Supporting information

Asymmetric Synthesis of Chiral Trifluoromethylated Heliotridane via Highly Catalytic Asymmetric Friedel - Crafts Alkylation with β-Trifluoromethylated Acrylates and Pyrroles

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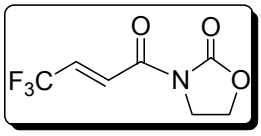
General Methods

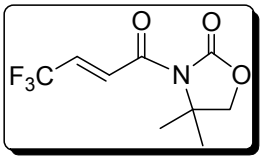
All reactions were performed in oven-dried glassware under a nitrogen atmosphere, except where noted. Chemicals and solvents were purchased from commercial suppliers and used as received, excepting as follows. Dichloromethane, THF, ether, and toluene were dried by passing through an activated column. All reactions were monitored by TLC, or ^{19}F NMR. TLC analysis was performed by illumination with a UV lamp (254 nm), staining with I_2, or PMA [phosphomolybdic acid (5 g) in ethanol (100 ml)] and heating. All flash chromatography was packed with silica-gel (60N spherical neutral size 63-210

μm) as the stationary phase. ^{1}H NMR (600 MHz) spectra were recorded on a Bruker Avance 600 instrument in $CDCl_3$ (7.26), or CD_2Cl_2 (5.24), and chemical shifts were measured relative to residual solvent peak. Chemical shifts (δ) are expressed in ppm downfield from internal TMS. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, m = multiplet, br = broad), coupling constant(s) and integration. ^{13}C NMR (150.9 MHz) spectra were recorded on a Bruker Avance 600 instrument. Chemical shifts are reported in parts per million (ppm) down field from TMS, using the middle resonance of $CDCl_3$ (77.23), or CD_2Cl_2 (53.73) as an internal standard. ^{19}F NMR (188 MHz) was recorded on a Varian Mercury 200 instrument using $CFCl_3$ (0) as an internal standard. HPLC analysis were performed on a JASCO U-2080 plus using 4.6 x 250 mm CHIRALPAK OD-H or CHIRALCEL AD-H column. Optical rotations were measured on a HORIBA SEPA-300. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A or SHIMADZU LCMS-2010EV. High resolution mass spectra (HRMS) (EI+) were obtained from the Mass Spectrometry Laboratory, Nagoya Institute of Technology, Nagoya.

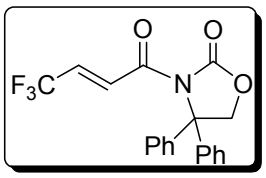
Synthesis of β–CF_3 Acrylates (1a, 1b, 1c, 1d)



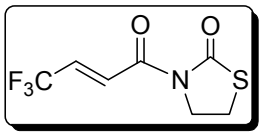
3-[(E)-4,4,4-Trifluorobut-2-enoyl]oxazolidin-2-one (1a): The known compound **1a** was synthesized according to the reported procedure.[1] ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.91 (dq, *J* = 1.8 Hz, 15.6 Hz, 1H), 6.93-6.86 (m, 1H), 4.50 (dt, *J* = 0.6 Hz, 7.8 Hz, 2H), 4.12 (dt, *J* = 0.6 Hz, 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 600 MHz): δ = 163.0, 153.4, 132.3 (q, *J* = 34.7 Hz), 127.6 (q, *J* = 6.2 Hz), 122.5 (q, *J* = 270.3 Hz), 62.8, 42.9; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −65.3 (s, 3F);



4,4-dimethyl-3-[(E)-4,4,4-Trifluorobut-2-enoyl]oxazolidin-2-one (1b): compound **1b** was synthesized according to the reported procedure. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.73 (dt, *J* = 1.8 Hz, 15.6 Hz, 1H), 6.83-6.77 (m, 1H), 4.09 (d, *J* = 1.2 Hz, 2H), 3.38 (d, *J* = 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 600 MHz): δ = 163.4, 153.7, 130.8 (q, *J* = 35.5 Hz), 129.4 (q, *J* = 6.0 Hz), 122.3 (q, *J* = 270.1 Hz), 75.6, 60.8, 24.5; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −65.1 (s, 3F); IR (KBr): 1765.5, 1693.2, 1671.0, 1399.1, 1382.7, 1354.7, 1320.7, 1268.9, 1181.2, 1133.9, 1099.2, 1031.7, 764.6, 628.6 cm^{-1}; mp = 80-81 ºC; MS (ESI, *m/z*): 237 (M^+); HRMS calcd. for $C_9H_{10}F_3NO_3^+$ 237.0613 found 237.0616.



4,4-diphenyl-3-[(E)-4,4,4-Trifluorobut-2-enoyl]oxazolidin-2-one (1c): compound **1c** was synthesized according to the reported procedure. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.83 (dd, *J* = 1.2 Hz, 15.6 Hz, 1H), 7.42-7.33 (m, 10H), 6.88-6.74 (m, 1H), 4.80 (s, 2H); ^{13}C NMR ($CDCl_3$, 600 MHz): δ = 162.4, 153.5, 138.3, 131.8 (q, *J* = 35.6 Hz), 128.6, 127.7, 122.1 (q, *J* = 270.3 Hz), 78.6, 71.5; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −65.2 (d, 6.6 Hz, 3F); IR (KBr): 1780.9, 1705.7, 1382.7, 1337.4, 1307.5, 1277.6, 1133.9, 1094.4, 1049.1, 961.3, 760.8, 698.1, 638.3 cm^{-1}; mp = 105-107 ºC; MS (EI, *m/z*): 361 (M^+); HRMS calcd. for $C_{19}H_{14}F_3NO_3^+$ 361.0926 found 361.0902.

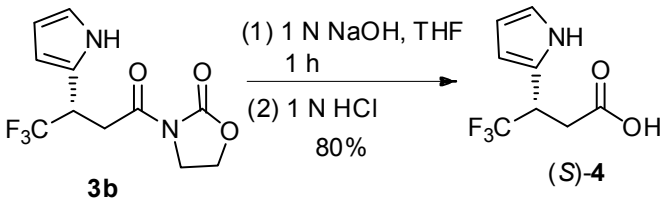


3-[(E)-4,4,4-Trifluorobut-2-enoyl]thiazolidin-2-one (1d): compound **1d** was synthesized according to the reported procedure. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.70-7.67 (m, 1H), 6.86-6.80 (m, 1H), 4.25 (dt, *J* = 1.2 Hz, 7.2 Hz, 2H), 3.38 (dt, *J* = 1.2 Hz, 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 600 MHz): δ = 173.0, 162.5, 131.3 (q, *J* = 35.6 Hz), 128.8 (q, *J* = 6.2 Hz), 120.4 (q, *J* = 270.3 Hz), 46.9, 25.4; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −65.2 (s, 3F); IR (KBr): 1683.5, 1471.4, 1447.3, 1366.3, 1309.4, 1287.2, 1271.8, 1230.3, 1187.9, 1133.9, 1065.5, 1018.2, 966.2, 933.4, 874.5, 768.5, 701.9, 674.0, 652.8, 626.8 cm^{-1}; mp = 59-60 ºC; MS (EI, *m/z*): 225 (M^+); HRMS calcd. for $C_7H_6F_3NO_2S^+$ 225.0071 found 225.0074.

General Catalytic Procedure for the Friedel-Crafts Reactions

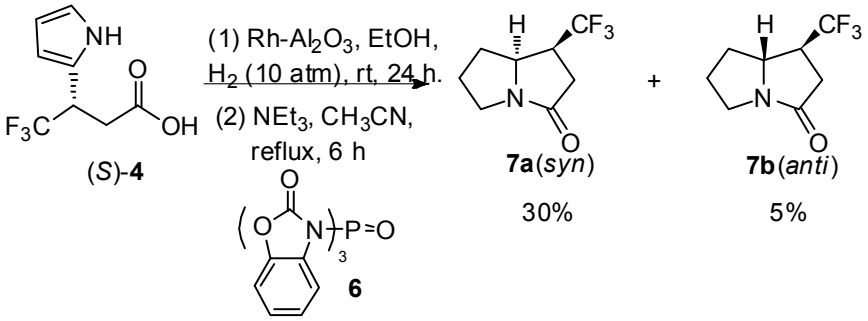
To an oven dried 10 mL test tube was added appropriate Lewis acid and 1.1 equiv of (*R,R*)-Ph–dbfox ligand. At N_2 atmosphere, dry CH_2Cl_2 was introduced, followed by stirring at RT for 1 h. 4 Å MS and β–CF_3 acrylates were added at RT, then the solution of pyrroles in CH_2Cl_2 was injected by syringe at the reaction temperature. While some Friedel-Crafts products have the same polarity as the starting material on TLC, the reaction would be monitored by ^{19}F NMR. After the starting material disappeared, the residue was directly subjected to the silica-gel column chromatography to afford the title product.

Synthesis of Optically Active Trifluoromethylated Heliotridane

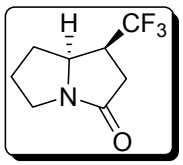


3b (*S*)-**4**

To a solution of (*S*)-**3b** (98% ee, 110.0mg, 0.40 mmol) in THF was added 1 N NaOH (aq., 0.80 mL, 0.80 mmol). After stirring at RT for 1h, 1 N HCl (aq.) was slowly added to adjust the PH value of the reaction mixture to 1-2. Compound (*S*)-**4** (66.2 mg, 80%) was isolated as a solid by flash column chromatography using 3:1 petroleum ether:ethyl acetate as eluent. $[\alpha]_D^{25}$ = +17.3 (*c* = 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.26 (br s, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 6.18-6.16 (m, 2H), 3.96-3.91 (m, 1H), 3.01 (dd, *J* = 4.2 Hz, 10.8 Hz, 1H), 2.88 (dd, *J* = 9.6 Hz, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ = 176.1, 125.8 (q, *J* = 279.5 Hz), 123.2, 118.8, 108.9, 108.1, 39.7 (q, *J* = 29.3 Hz), 33.8; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −70.7 (s, 3F); IR (KBr): 3470.3, 3119.3, 1719.2, 1660.4, 1560.1, 1418.4, 1363.4, 1293.0, 1272.8, 1181.2, 1164.8, 1035.6, 993.2, 930.5, 859.1, 810.9, 680.8 cm^{-1}; mp = 70-71 ºC; MS (ESI, *m/z*): 206.050 ($M-H^-$); HRMS calcd. $C_8H_8F_3NO_2^+$ for 207.0507 found 207.0513.

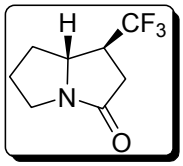


To a 10 mL test tube was added (*S*)-**4** (66.0 mg, 0.40 mmol), 5% of Rh-Al_2O_3 (8 mg), and 4 mL EtOH. The resulting mixture was put into an autoclave, and purged with H_2 (10 atm). After stirring at RT for 24 h, the catalyst was filtrated through celite, then the solvent was evaporated *in vacuo* to provide the 2-pyrrolidine carboxylic acid as white solid.[2] Without further purification, the compound obtained was heated under reflux with the phosphine oxide **6** (186 mg, 0.41 mmol) and triethyl amine (0.2 mL, 1.43 mmol) in 10 mL acetonitrile. After 6 h, the resulting solution was concentrated, then subjected to column chromatography using ether as eluent. The faster running fractions was determined as **7a** as a colorless oil (23.0 mg, 30%), while the lower fractions was as **7b** a colorless oil (4.0 mg, 5%).[3] The ratio and stereochemistry of the two isomers were identified from ^{19}F NMR spectrum. The value of −67.9 ppm in lower magnetic field due to steric deshielding effect indicates a *cis* arrangement of hydrogen and CF_3 group and thus the structure **7b** for the minor isomer.[4] Hence, the chemical shift value of −71.1 ppm belongs to the major *syn* isomer.

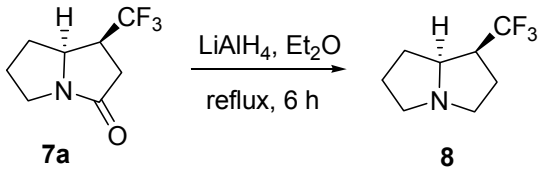


(*syn*)-1-Trifluoromethyl-hexahydropyrrolizin-3-one (7a): $[\alpha]_D^{25}$ = +26.0 (*c* = 0.35, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.95 (dt, *J* = 6.6 Hz, 9.0 Hz, 1H, 5-H), 3.59 (dt, *J* = 8.4 Hz, 11.4 Hz, 1H, 8-H), 3.13-3.09 (m, 1H, 8'-H), 2.91 (dd, *J* = 10.2 Hz, 16.2 Hz, 1H, 3-H), 2.87-2.79 (m, 1H, 4-H), 2.67 (dd, *J* = 9.0 Hz, 16.2 Hz, 1H, 3'-H),

2.21-2.15 (m, 2H, 6-H, 7-H), 2.12-2.04 (m, 1H, 7'-H), 1.50-1.43 (m, 1H, 6'-H); ^{13}C NMR ($CDCl_3$, 600 MHz): δ = 171.1, 126.1 (q, *J* = 276.6 Hz), 60.9 (d, *J* = 3.2 Hz), 44.8 (q, *J* = 29.1 Hz), 41.3, 35.2 (d, *J* = 2.26 Hz), 31.6, 26.6; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −71.1 (d, *J* = 6.6 Hz, 3F); IR (neat): 2976.6, 2884.9, 1782.9, 1702.8, 1428.0, 1343.2, 1270.9, 1166.7, 1123.3, 1085.7, 688.5 cm^{-1}; MS (ESI, *m/z*): 216.100 (M+Na$^+$); HRMS calcd. $C_8H_{10}F_3NO$ 193.0714 found 193.0756.

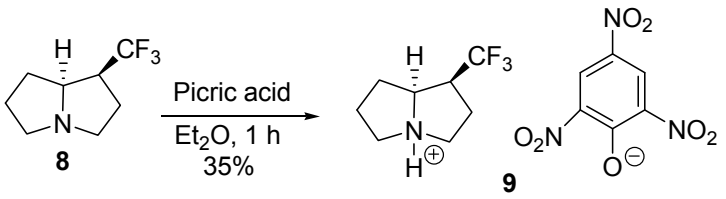


(*anti*)-1-Trifluoromethyl-hexahydropyrrolizin-3-one (7b): $[\alpha]_D^{25}$ = +24.0 (*c* = 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 4.04-4.00 (m, 1H, 5-H), 3.57 (dt, *J* = 8.4 Hz, 11.4 Hz, 1H, 8-H), 3.23-3.15 (m, 1H, 4-H), 3.14-3.10 (m, 1H, 8'-H), 2.93 (dd, *J* = 10.2 Hz, 17.4 Hz, 1H, 3-H), 2.64 (dd, *J* = 4.8 Hz, 17.4 Hz, 1H, 3'-H), 2.22-2.17 (m, 1H, 7-H), 2.06-1.98 (m, 1H, 7'-H), 1.96-1.92 (m, 1H, 6-H), 1.75-1.67 (m, 1H, 6'-H); ^{13}C NMR ($CDCl_3$, 600 MHz): δ = 172.0, 126.5 (q, *J* = 278.5 Hz), 61.1, 41.3, 38.3 (q, *J* = 28.5 Hz), 33.9, 29.7, 26.4; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –67.8 (d, *J* = 6.6 Hz, 3F); IR (neat): 2926.5, 1779.0, 1684.4, 1484.0, 1428.0, 1392.4, 1294.0, 167.0, 1178.3, 1150.3, 1126.2, 1103.1, 760.8 cm^{-1}; MS (ESI, *m/z*): 216.100 (M+Na$^+$); HRMS calcd. $C_8H_{10}F_3NO$ 193.0714 found 193.0698.



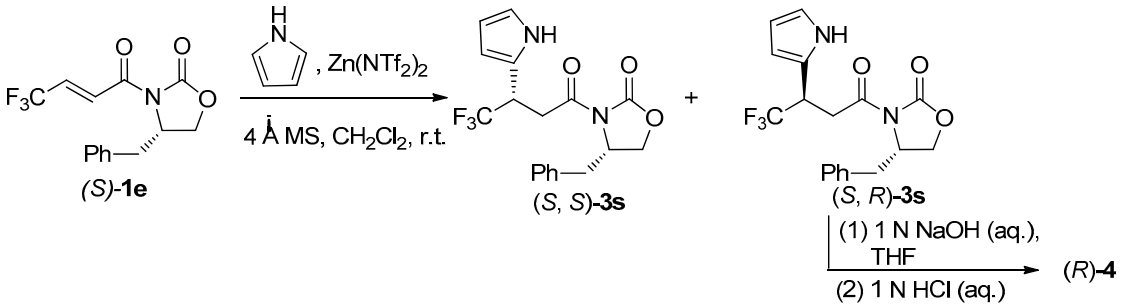
7a **8**

At N_2 atmosphere, to a solution of **7a** (20.0 mg, 0.104 mmol) in ether (2.0 mL) was added $LiAlH_4$ (15.8 mg, 0.416 mmol) directly at 0 °C. After stirring at 35 °C for 6 h, the solution was cooled to RT before $Na_2SO_4 \cdot 10H_2O$ (135.0 mg, 0.416 mmol) was slowly added to the reaction mixture. The resulting solution was stirred at RT for overnight. The solvent was removed by a steady stream of N_2 to obtain slightly yellow oil **8** (10.0 mg, 54% yield).[5] $[\alpha]_D^{25}$ = +20.3 (*c* = 0.3, Et_2O); ^{1}H NMR (CD_2Cl_2, 600 MHz): δ = ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.41-3.38 (m, 1H, 5-H), 3.04-3.01 (m, 1H, 2-H), 2.83 (dt, *J* = 6.6 Hz, 10.2 Hz, 1H, 8-H), 2.54 (dt, *J* = 6.6 Hz, 9.6 Hz, 1H, 2'-H), 2.46 (dt, *J* = 6.6 Hz, 10.2 Hz, 1H, 8'-H), 2.35-2.29 (m, 1H, 4-H), 2.06-2.00 (m, 1H, 3-H), 1.96-1.85 (m, 2H, 6-H, 3'-H), 1.80-1.73 (m, 1H, 7-H), 1.72-1.65 (m, 1H, 7'-H), 1.54-1.49 (m, 1H, 6'-H); ^{13}C NMR (CD_2Cl_2, 600 MHz): δ = 128.1 (q, *J* = 277.2 Hz), 64.8(d, *J* = 2.3 Hz), 54.7, 54.1, 49.6 (q, *J* = 26.1 Hz), 32.2, 27.7 (d, *J* = 2.1 Hz), 26.1; ^{19}F NMR (CD_2Cl_2, 188 MHz): δ = −70.1 (d, *J* = 9.2 Hz, 3F); MS (EI, *m/z*): 179 (M$^+$); HRMS calcd. $C_8H_{12}F_3N$ for 179.0922 found 179.0941.



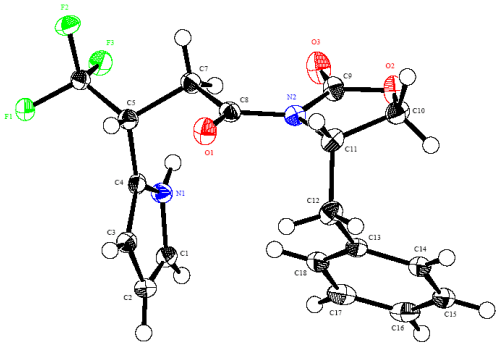
To a solution of **8** (10.0 mg, 0.056 mmol) in 1 mL ether was added the solution of Picric acid (20.0 mg, 0.056 mmol) in 1 mL ether. After stirring for 1 h at RT, the precipitate was filtrated as the target compound **9** (8.0 mg, 35% yield). $[\alpha]_D^{25} = -5.8$ (*c* = 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.88 (s, 2H, Ar-H), 4.50-4.47 (m, 1H, 5-H), 4.15-4.12 (m, 1H, 2-H), 3.80 (dt, *J* = 7.2 Hz, 12.0 Hz, 1H, 8-H), 3.16-3.12 (m, 1H, 8'-H), 3.06 (dt, *J* = 6.0 Hz, 10.8 Hz, 1H, 2-H), 2.81-2.75 (m, 1H, 4-H), 2.54-2.46 (m, 2H, 6-H, 3-H), 2.38-2.32 (m, 1H, 7-H), 2.21-2.14 (m, 1H, 7'-H), 2.05-2.00 (m, 1H, 6'-H); ^{13}C NMR ($CDCl_3$, 600 MHz): δ = 162.3, 141.6, 128.6, 126.7, 125.2 (q, *J* = 277.7 Hz), 67.0 (d, *J* = 2.4 Hz), 55.6, 54.9, 48.7 (q, *J* = 29.5 Hz), 30.8, 26.7, 25.0; ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −70.0 (d, *J* = 6.6 Hz, 3F); IR (KBr): 1716.3, 1637.3, 1557.2, 1489.7, 1434.8, 1329.7, 1276.7, 1162.9, 111.8 cm^{-1}; mp = 181-183 ºC; MS (ESI, *m/z*): 212.200 ($M+Na^+$); Anal. Calcd. (%) for $C_{14}H_{15}F_3N_4O_7$ C, 41.18; H, 3.70; N, 13.72; found C, 41.22; H, 3.90; N, 13.60.

