SUPPORTING INFORMATION

Directed, Palladium(II)-Catalyzed Enantioselective *anti*-Carboboration of Alkenyl Carbonyl Compounds

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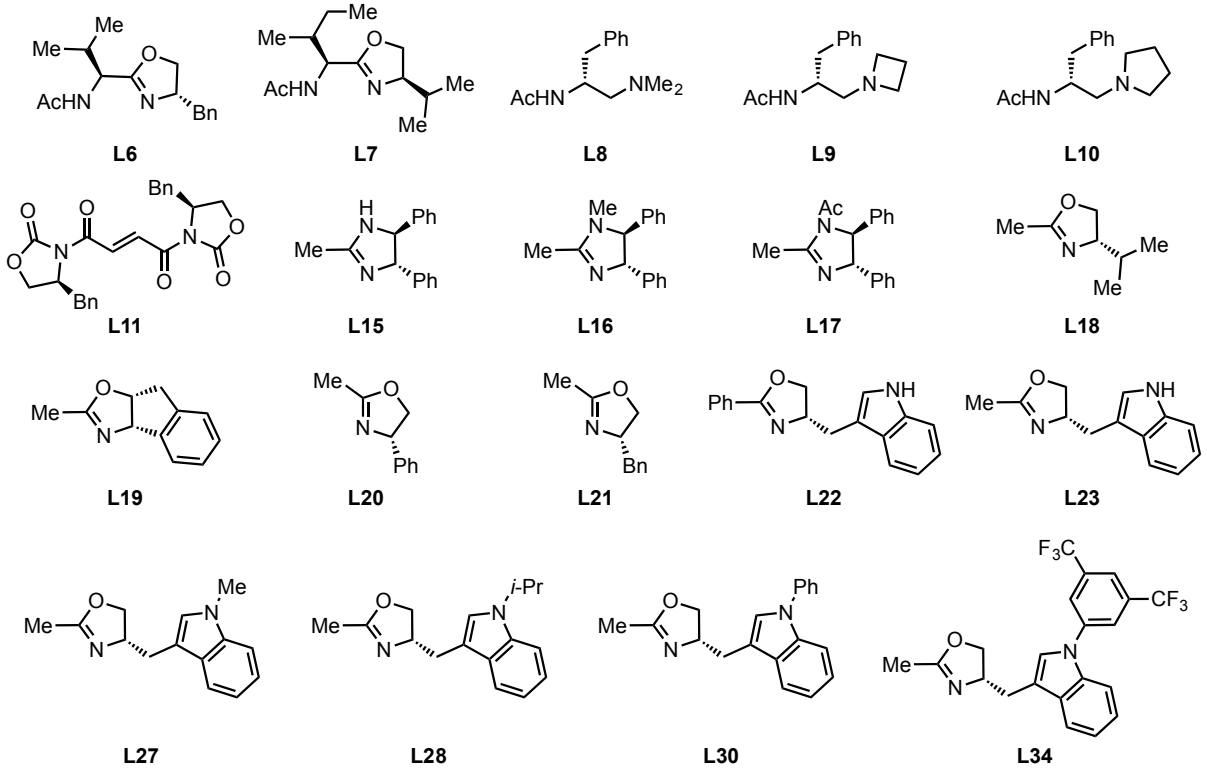
GENERAL INFORMATION

Unless otherwise noted, all materials were used as received from commercial sources without further purification. All commercial carbon nucleophiles, boron reagents, ligands and solvents were purchased from Aldrich, Alfa Aesar, Oakwood, and Combi-Blocks. $Pd(OAc)_2$ was obtained from Johnson Matthey. NMR spectra were recorded on Bruker AV-400, DRX-500 and AV-600 instruments. ^1H and ^{13}C spectra were internally referenced to $SiMe_4$ or solvent signals. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septet, m = multiplet. High-resolution mass spectra (HRMS) for new compounds were recorded on a Waters LC-TOF mass spectrometer, and the reported masses were automatically calibrated to be the neutral adduct of [M+H] by adding the mass of an electron. Enantiomeric ratios (*er*) were determined on a Waters UPC^2 system using commercially available chiral columns.

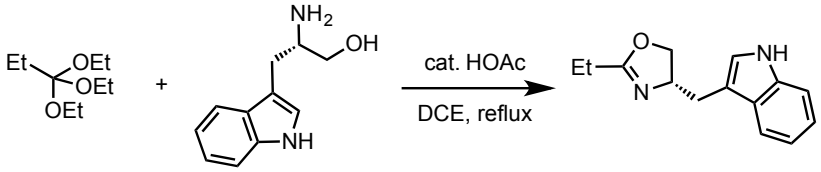
EXPERIMENTAL PROCEDURES

Chiral Ligand Synthesis

Table S1. Chiral ligands **L6–11**, **L15–23**, **L27–28**, **L30** and **L34**.

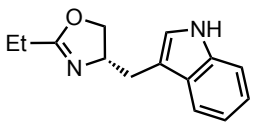


Chiral ligands **L6–11**,[1–3] **L15–23**,[4–7] **L27–28**,[7] **L30**[7] and **L34**[7] were prepared according to literature procedures.



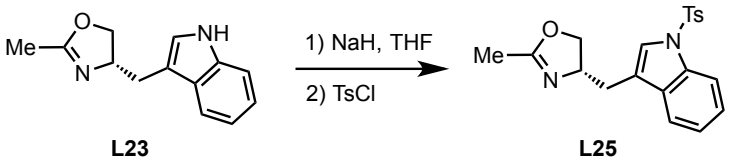
S1 **L24**

Scheme S1: Synthesis of (*S*)-4-((1*H*-indol-3-yl)methyl)-2-ethyl-4,5-dihydrooxazole (**L24**).[7]



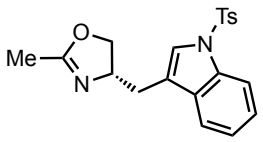
L24

(*S*)-4-((1*H*-indol-3-yl)methyl)-2-ethyl-4,5-dihydrooxazole (L24): The title compound was prepared from **S1** (475 mg, 2.5 mmol) and triethyl orthopropionate (529 mg, 3 mmol) according to a literature procedure.[7] Purification using silica gel column chromatography with 1:1.5 hexanes:EtOAc as the eluent gave the product as a light-yellow solid (457 mg, 80% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.64 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.35 (dp, *J* = 8.2, 0.9 Hz, 1H), 7.20 (ddt, *J* = 8.0, 7.0, 0.9 Hz, 1H), 7.15–7.09 (m, 1H), 7.02 (dt, *J* = 4.4, 1.9 Hz, 1H), 4.55–4.45 (m, 1H), 4.16 (ddd, *J* = 9.3, 8.4, 0.9 Hz, 1H), 3.98 (ddd, *J* = 8.3, 7.2, 1.0 Hz, 1H), 3.26 (ddt, *J* = 14.5, 4.8, 0.8 Hz, 1H), 2.79 (ddt, *J* = 14.5, 8.8, 0.9 Hz, 1H), 2.32–2.25 (m, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.0, 136.3, 127.6, 122.2, 122.0, 119.4, 118.9, 112.2, 111.1, 72.0, 66.3, 31.4, 21.5, 10.4; **HRMS** (ESI-TOF) Calcd for $C_{14}H_{17}N_2O$ [M+H] 229.1341, found 229.1336.



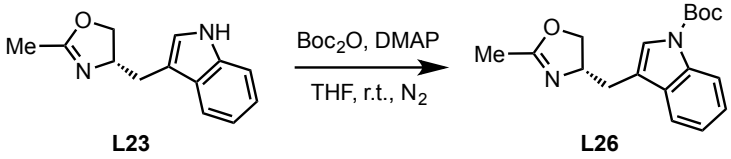
L23 **L25**

Scheme S2: Synthesis of (*S*)-2-methyl-4-((1-tosyl-1*H*-indol-3-yl)methyl)-4,5-dihydrooxazole (**L25**).[8]



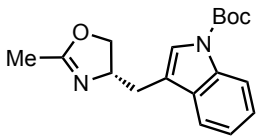
L25

(*S*)-2-methyl-4-((1-tosyl-1*H*-indol-3-yl)methyl)-4,5-dihydrooxazole (L25): The title compound was prepared from **L23** (107 mg, 0.5 mmol) and tosyl chloride (105 mg, 0.55 mmol) according to a literature procedure.[8] Purification using silica gel column chromatography with 1:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (184 mg, 78% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.54 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.40 (d, *J* = 1.1 Hz, 1H), 7.34 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.28–7.21 (m, 3H), 4.45 (ddddd, *J* = 9.7, 8.5, 7.2, 5.0, 1.3 Hz, 1H), 4.19 (dd, *J* = 9.4, 8.6 Hz, 1H), 3.91 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.12 (ddd, *J* = 14.8, 4.9, 1.2 Hz, 1H), 2.75 (ddd, *J* = 14.8, 8.6, 0.8 Hz, 1H), 2.36 (s, 3H), 1.97 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.3, 144.8, 135.2, 135.2, 130.9, 129.8, 126.7, 124.8, 123.6, 123.1, 119.5, 118.9, 113.7, 71.9, 65.6, 31.0, 21.5, 13.9; **HRMS** (ESI-TOF) Calcd for $C_{20}H_{21}N_2O_3S$ [M+H] 369.1273, found 369.1276.



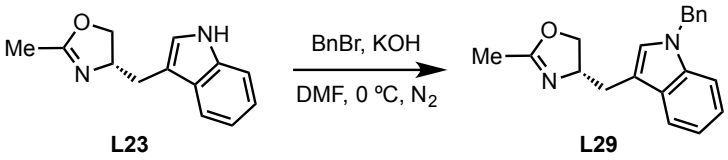
L23 **L26**

Scheme S3: Synthesis of *tert*-butyl (*S*)-3-((2-methyl-4,5-dihydrooxazol-4-yl)methyl)-1*H*-indole-1-carboxylate (**L26**).[9]



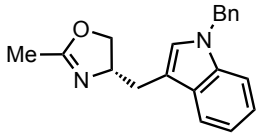
L26

***tert*-butyl (*S*)-3-((2-methyl-4,5-dihydrooxazol-4-yl)methyl)-1*H*-indole-1-carboxylate (L26):** The title compound was prepared from **L23** (107 mg, 0.5 mmol) and Boc_2O (218 mg, 1 mmol) according to a literature procedure.[9] Purification using silica gel column chromatography with 1:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (157 mg, 99% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.55 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.41 (s, 1H), 7.31 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.26–7.19 (m, 1H), 4.48 (ddddd, *J* = 9.7, 8.5, 7.0, 6.1, 1.3 Hz, 1H), 4.23 (dd, *J* = 9.4, 8.5 Hz, 1H), 3.97 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.12 (ddd, *J* = 14.8, 5.2, 1.2 Hz, 1H), 2.74 (ddd, *J* = 14.7, 8.5, 0.9 Hz, 1H), 1.98 (d, *J* = 1.3 Hz, 3H), 1.67 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.2, 149.7, 135.5, 130.6, 124.4, 123.3, 122.4, 119.0, 116.8, 115.2, 83.5, 72.2, 65.8, 31.2, 28.2, 13.9; **HRMS** (ESI-TOF) Calcd for $C_{18}H_{23}N_2O_3$ [M+H] 315.1709, found 315.1711.



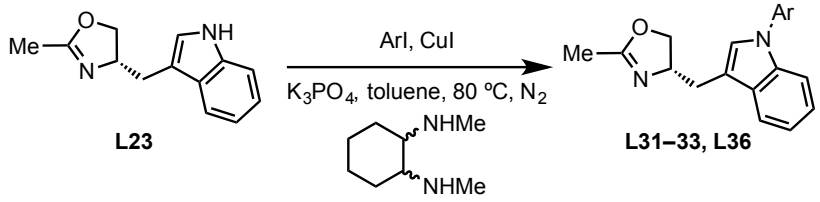
L23 L29

Scheme S4: Synthesis of (*S*)-4-((1-benzyl-1*H*-indol-3-yl)methyl)-2-methyl-4,5-dihydrooxazole (**L29**).[10]



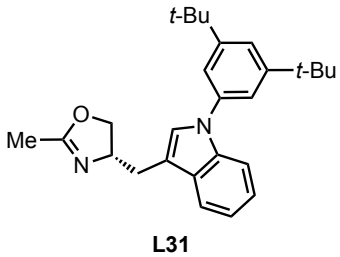
L29

(*S*)-4-((1-benzyl-1*H*-indol-3-yl)methyl)-2-methyl-4,5-dihydrooxazole (L29): The title compound was prepared from **L23** (214 mg, 1 mmol) and BnBr (256 mg, 1.5 mmol) according to a literature procedure.[10] Purification using silica gel column chromatography with 2:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (234 mg, 77% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67–7.62 (m, 1H), 7.32–7.26 (m, 4H), 7.19 (tt, *J* = 8.0, 0.9 Hz, 1H), 7.15–7.06 (m, 3H), 6.97 (s, 1H), 5.29 (d, *J* = 2.4 Hz, 2H), 4.53–4.44 (m, 1H), 4.17 (dd, *J* = 9.3, 8.5 Hz, 1H), 4.01–3.92 (m, 1H), 3.35–3.16 (m, 1H), 2.80 (dd, *J* = 14.6, 8.6 Hz, 1H), 1.96 (t, *J* = 0.9 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.89, 137.6, 136.6, 128.7, 128.3, 127.6, 126.7, 126.3, 121.8, 119.1, 119.0, 111.3, 109.7, 72.2, 66.6, 49.9, 31.2, 13.9; **HRMS** (ESI-TOF) Calcd for $C_{20}H_{21}N_2O$ [M+H] 305.1654, found 305.1653.



L23 L31–33, L36

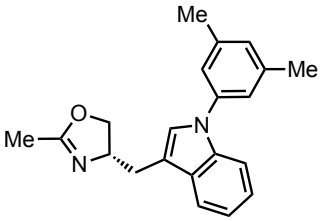
Scheme S5: Synthesis of **L31–33** and **L36**.[7]



L31

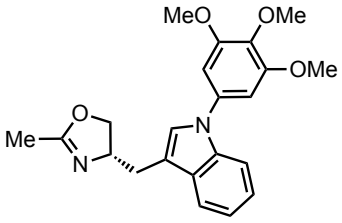
(*S*)-4-((1-(3,5-di-*tert*-butylphenyl)-1*H*-indol-3-yl)methyl)-2-methyl-4,5-dihydrooxazole (L31): The title compound was prepared from **L23** (107 mg, 0.5 mmol) and 1,3-di-*tert*-butyl-5-iodobenzene[11] (237 mg, 1.5 mmol) according to a literature procedure.[7] Purification using silica gel column chromatography with 3:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (151 mg, 75% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.55 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.43 (t, *J* = 1.8 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 2H), 7.27–7.23 (m, 2H), 7.20 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 4.62–4.52 (m, 1H), 4.26 (dd, *J* = 9.3, 8.5 Hz, 1H), 4.07 (dd, *J* = 8.4, 7.3 Hz, 1H),

3.33 (ddd, *J* = 14.6, 4.9, 1.0 Hz, 1H), 2.87 (dd, *J* = 14.6, 8.9 Hz, 1H), 2.03 (d, *J* = 1.2 Hz, 3H), 1.40 (s, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.0, 152.4, 139.0, 136.2, 128.9, 126.2, 122.4, 120.4, 119.8, 119.1, 118.7, 112.7, 110.7, 72.4, 66.6, 35.1, 31.4, 31.4, 14.0; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{35}N_2O$ [M+H] 403.2749, found 403.2750.



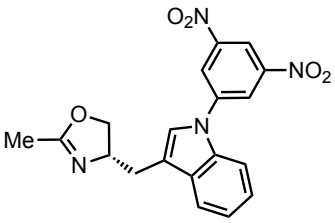
L32

(*S*)-4-((1-(3,5-dimethylphenyl)-1*H*-indol-3-yl)methyl)-2-methyl-4,5-dihydrooxazole (L32): The title compound was prepared from **L23** (107 mg, 0.5 mmol) and 1-iodo-3,5-dimethylbenzene (174 mg, 1.5 mmol) according to a literature procedure.[7] Purification using silica gel column chromatography with 2:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (156 mg, 98% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.56 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.24–7.19 (m, 1H), 7.19–7.15 (m, 2H), 7.10 (d, *J* = 1.5 Hz, 2H), 6.98 (s, 1H), 4.57–4.44 (m, 1H), 4.23 (t, *J* = 8.9 Hz, 1H), 4.03 (dd, *J* = 8.4, 7.3 Hz, 1H), 3.29 (ddd, *J* = 14.6, 4.9, 1.0 Hz, 1H), 2.82 (dd, *J* = 14.6, 8.9 Hz, 1H), 2.40 (s, 6H), 2.00 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.0, 139.6, 139.3, 136.1, 128.9, 127.9, 126.0, 122.4, 121.8, 119.9, 119.1, 112.9, 110.7, 72.4, 66.5, 31.4, 21.3, 14.0; **HRMS** (ESI-TOF) Calcd for $C_{21}H_{23}N_2O$ [M+H] 319.1810, found 319.1810.



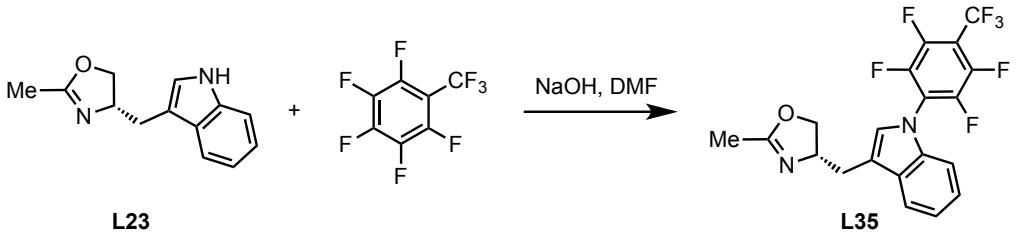
L33

(*S*)-2-methyl-4-((1-(3,4,5-trimethoxyphenyl)-1*H*-indol-3-yl)methyl)-4,5-dihydrooxazole (L33): The title compound was prepared from **L23** (107 mg, 0.5 mmol) and 5-iodo-1,2,3-trimethoxybenzene (221 mg, 1.5 mmol) according to a literature procedure.[7] Purification using silica gel column chromatography with 1.5:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (182 mg, 96% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.54 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.24 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.20–7.14 (m, 2H), 6.69 (s, 2H), 4.52 (ddddd, *J* = 9.7, 8.5, 6.9, 5.4, 1.3 Hz, 1H), 4.24 (dd, *J* = 9.4, 8.5 Hz, 1H), 4.02 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.90 (d, *J* = 9.6 Hz, 9H), 3.26 (ddd, *J* = 14.6, 5.3, 1.0 Hz, 1H), 2.85 (ddd, *J* = 14.6, 8.5, 0.8 Hz, 1H), 2.00 (d, *J* = 1.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.1, 153.8, 136.5, 136.3, 135.5, 128.9, 126.1, 122.6, 120.0, 119.2, 113.1, 110.6, 102.0, 72.4, 66.5, 61.0, 56.3, 31.3, 14.0; **HRMS** (ESI-TOF) Calcd for $C_{22}H_{25}N_2O_4$ [M+H] 381.1814, found 381.1812.

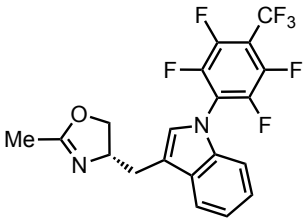


L36

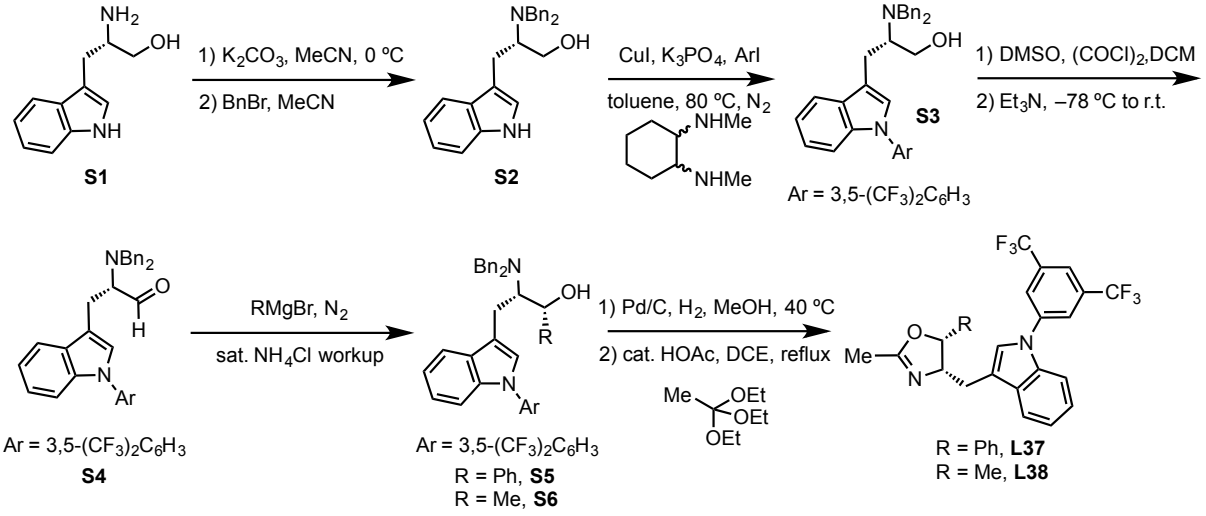
(*S*)-4-((1-(3,5-dinitrophenyl)-1*H*-indol-3-yl)methyl)-2-methyl-4,5-dihydrooxazole (L36): The title compound was prepared from **L23** (214 mg, 1 mmol) and 1-iodo-3,5-dinitrobenzene (441 mg, 1.5 mmol) according to a literature procedure.[7] Purification using silica gel column chromatography with 1:1 hexanes:EtOAc as the eluent gave the product as a yellow solid (289 mg, 76% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.95 (t, *J* = 2.0 Hz, 1H), 8.73 (d, *J* = 2.0 Hz, 2H), 7.74 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.66 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.41–7.37 (m, 2H), 7.33 (ddd, *J* = 7.9, 7.1, 0.9 Hz, 1H), 4.56 (p, *J* = 7.1 Hz, 1H), 4.34 (dd, *J* = 9.4, 8.5 Hz, 1H), 4.03 (dd, *J* = 8.4, 7.4 Hz, 1H), 3.19 (ddd, *J* = 14.8, 6.4, 1.1 Hz, 1H), 2.97 (dd, *J* = 14.8, 7.1 Hz, 1H), 2.03 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.4, 149.4, 142.1, 135.3, 130.1, 124.5, 124.4, 122.5, 122.0, 120.1, 117.4, 114.8, 109.8, 72.2, 66.1, 31.2, 14.0; **HRMS** (ESI-TOF) Calcd for $C_{19}H_{17}N_4O_5$ [M+H] 381.1199, found 381.1198.



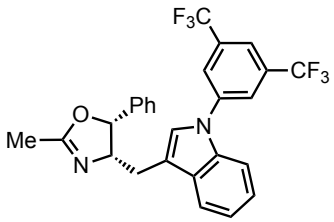
Scheme S6: Synthesis of (*S*)-2-methyl-4-((1-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)-1*H*-indol-3-yl)methyl)-4,5-dihydrooxazole (**L35**).[12]



(*S*)-2-methyl-4-((1-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)-1*H*-indol-3-yl)methyl)-4,5-dihydrooxazole (L35): The title compound was prepared from **L23** (214 mg, 1 mmol) and 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene (472 mg, 2 mmol) according to a literature procedure.[12] Purification using silica gel column chromatography with 2:1 hexanes:EtOAc as the eluent gave the product as a yellow solid (301 mg, 70% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (d, J = 7.8 Hz, 1H), 7.34–7.27 (m, 2H), 7.14 (dd, J = 7.0, 3.9 Hz, 1H), 7.08 (s, 1H), 4.52 (q, J = 7.6 Hz, 1H), 4.26 (t, J = 9.0 Hz, 1H), 4.00 (t, J = 7.9 Hz, 1H), 3.22 (dd, J = 14.8, 5.4 Hz, 1H), 2.89 (dd, J = 14.8, 8.0 Hz, 1H), 1.99 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.4, 144.9 (dd, $J_{C–F}$ = 260.5, 14.9 Hz), 142.6 (dd, $J_{C–F}$ = 255.1, 14.3 Hz), 136.0, 129.0, 125.4, 123.8, 122.6 (t, $J_{C–F}$ = 13.3 Hz), 121.6, 120.7 (q, $J_{C–F}$ = 275.3 Hz), 119.5, 116.5, 110.8 (t, $J_{C–F}$ = 2.7 Hz), 108.0 (dtd, $J_{C–F}$ = 47.8, 35.1, 12.6 Hz), 72.1, 66.0, 31.0, 13.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –56.2 (t, $J_{F–F}$ = 21.7 Hz, 3F), –136.0–(–140.4) (m, 2F), –142.8–(–145.5) (m, 2F); **HRMS** (ESI-TOF) Calcd for $C_{20}H_{14}F_7N_2O$ [M+H] 431.0994, found 431.0993.



Scheme S7: Synthesis of **L37** and **L38**.[7,13–15]



L37

(4*S*,5*R*)-4-((1-(3,5-bis(trifluoromethyl)phenyl)-1*H*-indol-3-yl)methyl)-2-methyl-5-phenyl-4,5-dihydrooxazole (L37): The title compound was prepared by adapting several literature procedures.

Benzyl protection:[13] A solution of benzyl bromide (1.88g, 11 mmol) in MeCN (1 mL) was prepared and added dropwise to a solution of *L*-tryptophanol (**S1**, 950 mg, 5 mmol) and K_2CO_3 (1.5 g, 11 mmol) in MeCN (10 mL) at 0 ºC. The reaction mixture was filtered, concentrated under vacuum, and purified by silica gel column chromatography (4:1 hexanes:EtOAc) to afford 900 mg (48% yield) of **S2**.

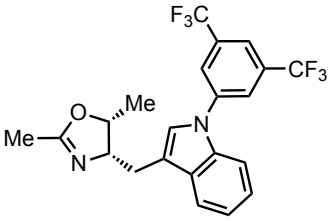
Ullmann coupling:[7] To a 50-mL round-bottom flask equipped with a Teflon-coated magnetic stir bar, were added **S2** (371 mg, 1 mmol), CuI (17 mg, 9 mol%), K_3PO_4 (423 mg, 2 mmol), *N,N'*-dimethyl-1,2-cyclohexanediamine (28.5 mg, 20 mol%), and 1-iodo-3,5-bis(trifluoromethyl)-benzene (510 mg, 1.5 mmol). The reaction flask was evacuated and backfilled with N_2 (×3), followed by addition of anhydrous toluene (5 mL). After being allowed to stir at 80 ºC for 24 h, the reaction mixture was diluted with EtOAc and filtered through a plug of silica gel. The solvent was removed in *vacuo* to leave a brown residue, which upon purification by silica gel column chromatography (5:1 hexanes:EtOAc), afforded **S3** (545 mg, 94%).

Swern oxidation:[14] A solution of DMSO (0.16 mL, 2 mmol) in DCM (6 mL) was added dropwise to a solution of oxalyl chloride (0.11 mL, 1.2 mmol) in DCM (3 mL) at –78 ºC and stirred for 15 min. To the reaction mixture, was added dropwise a solution of **S3** (545 mg, 0.94 mmol) in DCM (6.7 mL) at –78 ºC, and the resulting solution was stirred for another 35 min. Et_3N was then added, and reaction was slowly warmed to room temperature before treated with sat. NH_4Cl. The organic layer was separated, washed with sat. $NaHCO_3$ (20 mL, ×1) and brine (20 mL, ×1), dried over Na_2SO_4, and concentrated to afford **S4**, which was brought on to the next step without further purification.

Grignard addition:[15] To aldehyde **S4** in THF (1.4 mL), was slowly added PhMgBr (0.5 mL, 3 M in diethyl ether) at 0 ºC. The mixture was stirred for 12 h, followed by addition of sat. NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with EtOAc (10 mL, ×1). The combined organic layers were then washed with brine (20 mL, ×1) and dried over Na_2SO_4. The resulting organic solution was concentrated under vacuum and purified by silica gel column chromatography (10:1 hexanes:EtOAc) to afford **S5** (271 mg, 35% over two steps).

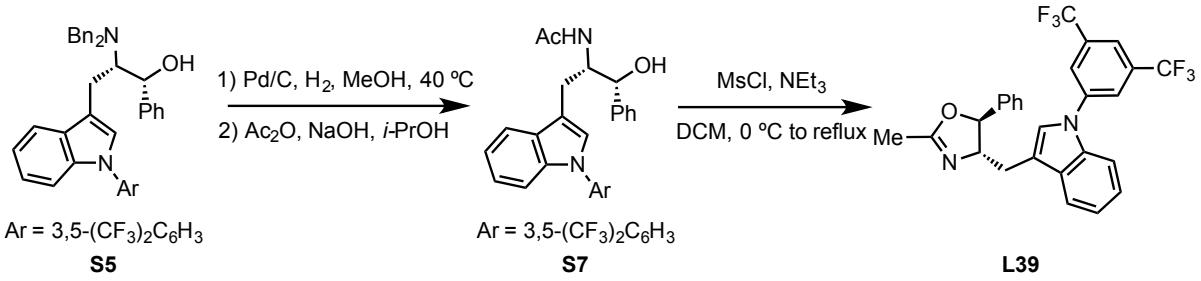
Benzyl deprotection[15] *and **L37** synthesis:*[7] In a 50-mL round-bottom flask, **S5** (165 mg, 0.25 mmol) was first treated with a solultion of HCl in diethylether to generate a white salt. After removal of the solvent, Pd/C (10 wt.%, 26 mg) and MeOH (2.5 mL) were added, and the reaction mixture was vigorously stirred under an H_2 atmosphere (1 atm) at 40 ºC for 48 h. The Pd/C catalyst was removed by filtration through a plug of celite, and the resulting solution was concentrated under vacuum. The crude product was carried forward to the next step without further purification. Finally, oxazoline formation was completed according to a literature procedure.[7] Purification using silica gel column chromatography with 2:1 hexanes:EtOAc as the eluent gave the product (**L37**) as a light-yellow solid (70 mg, 56% over two steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, J = 1.5 Hz, 2H), 7.78 (s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.41–7.33 (m, 3H), 7.27 (dd, J = 3.2, 1.4 Hz, 2H), 7.25 (d, J = 4.0 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 6.62 (s, 1H), 5.63 (d, J = 9.8 Hz, 1H), 4.83–4.73 (m, 1H), 2.74–2.53 (m, 2H), 2.16 (d, J = 1.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.8, 141.2, 136.7, 135.3, 133.1 (q, $J_{C–F}$ = 33.8 Hz), 129.5, 128.3, 128.2, 127.0, 125.0, 123.6, 123.2 (q, $J_{C–F}$ = 3.9 Hz), 123.0 (q, $J_{C–F}$ = 272.8 Hz), 121.0, 119.6, 118.9 (sept, $J_{C–F}$ = 3.8 Hz),

116.3, 109.8, 83.9, 69.1, 28.0, 14.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.2 (s, 6F); **HRMS** (ESI-TOF) Calcd for $C_{27}H_{21}F_6N_2O$ [M+H] 503.1558, found 503.1559.



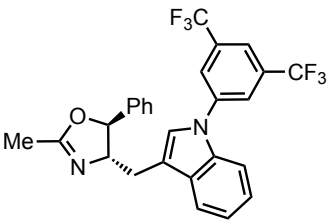
L38

(4*S*,5*R*)-4-((1-(3,5-bis(trifluoromethyl)phenyl)-1*H*-indol-3-yl)methyl)-2,5-dimethyl-4,5-dihydrooxazole (L38): The title compound was prepared from **S3** (493 mg, 0.85 mmol) according to the above synthetic sequence, using MeMgBr as the Grignard reagent in lieu of PhMgBr (Scheme S7). Purification using silica gel column chromatography with 2:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (137 mg, 37% yield over 4 steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, J = 1.6 Hz, 2H), 7.80 (s, 1H), 7.68 (dt, J = 7.8, 0.9 Hz, 1H), 7.53 (dt, J = 8.3, 0.8 Hz, 1H), 7.33 (d, J = 1.1 Hz, 1H), 7.30 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H), 7.24 (ddd, J = 7.9, 7.0, 0.9 Hz, 1H), 4.82 (dq, J = 9.2, 6.6 Hz, 1H), 4.51 (tdd, J = 9.2, 6.2, 1.6 Hz, 1H), 3.06–2.92 (m, 2H), 2.00 (d, J = 1.4 Hz, 3H), 1.36 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.5, 141.3, 135.5, 133.2 (q, $J_{C–F}$ = 33.9 Hz), 129.7, 124.8, 122.9 (q, $J_{C–F}$ = 272.8 Hz), 123.6, 123.5 (q, $J_{C–F}$ = 3.4 Hz), 121.1, 119.6, 119.1 (sept, $J_{C–F}$ = 7.7, 3.6 Hz), 117.2, 109.8, 78.5, 67.5, 26.0, 15.2, 14.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.2 (s, 6F); **HRMS** (ESI-TOF) Calcd for $C_{22}H_{19}F_6N_2O$ [M+H] 441.1402, found 441.1409.



Ar = 3,5-$(CF_3)_2C_6H_3$ **S5** | Ar = 3,5-$(CF_3)_2C_6H_3$ **S7** | **L39**

Scheme S8: Synthesis of **L39**.[15–17]



L39

(4*S*,5*S*)-4-((1-(3,5-bis(trifluoromethyl)phenyl)-1*H*-indol-3-yl)methyl)-2-methyl-5-phenyl-4,5-dihydrooxazole (L39): The title compound was prepared by adapting a literature procedure.[15–17] Benzyl deprotection of **S5** (107 mg, 0.16 mmol) was first conducted with 17 mg of Pd/C (10 wt.%) under H_2 atmosphere (1 atm) according to the above procedure.

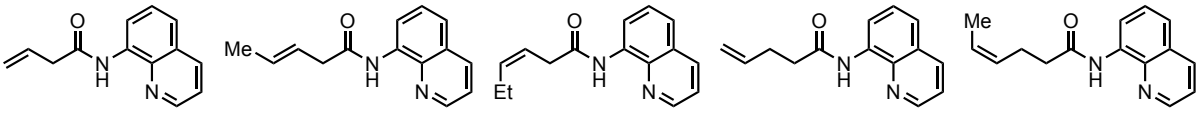
N-Acetylation:[16] The crude product was dissolved in *i*-PrOH (1.2 mL), and the resulting solution was added to a solution of NaOH (18 mg, 0.45 mmol) in water (0.2 mL). To this combined solution, was gradually added acetic anhydride (44 μL, 0.45 mmol), while maintaining the pH at approximately 8. After stirring at room temperature for 30 min, the reaction mixture was concentrated, extracted with EtOAc (5 mL, ×2), washed with water (5 mL, ×1) and brine (5 mL, ×1), and concentrated under vacuum again to afford crude **S7**, which was brought on to the next step without further purification.

Oxazoline ring formation:[17] To a flame-dried reaction tube equipped with a magnetic stir bar, were added **S7**, trimethylamine (55 μL, 0.48 mmol), and anhydrous DCM (0.8 mL) under N_2. Methanesulfonyl chloride (14.5 μL, 0.18 mmol) was slowly added at 0 ºC. The reaction was stirred at 0 ºC for 5 min and then heated up to 50 ºC for 24 h. Upon completion, the reaction was quenched with sat. $NaHCO_3$ (2 mL) and extracted with DCM (5 mL, ×2). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography (3:1 hexanes:EtOAc) to afford **L39** as a colorless oil

(53.2 mg, 65% yield over 3 steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.5 Hz, 2H), 7.81 (s, 1H), 7.67 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.33–7.28 (m, 4H), 7.26–7.22 (m, 1H), 7.16 (s, 1H), 7.12 (dd, *J* = 7.5, 2.0 Hz, 2H), 5.11 (d, *J* = 7.2 Hz, 1H), 4.44 (tdd, *J* = 7.5, 6.1, 1.5 Hz, 1H), 3.29 (ddd, *J* = 15.0, 6.3, 1.1 Hz, 1H), 3.15–3.04 (m, 1H), 2.11 (d, *J* = 1.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.5, 141.2, 140.6, 135.4, 133.2 (q, $J_{C–F}$ = 33.9 Hz), 129.9, 128.7, 128.3, 125.7, 125.3, 123.7, 123.5 (q, $J_{C–F}$ = 3.8 Hz), 122.9 (q, $J_{C–F}$ = 279.35 Hz), 121.3, 119.7, 119.2 (sept, $J_{C–F}$ = 3.8 Hz), 115.4, 109.8, 86.1, 74.9, 31.1, 14.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.2 (s, 6F); **HRMS** (ESI-TOF) Calcd for $C_{27}H_{21}F_6N_2O$ [M+H] 503.1558, found 503.1560.

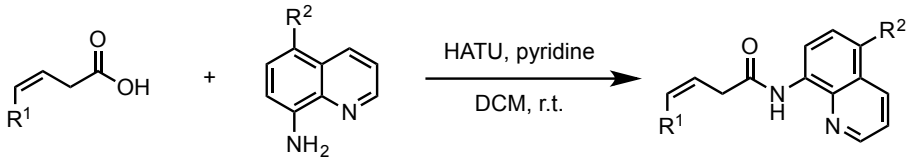
Alkene Substrate Synthesis

Table S2. Alkene substrates **1a–b**, **1d**, **1i**, and **1k**.



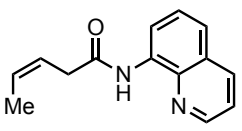
1a **1b** **1d** **1i** **1k**

Alkene substrates **1a–b**, **1d**, **1i**, and **1k** were prepared according to literature procedures.[18,19]



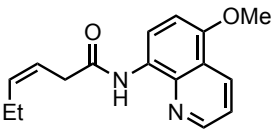
Scheme S9: General depiction of amide coupling.[18]

General Procedure for Amide Coupling: The appropriate carboxylic acid (1.05 equiv) was charged into a 25-mL round-bottom flask equipped with a Teflon-coated magnetic stir bar containing DCM (0.67 M). The appropriate amine (1 equiv), pyridine (2 equiv), and HATU (1.5 equiv) were added sequentially, and the reaction was stirred at ambient temperature for 20 h. The deep brown solution was diluted with EtOAc (30 mL), washed with sat. $NaHCO_3$ (20 mL, ×2) and brine (20 mL, ×1), and dried over Na_2SO_4. The solvent was removed under vacuum and the resulting residue was purified by column chromatography (10:1 hexanes:EtOAc) to afford the corresponding amide.



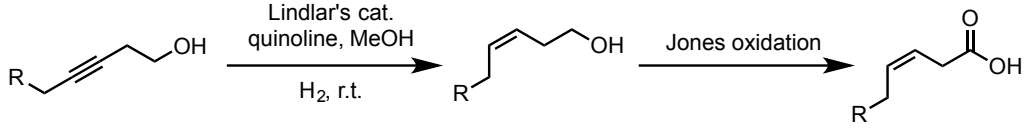
1c

(*Z*)-*N*-(quinolin-8-yl)pent-3-enamide (1c): The title compound was prepared from (*Z*)-pent-3-enoic acid (1 g, 10 mmol) and 8-aminoquinoline (1.4 g, 9.8 mmol) according to the general amide coupling procedure. Compound **1c** was isolated as a light-brown oil (908 mg, 41% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.84–8.72 (m, 2H), 8.15 (dd, $_J$ = 8.3, 1.7 Hz, 1H), 7.56–7.47 (m, 2H), 7.44 (ddd, *J* = 8.4, 4.2, 1.3 Hz, 1H), 5.98–5.88 (m, 1H), 5.81 (dtd, *J* = 11.0, 7.4, 1.9 Hz, 1H), 3.43–3.28 (m, 2H), 1.87–1.72 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.6, 148.2, 138.5, 136.2, 134.5, 129.6, 127.9, 127.4, 122.3, 121.5, 121.5, 116.4, 36.5, 13.1; **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}N_2O$ [M+H] 227.1184, found 227.1180.



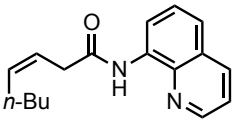
1e

(*Z*)-*N*-(5-methoxyquinolin-8-yl)hex-3-enamide (1e): The title compound was prepared from (*Z*)-hex-3-enoic acid (376 mg, 3.3 mmol) and 5-methoxyquinolin-8-amine (523 mg, 3 mmol) according to the general amide coupling procedure. Compound **1e** was isolated as a brown oil (324 mg, 40% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.80 (dq, *J* = 4.4, 1.6 Hz, 1H), 8.69 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.56 (dq, *J* = 8.4, 1.8 Hz, 1H), 7.42 (dt, *J* = 8.1, 3.8 Hz, 1H), 6.83 (dd, *J* = 8.6, 3.2 Hz, 1H), 5.82 (ddd, *J* = 10.5, 6.1, 1.5 Hz, 1H), 5.78–5.67 (m, 1H), 4.03–3.93 (m, 3H), 3.32 (d, *J* = 7.5 Hz, 2H), 2.26–2.15 (m, 2H), 1.07 (td, *J* = 7.5, 1.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.2, 150.2, 148.6, 139.2, 137.0, 131.1, 127.9, 120.8, 120.6, 120.4, 116.5, 104.3, 55.7, 36.7, 20.8, 14.0; **HRMS** (ESI-TOF) Calcd for $C_{16}H_{19}N_2O_2$ [M+H] 271.1447, found 271.1446.



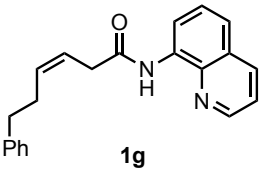
Scheme S10: Synthesis of (*Z*)-alkenyl carboxylic acid.[18,20]

General Procedure for Alkyne Semireduction[20] and Jones Oxidation:[18] To a stirred solution of alkyne substrate in anhydrous MeOH (0.33 M), were added Lindlar's catalyst (5 mol%) and quinoline (7 mol%). The reaction mixture was stirred under H_2 atmosphere (1 atm) for 3 days at room temperature. After the reaction had reacted completion (as monitored by TLC), the resulting suspension was filtered through a plug of celite and concentrated under vacuum. The crude alcohol was oxidized to the corresponding carboxylic acid following a literature procedure.



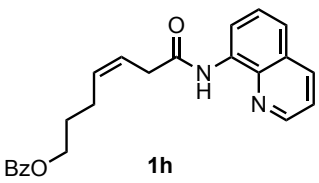
1f

(*Z*)-*N*-(quinolin-8-yl)oct-3-enamide (1f): The title compound was prepared from (*Z*)-oct-3-en-1-ol (1.28 g, 10 mmol) according to the general Jones oxidation and amide coupling procedures. Compound **1f** was isolated as a brown oil (1.09 g, 41% yield over 2 steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.81–8.73 (m, 2H), 8.15 (dt, *J* = 8.4, 1.4 Hz, 1H), 7.57–7.48 (m, 2H), 7.44 (ddd, *J* = 8.2, 4.2, 0.9 Hz, 1H), 5.88–5.82 (m, 1H), 5.81–5.71 (m, 1H), 3.35 (dd, *J* = 7.4, 1.2 Hz, 2H), 2.20 (qd, *J* = 7.2, 1.3 Hz, 2H), 1.45 (tt, *J* = 7.4, 5.8 Hz, 2H), 1.41–1.32 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.7, 148.2, 138.6, 136.2, 135.6, 134.5, 127.9, 127.4, 121.5, 121.5, 121.5, 116.4, 36.9, 31.5, 27.3, 22.3, 14.0; **HRMS** (ESI-TOF) Calcd for $C_{17}H_{21}N_2O$ [M+H] 269.1654, found 269.1653.



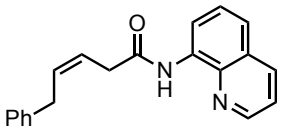
1g

(*Z*)-6-phenyl-*N*-(quinolin-8-yl)hex-3-enamide (1g): The title compound was prepared from 6-phenylhex-3-yn-1-ol (523 mg, 3 mmol) according to the general semi-reduction, Jones oxidation, and amide coupling procedures. Compound **1g** was isolated as a light-brown oil (209 mg, 22% yield over 3 steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.82–8.73 (m, 2H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.57–7.47 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28–7.23 (m, 2H), 7.23–7.18 (m, 2H), 7.14 (td, *J* = 7.2, 1.5 Hz, 1H), 5.91–5.84 (m, 1H), 5.84–5.77 (m, 1H), 3.28 (dd, *J* = 7.3, 1.2 Hz, 2H), 2.79 (t, *J* = 7.7 Hz, 2H), 2.55–2.48 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.5, 148.2, 141.5, 138.6, 136.3, 134.4, 134.2, 128.5, 128.4, 127.9, 127.4, 125.9, 122.1, 121.6, 121.6, 116.4, 36.8, 35.5, 29.4; **HRMS** (ESI-TOF) Calcd for $C_{21}H_{21}N_2O$ [M+H] 317.1654, found 317.1658.



1h

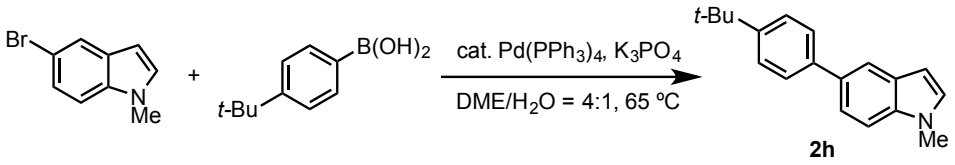
(*Z*)-7-oxo-7-(quinolin-8-ylamino)hept-4-en-1-yl benzoate (1h): Internal alkyne 7-hydroxyhept-4-yn-1-yl benzoate was synthesized following a literature procedure.[21] The title compound was prepared from 7-hydroxyhept-4-yn-1-yl benzoate (232 mg, 1 mmol) according to the general semi-reduction, Jones oxidation, and amide coupling procedures. Compound **1h** was isolated as a light-yellow oil (124 mg, 33% yield over 3 steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.76 (ddd, *J* = 8.7, 5.8, 1.5 Hz, 2H), 8.14 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.04–7.94 (m, 2H), 7.56–7.46 (m, 3H), 7.46–7.35 (m, 3H), 5.87 (q, *J* = 6.2 Hz, 2H), 4.39 (t, *J* = 6.4 Hz, 2H), 3.38 (d, *J* = 6.1 Hz, 2H), 2.40 (q, *J* = 6.9 Hz, 2H), 2.01–1.91 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.4, 166.7, 148.4, 138.6, 136.5, 136.4, 134.5, 134.0, 133.0, 130.4, 129.6, 128.5, 128.1, 127.5, 122.8, 121.7, 116.6, 64.4, 37.0, 28.6, 24.2; **HRMS** (ESI-TOF) Calcd for $C_{23}H_{23}N_2O_3$ [M+H] 375.1709, found 375.1710.



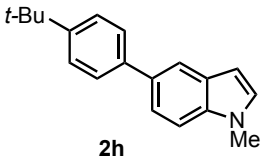
1j

(*Z*)-5-phenyl-*N*-(quinolin-8-yl)pent-3-enamide (1j): The title compound was prepared from 5-phenylpent-3-yn-1-ol (368 mg, 2.3 mmol) according to the general semi-reduction, Jones oxidation, and amide coupling procedure. **1j** was isolated as a light-brown oil (158 mg, 23% yield for 3 steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.76–8.64 (m, 2H), 8.05 (dt, *J* = 8.2, 1.6 Hz, 1H), 7.48–7.38 (m, 2H), 7.34 (ddd, *J* = 8.2, 4.2, 1.4 Hz, 1H), 7.21–7.13 (m, 4H), 7.09 (ddt, *J* = 8.0, 3.6, 2.1 Hz, 1H), 5.92 (dtt, *J* = 10.1, 7.2, 1.4 Hz, 1H), 5.84 (dtq, *J* = 10.7, 7.5, 1.6 Hz, 1H), 3.47 (dd, *J* = 7.6, 1.7 Hz, 2H), 3.38 (dd, *J* = 7.6, 1.4 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.2, 148.2, 139.9, 138.4, 136.2, 134.4, 133.4, 128.5, 128.4, 127.9, 127.3, 126.1, 122.3, 121.5, 121.5, 116.4, 36.8, 33.7; **HRMS** (ESI-TOF) Calcd for $C_{20}H_{19}N_2O$ [M+H] 303.1497, found 303.1495.

Indole Nucleophile Synthesis



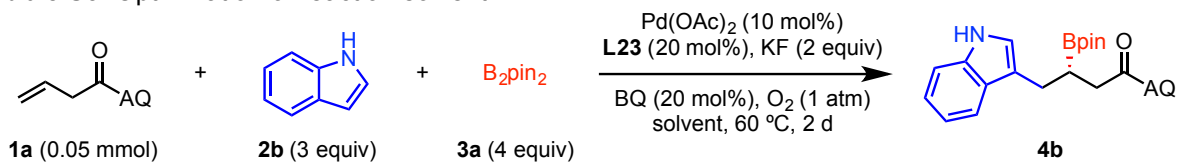
Scheme S11: Synthesis of 5-(4-(*tert*-butyl)phenyl)-1-methyl-1*H*-indole (**2h**).[22]



5-(4-(*tert*-butyl)phenyl)-1-methyl-1*H*-indole (2h):[22] To a 50-mL Schlenk flask equipped with a magnetic stir bar, were added 5-bromo-1-methyl-1*H*-indole (210 mg, 1 mmol), (4-(*tert*-butyl)phenyl)boronic acid (214 mg, 1.2 mmol), $Pd(PPh_3)_4$ (23 mg, 2 mol%), and K_3PO_4 (425 mg, 2 mmol). The reaction flask was evacuated and backfilled with N_2 (×3), followed by addition of DME and water (5 mL, 4:1 v/v). The reaction mixture was stirred at 65 ºC overnight, after which it was allowed to cool down to room temperature, concentrated under vacuum, and diluted with EtOAc (5 mL). The resulting solution was washed with sat. $NaHCO_3$ (10 mL, ×1) and brine (10 mL, ×1) and dried over Na_2SO_4. The organic solvent was removed under vacuum, and the residue was purified by column chromatography (10:1 hexanes:EtOAc) to afford the product as a light-orange solid (166 mg, 63% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85–7.80 (m, 1H), 7.62–7.55 (m, 2H), 7.47 (td, *J* = 8.3, 1.9 Hz, 3H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 6.52 (d, *J* = 3.0 Hz, 1H), 3.81 (s, 3H), 1.37 (d, *J* = 0.9 Hz, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.1, 139.7, 136.1, 132.7, 129.3, 128.9, 127.0, 125.6, 121.4, 119.2, 109.3, 101.2, 34.4, 32.9, 31.4; **HRMS** (ESI-TOF) Calcd for $C_{19}H_{22}N$ [M+H] 264.1752, found 264.1752.

Reaction Optimization Details

Table S3. Optimization of reaction solvent.[a]

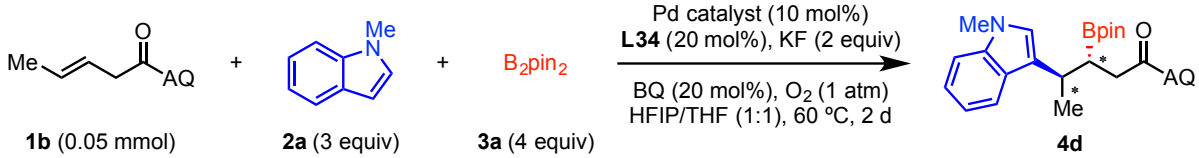


1a (0.05 mmol) **2b** (3 equiv) **3a** (4 equiv) **4b**

Entry	Solvent	Yield[b] (%)	*er*[c]
1	toluene	22	63:37
2	THF	17	66:34
3	MeCN	18	59:41
4	MeOH	trace	--
5	DMF	trace	--
6	HFIP	60	57:43
7	**THF/HFIP (1:1)**	**62**	**78:22**
8	THF/HFIP (1:2)	62	74:26
9	THF/HFIP (2:1)	33	78:22

[a]Reaction conditions: **1a** (0.1 mmol), **2b** (3 equiv), **3a** (4 equiv), $Pd(OAc)_2$ (10 mol%), **L23** (20 mol%), BQ (20 mol%), KF (2 equiv), O_2 (1 atm), 2 d. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as internal standard. [c]The *er* was determined by 2D LC/SFC analysis.

Table S4. Optimization of palladium source.[a]



1b (0.05 mmol) **2a** (3 equiv) **3a** (4 equiv) **4d**

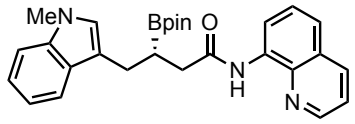
Entry	Pd Source	Yield[b] (%)	*er*[c]
1	$Pd(TFA)_2$	44	90:10
2	$PdCl_2$	trace	--
3	$Pd(MeCN)_4(BF_4)_2$	65	90:10
4	$Pd(PhCN)_2Cl_2$	58	92:8
5	$PdBr_2$	35	90:10
6	**$Pd(OAc)_2$**	**77**	**91:9**

[a]Reaction conditions: **1b** (0.1 mmol), **2a** (3 equiv), **3a** (4 equiv), **L34** (20 mol%), BQ (20 mol%), KF (2 equiv), HFIP/THF (1:1, 0.2 mL), O_2 (1 atm), 2 d. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as internal standard. [c]The *er* was determined by 2D LC/SFC analysis.

General Procedure for Asymmetric Alkene Carboboration

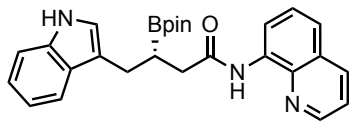
General Procedure: To an 8-mL reaction tube equipped with a Teflon-coated magnetic stir bar were added the alkene substrate (0.1 mmol), the appropriate carbon nucleophile (0.3 mmol), bis(pinacolato)diboron (0.4 mmol), $Pd(OAc)_2$ (10 mol%), **L34** (20 mol%), benzoquinone (20 mol%), and NaF (0.2 mmol). The tube was sealed with a screw-top septum cap and was then evacuated and backfilled with O_2 (×3). Under positive O_2 pressure, HFIP/THF/DMF (0.2 mL, 2:2:1, v/v/v) was added. All needle inlets/outlets were removed, and the reaction was placed in a heating block that was pre-heated to 45 °C. After 5 days, the dark black reaction mixture was allowed to cool to room temperature and directly purified by rapid silica gel column chromatography—with a total residence time less than 20 min to prevent alkyl boronate decomposition—affording the pure product.

Notes:[23] Column chromatography should be performed quickly to prevent product decomposition on silica. The recommended residence time is 10–15 min for reactions on 0.1 mmol scale. It is also important to use a short bed of silica gel (approximately 6 cm of silica for a 2.5 cm diameter column). If pinacol is still present after column, it can be removed by azetropic distillation.



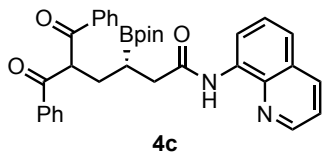
4a

(*S*)-4-(1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (4a): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), *N*-methylindole (39.2 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 3:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (37.1 mg, 79% yield, 86:14 *er*). $[\alpha]_D^{20}$ = +9.4 (c = 0.35 Chloroform, 86:14 *er*). **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IB column (3 μm, 4.6×250 mm), 35% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 2.088 min, t (minor) = 2.499 min.



4b

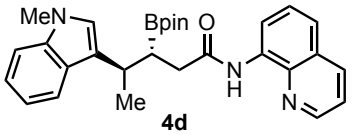
(*S*)-4-(1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (4b): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), indole (35.1 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 3:1 hexanes:EtOAc as the eluent gave the product as a light-orange solid (32.3 mg, 71% yield, 83:17 *er*). $[\alpha]_D^{20}$ = +10.6 (c = 0.35 Chloroform, 83:17 *er*). **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IB column (3 μm, 4.6×250 mm), 35% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 2.296 min, t (minor) = 2.539 min.



4c

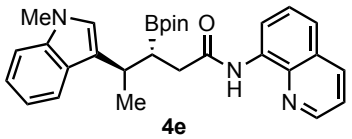
(*S*)-5-benzoyl-6-oxo-6-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (4c): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), 1,3-diphenylpropane-1,3-dione (67.3 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 7:1 hexanes:acetone as the eluent gave the product as a white solid (16.8 mg, 30% yield, 75:25 *er*). **SFC** (chiral column) The enantiomeric ratio was determined

by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 30% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 2.319 min, t (minor) = 2.515 min.



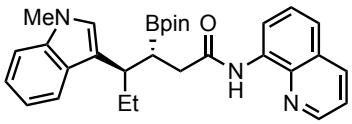
4d
dr = 20:1

(3*R*,4*R*)-4-(1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4d): The title compound was prepared from **1b** (22.6 mg, 0.1 mmol), *N*-methylindole (39.2 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 4:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (38.1 mg, 79% yield, 91:9 *er*). $[\alpha]_D^{20}$ = +16.3 (c = 0.4 Chloroform, 91:9 *er*). This product was isolated as an inseparable 20:1 mixture of diastereomers. The reported *dr* was determined by ^{1}H NMR analysis of purified **4d** and is consistent with that of the crude reaction mixture. The following analytical data correspond to the mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 9.47 (s, 0.05H), 8.79–8.67 (m, 2.1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1.05H), 7.69 (dd, *J* = 7.9, 1.0 Hz, 1.05H), 7.52–7.39 (m, 3.15H), 7.24–7.12 (m, 2.1H), 7.05 (ddd, *J* = 7.8, 6.9, 1.0 Hz, 1.05H), 6.98 (s, 1H), 6.88 (s, 0.05H), 3.71 (s, 3.15H), 3.43 (t, *J* = 6.9 Hz, 1H), 3.17 (dd, *J* = 10.8, 6.9 Hz, 0.05H), 2.76 (dd, *J* = 15.2, 10.6 Hz, 1H), 2.67 (dd, *J* = 15.2, 5.5 Hz, 1H), 2.63–2.58 (m, 0.1H), 2.09 (dt, *J* = 10.5, 6.0 Hz, 1H), 1.94 (td, *J* = 10.3, 5.8 Hz, 0.05H), 1.47 (d, *J* = 6.9 Hz, 0.15H), 1.43 (d, *J* = 7.0 Hz, 3H), 1.31 (s, 0.3H), 1.28 (s, 0.3H), 1.12 (s, 6H), 1.06 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.3, 147.9, 138.2, 136.8, 136.2, 134.8, 127.8, 127.5, 127.4, 126.0, 121.4, 121.2, 120.9, 119.8, 119.6, 118.4, 116.3, 108.8, 83.0, 37.2, 32.6, 31.1, 24.8, 24.5, 20.3; **HRMS** (ESI-TOF) Calcd for $C_{29}H_{35}BN_3O_3$ [M+H] 483.2808, found 483.2809; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 25% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 2.793 min, t (minor) = 3.783 min.



4e

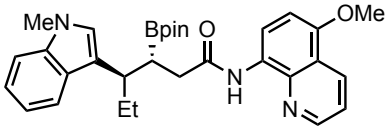
(3*R*,4*R*)-4-(1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4e): The title compound was prepared from **1c** (22.6 mg, 0.1 mmol), *N*-methylindole (39.2 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 4:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (37.1 mg, 77% yield, 91:9 *er*). **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 25% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 2.911 min, t (minor) = 3.875 min.



