Supporting Information

Catalytic enantioselective synthesis of β-trifluoromethyl pyrrolines

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Experimental Section

General Methods:

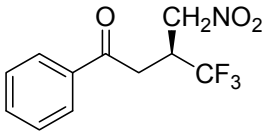
All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred *via* syringe and were introduced into the reaction vessels though a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). 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 for solution in $CDCl_3$ were recorded on a Buruker Avance 600 and a Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or $CHCl_3$. HPLC analyses were performed on a JASCO U-2080 Plus using 4.6 x 250 mm CHIRALPAK AD-3 or CHIRALCEL OJ-H or CHIRALPAK IB column. Mass spectra were recorded on a SHIMADZU LCMS-2010EV. Optical rotations were measured on a HORIBA SEPA-300. Infrared spectra were recorded on a JASCO FT/ IR-200 spectrometer. The β-trifluoromethylated enones **3** were prepared according to literature.[1]

[1] G. Blay, I. Fernández, M. C. Munoz, J. R. Pedro, C. Vila, *Chem. Eur. J.* **2010**, *16,* 9117.

General procedure for the asymmetric conjugated addition of nitromethane to β-trifluoromethylated enones 3:

To a stirred solution of β-trifluoromethylated enone **3** (0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%) in toluene (1.0 mL) was added nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) at ambient temperature under nitrogen atmosphere. After completion of reaction checked by TLC, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 90/10) to give (*S*)-**4**.

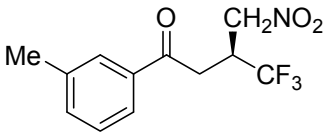
(*S*)-4,4,4-Trifluoro-3-(nitromethyl)-1-phenylbutan-1-one (4a)



Reaction of **3a** (20.0 mg, 0.10 mmol), catalyst **7** (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 20 h gave (*S*)-**4a** (26.1 mg, 99%, 97% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.35 (dd, *J* = 9.0, 18.6 Hz, 1H), 3.47 (dd, *J* = 3.9, 18.3 Hz, 1H), 3.88-3.99 (m, 1H), 4.63 (dd, *J* = 4.8, 13.8 Hz, 1H), 4.72 (dd, *J* = 6.8, 13.8 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 34.2 (m), 37.9 (q, *J* = 28.2 Hz), 72.3 (m), 126.1 (q, *J* = 280.0 Hz), 128.1, 128.9, 134.2, 135.5, 194.7; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.3 (d, *J* = 9.0 Hz, 3F) ; IR (KBr) 3068, 2962, 1691, 1558, 1451, 1396, 1172, 1102, 959, 930, 897, 799, 758, 724, 690, 653, 552, 510 cm^{-1}; mp = 48.0-49.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 300 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{11}H_{10}F_3NNaO_3$ [$(M+Na)^+$]: 284.0510 Found: 284.0506; The ee of the product was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 16.1 min, τ_{min} = 12.3 min); $[\alpha]_D^{25}$ = -7.4 (c = 0.64, $CHCl_3$), 97% ee.

(*S*)-4,4,4-Trifluoro-3-(nitromethyl)-1-*m*-tolylbutan-1-one (4b)

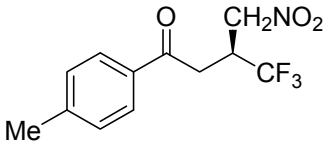


Reaction of **3b** (42.8 mg, 0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 70 h gave (*S*)-**4b** (52.4 mg, 95%, 98% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.43 (s, 3H), 3.32 (dd, *J* = 9.3, 18.3 Hz, 1H), 3.45 (dd, *J* = 4.1, 18.5 Hz, 1H), 3.87-3.98 (m, 1H), 4.62 (dd, *J* = 4.5, 14.1 Hz, 1H), 4.70 (dd, *J* = 6.5, 14.1 Hz, 1H), 7.36-7.46 (m, 2H), 7.74-7.77 (m, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.3, 34.2 (m), 37.9 (q, *J* =

28.7 Hz), 72.4 (m), 125.2, 126.1 (q, J = 280.0 Hz), 128.6, 128.8, 134.9, 135.6, 138.8, 194.8; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.3 (d, J = 7.9 Hz, 3F) ; IR (KBr) 3018, 2928, 1681, 1562, 1430, 1385, 1300, 1251, 1173, 1115, 972, 872, 798, 724, 686, 630, 597, 549, 505, 464 cm^{-1}; mp = 49.0-50.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 298 [$(M+K)^+$], HRMS (ESI) calcd. for $C_{12}H_{12}F_3NNaO_3$ [$(M+Na)^+$]: 298.0667 Found: 298.0670; The ee of the product was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 14.5 min, τ_{min} = 15.9 min); $[\alpha]_D^{25}$ = +0.3 (c = 1.19, $CHCl_3$), 98% ee.

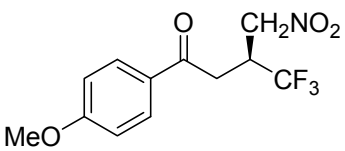
(*S*)-4,4,4-Trifluoro-3-(nitromethyl)-1-*p*-tolylbutan-1-one (4c)



Reaction of **3c** (42.8 mg, 0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 48 h gave (*S*)-**4c** (53.1 mg, 96%, 96% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.43 (s, 3H), 3.30 (dd, J = 9.3, 18.3 Hz, 1H), 3.43 (dd, J = 3.9, 18.3 Hz, 1H), 3.86-3.97 (m, 1H), 4.62 (dd, J = 4.5, 14.1 Hz, 1H), 4.69 (dd, J = 6.9, 13.7 Hz, 1H), 7.30 (d, J = 14.4 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.7, 34.0 (m), 37.9 (q, J= 28.7 Hz), 72.4 (m), 126.1 (q, J = 280.0 Hz), 128.2, 129.6, 133.1, 145.2, 194.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.4 (d, J = 9.0 Hz, 3F) ; IR (KBr) 3022, 2922, 1683, 1556, 1345, 1119, 972, 919, 891, 846, 808, 764, 730, 651, 590, 567, 506, 459 cm^{-1}; mp = 43.0-44.5 ºC ($CHCl_3$); MS (ESI, *m/z*) 298 [$(M+K)^+$], HRMS (ESI) calcd. for $C_{12}H_{12}F_3NNaO_3$ [$(M+Na)^+$]: 298.0667 Found: 298.0663; The ee of the product was determined by HPLC using an OJ-H column (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 18.2 min, τ_{min} = 14.9 min); $[\alpha]_D^{25}$ = -8.5 (c = 0.80, $CHCl_3$), 96% ee.

(*S*)-4,4,4-Trifluoro-1-(4-methoxyphenyl)-3-(nitromethyl)butan-1-one (4d)

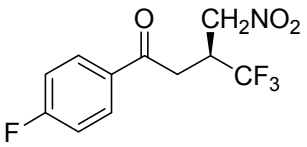


Reaction of **3d** (46.0 mg, 0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 48 h gave (*S*)-**4d** (56.1 mg, 96%, 97% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.27 (dd, J = 9.2, 18.5 Hz, 1H), 3.40 (dd, J = 4.1, 18.2 Hz, 1H), 3.83-3.97 (m, 1H), 3.89 (s, 3H), 4.63 (dd, J = 5.0, 14.3 Hz, 1H), 4.69 (dd, J = 6.8, 14.0 Hz, 1H),

6.94-6.99 (m, 2H), 7.91-7.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 33.7 (m), 37.9 (q, J = 28.2 Hz), 55.5, 72.4 (m), 114.0, 126.2 (q, J = 280.0 Hz), 128.6, 130.4, 164.3, 193.0; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.3 (d, J = 7.9 Hz, 3F) ; IR (KBr) 2965, 2844, 1667, 1550, 1255, 1120, 1030, 968, 919, 842, 818, 733, 652, 603, 569, 499, 419 cm^{-1}; mp = 90.0-92.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 314 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{12}H_{12}F_3NNaO_4$ [$(M+Na)^+$]: 314.0616 Found: 314.0626; The ee of the product was determined by HPLC using an OJ-H column (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 41.2 min, τ_{min} = 31.6 min); $[\alpha]_D^{25}$ = -10.8 (c = 1.43, $CHCl_3$), 97% ee.

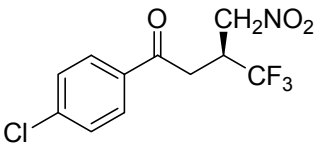
(*S*)-4,4,4-Trifluoro-1-(4-fluorophenyl)-3-(nitromethyl)butan-1-one (4e)



Reaction of **3e** (43.6 mg, 0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 70 h gave (*S*)-**4e** (49.1 mg, 88%, 97% ee) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.33 (dd, J = 9.0, 18.3 Hz, 1H), 3.44 (dd, J = 4.1, 18.5 Hz, 1H), 3.85-3.97 (m, 1H), 4.63 (dd, J = 4.8, 13.8 Hz, 1H), 4.72 (dd, J = 6.8, 14.0 Hz, 1H), 7.18 (t, J = 8.6 Hz, 2H), 8.01 (dd, J = 5.3, 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 34.1 (m), 37.9 (q, J = 28.2 Hz), 72.3 (m), 116.1 (d, J = 22.6 Hz), 126.0 (q, J = 280.0 Hz), 130.9 (d, J = 9.1 Hz), 132.0 (d, J = 3.0 Hz), 166.3 (d, J = 256.5 Hz), 193.1; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -103.5 (m, 1F), -71.3 (d, J = 7.9 Hz, 3F) ; IR (neat) 2928, 1688, 1599, 1562, 1508, 1380, 1342, 1301, 1228, 1176, 1124, 1003, 973, 911, 837, 735, 651, 587, 548, 474 cm^{-1}; MS (ESI, *m/z*) 302 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{11}H_9F_4NNaO_3$ [$(M+Na)^+$]: 302.0416 Found: 302.0414; The ee of the product was determined by HPLC using an OJ-H column (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 18.4 min, τ_{min} = 15.1 min); $[\alpha]_D^{25}$ = -6.6 (c = 1.20, $CHCl_3$), 97% ee.

(*S*)-1-(4-Chlorophenyl)-4,4,4-trifluoro-3-(nitromethyl)butan-1-one (4f)

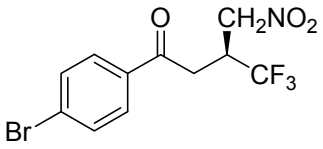


Reaction of **3f** (46.9 mg, 0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 71 h gave (*S*)-**4f** (59.1 mg, 99%, 97% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.32 (dd, J = 9.2, 18.5 Hz, 1H), 3.43 (dd, J = 4.5, 18.3 Hz, 1H),

3.85-3.96 (m, 1H), 4.63 (dd, *J* = 4.8, 13.8 Hz, 1H), 4.72 (dd, *J* = 6.6, 13.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 34.2 (m), 37.8 (q, *J* = 28.7 Hz), 72.3 (m), 126.0 (q, *J* = 280.0 Hz), 129.2, 129.5, 133.8, 140.7, 193.5; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.3 (d, *J* = 9.0 Hz, 3F) ; IR (KBr) 3097, 2947, 1927, 1691, 1554, 1380, 1308, 1265, 1227, 1121, 1029, 948, 890, 821, 781, 715, 621, 553, 499, 456 cm^{-1}; mp = 45.0-46.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 318 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{11}H_9ClF_3NNaO_3$ [$(M+Na)^+$]: 318.0121 Found: 318.0118; The ee of the product was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 17.7 min, τ_{min} = 19.7 min); $[\alpha]_D^{25}$ = -8.5 (c = 1.31, $CHCl_3$), 97% ee.

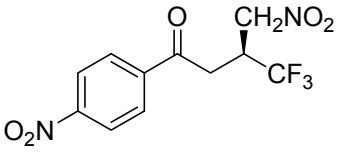
(*S*)-1-(4-Bromophenyl)-4,4,4-trifluoro-3-(nitromethyl)butan-1-one (4g)



Reaction of **3g** (55.8 mg, 0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 72 h gave (*S*)-**4g** (62.8 mg, 92%, 98% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.32 (dd, *J* = 8.9, 18.5 Hz, 1H), 3.43 (dd, *J* = 4.4, 18.2 Hz, 1H), 3.85-3.96 (m, 1H), 4.63 (dd, *J* = 4.8, 13.8 Hz, 1H), 4.72 (dd, *J* = 6.6, 13.8 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 34.2 (m), 37.8 (q, *J* = 28.2 Hz), 72.2 (m), 126.0 (q, *J* = 280.0 Hz), 129.5, 132.2, 134.2, 193.7; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.3 (d, *J* = 7.9 Hz, 3F) ; IR (KBr) 3032, 2974, 1928, 1676, 1558, 1487, 1344, 1172, 1121, 973, 895, 817, 784, 737, 704, 637, 564, 509, 472 cm^{-1}; mp = 40.0-41.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 362 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{11}H_9BrF_3NNaO_3$ [$(M+Na)^+$]: 361.9616 Found: 361.9615; The ee of the product was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 12.7 min, τ_{min} = 13.8 min); $[\alpha]_D^{25}$ = -8.9 (c = 1.37, $CHCl_3$), 98% ee.

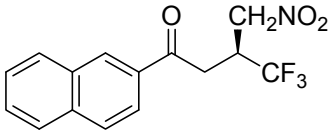
(*S*)-4,4,4-Trifluoro-3-(nitromethyl)-1-(4-nitrophenyl)butan-1-one (4h)



Reaction of **3h** (49.0 mg, 0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 90 h gave (*S*)-**4h** (57.3 mg, 94%, 97% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.44 (dd, *J* = 8.4, 18.6 Hz, 1H), 3.53 (dd, *J* = 4.5, 18.6 Hz, 1H), 3.88-3.98 (m, 1H), 4.66 (dd, *J* = 5.0, 14.0 Hz, 1H), 4.77 (dd, *J* = 6.5, 14.0 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.36 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 34.9 (m), 37.8 (q, *J* = 28.7 Hz), 72.1 (m), 124.1, 125.8 (q, *J* = 280.0 Hz), 129.2, 139.8, 150.8, 193.4; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.2 (d, *J* = 7.9 Hz, 3F) ; IR (KBr) 3113, 2931, 1687, 1563, 1525, 1345, 1254, 1217, 1125, 1059, 1006, 952, 851, 788, 748, 723, 687, 642, 489 cm^{-1}; mp = 80.0-81.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 329 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{11}H_9F_3N_2NaO_5$ [$(M+Na)^+$]: 329.0361 Found: 329.0368.; The ee of the product was determined by HPLC using an OJ-H column (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 47.5 min, τ_{min} = 64.5 min); $[\alpha]_D^{25}$ = -8.2 (c = 1.53, $CHCl_3$), 97% ee.

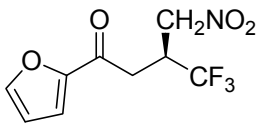
(*S*)-4,4,4-Trifluoro-1-(naphthalen-2-yl)-3-(nitromethyl)butan-1-one (4i)



Reaction of **3i** (50.0 mg, 0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 72 h gave (*S*)-**4i** (60.3 mg, 97%, 97% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.46 (dd, *J* = 9.2, 18.2 Hz, 1H), 3.58 (dd, *J* = 4.1, 18.5 Hz, 1H), 3.96-4.01 (m, 1H), 4.66 (dd, *J* = 4.7, 14.0 Hz, 1H), 4.74 (dd, *J* = 6.5, 14.0 Hz, 1H), 7.55-7.66 (m, 2H), 7.87-7.92 (m, 2H), 7.95-8.00 (m, 2H), 8.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 34.2 (m), 38.0 (q, *J* = 28.2 Hz), 72.4 (m), 123.3, 126.1 (q, J = 281 Hz), 127.2, 127.8, 128.9, 129.1, 129.6, 130.1, 132.3, 132.8, 135.9, 194.5; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.2 (d, *J* = 8.7 Hz, 3F) ; IR (KBr) 3035, 2931, 1675, 1569, 1469, 1430, 1384, 1254, 1168, 1117, 974, 941, 857, 823, 748, 625, 592, 549, 474 cm^{-1}; mp = 74.5-76.5 ºC ($CHCl_3$); MS (ESI, *m/z*) 334 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{15}H_{12}F_3NNaO_3$ [$(M+Na)^+$]: 334.0667 Found: 334.0669; The ee of the product was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 17.1 min, τ_{min} = 14.9 min); $[\alpha]_D^{25}$ = -24.3 (c = 1.65, $CHCl_3$), 97% ee.

(*S*)-4,4,4-Trifluoro-1-(furan-2-yl)-3-(nitromethyl)butan-1-one (4j)



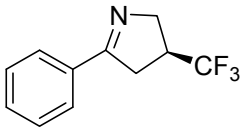
Reaction of **3j** (38.0 mg, 0.20 mmol), catalyst **7** (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 72 h gave (*S*)-**4j** (47.6 mg, 95%, 98% ee) as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.20 (dd, *J* = 9.0, 18.0 Hz, 1H), 3.35 (dd, *J* = 4.4, 18.2 Hz, 1H),

3.83-3.94 (m, 1H), 4.64 (dd, J = 5.1, 13.8 Hz, 1H), 4.71 (dd, J = 6.5, 14.0 Hz, 1H), 6.61 (dd, J = 1.7, 3.8 Hz, 1H), 7.29 (dd, J = 0.8, 4.1 Hz, 1H), 7.64-7.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 33.8 (m), 37.5 (q, J = 28.7 Hz), 72.3 (m), 112.8, 118.2, 125.9 (q, J = 280.0 Hz), 147.2, 151.6, 183.6; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.4 (d, J = 9.0 Hz, 3F) ; IR (neat) 3142, 2929, 1681, 1567, 1469, 1386, 1254, 1176, 1126, 1037, 974, 914, 883, 838, 767, 735, 639, 594 cm^{-1}; MS (ESI, *m/z*) 274 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_9H_8F_3NNaO_4$ [$(M+Na)^+$]: 274.0303 Found: 274.0304; The ee of the product was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 23.3 min, τ_{min} = 20.0 min); $[\alpha]_D^{25}$ = -8.7 (c = 1.12, $CHCl_3$), 98% ee.

General procedure for the enantioselective one-pot synthesis of β-trifluoromethyl pyrrolines 2:
To a stirred solution of β-trifluoromethylated enone **3** (0.10 mmol), catalyst **7** (1.1 mg, 0.002 mmol, 2 mol%) in toluene (0.5 mL) was added nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) at ambient temperature under nitrogen atmosphere. After completion of reaction checked by TLC, the reaction mixture was concentrated under reduced pressure. To a stirred solution of crude **4** in THF/MeOH (2/1, 1.5 mL) was added acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) successively at the ambient temperature, and the resulting mixture was heated at 65 ºC for 10 h under nitrogen atmosphere. After cooling down to room temperature, the reaction mixture was filtrated through Celite, rinsed with AcOEt. The whole mixture was washed with sat. $NaHCO_3$ aq., brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3$) to give β-trifluoromethyl pyrroline (*S*)-**2.**

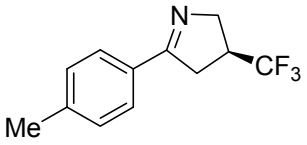
(*S*)-5-Phenyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole (2a)



Reaction of **3a** (20.0 mg, 0.10 mmol), catalyst **7** (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 50 h gave the crude product of **4a**. Reduction-cyclization-dehydration reaction of crude **4a**, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (*S*)-**2a** (19.0 mg, 89%, 98% ee) as a white solid.
^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.12-3.32 (m, 3H), 4.20-4.37 (m, 2H), 7.40-7.50 (m, 3H), 7.78-7.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 35.9 (m), 40.9 (q, J = 28.2 Hz), 61.2 (m), 127.5 (q, J = 277.2 Hz), 127.6, 128.6, 131.0, 133.4, 170.9; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -72.2 (d, J = 8.7 Hz, 3F) ; IR (KBr) 3032, 2944, 1628, 1578, 1496, 1439, 1385, 1351, 1276, 1108, 1024, 928, 797, 764, 694, 553, 520.7, 458 cm^{-1}; mp = 61.0-62.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 214 $[M+H]^+$, HRMS (ESI) calcd. for $C_{11}H_{11}F_3N$ $[M+H]^+$: 214.0844 Found: 214.0835; The ee of the product was determined by

HPLC using an OJ-H column (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 14.9 min, τ_{min} = 19.6 min); $[\alpha]_D^{25}$ = -42.4 (c = 0.32, $CHCl_3$), 98% ee.

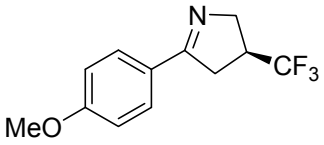
(*S*)-5-*p*-Tolyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole (2c)



Reaction of **3c** (21.4 mg, 0.10 mmol), catalyst **7** (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 50 h gave the crude product of **4c**. Reduction-cyclization-dehydration reaction of crude **3c**, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (*S*)-**2c** (20.9 mg, 92%, 98% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3H), 3.10-3.26 (m, 3H), 4.18-4.35 (m, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.5, 35.9 (m), 40.8 (q, *J* = 28.2 Hz), 61.1 (m), 127.57 (q, *J* = 277.2 Hz), 127.57, 129.3, 130.7, 141.3, 170.8; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -72.2 (d, *J* = 7.9 Hz, 3F) ; IR (KBr) 2950, 2879, 1924, 1622, 1569, 1514, 1459, 1387, 1343, 1320, 1109, 960, 821, 714, 609, 554, 517, 468 cm^{-1}; mp = 62.0-64.5 ºC ($CHCl_3$); MS (ESI, *m/z*) 228 $[M+H]^+$, HRMS (ESI) calcd. for $C_{12}H_{13}F_3N$ $[M+H]^+$: 228.1000 Found: 228.1007; The ee of the product was determined by HPLC using an OJ-H column (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 15.9 min, τ_{min} = 23.2 min); $[\alpha]_D^{25}$ = -43.5 (c = 0.36, $CHCl_3$), 98% ee.

(*S*)-5-(4-Methoxyphenyl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole (2d)

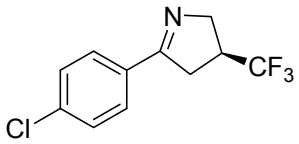


Reaction of **3d** (23.0 mg, 0.10 mmol), catalyst **7** (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 50 h gave the crude product of **4d**. Reduction-cyclization-dehydration reaction of crude **4d**, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (*S*)-**2d** (23.6 mg, 97%, 98% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.10-3.24 (m, 3H), 3.85 (s, 3H), 4.16-4.32 (m, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 35.8 (m), 40.9 (q, *J* = 28.2 Hz), 55.3, 61.0 (m), 113.9, 126.2, 127.6 (q, *J* = 276.7 Hz), 129.3, 161.8, 170.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -72.2 (d, *J* = 8.7 Hz, 3F) ; IR (KBr) 2962, 2841, 1623, 1575, 1516, 1462, 1385, 1345, 1319,

1158, 1111, 1037, 845, 821, 556 cm^{-1}; mp = 79.5-81.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 244 $[M+H]^+$, HRMS (ESI) calcd. for $C_{12}H_{13}F_3NO$ $[M+H]^+$: 244.0949 Found: 244.0948; The ee of the product was determined by HPLC using an AD-3 column (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 26.9 min, τ_{min} = 25.7 min); $[\alpha]_D^{25}$ = -42.7 (c = 0.53, $CHCl_3$), 98% ee.

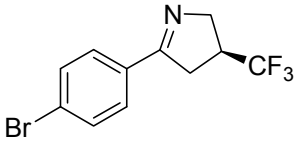
(*S*)-5-(4-Chlorophenyl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole (2f)



Reaction of **3f** (23.5 mg, 0.10 mmol), catalyst **7** (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 72 h gave the crude product of **4f**. Reduction-cyclization-dehydration reaction of crude **4f**, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (*S*)-**2f** (23.3 mg, 94%, 98% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.12-3.25 (m, 3H), 4.19-4.37 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 35.9 (m), 40.9 (q, *J* = 28.2 Hz), 61.3 (m), 127.4 (q, *J* = 277.2 Hz), 128.86, 128.91, 131.8, 137.1, 169.8; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -72.3 (d, *J* = 8.7 Hz, 3F) ; IR (KBr) 2955, 2880, 1625, 1492, 1439, 1387, 1321, 1274, 1116, 1034, 1014, 957, 828, 714, 553, 528, 455 cm^{-1}; mp = 67.0-68.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 248 $[M+H]^+$, HRMS (ESI) calcd. for $C_{11}H_{10}ClF_3N$ $[M+H]^+$: 248.0454 Found: 248.0459; The ee of the product was determined by HPLC using an OJ-H column (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 14.6 min, τ_{min} = 22.6 min); $[\alpha]_D^{25}$ = -38.2 (c = 0.45, $CHCl_3$), 98% ee.

(*S*)-5-(4-Bromophenyl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole (2g)

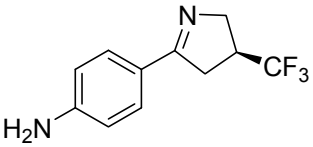


Reaction of **3g** (27.9 mg, 0.10 mmol), catalyst **7** (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 72 h gave the crude product of **4g**. Reduction-cyclization-dehydration reaction of crude **4g**, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (*S*)-**2g** (26.7 mg, 91%, 98% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.12-3.24 (m, 3H), 4.18-4.36 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 35.9 (m), 40.9 (q, *J* = 28.7 Hz), 61.3 (m),

125.6, 127.4 (q, J = 277.2 Hz), 129.1, 131.8, 132.2, 169.9; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -72.3 (d, J = 7.9 Hz, 3F) ; IR (KBr) 2956, 2877, 1624, 1590, 1564, 1488, 1438, 1385, 1343, 1321, 1272, 1114, 1072, 1033, 825, 709, 551, 456 cm^{-1}; mp = 78.0-79.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 292 $[M+H]^+$, HRMS (ESI) calcd. for $C_{11}H_{10}BrF_3N$ $[M+H]^+$: 291.9949 Found: 291.9942; The ee of the product was determined by HPLC using an OJ-H column (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 16.0 min, τ_{min} = 28.2 min); $[\alpha]_D^{25}$ = -33.3 (c = 0.61, $CHCl_3$), 98% ee.

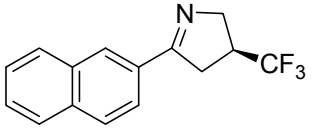
(*S*)-4-(3-(Trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-5-yl)aniline (2h)



Reaction of **3h** (24.5 mg, 0.10 mmol), catalyst **7** (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 90 h gave the crude product of **4h**. Reduction-cyclization-dehydration reaction of crude **4h**, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (*S*)-**2h** (19.5 mg, 85%, 98% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.08-3.21 (m, 3H), 4.06-4.30 (m, 5H), 6.67 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 35.7 (m), 40.8 (q, J = 27.7 Hz), 60.8 (m), 114.4, 123.7, 127.6 (q, J = 277.2 Hz), 129.3, 149.1, 170.4 ; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -72.1 (d, J = 7.9 Hz, 3F) ; IR (KBr) 3329, 3215, 2873, 1601, 1520, 1437, 1378, 1350, 1303, 1264, 1220, 1177, 1144, 1102, 1027, 984, 831, 550, 465 cm^{-1}; mp = 128.0-131.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 229 $[M+H]^+$, HRMS (ESI) calcd. for $C_{11}H_{12}F_3N_2$ $[M+H]^+$: 229.0953 Found: 229.0952; The ee of the product was determined by HPLC using an OJ-H column (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 10.6 min, τ_{min} = 16.0 min); $[\alpha]_D^{25}$ = -47.8 (c = 0.50, $CHCl_3$), 98% ee.

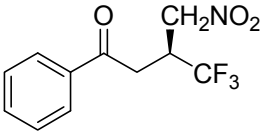
(*S*)-5-(Naphthalen-2-yl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole (2i)



Reaction of **3i** (25.0 mg, 0.10 mmol), catalyst **7** (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 72 h gave the crude product of **4i**. Reduction-cyclization-dehydration reaction of crude **4i**, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (*S*)-**2i** (25.0 mg, 95%, 97% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.17-3.43 (m, 3H), 4.25-4.43 (m, 2H), 7.50-7.57 (m, 2H), 7.84-7.91

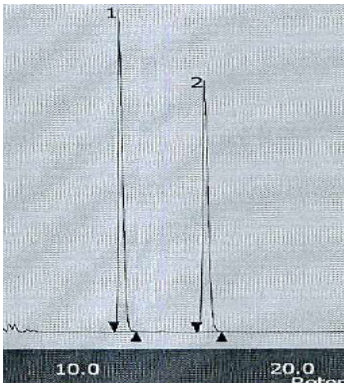
(m, 3H), 8.06 (d, *J* = 8.7 Hz, 1H), 8.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 36.0 (m), 40.9 (q, J = 28.2 Hz), 61.3 (m), 124.2, 126.6, 127.4, 127.6 (q, J = 277.2 Hz), 127.8, 128.41, 128.44, 128.7, 130.9, 132.8, 134.5, 170.9; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -72.1 (d, *J* = 9.9 Hz, 3F) ; IR (KBr) 3071, 2934, 1620, 1436, 1379, 1320, 1270, 1204, 1155, 1106, 1022, 960, 897, 869, 826, 754, 623, 576, 480 cm^{-1}; mp = 91.0-92.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 264 $[M+H]^+$, HRMS (ESI) calcd. for $C_{15}H_{13}F_3N$ $[M+H]^+$: 264.1000 Found: 264.0997; The ee of the product was determined by HPLC using an AD-3 column (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 23.9 min, τ_{min} = 33.6 min); $[\alpha]_D^{25}$ = -34.7 (c = 0.14, $CHCl_3$), 97% ee.