Absolute Stereochemistry Determination



At N_2 atmosphere, to a mixture of (4*S*)-benzyl-3-[(*E*)-4,4,4-Trifluorobut-2-enoyl]-oxazolidin-2-one (*S*)-**1e** (15.0 mg, 0.050 mmol), 4 Å MS (15.0 mg), and 20 mol % of catalyst $Zn(NTf_2)_2$ (6.2 mg, 0.010 mmol) in 0.5 mL CH_2Cl_2 was added pyrrole (17.0 mg, 0.250 mmol). The mixture was stirred at rt for 2 h, then passed through a plug of silica gel using 4:1 petroleum ether:ethyl acetate to afford a 2:1 mixture of diastereoisomers (13.40 mg, 73%). One diastereoisomer was separated as a white solid, which was determined as (*S, R*)-**3s** by single-crystal x-ray analysis. $[\alpha]_D^{25} = +81.5$ (*c* 0.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz) δ 8.46 (br s, 1H), 7.29-7.24 (m, 3H), 7.01 (d, 7.2 Hz, 2H), 6.77-6.76 (m, 1H), 6.22-6.17 (m, 2H), 4.67-4.63 (m, 1H), 4.23-4.15 (m, 3H), 3.85 (dd, 10.2 Hz, 17.4 Hz, 1H), 3.31 (dd, 4.2 Hz, 17.4 Hz, 1H), 3.02 (dd, 3.0 Hz, 13.2 Hz, 1H), 2.66 (dd, 9.0 Hz, 13.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 169.8, 153.4, 134.7, 129.4, 129.0, 127.4, 126.1 (q, 279.5 Hz), 123.6, 118.6, 118.6, 108.8, 108.5, 66.2 (d, 3.6

Hz), 39.5 (q, 29.0 Hz), 37.4, 35.1; ^{19}F NMR ($CDCl_3$, 188 MHz) δ -70.1 (d, 9.2 Hz, 3F); IR (KBr) 3387.4, 1776.1, 1692.2, 1441.5, 1401.0, 1358.6, 1302.7, 1262.2, 1218.8, 1195.7, 1163.8, 1153.2, 1132.0, 1101.2, 726.1 cm^{-1}; mp = 150-151 ºC; MS (ESI, *m/z*) 388.850 ($M+Na^+$); HRMS calcd. for $C_{18}H_{17}F_3N_2O_3^+$ 366.1191 found 366.1200.



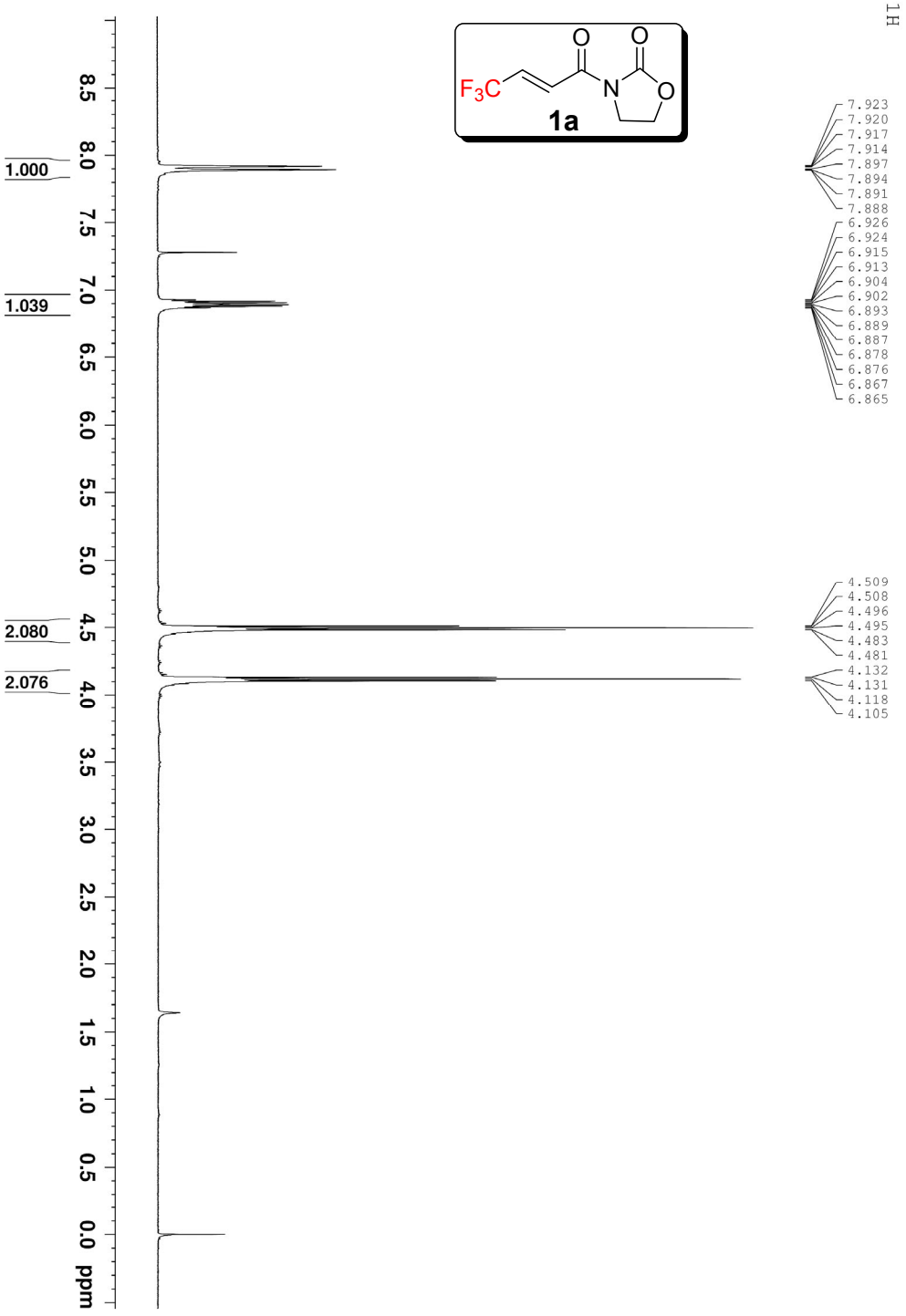
CIF file of (*S, R*)-**3s** is available as **CCDC 758056**.

To a solution of (*S, R*)-**3s** (11.0mg, 0.030 mmol) in THF was added 1 N NaOH (aq., 0.10 mL, 0.10 mmol). After stirring at rt for 1 h, 1N HCl (aq.) was slowly added to adjust the PH value of the reaction mixture to 1-2. Compound (*R*)-**4** (5.0 mg, 83%, $[\alpha]_D^{25}$ = -14.5 (*c* 0.05, $CHCl_3$)) was isolated by flash column chromatography, which has the opposite optical rotation as compound **4** transformed from **3b**. Thus the absolute stereochemistry of compound **3b** was determined as *S*.

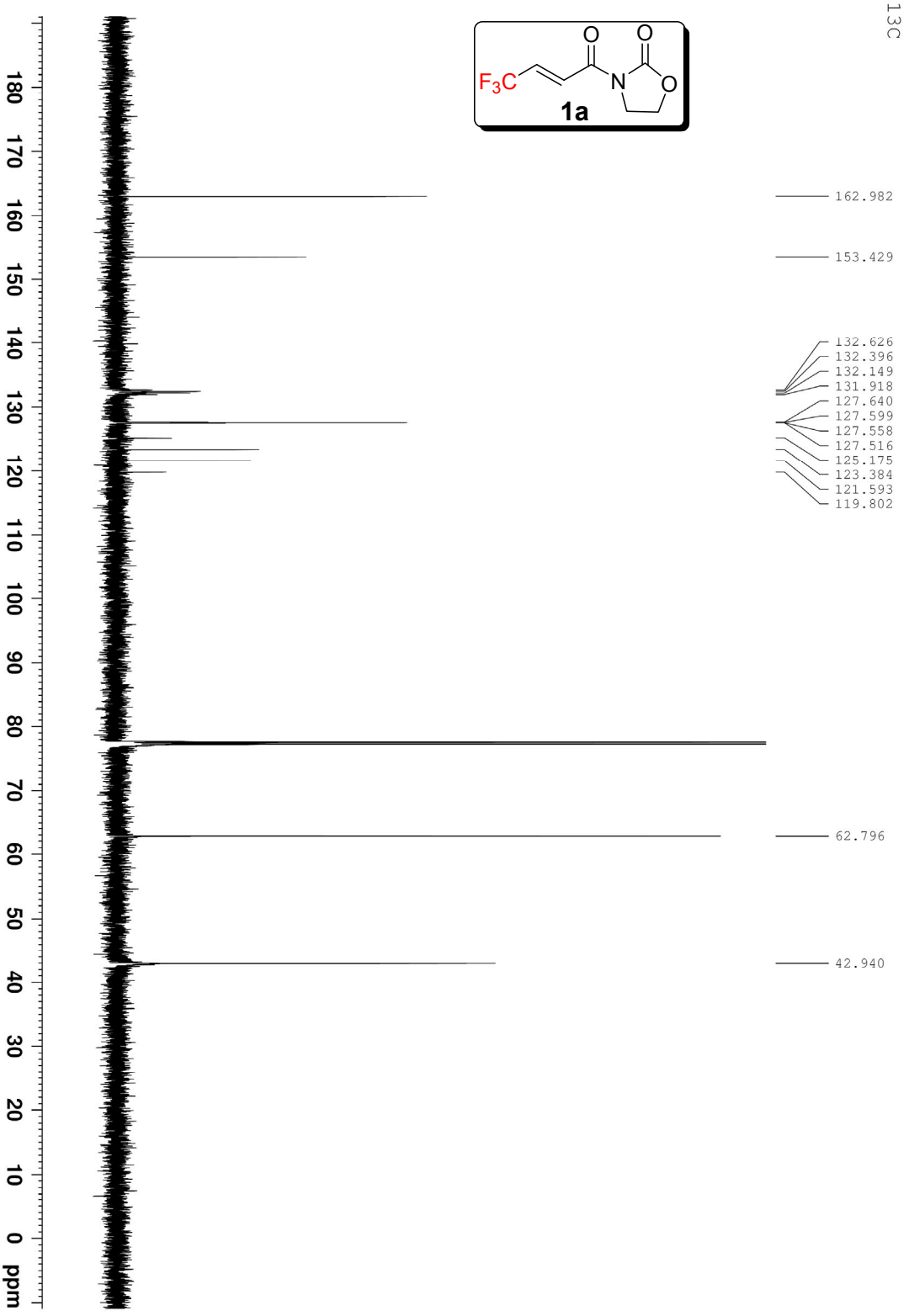
References

(1) K. Tamura, T. Yamazaki, T. Kitazume, T. Kubota, *J Fluorine Chem.* 2005, **126**, 918.
(2) D. A. Evans, K. R. Fandrick, *Org. Lett.* 2006, **8**, 2249.
(3) T. L. Gilchrist, A. Lemos, C. J. Ottaway, *J. Chem. Soc. Perkin Trans 1.* 1997, 3005.
(4) R. William, JR. Dolbier, *Guide to Fluorine NMR for Organic Chemistry*; WILEY: New Jersey, 2009; pp 1-256.
(5) P. G. Andenson, J. E. Backvalll, *J. Am. Chem. Soc*. 1992**, 114**, 8698.

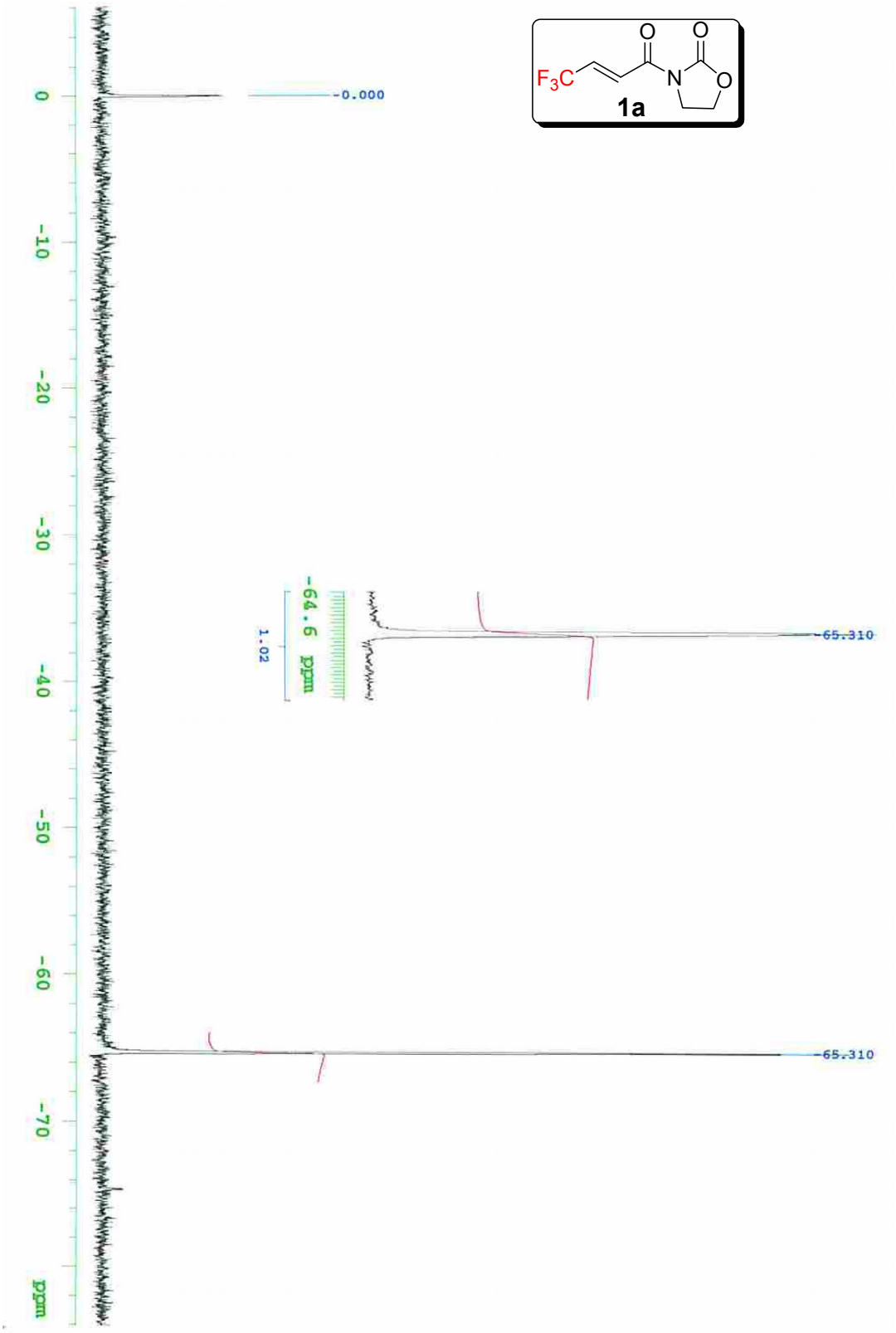
^{1}H, ^{13}C, and ^{19}F NMR Spectra



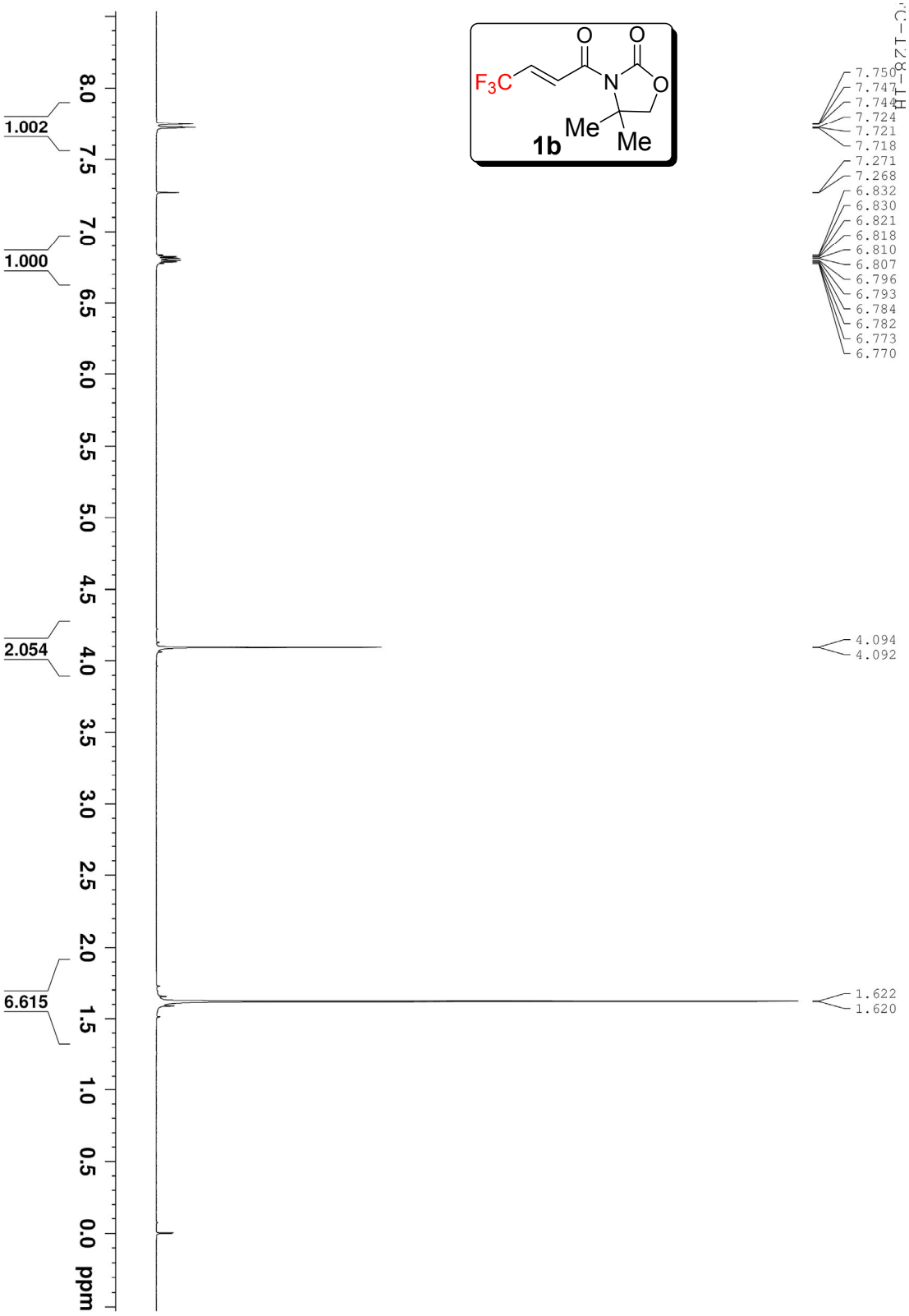
^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 150.9 MHz)



^{19}F NMR ($CDCl_3$, 188 MHz)



