Rh(III)-Catalyzed Diastereoselective C–H Bond Addition/Cyclization Cascade of Enone Tethered Aldehydes

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Supporting Information

I. General Information:

Unless otherwise indicated, all Rh(III)-catalyzed reactions were set up in a N_2 filled glovebox, using glassware that was oven-dried (150 °C) and evacuated while hot prior to use. Unless otherwise indicated, all reactions for substrate preparation were carried out on the benchtop under a N_2 atmosphere. Solvents were purified by elution through a column of activated alumina under N_2 before use. Methanol was distilled from CaH_2 under nitrogen prior to use. Glacial acetic acid was sparged with N_2 before use. Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Products and starting materials were visualized on TLC using UV-light or by staining with $KMnO_4$. Flash-column chromatography was preformed on SiliaFlash® P60 (230-400 mesh) silica gel, and preparative thin-layer chromatrography plates from Analtech (1 mm SiO_2, 20 x 20 cm) were used. NMR chemical shifts are reported in ppm relative to $CDCl_3$ (7.26 ppm for ^1H and 77.16 ppm for ^{13}C) or CD_2Cl_2 (5.32 ppm for ^1H and 53.84 ppm for ^{13}C). Trifluoroacetic acid (set to -76.55 ppm in $CDCl_3$) was used for standardizing ^{19}F NMR chemical shifts. For IR spectra, only partial data are provided. Melting points are reported uncorrected. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) on a time of flight (TOF) mass spectrometer.

II. Preparation of Substrates:

Catalysts:

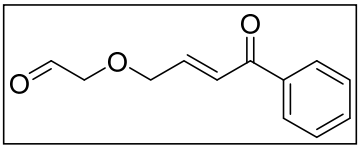
$[Cp^*RhCl_2]_2$[S1] and $AgB(C_6F_5)_4(Et_2O)_2$[S2] were synthesized according to a published literature procedure.

Substrates:

1-tosyl-2,5-dihydro-1*H*-pyrrole,[S3] (*E*)-7-oxo-7-phenylhept-5-enal,[S4] (*E*)-7-oxo-7-(4-(trifluoromethyl)phenyl)hept-5-enal,[S5] (*E*)-7-(methoxyphenyl)-7-oxohept-5-enal,[S6] (*E*)-7-oxo-7-(*o*-tolyl)hept-5-enal,[S7] (*E*)-7-oxooct-5-enal,[S8] (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)benzaldehyde,[S9] 2-(*m*-tolyl)pyridine,[S10] 2-(3-methoxyphenyl)pyridine,[S10] 2-(3-(trifluoromethyl)phenyl)pyridine,[S10] 2-(cyclohex-1-en-1-yl)pyridine,[S11] 1-(pyrimidin-2-yl)-1*H*-indole,[S12] *N*-methoxybenzamide,[S13] (*E*)-1-phenylethan-1-one *O*-methyl oxime,[S14] phenyl vinyl

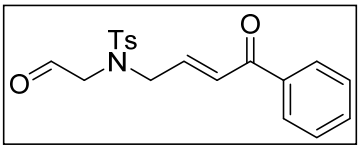
ketone,[S15] phenyl(pyrrolidin-1-yl)methanone,[S16] and (*E*)-ethyl-2-(tosylimino)acetate[S17] were synthesized according to literature procedure. All other C–H activation substrates were purchased from commercial sources and used without further purification.

Procedure for Synthesis of (*E*)-2-((4-Oxo-4-phenylbut-2-en-1-yl)oxy)acetaldehyde:



In a 500-mL round bottom flask equipped with a magnetic stir bar, 2,5-dihydrofuran (7.01 g, 0.100 mol, 10.0 equiv) was dissolved in 105 mL of CH_2Cl_2. The reaction mixture was cooled in a dry ice/acetone bath and ozone was bubbled in until a faint blue color persisted for 5 min. At this point the reaction mixture was purged with N_2 gas and kept under nitrogen for the duration of the reaction. Once the blue color had dissipated, triphenylphosphine (26.3 g, 0.100 mol, 10.0 equiv) was added, and the reaction mixture was placed in an ice/acetone bath and stirred for 1 h. At this point, (benzoylmethylene)triphenylphosphorane (3.81 g, 10.0 mmol, 1.00 equiv) was added and the reaction mixture was stirred for an additional 4 h. The reaction mixture was then warmed to ambient temperature and concentrated. The crude material was triturated with diethyl ether until no product remained in the residual solid as indicated by TLC. The combined ether washes were concentrated, dissolved in a minimal amount of CH_2Cl_2, and purified by silica gel chromatography using 1:1 ethyl acetate/hexane to obtain the aldehyde (**2f**) as a colorless oil (0.762 g, 37%). IR (film): 2856, 1734, 1671, 1624, 1282, 1017, 960.5, 765.0 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.98-7.96 (m, 2H), 7.60-7.56 (m, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.22 (dt, J = 15.5, 1.9 Hz, 1H), 7.04 (dt, 15.5, 4.1 Hz, 1H), 4.39 (dd, J = 4.1, 1.9 Hz, 2H), 4.21 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 199.62, 190.15, 142.71, 137.76, 133.14, 128.80, 125.92, 76.29, 70.92; HRMS (ESI/[M+H]+) calcd. for $C_{12}H_{12}O_3$: 205.0859 Found 205.0857.

