Supporting Information

Partially saturated fluorinated heterocycles: Diastereo- and enantioselective synthesis of β-trifluoromethyl-pyrroline carboxylates

*Hiroyuki Kawai, Yutaka Sugita, Etsuko Tokunaga, Hiroyasu Sato, Motoo Shiro, and Norio Shibata**

Department of Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology,

Gokiso, Showa-ku, Nagoya 466-8555, Japan

Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan

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]

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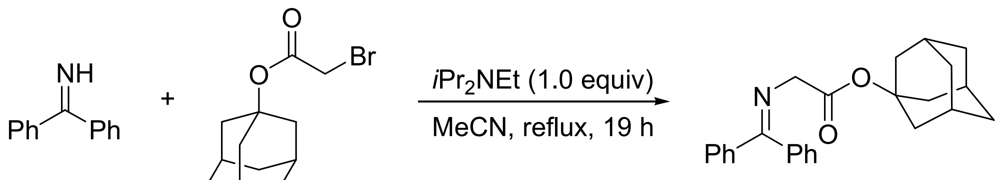
[1] G. Blay, I. Fernández, M. C. Munoz, J. R. Pedro, C. Vila, *Chem. Eur. J.* **2010**, *16,* 9117.

Synthesis of 1-adamantyl glycinate-benzophenone schiff base 5b:

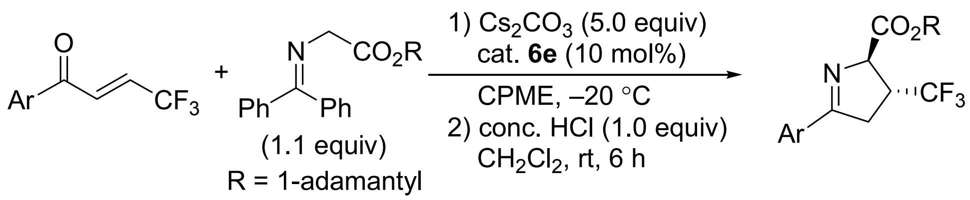


5b

To a stirred solution of 1-adamantyl 2-bromoacetate (3.45 g, 12.6 mmol) in MeCN (12 mL) was added benzophenone imine (2.11 mL, 12.6 mmol, 1.0 equiv) and *i*Pr_2NEt (2.20 mL, 12.6 mmol, 1.0 equiv) successively at ambient temperature and heated under reflux for 19 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and partitioned between CH_2Cl_2 and water. The resulting organic layer was washed with H_2O (two times) and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on flash silica gel (*n*-hexane/ethyl acetate = 9/1) to give **5b** as a white solid (1.83 g, 39%).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65 (s, 6H), 2.12 (s, 9H), 4.12 (s, 2H), 7.18-7.20 (m, 2H), 7.30-7.39 (m, 3H), 7.45 (s, 3H), 7.65 (d, J = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 30.8, 36.1, 41.3, 56.4, 81.1, 127.7, 128.0, 128.6, 128.7, 130.3, 136.1, 139.4, 169.5, 171.4; IR (KBr) 2911, 1749, 1624, 1490, 1445, 1394, 1353, 1284, 1184, 1103, 1057, 939, 884, 783, 699, 639, 575, 463 cm^{-1}; mp = 65.5-68.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 375 $(M+H)^+$, HRMS (ESI) calcd. for $C_{25}H_{28}NO_2$ [$(M+H)^+$]: 373.2042 Found: 374.2120;

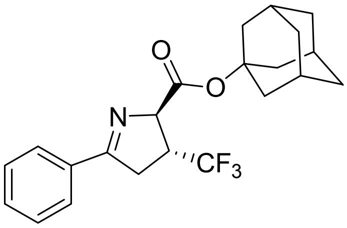
General procedure for the aymmetric synthesis of β-trifluoromethylated pyrrolines by organocatalytic conjugated addition of glycinate schiff base:



To a stirred solution of β-trifluoromethylated enone **4** (0.10 mmol), catalyst **6e** (5.8 mg, 0.01 mmol, 10 mol%) and glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv) in CPME (1.0 mL) was added Cs_2CO_3 (163 mg, 0.50 mmol, 5.0 equiv) at −20°C under nitrogen atmosphere. After reaction mixture was stirred at the same temperature, it was quenched with sat. NH_4Cl aq. Aqueous layer was extracted with AcOEt, and the combined organic layers was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to furnish the conjugated adduct intermediate. This intermediate was treated with conc. HCl (8.3 μL, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (0.5 mL) at ambient temperature for 6 h. After dilution with water, the resulting mixture was extracted with

CH_2Cl_2, 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 (*n*-hexane/ethyl acetate = 95/5) to give β-trifluoromethylated pyrroline (2*R*,3*R*)-**3**.

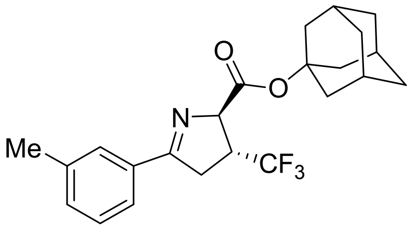
(2*R*,3*R*)-1-Adamantyl 5-phenyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (3b)



Reaction of **4a** (20.0 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0 mL) at −20 ˚C for 9 h gave (2*R*,3*R*)-**3b** (37.4 mg, 95%, 86% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 6H), 2.17 (s, 9H), 3.16-3.25 (m, 1H), 3.34-3.52 (m, 2H), 4.94-4.96 (m, 1H), 7.40-7.51 (m, 3H), 7. 84-7.87 (m, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 30.9, 36.1, 36.6 (q, *J* = 2.0 Hz), 41.1, 44.0 (q, *J* = 28.2 Hz), 76.3 (q, *J* = 1.5 Hz), 82.5, 126.9 (q, *J* = 277.7 Hz), 128.0, 128.5, 131.4, 132.9, 169.4, 173.1; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.6 (d, *J* = 8.7 Hz, 3F); IR (KBr) 2913, 2855, 1744, 1625, 1577, 1448, 1386, 1354, 1200, 1154, 1107, 1061, 965, 932, 889, 822, 769, 691, 556, 472 cm^{-1}; mp = 88.0-90.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 415 $[(M+Na)^+]$, HRMS (ESI) calcd. for $C_{22}H_{24}F_3NNaO_2$ $[(M+Na)^+]$: 414.1657 Found: 414.1651; 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} = 11.9 min, τ_{min} = 13.5 min); $[\alpha]_D^{25}$ = -54.2 (c = 0.65, $CHCl_3$), 86% ee.

(2*R*,3*R*)-1-Adamantyl 5-*m*-tolyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (3c)

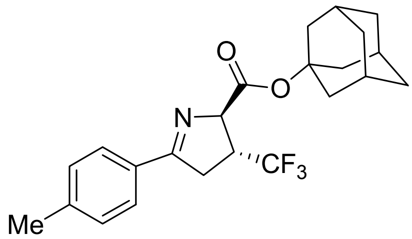


Reaction of **4c** (21.4 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0 mL) at −20 ˚C for 36 h gave (2*R*,3*R*)-**3c** (29.2 mg, 72%, 84% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 6H), 2.17 (s, 9H), 2.39 (s, 3H), 3.13-3.24 (m, 1H), 3.33-3.49 (m, 2H), 4.93-4.95 (m, 1H), 7.30-7.34 (m, 2H), 7.60-7.64 (m, 1H), 7.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.3, 30.9, 36.1, 36.6 (q, *J* = 2.0 Hz), 41.1, 44.0 (q, *J* = 28.2 Hz), 76.2, 82.5, 125.3, 126.9 (q, *J* = 277.7 Hz), 128.4, 128.5, 132.2, 132.8, 138.3, 169.5, 173.3; ^{19}F NMR ($CDCl_3$, 282

MHz) δ -71.6 (d, J = 9.0 Hz, 3F); IR (KBr) 2913, 1731, 1584, 1457, 1397, 1338, 1271, 1245, 1200, 1155, 1114, 1056, 967, 933, 883, 807, 741, 695, 469 cm^{-1}; mp = 80.5-82.0 °C ($CHCl_3$); MS (ESI, *m/z*) 407 $[(M+H)^+]$, HRMS (ESI) calcd. for $C_{23}H_{27}F_3NO_2$ $[(M+H)^+]$: 406.1994 Found: 406.1987; The ee of the product was determined by HPLC using an AD-3 column (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 13.8 min, τ_{min} = 16.5 min); $[\alpha]_D^{25}$ = -53.8 (c = 0.45, $CHCl_3$), 84% ee.

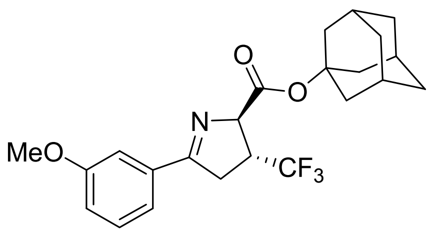
(2*R*,3*R*)-1-Adamantyl 5-*p*-tolyl-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole-2-carboxylate (3d)



Reaction of **4d** (21.4 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0 mL) at −20 °C for 12 h gave (2*R*,3*R*)-**3d** (38.4 mg, 95%, 87% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 6H), 2.17 (s, 9H), 2.39 (s, 3H), 3.12-3.24 (m, 1H), 3.31-3.48 (m, 2H), 4.92-4.94 (m, 1H), 7.23 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.5 30.8, 36.1, 36.5 (q, J = 1.5 Hz), 41.1, 44.0 (q, J = 28.2 Hz), 76.2, 82.4, 126.9 (q, J = 277.2 Hz), 128.0, 129.2, 130.2, 141.8, 169.5, 172.9; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.5 (d, J = 9.0 Hz, 3F); IR (KBr) 2918, 1725, 1619, 1567, 1515, 1457, 1397, 1334, 1217, 1154, 1110, 1052, 964, 932, 884, 821, 795, 736, 553, 507 cm^{-1}; mp = 97.0-99.5 ºC ($CHCl_3$); MS (ESI, *m/z*) 429 $[(M+Na)^+]$, HRMS (ESI) calcd. for $C_{23}H_{26}F_3NNaO_2$ $[(M+Na)^+]$: 428.1813 Found: 428.1806; 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} = 12.3 min, τ_{min} = 14.3 min); $[\alpha]_D^{25}$ = -38.7 (c = 1.20, $CHCl_3$), 87% ee.

(2*R*,3*R*)-1-Adamantyl 5-(3-methoxyphenyl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (3e)

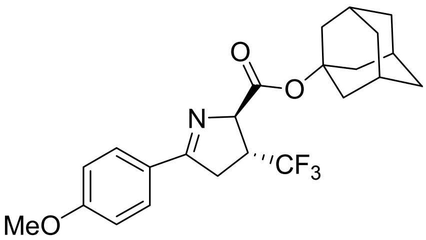


Reaction of **4e** (23.0 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0

mL) at −20 ˚C for 36 h gave (2*R*,3*R*)-**3e** (31.1 mg, 74%, 84% ee) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 6H), 2.17 (s, 9H), 3.14-3.23 (m, 1H), 3.33-3.48 (m, 2H), 3.86 (s, 3 H), 4.94-4.96 (m , 1H), 7.01-7.05 (m, 1H), 7.30-7.38 (m, 2H), 7.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 30.9, 36.1, 36.7, 41.1, 44.1 (q, *J* = 28.2 Hz), 55.4, 76.2, 82.6, 112.3, 117.9, 120.8, 126.9 (q, *J* = 277.7 Hz), 129.5, 134.2, 159.7, 169.4, 173.1; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.6 (d, *J* = 8.7 Hz, 3F); IR (neat) 2913, 2854, 1732, 1584, 1457, 1337, 1200, 1116, 1053, 965, 878, 788, 734, 689, 496 cm^{-1}; MS (ESI, *m/z*) 444 [(M+Na)$^{+}$], HRMS (ESI) calcd. for $C_{23}H_{26}F_3NNaO_3$ [(M+Na)$^{+}$]: 444.1762 Found: 444.1756; The ee of the product was determined by HPLC using an OZ-H column (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 15.3 min, τ_{min} = 12.3 min); $[\alpha]_D^{25}$ = -38.9 (c = 0.63, $CHCl_3$), 84% ee.

(2*R*,3*R*)-1-Adamantyl 5-(4-methoxyphenyl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (3f)

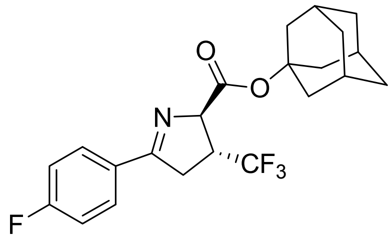


Reaction of **4f** (23.0 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0 mL) at −20 ˚C for 12 h gave (2*R*,3*R*)-**3f** (39.6 mg, 94%, 88% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 6H), 2.17 (s, 9H), 3.12-3.21 (m, 1H), 3.30-3.46 (m, 2H), 3.85 (s, 3 H), 4.90-4.92 (m, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 9.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 30.8, 36.1, 36.4 (q, *J* = 2.0 Hz), 41.1, 44.3 (q, *J* = 28.7 Hz), 55.4, 76.1, 82.4, 113.8, 125.7, 127.0 (q, *J* = 277.7 Hz), 129.8, 162.1, 169.7, 172.3; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.5 (d, *J* = 9.0 Hz, 3F); IR (KBr) 2913, 1739, 1608, 1571, 1515, 1457, 1246, 1054, 965, 930, 886, 841, 791, 738, 617, 557, 503 cm^{-1}; mp = 98.5-101.5 ºC ($CHCl_3$); MS (ESI, *m/z*) 423 [(M+H)$^{+}$], HRMS (ESI) calcd. for $C_{23}H_{27}F_3NO_3$ [(M+H)$^{+}$]: 422.1943 Found: 422.1932; 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} = 18.9 min, τ_{min} = 25.0 min); $[\alpha]_D^{25}$ = -34.7 (c = 0.27, $CHCl_3$), 88% ee.

(2*R*,3*R*)-1-Adamantyl

5-(4-fluorophenyl)-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole-2-carboxylate (3g)

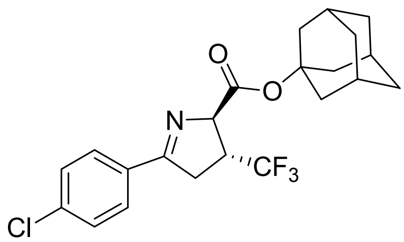


Reaction of **4g** (21.8 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0 mL) at −20 ˚C for 15 h gave (2*R*,3*R*)-**3g** (38.3 mg, 94%, 84% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.68 (s, 6H), 2.17 (s, 9H), 3.13-3.20 (m, 1H), 3.31-3.49 (m, 2H), 4.94 (brs, 1H), 7.11 (t, *J* = 8.6 Hz, 2H), 7.86 (dd, *J* = 5.7, 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 30.8, 36.0, 36.6 (q, *J* = 2.0 Hz), 41.1, 44.1 (q, *J* = 28.2 Hz), 76.2 (q, *J* = 1.1 Hz), 82.6, 115.7 (d, *J* = 21.1 Hz), 126.8 (q, *J* = 277.2 Hz), 129.2 (d, *J* = 3.0 Hz), 130.2 (d, *J* = 9.1 Hz), 164.6 (d, *J* = 252.0 Hz), 169.4, 171.9; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -108.6 (m, 1F), -71.6 (d, *J* = 8.7 Hz, 3F); IR (KBr) 2919, 1742, 1629, 1604, 1515, 1457, 1387, 1353, 1200, 1156, 1117, 1054, 966, 931, 890, 847, 820, 775, 551 cm^{-1}; mp = 65.0-67.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 433 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{22}H_{23}F_4NNaO_2$ [$(M+Na)^+$]: 432.1563 Found: 432.1563; 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} = 13.7 min, τ_{min} = 16.2 min); $[\alpha]_D^{25}$ = -50.9 (c = 0.83, $CHCl_3$), 84% ee.

(2*R*,3*R*)-1-Adamantyl

5-(4-chlorophenyl)-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole-2-carboxylate (3h)

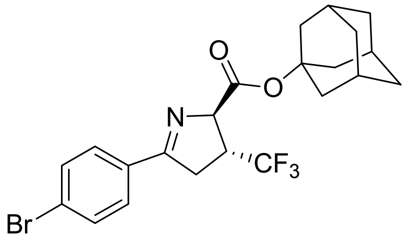


Reaction of **4h** (23.5 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0 mL) at −20 ˚C for 15 h gave (2*R*,3*R*)-**3h** (39.6 mg, 93%, 78% ee) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.68 (s, 6H), 2.17 (s, 9H), 3.12-3.19 (m, 1H), 3.31-3.49 (m, 2H), 4.94 -4.95 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 30.8, 36.0, 36.5 (q, *J* = 2.0 Hz), 41.1, 44.1 (q, *J* = 28.7 Hz), 76.3 (q, *J* = 1.5 Hz), 82.7, 126.8 (q, *J* =

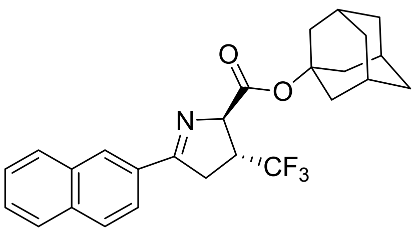
277.7 Hz), 128.8, 129.4, 131.3, 137.6, 169.2, 172.0; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.6 (d, *J* = 8.7 Hz, 3F); IR (neat) 2914, 2855, 1733, 1621, 1598, 1493, 1457, 1402, 1345, 1200, 1117, 1053, 1014, 965, 886, 830, 733, 553 cm^{-1}; MS (ESI, *m/z*) 448 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{22}H_{23}ClF_3NNaO_2$ [$(M+Na)^+$]: 448.1267 Found: 448.1264; 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} = 15.9 min, τ_{min} = 18.7 min); $[\alpha]_D^{25}$ = -37.6 (c = 0.45, $CHCl_3$), 78% ee.

(2*R*,3*R*)-1-Adamantyl
-(4-bromophenyl)-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole-2-carboxylate (3i)



Reaction of **4i** (28.0 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0 mL) at −20 ˚C for 15 h gave (2*R*,3*R*)-**3i** (45.2 mg, 96%, 77% ee) as a colorless oil.
^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 6H), 2.17 (s, 9H), 3.12-3.19 (m, 1H), 3.31-3.49 (m, 2H), 4.93 (brs, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 30.8, 36.0, 36.5 (q, *J* = 1.5 Hz), 41.1, 44.1 (q, *J* = 28.2 Hz), 76.3, 82.7, 126.1, 126.8 (q, *J* = 277.7 Hz), 129.5, 131.7, 131.8, 169.2, 172.1; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.6 (d, *J* = 8.7 Hz, 3F); IR (neat) 2913, 2854, 1733, 1620, 1592, 1488, 1457, 1398, 1333, 1200, 1117, 1053, 1011, 965, 823, 734 cm^{-1}; MS (ESI, *m/z*) 492 [$(M+Na)^+-1$], 494 [$(M+Na)^+ +1$], HRMS (ESI) calcd. for $C_{22}H_{23}BrF_3NNaO_2$ [$(M+Na)^+$]: 492.0762 Found: 492.0751; 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} = 17.6 min, τ_{min} = 21.6 min); $[\alpha]_D^{25}$ = -32.9 (c = 0.91, $CHCl_3$), 77% ee.

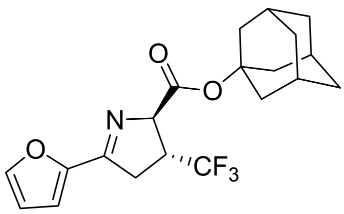
(2*R*,3*R*)-1-Adamantyl
5-(naphthalen-2-yl)-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole-2-carboxylate (3j)



Reaction of **4j** (25.0 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0 mL) at −20 ˚C for 14 h gave (2*R*,3*R*)-**3j** (35.7 mg, 81%, 72% ee) as a white solid.

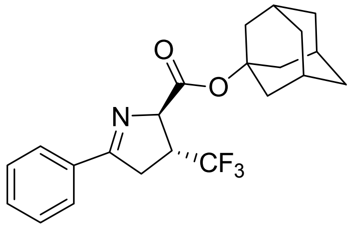
^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.68 (s, 6H), 2.19 (s, 9H), 3.31-3.38 (m, 1H), 3.44-3.57 (m, 2H), 5.01 (brs, 1H), 7.50-7.58 (m, 2H), 7.86-7.91 (m, 3H), 8.09 (d, *J* = 9.0 Hz, 1H), 8.19 (s, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 30.9, 36.1, 36.6, 41.1, 44.1 (q, *J* = 28.2 Hz), 76.4, 82.6, 124.5, 126.6, 126.9 (q, *J* = 277.2 Hz), 127.6, 127.8, 128.3, 128.8, 129.0, 130.4, 132.7, 134.7, 169.4, 173.1; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.5 (d, *J* = 8.7 Hz, 3F); IR (KBr) 2917, 1730, 1611, 1573, 1436, 1396, 1354, 1275, 1244, 1200, 1153, 1112, 1056, 969, 931, 869, 831, 755, 479 cm^{-1}; mp = 148.0-151.0 ºC ($CHCl_3$); MS (ESI, *m/z*) 464 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{26}H_{26}F_3NNaO_2$ [$(M+Na)^+$]: 464.1813 Found: 464.1812; 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} = 18.3 min, τ_{min} = 22.0 min); $[\alpha]_D^{25}$ = -61.4 (c = 0.59, $CHCl_3$), 72% ee.