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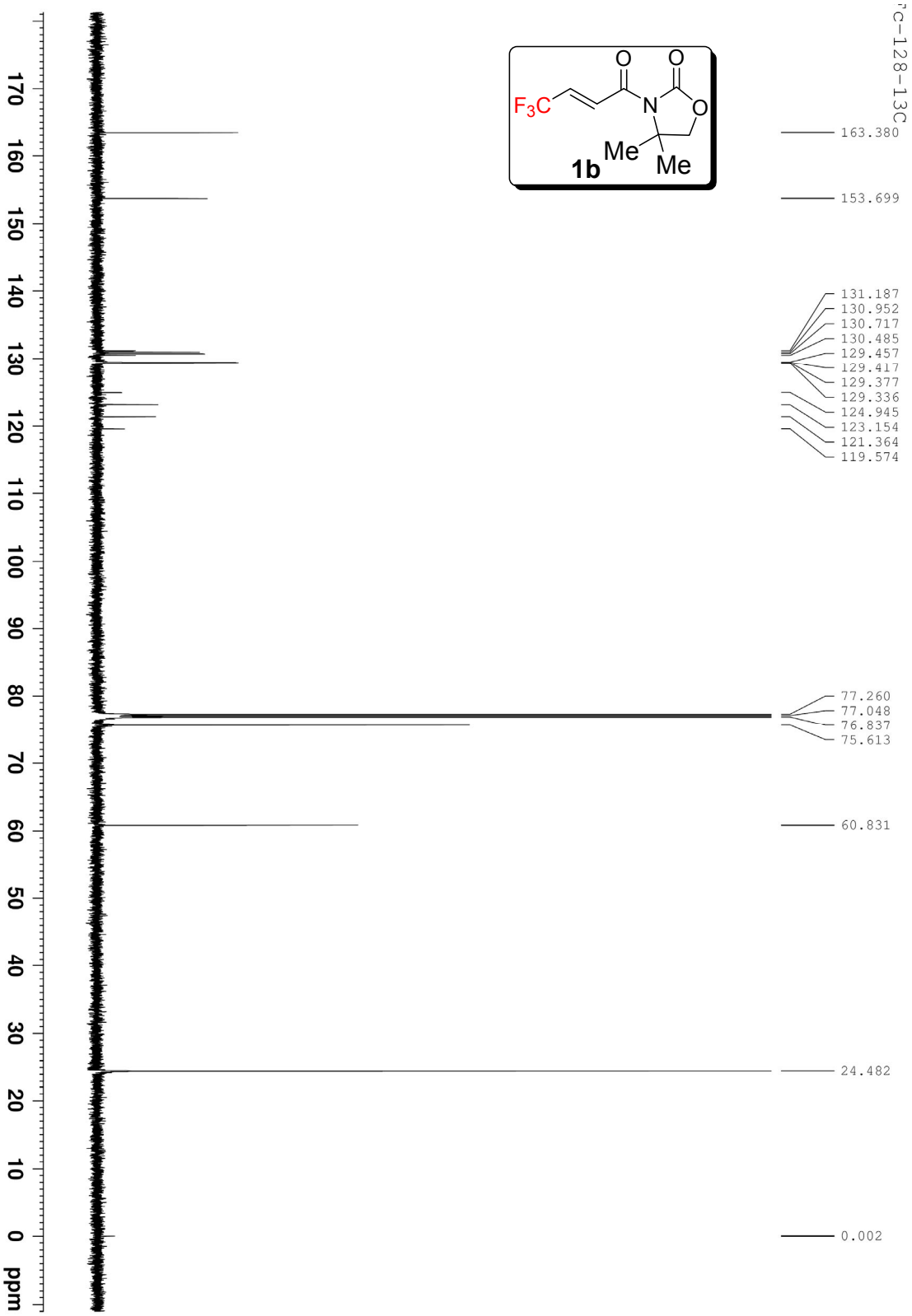

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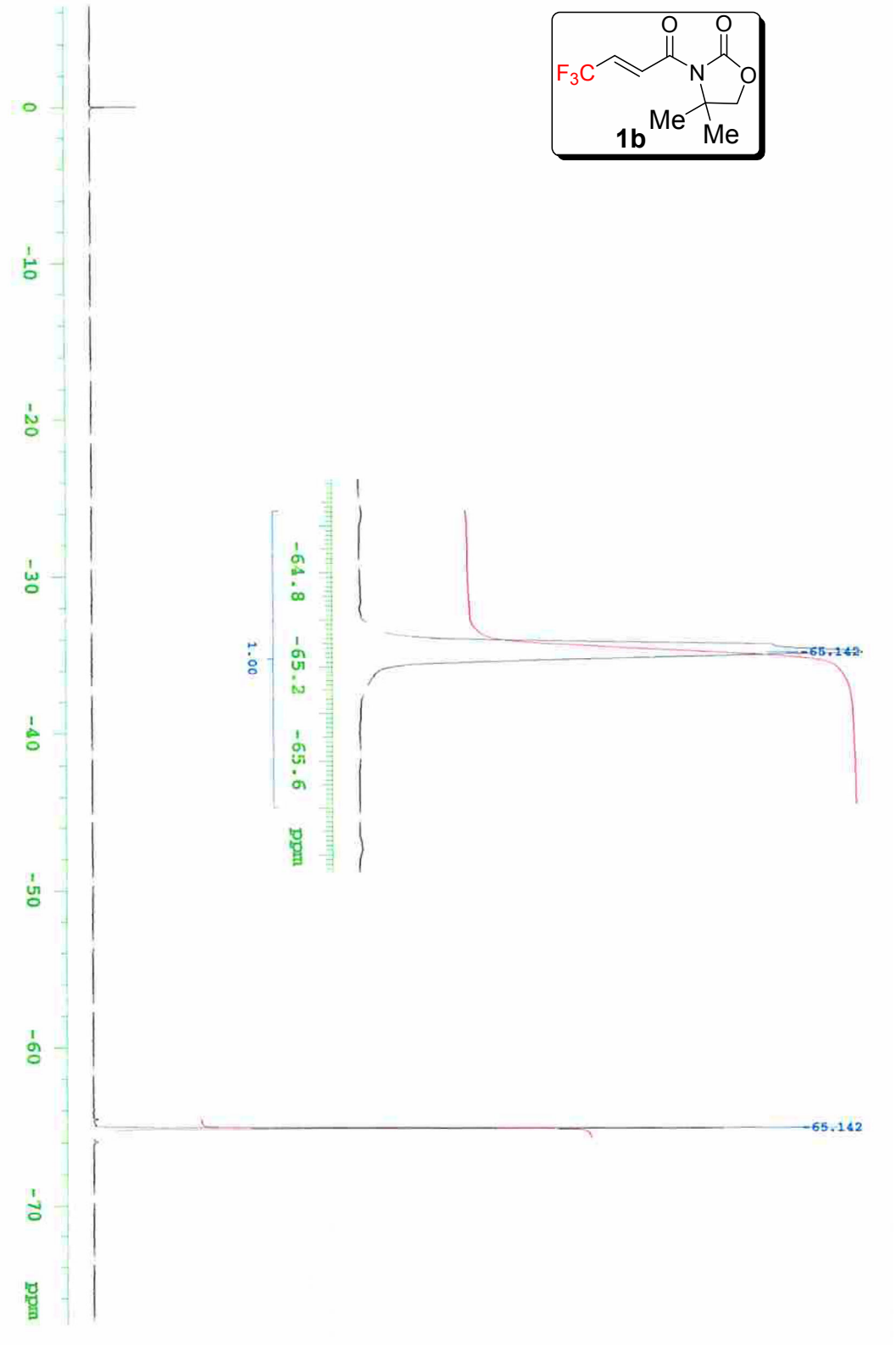
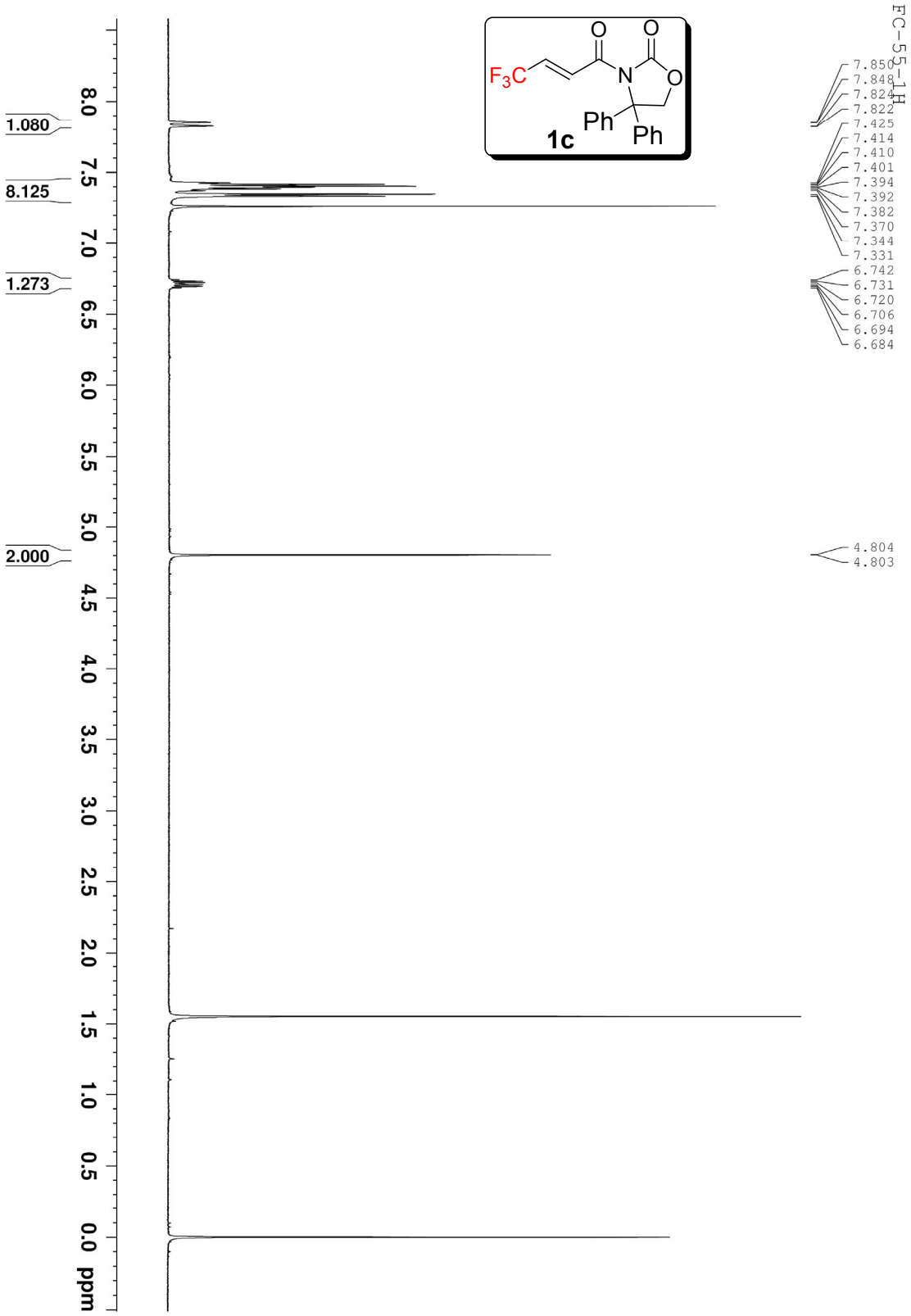
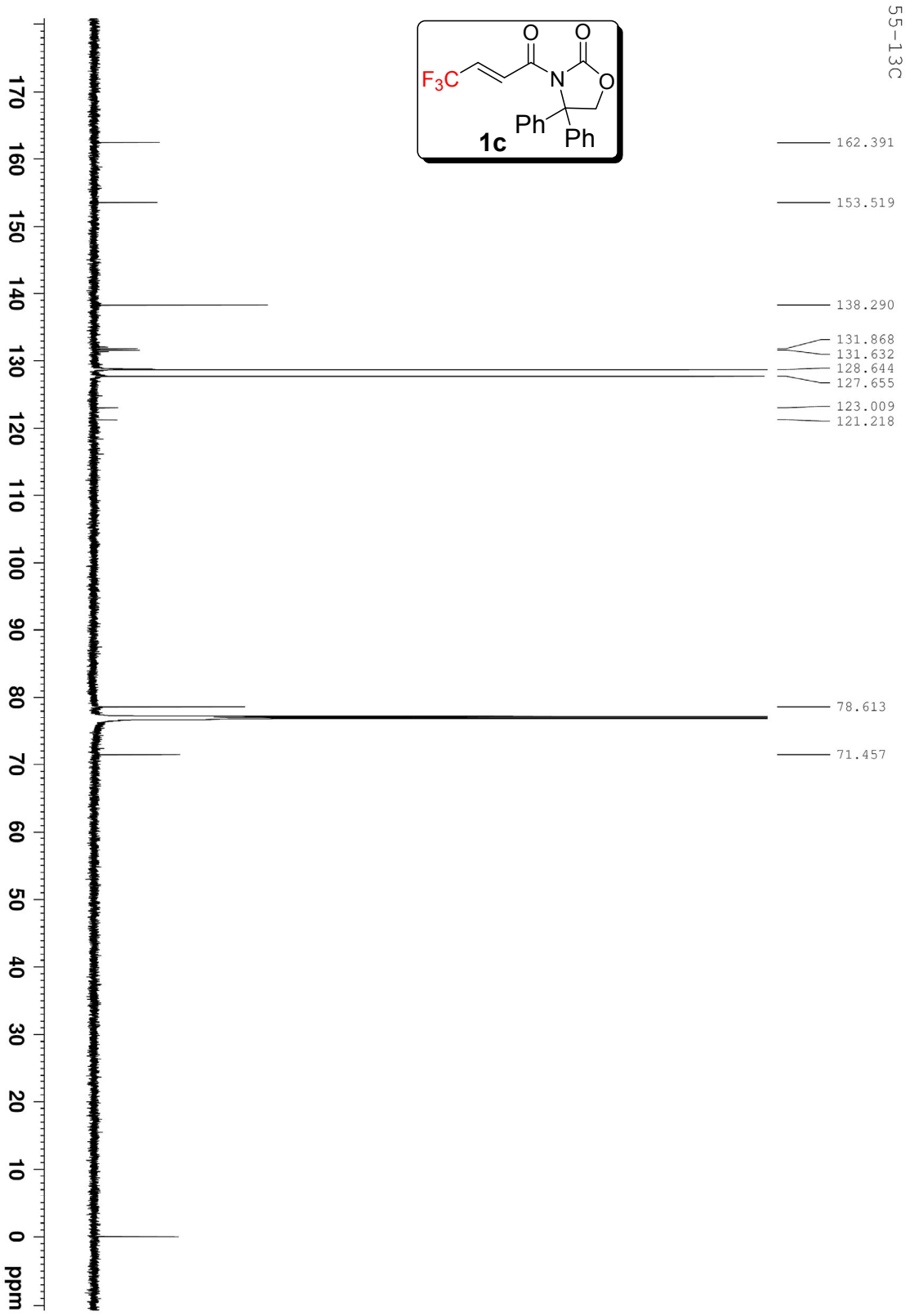


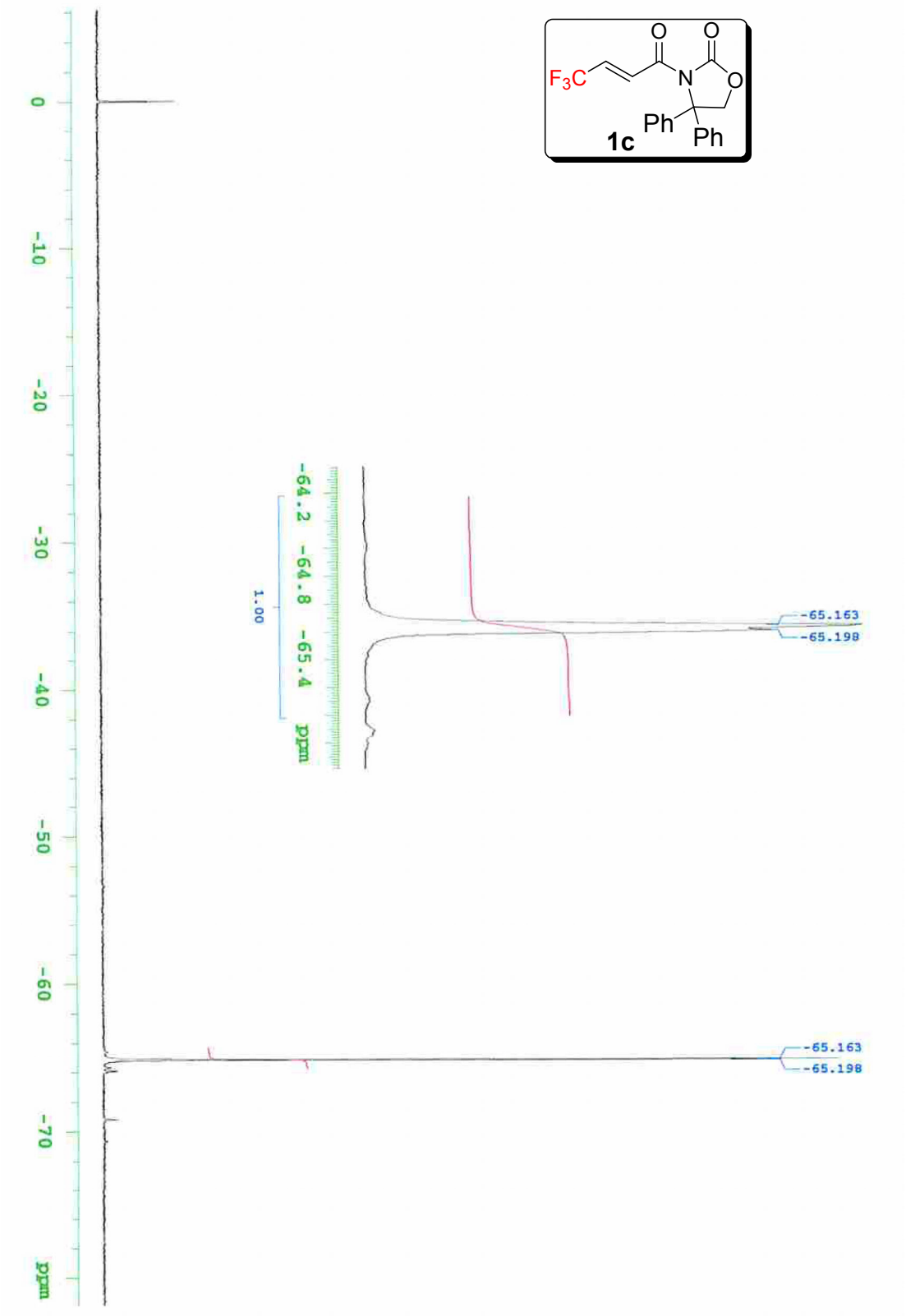
^{19}F NMR ($CDCl_3$, 188 MHz)



^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 150.9 MHz)



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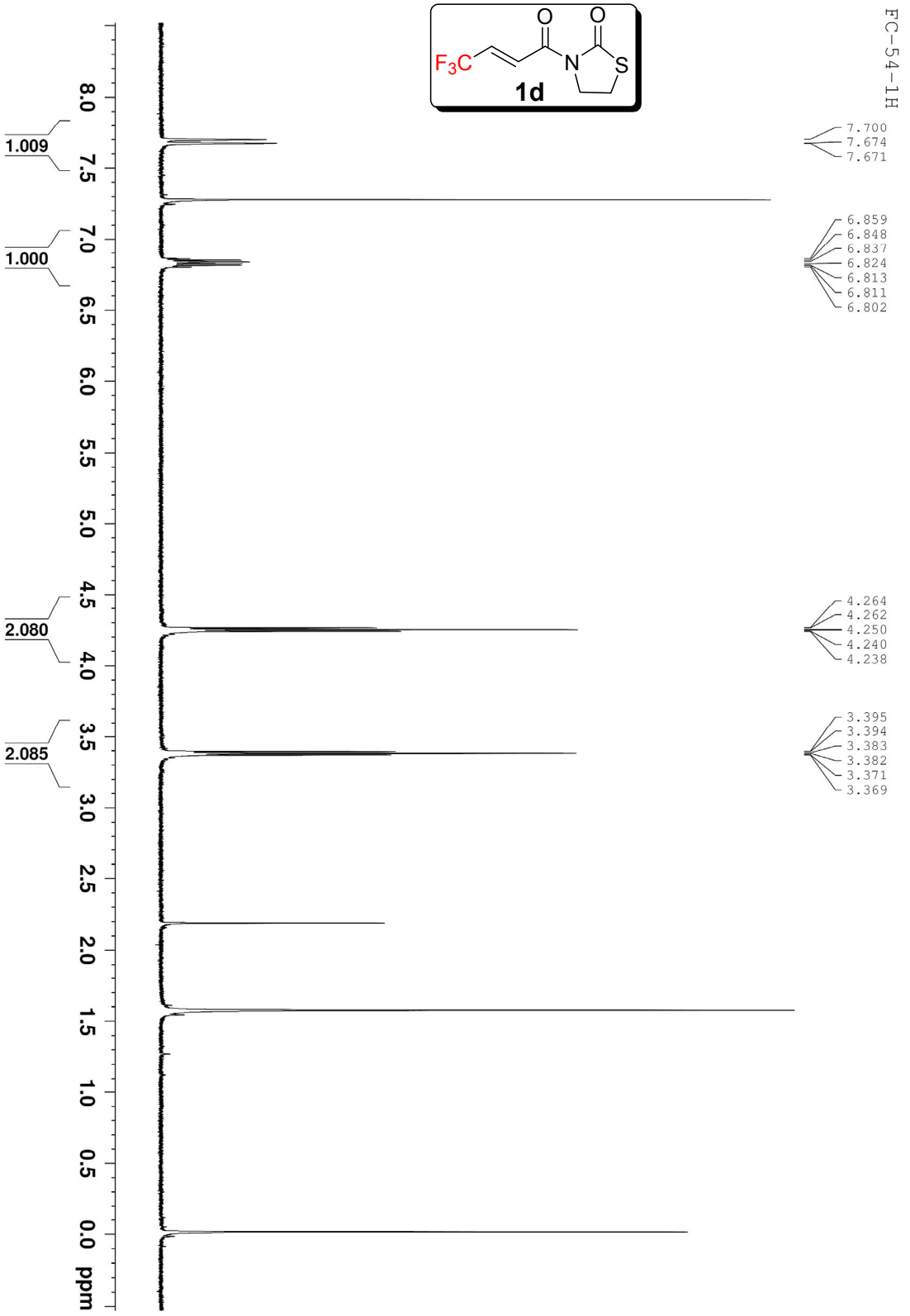