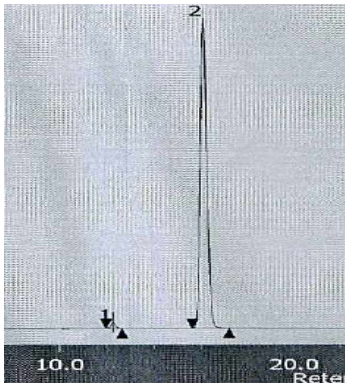


(*S*)-**4a**

HPLC using an IB

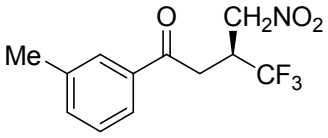
(*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	12.058	49.945	56.471
2	15.967	50.055	43.529

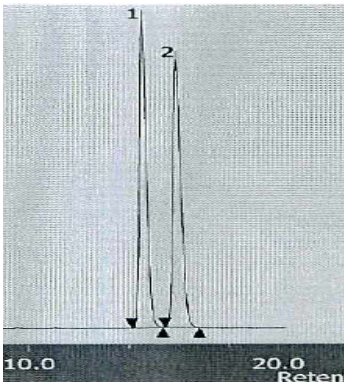
No.	tR (min)	Area (%)	High (%)
1	12.258	1.435	1.977
2	16.133	98.565	98.023

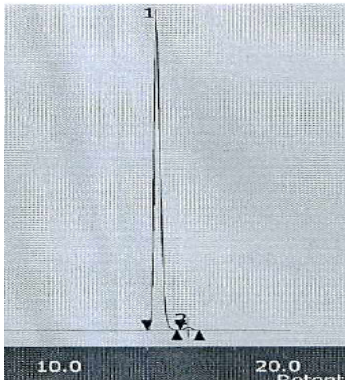


(*S*)-**4b**

HPLC using an IB

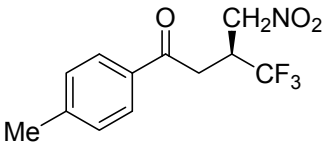
(*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	14.575	50.015	53.549
2	15.933	49.985	46.451

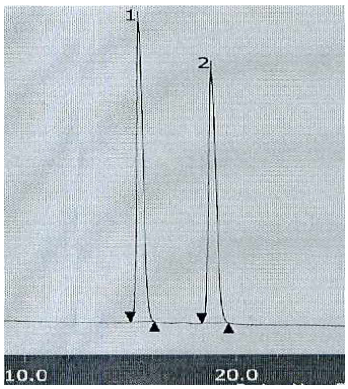
No.	tR (min)	Area (%)	High (%)
1	14.467	99.086	99.152
2	15.875	0.914	0.848

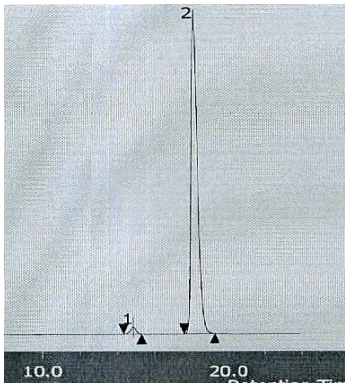


(*S*)-**4c**

HPLC using an OJ-H

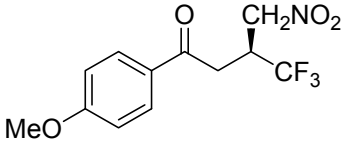
(*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	15.458	50.115	54.325
2	18.908	49.885	45.675

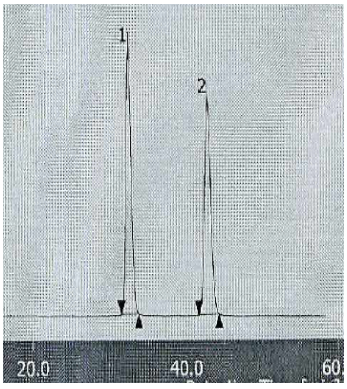
No.	tR (min)	Area (%)	High (%)
1	14.850	1.959	2.120
2	18.183	98.041	97.880

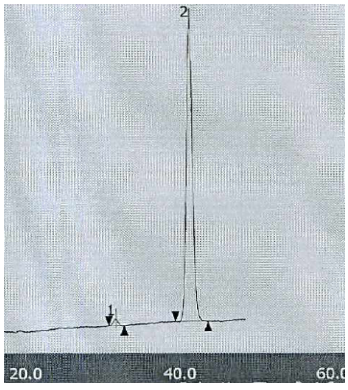


(*S*)-**4d**

HPLC using an OJ-H

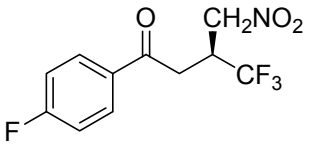
(*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	32.375	50.139	55.278
2	42.792	49.861	44.722

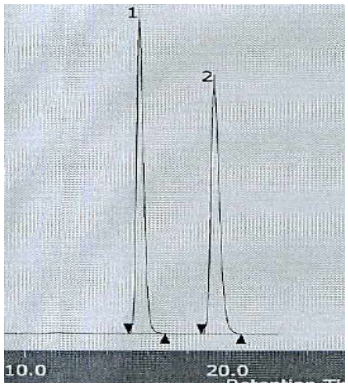
No.	tR (min)	Area (%)	High (%)
1	31.600	1.660	2.356
2	41.217	98.340	97.644

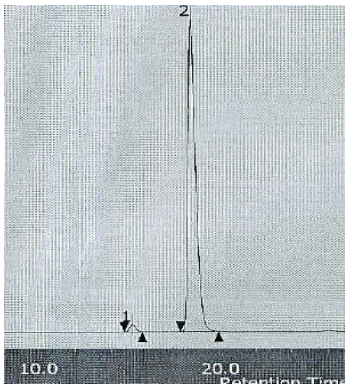


(*S*)-**4e**

HPLC using an OJ-H

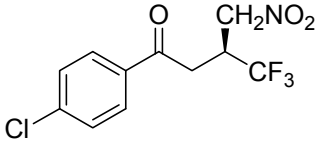
(*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	15.592	50.010	55.793
2	19.325	49.990	44.207

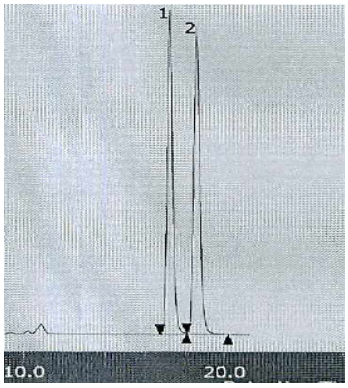
No.	tR (min)	Area (%)	High (%)
1	15.117	1.730	2.261
2	18.383	98.270	97.739

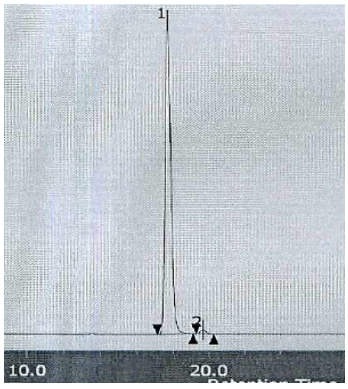


(*S*)-**4f**

HPLC using an IB

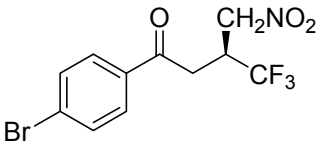
(*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	17.183	49.544	51.351
2	18.533	50.456	48.649

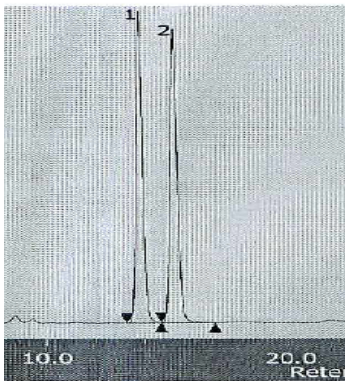
No.	tR (min)	Area (%)	High (%)
1	17.717	98.716	98.729
2	19.667	1.284	1.271

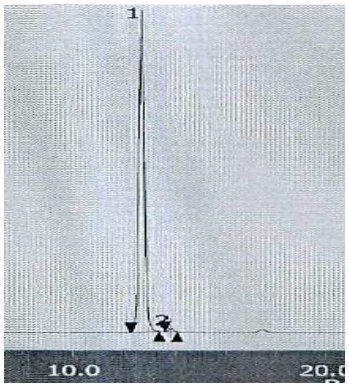


(*S*)-**4g**

HPLC using an IB

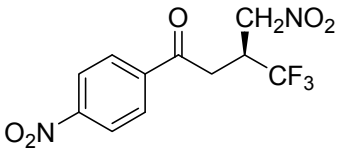
(*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	13.758	49.816	51.528
2	15.158	50.184	48.472

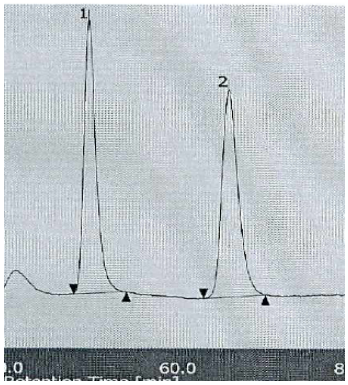
No.	tR (min)	Area (%)	High (%)
1	12.650	99.056	98.999
2	13.808	0.944	1.001

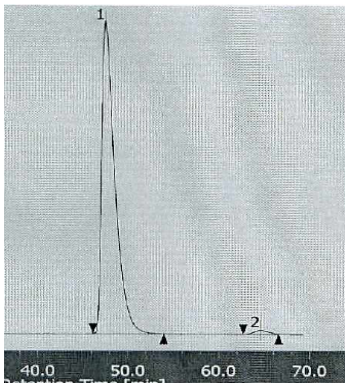


(*S*)-**4h**

HPLC using an OJ-H

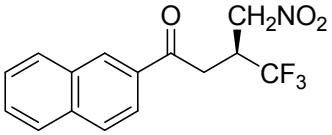
(*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	49.617	50.160	56.908
2	65.683	49.840	43.092

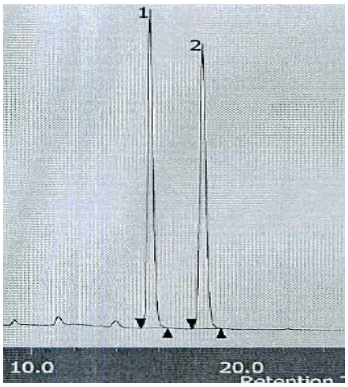
No.	tR (min)	Area (%)	High (%)
1	47.492	98.559	98.761
2	64.533	1.441	1.239

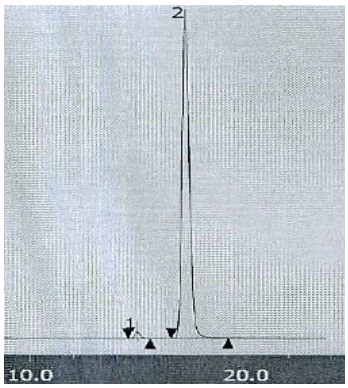


(*S*)-**4i**

HPLC using an IB

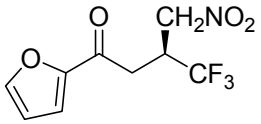
(*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	15.617	49.914	52.896
2	18.133	50.086	47.104

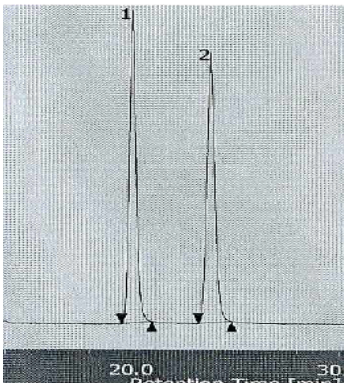
No.	tR (min)	Area (%)	High (%)
1	14.925	1.502	2.124
2	17.117	98.498	97.876

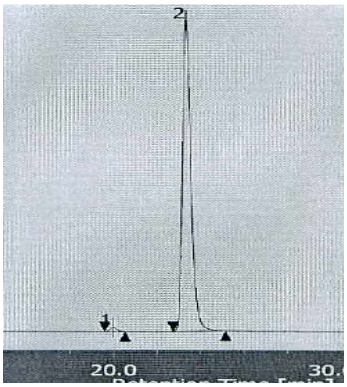


(*S*)-**4j**

HPLC using an IB

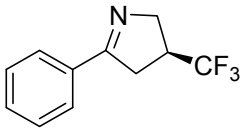
(*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	20.008	49.968	53.812
2	23.783	50.032	46.188

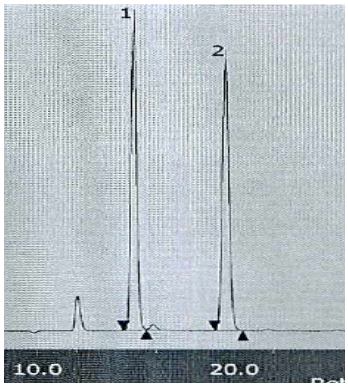
No.	tR (min)	Area (%)	High (%)
1	19.983	1.078	1.324
2	23.333	98.922	98.676



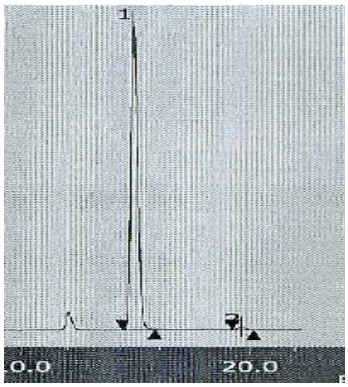
(*S*)-**2a**

HPLC using an OJ-H

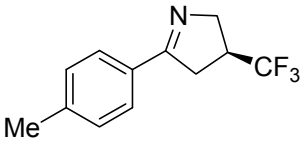
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)



No.	tR (min)	Area (%)	High (%)
1	14.875	49.943	53.414
2	19.542	50.057	46.586



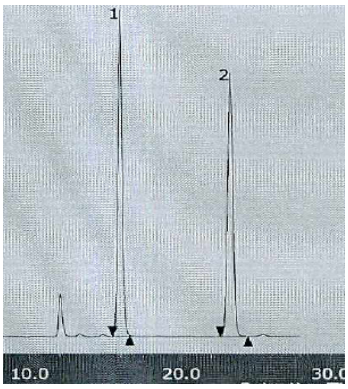
No.	tR (min)	Area (%)	High (%)
1	14.908	98.994	99.083
2	19.617	1.006	0.917



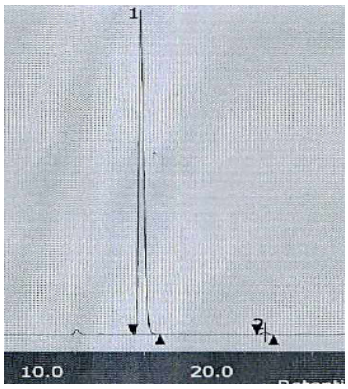
(*S*)-**2c**

HPLC using an OJ-H

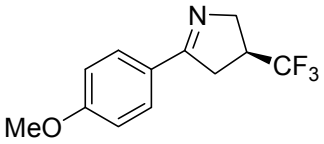
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)



No.	tR (min)	Area (%)	High (%)
1	15.917	50.198	55.503
2	23.233	49.802	44.497



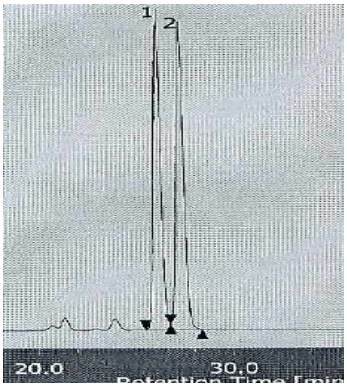
No.	tR (min)	Area (%)	High (%)
1	15.858	99.132	99.266
2	23.175	0.868	0.734

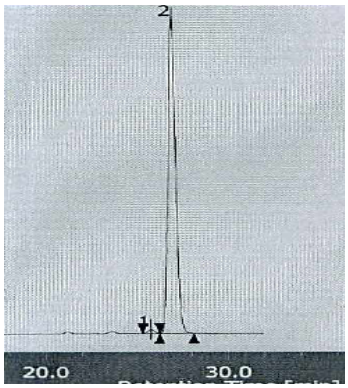


(*S*)-**2d**

HPLC using an AD-3

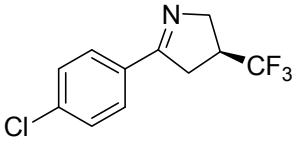
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	26.133	49.801	51.084
2	27.300	50.199	48.916

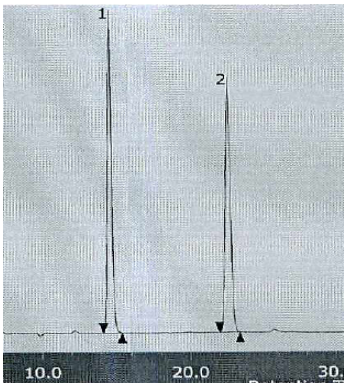
No.	tR (min)	Area (%)	High (%)
1	25.733	1.143	1.245
2	26.908	98.857	98.755

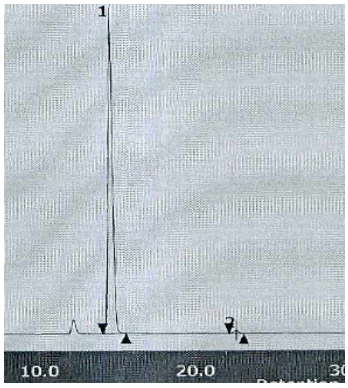


(*S*)-**2f**

HPLC using an OJ-H

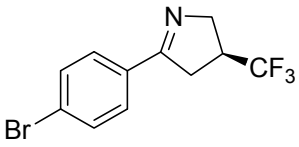
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	14.558	50.044	56.176
2	22.583	49.956	43.824

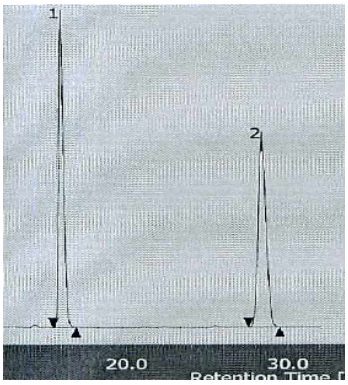
No.	tR (min)	Area (%)	High (%)
1	14.575	98.946	99.153
2	22.625	1.054	0.847

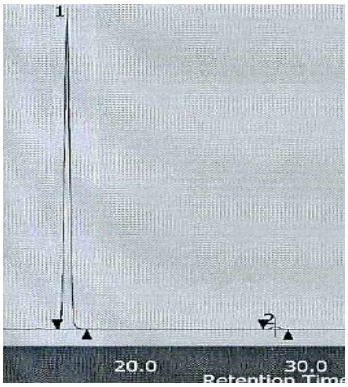


(*S*)-**2g**

HPLC using an OJ-H

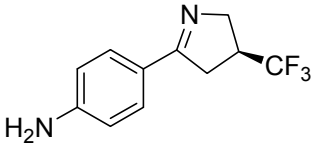
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	16.042	50.082	62.400
2	28.425	49.918	37.600

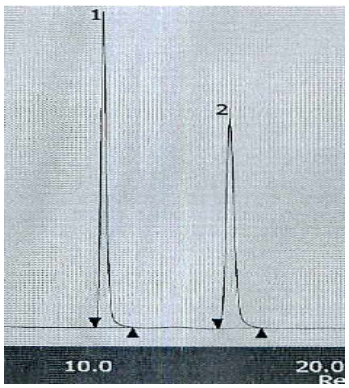
No.	tR (min)	Area (%)	High (%)
1	16.000	98.740	99.249
2	28.192	1.260	0.751

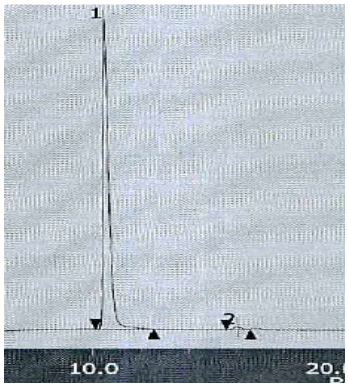


(*S*)-**2h**

HPLC using an OJ-H

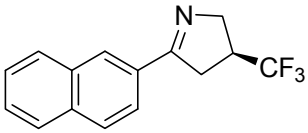
(*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	10.650	49.870	59.272
2	16.067	50.130	40.728

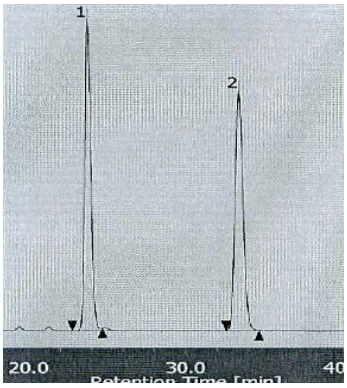
No.	tR (min)	Area (%)	High (%)
1	10.567	99.045	99.234
2	16.033	0.955	0.766



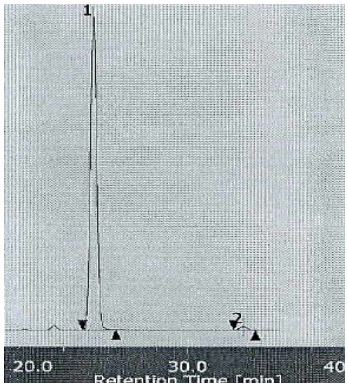
(*S*)-**2i**

HPLC using an AD-3

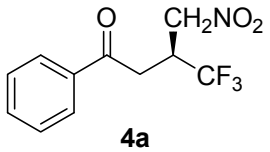
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)



No.	tR (min)	Area (%)	High (%)
1	23.758	49.751	56.554
2	33.408	50.249	43.446

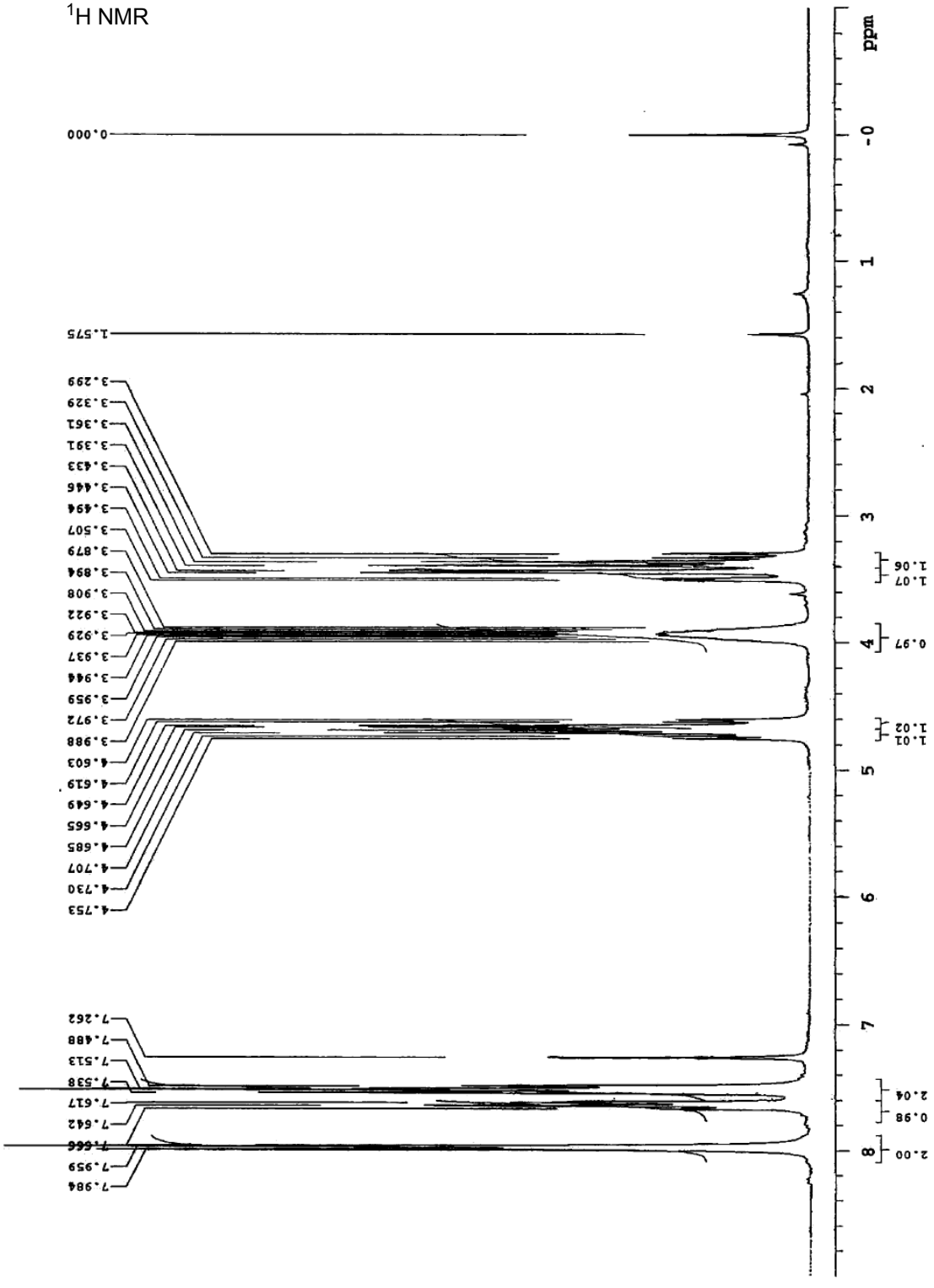


No.	tR (min)	Area (%)	High (%)
1	23.867	98.648	98.875
2	33.575	1.352	1.125


O
CH_2NO_2
CF_3

4a

^{1}H NMR


0.000
1.575
3.299
3.329
3.361
3.391
3.433
3.446
3.494
3.507
3.879
3.894
3.908
3.922
3.929
3.937
3.944
3.959
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7.513
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7.617
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ppm
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1.07
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1.01
1.02
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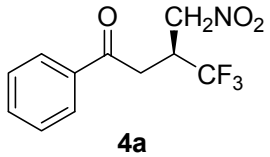
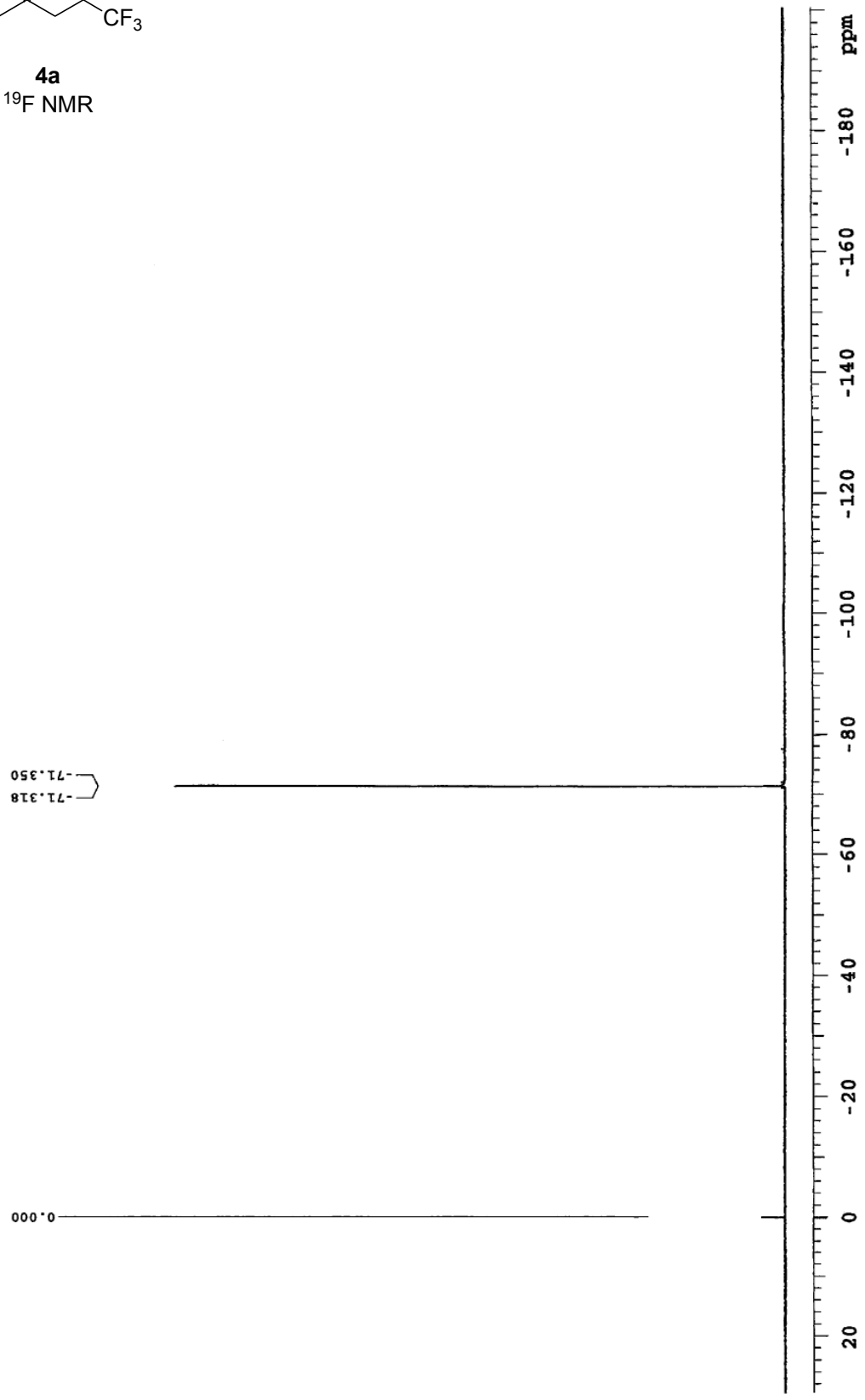
2.00


O
CH2NO2
CF3

4a

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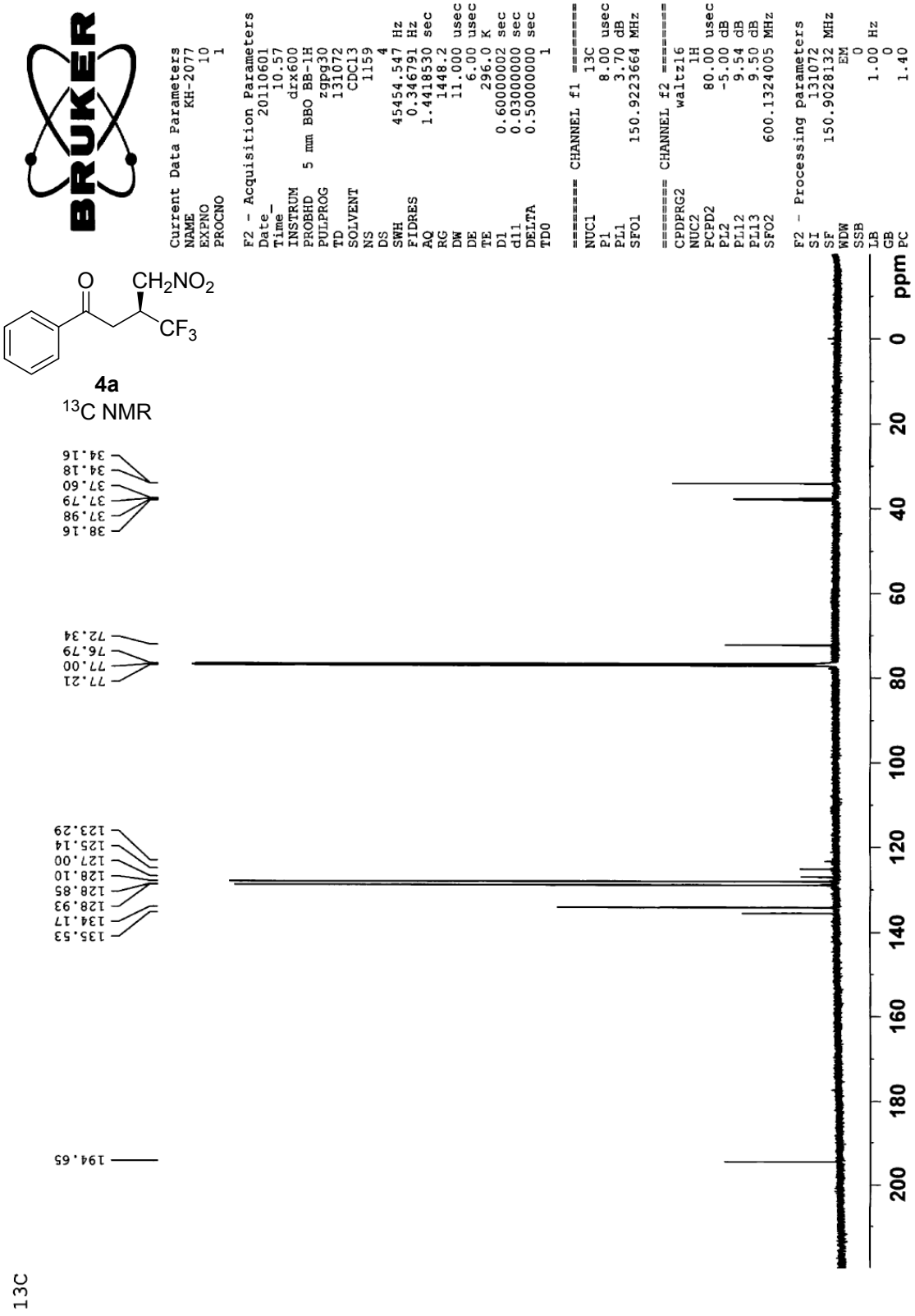
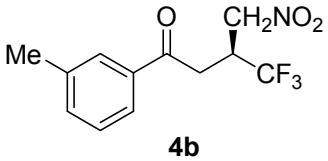
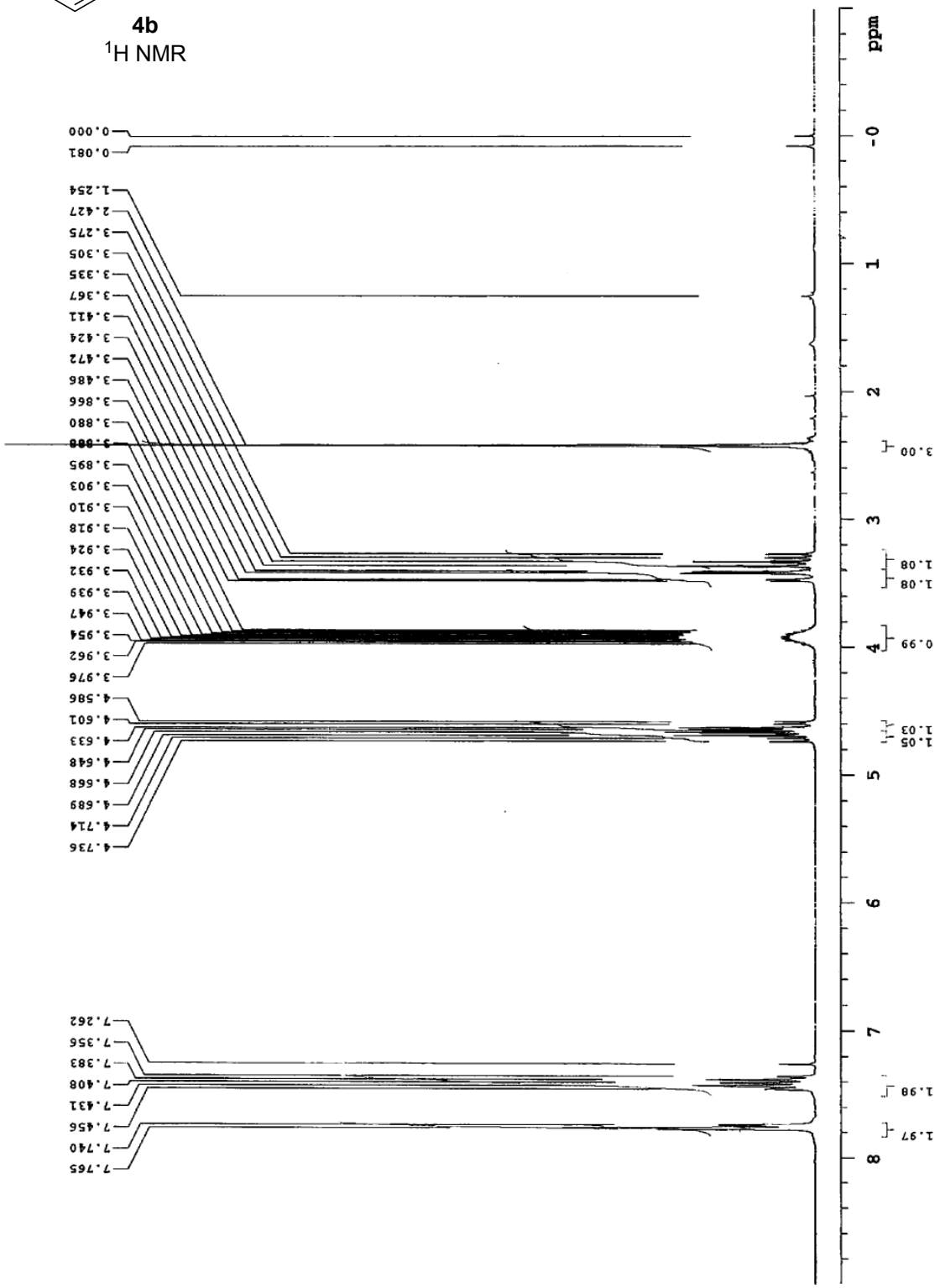
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180


