Supporting Information

Chiral β-Iodoamines by Urea-Catalyzed Iodocyclization of Trichloroacetimidates

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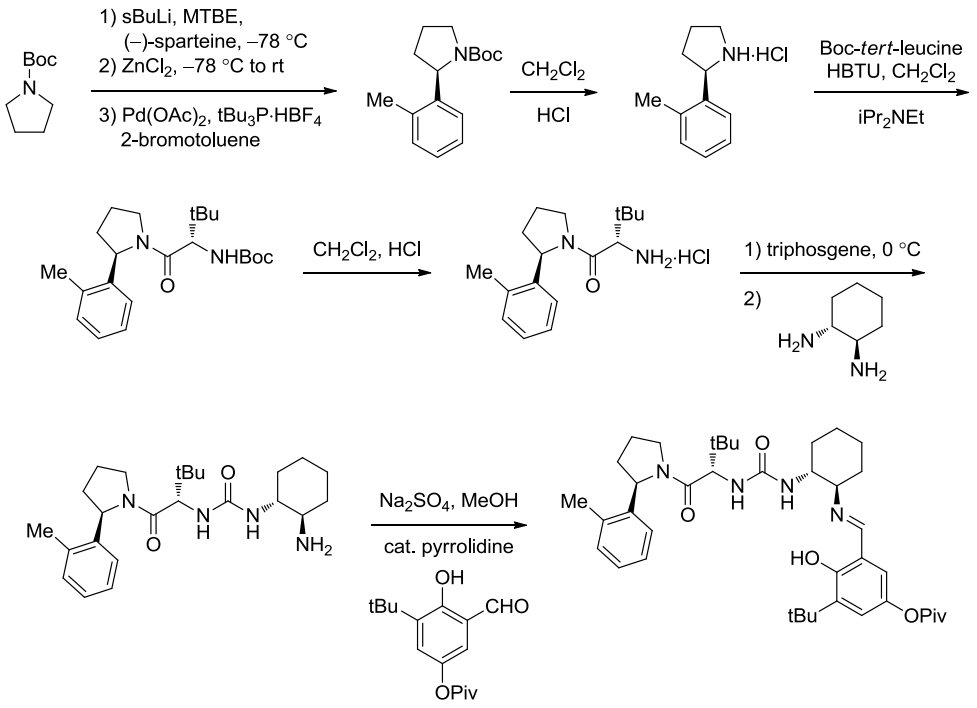
1. General considerations

Commercial reagents were purchased from Sigma-Aldrich, Alfa Aesar, Strem, or Frontier Scientific and used without purification. Acetonitrile, dichloromethane, toluene, tetrahydrofuran, diethyl ether, 1,4-dioxane, and methanol were dried by passing through columns of activated alumina. Triethylamine was distilled from CaH_2 at 760 torr. All reactions were performed in oven- or flame-dried round bottom flasks under air unless otherwise noted. Catalytic experiments were performed in oven-dried 1-dram vials. Stainless steel syringes were used to transfer air- and moisture-sensitive liquids. Reactions were monitored by thin-layer chromatography (ELC) on EMD Silica Gel 60 F_{254} plates under UV light (254 μm) or visualized with $KMnO_4$. Flash chromatography was performed using silica gel 60 (230-400 mesh) from EM Science or Davisil® (Grade 643, pore size 150 Å, 200-425 mesh) or activated neutral alumina (Brockmann I, standard grade, pore size 58 Å, 150 mesh) from Sigma-Aldrich. Preparative thin layer chromatography (TLC) was performed on EMD Silica Gel 60 F_{254} plates. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

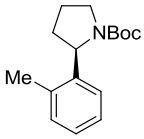
Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C{^{1}H} NMR) spectra were recorded on a Varian Mercury 400 (400 MHz), Inova 500 (500 MHz), or Inova 600 (600 MHz) spectrometer at ambient temperature. All chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Proton resonances are referenced to residual protium in the NMR solvent or tetramethylsilane. Carbon resonances are referenced to the carbon resonances of the NMR solvent. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using a Bruker Optics Tensor 27 FTIR spectrometer equipped with an attenuated total reflectance (ATR) single reflection unit. Optical rotations ($[\alpha]_D$) were measured using a 1 mL cell with a 0.5 dm path length on a Jasco DIP 370 digital polarimeter. Mass spectral (MS) data were obtained on an Agilent Technologies 6210 quadrupole LC/MS spectrometer equipped with an electrospray (ESI)/atmospheric-pressure chemical ionization (APCI) multimode source or a Bruker micrOTOF-Q II time-of-flight (ESI-TOF) LC/MS spectrometer. High-performance liquid chromatography (HPLC) analysis was performed using an Agilent 1200 series quaternary HPLC system with commercially available ChiralPak and ChiralCel columns.

Abbreviations used: *ee* = enantiomeric excess, eq = equivalents, sat'd = saturated, rt = room temperature, calc'd = calculated, *m/z* = mass to charge ratio, v/v = volume/volume, mmol = millimole, Boc = *tert*-butyloxycarbonyl, Piv = pivalate, sBuLi = *sec*-butyllithium, MTBE = *tert*-butyl methyl ether, DMSO = dimethylsulfoxide, THF = tetrahydrofuran, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, HBTU = *O*-(benzotriazol-1-yl)-*N*,*N*,*N'*,*N'*-tetramethyluronium hexafluorophosphate, dppp = 1,3-bis(diphenylphosphino)propane.

2. Catalyst synthesis



Catalyst **1f** and analogous catalysts were synthesized according to our previously described route.[1]

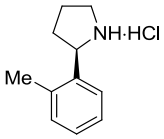


(*R*)-*Tert*-butyl 2-(*o*-tolyl)pyrrolidine-1-carboxylate: Prepared by a modified literature procedure.[2] A solution of *N*-Boc-pyrrolidine (4.9 mL, 28.0 mmol) and (–)-sparteine (7.0 mL, 30.5 mmol) in MTBE (84 mL, 0.3 M) was cooled to –78 ºC. sBuLi (1.4 M in cyclohexane, 20 mL, 28.0 mmol) was added via syringe pump over 1 h and the reaction mixture was stirred for 3 h at –78 ºC. $ZnCl_2$ (1 M in Et_2O, 30.2 mL, 30.2 mmol) was then added via syringe pump over 1 h and the mixture was stirred for an additional 30 min at –78 ºC, warmed to ambient temperature, and stirred for 1 h. Subsequently, $Pd(OAc)_2$ (226.6 mg, 1.0 mmol), $tBu_3P{\cdot}HBF_4$ (422.4 mg, 1.5 mmol), and 2-bromotoluene (5.0 mL, 25.1 mmol) were added and the mixture was stirred for 14 h at ambient temperature. Celite was added and the resulting slurry was filtered through a plug of celite. The filtrate was concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: 5-15% EtOAc/hexanes, v/v) to give 5.188 g (79% yield) of

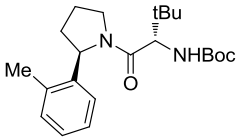
[1] Sigman, M.S.; Vachal, P.; Jacobsen, E.N. *Angew. Chem. Int. Ed.* **2000**, *39*, 1279-1281.

[2] Barker, G.; McGrath, J.L.; Klapars, A.; Stead, D.; Zhou, G.; Campos, K.R.; O'Brien, P. *J. Org. Chem.* **2011**, *76*, 5936-5953.

the desired product as a white solid in a 1.5:1 mixture of rotamers about the amide bond in d_6-DMSO. IR (thin film) 2971, 2872, 1695, 1479, 1457, 1394, 1365, 1311, 1247, 1161, 1122, 1102, 1001, 921, 901, 875, 799, 753, 726, 649 cm^{-1}. Major rotamer: ^1H NMR (500 MHz, d_6-DMSO) δ 7.17-6.92 (m, 4H), 4.92-4.83 (m, 1H), 3.62-3.40 (m, 2H), 2.27 (s, 3H), 1.88-1.50 (m, 4H), 1.04 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD) δ 153.2, 143.3, 133.6, 129.7, 125.7, 124.1, 77.8, 57.5, 46.8, 45.4, 33.8, 27.6, 25.2, 18.7. Minor rotamer: ^1H NMR (500 MHz, d_6-DMSO) δ 7.17-6.92 (m, 4H), 5.00-4.90 (m, 1H), 3.62-3.40 (m, 1H), 3.24-3.14 (m, 1H), 2.27 (s, 3H), 1.88-1.50 (m, 4H), 1.38 (s, 9H).$^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD) δ 153.5, 142.2, 133.8, 130.1, 126.0, 123.8, 78.3, 57.5, 47.0, 45.6, 32.4, 28.1, 24.4, 22.7. MS (APCI) *m/z* calc'd for $C_{11}H_{14}N$ (M–Boc): 160.1, found: 160.1. $[\alpha]_D^{22}$ = +44.6º (c = 1.10, CH_2Cl_2). This compound has been reported in the literature.[3]



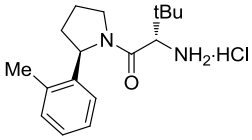
(*R*)-2-(*o*-Tolyl)pyrrolidinium hydrochloride: To a solution of (*R*)-*tert*-butyl 2-(*o*-tolyl)pyrrolidine-1-carboxylate (5.188 g, 19.9 mmol) in CH_2Cl_2 (40 mL, 0.5 M) was added HCl (4 M in dioxane, 20 mL, 80.0 mmol, 4 eq.). The reaction mixture was stirred for 14 h at ambient temperature. After removing excess HCl gas by sparging with nitrogen, the solution was concentrated *in vacuo* to give the desired product as a white foam. IR (thin film) 2889, 2740, 2552, 2069, 1589, 1496, 1461, 1398, 1120, 1032, 979, 761, 724 cm^{-1}. ^1H NMR (500 MHz, CD_3OD) δ 7.49 (m, 1H), 7.34-7.25 (m, 3H), 4.90 (t, *J* = 8.3 Hz, 1H), 3.46 (m, 1H), 3.24 (br s, 1H), 2.44 (s, 3H), 2.29 (m, 1H), 2.25-2.15 (m, 2H), 2.00 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD) δ 138.3, 134.3, 132.2, 130.4, 128.0, 126.8, 60.8, 46.7, 32.0, 25.1, 25.0. MS (APCI) *m/z* calc'd for $C_{11}H_{16}N$ (M–Cl): 162.1; found: 162.2. MS (ESI-TOF) *m/z* calc'd for $C_{11}H_{16}N$ (M–Cl): 162.1283; found: 162.1309. $[\alpha]_D^{23}$ = –13.5º (c = 1.90, CH_3OH).



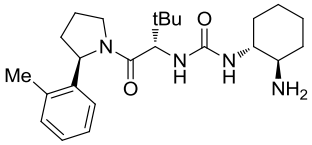
***Tert*-butyl ((*S*)-3,3-dimethyl-1-oxo-1-((*R*)-2-(*o*-tolyl)pyrrolidin-1-yl)butan-2-yl)carbamate:** To a suspension of (*L*)-*N*-Boc-*tert*-leucine (5.20 g, 22.5 mmol) and HBTU (8.08 g, 21.3 mmol) in CH_2Cl_2 (80 mL, 0.25 M) was added iPr_2NEt (11.0 mL, 63.2 mmol). The reaction mixture was stirred for 15 min. Subsequently, (*R*)-2-(*o*-tolyl)pyrrolidinium hydrochloride (19.9 mmol) was added and the suspension was stirred for 14 h at ambient temperature, diluted with Et_2O, and washed with sat'd NH_4Cl, sat'd $NaHCO_3$, and brine. The separated organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The

[3] Campos, K.R.; Klapars, A.; Waldman, J.H.; Dormer, P.G.; Chen, C. *J. Am. Chem. Soc.* **2006**, *128*, 3538-3539.

resulting residue was purified by column chromatography (eluent: 10-25% EtOAc/hexanes, v/v) to give the desired product as a white foam as a 3:1 mixture of rotamers about the amide bond in CD_3OD. IR (thin film) 3403, 2970, 2489, 1703, 1634, 1558, 1437, 1393, 1367, 1244, 1164, 1122, 1065, 999, 953, 910, 875, 738, 635 cm^{-1}. Major rotamer: ^1H NMR (400 MHz, CD_3OD) δ 7.24-6.92 (m, 4H), 6.28 (d, *J* = 9.5 Hz, 1H), 5.27 (dd, *J* = 1.5, 8.1 Hz, 1H), 4.38 (d, *J* = 9.5 Hz, 1H), 4.27 (m, 1H), 3.81 (q, *J* = 9.5 Hz, 1H), 2.35 (s, 3H), 2.34-2.24 (m, 1H), 2.02-1.88 (m, 2H), 1.76-1.68 (m, 1H), 1.49 (s, 9H), 1.03 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD) δ 172.3, 158.2, 141.7, 135.3, 131.5, 127.5, 126.7, 125.1, 80.7, 60.5, 59.9, 49.9, 35.2, 33.4, 28.8, 26.9, 24.0, 19.4. MS (APCI) *m/z* calc'd for $C_{22}H_{35}N_2O_3$ (M+H): 375.3; found: 375.3. MS (ESI-TOF) *m/z* calc'd for $C_{22}H_{35}N_2O_3$ (M+H): 375.2642; found: 375.2649. *m/z* calc'd for $C_{22}H_{34}N_2NaO_3$ (M+Na): 397.2462; found: 397.2469. *m/z* calc'd for $C_{22}H_{34}KN_2O_3$ (M+K): 413.2201; found: 413.2192. $[\alpha]_D^{22}$ = +28.3 (c = 1.30, CH_2Cl_2).

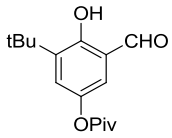


(*S*)-3,3-Dimethyl-1-oxo-1-((*R*)-2-(*o*-tolyl)pyrrolidin-1-yl)butan-2-ammonium chloride: To a solution of *tert*-butyl ((*S*)-3,3-dimethyl-1-oxo-1-((*R*)-2-(*o*-tolyl)pyrrolidin-1-yl)butan-2-yl)carbamate in CH_2Cl_2 (40 mL) was added HCl (4 M in dioxane, 20 mL, 80.0 mmol). The reaction mixture was stirred for 14 h at ambient temperature. After removing excess HCl gas by sparging with nitrogen, the solution was concentrated *in vacuo* to give 5.89 g (95% yield over 2 steps) of the desired product as a white foam as a 5:1 mixture of rotamers about the amide bond in CD_3OD. IR (thin film) 3462, 2988, 2952, 2880, 2071, 1651, 1601, 1486, 1448, 1373, 1358, 1121, 1052, 981, 787, 755, 634 cm^{-1}. Major rotamer: ^1H NMR (400 MHz, CD_3OD) δ 7.25-7.04 (m, 4H), 5.30 (dd, *J* = 2.2, 8.1 Hz, 1H), 4.15 (s, 1H), 4.02 (m, 1H), 3.85 (m, 1H), 2.37 (s, 3H), 2.33 (m, 1H), 2.01 (m, 2H), 1.75 (m, 1H), 1.15 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, d_6-DMSO) δ 167.4, 141.3, 135.3, 131.6, 127.8, 126.9, 125.1, 68.1, 60.7, 60.1, 35.4, 33.6, 26.7, 24.1, 19.4. MS (APCI) *m/z* calc'd for $C_{17}H_{27}N_2O$ (M–Cl): 275.2; found: 275.2. MS (ESI-TOF) *m/z* calc'd for $C_{17}H_{27}N_2O$ (M–Cl): 275.2118; found: 275.2122. *m/z* calc'd for $C_{17}H_{26}N_2NaO$ (M+Na): 297.1937; found: 297.1934. $[\alpha]_D^{24}$ = +108.6 (c = 1.10, CH_2Cl_2).



1-((1*R*,2*R*)-2-Aminocyclohexyl)-3-((*S*)-3,3-dimethyl-1-oxo-1-((*R*)-2-(*o*-tolyl)pyrrolidin-1-yl)butan-2-yl)urea: A suspension of (*S*)-3,3-dimethyl-1-oxo-1-((*R*)-2-(*o*-tolyl)pyrrolidin-1-yl)butan-2-ammonium chloride (583.9 mg, 1.9 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 ºC. Triphosgene (715.2 mg, 2.4 mmol)

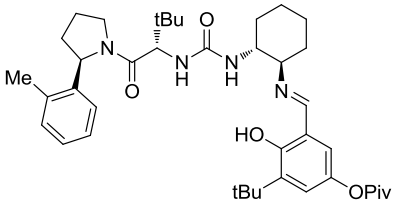
was added and the reaction mixture was warmed to ambient temperature and stirred for 14 h and washed with sat'd $NaHCO_3$. The separated organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. To a solution of the crude isonitrile in CH_2Cl_2 (20 mL) was added (1*R*,2*R*)-cyclohexane-1,2-diamine (678.8 mg, 4.5 mmol). The reaction mixture was stirred for 14 h at ambient temperature and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent: 0-10% MeOH/CH_2Cl_2, v/v) to give 585.2 mg (75% yield) of the desired product as a white foam as a 7:1 mixture of rotamers about the amide bond in $CDCl_3$. IR (thin film) 2942, 2218, 1621, 1557, 1447, 1396, 1325, 1241, 1168, 1106, 1032, 909, 728, 644 cm^{-1}. Major rotamer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.10 (d, *J* = 8.3 Hz, 1H), 5.81 (d, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 7.8 Hz, 1H), 4.37 (t, *J* = 8.8 Hz, 1H), 4.22 (d, *J* = 7.8 Hz, 1H), 3.74-3.56 (m, 2H), 2.62 (t, *J* = 8.3 Hz, 1H), 2.26 (s, 3H), 2.20-2.05 (m, 1H), 2.01-1.80 (m, 2H), 1.73 (dd, *J* = 5.9, 11.7 Hz, 1H), 1.60-1.50 (m, 2H), 1.44 (d, *J* = 11.2 Hz, 1H), 1.32-1.19 (m, 2H), 1.02 (s, 9H), 0.96-0.85 (m, 1H), 0.77-0.66 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 173.3, 157.3, 139.3, 132.5, 130.2, 128.4, 127.0, 124.2, 59.4, 59.0, 54.0, 51.8, 48.7, 40.0, 34.3, 33.3, 32.3, 28.6, 26.6, 24.1, 23.6, 22.7, 18.9. MS (APCI) *m/z* calc'd for $C_{24}H_{39}N_4O_2$ (M+H): 415.3; found: 415.3. MS (ESI-TOF) *m/z* calc'd for $C_{24}H_{39}N_4O_2$ (M+H): 415.3068; found: 415.3073. *m/z* calc'd for $C_{24}H_{38}N_4NaO_2$ (M+Na): 437.2887; found: 437.2893. $[\alpha]_D^{24}$ = +48.6 (c = 1.60, CH_2Cl_2).



3-(*tert*-Butyl)-5-formyl-4-hydroxyphenyl pivalate: To a suspension of 3-(*tert*-butyl)-4-hydroxyphenyl pivalate (1.2563 g, 5.0 mmol),[4] $MgCl_2$ (0.87 g, 9.1 mmol) and paraformaldehyde (1.31 g, 43.6 mmol) in acetonitrile (25 mL, 0.2 M) was added NEt_3 (2.8 mL, 20.1 mmol). The reaction mixture was heated to reflux for 14 h and cooled to ambient temperature, diluted with CH_2Cl_2, and washed with sat'd NH_4Cl. The separated organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent: 5-7% EtOAc/hexanes, v/v) to give 717.2 mg (51% yield) of the desired product. IR (thin film) 2963, 1751, 1657, 1435, 1319, 1272, 1221, 1146, 1113, 911, 762 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 11.70 (s, 1H), 9.79 (s, 1H), 7.17 (d, *J* = 2.7 Hz, 1H), 7.14 (d, *J* = 2.7 Hz, 1H), 1.41 (s, 9H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 196.3, 177.1, 158.6, 142.7, 139.8, 127.8, 123.0, 119.9, 38.9, 34.9, 28.9, 27.0. MS (APCI) *m/z* calc'd for $C_{16}H_{21}O_4$ (M–H): 277.1; found: 277.0. This compound has been reported in the literature.[4]

[4] Vachal, P.; Jacobsen, E.N. *Org. Lett.* **2000**, *2*, 867-870.

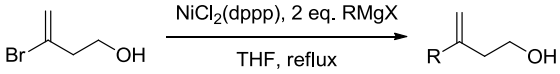
Note: Phenol formylation can be accomplished using $SnCl_4$ as the Lewis acid promoter, but subsequent urea Schiff base catalyst made using this method gave inconsistent enantioselectivity when used in iodoamination, presumably due to the presence of trace metal impurities.



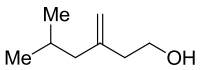
3-(*Tert*-butyl)-5-((*E*)-(((1*R*,2*R*)-2-(3-((*S*)-3,3-dimethyl-1-oxo-1-((*R*)-2-(*o*-tolyl)pyrrolidin-1-yl)butan-2-yl)ureido)cyclohexyl)imino)methyl)-4-hydroxyphenyl pivalate (3f): To a suspension of 1-((1*R*,2*R*)-2-aminocyclohexyl)-3-((*S*)-3,3-dimethyl-1-oxo-1-((*R*)-2-(*o*-tolyl)pyrrolidin-1-yl)butan-2-yl)urea (239.6 mg, 0.58 mmol), 3-(*tert*-butyl)-5-formyl-4-hydroxyphenyl pivalate (178 mg, 0.64 mmol), and Na_2SO_4 (579.4 mg, 4.08 mmol) in MeOH (6 mL) was added one drop of pyrrolidine. The reaction mixture was stirred for 14 h and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent: 5-45% EtOAc/hexanes, v/v) to give 306.9 mg (79% yield) of the desired product as a 2:1 mixture of rotamers about the amide bond in $CDCl_3$. IR (thin film) 3349, 2957, 2872, 1751, 1636, 1546, 1482, 1437, 1395, 1364, 1316, 1271, 1229, 1204, 1150, 1116, 1033, 908, 863, 794, 759, 633 cm^{-1}. Major rotamer: ^1H NMR (500 MHz, $CDCl_3$) δ 13.83 (br s, 1H), 8.17 (br s, 1H), 7.13-7.08 (m, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 2.7 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 2.6 Hz, 1H), 5.26 (d, *J* = 7.3 Hz, 1H), 5.10-4.97 (m, 1H), 4.59 (d, *J* = 9.6 Hz, 1H), 4.22-4.14 (m, 1H), 4.06 (d, *J* = 10.5 Hz, 1H), 3.70 (q, *J* = 7.2 Hz, 1H), 3.56-3.44 (m, 1H), 3.42-3.32 (m, 1H), 3.25-3.14 (m, 1H), 2.33 (s, 3H), 2.25-2.18 (m, 1H), 2.08-1.50 (m, 11H), 1.41 (s, 9H), 1.33 (s, 9H), 0.95 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 177.4, 171.0, 164.4, 158.2, 157.6, 141.8, 140.6, 138.6, 133.8, 130.4, 126.5, 125.9, 123.7, 122.7, 121.3, 118.2, 71.4, 58.0, 57.8, 53.8, 48.4, 38.9, 34.9, 34.7, 34.5, 33.4, 32.1, 29.2, 27.2, 26.4, 23.9, 23.1, 21.2, 19.3. MS (APCI) *m/z* calc'd for $C_{40}H_{59}N_4O_5$ (M+H): 675.4; found: 675.4. MS (ESI-TOF) *m/z* calc'd for $C_{40}H_{59}N_4O_5$ (M+H): 675.4480; found: 675.4472. *m/z* calc'd for $C_{40}H_{58}N_4NaO_5$ (M+Na): 697.4299; found: 697.4283. $[\alpha]_D^{23} = -36.1$ (c = 1.40, CH_2Cl_2).

3. Substrate preparation

a. General procedure for the synthesis of alcohols by Ni-catalyzed Kumada coupling:[5]

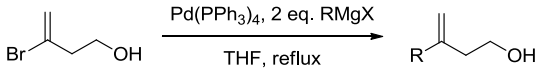


To a solution of $NiCl_2$(dppp) (137 mg, 0.25 mmol) in THF (17 mL, 0.3 M) was added 3-bromobut-3-en-1-ol (0.5 mL, 5.07 mmol). The Grignard reagent (10.13 mmol, 2 eq.) was added slowly and the reaction mixture was heated to reflux for 2 h, cooled to ambient temperature, and quenched with sat'd NH_4Cl. The separated aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent: 10-25% EtOAc/hexanes, v/v) to give the desired alcohol.



5-Methyl-3-methylenehexan-1-ol: IR (thin film) 3328, 3075, 2955, 2870, 1644, 1464, 1384, 1367, 1168, 1103, 1047, 893, 825 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.79 (s, 2H), 3.66 (t, *J* = 6.3 Hz, 2H), 2.23 (t, *J* = 6.3 Hz, 2H), 2.04 (m, 1H), 1.87 (d, *J* = 7.3 Hz, 2H), 1.72 (nonet, *J* = 6.8 Hz, 1H), 0.85 (d, *J* = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.0, 112.6, 60.3, 45.6, 38.7, 26.0, 22.3. MS (APCI) *m/z* calc'd for $C_8H_{17}O$ (M+H): 129.1; found: 129.1. MS (ESI-TOF) *m/z* calc'd for $C_8H_{16}NaO$ (M+Na): 151.1099; found: 151.1175.

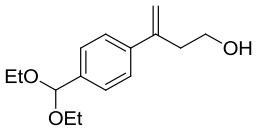
b. General procedure for the synthesis of alcohols by Pd-catalyzed Kumada coupling:[6]



To a solution of $Pd(PPh_3)_4$ (176 mg, 0.15 mmol) in THF (17 mL, 0.3 M) was added 3-bromobut-3-en-1-ol (0.5 mL, 5.07 mmol). The Grignard reagent (7.6 mmol, 1.5 eq.) was added slowly and the reaction mixture was heated to reflux for 1 h, cooled to ambient temperature, quenched with water, and diluted with Et_2O. The separated organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent: 10-30% EtOAc/hexanes, v/v) to give the desired alcohol.

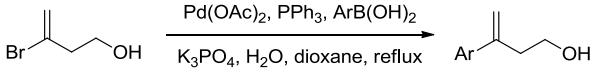
[5] Kumada, M.; Tamao, K.; Sumitani, K. *Org. Synth.* **1978**, *58*, 127.

[6] Yamamura, M.; Moritani, I.; Murahashi, S.I. *J. Organomet. Chem.* **1975**, *91*, C39-C42.

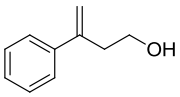


3-(4-(Diethoxymethyl)phenyl)but-3-en-1-ol: This compound was purified on high-purity grade silica gel (Davisil Grade 643, pore size 150 Å, 200-425 mesh, Sigma-Aldrich) to prevent hydrolysis of the acetal. IR (thin film) 3387, 2975, 2880, 1725, 1664, 1627, 1511, 1443, 1372, 1335, 1288, 1214, 1180, 1096, 1051, 900, 819, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.44 (m, 4H), 5.50 (s, 1H), 5.42 (d, *J* = 1.1 Hz, 1H), 5.17 (s, 1H), 3.72 (q, *J* = 6.2 Hz, 2H), 3.48-3.67 (m, 5H), 2.79 (t, *J* = 6.2 Hz, 2H), 1.24 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, d_6-benzene) δ 145.2, 140.9, 139.2, 127.3, 126.2, 114.3, 101.4, 61.1, 60.7, 38.9, 15.4. MS (APCI) *m/z* calc'd for $C_{13}H_{17}O_2$ (M–OEt): 205.1; found: 205.1. MS (ESI-TOF) *m/z* calc'd for $C_{15}H_{22}NaO_3$ (M+Na): 273.1467; found: 273.1464.

c. General procedure for the synthesis of alcohols by Pd-catalyzed Suzuki coupling:[7]



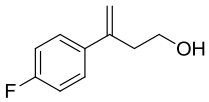
To a suspension of the boronic acid (10.13 mmol, 2 eq.), K_3PO_4 (4.3 g, 20.26 mmol, 4 eq.), PPh_3 (80 mg, 0.30 mmol, 0.06 eq.), and $Pd(OAc)_2$ (34 mg, 0.15 mmol, 0.03 eq.) in 1,4-dioxane (34 mL, 0.15 M) was added 3-bromobut-3-en-1-ol (0.5 mL, 5.07 mmol, 1 eq.) and water (0.27 mL, 15.20 mmol, 3 eq.) under a nitrogen atmosphere. The reaction mixture was heated to reflux for 5 h and cooled to ambient temperature. Celite was added and the resulting slurry was stirred vigorously for 30 min, filtered through a plug of celite, and the filter cake was rinsed with diethyl ether. The filtrate was diluted with an equal amount of hexane, washed three times with water, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent: EtOAc/hexanes) to give the desired alcohol.



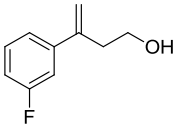
3-Phenylbut-3-en-1-ol: IR (thin film) 3334, 3083, 2947, 2882, 1627, 1600, 1574, 1494, 1444, 1185, 1045, 899, 857, 777, 704, 611 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.41 (m, 2H), 7.38-7.28 (m, 3H), 5.43 (d, *J* = 1.5 Hz, 1H), 5.17 (d, *J* = 1.5 Hz, 1H), 3.73 (t, *J* = 6.6 Hz, 2H), 2.80 (t, *J* = 6.6 Hz, 2H), 2.27 (br s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.7, 140.3, 128.3, 127.5, 125.9, 114.3, 60.8, 38.3. MS

[7] Lee, D.-w.; Yun, Y. *Bull. Korean Chem. Soc.* **2004**, *25*, 29-30.

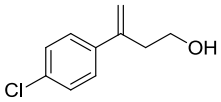
(APCI) *m/z* calc'd for $C_{10}H_{11}$ (M–OH): 131.1; found: 131.1. This compound has been reported in the literature.[8–10]



3-(4-Fluorophenyl)but-3-en-1-ol: IR (thin film) 3331, 2946, 1628, 1602, 1509, 1402, 1231, 1161, 1109, 1046, 901, 840, 740, 701, 667 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.4, 8.8 Hz, 2H), 7.01 (t, *J* = 8.8 Hz, 2H), 5.35 (s, 1H), 5.14 (s, 1H), 3.71 (t, *J* = 6.3 Hz, 2H), 2.75 (t, *J* = 6.3 Hz, 2H), 1.71 (br s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 247.0 Hz), 143.8, 136.5, 127.7 (d, *J* = 7.7 Hz), 115.2 (d, *J* = 21.4 Hz), 114.4, 60.8, 38.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ –115.2 (m). MS (APCI) *m/z* calc'd for $C_{10}H_{11}FO$ (M): 166.1; found: 166.1. This compound has been reported in the literature.[9–11]



3-(3-Fluorophenyl)but-3-en-1-ol: IR (thin film) 3360, 2948, 2882, 1611, 1580, 1488, 1434, 1266, 1213, 1046, 908, 875, 788, 731 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 14.3, 6.8 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 10.3 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 5.44 (s, 1H), 5.21 (s, 1H), 3.74 (t, *J* = 6.0 Hz, 2H), 2.77 (t, *J* = 6.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.0 (d, *J* = 245.4 Hz), 143.9, 142.9 (d, *J* = 7.3 Hz), 130.0 (d, *J* = 8.3 Hz), 121.9 (d, *J* = 2.7 Hz), 115.6, 114.6 (d, *J* = 21.2 Hz), 113.2 (d, *J* = 21.9 Hz), 61.0, 38.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.7 (m). MS (ESI-TOF) *m/z* calc'd for $C_{10}H_{11}FNaO$ (M+Na): 189.0686; found: 189.0688. This compound has been reported in the literature.[9]



3-(4-Chlorophenyl)but-3-en-1-ol: IR (thin film) 3336, 3085, 2946, 1626, 1593, 1492, 1396, 1182, 1092, 1046, 1012, 904, 834, 754, 735, 624, 607 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 5.35 (s, 1H), 5.12 (s, 1H), 3.66 (t, *J* = 6.3 Hz, 2H), 3.13 (br s, 1H), 2.69 (t, *J* = 6.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.4, 138.7, 133.1, 128.2, 127.1, 114.4, 60.5, 37.9. MS

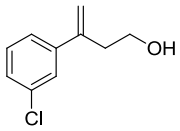
[8] (a) Lin, M.-H.; Lin, L.-Z.; Chuang, T.-H.; *Synlett* **2011**, 1871-1874. (b) Brodney, M.A.; Cole, M.L.; Freemont, J.A.; Kyi, S.; Junk, P.C.; Padwa, A.; Riches, A.G.; Ryan, J.H. *Tetrahedron Lett.* **2007**, *48*, 1939-1943. (d) Okachi, T.; Onaka, M. *J. Am. Chem. Soc.* **2004**, *126*, 2306-2307.

[9] Mo, J.; Xu, L.; Ruan, J.; Liu, S.; Xiao, J. *Chem. Commun.* **2006**, 3591-3593.

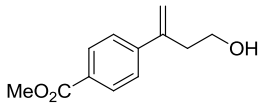
[10] Okachi, T.; Fujimoto, K.; Onaka, M. *Org. Lett.* **2002**, *4*, 1667-1670.

[11] Reetz, M.T.; Guo, H.; Jun-An, Ma.; Goddard, R.; Mynott, R.J. *J. Am. Chem. Soc.* **2009**, *131*, 4136-4142.

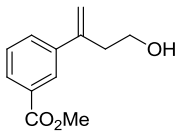
(APCI) *m/z* calc'd for $C_{10}H_{10}Cl$ (M–OH): 165.1; found: 165.1. This compound has been reported in the literature.[11]



3-(3-Chlorophenyl)but-3-en-1-ol: IR (thin film) 3336, 3086, 2948, 2883, 1628, 1593, 1562, 1476, 1414, 1319, 1181, 1120, 1047, 998, 906, 789, 724, 677 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.31-7.29 (m, 3H), 5.43 (s, 1H), 5.22 (s, 2H), 3.73 (t, *J* = 6.8 Hz, 2H), 2.77 (t, *J* = 6.8 Hz, 2H), 1.91 (br s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.6, 142.3, 134.3, 129.6, 127.6, 126.3, 124.2, 115.5, 60.8, 38.3. MS (APCI) *m/z* calc'd for $C_{10}H_{10}Cl$ (M–OH): 165.1; found 165.1. This compound has been reported in the literature.[12]

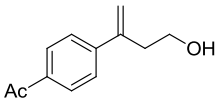


Methyl 4-(4-hydroxybut-1-en-2-yl)benzoate: IR (thin film) 3404, 2952, 1721, 1608, 1437, 1406, 1286, 1190, 1121, 1048, 1017, 862, 761, 721 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 6.7, 1.8 Hz, 2H), 7.48 (dd, *J* = 6.7, 1.7 Hz, 2H), 5.50 (s, 1H), 5.27 (s, 1H), 3.92 (s, 3H), 3.74 (t, *J* = 6.3 Hz, 2H), 2.81 (t, *J* = 6.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.0, 145.2, 144.2, 129.9, 129.3, 126.2, 116.4, 61.1, 52.2, 38.4. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{15}O_3$ (M+H): 207.1016; found: 207.1025. *m/z* calc'd for $C_{12}H_{14}NaO_3$ (M+Na): 229.0835; found: 229.0846. This compound has been reported in the literature.[9]

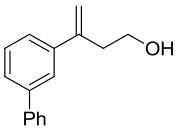


Methyl 3-(4-hydroxybut-1-en-2-yl)benzoate: IR (thin film) 3397, 2952, 1721, 1629, 1602, 1580, 1439, 1258, 1194, 1126, 1101, 1047, 984, 904, 865, 819, 765, 719 cm^{-1}. ^1H NMR (500 MHz, d_6-benzene) δ 8.26 (t, *J* = 1.8 Hz, 1H), 7.98 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.32 (ddd, *J* = 1.4, 1.8, 7.8 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 5.26 (s, 1H), 5.00 (s, 1H), 3.52 (q, *J* = 6.9 Hz, 2H), 3.50 (s, 3H), 2.56 (t, *J* = 6.9 Hz, 2H), 2.16 (t, *J* = 5.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, d_6-benzene) δ 166.9, 144.7, 141.6, 130.9, 130.7, 128.8, 128.7, 127.6, 115.1, 61.1, 51,7, 38.7. MS (APCI) *m/z* calc'd for $C_{12}H_{13}O_2$ (M–OH): 189.1; found: 189.1. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{15}O_3$ (M+H): 207.1016; found: 207.1022. *m/z* calc'd for $C_{12}H_{13}O_2$ (M+H–H_2O): 189.0910; found: 189.0912. *m/z* calc'd for $C_{12}H_{15}O_3$ (M+H): 207.1016; found: 207.1022. *m/z* calc'd for $C_{12}H_{14}NaO_3$ (M+Na): 229.0835; found: 229.0842.

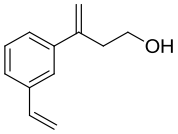
[12] Stelmach, J.E.; Rosauer, K.G.; Parmee, E.R.; Tata, J.R. Substituted aryl and heteroaryl derivatives. PCT Int. Appl. 2006102067, Sep 28, 2006.