Procedure for Synthesis of (*E*)-4-methyl-*N*-(4-oxo-4-phenylbut-2-en-1-yl)-*N*-(2-oxoethyl)benzenesulfonamide:



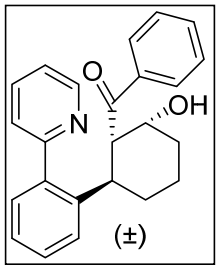
In a 500-mL round bottom flask equipped with a magnetic stir bar, 1-tosyl-2,5-dihydro-1*H*-pyrrole[S3] (3.90 g, 17.5 mol, 5.00 equiv) was dissolved in 60 mL of CH_2Cl_2. The reaction mixture was cooled in a dry ice/acetone bath and ozone was bubbled in until a faint blue color persisted for 5 min. At this point the reaction mixture was purged with N_2 gas and kept under nitrogen for the duration of the reaction. Once the blue color had dissipated, triphenylphosphine (26.3 g, 0.100 mol, 10.0 equiv) was added, and the reaction mixture was placed in an ice/acetone bath and stirred for 1 h. At this point, (benzoylmethylene)triphenylphosphorane (4.59 g, 17.5 mmol, 5.00 equiv) was added and the reaction mixture was stirred for an additional 4 h. The reaction mixture was then warmed to ambient temperature and concentrated. Afterwards the crude reaction product was dissolved in a minimal amount of CH_2Cl_2, and purified by a silica plug using 1:1 ethyl acetate/hexane to separate the desired product from triphenylphosphine oxide. The desired fractions were then concentrated and purified by four preparative TLC plates using a 40/60 mixture of ethyl acetate/hexane obtain the product as a pale yellow waxy solid (**2g**), likely the hydrate/oligomer (0.601 g, 48%). ^{1}H NMR (500 MHz, $CDCl_3$) crude shown in NMR Data Section; HRMS (ESI/[M+H]+) calcd. for $C_{19}H_{19}NO_4S$: 358.1108 Found 358.1115.

III. Procedures for Rh(III)-Catalyzed Tandem Addition/Cyclization:

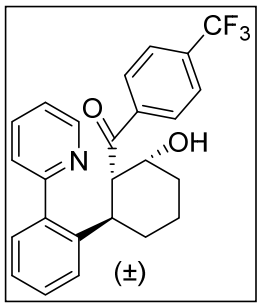
General Procedure:

In a N_2-filled glove box, a 2-5 mL microwave vial was charged with $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $[Cp^*RhCl_2]_2$[S1] (3.1 mg, 0.0050 mmol, 0.025 equiv), the corresponding aldehyde (0.20 mmol, 1.0 equiv), and the C–H activation substrate (0.40 mmol, 2.0 equiv). Acetic acid (1.0 mL) was then added and the vial was equipped with a stir bar. The reaction vial was sealed and then outside the glove box, the vial was heated at 50 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then cooled to room temperature, and filtered over a plug of celite (1 cm

celite in a glass pipette) with CH_2Cl_2. The filtrate then was concentrated and purified by flash column chromatography using an ethyl acetate/hexanes solvent system to afford the desired product.

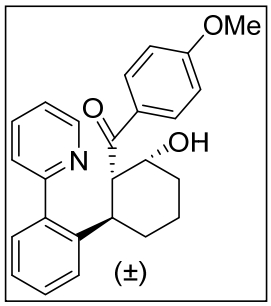


(±)-((1*S*,2*R*,6*R*)-2-Hydroxy-6-(2-(pyridin-2-yl)phenyl)cyclohexyl)(phenyl)methanone (3a): The general procedure using (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.0 equiv), and 2-phenylpyridine (62.1 mg, 0.400 mmol, 2.0 equiv) was followed. Chromatography eluting with a 1:2 solution of ethyl acetate/hexanes provided the product **3a** (70.1 mg, 98% yield) as a white solid (mp: 138-140 °C). IR (film): 3226, 2926, 2857, 1682, 1589, 996, 751, 702 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 8.70 (d, *J* = 4.3 Hz, 1H), 7.83 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.53-7.50 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.34-7.31 (m, 2H), 7.20-7.15 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.17 (s, 1H), 4.01 (d, *J* = 11.5 Hz, 1H), 3.74 (dt, *J* = 11.8, 3.5 Hz, 1H), 2.57 (s, 1H), 2.04 (apparent d, *J* = 11.0 Hz, 1H), 1.92 (apparent d, *J* = 13.1 Hz, 1H), 1.80-1.71 (m, 1H), 1.63 (apparent d, *J* = 13.6 Hz, 1H), 1.59-1.52 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): δ 204.30, 160.54, 149.48, 142.71, 141.65, 137.58, 136.37, 133.54, 130.49, 128.95, 128.54, 128.52, 126.67, 126.23, 124.81, 122.12, 67.51, 54.08, 35.97, 35.07, 32.55, 20.24; HRMS (ESI/[M+H]+) calcd. for $C_{24}H_{23}NO_2$: 358.1802 Found 358.1792.

