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SUPPORTING INFORMATION

Fluorine Effects in Organocatalysis - Asymmetric Brønsted acid assisted Lewis base catalysis for the synthesis of trifluoromethylated heterocycles by exploiting the negative hyperconjugation of the CF_3-group

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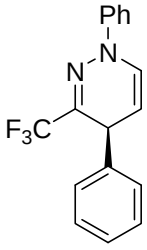
Methods: Unless otherwise stated, reactions were conducted in flame-dried glassware. Solvents after reactions and extraction were evaporated in a rotatory evaporator under vacuum. TLC for reaction monitoring was performed on 60 F_{254} (Merck) with detection by UV light and charring with $KMnO_4$ or Pancaldi reagent. ^1H and ^{13}C NMR spectra were recorded by using Varian Inova 400 and Inova 600 spectrometers and are reported relative to Me_4Si (δ 0.0) or to the solvents residual ^1H-signal ($CH\text{-}Cl_3$, δ(H) 7.27, CH_2Cl_2 δ(H) 5.3). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin-Elmer-100 spectrometer and are reported in frequency of absorption (cm^{-1}). LC-MS mass spectra were measured on a LCQ FLEET instrument. The enantiomeric excesses were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. CHIRALCEL OD-H, CHIRALPAK AD-H or CHIRALPAK AS-H; eluent: *n*hexane/ 2-propanol). The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Optical rotations were measured on a Perkin Elmer 241 polarimeter.

Typical Experimental Procedure: In a screw-cap tube were placed 20 mol% of TMS-prolinol ether catalyst (0.026 mmol) and 1.0 equiv. (0.13 mmol) of the trifluoromethylacetaldehyde hydrazone. 1.0 mL of dry DCM was added to the tube followed by 2.0 equiv. (0.26 mmol) of freshly distilled α,β-unsaturated aldehyde. The tube was stirred at 0 °C for 10 mins. After 10 mins 1.0 equiv. of acetic acid (0.13 mmol) was added to the reaction. The reaction was stirred until the complete disappearance of the trifluoromethylacetaldehyde hydrazone by TLC. 40 mol% of TFA (0.052 mmol) was added to the reaction and then it was stirred at the same temperature overnight. The crude reaction mixture was subjected to column chromatography over silica gel to get the pure product.

1,4-Diphenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9a)



^1H NMR (400 MHz, $CDCl_3$): δ = 4.42 (d, *J* = 5.3 Hz, 1H), 5.23 (dd, *J* = 7.8, 5.3 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 7.18-7.12 (m, 1H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.36 - 7.44 (m, 4H)

^{13}C NMR (100.6 MHz, $CDCl_3$): 143.64, 142.83, 132.86 (q, $J_{C\text{-}F}$ = 33.8 Hz), 129.32, 128.95, 127.63, 127.51, 124.71, 123.93, 121.47 (q, $J_{C\text{-}F}$ = 274.5 Hz), 116.25, 104.73, 36.55

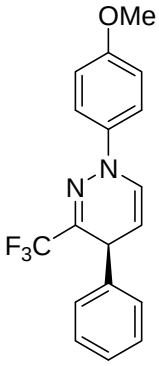
IR (film): 3442, 3034, 2922, 2856, 1729, 1671, 1597, 1494, 1383, 1245, 1132, 1060, 997, 832, 755, 697, 604, 520 cm^{-1}

MS (EI): ($C_{17}H_{13}F_3N_2$), 302.4 (22, M^+), 225.4 (99, M^+ - 77).

$[\alpha]_D$ = -234.0 (c = 7.6, $CHCl_3$, 96% ee)

HPLC conditions: OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, major enantiomer: t_R = 6.55 min, minor enantiomer: t_R = 7.51 min.

1-(4-Methoxyphenyl)-4-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9b)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.82 (s, 3H, OMe), 4.40 (d, *J* = 5.3 Hz, 1H), 5.17 (dd, *J* = 7.7, 5.4 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 6.9 Hz, 2H), 7.25 - 7.29 (m, 1H), 7.30 - 7.36 (m, 4H)

^{13}C NMR (150.9 MHz, $CDCl_3$): 156.57, 143.16, 137.79, 131.90 (q, $J_{C\text{-}F}$ = 33.5 Hz), 128.90, 127.53, 127.45, 125.53, 121.54 (q, $J_{C\text{-}F}$ = 274.1 Hz), 118.33, 114.49, 103.95, 55.59, 36.37

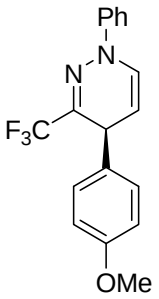
IR (film): 3444, 2924, 2850, 2296, 1727, 1670, 1606, 1509, 1460, 1383, 1246, 1129, 1051, 829, 759, 702, 533 cm^{-1}

MS (EI): ($C_{18}H_{15}F_3N_2O$), 333.4 (29, M^+ +1), 332.3 (89, M^+), 255.3 (99, M^+ - 77).

$[\alpha]_D$ = -86.0 (c = 21.1, $CHCl_3$, 96% ee)

HPLC conditions: OD-H column, 95/5 *n*-hexane/2-propanol, flow 1.0 mL/min, major enantiomer: t_R = 7.52 min, minor enantiomer: t_R = 9.12 min.

4-(4-Methoxyphenyl)-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9c)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.79 (s, 3H, OMe), 4.35 (dd, *J* = 5.2, 2.6 Hz, 1H), 5.21 (ddd, *J* = 7.8, 5.3, 2.5 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.8 Hz, 2H), 6.92 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.14-7.11 (m, 1H), 7.16 (dd, *J* = 8.9, 2.4 Hz, 2H), 7.36 - 7.44 (m, 4H)

^{13}C NMR (150.9 MHz, $CDCl_3$): 159.07, 143.66, 135.16, 133.18 (q, $J_{C\text{-}F}$ = 33.4 Hz), 129.30, 128.65, 124.53, 123.84, 121.49 (q, $J_{C\text{-}F}$ = 274.7 Hz), 116.20, 114.28, 104.89, 55.23, 35.62

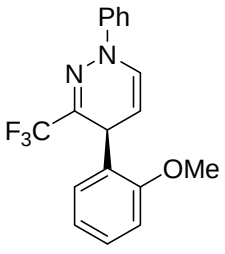
IR (film): 3442, 3008, 2926, 2843, 1726, 1663, 1601, 1503, 1463, 1383, 1299, 1252, 1175, 1129, 1054, 953, 833, 755, 691, 541 cm^{-1}

MS (EI): ($C_{18}H_{15}F_3N_2O$), 333.4 (34, M^++1), 332.3 (99, M^+), 225.3 (97, M^+ - 107).

$[\alpha]_D$ = -41.3 (c = 9.0, $CHCl_3$, 94% ee)

HPLC conditions: OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, minor enantiomer: t_R = 6.35 min, major enantiomer: t_R = 8.65 min.

4-(2-Methoxyphenyl)-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9d)



^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.84 (s, 3H, OMe), 4.86 (d, *J* = 5.4 Hz, 1H), 5.25 (dd, *J* = 7.8, 5.4 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 2H), 7.08 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.10 - 7.15 (m, 1H), 7.24 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 7.37 - 7.40 (m, 4H)

^{13}C NMR (100.6 MHz, CD_2Cl_2): 155.98, 143.80, 132.14 (q, $J_{C\text{-}F}$ = 33.5 Hz), 130.73, 129.18, 128.72, 128.55, 124.78, 123.64, 121.15 (q, $J_{C\text{-}F}$ = 274.2 Hz), 120.93, 116.09, 110.74, 104.31, 55.41, 29.96

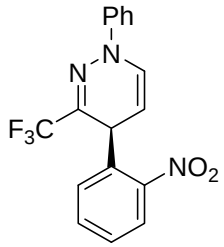
IR (film): 3442, 3306, 2923, 2850, 1731, 1663, 1596, 1494, 1382, 1247, 1129, 1054, 950, 837, 753, 693, 617, 570 cm^{-1}

MS (EI): ($C_{18}H_{15}F_3N_2O$), 333.3 (21, M^++1), 332.3 (99, M^+), 225.3 (98, M^+ - 107).

$[\alpha]_D$ = -77.3 (c = 25.5, $CHCl_3$, 96% ee)

HPLC conditions: OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, major enantiomer: t_R = 5.46 min, minor enantiomer: t_R = 7.40 min.

4-(2-Nitrophenyl)-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9e)



^{1}H NMR (400 MHz, CD_2Cl_2): δ = 5.13 (d, *J* = 5.4 Hz, 1H), 5.48 (dd, *J* = 7.8, 5.4 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 7.18 (dd, *J* = 8.8, 4.5 Hz, 1H), 7.37 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.40 - 7.43 (m, 4H), 7.42 - 7.47 (m, 1H), 7.62 (dt, *J* = 7.7, 7.6, 1.4 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.4 Hz, 1H)

^{13}C NMR (100.6 MHz, CD_2Cl_2): 147.07, 143.45, 136.79, 134.04, 131.09 (q, $J_{C\text{-}F}$ = 22.6 Hz), 130.68, 129.29, 128.39, 125.77, 124.74, 124.35, 121.27 (q, $J_{C\text{-}F}$ = 274.2 Hz), 116.53, 103.60, 32.17

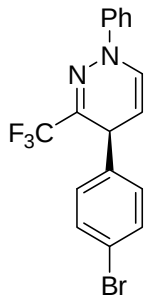
IR (film): 3440, 3071, 3022, 1952, 1685, 1599, 1529, 1496, 1385, 1350, 1241, 1136, 1062, 1002, 951, 855, 828, 755, 694, 618, 517 cm^{-1}

MS (EI): ($C_{17}H_{12}F_3N_3O_2$), 347.3 (20, M^+), 330.3 (99, M^+ - 17).

$[\alpha]_D$ = -4.1 (c = 25.7, $CHCl_3$, 99.5% ee)

HPLC conditions: OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, major enantiomer: t_R = 7.10 min, minor enantiomer: t_R = 21.58 min.

4-(4-Bromophenyl)-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9f)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.40 (d, *J* = 5.3 Hz, 1H), 5.20 (dd, *J* = 7.6, 5.2 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.14 - 7.18 (m, 1H), 7.38 - 7.42 (m, 4H), 7.46 (d, *J* = 8.3 Hz, 2H)

^{13}C NMR (150.9 MHz, $CDCl_3$): 143.50, 141.79, 132.22 (q, $J_{C\text{-}F}$ = 34.0 Hz), 131.87, 129.36, 129.22, 125.06, 124.15, 121.68, 121.36 (q, $J_{C\text{-}F}$ = 274.5 Hz), 116.35, 104.16, 36.01

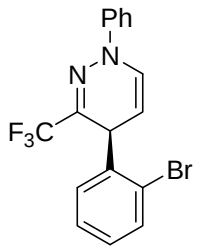
IR (film): 3439, 3049, 2923, 2855, 1663, 1597, 1493, 1377, 1304, 1270, 1242, 1180, 1130, 1058, 1007, 950, 829, 755, 692, 609, 519 cm^{-1}

MS (EI): ($C_{17}H_{12}BrF_3N_2$), 382.2 (44, M^+ + 2), 380.3 (44, M^+), 225.3 (99, M^+ - 155).

$[\alpha]_D$ = -69.7 (c = 6.5, $CHCl_3$, 96% ee)

HPLC conditions: OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, minor enantiomer: t_R = 5.16 min, major enantiomer: t_R = 7.05 min.

4-(2-Bromophenyl)-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9g)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.95 (d, *J* = 5.4 Hz, 1H), 5.35 (dd, *J* = 7.8, 5.4 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 7.07 - 7.18 (m, 3H), 7.23 - 7.30 (m, 1H), 7.37 - 7.40 (m, 4H), 7.55 (dd, *J* = 8.0, 1.4 Hz, 1H)

^{13}C NMR (100.6 MHz, $CDCl_3$): 143.55, 141.44, 133.06, 131.72 (q, $J_{C\text{-}F}$ = 34.6 Hz), 129.55, 129.32, 128.92, 128.44, 125.14, 124.12, 121.25 (q, $J_{C\text{-}F}$ = 274.3 Hz), 121.43, 116.40, 103.45, 35.97

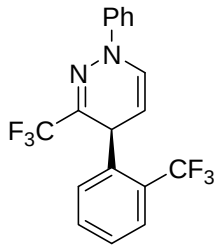
IR (film): 3448, 3061, 2921, 2855, 1953, 1731, 1656, 1595, 1493, 1383, 1246, 1186, 1128, 1053, 1009, 951, 826, 748 cm^{-1}

MS (EI): ($C_{17}H_{12}BrF_3N_2$), 382.2 (5, M^+ + 2), 380.3 (6, M^+), 225.3 (99, M^+ - 155).

$[\alpha]_D$ = -287.8 (c = 17.9, $CHCl_3$, 96% ee)

HPLC conditions: OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, major enantiomer: t_R = 5.49 min, minor enantiomer: t_R = 10.57 min.

1-Phenyl-3-(trifluoromethyl)-4-(2-(trifluoromethyl)phenyl)-1,4-dihydropyridazine (9h)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.83 (d, *J* = 5.3 Hz, 1H), 5.25 (dd, *J* = 7.8, 5.3 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 7.13 - 7.19 (m, 1H), 7.36 (t, *J* = 8.9, 8.9 Hz, 2H), 7.39 - 7.43 (m, 4H), 7.53 (t, *J* = 7.6, 7.6 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H)

^{13}C NMR (150.9 MHz, $CDCl_3$): 143.48, 142.03, 132.99, 132.13 (q, $J_{C\text{-}F}$ = 34.8 Hz), 130.49, 129.36, 127.41, 126.23 (q, $J_{C\text{-}F}$ = 30.1 Hz), 125.82 (q, $J_{C\text{-}F}$ = 5.5 Hz), 124.60, 124.19, 124.16 (q, $J_{C\text{-}F}$ = 273.8 Hz), 116.41, 104.97, 32.56

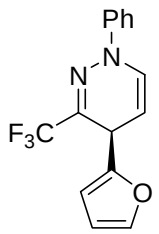
IR (film): 3781, 3442, 2921, 2853, 2426, 2226, 1861, 1727, 1657, 1600, 1488, 1385, 1301, 1244, 1119, 1049, 952, 832, 729, 508 cm^{-1}

MS (EI): ($C_{18}H_{12}F_6N_2$), 370.2 (99, M^+).

$[\alpha]_D$ = -98.2 (c = 9.0, $CHCl_3$, 98% ee)

HPLC conditions: OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, major enantiomer: t_R = 4.50 min, minor enantiomer: t_R = 5.66 min.

4-(Furan-2-yl)-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9i)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.57 (d, *J* = 5.3 Hz, 1H), 5.18 (dd, *J* = 7.7, 5.3 Hz, 1H), 6.14 (d, *J* = 3.2 Hz, 1H), 6.30 - 6.33 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 7.11 - 7.16 (m, 1H), 7.33 - 7.35 (m, 1H), 7.35 - 7.40 (m, 4H)

^{13}C NMR (150.9 MHz, $CDCl_3$): 153.74, 143.60, 142.41, 129.62 (q, $J_{C\text{-}F}$ = 34.3 Hz), 129.26, 126.12, 124.09, 121.22 (q, $J_{C\text{-}F}$ = 273.9 Hz), 116.43, 110.59, 106.67, 100.78, 29.73

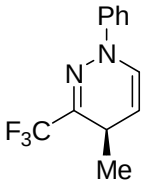
IR (film): 3438, 2923, 2854, 1724, 1661, 597, 1496, 1374, 1241, 1185, 1133, 1054, 1005, 959, 911, 796, 751, 692, 600, 517 cm^{-1}

MS (EI): ($C_{15}H_{11}F_3N_2O$), 292.3 (99, M^+), 225.3 (35, M^+ - 67).

$[\alpha]_D$ = -61.2 (c = 5.5, $CHCl_3$, 82% ee)

HPLC conditions: OD-H column, 95/5 *n*-hexane/2-propanol, flow 1.0 mL/min, major enantiomer: t_R = 5.65 min, minor enantiomer: t_R = 6.16 min.

4-Methyl-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9j)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, *J* = 6.8 Hz, 3H, Me), 3.13 - 3.37 (m, 1H), 5.07 (dd, *J* = 7.6, 5.5 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 7.06 - 7.12 (m, 1H), 7.33 - 7.36 (m, 4H)

^{13}C NMR (100.6 MHz, $CDCl_3$): 143.90, 134.63 (q, $J_{C\text{-}F}$ = 33.7 Hz), 129.20, 125.68, 123.59, 121.67 (q, $J_{C\text{-}F}$ = 273.9 Hz), 116.01, 105.00, 24.90, 21.30

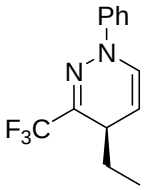
IR (film): 3435, 2924, 2854, 1650, 1597, 1496, 1383, 1273, 1240, 1183, 1127, 1035, 756, 724, 692, 589 cm^{-1}

MS (EI): ($C_{12}H_{11}F_3N_2$), 239.9 (22, M^+), 224.9 (99, M^+ - 15).

$[\alpha]_D$ = -173.6 (c = 9.6, $CHCl_3$, 76% ee)

SFC conditions: OJ-H column, 2.5 mLCO_2 – 1% *n*-hexane/2-propanol (1:1), minor enantiomer: t_R = 3.53 min, major enantiomer: t_R = 3.73 min.

4-Ethyl-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9k)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.5, 7.5 Hz, 3H), 1.52 - 1.60 (m, 2H), 3.28 (ddd, *J* = 7.6, 5.6, 3.8 Hz, 1H), 5.04 (t, *J* = 6.6, 6.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 7.07 - 7.11 (m, 1H), 7.32 - 7.36 (m, 4H)

^{13}C NMR (150.9 MHz, $CDCl_3$): 143.85, 129.30 (q, $J_{C\text{-}F}$ = 34.6 Hz), 129.19, 126.38, 123.56, 121.61 (q, $J_{C\text{-}F}$ = 274.0 Hz), 116.00, 102.88, 31.38, 27.84, 8.91

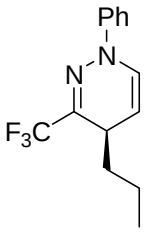
IR (film): 3448, 2922, 2858, 2052, 1597, 1459, 1383, 1264, 1120, 753, 690, 602 cm^{-1}

MS (EI): ($C_{13}H_{13}F_3N_2$), 509.5 (29, $2M^+1$), 508.5 (99, $2M^+$).

$[\alpha]_D$ = -70.0 (c = 3.1, $CHCl_3$, 90% ee)

SFC conditions: OJ-H column, 2.5 mLCO_2 – 1% *n*-hexane/2-propanol (1:1), minor enantiomer: t_R = 3.54 min, major enantiomer: t_R = 4.07 min.

1-Phenyl-4-propyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9l)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.2, 7.2 Hz, 3H), 1.30 - 1.58 (m, 4H), 3.29 (ddd, *J* = 9.5, 5.7, 3.8 Hz, 1H), 5.07 (dd, *J* = 7.6, 5.8 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 7.06 - 7.12 (m, 1H), 7.33 - 7.36 (m, 4H)

^{13}C NMR (150.9 MHz, $CDCl_3$): 143.89, 134.06 (q, $J_{C\text{-}F}$ = 33.6 Hz), 129.19, 126.23, 123.54, 121.61 (q, $J_{C\text{-}F}$ = 274.3 Hz), 115.96, 103.34, 37.13, 30.14, 17.85, 13.83

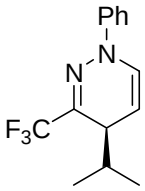
IR (film): 3443, 2922, 2855, 2031, 1621, 1452, 1383, 1027, 698, 513 cm^{-1}

MS (EI): ($C_{14}H_{15}F_3N_2$), 268.5 (9, M^+), 225.3 (99, M^+ - 43).

$[\alpha]_D$ = -87.9 (c = 6.8, $CHCl_3$, 93% ee)

SFC conditions: OJ-H column, 2.5 $mLCO_2$ – 1% *n*-hexane/2-propanol (1:1), minor enantiomer: t_R = 3.83 min, major enantiomer: t_R = 4.53 min.

4-Isopropyl-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9m)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.83 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 1.96 (dt, *J* = 13.1, 13.1, 6.5 Hz, 1H), 3.29 (dd, *J* = 5.6, 4.2 Hz, 1H), 4.96 (dd, *J* = 7.7, 5.7 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 7.06 - 7.11 (m, 1H), 7.25 - 7.27 (m, 4H)

^{13}C NMR (150.9 MHz, $CDCl_3$): 143.74, 133.85, 133.63, 129.18, 127.09, 123.56, 119.30, 118.72, 115.98, 99.87, 36.76, 32.28, 18.12, 16.75

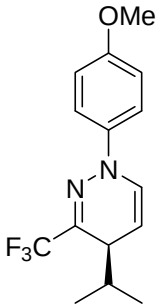
IR (film): 3446, 2921, 2853, 1615, 1507, 1454, 1384, 1248, 1120, 1067, 830, 762, 699 cm^{-1}

MS (EI): ($C_{14}H_{15}F_3N_2$), 268.5 (10, M^+), 225.3 (99, M^+ - 43).

$[\alpha]_D$ = -114.7 (c = 5.1, $CHCl_3$, 96% ee)

SFC conditions: OJ-H column, 2.5 $mLCO_2$ – 1% *n*-hexane/2-propanol (1:1), minor enantiomer: t_R = 3.25 min, major enantiomer: t_R = 4.18 min.

4-Isopropyl-1-(4-methoxyphenyl)-3-(trifluoromethyl)-1,4-dihydropyridazine (9n)



^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.82 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H), 1.90 (dq, *J* = 11.0, 6.8 Hz, 1H), 3.27 (dd, *J* = 5.7, 4.1 Hz, 1H), 3.77 (s, 3H), 4.91 (dd, *J* = 7.7, 5.7 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 9.2 Hz, 2H), 7.22 (d, *J* = 9.2 Hz, 2H)

^{13}C NMR (100.6 MHz, CD_2Cl_2): 158.34, 139.76, 134.40 (q, $J_{C\text{-}F}$ = 33.5 Hz), 129.69, 123.76 (q, $J_{C\text{-}F}$ = 274.0 Hz), 119.89, 116.17, 100.95, 57.36, 38.45, 34.32, 19.59, 18.38

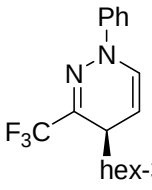
IR (film): 2966, 2931, 1656, 1508, 1462, 1372, 1251, 1182, 1119, 1040, 977, 901, 831, 737, 707, 671 cm^{-1}

MS (EI): ($C_{15}H_{17}F_3N_2O$), 297,9 (25, M^+), 254.8 (99, M^+ - 43).

$[\alpha]_D$ = -271.8 (c = 5.7, $CHCl_3$, 99% ee)

HPLC conditions: AD-H column, 99.5/0.5 *n*-hexane/2-propanol, flow 1.0 mL/min, minor enantiomer: t_R = 5.40 min, major enantiomer: t_R = 5.93 min.

(*E*)-4-(Hex-3-enyl)-1-phenyl-3-(trifluoromethyl)-1,4-dihydropyridazine (9o)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.5, 7.5 Hz, 3H), 1.46 - 1.59 (m, 2H), 1.98 – 2.16 (m, 4H), 3.31 (ddd, *J* = 8.2, 5.7, 4.2 Hz, 1H), 5.07 (dd, *J* = 7.6, 5.8 Hz, 1H), 5.25 - 5.34 (m, 1H), 5.35 - 5.44 (m, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 7.10 (dd, *J* = 8.6, 4.4 Hz, 1H), 7.34 - 7.36 (m, 4H),

^{13}C NMR (100.6 MHz, $CDCl_3$): 143.87, 133.82 (q, J_{C-F} = 33.8 Hz), 132.70, 129.20, 127.56, 126.49, 123.64, 121.60 (q, J_{C-F} = 273.9 Hz), 116.05, 103.01, 34.80, 29.91, 22.29, 20.48, 14.26

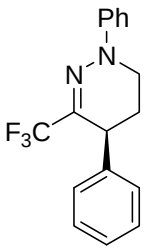
IR (film): 3007, 2937, 2875, 1655, 1599, 1495, 1456, 1378, 1341, 1270, 1240, 1190, 1124, 1060, 1039, 969, 753, 723, 693, 615, 517 cm^{-1}

MS (EI): ($C_{17}H_{19}F_3N_2$), 307.9 (86, M+), 278.9 (7, M^+ - 29), 225.2 (99, M^+ - 83).

$[\alpha]_D$ = -229.2 (c = 11.2, $CHCl_3$, 91% ee)

SFC conditions: OJ-H column, 2.5 mLCO_2 – 1% *n*-hexane/2-propanol (1:1), minor enantiomer: t_R = 3.88 min, major enantiomer: t_R = 4.90 min.

1,4-Diphenyl-3-(trifluoromethyl)-1,4,5,6-tetrahydropyridazine (10a)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.03 - 2.13 (m, 1H), 2.18 - 2.25 (m, 1H), 3.28 - 3.37 (m, 1H), 3.81 - 3.87 (m, 1H), 3.89 (d, *J* = 5.2 Hz, 1H), 6.96 - 7.05 (m, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 7.25 - 7.30 (m, 1H), 7.31 - 7.37 (m, 6H)

^{13}C NMR (150.9 MHz, $CDCl_3$): 146.07, 141.53, 129.81, 129.28, 129.07, 128.73, 127.80, 127.17, 121.78, 121.66 (q, J_{C-F} = 272.6 Hz), 114.40, 38.95, 35.19, 25.77

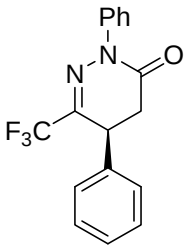
IR (film): 2927, 2858, 1736, 1593, 1497, 1459, 1398, 1280, 1176, 1108, 1041, 965, 889, 830, 749, 693 cm^{-1}

MS (EI): ($C_{17}H_{15}F_3N_2$), 304.1 (75, M^+), 235.1 (5, M^+ - 69), 77.0 (99, M^+ -227).

$[\alpha]_D$ = +97.2 (c = 12.0, $CHCl_3$, 96% ee)

HPLC conditions: OD-H column, 97/3 *n*-hexane/2-propanol, flow 0.4 mL/min, major enantiomer: t_R = 20.70 min, minor enantiomer: t_R = 23.02 min.

2,5-Diphenyl-6-(trifluoromethyl)-4,5-dihydropyridazin-3(*2H*)-one (12a)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.97 (dd, *J* = 16.8, 1.9 Hz, 1H), 3.17 (dd, *J* = 16.8, 8.1 Hz, 1H), 4.21 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.29 - 7.39 (m, 4H), 7.41 - 7.46 (m, 2H), 7.47 - 7.50 (m, 2H)

^{13}C NMR (100.6 MHz, $CDCl_3$): 163.22, 142.55 (q, J_{C-F} = 35.3 Hz), 139.76, 135.97, 129.58, 128.83, 128.47, 127.49, 126.61, 124.63, 120.41 (q, J_{C-F} = 275.3 Hz), 38.02, 36.28

IR (film): 3407, 3067, 2926, 2254, 1708, 1595, 1495, 1387, 1304, 1201, 1142, 1063, 1015, 910, 743, 698, 651, 592 cm^{-1}

MS (EI): ($C_{17}H_{13}F_3N_2O$), 318.0 (99, M^+).

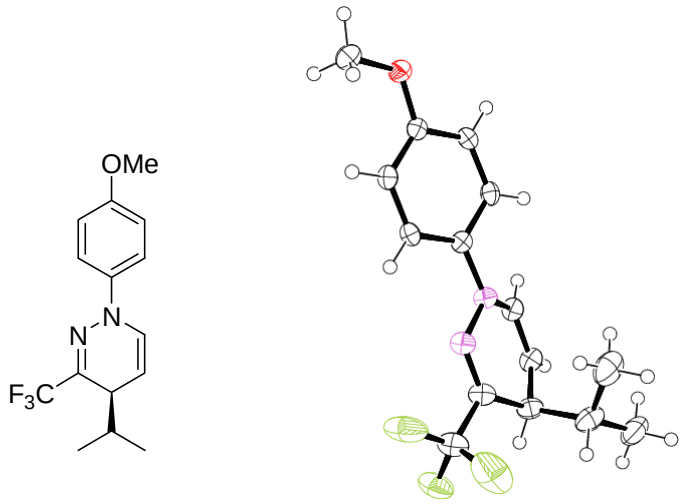
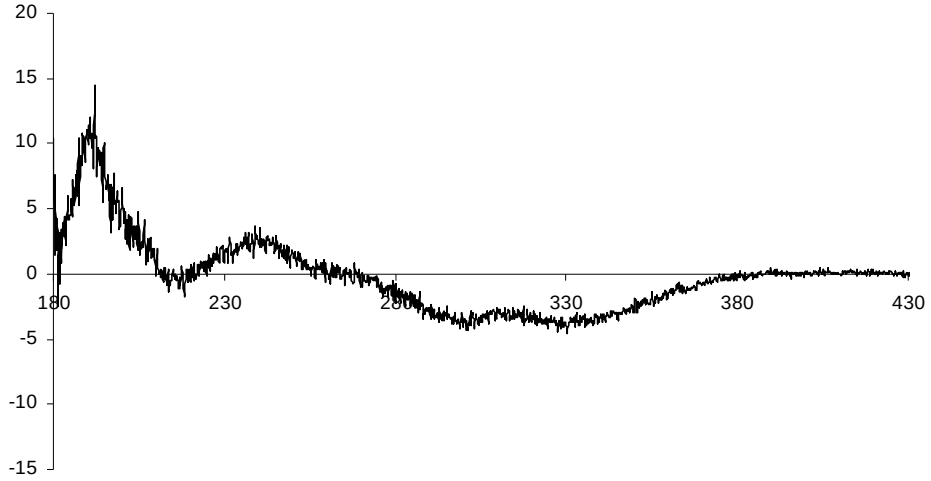


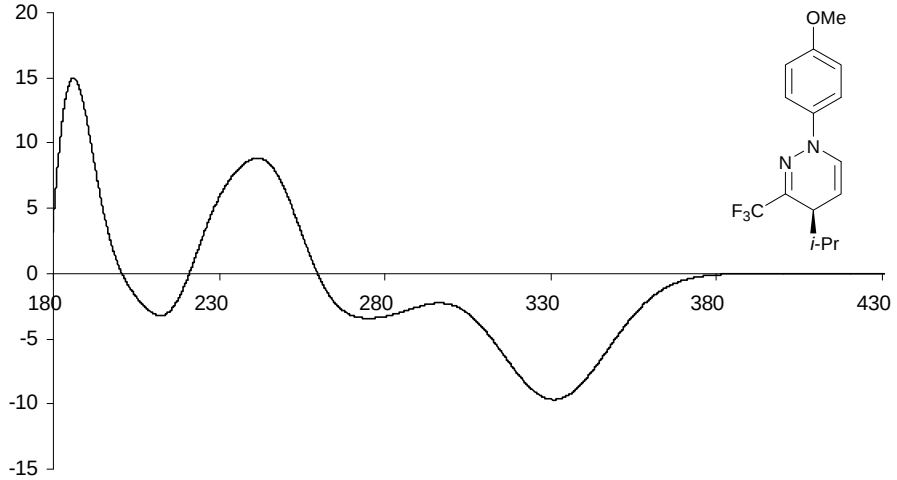
Figure 1. Structure of compound **9n** as determined by X-ray crystal structure analysis.

