The Enantioselective α–Trifluoromethylation of Aldehydes via Photoredox Organocatalysis

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Supporting Information

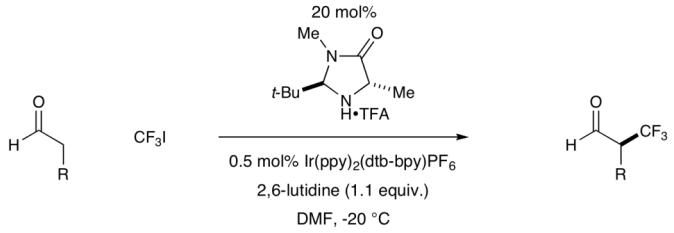
I. General Information. Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] Perfluoroalkyl iodides were purified by passing through a small pad of basic alumina. All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using force-flow chromatography on Silicycle silica gel according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates. TLC visualization was performed by fluorescence quenching, $KMnO_4$ or iodine stain. All yields reported are averages of at least two experimental runs.

^1H and ^{19}F NMR spectra were recorded on a Varian Inova 400 (400 MHz or 376 MHz) and are referenced relative to residual $CDCl_3$ proton signals at δ 7.27 ppm and $CFCl_3$ (δ 0.0 ppm) respectively. Data for ^1H and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, ap = apparent), integration, coupling constant (Hz) and assignment.

(1) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford, 1988.
(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1996**, *15*, 1518.
(3) Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

^{13}C spectra were recorded on a Bruker 500 (125 MHz) and are referenced relative to $CDCl_3$ at δ 77.23 ppm. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High Resolution Mass spectra were obtained from the Princeton University Mass Spectral Facility. Supercritical fluid chromatography (SFC) was performed on a Berger Minigram equipped with a diode array UV detector (λ = 214–258 nm) using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. High Pressure Liquid chromatography (HPLC) was performed on a Hewlett-Packard 1100 Series chromatographs using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. Optical rotations were measured on a Jasco P-1010 polarimeter with $[\alpha]_D$ values reported in degrees; concentration (c) is in g/100 mL.

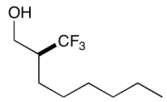
II. Enantioselective α–Trifluoromethylation of Aldehydes.



General procedure for enantioselective trifluoromethylation: To an oven-dried 13 mm × 100 mm borosilicate test tube equipped with a magnetic stir bar was added (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.2 mg, 0.200 equiv.) and $Ir(ppy)_2(dtb\text{-}bpy)PF_6$[4] (3.5 mg, 0.005 equiv.). The tube was fitted with a septum and degassed through alternating vacuum evacuation/argon backfill (×3) and was cooled to –78 °C before DMF (2.53 mL) was added. The resulting yellow solution was further degassed by alternating vacuum evacuation/argon backfill (×3) at -78 °C. Approximately

[4] **$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (1)** was prepared according to literature procedures: Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. *J. Am. Chem. Soc.* **2004**, *126*, 2763–2767.

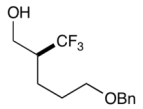
CF_3I (1.20 g, 8.1 equiv.)[5] was then condensed using a cold finger fitted with an 18 gauge needle. The aldehyde (0.76 mmol, 1.0 equiv.) and 2,6-lutidine (97.4 μL, 1.1 equiv.) were added by syringe and the test tube was placed in a -20 °C acetone-containing cryocool approximately 3 cm from a 26 W compact fluorescent light bulb (daylight GE Energy Smart™ 1600 lumens) that was inserted into a Pyrex glass tube insert. After 7.5-8 hours, the test tube was removed, cooled to -78 °C, and transferred by pre-cooled pipette to a round bottom flask containing CH_2Cl_2 (4.0 mL) at -78 °C. Cold CH_2Cl_2 (8.0 mL, -78 °C) was then used to transfer the remaining residue and $NaBH_4$ (288 mg, 10 equiv.) was added followed by cold MeOH (10 mL, -78 °C). The reaction was stirred for one hour at -78 °C before being quenched with saturated aqueous NH_4Cl solution (10 mL). The resulting solution was warmed to room temperature, extracted with Et_2O (×3), and the combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude oil was then purified by column chromatography on silica gel using the noted solvent mixture to furnish the desired alcohol product.



(S)-2-(Trifluoromethyl)octan-1-ol (Table 2, entry 1). Prepared following the general procedure outlined above using octanal (0.0984 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.3 g, 8.7 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7.5 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentanes to provide the title compound (0.120 g, 79% yield, 98% ee) as a clear oil. IR (thin film) 3367, 2930, 2861, 1468, 1253, 1162, 1133, 1103, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 3.81 (m, 2H, HO–C**H**$_2$), 2.22 (m, 1H, C**H**CF_3), 1.66–1.24 (m,

[5] Although the reaction efficiency and selectivity are moderately dependent on the amount of CF_3I employed in the reaction, effects were found to be minimal between 8-12 equivalents of CF_3I.

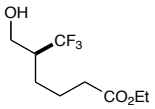
10H, –C**H**$_2$–), 0.89 (t, 3H, J = 6.8 Hz, –C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 128.2 (q, J^1 = 280.7 Hz), 60.1 (q, J^3 = 2.5 Hz), 45.6 (q, J^2 = 23.9 Hz), 31.8, 29.4, 27.0, 24.8 (q, J^3 = 1.3 Hz), 22.8, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.6 (d, J = 9.5 Hz); HRMS (ESI-TOF) calculated for $C_9H_{16}F_3$ $[M–OH]^+$ m/z 180.1126, found 180.1128. $[\alpha]_D^{23}$ = +8.2 (c = 1.10, $CHCl_3$); literature: $[\alpha]_D^{23}$ = +3.1 (c = 0.6, $CHCl_3$).[6] The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by preparative TLC. HPLC analysis of the 2-naphthoyl ester derivative (OD, 1% EtOH/hexanes, 1.0 mL/min, 254 nm) indicated 98% ee: t_R (minor) = 23.2 minutes, t_R (major) = 29.1 minutes.



(S)-5-(Benzyloxy)-2-(trifluoromethyl)pentan-1-ol (Table 2, entry 2). Prepared following the general procedure outlined above using 5-(benzyloxy)pentanal (0.162 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.2 g, 8.3 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7.5 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% EtOAc in hexanes to provide the title compound (0.156 g, 71% yield, 95% ee) as a clear oil. IR (thin film) 3418, 2944, 2867, 1455, 1361, 1254, 1160, 1126, 1093, 909, 736, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–7.26 (m, 5H, Ar**H**), 4.51 (s, 2H, OC**H**$_2$Ph), 3.81 (m, 2H, C**H**$_2$OH), 3.51 (m, 2H, C**H**$_2$OBn), 2.28 (m, 1H, C**H**CF_3), 1.81–1.57 (m, 5H, C**H**$_2$C**H**$_2$ and O**H**); ^{13}C NMR (125

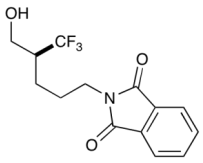
[6] Absolute stereochemical correlation made by comparison to:
Konno, T.; Umetani, H.; Kitazume, T. *J. Org. Chem.* **1997**, *62*, 137–150.

MHz, $CDCl_3$) δ: 138.3, 128.7, 128.0 (q, J^1 = 280.7 Hz), 127.9, 127.8, 73.3, 70.0, 59.9 (q, J^3 = 2.5 Hz), 45.3 (q, J^2 = 23.9 Hz), 26.9, 21.8 (q, J^3 = 2.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.6 (d, J = 9.5 Hz); HRMS (ESI-TOF) calculated for $C_{13}H_{18}F_3O_2$ $[M+H]^+$ m/z 262.1181, found 262.1182. $[\alpha]_D^{24}$ = +2.85 (c = 1.17, $CHCl_3$). HPLC analysis of the alcohol (AS, 3% EtOH, 1.0 mL/min, 214 nm) indicated 95% ee: t_R (major) = 11.1 minutes, t_R (minor) = 12.9 minutes.

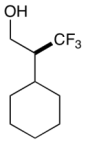


(S)-Ethyl 6,6,6-trifluoro-5-(hydroxymethyl)hexanoate (Table 2, entry 3). Prepared following the general procedure outlined above using ethyl 6-oxohexanoate (0.127 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.3 g, 8.4 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7.5 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 35% EtOAc in hexanes to provide the title compound (0.161 g, 88% yield, 96% ee) as a clear oil. IR (thin film) 3454, 2970, 1733, 1465, 1376, 1255, 1152, 1118, 1040, 857 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.15 (q, 2H, J = 7.2 Hz, $OC\mathbf{H_2}CH_3$), 3.85 (m, 2H, $C\mathbf{H_2}OH$), 2.36 (t, 2H, J = 6.8 Hz, $C\mathbf{H_2}CO_2Et$), 2.25 (m, 1H, $C\mathbf{H}CF_3$), 2.03 (bs, 1H, O**H**), 1.86–1.58 (m, 4H, $C\mathbf{H_2}C\mathbf{H_2}CH_2CO_2Et$), 1.26 (t, 3H, J = 7.2 Hz, $OCH_2C\mathbf{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.7, 127.8 (q, J^1 = 280.4 Hz), 60.8, 59.6 (q, J^3 = 2.5 Hz), 45.3 (q, J^2 = 23.9 Hz), 34.0, 24.2 (q, J^3 = 2.5 Hz), 21.9, 14.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.6 (d, J = 9.5 Hz); HRMS (ESI-TOF) calculated for $C_9H_{16}F_3O_3$ $[M+H]^+$ m/z 228.0973, found 228.0975. $[\alpha]_D^{2\,3}$ = +3.23 (c = 1.35, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in*

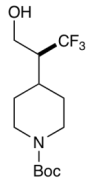
vacuo and purified by preparative TLC. SFC analysis of the 2-naphthoyl ester derivative (ODH, 10% *i*-PrOH, 1.0 mL/min, 220 nm) indicated 96% ee: t_R(major) = 2.8 minutes, t_R (minor) = 3.4 minutes.



(S)-2-(5,5,5-Trifluoro-4-(hydroxymethyl)pentyl)isoindoline-1,3-dione (Table 2, entry 4). Prepared following the general procedure outlined above using 5-(1,3-dioxoisoindolin-2-yl)pentanal (0.182 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethyl-imidazolidin-4-one·TFA (43.4 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.3 g, 8.6 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7.5 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 40% EtOAc and 2% MeOH in hexanes to provide the title compound (0.186 g, 79% yield, 99% ee) as a clear oil. IR (thin film) 3463, 2948, 1772, 1701, 1439, 1397, 1361, 1242, 1164, 1134, 1117, 1036, 1020, 718 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.85 (m, 2H, Ar**H**), 7.73 (m, 2H, Ar**H**), 3.90 (AB, 1H, *J* = 11.9, 5.2 Hz, C**H**HOH), 3.74 (AB, 1H, *J* = 11.9, 4.4 Hz, C**H**HOH), 3.73 (t, 2H, *J* = 7.2 Hz, C$\mathbf{H_2}$–NPhth), 2.32 (m, 1H, C**H**CF_3), 1.92–1.61 (m, 4H, C$\mathbf{H_2}$C$\mathbf{H_2}$CHCF_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.7, 134.3, 132.1, 127.8 (q, J^1 = 280.6 Hz), 123.5, 59.9 (q, J^3 = 3.8 Hz), 45.1 (q, J^2 = 24.3 Hz), 37.7, 26.0, 22.0 (q, J^3 = 2.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.4 (d, *J* = 9.2 Hz); HRMS (ESI-TOF) calculated for $C_{14}H_{15}F_3O_3N$ $[M+H]^+$ m/z 302.0926, found 302.0926. $[\alpha]_D^{22}$ = +3.00 (c = 0.97, $CHCl_3$). SFC analysis of the alcohol (ASH, 5–20% MeOH gradient over 9.0 minutes then isocratic 20% MeOH, 1.0 mL/min, 220 nm) indicated 99% ee: t_R(major) = 8.4 minutes, t_R (minor) = 9.4 minutes.

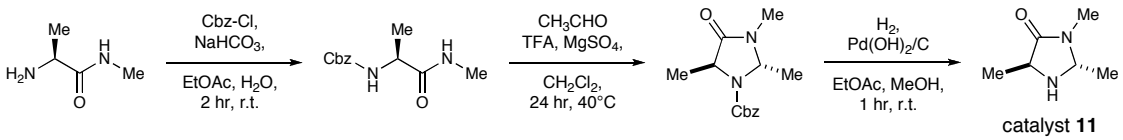


(S)-2-Cyclohexyl-3,3,3-trifluoropropan-1-ol (Table 2, entry 5). Prepared following the general procedure outlined above using 2-cyclohexylacetaldehyde (0.0966 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.2 g, 8.1 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7.5 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 15% Et_2O in pentanes to provide the title compound (0.105 g, 70% yield, 99% ee) as a clear oil. IR (thin film) 3344, 2930, 2857, 1452, 1363, 1254, 1159, 1112, 1045 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 3.90 (ABX, 1H, J = 11.7, 6.4 Hz, HO–C**H**H), 3.83 (ABX, 1H, J = 11.7, 3.2 Hz, HO–C**H**H), 2.14 (m, 1H, C**H**CF_3), 1.84–1.64 (m, 6H, *c*-Hex**H**), 1.60 (bs, 1H, O**H**), 1.31–1.08 (m, 5H, *c*-Hex**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 128.3 (q, J^1 = 283.1 Hz), 58.9 (q, J^3 = 3.8 Hz), 51.1 (q, J^2 = 22.7 Hz), 35.6 (q, J^3 = 2.5 Hz), 29.8 (q, J^4 = 1.3 Hz), 26.9, 26.7, 26.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -65.5 (d, J = 10.3 Hz); HRMS (ESI-TOF) calculated for $C_9H_{14}F_3$ $[M–OH]^+$ m/z 178.0970, found 178.0970. $[\alpha]_D^{22}$ = +1.85 (c = 0.90, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by preparative TLC. HPLC analysis of the 2-naphthoyl ester derivative (OD, 2% EtOH, 1.0 mL/min, 254 nm) indicated 99% ee: t_R (major) = 7.6 minutes, t_R (minor) = 10.0 minutes.



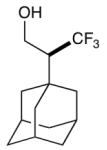
(S)-*tert*-Butyl-4-(1,1,1-trifluoro-3-hydroxypropan-2-yl)piperidine-1-carboxylate (Table 2, entry 6). Prepared following the general procedure outlined above using *tert*-butyl 4-(2-oxoethyl)piperidine-1-carboxylate (0.175 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.2 g, 8.9 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7.5 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 10% Et_2O in pentanes to provide the title compound (0.159 g, 70% yield, 97% ee) as a clear oil. IR (thin film) 3432, 2978, 1668, 1429, 1367, 1249, 1160, 868 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 4.16 (bs, 2H, C**H**$_2$–NBoc), 3.90 (ABX, 1H, *J* = 11.7, 5.2 Hz, HO–C**H**H), 3.86 (ABX, 1H, *J* = 11.7, 4.8 Hz, HO–C**H**H), 2.67 (bs, 2H, C**H**$_2$–NBoc), 2.18 (m, 1H, C**H**CF_3), 1.98 (m, 1H, C**H**$CHCF_3CH_2OH$), 1.85 (bs, 1H, O**H**), 1.74 (m, 2H, C**H**$_2CH_2NBoc$), 1.52–1.29 (m, 2H, C**H**$_2CH_2NBoc$), 1.46 [s, 9H, $C(C\mathbf{H}_3)_3$]; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.9, 127.8 (q, J^1 = 281.9 Hz), 79.8, 58.4 (q, J^3 = 3.8 Hz), 50.2 (q, J^2 = 22.7 Hz), 44.6 & 43.6 (broad singlets, rotamers), 33.8, 30.1 & 29.1 (broad singlets, rotamers), 28.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -65.4 (d, *J* = 9.5 Hz); HRMS (ESI-TOF) calculated for $C_{13}H_{23}F_3O_3N$ $[M+H]^+$ m/z 297.1552, found 297.1552. $[\alpha]_D^{22}$ = +1.99 (c = 1.09, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by preparative TLC. SFC analysis of the 2-naphthoyl ester derivative (ODH, 5–10% MeOH gradient over 9.0 minutes then isocratic 10% MeOH, 1.0 mL/min, 220 nm) indicated 97% ee: t_R (major) = 5.6 minutes, t_R (minor)

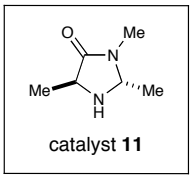
= 6.3 minutes.



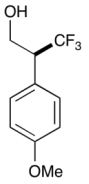
(2*R*,5*S*)-2,3,5-trimethylimidazolidin-4-one (catalyst 11, employed in Table 2, entry 7). A flask containing L-alanine-*N*-methylamide (12.9 g, 1.0 equiv, 126 mmol) is equipped with a magnetic stir bar and $NaHCO_3$ (27.7 g, 3.0 equiv). After suspension in EtOAc (250 mL) and H_2O (250 mL), benzyl chloroformate (19.8 mL, 1.1 equiv) was added. The mixture was stirred at ambient temperature for 2 hours before being quenched with saturated aqueous NH_4Cl solution (50 mL). The resulting solution was extracted with EtOAc (×3), dried over $MgSO_4$, and concentrated *in vacuo*. To the crude oil was then added a magnetic stir bar, anhydrous magnesium sulfate (26 g, 1 wt. equiv), CH_2Cl_2 (280 mL), acetaldehyde (12.3 mL, 2.0 equiv), and trifluoroacetic acid (81.7 mL, 10.0 equiv). The mixture was then refluxed for 24-48 hours (until SM consumption as judged by TLC analysis) before being quenched with 1M $NaHCO_3$ solution (50 mL), extracted with EtOAc (×3), dried over $MgSO_4$, and concentrated *in vacuo*. The mixture of *cis*- and *trans*- diastereomers of the cyclized product were then separated by flash chromatography using 30-50% EtOAc in hexanes to provide the desired *trans*-di-Me imidazolidinone (7.8 g, 27% yield) as a pale yellow oil. The Cbz-protecting group was then removed by addition of $Pd(OH)_2/C$ (100 mg, 20 wt %) to the imidazolidinone (1.0 g, 3.81 mmol), followed by dissolving in EtOAc (100 mL) and MeOH (10 mL), and stirring under hydrogen atmosphere at ambient temperature for 6 hours. After passage of the mixture through a pad of Celite and concentration *in vacuo*, flash chromatography using 100% acetone provided the desired *trans*-di-Me imidazolidinone catalyst **11** (0.200 g, 41% yield) as a yellow oil. IR (thin film) 3299, 2976, 1683, 1483, 1431, 1403, 1380, 1328, 1290, 1257, 1217, 1129, 1083, 1060, 1016 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.52 (d, 1H, *J* = 5.7 Hz, C**H**NH), 3.62 (d, 1H, *J* = 6.9 Hz, C**H**NH), 2.81 (s, 3H, *J* = 5.7

Hz, CHC**H**$_3$), 2.08 (m, 2H, N**H** & O**H**), 1.34 (d, 3H, J = 5.8 Hz, CHC**H**$_3$), 1.29 (d, 3H, J = 7.0 Hz, CHC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.7, 70.5, 54.2, 26.8, 20.0, 17.4; HRMS (ESI-TOF) calculated for $C_6H_{13}N_2O$ $[M+H]^+$ m/z 128.0950, found 128.0951. $[\alpha]_D^{23}$ = +6.6 (c = 1.0, $CHCl_3$).

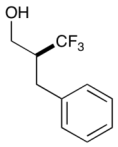




(S)-2-Adamantyl-3,3,3-trifluoropropan-1-ol (Table 2, entry 7). Prepared following the general procedure outlined above using 2-(adamantyl)acetaldehyde (0.133 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2,3,5-trimethylimidazolidin-4-one·TFA **11** (43.4 mg, 0.200 equiv.), $Ir(ppy)_2$(dtb-bpy)PF_6 (3.5 mg, 0.005 equiv.), CF_3I (1.31 g, 8.8 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 10 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentanes to provide the title compound (0.135 g, 73% yield, 90% ee) as a white solid. IR (thin film) 3381, 2905, 2852, 1449, 1243, 1154, 1115, 1093, 1024 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.90 (bs, 2H, C**H**$_2$OH), 2.0 (bs, 3H, AdmC**H**), 1.65 (m, 1H, C**H**CF_3), 1.82–1.62 (m, 13H, O**H** and AdmC**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 128.9 (q, J^1 = 284.2 Hz), 58.8 (q, J^3 = 3.8 Hz), 56.2 (q, J^2 = 21.4 Hz), 40.1 (q, J^3 = 1.3 Hz), 36.8, 34.5, 28.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -61.3 (d, J = 11.2 Hz); HRMS (ESI-TOF) calculated for $C_{13}H_{18}F_3O$ $[M–H]^+$ m/z 246.1232, found 246.1228. $[\alpha]_D^{23}$ = +1.92 (c = 1.08, $CHCl_3$). SFC analysis of the alcohol (ODH, 5–10% *i*-PrOH gradient over 9.0 minutes then isocratic 10% *i*-PrOH, 1.0 mL/min, 220 nm) indicated 90% ee: t_R(major) = 6.7 minutes, t_R (minor) = 7.7 minutes.

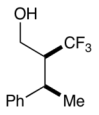


(S)-3,3,3-Trifluoro-2-(4-methoxyphenyl)propan-1-ol (Table 2, entry 8). Prepared following the general procedure outlined above using 2-(4-methoxyphenyl)acetaldehyde (0.113 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 mg, 0.300 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.36 g, 9.2 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% EtOAc in hexanes to provide the title compound (0.102 g, 61% yield, 94% ee) as a white solid. IR (thin film) 3384, 2941, 2842, 1614, 1516, 1466, 1304, 1246, 1157, 1109, 1032, 830, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.26 (d, 2H, *J* = 8.5 Hz, Ar**H**), 6.93 (d, 2H, *J* = 8.5 Hz, Ar**H**), 4.16 (m, 1H, C**H**HOH), 3.99 (m, 1H, C**H**HOH), 3.82 (s, 3H, OC$\mathbf{H_3}$), 3.50 (m, 1H, C**H**CF_3), 1.54 (bs, 1H, O**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.0, 130.5, 126.3 (q, J^1 = 279.4 Hz), 124.4 (q, J^3 = 2.5 Hz), 114.6, 61.5 (q, J^3 = 2.5 Hz), 55.5, 51.9 (q, J^2 = 25.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -68.4 (d, *J* = 9.2 Hz); HRMS (ESI-TOF) calculated for $C_{10}H_{12}F_3O_2$ $[M+H]^+$ m/z 220.0711, found 220.0701. $[\alpha]_D^{23}$ = -29.1 (c = 1.07, $CHCl_3$). HPLC analysis of the alcohol (OD, 2% EtOH, 1.0 mL/min, 254 nm) indicated 94% ee: t_R(minor) = 24.0 minutes, t_R (major) = 33.4 minutes.



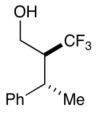
(S)-2-Benzyl-3,3,3-trifluoropropan-1-ol (Table 2, entry 9). Prepared following the general procedure outlined above using 3-phenylpropanal (100 μL, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 mg, 0.200 equiv.),

$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.4 g, 9.0 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7.5 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 10% Et_2O in pentanes to provide the title compound (0.116 g, 75% yield, 97% ee) as a clear oil. IR (thin film) 3387, 2933, 1456, 1391, 1253, 1152, 1116, 1031, 745, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.23 (m, 5H, Ar**H**), 3.80 (AB, 1H, *J* = 11.9 Hz, HO–C**H**H), 3.68 (AB, 1H, *J* = 11.9 Hz, HO–CH**H**), 3.00 (ABX, 1H, *J* = 13.7, 5.6 Hz, PhC**H**H), 2.82 (ABX, 1H, *J* = 13.7, 10.4 Hz, PhCH**H**), 2.51 (m, 1H, C**H**CF_3), 1.53 (bs, 1H, O**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.8, 129.3, 129.0, 127.8 (q, J^1 = 280.6 Hz), 127.1, 58.9 (q, J^3 = 2.5 Hz), 47.4 (q, J^2 = 23.9 Hz), 30.7 (q, J^3 = 2.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.6 (d, *J* = 9.2 Hz); HRMS (ESI-TOF) calculated for $C_{10}H_{12}F_3O$ $[M+H]^+$ m/z 204.0762, found 204.0761. $[\alpha]_D^{23}$ = +26.4 (c = 1.10, $CHCl_3$). HPLC analysis (AS, 2% EtOH/hexanes, 1.0 mL/min, 214 nm) indicated 97% ee: t_R(major) = 14.9 minutes, t_R (minor) = 19.2 minutes.



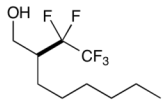
(2S,3R)-3-Phenyl-2-(trifluoromethyl)butan-1-ol (Table 2, entry 10). Prepared following the general procedure outlined above using (*R*)-3-phenylbutanal (0.114 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.3 g, 8.5 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7.5 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentane to provide the title compound (0.114 g, 68% yield, >20:1 dr determined by crude ^{19}F NMR) as a white solid. IR (thin film) 3388, 2976, 1496, 1454, 1386, 1251, 1159, 1130, 1047, 1022, 763, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.35–7.32 (m, 2H, Ar**H**), 7.28–7.24 (m, 3H, Ar**H**), 3.92 (m, 2H, C**H**$_2$OH), 3.36 (dq, 1H, *J* = 7.2, 6.8 Hz, C**H**Ph), 2.54 (m, 1H, C**H**CF_3), 1.42 (bs, 1H, O**H**),

1.39 (d, 3H, J = 7.2 Hz, –C**H$_3$**); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.9, 128.8, 127.8 (q, J^1 = 281.9 Hz), 127.6, 127.0, 58.2 (q, J^3 = 3.8 Hz), 51.5 (q, J^2 = 22.7 Hz), 35.9 (q, J^3 = 1.3 Hz), 16.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -66.0 (d, J = 9.7 Hz); HRMS (ESI-TOF) calculated for $C_{11}H_{14}F_3O$ $[M+H]^+$ m/z 218.0919, found 218.0920. $[\alpha]_D^{22}$ = -3.83 (c = 1.04, $CHCl_3$).

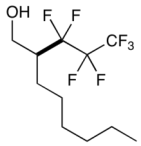


(2S,3S)-3-Phenyl-2-(trifluoromethyl)butan-1-ol (Table 2, entry 11). Prepared following the general procedure outlined above using (*S*)-3-phenylbutanal (0.111 g, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3I (1.3 g, 8.5 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 7.5 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentane to provide the title compound (0.102 g, 62% yield, >20:1 dr determined by crude ^{19}F NMR) as a white solid. IR (thin film) 3397, 2973, 1495, 1384, 1247, 1155, 1128, 1078, 1018, 765, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.30 (m, 2H, Ar**H**), 7.28–7.21 (m, 3H, Ar**H**), 3.74 (AB, 1H, J = 11.9 Hz, C**H**HOH), 3.49 (AB, 1H, J = 11.9 Hz, C**H**HOH), 3.20 (dq, 1H, J = 9.2, 7.0 Hz, C**H**Ph), 2.43 (m, 1H, C**H**CF_3), 1.42 (bs, 1H, O**H**), 1.41 (d, 3H, J = 7.0 Hz, –C**H$_3$**); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.0, 131.3, 128.0 (q, J^1 = 282.1 Hz), 127.6, 126.8, 59.7 (q, J^3 = 3.8 Hz), 51.5 (q, J^2 = 22.6 Hz), 36.7 (q, J^3 = 1.3 Hz), 20.5 (q, J^4 = 1.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -64.3 (d, J = 9.2 Hz); HRMS (ESI-TOF) calculated for $C_{11}H_{14}F_3O$ $[M+H]^+$ m/z 218.0919, found 218.0919. $[\alpha]_D^{23}$ = +6.90 (c = 1.14, $CHCl_3$).

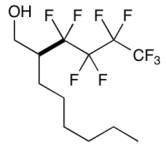
III. Enantioselective α–Perfluoroalkylation of Aldehydes.



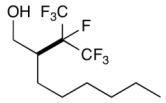
(*S*)-2-(Perfluoroethyl)octan-1-ol (Table 3, entry 1). Prepared following the general procedure outlined above using octanal (118.5 μL, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.2 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_3CF_2I (2.0 g, 10.7 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 8 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentanes to provide the title compound (0.137 g, 73% yield, 96% ee) as a clear oil. IR (thin film) 3020, 2401, 2160, 1974, 1214 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.81 (m, 2H, HO–C**H**$_2$), 2.14 (m, 1H, C**H**CF_2), 1.57–1.23 (m, 10H, –C**H**$_2$–), 0.82 (t, 3H, J = 6.7 Hz, –C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 123.0-115.3 (m), 59.0 (td, J^3 = 4.9 Hz, J^4 = 1.3 Hz), 43.4 (ttt, J^2 = 19.0 Hz, J^3 = 4.5 Hz, J^4 = 1.4 Hz), 31.6, 29.2, 27.0, 23.8 (td, J^3 = 4.0 Hz, J^4 = 1.6 Hz), 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -82.9 (s, 3F, $–CF_2C\mathbf{F}_3$), -118.1 (d, 2F, J = 16.1 Hz, $–C\mathbf{F}_2CF_3$); HRMS (ESI-TOF) calculated for $C_{10}H_{16}F_5$ $[M–OH]^+$ m/z 230.1094, found 230.1095. $[\alpha]_D^{23}$ = +4.0 (c = 1.00, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 10% Et_2O in pentanes. HPLC analysis of the 2-naphthoyl ester derivative (OD, 3% EtOH/hexanes, 1.0 mL/min, 254 nm) indicated 96% ee: t_R (major) = 5.5 minutes, t_R (minor) = 6.1 minutes.



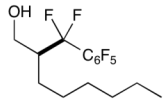
(*S*)-2-(Perfluoropropyl)octan-1-ol (Table 3, entry 2). Prepared following the general procedure outlined above using octanal (118.5 μL, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.2 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), $CF_3CF_2CF_2I$ (878 μL, 8.0 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 8 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentanes to provide the title compound (0.155 g, 69% yield, 99% ee) as a clear oil. IR (thin film) 3361, 2959, 2929, 2860, 1716, 1469, 1349, 1297, 1218, 1174, 1116, 1051 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.92 (m, 2H, HO–C**H**$_2$), 2.32 (m, 1H, C**H**CF_2), 1.62–1.33 (m, 10H, –C**H**$_2$–), 0.92 (t, 3H, J = 6.8 Hz, –C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 121.5-109.2 (m), 59.0 (tt, J^3 = 5.3 Hz, J^4 = 2.1 Hz), 43.6 (t, J^2 = 19.1 Hz), 31.6, 29.2, 27.0, 23.7 (tt, J^3 = 4.0 Hz, J^4 = 1.9 Hz), 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.1 (t, 3F, J = 10.8 Hz, –C**F**$_3$), -115.1 (dt, 2F, J = 16.0, 10.3 Hz, –CHC**F**$_2$–), -125.7 (m, 2F, –C**F**$_2CF_3$); HRMS (ESI-TOF) calculated for $C_{11}H_{16}F_7$ $[M–OH]^+$ m/z 280.1062, found 280.1063. $[\alpha]_D^{23}$ = +6.3 (c = 1.00, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 10% Et_2O in pentanes. HPLC analysis of the 2-naphthoyl ester derivative (OD, 2% *i*-PrOH/hexanes, 1.0 mL/min, 254 nm) indicated 99% ee: t_R (major) = 6.2 minutes, t_R (minor) = 9.9 minutes.



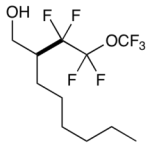
(*S*)-2-(Perfluorobutyl)octan-1-ol (Table 3, entry 3). Prepared following the general procedure outlined above using octanal (118.5 μL, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.2 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), $CF_3CF_2CF_2CF_2I$ (1.04 mL, 8.0 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 8 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 15% Et_2O in pentanes to provide the title compound (0.178 g, 67% yield, 96% ee) as a clear oil. IR (thin film) 3020, 2401, 2165, 1214, 1134 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.93 (m, 2H, HO–C**H**$_2$), 2.34 (m, 1H, C**H**CF_2), 1.67–1.33 (m, 10H, –C**H**$_2$–), 0.92 (t, 3H, J = 6.7 Hz, –C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 121.6-108.4 (m), 59.0 (t, J^3 = 5.0 Hz), 43.8 (t, J^2 = 19.2 Hz), 31.6, 29.3, 27.0, 23.8 (tt, J^3 = 3.8 Hz, J^3 = 1.8 Hz), 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -81.5 (tt, 3F, J = 9.6, 2.8 Hz, –C**F**$_3$), -114.6 (tt, 2F, J = 19.9, 16.6 Hz, –CHC**F**$_2$–), -122.5 (dd, 2F, J = 15.4, 10.4 Hz, –C**F**$_2$–), -126.6 (ddd, 2F, J = 12.3, 4.5, 2.3 Hz, –C**F**$_2$–); HRMS (ESI-TOF) calculated for $C_{12}H_{16}F_9$ $[M–OH]^+$ m/z 330.1030, found 330.1031. $[\alpha]_D^{23}$ = +5.6 (c = 1.00, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 10% Et_2O in pentanes. HPLC analysis of the 2-naphthoyl ester derivative (OD, 3% *i*-PrOH/hexanes, 1.0 mL/min, 254 nm) indicated 96% ee: t_R (major) = 4.7 minutes, t_R (minor) = 5.8 minutes.



