Supporting Information for

Remote *meta*-C–H activation using a pyridine-based template: achieving site-selectivity via recognition of distance and geometry

Ling Chu[1], Ming Shang[1], Keita Tanaka[1], Qinghao Chen[2], Natalya Pissarnitski[3], Eric Streckfuss[3] and Jin-Quan Yu[1]†

[1]Department of Chemistry, The Scripps Research Institute, 10550 N. Torrey Pines Road, La Jolla, California 92037, USA.

[2]Department of Process Chemistry, Merck & Co. Inc., 126 East Lincoln Avenue, Rahway, New Jersey 07065, USA.

[3]Department of Discovery Chemistry,Merck & Co. Inc., 126 East Lincoln Avenue, Rahway, New Jersey, 07065, USA.

†Corresponding author. Email: yu200@scripps.edu

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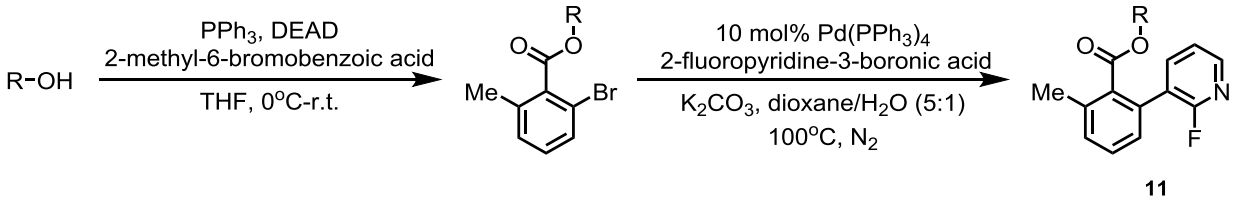
General Information:

Unless otherwise noted all commercial materials were used without further purification. Solvents were obtained from Acros or Sigma-Aldrich and used directly without further purification. Nuclear magnetic resonance (NMR) spectra were recorded with Varian Inova-400, Bruker DRX-600. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CHCl_3$ = 7.26) unless otherwise noted. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. High resolution mass spectra for new compounds were recorded on an Agilent LC/MSD TOF mass spectrometer. All amino acids were purchased from Bachem or Sigma-Aldrich or synthesized according to literature procedures. All the substrates were synthesized according to the procedure described below.

Experimental Section:

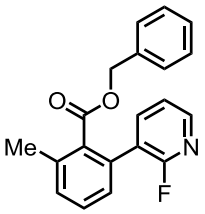
Procedures for the Preparation of Substrates:



11

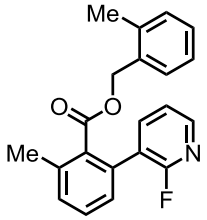
Step 1: To a 250 mL round bottom flask was added the corresponding alcohol (5 mmol, 1 equiv.), PPh_3 (1.1 equiv.), 2-methyl-6-bromobenzoic acid (1 equiv.) and THF. The flask was evacuated and backfilled with N_2 three times. The reaction mixture was cooled to 0 °C, at which time DEAD (1.1 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 1h. After completion, the mixture was concentrated in *vacuo* and the resulting residue was purified by column chromatography using an eluent of hexane:ethyl aceate.

Step 2: To a 250 mL Schlenk tube was added the corresponding benzoic ester (1 equiv.) obtained from step 1, 2-fluoropyridine-3-boronic acid (1.5 equiv.), potassium carbonate (3 equiv.), $Pd(PPh_3)_4$ (0.1 equiv.), 50 mL dioxane and 10 mL water. The flask was evacuated and backfilled with N_2 three times. The mixture was heated to 100 °C for 18 h. After being allowed to cool to room temperature, the mixture was diluted with ethyl acetate and washed with brine. The organic residue was dried over $MgSO_4$, concentrated in *vacuo* and purified by column chromatography to obtain the desired product **11**.



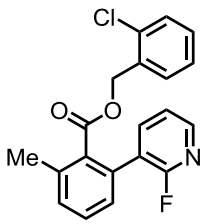
11a benzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.61 (m, 1H), 7.38 (m, 1H), 7.28 (s, 4H), 7.21 – 7.09 (m, 3H), 7.05 (s, 1H), 5.07 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.28 , 160.07 (d, *J* = 239.0 Hz), 146.64 (d, *J* = 14.4 Hz), 141.05 (d, *J* = 4.2 Hz), 136.72 , 134.85 , 132.92 , 132.56 (d, *J* = 4.0 Hz), 130.74 , 129.73 , 128.63 , 128.47 , 128.29 , 127.96 , 123.13 (d, *J* = 31.1 Hz), 121.12 (d, *J* = 4.3 Hz), 67.05 , 20.22 . HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{17}FNO_2^+$ $[M+H]^+$ 322.1238 , found 322.1240.



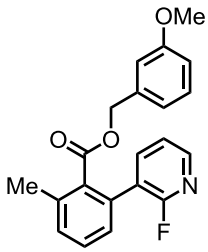
11b 2-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (ddd, *J* = 4.9, 2.0, 1.2 Hz, 1H), 7.60 (ddd, *J* = 9.5, 7.4, 2.0 Hz, 1H), 7.37 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.28 (ddd, *J* = 7.7, 1.2, 0.7 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.14 – 7.08 (m, 3H), 7.01 (ddd, *J* = 7.4, 4.9, 1.8 Hz, 1H), 5.11 (s, 2H), 2.43 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.36 , 160.02 (d, *J* = 238.9 Hz), 146.65 (d, *J* = 14.4 Hz), 140.98 (d, *J* = 4.2 Hz), 137.10 , 136.58 , 133.09 , 132.87 , 132.42 (d, *J* = 3.9 Hz), 130.67 , 130.30 , 129.82 , 129.64 , 128.60 , 127.94 , 125.91 , 122.96 (d, *J* = 31.5 Hz) , 121.01 (d, *J* = 4.4 Hz), 65.13 , 20.16 , 18.65 . HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}FNO_2^+$ $[M+H]^+$ 336.1394, found 336.1395.



11c 2-chlorobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

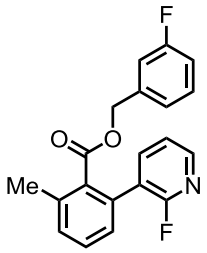
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 4.9 Hz, 1H), 7.64 (ddd, *J* = 9.5, 7.3, 1.9 Hz, 1H), 7.37 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.20 – 7.14 (m, 3H), 7.07 (ddd, *J* = 7.3, 4.9, 1.8 Hz, 1H), 5.20 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.05 , 159.98 (d, *J* = 238.9 Hz), 146.60 (d, *J* = 14.4 Hz), 141.00 (d, *J* = 4.2 Hz), 136.70 , 133.85 , 132.68 , 132.54 , 132.51 (d, *J* = 4.2 Hz), 130.69 , 130.47 , 129.75 , 129.64 , 129.40 , 127.92 , 126.78 , 123.00 (d, *J* = 31.5 Hz) , 121.05 (d, *J* = 4.3 Hz), 64.10 , 20.17 . HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{16}ClFNO_2^+$ $[M+H]^+$ 356.0848, found 356.0848.



11d 3-methoxybenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

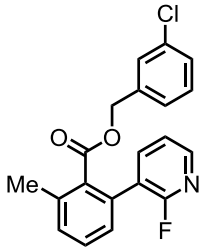
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (ddd, *J* = 4.9, 2.0, 1.1 Hz, 1H), 7.61 (ddd, *J* = 9.4, 7.3, 2.0 Hz, 1H),

7.38 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.06 (ddd, *J* = 7.3, 4.9, 1.8 Hz, 1H), 6.83 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 6.70 – 6.65 (m, 1H), 5.04 (s, 2H), 3.78 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.23 , 160.03 (d, *J* = 238.8 Hz), 159.58 , 146.63 (d, *J* = 14.4 Hz), 141.00 (d, *J* = 4.2 Hz), 136.68 , 136.25 , 132.89 , 132.55 (d, *J* = 4.0 Hz), 130.71 , 129.72 , 129.47 , 127.93 , 123.07 (d, *J* = 31.5 Hz) , 121.09 (d, *J* = 4.4 Hz), 120.81 , 114.17 , 113.73 , 66.91 , 55.17 , 20.20 . HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}FNO_3^+$ $[M+H]^+$ 352.1343, found 352.1344.



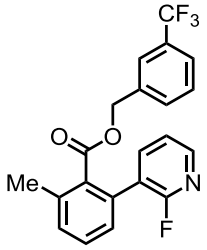
11e 3-fluorobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 4.9 Hz, 1H), 7.63 (ddd, *J* = 9.5, 7.1, 2.0 Hz, 1H), 7.40 (ddd, *J* = 7.7, 7.7, 3.6 Hz, 1H), 7.30 (dd, *J* = 7.7, 2.6 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.18 (d, *J* = 7.1 Hz, 1H), 7.09 (ddd, *J* = 7.1, 4.9, 1.7 Hz, 1H), 6.98 (dddd, *J* = 8.6, 8.6, 2.3, 2.3 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 9.4 Hz, 1H), 5.06 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.08 , 162.13 (d, *J* = 389.7 Hz), 160.53 (d, *J* = 382.1 Hz), 146.73 (d, *J* = 14.4 Hz), 141.04 (d, *J* = 4.2 Hz), 137.25 (d, *J* = 7.2 Hz), 136.87 , 132.70 (d, *J* = 4.0 Hz), 132.56 , 130.85 , 130.06 (d, *J* = 8.0 Hz), 129.93 , 128.05 , 124.06 (d, *J* = 2.8 Hz), 123.19 (d, *J* = 31.5 Hz) , 121.15 (d, *J* = 3.5 Hz), 115.37 (d, *J* = 21.1 Hz), 115.23 (d, *J* = 20.6 Hz) , 66.13 , 20.29 . HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{16}F_2NO_2^+$ $[M+H]^+$ 340.1144, found 340.1145.



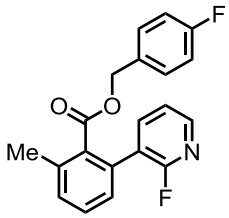
11f 3-chlorobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 4.9 Hz, 1H), 7.61 (ddd, *J* = 9.5, 7.2, 2.0 Hz, 1H), 7.39 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.21 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 (ddd, *J* = 7.2, 4.9, 1.8 Hz, 1H), 7.06 (s, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 5.03 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.96 , 159.95 (d, *J* = 238.7 Hz), 146.68 (d, *J* = 14.4 Hz), 140.93 (d, *J* = 4.2 Hz), 136.89 , 136.73 , 134.20 , 132.69 (d, *J* = 4.1 Hz), 132.42 , 130.81 , 129.92 , 129.75 , 128.56 , 128.42 , 128.01 , 126.65 , 123.12 (d, *J* = 31.5 Hz) , 121.11 (d, *J* = 4.4 Hz), 66.02 , 20.26 . HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{16}ClFNO_2^+$ $[M+H]^+$ 356.0848, found 356.0846.



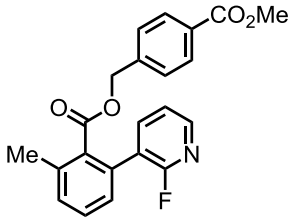
11g 3-(trifluoromethyl)benzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (ddd, *J* = 4.9, 2.0, 1.1 Hz, 1H), 7.62 (ddd, *J* = 9.5, 7.3, 2.0 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.35 – 7.28 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.07 (ddd, *J* = 7.2, 4.9, 1.8 Hz, 1H), 5.11 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.99 , 159.98 (d, *J* = 238.6 Hz), 146.69 (d, *J* = 14.4 Hz), 140.95 (d, *J* = 4.3 Hz), 137.01 , 135.82 , 132.81 (d, *J* = 4.1 Hz), 132.32 , 131.87 , 130.91 , 130.80 (q, *J* = 32.7 Hz), 130.05 , 129.06 , 128.08 , 125.24 (q, *J* = 3.7 Hz), 125.13 (q, *J* = 3.7 Hz), 123.86 (q, *J* = 270 Hz), 123.22 (d, *J* = 31.5 Hz) , 121.14 (d, *J* = 4.4 Hz), 66.06 , 20.29 . HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{16}F_4NO_2^+$ $[M+H]^+$ 390.1112, found 390.1112.



11h 4-fluorobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

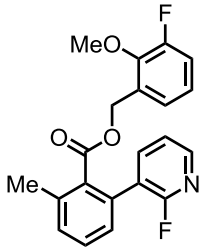
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 4.9 Hz, 1H), 7.60 (ddd, *J* = 9.4, 7.1, 2.0 Hz, 1H), 7.39 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.11 (ddd, *J* = 8.3, 5.3, 2.4 Hz, 2H), 7.06 (ddd, J = 7.1, 4.9, 1.7 Hz, 1H), 7.02 – 6.92 (m, 2H), 5.04 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.18 , 162.15 (d, *J* = 393.8 Hz), 160.54 (d, *J* = 385.4 Hz), 146.63 (d, *J* = 14.3 Hz), 141.04 (d, *J* = 4.3 Hz), 136.72 , 132.73 , 132.56 (d, *J* = 3.8 Hz), 130.79 , 130.67 (d, *J* = 8.2 Hz), 129.82 , 127.99 , 123.14 (d, *J* = 31.5 Hz) , 121.11 (d, *J* = 4.4 Hz), 115.39 (d, *J* = 21.5 Hz), 66.23 , 20.20 . HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{16}F_2NO_2^+$ $[M+H]^+$ 340.1144, found 340.1146.



11i 4-(methoxycarbonyl)benzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

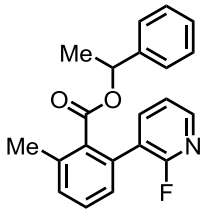
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 3.6, 2.1 Hz, 1H), 7.95 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.69 – 7.58 (m, 1H), 7.40 (ddd, *J* = 7.7, 4.2 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.18 (dd, *J* = 8.4, 2.5 Hz, 3H), 7.08 (ddd, *J*

= 7.3, 3.6, 2.1 Hz, 1H), 5.12 (s, 2H), 3.92 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.05 , 166.61 , 160.02 (d, *J* = 238.8 Hz), 146.69 (d, *J* = 14.4 Hz), 141.01 (d, *J* = 4.2 Hz), 139.82 , 136.85 , 132.66 (d, *J* = 4.0 Hz), 132.49 , 130.84 , 129.94 , 129.72 , 128.13 , 128.03 , 123.18 (d, *J* = 31.5 Hz), 121.16 (d, *J* = 4.3 Hz), 66.18 , 52.12 , 20.27 . HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{19}FNO_4^+$ $[M+H]^+$ 380.1293, found 380.1294.



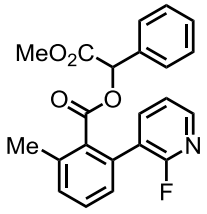
11j 3-fluoro-2-methoxybenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 1H), 7.64 (ddd, *J* = 9.4, 7.3, 1.9 Hz, 1H), 7.38 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.08 (ddd, *J* = 6.6, 4.9, 1.7 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.95 – 6.89 (m, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 5.14 (s, 2H), 3.88 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.23 , 160.05 (d, *J* = 238.9 Hz), 154.99 (d, *J* = 246.9 Hz), 146.63 (d, *J* = 14.4 Hz), 145.84 (d, *J* = 10.4 Hz), 141.06 (d, *J* = 4.2 Hz), 136.67 , 132.92 , 132.48 (d, *J* = 4.1 Hz), 130.73 , 129.72 , 129.32 (d, *J* = 3.0 Hz), 127.96 , 125.45 (d, *J* = 3.1 Hz), 123.26 (d, *J* = 7.7 Hz), 123.06 (d, *J* = 31.0 Hz), 121.06 (d, *J* = 4.4 Hz), 117.24 (d, *J* = 19.1 Hz), 61.52 (d, *J* = 3.2 Hz), 61.43 (d, *J* = 6.5 Hz), 20.17 . HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{18}F_2NO_3^+$ $[M+H]^+$ 370.1249, found 370.1250.



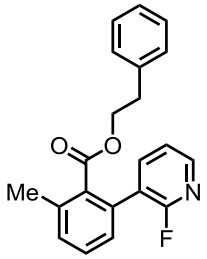
11k 1-phenylethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (ddd, *J* = 4.9, 2.0, 1.1 Hz, 1H), 7.60 (ddd, *J* = 9.5, 7.3, 2.0 Hz, 1H), 7.36 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.33 – 7.22 (m, 4H), 7.17 (m, 3H), 7.03 (ddd, *J* = 7.3, 4.9, 1.7 Hz, 1H), 5.89 (q, *J* = 6.6 Hz, 1H), 2.37 (s, 3H), 1.32 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.64 , 160.11 (d, *J* = 239.2 Hz), 146.58 (d, *J* = 14.3 Hz), 141.12 (d, *J* = 4.2 Hz), 140.49 , 136.43 , 133.33 , 132.23 (d, *J* = 4.0 Hz), 130.62 , 129.48 , 128.38 , 127.87 , 127.80 , 126.18 , 123.05 (d, *J* = 30.0 Hz) , 121.00 (d, *J* = 4.3 Hz), 73.33 , 21.51 , 20.02 . HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}FNO_2^+$ $[M+H]^+$ 336.1394, found 336.1396.



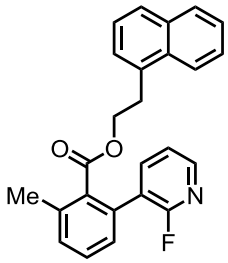
11l 2-methoxy-2-oxo-1-phenylethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (ddd, *J* = 4.9, 1.9, 1.1 Hz, 1H), 7.64 (ddd, *J* = 9.5, 7.2, 1.9 Hz, 1H), 7.42 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.37 – 7.28 (m, 4H), 7.24 – 7.20 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.05 (ddd, *J* = 7.2, 4.9, 1.7 Hz, 1H), 5.88 (s, 1H), 3.70 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.80 , 167.58 , 160.00 (d, *J* = 238.6 Hz), 146.58 (d, *J* = 14.4 Hz), 141.14 (d, *J* = 4.1 Hz), 137.76 , 133.20 (d, *J* = 3.9 Hz), 133.04 , 131.64 , 131.00 , 130.26 , 129.19 , 128.68 , 128.09 , 127.62 , 123.16 (d, *J* = 30.0 Hz) , 121.09 (d, *J* = 4.3 Hz), 75.08 , 52.60 , 20.45 . HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{19}FNO_4^+$ $[M+H]^+$ 380.1293, found 380.1293.



11m phenethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

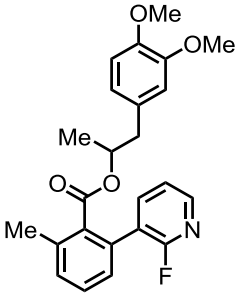
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.8 Hz, 1H), 7.66 (ddd, *J* = 9.5, 7.4, 1.9 Hz, 1H), 7.38 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.23 – 7.15 (m, 3H), 7.11 (d, *J* = 7.0 Hz, 2H), 4.25 (t, *J* = 7.3 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.40 , 160.15 (d, *J* = 239.0 Hz), 146.64 (d, *J* = 14.4 Hz), 141.09 (d, *J* = 4.2 Hz), 137.25 , 136.67 , 133.06 , 132.51 (d, *J* = 4.1 Hz), 130.73 , 129.66 , 128.70 , 128.42 , 127.84 , 126.50 , 123.39 (d, *J* = 30.0 Hz) , 121.16 (d, *J* = 4.3 Hz), 65.48 , 34.57 , 20.11 . HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}FNO_2^+$ $[M+H]^+$ 336.1394, found 336.1397.



11n 2-(naphthalen-1-yl)ethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

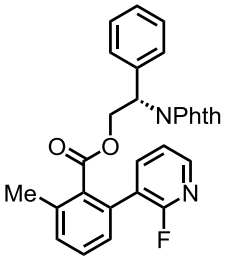
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 1H), 7.99 – 7.91 (m, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.63 (ddd, *J* = 9.4, 7.4, 1.9 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.44 (m, 1H), 7.41 – 7.33 (m, 2H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.08 (ddd, *J* =

6.7, 4.9, 1.7 Hz, 1H), 4.46 – 4.30 (m, 2H), 3.21 – 3.08 (m, 2H), 2.47 – 2.36 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.44 , 160.22 (d, *J* = 238.8 Hz), 146.66 (d, *J* = 14.3 Hz), 141.09 , 136.73 , 133.78 , 133.07 , 133.04 , 132.58 , 131.82 , 130.80 , 129.75 , 128.77 , 127.90 , 127.46 , 126.88 , 126.21 , 125.64 , 125.45 , 123.44 (d, *J* = 31.4 Hz), 123.38 , 121.16 , 64.85 , 31.73 , 20.20 . HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{21}FNO_2^+$ $[M+H]^+$ 386.1551, found 386.1554.



11o 1-(3,4-dimethoxyphenyl)propan-2-yl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

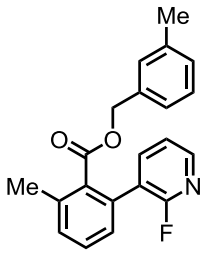
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.8 Hz, 1H), 7.65 (ddd, *J* = 9.4, 7.4, 1.8 Hz, 1H), 7.38 (dd, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 7.0 Hz, 1H), 7.21 – 7.14 (m, 2H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.69 – 6.62 (m, 2H), 5.11 (tdd, *J* = 6.5 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 2.70 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.49 (dd, *J* = 13.7, 6.9 Hz, 1H), 2.28 (s, 3H), 0.94 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.94 , 160.30 (d, *J* = 239.1 Hz), 148.67 , 147.62 , 146.67 (d, *J* = 14.3 Hz), 141.30 (d, *J* = 4.2 Hz), 136.26 , 133.62 , 132.12 (d, *J* = 3.6 Hz), 130.63 , 129.77 , 129.39 , 127.70 , 123.32 (d, *J* = 31.5 Hz), 121.31 , 121.07 (d, *J* = 4.3 Hz), 112.38 , 111.07 , 72.65 , 55.84 , 55.71 , 41.48 , 19.82 , 18.78 . HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{23}FNO_4^+$ $[M+H]^+$ 396.1606, found 396.1605.



11p (S)-2-(1,3-dioxoisoindolin-2-yl)-2-phenylethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

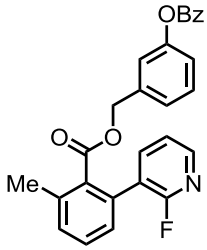
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 4.9 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.73 – 7.68 (m, 2H), 7.64 (ddd, *J* = 9.5, 7.4, 1.9 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.37 – 7.27 (m, 4H), 7.24 – 7.19 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 5.42 (dd, *J* = 10.1, 5.5 Hz, 1H), 5.16 (dd, *J* = 11.3, 10.2 Hz, 1H), 4.79 (dd, *J* = 11.4, 5.5 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.12 , 167.90 , 160.03 (d, *J* = 239.2 Hz), 146.86 (d, *J* = 14.4 Hz), 141.03 (d, *J* = 4.8 Hz), 136.79 , 135.98 , 134.09 , 132.74 (d, *J* = 4.1 Hz), 132.54 , 131.72 , 130.74 , 129.88 , 128.81 , 128.55 , 128.08 , 127.99 , 123.39 , 123.08 (d, *J* = 31.0 Hz), 121.31 (d, *J* = 4.3 Hz), 63.24 , 53.54 , 20.17 . HRMS (ESI-TOF) m/z Calcd for $C_{29}H_{22}FN_2O_4^+$ $[M+H]^+$ 481.1558, found

481.1557.



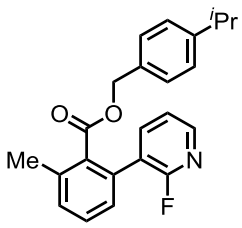
11q 3-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (ddd, *J* = 4.9, 2.0, 1.1 Hz, 1H), 7.62 (ddd, *J* = 9.5, 7.3, 2.0 Hz, 1H), 7.37 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.06 (ddd, *J* = 7.3, 4.9, 1.8 Hz, 1H), 6.95 – 6.90 (m, 2H), 5.04 (s, 2H), 2.44 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.26 , 160.05 (d, *J* = 238.9 Hz), 146.55 (d, *J* = 14.4 Hz), 141.01 (d, *J* = 4.3 Hz), 138.07 , 136.71 , 134.69 , 132.92 , 132.53 (d, *J* = 3.9 Hz), 130.70 , 129.68 , 129.30 , 129.01 , 128.33 , 127.93 , 125.64 , 123.14 (d, *J* = 30.0 Hz) , 121.07 (d, *J* = 4.1 Hz), 67.09 , 21.21 , 20.19 . HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}FNO_2^+$ $[M+H]^+$ 336.1394 , found 336.1394.



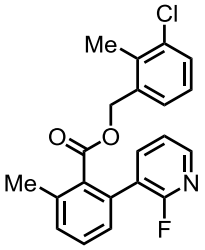
11r 3-(benzoyloxy)benzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.3 Hz, 2H), 8.09 (d, *J* = 4.9 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.53 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.39 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.35 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.08 – 7.02 (m, 2H), 6.99 (d, *J* = 1.7 Hz, 1H), 5.11 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.16 , 165.00 , 160.04 (d, *J* = 238.8 Hz), 150.90 , 146.69 (d, *J* = 14.3 Hz), 141.07 (d, *J* = 4.2 Hz), 136.91 , 136.57 , 133.67 , 132.69 (d, *J* = 3.8 Hz), 132.65 , 130.81 , 130.14 , 129.86 , 129.59 , 129.36 , 128.60 , 128.01 , 126.02 , 123.14 (d, *J* = 31.0 Hz), 121.87 , 121.74 , 121.23 (d, *J* = 4.3 Hz), 66.34 , 20.30 . HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{21}FNO_4^+$ $[M+H]^+$ 442.1449, found 442.1447.



11s 4-isopropylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 4.9 Hz, 1H), 7.60 (ddd, *J* = 9.4, 7.4, 1.8 Hz, 1H), 7.36 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 – 7.00 (m, 3H), 5.04 (s, 2H), 2.88 (hept, *J* = 6.9 Hz, 1H), 2.43 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 168.30 , 160.06 (d, *J* = 239.1 Hz), 149.05 , 146.54 (d, *J* = 14.3 Hz), 141.03 (d, *J* = 4.2 Hz), 136.61 , 133.02 , 132.45 (d, *J* = 4.0 Hz), 132.19 , 130.66 , 129.61 , 128.76 , 127.88 , 126.49 , 123.09 (d, *J* = 31.5 Hz) , 121.05 (d, *J* = 4.2 Hz), 66.95 , 33.81 , 23.89 , 20.16 . HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{23}FNO_2^+$ $[M+H]^+$ 364.1707, found 364.1707.

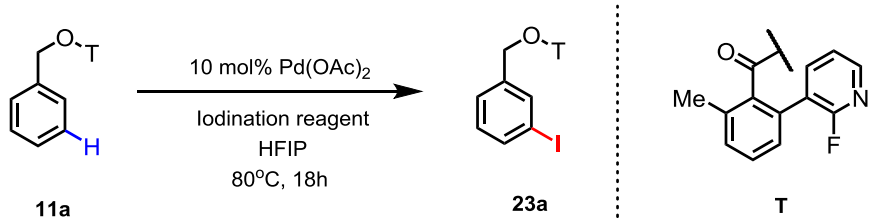


11t 3-chloro-2-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

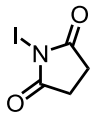
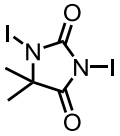
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 1H), 7.60 – 7.53 (m, 1H), 7.39 (ddd, *J* = 7.7, 2.8, 2.8 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 – 7.03 (m, 2H), 7.01 – 6.97 (m, 1H), 5.12 (s, 2H), 2.44 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.09 , 159.93 (d, *J* = 238.8 Hz), 146.67 (d, *J* = 14.4 Hz), 140.82 (d, *J* = 4.2 Hz), 136.67 , 135.31 , 135.06 , 134.79 , 132.72 , 132.46 (d, *J* = 4.1 Hz), 130.72 , 129.78 , 129.57 , 128.59 , 128.00 , 126.60 , 122.88 (d, *J* = 31.0 Hz), 120.89 (d, *J* = 4.2 Hz), 65.17 , 20.18 , 15.50 . HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{18}ClFNO_2^+$ $[M+H]^+$ 370.1005, found 370.1005.

Optimization of Remote *meta*-C–H Iodination Reaction:

Table S1. Screening of iodination reagents

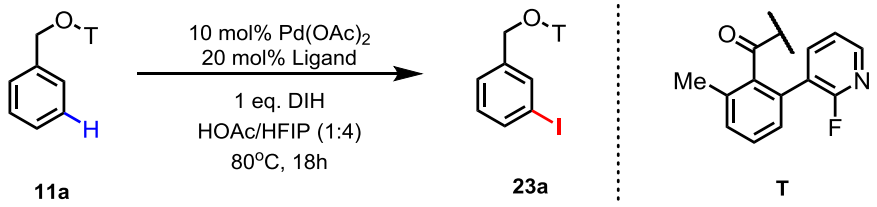


11a **23a** **T**

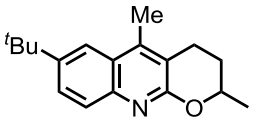
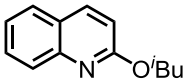
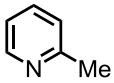
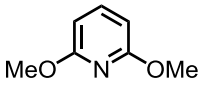
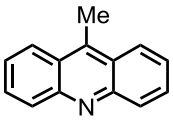
entry	iodination reagent	yield[a] (%)
1	I_2+CsOAc	0
2	I_2+PhI(OAc)$_2$	0
3	 (NIS)	16
4	 (DIH)	21(51[b])

[a]Yields were determined by ^{1}H-NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard. [b]HOAc/HFIP (1/4) was utilized as the solvent.

Table S2. Ligand screening

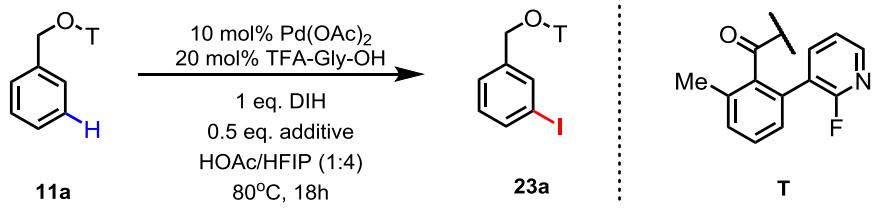


11a **23a** **T**

entry	ligand	yield[a] (%)	
		mono	di
1	no ligand	42	9
2	Ac-Val-OH	10	0
3	Ac-Gly-OH	16	0
4	Ac-Leu-OH	8	0
5	Boc-Gly-OH	9	0
6	Bz-Gly-OH	26	2
7	TFA-Gly-OH	44	12
8	Trc-Gly-OH	38	5
9	Fmoc-Gly-OH	15	0
10		5	0
11		26	0
12		trace	0
13		20	0
14	F_5-pyridine	0	0
15		18	0

[a]Yields were determined by ^{1}H-NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard.

Table S3. Screening of additives

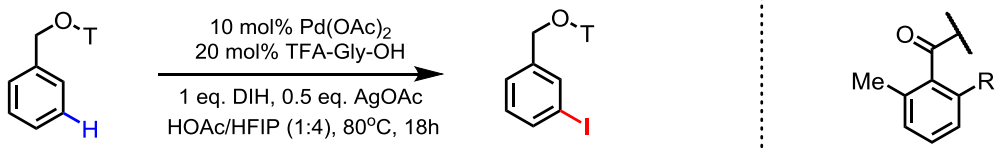


11a **23a** **T**

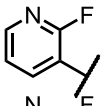
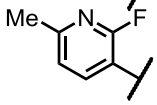
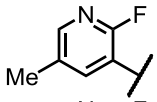
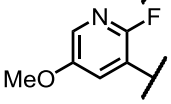
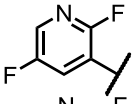
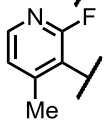
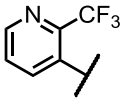
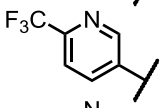
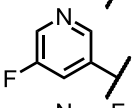
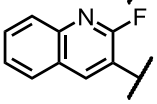
entry	additive	yield[a] (%)	
		mono	di
1	no additive	44	12
2	LiOAc	39	3
3	NaOAc	30	0
4	KOAc	38	3
5	CsOAc	53	11
6	**AgOAc**	**68**	**17**
7	NH_4OAc	32	0
8	$Cu(OAc)_2$	48	10
9	AgTFA	59	8
10	Ag_3PO_4	48	3

[a]Yields were determined by ^{1}H-NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard.

Table S4. Tuning of templates



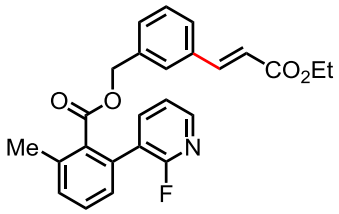
11a **23a** **T**

entry	R	yield[a] (%)		selectivity[b] (*m*:others)
		mono	di	
1		69	19	>20:1
2		60	10	>20:1
3		28	2	>20:1
4		25	0	>20:1
5		50	5	>20:1
6		n.d.	n.d.	mixture of products
7		32	1	5:1
8		28	0	6:1
9		20	0	10:1
10		64	15	>20:1

[a]Yields were determined by ^{1}H-NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard.
[b]Selectivity was determined by GC-MS.

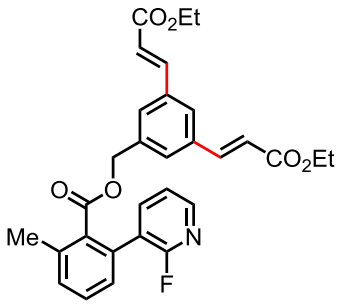
General Procedure for Template-directed *meta*-C–H Olefination of Alcohols:

A 10 mL sealed tube was charged with substrate (0.2 mmol, 1.0 equiv), olefin (3.0 equiv), $Pd(OAc)_2$ (10 mol%), Ac-Gly-OH (20 mol%), AgOAc (3.0 equiv), and HFIP (2 mL). The tube was then sealed and submerged into a pre-heated 80 °C heating plate. The reaction mixture was stirred at 80 °C for 18 h. After being cooled to room temperature, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite. The filtrate was concentrated in vacuo, and the resulting residue was purified by preparative TLC using EtOAc/hexanes as the eluent to give the desired product. The positional selectivity was determined by GC-MS with a flame ionization detector.



22a-mono (E)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)benzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **22a-mono** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 46 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (ddd, *J* = 4.9, 1.9, 1.1 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.28 (s, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.08 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.16 , 166.82 , 160.05 (d, *J* = 238.9 Hz), 146.68 (d, *J* = 14.4 Hz), 143.90 , 141.01 (d, *J* = 4.3 Hz), 136.91 , 135.66 , 134.74 , 132.72 (d, *J* = 3.9 Hz), 132.60 , 130.87 , 130.38 , 129.94 , 129.12 , 128.21 , 128.06 , 127.90 , 123.23 (d, *J* = 31.5 Hz), 121.13 (d, *J* = 4.5 Hz), 118.86 , 66.56 , 60.57 , 20.32 , 14.31 . HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{23}FNO_4^+$ $[M+H]^+$ 420.1606, found 420.1605.



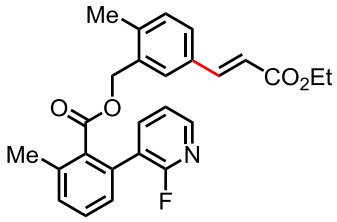
22a-di

diethyl

3,3'-(5-(((2-(2-fluoropyridin-3-yl)-6-methylbenzoyl)oxy)methyl)-1,3-phenylene)(2E,2'E)-diacrylate

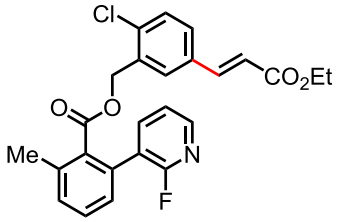
The compound **22a-di** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 28 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 1H), 7.68 – 7.59 (m, 3H),

7.58 (s, 1H), 7.42 (dd, J = 7.7, 7.5 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.07 (ddd, *J* = 6.7, 4.9, 1.8 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 2H), 5.09 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 4H), 2.46 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 168.04 , 166.55 , 160.03 (d, *J* = 238.7 Hz), 146.69 (d, *J* = 14.4 Hz), 143.01 , 140.95 (d, *J* = 4.2 Hz), 137.08 , 136.46 , 135.51 , 132.87 (d, *J* = 3.9 Hz), 132.29 , 130.98 , 130.12 , 129.42 , 128.14 , 127.36 , 123.33 (d, *J* = 31.5 Hz), 121.15 (d, *J* = 4.4 Hz), 119.86 , 66.17 , 60.70 , 20.41 , 14.30 . HRMS (ESI-TOF) m/z Calcd for $C_{30}H_{29}FNO_6^+$ $[M+H]^+$ 518.1973, found 518.1975.



22b (E)-5-(3-ethoxy-3-oxoprop-1-en-1-yl)-2-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

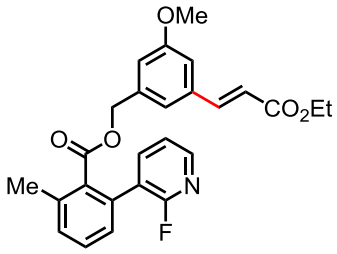
The compound **22b** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 76 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.95 (m, 1H), 7.66 – 7.54 (m, 2H), 7.44 – 7.33 (m, 2H), 7.26 (s, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 5.11 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 2.21 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.21 , 167.01 , 159.98 (d, *J* = 238.9 Hz), 146.67 (d, *J* = 14.4 Hz), 143.96 , 140.96 (d, *J* = 4.2 Hz), 139.69 , 136.77 , 133.60 , 132.74 , 132.59 (d, *J* = 4.1 Hz), 132.31 , 130.99 , 130.81 , 129.85 , 129.42 , 128.03 , 123.03 (d, *J* = 31.0 Hz), 121.00 (d, *J* = 4.4 Hz), 117.78 , 64.70 , 60.47 , 20.25 , 18.74 , 14.32 . HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{25}FNO_4^+$ $[M+H]^+$ 434.1762, found 434.1762.



22c-mono (E)-2-chloro-5-(3-ethoxy-3-oxoprop-1-en-1-yl)benzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

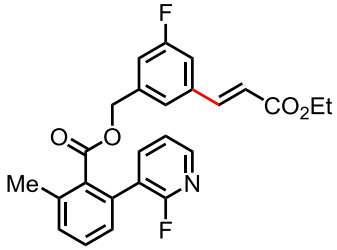
The compound **22c-mono** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 66 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 4.9 Hz, 1H), 7.67 (ddd, *J* = 9.4, 7.0, 1.9 Hz, 1H), 7.58 (d, *J* = 16.0 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.37 – 7.28 (m, 3H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.09 (ddd, *J* = 7.0, 4.9, 1.7 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 5.20 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.03 , 166.59 , 160.04 (d, *J* = 239.1 Hz), 146.73 (d, *J* = 14.4 Hz), 142.66 , 141.01 (d, *J* = 4.2 Hz), 136.99 , 135.55 , 133.36 , 133.35 ,

132.78 (d, *J* = 3.9 Hz), 132.42 , 130.91 , 130.07 , 130.04 , 129.85 , 128.77 , 128.10 , 123.19 (d, *J* = 31.3 Hz), 121.14 (d, *J* = 4.4 Hz), 119.39 , 63.87 , 60.66 , 20.36 , 14.29 . HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{22}ClFNO_4^+$ $[M+H]^+$ 454.1216, found 454.1217.



22d **(E)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-methoxybenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate**

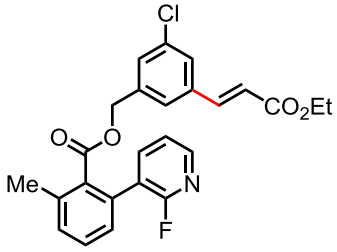
The compound **22d** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 62 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 4.8 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.40 (dd, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.97 (s, 1H), 6.88 (s, 1H), 6.71 (s, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.04 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.45 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.14 , 166.76 , 160.02 (d, *J* = 238.8 Hz), 159.98 , 146.68 (d, *J* = 14.4 Hz), 143.88 , 140.98 (d, *J* = 4.0 Hz), 136.89 , 136.88 , 135.94 , 132.71 (d, *J* = 4.0 Hz), 132.59 , 130.85 , 129.92 , 128.03 , 123.16 (d, *J* = 31.4 Hz), 121.11 (d, *J* = 4.3 Hz), 120.73 , 119.08 , 115.74 , 113.25 , 66.51 , 60.57 , 55.40 , 20.31 , 14.29 . HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{25}FNO_5^+$ $[M+H]^+$ 450.1711, found 450.1713.



22e (E)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-fluorobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

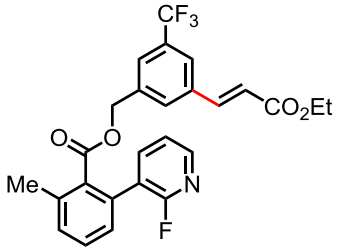
The compound **22e** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 67 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 1H), 7.64 (ddd, *J* = 9.4, 7.0, 2.0 Hz, 1H), 7.58 (d, *J* = 16.0 Hz, 1H), 7.42 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.10 (ddd, *J* = 7.0, 4.9, 1.8 Hz, 1H), 7.06 (s, 1H), 6.85 – 6.78 (m, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.06 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.95 , 166.41 , 162.78 (d, *J* = 247.7 Hz), 160.02 (d, *J* = 238.9 Hz), 146.74 (d, *J* = 14.4 Hz), 142.56 (d, *J* = 2.9 Hz), 140.99 (d, *J* = 4.3 Hz), 137.90 (d, *J* = 7.9 Hz), 137.03 , 136.84 (d, *J* = 7.9 Hz), 132.82 (d, *J* = 3.9 Hz), 132.24 , 130.95 , 130.11 , 128.12 , 123.93 (d, *J* = 2.9 Hz),

123.27 (d, *J* = 31.4 Hz), 121.17 (d, *J* = 4.4 Hz), 120.23 , 116.93 (d, *J* = 22.2 Hz), 114.10 (d, *J* = 22.0 Hz), 65.76 , 60.72 , 20.37 , 14.26 . HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{22}F_2NO_4^+$ $[M+H]^+$ 438.1511, found 438.1511.



22f (E)-3-chloro-5-(3-ethoxy-3-oxoprop-1-en-1-yl)benzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

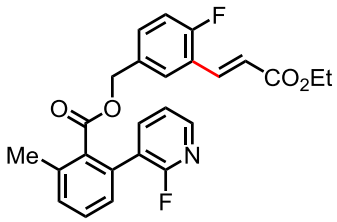
The compound **22f** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 75 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 4.8 Hz, 1H), 7.63 (ddd, *J* = 9.4, 7.3, 1.9 Hz, 1H), 7.56 (d, *J* = 16.0 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.16 (s, 1H), 7.10 (ddd, *J* = 6.9, 4.9, 1.7 Hz, 1H), 7.07 (s, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.04 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.91 , 166.36 , 159.99 (d, *J* = 238.8 Hz), 146.73 (d, *J* = 14.4 Hz), 142.31 , 140.93 (d, *J* = 4.2 Hz), 137.37 , 137.10 , 136.44 , 134.96 , 132.86 (d, *J* = 4.1 Hz), 132.16 , 130.96 , 130.14 , 129.90 , 128.13 , 127.55 , 126.29 , 123.26 (d, *J* = 31.5 Hz), 121.17 (d, *J* = 4.3 Hz), 120.31 , 65.72 , 60.72 , 20.39 , 14.26 . HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{22}ClFNO_4^+$ $[M+H]^+$ 454.1216, found 454.1218.



22g (E)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-(trifluoromethyl)benzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

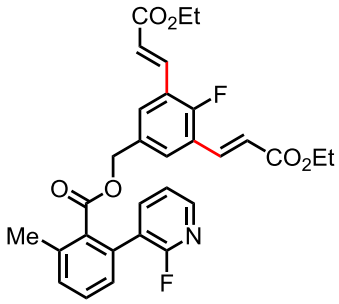
The compound **22g** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 70 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.9 Hz, 1H), 7.69 (s, 1H), 7.67 – 7.61 (m, 2H), 7.46 (s, 1H), 7.43 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.38 (s, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 5.12 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.89 , 166.23 , 159.97 (d, *J* = 238.7 Hz), 146.71 (d, *J* = 14.4 Hz), 142.08 , 140.91 (d, *J* = 4.3 Hz), 137.19 , 136.78 , 135.72 , 132.95 (d, *J* = 4.1 Hz), 132.01 , 131.68 (q, *J* = 31.8 Hz), 131.03 , 131.01 , 130.25 , 128.17 , 126.46 (q, *J* = 3.5 Hz), 124.38 (d, *J* = 3.8 Hz), 123.49 (q, *J* = 281.8 Hz), 123.33 (d, *J* = 31.5 Hz), 121.18 (d, *J* = 4.5 Hz), 120.86 ,

65.71 , 60.81 , 20.40 , 14.25 . HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{22}F_4NO_4^+$ $[M+H]^+$ 488.1479, found 488.1479.



22h-mono **(E)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-fluorobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate**

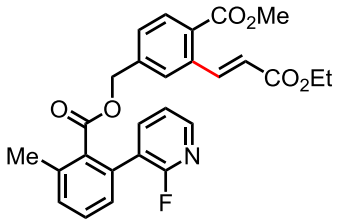
The compound **22h-mono** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 40 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 1H), 7.75 (d, *J* = 16.2 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.41 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.13 (ddd, *J* = 7.6, 4.8, 1.9 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.05 – 6.99 (m, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 5.04 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.08 , 166.63 , 161.06 (d, *J* = 255.2 Hz), 160.03 (d, *J* = 238.9 Hz), 146.64 (d, *J* = 14.4 Hz), 141.00 (d, *J* = 4.2 Hz), 136.90 , 136.54 (d, *J* = 2.5 Hz), 132.71 (d, *J* = 3.8 Hz), 132.44 , 132.06 (d, *J* = 9.2 Hz), 131.31 (d, *J* = 3.4 Hz), 130.91 , 130.01 , 129.59 (d, *J* = 3.3 Hz), 128.08 , 123.23 (d, *J* = 31.2 Hz), 122.55 (d, *J* = 12.2 Hz), 121.44 (d, *J* = 6.6 Hz), 121.11 (d, *J* = 4.4 Hz), 116.39 (d, *J* = 22.3 Hz), 65.92 , 60.69 , 20.31 , 14.29 . HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{22}F_2NO_4^+$ $[M+H]^+$ 438.1511, found 438.1510.



22h-di **diethyl 3,3'-(2-fluoro-5-(((2-(2-fluoropyridin-3-yl)-6-methylbenzoyl)oxy)methyl)-1,3-phenylene)(2E,2'E)-diacrylate**

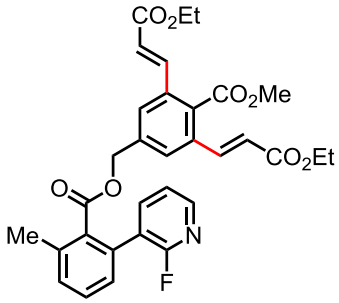
The compound **22h-di** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 42 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 4.9 Hz, 1H), 7.77 (d, *J* = 16.2 Hz, 2H), 7.62 (ddd, *J* = 9.4, 7.1, 1.9 Hz, 1H), 7.42 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.07 (ddd, *J* = 7.1, 4.9, 1.7 Hz, 1H), 6.53 (d, *J* = 16.2 Hz, 2H), 5.04 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 2.46 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 167.97 , 166.39 ,

159.99 (d, *J* = 239.0 Hz), 159.16 (d, *J* = 262.0 Hz), 146.63 (d, *J* = 14.4 Hz), 140.94 (d, *J* = 4.2 Hz), 137.06 , 135.80 (d, *J* = 3.8 Hz), 132.85 (d, *J* = 3.8 Hz), 132.14 , 131.48 (d, *J* = 3.8 Hz), 131.00 , 130.52 (d, *J* = 3.7 Hz), 130.17 , 128.14 , 123.47 (d, *J* = 13.2 Hz), 123.32 (d, *J* = 32.8 Hz), 122.20 (d, *J* = 6.2 Hz), 121.12 (d, *J* = 4.4 Hz), 65.69 , 60.81 , 20.38 , 14.27 . HRMS (ESI-TOF) m/z Calcd for $C_{30}H_{28}F_2NO_6^+$ $[M+H]^+$ 536.1879, found 536.1881.



22i-mono **methyl (E)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-(((2-(2-fluoropyridin-3-yl)-6-methylbenzoyl)oxy)methyl)benzoate**

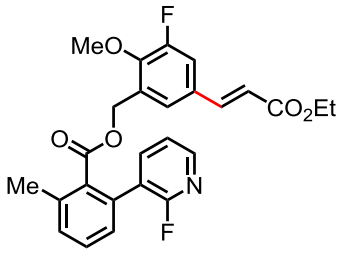
The compound **22i-mono** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 37 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 15.9 Hz, 1H), 8.07 (d, *J* = 4.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.42 (dd, *J* = 7.7 Hz, 1H), 7.35 (s, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.08 – 7.05 (m, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 5.11 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 2.46 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.91 , 167.85 , 166.01 , 159.93 (d, *J* = 238.3 Hz), 146.73 (d, *J* = 14.4 Hz), 140.75 (d, *J* = 4.2 Hz), 140.19 , 137.18 , 137.05 , 133.82 , 133.63 , 132.87 (d, *J* = 3.0 Hz), 132.08 , 130.96 , 130.18 , 128.13 , 127.91 , 123.11 (d, *J* = 31.5 Hz), 122.39 , 121.06 (d, *J* = 4.3 Hz), 65.73 , 60.79 , 52.93 , 20.36 , 14.23 . HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{25}FNO_6^+$ $[M+H]^+$ 478.1660, found 478.1661.



22i-di **diethyl 3,3'-(5-(((2-(2-fluoropyridin-3-yl)-6-methylbenzoyl)oxy)methyl)-2-(methoxycarbonyl)-1,3-phenylene)(2E,2'E)-diacrylate**

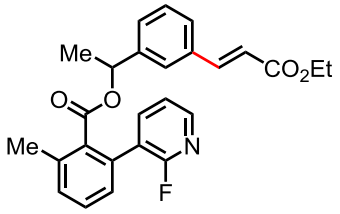
The compound **22i-di** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 44 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 1H), 7.68 (d, *J* = 15.8 Hz, 2H), 7.57 (ddd, *J* = 9.3, 7.0, 1.9 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.34 – 7.30 (m, 1H), 7.17 (d, *J* = 7.6 Hz,

1H), 7.00 (ddd, *J* = 7.0, 4.9, 1.6 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 2H), 5.10 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 4H), 4.01 (s, 3H), 2.47 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 167.91 , 167.85 , 166.01 , 159.93 (d, *J* = 238.3 Hz), 146.73 (d, *J* = 14.4 Hz), 140.75 (d, *J* = 4.2 Hz), 140.19 , 137.18 , 137.05 , 133.82 , 133.63 , 132.87 (d, *J* = 3.9 Hz), 132.08 , 130.96 , 130.18 , 128.13 , 127.91 , 123.11 (d, *J* = 31.5 Hz), 122.39 , 121.06 (d, *J* = 4.3 Hz), 65.73 , 60.79 , 52.93 , 20.36 , 14.23 . HRMS (ESI-TOF) m/z Calcd for $C_{32}H_{31}FNO_8^+$ $[M+H]^+$ 576.2028, found 576.2026.



22j **(E)-5-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-fluoro-2-methoxybenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate**

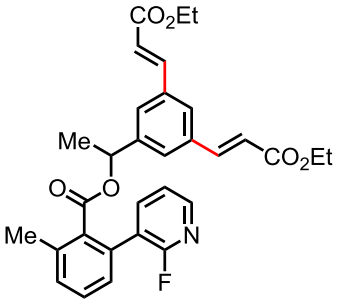
The compound **22j** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 78 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 1H), 7.64 (ddd, *J* = 9.5, 7.3, 1.9 Hz, 1H), 7.52 (d, *J* = 16.0 Hz, 1H), 7.41 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.08 (ddd, *J* = 7.1, 4.9, 1.7 Hz, 1H), 7.05 – 7.01 (m, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 5.13 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.94 (d, *J* = 2.9 Hz, 3H), 2.46 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.11 , 166.65 , 160.02 (d, *J* = 238.8 Hz), 154.52 (d, *J* = 247.7 Hz), 147.12 (d, *J* = 10.4 Hz), 146.65 (d, *J* = 14.4 Hz), 142.50 (d, *J* = 2.0 Hz), 141.00 (d, *J* = 4.2 Hz), 136.85 , 132.65 (d, *J* = 3.8 Hz), 132.59 , 130.86 , 129.93 , 129.64 (d, *J* = 7.5 Hz), 129.43 (d, *J* = 3.2 Hz), 128.05 , 125.52 (d, *J* = 2.3 Hz), 123.15 (d, *J* = 31.1 Hz), 121.06 (d, *J* = 4.4 Hz), 118.51 , 116.20 (d, *J* = 20.1 Hz), 61.38 (d, *J* = 7.4 Hz), 61.33 (d, *J* = 2.9 Hz), 60.59 , 20.27 , 14.28 . HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{24}F_2NO_5^+$ $[M+H]^+$ 468.1617, found 468.1617.



22k-mono **(E)-1-(3-(3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)ethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate**

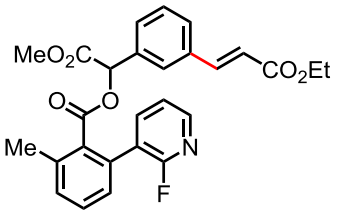
The compound **22k-mono** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 36 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.40 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.34 – 7.28 (m, 3H),

7.21 – 7.16 (m, 2H), 7.08 – 7.03 (m, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.88 (q, *J* = 6.6 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.38 – 1.31 (m, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 167.60 , 166.84 , 160.13 (d, *J* = 239.0 Hz), 146.65 (d, *J* = 14.3 Hz), 144.09 , 141.38 , 141.09 (d, *J* = 4.2 Hz), 136.63 , 134.65 , 133.06 , 132.41 (d, *J* = 4.0 Hz), 130.78 , 129.71 , 129.10 , 128.07 , 127.93 , 127.56 , 125.90 , 123.18 (d, *J* = 31.6 Hz), 121.04 (d, *J* = 4.4 Hz), 118.70 , 72.97 , 60.54 , 21.58 , 20.15 , 14.30 . HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{25}FNO_4^+$ $[M+H]^+$ 434.1762, found 434.1763.



22k-di **diethyl 3,3'-(5-(1-((2-(2-fluoropyridin-3-yl)-6-methylbenzoyl)oxy)ethyl)-1,3-phenylene)(2E,2'E)-diacrylate**

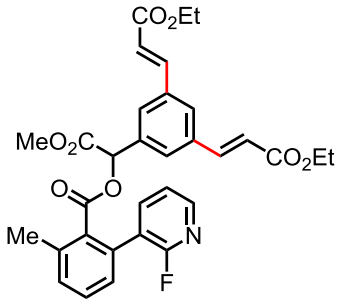
The compound **22k-di** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 36 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 1H), 7.66 – 7.60 (m, 3H), 7.56 (s, 1H), 7.41 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.07 (ddd, *J* = 6.8, 4.9, 1.7 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 2H), 5.87 (q, *J* = 6.6 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 4H), 2.40 (s, 3H), 1.39 – 1.31 (m, 9H). ^{13}C NMR (151 MHz, CDCl3) δ 167.49 , 166.56 , 160.10 (d, *J* = 238.9 Hz), 146.66 (d, *J* = 14.3 Hz), 143.18 , 142.23 , 141.02 (d, *J* = 4.2 Hz), 136.77 , 135.45 , 132.75 , 132.55 (d, *J* = 3.7 Hz), 130.89 , 129.89 , 128.00 , 127.21 , 127.03 , 123.28 (d, *J* = 31.6 Hz), 121.05 (d, *J* = 4.3 Hz), 119.71 , 72.64 , 60.67 , 21.61 , 20.22 , 14.28 . HRMS (ESI-TOF) m/z Calcd for $C_{31}H_{31}FNO_6^+$ $[M+H]^+$ 532.2130, found 532.2129.



22l-mono **(E)-1-(3-(3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)-2-methoxy-2-oxoethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate**

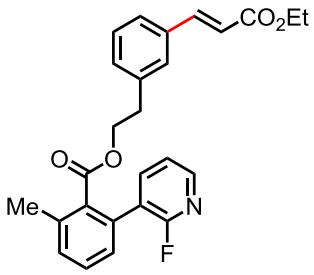
The compound **22l-mono** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 44 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 1H), 7.69 – 7.59 (m, 2H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.44 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.07 – 7.02 (m, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.89 (s, 1H), 4.28 (q, *J* = 7.1 Hz,

2H), 3.71 (s, 3H), 2.56 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.48 , 167.37 , 166.69 , 159.94 (d, *J* = 238.6 Hz), 146.53 (d, *J* = 14.4 Hz), 143.54 , 141.03 (d, *J* = 4.2 Hz), 137.90 , 134.95 , 133.85 , 133.28 (d, *J* = 3.9 Hz), 131.31 , 131.09 , 130.44 , 129.28 , 129.20 , 128.66 , 128.15 , 127.00 , 123.25 (d, *J* = 31.1 Hz), 121.09 (d, *J* = 4.3 Hz), 119.24 , 74.60 , 60.60 , 52.73 , 20.49 , 14.29 . HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{25}FNO_6^+$ $[M+H]^+$ 478.1660, found 478.1658.



22l-di **diethyl 3,3'-(5-(1-((2-(2-fluoropyridin-3-yl)-6-methylbenzoyl)oxy)-2-methoxy-2-oxoethyl)-1,3-phenylene)(2E,2'E)-diacrylate**

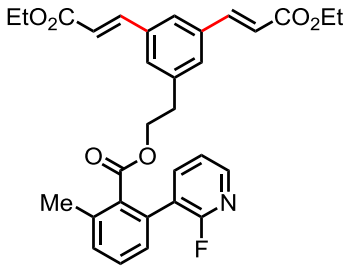
The compound **22l-di** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 28 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 4.9 Hz, 1H), 7.70 – 7.57 (m, 4H), 7.45 (dd, *J* = 7.7, 7.5 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.05 (ddd, *J* = 6.8, 4.9, 1.5 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 2H), 5.88 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.72 (s, 3H), 2.57 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 168.22 , 167.22 , 166.43 , 159.93 (d, *J* = 238.5 Hz), 146.54 (d, *J* = 14.4 Hz), 142.68 , 140.95 (d, *J* = 4.1 Hz), 138.05 , 135.72 , 134.67 , 133.37 (d, *J* = 4.0 Hz), 131.19 , 131.08 , 130.61 , 128.22 , 128.11 , 128.05 , 123.35 (d, *J* = 31.4 Hz), 121.12 (d, *J* = 4.3 Hz), 120.23 , 74.26 , 60.74 , 52.89 , 20.54 , 14.28 . HRMS (ESI-TOF) m/z Calcd for $C_{32}H_{31}FNO_8^+$ $[M+H]^+$ 576.2028, found 576.2028.



22m-mono **(E)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)phenethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate**

The compound **22m-mono** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 36 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 – 8.14 (m, 1H), 7.73 – 7.59 (m, 2H), 7.45 – 7.34 (m, 2H), 7.33 – 7.24 (m, 4H), 7.23 – 7.16 (m, 2H), 7.13 (d, *J* = 7.3 Hz, 1H),

6.41 (d, *J* = 16.0 Hz, 1H), 4.35 – 4.20 (m, 4H), 2.72 (t, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.42 – 1.29 (m, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.40 , 166.92 , 160.18 (d, *J* = 238.9 Hz), 146.71 (d, *J* = 14.3 Hz), 144.29 , 141.11 (d, *J* = 4.3 Hz), 138.10 , 136.77 , 134.68 , 132.92 , 132.62 (d, *J* = 4.0 Hz), 130.85 , 130.65 , 129.83 , 129.06 , 128.43 , 127.95 , 126.34 , 123.47 (d, *J* = 31.2 Hz), 121.21 (d, *J* = 4.4 Hz), 118.44 , 65.20 , 60.50 , 34.47 , 20.19 , 14.31 . HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{25}FNO_4^+$ $[M+H]^+$ 434.1762, found 434.1764.

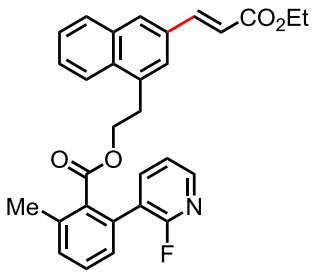


22m-di

diethyl

3,3'-(5-(2-((2-(2-fluoropyridin-3-yl)-6-methylbenzoyl)oxy)ethyl)-1,3-phenylene)(2E,2'E)-diacrylate

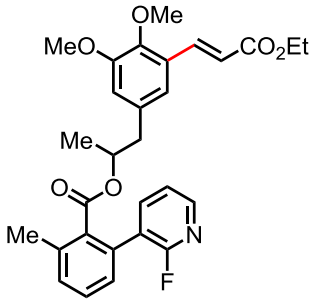
The compound **22m-di** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 50 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.4 Hz, 1H), 7.73 – 7.56 (m, 3H), 7.51 (s, 1H), 7.40 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.34 – 7.23 (m, 3H), 7.23 – 7.13 (m, 2H), 6.44 (d, *J* = 16.0 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 6H), 2.74 (t, *J* = 7.0 Hz, 2H), 2.36 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 168.31 , 166.61 , 160.13 (d, *J* = 239.1 Hz), 146.69 (d, *J* = 14.4 Hz), 143.36 , 141.06 (d, *J* = 4.3 Hz), 138.88 , 136.79 , 135.38 , 132.71 , 132.67 (d, *J* = 3.9 Hz), 130.89 , 129.92 , 129.81 , 127.98 , 125.92 , 123.48 (d, *J* = 31.1 Hz), 121.22 (d, *J* = 4.3 Hz), 119.44 , 64.88 , 60.61 , 34.34 , 20.21 , 14.27 . HRMS (ESI-TOF) m/z Calcd for $C_{31}H_{31}FNO_6^+$ $[M+H]^+$ 532.2130, found 532.2127.



22n **(E)-2-(3-(3-ethoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)ethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate**

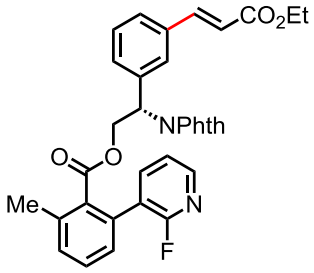
The compound **22n** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 57 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 4.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.83 (s, 1H), 7.79 (d, *J* = 16.0 Hz, 1H), 7.67 (ddd, *J* = 9.4, 7.3, 1.9 Hz, 1H), 7.56 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.45 (s, 1H), 7.41 (dd, *J* = 7.7, 7.7 Hz, 1H),

7.31 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.14 (ddd, *J* = 7.0, 4.9, 1.7 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.38 (t, *J* = 7.6 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.43 , 167.00 , 160.22 (d, *J* = 238.9 Hz), 146.69 (d, *J* = 14.3 Hz), 144.27 , 141.09 (d, *J* = 4.3 Hz), 136.83 , 134.08 , 133.73 , 132.90 , 132.67 (d, *J* = 3.7 Hz), 131.49 , 130.88 , 129.87 , 129.47 , 129.35 , 127.96 , 127.58 , 126.54 , 124.47 , 123.53 , 123.51 (d, J = 31.1 Hz), 121.18 (d, *J* = 4.4 Hz), 118.53 , 64.60 , 60.52 , 31.86 , 20.25 , 14.34 . HRMS (ESI-TOF) m/z Calcd for $C_{30}H_{27}FNO_4^+$ $[M+H]^+$ 484.1919, found 484.1920.



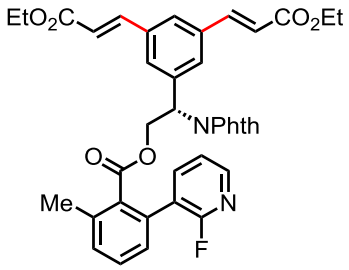
22o (E)-1-(3-(3-ethoxy-3-oxoprop-1-en-1-yl)-4,5-dimethoxyphenyl)propan-2-yl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **22o** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 89 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.8 Hz, 1H), 7.93 (d, *J* = 16.2 Hz, 1H), 7.67 (ddd, *J* = 9.4, 7.3, 1.9 Hz, 1H), 7.38 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.23 – 7.14 (m, 2H), 6.89 (d, *J* = 1.7 Hz, 1H), 6.70 (d, *J* = 1.8 Hz, 1H), 6.42 (d, *J* = 16.2 Hz, 1H), 5.18 – 5.09 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 2.71 (dd, *J* = 13.7, 7.2 Hz, 1H), 2.52 (dd, *J* = 13.7, 6.6 Hz, 1H), 2.23 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.94 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.87 , 167.07 , 160.29 (d, *J* = 239.3 Hz), 152.80 , 147.04 , 146.72 (d, *J* = 14.3 Hz), 141.31 (d, *J* = 4.2 Hz), 139.06 , 136.24 , 133.45 , 133.29 , 132.16 (d, *J* = 3.8 Hz), 130.68 , 129.51 , 128.16 , 127.73 , 123.35 (d, *J* = 31.2 Hz), 121.11 (d, *J* = 4.3 Hz), 119.79 , 119.60 , 114.89 , 72.18 , 61.24 , 60.39 , 55.79 , 41.76 , 19.77 , 18.88 , 14.29 . HRMS (ESI-TOF) m/z Calcd for $C_{29}H_{31}FNO_6^+$ $[M+H]^+$ 508.2130, found 508.2132.



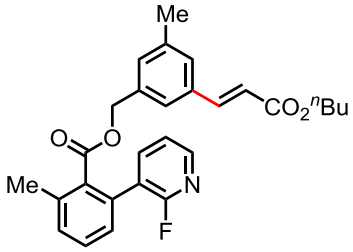
22p-mono (S,E)-2-(1,3-dioxoisoindolin-2-yl)-2-(3-(3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)ethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **22p-mono** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 40 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 4.9 Hz, 1H), 7.82 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.67 – 7.59 (m, 3H), 7.50 – 7.43 (m, 2H), 7.39 – 7.33 (m, 2H), 7.25 – 7.19 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.43 (dd, *J* = 9.9, 5.7 Hz, 1H), 5.14 (dd, *J* = 11.4, 9.9 Hz, 1H), 4.81 (dd, *J* = 11.4, 5.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.05 , 167.81 , 166.73 , 160.00 (d, *J* = 238.9 Hz), 146.87 (d, *J* = 14.4 Hz), 143.76 , 141.00 (d, *J* = 4.2 Hz), 136.81 , 135.10 , 134.18 , 132.77 (d, *J* = 4.1 Hz), 132.37 , 131.61 , 130.77 , 129.95 , 129.82 , 129.40 , 128.02 , 128.01 , 127.79 , 123.48 , 123.06 (d, *J* = 31.0 Hz), 121.32 (d, *J* = 4.3 Hz), 119.11 , 63.00 , 60.55 , 53.21 , 20.19 , 14.29 . HRMS (ESI-TOF) m/z Calcd for $C_{34}H_{28}FN_2O_6^+$ $[M+H]^+$ 579.1926, found 579.1925.