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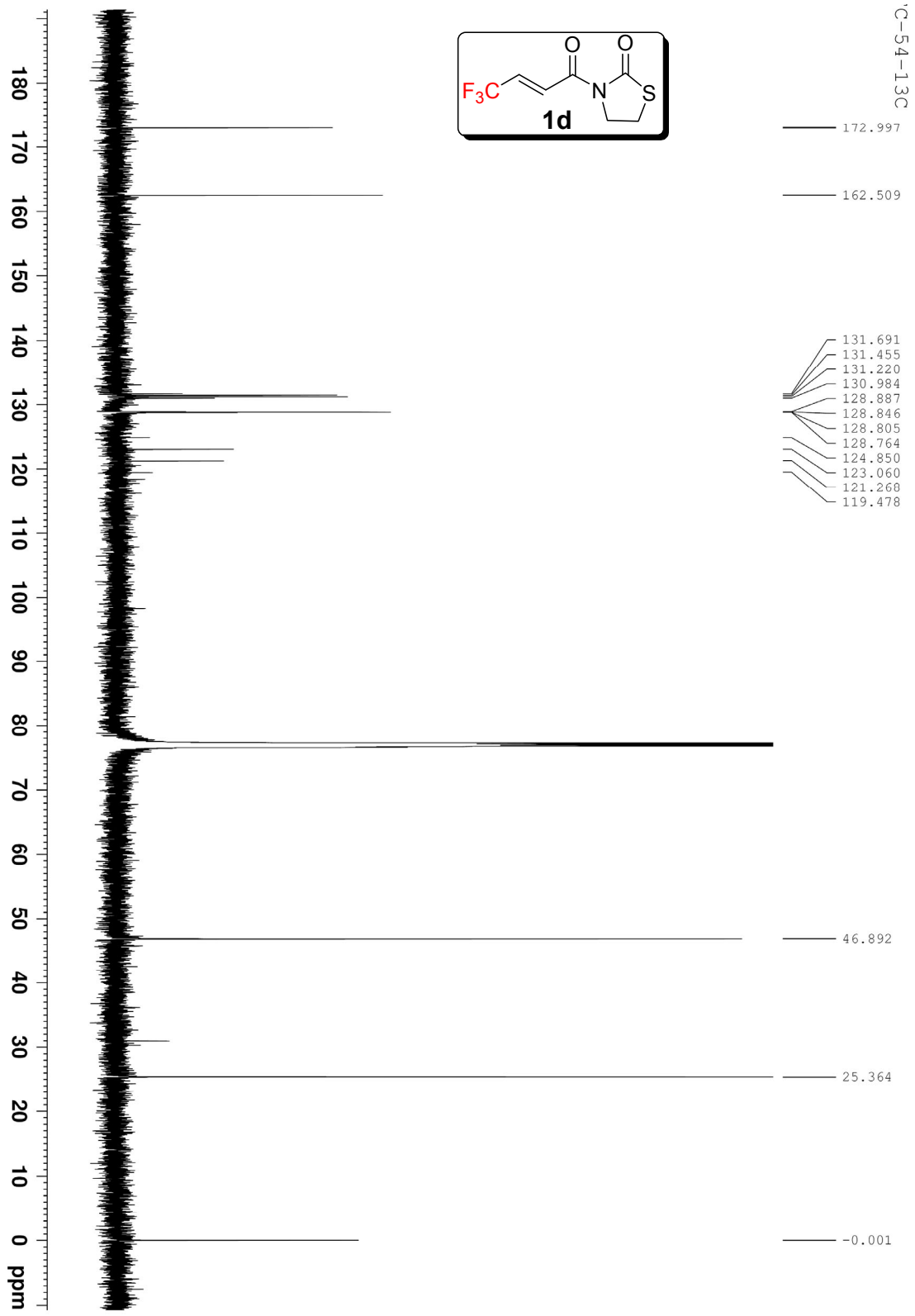

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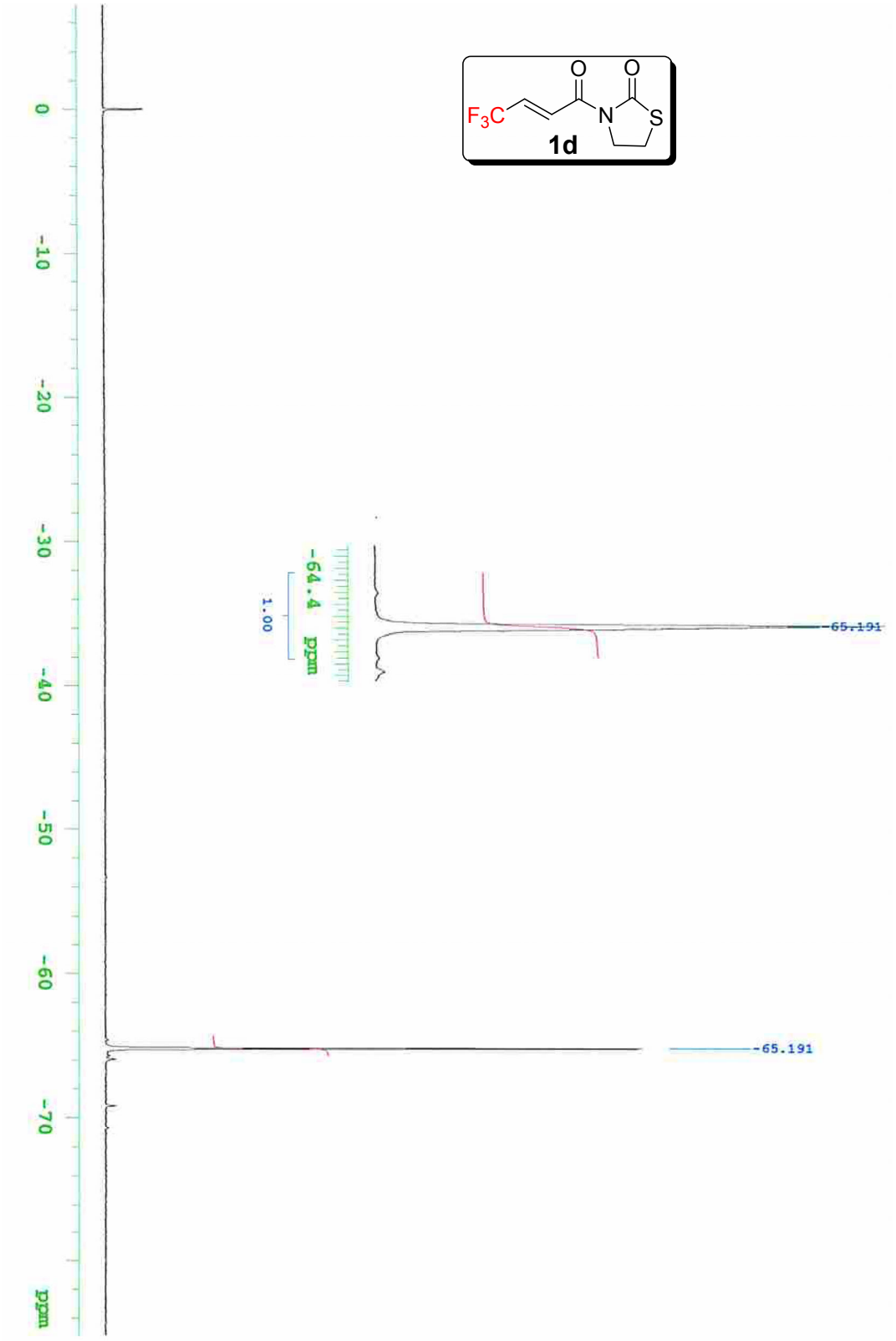

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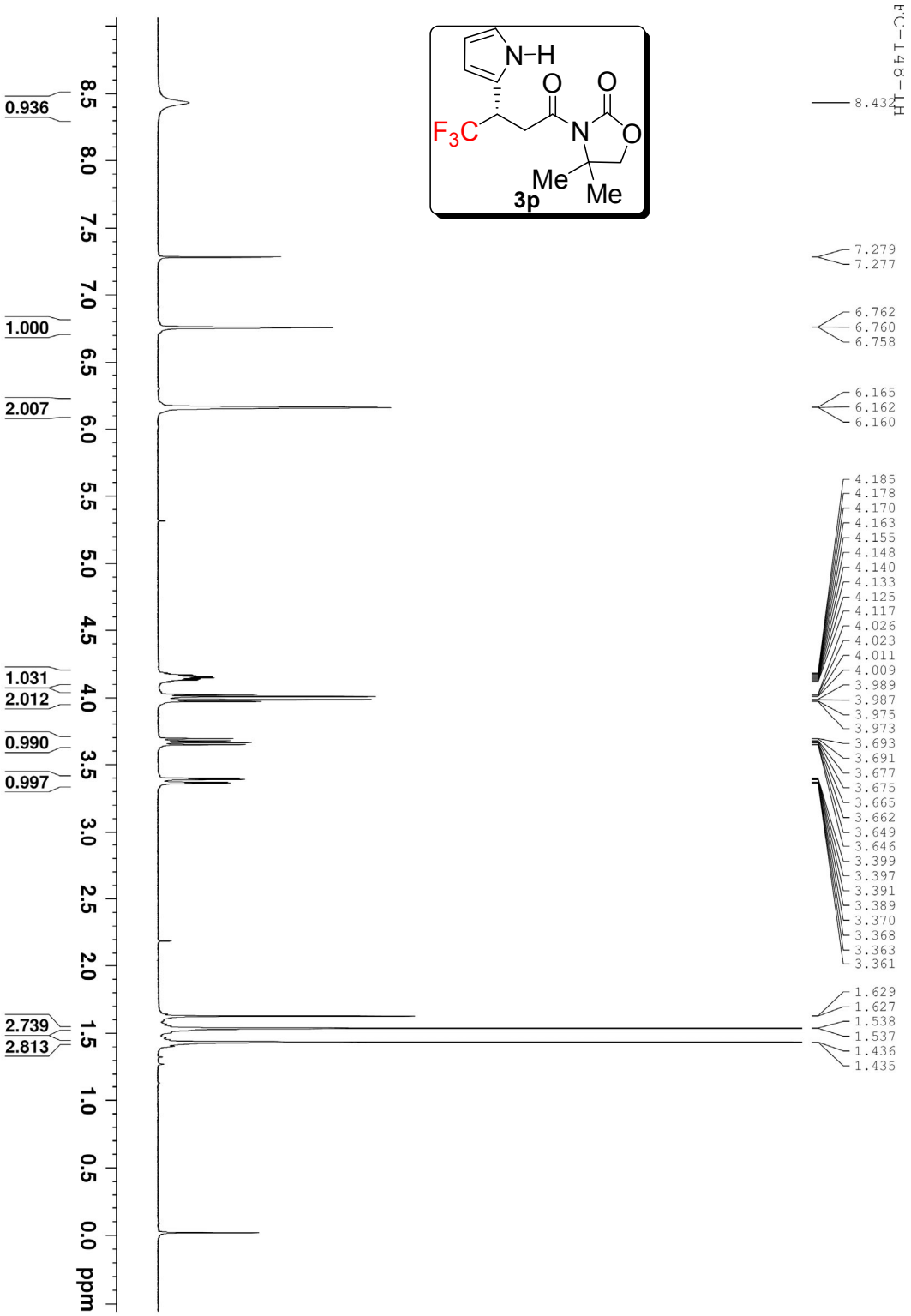

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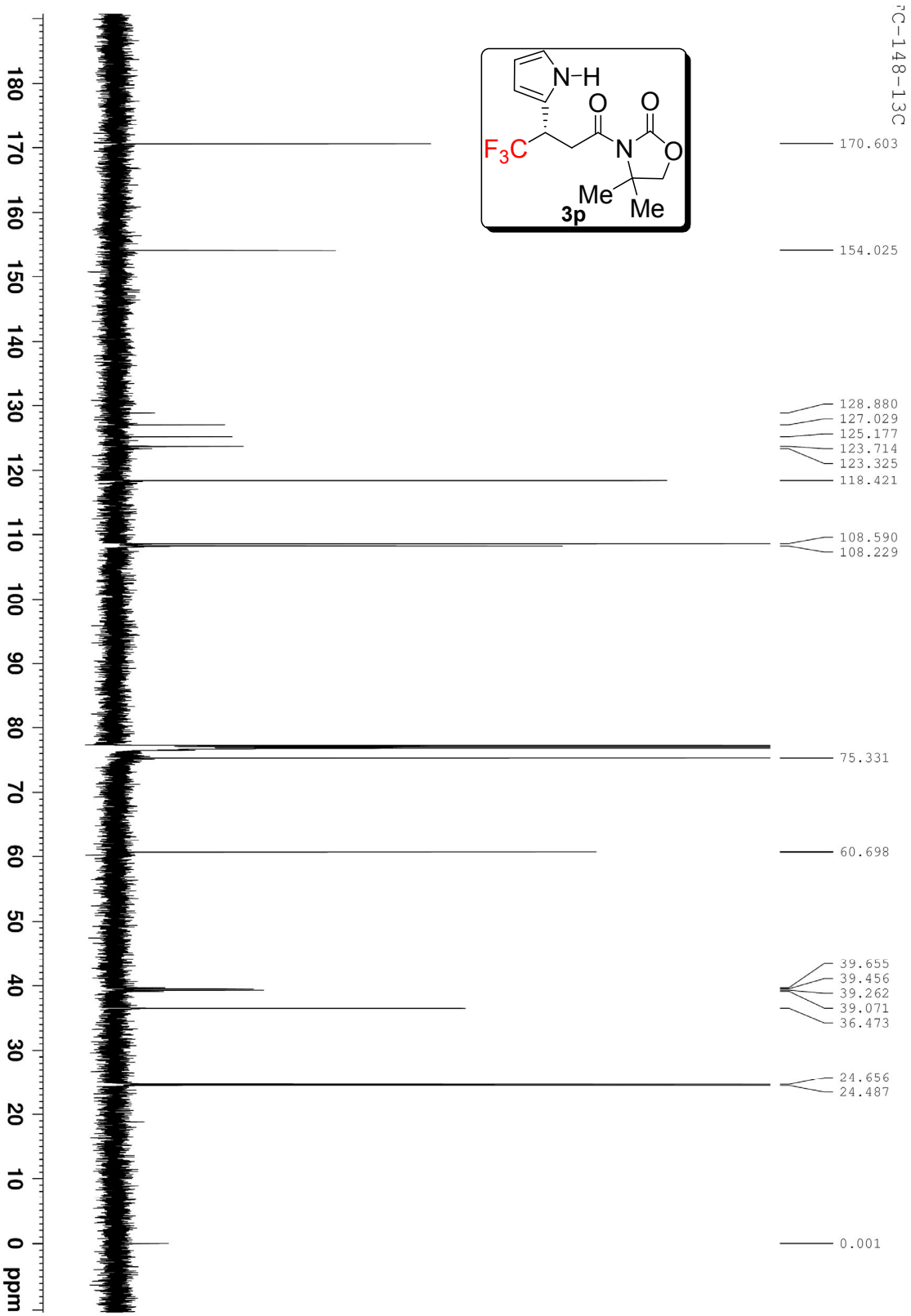

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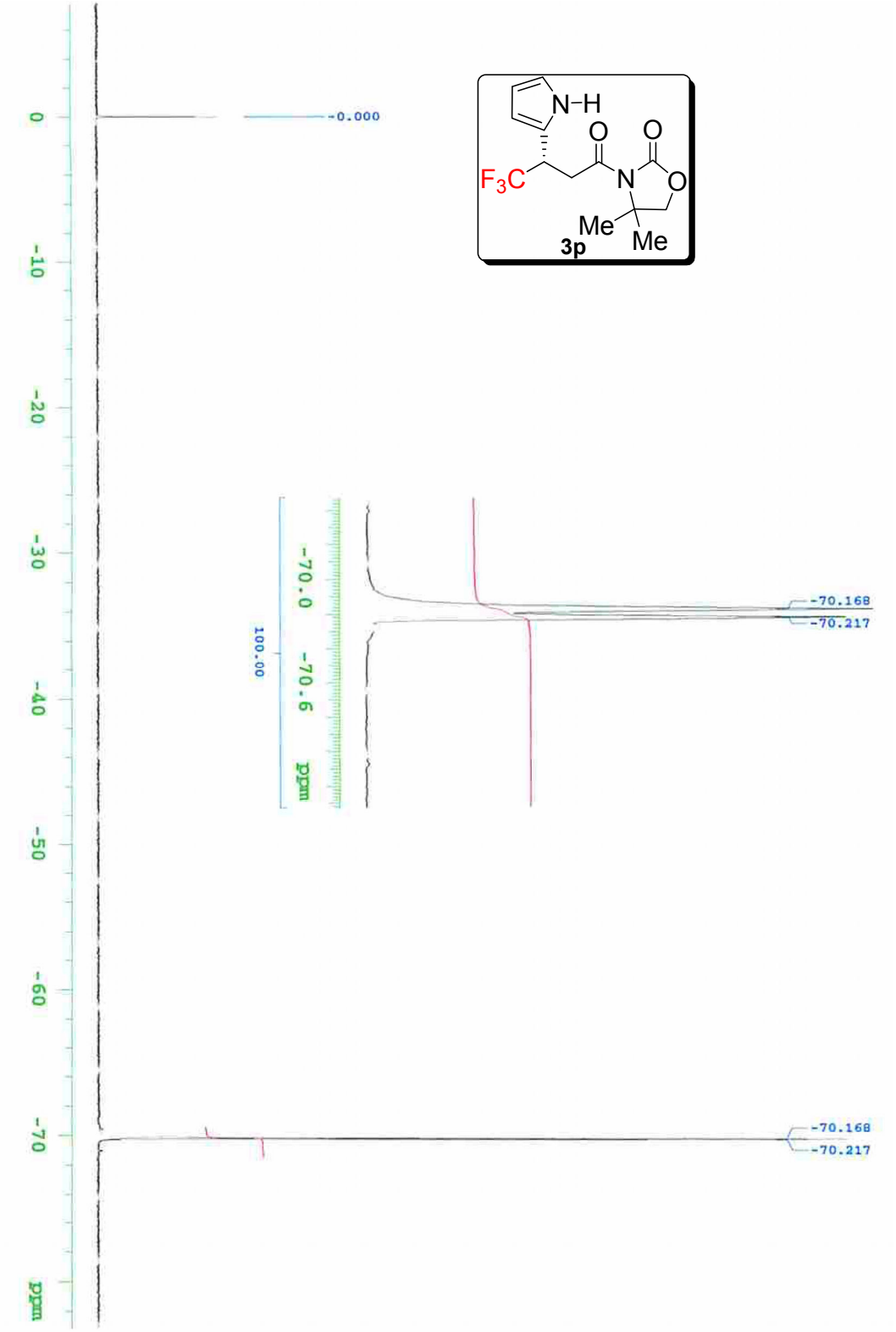