4f

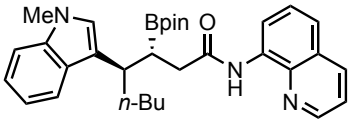
(3*R*,4*R*)-4-(1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (4f): The title compound was prepared from **1d** (24.0 mg, 0.1 mmol), *N*-methylindole (39.2 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (37.7 mg, 76% yield, 94:6 *er*). $[\alpha]_D^{20}$ = +31.7 (c = 0.5 Chloroform, 94:6 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.83–8.69 (m, 2H), 8.13 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.54–7.38 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07–6.95 (m, 2H), 3.73 (s, 3H), 3.12 (ddd, *J* = 9.7, 7.7, 4.3 Hz, 1H), 2.81–2.66 (m, 2H), 2.15–2.03 (m, 1H), 1.92 (dqd, *J* = 14.6, 7.3, 4.4 Hz, 1H), 1.78 (dtd, *J* = 13.6, 7.1, 2.2 Hz, 1H), 1.03 (s, 6H), 0.97 (s,

6H), 0.86 (t, *J* = 7.3 Hz, 3H) ; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.2, 147.9, 138.3, 136.6, 136.2, 134.8, 128.6, 127.9, 127.4, 126.6, 121.4, 121.1, 120.9, 119.6, 118.4, 117.6, 116.3, 108.7, 82.9, 38.7, 38.4, 32.6, 27.8, 24.8, 24.5, 12.1; **HRMS** (ESI-TOF) Calcd for $C_{30}H_{37}BN_3O_3$ [M+H] 497.2964, found 497.2970; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm, 25% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 2.293 min, t (minor) = 3.275 min; **X-ray** (single-crystal) Colorless needle crystals of X-ray diffraction quality were obtained by vapor diffusion of hexanes into a saturated solution of **4f** in EtOH (CCDC 1888952).[24]



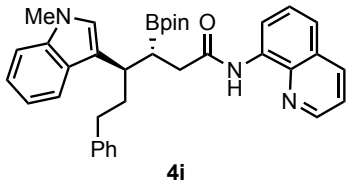
4g

(3*R*,4*R*)-*N*-(5-methoxyquinolin-8-yl)-4-(1-methyl-1*H*-indol-3-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (4g): The compound was prepared from **1e** (27.0 mg, 0.1 mmol), *N*-methylindole (39.2 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a yellow solid (31.5 mg, 60% yield, 94:6 *er*). **$[\alpha]_D^{20}$** = +26.4 (c = 0.45 Chloroform, 94:6 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.76 (d, *J* = 4.1 Hz, 1H), 8.68 (d, *J* = 8.6 Hz, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.40 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 3H), 3.73 (s, 3H), 3.11 (td, *J* = 8.8, 4.2 Hz, 1H), 2.71 (dd, *J* = 8.0, 5.2 Hz, 2H), 2.08 (q, *J* = 8.0 Hz, 1H), 1.99–1.88 (m, 1H), 1.77 (dt, *J* = 14.2, 7.5 Hz, 1H), 1.02 (s, 6H), 0.96 (s, 6H), 0.85 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.7, 149.8, 148.4, 139.0, 136.6, 131.0, 128.6, 128.3, 126.6, 121.0, 120.5, 120.3, 119.6, 118.4, 117.7, 116.4, 108.7, 104.4, 82.8, 55.7, 38.7, 38.4, 32.6, 27.8, 24.7, 24.5, 12.1; **HRMS** (ESI-TOF) Calcd for $C_{31}H_{39}BN_3O_4$ [M+H] 527.3070, found 527.3071; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on Daicel IBN column (3 μm, 4.6×250 mm), 25% MeOH/CO_2, 4.0 mL/min, λ = 250 nm, t (major) = 3.164 min, t (minor) = 4.576 min; **X-ray** (single-crystal) Colorless plank crystals of X-ray diffraction quality were obtained by vapor diffusion of hexanes into a saturated solution of **4g** in EtOAc (CCDC 1888953).[24]



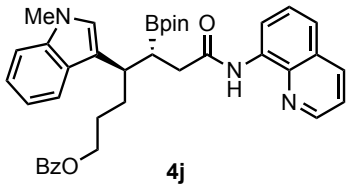
4h

(3*R*,4*R*)-4-(1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanamide (4h): The title compound was prepared from **1f** (26.8 mg, 0.1 mmol), *N*-methylindole (39.2 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a light-yellow solid (29.9 mg, 57% yield, 94:6 *er*). **$[\alpha]_D^{20}$** = +9.6 (c = 0.25 Chloroform, 94:6 *er*). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.79–8.68 (m, 2H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.66 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.54–7.35 (m, 3H), 7.21 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.14 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.03 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 6.97 (s, 1H), 3.72 (s, 3H), 3.19 (ddd, *J* = 9.9, 7.3, 4.3 Hz, 1H), 2.73 (d, *J* = 8.2 Hz, 2H), 2.07 (q, *J* = 7.7 Hz, 1H), 1.92–1.70 (m, 2H), 1.32–1.21 (m, 4H), 1.05 (s, 6H), 0.97 (s, 6H), 0.82 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.3, 147.9, 138.3, 136.7, 136.2, 134.8, 128.5, 127.9, 127.4, 126.5, 121.4, 121.1, 120.9, 119.6, 118.4, 118.0, 116.3, 108.8, 82.9, 38.3, 36.9, 34.8, 32.6, 29.9, 24.8, 24.5, 22.9, 14.1; **HRMS** (ESI-TOF) Calcd for $C_{32}H_{41}BN_3O_3$ [M+H] 525.3277, found 525.3281; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IB column (3 μm, 4.6×250 mm), 35% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 1.578 min, t (minor) = 1.993 min.



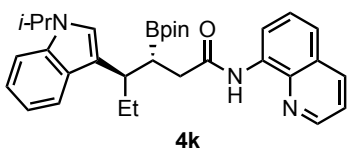
4i

(3*R*,4*R*)-4-(1-methyl-1*H*-indol-3-yl)-6-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (4i): The title compound was prepared from **1g** (31.6 mg, 0.1 mmol), *N*-methylindole (39.2 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (29.2 mg, 51% yield, 94:6 *er*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.79–8.71 (m, 2H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.67 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.54–7.39 (m, 3H), 7.26–7.10 (m, 7H), 7.09–7.02 (m, 2H), 3.76 (s, 3H), 3.25 (ddd, *J* = 9.9, 7.2, 4.3 Hz, 1H), 2.79–2.50 (m, 4H), 2.31–2.04 (m, 3H), 1.06 (s, 6H), 0.97 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.1, 147.9, 142.9, 138.2, 136.7, 136.2, 134.7, 128.5, 128.4, 128.1, 127.8, 127.4, 126.5, 125.4, 121.4, 121.2, 120.9, 119.6, 118.5, 117.5, 116.3, 108.8, 82.9, 38.3, 37.0, 36.6, 34.0, 32.7, 27.2, 24.8, 24.5; **HRMS** (ESI-TOF) Calcd for $C_{36}H_{41}BN_3O_3$ [M+H] 573.3277, found 573.3276; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IB column (3 μm, 4.6×250 mm), 35% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 2.273 min, t (minor) = 2.699 min.



4j

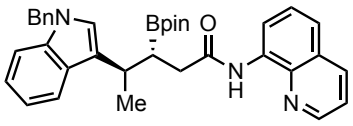
(4*R*,5*R*)-4-(1-methyl-1*H*-indol-3-yl)-7-oxo-7-(quinolin-8-ylamino)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl benzoate (4j): The title compound was prepared from **1h** (37.5 mg, 0.1 mmol), *N*-methylindole (39.2 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a white solid (26.4 mg, 42% yield, 94:6 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.81–8.69 (m, 2H), 8.13 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.03–7.96 (m, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.56–7.36 (m, 6H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.16 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 7.04–6.99 (m, 2H), 4.27 (t, *J* = 6.5 Hz, 2H), 3.72 (s, 3H), 3.26 (ddd, *J* = 11.0, 7.1, 4.4 Hz, 1H), 2.79–2.69 (m, 2H), 2.17–2.03 (m, 2H), 1.95 (dtd, *J* = 13.3, 9.9, 9.5, 5.8 Hz, 1H), 1.75 (ddt, *J* = 13.2, 9.3, 4.5 Hz, 2H), 1.05 (s, 6H), 0.98 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.0, 166.6, 147.9, 138.3, 136.7, 136.2, 134.8, 132.7, 130.5, 129.5, 128.4, 128.2, 127.8, 127.4, 126.6, 121.4, 121.3, 121.0, 119.5, 118.6, 117.2, 116.3, 108.8, 83.0, 65.2, 38.2, 36.8, 32.7, 31.4, 27.1, 24.8, 24.5; **HRMS** (ESI-TOF) Calcd for $C_{38}H_{43}BN_3O_5$ [M+H] 631.3332, found 631.3332; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 35% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 3.540 min, t (minor) = 4.849 min.



4k

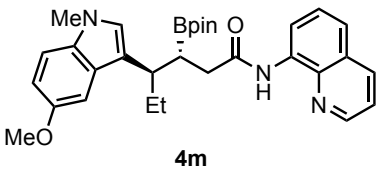
(3*R*,4*R*)-4-(1-isopropyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (4k): The title compound was prepared from **1d** (24.0 mg, 0.1 mmol), *N*-isopropylindole (47.8 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a light-yellow solid (33.0 mg, 63% yield, 95:5 *er*). **$[\alpha]_D^{20}$** = +12.6 (c = 0.35 Chloroform, 95:5 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.82–8.72 (m, 2H), 8.12 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.47–7.38 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.19–7.10 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.63 (p, *J* = 6.7 Hz, 1H), 3.12 (td, *J* = 8.8, 4.3 Hz, 1H),

2.76 (qd, *J* = 15.2, 8.1 Hz, 2H), 2.11 (ddd, *J* = 10.3, 8.3, 5.9 Hz, 1H), 1.92 (ddd, *J* = 13.6, 7.3, 4.4 Hz, 1H), 1.82–1.75 (m, 1H), 1.51 (dd, *J* = 8.5, 6.7 Hz, 6H), 0.99 (s, 6H), 0.95 (s, 6H), 0.83 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.2, 147.9, 138.3, 136.2, 135.5, 134.8, 128.7, 127.9, 127.5, 121.4, 121.4, 121.0, 120.8, 119.7, 118.3, 117.8, 116.4, 109.0, 82.8, 46.7, 38.8, 38.7, 27.8, 24.7, 24.6, 22.9, 22.8, 11.9; **HRMS** (ESI-TOF) Calcd for $C_{32}H_{41}BN_3O_3$ [M+H] 525.3277, found 525.3276; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 30% MeOH/CO_2, 4.0 mL/min, λ = 298 nm, t (major) = 1.754 min, t (minor) = 2.374 min.



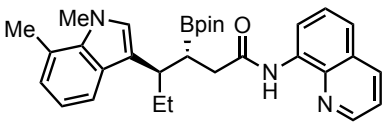
4l

(3*R*,4*R*)-4-(1-benzyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4l): The title compound was prepared from **1c** (22.6 mg, 0.1 mmol), *N*-benzylindole (62.2mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel chromatography with 9:1 hexanes:acetone as the eluent gave the product as a light-green oil (33.5 mg, 60% yield, 92:8 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.78–8.68 (m, 2H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.44 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.24–7.17 (m, 2H), 7.15–7.09 (m, 3H), 7.08–7.03 (m, 2H), 5.25 (s, 2H), 3.45 (t, *J* = 6.9 Hz, 1H), 2.76 (dd, *J* = 15.2, 10.7 Hz, 1H), 2.67 (dd, *J* = 15.2, 5.4 Hz, 1H), 2.14–2.04 (m, 1H), 1.43 (d, *J* = 7.1 Hz, 3H), 1.09 (s, 6H), 1.02 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.2, 147.9, 138.3, 137.9, 136.5, 136.2, 134.8, 128.6, 127.8, 127.8, 127.4, 127.4, 126.8, 125.3, 121.5, 121.4, 120.9, 120.6, 119.7, 118.7, 116.3, 109.4, 83.0, 49.9, 37.3, 31.1, 24.8, 24.5, 20.3; **HRMS** (ESI-TOF) Calcd for $C_{35}H_{39}BN_3O_3$ [M+H] 559.3121, found 559.3123; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 30% MeOH/CO_2, 4.0 mL/min, λ = 295 nm, t (major) = 3.982 min, t (minor) = 5.630 min.



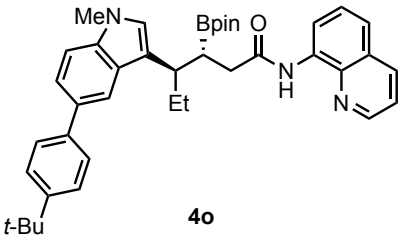
4m

(3*R*,4*R*)-4-(5-methoxy-1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (4m): The title compound was prepared from **1d** (24.0 mg, 0.1 mmol), 5-methoxy-*N*-methylindole (48.4 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (44.7 mg, 85% yield, 93:7 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.82–8.69 (m, 2H), 8.12 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.53–7.38 (m, 3H), 7.13–7.03 (m, 2H), 6.97 (s, 1H), 6.79 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.76 (s, 3H), 3.70 (s, 3H), 3.07 (td, *J* = 8.7, 4.3 Hz, 1H), 2.74 (dd, *J* = 8.1, 6.3 Hz, 2H), 2.08 (dt, *J* = 9.4, 7.2 Hz, 1H), 1.92 (ddd, *J* = 13.5, 7.2, 4.4 Hz, 1H), 1.75 (dtd, *J* = 13.6, 7.1, 2.1 Hz, 1H), 1.04 (s, 6H), 0.98 (s, 6H), 0.86 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.2, 153.4, 147.9, 138.2, 136.2, 134.8, 132.0, 128.9, 127.8, 127.4, 127.2, 121.4, 120.9, 117.1, 116.2, 111.3, 109.4, 101.3, 82.9, 55.9, 38.5, 38.4, 32.8, 27.9, 24.8, 24.5, 12.1; **HRMS** (ESI-TOF) Calcd for $C_{31}H_{39}BN_3O_4$ [M+H] 527.3070, found 527.3070; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 30% MeOH/CO_2, 4.0 mL/min, λ = 305 nm, t (major) = 2.022 min, t (minor) = 2.753 min.



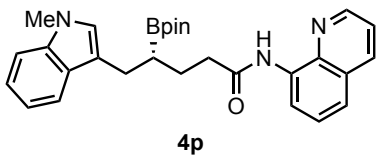
4n

(3*R*,4*R*)-4-(1,7-dimethyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (4n): The title compound was prepared from **1d** (24.0 mg, 0.1 mmol), 7-methyl-*N*-methylindole (43.6 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a light-yellow solid (43.3 mg, 85% yield, 93:7 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.82–8.73 (m, 2H), 8.15 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.54–7.42 (m, 4H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 7.0 Hz, 1H), 4.01 (s, 3H), 3.14 (ddd, *J* = 9.4, 7.2, 4.3 Hz, 1H), 2.79–2.67 (m, 5H), 2.13–2.08 (m, 1H), 1.92 (ddq, *J* = 14.8, 7.5, 3.1 Hz, 1H), 1.80 (ddd, *J* = 13.6, 9.4, 7.1 Hz, 1H), 1.11 (s, 6H), 1.05 (s, 6H), 0.89 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.3, 147.9, 138.3, 136.2, 135.4, 134.8, 129.7, 128.3, 127.9, 127.4, 123.8, 121.4, 120.9, 120.7, 118.7, 117.6, 117.2, 116.3, 83.0, 38.4, 38.2, 36.6, 27.6, 24.8, 24.5, 19.7, 12.2; **HRMS** (ESI-TOF) Calcd for $C_{31}H_{39}BN_3O_3$ [M+H] 511.3121, found 511.3127; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 30% MeOH/CO_2, 4.0 mL/min, λ = 298 nm, t (major) = 2.063 min, t (minor) = 2.883 min.



4o

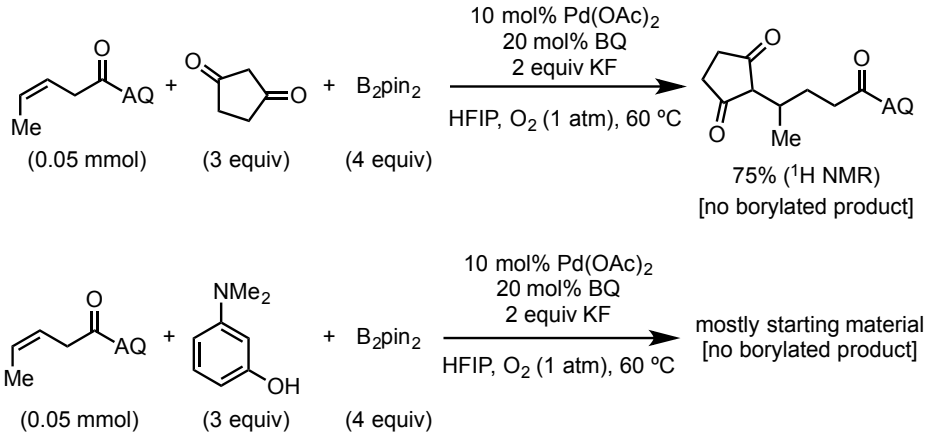
(3*R*,4*R*)-4-(5-(4-(*tert*-butyl)phenyl)-1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (4o): The title compound was prepared from **1d** (24.0 mg, 0.1 mmol), 5-(4-(*tert*-butyl)phenyl)-*N*-methylindole (79.0 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (34.5 mg, 55% yield, 92:8 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.78 (d, *J* = 7.7 Hz, 1H), 8.71 (d, *J* = 4.1 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.81 (s, 1H), 7.51 (dd, *J* = 16.8, 8.0 Hz, 3H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.42–7.37 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.24 (s, 1H), 7.02 (s, 1H), 3.75 (s, 3H), 3.17 (td, *J* = 8.7, 4.3 Hz, 1H), 2.82–2.71 (m, 2H), 2.11 (q, *J* = 8.0 Hz, 1H), 1.94 (dq, *J* = 13.0, 6.5 Hz, 1H), 1.81 (dq, *J* = 14.3, 7.5 Hz, 1H), 1.34 (s, 9H), 1.04 (s, 6H), 0.98 (s, 6H), 0.87 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.2, 148.8, 147.9, 139.9, 138.3, 136.1, 136.0, 134.8, 131.8, 129.2, 127.8, 127.4, 127.2, 127.0, 125.4, 121.4, 120.9, 120.9, 118.2, 117.9, 116.3, 108.9, 82.9, 38.5, 38.5, 34.4, 32.8, 31.4, 28.1, 24.8, 24.5, 12.2; **HRMS** (ESI-TOF) Calcd for $C_{40}H_{49}BN_3O_3$ [M+H] 629.3903, found 629.3903; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 25% MeOH/CO_2, 4.0 mL/min, λ = 300 nm, t (major) = 4.003 min, t (minor) = 5.914 min.



4p

(*R*)-5-(1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4p): The title compound was prepared from **1i** (22.6 mg, 0.1 mmol), *N*-methylindole (39.2 mg, 0.3 mmol), and bis(pinacolato)diboron (101.6 mg, 0.4 mmol) according to the general asymmetric carboboration procedure. Purification using silica gel column chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (36.7 mg, 76% yield, 76:24 *er*). **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 25% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (minor) = 4.982 min, t (major) = 5.271 min.

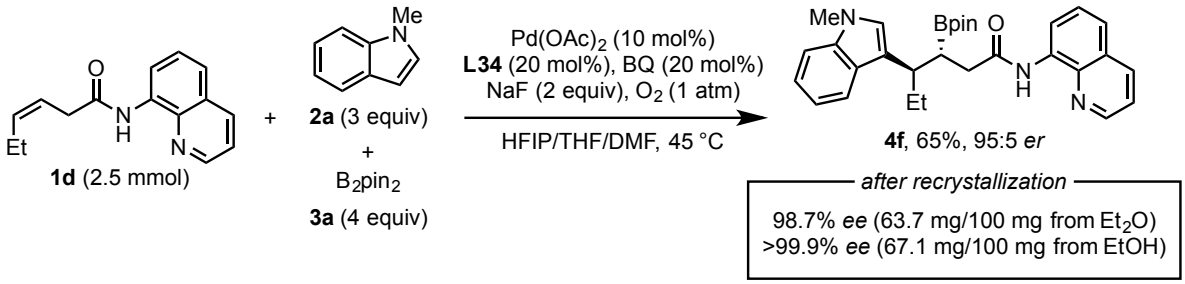
Unsuccessful Non-Indole Carbon Nucleophiles



Scheme S12: Unsuccessful carbon nucleophiles for carboboration reaction.

a) b) c) d)

Large-Scale Synthesis and Recrystallization



Scheme S13: Large-Scale Synthesis of Chiral Boronate **4f**.

Procedure for Large-Scale Synthesis and Recrystallization of 4f: Alkene substrate **1b** (600 mg, 2.5 mmol), *N*-methylindole (980 mg, 7.5 mmol), bis(pinacolato)diboron (2.54 g, 10 mmol), $Pd(OAc)_2$ (55 mg, 0.25 mmol), **L34** (214 g, 0.5 mmol), benzoquinone (55 mg, 0.5 mmol), and NaF (210 mg, 5 mmol) were added to a 500-mL Schlenk flask. The reaction flask was sealed with a rubber septum and was then evacuated and backfilled with O_2 (×3). Under positive O_2 pressure HFIP/THF/DMF (5 mL, 2:2:1, v/v/v) was added. The flask was submerged into a silicon oil bath that was pre-heated to 45 °C. After 5 days, the dark brown reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL) and washed with brine (20 mL). The organic layer was dried over Na_2SO_4 and concentrated to afford a brown residue that upon purification by rapid silica gel column chromatography—with a residence time less than 20 min to prevent alkyl boronate decomposition—afforded **4f** (809 mg, 65%, 95:5 *er*) as a light-yellow solid. Analytical data was consistent with the information reported above.

Recrystallization: A sample of **4f** (100 mg) was dissolved in a minimum volume of Et_2O or EtOH to afford a saturated solution in a 4-dram vial. The organic solvent was slowly evaporated until small amount of crystals precipitated. The vial was placed in a 4 ºC refrigerator for 2 days and the recrystallized product **4f** (63.7 mg, 98.7% *ee* from Et_2O; 67.1 mg, >99% *ee* from EtOH) was collected by filtration.

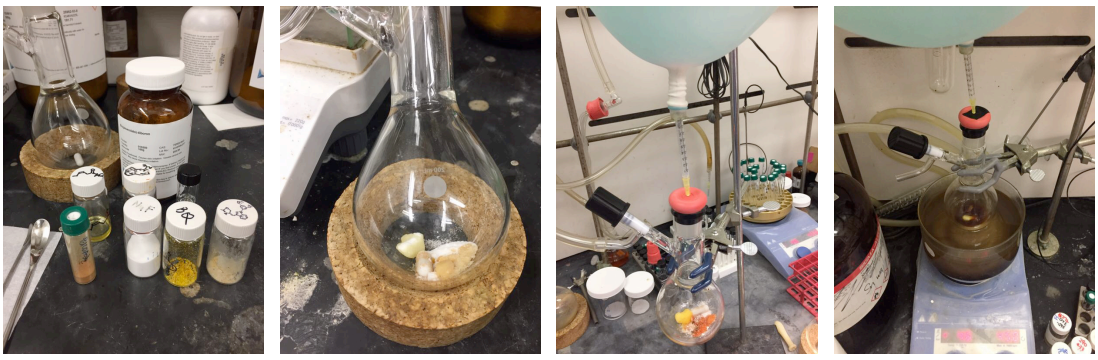
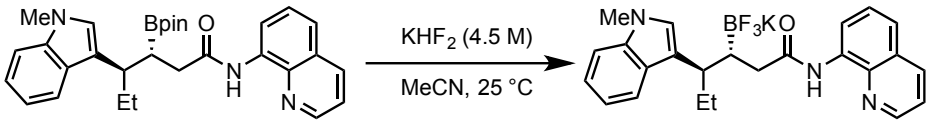


Figure S1: Photographic depiction of the procedure for gram-scale synthesis of **4f**.

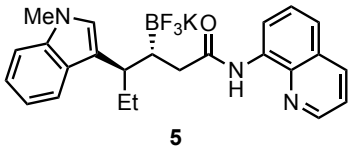
a) Reagents. b) Adding reagents to Schlenk flask. c) Degassing and back-filling with O_2. d) Heating in oil bath.

Procedures for Transformations of Borylated Products



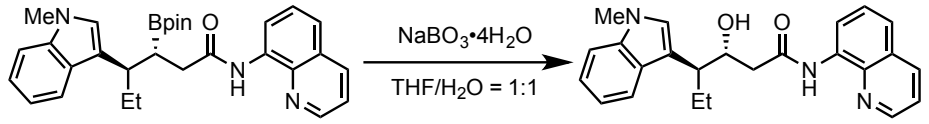
4f, 95:5 *er* **5**, 95%

Scheme S14: Synthesis of potassium trifluoroborate salt **5**.



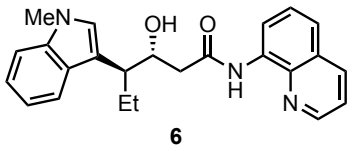
5

(3*R*,4*R*)-4-(1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)-3-(trifluoro-λ^4-boraneyl)hexanamide, potassium salt (5): The title compound was prepared by adapting a literature procedure.[25] In a 15-mL reaction tube containing a Teflon-coated magnetic stir bar, the borylated compound **4f** (49.8 mg, 0.1 mmol) was dissolved in MeCN (0.2 mL), and saturated aq. KHF_2 (4.5 M, 0.09 mL, 4 equiv) was added. The reaction mixture was stirred for 5 h, concentrated, and azeotroped with EtOH (×3). The resulting material was then placed on the high vacuum for 6 h. The crude product was extracted with hot acetone, filtered and then concentrated. Et_2O (3 mL) was added to the crude material, and the mixture was sonicated for 30 min. After removal of the solvent, the trifluoroborate salt was achieved as a pale-yellow solid (45.4 mg, 95% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.51 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.70–7.57 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 11.1 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.77 (s, 1H), 3.52 (s, 3H), 3.04 (s, 1H), 2.34 (d, *J* = 11.7 Hz, 2H), 1.83 (s, 1H), 1.56 (s, 1H), 1.38 (s, 1H), 0.73 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 176.1, 147.8, 138.2, 136.9, 135.8, 134.6, 128.5, 127.7, 127.3, 126.4, 121.2, 120.7, 120.7, 119.9, 119.3, 118.0, 116.0, 108.8, 39.1, 37.5, 32.3, 24.8, 24.8, 13.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –140.4 (s, 3F).



4f, 95:5 *er* **6**, 88%, 94:6 *er*

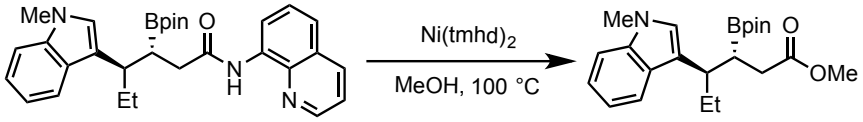
Scheme S15: Oxidation of chiral boronate **4f**.



6

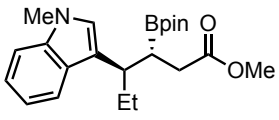
(3*R*,4*S*)-3-hydroxy-4-(1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)hexanamide (6): The title compound was prepared by adapting a literature procedure.[26] To a reaction tube containing **4f** (49.8 mg, 0.1 mmol), were added $NaBO_3$•$4H_2O$ (77 mg, 0.5 mmol), THF (0.5 mL) and H_2O (0.5 mL). The resulting mixture was allowed to stir at room temperature for 3 h. The aqueous layer was then washed with Et_2O (5 mL, ×2). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by preparative TLC (1.5:1 hexanes:EtOAc) gave the product as a white solid (34.1 mg, 88%, 94:6 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.79–8.69 (m, 2H), 8.13 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.67 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.54–7.47 (m, 2H), 7.41 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.31 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.22 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.10 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.05 (s, 1H), 4.54 (ddd, *J* = 9.5, 4.7, 2.8 Hz, 1H), 3.78 (s, 3H), 3.21 (s, 1H), 3.00 (dt, *J* = 9.9, 5.0 Hz, 1H), 2.74 (dd, *J* = 15.4, 2.8 Hz, 1H), 2.62 (dd, *J* = 15.4, 9.4 Hz, 1H), 1.99 (ddd, *J* = 13.0, 7.3, 5.3 Hz, 1H), 1.93–1.82 (m,

1H), 0.91 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.4, 148.3, 138.6, 137.1, 136.4, 134.6, 128.6, 128.1, 127.7, 127.4, 121.7, 121.7, 121.6, 119.5, 119.0, 116.9, 113.4, 109.4, 71.3, 44.6, 43.1, 32.9, 25.6, 12.8; **HRMS** (ESI-TOF) Calcd for $C_{24}H_{26}N_3O_2$ [M+H] 388.2025, found 388.2023; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IBN column (3 μm, 4.6×250 mm), 35% MeOH/CO_2, 4.0 mL/min, λ = 241 nm, t (major) = 3.573 min, t (minor) = 4.196 min.



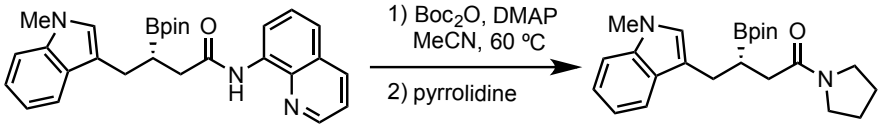
4f, 95:5 *er* **7**, 82%, 96:4 *er*

Scheme S16: Methanolysis of the 8-amionquinoline (AQ) amide.



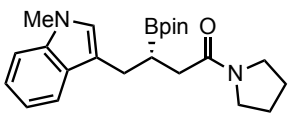
7

methyl (3*R*,4*R*)-4-(1-methyl-1*H*-indol-3-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (7): The title compound was prepared by adapting a literature procedure.[27] To a 15-mL reaction tube containing a Teflon-coated magnetic stir bar, were added compound **4f** (99.6 mg, 0.2 mmol), and Ni(tmhd)$_2$ (128 mg, 0.3 mmol). The reaction vessel was evacuated and backfilled with N_2 (×3), followed by addition of anhydrous MeOH (2 mL). The reaction mixture was heated at 100 ºC for 6 days. After cooling to room temperature, the reaction was diluted with EtOAc (5 mL) and filtered through a plug of celite with EtOAc as the eluent. The resulting solution was concentrated under vacuum and purified by preparative TLC (4:1 hexanes:EtOAc) to afford the product as a colorless oil (7.1 mg, 55% yield, 96:4 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (dt, J = 7.9, 0.9 Hz, 1H), 7.24 (dt, J = 8.2, 0.9 Hz, 1H), 7.17 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 7.06 (ddd, J = 7.9, 6.9, 1.1 Hz, 1H), 6.89 (s, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 3.02 (ddd, J = 9.6, 7.7, 4.1 Hz, 1H), 2.54–2.40 (m, 2H), 1.90–1.76 (m, 2H), 1.68 (ddd, J = 13.5, 9.7, 7.3 Hz, 1H), 1.04 (s, 6H), 0.97 (s, 6H), 0.82 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.6, 136.7, 128.3, 126.4, 121.2, 119.5, 118.4, 117.4, 108.8, 82.9, 51.3, 38.3, 34.0, 32.6, 27.0, 24.8, 24.4, 12.0; **HRMS** (ESI-TOF) Calcd for $C_{22}H_{33}BNO_4$ [M+H] 385.2539, found 385.2532; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IG column (3 μm, 4.6×250 mm), 3% *i*-PrOH / CO_2, 4.0 mL/min, λ = 222 nm, t (minor) = 3.987 min, t (major) = 4.442 min.



4a, 86:14 *er* **8**, 82%, 86:14 *er*

Scheme S17: Transamidation of the 8-amionquinoline (AQ) amide.



8

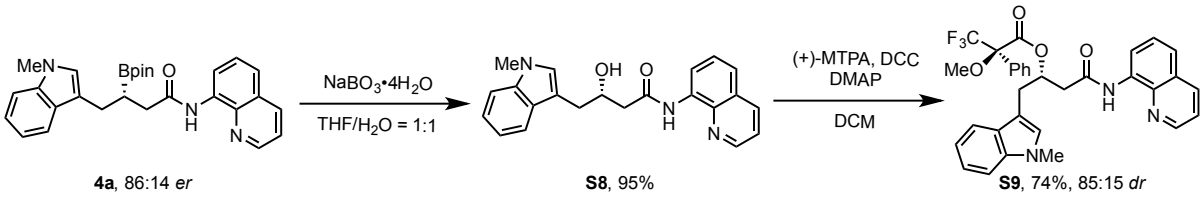
(*S*)-4-(1-methyl-1*H*-indol-3-yl)-1-(pyrrolidin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (8): The title compound was prepared by adapting a literature procedure.[28]

Boc Protection: To a 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar, were added compound **4a** (235 mg,

0.5 mmol), 4-(dimethylamino)pyridine (6.1 mg, 0.05 mmol) and Boc anhydride (218 mg, 1 mmol). The reaction flask was evacuated and backfilled with N_2 (×1), followed by addition of anhydrous MeCN (5 mL). The reaction mixture was heated at 60 ºC for 2 hours. After cooling to room temperature, the reaction was concentrated under vacuum and purified by column chromatography (2:1 hexanes:EtOAc) to afford the Boc-protected amide as a light yellow solid.

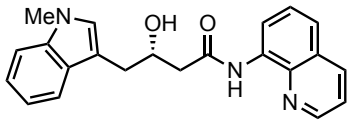
Aminolysis: To a 4-dram vial equipped with a Teflon-coated magnetic stir bar, were added pyrrolidine (65 μL, 0.75 mmol) and toluene (1 mL). The reaction mixture was heated under N_2 atmosphere at 60 ºC overnight. After cooling to room temperature, the reaction was concentrated under vacuum and purified by column chromatography (1:2 hexanes:EtOAc) to afford amide **8** as a colorless oil (162 mg, 82% yield, 86:14 *er*). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 3.72 (s, 3H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.18 (t, *J* = 6.6 Hz, 2H), 3.02 (dd, *J* = 15.0, 5.2 Hz, 1H), 2.71 (dd, *J* = 15.0, 10.7 Hz, 1H), 2.43 (dd, *J* = 16.9, 6.8 Hz, 1H), 2.30 (dd, *J* = 16.6, 8.0 Hz, 1H), 1.89–1.73 (m, 4H), 1.70–1.57 (m, 1H), 1.25 (d, *J* = 8.7 Hz, 12H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.6, 137.0, 128.4, 126.6, 121.2, 119.4, 118.3, 115.4, 108.9, 81.9, 46.6, 46.0, 36.4, 32.6, 25.8, 25.4, 25.0, 25.0, 24.4; **SFC** (chiral column) The enantiomeric ratio was determined by chiral SFC on a Daicel IG column (3 μm, 4.6×250 mm), 30% MeOH/CO_2, 4.0 mL/min, λ = 224 nm, t (minor) = 1.722 min, t (major) = 2.073 min.

*Determination of Absolute Stereochemistry of **4a** by Mosher Ester Analysis*



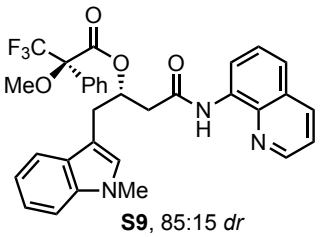
4a, 86:14 *er* — **S8**, 95% — **S9**, 74%, 85:15 *dr*

Scheme S18: Synthesis of Mosher ester **S9**.



S8

(*S*)-3-hydroxy-4-(1-methyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)butanamide (S8): The title compound was prepared from **4a** (31.8 mg, 0.068 mmol), and $NaBO_3•4H_2O$ (83.5 mg, 0.54 mmol) according to the previously described procedure.[26] Purification using silica gel column chromatography with 1:1 hexanes:EtOAc as the eluent gave the product as a white solid (23.1 mg, 95% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.92–8.59 (m, 2H), 8.14 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.58–7.47 (m, 2H), 7.43 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.26–7.22 (m, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 4.53 (d, *J* = 7.6 Hz, 1H), 3.77 (s, 3H), 3.56 (s, 1H), 3.19–2.95 (m, 2H), 2.81 (dd, *J* = 15.4, 3.1 Hz, 1H), 2.74 (dd, *J* = 15.4, 8.6 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.0, 148.2, 138.4, 137.1, 136.3, 134.3, 128.1, 128.0, 127.8, 127.3, 121.8, 121.7, 121.6, 119.1, 119.0, 116.8, 110.1, 109.3, 77.3, 77.0, 76.8, 69.0, 43.6, 32.8, 32.7.

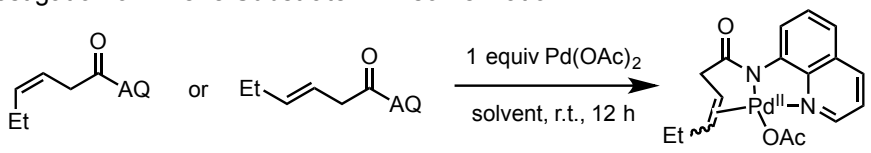


S9, 85:15 *dr*

(*S*)-1-(1-methyl-1*H*-indol-3-yl)-4-oxo-4-(quinolin-8-ylamino)butan-2-yl (*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (S9): The title compound was prepared by adapting a literature procedure.[29] Under a N_2 atmosphere, (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (Mosher's acid, 15 mg, 0.064 mmol) was dissolved in anhydrous DCM (0.62 mL), and the mixture was cooled to 0 ºC. Subsequent addition of DCC (15 mg, 0.073 mmol) was followed by stirring for 15 min, at which time a solution of alcohol **S8** (20.8 mg, 0.058 mmol) in DCM (0.65 mL) and a catalytic amount of 4-(dimethylamino)pyridine were added. The reaction mixture was stirred at room temperature overnight. After the reaction had reacted completion, the resulting suspension was filtered through a plug of celite, and the filtrate was concentrated under vacuum. Purification by preparative TLC (3:1 hexanes:EtOAc) gave the product as a colorless oil (24.8 mg, 74% yield, 85:15 *dr*). The reported *dr* was determined by ^{1}H NMR analysis of purified **S9** and is consistent with that of the crude reaction mixture. The following analytical data correspond to the mixture. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.70 (s, 0.15H), 9.62 (s, 0.85H), 8.70 (dtd, *J* = 9.1, 6.5, 6.1, 3.5 Hz, 2H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 0.85H), 7.69 (d, *J* = 7.9 Hz, 0.15H), 7.57–7.33 (m, 5H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.25–6.99 (m, 5H), 6.96 (s, 0.85H), 6.68 (s, 0.15H), 6.02 (tt, *J* = 7.3, 5.7 Hz, 1H), 3.72 (s, 2.55H), 3.68 (s, 0.45H), 3.45 (s, 3H), 3.43–3.31 (m, 1H), 3.22 (dd, *J* = 14.4, 7.6 Hz, 0.85H), 3.05 (dd, *J* = 14.4, 8.0 Hz, 0.15H), 2.96–2.78 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –71.4 (s, 0.45 F), –72.0 (s, 2.55 F). The absolute configurations of compound **4a** and alcohol **S8** were assigned as (*S*) by ^{1}H NMR analysis according to the literature.[30]

Mechanistic Studies of Alkene E/Z Isomerization

Table S5. Investigation of Alkene Substrate *E/Z* Isomerization.

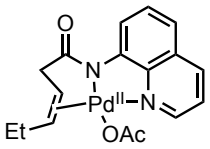


1d (0.05 mmol) **1l** (0.05 mmol) **Pd-I**

Entry	Substrate	Solvent	**L34**	Pd complex Z/E
1	**1d**	MeCN	w/o	>20:1
2	**1d**	MeCN	w	>20:1
3	**1l**	MeCN	w/o	1.6:1
4	**1l**	MeCN	w	>20:1
5	**1d**	MeOH	w/o	>20:1
6	**1d**	MeOH	w	>20:1
7	**1l**	MeOH	w/o	7.4:1 (1:3)[a]
8	**1l**	MeOH	w	>20:1
9	**1d**	HFIP/THF/DMF[b]	w/o	17:1
10	**1d**	HFIP/THF/DMF[b]	w	>20:1
11	**1l**	HFIP/THF/DMF[b]	w/o	1.2:1
12	**1l**	HFIP/THF/DMF[b]	w	10:1

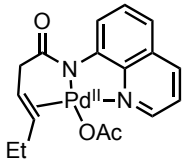
[a]The ratio in parentheses is the product ratio of a trial that was stopped after 3 h. [b]HFIP/THF/DMF = 2:2:1

General Procedure for Palladium Complex formation: Alkene substrate (12 mg, 0.05 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and solvent (0.2 mL) were added to a 1-dram vial. The reaction mixture was stirred at room temperature for 12 hours under air. The *Z*/*E* ratio of palladium(II) complex was determined by ^{1}H NMR analysis of the crude reaction mixture.



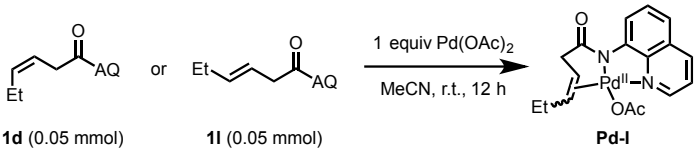
Pd-I

Pd Complex I (Pd-I): The title compound was isolated as a yellow solid (16 mg, 80% yield). **^{1}H NMR** (500 MHz, CD_3CN) δ 8.77 (dd, *J* = 5.7, 3.2 Hz, 1H), 8.56 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.49 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.65 (dd, *J* = 8.3, 5.1 Hz, 1H), 7.55–7.52 (m, 2H), 6.40–6.32 (m, 1H), 5.95 (q, *J* = 7.6 Hz, 1H), 3.47 (dd, *J* = 17.5, 7.6 Hz, 1H), 3.16 (ddd, *J* = 17.4, 5.2, 1.3 Hz, 1H), 2.47 (dtd, *J* = 14.9, 7.5, 0.9 Hz, 1H), 1.98 (s, 3H), 1.30 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (150 MHz, CD_3CN) δ 181.3, 177.4, 147.6, 147.3, 141.6, 131.2, 130.3, 122.6, 122.3, 121.3, 120.1, 92.2, 37.4, 25.5, 23.6, 13.2; **HRMS** (ESI-TOF) Calcd for $C_{15}H_{15}N_2OPd$ [M–OAc] 343.0225, found 343.0225. **X-ray** (single-crystal) Yellow block crystals of X-ray diffraction quality were obtained by vapor diffusion of hexanes into a saturated solution of **Pd-I** in benzene (CCDC 1888954).[24]

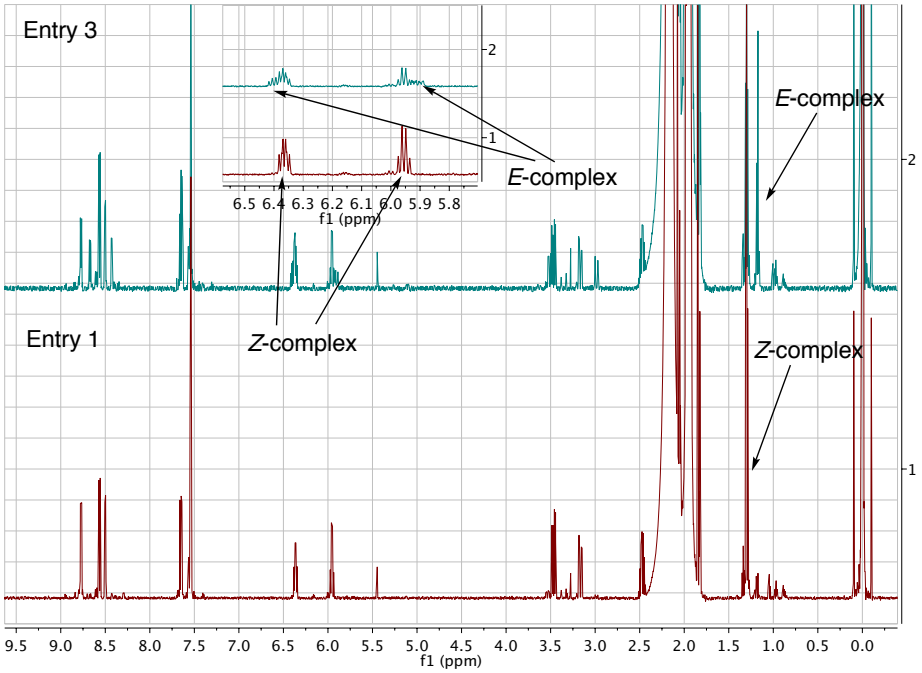


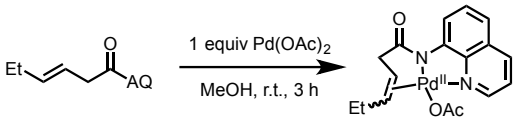
***E*-Alkene Pd Complex: ^{1}H NMR** (600 MHz, CD_3OD) δ 8.66 (ddd, *J* = 8.1, 5.2, 1.4 Hz, 2H), 8.41 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.74–7.66 (m, 1H), 7.64–7.57 (m, 2H), 6.58 (dt, *J* = 14.1, 6.8 Hz, 1H), 5.93 (ddd, *J* = 14.8, 6.7, 2.5 Hz, 1H), 3.66 (dd, *J* = 17.9, 6.7 Hz, 1H), 2.26–2.17 (m, 1H), 2.08 (s, 3H), 1.97–1.89 (m, 1H), 1.26 (t, *J* = 7.4 Hz, 3H). One of the aliphatic protons could not be confidently assigned due to overlap with methanol peaks.

Representative ^{1}H NMR spectra for determination of *E/Z* ratios

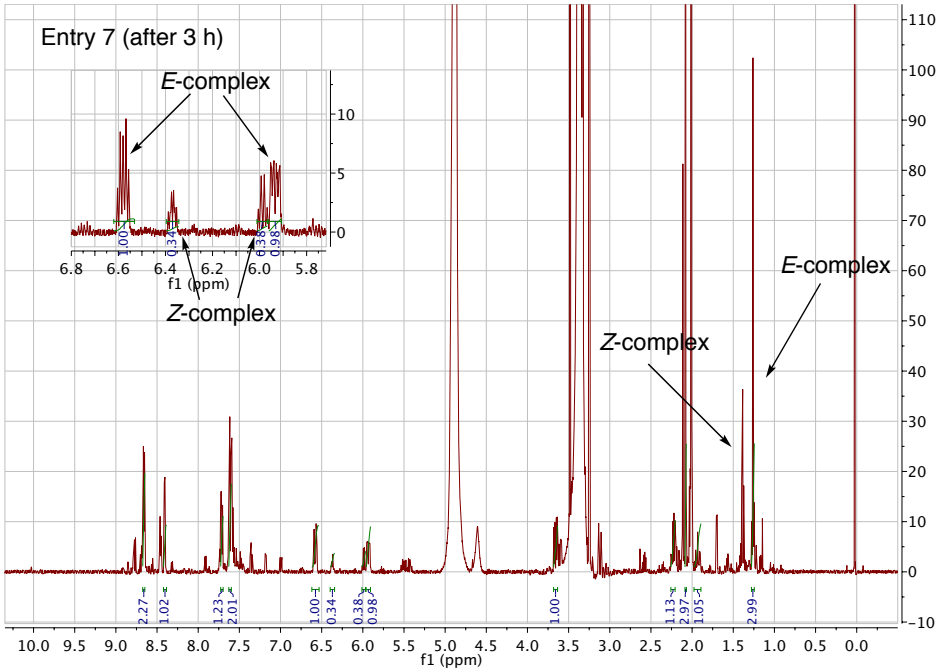


1d (0.05 mmol) **1l** (0.05 mmol) **Pd-I**





1l (0.05 mmol) **Pd-I**


Entry 7 (after 3 h)
E-complex
Z-complex
E-complex
Z-complex
f1 (ppm)
f1 (ppm)

X-RAY CRYSTALLOGRAPHY

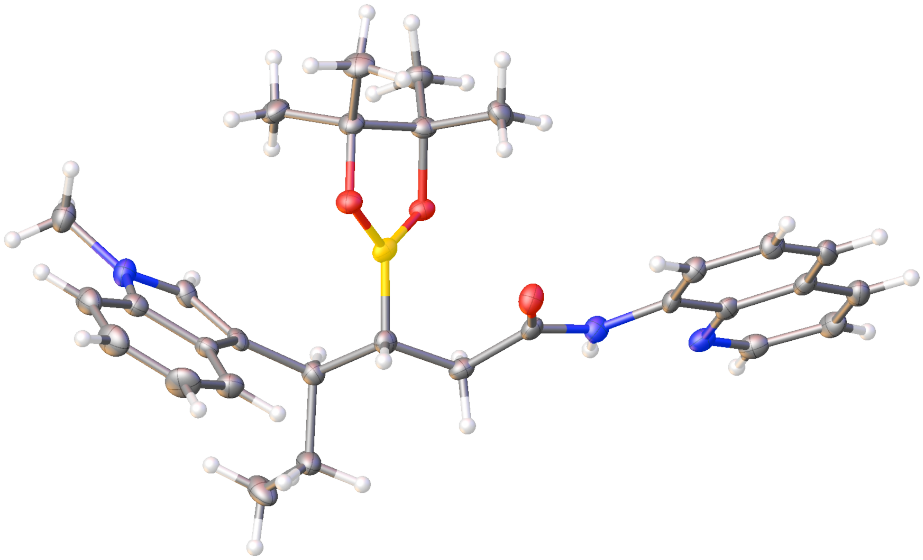


Table S6. Crystal data and structure refinement for **4f**.

Identification code	LZ-Et-S	
Empirical formula	C30 H36 B N3 O3	
Formula weight	497.43	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 6.37430(10) Å	α= 90°.
	b = 23.6017(6) Å	β= 101.680(2)°.
	c = 9.0486(2) Å	γ = 90°.
Volume	1333.12(5) $Å^3$	
Z	2	
Density (calculated)	1.239 Mg/m^3	
Absorption coefficient	0.629 mm^{-1}	
F(000)	532	
Crystal size	0.27 x 0.13 x 0.08 mm^3	
Theta range for data collection	3.746 to 68.277°.	
Index ranges	-7<=h<=7, -28<=k<=28, -10<=l<=10	
Reflections collected	18399	
Independent reflections	4851 [R(int) = 0.0255]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6828	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4851 / 1 / 340	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0607	
R indices (all data)	R1 = 0.0255, wR2 = 0.0611	
Absolute structure parameter	0.01(5) [stereochem. confirmed]	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.163 and -0.154 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4f**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(2)	3837(2)	4534(1)	5889(1)	16(1)
O(1)	4310(2)	5266(1)	4336(1)	18(1)
O(3)	8649(2)	4865(1)	7238(1)	21(1)
N(3)	8293(2)	3384(1)	10978(2)	20(1)
N(2)	8134(2)	4259(1)	9092(2)	18(1)
N(1)	-868(2)	6354(1)	4161(2)	20(1)
C(22)	826(3)	6716(1)	4199(2)	19(1)
C(5)	13068(3)	3051(1)	9363(2)	22(1)
C(8)	9791(3)	3868(1)	9103(2)	17(1)
C(9)	9849(3)	3406(1)	10144(2)	17(1)
C(21)	1050(3)	7171(1)	3256(2)	25(1)
C(7)	11324(3)	3905(1)	8239(2)	19(1)
C(2)	9937(3)	2531(1)	12134(2)	24(1)
C(1)	8354(3)	2957(1)	11929(2)	22(1)
C(4)	11507(3)	2997(1)	10261(2)	19(1)
C(17)	2461(3)	6562(1)	5447(2)	18(1)
C(16)	1668(3)	6087(1)	6167(2)	17(1)
C(30)	-338(3)	5979(1)	5346(2)	18(1)
C(6)	12965(3)	3495(1)	8382(2)	21(1)
C(10)	7679(3)	4733(1)	8218(2)	16(1)
C(25)	3819(3)	4281(1)	4411(2)	18(1)
C(14)	3142(3)	6138(1)	8958(2)	24(1)
C(11)	5884(3)	5093(1)	8579(2)	18(1)
C(12)	4877(3)	5476(1)	7249(2)	16(1)
C(18)	4364(3)	6876(1)	5708(2)	24(1)
C(28)	3332(3)	4803(1)	3356(2)	19(1)
C(13)	2793(3)	5761(1)	7534(2)	17(1)
C(29)	946(3)	4935(1)	2908(2)	26(1)
C(20)	2939(4)	7474(1)	3568(2)	30(1)
C(24)	6046(3)	4036(1)	4463(2)	24(1)
C(26)	2148(3)	3816(1)	4130(2)	24(1)
C(15)	1096(4)	6189(1)	9584(2)	32(1)
C(23)	-2763(3)	6322(1)	2962(2)	27(1)
C(3)	11487(3)	2552(1)	11303(2)	23(1)
B(1)	4348(3)	5095(1)	5785(2)	15(1)
C(27)	4327(3)	4787(1)	1972(2)	27(1)
C(19)	4580(4)	7328(1)	4778(2)	31(1)

Table S8. Bond lengths [Å] and angles [°] for **4f**.

O(2)-C(25)	1.462(2)
O(2)-B(1)	1.373(2)
O(1)-C(28)	1.464(2)
O(1)-B(1)	1.367(2)
O(3)-C(10)	1.219(2)
N(3)-C(9)	1.363(2)
N(3)-C(1)	1.321(2)
N(2)-H(2)	0.8800
N(2)-C(8)	1.401(2)
N(2)-C(10)	1.366(2)
N(1)-C(22)	1.371(2)
N(1)-C(30)	1.379(2)
N(1)-C(23)	1.453(2)

C(22)-C(21)	1.397(3)
C(22)-C(17)	1.420(3)
C(5)-H(5)	0.9500
C(5)-C(4)	1.412(3)
C(5)-C(6)	1.366(3)
C(8)-C(9)	1.436(2)
C(8)-C(7)	1.373(3)
C(9)-C(4)	1.418(3)
C(21)-H(21)	0.9500
C(21)-C(20)	1.381(3)
C(7)-H(7)	0.9500
C(7)-C(6)	1.411(3)
C(2)-H(2A)	0.9500
C(2)-C(1)	1.410(3)
C(2)-C(3)	1.359(3)
C(1)-H(1)	0.9500
C(4)-C(3)	1.413(3)
C(17)-C(16)	1.440(3)
C(17)-C(18)	1.399(3)
C(16)-C(30)	1.366(3)
C(16)-C(13)	1.508(2)
C(30)-H(30)	0.9500
C(6)-H(6)	0.9500
C(10)-C(11)	1.513(2)
C(25)-C(28)	1.552(2)
C(25)-C(24)	1.525(2)
C(25)-C(26)	1.514(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(14)-C(13)	1.544(2)
C(14)-C(15)	1.528(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(11)-C(12)	1.538(2)
C(12)-H(12)	1.0000
C(12)-C(13)	1.557(2)
C(12)-B(1)	1.579(3)
C(18)-H(18)	0.9500
C(18)-C(19)	1.383(3)
C(28)-C(29)	1.524(3)
C(28)-C(27)	1.514(3)
C(13)-H(13)	1.0000
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(20)-H(20)	0.9500
C(20)-C(19)	1.396(3)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(3)-H(3)	0.9500

C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(19)-H(19)	0.9500

B(1)-O(2)-C(25)	106.84(13)
B(1)-O(1)-C(28)	106.54(13)
C(1)-N(3)-C(9)	117.44(16)
C(8)-N(2)-H(2)	116.0
C(10)-N(2)-H(2)	116.0
C(10)-N(2)-C(8)	127.92(15)
C(22)-N(1)-C(30)	108.17(14)
C(22)-N(1)-C(23)	125.62(15)
C(30)-N(1)-C(23)	125.70(16)
N(1)-C(22)-C(21)	129.79(17)
N(1)-C(22)-C(17)	108.03(15)
C(21)-C(22)-C(17)	122.17(17)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(6)-C(5)-C(4)	119.71(17)
N(2)-C(8)-C(9)	115.11(15)
C(7)-C(8)-N(2)	125.21(16)
C(7)-C(8)-C(9)	119.66(16)
N(3)-C(9)-C(8)	117.78(15)
N(3)-C(9)-C(4)	123.17(16)
C(4)-C(9)-C(8)	119.04(15)
C(22)-C(21)-H(21)	121.1
C(20)-C(21)-C(22)	117.83(18)
C(20)-C(21)-H(21)	121.1
C(8)-C(7)-H(7)	119.9
C(8)-C(7)-C(6)	120.23(16)
C(6)-C(7)-H(7)	119.9
C(1)-C(2)-H(2A)	120.6
C(3)-C(2)-H(2A)	120.6
C(3)-C(2)-C(1)	118.81(17)
N(3)-C(1)-C(2)	123.78(18)
N(3)-C(1)-H(1)	118.1
C(2)-C(1)-H(1)	118.1
C(5)-C(4)-C(9)	119.79(16)
C(5)-C(4)-C(3)	123.57(17)
C(3)-C(4)-C(9)	116.64(17)
C(22)-C(17)-C(16)	106.84(16)
C(18)-C(17)-C(22)	118.13(17)
C(18)-C(17)-C(16)	135.02(18)
C(17)-C(16)-C(13)	127.98(16)
C(30)-C(16)-C(17)	105.96(16)
C(30)-C(16)-C(13)	126.05(16)
N(1)-C(30)-H(30)	124.5
C(16)-C(30)-N(1)	110.99(15)
C(16)-C(30)-H(30)	124.5
C(5)-C(6)-C(7)	121.56(17)
C(5)-C(6)-H(6)	119.2
C(7)-C(6)-H(6)	119.2
O(3)-C(10)-N(2)	123.36(16)
O(3)-C(10)-C(11)	122.06(15)
N(2)-C(10)-C(11)	114.57(15)
O(2)-C(25)-C(28)	101.65(13)
O(2)-C(25)-C(24)	106.93(14)
O(2)-C(25)-C(26)	108.93(14)
C(24)-C(25)-C(28)	112.88(15)

C(26)-C(25)-C(28)	115.20(15)
C(26)-C(25)-C(24)	110.50(15)
H(14A)-C(14)-H(14B)	108.0
C(13)-C(14)-H(14A)	109.3
C(13)-C(14)-H(14B)	109.3
C(15)-C(14)-H(14A)	109.3
C(15)-C(14)-H(14B)	109.3
C(15)-C(14)-C(13)	111.45(17)
C(10)-C(11)-H(11A)	109.2
C(10)-C(11)-H(11B)	109.2
C(10)-C(11)-C(12)	112.05(14)
H(11A)-C(11)-H(11B)	107.9
C(12)-C(11)-H(11A)	109.2
C(12)-C(11)-H(11B)	109.2
C(11)-C(12)-H(12)	109.3
C(11)-C(12)-C(13)	111.11(14)
C(11)-C(12)-B(1)	107.86(14)
C(13)-C(12)-H(12)	109.3
C(13)-C(12)-B(1)	109.91(14)
B(1)-C(12)-H(12)	109.3
C(17)-C(18)-H(18)	120.2
C(19)-C(18)-C(17)	119.65(18)
C(19)-C(18)-H(18)	120.2
O(1)-C(28)-C(25)	102.23(13)
O(1)-C(28)-C(29)	106.83(14)
O(1)-C(28)-C(27)	108.78(15)
C(29)-C(28)-C(25)	112.93(15)
C(27)-C(28)-C(25)	115.02(15)
C(27)-C(28)-C(29)	110.36(15)
C(16)-C(13)-C(14)	110.85(14)
C(16)-C(13)-C(12)	111.41(14)
C(16)-C(13)-H(13)	106.8
C(14)-C(13)-C(12)	113.80(14)
C(14)-C(13)-H(13)	106.8
C(12)-C(13)-H(13)	106.8
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(21)-C(20)-H(20)	119.5
C(21)-C(20)-C(19)	121.05(18)
C(19)-C(20)-H(20)	119.5
C(25)-C(24)-H(24A)	109.5
C(25)-C(24)-H(24B)	109.5
C(25)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5

H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
N(1)-C(23)-H(23A)	109.5
N(1)-C(23)-H(23B)	109.5
N(1)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(2)-C(3)-C(4)	120.15(18)
C(2)-C(3)-H(3)	119.9
C(4)-C(3)-H(3)	119.9
O(2)-B(1)-C(12)	120.33(16)
O(1)-B(1)-O(2)	113.03(16)
O(1)-B(1)-C(12)	126.64(16)
C(28)-C(27)-H(27A)	109.5
C(28)-C(27)-H(27B)	109.5
C(28)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(18)-C(19)-C(20)	121.15(19)
C(18)-C(19)-H(19)	119.4
C(20)-C(19)-H(19)	119.4

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4f**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	20(1)	15(1)	14(1)	-1(1)	5(1)	-2(1)
O(1)	24(1)	16(1)	15(1)	0(1)	5(1)	-1(1)
O(3)	19(1)	22(1)	22(1)	7(1)	6(1)	1(1)
N(3)	21(1)	20(1)	18(1)	1(1)	3(1)	-3(1)
N(2)	19(1)	21(1)	17(1)	3(1)	6(1)	1(1)
N(1)	20(1)	21(1)	20(1)	4(1)	2(1)	2(1)
C(22)	23(1)	16(1)	18(1)	-1(1)	6(1)	4(1)
C(5)	18(1)	21(1)	24(1)	-1(1)	-1(1)	2(1)
C(8)	18(1)	16(1)	15(1)	1(1)	-1(1)	-1(1)
C(9)	17(1)	17(1)	16(1)	-1(1)	0(1)	-5(1)
C(21)	35(1)	19(1)	21(1)	4(1)	5(1)	5(1)
C(7)	21(1)	20(1)	17(1)	3(1)	3(1)	-1(1)
C(2)	34(1)	17(1)	21(1)	4(1)	1(1)	-5(1)
C(1)	26(1)	21(1)	19(1)	1(1)	5(1)	-7(1)
C(4)	20(1)	16(1)	18(1)	-1(1)	-2(1)	-3(1)
C(17)	25(1)	13(1)	17(1)	-3(1)	6(1)	2(1)
C(16)	22(1)	14(1)	16(1)	-1(1)	7(1)	3(1)
C(30)	19(1)	15(1)	21(1)	2(1)	7(1)	2(1)
C(6)	17(1)	25(1)	22(1)	0(1)	4(1)	-1(1)
C(10)	16(1)	17(1)	14(1)	1(1)	-1(1)	-3(1)
C(25)	22(1)	18(1)	14(1)	-4(1)	4(1)	-1(1)
C(14)	33(1)	21(1)	19(1)	-2(1)	5(1)	6(1)
C(11)	21(1)	19(1)	14(1)	0(1)	2(1)	-2(1)
C(12)	17(1)	15(1)	16(1)	1(1)	3(1)	0(1)
C(18)	29(1)	18(1)	22(1)	-2(1)	2(1)	-2(1)
C(28)	24(1)	19(1)	14(1)	-2(1)	4(1)	0(1)
C(13)	21(1)	15(1)	16(1)	0(1)	4(1)	1(1)
C(29)	28(1)	28(1)	19(1)	-2(1)	-1(1)	4(1)

C(20)	46(1)	17(1)	29(1)	6(1)	12(1)	-2(1)
C(24)	24(1)	23(1)	26(1)	-3(1)	5(1)	6(1)
C(26)	27(1)	21(1)	24(1)	-5(1)	4(1)	-6(1)
C(15)	50(1)	26(1)	24(1)	2(1)	18(1)	12(1)
C(23)	24(1)	30(1)	25(1)	5(1)	0(1)	3(1)
C(3)	27(1)	16(1)	23(1)	2(1)	-1(1)	1(1)
B(1)	13(1)	16(1)	17(1)	1(1)	4(1)	1(1)
C(27)	36(1)	30(1)	18(1)	-1(1)	10(1)	0(1)
C(19)	36(1)	19(1)	36(1)	-1(1)	7(1)	-10(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4f**.

	x	y	z	U(eq)
H(2)	7281	4191	9724	22
H(5)	14185	2779	9440	26
H(21)	-62	7268	2427	30
H(7)	11281	4208	7541	23
H(2A)	9920	2234	12841	29
H(1)	7269	2936	12508	26
H(30)	-1246	5684	5563	22
H(6)	14022	3529	7783	25
H(14A)	4293	5973	9740	29
H(14B)	3609	6520	8707	29
H(11A)	6449	5331	9471	22
H(11B)	4765	4842	8837	22
H(12)	5929	5775	7109	19
H(18)	5502	6778	6520	28
H(13)	1806	5449	7698	21
H(29A)	312	4929	3808	39
H(29B)	244	4649	2188	39
H(29C)	747	5310	2439	39
H(20)	3125	7788	2950	36
H(24A)	7114	4339	4690	37
H(24B)	6107	3867	3484	37
H(24C)	6349	3745	5250	37
H(26A)	2539	3517	4888	36
H(26B)	2074	3657	3121	36
H(26C)	749	3974	4201	36
H(15A)	-75	6324	8787	48
H(15B)	1329	6459	10425	48
H(15C)	723	5818	9941	48
H(23A)	-3400	6700	2777	40
H(23B)	-3805	6064	3261	40
H(23C)	-2362	6182	2038	40
H(3)	12561	2267	11423	28
H(27A)	3906	5126	1360	41
H(27B)	3828	4448	1375	41
H(27C)	5891	4774	2286	41
H(19)	5868	7542	4966	37

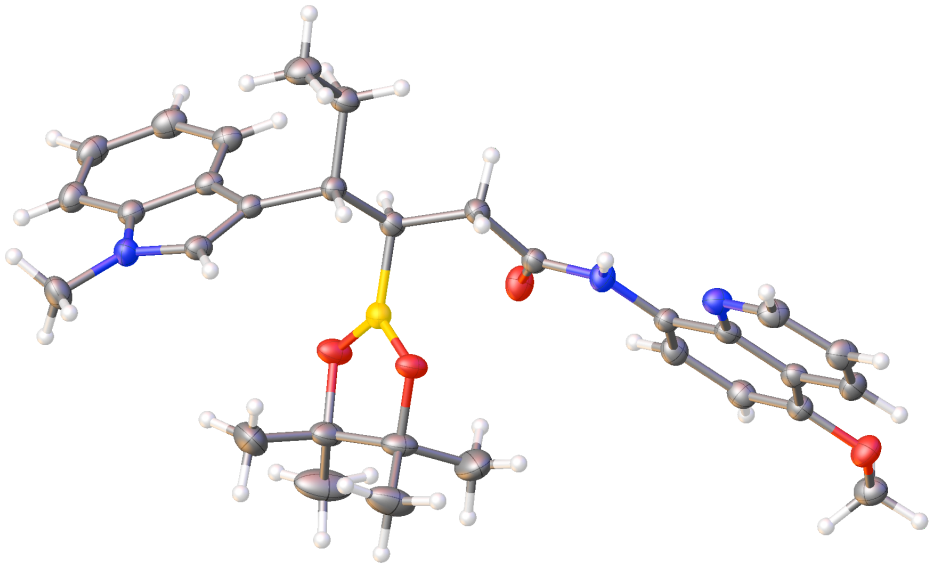


Table S11. Crystal data and structure refinement for **4g**.

