Supporting Information

for

Regioselective 1,4-trifluoromethylation of α,β-unsaturated ketones via a *S*-(trifluoromethyl)diphenylsulfonium salts/copper system

Satoshi Okusu[1], Yutaka Sugita[1], Etsuko Tokunaga[1] and Norio Shibata*[1]

Address: [1] Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan

Email: Norio Shibata* - nozshiba@nitech.ac.jp

* Corresponding author

Experimental section

General methods:

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels though a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F_{254}). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat. Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63–210 μm. The ^{1}H-NMR (300 MHz), ^{19}F NMR (282 MHz), ^{13}C NMR (150.9 MHz) spectra in $CDCl_3$ were recorded on a Buruker Avance 600 and a Varian Mercury 300 spectrometer. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or $CHCl_3$. The α,β-unsaturated ketones **1** were prepared according to literature. [1,2]

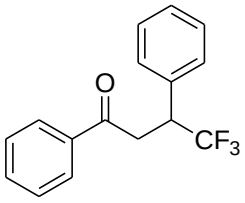
[1] A. Wilhelm, L. A. Lopez-Garcia, K. Busschots, W. Fröhner, F. Maurer, S. Boettcher, H. Zhang, J. O. Schulze, R. M. Biondi, M. Engel, *J. Med. Chem.* **2012**, *55*, 9817.

[2] B. A. Provencher, K. J. Bartelson, Y. Liu, B. M. Foxman, L. Deng, *Angew. Chem. Int. Ed.* **2011**, *50*, 10565.

General procedure for the copper mediated conjugate trifluoromethylation

A stirred solution of α,β-unsaturated ketones **1** (0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) was heated at 60 °C for 12 h. After cooling down to room temperature, the reaction mixture was extracted with Et_2O, and the combined organic layers was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give β-trifluoromethylated ketone **2**.

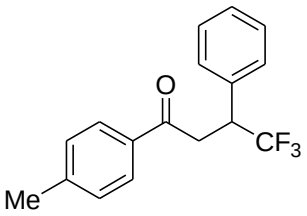
4,4,4-Trifluoro-1,3-diphenyl-1-butanone (2a)[3]



A reaction of **1a** (41.7 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give β-trifluoromethylated ketone **2a** (10.2 mg, 37%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.60 (dd, *J* = 3.9, 17.4 Hz, 1H), 3.71 (ddd, *J* = 1.1, 8.3, 18.3 Hz, 1H), 4.19-4.32 (m, 1H), 7.26-7.49 (m, 7H), 7.55-7.61 (m, 1H), 7.93 (d, 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 38.3, 44.8 (q, *J* = 27.2 Hz), 126.9 (q, *J* = 277.2 Hz), 128.02, 128.3, 128.68, 128.71, 129.0, 133.6, 134.6, 136.3, 195.3; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.2 (d, *J* = 9.9 Hz, 3F); IR (KBr) 3347, 3068, 2959, 1966, 1682, 1595, 1500, 1450, 1433, 1357, 1306, 1254, 1162, 1106, 962, 880, 749, 704, 597, 517 cm^{-1}; mp = 67.0-68.0 ºC ($CHCl_3$); MS (EI, *m/z*) 278 (M^+), HRMS (EI) calcd. for $C_{16}H_{13}F_3O$ $(M)^+$: 278.0918 Found: 278.0929

4,4,4-Trifluoro-1-(4-methylphenyl)-3-phenyl-1-butanone (2b)



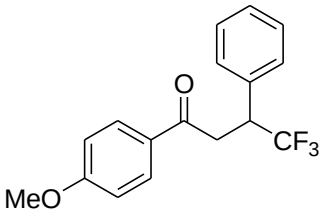
A reaction of **1b** (44.5 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give

[3] A. Morigaki, T. Tanaka, T. Miyabe, T. Ishihara, T. Konno, *Org. Biomol. Chem.* **2013**, *11*, 586.

β-trifluoromethylated ketone **2b** (11.7 mg, 20%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.40, (s, 3H), 3.53-3.60 (m, 1H), 3.68 (ddd, *J* = 1.9, 8.9, 17.8 Hz, 1H), 4.21-4.28 (m, 1H), 7.24-7.38 (m, 7H), 7.81-7.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.6, 38.1, 44.8 (q, *J* = 27.7 Hz), 127.0 (q, *J* = 279.2 Hz), 128.1, 128.2, 128.6, 129.0, 129.4, 129.8, 133.8, 134.6, 144.5, 194.9; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.1 (d, *J* = 8.7 Hz, 3F); IR (KBr) 3343, 3044, 2956, 2909, 1678, 1605, 1499, 1456, 1433, 1356, 1304, 1253, 1152, 1105, 962, 879, 821, 756, 700, 675, 591, 517 cm^{-1}; mp = 100.0-101.0 ºC ($CHCl_3$); MS (EI, *m/z*) 292 (M^+), HRMS (EI) calcd. for $C_{17}H_{15}F_3O$ $(M)^+$: 292.1075 Found: 292.1097

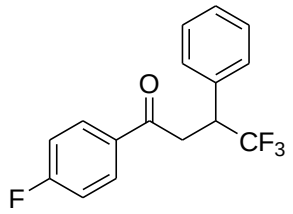
4,4,4-Trifluoro-1-(4-methoxyphenyl)-3-phenyl-1-butanone (2c)



A reaction of **1c** (47.3 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give β-trifluoromethylated ketone **2c** (6.7 mg, 11%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.53 (dd, *J* = 3.9, 17.4 Hz, 1H), 3.65 (dd, *J* = 9.0, 17.4 Hz, 1H), 3.86 (s, 3H), 4.18-4.31 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 7.29-7.40 (m, 5H), 7.91 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 37.8, 44.8 (q, *J* = 27.7 Hz), 55.5, 113.8, 127.0 (q, *J* = 283.7 Hz), 128.2, 128.6, 129.0, 129.4, 130.3, 134.7, 163.8, 193.7; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.1 (d, *J* = 8.7 Hz, 3F); IR (KBr) 3331, 3044, 2977, 2941, 2909, 2845, 2582, 1673, 1604, 1573, 1512, 1423, 1305, 1258, 1149, 1105, 1032, 961, 848, 757, 700, 595 cm^{-1}; mp = 86.5-87.5 ºC ($CHCl_3$); MS (EI, *m/z*) 308 (M^+), HRMS (EI) calcd. for $C_{17}H_{15}F_3O_2$ $(M)^+$: 308.1024 Found: 308.1043

4,4,4-Trifluoro-1-(4-fluorophenyl)-3-phenyl-1-butanone (2d)

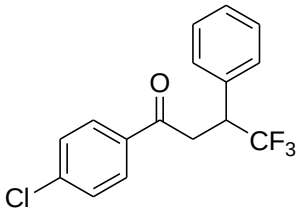


A reaction of **1d** (45.3 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give

β-trifluoromethylated ketone **2d** (7.9 mg, 13%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.47-3.59 (m, 1H), 3.62-3.71 (m, 1H), 4.23 (m, 1H), 7.10-7.15 (m, 2H), 7.32-7.37 (m, 5H), 7.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 38.2, 44.8 (q, *J* = 27.7 Hz), 115.9 (d, 22.6 Hz), 126.9 (q, *J* = 278.7 Hz), 128.3, 128.7, 129.0, 130.7 (d, 9.1 Hz), 132.7 (d, 3.0 Hz), 134.5, 166.0 (d, 255.0 Hz), 193.7; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.2 (d, *J* = 9.0 Hz, 3F), 104.7 (s, 1H); IR (KBr) 3363, 3074, 3033, 2946, 2343, 1688, 1600, 1508, 1451, 1432, 1375, 1306, 1243, 1164, 1101, 991, 878, 841, 702, 672, 625, 588, 516, 436 cm^{-1}; mp = 68.5-69.5 ºC ($CHCl_3$); MS (EI, *m/z*) 296 (M^+), HRMS (EI) calcd. for $C_{16}H_{12}F_4O$ $(M)^+$: 296.0824 Found: 296.0845

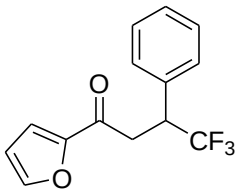
1-(4-Chlorophenyl)-4,4,4-trifluoro-3-phenyl-1-butanone (2e)



A reaction of **1e** (48.5 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give β-trifluoromethylated ketone **2e** (10.9 mg, 22%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.56 (dd, *J* = 5.3, 17.6 Hz, 1H), 3.65-3.71 (m, 1H), 4.16-4.30 (m, 1H), 7.26-7.45 (m, 7H), 7.85-7.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 38.2, 44.8 (q, *J* = 27.7 Hz), 126.9 (q, *J* = 275.6 Hz), 128.4, 128.7, 128.96, 129.04, 129.4, 134.4, 134.6, 140.1, 194.1; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.2 (d, *J* = 9.9 Hz, 3F); IR (KBr) 3358, 3096, 3066, 3036, 2937, 1686, 1590, 1490, 1455, 1402, 1303, 1246, 1222, 1164, 1105, 987, 877, 833, 754, 699, 665, 620, 458 cm^{-1}; mp = 74.0-75.0 ºC ($CHCl_3$); MS (EI, *m/z*) 312 (M^+), HRMS (EI) calcd. for $C_{16}H_{12}ClF_3O$ $(M)^+$: 312.0529 Found: 312.0524

4,4,4-Trifluoro-1-(2-furanyl)-3-phenyl-1-butanone (2f)

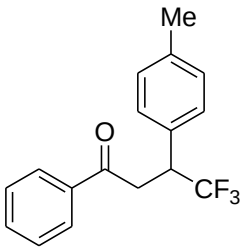


A reaction of **1f** (39.6 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:/1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give

β-trifluoromethylated ketone **2f** (7.2 mg, 13%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.45 (dd, *J* = 4.8, 17.4 Hz, 1H), 3.56 (dd, *J* = 8.7, 17.4 Hz, 1H), 4.16-4.24 (m, 1H), 6.52-6.54 (m, 1H), 7.18-7.19 (m, 1H), 7.26-7.37 (m, 5H), 7.58 (s, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 38.0, 44.4 (q, *J* = 27.7 Hz), 112.5, 117.5, 126.8 (q, *J* = 277.2 Hz), 128.3, 128.7, 129.0, 134.2, 146.7, 152.2, 184.6; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.3 (d, *J* = 9.9 Hz, 3F); IR (KBr) 3316, 3099, 3065, 3046, 2960, 2924, 2856, 2727, 2643, 2547, 2467, 2358, 2113, 1965, 1901, 1500, 843, 800, 541, 455 cm^{-1}; mp = 84.5-85.5 ºC ($CHCl_3$); MS (EI, *m/z*) 268 (M^+), HRMS (EI) calcd. for $C_{14}H_{11}F_3O_2$ $(M)^+$: 268.0711 Found: 268.0688

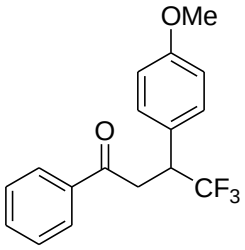
4,4,4-Trifluoro-3-(4- methylphenyl)-1-phenyl-1-butanone (2g)[3]



A reaction of **1g** (44.5 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give β-trifluoromethylated ketone **2g** (6.9 mg, 12%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.31, (s, 3H), 3.55-3.61 (m, 1H), 3.69 (dd, *J* = 9.2, 17.6 Hz, 1H), 4.18-4.21 (m, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.55-7.57 (m, 1H), 7.93 (d, 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.1, 38.2, 44.4 (q, *J* = 28.7 Hz), 127.1 (q, *J* = 284.7 Hz), 128.0, 128.7, 128.8, 129.4, 131.5, 133.5, 136.3, 138.1, 195.4; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.3 (d, *J* = 9.9 Hz, 3F); IR (KBr) 3347, 3040, 2921, 1683, 1595, 1519, 1450, 1428, 1306, 1254, 1186, 1150, 1098, 1000, 885, 809, 765, 742, 685, 632, 599, 511 cm^{-1}; mp = 94.5-95.0 ºC ($CHCl_3$); MS (EI, *m/z*) 292 (M^+), MS (EI, *m/z*) 292 (M^+), HRMS (EI) calcd. for $C_{17}H_{15}F_3O$ $(M)^+$: 292.1075 Found: 292.1074

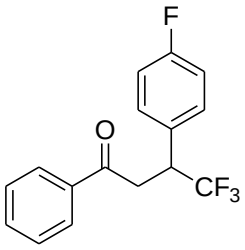
4,4,4-Trifluoro-3-(4-methoxyphenyl)-1-phenyl-1-butanone (2h)[3]



A reaction of **1h** (47.7 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give β-trifluoromethylated ketone **2h** (7.4 mg, 12%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.56 (dd, *J* = 4.1, 17.6 Hz, 1H), 3.67 (dd, *J* = 9.0, 17.4 Hz, 1H), 3.77 (s, 3H), 4.13-4.26 (m, 1H), 6.86 (d, 8.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 38.3, 44.0 (q, *J* = 27.7 Hz), 55.2, 114.1, 126.5, 127.0 (q, *J* = 279.2 Hz), 128.0, 128.7, 130.1, 133.5, 136.3, 159.4, 195.4; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.5 (d, *J* = 9.9 Hz, 3F); IR (KBr) 3005, 2961, 2840, 1684, 1614, 1518, 1449, 1431, 1307, 1245, 1181, 1163, 1097, 1034, 962, 884, 819, 765, 685, 598, 531 cm^{-1}; mp = 89.0-90.0 ºC ($CHCl_3$); MS (EI, *m/z*) 308 (M^+), HRMS (EI) calcd. for $C_{17}H_{15}F_3O_2$ $(M)^+$: 308.1024 Found: 308.1048

4,4,4-Trifluoro-3-(4-fluorophenyl)-1-phenyl-1-butanone (2i)

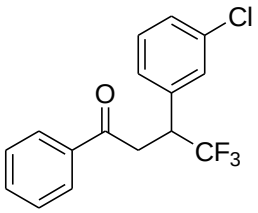


A reaction of **1i** (45.3 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give β-trifluoromethylated ketone **2i** (10.1 mg, 17%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.59 (dd, *J* = 4.5, 17.6 Hz, 1H), 3.66-3.72 (m, 1H), 4.17-4.31 (m, 1H), 7.00-7.06 (m, 2H), 7.37 (t, *J* = 6.5 Hz, 2H), 7.44-7.49 (m, 2H), 7.57-7.61 (m, 1H), 7.92 (d, 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 38.3, 44.1 (q, *J* = 27.7 Hz), 115.7 (d, *J* = 21.1 Hz), 126.8 (q, J = 279.7 Hz), 128.0, 128.8, 130.3, 130.7 (d, J = 7.5 Hz), 133.7, 136.2, 162.6 (d, *J* = 247.5 Hz), 195.1; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.4 (d, *J* = 9.9 Hz, 3F), -114.3 (s, 1F); IR (KBr) 3351, 3060, 2925,

1687, 1596, 1518, 1450, 1427, 1308, 1257, 1167, 1149, 1112, 961, 922, 890, 828, 744, 722, 686, 598, 525, 492 cm^{-1}; mp = 97.5-98.5 ºC ($CHCl_3$); MS (EI, *m/z*) 296 (M^+), HRMS (EI) calcd. for $C_{16}H_{12}F_4O$ $(M)^+$: 296.0824 Found: 296.0842

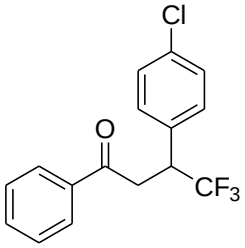
3-(3-Chlorophenyl)-4,4,4-trifluoro-1-phenyl-1-butanone (2j)[3]



A reaction of **1j** (48.4 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give β-trifluoromethylated ketone **2j** (11.5 mg, 18%) as a colorless oil.

^1H NMR ($CDCl_3$, 300 MHz) δ 3.58-3.72 (m, 2H), 4.22-4.27 (m, 1H), 7.27-7.29 (m, 3H), 74.0 (s, 1H), 7.47 (t, *J* = 6.9 Hz, 2H), 7.57-7.62 (m, 1H), 7.92-7.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 38.2, 44.5 (q, *J* = 27.7 Hz), 126.6 (q, *J* = 279.7 Hz), 127.4, 128.0, 128.6, 128.8, 129.1, 129.9, 133.7, 134.5, 136.0, 136.5, 194.9; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.0 (d, *J* = 9.0 Hz, 3F); IR (neat) 3065, 2921, 1692, 1598, 1577, 1478, 1449, 1301, 1256, 1158, 1109, 1002, 908, 782, 755, 688, 608, 496, 486, 468, 458, 428 cm^{-1}; MS (EI, *m/z*) 312 (M^+), HRMS (EI) calcd. for $C_{16}H_{12}ClF_3O$ $(M)^+$: 312.0529 Found: 312.0558

3-(4-Chlorophenyl)-4,4,4-trifluoro-1-phenyl-1-butanone (2k)[3]

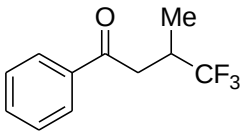


A reaction of **1k** (48.4 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give β-trifluoromethylated ketone **2k** (7.9 mg, 13%) as a white solid.

^1H NMR ($CDCl_3$, 300 MHz) δ 3.56-3.66 (m, 2H), 4.20-4.24 (m, 1H), 7.26-7.33 (m, 4H), 7.47 (t, *J* = 6.9 Hz, 2H), 7.59 (t, *J* = 6.6 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 38.1, 44.3 (q, *J* = 27.2 Hz), 126.6 (q, *J* = 272.1 Hz), 128.0, 128.8, 128.9, 130.3, 133.0, 133.7, 134.3, 136.1,

195.0; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -70.2 (d, *J* = 9.9 Hz, 3F); IR (KBr) 3347, 3064, 2923, 1685, 1595, 1496, 1450, 1426, 1308, 1250, 1154, 1101, 1015, 888, 823, 778, 753, 728, 685, 625, 596, 518, 425 cm^{-1}; mp = 101.0-102.0 ºC ($CHCl_3$); MS (EI, *m/z*) 312 (M^+), HRMS (EI) calcd. for $C_{16}H_{12}ClF_3O$ $(M)^+$: 312.0529 Found: 312.0544

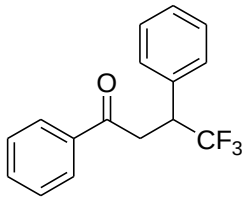
4,4,4-Trifluoro-3-methyl-1-phenyl-1-butanone (2l)[4]



A reaction of **1l** (29.2 mg, 0.20 mmol), trifluoromethylsulfonium triflate **3a** (323 mg, 0.80 mmol, 4.0 equiv) and Cu (76.3 mg, 1.20 mmol, 6.0 equiv) in DMSO/H_2O (1:1, 1.0 mL) at 60 ºC for 12 h, and a purification by column chromatography on silica gel (*n*-hexane/benzene 8:2) to give β-trifluoromethylated ketone **2l** (15.4 mg, 36%) as a colorless oil.