(2*R*,3*R*)-1-Adamantyl 5-(furan-2-yl)-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole-2-carboxylate (3k)



Reaction of **4k** (19.0 mg, 0.10 mmol), catalyst **6e** (5.8 mg, 0.010 mmol, 10 mol%), glycinate schiff base **5b** (41.1 mg, 0.11 mmol, 1.1 equiv), Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv) in CPME (1.0 mL) at −20 ˚C for 16 h gave **3k** (36.5 mg, 96%, 80% ee) as a colorless oil.

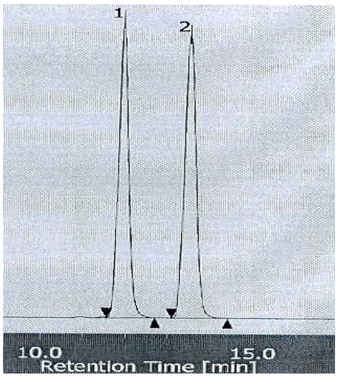
^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 6H), 2.16 (s, 9H), 3.09-3.16 (m, 1H), 3.28-3.46 (m, 2H), 4.92-4.94 (m, 1H), 6.51 (dd, *J* = 1.7, 3.5 Hz, 1H), 6.95 (d, *J* = 3.6 Hz, 1H), 7.56 (d, *J* =1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 30.8, 36.0, 36.4, 41.1, 43.8 (q, *J* = 28.7 Hz), 76.3, 82.6, 111.9, 114.6, 126.7 (q, *J* = 277.2 Hz), 145.4, 148.4, 163.6, 169.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.6 (d, *J* = 9.0 Hz, 3F); IR (neat) 2914, 2855, 1732, 1629, 1483, 1457, 1389, 1330, 1200, 1115, 1053, 965, 912, 885, 734, 595, 498 cm^{-1}; MS (ESI, *m/z*) 405 [$(M+Na)^+$], HRMS (ESI) calcd. for $C_{20}H_{22}F_3NNaO_3$ [$(M+Na)^+$]: 404.1449 Found: 404.1444; The ee of the product was determined by HPLC using an AD-3 column (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, τ_{maj} = 8.7 min, τ_{min} = 4.7 min); $[\alpha]_D^{25}$ = -57.0 (c = 0.82, $CHCl_3$), 80% ee.

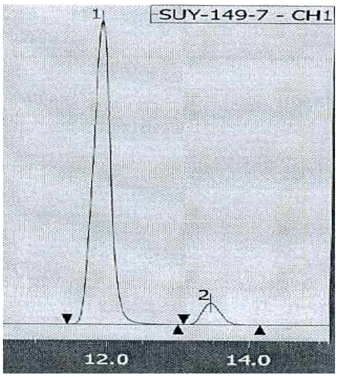


(2*R*,3*R*)-**3b**

HPLC using an AD-3

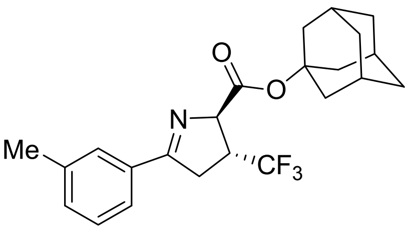
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	11.925	49.845	51.296
2	13.492	50.155	48.704

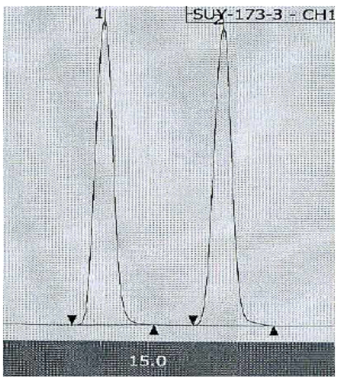
No.	tR (min)	Area (%)	High (%)
1	11.883	93.100	93.443
2	13.450	6.900	6.557

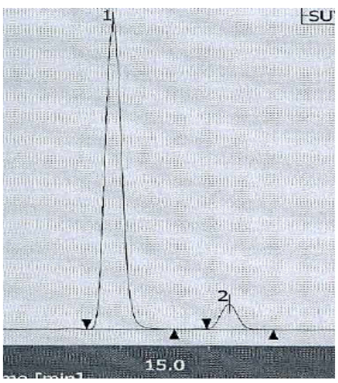


(2*R*,3*R*)-**3c**

HPLC using an AD-3

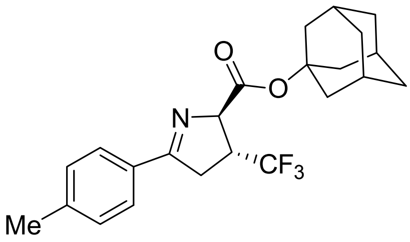
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	14.042	49.838	50.613
2	16.567	50.162	49.387

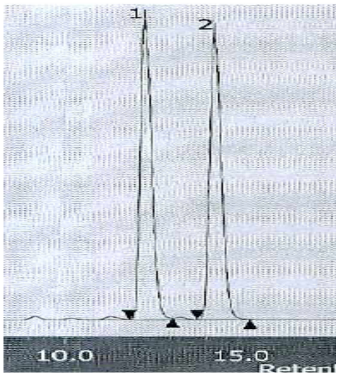
No.	tR (min)	Area (%)	High (%)
1	13.808	92.197	92.522
2	16.458	7.803	7.478

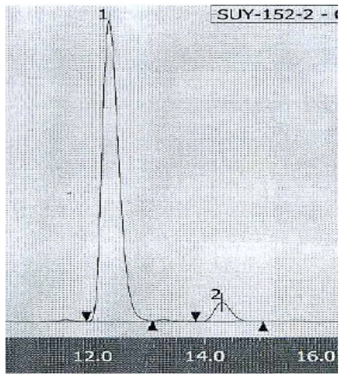


(2*R*,3*R*)-**3d**

HPLC using an AD-3

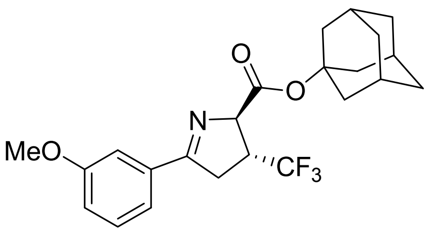
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	12.283	50.027	51.119
2	14.267	49.973	48.881

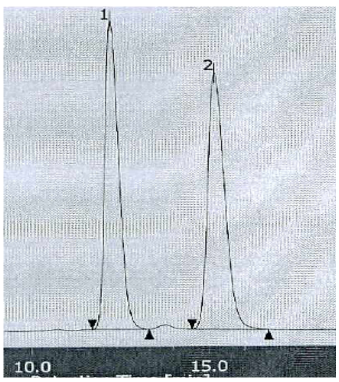
No.	tR (min)	Area (%)	High (%)
1	12.308	93.671	93.917
2	14.308	6.329	6.083

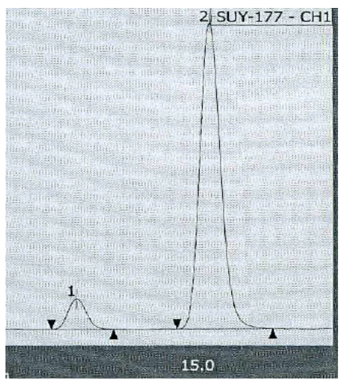


(2*R*,3*R*)-**3e**

HPLC using an OZ-H

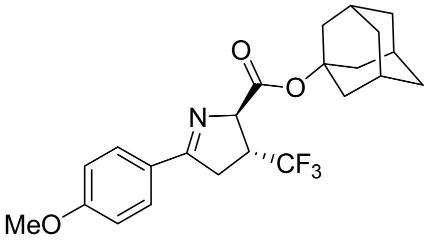
(*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	12.308	49.900	54.616
2	15.225	50.100	45.384

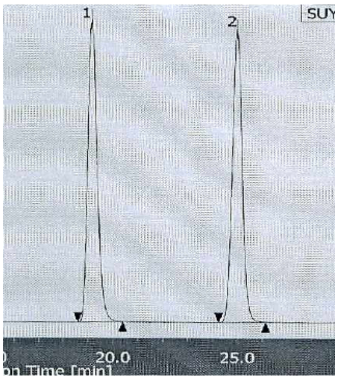
No.	tR (min)	Area (%)	High (%)
1	12.325	7.946	9.075
2	15.267	92.054	90.925

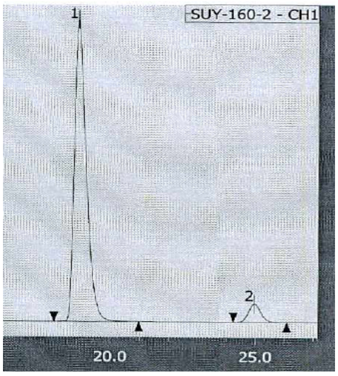


(2*R*,3*R*)-**3f**

HPLC using an AD-3

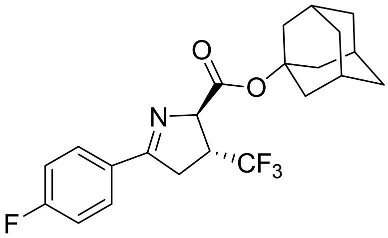
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	19.117	49.924	50.858
2	24.958	50.076	49.142

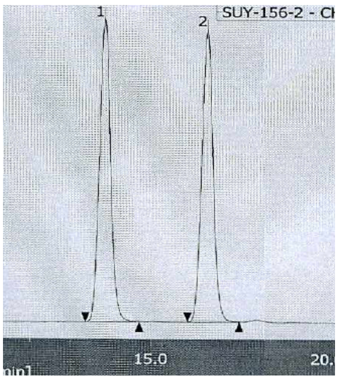
No.	tR (min)	Area (%)	High (%)
1	18.892	94.010	94.294
2	24.950	5.990	5.706

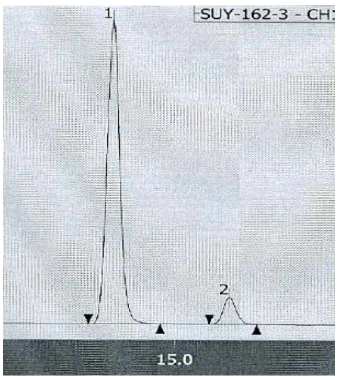


(2*R*,3*R*)-**3g**

HPLC using an AD-3

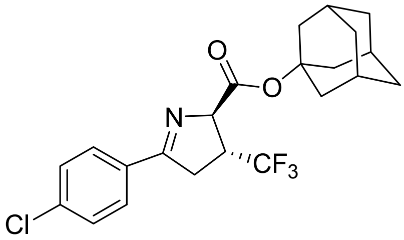
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	13.825	50.214	50.958
2	16.375	49.786	49.042

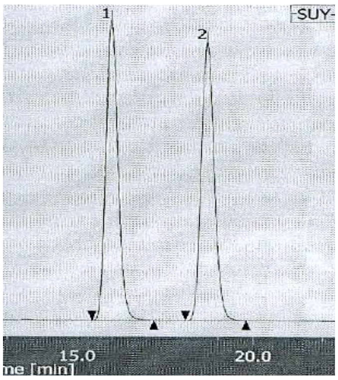
No.	tR (min)	Area (%)	High (%)
1	13.650	91.756	91.831
2	16.158	8.244	8.169

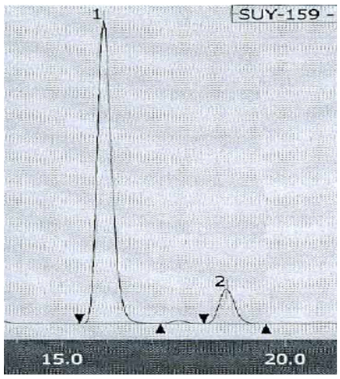


(2*R*,3*R*)-**3h**

HPLC using an AD-3

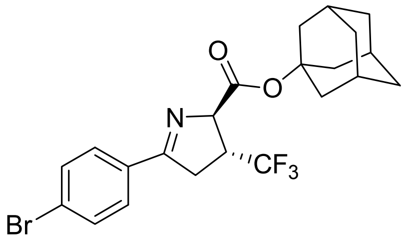
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	15.950	50.031	51.936
2	18.675	49.969	48.064

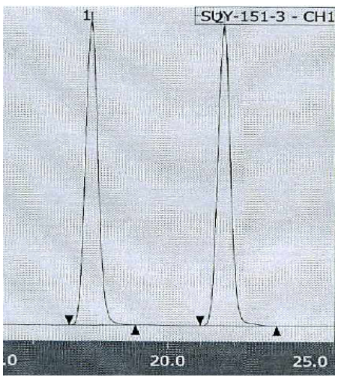
No.	tR (min)	Area (%)	High (%)
1	15.925	89.064	89.768
2	18.667	10.936	10.232

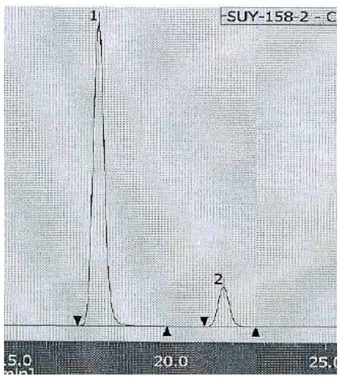


(2*R*,3*R*)-**3i**

HPLC using an AD-H

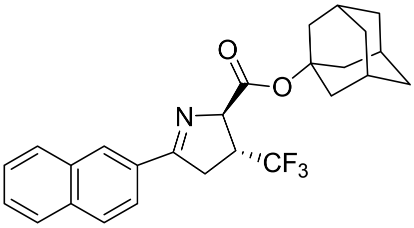
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	17.683	49.761	50.311
2	21.650	50.239	49.689

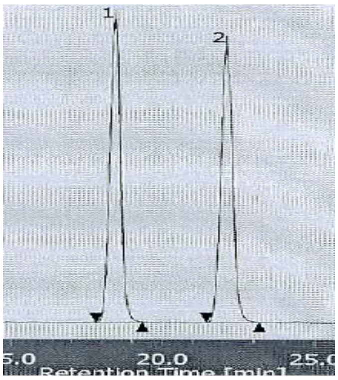
No.	tR (min)	Area (%)	High (%)
1	17.617	88.458	88.545
2	21.658	11.542	11.455

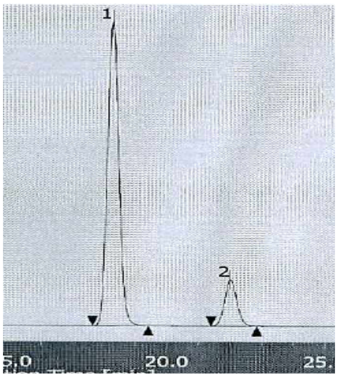


(2*R*,3*R*)-**3j**

HPLC using an AD-3

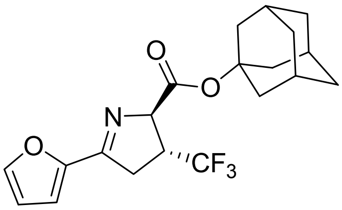
(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5/min, λ = 254 nm)





No.	tR (min)	Area (%)	High (%)
1	18.408	50.003	52.285
2	22.075	49.997	47.715

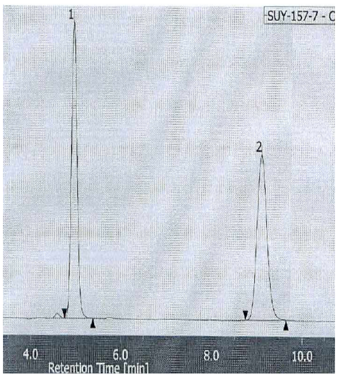
No.	tR (min)	Area (%)	High (%)
1	18.250	85.984	86.832
2	21.992	14.016	13.168

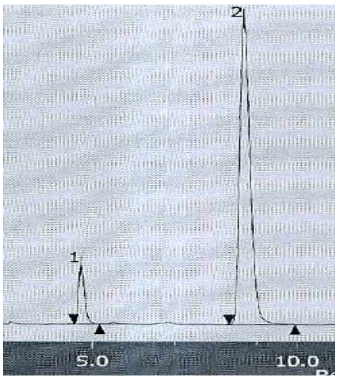


(2*R*,3*R*)-**3k**

HPLC using an OD-3

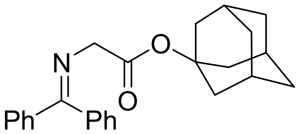
(*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm)





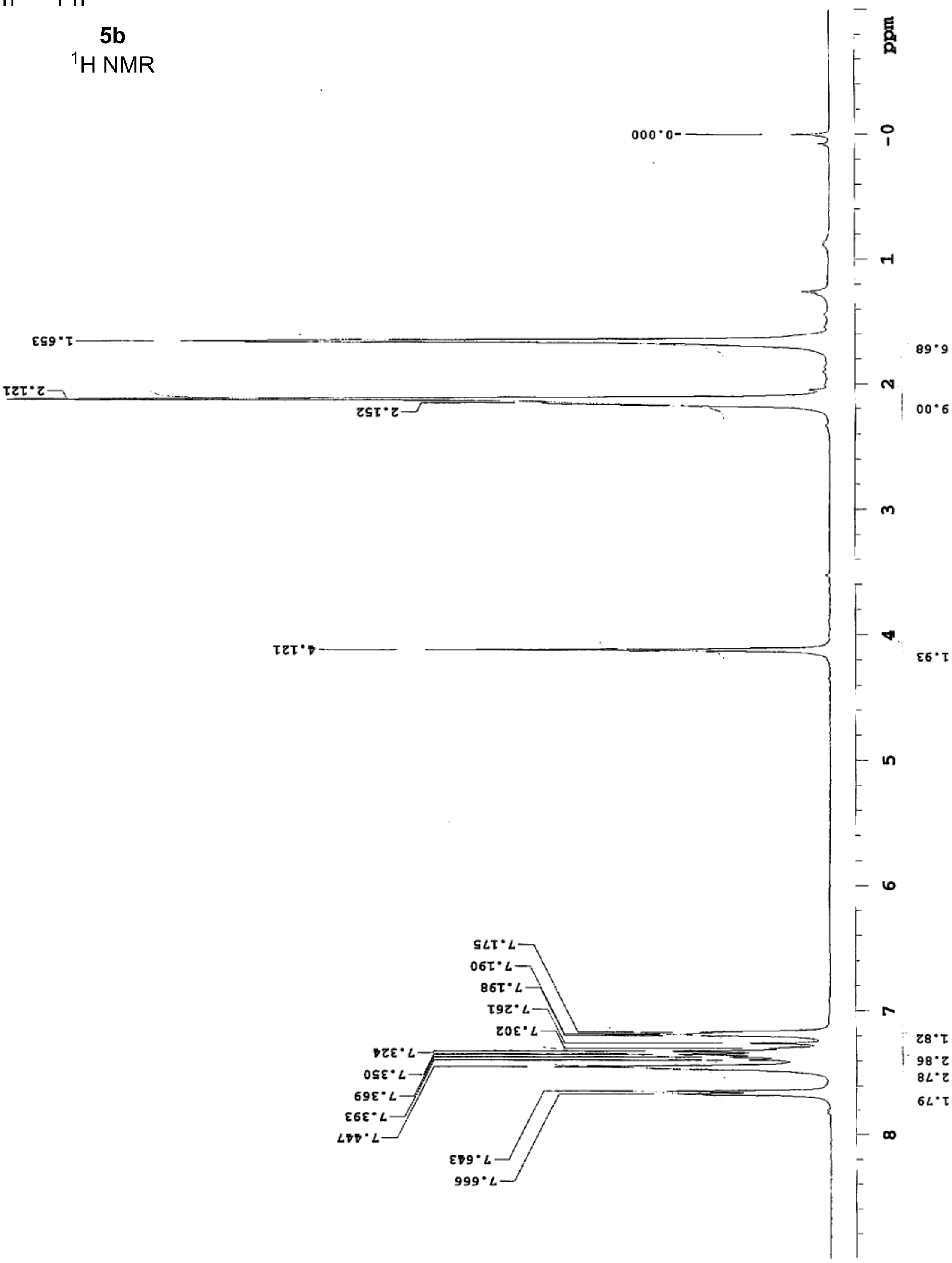
No.	tR (min)	Area (%)	High (%)
1	4.950	50.267	64.283
2	9.100	49.733	35.717