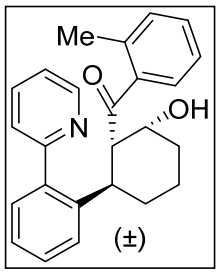


(±)-((1S,2R,6R)-2-Hydroxy-6-(2-(pyridin-2-yl)phenyl)cyclohexyl)(4-(trifluoromethyl)phenyl)methanone (3b): The general procedure using (*E*)-7-oxo-7-(4-(trifluoromethyl)phenyl)hept-5-enal[S5] (54.1 mg, 0.200 mmol, 1.00 equiv), and 2-phenylpyridine (62.1 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 1:1 solution of ethyl acetate/hexanes provided the product **3b** (76.6 mg, 90% yield) as a white solid (148-150 °C). IR (film): 3223, 2930, 1691, 1325, 1159, 1131, 1065, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.8 Hz, 1H), 7.84-7.79 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 6.8 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 4.20 (s, 1H), 3.94 (d, *J* = 11.8 Hz, 1H), 3.77 (dt, *J* = 11.9, 3.3 Hz, 1H), 2.85 (s, 1H), 2.09-2.05 (m, 1H), 1.99 (apparent d, *J* = 12.3 Hz, 1H), 1.86-1.77 (m, 1H), 1.60-1.55 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 126 MHz): δ 204.12, 159.84, 149.28, 141.40, 141.06, 140.09, 136.28, 134.35 (q, *J* = 32.7 Hz), 130.33, 128.52, 128.36, 126.39, 125.60 (q, *J* = 3.6 Hz), 124.47, 123.64

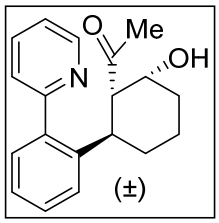
(q, J = 272.8 Hz), 121.97, 66.95, 54.41, 35.88, 34.43, 32.07, 19.75; ^{19}F NMR ($CDCl_3$, 470 MHz): δ -64.37 (s, 3F); HRMS (ESI/[M+H]+) calcd. for $C_{25}H_{22}F_3NO_2$: 426.1675 Found 426.1667.



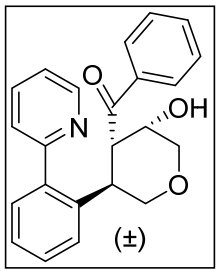
(±)-((1S,2R,6R)-2-Hydroxy-6-(2-(pyridin-2-yl)phenyl)cyclohexyl)(4-methoxyphenyl)methanone (3c): The general procedure using (*E*)-7-(methoxyphenyl)-7-oxohept-5-enal[S6] (46.5 mg, 0.200 mmol, 1.00 equiv), and 2-phenylpyridine (62.1 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 40/60 solution of ethyl acetate/hexanes provided the product **3c** (68.5 mg, 88% yield) as a white solid (mp: 140-142 °C). IR (film): 3458, 2932, 2858, 1673, 1598, 1253, 1170, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.1 Hz, 1H), 7.82-7.78 (m, 3H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.34-7.32 (m, 1H), 7.30-7.28 (m, 1H), 7.21-7.14 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.14 (s, 1H), 3.95 (d, *J* = 11.5 Hz, 1H), 3.83 (s, 3H), 3.76 (dt, *J* = 11.9, 3.5 Hz, 1H), 3.14 (s, 1H), 2.03-1.95 (m, 2H), 1.80 (apparent q, *J* = 14.3 Hz, 1H), 1.58-1.50 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$), 101 MHz): δ 203.09, 163.86, 149.31, 141.71, 141.09, 136.15, 130.81, 130.58, 130.20, 130.00, 128.24, 126.15, 124.59, 121.86, 113.81, 113.63, 67.11, 55.61, 52.74, 35.71, 34.76, 31.95, 19.90; HRMS (ESI/[M+H]+) calcd. for $C_{25}H_{25}NO_3$: 388.1907 Found 388.1897.