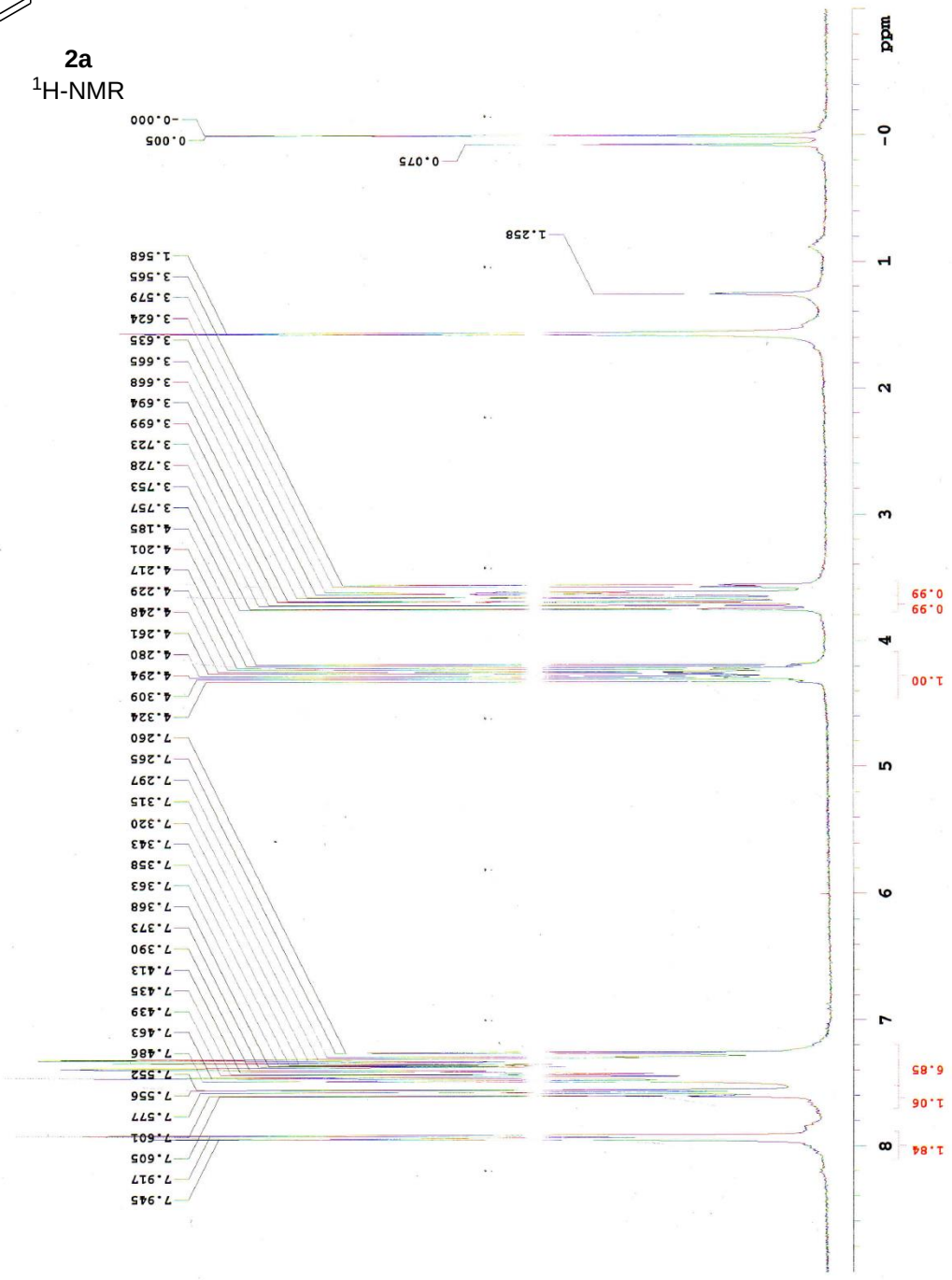
^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.19 (d, J = 5.7 Hz, 3H), 3.01-3.05 (m, 2H), 3.29-3.33 (m, 1H), 7.47-7.61 (m, 3H), 7.97 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 13.2 (d, J = 1.5 Hz), 33.9 (q, *J* = 27.7 Hz), 38.4 (d, 1.5 Hz), 128.0, 128.3 (q, *J* = 278.7 Hz), 128.7, 133.5, 136.4, 196.3; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -74.0 (d, *J* = 7.9 Hz, 3F); IR (neat) 2988, 2950, 1779, 1690, 1598, 1581, 1449, 1387, 1347, 1301, 1268, 1216, 1173, 1127, 1081, 1022, 992, 920, 754, 689, 624, 501, 460 cm^{-1}; MS (EI, *m/z*) 216 (M^+), HRMS (EI) calcd. for $C_{11}H_{11}F_3O$ $(M)^+$: 216.0762 Found: 216.0743

[4] V. Bizet, X. Pannecoucke, J.-L. Renaud, D. Cahard, *Angew. Chem. Int. Ed.* **2012**, *51*, 6467.


O
CF3

2a

^{1}H-NMR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0.005
0.075
1.258
1.568
3.565
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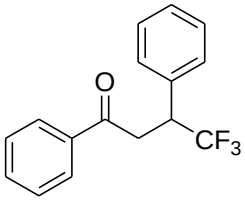
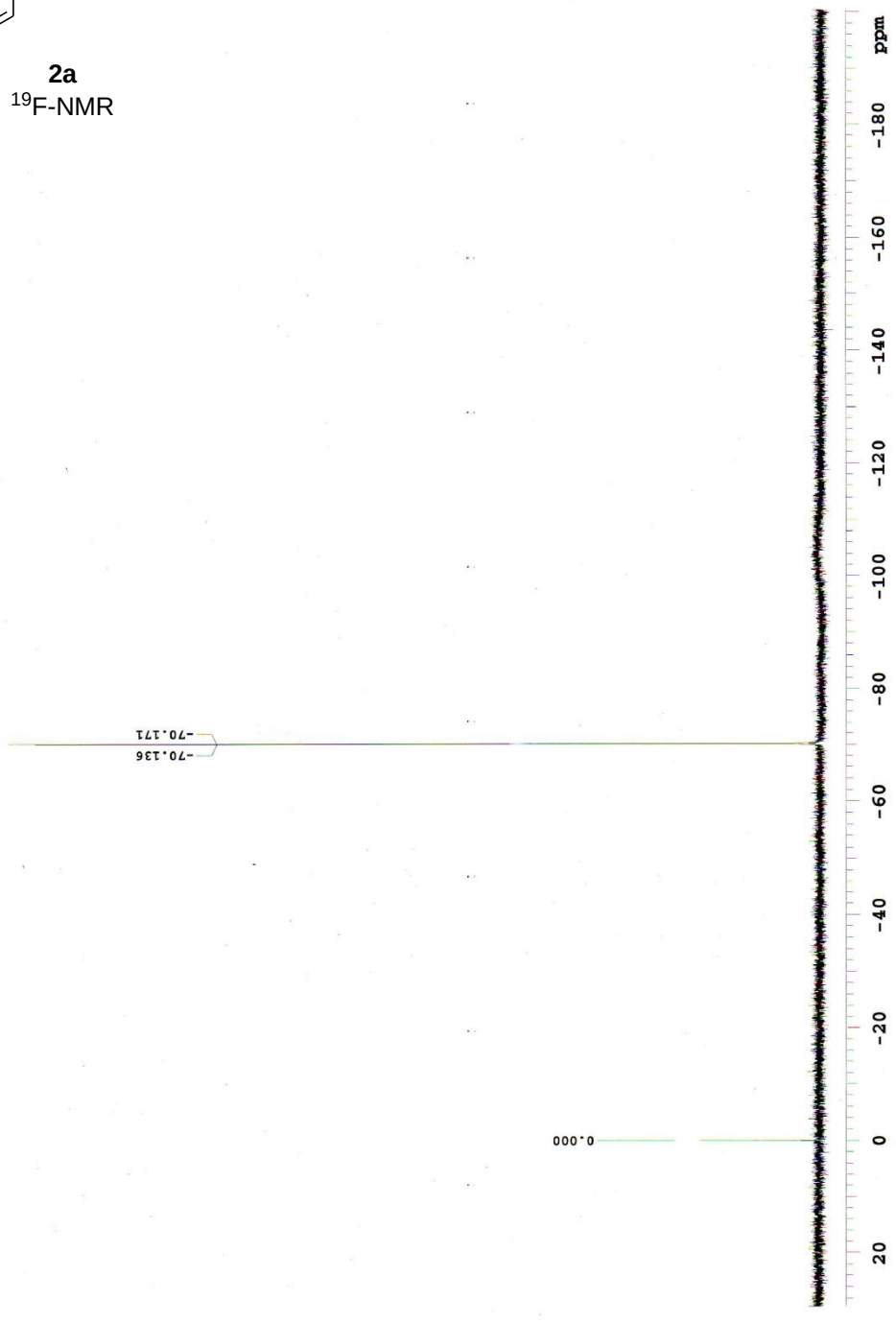
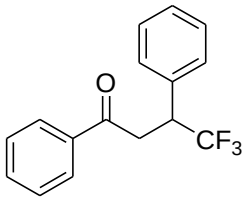
3.624
3.635
3.665
3.668
3.694
3.699
3.723
3.728
3.753
3.757
4.185
4.201
4.217
4.229
4.248
4.261
4.280
4.294
4.309
4.324
7.260
7.265
7.297
7.315
7.320
7.343
7.358
7.363
7.368
7.373
7.390
7.413
7.435
7.439
7.463
7.486
7.552
7.556
7.577
7.601
7.605
7.917
7.945
ppm
0.99
0.99
1.00
6.85
1.06
1.84



2a

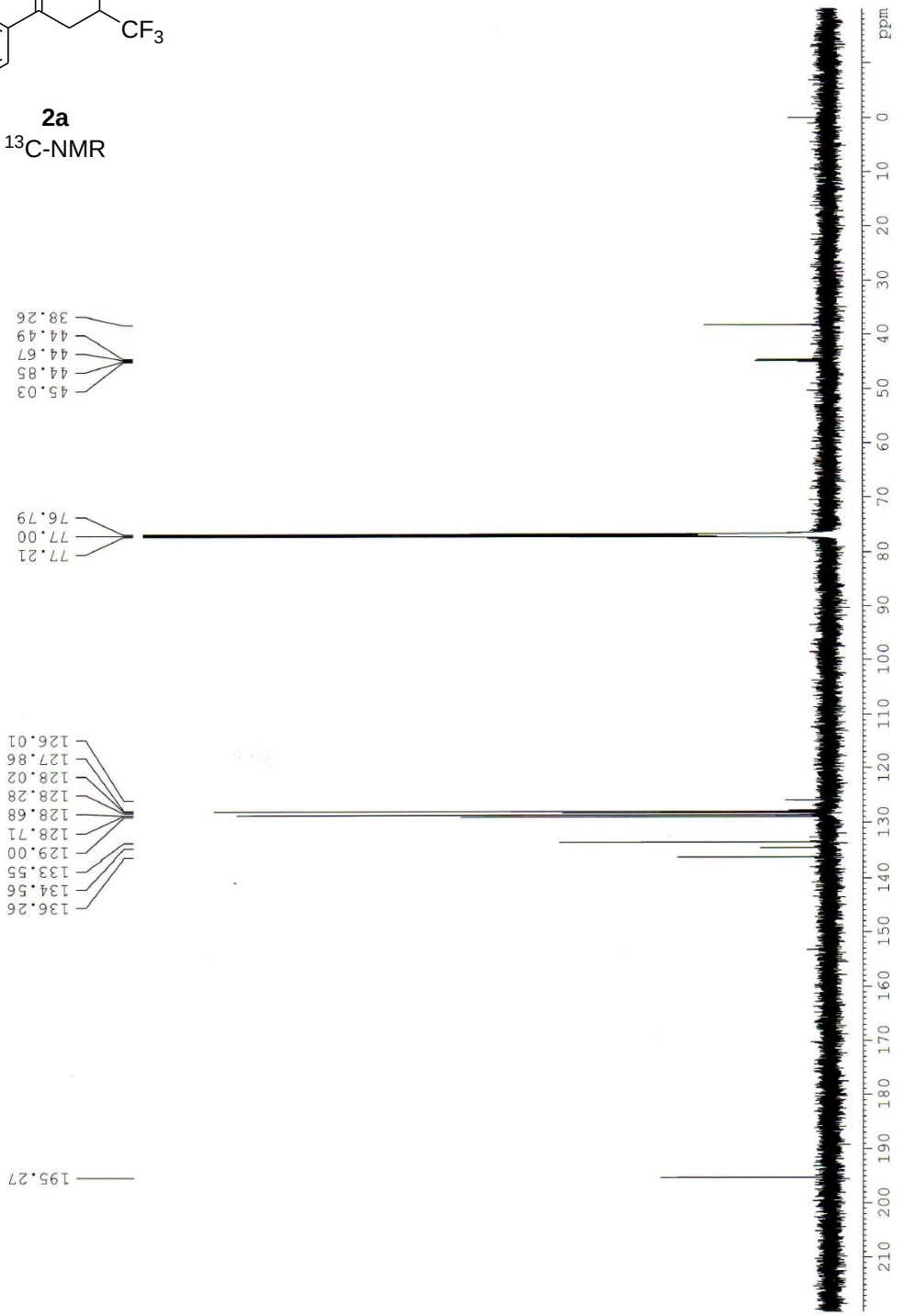
^{19}F-NMR

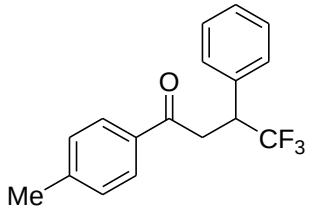



O
CF3

2a

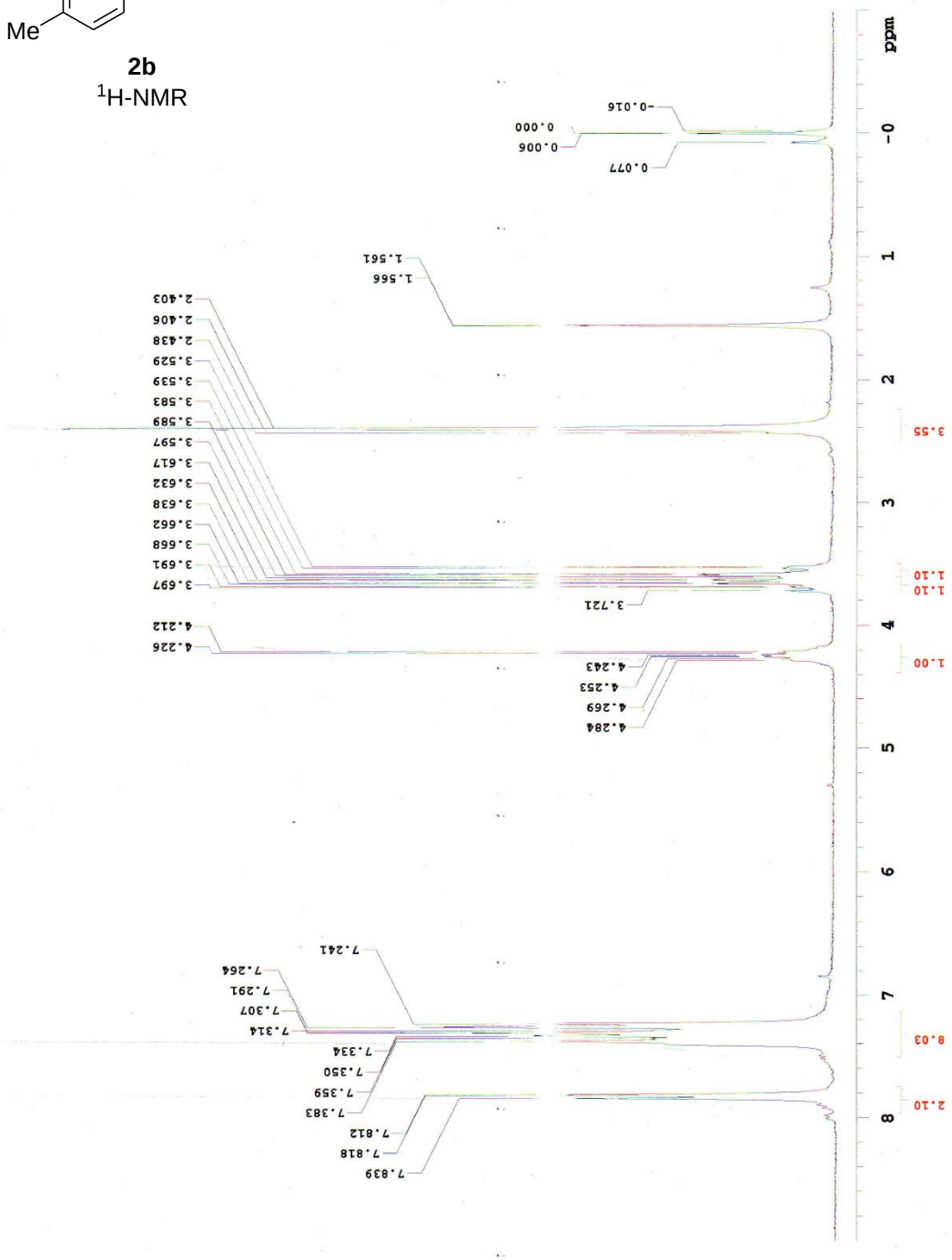
^{13}C-NMR


38.26
44.49
44.67
44.85
45.03
76.79
77.00
77.21
126.01
127.86
128.02
128.28
128.68
128.71
129.00
133.55
134.56
136.26
195.27
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


O
CF3
Me

2b

^{1}H-NMR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0.006
0.077
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1.566
2.403
2.406
2.438
3.529
3.539
3.583
3.589
3.597
3.617
3.632
3.638
3.662
3.668
3.691
3.697
3.721
4.212
4.226
4.243
4.253
4.269
4.284
7.241
7.264
7.291
7.307
7.314
7.334
7.350
7.359
7.383
7.812
7.818
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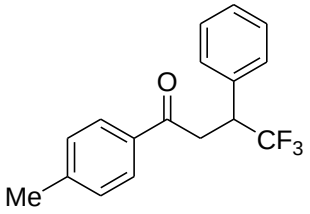
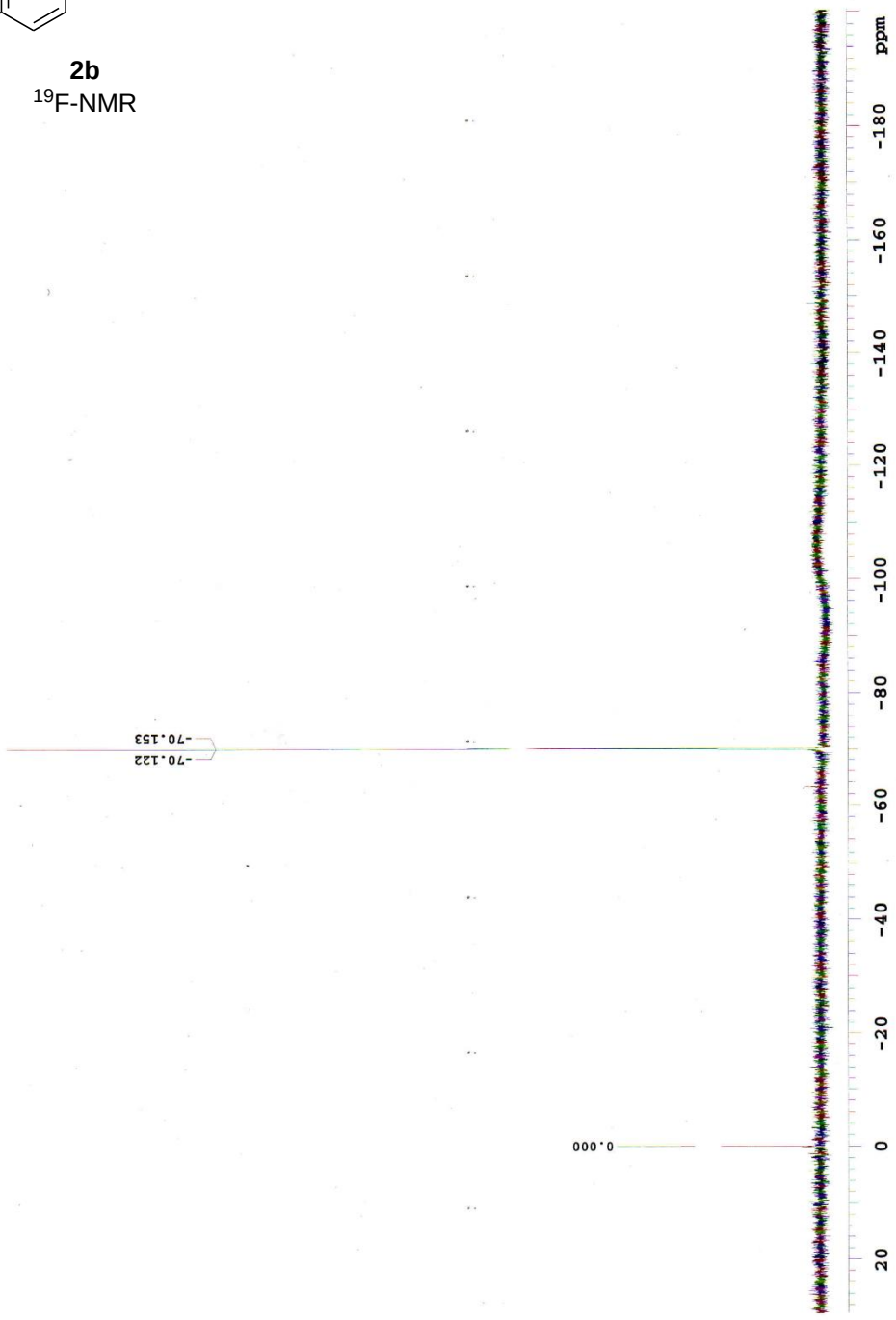
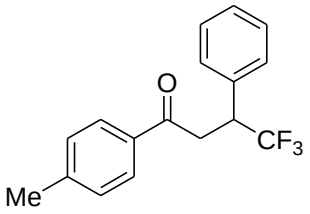
3.55
1.10
1.10
1.00
8.03
2.10