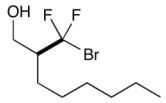
(*S*)-2-(Perfluoropropan-2-yl)octan-1-ol (Table 3, entry 4). Prepared following the general procedure outlined above using octanal (118.5 μL, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.2 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), $(CF_3)_2CF\text{-}I$ (878 μL, 8.0 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 8 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentanes to provide the title compound (0.163 g, 72% yield, 98% ee) as a clear oil. IR (thin film) 3361, 2961, 2931, 2861, 1469, 1298, 1214, 1161, 1131, 1112, 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.00 (ABX, dd, 1H, J = 15.1, 3.9 Hz, HO–C**H**H), 3.76 (ABX, dd, 1H, J = 15.1, 1.8 Hz, HO–CH**H**), 2.36 (m, 1H, C**H**CF_2), 1.71–1.25 (m, 10H, –C$\mathbf{H_2}$–), 0.88 (t, 3H, J = 6.5 Hz, –C$\mathbf{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 121.3 (qd, J^1 = 287.4 Hz, J^2 = 28.4 Hz, –**C**F_3), 121.2 (qd, J^1 = 286.9 Hz, J^2 = 27.7 Hz, –**C**F_3), 93.3 (dhd, J^1 = 290.2 Hz, J^2 = 31.0 Hz, J^3 = 0.5 Hz, –**C**F–), 60.3 (ddd, J^3 = 8.2 Hz, J^4 = 3.7, 1.7 Hz), 43.9 (d, J^3 = 17.6 Hz), 31.6, 29.2, 28.4, 25.4 (dh, J^3 = 5.8 Hz, J^4 = 3.8 Hz), 22.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -73.2 (dd, 3F, J = 16.1, 8.3 Hz, –C$\mathbf{F_3}$), -74.5 (dd, 3F, J = 16.1, 8.2 Hz, –C$\mathbf{F_3}$), -176.6 (td, 1F, J = 13.0, 6.5 Hz, –C**F**–); HRMS (ESI-TOF) calculated for $C_{11}H_{16}F_7$ $[M–OH]^+$ m/z 280.1062, found 280.1063. $[\alpha]_D^{23}$ = +6.3 (c = 1.00, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 10% Et_2O in pentanes. HPLC analysis of the 2-naphthoyl ester derivative (AD, 3% *i*-PrOH/hexanes, 1.0 mL/min, 254 nm) indicated 98% ee: t_R (major) = 4.5 minutes, t_R (minor) = 5.4 minutes.



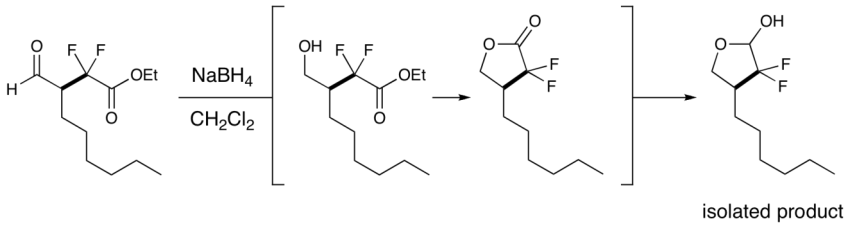
(*S*)-2-(Perfluorobenzyl)octan-1-ol (Table 3, entry 5). Prepared following the general procedure outlined above using octanal (118.5 μL, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.2 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), $(C_6F_5)CF_2I$ (0.95 mL, 8.0 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 8 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentanes to provide the title compound (0.224 g, 85% yield, 98% ee) as a clear oil. IR (thin film) 3389, 2930, 2861, 1748, 1656, 1527, 1591, 1422, 1324, 1171, 1122, 1099, 1046 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.83 (d, 2H, J = 4.8 Hz, HO–C**H**$_2$), 2.30 (m, 1H, C**H**CF_2), 1.61–1.26 (m, 10H, –C**H**$_2$–), 0.87 (t, 3H, J = 6.6 Hz, –C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.6 (ddd, J^1 = 255.7 Hz, J^2 = 11.5 Hz, J^3 = 7.7 Hz), 142.1 (dt, J^1 = 257.7 Hz, J^2 = 13.2 Hz), 137.8 (m), 122.4 (t, J^1 = 250.6 Hz), 111.4 (m), 59.8 (t, J^3 = 4.4 Hz), 48.6 (t, J^2 = 22.2 Hz), 31.6, 29.3, 27.1, 24.4 (t, J^3 = 3.2 Hz), 22.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -95.9 (m, 2F, –CHC**F**$_2$–), -140.5 (m, 2F, –C_6**F**$_5$), -151.3 (t, 1F, J = 9.5 Hz, –C_6**F**$_5$), -161.3 (m, 2F, –C_6**F**$_5$); HRMS (ESI-TOF) calculated for $C_{15}H_{17}F_7O$ $[M]^+$ m/z 346.1168, found 346.1169. $[\alpha]_D^{23}$ = +14.1 (c = 1.00, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 10% Et_2O in pentanes. HPLC analysis of the 2-naphthoyl ester derivative (OD, 2% EtOH/hexanes, 1.0 mL/min, 254 nm) indicated 98% ee: t_R (major) = 10.6 minutes, t_R (minor) = 11.5 minutes.



(*S*)-2-(1,1,2,2-Tetrafluoro-2-(trifluoromethoxy)ethyl)octan-1-ol (Table 3, entry 6). Prepared following the general procedure outlined above using octanal (118.5 μL, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.2 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), $ICF_2CF_2OCF_3$ (1.13 mL, 10.0 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 8 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentanes to provide the title compound (0.169 g, 71% yield, 99% ee) as a clear oil. IR (thin film) 3361, 2961, 2931, 2861, 1469, 1298, 1214, 1161, 1131, 1112, 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.81 (ABX, dd, 1H, J = 9.0, 4.1 Hz, HO–C**H**H), 3.80 (ABX, dd, 1H, J = 9.0, 1.6 Hz, HO–C**H**H), 2.16 (m, 1H, C**H**CF_2), 1.44–1.23 (m, 10H, –C$\mathbf{H_2}$–), 0.82 (t, 3H, J = 6.8 Hz, –C$\mathbf{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 117.5 (m, –$\mathbf{CF_2CF_2OCF_3}$), 59.0 (t, J^3 = 5.0 Hz), 43.2 (t, J^2 = 19.1 Hz), 31.6, 29.2, 27.0, 23.8 (t, J^3 = 3.8 Hz), 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -55.4 (t, 3F, J = 9.0 Hz, –OC$\mathbf{F_3}$), -87.5 (dq, 2F, J = 18.0, 9.0 Hz, –CF_2C$\mathbf{F_2}$$OCF_3$), -117.9 (d, 2F, J = 16.1 Hz, –C$\mathbf{F_2}$$CF_2OCF_3$); HRMS (ESI-TOF) calculated for $C_{11}H_{16}F_7O$ $[M–OH]^+$ m/z 296.1011, found 296.1012. $[\alpha]_D^{23}$ = +7.7 (c = 1.00, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 10% Et_2O in pentanes. HPLC analysis of the 2-naphthoyl ester derivative (OD, 2% *i*-PrOH/hexanes, 1.0 mL/min, 254 nm) indicated 99% ee: t_R (major) = 5.2 minutes, t_R (minor) = 7.7 minutes.

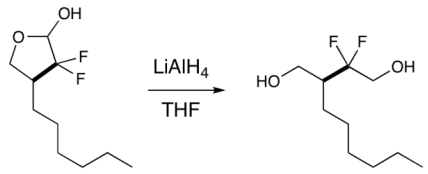


(*S*)-2-(Bromodifluoromethyl)octan-1-ol (Table 3, entry 7). Prepared following the general procedure outlined above using octanal (118.5 μL, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.2 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), CF_2Br_2 (0.70 mL, 8.0 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 8 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20% Et_2O in pentanes to provide the title compound (0.133 g, 68% yield, 99% ee) as a clear oil. IR (thin film) 3348, 2956, 2928, 2859, 1467, 1380, 1170, 1108, 1038 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.84 (ABX, dd, 1H, *J* = 10.6, 5.0 Hz, HO–C**H**H), 3.82 (ABX, dd, 1H, *J* = 10.6, 1.6 Hz, HO–C**H**H), 2.16 (m, 1H, C**H**CF_2), 2.25 (m, 1H, C**H**CF_2), 1.84–1.20 (m, 10H, –C$\mathbf{H_2}$–), 0.88 (t, 3H, *J* = 6.7 Hz, –C$\mathbf{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 126.5 (t, J^1 = 249.7 Hz), 61.4 (t, J^3 = 4.4 Hz), 53.3 (t, J^2 = 17.1 Hz), 31.6, 29.3, 27.0, 26.8 (t, J^3 = 4.9 Hz), 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -44.7 (d, 1F, *J* = 160.3, 10.9 Hz), -45.3 (d, 1F, *J* = 160.3, 10.9 Hz); HRMS (ESI-TOF) calculated for $C_9H_{17}BrFO$ $[M\text{-}F]^+$ m/z 238.0369, found 238.0371. $[\alpha]_D^{23}$ = +5.6 (c = 1.00, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding alcohol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 10% Et_2O in pentanes. HPLC analysis of the 2-naphthoyl ester derivative (OD, 2% *i*-PrOH/hexanes, 1.0 mL/min, 254 nm) indicated 99% ee: t_R (major) = 7.8 minutes, t_R (minor) = 15.8 minutes.



(4*S*)-3,3-Difluoro-4-hexyltetrahydrofuran-2-ol (Table 3, entry 8). Prepared as a mixture of diastereomers, following the general procedure outlined above using octanal (118.5 μL, 0.76 mmol, 1.00 equiv.), (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.2 mg, 0.200 equiv.), $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.), ethyl bromodifluoroacetate (0.78 mL, 8.0 equiv.), 2,6-lutidine (97.4 μL, 1.1 equiv.) and DMF (2.53 mL). After 8 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 35% Et_2O in pentanes to provide the title compound (0.140 g, 89% yield, 2:1 dr) as a clear oil. IR (thin film) 3386, 2930, 2860, 1467, 1380, 1338, 1189, 1135, 1048 cm^{-1}; *major diastereomer*: ^1H NMR (500 MHz, $CDCl_3$) δ: 5.10 (d, 1H, J = 7.7 Hz, –OC**H**(OH)CF_2), 4.22 (ap t, 1H, J = 8.7 Hz, –OC**H**H), 3.56 (ap t, 1H, J = 8.9 Hz, –OCH**H**), 3.22 (bs, 1H, O**H**), 2.53 (m, 1H, C**H**CF_2), 1.63–1.21 (m, 10H, –C$\mathbf{H_2}$–), 0.82 (t, 3H, J = 6.8 Hz, –C$\mathbf{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 125.6 (dd, J^1 = 261.1, 249.2 Hz), 96.2 (dd, J^2 = 41.6, 25.2 Hz), 70.5 (d, J^3 = 9.4 Hz), 40.7 (dd, J^2 = 21.6, 2.3 Hz), 31.6, 29.3, 27.5, 24.5 (d, J^3 = 5.0 Hz), 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -121.7 (dd, J = 42.0, 16.6 Hz); *minor diastereomer*: ^1H NMR (500 MHz, $CDCl_3$) δ: 5.20 (dd, 1H, J = 6.5, 2.5 Hz, –OC**H**(OH)CF_2), 4.11 (ap t, 1H, J = 8.5 Hz, –OC**H**H), 3.77 (ap t, 1H, J = 8.9 Hz, –OCH**H**), 3.22 (bs, 1H, O**H**), 2.40 (m, 1H, C**H**CF_2), 1.63–1.21 (m, 10H, –C$\mathbf{H_2}$–), 0.82 (t, 3H, J = 6.8 Hz, –C$\mathbf{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 125.6 (dd, J^1 = 261.1, 249.2 Hz), 97.2 (m), 70.8 (dd, J^3 = 6.5, 2.3 Hz), 43.7 (m), 31.6, 29.2, 27.5, 25.9 (d, J^3 = 5.0 Hz), 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.6 (dddd, J = 8810.8, 243.2, 22.0, 7.0 Hz); HRMS (ESI-TOF) calculated for $C_{10}H_{17}F_2O$ $[M–OH]^+$ m/z 190.1169, found 190.1170. $[\alpha]_D^{25}$ = +24.9 (c = 0.67, $CHCl_3$). The diastereomeric ratio of this mixture of

syn- and *anit*- lactols was determined by ^{1}H, ^{13}C, and ^{19}F NMR, as reported above, and was found to be approximately 2:1.

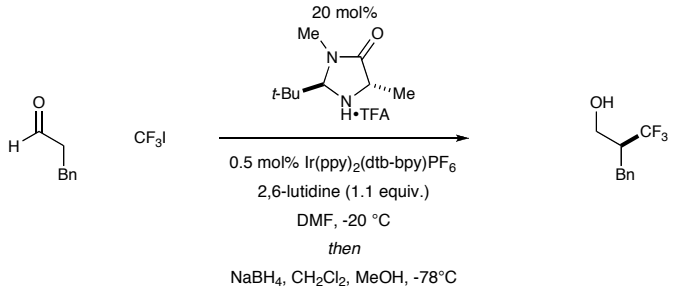


(*S*)-2,2-Difluoro-3-hexylbutane-1,4-diol (Table 3, entry 8, continued). In order to determine the enantiomeric excess, the diastereomeric mixture of the above lactol was reduced to the corresponding diol, by treating a solution of the lactol (1.0 equiv.) in THF (0.20 M) with $LiAlH_4$ (4.0 equiv.). After consumption of the lactol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 35-50% Et_2O in pentanes to provide the title compound (0.129 g, 91% yield, 99% ee) as a clear oil. IR (thin film) ~3314(br), 2956, 2928, 2859, 1467, 1379, 1216, 1151, 1114, 1060 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.81-3.63 (m, 4H, 2 × HO–C**H**$_2$), 3.66 (dd, 2H, J = 19.1, 12.0 Hz, HO–C**H**$_2$), 2.99 (bs, 1H, –O**H**), 2.01 (dddd, 2H, J = 15.9, 9.4, 6.1, 2.9 Hz, –C**H**CF$_2$), 1.88 (bs, 1H, –O**H**), 1.35–1.22 (m, 10H, –C**H**$_2$-), 0.82 (t, 3H, J = 6.8 Hz, –C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 123.9 (dd, J^1 = 246.6, 244.6 Hz), 62.8 (dd, J^2 = 37.1, 31.0 Hz), 59.6 (t, J^3 = 5.7 Hz), 45.7 (t, J^2 = 22.1 Hz), 31.7, 29.4, 27.3, 24.1 (dd, J^3 = 4.9, 3.5 Hz), 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -109.8 (ddd, J = 2202.5, 262.8, 21.7, 10.4 Hz); HRMS (ESI-TOF) calculated for $C_{10}H_{20}F_2O_2$ $[M]^+$ m/z 210.1431, found 210.1432. $[\alpha]_D^{23}$ = +20.4 (c = 1.00, $CHCl_3$). The enantiomeric excess was determined on the 2-naphthoyl ester derivative, which was prepared by treating a solution of the corresponding diol (1.0 equiv.) in CH_2Cl_2 (0.20 M) with DMAP (2.0 equiv.) and 2-naphthoyl chloride (2.0 equiv.). After consumption of the alcohol was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 5% Et_2O in pentanes. HPLC analysis of the *di*-2-

naphthoyl ester derivative (OJ, 2% EtOH/hexanes, 1.0 mL/min, 254 nm) indicated 99% ee: t_R (major) = 6.9 minutes, t_R (minor) = 7.6 minutes.

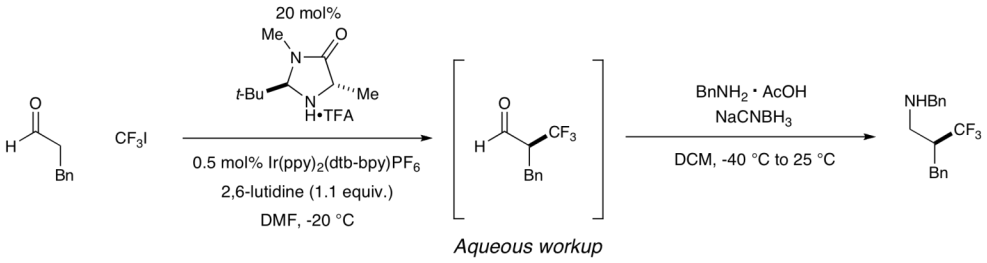
IV. Access to Enantioenriched Organofluorine Synthons.

Enantioselective α-trifluoromethylation, followed by (a) in situ reduction, (b) sequential reductive amination, (c) in situ oxidation, or (d) in situ oxidation and sequential Curtius rearrangement.



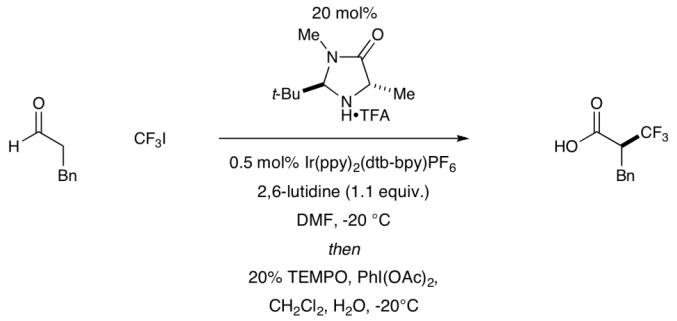
(a) β-CF_3 alcohol: General procedure for enantioselective trifluoromethylation, followed by an in situ reduction: To an oven-dried 13 mm × 100 mm borosilicate test tube equipped with a magnetic stir bar was added (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 g, 0.200 equiv.) and $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.4 mg, 0.005 equiv.). The tube was fitted with a septum and degassed through alternating vacuum evacuation/argon backfill (×3) and was cooled to -78 °C before DMF (2.53 mL) was added. The resulting yellow solution was further degassed by alternating vacuum evacuation/argon backfill (×3) at -78 °C. Approximately CF_3I (1.20 g, 8.1 equiv.) was then condensed using a cold finger fitted with an 18 gauge needle. Next, 3-phenylpropanal (100 μL, 0.76 mmol, 1.0 equiv.) and 2,6-lutidine (97 μL, 1.1 equiv.) were added by syringe and the test tube was placed in a -20 °C acetone-containing cryocool approximately 3 cm from a 26 W compact fluorescent light bulb (daylight GE Energy Smart™ 1600 lumens) that was inserted into a Pyrex glass tube insert. After 8 hours, the test tube was removed, cooled to -78 °C, and transferred by pre-cooled pipette to a round bottom flask containing CH_2Cl_2 (4.0 mL) at -78 °C. Cold CH_2Cl_2 (8.0 mL, -78 °C) was

then used to transfer the remaining residue and $NaBH_4$ (0.288 g, 10 equiv.) was added followed by cold MeOH (10 mL, -78 °C). The reaction was stirred for one hour at -78 °C before being quenched with saturated aqueous NH_4Cl solution (10 mL). The resulting solution was warmed to room temperature, extracted with Et_2O (×3), and the combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude oil was then purified by column chromatography on silica gel using 10% Et_2O in pentanes to furnish the desired alcohol product (0.116 g, 75% yield over 2 steps, 99% yield from α-CF_3 hydrocinnamaldehyde, 97% ee) as a clear oil, whose spectral data was consistent with previous values (Table 2, entry 9).



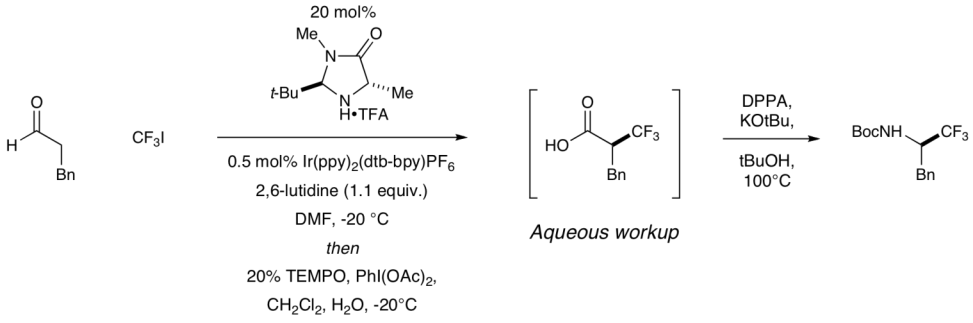
(b) β-CF_3 amine: General procedure for sequential enantioselective trifluoromethylation/reductive amination: To an oven-dried 13 mm × 100 mm borosilicate test tube equipped with a magnetic stir bar was added (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 g, 0.200 equiv.) and $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.4 mg, 0.005 equiv.). The tube was fitted with a septum and degassed through alternating vacuum evacuation/argon backfill (×3) and was cooled to -78 °C before DMF (2.53 mL) was added. The resulting yellow solution was further degassed by alternating vacuum evacuation/argon backfill (×3) at -78 °C. Approximately CF_3I (1.37 g, 9.2 equiv.) was then condensed using a cold finger fitted with an 18 gauge needle. 3-Phenylpropanal (100 μL, 1.00 equiv.) and 2,6-lutidine (97 μL, 1.1 equiv.) were added by syringe and the test tube was placed in a -20 °C acetone-containing cryocool approximately 3 cm from a 26 W compact fluorescent light bulb (daylight GE Energy Smart™ 1600 lumens) that was

inserted into a Pyrex glass tube. After 7.5 hours, the test tube was removed, cooled to -78 °C, and transferred by pre-cooled pipette to a separatory funnel containing cold Et_2O and the resulting yellow solution was washed with cold pH = 4 buffer (potassium biphthalate buffer, Fisher Scientific) (×4). The combined organic washings were dried over a mixture of Na_2SO_4 and $MgSO_4$, filtered, and concentrated *in vacuo*. ^{19}F NMR yield using 3,5-bis(trifluoromethyl)bromobenzene as internal standard showed a crude yield of the desired aldehyde of 77% (internal standard δ = -63.4 (singlet); aldehyde δ = -66.7 (doublet)). The crude product was then taken up in CH_2Cl_2 (2.5 mL) and cooled to -40 °C before the $NaCNBH_3$ (0.095 g, 2.0 equiv.) and $BnNH_2$·AcOH (0.762 g, 6.00 equiv.) were added. The reaction flask was kept at -40 °C for two hours before being allowed to warm to room temperature overnight. The reaction was quenched by addition of saturated $NaHCO_3$ solution (~ 4 mL) followed by brine. The aqueous layer was then extracted with CH_2Cl_2 (×3) followed by EtOAc (×3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification of the product was achieved using flash chromatography using basic silica (packed as a slurry in 3% triethylamine in hexanes), eluting with 15% CH_2Cl_2 and 5% EtOAc in hexanes to provide the title compound (0.168 g, 71% yield over 2 steps, 95% yield from α-CF_3 hydrocinnamaldehyde, 87% ee) as a clear oil. IR (thin film) 3029, 2917, 2849, 1497, 1455, 1254, 1155, 1118, 1078, 736, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.14 (m, 10H, Ar**H**), 3.68 (AB, 1H, *J* = 13.3 Hz, NC**H**HPh), 3.64 (AB, 1H, *J* = 13.3 Hz, NCH**H**Ph), 3.00 (ABX, 1H, *J* = 13.3, 3.6 Hz, CH(CF_3)C**H**HPh), 2.78 (m, 3H, NC**H**$_2$CH(CF_3)CH**H**Ph), 2.55 (m, 1H, C**H**CF_3), 1.35 (bs, 1H, N**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 140.1, 138.4, 129.3, 128.8, 128.6, 128.2, 128.1 (q, J^1 = 284.4 Hz), 127.2, 126.8, 54.0, 46.3 (q, J^3 = 2.5 Hz), 45.6 (q, J^2 = 23.9 Hz), 32.5 (q, J^3 = 2.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.8 (d, *J* = 9.2 Hz); HRMS (ESI-TOF) calculated for $C_{17}H_{19}F_3N$ $[M+H]^+$ m/z 293.1391, found 293.1393. $[\alpha]_D^{24}$ = +41.8 (c = 1.23, $CHCl_3$). HPLC analysis (OJ, 2% *i*-PrOH/hexanes, 1.0 mL/min, 214 nm) indicated 87% ee: t_R(minor) = 10.8 minutes, t_R (major) = 11.4 minutes.



(c) α-CF_3 acid: General procedure for enantioselective trifluoromethylation, followed by an in situ oxidation: To an oven-dried 13 mm × 100 mm borosilicate test tube equipped with a magnetic stir bar was added (2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 g, 0.200 equiv.) and $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.). The tube was fitted with a septum and degassed through alternating vacuum evacuation/argon backfill (×3) and was cooled to -78 °C before DMF (2.53 mL) was added. The resulting yellow solution was further degassed by alternating vacuum evacuation/argon backfill (×3) at -78 °C. Approximately CF_3I (1.58 g, 10.6 equiv.) was then condensed using a cold finger fitted with an 18 gauge needle. Next, 3-phenylpropanal (100 μL, 0.76 mmol, 1.0 equiv.) and 2,6-lutidine (97 μL, 1.1 equiv.) were added by syringe and the test tube was placed in a -20 °C acetone-containing cryocool approximately 3 cm from a 26 W compact fluorescent light bulb (daylight GE Energy Smart™ 1600 lumens) that was inserted into a Pyrex glass tube insert. After 8 hours, the test tube was transferred by pre-cooled pipette to a round-bottom flask containing CH_2Cl_2 (4.0 mL) at -20 °C. Cold CH_2Cl_2 (4.0 mL, -20 °C) was then used to transfer the remaining residue, and $PhI(OAc)_2$ (0.490 g, 2 equiv.) was added followed by 2,2,6,6-tetramethylpiperidine-1-oxyl (0.024 g, 0.2 equiv., i.e. TEMPO), and cold H_2O (3.8 mL). The reaction was stirred for two hours at -20 °C before being quenched with a 1M aqueous Na_2SO_3 solution (10 mL). The resulting solution was warmed to room temperature, poured into a separatory funnel containing 1M NaOH (25 mL) and CH_2Cl_2 (25 mL) and the organic materials were removed by extraction with CH_2Cl_2 (×3). The

remaining aqueous layer was then acidified with 1M HCl and extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo*. The crude oil was then purified by column chromatography on silica gel using 50% Et_2O in pentanes to furnish the desired acid product (0.117 g, 71% yield over 2 steps, 94% yield from α-CF_3 hydrocinnamaldehyde, 96% ee) as a clear oil. IR (thin film) 3034, 2947, 1726, 1606, 1587, 1498, 1457, 1422, 1363, 1303, 1256, 1236, 1209, 1187, 1161, 1153, 1117, 1080, 1054, 1032 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 9.02 (bs, 1H, COO**H**), 7.34–7.19 (m, 5H, Ar**H**), 3.48 (m, 1H, C**H**CF_3), 3.20 (m, 2H, C**H**$_2$$CHCF_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.2, 135.9, 128.9, 128.8, 127.2, 124.2 (q, J^1 = 280.7 Hz), 52.5 (q, J^2 = 19.7 Hz), 32.1 (q, J^3 = 2.1 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) δ: -68.6 (d, J = 7.7 Hz); HRMS (ESI-TOF) calculated for $C_{10}H_9F_3O_2Na$ $[M+Na]^+$ m/z 240.0374, found 240.0376. $[\alpha]_D^{25}$ = +55.6 (c = 1.0, $CHCl_3$). In order to determine the enantiomeric excess, the acid was reduced to the corresponding alcohol, by treating a solution of the acid (1.0 equiv.) in THF (0.20 M) with $LiAlH_4$ (4.0 equiv.). After consumption of the acid was complete (as judged by TLC analysis), the reaction was concentrated *in vacuo* and purified by flash chromatography using 10% Et_2O in pentanes to provide the same alcohol as Table 2, entry 9. HPLC analysis (AS, 2% EtOH/hexanes, 1.0 mL/min, 214 nm) indicated 96% ee: t_R (minor) = 14.9 minutes, t_R (major) = 19.2 minutes.



(d) α-CF_3 amine: General procedure for enantioselective trifluoromethylation, followed by (1) an in situ oxidation and (2) Curtius rearrangement: To an oven-dried 13 mm × 100 mm borosilicate test tube equipped with a magnetic stir bar was added

(2*R*,5*S*)-2-*t*-butyl-3,5-dimethylimidazolidin-4-one·TFA (43.4 g, 0.200 equiv.) and $Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (3.5 mg, 0.005 equiv.). The tube was fitted with a septum and degassed through alternating vacuum evacuation/argon backfill (×3) and was cooled to -78 °C before DMF (2.53 mL) was added. The resulting yellow solution was further degassed by alternating vacuum evacuation/argon backfill (×3) at -78 °C. Approximately CF_3I (1.58 g, 10.6 equiv.) was then condensed using a cold finger fitted with an 18 gauge needle. Next, 3-phenylpropanal (100 μL, 0.76 mmol, 1.0 equiv.) and 2,6-lutidine (97 μL, 1.1 equiv.) were added by syringe and the test tube was placed in a -20 °C acetone-containing cryocool approximately 3 cm from a 26 W compact fluorescent light bulb (daylight GE Energy Smart™ 1600 lumens) that was inserted into a Pyrex glass tube insert. After 8 hours, the test tube was transferred by pre-cooled pipette to a round-bottom flask containing CH_2Cl_2 (4.0 mL) at -20 °C. Cold CH_2Cl_2 (4.0 mL, -20 °C) was then used to transfer the remaining residue, and $PhI(OAc)_2$ (0.490 g, 2 equiv.) was added followed by 2,2,6,6-tetramethylpiperidine-1-oxyl (0.024 g, 0.2 equiv., i.e. TEMPO), and cold H_2O (3.8 mL). The reaction was stirred for two hours at -20 °C before being quenched with a 1M aqueous Na_2SO_3 solution (10 mL). The resulting solution was warmed to room temperature, poured into a separatory funnel containing 1M NaOH (25 mL) and CH_2Cl_2 (25 mL) and the organic materials were removed by extraction with CH_2Cl_2 (×3). The remaining aqueous layer was then acidified with 1M HCl and extracted with CH_2Cl_2 (3× 30 mL). The combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo*. The crude oil was then subjected to the Curtius rearrangement protocol, by transferring the oil with *t*-butanol (7.6 mL, 0.1M) to a Pyrex sealed tube, equipped with a magnetic stir bar, potassium *t*-butoxide (94 mg, 1.1 equiv.), and 4Å molecular sieves (1.0 wt. equiv.). After addition of diphenyl phosphoryl azide (0.36 mL, 2.2 equiv., i.e. DPPA) and purging with argon before sealing the tube, the reaction was stirred for 10 hours at 110 °C, then cooled to room temperature and quenched with a 1M citric acid solution (20 mL). The resulting solution was extracted with CH_2Cl_2 (×3), and the combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude oil was then purified by column chromatography on

silica gel using 15% Et_2O in pentanes to furnish the desired amine product (0.145 g, 66% yield over 3 steps, 88% yield from α-CF_3 hydrocinnamaldehyde, 92% ee) as a white solid. IR (thin film) 3364, 2985, 1697, 1525, 1446, 1372, 1305, 1282, 1254, 1210, 1170, 1152, 1128, 1083, 1051, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.33–7.19 (m, 5H, Ar**H**), 4.56 (m, 2H, C**H**CF_3 and N**H**), 3.17 (dd, 1H, J = 16.0, 3.2 Hz, PhC**H**HCHCF_3), 2.72 (dd, 1H, J = 16.0, 9.9 Hz, PhCH**H**CHCF_3), 1.29 [s, 9H, J = 30.5 Hz, –C(C**H**$_3$)]; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.8, 135.1 (q, J^4 = 1.5 Hz), 129.2, 128.7, 127.1, 125.2 (q, J^1 = 282.2 Hz), 80.5, 53.0 (q, J^2 = 20.8 Hz), 34.8 (q, J^3 = 2.4 Hz), 28.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -76.5 (d, J = 6.1 Hz); HRMS (ESI-TOF) calculated for $C_9H_{11}F_3N$ [M-Boc+H]$^+$ m/z 189.0765, found 189.0769. $[\alpha]_D^{23}$ = +1.5 (c = 1.0, $CHCl_3$); literature for (*S*)-enantiomer: $[\alpha]_D^{23}$ = –3.1 (c = 0.6, $CHCl_3$).[7] HPLC analysis of amine dissolved in pentanes (AS, 2% *i*-PrOH/hexanes, 1.0 mL/min, 214 nm) indicated 92% ee: t_R(major) = 8.0 minutes, t_R (minor) = 9.7 minutes.

[7] Fustero, S.; del Pozo, C.; Catalán, S.; Alemán, J.; Parra, A.; Marcos, V.; García Ruano, J. L. *J. Org. Chem.* **2009**, *11*, 641–644.