Current Data Parameters
NAME KH-2077
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110601
Time_ 10.57
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1159
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1448.2
DW 11.000 usec
DE 6.00 usec
TE 296.0 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028132 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
CF3
4a
13C NMR
34.16
34.18
37.60
37.79
37.98
38.16
72.34
76.79
77.00
77.21
123.29
125.14
127.00
128.10
128.85
128.93
134.17
135.53
194.65
ppm
13C


O
CH_2NO_2
Me
CF_3

4b

^{1}H NMR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3.275
3.305
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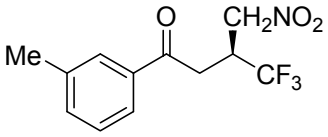
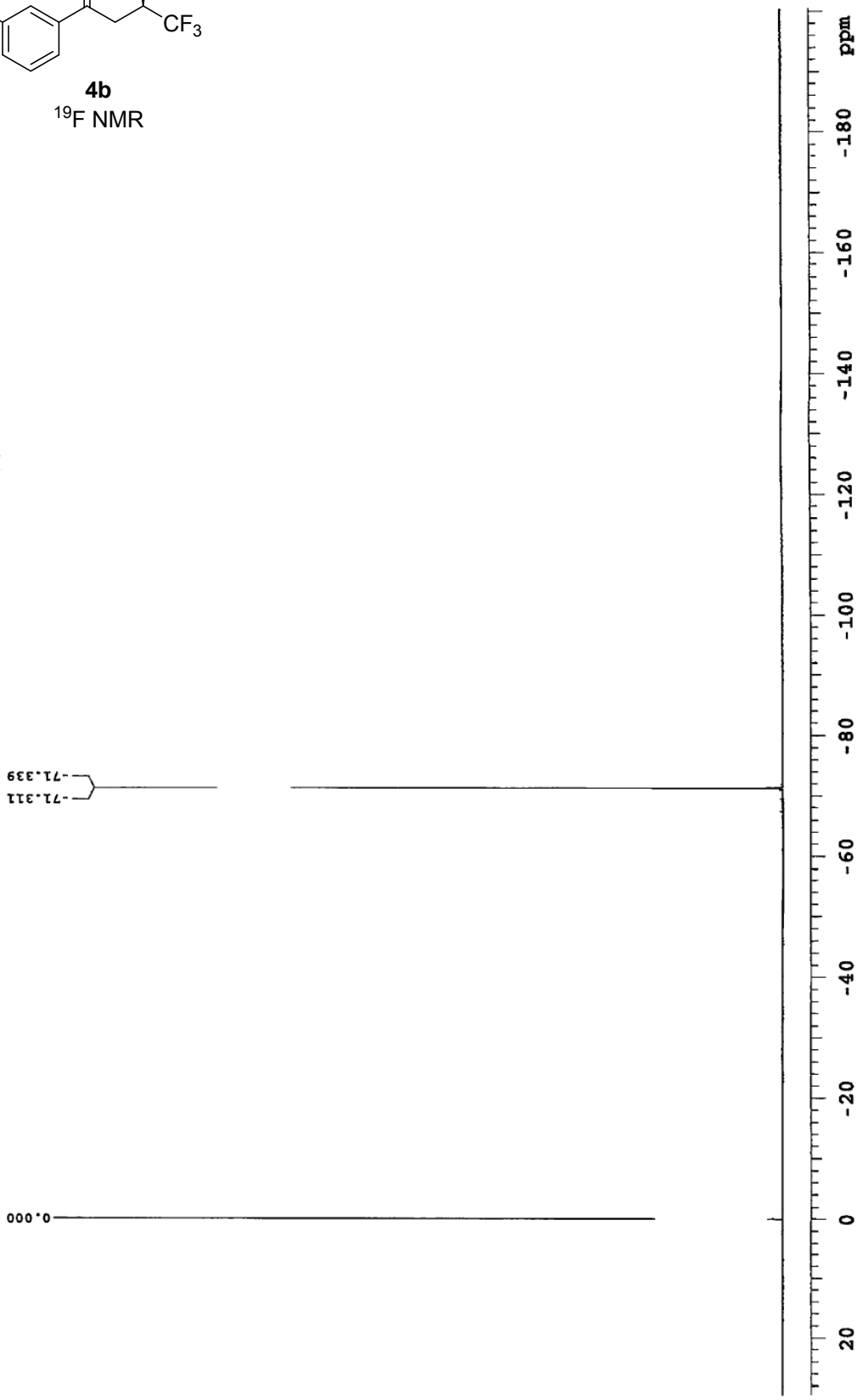
3.367
3.411
3.424
3.472
3.486
3.866
3.880
3.888
3.895
3.903
3.910
3.918
3.924
3.932
3.939
3.947
3.954
3.962
3.976
4.586
4.601
4.633
4.648
4.668
4.689
4.714
4.736
7.262
7.356
7.383
7.408
7.431
7.456
7.740
7.765
3.00
1.08
1.08
0.99
1.05
1.03
1.98
1.97


O
CH2NO2
Me
CF3

4b

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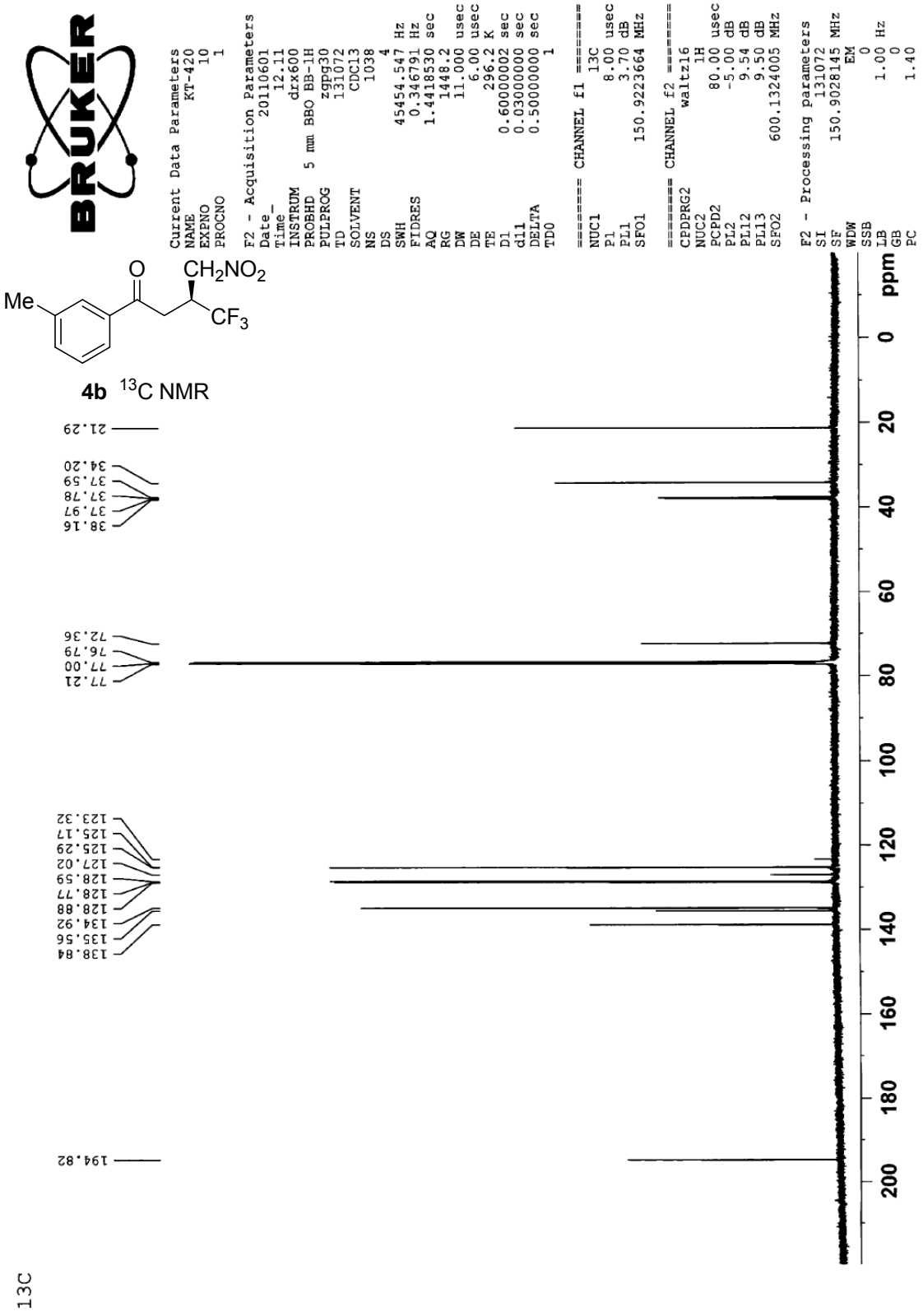
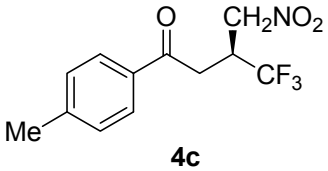
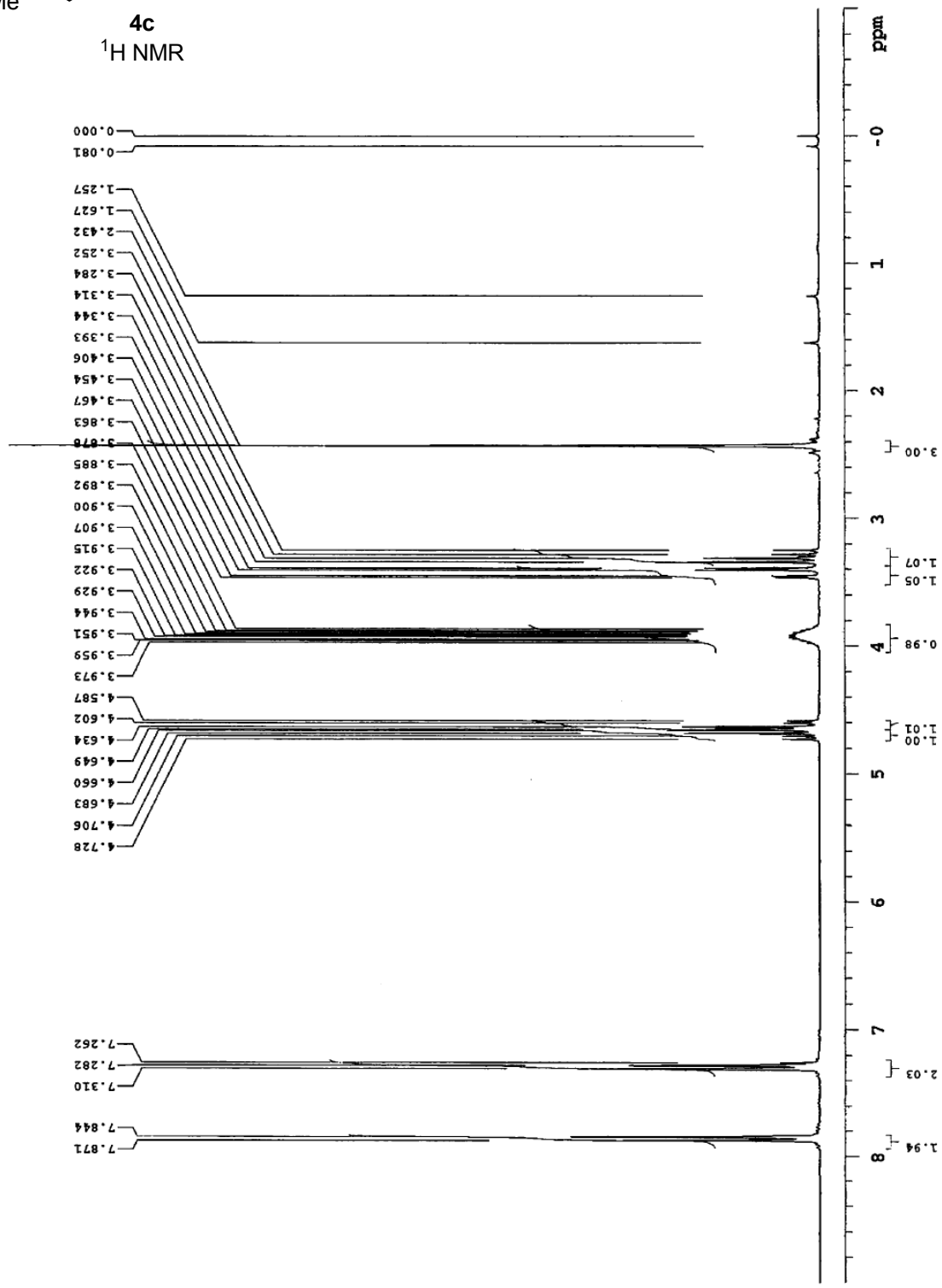
0.000
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180


Current Data Parameters
NAME KT-420
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110601
Time 12.11
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1038
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1448.2
DW 11.000 usec
DE 6.00 usec
TE 296.2 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028145 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
Me
CF3
4b 13C NMR
21.29
34.20
37.59
37.78
37.97
38.16
72.36
76.79
77.00
77.21
123.32
125.17
125.29
127.02
128.59
128.77
128.88
134.92
135.56
138.84
194.82
ppm
0
20
40
60
80
100
120
140
160
180
200
13C


O
CH_2NO_2
CF_3
Me

4c

^{1}H NMR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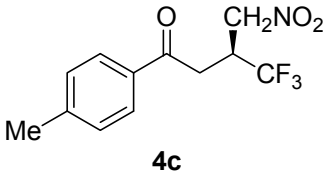
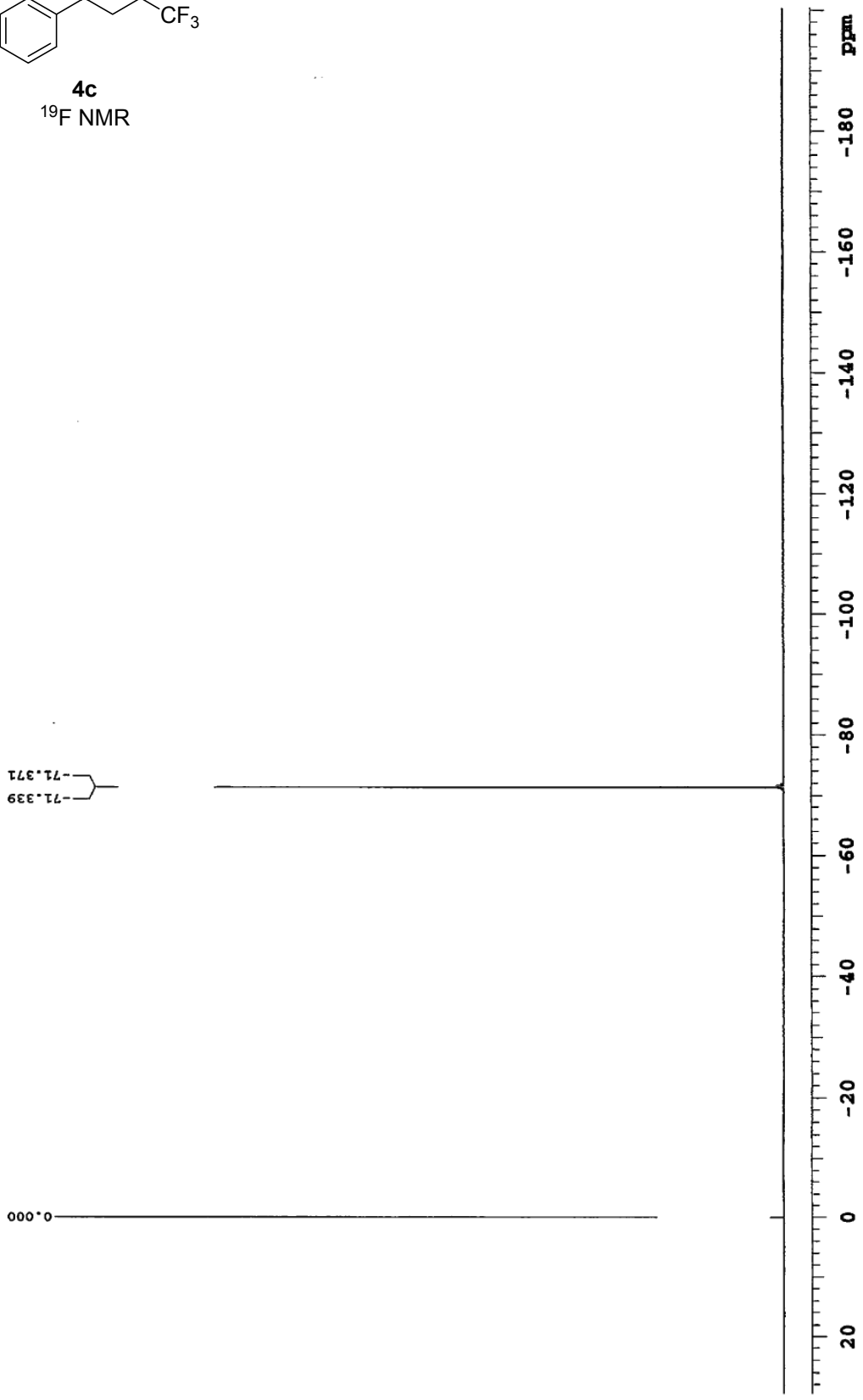
0.081
1.257
1.627
2.432
3.252
3.284
3.314
3.444
3.393
3.406
3.454
3.467
3.863
3.878
3.885
3.892
3.900
3.907
3.915
3.922
3.929
3.944
3.951
3.959
3.973
4.587
4.602
4.634
4.649
4.660
4.683
4.706
4.728
7.262
7.282
7.310
7.844
7.871
ppm
3.00
1.07
1.05
0.98
1.01
1.00
2.03
1.94


O
CH2NO2
CF3
Me

4c

^{19}F NMR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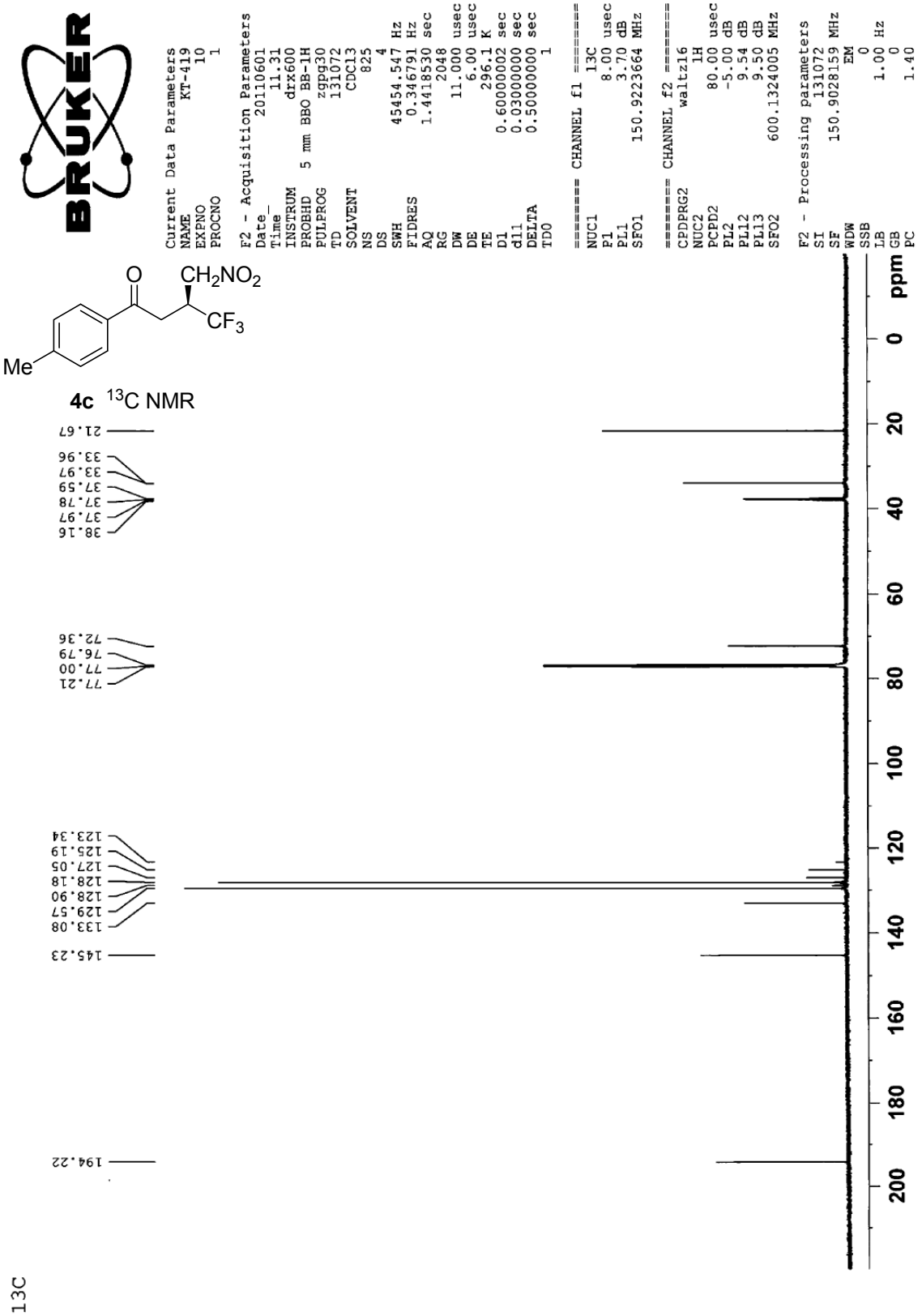
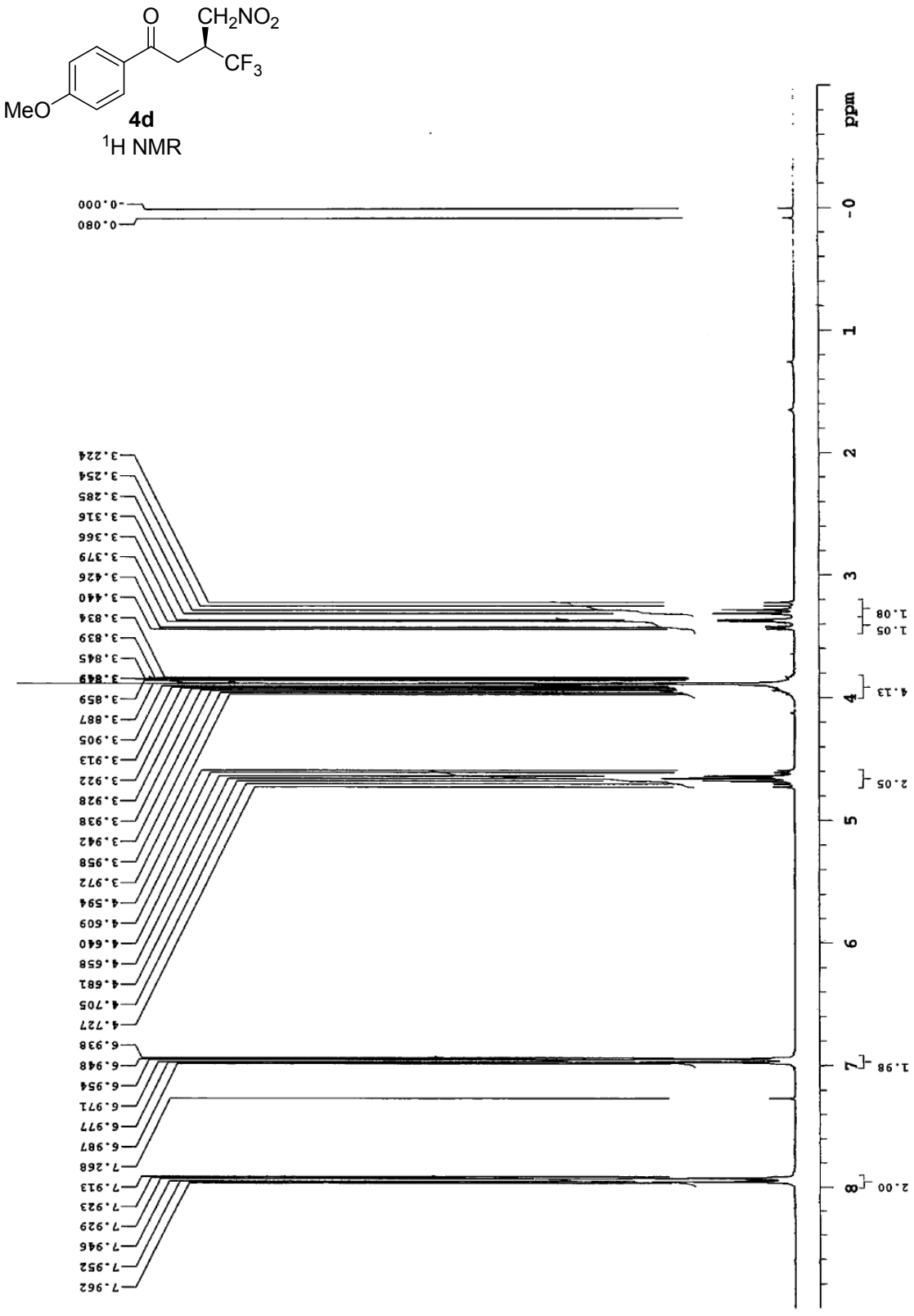
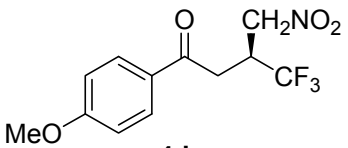
-71.371
0.000
ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20

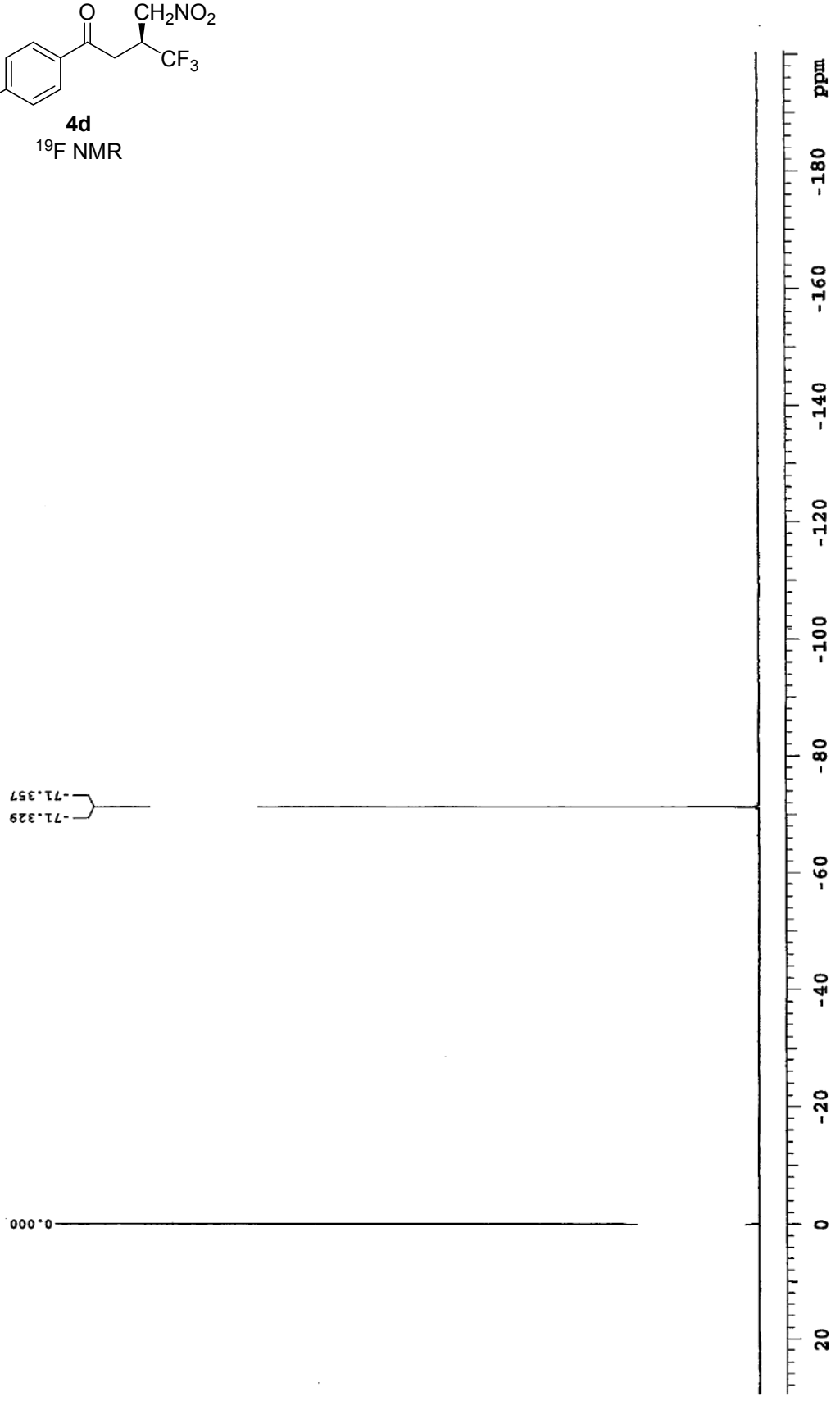

Current Data Parameters
NAME KT-419
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110601
Time 11.31
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 825
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.44718530 sec
RG 2048
DW 11.000 usec
DE 6.00 usec
TE 296.1 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028159 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
CF3
Me
4c 13C NMR
21.67
33.96
33.97
37.59
37.78
37.97
38.16
72.36
76.79
77.00
77.21
123.34
125.19
127.05
128.18
128.90
129.57
133.08
145.23
194.22
ppm
13C