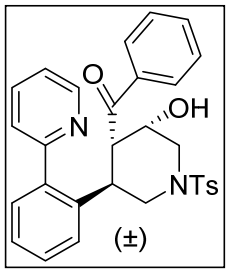
(±)-((1S,2R,6R)-2-Hydroxy-6-(2-(pyridin-2-yl)phenyl)cyclohexyl)(*o*-tolyl)methanone (3d): A modification to the general procedure was used. (*E*)-7-oxo-7-(*o*-tolyl)hept-5-enal[S7] (43.3 mg, 0.200 mmol, 1.00 equiv), and 2-phenylpyridine (62.1 mg, 0.400 mmol, 2.00 equiv) was added and stirred at 40 °C instead of 50 °C for 20 h. Chromatography eluting with a 40/60 solution of ethyl acetate/hexanes provided the product **3d** (66.2 mg, 89% yield) as a white solid (mp: 58-60 °C). IR (film): 3497, 2928, 2858, 1690, 1426, 994, 749, 730 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.7 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.30-7.28 (m, 3H), 7.20-7.13 (m, 3H), 7.08 (t, *J* = 8.7 Hz, 2H), 4.31 (s, 1H), 3.81 (d, *J* = 11.7 Hz, 1H), 3.69 (dt, *J* = 11.8, 3.2 Hz, 1H), 3.15 (s, 1H), 2.06 (apparent d, *J* = 12.7 Hz, 1H), 1.99 (s, 3H), 1.99-1.96 (m, 1H), 1.83-1.75 (m, 1H), 1.56-1.46 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$), 126 MHz): δ 209.92, 159.90, 149.37, 141.28, 141.17, 139.63, 137.85, 136.25, 131.63, 131.16, 130.22, 128.14, 127.49, 126.72, 126.26, 125.49, 124.48, 121.92, 67.36, 56.84, 36.45, 35.17, 31.98, 20.00, 19.89; HRMS (ESI/[M+H]+) calcd. for $C_{25}H_{25}NO_2$: 372.1958 Found 372.1968.



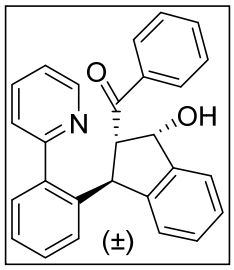
(±)-1-((1S,2R,6R)-2-Hydroxy-6-(2-(pyridin-2-yl)phenyl)cyclohexyl)ethan-1-one (3e): The general procedure using (*E*)-7-oxooct-5-enal[S8] (28.0 mg, 0.200 mmol, 1.00 equiv), and 2-phenylpyridine (62.1 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 70/30 solution of ethyl acetate/hexanes provided the product **3e** (36.1 mg, 61% yield) as an off-white solid (mp: 46-47 °C). IR (film): 3452, 2929, 1692, 1585, 1425, 1083, 795, 749 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.8 Hz, 1H), 7.75 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.43-7.37 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.28-7.24 (m, 2H), 4.16 (s, 1H), 3.50 (dt, *J* = 11.9, 3.3 Hz, 1H), 3.16 (s, 1H), 2.99 (d, *J* = 11.6 Hz, 1H), 1.97 (apparent d, *J* = 12.0 Hz, 1H), 1.89 (apparent d, *J* = 14.0 Hz, 1H), 1.80 (s, 3H), 1.77-1.69 (m, 1H), 1.52-1.41 (m, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 214.74, 159.61, 149.29, 141.86, 141.10, 136.23, 130.45, 128.61, 126.50, 124.34, 121.96, 66.62, 59.08, 35.63, 34.63, 32.15, 31.93, 19.73; HRMS (ESI/[M+H]+) calcd. for $C_{19}H_{21}NO_2$: 296.1645 Found 296.1626.



(±)-((3S,4S,5R)-3-Hydroxy-5-(2-(pyridin-2-yl)phenyl)tetrahydro-2*H*-pyran-4-yl)(phenyl)methanone (3f): The general procedure using (*E*)-2-((4-oxo-4-phenylbut-2-en-1-yl)oxy)acetaldehyde (40.8 mg, 0.200 mmol, 1.00 equiv), and 2-phenylpyridine (62.1 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 70/30 solution of ethyl acetate/hexanes provided the product **3f** (57.7 mg, 80% yield) as a white solid (mp: 179-181 °C). IR (film): 3365, 2962, 1674, 1587, 1092, 1023, 758, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.5 Hz, 1H), 7.87-7.84 (m, 3H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.34-7.31 (m, 2H), 7.28-7.27 (m, 1H), 7.25-7.24 (m, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.21 (dd, *J* = 11.7, 2.9 Hz, 2H), 4.09 (s, 1H), 4.03-3.99 (m, 2H), 3.71 (d, *J* = 12.0 Hz, 1H), 3.45 (t, *J* = 11.4 Hz, 1H), 2.71 (s, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz): δ 200.37, 159.56, 149.23, 142.02, 136.83, 136.77, 136.48, 133.50, 130.63, 128.87, 128.57, 128.33, 127.03, 126.25, 124.65, 122.31, 72.88, 72.04, 66.58, 51.36, 34.89; HRMS (ESI/[M+H]+) calcd. for $C_{23}H_{21}NO_3$: 360.1594 Found 360.1584.