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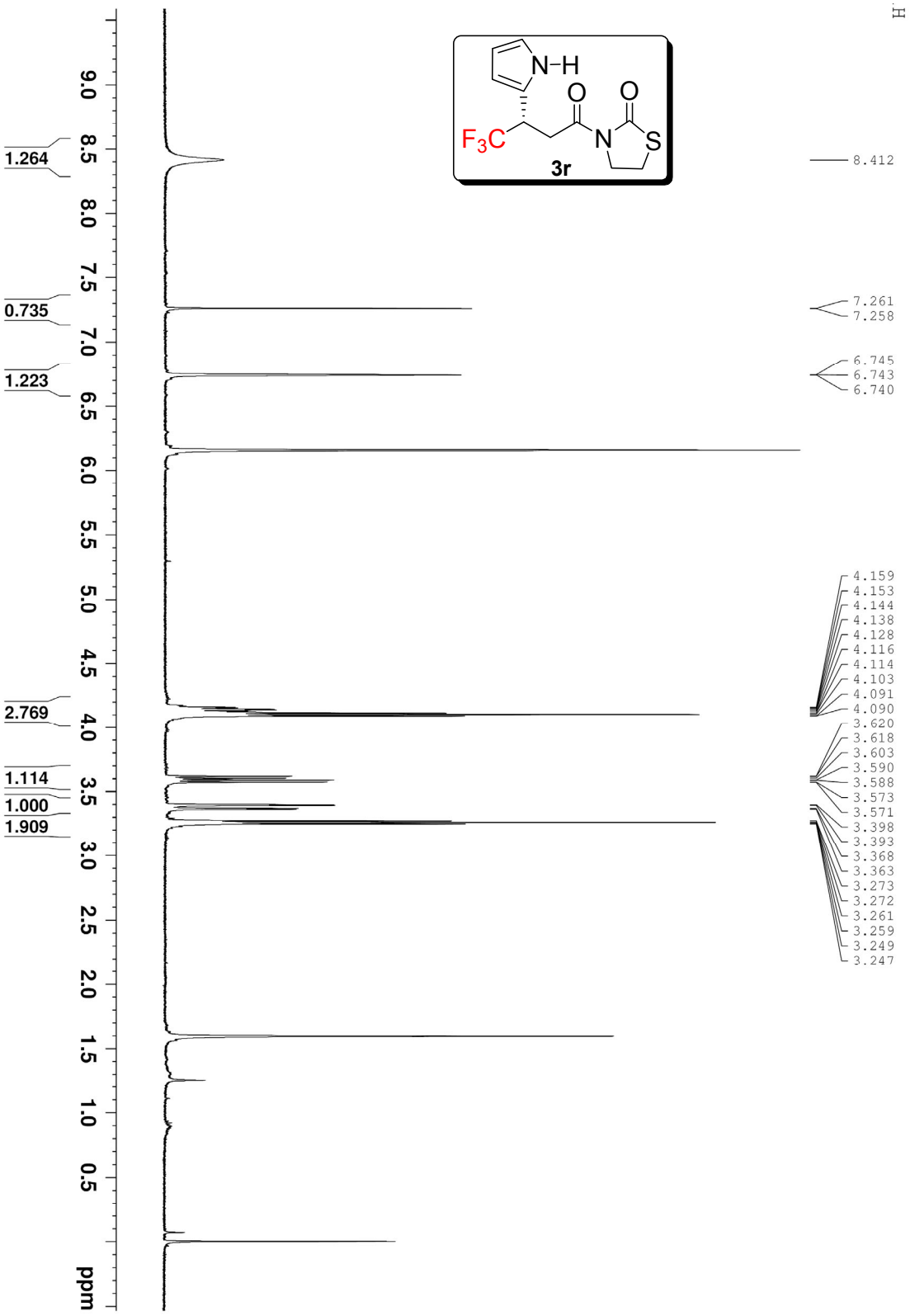

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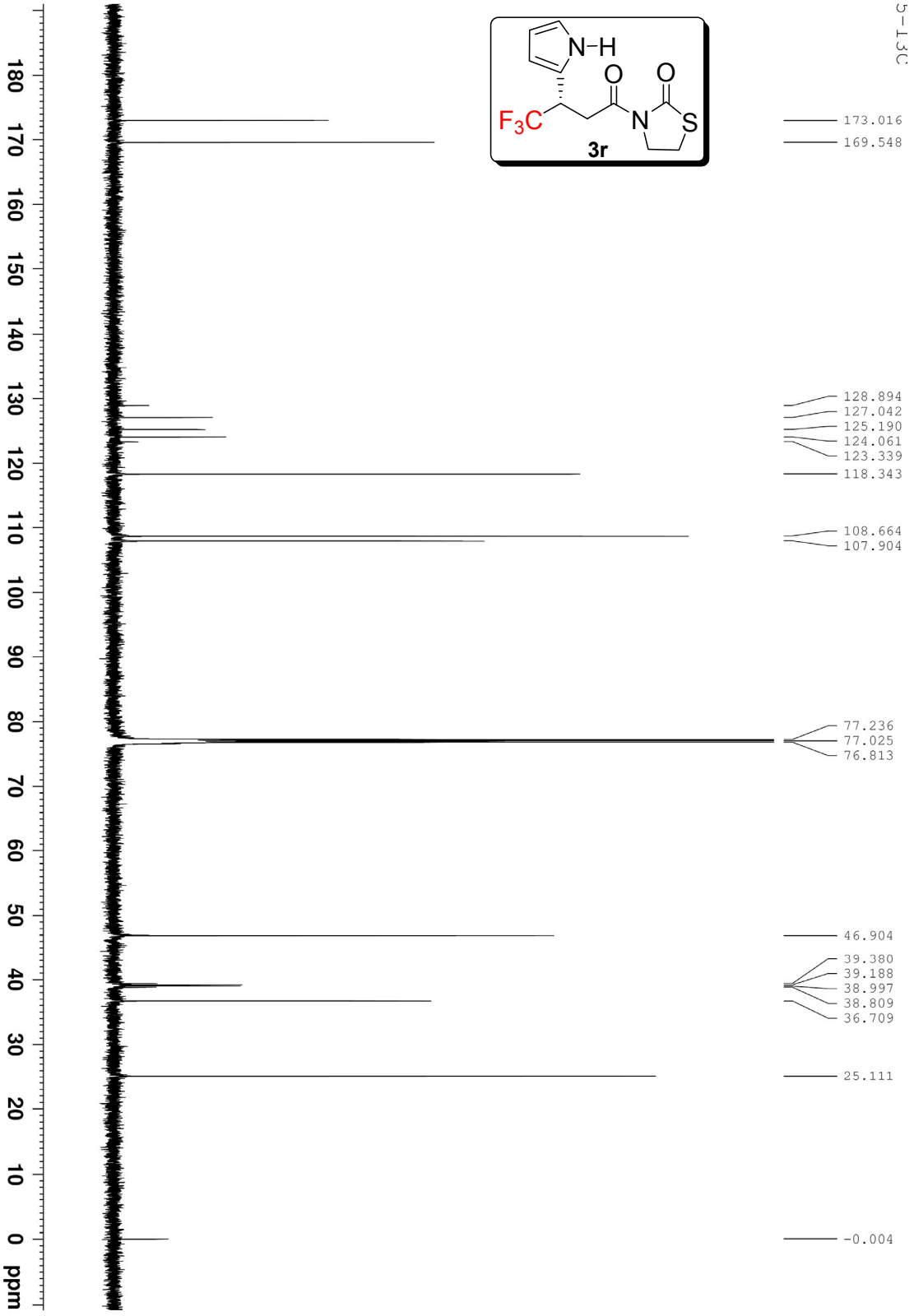

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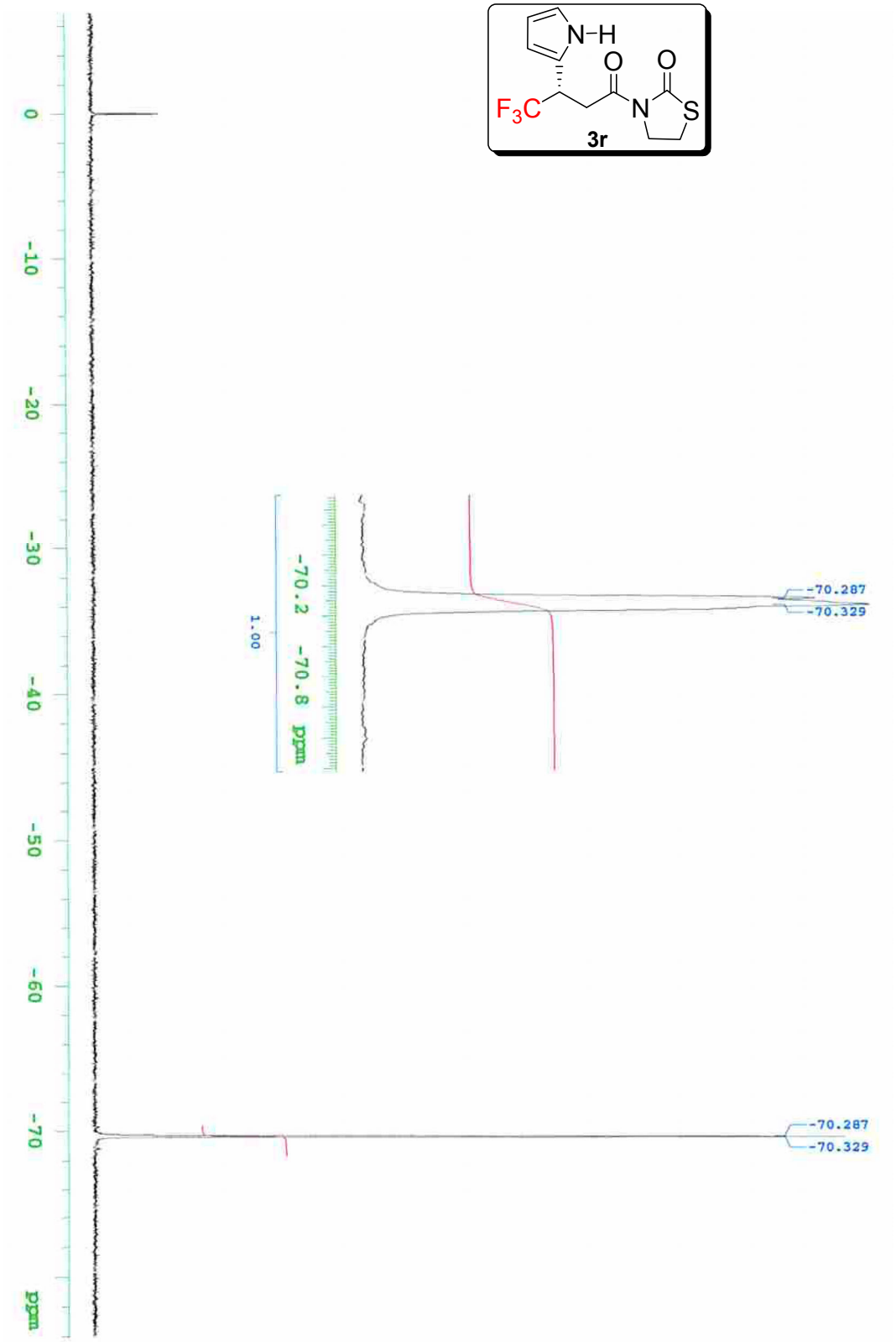

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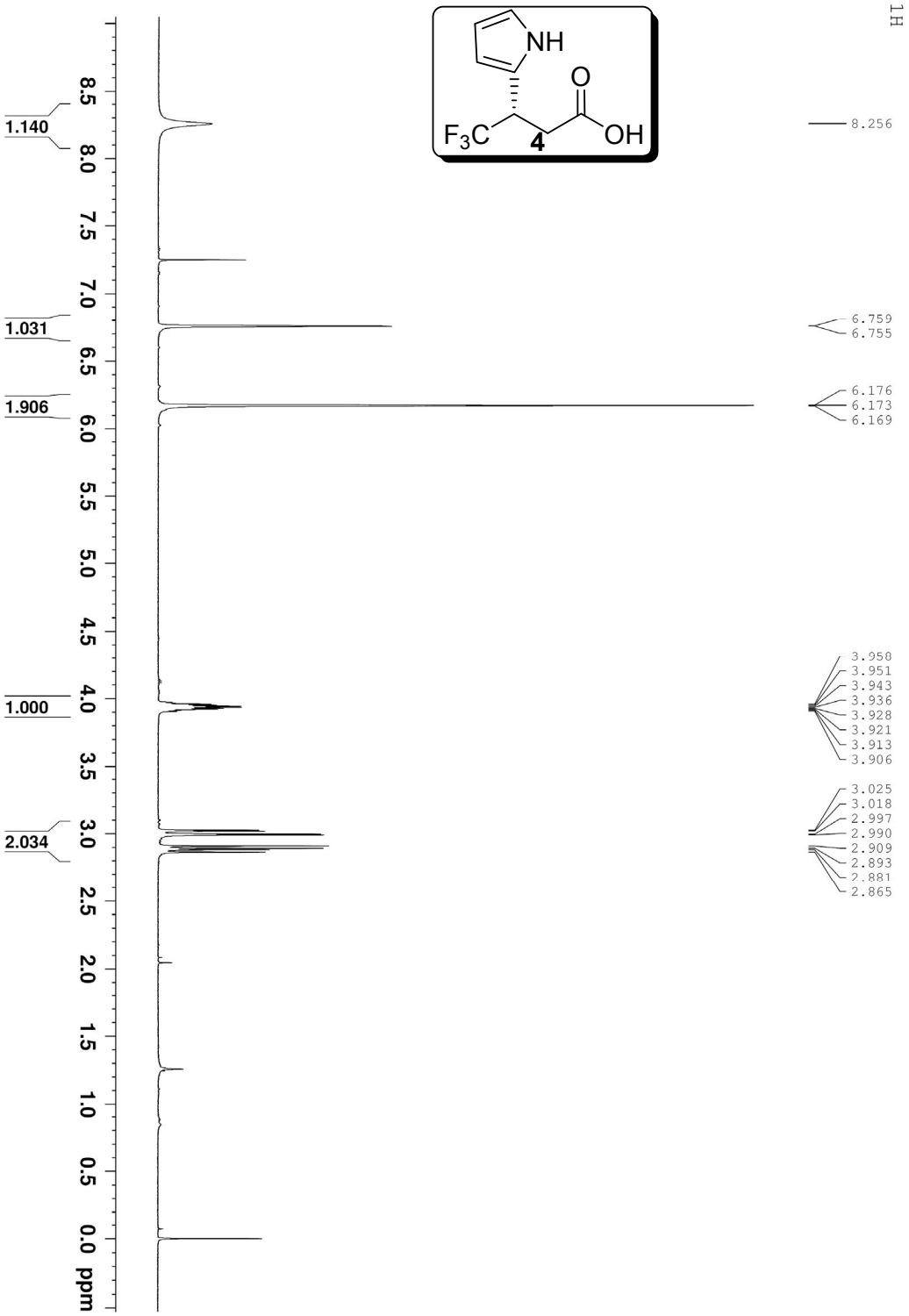

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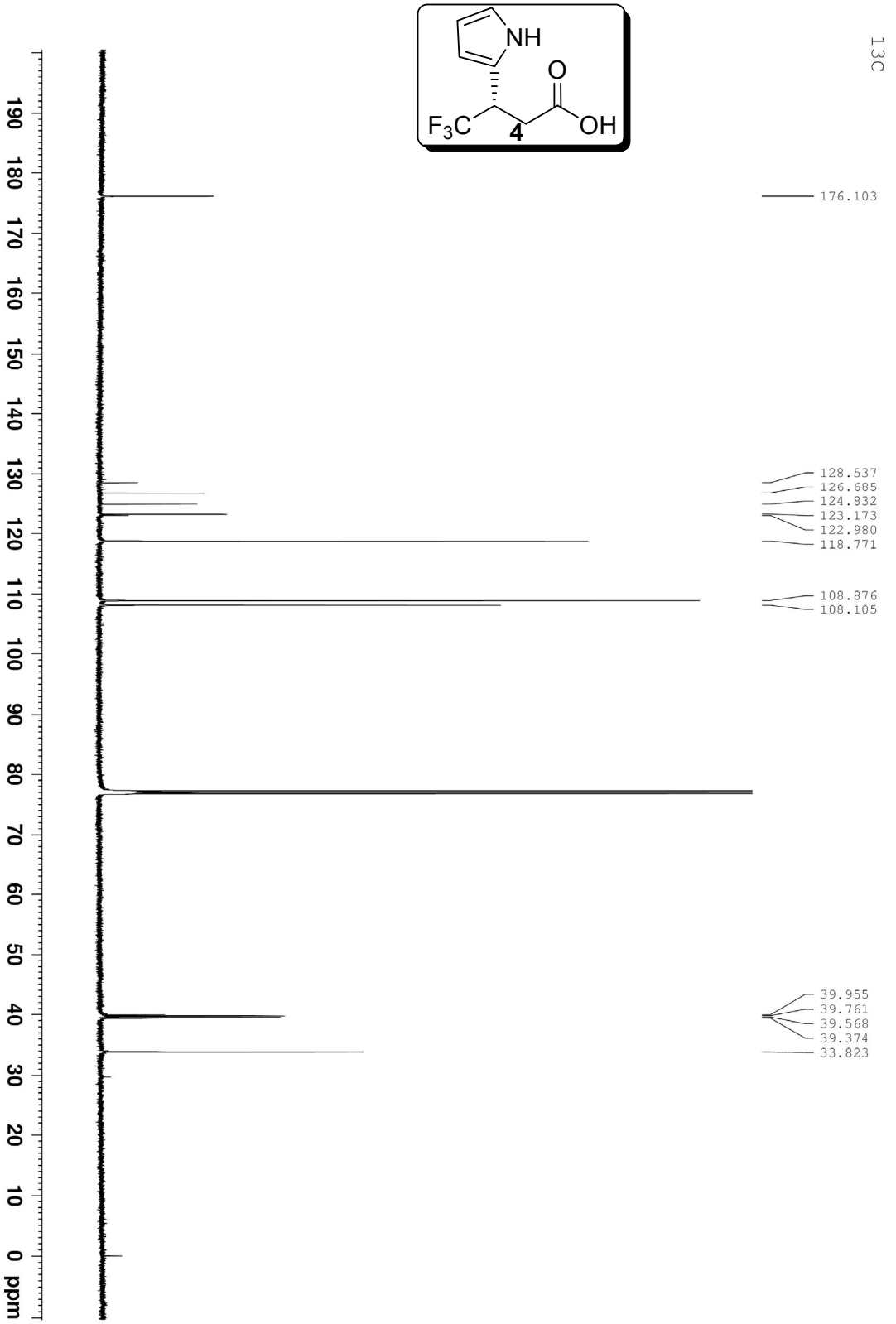
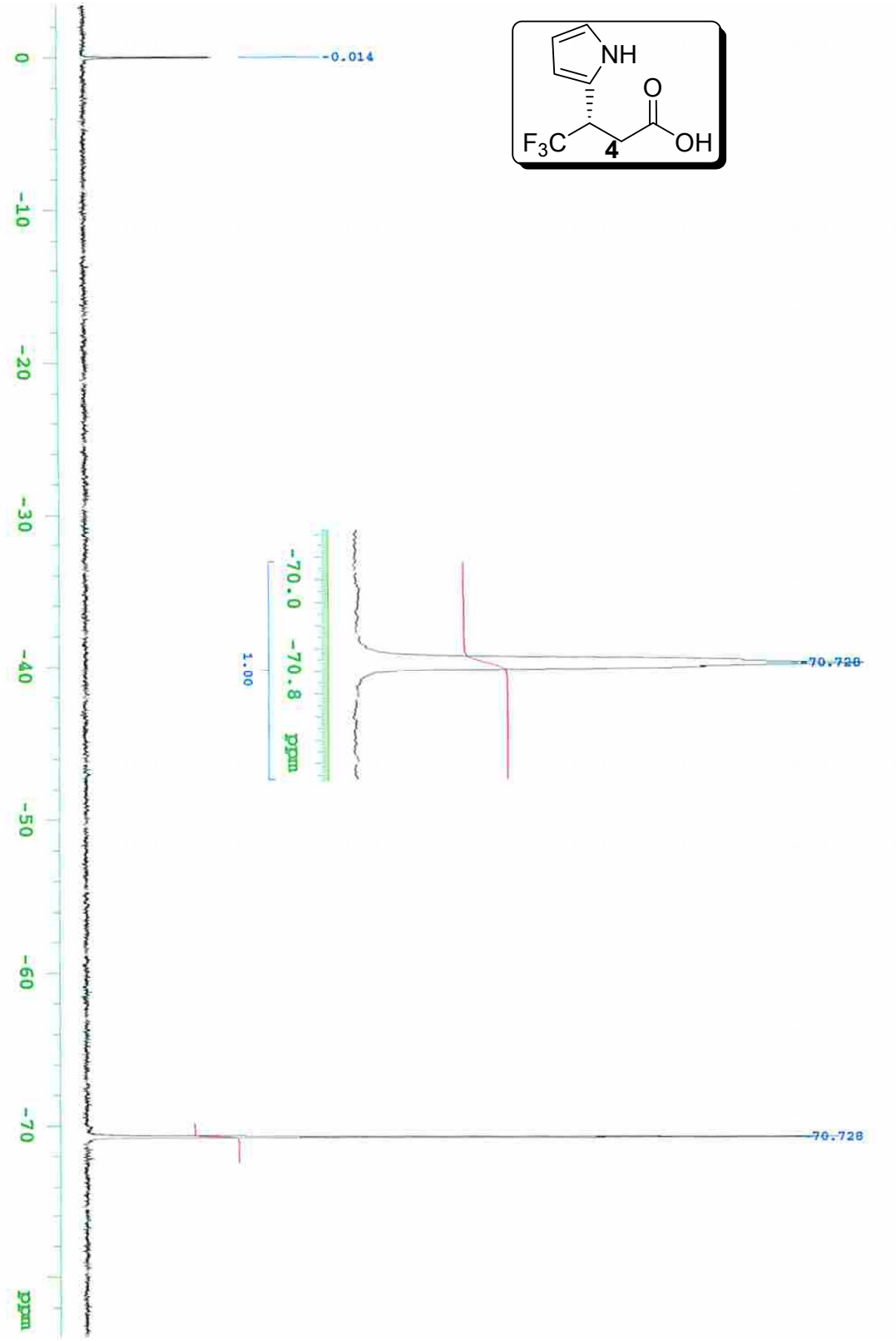
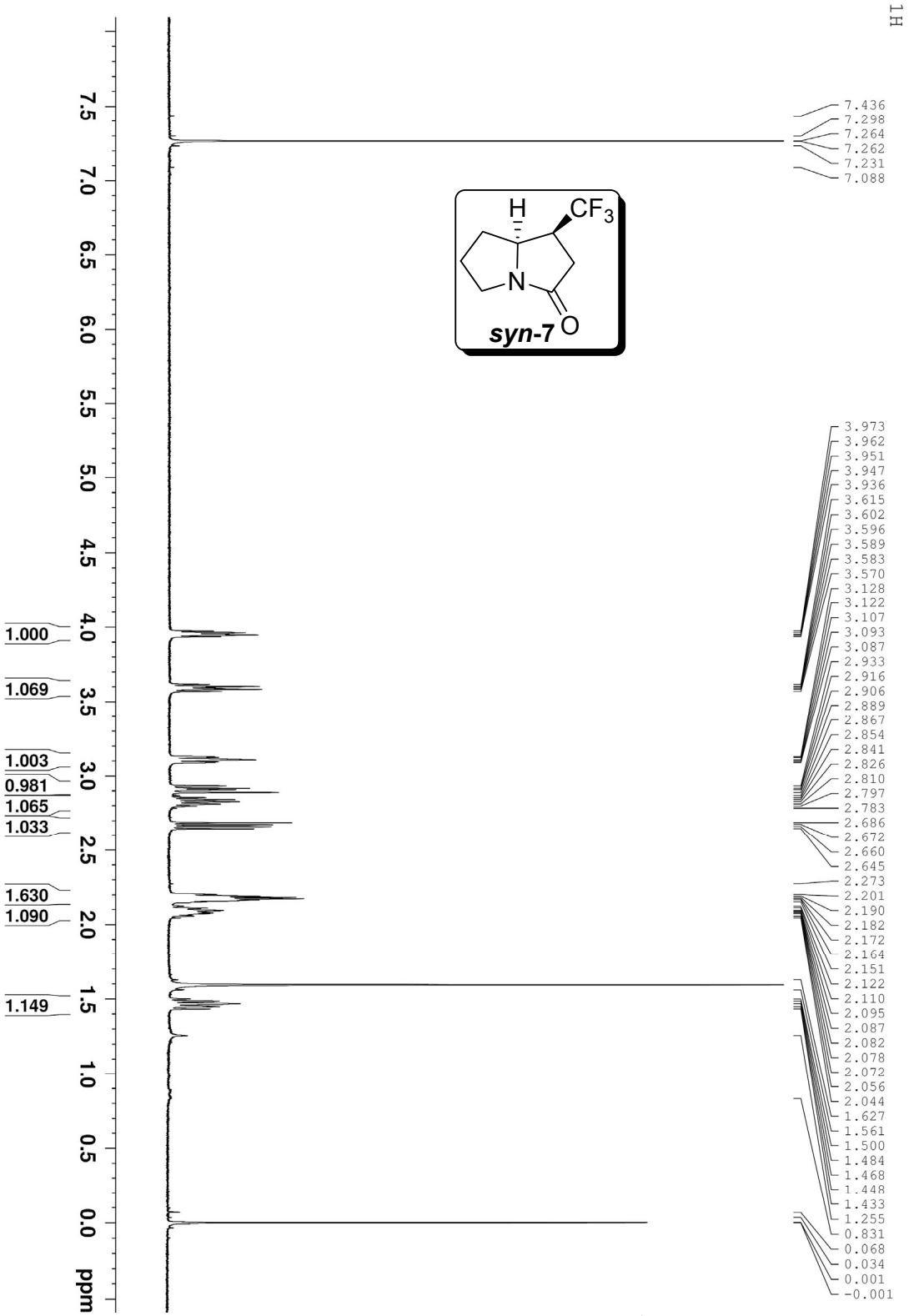