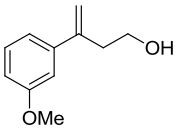
3-(4-Acetylphenyl)but-3-en-1-ol: IR (thin film) 3413, 2881, 1679, 1604, 1558, 1403, 1359, 1270, 1187, 1106, 1047, 960, 909, 847, 819, 732, 645 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 5.49 (s, 1H), 5.26 (s, 1H), 3.73 (t, *J* = 6.3 Hz, 2H), 2.80 (t, *J* = 6.3 Hz, 2H), 2.58 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 197.7, 145.2, 144.0, 129.0, 128.5, 126.2, 116.4, 60.9, 38.2, 26.6. MS (APCI) *m/z* calc'd for $C_{12}H_{15}O_2$ (M+H): 191.1; found: 191.1. This compound has been reported in the literature.[9]



3-([1,1'-Biphenyl]-3-yl)but-3-en-1-ol: IR (thin film) 3337, 3031, 2946, 1948, 1808, 1627, 1598, 1572, 1509, 1479, 1450, 1414, 1233, 1177, 1046, 895, 861, 842, 804, 760, 723, 697, 615 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 6.3 Hz, 1H), 7.47 (t, *J* = 6.8 Hz, 2H), 7.43 (d, *J* = 5.4 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 5.50 (s, 1H), 5.23 (s, 1H), 3.78 (t, *J* = 6.3 Hz, 2H), 2.86 (t, *J* = 6.3 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.8, 141.4, 141.1, 140.9, 128.8, 128.7 (2 overlapping signals), 127.4, 127.2, 126.5, 125.0, 114.8, 60.9, 38.6. MS (APCI) *m/z* calc'd for $C_{16}H_{15}$ (M–OH): 207.1; found: 207.1. MS (ESI-TOF) *m/z* calc'd for $C_{16}H_{17}O$ (M+H): 225.1274; found: 225.1268.

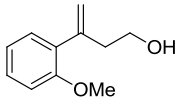


3-(3-Vinylphenyl)but-3-en-1-ol: IR (thin film) 3334, 3087, 2946, 1815, 1629, 1594, 1575, 1481, 1417, 1310, 1192, 1045, 990, 897, 802, 731, 712 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.35-7.31 (m, 1H), 7.30-7.26 (m, 2H), 6.71 (dd, *J* = 10.7, 17.6 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.40 (s, 1H), 5.25 (d, *J* = 11.2 Hz, 1H), 5.15 (s, 1H), 3.70 (t, *J* = 6.8 Hz, 2H), 2.77 (t, *J* = 6.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.7, 140.7, 137.6, 136.6, 128.5, 125.5, 125.3, 124.1, 114.6, 114.1, 60.8, 38.5. MS (APCI) *m/z* calc'd for $C_{12}H_{13}$ (M–OH): 157.1; found: 157.1. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{14}NaO$ (M+Na): 197.0937; found: 197.0931.

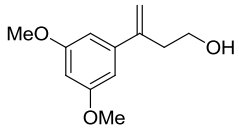


3-(3-Methoxyphenyl)but-3-en-1-ol: IR (thin film) 3380, 2943, 2835, 1598, 1577, 1488, 1452, 1429, 1320, 1287, 1229, 1173, 1108, 1043, 877, 829, 782, 727, 690 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t,

J = 8.1 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.96 (s, 1H), 6.84 (dd, *J* = 2.4, 8.3 Hz, 1H), 5.41 (s, 1H), 5.16 (s, 1H), 3.82 (s, 3H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.77 (t, *J* = 6.3 Hz, 2H), 1.74 (br s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.5, 144.7, 141.9, 129.3, 118.6, 114.6, 112.8, 112.1, 60.9, 55.1, 38.5. MS (APCI) *m/z* calc'd for $C_{11}H_{15}O_2$ (M+H): 179.1; found: 179.1. This compound has been reported in the literature.[9]

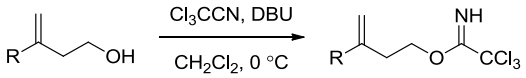


3-(2-Methoxyphenyl)but-3-en-1-ol: IR (thin film) 3385, 2938, 2836, 1630, 1598, 1578, 1490, 1463, 1435, 1292, 1240, 1181, 1126, 1096, 1047, 1026, 904, 861, 799, 752, 648 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30-7.22 (m, 1H), 7.16-7.10 (m, 1H), 6.96-6.84 (m, 2H), 5.27 (s, 1H), 5.13 (s, 1H), 3.81 (s, 3H), 3.59 (t, *J* = 6.3 Hz, 2H), 2.72 (t, *J* = 6.3 Hz, 2H), 2.13 (br s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 156.2, 144.6, 131.1, 129.8, 128.5, 120.6, 117.0, 110.6, 60.4, 55.3, 40.1. MS (APCI) *m/z* calc'd for $C_{11}H_{13}O$ (M–OH): 161.1; found: 161.1. This compound has been reported in the literature.[9]



3-(3,3-Dimethoxyphenyl)but-3-en-1-ol: IR (thin film) 3370, 3000, 2944, 2838, 1591, 1455, 1421, 1347, 1204, 1155, 1113, 1050, 906, 848, 791, 733, 688 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 6.56-6.66 (m, 2H), 6.41-6.40 (m, 1H), 5.39 (s, 1H), 5.14 (s, 1H), 3.79 (s, 6 H), 3.71 (t, *J* = 6.3 Hz, 2H), 2.73 (t, *J* = 6.3 Hz), 1.76 (br s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 160.7, 144.9, 142.7, 114.7, 104.5, 99.4, 60.9, 55.2, 38.6. MS (APCI) *m/z* calc'd for $C_{12}H_{16}O_3$ (M+H): 209.1; found: 209.1. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{15}O_2$ (M+H–H_2O): 191.1067; found: 191.1062. *m/z* calc'd for $C_{12}H_{17}O_3$ (M+H): 209.1172; found: 209.1171. *m/z* calc'd for $C_{12}H_{16}NaO_3$ (M+Na): 231.0992; found: 231.0996.

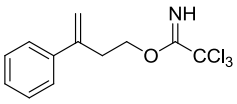
d. General procedure for the synthesis of trichloroacetimidates:[13]



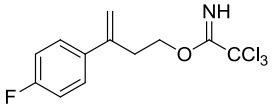
A solution of the alcohol (1 eq.) in CH_2Cl_2 (0.1 M) was cooled to 0 ºC. Subsequently, trichloroacetonitrile (1.5 eq.) and DBU (0.2 eq.) were added and the resulting solution was stirred for 1 h and quenched with sat'd $NaHCO_3$. The separated aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by

[13] Arnold, J.S.; Stone, R.F.; Nguyen, H.M. *Org. Lett.* **2010**, *12*, 4580-4583.

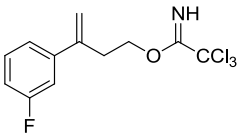
column chromatography (eluent: EtOAc/hexanes) on high-purity grade silica gel (Davisil Grade 643, pore size 150 Å, 200-425 mesh, Sigma-Aldrich) to prevent hydrolysis of the trichloroacetimidate.



3-Phenylbut-3-en-1-yl 2,2,2-trichloroacetimidate (1a): IR (thin film) 3342, 3084, 3058, 2961, 1948, 1881, 1805, 1766, 1663, 1629, 1601, 1574., 1495, 1445, 1385, 1310, 1241, 1083, 999, 902, 862, 827, 795, 777, 703, 647, 614 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29, 7.46 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 6.9 Hz, 1H), 5.44 (s, 1H), 5.23 (s, 1H), 4.44 (t, *J* = 6.9 Hz, 2H), 3.02 (t, *J* = 6.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 162.7, 143.9, 140.4, 128.4, 127.6, 126.1, 114.7, 91.4, 67.9, 33.9. MS (APCI) *m/z* calc'd for $C_{12}H_{13}Cl_3NO$ (M+H): 292.0; found: 292.0. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{13}Cl_3NO$ (M+H): 292.0057; found: 292.0060. *m/z* calc'd for $C_{12}H_{12}Cl_3NNaO$ (M+Na): 313.9877; found: 313.9878.

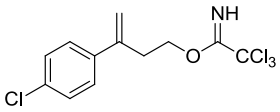


3-(4-Fluorophenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1b): IR (thin film) 3344, 3087, 2959, 1892, 1766, 1727, 1664, 1602, 1509, 1448, 1387, 1311, 1231, 1162, 1082, 1000, 906, 839, 795, 736, 683, 648 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (br s, 1H), 7.40 (dd, *J* = 5.4, 8.8 Hz, 2H), 7.02 (t, *J* = 8.8 Hz, 2H), 5.35 (s, 1H), 5.18 (s, 1H), 4.39 (t, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 7.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 162.7, 162.4 (d, *J* = 246.8 Hz), 143.0, 136.5, 127.7 (d, *J* = 8.2 Hz), 115.2 (d, *J* = 21.2 Hz), 114.7, 91.4, 67.8, 34.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ –115.2 (m). MS (APCI) *m/z* calc'd for $C_{12}H_{12}Cl_3FNO$ (M+H): 310.0; found: 310.0. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{12}Cl_3FNO$ (M+H): 309.9963; found: 309.9962.

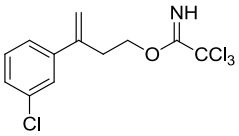


3-(3-Fluorophenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1c): IR (thin film) 3345, 2981, 2868, 1665, 1612, 1581, 1488, 1441, 1312, 1086, 1002, 798, 649 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.31 (td, *J* = 8.0, 6.1 Hz, 1H), 7.25-7.21 (m, 1H), 7.18-7.14 (m, 1H), 6.99 (tdd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 5.45 (s, 1H), 5.26 (s, 1H), 4.46-4.36 (m, 2H), 2.99 (td, *J* = 6.8, 0.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 163.1 (d, *J* = 245.4 Hz), 162.9, 143.2 (d, *J* = 2.5 Hz), 142.9 (d, *J* = 7.5 Hz), 130.00 (d, *J* = 8.3 Hz), 121.9 (d, *J* = 2.9 Hz), 115.9, 114.6 (d, *J* = 21.4 Hz), 113.3 (d, *J* = 22.0 Hz), 91.5, 68.0, 34.0. ^{19}F

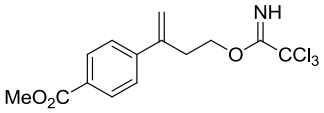
NMR (376 MHz, $CDCl_3$) δ –113.8 (m). MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{11}Cl_3FNNaO$ (M+Na): 331.9782; found: 331.9774.



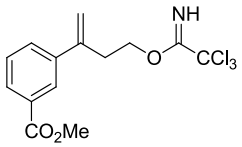
Methyl 3-(4-chlorophenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1d): IR (thin film) 3342, 2972, 1664, 1493, 1442, 1385, 1310, 1087, 1001, 907, 833, 797, 764, 736, 949 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (br s, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.39 (s, 1H), 5.22 (s, 1H), 4.39 (t, *J* = 6.8 Hz, 2H), 2.96 (t, *J* = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$); δ 162.7, 142.9, 138.8, 133.4, 128.5, 127.4, 115.2, 91.3, 67.8, 33.8. MS (APCI) *m/z* calc'd for $C_{12}H_{12}Cl_4NO$ (M+H): 326.0; found: 326.0. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{12}Cl_4NO$ (M+H): 325.9668; found: 325.9684.



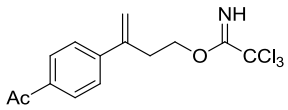
3-(3-Chlorophenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1e): IR (thin film) 3342, 2958, 1664, 1593, 1563, 1476, 1414, 1310, 1082, 1000, 908, 863, 794, 719, 677, 648 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.40 (s, 1H), 7.31-7.26 (m, 1H), 7.26-7.22 (m, 2H), 5.39 (s, 1H), 5.22 (s, 1H), 4.38 (t, *J* = 6.8 Hz, 2H), 2.94 (t, *J* = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.7, 143.0, 142.4, 134.3, 129.6, 127.6, 126.4, 124.3, 115.9, 91.3, 67.8, 33.8. MS (APCI) *m/z* calc'd for $C_{12}H_{12}Cl_4NO$ (M+H): 326.0; found: 326.0. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{12}Cl_4NO$ (M+H): 325.9668; found: 325.9685.



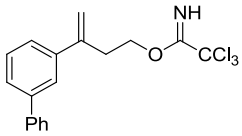
Methyl 4-(4-(2,2,2-trichloro-1-iminoethoxy)but-1-en-2-yl)benzoate (1f): IR (thin film) 3341, 2953, 1721, 1664, 1609, 1436, 1406, 1279, 1188, 1085, 1017, 1001, 909, 862, 827, 797, 783, 718, 648 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (br s, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 5.48 (s, 1H), 5.29 (s, 1H), 4.39 (t, *J* = 6.8 Hz, 2H), 3.90 (s, 3H), 2.99 (t, *J* = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.7, 162.6, 144.9, 143.3, 129.7, 129.2, 126.0, 116.5, 91.3, 67.7, 52.0, 33.7. MS (APCI) *m/z* calc'd for $C_{14}H_{15}Cl_3NO_3$ (M+H): 350.0; found: 350.0. MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{15}Cl_3NO_3$ (M+H): 350.0112; found: 350.0115. *m/z* calc'd for $C_{14}H_{14}Cl_3NNaO_3$ (M+Na): 371.9931; found: 371.9935.



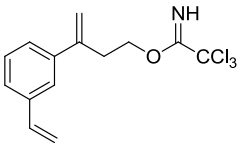
Methyl 3-(4-(2,2,2-trichloro-1-iminoethoxy)but-1-en-2-yl)benzoate (1g): IR (thin film) 3342, 2953, 1720, 1665, 1581, 1439, 1385, 1295, 1256, 1129, 1083, 1000, 908, 864, 796, 764, 716, 648 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (br s, 1H), 8.09 (d, *J* = 1.4 Hz, 1H), 7.93 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.60 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.38 (dt, *J* = 2.3, 7.8 Hz, 1H), 5.44 (s, 1H), 5.24 (s, 1H), 4.38 (t, *J* = 6.9 Hz, 2H), 3.90 (d, *J* = 2.7 Hz, 3H), 2.99 (t, *J* = 6.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 166.8, 162.6, 143.2, 140.7, 130.5, 130.2, 128.6, 128.4, 127.2, 115.6, 91.3, 67.7, 52.0, 33.7. MS (APCI) *m/z* calc'd for $C_{14}H_{15}Cl_3NO_3$ (M+H): 350.0; found: 350.0. MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{14}Cl_3NNaO_3$ (M+Na): 371.9931; found: 371.9940.



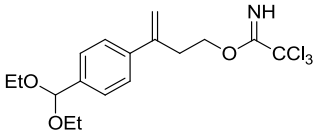
3-(4-acetylphenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1h): IR (thin film) 3343, 2981, 2869, 1766, 1683, 1669, 1607, 1581, 1310, 1268, 1084, 1002, 830, 799, 649 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.94 (dd, *J* = 6.7, 1.9 Hz, 2H), 7.54 (dd, *J* = 6.7, 1.9 Hz, 2H), 5.52 (s, 1H), 5.33 (s, 1H), 4.41 (t, *J* = 6.8 Hz, 2H), 3.02 (dt, *J* = 6.8, 0.8 Hz, 2H), 2.60 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 197.7, 162.9, 145.3, 143.4, 136.4, 128.7, 126.4, 116.9, 91.5, 67.9, 33.9, 26.8. MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{14}Cl_3NNaO_2$ (M+Na): 355.9982; found: 355.9994.



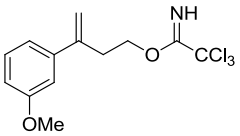
3-([1,1'-Biphenyl]-3-yl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1i): IR (thin film) 3340, 3032, 2954, 1765, 1663, 1598, 1573, 1480, 1451, 1386, 1309, 1083, 999, 905, 863, 796, 760, 720, 698, 647, 616 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.68 (s, 1H), 7.65-7.59 (m, 2H), 7.53 (dt, *J* = 6.3, 2.0 Hz, 1H), 7.50-7.40 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 5.50 (s, 1H), 5.27 (s, 1H), 4.47 (t, *J* = 6.8 Hz, 2H), 3.07 (t, *J* = 6.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 162.8, 144.0, 141.4, 141.1, 141.0, 128.8, 128.7, 127.3, 127.2, 126.5, 125.1, 125.0, 115.0, 91.4, 68.0, 34.0. MS (APCI) *m/z* calc'd for $C_{18}H_{17}Cl_3NO$ (M+H): 368.0; found: 368.0. MS (ESI-TOF) *m/z* calc'd for $C_{18}H_{17}Cl_3NO$ (M+H): 368.0372; found: 368.0376.



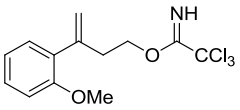
3-(3-Vinylphenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1j): IR (thin film) 3341, 3088, 1663, 1631, 1595, 1575, 1480, 1388, 1310, 1194, 1083, 998, 907, 864, 826, 796, 762, 711, 648 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.48 (s, 1H), 7.38-7.28 (m, 3 H), 6.74 (dd, *J* = 11.0, 17.6 Hz, 1H), 5.79 (dd, *J* = 0.7, 17.6 Hz, 1H), 5.43 (s, 1H), 5.28 (dd, *J* = 0.7, 11.0 Hz, 1H), 5.23 (s, 1H), 4.42 (t, *J* = 7.0 Hz, 2H), 3.01 (t, *J* = 7.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 162.7, 143.9, 140.8, 137.7, 136.7, 128.5, 125.6, 125.4, 124.2, 114.9, 114.1, 91.4, 68.0, 34.0. MS (APCI) *m/z* calc'd for $C_{14}H_{15}Cl_3NO$ (M+H): 318.0; found: 318.0. MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{15}Cl_3NO$ (M+H): 318.0214; found: 318.0222. *m/z* calc'd for $C_{14}H_{14}Cl_3NNaO$ (M+Na): 340.0033; found: 340.0027.



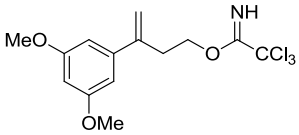
3-(4-(Diethoxymethyl)phenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1k): IR (thin film) 3347, 2975, 2881, 1665, 1444, 1390, 1309, 1215, 1180, 1089, 1054, 1000, 906, 850, 797, 734, 649 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (br s, 1H), 7.43 (m, 4H), 5.50 (s, 1H), 5.41 (s, 1H), 5.19 (s, 1H), 4.39 (t, *J* = 7.0 Hz, 2H), 3.66-3.43 (m, 5H), 2.98 (t, *J* = 7.0 Hz, 2H), 1.24 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 162.7, 143.6, 140.3, 138.5, 126.7, 125.9, 114.8, 101.3, 91.4, 67.9, 60.9, 33.9, 15.1. MS (APCI) *m/z* calc'd for $C_{15}H_{17}Cl_3NO_2$ (M–OEt): 348.0; found: 348.0. MS (ESI-TOF) *m/z* calc'd for $C_{17}H_{22}Cl_3NNaO_3$ (M+Na): 417.0557; found: 417.0563.



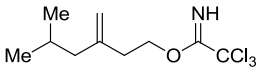
3-(3-Methoxyphenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1l): IR (thin film) 3341, 2959, 2835, 1663, 1598, 1577, 1489, 1463, 1430, 1385, 1289, 1235, 1181, 1084, 1049, 1000, 906, 863, 795, 725, 648 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (br s, 1H), 7.26 (t, *J* = 8.2 Hz, 1H), 7.04 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.00 (t, *J* = 2.1 Hz, 1H), 6.85 (dd, *J* = 2.7, 8.2 Hz, 1H), 5.43 (s, 1H), 5.21 (s, 1H), 4.42 (t, *J* = 6.9 Hz, 2H), 3.83 (s, 3H), 2.99 (t, *J* =6.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 162.7, 159.6, 143.8, 141.9, 129.3, 118.5, 114.8, 112.8, 112.1, 91.4, 67.9, 55.1, 34.0. MS (APCI) *m/z* calc'd for $C_{13}H_{15}Cl_3NO_2$ (M+H): 322.0; found: 322.0. MS (ESI-TOF) *m/z* calc'd for $C_{13}H_{15}Cl_3NO_2$ (M+H): 322.0163; found: 322.0167.



3-(2-Methoxyphenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1m): IR (thin film) 3360, 2935, 2838, 1764, 1726, 1598, 1490, 1464, 1436, 1242, 1182, 1098, 1048, 1027, 989, 910, 828, 736, 682, 650 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.31-7.21 (m, 1H), 7.21-7.12 (m, 1H), 6.91 (td, *J* = 7.4, 1.0 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.25 (dd, *J* = 2.9, 1.3 Hz, 1H), 5.13 (d, *J* = 1.7 Hz, 1H), 4.29 (t, *J* = 6.7 Hz, 2H), 3.83 (s, 3H), 2.97 (dd, *J* = 7.0, 6.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.0, 156.6, 144.8, 131.1, 130.5, 128.9, 120.8, 116.9, 110.7, 91.7, 68.2, 55.5, 35.0. MS (ESI-TOF) *m/z* calc'd for $C_{13}H_{15}Cl_3NO_2$ (M+H): 322.0163; found: 322.0173. *m/z* calc'd for $C_{13}H_{14}Cl_3NNaO_2$ (M+Na): 343.9982; found: 343.9995.

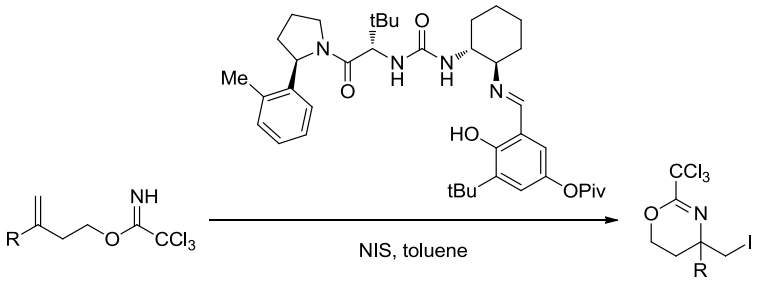


3-(3,5-Dimethoxyphenyl)but-3-en-1-yl 2,2,2-trichloroacetimidate (1n): IR (thin film) 3340, 2935, 2838, 1664, 1591, 1456, 1421, 1384, 1309, 1205, 1156, 1069, 999, 907, 827, 796, 733, 648 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 6.59 (d, *J* = 2.0 Hz, 2H), 6.41 (t, *J* = 2.0 Hz, 1H), 5.40 (s, 1H), 5.19 (s, 1H), 4.40 (t, *J* = 6.8 Hz, 2H), 3.80 (s, 6H), 2.95 (t, *J* = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.7, 160.7, 143.9, 142.6, 114.9, 104.5, 99.4, 91.4, 67.9, 55.3, 34.0. MS (APCI) *m/z* calc'd for $C_{14}H_{17}Cl_3NO_3$ (M+H): 352.0; found: 352.0. MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{17}Cl_3NO_3$ (M+H): 352.0269; found: 352.0274.

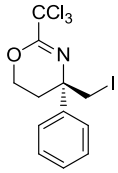


5-Methyl-3-methylenehexyl 2,2,2-trichloroacetimidate (1o): IR (thin film) 3347, 3077, 2956, 2870, 1664, 1465, 1385, 1367, 1310, 1167, 1083, 1000, 898, 861, 797, 718, 648 c cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (br s, 1H), 4.85 (s, 1H), 481 (s, 1H), 4.39 (t, *J* = 6.8 Hz, 2H), 2.45 (t, *J* = 6.8 Hz, 2H), 1.95 (d, *J* = 7.3 Hz, 2H), 1.78 (nonet, *J* = 6.8 Hz, 1H), 0.88 (d, *J* = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.9, 144.2, 112.6, 91.5, 68.1, 46.1, 34.0, 26.0, 22.4. MS (APCI) *m/z* calc'd for $C_{10}H_{17}Cl_3NO$ (M+H): 272.0; found: 272.0. MS (ESI-TOF) *m/z* calc'd for $C_{10}H_{16}Cl_3NNaO$ (M+Na): 294.0190; found: 294.0196.

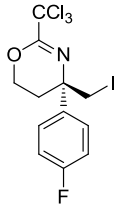
4. Catalytic iodoamination and characterization of products



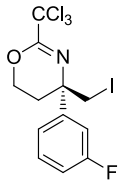
In a 1-dram vial was added catalyst (5-20 mol%), NIS (34.0 mg, 0.15 mmol), and toluene (0.2 mL). The resulting suspension was cooled to –78 ºC. Substrate (0.1 mmol) was then added as a solution in toluene (0.1 mL, followed by two 0.05 mL rinses). The reaction mixture was transferred to a cryocool at the desired temperature and stirred for the designated time period and quenched with 2 mL freshly prepared sat'd $Na_2S_2O_3$. The organic layer was separated and purified by preparative TLC or column chromatography (eluent: EtOAc/hexanes or Et_2O/hexanes) to give the desired product. Note: The vicinal iodoamine products are prone to decolorize over time and readily decompose at rt. It is preferable to store these products in the fridge.



(*S*)-4-(Iodomethyl)-4-(3-methoxyphenyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2a): $[\alpha]_D^{24}$ (90% ee) = +40.1º (c = 0.992, $CHCl_3$). IR (thin film) 3024, 2969, 2899, 1679, 1601, 1493, 1447, 1376, 1314, 1263, 1245, 1202, 1184, 1170, 1140, 1124, 1074, 1037, 1001, 944, 932, 919, 871, 826, 791, 757, 740, 699, 674, 627 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.43-7.30 (m, 5H), 4.41 (ddd, *J* = 2.9, 4.4, 10.7 Hz, 1H), 3.94 (dt, *J* = 2.9, 11.2 Hz, 1H), 3.66 (d, *J* = 10.0 Hz, 1H), 3.63 (d, *J* = 10.0 Hz, 1H), 2.50 (ddd, *J* = 4.9, 12.2, 14.2 Hz, 1H), 2.32 (dt, *J* = 14.2, 2.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$); δ 153.6, 142.3, 128.8, 127.8, 125.8, 92.2, 64.4, 57.9, 31.7, 20.7. MS (APCI) *m/z* calc'd for $C_{12}H_{12}Cl_3INO$ (M+H): 417.9; found: 417.9. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{12}Cl_3INO$ (M+H): 417.9024; found: 417.9026. *m/z* calc'd for $C_{12}H_{11}Cl_3INNaO$ (M+Na): 439.8843; found: 439.8850. This material was determined to be 90% ee by chiral HPLC analysis (ChiralCel OD-H, 1% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 27.60 min, t_R (major) = 22.42 min. $[\alpha]_D^{26}$ = +34.1º (c = 0.986, $CHCl_3$).



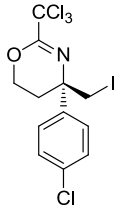
(*S*)-4-(4-Fluorophenyl)-4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2b): IR (thin film) 2962, 2899, 1674, 1603, 1506, 1467, 1408, 1377, 1338, 1302, 1262, 1235, 1203, 1186, 1162, 1140, 1122, 1103, 1078, 1038, 1014, 959, 932, 917, 874, 831, 791, 757, 725, 692, 669, 658, 635, 607 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 5.5, 9.1 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 4.42 (dt, *J* = 10.6, 4.4 Hz, 1H), 3.96 (dt, *J* = 3.3, 11.3 Hz, 1H), 3.60 (d, *J* = 10.1 Hz, 1H), 3.56 (d, *J* = 10.1 Hz, 1H), 2.49 (ddd, *J* = 4.4, 11.3, 13.9 Hz, 1H), 2.30 (dt, *J* = 3.3, 13.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 247.4 Hz), 153.8, 138.2 (d, *J* = 2.9 Hz), 127.6 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 21.2 Hz), 92.1, 64.4, 57.5, 31.6, 20.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ –114.5 (m). MS (APCI) *m/z* calc'd for $C_{12}H_{11}Cl_3FINO$ (M+H): 435.9; found: 435.9. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{11}Cl_3FINO$ (M+H) 435.8929; found: 435.8941. *m/z* calc'd for $C_{12}H_{10}Cl_3FINNaO$ (M+Na): 457.8749; found: 457.8759. This material was determined to be 90% ee by chiral HPLC analysis (ChiralCel OD-H, 0.1% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 22.17 min, t_R (major) = 23.58 min. $[\alpha]_D^{26}$ = +34.1° (c = 0.986, $CHCl_3$).



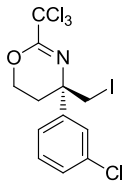
(*S*)-4-(3-Fluorophenyl)-4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4H-1,3-oxazine (2c): IR (thin film) 2978, 1677, 1612, 1588, 1484, 1439, 1246, 1117, 1137, 942, 896, 794, 758, 670, 674, 637. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (td, *J* = 8.1, 6.0 Hz, 1H), 7.16 (ddd, *J* = 7.8, 1.7, 0.9 Hz, 1H), 7.14-7.09 (m, 1H), 7.03 (tdd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 4.44 (ddd, *J* = 11.1, 4.4, 3.7 Hz, 1H), 3.99 (td, *J* = 11.3, 3.1 Hz, 1H), 3.67-3.54 (m, 2H), 2.51 (ddd, *J* = 14.2, 11.4, 4.5 Hz, 1H), 2.32 (dt, *J* = 14.2, 3.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 164.0, 162.1, 154.2, 145.2 (d, *J* = 7.0 Hz), 121.6 (d, *J* = 2.8 Hz), 115.0 (d, *J* = 21.1 Hz), 113.6 (d, *J* = 23.2 Hz), 92.3, 64.5, 57.9, 31.8, 19.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –111.7 (m). MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{11}Cl_3FINO$ (M+H): 435.8929; found: 435.8939.

1 mmol scale: In a scintillation vial was added catalyst (5 mol%), NIS (337.0 mg, 1.5 mmol), and toluene (2 mL). The resulting suspension was cooled to –78 ºC. Substrate (0.1 mmol) was then added as a solution in cold toluene (1 mL, followed by two 0.5 mL rinses). The reaction mixture was transferred to a cryocool at –40 ºC for 7 d, diluted with 10 mL hexanes, and quenched with 10 mL freshly prepared sat'd

$Na_2S_2O_3$. The aqueous layer was extracted thrice with hexanes. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent: 0-20% EtOAc/hexanes, v/v) to afford 432.1 mg (99%) of the desired product as a pale yellow oil. This material was determined to be 98% ee by chiral HPLC analysis (ChiralCel OD-H, 1% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 31.87 min, t_R (major) = 33.34 min. $[\alpha]_D^{26}$ = +37.5º (c = 1.15, $CHCl_3$).

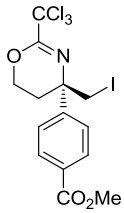


(*S*)-4-(4-Chlorophenyl)-4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2d): IR (thin film) 2961, 2899, 1674, 1591, 1490, 1435, 1399, 1261, 1244, 1201, 1095, 1038, 1013, 959, 913, 875, 829, 793, 761, 738, 721, 684, 644 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz,, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 4.42 (dt, *J* = 10.7, 3.9 Hz, 1H), 3.96 (dt, *J* = 2.9, 11.2 Hz, 1H), 3.60 (d, *J* = 10.0 Hz, 1H), 3.55 (d, *J* = 10.0 Hz, 1H), 2.49 (ddd, *J* = 4.4, 11.2, 14.2 Hz, 1H), 2.30 (dt, *J* = 14.2, 2.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 153.9, 141.0, 133.8, 129.0, 127.4, 94.7, 64.4, 57.6, 31.5, 19.9. MS (APCI) *m/z* calc'd for $C_{12}H_{11}Cl_4INO$ (M+H): 451.9; found: 451.9. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{11}Cl_4INO$: 451.8634; found: 451.8646. This material was determined to be 95% ee by chiral HPLC analysis (ChiralCel OD-H, 0.1% iPrOH in hexanes, 1 mL/min, 200 nm): t_R (minor) = 26.17 min, t_R (major) = 28.06 min. $[\alpha]_D^{25}$ = +52.8º (c = 0.899, $CHCl_3$).

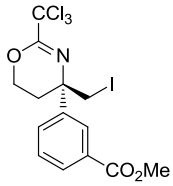


(*S*)-4-(3-Chlorophenyl)-4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2e): IR (thin film) 2966, 1674, 1593, 1570, 1473, 1419, 1377, 1339, 1244, 1188, 1142, 1082, 1037, 959, 909, 883, 828, 790, 734, 698, 667, 631 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40-7.26 (m, 4H), 4.45 (dt, *J* = 11.2, 4.6 Hz, 1H), 4.00 (dt, *J* = 3.2, 11.2 Hz, 1H), 3.63 (d, *J* = 10.3 Hz, 1H), 3.59 (d, *J* = 10.3 Hz, 1H), 2.52 (ddd, *J* = 4.1, 11.0, 14.2 Hz, 1H), 2.32 (dt, *J* = 14.2, 3.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 154.0, 144.5, 134.9, 130.1, 128.1, 126.2, 124.2, 92.1, 64.3, 57.6, 31.5, 19.7. MS (APCI) *m/z* calc'd for $C_{12}H_{11}Cl_4INO$ (M+H): 451.9; found: 451.9. MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{11}Cl_4INO$ (M+H): 451.8634; found: 451.8635. This material was determined to be 97% ee by chiral HPLC analysis

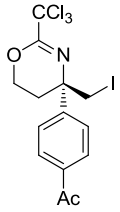
(ChiralCel OD-H, 1% iPrOH in hexanes, 1 mL/min, 200 nm): t_R (minor) = 32.52 min, t_R (major) = 33.69 min. $[\alpha]_D^{26}$ = +41.0° (c = 0.992, $CHCl_3$).



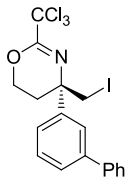
(*S*)-Methyl 4-(4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazin-4-yl)benzoate (2f): IR (thin film) 2953, 2899, 1721, 1672, 1610, 1436, 1406, 1377, 1314, 1282, 1244, 1191, 1114, 1079, 1037, 1018, 962, 932, 913, 875, 857, 828, 791, 774, 759, 734, 707, 681, 640 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 4.43 (dt, *J* = 11.3, 4.0 Hz, 1H), 3.94 (dt, *J* = 2.9, 11.0 Hz, 1H), 3.92 (s, 3H), 3.63 (d, *J* = 10.2 Hz, 1H), 3.59 (d, *J* = 10.2 Hz, 1H), 2.51 (ddd, *J* = 4.4, 11.3, 14.3 Hz, 1H), 2.35 (dt, *J* = 14.3, 3.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.4, 154.0, 147.4, 130.0, 129.7, 126.0, 92.1, 64.3, 58.0, 52.2, 31.6, 19.5. MS (APCI) *m/z* calc'd for $C_{14}H_{14}Cl_3INO_3$ (M+H): 475.9; found: 475.9. MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{14}Cl_3INO_3$ (M+H): 475.9078; found: 475.9089. *m/z* calc'd for $C_{14}H_{13}Cl_3INNaO_3$ (M+Na): 497.8898; found: 497.8913. This material was determined to be 96% ee by chiral HPLC analysis (ChiralPak AS-H, 10% iPrOH in hexanes, 1 mL/min, 230 nm): t_R (minor) = 8.88 min, t_R (major) = 10.81 min. $[\alpha]_D^{26}$ = +53.4° (c = 0.913, $CHCl_3$).



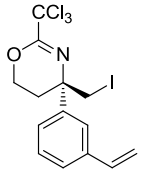
(*S*)-Methyl 3-(4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazin-4-yl)benzoate (2g): IR (thin film) 2952, 1720, 1673, 1605, 1586, 1440, 1288, 1256, 1193, 1137, 1113, 1087, 1038, 985, 960, 910, 887, 828, 793, 757, 734, 699, 683, 663, 649, 630 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (t, *J* = 1.8 Hz, 1H), 7.99 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.60 (ddd, *J* = 1.4, 1.8, 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 4.43 (ddd, *J* = 3.7, 4.6, 11.0 Hz, 1H), 3.95 (dt, *J* = 3.2, 11.4 Hz, 1H), 3.92 (s, 3H), 3.64 (d, *J* = 10.3 Hz, 1H), 3.61 (d, *J* = 10.3 Hz, 1H), 2.53 (ddd, *J* = 4.6, 11.4, 14.2 Hz, 1H), 2.38 (dt, *J* = 14.2, 3.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.6, 154.1, 143.0, 131.0, 130.7, 129.0, 129.0, 126.6, 92.1, 64.4, 57.8, 52.3, 31.5, 19.9. MS (APCI) *m/z* calc'd for $C_{14}H_{14}Cl_3INO_3$ (M+H): 475.9; found: 475.9. MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{14}Cl_3INO_3$ (M+H): 475.9078; found: 475.9093. *m/z* calc'd for $C_{14}H_{13}Cl_3INNaO_3$ (M+Na): 497.8898; found: 497.8913. This material was determined to be 90% ee by chiral HPLC analysis (ChiralPak AS-H, 4% iPrOH in hexanes, 1 mL/min, 254 nm): t_R (minor) = 10.25 min, t_R (major) = 11.10 min. $[\alpha]_D^{26}$ = +31.8° (c = 1.08, $CHCl_3$).



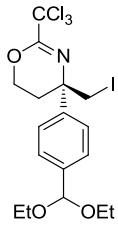
(*S*)-1-(4-(4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4H-1,3-oxazin-4-yl)phenyl)ethanone (2h): IR (thin film) 2976, 1766, 1678, 1606, 1404, 1358, 1267, 1244, 1119, 828, 794, 685 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-7.95 (m, 2H), 7.55-7.46 (m, 2H), 4.52-4.39 (m, 1H), 4.01-3.91 (m, 1H), 3.62 (q, *J* = 10.2 Hz, 2H), 2.63 (s, 3H), 2.53 (ddd, *J* = 14.3, 11.3, 4.5 Hz, 1H), 2.38 (dt, *J* = 14.2, 3.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 197.6, 154.2, 147.8, 136.7, 129.0, 126.4, 92.2, 64.5, 58.1, 31.8, 26.8, 19.5. MS (APCI) *m/z* calc'd for $C_{14}H_{14}Cl_3INO_2$ (M+H): 459.9129; found: 459.9130. *m/z* calc'd for $C_{14}H_{13}Cl_3INNaO_2$ (M+Na): 481.8949; found: 481.8955. This material was determined to be 92% ee by chiral HPLC analysis (ChiralPak AS-H, 10% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 17.61 min, t_R (major) = 21.04 min. $[\alpha]_D^{26}$ = +51.2° (c = 1.03, $CHCl_3$).