2b

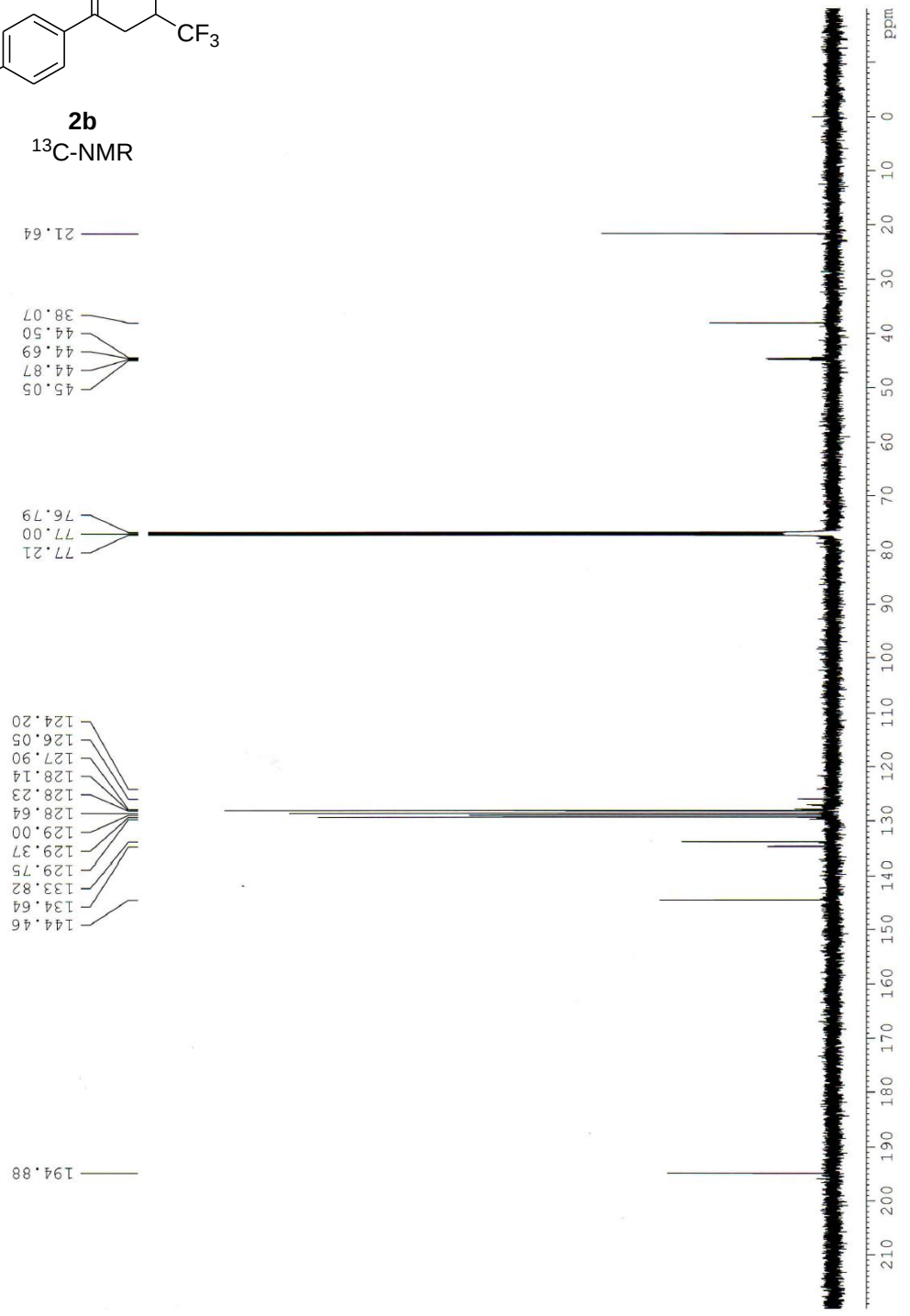
^{19}F-NMR

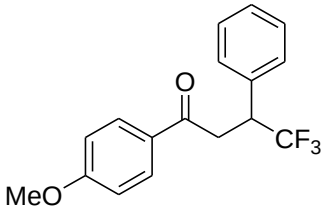



O
CF3
Me

2b

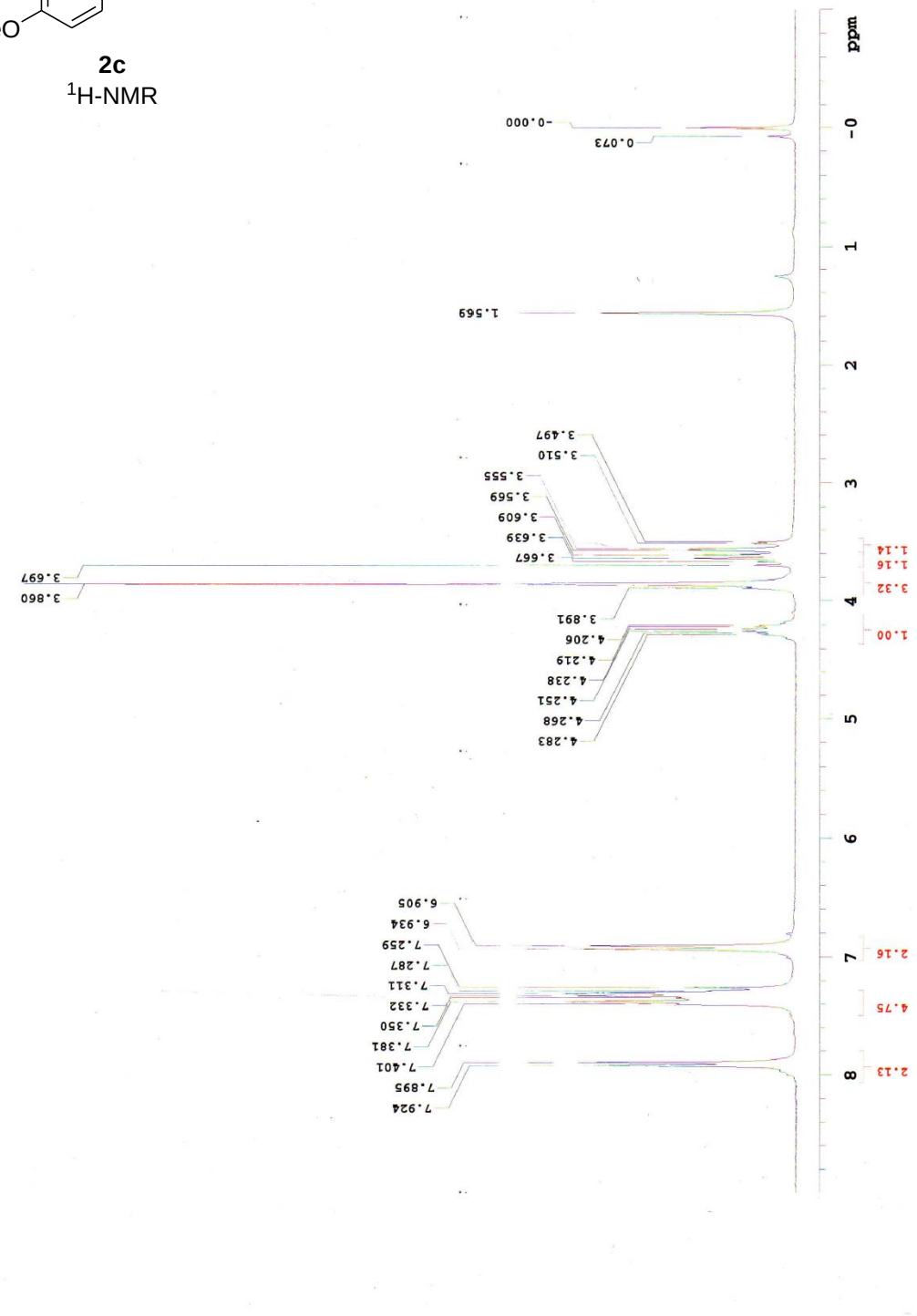
^{13}C-NMR


21.64
38.07
44.50
44.69
44.87
45.05
76.79
77.00
77.21
124.20
126.05
127.90
128.14
128.23
128.64
129.00
129.37
129.75
133.82
134.64
144.46
194.88
ppm


O
CF3
MeO

2c

^{1}H-NMR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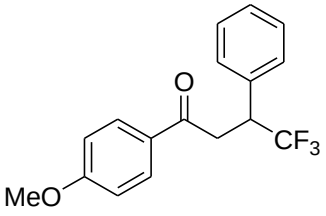
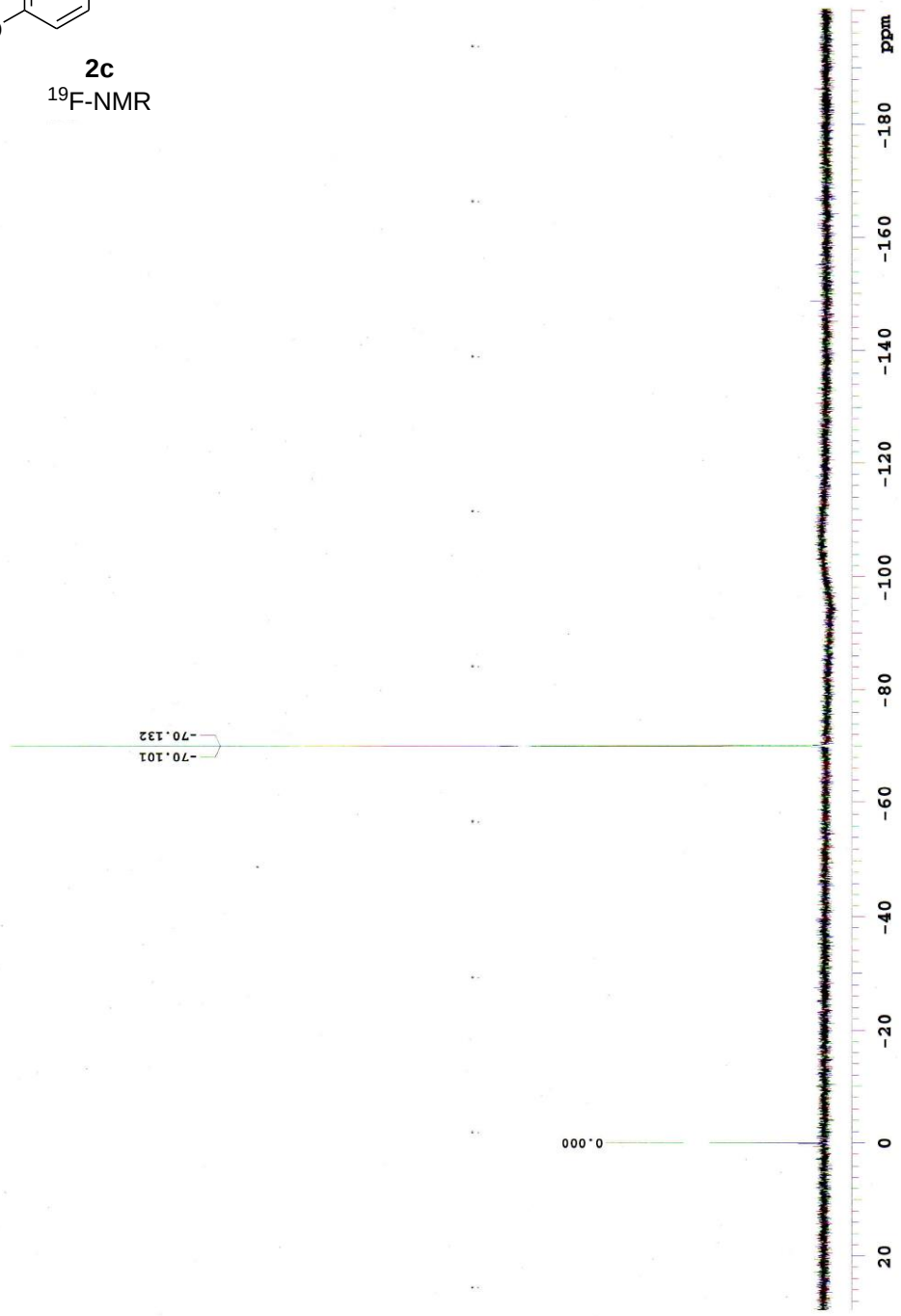
3.497
3.510
3.555
3.569
3.609
3.639
3.667
3.687
3.860
3.891
4.206
4.219
4.238
4.251
4.268
4.283
6.905
6.934
7.259
7.287
7.311
7.332
7.350
7.381
7.401
7.895
7.924
1.14
1.16
3.32
1.00
2.16
4.75
2.13


O
CF3
MeO

2c

^{19}F-NMR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-70.132
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ppm
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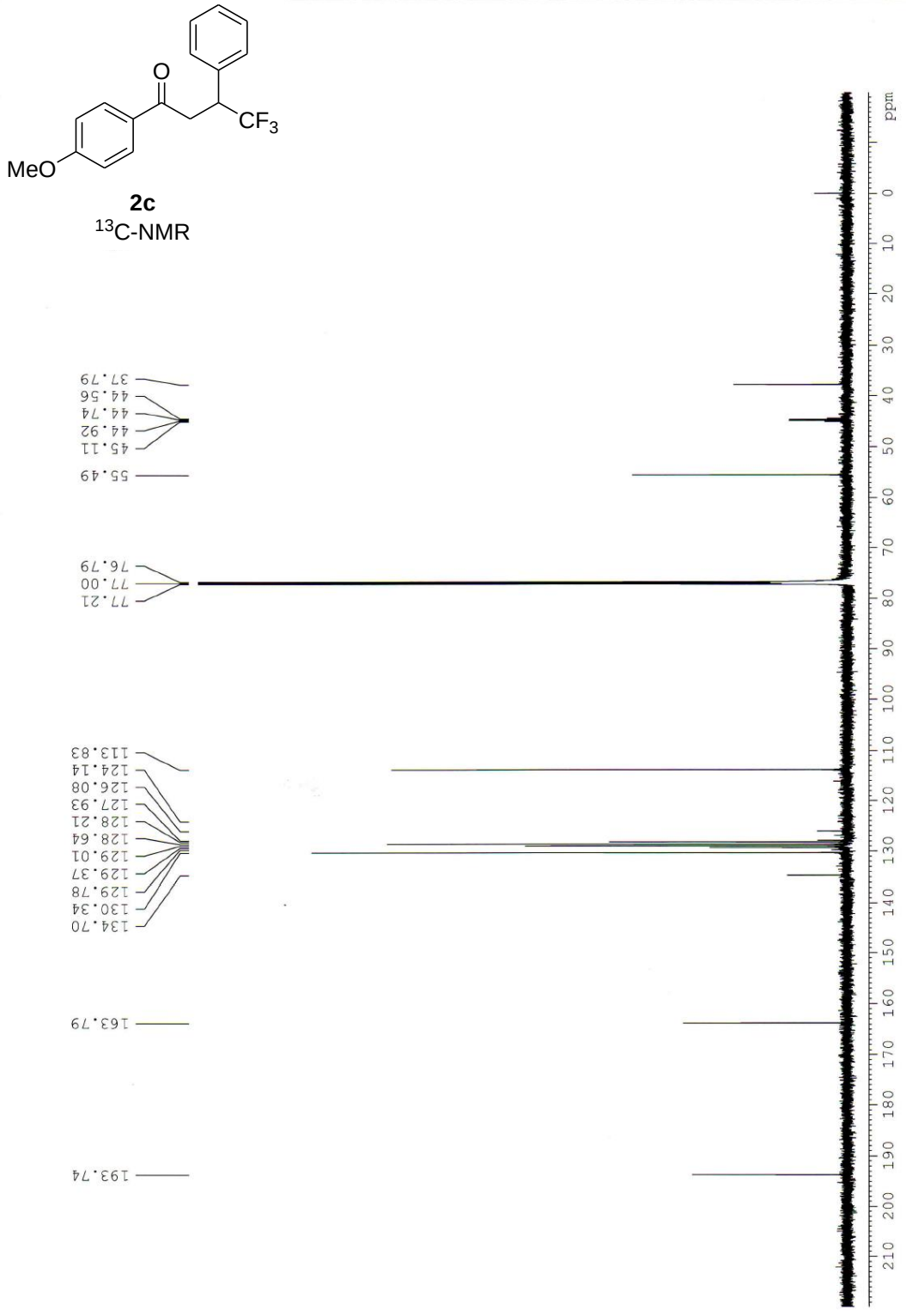
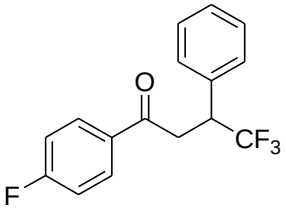
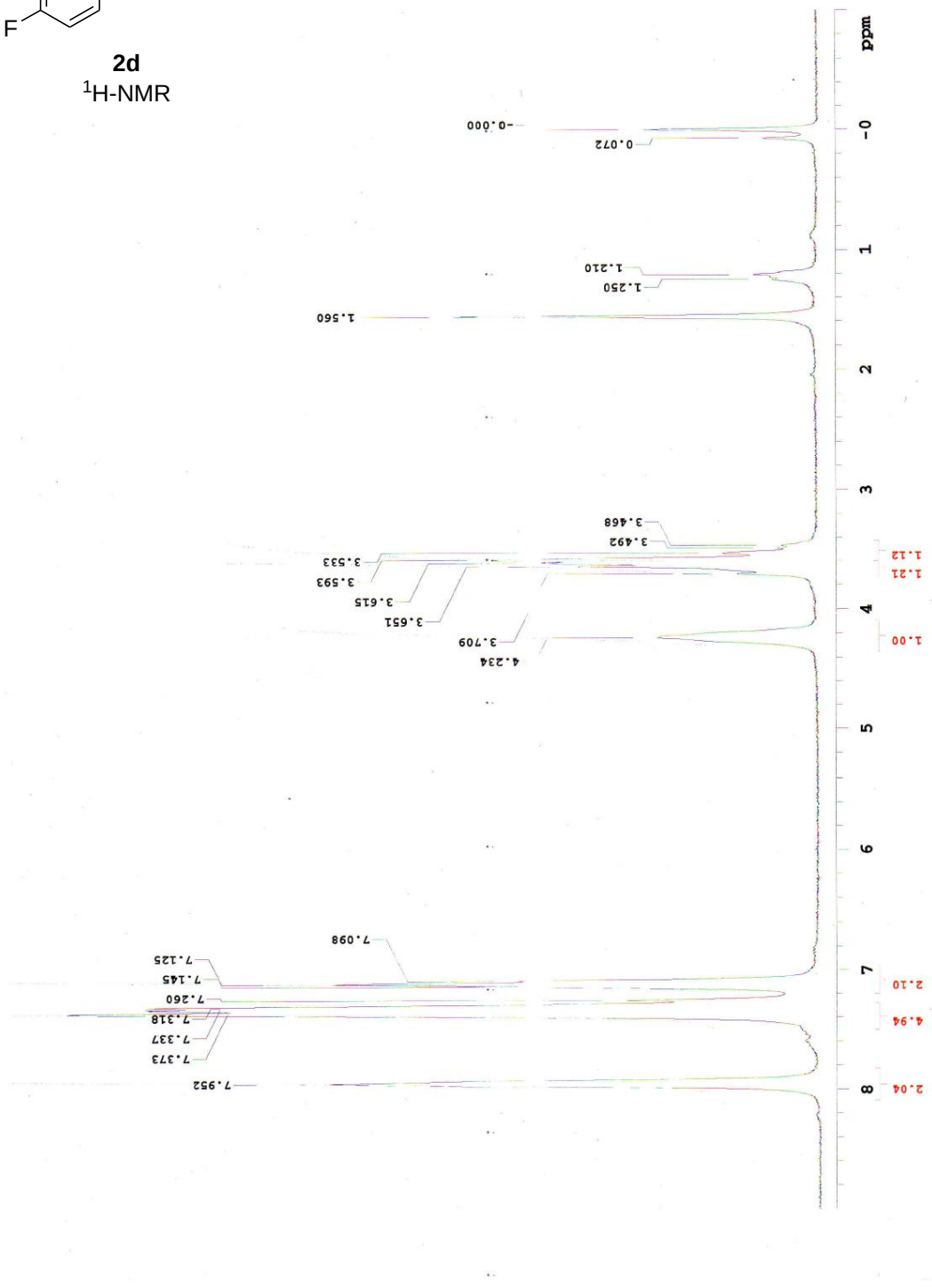
0
-20
-40
-60
-80
-100
-120
-140
-160
-180


O
CF3
MeO
2c
13C-NMR
37.79
44.56
44.74
44.92
45.11
55.49
76.79
77.00
77.21
113.83
124.14
126.08
127.93
128.21
128.64
129.01
129.37
129.78
130.34
134.70
163.79
193.74
ppm