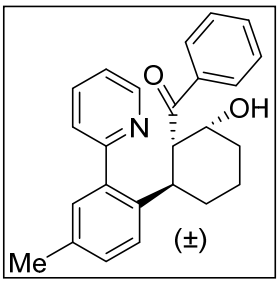


(±)-((3S,4S,5R)-3-Hydroxy-5-(2-(pyridin-2-yl)phenyl)-1-tosylpiperidin-4-yl)(phenyl)methanone (3g): A modification to the general procedure was used. ((*E*)-4-methyl-*N*-(4-oxo-4-phenylbut-2-en-1-yl)-*N*-(2-oxoethyl)benzenesulfonamide (71.5 mg, 0.200 mmol, 1.00 equiv), and 2-phenylpyridine (62.1 mg, 0.400 mmol, 2.00 equiv) was added, followed by the addition of a 95:5 acetic acid/water mixture (1.00 mL) instead of acetic acid. Chromatography eluting with a 40/60 solution of ethyl acetate/hexanes provided the product **3g** (46.1 mg, 45% yield) as an off-white solid (mp: 110-112 °C). IR (film): 3513, 3066, 1729, 1683, 1596, 1157, 753, 679 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 3.6 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.65-7.62 (m, 3H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.32-7.29 (m, 4H), 7.22-7.16 (m, 3H), 4.30 (d, *J* = 11.1 Hz, 1H), 4.25 (d, *J* = 5.2 Hz, 1H), 3.98-3.89 (m, 3H), 2.71 (d, *J* = 12.2 Hz 1H), 2.53 (d, *J* = 7.0 Hz, 1H), 2.45 (s, 3H), 2.43-2.39 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 199.30, 159.51, 149.43, 143.73, 142.17, 137.69, 136.73, 136.38, 133.91, 133.42, 130.59, 129.84, 128.86, 128.46, 128.18, 127.89, 127.14, 124.21, 122.26, 65.95, 51.90, 51.81, 51.75, 34.60, 21.71; HRMS (ESI/[M+H]+) calcd. For $C_{30}H_{28}N_2O_4S$: 513.1843 Found 513.1853.

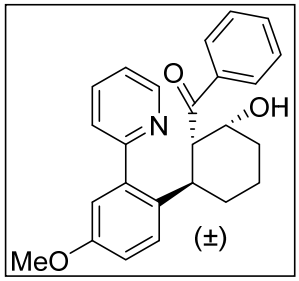


(±)-((1S,2S,3R)-1-Hydroxy-3-(2-(pyridin-2-yl)phenyl)-2,3-dihydro-1*H*-inden-2-yl)(phenyl)methanone (3h): A modification to the general procedure was used. A 2-5 mL microwave vial was charged with $[Cp^*RhCl_2]_2$[S1] (12.4 mg, 0.200 mmol, 1.00 equiv), $AgSbF_6$ (13.7 mg, 0.400 mmol, 2.00 equiv), (*E*)-2-(3-oxo-3-phenylprop-1-en-1-yl)benzaldehyde[S9] (47.3 mg, 0.20 mmol, 1.0 equiv), and 2-phenylpyridine (62.1 mg, 0.40 mmol, 2.0 equiv), followed by the addition of a 3:2 dioxane/water mixture (1.00 ml) instead of acetic acid. The reaction mixture was stirred at 40 °C instead of 50 °C for 20 h. Chromatography with a 1:1 solution of ethyl acetate/hexanes provided the product **3h** (39.0 mg, 50% yield) as a white solid (mp: 183-185 °C). IR (film): 3252, 3063, 1668, 1591, 1363, 1061, 754, 706 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 4.3 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39-7.33 (m, 4H), 7.32-7.28 (m, 3H), 7.26-7.24 (m, 2H), 7.11 (dd, *J* = 7.6, 4.9 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 5.47 (t, *J* = 6.1 Hz, 1H), 5.08 (d, *J* = 7.0 Hz, 1H), 4.40 (t, *J* = 6.2 Hz, 1H), 2.53 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 151 MHz): δ 199.98, 159.40, 148.82, 145.09, 143.14, 142.18, 141.19, 137.12, 136.24, 133.14, 129.91, 129.21, 129.09, 128.93, 128.48,

127.61, 126.85, 125.75, 124.28, 124.12, 121.87, 78.79, 67.05, 48.82; HRMS (ESI/[M+H]+) calcd. for $C_{27}H_{21}NO_2$: 392.1645 Found 392.1624.

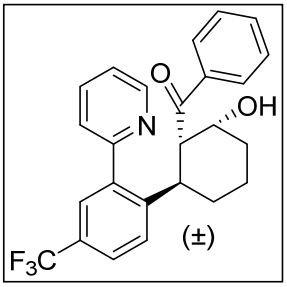


(±)-((1S,2R,6R)-2-Hydroxy-6-(4-methyl-2-(pyridin-2-yl)phenyl)cyclohexyl)(phenyl)methanone (3i): The general procedure using (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.00 equiv), and 2-(*m*-tolyl)pyridine[S10] (67.7 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 40/60 solution of ethyl acetate/hexanes provided the product **3i** (70.5 mg, 95% yield) as a white solid (63-65 °C). IR (film): 3495, 2929, 2859, 1681, 1588, 1200, 993, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.8 Hz, 1H), 7.81-7.79 (m, 3H), 7.55-7.50 (m, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.28 (ddd, *J* = 8.0, 5.2, 1.4 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.03 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 4.18 (s, 1H), 4.00 (d, *J* = 11.4 Hz, 1H), 3.72 (dt, *J* = 11.8, 3.2 Hz, 1H), 2.90 (s, 1H), 2.20 (s, 3H), 1.98 (apparent t, *J* = 11.0 Hz, 2H), 1.82-1.73 (m, 1H), 1.61-1.53 (m, 2H), 1.52-1.46 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 151 MHz): δ 204.83, 159.97, 149.38, 140.88, 138.57, 137.14, 136.10, 135.65, 133.33, 130.85, 129.04, 128.63, 128.37, 126.10, 124.54, 121.82, 67.05, 53.55, 35.27, 34.92, 31.99, 20.94, 19.91; HRMS (ESI/[M+H]+) calcd. for $C_{25}H_{25}NO_2$: 372.1958 Found 372.1938.