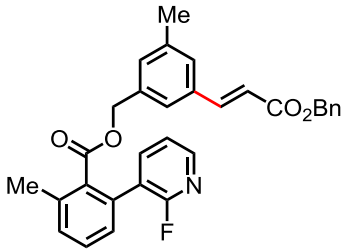
22p-di **diethyl 3,3'-(5-((S)-1-(1,3-dioxoisoindolin-2-yl)-2-((2-(2-fluoropyridin-3-yl)-6-methylbenzoyl)oxy)ethyl)-1,3-phenylene)(2E,2'E)-diacrylate**

The compound **22p-di** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 34 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.6 Hz, 1H), 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.69 – 7.63 (m, 4H), 7.60 (s, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 16.1 Hz, 2H), 5.45 (dd, *J* = 9.6, 5.8 Hz, 1H), 5.14 (dd, *J* = 11.3, 9.8 Hz, 1H), 4.85 (dd, *J* = 11.4, 5.9 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 4H), 2.33 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 168.00 , 167.76 , 166.46 , 159.99 (d, *J* = 238.9 Hz), 146.91 (d, *J* = 14.4 Hz), 142.90 , 140.99 (d, *J* = 4.1 Hz), 137.66 , 136.84 , 135.85 , 134.29 , 132.82 (d, *J* = 4.1 Hz), 132.23 , 131.53 , 130.81 , 130.04 , 129.04 , 128.05 , 127.43 , 123.58 , 123.06 (d, *J* = 31.0 Hz), 121.33 (d, *J* = 4.3 Hz), 120.09 , 62.80 , 60.68 , 52.97 , 20.21 , 14.27 . HRMS (ESI-TOF) m/z Calcd for $C_{39}H_{34}FN_2O_8^+$ $[M+H]^+$ 677.2294, found 677.2294.



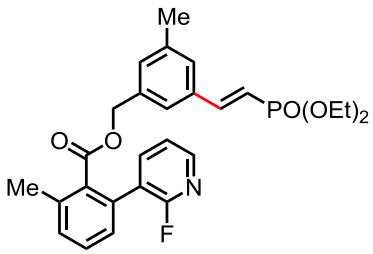
22q$_1$ **(E)-3-(3-butoxy-3-oxoprop-1-en-1-yl)-5-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate**

The compound **22q$_1$** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 70 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 4.1 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.40 (dd, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.94 (s, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.04 (s, 2H), 4.21 (t, *J* = 6.7 Hz, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 1.76 – 1.64 (m, 2H), 1.50 – 1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.17 , 166.98 , 160.05 (d, *J* = 238.9 Hz), 146.60 (d, *J* = 14.4 Hz), 144.04 , 140.99 (d, *J* = 4.3 Hz), 138.88 , 136.91 , 135.48 , 134.65 , 132.70 (d, *J* = 4.1 Hz), 132.62 , 131.20 , 130.85 , 129.90 , 128.63 , 128.05 , 125.44 , 123.24 (d, *J* = 31.3 Hz), 121.10 (d, *J* = 4.3 Hz), 118.60 , 66.63 , 64.43 , 30.74 , 21.14 , 20.31 , 19.19 , 13.73 . HRMS (ESI-TOF) m/z Calcd for $C_{28}H_{29}FNO_4^+$ $[M+H]^+$ 462.2075, found 462.2076.



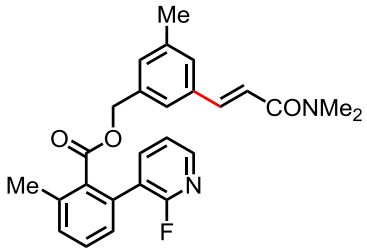
22q$_2$ **(E)-3-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-5-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate**

The compound **22q$_2$** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 61 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.8 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.45 – 7.36 (m, 5H), 7.34 (dd, *J* = 8.3, 6.0 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.07 (s, 1H), 7.05 (ddd, *J* = 6.9, 4.9, 1.6 Hz, 1H), 6.94 (s, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 5.26 (s, 2H), 5.03 (s, 2H), 2.45 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.17 , 166.66 , 160.06 (d, *J* = 238.9 Hz), 146.61 (d, *J* = 14.4 Hz), 144.69 , 140.99 (d, *J* = 4.2 Hz), 138.92 , 136.92 , 136.01 , 135.53 , 134.54 , 132.71 (d, *J* = 4.1 Hz), 132.61 , 131.33 , 130.86 , 129.91 , 128.66 , 128.58 , 128.24 , 128.06 , 125.51 , 123.25 (d, *J* = 31.3 Hz), 121.10 (d, *J* = 4.4 Hz), 118.19 , 66.61 , 66.36 , 21.15 , 20.33 . HRMS (ESI-TOF) m/z Calcd for $C_{31}H_{27}FNO_4^+$ $[M+H]^+$ 496.1919, found 496.1921.



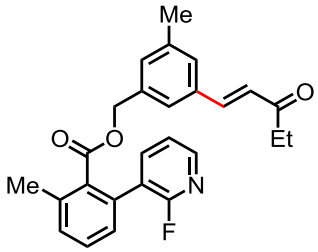
22q$_3$ (E)-3-(2-(diethoxyphosphoryl)vinyl)-5-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **22q$_3$** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 57 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 1H), 7.67 – 7.58 (m, 1H), 7.47 – 7.35 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.23 (s, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.94 (s, 1H), 6.24 (dd, *J* = 17.5, 17.5 Hz, 1H), 5.04 (s, 2H), 4.21 – 4.07 (m, 4H), 2.45 (s, 3H), 2.33 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 168.19 , 160.06 (d, *J* = 238.9 Hz), 148.16 (d, *J* = 6.7 Hz), 146.62 (d, *J* = 14.4 Hz), 141.01 (d, *J* = 4.2 Hz), 138.89 , 136.90 , 135.48 , 135.09 (d, *J* = 23.2 Hz), 132.70 (d, *J* = 4.1 Hz), 131.13 , 130.86 , 129.92 , 128.42 , 128.05 , 124.93 , 123.25 (d, *J* = 31.5 Hz), 121.14 (d, *J* = 4.4 Hz), 115.07 , 113.80 , 66.64 , 61.86 , 21.15 , 20.32 , 16.43 . HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{30}FNO_5P^+$ $[M+H]^+$ 498.1840, found 498.1841.



22q$_4$ (E)-3-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-5-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

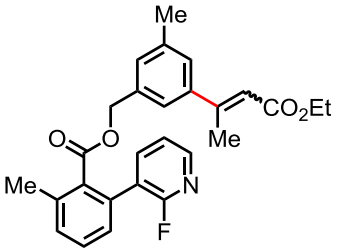
The compound **22q$_4$** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 65 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 1H), 7.67 – 7.55 (m, 2H), 7.40 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.24 (s, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 7.06 (ddd, *J* = 7.0, 4.9, 1.7 Hz, 1H), 6.92 (s, 1H), 6.89 (d, *J* = 15.4 Hz, 1H), 5.04 (s, 2H), 3.21 (s, 3H), 3.08 (s, 3H), 2.45 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.23 , 166.59 , 160.07 (d, *J* = 238.6 Hz), 146.63 (d, *J* = 14.4 Hz), 141.82 , 140.99 (d, *J* = 4.2 Hz), 138.74 , 136.87 , 135.61 , 135.30 , 132.73 , 132.67 (d, *J* = 3.8 Hz), 130.83 , 130.54 , 129.86 , 128.81 , 128.01 , 124.80 , 123.20 (d, *J* = 31.4 Hz), 121.14 (d, *J* = 4.4 Hz), 117.80 , 66.78 , 37.46 , 35.94 , 21.16 , 20.28 . HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{26}FN_2O_3^+$ $[M+H]^+$ 433.1922, found 433.1921.



22q$_5$ (E)-3-(3-oxopent-1-en-1-yl)-5-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

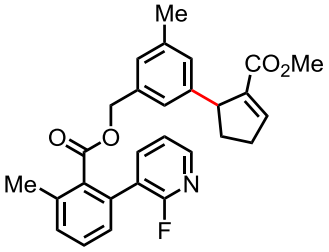
The compound **22q$_5$** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 70 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 4.9 Hz, 1H), 7.63 (ddd, *J* = 9.4,

7.1, 1.9 Hz, 1H), 7.48 (d, *J* = 16.2 Hz, 1H), 7.40 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 7.06 (ddd, *J* = 7.1, 4.9, 1.7 Hz, 1H), 6.95 (s, 1H), 6.72 (d, *J* = 16.2 Hz, 1H), 5.04 (s, 2H), 2.71 (q, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 1.18 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 200.84 , 168.21 , 160.07 (d, *J* = 238.9 Hz), 146.61 (d, *J* = 14.5 Hz), 141.67 , 141.02 (d, *J* = 4.2 Hz), 138.93 , 136.90 , 135.55 , 134.83 , 132.69 (d, *J* = 4.1 Hz), 132.65 , 131.28 , 130.87 , 129.92 , 128.83 , 128.06 , 126.22 , 125.53 , 123.26 (d, *J* = 31.3 Hz), 121.12 (d, *J* = 4.4 Hz), 66.62 , 34.18 , 21.16 , 20.31 , 8.19 . HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{25}FNO_3^+$ $[M+H]^+$ 418.1813, found 418.1813.



6q$_6$ 3-(4-ethoxy-4-oxobut-2-en-2-yl)-5-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

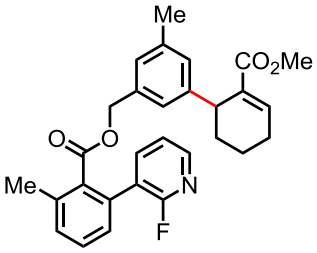
The compound **6q$_6$** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 47 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 1H), 7.69 – 7.62 (m, 1H), 7.42 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.36 – 7.26 (m, 2H), 7.26 – 7.17 (m, 2H), 7.14 – 7.04 (m, 2H), 6.94 (s, 1H), 6.33 (s, 0.2H), 6.11 (s, 0.8H), 5.07 (s, 2H), 4.29 – 4.21 (m, 2H), 2.56 (s, 2H), 2.51 – 2.43 (m, 4H), 2.36 (s, 3H), 1.37 – 1.33 (m, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.78 , 166.31 , 159.63 (d, *J* = 238.9 Hz), 154.64 , 149.78 , 146.14 (d, *J* = 14.4 Hz), 142.07 , 140.58 , 138.05 , 136.46 , 134.61 , 132.29 , 130.41 , 129.57 , 129.44 , 127.61 , 127.26 , 126.86 , 126.63 , 123.95 , 122.82 (d, *J* = 31.0 Hz), 121.33 , 120.65 (d, *J* = 4.6 Hz), 116.88 , 68.66 , 66.46 , 66.32 , 64.08 , 60.42 , 59.42 , 20.83 , 19.86 , 19.78 , 17.54 , 13.89 , 13.71 . HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{25}FNO_4^+$ $[M+H]^+$ 434.1762, found 434.1765.



22q$_7$ 3-(2-(methoxycarbonyl)cyclopent-2-en-1-yl)-5-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **22q$_7$** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 84 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 4.3 Hz, 1H), 7.63 (ddd, *J* = 9.4, 7.4, 1.9 Hz, 1H), 7.38 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.08

(ddd, *J* = 6.9, 4.9, 1.7 Hz, 1H), 6.99 (dd, *J* = 4.2, 2.4 Hz, 1H), 6.89 (s, 1H), 6.78 (s, 1H), 6.72 (s, 1H), 5.00 (s, 2H), 4.08 (dd, *J* = 5.8, 3.7 Hz, 1H), 3.60 (s, 3H), 2.72 – 2.62 (m, 1H), 2.58 – 2.45 (m, 2H), 2.42 (s, 3H), 2.27 (s, 3H), 1.89 – 1.81 (m, 1H). ^{13}C NMR (151 MHz, CDCl3) δ 168.33 , 165.06 , 160.08 (d, *J* = 238.9 Hz), 146.57 (d, *J* = 14.4 Hz), 145.33 , 145.13 , 141.04 (d, *J* = 4.1 Hz), 138.84 , 138.21 , 136.71 , 134.75 , 133.05 , 132.54 (d, *J* = 4.1 Hz), 130.70 , 129.66 , 127.93 , 127.71 , 127.42 , 124.48 , 123.14 (d, *J* = 31.0 Hz), 121.14 (d, *J* = 4.3 Hz), 67.25 , 51.30 , 49.78 , 34.04 , 32.15 , 21.28 , 20.20 . HRMS (ESI-TOF) m/z Calcd for $C_{28}H_{27}FNO_4^+$ $[M+H]^+$ 460.1919, found 460.1920.

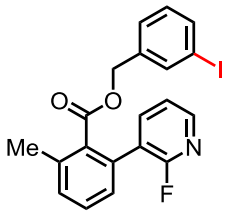


22q$_8$ methyl 3'-(((2-(2-fluoropyridin-3-yl)-6-methylbenzoyl)oxy)methyl)-5'-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate

The compound **22q$_8$** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 78 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 – 8.08 (m, 1H), 7.68 – 7.58 (m, 1H), 7.38 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.11 – 7.02 (m, 1H), 6.87 (s, 1H), 6.78 (s, 1H), 6.72 (s, 1H), 5.00 (s, 2H), 3.87 (s, 1H), 3.59 (s, 3H), 2.53 – 2.18 (m, 8H), 1.98 – 1.81 (m, 1H), 1.80 – 1.66 (m, 1H), 1.60 – 1.38 (m, 2H). ^{13}C NMR (151 MHz, CDCl3) δ 168.35 , 167.40 , 160.09 (d, *J* = 239.1 Hz), 146.56 (d, *J* = 14.3 Hz), 145.22 , 141.83 , 141.04 (d, *J* = 4.2 Hz), 137.91 , 136.68 , 134.48 , 133.07 , 132.53 (d, *J* = 3.8 Hz), 131.52 , 130.69 , 129.65 , 128.53 , 127.93 , 127.23 , 125.28 , 123.13 (d, *J* = 30.9 Hz), 121.14 (d, *J* = 4.3 Hz), 67.30 , 51.48 , 39.18 , 31.24 , 25.84 , 21.30 , 20.20 , 16.80 . HRMS (ESI-TOF) m/z Calcd for $C_{29}H_{29}FNO_4^+$ $[M+H]^+$ 474.2075, found 474.2074.

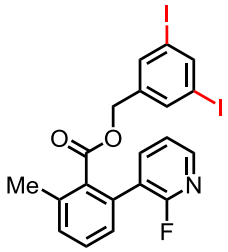
General Procedure for Template-directed *meta*-C–H Iodination of Alcohols:

A 10 mL sealed tube was charged with substrate (0.2 mmol, 1.0 equiv), DIH (1.0 equiv), $Pd(OAc)_2$ (10 mol%), TFA-Gly-OH (20 mol%), AgOAc (0.5 equiv), HOAc (0.4 mL) and HFIP (1.6 mL). The tube was then sealed and submerged into a pre-heated 80 °C heating plate. The reaction mixture was stirred at 80 °C for 18 h. After being cooled to room temperature, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite. The filtrate was concentrated in vacuo, and the resulting residue was purified by preparative LC-MS to give the desired product. The positional selectivity was determined by GC-MS with a flame ionization detector.



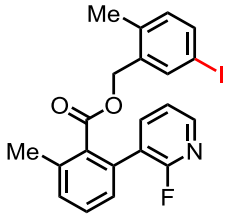
23a-mono 3-iodobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **23a-mono** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 68 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 4.9 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.44 (s, 1H), 7.41 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.02 (dd, *J* = 7.8,7.8 Hz, 1H), 5.00 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.01 , 159.98 (d, *J* = 239.3 Hz), 146.66 (d, *J* = 14.2 Hz), 141.06 (d, *J* = 4.3 Hz), 137.42 , 137.38 , 137.07 , 136.99 , 132.70 (d, *J* = 4.0 Hz), 132.44 , 130.90 , 130.24 , 129.99 , 128.06 , 128.05 , 127.87 , 123.22 (d, *J* = 31.0 Hz), 121.21 (d, *J* = 4.4 Hz), 94.21 , 65.93 , 20.33 . ESI-MS $[M+H]^+$ calcd 448.0, found 448.0.



23a-di 3,5-diiodobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

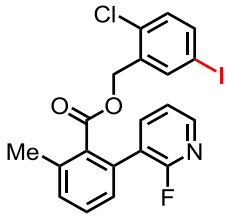
The compound **23a-di** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 17 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.6 Hz, 1H), 7.98 (s, 1H), 7.63 (ddd, *J* = 9.3, 7.5, 1.8 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.12 (m, 1H), 4.92 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.82 , 159.96 (d, *J* = 239.3 Hz), 146.80 (d, *J* = 14.3 Hz), 145.03 , 140.94 (d, *J* = 4.1 Hz), 138.69 , 137.23 , 136.69 , 132.91 (d, *J* = 4.1 Hz), 132.04 , 131.01 , 130.21 , 128.17 (d, *J* = 0.8 Hz), 123.28 (d, *J* = 31.1 Hz), 121.27 (d, *J* = 4.4 Hz), 94.70 , 64.96 , 20.41 . ESI-MS $[M+H]^+$ calcd 574.0, found 574.0.



23b 5-iodo-2-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

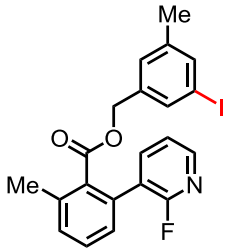
The compound **23b** was prepared according to the general procedure and was purified by preparative

LC-MS to give colorless oil in 77 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 4.8 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.51 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.03 (s, 2H), 2.46 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.03 , 159.85 (d, *J* = 240.4 Hz), 146.39 (d, *J* = 13.5 Hz), 141.28 , 138.06 , 137.45 , 136.91 , 136.69 , 135.20 , 132.55 , 132.45 (d, *J* = 3.9 Hz), 132.26 , 130.90 , 129.93 , 128.00 (d, *J* = 1.0 Hz) , 123.15 (d, *J* = 30.4 Hz), 121.17 (d, *J* = 4.4 Hz), 90.43 , 64.03 , 20.26 , 18.30 . ESI-MS $[M+H]^+$ calcd 462.0, found 462.0.



23c 2-chloro-5-iodobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

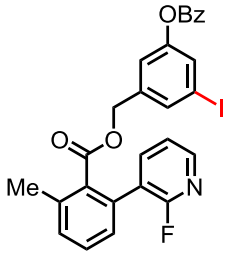
The compound **23c** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 67 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 4.8 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.46 (s, 1H), 7.42 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 5.12 (s, 2H), 2.48 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.87 , 159.96 (d, *J* = 239.8 Hz), 146.60 (d, *J* = 14.0 Hz), 141.17 (d, *J* = 4.3 Hz), 138.79 , 138.56 , 137.13 , 134.78 , 133.80 , 132.74 (d, *J* = 4.0 Hz), 132.25 , 131.16 , 130.98 , 130.12 , 128.00 (d, *J* = 4.0), 123.27 (d, *J* = 30.8 Hz), 121.27 (d, *J* = 4.4 Hz), 91.31 , 63.34 , 20.38 . ESI-MS $[M+H]^+$ calcd 482.0, found 482.0.



23d 3-iodo-5-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

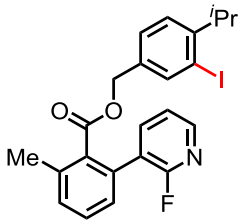
The compound **23d** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 64 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 4.1 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.47 (s, 1H), 7.40 (dd, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.15 – 7.11 (m, 1H), 6.89 (s, 1H), 4.96 (s, 2H), 2.45 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.01 , 159.93 (d, *J* = 240.2 Hz), 146.37 (d, *J* = 13.7 Hz), 141.26 (d, *J* = 4.3 Hz), 140.42 , 137.99 , 137.04 , 136.69 , 134.45 , 132.56 (d, *J* = 3.9 Hz), 132.46 , 130.94 , 129.98 , 128.77 , 128.04 (d, *J* = 1 Hz), 127.64 , 123.34 (d, *J* = 30.5 Hz), 121.25 , 94.14 , 66.00 , 20.80 , 20.32 . ESI-MS

$[M+H]^+$ calcd 462.0, found 462.1.



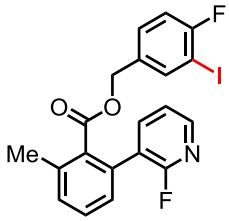
23e 3-(benzoyloxy)-5-iodobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **23e** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 57 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 – 8.15 (m, 2H), 8.13 (d, *J* = 4.9 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.58 – 7.49 (m, 3H), 7.41 (dd, *J* = 7.7 Hz, 1H), 7.35 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.11 (ddd, *J* = 6.9, 4.9, 1.5 Hz, 1H), 6.99 (s, 1H), 5.03 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.94 , 164.63 , 160.00 (d, *J* = 238.8 Hz), 151.06 , 146.81 (d, *J* = 14.3 Hz), 140.96 (d, *J* = 4.2 Hz), 138.13 , 137.16 , 134.85 , 133.92 , 132.90 (d, *J* = 4.0 Hz), 132.23 , 130.90 (d, *J* = 7.5 Hz), 130.19 , 130.09 , 128.88 , 128.68 , 128.12 , 123.19 (d, *J* = 31.0 Hz), 121.60 , 121.28 (d, *J* = 4.4 Hz), 93.49 , 65.34 , 20.39 . ESI-MS $[M+H]^+$ calcd 568.0, found 568.0.



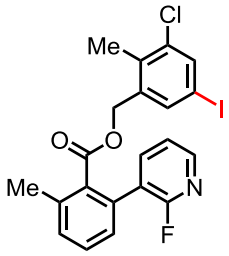
23f 3-iodo-4-isopropylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **23f** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 47 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 4.1 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.56 (s, 1H), 7.40 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.06 (m, 2H), 4.97 (s, 2H), 3.17 (hept, *J* = 6.8 Hz, 1H), 2.45 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 168.09 , 159.98 (d, *J* = 240.1 Hz), 150.59 , 146.38 (d, *J* = 13.7 Hz), 141.27 (d, *J* = 4.3 Hz), 139.53 , 136.97 , 134.26 , 132.58 , 132.51 (d, *J* = 3.9 Hz), 130.91 , 129.92 , 128.98 , 128.01 , 125.87 , 123.32 (d, *J* = 30.5 Hz), 121.21 (d, *J* = 4.4 Hz), 100.81 , 65.69 , 37.81 , 22.99 , 20.31 . ESI-MS $[M+H]^+$ calcd 490.1, found 490.1.



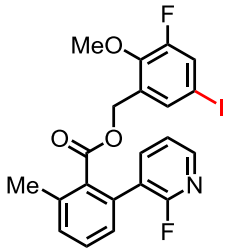
23g-mono 4-fluoro-3-iodobenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **23g-mono** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 59 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 4.8 Hz, 1H), 7.61 (ddd, *J* = 9.3, 7.5, 1.7 Hz, 1H), 7.49 (dd, *J* = 5.9, 2.0 Hz, 1H), 7.41 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.97 (dd, *J* = 8.1, 8.1 Hz, 1H), 4.99 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.96 , 161.57 (d, *J* = 245.6 Hz), 159.96 (d, *J* = 238.2 Hz), 146.59 (d, *J* = 14.1 Hz), 141.06 (d, *J* = 4.2 Hz), 139.68 (d, *J* = 2.0 Hz), 136.96 , 132.70 (d, *J* = 3.6 Hz), 132.65 (d, *J* = 3.9 Hz), 132.32 , 130.92 , 130.69 (d, *J* = 7.7 Hz), 130.03 , 128.06 (d, *J* = 0.9 Hz), 123.22 (d, *J* = 31.0 Hz), 121.17 (d, *J* = 4.4 Hz), 115.58 (d, *J* = 24.2 Hz), 81.20 (d, *J* = 26.0 Hz), 65.25 , 20.30 . ESI-MS $[M+H]^+$ calcd 466.0, found 466.0.



23h 3-chloro-5-iodo-2-methylbenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

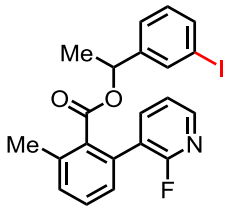
The compound **23h** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 61 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (ddd, *J* = 4.9, 1.8, 1.1 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.58 (ddd, *J* = 9.5, 7.3, 2.0 Hz, 1H), 7.41 (dd, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.05 (ddd, *J* = 7.2, 4.9, 1.7 Hz, 1H), 5.04 (s, 2H), 2.46 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.92 , 159.94 (d, *J* = 238.8 Hz), 146.80 (d, *J* = 14.4 Hz), 140.85 (d, *J* = 4.0 Hz), 137.60 , 136.95 , 136.88 , 136.52 , 135.94 , 135.07 , 132.71 (d, *J* = 4.1 Hz), 132.33 , 130.88 , 130.04 , 128.11 , 122.99 (d, *J* = 31.1 Hz), 121.03 (d, *J* = 4.4 Hz), 89.74 , 64.15 , 20.29 , 15.37 . ESI-MS $[M+H]^+$ calcd 496.0, found 496.0.



23i 3-fluoro-5-iodo-2-methoxybenzyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

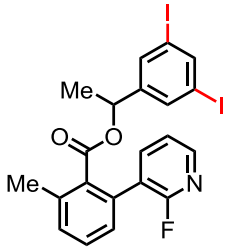
The compound **23i** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 77 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (ddd, *J* = 4.9, 2.0, 1.1 Hz, 1H), 7.65 (ddd, *J* = 9.5, 7.3, 2.0 Hz, 1H), 7.41 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.36 (dd, *J* = 10.8, 2.1 Hz, 1H),

7.31 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.13 (m, 2H), 5.07 (s, 2H), 3.87 (d, *J* = 2.4 Hz, 3H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.96 , 159.96 (d, *J* = 238.8 Hz), 154.60 (d, *J* = 252.8 Hz), 146.73 (d, *J* = 14.4 Hz), 145.81 (d, *J* = 10.2 Hz), 140.95 (d, *J* = 4.3 Hz), 136.95 , 134.10 (d, *J* = 3.3 Hz), 132.71 (d, *J* = 4.1 Hz), 132.43 , 131.15 (d, *J* = 3.1 Hz), 130.86 , 129.97 , 128.05 , 126.28 (d, *J* = 21.8 Hz), 123.11 (d, *J* = 31.4 Hz), 121.17 (d, *J* = 4.4 Hz), 84.00 , 61.45 (d, *J* = 7.0 Hz), 60.62 (d, *J* = 2.9 Hz), 20.28 . ESI-MS $[M+H]^+$ calcd 496.0, found 496.0.



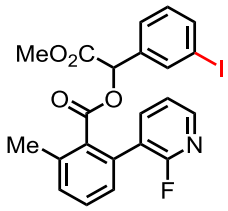
23j-mono 1-(3-iodophenyl)ethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **23j-mono** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 70 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 4.9 Hz, 1H), 7.65 (ddd, *J* = 9.3, 7.5, 1.7 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.49 (s, 1H), 7.40 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.02 (dd, *J* = 7.9, 7.8 Hz, 1H), 5.79 (q, *J* = 6.6 Hz, 1H), 2.41 (s, 3H), 1.32 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.48 , 160.00 (d, *J* = 240.7 Hz), 146.30 (d, *J* = 13.4 Hz), 142.78 , 141.45 (d, *J* = 4.4 Hz), 137.04 , 136.77 , 135.20 , 132.89 , 132.22 (d, *J* = 3.8 Hz), 130.90 , 130.29 , 129.81 , 127.92 (d, *J* = 1.0 Hz), 125.55 , 123.33 (d, *J* = 30.5 Hz), 121.20 (d, *J* = 4.4 Hz), 94.25 , 72.49 , 21.57 , 20.17 . ESI-MS $[M+H]^+$ calcd 462.0, found 462.1.



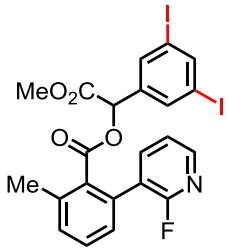
23j-di 1-(3,5-diiodophenyl)ethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **23j-di** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 10 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 – 8.11 (m, 1H), 7.95 (s, 1H), 7.68 – 7.59 (m, 1H), 7.52 – 7.39 (m, 3H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.17 – 7.11 (m, 1H), 5.68 (q, *J* = 6.7 Hz, 1H), 2.41 (s, 3H), 1.28 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.34 , 160.08 (d, *J* = 239.4 Hz), 146.76 (d, *J* = 14.2 Hz), 144.68 , 144.58 , 141.01 (d, *J* = 4.2 Hz), 136.90 , 134.55 , 132.62 (d, *J* = 4.1 Hz), 132.57 , 130.93 , 129.98 , 128.04 , 123.23 (d, *J* = 31.4 Hz), 121.16 (d, *J* = 4.5 Hz), 94.79 , 71.62 , 21.59 , 20.24 . ESI-MS $[M+H]^+$ calcd 588.0, found 588.0.



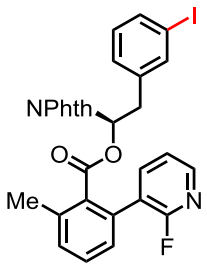
23k-mono 1-(3-iodophenyl)-2-methoxy-2-oxoethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **23k-mono** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 53 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 4.7 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.50 (s, 1H), 7.44 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.16 – 7.10 (m, 1H), 7.05 (dd, *J* = 7.7, 7.7 Hz, 1H), 5.80 (s, 1H), 3.71 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 168.24 , 167.17 , 159.84 (d, *J* = 239.8 Hz), 146.31 (d, *J* = 13.8 Hz), 141.27 (d, *J* = 4.3 Hz), 138.24 , 138.03 , 136.21 , 135.06 , 133.18 (d, *J* = 3.9 Hz), 131.18 , 131.14 , 130.53 , 130.36 , 128.15 , 126.84 , 123.36 (d, *J* = 30.8 Hz), 121.26 (d, *J* = 4.4 Hz), 94.24 , 74.00 , 52.79 , 20.49 . ESI-MS $[M+H]^+$ calcd 506.0, found 506.0.



23k-di 1-(3,5-diiodophenyl)-2-methoxy-2-oxoethyl 2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **23k-di** was prepared according to the general procedure and was purified by preparative LC-MS to give colorless oil in 20 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 8.02 (t, *J* = 1.5 Hz, 1H), 7.68 (ddd, *J* = 9.4, 7.3, 2.0 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.37 – 7.34 (m, 1H), 7.22 – 7.15 (m, 2H), 5.72 (s, 1H), 3.73 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 167.34 , 166.51 , 159.42 (d, *J* = 239.1 Hz), 146.11 (d, *J* = 14.3 Hz), 146.09 (d, *J* = 14.1 Hz), 145.47 , 140.61 (d, *J* = 3.9 Hz), 137.75 , 136.14 , 135.10 , 132.95 (d, *J* = 3.6 Hz), 130.80 , 130.41 , 130.27 , 127.81 , 122.92 (d, *J* = 30.9 Hz), 120.87 (d, *J* = 4.3 Hz), 94.29 , 72.66 , 52.55 , 20.10 . ESI-MS $[M+H]^+$ calcd 632.0, found 632.0.

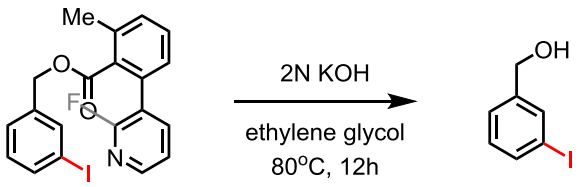


23l-mono **(R)-1-(1,3-dioxoisoindolin-2-yl)-2-(3-iodophenyl)ethyl**

2-(2-fluoropyridin-3-yl)-6-methylbenzoate

The compound **23l-mono** was prepared according to the general procedure and was purified by prep-TLC to give colorless oil in 61 % yield as a 5:1 mixture of regioisomers (*meta*-iodinated product is the major product). 1H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 4.8 Hz, 1H), 7.85 – 7.78 (m, 3H), 7.75 – 7.69 (m, 2H), 7.68 – 7.60 (m, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.36 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 5.34 (dd, *J* = 9.8, 5.7 Hz, 1H), 5.08 (dd, *J* = 11.4, 9.8 Hz, 1H), 4.77 (dd, *J* = 11.4, 5.7 Hz, 1H), 2.31 (s, 3H). 13C NMR (151 MHz, $CDCl_3$) δ 168.00, 167.71, 159.98 (d, *J* = 238.9 Hz), 146.83, 140.99 (d, *J* = 4.2 Hz), 139.63, 138.99, 138.14, 137.91, 137.71, 137.03, 136.82, 135.60, 134.20, 132.77 (d, *J* = 3.8 Hz), 132.30, 131.57, 130.77, 130.48, 129.98, 129.97, 128.95, 128.01, 127.35, 123.50, 123.46, 123.04 (d, *J* = 31.3 Hz), 121.32 (d, *J* = 4.4 Hz), 94.50, 94.43, 62.88, 62.62, 52.91, 52.74, 52.13, 20.20, 14.18. ESI-MS $[M+H]^+$ calcd 607.1, found 607.0.

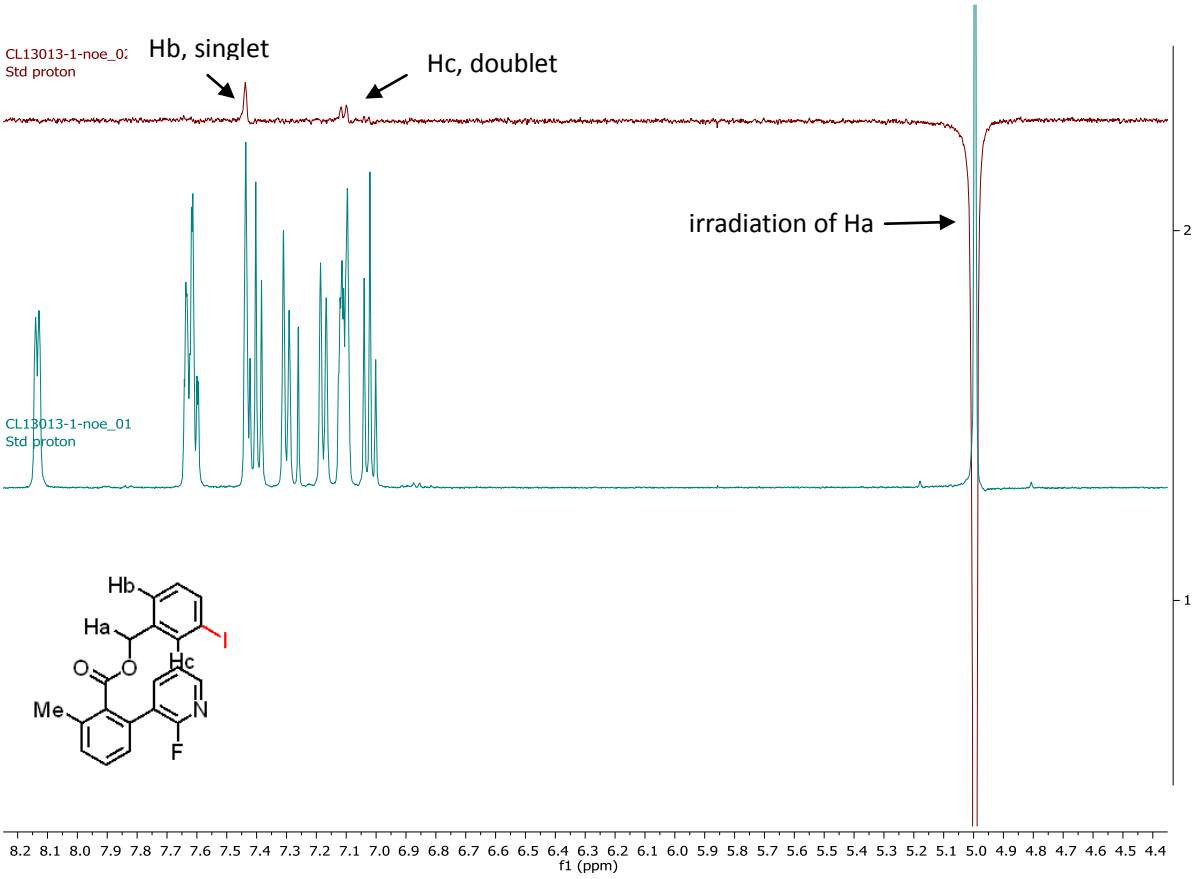
General Procedure for Removal of Template:

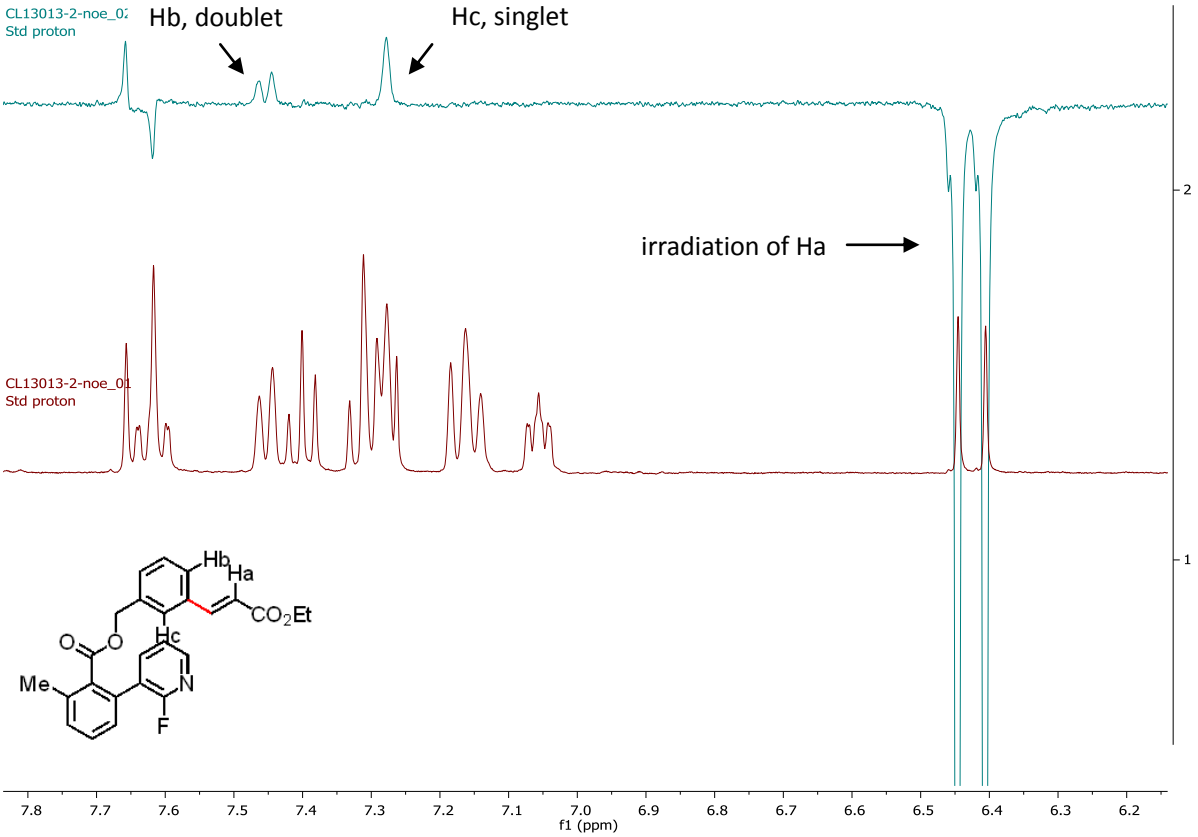


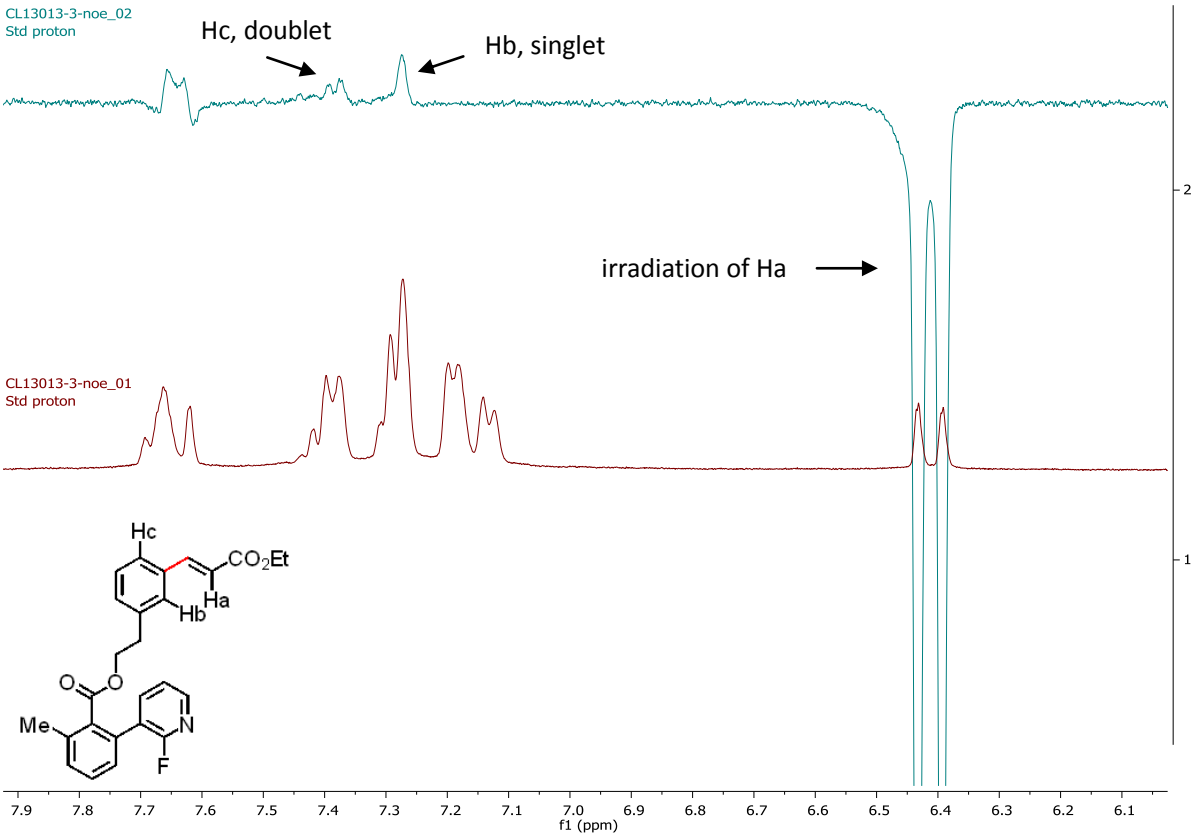
23a$_{mono}$ **24**, 94%

To a 10 mL sealed tube was added **23a$_{mono}$** (0.2 mmol), KOH (2 mmol) and ethylene glycol (1 mL). The mixture was heated to 80 °C for 12 h. After being allowed to cool to room temperature, the mixture was acidified with 1N HCl and diluted with Et_2O. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 times). The combined organic layer was dried over Na_2SO_4, concentrated in vacuo and purified by preparative TLC to give **24** as colorless oil in 94% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 4.60 (s, 2H), 2.22 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.05, 136.53, 135.76, 130.21, 125.95, 94.44, 64.23.

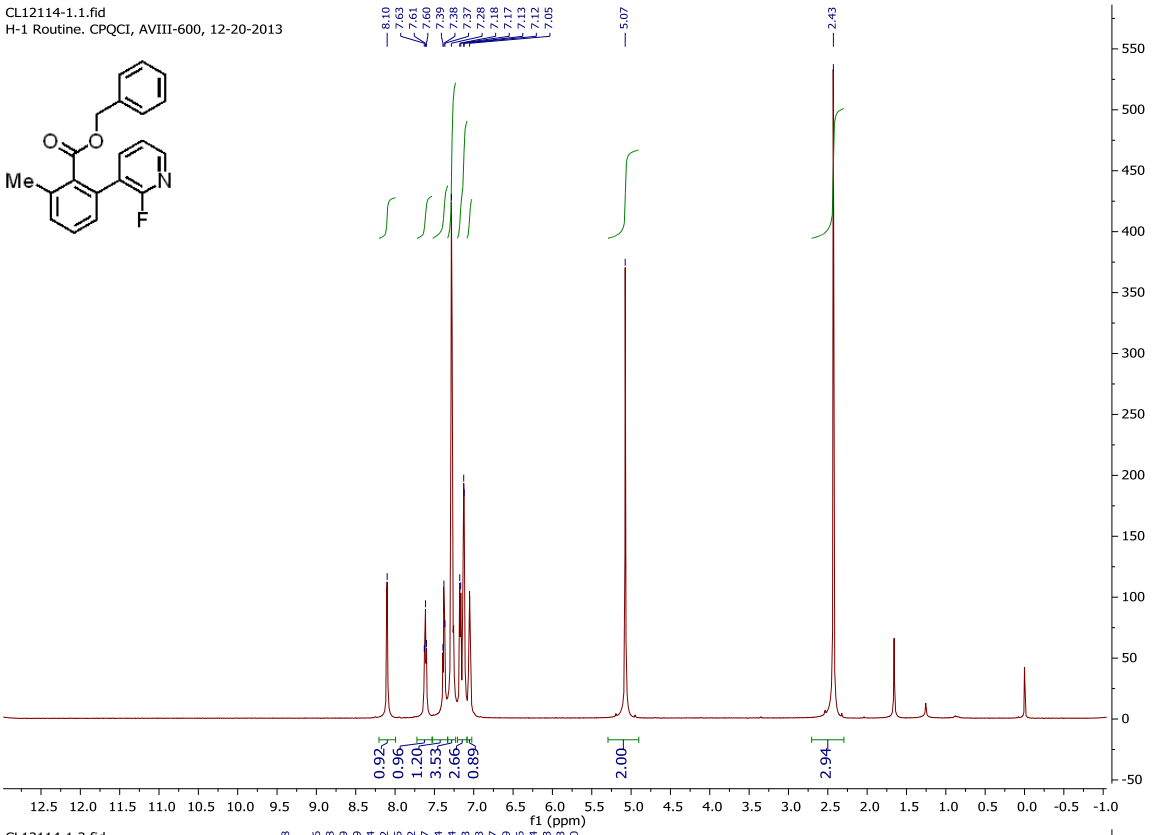
NMR Study of Regioselectivity (1D selective NOESY):

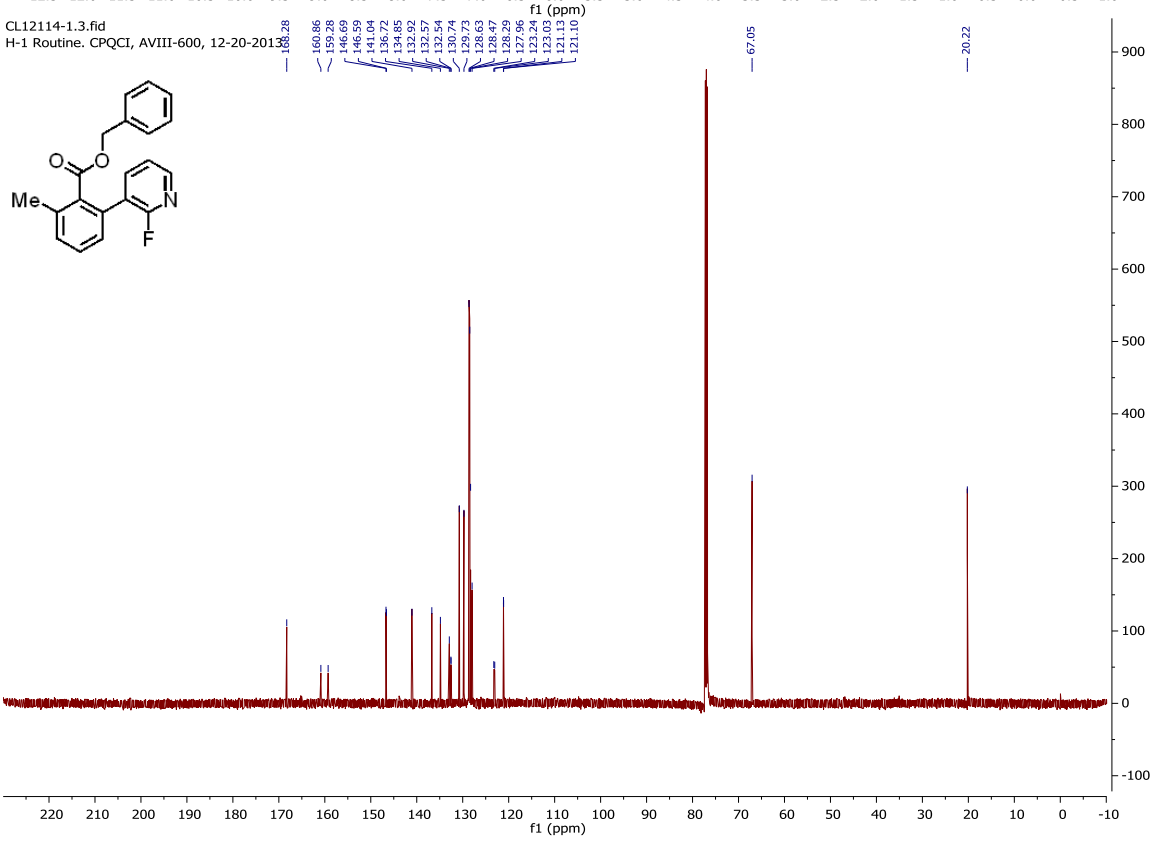


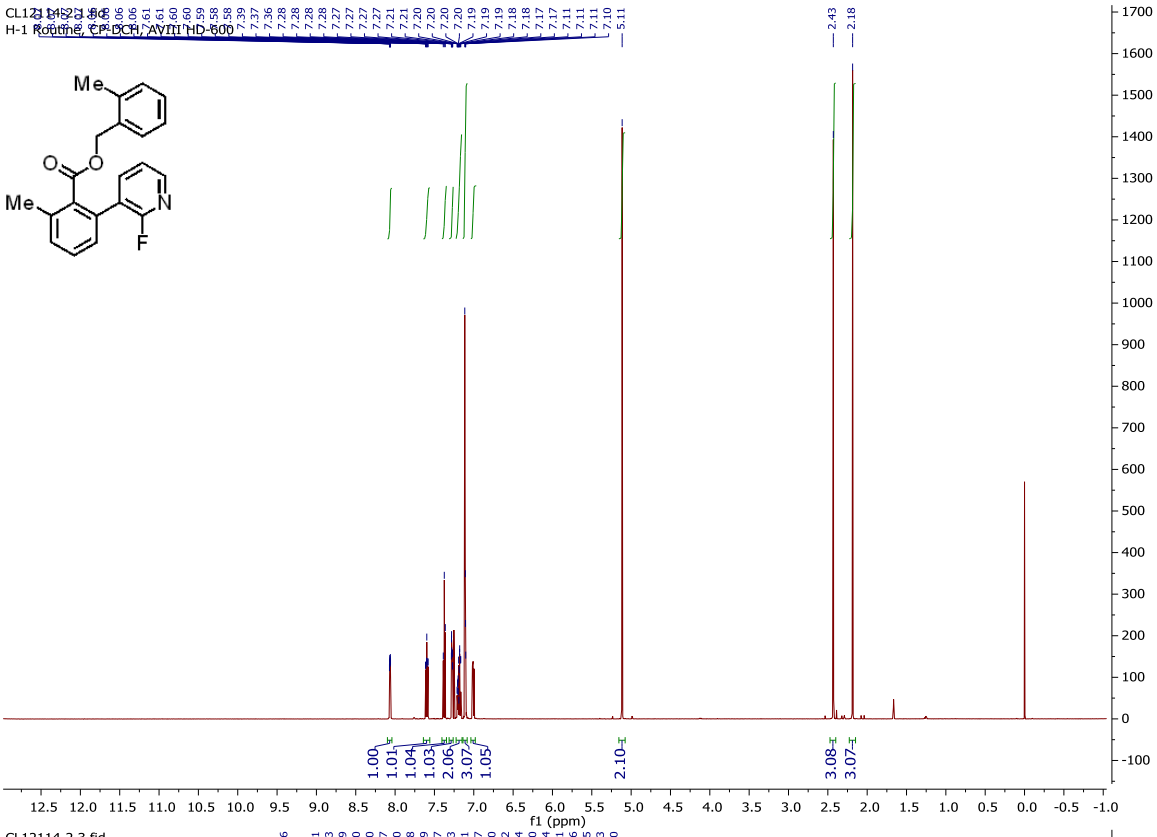

CL13013-2-noe_0
Std proton
Hb, doublet
Hc, singlet
irradiation of Ha
CL13013-2-noe_01
Std proton
Hb
Ha
CO2Et
Hc
O
O
Me
N
F
2
1
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
f1 (ppm)

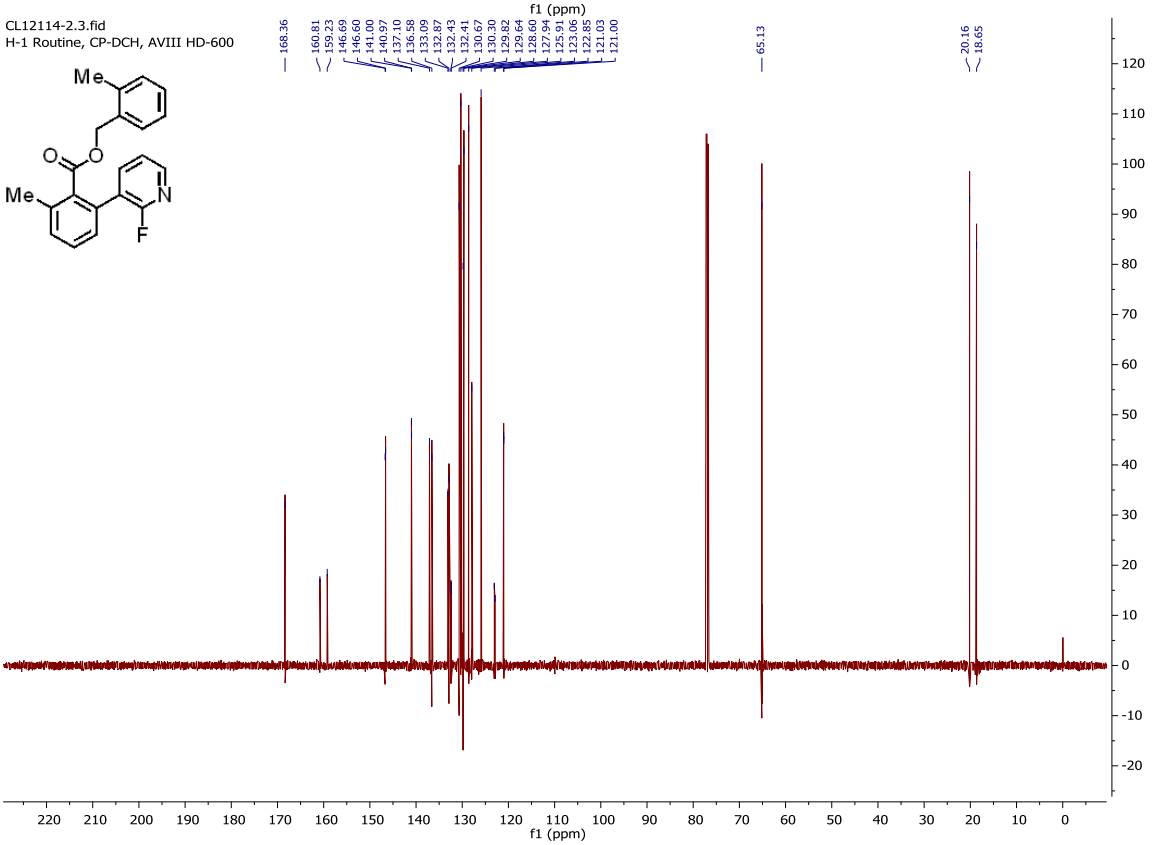

CL13013-3-noe_02
Std proton
Hc, doublet
Hb, singlet
irradiation of Ha
CL13013-3-noe_01
Std proton
Hc
CO2Et
Ha
Hb
O
O
Me
N
F
2
1
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
f1 (ppm)

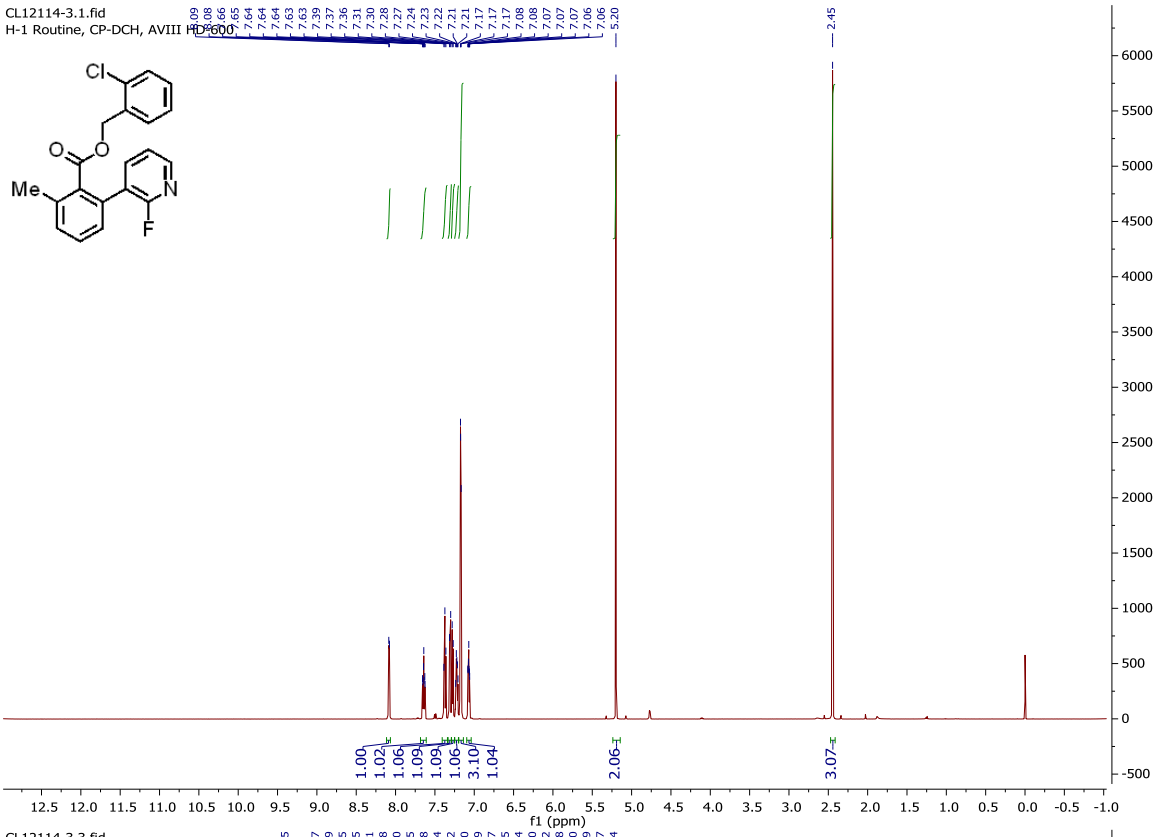
NMR Spectra:

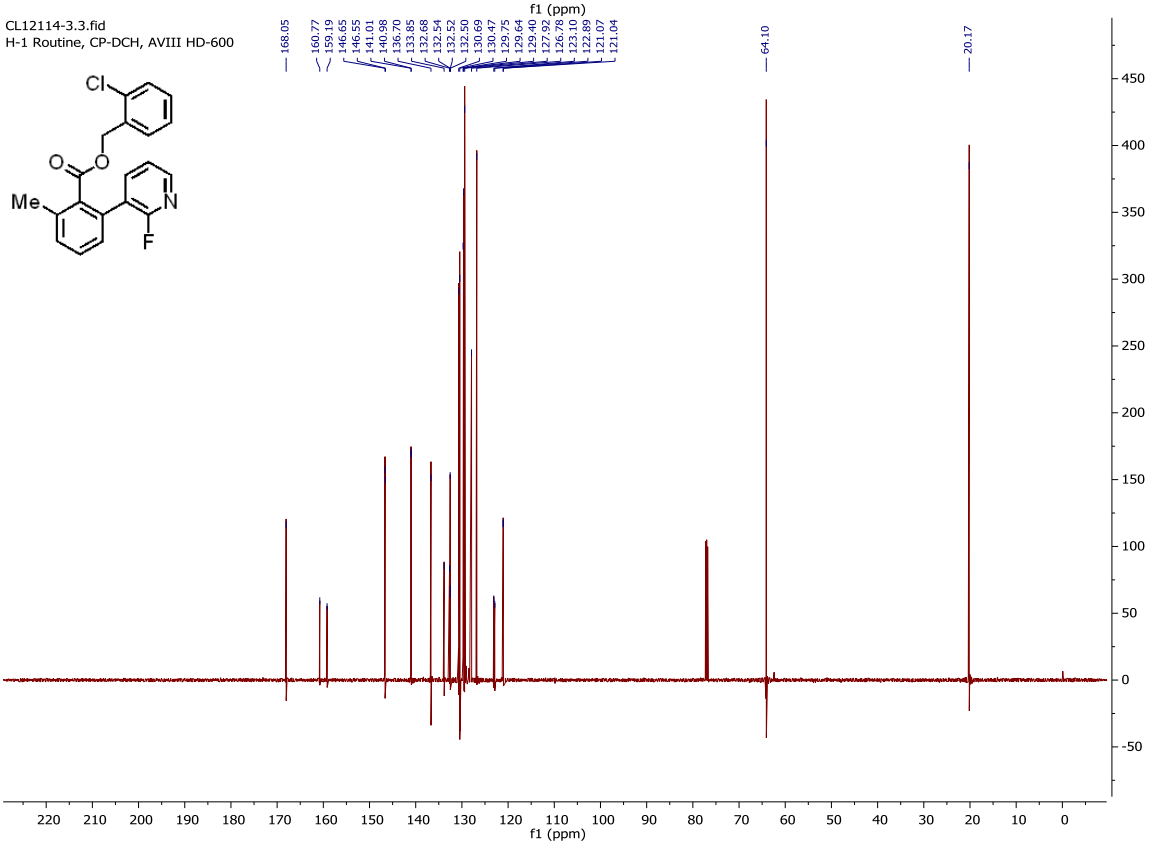

CL12114-1.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
8.10
7.63
7.61
7.60
7.39
7.38
7.37
7.28
7.18
7.17
7.13
7.12
7.05
5.07
2.43
Me
O
O
N
F
0.92
0.96
1.20
3.53
2.66
0.89
2.00
2.94
f1 (ppm)

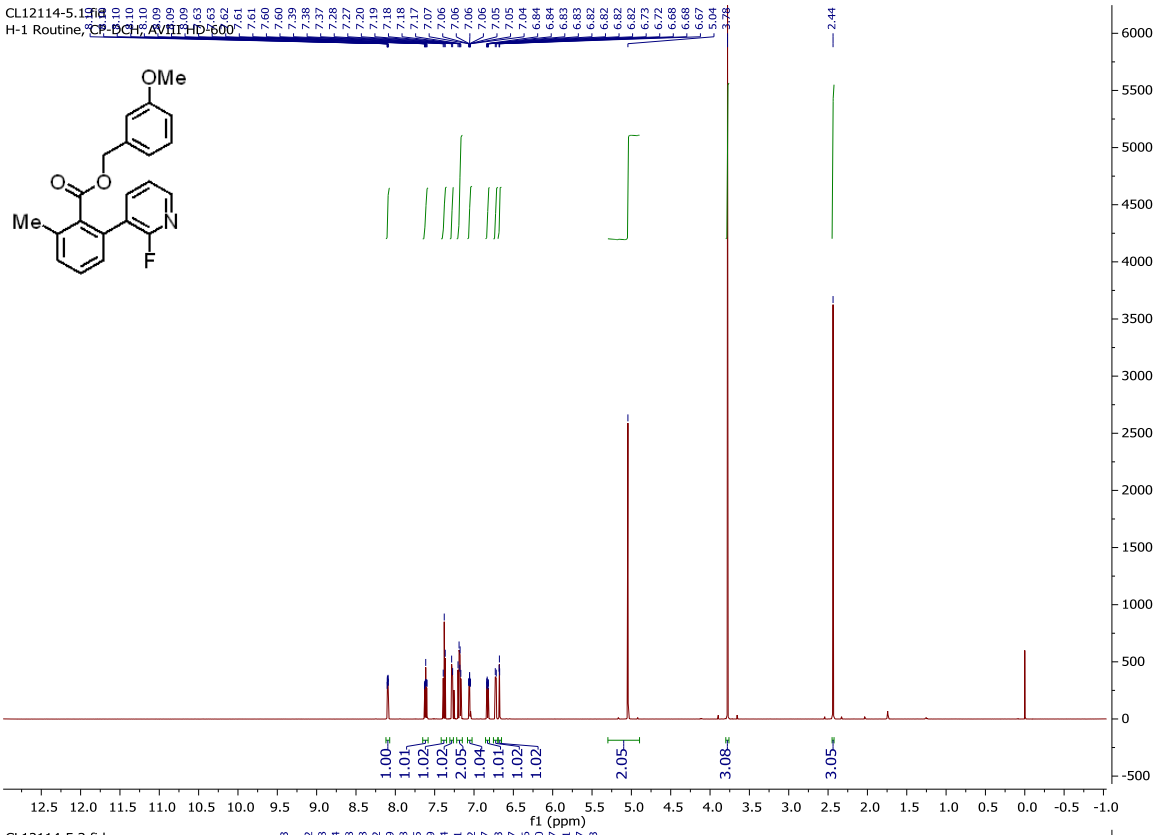

CL12114-1.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
168.28
160.86
159.28
146.69
146.59
141.94
136.72
134.85
132.92
132.57
132.54
130.74
129.73
128.63
128.47
128.29
127.96
123.24
123.03
121.13
121.10
67.05
20.22
Me
O
O
N
F
f1 (ppm)

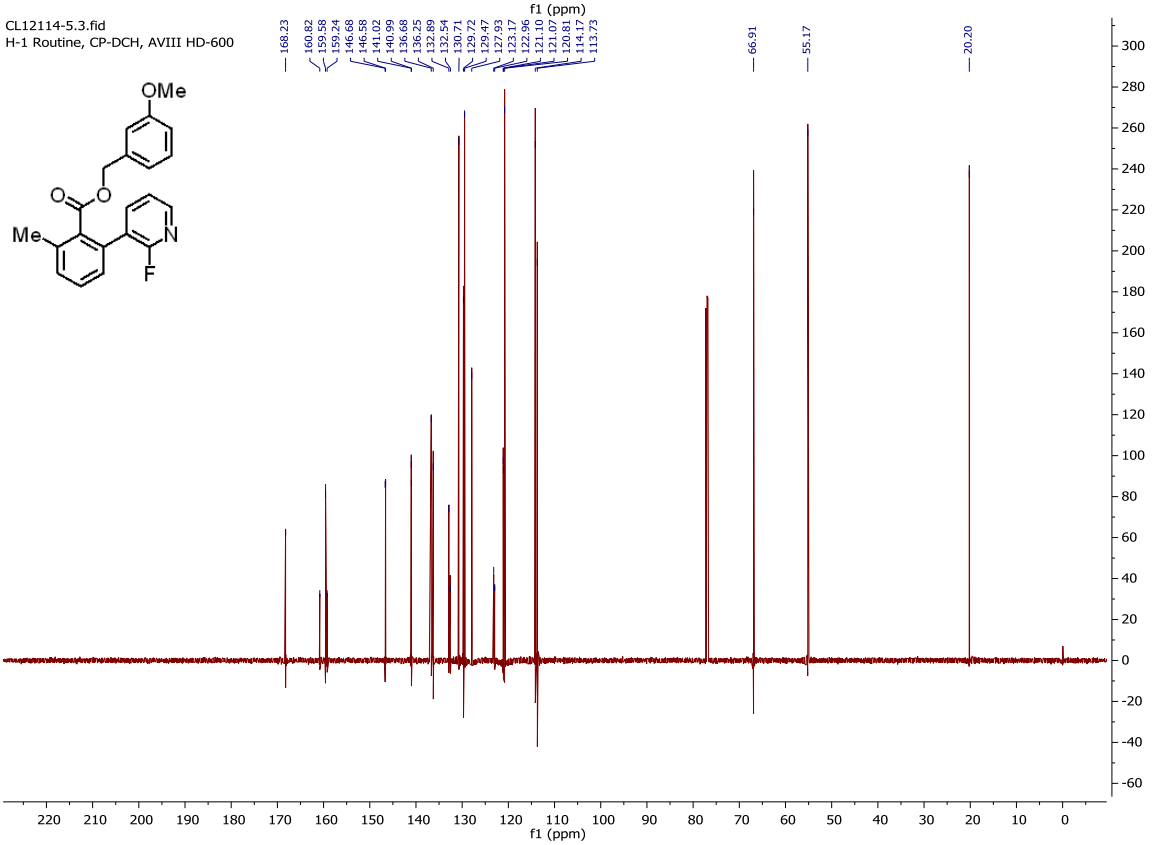

CL12114-2.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
Me
N
F
2.43
2.18
5.11
1.00
1.01
1.04
1.03
2.06
3.07
1.05
2.10
3.08
3.07
f1 (ppm)