No.	tR (min)	Area (%)	High (%)
1	4.725	10.151	16.088
2	8.692	89.849	83.912



5b

^{1}H NMR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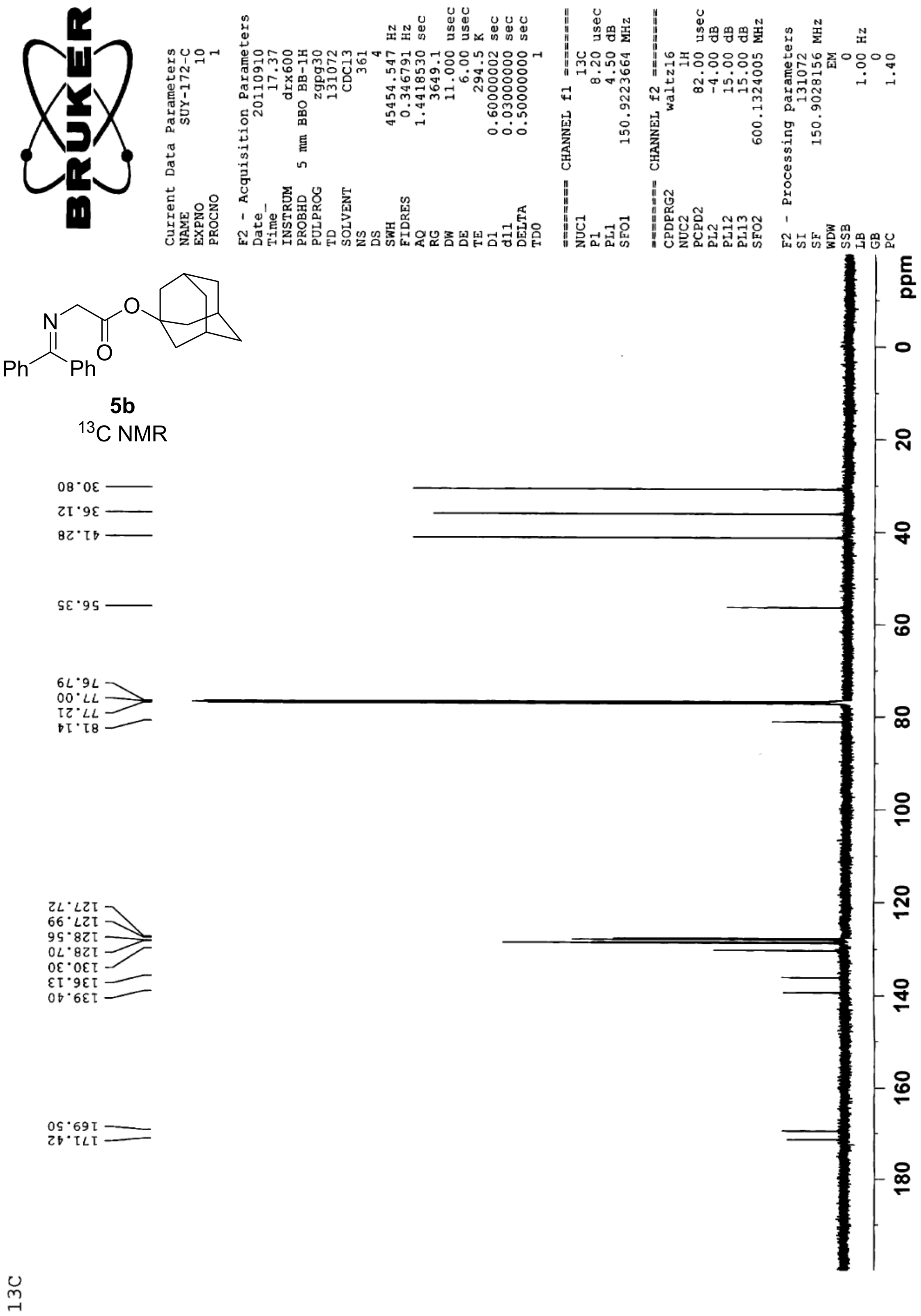
1.79


BRUKER
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PROCNO 1
F2 - Acquisition Parameters
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FIDRES 0.346791 Hz
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DE 6.00 usec
TE 294.5 K
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PL1 4.50 dB
SFO1 150.9223664 MHz
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PL2 -4.00 dB
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PL13 15.00 dB
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F2 - Processing parameters
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Ph
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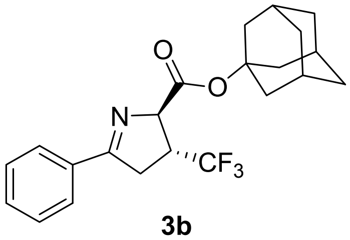
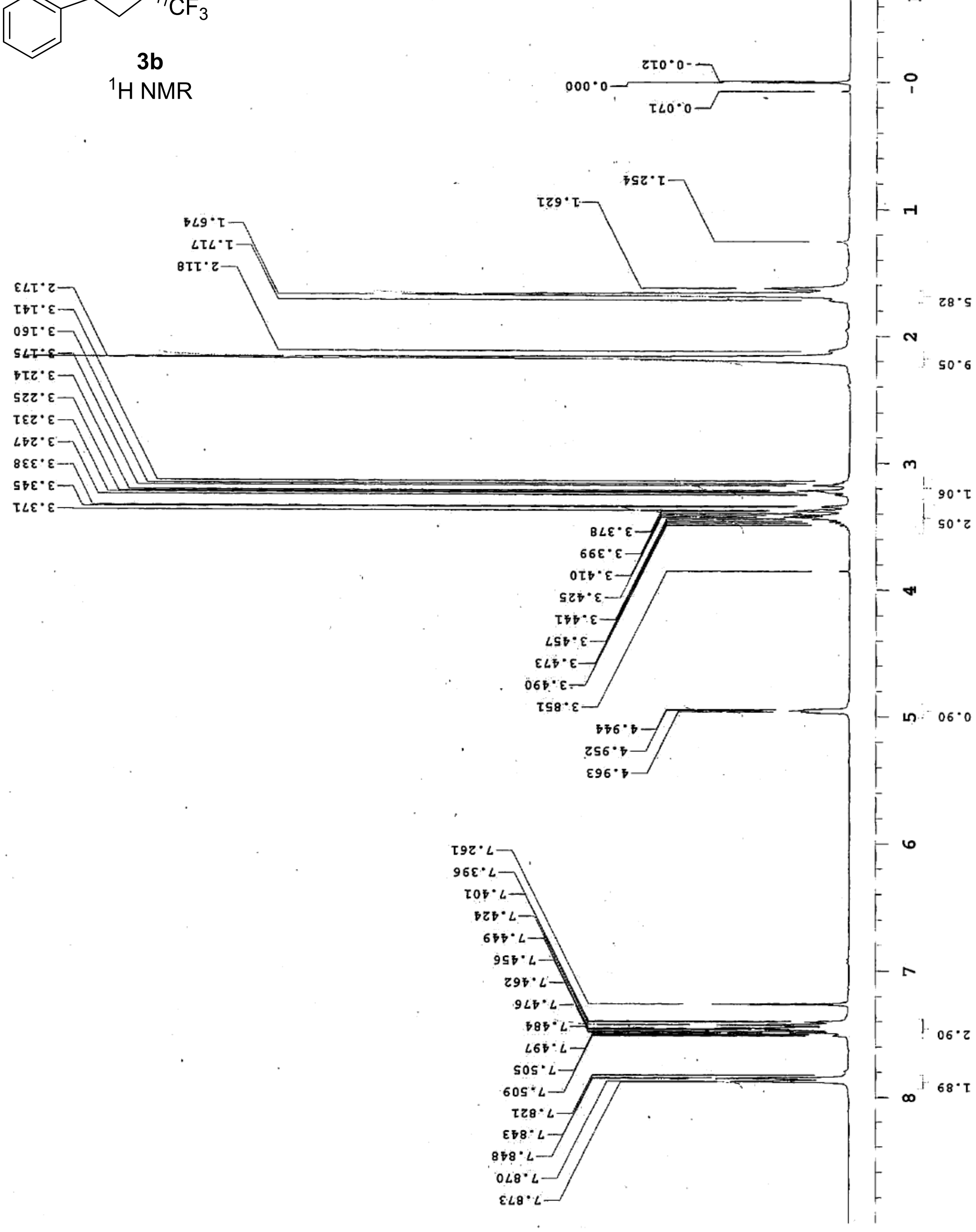
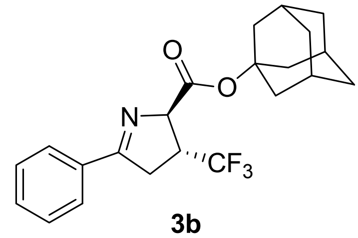


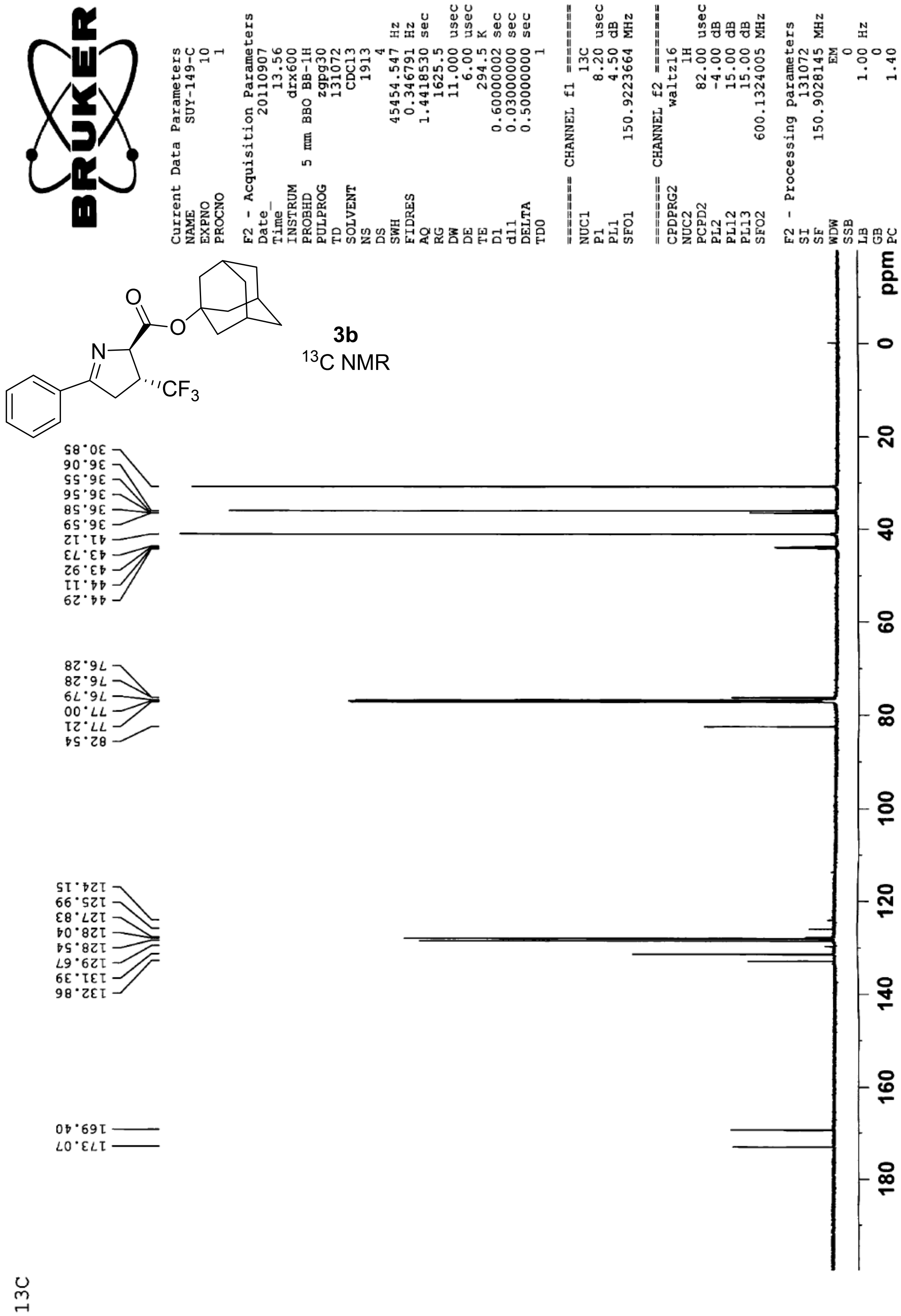
3b

^{1}H NMR





3b
^{19}F NMR


3b
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DE 6.00 usec
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PL1 4.50 dB
SFO1 150.9223664 MHz
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PCPD2 82.00 usec
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PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
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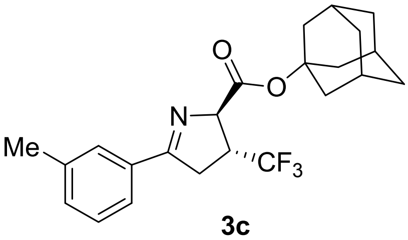
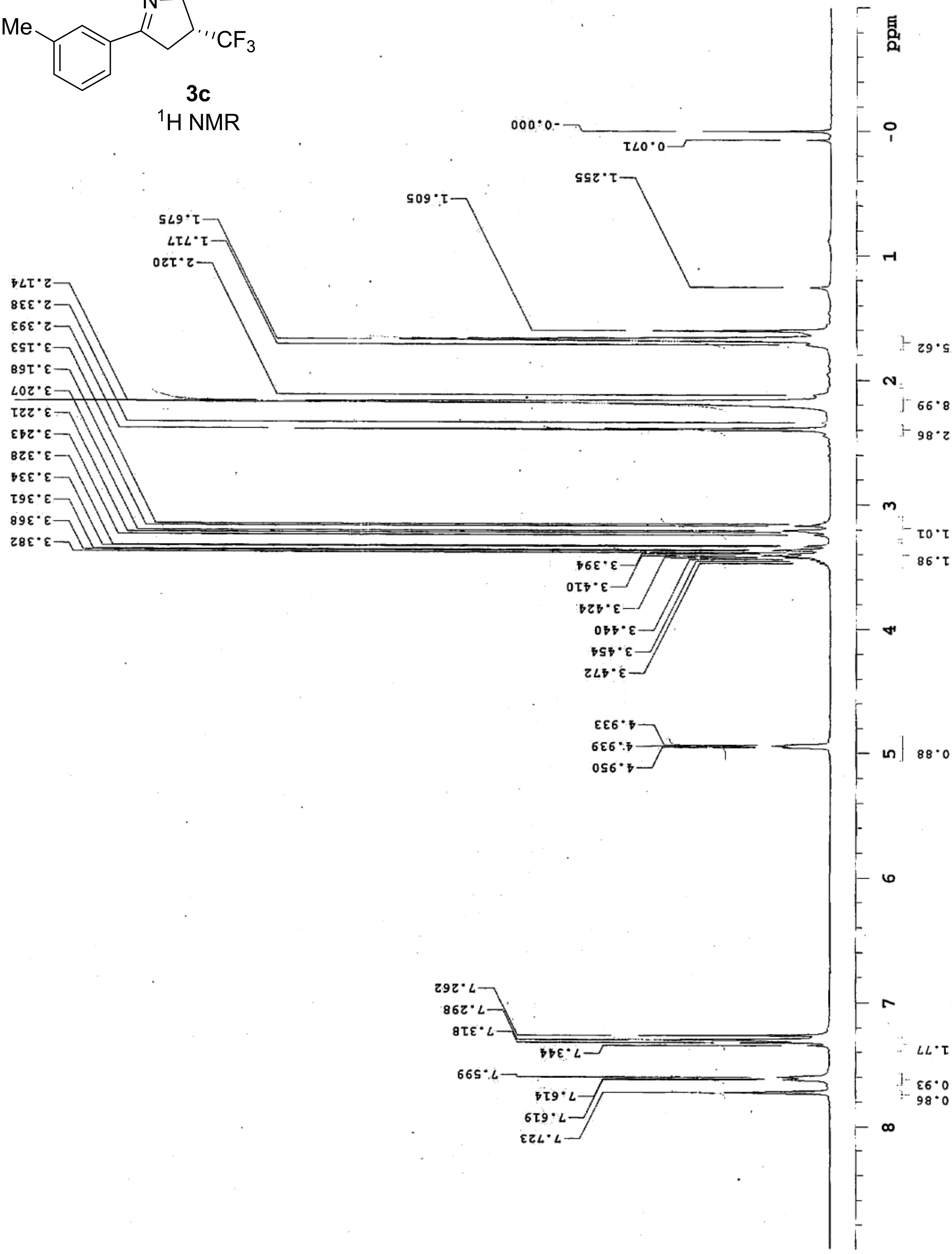
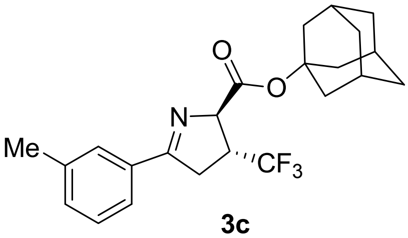
180
13C