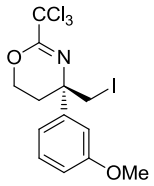
(*S*)-4-([1,1'-Biphenyl]-3-yl)-4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2i): IR (thin film) 3059, 3030, 2955, 2899, 1674, 1597, 1479, 1412, 1377, 1337, 1242, 1186, 1165, 1138, 1078, 1036, 924, 882, 826, 791, 756, 733, 704, 673, 644, 615 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.57 (m, 3H), 7.57-7.53 (m, 1H), 7.49-7.43 (m, 3H), 7.40-7.36 (m, 1H), 7.36-7.33 (m, 1H), 4.44 (dt, *J* = 10.7, 3.8 Hz, 1H), 4.02 (dt, *J* = 11.2, 2.9 Hz, 1H), 3.71 (d, *J* = 10.3 Hz, 1H), 3.68 (d, *J* = 10.3 Hz, 1H), 2.54 (ddd, *J* = 4.9, 12.2, 14.2 Hz, 1H), 2.38 (dt, *J* = 14.2, 2.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 153.8, 143.0, 141.7, 140.7, 129.3, 128.9, 127.6, 127.1, 126.6, 124.7, 124.7, 92.2, 64.5, 58.0, 31.7, 20.5. MS (APCI) *m/z* calc'd for $C_{18}H_{16}Cl_3INO$ (M+H): 493.9; found: 493.9. MS (ESI-TOF) *m/z* calc'd for $C_{18}H_{16}Cl_3INO$ (M+H): 493.9354; found: 493.9337. *m/z* calc'd for $C_{18}H_{15}Cl_3INNaO$ (M+Na): 515.9171; found: 515.9156. This material was determined to be 86% ee by chiral HPLC analysis (ChiralPak AS-H, 2% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 8.44 min, t_R (major) = 9.31 min. $[\alpha]_D^{26}$ (86% ee) = +47.9° (c = 1.03, $CHCl_3$). Crystals suitable for X-ray diffraction were obtained from hexanes (99% ee).



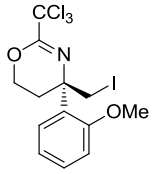
(*S*)-4-(Iodomethyl)-2-(trichloromethyl)-4-(3-vinylphenyl)-5,6-dihydro-4*H*-1,3-oxazine (2j): IR (thin film) 2959, 2924, 2853, 1676, 1246, 1038, 793, 756, 700, 673 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.20 (m, 5H), 6.71 (dd, *J* = 10.7, 17.6 Hz, 1H), 5.76 (d, *J* =17.6 Hz, 1H), 5.28 (d, *J* = 10.7 Hz, 1H), 4.41 (dt, *J* = 10.7, 3.9 Hz, 1H), 3.95 (dt, *J* = 2.9, 11.2 Hz, 1H), 3.67 (d, *J* = 10.3 Hz, 1H), 3.63 (d, *J* = 10.3 Hz, 1H), 2.51 (ddd, *J* = 4.9, 12.2, 14.2 Hz, 1H), 2.31 (dt, *J* = 14.2, 2.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 153.8, 142.7, 138.1, 136.5, 129.1, 125.7, 125.1, 123.9, 114.6, 92.2, 64.5, 57.9, 31.8, 20.4. MS (APCI) *m/z* calc'd for $C_{14}H_{14}Cl_3INO$ (M+H): 443.9; found: 443.9. MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{14}Cl_3INO$ (M+H): 443.9186; found: 443.9198. This material was determined to be 94% ee by chiral HPLC analysis (ChiralCel OD-H, 0.1% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 20.83 min, t_R (major) = 21.93 min. $[\alpha]_D^{25}$ = +44.5° (c = 0.933, $CHCl_3$).



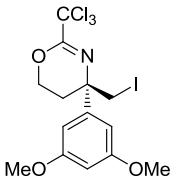
(*S*)-4-(4-(Diethoxymethyl)phenyl)-4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2k): IR (thin film) 2975, 2882, 1725, 1681, 1443, 1371, 1339, 1292, 1265, 1213, 1187, 1140, 1112, 1055, 1018, 957, 918, 875, 829, 793, 760, 736, 709, 682, 632 cm^{-1}. ^1H NMR (500 MHz, d_6-benzene) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 5.42 (s, 1H), 3.58-3.46 (m, 3H), 3.41-3.33 (m, 2H), 3.31 (dt, *J* = 11.4, 3.2 Hz, 1H), 3.28 (d, *J* = 9.8 Hz, 1H), 3.09 (d, *J* = 9.8 Hz, 1H), 1.88 (ddd, *J* = 4.6, 11.9, 14.2 Hz, 1H), 1.41 (dt, *J* = 14.2, 2.7 Hz, 1H), 1.11 (dt, *J* = 1.8, 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, d_6-benzene) δ 154.0, 142.7, 139.5, 127.5, 125.9, 101.2, 93.1, 64.3, 60.9, 60.8, 58.0, 31.4, 20.6, 15.4. MS (APCI) *m/z* calc'd for $C_{17}H_{22}Cl_3INO_3$ (M+H): 520.0; found: 520.0. MS (ESI-TOF) *m/z* calc'd for $C_{17}H_{22}Cl_3INO_3$ (M+H): 519.9710; found: 519.9689. This material was determined to be 90% ee by chiral HPLC analysis (ChiralPak AD-H, 3% iPrOH in hexanes, 1 mL/min, 254 nm): t_R (minor) = 17.85 min, t_R (major) = 19.18 min. $[\alpha]_D^{26}$ = +45.1° (c = 1.17, $CHCl_3$).



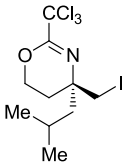
(*S*)-4-(Iodomethyl)-4-(3-methoxyphenyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2l): IR (thin film) 3004, 2955, 2899, 2835, 1676, 1598, 1582, 1486, 1463, 1449, 1433, 1335, 1313, 1291, 1271, 1248, 1237, 1201, 1187, 1159, 1138, 1120, 1040, 996, 960, 938, 910, 891, 829, 791, 756, 731, 701, 673, 646, 621 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.1 Hz, 1H), 6.94-6.89 (m, 2H), 6.87-6.82 (m, 1H), 4.41 (ddd, *J* = 2.9, 4.8, 11.0 Hz, 1H), 3.96 (ddd, *J* = 2.9, 11.0, 11.7 Hz, 1H), 3.81 (s, 3H), 3.66 (d, *J* = 9.9 Hz, 1H), 3.61 (d, *J* = 9.9 Hz, 1H), 2.48 (ddd, *J* = 4.8, 12.1, 14.3 Hz, 1H), 2.29 (dt, *J* = 14.3, 2.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.8, 153.8, 144.0, 129.8, 117.7, 113.0, 112.3, 92.2, 64.5, 57.9, 55.2, 31.8, 20.4. MS (APCI) *m/z* calc'd for $C_{13}H_{14}Cl_3INO_2$ (M+H): 447.9; found 447.9. MS (ESI-TOF) *m/z* calc'd for $C_{13}H_{14}Cl_3INO_2$ (M+H): 447.9129; found: 447.9137. *m/z* calc'd for $C_{13}H_{13}Cl_3INNaO_2$ (M+Na): 469.8949; found: 469.8952. This material was determined to be 90% ee by chiral HPLC analysis (ChiralPak AD-H, 3% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 9.35 min, t_R (major) = 11.51 min. $[\alpha]_D^{25}$ = +46.1° (c = 0.926, $CHCl_3$). Crystals suitable for X-ray diffraction were obtained from hexanes (>99% ee).



(*S*)-4-(Iodomethyl)-4-(2-methoxyphenyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2m): IR (thin film) 2966, 2837, 1677, 1597, 1582, 1486, 1464, 1436, 1377, 1287, 1244, 1204, 1183, 1165, 1118, 1071, 1025, 912, 884, 829, 792, 755, 735, 699, 671, 629 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (dt, *J* = 1.8, 7.8 Hz, 1H), 7.17 (dd, *J* = 1.8, 7.8 Hz, 1H), 6.96 (dt, *J* = 7.8, 0.9 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 4.35 (ddd, *J* = 2.7, 4.6, 11.0 Hz, 1H), 4.02 (d, *J* = 9.6 Hz, 1H), 3.91 (d, *J* = 9.6 Hz, 1H), 3.88 (s, 3H), 3.84 (ddd, *J* = 2.7, 11.0, 12.4 Hz, 1H), 2.78 (dt, *J* = 14.2, 2.7 Hz, 1H), 2.32 (ddd, *J* = 4.6, 12.4, 14.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.7, 153.7, 130.0, 129.3, 129.2, 121.0, 111.5, 92.4, 65.1, 58.1, 55.2, 29.5, 19.3. MS (APCI) *m/z* calc'd for $C_{13}H_{14}Cl_3INO_2$ (M+H): 447.9; found: 447.9. MS (ESI-TOF) *m/z* calc'd for $C_{13}H_{14}Cl_3INO_2$ (M+H): 447.9129; found: 447.9141. *m/z* calc'd for $C_{13}H_{13}Cl_3INNaO_2$ (M+Na): 469.8949; found: 469.8951. This material was determined to be 70% ee by chiral HPLC analysis (ChiralCel OD-H, 0.1% iPrOH in hexanes, 1 mL/min, 230 nm): t_R (minor) = 16.35 min, t_R (major) = 17.39 min. $[\alpha]_D^{26}$ = –6.2° (c = 1.11, $CHCl_3$).

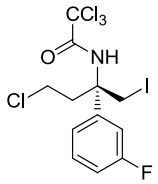


(*S*)-4-(3,5-Dimethoxyphenyl)-4-(iodomethyl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2n): IR (thin film) 3001, 2962, 2899, 2837, 1676, 1594, 1457, 1424, 1339, 1314, 1297, 1268, 1251, 1205, 1156, 1067, 1046, 943, 911, 894, 828, 792, 754, 734, 699, 683, 648, 621 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (d, *J* = 2.2 Hz, 2H), 6.39 (t, *J* = 2.2 Hz, 1H), 4.40 (ddd, *J* = 2.9, 4.8, 11.0 Hz, 1H), 3.97 (dt, *J* = 2.9, 11.7 Hz, 1H), 3.78 (s, 6H), 3.65 (d, *J* = 10.2 Hz, 1H), 3.60 (d, *J* = 10.2 Hz, 1H), 2.46 (ddd, *J* = 4.4, 12.1, 13.9 Hz, 1H), 2.26 (dt, *J* = 2.9, 13.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.9, 153.7, 144.7, 104.2, 99.3, 92.2, 64.6, 58.0, 55.3, 31.8, 20.3. MS (APCI) *m/z* calc'd for $C_{14}H_{16}Cl_3INO$ (M+H): 477.9; found: 477.9. MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{16}Cl_3INO_3$ (M+H): 477.9235; found: 477.9234. *m/z* calc'd for $C_{14}H_{15}Cl_3INNaO_3$ (M+Na): 499.9054; found: 499.9054. This material was determined to be 90% ee by chiral HPLC analysis (ChiralCel OD-H, 2% iPrOH in hexanes, 1 mL/min, 230 nm): t_R (minor) = 13.90 min, t_R (major) = 15.39 min. $[\alpha]_D^{25}$ = +49.4° (c = 1.07, $CHCl_3$).

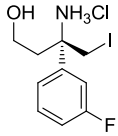


(*S*)-4-(Iodomethyl)-4-isobutyl-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (2o): IR (thin film) 2955, 2926, 2868, 1667, 1468, 1435, 1366, 1346, 1240, 1206, 1184, 1173, 1136, 1082, 1053, 1028, 991, 955, 937, 893, 826, 789, 762, 741, 677, 629 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.40-4.30 (m, 2H), 3.47 (d, *J* = 10.3 Hz, 1H), 3.23 (d, *J* = 10.3 Hz, 1H), 2.04 (ddd, *J* = 5.5, 7.8, 14.7 Hz, 1H), 1.90-1.80 (m, 2H), 1.70 (dd, *J* = 4.6, 14.2 Hz, 1H), 1.51 (dd, *J* = 7.3, 14.2 Hz, 1H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 152.5, 92.3, 64.0, 54.4, 48.4, 30.8, 24.7, 24.4, 24.0, 16.7. MS (APCI) *m/z* calc'd for $C_{10}H_{16}Cl_3INO$ (M+H): 397.9; found: 397.9. MS (ESI-TOF) *m/z* calc'd for $C_{10}H_{16}Cl_3INO$ (M+H): 397.9337; found: 397.9347. This material was determined to be 73% ee by chiral HPLC analysis (ChiralPak AD-H, 0.02% iPrOH in hexanes, 1 mL/min, 200 nm): t_R (minor) = 5.96 min, t_R (major) = 6.95 min. $[\alpha]_D^{26}$ = +14.7° (c = 1.06, $CHCl_3$).

5. Product derivatization



(*S*)-2,2,2-Trichloro-N-(4-chloro-2-(3-fluorophenyl)-1-iodobutan-2-yl)acetamide (5c): To a solution of **2c** (21.4 mg, 0.049 mmol) in CH_2Cl_2 (327 μL, 0.15 M) was added HCl (4 M in dioxane, 49 μL, 0.196 mmol). The resulting solution was stirred at rt for 12 h, concentrated *in vacuo*, and purified by column chromatography (eluent: 5% EtOAc/hexanes, v/v) to give 20.7 mg (89%) of the desired product as a white solid. IR (thin film) 1718, 1614, 1591, 1519, 1440, 1279, 1248, 1217, 910, 823, 785, 734, 685, 649 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.42 (td, *J* = 8.1, 6.0 Hz, 1H), 7.11 (ddd, *J* = 7.9, 1.9, 0.8 Hz, 1H), 7.08 (ddd, *J* = 8.3, 2.4, 0.7 Hz, 1H), 7.03 (dt, *J* = 10.2, 2.1 Hz, 1H), 4.29 (d, *J* = 10.7 Hz, 1H), 4.01 (d, *J* = 10.7 Hz, 1H), 3.45 (ddd, *J* = 11.6, 6.9, 5.4 Hz, 1H), 3.27 (ddd, *J* = 11.4, 8.1, 6.6 Hz, 1H), 2.88 (ddd, *J* = 14.9, 8.1, 6.9 Hz, 1H), 2.50 (ddd, *J* = 14.9, 6.5, 5.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.3 (d, *J* = 247.9 Hz), 160.8, 140.7 (d, *J* = 6.4 Hz), 131.1 (d, *J* = 8.3 Hz), 121.0 (d, *J* = 3.0 Hz), 115.7 (d, *J* = 21.0 Hz), 113.0 (d, *J* = 23.7 Hz), 92.7, 62.0, 42.4, 39.5, 14.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –110.9 (m). MS (ESI-TOF) *m/z* calc'd for $C_{12}H_{12}Cl_4FINO$ (M+H): 471.8702; found: 471.8696. This material was determined to be 98% ee by chiral HPLC analysis (ChiralCel OD-H, 3% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 25.49 min, t_R (major) = 21.01 min. $[\alpha]_D^{26}$ (98% ee) = +7.8º (c = 0.946, $CHCl_3$). Crystals suitable for X-ray diffraction were obtained from hexanes.

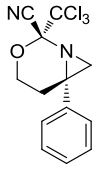


(*S*)-3-Amino-3-(3-fluorophenyl)-4-iodobutan-1-ol hydrochloride salt (6c): Prepared by a modified literature procedure.[14] To a solution of **2c** (25 mg, 0.057 mmol) in MeOH (286 μL, 0.2 M) was added HCl (2 M in H_2O, 58 μL, 0.115 mmol). The reaction mixture was stirred at ambient temperature for 13 h, and concentrated *in vacuo* to afford 19.5 mg (99%) of the desired product as a yellow oil. Note that the generated trichloroacetic acid may be removed by azeotropic distillation.[15] IR (thin film) 3390, 1617, 1594, 1496, 1446, 1229, 1117, 1058, 976, 866, 844, 788, 682 cm^{-1}. ^1H NMR (500 MHz, CD_3OD) δ 7.54 (td, *J* = 8.2, 6.0 Hz, 1H), 7.28-7.23 (m, 2H), 7.20 (tdd, *J* = 8.3, 2.3, 0.7 Hz, 1H), 3.96 (d, *J* = 11.7 Hz, 1H), 3.88 (d, *J* = 11.7 Hz, 1H), 3.71 (dt, *J* = 11.0, 5.2 Hz, 1H), 3.42 (ddd, *J* = 10.9, 8.8, 4.4 Hz, 1H), 2.42 (ddd,

[14] Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *J. Chem. Soc. Chem. Commun.* **1982**, 1308-1309.

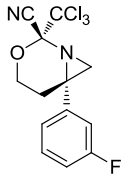
[15] Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S.; Tomasini, C. *J. Chem. Soc. Perkin Trans. 1* **1986**, 1339-1344.

J = 14.8, 8.8, 5.0 Hz, 1H), 2.33 (dt, *J* = 15.0, 4.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 164.5 (d, *J* = 246.0 Hz), 141.6 (d, *J* = 7.3 Hz), 132.3 (d, *J* = 8.5 Hz), 122.3 (d, *J* = 3.0 Hz), 116.8 (d, *J* = 21.1 Hz), 113.9 (d, *J* = 24.3 Hz), 63.1, 59.1, 40.7, 12.8. ^{19}F NMR (376 MHz, CD_3OD) δ –113.3 (m). MS (ESI-TOF) *m/z* calc'd for $C_{10}H_{14}FINO$ (M–Cl): 310.0099; found: 310.0121. This material was determined to be 98% ee by chiral HPLC analysis of the corresponding trifluoroacetylated derivative.[16] $[\alpha]_D^{23}$ = +4.8º (c = 1.00, CH_3OH).



(2*R*,6*S*)-6-Phenyl-2-(trichloromethyl)-3-oxa-1-azabicyclo[4.1.0]heptane-2-carbonitrile (7a): To a solution of **2a** (25.7 mg, 0.061 mmol) in DMF (307 μL, 0.2 M) was added NaCN (15.1 mg, 0.307 mmol). The reaction mixture was heated to 50 ºC for 18 h, cooled to ambient temperature, and quenched by addition of sat'd $NaHCO_3$ and Et_2O. The aqueous layer was separated and extracted thrice with Et_2O. The combined organic layers were washed five times with water, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by preparative TLC (eluent: 5% EtOAc/hexanes, v/v) to give 15.5 mg (79%) of the desired product as a pale yellow oil that solidifies to afford a white solid. IR (thin film) 1496, 1447, 1384, 1229, 1162, 1115, 1093, 1042, 989, 913, 858, 809, 773, 735, 701 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 4.20 (ddd, *J* = 1.0, 5.9, 12.7 Hz, 1H), 3.81 (dt, *J* = 3.4, 12.7 Hz, 1H), 2.91 (s, 1H), 2.62 (ddd, *J* = 1.4, 3.2, 14.2 Hz, 1H), 2.54 (dt, *J* = 6.0, 13.3 Hz, 1H), 2.36 (s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$); δ 141.0, 128.5, 127.7, 125.4, 114.2, 101.1, 94.2, 59.3, 42.9, 39.0, 25.0. MS (APCI) *m/z* calc'd for $C_{13}H_{12}Cl_3N_2O$ (M+H): 317.0; found: 317.0. MS (ESI-TOF) *m/z* calc'd for $C_{13}H_{12}Cl_3N_2O$ (M+H): 317.0010; found: 316.9997. This material was determined to be 90% ee by chiral HPLC analysis (ChiralPak AS-H, 5% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 25.49 min, t_R (major) = 21.01 min. $[\alpha]_D^{26}$ = +57.5º (c = 0.689, $CHCl_3$). Crystals suitable for X-ray diffraction were obtained from Et_2O/hexanes (>99% ee).

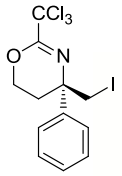
[16] **5c** was treated with an excess of trifluoroacetic anhydride to afford the trifluoroacetylated derivative (containing both trifluoroacetamide and trifluoroacetate functionalities). MS (ESI-TOF) *m/z* calc'd for $C_{14}H_{12}F_7INO_3$ (M+H): 501.9745; found: 501.9734. *m/z* calc'd for $C_{14}H_{11}F_7INNaO_3$ (M+Na): 523.9570; found: 523.9524. This material was determined to be 98% ee by chiral HPLC analysis (ChiralPak AS-H, 10% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 6.78 min, t_R (major) = 6.07 min.

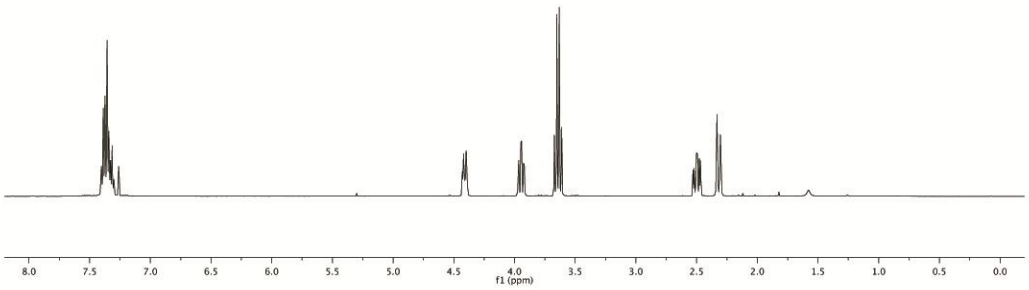


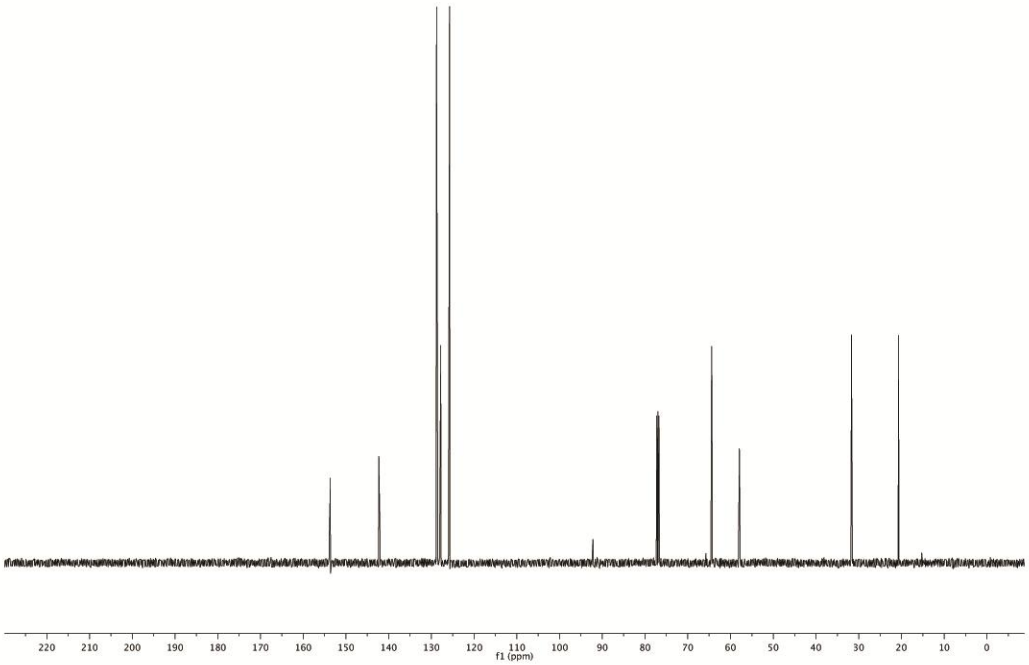
(2*R*,6*S*)-6-(3-fluorophenyl)-2-(trichloromethyl)-3-oxa-1-azabicyclo[4.1.0]heptane-2-carbonitrile (7c): To a solution of **2c** (31.2 mg, 0.071 mmol) in DMF (179 μL, 0.4 M) was added NaCN (17.5 mg, 0.357 mmol). The reaction mixture was heated to 50 ºC for 12 h, cooled to ambient temperature, and quenched by addition of sat'd $NaHCO_3$ and Et_2O. The aqueous layer was separated and extracted thrice with Et_2O. The combined organic layers were washed five times with water, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (eluent: 0-20% EtOAc/hexanes, v/v) to give 20.1 mg (84%) of the desired product as a colorless oil. IR (thin film) 1615, 1615, 1589, 1488, 1445, 1384, 1193, 1154, 1112, 1094, 1044, 911, 809, 735, 706 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (td, *J* = 8.0, 6.0 Hz, 1H), 7.21 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.14 (ddd, *J* = 10.2, 2.5, 1.6 Hz, 1H), 7.00 (tdd, *J* = 8.5, 2.5, 1.0 Hz, 1H), 4.21 (ddd, *J* = 12.6, 5.9, 1.4 Hz, 1H), 3.81 (td, *J* = 12.6, 3.0 Hz, 1H), 2.93 (s, 1H), 2.62 (ddd, *J* = 13.9, 2.8, 1.4 Hz, 1H), 2.53 (ddd, *J* = 14.0, 12.8, 5.9 Hz, 1H), 2.36 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.1 (d, *J* = 246.0 Hz), 143.8 (d, *J* = 7.4 Hz), 130.3 (d, *J* = 8.2 Hz), 121.2 (d, *J* = 3.1 Hz), 114.9 (d, *J* = 21.2 Hz), 114.2, 112.8 (d, *J* = 23.2 Hz), 101.2, 94.2, 59.3, 42.5, 39.2, 24.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ –112.7 (m). MS (ESI-TOF) *m/z* calc'd for $C_{13}H_{11}Cl_3FN_2O$ (M+H): 334.9916; found: 334.9923. This material was determined to be 98% ee by chiral HPLC analysis (ChiralPak AS-H, 5% iPrOH in hexanes, 1 mL/min, 210 nm): t_R (minor) = 11.18 min, t_R (major) = 13.53 min. $[\alpha]_D^{26}$ = +80.9º (c = 0.539, $CHCl_3$).

6. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of iodoamination products

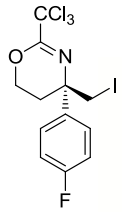
NMR spectra for **2a**

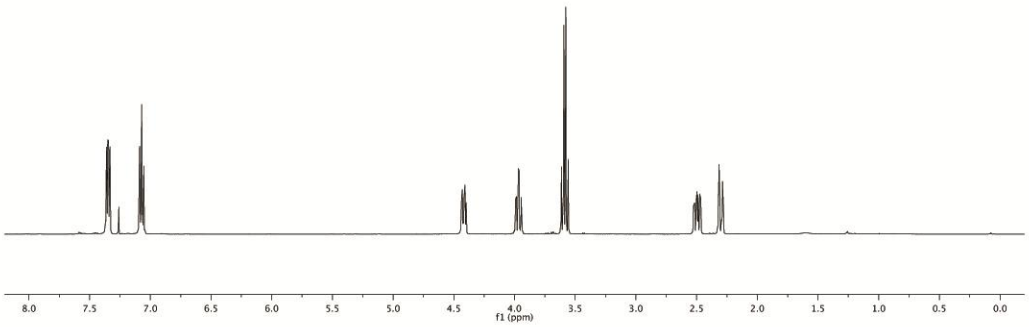


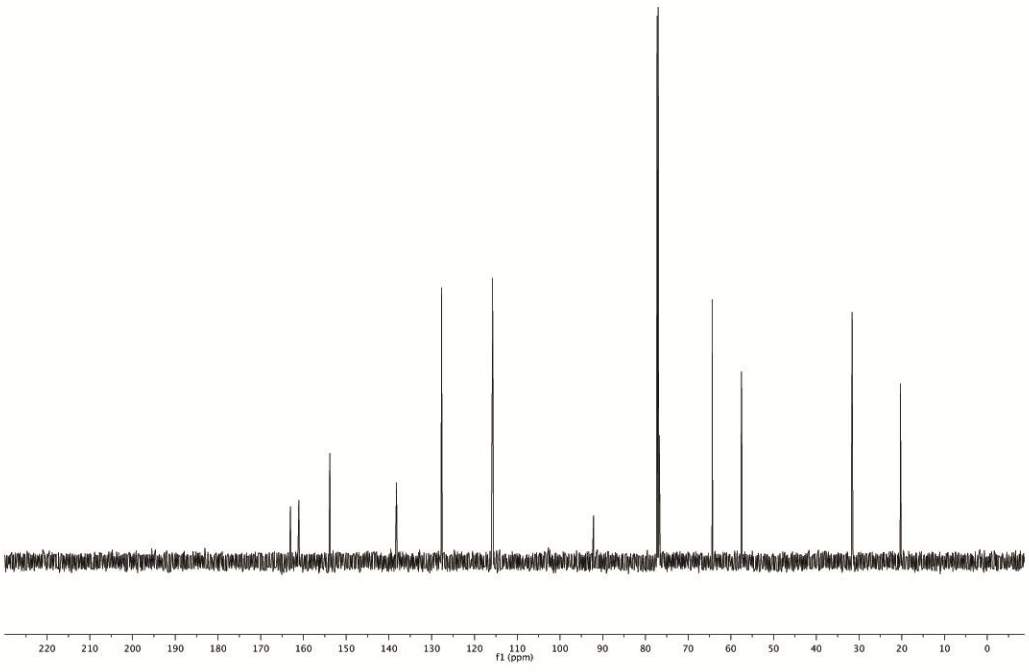




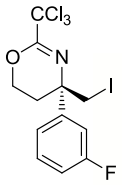
NMR spectra for **2b**

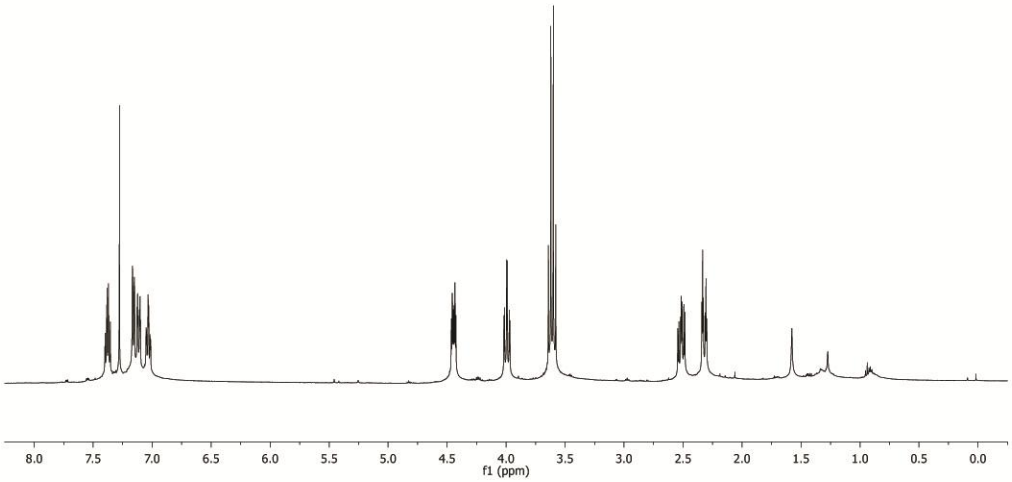


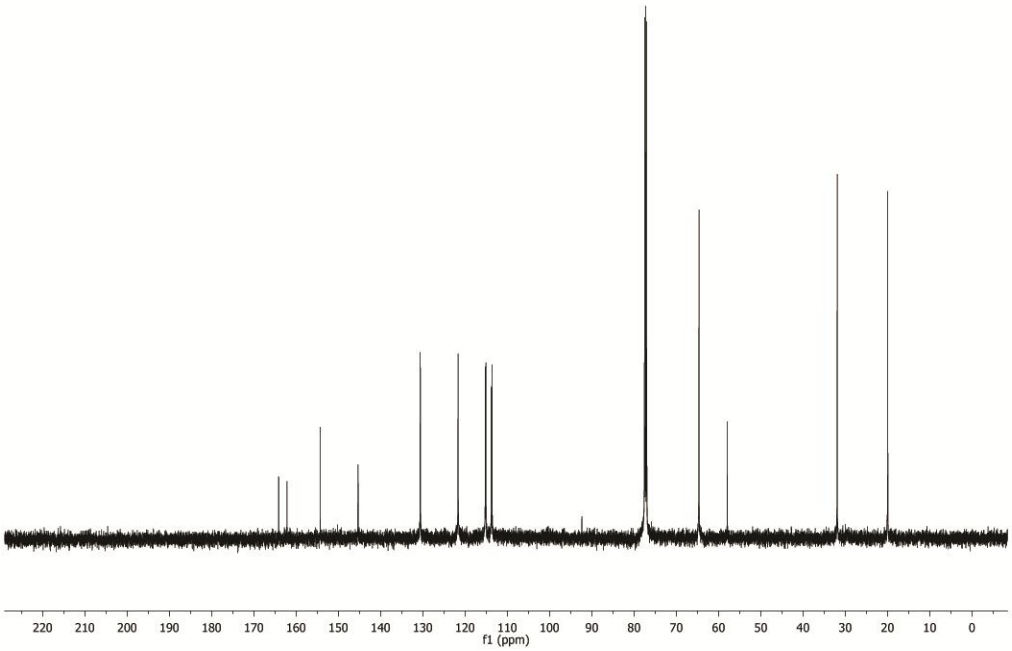




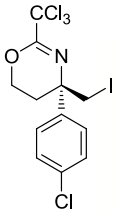
NMR spectra for **2c**

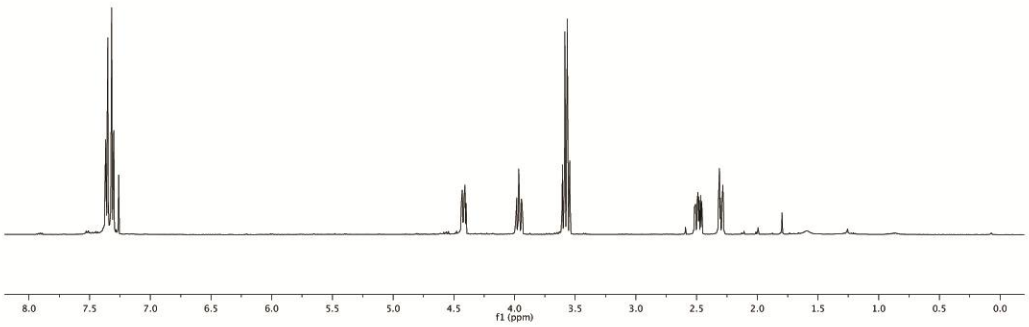


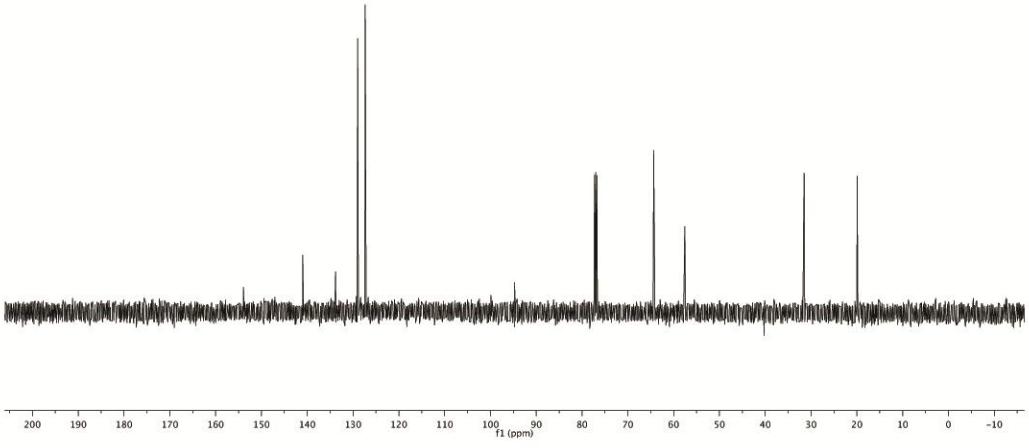




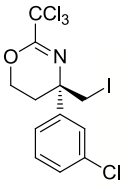
NMR spectra for **2d**

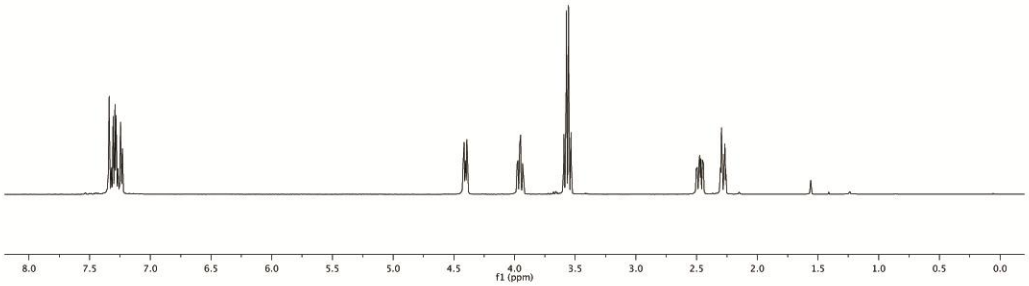


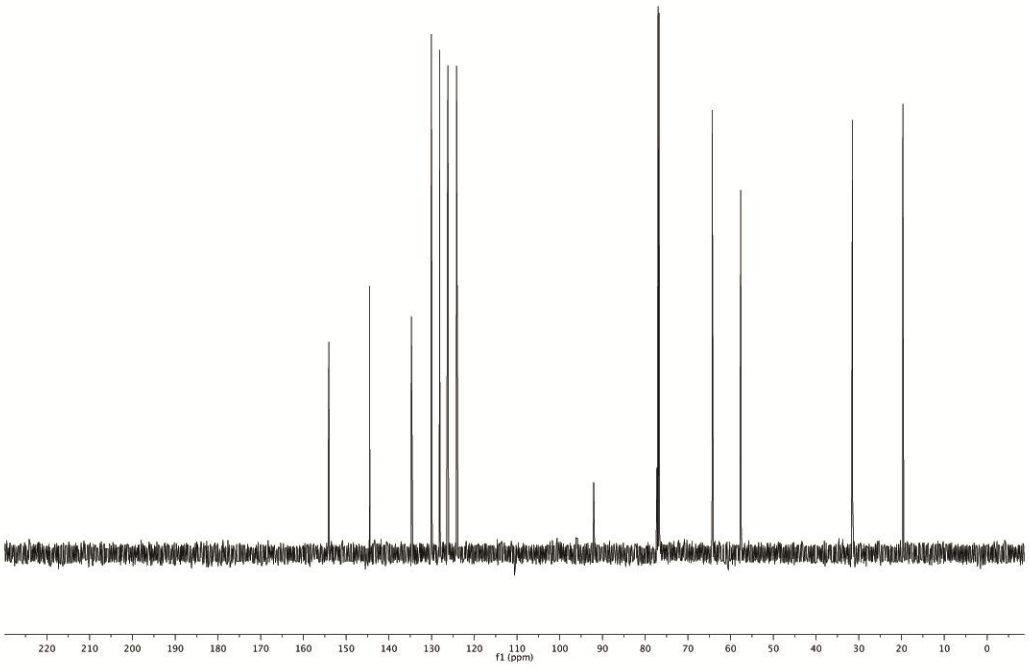




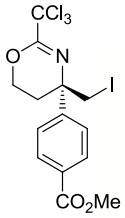
NMR spectra for **2e**

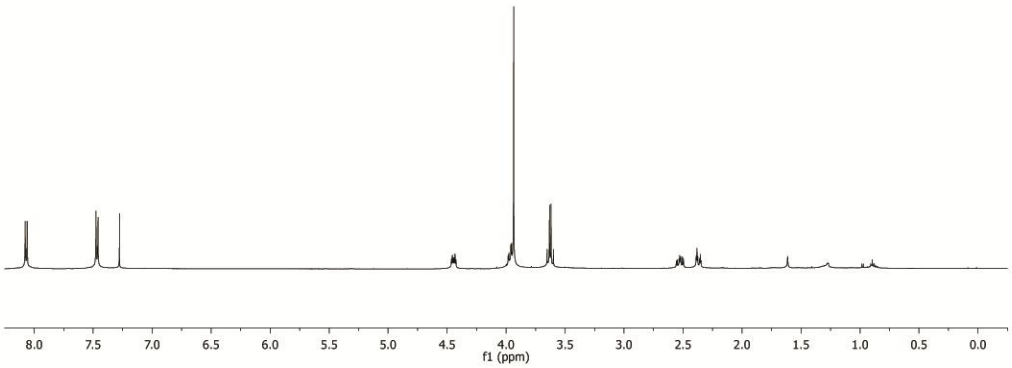


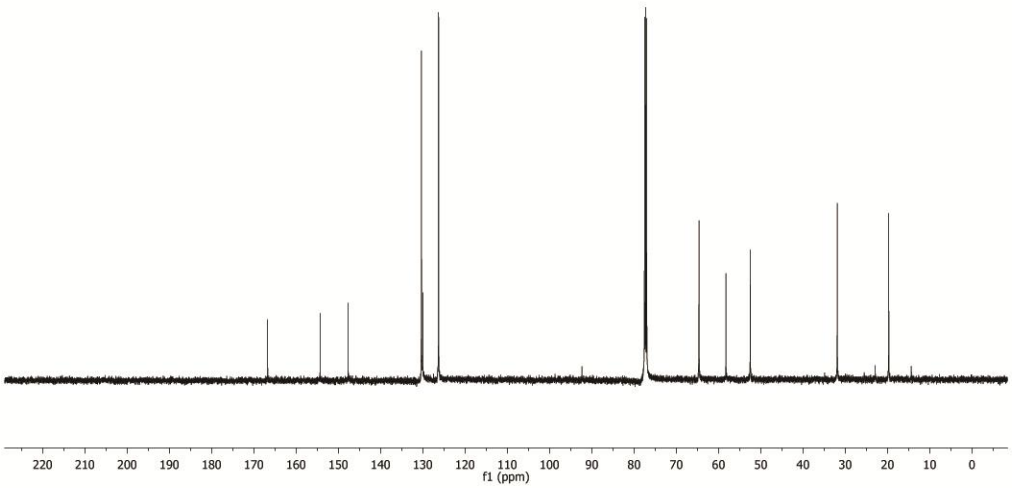




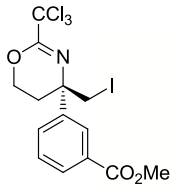
NMR spectra for **2f**

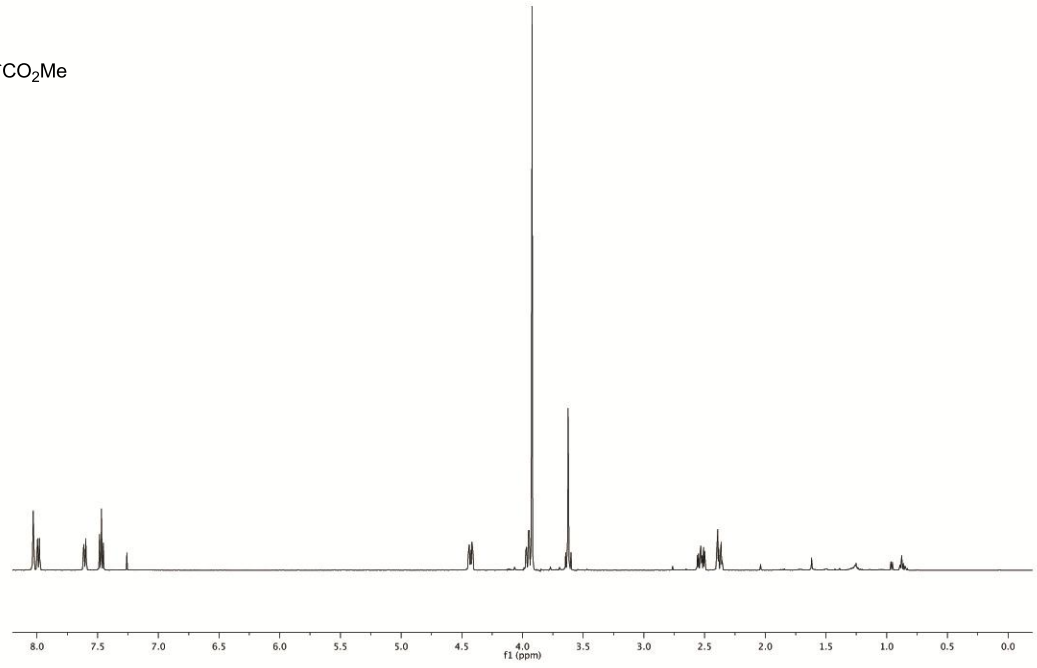


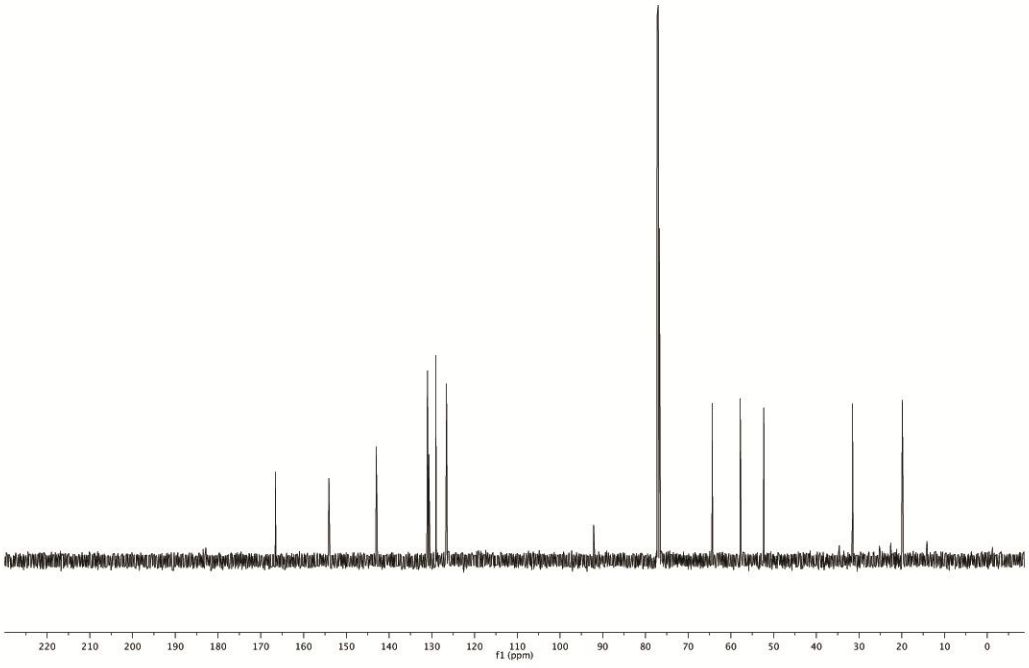




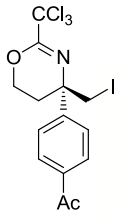
NMR spectra for **2g**

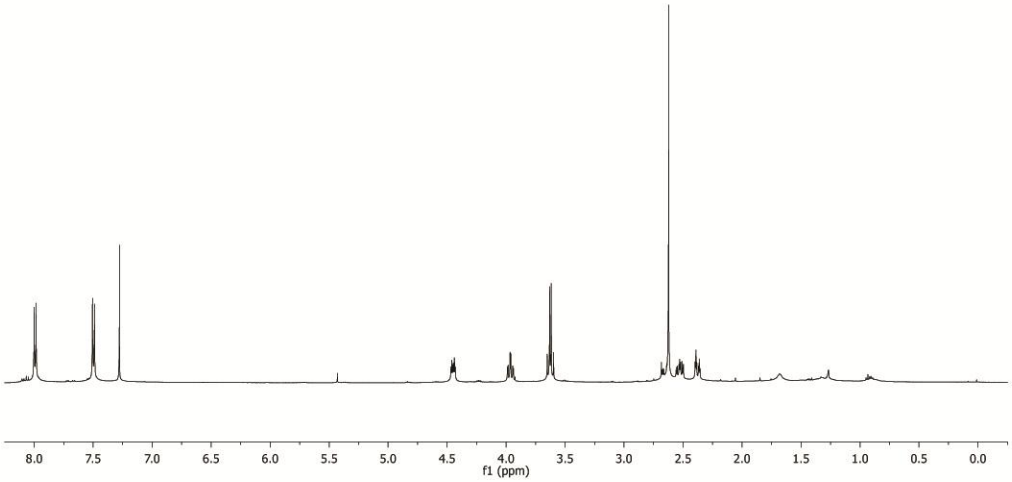


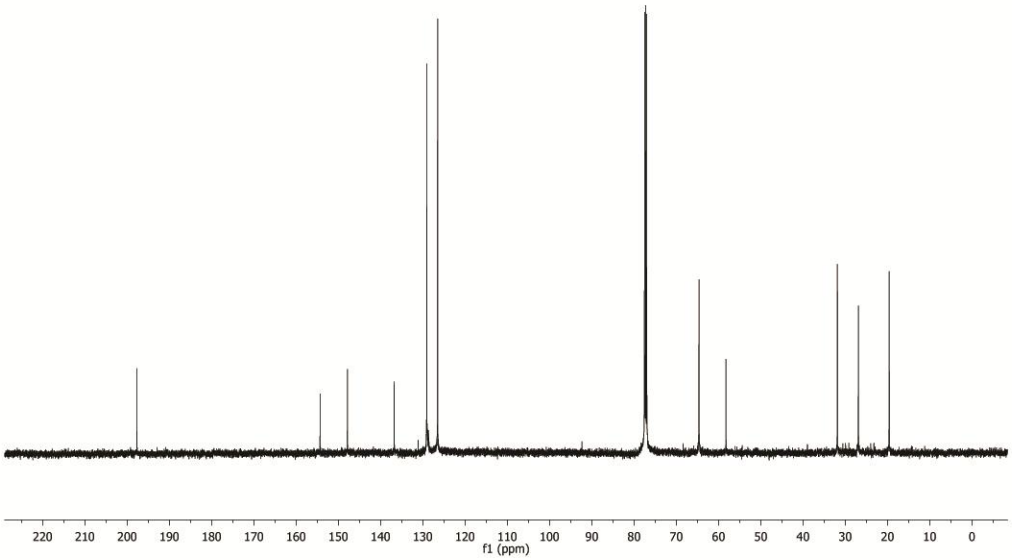




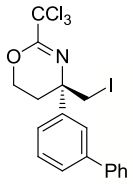
NMR spectra for **2h**

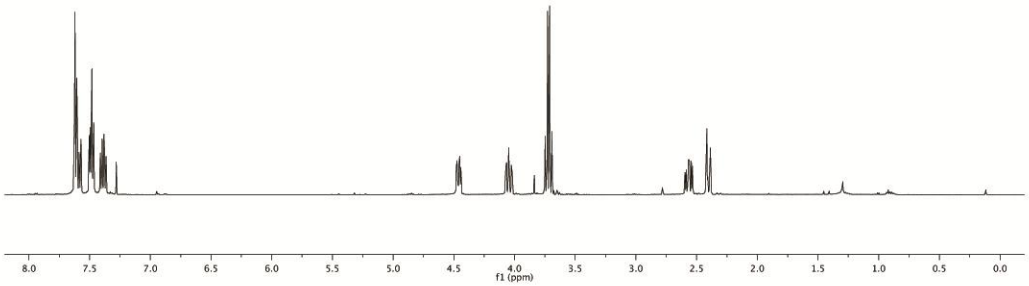


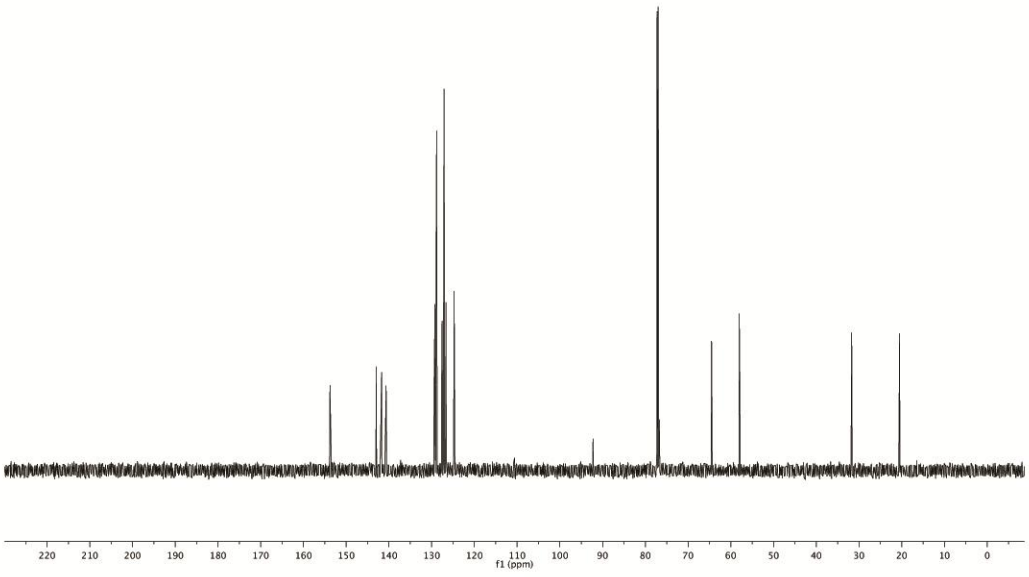




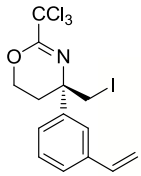
NMR spectra for **2i**

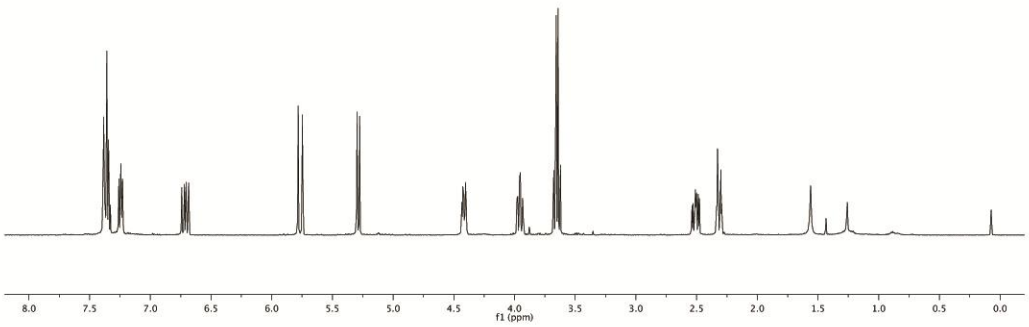


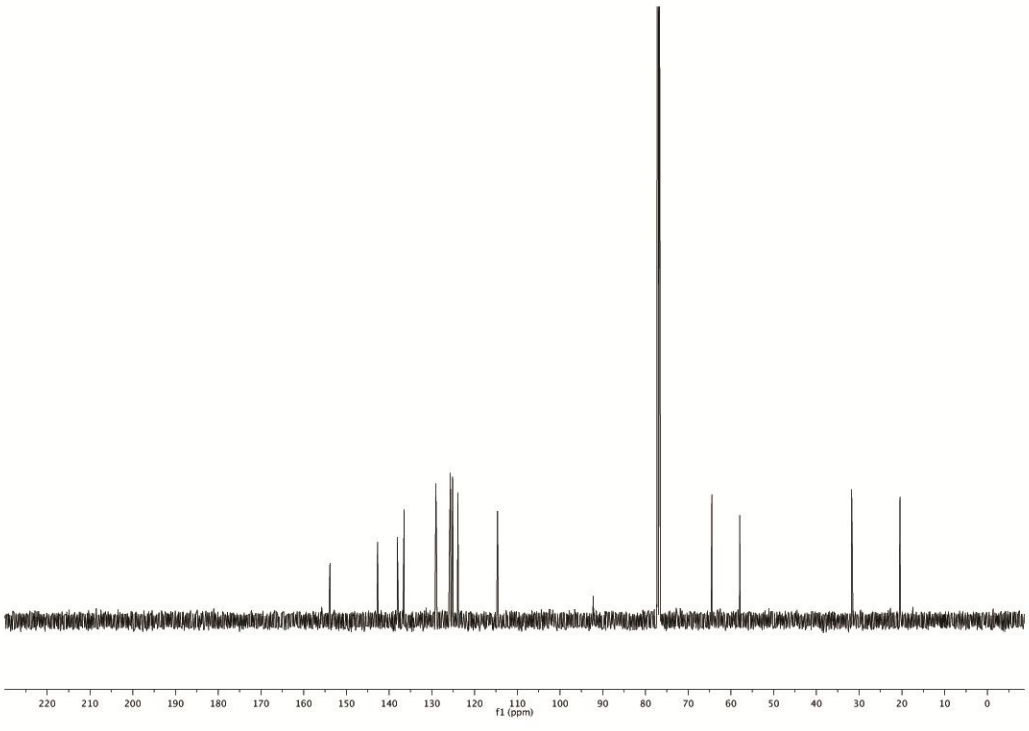




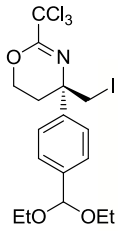
NMR spectra for **2j**

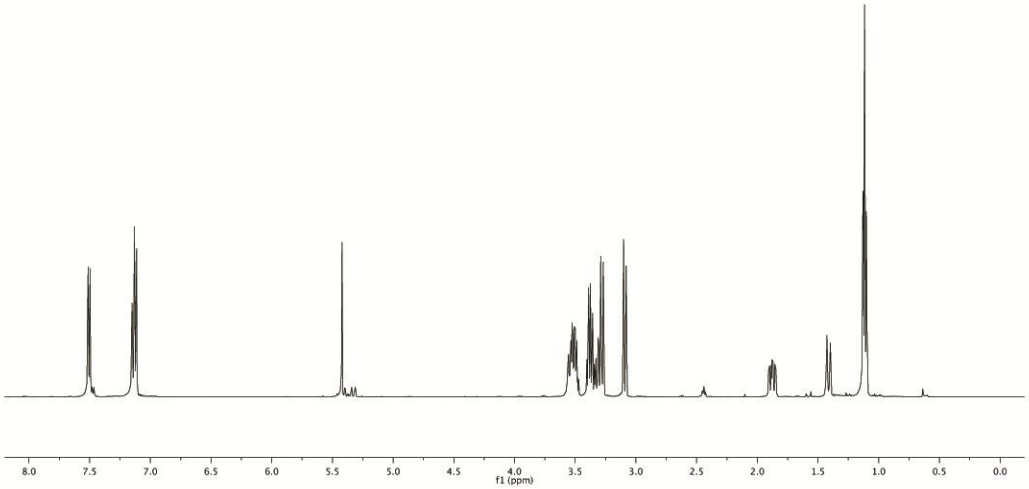


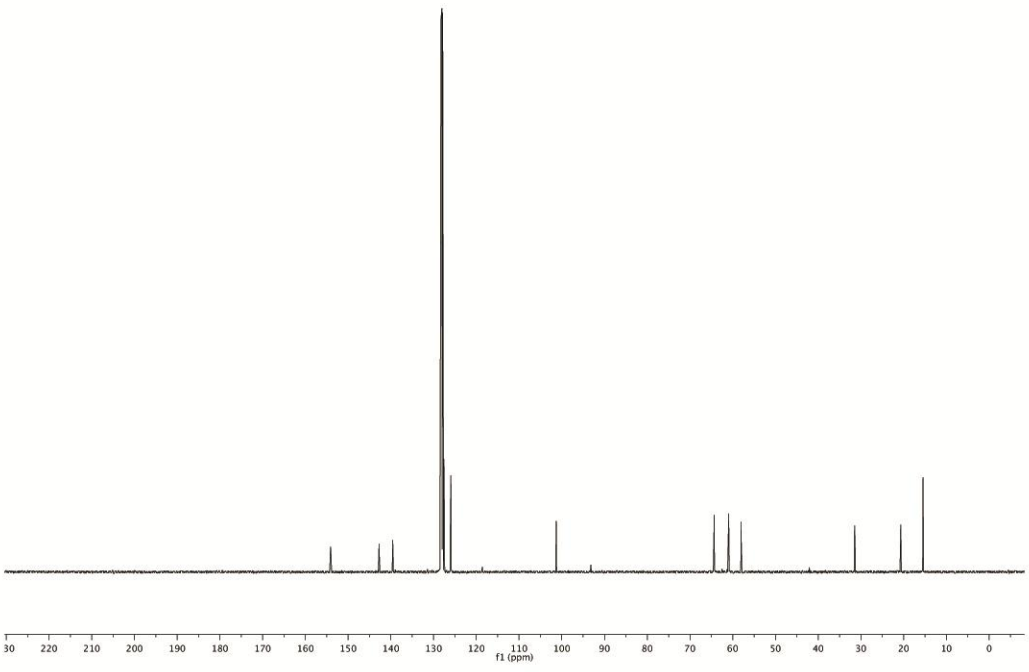




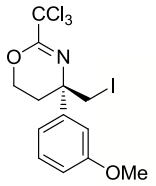
NMR spectra for **2k**

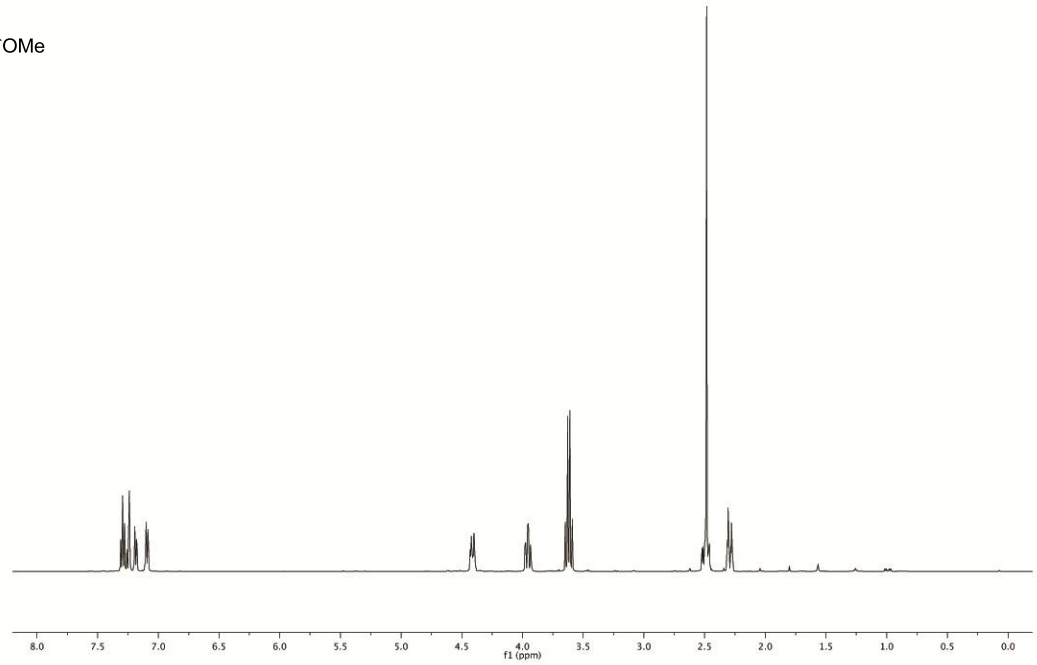


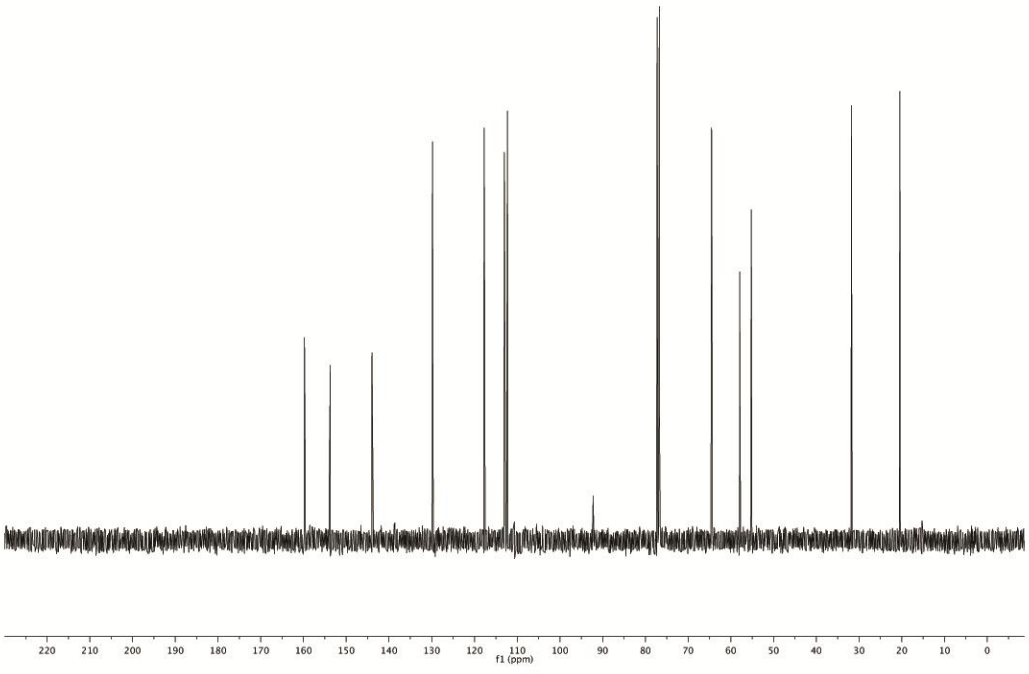




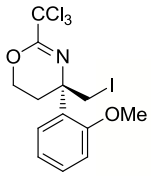
NMR spectra for **2l**

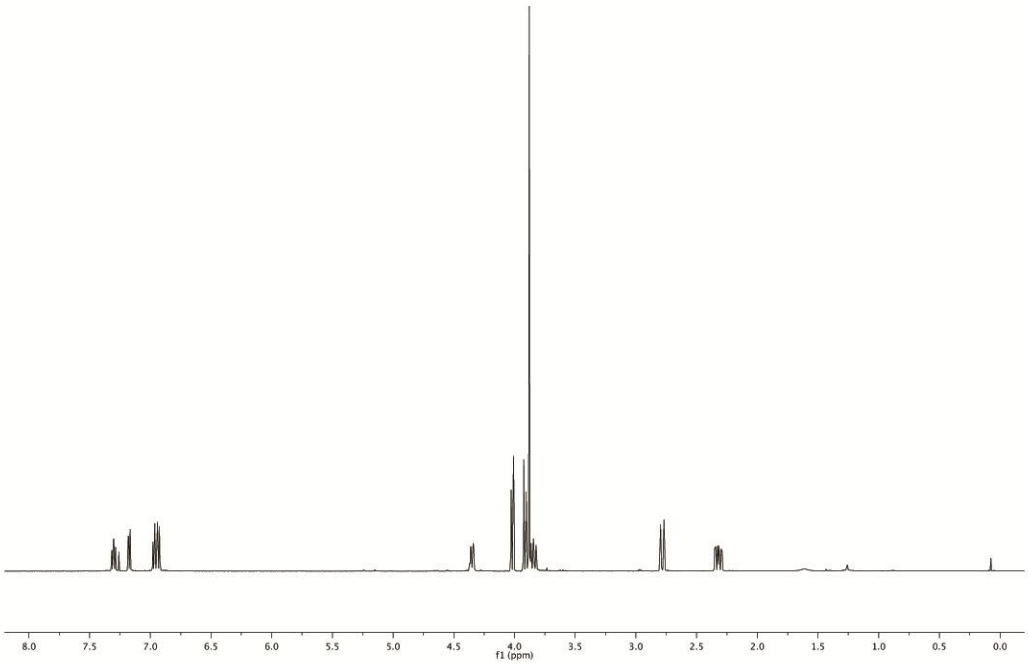


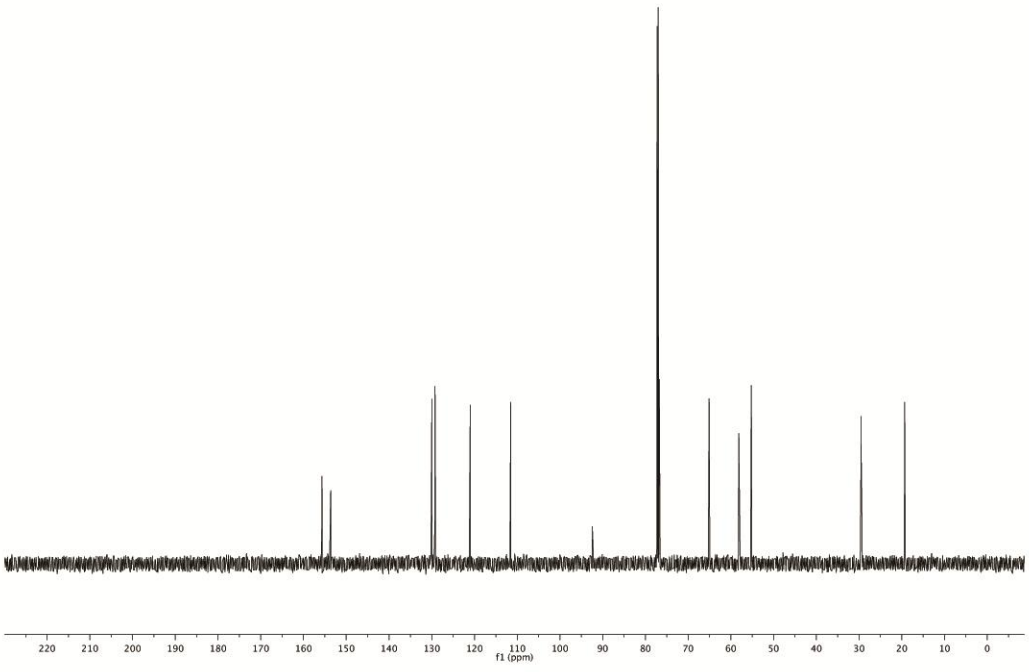




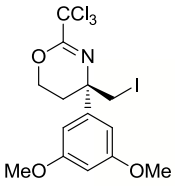
NMR spectra for **2m**

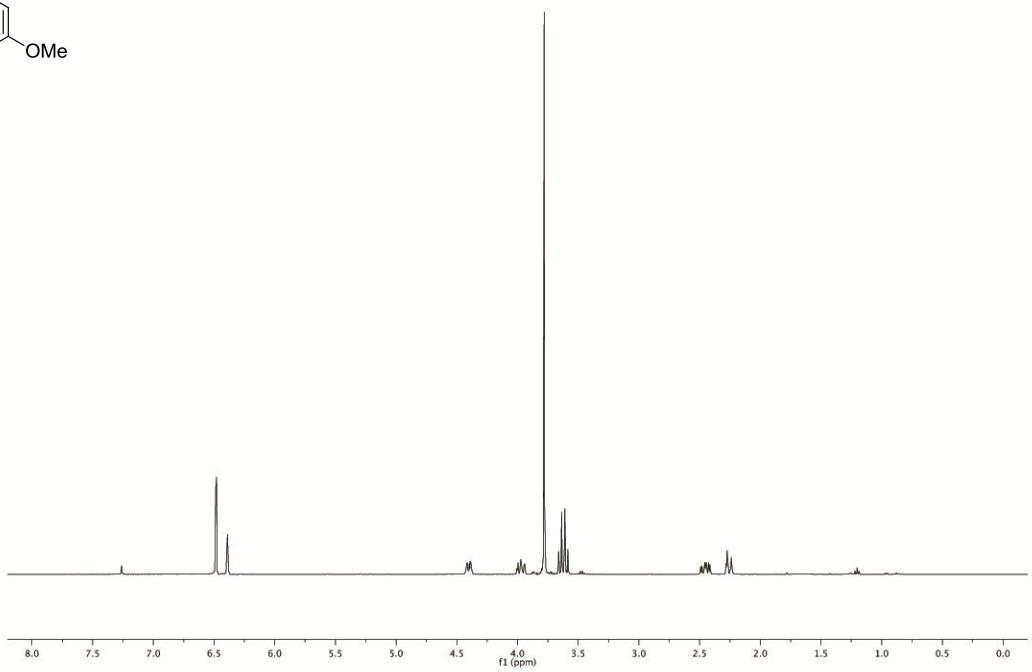


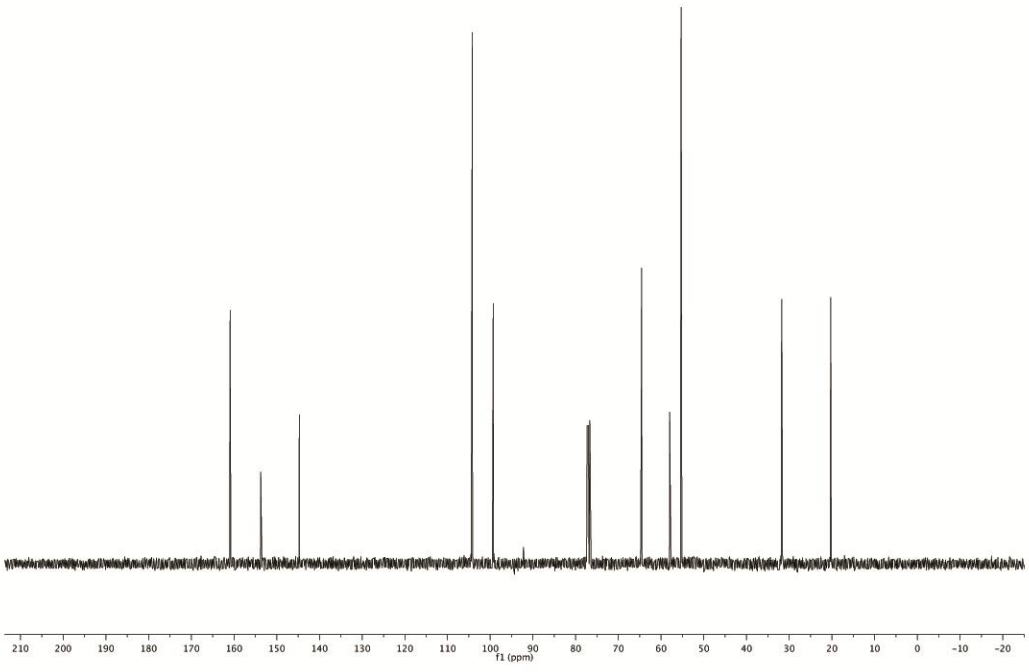




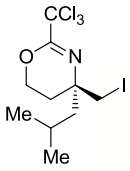
NMR spectra for **2n**

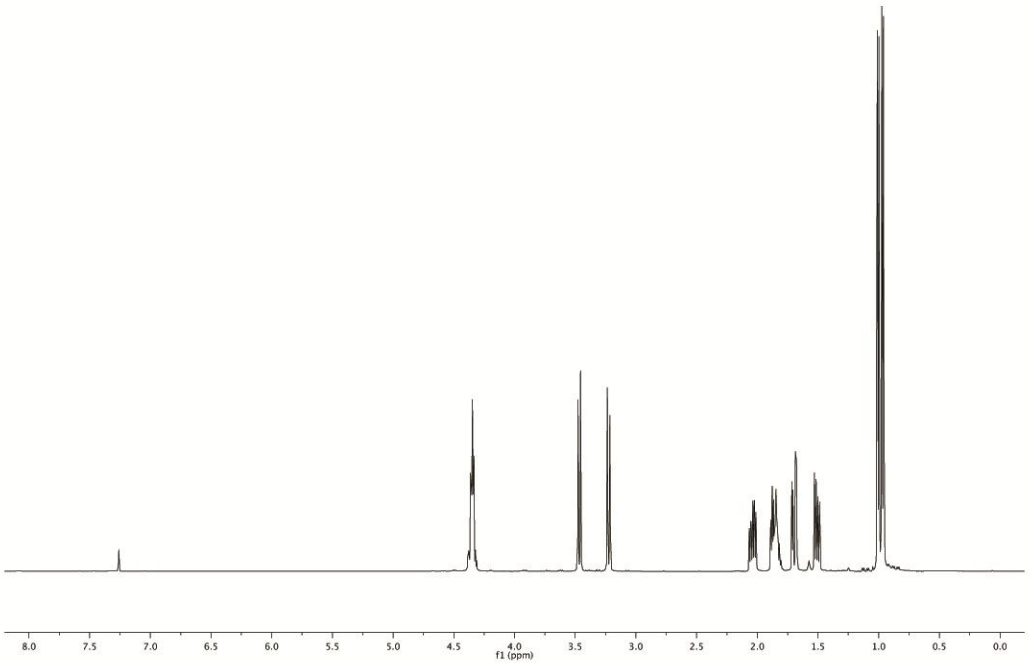


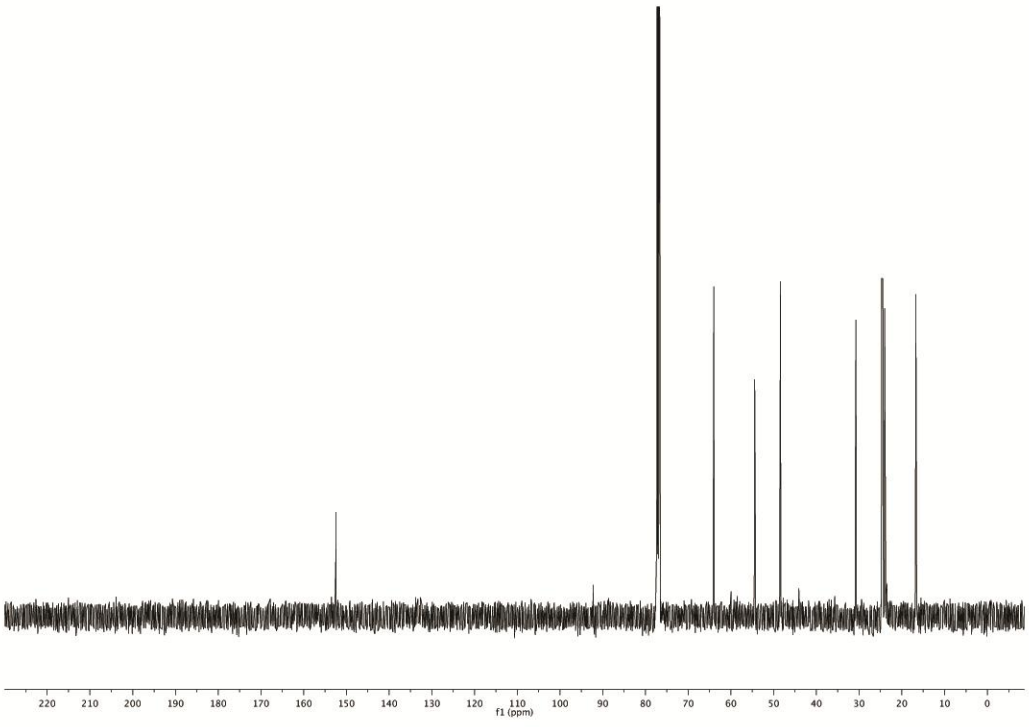




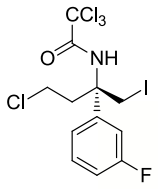
NMR spectra for **2o**

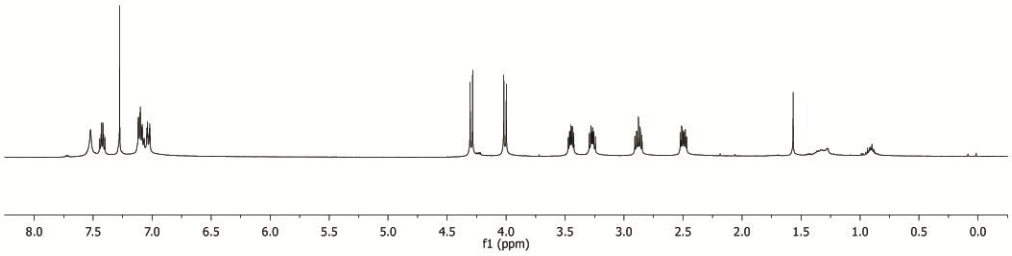


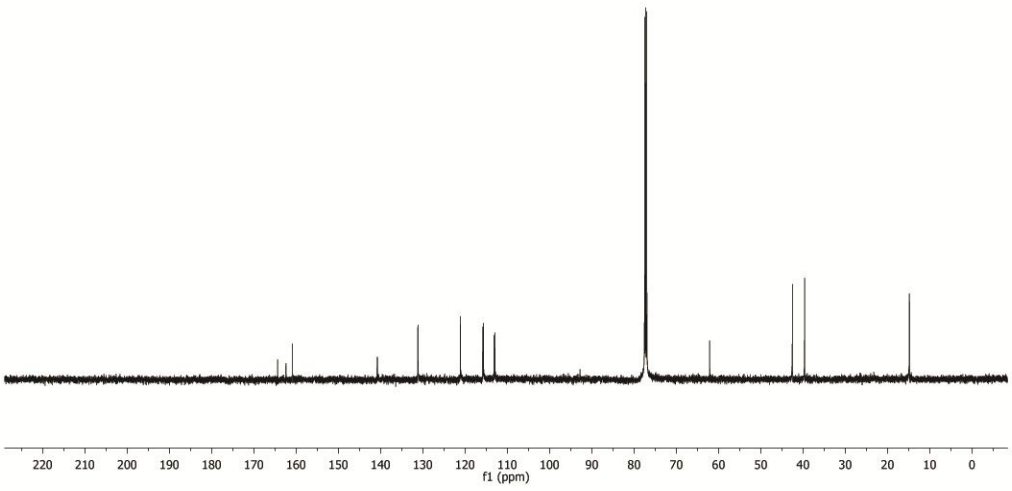




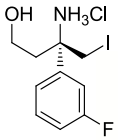
NMR spectra for **5c**

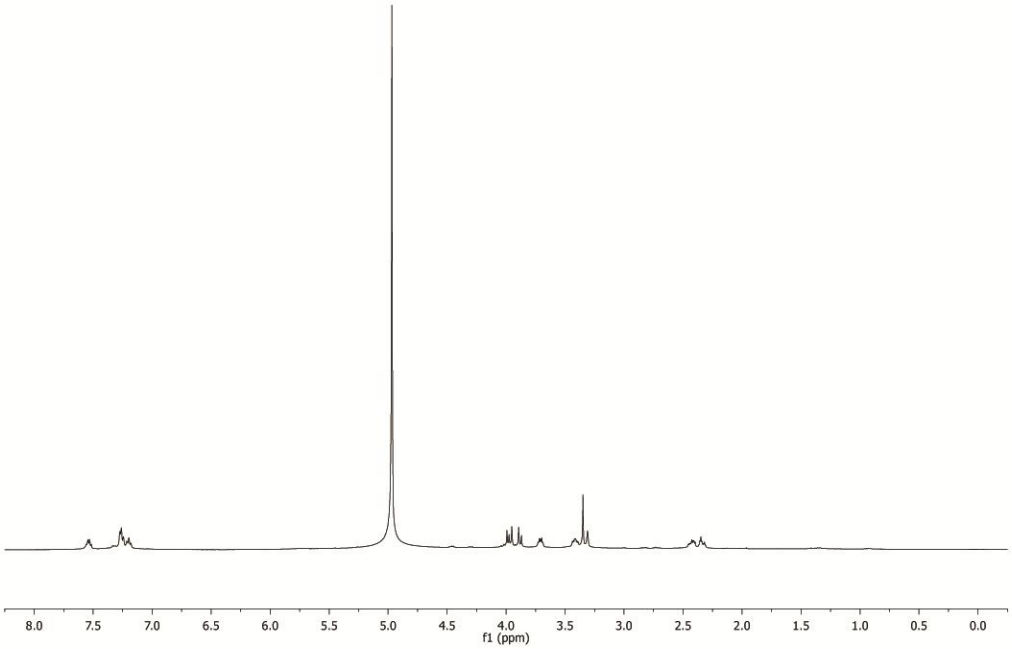


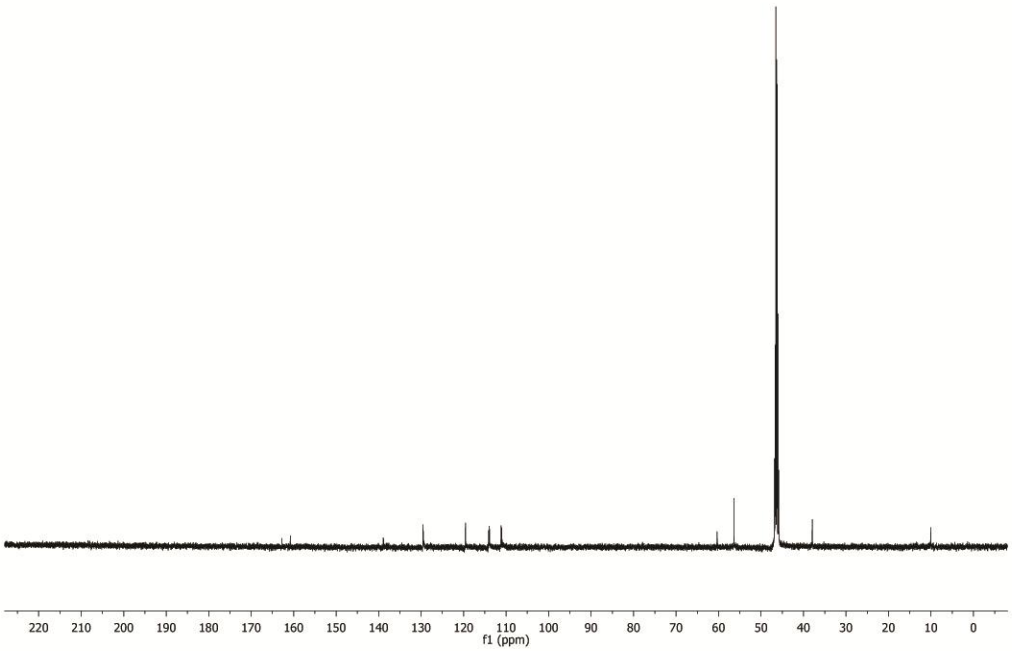




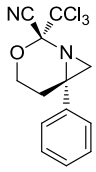
NMR spectra for **6c**

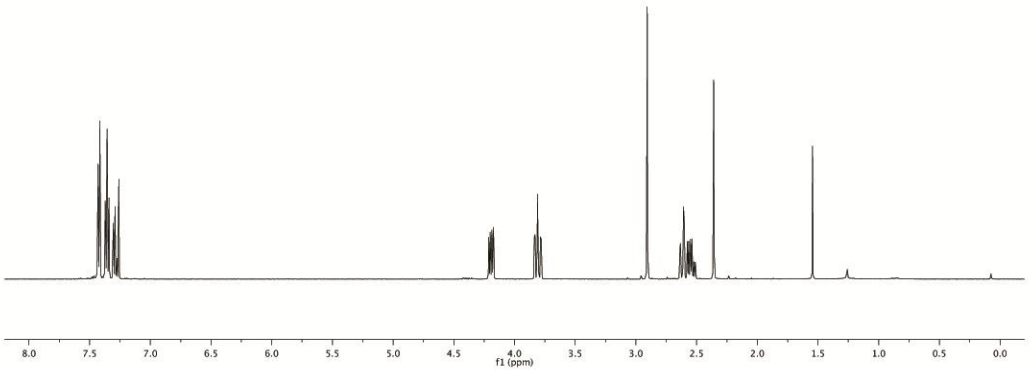


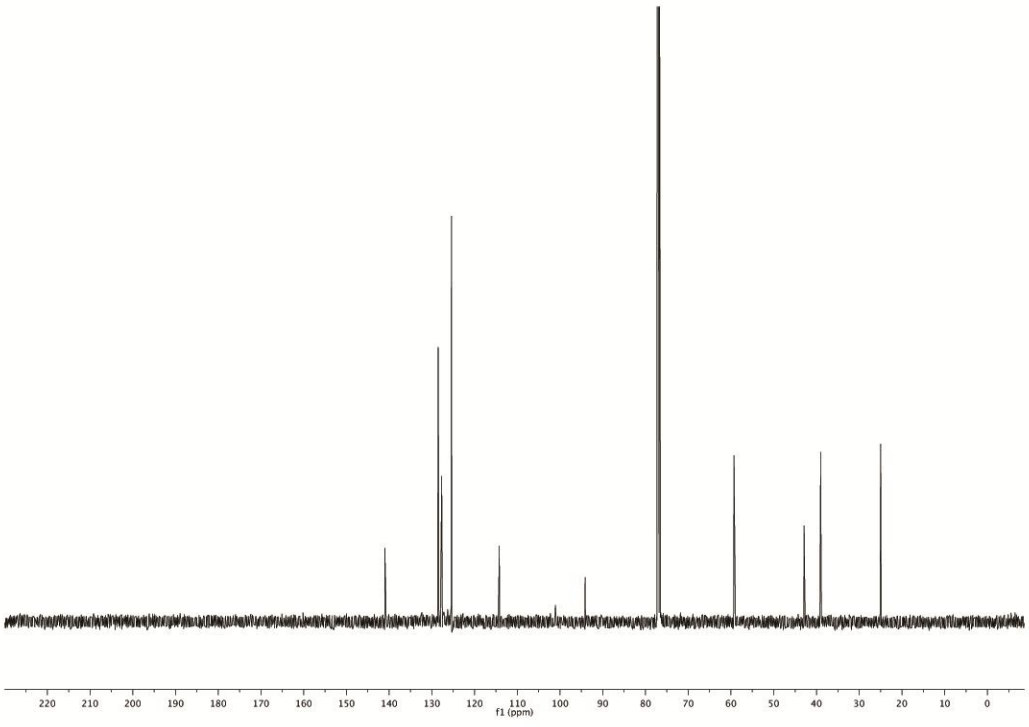




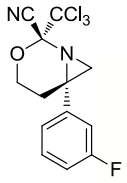
NMR spectra for **7a**

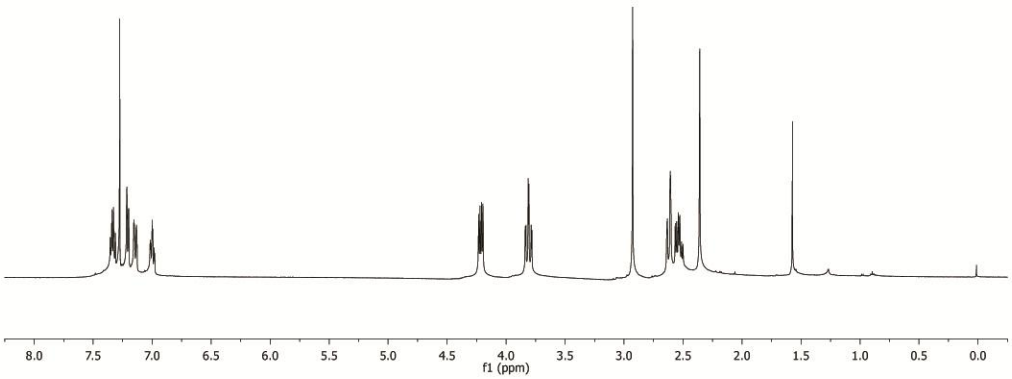


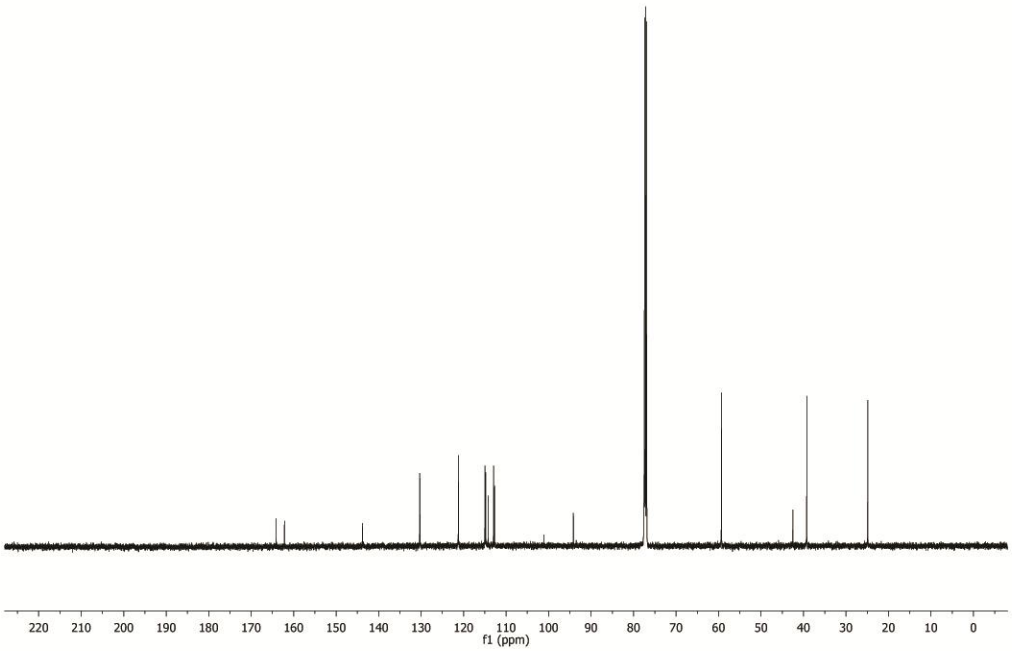




NMR spectra for **7c**

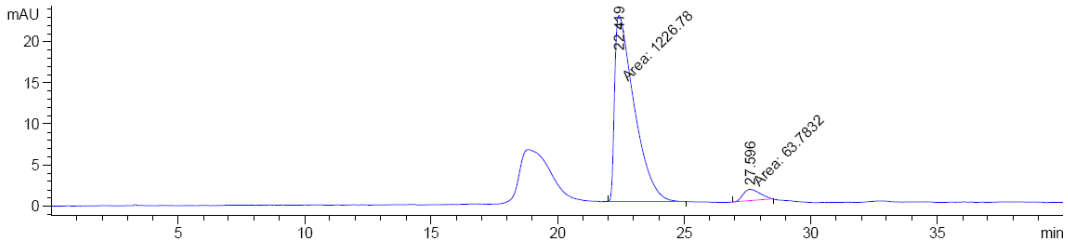






7. HPLC traces of enantioenriched and racemic iodoamination products and derivatives

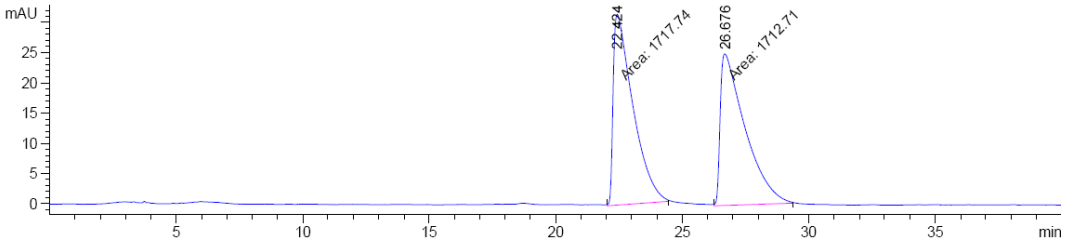
2a (90% ee, ChiralCel OD-H, 1% iPrOH in hexanes, 1 mL/min)



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.419	MM	0.9004	1226.78088	22.70684	95.0577
2	27.596	MM	0.7678	63.78321	1.38462	4.9423
Totals :				1290.56409	24.09145	

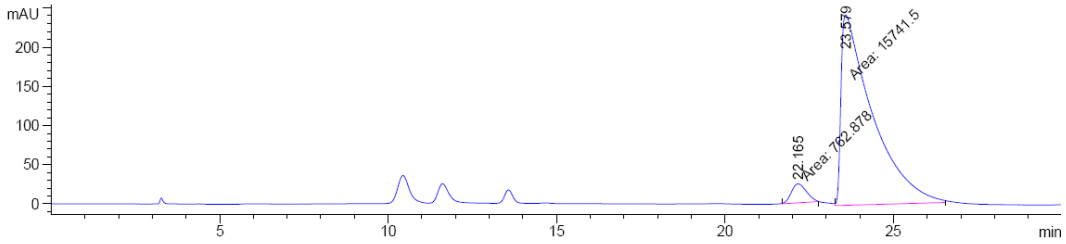
2a (racemic)



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.424	MM	0.9062	1717.74402	31.59356	50.0733
2	26.676	MM	1.1359	1712.71301	25.12990	49.9267
Totals :				3430.45703	56.72347	

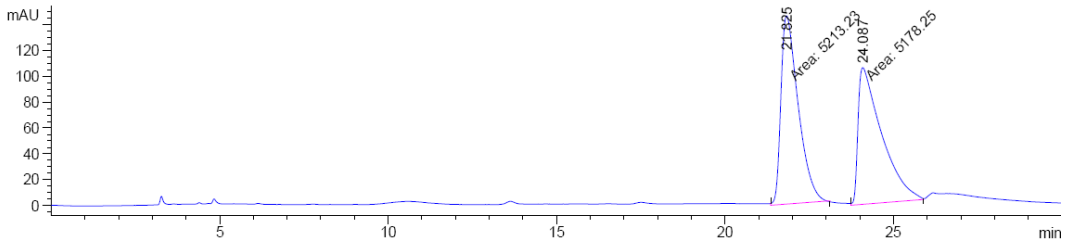
2b (90% ee, ChiralCel OD-H, 0.1% iPrOH in hexanes, 1 mL/min)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.165	MM	0.5236	762.87793	24.28442	4.6223
2	23.579	MM	1.0796	1.57415e4	243.00655	95.3777
Totals :				1.65044e4	267.29096	

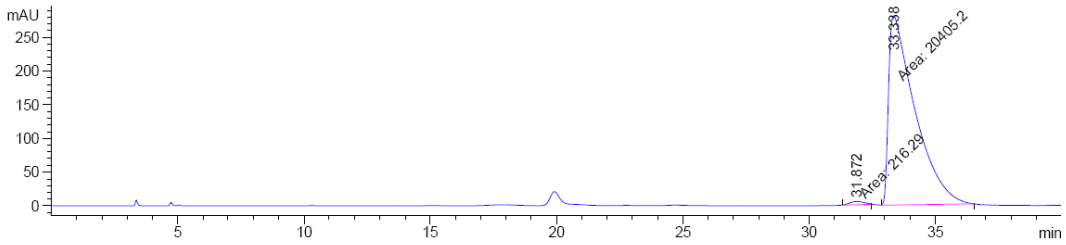