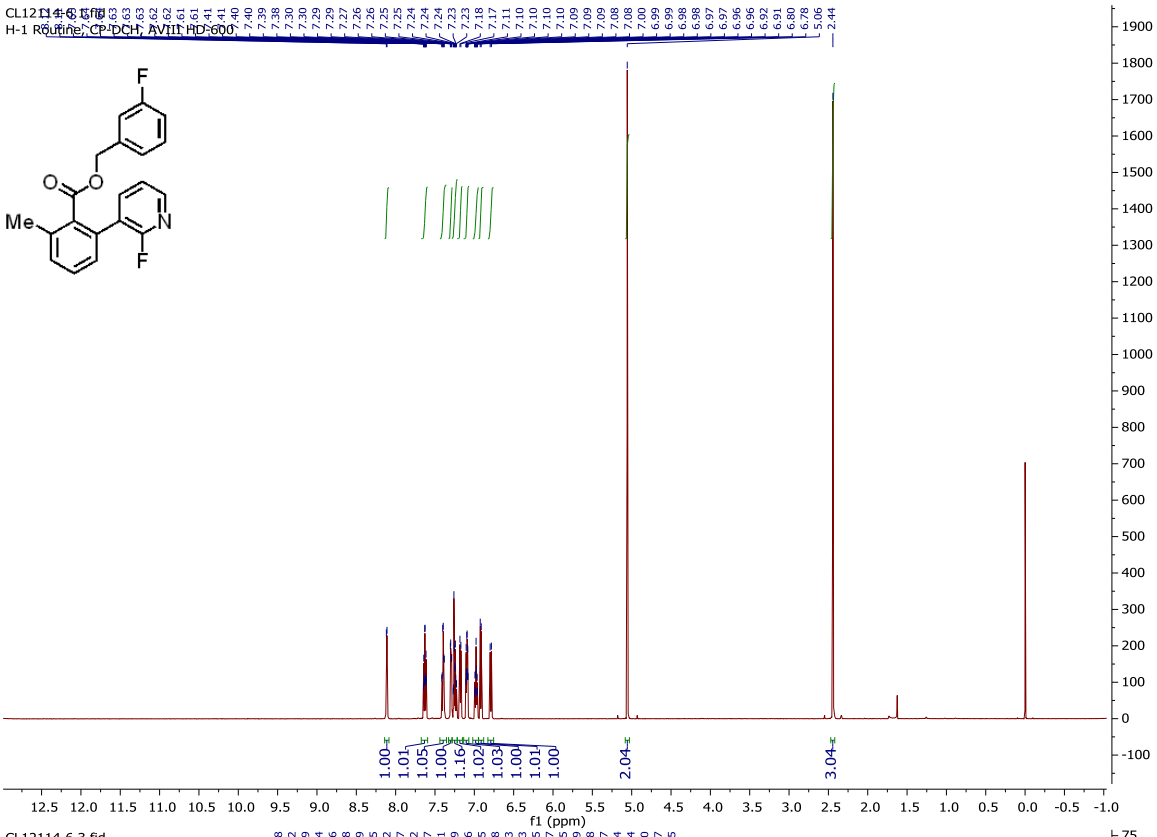

CL12114-2.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
Me
N
F
168.36
160.81
159.23
146.69
146.60
141.00
140.97
137.10
136.58
133.09
132.87
132.43
132.41
130.67
130.30
129.82
129.64
128.60
127.94
125.91
123.06
122.85
121.03
121.00
65.13
20.16
18.65
f1 (ppm)

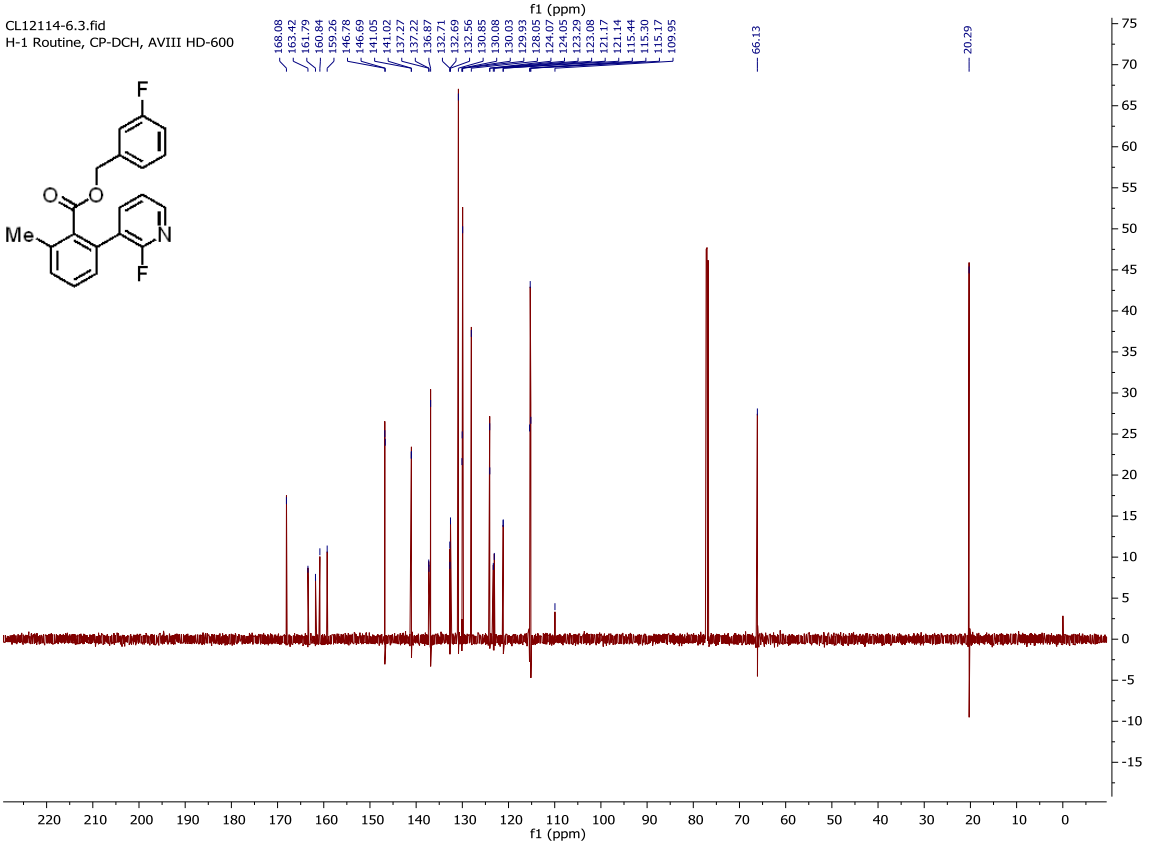

CL12114-3.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Cl
O
O
Me
N
F
f1 (ppm)

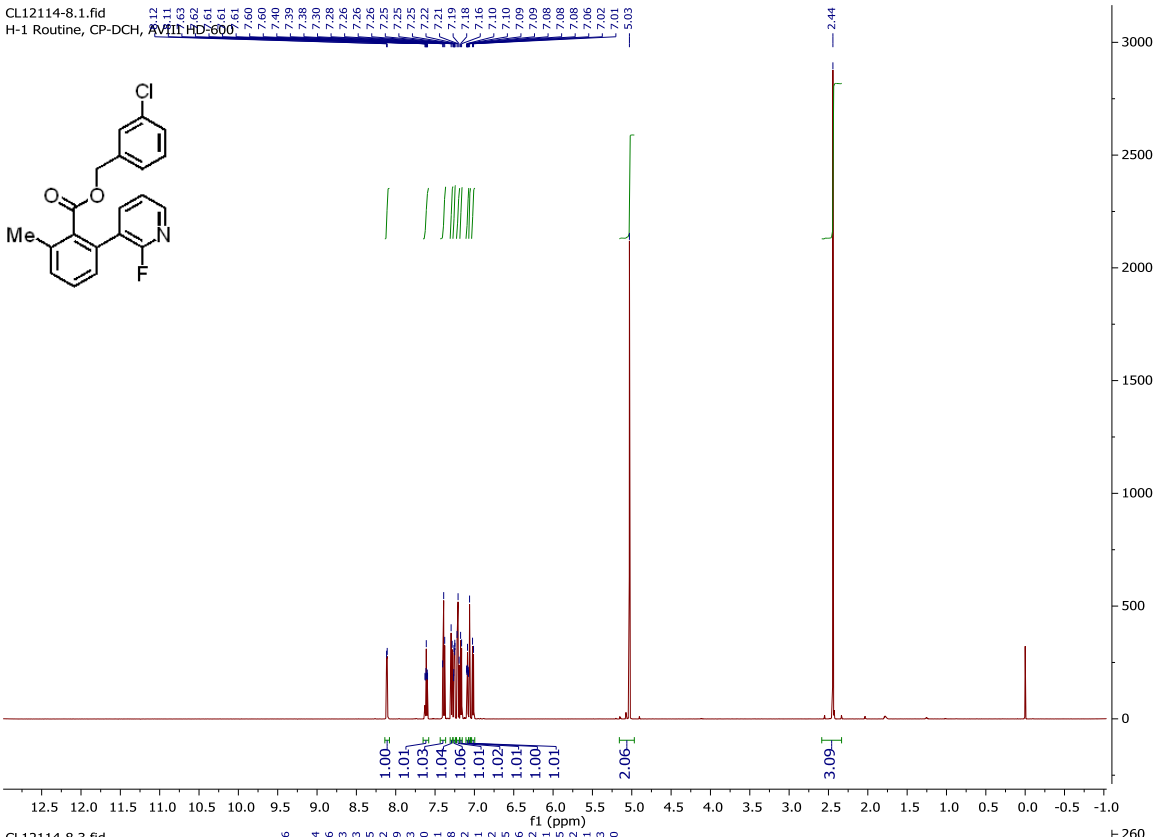

CL12114-3.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Cl
O
O
Me
N
F
f1 (ppm)

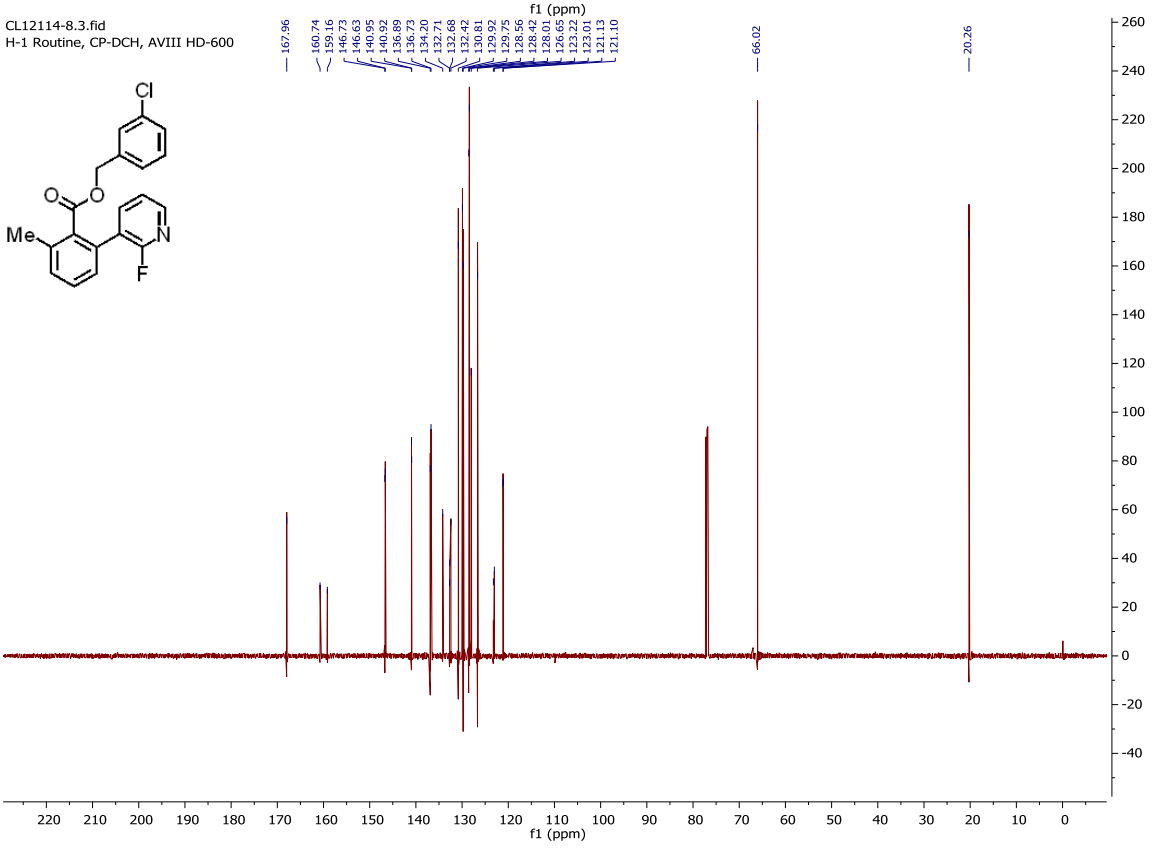

CL12114-5.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
OMe
Me
F
N
O
2.44
1.00
1.01
1.02
1.02
2.05
1.04
1.01
1.02
1.02
2.05
3.08
3.05
f1 (ppm)

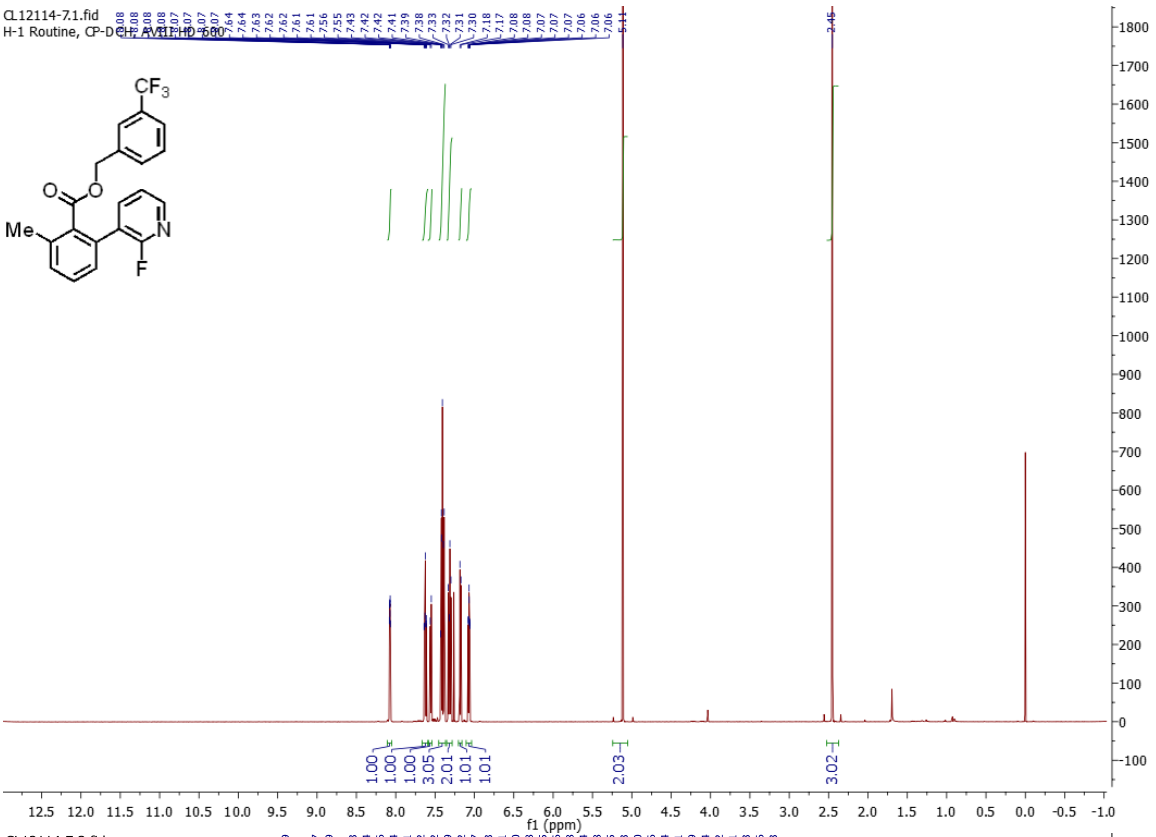

CL12114-5.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
OMe
Me
F
N
O
168.23
160.82
159.58
159.24
146.68
146.58
141.02
140.99
136.68
136.25
132.89
132.54
130.71
129.72
129.47
127.93
123.17
122.96
121.10
121.07
120.81
114.17
113.73
66.91
55.17
20.20
f1 (ppm)

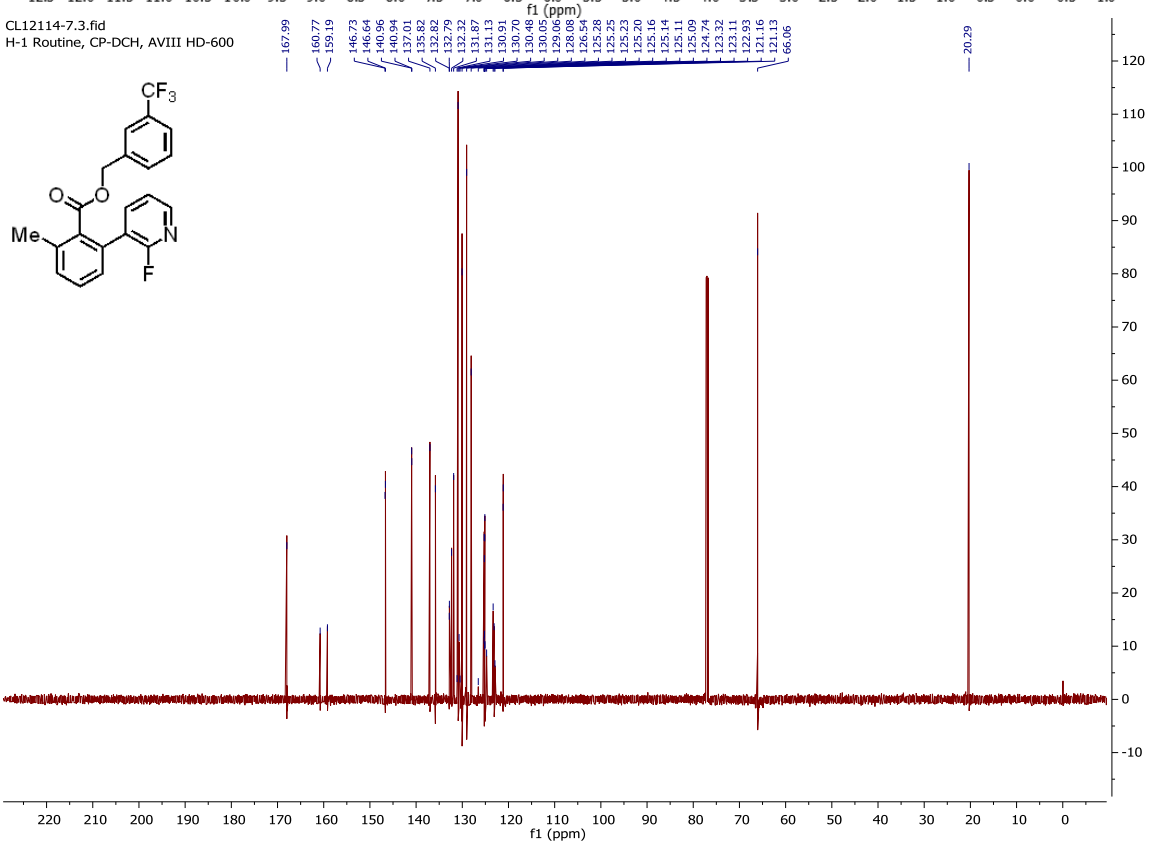

CL12114-6.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
F
O
O
Me
N
F
1.00
1.01
1.05
1.00
1.16
1.02
1.03
1.00
1.01
1.00
2.04
3.04
f1 (ppm)

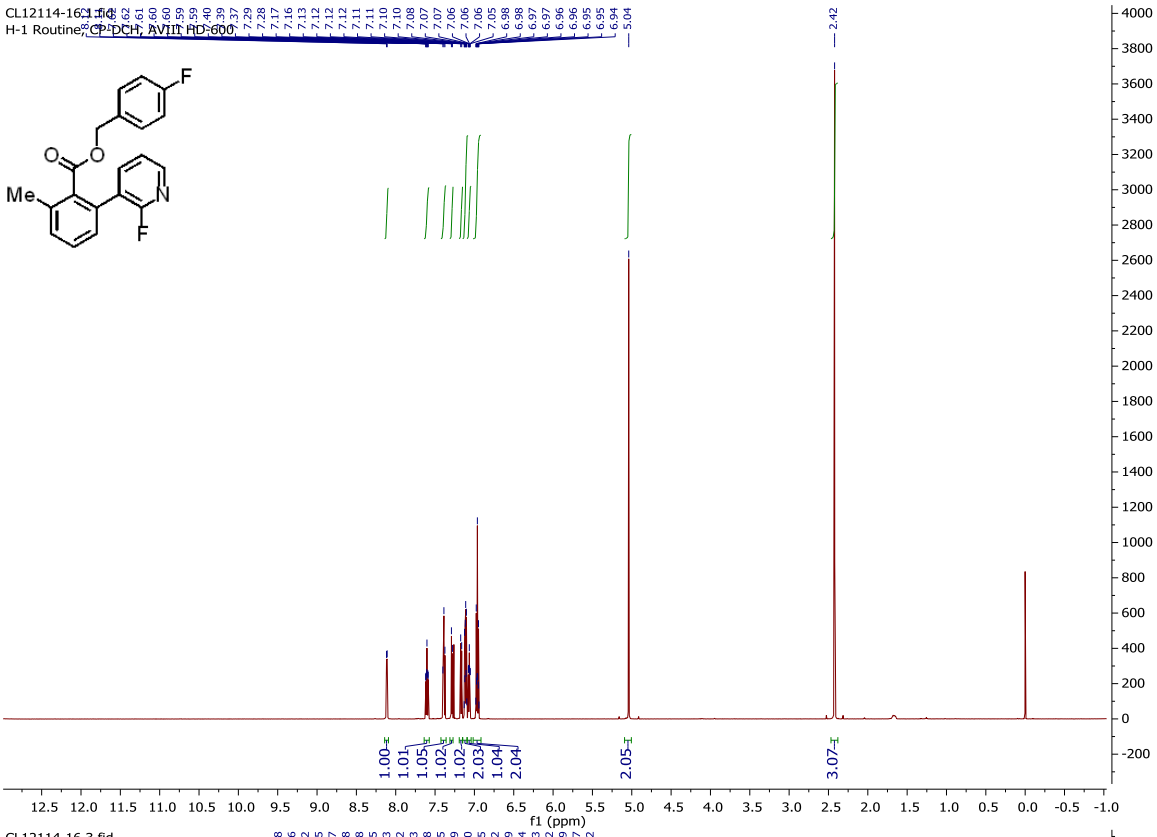

CL12114-6.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
168.08
163.42
161.79
160.84
159.26
146.78
146.69
141.05
141.02
137.27
137.22
136.87
132.71
132.69
132.55
130.85
130.08
130.03
129.93
128.05
124.07
124.05
123.29
123.08
121.17
121.14
115.44
115.30
115.17
109.95
66.13
20.29
F
O
O
Me
N
F
f1 (ppm)

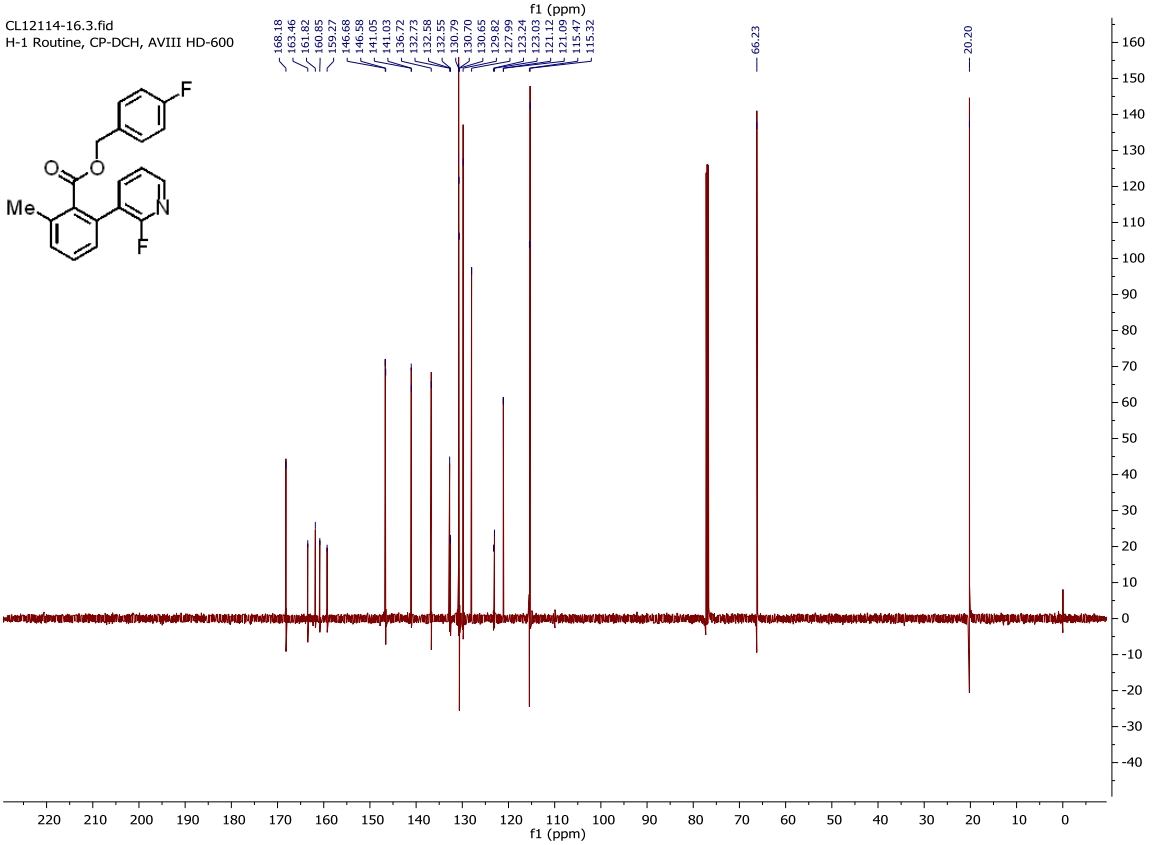

CL12114-8.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Cl
O
O
Me
N
F
f1 (ppm)

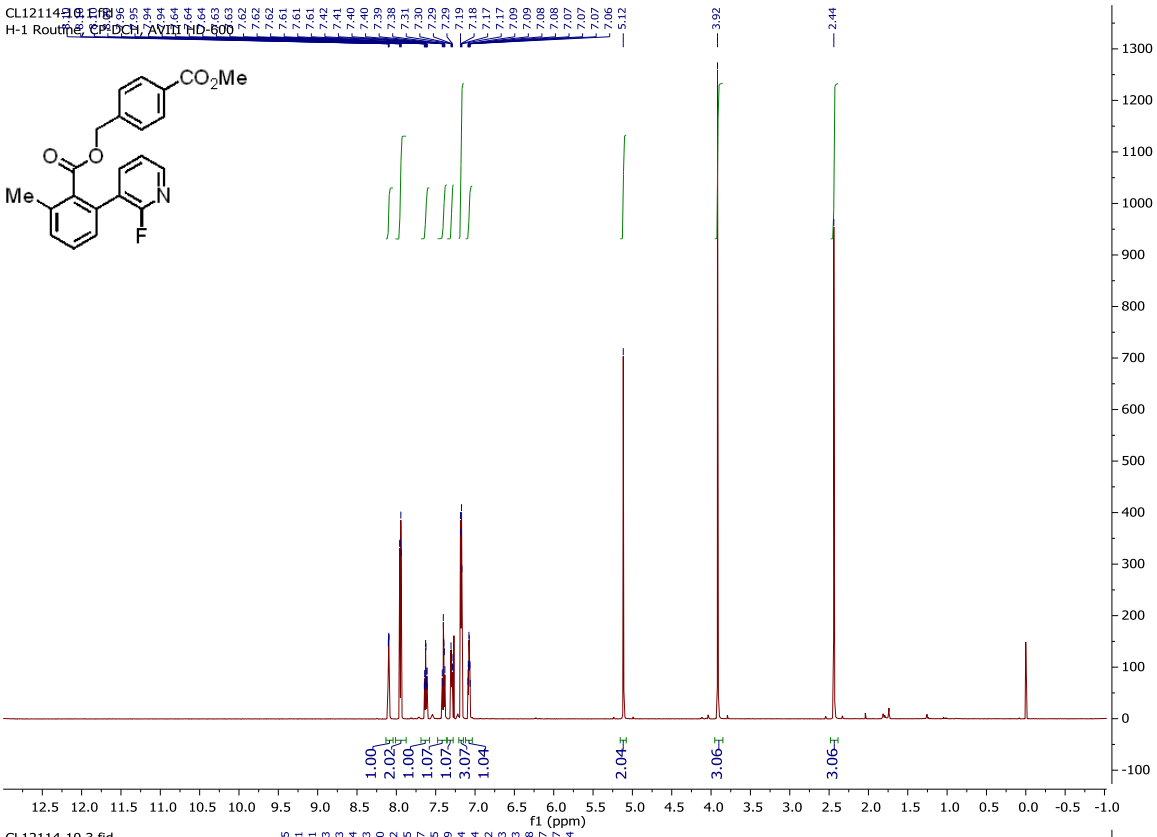

CL12114-8.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Cl
O
O
Me
N
F
f1 (ppm)

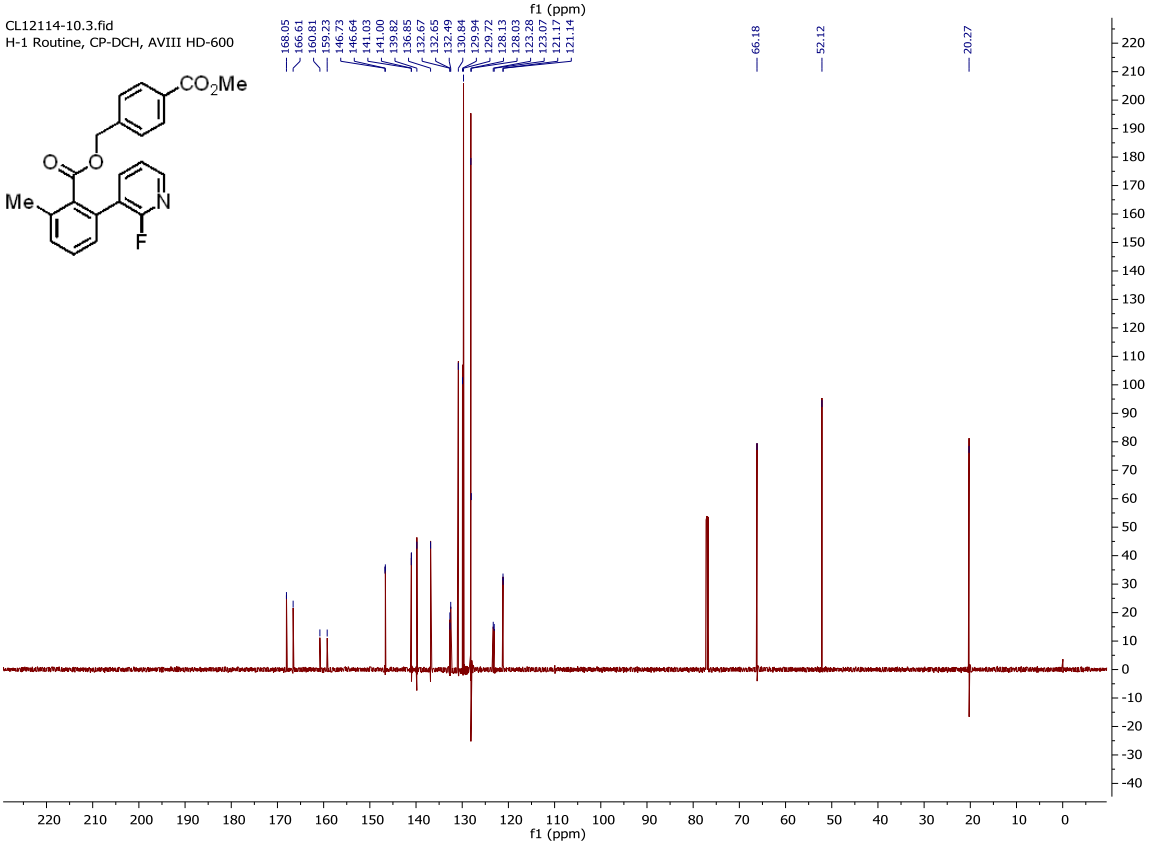

CL12114-7.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
CF3
O
O
Me
N
F
1.00
1.00
1.00
3.05
2.01
1.01
1.01
2.03
3.02
f1 (ppm)

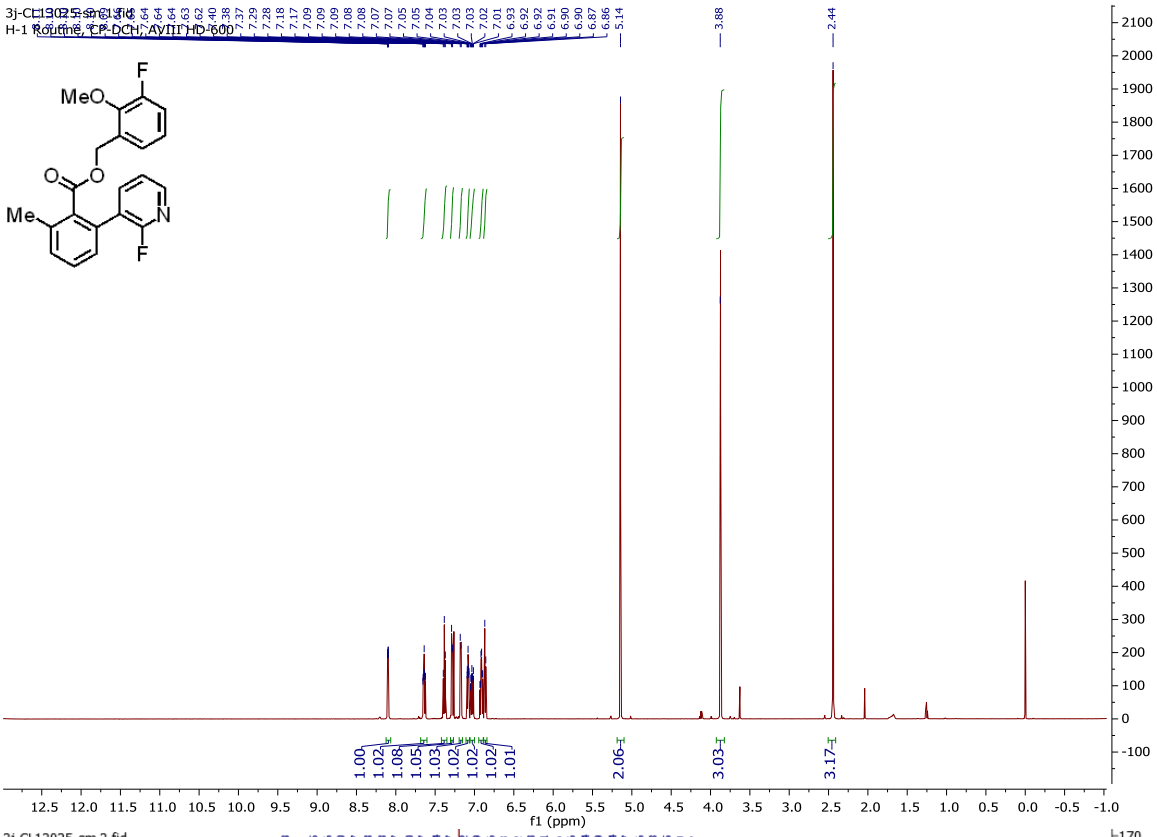

CL12114-7.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
167.99
160.77
159.19
146.73
146.64
140.96
140.94
137.01
135.82
132.82
132.79
132.32
131.87
131.13
130.91
130.70
130.48
130.05
129.06
128.08
126.54
125.28
125.25
125.23
125.20
125.16
125.14
125.11
125.09
124.74
123.32
123.11
122.93
121.16
121.13
66.06
20.29
CF3
O
O
Me
N
F
f1 (ppm)

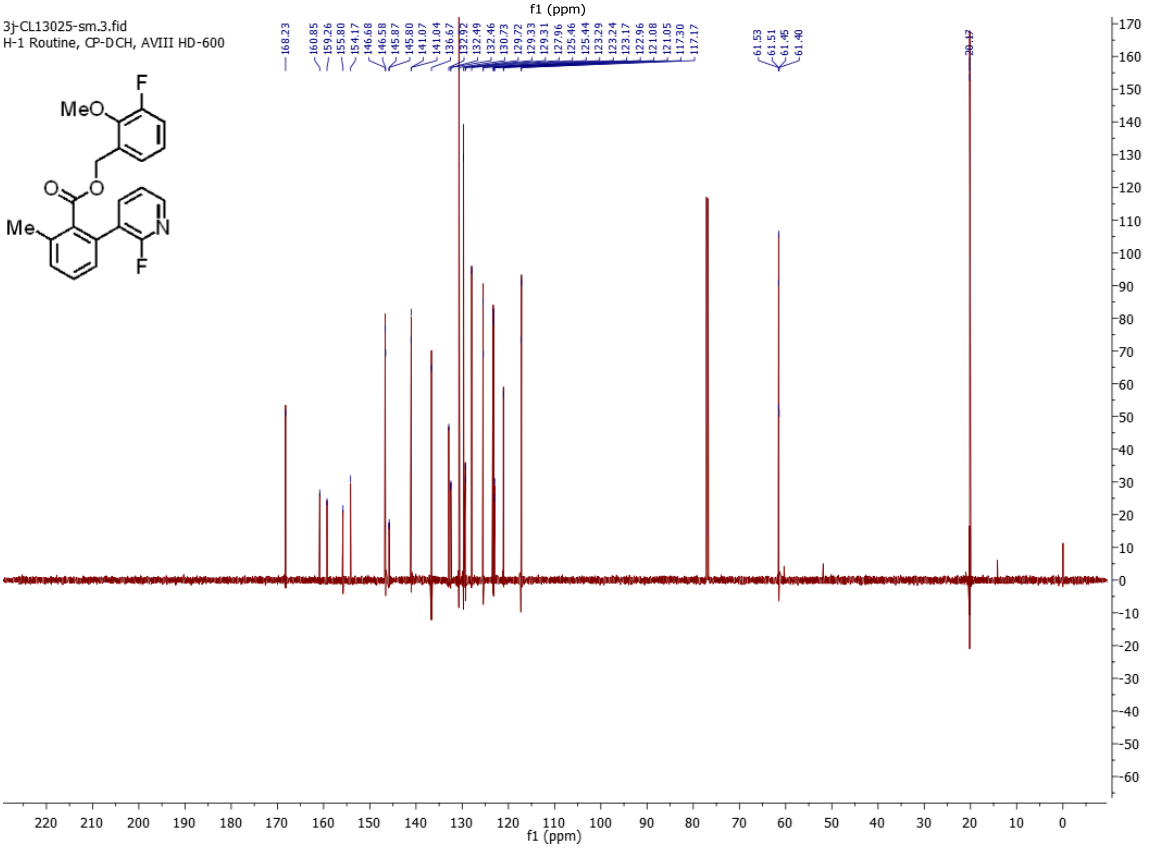

CL12114-16.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
F
O
O
Me
N
F
2.42
5.04
1.00
1.01
1.05
1.02
2.03
1.04
2.04
2.05
3.07
f1 (ppm)

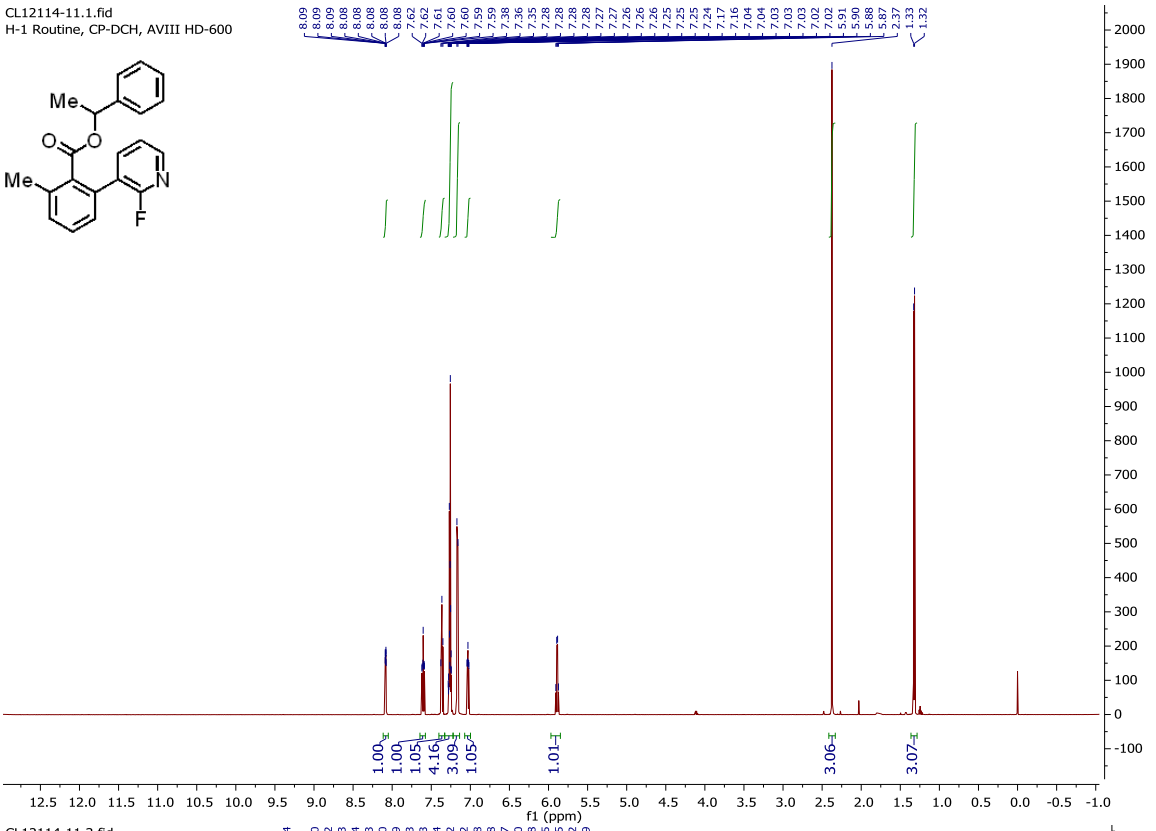

CL12114-16.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
F
O
O
Me
N
F
168.18
163.46
161.82
160.85
159.27
146.68
146.58
141.05
141.03
136.72
132.73
132.58
132.55
130.79
130.70
130.65
129.82
127.99
123.24
123.03
121.12
121.09
115.47
115.32
66.23
20.20
f1 (ppm)

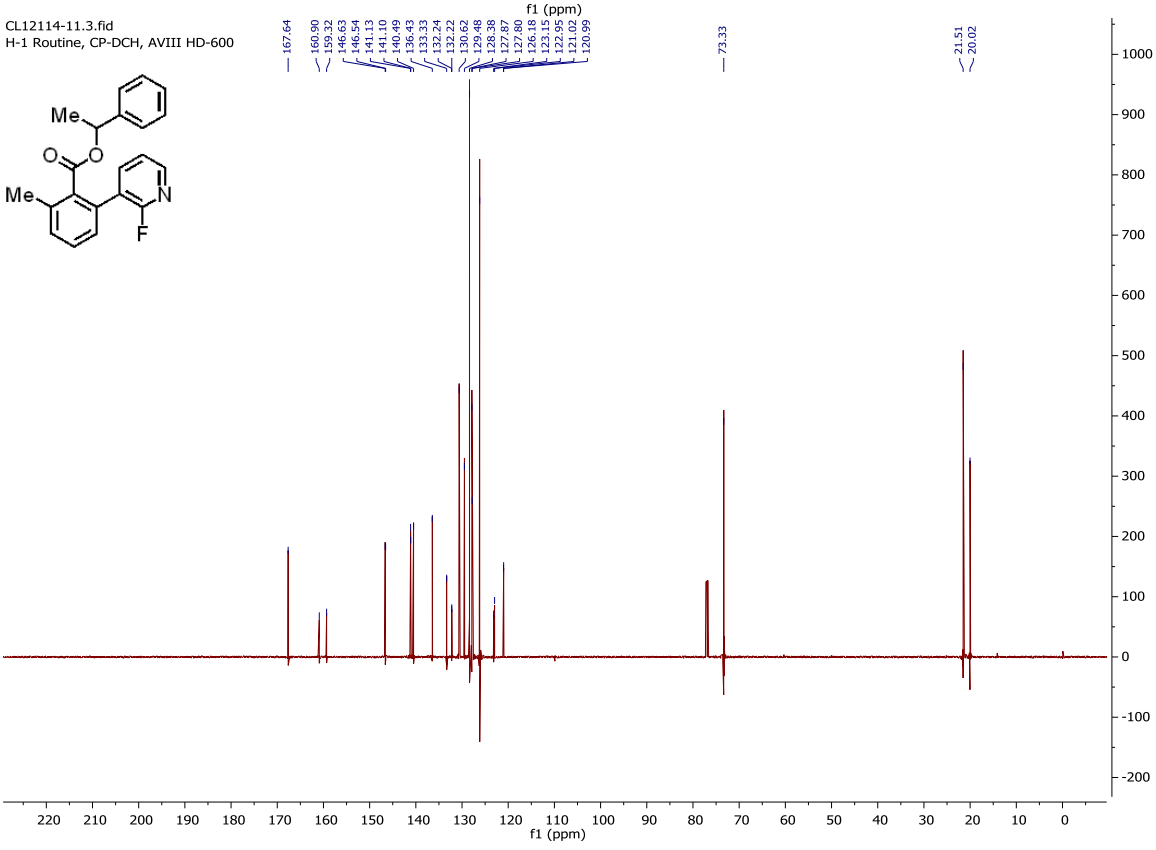

CL12114-10.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
CO2Me
O
O
Me
N
F
5.12
3.92
2.44
1.00
2.02
1.00
1.07
1.07
3.07
1.04
2.04
3.06
3.06
f1 (ppm)

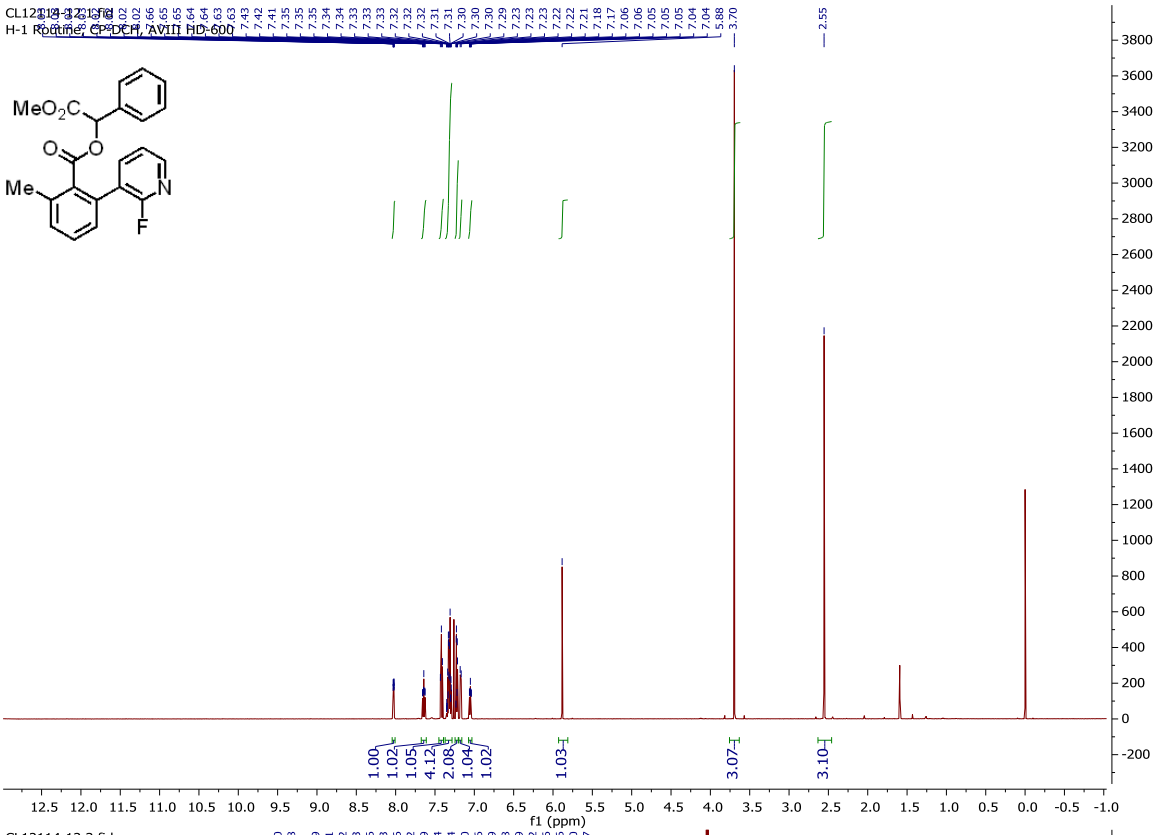

CL12114-10.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
CO2Me
O
O
Me
N
F
168.05
166.61
160.81
159.23
146.64
146.73
141.03
141.00
139.82
136.85
132.67
132.65
132.49
130.84
129.94
129.72
128.13
128.03
123.28
123.07
121.17
121.14
66.18
52.12
20.27
f1 (ppm)

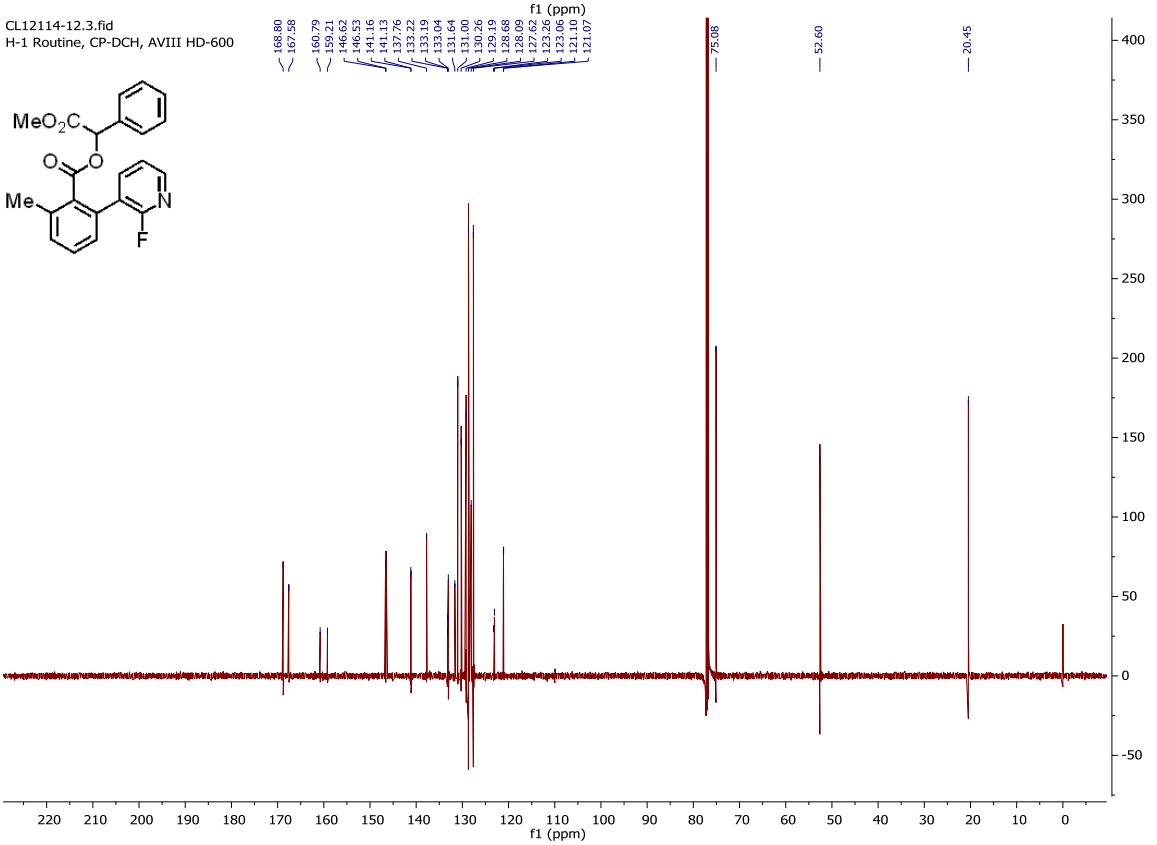

3j-CL13025-sm.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO
F
O
O
Me
N
F
f1 (ppm)

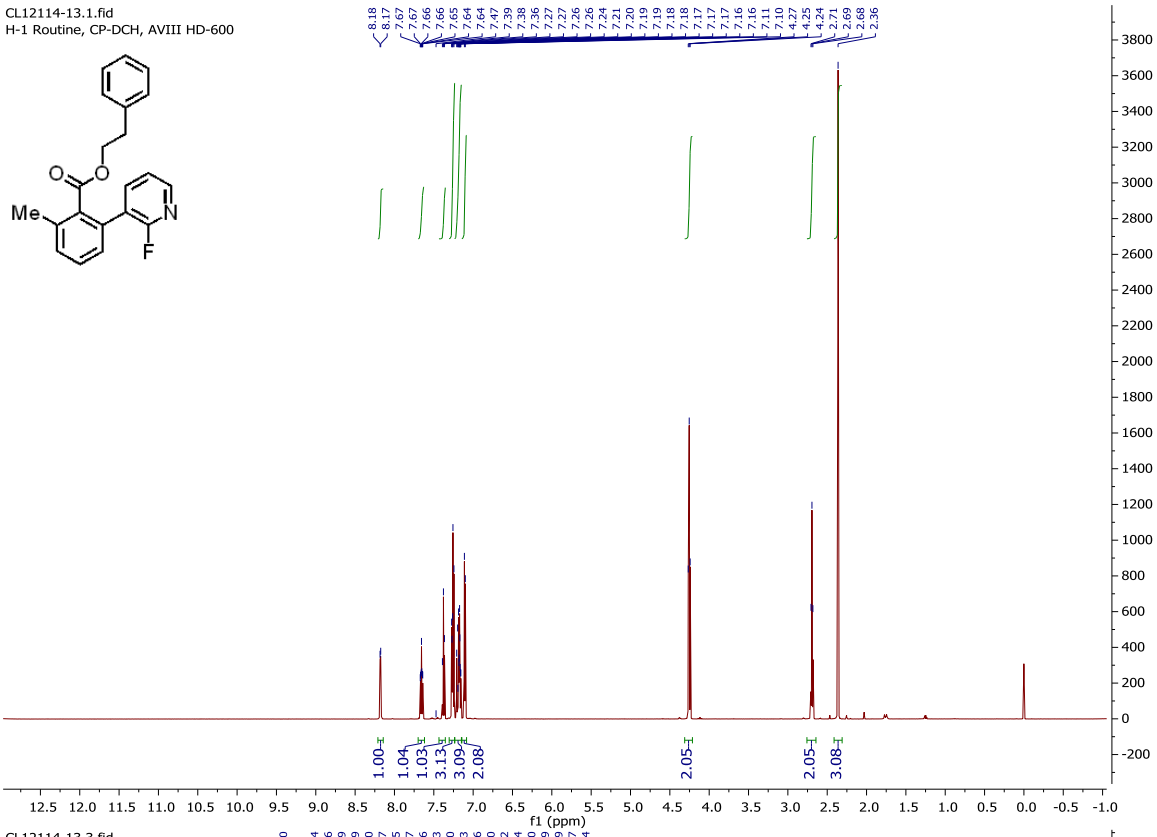

3j-CL13025-sm.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO
F
O
O
Me
N
F
f1 (ppm)

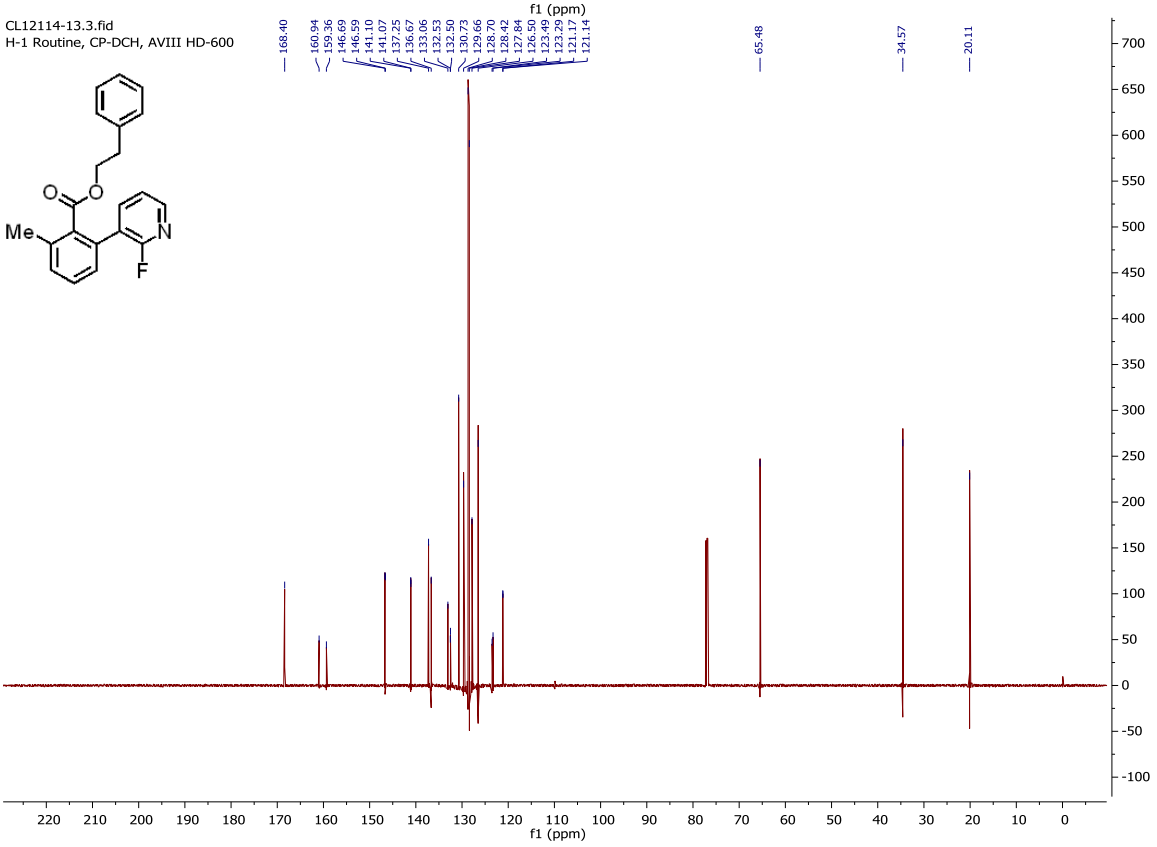

CL12114-11.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
Me
N
F
1.00
1.00
1.05
4.16
3.09
1.05
1.01
3.06
3.07
f1 (ppm)

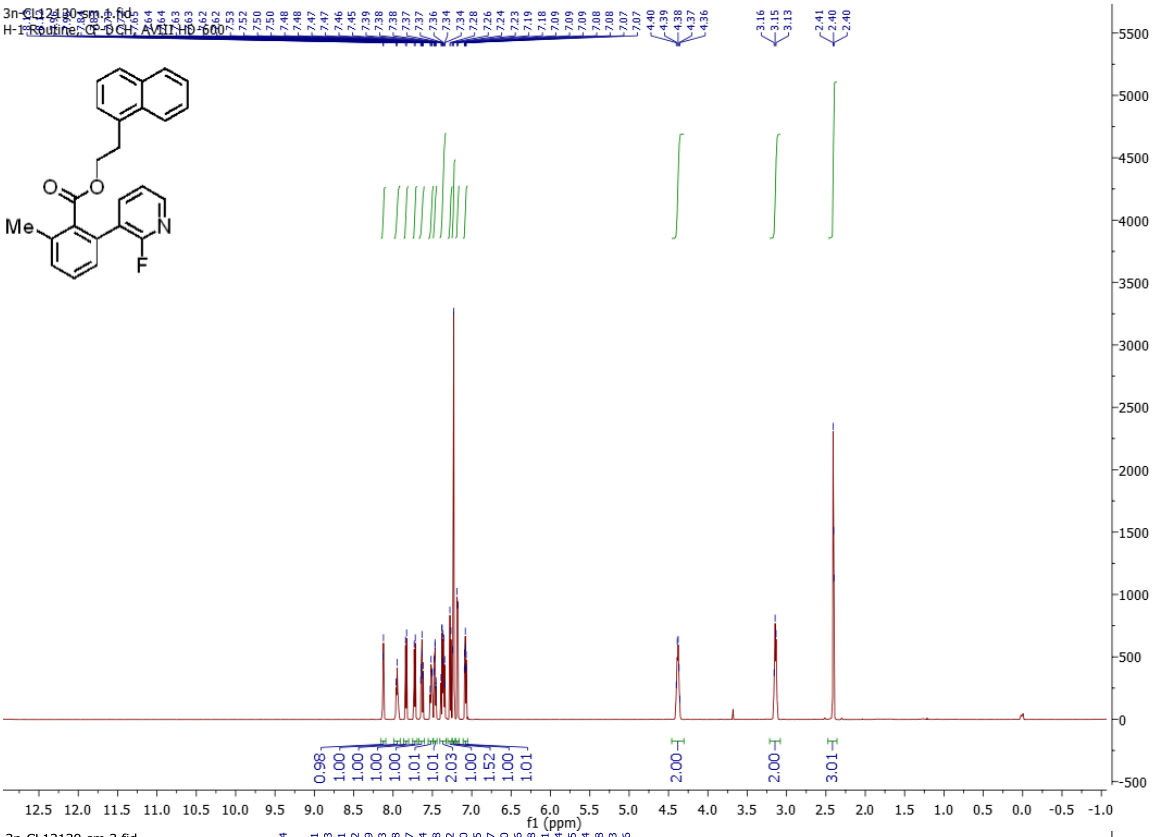

CL12114-11.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
Me
N
F
167.64
160.90
159.32
146.63
146.54
141.13
141.10
140.49
136.43
133.33
132.24
132.22
130.62
129.48
128.38
127.87
127.80
126.18
123.15
122.95
121.02
120.99
73.33
21.51
20.02
f1 (ppm)


CL12114-12.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO2C
O
O
Me
N
F
7.66 7.65 7.64 7.63 7.45 7.43 7.42 7.41 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.23 7.23 7.22 7.22 7.21 7.18 7.17 7.06 7.06 7.05 7.05 7.05 7.04 7.04 5.88 3.70
2.55
1.00 1.02 1.05 4.12 2.08 1.04 1.02 1.03 3.07 3.10
f1 (ppm)


CL12114-12.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO2C
O
O
Me
N
F
168.80 167.58 160.79 159.21 146.62 146.53 141.16 137.76 133.22 133.19 133.04 131.64 131.00 130.26 129.19 128.68 128.09 127.62 123.26 123.06 121.10 121.07
75.08
52.60
20.45
f1 (ppm)


CL12114-13.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
N
F
8.18
8.17
7.67
7.67
7.66
7.66
7.65
7.64
7.64
7.47
7.39
7.38
7.36
7.27
7.27
7.26
7.26
7.24
7.21
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.17
7.16
7.16
7.11
7.10
4.27
4.25
4.24
2.71
2.69
2.68
2.36
1.00
1.04
1.03
3.13
3.09
2.08
2.05
2.05
3.08
f1 (ppm)


CL12114-13.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
N
F
168.40
160.94
159.36
146.59
146.59
141.10
141.07
137.25
136.67
133.06
132.53
132.50
130.73
129.66
128.70
128.42
127.84
126.50
123.49
123.29
121.17
121.14
65.48
34.57
20.11
f1 (ppm)