O
CF3
F

2d

^{1}H-NMR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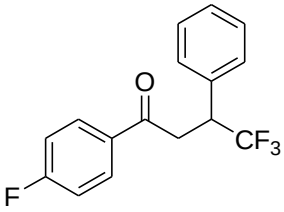
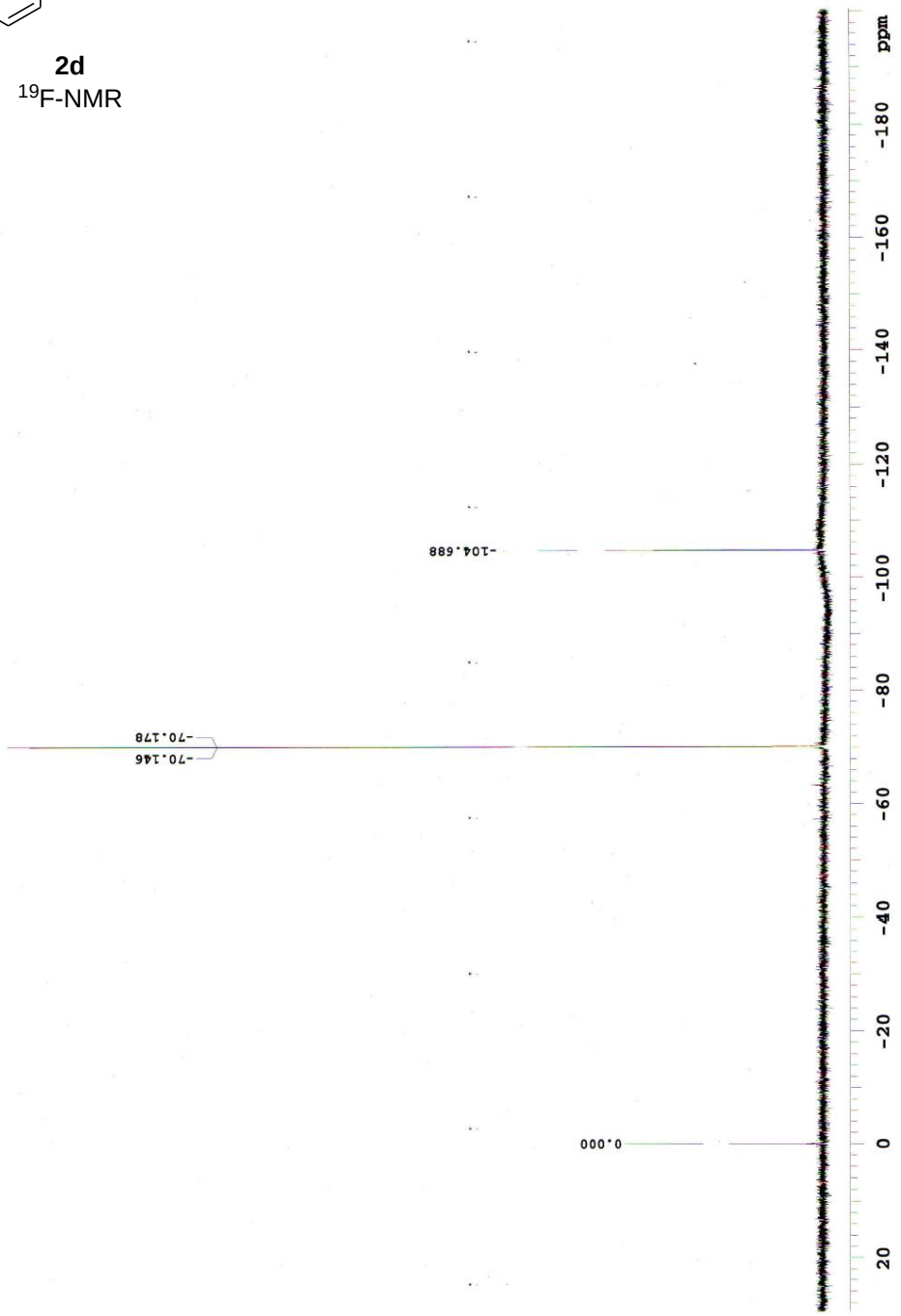
1.560
3.468
3.492
3.533
3.593
3.615
3.651
3.709
4.234
7.098
7.125
7.145
7.260
7.318
7.337
7.373
7.952
ppm
1.12
1.21
1.00
2.10
4.94
2.04


O
CF3
F

2d

^{19}F-NMR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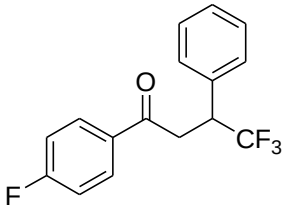
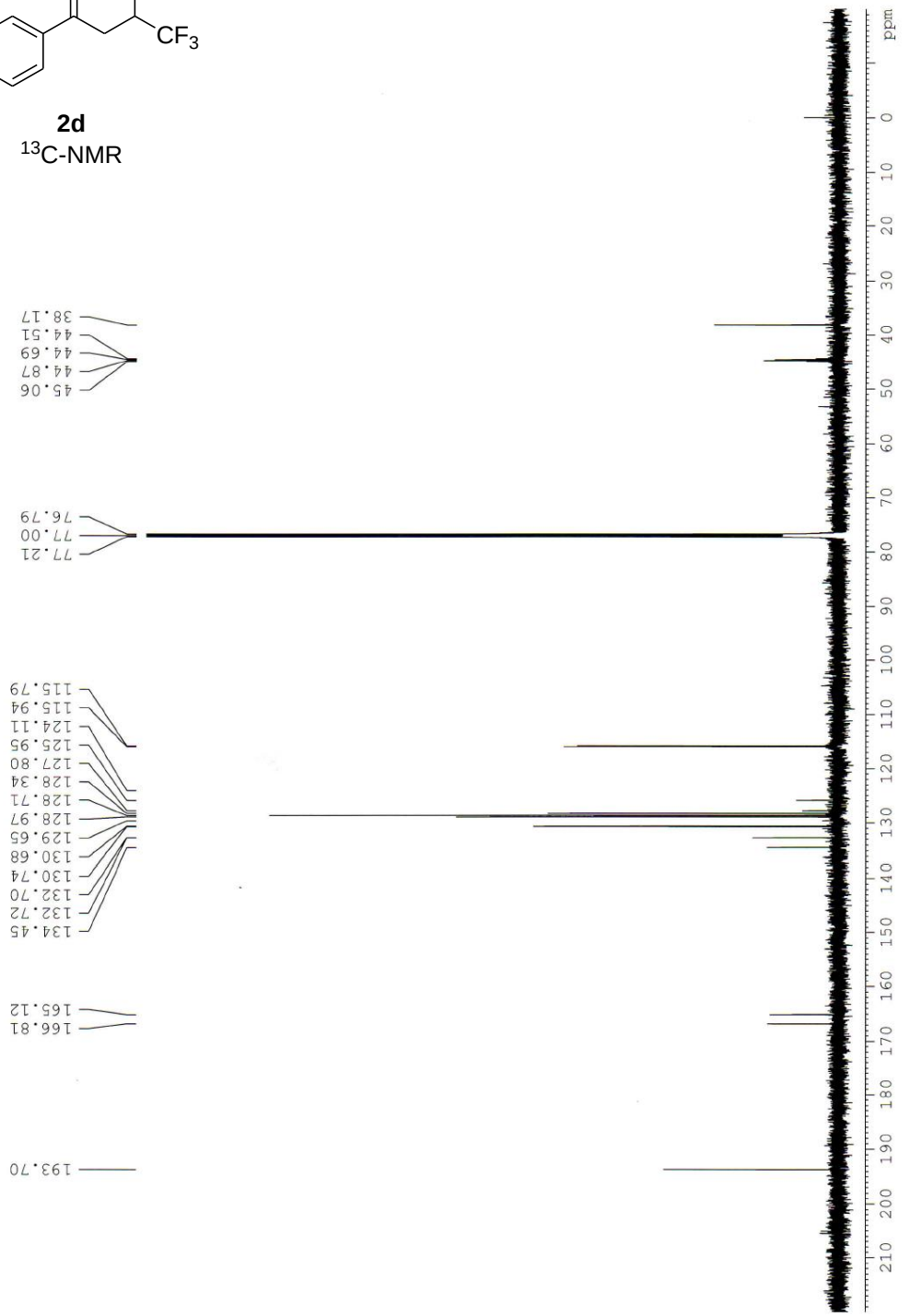
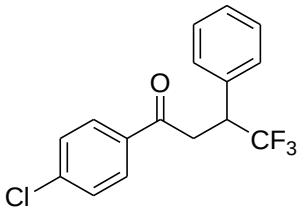
-70.146
0.000
ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20


O
CF3
F

2d

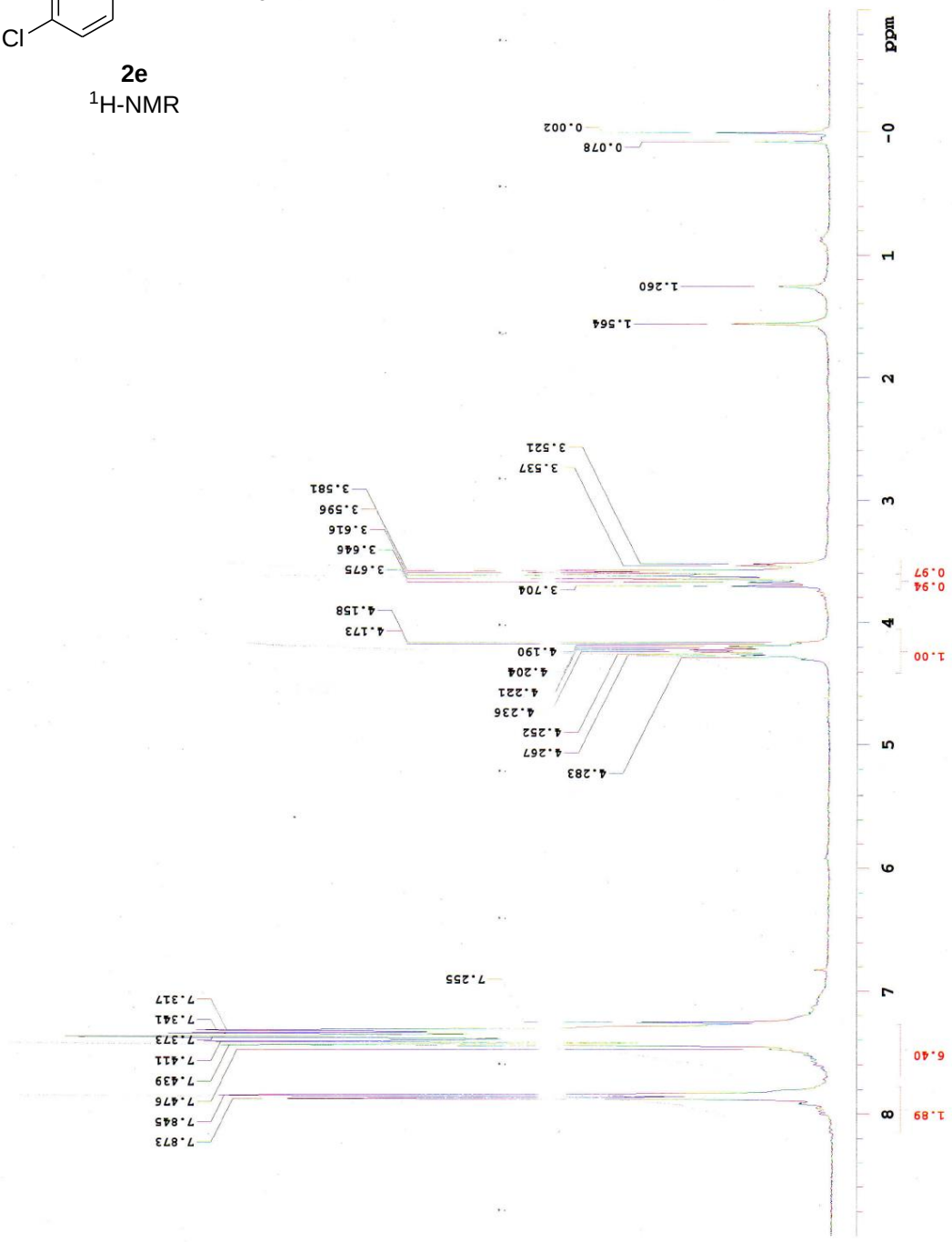
^{13}C-NMR


38.17
44.51
44.69
44.87
45.06
76.79
77.00
77.21
115.79
115.94
124.11
125.95
127.80
128.34
128.71
128.97
129.65
130.68
130.74
132.70
132.72
134.45
165.12
166.81
193.70
ppm


O
CF3
Cl

2e

^{1}H-NMR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3.616
3.646
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4.221
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4.252
4.267
4.283
7.255
7.317
7.341
7.373
7.411
7.439
7.476
7.845
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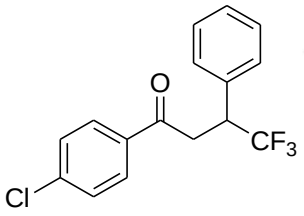
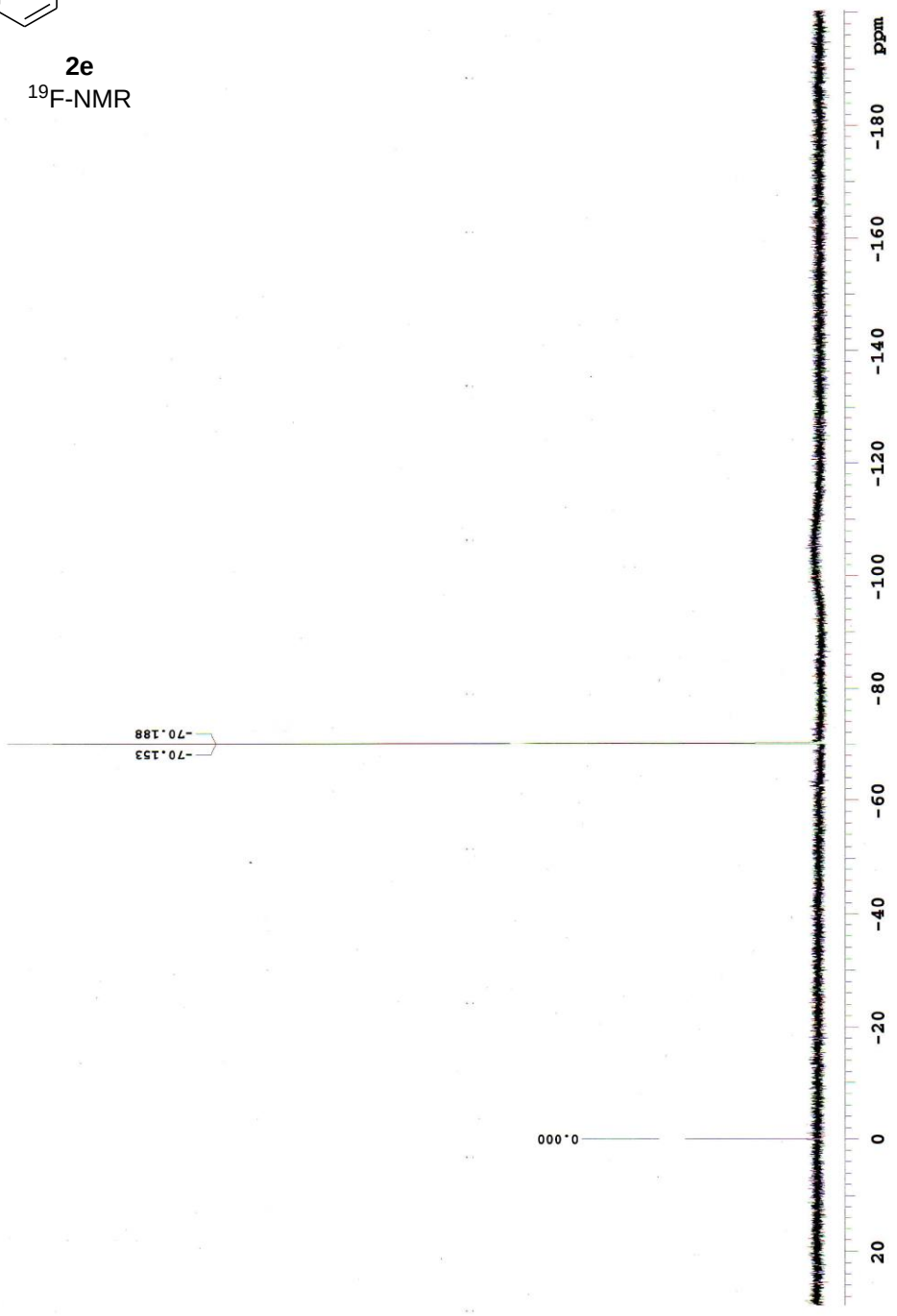
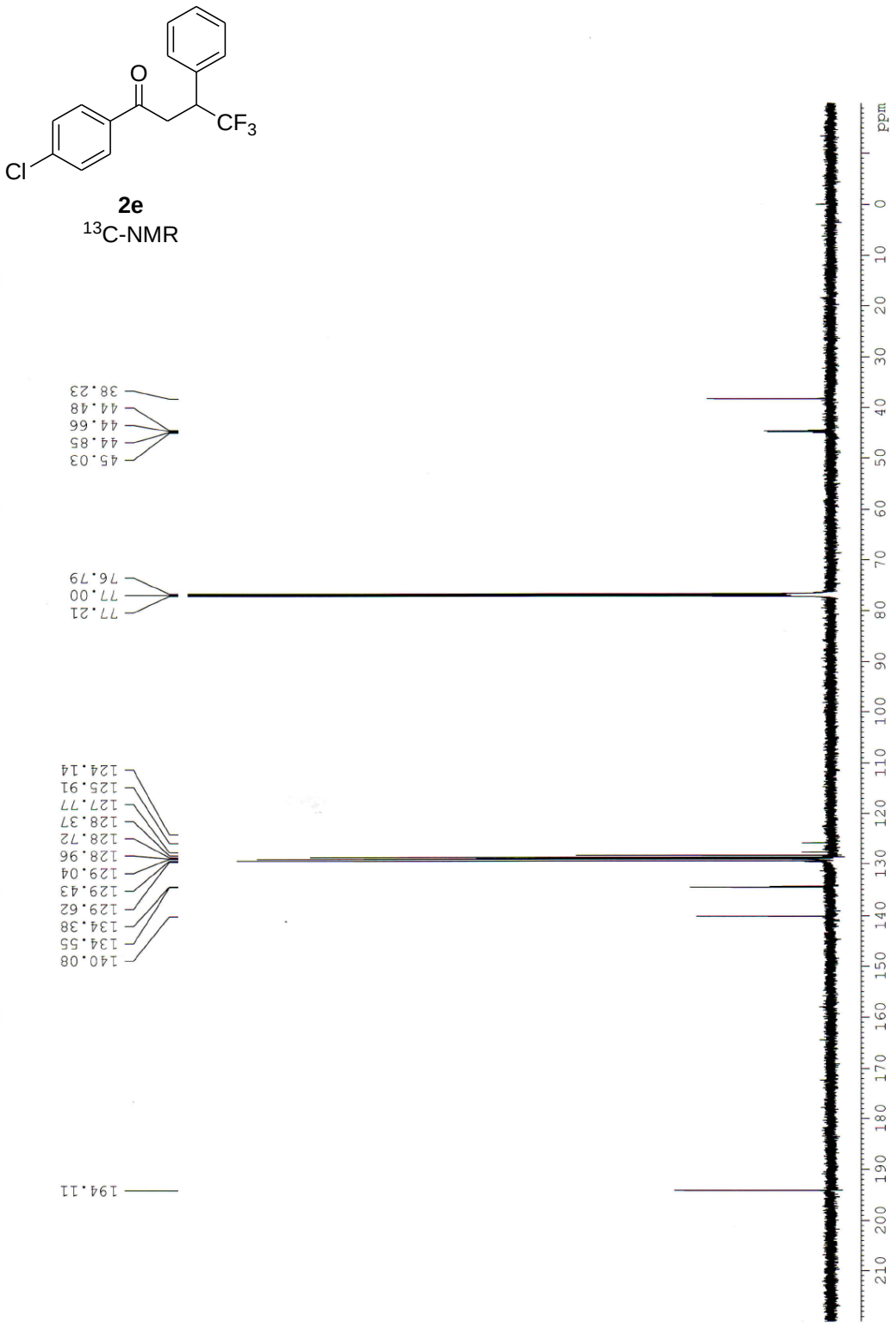
1.00
6.40
1.89

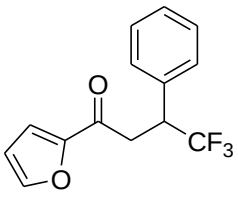


2e

^{19}F-NMR

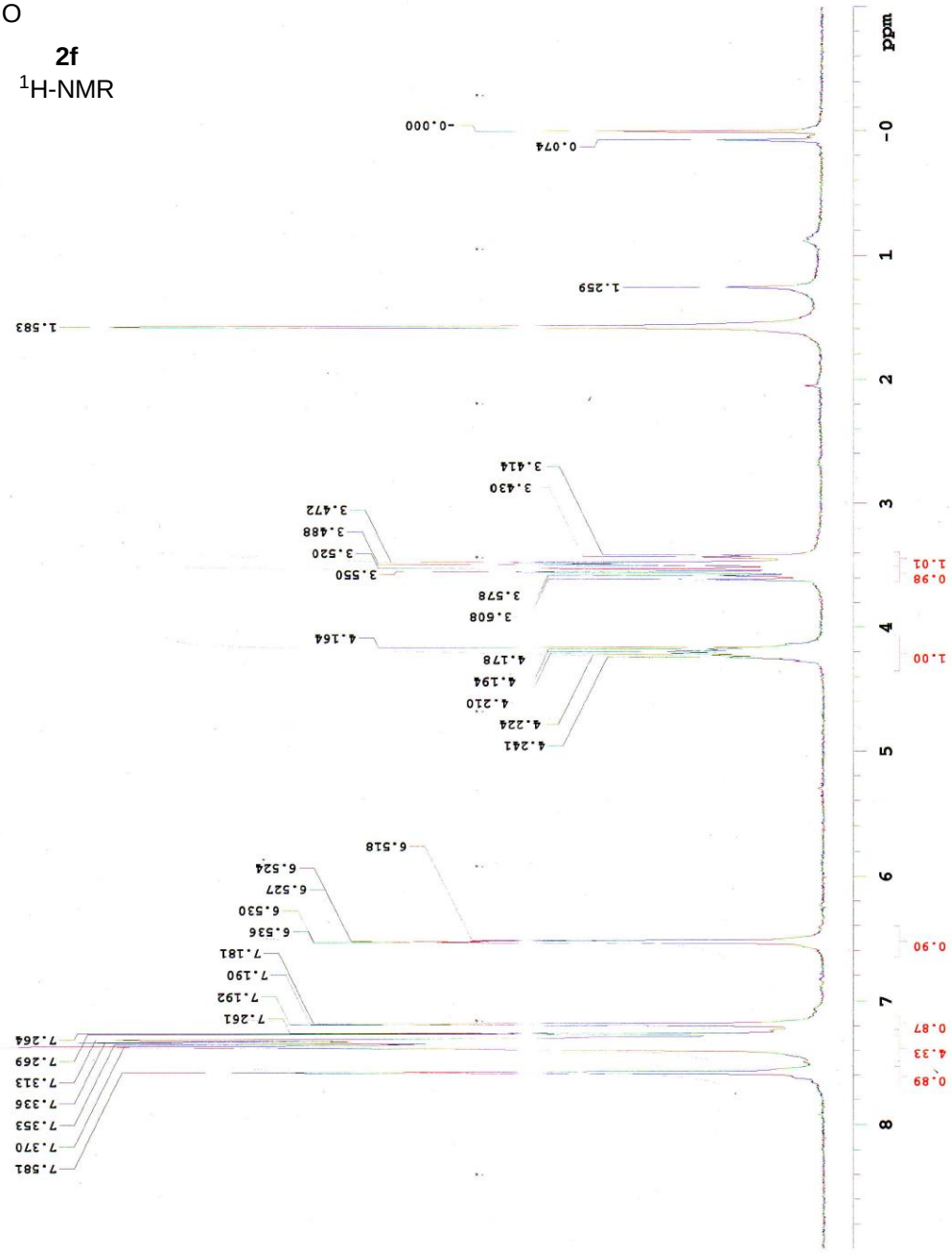



O
CF3
Cl
2e
13C-NMR
38.23
44.48
44.66
44.85
45.03
76.79
77.00
77.21
124.14
125.91
127.77
128.37
128.72
128.96
129.04
129.43
129.62
134.38
134.55
140.08
194.11
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