2b (racemic)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.825	MM	0.5957	5213.22607	145.85895	50.1683
2	24.087	MM	0.8149	5178.24854	105.90828	49.8317
Totals :				1.03915e4	251.76723	

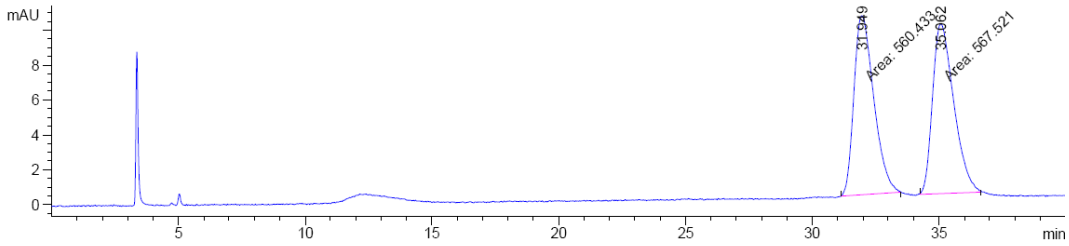
2c (98% ee, ChiralCel OD-H, 1% iPrOH in hexanes, 1 mL/min)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.872	MM	0.6983	216.28998	5.16239	1.0489
2	33.338	MM	1.2102	2.04052e4	281.01898	98.9511
Totals :				2.06215e4	286.18138	

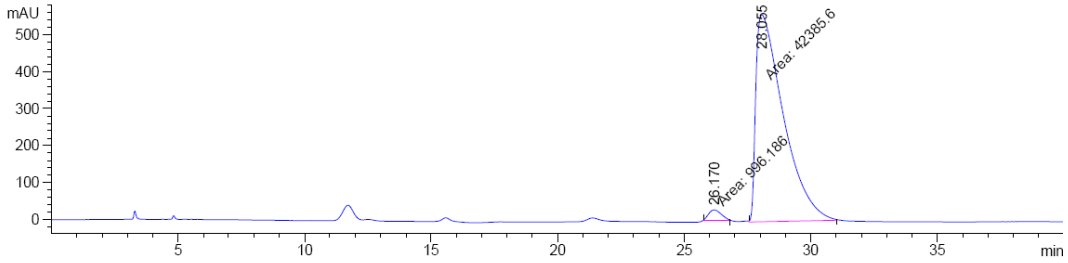
2c (racemic)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.949	MM	0.9096	560.43304	10.26849	49.6858
2	35.062	MM	0.9726	567.52142	9.72489	50.3142
Totals :				1127.95447	19.99338	

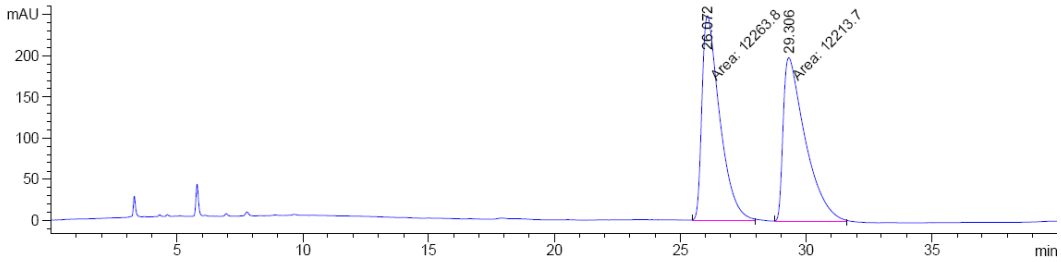
2d (95% ee, ChiralCel OD-H, 0.1% iPrOH in hexanes, 1 mL/min)



Signal 5: DAD1 E, Sig=200,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.170	MM	0.5841	996.18585	28.42566	2.2963
2	28.055	MM	1.2628	4.23856e4	559.39990	97.7037
Totals :				4.33818e4	587.82556	

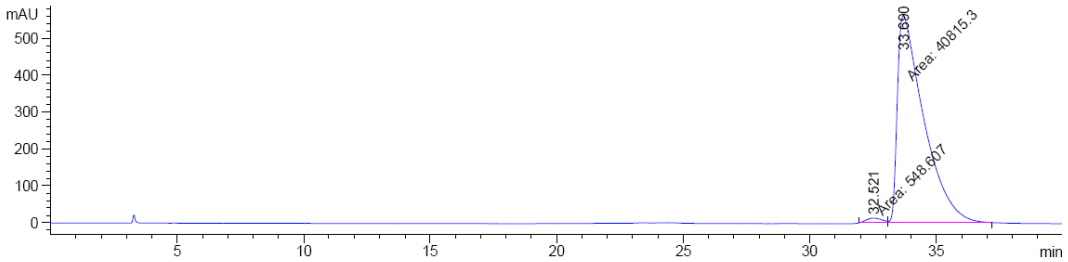
2d (racemic)



Signal 5: DAD1 E, Sig=200,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.072	MM	0.8218	1.22638e4	248.71312	50.1022
2	29.306	MM	1.0213	1.22137e4	199.30708	49.8978
Totals :				2.44775e4	448.02020	

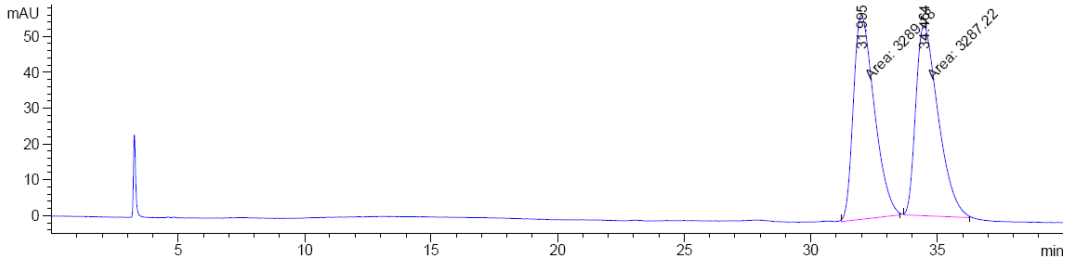
2e (97% ee, ChiralCel OD-H, 1% IPrOH in hexanes, 1 mL/min)



Signal 5: DAD1 E, Sig=200,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.521	MM	0.7291	548.60675	12.54013	1.3263
2	33.690	MM	1.2134	4.08153e4	560.64050	98.6737
Totals :				4.13639e4	573.18063	

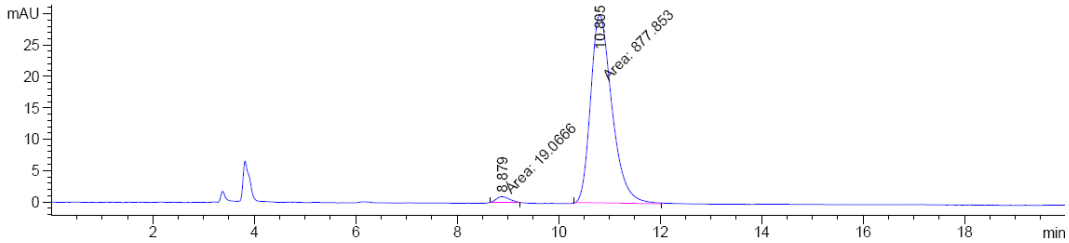
2e (racemic)



Signal 5: DAD1 E, Sig=200,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.995	MM	0.9608	3289.18359	57.05827	50.0149
2	34.464	MM	1.0309	3287.21729	53.14278	49.9851
Totals :				6576.40088	110.20105	

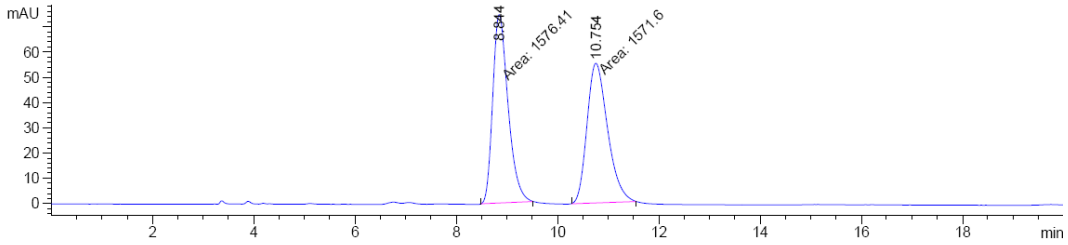
2f (96% ee, ChiralPak AS-H, 10% iPrOH in hexanes, 1 mL/min)



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.879	MM	0.3209	19.06658	9.90400e-1	2.1258
2	10.805	MM	0.4878	877.85327	29.99088	97.8742
Totals :				896.91985	30.98128	

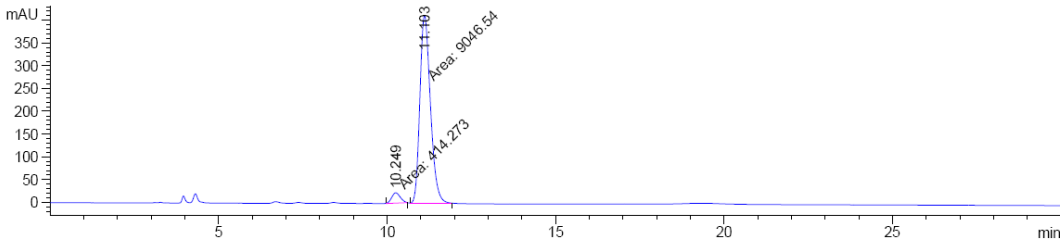
2f (racemic)



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.844	MM	0.3516	1576.40869	74.72331	50.0763
2	10.754	MM	0.4727	1571.60315	55.41798	49.9237
Totals :				3148.01184	130.14129	

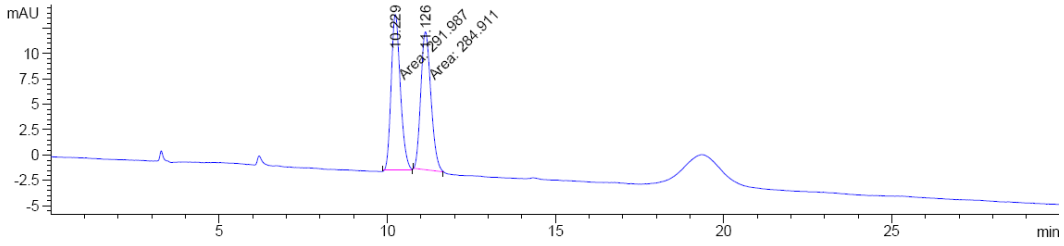
2g (90% ee, ChiralPak AS-H, 4% iPrOH in hexanes, 1 mL/min)



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.249	MM	0.2984	414.27347	23.13625	4.3788
2	11.103	MM	0.3652	9046.53906	412.86142	95.6212
Totals :				9460.81253	435.99767	

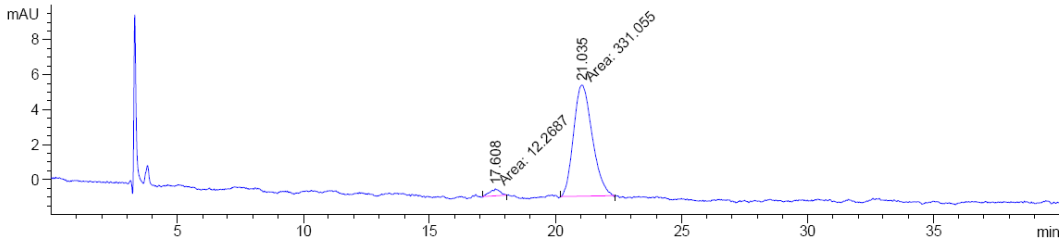
2g (racemic)



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.229	MM	0.3171	291.98740	15.34642	50.6133
2	11.126	MM	0.3491	284.91150	13.60330	49.3867
Totals :				576.89890	28.94972	

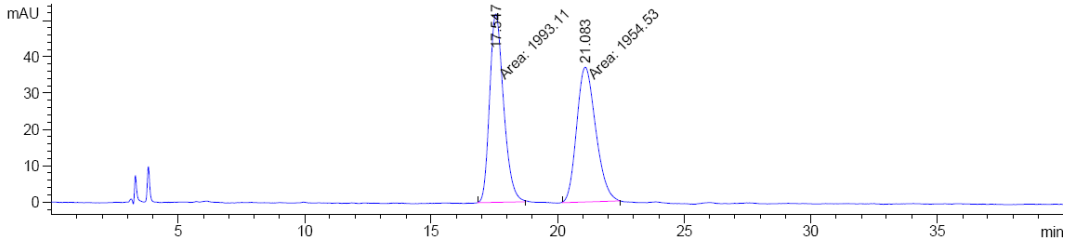
2h (92% ee, ChiralPak AS-H, 10% iPrOH in hexanes, 1 mL/min)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.608	MM	0.4807	12.26865	4.25402e-1	3.5735
2	21.035	MM	0.8643	331.05542	6.38419	96.4265
Totals :				343.32407	6.80960	

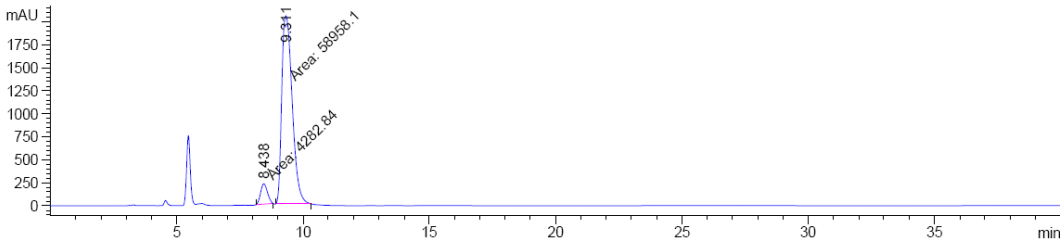
2h (racemic)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.547	MM	0.6406	1993.11304	51.85198	50.4886
2	21.083	MM	0.8772	1954.53381	37.13685	49.5114
Totals :				3947.64685	88.98883	

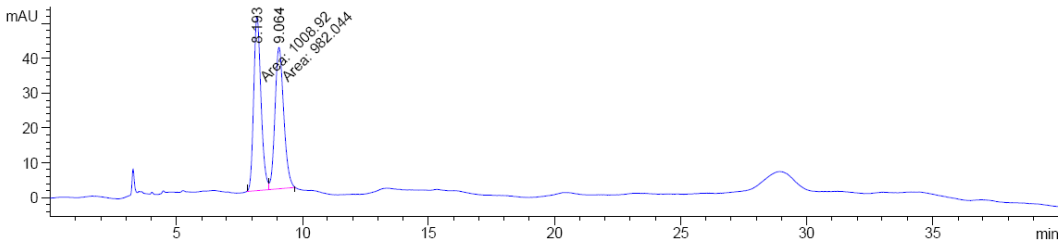
2i (86% ee, ChiralPak AS-H, 2% iPrOH in hexanes, 1 mL/min)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.438	MM	0.3191	4282.83789	223.68797	6.7723
2	9.311	MM	0.4795	5.89581e4	2049.17725	93.2277
Totals :				6.32410e4	2272.86522	

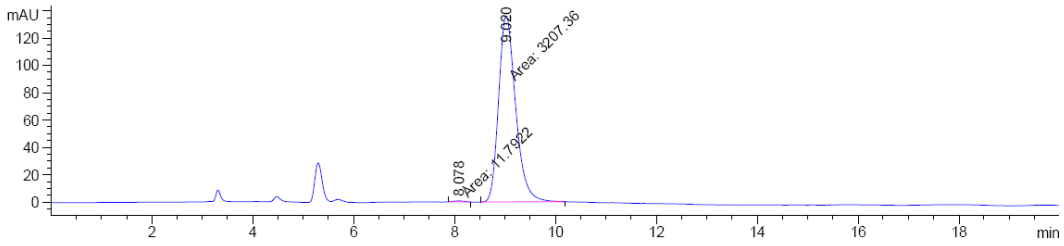
2i (racemic)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.193	MF	0.3365	1008.91595	49.96815	50.6749
2	9.064	FM	0.4026	982.04364	40.65314	49.3251
Totals :				1990.95959	90.62130	