Crystallographic data for **9n** were collected at 100 K with a Bruker Kappa APEX II CCD-diffractometer with monochromatic Cu–Kα radiation (λ = 1.540562 Å) and a CCD detector. The structure was solved by direct methods using SHELXS-97 and refined against F2 on all data by full-matrix least-squares methods using SHELXL-97[1,2] The (*R*) absolute configuration of the compound determined in this way (Flack Xabs = 0.11(17)) was confirmed by CD-spectroscopy (Fig 2).

Fig 2. Recorded and averaged calculated CD-spectra for (*R*)-**9n**.



a) Recorded CD-spectrum for **9n**.



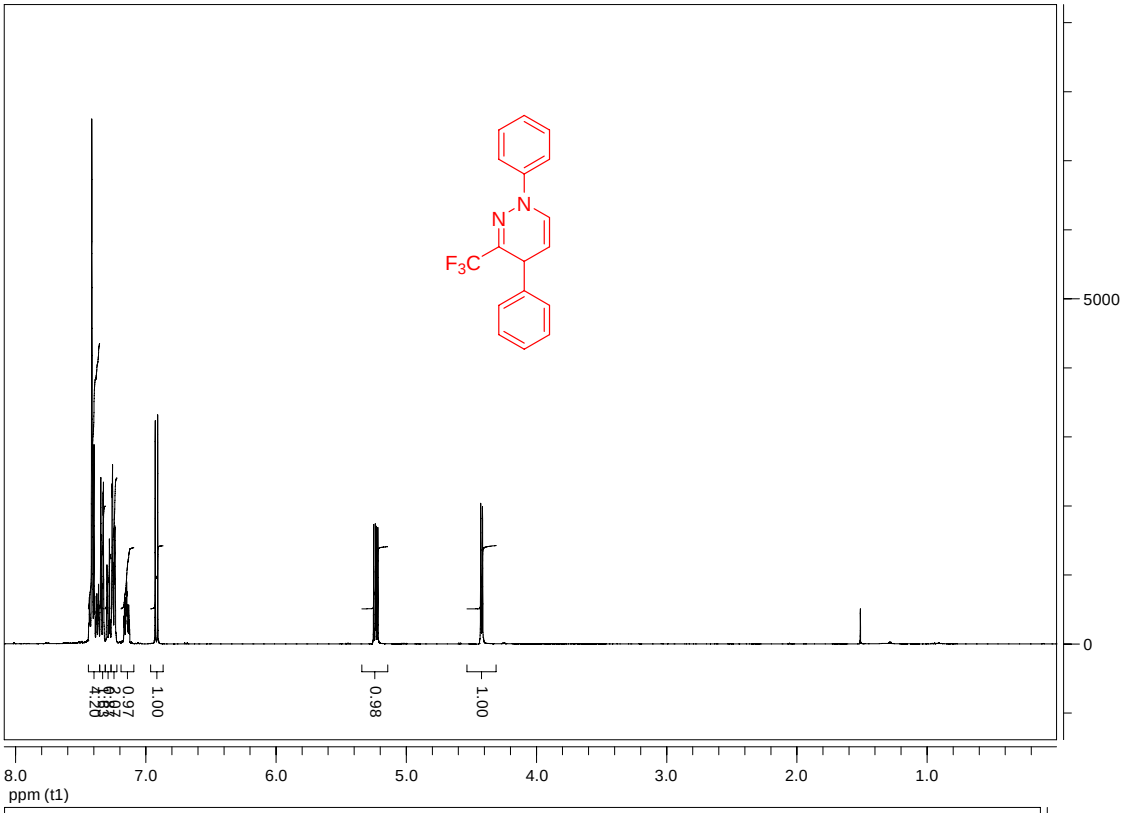
b) Averaged calculated CD-spectrum for (*R*)-**9n** at the TD-DFT/B3LYP/6-31G*//B3LYP/6-31G* level (the 4 most stable conformers lying in a range of 1.5 kcal/mol have been taken into account).[3,4]

[1] Sheldrick, G.M. *SHELXS/L-97, Programs for the Solution and Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

[2] Sheldrick, G.M. A short history of *SHELX*. *Acta Cryst.* **2008**, *A64*, 112–122.

[3] Theoretical calculations have been performed by employing the Gaussian 09 program package. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J.

Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
[4] The calculations have been performed by using the facilities and computing resources offered by the Center for Computing and Communication of the RWTH Aachen University.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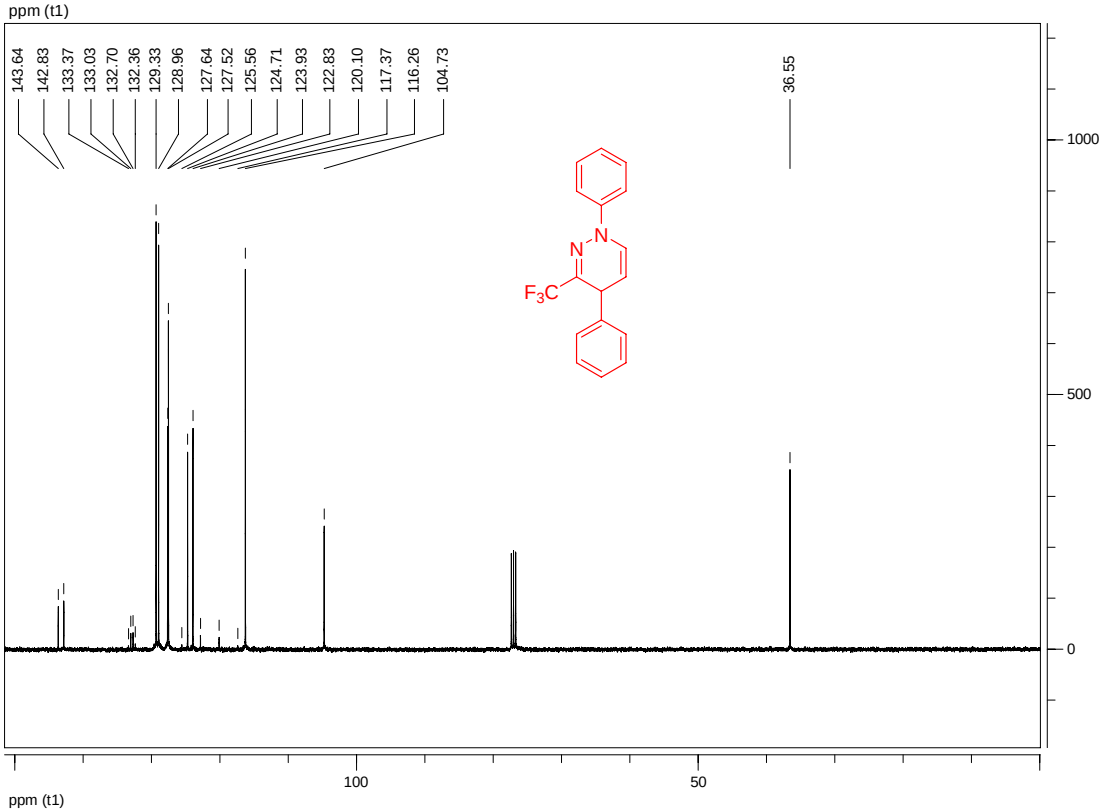
1.0
ppm (t1)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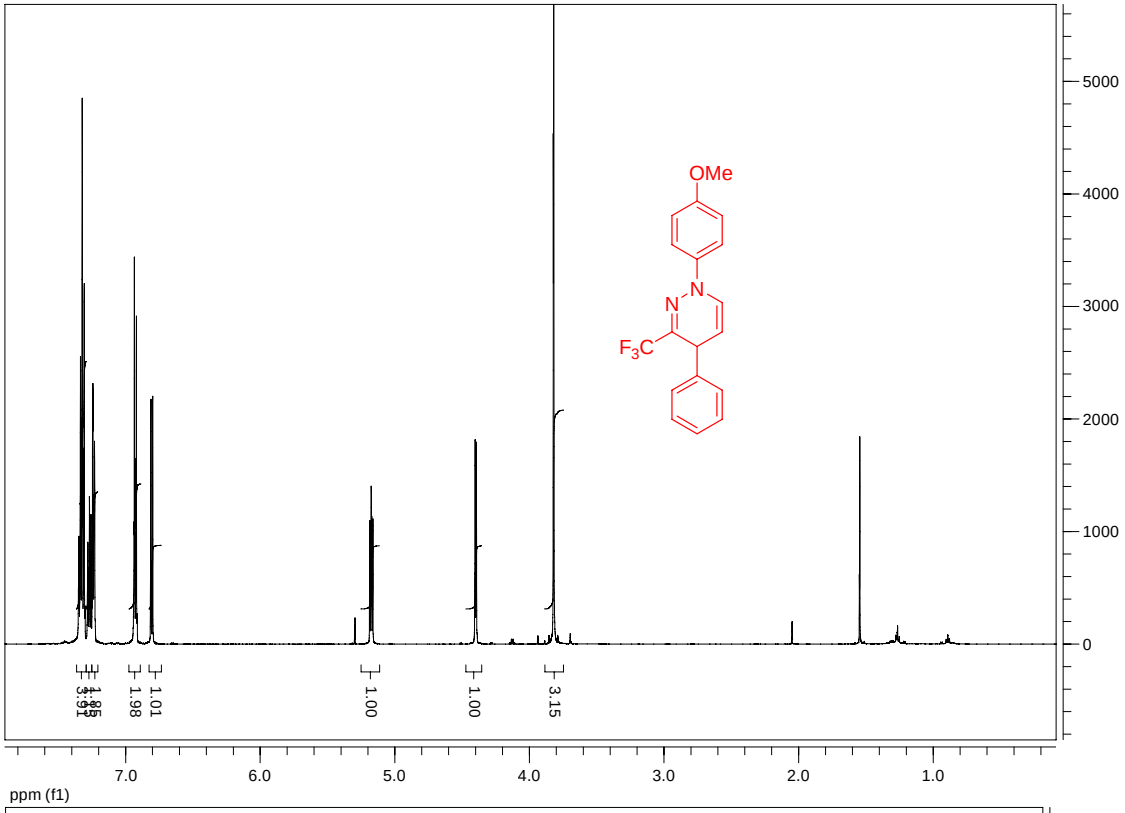
ppm (t1)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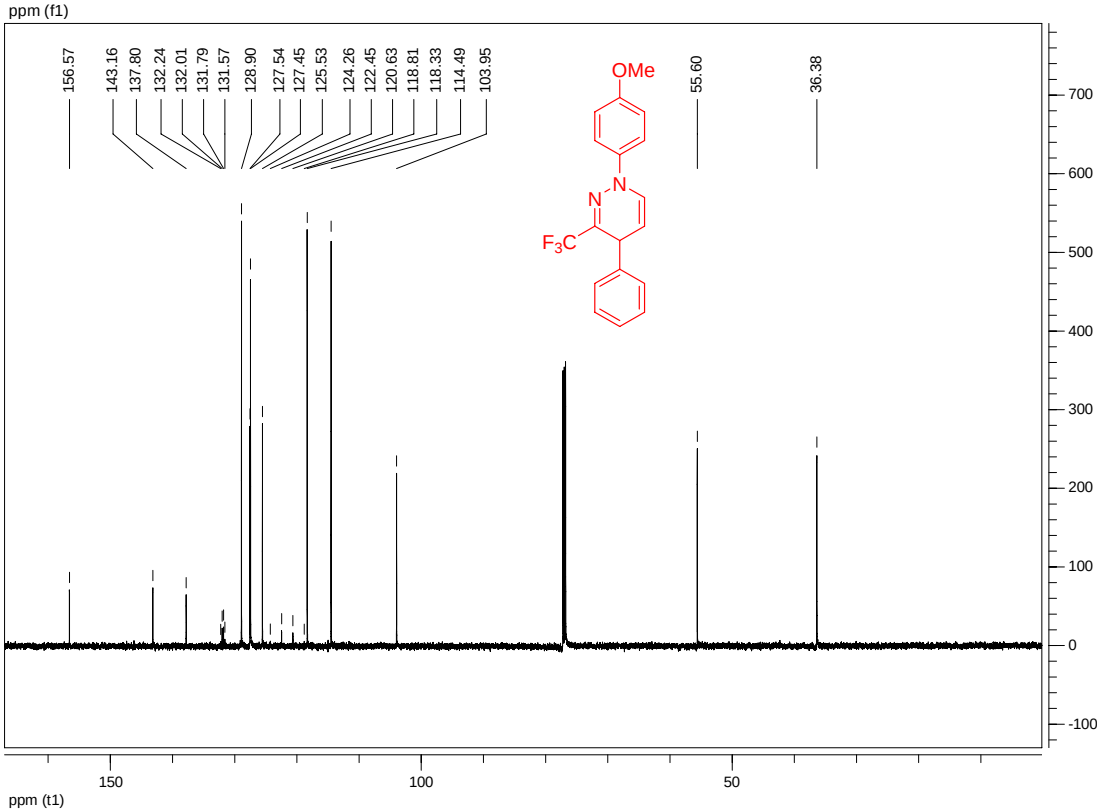
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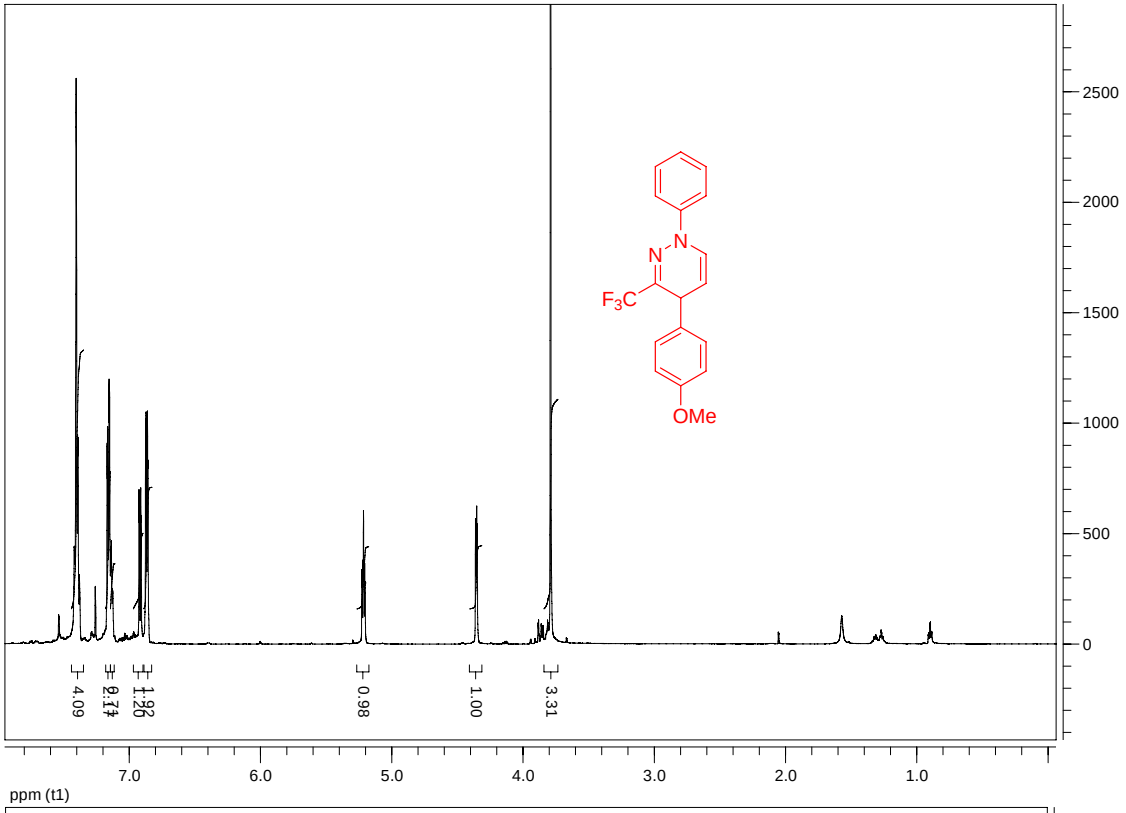
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F3C
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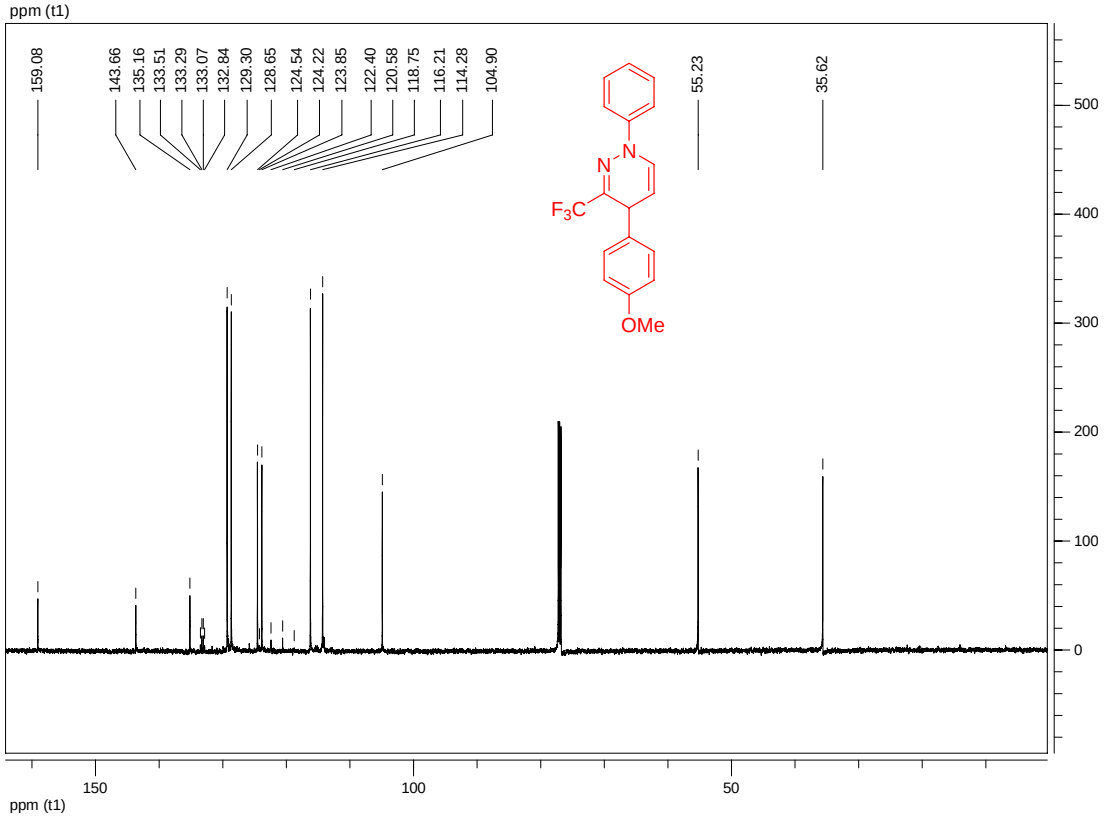
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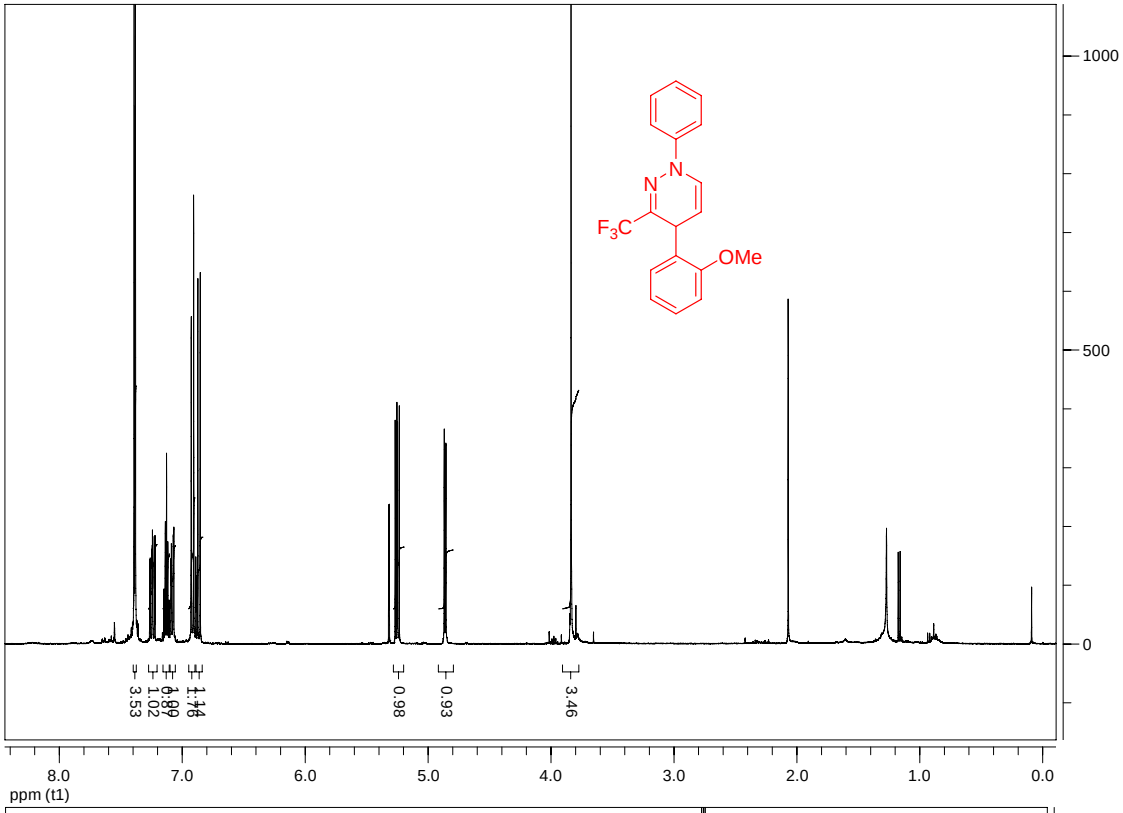
F3C
OMe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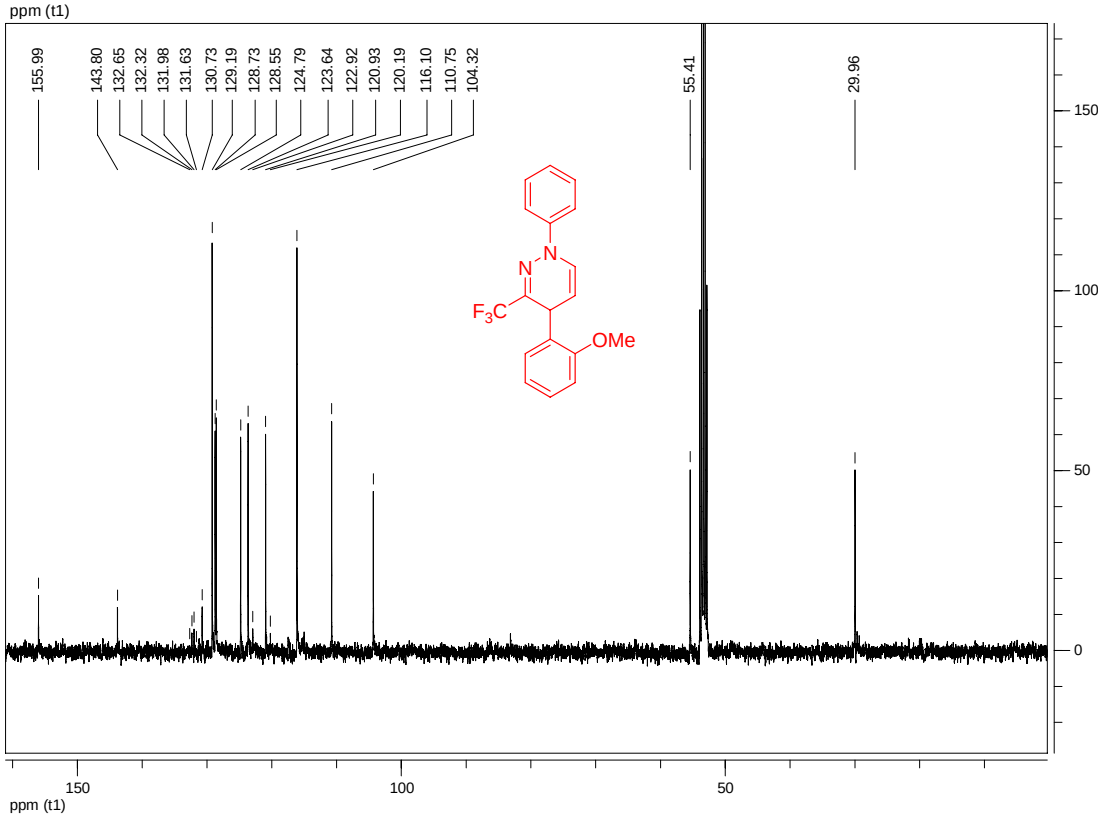
F3C
OMe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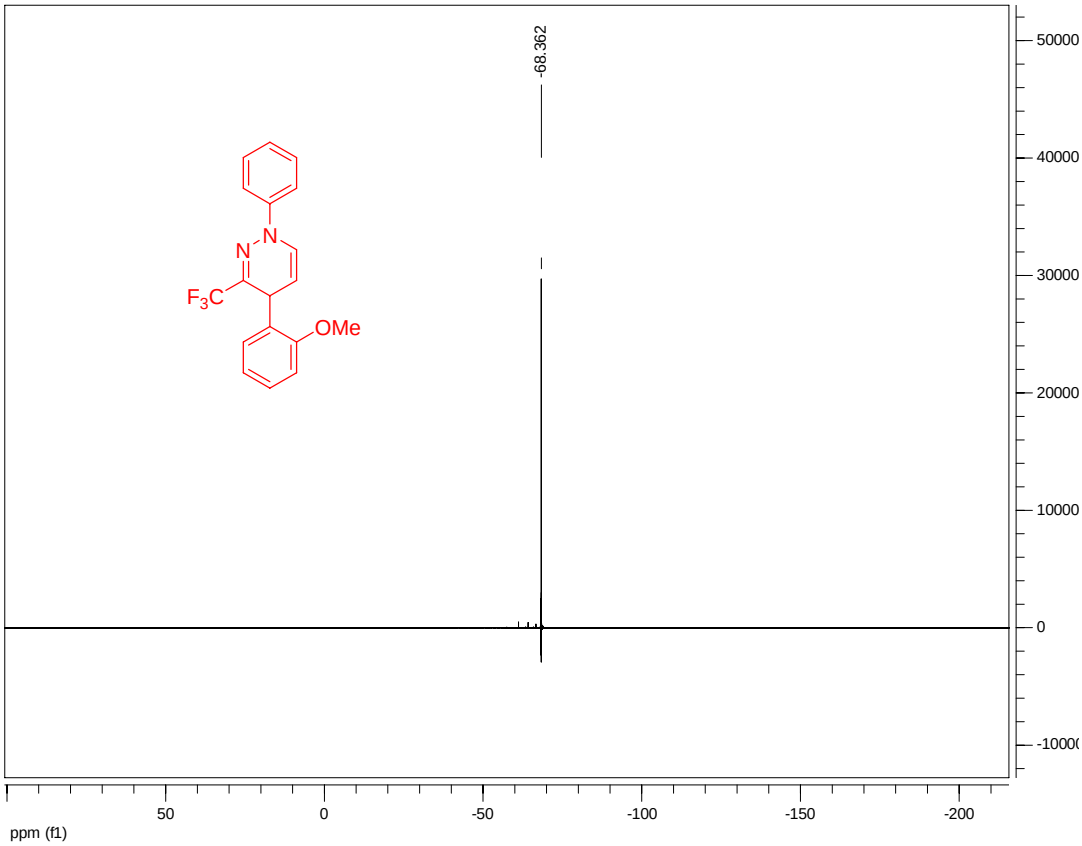
OMe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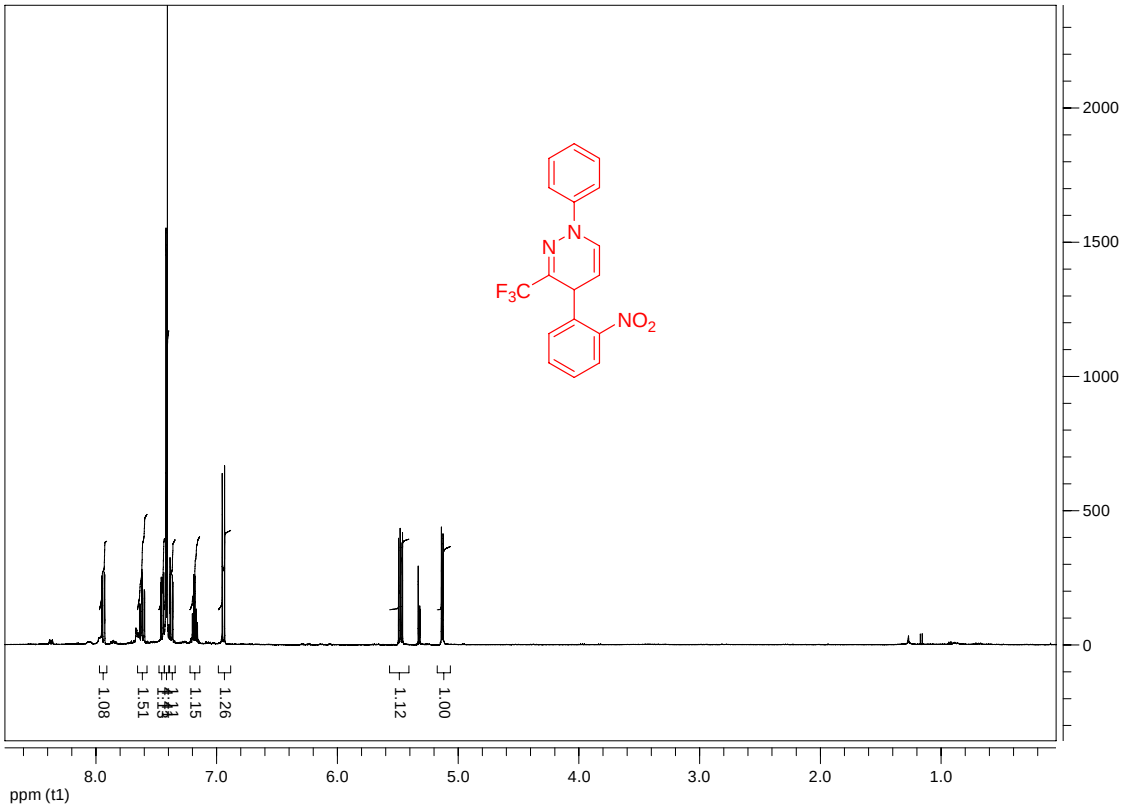
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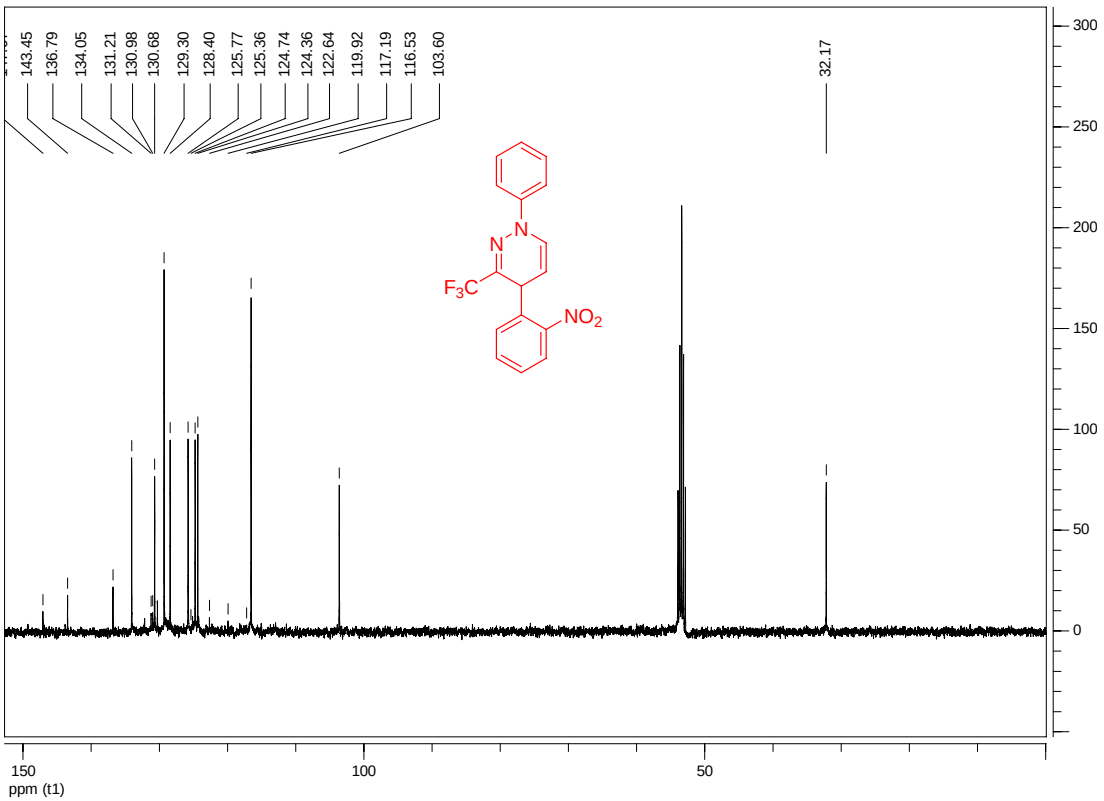
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116.53
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F3C
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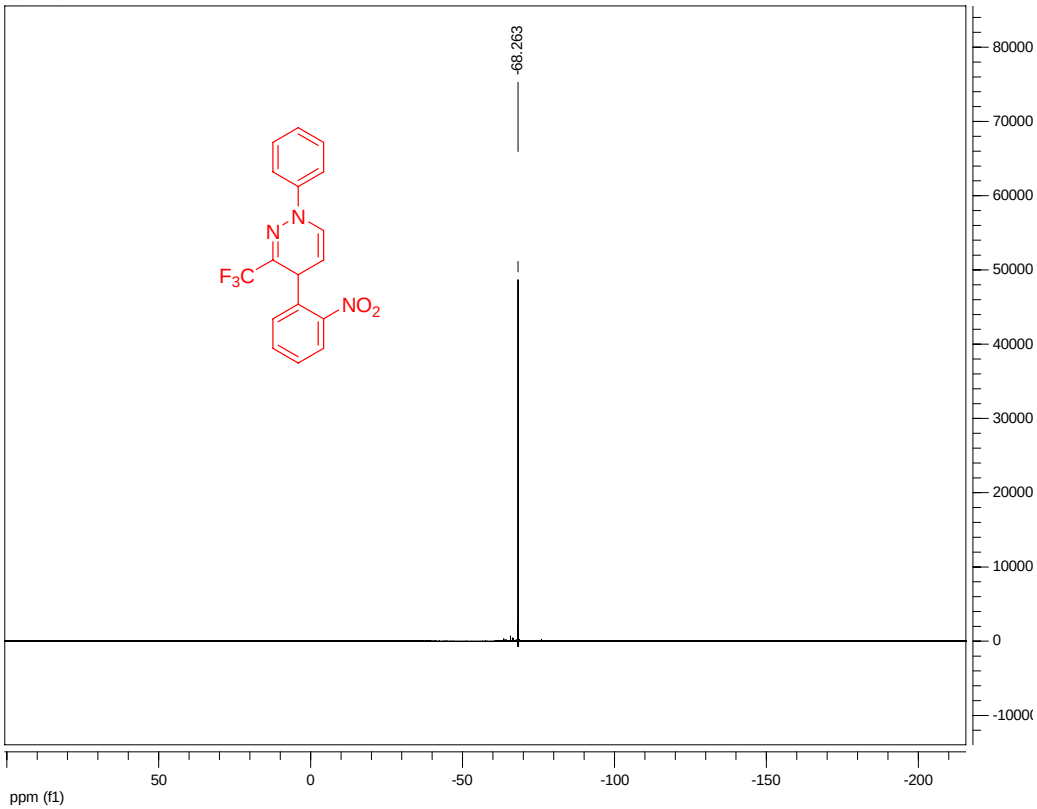
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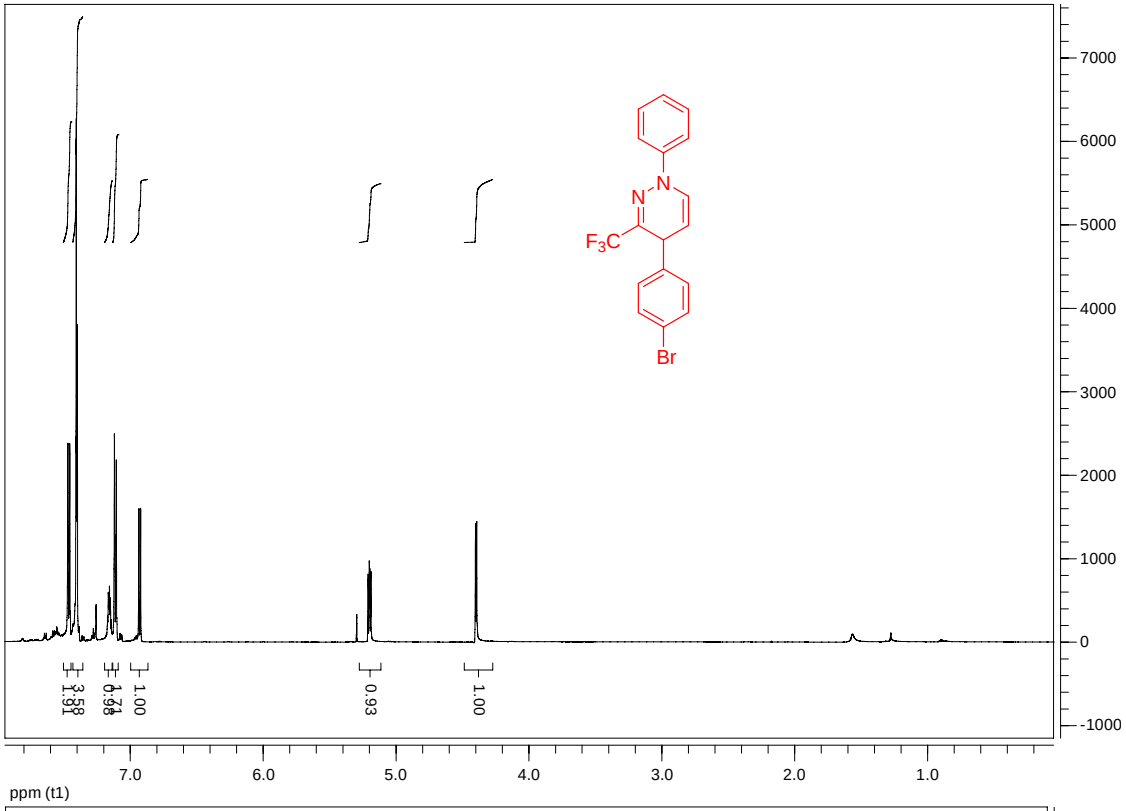
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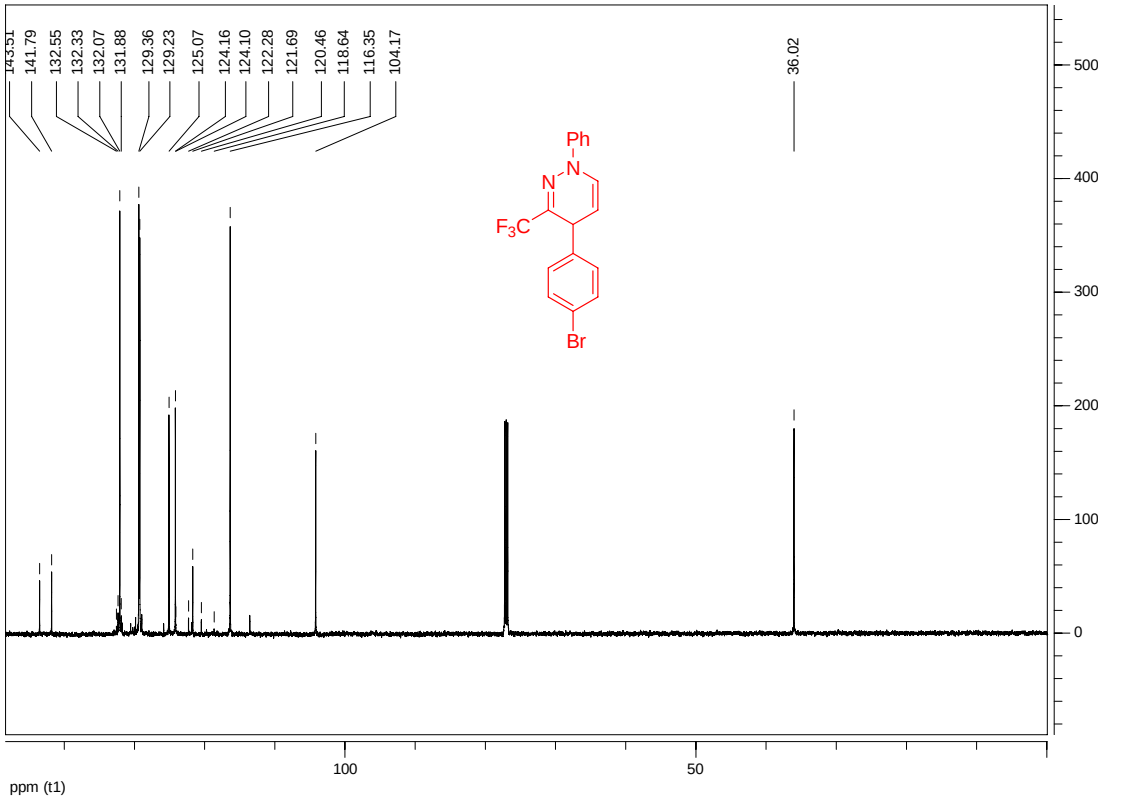
Br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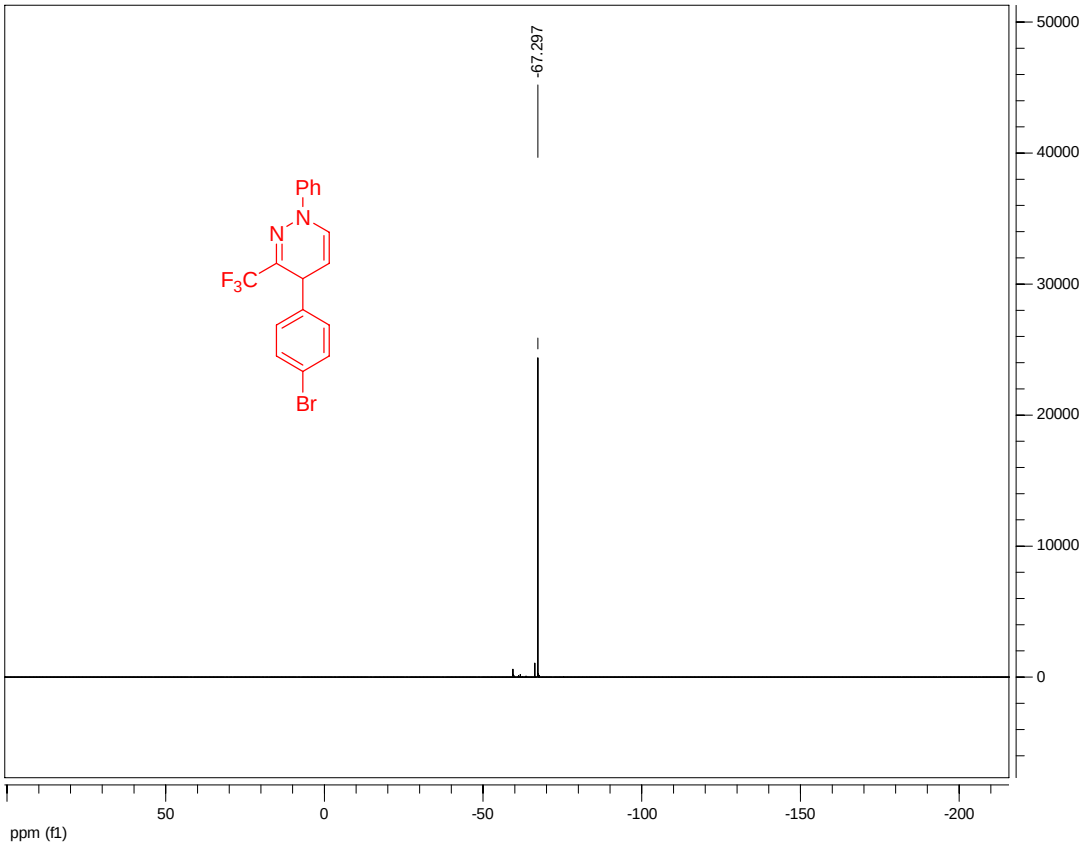
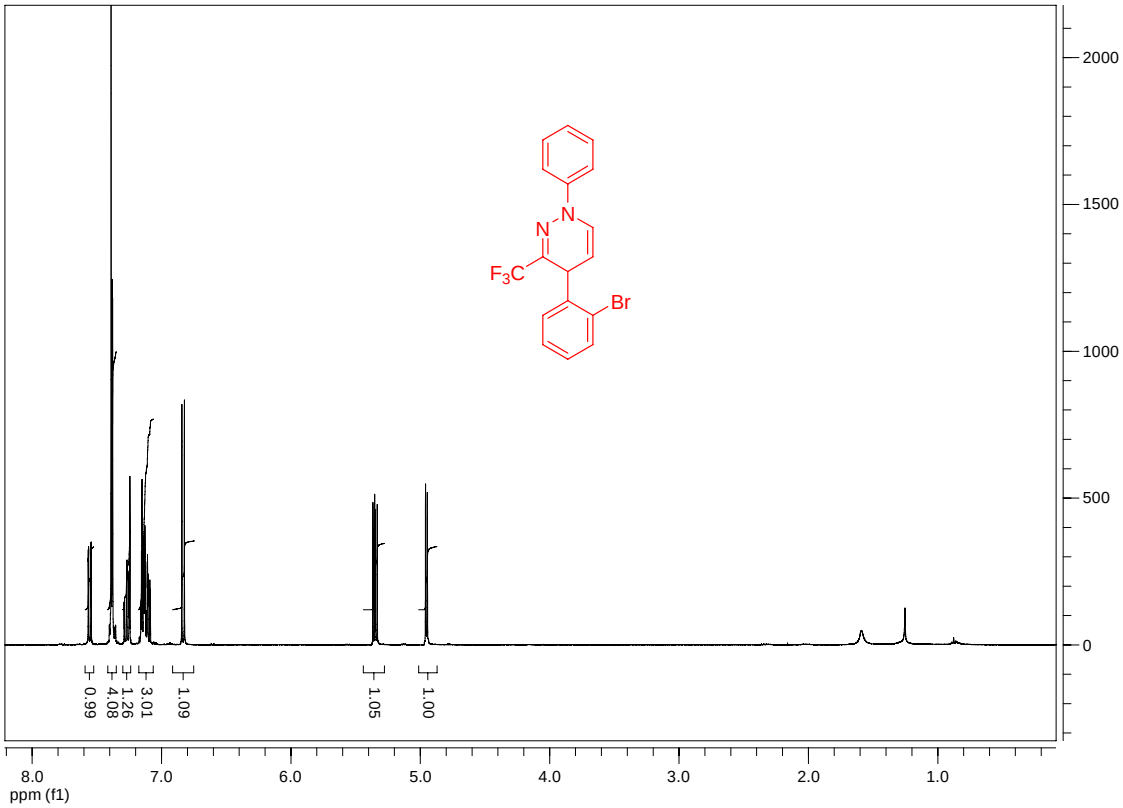
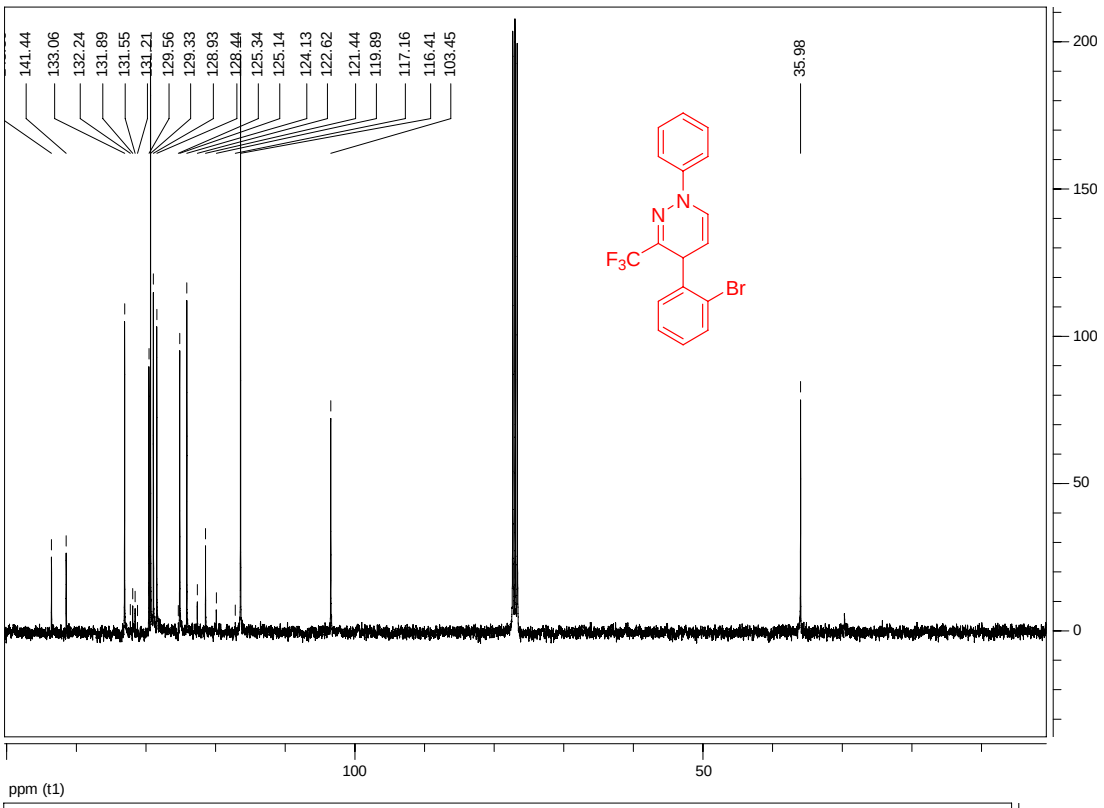
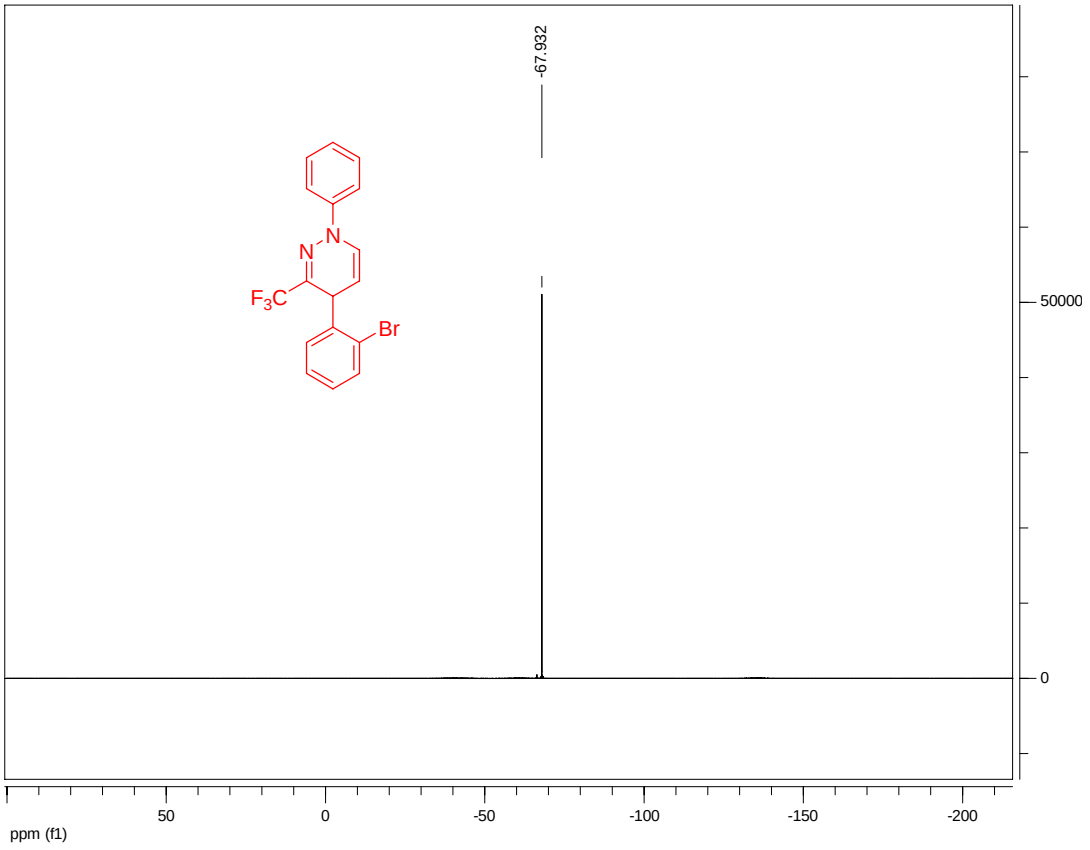
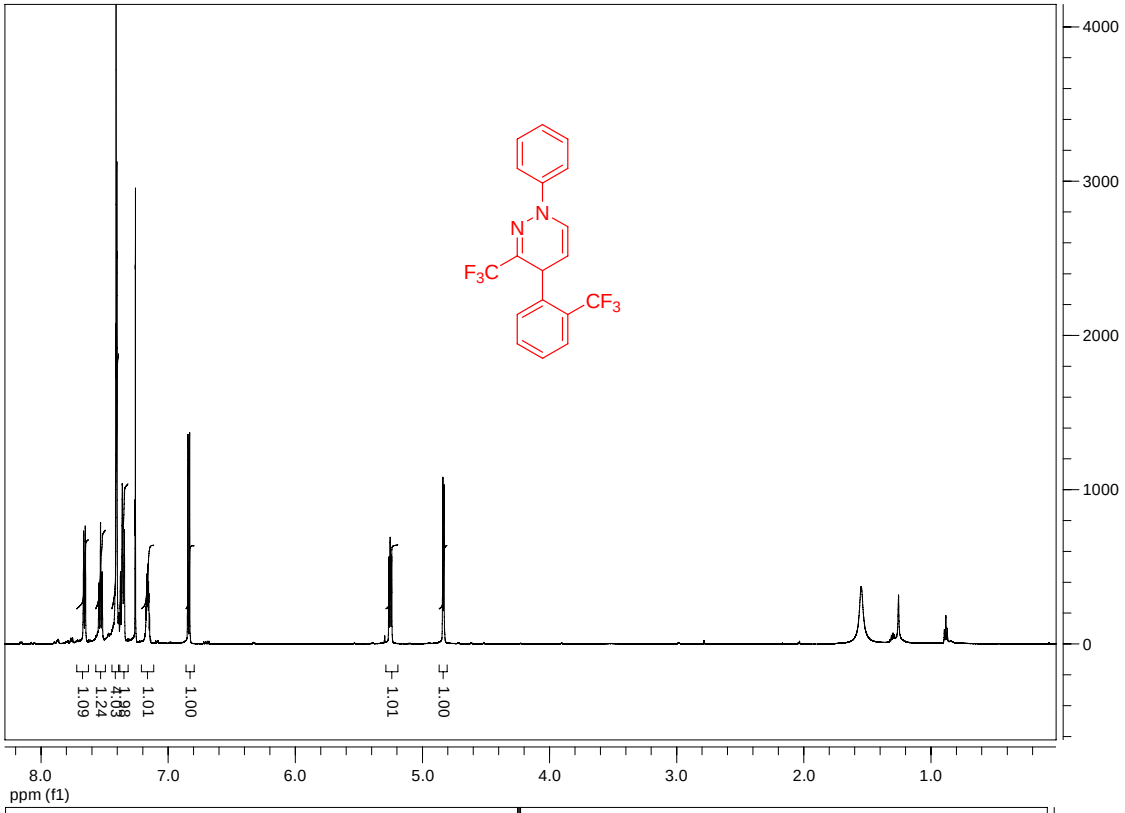
400
300
200
100
0
100
50
ppm (t1)
Ph
N
N
F3C
Br