Report date	2018-09-19	
Identification code	engle140	
Empirical formula	C31 H38 B N3 O4	
Molecular formula	C31 H38 B N3 O4	
Formula weight	527.45	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 6.5323(2) Å	α= 90°.
	b = 24.4180(6) Å	β= 104.3870(10)°.
	c = 9.1910(2) Å	γ = 90°.
Volume	1420.04(6) $Å^3$	
Z	2	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.646 mm^{-1}	
F(000)	564	
Crystal size	0.125 x 0.08 x 0.04 mm^3	
Crystal color, habit	colorless plank	
Theta range for data collection	3.620 to 70.172°.	
Index ranges	-7<=h<=7, -25<=k<=28, -11<=l<=11	
Reflections collected	22034	
Independent reflections	5204 [R(int) = 0.0494]	
Completeness to theta = 67.500°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5856 and 0.5041	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5204 / 2 / 363	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0878	
R indices (all data)	R1 = 0.0483, wR2 = 0.0923	
Absolute structure parameter	0.02(13)	
Largest diff. peak and hole	0.270 and -0.188 $e.Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4g**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	1506(4)	4894(1)	2317(2)	30(1)
O(2)	-3862(3)	2622(1)	222(2)	30(1)
O(3)	6345(3)	4538(1)	3714(2)	26(1)
O(4)	5641(4)	5207(1)	5252(2)	31(1)
N(1)	1840(4)	3472(1)	-1340(3)	25(1)
N(2)	1934(4)	4321(1)	469(3)	24(1)
N(3)	11175(4)	6241(1)	5625(3)	25(1)
C(1)	1851(5)	3050(1)	-2243(3)	28(1)
C(2)	435(5)	2612(1)	-2402(3)	31(1)
C(3)	-1041(5)	2605(1)	-1576(3)	28(1)
C(4)	-1100(5)	3044(1)	-584(3)	23(1)
C(5)	-2554(5)	3067(1)	341(3)	24(1)
C(6)	-2540(5)	3508(1)	1259(3)	26(1)
C(7)	-1062(5)	3937(1)	1331(3)	26(1)
C(8)	377(5)	3924(1)	478(3)	22(1)
C(9)	367(5)	3472(1)	-515(3)	22(1)
C(10)	2424(5)	4773(1)	1348(3)	23(1)
C(11)	4169(5)	5122(1)	1038(3)	24(1)
C(12)	5277(5)	5463(1)	2419(3)	22(1)
C(13)	7348(5)	5717(1)	2212(3)	22(1)
C(14)	8549(5)	6012(1)	3608(3)	22(1)
C(15)	7889(5)	6481(1)	4324(3)	23(1)
C(16)	6093(5)	6816(1)	4030(4)	27(1)
C(17)	6061(6)	7273(1)	4924(4)	32(1)
C(18)	7778(6)	7400(1)	6118(4)	32(1)
C(19)	9550(5)	7070(1)	6478(4)	29(1)
C(20)	9585(5)	6614(1)	5568(3)	24(1)
C(21)	10523(5)	5882(1)	4435(3)	24(1)
C(22)	13172(5)	6219(2)	6748(3)	33(1)
C(23)	-5194(5)	2596(1)	1233(4)	32(1)
C(24)	7041(5)	6094(1)	821(3)	29(1)
C(25)	9100(6)	6212(2)	400(4)	36(1)
C(26)	6574(6)	4749(1)	6235(3)	34(1)
C(27)	6290(6)	4266(1)	5110(3)	32(1)
C(28)	5472(9)	4694(2)	7472(4)	64(1)
C(29)	8897(7)	4897(2)	6861(5)	59(1)
C(30)	4109(7)	4000(2)	4845(5)	58(1)
C(31)	7961(8)	3833(2)	5461(4)	53(1)
B(1)	5738(6)	5072(1)	3835(4)	24(1)

Table S13. Bond lengths [Å] and angles [°] for **4g**.

O(1)-C(10)	1.226(4)
O(2)-C(5)	1.370(4)
O(2)-C(23)	1.423(4)
O(3)-C(27)	1.453(3)
O(3)-B(1)	1.376(4)
O(4)-C(26)	1.470(4)
O(4)-B(1)	1.360(4)
N(1)-C(1)	1.324(4)
N(1)-C(9)	1.365(4)
N(2)-H(2)	0.87(2)
N(2)-C(8)	1.406(4)

N(2)-C(10)	1.359(4)
N(3)-C(20)	1.373(4)
N(3)-C(21)	1.383(4)
N(3)-C(22)	1.449(4)
C(1)-H(1)	0.9500
C(1)-C(2)	1.399(5)
C(2)-H(2A)	0.9500
C(2)-C(3)	1.367(4)
C(3)-H(3)	0.9500
C(3)-C(4)	1.415(4)
C(4)-C(5)	1.425(4)
C(4)-C(9)	1.407(4)
C(5)-C(6)	1.366(4)
C(6)-H(6)	0.9500
C(6)-C(7)	1.417(4)
C(7)-H(7)	0.9500
C(7)-C(8)	1.366(4)
C(8)-C(9)	1.433(4)
C(10)-C(11)	1.506(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(11)-C(12)	1.540(4)
C(12)-H(12)	1.0000
C(12)-C(13)	1.543(4)
C(12)-B(1)	1.581(4)
C(13)-H(13)	1.0000
C(13)-C(14)	1.510(4)
C(13)-C(24)	1.548(4)
C(14)-C(15)	1.440(4)
C(14)-C(21)	1.361(4)
C(15)-C(16)	1.400(4)
C(15)-C(20)	1.418(4)
C(16)-H(16)	0.9500
C(16)-C(17)	1.389(4)
C(17)-H(17)	0.9500
C(17)-C(18)	1.395(5)
C(18)-H(18)	0.9500
C(18)-C(19)	1.381(5)
C(19)-H(19)	0.9500
C(19)-C(20)	1.397(4)
C(21)-H(21)	0.9500
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(24)-C(25)	1.516(5)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(27)	1.550(5)
C(26)-C(28)	1.495(5)
C(26)-C(29)	1.526(6)
C(27)-C(30)	1.529(5)
C(27)-C(31)	1.496(5)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800

C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800

C(5)-O(2)-C(23)	116.9(2)
B(1)-O(3)-C(27)	106.9(2)
B(1)-O(4)-C(26)	107.1(2)
C(1)-N(1)-C(9)	117.6(3)
C(8)-N(2)-H(2)	116(2)
C(10)-N(2)-H(2)	115(2)
C(10)-N(2)-C(8)	128.3(3)
C(20)-N(3)-C(21)	108.0(2)
C(20)-N(3)-C(22)	126.1(3)
C(21)-N(3)-C(22)	125.9(3)
N(1)-C(1)-H(1)	118.2
N(1)-C(1)-C(2)	123.6(3)
C(2)-C(1)-H(1)	118.2
C(1)-C(2)-H(2A)	120.3
C(3)-C(2)-C(1)	119.4(3)
C(3)-C(2)-H(2A)	120.3
C(2)-C(3)-H(3)	120.5
C(2)-C(3)-C(4)	118.9(3)
C(4)-C(3)-H(3)	120.5
C(3)-C(4)-C(5)	122.9(3)
C(9)-C(4)-C(3)	117.7(3)
C(9)-C(4)-C(5)	119.4(3)
O(2)-C(5)-C(4)	114.6(3)
C(6)-C(5)-O(2)	125.6(3)
C(6)-C(5)-C(4)	119.8(3)
C(5)-C(6)-H(6)	119.6
C(5)-C(6)-C(7)	120.8(3)
C(7)-C(6)-H(6)	119.6
C(6)-C(7)-H(7)	119.5
C(8)-C(7)-C(6)	121.0(3)
C(8)-C(7)-H(7)	119.5
N(2)-C(8)-C(9)	114.6(2)
C(7)-C(8)-N(2)	126.1(3)
C(7)-C(8)-C(9)	119.3(3)
N(1)-C(9)-C(4)	122.8(3)
N(1)-C(9)-C(8)	117.5(3)
C(4)-C(9)-C(8)	119.8(3)
O(1)-C(10)-N(2)	122.9(3)
O(1)-C(10)-C(11)	122.1(3)
N(2)-C(10)-C(11)	115.1(3)
C(10)-C(11)-H(11A)	109.2
C(10)-C(11)-H(11B)	109.2
C(10)-C(11)-C(12)	111.9(2)
H(11A)-C(11)-H(11B)	107.9
C(12)-C(11)-H(11A)	109.2
C(12)-C(11)-H(11B)	109.2
C(11)-C(12)-H(12)	109.0
C(11)-C(12)-C(13)	111.3(2)
C(11)-C(12)-B(1)	107.9(2)

C(13)-C(12)-H(12)	109.0
C(13)-C(12)-B(1)	110.5(2)
B(1)-C(12)-H(12)	109.0
C(12)-C(13)-H(13)	106.7
C(12)-C(13)-C(24)	113.8(2)
C(14)-C(13)-C(12)	111.9(2)
C(14)-C(13)-H(13)	106.7
C(14)-C(13)-C(24)	110.6(2)
C(24)-C(13)-H(13)	106.7
C(15)-C(14)-C(13)	128.1(3)
C(21)-C(14)-C(13)	125.7(3)
C(21)-C(14)-C(15)	106.2(3)
C(16)-C(15)-C(14)	135.1(3)
C(16)-C(15)-C(20)	118.1(3)
C(20)-C(15)-C(14)	106.8(3)
C(15)-C(16)-H(16)	120.3
C(17)-C(16)-C(15)	119.3(3)
C(17)-C(16)-H(16)	120.3
C(16)-C(17)-H(17)	119.4
C(16)-C(17)-C(18)	121.1(3)
C(18)-C(17)-H(17)	119.4
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-C(17)	121.3(3)
C(19)-C(18)-H(18)	119.3
C(18)-C(19)-H(19)	121.3
C(18)-C(19)-C(20)	117.3(3)
C(20)-C(19)-H(19)	121.3
N(3)-C(20)-C(15)	108.1(2)
N(3)-C(20)-C(19)	129.2(3)
C(19)-C(20)-C(15)	122.7(3)
N(3)-C(21)-H(21)	124.5
C(14)-C(21)-N(3)	110.9(3)
C(14)-C(21)-H(21)	124.5
N(3)-C(22)-H(22A)	109.5
N(3)-C(22)-H(22B)	109.5
N(3)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(2)-C(23)-H(23A)	109.5
O(2)-C(23)-H(23B)	109.5
O(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(13)-C(24)-H(24A)	109.1
C(13)-C(24)-H(24B)	109.1
H(24A)-C(24)-H(24B)	107.8
C(25)-C(24)-C(13)	112.5(3)
C(25)-C(24)-H(24A)	109.1
C(25)-C(24)-H(24B)	109.1
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
O(4)-C(26)-C(27)	101.9(2)
O(4)-C(26)-C(28)	109.3(3)
O(4)-C(26)-C(29)	105.9(3)

C(28)-C(26)-C(27)	116.0(3)
C(28)-C(26)-C(29)	110.9(3)
C(29)-C(26)-C(27)	112.0(3)
O(3)-C(27)-C(26)	102.5(2)
O(3)-C(27)-C(30)	106.3(3)
O(3)-C(27)-C(31)	109.7(3)
C(30)-C(27)-C(26)	112.5(3)
C(31)-C(27)-C(26)	115.8(3)
C(31)-C(27)-C(30)	109.6(3)
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(27)-C(30)-H(30A)	109.5
C(27)-C(30)-H(30B)	109.5
C(27)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(27)-C(31)-H(31A)	109.5
C(27)-C(31)-H(31B)	109.5
C(27)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
O(3)-B(1)-C(12)	120.3(3)
O(4)-B(1)-O(3)	112.9(3)
O(4)-B(1)-C(12)	126.7(3)

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4g**. The anisotropic displacement factor exponent takes the form: $-2^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	32(1)	29(1)	30(1)	-10(1)	12(1)	-3(1)
O(2)	30(1)	28(1)	35(1)	-1(1)	13(1)	-6(1)
O(3)	37(1)	23(1)	20(1)	3(1)	8(1)	6(1)
O(4)	47(2)	26(1)	21(1)	2(1)	10(1)	8(1)
N(1)	31(2)	23(1)	22(1)	0(1)	9(1)	3(1)
N(2)	28(2)	24(1)	22(1)	-6(1)	9(1)	-3(1)
N(3)	26(2)	22(1)	24(1)	-2(1)	2(1)	-1(1)
C(1)	36(2)	28(2)	24(2)	-1(1)	12(1)	3(1)
C(2)	41(2)	25(2)	27(2)	-4(1)	10(1)	4(1)
C(3)	32(2)	20(2)	28(2)	-2(1)	5(1)	-1(1)
C(4)	25(2)	20(2)	22(2)	2(1)	4(1)	3(1)
C(5)	25(2)	24(2)	23(2)	2(1)	3(1)	-2(1)
C(6)	25(2)	30(2)	23(2)	0(1)	7(1)	1(1)
C(7)	29(2)	26(2)	22(2)	-4(1)	6(1)	2(1)
C(8)	27(2)	19(2)	19(1)	0(1)	3(1)	0(1)
C(9)	28(2)	20(2)	17(1)	2(1)	3(1)	3(1)

C(10)	26(2)	20(2)	21(1)	0(1)	2(1)	1(1)
C(11)	29(2)	24(2)	19(1)	-1(1)	3(1)	-2(1)
C(12)	26(2)	19(2)	21(2)	-1(1)	4(1)	1(1)
C(13)	28(2)	19(2)	19(1)	-1(1)	5(1)	-1(1)
C(14)	28(2)	18(2)	20(1)	1(1)	7(1)	-2(1)
C(15)	28(2)	19(2)	23(2)	3(1)	10(1)	0(1)
C(16)	28(2)	23(2)	29(2)	3(1)	8(1)	2(1)
C(17)	36(2)	26(2)	38(2)	2(1)	16(2)	5(1)
C(18)	45(2)	22(2)	33(2)	-5(1)	17(2)	-2(1)
C(19)	36(2)	25(2)	28(2)	-5(1)	11(1)	-4(1)
C(20)	30(2)	21(2)	22(2)	0(1)	8(1)	-2(1)
C(21)	33(2)	18(2)	20(1)	0(1)	7(1)	2(1)
C(22)	33(2)	36(2)	26(2)	-4(1)	-2(1)	2(1)
C(23)	31(2)	32(2)	34(2)	5(1)	11(1)	0(1)
C(24)	37(2)	28(2)	21(2)	3(1)	6(1)	-1(1)
C(25)	46(2)	33(2)	33(2)	6(2)	17(2)	-1(2)
C(26)	54(2)	27(2)	20(2)	4(1)	8(2)	2(2)
C(27)	44(2)	29(2)	24(2)	9(1)	11(2)	7(1)
C(28)	105(4)	59(3)	38(2)	16(2)	39(2)	29(3)
C(29)	66(3)	55(3)	41(2)	13(2)	-17(2)	-13(2)
C(30)	60(3)	52(3)	53(2)	20(2)	1(2)	-22(2)
C(31)	80(3)	43(2)	34(2)	11(2)	13(2)	27(2)
B(1)	24(2)	24(2)	22(2)	0(1)	4(1)	-2(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **4g**.

	x	y	z	U(eq)
H(2)	2740(50)	4264(15)	-140(40)	35(10)
H(1)	2878	3045	-2816	34
H(2A)	498	2321	-3077	37
H(3)	-2012	2309	-1667	33
H(6)	-3534	3526	1857	31
H(7)	-1071	4239	1983	31
H(11A)	3575	5371	189	29
H(11B)	5222	4883	741	29
H(12)	4309	5763	2569	27
H(13)	8261	5406	2047	27
H(16)	4909	6731	3226	32
H(17)	4848	7502	4720	38
H(18)	7727	7721	6694	38
H(19)	10698	7150	7312	35
H(21)	11343	5585	4223	29
H(22A)	13895	6572	6783	50
H(22B)	14057	5930	6486	50
H(22C)	12913	6140	7732	50
H(23A)	-6018	2257	1063	48
H(23B)	-6155	2911	1063	48
H(23C)	-4326	2604	2269	48
H(24A)	6043	5919	-41	35
H(24B)	6407	6445	1032	35
H(25A)	9681	5869	116	54
H(25B)	10110	6375	1260	54
H(25C)	8838	6467	-449	54
H(28A)	5714	5025	8097	96
H(28B)	6026	4375	8089	96
H(28C)	3952	4648	7039	96

H(29A)	9601	4915	6037	89
H(29B)	9580	4616	7583	89
H(29C)	9001	5253	7365	89
H(30A)	3015	4283	4579	86
H(30B)	3987	3812	5762	86
H(30C)	3928	3734	4023	86
H(31A)	7693	3560	4653	79
H(31B)	7933	3654	6410	79
H(31C)	9350	4000	5550	79

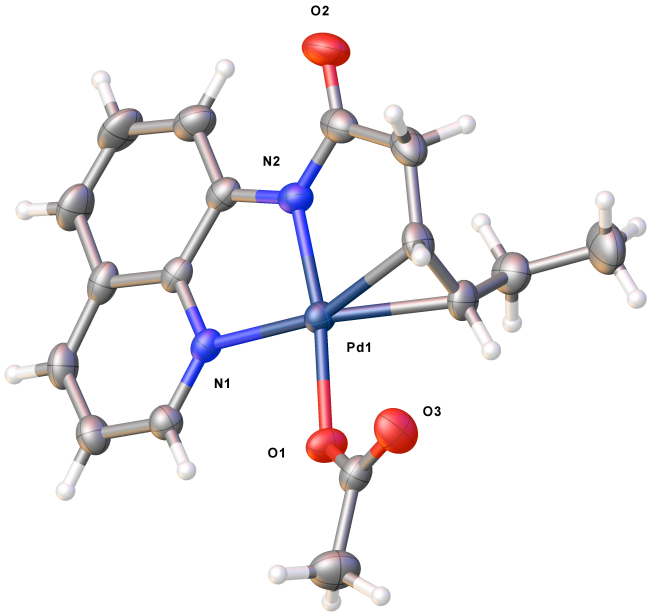


Table S16. Crystal data and structure refinement for **Pd-I**.

Report date	2016-05-26	
Identification code	AQ-Et-Pd	
Empirical formula	C17 H18 N2 O3 Pd	
Molecular formula	C17 H18 N2 O3 Pd	
Formula weight	404.73	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.6104(4) Å	α= 90°.
	b = 10.5955(5) Å	β= 99.0510 (10)°.
	c = 17.7100(9) Å	γ = 90°.
Volume	1595.59(13) $Å^3$	
Z	4	
Density (calculated)	1.685 Mg/m^3	
Absorption coefficient	1.179 mm^{-1}	
F(000)	816	
Crystal size	0.347 x 0.295 x 0.261 mm^3	
Crystal color, habit	Yellow Block	
Theta range for data collection	2.493 to 25.347°.	
Index ranges	-8<=h<=10, -12<=k<=12, -21<=l<=21	
Reflections collected	16069	
Independent reflections	2929 [R(int) = 0.0238]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2590 and 0.2292	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2929 / 0 / 210
Goodness-of-fit on F^2	1.141
Final R indices [I>2sigma(I)]	R1 = 0.0214, wR2 = 0.0516
R indices (all data)	R1 = 0.0240, wR2 = 0.0529
Extinction coefficient	n/a
Largest diff. peak and hole	0.338 and -0.367 e.Å^{-3}

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **Pd-I**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6604(1)	7152(1)	4372(1)	25(1)
O(1)	8343(2)	7913(2)	5139(1)	35(1)
O(2)	2747(2)	6109(2)	2825(1)	49(1)
O(3)	7307(2)	9803(2)	5286(1)	43(1)
N(1)	7225(2)	5422(2)	4823(1)	25(1)
N(2)	5021(2)	6147(2)	3703(1)	29(1)
C(1)	8350(3)	5151(2)	5398(1)	29(1)
C(2)	8767(3)	3899(2)	5595(1)	34(1)
C(3)	7983(3)	2937(2)	5193(2)	36(1)
C(4)	6753(3)	3191(2)	4593(1)	32(1)
C(5)	6398(3)	4472(2)	4414(1)	25(1)
C(6)	5207(3)	4826(2)	3804(1)	29(1)
C(7)	4387(3)	3876(3)	3382(2)	41(1)
C(8)	4713(4)	2597(3)	3565(2)	48(1)
C(9)	5852(4)	2252(2)	4150(2)	43(1)
C(10)	3787(3)	6679(3)	3239(1)	35(1)
C(11)	3775(3)	8115(3)	3290(2)	40(1)
C(12)	5140(3)	8685(2)	3818(1)	33(1)
C(13)	6605(3)	8808(2)	3609(1)	32(1)
C(14)	6979(3)	8477(3)	2834(2)	41(1)
C(15)	6670(4)	9626(3)	2305(2)	60(1)
C(16)	8298(3)	8989(2)	5468(1)	31(1)
C(17)	9603(3)	9183(3)	6134(2)	51(1)

Table S18. Bond lengths [Å] and angles [°] for **Pd-I**.

Pd(1)-O(1)	2.0243(17)
Pd(1)-N(1)	2.0382(18)
Pd(1)-N(2)	1.9712(19)
Pd(1)-C(12)	2.191(2)
Pd(1)-C(13)	2.214(2)
O(1)-C(16)	1.283(3)
O(2)-C(10)	1.224(3)
O(3)-C(16)	1.220(3)
N(1)-C(1)	1.321(3)
N(1)-C(5)	1.372(3)
N(2)-C(6)	1.417(3)
N(2)-C(10)	1.359(3)
C(1)-H(1)	0.9500
C(1)-C(2)	1.404(3)
C(2)-H(2)	0.9500
C(2)-C(3)	1.360(4)
C(3)-H(3)	0.9500
C(3)-C(4)	1.403(4)

C(4)-C(5)	1.416(3)
C(4)-C(9)	1.420(4)
C(5)-C(6)	1.417(3)
C(6)-C(7)	1.380(3)
C(7)-H(7)	0.9500
C(7)-C(8)	1.411(4)
C(8)-H(8)	0.9500
C(8)-C(9)	1.359(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.524(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(11)-C(12)	1.507(4)
C(12)-H(12)	1.0000
C(12)-C(13)	1.375(3)
C(13)-H(13)	1.0000
C(13)-C(14)	1.500(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(14)-C(15)	1.534(4)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.510(4)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800

O(1)-Pd(1)-N(1)	88.51(7)
O(1)-Pd(1)-C(12)	108.56(8)
O(1)-Pd(1)-C(13)	91.29(8)
N(1)-Pd(1)-C(12)	160.00(9)
N(1)-Pd(1)-C(13)	157.97(8)
N(2)-Pd(1)-O(1)	170.66(7)
N(2)-Pd(1)-N(1)	82.14(8)
N(2)-Pd(1)-C(12)	80.62(9)
N(2)-Pd(1)-C(13)	97.40(9)
C(12)-Pd(1)-C(13)	36.39(9)
C(16)-O(1)-Pd(1)	125.87(16)
C(1)-N(1)-Pd(1)	127.78(16)
C(1)-N(1)-C(5)	120.3(2)
C(5)-N(1)-Pd(1)	111.73(15)
C(6)-N(2)-Pd(1)	113.84(15)
C(10)-N(2)-Pd(1)	122.68(17)
C(10)-N(2)-C(6)	123.2(2)
N(1)-C(1)-H(1)	119.2
N(1)-C(1)-C(2)	121.7(2)
C(2)-C(1)-H(1)	119.2
C(1)-C(2)-H(2)	120.3
C(3)-C(2)-C(1)	119.4(2)
C(3)-C(2)-H(2)	120.3
C(2)-C(3)-H(3)	119.8
C(2)-C(3)-C(4)	120.4(2)
C(4)-C(3)-H(3)	119.8
C(3)-C(4)-C(5)	117.6(2)
C(3)-C(4)-C(9)	124.5(2)
C(5)-C(4)-C(9)	117.9(2)
N(1)-C(5)-C(4)	120.6(2)
N(1)-C(5)-C(6)	117.5(2)
C(4)-C(5)-C(6)	121.9(2)

C(5)-C(6)-N(2)	114.29(19)
C(7)-C(6)-N(2)	127.9(2)
C(7)-C(6)-C(5)	117.8(2)
C(6)-C(7)-H(7)	119.7
C(6)-C(7)-C(8)	120.6(3)
C(8)-C(7)-H(7)	119.7
C(7)-C(8)-H(8)	119.1
C(9)-C(8)-C(7)	121.8(2)
C(9)-C(8)-H(8)	119.1
C(4)-C(9)-H(9)	120.0
C(8)-C(9)-C(4)	119.9(3)
C(8)-C(9)-H(9)	120.0
O(2)-C(10)-N(2)	125.9(3)
O(2)-C(10)-C(11)	121.1(2)
N(2)-C(10)-C(11)	112.9(2)
C(10)-C(11)-H(11A)	108.5
C(10)-C(11)-H(11B)	108.5
H(11A)-C(11)-H(11B)	107.5
C(12)-C(11)-C(10)	115.2(2)
C(12)-C(11)-H(11A)	108.5
C(12)-C(11)-H(11B)	108.5
Pd(1)-C(12)-H(12)	115.2
C(11)-C(12)-Pd(1)	108.51(16)
C(11)-C(12)-H(12)	115.2
C(13)-C(12)-Pd(1)	72.71(14)
C(13)-C(12)-C(11)	122.0(2)
C(13)-C(12)-H(12)	115.2
Pd(1)-C(13)-H(13)	113.8
C(12)-C(13)-Pd(1)	70.90(14)
C(12)-C(13)-H(13)	113.8
C(12)-C(13)-C(14)	124.2(2)
C(14)-C(13)-Pd(1)	113.20(17)
C(14)-C(13)-H(13)	113.8
C(13)-C(14)-H(14A)	109.8
C(13)-C(14)-H(14B)	109.8
C(13)-C(14)-C(15)	109.4(2)
H(14A)-C(14)-H(14B)	108.2
C(15)-C(14)-H(14A)	109.8
C(15)-C(14)-H(14B)	109.8
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(1)-C(16)-C(17)	113.8(2)
O(3)-C(16)-O(1)	125.3(2)
O(3)-C(16)-C(17)	120.9(2)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Table S19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **Pd-I**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	26(1)	20(1)	29(1)	-2(1)	4(1)	1(1)
O(1)	34(1)	22(1)	47(1)	-7(1)	-2(1)	0(1)
O(2)	40(1)	63(1)	41(1)	-2(1)	-8(1)	-4(1)
O(3)	55(1)	29(1)	45(1)	-6(1)	4(1)	10(1)
N(1)	27(1)	20(1)	28(1)	-4(1)	9(1)	-2(1)
N(2)	26(1)	31(1)	28(1)	-2(1)	3(1)	-3(1)
C(1)	32(1)	26(1)	30(1)	-1(1)	5(1)	1(1)
C(2)	37(1)	30(1)	35(1)	4(1)	7(1)	6(1)
C(3)	48(2)	22(1)	40(1)	4(1)	16(1)	4(1)
C(4)	43(1)	22(1)	35(1)	-4(1)	19(1)	-5(1)
C(5)	30(1)	23(1)	26(1)	-6(1)	12(1)	-3(1)
C(6)	30(1)	30(1)	28(1)	-5(1)	10(1)	-7(1)
C(7)	40(2)	44(2)	38(1)	-10(1)	4(1)	-12(1)
C(8)	58(2)	35(2)	52(2)	-18(1)	12(2)	-21(1)
C(9)	58(2)	23(1)	50(2)	-7(1)	15(1)	-10(1)
C(10)	29(1)	48(2)	28(1)	2(1)	6(1)	1(1)
C(11)	32(1)	49(2)	39(1)	12(1)	7(1)	10(1)
C(12)	40(1)	24(1)	36(1)	6(1)	9(1)	10(1)
C(13)	41(1)	21(1)	37(1)	3(1)	9(1)	0(1)
C(14)	40(2)	47(2)	38(1)	1(1)	13(1)	-1(1)
C(15)	65(2)	72(2)	46(2)	18(2)	21(2)	1(2)
C(16)	35(1)	26(1)	34(1)	-2(1)	11(1)	-5(1)
C(17)	48(2)	47(2)	55(2)	-15(1)	-1(1)	-3(1)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **Pd-I**.

	x	y	z	U(eq)
H(1)	8891	5820	5684	35
H(2)	9589	3726	6007	41
H(3)	8271	2089	5319	43
H(7)	3596	4085	2964	49
H(8)	4121	1960	3272	58
H(9)	6045	1384	4261	52
H(11A)	3766	8464	2771	48
H(11B)	2788	8380	3465	48
H(12)	4854	9354	4170	40
H(13)	7220	9542	3854	39
H(14A)	6316	7761	2619	49
H(14B)	8095	8220	2878	49
H(15A)	7376	10315	2504	90
H(15B)	5576	9899	2281	90
H(15C)	6860	9397	1791	90
H(17A)	10535	8708	6046	76
H(17B)	9260	8885	6604	76
H(17C)	9863	10083	6183	76

REFERENCES

(1) Wu, Q.-F.; Shen, P.-X.; He, J.; Wang, X.-B.; Zhang, F.; Shao, Q.; Zhu, R.-Y.; Mapelli, C.; Qiao, J. X.; Poss, M. A.; Yu, J.-Q. Formation of α-chiral centers by asymmetric β-C(sp^3)–H arylation, alkenylation, and alkynylation. *Science* **2017**, *355*, 499–503.

(2) Shen, P.-X.; Hu, L.; Shao, Q.; Hong, K.; Yu, J.-Q. Enantioselective C(sp^3)–H Arylation of Free Carboxylic Acids. *J. Am. Chem. Soc.* **2018**, *140*, 6545–6549.

(3) Martinelli, M. J. Asymmetric Diels-Alder reactions with γ-functionalized α,β-unsaturated chiral N-acyloxazolidinones: synthesis of (+)-S-145. *J. Org. Chem.* **1990**, *55*, 5065–5073.

(4) Mitchell, J. M.; Finney, N. S. An efficient method for the preparation of *N,N*-disubstituted 1,2-diamines. *Tetrahedron Lett.* **2000**, *41*, 8431–8434.

(5) Jung, M. E.; Huang, Use of Optically Active Cyclic *N,N*-Dialkyl Aminals in Asymmetric Induction. A. *Org. Lett.* **2000**, *2*, 2659–2661.

(6) Clemens, N.; Sereda, O.; Wilhelm, R. Unexpected behaviour of tosylated and acetylated imidazolinium salts. *Org. Biomol. Chem.* **2006**, *4*, 2285–2290.

(7) Wang, H.; Bai, Z.; Jiao, T.; Deng, Z.; Tong, H.; He, G.; Peng, Q.; Chen, G. Palladium-Catalyzed Amide-Directed Enantioselective Hydrocarbofunctionalization of Unactivated Alkenes Using a Chiral Monodentate Oxazoline Ligand. *J. Am. Chem. Soc.* **2018**, *140*, 3542–3546.

(8) Williams, C. W.; Shenje, R.; France, S. Catalytic, Interrupted Formal Homo-Nazarov Cyclization with (Hetero)arenes: Access to α-(Hetero)aryl Cyclohexanones. *J. Org. Chem.* **2016**, *81*, 8253–8267.

(9) Jacquemard, U.; Bénéteau, V.; Lefoix, M.; Routier, S.; Mérour, J.-Y.; Coudert, G. Mild and selective deprotection of carbamates with Bu_4NF. *Tetrahedron* **2004**, *60*, 10039–10047.

(10) Choy, P. Y.; Lau, C. P.; Kwong, F. Y. Palladium-Catalyzed Direct and Regioselective C−H Bond Functionalization/Oxidative Acetoxylation of Indoles. *J. Org. Chem.* **2011**, *76*, 80–84.

(11) Stavber, S.; Kralj, P.; Zupan, M. Progressive Direct Iodination of Sterically Hindered Alkyl Substituted Benzenes. *Synthesis* **2002**, *11*, 1513–1518.

(12) Liu, C.; Wang, H.; Xing, X.; Xu, Y.; Ma, J.-A.; Zhang, B. Selective C4–F bond cleavage of pentafluorobenzene: synthesis of N-tetrafluoroarylated heterocyclic compounds. *Tetrahedron Lett.* **2013**, *54*, 4649–4652.

(13) Sun, X.; Chen, Y.; Wu, N.; Kang, C. S.; Song, H. A.; Jin, S.; Fu, Y.; Bryant, H., Jr.; Frank, J. A.; Chong, H.-S. Application of aziridinium ring opening for preparation of optically active diamine and triamine analogues: Highly efficient synthesis and evaluation of DTPA-based MRI contrast enhancement agents. *RSC Adv.* **2015**, *5*, 94571–94581.

(14) Richmond, E.; Ling, K. B.; Duguet, N.; Manton, L. B.; Çelebi-Ölçüm, N.; Lam, Y.-H.; Alsancak, S.; Slawin, A. M. Z.; Houk, K. N.; Smith, A. D. An asymmetric pericyclic cascade approach to 3-alkyl-3-aryloxindoles: generality, applications and mechanistic investigations. *Org. Biomol. Chem.* **2015**, *13*, 1807–1817.

(15) Chen, C.-A.; Wu, K.-H.; Gau, H.-M. Synthesis and application of polymer-supported *N*-sulfonylated aminoalcohols as enantioselective catalysts. *Polymer* **2008**, *49*, 1512–1519.

(16) Srivastava, V.; Tandon, A.; Ray, S. Convenient and Selective Acetylations of Phenols, Amines and Alcohols. *Synth. Commun.* **1992**, *22*, 2703–2710.

(17) White, D. E.; Stewart, I. C.; Grubbs, R. H.; Stoltz, B. M. The Catalytic Asymmetric Total Synthesis of Elatol. *J. Am. Chem. Soc.* **2008**, *130*, 810–811.

(18) Yang, K. S.; Gurak, J. A., Jr.; Liu, Z.; Engle, K. M. Catalytic, Regioselective Hydrocarbofunctionalization of Unactivated Alkenes with Diverse C−H Nucleophiles. *J. Am. Chem. Soc.* **2016**, *138*, 14705–14712.

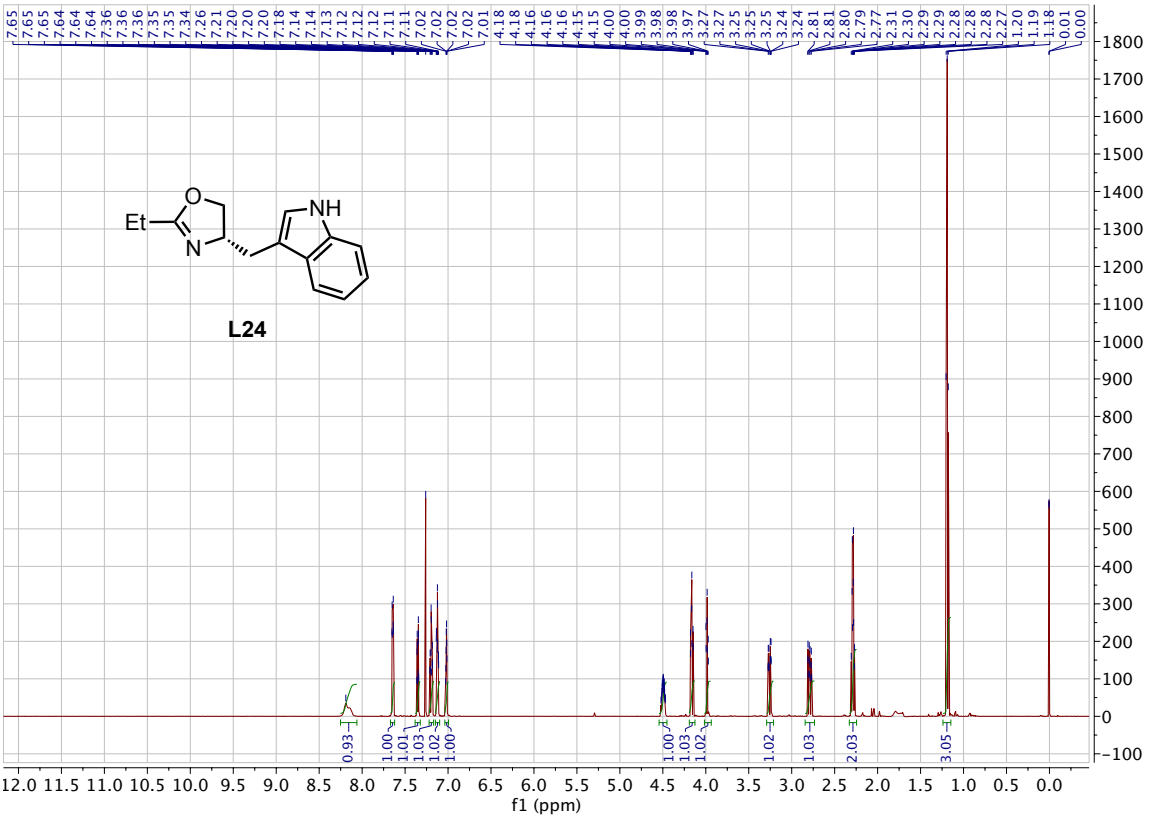
(19) Liu, M.; Yang, P.; Karunananda, M. K.; Wang, Y.; Liu, P.; Engle, K. M. C(alkenyl)–H Activation via Six-Membered Palladacycles: Catalytic 1,3-Diene Synthesis. *J. Am. Chem. Soc.* **2018**, *140*, 5805–5813.

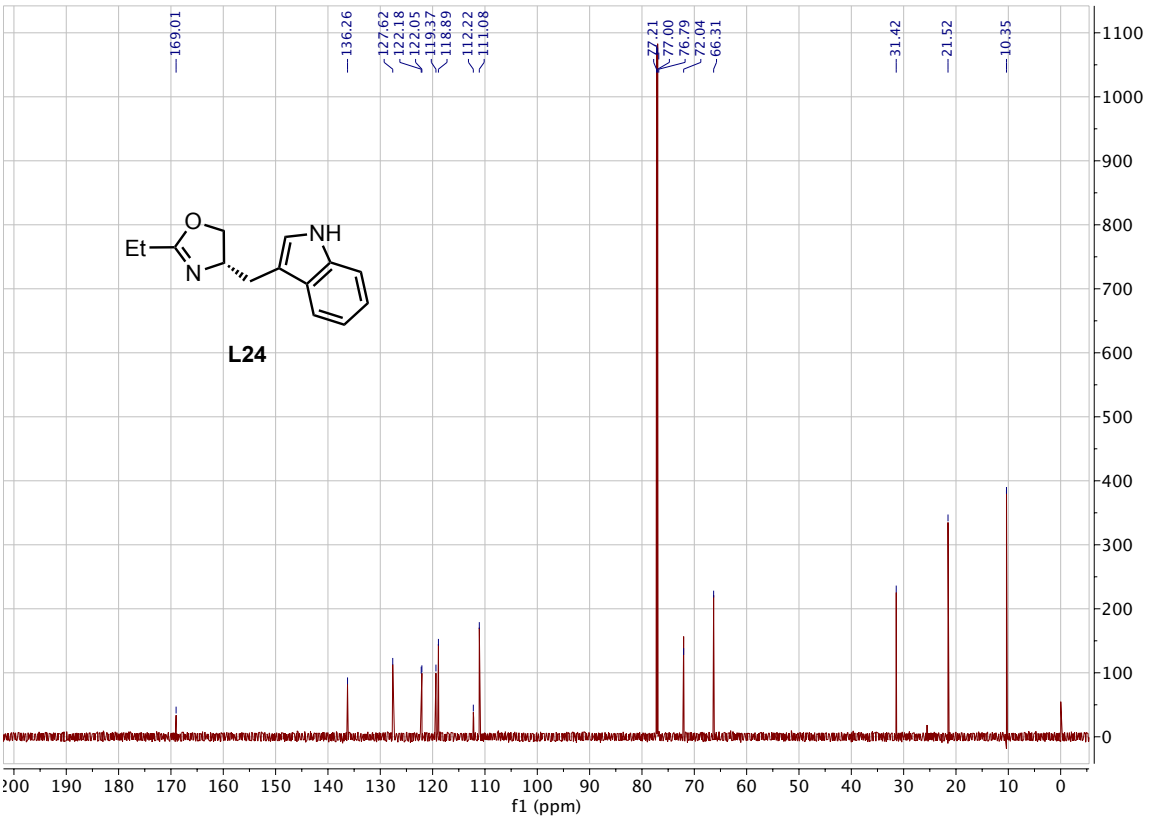
(20) Kim, I. S.; Dong, G. R.; Jung, Y. H. Palladium(II)-Catalyzed Isomerization of Olefins with Tributyltin Hydride. *J. Org. Chem.* **2007**, *72*, 5424–5426.

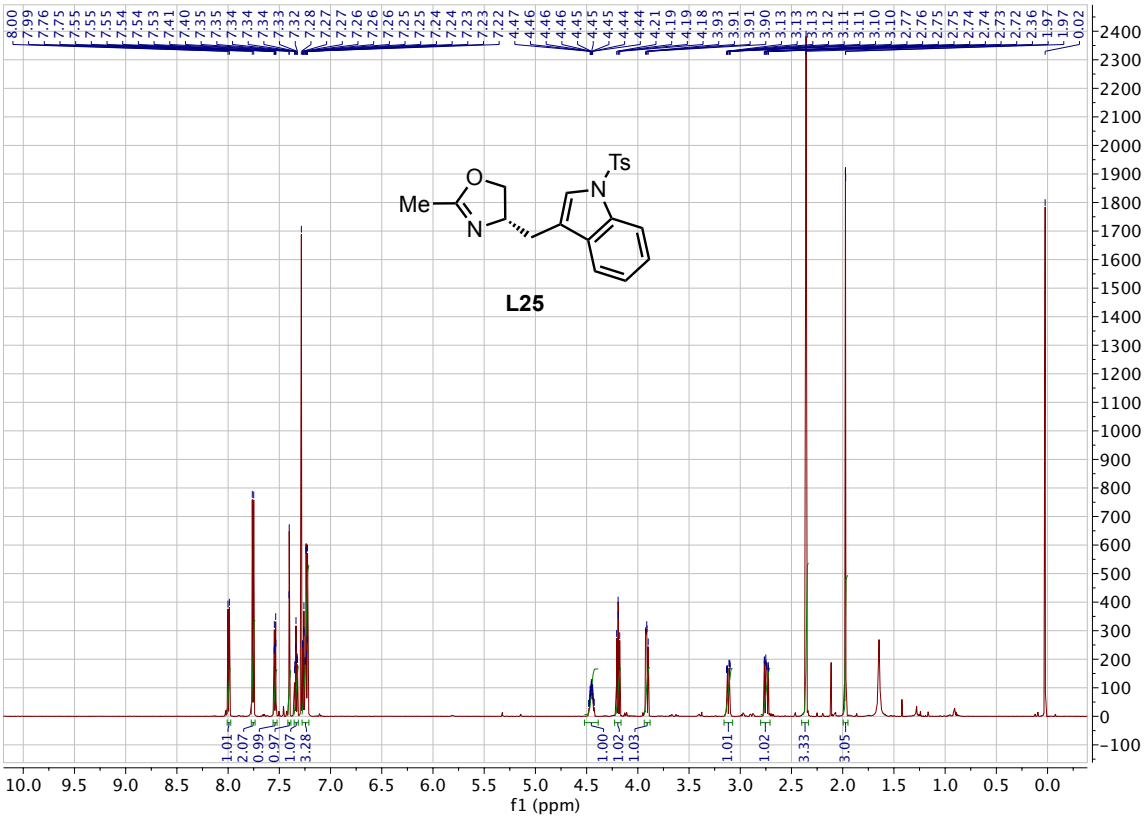
(21) Yadagiri, P.; Yadav, J. S. A Convenient Synthesis of (*Z*)-7-Nonadecen-Ll-One and (*Z*)-7-Eicosen-Ll-Cne–The Pheromones of Peach Fruit Moth. *Synth. Commun.* **1983**, *13*, 1067–1074.

(22) Shao, C.; Shi, G.; Zhang, Y.; Pan, S.; Guan, X. Palladium-Catalyzed C–H Ethoxycarbonyldifluoromethylation of Electron-Rich Heteroarenes. *Org. Lett.* **2015**, *17*, 2652–2655.
(23) Fawcett, A.; Pradeilles, J.; Wang, Y.; Mutsuga, T.; Myers, E. L.; Aggarwal, V. K. Photoinduced decarboxylative borylation of carboxylic acids. *Science* **2017**, *357*, 283–286.
(24) CCDC 1888952 (**4f**), CCDC 1888953 (**4g**) and CCDC 1888954 (**Pd-I**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
(25) He, J.; Shao, Q.; Wu, Q.; Yu, J.-Q. Pd(II)-Catalyzed Enantioselective C(sp^3)–H Borylation. *J. Am. Chem. Soc.* **2017**, *139*, 3344–3347.
(26) Bonet, A.; Gulyás, H.; Fernández, E. Metal-Free Catalytic Boration at the β-Position of α,β-Unsaturated Compounds: A Challenging Asymmetric Induction. *Angew. Chem. Int. Ed.* **2010**, *49*, 5130–5134.
(27) Deguchi, T.; Xin, H.-L.; Morimoto, H.; Ohshima, T. Direct Catalytic Alcoholysis of Unactivated 8-Aminoquinoline Amides. *ACS. Catal.* **2017**, *7*, 3157–3161.
(28) Verho, O.; Lati, M. P.; Oschmann, M. J. A Two-Step Procedure for the Overall Transamidation of 8-Aminoquinoline Amides Proceeding via the Intermediate *N*-Acyl-Boc-Carbamates. *J. Org. Chem.* **2018**, *83*, 4464–4476.
(29) Dietz, C.; Hart, T. K.; Nemati, R.; Yao, X.; Nichols, F. C.; Smith, M. B. Structural verification via convergent total synthesis of dipeptide–lipids isolated from *Porphyromonas gingivalis. Tetrahedron* **2016**, *72*, 7557–7569.
(30) Hoye, T. R.; Jeffrey, C. S.; Shao F. Mosher ester analysis for the determination of absolute configuration of stereogenic (chiral) carbinol carbons. *Nat. Protoc.* **2007**, *2*, 2451–2458.

NMR Spectra and SFC Chromatograms



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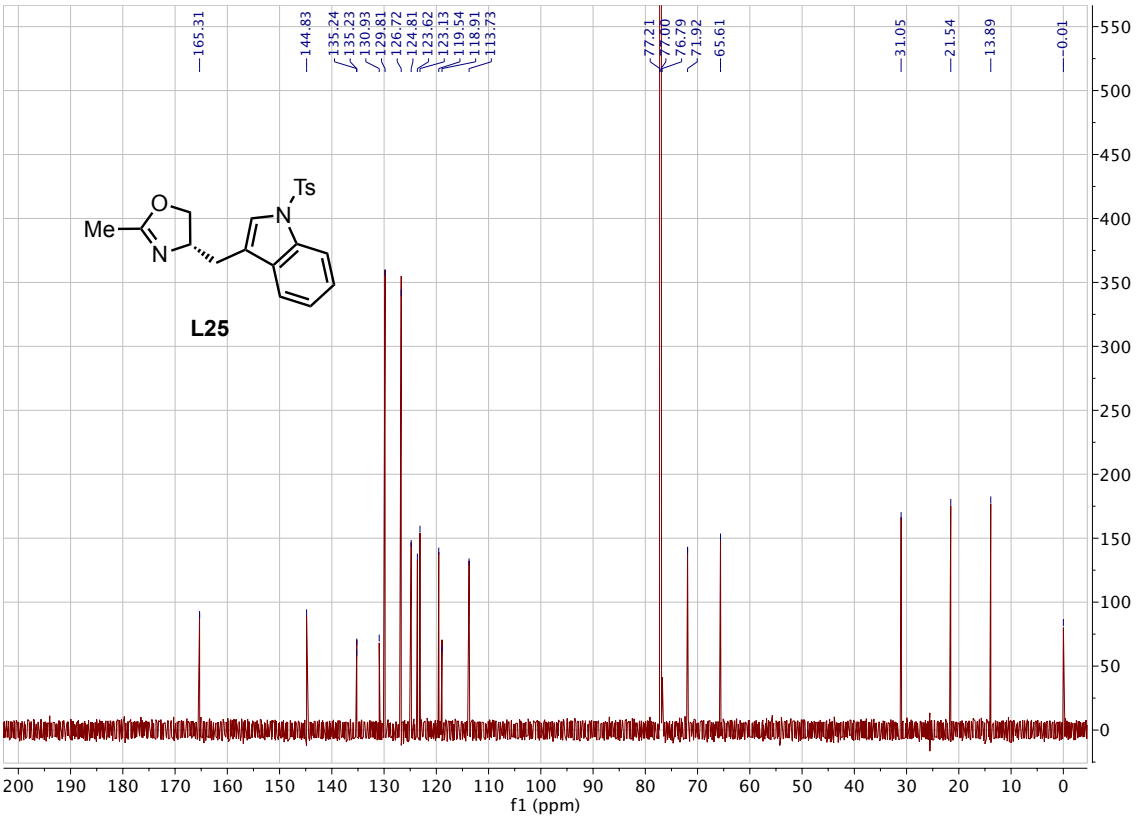
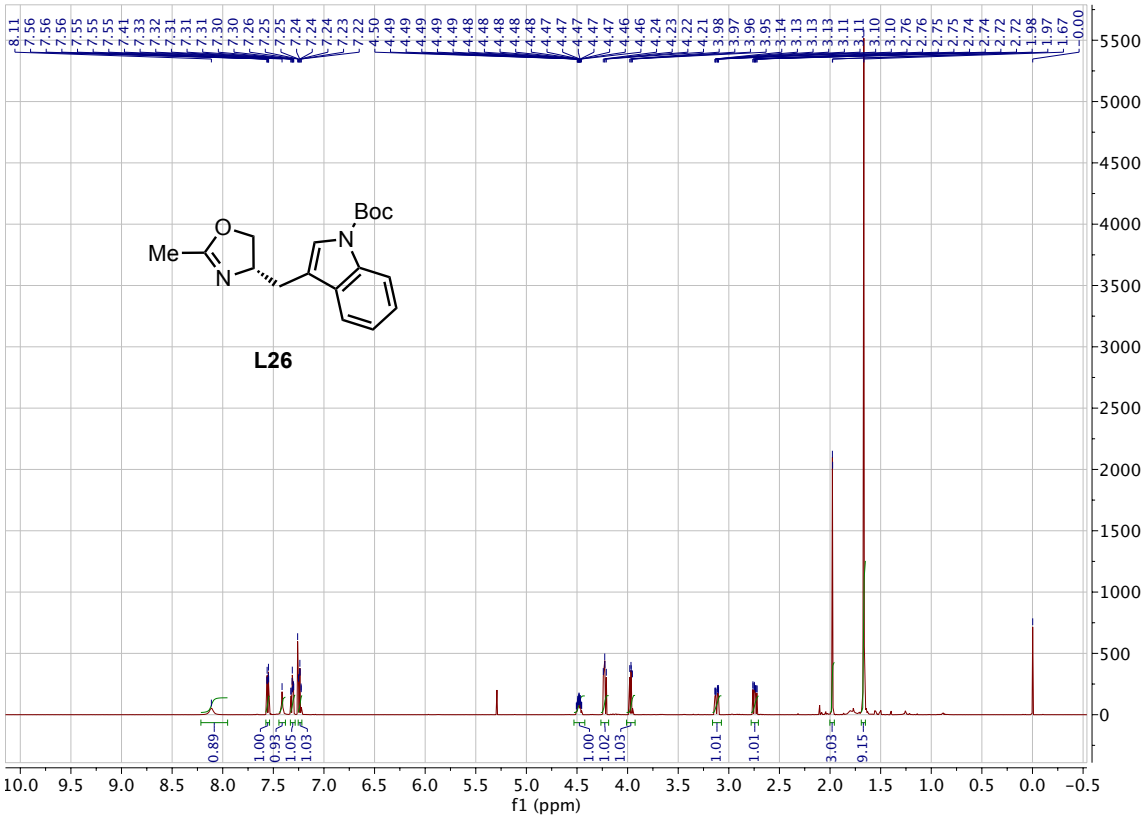
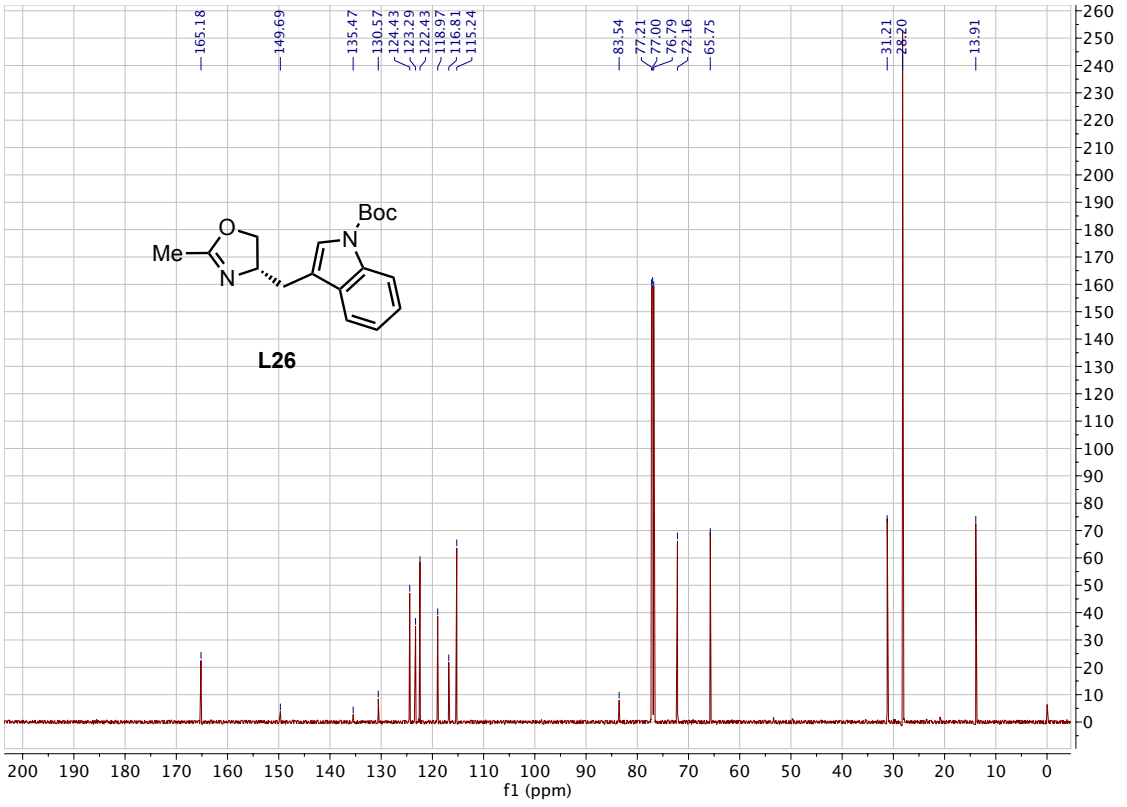
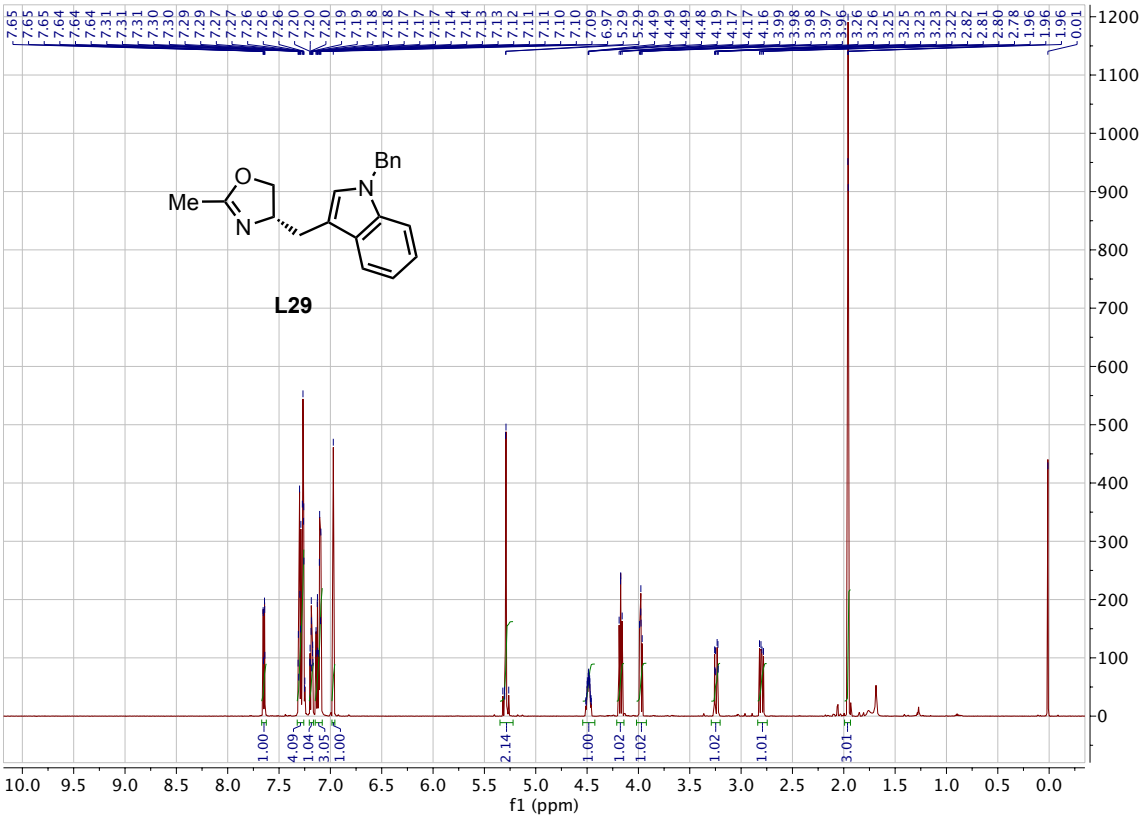
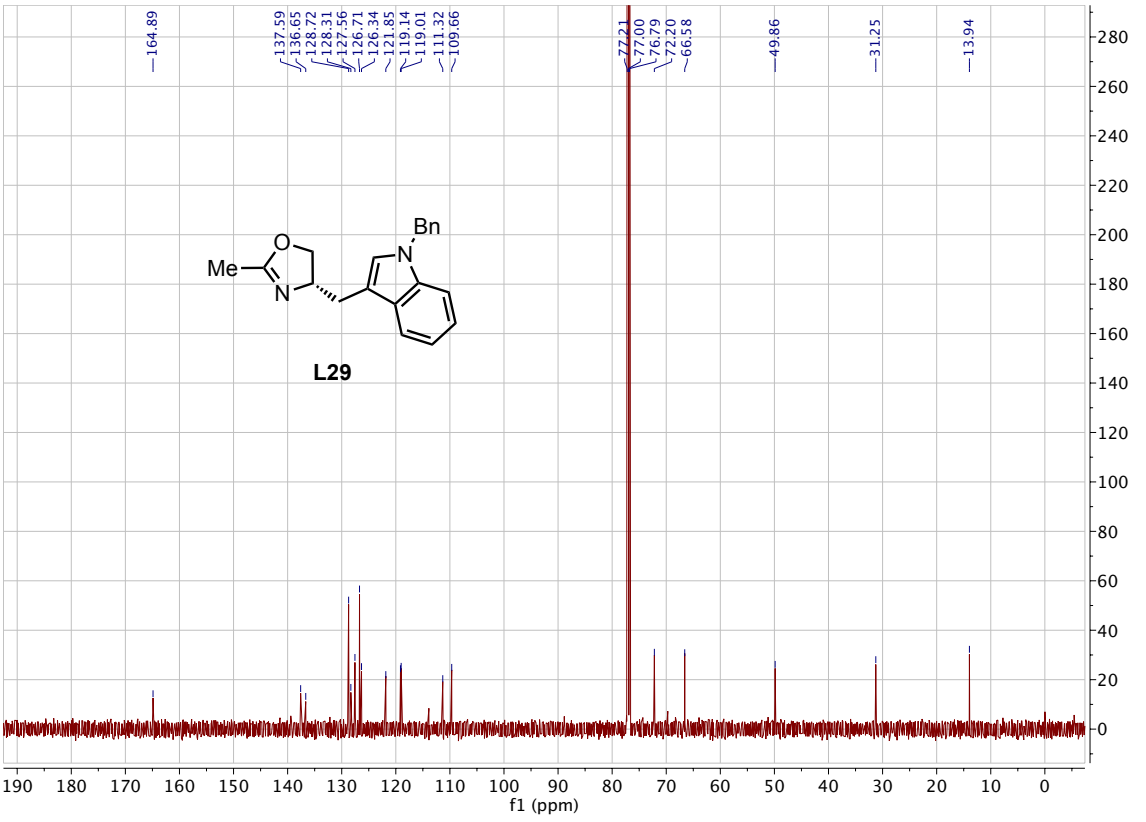
L25
f1 (ppm)