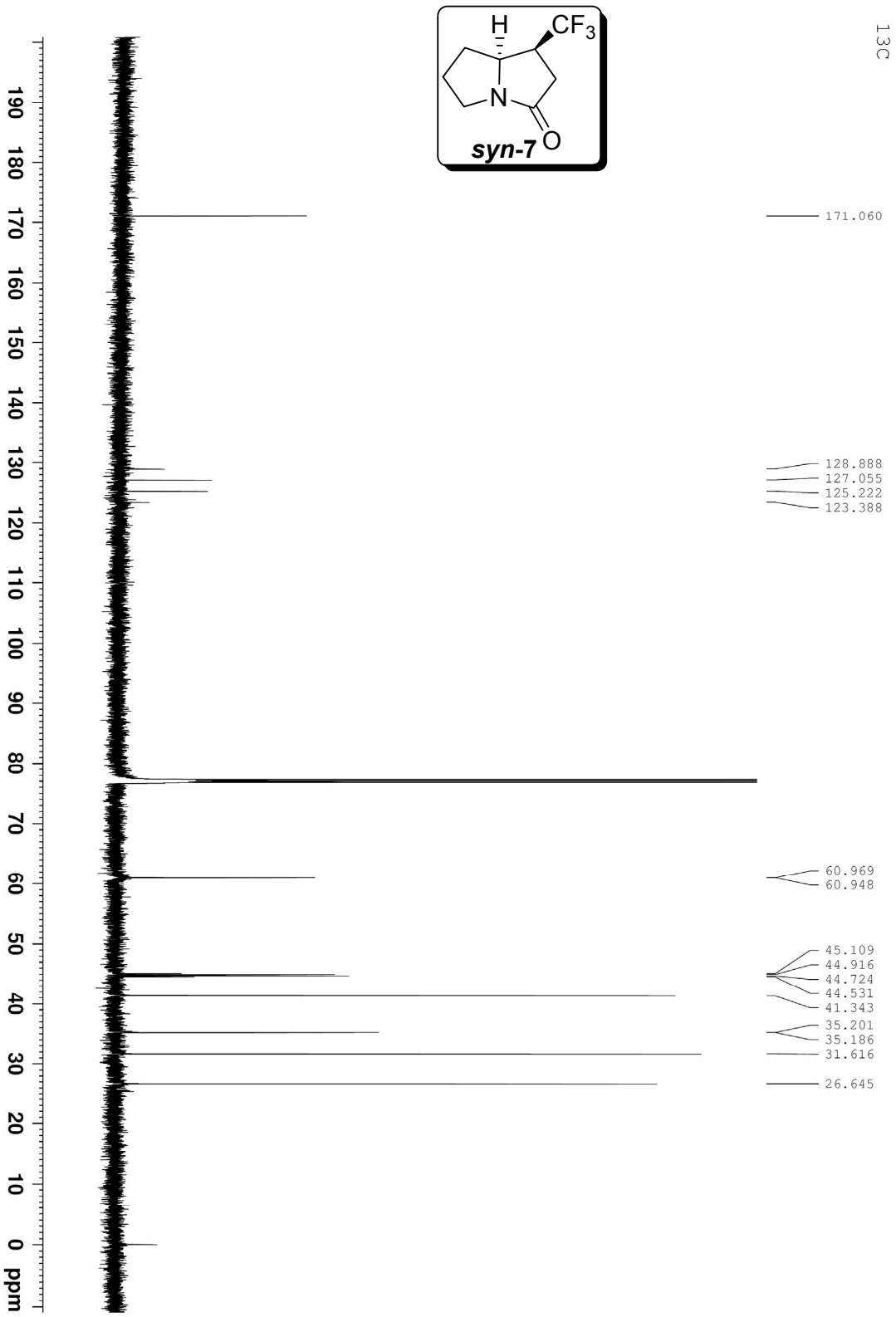
^{13}C NMR ($CDCl_3$, 150.9 MHz)



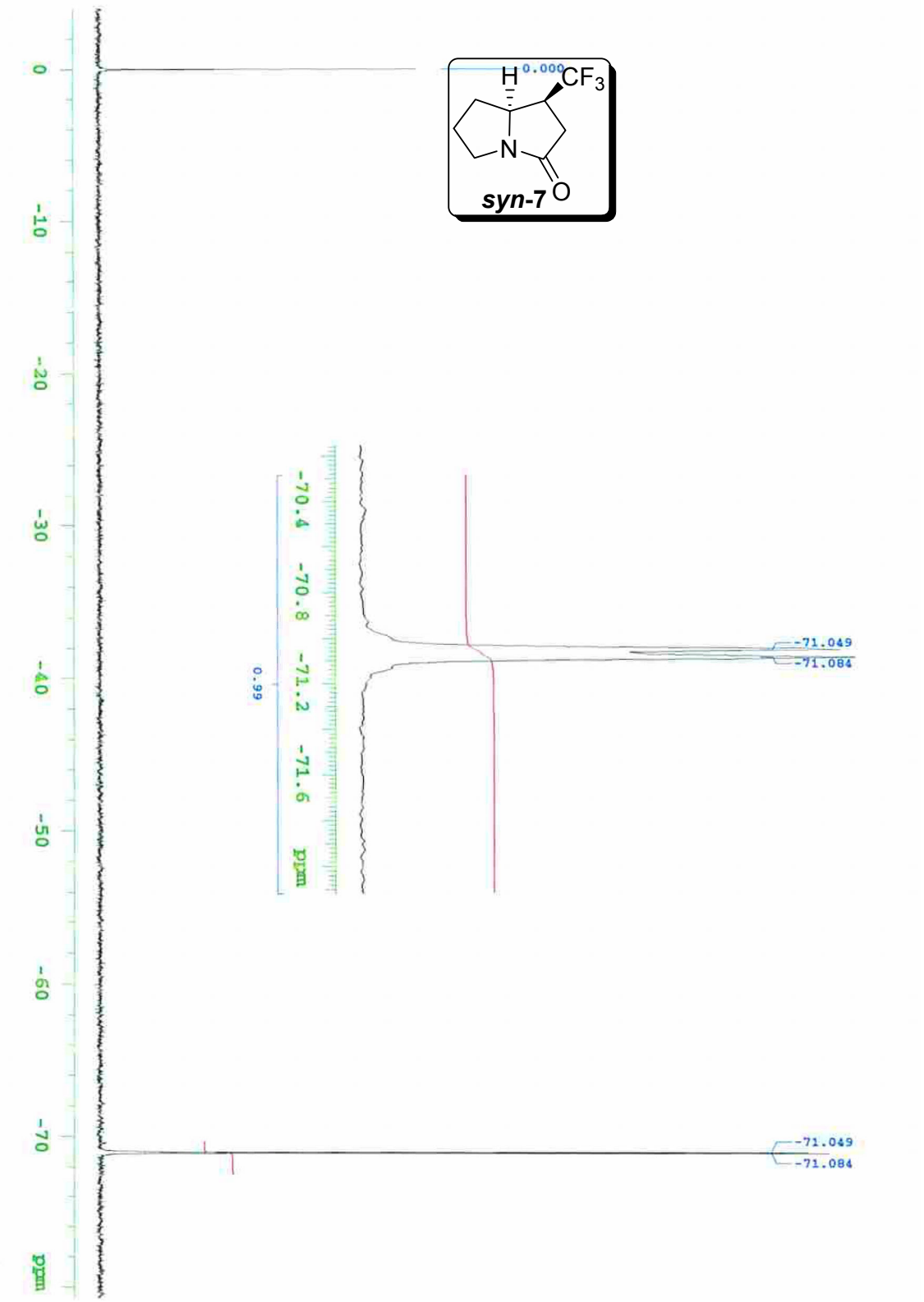
^{19}F NMR ($CDCl_3$, 188 MHz)



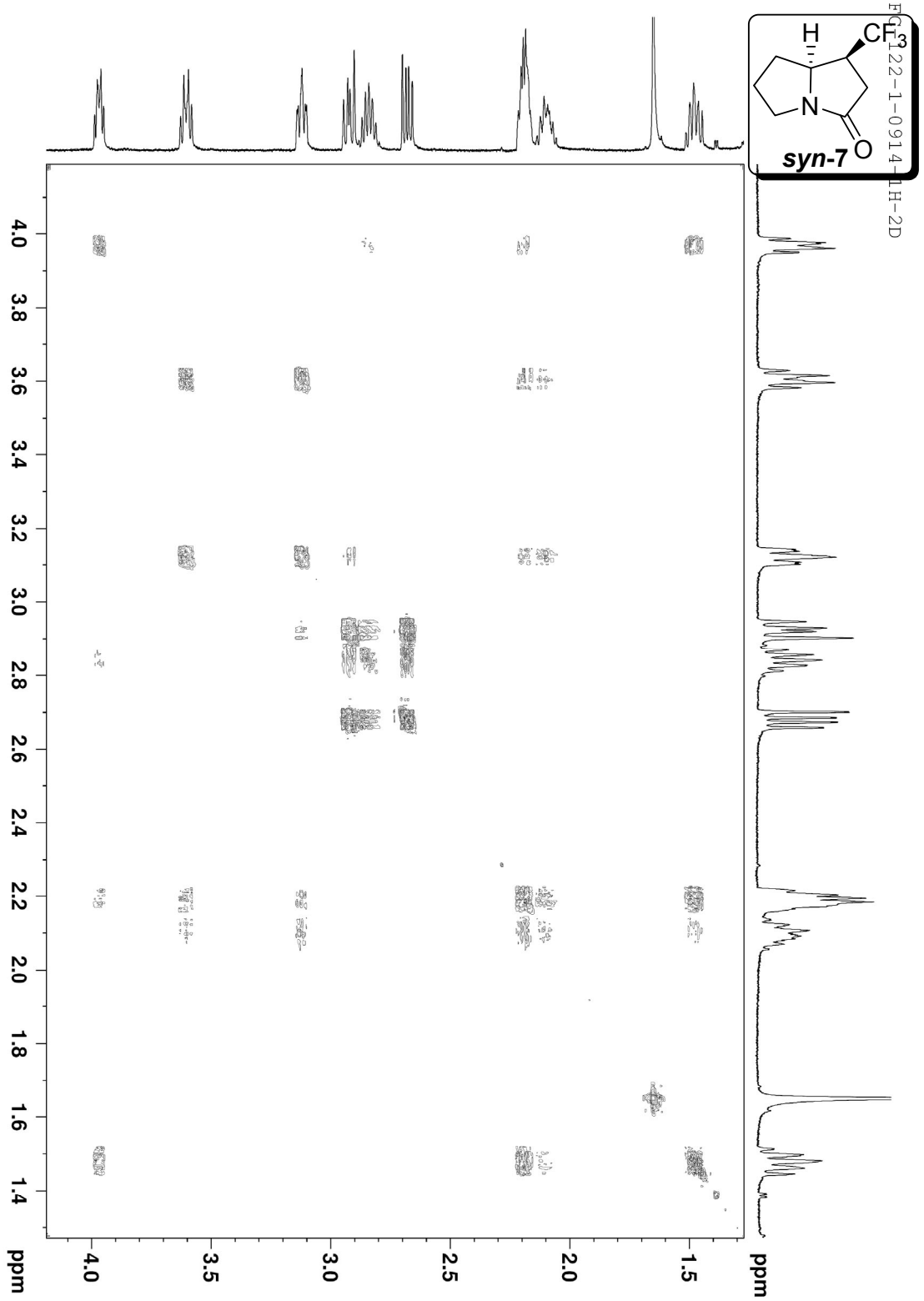
^{1}H NMR ($CDCl_3$, 600 MHz)



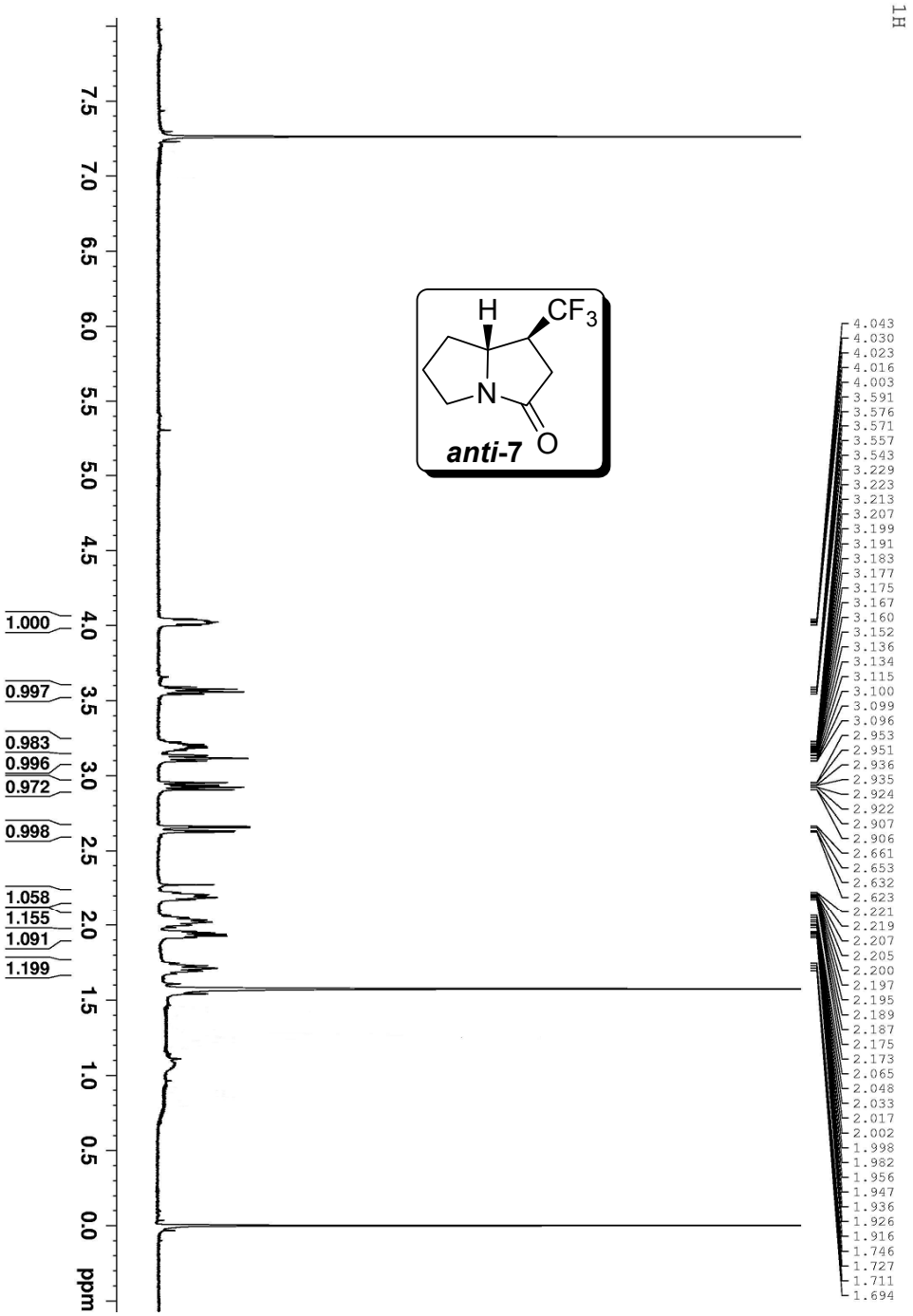
^{13}C NMR ($CDCl_3$, 150.9 MHz)