3c

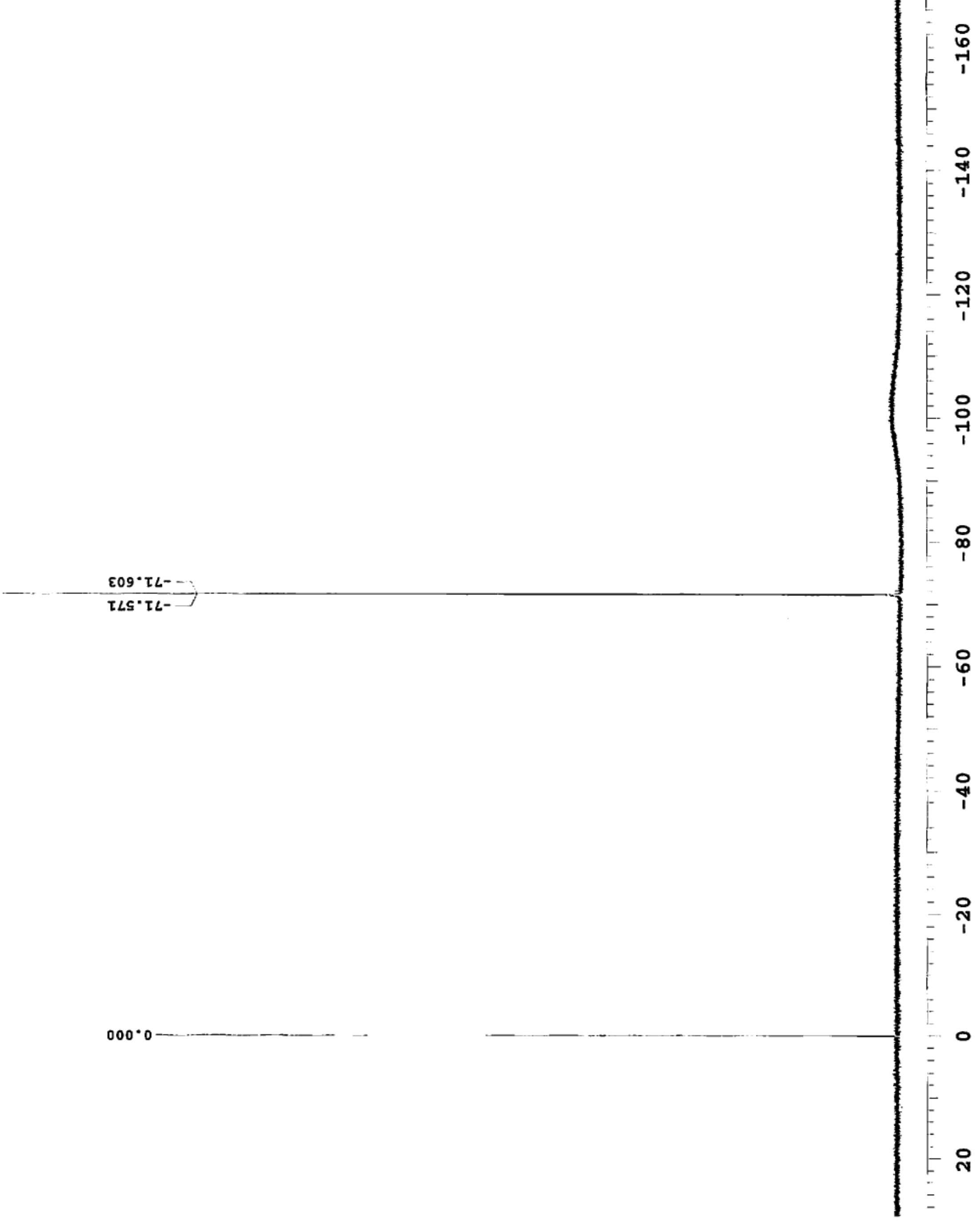
^{1}H NMR




Me
N
O
O
CF3

3c

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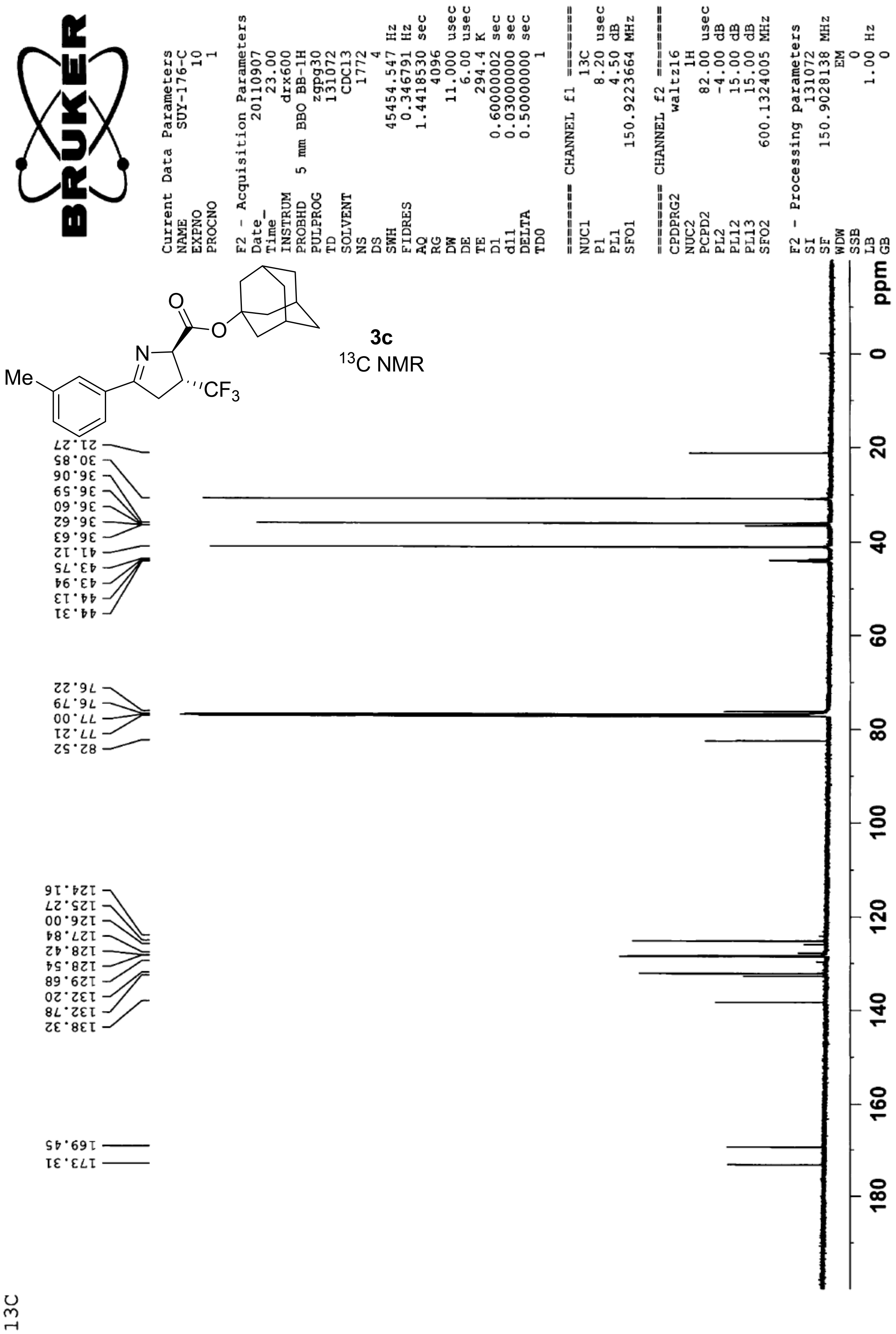
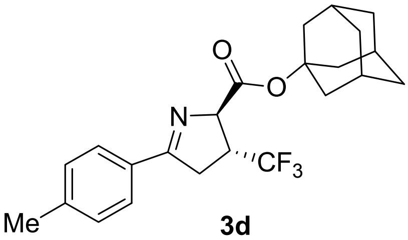
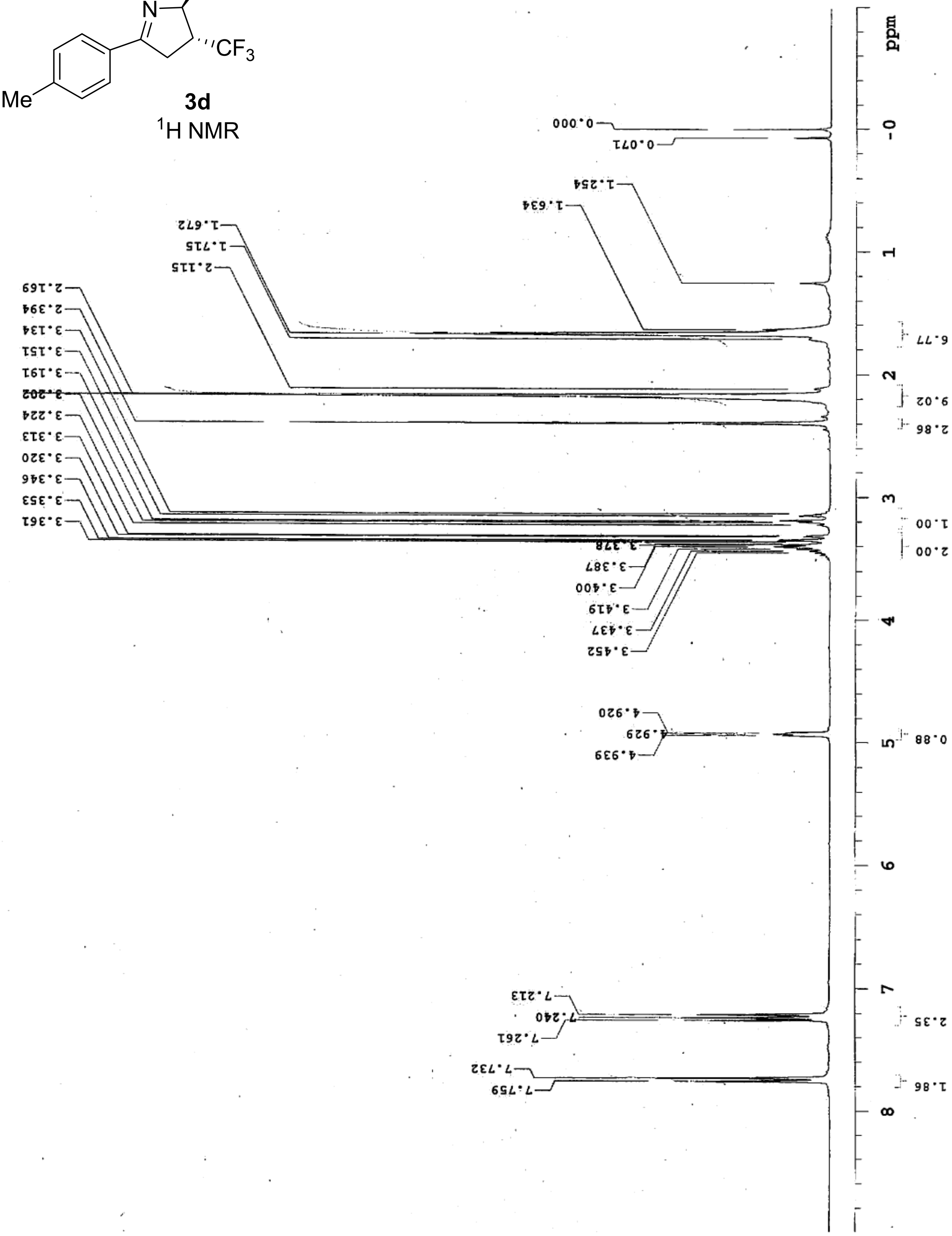
0.000
ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20


3c
^{13}C NMR
Me
N
O
CF3
Current Data Parameters
NAME SUY-176-C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110907
Time 23.00
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1772
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 4096
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 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028138 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
21.27
30.85
36.06
36.59
36.60
36.62
36.63
41.12
43.75
43.94
44.13
44.31
76.22
76.79
77.00
77.21
82.52
124.16
125.27
126.00
127.84
128.42
128.54
129.68
132.20
132.78
138.32
169.45
173.31
ppm
13C


O
O
N
CF3
Me

3d

^{1}H NMR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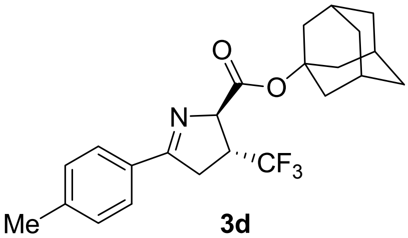
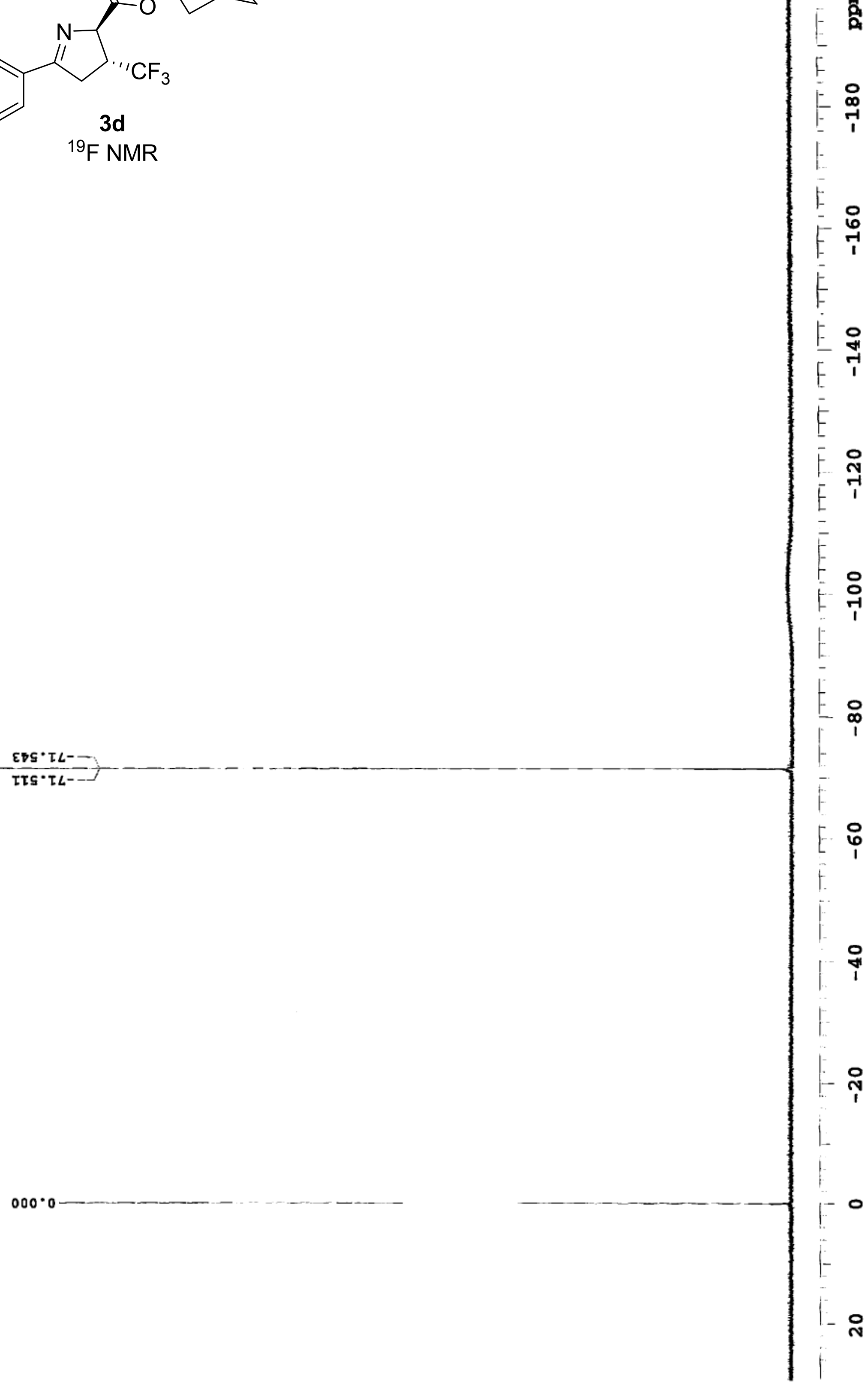
0.071
1.254
1.634
1.672
1.715
2.115
2.169
2.394
3.134
3.151
3.191
3.202
3.224
3.313
3.320
3.346
3.353
3.361
3.378
3.387
3.400
3.419
3.437
3.452
4.920
4.929
4.939
7.213
7.240
7.261
7.732
7.759
ppm
-0
1
2
3
4
5
6
7
8
6.77
9.02
2.86
1.00
2.00
0.88
2.35
1.86


O
O
N
CF3
Me

3d

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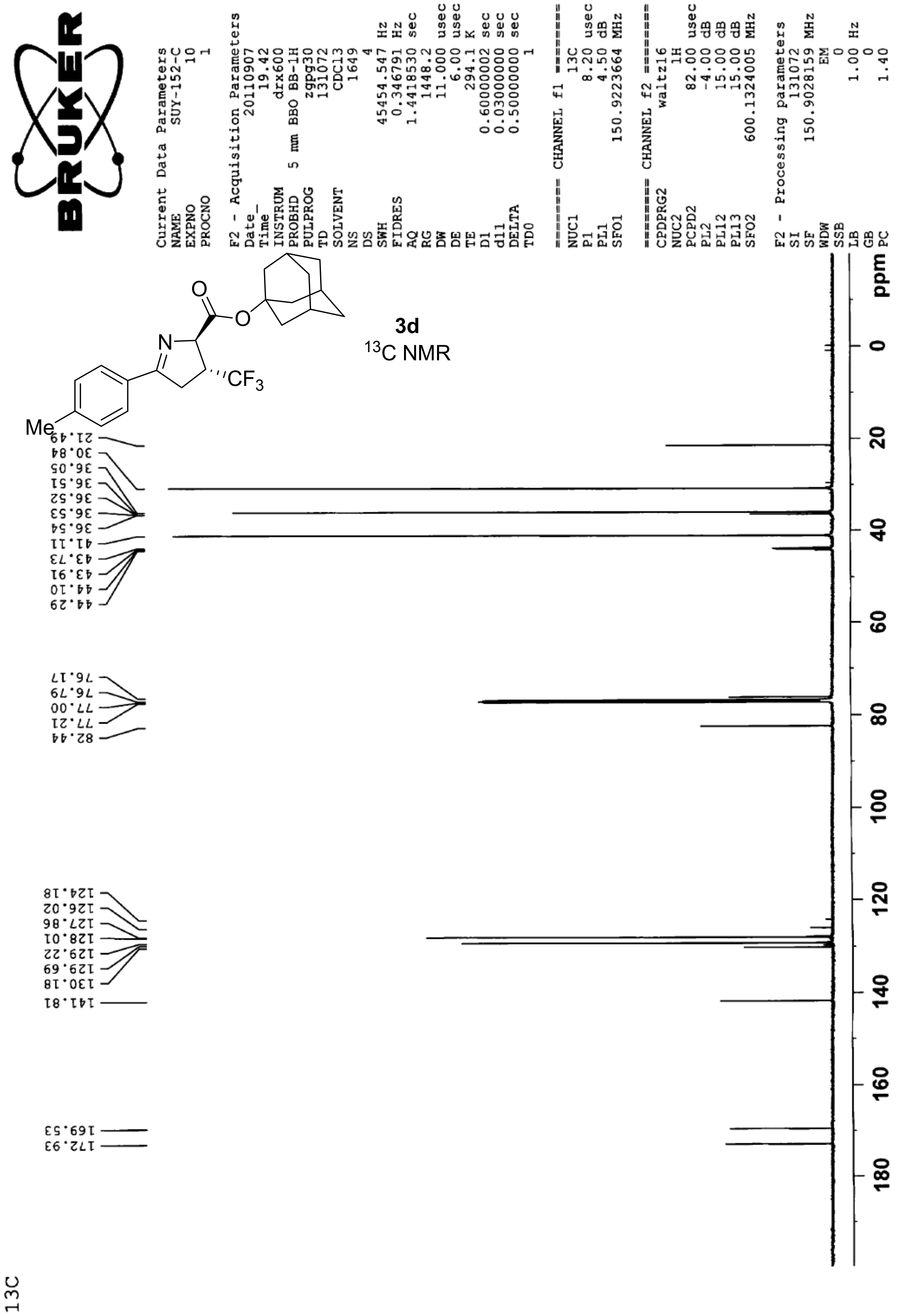
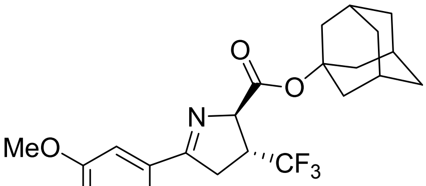
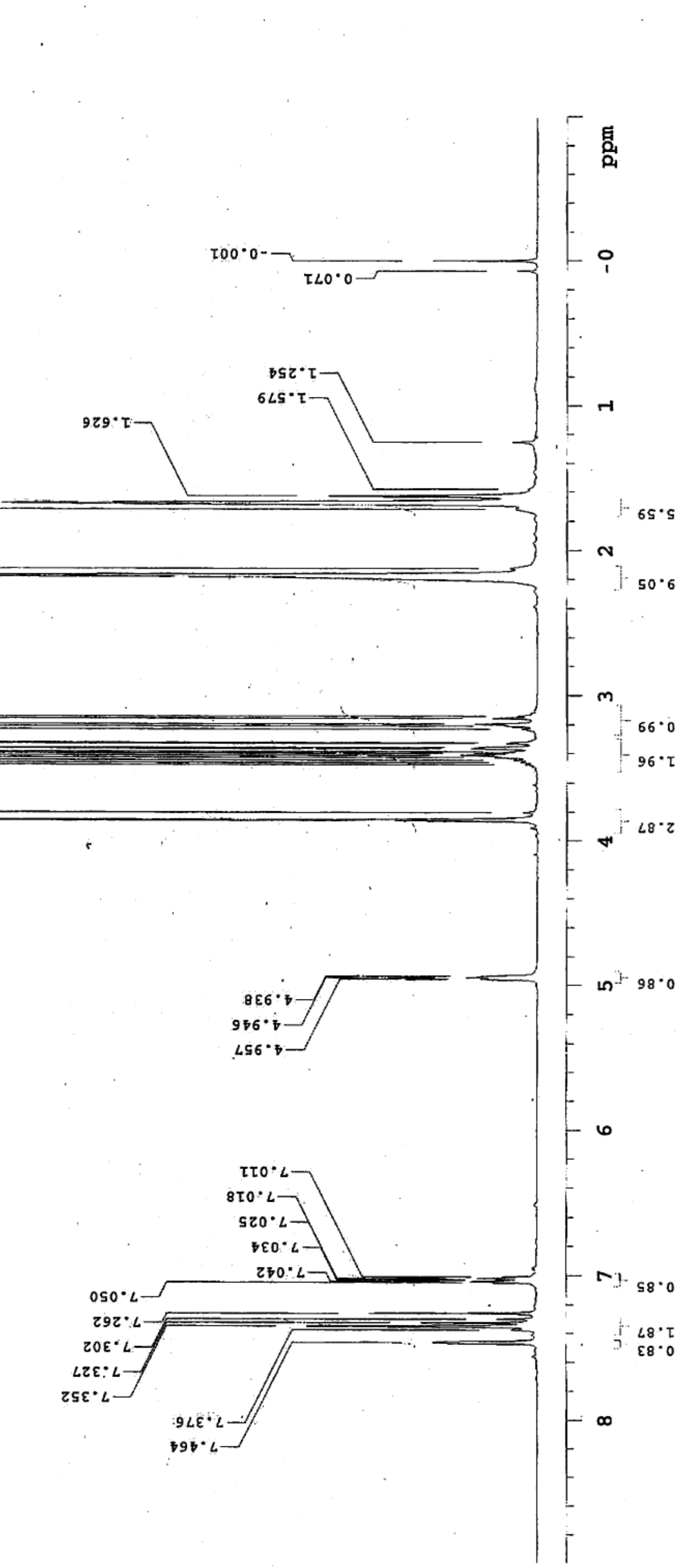
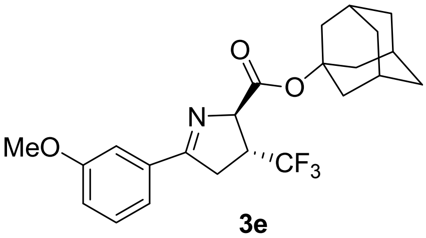
-160
-140
-120
-100
-80
-60
-40
-20
0
20


3d
13C NMR
Current Data Parameters
NAME SUY-152-C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110907
Time 19.42
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1649
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 294.1 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 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
21.49
30.84
36.05
36.51
36.52
36.53
36.54
41.11
43.73
43.91
44.10
44.29
76.17
76.79
77.00
77.21
82.44
124.18
126.02
127.86
128.01
129.22
129.69
130.18
141.81
169.53
172.93
ppm
13C