O
CH2NO2
CF3
MeO

4d

^{19}F NMR


-71.357
-71.329
0.000
ppm
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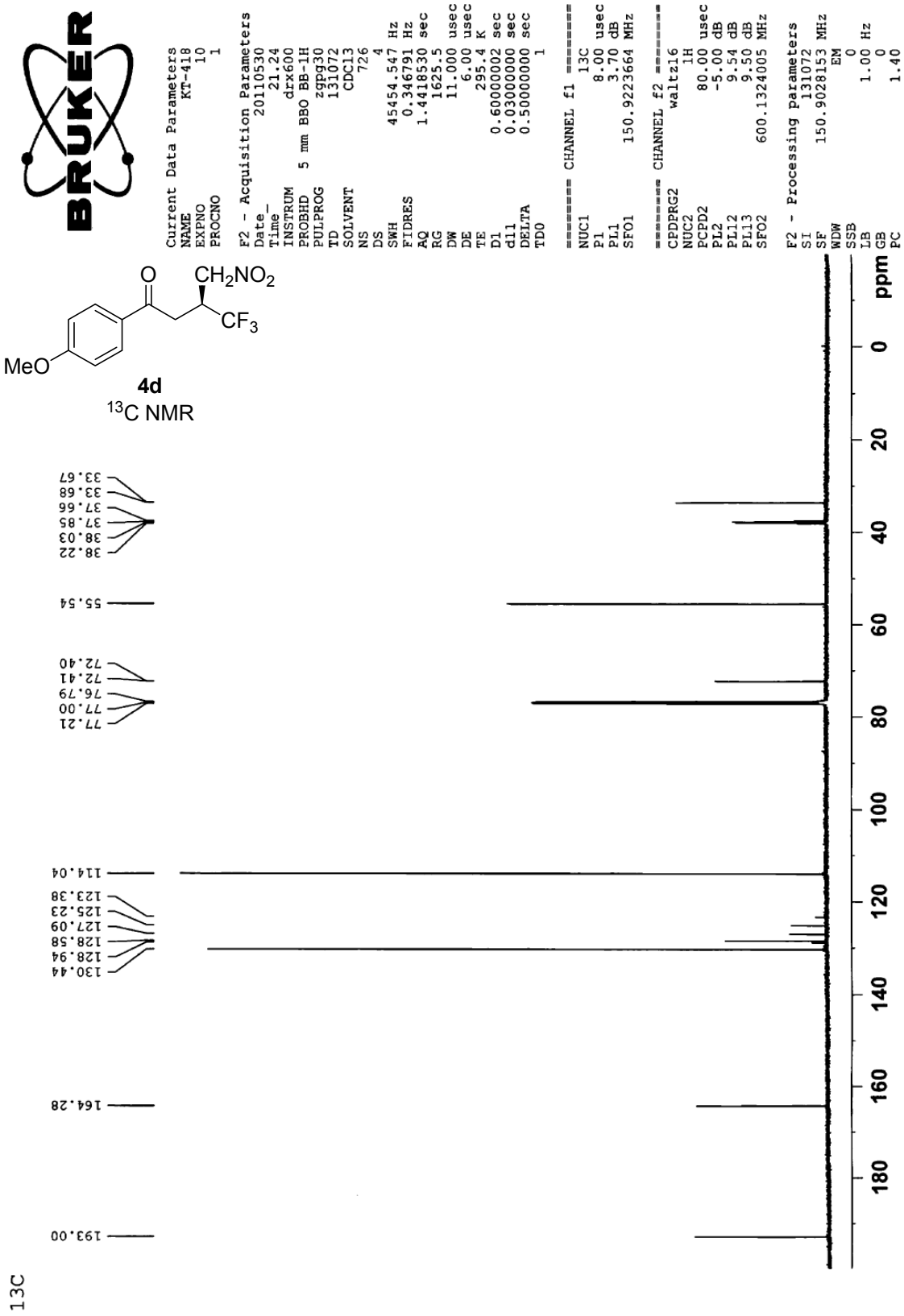
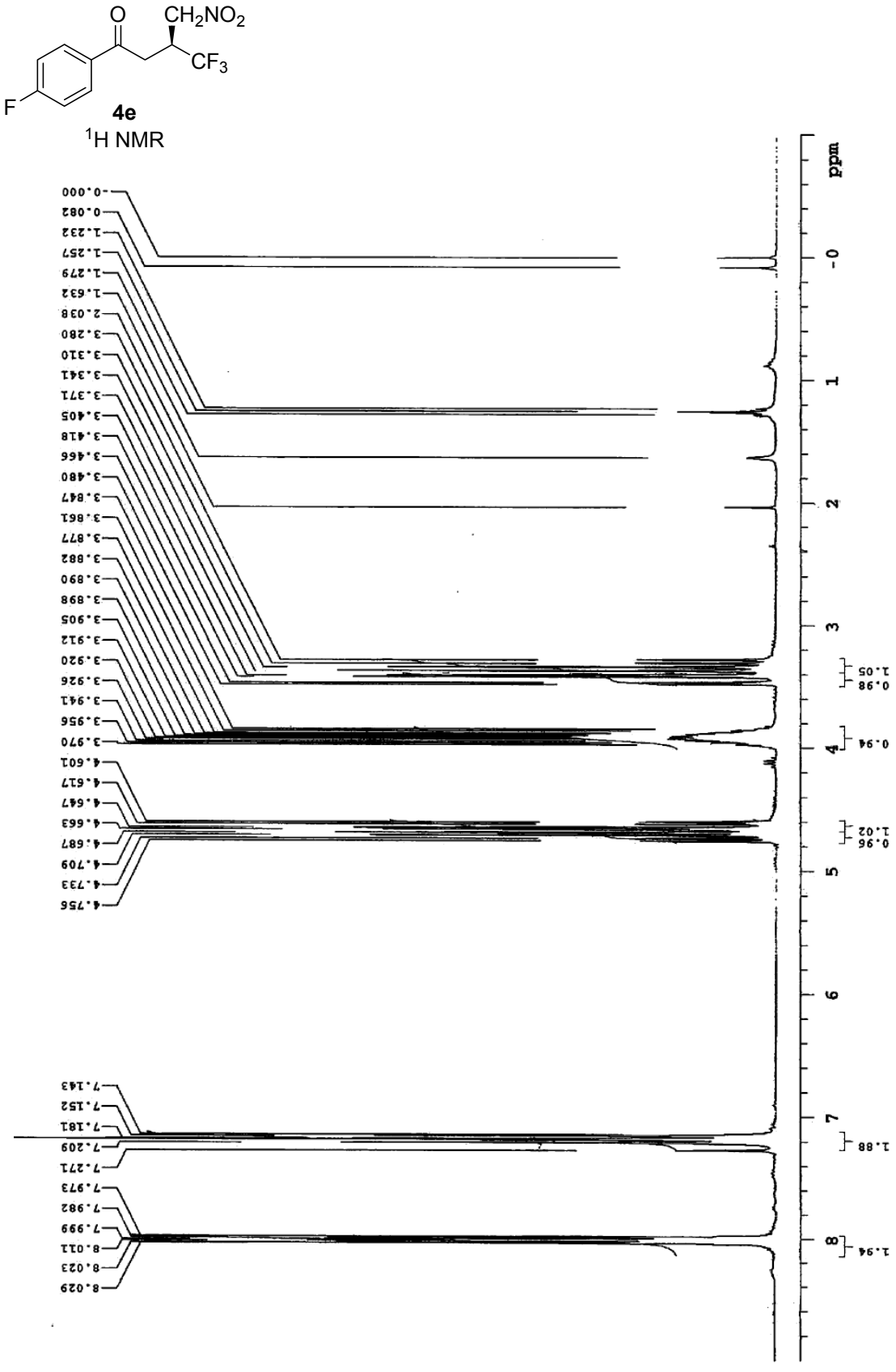
0
-20
-40
-60
-80
-100
-120
-140
-160
-180


Current Data Parameters
NAME KT-418
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110530
Time 21.24
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 726
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1625.5
DW 11.000 usec
DE 6.00 usec
TE 295.4 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028153 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
CF3
MeO
4d
13C NMR
33.67
33.68
37.66
37.85
38.03
38.22
55.54
72.40
72.41
76.79
77.00
77.21
114.04
123.38
125.23
127.09
128.58
128.94
130.44
164.28
193.00
13C
ppm
0
20
40
60
80
100
120
140
160
180


O
CH2NO2
CF3
F
4e
1H NMR
ppm
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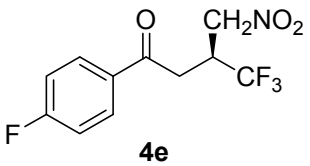
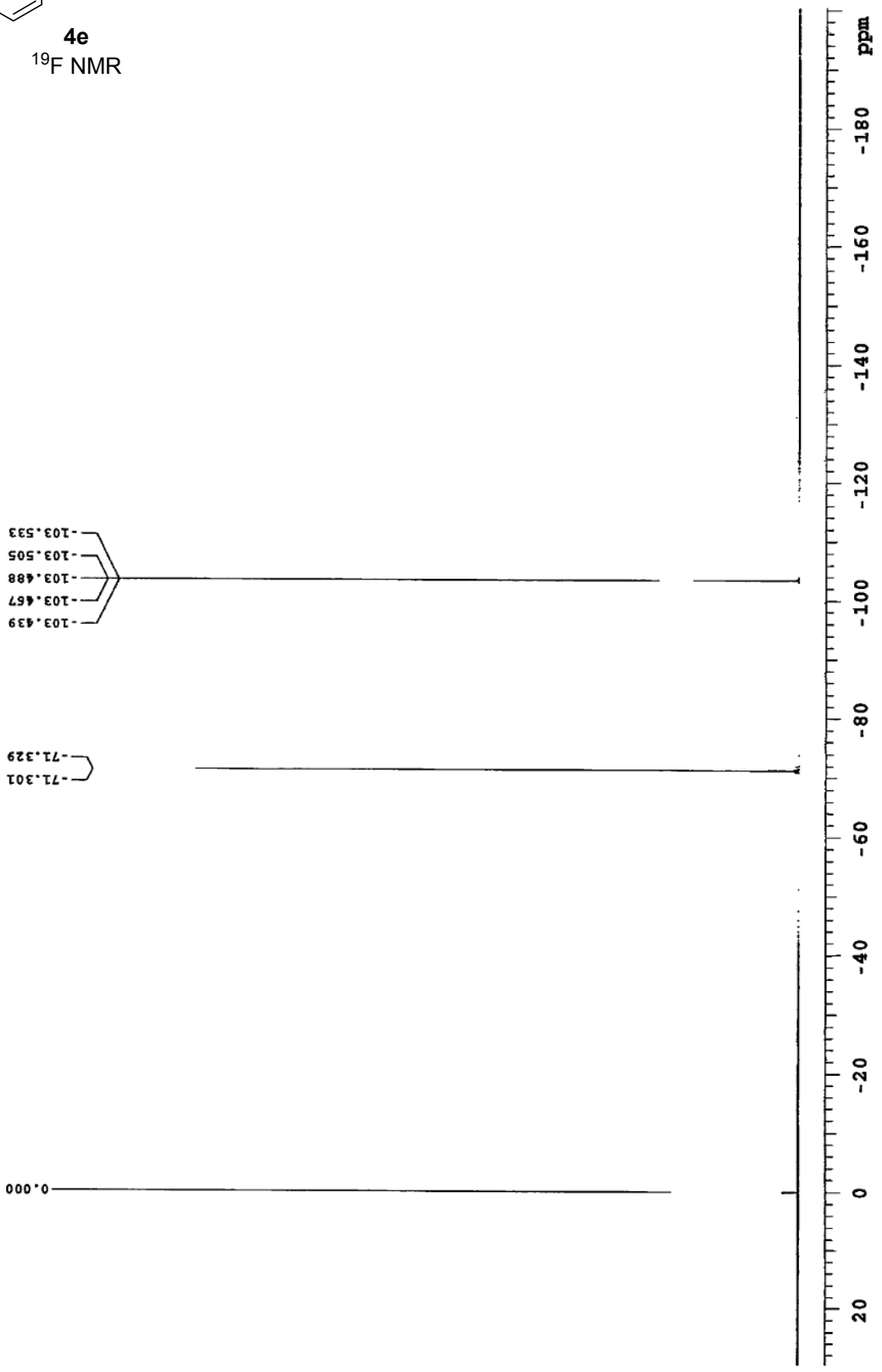
0.082
1.232
1.257
1.279
1.632
2.038
3.280
3.310
3.341
3.371
3.405
3.418
3.466
3.480
3.847
3.861
3.877
3.882
3.890
3.898
3.905
3.912
3.920
3.926
3.941
3.956
3.970
4.601
4.617
4.647
4.663
4.687
4.709
4.733
4.756
7.143
7.152
7.181
7.209
7.271
7.973
7.982
7.999
8.011
8.023
8.029
1.05
0.98
0.94
1.02
0.96
1.88
1.94


O
CH2NO2
CF3
F

4e

^{19}F NMR


-103.533
-103.505
-103.488
-103.467
-103.439
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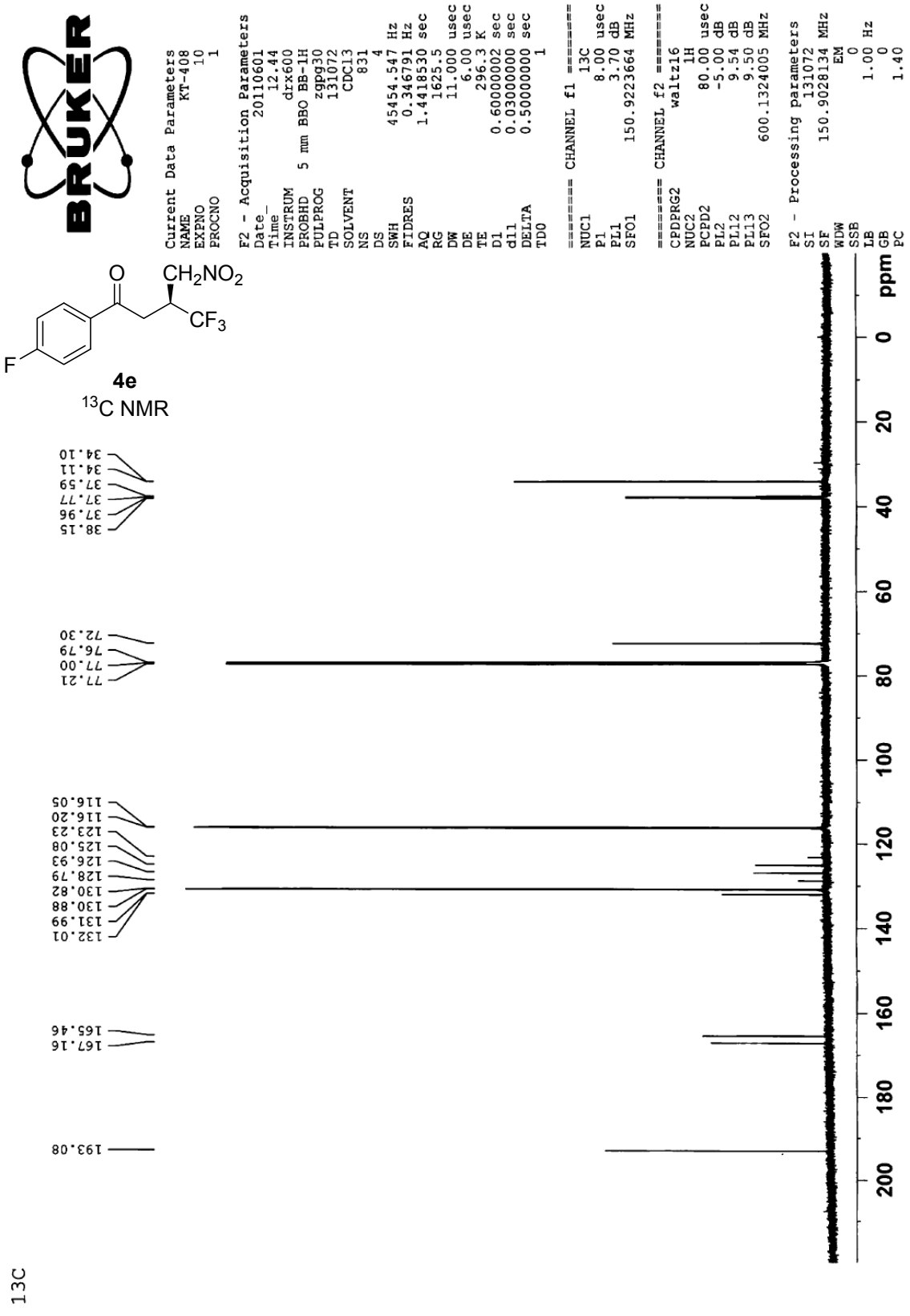
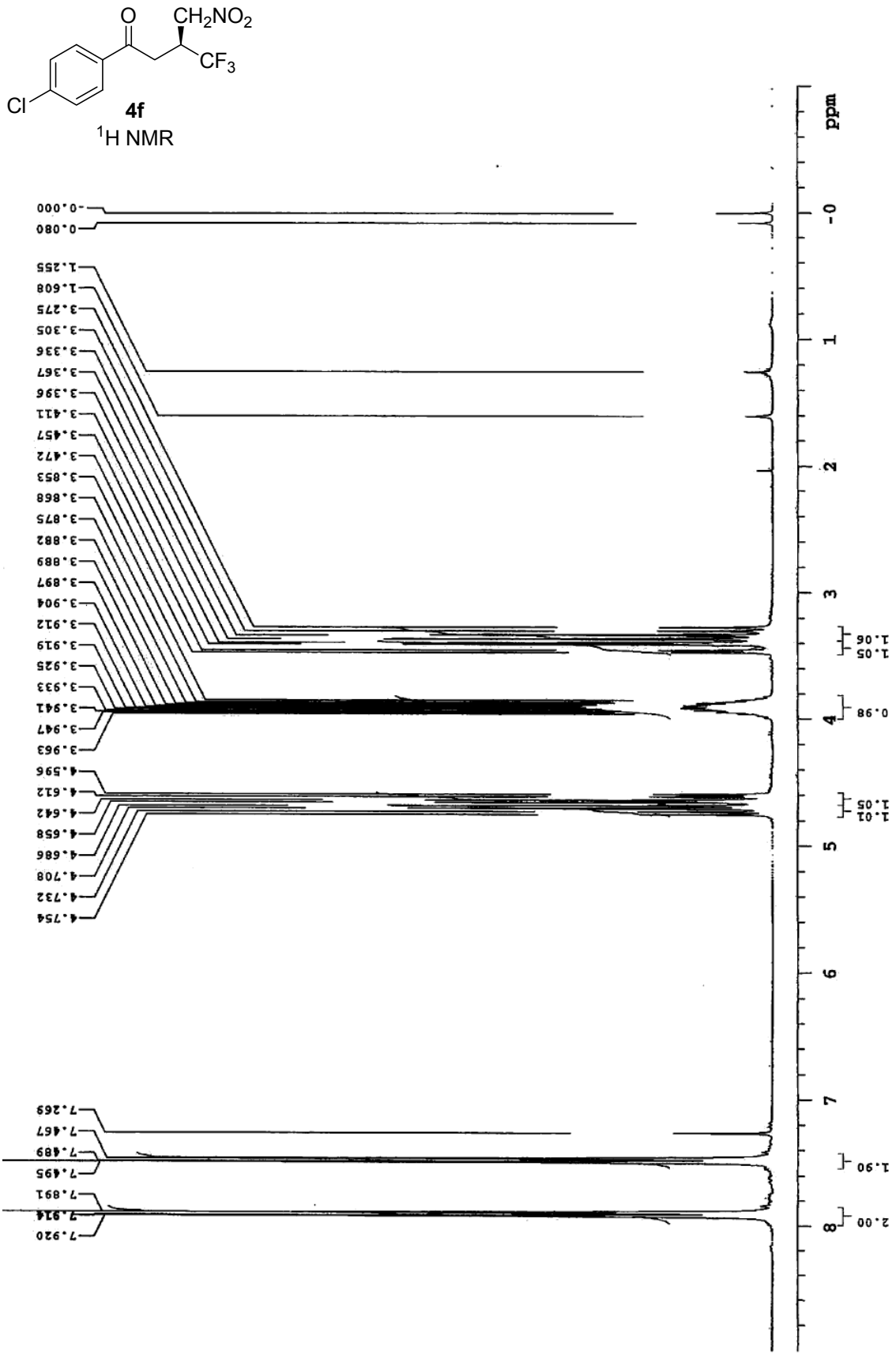
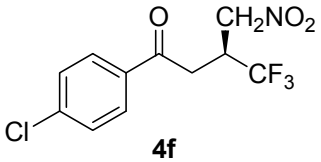
-71.301
0.000
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180

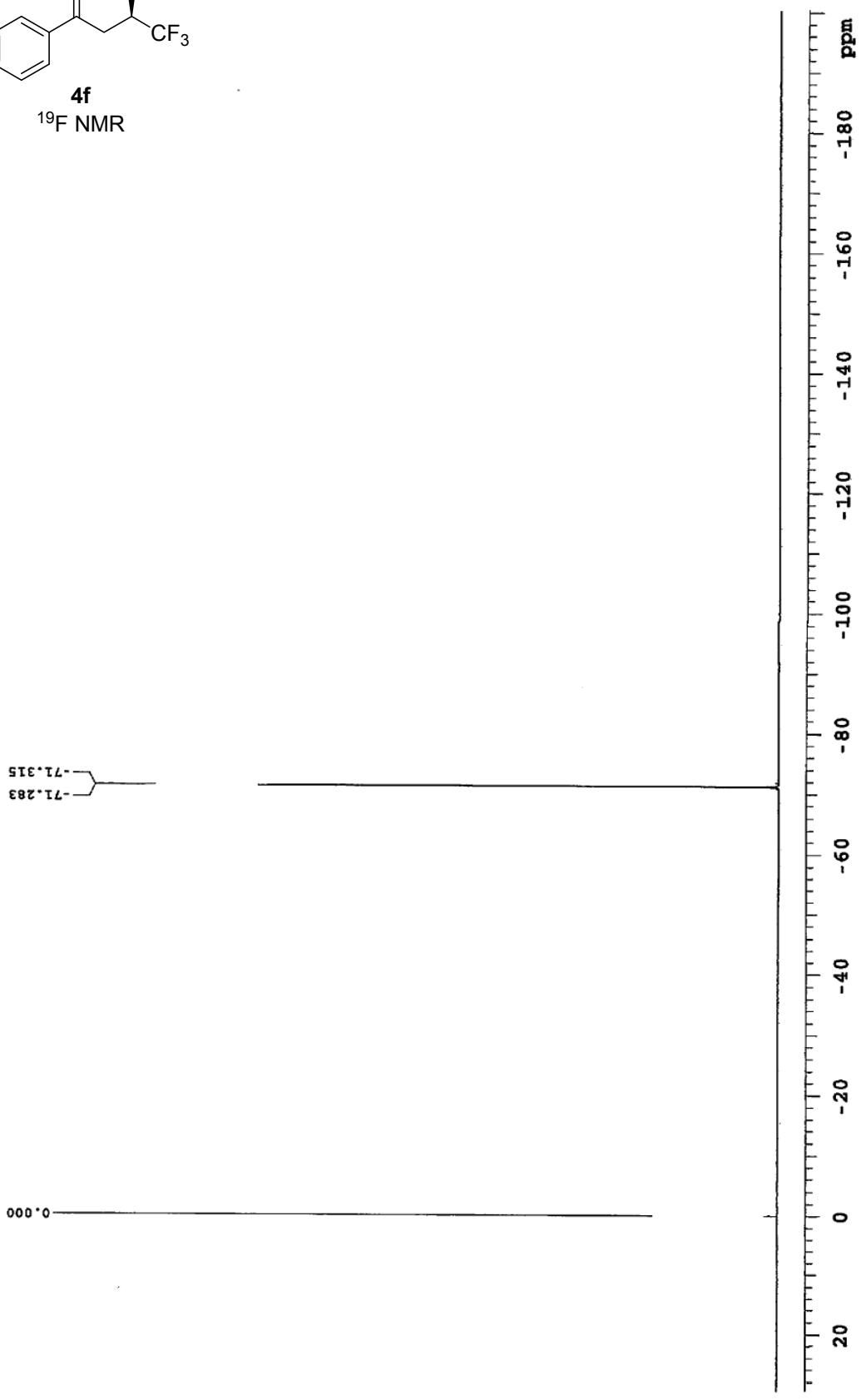

Current Data Parameters
NAME KT-408
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110601
Time_ 12.44
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 831
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1625.5
DW 11.000 usec
DE 6.00 usec
TE 296.3 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028134 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
CF3
F
4e
13C NMR
34.10
34.11
37.59
37.77
37.96
38.15
72.30
76.79
77.00
77.21
116.05
116.20
123.23
125.08
126.93
128.79
130.82
130.88
131.99
132.01
165.46
167.16
193.08
ppm
0
20
40
60
80
100
120
140
160
180
200
13C

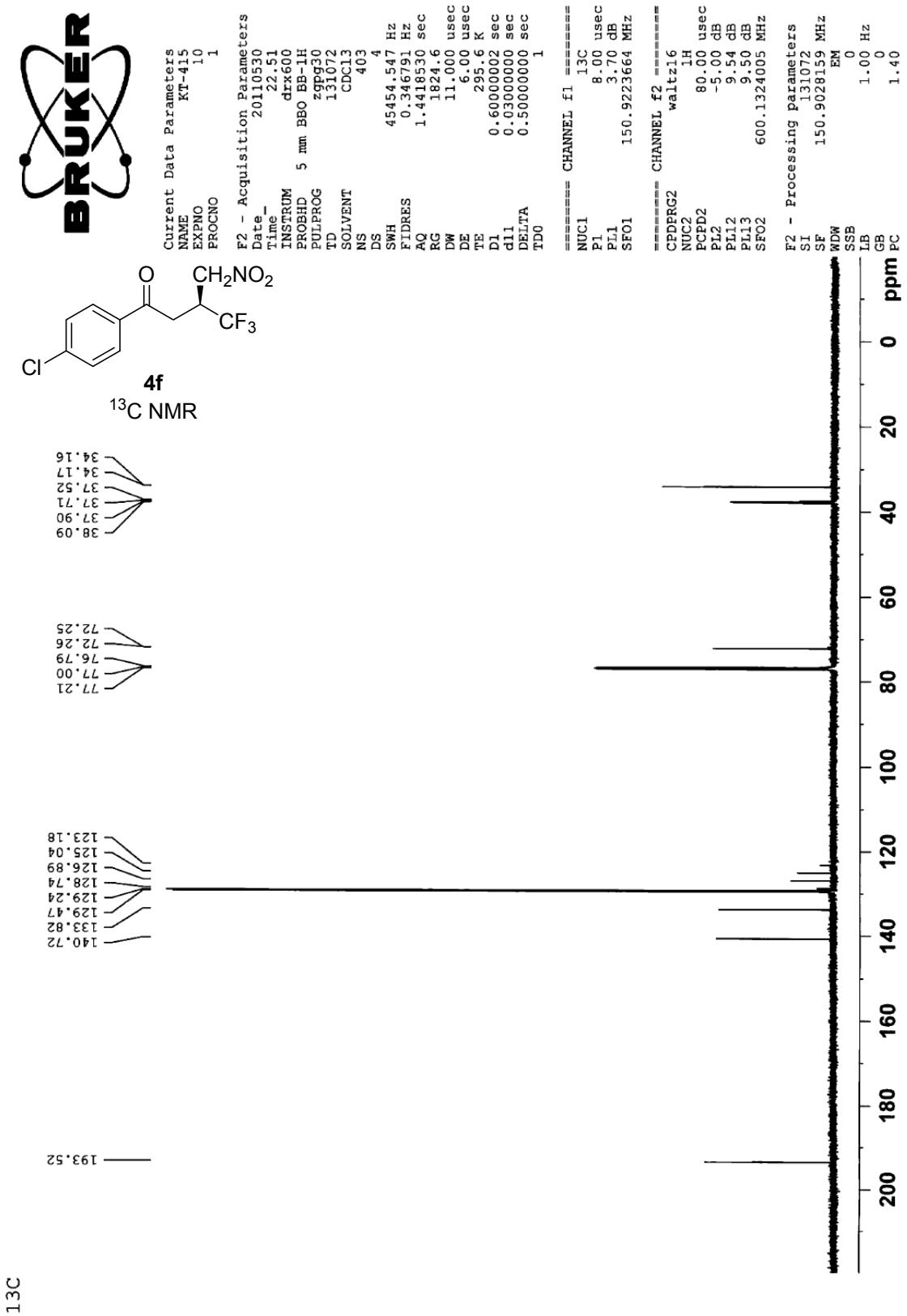


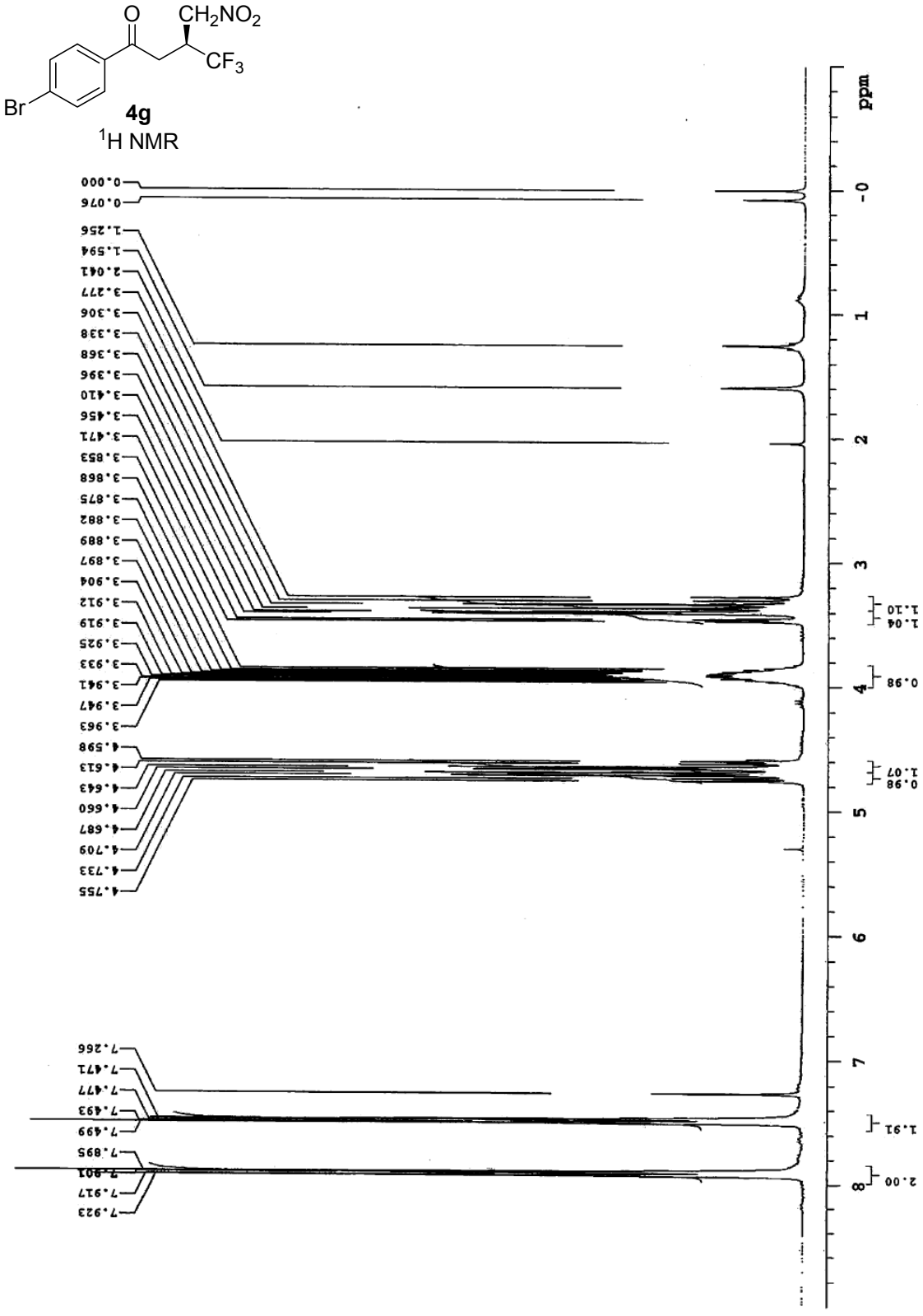

O
CH2NO2
CF3
Cl

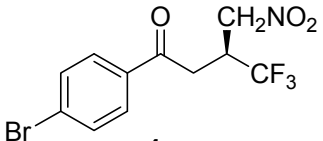
4f

^{19}F NMR


-71.283
-71.315
0.000
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180

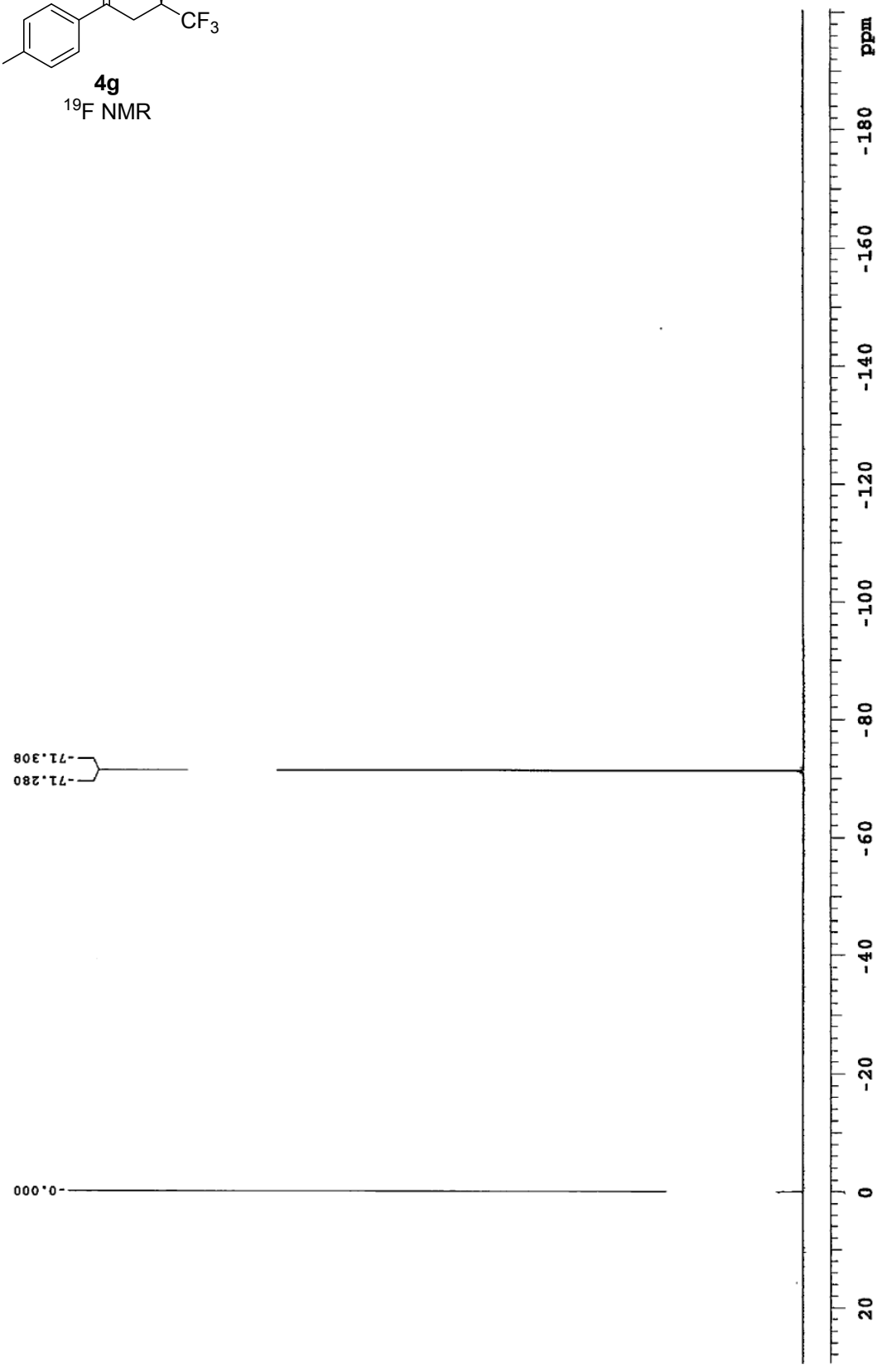

Current Data Parameters
NAME KT-415
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110530
Time 22.51
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 403
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1824.6
DW 11.000 usec
DE 6.00 usec
TE 295.6 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028159 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
CF3
Cl
4f
13C NMR
34.16
34.17
37.52
37.71
37.90
38.09
72.25
72.26
76.79
77.00
77.21
123.18
125.04
126.89
128.74
129.24
129.47
133.82
140.72
193.52
ppm
13C