3n-CL12130-sm.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
N
F
0.98
1.00
1.00
1.00
1.00
1.01
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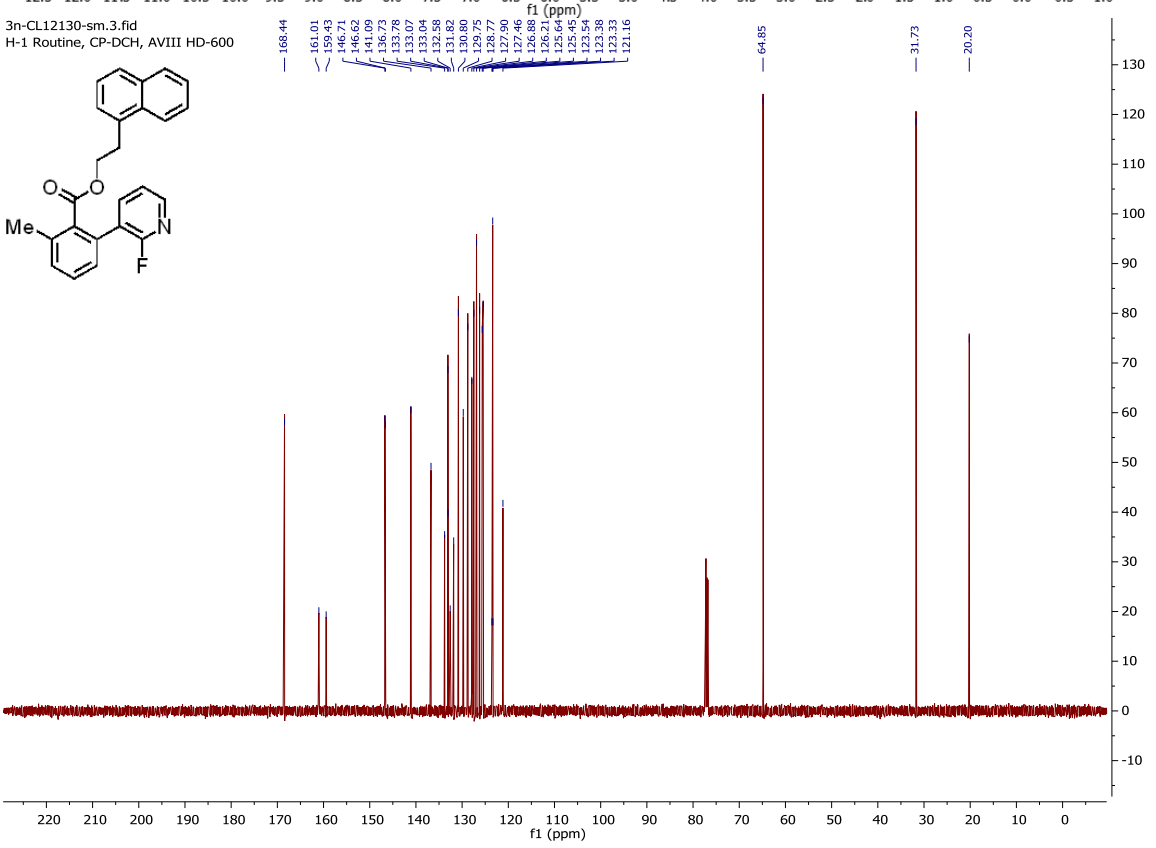
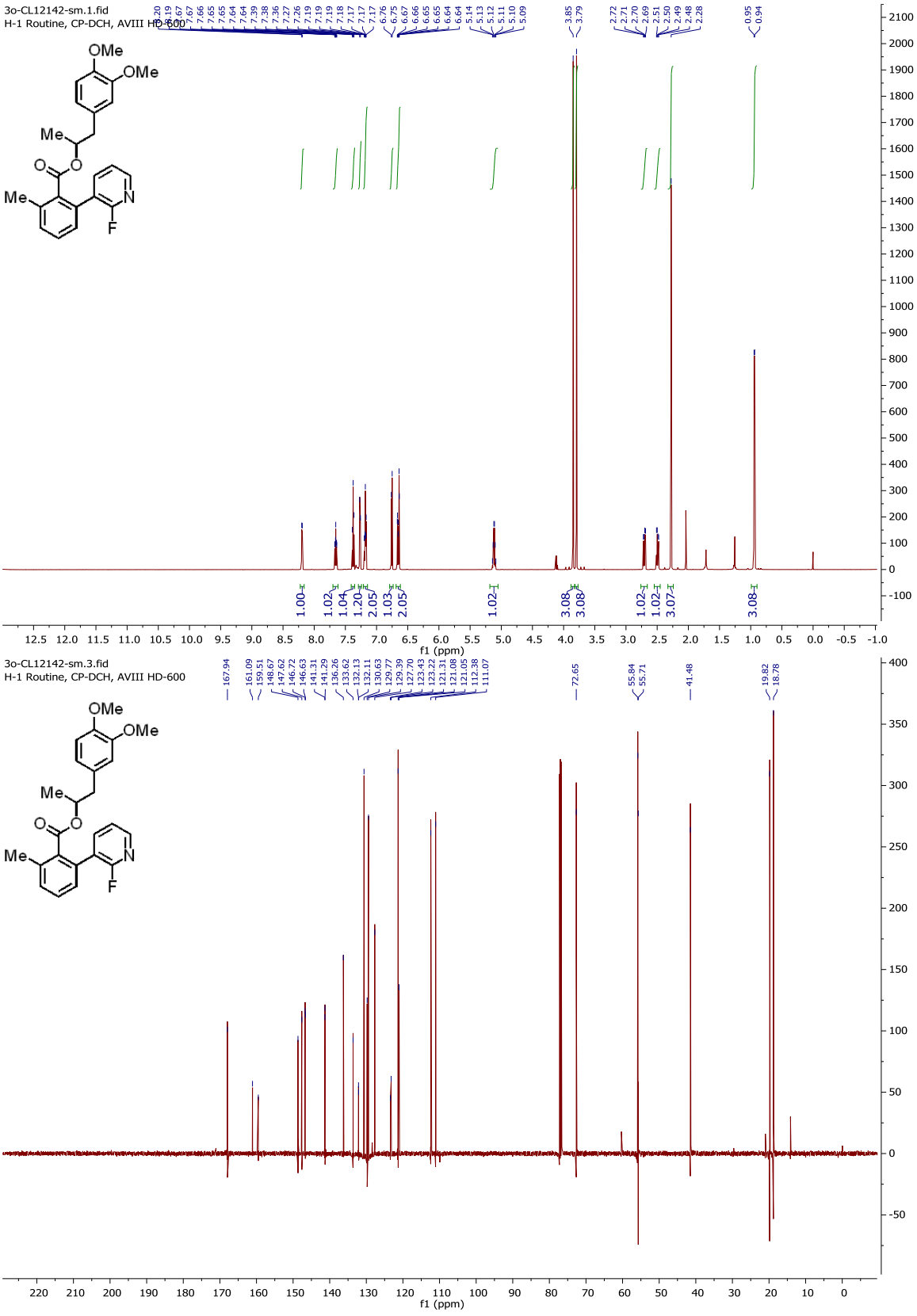
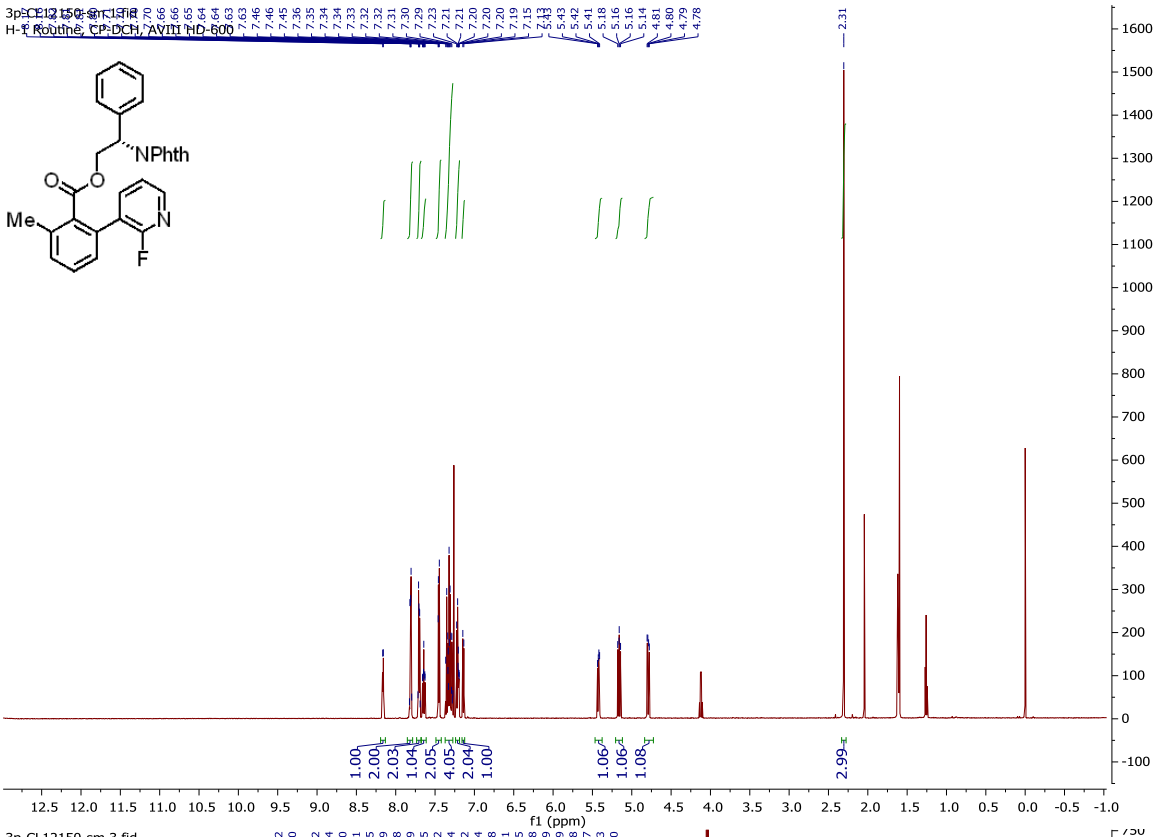
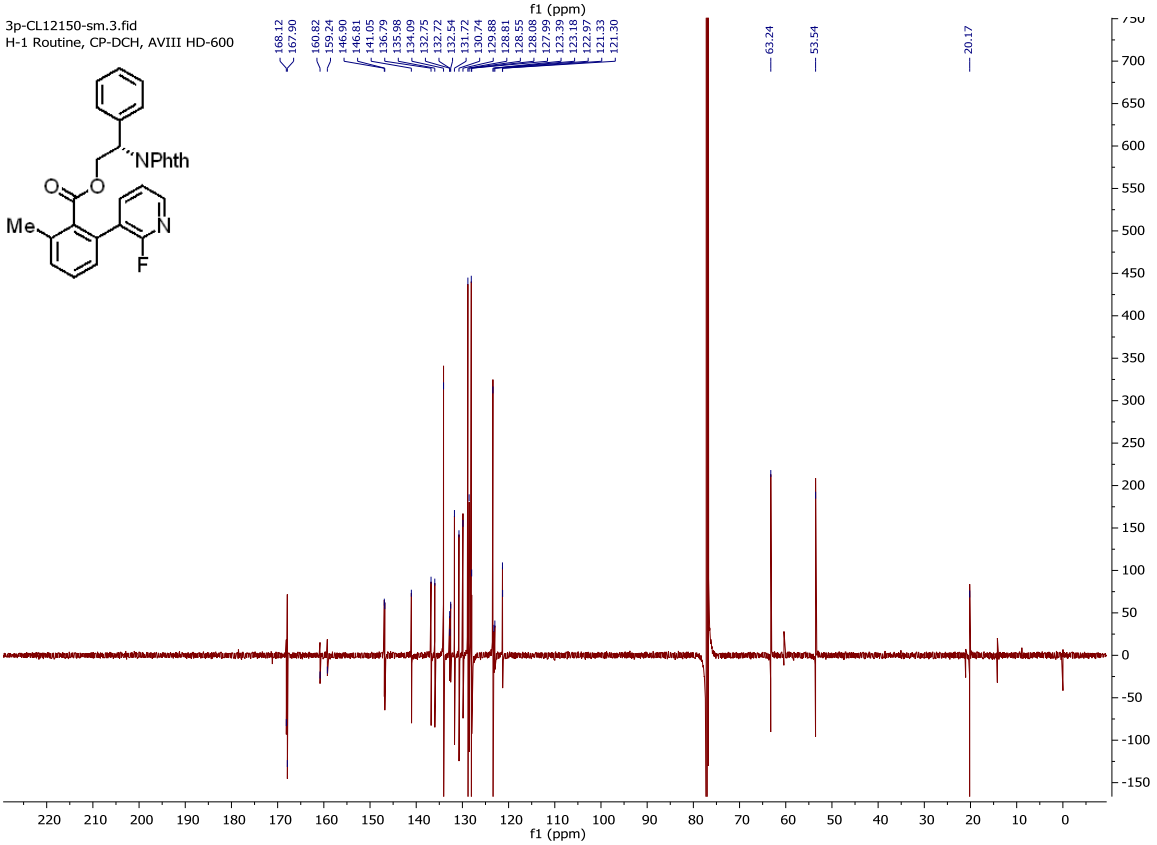
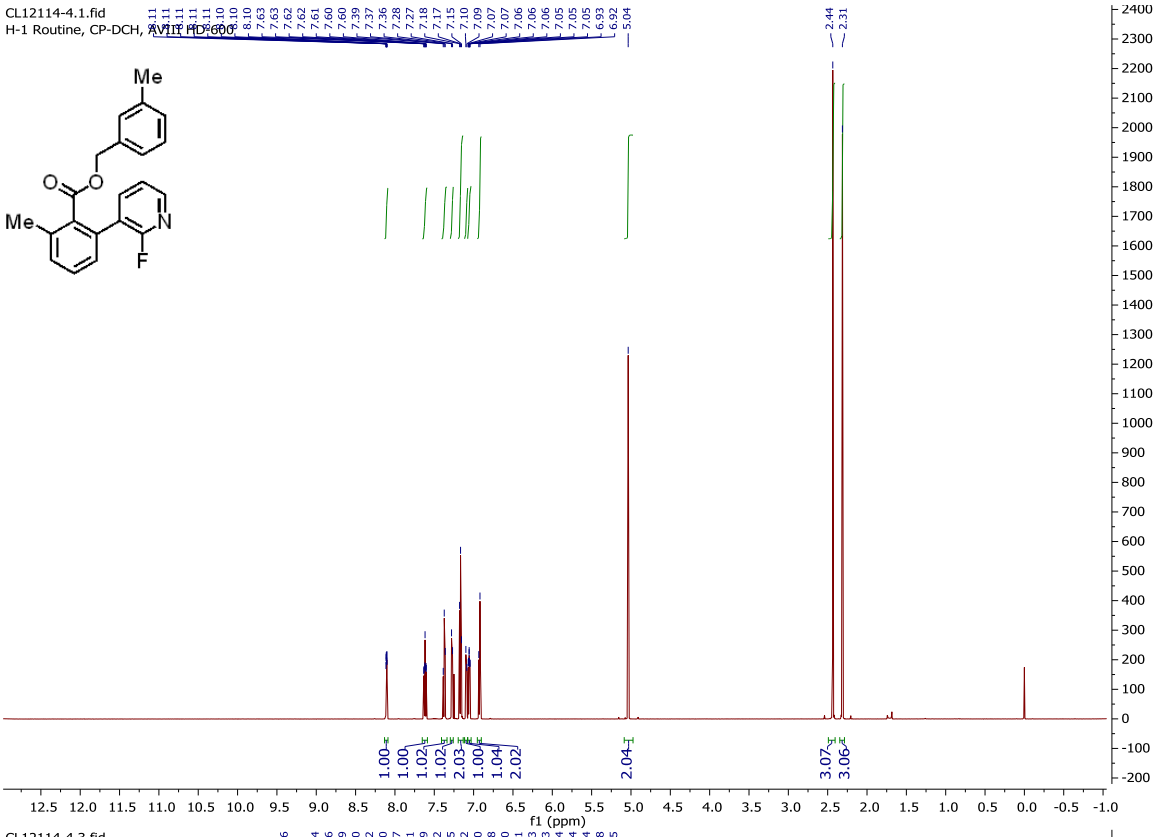
2.03
1.00
1.52
1.00
1.01
2.00
2.00
3.01
f1 (ppm)

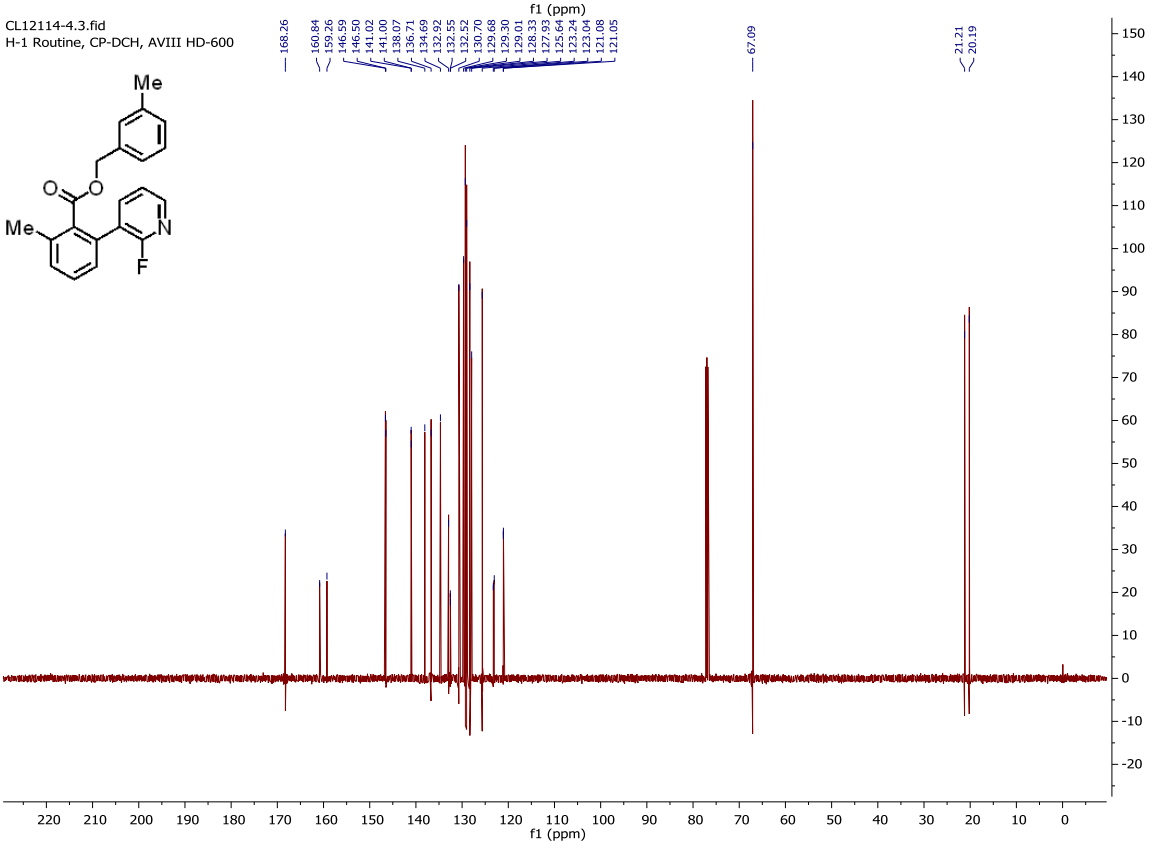

3n-CL12130-sm.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
N
F
168.44
161.01
159.43
146.71
146.62
141.09
136.73
133.78
133.07
133.04
132.58
131.82
130.80
129.75
128.77
127.90
127.46
126.88
126.21
125.64
125.45
123.54
123.38
123.33
121.16
64.85
31.73
20.20
f1 (ppm)

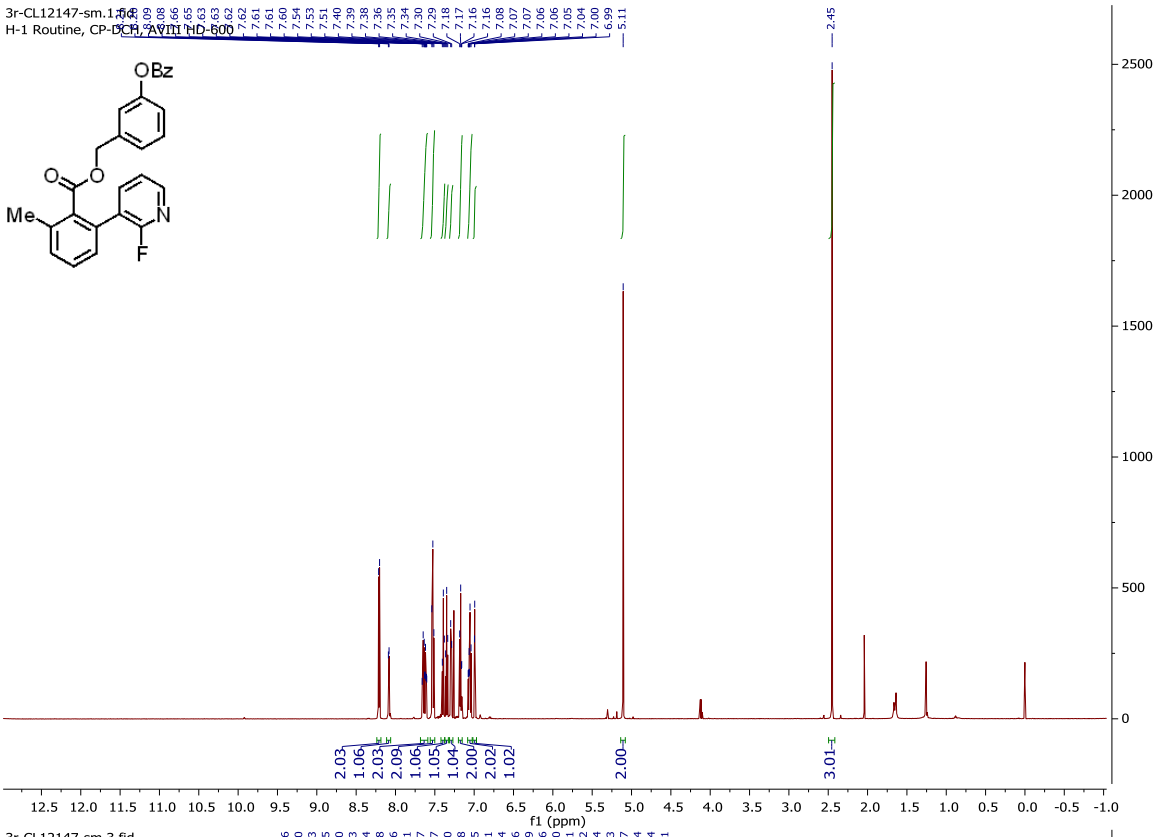

3o-CL12142-sm.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
OMe
OMe
Me
O
O
Me
N
F
f1 (ppm)
3o-CL12142-sm.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
OMe
OMe
Me
O
O
Me
N
F
f1 (ppm)

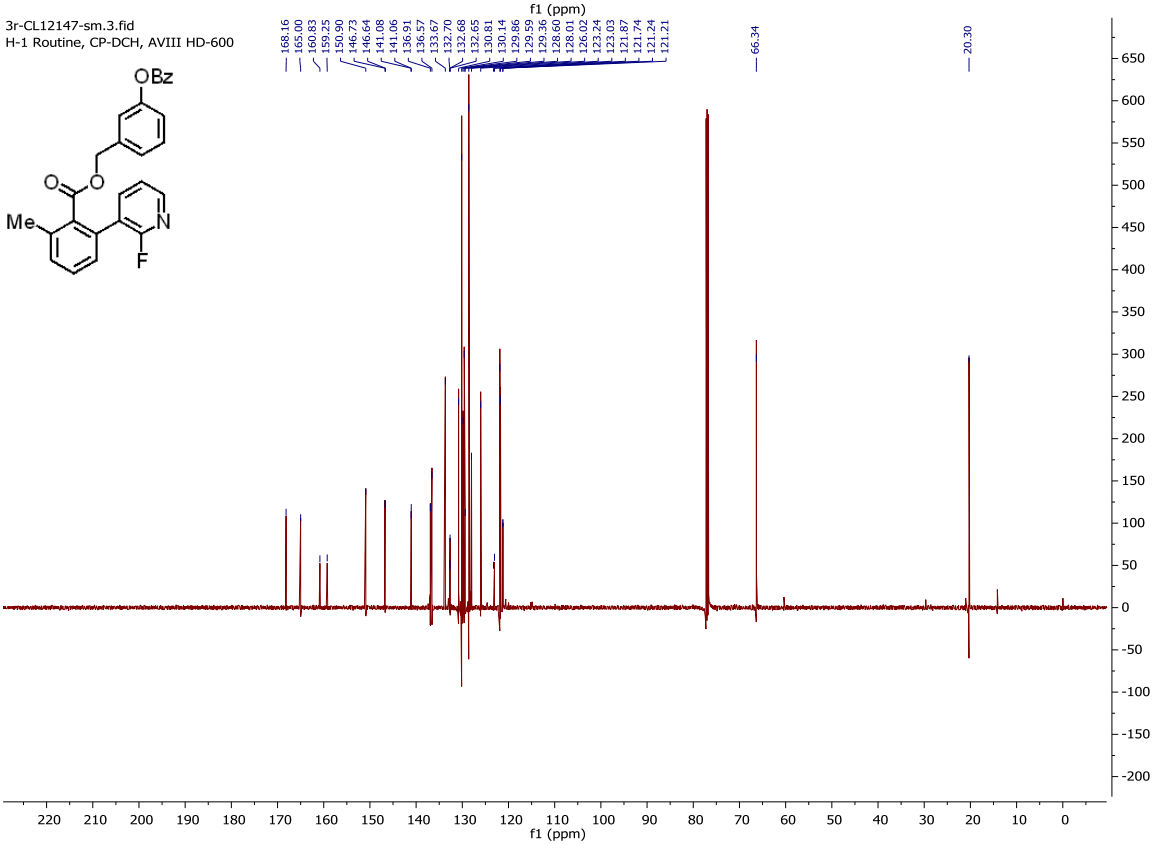

3p-CL12150-sm.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
NPhth
O
O
Me
N
F
2.31
1.00
2.00
2.03
1.04
2.05
4.05
2.04
1.00
1.06
1.06
1.08
2.99
f1 (ppm)


3p-CL12150-sm.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
NPhth
O
O
Me
N
F
168.12
167.90
160.82
159.24
146.90
146.81
141.05
136.79
135.98
134.09
132.75
132.72
132.54
131.72
130.74
129.88
128.81
128.55
128.08
127.99
123.39
123.18
122.97
121.33
121.30
63.24
53.54
20.17
f1 (ppm)


CL12114-4.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
Me
N
F
f1 (ppm)


CL12114-4.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
Me
N
F
f1 (ppm)


3r-CL12147-sm.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
OBz
O
O
Me
N
F
2.45
5.11
2.03
1.06
2.03
2.09
1.06
1.05
1.04
2.00
2.02
1.02
2.00
3.01
f1 (ppm)


3r-CL12147-sm.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
OBz
O
O
Me
N
F
168.16
165.00
160.83
159.25
150.90
146.73
146.64
141.08
141.06
136.91
136.57
133.67
132.70
132.68
132.65
130.81
130.14
129.86
129.59
129.36
128.60
128.01
126.02
123.24
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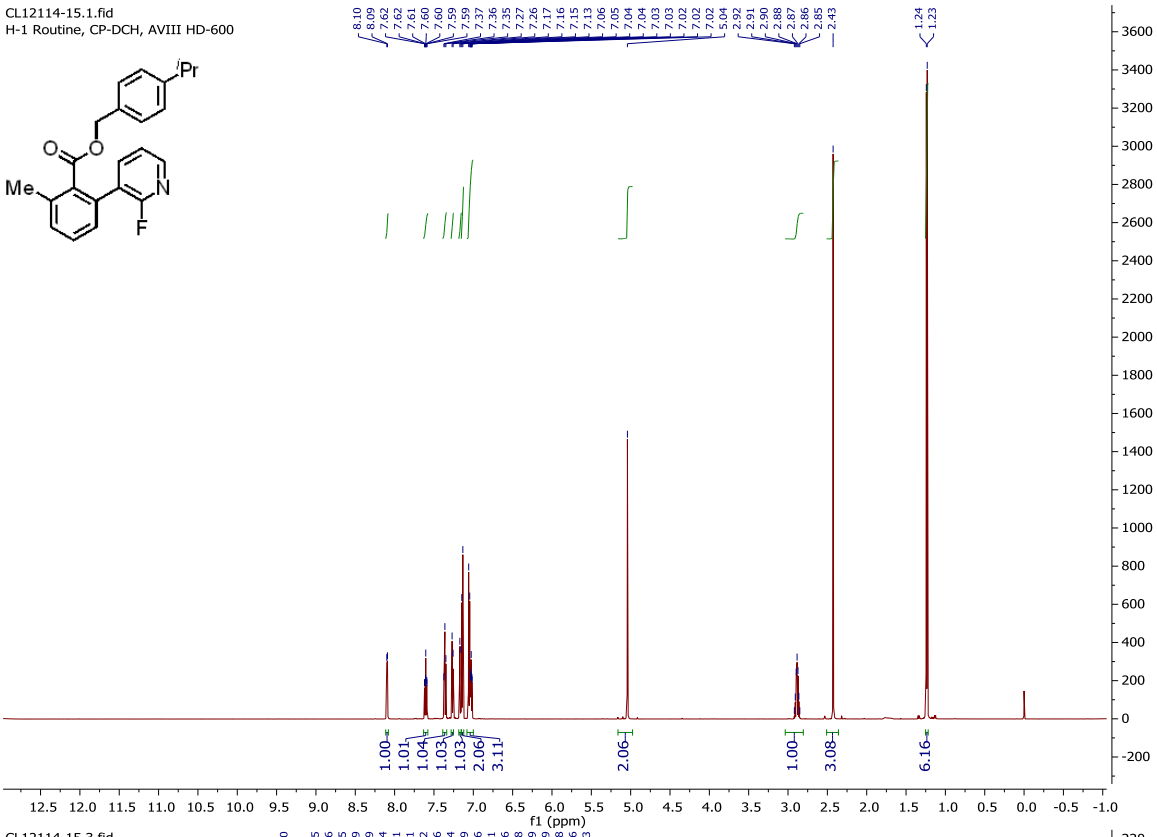
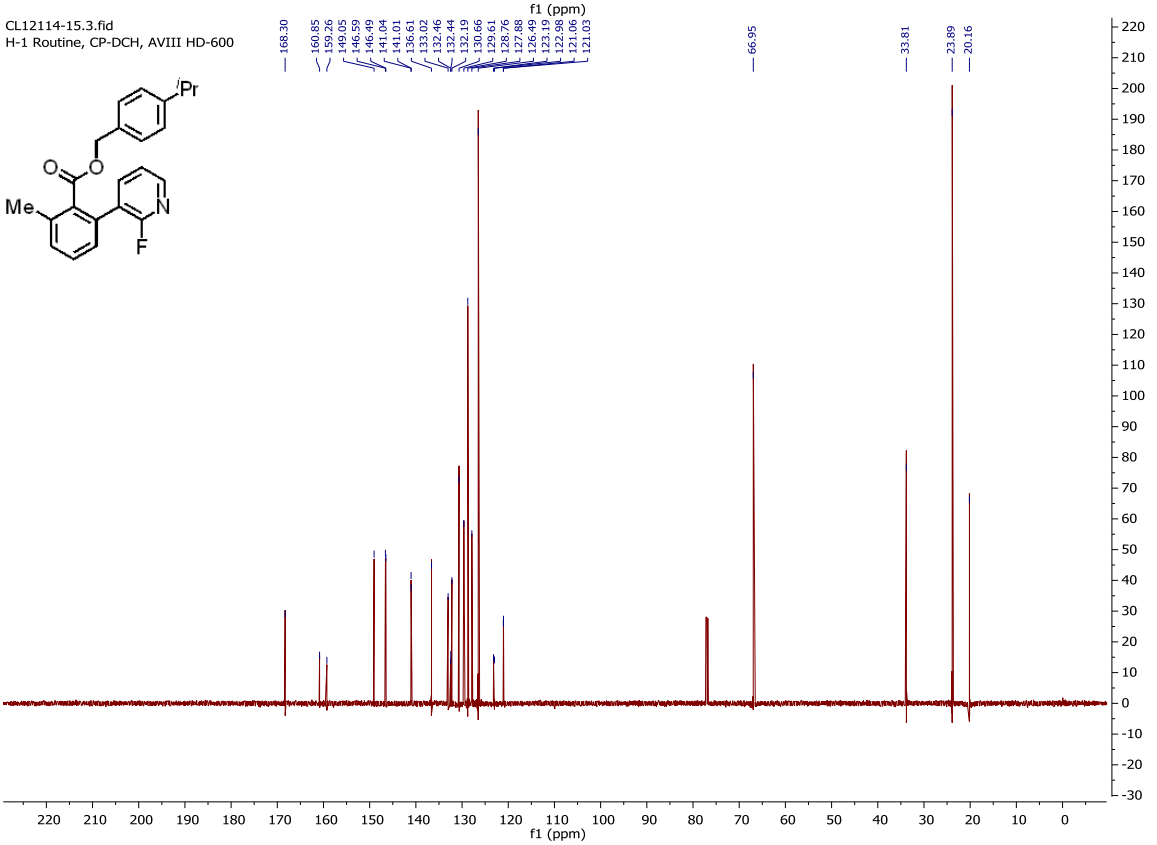
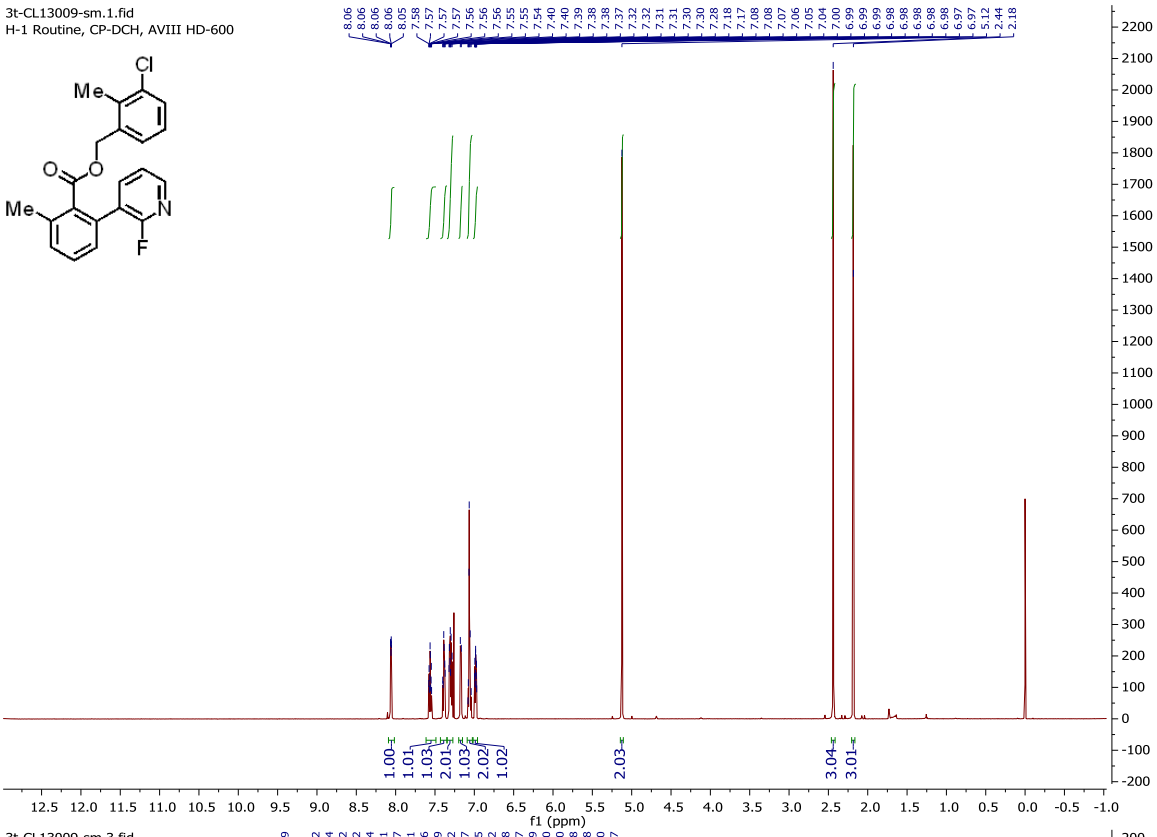
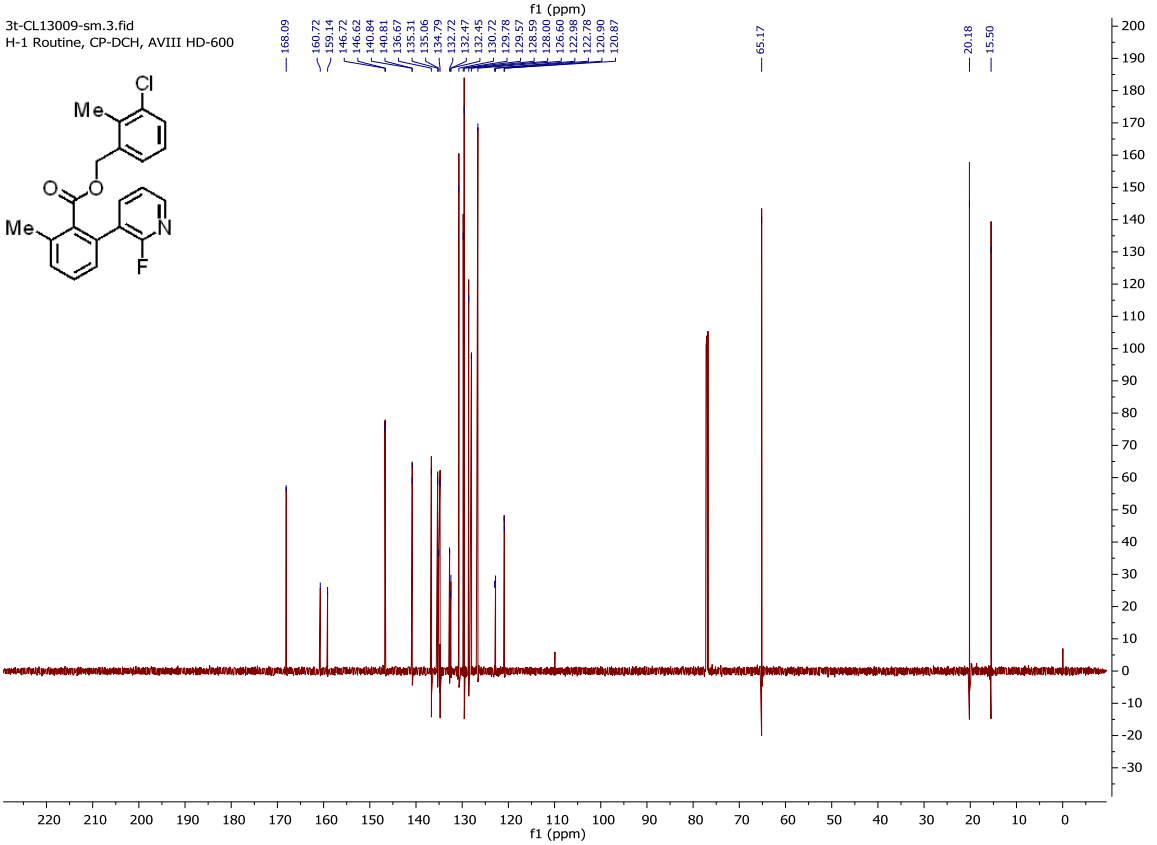
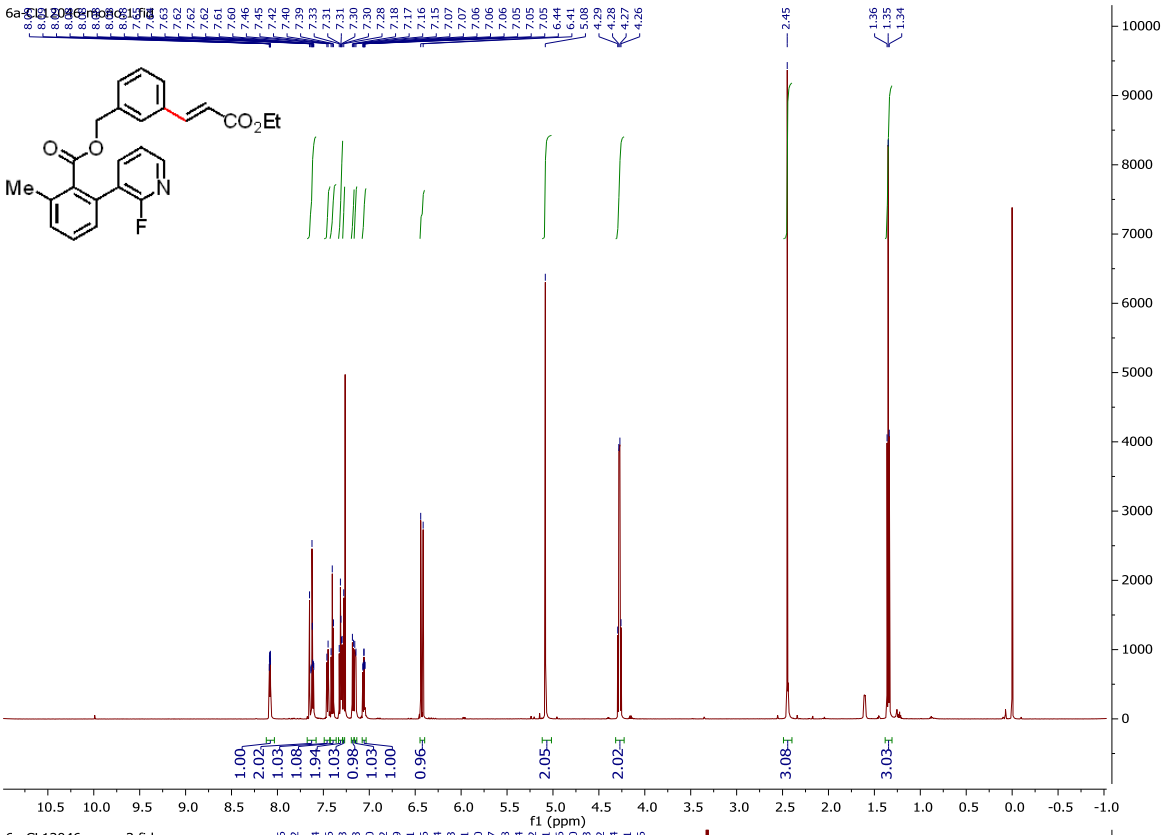
121.74
121.24
121.21
66.34
20.30
f1 (ppm)

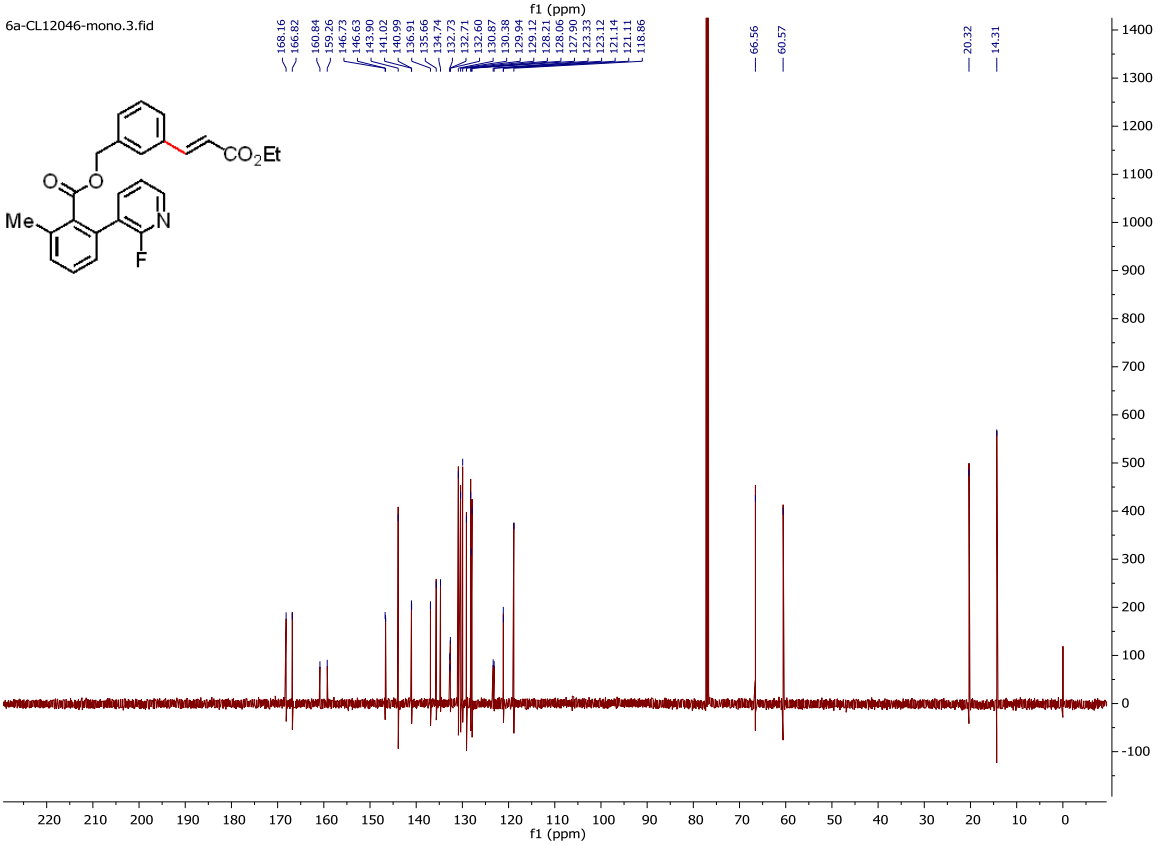

CL12114-15.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
iPr
O
O
Me
N
F
8.10
8.09
7.62
7.61
7.60
7.59
7.37
7.36
7.35
7.27
7.26
7.17
7.16
7.15
7.13
7.06
7.05
7.04
7.03
7.02
5.04
2.92
2.91
2.90
2.88
2.87
2.86
2.85
2.43
1.24
1.23
1.00
1.01
1.04
1.03
1.03
2.06
3.11
2.06
1.00
3.08
6.16
f1 (ppm)

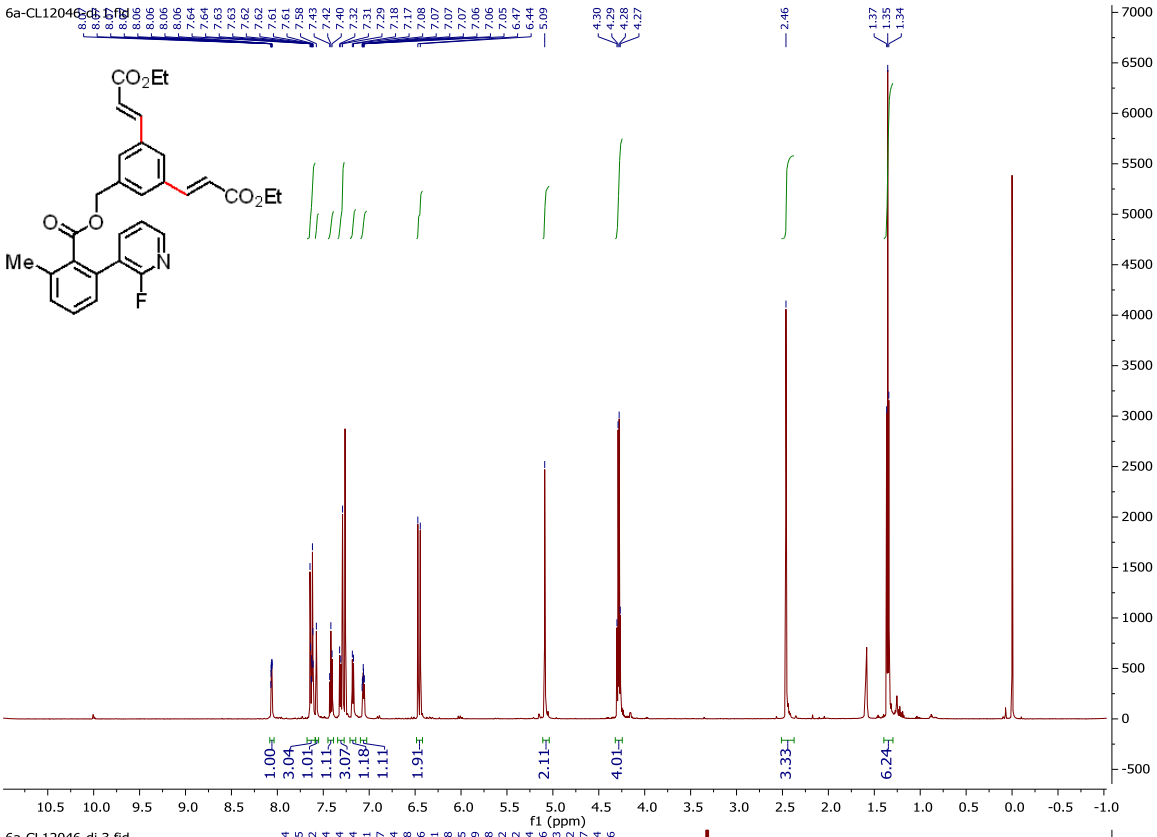

CL12114-15.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
iPr
O
O
Me
N
F
168.30
160.85
159.26
149.05
146.59
146.49
141.04
141.01
136.61
133.02
132.46
132.44
132.19
130.66
129.61
128.76
127.88
126.49
123.19
122.98
121.06
121.03
66.95
33.81
23.89
20.16
f1 (ppm)

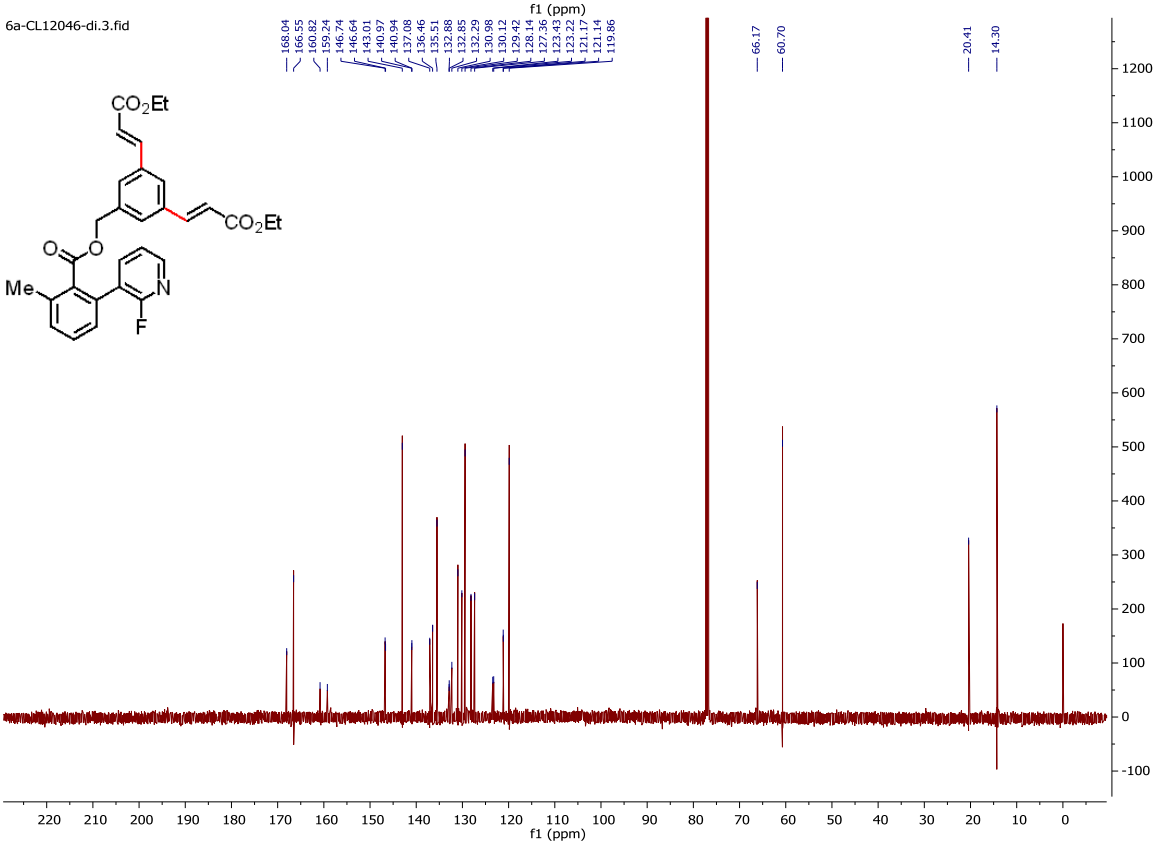

3t-CL13009-sm.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Cl
Me
O
O
Me
N
F
f1 (ppm)

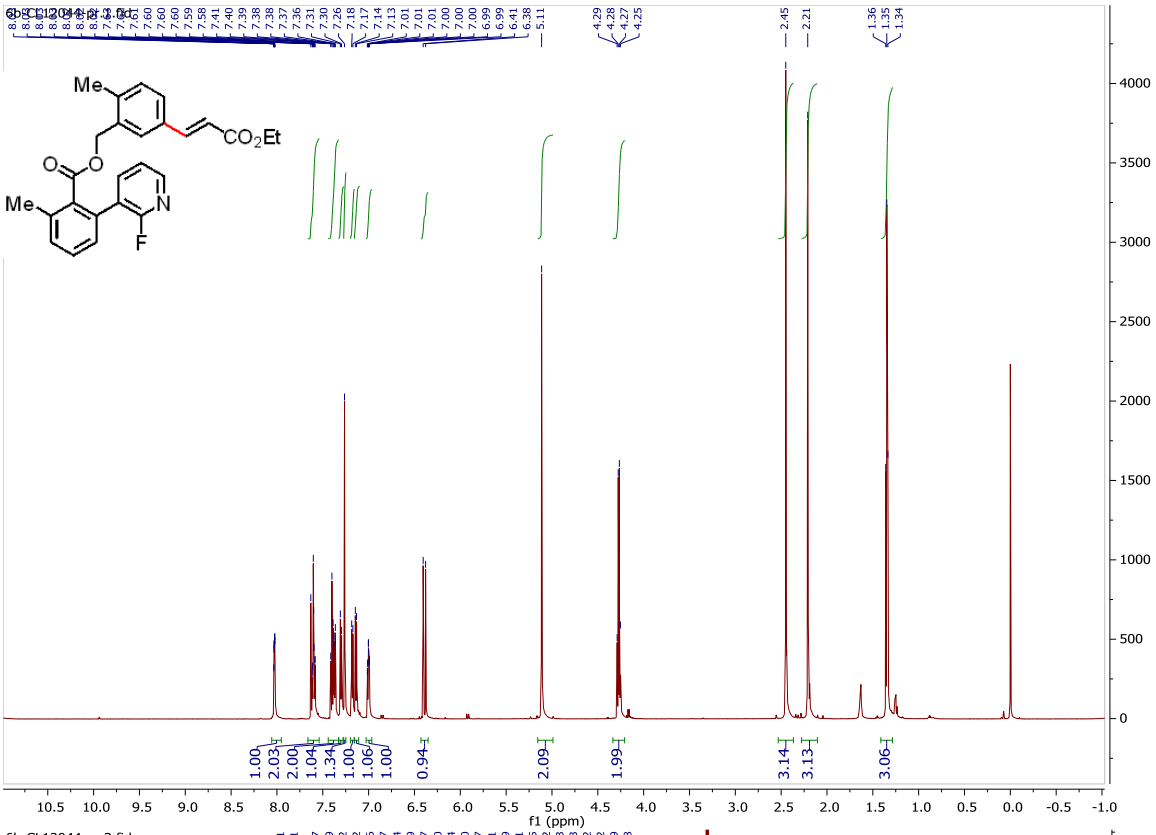

3t-CL13009-sm.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Cl
Me
O
O
Me
N
F
f1 (ppm)

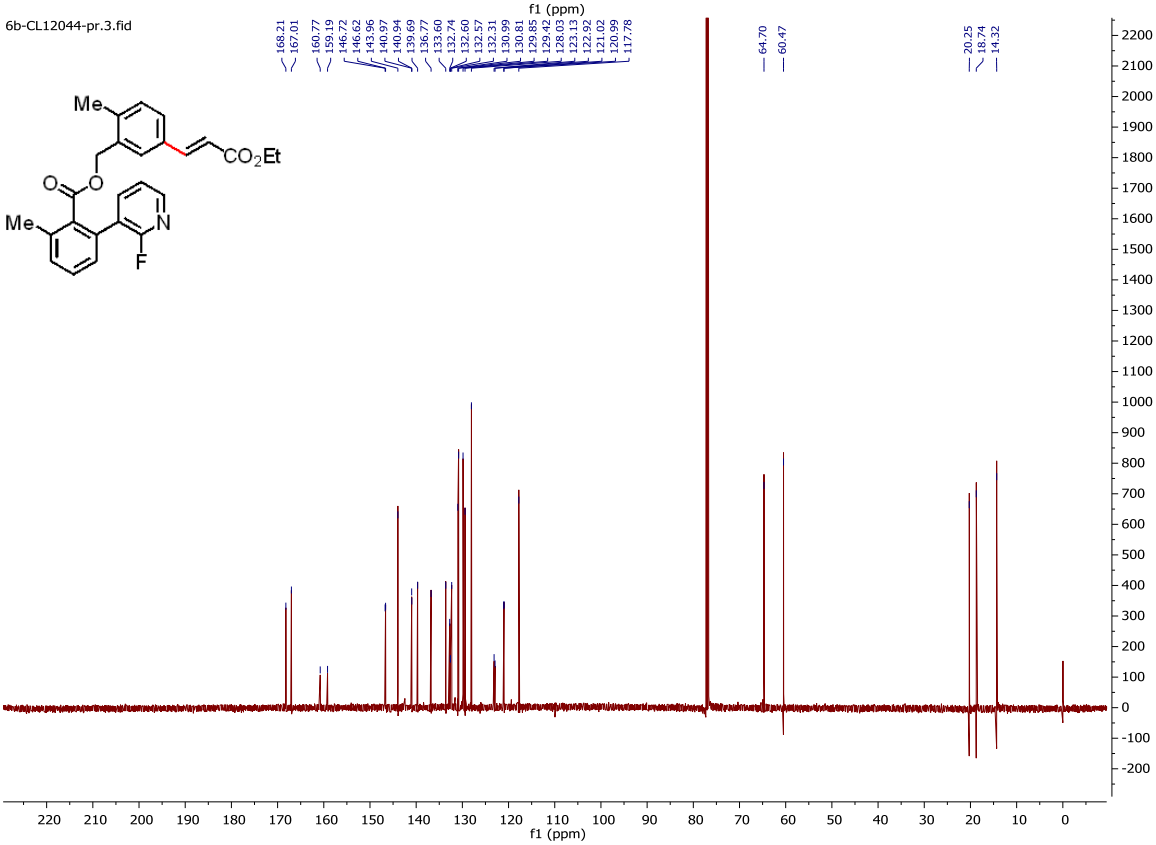

6a-CL12046-mono.1.fid
CO2Et
O
O
Me
N
F
f1 (ppm)

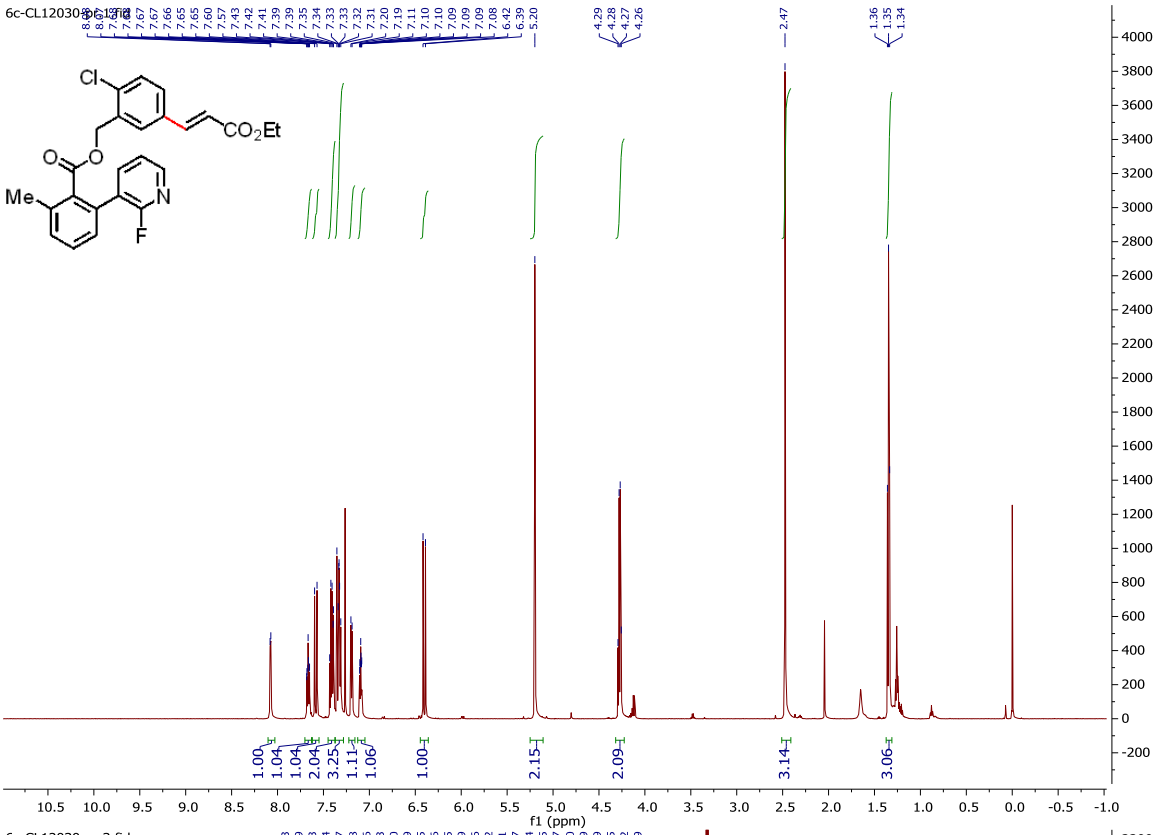

6a-CL12046-mono.3.fid
CO2Et
O
O
Me
N
F
f1 (ppm)

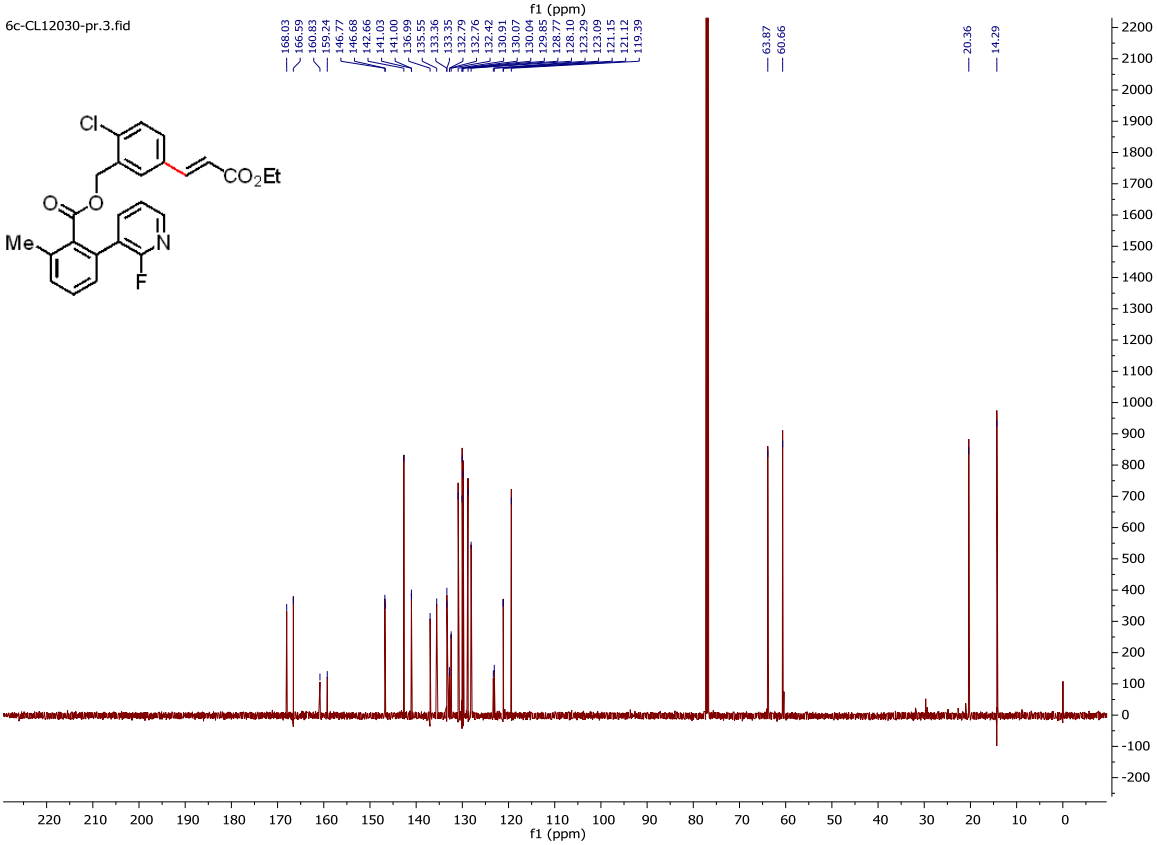

6a-CL12046-di.1.fid
CO2Et
CO2Et
O
O
Me
N
F
1.00
3.04
1.01
1.11
3.07
1.18
1.11
1.91
2.11
4.01
3.33
6.24
f1 (ppm)

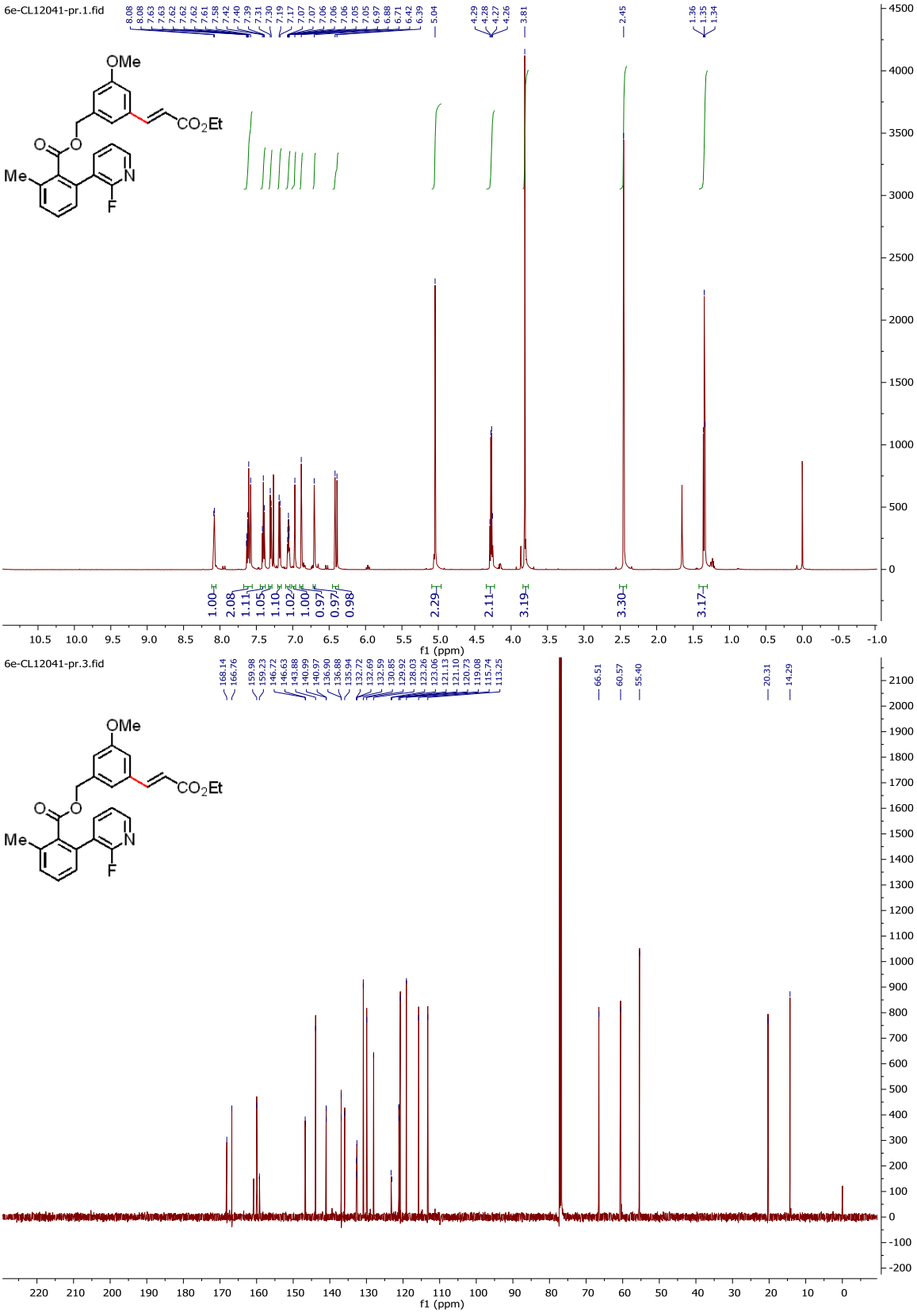

6a-CL12046-di.3.fid
CO2Et
CO2Et
O
O
Me
N
F
f1 (ppm)