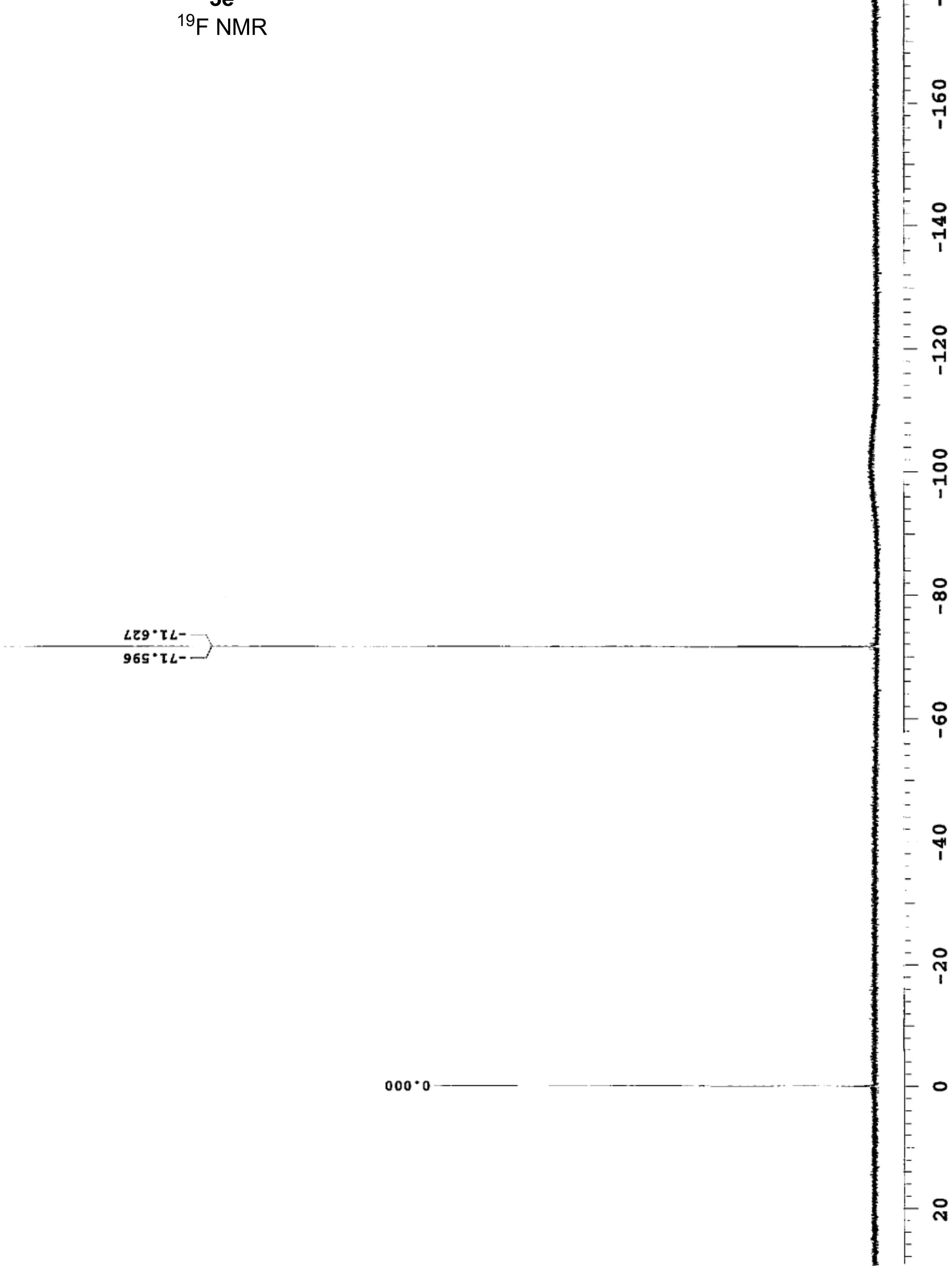
3e
^{1}H NMR

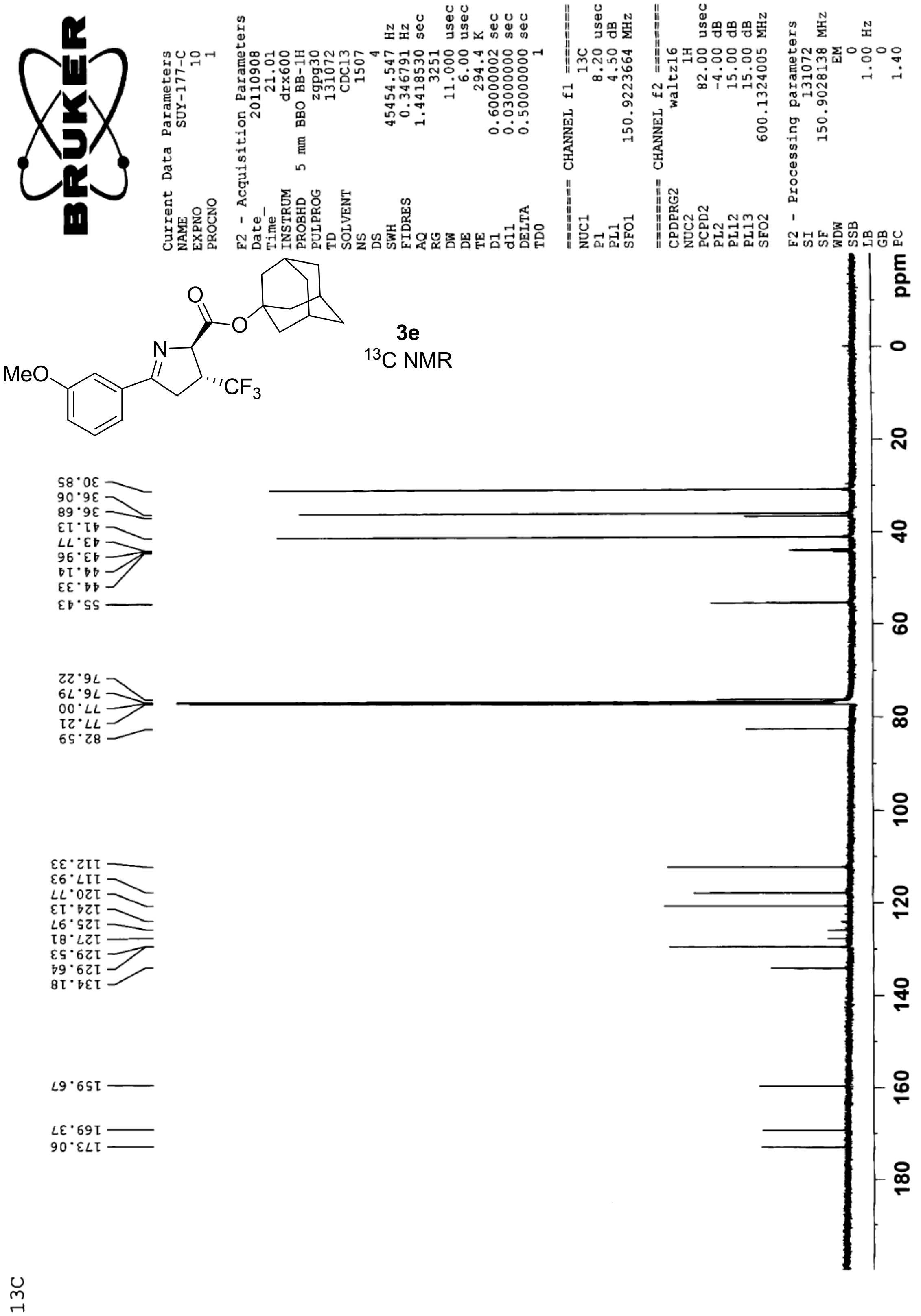


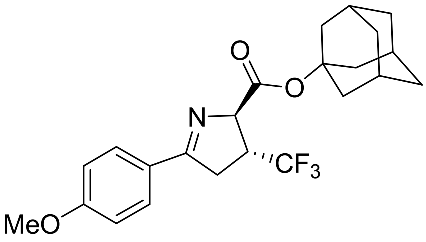

MeO
N
O
O
CF3

3e

^{19}F NMR

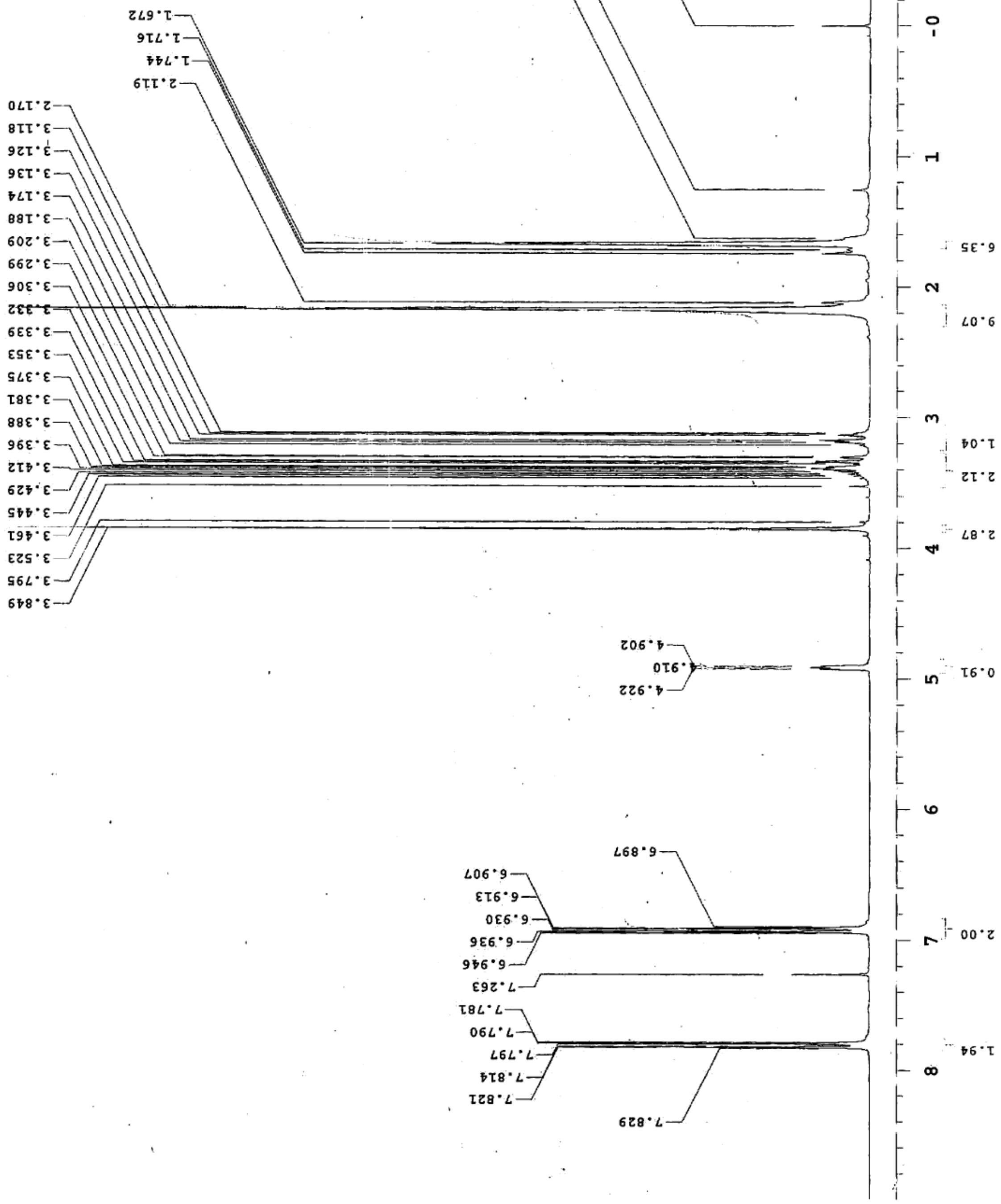

-71.627
-71.596
0.000
ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20


3e
^{13}C NMR
MeO
N
O
CF$_3$
Current Data Parameters
NAME SUY-177-C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110908
Time 21.01
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1507
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 3251
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 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 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
30.85
36.06
36.68
41.13
43.77
43.96
44.14
44.33
55.43
76.22
76.79
77.00
77.21
82.59
112.33
117.93
120.77
124.13
125.97
127.81
129.53
129.64
134.18
159.67
169.37
173.06
ppm
0
20
40
60
80
100
120
140
160
180
13C


O
O
N
CF3
MeO

3f

^{1}H NMR


ppm
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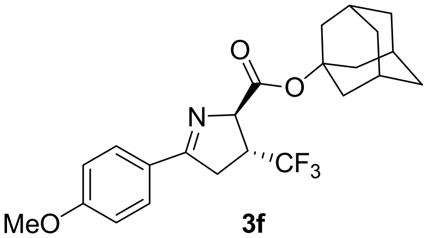
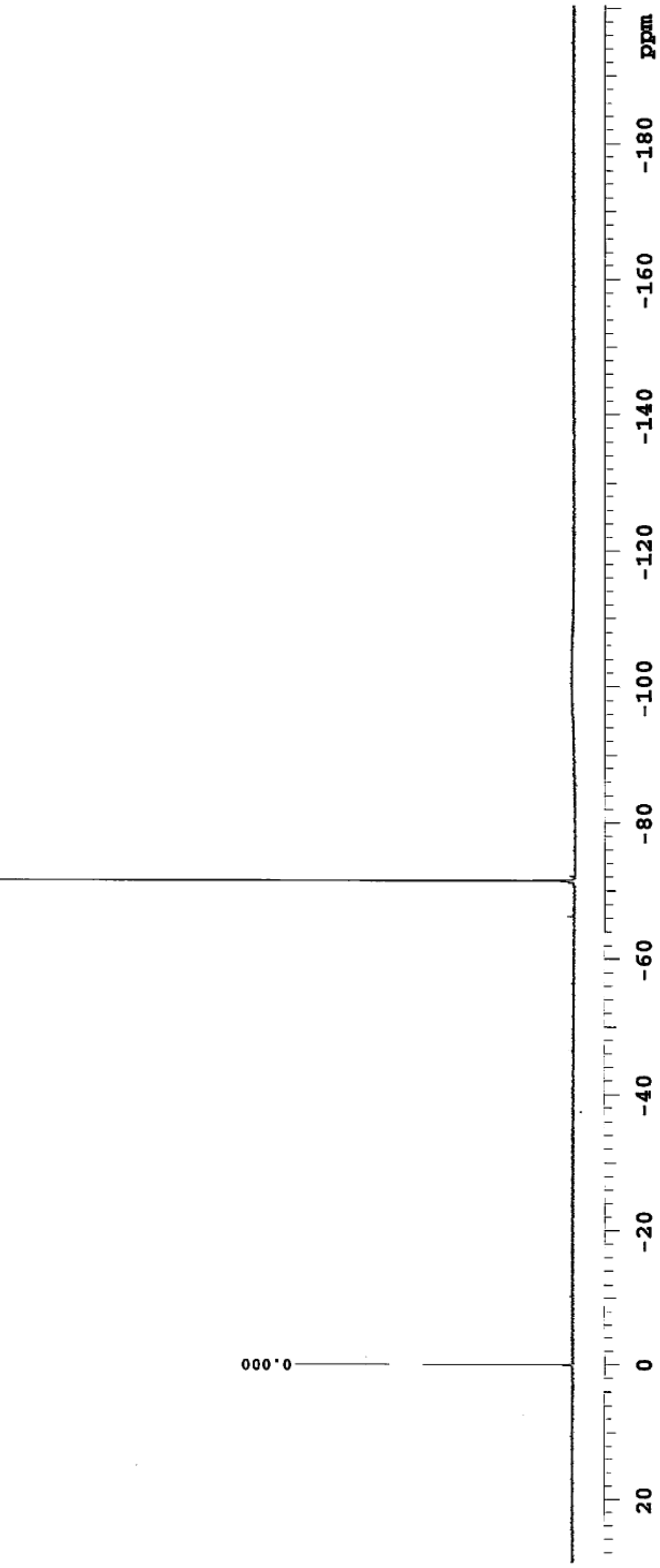
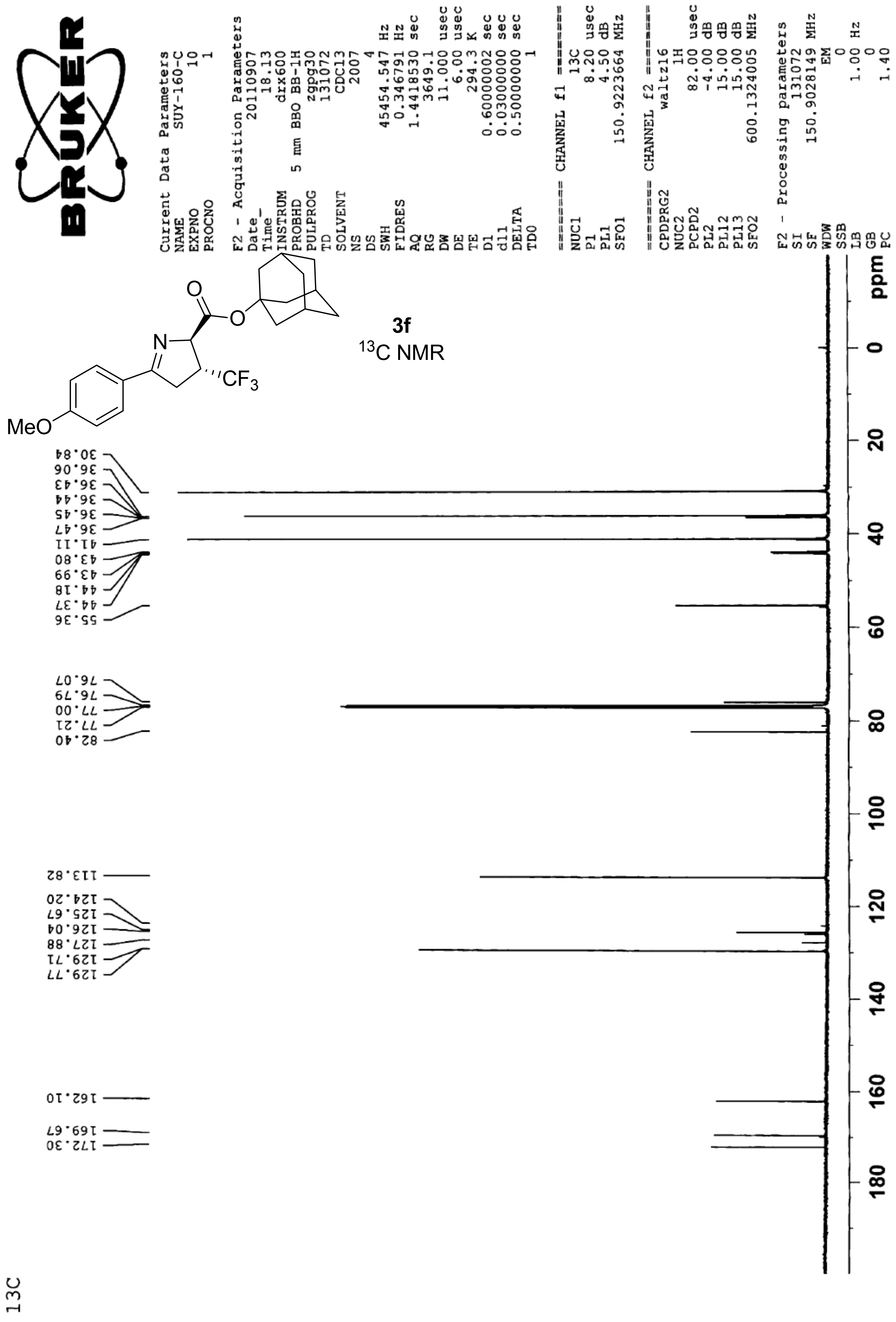
2
3
4
5
6
7
8
0.000
1.255
1.627
1.672
1.716
1.744
2.119
2.170
3.118
3.126
3.136
3.174
3.188
3.209
3.299
3.306
3.332
3.339
3.353
3.375
3.381
3.388
3.396
3.412
3.429
3.445
3.461
3.523
3.795
3.849
4.902
4.910
4.922
6.897
6.907
6.913
6.930
6.936
6.946
7.263
7.781
7.790
7.797
7.814
7.821
7.829
6.35
9.07
1.04
2.12
2.87
0.91
2.00
1.94