O
CH2NO2
CF3
Br
4g
1H NMR
ppm
0.000
0.076
1.256
1.594
2.041
3.277
3.306
3.338
3.368
3.396
3.410
3.456
3.471
3.853
3.868
3.875
3.882
3.889
3.897
3.904
3.912
3.919
3.925
3.933
3.941
3.947
3.963
4.598
4.613
4.643
4.660
4.687
4.709
4.733
4.755
7.266
7.471
7.477
7.493
7.499
7.895
7.901
7.917
7.923
1.04
1.10
0.98
0.98
1.07
1.91
2.00


O
CH2NO2
CF3
Br

4g

^{19}F NMR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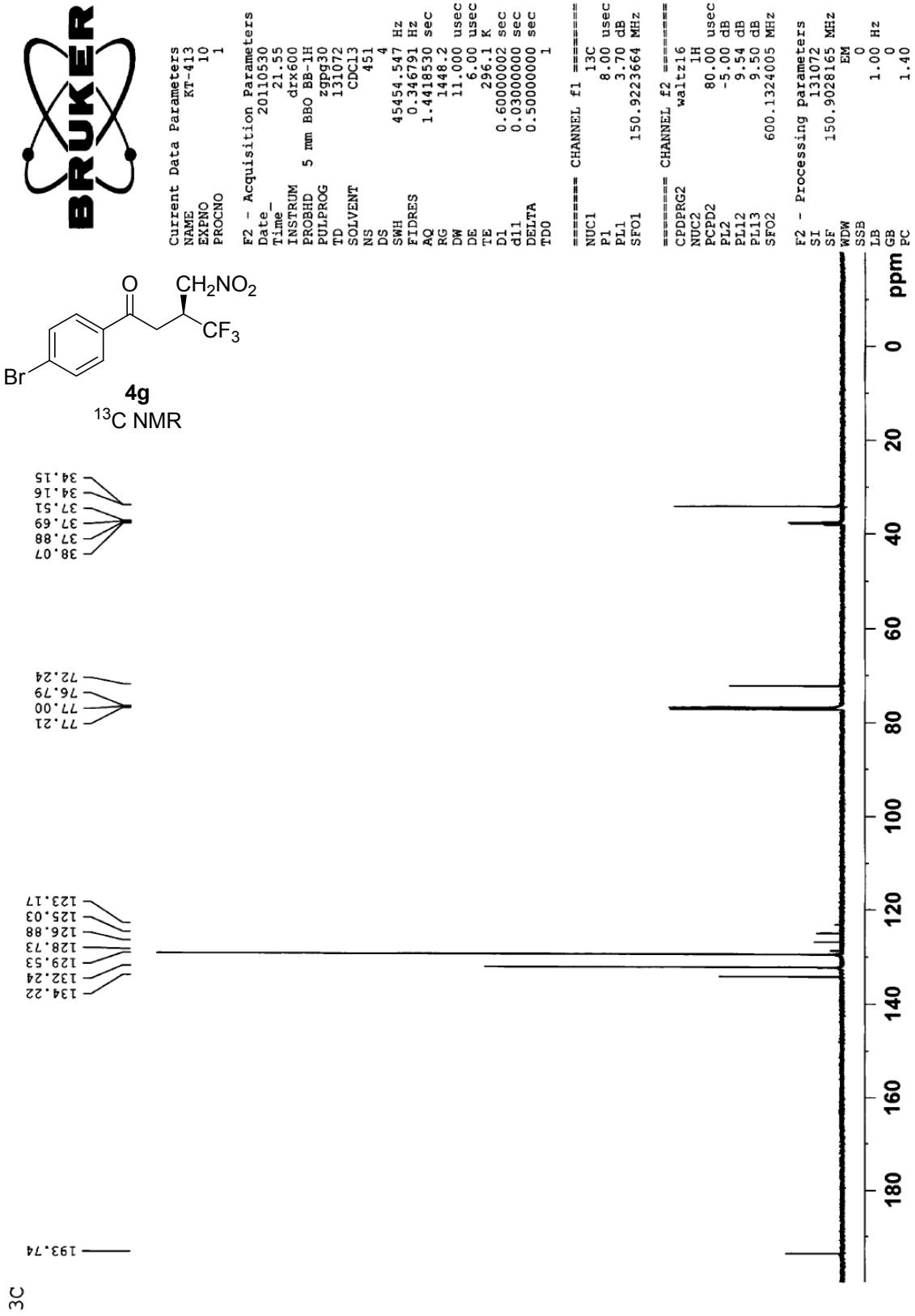
-140
-160
-180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NAME KT-413
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110530
Time_ 21.55
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 451
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.44418530 sec
RG 1448.2
DW 11.000 usec
DE 6.00 usec
TE 296.1 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028165 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
CF3
Br
4g
13C NMR
193.74
134.22
132.24
129.53
128.73
126.88
125.03
123.17
77.21
76.79
77.00
72.24
38.07
37.88
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34.16
34.15
3C
ppm
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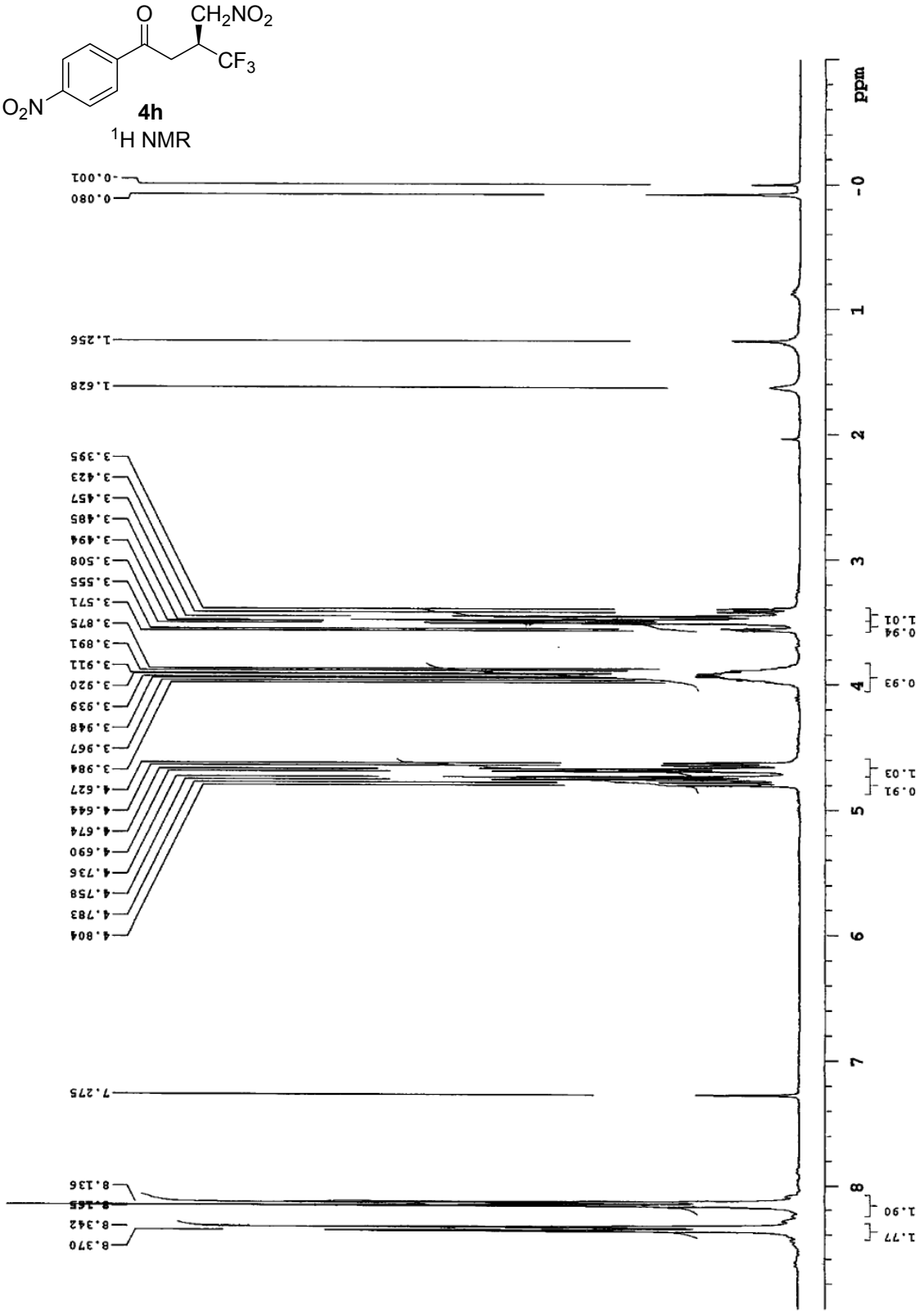
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CF3
O2N
4h
1H NMR
ppm
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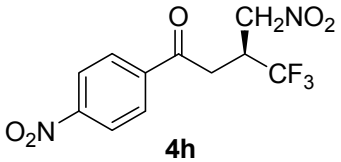
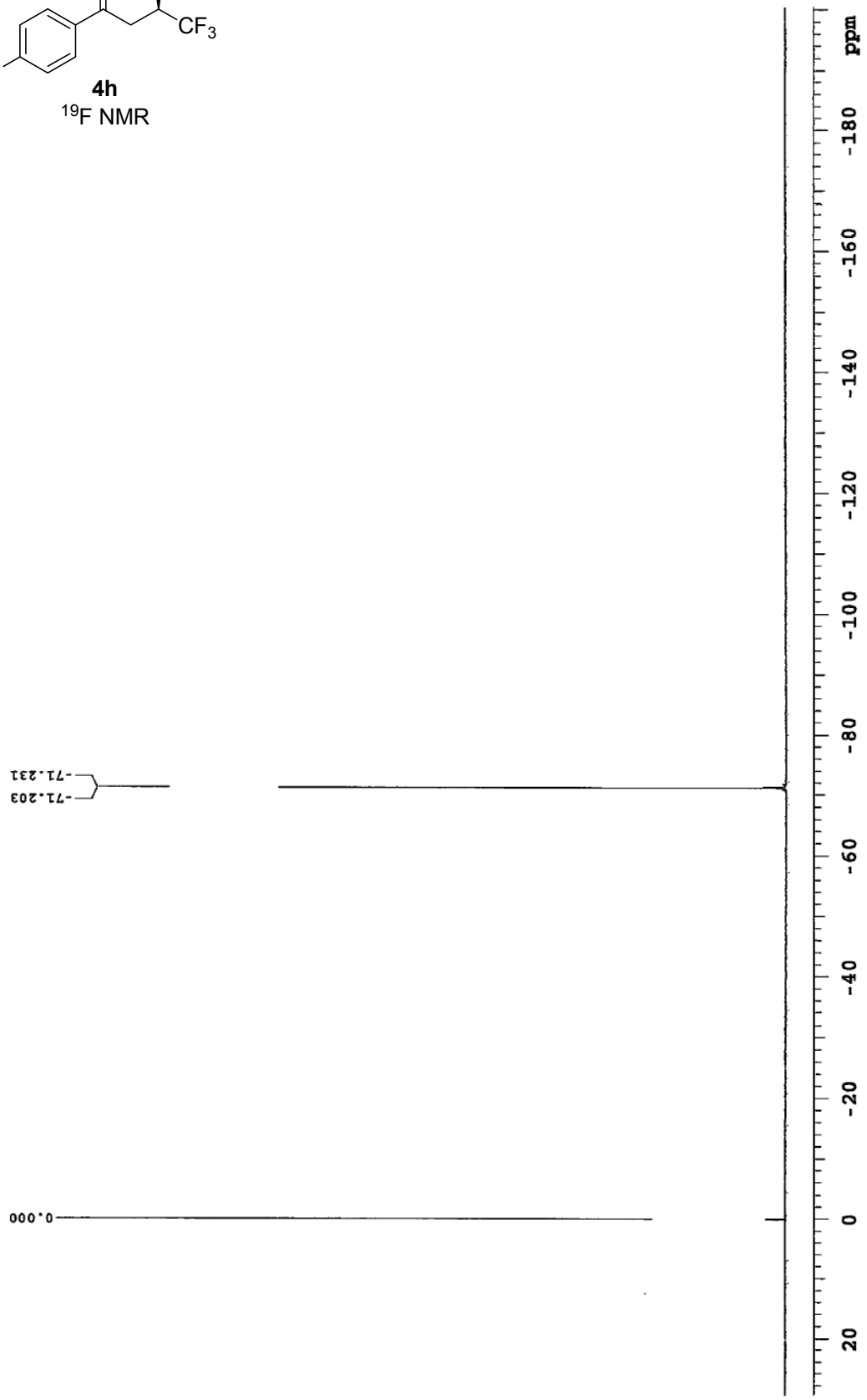
1.628
3.395
3.423
3.457
3.485
3.494
3.508
3.555
3.571
3.875
3.891
3.911
3.920
3.939
3.948
3.967
3.984
4.627
4.644
4.674
4.690
4.736
4.758
4.783
4.804
7.275
8.136
8.165
8.342
8.370
1.01
0.94
0.93
1.03
0.91
1.90
1.77


O
CH2NO2
CF3
O2N

4h

^{19}F NMR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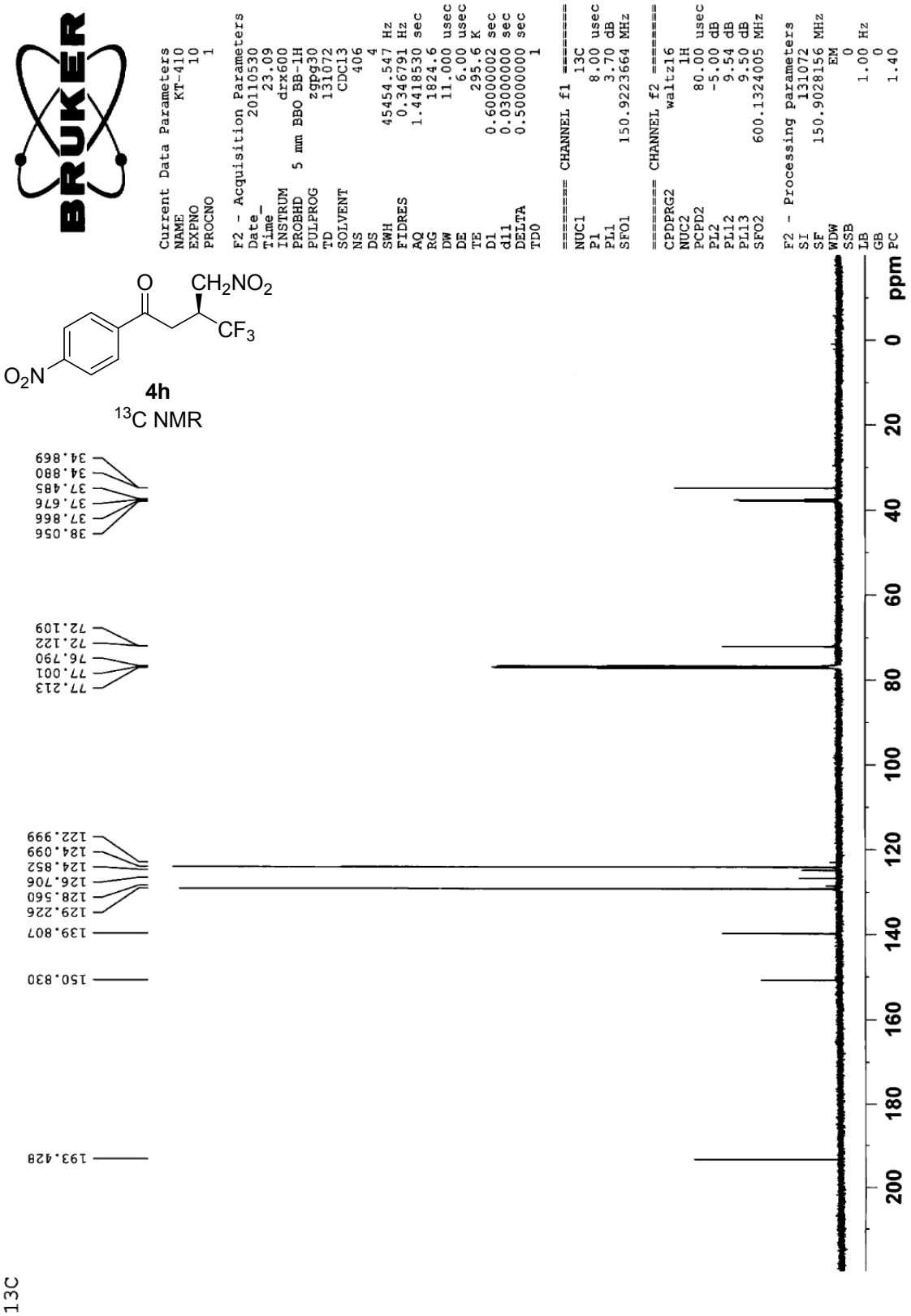
-120
-140
-160
-180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NAME KT-410
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110530
Time_ 23.09
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 406
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1824.6
DW 11.000 usec
DE 6.00 usec
TE 295.6 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028156 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
CF3
O2N
4h
13C NMR
34.869
34.880
37.485
37.676
37.866
38.056
72.109
72.122
76.790
77.001
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124.099
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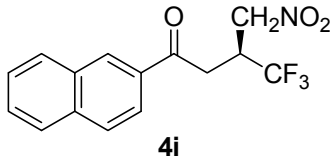
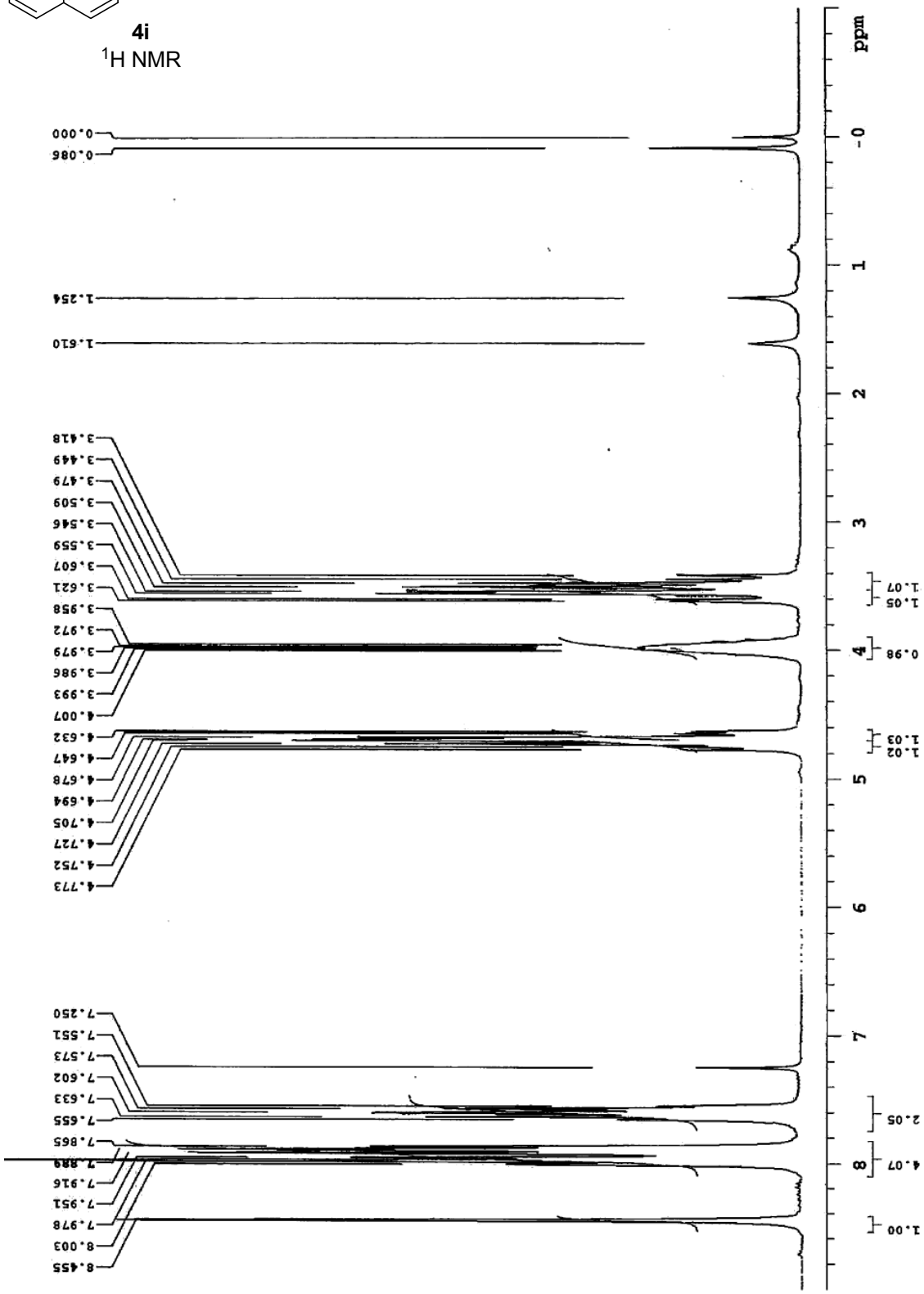
139.807
150.830
193.428
ppm
13C


O
CH2NO2
CF3

4i

^{1}H NMR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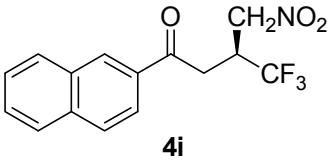
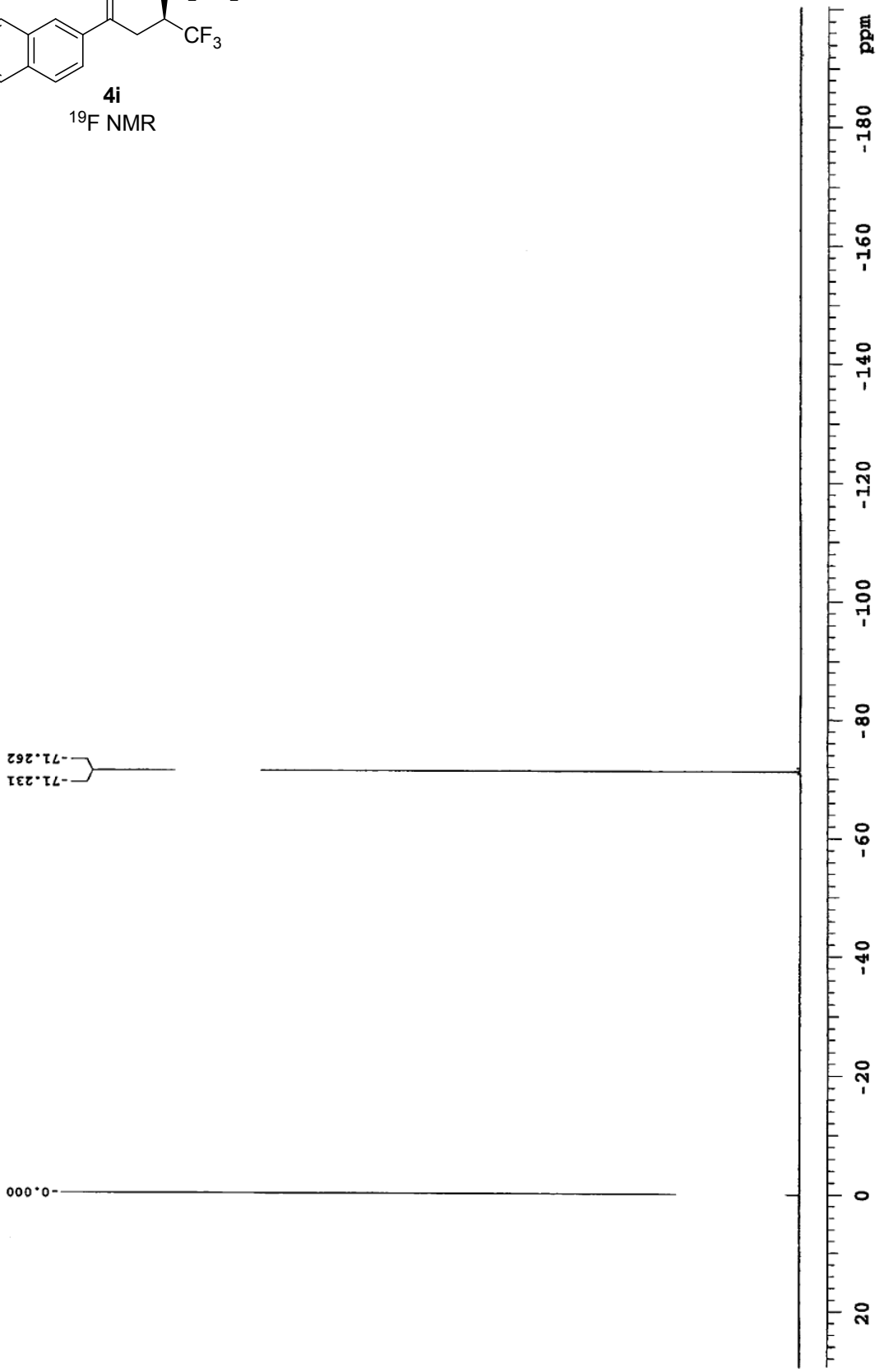
3.509
3.546
3.559
3.607
3.621
3.958
3.972
3.979
3.986
3.993
4.007
4.632
4.647
4.678
4.694
4.705
4.727
4.752
4.773
7.250
7.551
7.573
7.602
7.633
7.655
7.865
7.889
7.916
7.951
7.978
8.003
8.455
1.07
1.05
0.98
1.03
1.02
2.05
4.07
1.00