O
CF3
O

2f

^{1}H-NMR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1.583
3.414
3.430
3.472
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3.520
3.550
3.578
3.608
4.164
4.178
4.194
4.210
4.224
4.241
6.518
6.524
6.527
6.530
6.536
7.181
7.190
7.192
7.261
7.264
7.269
7.313
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7.353
7.370
7.581
ppm
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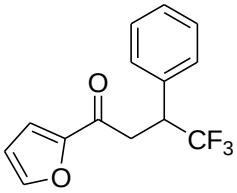
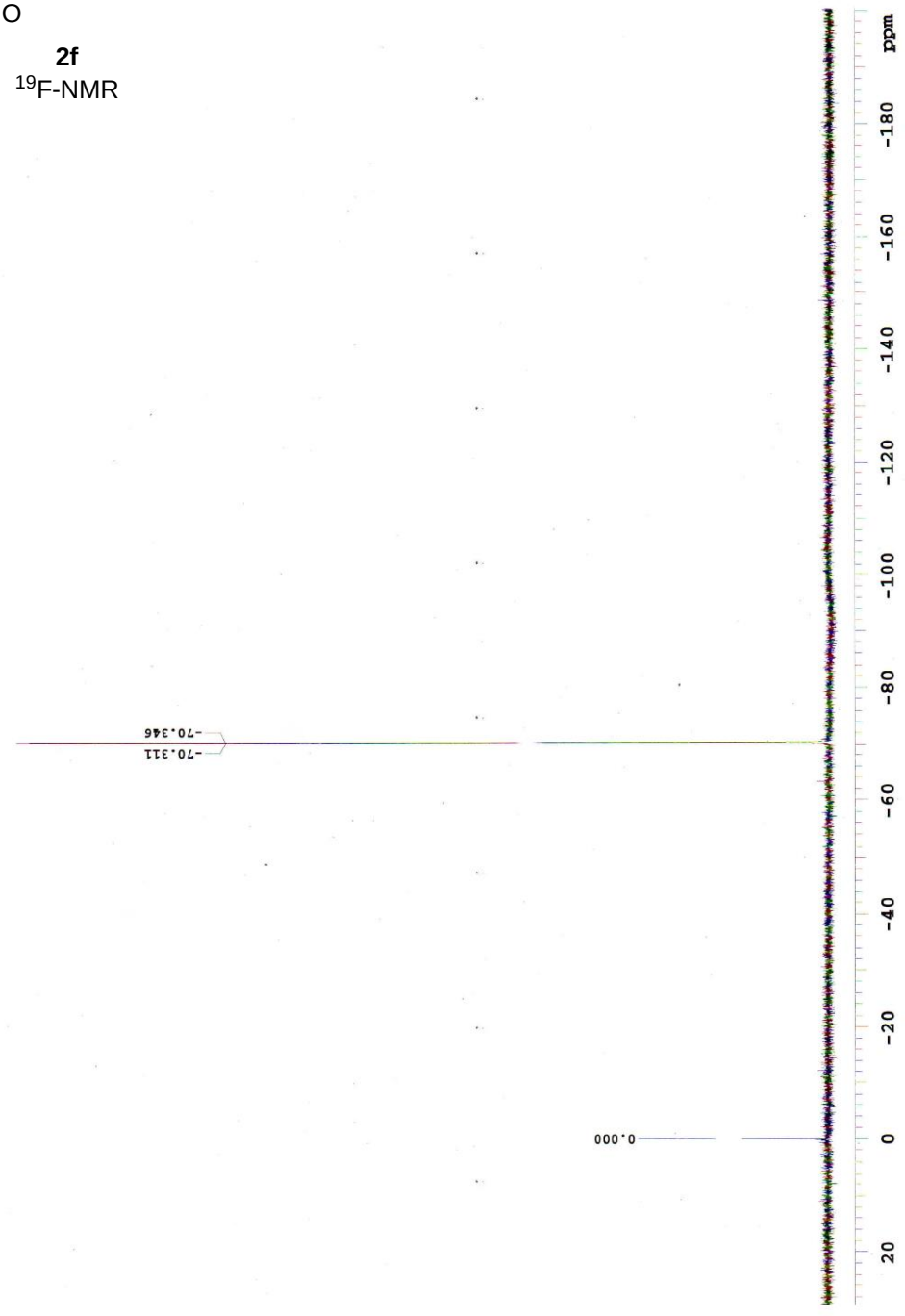
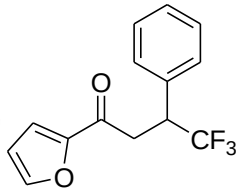
1
2
3
4
5
6
7
8
0.98
1.01
1.00
0.90
0.87
4.33
0.89



2f

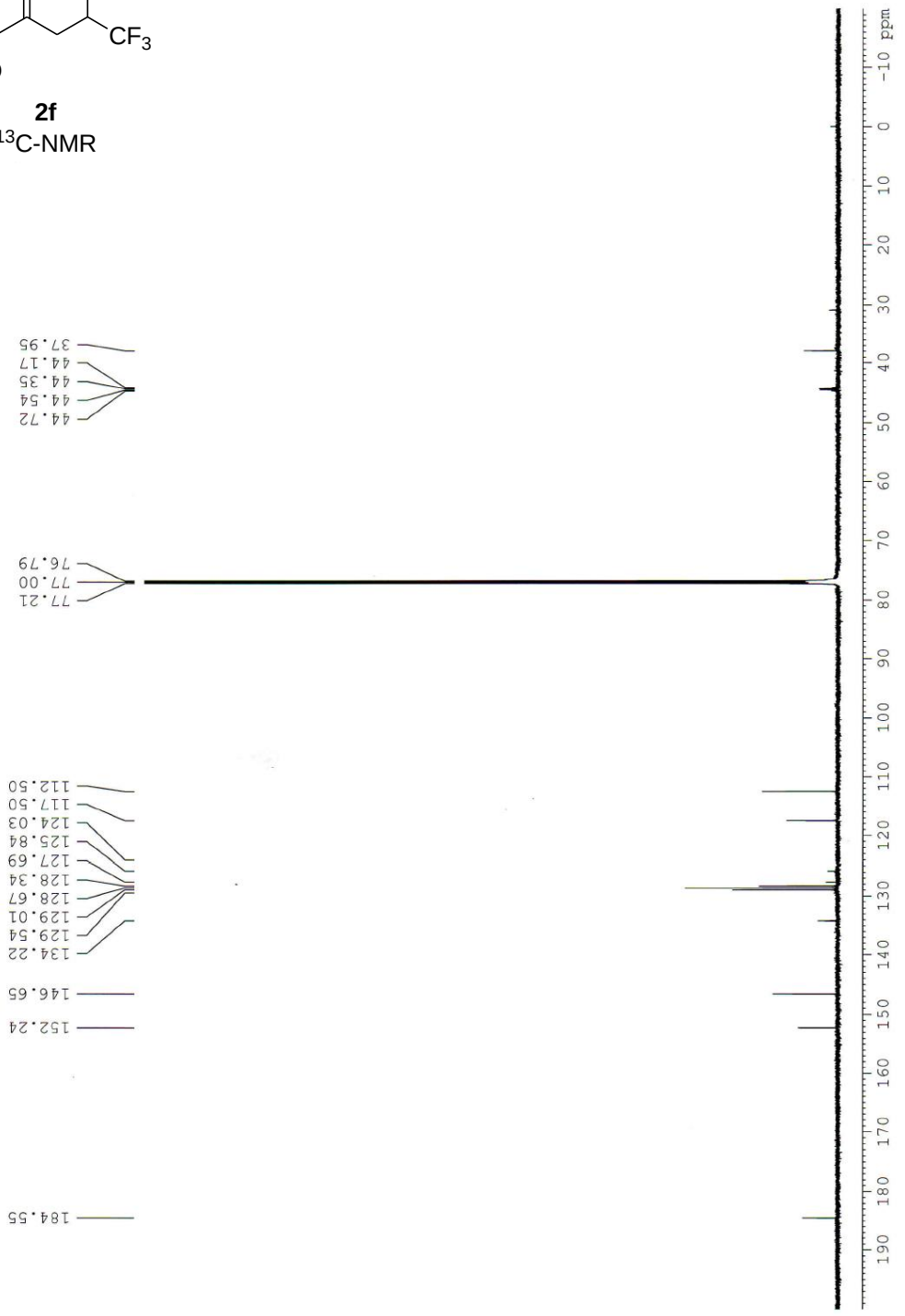
^{19}F-NMR

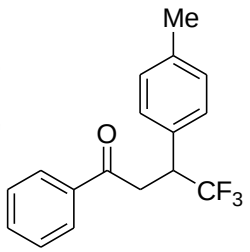



O
CF3
O

2f

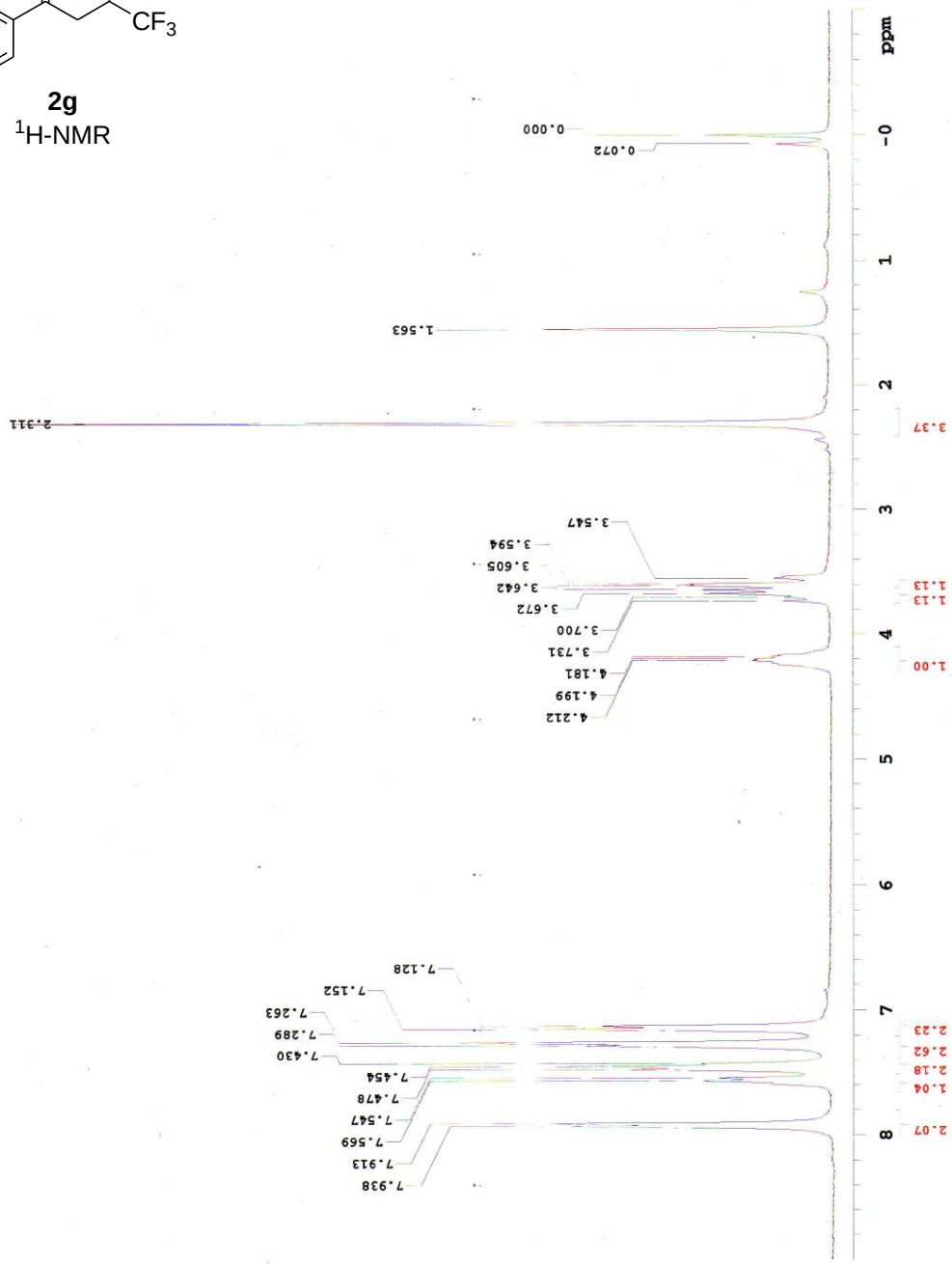
^{13}C-NMR

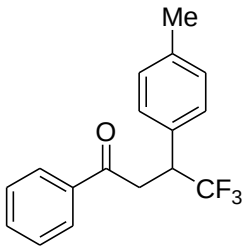

37.95
44.17
44.35
44.54
44.72
76.79
77.00
77.21
112.50
117.50
124.03
125.84
127.69
128.34
128.67
129.01
129.54
134.22
146.65
152.24
184.55
ppm


Me
O
CF3

2g

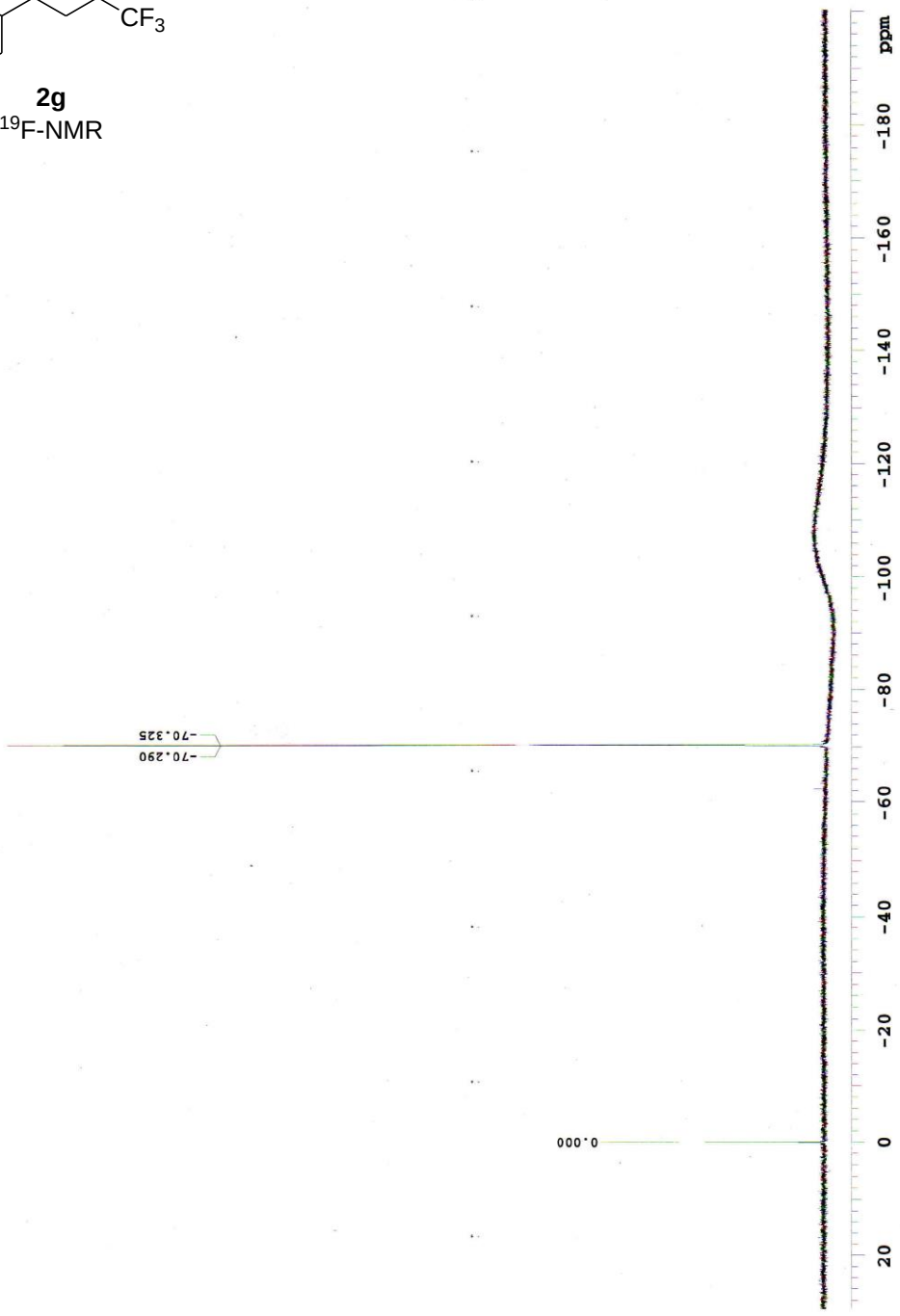
^{1}H-NMR

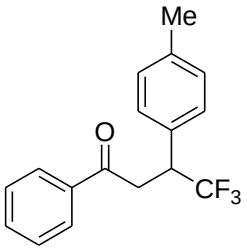

0.000
0.072
1.563
2.311
3.547
3.594
3.605
3.642
3.672
3.700
3.731
4.181
4.199
4.212
7.128
7.152
7.263
7.289
7.430
7.454
7.478
7.547
7.569
7.913
7.938
ppm
0
1
2
3
4
5
6
7
8
3.37
1.13
1.13
1.00
2.23
2.62
2.18
1.04
2.07