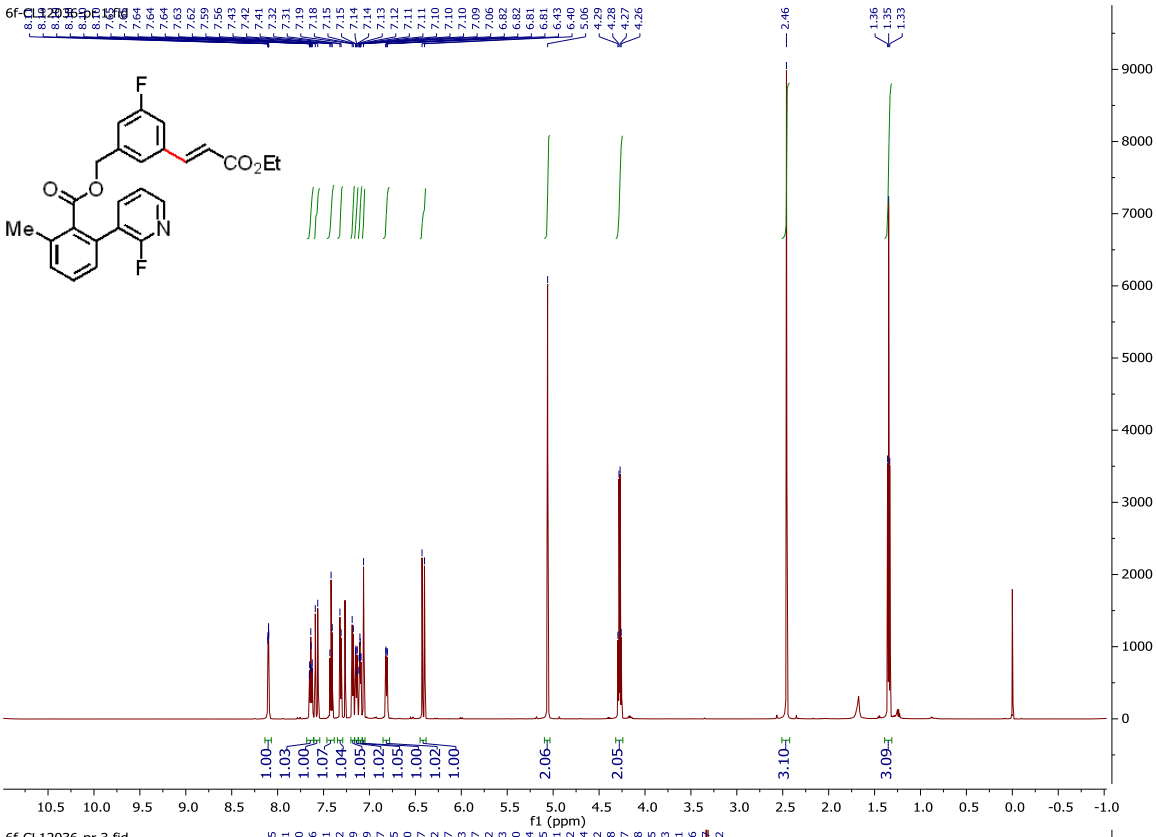

Me
CO2Et
O
O
Me
N
F
f1 (ppm)


6b-CL12044-pr.3.fid
Me
CO2Et
O
O
Me
N
F
f1 (ppm)


6c-CL12030-pr.1.fid
Cl
CO2Et
O
O
Me
N
F
1.00
1.04
1.04
2.04
3.25
1.11
1.06
1.00
2.15
2.09
3.14
3.06
f1 (ppm)


6c-CL12030-pr.3.fid
Cl
CO2Et
O
O
Me
N
F
f1 (ppm)


6e-CL12041-pr.1.fid
OMe
CO2Et
O
O
Me
N
F
f1 (ppm)
6e-CL12041-pr.3.fid
OMe
CO2Et
O
O
Me
N
F
f1 (ppm)


F
CO2Et
O
O
Me
N
F
2.46
1.36
1.35
1.33
1.00
1.03
1.00
1.07
1.04
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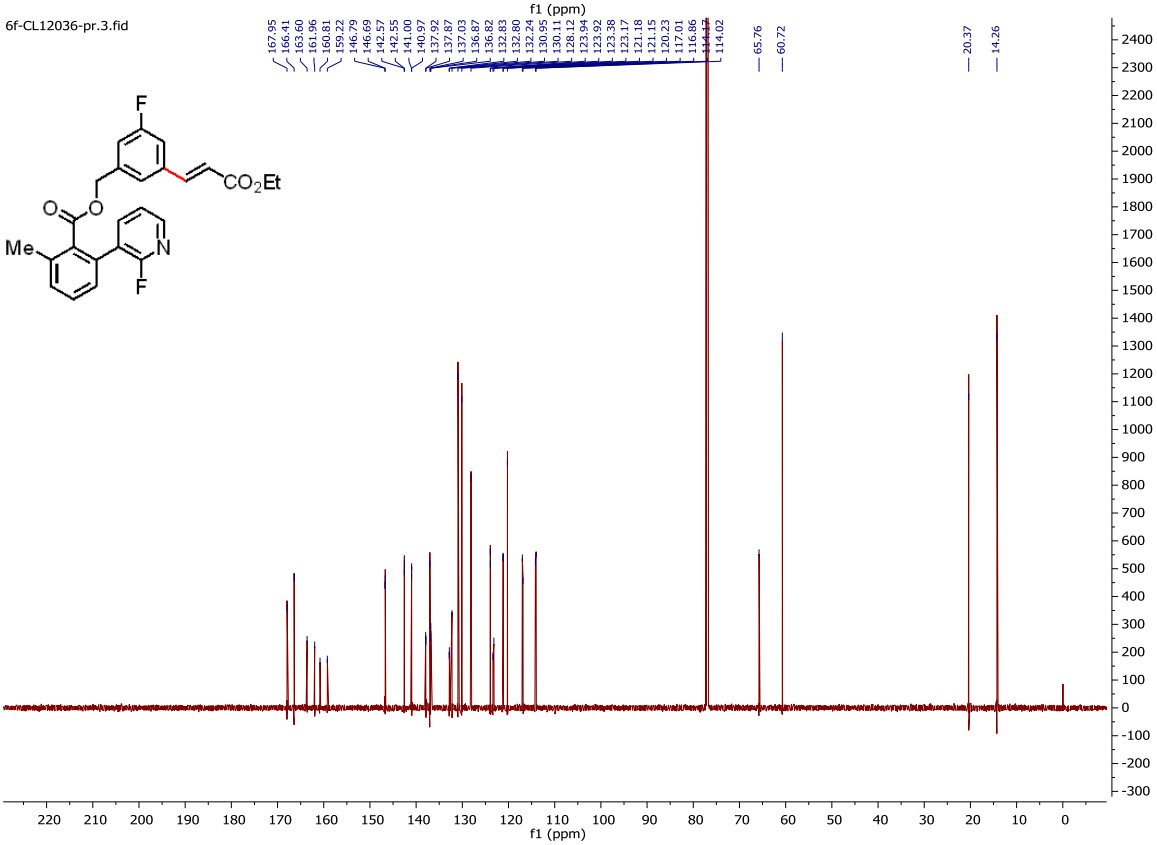
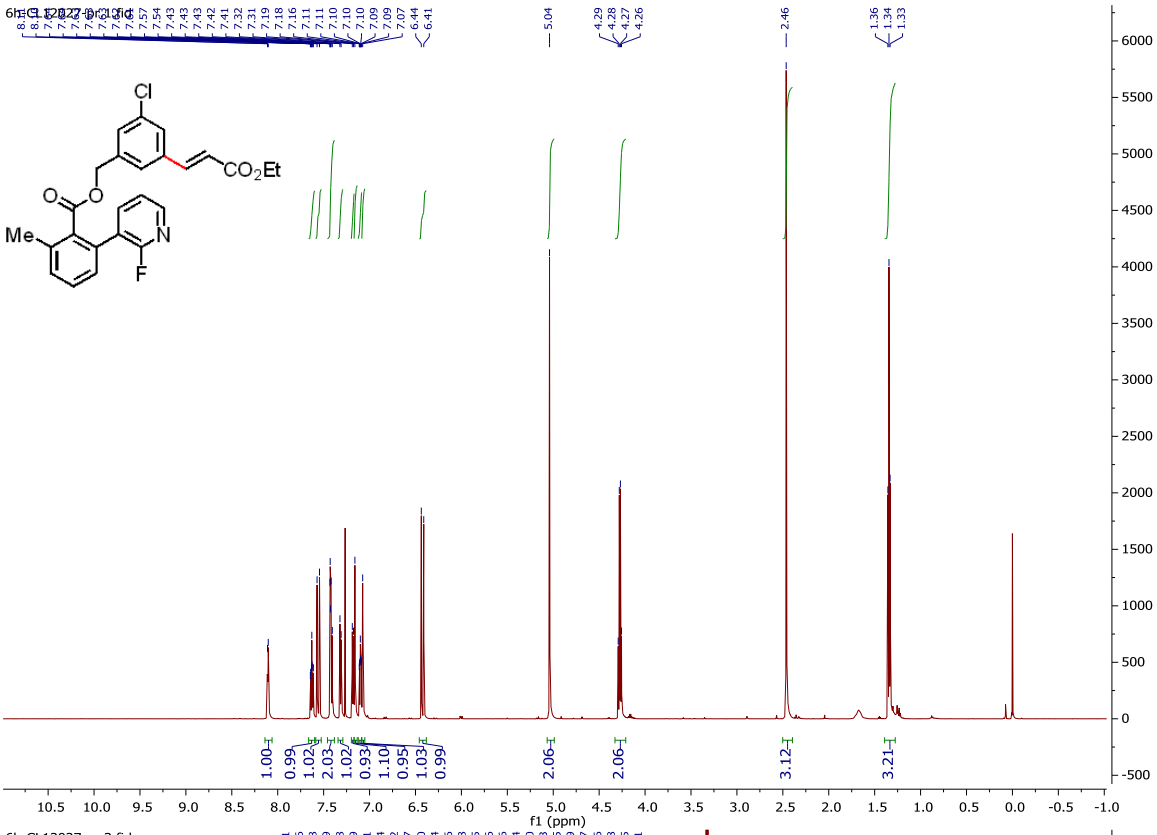
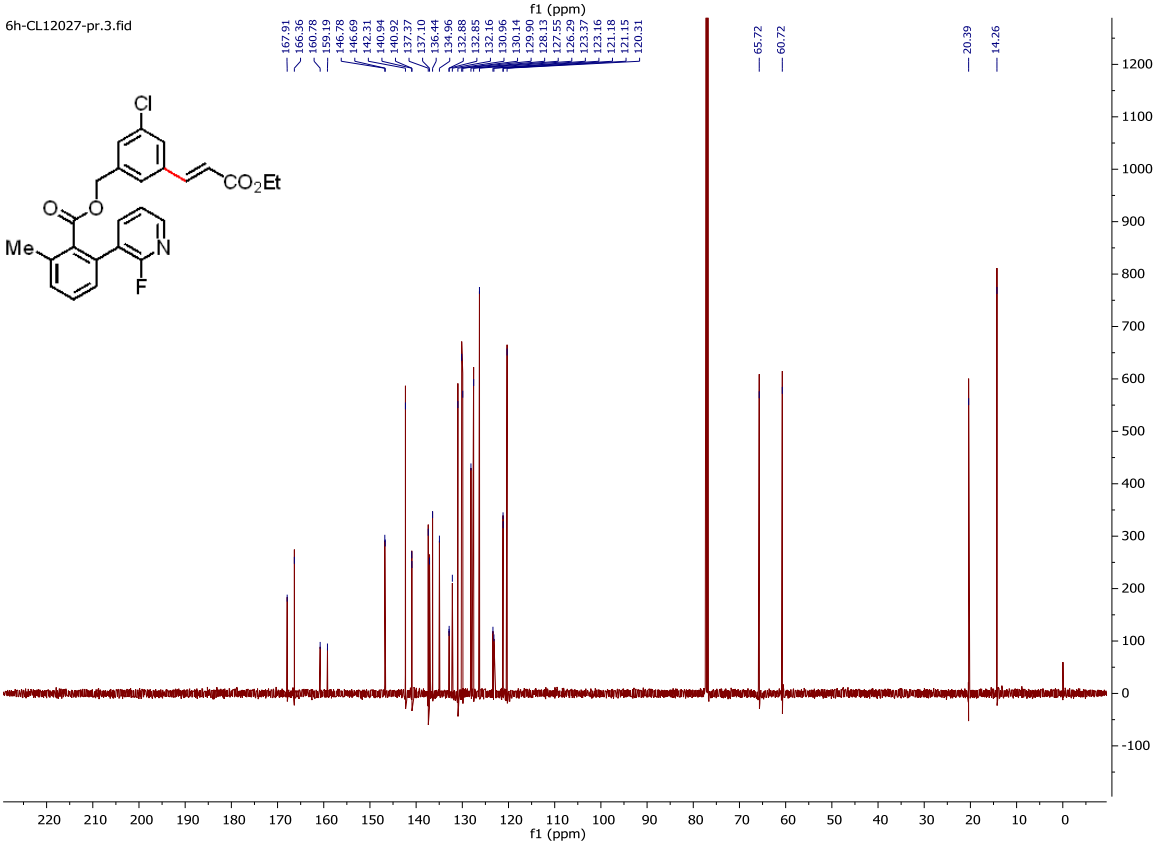
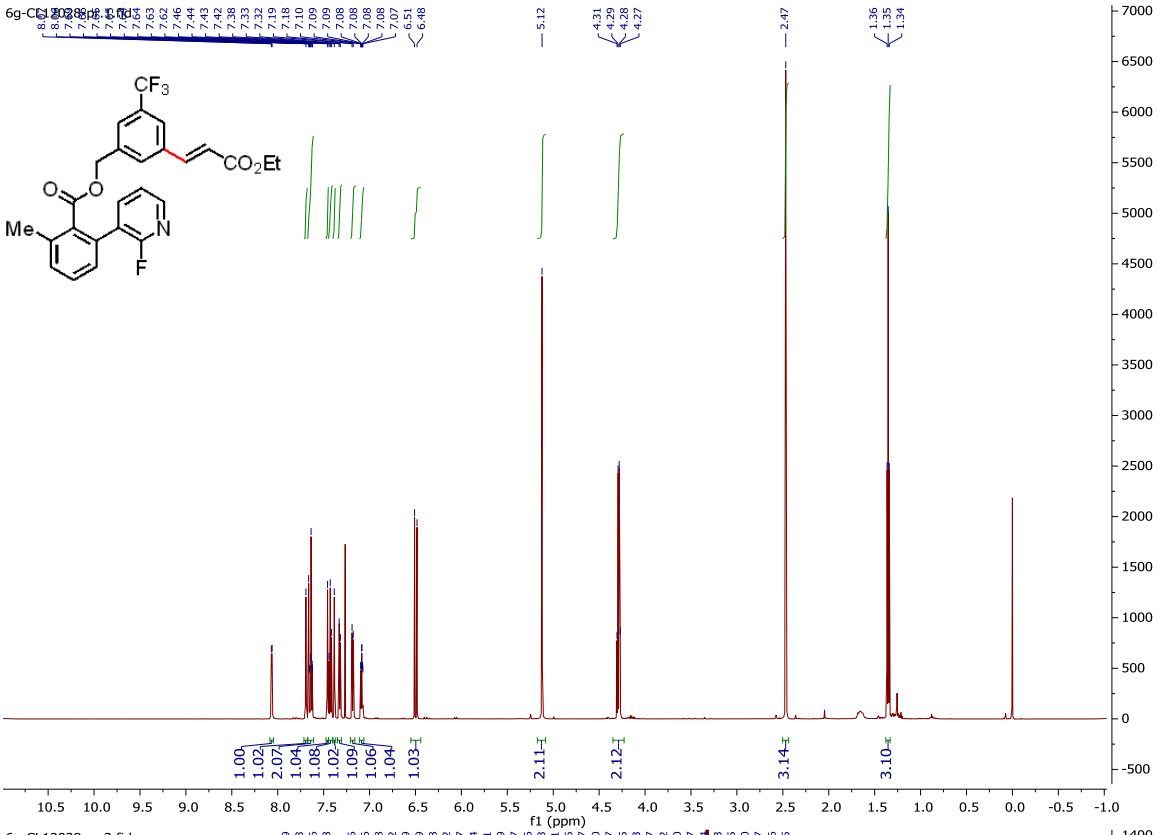
2.06
2.05
3.10
3.09
f1 (ppm)


6f-CL12036-pr.3.fid
F
CO2Et
O
O
Me
N
F
167.95
166.41
163.60
161.96
160.81
159.22
146.79
146.69
142.57
142.55
141.00
140.97
137.92
137.87
137.03
136.87
136.82
132.83
132.80
132.24
130.95
130.11
128.12
123.94
123.92
123.38
123.17
121.18
121.15
120.23
117.01
116.86
114.17
114.02
65.76
60.72
20.37
14.26
f1 (ppm)


6h-CL12027-pr.1.fid
Cl
CO2Et
O
O
Me
N
F
5.04
4.29
4.28
4.27
4.26
2.46
1.36
1.34
1.33
1.00
0.99
1.02
2.03
1.02
0.93
1.10
0.95
1.03
0.99
2.06
2.06
3.12
3.21
f1 (ppm)


6h-CL12027-pr.3.fid
Cl
CO2Et
O
O
Me
N
F
167.91
166.36
160.78
159.19
146.78
146.69
142.31
140.94
140.92
137.37
137.10
136.44
134.96
132.88
132.85
132.16
130.96
130.14
129.90
128.13
127.55
126.29
123.37
123.16
121.18
121.15
120.31
65.72
60.72
20.39
14.26
f1 (ppm)


6g-CL12028-pr.1.fid
CF3
CO2Et
O
O
Me
N
F
5.12
4.31
4.29
4.28
4.27
2.47
1.36
1.35
1.34
6.51
6.48
1.00
1.02
2.07
1.04
1.08
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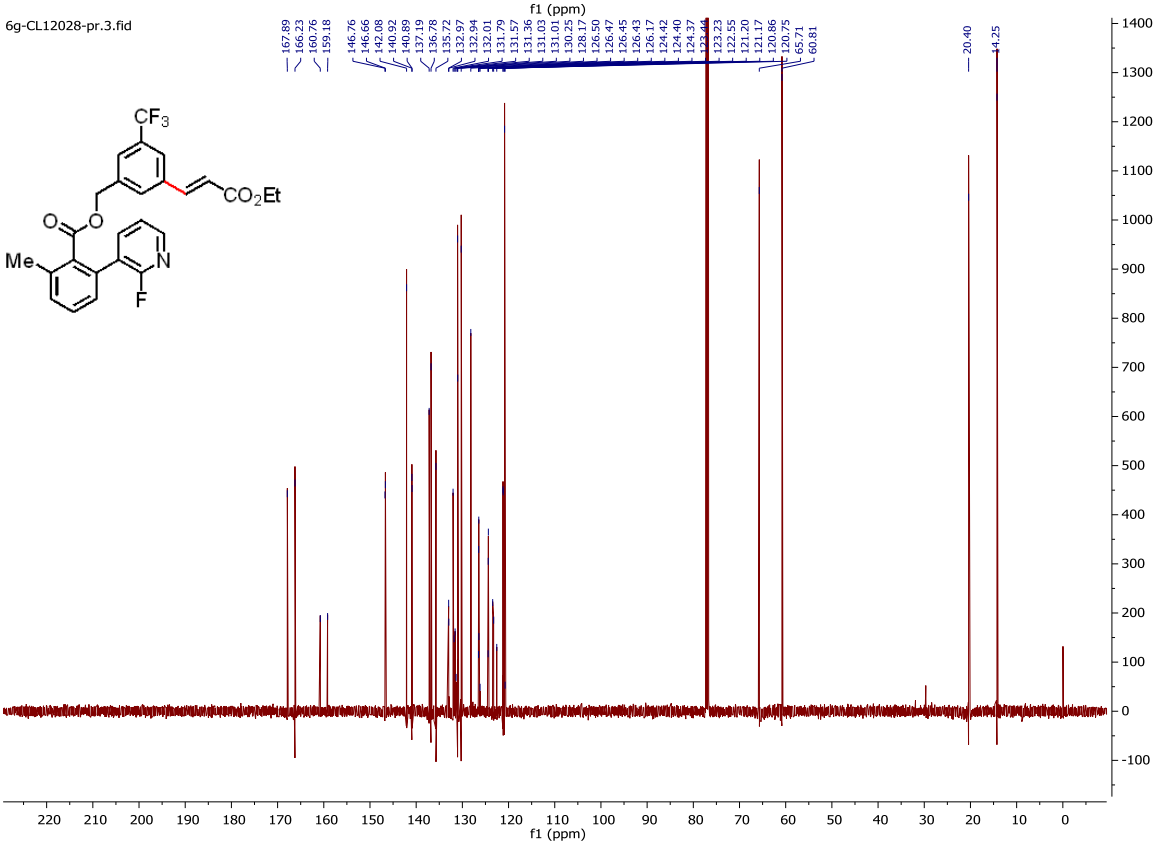
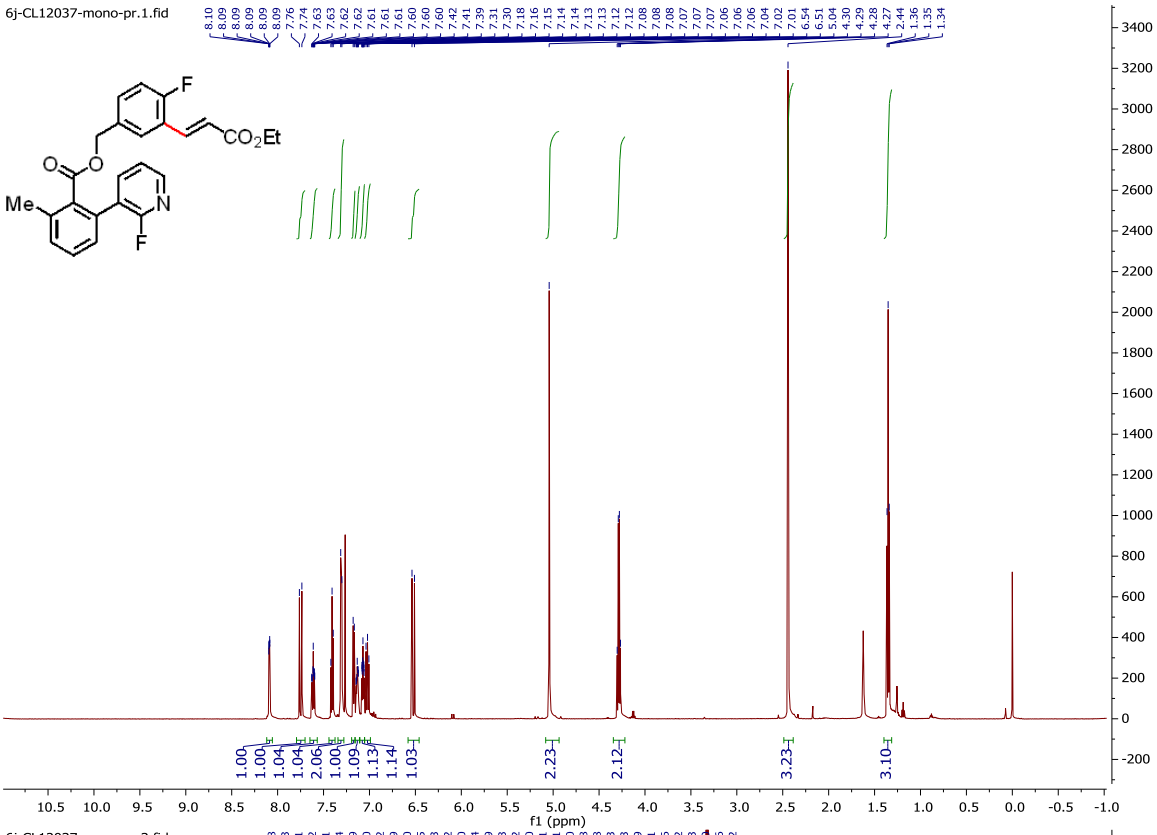
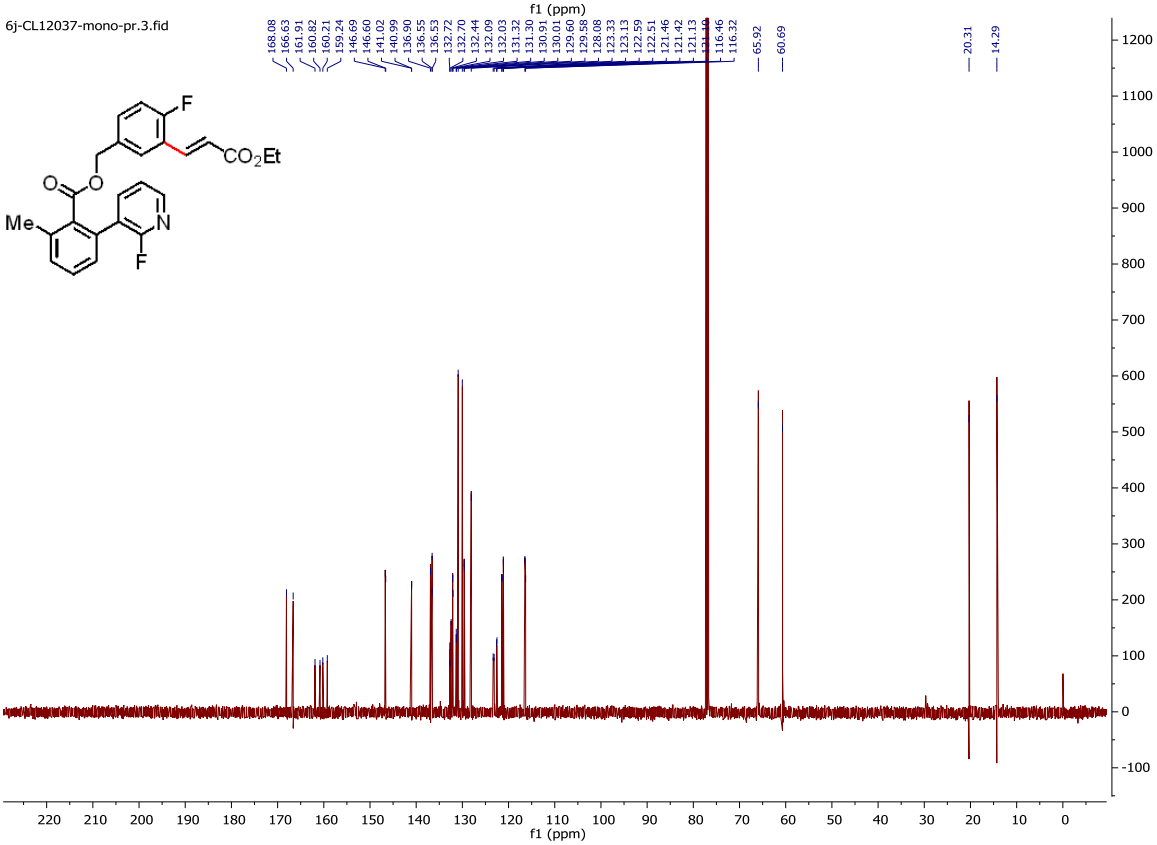
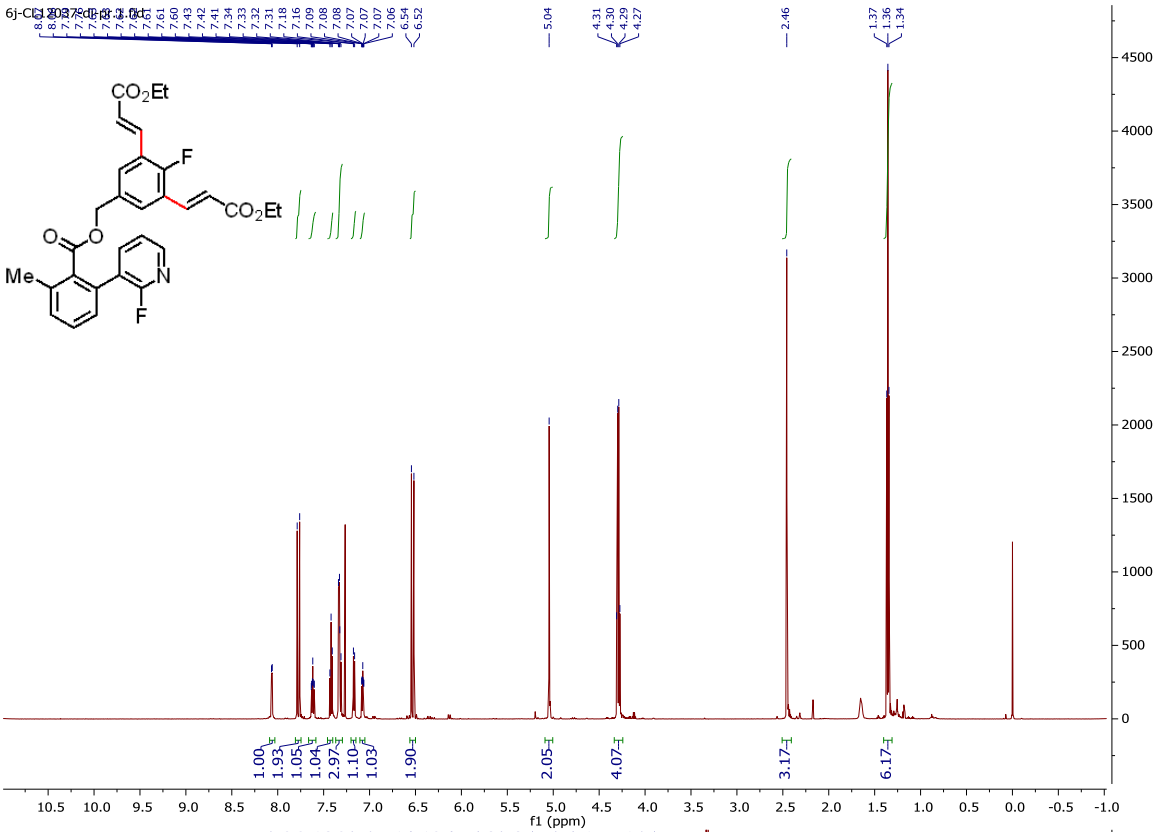
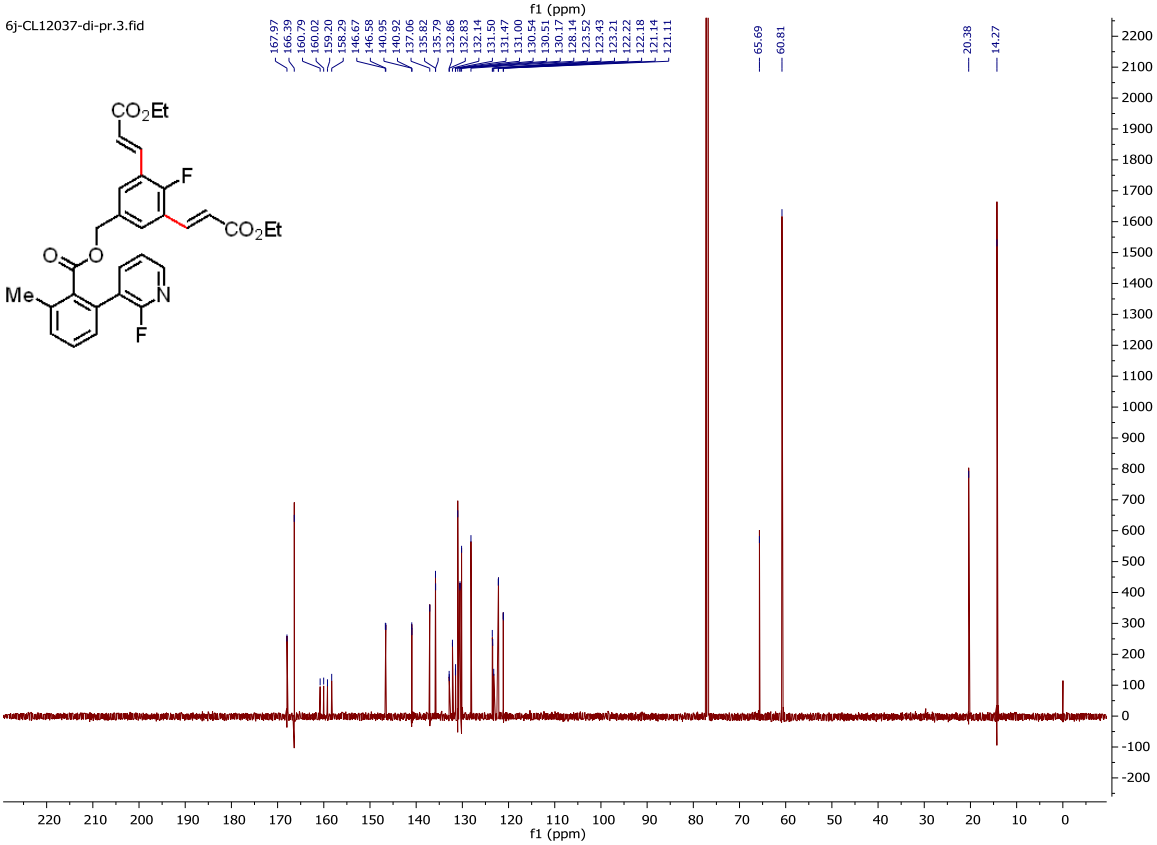
1.09
1.06
1.04
1.03
2.11
2.12
3.14
3.10
f1 (ppm)

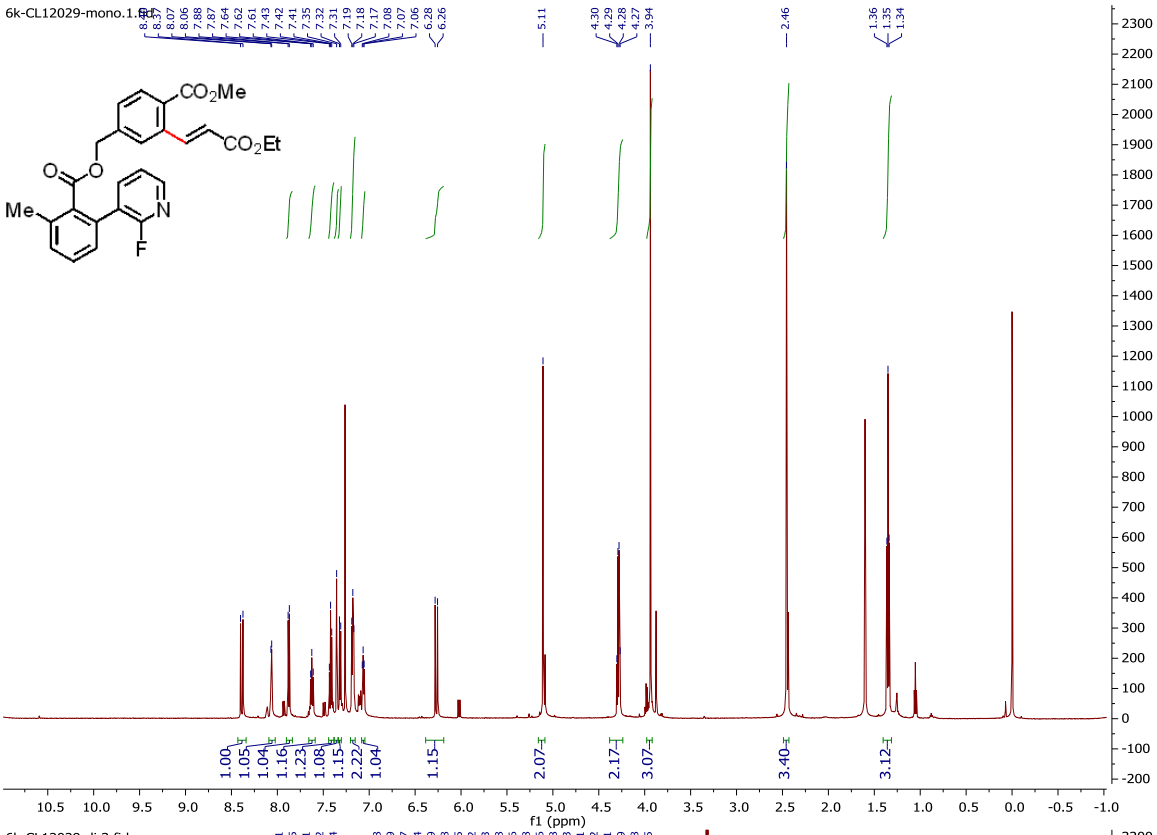

6g-CL12028-pr.3.fid
CF3
CO2Et
O
O
Me
N
F
167.89
166.23
160.76
159.18
146.76
146.66
142.08
140.92
140.89
137.19
136.78
135.72
132.97
132.94
132.01
131.79
131.57
131.36
131.03
131.01
130.25
128.17
126.50
126.47
126.45
126.43
126.17
124.42
124.40
124.37
123.44
123.23
122.55
121.20
121.17
120.86
120.75
65.71
60.81
20.40
14.25
f1 (ppm)

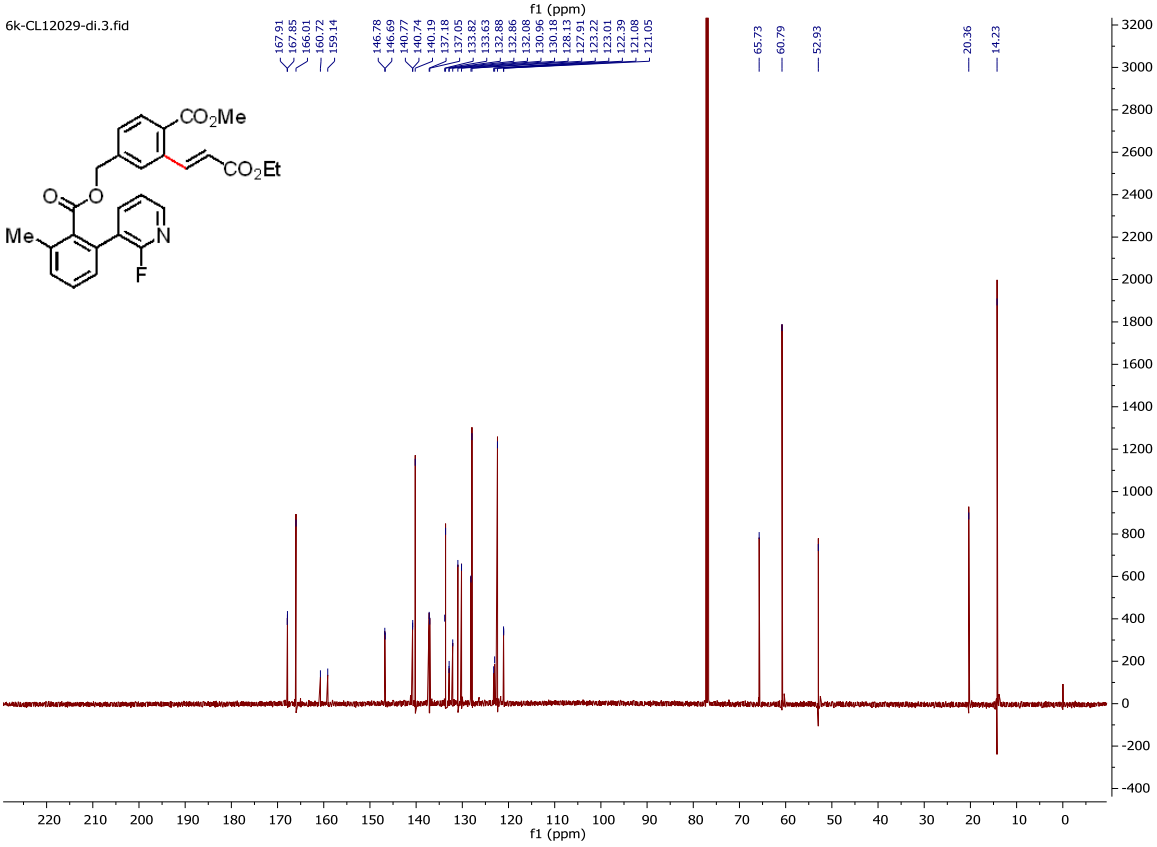

6j-CL12037-mono-pr.1.fid
F
CO2Et
O
O
Me
N
F
f1 (ppm)

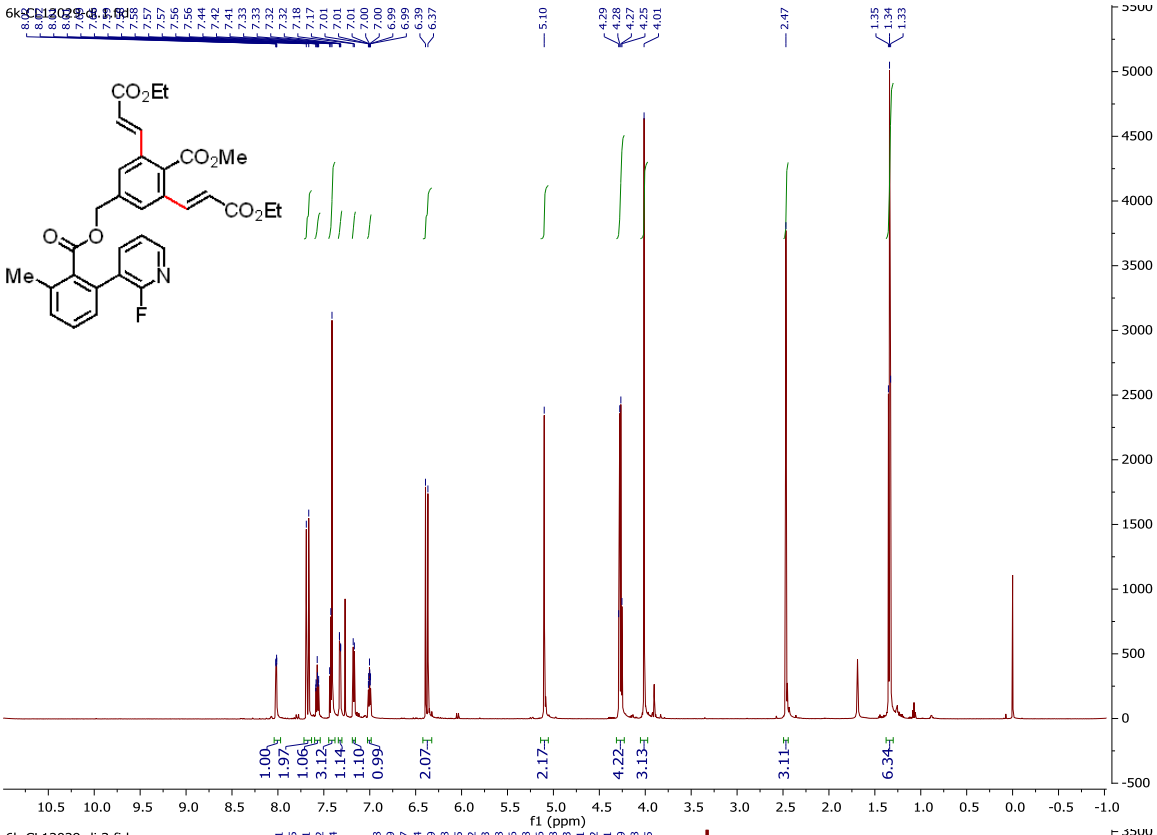

6j-CL12037-mono-pr.3.fid
F
CO2Et
O
O
Me
N
F
f1 (ppm)

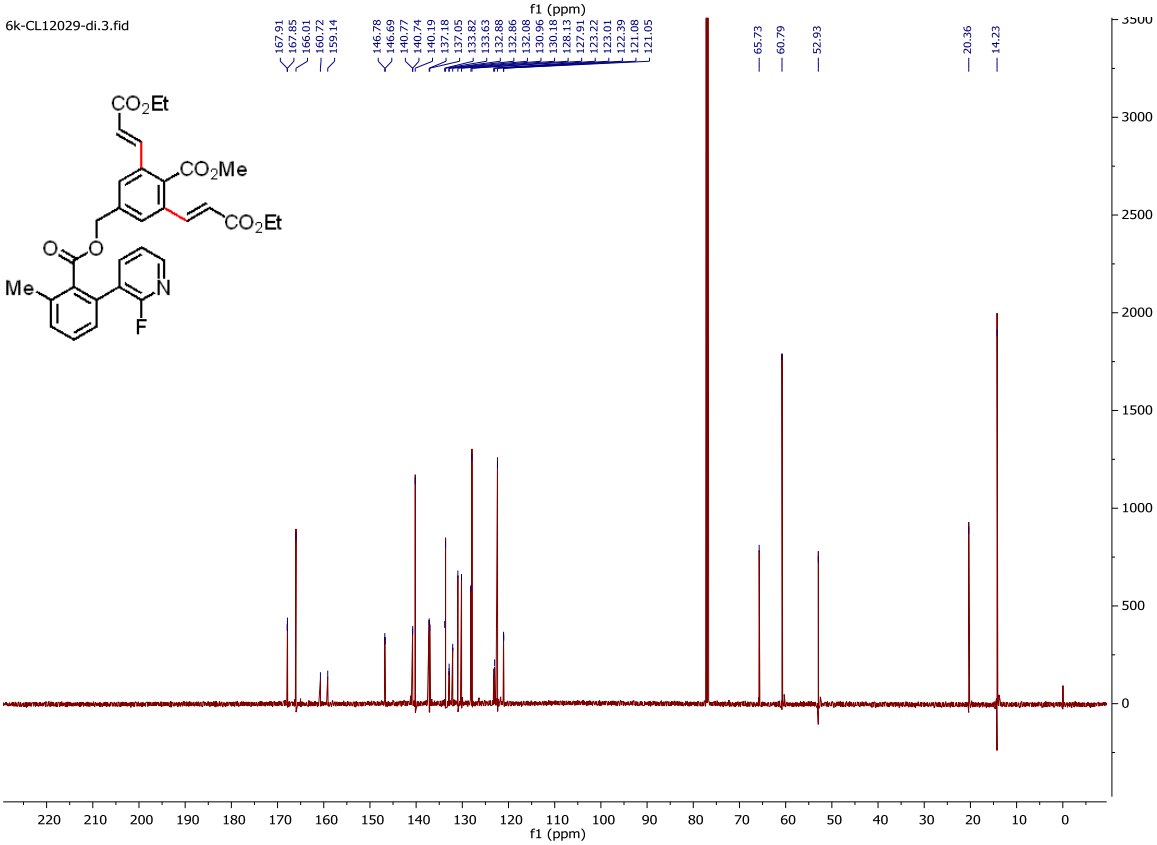

6j-CL12037-di-pr.3.fid
CO2Et
F
CO2Et
O
O
Me
N
F
1.00
1.93
1.05
1.04
2.97
1.10
1.03
1.90
2.05
4.07
3.17
6.17
f1 (ppm)

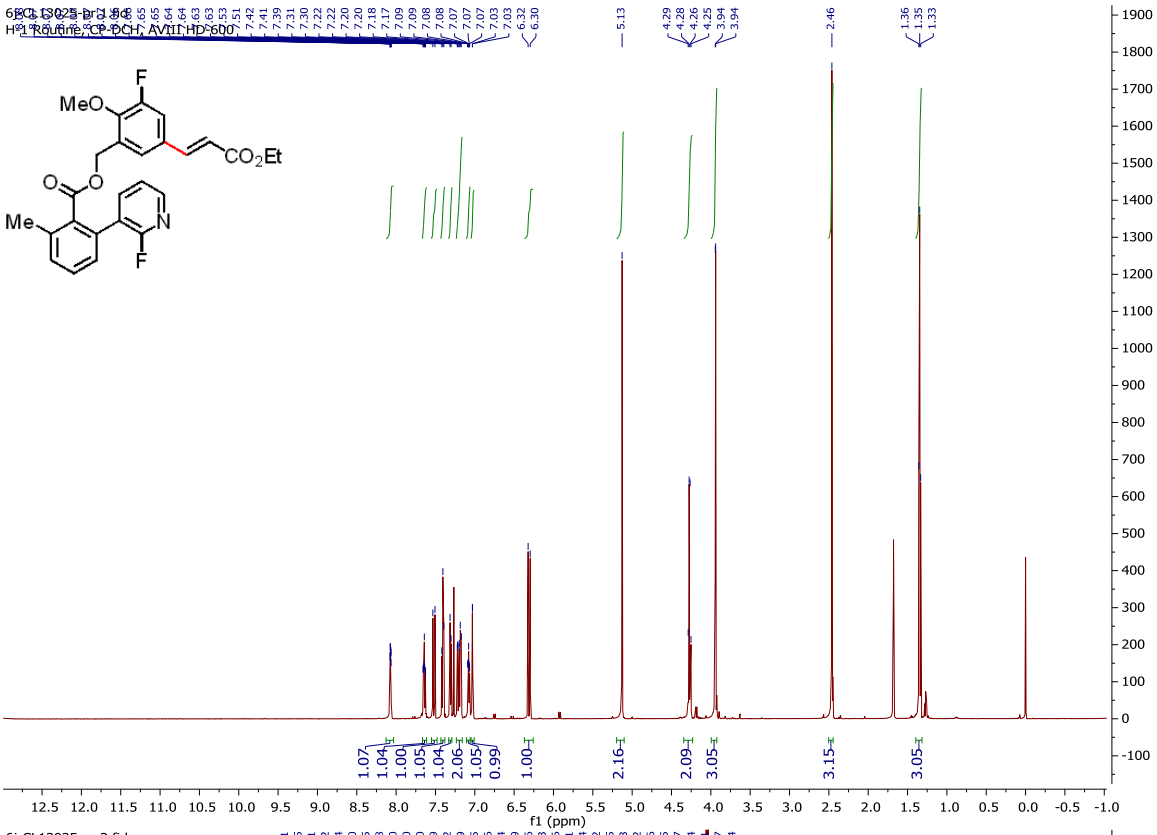

6j-CL12037-di-pr.3.fid
CO2Et
F
CO2Et
O
O
Me
N
F
f1 (ppm)

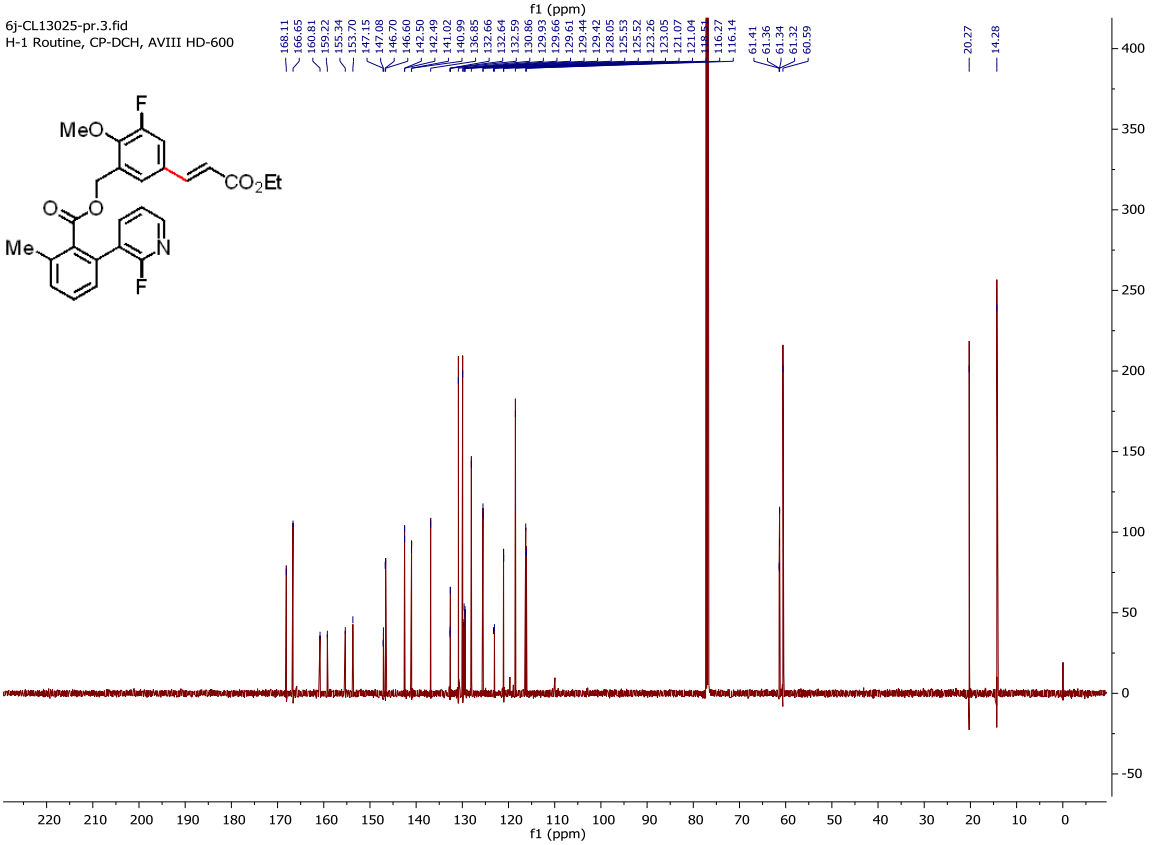

6k-CL12029-mono.1.fid
CO2Me
CO2Et
O
O
Me
N
F
f1 (ppm)

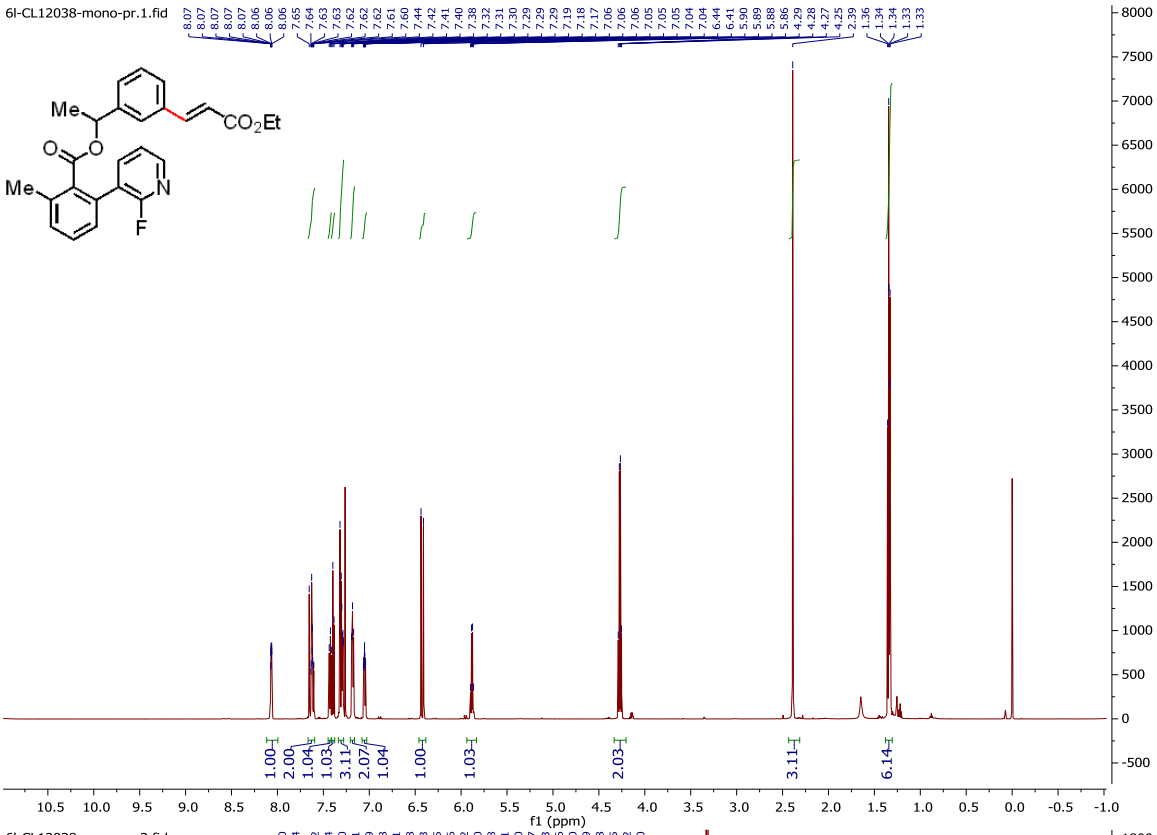

6k-CL12029-di.3.fid
CO2Me
CO2Et
O
O
Me
N
F
f1 (ppm)

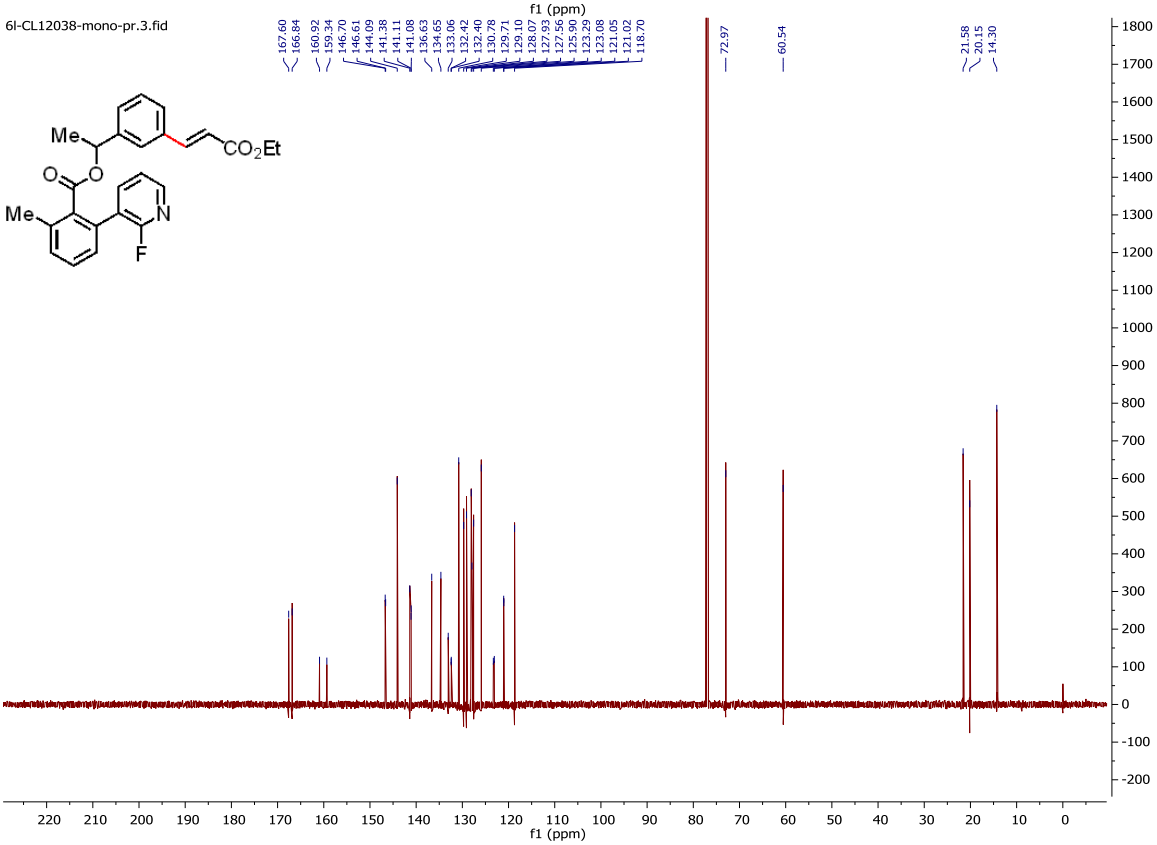

6k-CL12029-di.1.fid
CO2Et
CO2Me
CO2Et
O
O
Me
N
F
5.10
4.29
4.28
4.27
4.25
4.01
2.47
1.35
1.34
1.33
1.00
1.97
1.06
3.12
1.14
1.10
0.99
2.07
2.17
4.22
3.13
3.11
6.34
f1 (ppm)

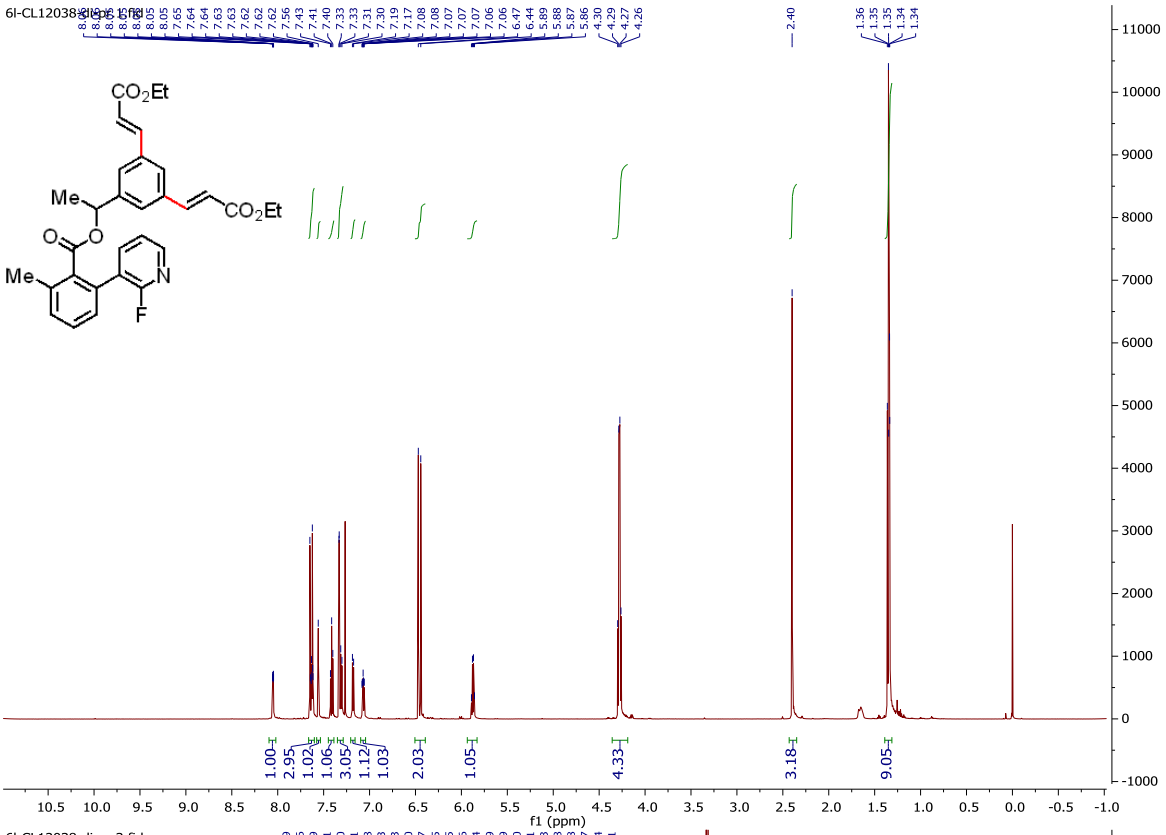

6k-CL12029-di.3.fid
CO2Et
CO2Me
CO2Et
O
O
Me
N
F
167.91
167.85
166.01
160.72
159.14
146.78
146.69
140.77
140.74
140.19
137.18
137.05
133.82
133.63
132.88
132.86
132.08
130.98
130.18
128.13
127.91
123.22
123.01
122.39
121.08
121.05
65.73
60.79
52.93
20.36
14.23
f1 (ppm)

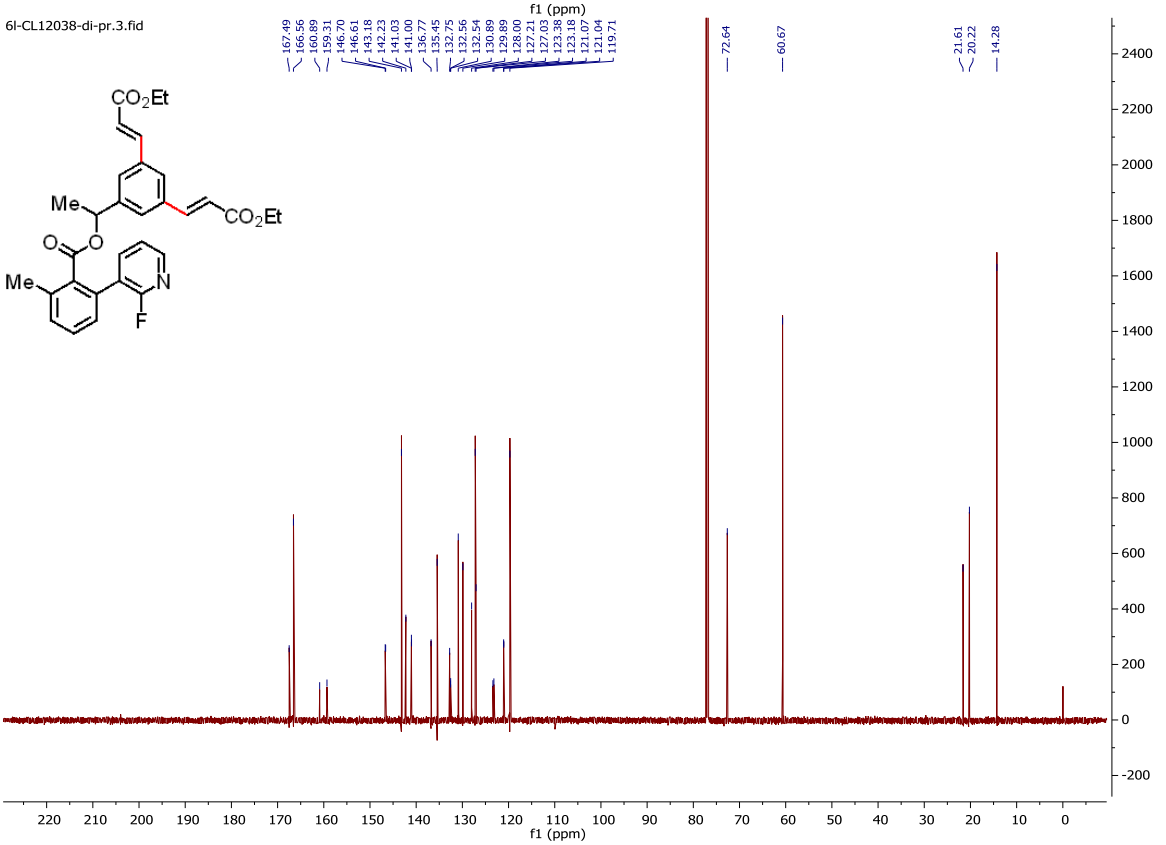

6j-CL13025-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO
F
CO2Et
O
O
Me
N
F
f1 (ppm)

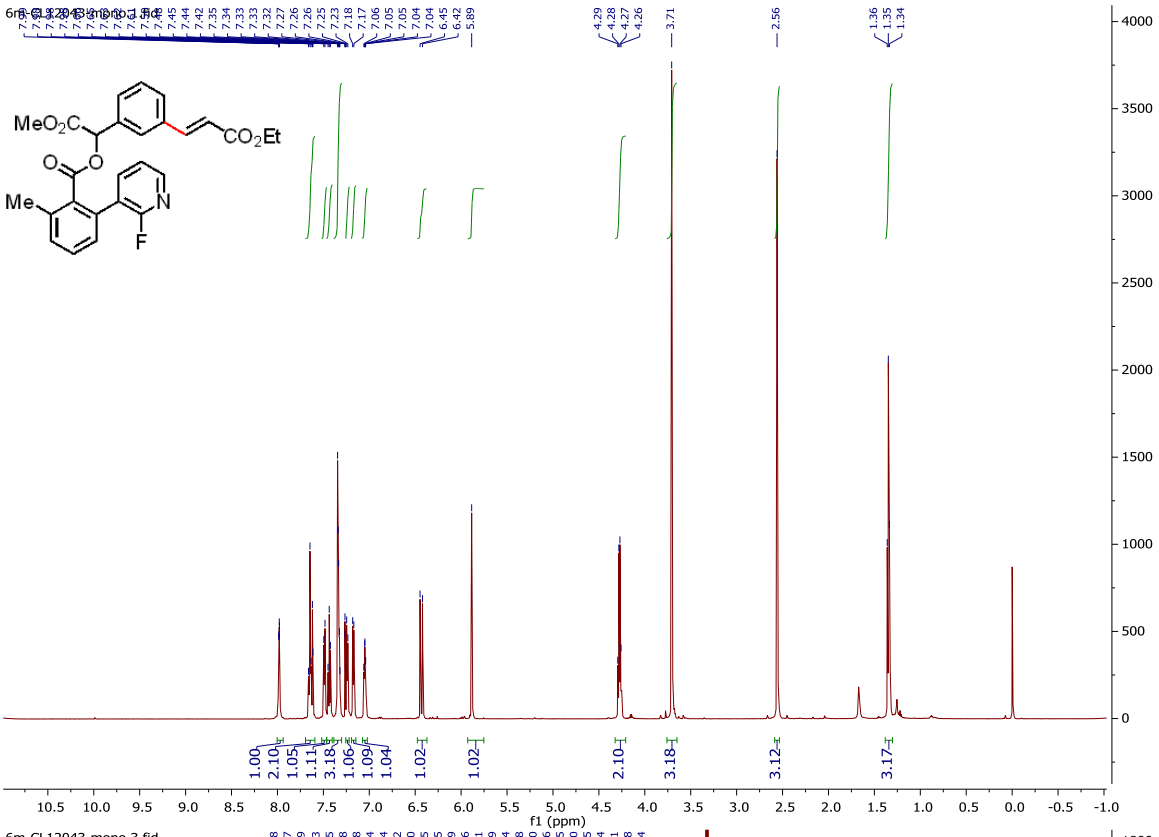

6j-CL13025-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO
F
CO2Et
O
O
Me
N
F
f1 (ppm)