V. Cryogenic Reaction Set-up & Safety Procedures.

In a typical experiment, a –20 °C acetone-containing cryocool was employed to maintain constant cryogenic temperatures. A standard –20 °C dry-ice/acetone bath was also found to be amenable to these conditions, however the ease of the cryocool system was preferred. As a light source, a variety of fluorescent light fixtures could be employed, including aquarium lights, flashlights, work lamps, and compact fluorescent light bulbs of varying power output. Ultimately, a 26 W compact fluorescent light bulb (daylight GE Energy Smart™ 1600 lumens) was chosen because of the combination of its intense luminosity and compact size. Placing the light source approximately 3 cm from the reaction ensured efficient photo-excitation, with minimal warming effects. Although the light bulb could be simply clamped above the acetone bath, it was deemed safer to encase the bulb within a Pyrex glass tube, sealed with a rubber stopper (as shown below). Further advantage of this encasement involves the capacity to bring the light source within closer proximity to the reaction vessel. ***CAUTION: When using an electrical device near a cooling bath, be certain the outlet is equipped with a proper ground fault circuit interrupter (GFI or GFCI) to prevent severe or fatal electric shocks.***

26 W fluorescent light bulbs

Pyrex glass tube encasement with rubber stopper

Reaction set-up (side view)

Reaction set-up (top view)

VI. Emission Quenching Experiments.

Emission intensities were recorded using a Perkin Elmer LS50 Luminescence spectrometer. All $Ir(bpy)_2(dtb\text{-}bpy)PF_6$ solutions were excited at 445 nm and the emission intensity at 580 nm was observed. In a typical experiment, a 0.0373 M solution of $Ir(bpy)_2(dtbbpy)PF_6$ in DMF was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing with a stream of nitrogen for 10 minutes, the emission spectrum of the sample was collected.

Figure S1: $Ir(bpy)_2(dtb\text{-}bpy)PF_6$ Emission Quenching by Imidazolidinone

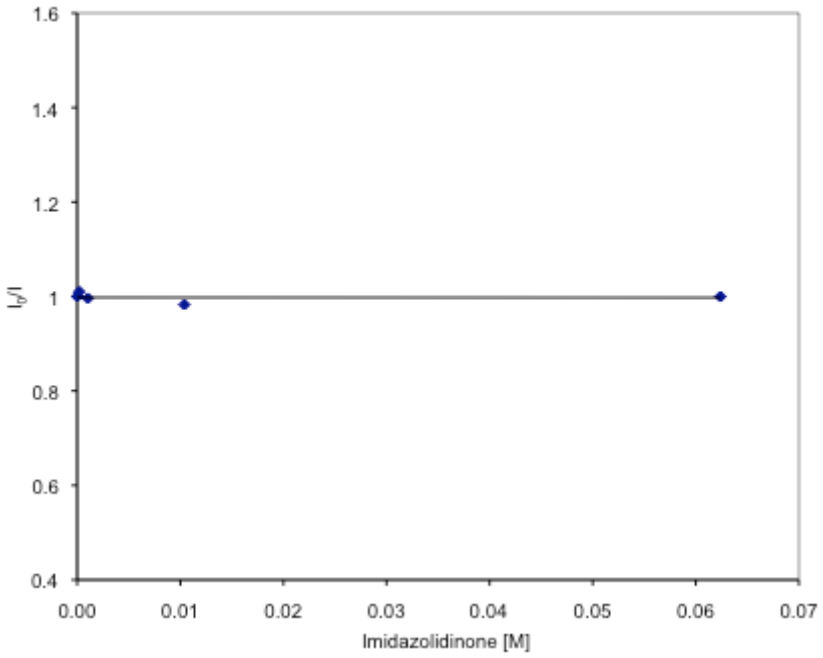


Figure S2: $Ir(bpy)_2(dtb\text{-}bpy)PF_6$ Emission Quenching by Imidazolidinone•TFA

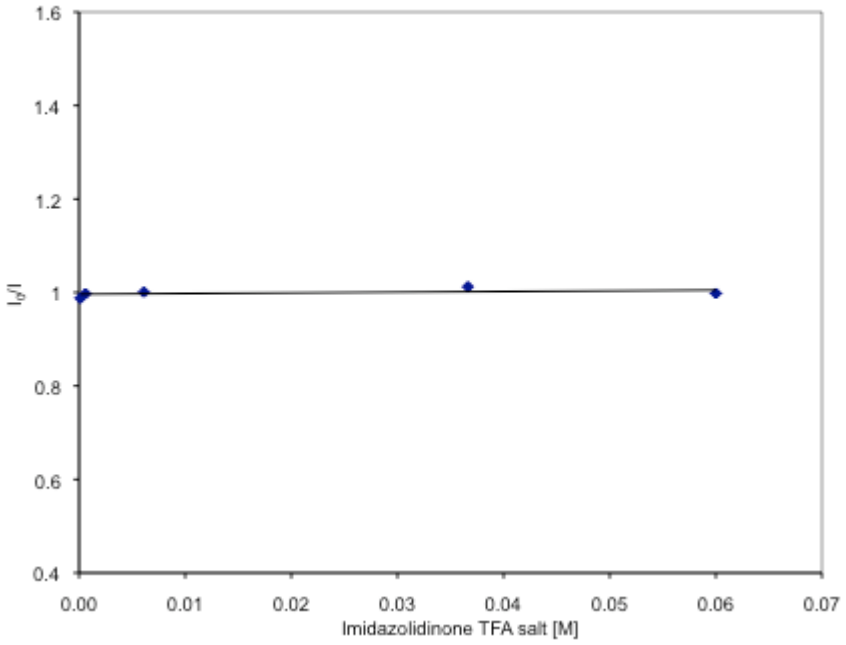


Figure S3: $Ir(bpy)_2(dtb\text{-}bpy)PF_6$ Emission Quenching by Lutidine

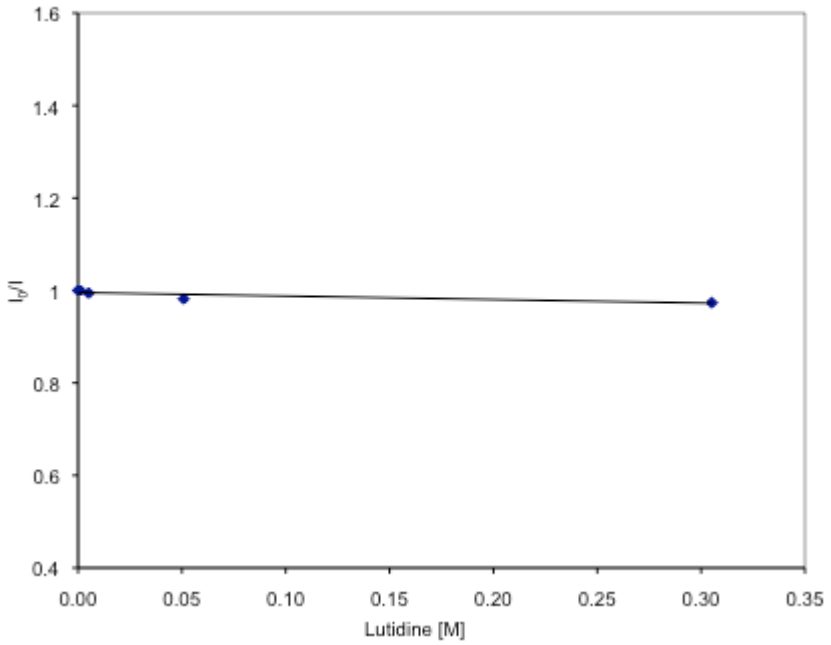


Figure S4: $Ir(bpy)_2(dtb\text{-}bpy)PF_6$ Emission Quenching by 3-Phenylpropanal

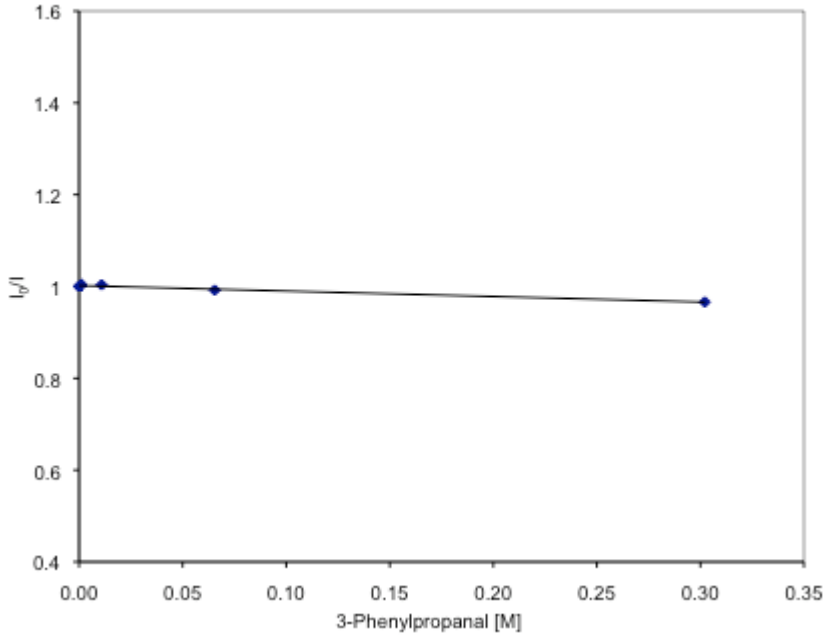
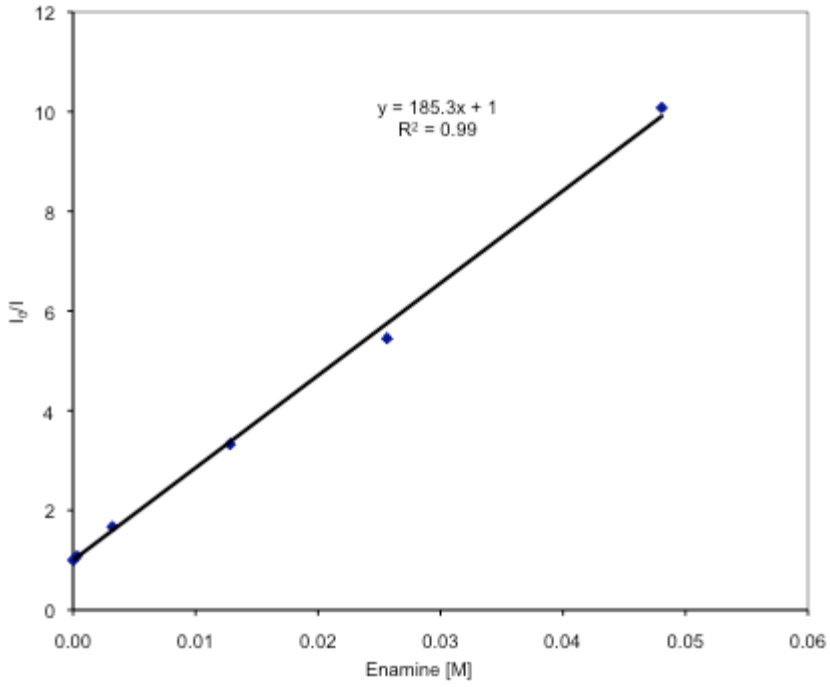
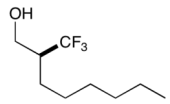


Figure S5: $Ir(bpy)_2(dtb\text{-}bpy)PF_6$ Emission Quenching by Enamine



VII. Spectroscopic Data.

^{1}H and ^{13}C NMR spectra, as well as HPLC or SFC traces, for all new compounds are included below.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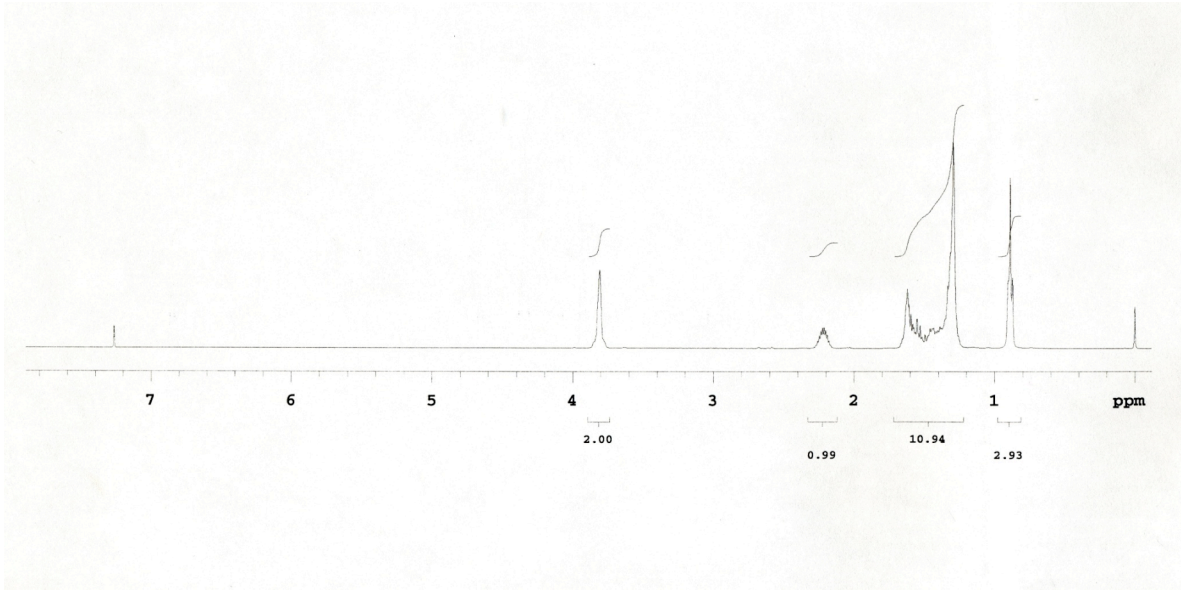
CF3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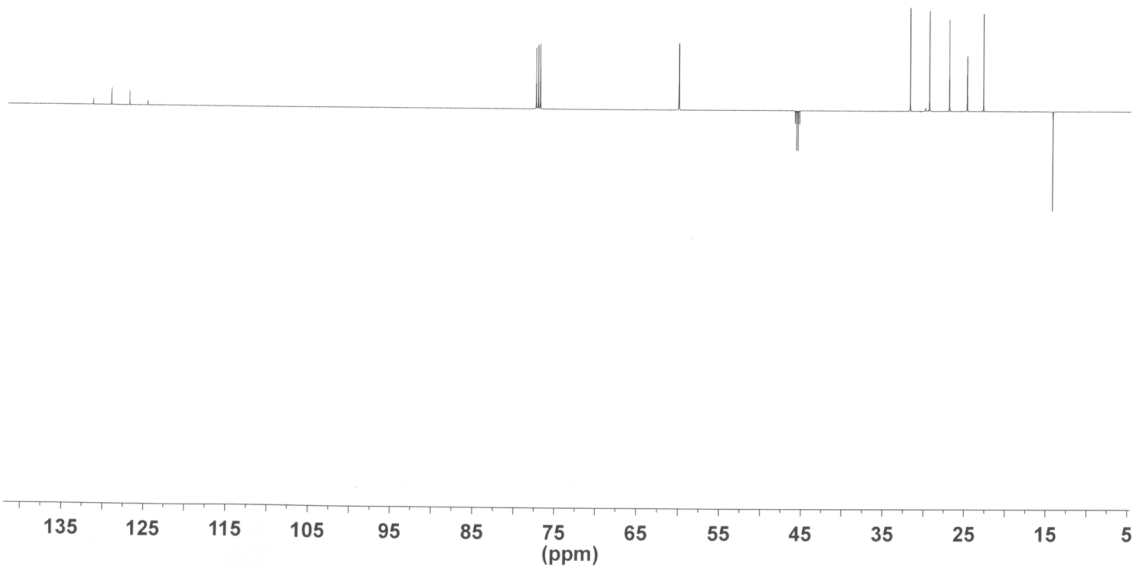
2.93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35
25
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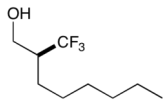
5
(ppm)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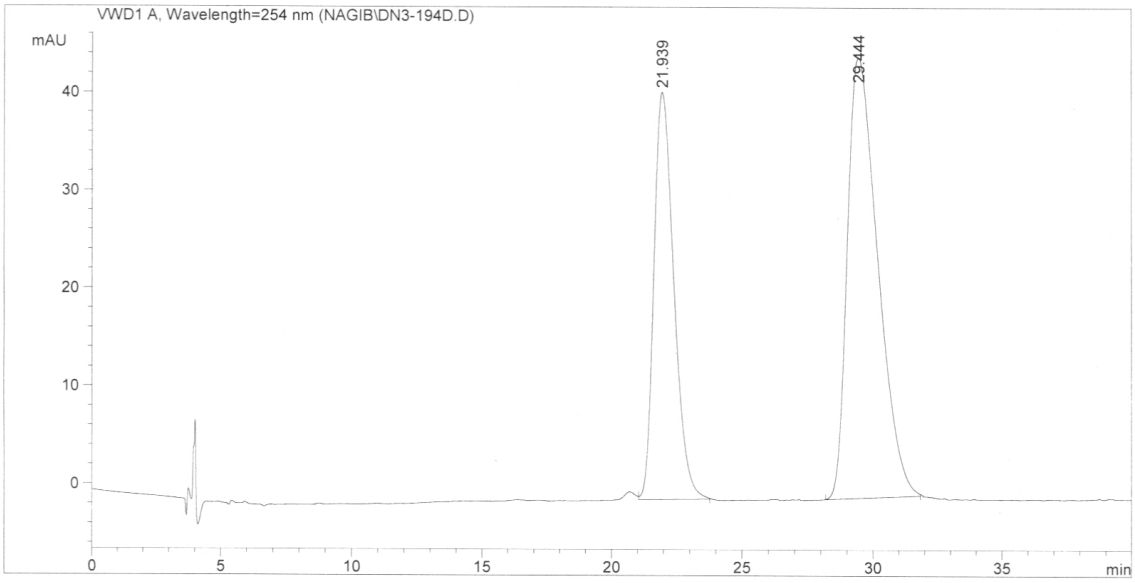
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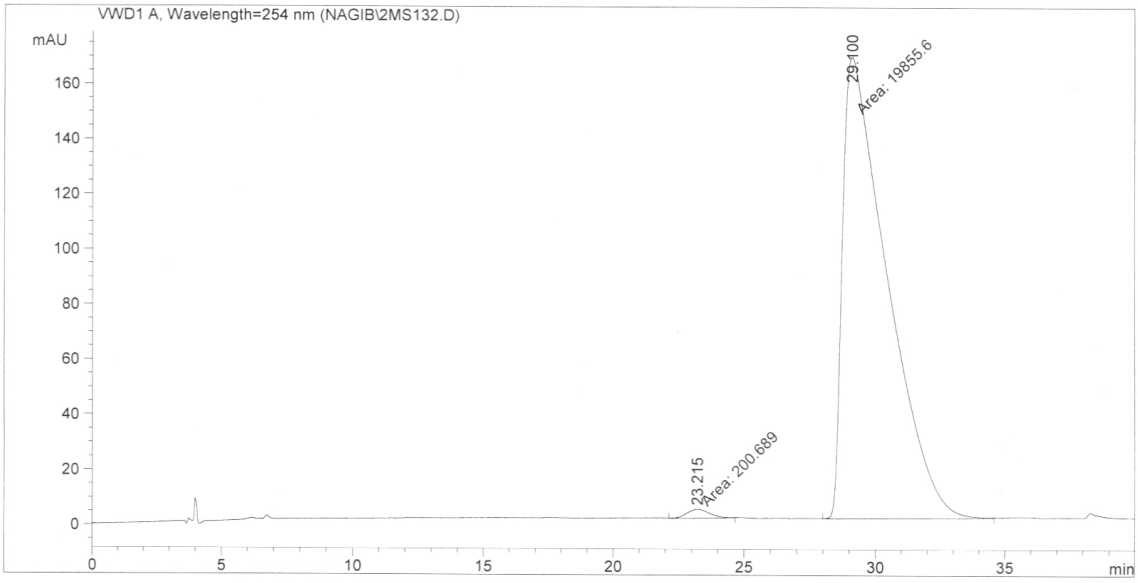
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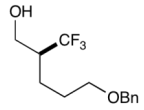
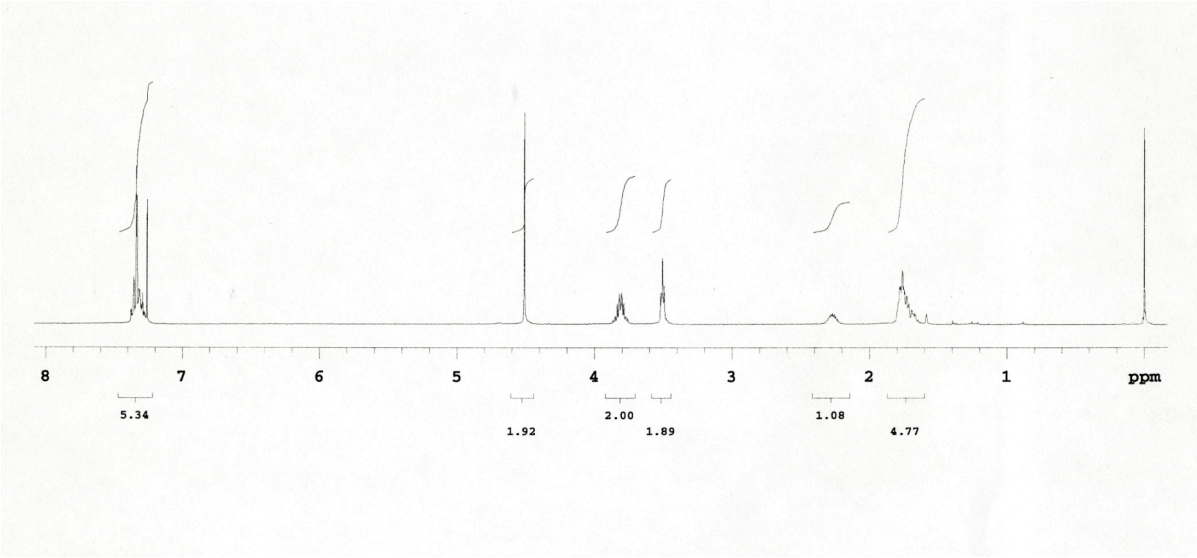
23.215
Area: 200.689
min


OH
CF3
OBn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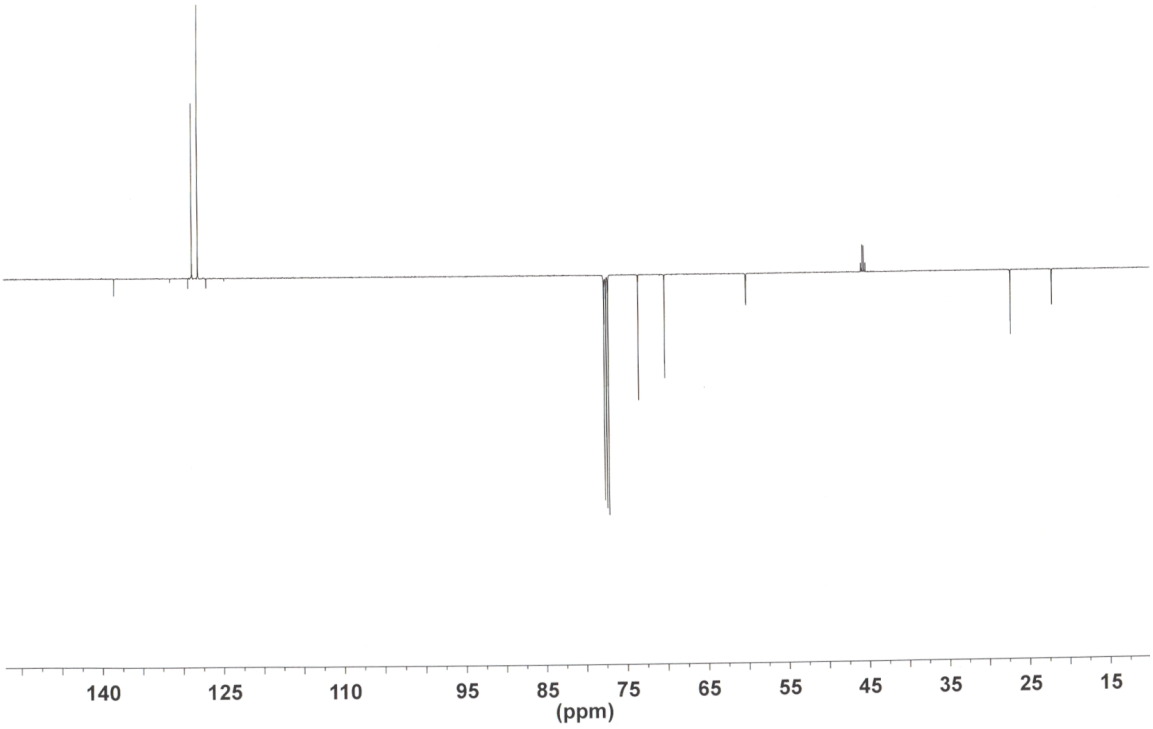
4.77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75
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55
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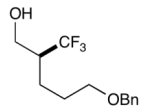
35
25
15
(ppm)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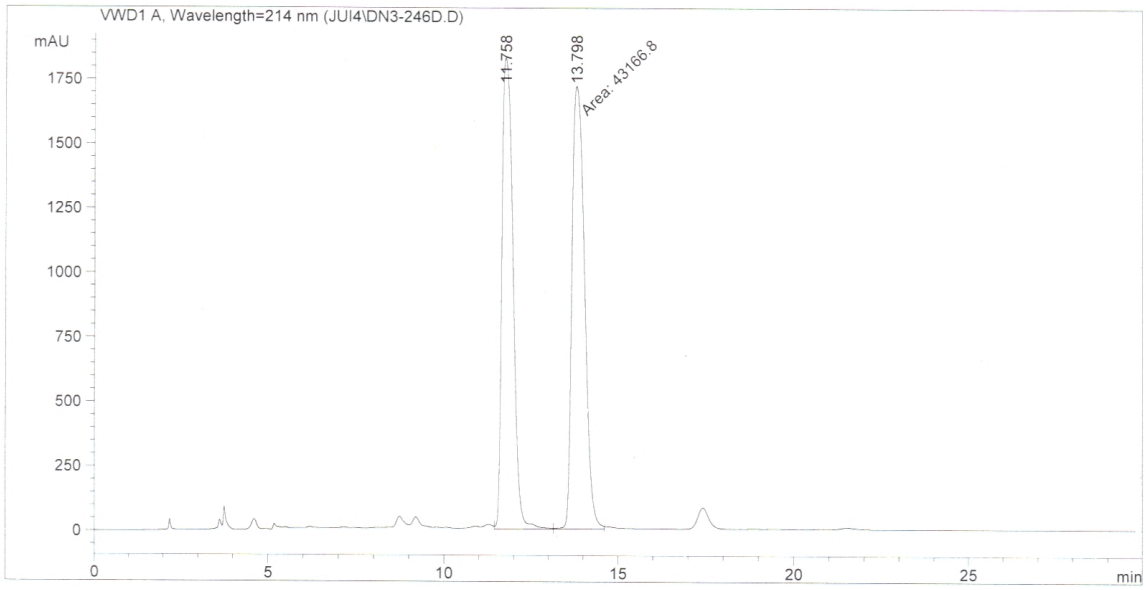
CF3
OBn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0
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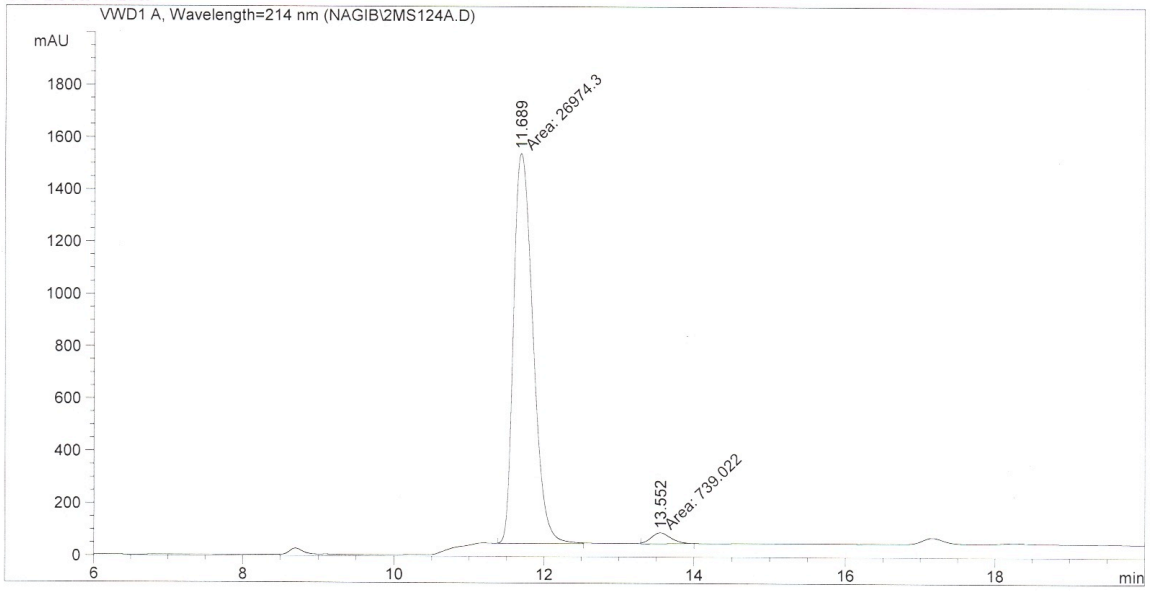
10
15
20
25
min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800
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6
8
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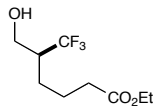
12
14
16
18
min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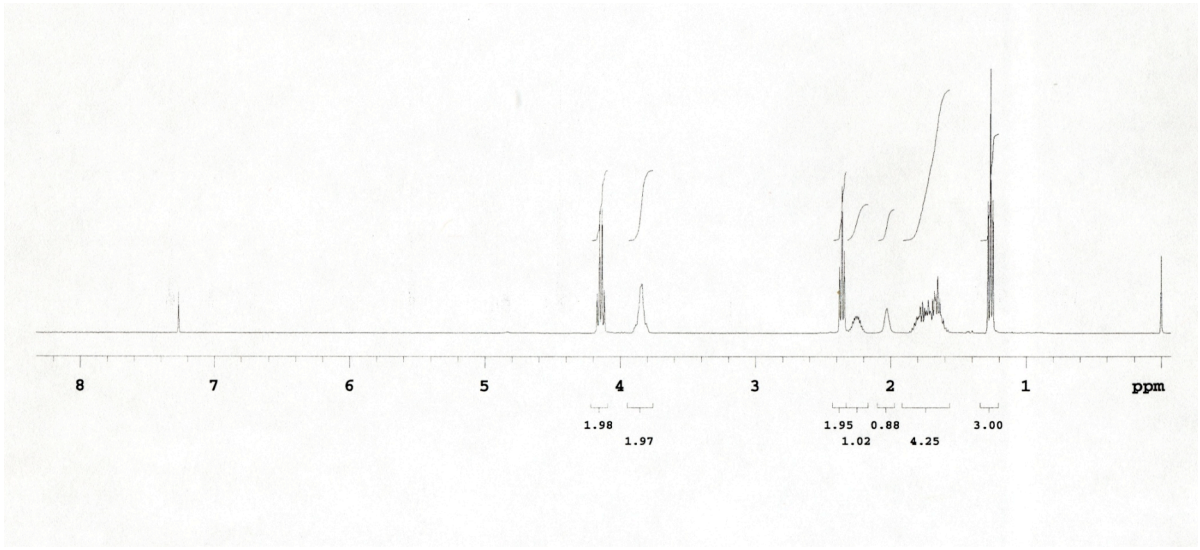
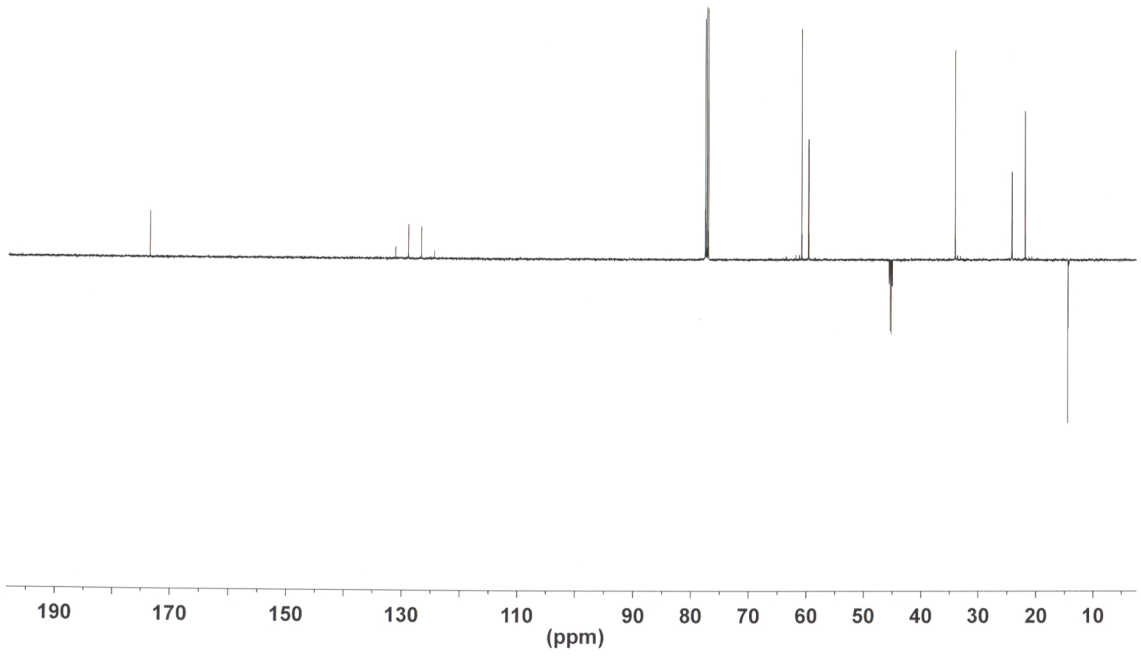
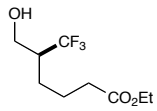
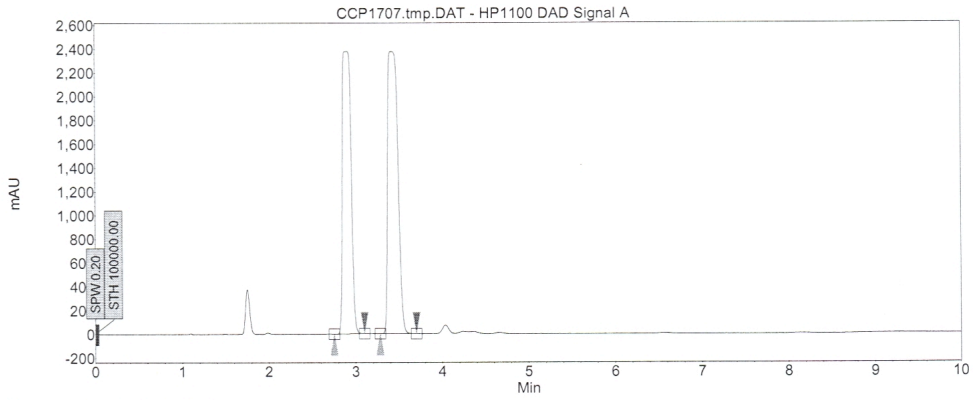