2i (99% ee)

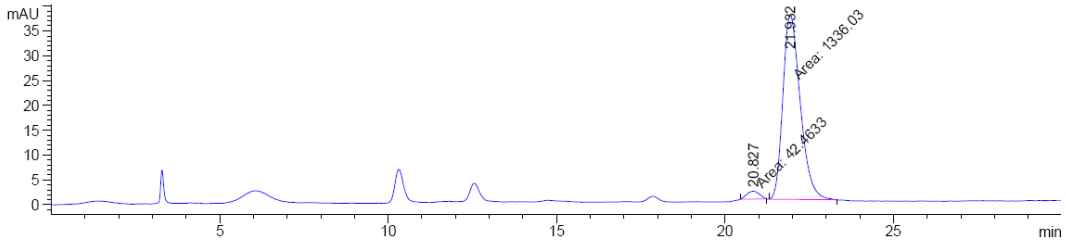


Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.078	MM	0.2316	11.79223	8.48632e-1	0.3663
2	9.020	MM	0.3920	3207.36133	136.35141	99.6337

Totals : 3219.15356 137.20004

2j (94% ee, ChiralCel OD-H, 0.1% iPrOH in hexanes, 1 mL/min)

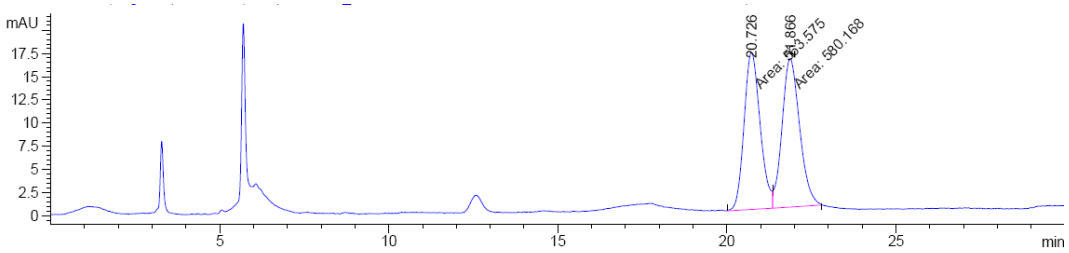


Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.827	MM	0.4432	42.46333	1.59683	3.0804
2	21.932	MM	0.5989	1336.03259	37.17826	96.9196

Totals : 1378.49592 38.77509

2j (racemic)

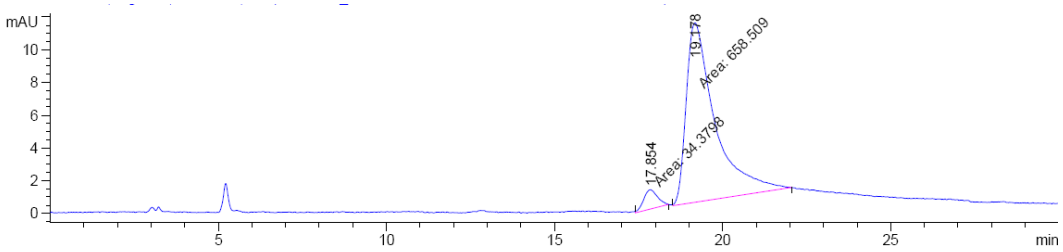


Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.726	MF	0.5540	563.57483	16.95534	49.2746
2	21.866	FM	0.6034	580.16809	16.02493	50.7254

Totals : 1143.74292 32.98027

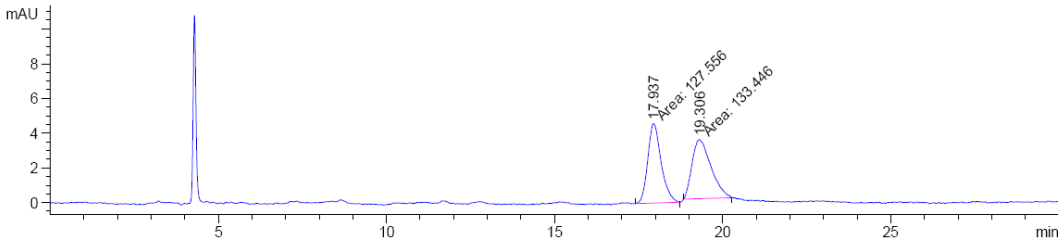
2k (90% ee, ChiralPak AD-H, 3% iPrOH in hexanes, 1 mL/min)



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.854	MM	0.4819	34.37984	1.18908	4.9618
2	19.178	MM	0.9987	658.50934	10.98934	95.0382
Totals :				692.88918	12.17842	

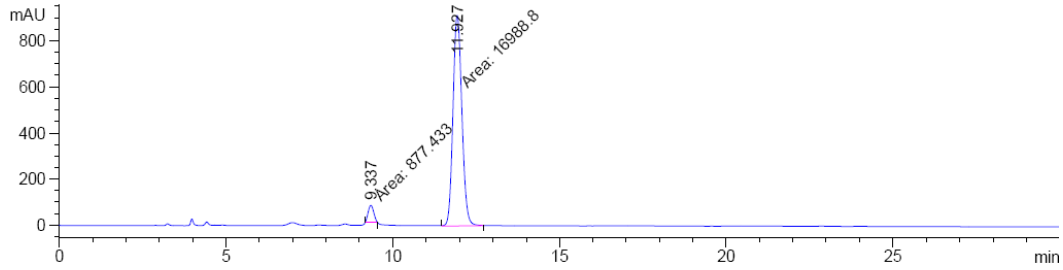
2k (racemic)



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.937	MM	0.4637	127.55595	4.58474	48.8716
2	19.306	MM	0.6515	133.44608	3.41392	51.1284
Totals :				261.00202	7.99866	

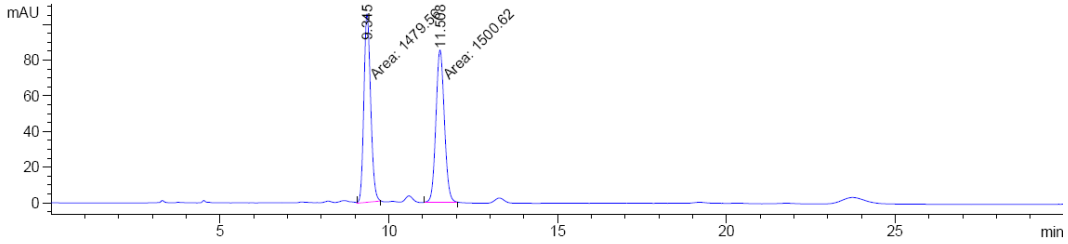
2l (90% ee, ChiralCel OD-H, 3% iPrOH in hexanes, 1 mL/min)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.337	MM	0.1954	877.43311	74.83657	4.9111
2	11.927	MM	0.3099	1.69888e4	913.81714	95.0889
Totals :				1.78663e4	988.65371	

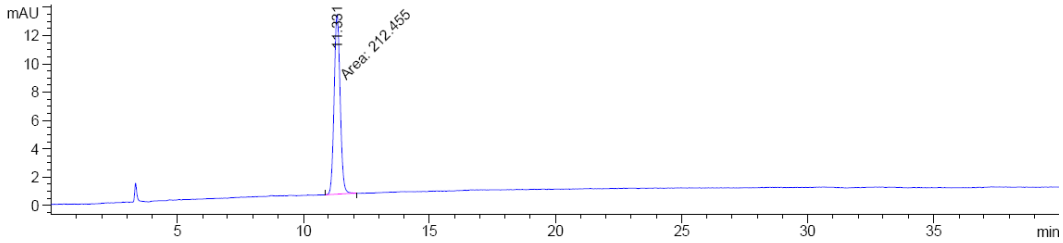
2l (racemic)



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.345	MM	0.2330	1479.55530	105.84991	49.6466
2	11.508	MM	0.2921	1500.61938	85.62201	50.3534
Totals :				2980.17468	191.47192	

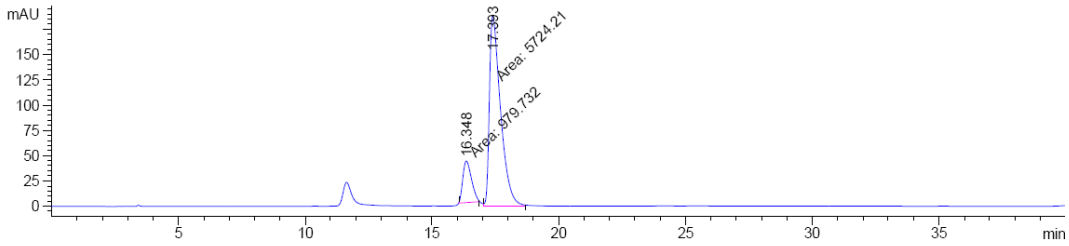
2l (>99% ee)



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.331	MM	0.2784	212.45515	12.71807	100.0000
Totals :				212.45515	12.71807	

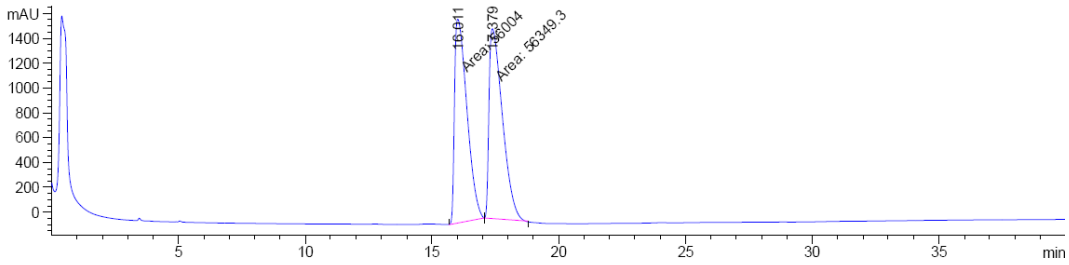
2m (70% ee, ChiralCel OD-H, 0.1% iPrOH in hexanes, 1 mL/min)



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.348	MM	0.3966	979.73169	41.16856	14.6143
2	17.393	MM	0.5070	5724.21143	188.16844	85.3857
Totals :				6703.94312	229.33700	

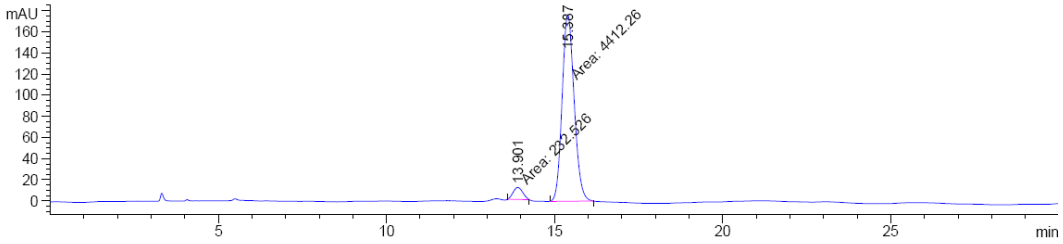
2m (racemic)



Signal 5: DAD1 E, Sig=200,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.011	MM	0.5669	5.60040e4	1646.64185	49.8464
2	17.379	MM	0.6125	5.63493e4	1533.39575	50.1536
Totals :				1.12353e5	3180.03760	

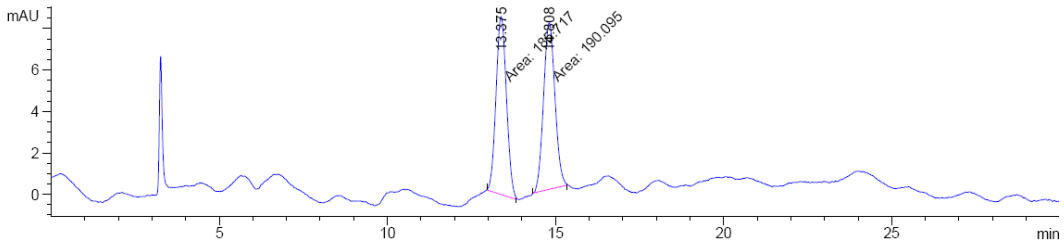
2n (90% ee, ChiralCel OD-H, 2% iPrOH in hexanes, 1 mL/min)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.901	MM	0.3373	232.52573	11.49026	5.0062
2	15.387	MM	0.4164	4412.25586	176.61739	94.9938
Totals :				4644.78159	188.10765	

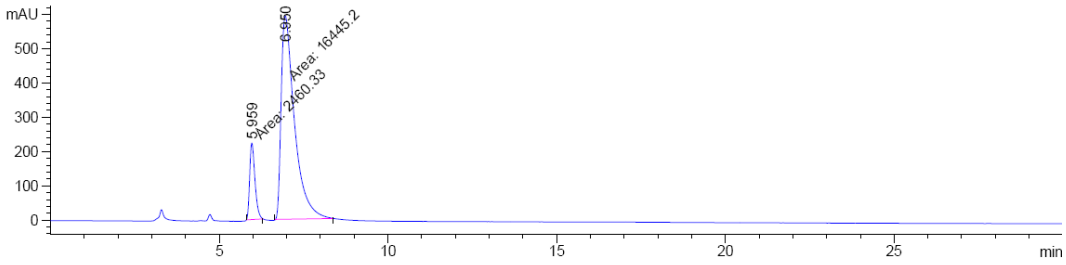
2n (racemic)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.375	MM	0.3604	185.71681	8.58802	49.4175
2	14.808	MM	0.3939	190.09496	8.04335	50.5825
Totals :				375.81177	16.63136	

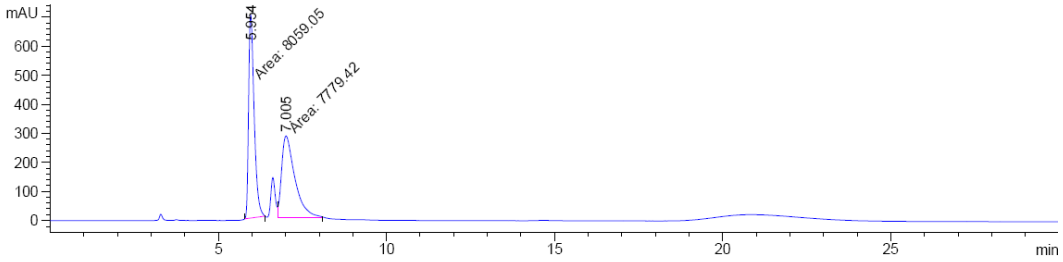
2o (73% ee, ChiralPak AD-H, 0.02% iPrOH in hexanes, 1 mL/min)



Signal 5: DAD1 E, Sig=200,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.959	MM	0.1828	2460.33350	224.37224	13.0139
2	6.950	MM	0.4611	1.64452e4	594.46338	86.9861
Totals :				1.89055e4	818.83562	

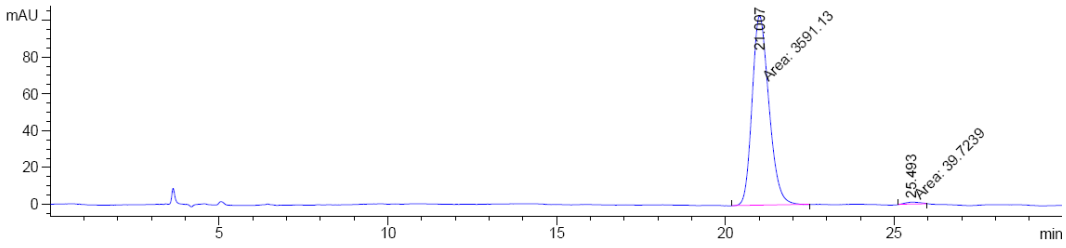
2o (racemic)



Signal 5: DAD1 E, Sig=200,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.954	MM	0.1916	8059.04688	701.01831	50.8827
2	7.005	MM	0.4597	7779.42188	282.03738	49.1173
Totals :				1.58385e4	983.05569	

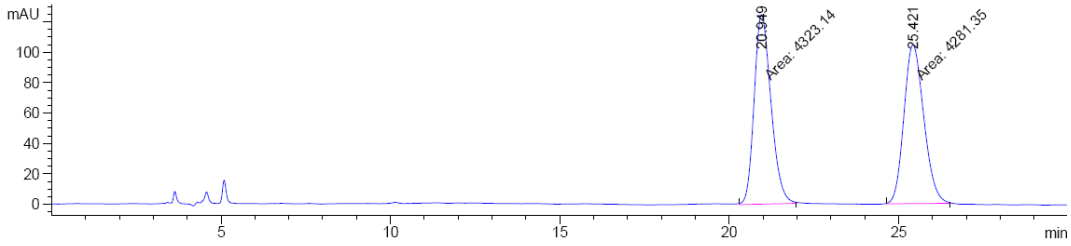
5c (98% ee, ChiralCel OD-H, 3% iPrOH in hexanes, 1 mL/min)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.007	MM	0.5809	3591.13306	103.02996	98.9059
2	25.493	MM	0.5369	39.72391	1.23312	1.0941
Totals :				3630.85696	104.26308	

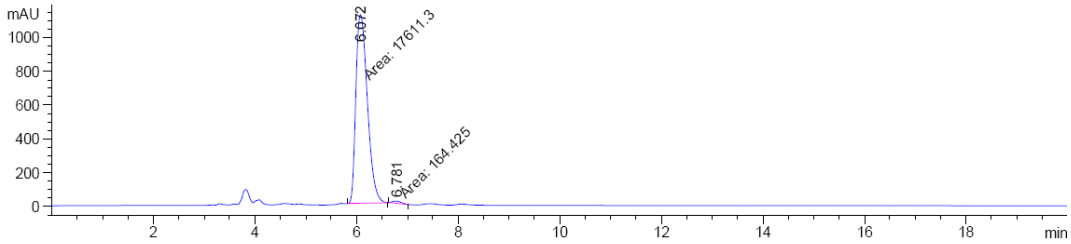
5c (racemic)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.949	MM	0.5781	4323.13721	124.64666	50.2428
2	25.421	MM	0.6828	4281.35498	104.50150	49.7572
Totals :				8604.49219	229.14816	

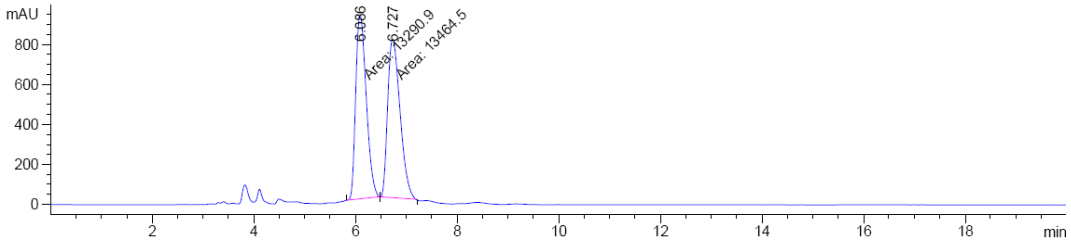
Trifluoroacetylated 6c (98% ee, ChiralPak AS-H, 10% iPrOH in hexanes, 1 mL/min)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.072	MM	0.2629	1.76113e4	1116.43457	99.0750
2	6.781	MM	0.2120	164.42485	12.92935	0.9250
Totals :				1.77757e4	1129.36392	

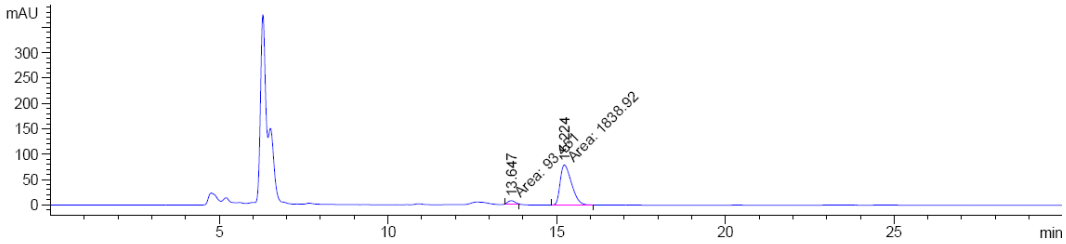
Trifluoroacetylated 6c (racemic)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.086	MM	0.2403	1.32909e4	921.99310	49.6756
2	6.727	MM	0.2829	1.34645e4	793.28748	50.3244
Totals :				2.67555e4	1715.28058	

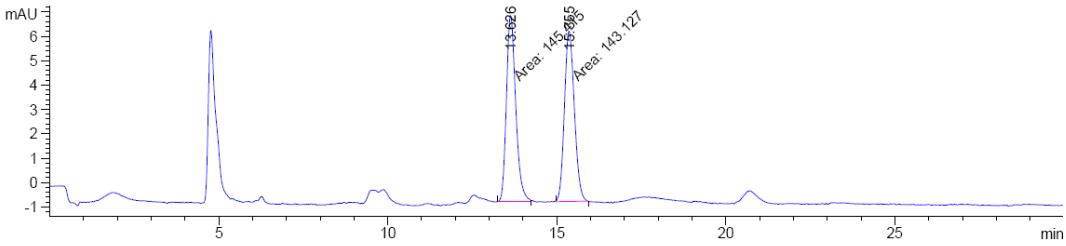
7a (90% ee, ChiralPak AS-H, 5% iPrOH in hexanes, 1 mL/min)



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.647	MM	0.2397	93.45100	6.49913	4.8361
2	15.224	MM	0.3879	1838.91785	79.01415	95.1639
Totals :				1932.36885	85.51328	

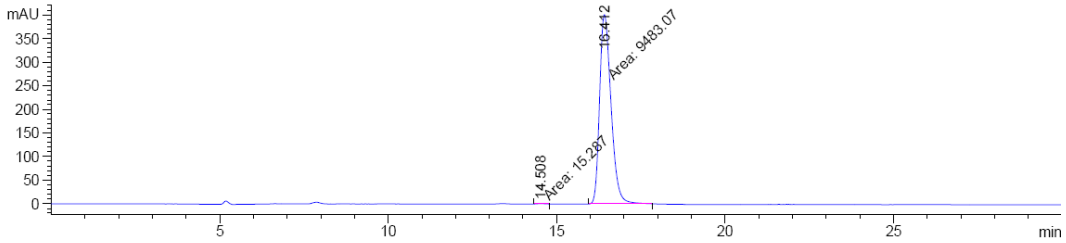
7a (racemic)



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.626	MM	0.3178	145.41547	7.62597	50.3966
2	15.355	MM	0.3406	143.12691	7.00372	49.6034
Totals :				288.54237	14.62969	

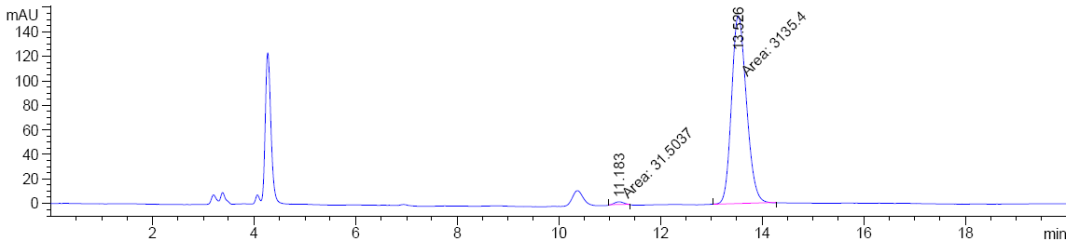
7a (>99% ee)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.508	MM	0.2613	15.28702	9.75178e-1	0.1609
2	16.412	MM	0.3940	9483.06543	401.09970	99.8391
Totals :				9498.35245	402.07488	

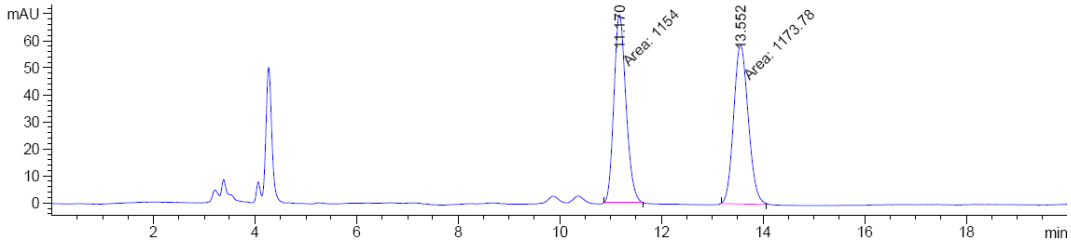
7c (98% ee, ChiralPak AS-H, 5% iPrOH in hexanes, 1 mL/min)



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.183	MM	0.2133	31.50368	2.46114	0.9948
2	13.526	MM	0.3406	3135.39624	153.44450	99.0052
Totals :				3166.89992	155.90564	

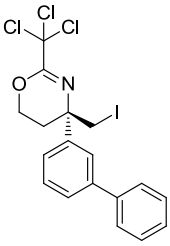
7c (racemic)

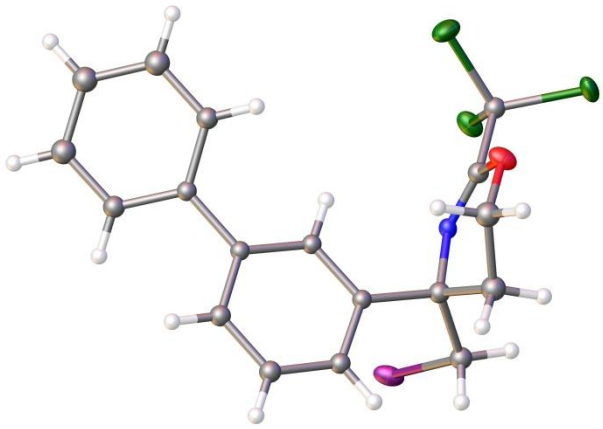


Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.170	MM	0.2761	1154.00464	69.66000	49.5752
2	13.552	MM	0.3323	1173.77979	58.87663	50.4248
Totals :				2327.78442	128.53663	

8. X-Ray crystallographic data for 2i





A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A[17] with reflection spot size optimization. Absorption corrections were made with the program SADABS.[17] The structure was solved by the direct methods procedure and refined by least-squares methods again F^2 using SHELXS-97 and SHELXL-97[18] with OLEX 2 interface.[19] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S1, and geometric parameters are shown in Table S2. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[20]

[17] Bruker AXS APEX II, Bruker AXS, Madison, Wisconsin, 2009.

[18] Sheldrick, G.M. *Acta Cryst.* **2008**, *A64*, 112-122.

[19] Dolomanov, O.V.; Bourhis, L,J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

[20] Accelrys DS Visualizer v2.0.1, Accelrys Software. Inc., 2007.

Table S1. Experimental details

Crystal data	
Chemical formula	$C_{18}H_{15}Cl_3INO$
M_r	494.56
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, *b*, *c* (Å)	6.2501 (1), 10.0275 (2), 30.1617 (7)
V (Å^3)	1890.32 (7)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	2.12
Crystal size (mm)	0.20 × 0.12 × 0.12
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.676, 0.785
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21519, 3605, 3397
R_{int}	0.040
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.021, 0.038, 1.07
No. of reflections	3605
No. of parameters	217
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, -0.37
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Flack parameter	-0.010 (13)

Computer programs: *APEX2* v2009.3.0,[17] *SAINT* 7.46A,[17] *SHELXS97*,[18] *SHELXL97*,[18] Bruker *SHELXTL*.[18]

Table S2. Geometric parameters (Å, º)

C1—C2	1.381 (4)	C11—H11	0.9500
C1—C6	1.402 (4)	C12—H12	0.9500
C1—H1	0.9500	C13—N1	1.478 (3)
C2—C3	1.393 (4)	C13—C17	1.531 (4)
C2—C13	1.520 (4)	C13—C14	1.544 (4)
C3—C4	1.380 (4)	C14—C15	1.502 (4)
C3—H3	0.9500	C14—H14A	0.9900
C4—C5	1.388 (4)	C14—H14B	0.9900
C4—H4	0.9500	C15—O1	1.452 (3)
C5—C6	1.396 (4)	C15—H15A	0.9900
C5—H5	0.9500	C15—H15B	0.9900
C6—C7	1.480 (4)	C16—N1	1.256 (3)
C7—C8	1.395 (4)	C16—O1	1.346 (4)
C7—C12	1.396 (4)	C16—C18	1.523 (4)
C8—C9	1.385 (4)	C17—I1	2.150 (3)
C8—H8	0.9500	C17—H17A	0.9900
C9—C10	1.382 (4)	C17—H17B	0.9900
C9—H9	0.9500	C18—Cl1	1.764 (3)
C10—C11	1.385 (4)	C18—Cl2	1.776 (3)
C10—H10	0.9500	C18—Cl3	1.777 (3)
C11—C12	1.387 (4)		
C2—C1—C6	122.3 (2)	N1—C13—C2	111.4 (2)
C2—C1—H1	118.9	N1—C13—C17	105.6 (2)
C6—C1—H1	118.9	C2—C13—C17	111.7 (2)
C1—C2—C3	118.2 (2)	N1—C13—C14	110.0 (2)
C1—C2—C13	122.3 (2)	C2—C13—C14	110.3 (2)
C3—C2—C13	119.5 (2)	C17—C13—C14	107.7 (2)
C4—C3—C2	121.1 (3)	C15—C14—C13	108.9 (3)
C4—C3—H3	119.4	C15—C14—H14A	109.9
C2—C3—H3	119.4	C13—C14—H14A	109.9
C3—C4—C5	119.9 (3)	C15—C14—H14B	109.9
C3—C4—H4	120.0	C13—C14—H14B	109.9
C5—C4—H4	120.0	H14A—C14—H14B	108.3
C4—C5—C6	120.7 (3)	O1—C15—C14	110.0 (2)
C4—C5—H5	119.7	O1—C15—H15A	109.7

C6—C5—H5	119.7	C14—C15—H15A	109.7
C5—C6—C1	117.8 (2)	O1—C15—H15B	109.7
C5—C6—C7	120.8 (2)	C14—C15—H15B	109.7
C1—C6—C7	121.4 (2)	H15A—C15—H15B	108.2
C8—C7—C12	118.2 (3)	N1—C16—O1	130.5 (3)
C8—C7—C6	120.4 (2)	N1—C16—C18	120.8 (3)
C12—C7—C6	121.5 (2)	O1—C16—C18	108.7 (2)
C9—C8—C7	120.9 (3)	C13—C17—I1	113.10 (19)
C9—C8—H8	119.6	C13—C17—H17A	109.0
C7—C8—H8	119.6	I1—C17—H17A	109.0
C10—C9—C8	120.2 (3)	C13—C17—H17B	109.0
C10—C9—H9	119.9	I1—C17—H17B	109.0
C8—C9—H9	119.9	H17A—C17—H17B	107.8
C9—C10—C11	119.8 (3)	C16—C18—Cl1	111.90 (19)
C9—C10—H10	120.1	C16—C18—Cl2	109.0 (2)
C11—C10—H10	120.1	Cl1—C18—Cl2	108.39 (15)
C10—C11—C12	120.0 (3)	C16—C18—Cl3	109.50 (19)
C10—C11—H11	120.0	Cl1—C18—Cl3	108.75 (15)
C12—C11—H11	120.0	Cl2—C18—Cl3	109.28 (15)
C11—C12—C7	120.9 (3)	C16—N1—C13	118.7 (2)
C11—C12—H12	119.5	C16—O1—C15	114.9 (2)
C7—C12—H12	119.5		
C6—C1—C2—C3	-0.2 (4)	C3—C2—C13—C17	50.3 (3)
C6—C1—C2—C13	179.7 (3)	C1—C2—C13—C14	110.7 (3)
C1—C2—C3—C4	0.5 (4)	C3—C2—C13—C14	-69.4 (3)
C13—C2—C3—C4	-179.4 (3)	N1—C13—C14—C15	49.7 (3)
C2—C3—C4—C5	-0.4 (4)	C2—C13—C14—C15	-73.6 (3)
C3—C4—C5—C6	0.0 (4)	C17—C13—C14—C15	164.3 (2)
C4—C5—C6—C1	0.2 (4)	C13—C14—C15—O1	-58.5 (3)
C4—C5—C6—C7	179.3 (3)	N1—C13—C17—I1	-64.8 (2)
C2—C1—C6—C5	-0.1 (4)	C2—C13—C17—I1	56.4 (3)
C2—C1—C6—C7	-179.2 (2)	C14—C13—C17—I1	177.70 (17)
C5—C6—C7—C8	-36.4 (4)	N1—C16—C18—Cl1	-2.8 (3)
C1—C6—C7—C8	142.6 (3)	O1—C16—C18—Cl1	176.11 (18)
C5—C6—C7—C12	143.9 (3)	N1—C16—C18—Cl2	-122.7 (3)
C1—C6—C7—C12	-37.0 (4)	O1—C16—C18—Cl2	56.3 (3)

C12—C7—C8—C9	-0.3 (4)	N1—C16—C18—Cl3	117.8 (2)
C6—C7—C8—C9	-179.9 (2)	O1—C16—C18—Cl3	-63.2 (3)
C7—C8—C9—C10	0.9 (4)	O1—C16—N1—C13	-4.3 (4)
C8—C9—C10—C11	-0.5 (4)	C18—C16—N1—C13	174.4 (2)
C9—C10—C11—C12	-0.4 (4)	C2—C13—N1—C16	103.0 (3)
C10—C11—C12—C7	1.1 (4)	C17—C13—N1—C16	-135.6 (2)
C8—C7—C12—C11	-0.7 (4)	C14—C13—N1—C16	-19.7 (3)
C6—C7—C12—C11	178.9 (2)	N1—C16—O1—C15	-4.2 (4)
C1—C2—C13—N1	-11.7 (4)	C18—C16—O1—C15	177.0 (2)
C3—C2—C13—N1	168.2 (2)	C14—C15—O1—C16	36.4 (3)
C1—C2—C13—C17	-129.6 (3)		

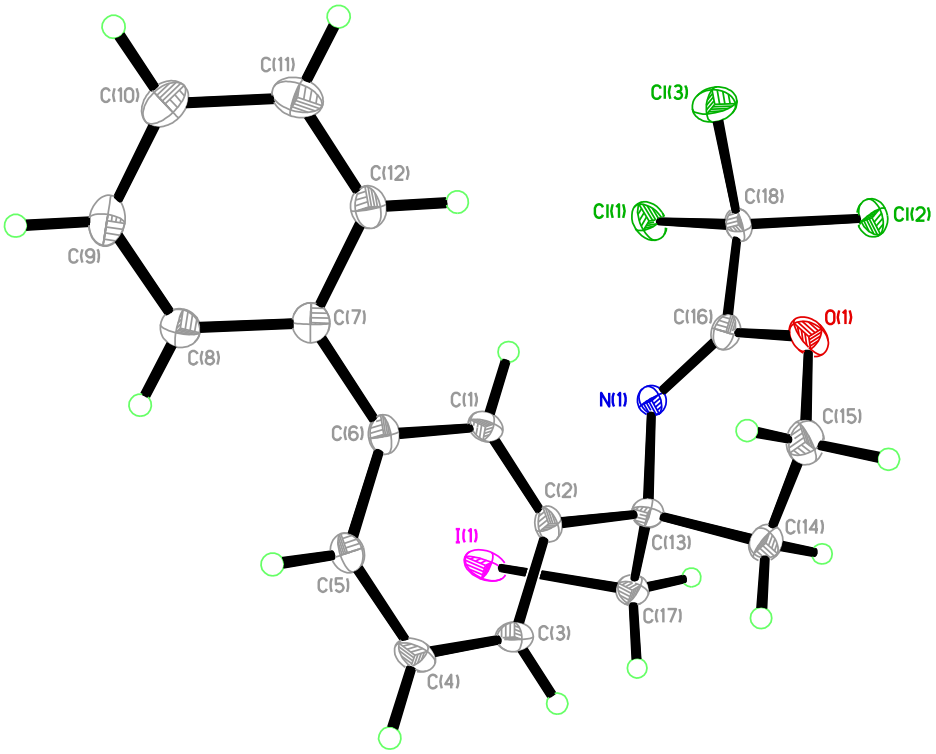


Figure S1. Perspective views showing 50% probability displacement.