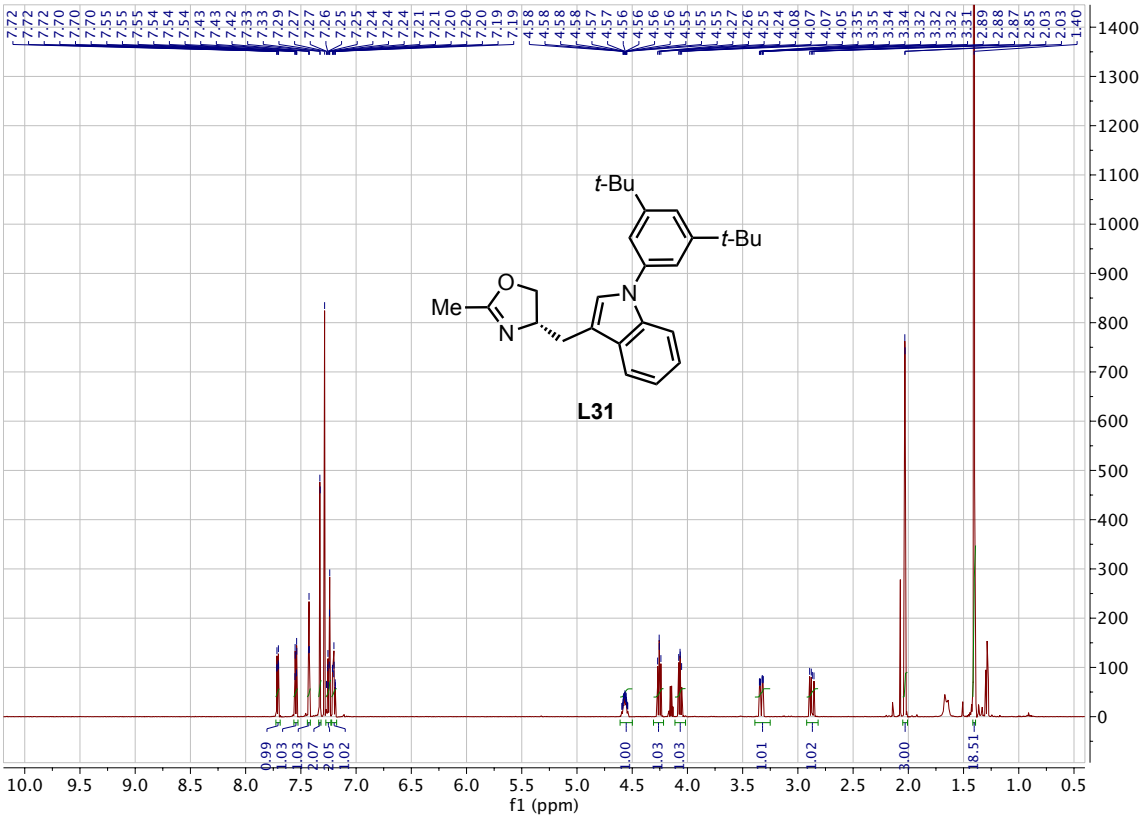

Me
O
N
Ts
N
L25
f1 (ppm)

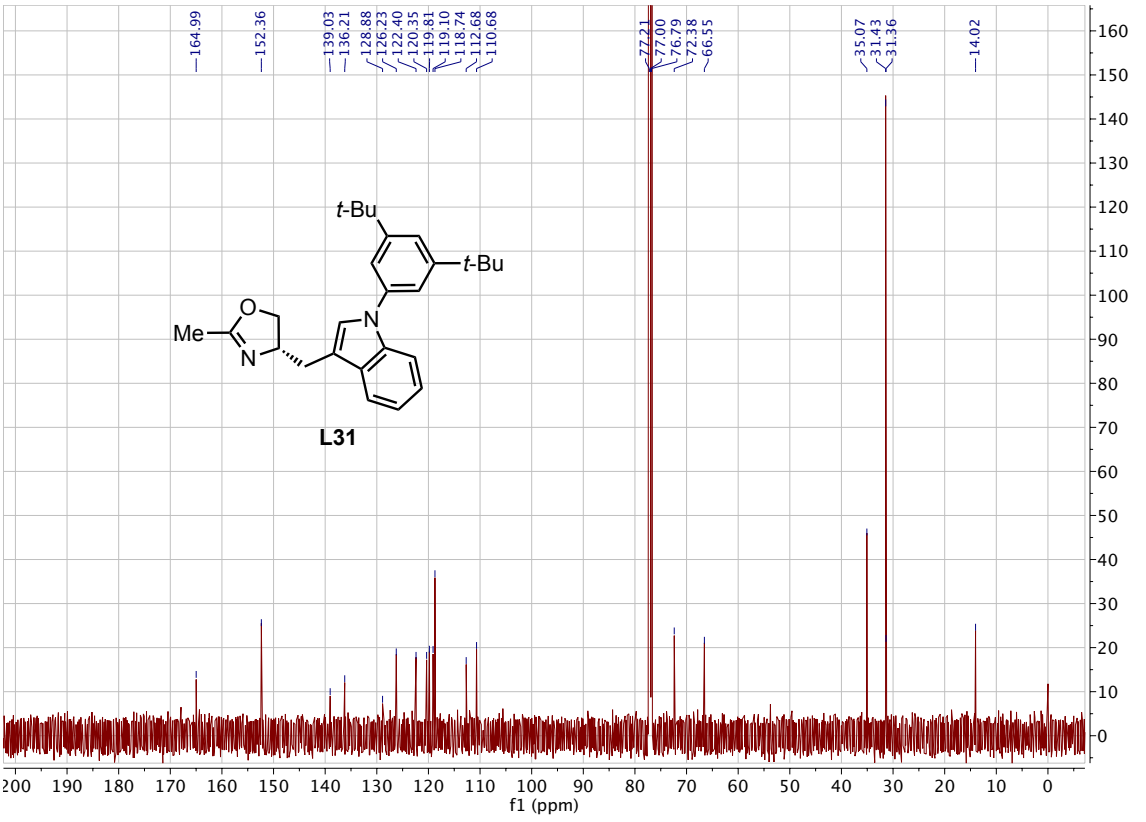

Boc
N
O
Me
N
L26
f1 (ppm)

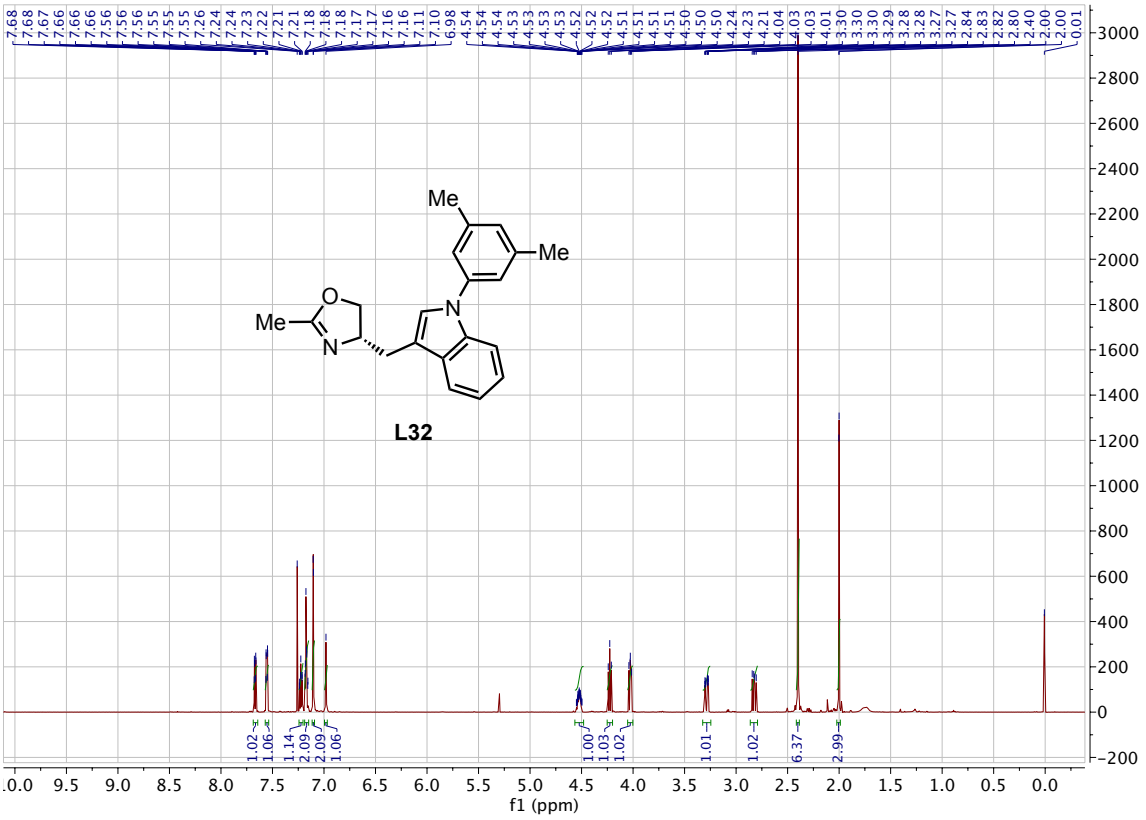

Boc
N
O
Me
N
L26
f1 (ppm)

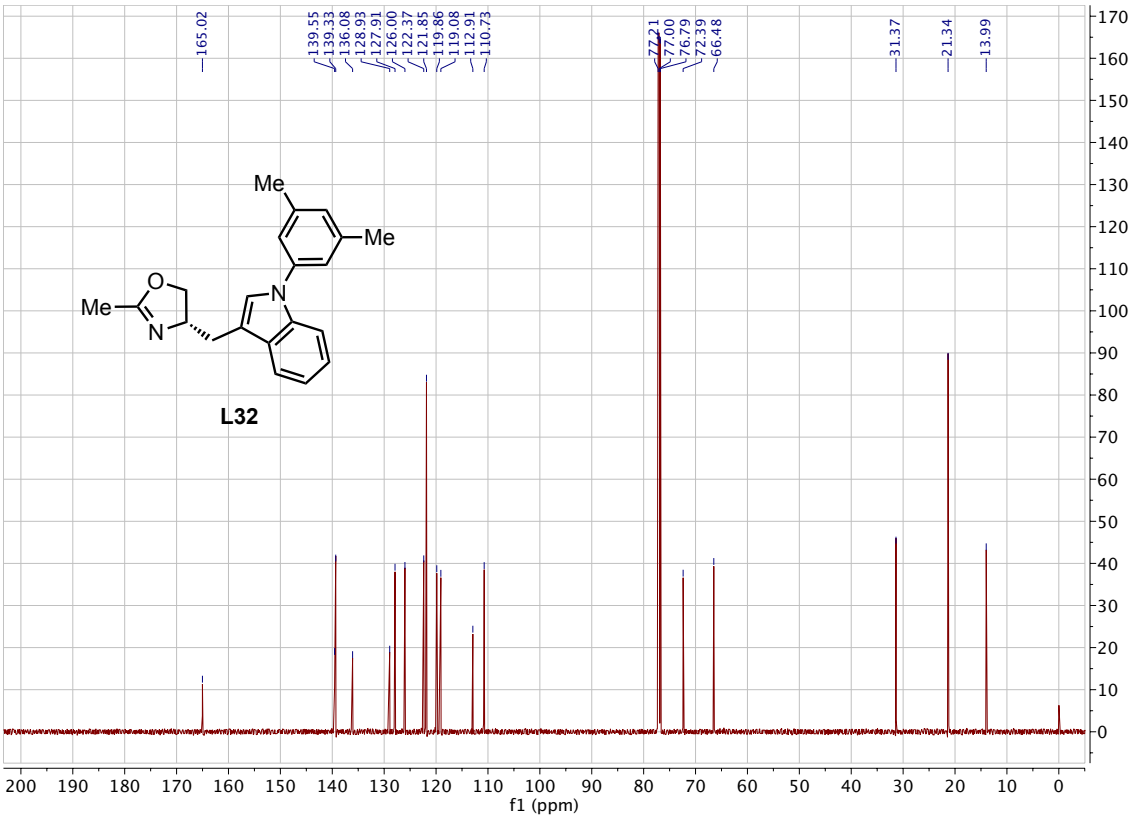

Me
O
N
Bn
N
L29
f1 (ppm)

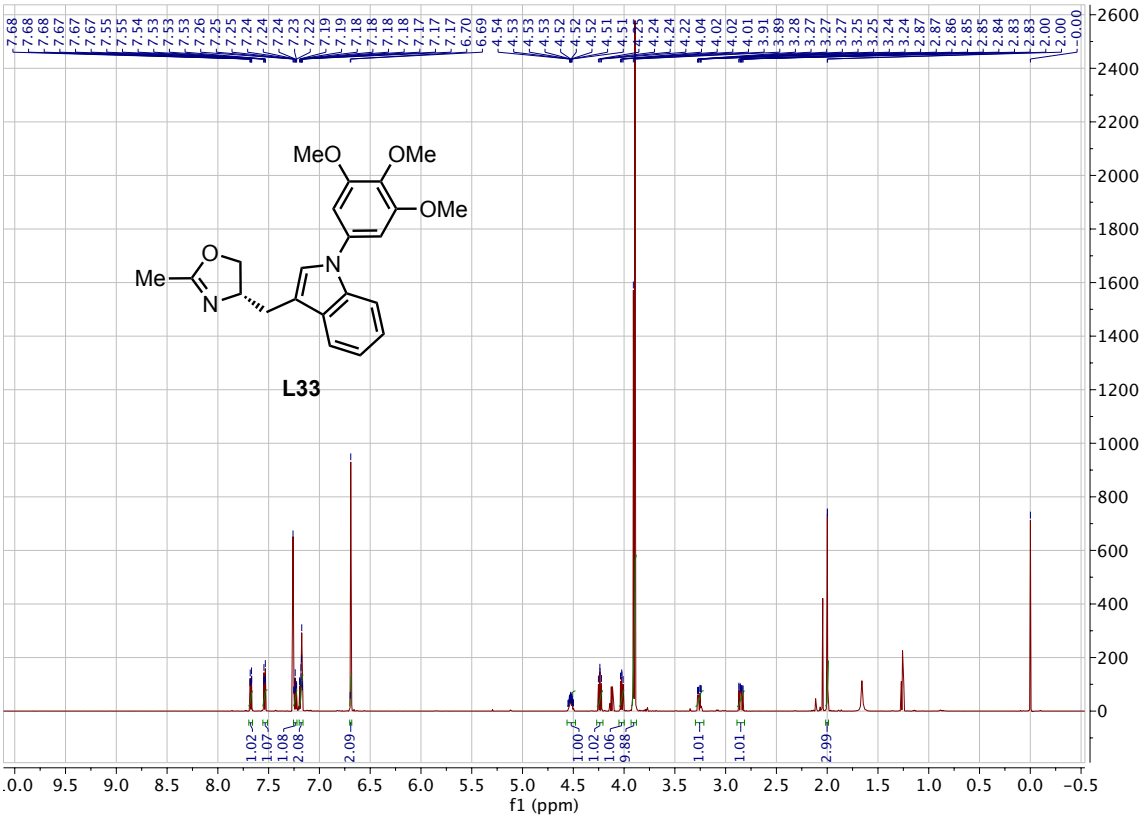

Me
O
N
Bn
N
L29
f1 (ppm)

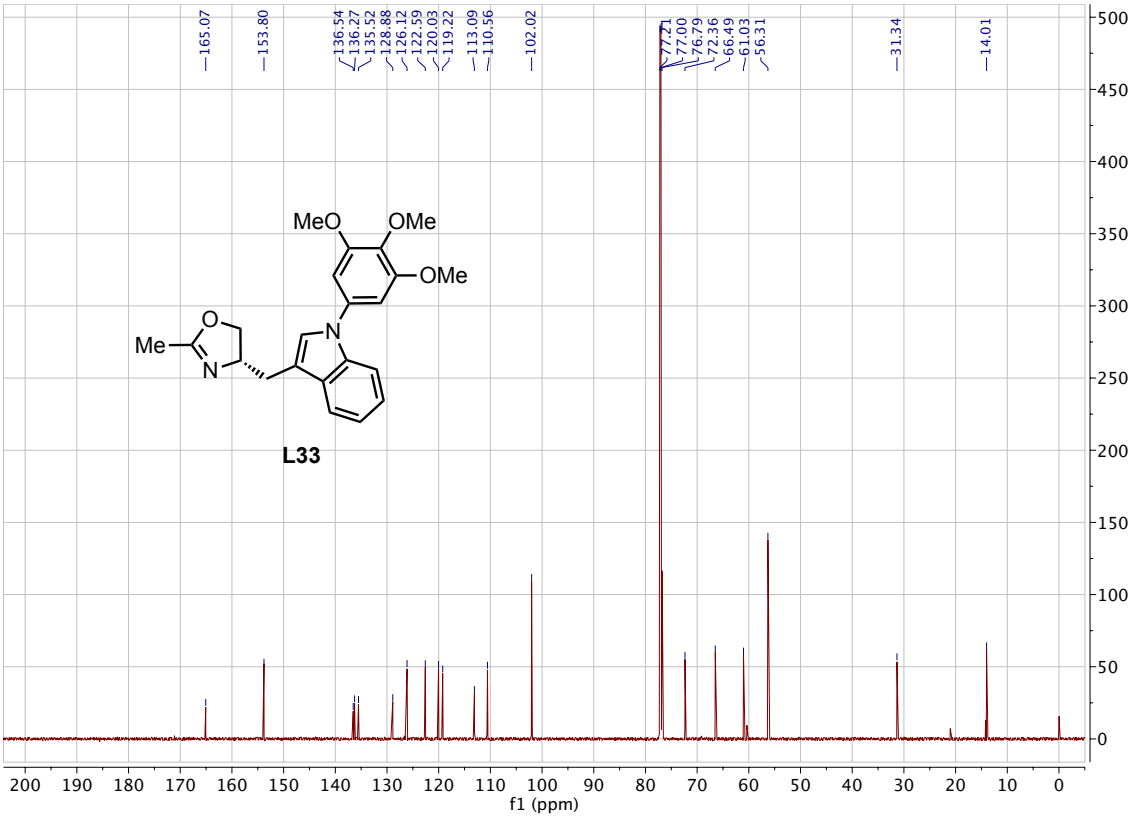

t-Bu
t-Bu
Me
O
N
N
L31
f1 (ppm)

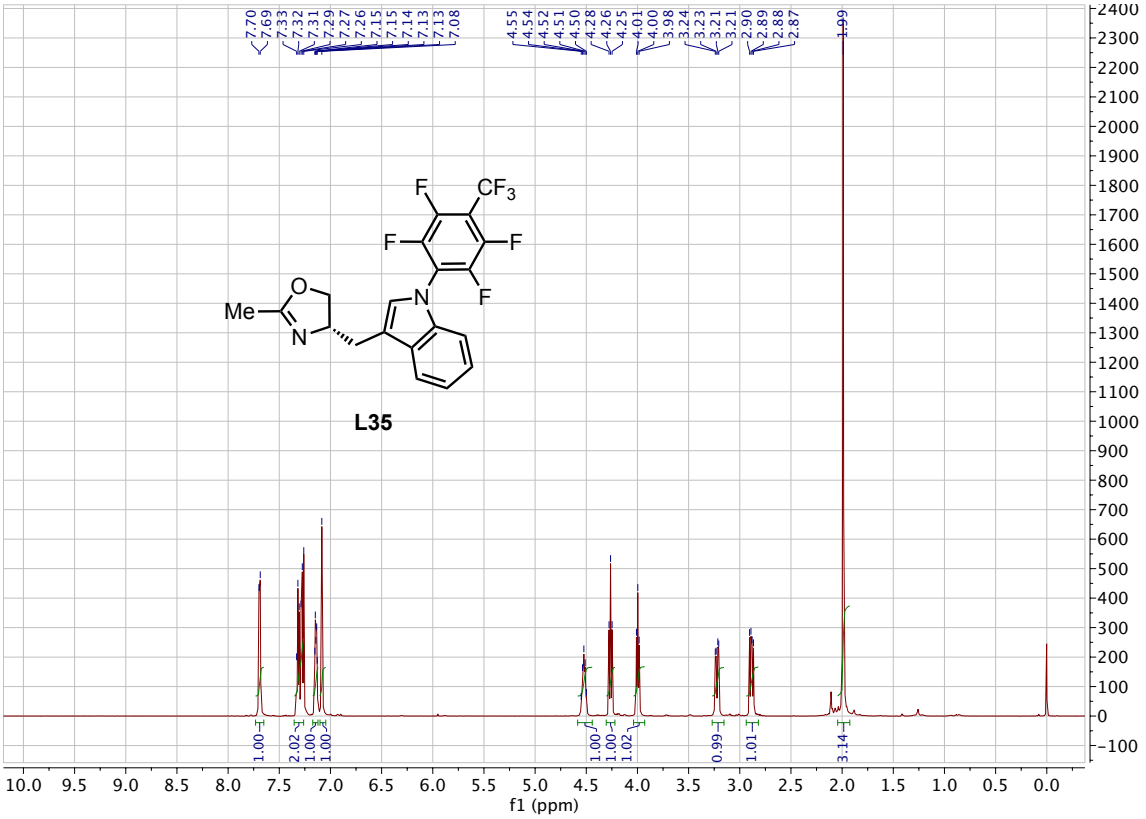

t-Bu
t-Bu
Me
O
N
N
L31
f1 (ppm)

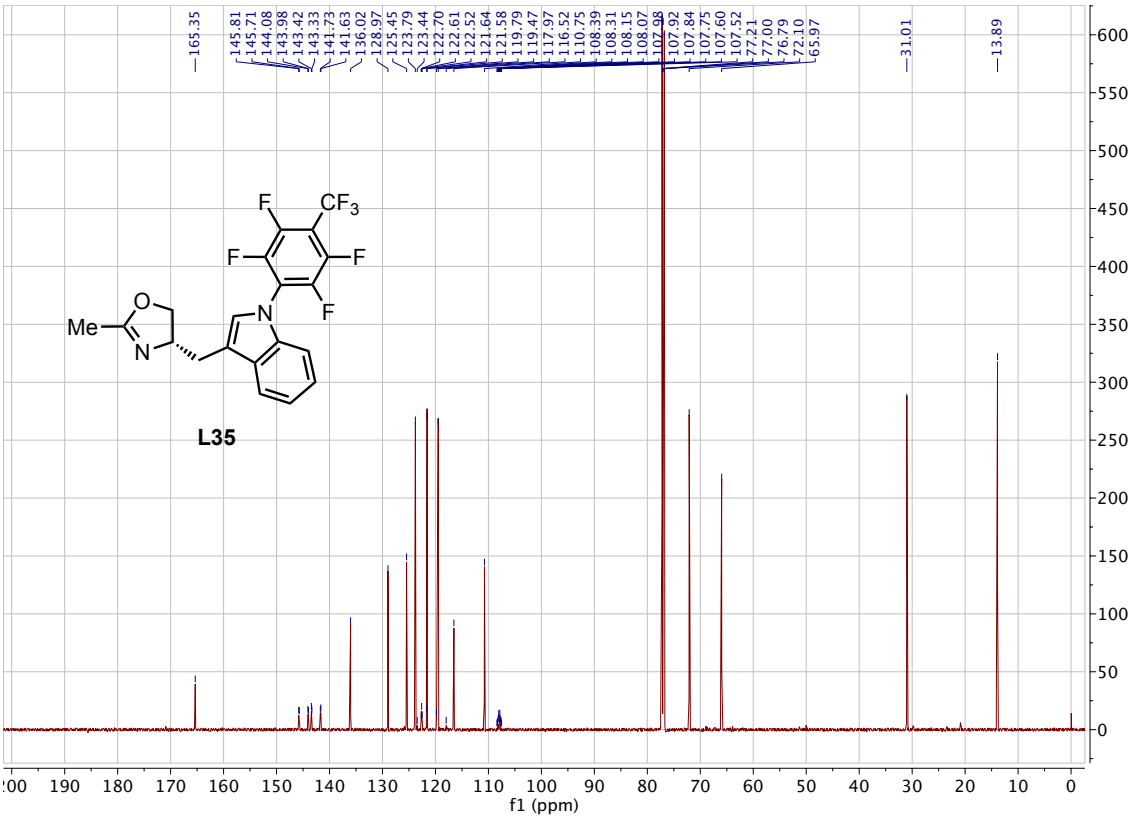

Me
Me
O
Me
N
N
L32
f1 (ppm)

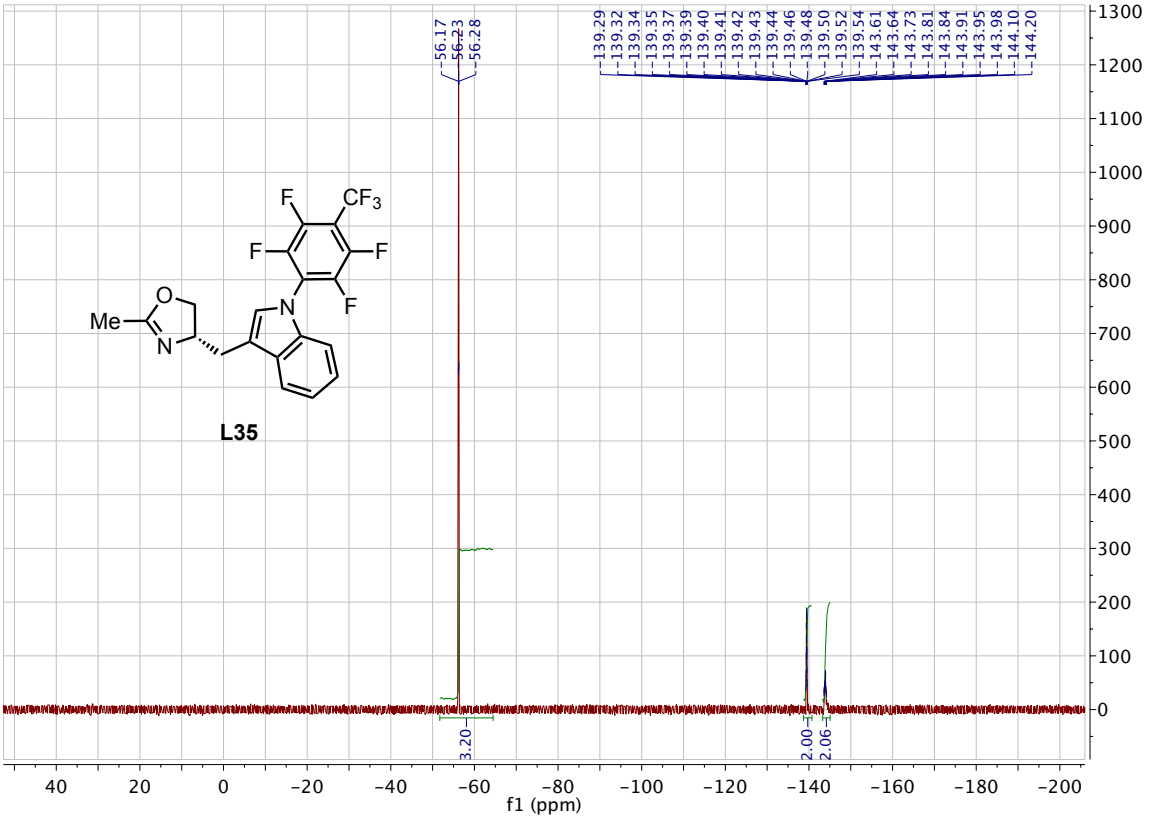

165.02
139.55
139.33
136.08
128.93
127.91
126.00
122.37
121.85
119.86
119.08
112.91
110.73
77.21
77.00
76.79
72.39
66.48
31.37
21.34
13.99
Me
Me
O
Me
N
N
L32
f1 (ppm)

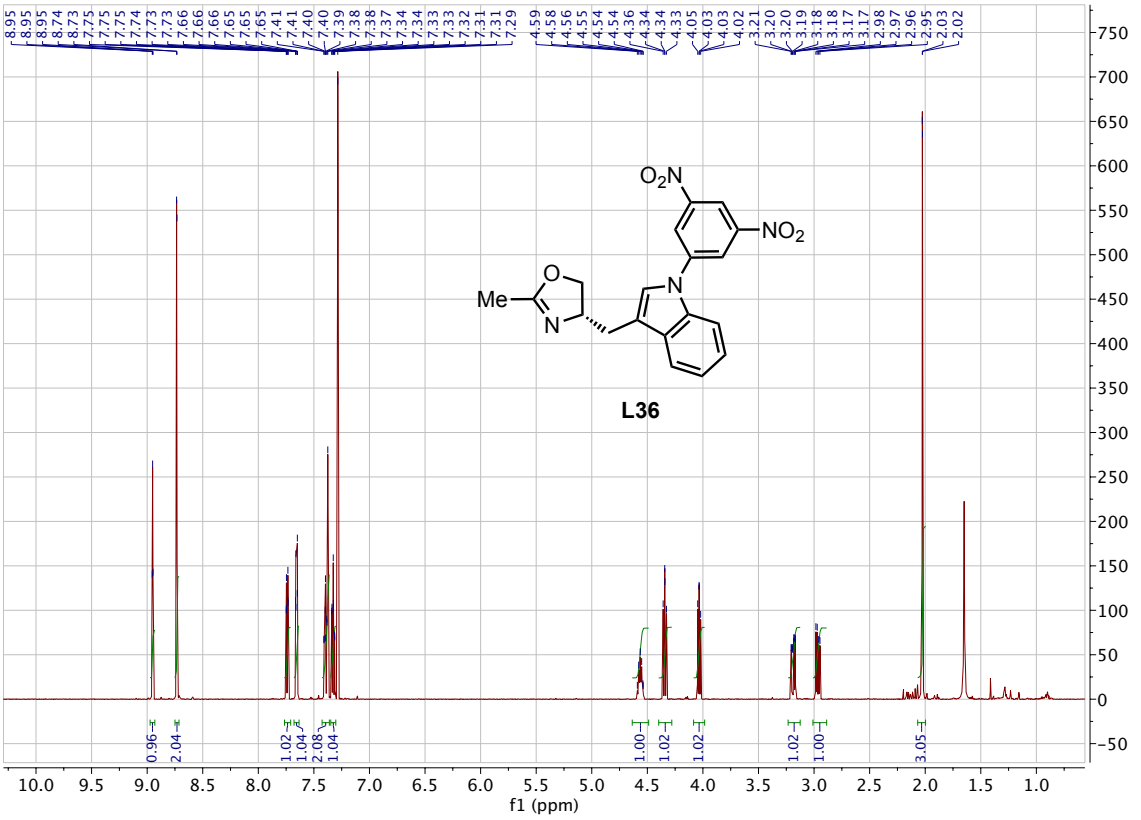

MeO
OMe
OMe
Me
O
N
N
L33
f1 (ppm)

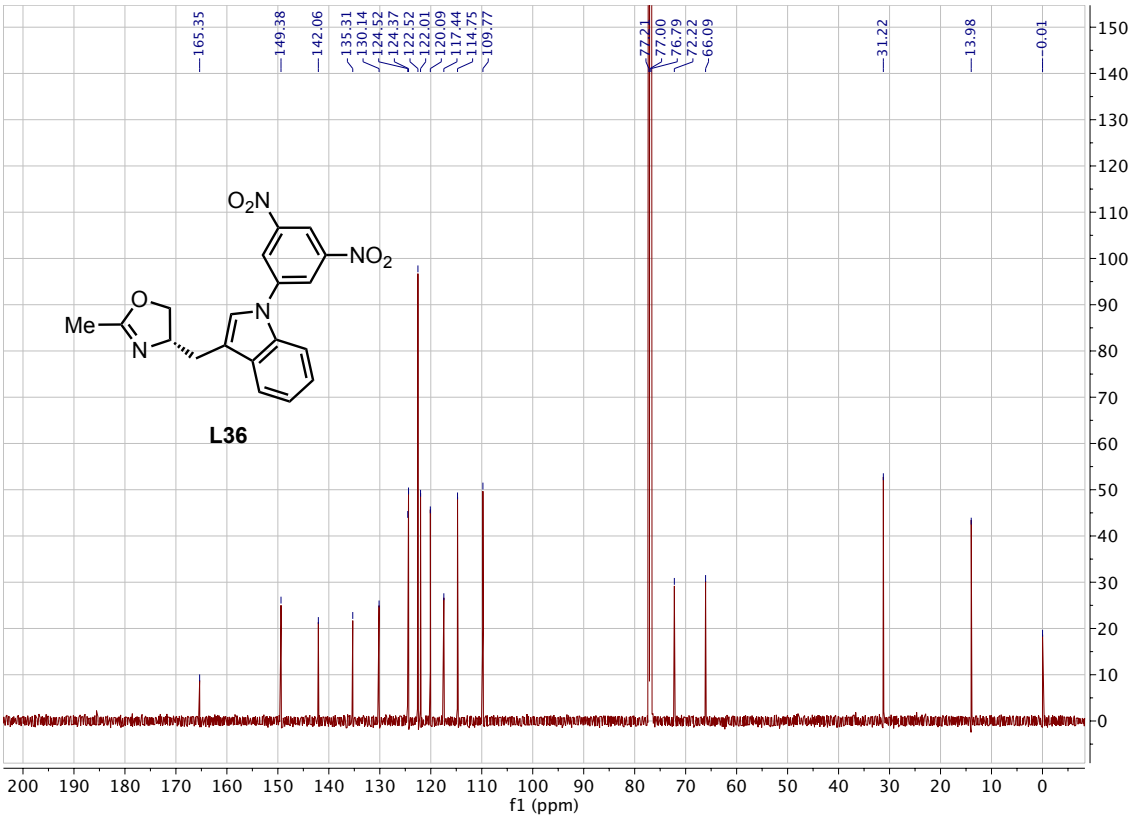

MeO
OMe
OMe
Me
O
N
N
L33
f1 (ppm)

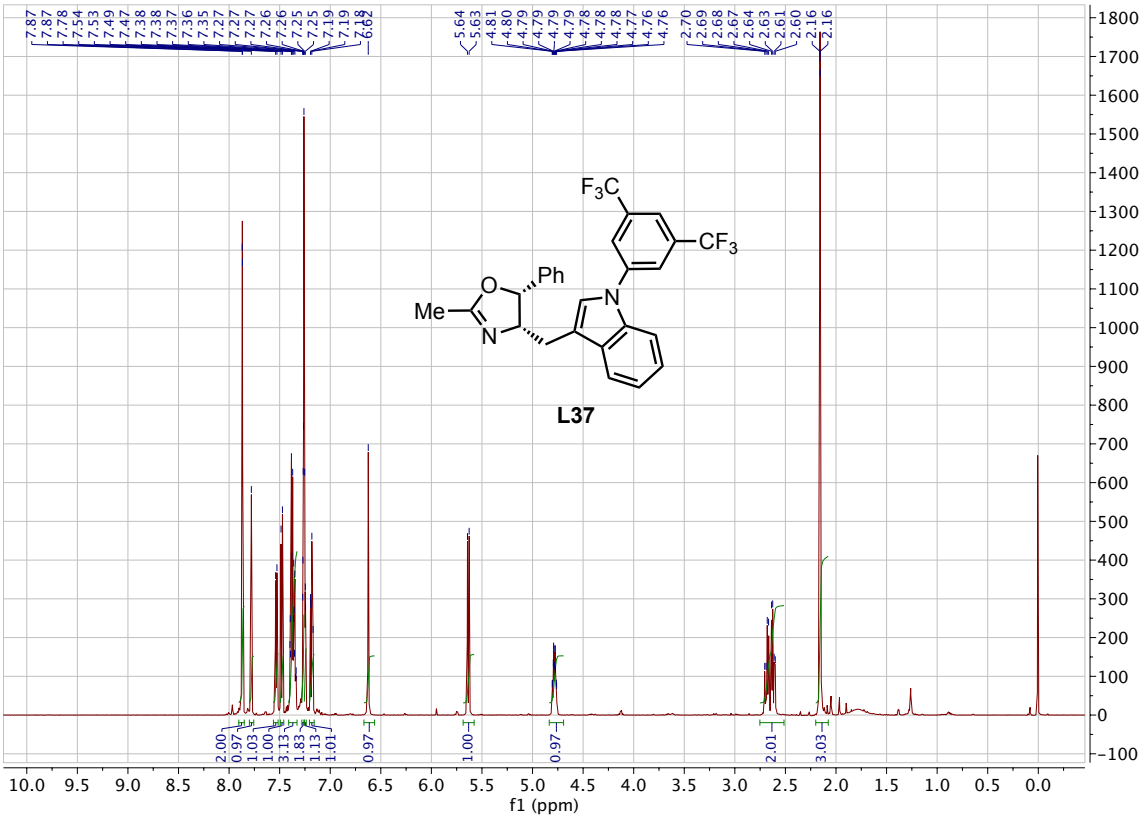

F
CF3
F
F
F
N
O
Me
N
L35
f1 (ppm)

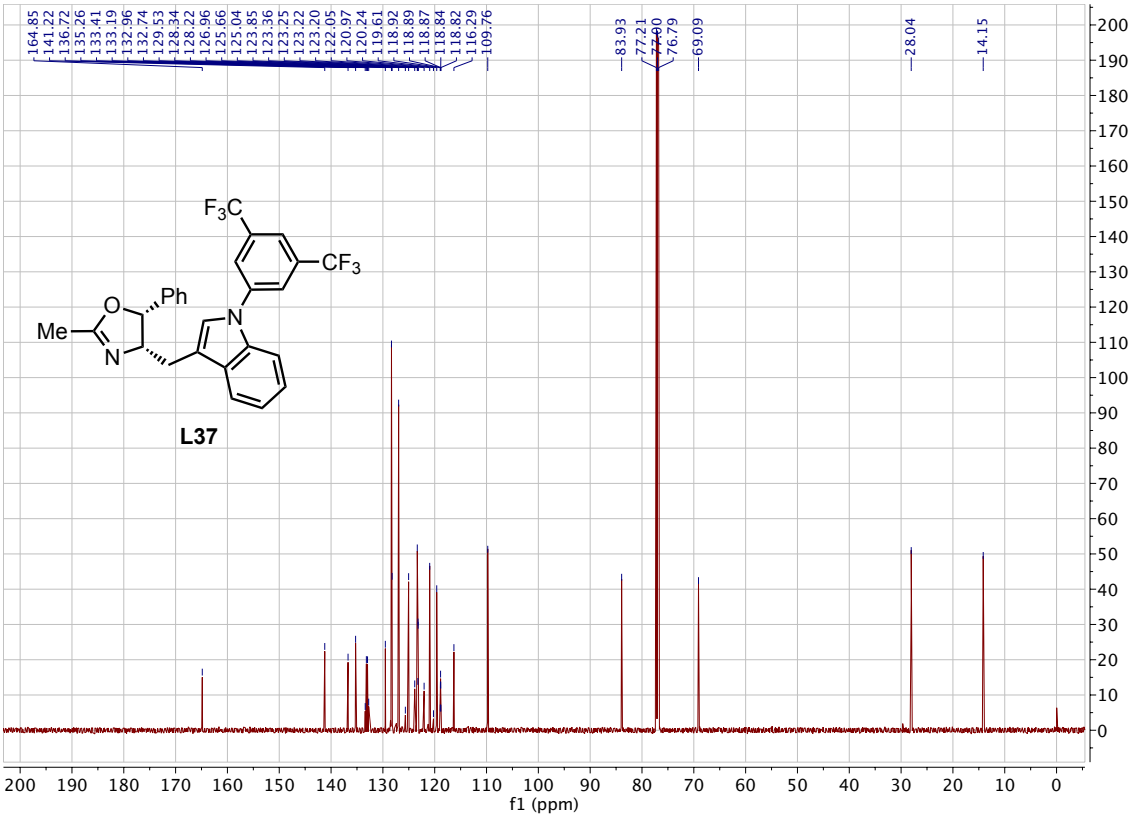

F
CF3
F
F
F
N
O
Me
N
L35
f1 (ppm)

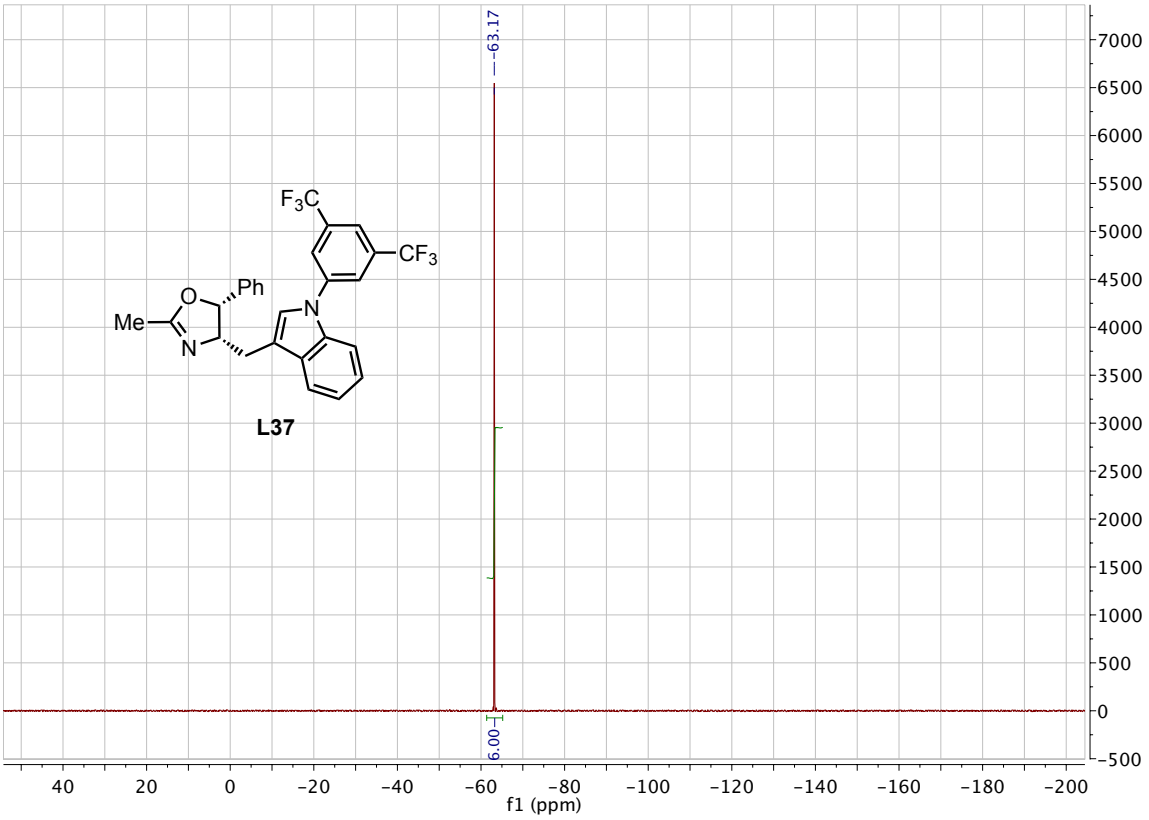

F
CF3
F
F
F
N
O
Me
N
L35
56.17
56.23
56.28
139.29
139.32
139.34
139.35
139.37
139.39
139.40
139.41
139.42
139.43
139.44
139.46
139.48
139.50
139.52
139.54
143.61
143.64
143.73
143.81
143.84
143.91
143.95
143.98
144.10
144.20
3.20
2.00
2.06
f1 (ppm)

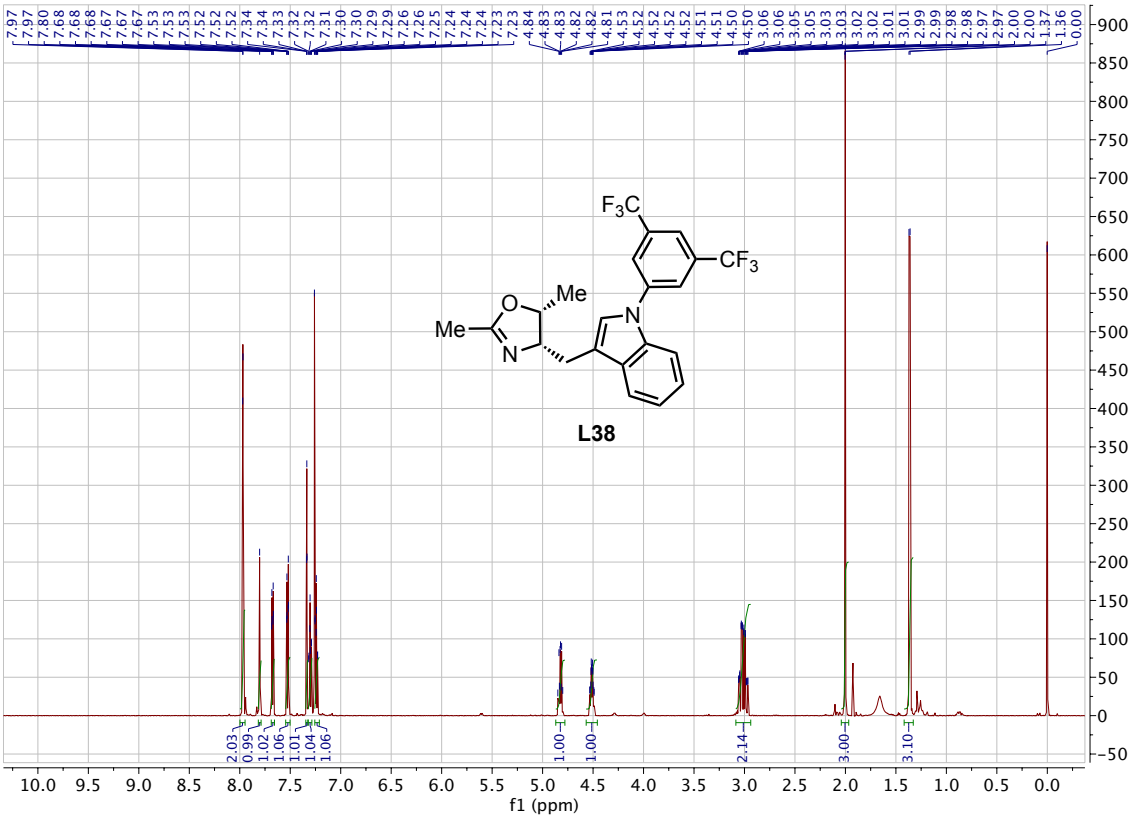

L36
f1 (ppm)

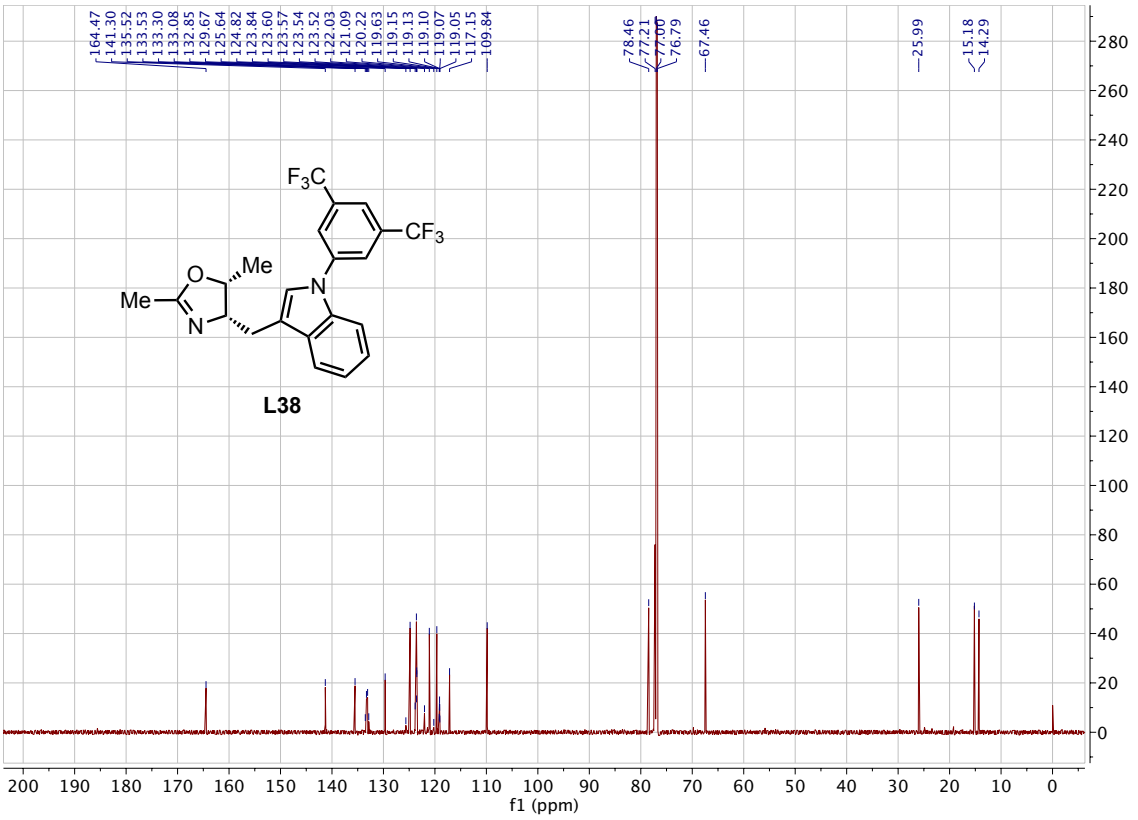

L36
f1 (ppm)

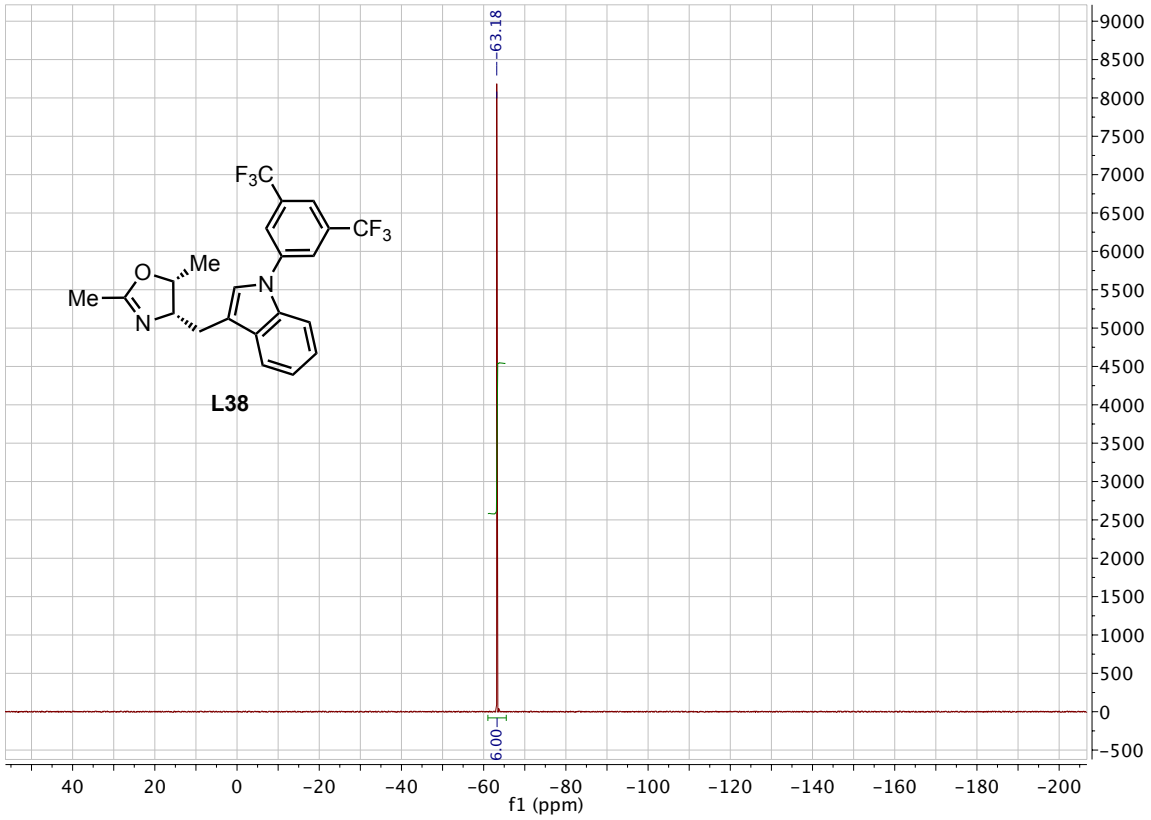

F3C
CF3
Ph
O
N
Me
N
L37
f1 (ppm)

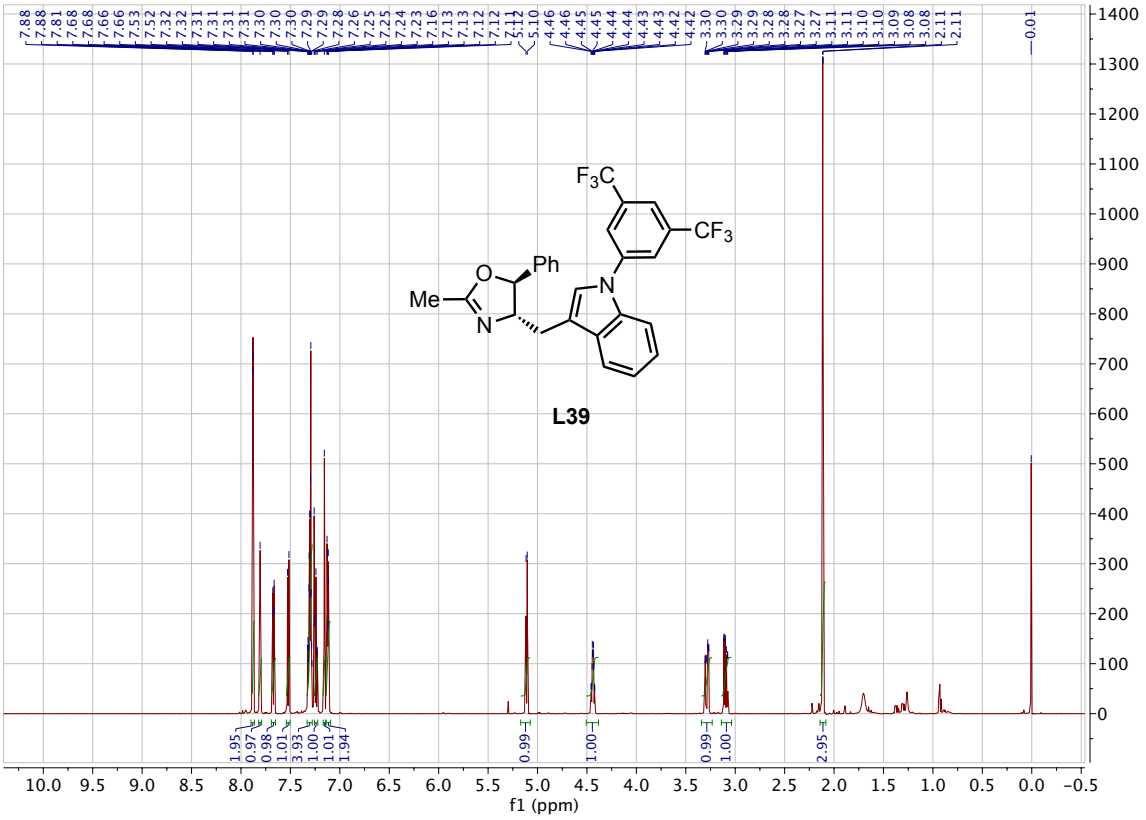

F3C
CF3
Ph
O
N
Me
N
L37
f1 (ppm)

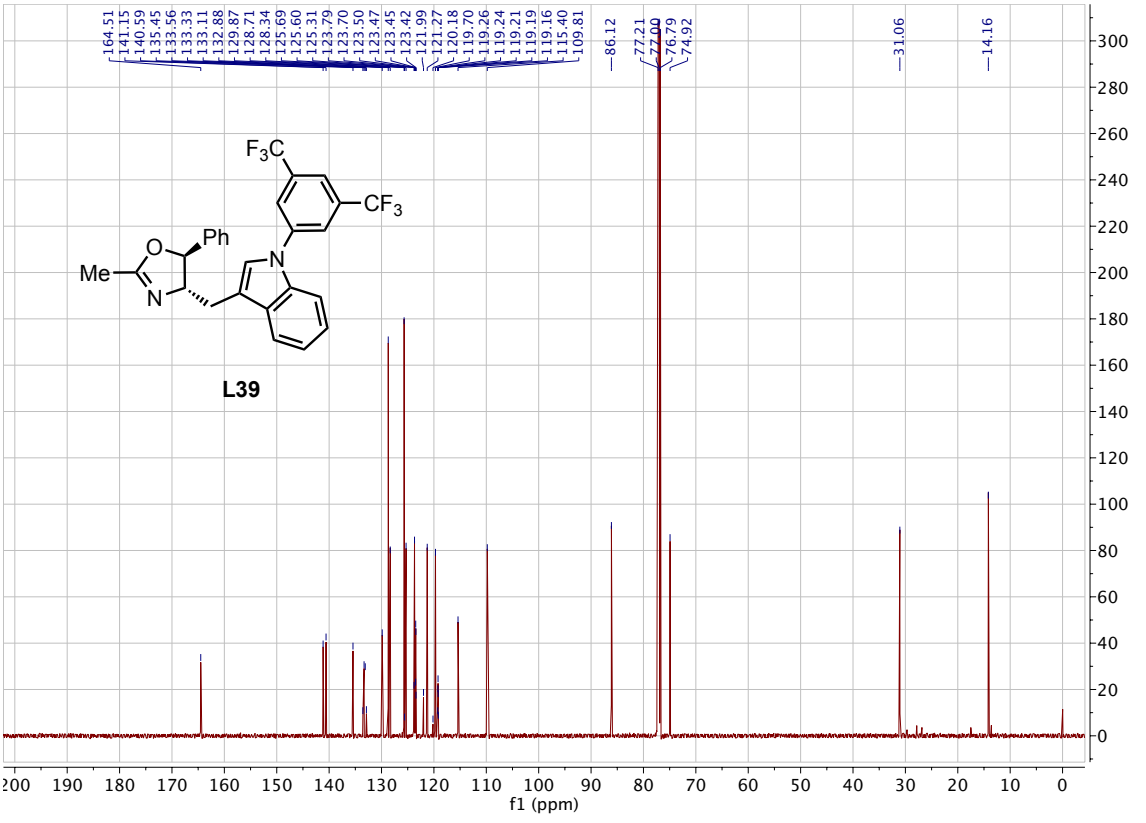

F3C
CF3
Ph
O
Me
N
N
L37
-63.17
6.00
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