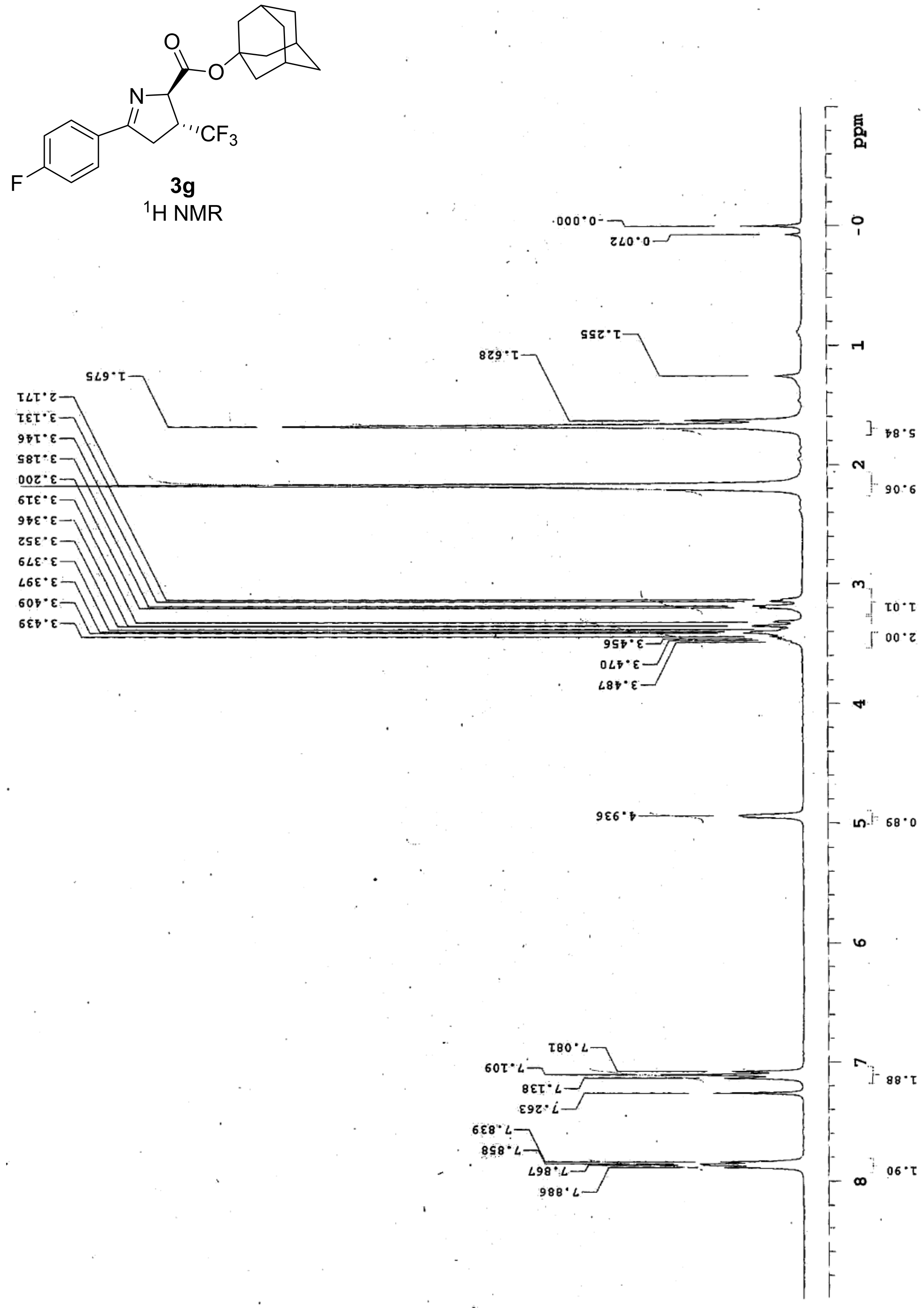

O
O
N
CF3
MeO

3f

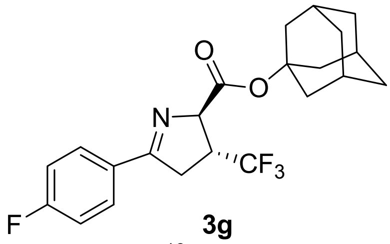
^{19}F NMR


-71.515
-71.483
0.000
ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20

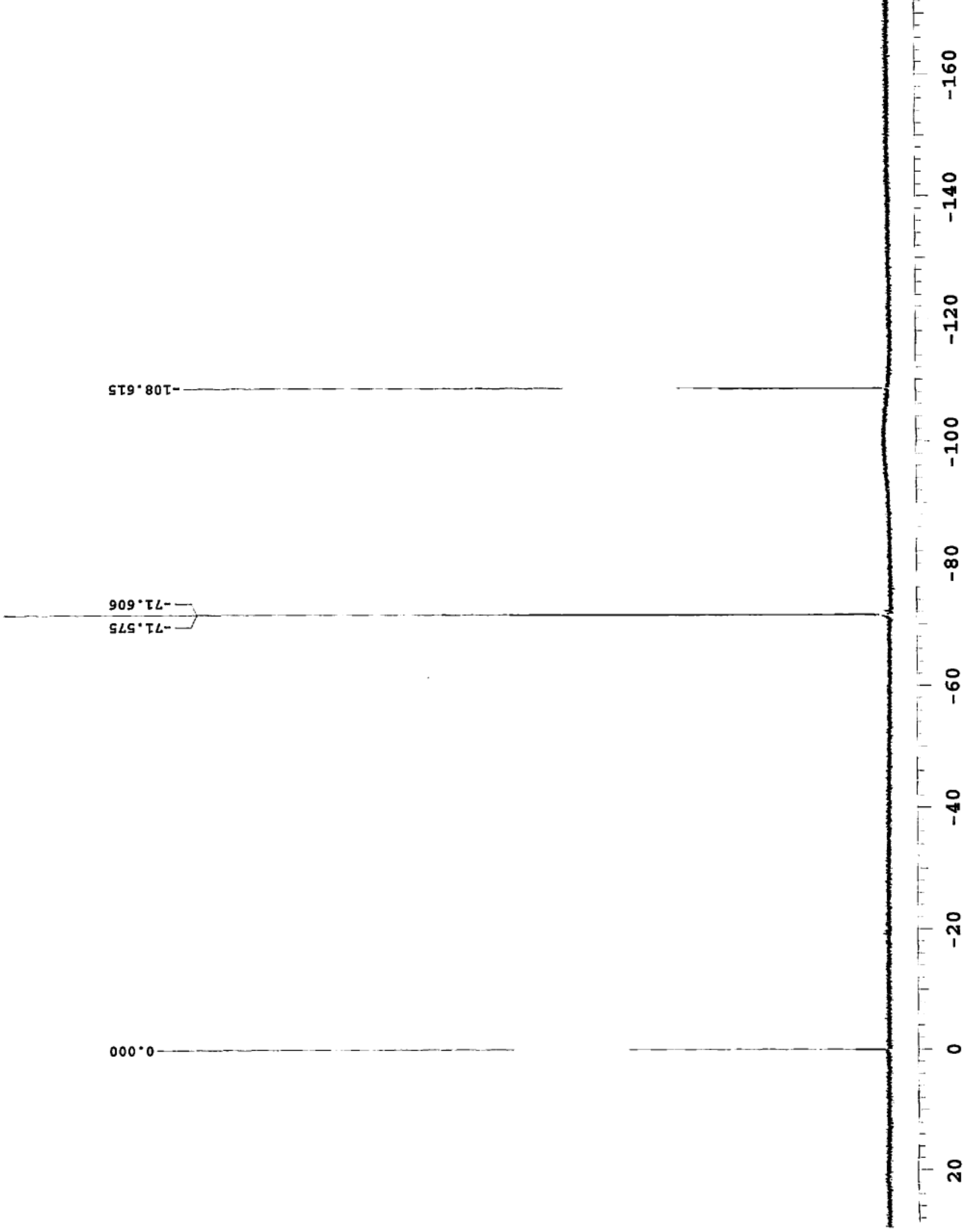

3f
13C NMR
MeO
N
O
CF3
Current Data Parameters
NAME SUY-160-C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110907
Time_ 18.13
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 2007
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 3649.1
DW 11.000 usec
DE 6.00 usec
TE 294.3 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028149 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
30.84
36.06
36.43
36.44
36.45
36.47
41.11
43.80
43.99
44.18
44.37
55.36
76.07
76.79
77.00
77.21
82.40
113.82
124.20
125.67
126.04
127.88
129.71
129.77
162.10
169.67
172.30
ppm
0
20
40
60
80
100
120
140
160
180
13C

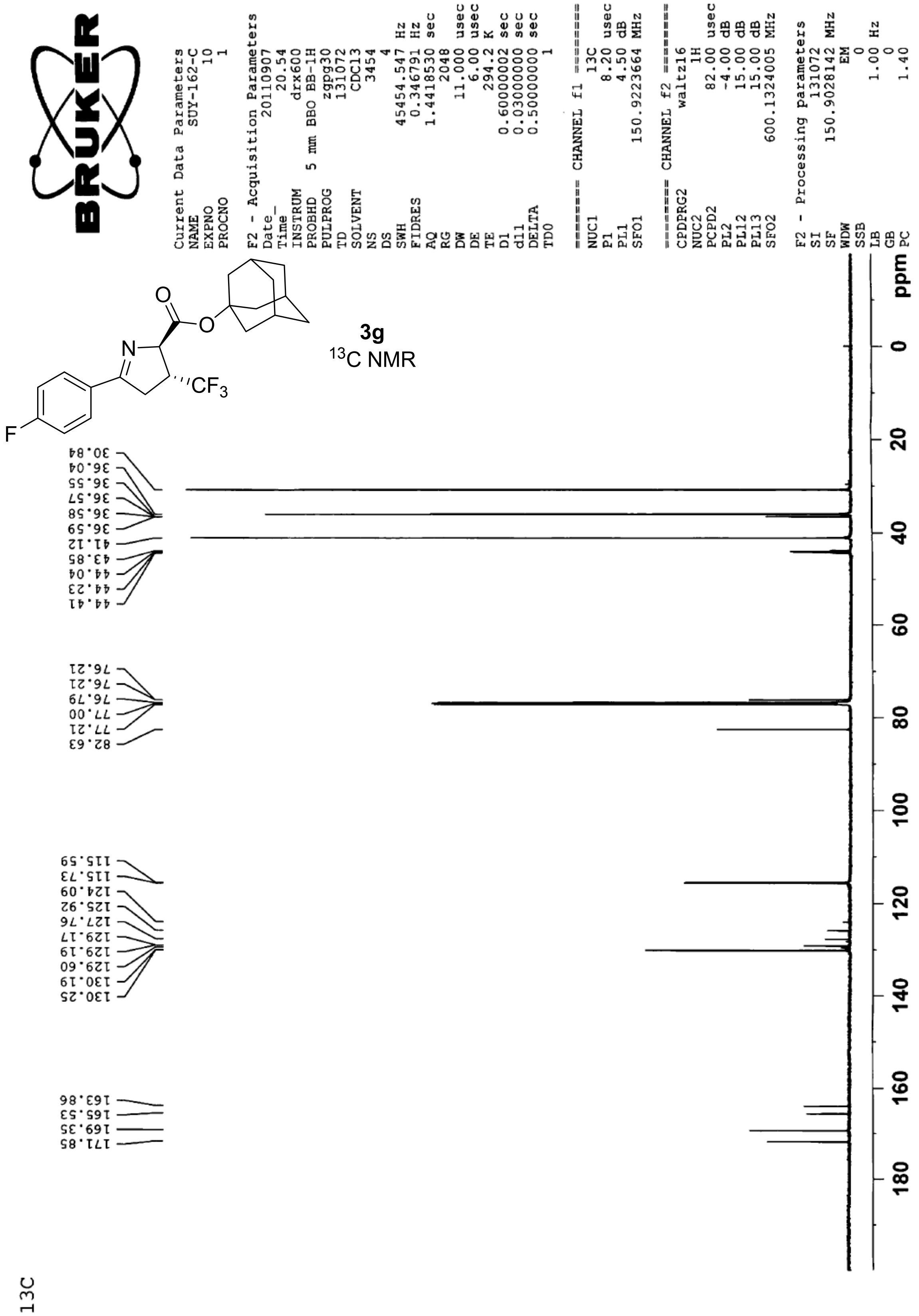


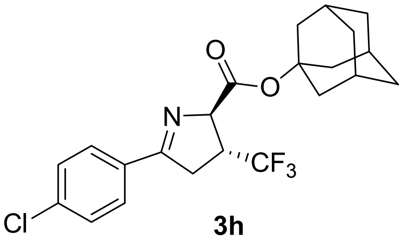
3g
^{1}H NMR


O
O
N
CF3
F

3g
^{19}F NMR

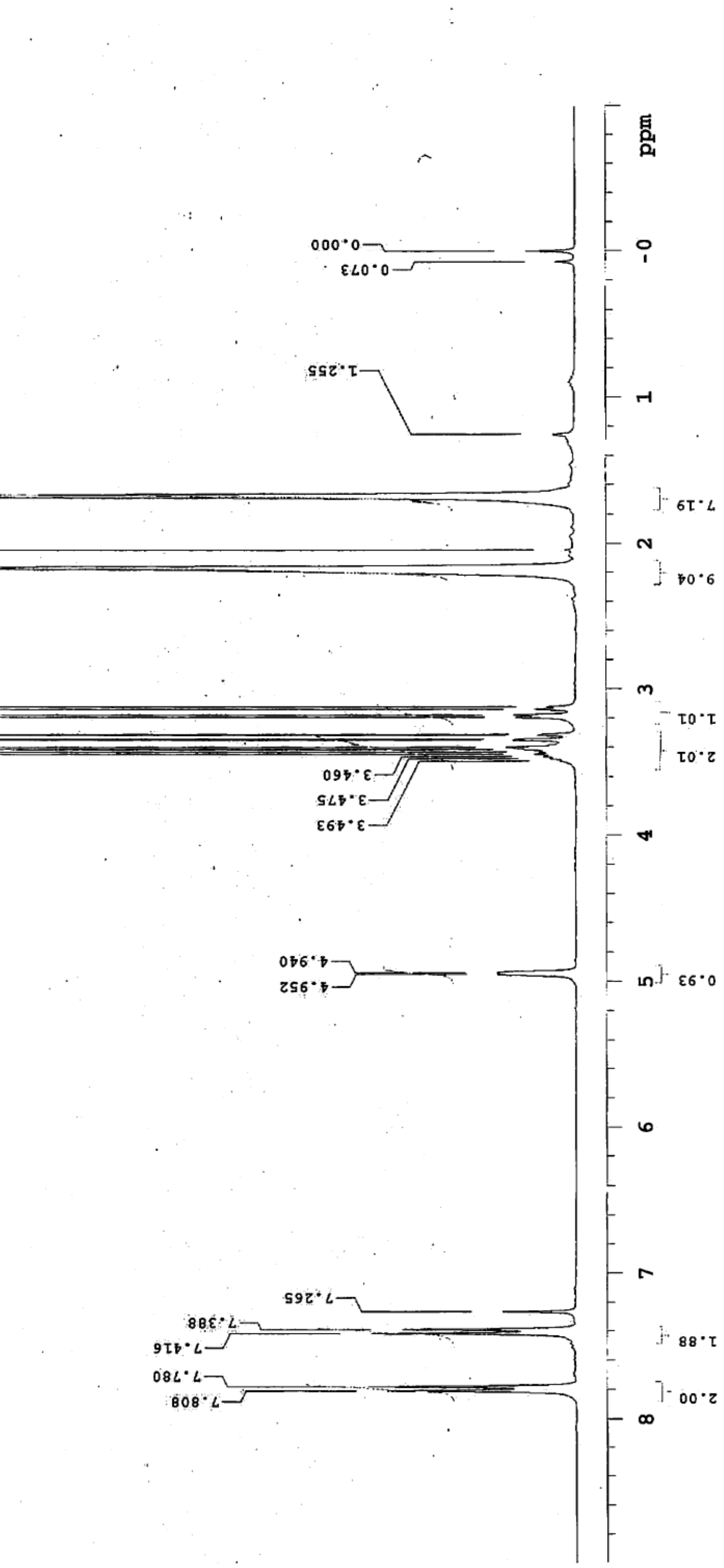

-108.615
-71.606
-71.575
0.000
ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20

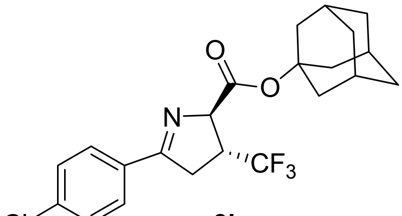

Current Data Parameters
NAME SUY-162-C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110907
Time 20.54
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 3454
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 2048
DW 11.000 usec
DE 6.00 usec
TE 294.2 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028142 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
3g
13C NMR
F
N
O
O
CF3
30.84
36.04
36.55
36.57
36.58
36.59
41.12
43.85
44.04
44.23
44.41
76.21
76.21
76.79
77.00
77.21
82.63
115.59
115.73
124.09
125.92
127.76
129.17
129.19
129.60
130.19
130.25
163.86
165.53
169.35
171.85
ppm
0
20
40
60
80
100
120
140
160
180
13C