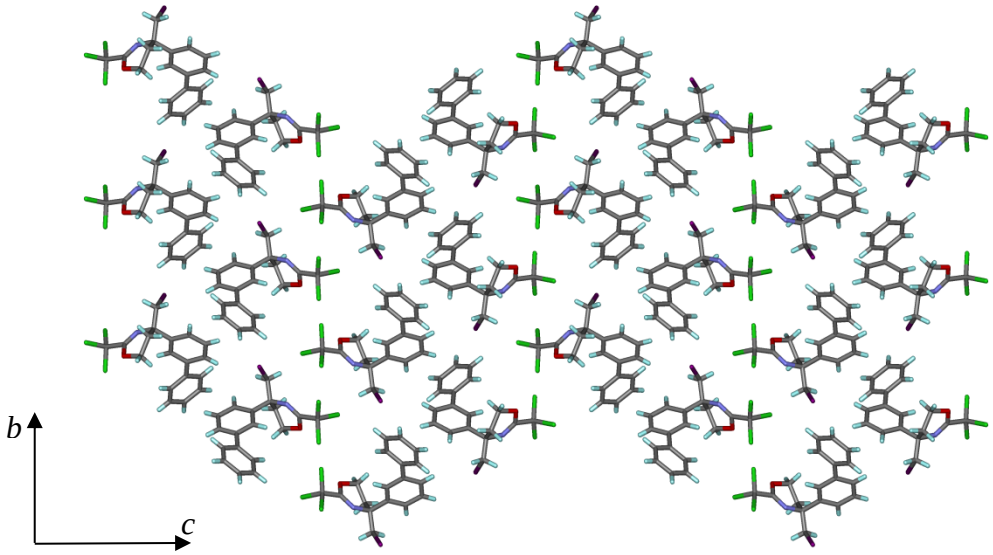
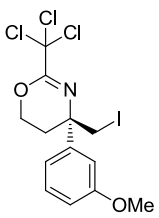
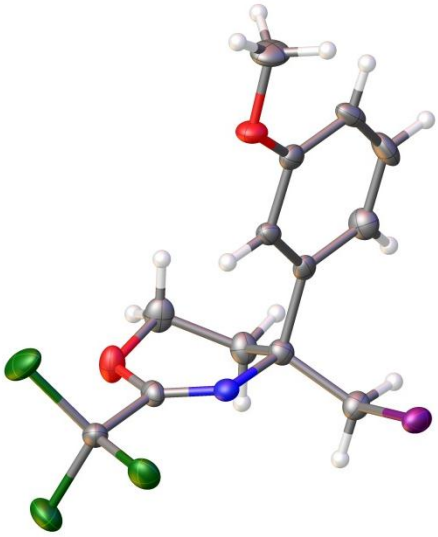


Figure S2. Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

9. X-Ray Crystallographic Data for 2l





A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.78 Å resolution was carried out using SAINT V7.46 A[17] with reflection spot size optimization. Absorption corrections were made with the program SADABS.[17] The structure was solved by the direct methods procedure and refined by least-squares methods again F^2 using SHELXS-97 and SHELXL-97[18] with OLEX 2 interface.[19] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S3, and geometric parameters are shown in Table S4. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[20]

Table S3. Experimental details

Crystal data	
Chemical formula	$C_{13}H_{13}Cl_3INO_2$
M_r	448.49
Crystal system, space group	Monoclinic, *C*2
Temperature (K)	100
a, *b*, *c* (Å)	25.646 (3), 6.3769 (7), 10.8278 (11)
β (°)	112.766 (1)
V (Å^3)	1632.8 (3)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	2.45
Crystal size (mm)	0.24 × 0.18 × 0.16
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.591, 0.695
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9229, 3530, 3253
R_{int}	0.034
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.642
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.029, 0.062, 1.03
No. of reflections	3530
No. of parameters	182
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.98, -0.61
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Flack parameter	-0.03 (2)

Computer programs: *APEX2* v2009.3.0,[17] *SAINT* 7.46A,[17] *SHELXS97*,[18] *SHELXL97*,[18] Bruker *SHELXTL*.[18]

Table S4. Geometric parameters (Å, º)

C1—C6	1.371 (7)	C8—H8B	0.9900
C1—C2	1.412 (6)	C9—O2	1.452 (5)
C1—H1	0.9500	C9—H9A	0.9900
C2—O1	1.361 (5)	C9—H9B	0.9900
C2—C3	1.372 (6)	C10—N1	1.256 (5)
C3—C4	1.378 (7)	C10—O2	1.338 (5)
C3—H3	0.9500	C10—C13	1.520 (5)
C4—C5	1.379 (6)	C11—O1	1.438 (5)
C4—H4	0.9500	C11—H11A	0.9800
C5—C6	1.401 (6)	C11—H11B	0.9800
C5—H5	0.9500	C11—H11C	0.9800
C6—C7	1.540 (5)	C12—I1	2.143 (4)
C7—N1	1.465 (5)	C12—H12A	0.9900
C7—C8	1.532 (7)	C12—H12B	0.9900
C7—C12	1.533 (5)	C13—Cl1	1.753 (4)
C8—C9	1.514 (5)	C13—Cl3	1.766 (4)
C8—H8A	0.9900	C13—Cl2	1.774 (4)
C6—C1—C2	121.2 (4)	O2—C9—C8	110.0 (3)
C6—C1—H1	119.4	O2—C9—H9A	109.7
C2—C1—H1	119.4	C8—C9—H9A	109.7
O1—C2—C3	125.6 (4)	O2—C9—H9B	109.7
O1—C2—C1	114.4 (4)	C8—C9—H9B	109.7
C3—C2—C1	119.9 (4)	H9A—C9—H9B	108.2
C2—C3—C4	118.5 (4)	N1—C10—O2	130.6 (4)
C2—C3—H3	120.8	N1—C10—C13	119.8 (4)
C4—C3—H3	120.8	O2—C10—C13	109.6 (3)
C3—C4—C5	122.4 (4)	O1—C11—H11A	109.5
C3—C4—H4	118.8	O1—C11—H11B	109.5
C5—C4—H4	118.8	H11A—C11—H11B	109.5
C4—C5—C6	119.5 (4)	O1—C11—H11C	109.5
C4—C5—H5	120.3	H11A—C11—H11C	109.5
C6—C5—H5	120.3	H11B—C11—H11C	109.5
C1—C6—C5	118.5 (4)	C7—C12—I1	113.4 (3)
C1—C6—C7	121.6 (3)	C7—C12—H12A	108.9
C5—C6—C7	119.9 (4)	I1—C12—H12A	108.9

N1—C7—C8	110.8 (3)	C7—C12—H12B	108.9
N1—C7—C12	107.4 (3)	I1—C12—H12B	108.9
C8—C7—C12	107.6 (3)	H12A—C12—H12B	107.7
N1—C7—C6	109.9 (3)	C10—C13—Cl1	112.2 (3)
C8—C7—C6	110.9 (3)	C10—C13—Cl3	108.3 (3)
C12—C7—C6	110.2 (3)	Cl1—C13—Cl3	108.7 (2)
C9—C8—C7	108.9 (5)	C10—C13—Cl2	109.4 (3)
C9—C8—H8A	109.9	Cl1—C13—Cl2	109.1 (2)
C7—C8—H8A	109.9	Cl3—C13—Cl2	109.1 (2)
C9—C8—H8B	109.9	C10—N1—C7	118.9 (3)
C7—C8—H8B	109.9	C2—O1—C11	117.3 (4)
H8A—C8—H8B	108.3	C10—O2—C9	114.8 (3)
C6—C1—C2—O1	-178.9 (4)	N1—C7—C12—I1	-59.7 (4)
C6—C1—C2—C3	0.5 (6)	C8—C7—C12—I1	-179.0 (2)
O1—C2—C3—C4	179.8 (4)	C6—C7—C12—I1	59.9 (4)
C1—C2—C3—C4	0.4 (6)	N1—C10—C13—Cl1	-0.2 (5)
C2—C3—C4—C5	-0.5 (7)	O2—C10—C13—Cl1	-178.9 (3)
C3—C4—C5—C6	-0.2 (7)	N1—C10—C13—Cl3	119.8 (4)
C2—C1—C6—C5	-1.2 (6)	O2—C10—C13—Cl3	-58.9 (4)
C2—C1—C6—C7	178.4 (4)	N1—C10—C13—Cl2	-121.4 (4)
C4—C5—C6—C1	1.1 (6)	O2—C10—C13—Cl2	59.9 (4)
C4—C5—C6—C7	-178.5 (4)	O2—C10—N1—C7	-3.9 (6)
C1—C6—C7—N1	-7.0 (5)	C13—C10—N1—C7	177.7 (3)
C5—C6—C7—N1	172.6 (3)	C8—C7—N1—C10	-19.2 (5)
C1—C6—C7—C8	115.9 (4)	C12—C7—N1—C10	-136.5 (4)
C5—C6—C7—C8	-64.5 (5)	C6—C7—N1—C10	103.7 (4)
C1—C6—C7—C12	-125.1 (4)	C3—C2—O1—C11	2.9 (6)
C5—C6—C7—C12	54.5 (5)	C1—C2—O1—C11	-177.8 (4)
N1—C7—C8—C9	48.4 (4)	N1—C10—O2—C9	-5.3 (7)
C12—C7—C8—C9	165.5 (3)	C13—C10—O2—C9	173.2 (4)
C6—C7—C8—C9	-73.9 (4)	C8—C9—O2—C10	36.4 (6)
C7—C8—C9—O2	-57.3 (5)		

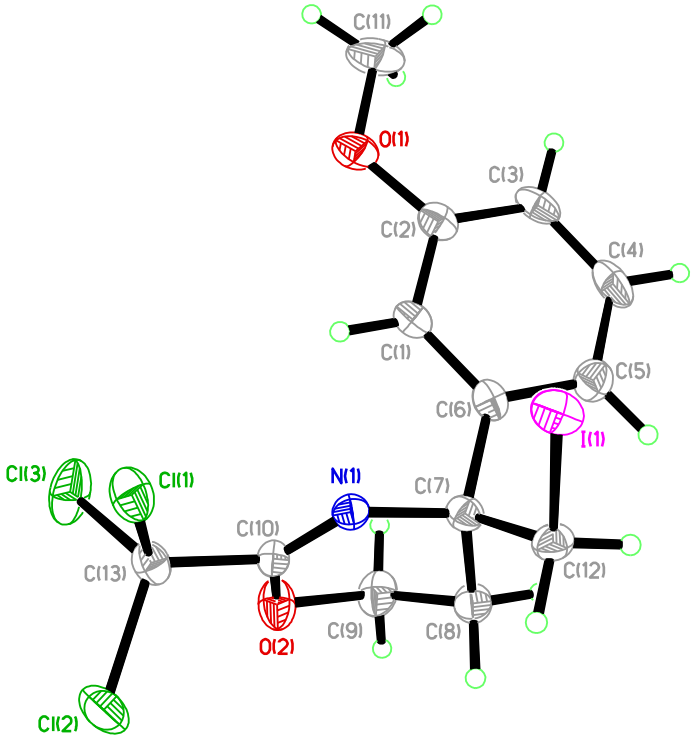


Figure S3. Perspective views showing 50% probability displacement.

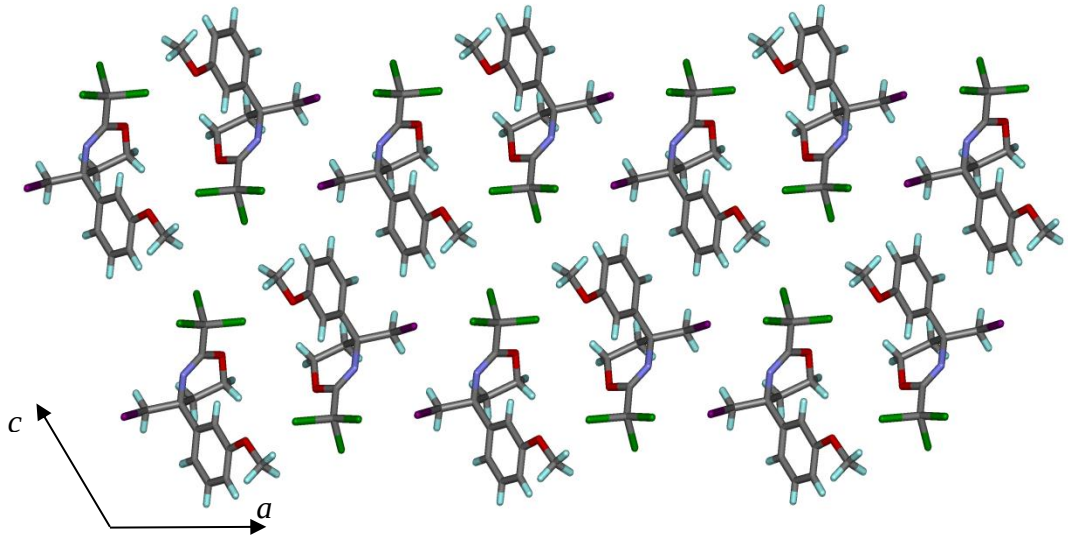
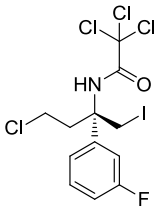
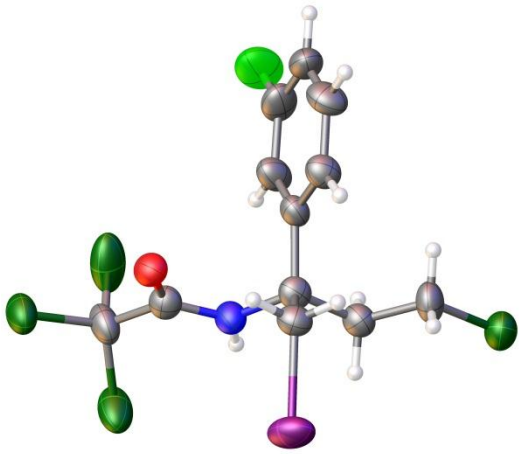


Figure S4. Three-dimensional supramolecular architecture viewed along the *b*-axis direction.

10. X-Ray Crystallographic Data for 5c





A crystal mounted on a diffractometer was collected data at 180 K. The intensities of the reflections were collected by means of a Bruker APEX II DUO CCD diffractometer ($Cu_{K\alpha}$ radiation, λ=1.54178 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 1.0° scans in ω at 30°, 55°, 80° and 115° in 2θ. Data integration down to 0.84 Å resolution was carried out using SAINT V7.46 A[17] with reflection spot size optimisation. Absorption corrections were made with the program SADABS.[17] The structure was solved by the direct methods procedure and refined by least-squares methods again F^2 using SHELXS-97 and SHELXL-97.[18] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S5, geometric parameters are shown in Table S6, and hydrogen-bond parameters are listed in Table S7. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[20]

Table S5. Experimental details

Crystal data	
Chemical formula	$C_{12}H_{11}Cl_4FINO$
M_r	472.92
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	9.9921 (4), 17.5041 (6), 18.6434 (7)
V (Å^3)	3260.8 (2)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	21.52
Crystal size (mm)	0.26 × 0.05 × 0.03
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.071, 0.565
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	57065, 5723, 4899
R_{int}	0.102
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.144, 1.06
No. of reflections	5723
No. of parameters	374
No. of restraints	22
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.29, -0.65
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Flack parameter	-0.018 (9)

Computer programs: *APEX2* v2009.3.0,[17] *SAINT* 7.46A,[17] *SHELXS97*,[18] *SHELXL97*,[18] Bruker *SHELXTL*.[18]

Table S6. Geometric parameters (Å, º)

C1—C2	1.358 (14)	C21—H21	0.9500
C1—C6	1.366 (13)	C22—F2	1.332 (13)
C1—H1	0.9500	C22—C23	1.382 (18)
C2—F1	1.361 (12)	C23—C24	1.31 (2)
C2—C3	1.376 (17)	C23—H23	0.9500
C3—C4	1.340 (16)	C24—C25	1.392 (16)
C3—H3	0.9500	C24—H24	0.9500
C4—C5	1.381 (14)	C25—C26	1.375 (14)
C4—H4	0.9500	C25—H25	0.9500
C5—C6	1.401 (13)	C26—C27	1.549 (12)
C5—H5	0.9500	C27—N2	1.491 (10)
C6—C7	1.543 (12)	C27—C29	1.522 (13)
C7—N1	1.490 (11)	C27—C28	1.532 (13)
C7—C8	1.535 (12)	C28—I2	2.126 (8)
C7—C9	1.539 (13)	C28—H28A	0.9900
C8—I1	2.125 (9)	C28—H28B	0.9900
C8—H8A	0.9900	C29—C30	1.503 (14)
C8—H8B	0.9900	C29—H29A	0.9900
C9—C10	1.537 (12)	C29—H29B	0.9900
C9—H9A	0.9900	C30—Cl5	1.720 (11)
C9—H9B	0.9900	C30—H30A	0.9900
C10—Cl1	1.788 (10)	C30—H30B	0.9900
C10—H10A	0.9900	C31—O2	1.216 (11)
C10—H10B	0.9900	C31—N2	1.326 (10)
C11—O1	1.217 (11)	C31—C32B	1.575 (17)
C11—N1	1.323 (12)	C31—C32	1.581 (16)
C11—C12	1.561 (13)	N2—H2	0.8800
C12—Cl3	1.742 (11)	C32—Cl8	1.742 (15)
C12—Cl2	1.749 (10)	C32—Cl6	1.759 (14)
C12—Cl4	1.803 (12)	C32—Cl7	1.796 (15)
N1—H1A	0.8800	C32B—Cl8B	1.738 (16)
C21—C22	1.357 (16)	C32B—Cl6B	1.754 (15)
C21—C26	1.366 (15)	C32B—Cl7B	1.790 (16)
C2—C1—C6	120.7 (10)	F2—C22—C23	118.9 (11)
C2—C1—H1	119.7	C21—C22—C23	120.9 (11)

C6—C1—H1	119.7	C24—C23—C22	120.2 (11)
C1—C2—F1	119.0 (11)	C24—C23—H23	119.9
C1—C2—C3	121.9 (9)	C22—C23—H23	119.9
F1—C2—C3	119.1 (10)	C23—C24—C25	119.6 (13)
C4—C3—C2	118.4 (9)	C23—C24—H24	120.2
C4—C3—H3	120.8	C25—C24—H24	120.2
C2—C3—H3	120.8	C26—C25—C24	121.0 (12)
C3—C4—C5	121.1 (10)	C26—C25—H25	119.5
C3—C4—H4	119.4	C24—C25—H25	119.5
C5—C4—H4	119.4	C21—C26—C25	118.3 (9)
C4—C5—C6	120.4 (9)	C21—C26—C27	119.8 (9)
C4—C5—H5	119.8	C25—C26—C27	121.9 (9)
C6—C5—H5	119.8	N2—C27—C29	110.4 (7)
C1—C6—C5	117.5 (8)	N2—C27—C28	104.0 (7)
C1—C6—C7	120.2 (8)	C29—C27—C28	111.7 (7)
C5—C6—C7	121.9 (8)	N2—C27—C26	108.6 (7)
N1—C7—C8	110.4 (7)	C29—C27—C26	113.1 (8)
N1—C7—C9	106.0 (7)	C28—C27—C26	108.5 (7)
C8—C7—C9	112.4 (7)	C27—C28—I2	115.5 (6)
N1—C7—C6	108.4 (7)	C27—C28—H28A	108.4
C8—C7—C6	109.7 (7)	I2—C28—H28A	108.4
C9—C7—C6	109.9 (7)	C27—C28—H28B	108.4
C7—C8—I1	116.2 (6)	I2—C28—H28B	108.4
C7—C8—H8A	108.2	H28A—C28—H28B	107.5
I1—C8—H8A	108.2	C30—C29—C27	116.2 (8)
C7—C8—H8B	108.2	C30—C29—H29A	108.2
I1—C8—H8B	108.2	C27—C29—H29A	108.2
H8A—C8—H8B	107.4	C30—C29—H29B	108.2
C10—C9—C7	112.2 (8)	C27—C29—H29B	108.2
C10—C9—H9A	109.2	H29A—C29—H29B	107.4
C7—C9—H9A	109.2	C29—C30—Cl5	115.2 (8)
C10—C9—H9B	109.2	C29—C30—H30A	108.5
C7—C9—H9B	109.2	Cl5—C30—H30A	108.5
H9A—C9—H9B	107.9	C29—C30—H30B	108.5
C9—C10—Cl1	108.9 (7)	Cl5—C30—H30B	108.5
C9—C10—H10A	109.9	H30A—C30—H30B	107.5
Cl1—C10—H10A	109.9	O2—C31—N2	126.2 (8)

C9—C10—H10B	109.9	O2—C31—C32B	120.5 (10)
Cl1—C10—H10B	109.9	N2—C31—C32B	113.2 (10)
H10A—C10—H10B	108.3	O2—C31—C32	118.9 (9)
O1—C11—N1	124.8 (9)	N2—C31—C32	114.5 (10)
O1—C11—C12	119.1 (8)	C31—N2—C27	121.0 (7)
N1—C11—C12	115.9 (8)	C31—N2—H2	119.5
C11—C12—Cl3	112.4 (7)	C27—N2—H2	119.5
C11—C12—Cl2	110.8 (7)	C31—C32—Cl8	110.4 (10)
Cl3—C12—Cl2	111.1 (5)	C31—C32—Cl6	110 (3)
C11—C12—Cl4	106.7 (6)	Cl8—C32—Cl6	110.5 (11)
Cl3—C12—Cl4	108.6 (6)	C31—C32—Cl7	109.5 (10)
Cl2—C12—Cl4	107.0 (6)	Cl8—C32—Cl7	110.0 (9)
C11—N1—C7	122.8 (8)	Cl6—C32—Cl7	106.4 (14)
C11—N1—H1A	118.6	C31—C32B—Cl8B	112.1 (11)
C7—N1—H1A	118.6	C31—C32B—Cl6B	110 (3)
C22—C21—C26	119.9 (11)	Cl8B—C32B—Cl6B	109.6 (15)
C22—C21—H21	120.1	C31—C32B—Cl7B	107.0 (10)
C26—C21—H21	120.1	Cl8B—C32B—Cl7B	110.1 (10)
F2—C22—C21	120.1 (12)	Cl6B—C32B—Cl7B	107.5 (13)
C6—C1—C2—F1	178.8 (9)	C22—C21—C26—C27	177.7 (9)
C6—C1—C2—C3	1.0 (17)	C24—C25—C26—C21	-0.1 (14)
C1—C2—C3—C4	-0.6 (17)	C24—C25—C26—C27	-178.0 (9)
F1—C2—C3—C4	-178.4 (10)	C21—C26—C27—N2	43.9 (11)
C2—C3—C4—C5	1.1 (17)	C25—C26—C27—N2	-138.2 (9)
C3—C4—C5—C6	-2.1 (16)	C21—C26—C27—C29	166.9 (8)
C2—C1—C6—C5	-1.9 (14)	C25—C26—C27—C29	-15.2 (12)
C2—C1—C6—C7	-174.8 (9)	C21—C26—C27—C28	-68.5 (10)
C4—C5—C6—C1	2.4 (14)	C25—C26—C27—C28	109.4 (10)
C4—C5—C6—C7	175.2 (9)	N2—C27—C28—I2	180.0 (5)
C1—C6—C7—N1	-39.8 (11)	C29—C27—C28—I2	60.8 (9)
C5—C6—C7—N1	147.6 (8)	C26—C27—C28—I2	-64.5 (8)
C1—C6—C7—C8	-160.4 (8)	N2—C27—C29—C30	-46.5 (11)
C5—C6—C7—C8	27.0 (11)	C28—C27—C29—C30	68.8 (10)
C1—C6—C7—C9	75.6 (10)	C26—C27—C29—C30	-168.4 (8)
C5—C6—C7—C9	-97.0 (10)	C27—C29—C30—Cl5	-171.7 (7)
N1—C7—C8—I1	58.7 (9)	O2—C31—N2—C27	3.4 (14)

C9—C7—C8—I1	-59.4 (9)	C32B—C31—N2—C27	-172.4 (9)
C6—C7—C8—I1	178.1 (6)	C32—C31—N2—C27	175.6 (9)
N1—C7—C9—C10	-176.9 (7)	C29—C27—N2—C31	-60.3 (10)
C8—C7—C9—C10	-56.2 (10)	C28—C27—N2—C31	179.7 (7)
C6—C7—C9—C10	66.2 (9)	C26—C27—N2—C31	64.3 (10)
C7—C9—C10—Cl1	-176.1 (6)	O2—C31—C32—Cl8	108.5 (12)
O1—C11—C12—Cl3	-138.6 (8)	N2—C31—C32—Cl8	-64.3 (13)
N1—C11—C12—Cl3	45.6 (10)	C32B—C31—C32—Cl8	-150 (7)
O1—C11—C12—Cl2	-13.7 (11)	O2—C31—C32—Cl6	-13.7 (16)
N1—C11—C12—Cl2	170.5 (7)	N2—C31—C32—Cl6	173.5 (11)
O1—C11—C12—Cl4	102.4 (9)	C32B—C31—C32—Cl6	88 (6)
N1—C11—C12—Cl4	-73.4 (9)	O2—C31—C32—Cl7	-130.2 (10)
O1—C11—N1—C7	-3.5 (14)	N2—C31—C32—Cl7	57.0 (12)
C12—C11—N1—C7	172.0 (8)	C32B—C31—C32—Cl7	-29 (6)
C8—C7—N1—C11	59.5 (11)	O2—C31—C32B—Cl8B	134.4 (11)
C9—C7—N1—C11	-178.6 (8)	N2—C31—C32B—Cl8B	-49.5 (14)
C6—C7—N1—C11	-60.7 (11)	C32—C31—C32B—Cl8B	50 (6)
C26—C21—C22—F2	-178.8 (9)	O2—C31—C32B—Cl6B	12.0 (16)
C26—C21—C22—C23	-0.8 (16)	N2—C31—C32B—Cl6B	-172.0 (12)
F2—C22—C23—C24	-179.6 (11)	C32—C31—C32B—Cl6B	-73 (6)
C21—C22—C23—C24	2.5 (18)	O2—C31—C32B—Cl7B	-104.7 (13)
C22—C23—C24—C25	-2.8 (17)	N2—C31—C32B—Cl7B	71.3 (12)
C23—C24—C25—C26	1.6 (16)	C32—C31—C32B—Cl7B	171 (7)
C22—C21—C26—C25	-0.3 (15)		

Table S7. Hydrogen-bond parameters

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N1—H1A···O2	0.88	2.14	2.940 (10)	150.1

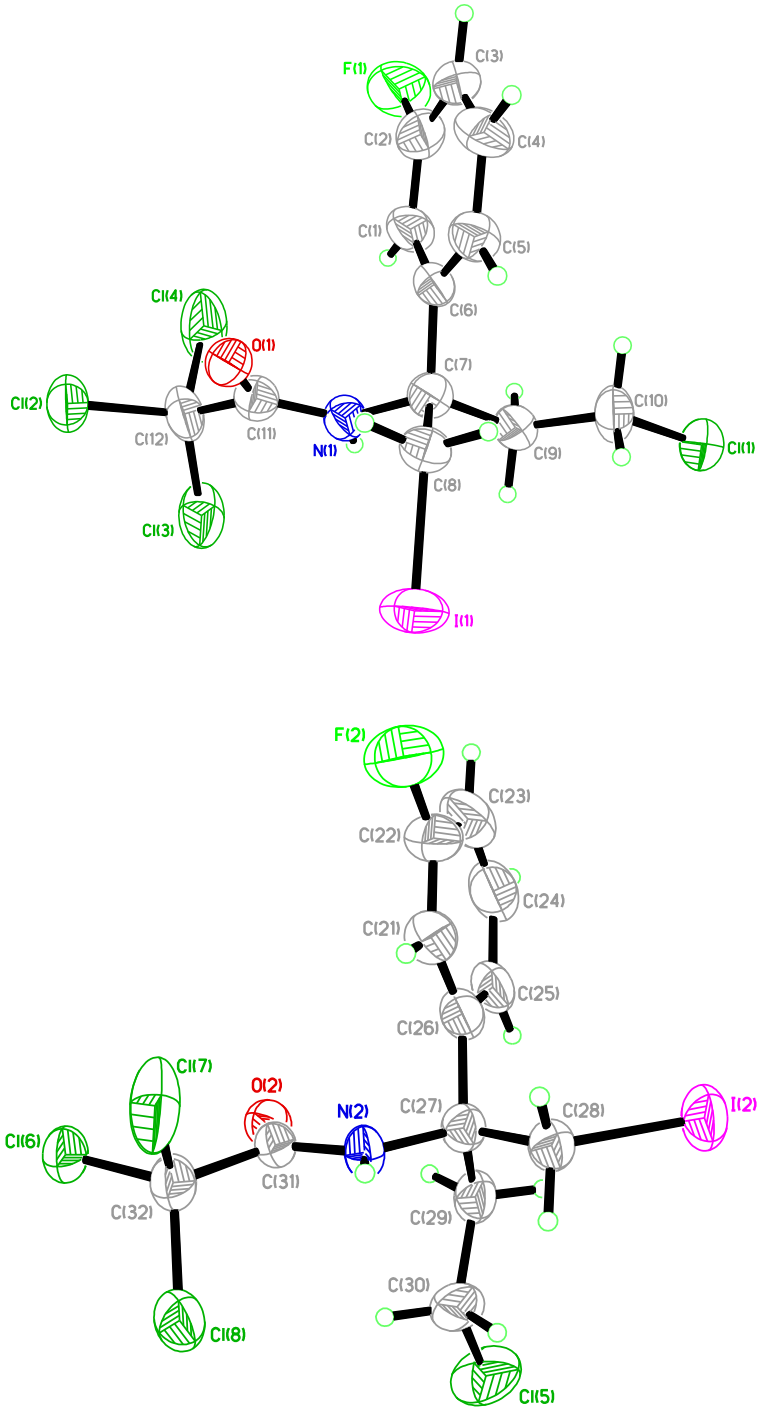


Figure S5. Perspective views showing 50% probability displacement.

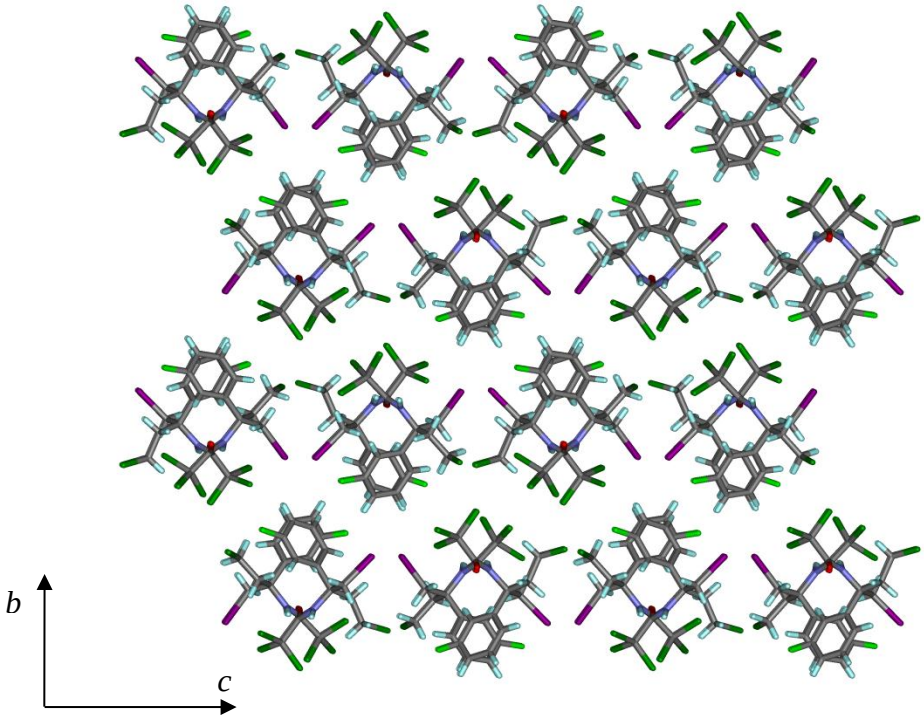
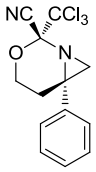
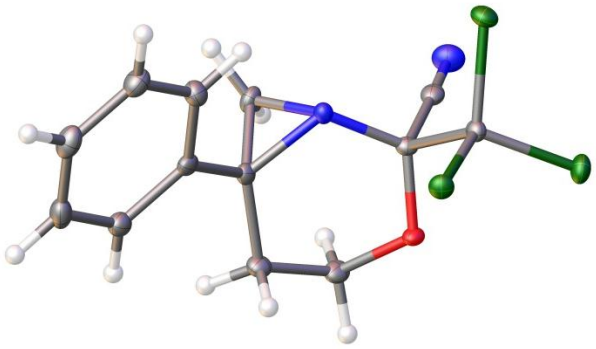


Figure S6. Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

11. X-Ray Crystallographic Data for 7a





A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.78 Å resolution was carried out using SAINT V7.46 A[17] with reflection spot size optimization. Absorption corrections were made with the program SADABS.[17] The structure was solved by the direct methods procedure and refined by least-squares methods again F^2 using SHELXS-97 and SHELXL-97[18] with OLEX 2 interface.[19] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S8, and geometric parameters are shown in Table S9. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[20]

Table S8. Experimental details

Crystal data	
Chemical formula	$C_{13}H_{11}Cl_3N_2O$
M_r	317.59
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, *b*, *c* (Å)	11.2235 (16), 11.7597 (17), 20.531 (3)
V (Å^3)	2709.8 (7)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.67
Crystal size (mm)	0.18 × 0.10 × 0.08
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.889, 0.949
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32256, 5996, 5337
R_{int}	0.057
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.061, 1.04
No. of reflections	5996
No. of parameters	343
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, -0.23
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Flack parameter	-0.03 (4)

Computer programs: *APEX2* v2009.3.0,[17] *SAINT* 7.46A,[17] *SHELXS97*,[18] *SHELXL97*,[18] Bruker *SHELXTL*).[18]

Table S9. Geometric parameters (Å, º)

C21—C22	1.388 (3)	C1—C2	1.391 (3)
C21—C26	1.391 (3)	C1—C6	1.395 (3)
C21—H21	0.9500	C1—H1	0.9500
C22—C23	1.390 (3)	C2—C3	1.389 (3)
C22—H22	0.9500	C2—H2	0.9500
C23—C24	1.382 (3)	C3—C4	1.383 (3)
C23—H23	0.9500	C3—H3	0.9500
C24—C25	1.389 (3)	C4—C5	1.395 (3)
C24—H24	0.9500	C4—H4	0.9500
C25—C26	1.398 (3)	C5—C6	1.396 (3)
C25—H25	0.9500	C5—H5	0.9500
C26—C27	1.502 (3)	C6—C7	1.507 (3)
C27—C31	1.493 (3)	C7—C11	1.479 (3)
C27—N3	1.499 (3)	C7—N1	1.496 (3)
C27—C28	1.516 (3)	C7—C8	1.520 (3)
C28—C29	1.510 (3)	C8—C9	1.518 (3)
C28—H28A	0.9900	C8—H8A	0.9900
C28—H28B	0.9900	C8—H8B	0.9900
C29—O2	1.449 (2)	C9—O1	1.448 (3)
C29—H29A	0.9900	C9—H9A	0.9900
C29—H29B	0.9900	C9—H9B	0.9900
C30—O2	1.404 (2)	C10—O1	1.393 (3)
C30—N3	1.453 (3)	C10—N1	1.462 (3)
C30—C33	1.505 (3)	C10—C13	1.509 (3)
C30—C32	1.565 (3)	C10—C12	1.570 (3)
C31—N3	1.478 (3)	C11—N1	1.498 (3)
C31—H31A	0.9900	C11—H11A	0.9900
C31—H31B	0.9900	C11—H11B	0.9900
C32—Cl4	1.763 (2)	C12—Cl2	1.767 (2)
C32—Cl6	1.768 (2)	C12—Cl3	1.769 (2)
C32—Cl5	1.776 (2)	C12—Cl1	1.772 (2)
C33—N4	1.144 (3)	C13—N2	1.138 (3)
C26—C21—C22—C23	0.4 (3)	C6—C1—C2—C3	-0.7 (3)
C21—C22—C23—C24	-0.8 (3)	C1—C2—C3—C4	0.2 (3)
C22—C23—C24—C25	0.9 (3)	C2—C3—C4—C5	0.2 (4)

C23—C24—C25—C26	-0.6 (3)	C3—C4—C5—C6	-0.1 (3)
C22—C21—C26—C25	-0.1 (3)	C2—C1—C6—C5	0.7 (3)
C22—C21—C26—C27	-174.9 (2)	C2—C1—C6—C7	-176.8 (2)
C24—C25—C26—C21	0.2 (3)	C4—C5—C6—C1	-0.3 (3)
C24—C25—C26—C27	174.9 (2)	C4—C5—C6—C7	177.3 (2)
C21—C26—C27—C31	120.3 (2)	C1—C6—C7—C11	-108.9 (2)
C25—C26—C27—C31	-54.4 (3)	C5—C6—C7—C11	73.6 (3)
C21—C26—C27—N3	-172.73 (18)	C1—C6—C7—N1	-40.2 (3)
C25—C26—C27—N3	12.6 (3)	C5—C6—C7—N1	142.4 (2)
C21—C26—C27—C28	-30.1 (3)	C1—C6—C7—C8	101.8 (2)
C25—C26—C27—C28	155.3 (2)	C5—C6—C7—C8	-75.6 (2)
C31—C27—C28—C29	45.6 (3)	C11—C7—C8—C9	44.5 (3)
N3—C27—C28—C29	-22.1 (3)	N1—C7—C8—C9	-25.7 (3)
C26—C27—C28—C29	-163.72 (18)	C6—C7—C8—C9	-166.71 (18)
C27—C28—C29—O2	53.8 (2)	C7—C8—C9—O1	54.8 (2)
C26—C27—C31—N3	103.1 (2)	C6—C7—C11—N1	105.0 (2)
C28—C27—C31—N3	-106.9 (2)	C8—C7—C11—N1	-107.5 (2)
O2—C30—C32—Cl4	-66.87 (18)	O1—C10—C12—Cl2	-65.12 (19)
N3—C30—C32—Cl4	58.71 (18)	N1—C10—C12—Cl2	61.5 (2)
C33—C30—C32—Cl4	176.86 (14)	C13—C10—C12—Cl2	177.77 (15)
O2—C30—C32—Cl6	54.34 (19)	O1—C10—C12—Cl3	173.94 (14)
N3—C30—C32—Cl6	179.92 (13)	N1—C10—C12—Cl3	-59.5 (2)
C33—C30—C32—Cl6	-61.93 (19)	C13—C10—C12—Cl3	56.8 (2)
O2—C30—C32—Cl5	173.85 (14)	O1—C10—C12—Cl1	54.4 (2)
N3—C30—C32—Cl5	-60.58 (19)	N1—C10—C12—Cl1	-179.03 (14)
C33—C30—C32—Cl5	57.6 (2)	C13—C10—C12—Cl1	-62.7 (2)
O2—C30—N3—C31	-77.7 (2)	O1—C10—N1—C7	-12.8 (3)
C33—C30—N3—C31	47.3 (2)	C13—C10—N1—C7	113.2 (2)
C32—C30—N3—C31	165.65 (17)	C12—C10—N1—C7	-131.40 (19)
O2—C30—N3—C27	-7.8 (3)	O1—C10—N1—C11	-80.2 (2)
C33—C30—N3—C27	117.25 (19)	C13—C10—N1—C11	45.8 (2)
C32—C30—N3—C27	-124.41 (18)	C12—C10—N1—C11	161.21 (18)
C27—C31—N3—C30	108.5 (2)	C11—C7—N1—C10	-105.8 (2)
C31—C27—N3—C30	-108.8 (2)	C6—C7—N1—C10	144.71 (19)
C26—C27—N3—C30	141.12 (18)	C8—C7—N1—C10	4.2 (3)
C28—C27—N3—C30	-1.2 (3)	C6—C7—N1—C11	-109.5 (2)
C26—C27—N3—C31	-110.1 (2)	C8—C7—N1—C11	110.0 (2)

C28—C27—N3—C31	107.6 (2)	C7—C11—N1—C10	108.0 (2)
N3—C30—O2—C29	41.7 (2)	N1—C10—O1—C9	45.1 (2)
C33—C30—O2—C29	-83.4 (2)	C13—C10—O1—C9	-79.8 (2)
C32—C30—O2—C29	159.91 (17)	C12—C10—O1—C9	165.71 (17)
C28—C29—O2—C30	-65.2 (2)	C8—C9—O1—C10	-66.5 (2)

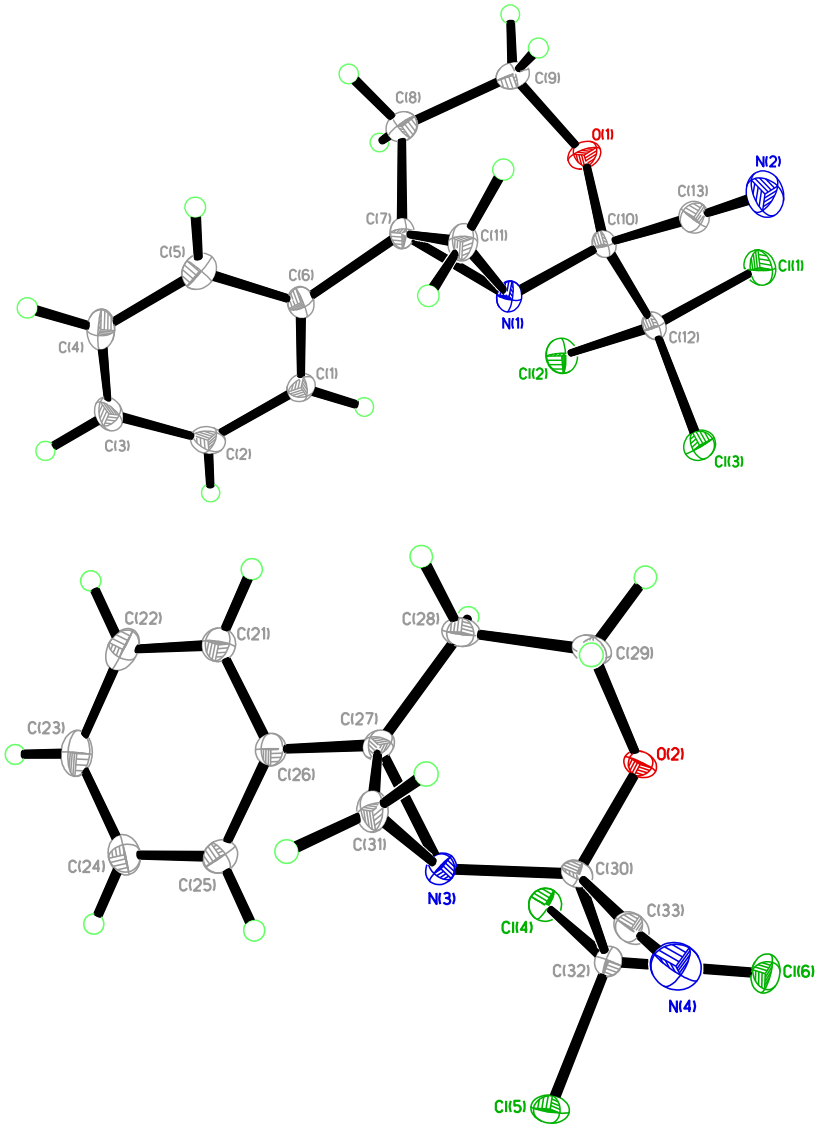


Figure S7. Perspective views showing 50% probability displacement.