8
7
6
5
4
3
2
1
ppm
1.98
1.97
1.95
0.88
1.02
4.25
3.00


190
170
150
130
110
90
80
70
60
50
40
30
20
10
(ppm)

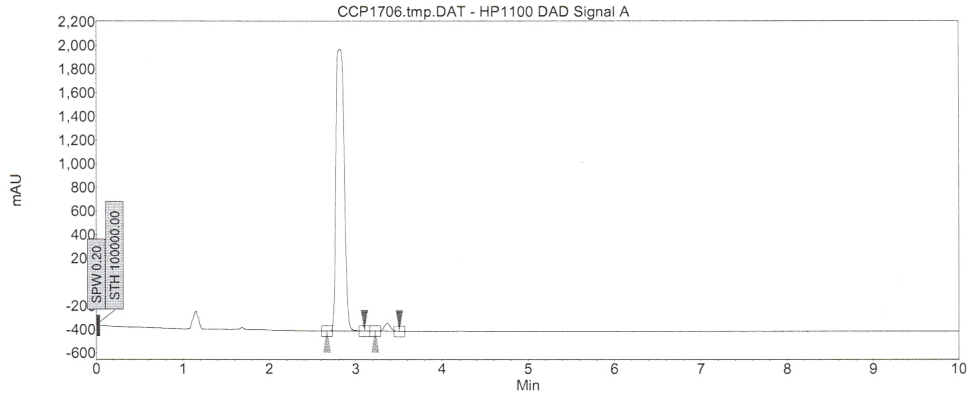




Chromatogram Noise is 0
STD Deviation is 0.04

Results Table:

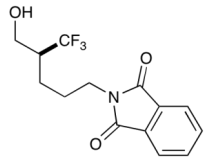
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.75	2.91	3.10	0.00	45.91	2375.8	274.0	45.914
2	UNKNOWN	3.28	3.43	3.70	0.00	54.09	2373.7	322.7	54.086
Total						100.00	4749.5	596.7	100.000

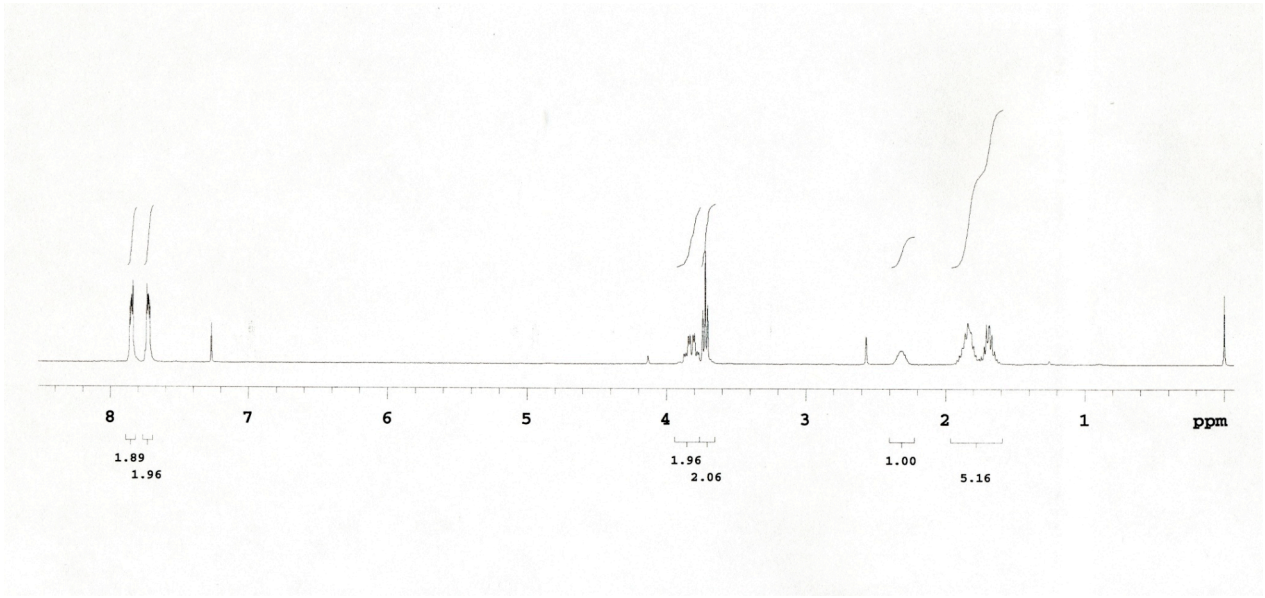


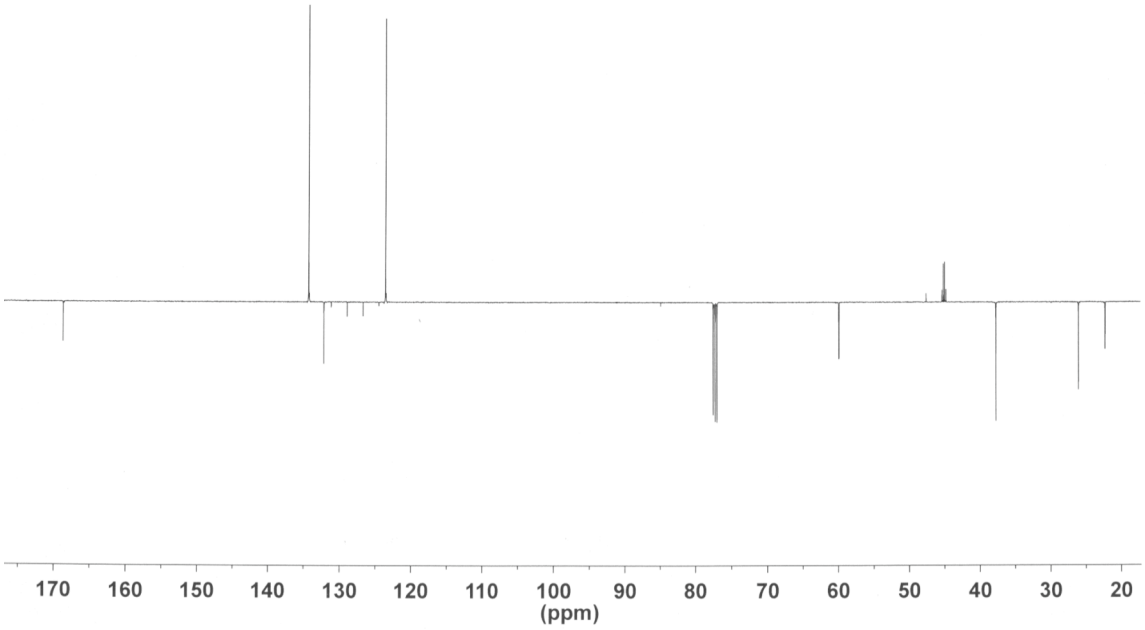
Chromatogram Noise is 0
STD Deviation is 0.03

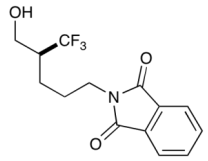
Results Table:

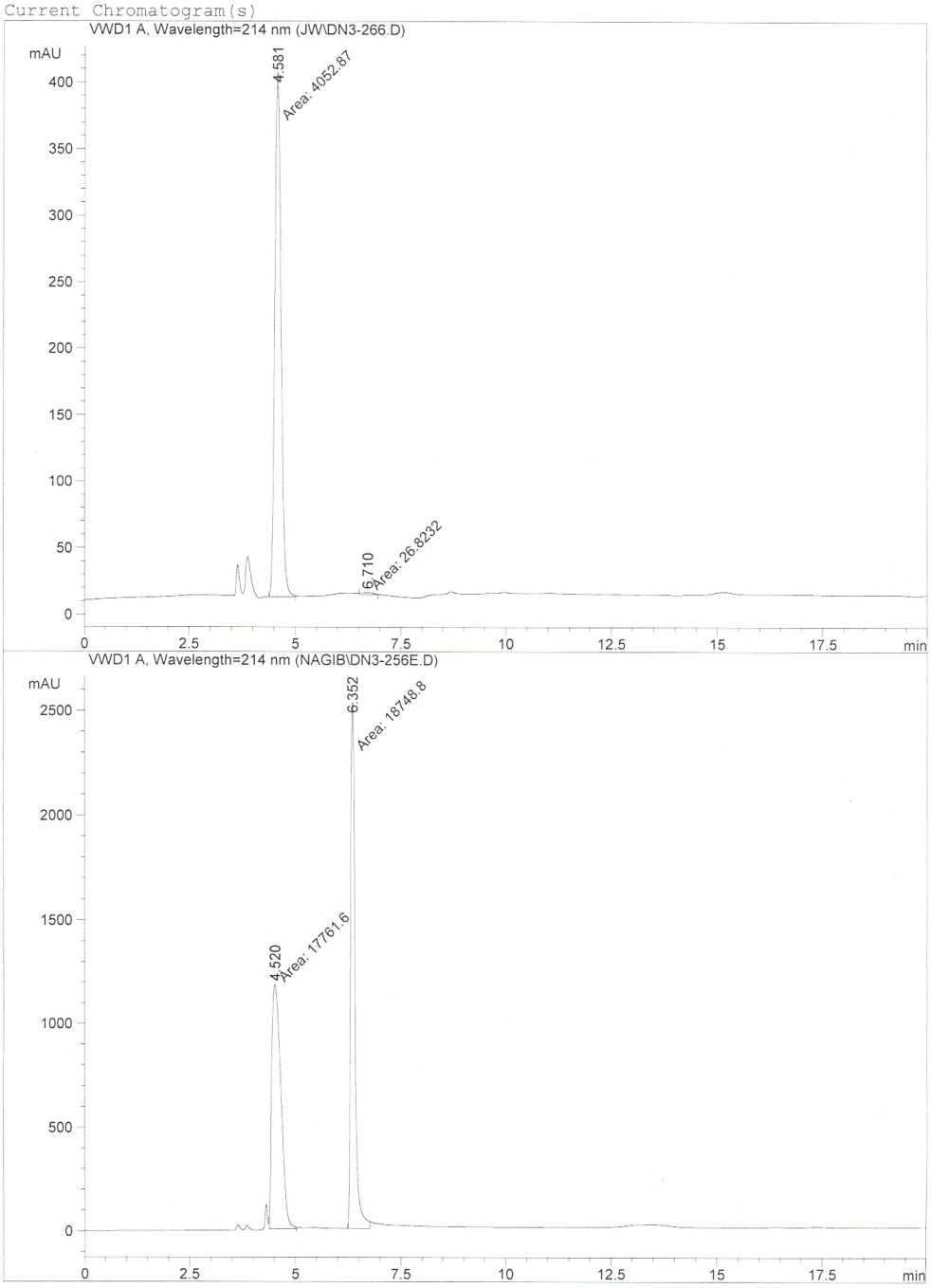
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.67	2.81	3.10	0.00	97.79	2381.1	262.9	97.795
2	UNKNOWN	3.23	3.37	3.51	0.00	2.21	69.3	5.9	2.205
Total						100.00	2450.5	268.9	100.000

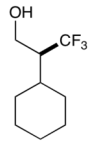

OH
CF3
O
N
O

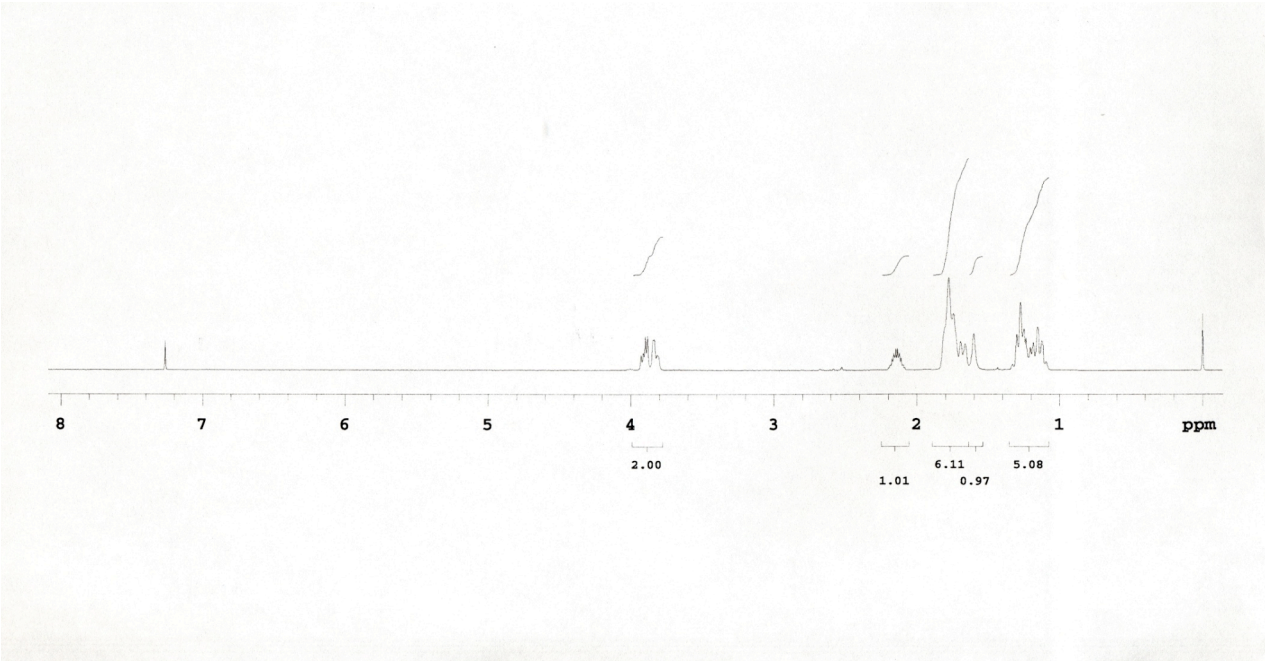

8
7
6
5
4
3
2
1
ppm
1.89
1.96
1.96
2.06
1.00
5.16

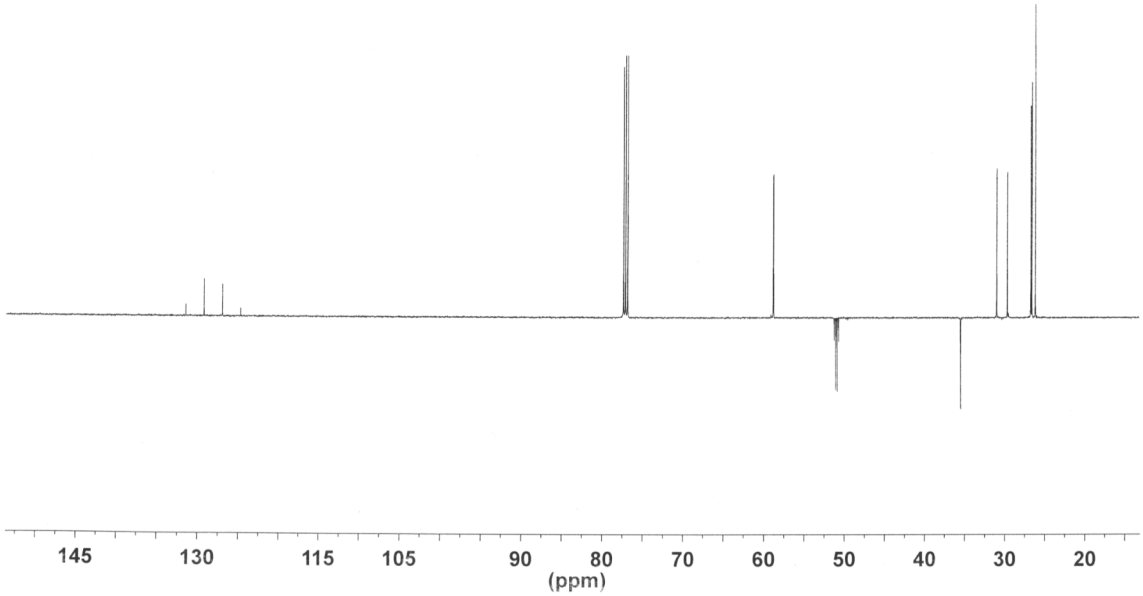

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

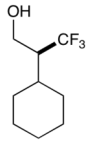

OH
CF3
O
N
O

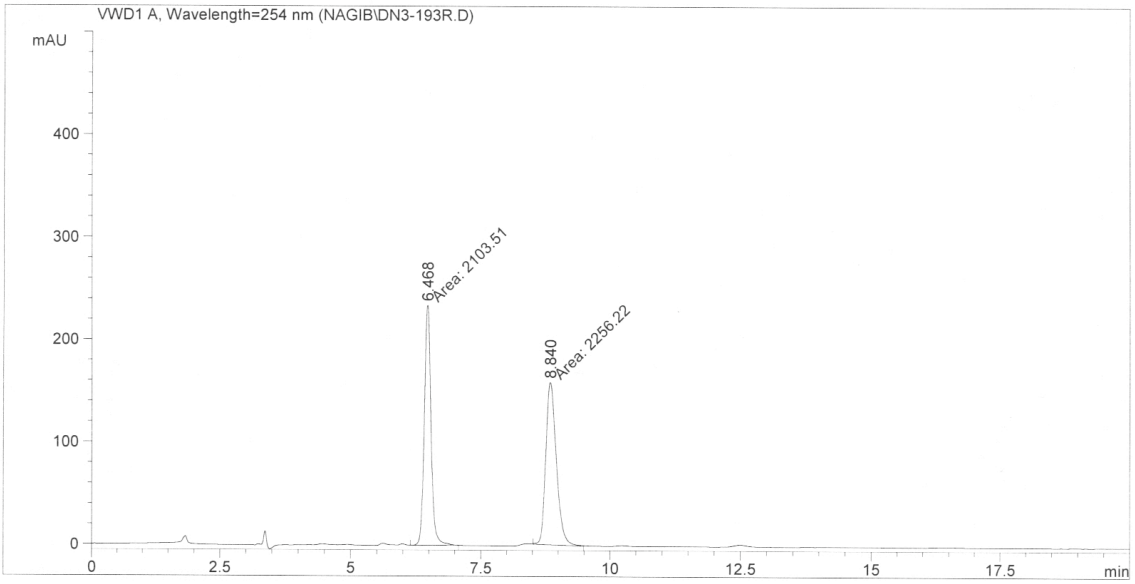

Current Chromatogram(s)
VWD1 A, Wavelength=214 nm (JW\DN3-266.D)
mAU
4.581
Area: 4052.87
6.710
Area: 26.8232
min
VWD1 A, Wavelength=214 nm (NAGIB\DN3-256E.D)
mAU
6.352
Area: 18748.8
4.520
Area: 17761.6
min

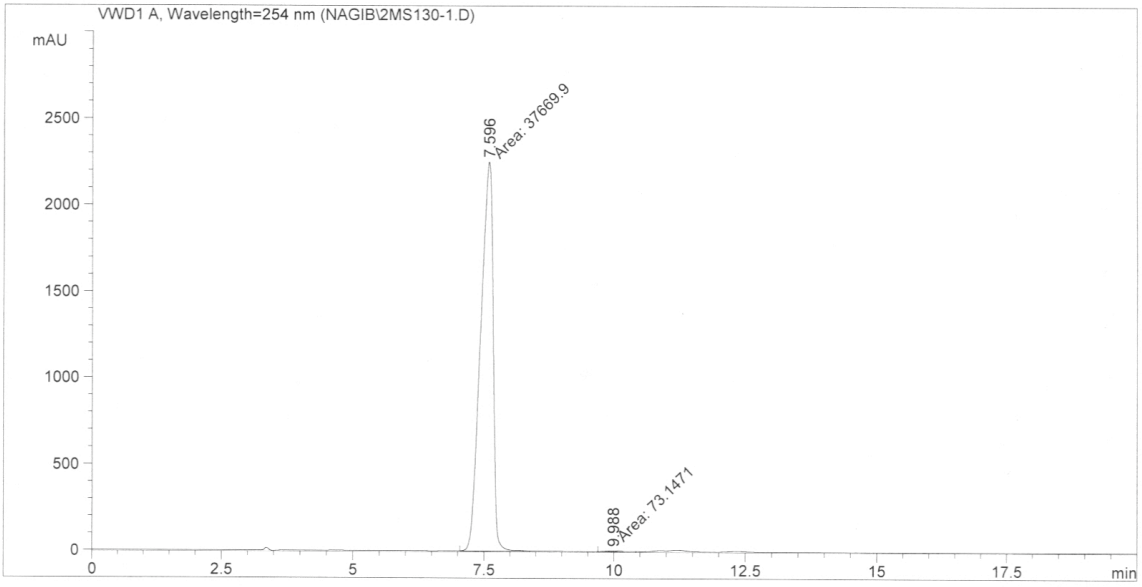

OH
CF3

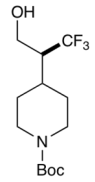

8
7
6
5
4
3
2
1
ppm
2.00
1.01
6.11
0.97
5.08

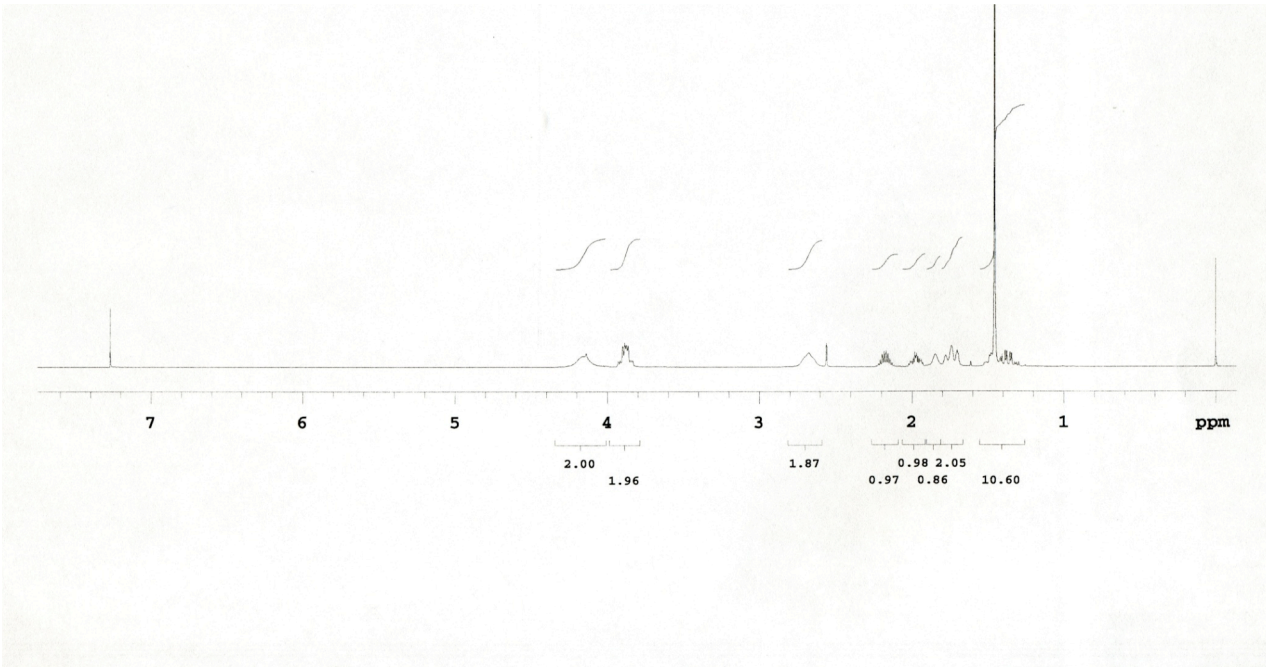

145
130
115
105
90
80
70
60
50
40
30
20
(ppm)

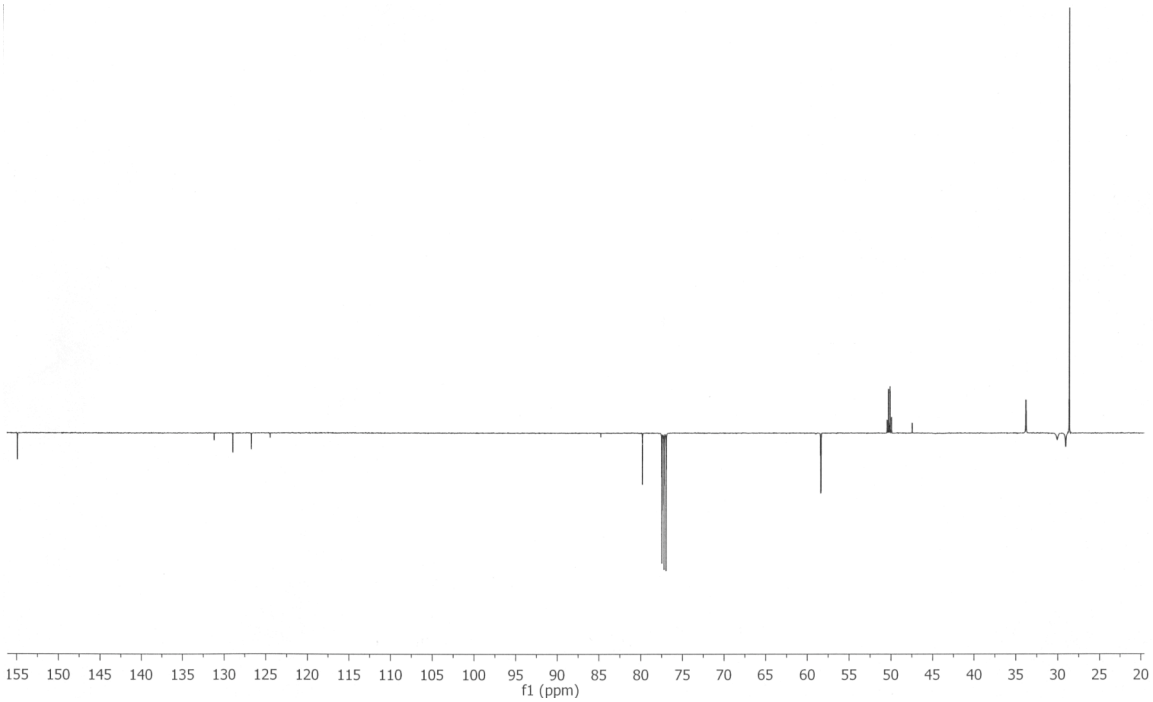

OH
CF3

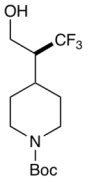

VWD1 A, Wavelength=254 nm (NAGIB\DN3-193R.D)
mAU
400
300
200
100
0
6.468
Area: 2103.51
8.840
Area: 2256.22
0
2.5
5
7.5
10
12.5
15
17.5
min

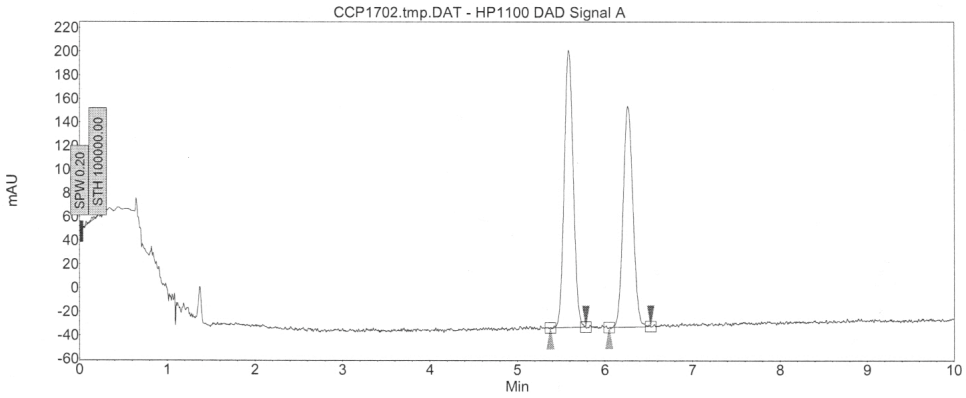

VWD1 A, Wavelength=254 nm (NAGIB\2MS130-1.D)
mAU
2500
2000
1500
1000
500
0
7.596
Area: 37669.9
9.988
Area: 73.1471
0
2.5
5
7.5
10
12.5
15
17.5
min


OH
CF3
N
Boc


7
6
5
4
3
2
1
ppm
2.00
1.96
1.87
0.98
2.05
0.97
0.86
10.60


155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

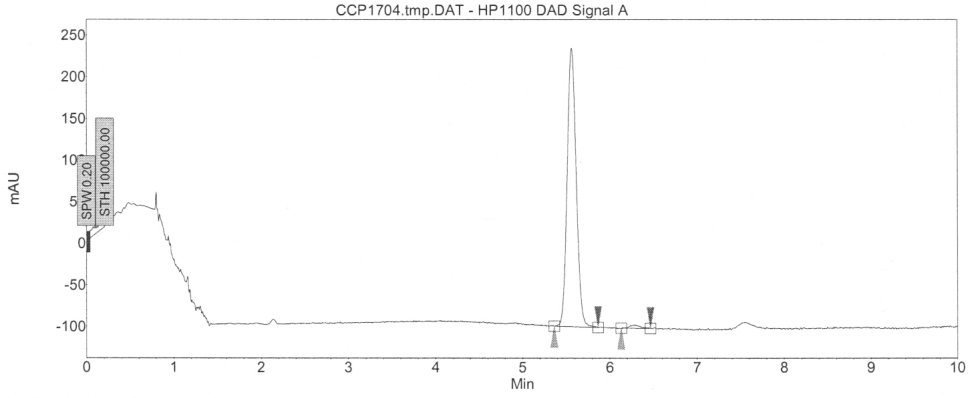




Chromatogram Noise is 0
STD Deviation is 0.06

Results Table:

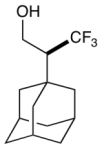
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.38	5.59	5.78	0.00	53.47	234.4	28.0	53.473
2	UNKNOWN	6.05	6.26	6.52	0.00	46.53	186.6	24.3	46.527
Total						100.00	421.0	52.3	100.000