2g

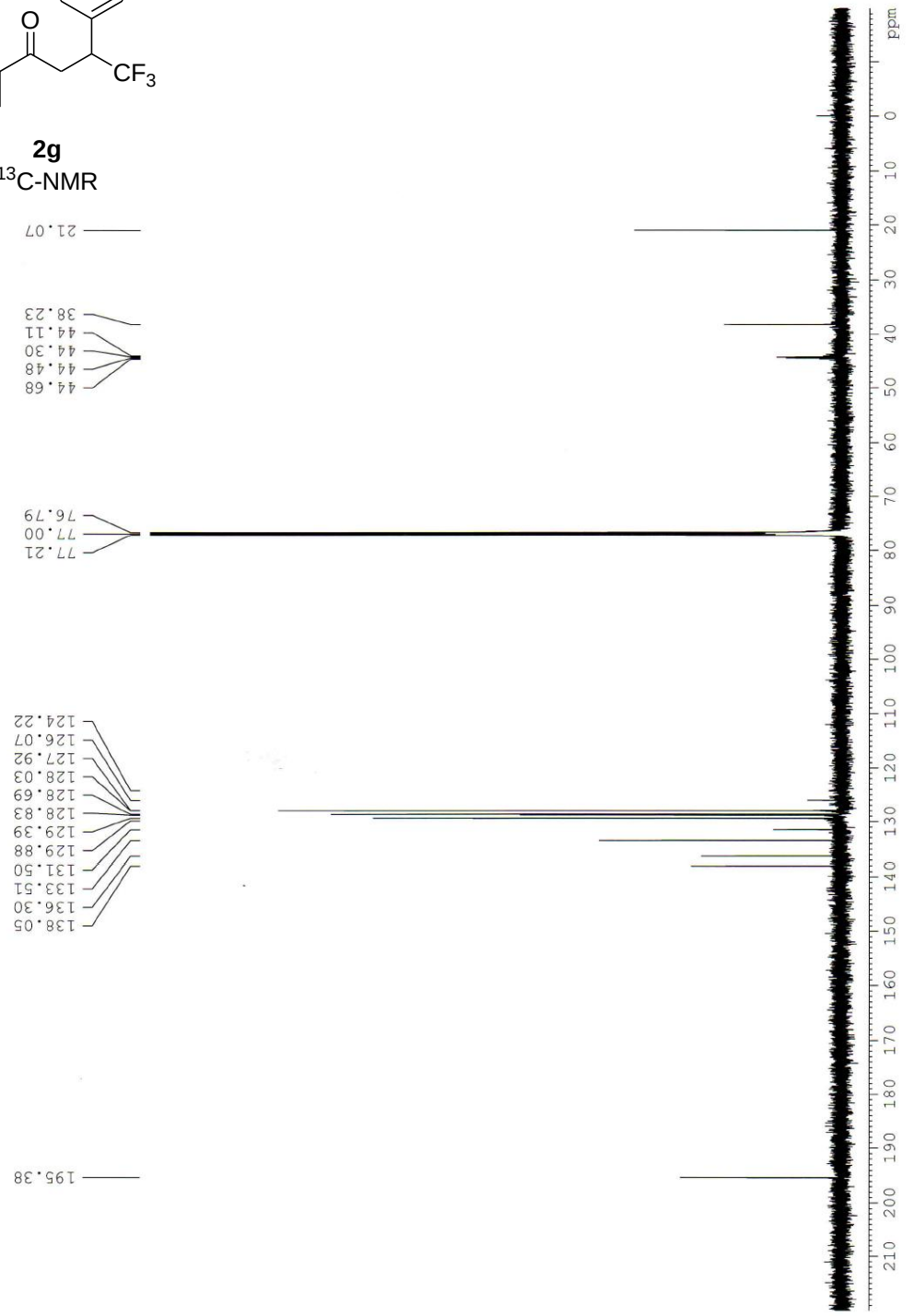
^{19}F-NMR

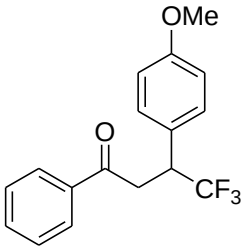



Me
O
CF3

2g

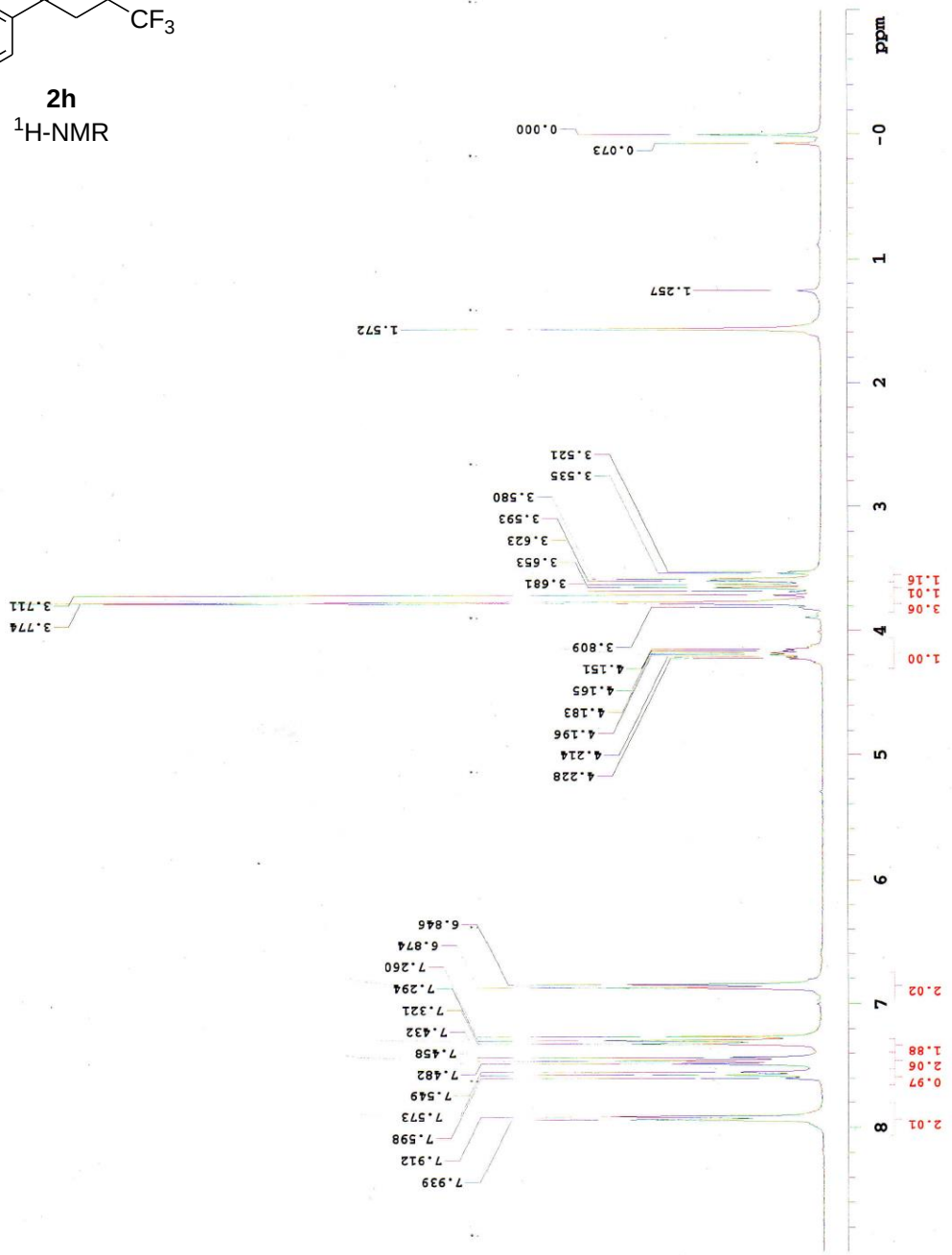
^{13}C-NMR

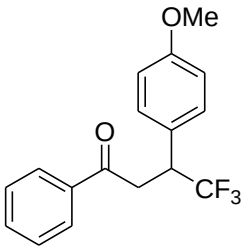

21.07
38.23
44.11
44.30
44.48
44.68
76.79
77.00
77.21
124.22
126.07
127.92
128.03
128.69
128.83
129.39
129.88
131.50
133.51
136.30
138.05
195.38
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


OMe
O
CF3

2h

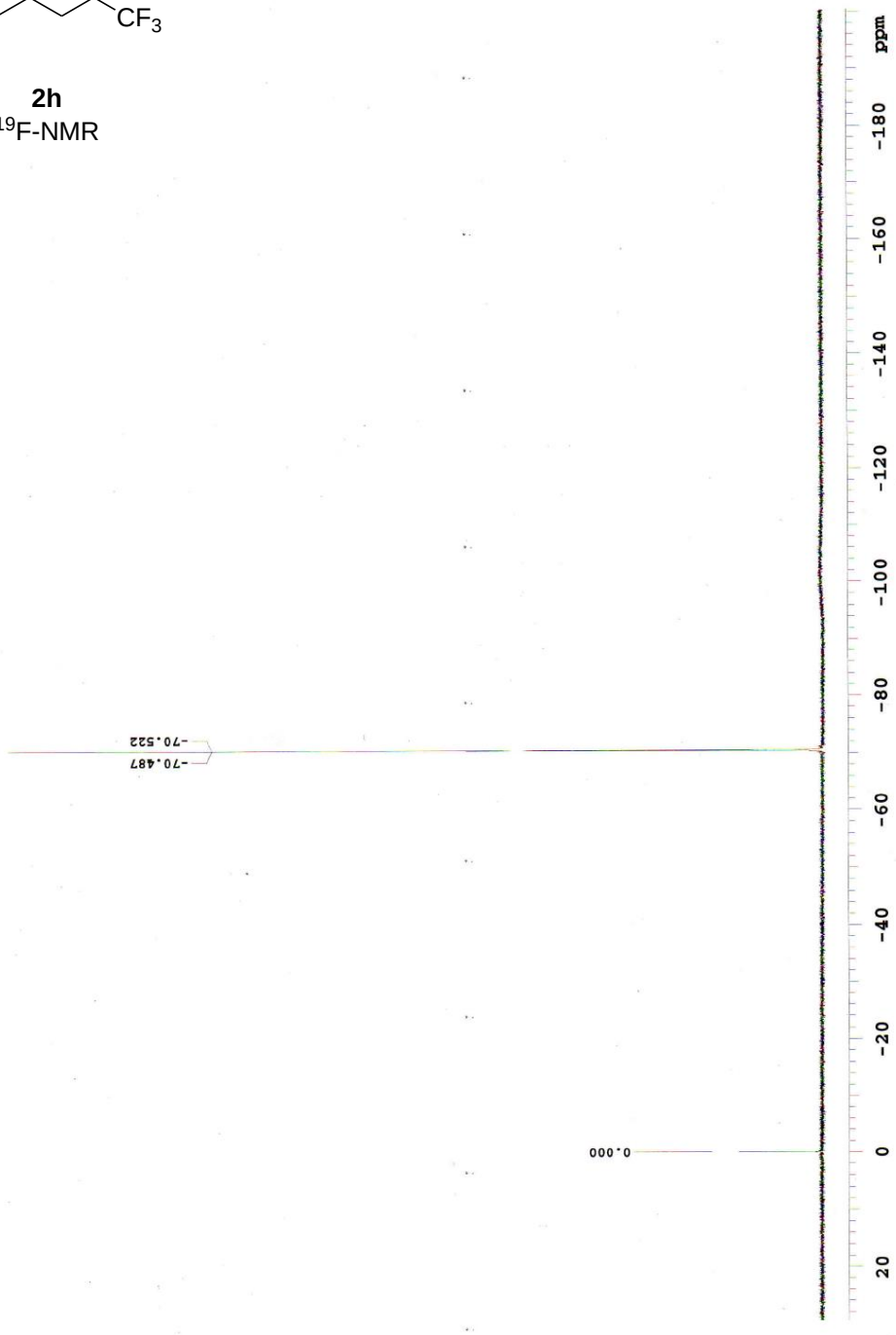
^{1}H-NMR

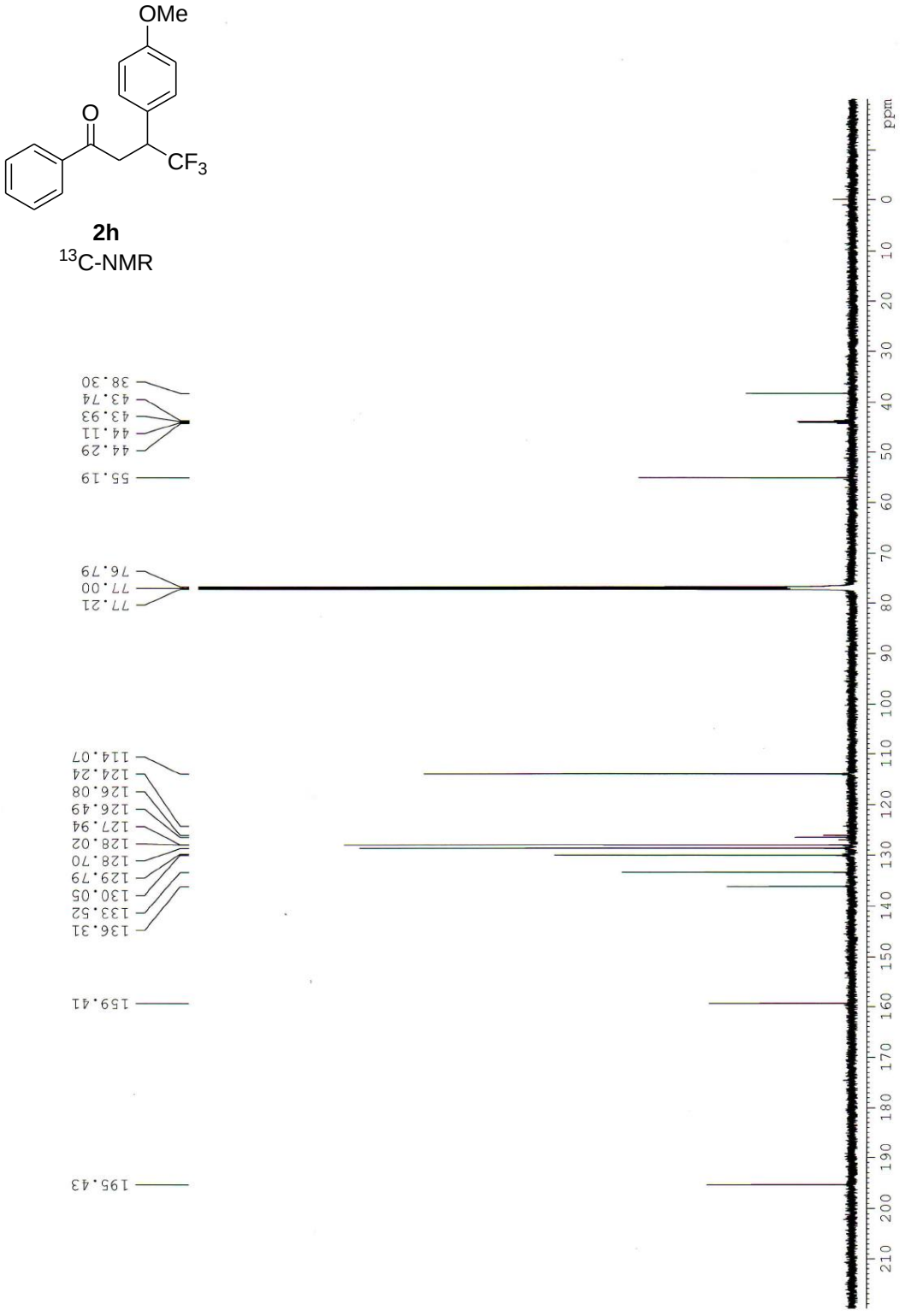

0.000
0.073
1.257
1.572
3.521
3.535
3.580
3.593
3.623
3.653
3.681
3.711
3.774
3.809
4.151
4.165
4.183
4.196
4.214
4.228
6.846
6.874
7.260
7.294
7.321
7.432
7.458
7.482
7.549
7.573
7.598
7.912
7.939
ppm
1.16
1.01
3.06
1.00
2.02
1.88
2.06
0.97
2.01

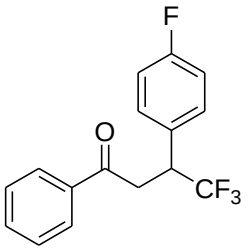

OMe
O
CF3

2h

^{19}F-NMR

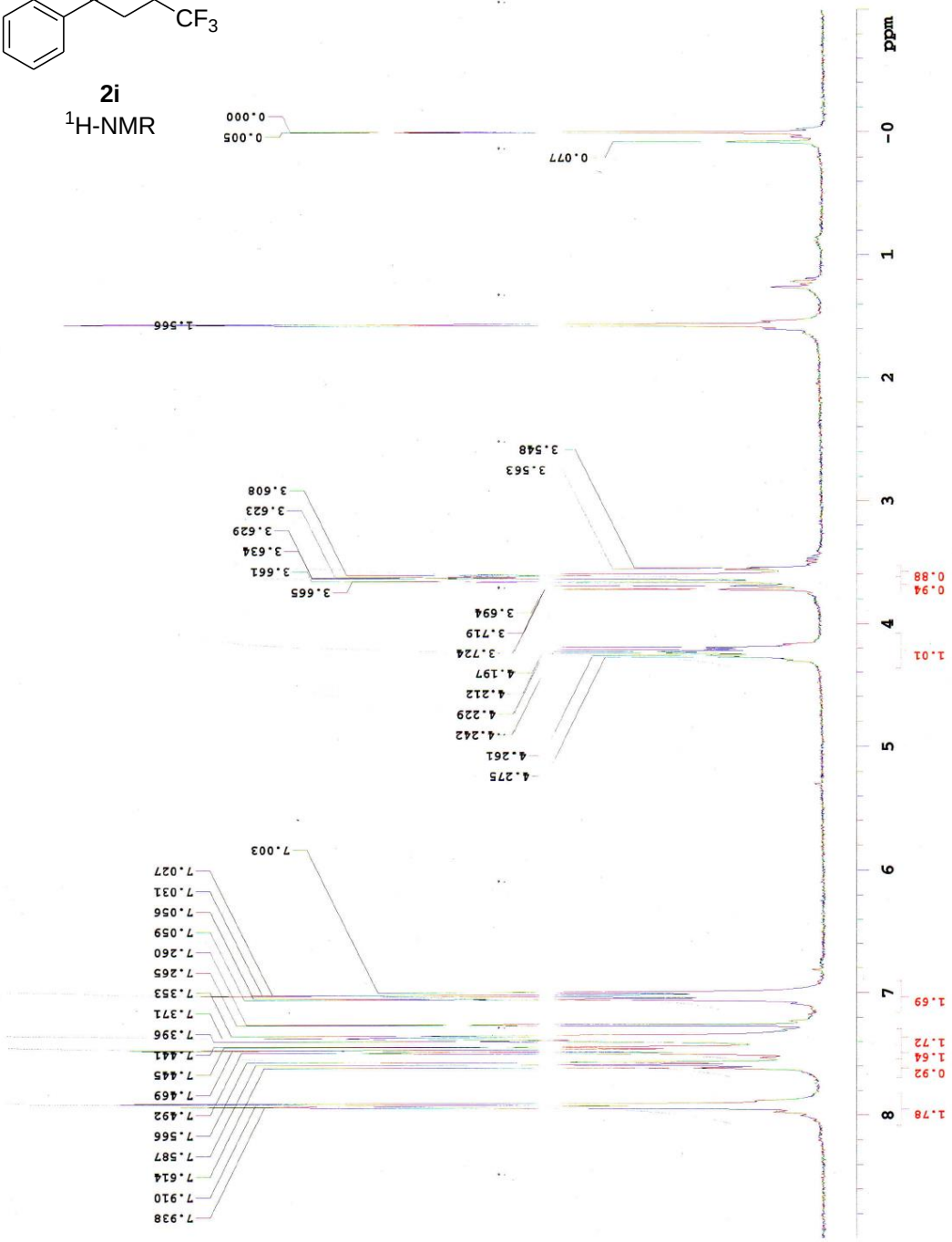

-70.522
-70.487
0.000
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180

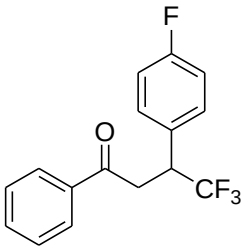

OMe
O
CF3
2h
13C-NMR
38.30
43.74
43.93
44.11
44.29
55.19
76.79
77.00
77.21
114.07
124.24
126.08
126.49
127.94
128.02
128.70
129.79
130.05
133.52
136.31
159.41
195.43
ppm


F
O
CF3

2i

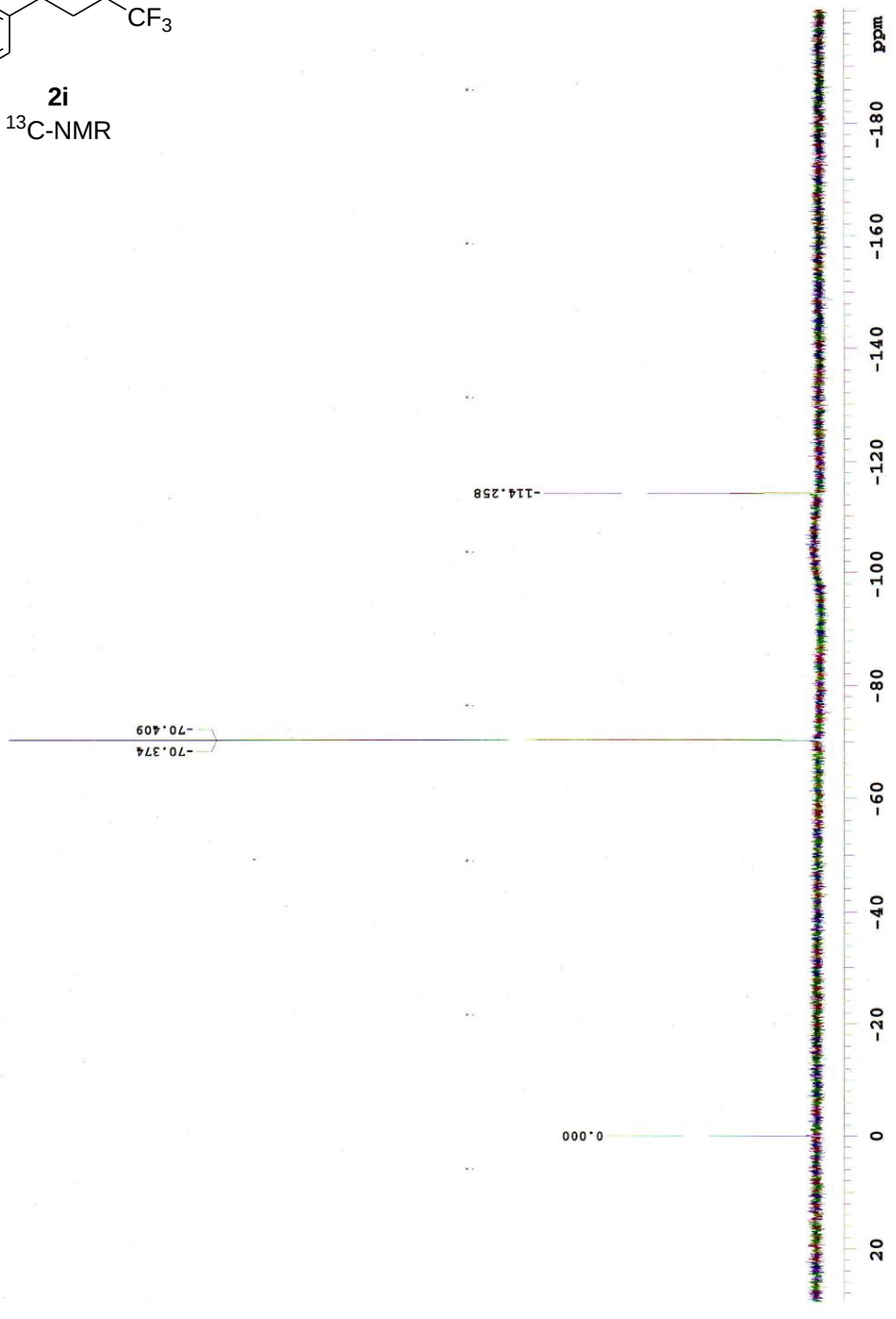
^{1}H-NMR

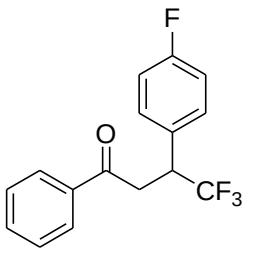

0.000
0.005
0.077
1.566
3.548
3.563
3.608
3.623
3.629
3.634
3.661
3.665
3.694
3.719
3.724
4.197
4.212
4.229
4.242
4.261
4.275
7.003
7.027
7.031
7.056
7.059
7.260
7.265
7.353
7.371
7.396
7.441
7.445
7.469
7.492
7.566
7.587
7.614
7.910
7.938
ppm
0
1
2
3
4
5
6
7
8
0.88
0.94
1.01
1.69
0.92
1.64
1.72
1.78