3h

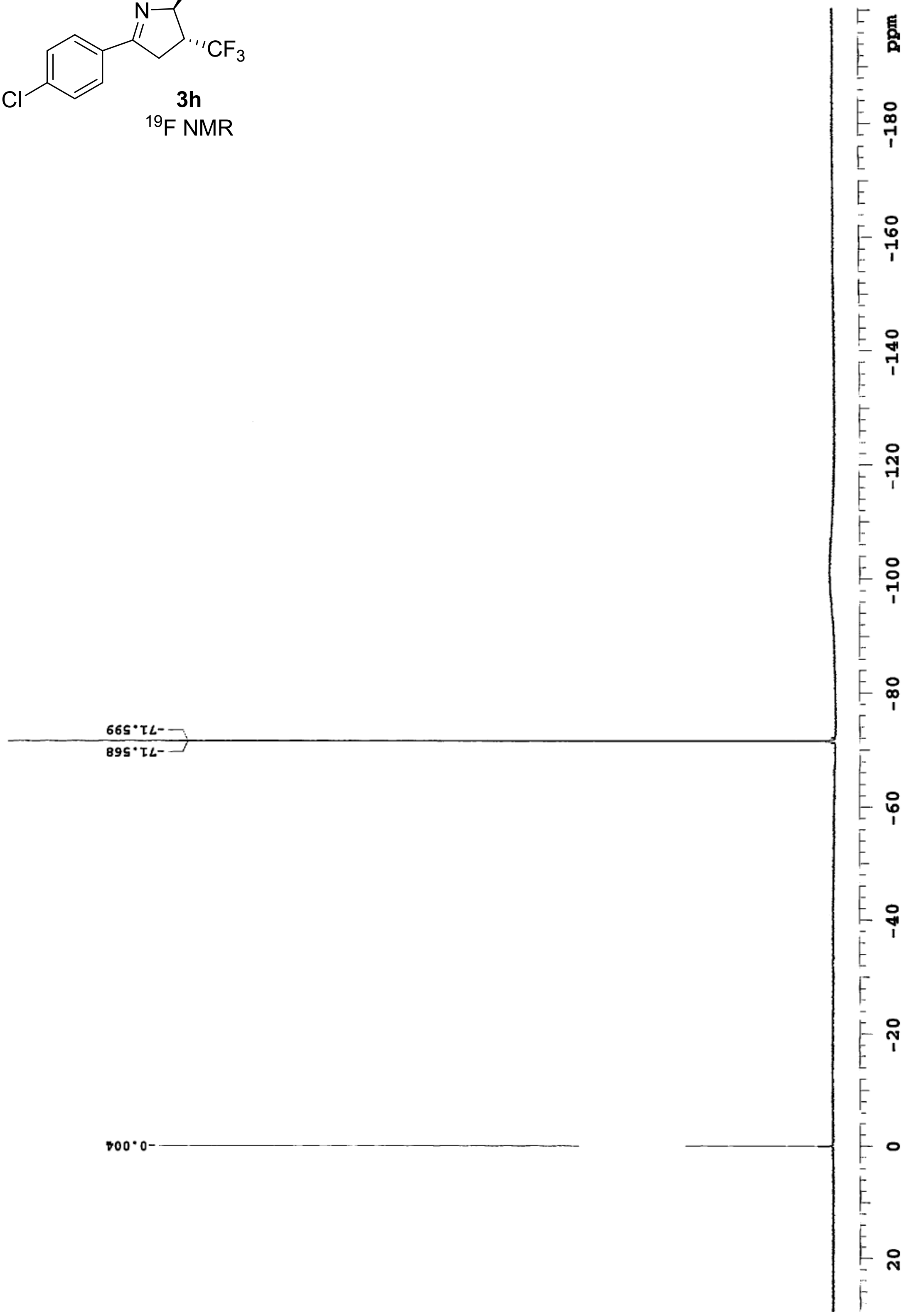
^{1}H NMR

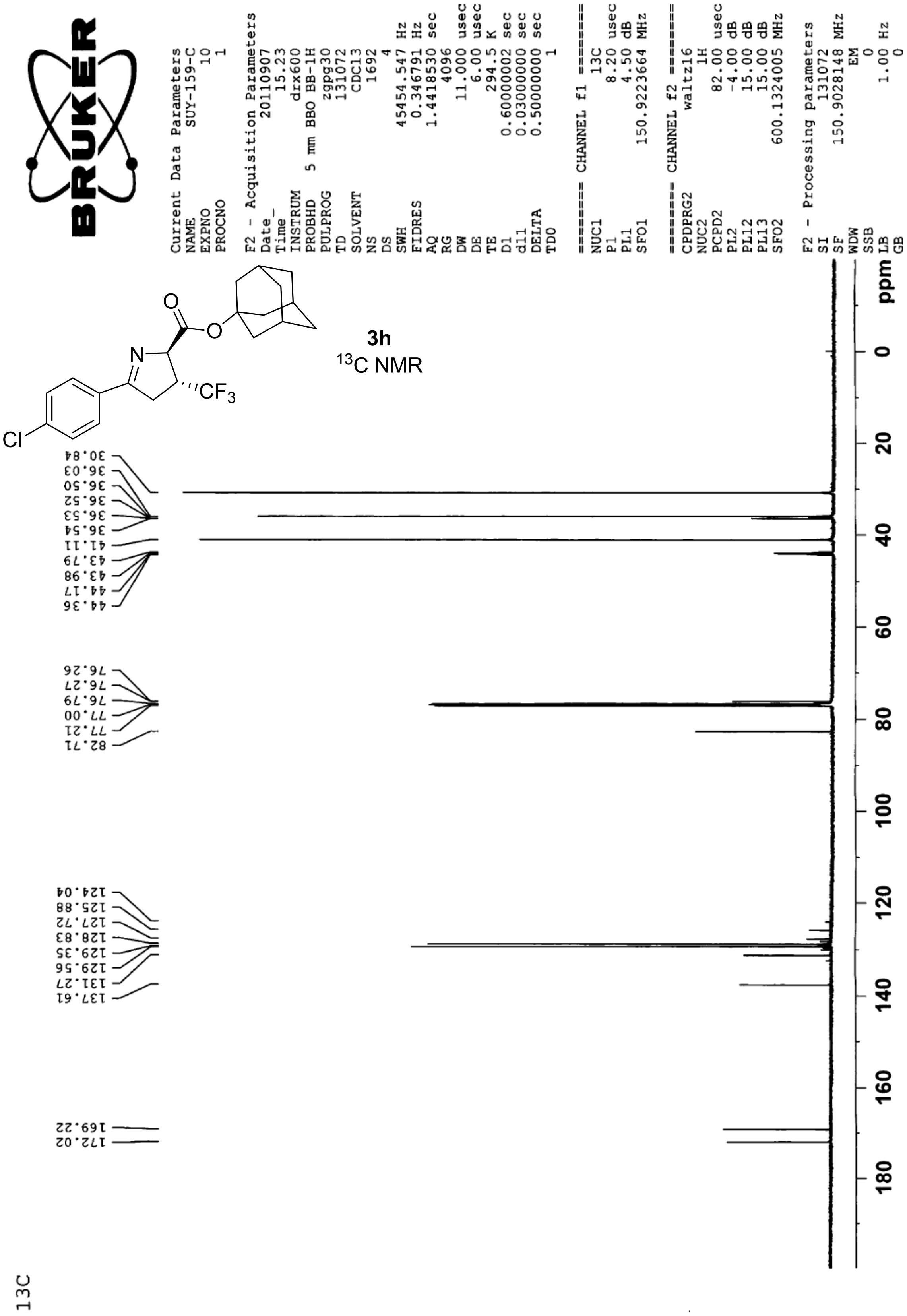


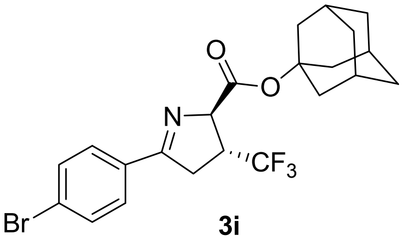


3h

^{19}F NMR

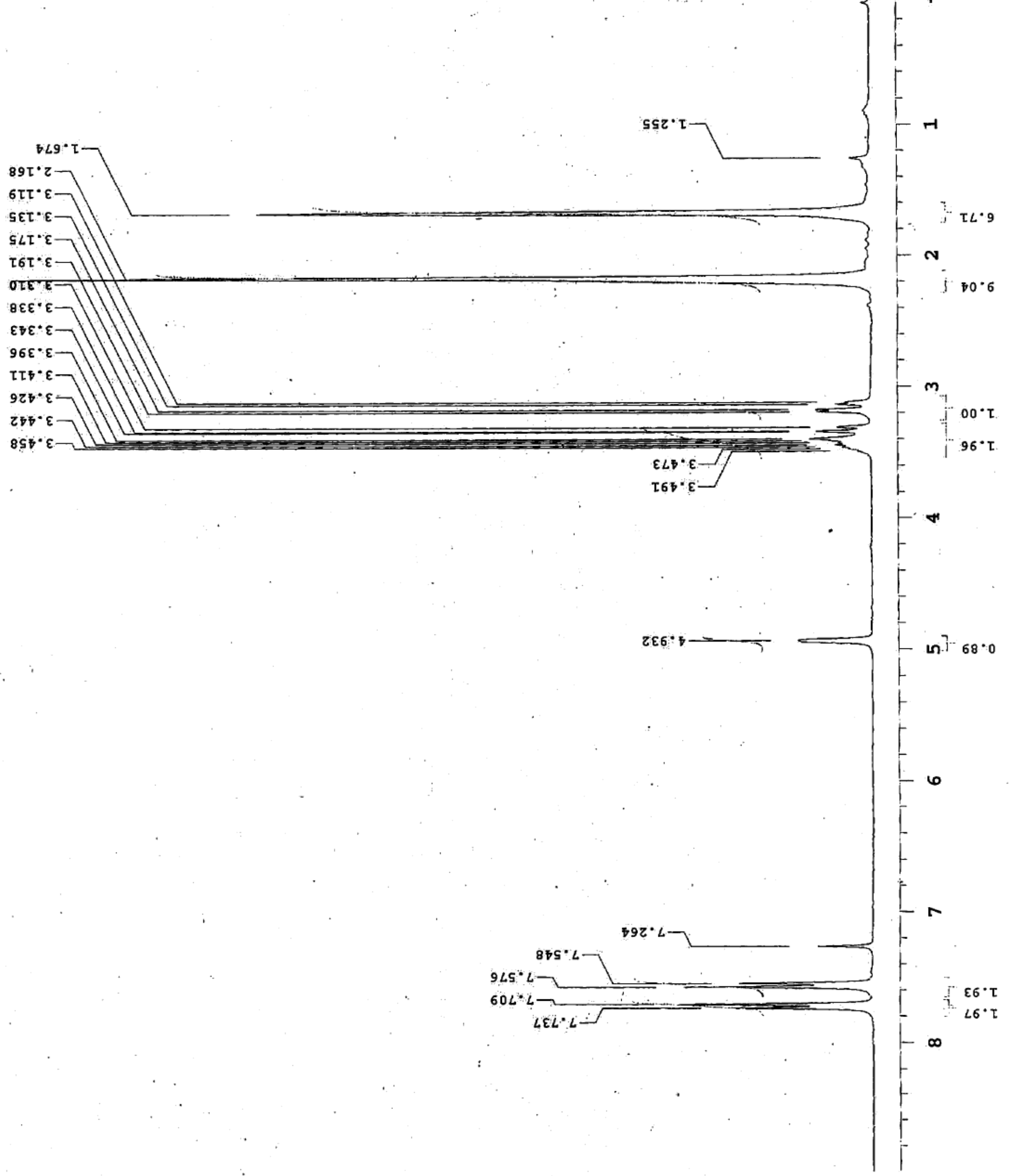



3h
13C NMR
Cl
N
O
O
CF3
Current Data Parameters
NAME SUY-159-C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110907
Time 15.23
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1692
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 4096
DW 11.000 usec
DE 6.00 usec
TE 294.5 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028148 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
30.84
36.03
36.50
36.52
36.53
36.54
41.11
43.79
43.98
44.17
44.36
76.26
76.27
76.79
77.00
77.21
82.71
124.04
125.88
127.72
128.83
129.35
129.56
131.27
137.61
169.22
172.02
ppm
0
20
40
60
80
100
120
140
160
180
13C


O
O
N
CF3
Br

3i

^{1}H NMR


-0.000
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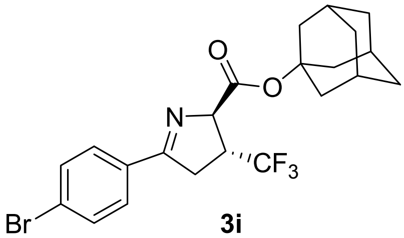
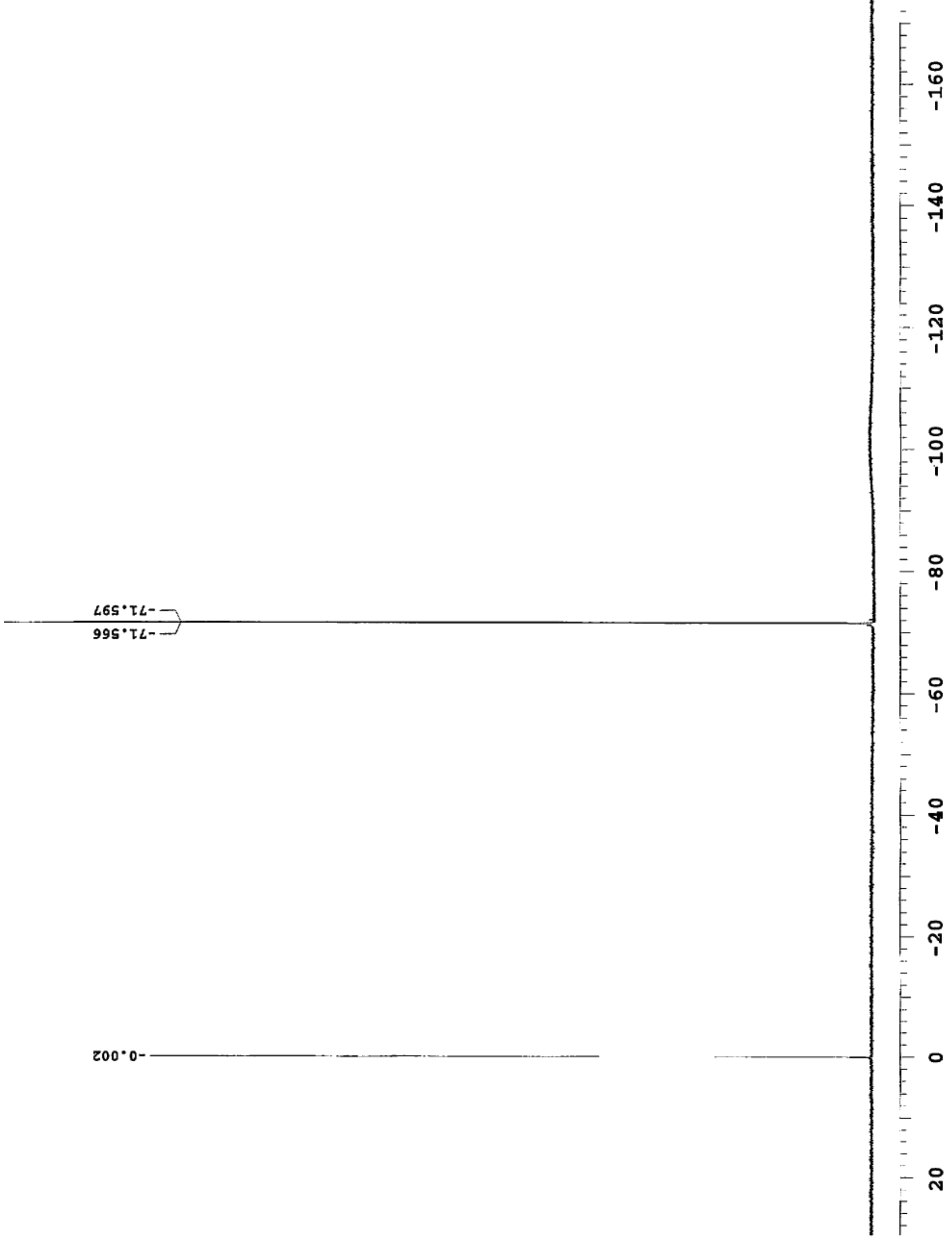
3.119
3.135
3.175
3.191
3.310
3.338
3.343
3.396
3.411
3.426
3.442
3.458
3.473
3.491
4.932
7.264
7.548
7.576
7.709
7.737
6.71
9.04
1.00
1.96
0.89
1.93
1.97
ppm

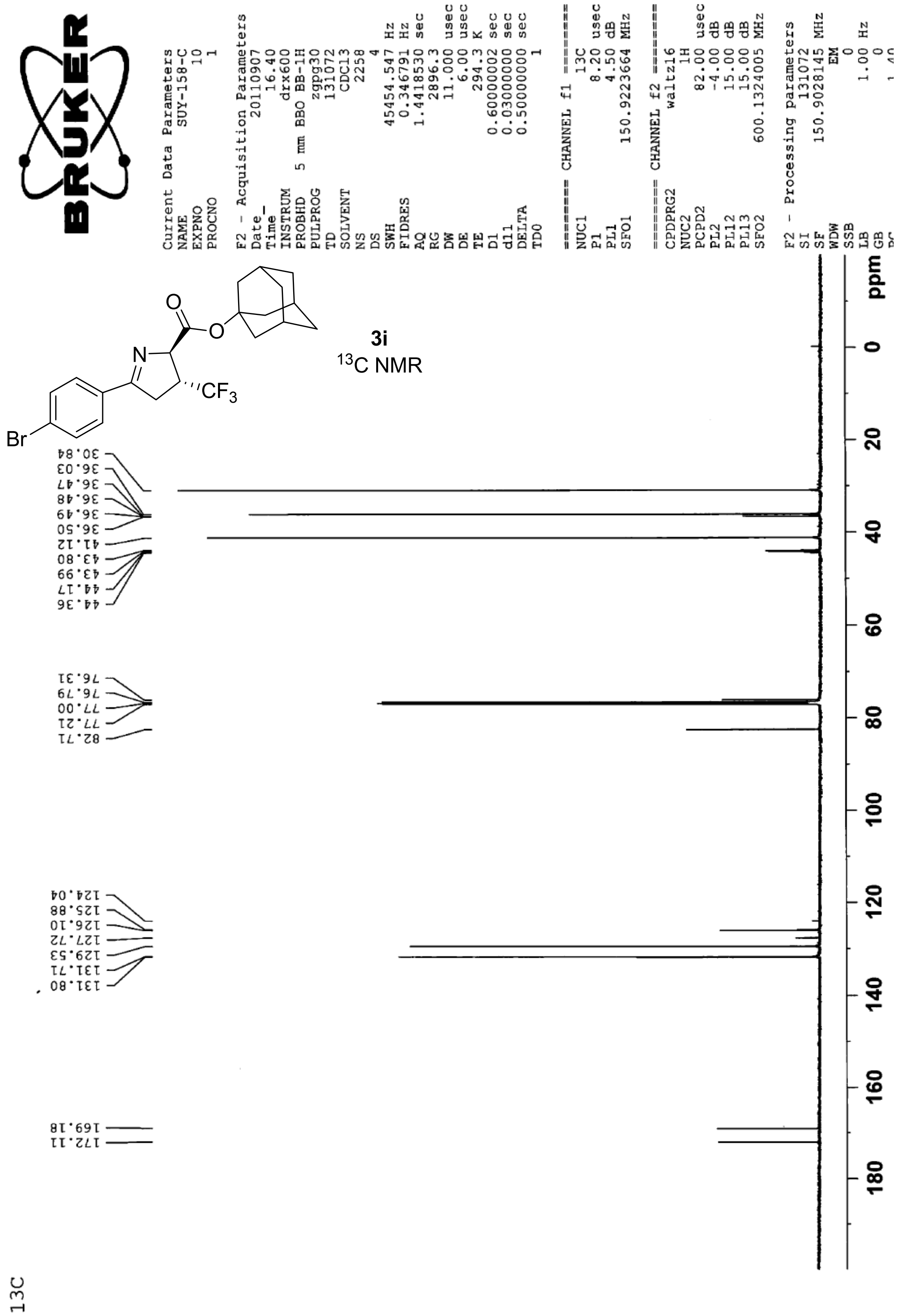
Electronic Supplementary Material (ESI) for Chemical Communications

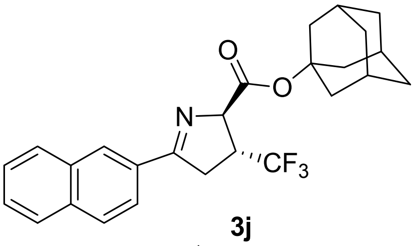


3i

^{19}F NMR

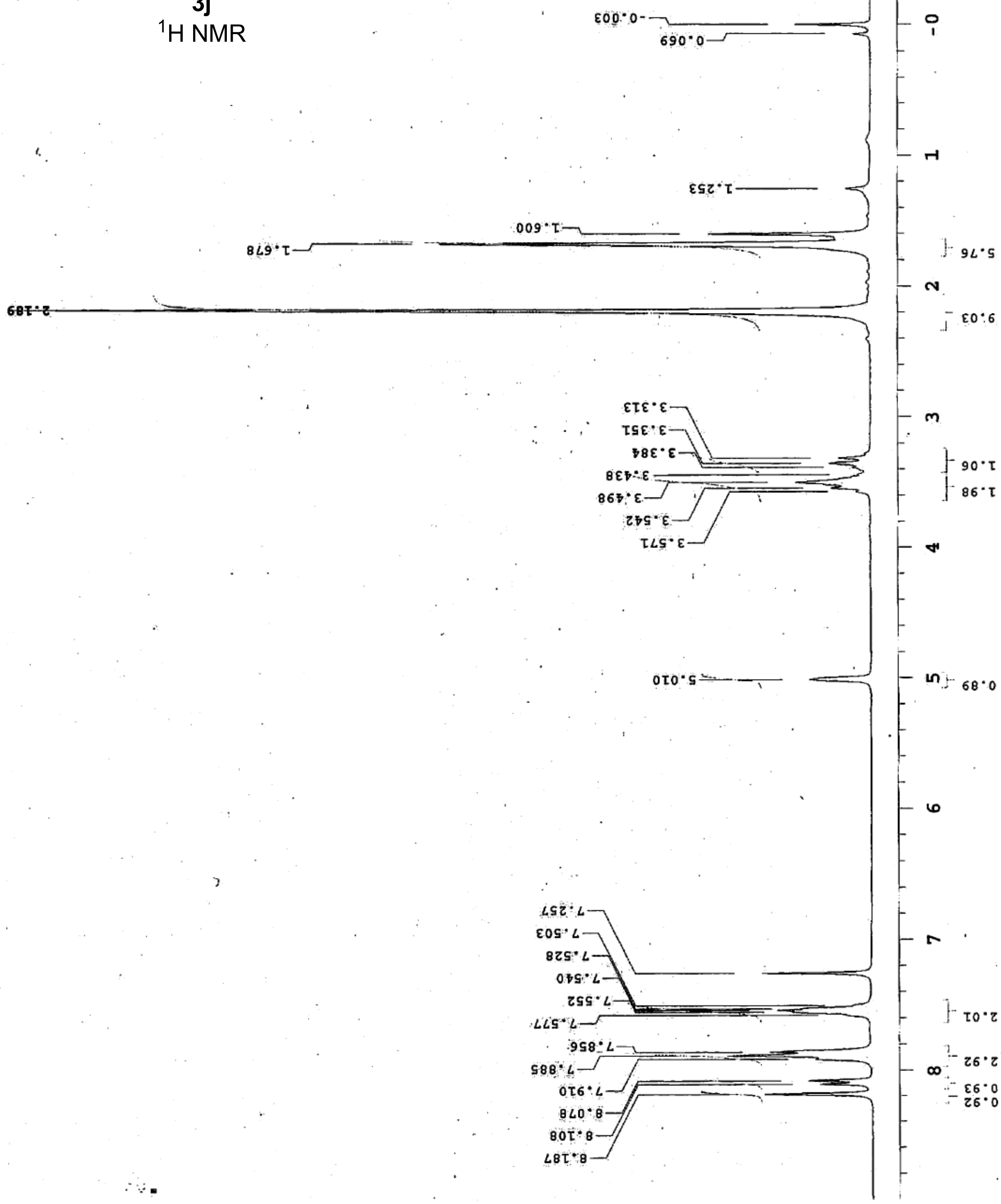


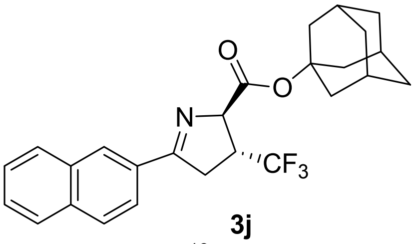

BRUKER
Current Data Parameters
NAME SUY-158-C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110907
Time 16.40
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 2258
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 2896.3
DW 11.000 usec
DE 6.00 usec
TE 294.3 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028145 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
Br
N
O
CF_3
3i
^{13}C NMR
30.84
36.03
36.47
36.48
36.49
36.50
41.12
43.80
43.99
44.17
44.36
76.31
76.79
77.00
77.21
82.71
124.04
125.88
126.10
127.72
129.53
131.71
131.80
169.18
172.11
ppm
0
20
40
60
80
100
120
140
160
180
13C


O
O
N
CF3

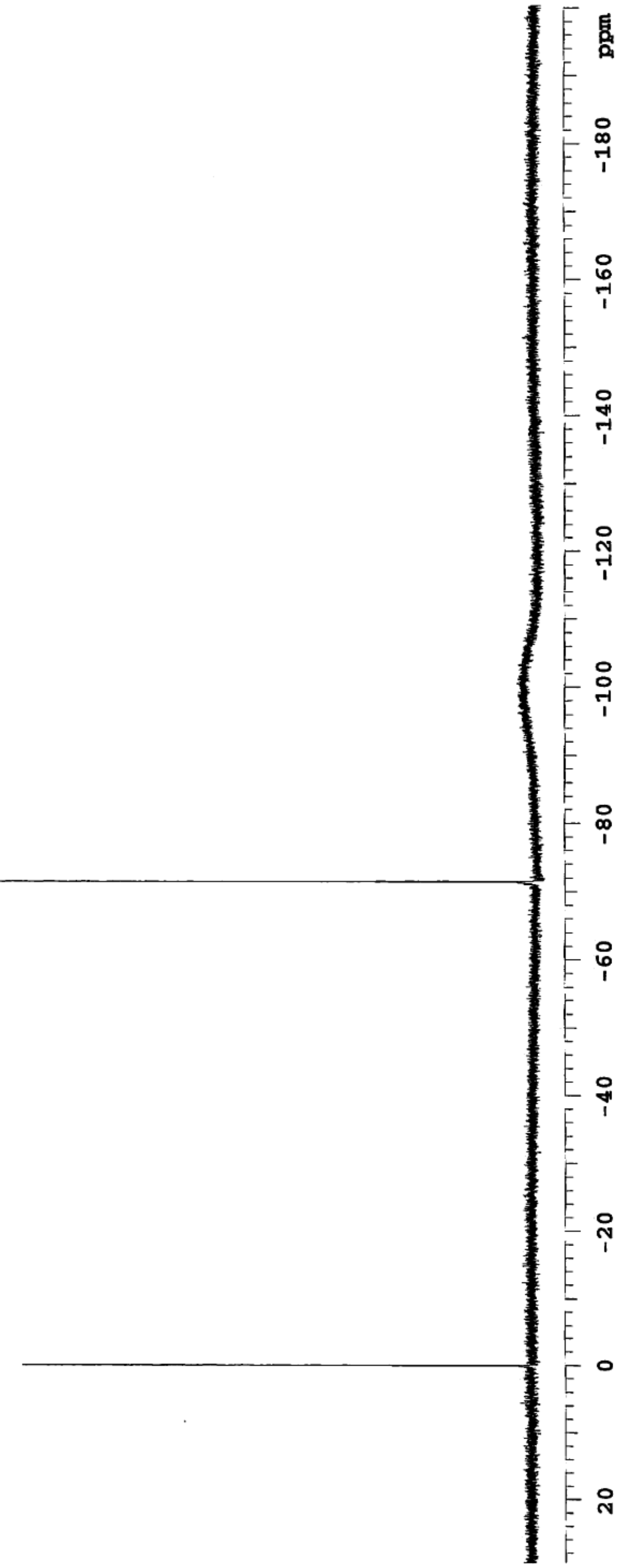
3j

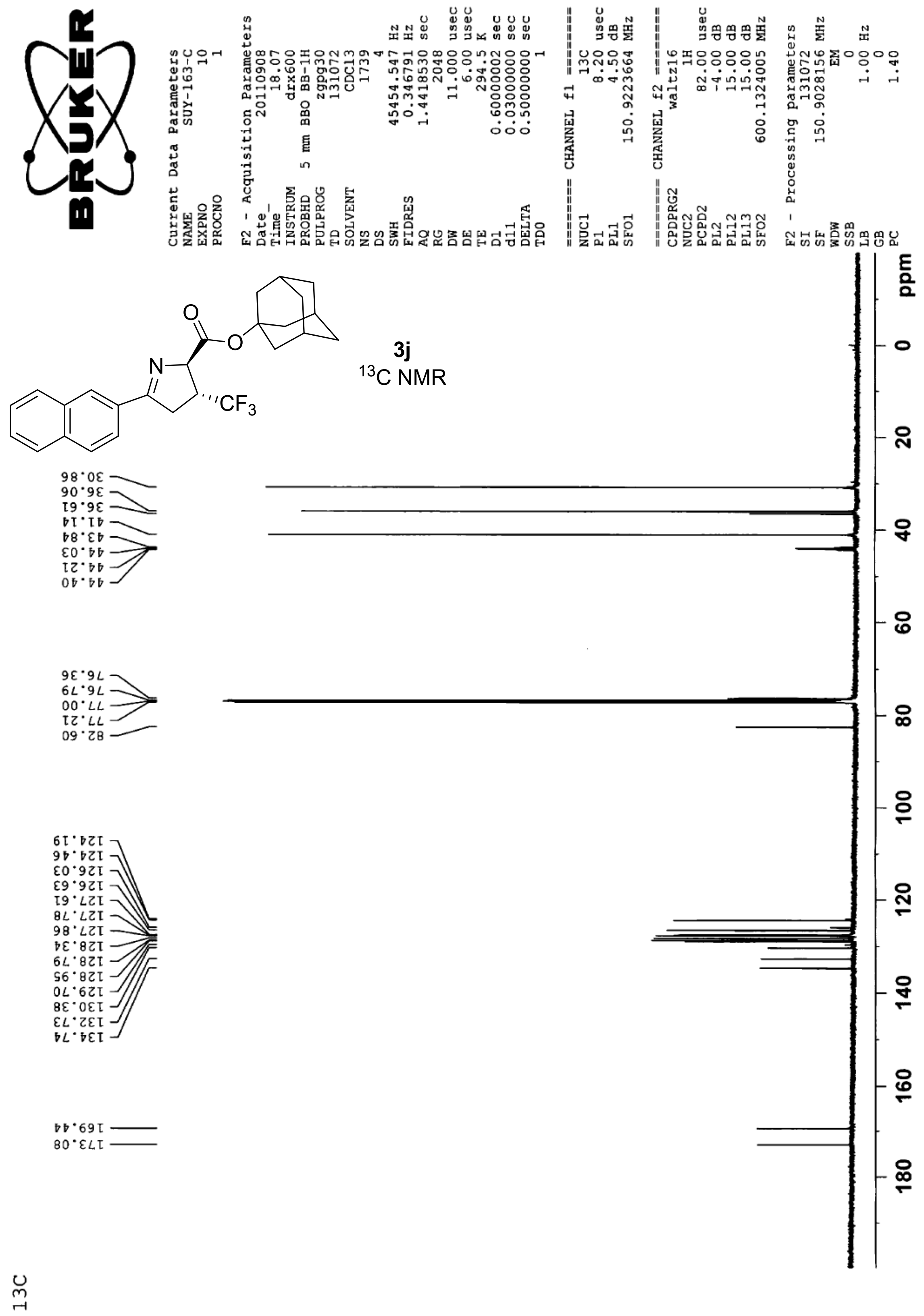
^{1}H NMR

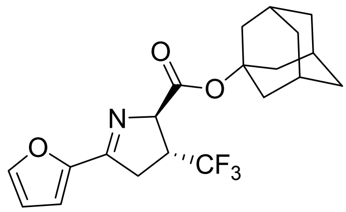

ppm
8.187
8.108
8.078
7.910
7.885
7.856
7.577
7.552
7.540
7.528
7.503
7.257
5.010
3.571
3.542
3.498
3.438
3.384
3.351
3.313
2.189
1.678
1.600
1.253
0.069
-0.003
5.76
9.03
1.06
1.98
0.89
2.01
2.92
0.93
0.92