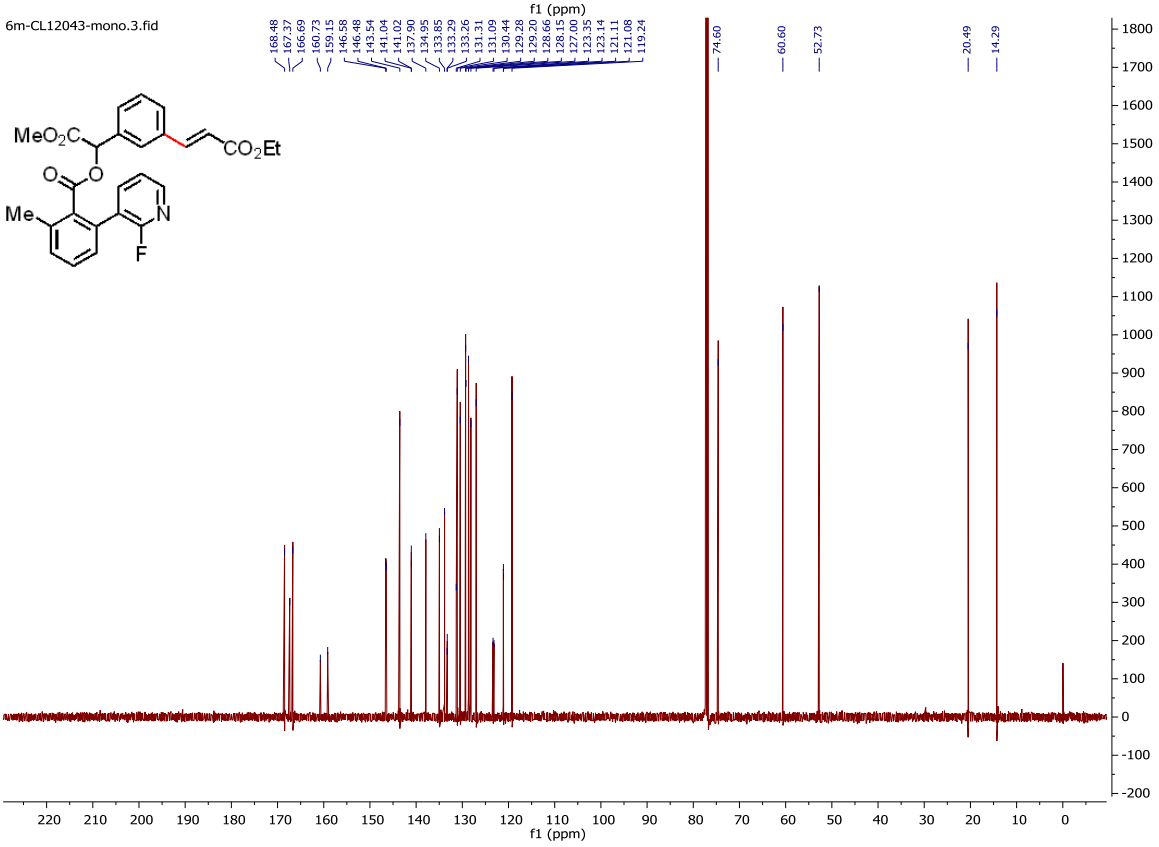

6l-CL12038-mono-pr.1.fid
Me
O
O
Me
N
F
CO2Et
1.00
2.00
1.04
1.03
3.11
2.07
1.04
1.00
1.03
2.03
3.11
6.14
f1 (ppm)

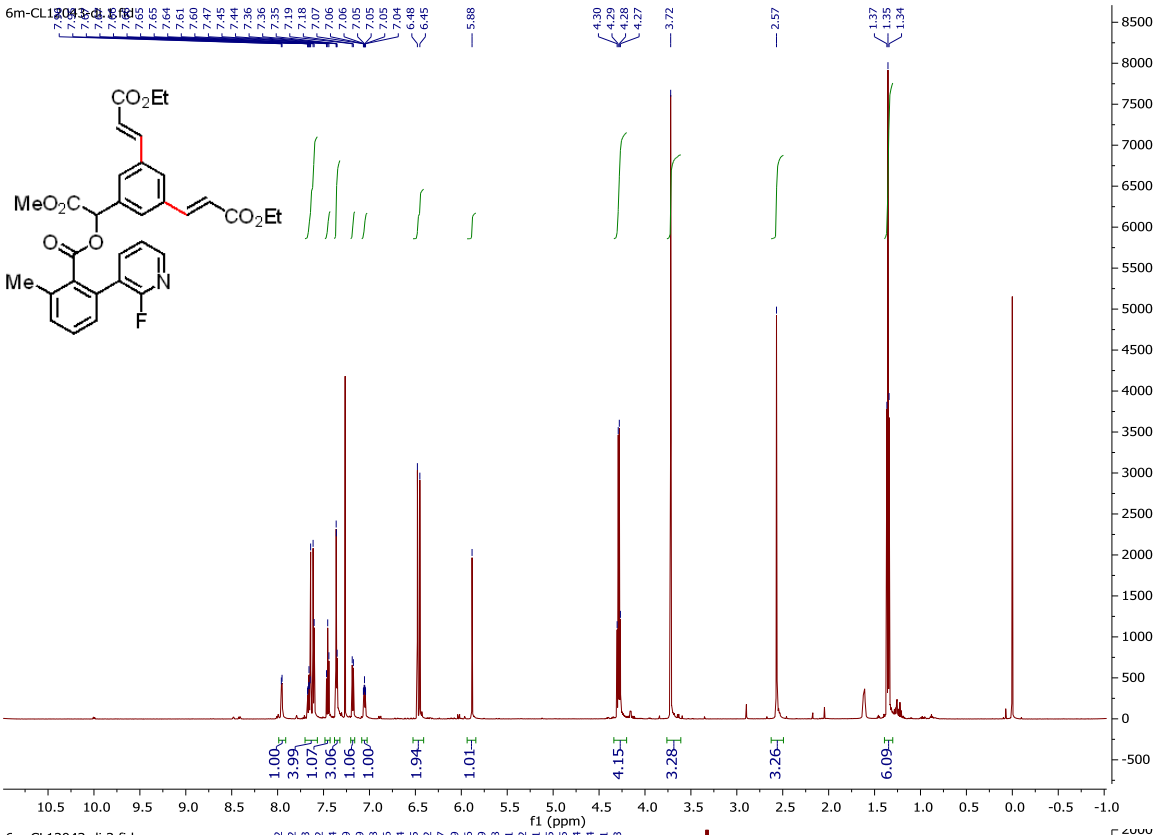

6l-CL12038-mono-pr.3.fid
Me
O
O
Me
N
F
CO2Et
167.60
166.84
160.92
159.34
146.70
146.61
144.09
141.38
141.11
141.08
136.63
134.65
133.06
132.42
132.40
130.78
129.71
129.10
128.07
127.93
127.56
125.90
123.29
123.08
121.05
121.02
118.70
72.97
60.54
21.58
20.15
14.30
f1 (ppm)

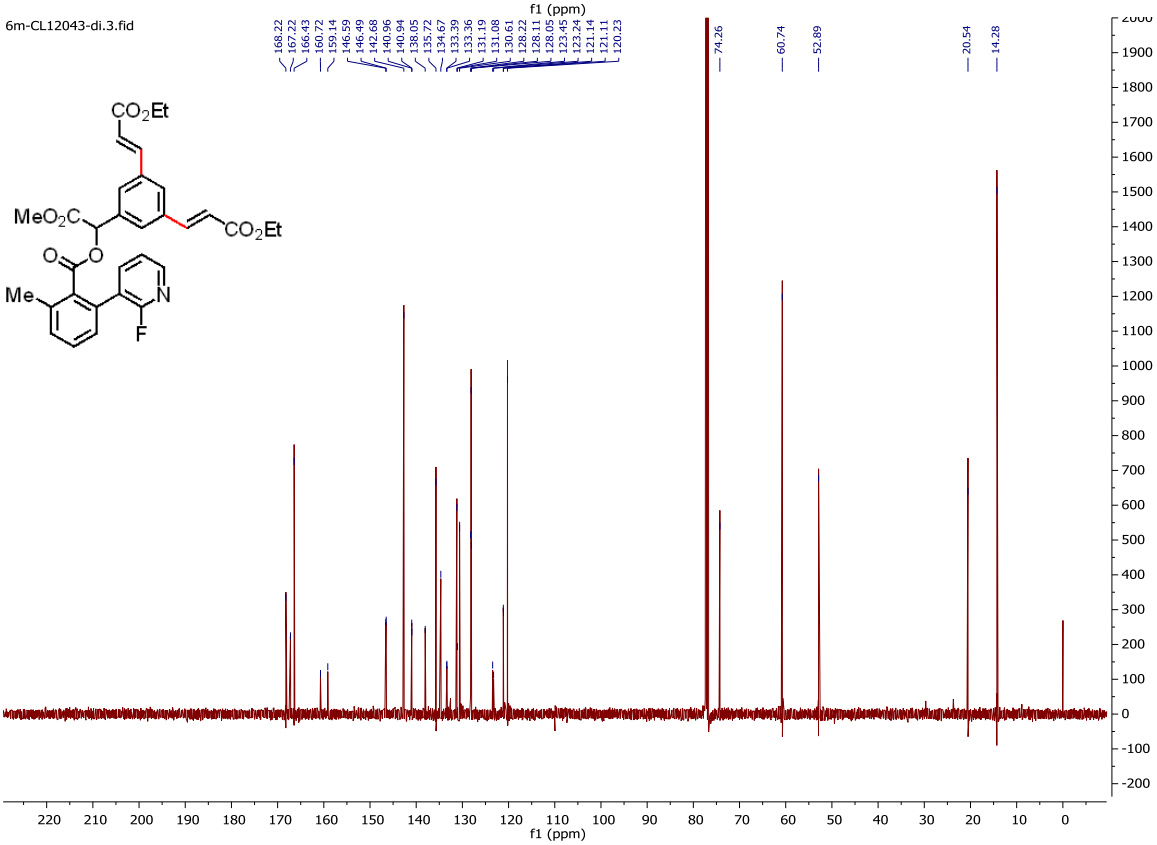

6l-CL12038-di-pr.1.fid
CO2Et
Me
O
O
CO2Et
Me
N
F
2.40
1.36
1.35
1.35
1.34
1.34
1.00
2.95
1.02
1.06
3.05
1.12
1.03
2.03
1.05
4.33
3.18
9.05
f1 (ppm)

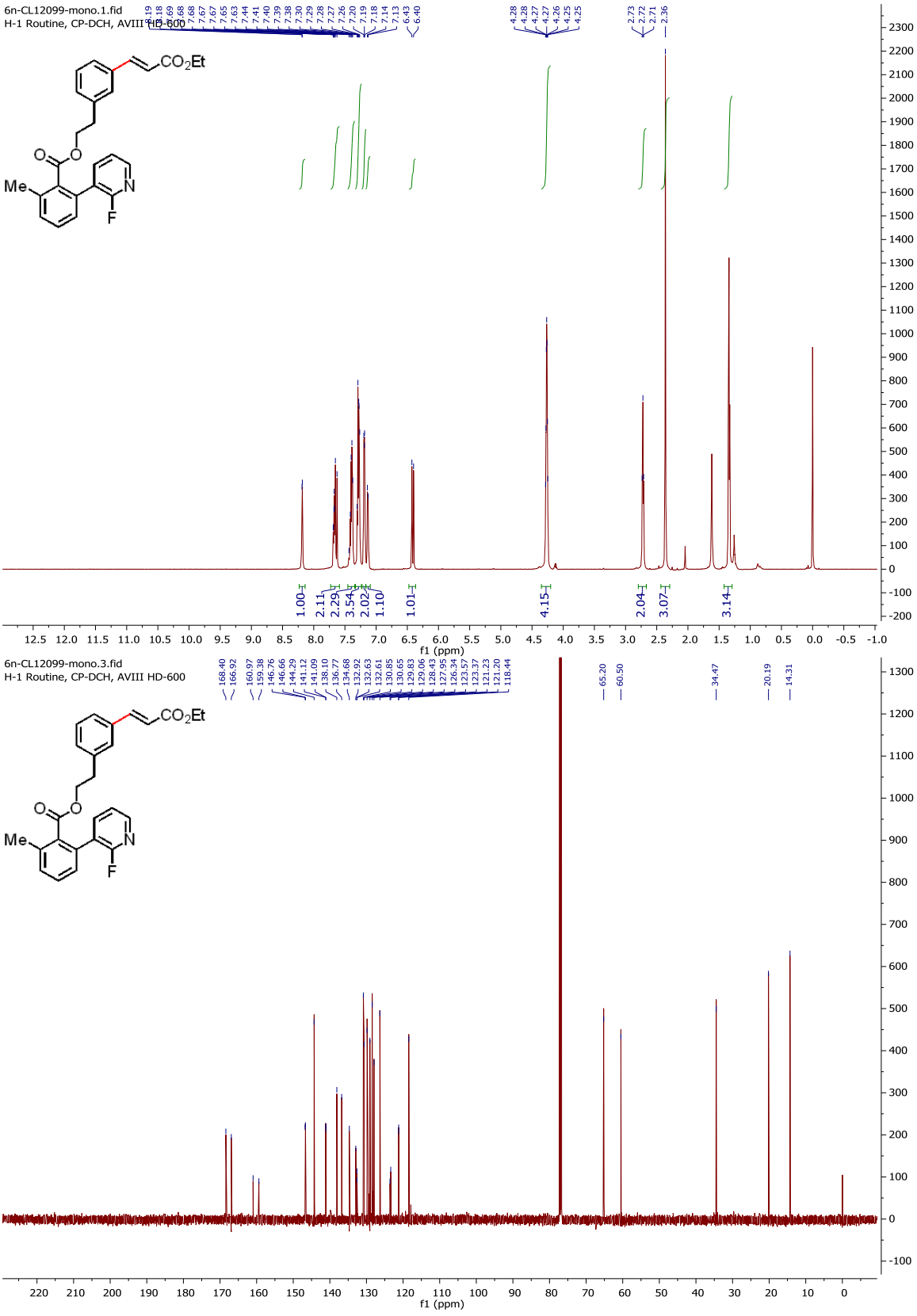

6l-CL12038-di-pr.3.fid
CO2Et
Me
O
O
CO2Et
Me
N
F
167.49
166.56
160.89
159.31
146.70
146.61
143.18
142.23
141.03
141.00
136.77
135.45
132.75
132.56
132.54
130.89
129.89
128.00
127.21
127.03
123.38
123.18
121.07
121.04
119.71
72.64
60.67
21.61
20.22
14.28
f1 (ppm)

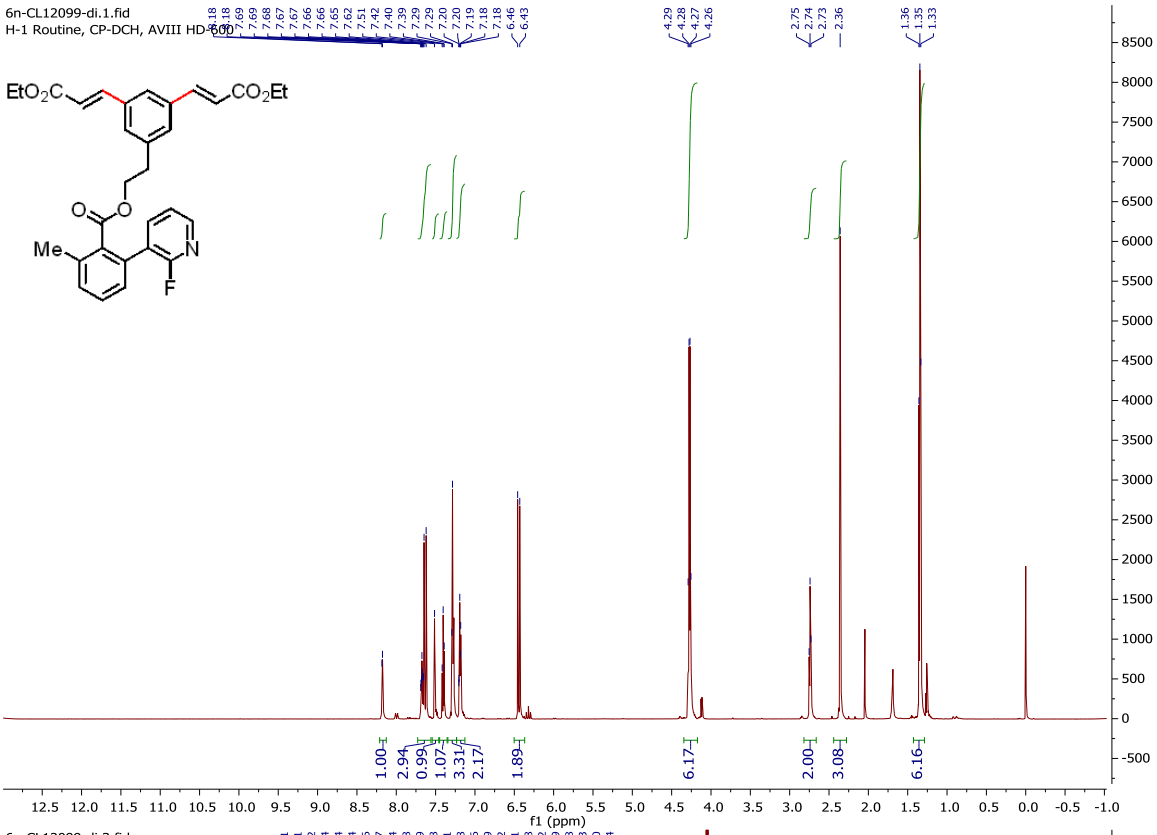

MeO2C
CO2Et
O
O
Me
N
F
f1 (ppm)

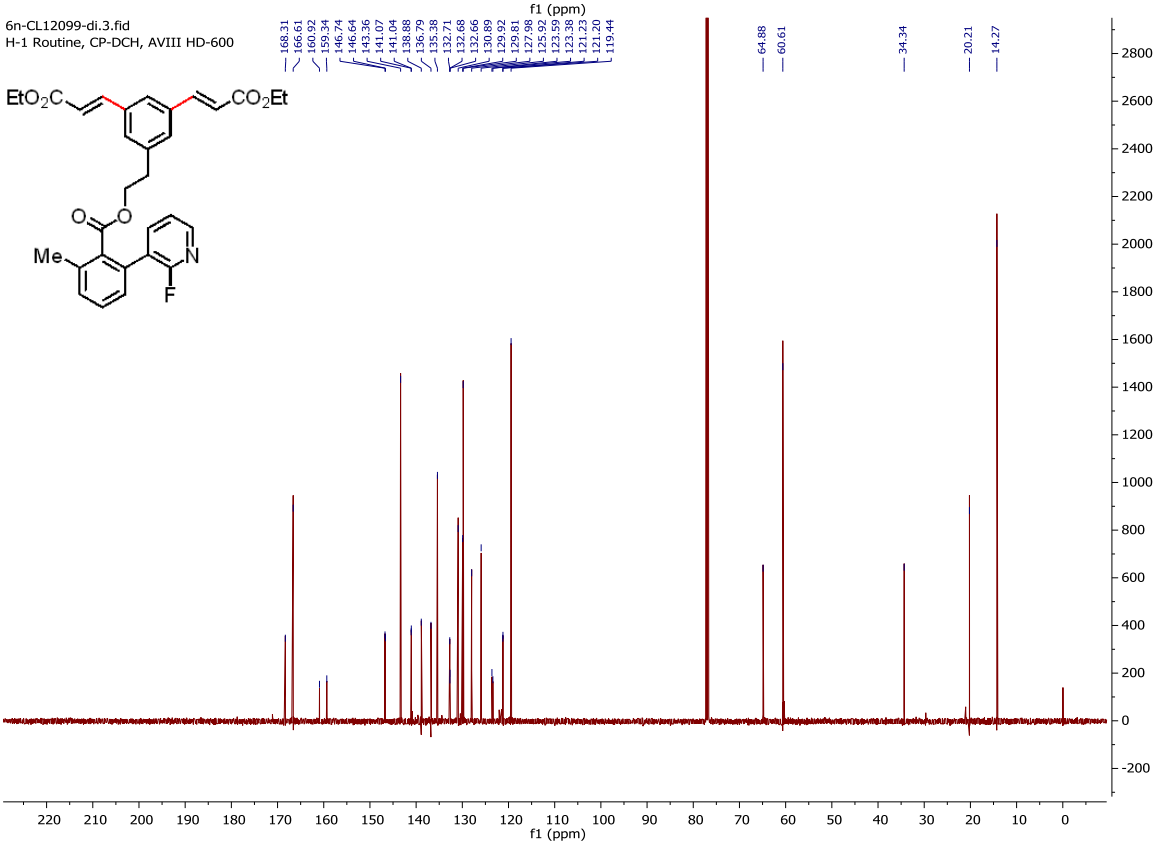

6m-CL12043-mono.3.fid
MeO2C
CO2Et
O
O
Me
N
F
f1 (ppm)

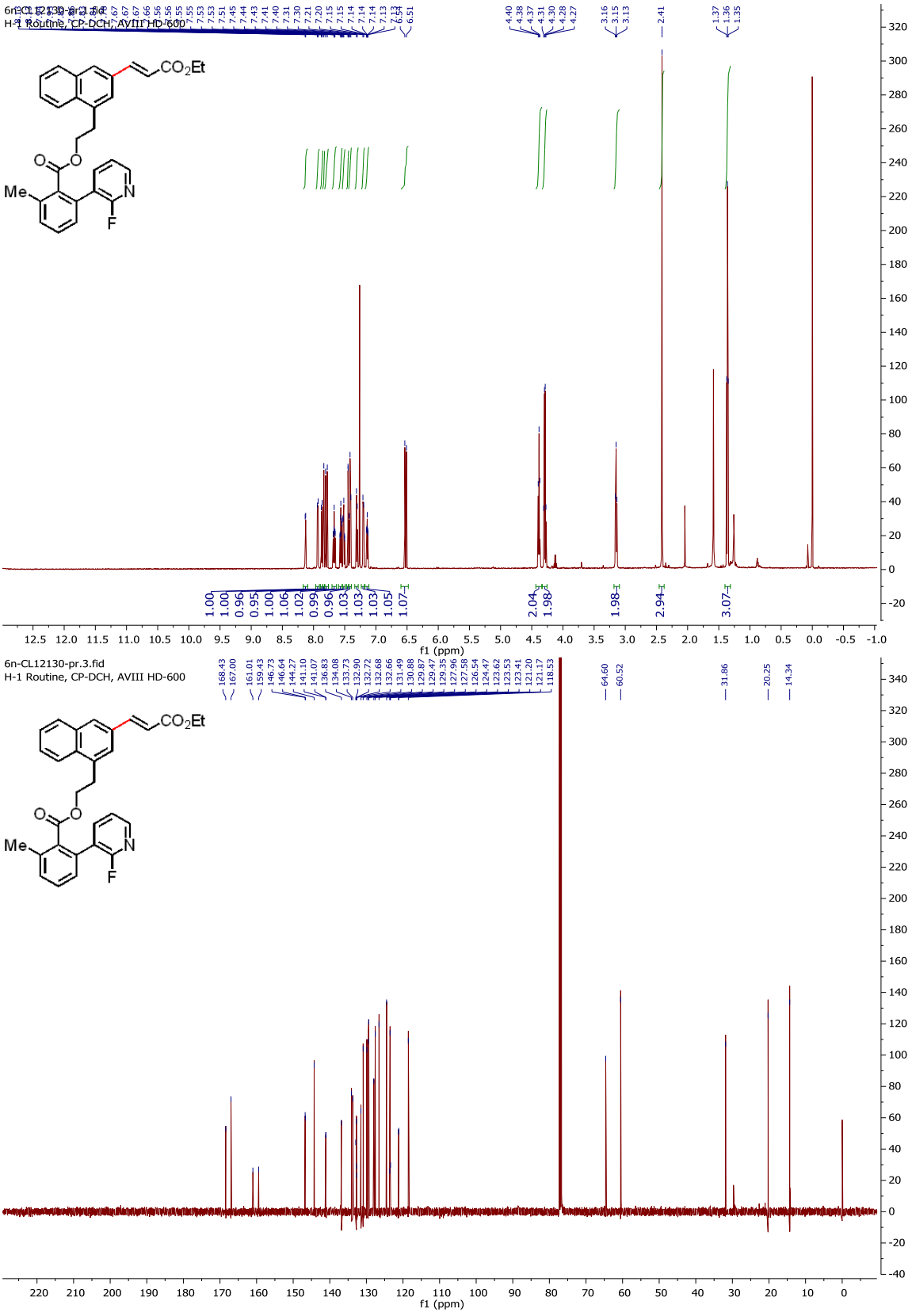

6m-CL12043-di.3.fid
CO2Et
MeO2C
CO2Et
O
O
Me
N
F
f1 (ppm)

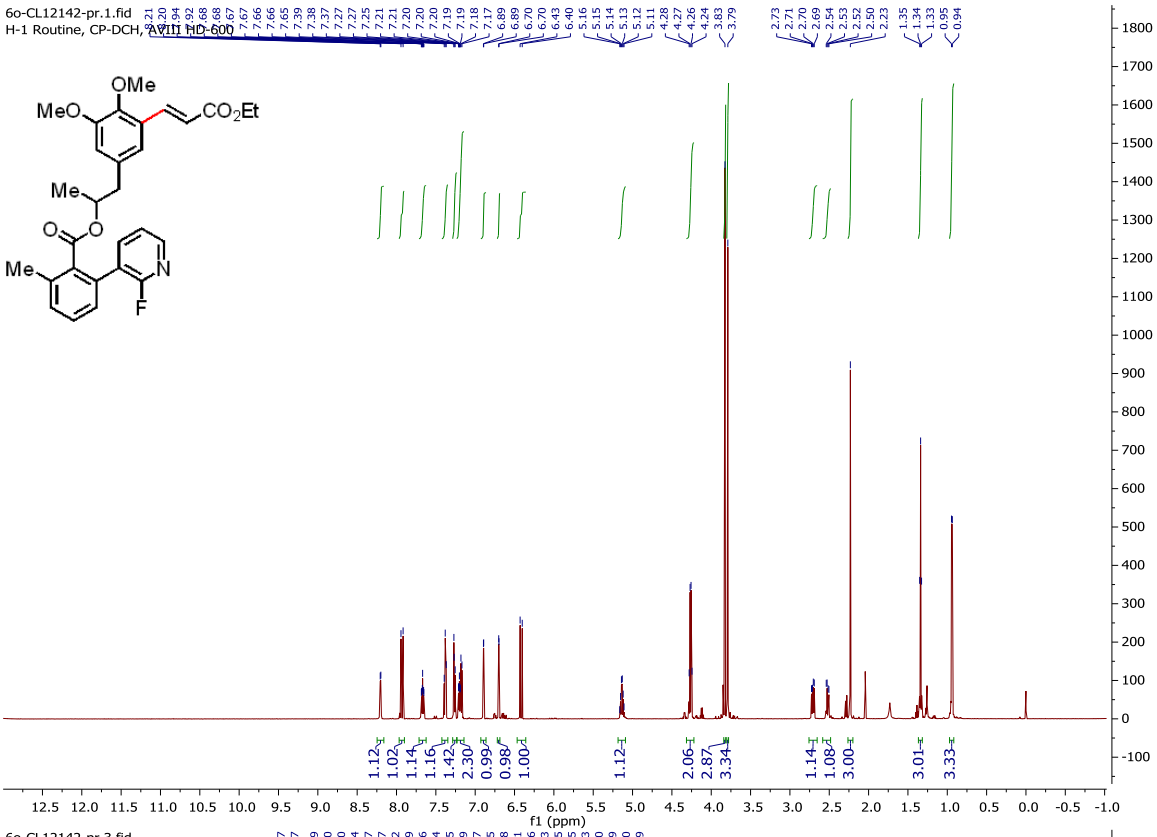

6m-CL12043-di.3.fid
CO2Et
MeO2C
CO2Et
O
O
Me
N
F
f1 (ppm)

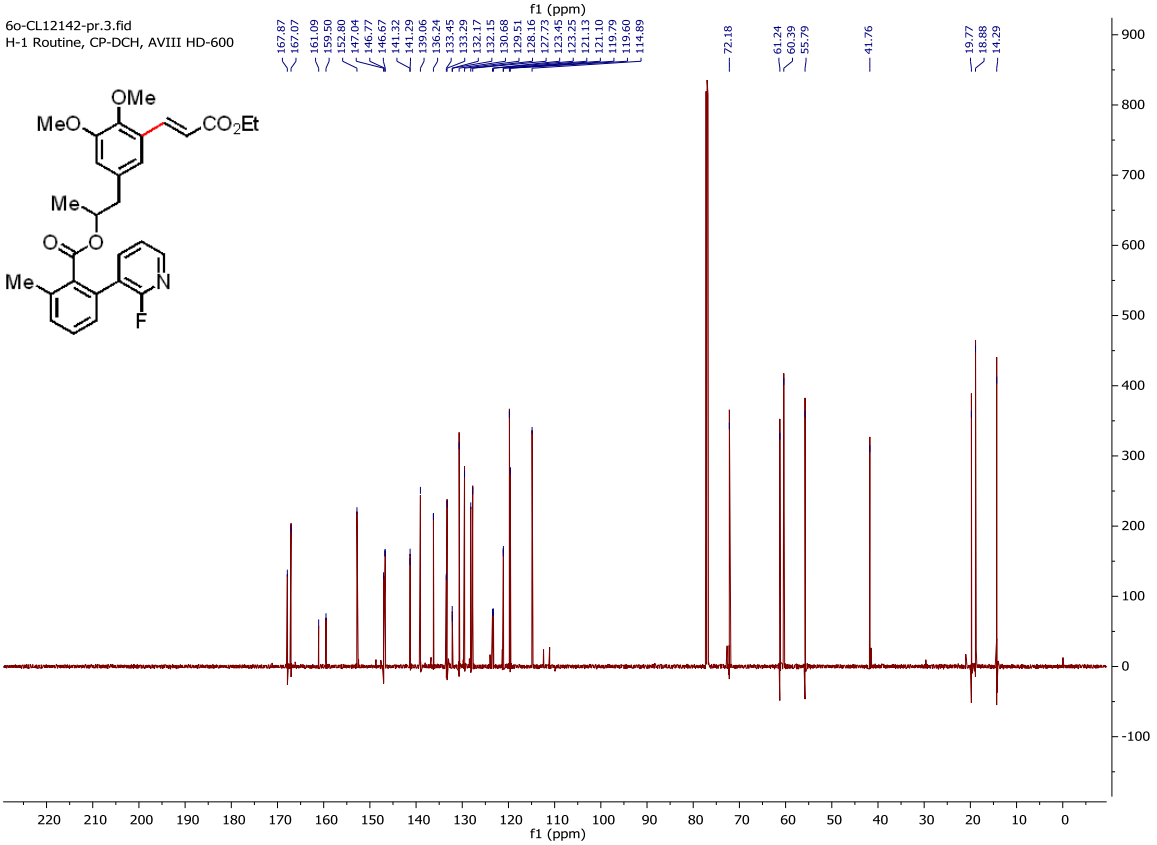

6n-CL12099-mono.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
7.19 7.18 7.69 7.68 7.68 7.67 7.67 7.65 7.63 7.44 7.41 7.40 7.39 7.38 7.30 7.29 7.28 7.27 7.26 7.20 7.19 7.18 7.14 7.13 6.43 6.40
4.28 4.28 4.27 4.27 4.26 4.25 4.25
2.73 2.72 2.71 2.36
CO2Et
O
O
Me
N
F
1.00 2.11 2.29 3.54 2.02 1.10 1.01 4.15 2.04 3.07 3.14
f1 (ppm)
6n-CL12099-mono.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
168.40 166.92 160.97 159.38 145.76 145.66 144.29 141.12 141.09 138.10 136.77 134.68 132.92 132.63 132.61 130.85 130.65 129.83 129.06 128.43 127.95 126.34 123.57 123.37 121.23 121.20 118.44
65.20 60.50 34.47 20.19 14.31
f1 (ppm)

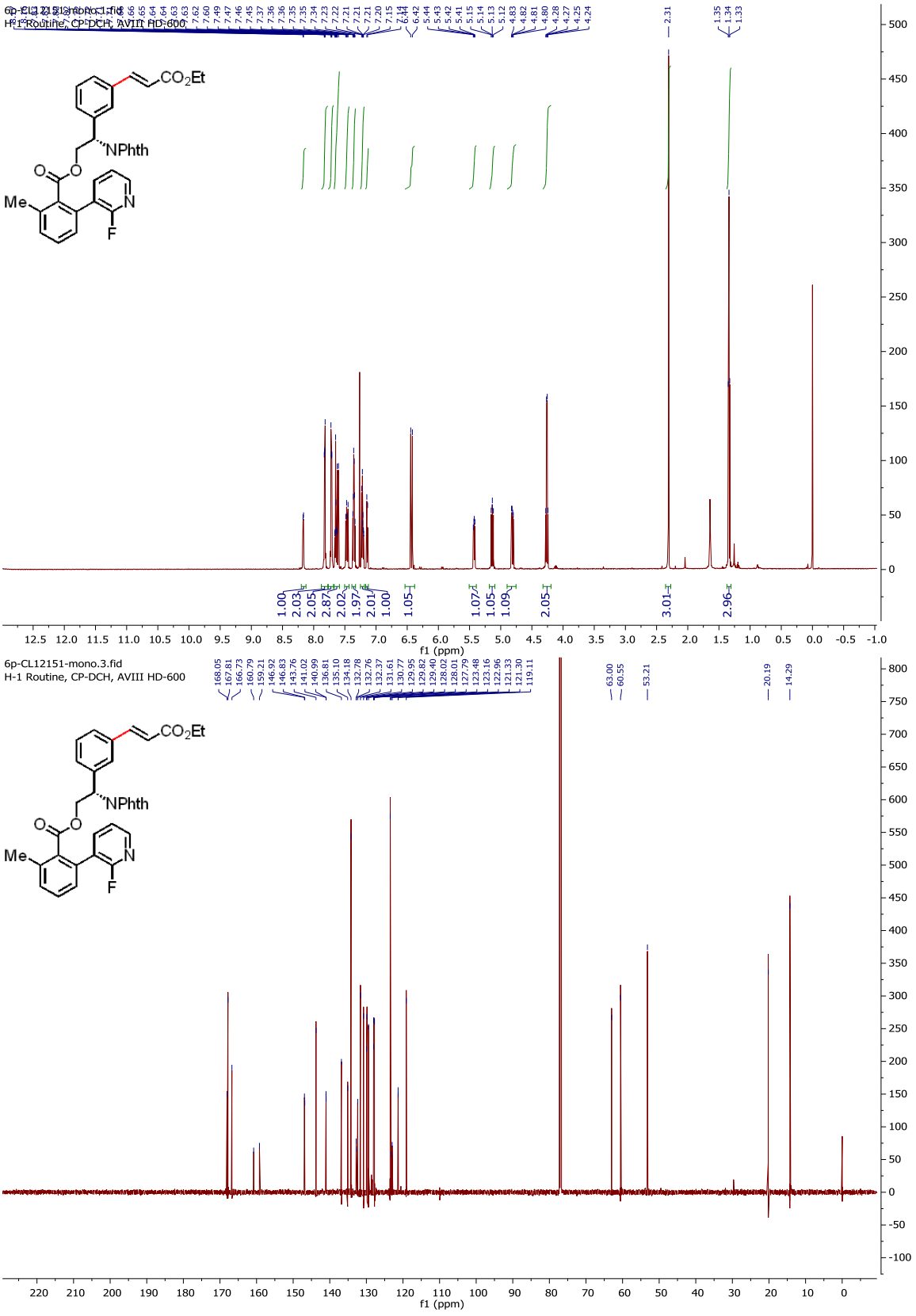

6n-CL12099-di.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
EtO2C
CO2Et
Me
N
F
1.00
2.94
0.99
1.07
3.31
2.17
1.89
6.17
2.00
3.08
6.16
f1 (ppm)

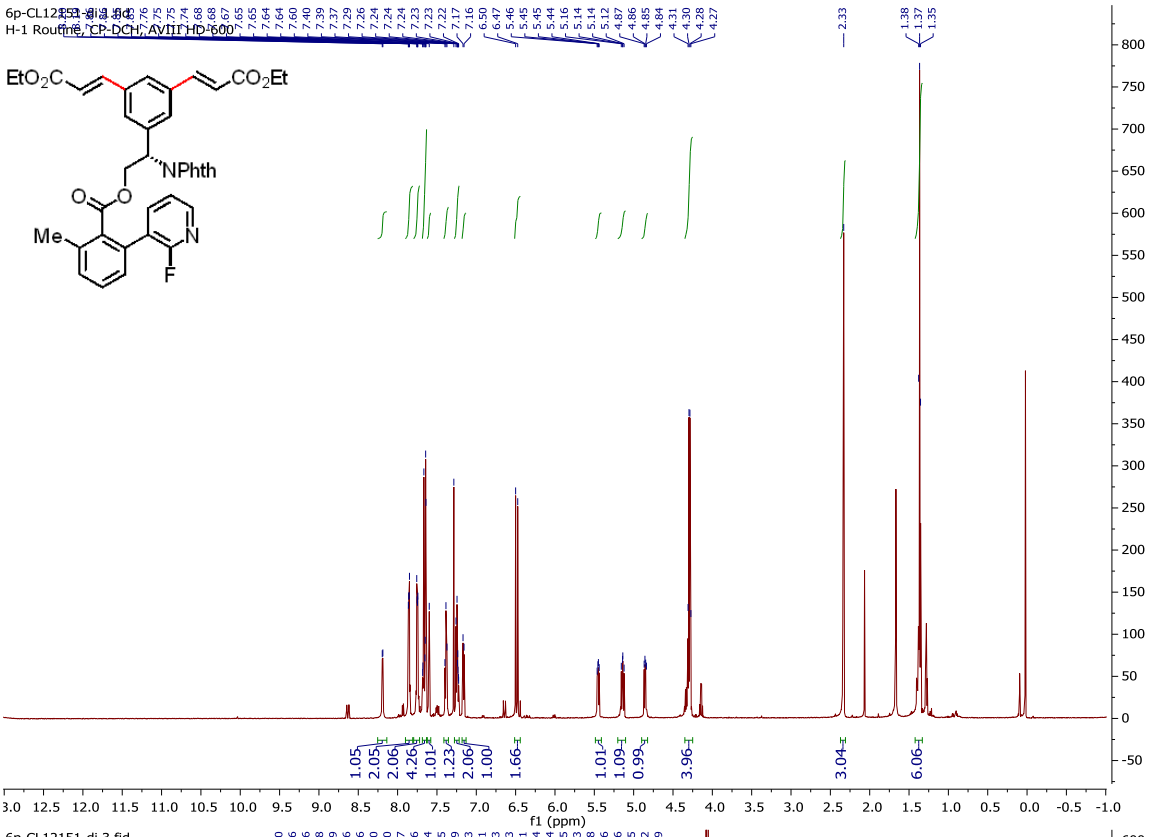

6n-CL12099-di.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
EtO2C
CO2Et
Me
N
F
f1 (ppm)

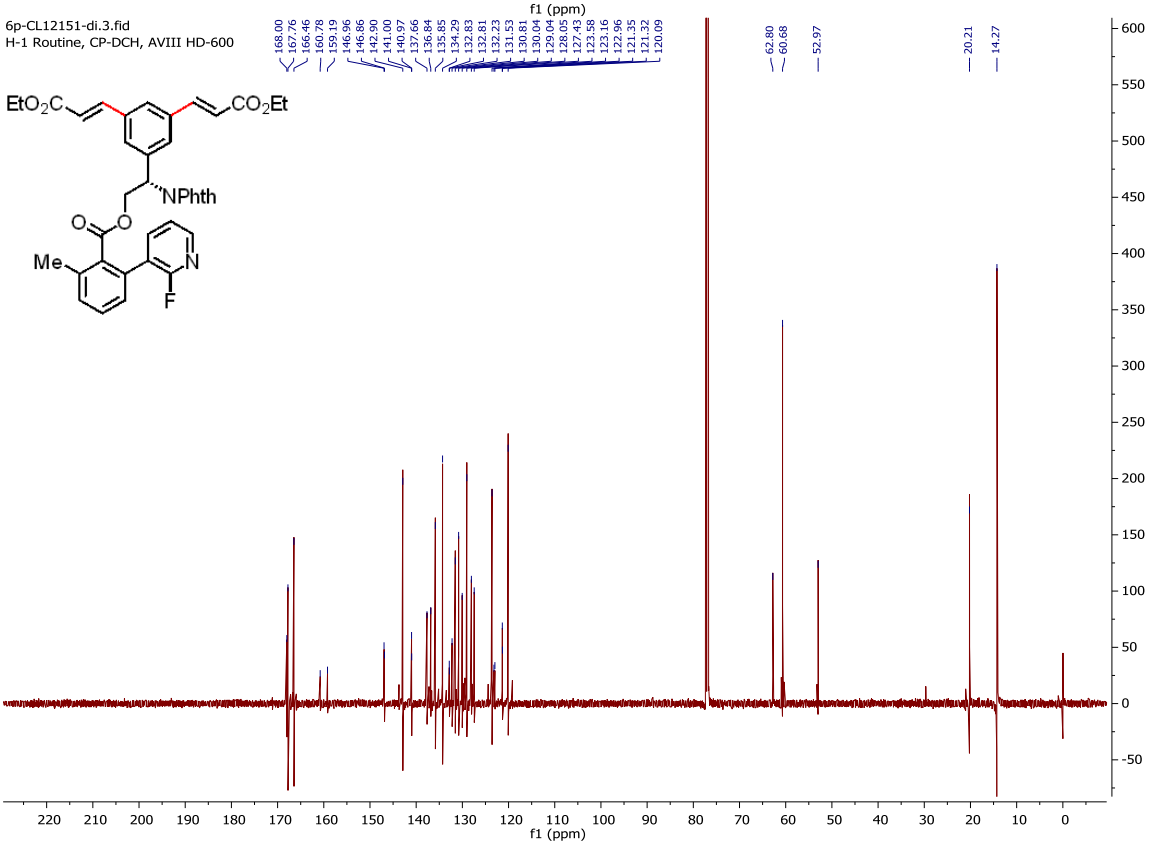

6n-CL12130-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
CO2Et
O
O
Me
N
F
f1 (ppm)
6n-CL12130-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
CO2Et
O
O
Me
N
F
f1 (ppm)

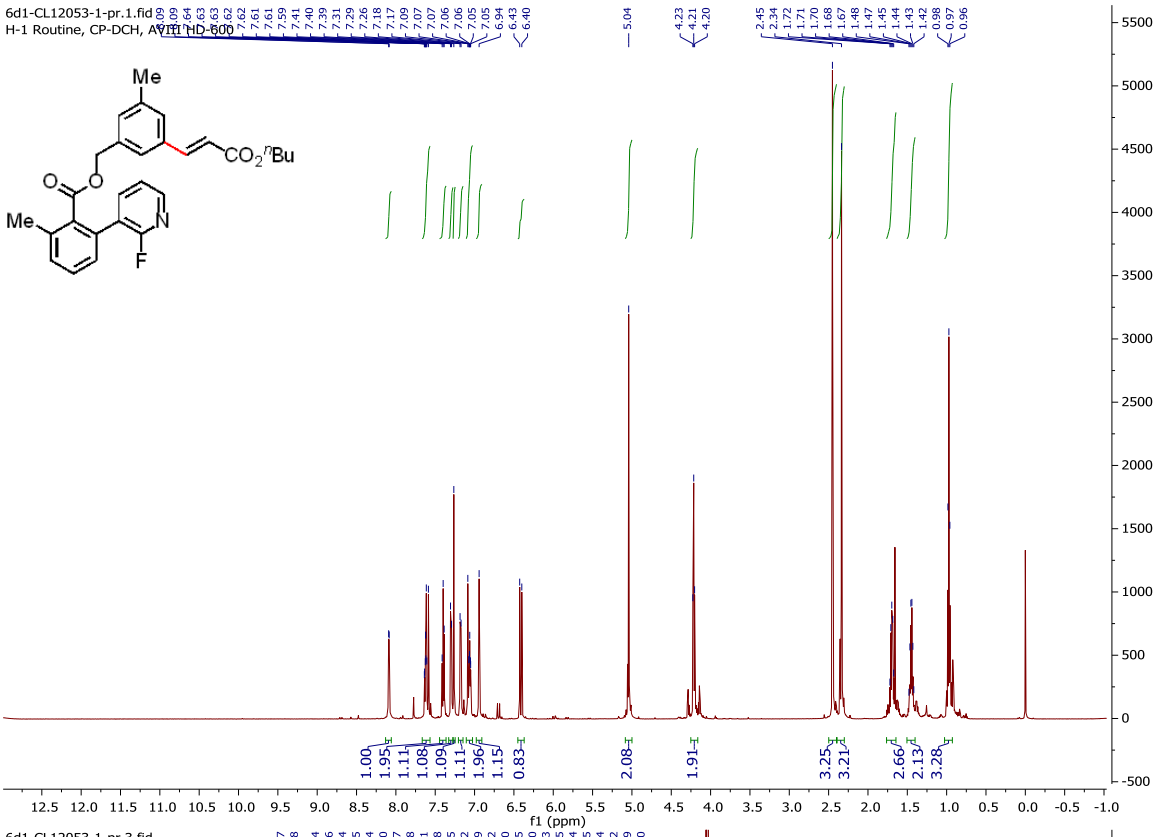

6o-CL12142-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
OMe
MeO
CO2Et
Me
O
O
Me
N
F
f1 (ppm)

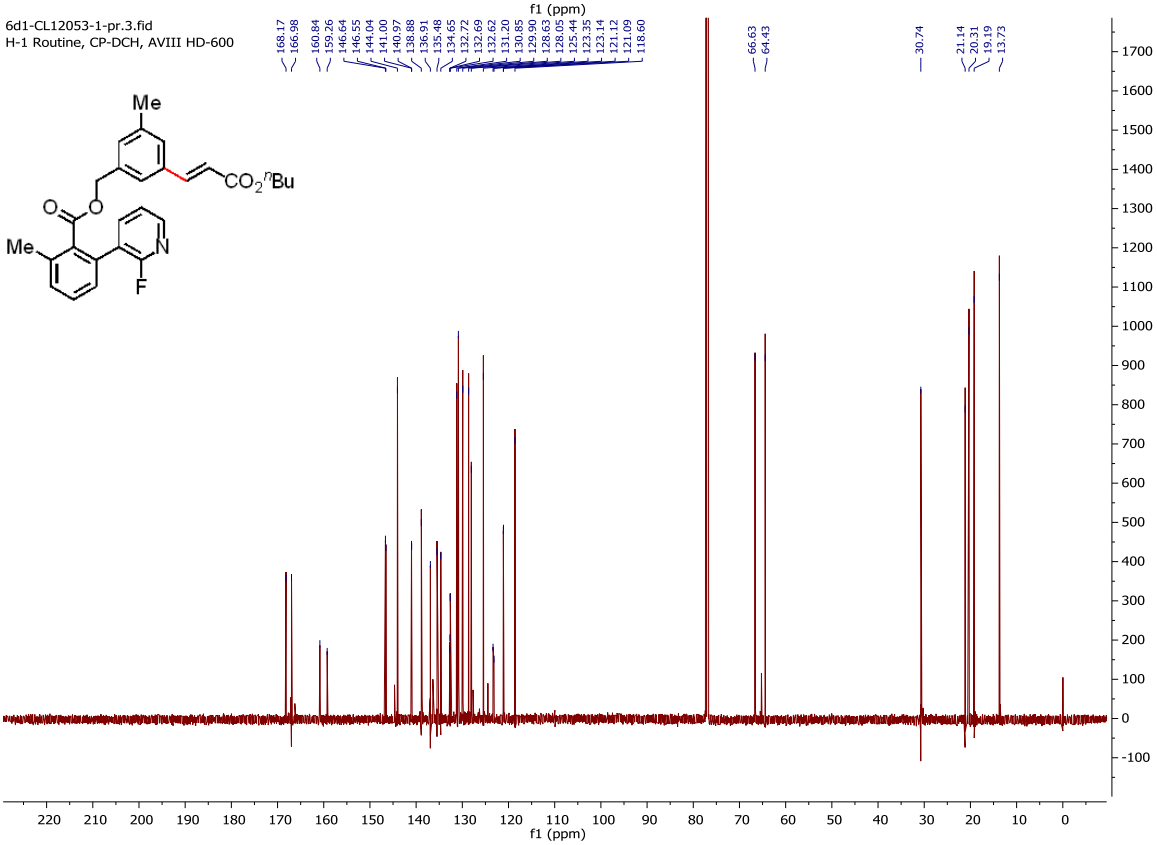

6o-CL12142-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
OMe
MeO
CO2Et
Me
O
O
Me
N
F
f1 (ppm)

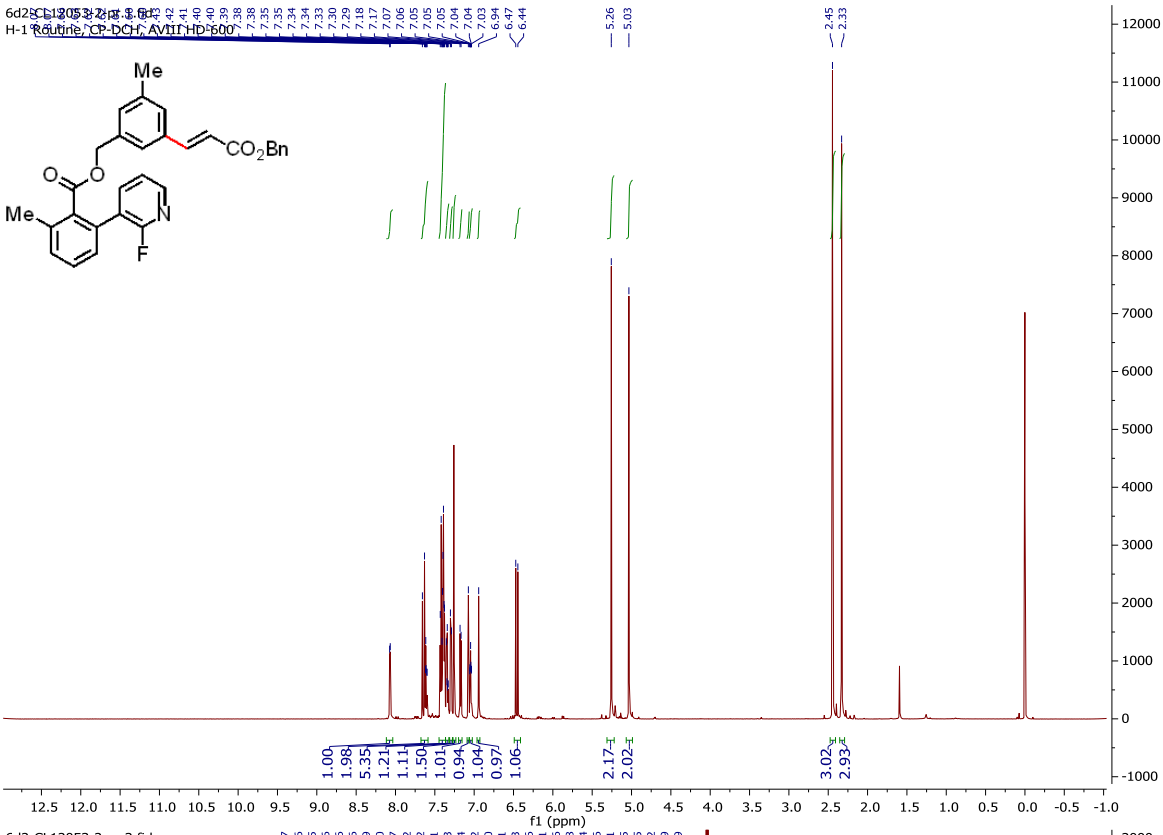

6p-CL12151-mono.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
CO2Et
NPhth
O
O
Me
N
F
2.31
1.35
1.34
1.33
1.00
2.03
2.05
2.87
2.02
1.97
2.01
1.00
1.05
1.07
1.05
1.09
2.05
3.01
2.96
f1 (ppm)
6p-CL12151-mono.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
168.05
167.81
166.73
160.79
159.21
146.82
143.76
141.02
140.99
136.81
135.10
134.18
132.78
132.76
132.37
131.61
130.77
129.95
129.82
129.40
128.02
128.01
127.79
123.48
123.16
122.96
121.33
121.30
119.11
63.00
60.55
53.21
20.19
14.29
f1 (ppm)

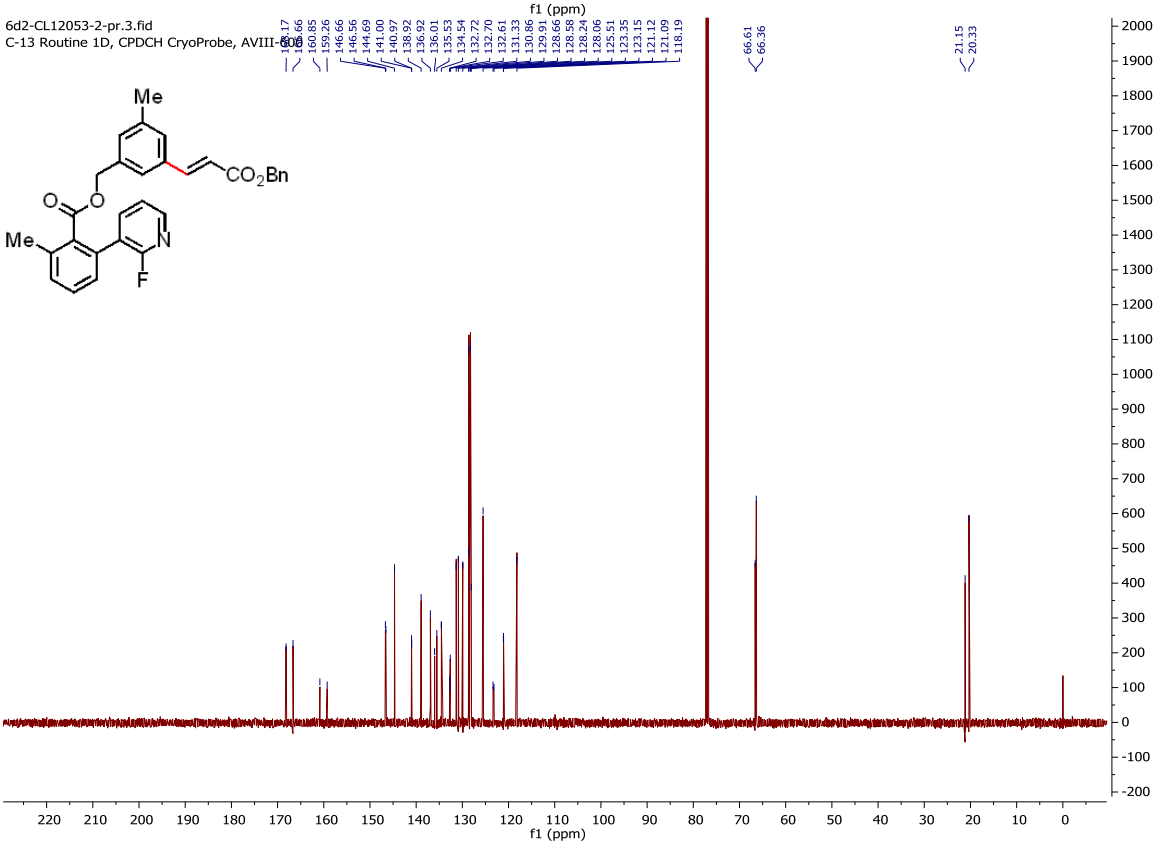

6p-CL12151-di.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
EtO2C
CO2Et
NPhth
O
O
Me
N
F
2.33
1.38
1.37
1.35
1.05
2.05
2.06
4.26
1.01
1.23
2.06
1.00
1.66
1.01
1.09
0.99
3.96
3.04
6.06
f1 (ppm)

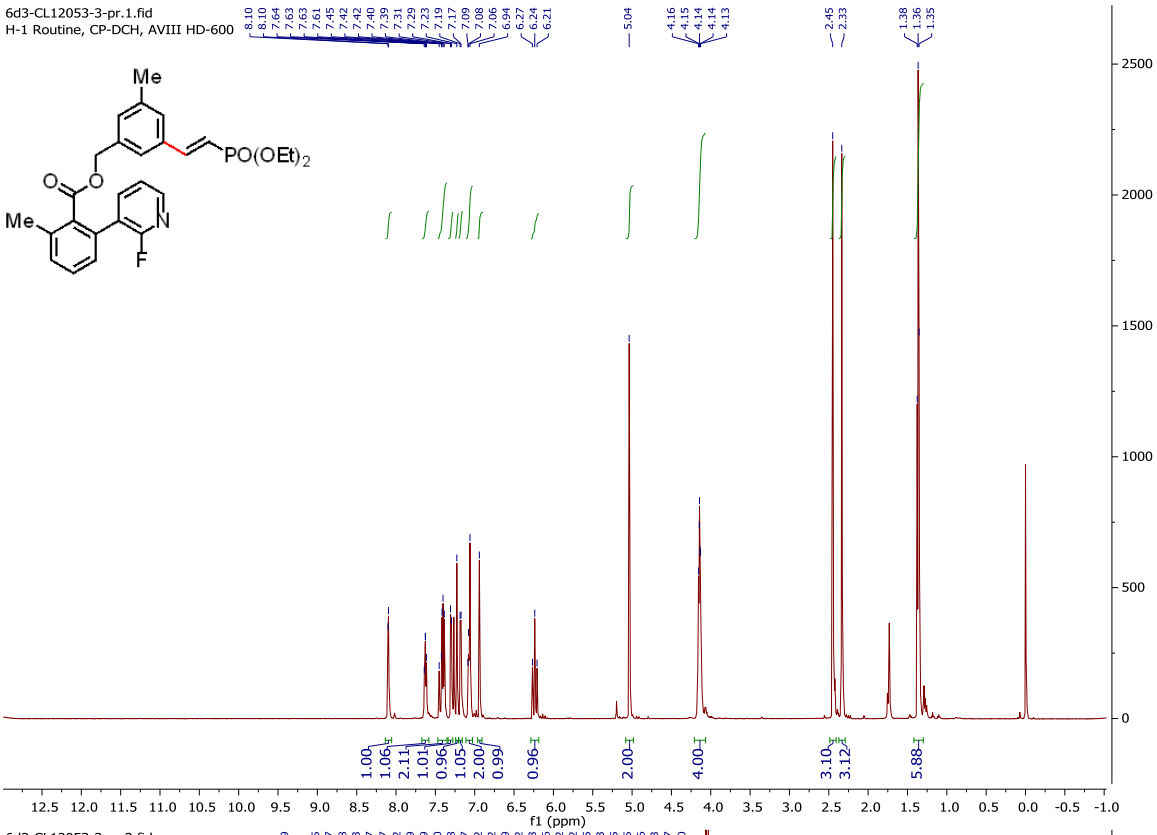

6p-CL12151-di.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
EtO2C
CO2Et
NPhth
O
O
Me
N
F
168.00
167.76
166.46
160.78
159.19
146.96
146.86
142.90
141.00
140.97
137.66
136.84
135.85
134.29
132.83
132.81
132.21
131.53
130.81
130.04
129.04
128.05
127.43
123.58
123.16
122.96
121.35
121.32
120.09
62.80
60.68
52.97
20.21
14.27
f1 (ppm)

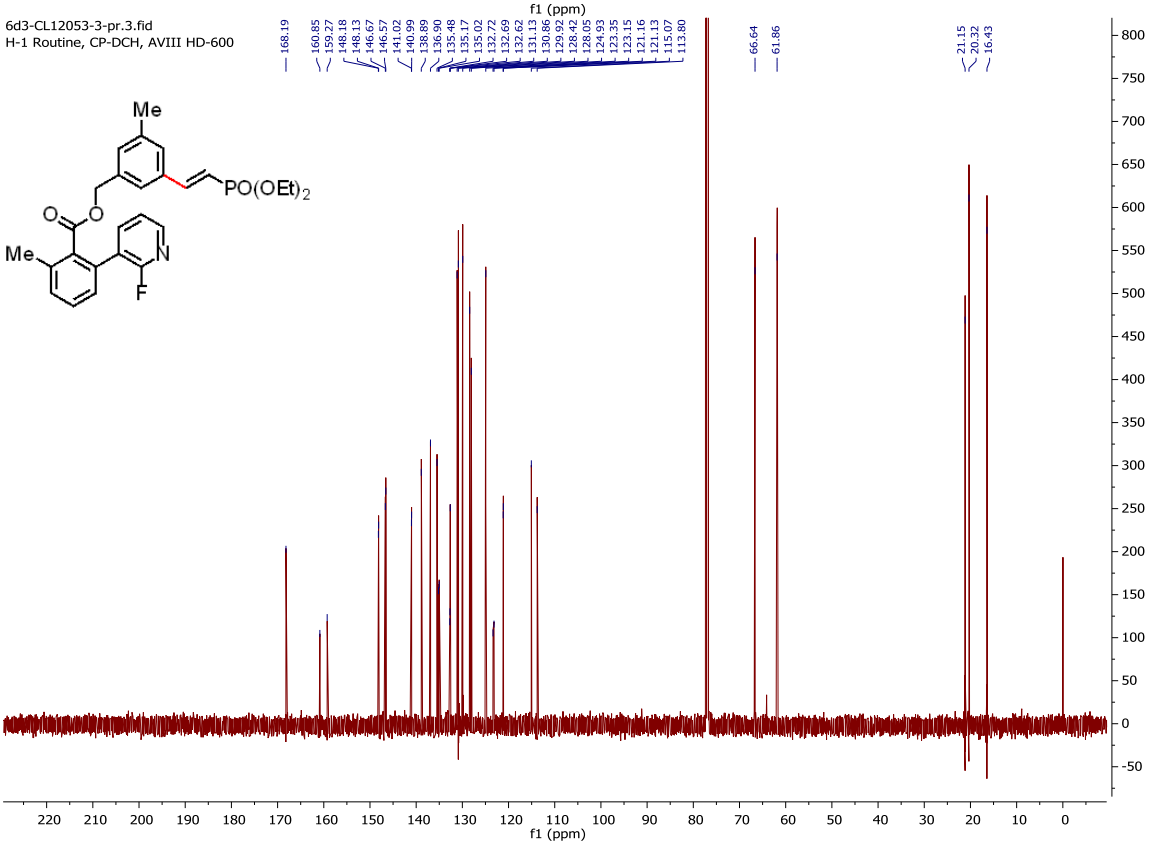

6d1-CL12053-1-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CO2nBu
O
O
Me
N
F
f1 (ppm)

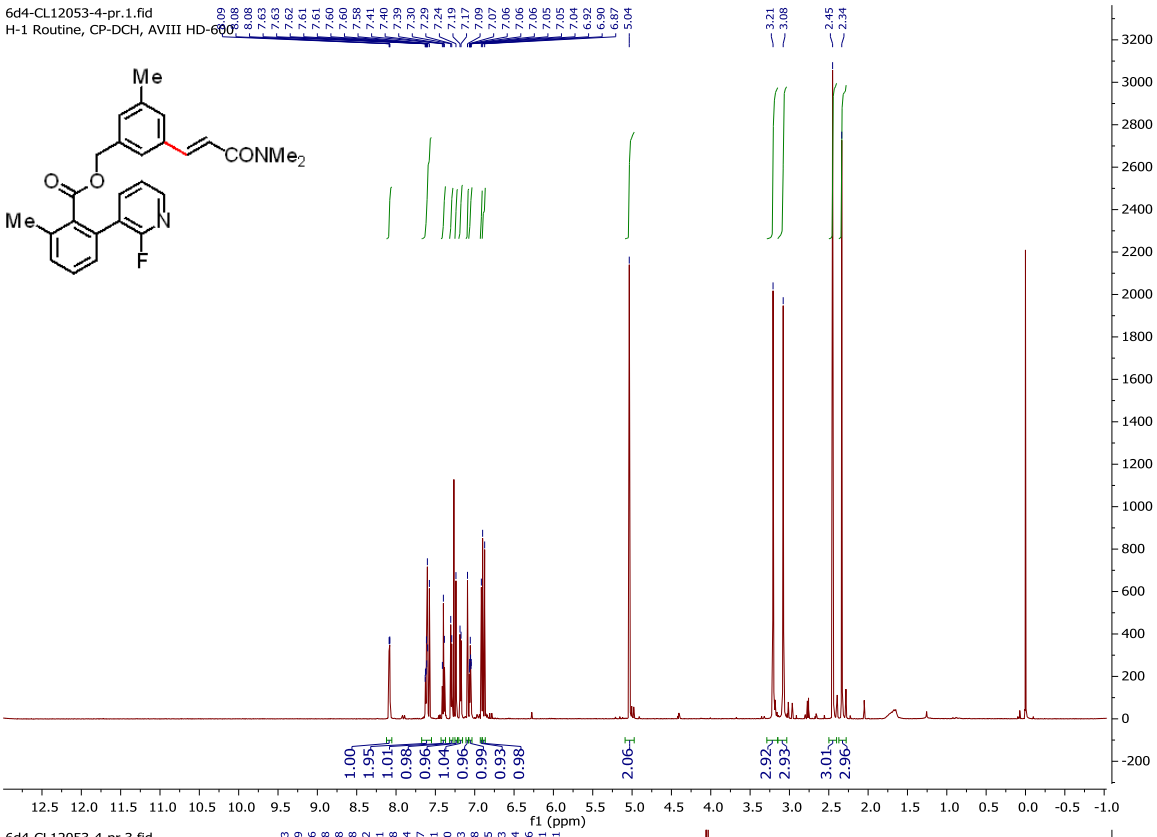

6d1-CL12053-1-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CO2nBu
O
O
Me
N
F
f1 (ppm)