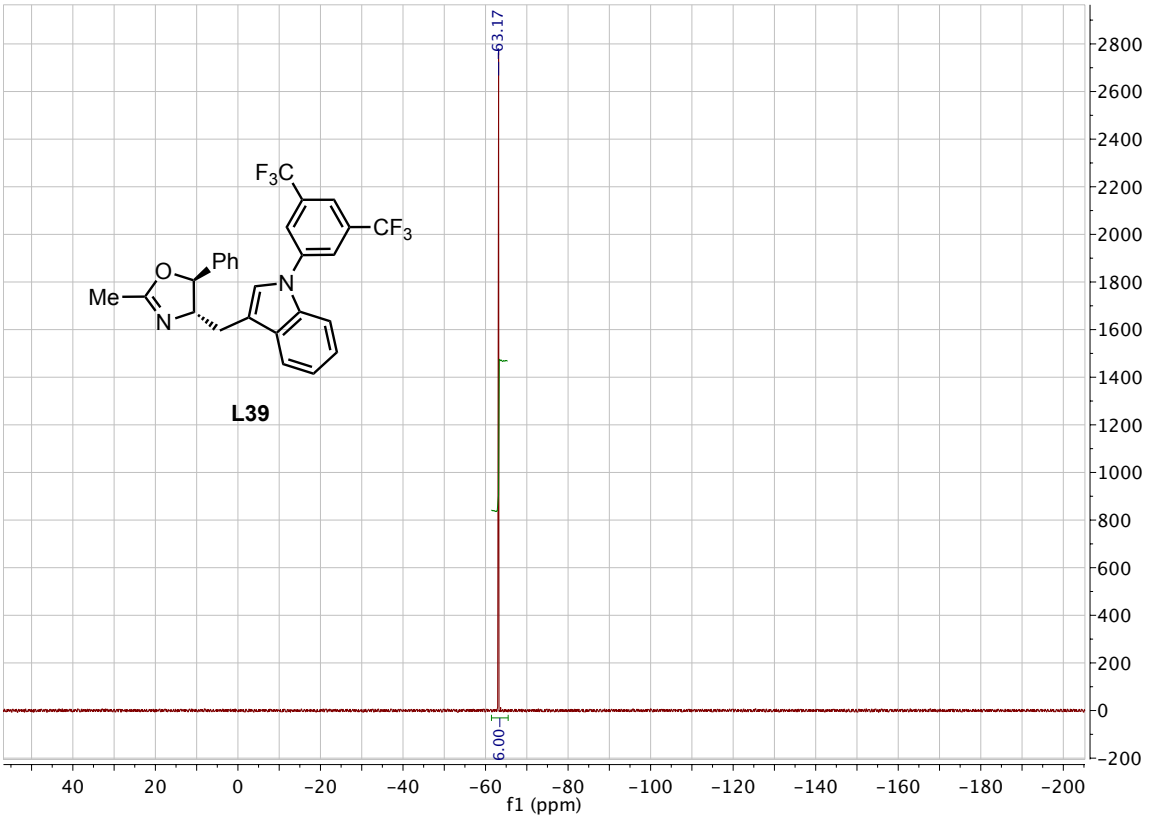

F3C
CF3
Me
Me
O
N
N
L38
f1 (ppm)

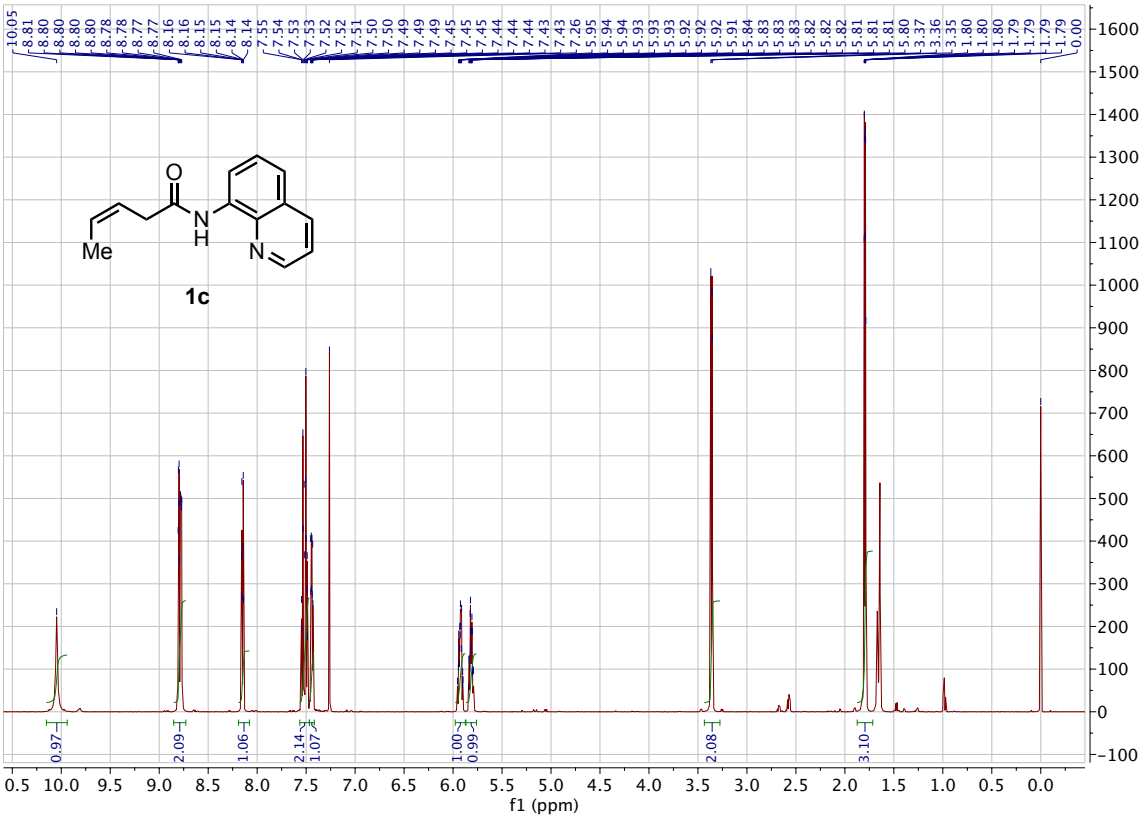

F3C
CF3
Me
Me
O
N
N
L38
f1 (ppm)

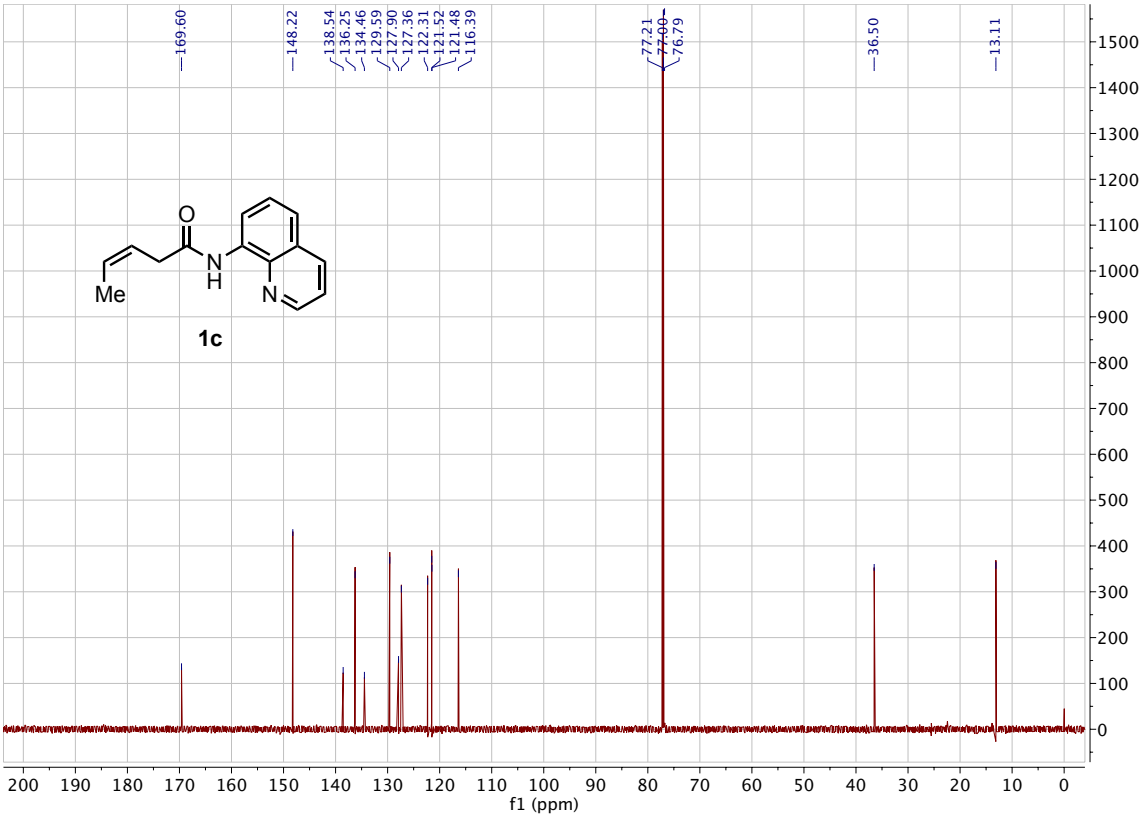

F3C
CF3
O
Me
Me
N
N
L38
-63.18
6.00
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

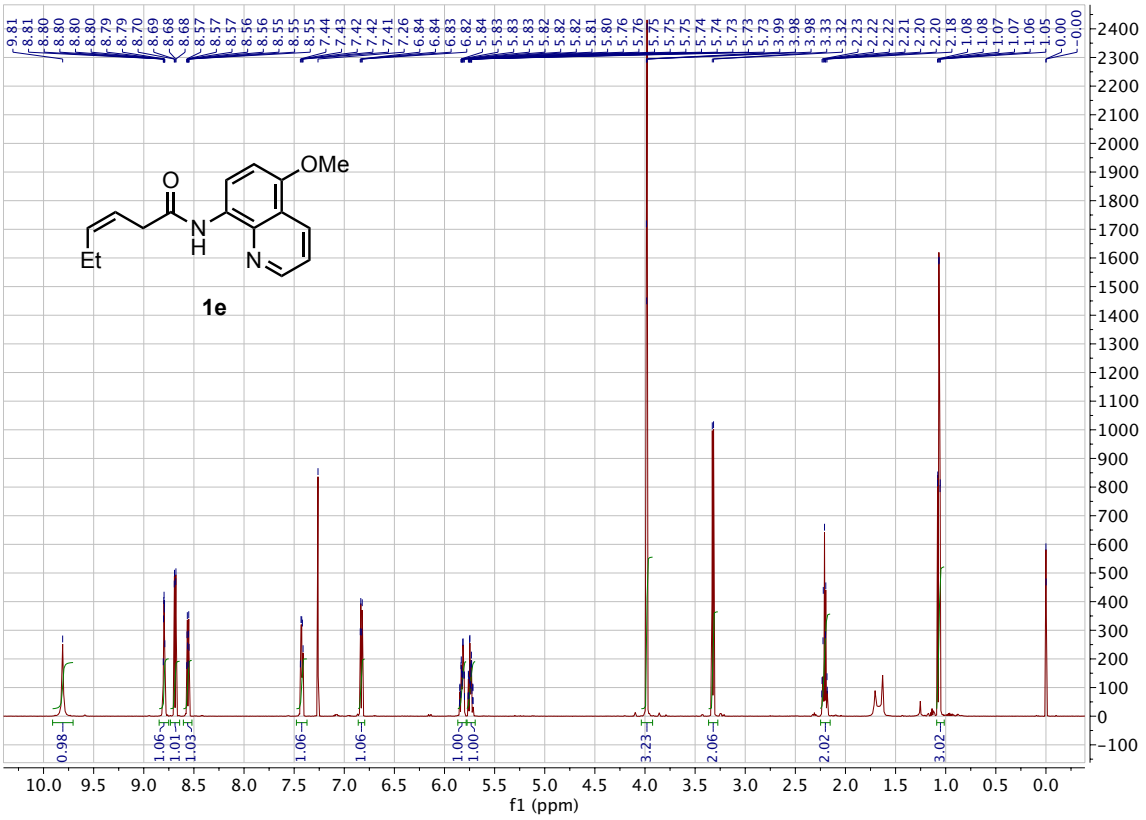

F3C
CF3
Ph
O
Me
N
N
L39
f1 (ppm)

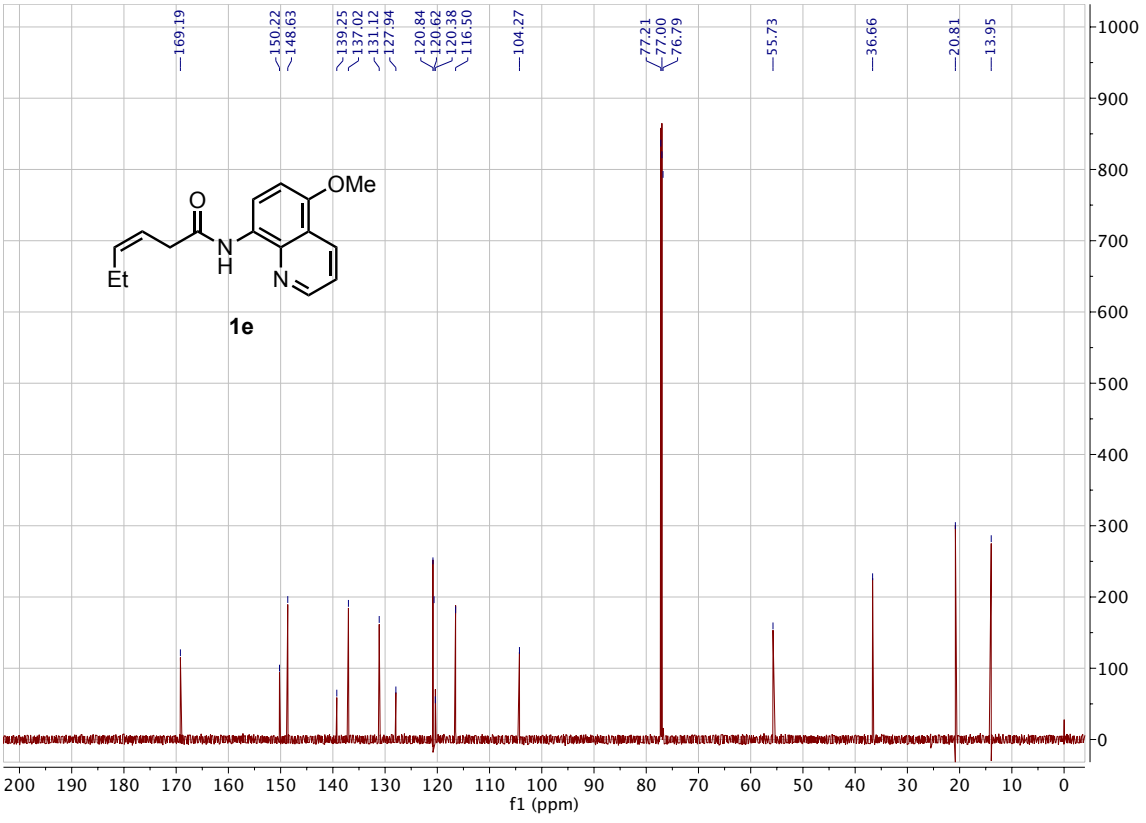

F3C
CF3
Ph
O
Me
N
N
L39
f1 (ppm)

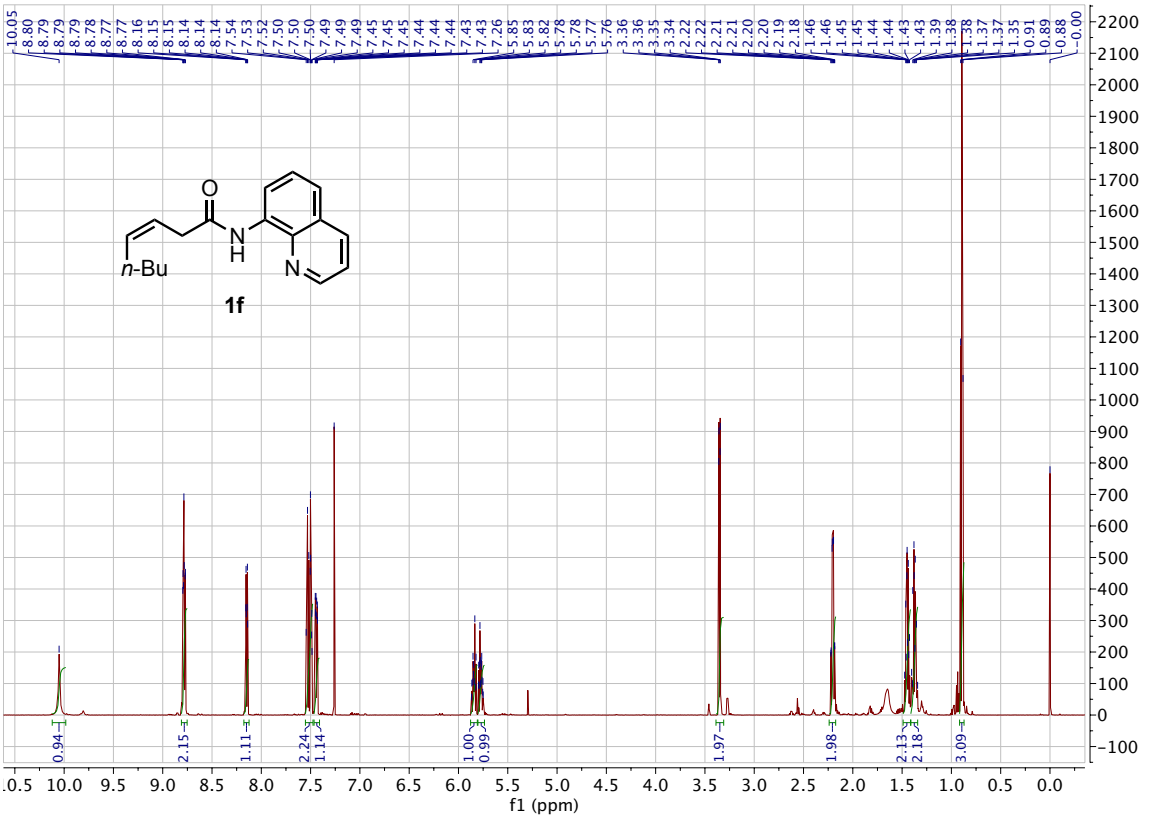

63.17
6.00
F3C
CF3
Ph
O
Me
N
N
L39
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

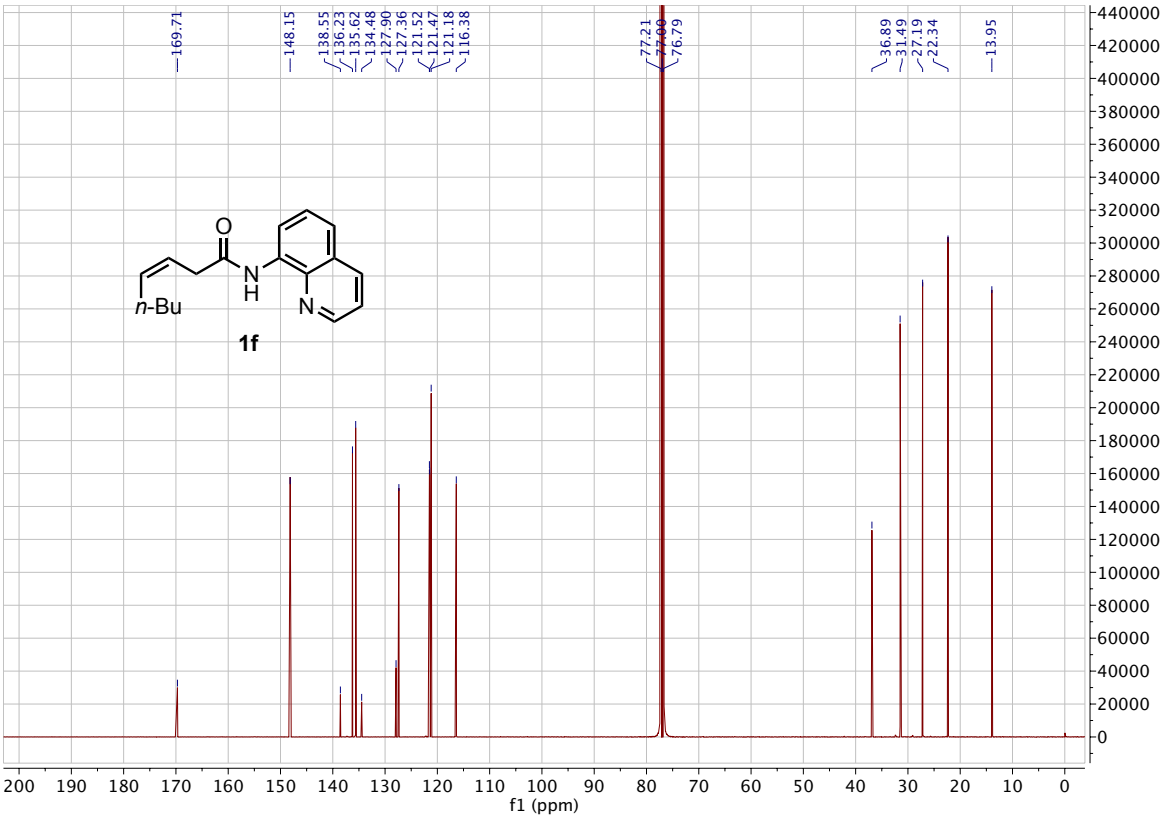

O
N
H
Me
N
1c
f1 (ppm)

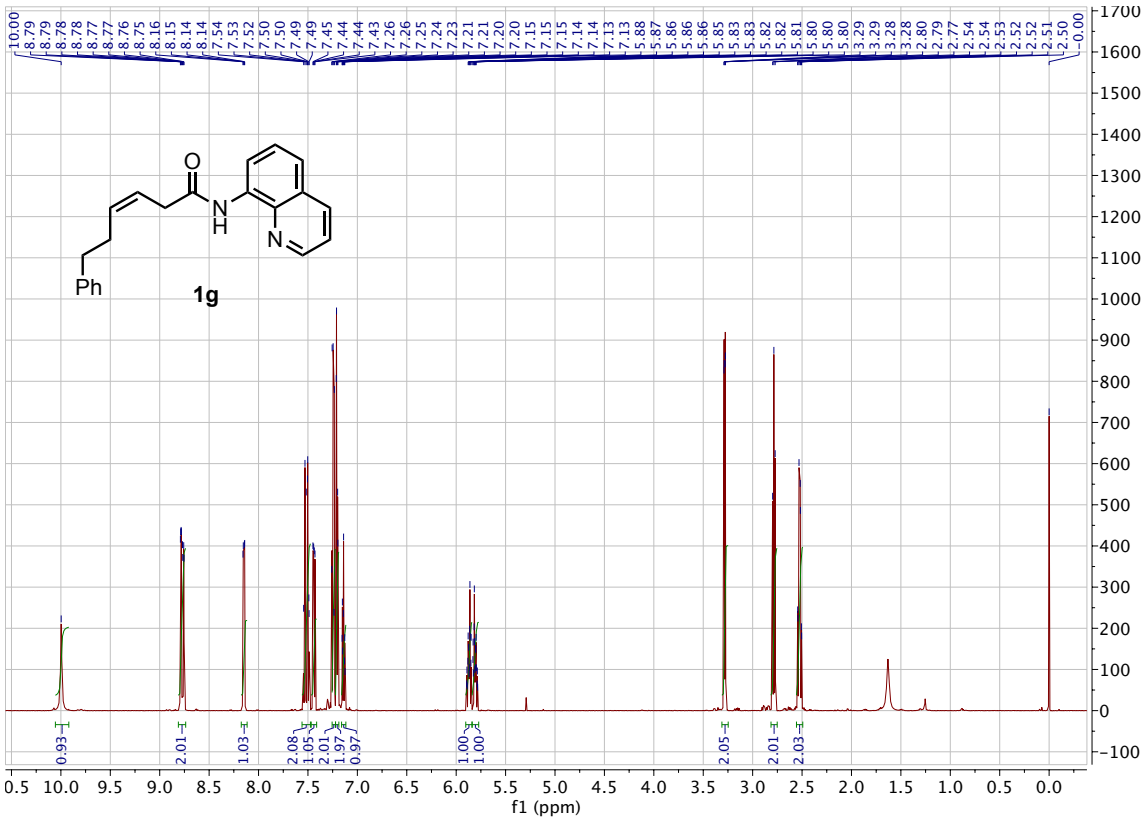

O
N
H
Me
N
1c
f1 (ppm)

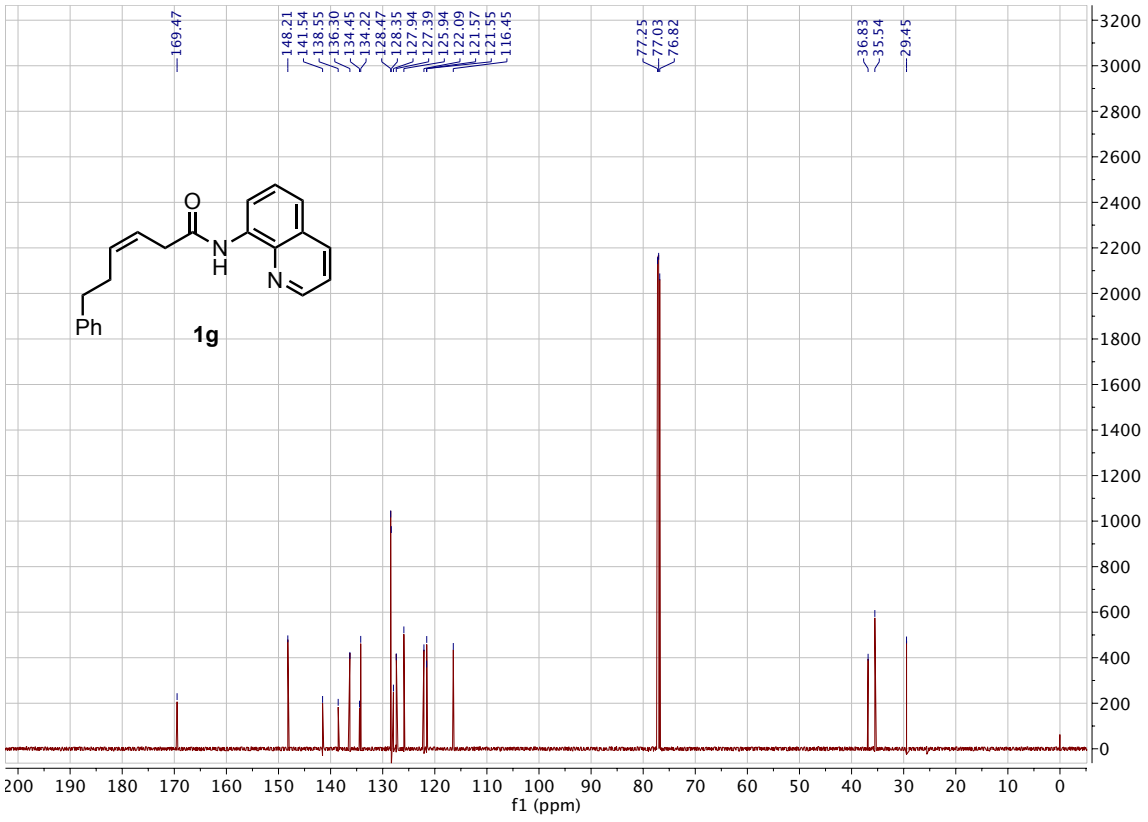

OMe
O
N
H
Et
N
1e
f1 (ppm)

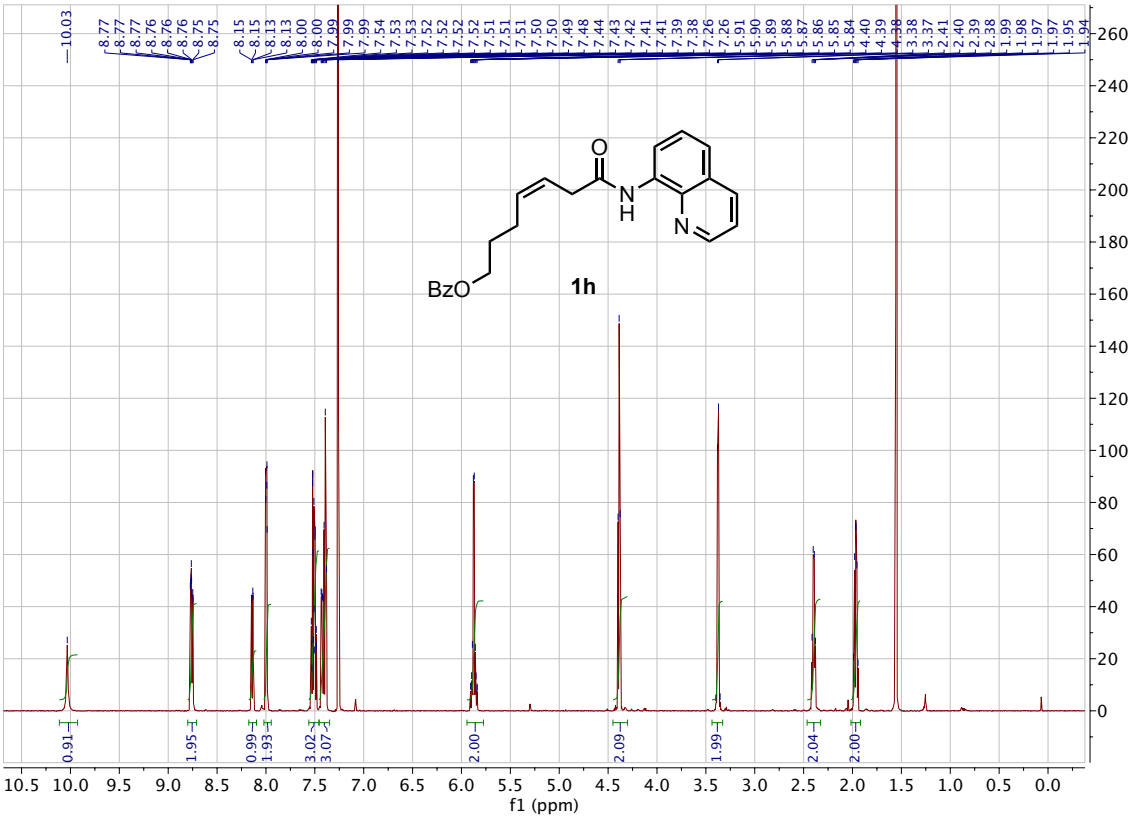

OMe
O
N
H
Et
N
1e
f1 (ppm)

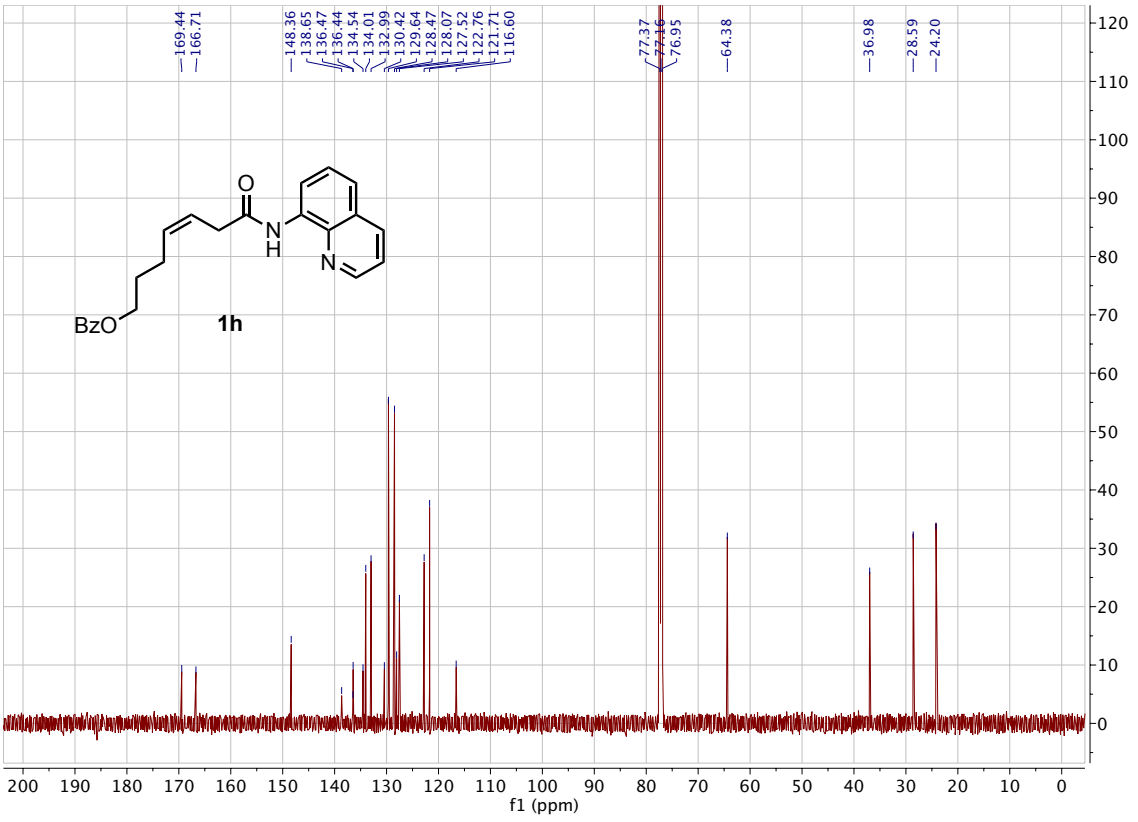

10.05
8.80
8.79
8.79
8.78
8.78
8.77
8.77
8.16
8.15
8.15
8.14
8.14
8.14
7.54
7.53
7.52
7.50
7.50
7.50
7.49
7.49
7.49
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.26
5.85
5.83
5.82
5.78
5.78
5.77
5.76
3.36
3.36
3.35
3.34
2.22
2.22
2.21
2.21
2.20
2.20
2.19
2.18
1.46
1.46
1.45
1.45
1.44
1.44
1.43
1.43
1.39
1.38
1.38
1.37
1.37
1.35
0.91
0.89
0.88
0.00
O
N
H
N
n-Bu
1f
0.94
2.15
1.11
2.24
1.14
1.00
0.99
1.97
1.98
2.13
2.18
3.09
f1 (ppm)

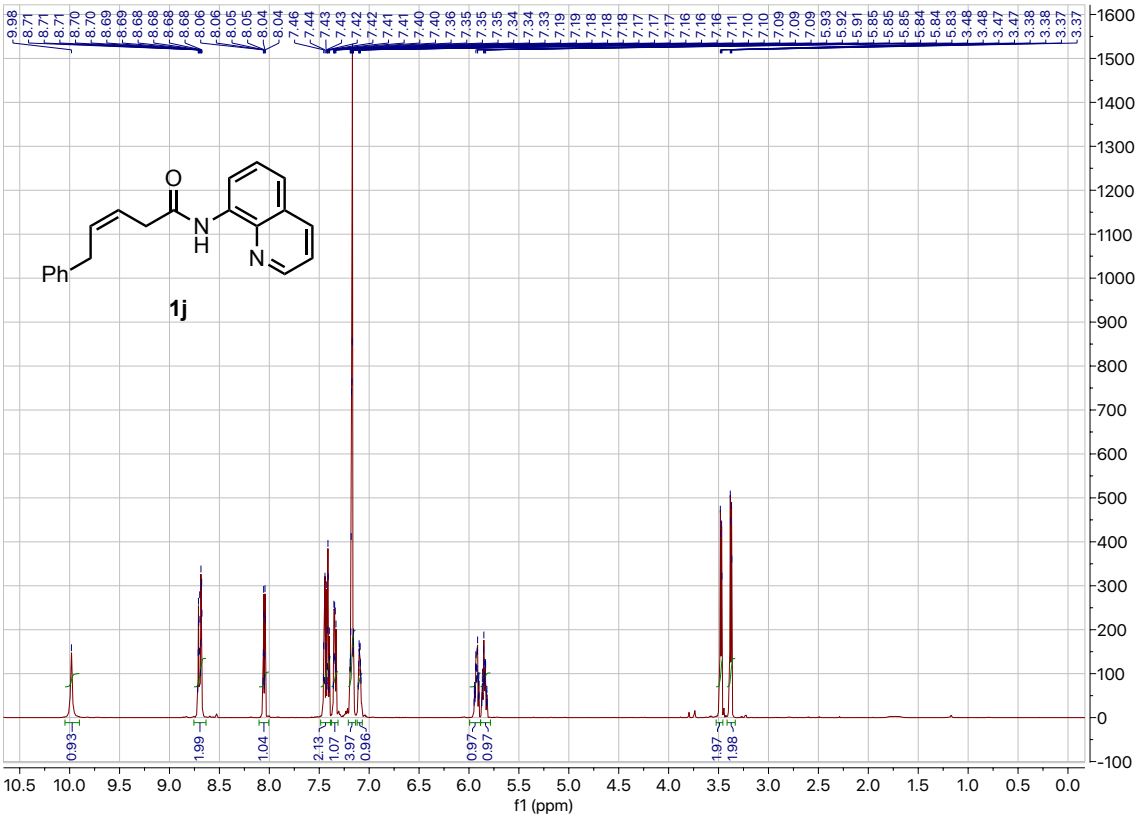

169.71
148.15
138.55
136.23
135.62
134.48
127.90
127.36
121.52
121.47
121.18
116.38
77.21
77.00
76.79
36.89
31.49
27.19
22.34
13.95
O
N
H
N
n-Bu
1f
f1 (ppm)

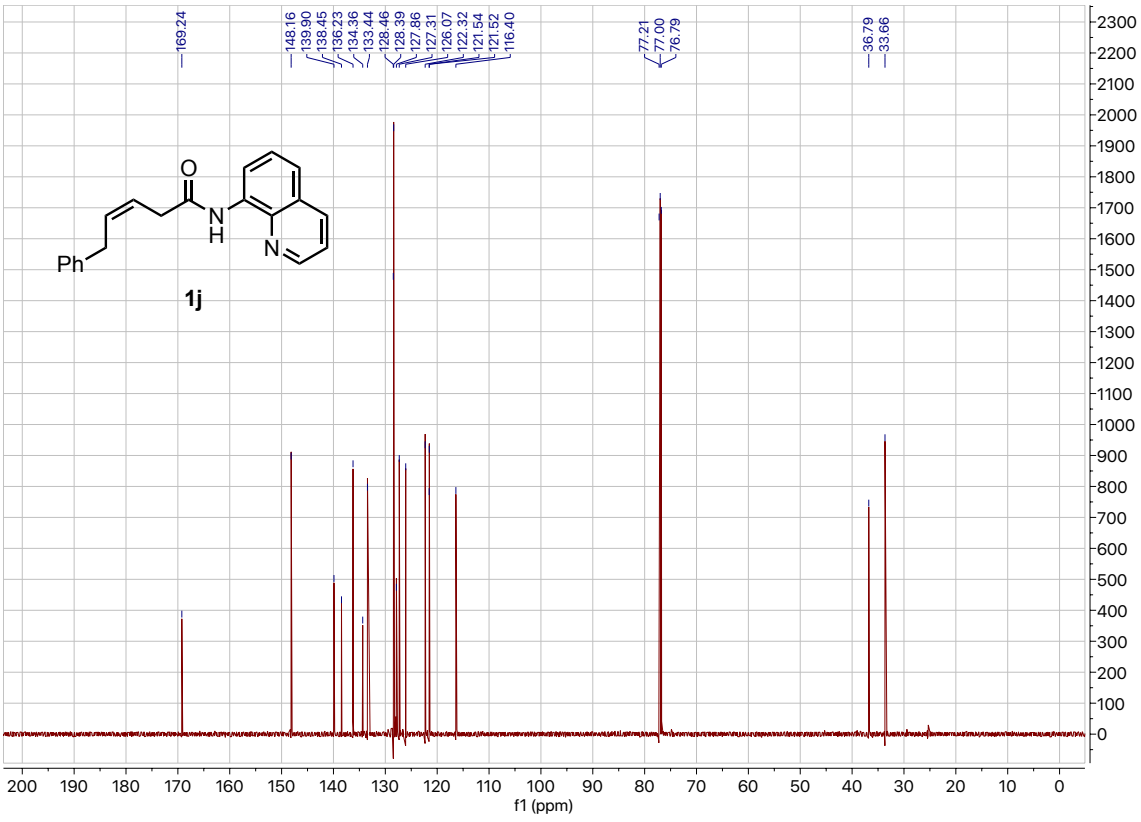

1g
f1 (ppm)

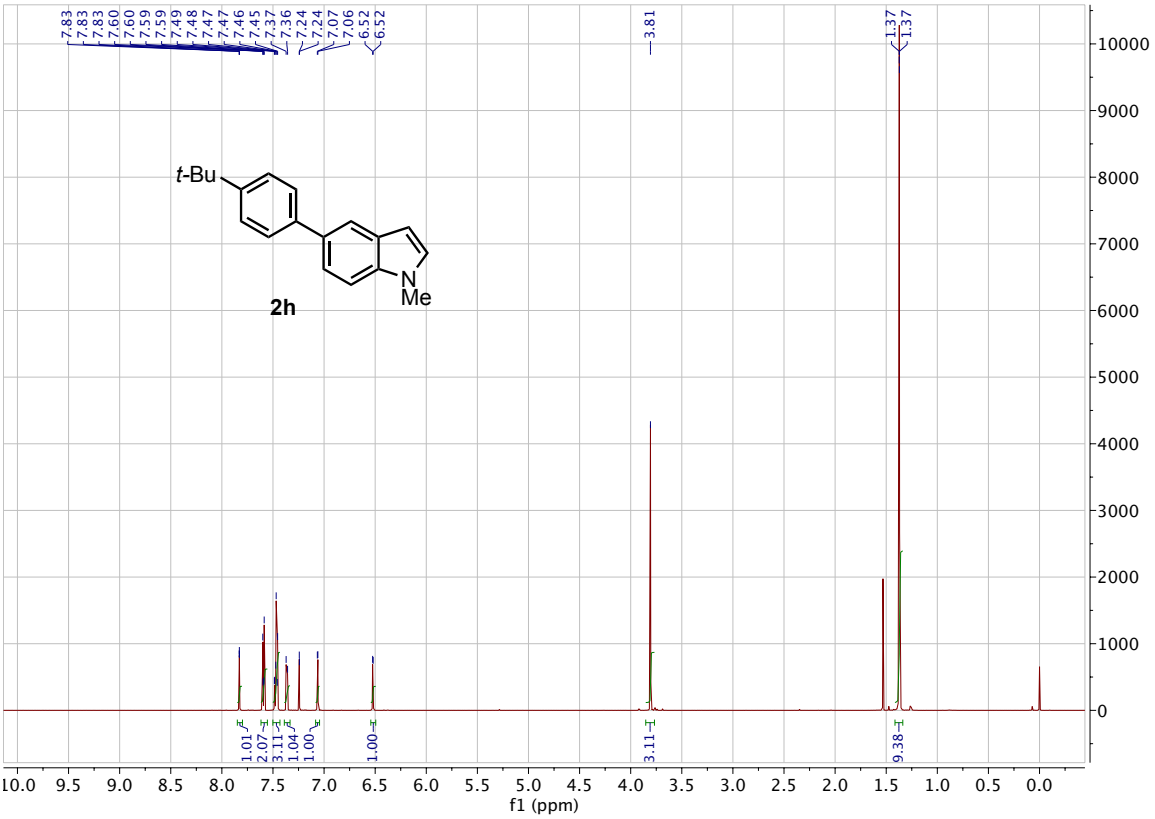

1g
f1 (ppm)

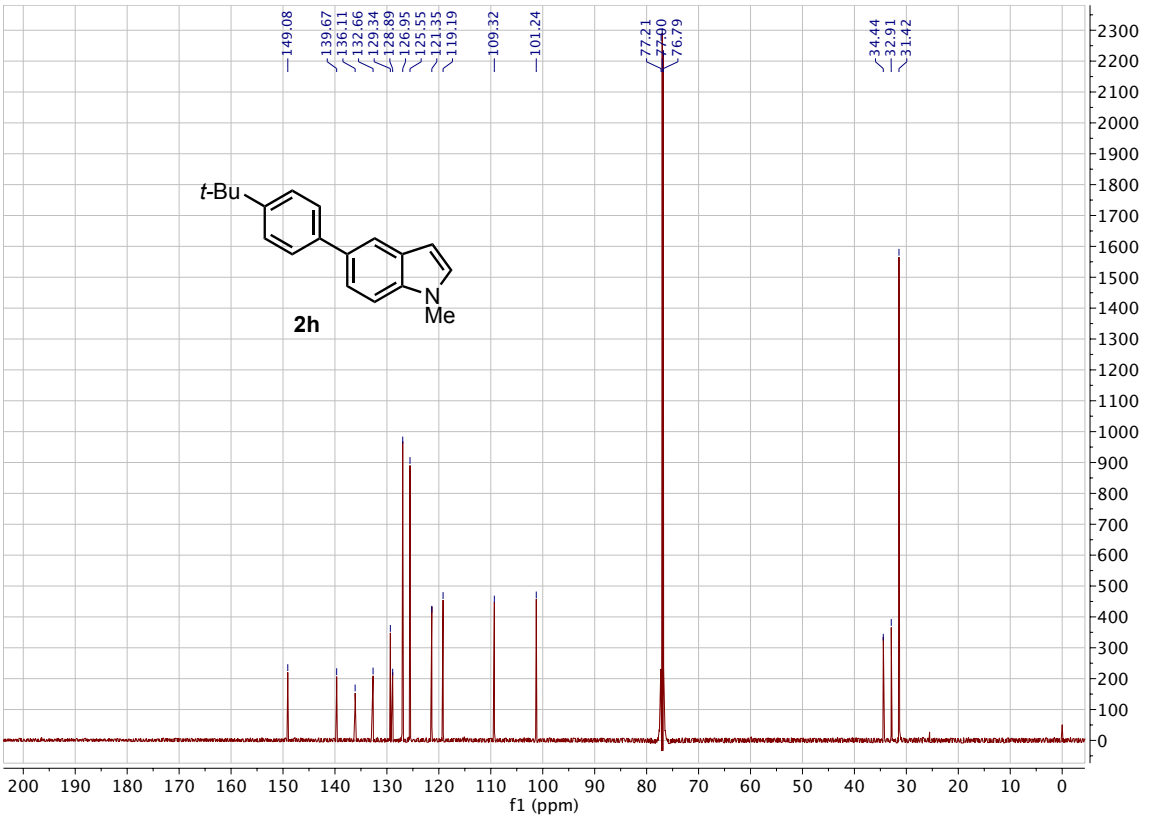

10.03
8.77
8.77
8.77
8.76
8.76
8.76
8.75
8.75
8.15
8.15
8.13
8.13
8.00
8.00
7.99
7.99
7.99
7.54
7.53
7.53
7.52
7.52
7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.49
7.48
7.44
7.43
7.42
7.41
7.41
7.39
7.38
7.26
5.91
5.90
5.89
5.88
5.87
5.86
5.85
5.84
4.40
4.39
4.38
3.38
3.37
2.41
2.40
2.39
2.38
1.99
1.98
1.97
1.97
1.95
1.94
O
N
H
N
BzO
1h
0.91
1.95
0.99
1.93
3.02
3.07
2.00
2.09
1.99
2.04
2.00
f1 (ppm)


169.44
166.71
148.36
138.65
136.47
136.44
134.54
134.01
132.99
130.42
129.64
128.47
128.07
127.52
122.76
121.71
116.60
77.37
77.16
76.95
64.38
36.98
28.59
24.20
O
N
H
N
BzO
1h
f1 (ppm)

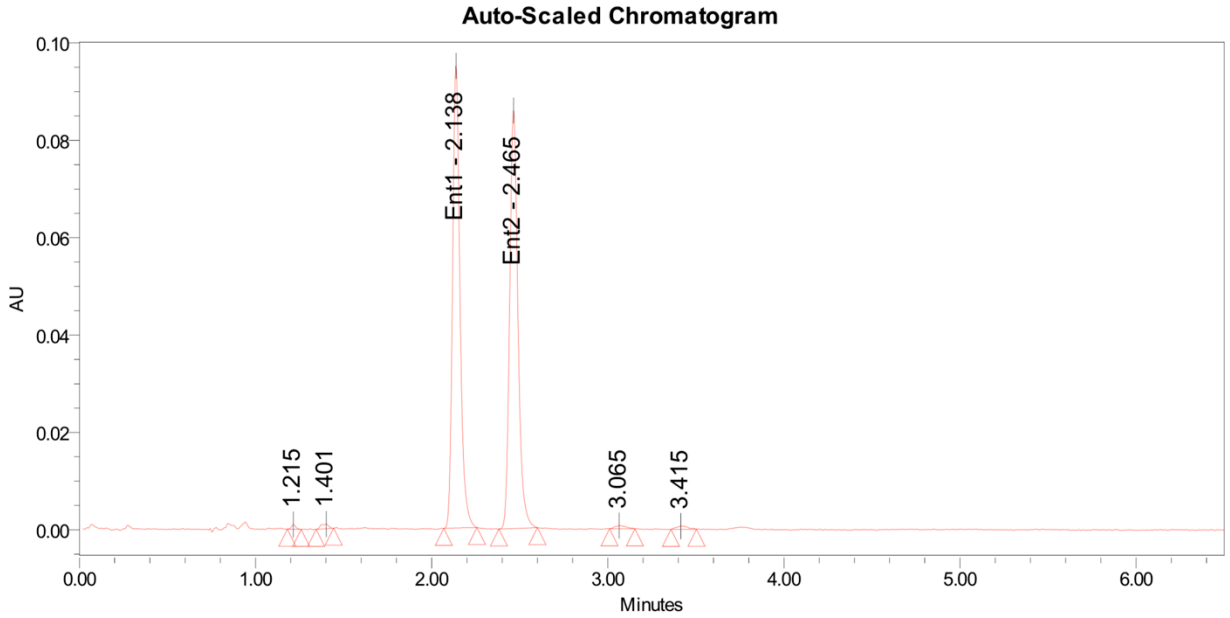

1j
f1 (ppm)

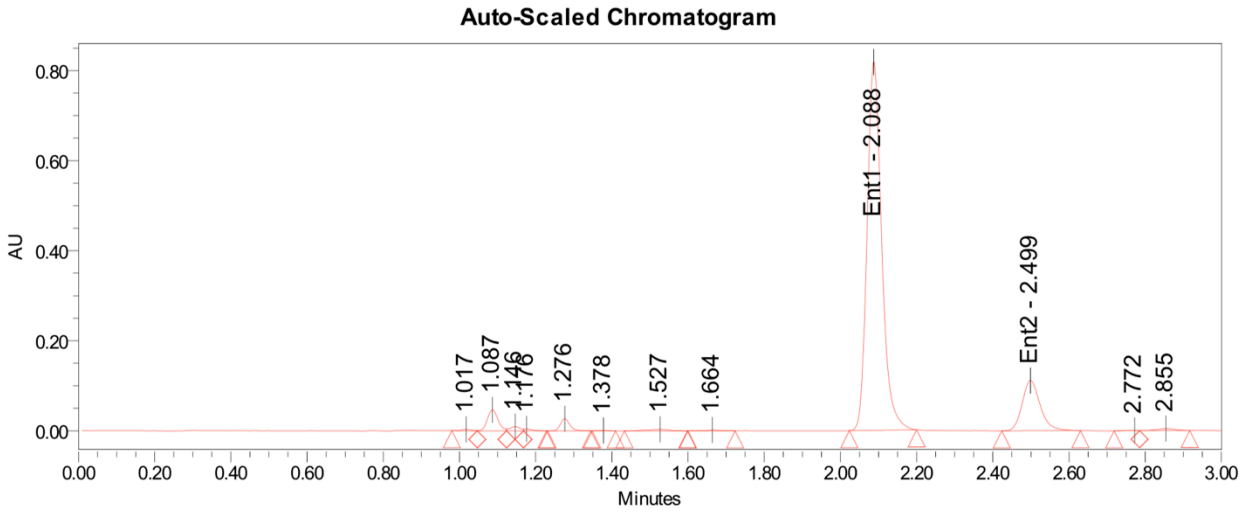

1j
f1 (ppm)


7.83
7.83
7.83
7.60
7.60
7.59
7.59
7.49
7.48
7.47
7.47
7.46
7.45
7.37
7.36
7.24
7.24
7.07
7.06
6.52
6.52
3.81
1.37
1.37
t-Bu
N
Me
2h
1.01
2.07
3.11
1.04
1.00
1.00
3.11
9.38
f1 (ppm)


149.08
139.67
136.11
132.66
129.34
128.89
126.95
125.55
121.35
119.19
109.32
101.24
77.21
77.00
76.79
34.44
32.91
31.42
t-Bu
N
Me
2h
f1 (ppm)

SFC Chromatograms of **4a**

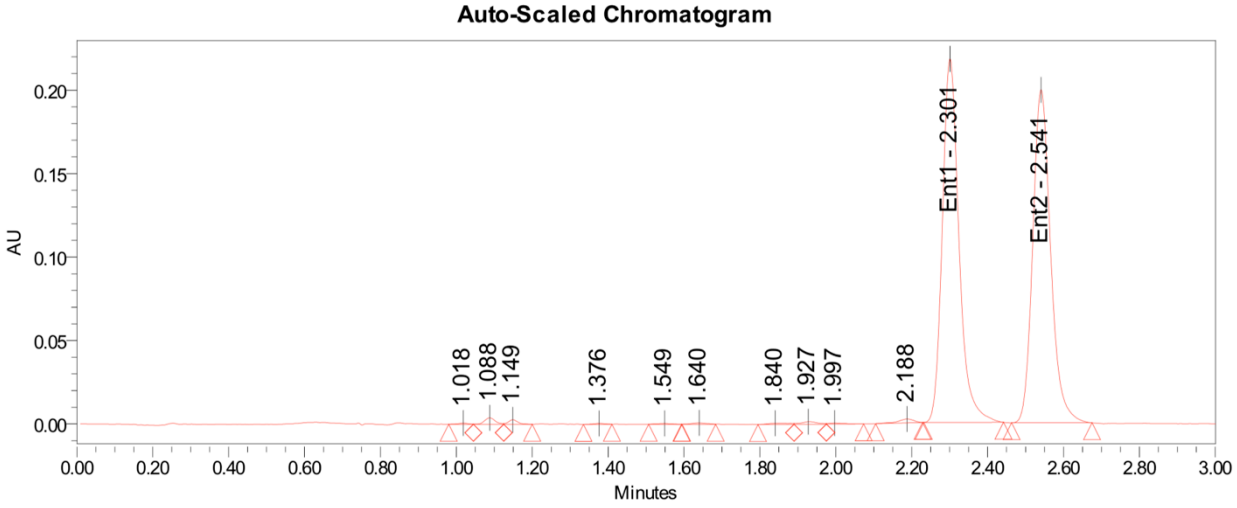


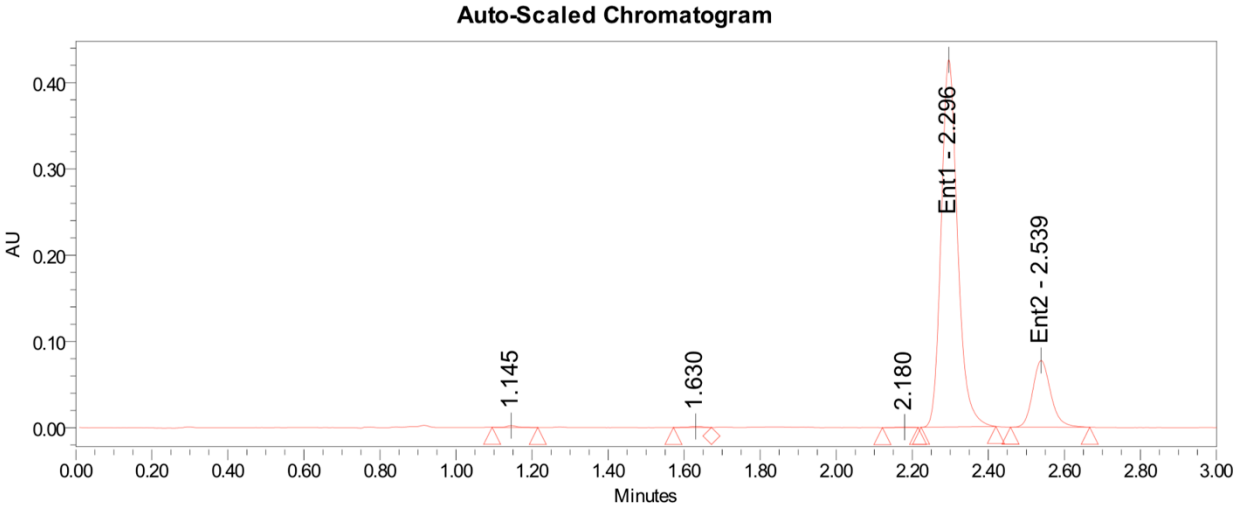


Area Summarized by Name

	SampleName	ent1	ent2	ee	Ent1	Ent2
1	ZL-5-member	49.83	50.17	-0.35	277875	279800
2	LZ-57-1	85.58	14.42	71.16	2173472	366285

SFC Chromatograms of **4b**

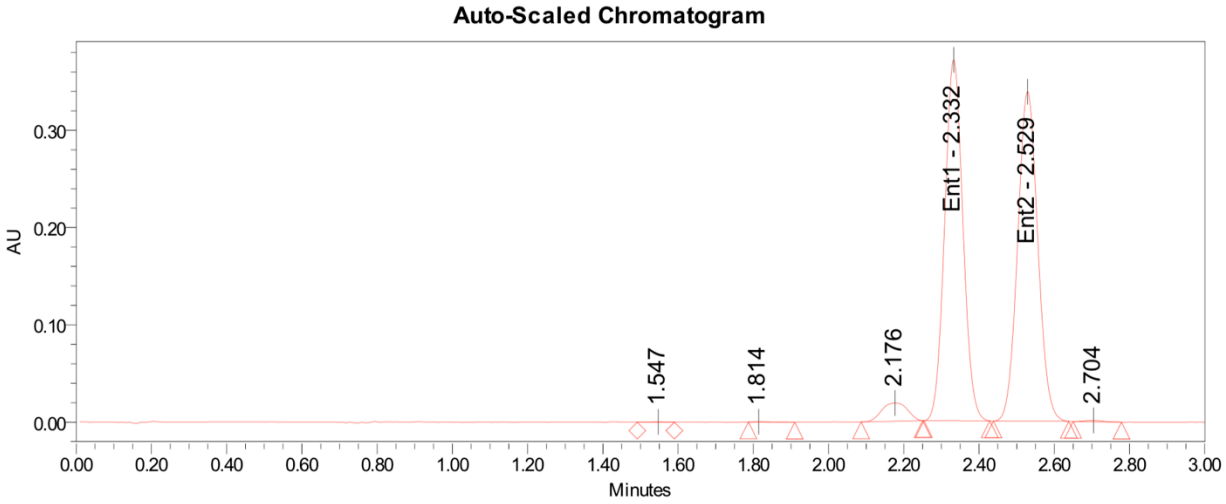


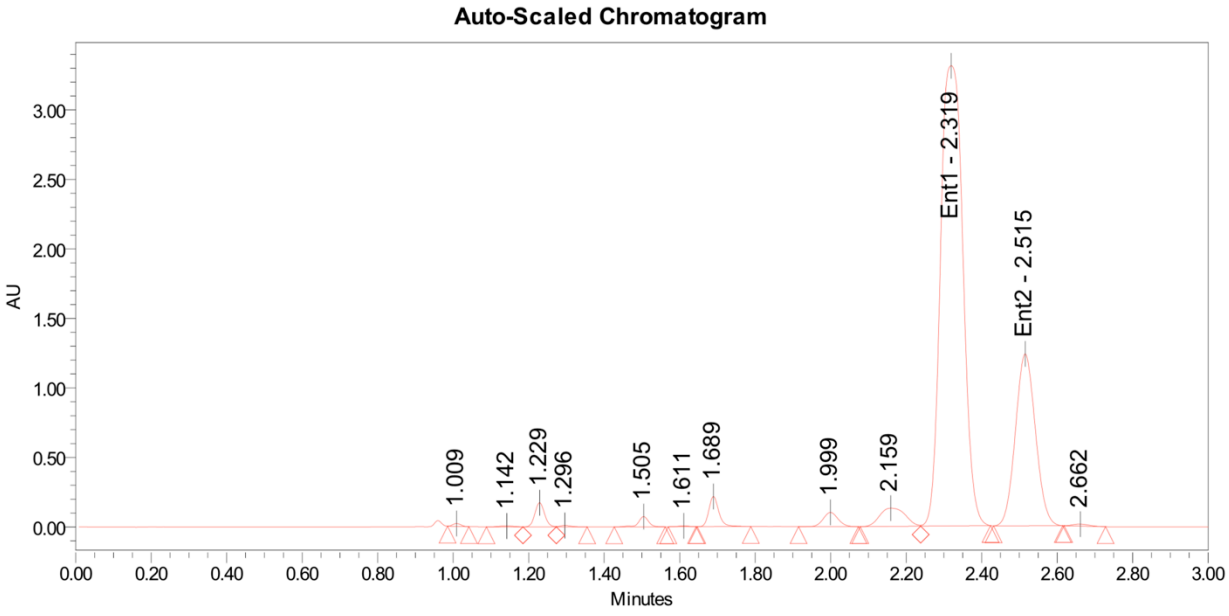


Area Summarized by Name

	SampleName	ent1	ent2	ee	Ent1	Ent2
1	Rac-B	50.38	49.62	0.75	663517	653579
2	LZ-57-2	83.40	16.60	66.81	1276993	254111