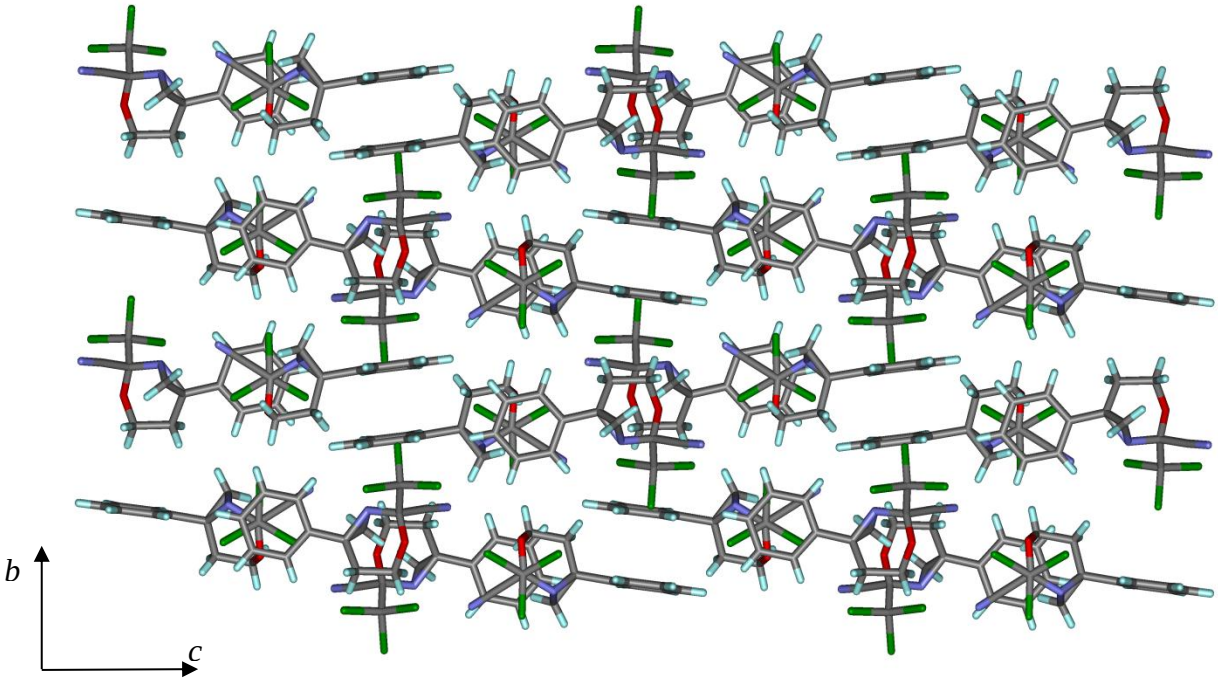
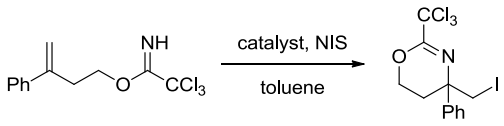
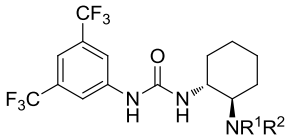


Figure S8. Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

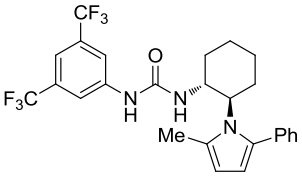
12. Results with sub-optimal catalysts





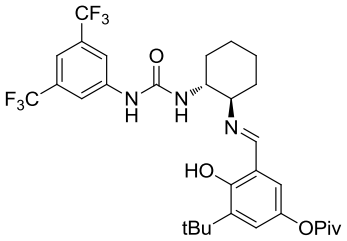
R^1	R^2	time	yield (%)	ee (%)
nC_5H_{11}	nC_5H_{11}	9 d	91	–15
H	H	5 d	83	–4
H	(*R*)-tBu-sulfinate	9 d	53	0

Conditions: 10 mol% catalyst, –20 °C, 0.05 M, 1.1 eq. NIS



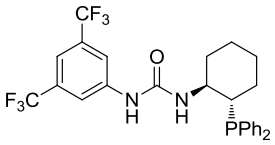
9 d, 80% yield, –12% ee

Conditions: 10 mol% catalyst –20 °C, 0.05 M, 1.1 eq. NIS



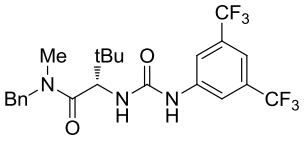
6 d, 61% yield, –5% ee

Conditions: 10 mol% catalyst –20 °C, 0.05 M, 1.1 eq. NIS



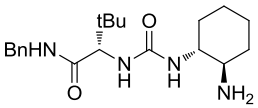
9 d, 75% yield, 1% ee

Conditions: 10 mol% catalyst –20 °C, 0.05 M, 1.1 eq. NIS (w/ 2 mol% I_2)



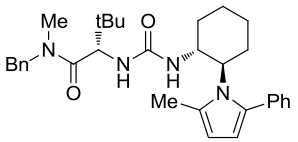
9 d, 78% yield, 4% ee

Conditions: 10 mol% catalyst –20 °C, 0.05 M, 1.1 eq. NIS (w/ 2 mol% I_2)



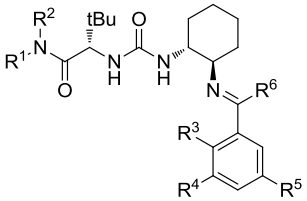
13 d, 66% yield, 0% ee

Conditions: 10 mol% catalyst –20 °C, 0.05 M, 1.1 eq. NIS (w/ 2 mol% I_2)



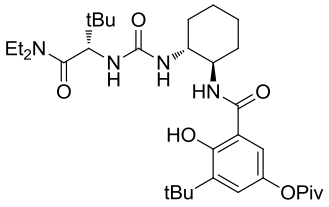
13 d, 91% yield, –1% ee

Conditions: 10 mol% catalyst –20 °C, 0.05 M, 1.1 eq. NIS



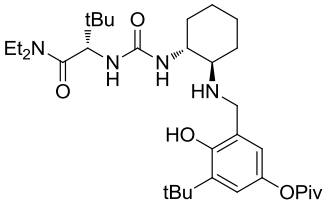
R^1	R^2	R^3	R^4	R^5	R^6	time	eq. NIS	yield (%)	ee (%)
Bn	H	OH	tBu	OPiv	H	9 d	1.1	56	27
Bn	H	H	H	H	Ph	14 d	1.1	55	0
Bn	H	H	H	H	H	14 d	1.1	81	–1
Bn	Me	OH	tBu	OPiv	H	14 d	1.1	50	28
Et	Et	OH	tBu	OPiv	H	1.5 d	5	33	74
Et	Et	OH	tBu	OPiv	Me	1 d	5	30	21
Et	Et	OH	tBu	OAc	H	1 d	3	8	36
Et	Et	OMe	tBu	OPiv	H	6 d	3	12	5
Et	Et	OH	tBu	NHPiv	H	1 d	3	11	24
Et	Et	OH	tBu	OtBu	H	1 d	3	1	7
Et	Et	OH	tBu	OTBDPS	H	1.5 d	5	30	27
Et	Et	OH	tBu	OCOAd	H	1.5 d	5	20	67
$–(CH_2)_4–$		OH	tBu	OPiv	H	1.5 d	5	31	74

Conditions: 10 mol% catalyst, 0.05 M, –20 °C



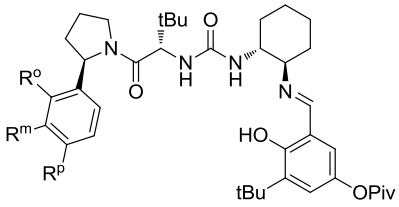
1.5 d, 10% yield, 6% ee

Conditions: 10 mol% catalyst –20 °C, 0.05 M, 3 eq. NIS



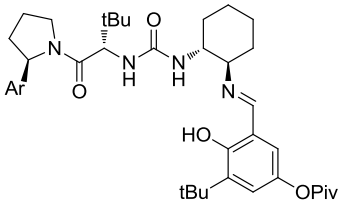
1.5 d, 90% yield, 0% ee

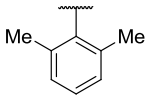
Conditions: 10 mol% catalyst –20 °C, 0.05 M, 3 eq. NIS



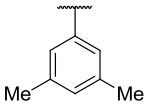
R^o	R^m	R^p	time	temp (°C)	yield (%)	ee (%)
H	H	H	1.5 d	–20	44	79
H	H	CF_3	1.5 d	–20	43	81
H	H	F	1.5 d	–20	84	60
H	H	Me	1.5 d	–20	74	76
H	H	tBu	1.5 d	–20	49	80
H	H	OMe	1.5 d	–20	45	69
H	H	NMe_2	1.5 d	–20	59	80
H	Me	H	1.5 d	–20	79	79
Me	H	H	1.5 d	–20	100	79
Me	H	H	1.5 d	–40	100	90

Conditions: 10 mol% catalyst, –20 °C, 0.05 M, 5 eq. NIS, 1.5 d

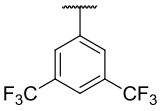




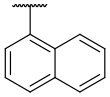
30% yield, 80% ee
(–40 °C, 0.1 M, 3 eq. NIS, 12 h)



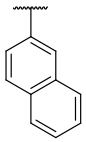
46% yield, 79% ee



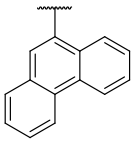
55% yield, 69% ee



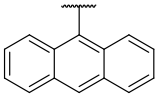
52% yield, 77% ee



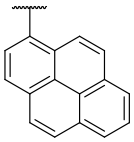
74% yield, 72% ee



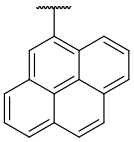
87% yield, 88% ee
(–30 °C, 3 d)



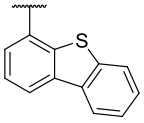
66% yield, 63% ee



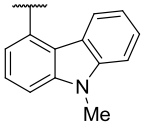
63% yield, 64% ee



94% yield, 62% ee



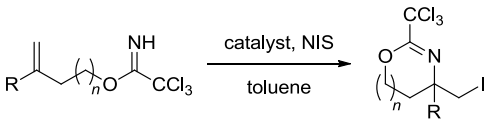
45% yield, 78% ee

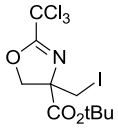


96% yield, 65% ee

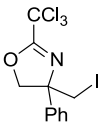
Conditions: 10 mol% catalyst, –20 °C, 0.05 M, 5 eq. NIS, 1.5 d

13. Results with sub-optimal and unreactive substrates

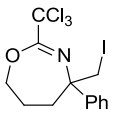




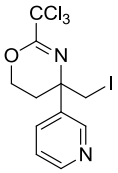
0% yield
(5 mol% **3f**, 1.5 eq. NIS,
0.2 M, 0 °C, 2 d)



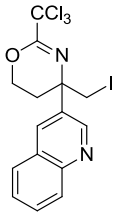
14% yield, 2% ee
(10 mol% **3a**, 1 eq. NIS,
0.05 M, –60 to –10 °C, 14 d)



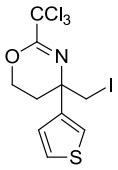
0% yield
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –20 °C, 18 h)



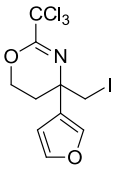
23% yield, 33% ee
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –30 to 0 °C, 2 d)



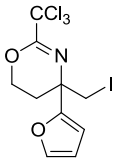
43% yield, 34% ee
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –30 to 0 °C, 2 d)



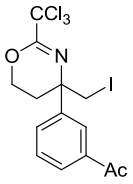
47% yield, 51% ee
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –40 °C, 14 h)



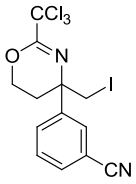
47% yield, 48% ee
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –40 °C, 16 h)



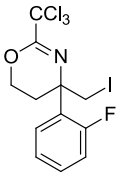
100% yield, 5% ee
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –40 °C, 16 h)



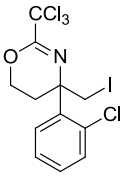
52% yield, 72% ee
(15 mol% **3f**, 1.5 eq. NIS,
0.25 M, –40 °C, 6 d)



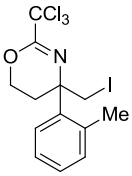
15% yield, 90% ee
(5 mol% **3f**, 1.5 eq. NIS,
0.25 M, –40 °C, 6 d)



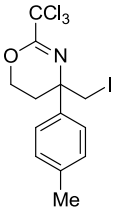
0% yield
(5 mol% **3f**, 1.5 eq. NIS,
0.25 M, –40 °C, 6 d)



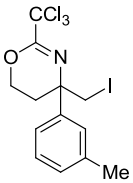
0% yield
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, 0 °C, 13 h)



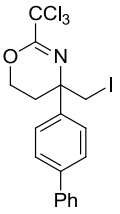
0% yield
(5 mol% **3f**, 3 eq. NIS,
0.2 M, –40 °C, 12 h)



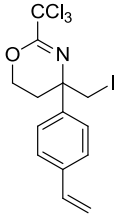
93%, 66% ee
(15 mol% **3f**, 1.5 eq. NIS,
0.25 M, –50 °C, 3 d)



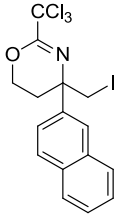
58% yield, 62% ee
(5 mol **3f**, 3 eq. NIS,
0.2 M, –40 °C, 12 h)



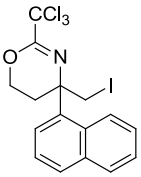
45% yield, 77% ee
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –40 °C, 16 h)



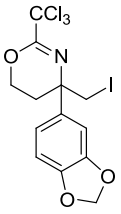
75% yield, 79% ee
(5 mol% **3f**, 3 eq. NIS,
0.2 M, –40 °C, 12 h)



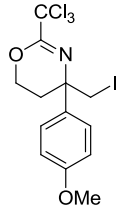
83% yield, 67% ee
(5 mol% **3f**, 3 eq. NIS,
0.2 M, –40 °C, 12 h)



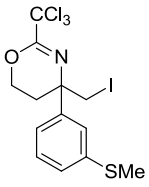
75% yield, 79% ee
(5 mol% **3f**, 3 eq. NIS,
0.2 M, –40 °C, 12 h)



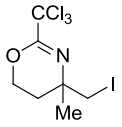
28% yield, 43% ee
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –40 °C, 16 h)



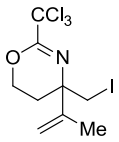
65% yield, 11% ee
(10 mol% **3f**, 1.5 eq. NIS,
0.25 M, –60 °C, 15 h)



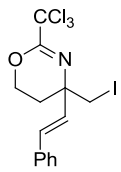
22% yield, 88% ee
(15 mol% **3f**, 1.5 eq. NIS,
0.2 M, –40 °C, 5 d)



87% yield, 27% ee
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –40 °C, 15 h)



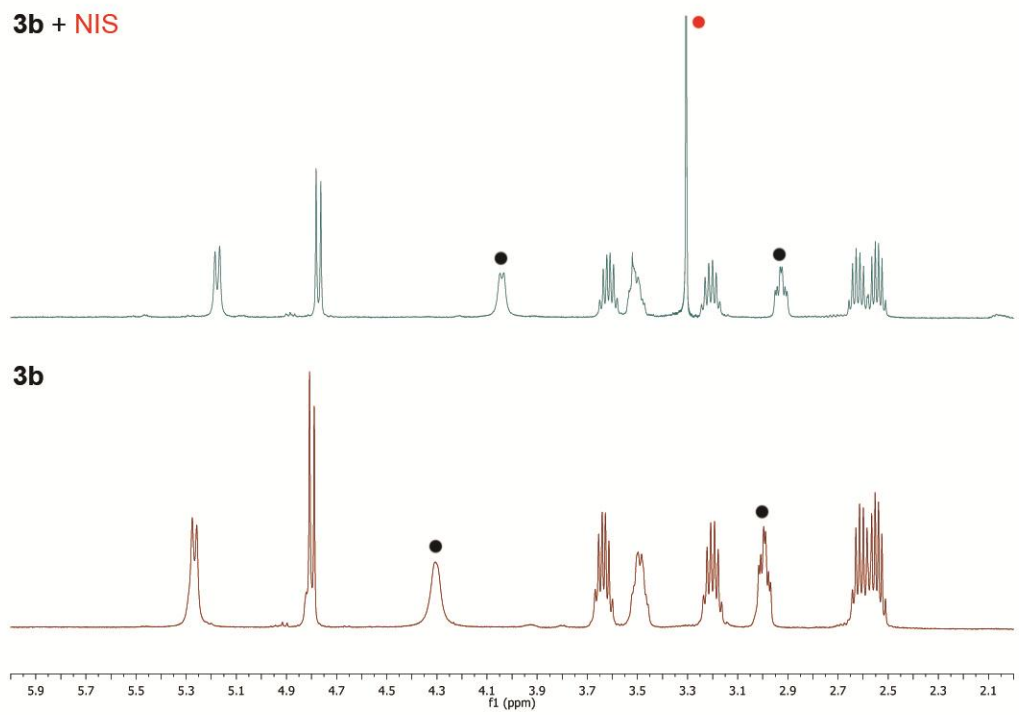
19% yield, 77% ee
(10 mol% **3f**, 1.5 eq. NIS,
0.25 M, –40 °C, 4.5 d)



44% yield, 50% ee
(5 mol% **3f**, 1.1 eq. NIS,
0.2 M, –40 °C, 16 h)

14. NMR and DFT studies of NIS binding to 3b

A 1:1 mixture of **3b** and *N*-iodosuccinimide displays the following ^{1}H NMR spectrum at a concentration of 0.1 M (C_6D_6). The peaks marked with the black dots indicate the shift of the urea N–H protons of catalyst **3b**. The peak marked with the red dot corresponds to the protons on the carbon skeleton of NIS.



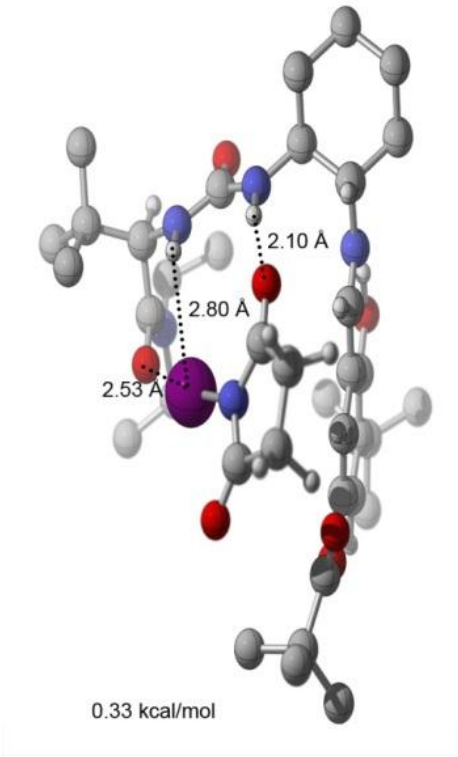
Density functional theory (DFT) calculations were performed at Harvard University using Gaussian 09[21] using the hybrid Hartree-Fock/DFT method B3LYP[22] with a 3-21g[23] basis set. The effective core

[21] Gaussian 09, Revision **A.1**, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, Ö.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J. Gaussian, Inc., Wallingford CT, 2009.

[22] (a) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B.* **1988**, *37*, 785-789. (c) Vosko, S.H.; Wilk, L.; Nusair, M. *Can J. Phys.* **1980**, *58*, 1200-1211. (d) Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. *J. Phys. Chem.* **1994**, *98*, 11623-11627.

[23] (a) Binkley, J.S.; Pople, J.A.; Hehre, W.J. *J. Am. Chem. Soc.* **1980**, *102*, 939-947. (b) Gordon, M.S.; Binkley, J.S.; Pople, J.A.; Pietro, W.J.; Hehre, W.J. *J. Am. Chem. Soc.* **1982**, *104*, 2797-2803. (c) Pietro, W.J.; Francl, M.M.; Hehre, W.J.; Defrees, D.J.; Pople, J.A.; Binkley, J.S. *J. Am. Chem. Soc.* **1982**, *104*, 5039-5048. (d) Dobbs, K.D.; Hehre, W.J. *J. Comp. Chem.* **1986**, *7*, 359-378. (e) Dobbs, K.D.; Hehre, W.J. *J. Comp. Chem.* **1987**, *8*, 861-879. (f) Dobbs, K.D.; Hehre, W.J. *J. Comp. Chem.* **1987**, *8*, 880-893.

pseudopotential of Hay and Wadt LANL2[24] was used to model the iodine atom. Figures were generated using CYLview.[25] The Hessian matrix was calculated to verify the nature of all stationary points.



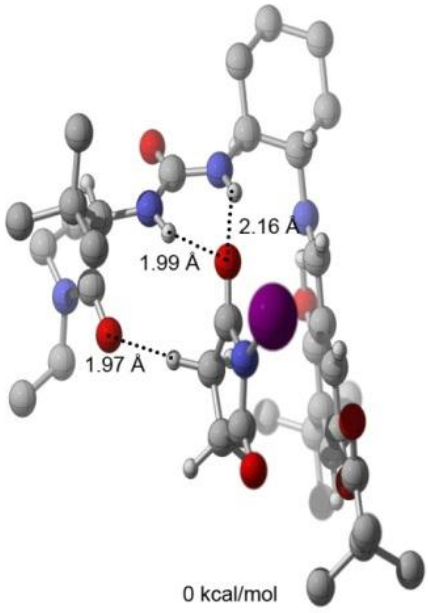
Conformer 1

```
 Electronic energy=                            -2243.501165
 Zero-point correction=                            0.935345
 (Hartree/Particle)
 Thermal correction to Energy=                     0.989280
 Thermal correction to Enthalpy=                   0.990224
 Thermal correction to Gibbs Free Energy=          0.846028
 Sum of electronic and zero-point Energies=    -2243.501165
 Sum of electronic and thermal Energies=       -2243.447230
 Sum of electronic and thermal Enthalpies=     -2243.446286
 Sum of electronic and thermal Free Energies= -2243.590482

 Lowest vibrational mode= 9.62 cm-1

 C                 -0.75451000    2.85142600    1.14232100
 C                 -1.65030300    2.70734400    2.23843400
 C                 -2.81747500    1.97756200    2.03176800
 H                 -3.51914000    1.82254600    2.83793200
 C                 -3.13558600    1.39902900    0.79302300
 C                 -2.28646000    1.55835200   -0.28223500
 H                 -2.53291500    1.13313100   -1.23933800
 C                 -1.09205400    2.27071200   -0.10601000
```

[24] Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 299-310.
[25] CYLview, 1.0b; Legault, C.Y., Université de Sherbrooke, 2009 (http://www.cylview.org)

C	-0.17101400	2.36824600	-1.21915700
H	-0.45407100	1.84931100	-2.13591500
C	1.85803400	2.99785000	-2.30985700
H	1.33042600	2.55907300	-3.17229800
C	2.26091200	4.45461000	-2.62383200
H	2.73884000	4.87466400	-1.72995100
H	1.35516700	5.03799600	-2.82465200
C	3.23360100	4.52022400	-3.81961700
H	2.73024800	4.14565400	-4.72152300
H	3.51867500	5.56199600	-4.00808400
C	4.48658200	3.66113600	-3.54098300
H	5.02871700	4.08324100	-2.68402900
H	5.16246500	3.68222100	-4.40409900
C	4.08389800	2.20559800	-3.21984300
H	3.59775900	1.75208900	-4.09437600
H	4.96629800	1.60453600	-2.97487800
C	3.10995100	2.14002500	-2.02021500
H	3.60857400	2.51430700	-1.12214200
C	3.37224800	0.12376600	-0.67252700
C	3.48750500	-1.89367500	0.73302900
H	4.25516700	-1.23616100	1.13670800
C	2.28320900	-1.97431000	1.69140300
C	-1.31054400	3.33293200	3.60250600
C	0.01696800	2.71941600	4.13028800
H	-0.10900500	1.64343900	4.30121300
H	0.29005300	3.19547600	5.07981700
H	0.81102900	2.88150800	3.39932000
C	-2.41417000	3.07767100	4.65412700
H	-3.36995800	3.51596000	4.34419900
H	-2.11481300	3.54714900	5.59787200
H	-2.55513600	2.00601100	4.83737500
C	-1.14572200	4.86929700	3.43449100
H	-0.36009100	5.07689000	2.70719300
H	-0.87916900	5.31800600	4.39920800
H	-2.08734800	5.31258600	3.09091900
C	-4.86808700	0.02368500	-0.34270100
C	-5.95891300	-0.95571600	0.06787400
C	-5.27949600	-2.06166100	0.92173600
H	-4.52394500	-2.57529500	0.31943900
H	-6.03705500	-2.78693700	1.23876900
H	-4.80897600	-1.62079900	1.80395100
C	-6.56086900	-1.57707200	-1.20555100
H	-6.97687600	-0.80265700	-1.85829800
H	-7.35984100	-2.27224700	-0.92701300
H	-5.78218500	-2.12334200	-1.74445300
C	-7.02685200	-0.20797000	0.90021200
H	-6.56199600	0.27013200	1.76545700
H	-7.78220900	-0.92226300	1.24509800
H	-7.52401300	0.55853300	0.29462100
C	4.12511200	-3.29423400	0.45405000
C	5.38976600	-3.07877400	-0.40732900
H	5.12555100	-2.57970500	-1.34393900

H	5.85338900	-4.04501600	-0.63698500
H	6.12074500	-2.45714700	0.12356900
C	3.14580300	-4.23058200	-0.28937700
H	2.21072600	-4.32402700	0.26567100
H	3.60338600	-5.21943600	-0.40686400
H	2.92482300	-3.84318100	-1.29050700
C	4.52506000	-3.93732200	1.80287500
H	5.23392100	-3.29911400	2.34444600
H	5.00895600	-4.90305700	1.62046300
H	3.64760900	-4.10807400	2.43626300
C	3.56768300	-0.78360400	3.52520100
H	4.46504200	-1.27356200	3.14610800
H	3.51709400	-0.98782900	4.59981600
C	3.61838600	0.73272400	3.25542100
H	4.44828100	1.17509900	3.81857000
H	2.68862700	1.21261200	3.57777000
H	3.77393100	0.92067100	2.18879300
C	1.13020900	-1.43493000	3.76110500
H	0.27781500	-1.27600000	3.09924900
H	1.20398700	-0.59573700	4.45712400
C	0.97298600	-2.77413500	4.50285500
H	0.08140100	-2.75176000	5.13873600
H	1.84613200	-2.97925300	5.13121200
H	0.86080700	-3.57187400	3.76425900
N	0.95903900	2.99288400	-1.13074500
N	2.74081300	0.74693800	-1.71828200
N	3.05054900	-1.21452000	-0.49189200
N	2.36430000	-1.42429900	2.92204900
O	0.41782600	3.52586400	1.27739200
H	0.92650900	3.47263300	0.33233000
O	-4.32543300	0.62413200	0.78622900
O	-4.47466800	0.25426600	-1.48596500
O	4.20061100	0.70922600	0.06972400
O	1.19641300	-2.54389100	1.33953400
H	2.34146800	-1.65471000	-1.06739500
C	-0.92745900	-0.71339700	-3.26404700
H	1.97616500	0.30849600	-2.23688200
O	0.18622300	-0.16826200	-3.22175000
C	-1.96175300	-0.57900900	-4.39317100
H	-2.11151900	0.47869900	-4.62207800
H	-1.55722500	-1.06879800	-5.28545900
C	-3.22483500	-1.27948600	-3.85769900
H	-3.99384400	-0.56677100	-3.54616800
H	-3.65772700	-2.00782600	-4.54586000
C	-2.77855900	-1.97375000	-2.56834300
O	-3.43416400	-2.72775400	-1.85387000
N	-1.46007400	-1.55443000	-2.29562700
I	-0.38503900	-2.10054000	-0.58699000



Conformer 2

```
 Electronic energy=                            -2244.433259
 Zero-point correction=                            0.934684
(Hartree/Particle)
 Thermal correction to Energy=                     0.988973
 Thermal correction to Enthalpy=                   0.989917
 Thermal correction to Gibbs Free Energy=          0.842256
 Sum of electronic and zero-point Energies=    -2243.498575
 Sum of electronic and thermal Energies=       -2243.444286
 Sum of electronic and thermal Enthalpies=     -2243.443342
 Sum of electronic and thermal Free Energies= -2243.591003

 Lowest vibrational mode= 8.83 cm-1

 C                 -1.29660200    3.34999300    0.18782700
 C                 -2.23096900    3.53655300    1.24681800
 C                 -3.28816100    2.64035000    1.34116500
 H                 -4.02056100    2.73395800    2.12953000
 C                 -3.46549300    1.57739000    0.43861300
 C                 -2.57639100    1.39648700   -0.60291800
 H                 -2.71392300    0.58780100   -1.30095400
 C                 -1.48822200    2.27770000   -0.72550400
 C                 -0.53307800    2.07477800   -1.79918400
 H                 -0.72056800    1.22899100   -2.46997400
 C                  1.47488100    2.59856400   -3.03214000
 H                  1.08806700    1.82344900   -3.71444000
 C                  1.69751700    3.91514900   -3.80843600
 H                  2.02111600    4.68001500   -3.09143000
 H                  0.74218800    4.23958900   -4.23620000
 C                  2.76548700    3.74531200   -4.91009100
 H                  2.41280000    3.01560000   -5.65180200
 H                  2.91144500    4.70013400   -5.42875700
```

C	4.09516900	3.25059500	-4.29964700
H	4.48338200	4.01465300	-3.61254000
H	4.84366900	3.10367200	-5.08707600
C	3.87396700	1.93457800	-3.52838900
H	3.54551100	1.14422500	-4.21621600
H	4.78908100	1.60581400	-3.02785800
C	2.80268600	2.09762900	-2.42323100
H	3.15904400	2.83603500	-1.69589300
C	3.54521100	0.35565200	-0.86085600
C	4.13417100	-1.47302200	0.68489600
H	5.07314800	-0.93201100	0.58181100
C	3.52559000	-1.26723300	2.08493100
C	-2.05293700	4.69442800	2.24377100
C	-0.69070200	4.53539000	2.97537000
H	-0.67819400	3.60216900	3.55051800
H	-0.54578600	5.37373700	3.66729900
H	0.11944700	4.52355300	2.24544300
C	-3.17434700	4.72277800	3.30792600
H	-4.16028000	4.85880500	2.84826200
H	-2.99482400	5.56721000	3.98234300
H	-3.18257900	3.80537100	3.90832000
C	-2.08132600	6.04299300	1.47135000
H	-1.28976600	6.05441100	0.72130300
H	-1.92949300	6.87126700	2.17381800
H	-3.05198600	6.17510100	0.97982000
C	-4.92288100	-0.39886100	0.01711300
C	-6.14140200	-1.05434100	0.65071900
C	-5.81320600	-1.36507400	2.13454800
H	-4.97007700	-2.06039900	2.18219200
H	-6.68612000	-1.82958700	2.60611300
H	-5.56536500	-0.44370300	2.66738100
C	-6.42898600	-2.35867800	-0.11507500
H	-6.63259000	-2.15102600	-1.17010500
H	-7.29904600	-2.85698700	0.32494400
H	-5.55986500	-3.01855800	-0.05004700
C	-7.33048500	-0.06600600	0.56072200
H	-7.07864500	0.87110300	1.06352900
H	-8.20719300	-0.51064300	1.04396400
H	-7.57981300	0.14604200	-0.48520300
C	4.38028800	-2.98654300	0.36981500
C	5.11499000	-3.08112700	-0.98657800
H	4.52085300	-2.60171300	-1.76985400
H	5.27324300	-4.13253600	-1.25345200
H	6.09119700	-2.58347200	-0.93557000
C	3.04634100	-3.76683400	0.29134100
H	2.47696600	-3.62774800	1.21239600
H	3.25417600	-4.83227000	0.14022800
H	2.44046900	-3.41841400	-0.55320100
C	5.26956200	-3.59742600	1.47816200
H	6.22453700	-3.06244400	1.55101400
H	5.48537100	-4.64536400	1.24171700
H	4.77096900	-3.56112600	2.45279900

C	5.66315400	-0.17331400	2.91627400
H	6.21531300	-0.83080200	2.24311400
H	6.12645800	-0.26484500	3.90464200
C	5.72061600	1.28449800	2.41831400
H	6.75840900	1.63776000	2.42871600
H	5.12964100	1.93228200	3.07517100
H	5.33350600	1.34976700	1.39629800
C	3.59670700	-0.42768100	4.36194000
H	2.55354700	-0.18181500	4.15493000
H	4.08567500	0.42883600	4.83374700
C	3.66226300	-1.67739100	5.25883900
H	3.18935000	-1.47919800	6.22715400
H	4.70045300	-1.98032100	5.43049700
H	3.12549400	-2.48959900	4.76148000
N	0.49649500	2.84496600	-1.94812900
N	2.58244300	0.82782600	-1.71937600
N	3.23465800	-0.86104800	-0.29041300
N	4.26759200	-0.66747500	3.05550700
O	-0.23237500	4.17769400	0.04701000
H	0.32877300	3.82894900	-0.80669900
O	-4.58472400	0.75474700	0.72970500
O	-4.29295400	-0.79352700	-0.95957100
O	4.61409700	0.97923400	-0.63790800
O	2.34325600	-1.63912700	2.33160700
H	2.31175500	-1.25800800	-0.44911200
C	-0.34394100	-1.51866700	-0.32685300
H	1.73768200	0.27997300	-1.86633300
O	0.48458500	-1.36245400	-1.23890900
C	-0.33655000	-0.88817900	1.05584500
H	0.58740400	-1.19512900	1.56880400
H	-0.33002800	0.19886100	0.93649100
C	-1.62086000	-1.39897800	1.73938300
H	-1.42827500	-1.91739300	2.68223700
H	-2.34089000	-0.59523600	1.92003300
C	-2.25709200	-2.38052300	0.75152100
O	-3.26189800	-3.06663900	0.89604400
N	-1.45278900	-2.35917200	-0.41463800
I	-1.90892100	-3.44451900	-2.10376700