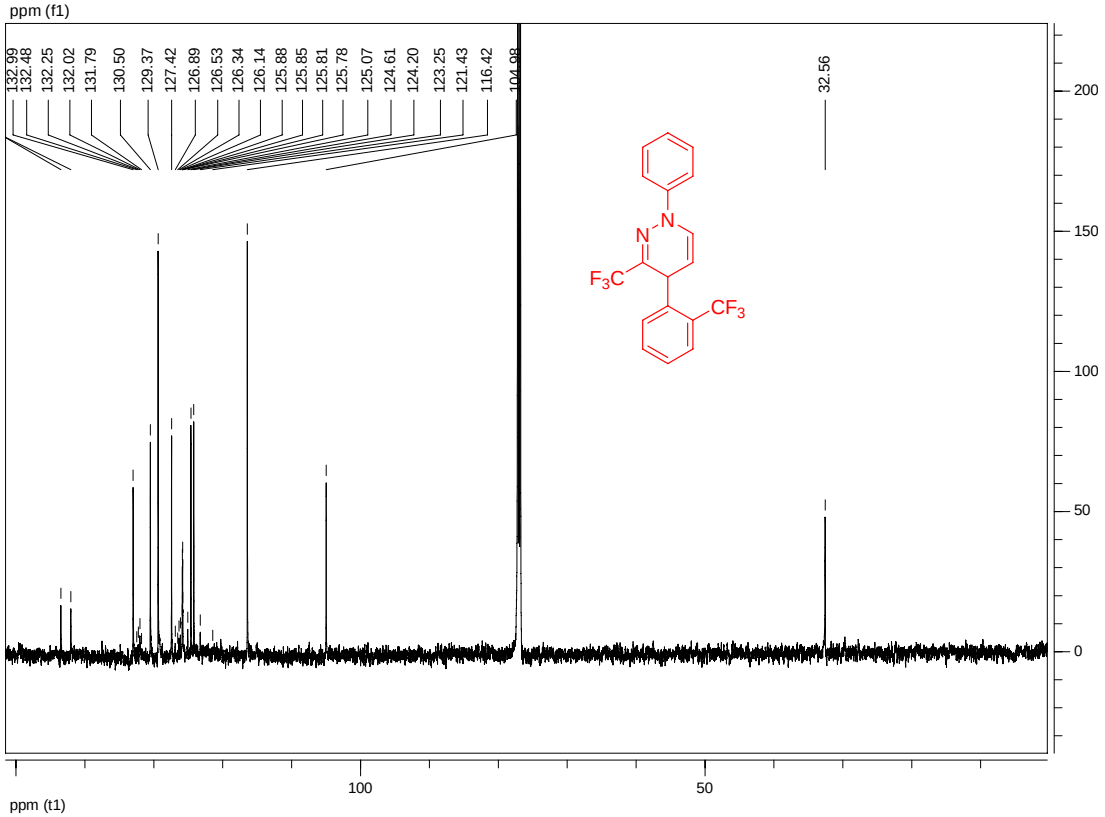

-67.297
Ph
N
N
F3C
Br
50000
40000
30000
20000
10000
0
50
0
-50
-100
-150
-200
ppm (f1)

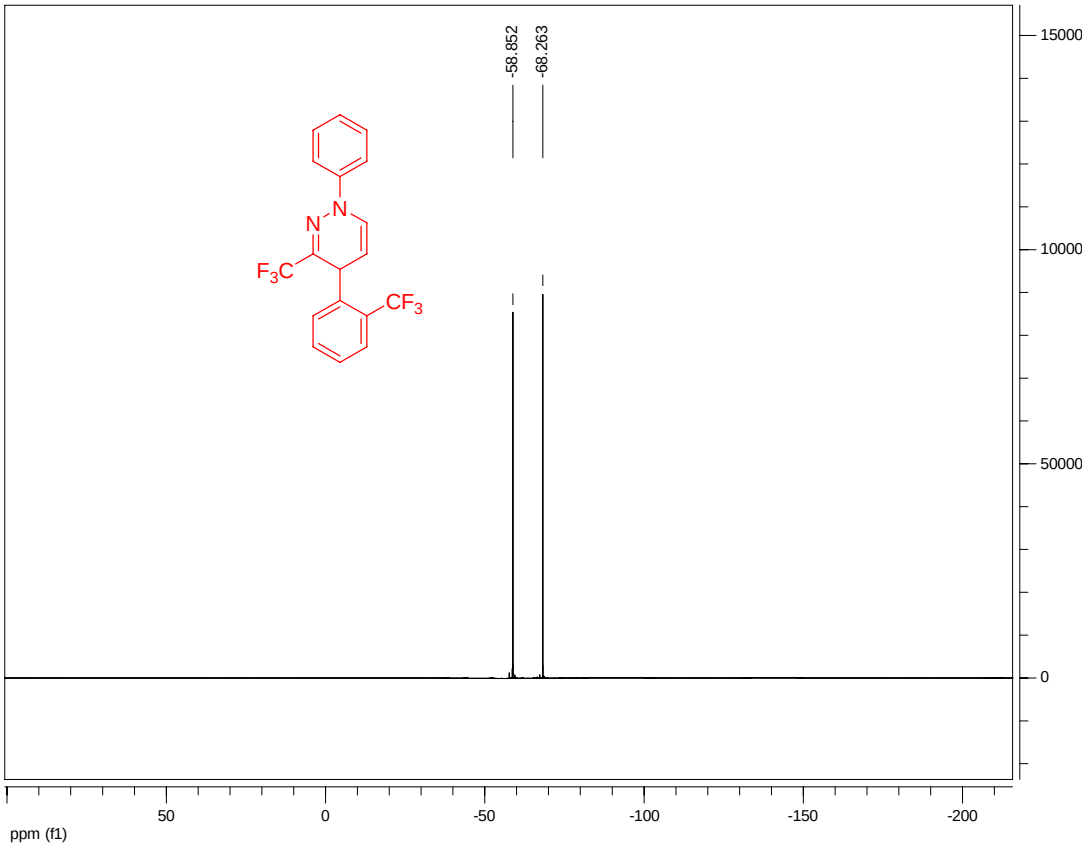

N
N
F3C
Br
2000
1500
1000
500
0
0.99
4.08
1.26
3.01
1.09
1.05
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

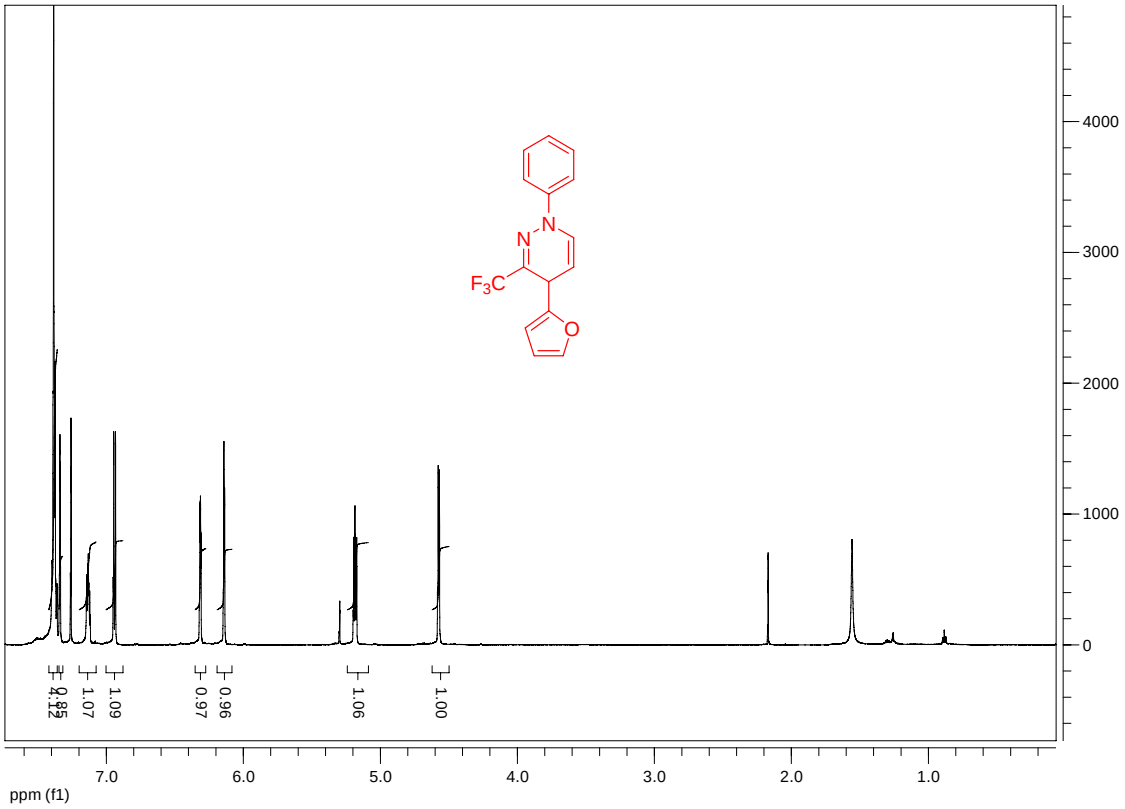

141.44
133.06
132.24
131.89
131.55
131.21
129.56
129.33
128.93
128.44
125.34
125.14
124.13
122.62
121.44
119.89
117.16
116.41
103.45
35.98
N
N
F3C
Br
200
150
100
50
0
100
50
ppm (t1)

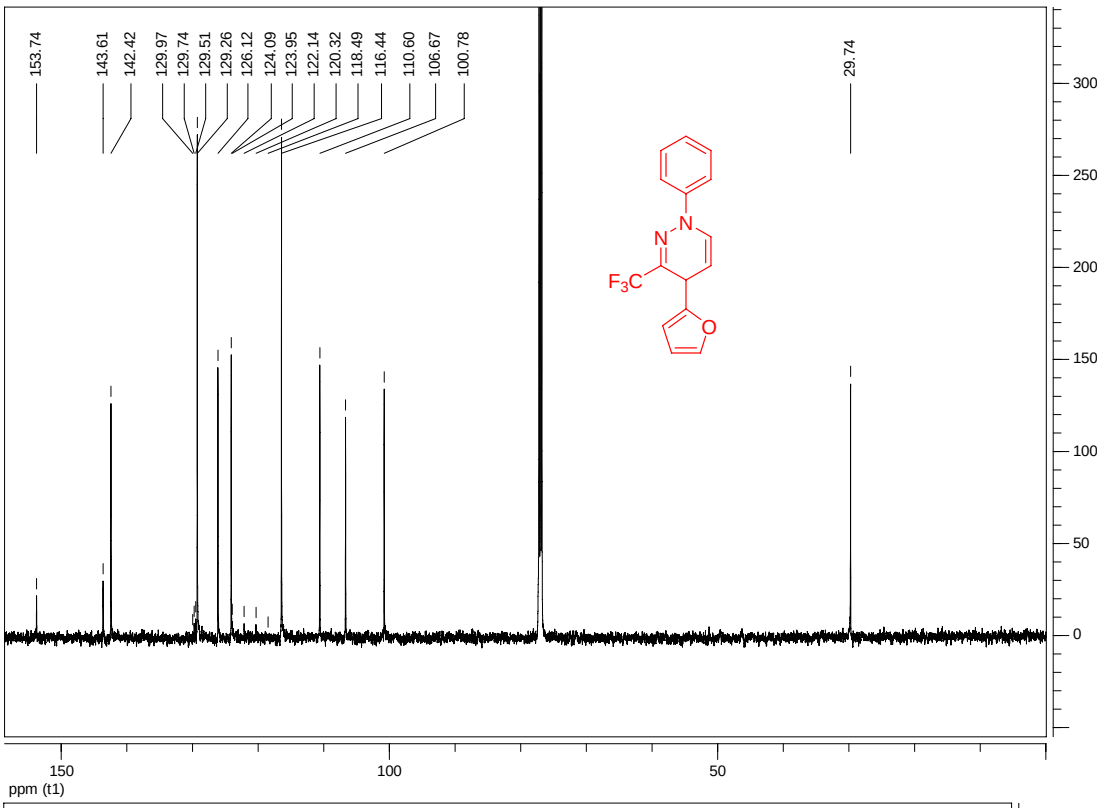

-67.932
N
N
F3C
Br
50000
0
50
0
-50
-100
-150
-200
ppm (f1)

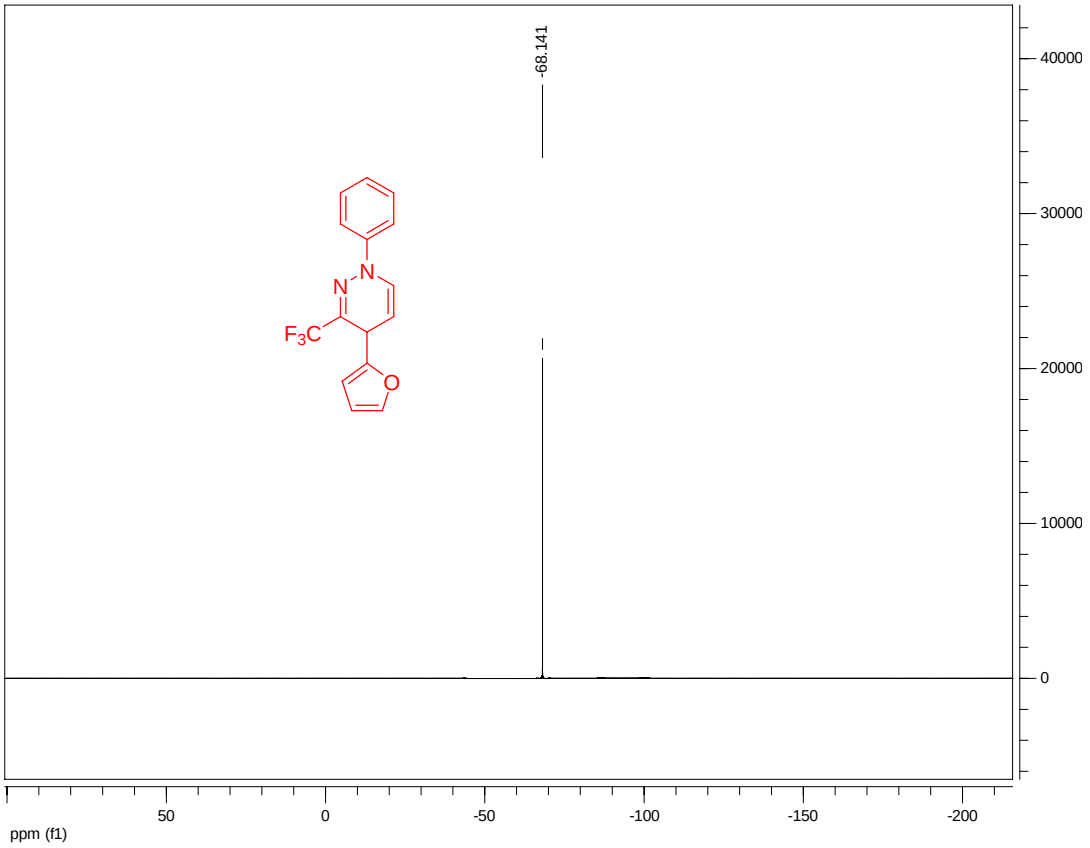

4000
3000
2000
1000
0
1.60
1.24
1.03
1.01
1.00
1.01
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
N
N
F3C
CF3

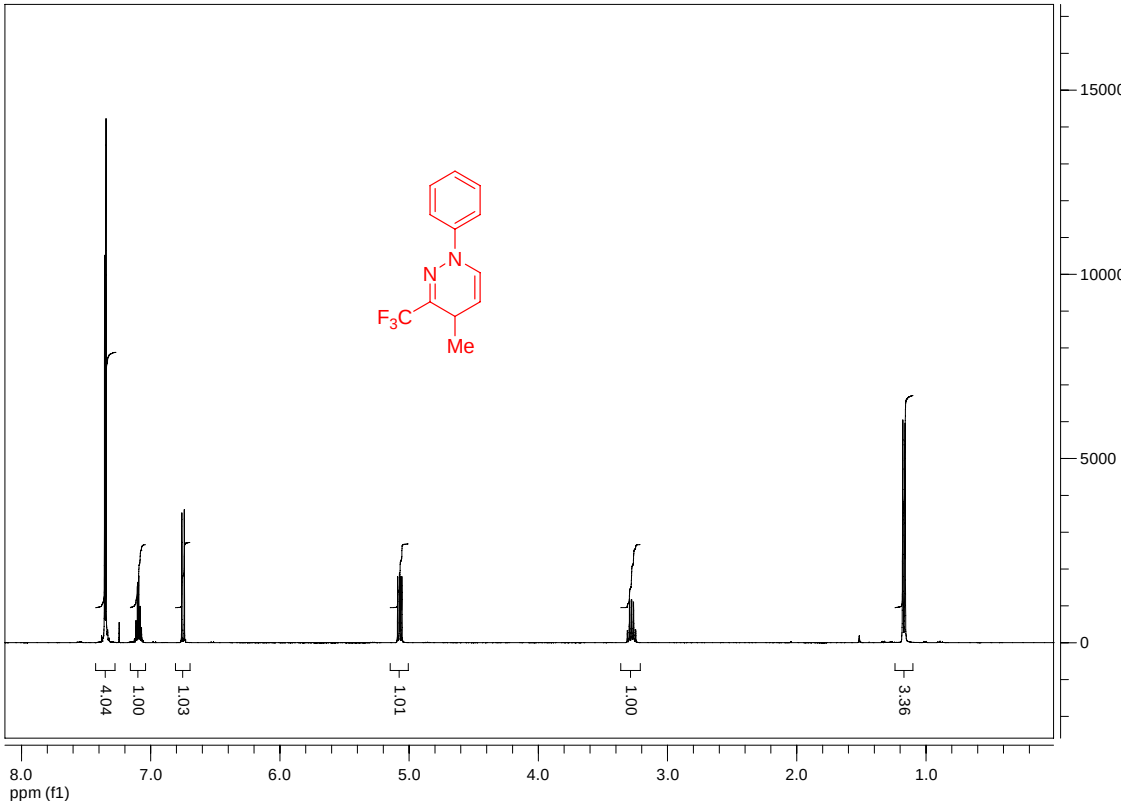

132.99
132.48
132.25
132.02
131.79
130.50
129.37
127.42
126.89
126.53
126.34
126.14
125.88
125.85
125.81
125.78
125.07
124.61
124.20
123.25
121.43
116.42
104.98
32.56
200
150
100
50
0
100
50
ppm (t1)
N
N
F3C
CF3

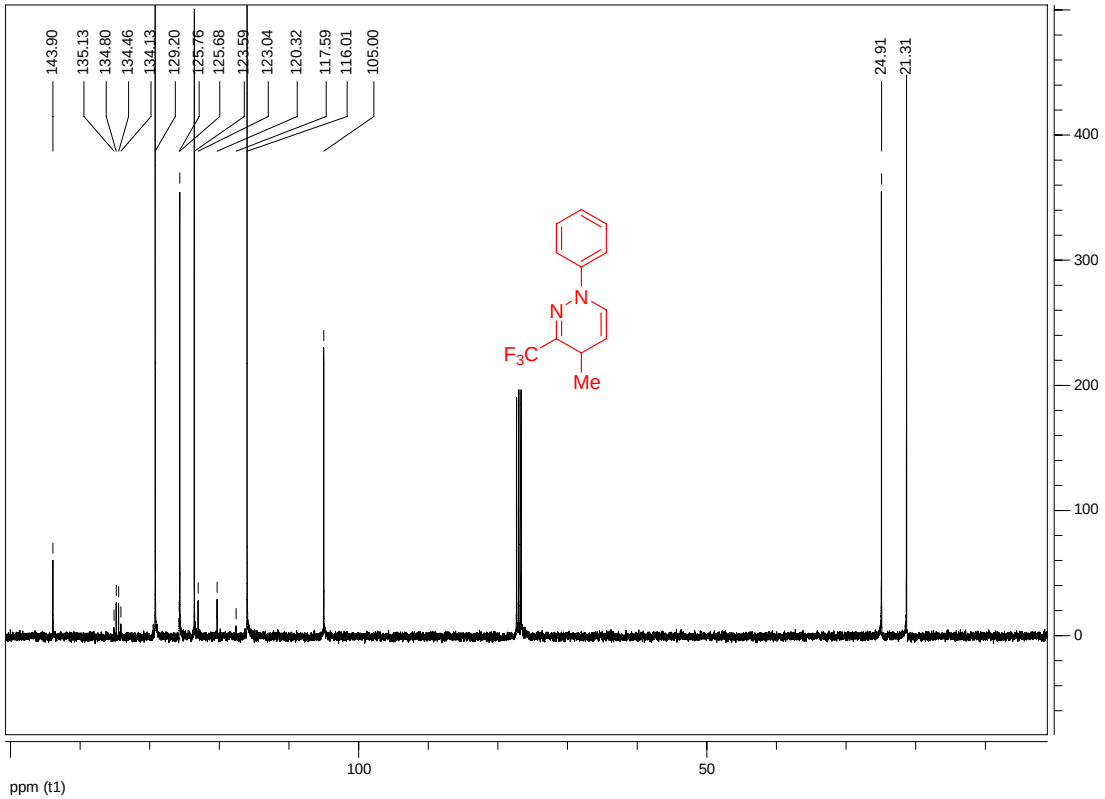

-58.852
-68.263
15000
10000
50000
0
N
N
F3C
CF3
50
0
-50
-100
-150
-200
ppm (f1)

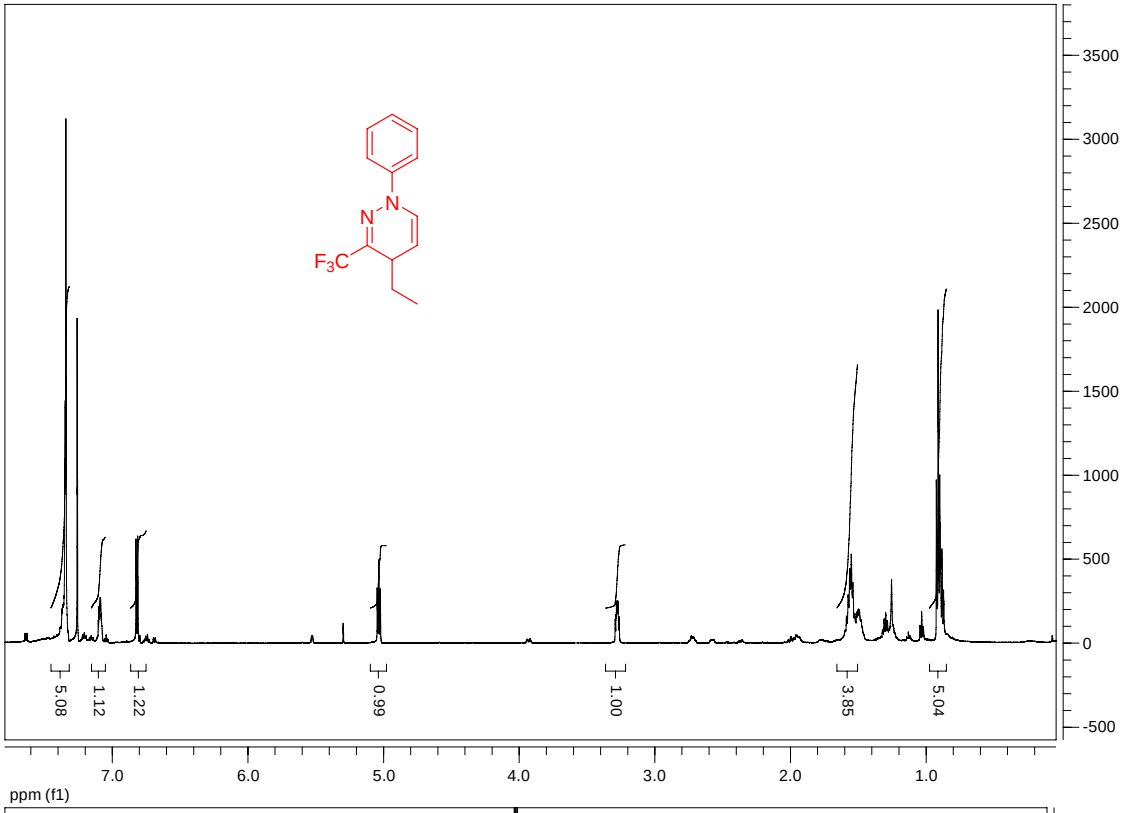

4000
3000
2000
1000
0
N
N
F3C
O
0.85
1.07
1.09
0.97
0.96
1.06
1.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

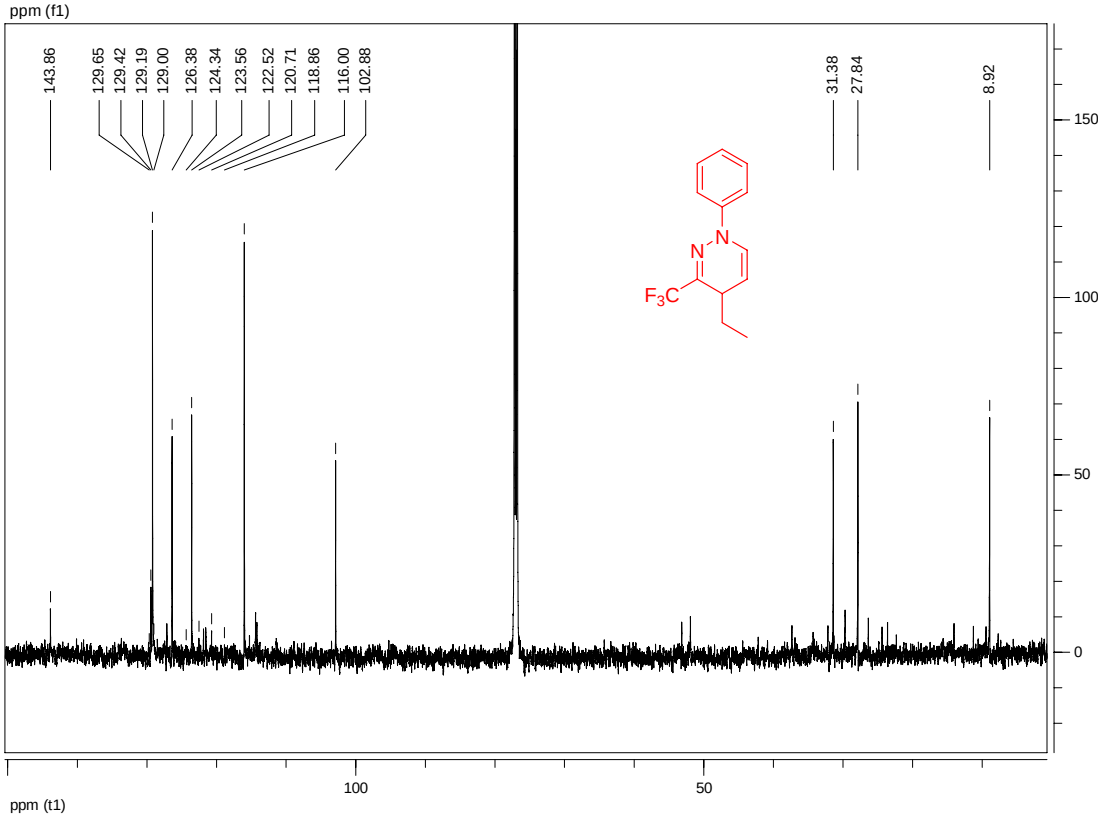

153.74
143.61
142.42
129.97
129.74
129.51
129.26
126.12
124.09
123.95
122.14
120.32
118.49
116.44
110.60
106.67
100.78
29.74
N
N
F3C
O
300
250
200
150
100
50
0
150
100
50
ppm (t1)

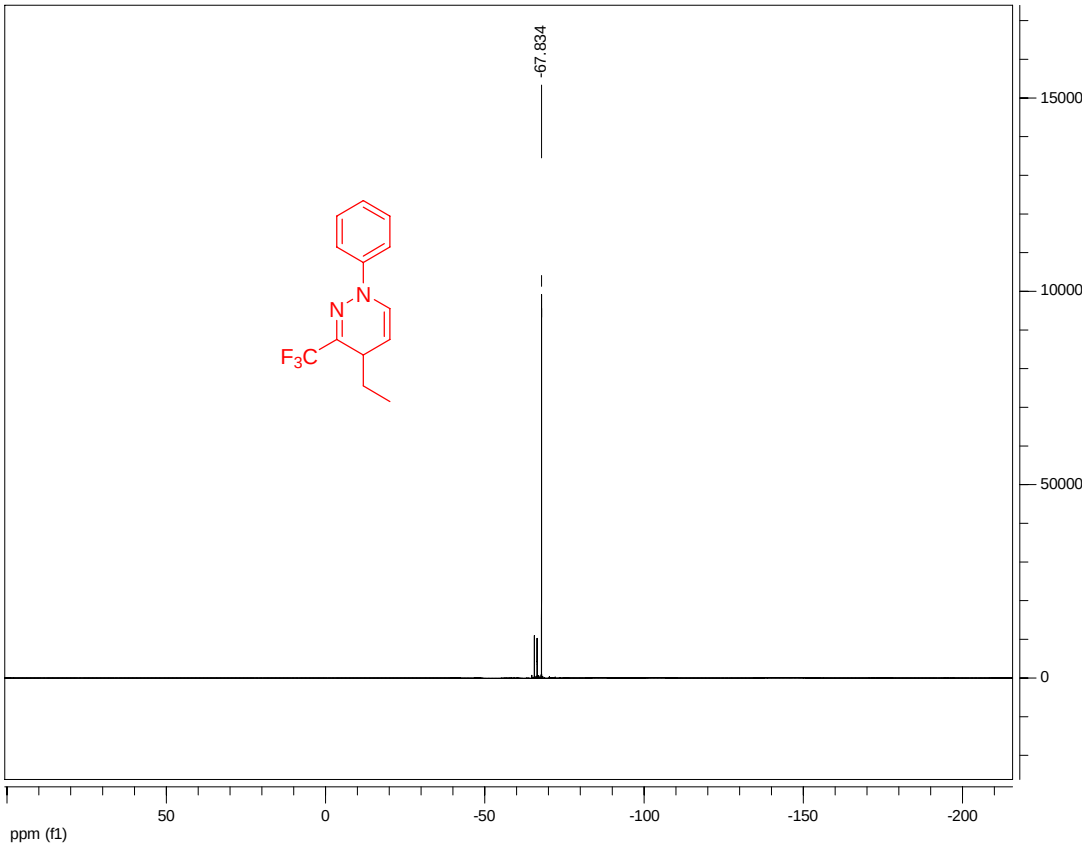

-68.141
N
N
F3C
O
40000
30000
20000
10000
0
50
0
-50
-100
-150
-200
ppm (f1)