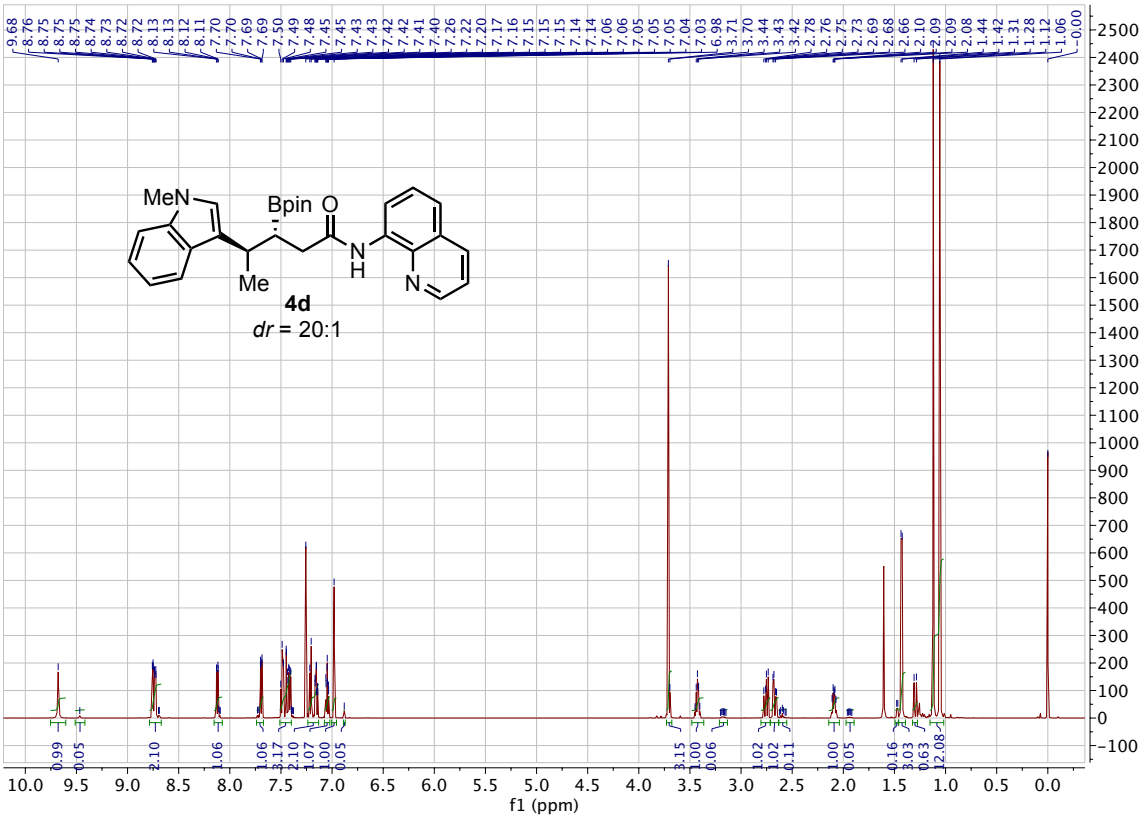
SFC Chromatograms of **4c**

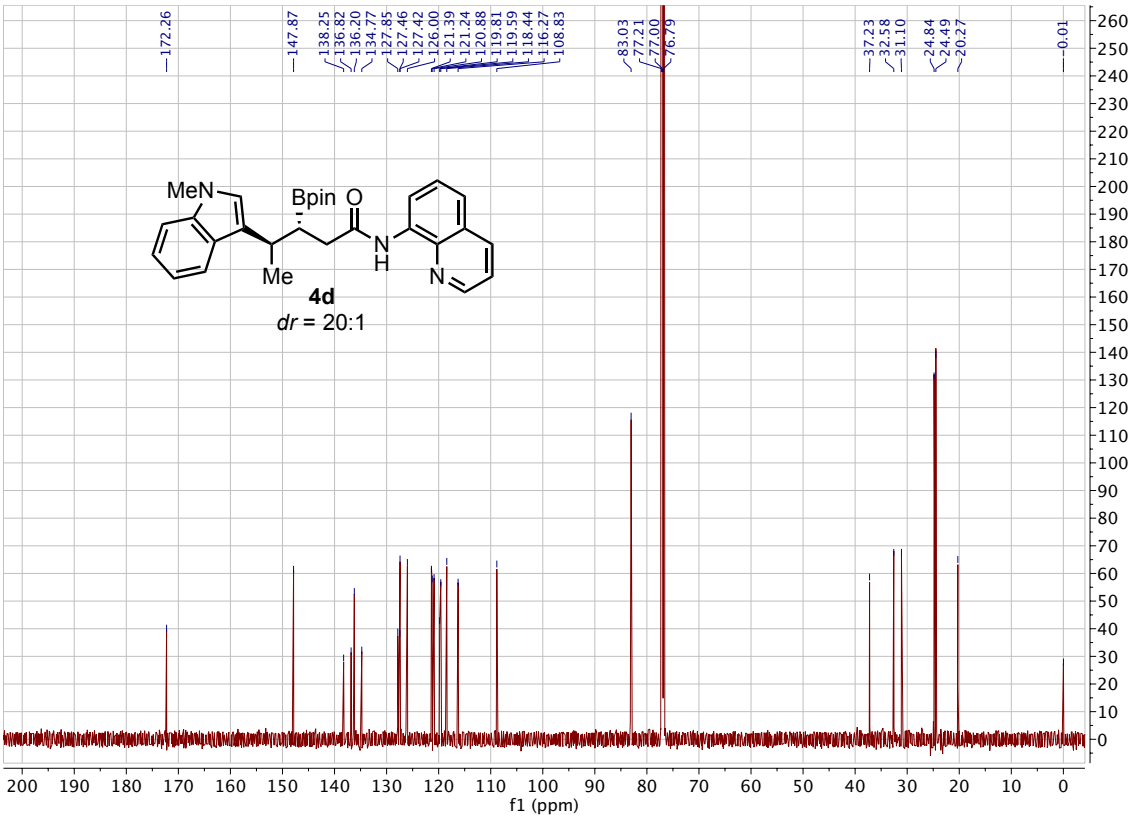




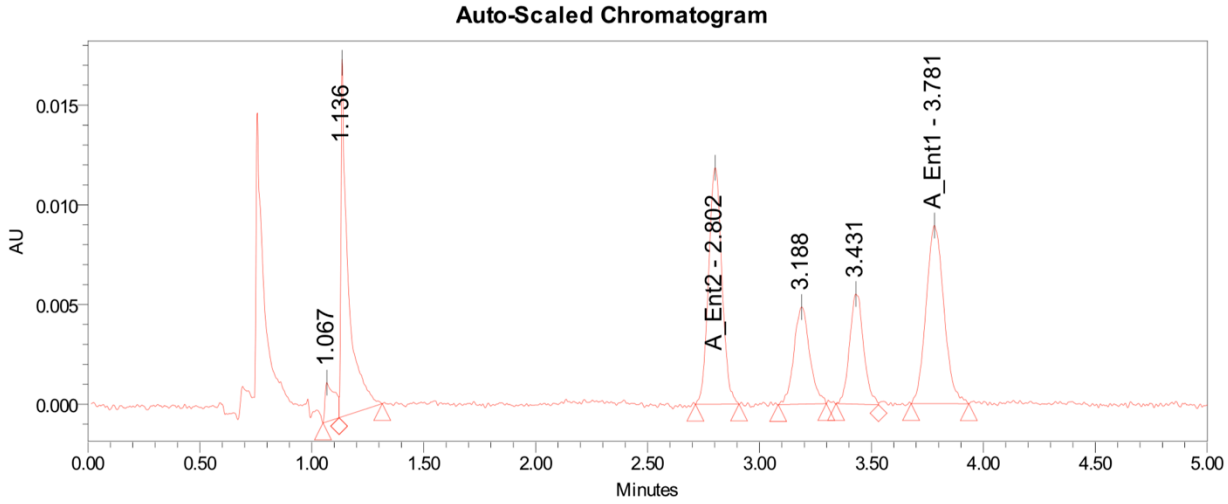
Area Summarized by Name

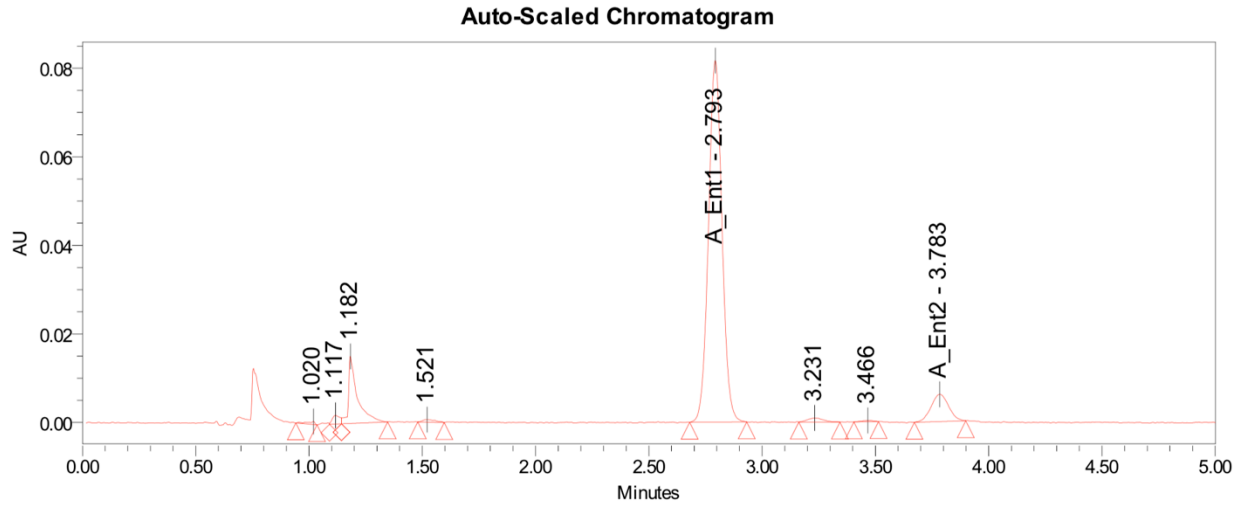
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-70-3-rac	49.81	50.19	-0.38	1250546	1260159
2	LZ-42-2	74.97	25.03	49.94	13664993	4562767


MeN
Bpin
O
N
H
Me
N
4d
dr = 20:1
f1 (ppm)


MeN
Bpin
O
N
H
Me
N
4d
dr = 20:1
f1 (ppm)

SFC Chromatograms of **4d**

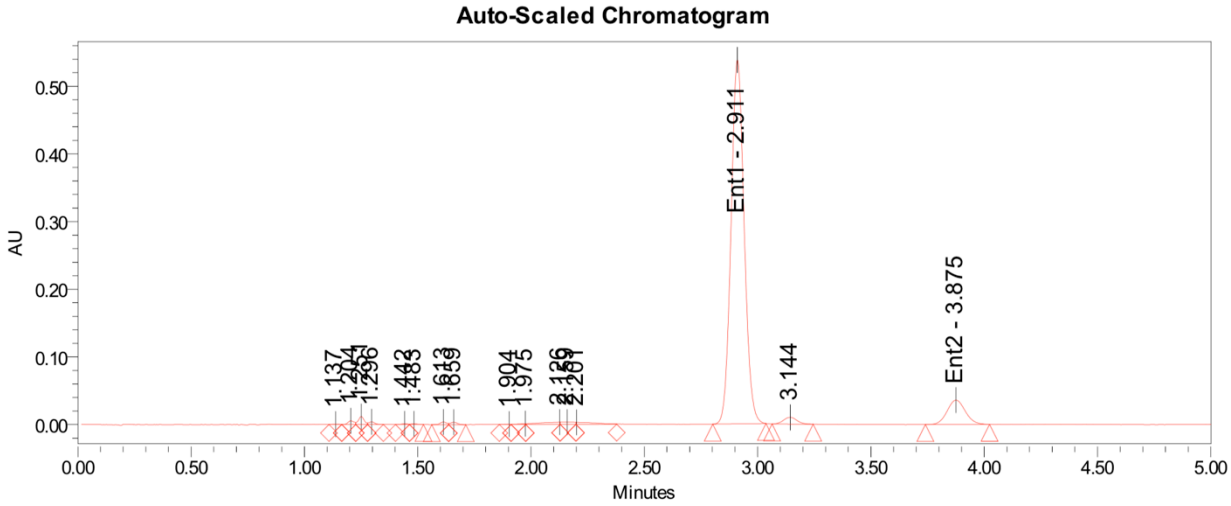




Area Summarized by Name

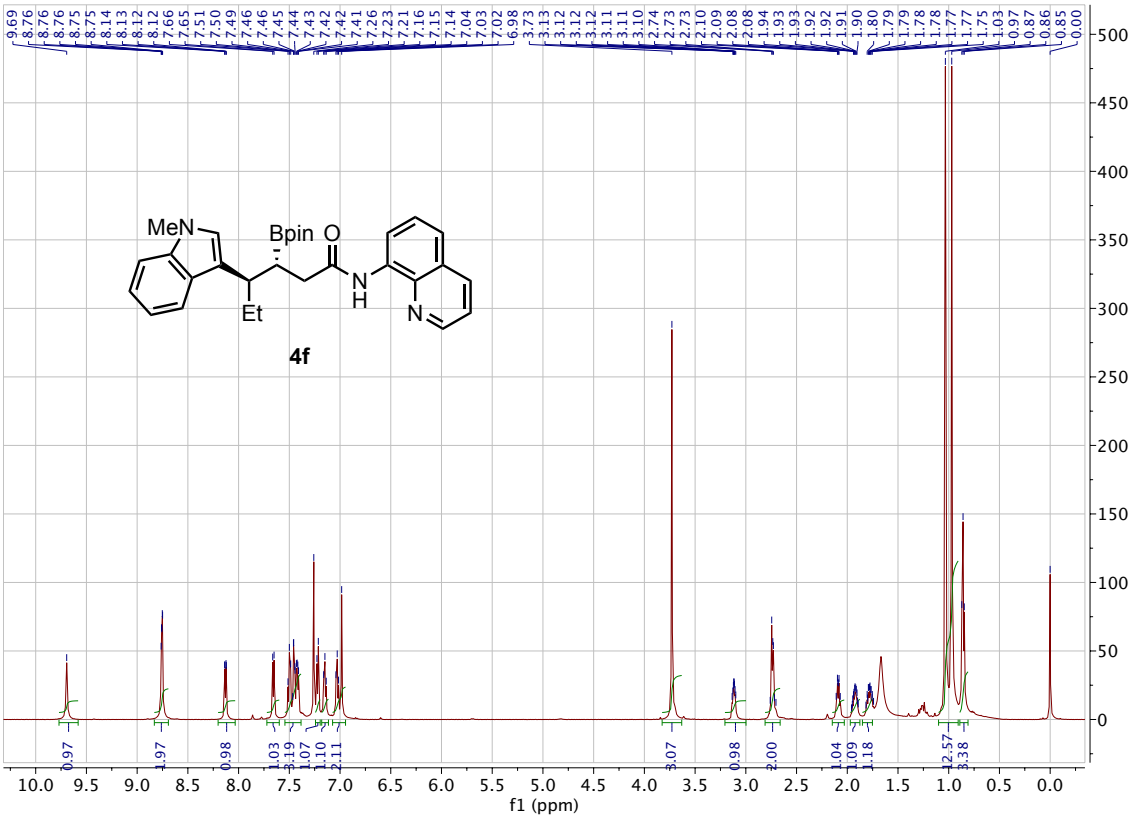
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	ENG0177A_SFC	50.35	49.65	0.70	49043	49731
2	LZ-22-4	91.05	8.95	82.10	338533	33271

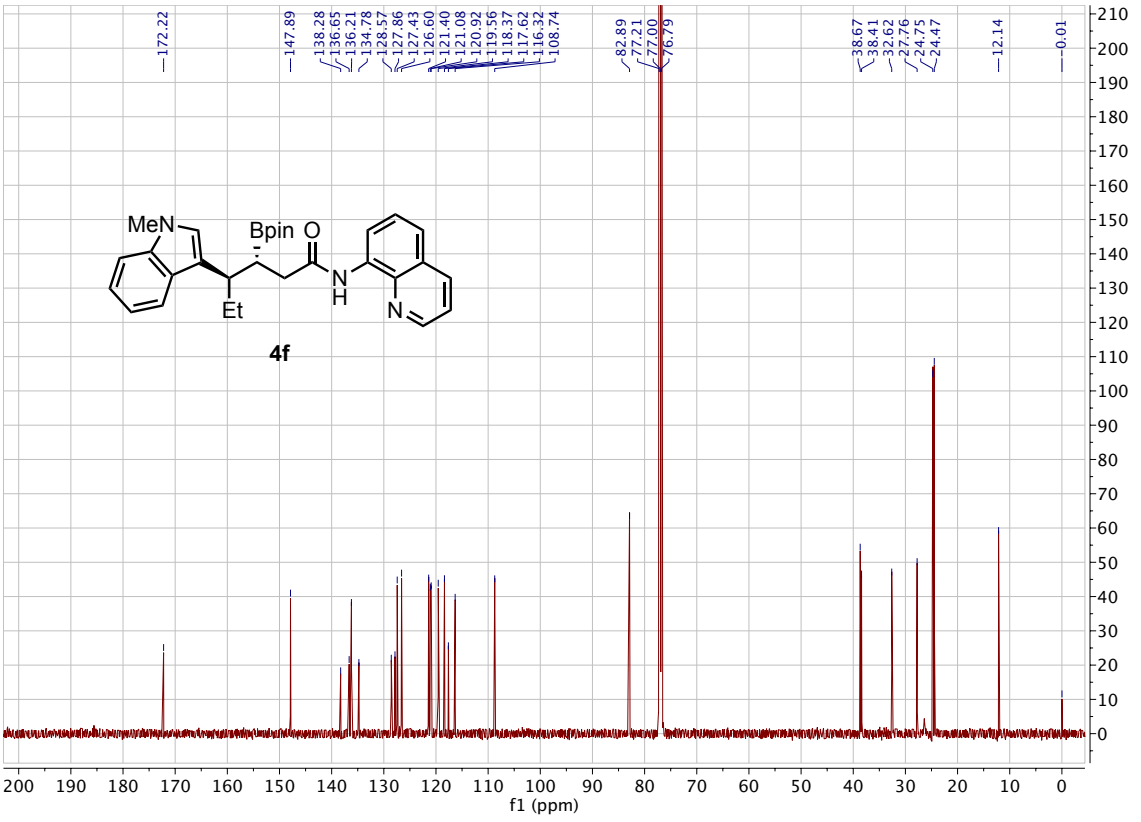
SFC Chromatograms of **4e**



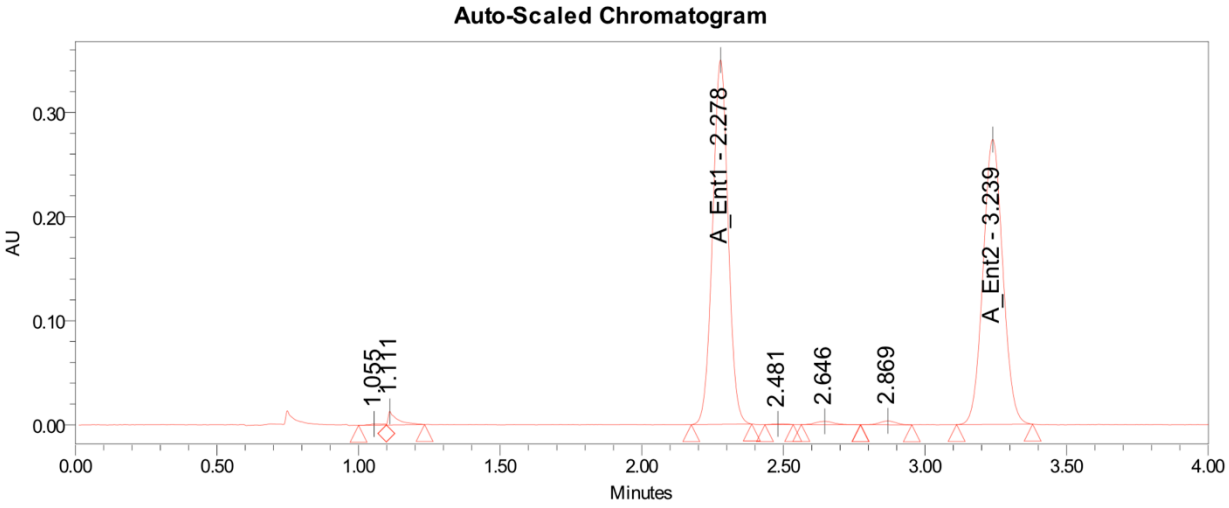
Area Summarized by Name

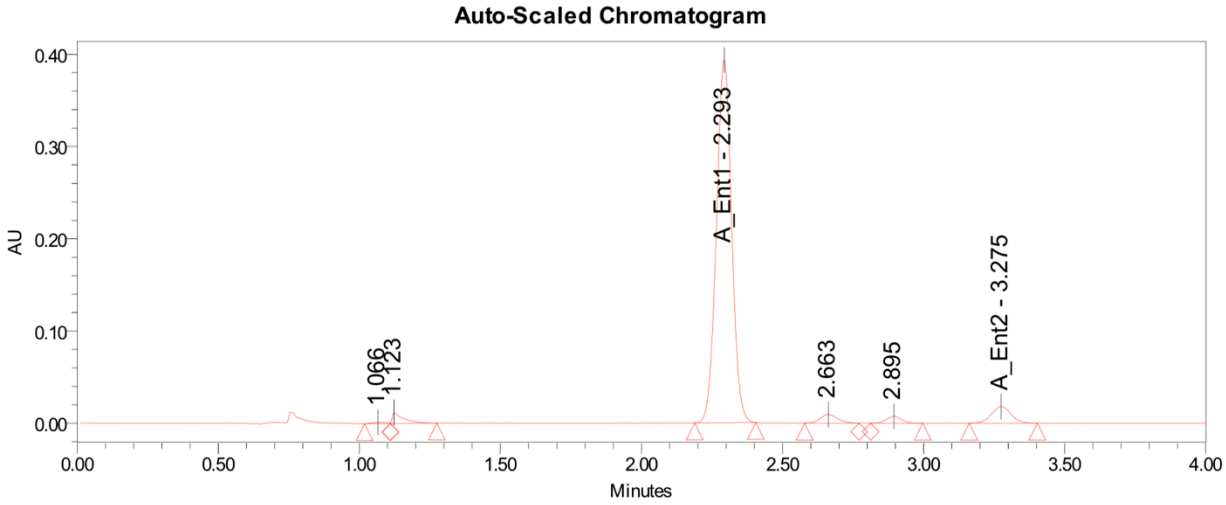
SampleName	ent1	ent2	ee	Ent1	Ent2
LZ-60-1	91.49	8.51	82.98	2163391	201223


MeN
Bpin
O
N
H
Et
N
4f
f1 (ppm)


MeN
Bpin
O
N
H
Et
N
4f
f1 (ppm)

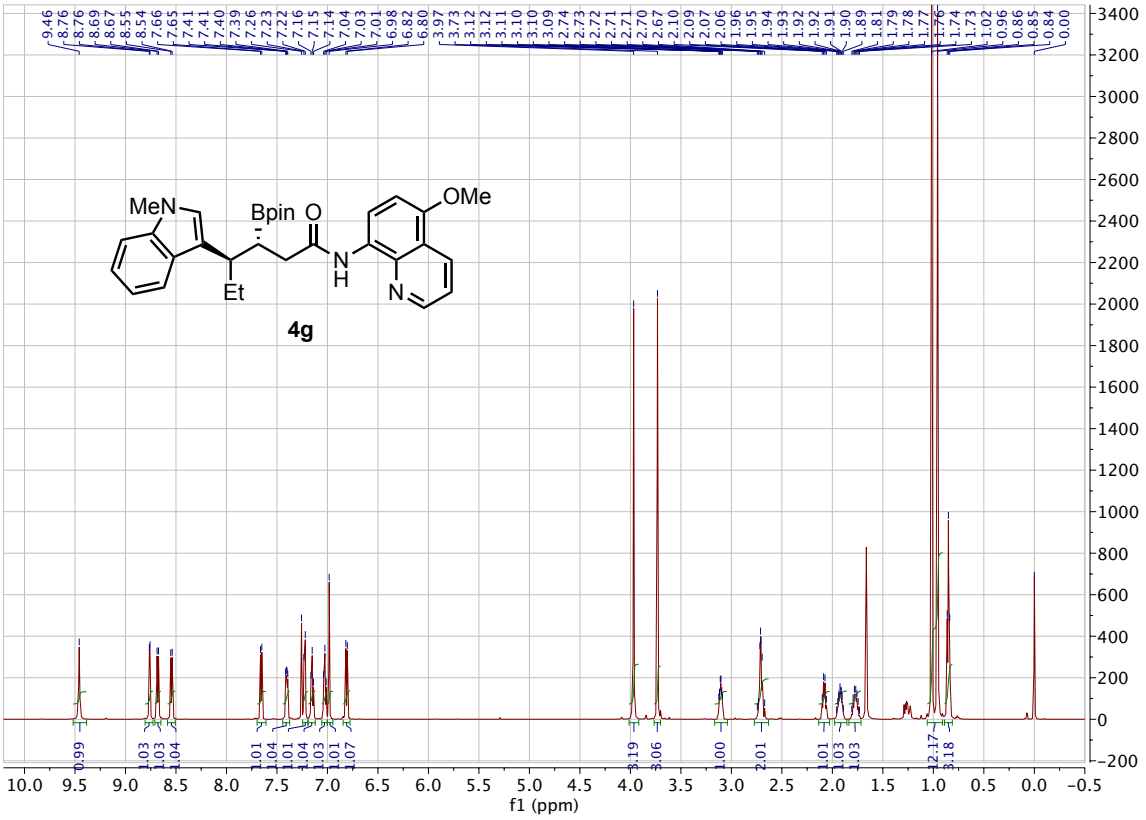
SFC Chromatograms of **4f**

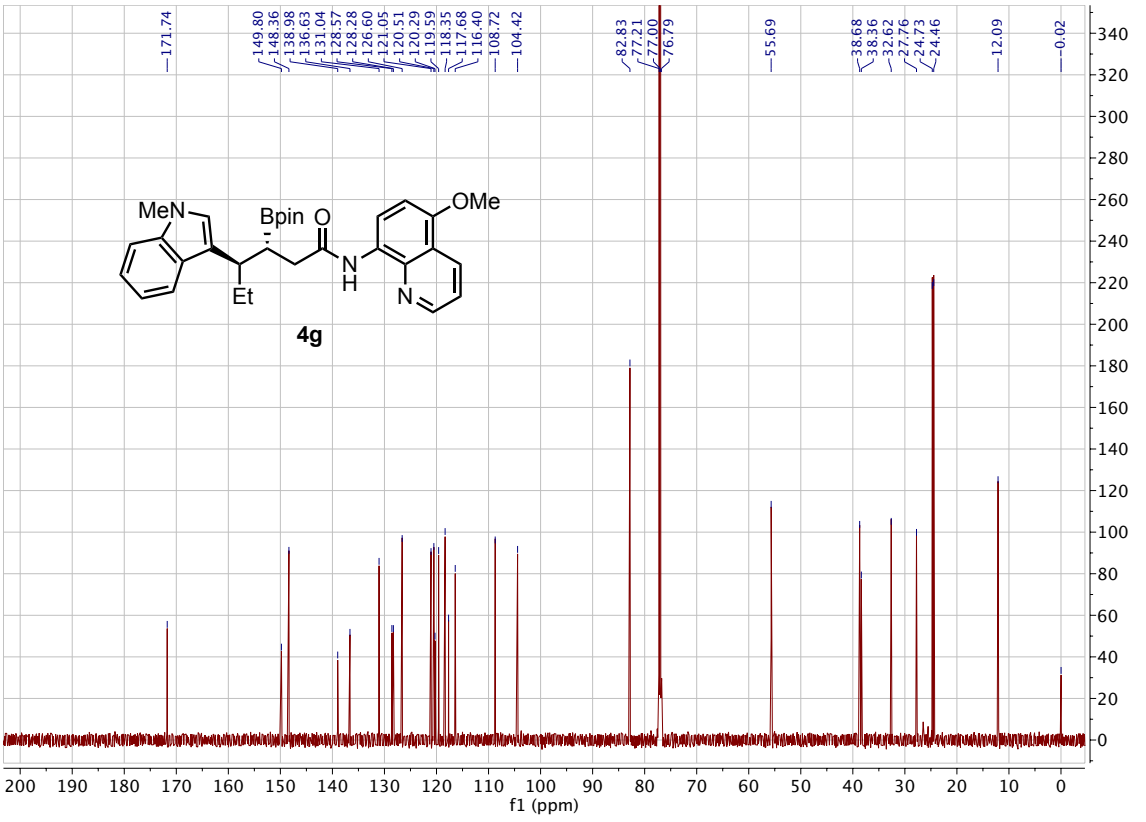




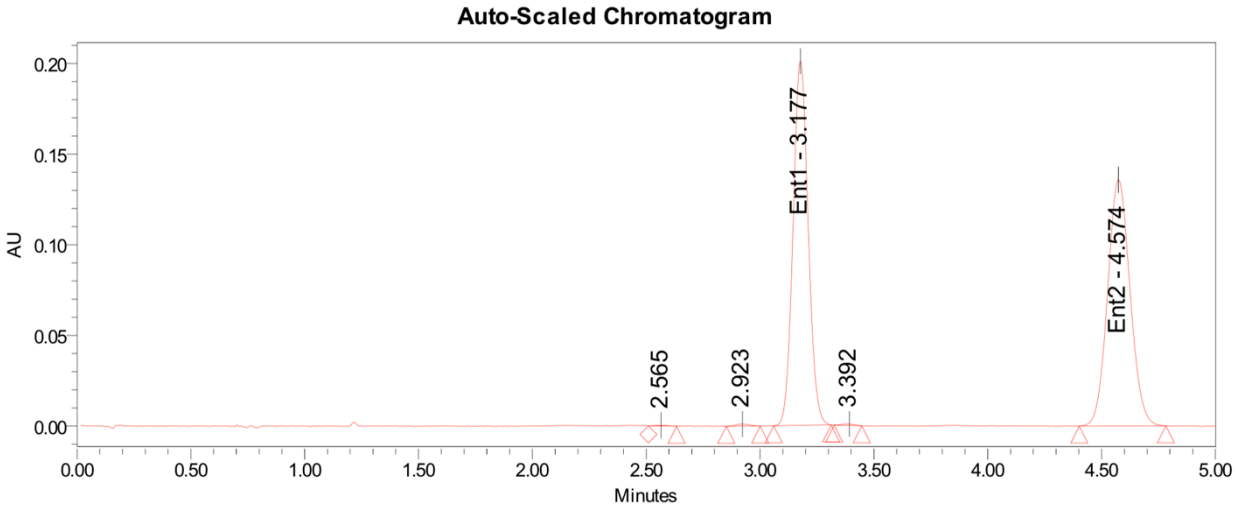
Area Summarized by Name

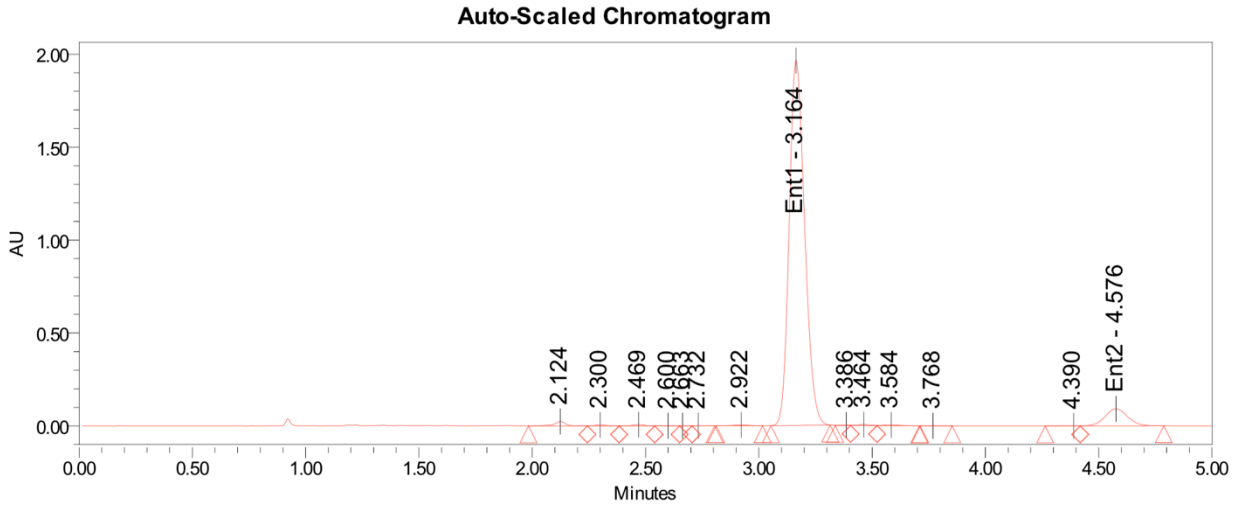
	SampleName	ent1	ent2	ee	A_Ent1	A_Ent2
1	rac	50.06	49.94	0.11	1331485	1328491
2	LZ-39-1	94.43	5.57	88.86	1475223	86989


MeN
Bpin
O
OMe
N
H
Et
N
4g
f1 (ppm)


MeN
Bpin
O
OMe
N
H
Et
N
4g
f1 (ppm)

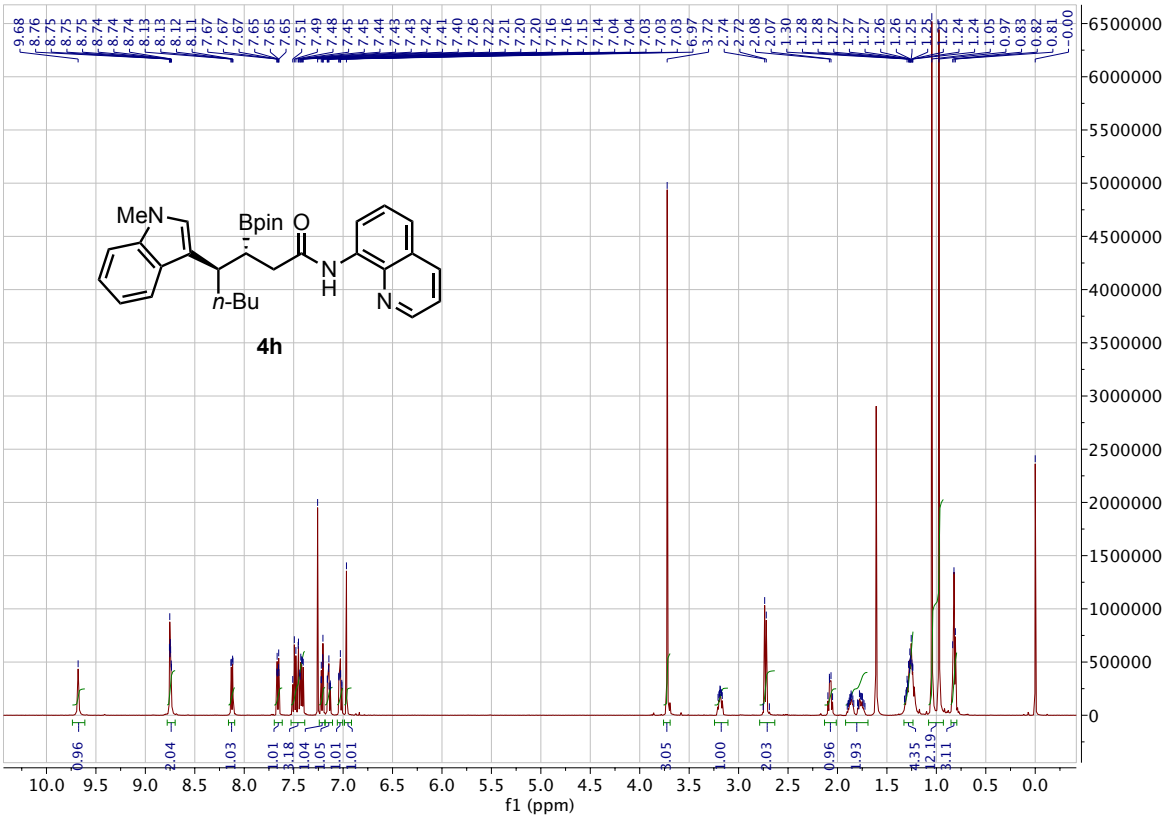
SFC Chromatograms of **4g**

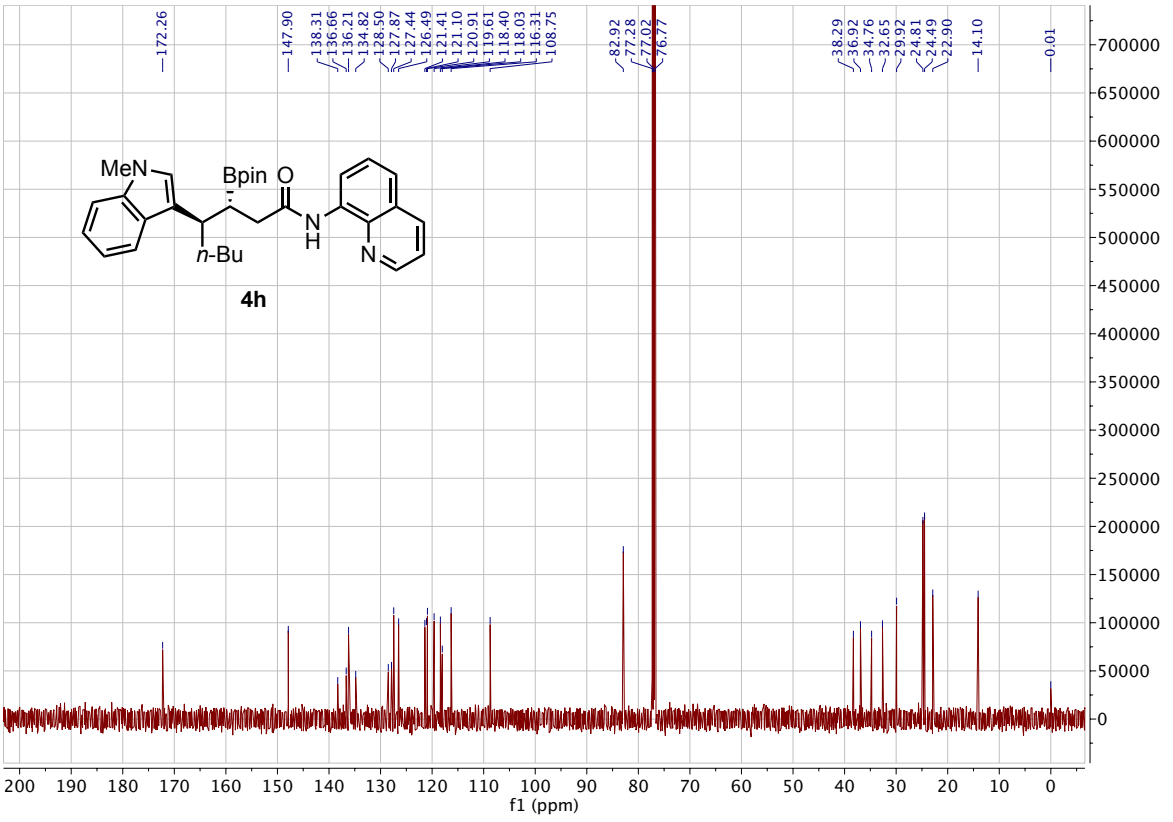




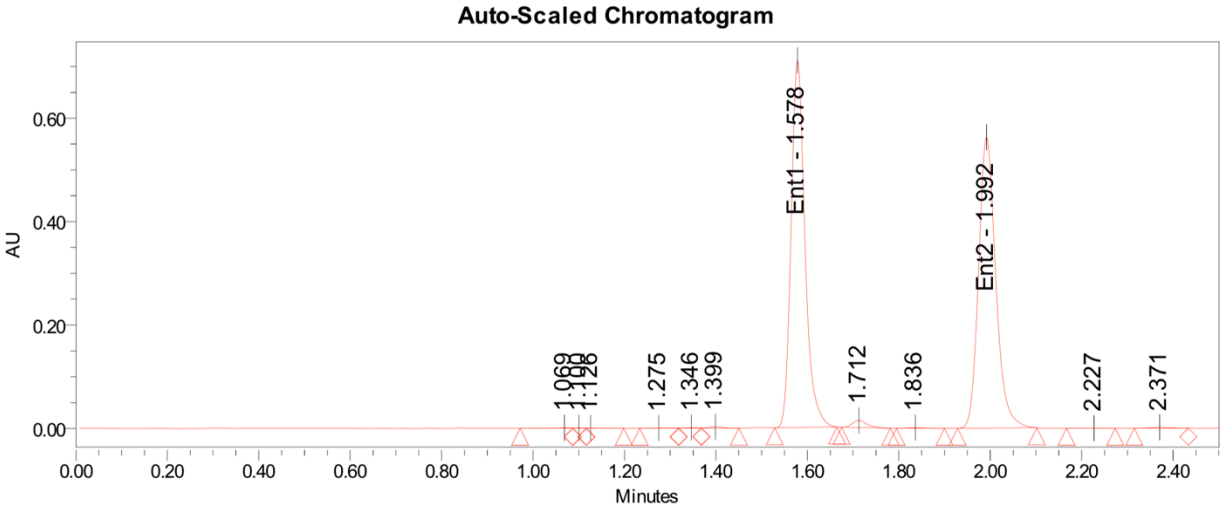
Area Summarized by Name

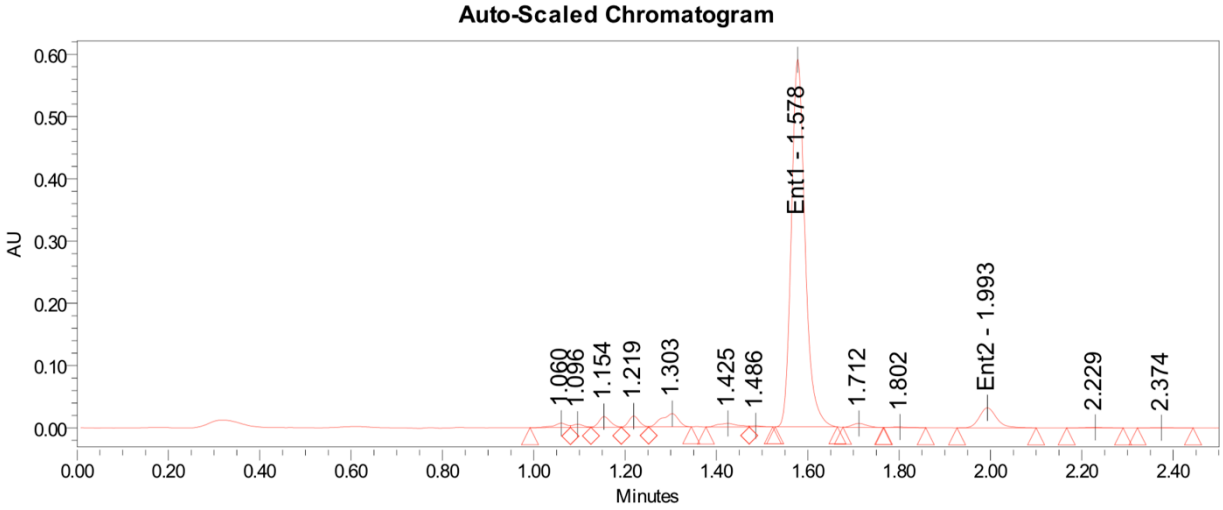
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-43-2-rac	49.93	50.07	-0.14	927764	930336
2	LZ-43-2	93.56	6.44	87.13	9289195	639042


MeN
Bpin
O
N
H
n-Bu
N
4h
f1 (ppm)


MeN
Bpin
O
N
H
n-Bu
N
4h
f1 (ppm)

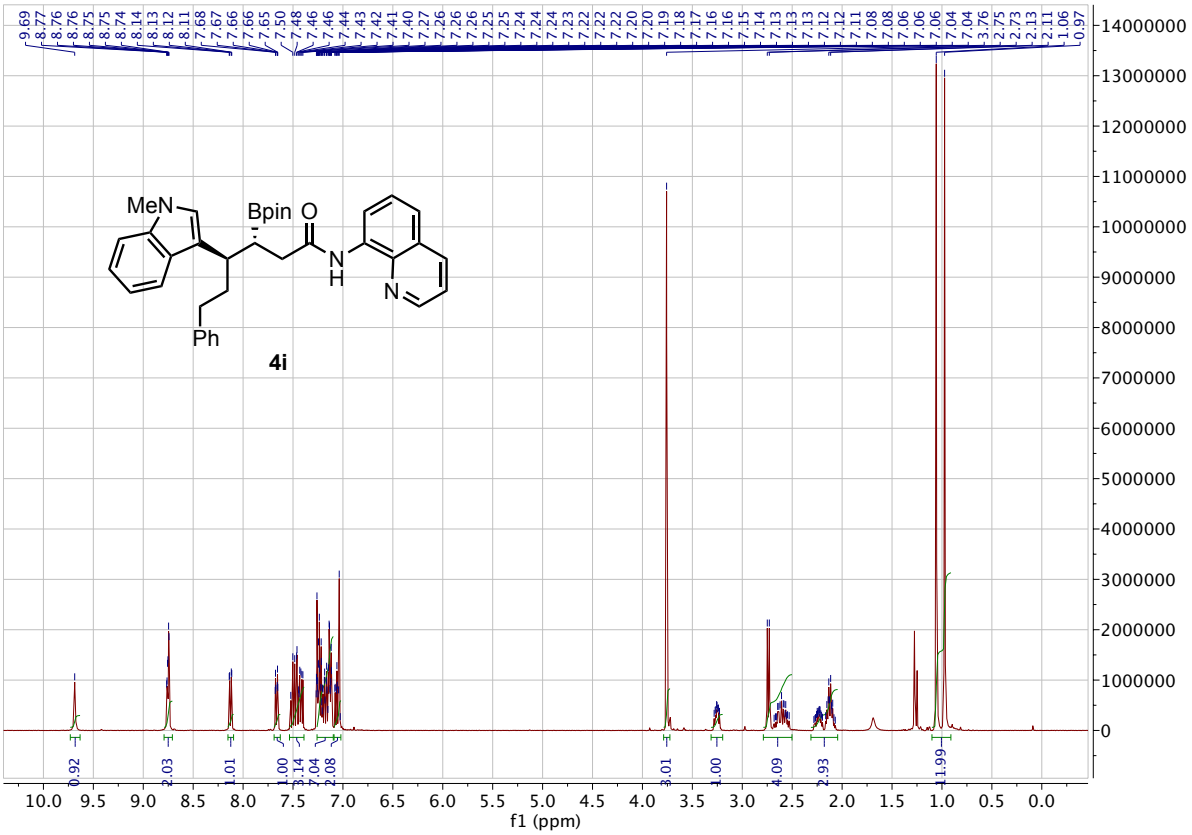
SFC Chromatograms of **4h**

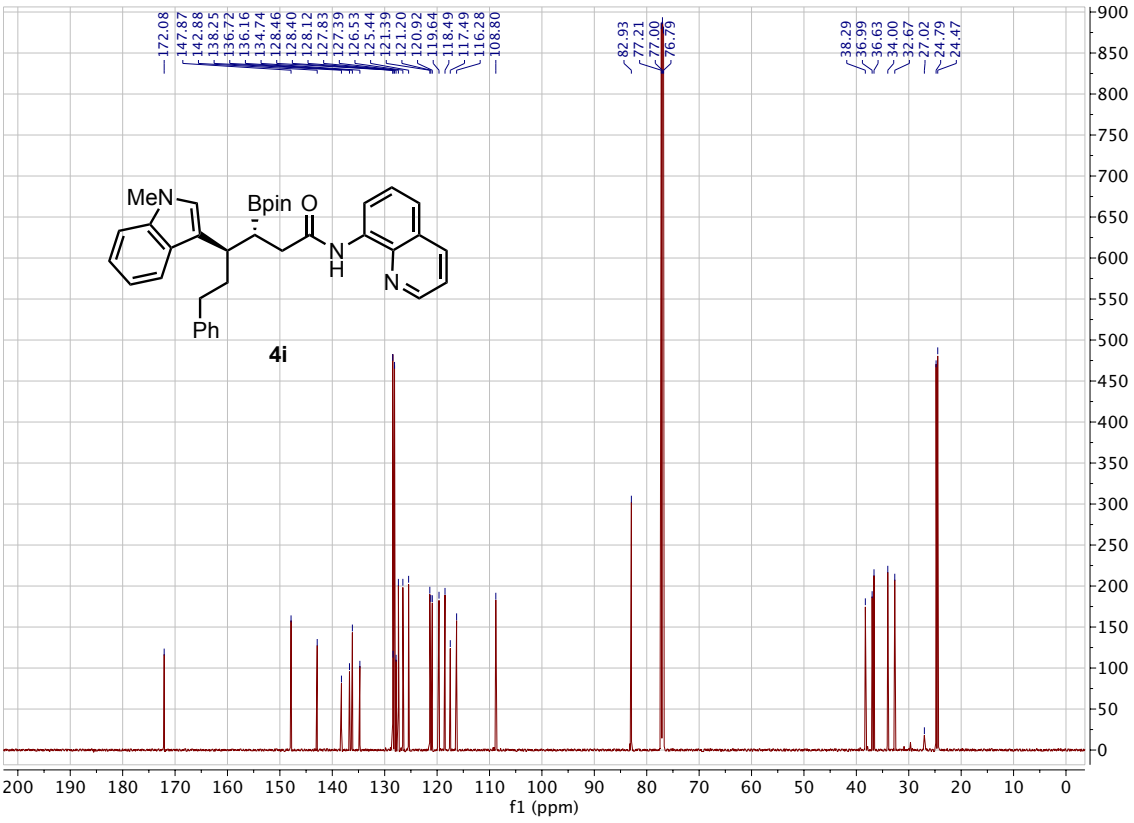




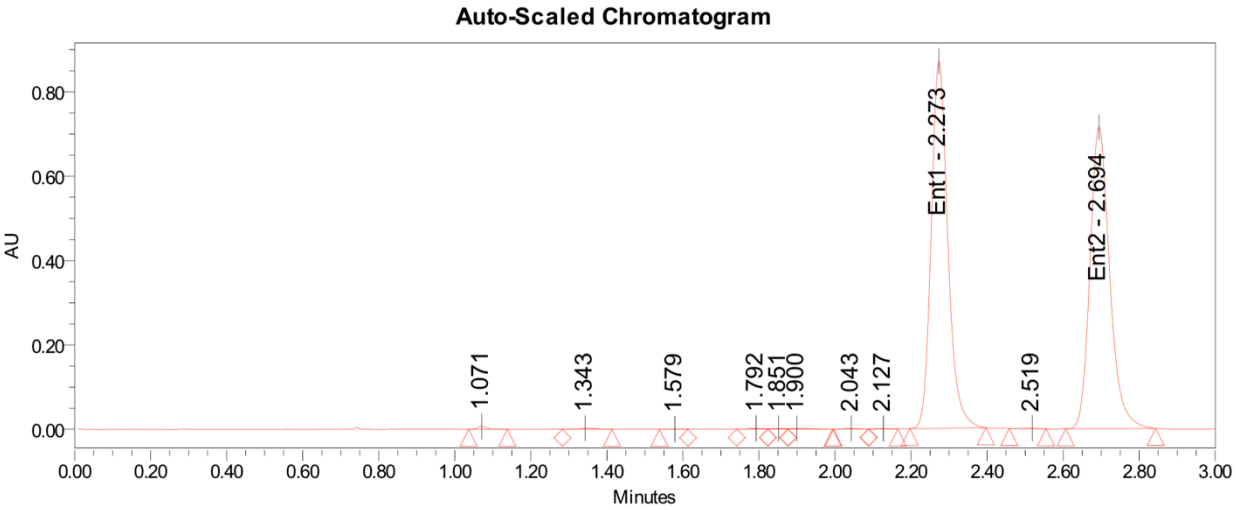
Area Summarized by Name

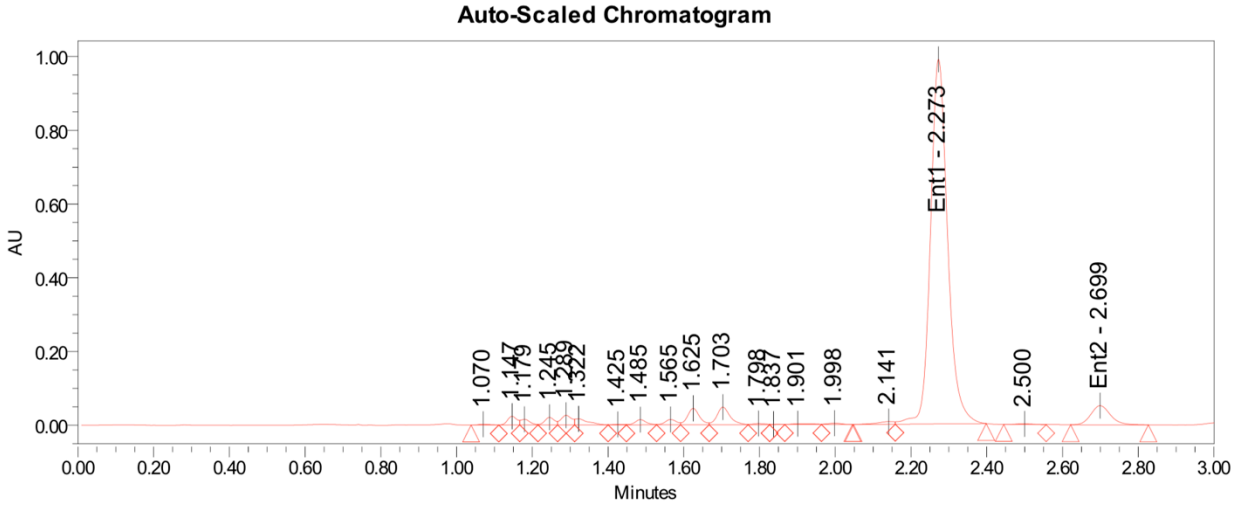
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	Bu-rac	50.48	49.52	0.96	1491500	1463005
1	57-3	93.62	6.38	87.25	1230857	83823


MeN
Bpin
O
N
H
N
Ph
4i
f1 (ppm)


MeN
Bpin
O
N
H
N
Ph
4i
f1 (ppm)

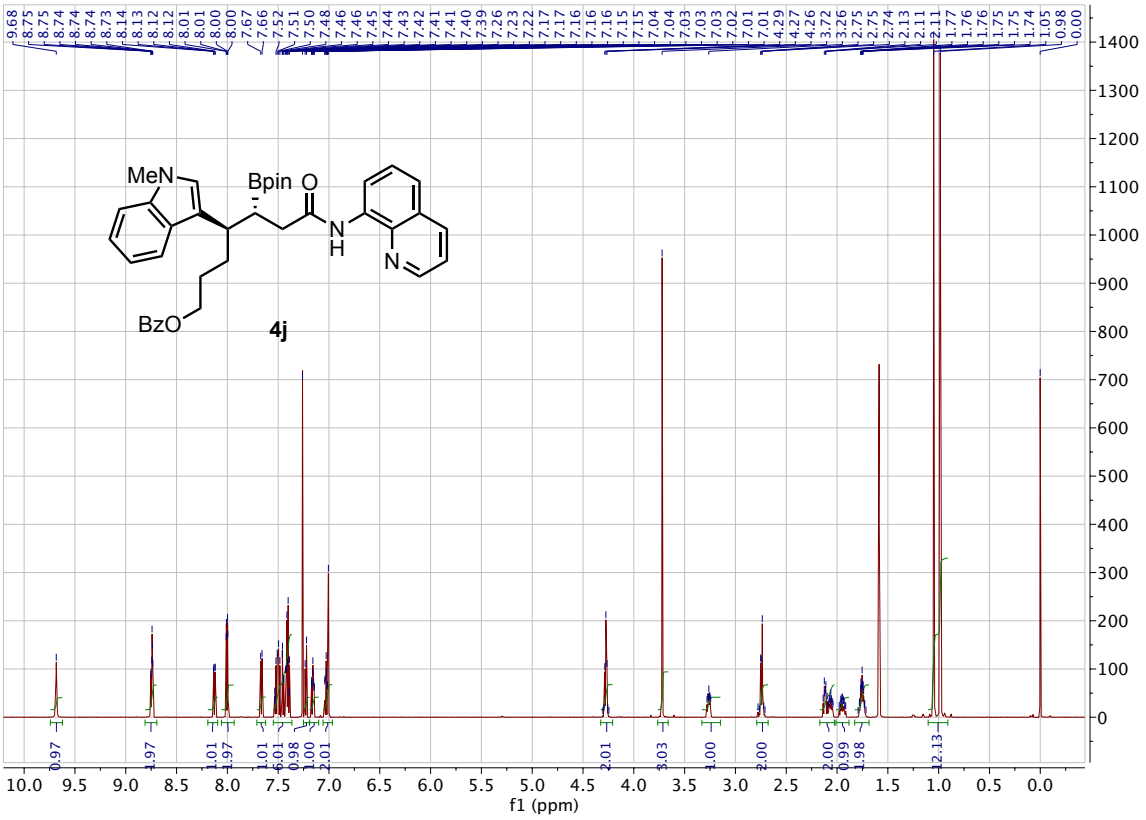
SFC Chromatograms of **4i**

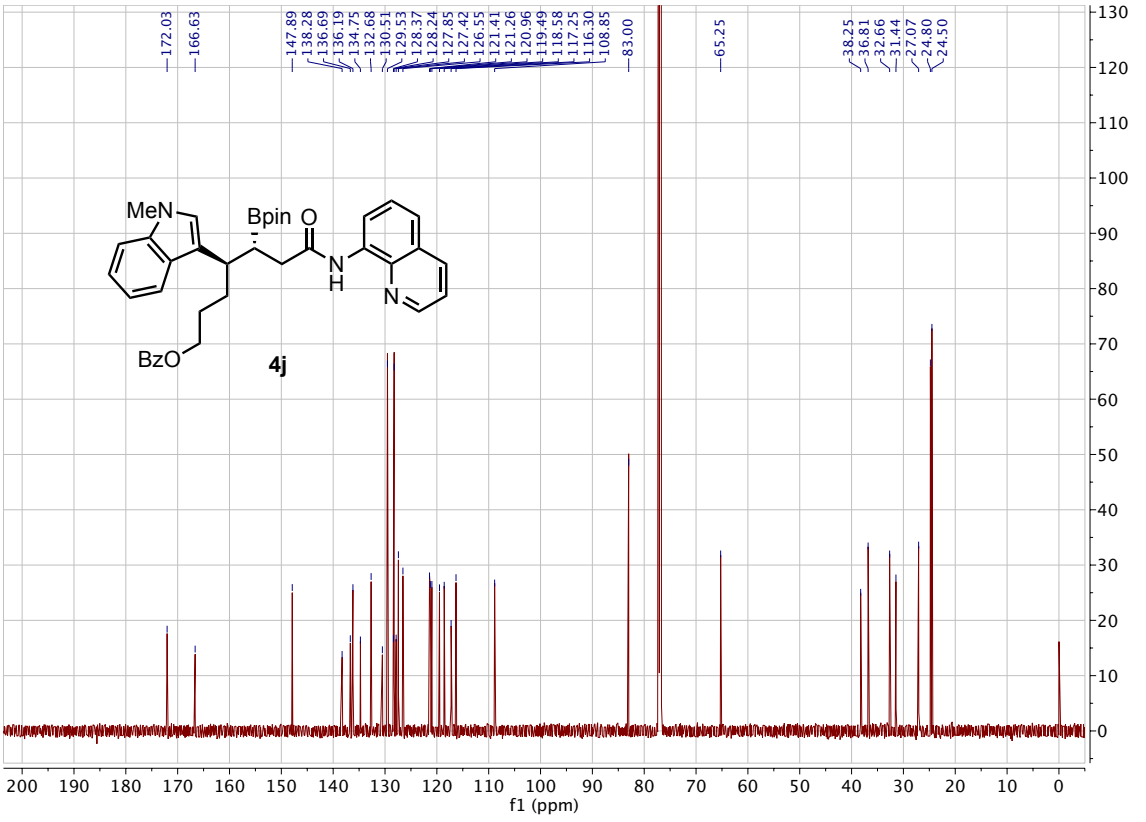




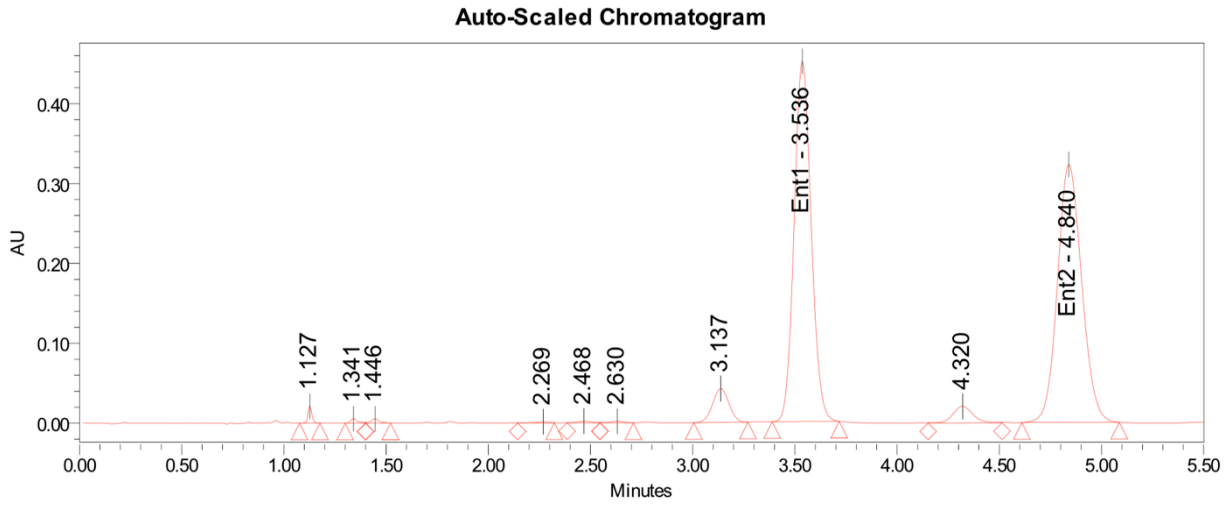
Area Summarized by Name

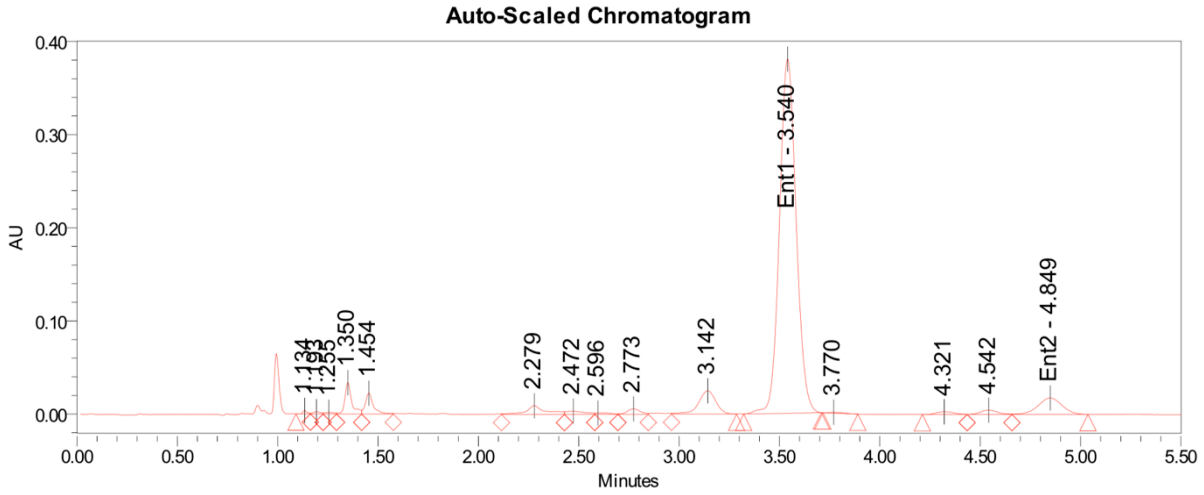
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-67-3-rac	50.69	49.31	1.38	2643173	2571036
2	LZ-67-2	94.34	5.66	88.69	3113494	186680