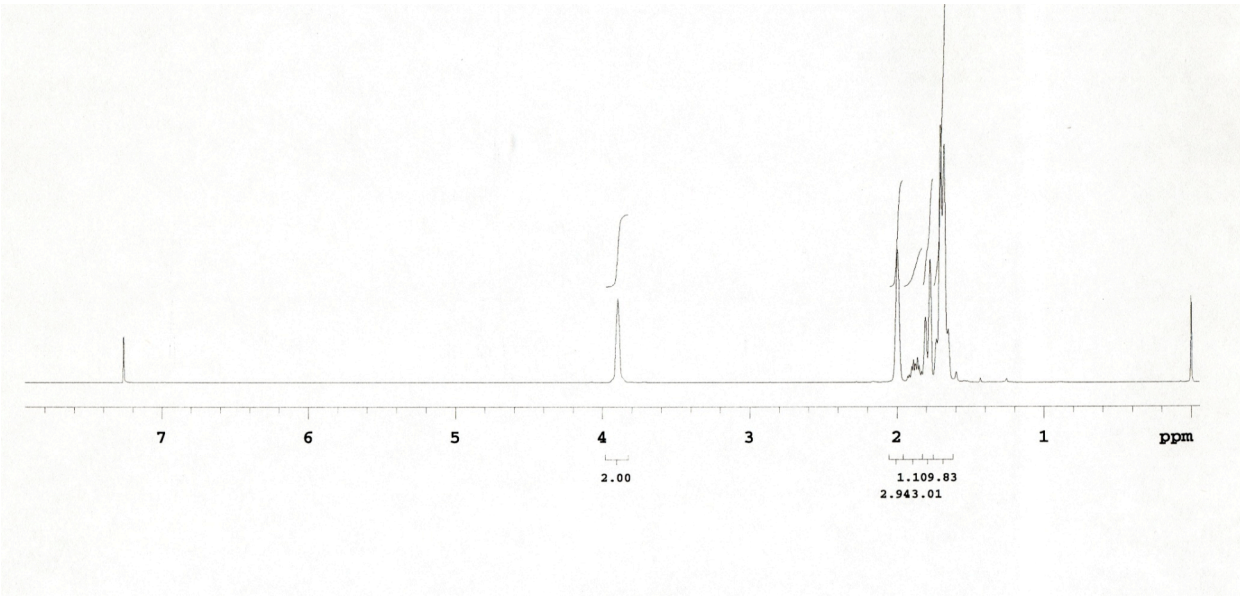


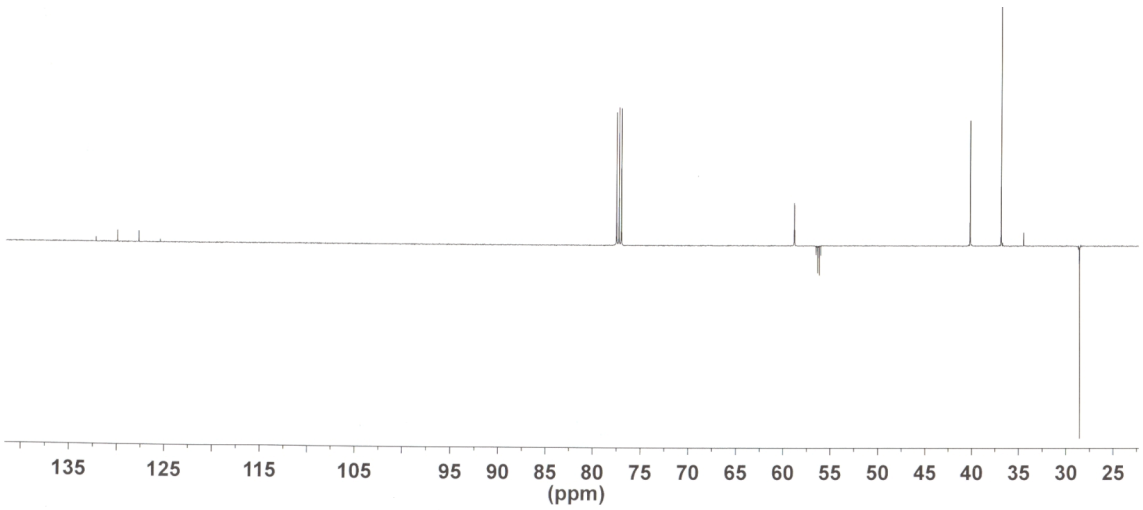
Chromatogram Noise is 0
STD Deviation is 0.03

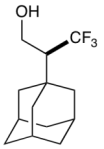
Results Table:

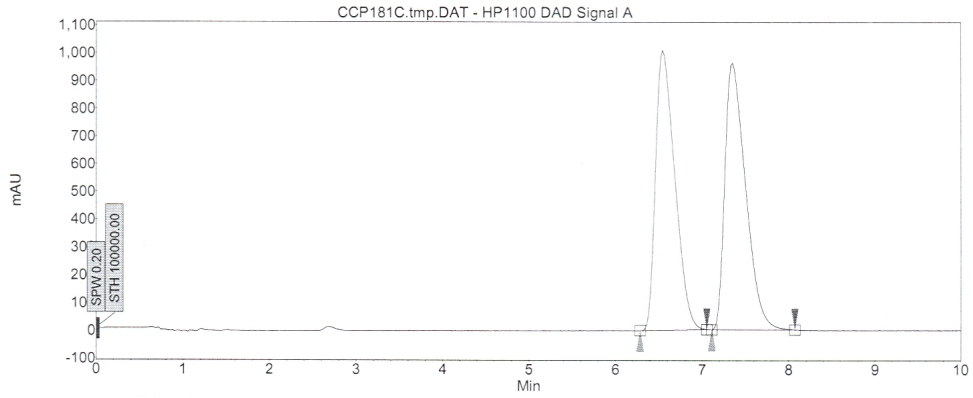
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.36	5.57	5.87	0.00	98.70	335.0	40.3	98.702
2	UNKNOWN	6.13	6.29	6.47	0.00	1.30	4.0	0.5	1.298
Total						100.00	339.0	40.8	100.000


OH
CF3


7
6
5
4
3
2
1
ppm
2.00
1.109.83
2.943.01


135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
(ppm)

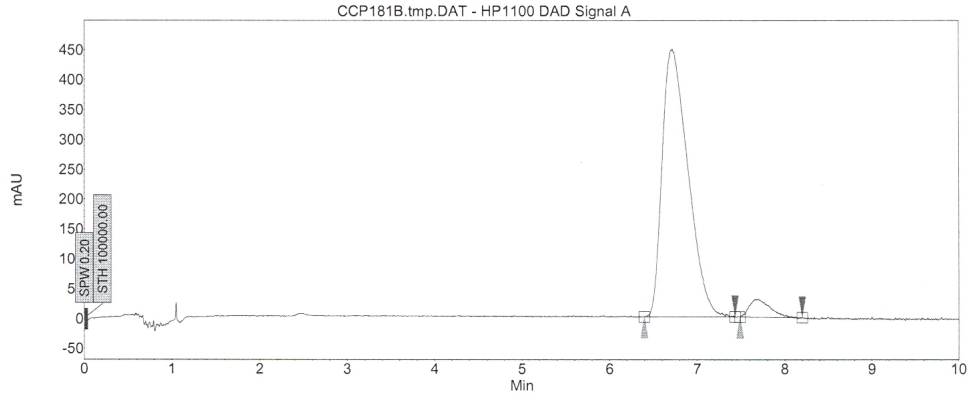




Chromatogram Noise is 0
STD Deviation is 0.02

Results Table:

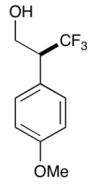
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.29	6.54	7.05	0.00	49.29	1007.9	259.3	49.285
2	UNKNOWN	7.11	7.35	8.07	0.00	50.71	960.5	266.8	50.715
Total						100.00	1968.4	526.1	100.000

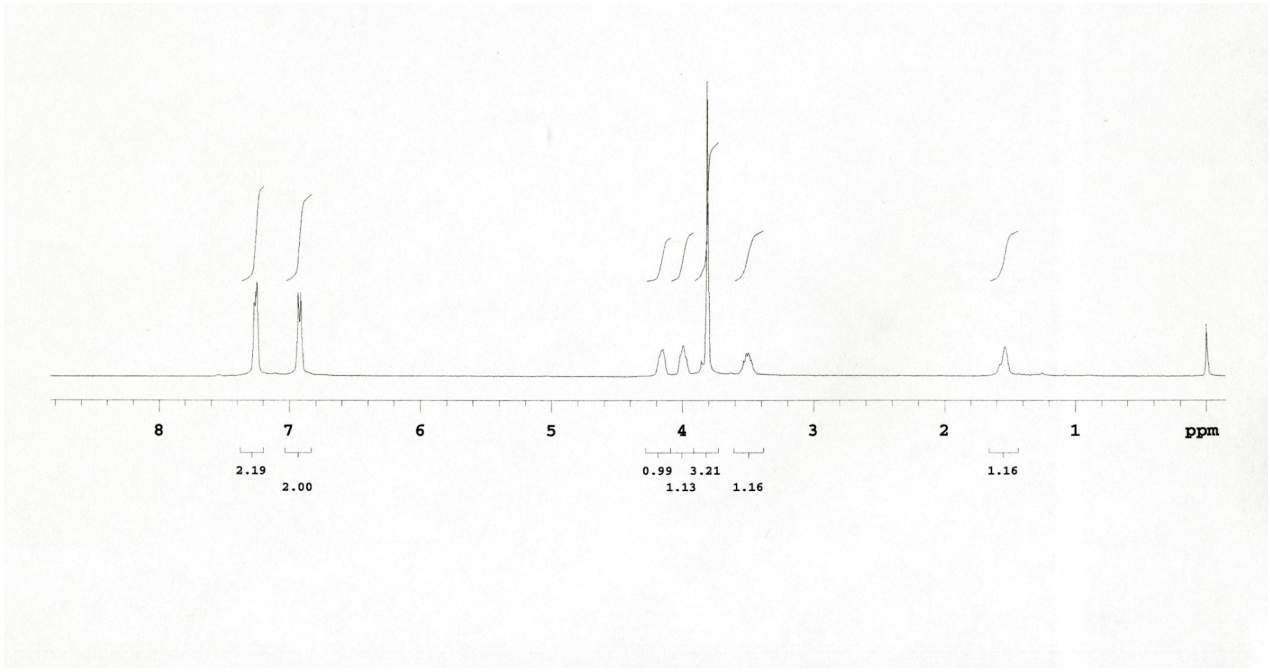


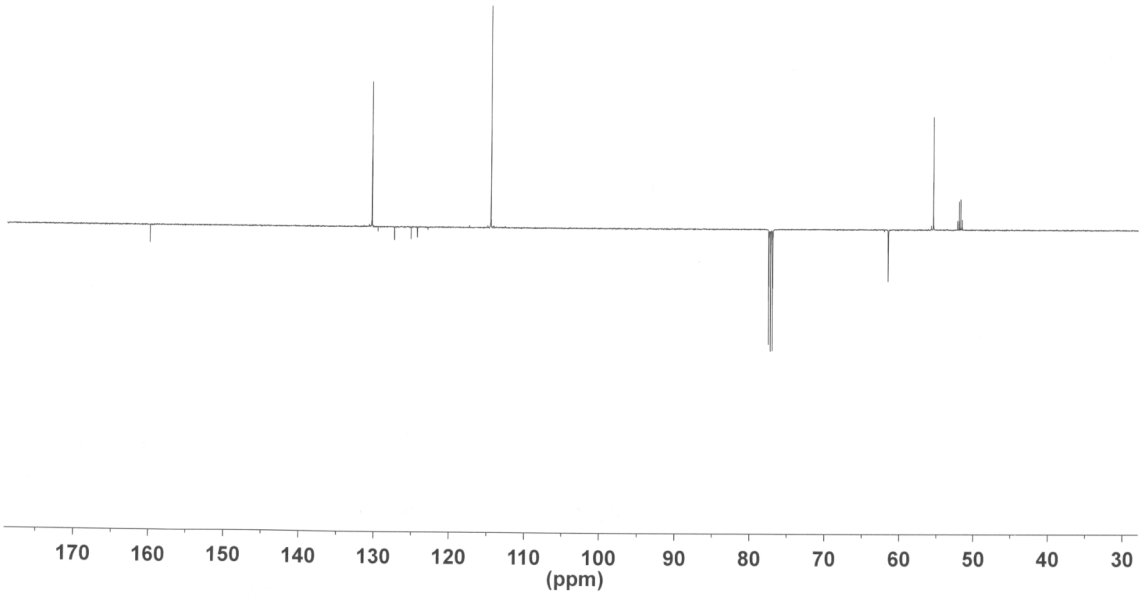
Chromatogram Noise is 0
STD Deviation is 0.03

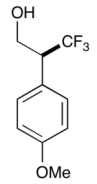
Results Table:

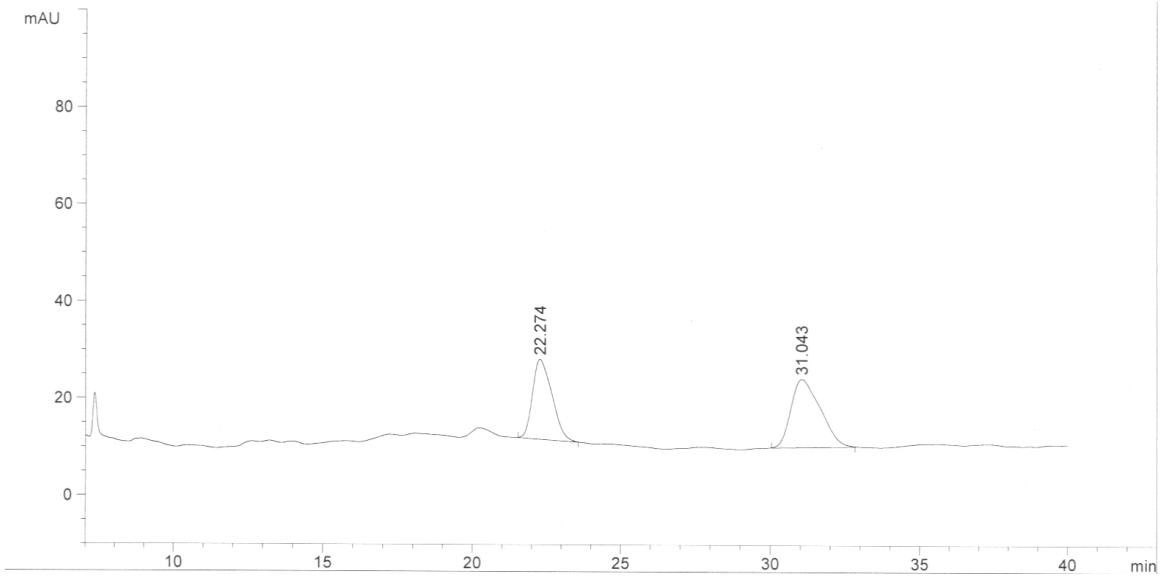
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.40	6.72	7.43	0.00	94.86	448.3	153.2	94.856
2	UNKNOWN	7.49	7.70	8.20	0.00	5.14	30.5	8.3	5.144
Total						100.00	478.9	161.5	100.000

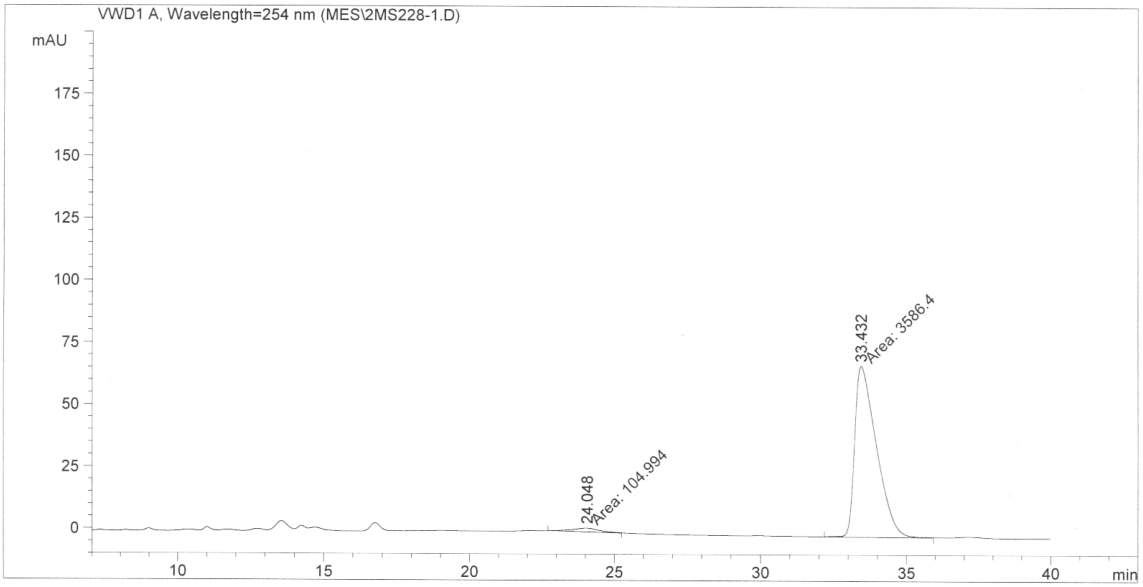

OH
CF3
OMe

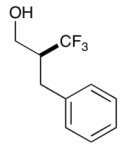

8
7
6
5
4
3
2
1
ppm
2.19
2.00
0.99
3.21
1.13
1.16
1.16

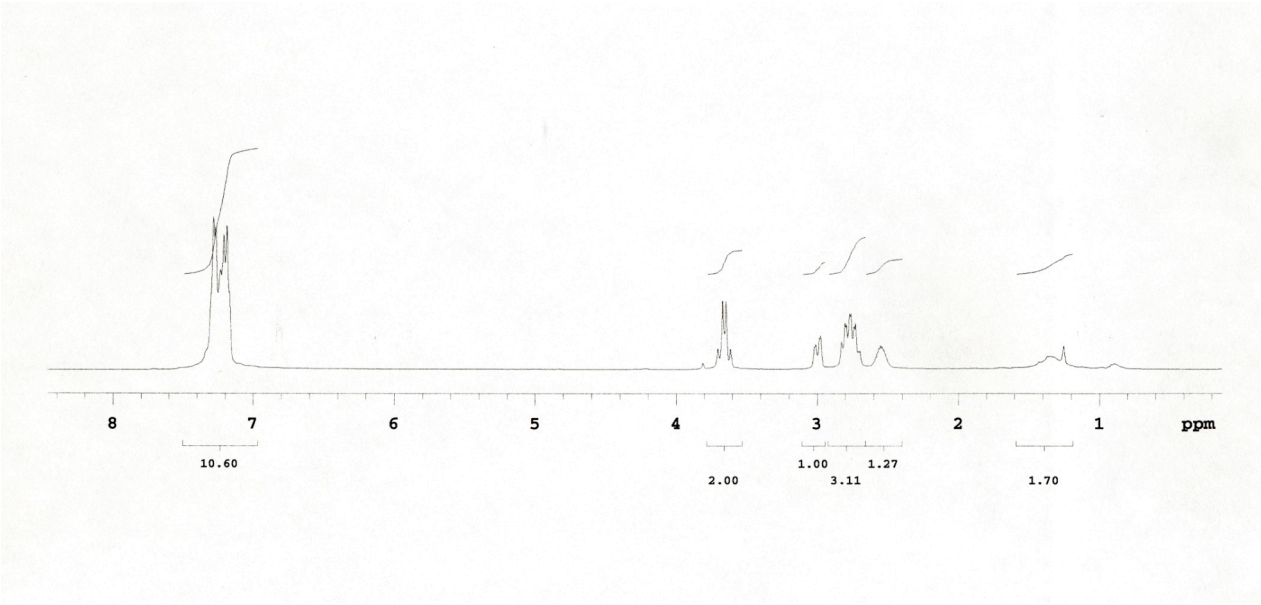

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
(ppm)

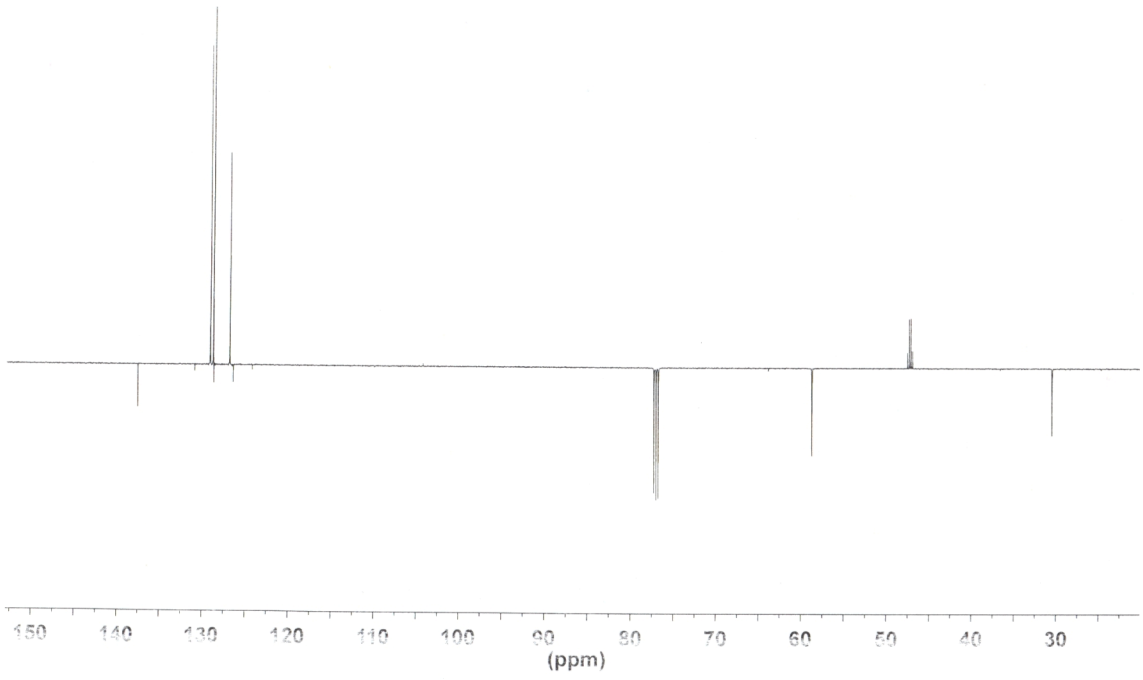

OH
CF3
OMe

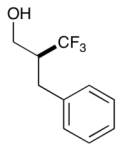

mAU
80
60
40
20
0
22.274
31.043
10
15
20
25
30
35
40
min

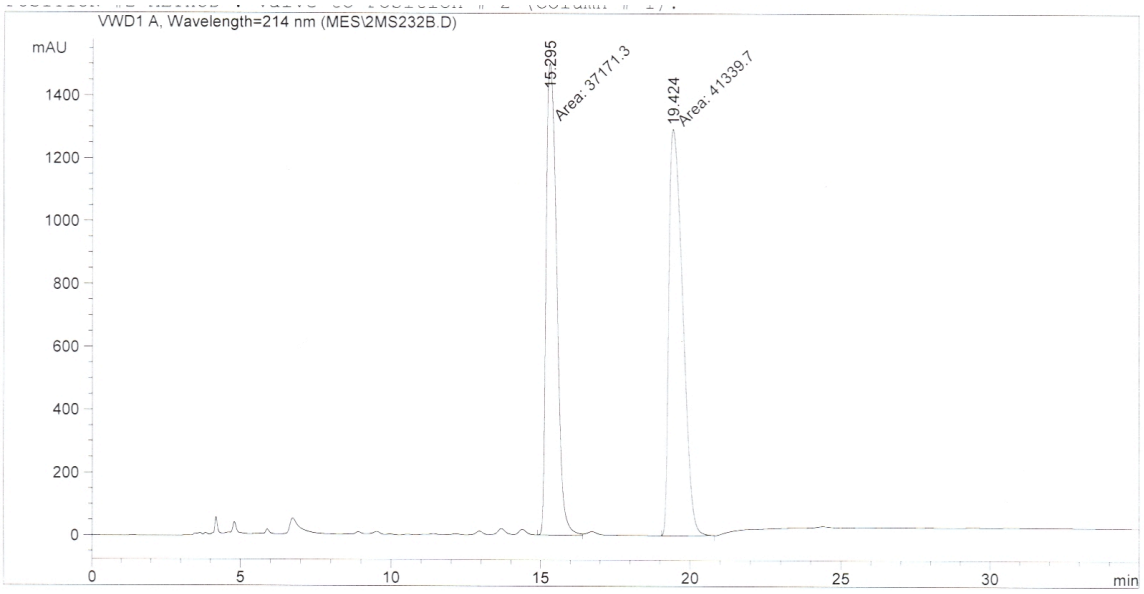

VWD1 A, Wavelength=254 nm (MES\2MS228-1.D)
mAU
175
150
125
100
75
50
25
0
24.048
Area: 104.994
33.432
Area: 3586.4
10
15
20
25
30
35
40
min

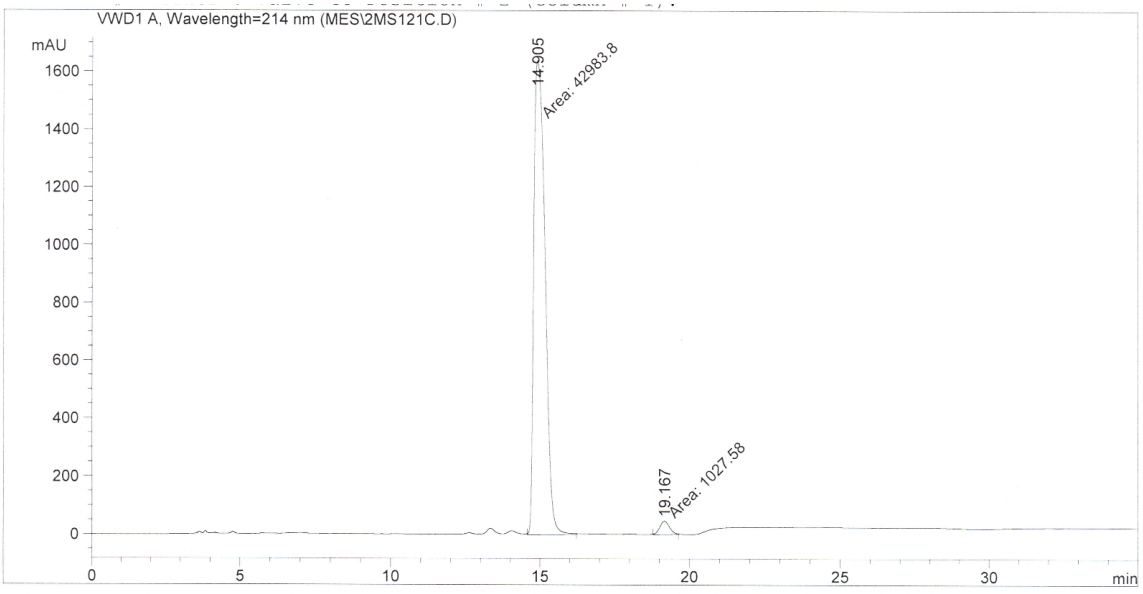

OH
CF3

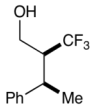

8
7
6
5
4
3
2
1
ppm
10.60
2.00
1.00
3.11
1.27
1.70

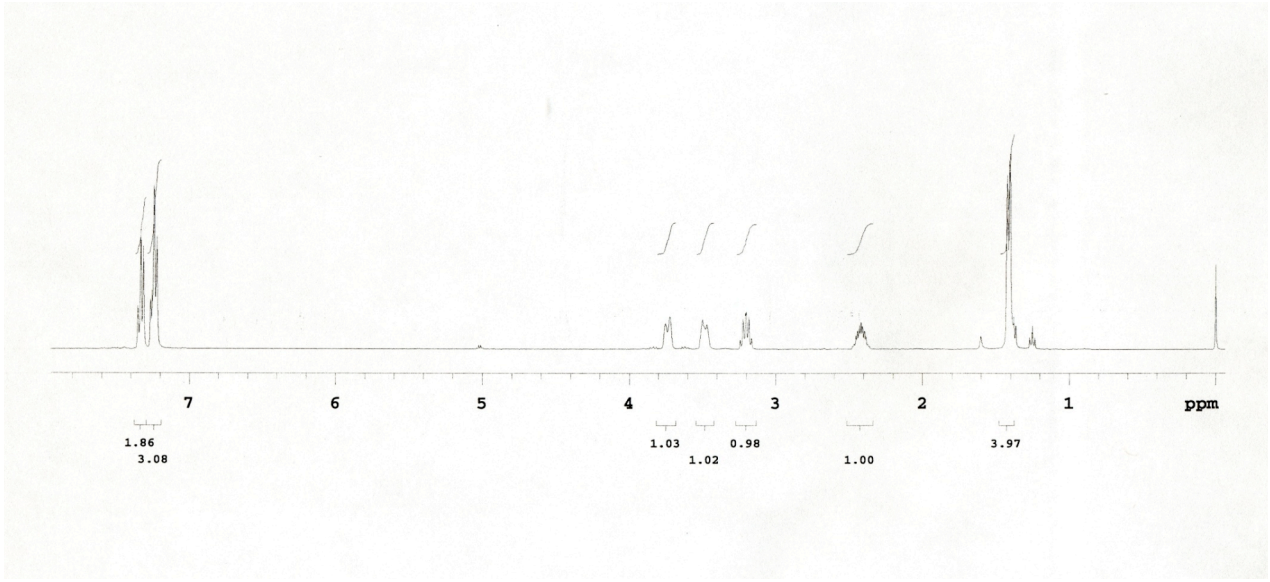

150
140
130
120
110
100
90
80
70
60
50
40
30
(ppm)

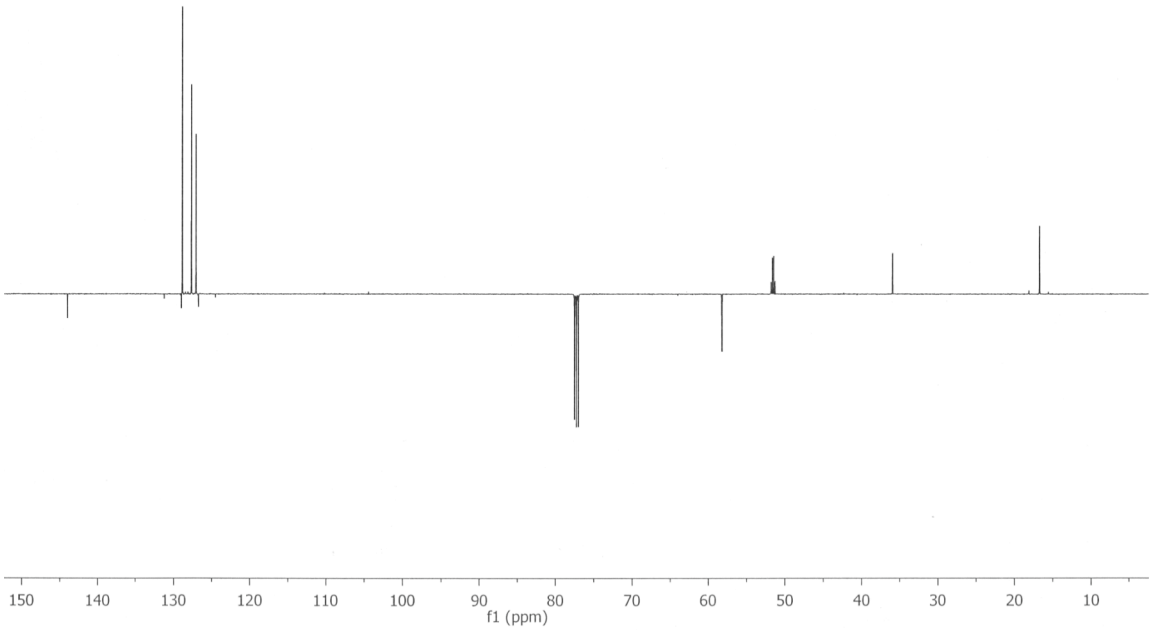

OH
CF3

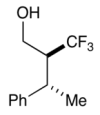

VWD1 A, Wavelength=214 nm (MES\2MS232B.D)
mAU
15.295
Area: 37171.3
19.424
Area: 41339.7
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
min

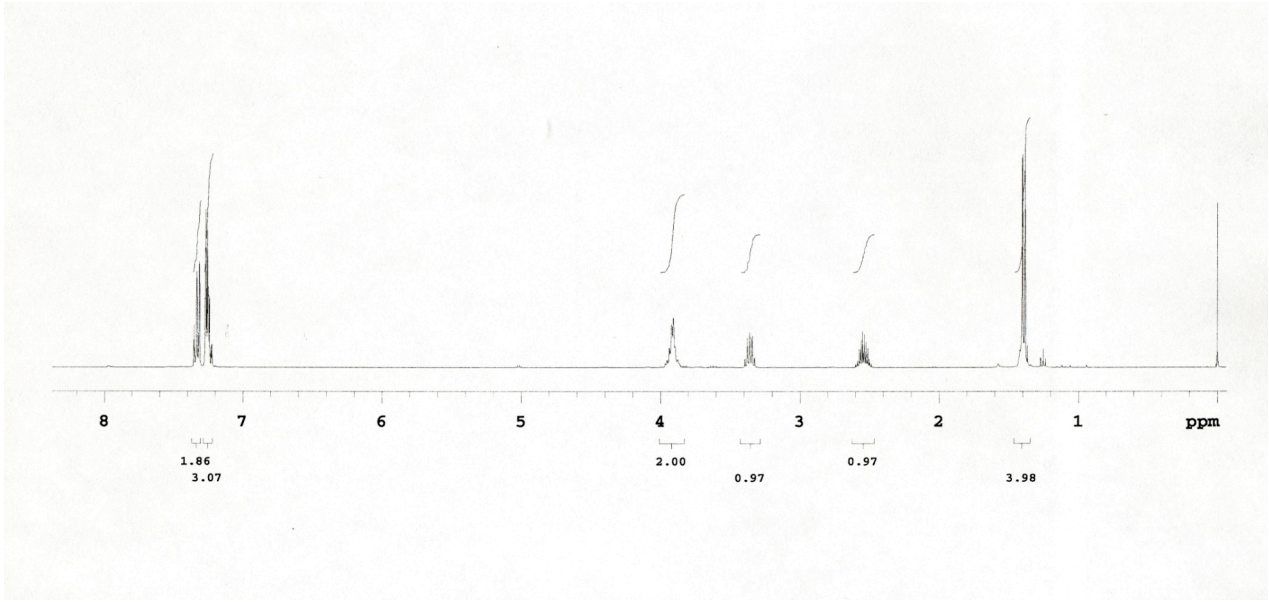

VWD1 A, Wavelength=214 nm (MES\2MS121C.D)
mAU
14.905
Area: 42983.8
19.167
Area: 1027.58
1600
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
min