F
O
CF3

2i

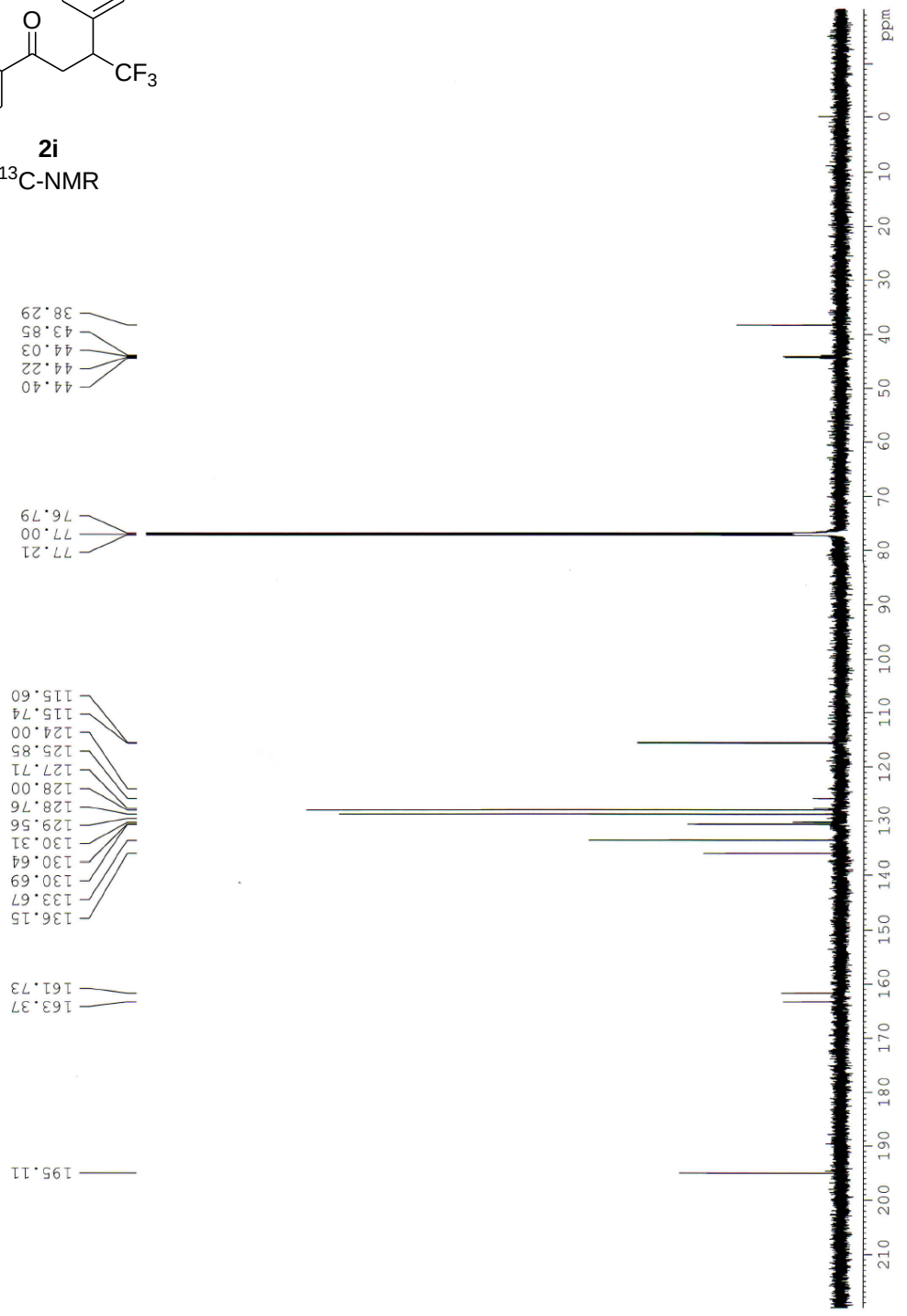
^{13}C-NMR

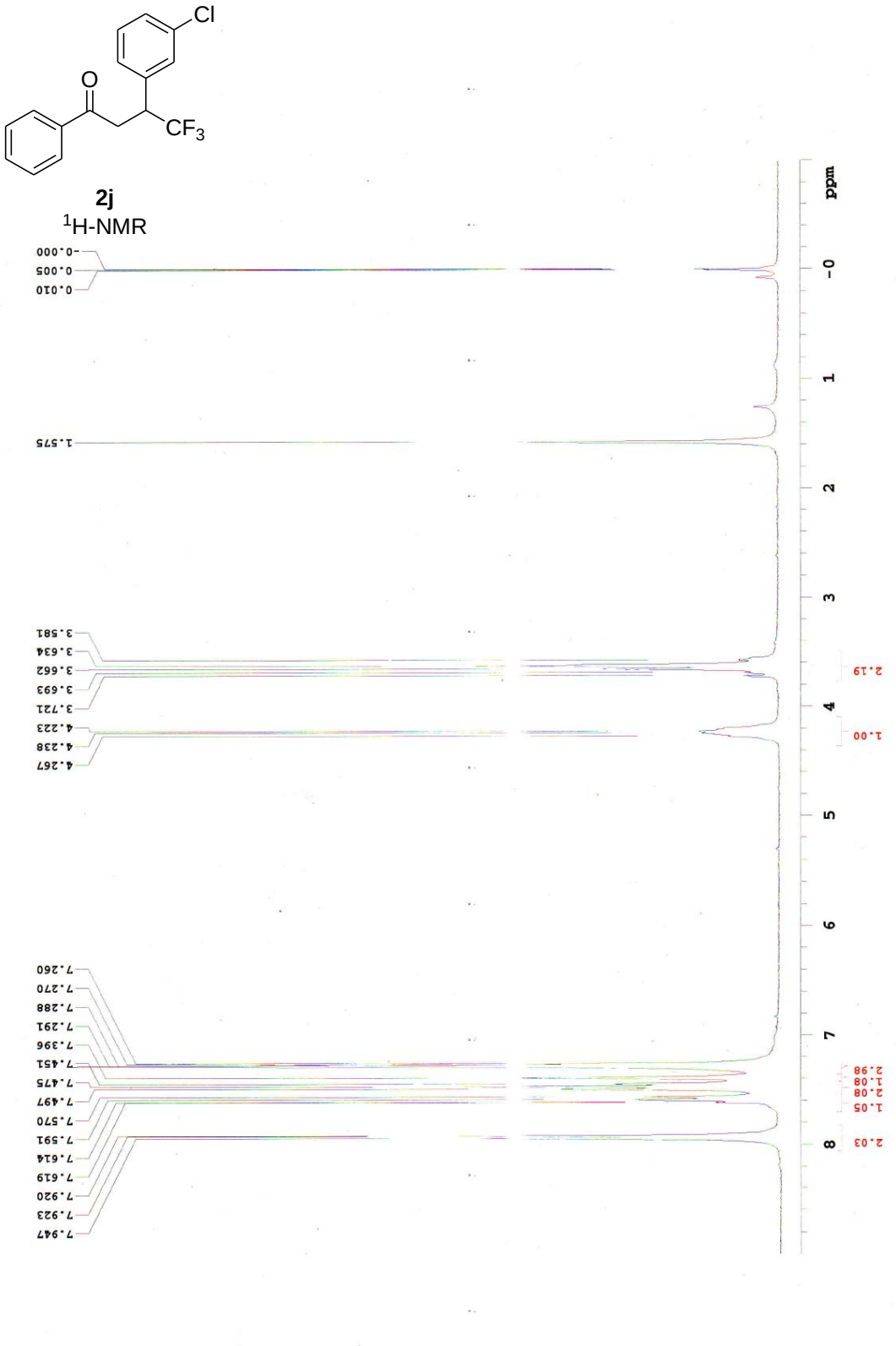

-114.258
-70.374
-70.409
0.000
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180

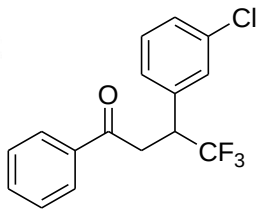

F
O
CF3

2i

^{13}C-NMR

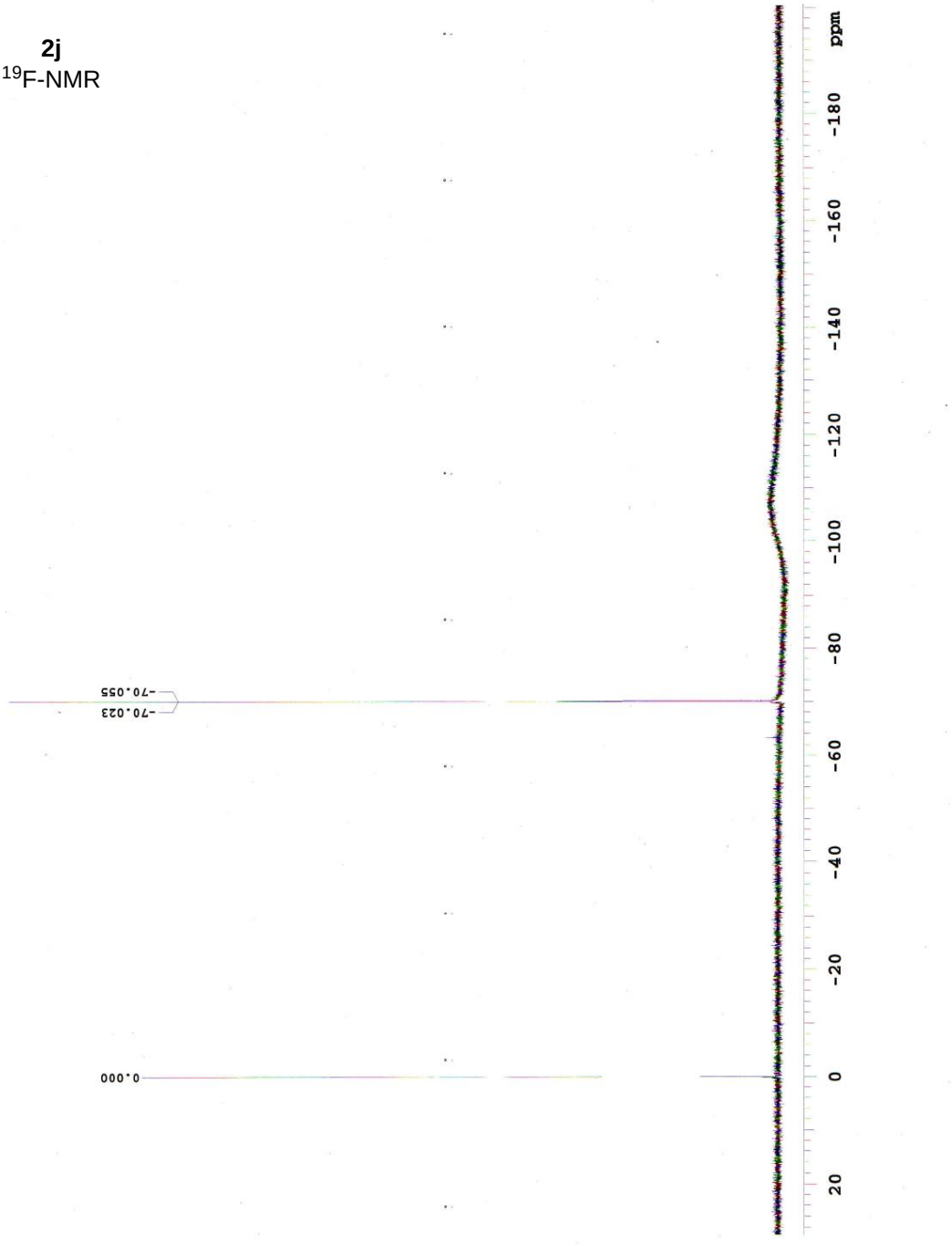

38.29
43.85
44.03
44.22
44.40
76.79
77.00
77.21
115.60
115.74
124.00
125.85
127.71
128.00
128.76
129.56
130.31
130.64
130.69
133.67
136.15
161.73
163.37
195.11
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

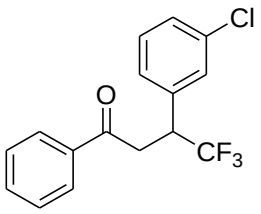

Cl
O
CF3
2j
1H-NMR
-0.000
0.005
0.010
1.575
3.581
3.634
3.662
3.693
3.721
4.223
4.238
4.267
7.260
7.270
7.288
7.291
7.396
7.451
7.475
7.497
7.570
7.591
7.614
7.619
7.920
7.923
7.947
2.19
1.00
2.98
1.08
2.08
1.05
2.03
ppm



2j

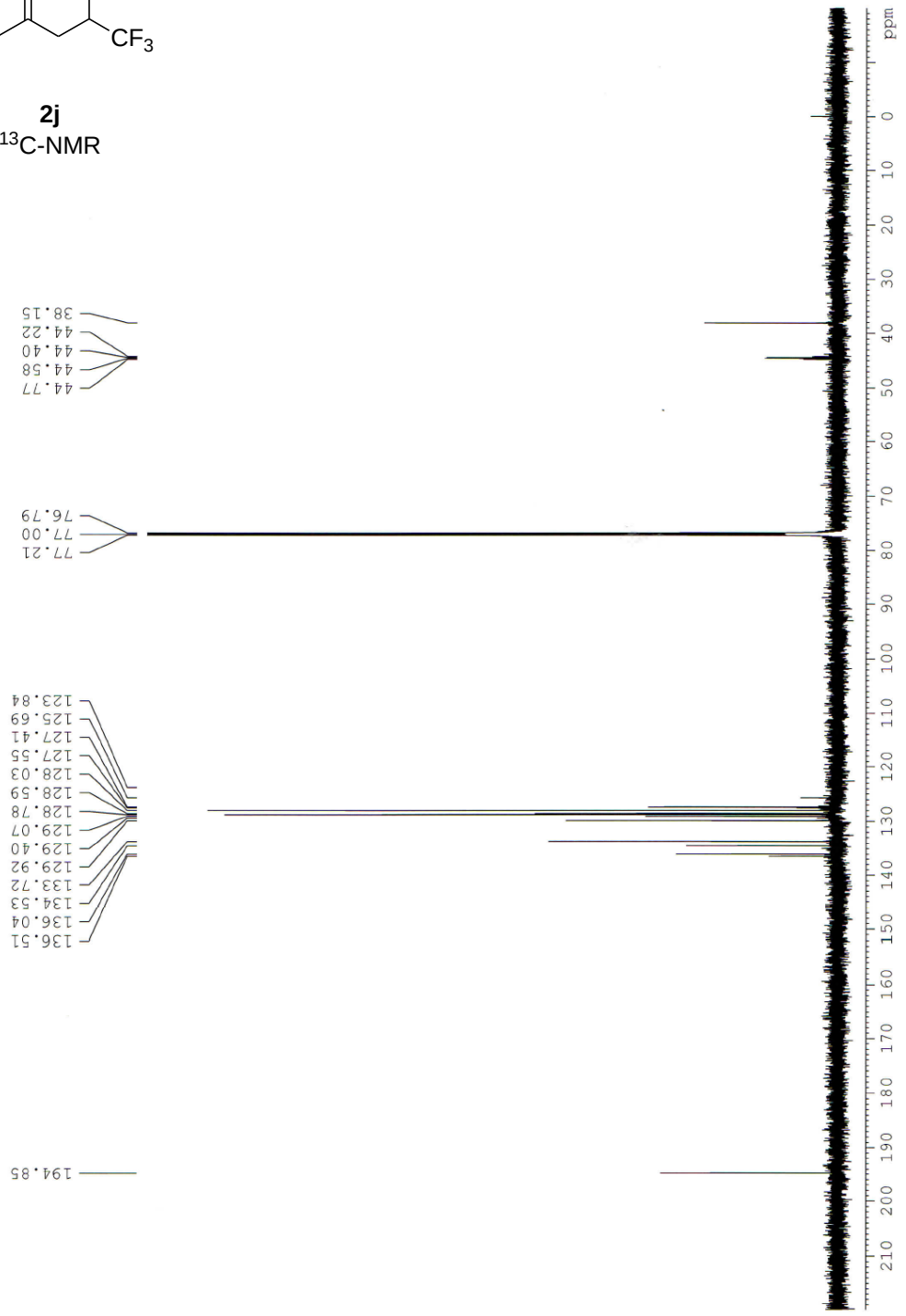
^{19}F-NMR

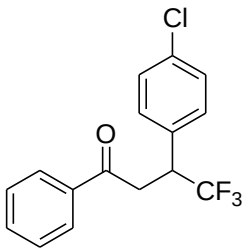



Cl
O
CF3

2j

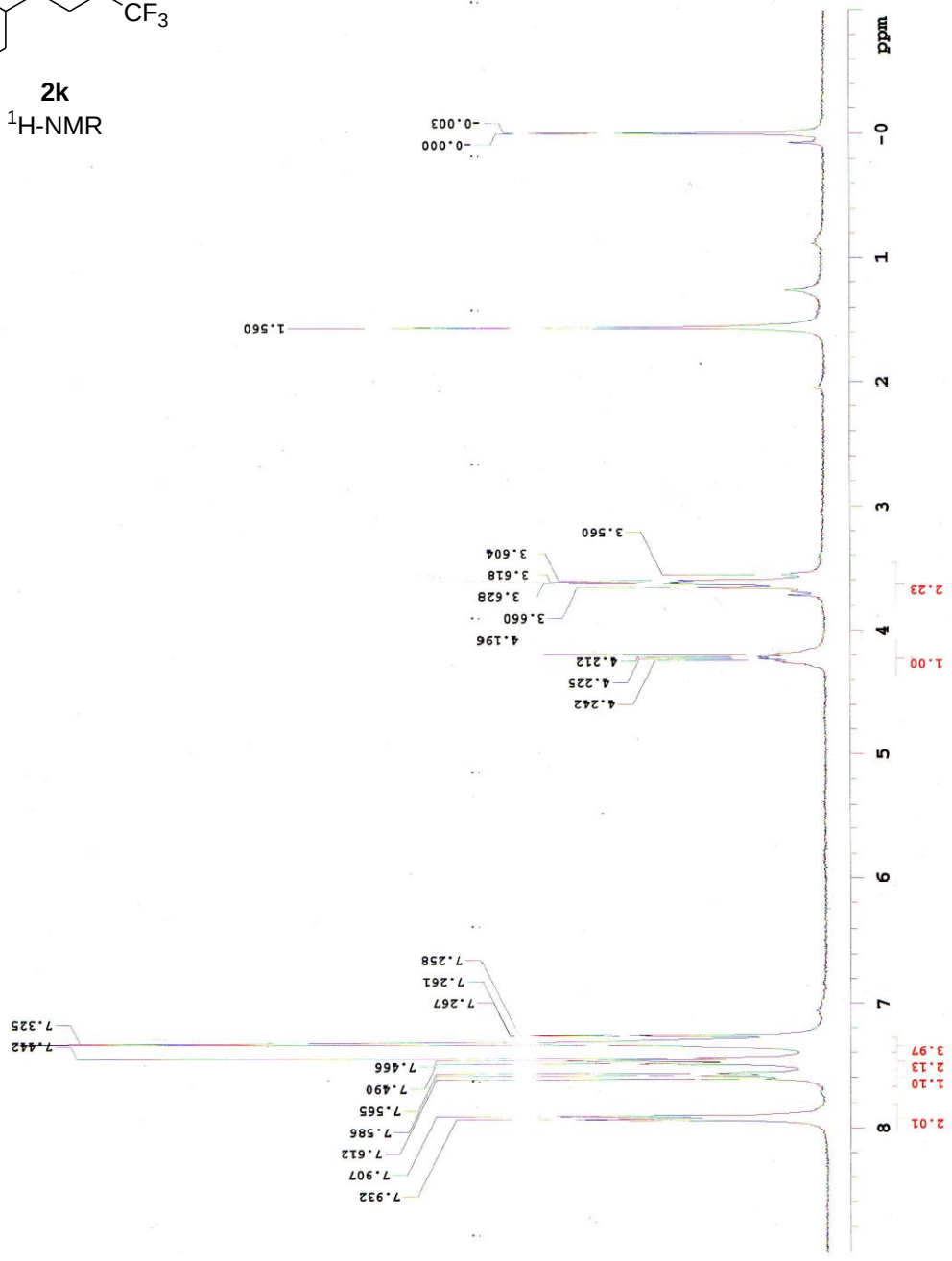
^{13}C-NMR

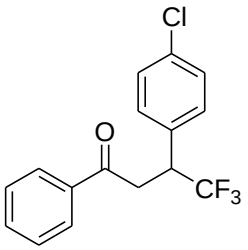

38.15
44.22
44.40
44.58
44.77
76.79
77.00
77.21
123.84
125.69
127.41
127.55
128.03
128.59
128.78
129.07
129.40
129.92
133.72
134.53
136.04
136.51
194.85
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