MeN
Bpin
O
N
H
N
BzO
4j
f1 (ppm)


MeN
Bpin
O
N
H
N
BzO
4j
f1 (ppm)

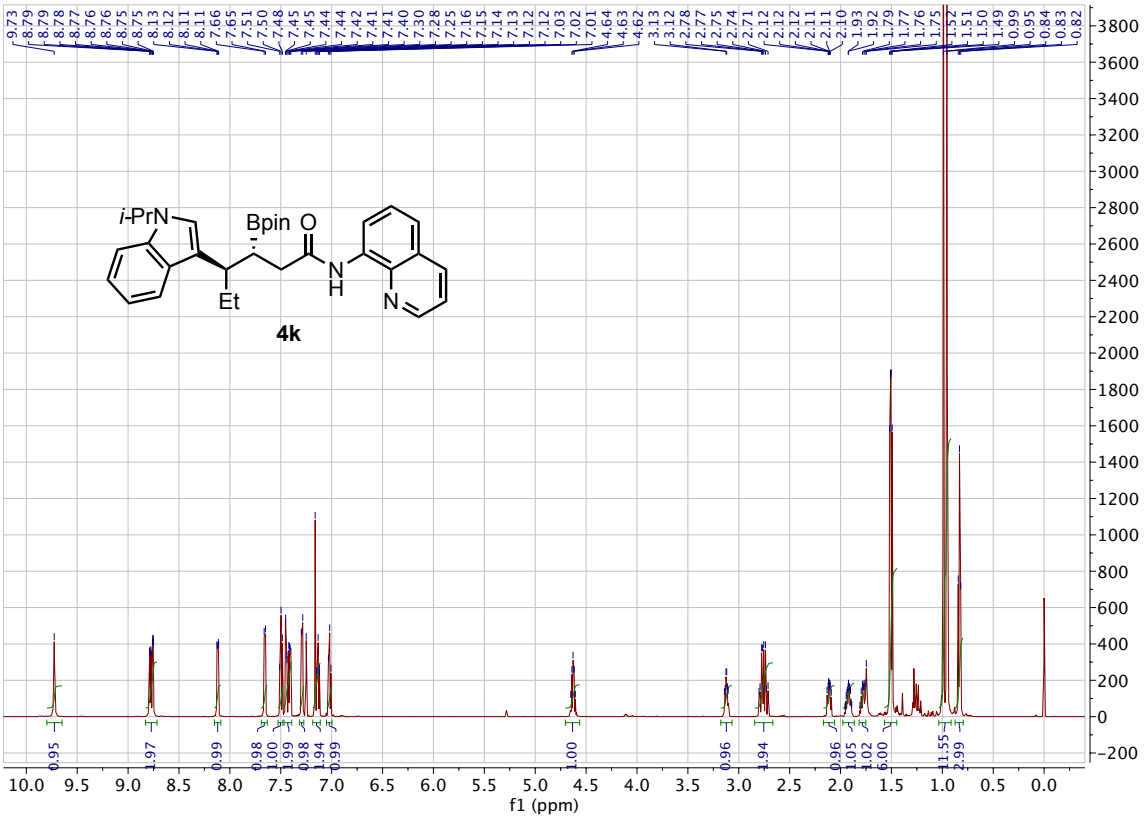
SFC Chromatograms of **4j**

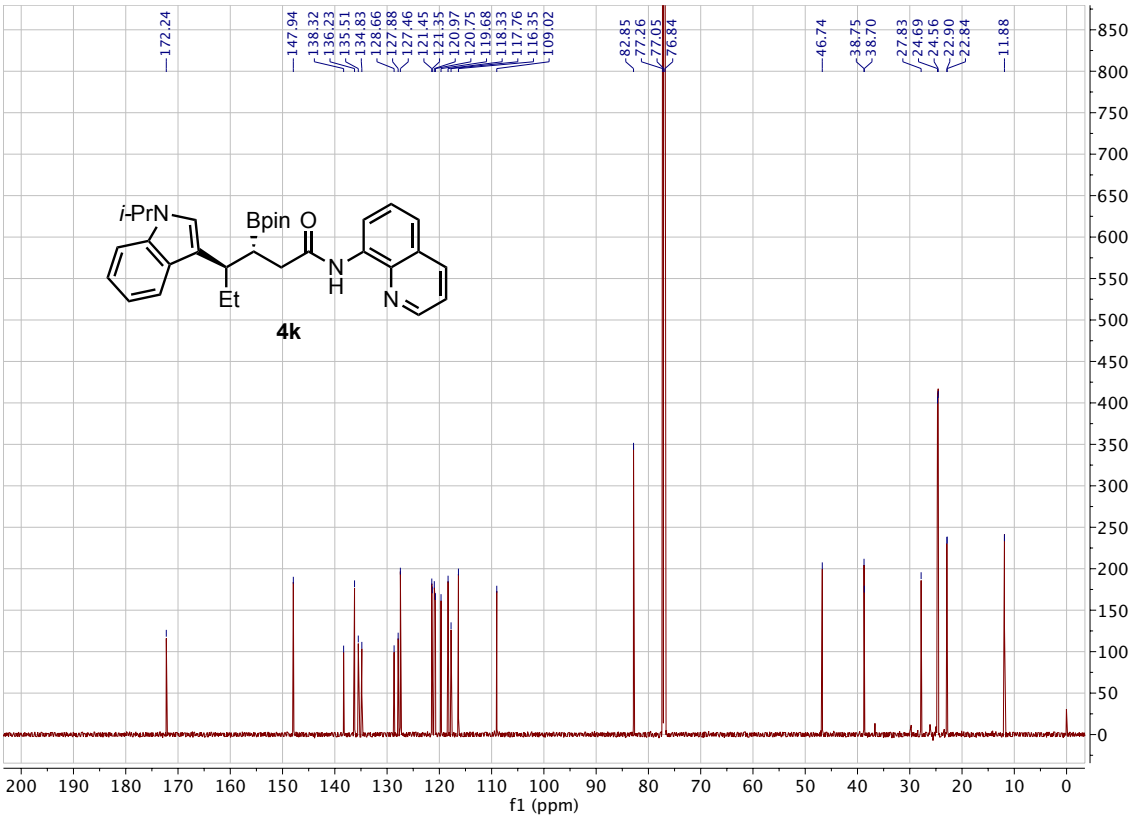




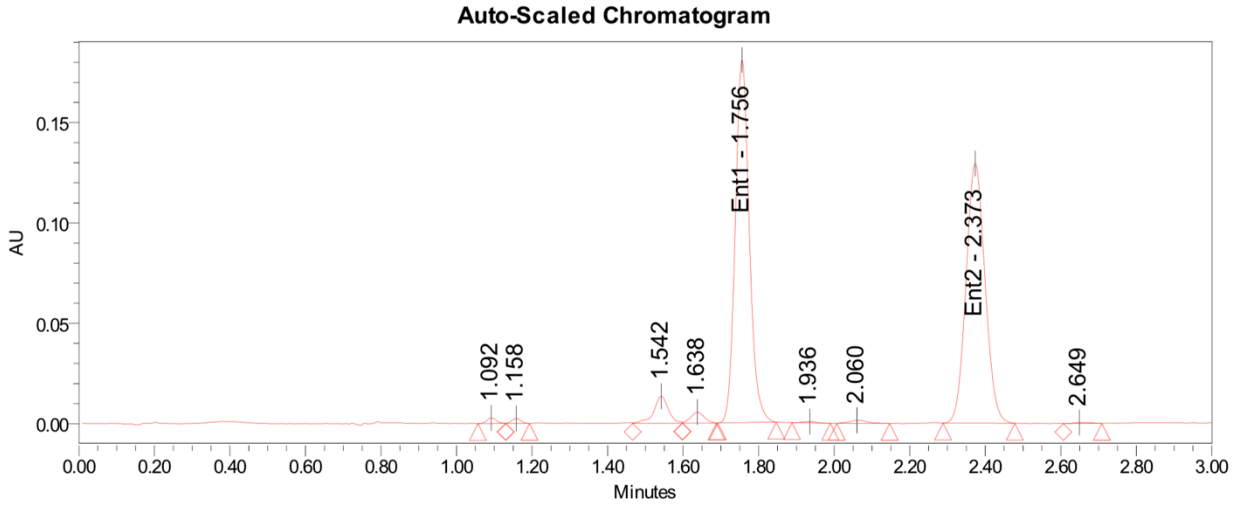
Area Summarized by Name

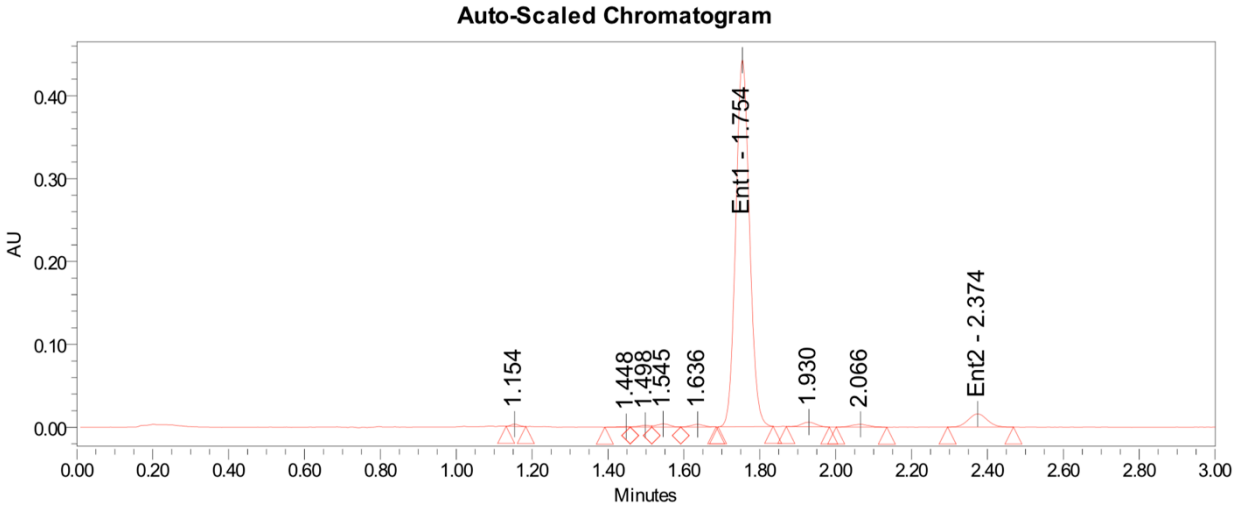
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-78-1-rac	49.54	50.46	-0.92	2612581	2661317
2	LZ-78-2	93.73	6.27	87.47	2196930	146845


i-PrN
Bpin
O
N
H
Et
N
4k
f1 (ppm)


i-PrN
Bpin
O
N
H
Et
N
4k
f1 (ppm)

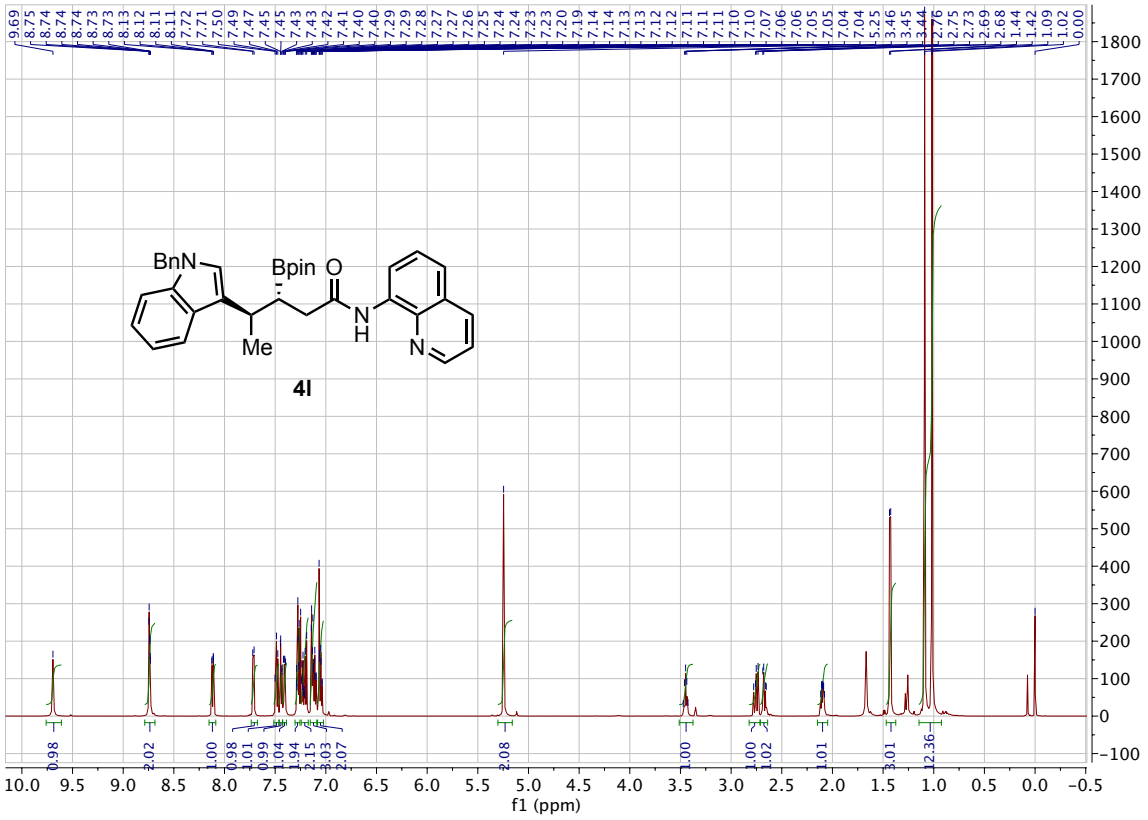
SFC Chromatograms of **4k**

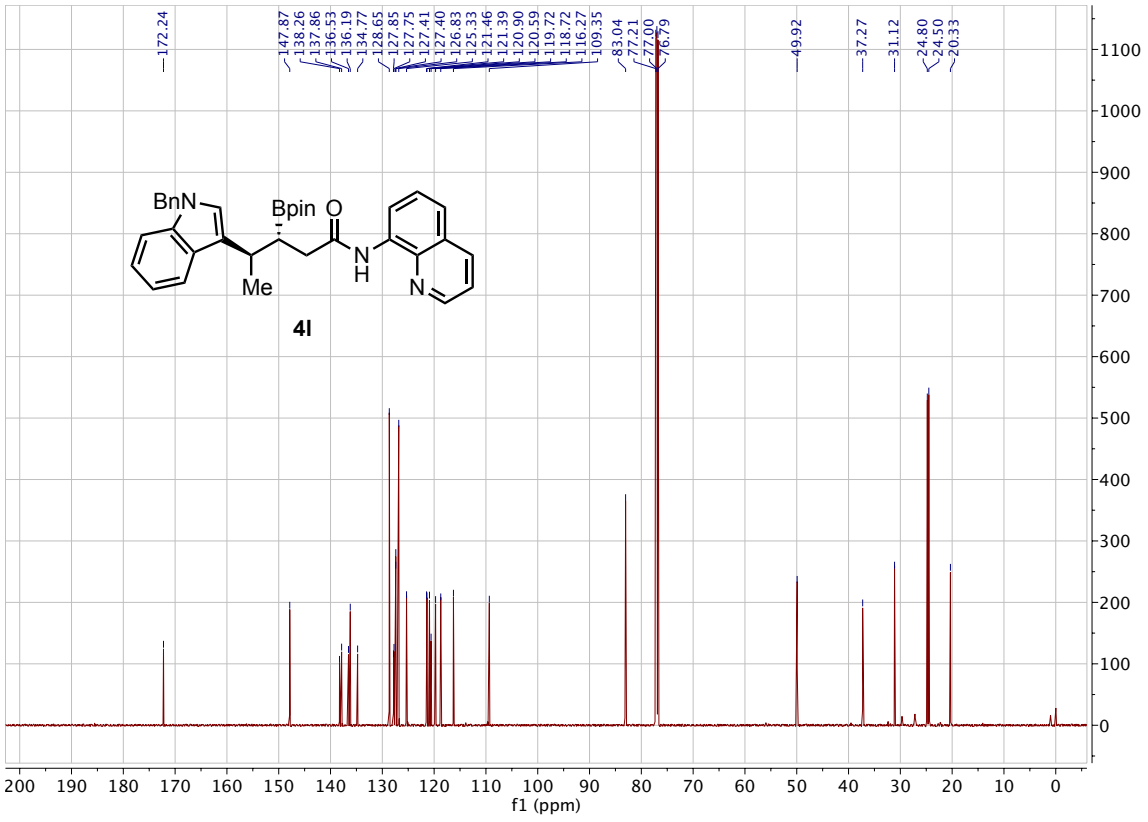




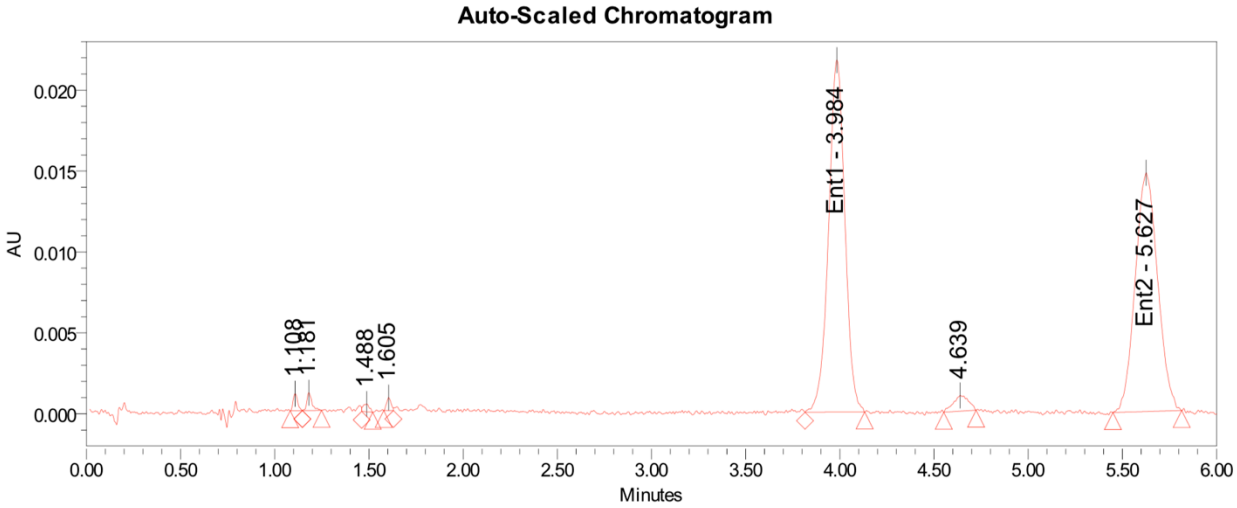
Area Summarized by Name

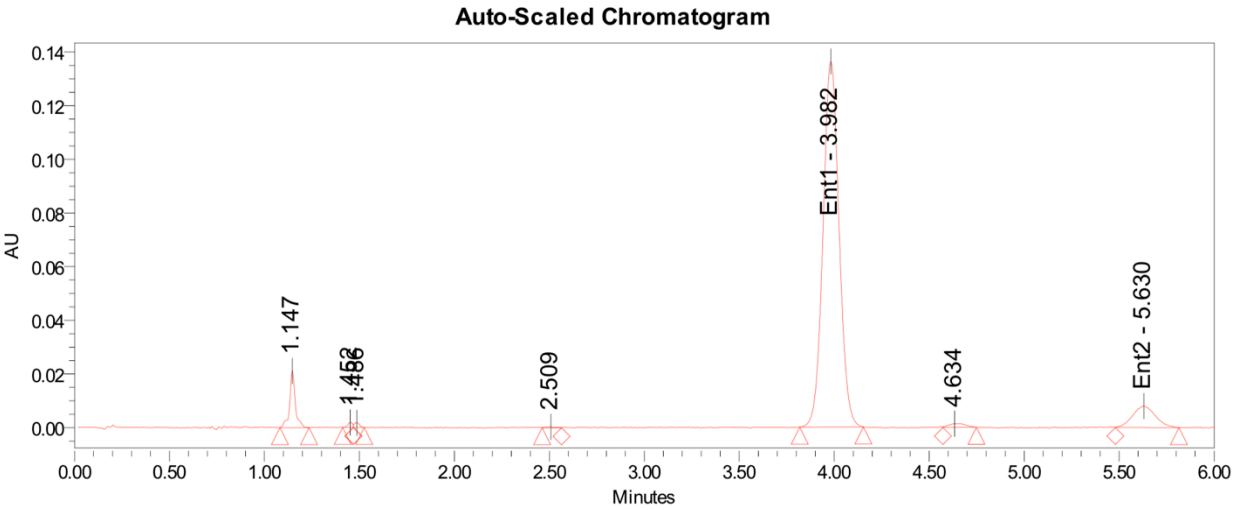
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-IPR-Rac	50.77	49.23	1.54	466922	452776
2	LZ-IPR-1	95.28	4.72	90.56	1117490	55368


BnN
Bpin
O
N
H
Me
N
4l
f1 (ppm)


BnN
Bpin
O
N
H
Me
N
4l
f1 (ppm)

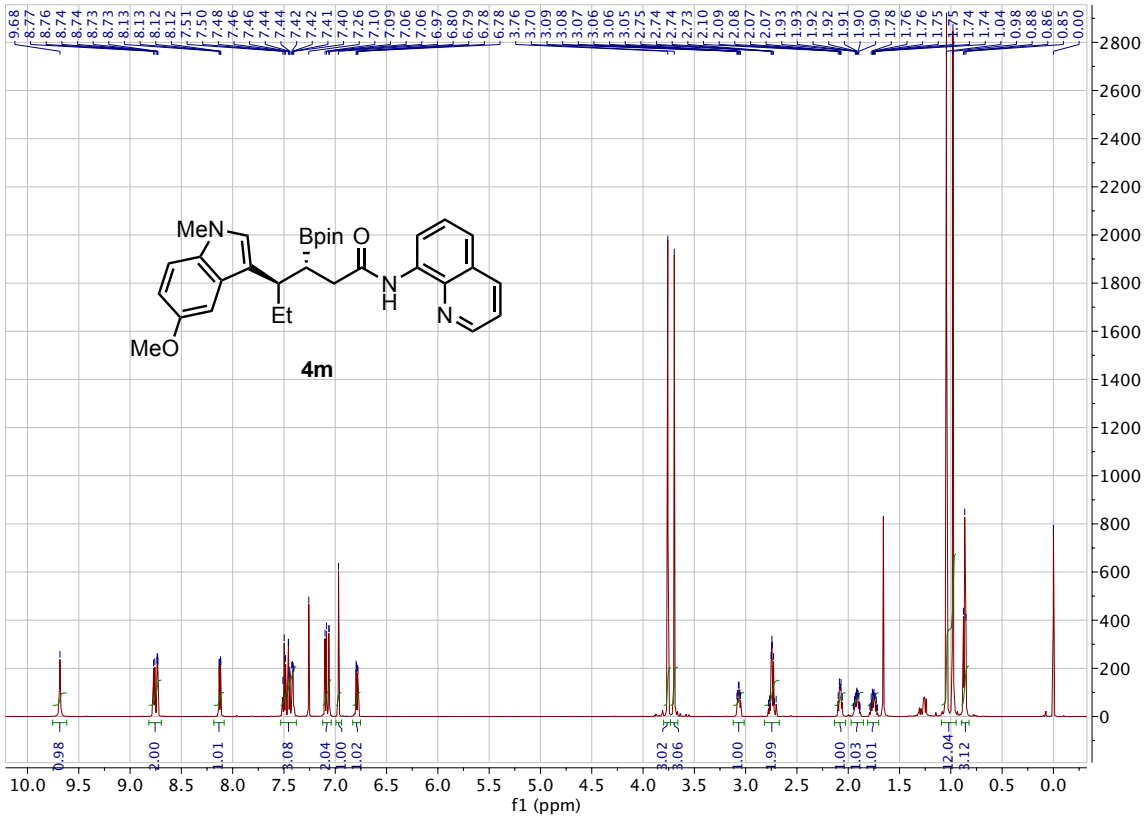
SFC Chromatograms of **4l**

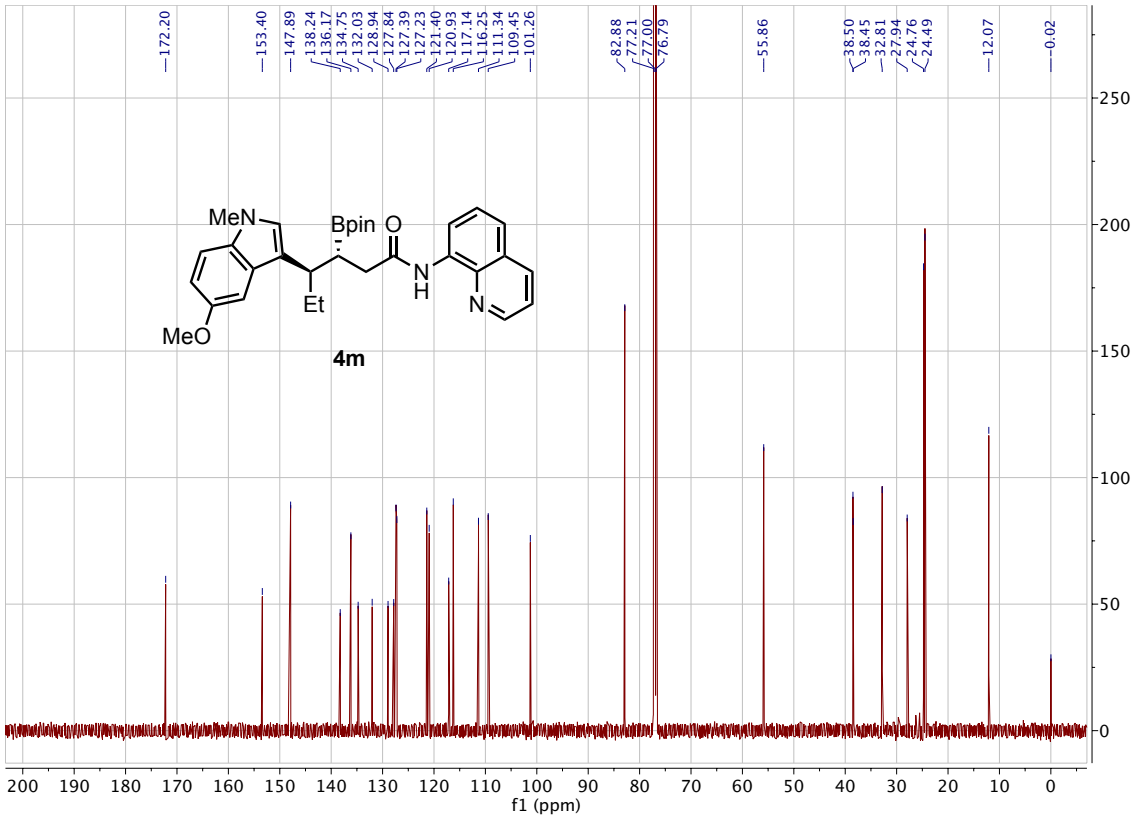




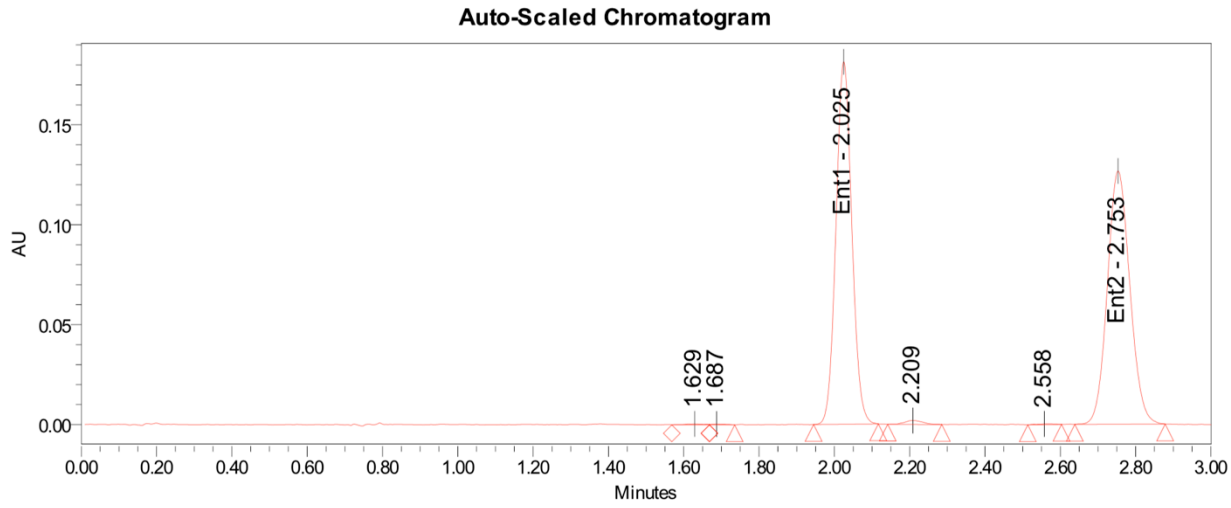
Area Summarized by Name

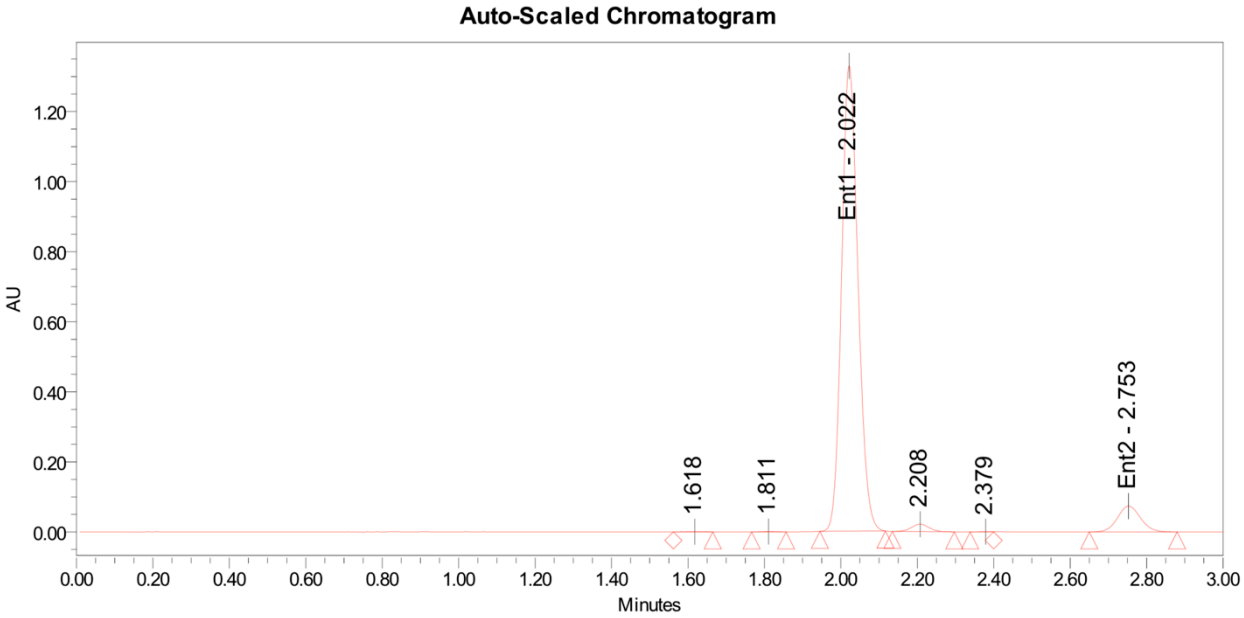
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-NBu-Rac	51.79	48.21	3.59	131292	122203
2	LZ-NBu-1	92.27	7.73	84.53	799931	67043


MeN
Bpin
O
N
H
Et
N
MeO
4m
f1 (ppm)


MeN
Bpin
O
N
H
Et
N
MeO
4m
f1 (ppm)

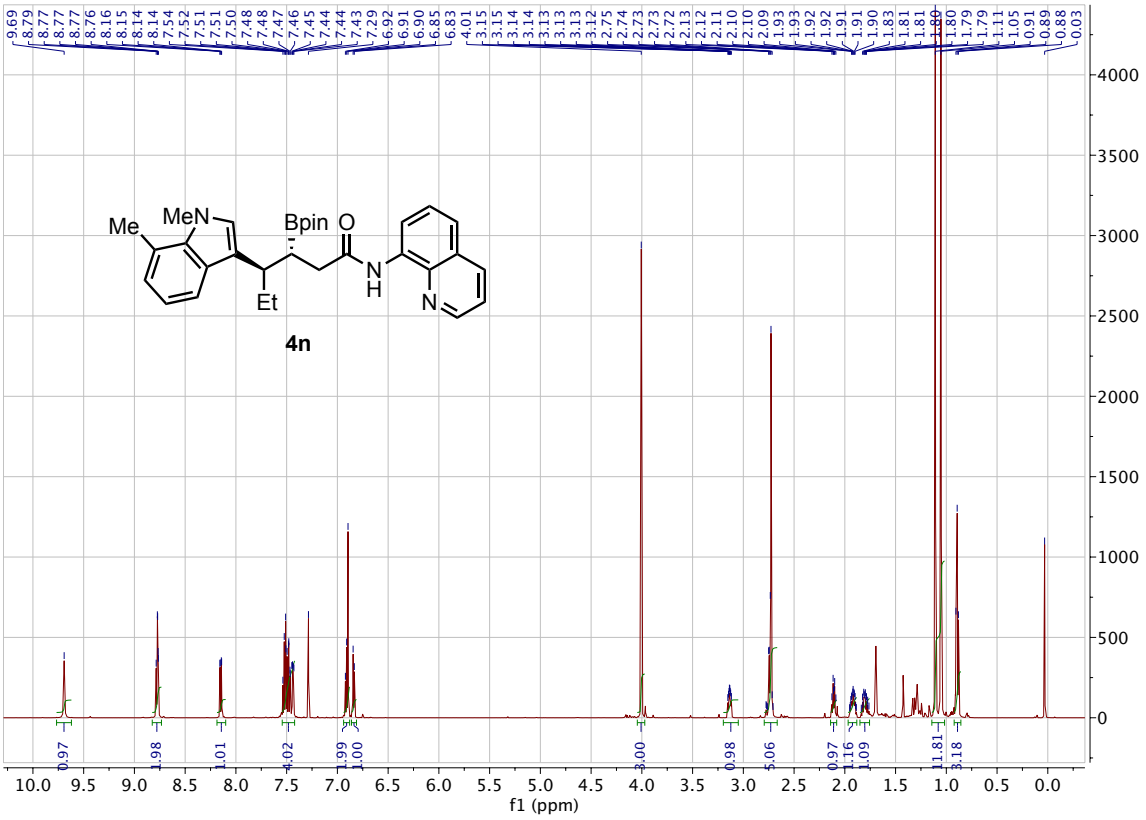
SFC Chromatograms of **4m**

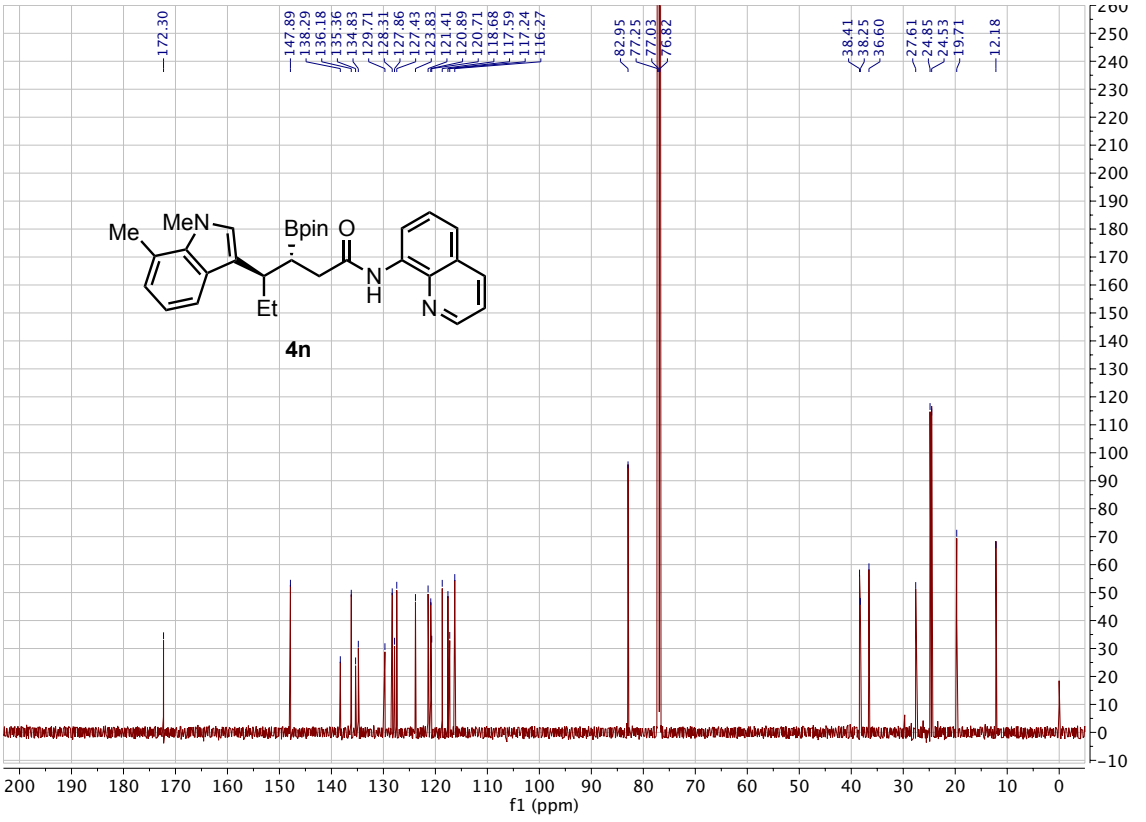




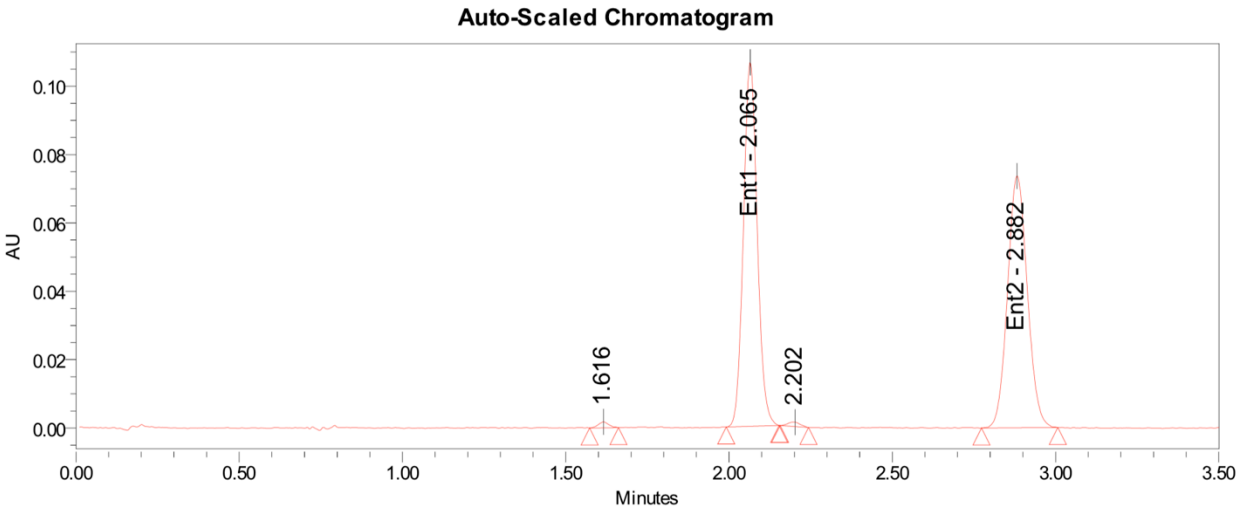
Area Summarized by Name

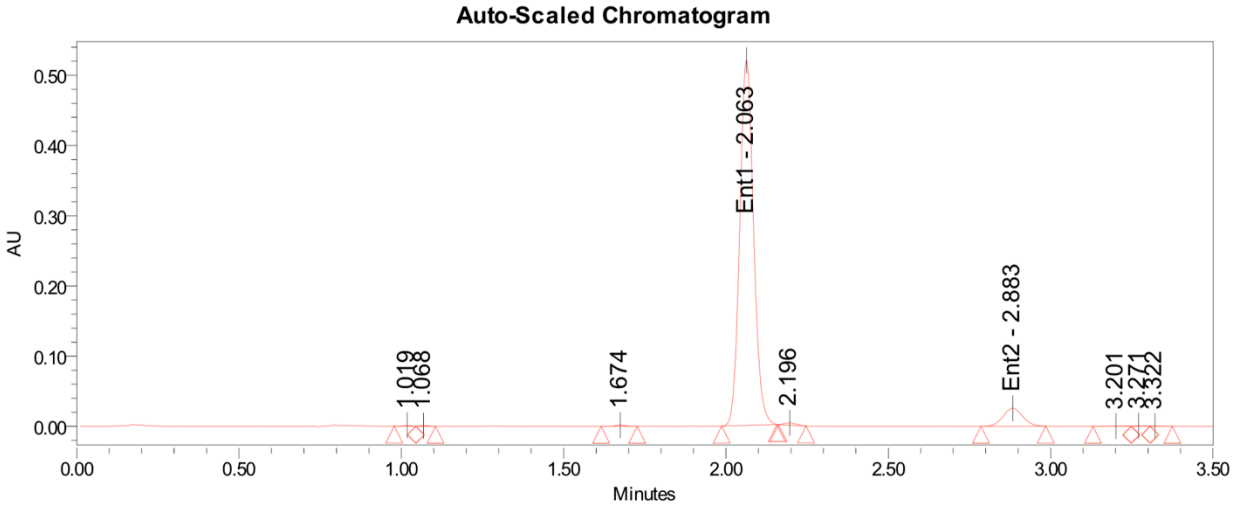
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-5OMe-Rac	50.23	49.77	0.46	530628	525733
2	LZ-37-1	92.81	7.19	85.62	3959224	306764


Me
MeN
Bpin
O
N
H
Et
N
4n
f1 (ppm)


Me
MeN
Bpin
O
N
H
Et
N
4n
f1 (ppm)

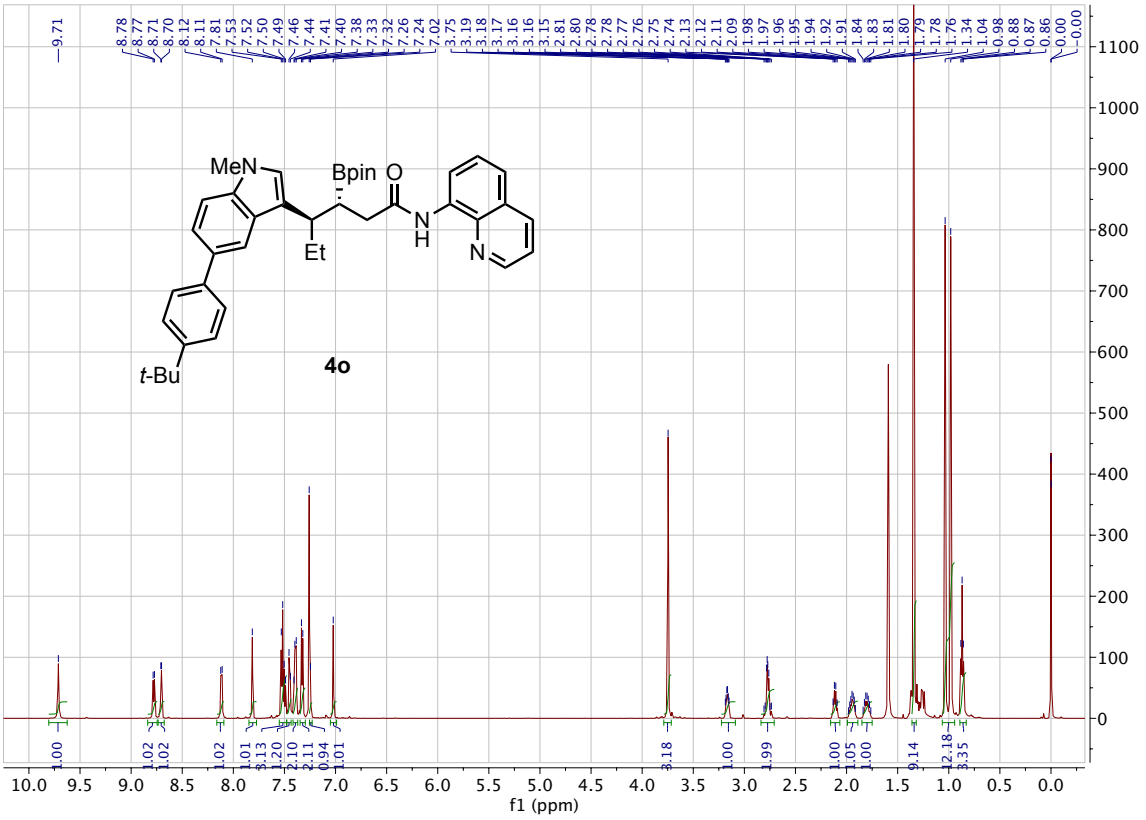
SFC Chromatograms of **4n**

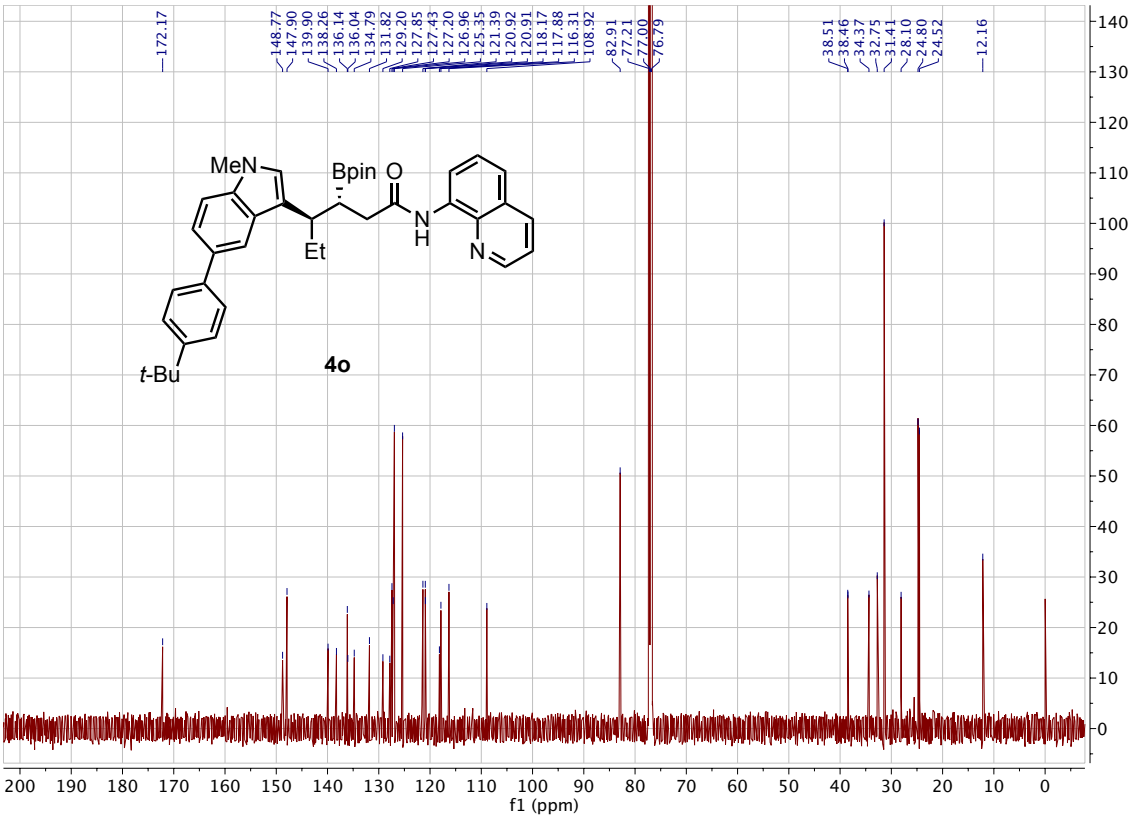




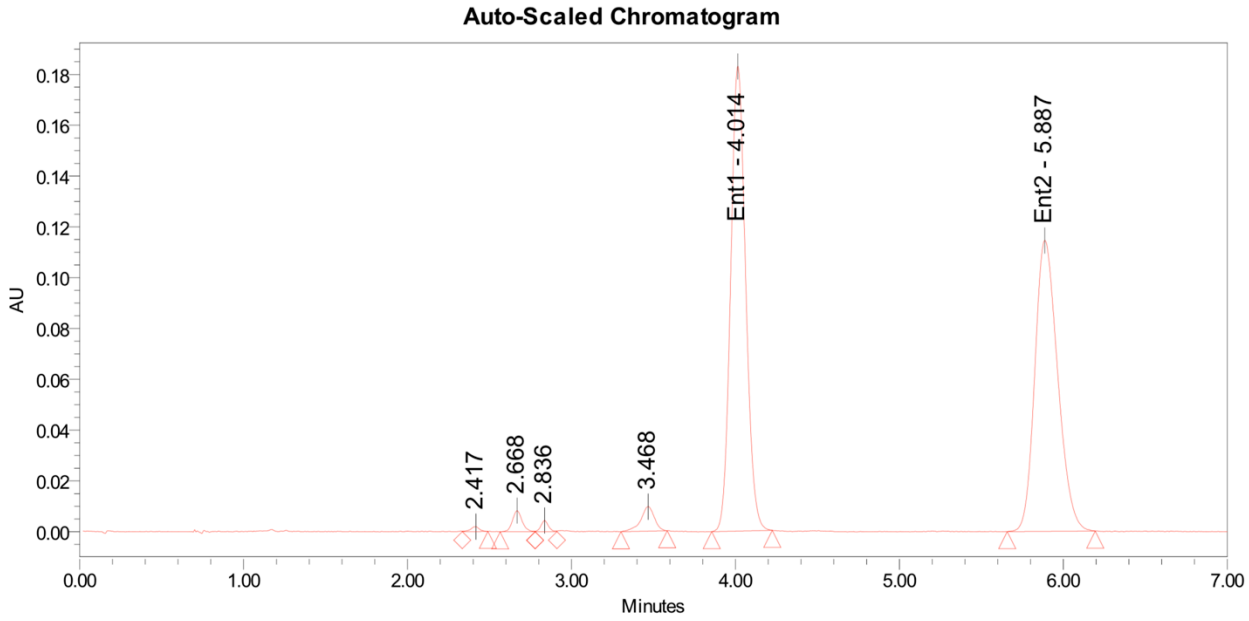
Area Summarized by Name

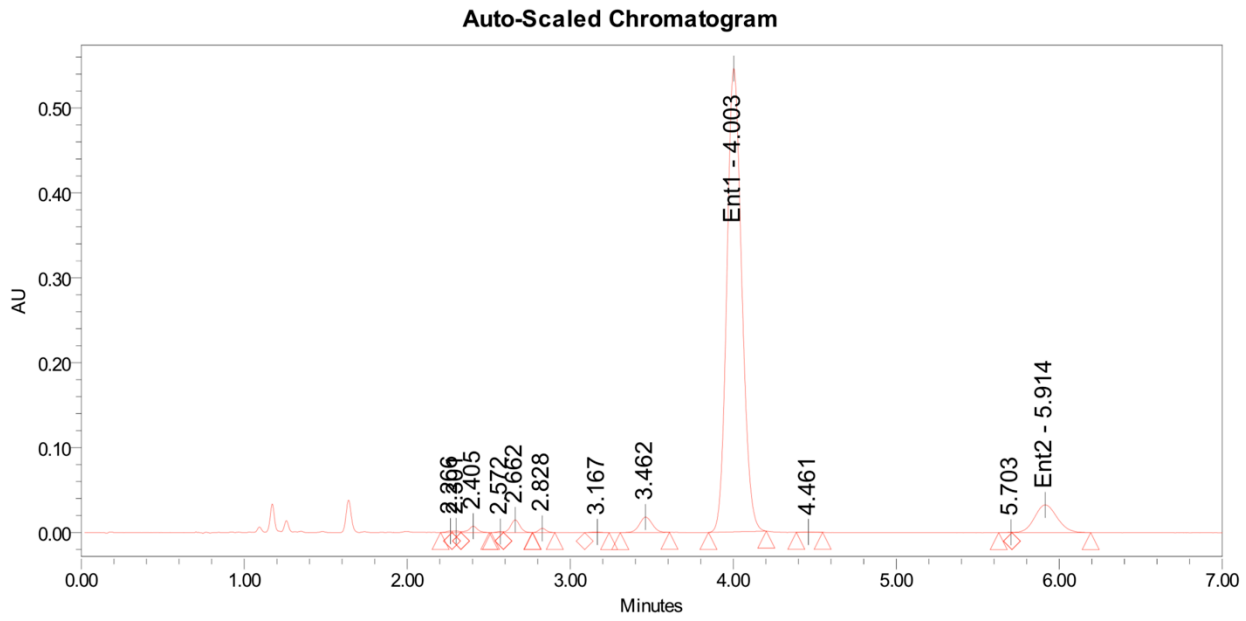
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-7Me-Rac	50.18	49.82	0.36	313197	310925
2	LZ-7Me-1	93.46	6.54	86.92	1537208	107576


MeN
Bpin
O
N
H
Et
N
t-Bu
4o
f1 (ppm)


MeN
Bpin
O
N
H
Et
N
t-Bu
4o
f1 (ppm)

SFC Chromatograms of **4o**

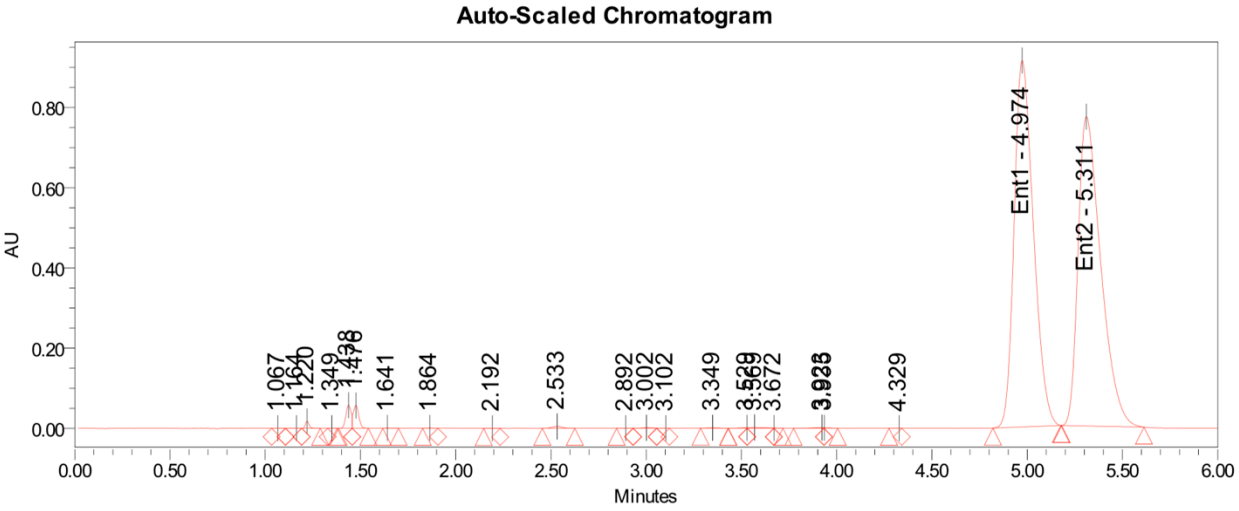


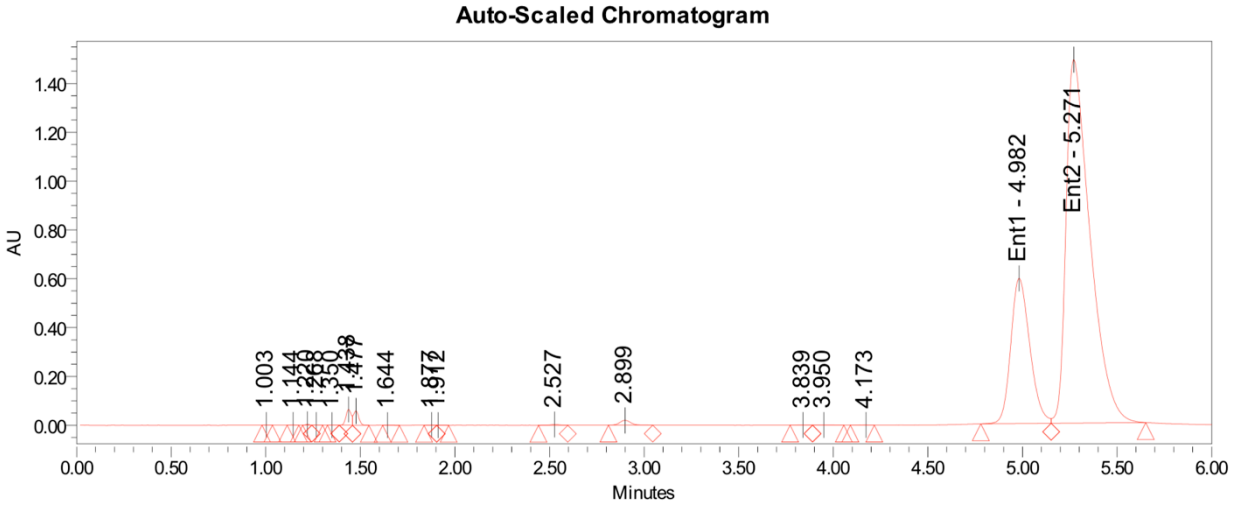


Area Summarized by Name

	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-42-1	51.11	48.89	2.22	1162181	1111601
2	LZ-43-1	91.67	8.33	83.34	3462388	314726