O
CH2NO2
CF3

4i

^{19}F NMR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ppm
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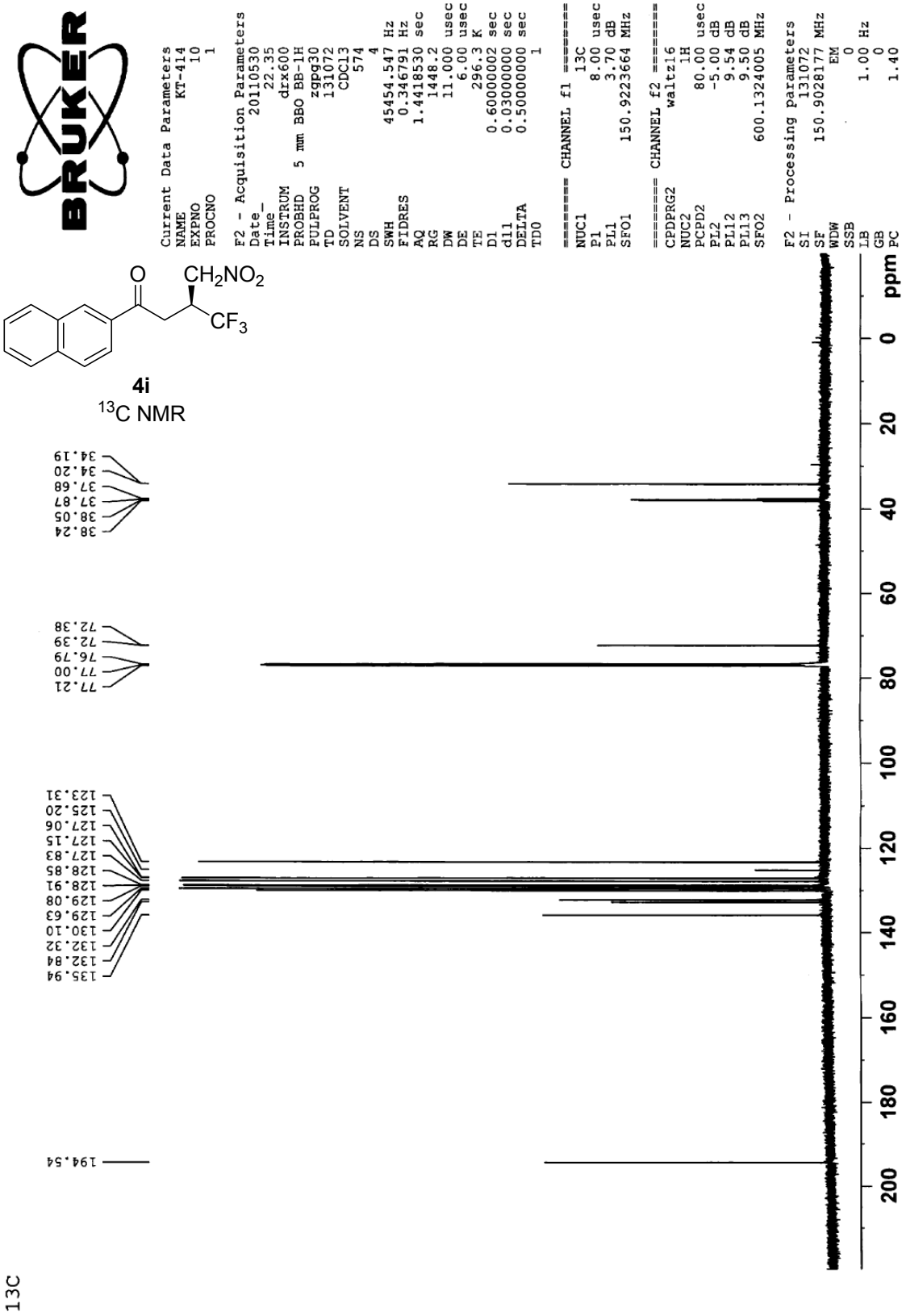
-40
-60
-80
-100
-120
-140
-160
-180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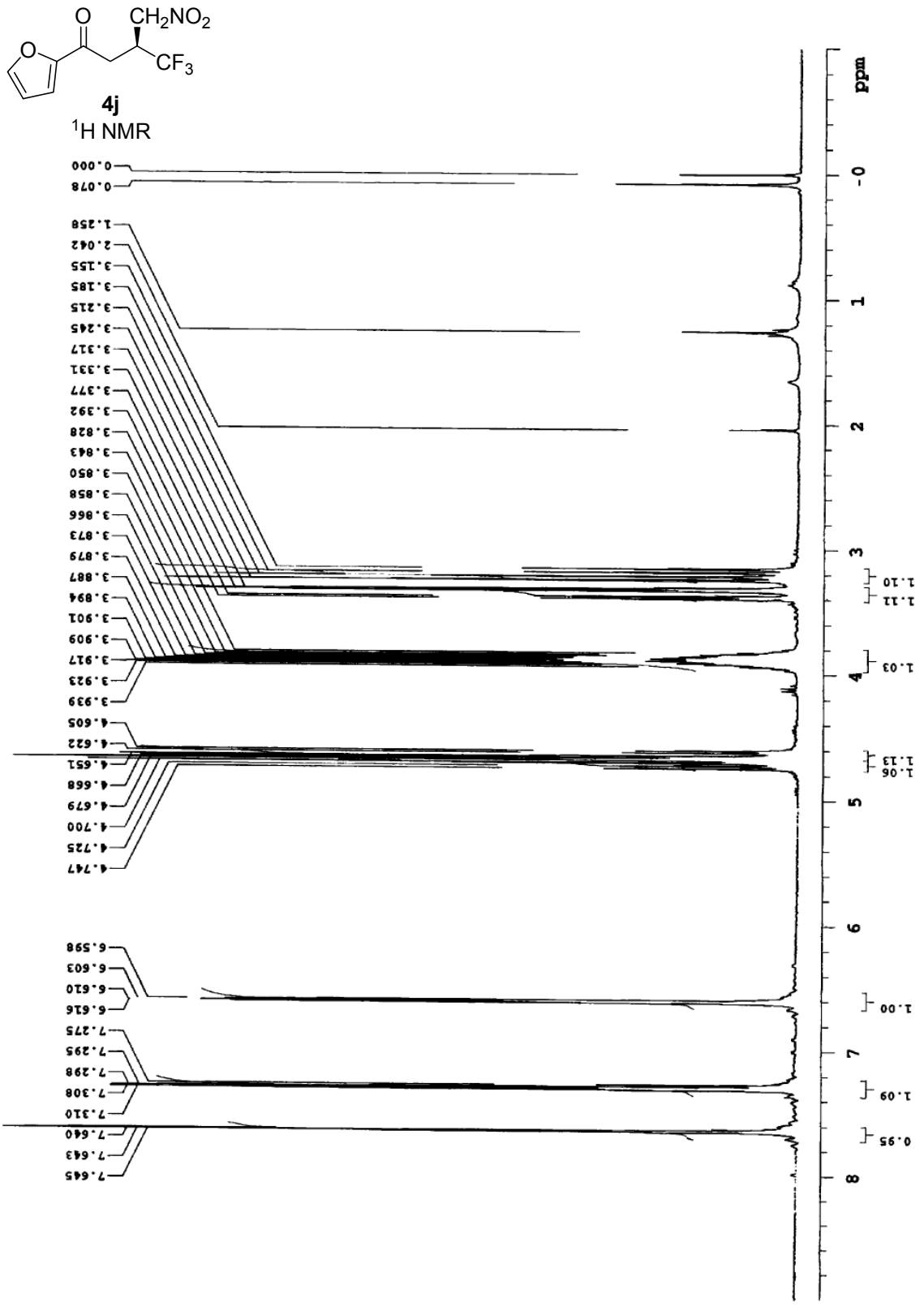
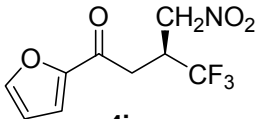
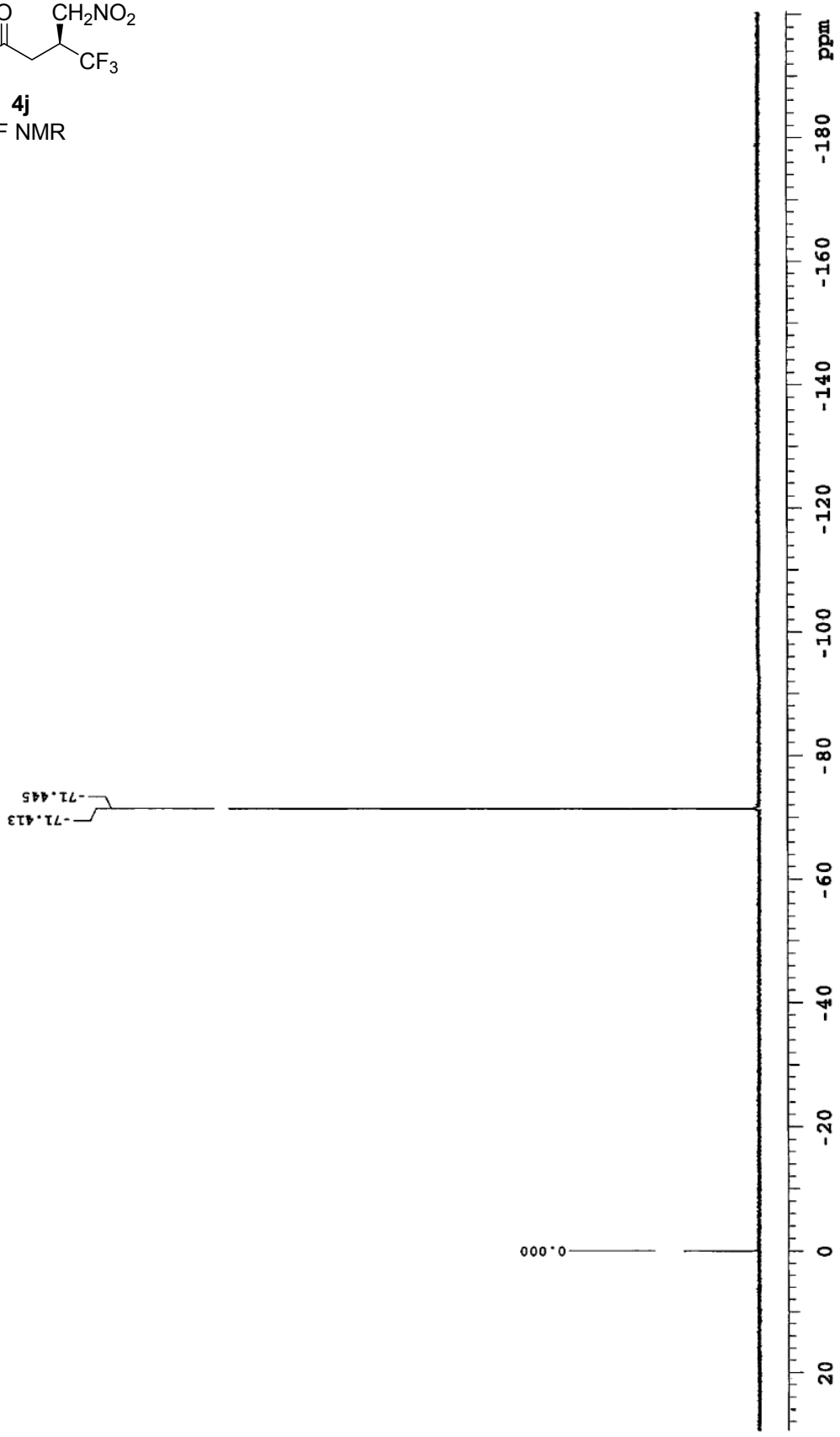
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110530
Time 22.35
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 574
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.44118530 sec
RG 1448.2
DW 11.000 usec
DE 6.00 usec
TE 296.3 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028177 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
CF3
4i
13C NMR
34.19
34.20
37.68
37.87
38.05
38.24
72.38
72.39
76.79
77.00
77.21
123.31
125.20
127.06
127.15
127.83
128.85
128.91
129.08
129.63
130.10
132.32
132.84
135.94
194.54
ppm
13C




O
CH2NO2
O
CF3

4j

^{19}F NMR


-71.445
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ppm
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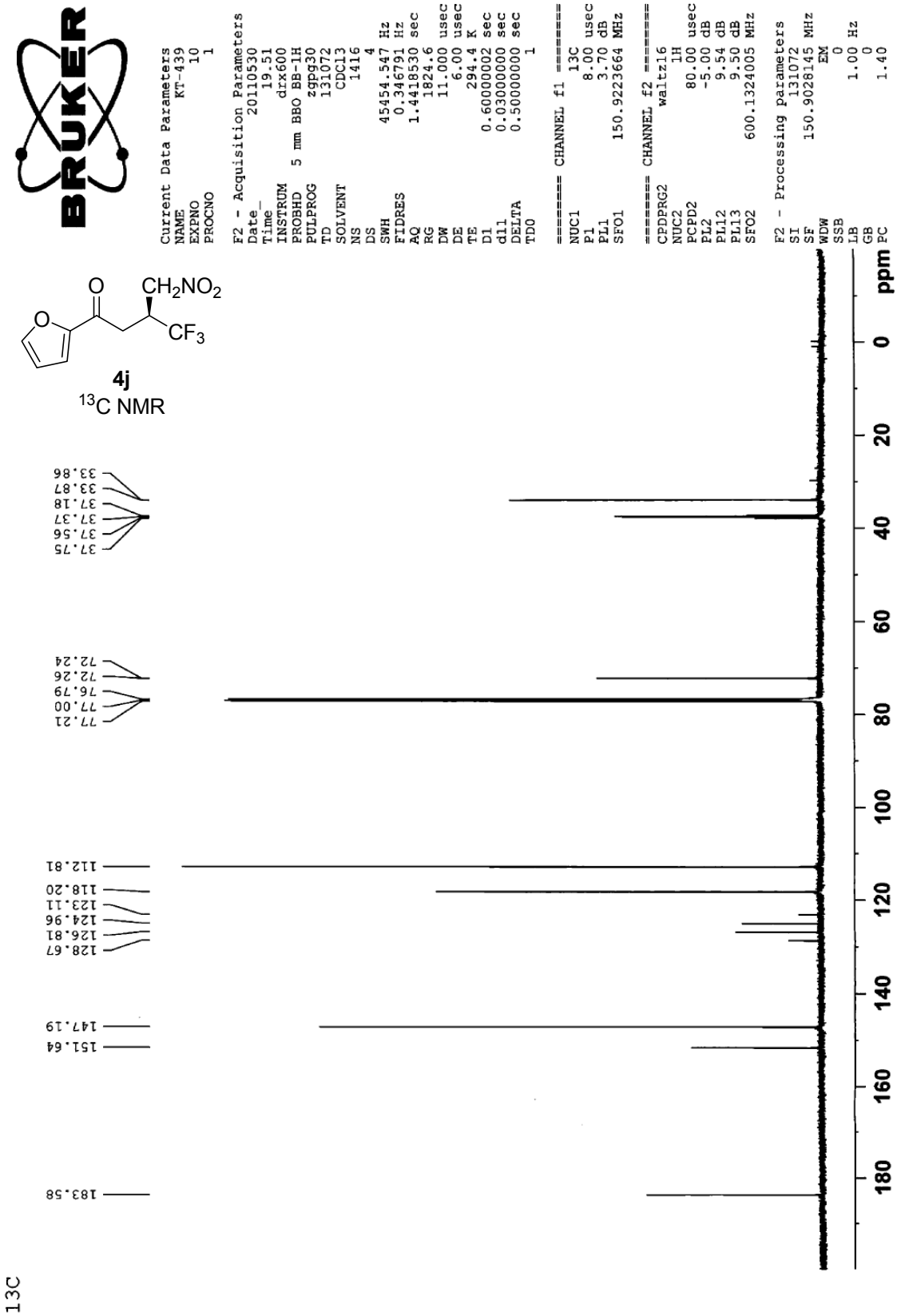
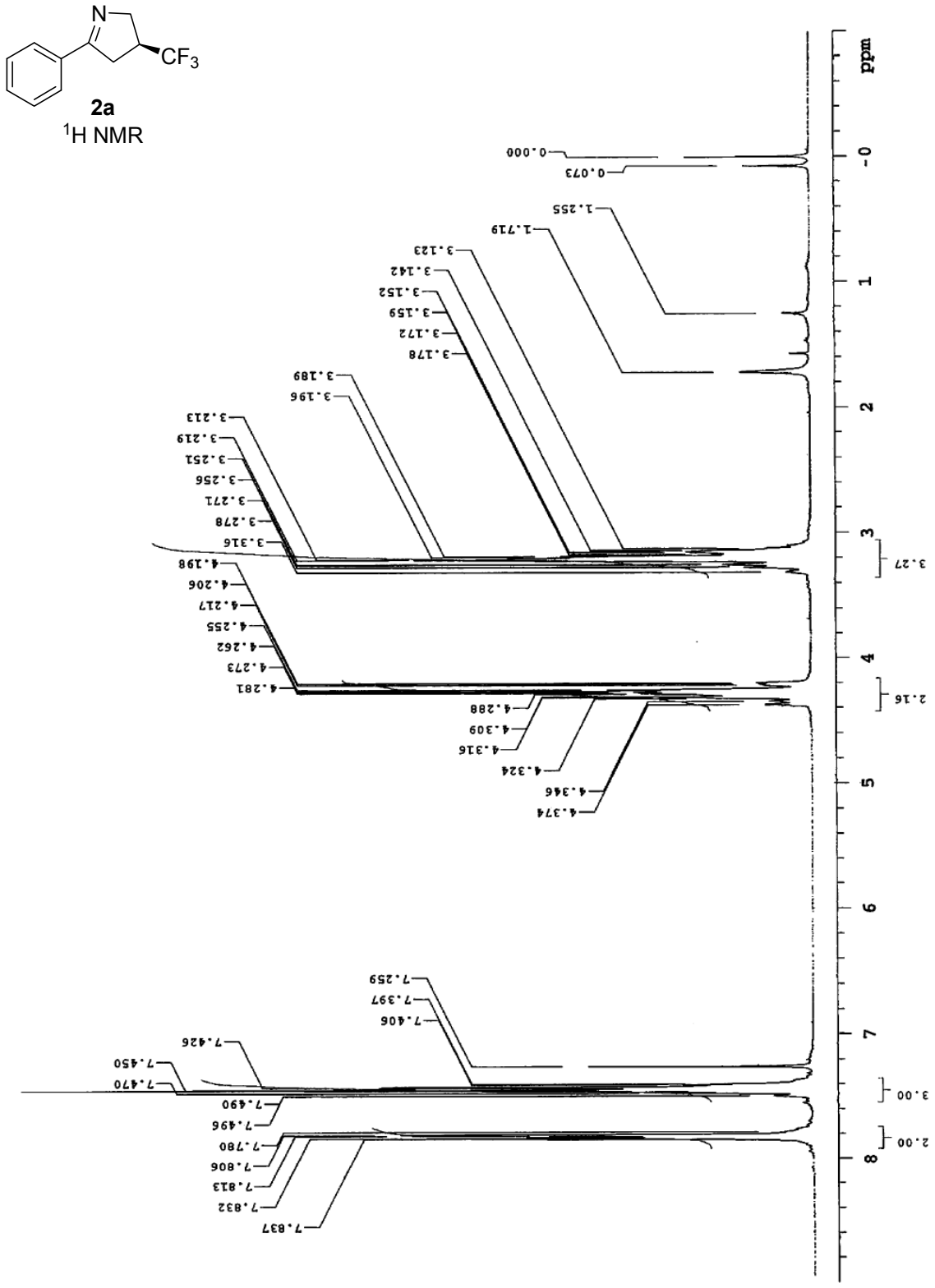
0
-20
-40
-60
-80
-100
-120
-140
-160
-180


Current Data Parameters
NAME KT-439
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110530
Time 19.51
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1416
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1824.6
DW 11.000 usec
DE 6.00 usec
TE 294.4 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028145 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
CH2NO2
O
CF3
4j
13C NMR
33.86
33.87
37.18
37.37
37.56
37.75
72.24
72.26
76.79
77.00
77.21
112.81
118.20
123.11
124.96
126.81
128.67
147.19
151.64
183.58
ppm
0
20
40
60
80
100
120
140
160
180
13C


N
CF3
2a
1H NMR
ppm
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1.719
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3.142
3.152
3.159
3.172
3.178
3.189
3.196
3.213
3.219
3.251
3.256
3.271
3.278
3.316
4.198
4.206
4.217
4.255
4.262
4.273
4.281
4.288
4.309
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7.450
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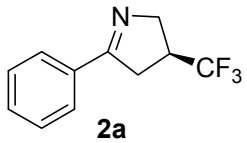
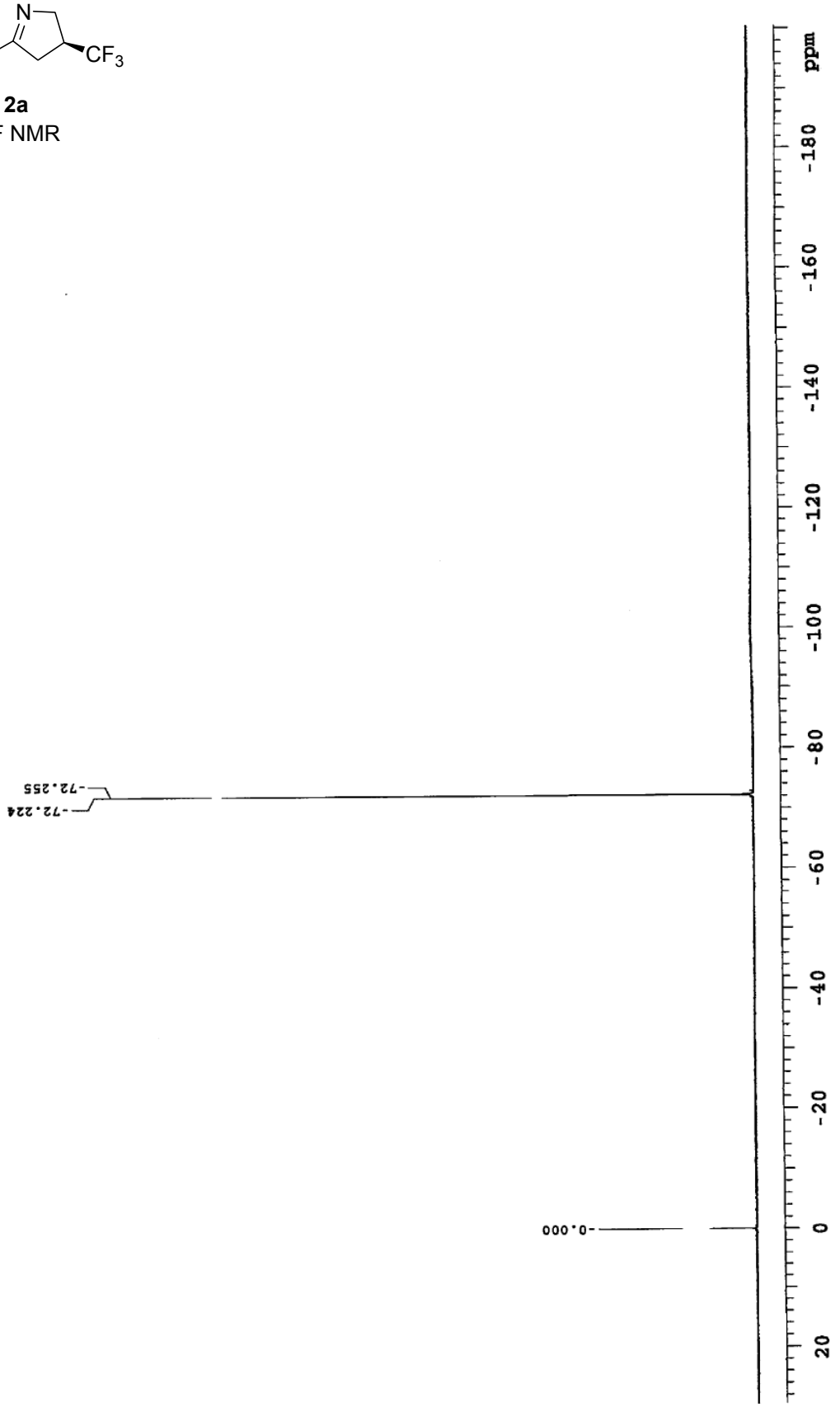
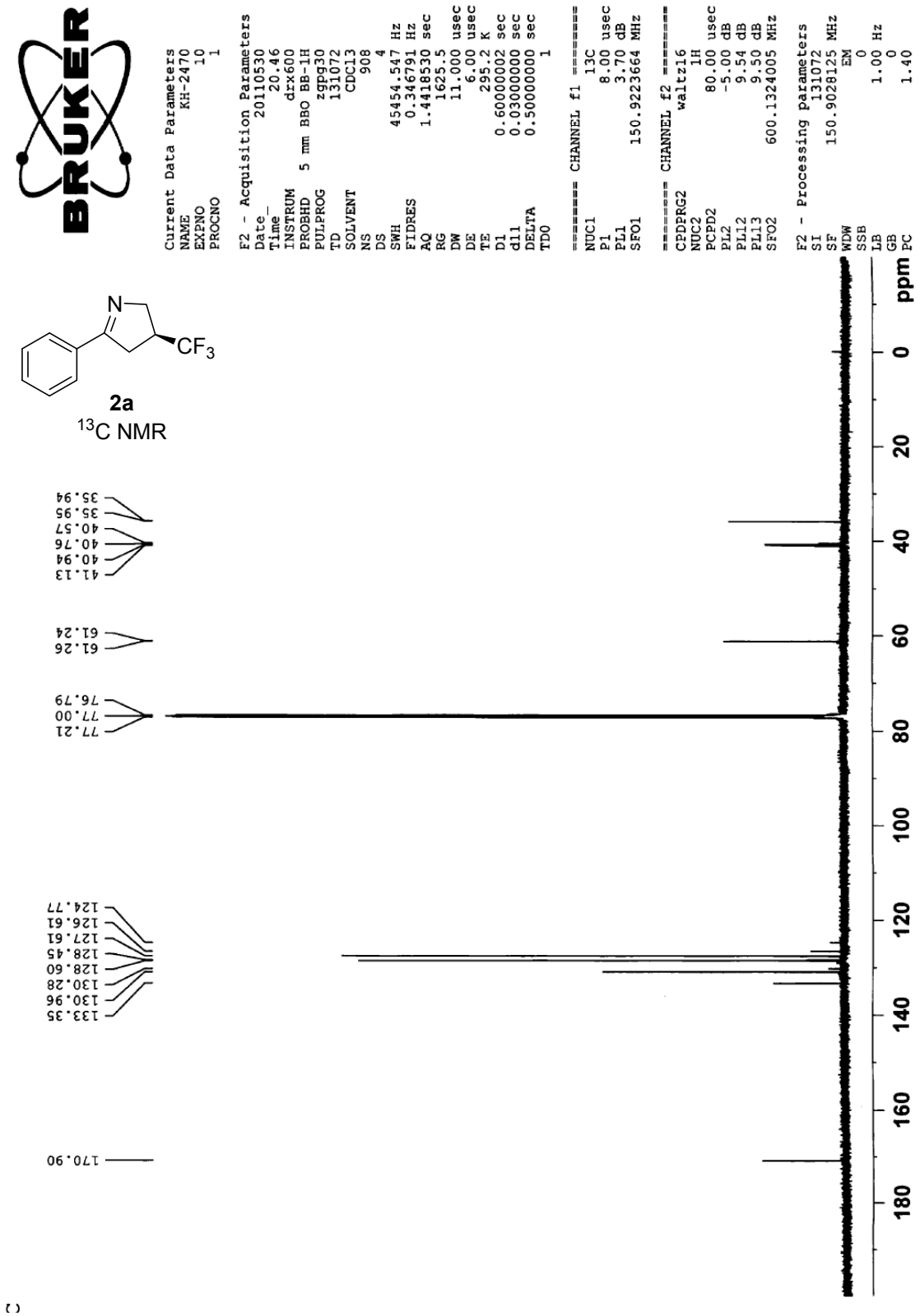
2.00



2a

^{19}F NMR

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NAME KH-2470
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110530
Time_ 20.46
INSTRUM dzx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 908
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1625.5
DW 11.000 usec
DE 6.00 usec
TE 295.2 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028125 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N
CF3
2a
13C NMR
35.94
35.95
40.57
40.76
40.94
41.13
61.24
61.26
76.79
77.00
77.21
124.77
126.61
127.61
128.45
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130.96
133.35
170.90
ppm
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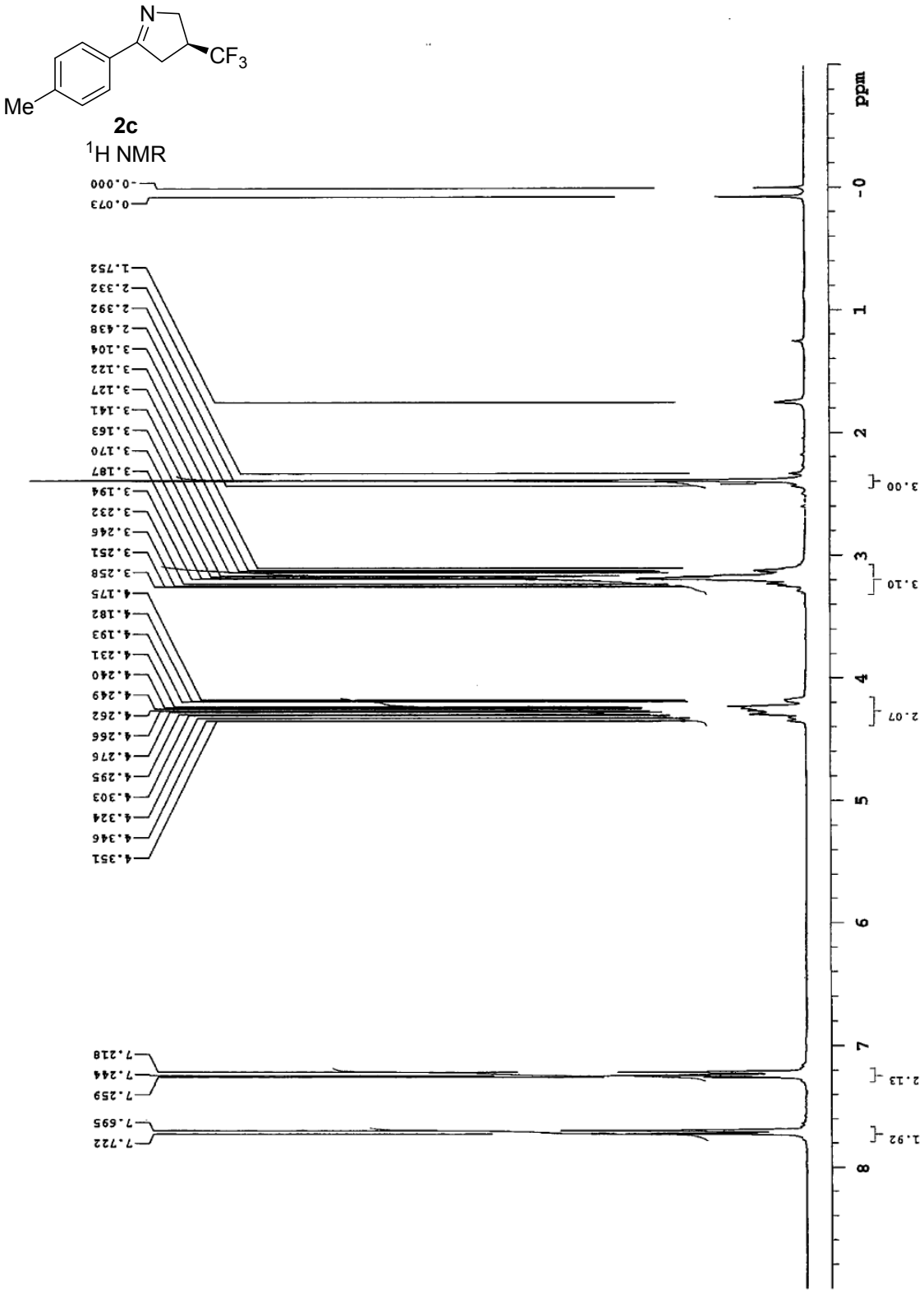
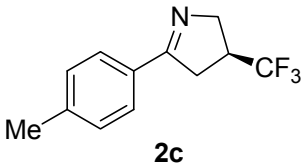
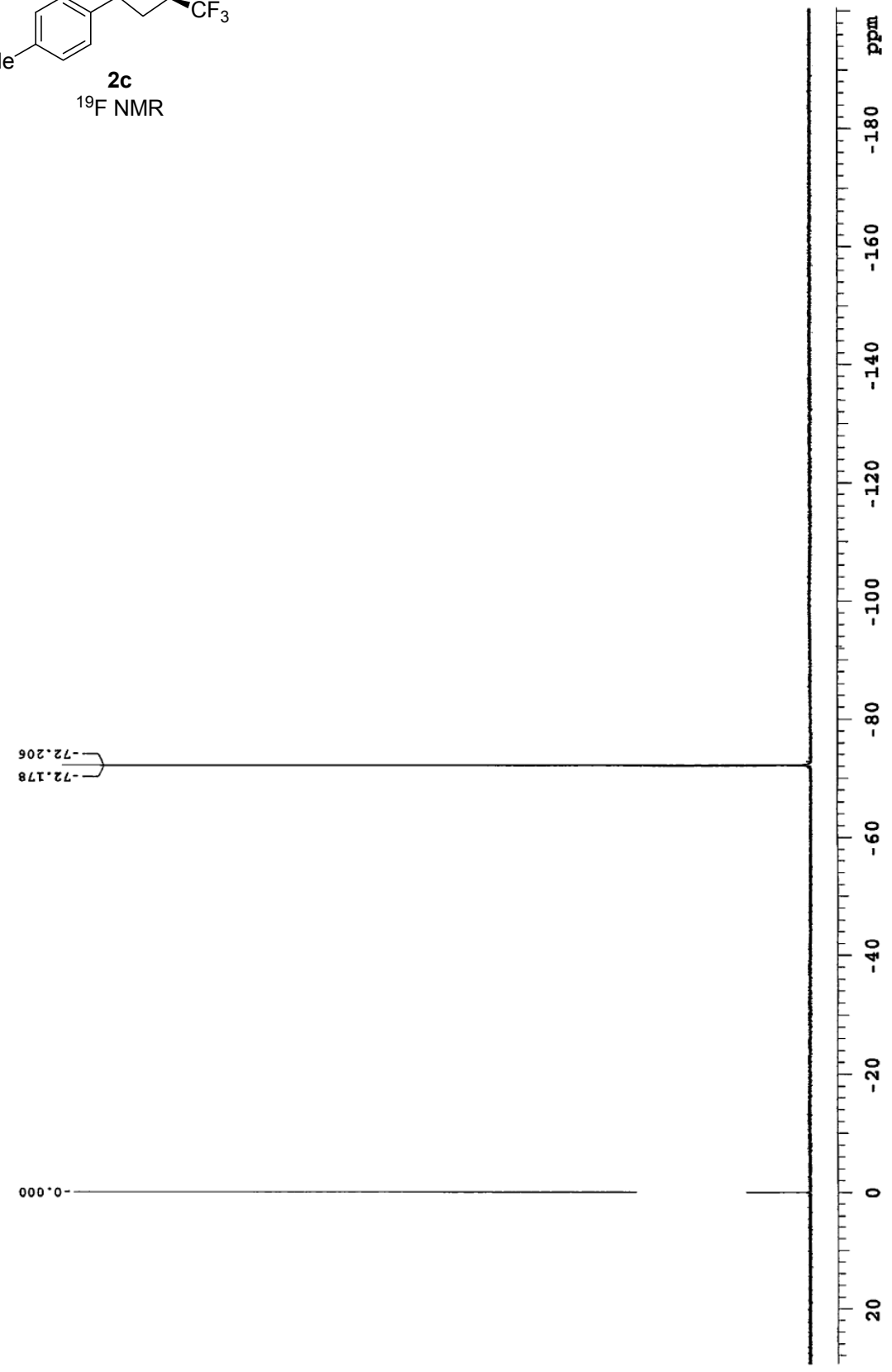
40
60
80
100
120
140
160
180

