128.19(18)	O20	-C21	-C23	114.20(19)
N1	-C5	-C4	108.14(17)	O22	-C21	-C23	123.32(19)
N1	-C6	-C7	119.38(18)	C21	-C23	-C24	117.49(19)
N1	-C6	-C11	121.23(17)	C21	-C23	-C28	122.79(18)
C7	-C6	-C11	119.39(19)	C24	-C23	-C28	119.72(19)
C6	-C7	-C8	120.1(2)	C23	-C24	-C25	120.4(2)
C7	-C8	-C9	121.9(2)	C24	-C25	-C26	118.87(18)
C8	-C9	-C10	116.8(2)	N29	-C26	-C25	119.03(18)
C8	-C9	-C12	120.81(19)	N29	-C26	-C27	119.0(2)
C10	-C9	-C12	122.4(2)	C25	-C26	-C27	121.9(2)
C9	-C10	-C11	122.1(2)	C26	-C27	-C28	118.7(2)
C6	-C11	-C10	119.76(18)	C23	-C28	-C27	120.36(19)
F14	-C13	-F15	106.94(18)	F14	-C13	-C3	112.16(15)
F14	-C13	-F14_a	103.1(2)				

a = x,1/2-y,z

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