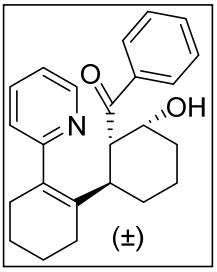


(±)-((1S,2R,6R)-2-Hydroxy-6-(4-methoxy-2-(pyridin-2-yl)phenyl)cyclohexyl)(phenyl)methanone (3j): The general procedure using (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.00 equiv), and 2-(3-methoxyphenyl)pyridine[S10] (74.1 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 40/60 solution of ethyl acetate/hexanes provided the product **3j** (69.7 mg, 90% yield) as a white solid (mp: 59-61 °C). IR (film): 3482, 2932, 1680, 1589, 1470, 1214, 791, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.2 Hz, 1H), 7.84-7.78 (m, 3H), 7.53-7.49 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 6.74 (d, *J* = 2.7 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.7 Hz, 1H), 4.17 (s, 1H), 3.96 (d, *J* = 11.4 Hz, 1H), 3.69 (s, 3H), 3.68-3.63 (m, 1H), 2.99 (s, 1H), 1.99-1.95 (m, 2H), 1.82-1.73 (m, 1H), 1.57-1.46 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 151 MHz): δ 205.08, 159.67, 157.50, 149.32, 142.01, 137.18, 136.25, 133.79,

133.37, 128.64, 128.33, 127.45, 124.52, 122.04, 114.82, 114.67, 67.04, 55.36, 53.65, 35.13, 34.94, 31.95, 19.90; HRMS (ESI/[M+H]+) calcd. for $C_{25}H_{25}NO_3$: 388.1907 Found 388.1886.

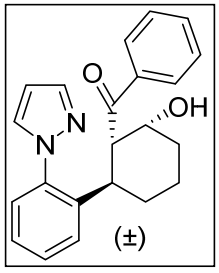


(±)-((1S,2R,6R)-2-Hydroxy-6-(2-(pyridin-2-yl)-4-(trifluoromethyl)phenyl)cyclohexyl)(phenyl)methanone (3k): The general procedure using (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.00 equiv), and 2-(3-(trifluoromethyl)phenyl)pyridine[S10] (89.3 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 40/60 solution of ethyl acetate/hexanes provided the product **3k** (76.9 mg, 90% yield) as a white solid (mp: 64-66 °C). IR (film): 3483, 2935, 1681, 1337, 1165, 1117, 1079, 688 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.8 Hz, 1H), 7.86 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49 (s, 1H), 7.41-7.34 (m, 5H), 4.24 (s, 1H), 4.01 (d, *J* = 11.6 Hz, 1H), 3.81 (dt, *J* = 11.8, 3.2 Hz, 1H), 2.67 (s, 1H), 2.06-2.03 (m, 1H), 2.00-1.97 (m, 1H), 1.82-1.73 (m, 1H), 1.64-1.57 (m, 2H), 1.50 (apparent dq, *J* = 12.9, 3.4 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 151 MHz): δ 203.98, 158.49, 149.53, 146.10, 141.63, 136.87, 136.60, 133.64, 128.81, 128.42 (q, *J* = 32.6 Hz), 128.23, 127.22 (q, *J* = 3.7 Hz), 126.60, 125.03 (q, *J* = 3.6 Hz), 124.58, 124.057 (q, *J* = 272.0 Hz), 122.53, 67.06, 53.59, 35.70, 34.57, 32.04, 19.79; ^{19}F NMR ($CDCl_3$, 470 MHz): δ -63.73 (s, 3F); HRMS (ESI/[M+H]+) calcd. for $C_{25}H_{22}F_3NO_2$: 426.1675 Found 426.1659.

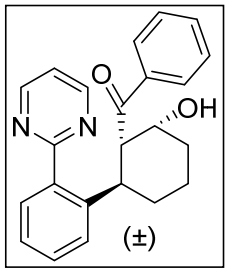


(±)-((1R,2S,3R)-3-Hydroxy-2'-(pyridin-2-yl)-[1,1'-bi(cyclohexan)]-1'-en-2-yl)(phenyl)methanone (3l): The general procedure using (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.00 equiv), and 2-(cyclohex-1-en-1-yl)pyridine[S11] (63.7 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 40/60 solution of ethyl acetate/hexanes provided the product **3l** (57.9 mg, 80% yield) as a pale yellow solid (47-49 °C). IR (film): 3462, 2928, 2857, 1682, 1585, 1446, 1000, 780 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 8.58 (d, *J* = 4.8 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.70 (dt, *J* = 7.6, 1.8 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.16 (dd, *J* = 7.4, 5.0 Hz, 1H), 4.10 (s, 1H), 3.62 (d, *J* = 11.4 Hz, 1H), 3.20 (dt, *J* = 11.7, 2.7 Hz, 1H), 3.12 (s, 1H), 2.12-2.04 (m, 3H), 1.81 (apparent d, *J* = 13.6 Hz, 1H), 1.74-1.69 (m, 1H), 1.67-1.61 (m, 2H), 1.55-1.50 (m, 1H), 1.49-1.45 (m, 2H), 1.43-1.38 (m, 2H), 1.26-1.19 (m, 1H), 1.06-0.99 (m, 1H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), 126 MHz): δ 205.98,