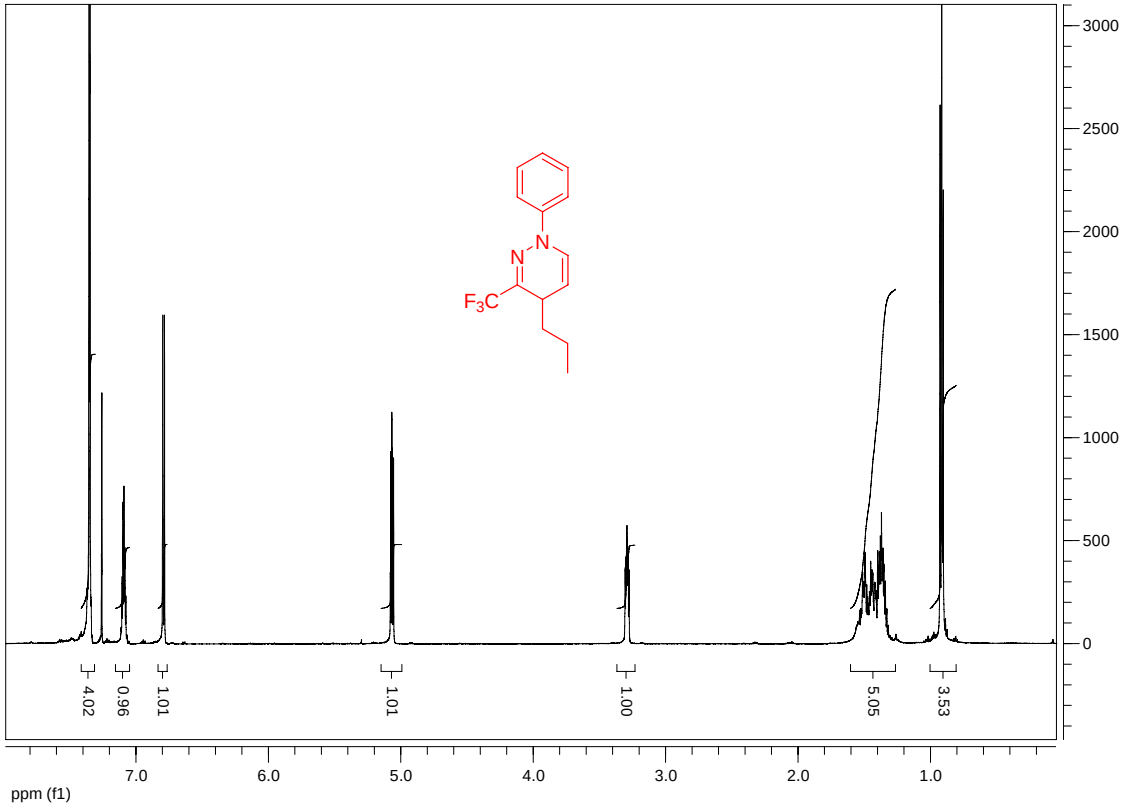

15000
10000
5000
0
4.04
1.00
1.03
1.01
1.00
3.36
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
N
N
F3C
Me

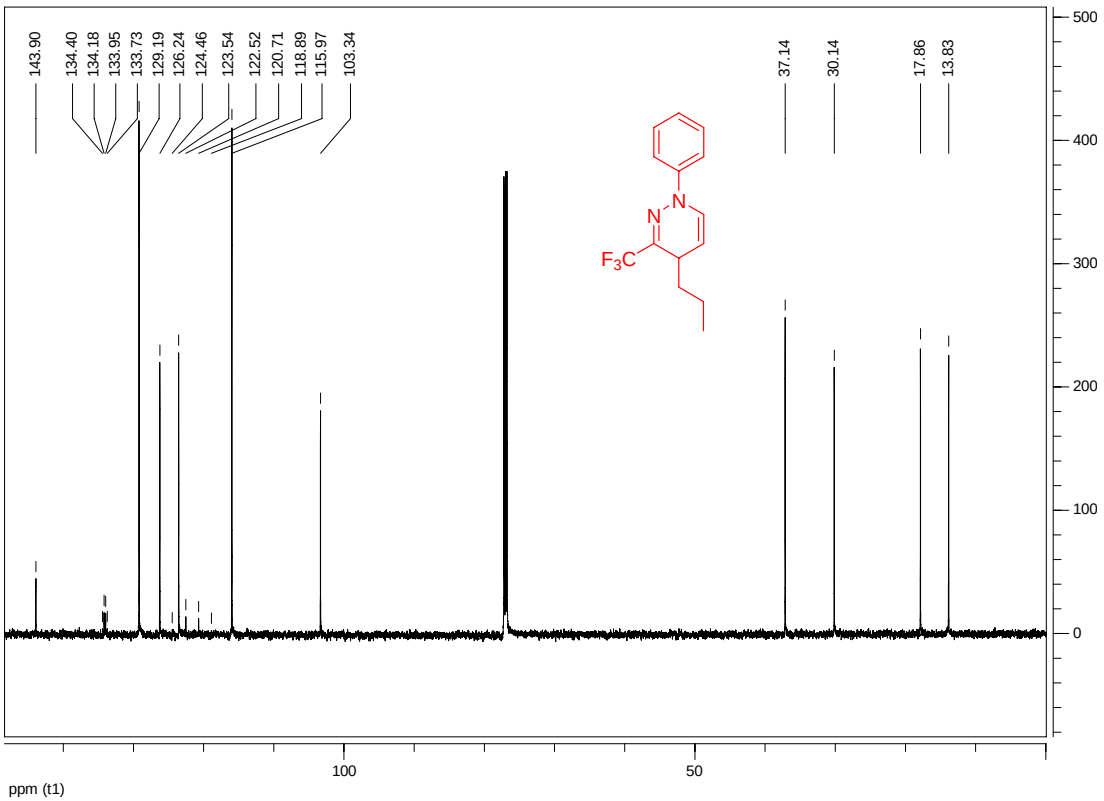

143.90
135.13
134.80
134.46
134.13
129.20
125.76
125.68
123.59
123.04
120.32
117.59
116.01
105.00
24.91
21.31
400
300
200
100
0
100
50
ppm (t1)
N
N
F3C
Me

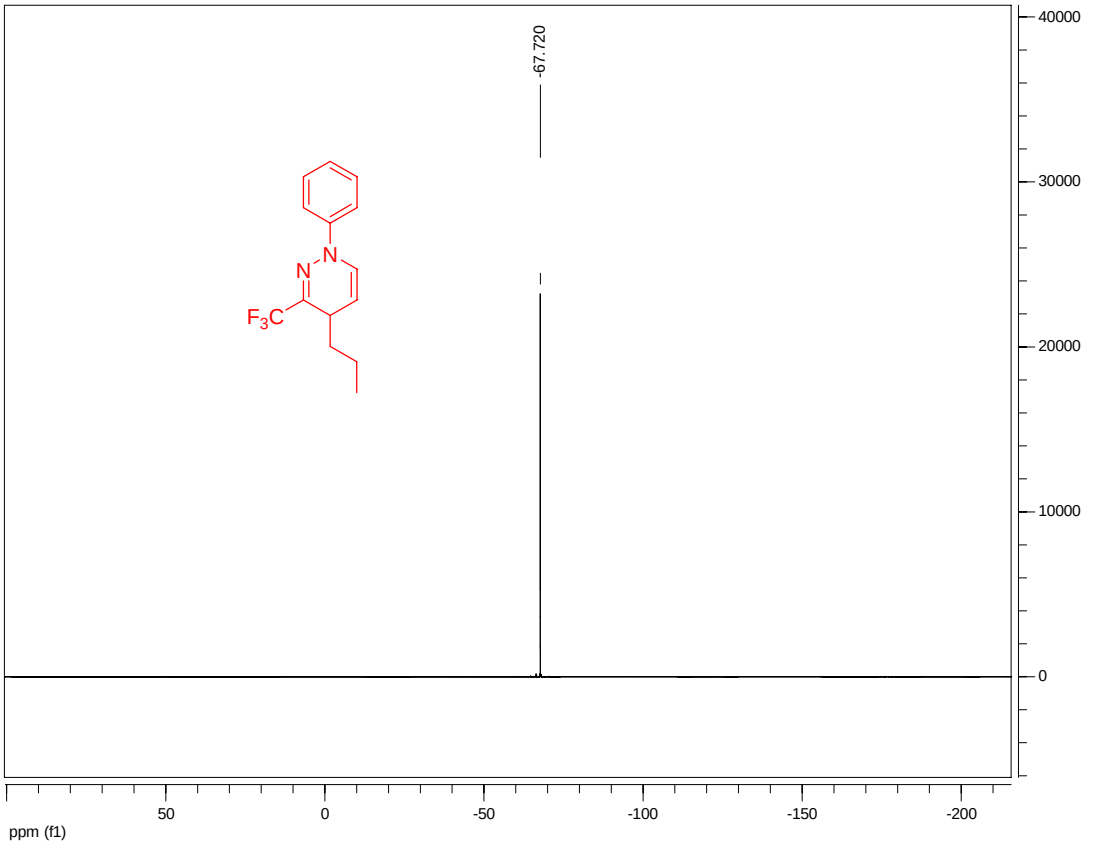

3500
3000
2500
2000
1500
1000
500
0
-500
5.08
1.12
1.22
0.99
1.00
3.85
5.04
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

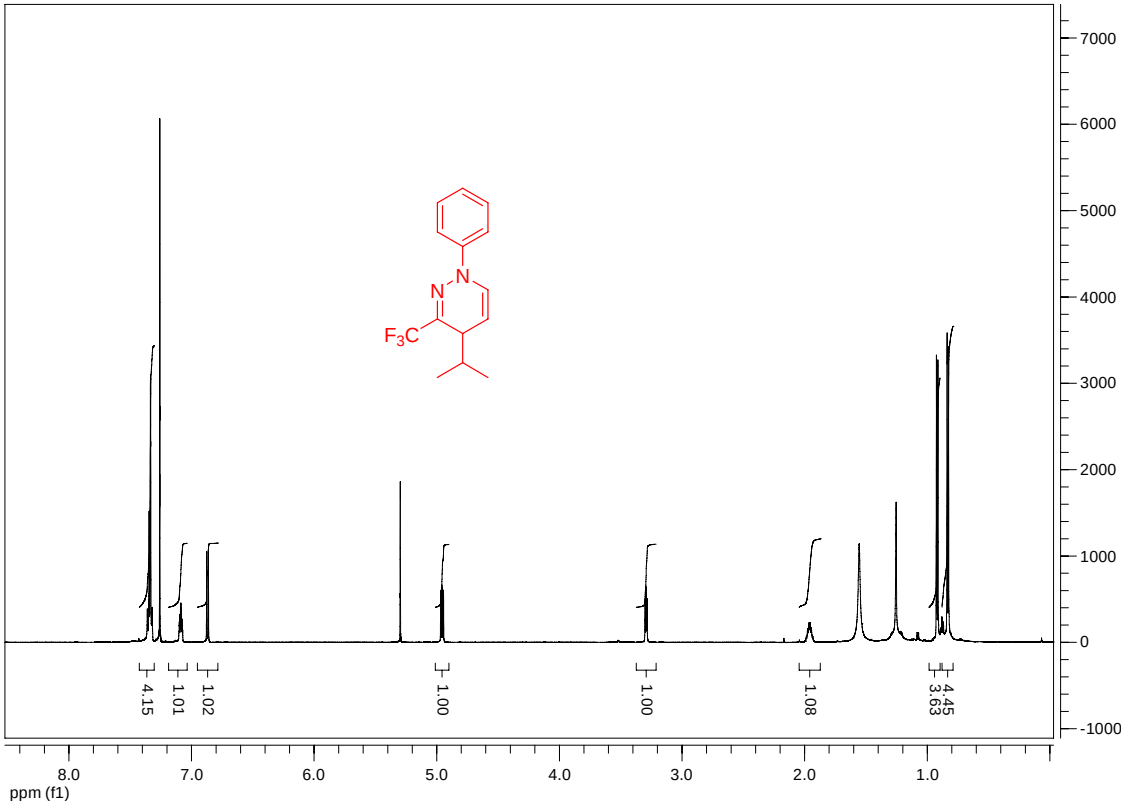

143.86
129.65
129.42
129.19
129.00
126.38
124.34
123.56
122.52
120.71
118.86
116.00
102.88
31.38
27.84
8.92
150
100
50
0
100
50
ppm (t1)

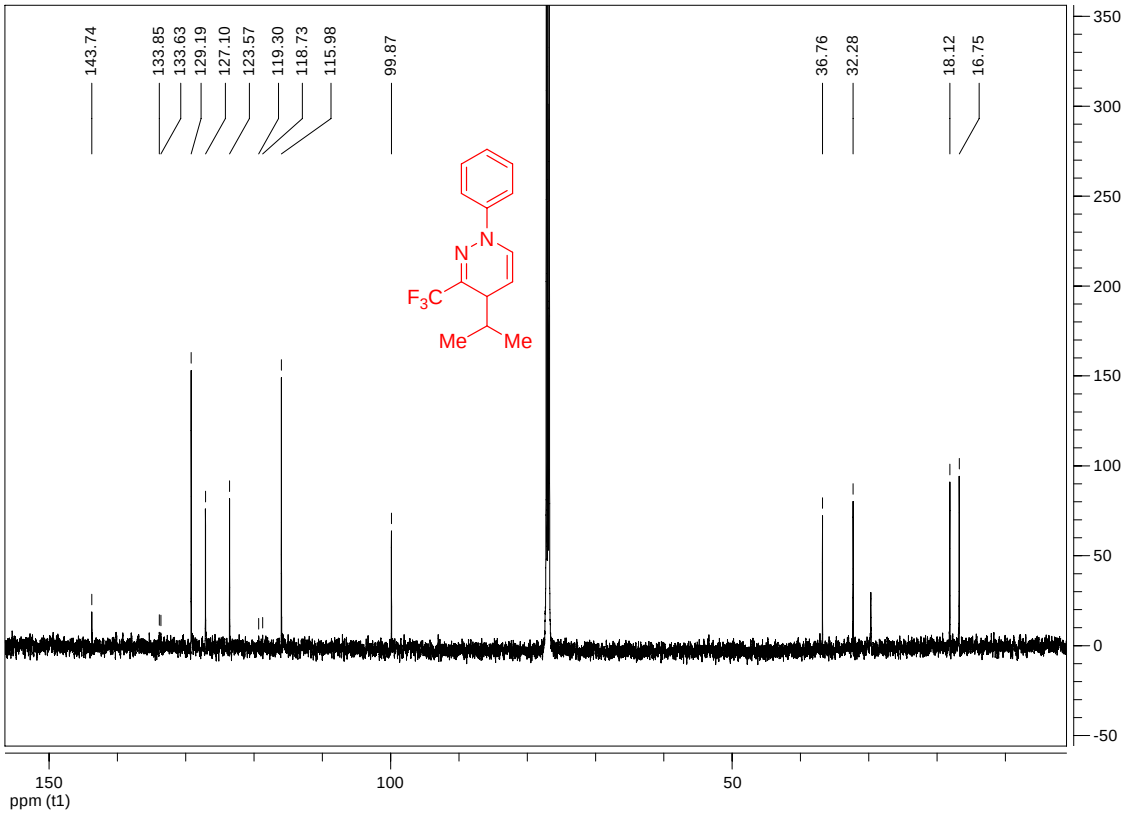

-67.834
15000
10000
50000
0
50
0
-50
-100
-150
-200
ppm (f1)
N
N
F3C

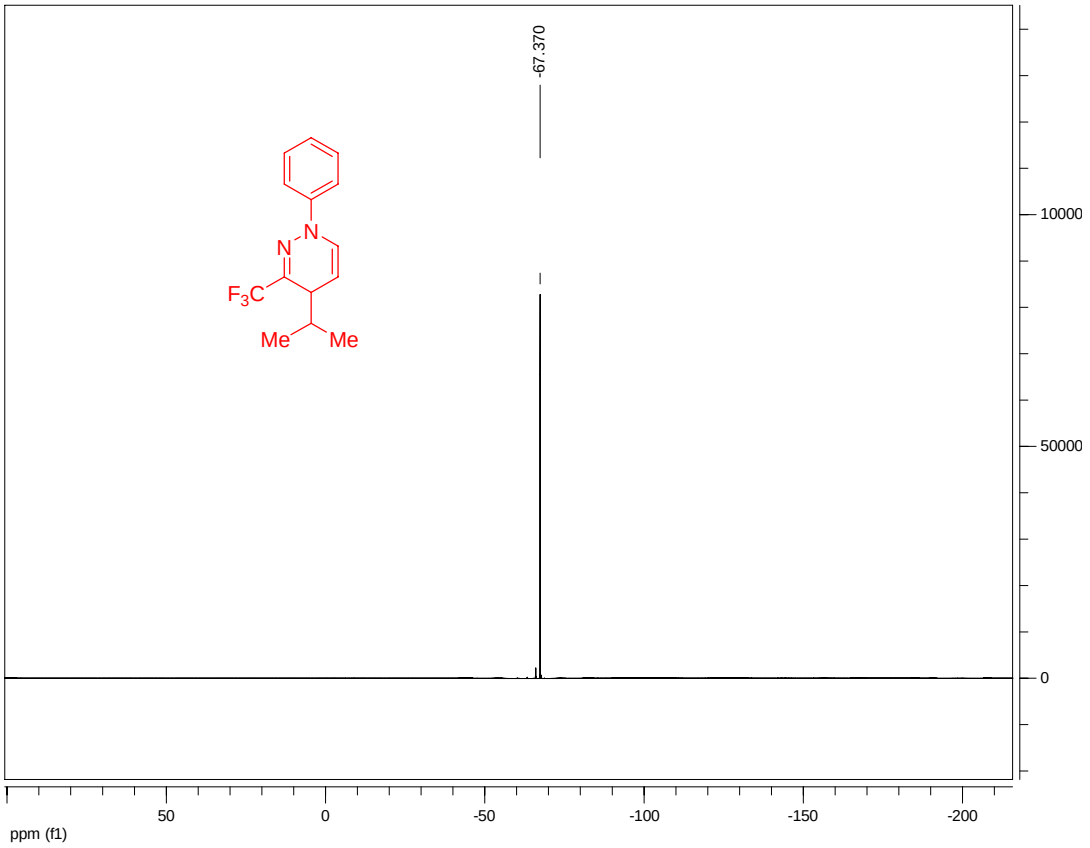

3000
2500
2000
1500
1000
500
0
4.02
0.96
1.01
1.01
1.00
5.05
3.53
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
N
N
F3C

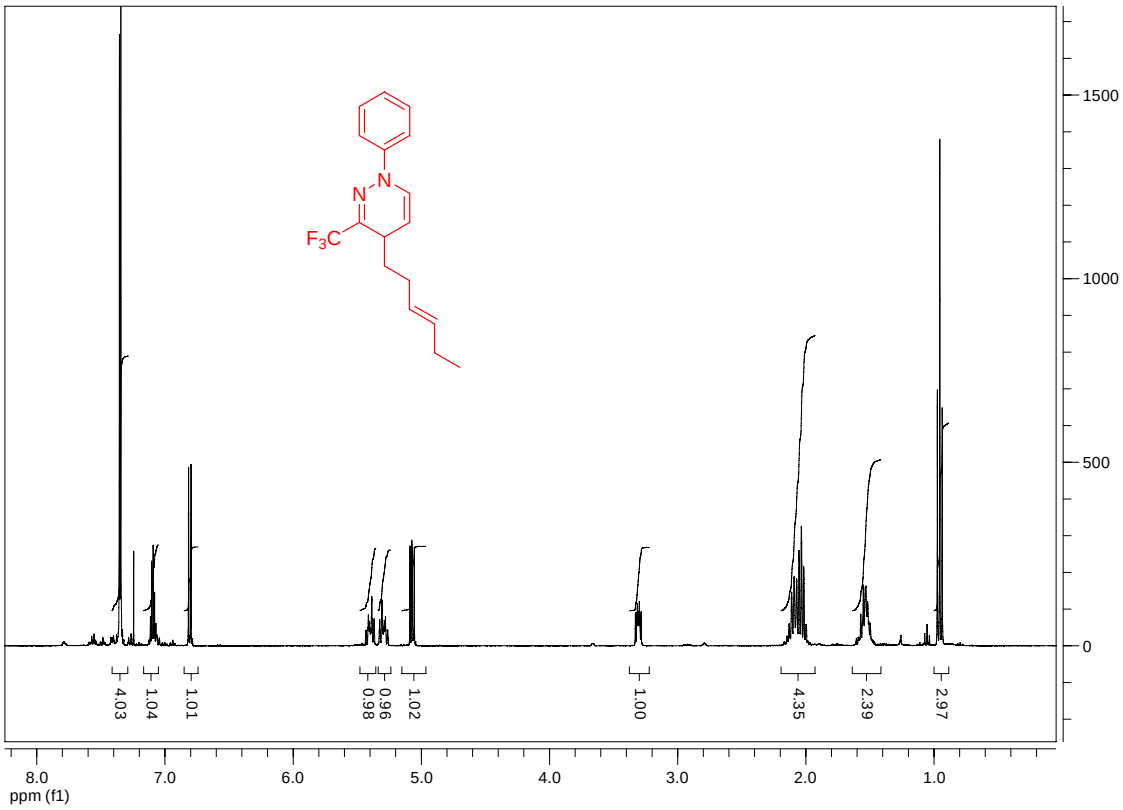

143.90
134.40
134.18
133.95
133.73
129.19
126.24
124.46
123.54
122.52
120.71
118.89
115.97
103.34
37.14
30.14
17.86
13.83
N
N
F3C
500
400
300
200
100
0
100
50
ppm (t1)

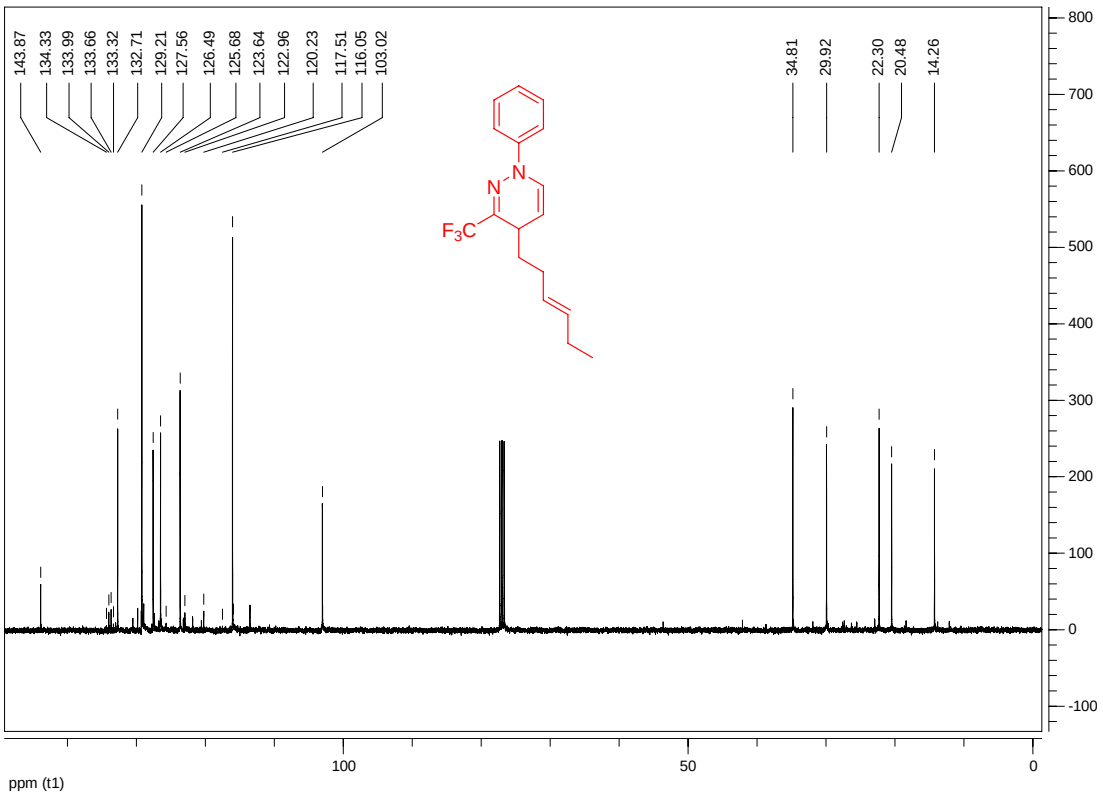

-67.720
N
N
F3C
40000
30000
20000
10000
0
50
0
-50
-100
-150
-200
ppm (f1)

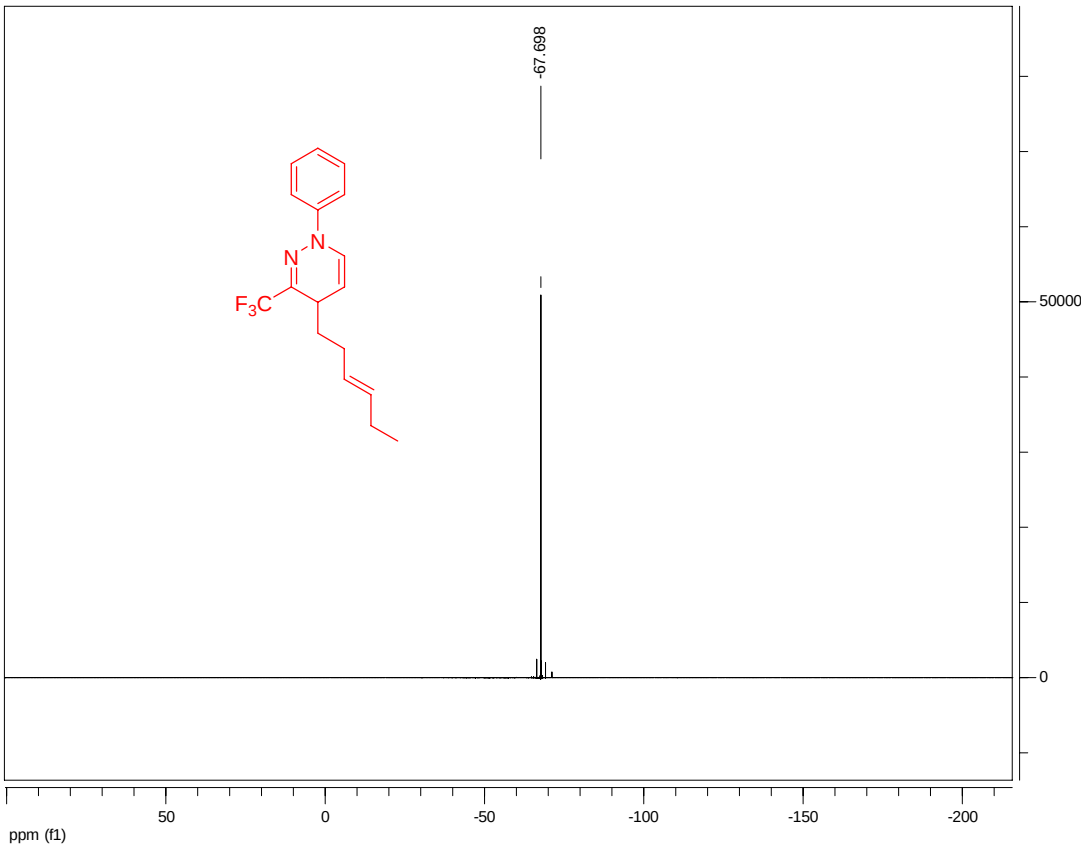

7000
6000
5000
4000
3000
2000
1000
0
-1000
4.15
1.01
1.02
1.00
1.00
1.08
4.45
3.63
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
N
N
F3C


143.74
133.85
133.63
129.19
127.10
123.57
119.30
118.73
115.98
99.87
36.76
32.28
18.12
16.75
350
300
250
200
150
100
50
0
-50
150
100
50
ppm (t1)
N
N
F3C
Me
Me


-67.370
N
N
F3C
Me
Me
10000
50000
0
50
0
-50
-100
-150
-200
ppm (f1)


N
N
F3C
1500
1000
500
0
4.03
1.04
1.01
0.98
0.96
1.02
1.00
4.35
2.39
2.97
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