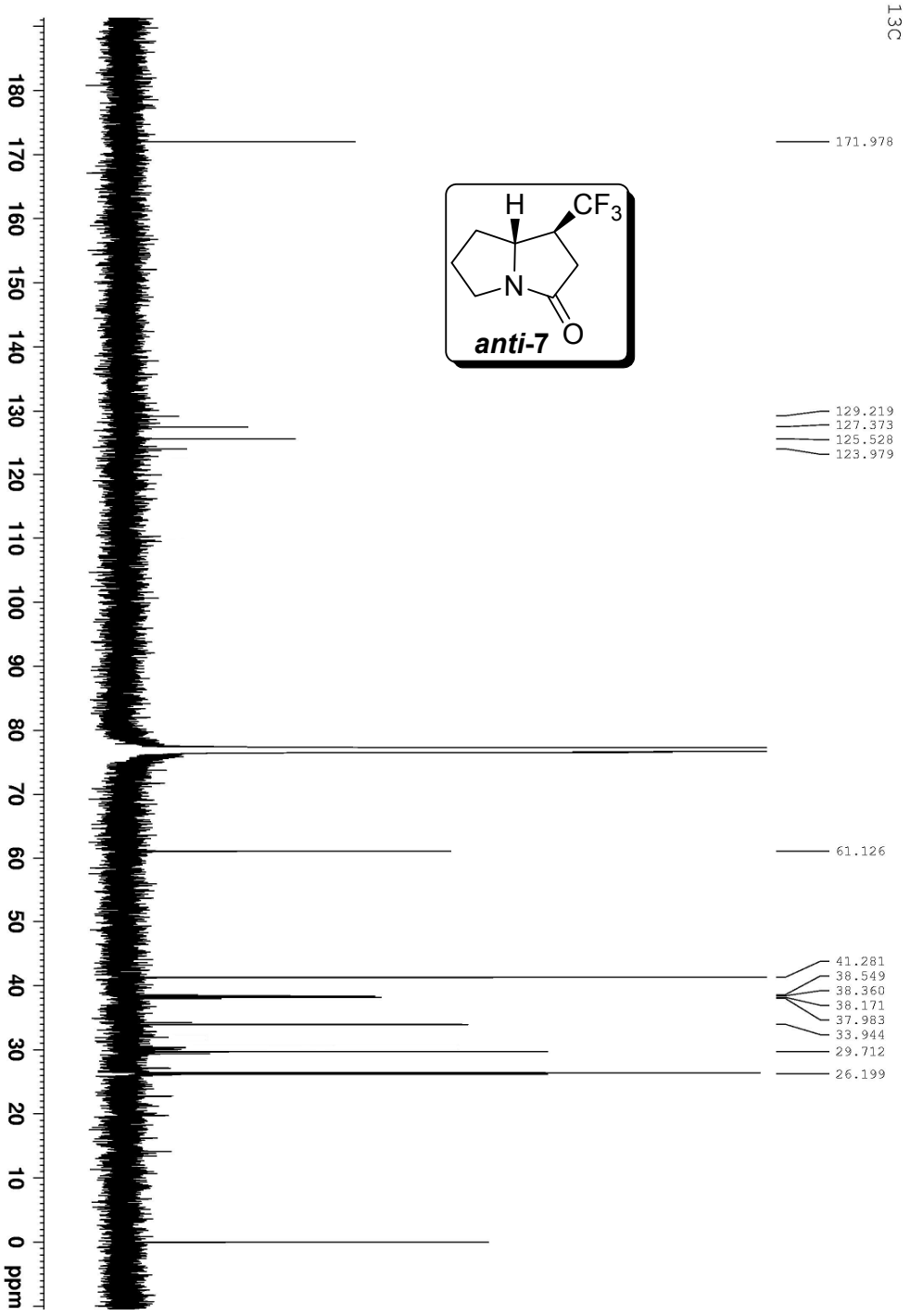
^{19}F NMR ($CDCl_3$, 188 MHz)



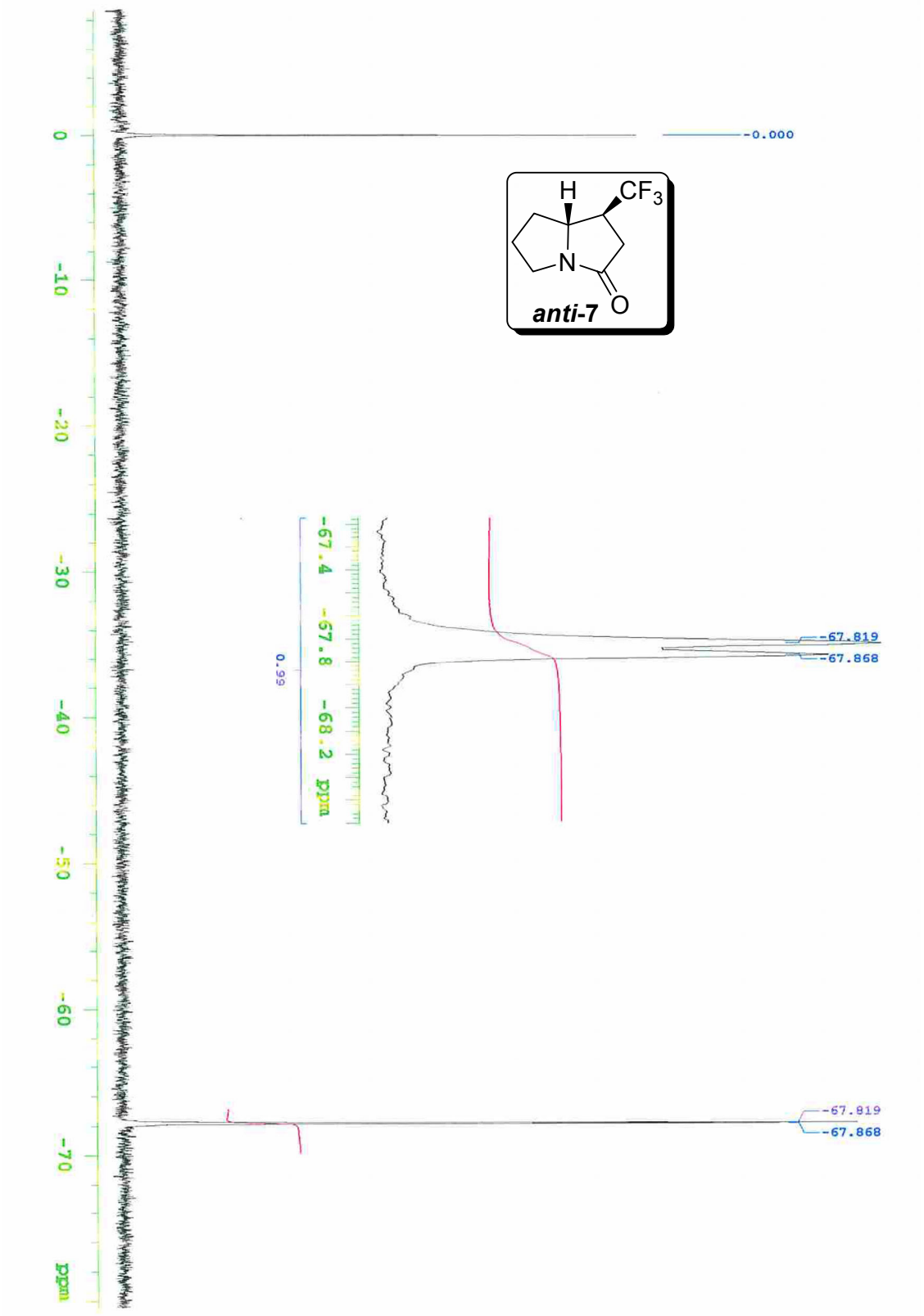
2D NMR, ^{1}H-^{1}H COSY ($CDCl_3$,600 MHz)



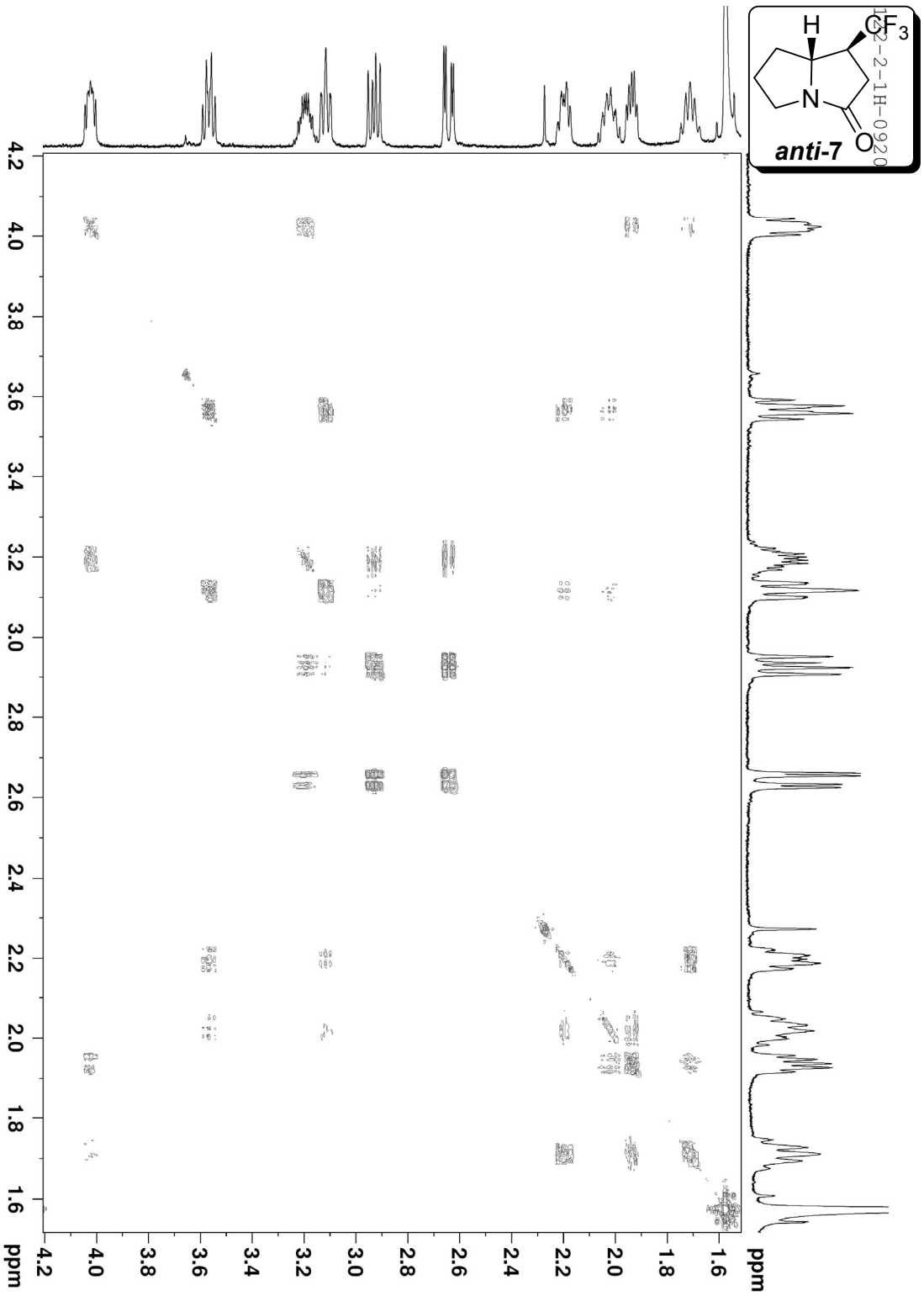
^{1}H NMR ($CDCl_3$, 600 MHz)



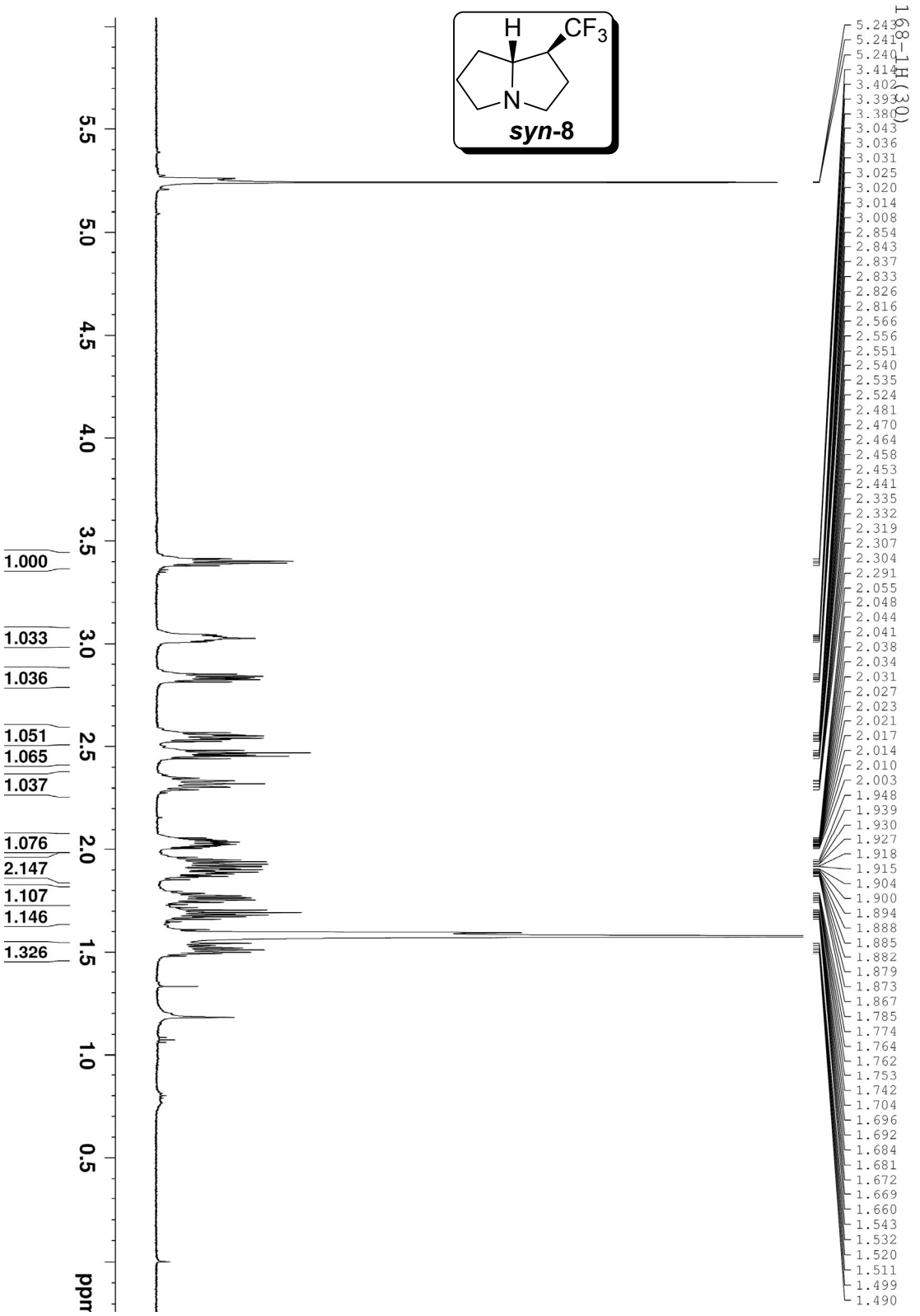
^{13}C NMR ($CDCl_3$, 150.9 MHz)



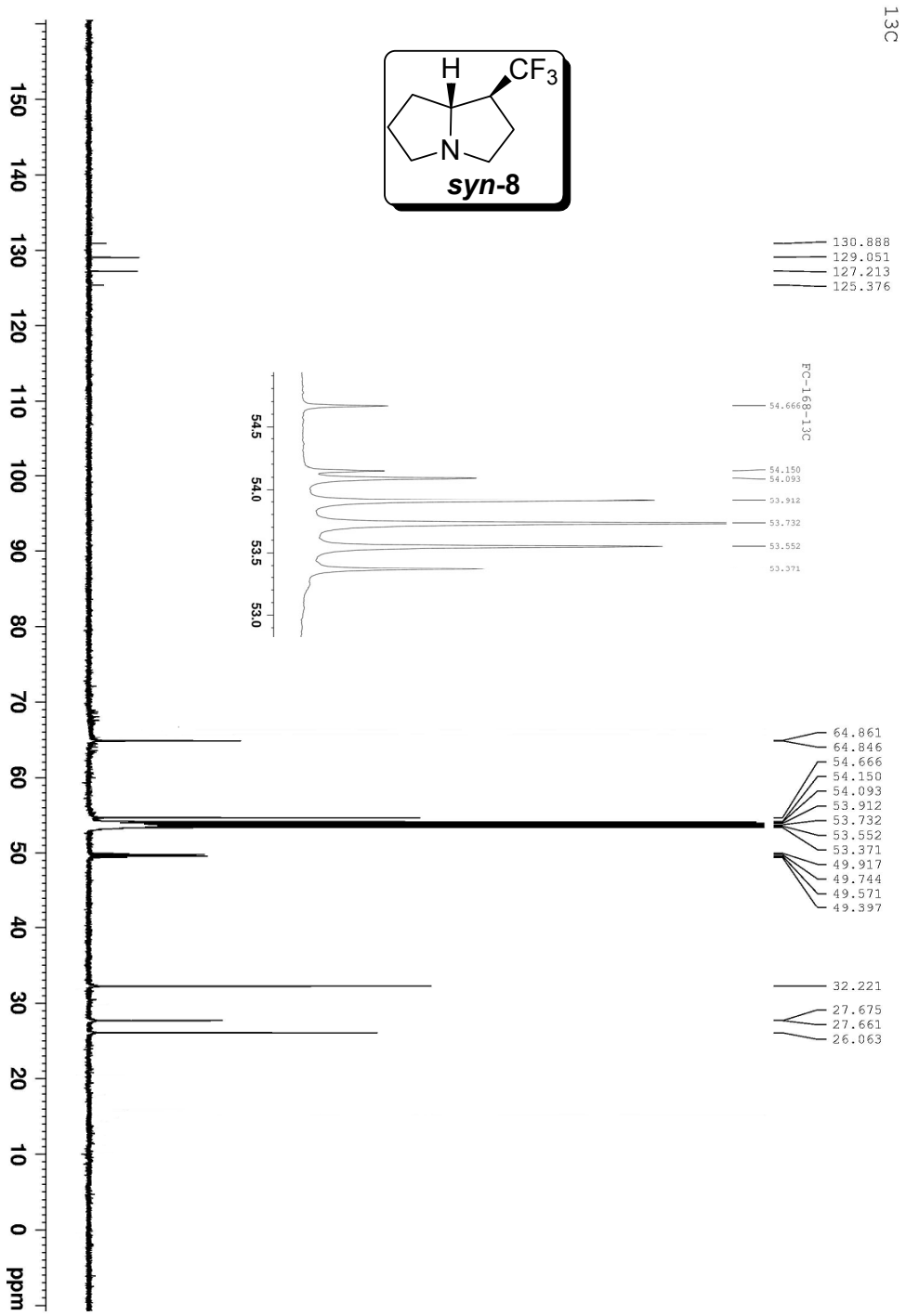
^{19}F NMR ($CDCl_3$, 188 MHz)



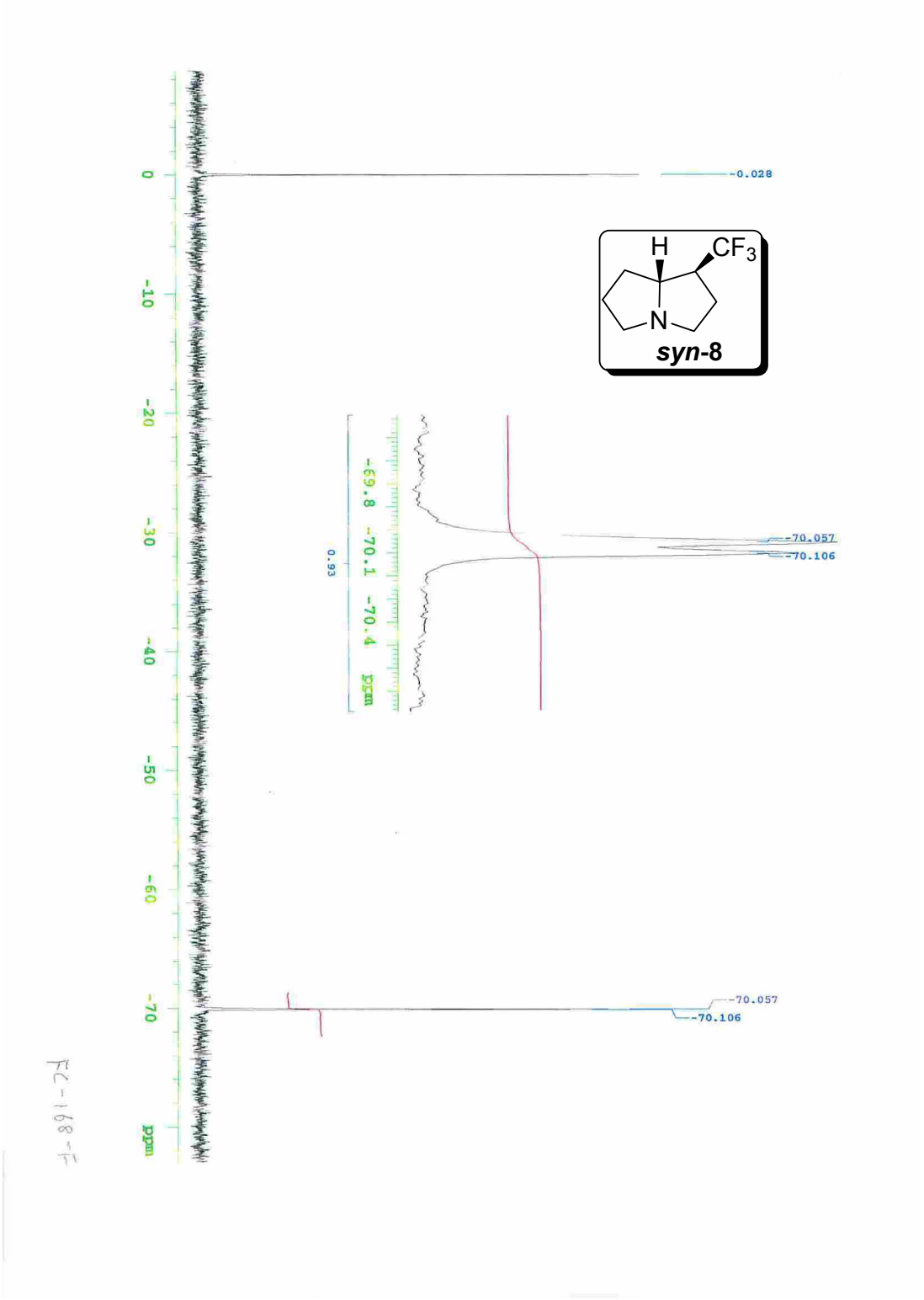
2D NMR, ^{1}H-^{1}H COSY ($CDCl_3$,600 MHz)