Cl
O
CF3

2k

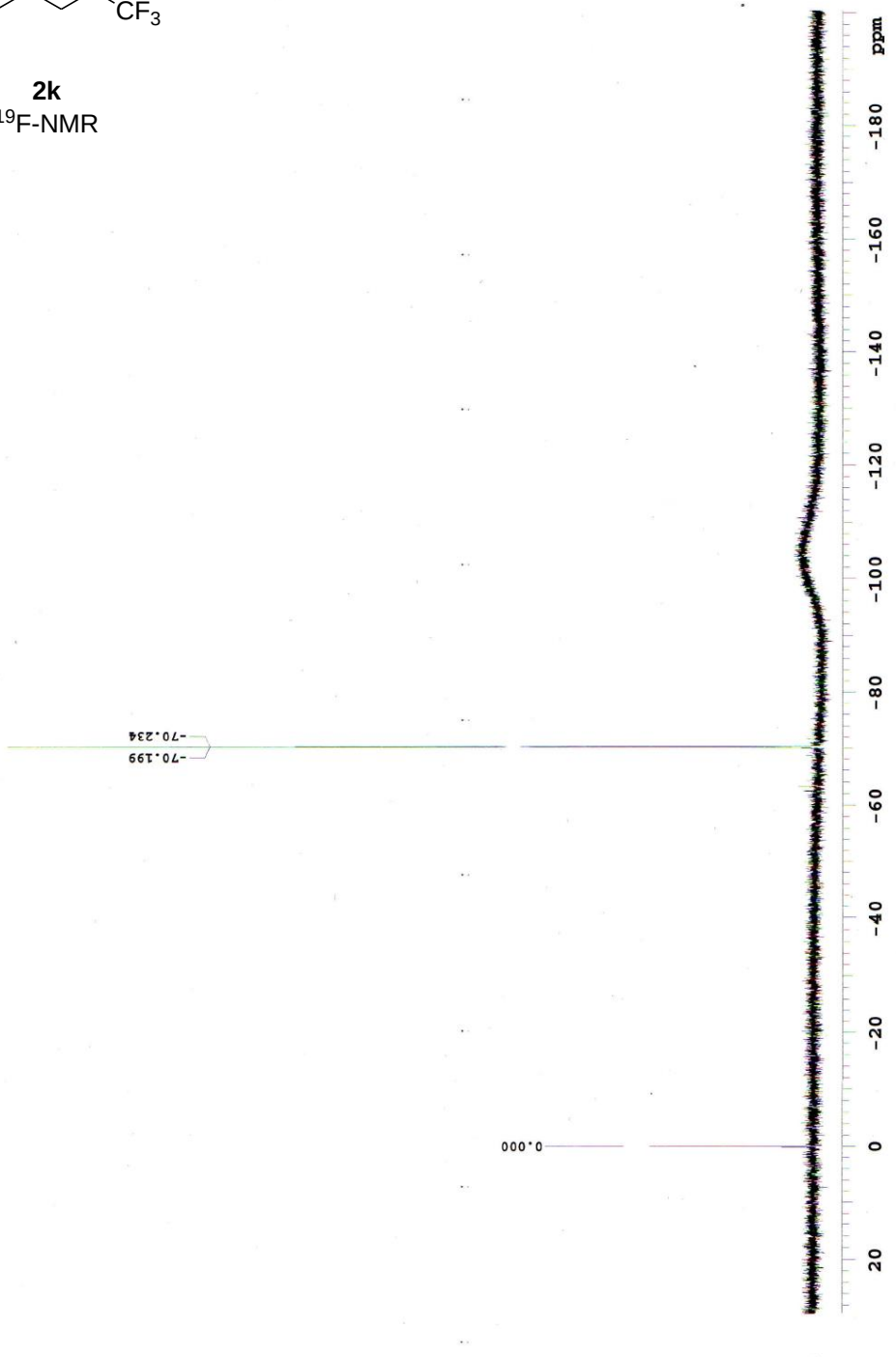
^{1}H-NMR

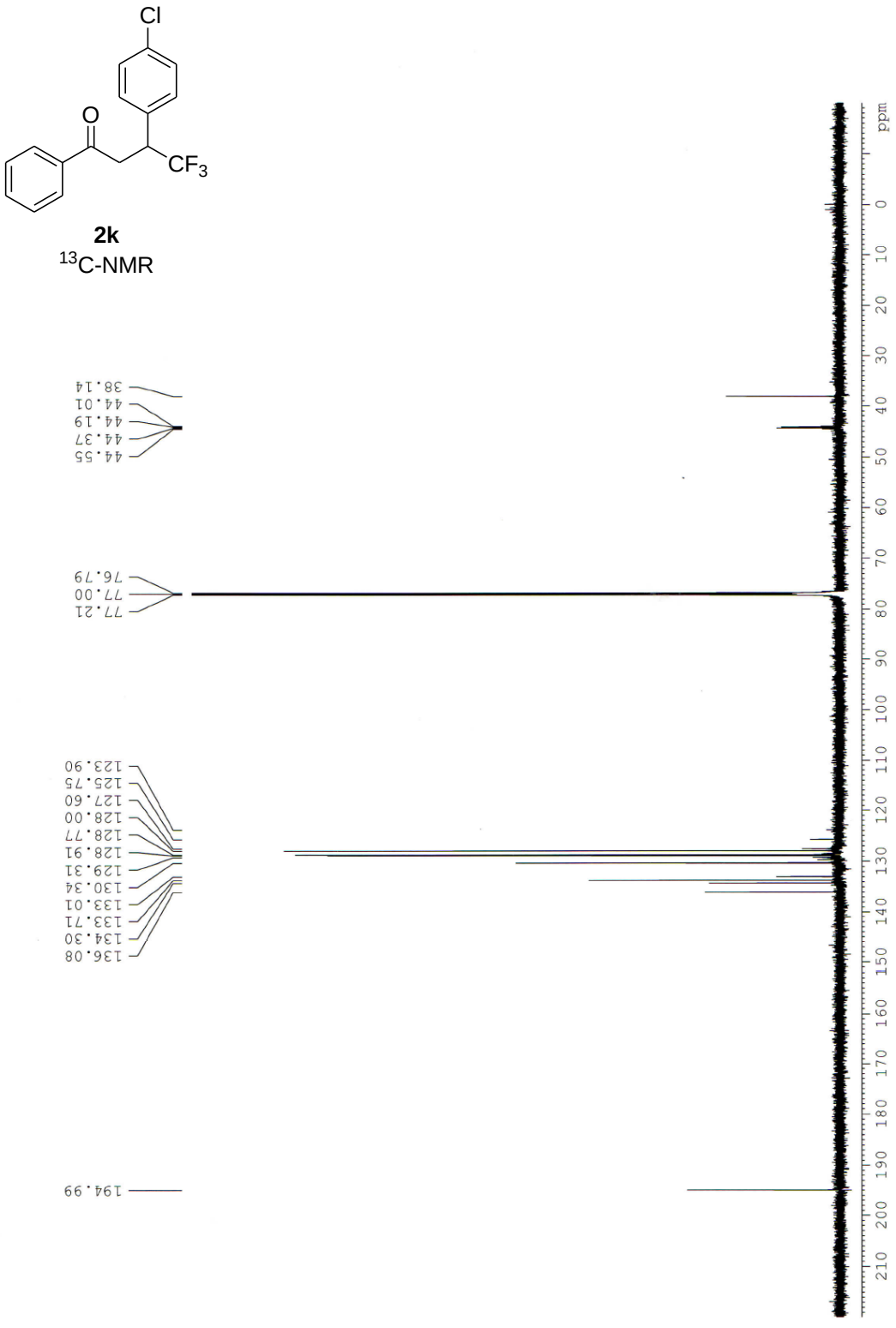

ppm
-0.003
-0.000
1.560
3.560
3.604
3.618
3.628
3.660
4.196
4.212
4.225
4.242
7.258
7.261
7.267
7.325
7.442
7.466
7.490
7.565
7.586
7.612
7.907
7.932
2.23
1.00
3.97
2.13
1.10
2.01

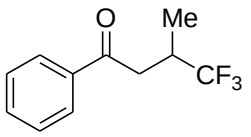


2k

^{19}F-NMR

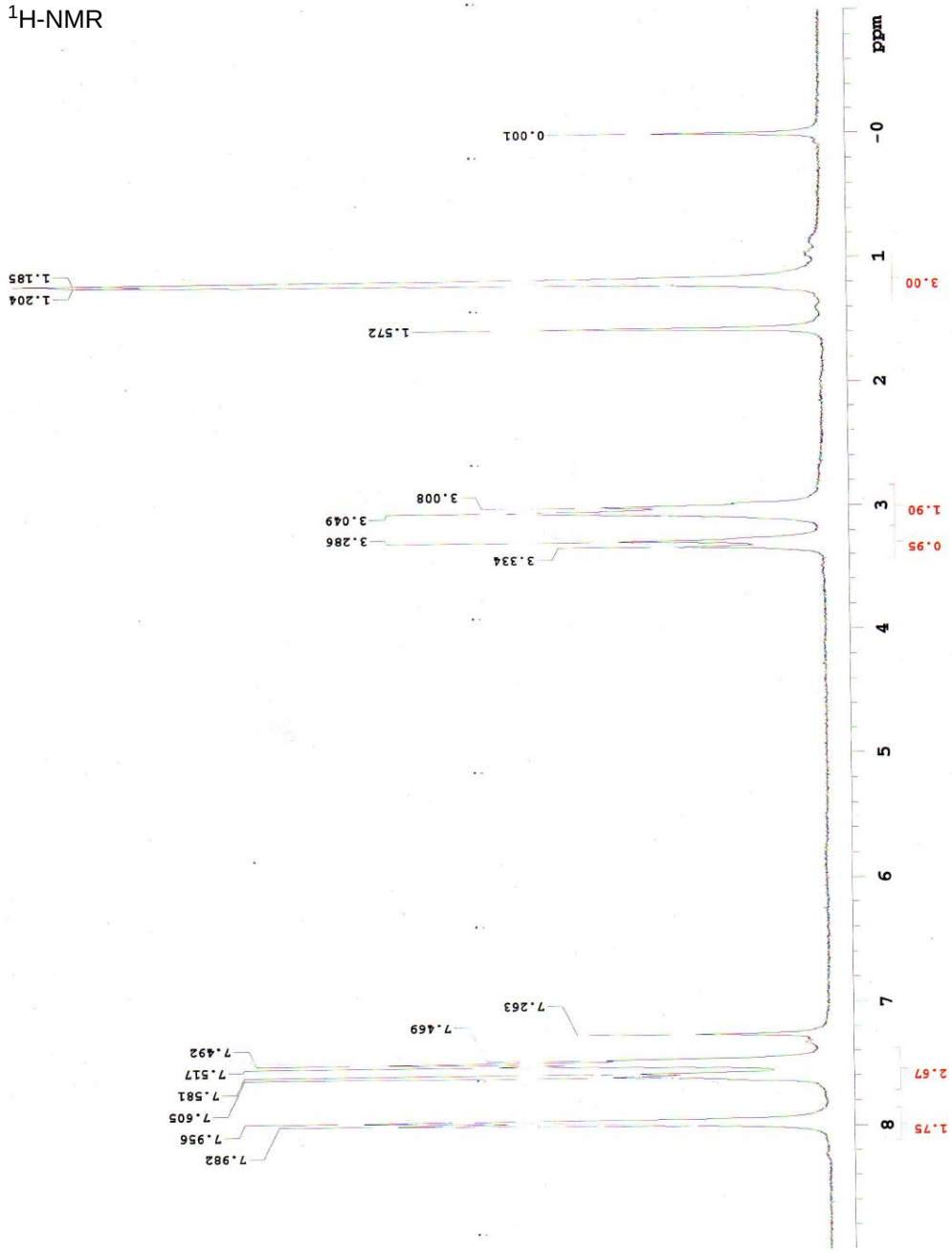


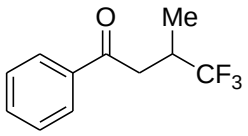

Cl
O
CF3
2k
13C-NMR
38.14
44.01
44.19
44.37
44.55
76.79
77.00
77.21
123.90
125.75
127.60
128.00
128.77
128.91
129.31
130.34
133.01
133.71
134.30
136.08
194.99
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


O
Me
CF3

2l

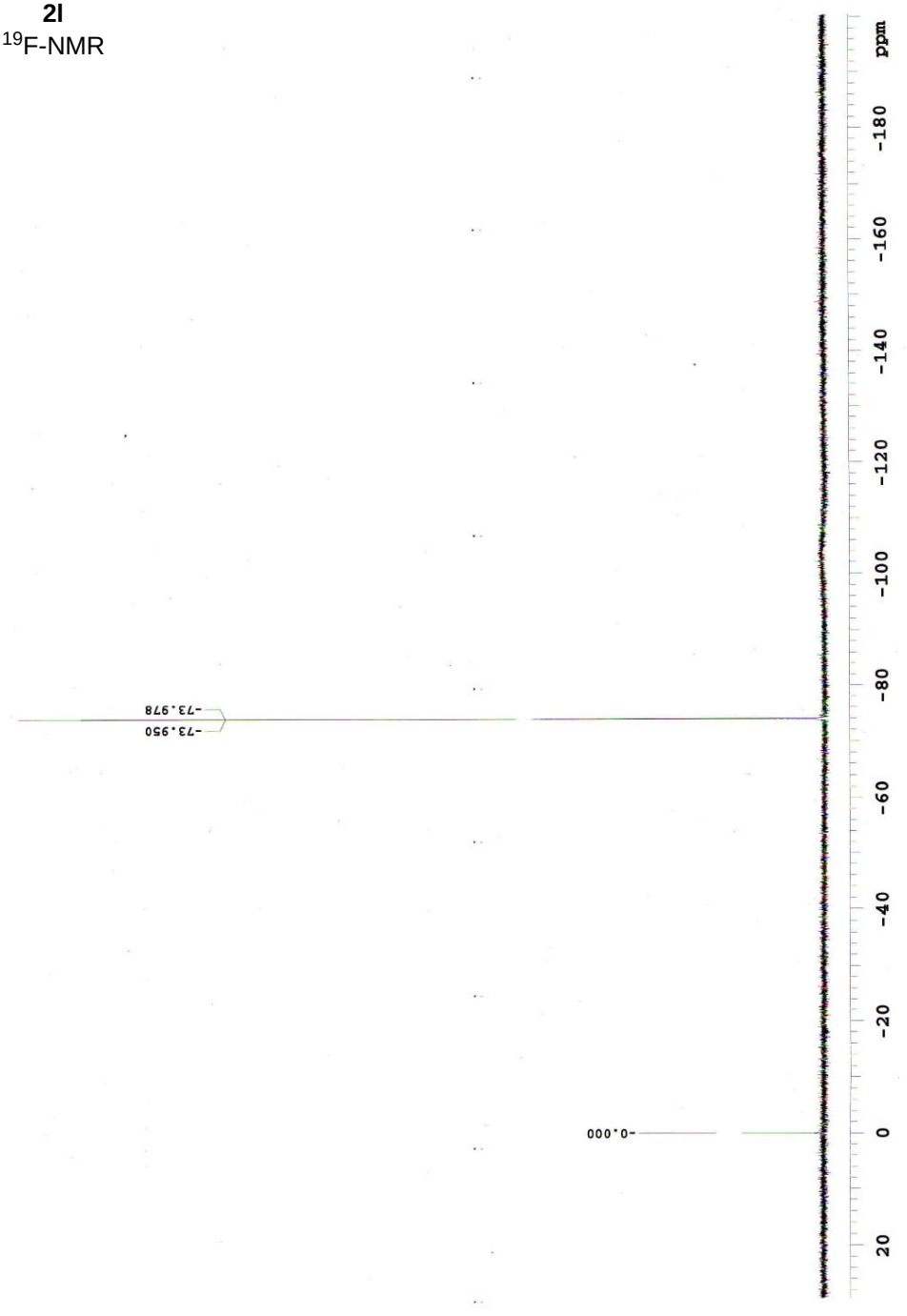
^{1}H-NMR

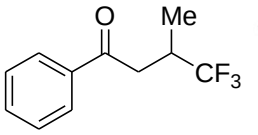

ppm
0.001
1.185
1.204
1.572
3.008
3.049
3.286
3.334
7.263
7.469
7.492
7.517
7.581
7.605
7.956
7.982
3.00
1.90
0.95
2.67
1.75



2l

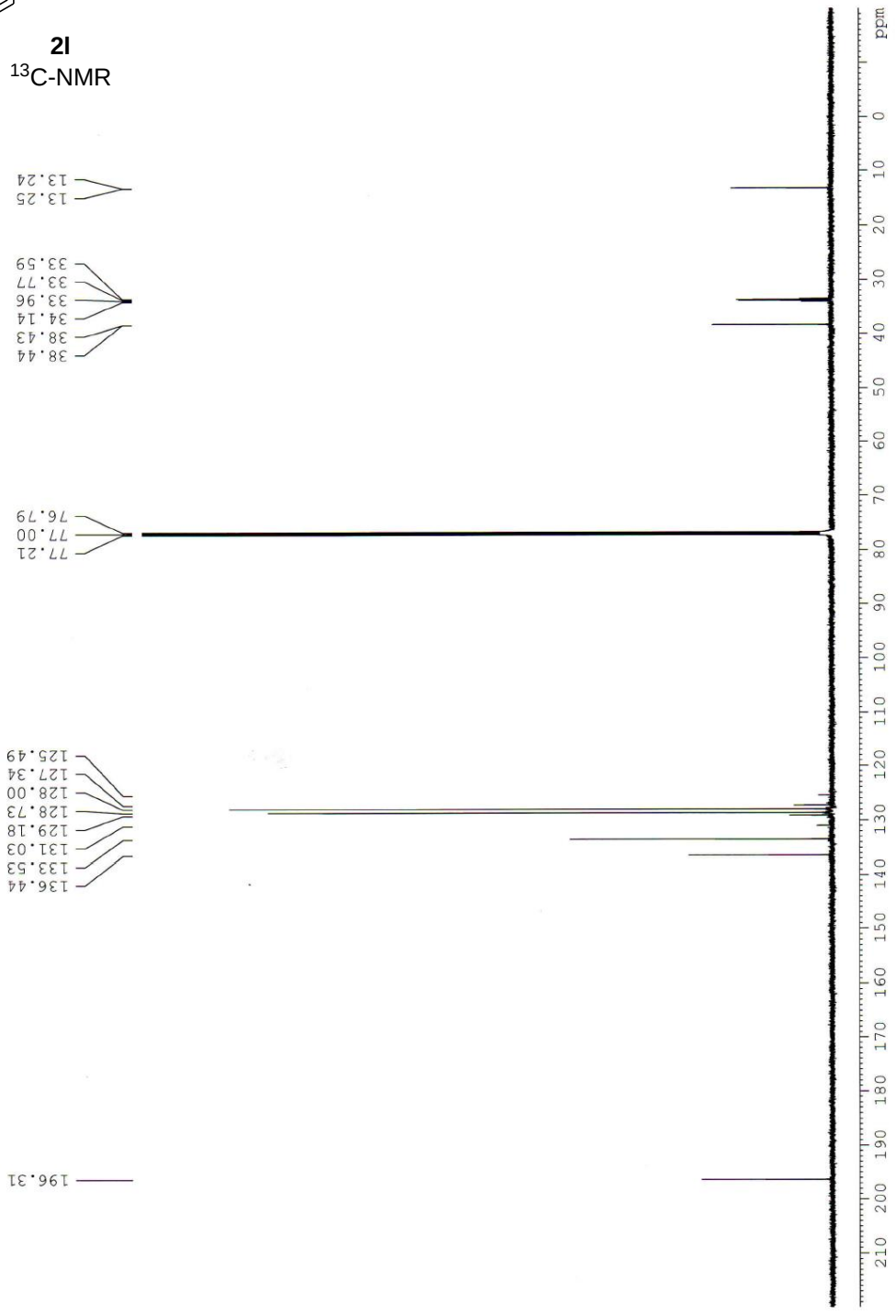
^{19}F-NMR




O
Me
CF3

2l

^{13}C-NMR


13.24
13.25
33.59
33.77
33.96
34.14
38.43
38.44
76.79
77.00
77.21
125.49
127.34
128.00
128.73
129.18
131.03
133.53
136.44
196.31
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210