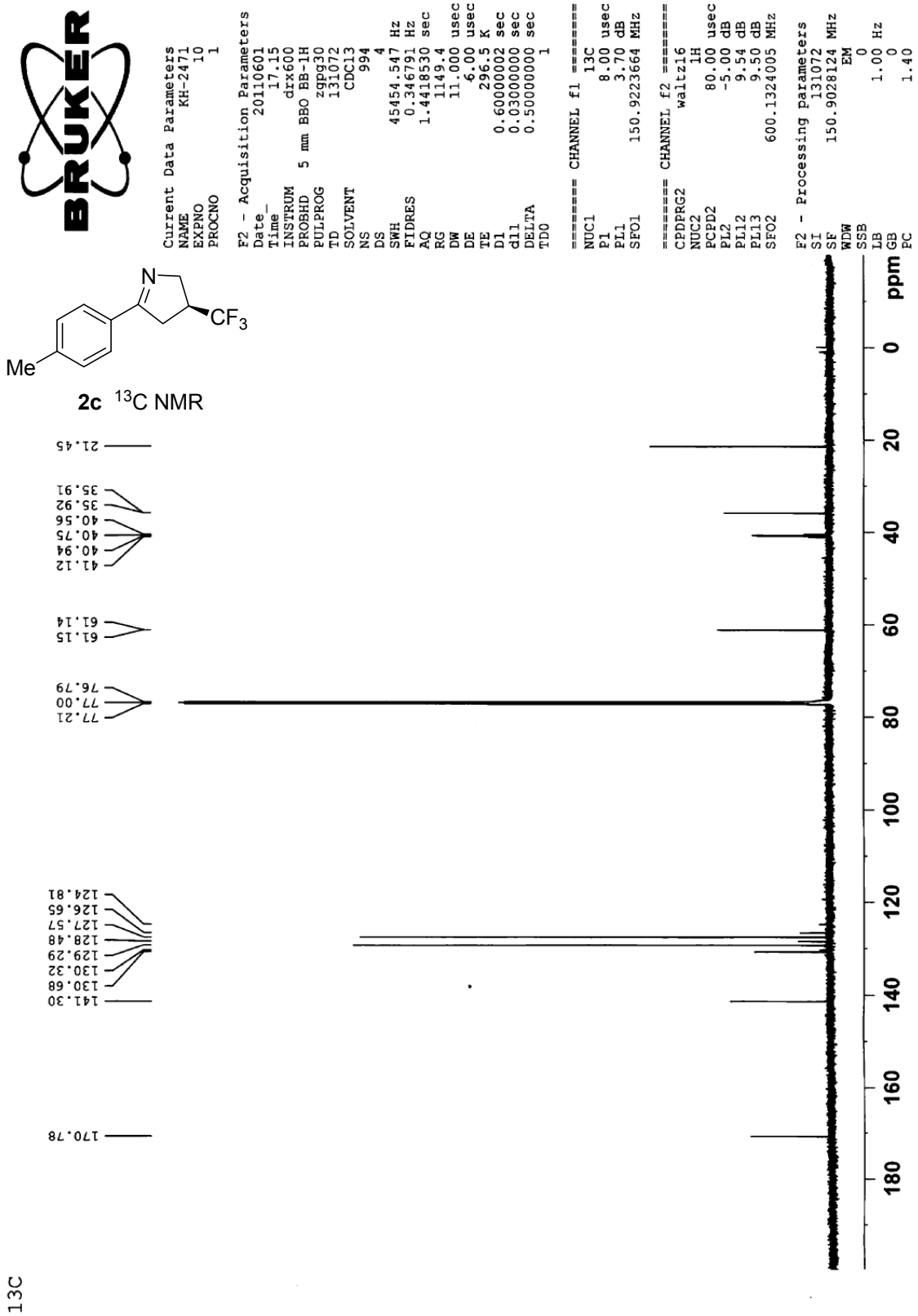




2c

^{19}F NMR

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NAME KH-2471
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110601
Time_ 17.15
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 994
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1149.4
DW 11.000 usec
DE 6.00 usec
TE 296.5 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028124 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N
CF3
Me
2c 13C NMR
21.45
35.91
35.92
40.56
40.75
40.94
41.12
61.14
61.15
76.79
77.00
77.21
124.81
126.65
127.57
128.48
129.29
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141.30
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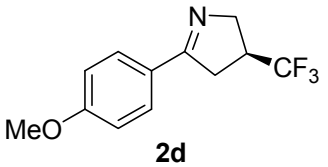
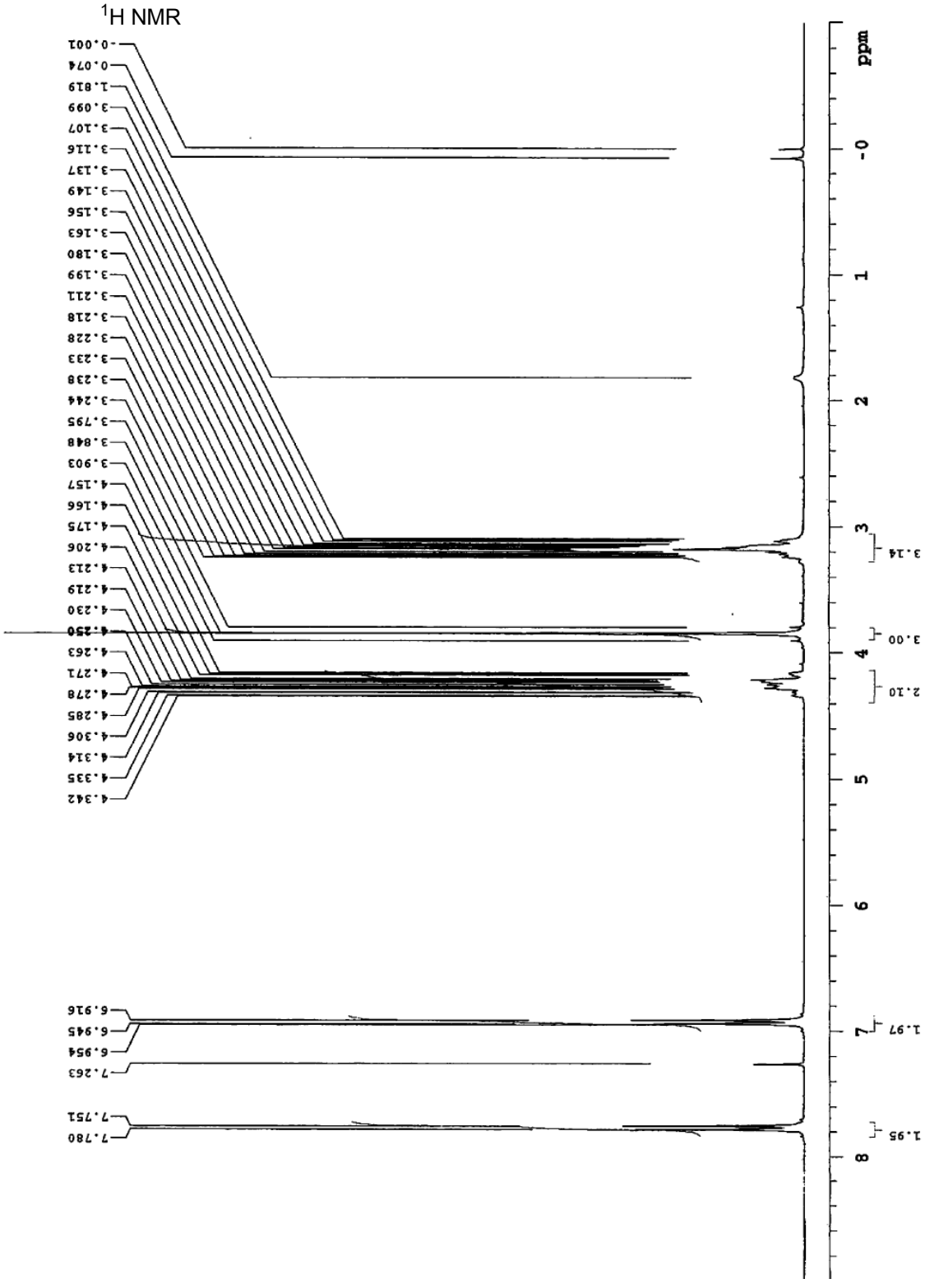
40
60
80
100
120
140
160
180
13C


N
CF3
MeO

2d

^{1}H NMR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3.163
3.180
3.199
3.211
3.218
3.228
3.233
3.238
3.244
3.795
3.848
3.903
4.157
4.166
4.175
4.206
4.213
4.219
4.230
4.250
4.263
4.271
4.278
4.285
4.306
4.314
4.335
4.342
6.916
6.945
6.954
7.263
7.751
7.780
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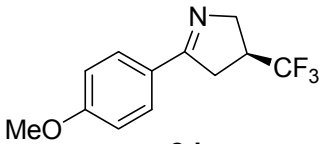
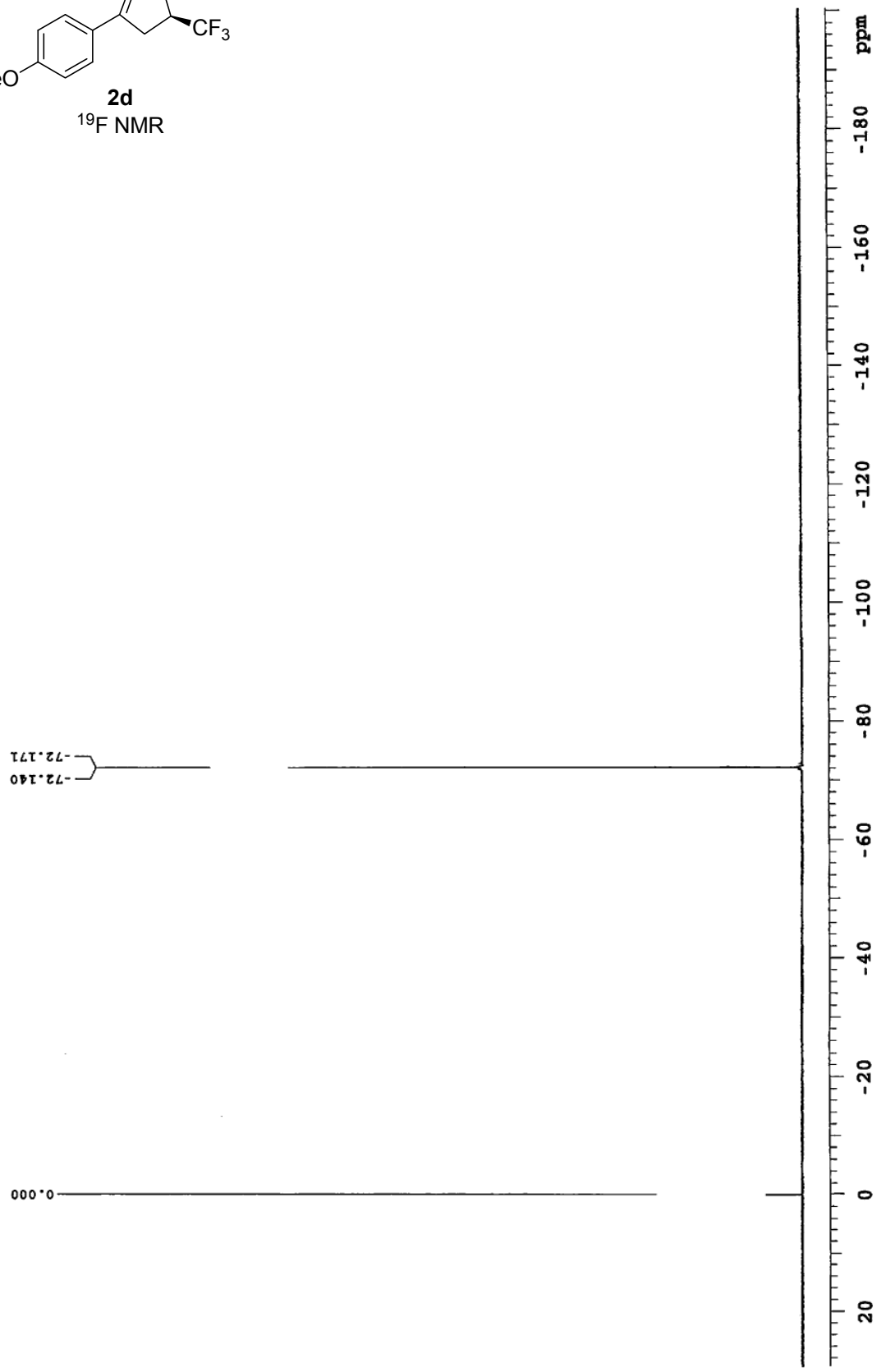
2.10
1.97
1.95


N
CF3
MeO

2d

^{19}F NMR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-72.140
0.000
ppm
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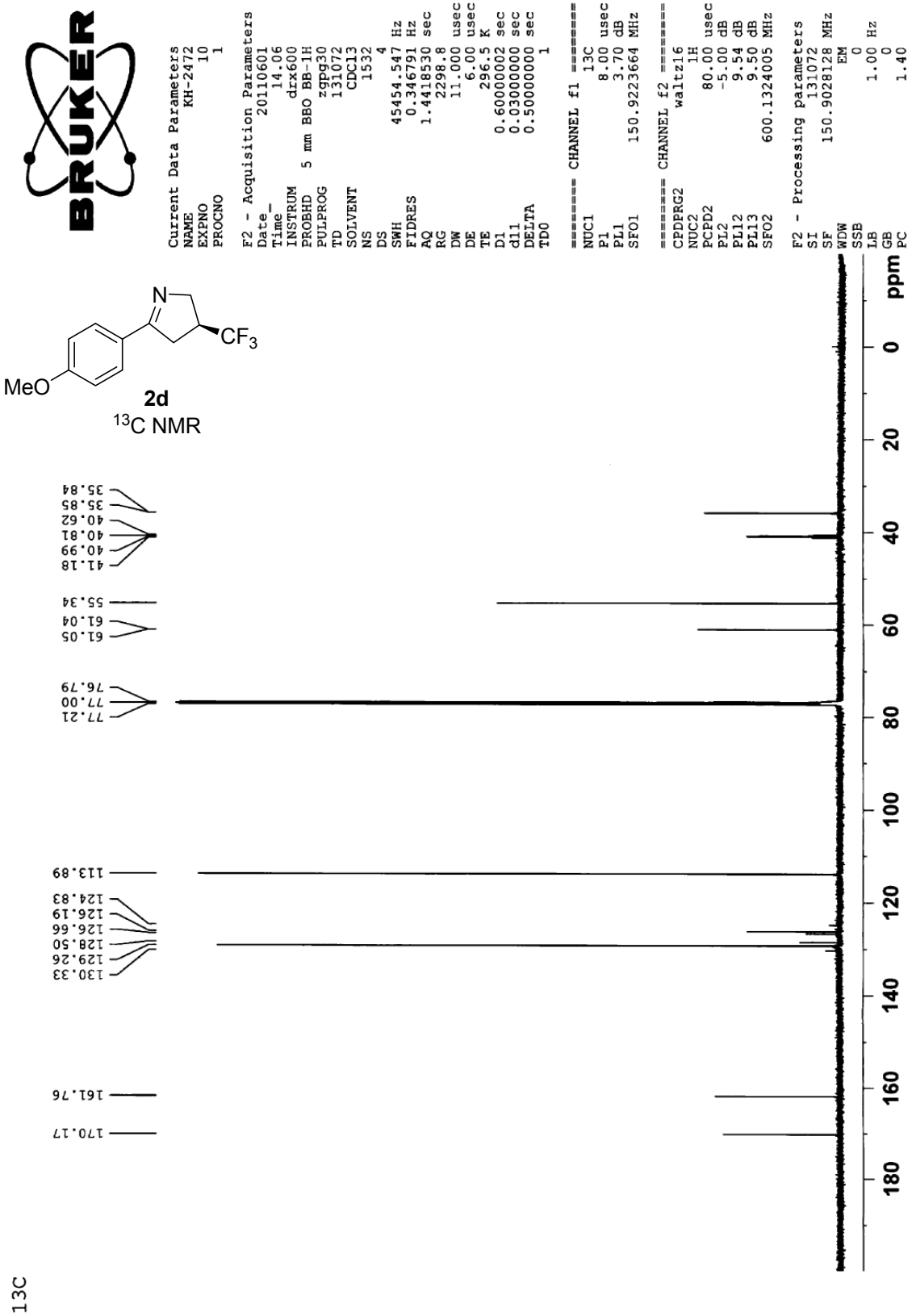
0
-20
-40
-60
-80
-100
-120
-140
-160
-180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EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110601
Time_ 14.06
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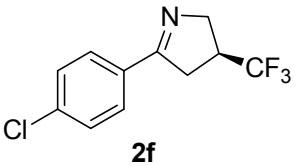
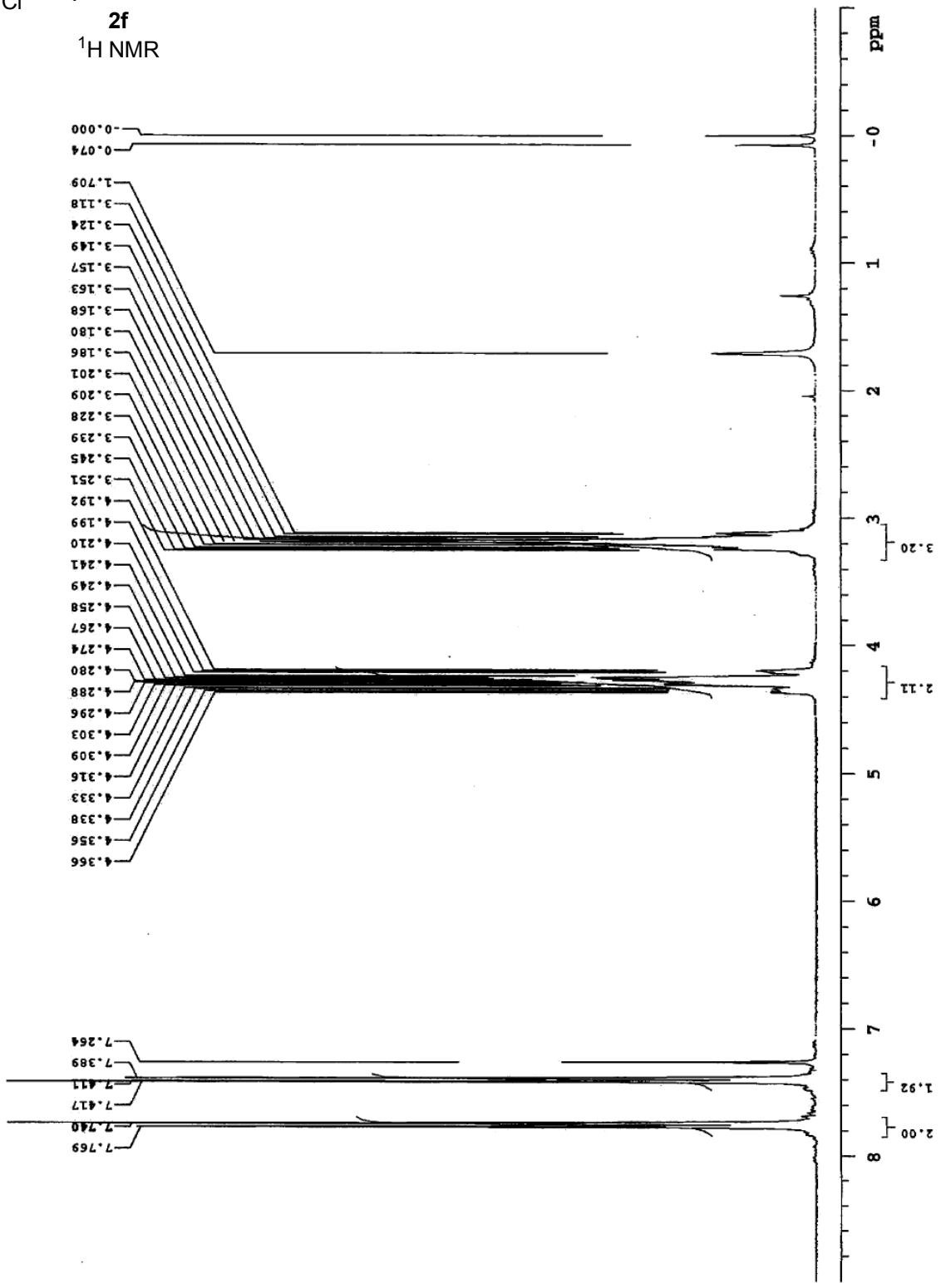
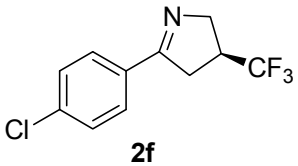
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1532
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 2298.8
DW 11.000 usec
DE 6.00 usec
TE 296.5 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028128 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N
CF3
MeO
2d
13C NMR
35.84
35.85
40.62
40.81
40.99
41.18
55.34
61.04
61.05
76.79
77.00
77.21
113.89
124.83
126.19
126.66
128.50
129.26
130.33
161.76
170.17
ppm
0
20
40
60
80
100
120
140
160
180
13C



2f

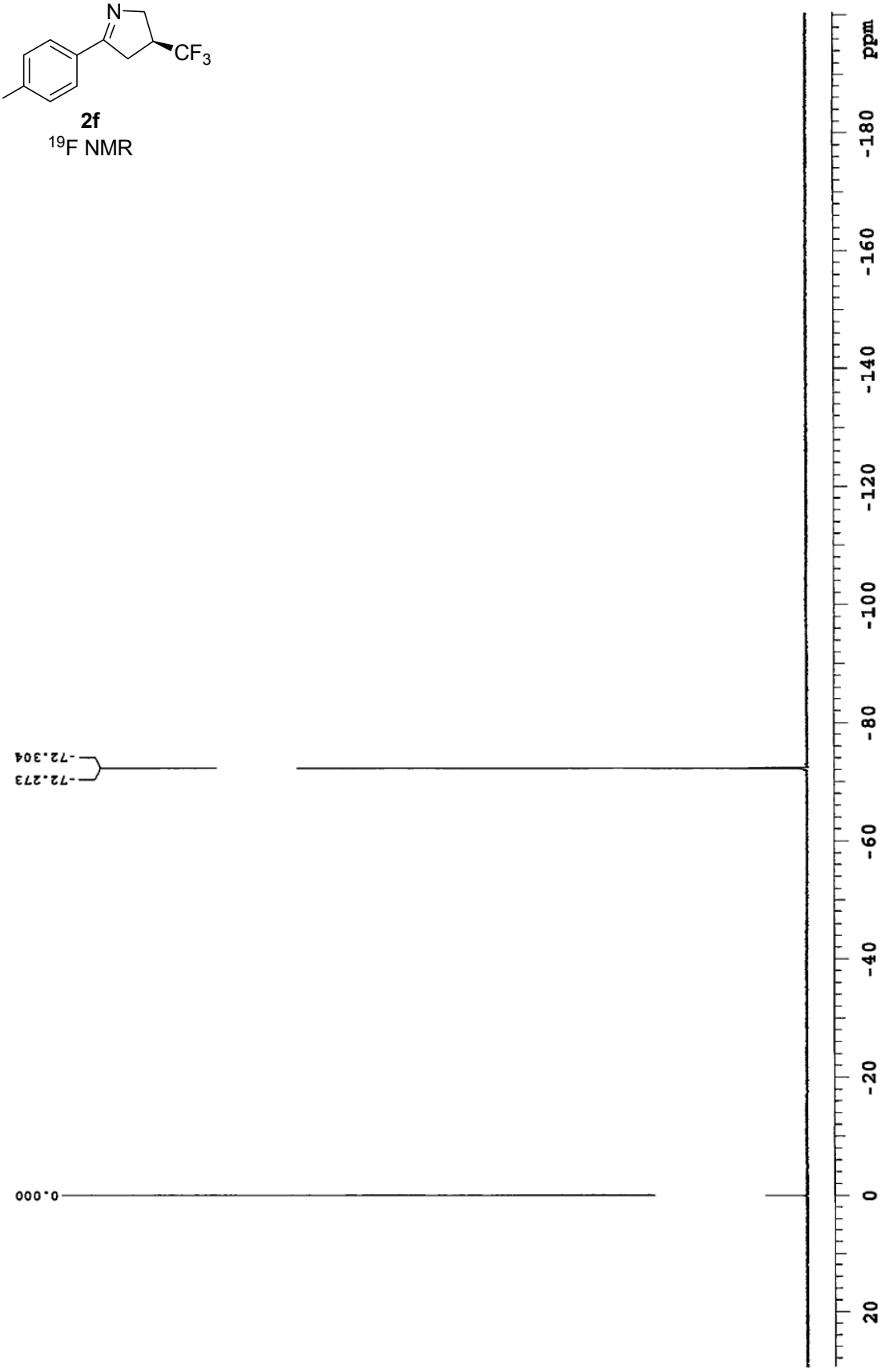
^{1}H NMR

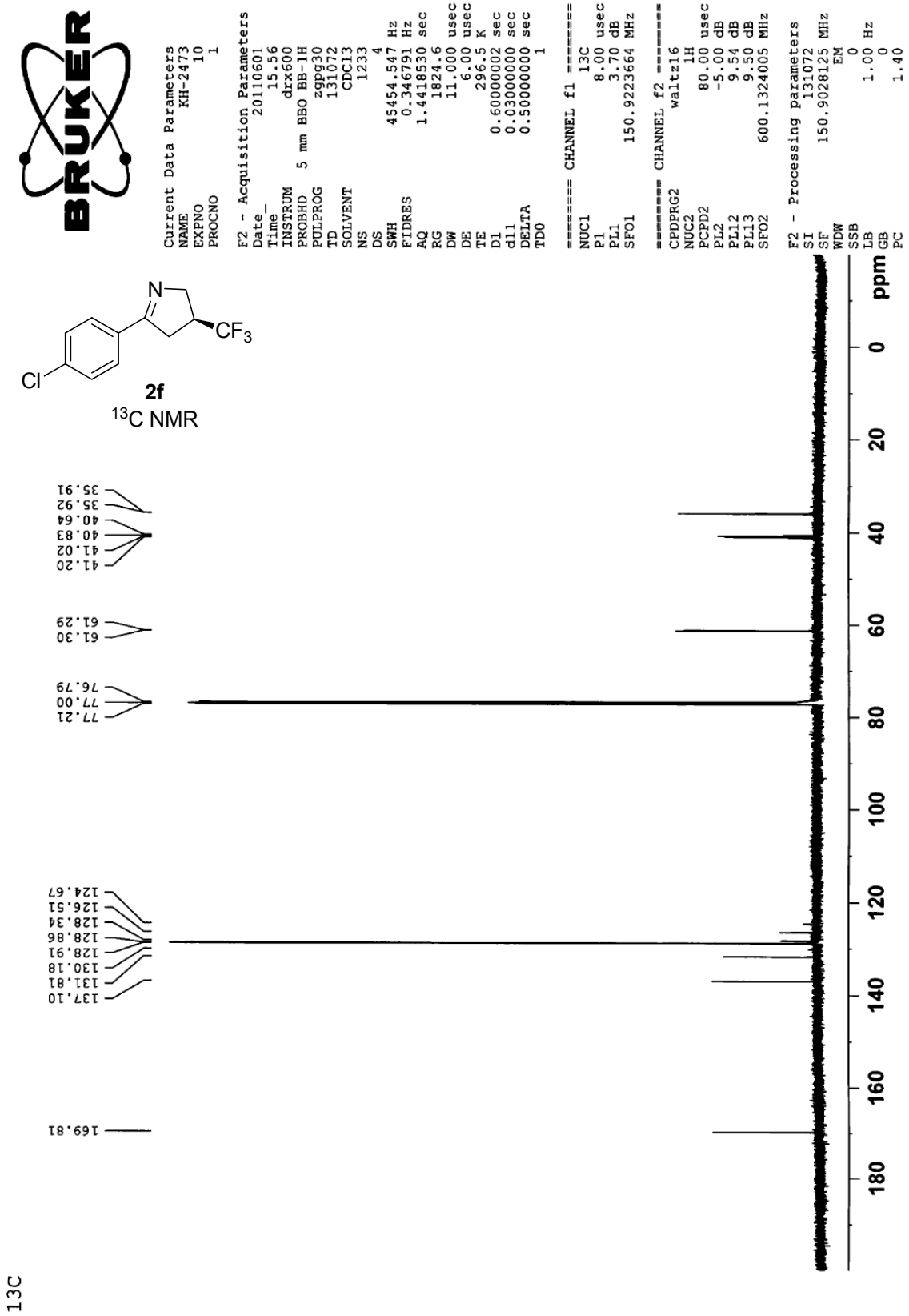




2f

^{19}F NMR

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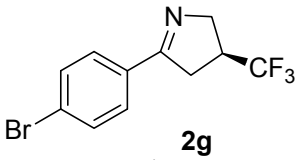
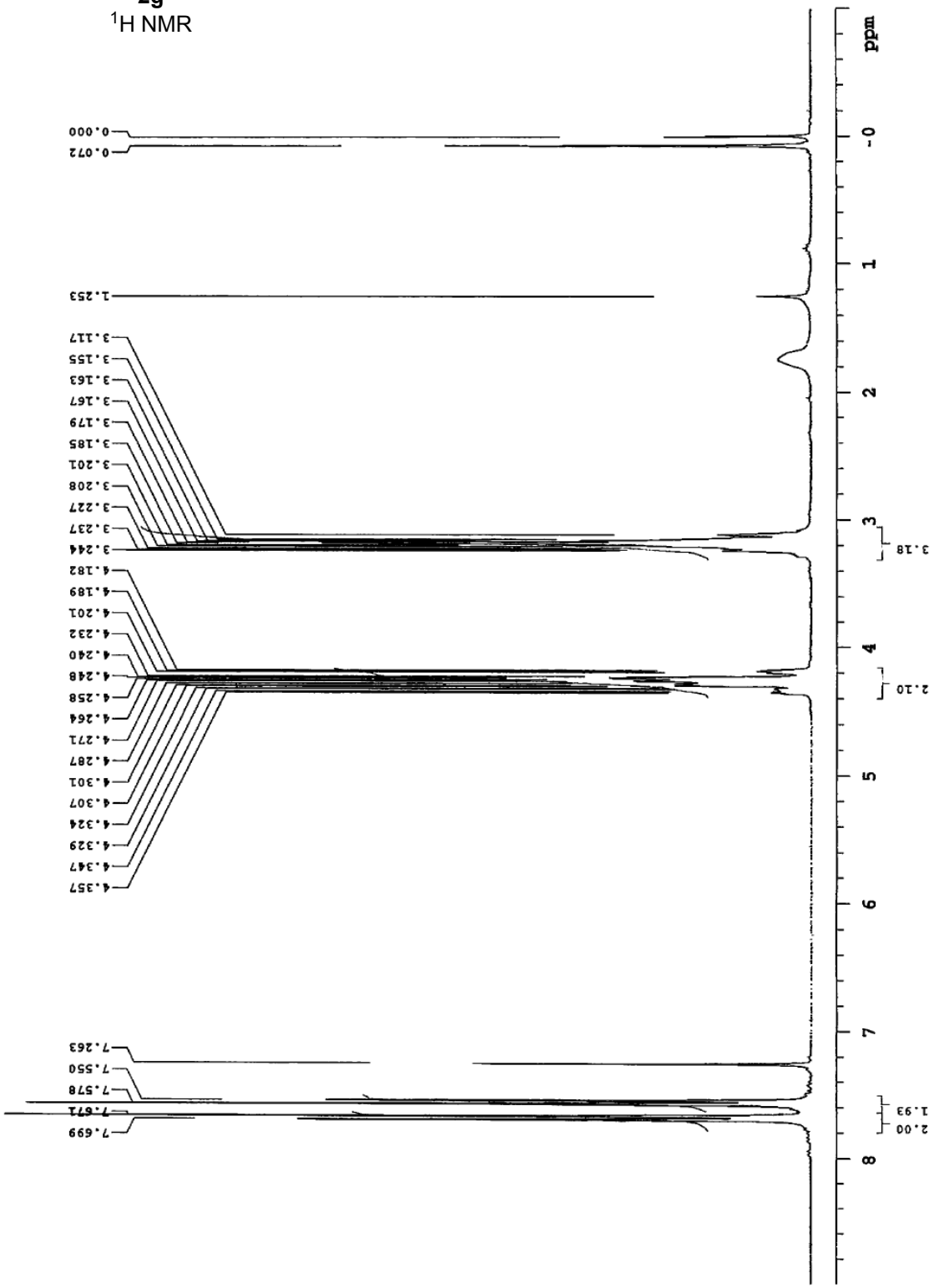
NAME KH-2473
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110601
Time_ 15.56
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1233
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1824.6
DW 11.000 usec
DE 6.00 usec
TE 296.5 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028125 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N
CF3
Cl
2f
13C NMR
35.91
35.92
40.64
40.83
41.02
41.20
61.29
61.30
76.79
77.00
77.21
124.67
126.51
128.34
128.86
128.91
130.18
131.81
137.10
169.81
ppm
0
20
40
60
80
100
120
140
160
180
13C


N
CF3
Br

2g

^{1}H NMR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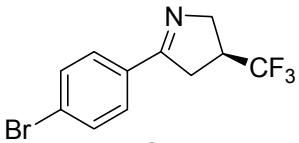
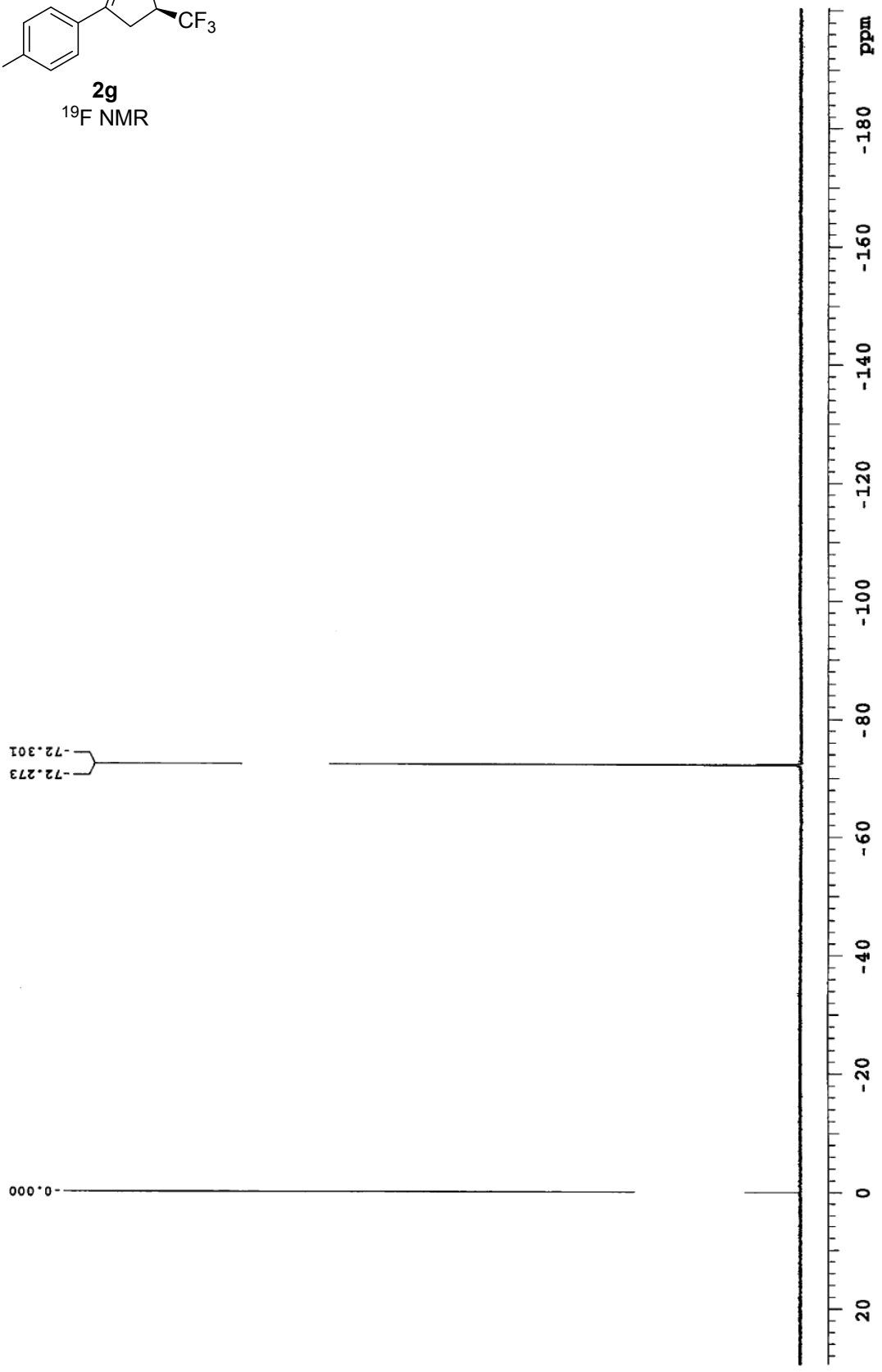
0.072
1.253
3.117
3.155
3.163
3.167
3.179
3.185
3.201
3.208
3.227
3.237
3.244
4.182
4.189
4.201
4.232
4.240
4.248
4.258
4.264
4.271
4.287
4.301
4.307
4.324
4.329
4.347
4.357
7.263
7.550
7.578
7.671
7.699
3.18
2.10
1.93
2.00