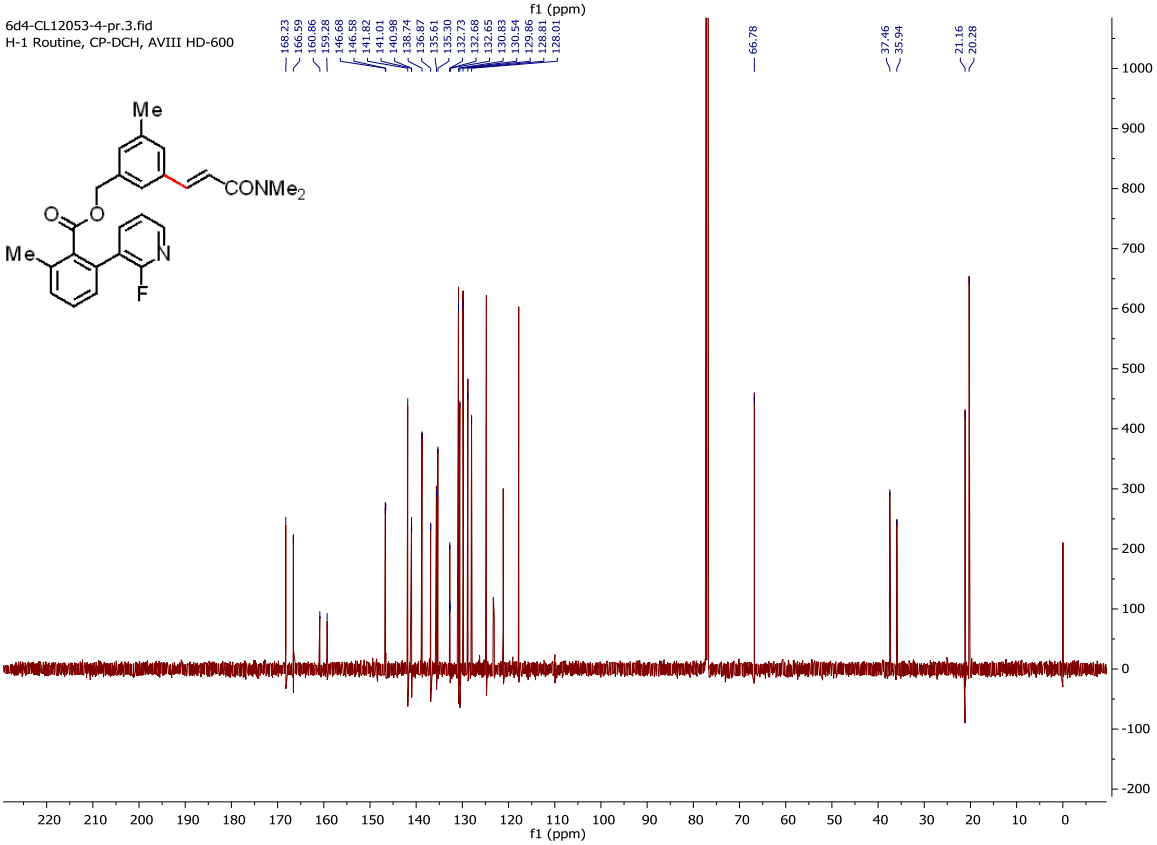

6d2-CL12053-2-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD 600
Me
CO2Bn
O
O
Me
N
F
f1 (ppm)

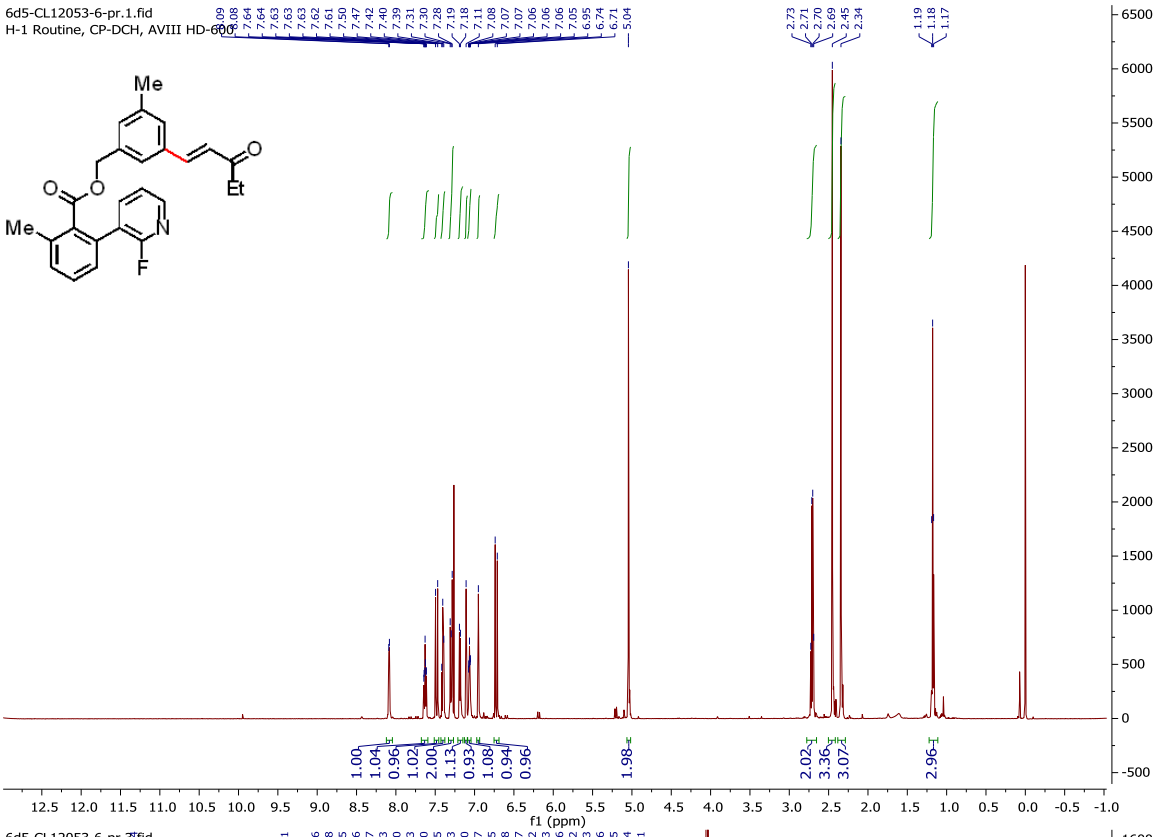

6d2-CL12053-2-pr.3.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
CO2Bn
O
O
Me
N
F
f1 (ppm)

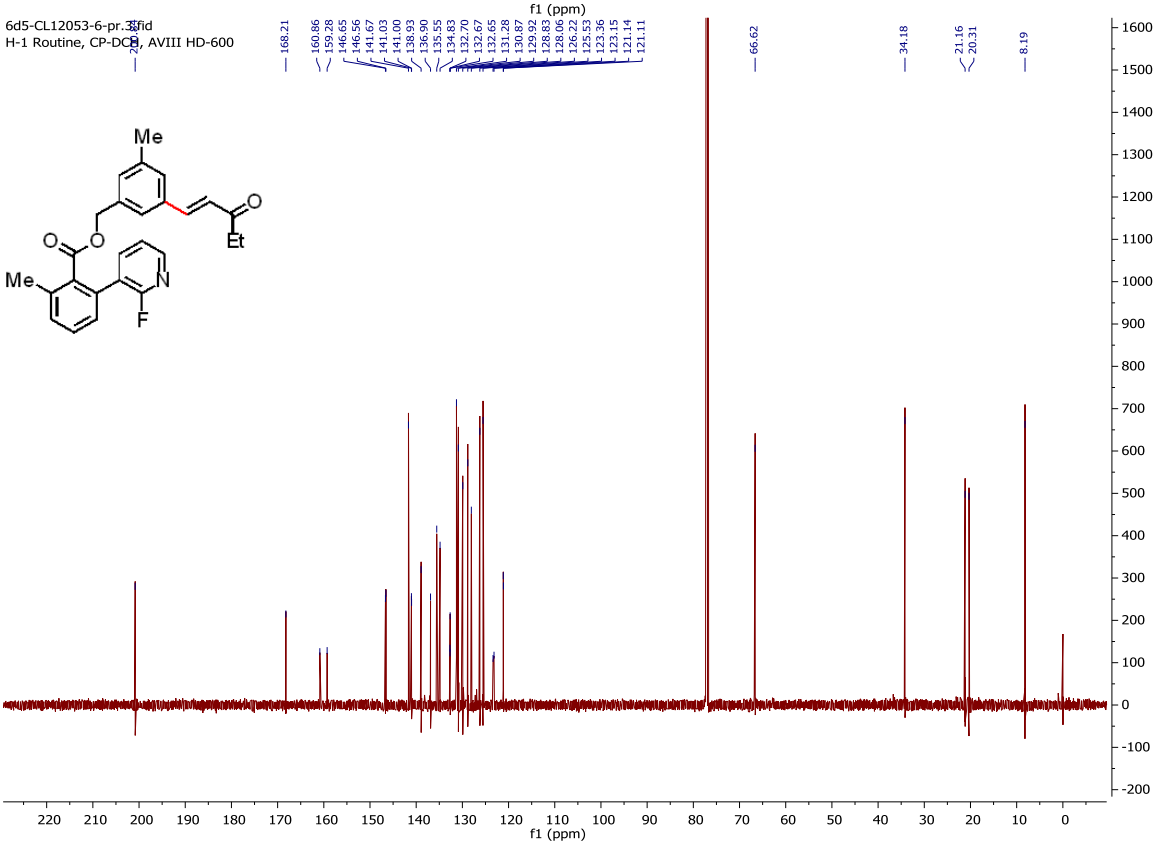

6d3-CL12053-3-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
PO(OEt)2
O
O
Me
N
F
f1 (ppm)

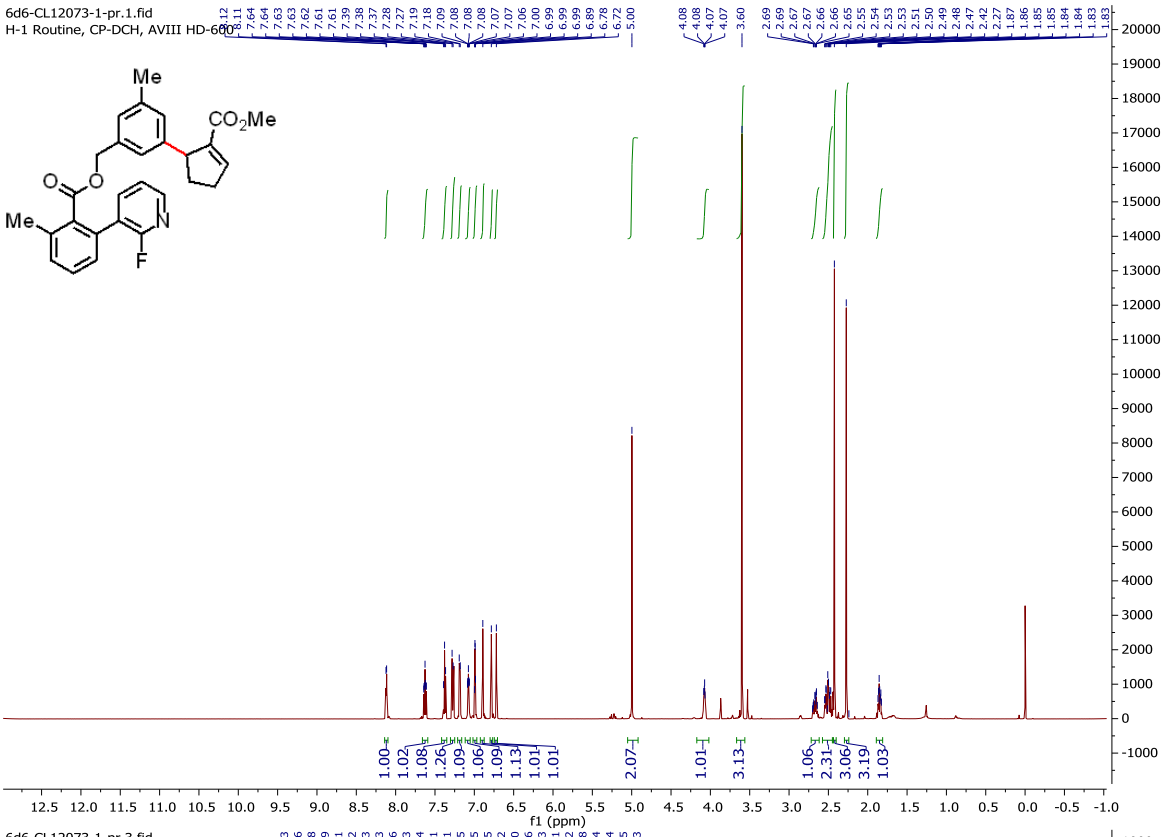

6d3-CL12053-3-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
PO(OEt)2
O
O
Me
N
F
f1 (ppm)

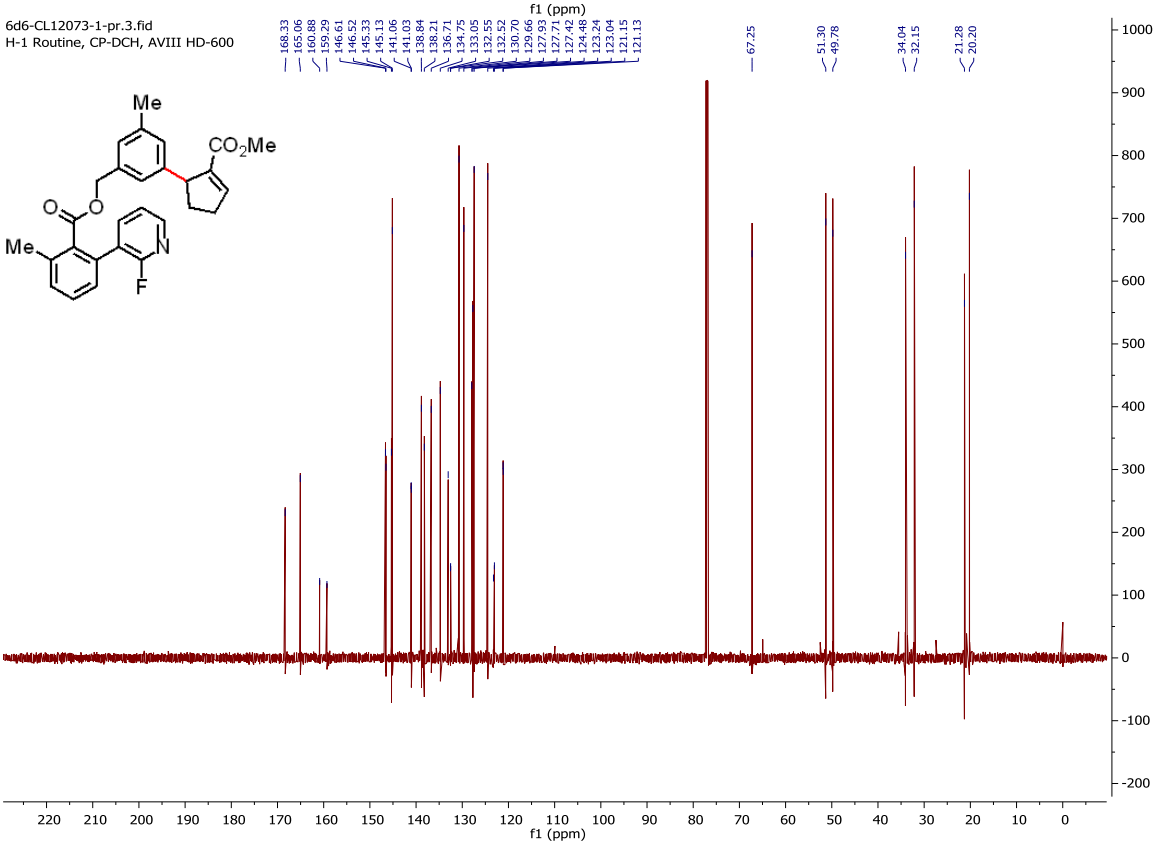

6d4-CL12053-4-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CONMe2
O
O
Me
N
F
f1 (ppm)

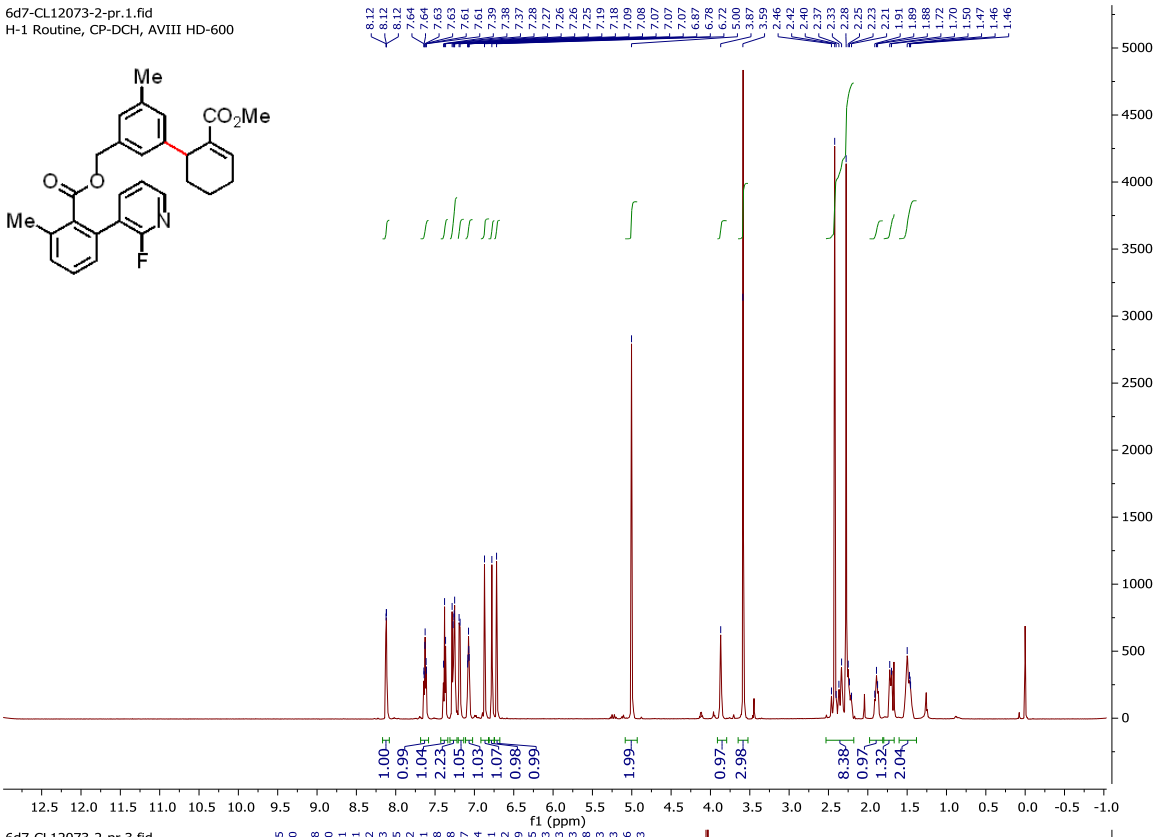

6d4-CL12053-4-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CONMe2
O
O
Me
N
F
f1 (ppm)

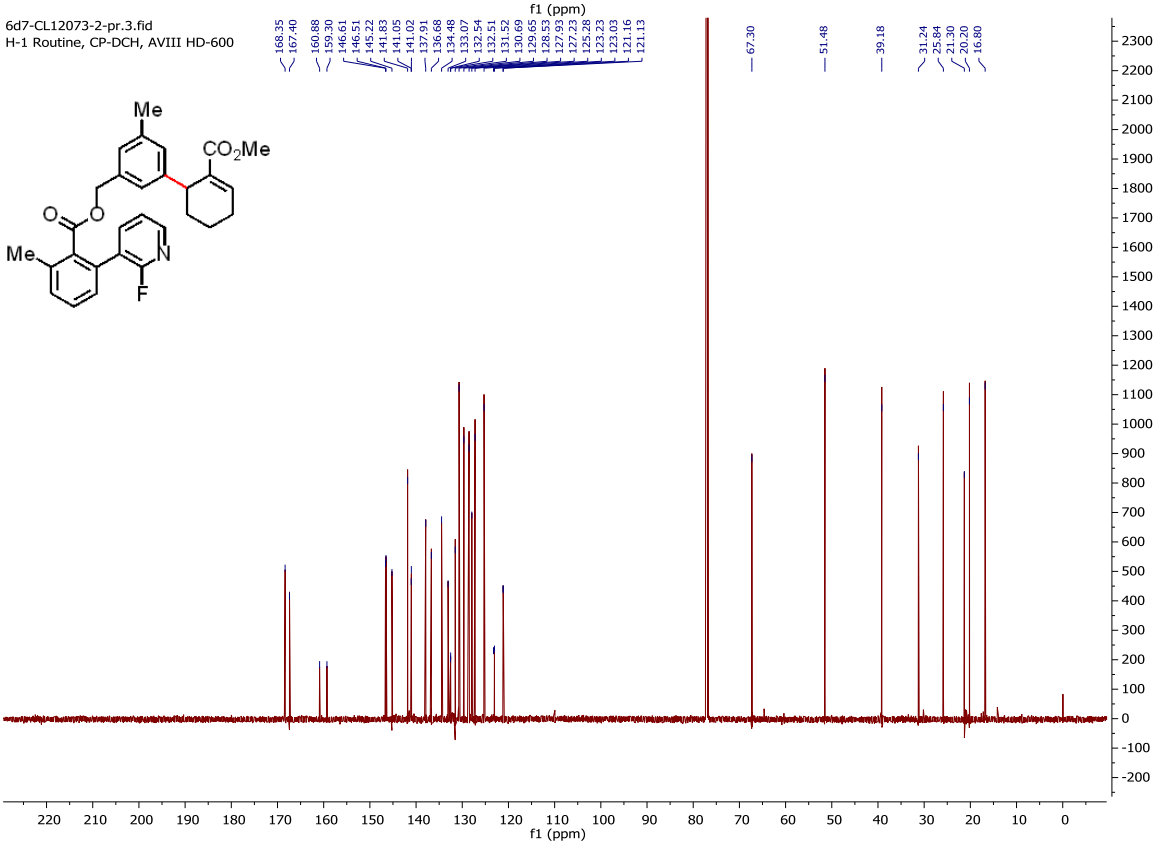

6d5-CL12053-6-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
Et
Me
N
F
f1 (ppm)

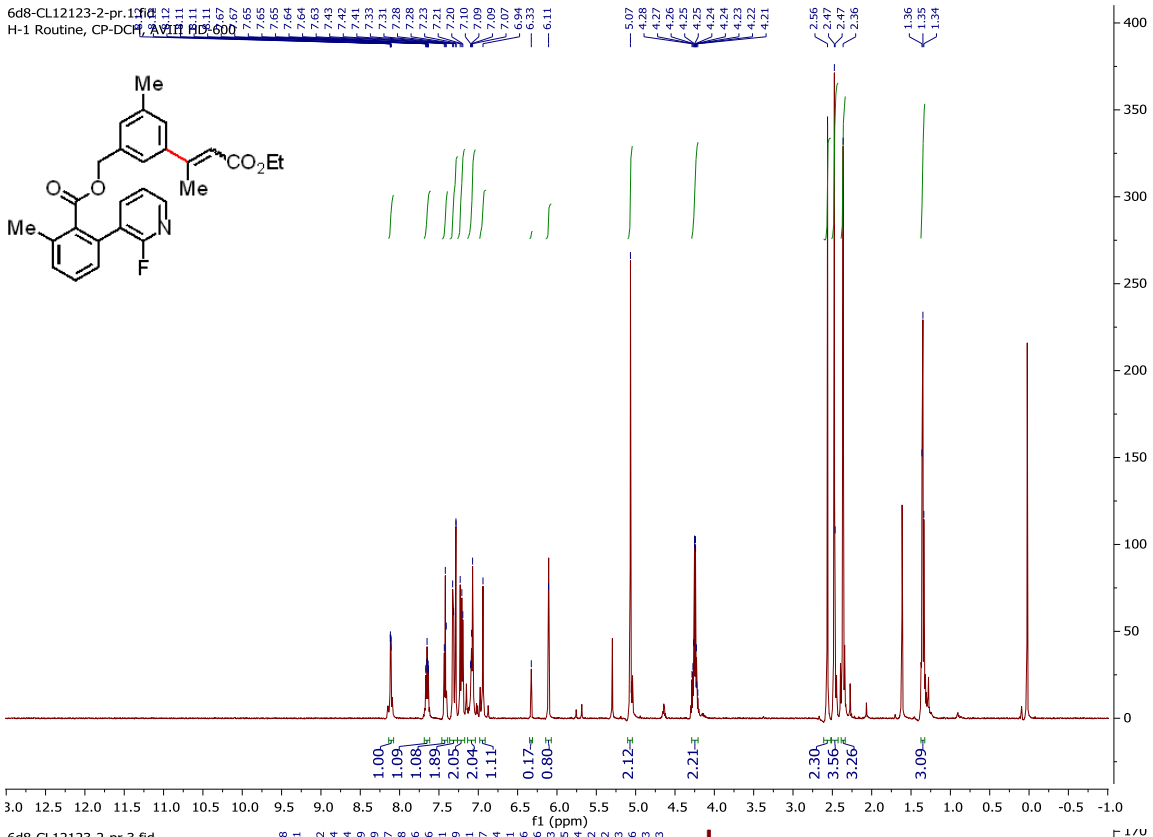

6d5-CL12053-6-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
O
O
Et
Me
N
F
f1 (ppm)

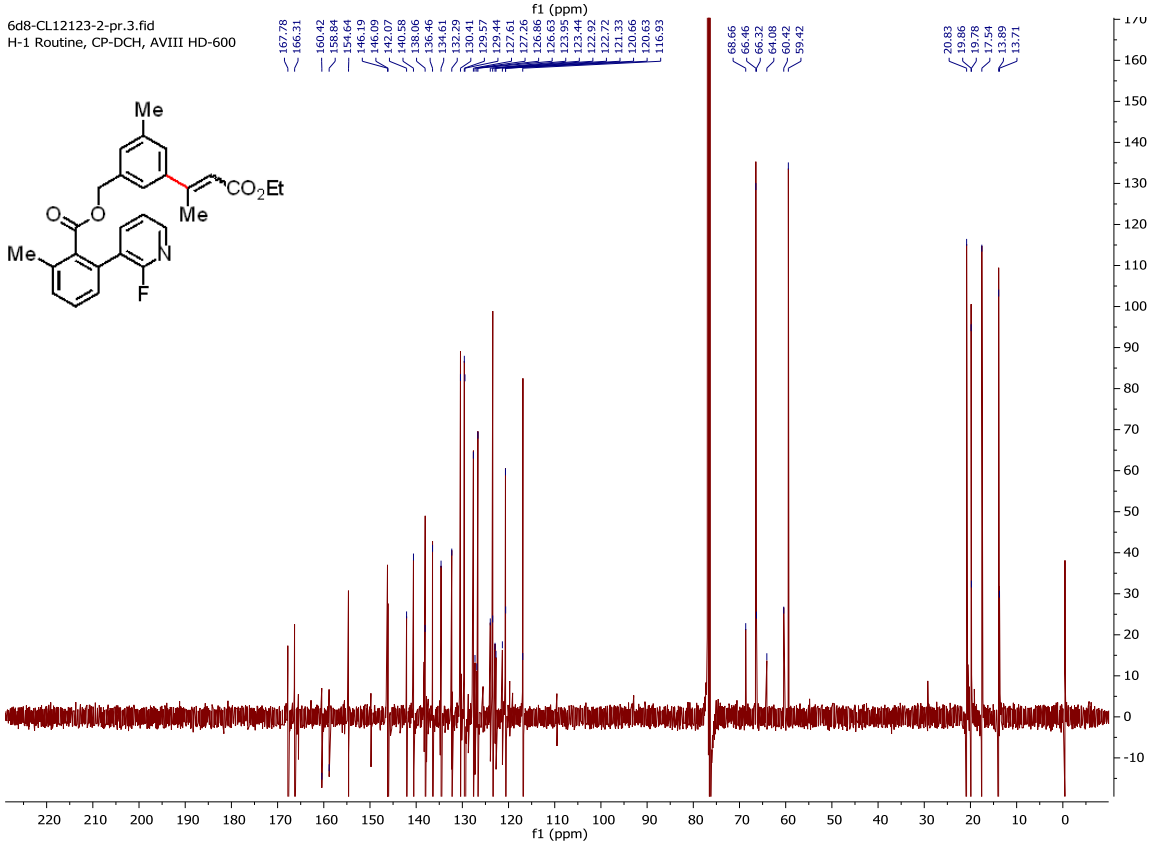

6d6-CL12073-1-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CO2Me
O
O
Me
N
F
f1 (ppm)

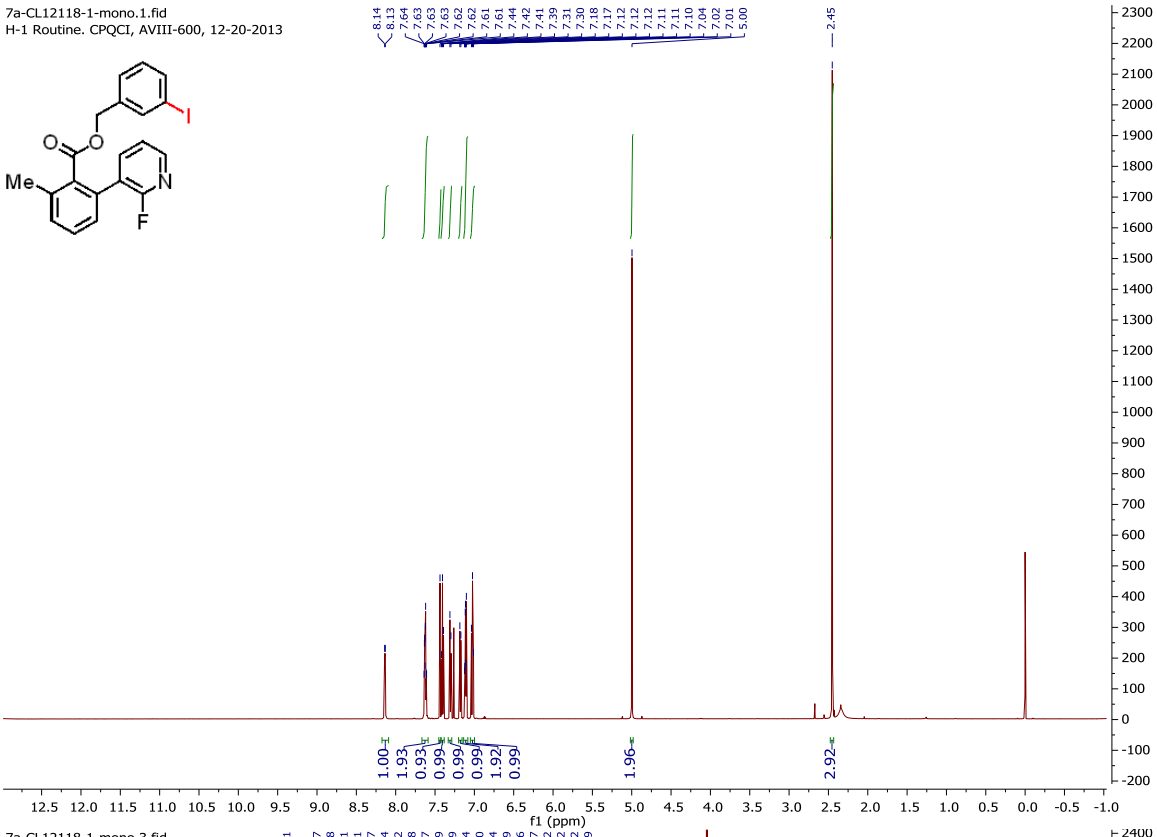

6d6-CL12073-1-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CO2Me
O
O
Me
N
F
f1 (ppm)

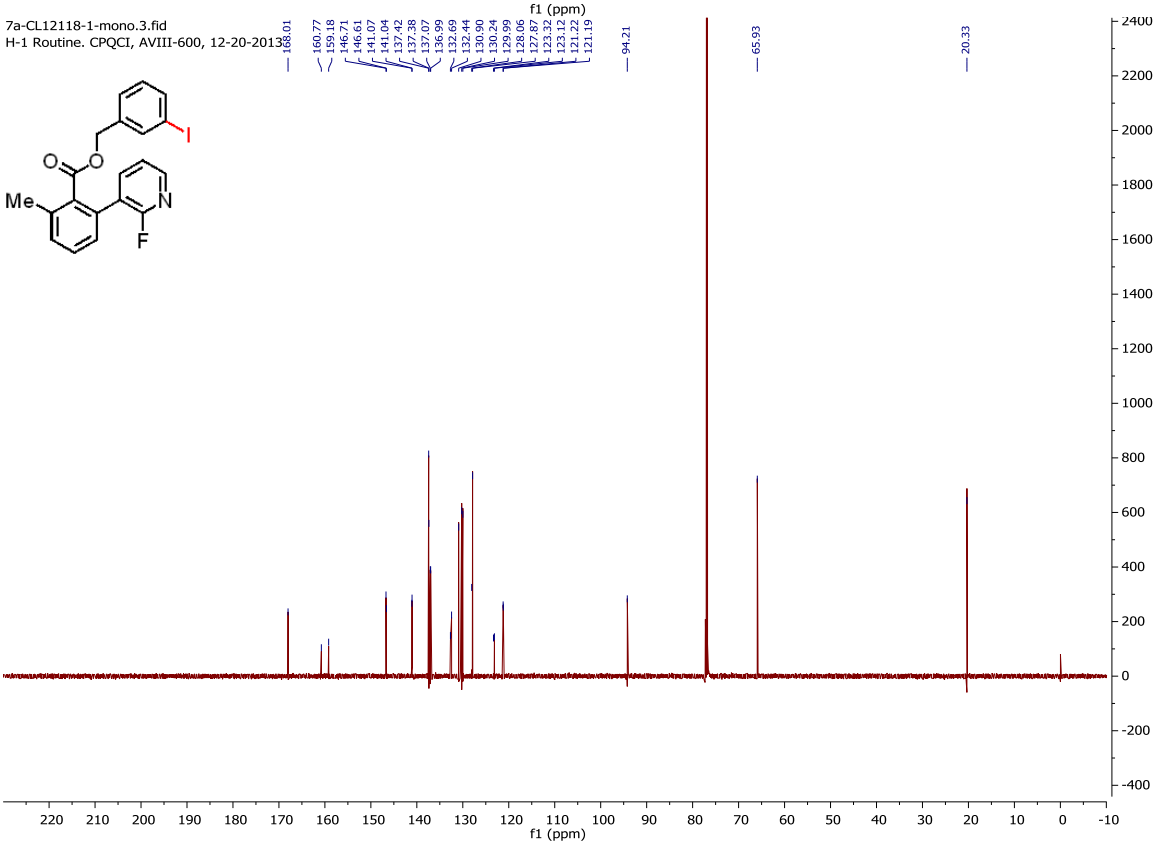

6d7-CL12073-2-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CO2Me
O
O
Me
N
F
f1 (ppm)

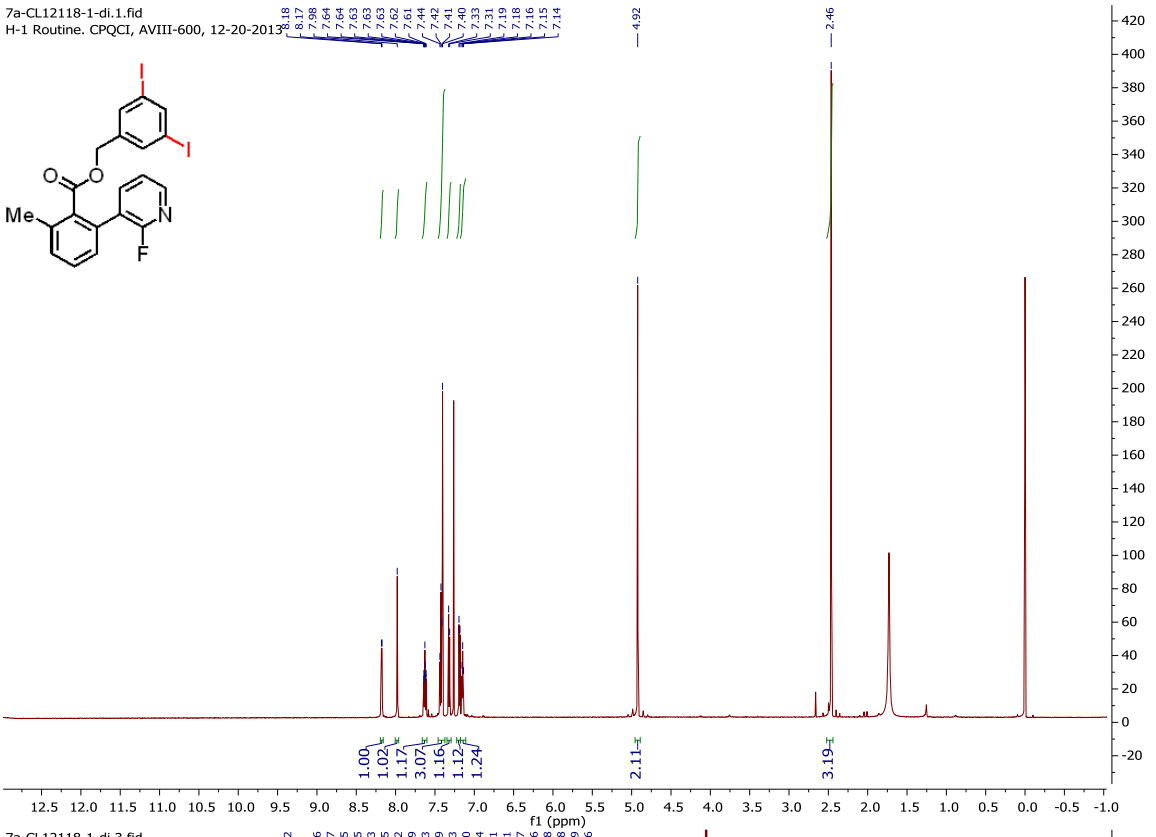

6d7-CL12073-2-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CO2Me
O
O
Me
N
F
f1 (ppm)

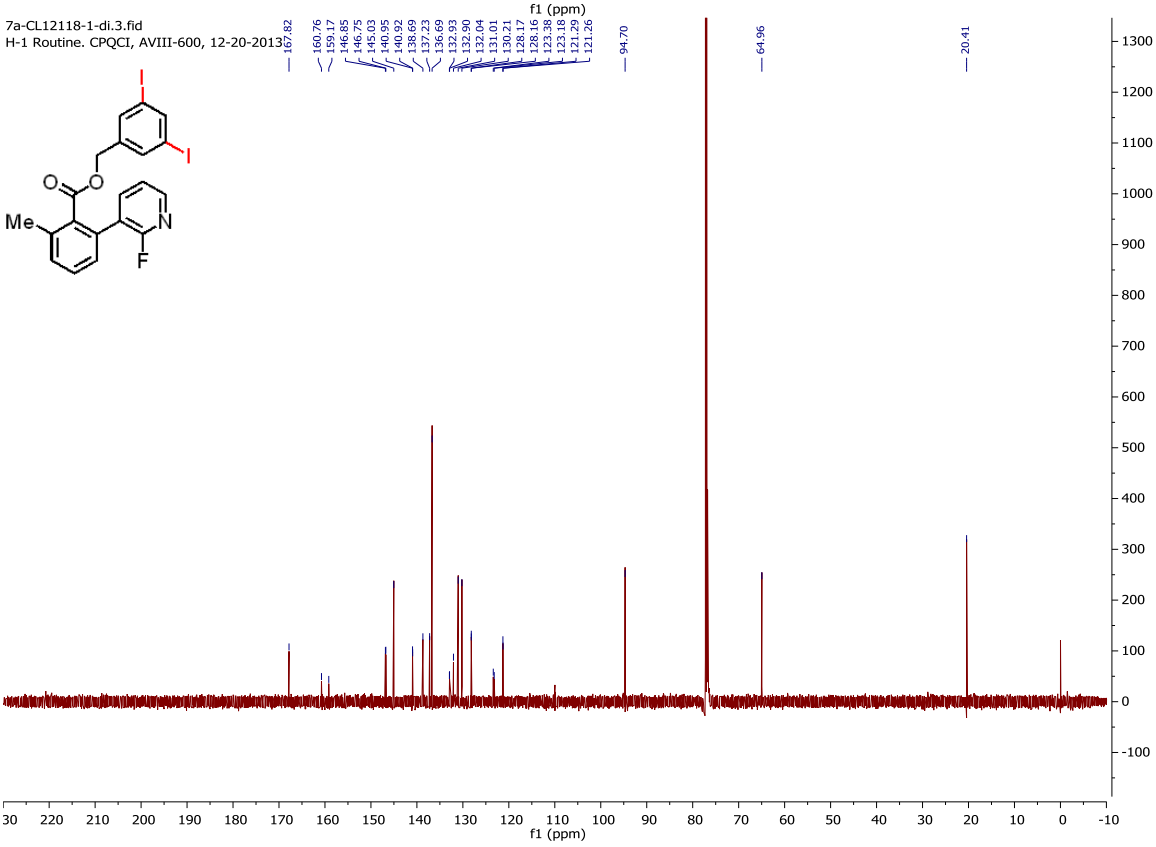

6d8-CL12123-2-pr.12.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CO2Et
Me
O
O
Me
N
F
f1 (ppm)

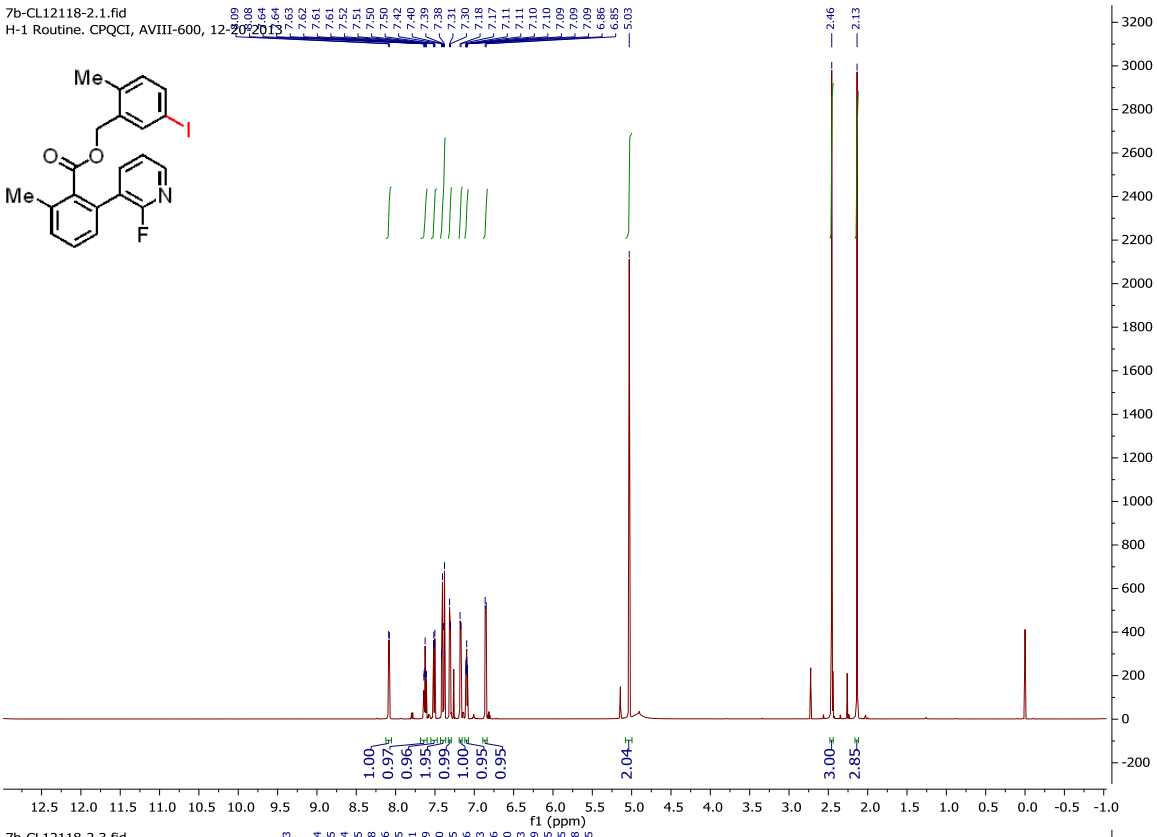

6d8-CL12123-2-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Me
CO2Et
Me
O
O
Me
N
F
f1 (ppm)

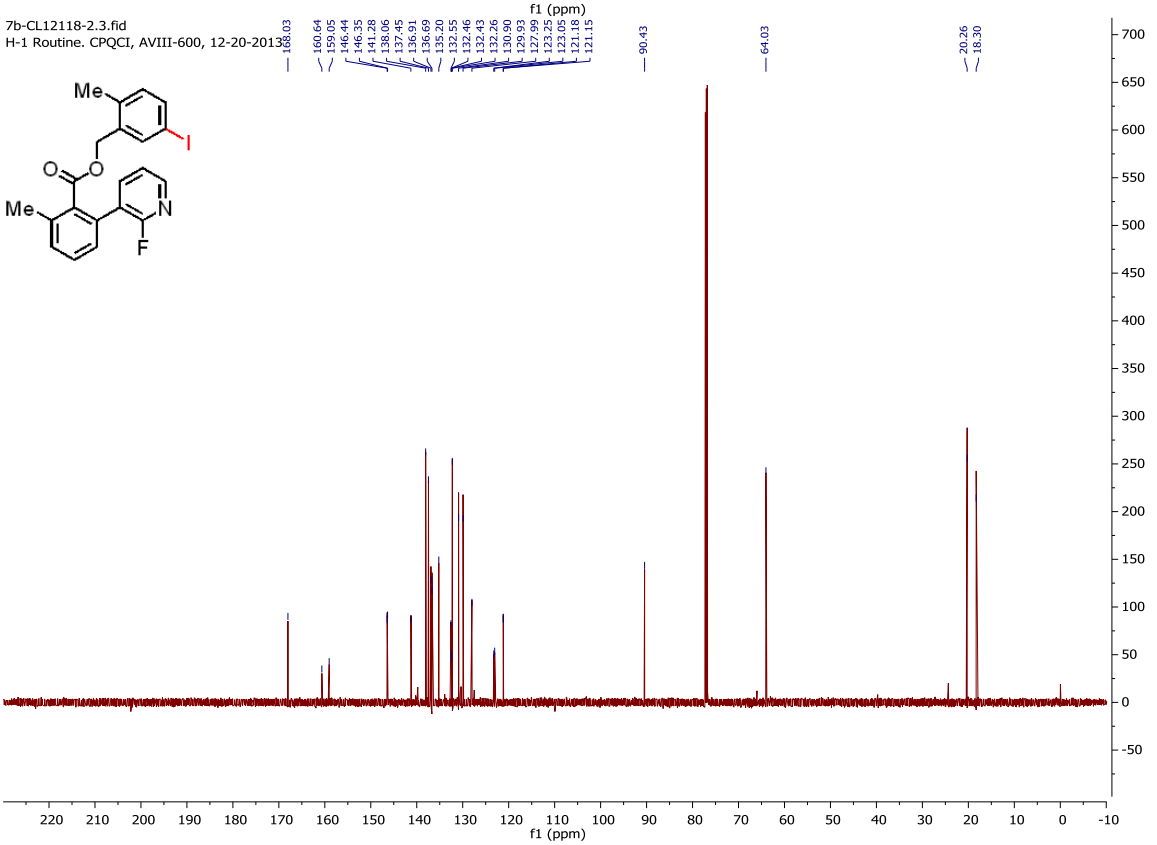

7a-CL12118-1-mono.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
N
F
I
f1 (ppm)

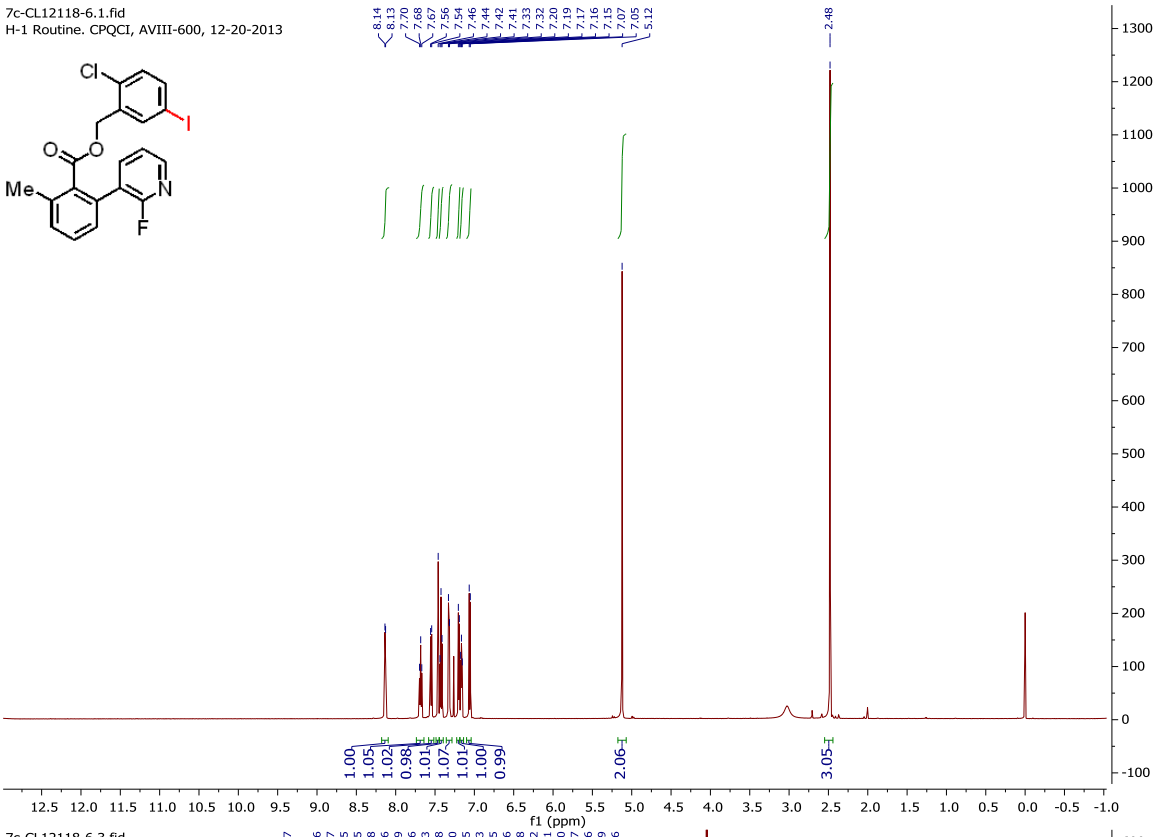

7a-CL12118-1-mono.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
N
F
I
f1 (ppm)

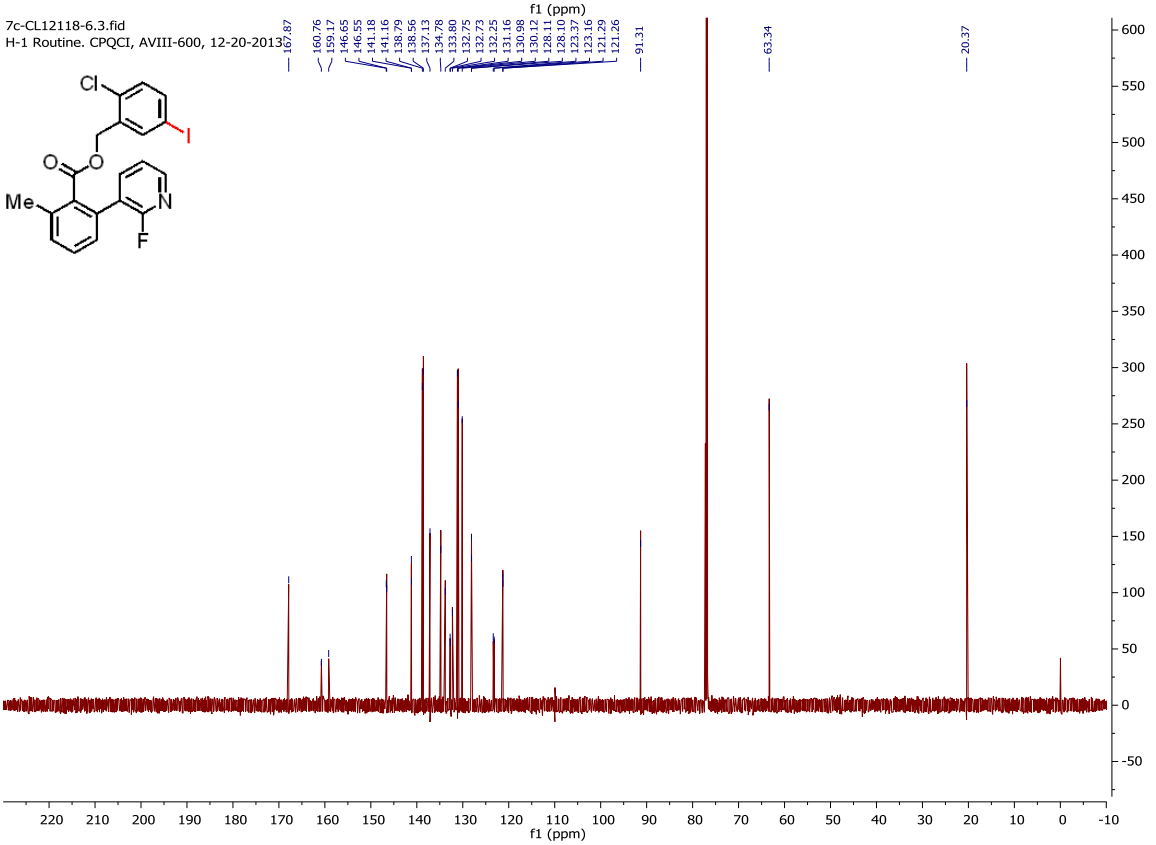

7a-CL12118-1-di.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
8.18
8.17
7.98
7.64
7.64
7.63
7.63
7.63
7.62
7.61
7.44
7.42
7.41
7.40
7.33
7.31
7.19
7.18
7.16
7.15
7.14
4.92
2.46
Me
F
1.00
1.02
1.17
3.07
1.16
1.12
1.24
2.11
3.19
f1 (ppm)

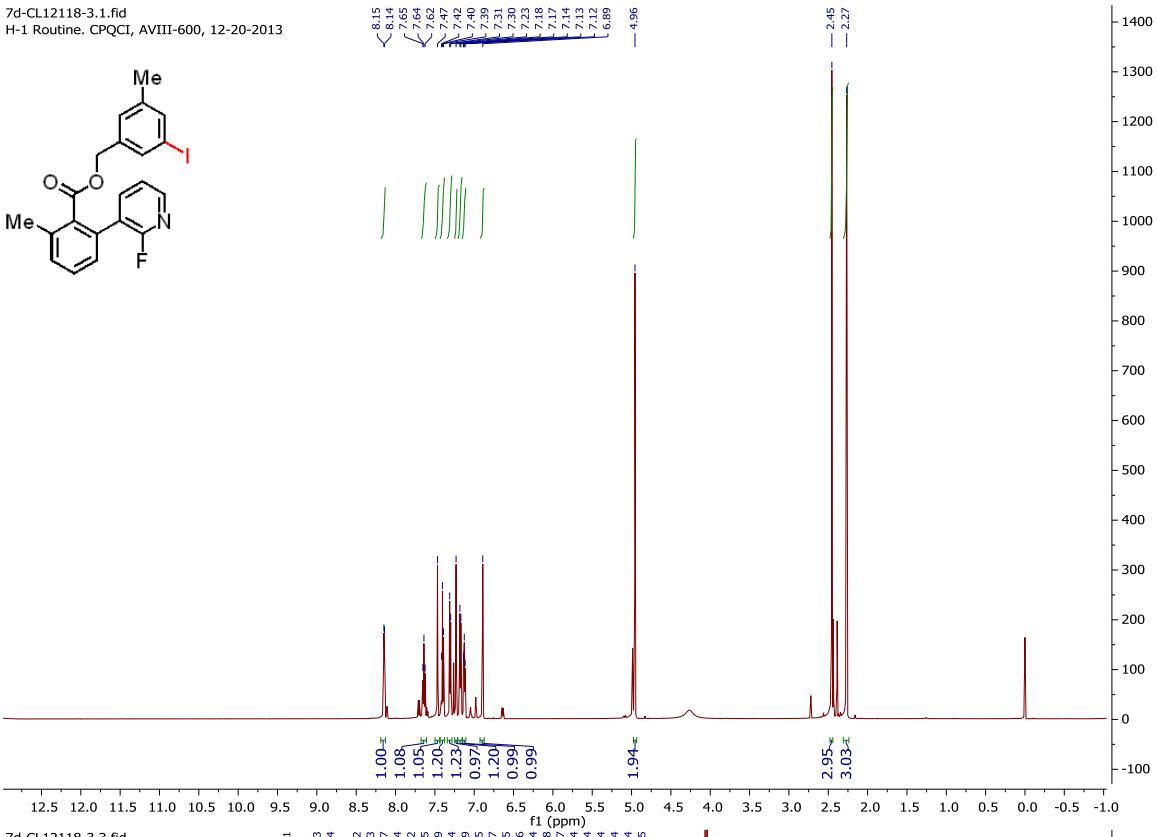

7a-CL12118-1-di.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
167.82
160.76
159.17
146.85
146.75
145.03
140.95
140.92
138.69
137.23
136.69
132.93
132.90
132.04
131.01
130.21
128.17
128.16
123.38
123.18
121.29
121.26
94.70
64.96
20.41
Me
F
f1 (ppm)

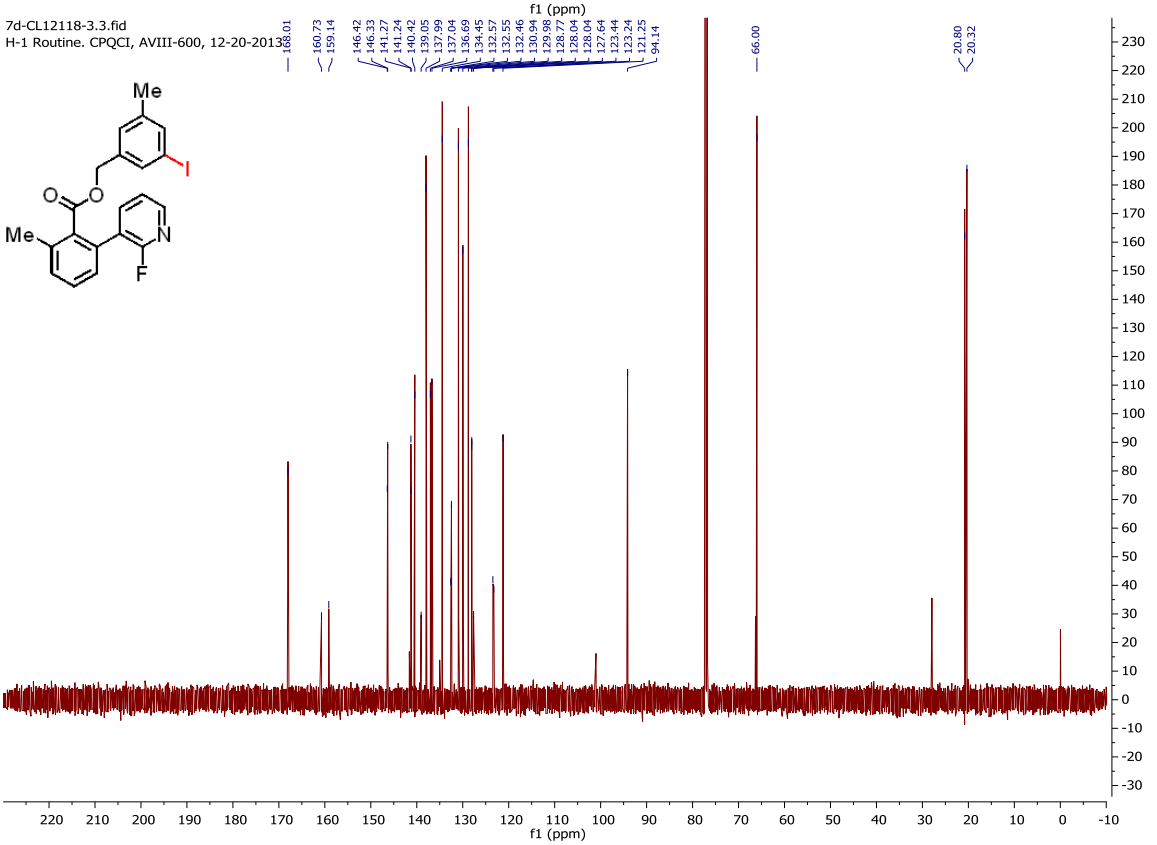

7b-CL12118-2.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
Me
N
F
I
f1 (ppm)

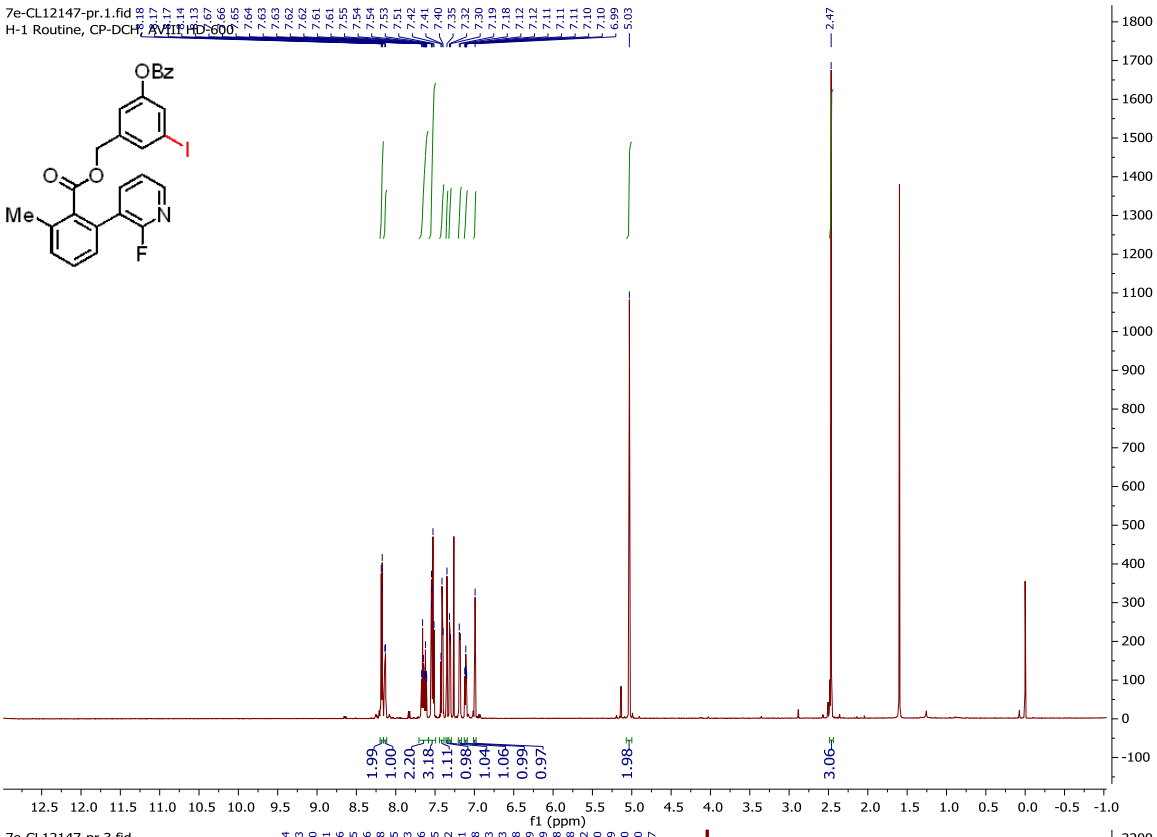

7b-CL12118-2.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
Me
N
F
I
f1 (ppm)

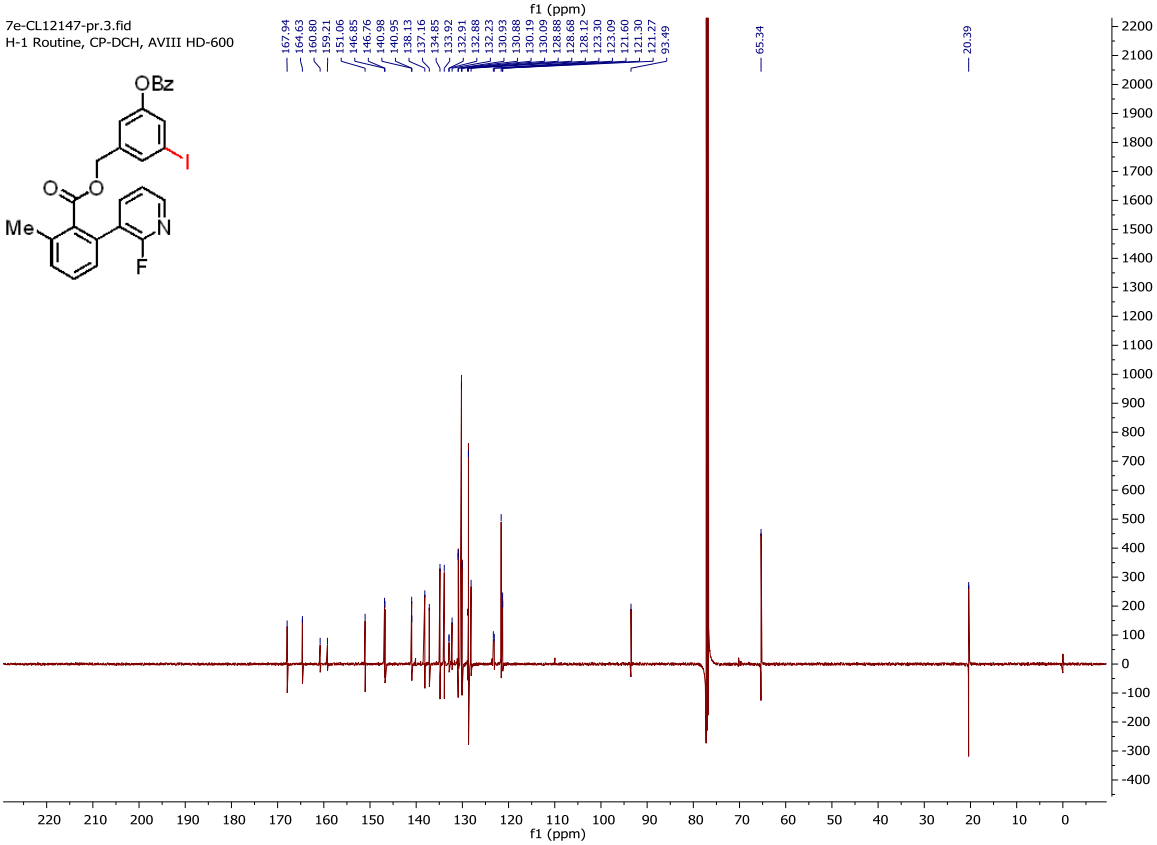

7c-CL12118-6.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Cl
I
O
O
Me
N
F
8.14
8.13
7.70
7.68
7.67
7.56
7.54
7.46
7.44
7.42
7.41
7.33
7.32
7.20
7.19
7.17
7.16
7.15
7.07
7.05
5.12
2.48
1.00
1.05
1.02
0.98
1.01
1.07
1.01
1.00
0.99
2.06
3.05
f1 (ppm)