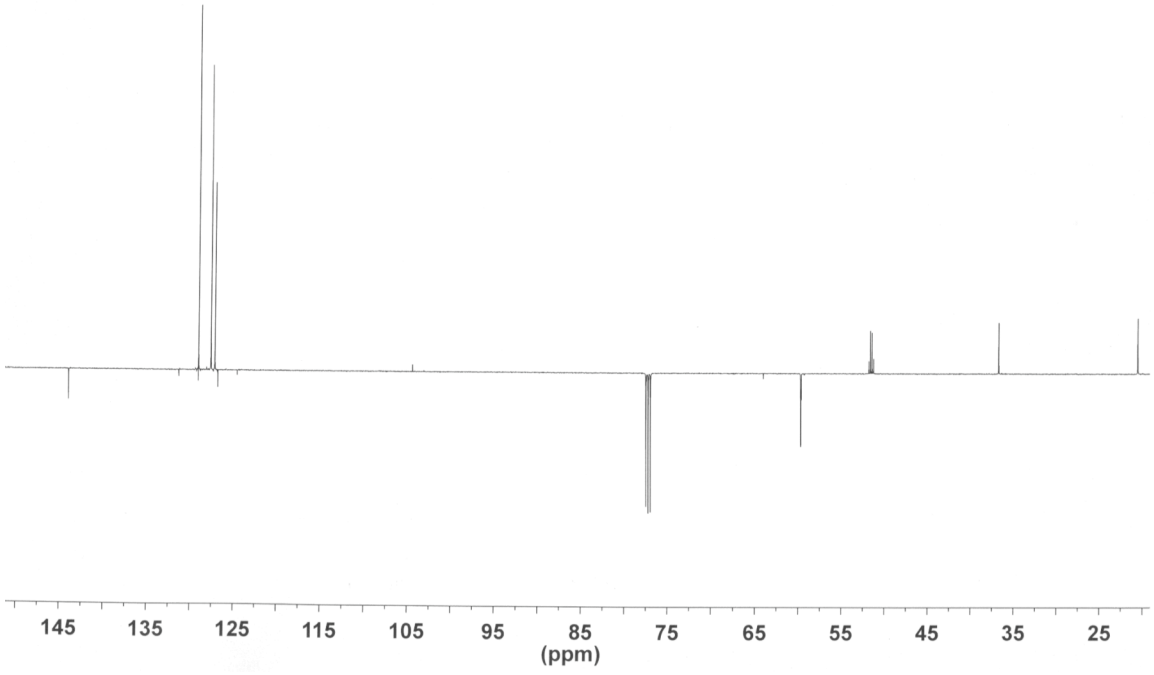

OH
CF3
Ph
Me

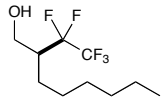

7
6
5
4
3
2
1
ppm
1.86
3.08
1.03
1.02
0.98
1.00
3.97

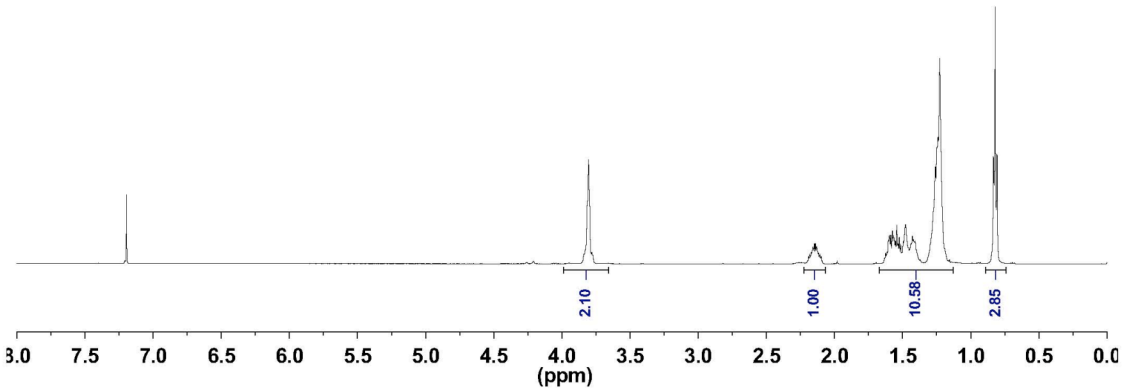

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

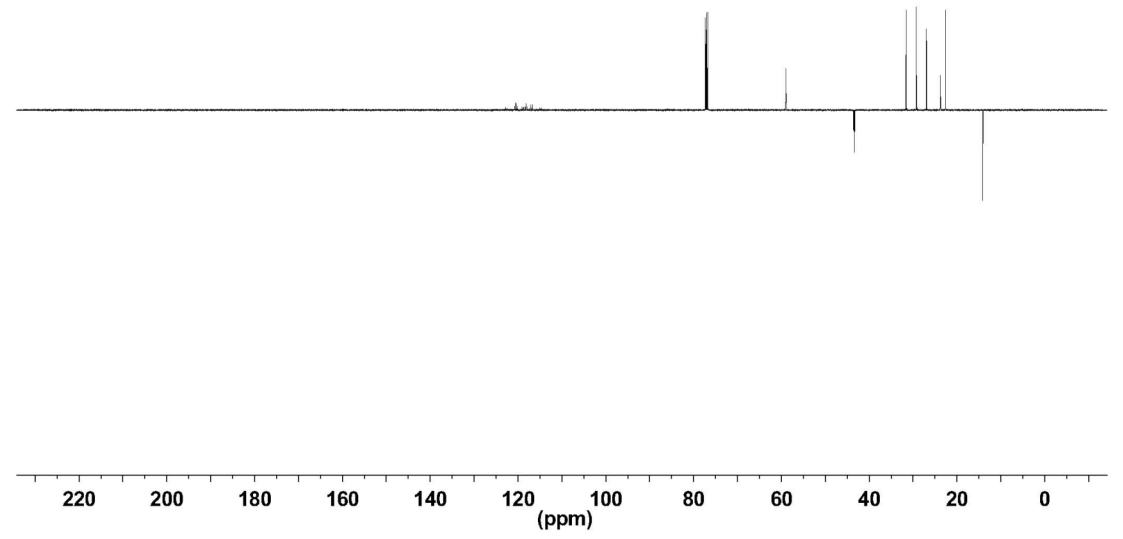

OH
CF3
Ph
Me

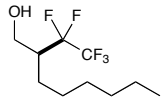

8
7
6
5
4
3
2
1
ppm
1.86
3.07
2.00
0.97
0.97
3.98

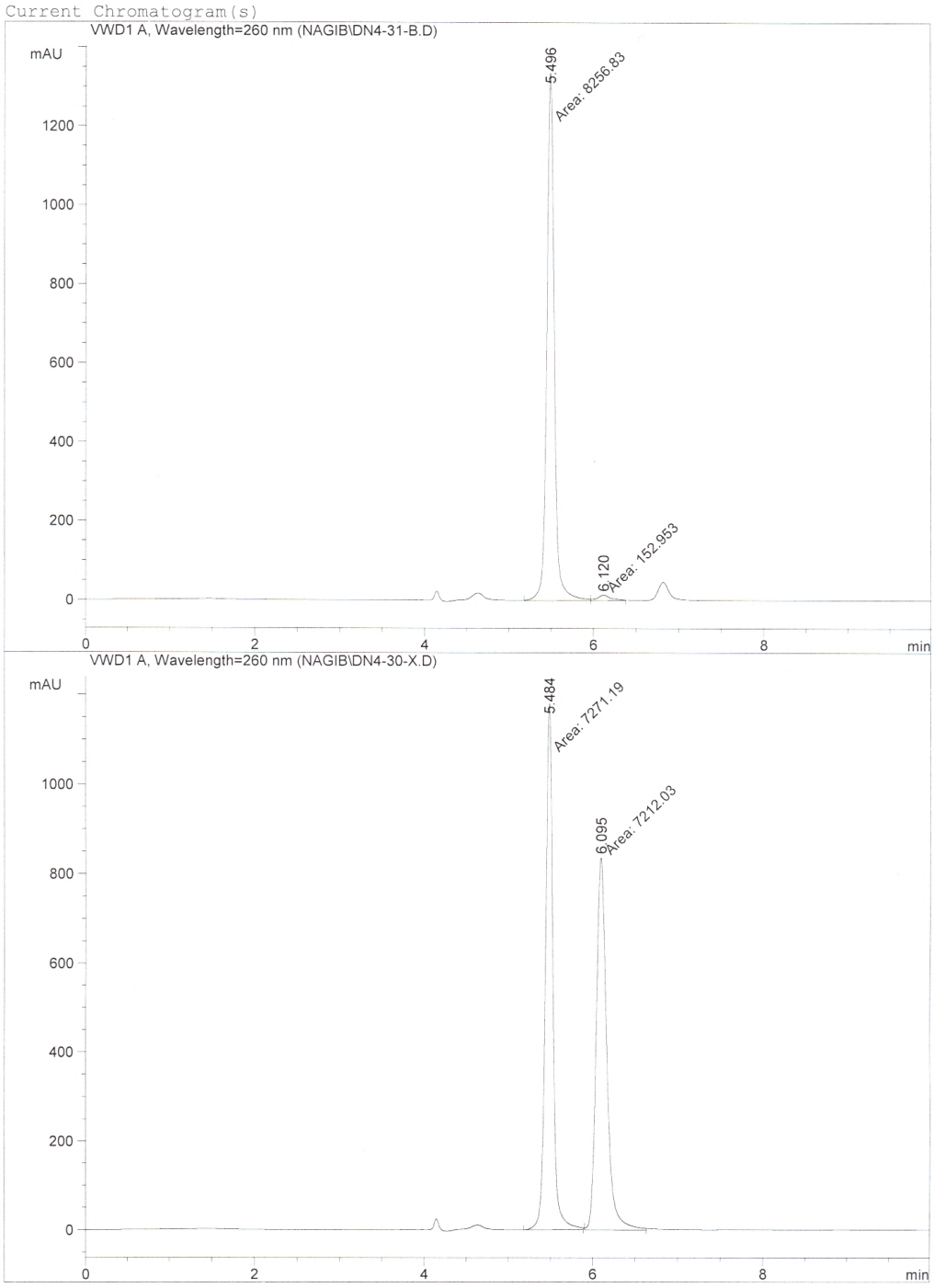

145
135
125
115
105
95
85
75
65
55
45
35
25
(ppm)

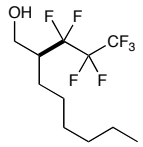

OH
F
F
CF3

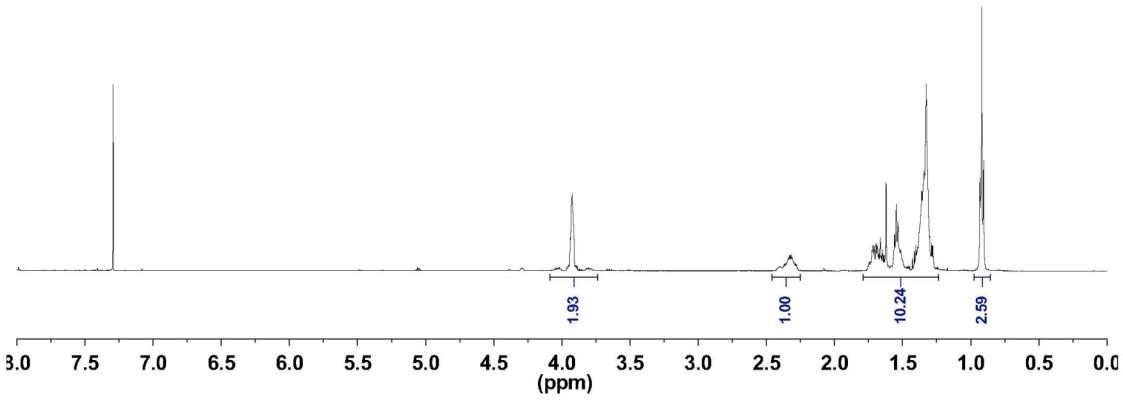

2.10
1.00
10.58
2.85
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

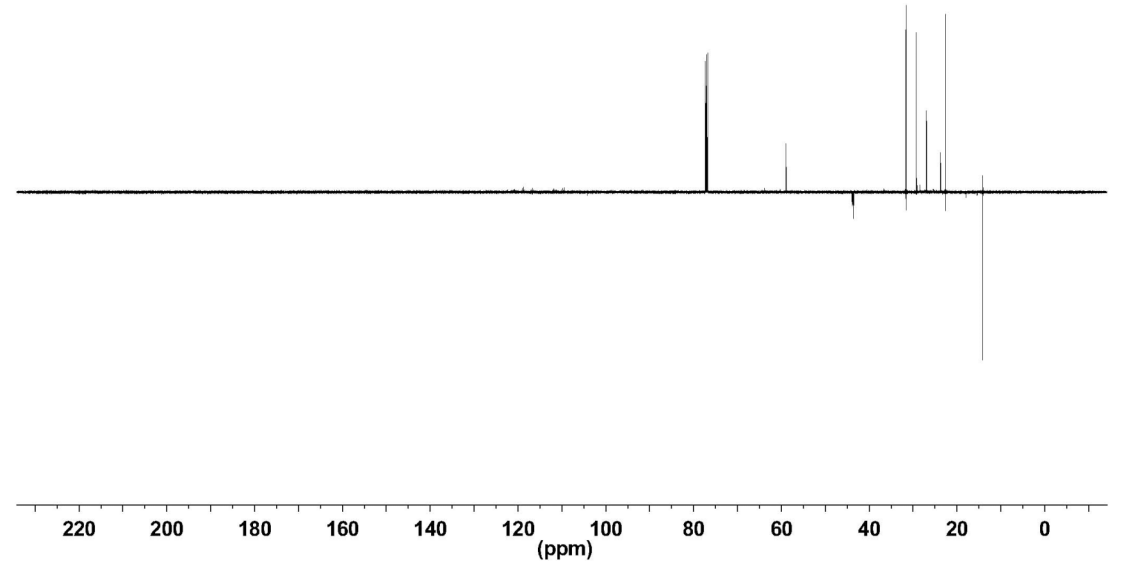

220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

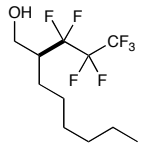

OH
F
F
CF3

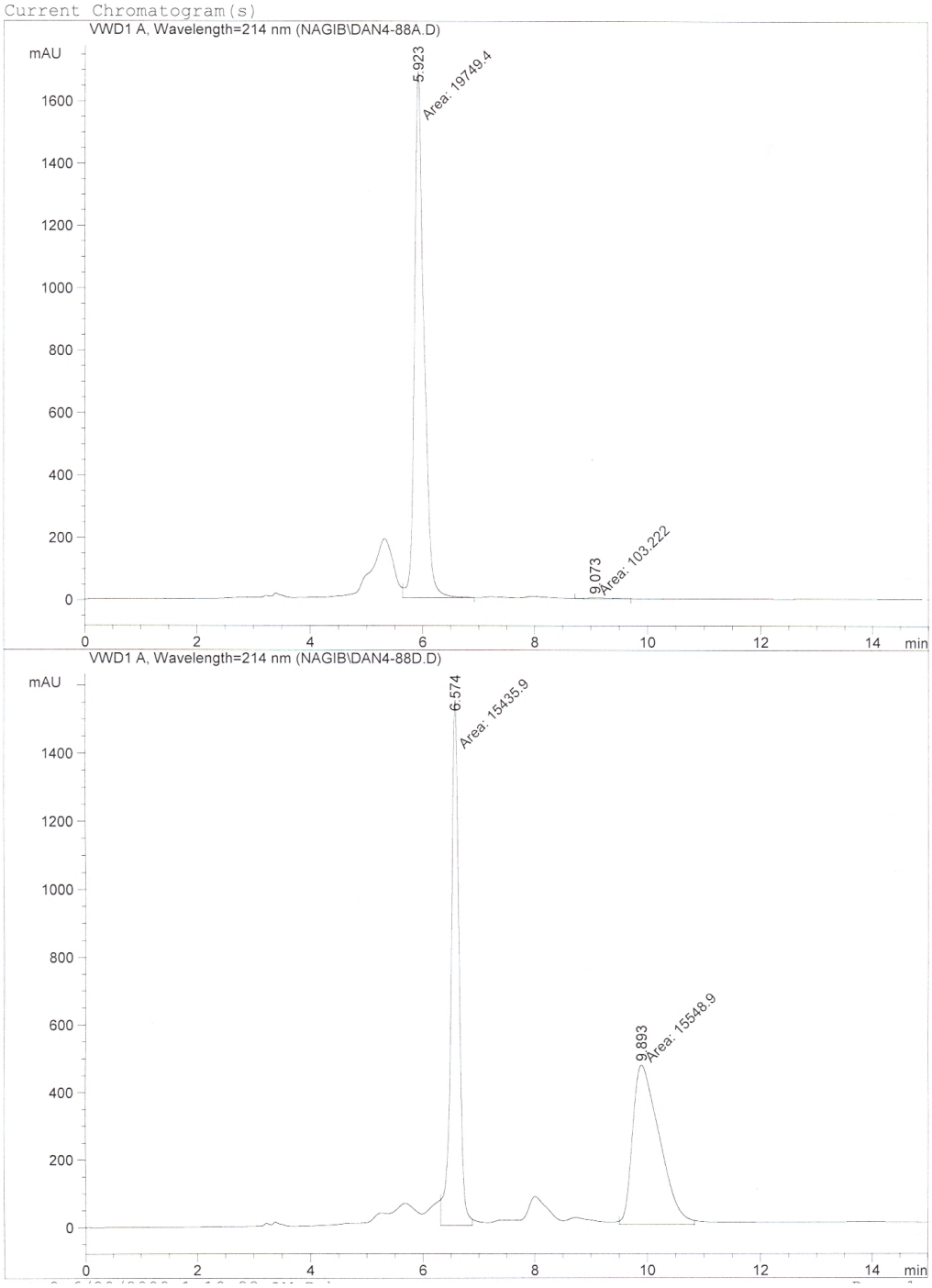

Current Chromatogram(s)
VWD1 A, Wavelength=260 nm (NAGIB\DN4-31-B.D)
mAU
5.496
Area: 8256.83
6.120
Area: 152.953
min
VWD1 A, Wavelength=260 nm (NAGIB\DN4-30-X.D)
mAU
5.484
Area: 7271.19
6.095
Area: 7212.03
min

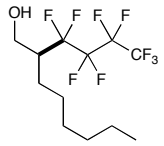

OH
F
F
CF3
F
F

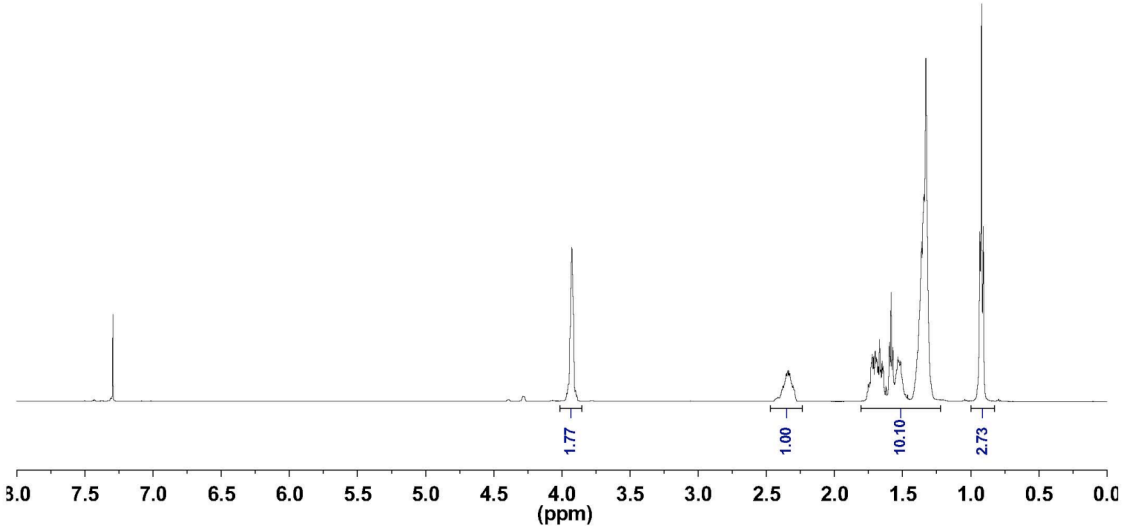

1.93
1.00
10.24
2.59
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

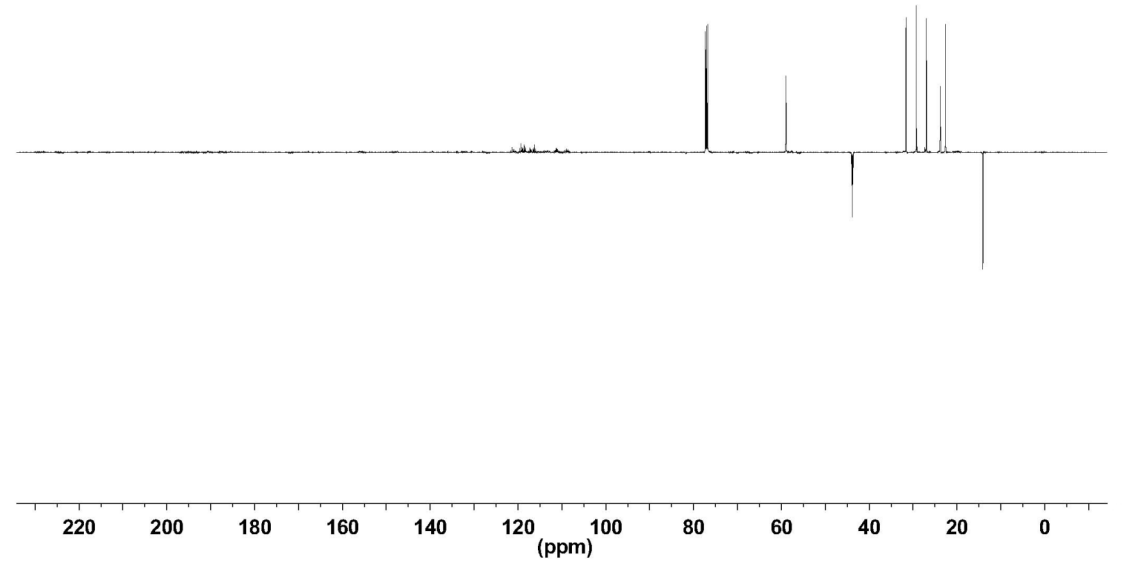

220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

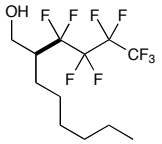

OH
F
F
CF3
F
F

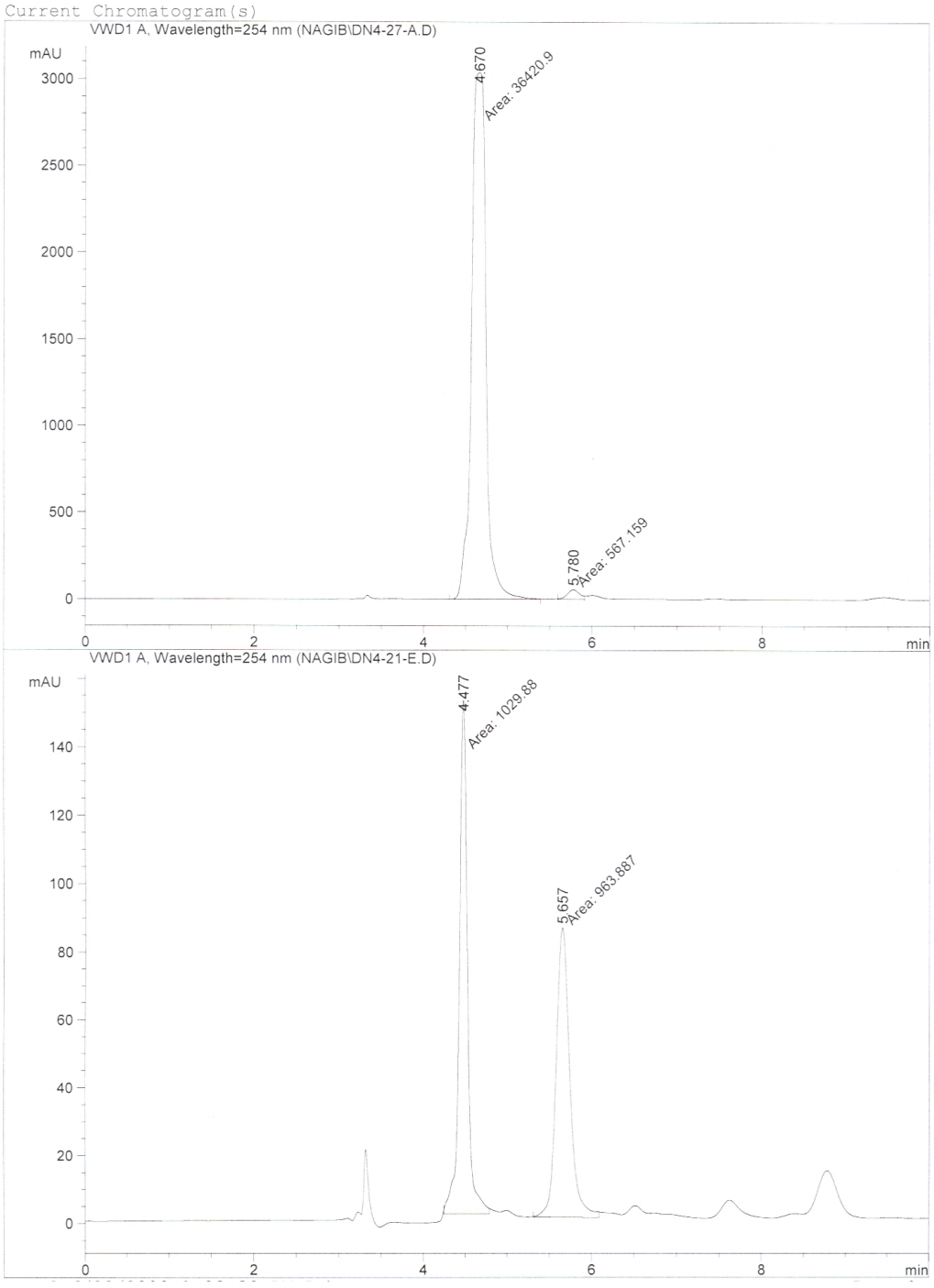

Current Chromatogram(s)
VWD1 A, Wavelength=214 nm (NAGIB\DAN4-88A.D)
mAU
5.923
Area: 19749.4
9.073
Area: 103.222
min
VWD1 A, Wavelength=214 nm (NAGIB\DAN4-88D.D)
mAU
6.574
Area: 15435.9
9.893
Area: 15548.9
min

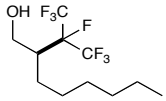

OH
F
F
F
F
CF3
F
F

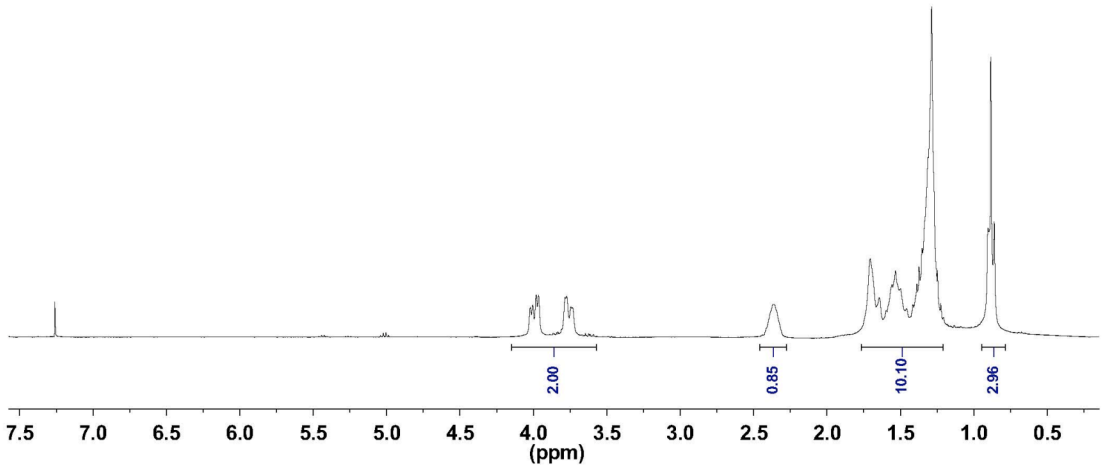

1.77
1.00
10.10
2.73
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

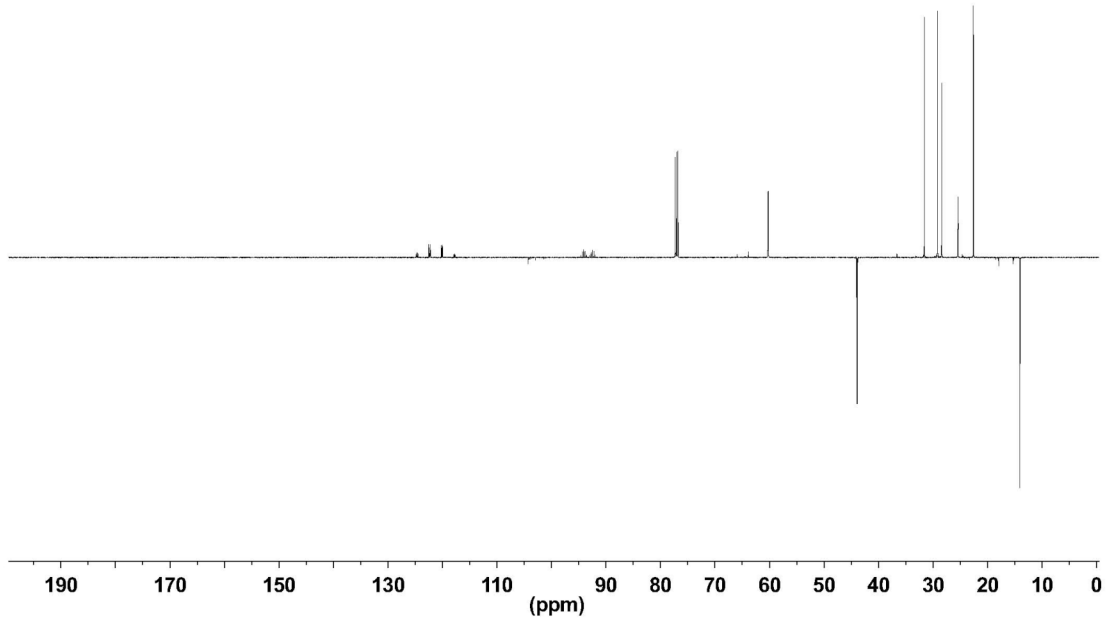

220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

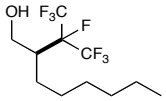

OH
F
F
F
F
CF3
F
F

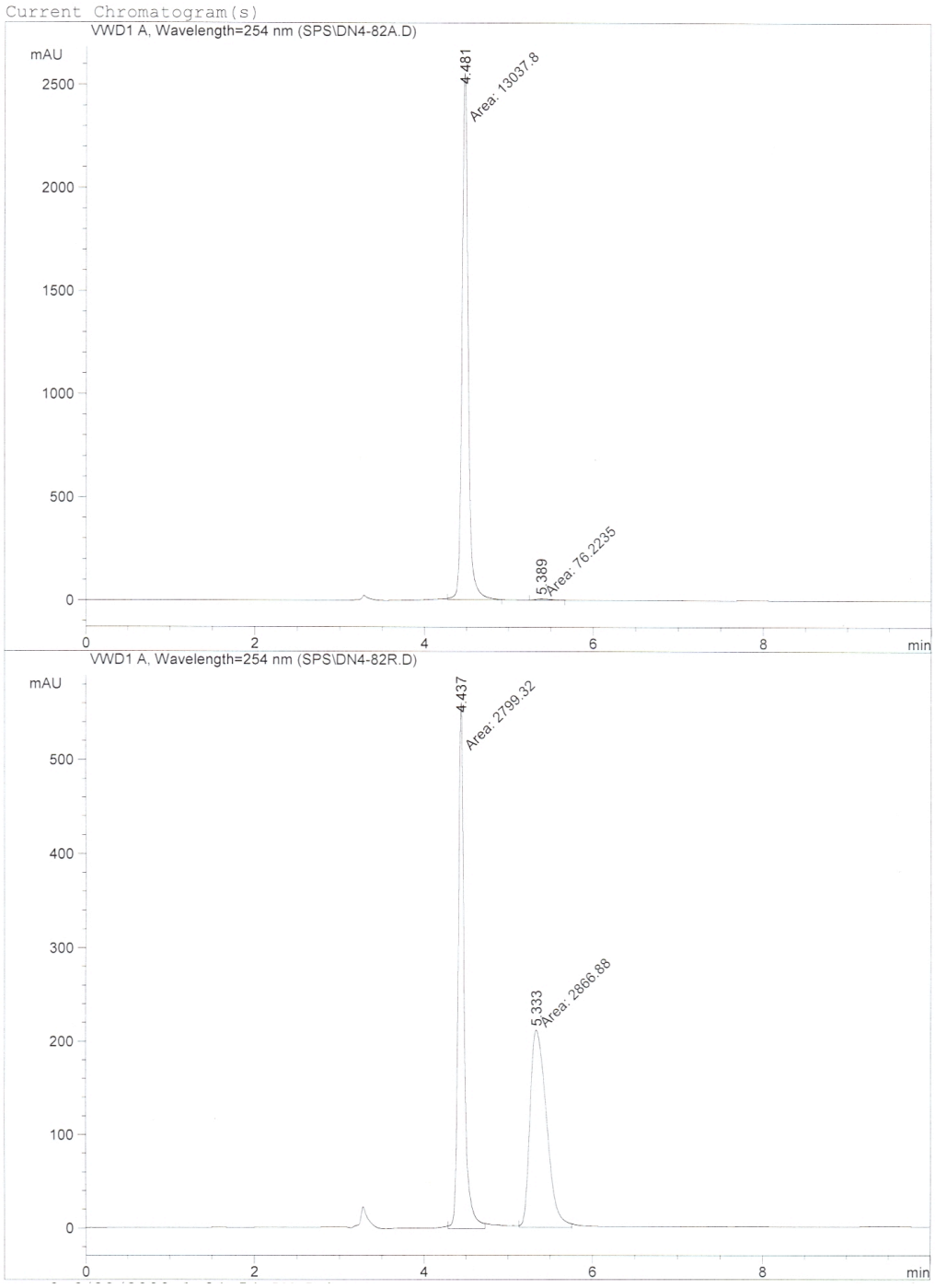

Current Chromatogram(s)
VWD1 A, Wavelength=254 nm (NAGIB\DN4-27-A.D)
mAU
3000
2500
2000
1500
1000
500
0
4.670
Area: 36420.9
5.780
Area: 567.159
0
2
4
6
8
min
VWD1 A, Wavelength=254 nm (NAGIB\DN4-21-E.D)
mAU
140
120
100
80
60
40
20
0
4.477
Area: 1029.88
5.657
Area: 963.887
0
2
4
6
8
min