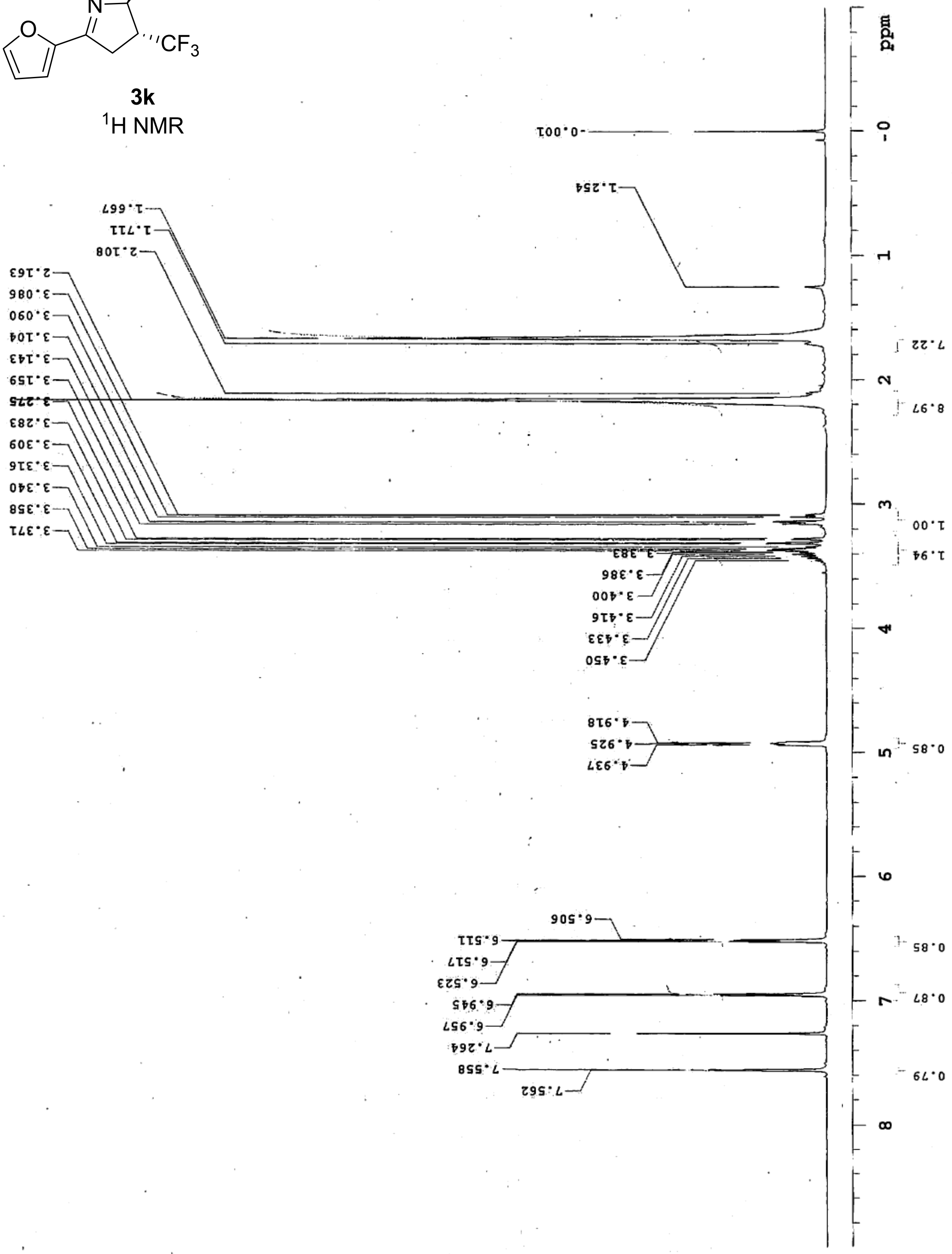
3j
^{19}F NMR

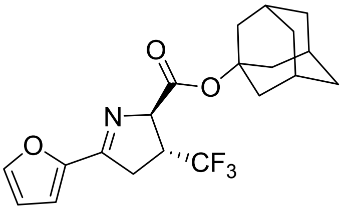



3j
13C NMR
O
N
O
CF3
Current Data Parameters
NAME SUY-163-C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110908
Time_ 18.07
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1739
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 2048
DW 11.000 usec
DE 6.00 usec
TE 294.5 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 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
30.86
36.06
36.61
41.14
43.84
44.03
44.21
44.40
76.36
76.79
77.00
77.21
82.60
124.19
124.46
126.03
126.63
127.61
127.78
127.86
128.34
128.79
128.95
129.70
130.38
132.73
134.74
169.44
173.08
ppm
0
20
40
60
80
100
120
140
160
180
13C



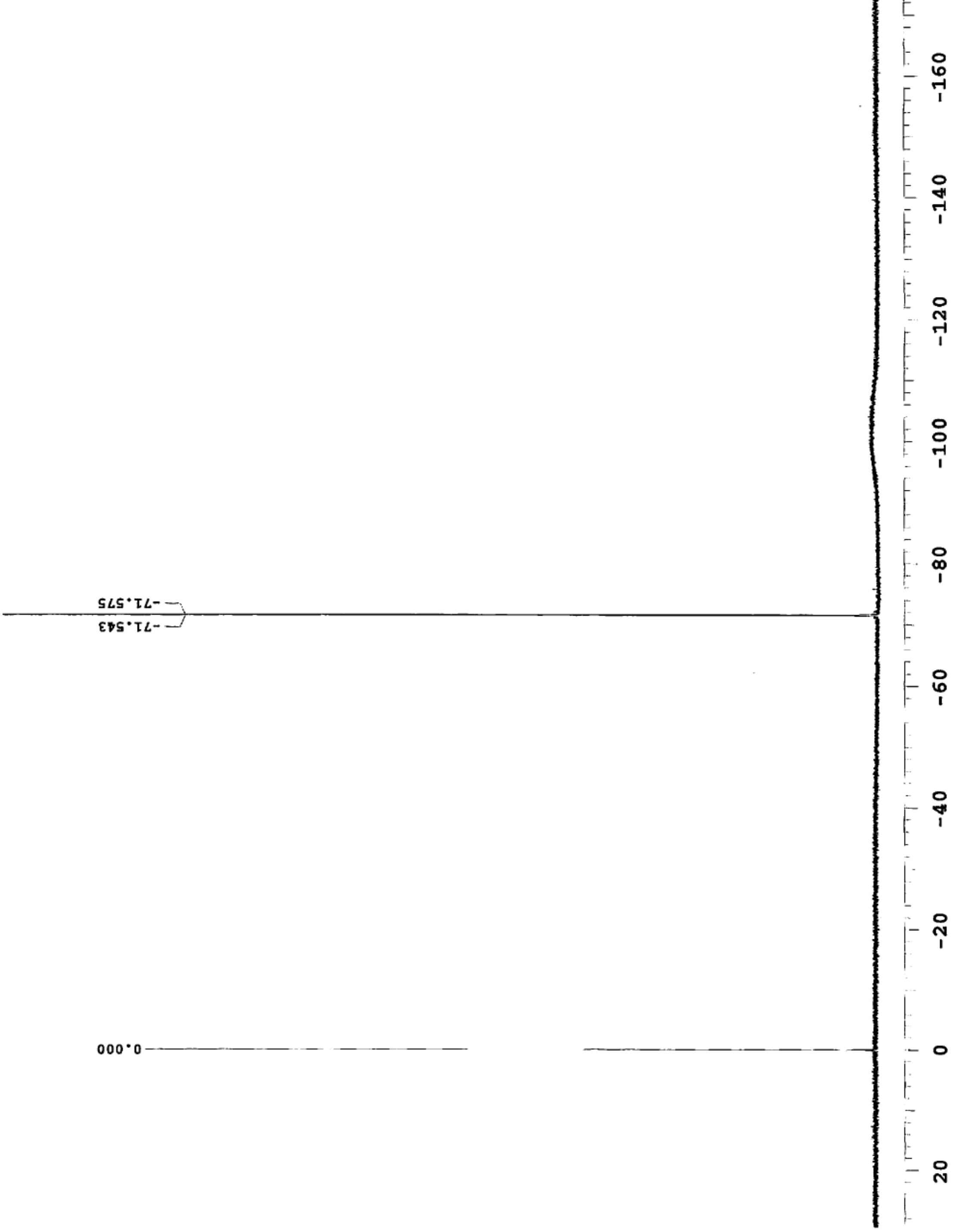
3k
^{1}H NMR

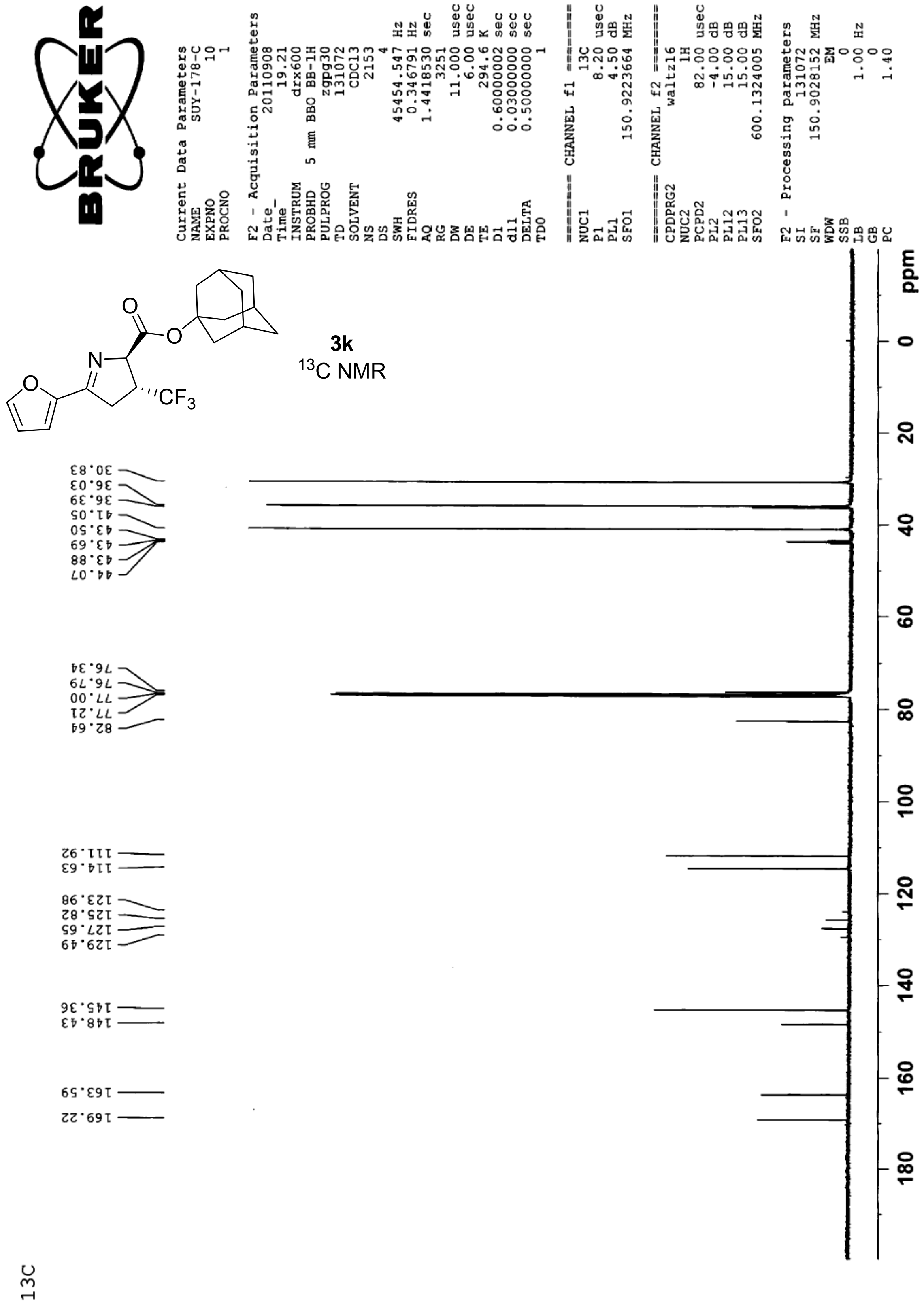



O
O
N
O
CF3

3k

^{19}F NMR

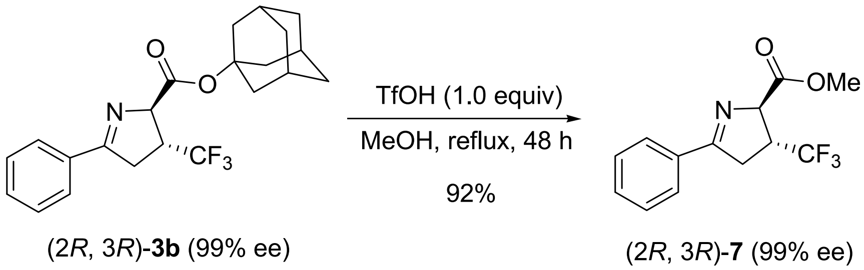

ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20
-71.575
-71.543
0.000



BRUKER
Current Data Parameters
NAME SUY-178-C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110908
Time 19.21
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 2153
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 3251
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 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028152 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
3k
13C NMR
30.83
36.03
36.39
41.05
43.50
43.69
43.88
44.07
76.34
76.79
77.00
77.21
82.64
111.92
114.63
123.98
125.82
127.65
129.49
145.36
148.43
163.59
169.22
ppm
0
20
40
60
80
100
120
140
160
180
13C

Transesterification of 3b to methylester 7:

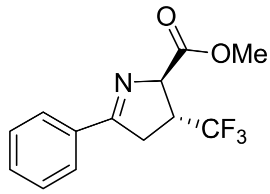
(2*R*,3*R*)-Methyl 5-phenyl-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole-2-carboxylate (7)



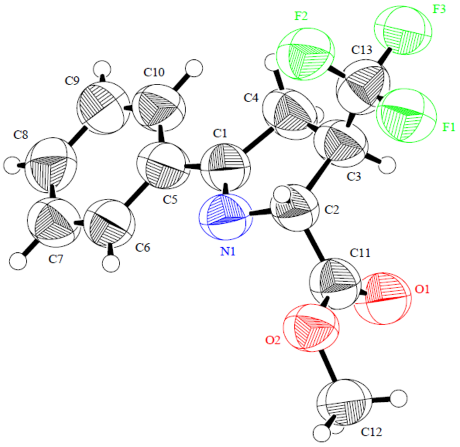
A stirring solution of (2*R*, 3*R*)-**3b** (99% ee) (25.0 mg, 0.064 mmol) and TfOH (5.7 μL, 0.064 mmol, 1.0 equiv) in MeOH (0.5 mL) was heated under reflux for 48 h. After cooling to room temperature, the reaction mixture was quenched with sat. $NaHCO_3$ aq., the whole reaction mixture was extracted three times with CH_2Cl_2, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/ethyl acetate = 95/5) on silica gel to give methylester (2*R*, 3*R*)-**7** (15.9 mg, 92%, 99% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.23 (dd, *J* = 5.6, 17.3 Hz, 1H), 3.45 (ddd, *J* = 2.0, 10.4, 17.7 Hz, 1H), 3.53-3.67 (m, 1H), 5.08 (d, *J* = 4.8 Hz, 1H), 7.41-7.52 (m, 3H), 7.86 (d, *J* = 6.9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -71.7 (d, *J* = 9.9 Hz, 3F); IR (KBr) 2968, 1745, 1618, 1576, 1441, 1402, 1340, 1276, 1211, 1152, 1113, 1043, 951, 923, 846, 764, 691, 555, 514 cm^{-1}; MS (ESI, *m/z*) 294 [$(M+Na)^+$]; 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} = 15.1 min, τ_{min} = 18.5 min).

X-ray crystallographic structure of (2*R*, 3*R*)-**7**



(2*R*, 3*R*)-**7**



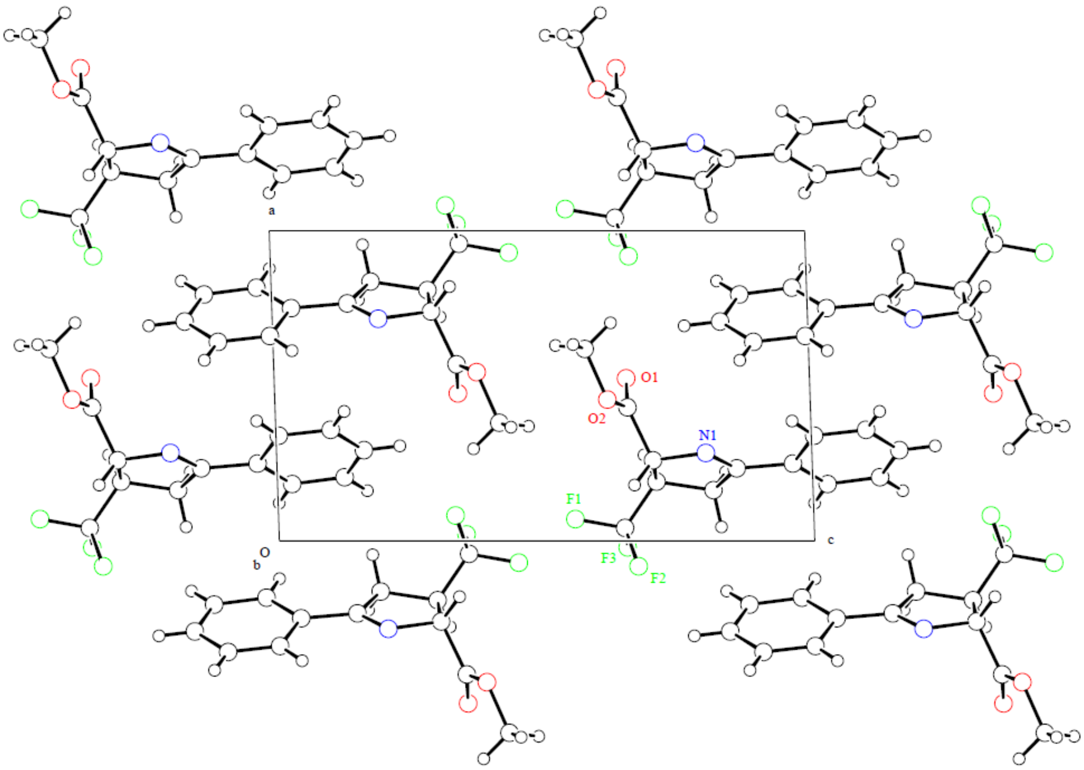


Figure S1