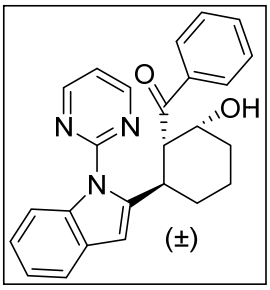
162.31, 149.45, 138.22, 136.08, 135.20, 134.98, 133.48, 129.03, 128.49, 123.61, 121.45, 67.11, 50.39, 37.94, 32.17, 31.10, 30.74, 25.06, 23.06, 22.77, 19.60; HRMS (ESI/[M+H]+) calcd. for $C_{24}H_{27}NO_2$: 362.2115 Found 362.2104.



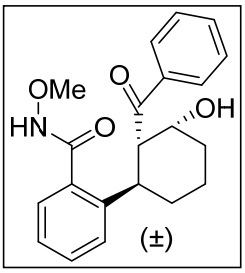
(±)-((1S,2R,6R)-2-(2-(1*H*-Pyrazol-1-yl)phenyl)-6-hydroxycyclohexyl)(phenyl)methanone (3m): The general procedure using (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.00 equiv), and 1-phenyl-1*H*-pyrazole (57.7 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 40/60 solution of ethyl acetate/hexanes provided the product **3m** (57.0 mg, 82% yield) as a white solid (mp: 56-58 °C). IR (film): 3490, 2931, 1679, 1396, 1201, 938, 758, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83-7.81 (m, 3H), 7.75 (s, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.50 (s, 1H), 4.23 (s, 1H), 4.00 (d, *J* = 11.5 Hz, 1H), 3.44 (dt, *J* = 11.7, 3.4 Hz, 1H), 2.64 (s, 1H), 2.02-1.97 (m, 2H), 1.85-1.76 (m, 1H), 1.61-1.56 (m, 2H), 1.48-1.41 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 126 MHz): δ 203.86, 140.68, 140.42, 139.85, 136.79, 133.53, 131.79, 128.84, 128.76, 128.31, 128.19, 127.50, 126.86, 106.33, 67.04, 53.38, 34.64, 33.88, 32.05, 19.83; HRMS (ESI/[M+H]+) calcd. for $C_{22}H_{22}N_2O_2$: 347.1754 Found 347.1747.



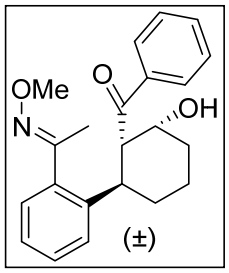
(±)-((1S,2R,6R)-2-Hydroxy-6-(2-(pyrimidin-2-yl)phenyl)cyclohexyl)(phenyl)methanone (3n): The general procedure using (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.00 equiv), and 2-phenylpyrimidine (62.5 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 1:1 solution of ethyl acetate/hexanes provided the product **3n** (52.1 mg, 71% yield) as a white solid (mp: 120-122 °C). IR (film): 3242, 2930, 1685, 1557, 1414, 748, 685, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.8 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.32-7.27 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.27 (t, *J* = 11.1 Hz, 1H), 4.18 (s, 1H), 3.91 (d, *J* = 10.6 Hz, 1H), 3.19 (s, 1H), 2.23 (apparent d, *J* = 11.1 Hz, 1H), 2.03-1.95 (m, 2H), 1.70-1.63 (m, 2H), 1.60-1.57 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 151 MHz): δ 205.25, 167.75, 156.99, 142.58, 138.84, 137.28, 133.14, 130.87, 129.28, 128.42, 128.24, 128.06, 126.21, 118.76, 67.03, 53.96, 35.45, 33.97, 32.02, 19.89; HRMS (ESI/[M+H]+) calcd. for $C_{23}H_{22}N_2O_2$: 359.1754 Found 359.1744.