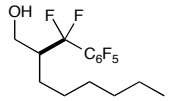

OH
F3C
F
CF3

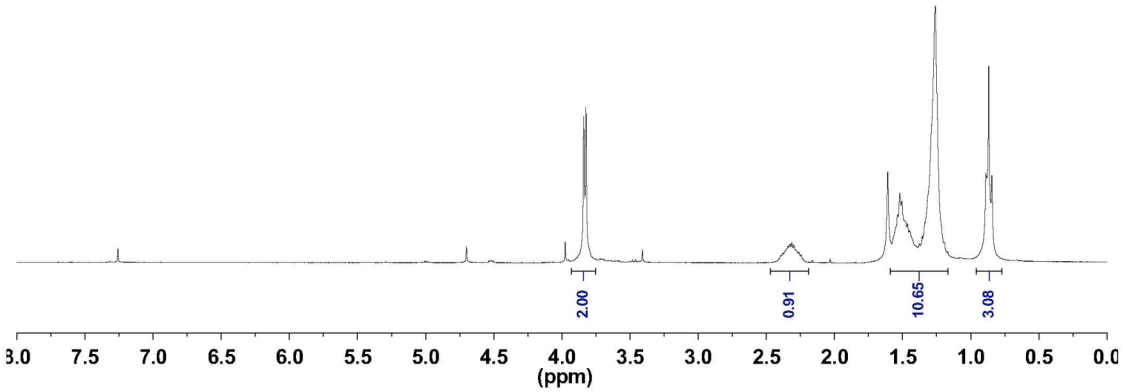

2.00
0.85
10.10
2.96
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

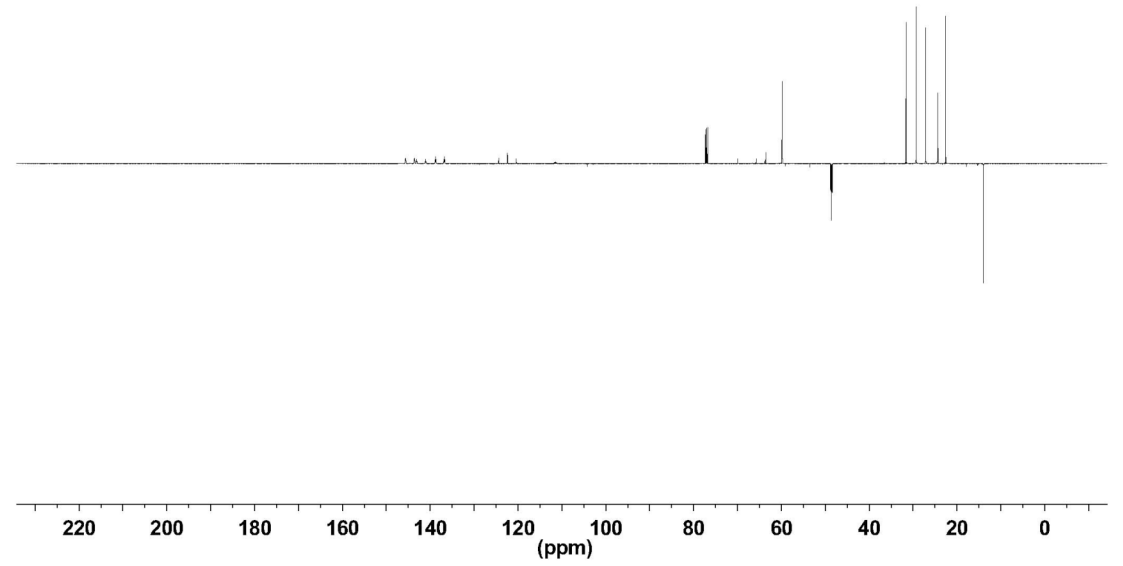

190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

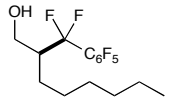

OH
F3C
F
CF3

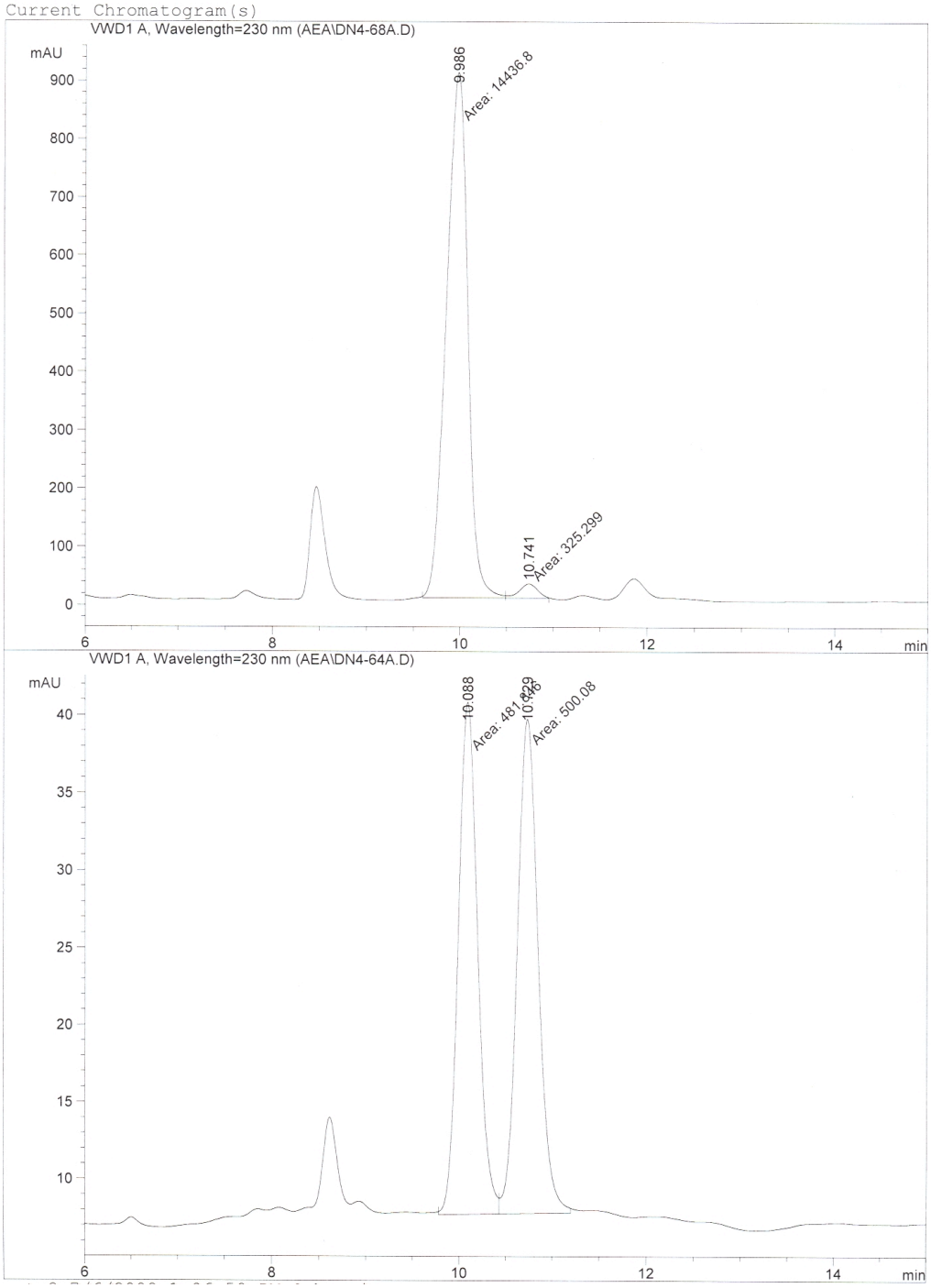

Current Chromatogram(s)
VWD1 A, Wavelength=254 nm (SPS\DN4-82A.D)
mAU
2500
2000
1500
1000
500
0
4.481
Area: 13037.8
5.389
Area: 76.2235
0
2
4
6
8
min
VWD1 A, Wavelength=254 nm (SPS\DN4-82R.D)
mAU
500
400
300
200
100
0
4.437
Area: 2799.32
5.333
Area: 2866.88
0
2
4
6
8
min

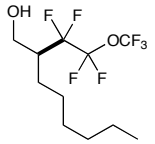

OH
F
F
C_6F_5

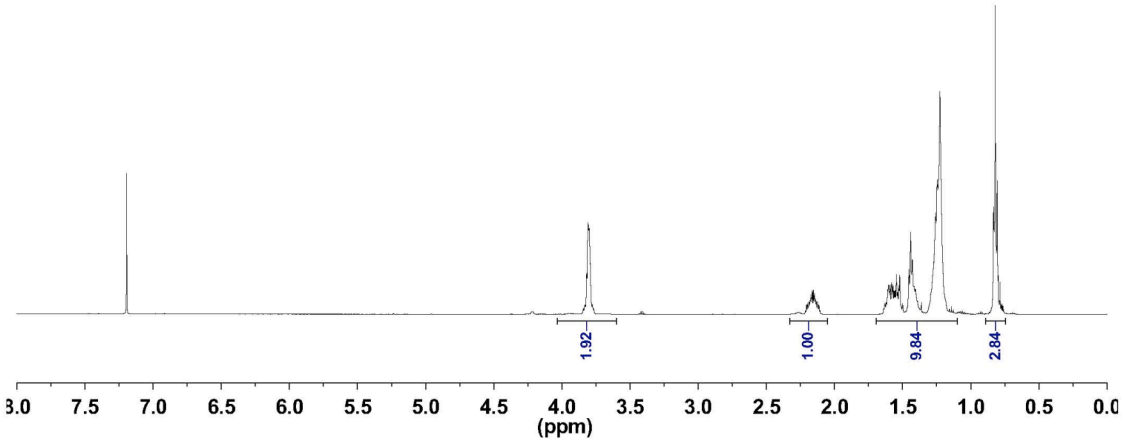

2.00
0.91
10.65
3.08
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

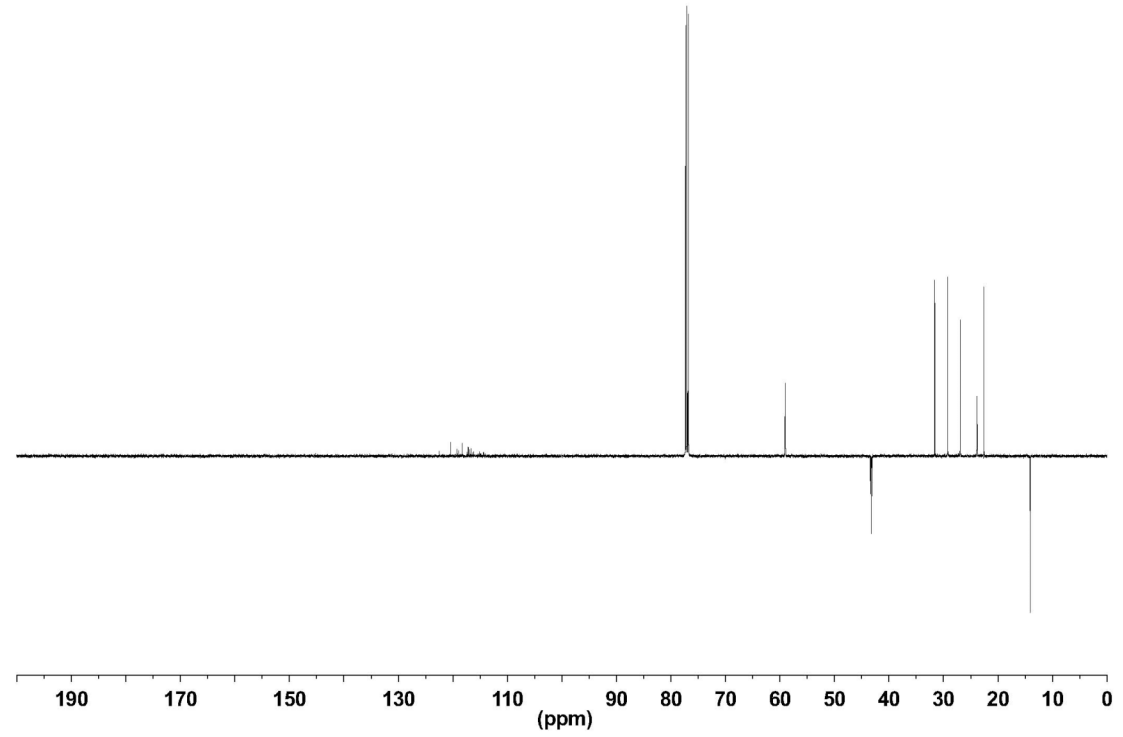

220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

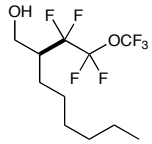

OH
F
F
C_6F_5

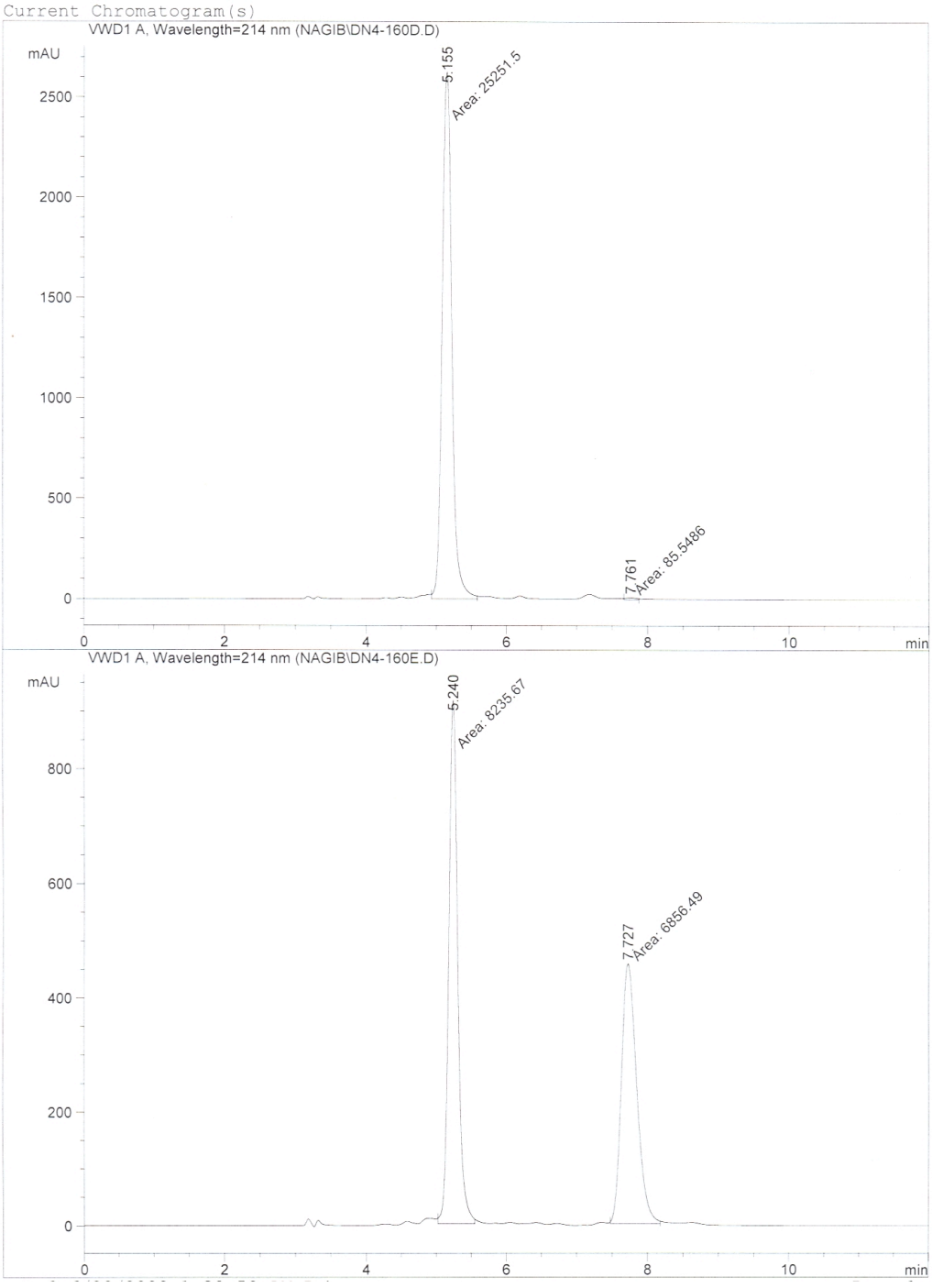

Current Chromatogram(s)
VWD1 A, Wavelength=230 nm (AEA\DN4-68A.D)
mAU
9.986
Area: 14436.8
10.741
Area: 325.299
min
VWD1 A, Wavelength=230 nm (AEA\DN4-64A.D)
mAU
10.088
Area: 481.929
10.446
Area: 500.08
min

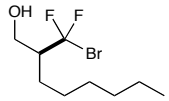

OH
F
F
OCF3
F
F

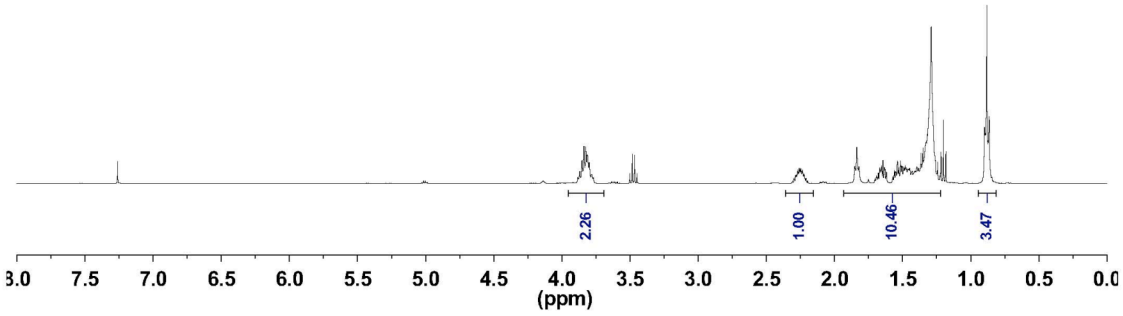

1.92
1.00
9.84
2.84
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

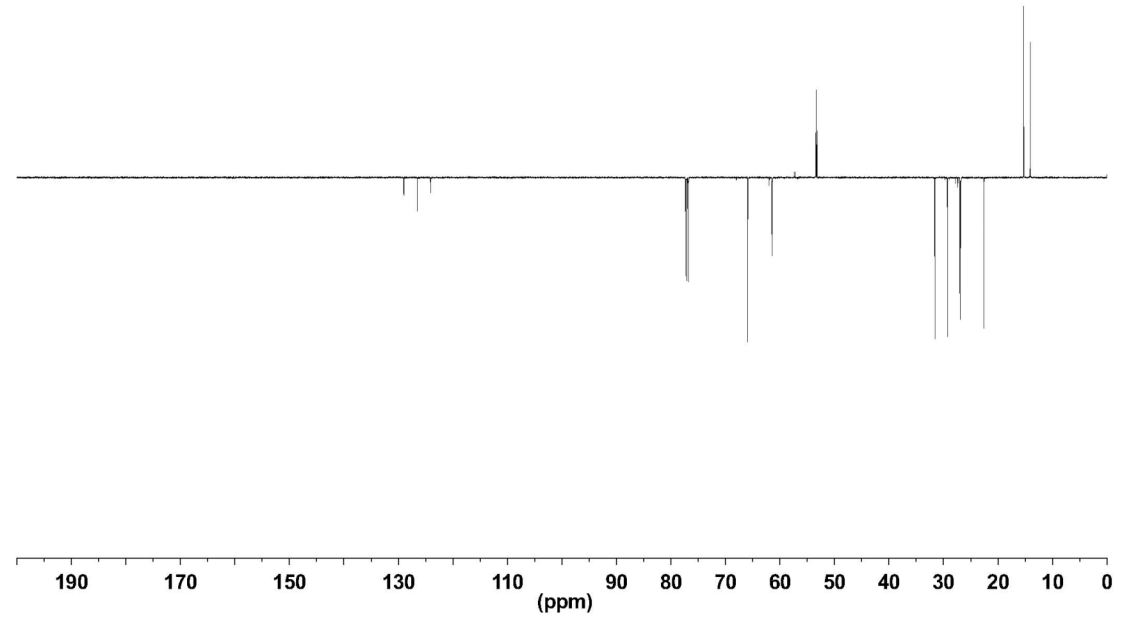

190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

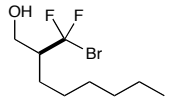

OH
F
F
OCF3
F
F

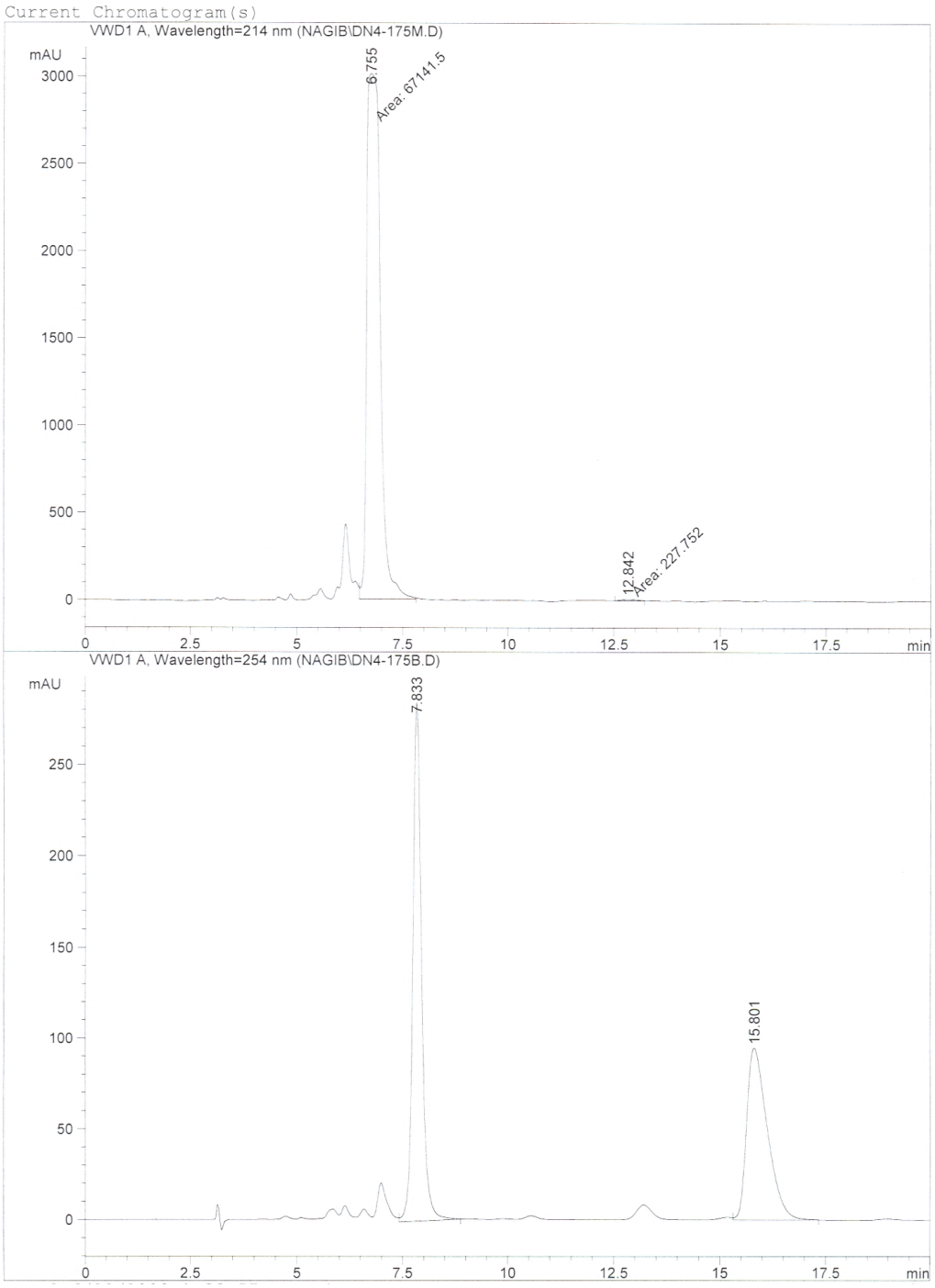

Current Chromatogram(s)
VWD1 A, Wavelength=214 nm (NAGIB\DN4-160D.D)
mAU
5.155
Area: 25251.5
7.761
Area: 85.5486
min
VWD1 A, Wavelength=214 nm (NAGIB\DN4-160E.D)
mAU
5.240
Area: 8235.67
7.727
Area: 6856.49
min

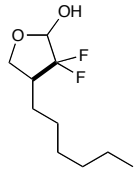

OH
F
F
Br

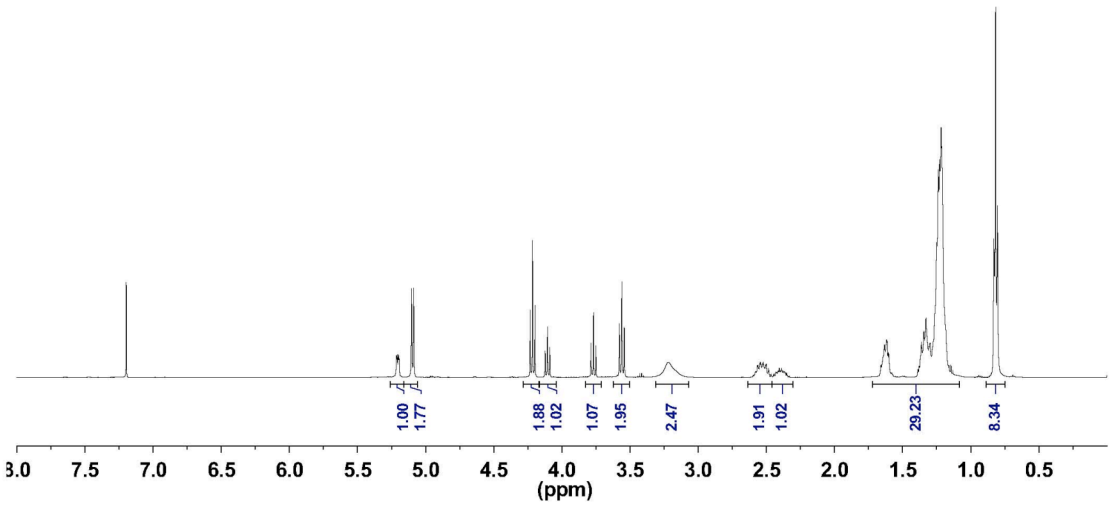

2.26
1.00
10.46
3.47
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

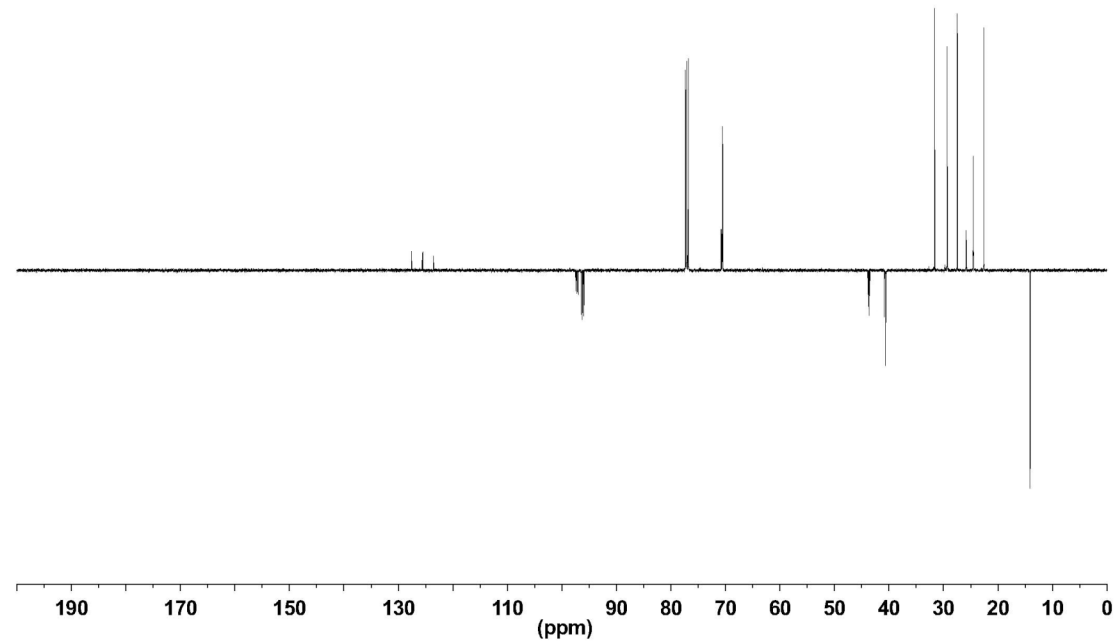

190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

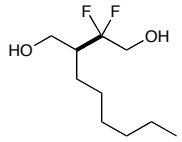

OH
F
F
Br

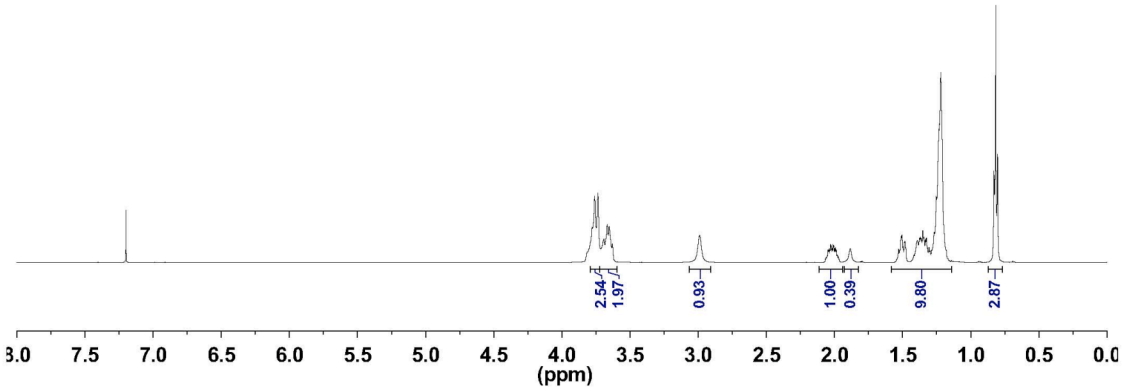

Current Chromatogram(s)
VWD1 A, Wavelength=214 nm (NAGIB\DN4-175M.D)
mAU
3000
2500
2000
1500
1000
500
0
6.755
Area: 67141.5
12.842
Area: 227.752
0
2.5
5
7.5
10
12.5
15
17.5
min
VWD1 A, Wavelength=254 nm (NAGIB\DN4-175B.D)
mAU
250
200
150
100
50
0
7.833
15.801
0
2.5
5
7.5
10
12.5
15
17.5
min