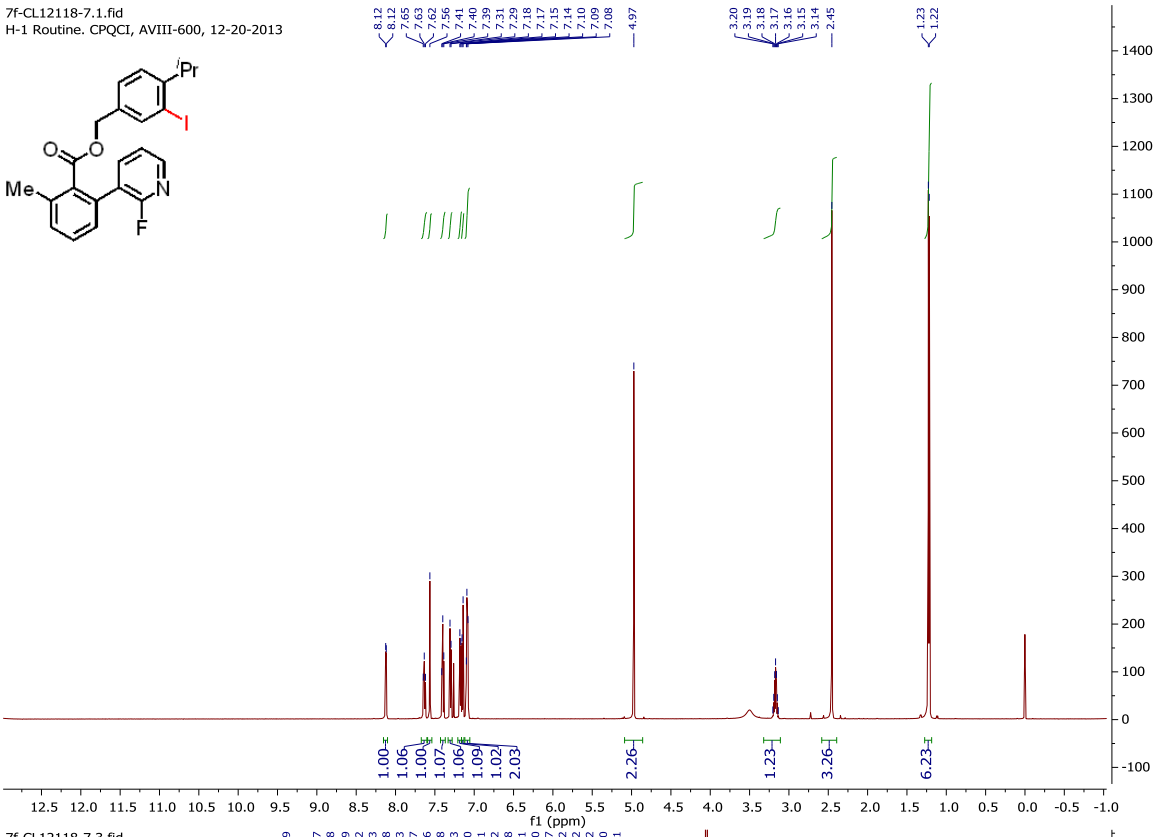

7c-CL12118-6.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Cl
I
O
O
Me
N
F
167.87
160.76
159.17
146.65
146.55
141.18
141.16
138.79
138.56
137.13
134.78
133.80
132.75
132.73
132.25
131.16
130.98
130.12
128.11
128.10
123.37
123.16
121.29
121.26
91.31
63.34
20.37
f1 (ppm)

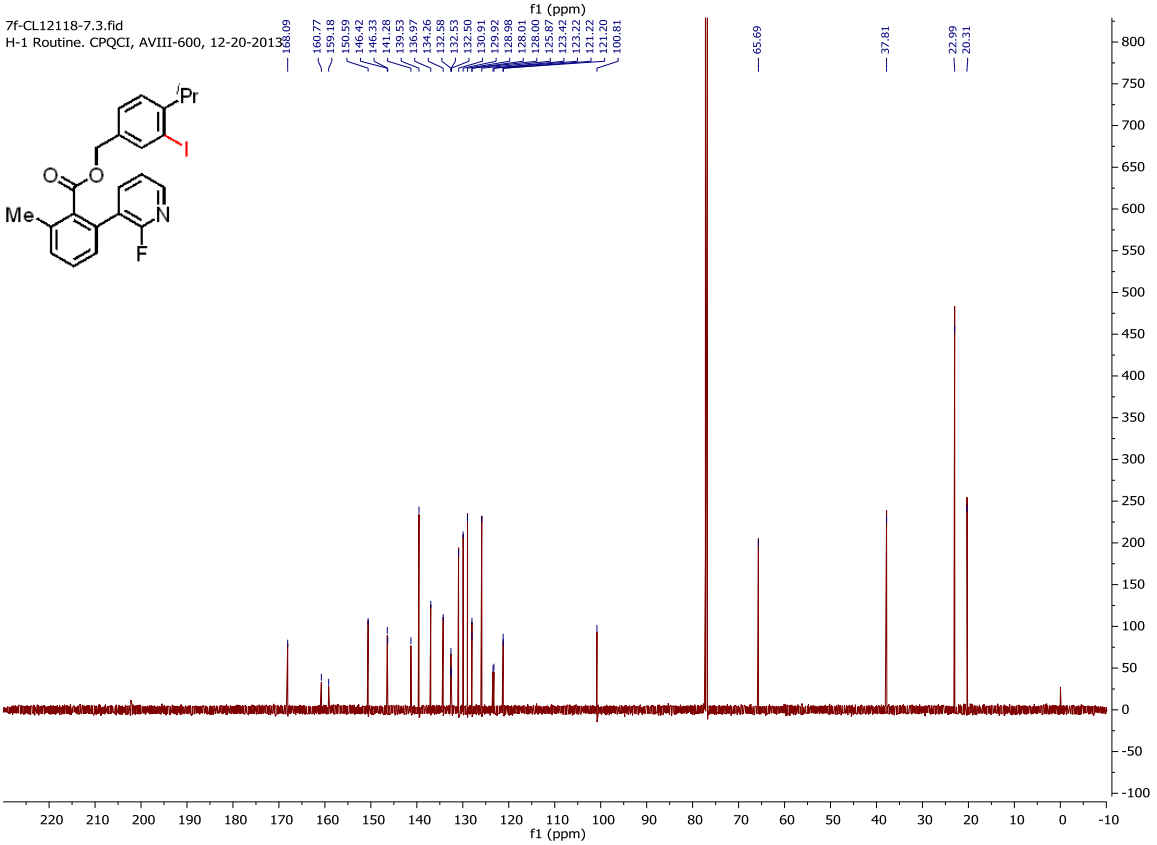

7d-CL12118-3.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
Me
N
F
I
8.15
8.14
7.65
7.64
7.62
7.47
7.42
7.40
7.39
7.31
7.30
7.23
7.18
7.17
7.14
7.13
7.12
6.89
4.96
2.45
2.27
1.00
1.08
1.05
1.20
1.23
0.97
1.20
0.99
0.99
1.94
2.95
3.03
f1 (ppm)

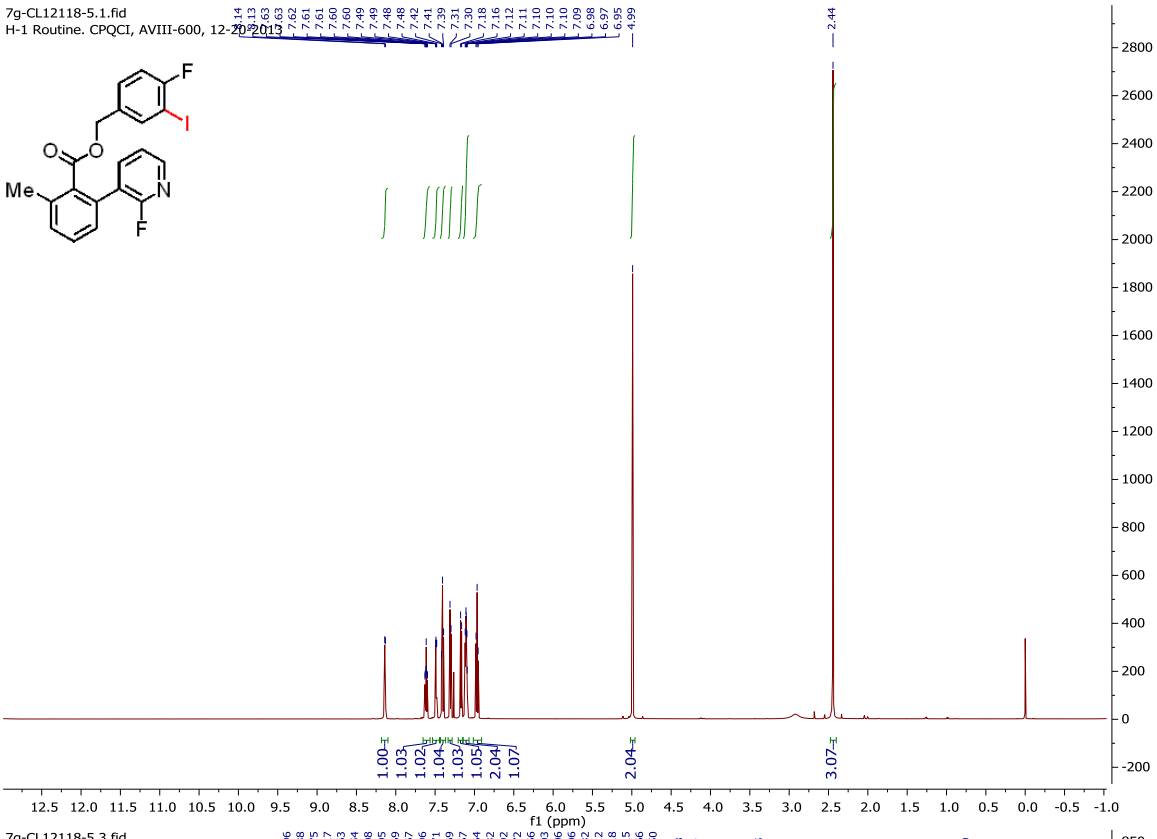

7d-CL12118-3.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
Me
N
F
I
168.01
160.73
159.14
146.42
146.33
141.23
141.24
140.42
139.05
137.99
137.04
136.69
134.45
132.57
132.55
132.46
130.94
129.98
128.77
128.04
128.04
127.64
123.44
123.24
121.25
94.14
66.00
20.80
20.32
f1 (ppm)

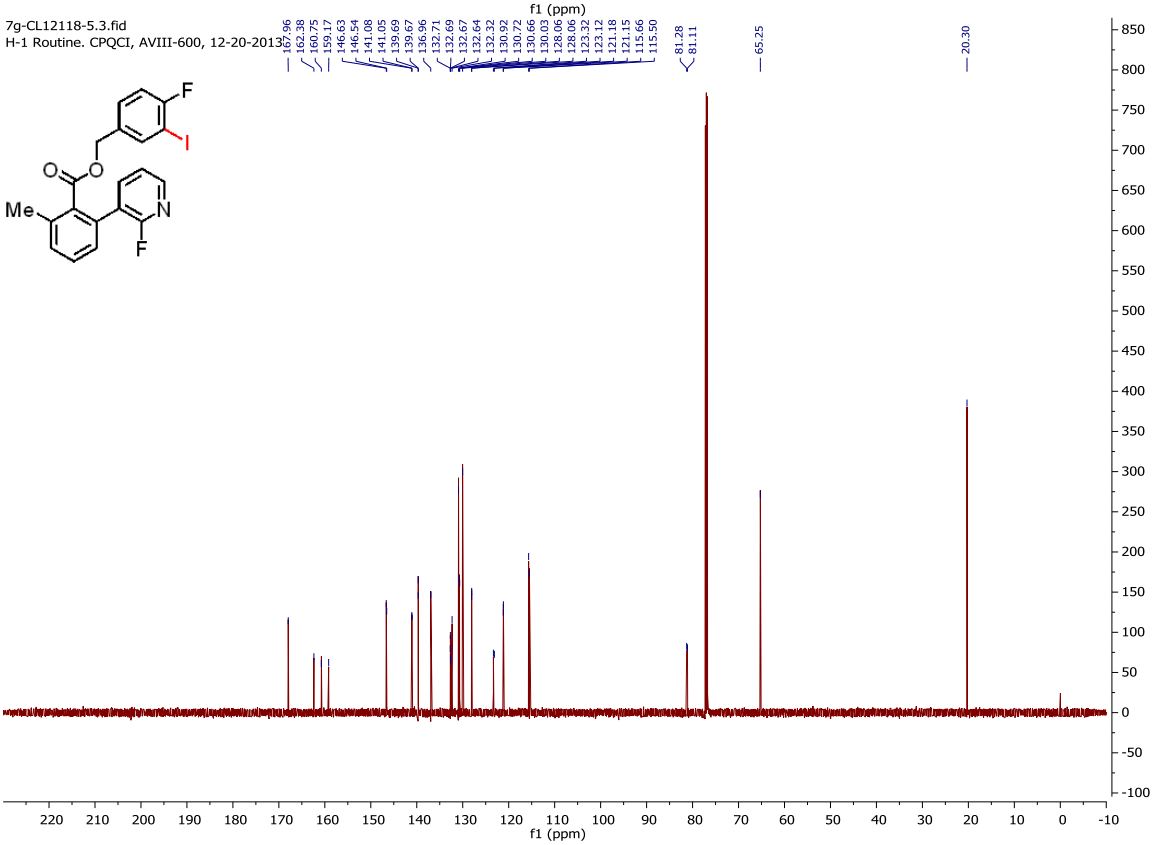

7e-CL12147-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
OBz
O
O
Me
N
F
I
1.99
1.00
2.20
3.18
1.11
0.98
1.04
1.06
0.99
0.97
1.98
3.06
f1 (ppm)

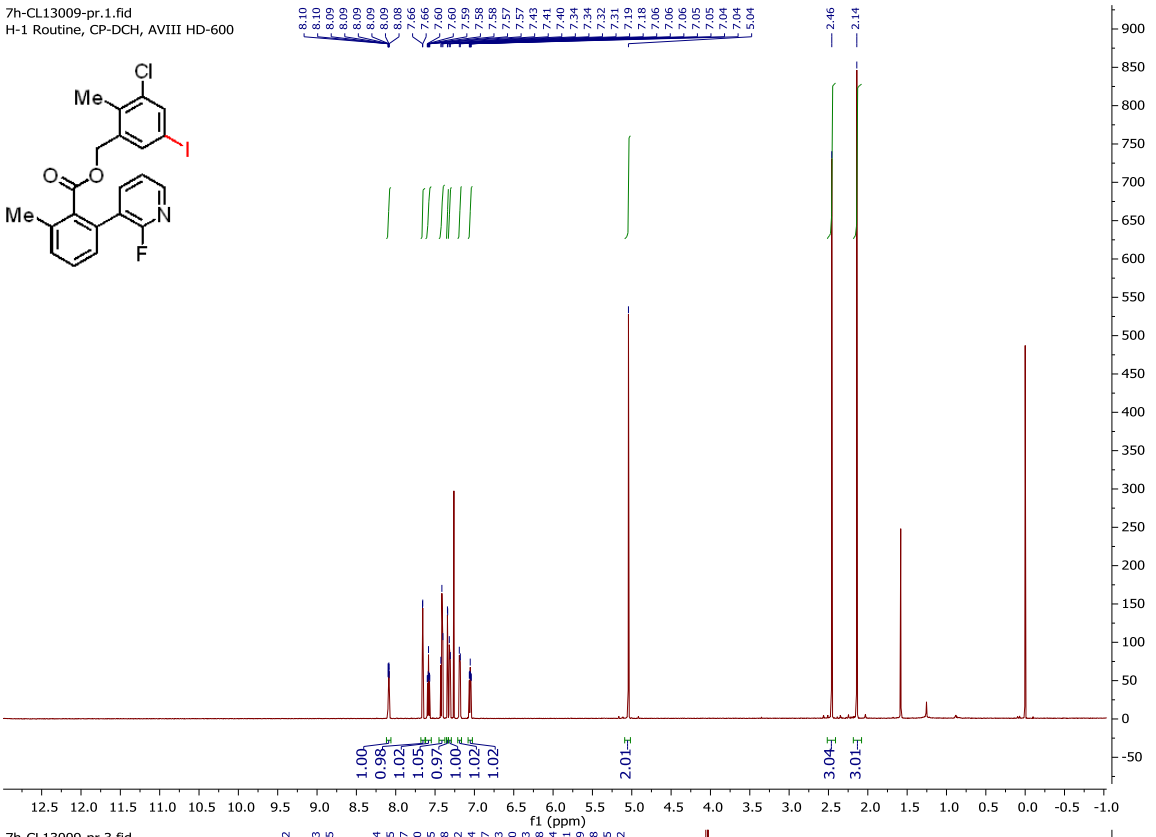

7e-CL12147-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
OBz
O
O
Me
N
F
I
f1 (ppm)

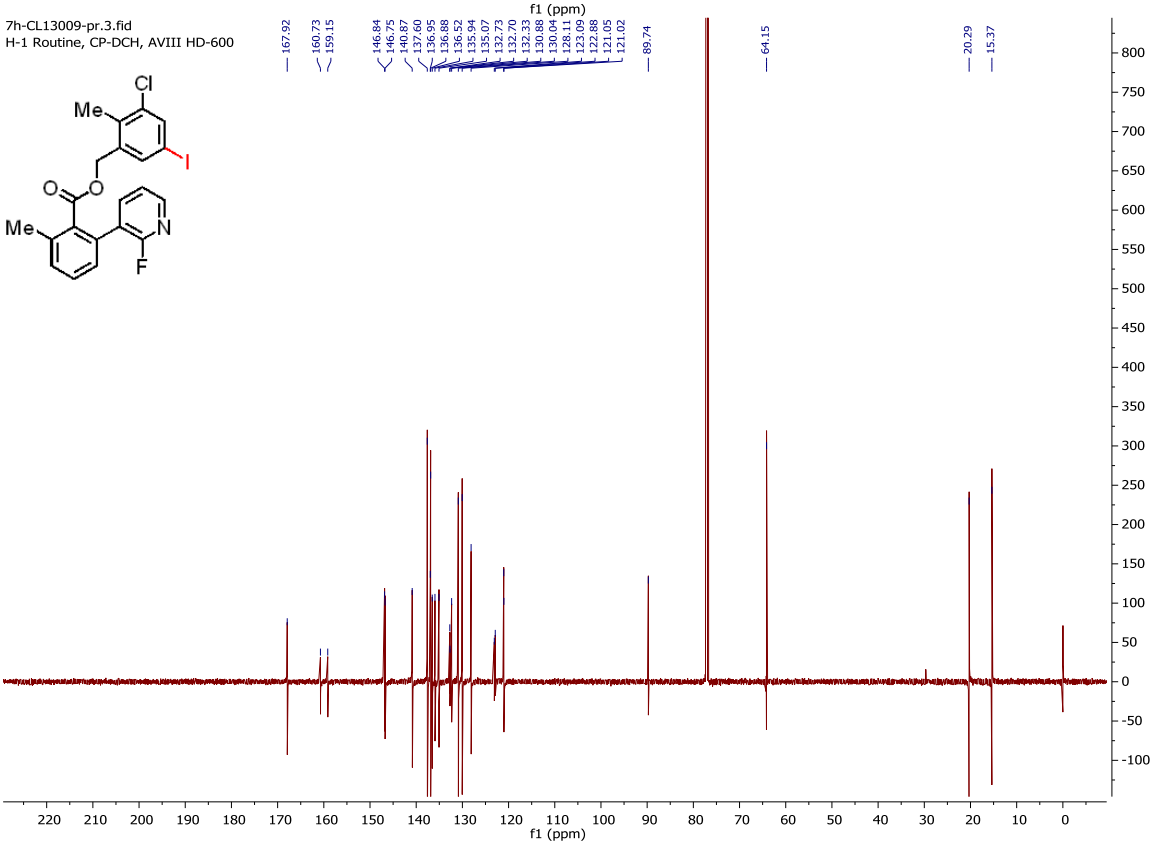

7f-CL12118-7.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
iPr
I
O
O
Me
N
F
f1 (ppm)

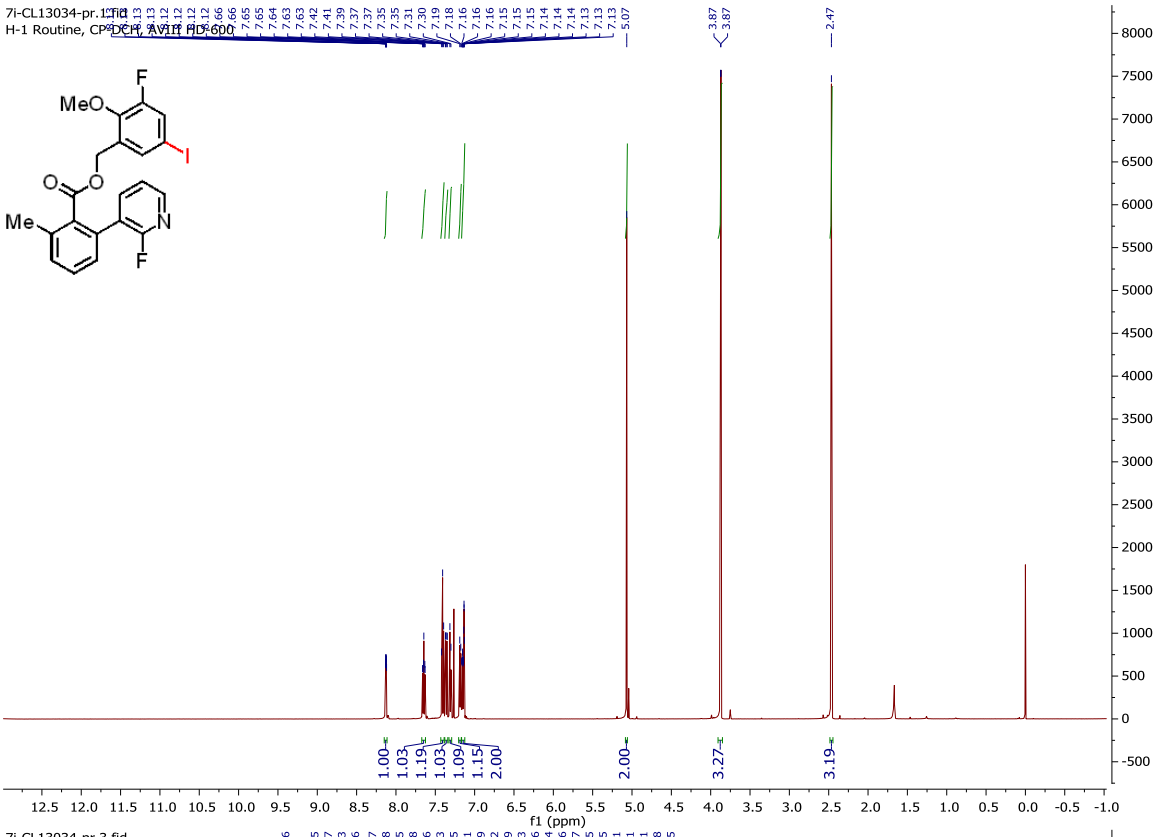

7f-CL12118-7.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
iPr
I
O
O
Me
N
F
f1 (ppm)

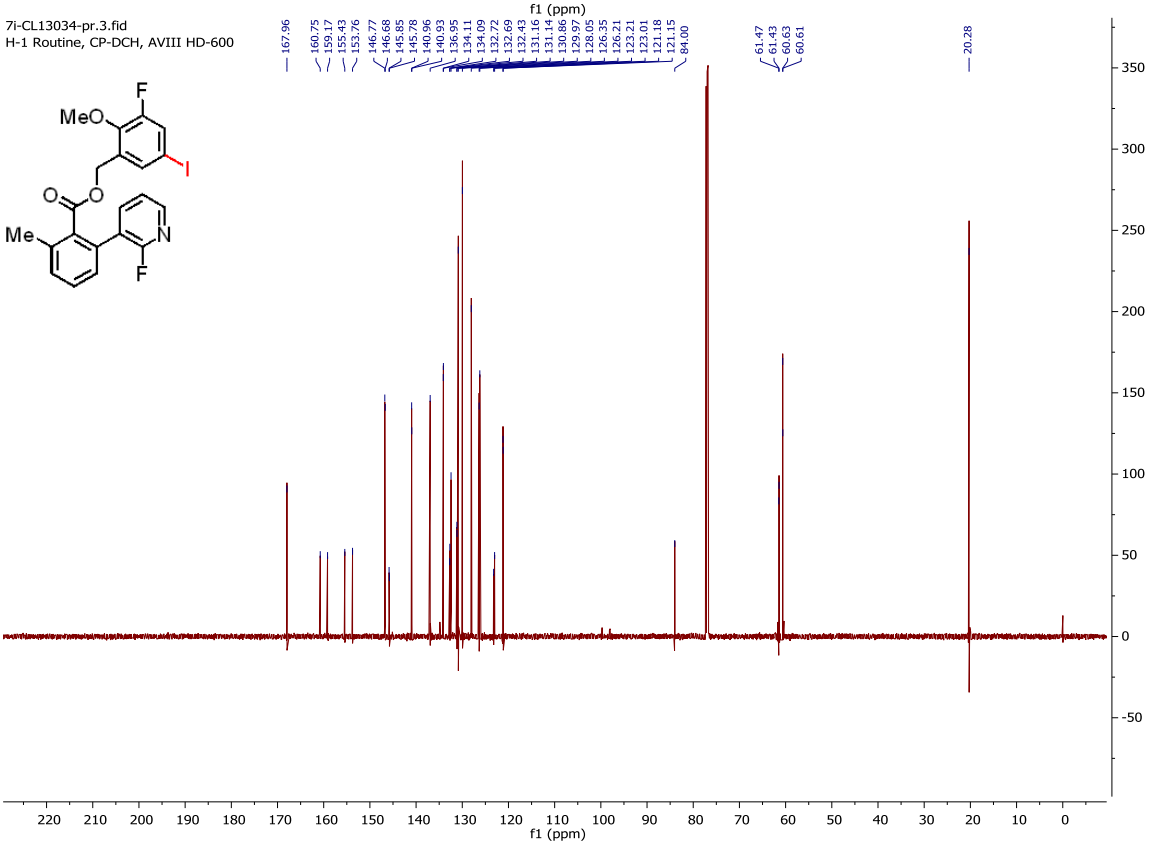

7g-CL12118-5.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
F
I
O
O
Me
N
F
f1 (ppm)

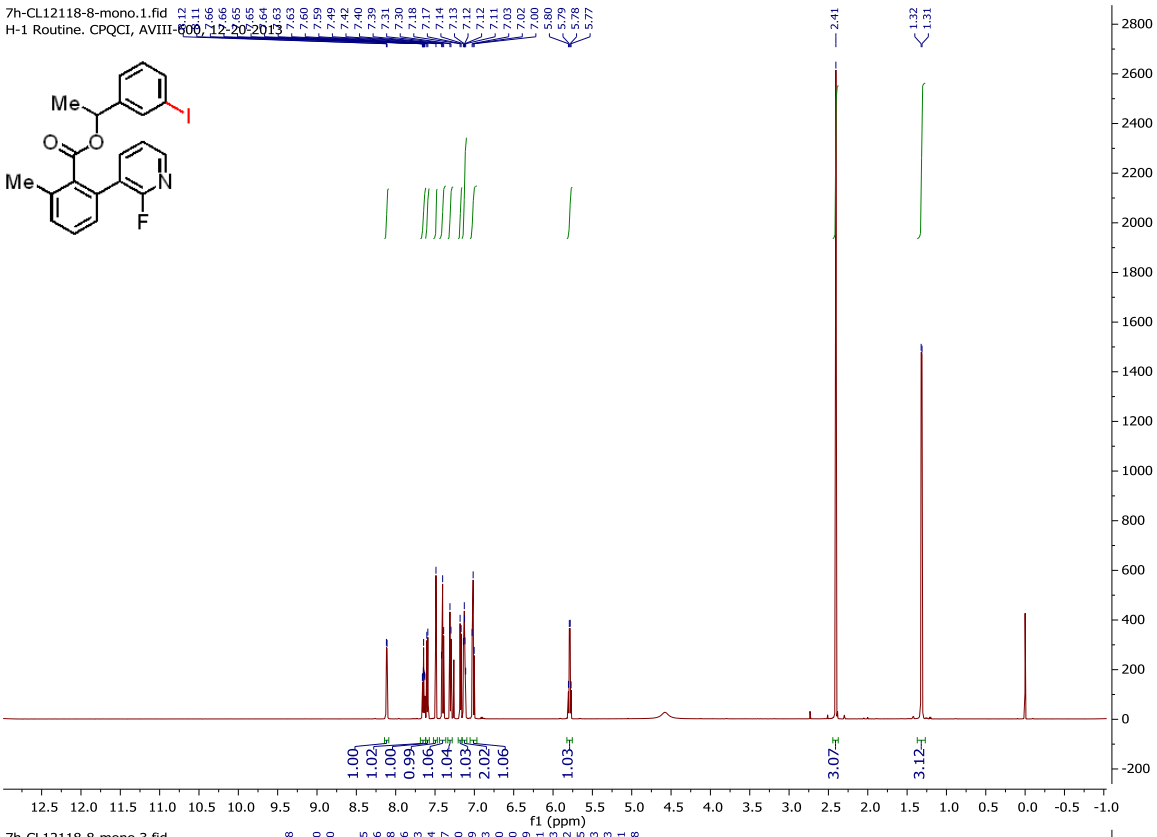

7g-CL12118-5.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
F
I
O
O
Me
N
F
f1 (ppm)

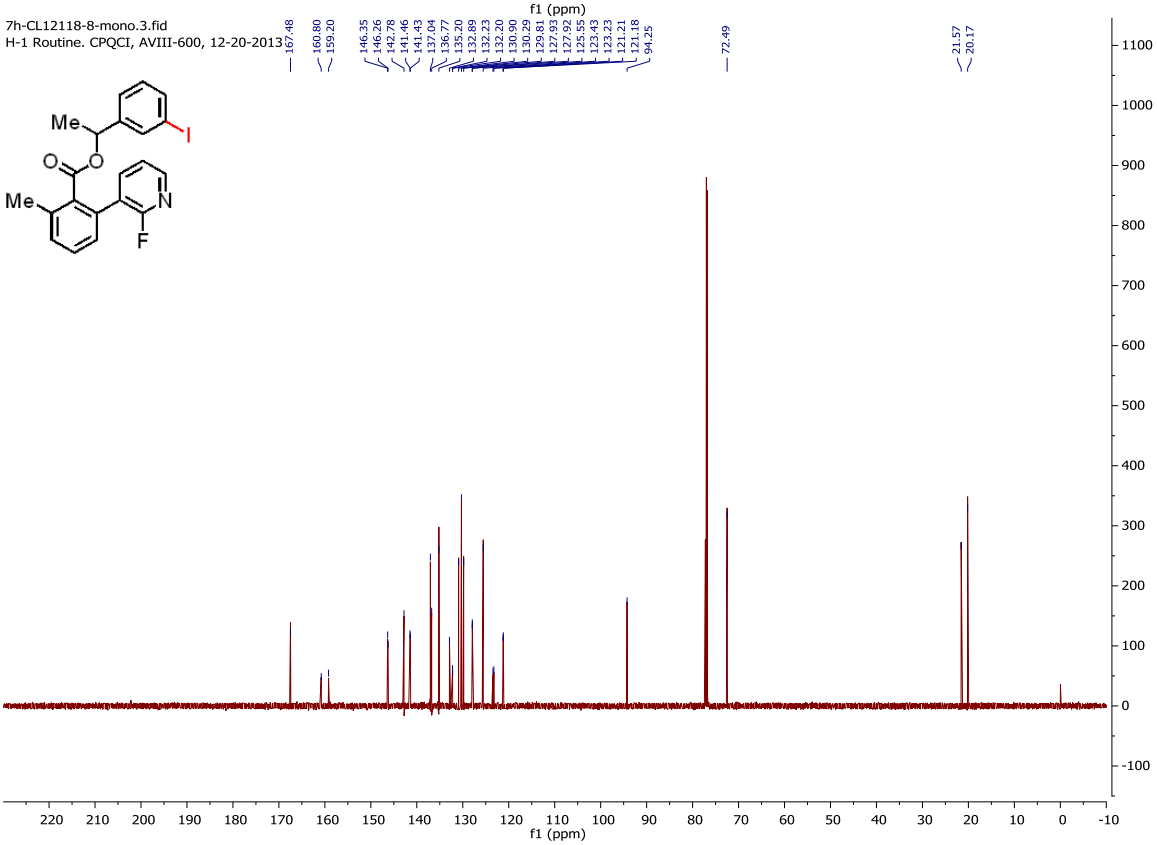

7h-CL13009-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
Cl
Me
I
O
O
Me
N
F
8.10 8.10 8.09 8.09 8.09 8.09 8.09 8.08 8.08 7.66 7.66 7.60 7.60 7.59 7.58 7.58 7.57 7.57 7.43 7.41 7.40 7.34 7.34 7.32 7.31 7.19 7.18 7.06 7.06 7.06 7.05 7.05 7.04 7.04 7.04 5.04
2.46
2.14
1.00 0.98 1.02 1.05 0.97 1.00 1.02 1.02
2.01
3.04
3.01
f1 (ppm)

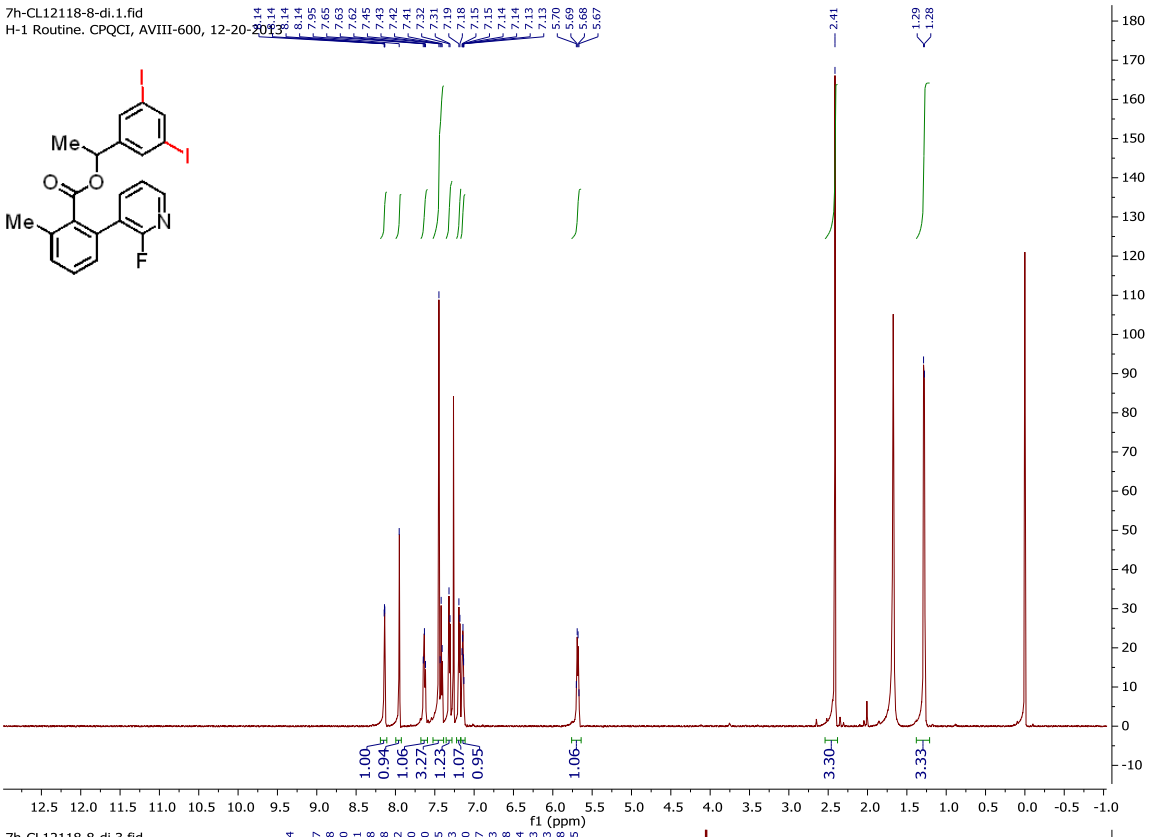

7h-CL13009-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
Cl
Me
I
O
O
Me
N
F
167.92
160.73
159.15
146.84
146.75
140.87
137.60
136.95
136.88
136.52
135.94
135.07
132.73
132.70
132.33
130.88
130.04
129.11
123.09
122.88
121.05
121.02
89.74
64.15
20.29
15.37
f1 (ppm)

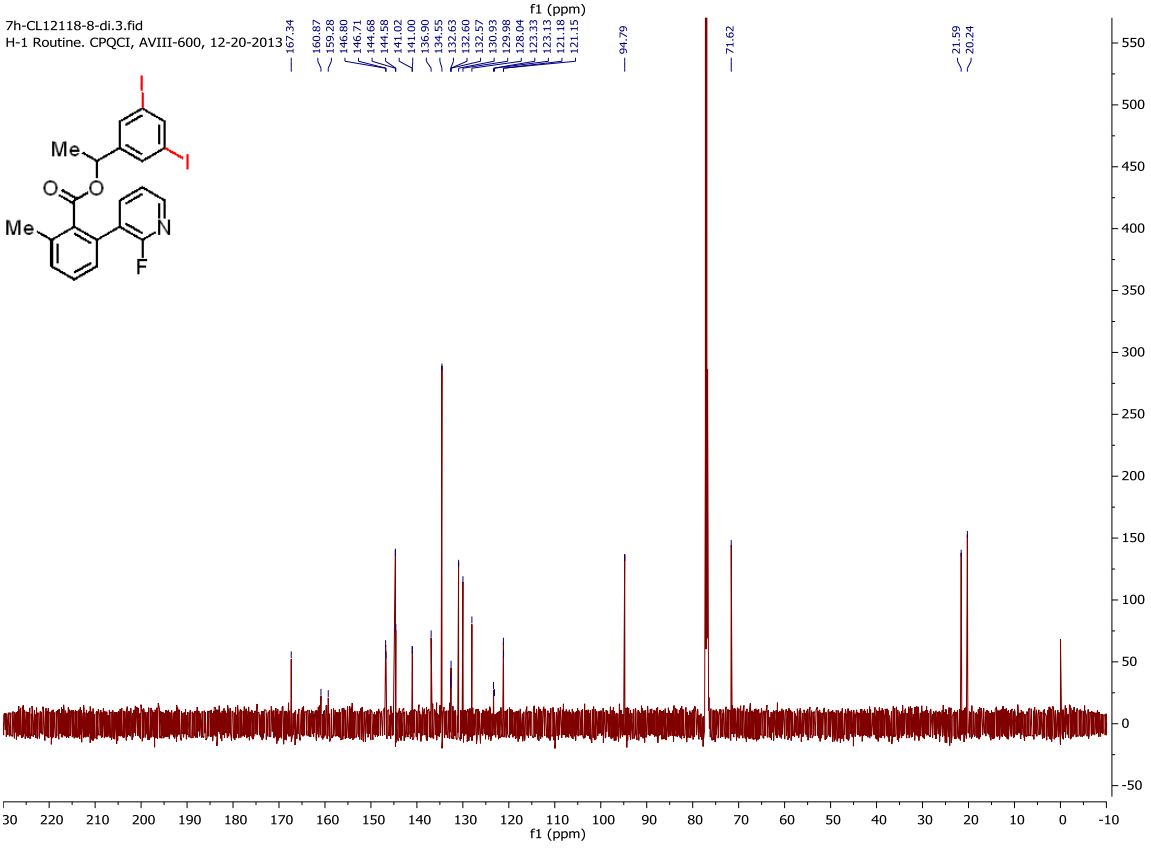

7i-CL13034-pr.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO
F
I
O
O
Me
N
F
5.07
3.87
3.87
2.47
1.00
1.03
1.19
1.03
1.09
1.15
2.00
2.00
3.27
3.19
f1 (ppm)

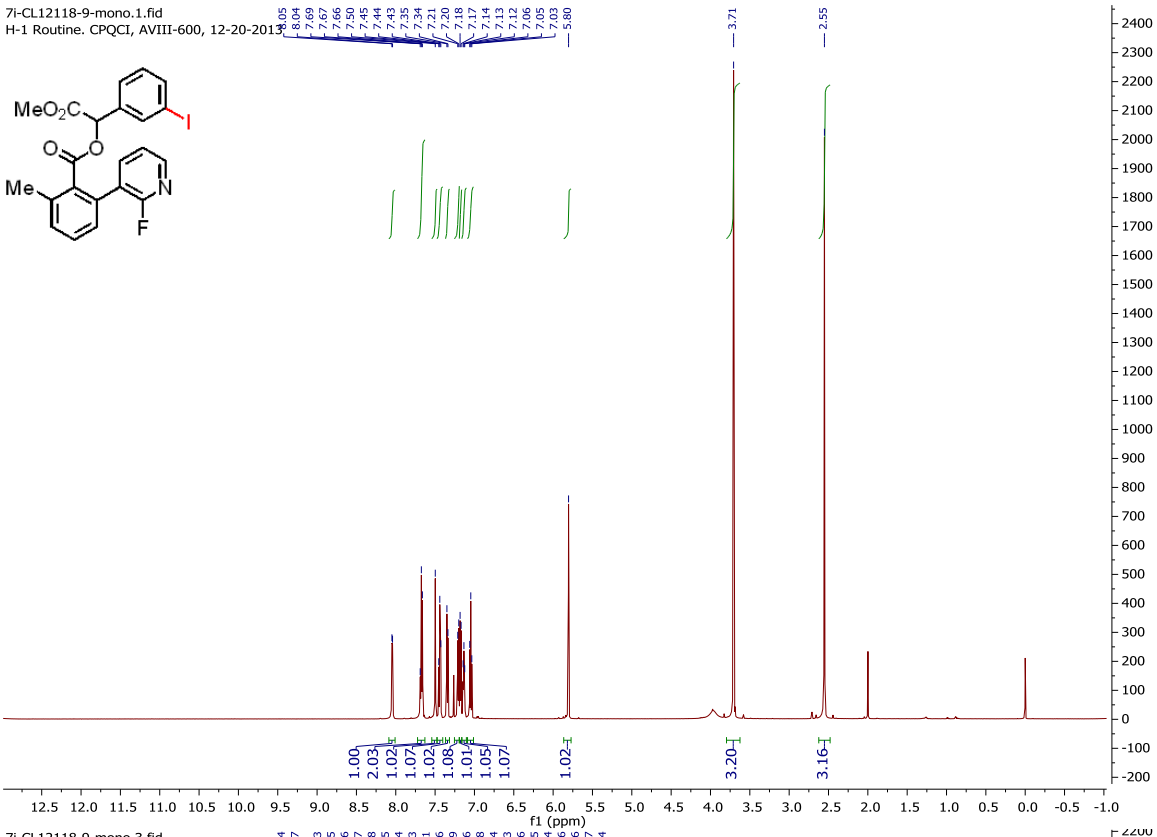

7i-CL13034-pr.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO
F
I
O
O
Me
N
F
167.96
160.75
159.17
155.43
153.76
146.77
146.68
145.85
145.78
140.86
140.93
136.95
134.11
134.09
132.72
132.69
132.43
131.16
131.14
130.86
129.97
128.05
126.35
126.21
123.21
123.01
121.18
121.15
84.00
61.47
61.43
60.63
60.61
20.28
f1 (ppm)

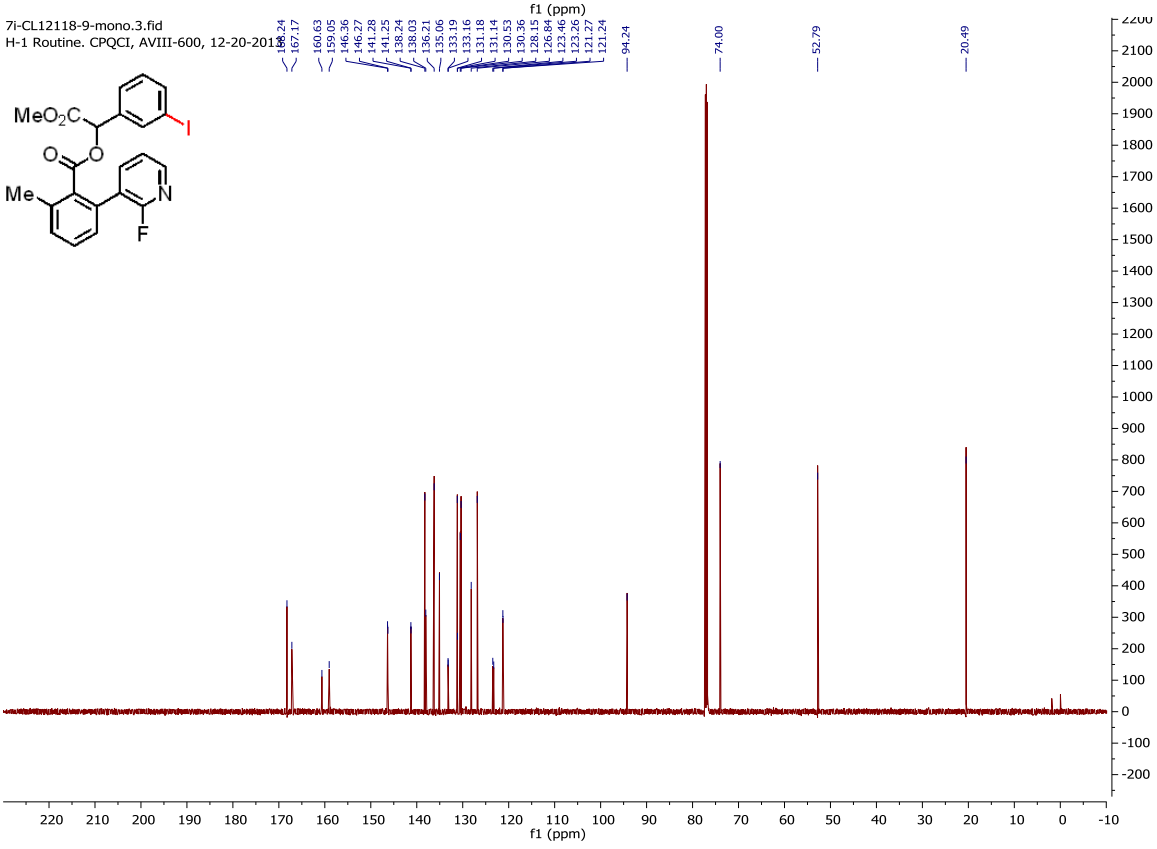

7h-CL12118-8-mono.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
Me
N
F
I
f1 (ppm)

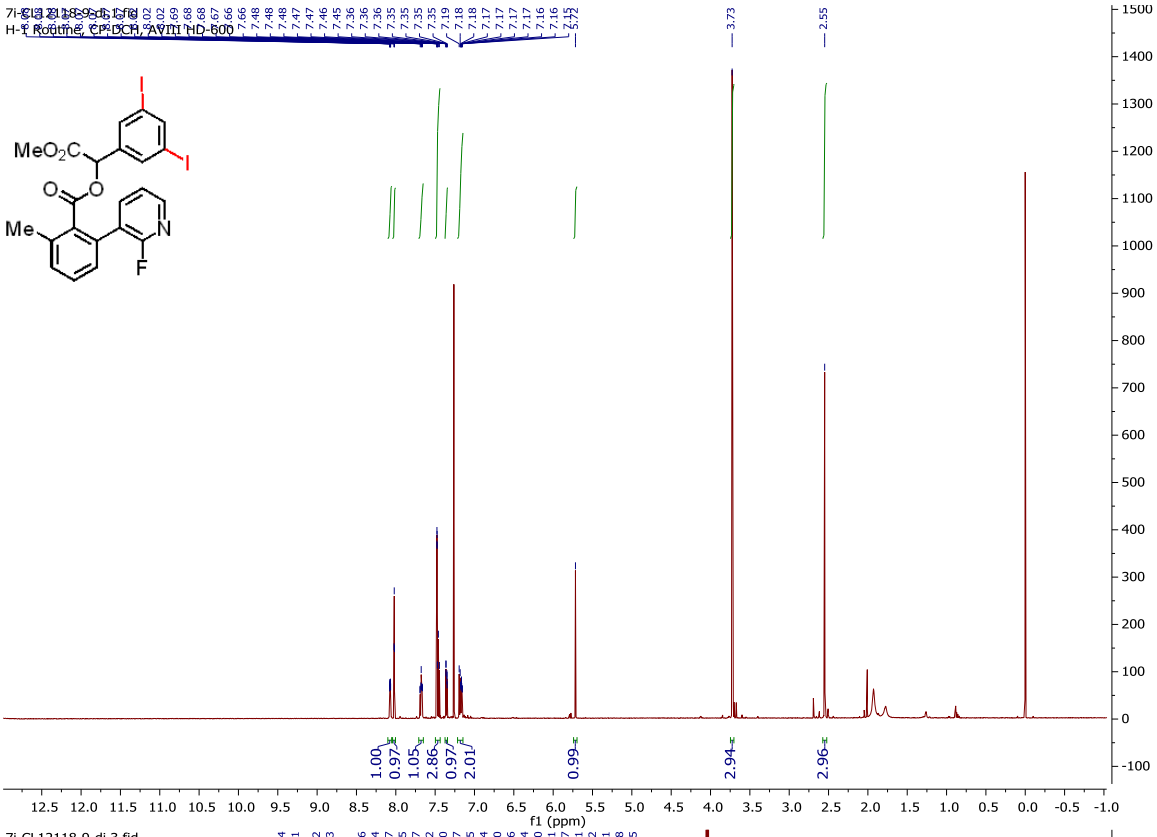

7h-CL12118-8-mono.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
Me
N
F
I
f1 (ppm)

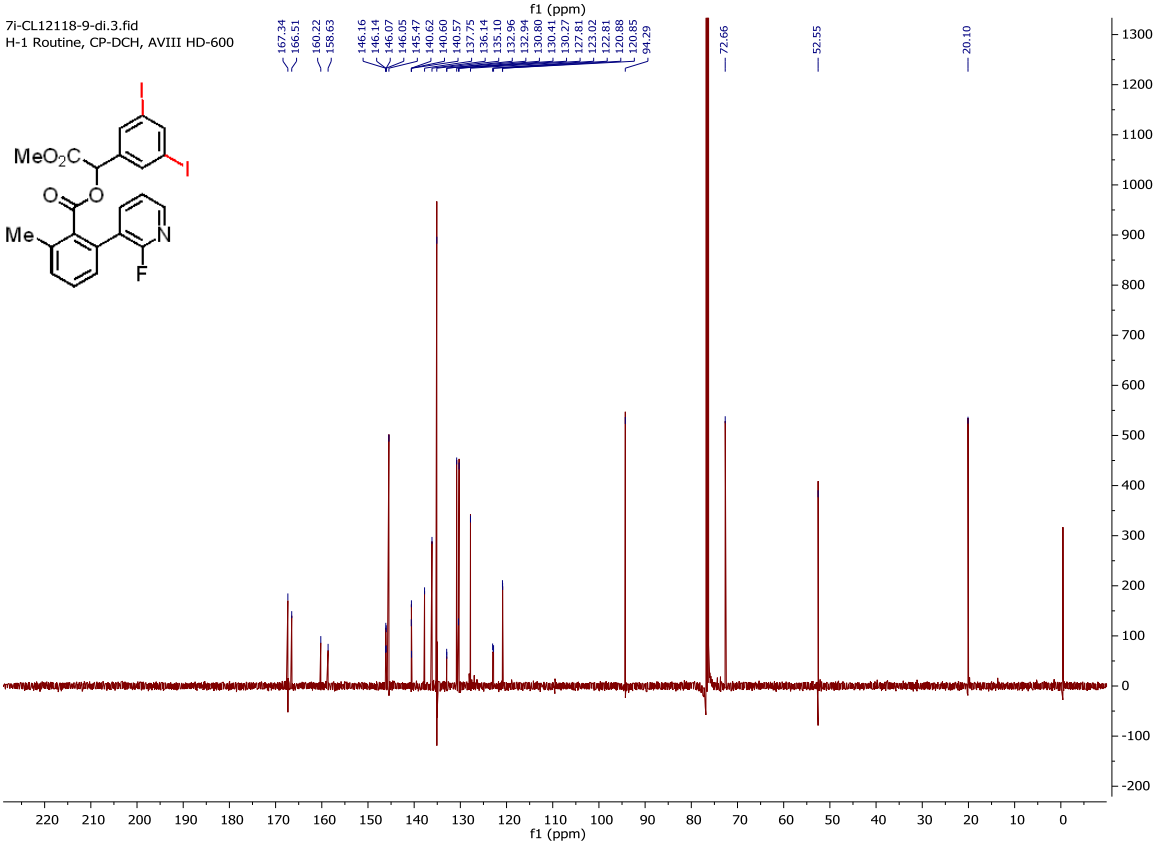

7h-CL12118-8-di.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
Me
N
F
I
8.14
8.14
8.14
7.95
7.65
7.63
7.62
7.45
7.43
7.42
7.41
7.32
7.31
7.19
7.18
7.15
7.15
7.14
7.14
7.13
7.13
5.70
5.69
5.68
5.67
2.41
1.29
1.28
1.00
0.94
1.06
3.27
1.23
1.07
0.95
1.06
3.30
3.33
f1 (ppm)

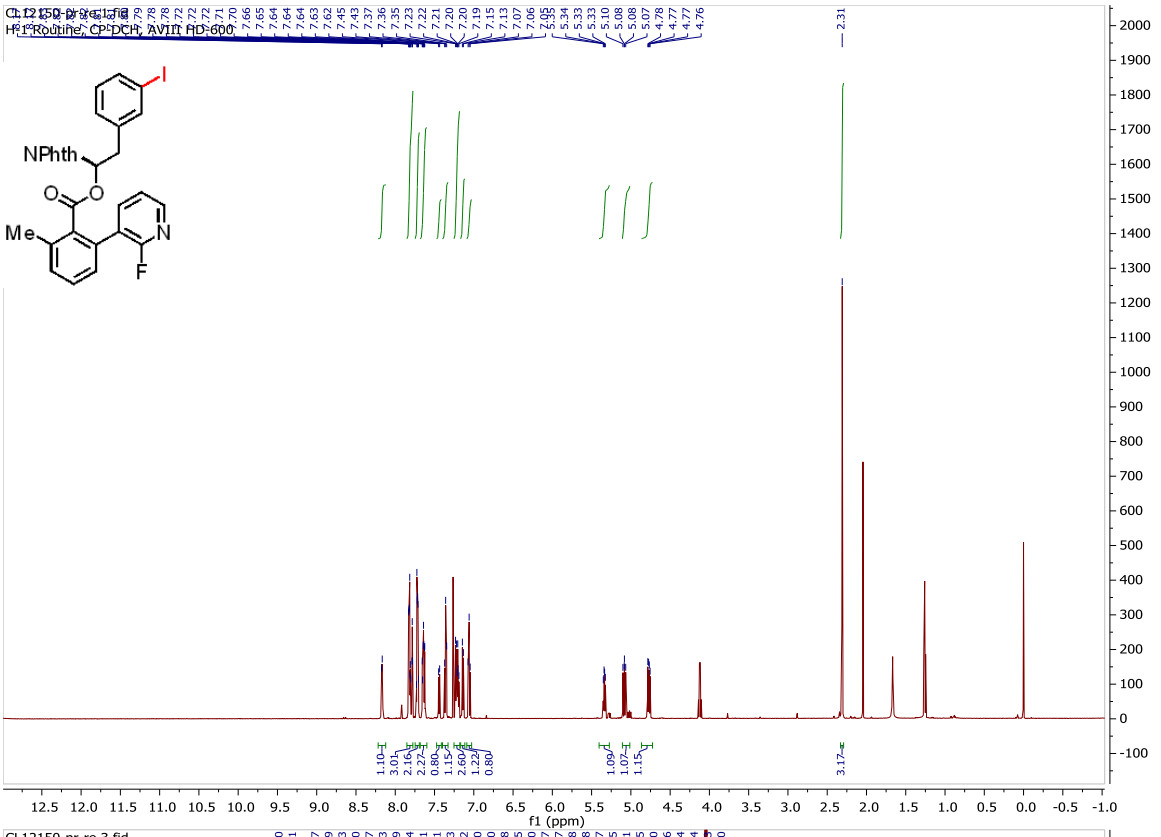

7h-CL12118-8-di.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
Me
O
O
Me
N
F
I
167.34
160.87
159.28
146.80
146.71
144.68
144.58
141.02
141.00
136.90
134.55
132.63
132.60
132.57
130.93
129.98
128.04
123.33
123.13
121.18
121.15
94.79
71.62
21.59
20.24
f1 (ppm)

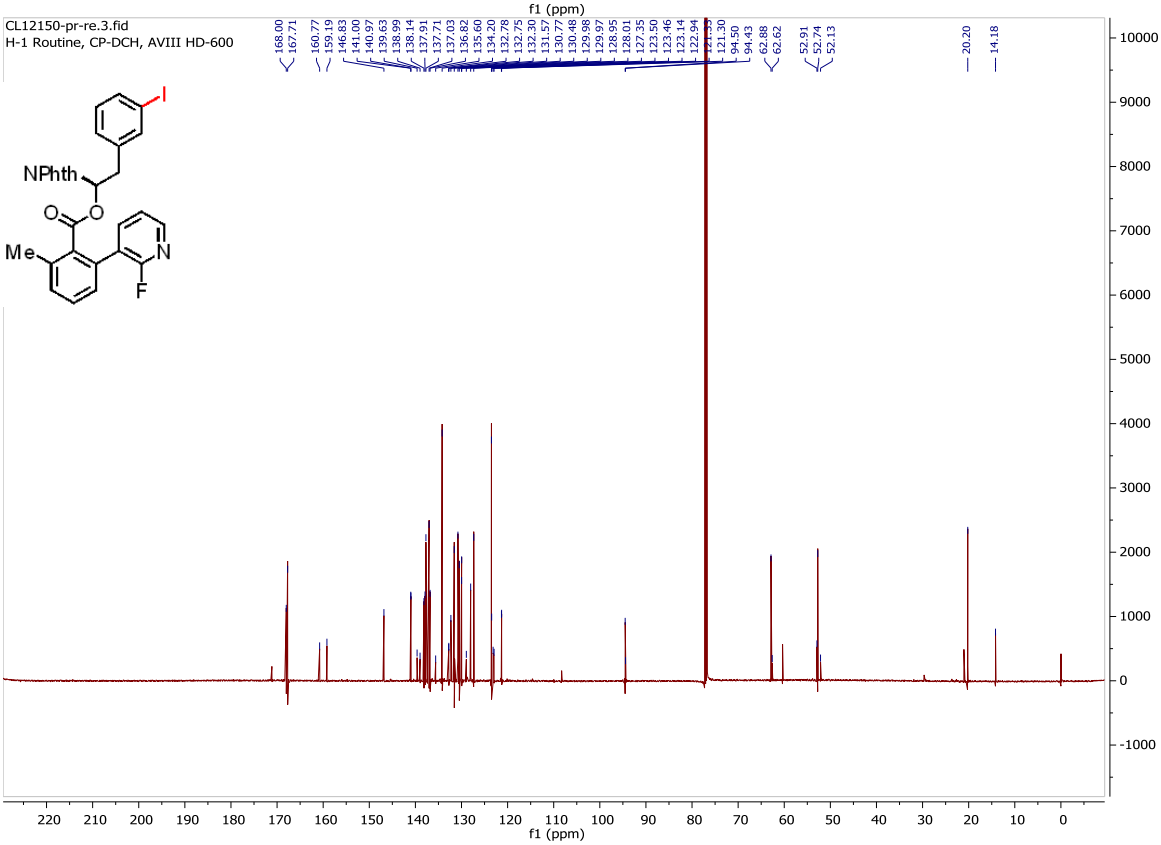

7i-CL12118-9-mono.1.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
MeO2C
O
O
Me
N
F
I
8.05
8.04
7.69
7.67
7.66
7.50
7.45
7.44
7.43
7.35
7.34
7.21
7.20
7.18
7.17
7.14
7.13
7.12
7.06
7.05
7.03
5.80
3.71
2.55
1.00
2.03
1.02
1.07
1.02
1.08
1.01
1.05
1.07
1.02
3.20
3.16
f1 (ppm)

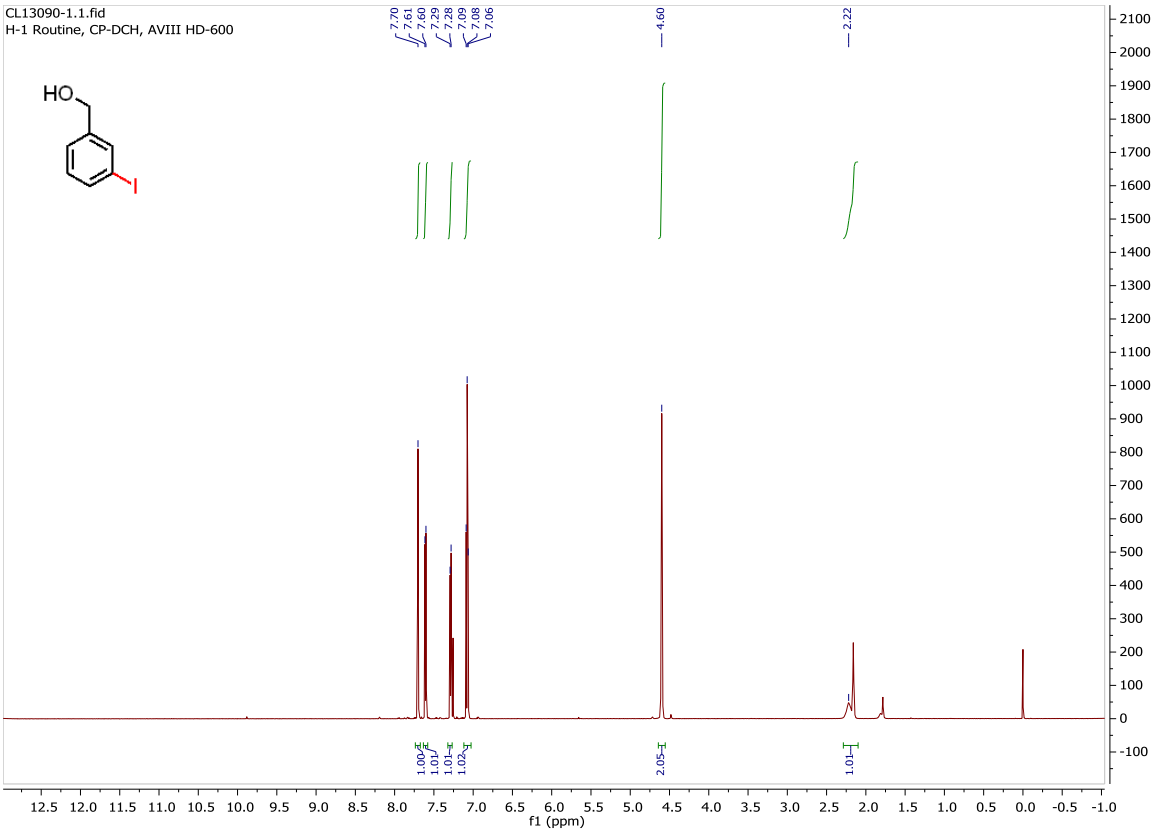

7i-CL12118-9-mono.3.fid
H-1 Routine. CPQCI, AVIII-600, 12-20-2013
MeO2C
O
O
Me
N
F
I
168.24
167.17
160.63
159.05
146.36
146.27
141.28
141.25
138.24
138.03
136.21
135.06
133.19
133.16
131.18
131.14
130.53
130.36
128.15
126.84
123.46
123.26
121.27
121.24
94.24
74.00
52.79
20.49
f1 (ppm)

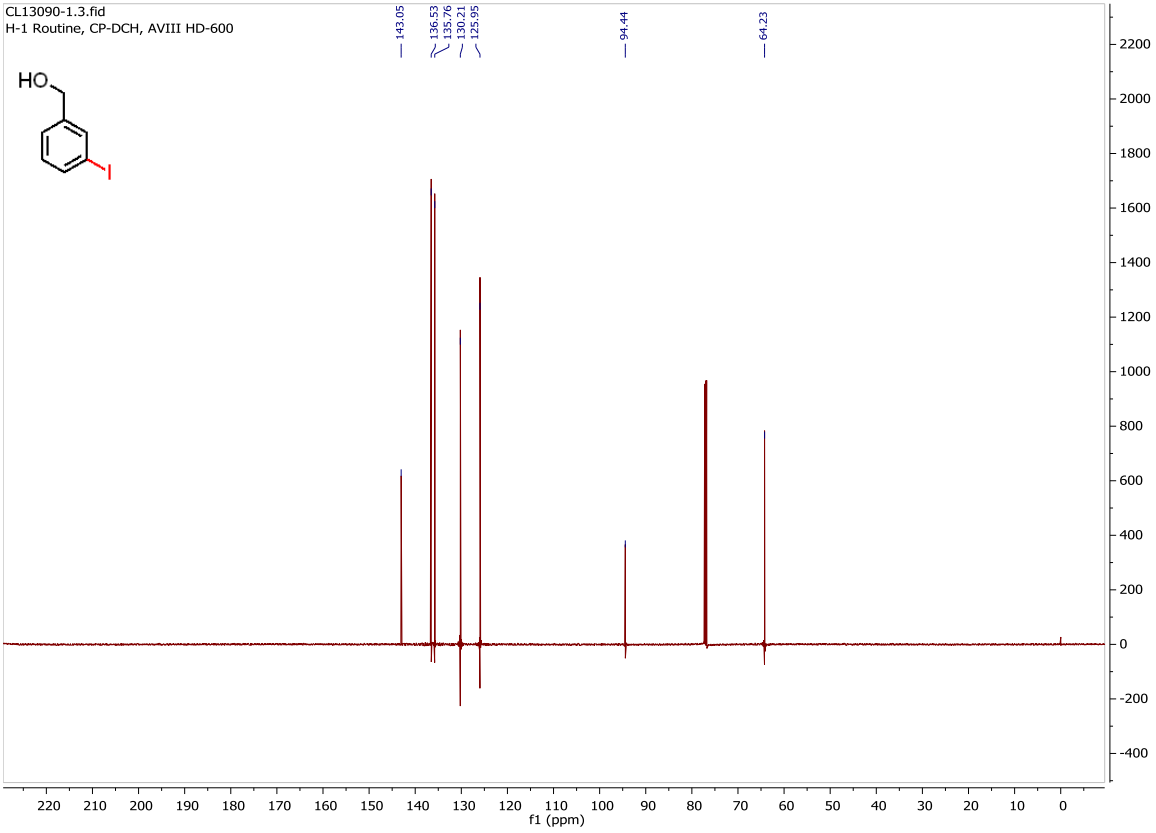

7i-CL12118-9-di.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO2C
O
O
Me
N
F
I
I
3.73
2.55
1.00
0.97
1.05
2.86
0.97
2.01
0.99
2.94
2.96
f1 (ppm)


7i-CL12118-9-di.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
MeO2C
O
O
Me
N
F
I
I
167.34
166.51
160.22
158.63
146.16
146.14
146.07
146.05
145.47
140.62
140.60
140.57
137.75
136.14
135.10
132.96
132.94
130.80
130.41
130.27
127.81
123.02
122.81
120.88
120.85
94.29
72.66
52.55
20.10
f1 (ppm)


CL12150-pr-re.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
NPhth
O
O
Me
I
N
F
f1 (ppm)


CL12150-pr-re.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
NPhth
O
O
Me
I
N
F
f1 (ppm)


CL13090-1.1.fid
H-1 Routine, CP-DCH, AVIII HD-600
HO
I
7.70
7.61
7.60
7.29
7.28
7.09
7.08
7.06
4.60
2.22
1.00
1.01
1.01
1.02
2.05
1.01
f1 (ppm)


CL13090-1.3.fid
H-1 Routine, CP-DCH, AVIII HD-600
HO
I
143.05
136.53
135.76
130.21
125.95
94.44
64.23
f1 (ppm)