143.87
134.33
133.99
133.66
133.32
132.71
129.21
127.56
126.49
125.68
123.64
122.96
120.23
117.51
116.05
103.02
34.81
29.92
22.30
20.48
14.26
N
N
F3C
800
700
600
500
400
300
200
100
0
-100
100
50
0
ppm (t1)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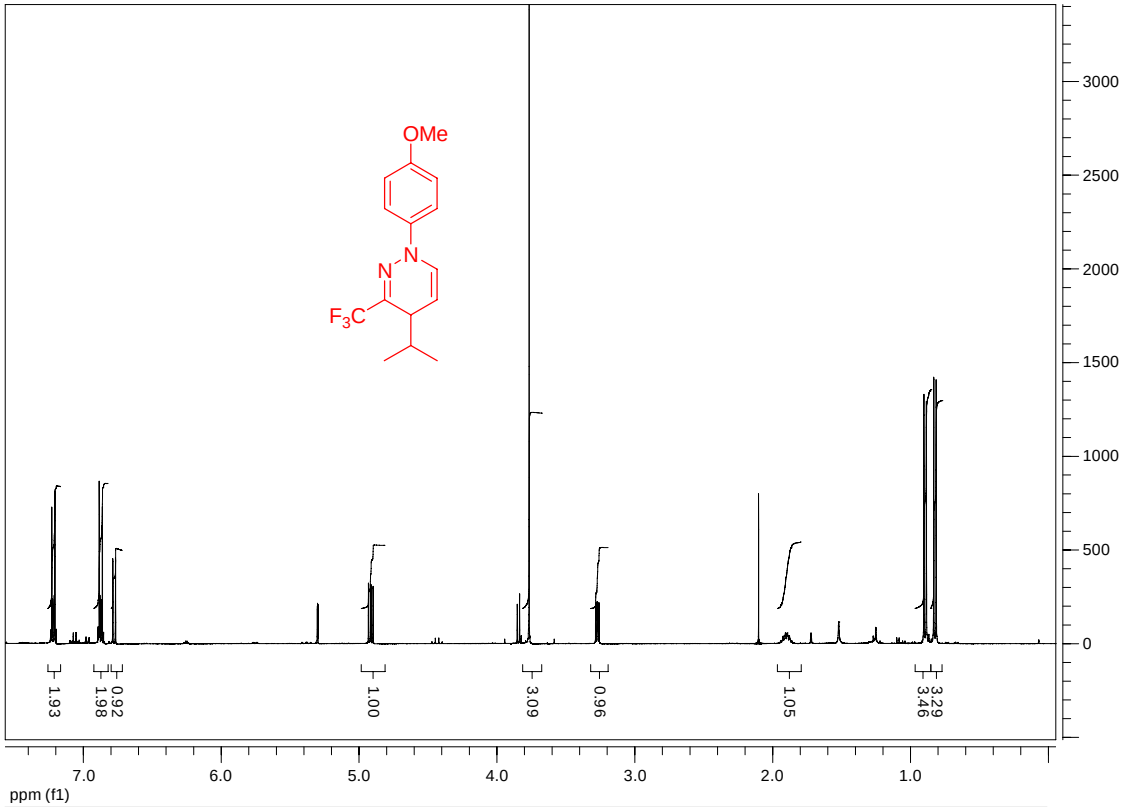
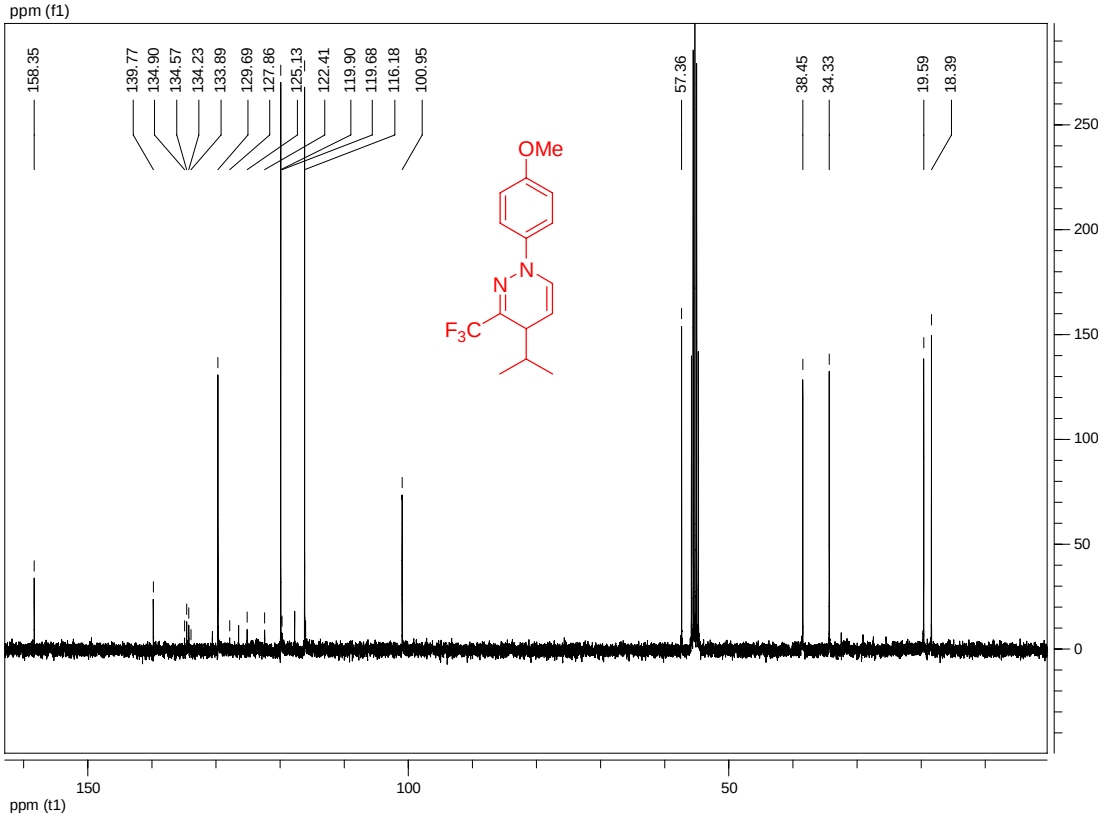
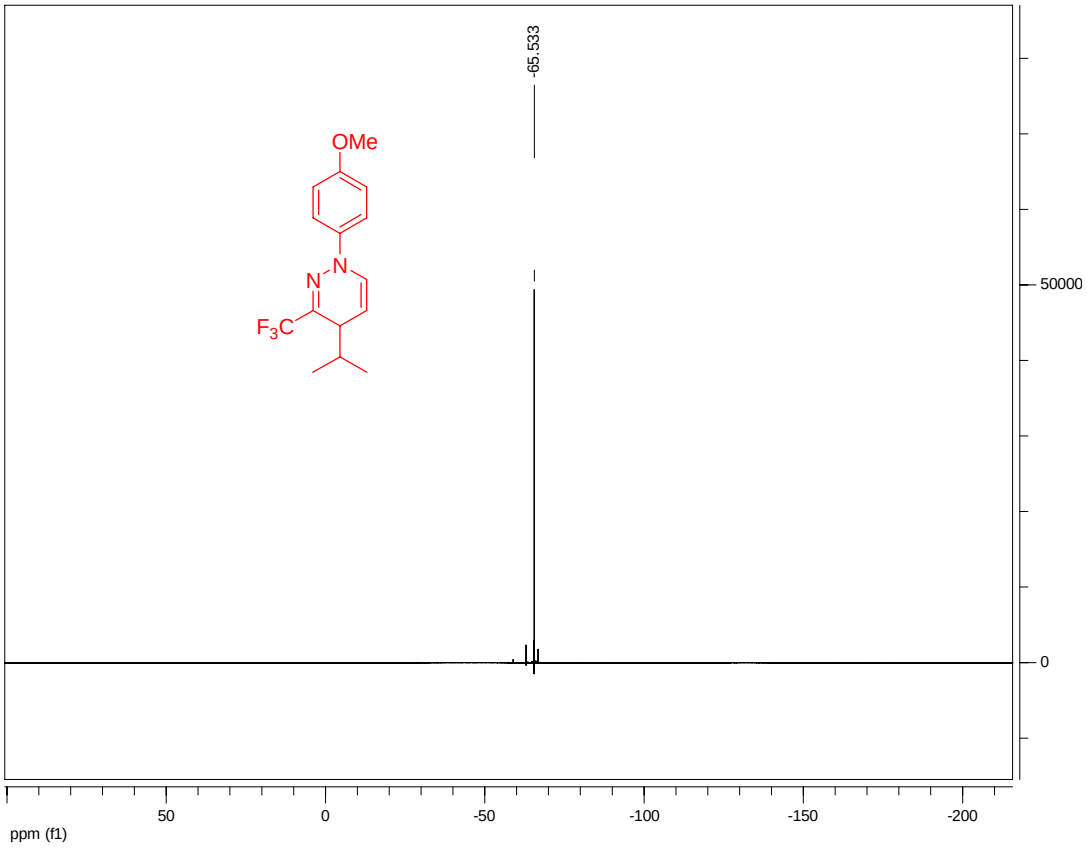
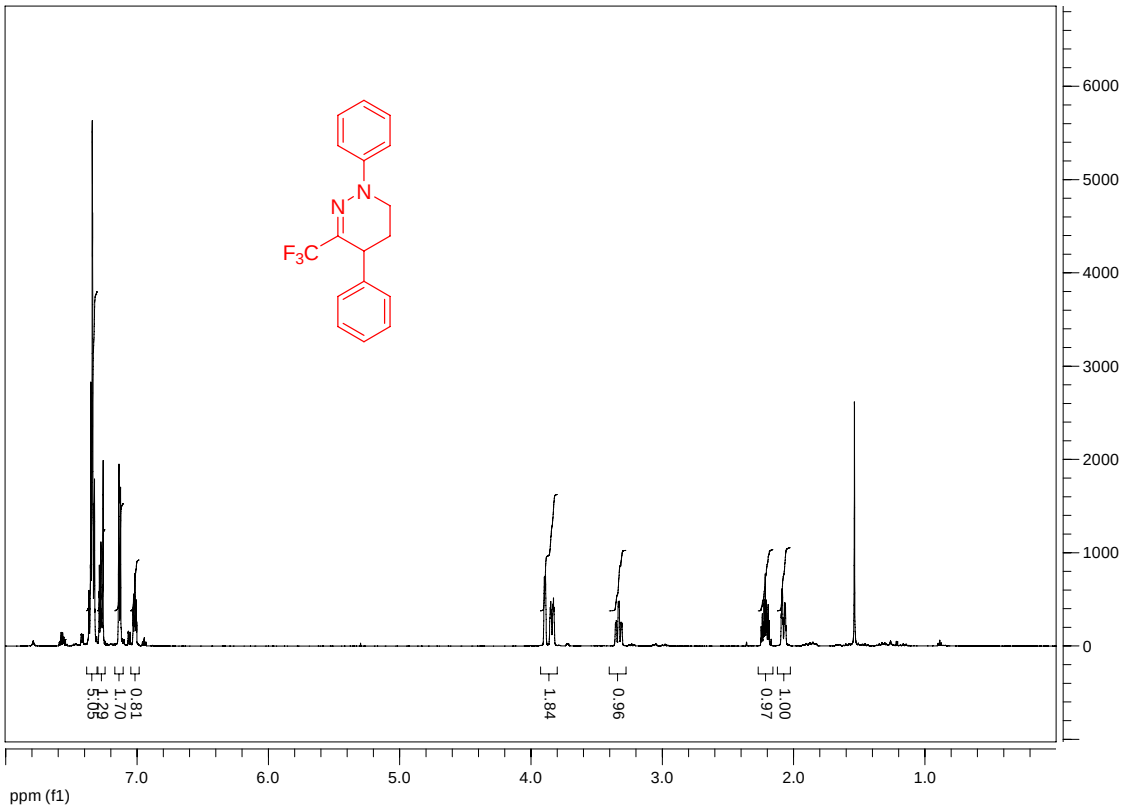
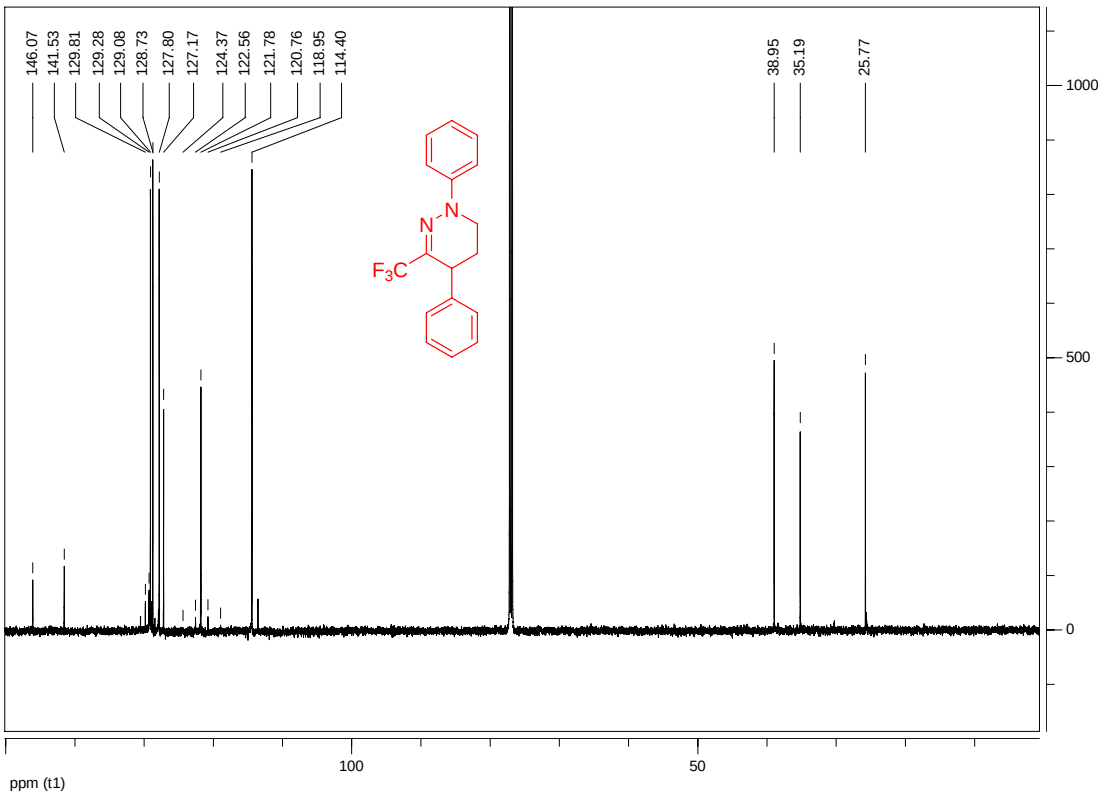
N
N
F3C
50000
0
50
0
-50
-100
-150
-200
ppm (f1)

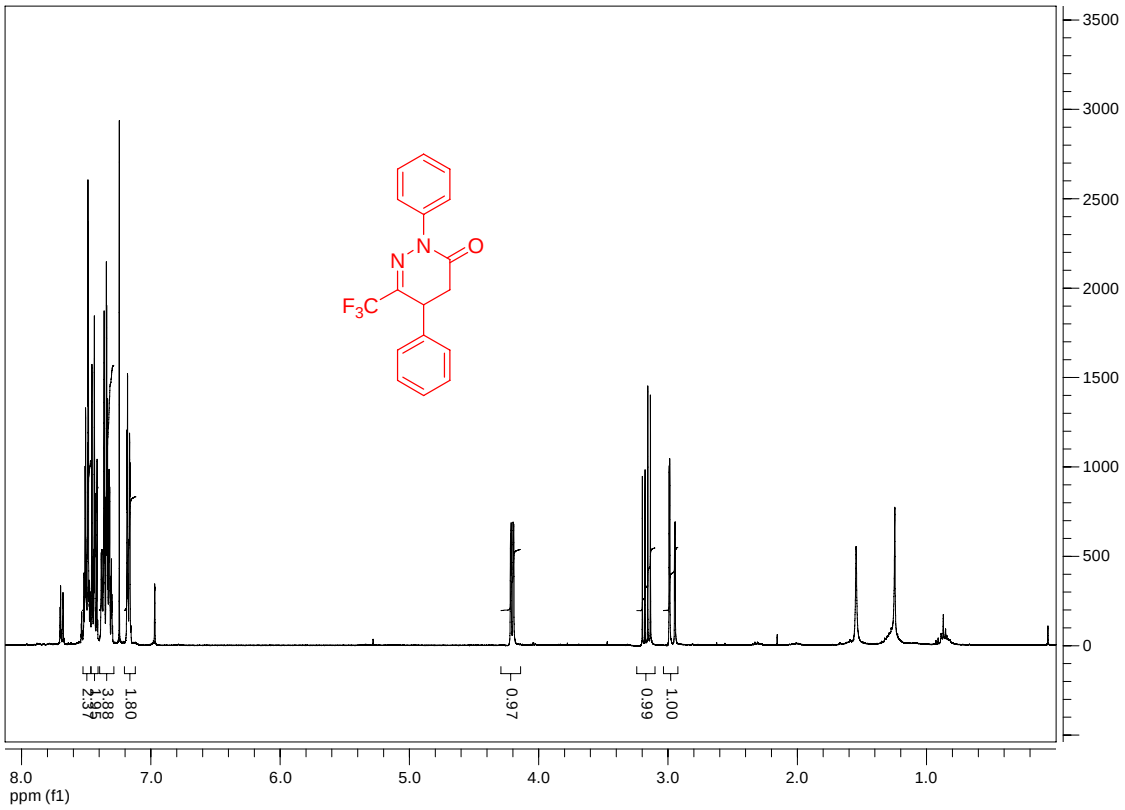

OMe
N
N
F3C
3000
2500
2000
1500
1000
500
0
1.93
1.98
0.92
1.00
3.09
0.99
1.05
3.29
3.46
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

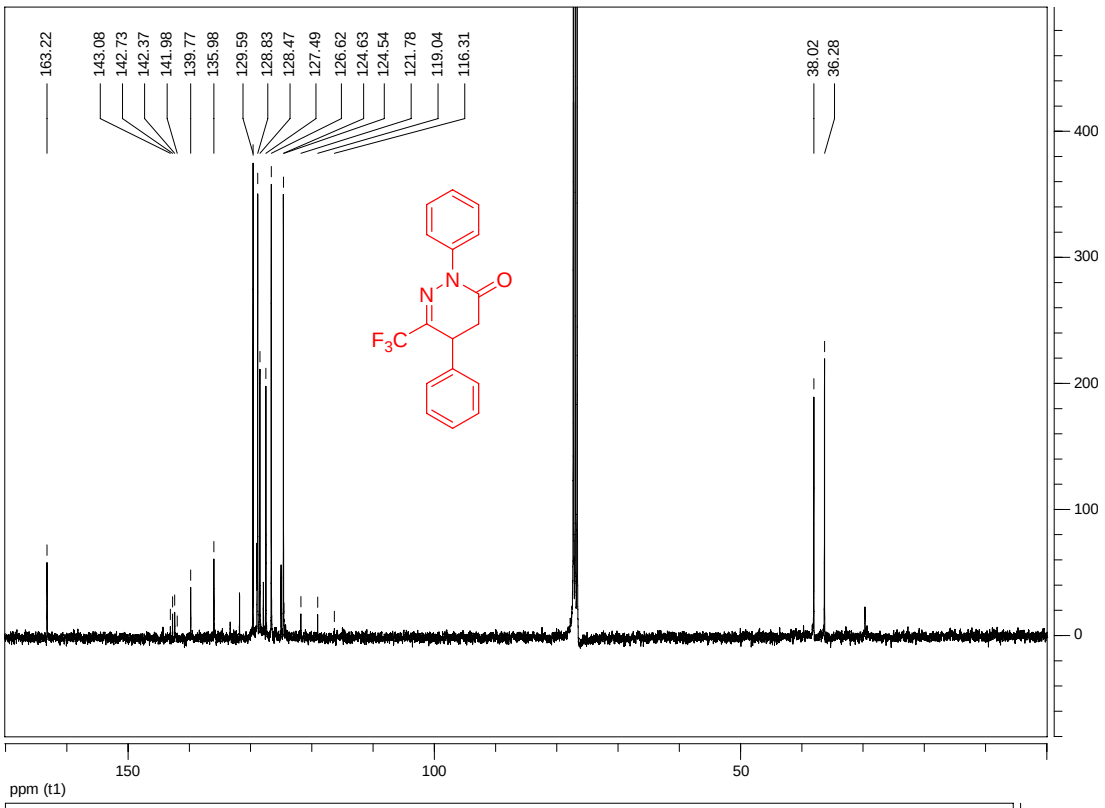

158.35
139.77
134.90
134.57
134.23
133.89
129.69
127.86
125.13
122.41
119.90
119.68
116.18
100.95
57.36
38.45
34.33
19.59
18.39
OMe
N
N
F3C
250
200
150
100
50
0
150
100
50
ppm (t1)

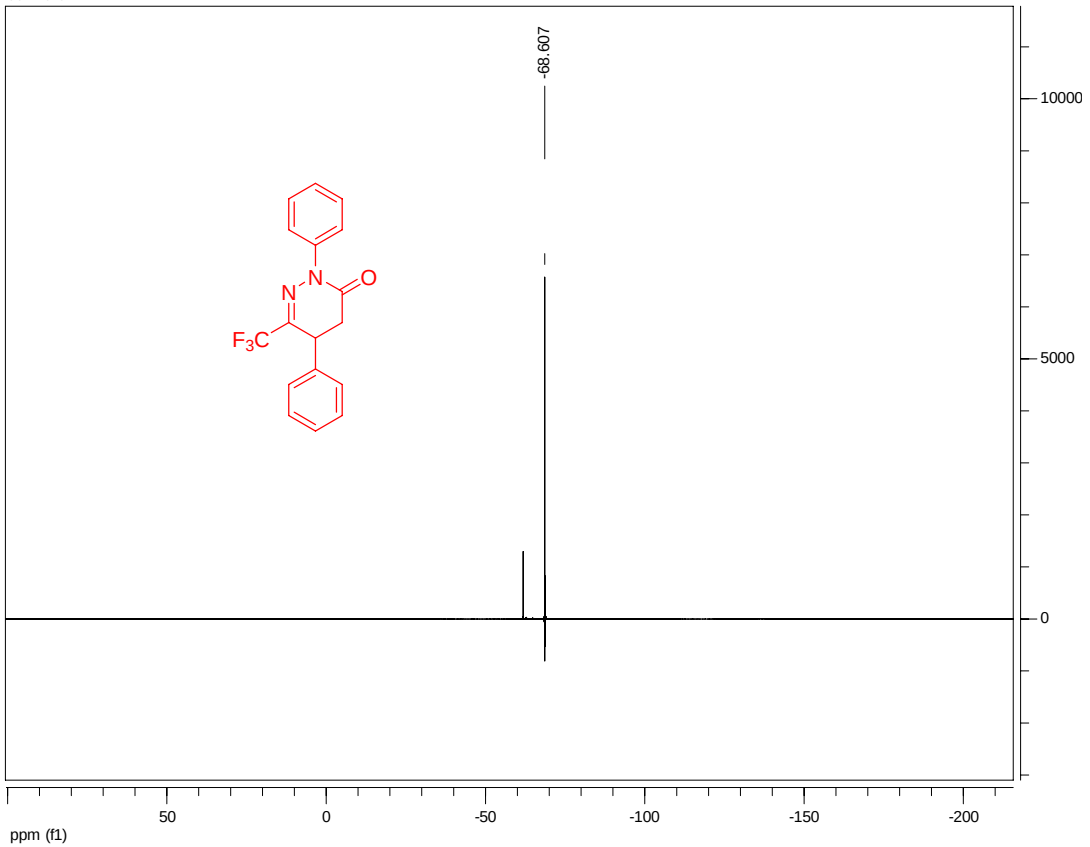

-65.533
OMe
N
N
F3C
50000
0
50
0
-50
-100
-150
-200
ppm (f1)


N
N
F3C
6000
5000
4000
3000
2000
1000
0
5.03
1.09
1.70
0.81
1.84
0.96
0.97
1.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


146.07
141.53
129.81
129.28
129.08
128.73
127.80
127.17
124.37
122.56
121.78
120.76
118.95
114.40
38.95
35.19
25.77
1000
500
0
100
50
ppm (t1)

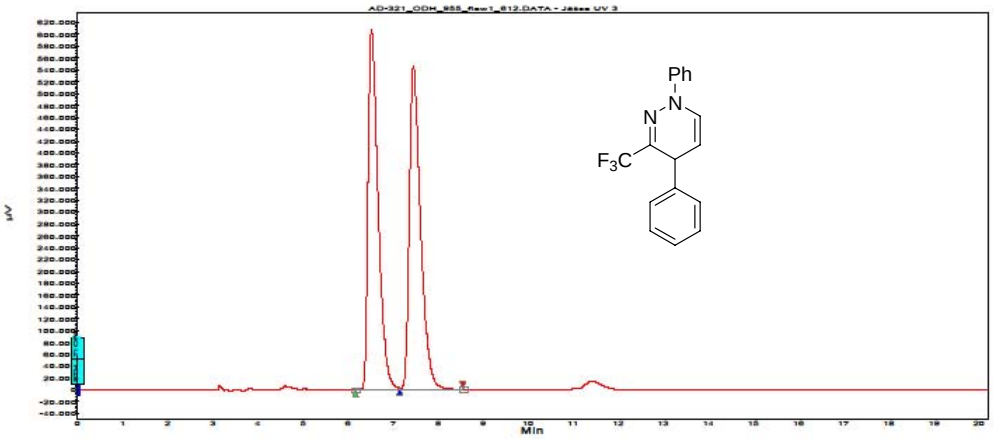

3500
3000
2500
2000
1500
1000
500
0
2.37
1.95
3.88
1.80
0.97
0.99
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


163.22
143.08
142.73
142.37
141.98
139.77
135.98
129.59
128.83
128.47
127.49
126.62
124.63
124.54
121.78
119.04
116.31
38.02
36.28
400
300
200
100
0
150
100
50
ppm (t1)


-68.607
10000
5000
0
50
0
-50
-100
-150
-200
ppm (f1)

Chromatogram : AD-321_ODH_955_flow1_612

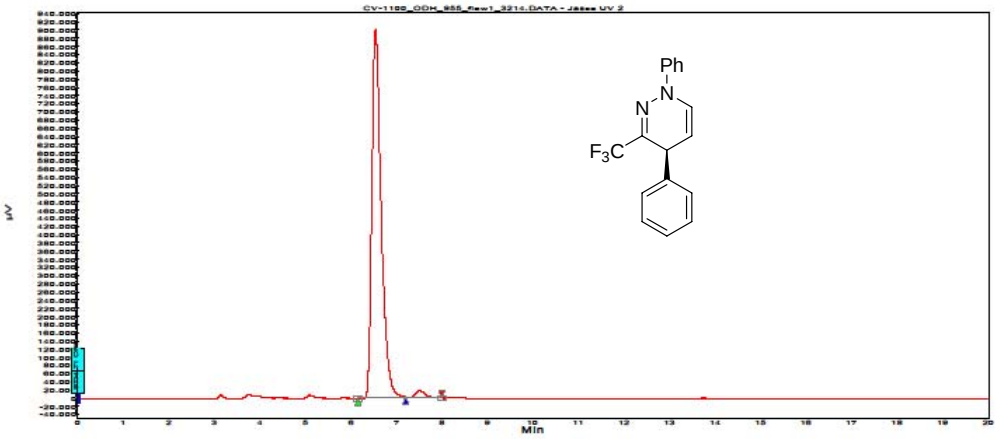
Data file: AD-321_ODH_955_flow1_612.DATA
Method: HPLC1_ODH_955_flow1_acq_120
Date: 23.04.2012 15:09:07



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6,172	6,525	7,151	0,000	49,85	608189,5	157066,1	49,847
2	UNKNOWN	7,151	7,458	8,548	0,000	50,15	545548,7	158032,3	50,153
Total						100,00	1153738,2	315098,4	100,000

Chromatogram : CV-1100_ODH_955_flow1_3214

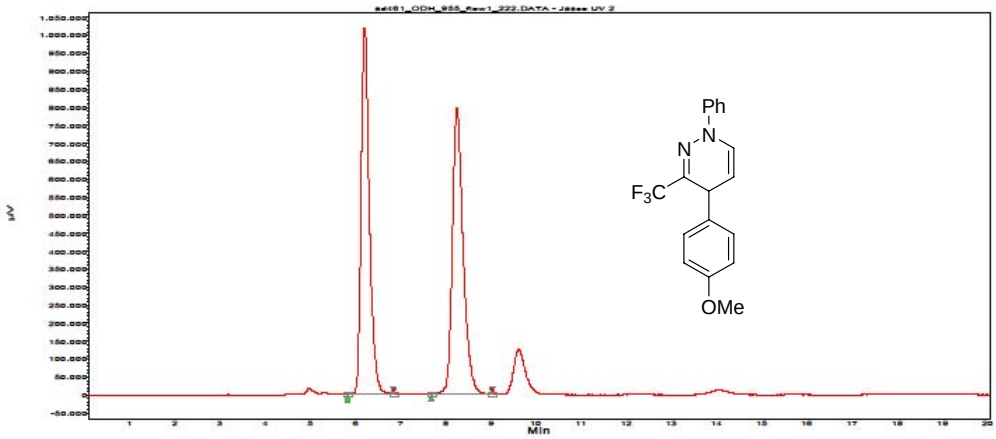
Data file: CV-1100_ODH_955_flow1_3214.DATA
Method: HPLC1_ODH_955_flow1_acq_20
Date: 12.07.2012 21:26:29



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	6,161	6,550	7,207	97,807
2	7,207	7,517	7,998	2,193
Total				100,000