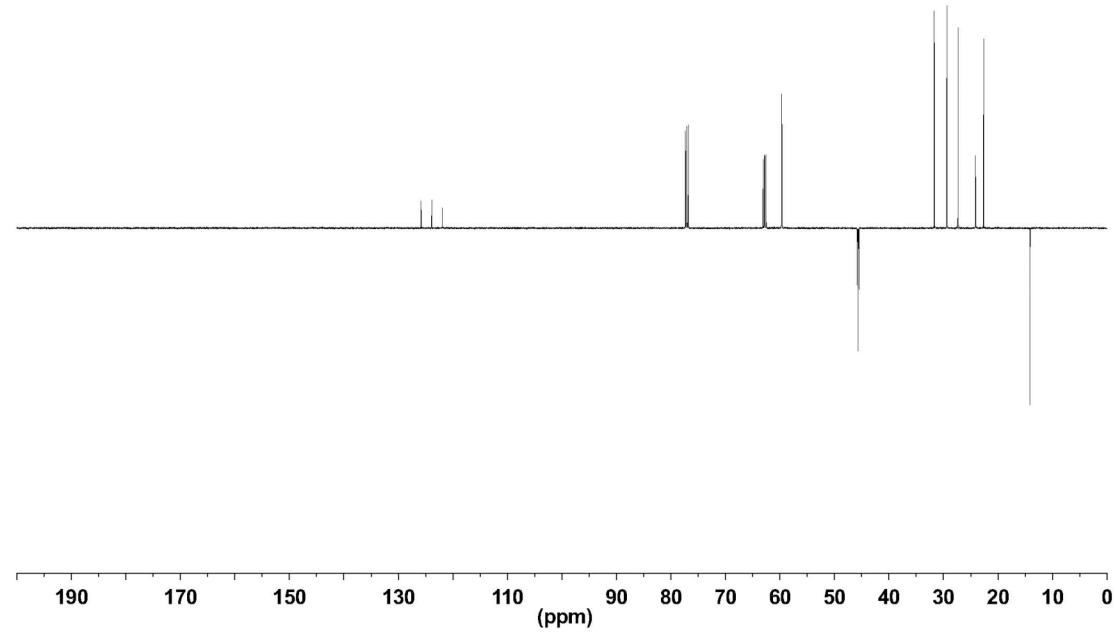

OH
O
F
F

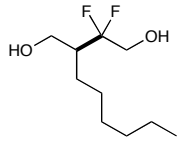

1.00
1.77
1.88
1.02
1.07
1.95
2.47
1.91
1.02
29.23
8.34
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

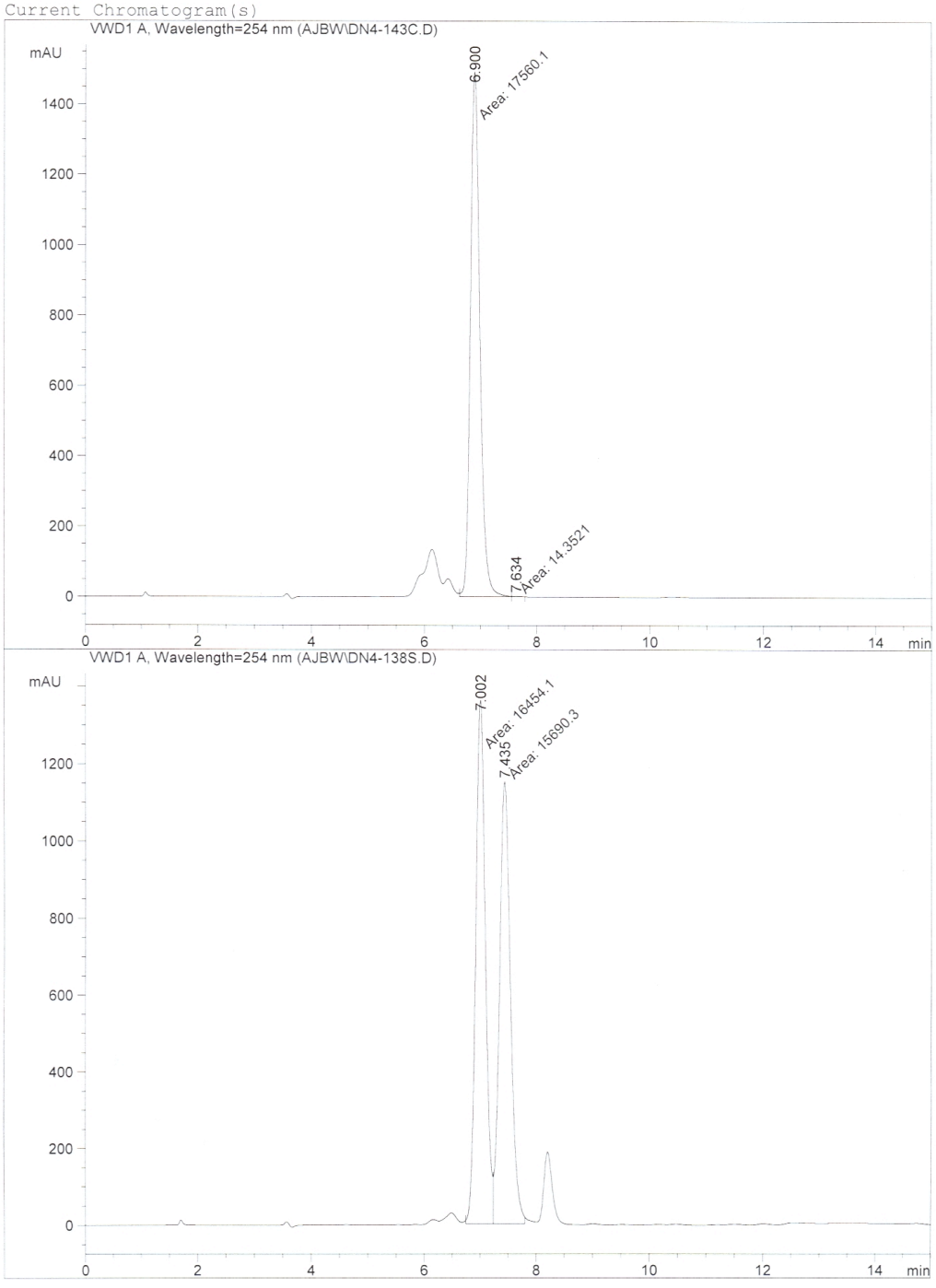

190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

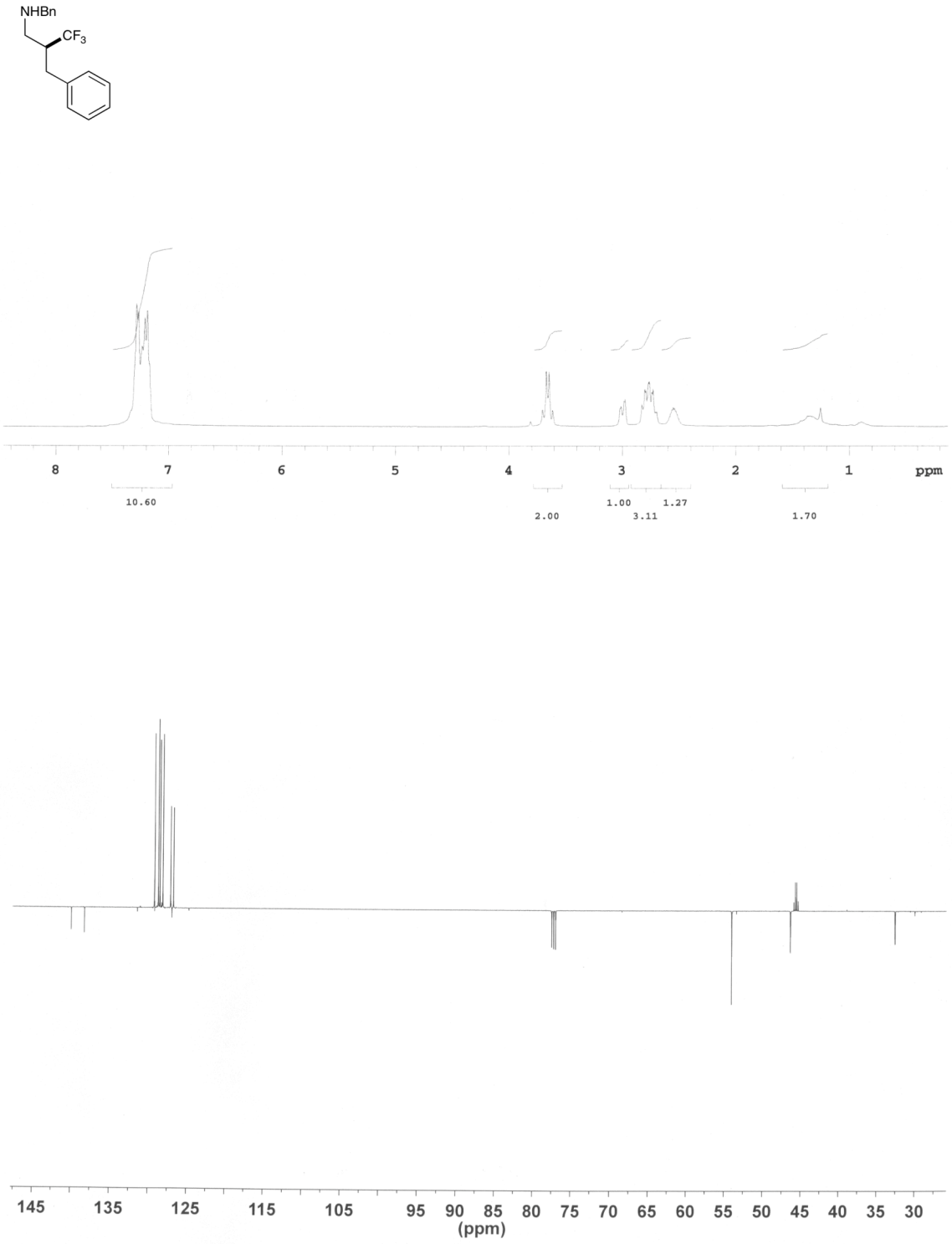

F
F
HO
OH

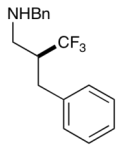

2.54
1.97
0.93
1.00
0.39
9.80
2.87
(ppm)

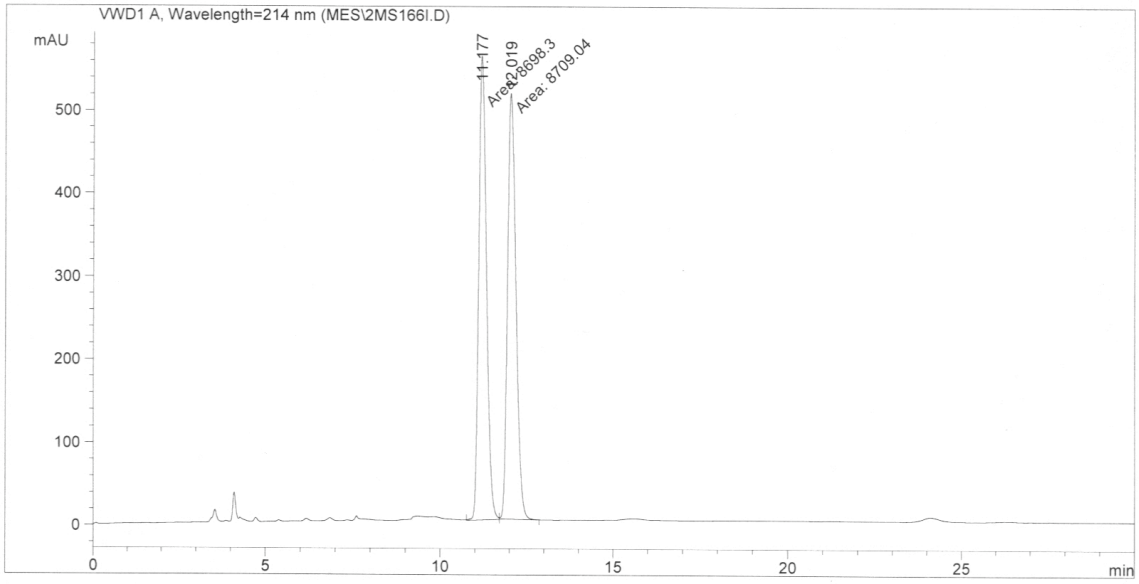

(ppm)

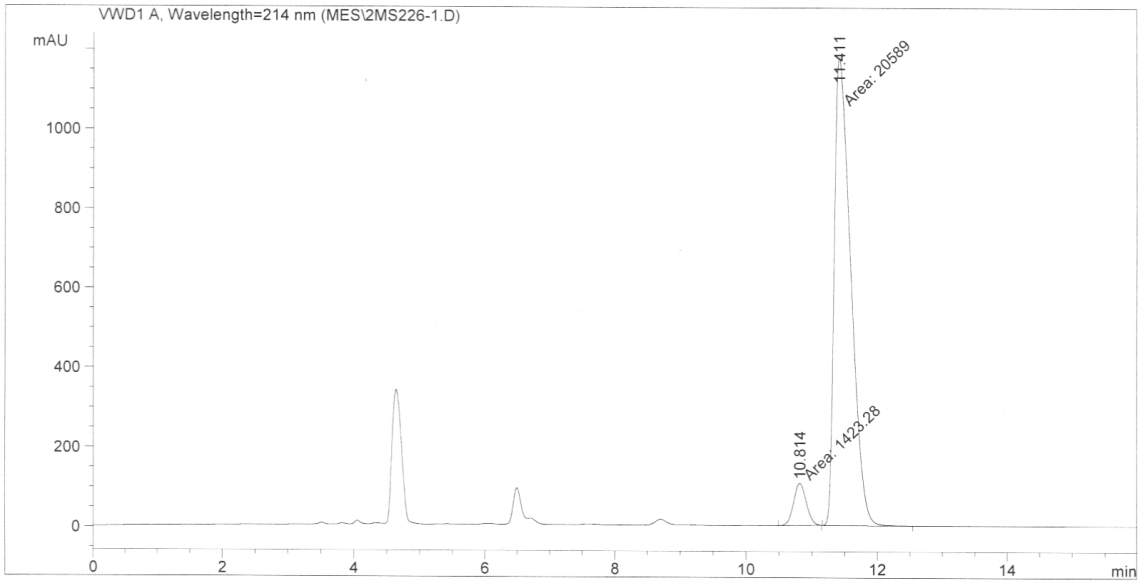

F
F
HO
OH

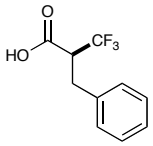

Current Chromatogram(s)
VWD1 A, Wavelength=254 nm (AJBW\DN4-143C.D)
mAU
6.900
Area: 17560.1
7.634
Area: 14.3521
min
VWD1 A, Wavelength=254 nm (AJBW\DN4-138S.D)
mAU
7.002
Area: 16454.1
7.435
Area: 15690.3
min

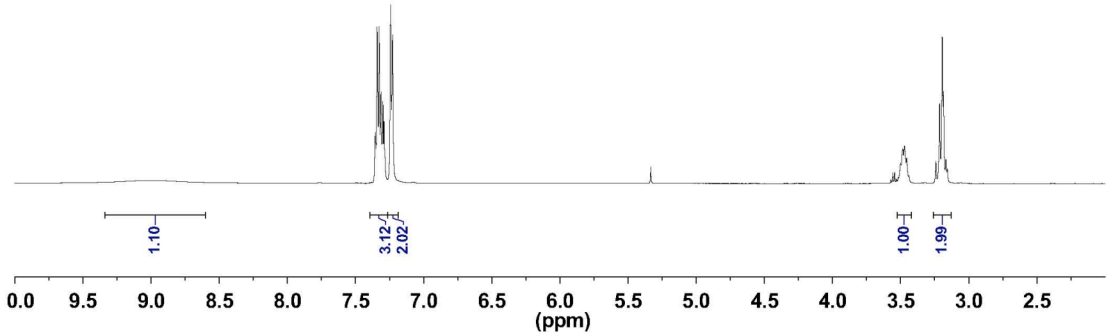

NHBn
CF3
8
7
6
5
4
3
2
1
ppm
10.60
2.00
1.00
1.27
3.11
1.70
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
(ppm)

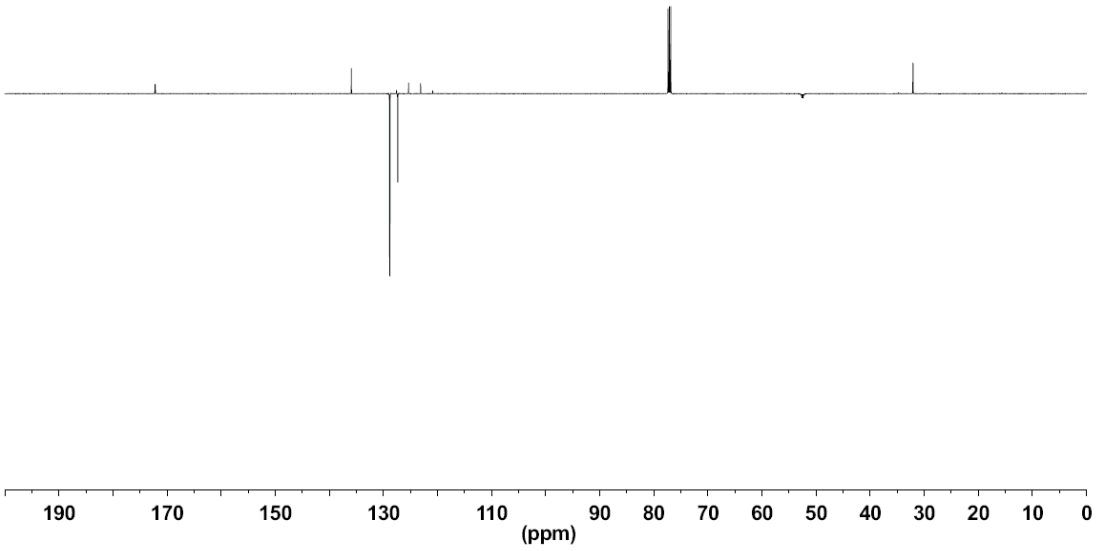

NHBn
CF3

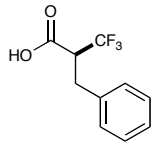

VWD1 A, Wavelength=214 nm (MES\2MS166I.D)
mAU
11.177
Area: 8698.3
12.019
Area: 8709.04
500
400
300
200
100
0
0
5
10
15
20
25
min

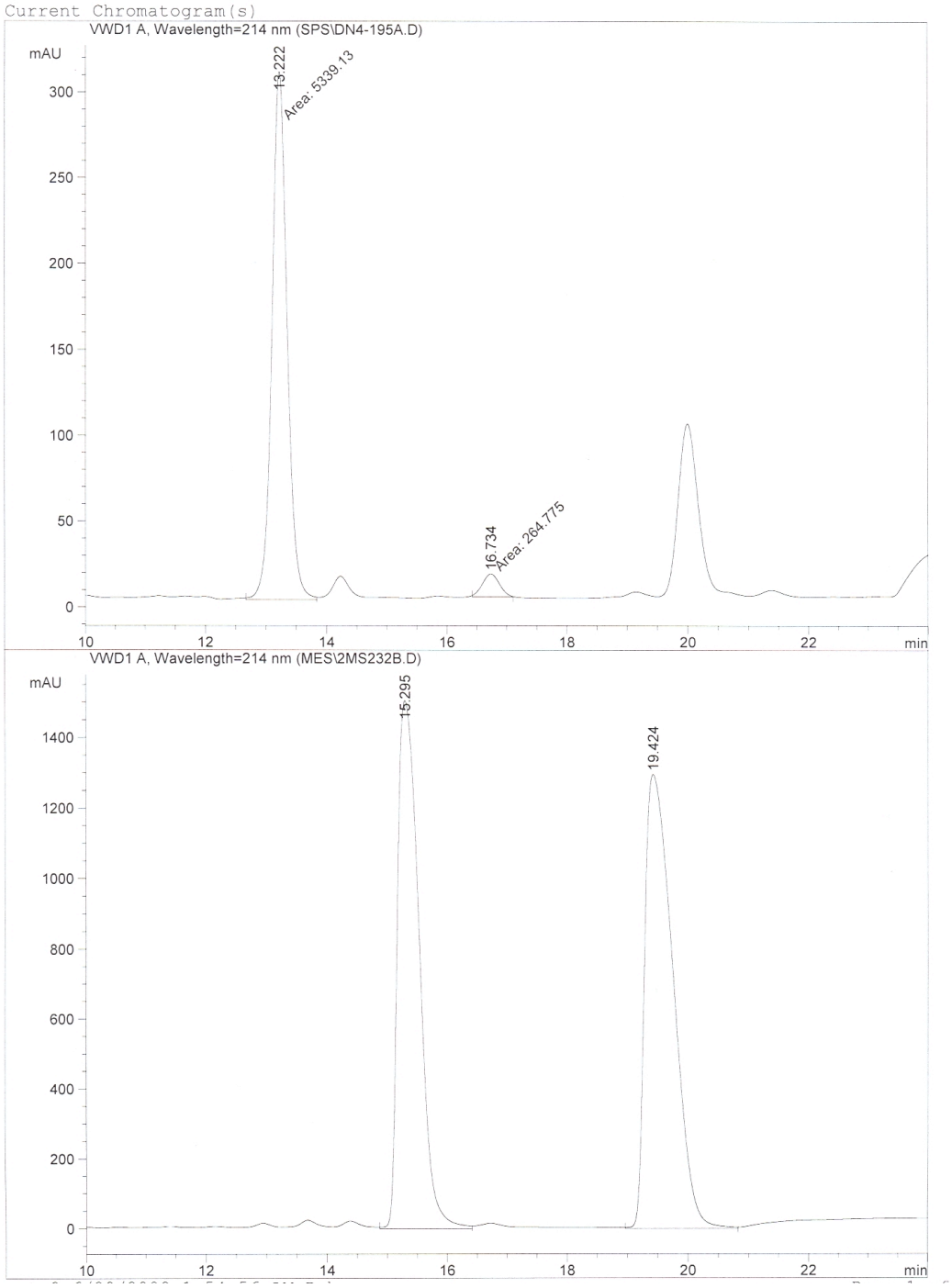

VWD1 A, Wavelength=214 nm (MES\2MS226-1.D)
mAU
11.411
Area: 20589
10.814
Area: 1423.28
1000
800
600
400
200
0
0
2
4
6
8
10
12
14
min

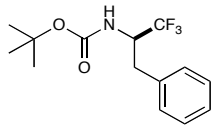

O
HO
CF3

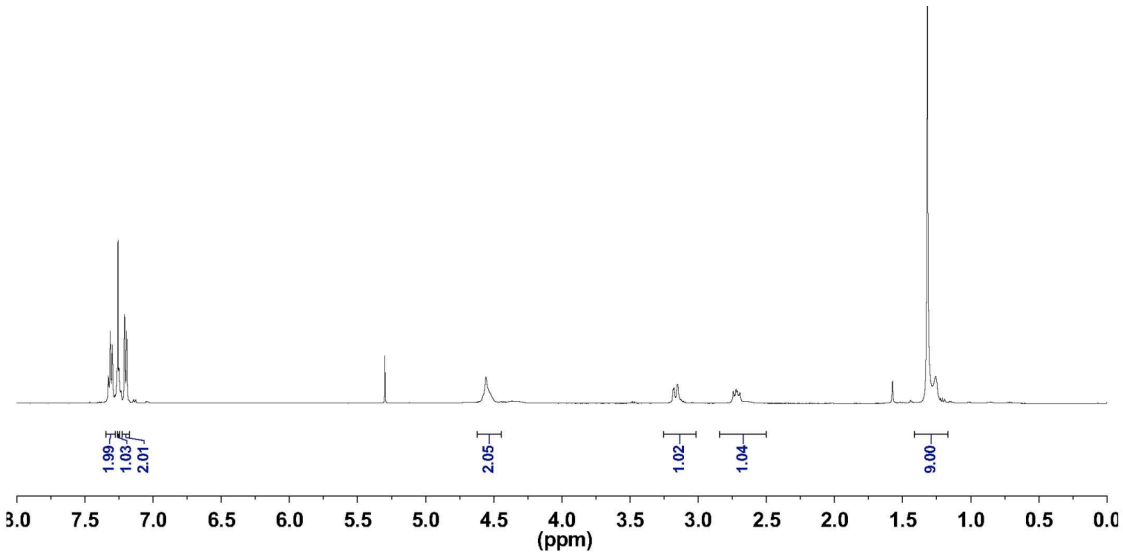

1.10
3.12
2.02
1.00
1.99
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
(ppm)

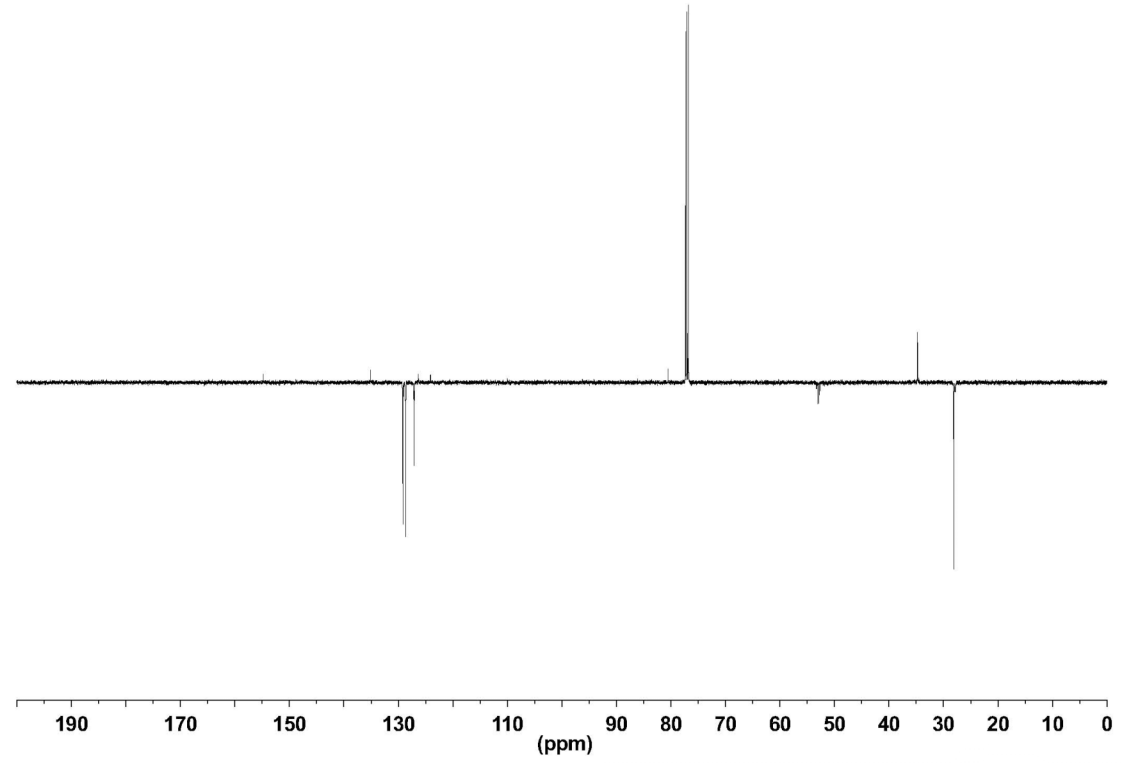

190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
(ppm)

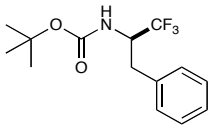

O
HO
CF3

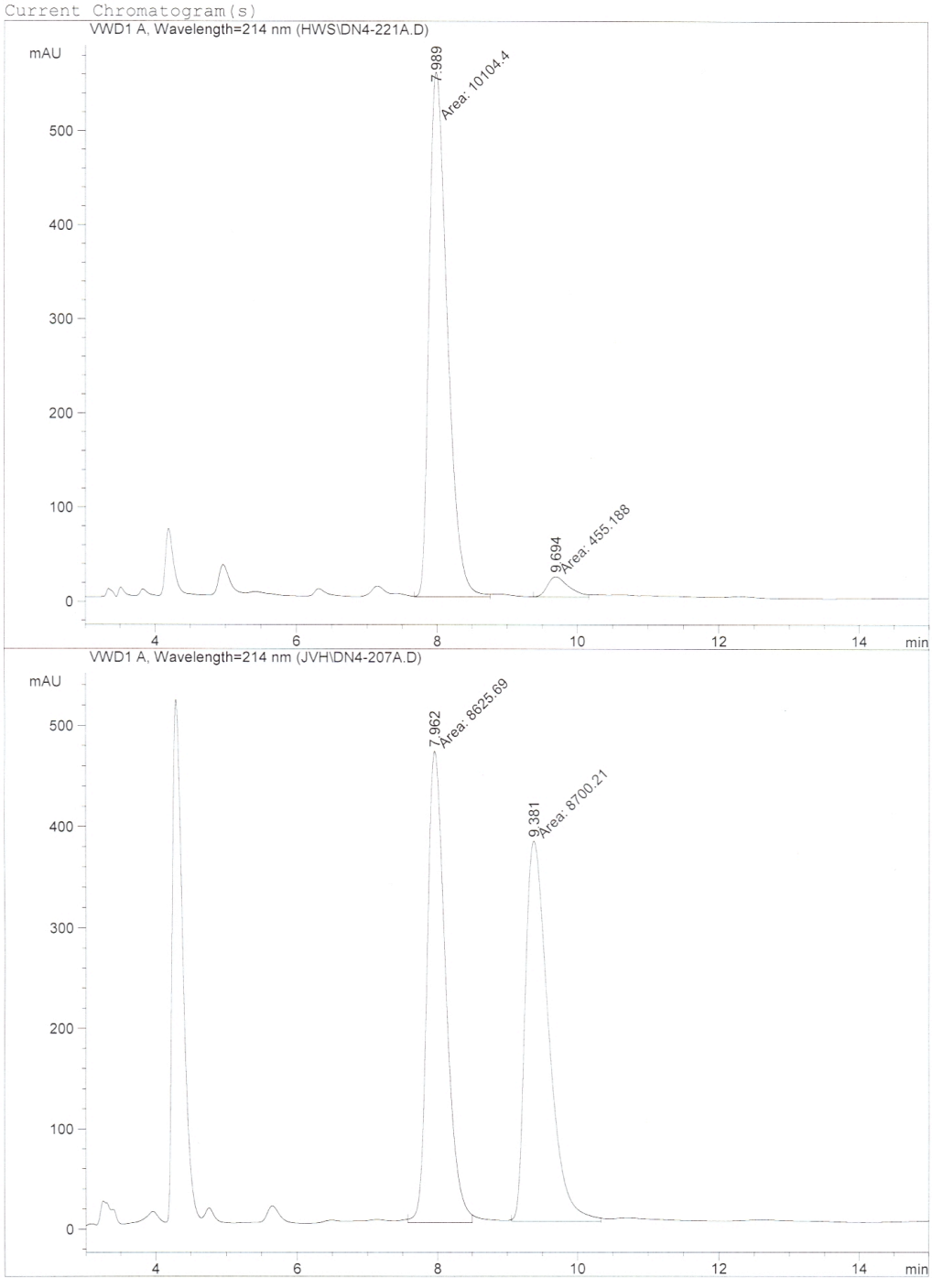

Current Chromatogram(s)
VWD1 A, Wavelength=214 nm (SPS\DN4-195A.D)
mAU
13.222
Area: 5339.13
16.734
Area: 264.775
min
VWD1 A, Wavelength=214 nm (MES\2MS232B.D)
mAU
15.295
19.424
min


H
N
O
O
O
CF3


1.99
1.03
2.01
2.05
1.02
1.04
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)


H
N
O
O
O
CF3


Current Chromatogram(s)
VWD1 A, Wavelength=214 nm (HWS\DN4-221A.D)
mAU
7.989
Area: 10104.4
9.694
Area: 455.188
min
VWD1 A, Wavelength=214 nm (JVH\DN4-207A.D)
mAU
7.962
Area: 8625.69
9.381
Area: 8700.21
min