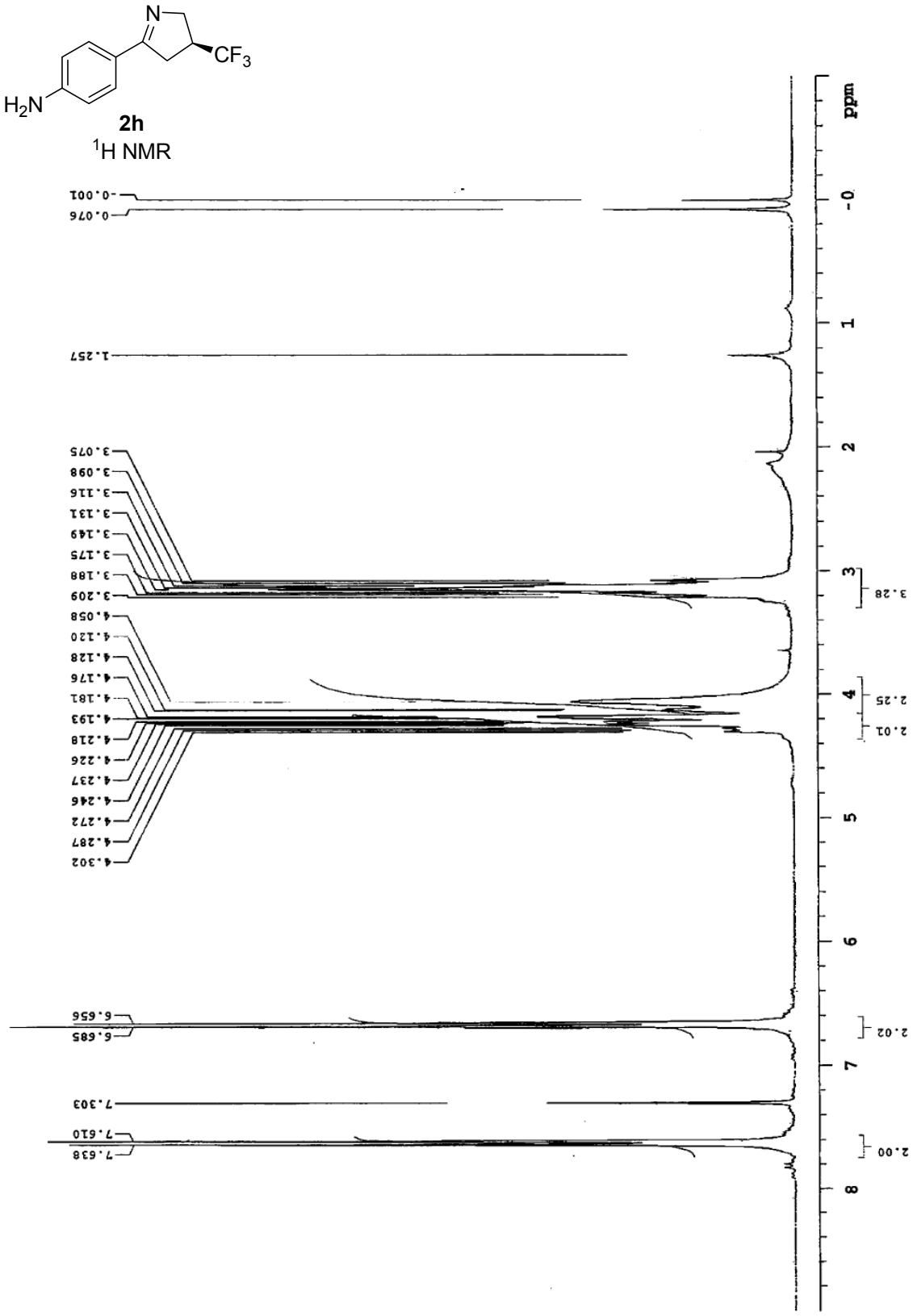


2g

^{19}F NMR




BRUKER
Current Data Parameters
NAME KH-2474
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110601
Time_ 16.36
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 997
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1625.5
DW 11.000 usec
DE 6.00 usec
TE 296.5 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028128 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
N
CF3
Br
2g
13C NMR
35.87
35.88
40.63
40.82
41.01
41.20
61.32
61.33
76.79
77.00
77.21
124.66
125.56
126.50
128.33
129.12
130.17
131.83
132.22
169.93
ppm
0
20
40
60
80
100
120
140
160
180
13C


N
CF3
H2N
2h
1H NMR
ppm
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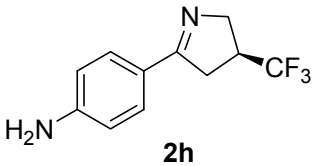
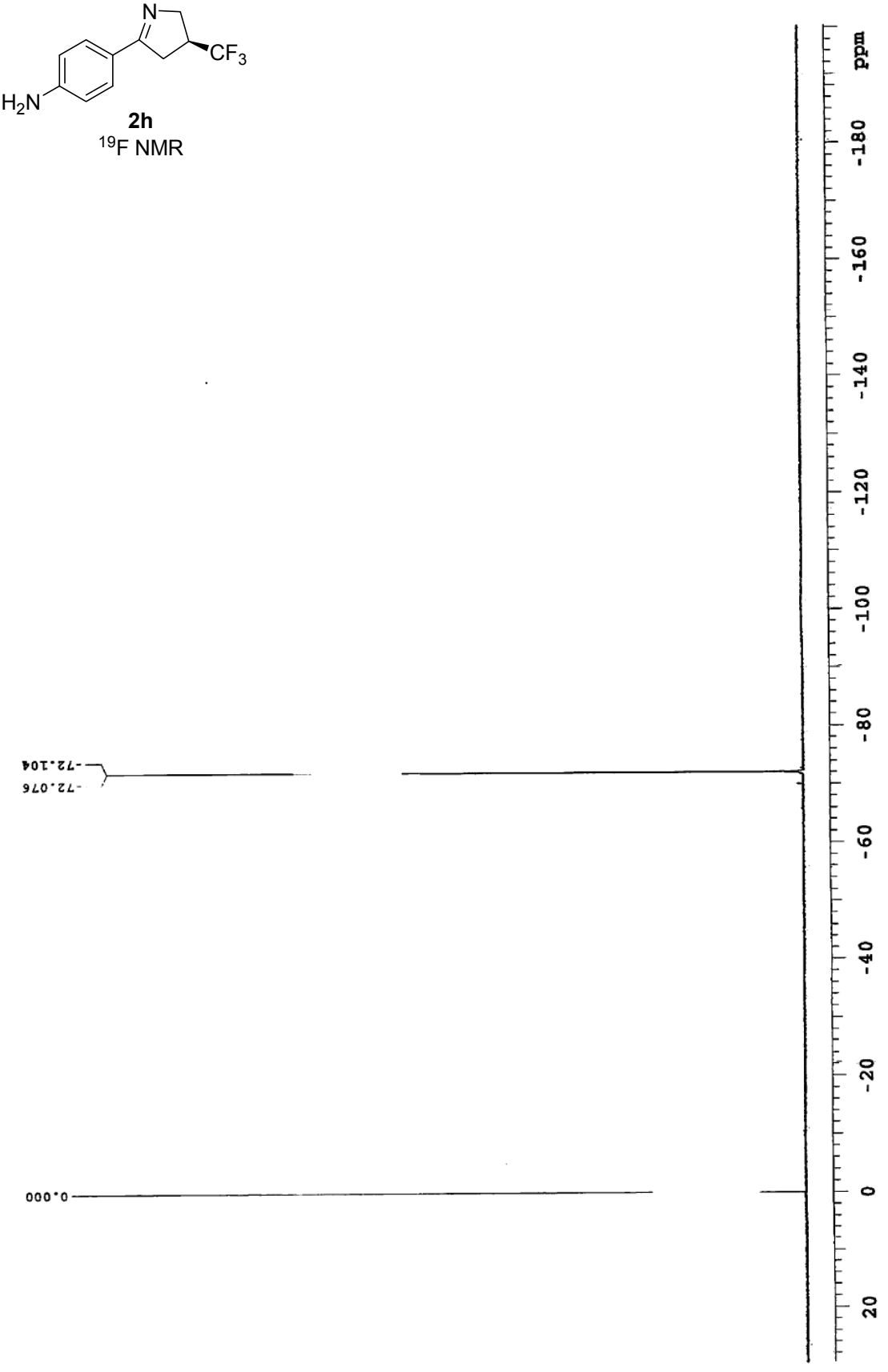
0.076
1.257
3.075
3.098
3.116
3.131
3.149
3.175
3.188
3.209
4.058
4.120
4.128
4.176
4.181
4.193
4.218
4.226
4.237
4.246
4.272
4.287
4.302
6.656
6.685
7.303
7.610
7.638
3.28
2.25
2.01
2.02
2.00


N
CF3
H2N

2h

^{19}F NMR


-72.104
-72.076
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ppm
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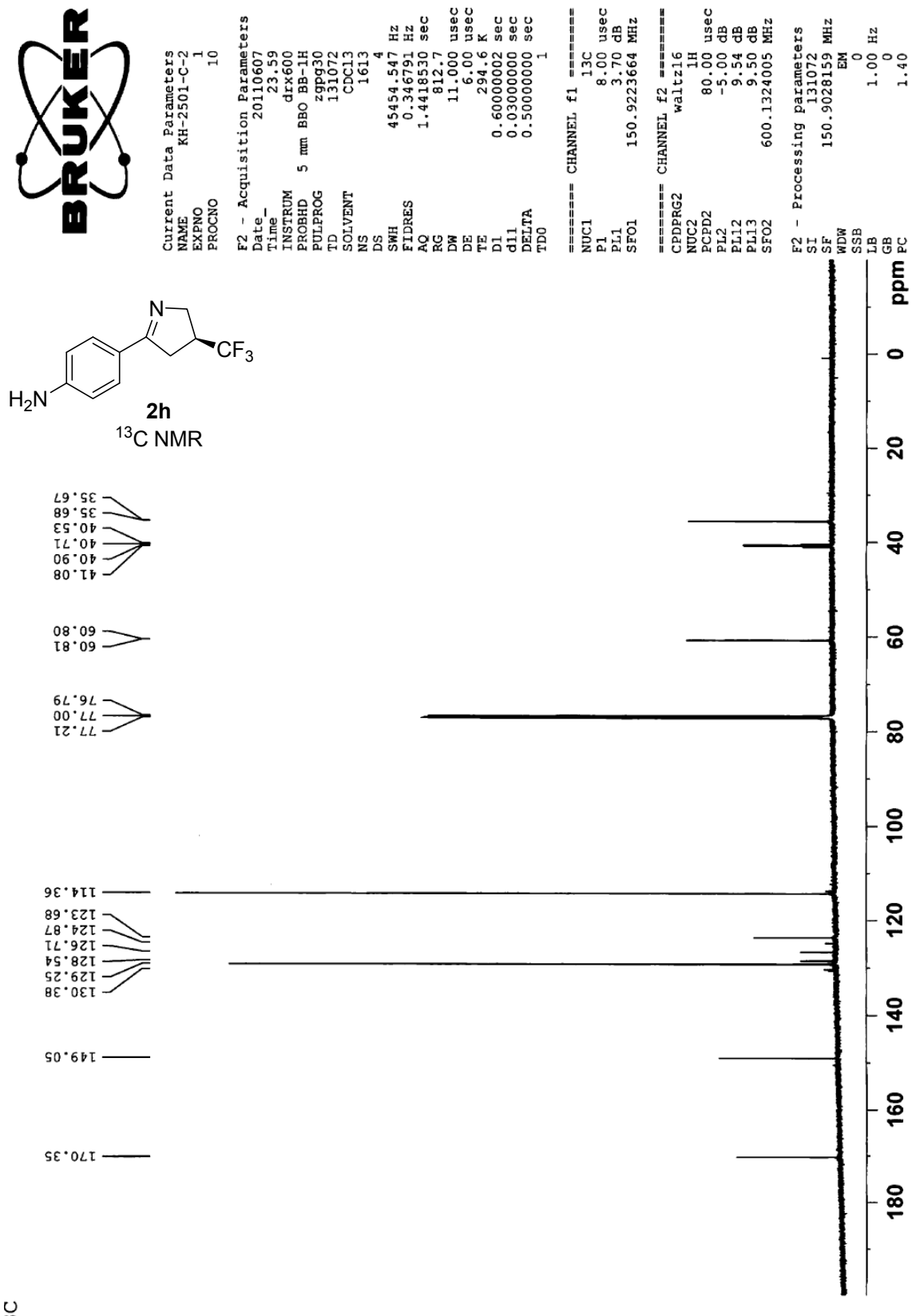
0
-20
-40
-60
-80
-100
-120
-140
-160
-180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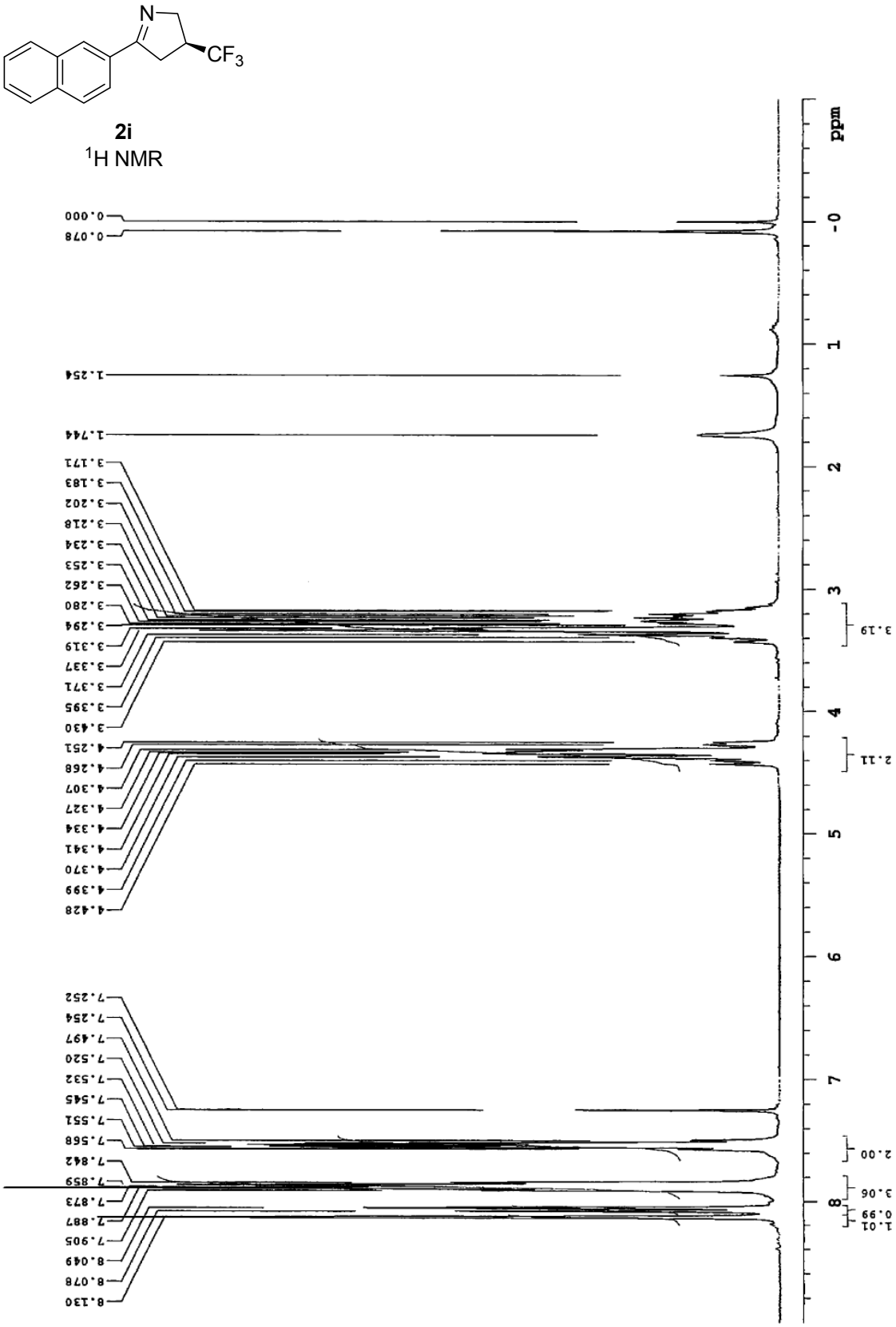
EXPNO 1
PROCNO 10
F2 - Acquisition Parameters
Date_ 20110607
Time 23.59
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1613
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.44188530 sec
RG 812.7
DW 11.000 usec
DE 6.00 usec
TE 294.6 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028159 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N
CF3
H2N
2h
13C NMR
35.67
35.68
40.53
40.71
40.90
41.08
60.80
60.81
76.79
77.00
77.21
114.36
123.68
124.87
126.71
128.54
129.25
130.38
149.05
170.35
ppm
0
20
40
60
80
100
120
140
160
180
13C


N
CF3
2i
1H NMR
ppm
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0.078
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3.183
3.202
3.218
3.234
3.253
3.262
3.280
3.294
3.319
3.337
3.371
3.395
3.430
4.251
4.268
4.307
4.327
4.334
4.341
4.370
4.399
4.428
7.252
7.254
7.497
7.520
7.532
7.545
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7.859
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8.049
8.078
8.130
3.19
2.11
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1.01
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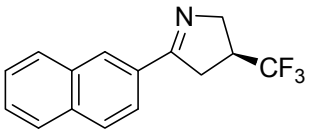
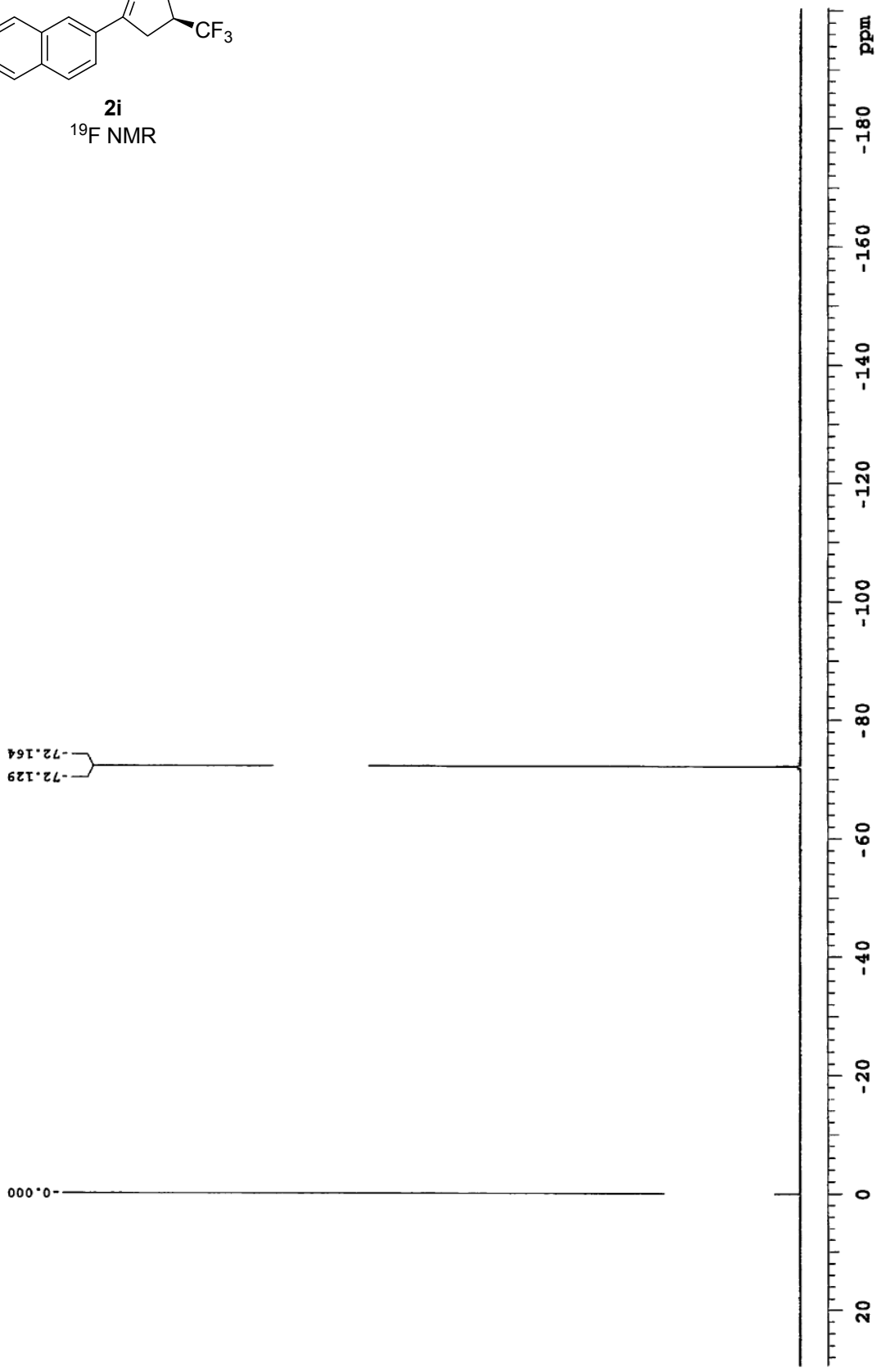
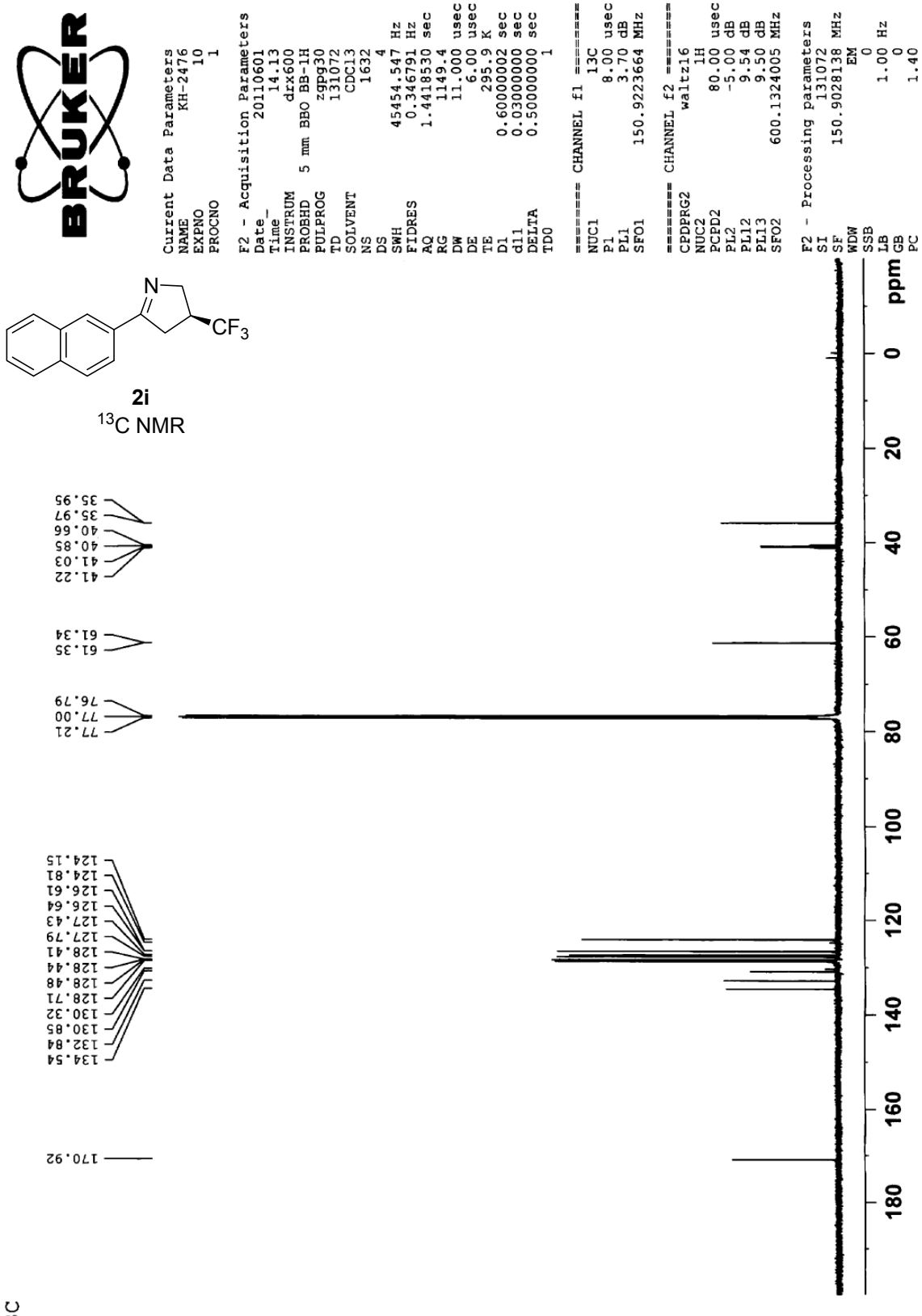


2i

^{19}F NMR

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PROCNO 1
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Time 14.13
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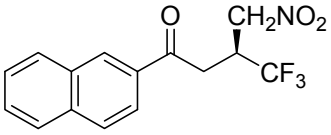
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1632
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 1149.4
DW 11.000 usec
DE 6.00 usec
TE 295.9 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 3.70 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 9.54 dB
PL13 9.50 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028138 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N
CF3
2i
13C NMR
35.95
35.97
40.66
40.85
41.03
41.22
61.34
61.35
76.79
77.00
77.21
124.15
124.81
126.61
126.64
127.43
127.79
128.41
128.44
128.48
128.71
130.32
130.85
132.84
134.54
170.92
ppm
0
20
40
60
80
100
120
140
160
180
13C

X-ray crystallographic structure of (*S*)-**4i**



(*S*)-**4i**

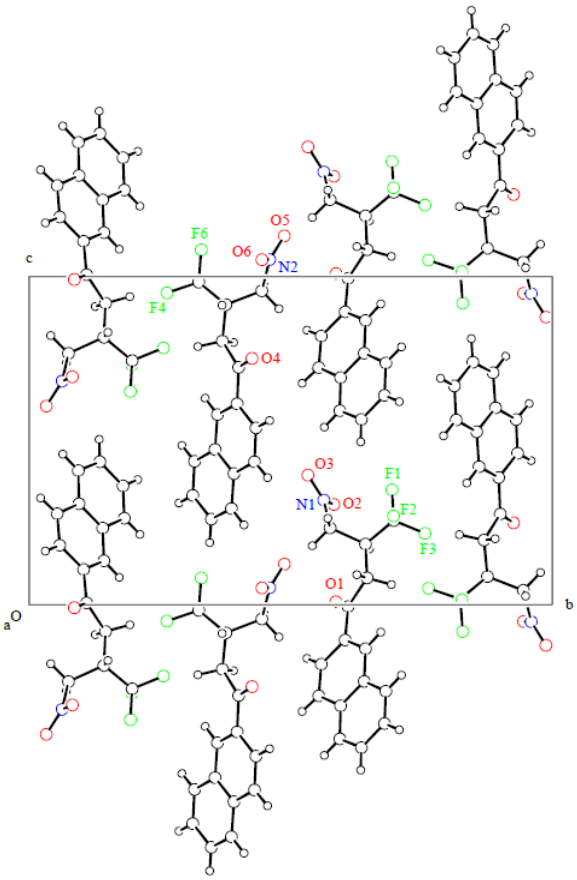
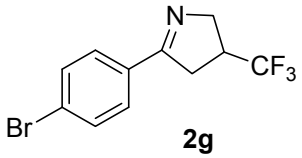
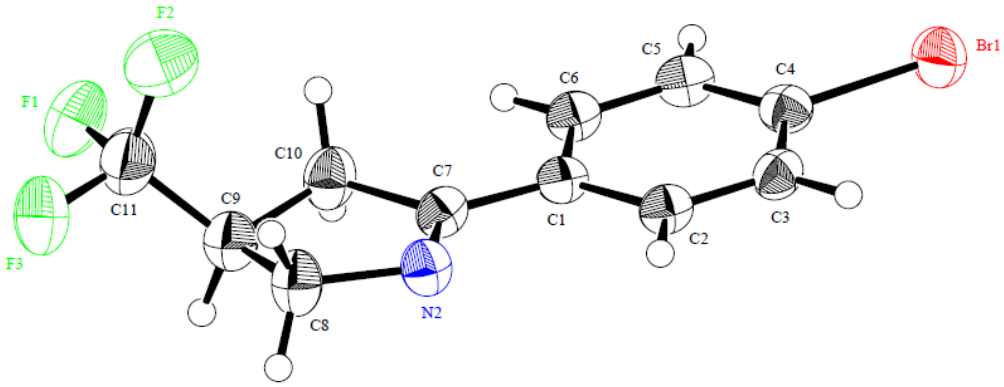


Figure S1

X-ray crystallographic structure of racemic **2g**



2g



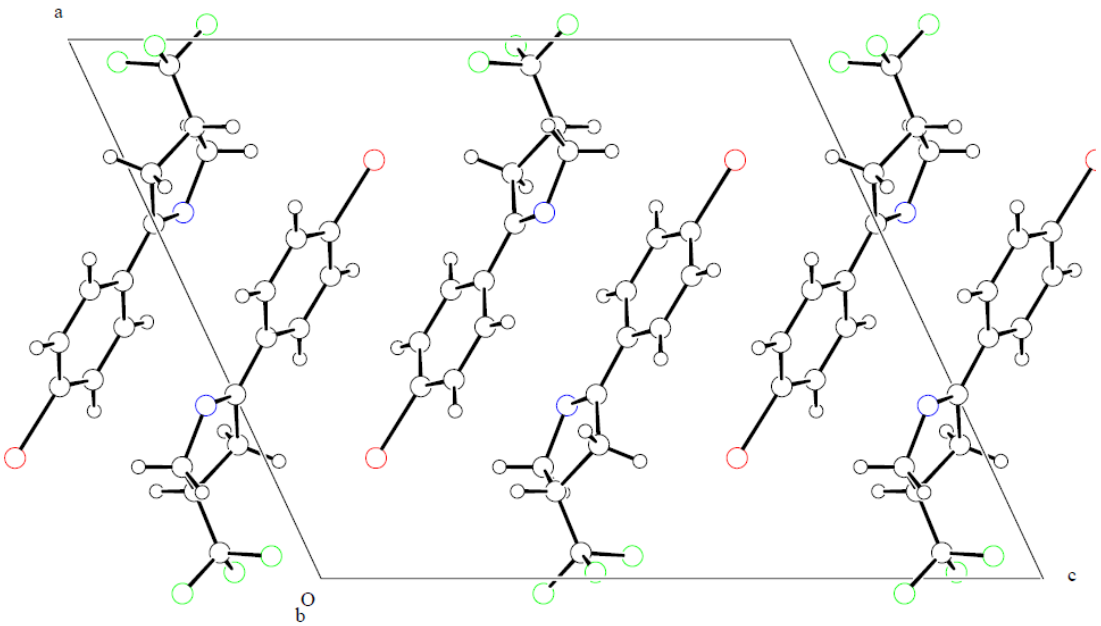


Figure S2