Chromatogram : ad461_ODH_955_flow1_222

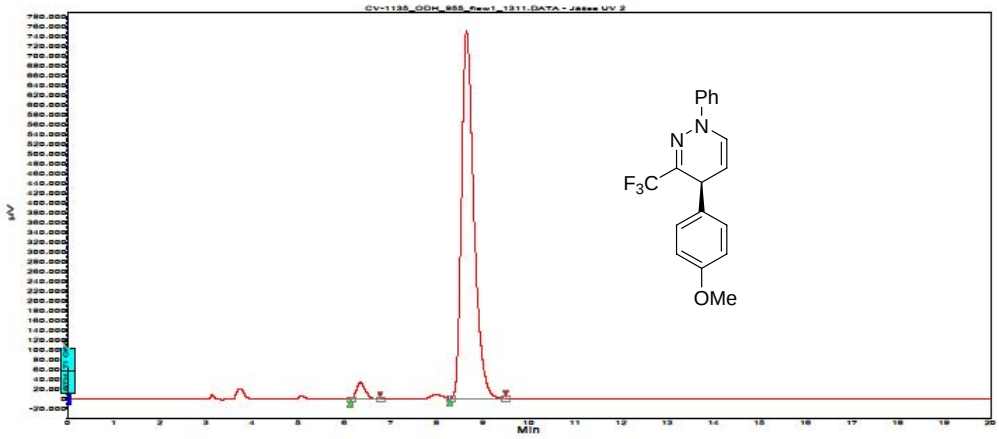
Data file: ad461_ODH_955_flow1_222.DATA
Method: HPLC1_ODH_955_flow1_acq_45
Date: 28.07.2012 01:48:53



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	5,826	6,208	6,844	49,552
2	7,683	8,250	9,026	50,448
Total				100,000

Chromatogram : CV-1135_ODH_955_flow1_1311

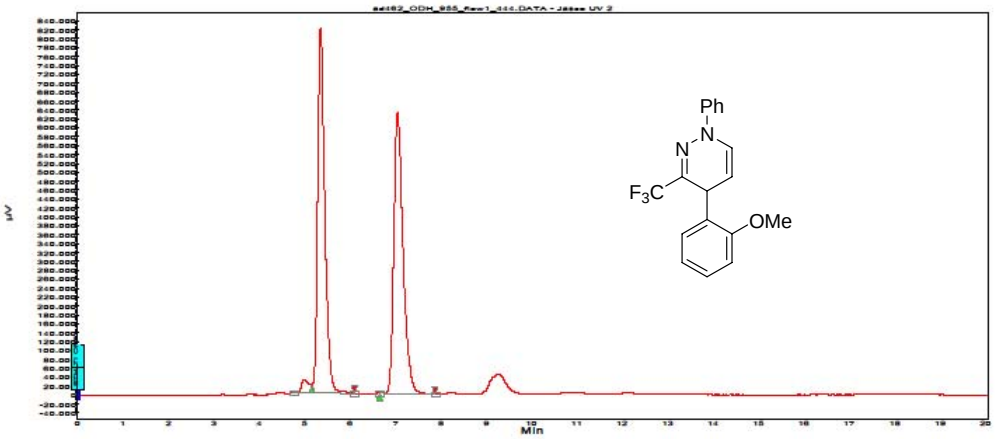
Data file: CV-1135_ODH_955_flow1_1311.DATA
Method: HPLC1_ODH_955_flow1_acq_20
Date: 31.07.2012 12:32:02



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	6,136	6,350	6,777	3,097
2	8,290	8,658	9,500	96,903
Total				100,000

Chromatogram : ad462_ODH_955_flow1_444

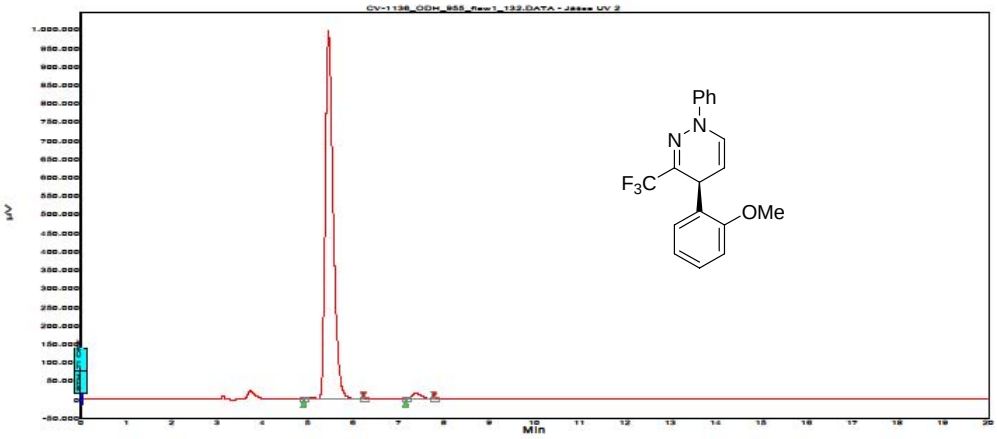
Data file: ad462_ODH_955_flow1_444.DATA
Method: HPLC1_ODH_955_flow1_acq_45
Date: 28.07.2012 03:24:10



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	5,168	5,358	6,107	50,212
1	6,661	7,050	7,870	49,788
Total				100,000

Chromatogram : CV-1136_ODH_955_flow1_132

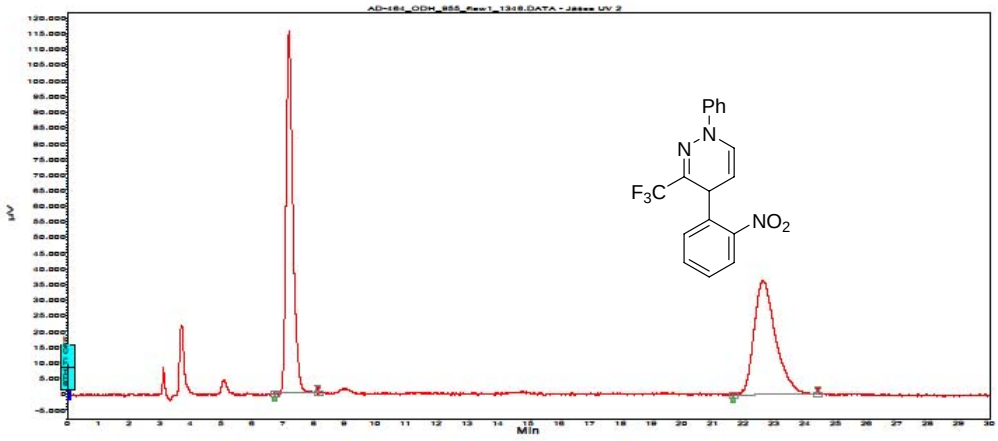
Data file: CV-1136_ODH_955_flow1_132.DATA
Method: HPLC1_ODH_955_flow1_acq_20
Date: 31.07.2012 13:07:03



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	4,917	5,467	6,240	98,051
2	7,169	7,400	7,789	1,949
Total				100,000

Chromatogram : AD-464_ODH_955_flow1_1346

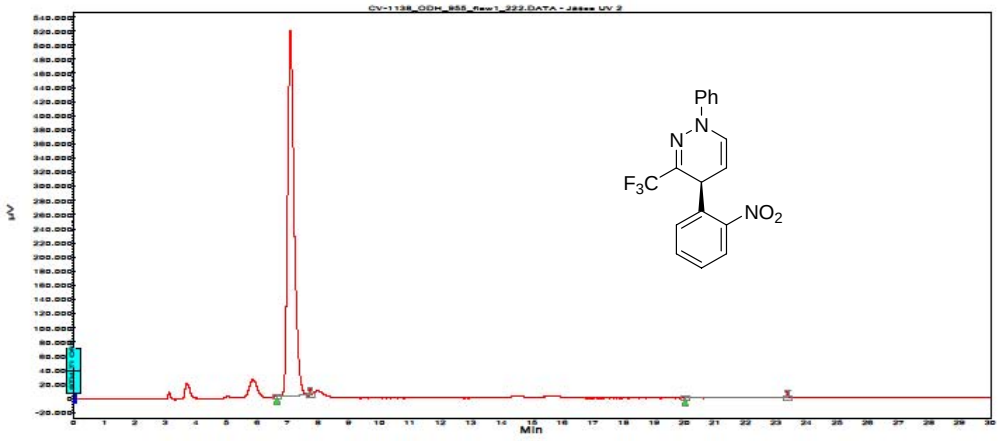
Data file: AD-464_ODH_955_flow1_1346.DATA
Method: HPLC1_ODH_955_flow1_acq_30
Date: 01.08.2012 07:00:51



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	6,756	7,217	8,151	50,130
2	21,663	22,617	24,421	49,870
Total				100,000

Chromatogram : CV-1138_ODH_955_flow1_222

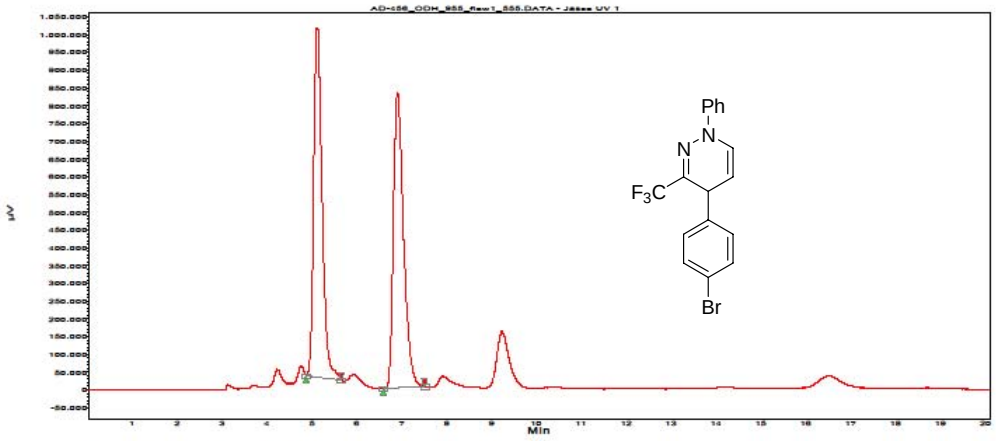
Data file: CV-1138_ODH_955_flow1_222.DATA
Method: HPLC1_ODH_955_flow1_acq_30
Date: 01.08.2012 12:41:34



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	6,663	7,100	7,748	99,718
2	20,021	21,583	23,368	0,282
Total				100,000

Chromatogram : AD-456_ODH_955_flow1_555

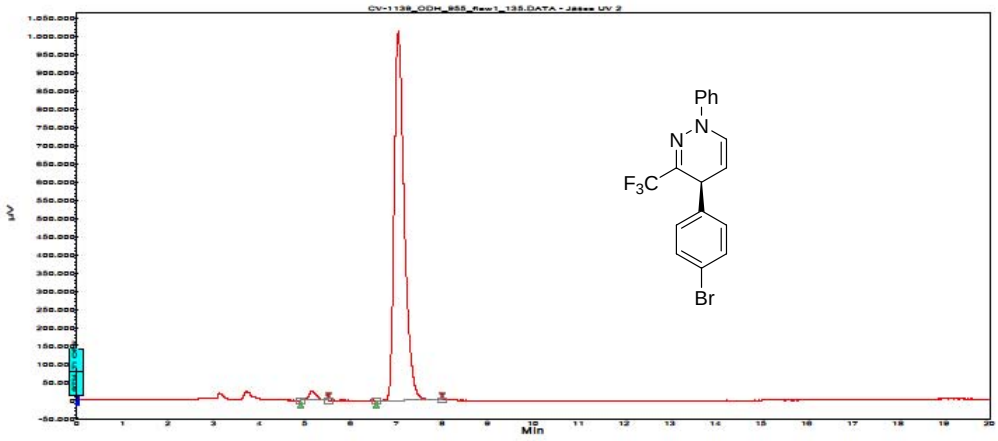
Data file: AD-456_ODH_955_flow1_555.DATA
Method: HPLC1_ODH_955_flow1_acq_30
Date: 01.08.2012 14:19:43



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	4,878	5,133	5,665	49,673
2	6,597	6,908	7,509	50,327
Total				100,000

Chromatogram : CV-1139_ODH_955_flow1_135

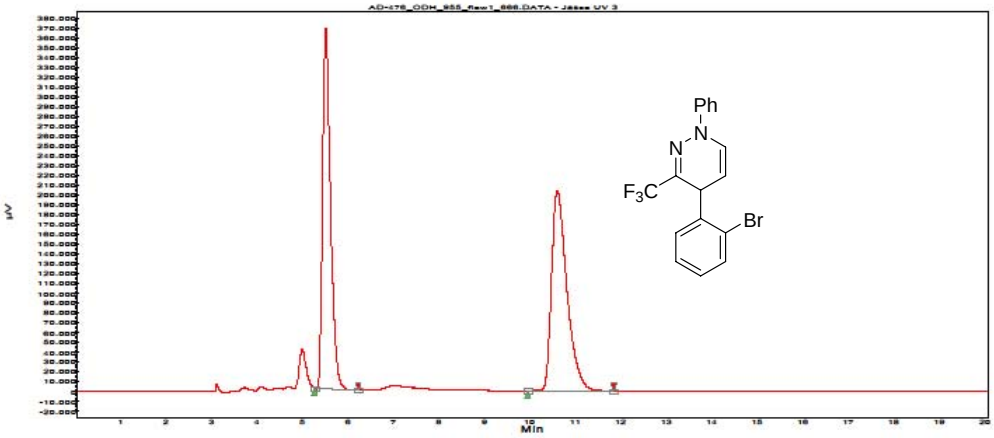
Data file: CV-1139_ODH_955_flow1_135.DATA
Method: HPLC1_ODH_955_flow1_acq_20
Date: 31.07.2012 14:38:01



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	4,917	5,167	5,517	1,946
2	6,570	7,058	8,017	98,054
Total				100,000

Chromatogram : AD-476_ODH_955_flow1_666

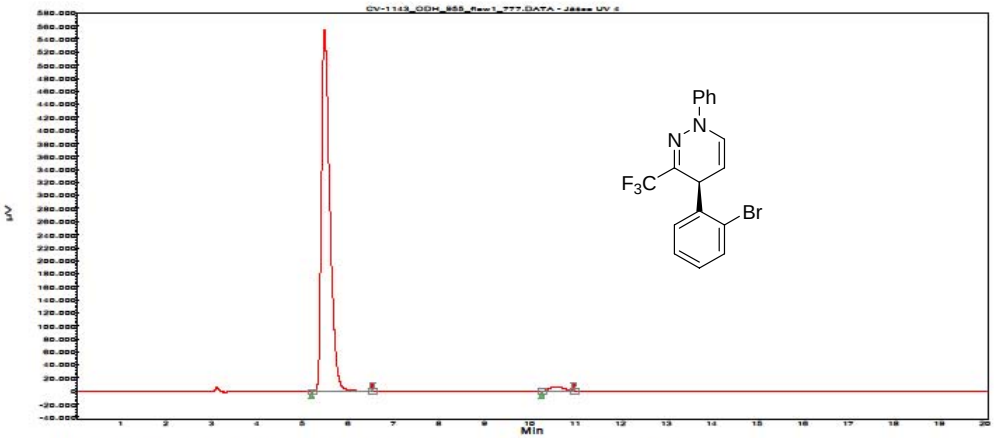
Data file: AD-476_ODH_955_flow1_666.DATA
Method: HPLC1_ODH_955_flow1_acq_30
Date: 01.08.2012 14:52:26



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5,269	5,517	6,229	0,000	47,96	366772,3	73741,9	47,958
2	UNKNOWN	9,948	10,608	11,839	0,000	52,04	204067,1	80021,8	52,042
Total						100,00	570839,4	153763,8	100,000

Chromatogram : CV-1143_ODH_955_flow1_777

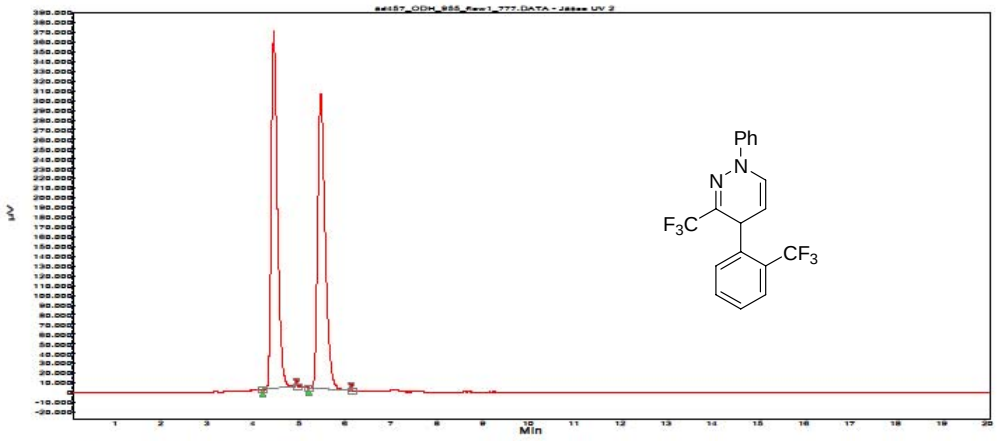
Data file: CV-1143_ODH_955_flow1_777.DATA
Method: HPLC1_ODH_955_flow1_acq_30
Date: 01.08.2012 15:25:10



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5,207	5,492	6,539	0,000	98,19	554271,5	117525,2	98,188
2	UNKNOWN	10,258	10,575	10,971	0,000	1,81	6532,9	2168,7	1,812
Total						100,00	560804,5	119693,9	100,000

Chromatogram : ad457_ODH_955_flow1_777

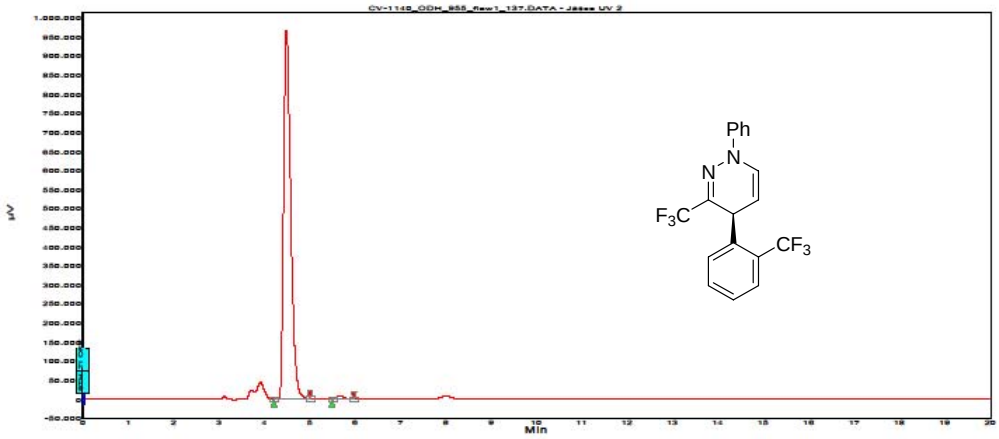
Data file: ad457_ODH_955_flow1_777.DATA
Method: HPLC1_ODH_955_flow1_acq_45
Date: 28.07.2012 05:47:08



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	4,213	4,458	4,955	49,914
2	5,223	5,483	6,150	50,086
Total				100,000

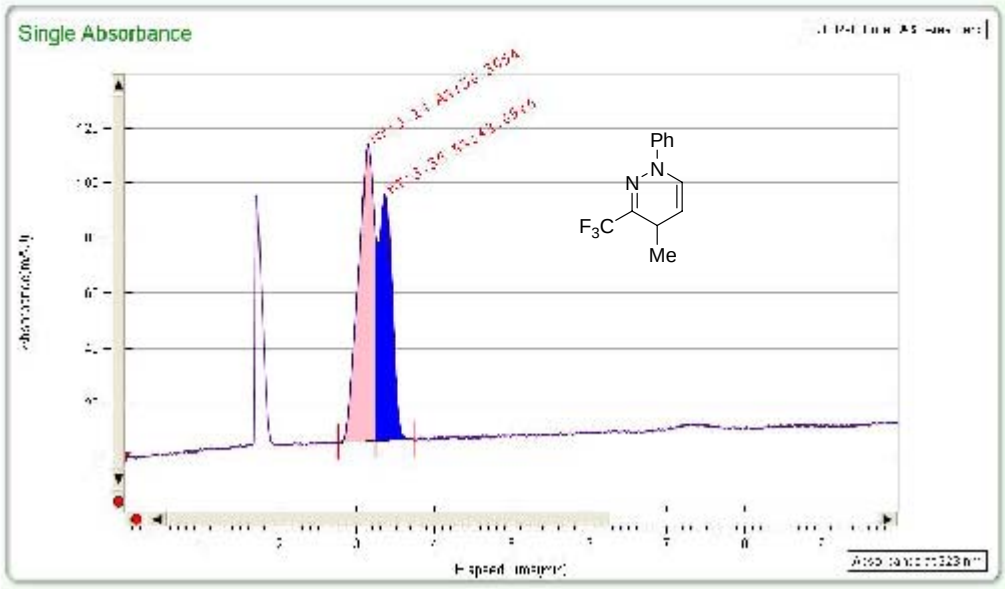
Chromatogram : CV-1140_ODH_955_flow1_137

Data file: CV-1140_ODH_955_flow1_137.DATA
Method: HPLC1_ODH_955_flow1_acq_20
Date: 31.07.2012 15:23:29



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	4,220	4,500	5,015	99,091
2	5,496	5,667	5,976	0,909
Total				100,000

ThарSFC



General Info	
Log Author	
Log Date	7/12/2012 11:45:56 AM
Report By	current_User
Report Date	8/9/2012
Method Name	2-5mlCO2-1MeOH-38.met
Notes	AK-Rue / Vermeeren

Injection Info			
Inj Vol	5	Temp	36.5
Solvent	n-Hexan-Isoprop-1-1	Flow	2.5
Column	OJ-H	% Modifier	1
Sample	AD-322	Pressure	150
Well location	P1: 1E		

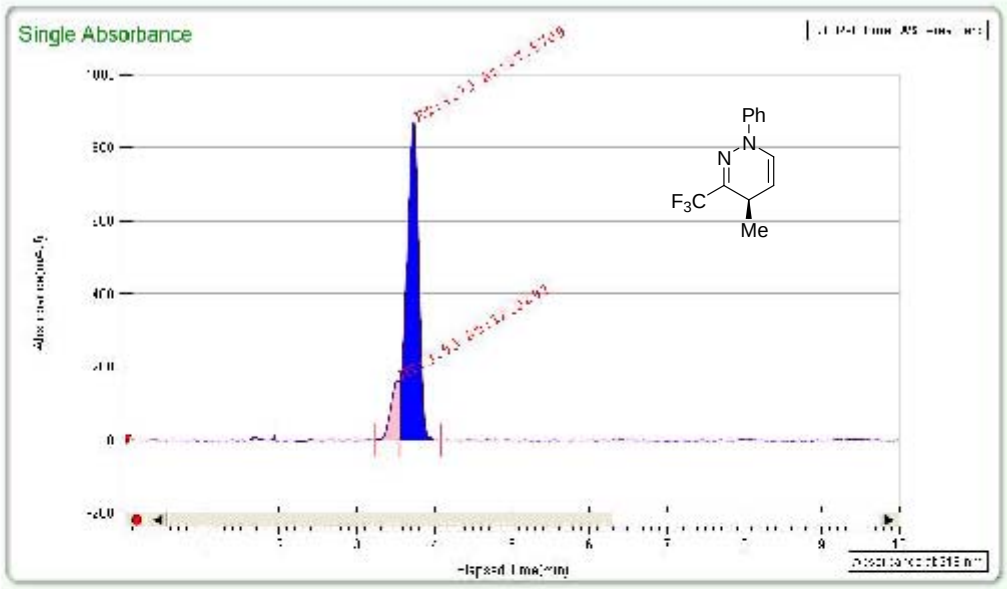
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	56.3054	1461.2776	3.14	107.6975	0.0044
2	43.6946	1133.9915	3.36	89.2942	0.0048
Total:	100	2595.2691			

ThарSFC

C:\Program Files\SuperChrom\logs\QA\AMDSQA_COL\Das\AD-322_7-12-2012_4.tta

TharSFC



General Info	
Log Author	
Log Date	7/28/2012 5:44:00 PM
Report By	current_User
Report Date	8/9/2012
Method Name	2-5mlCO2-1MeOH.met
Notes	AK-Rue / Vermeeren

Injection Info			
Inj Vol	5	Temp	35.2
Solvent	n-Hexan-Isoprop-1-1	Flow	2
Column	OJ-H	% Modifier	1
Sample	CV-1130	Pressure	149
Well location	P1: 4F		

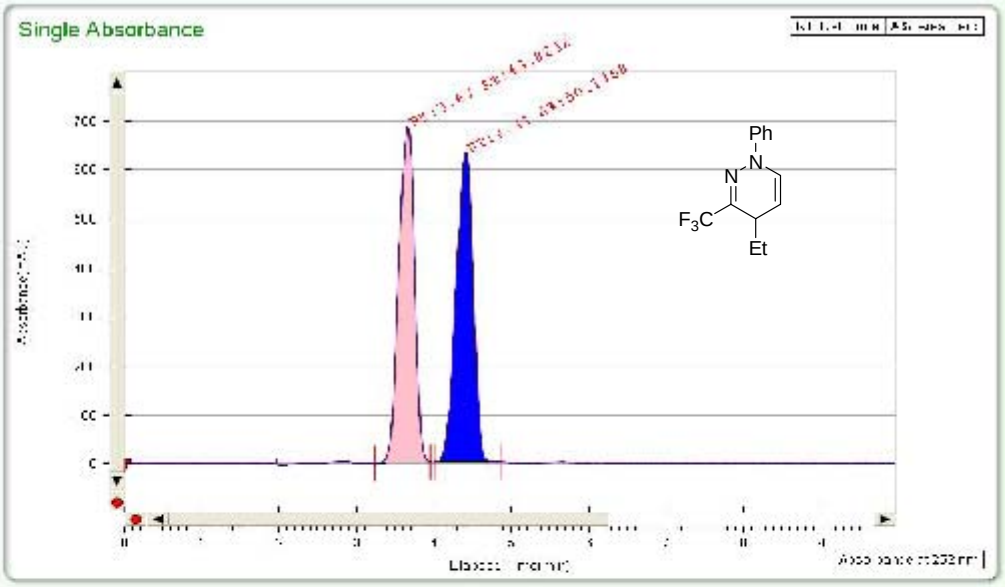
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	12.0292	1274.5943	3.53	163.3817	0.0033
2	87.9708	9321.2783	3.73	870.8905	0.0035
Total:	100	10595.8726			

TharSFC

C:\Program Files\SuperChrom\logs\QA\AMDSQA_COL\moli\CV-1130_7-28-2012_2.tta

TharSFC



General Info

Log Author	
Log Date	7/28/2012 6:01:56 PM
Report By	current_User
Report Date	7/31/2012
Method Name	2-5mlCO2-1MeOH.met
Notes	AK-Rue / Vermeeren

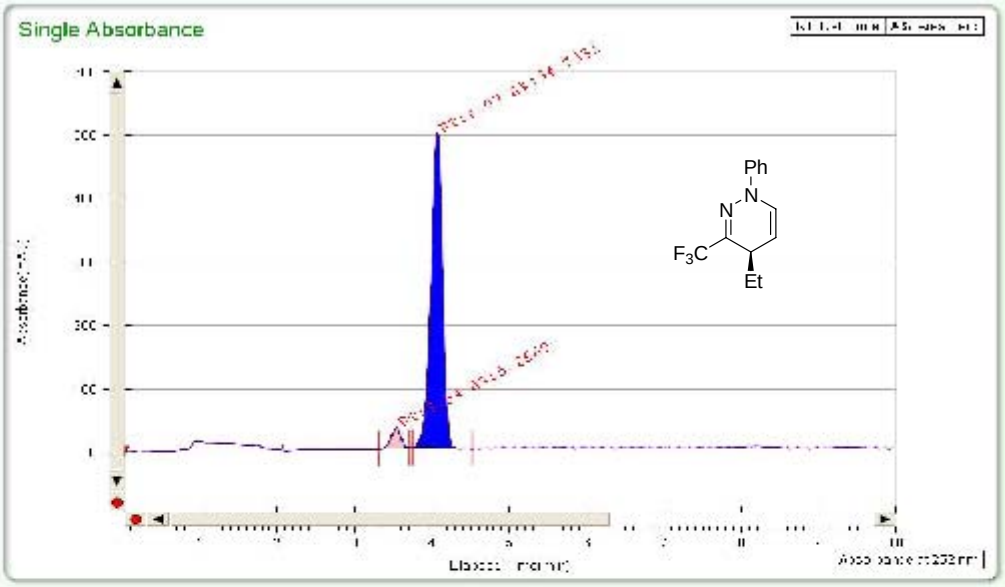
Injection Info

Inj Vol	5	**Temp**	35.3
Solvent	n-Hexan-Isoprop-1-1	**Flow**	2
Column	OJ-H	**% Modifier**	1
Sample	AD-458	**Pressure**	150
Well location	P1: 3E		

Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.8232	9636.8168	3.67	684.6472	0.0034
2	50.1768	9705.2126	4.41	629.8868	0.0041
Total:	100	19342.0294			

TharSFC



General Info	
Log Author	
Log Date	7/28/2012 5:26:03 PM
Report By	current_User
Report Date	7/31/2012
Method Name	2-5mlCO2-1MeOH.met
Notes	AK-Rue / Vermeeren

Injection Info			
Inj Vol	5	Temp	35.3
Solvent	n-Hexan-Isoprop-1-1	Flow	2
Column	OJ-H	% Modifier	1
Sample	CV-1131	Pressure	151
Well location	P1: 4E		