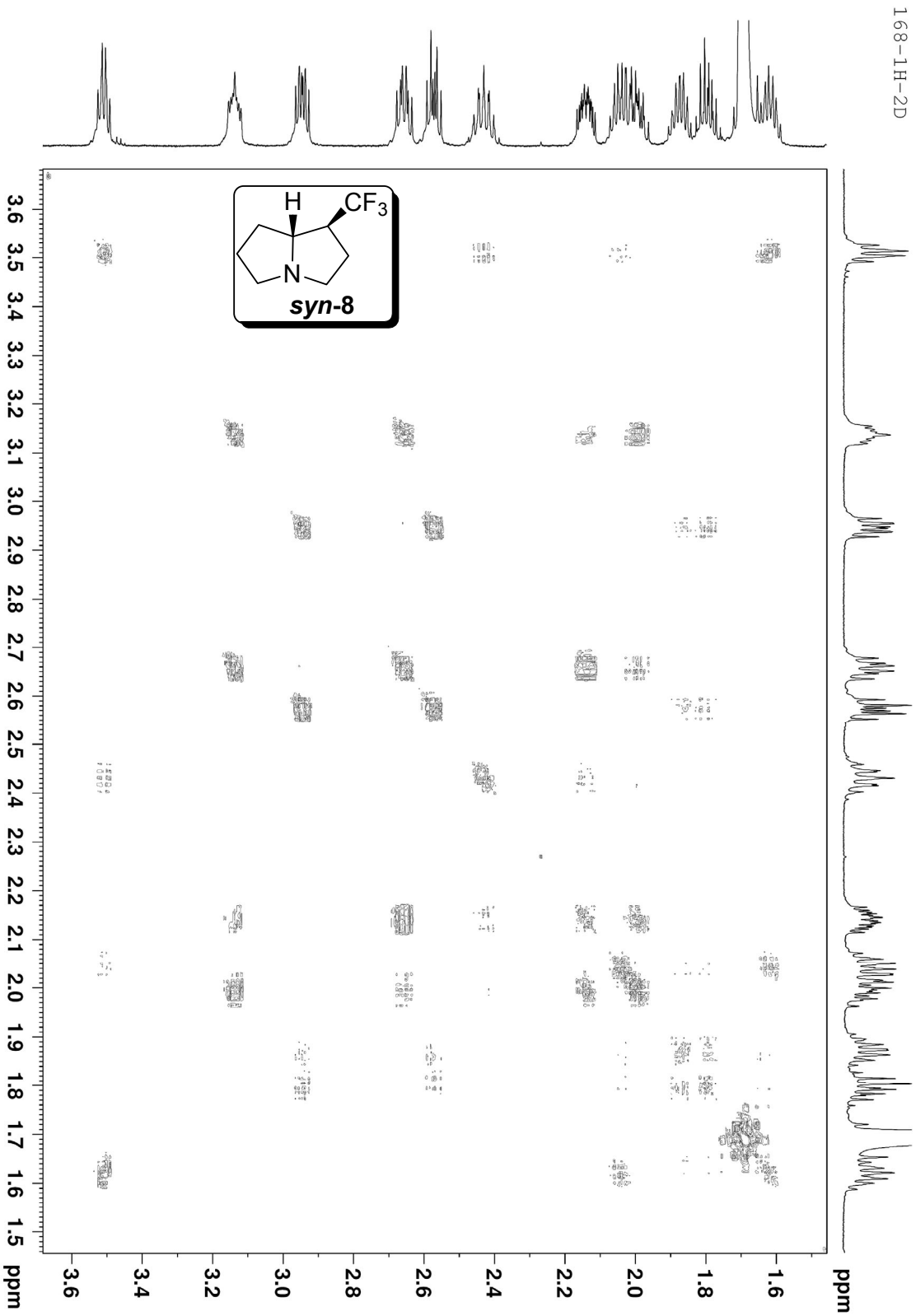
^{1}H NMR (CD_2Cl_2, 600 MHz)



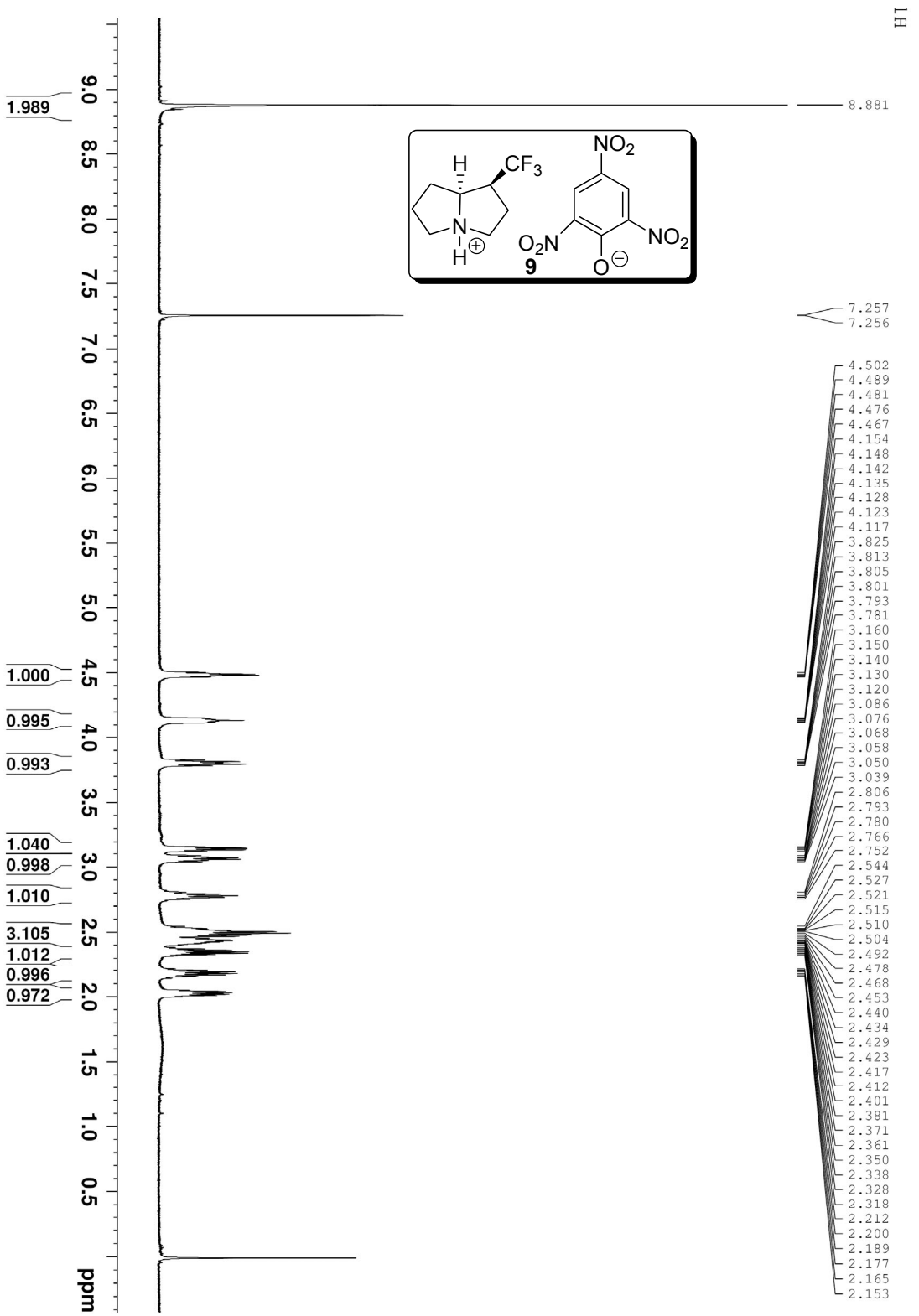
^{13}C NMR (CD_2Cl_2, 150.9 MHz)



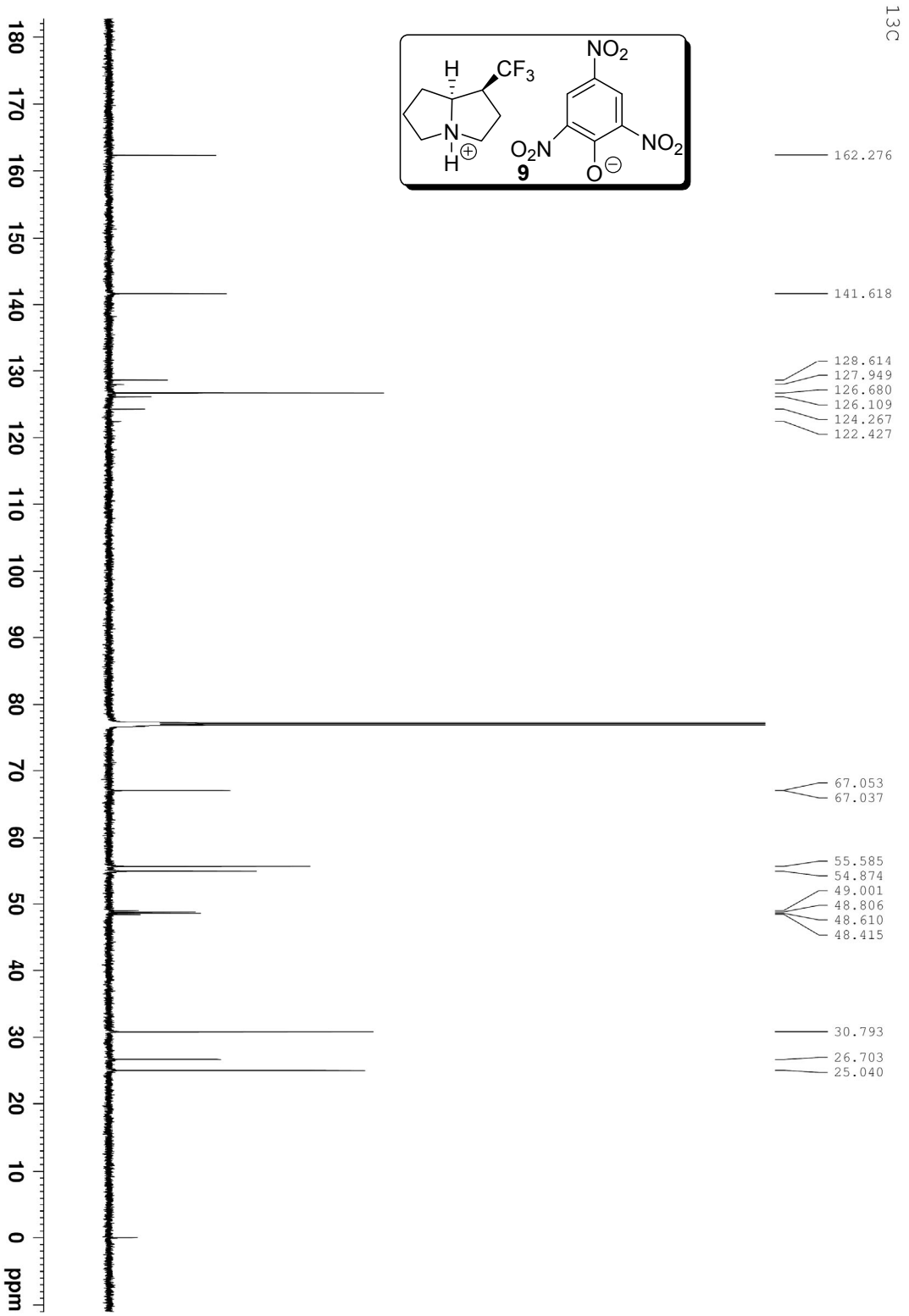
^{19}F NMR (CD_2Cl_2, 188 MHz)



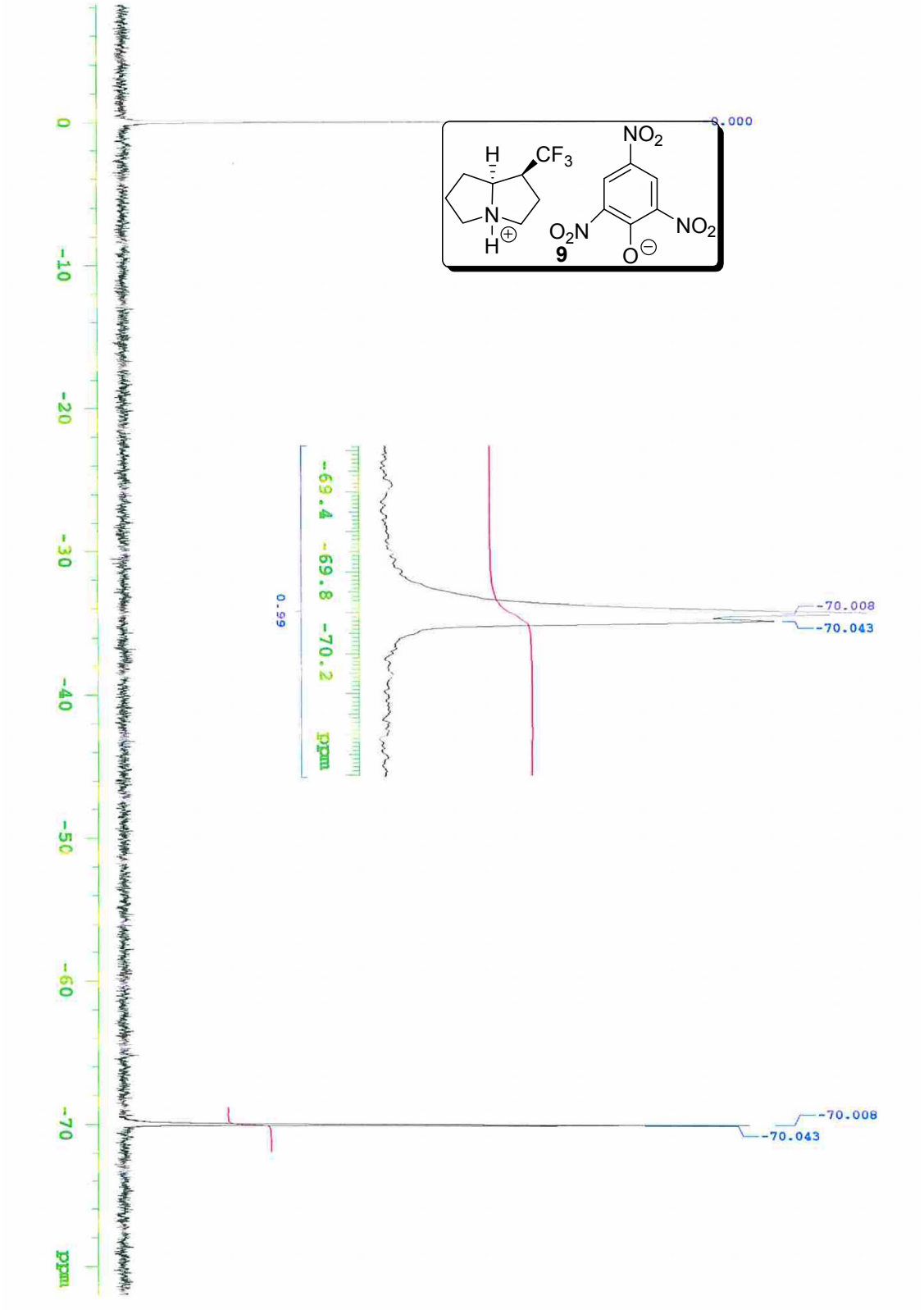
2D NMR, ^{1}H-^{1}H COSY (CD_2Cl_2,600 MHz)



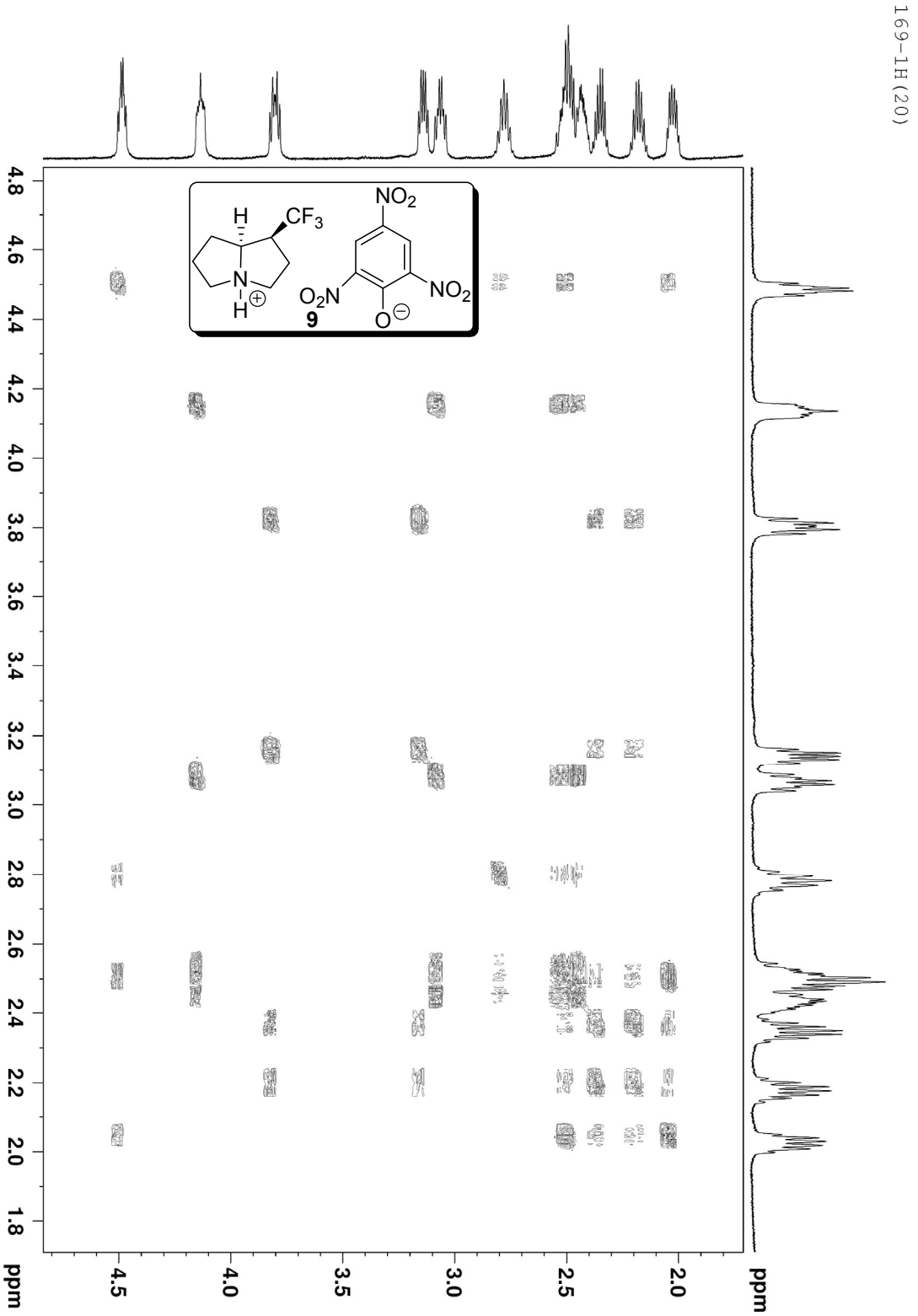
^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 150.9 MHz)



^{19}F NMR ($CDCl_3$, 188 MHz)



2D NMR, ^{1}H-^{1}H COSY ($CDCl_3$, 600 MHz)