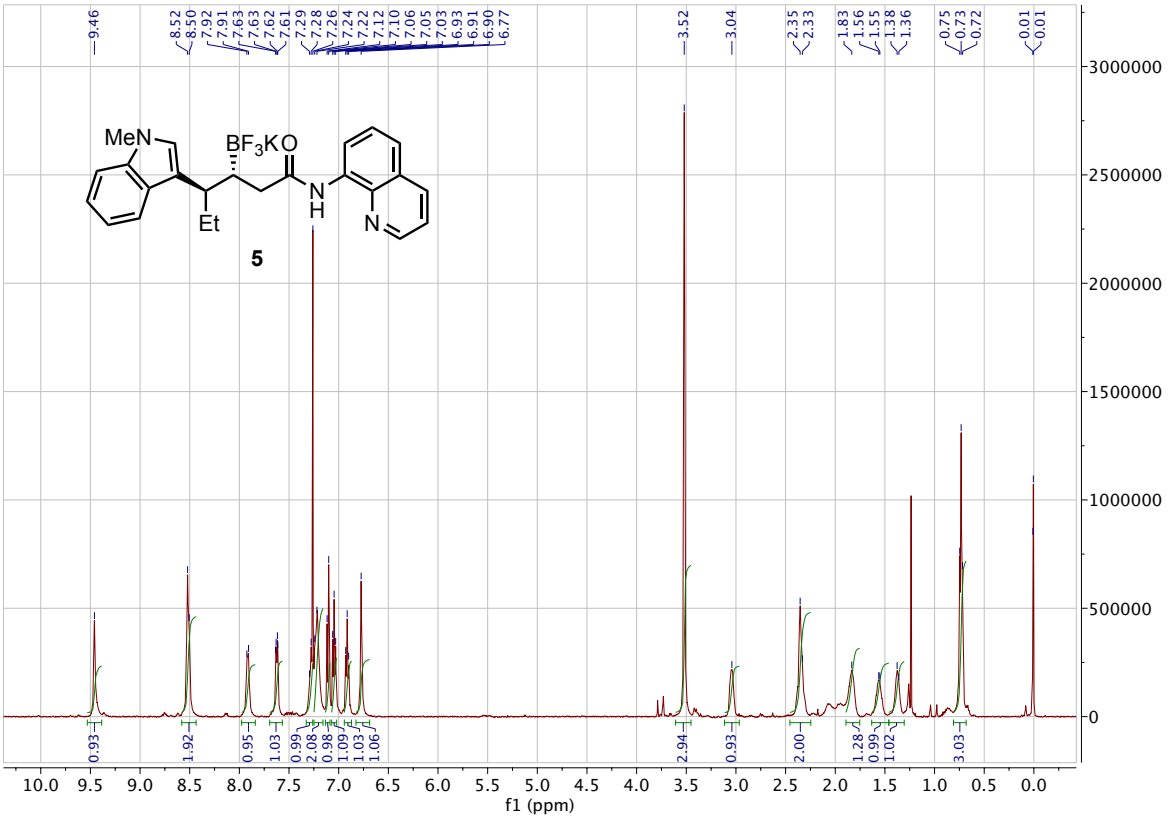
SFC Chromatograms of **4p**

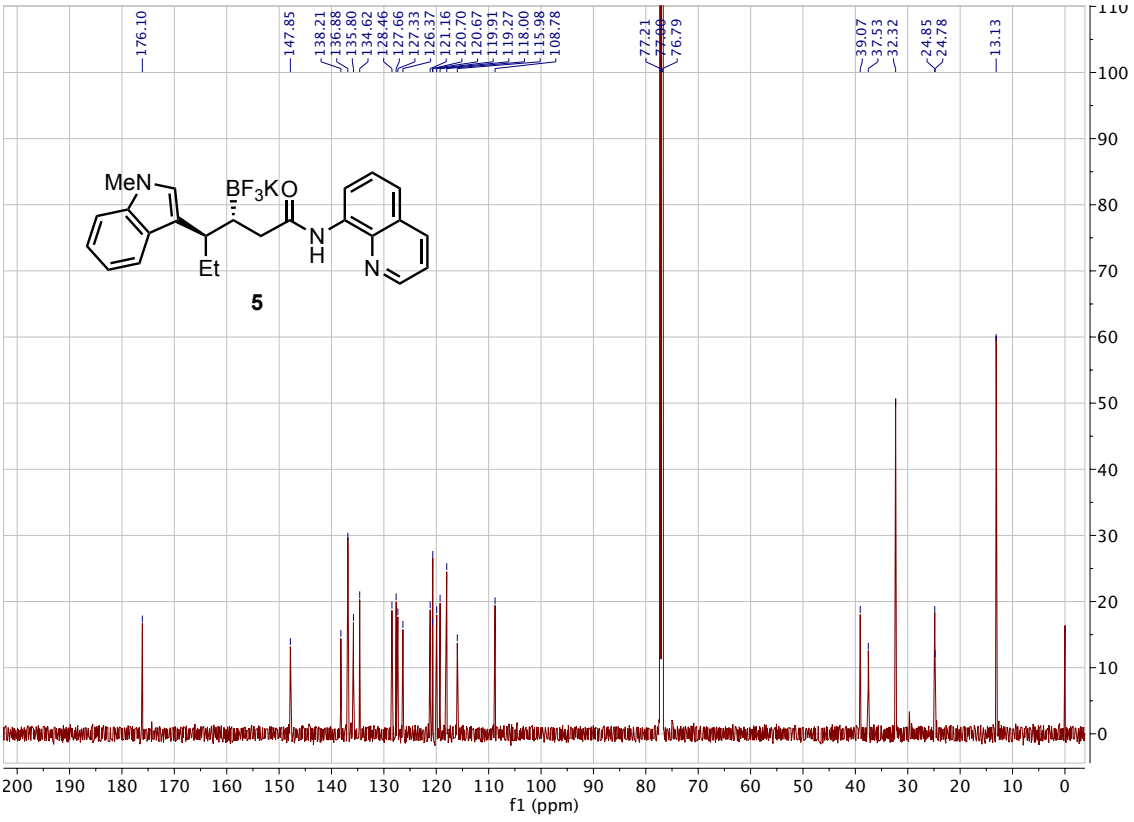


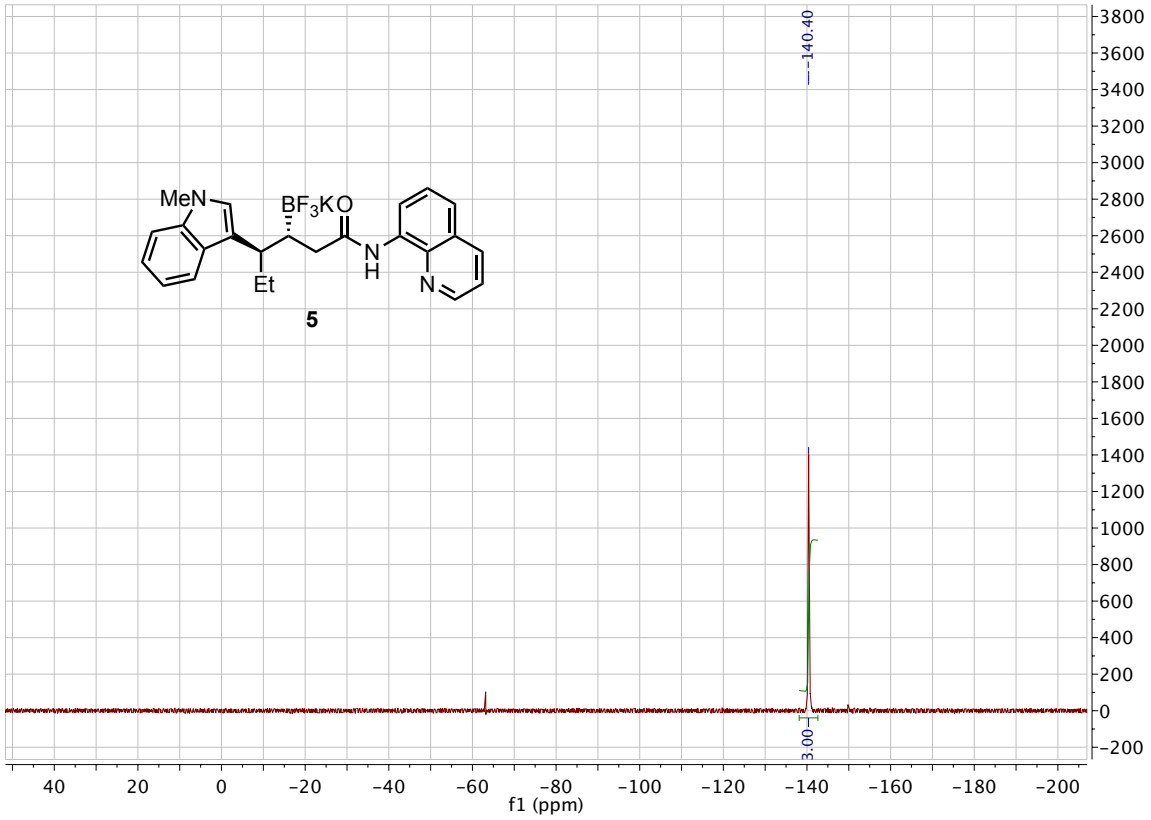


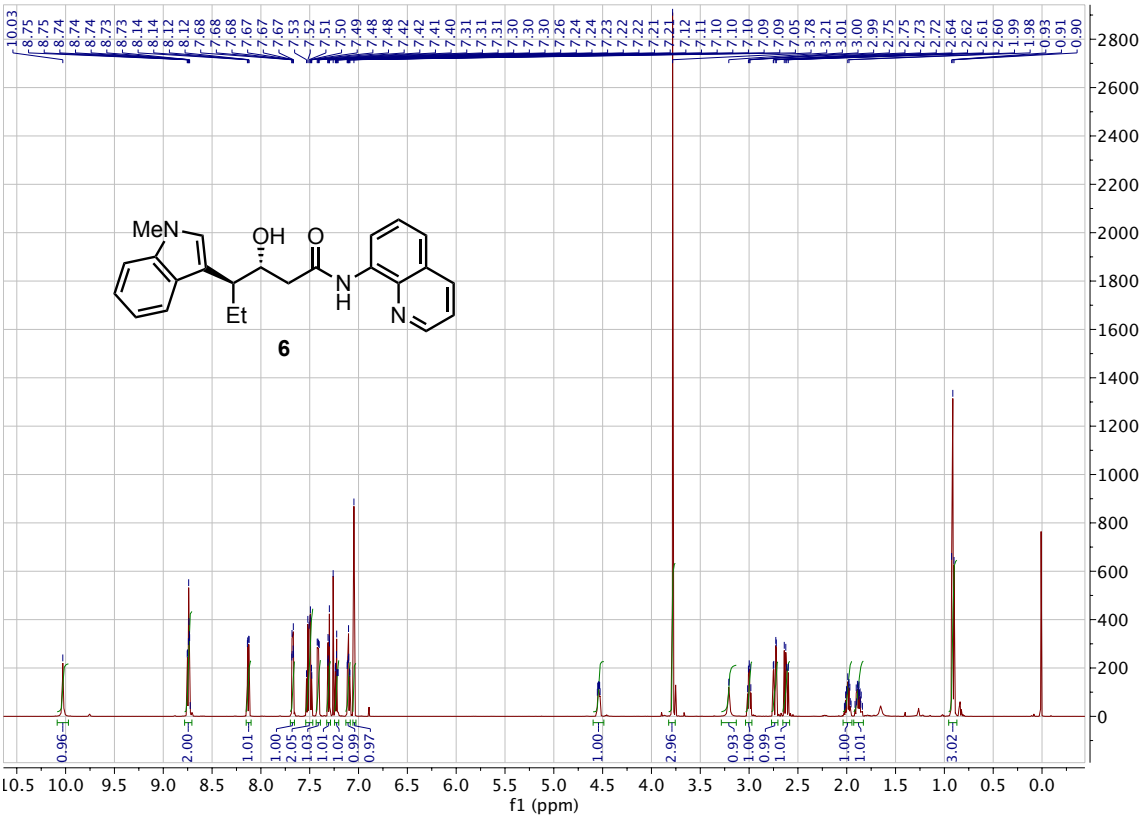
Area Summarized by Name

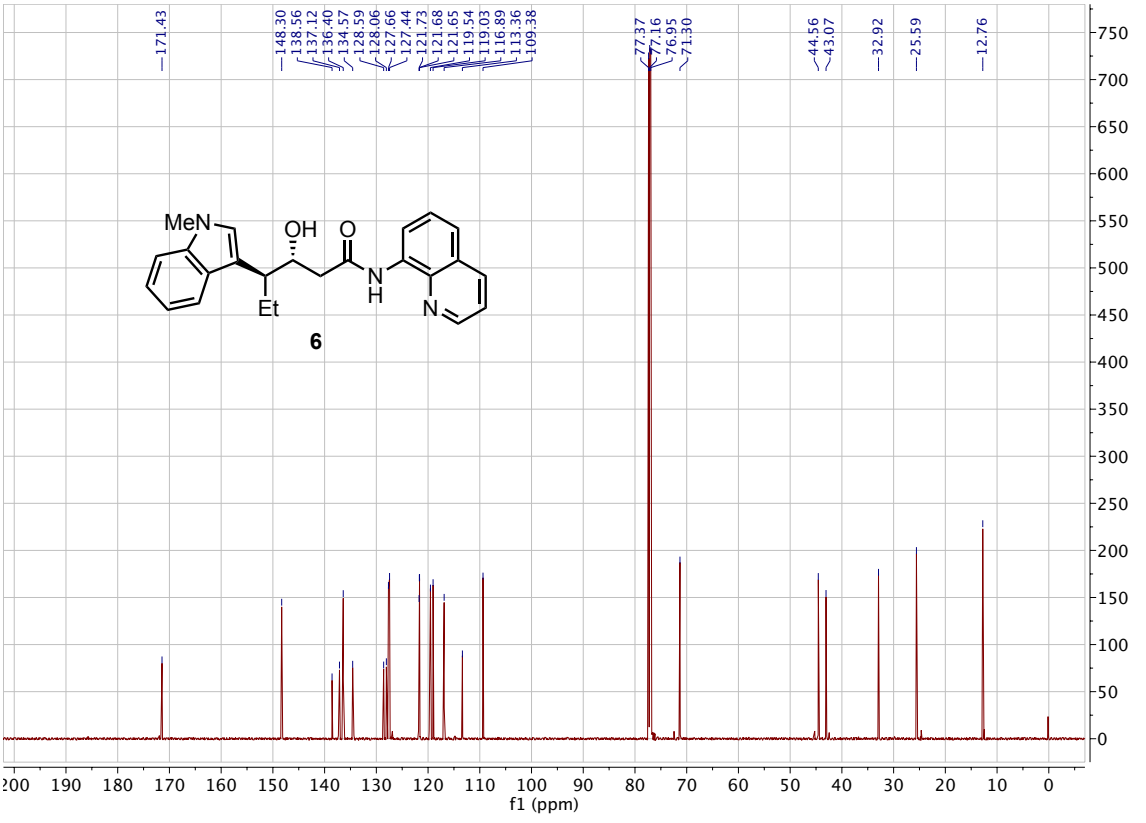
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-rac	50.10	49.90	0.20	6410665	6384853
2	LZ-143-2	24.06	75.94	-51.87	4157236	13119578


MeN
BF3KO
Et
N
H
N
5
f1 (ppm)

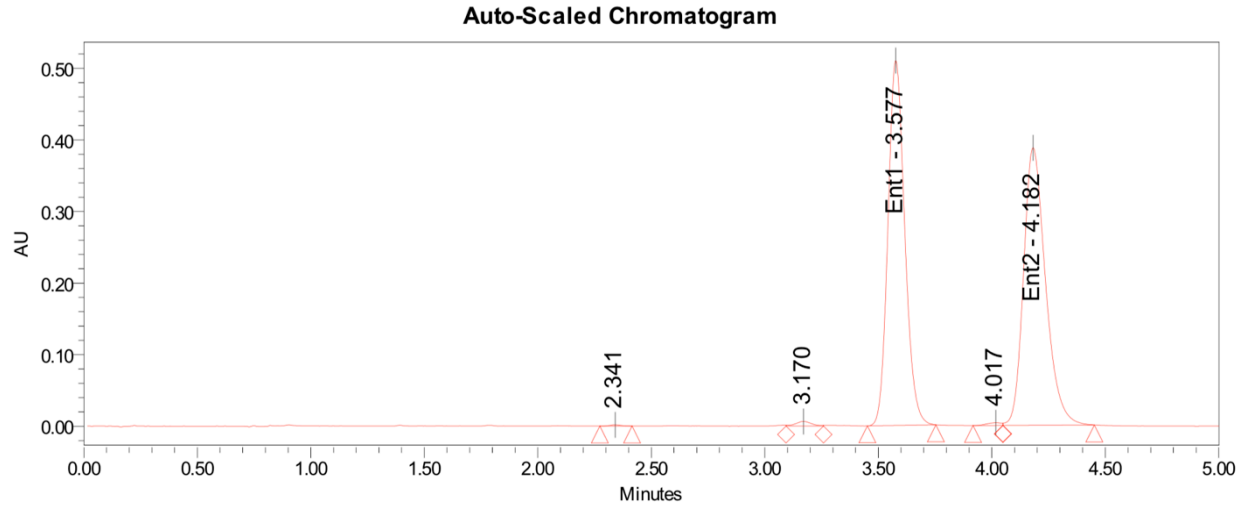

MeN
BF3KO
Et
N
H
N
5
f1 (ppm)

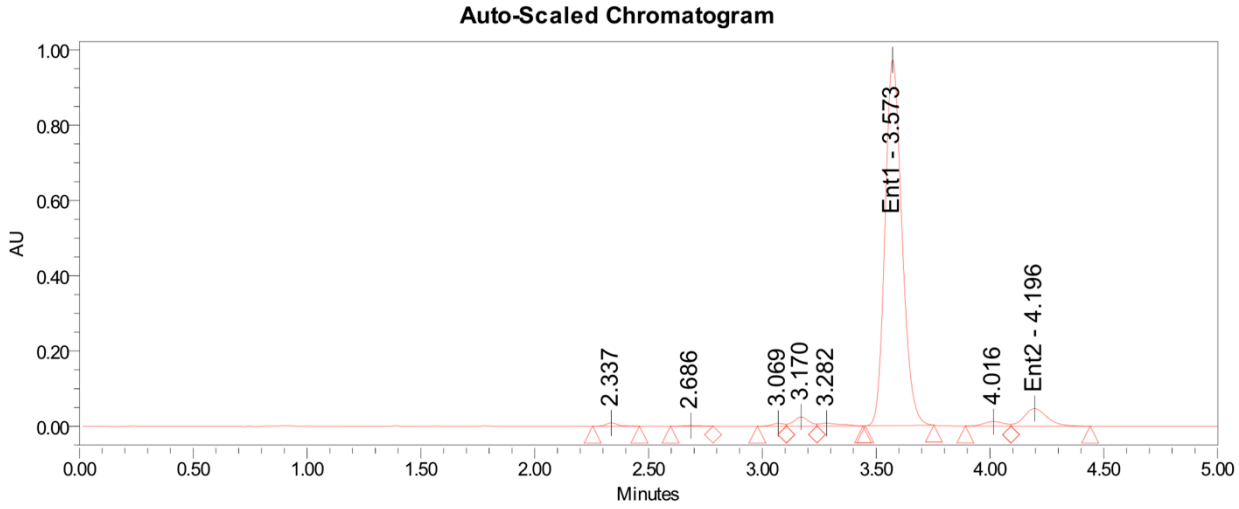

MeN
BF3KO
Et
N
H
N
5
-140.40
3.00
f1 (ppm)


MeN
OH
O
N
H
Et
N
6
f1 (ppm)


MeN
OH
O
N
H
Et
N
6
f1 (ppm)

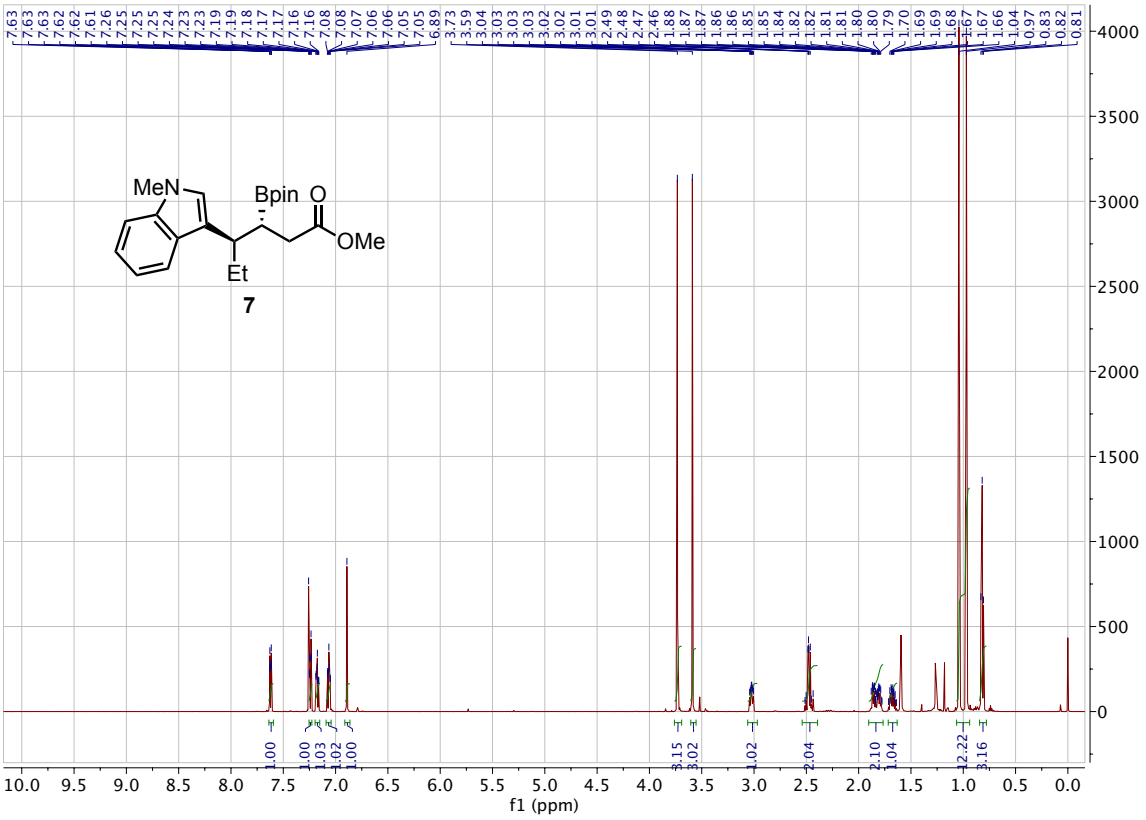
SFC Chromatograms of **6**

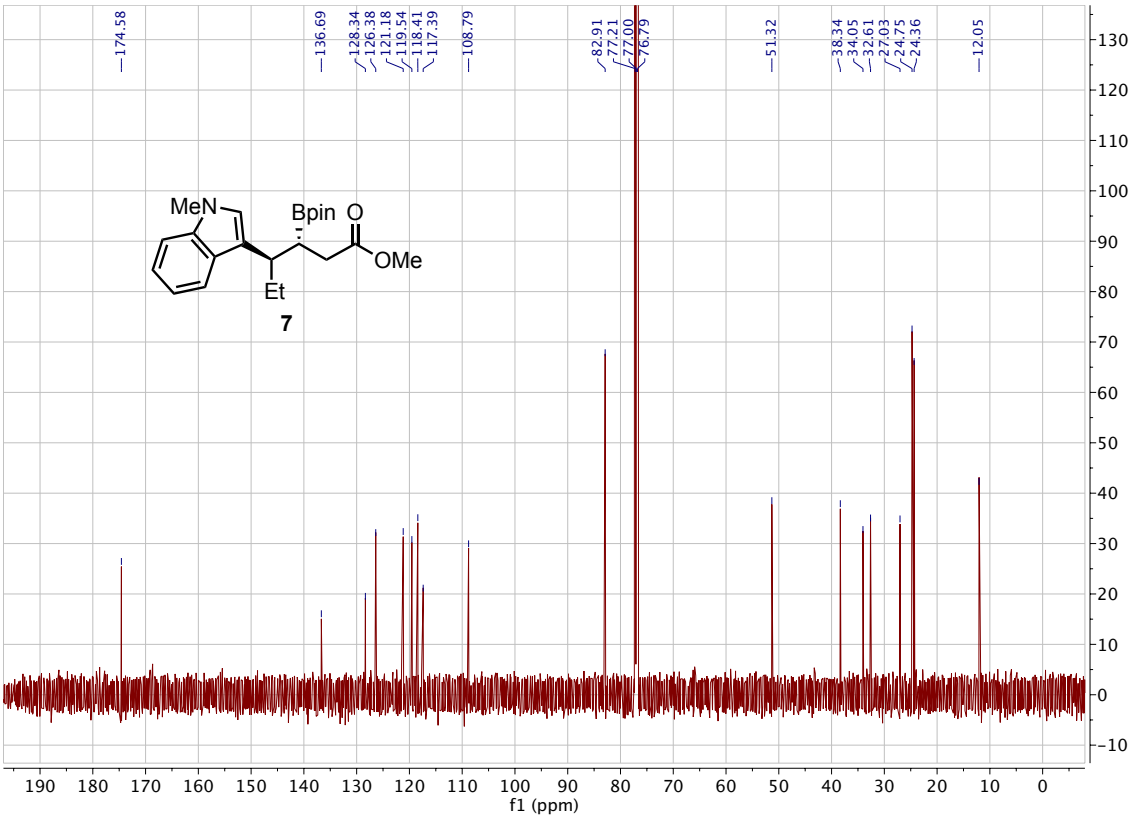




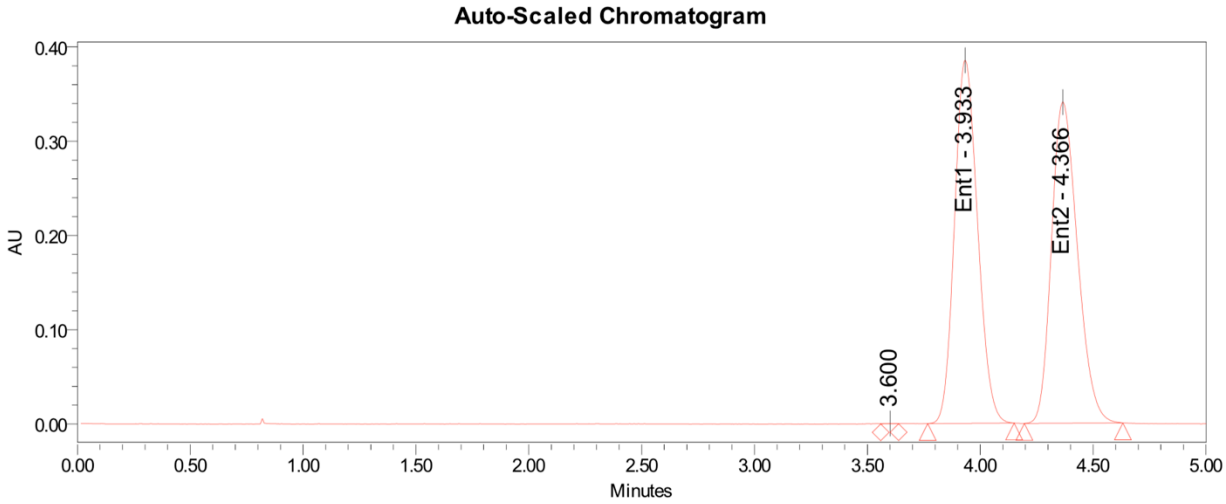
Area Summarized by Name

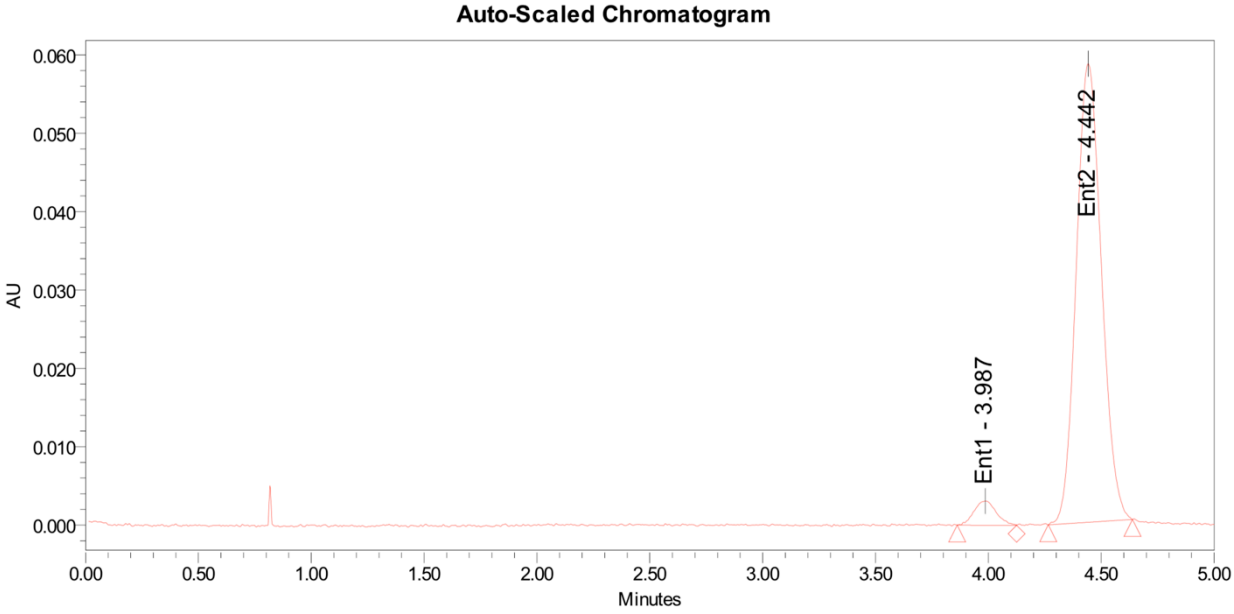
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LZ-Et-O-R	50.10	49.90	0.20	2624365	2613891
2	LZ-ET-O-C	93.89	6.11	87.77	5016360	326701


MeN
Bpin
O
OMe
Et
7
f1 (ppm)


MeN
Bpin
O
OMe
Et
7
f1 (ppm)

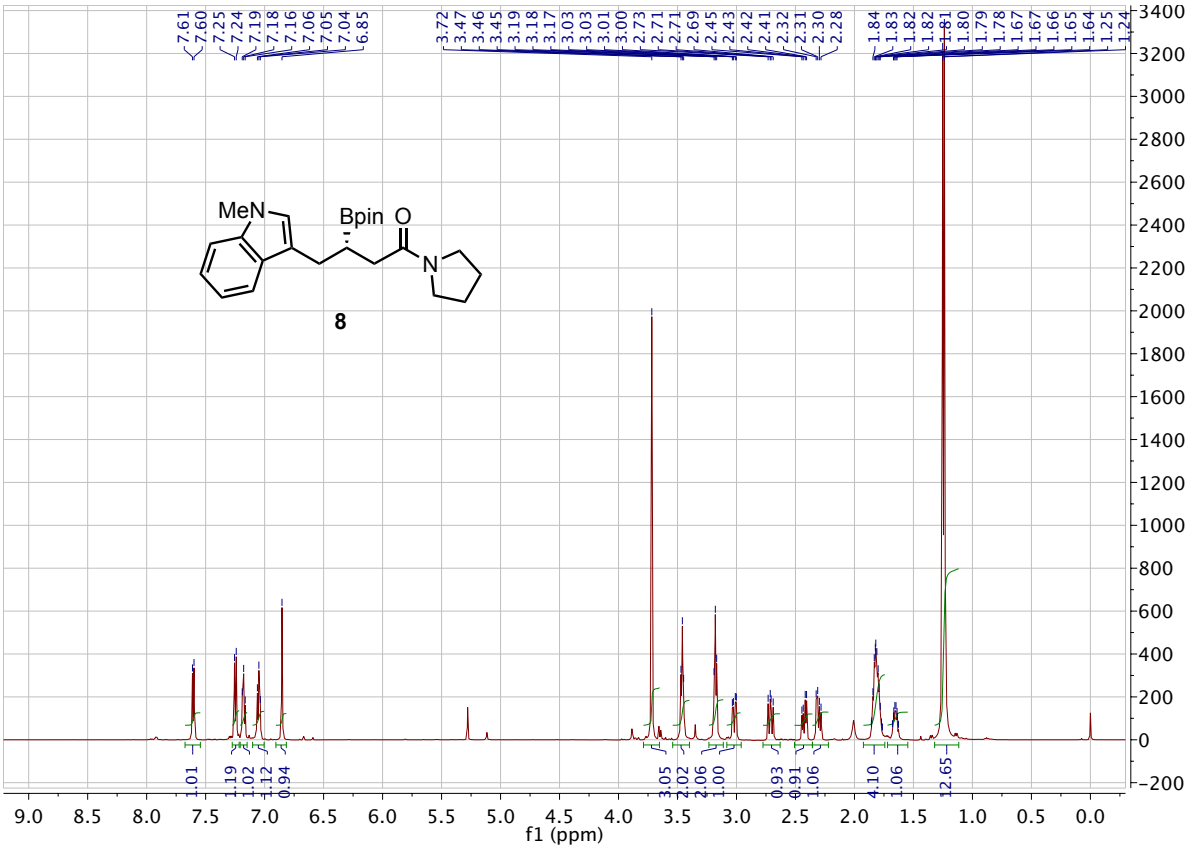
SFC Chromatograms of **7**

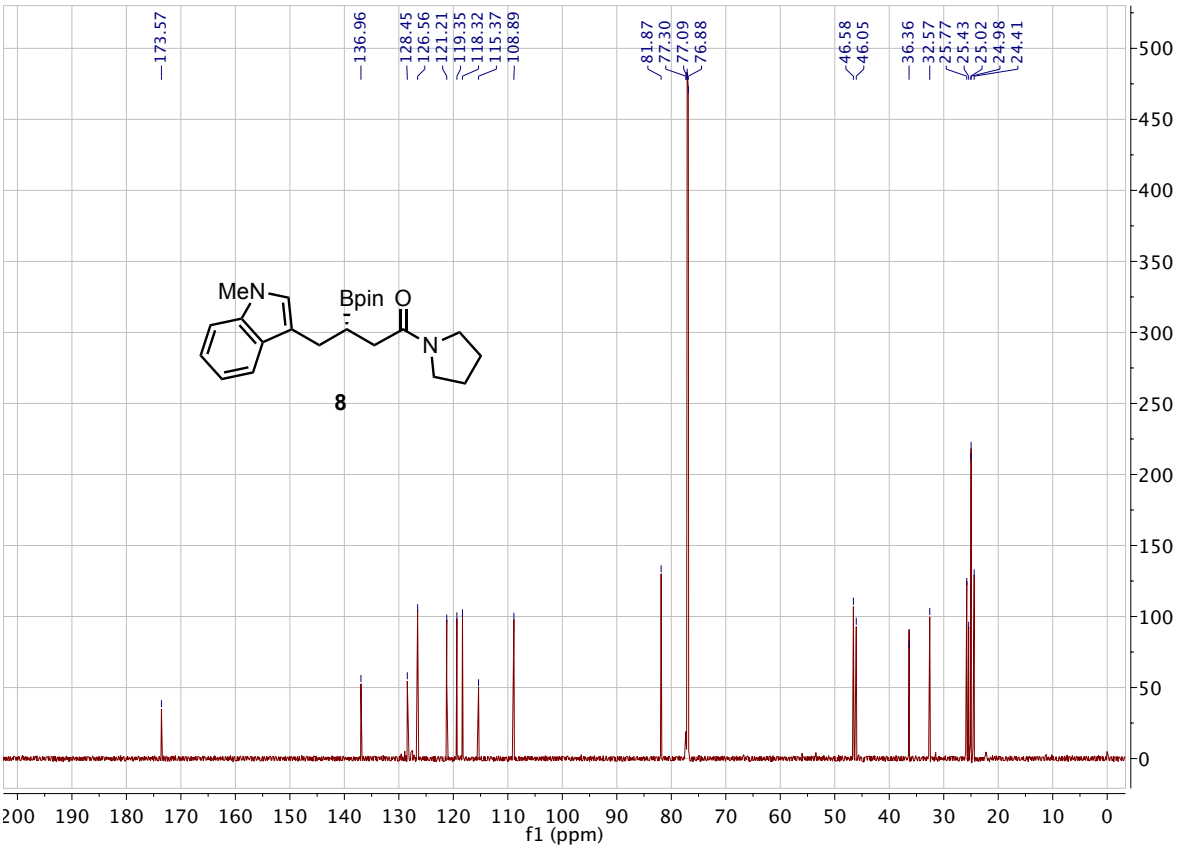




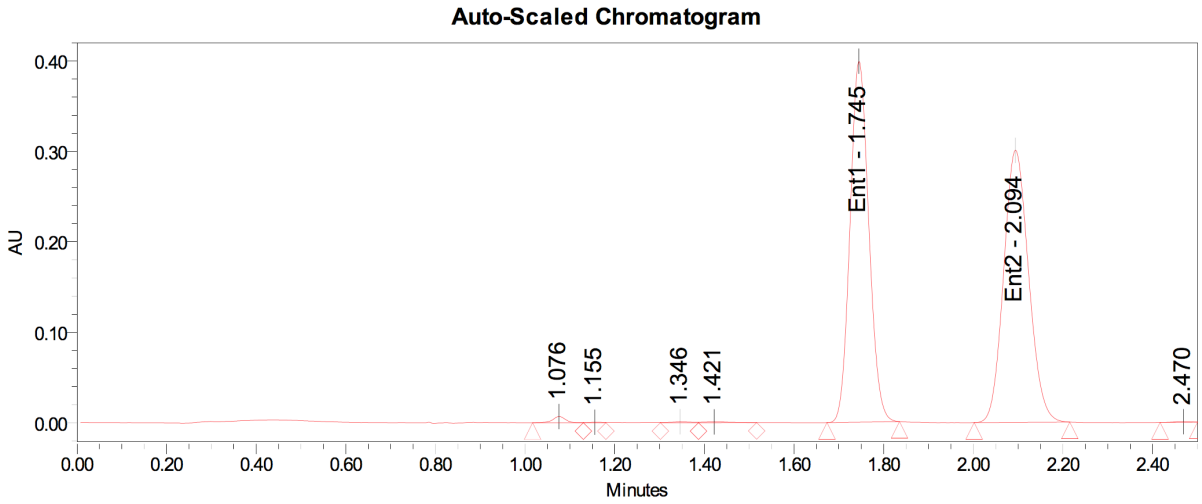
Area Summarized by Name

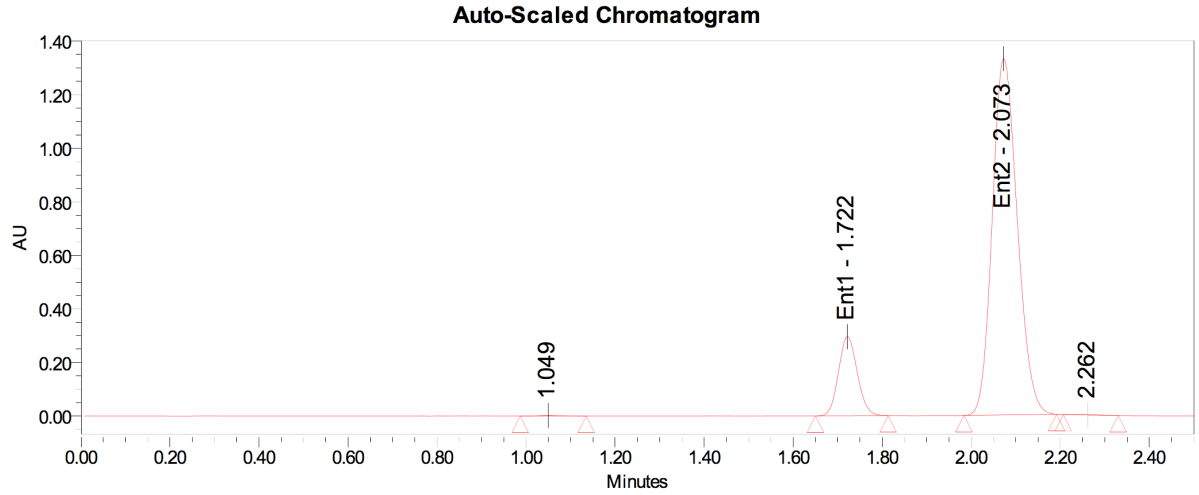
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	LXH-60(r)	50.09	49.91	0.17	2739668	2730184
2	LXH-60(c)	4.45	95.55	-91.10	21151	454211


MeN
Bpin
O
N
8
f1 (ppm)


MeN
Bpin
O
N
8
f1 (ppm)

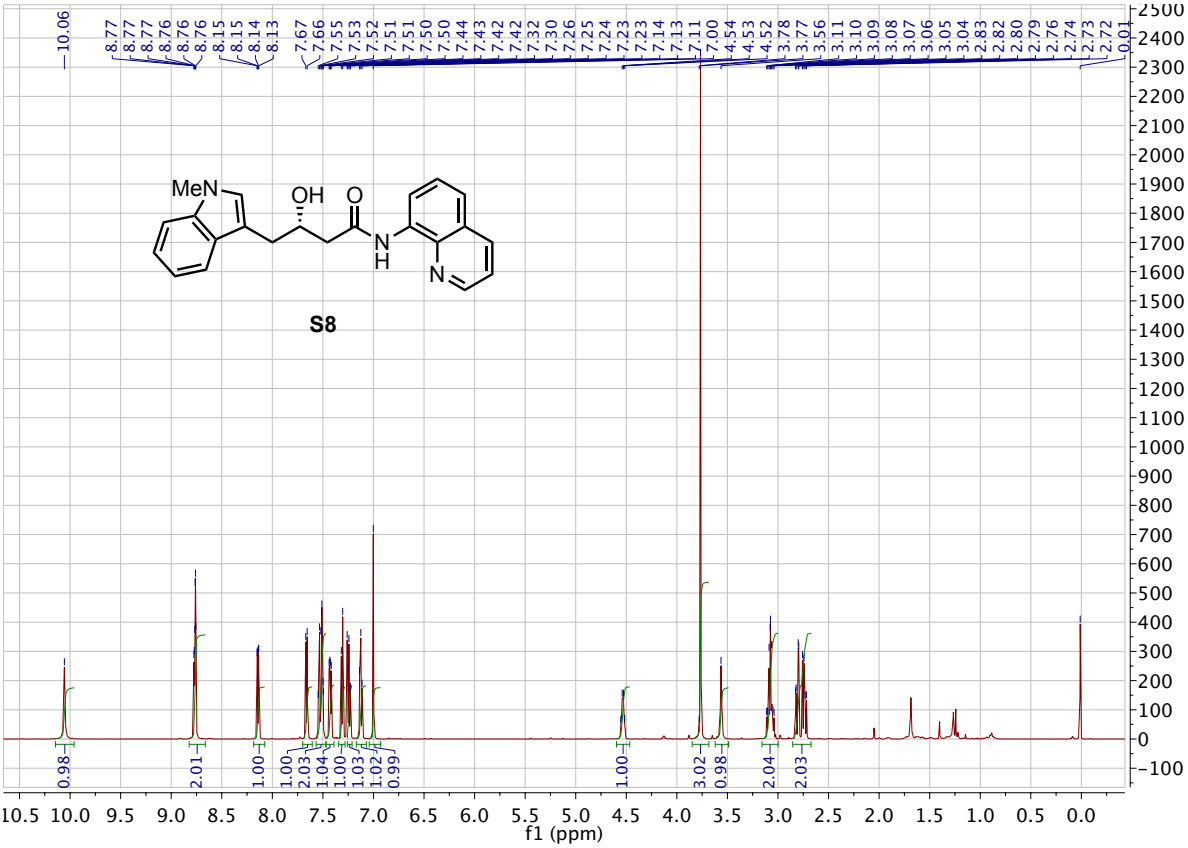
SFC Chromatograms of **8**

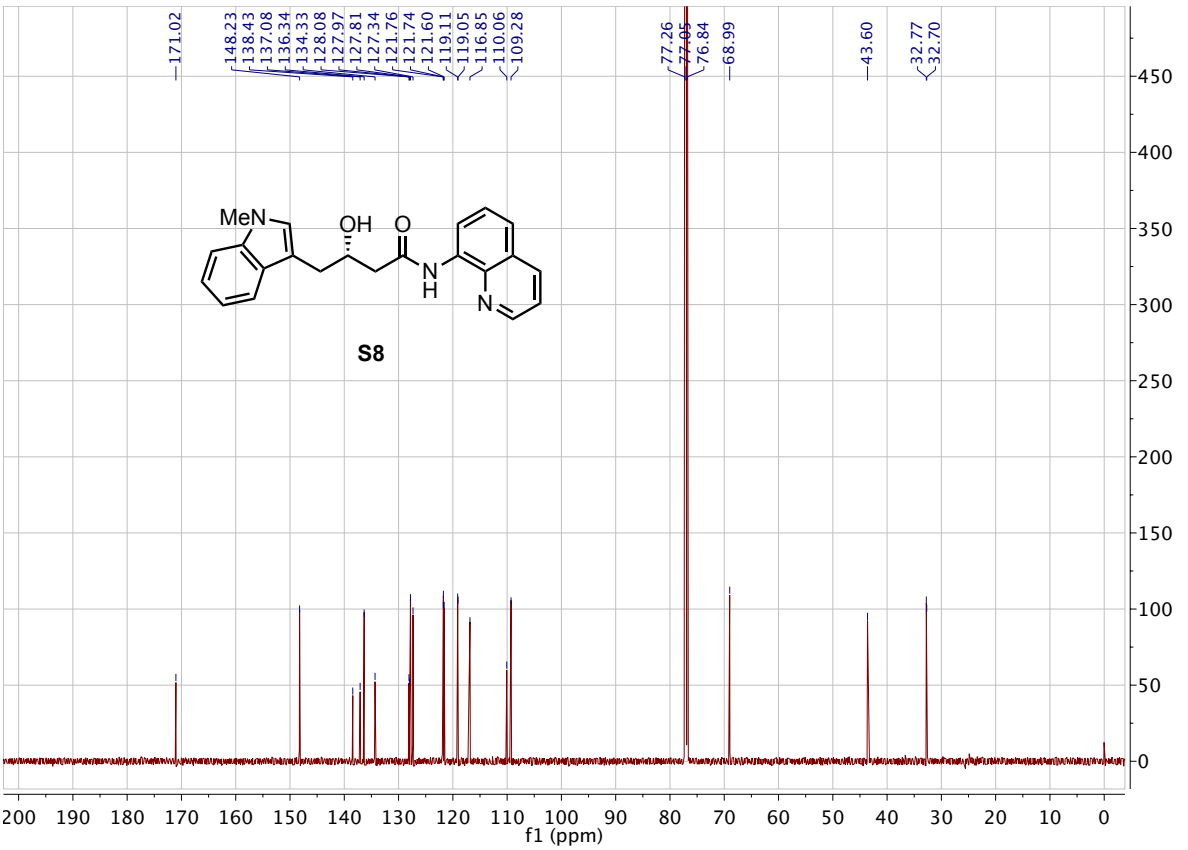


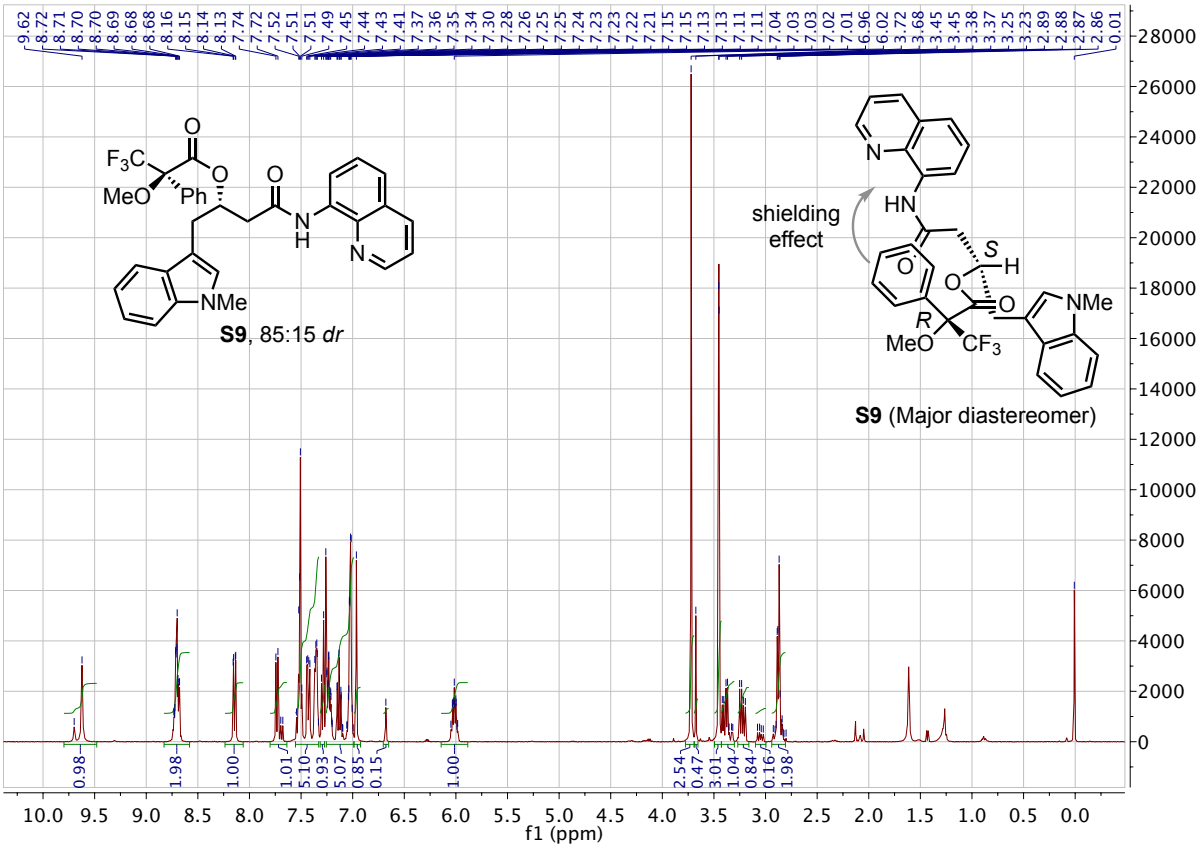


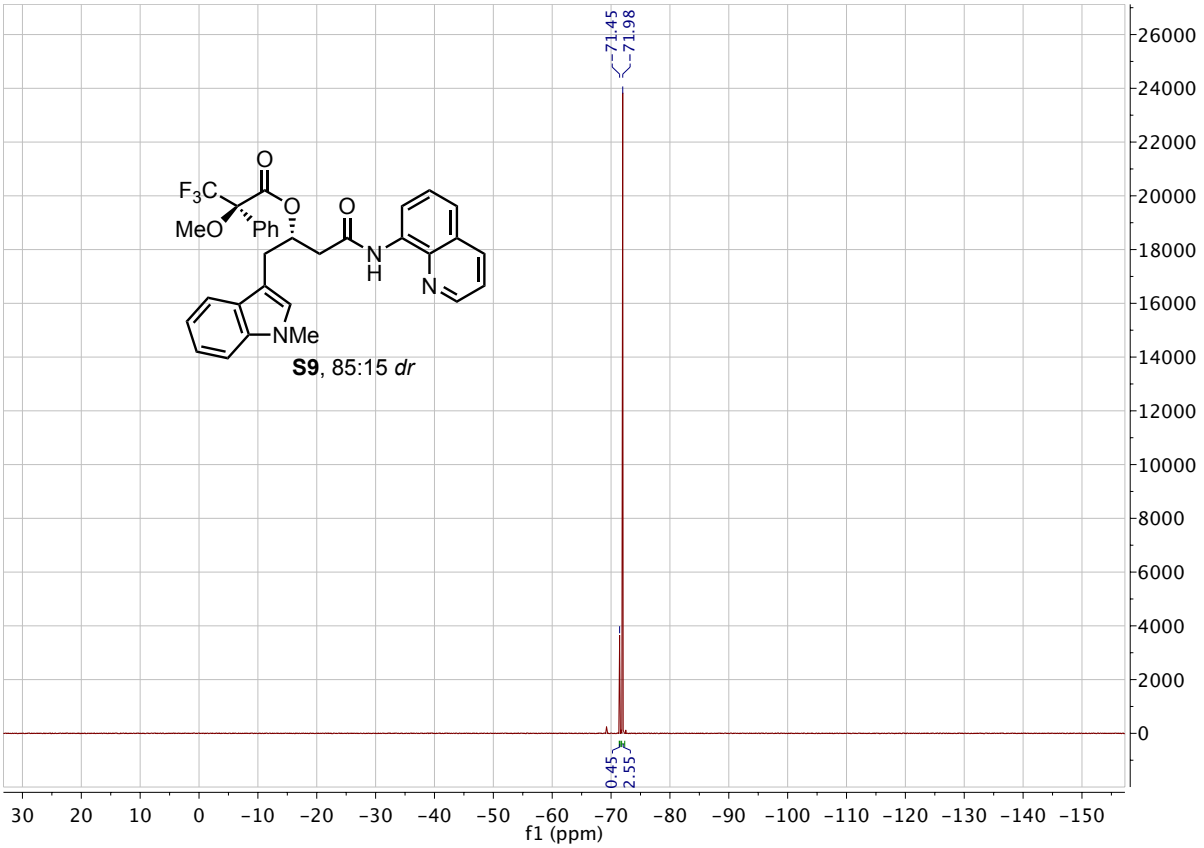
Area Summarized by Name

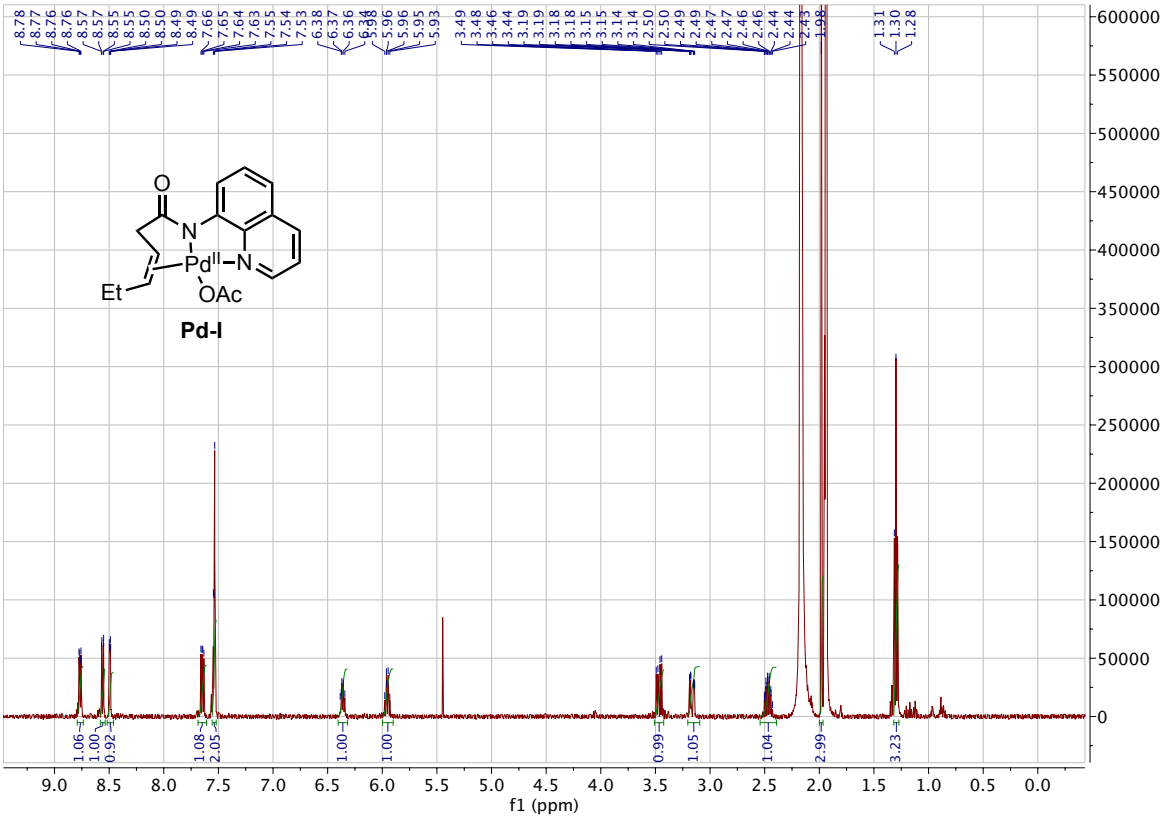
	SampleName	ent1	ent2	ee	Ent1	Ent2
1	ZL-AR	49.87	50.13	-0.25	1159648	1165488
2	ZL-AC	14.29	85.71	-71.41	864400	5182664

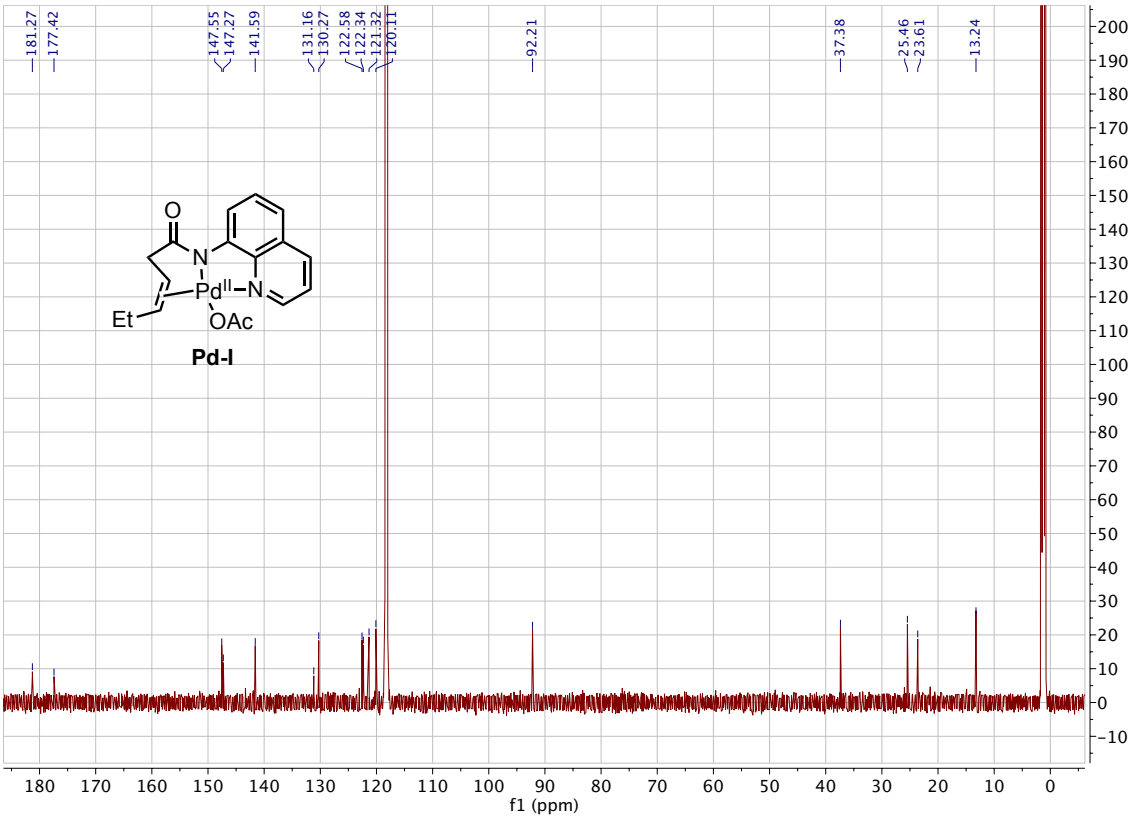

MeN
OH
O
N
H
N
S8
f1 (ppm)


MeN
OH
O
N
H
N
S8
f1 (ppm)


shielding effect
S9, 85:15 dr
S9 (Major diastereomer)
f1 (ppm)


S9, 85:15 dr
f1 (ppm)


Pd-I
f1 (ppm)


Pd-I
f1 (ppm)