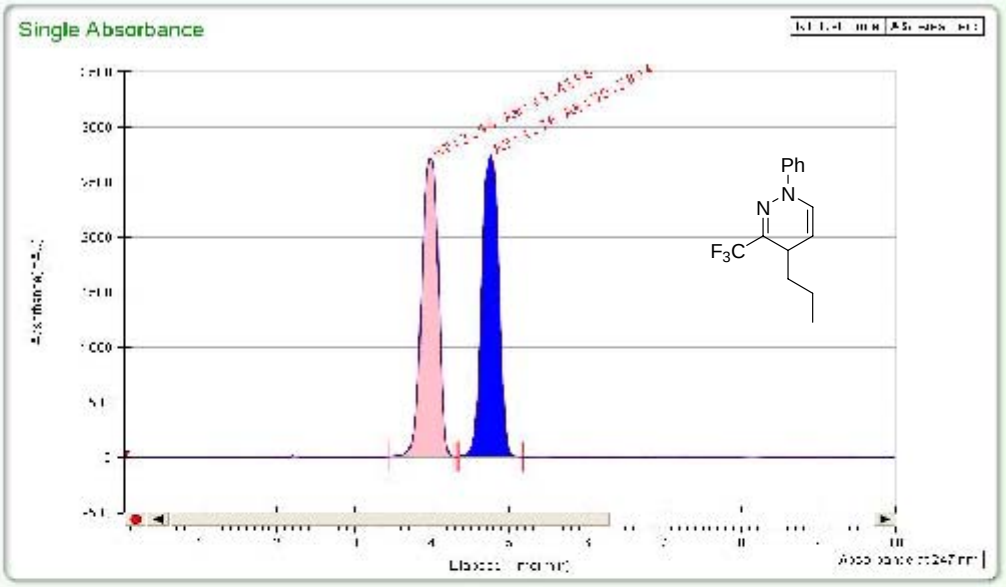
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	5.2669	280.8215	3.54	32.6776	0.0034
2	94.7331	5051.0363	4.07	496.6204	0.0039
Total:	100	5331.8578			

TharSFC

C:\Program Files\SuperChrom\logs\QA\AMDSQA_COL\moli\CV-1131_7-28-2012_1.tta

ThарSFC



General Info	
Log Author	
Log Date	7/31/2012 11:25:54 AM
Report By	current_User
Report Date	7/31/2012
Method Name	2-5mlCO2-1MeOH.met
Notes	AK-Rue / Vermeeren

Injection Info			
Inj Vol	5	Temp	35.1
Solvent	n-Hexan-Isoprop-1-1	Flow	2
Column	OJ-H	% Modifier	1
Sample	AD-459	Pressure	149
Well location	P1: 3D		

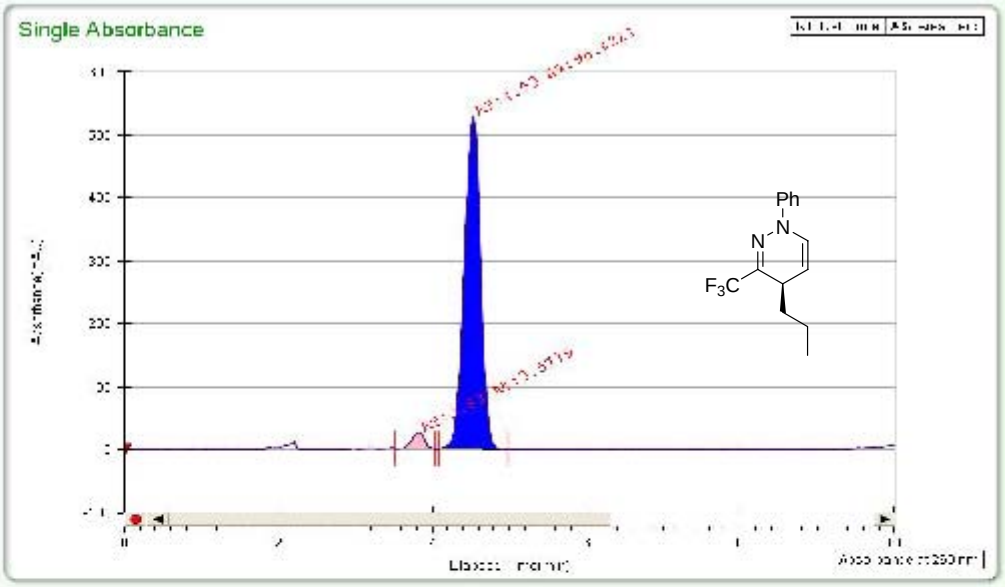
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.4196	40295.3848	3.98	2713.5611	0.0058
2	50.5804	41241.9159	4.76	2745.4276	0.0069
Total:	100	81537.3007			

ThарSFC

C:\Program Files\SuperChrom\logs\AK-Rue\AD-459_7-31-2012_1.tta

TharSFC



General Info	
Log Author	
Log Date	7/31/2012 11:44:50 AM
Report By	current_User
Report Date	7/31/2012
Method Name	2-5mlCO2-1MeOH.met
Notes	AK-Rue / Vermeeren

Injection Info			
Inj Vol	5	Temp	35
Solvent	n-Hexan-Isoprop-1-1	Flow	2
Column	OJ-H	% Modifier	1
Sample	CV-1132	Pressure	150
Well location	P1: 3C		

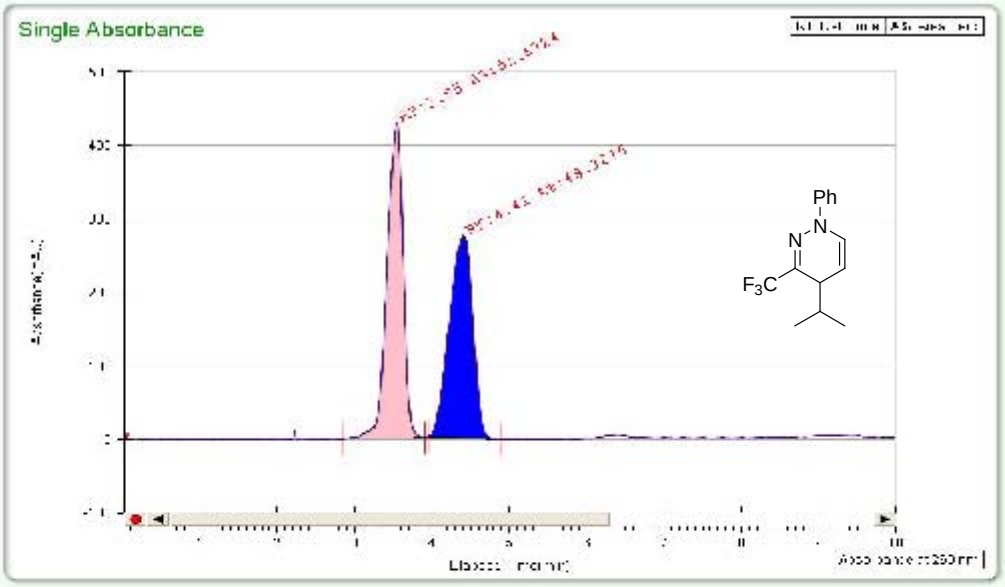
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	3.5779	288.9651	3.83	25.7088	0.0054
2	96.4221	7787.3334	4.53	529.1004	0.0064
Total:	100	8076.2985			

TharSFC

C:\Program Files\SuperChrom\logs\AK-Rue\CV-1132_7-31-2012_1.tta

TharSFC



General Info	
Log Author	
Log Date	7/31/2012 12:03:46 PM
Report By	current_User
Report Date	7/31/2012
Method Name	2-5mlCO2-1MeOH.met
Notes	AK-Rue / Vermeeren

Injection Info			
Inj Vol	5	Temp	34.9
Solvent	n-Hexan-Isoprop-1-1	Flow	2
Column	OJ-H	% Modifier	1
Sample	AD-460	Pressure	151
Well location	P1: 3B		

Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	51.6724	6211.9253	3.55	430.3012	0.0049
2	48.3276	5809.8148	4.41	276.5344	0.0061
Total:	100	12021.7401			

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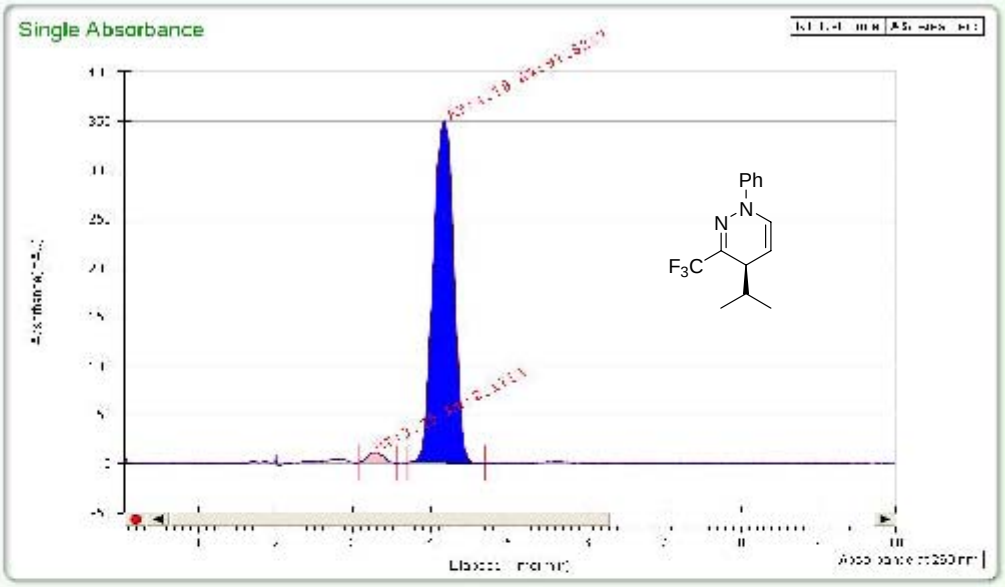
C:\Program Files\SuperChrom\logs\AK-Rue\AD-460_7-31-2012_1.tta

TharSFC



General Info	
Log Author	
Log Date	7/28/2012 6:37:50 PM
Report By	current_User
Report Date	7/31/2012
Method Name	2-5mlCO2-1MeOH.met
Notes	AK-Rue / Vermeeren

Injection Info			
Inj Vol	5	Temp	35.2
Solvent	n-Hexan-Isoprop-1-1	Flow	2
Column	OJ-H	% Modifier	1
Sample	CV-1133	Pressure	151
Well location	P1: 4C		

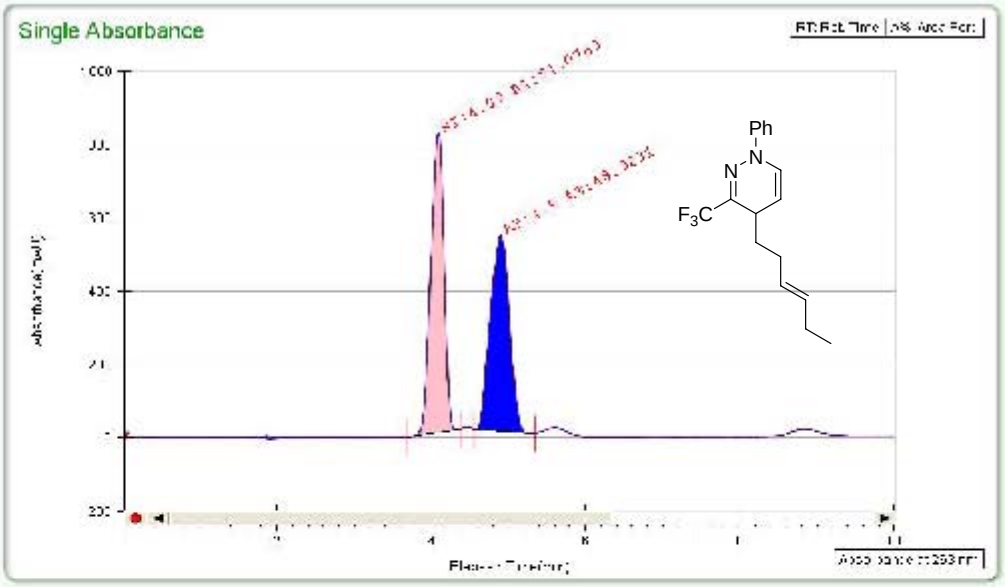
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	2.1713	142.3527	3.25	10.6362	0.0029
2	97.8287	6413.7236	4.18	350.7453	0.0037
Total:	100	6556.0763			

TharSFC

C:\Program Files\SuperChrom\logs\QA\AMDSQA_COL\moli\CV-1133_7-28-2012_1.tta

ThарSFC



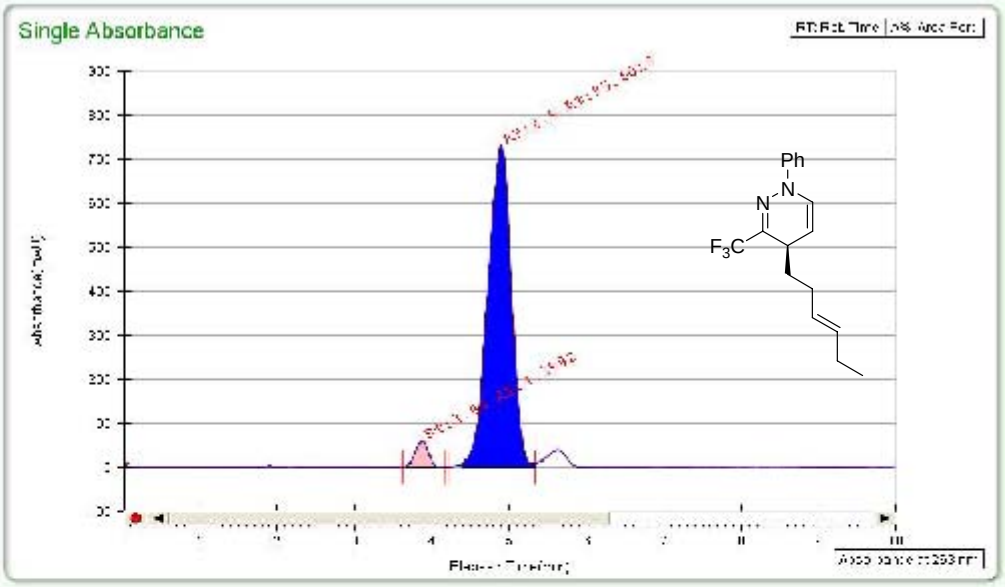
General Info		Report Date	8/2/2012
Log Author		Method Name	2-5mlCO2-1MeOH.met
Log Date	8/2/2012 3:27:23 PM	Notes	AK-Rue / Vermeeren
Report By	current_User		

Injection Info			
Inj Vol	5	Temp	35
Solvent	n-Hexan-Isoprop-1-1	Flow	2
Column	OJ-H	% Modifier	1
Sample	AD-482	Pressure	150
Well location	P1: 3F		

Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	51.0769	9584.5921	4.09	818.2727	0.0044
2	48.9231	9180.4358	4.9	537.0471	0.0053
Total:	100	18765.0279			

ThorSFC



General Info		**Report Date**	8/2/2012
Log Author		**Method Name**	2-5mlCO2-1MeOH.met
Log Date	8/2/2012 3:46:19 PM	**Notes**	AK-Rue / Vermeeren
Report By	current_User		

Injection Info		**Temp**	34.9
Inj Vol	5	**Flow**	2
Solvent	n-Hexan-Isoprop-1-1	**% Modifier**	1
Column	OJ-H	**Pressure**	150
Sample	CV-1134		
Well location	P1: 3E		

Peak Info

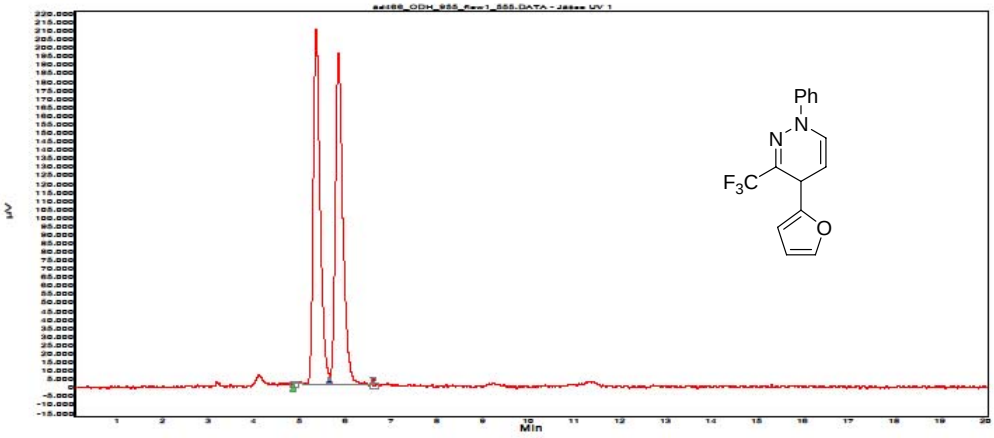
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	4.3982	711.6003	3.88	60.965	0.0041
2	95.6018	15467.703	4.9	734.0619	0.0052
Total:	100	16179.3033			

ThorSFC

C:\Program Files\SuperChrom\logs\AK-Rue\CV-1134_8-2-2012_1.tta

Chromatogram : ad466_ODH_955_flow1_555

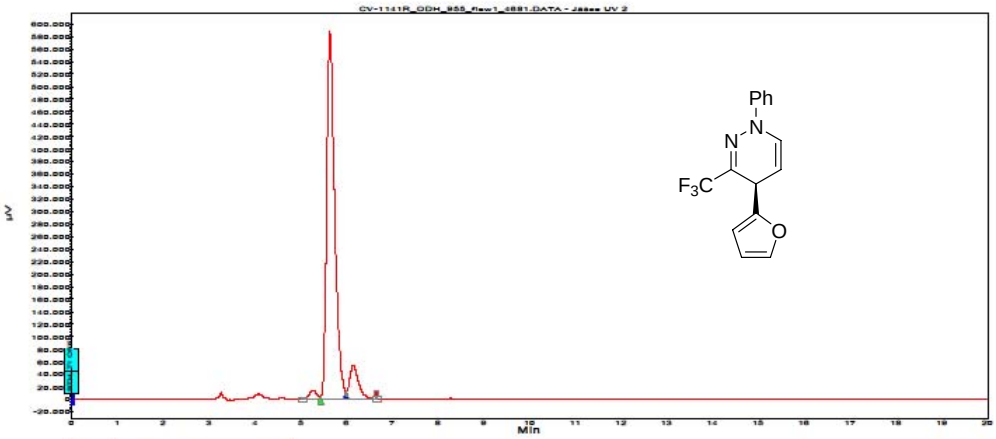
Data file: ad466_ODH_955_flow1_555.DATA
Method: HPLC1_ODH_955_flow1_acq_45
Date: 28.07.2012 04:11:48



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	4,869	5,367	5,663	49,250
2	5,663	5,858	6,615	50,750
Total				100,000

Chromatogram : CV-1141R_ODH_955_flow1_4681

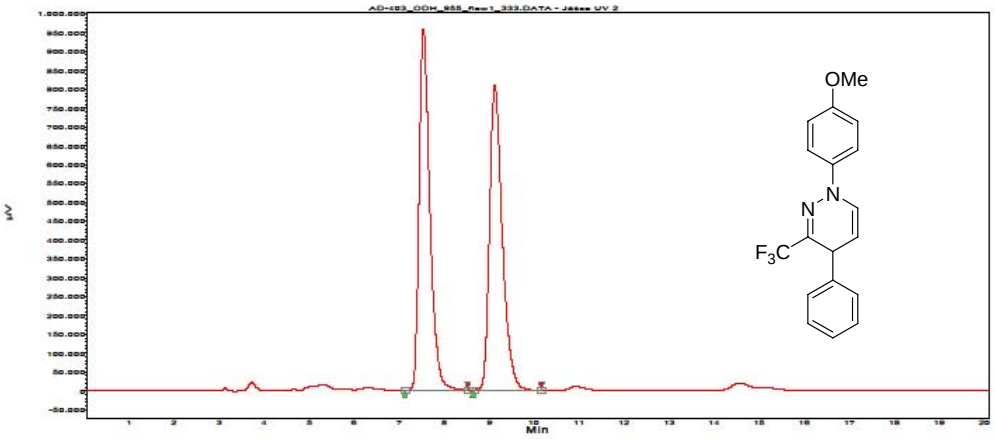
Data file: CV-1141R_ODH_955_flow1_4681.DATA
Method: HPLC1_ODH_955_flow1_acq_20
Date: 08.08.2012 20:15:03



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	5,442	5,650	6,000	90,833
2	6,000	6,158	6,661	9,167
Total				100,000

Chromatogram : AD-403_ODH_955_flow1_333

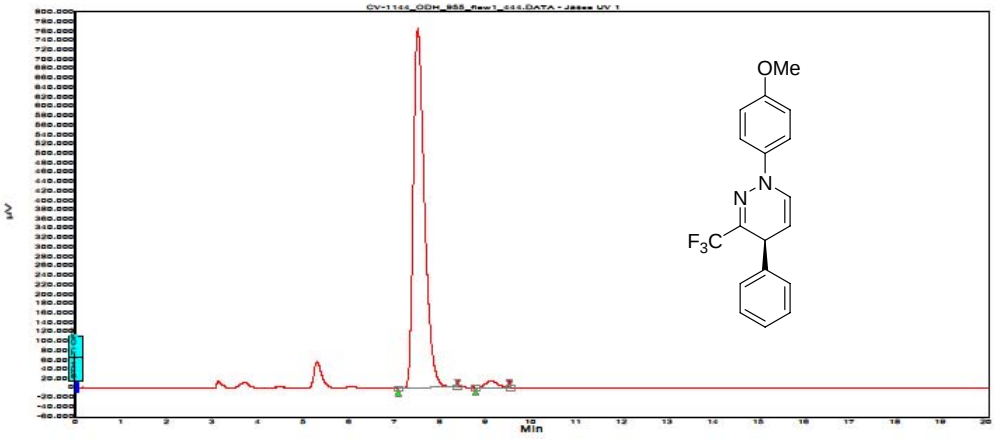
Data file: AD-403_ODH_955_flow1_333.DATA
Method: HPLC1_ODH_955_flow1_acq_30
Date: 01.08.2012 13:14:17



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	7,128	7,542	8,523	49,921
2	8,647	9,133	10,165	50,079
Total				100,000

Chromatogram : CV-1144_ODH_955_flow1_444

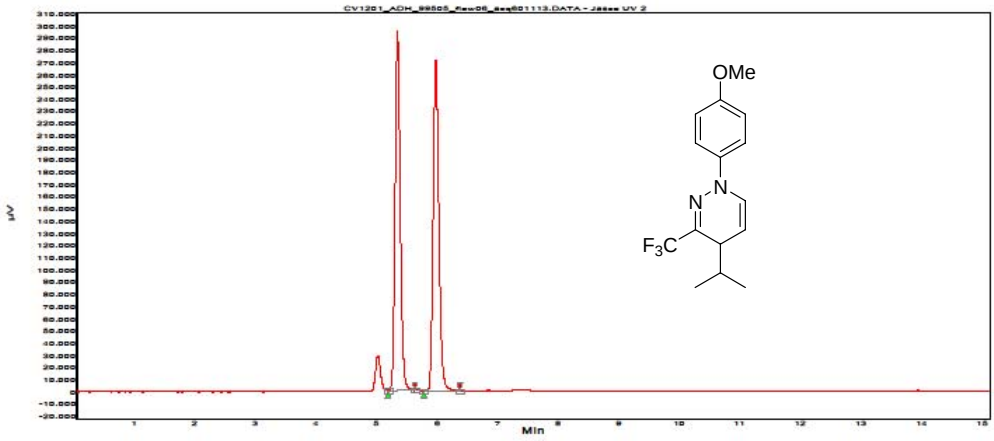
Data file: CV-1144_ODH_955_flow1_444.DATA
Method: HPLC1_ODH_955_flow1_acq_30
Date: 01.08.2012 13:47:00



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	7,097	7,525	8,399	97,971
2	8,802	9,125	9,545	2,029
Total				100,000

Chromatogram : CV1201_ADH_99505_flow06_acq601113

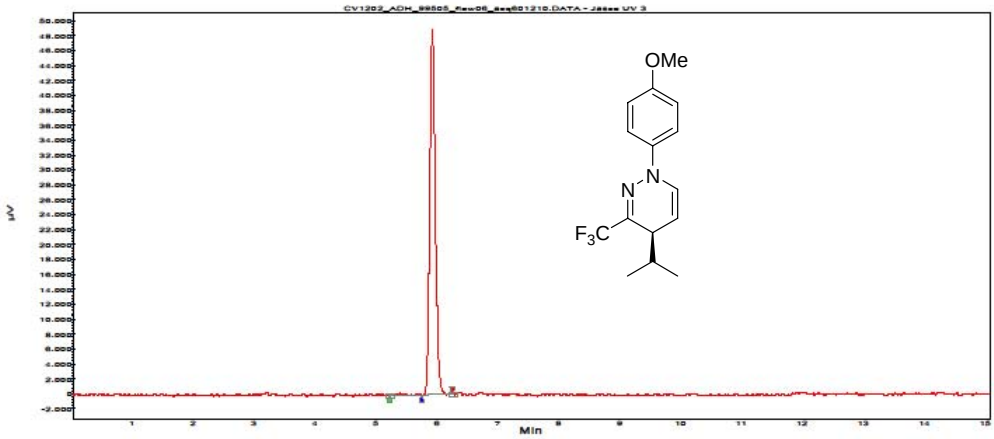
Data file: CV1201_ADH_99505_flow06_acq601113.DATA
Method: HPLC1_ADH_99505_flow1_acq_60
Date: 02.09.2012 20:41:31



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	5,192	5,350	5,636	49,465
2	5,786	5,983	6,379	50,535
Total				100,000

Chromatogram : CV1202_ADH_99505_flow06_acq601210

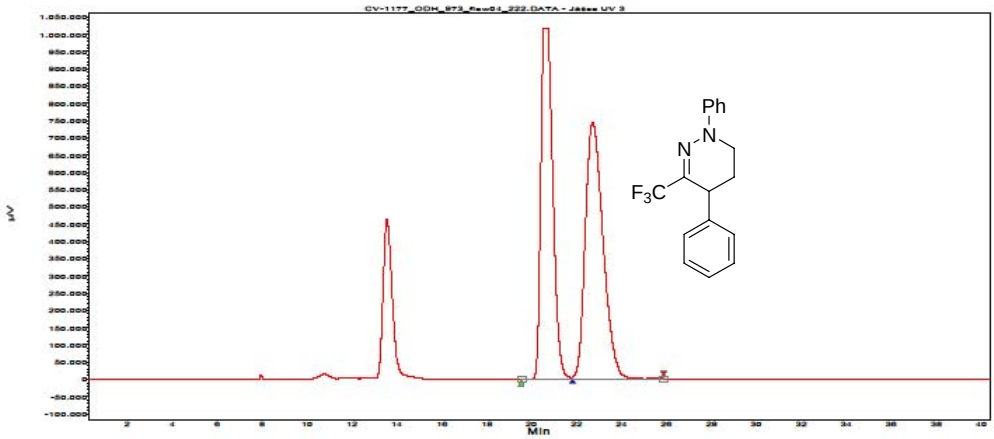
Data file: CV1202_ADH_99505_flow06_acq601210.DATA
Method: HPLC1_ADH_99505_flow1_acq_60
Date: 02.09.2012 21:43:38



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5,227	5,400	5,757	0,000	0,50	260,4	25,8	0,497
2	UNKNOWN	5,757	5,933	6,257	0,000	99,50	48926,2	5161,1	99,503
Total						100,00	49186,7	5186,9	100,000

Chromatogram : CV-1177_ODH_973_flow04_222

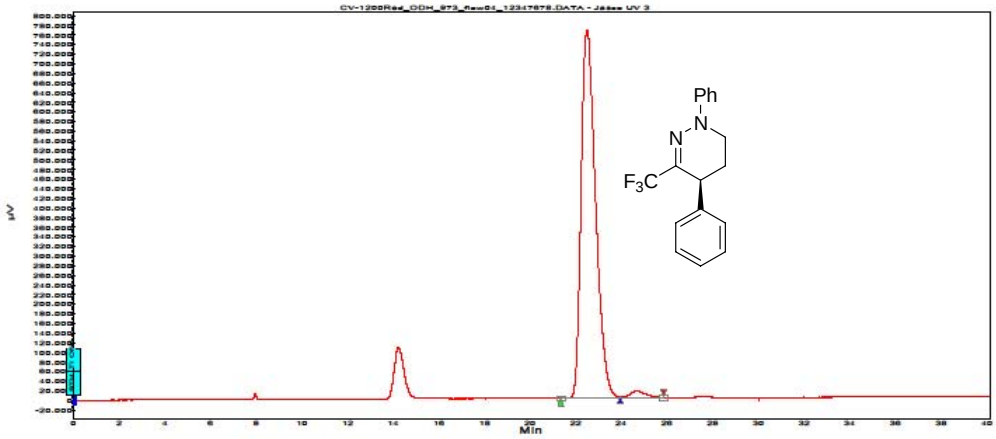
Data file: CV-1177_ODH_973_flow04_222.DATA
Method: HPLC1_ODH_973_flow04_aoq_90
Date: 30.08.2012 05:00:03



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	19,529	20,600	21,805	0,000	48,04	1017245,1	629188,9	48,039
2	UNKNOWN	21,805	22,708	25,862	0,000	51,96	746006,5	680565,4	51,961
Total						100,00	1763251,6	1309754,3	100,000

Chromatogram : CV-1200Red_ODH_973_flow04_12347678

Data file: CV-1200Red_ODH_973_flow04_12347678.DATA
Method: HPLC1_ODH_973_flow04_aoq_90
Date: 01.09.2012 20:50:29



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	21,339	22,492	23,949	0,000	98,16	764742,7	562738,2	98,159
2	UNKNOWN	23,949	24,683	25,855	0,000	1,84	13085,9	10552,9	1,841
Total						100,00	777828,6	573291,1	100,000