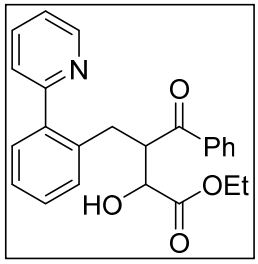
(±)-((1S,2R,6R)-2-Hydroxy-6-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)cyclohexyl)(phenyl)methanone (3o): The general procedure using (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.00 equiv), and 1-(pyrimidin-2-yl)-1*H*-indole[S12] (78.1 mg, 0.400 mmol, 2.00 equiv) was followed. Chromatography eluting with a 1:1 solution of ethyl acetate/hexanes provided the product **3o** (38.4 mg, 48% yield) as an off-white solid (68-70 °C). IR (film): 3462, 2932, 1679, 1563, 1454, 1420, 746, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.8 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.33 (apparent t, *J* = 7.9 Hz, 3H), 7.21 (t, J = 4.8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.40 (s, 1H), 4.65 (dt, *J* = 11.7, 3.2 Hz, 1H), 4.25 (s, 1H), 3.97 (d, *J* = 11.5 Hz, 1H), 3.01 (s, 1H), 2.32 (apparent d, *J* = 13.8 Hz, 1H), 2.07-1.95 (m, 2H), 1.67-1.58 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 126 MHz): δ 204.37, 158.35, 158.12, 144.95, 136.70, 136.67, 133.40, 128.91, 128.58, 128.31, 122.70, 121.62, 119.76, 117.62, 113.53, 104.06, 67.20, 54.40, 33.98, 32.72, 32.12, 19.91; HRMS (ESI/[M+H]+) calcd. for $C_{25}H_{23}N_3O_2$: 398.1863 Found 398.1848.



(±)-2-((1R,2S,3R)-2-Benzoyl-3-hydroxycyclohexyl)-*N*-methoxybenzamide (3p): A modification to the general procedure was used. (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.00 equiv), and *N*-methoxybenzamide[S13] (60.5 mg, 0.400 mmol, 2.00 equiv) was added, followed by the addition of a 3:2 mixture of dioxane/water (0.500 mL) instead of acetic acid. Chromatography eluting with a 70/30 solution of ethyl acetate/hexanes provided the product **3p** (35.4 mg, 50% yield) as a white solid (mp: 71-73 °C). IR (film): 3435, 3212, 2933, 1658, 1597, 1447, 1030, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.24-7.20 (m, 2H), 7.14 (t, *J* = 7.0 Hz, 1H), 4.38 (s, 1H), 4.07 (d, *J* = 10.2 Hz, 1H), 4.02 (s, 3H), 3.83 (t, *J* = 10.8 Hz, 1H), 2.00 (apparent t, *J* = 15.9 Hz, 2H), 1.91-1.88 (m, 1H), 1.74 (apparent t, *J* = 13.8 Hz, 1H), 1.66-1.63 (m, 2H), 1.51-1.44 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 126 MHz): δ 204.02, 167.94, 141.81, 136.09, 134.18, 133.99, 130.49, 128.99, 128.58, 128.51, 126.65, 125.41, 67.83, 64.37, 55.34, 35.34, 35.21, 32.84, 19.93; HRMS (ESI/[M+H]+) calcd. for $C_{21}H_{23}NO_4$: 354.1700 Found 354.1706.



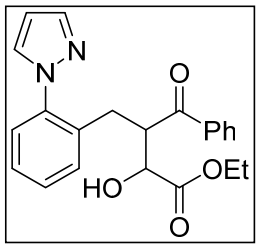
(±)-((1S,2R,6R)-2-Hydroxy-6-(2-((*E*)-1-(methoxyimino)ethyl)phenyl)cyclohexyl)(phenyl)methanone (3q): A modification to the general procedure was used. (*E*)-7-oxo-7-phenylhept-5-enal[S4] (40.5 mg, 0.200 mmol, 1.00 equiv), and (*E*)-1-phenylethan-1-one *O*-methyl oxime[S14] (59.7 mg, 0.400 mmol, 2.00 equiv) was added, followed by the addition of a 3:2 mixture of dioxane/water (1.00 mL) instead of acetic acid. Chromatography eluting with a 20/80 solution of ethyl acetate/hexanes provided the product **3q** (24.2 mg, 34% yield) as a waxy white solid. IR (film): 3462, 2934, 1682, 1597, 1446, 1201, 1041, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.51-7.46 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.07-7.00 (m, 3H), 4.26 (s, 1H), 4.02-3.99 (m, 1H), 3.99 (s, 3H), 3.75 (dt, *J* = 11.8, 3.3 Hz, 1H), 3.08 (s, 1H), 2.28 (s, 3H), 2.06 (apparent d, *J* = 12.7 Hz, 2H), 2.01-1.94 (m, 1H), 1.65-1.60 (m, 2H), 1.55-1.47 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 151 MHz): δ 204.57, 157.06, 141.97, 137.82, 137.10, 133.38, 128.65, 128.55, 128.38, 128.31, 128.26, 126.24, 67.05, 61.89, 53.45, 36.26, 34.97, 32.08, 19.85, 16.85; HRMS (ESI/[M+H]+) calcd. for $C_{22}H_{25}NO_3$: 352.1907 Found 352.1905.



Ethyl-2-hydroxy-4-oxo-4-phenyl-3-(2-(pyridin-2-yl)benzyl)butanoate (3r): In a N_2-filled glove box, a 2-5 mL microwave vial was charged with $AgSbF_6$ (13.8 mg, 0.0402 mmol, 0.200 equiv), $[Cp^*RhCl_2]_2$[S1] (6.2 mg, 0.010 mmol, 0.050 equiv), 2-phenylpyridine (31.0 mg, 0.200 mmol, 1.0 equiv), phenyl vinyl ketone[S15] (29.1 mg, 0.220 mmol, 1.1 equiv), and ethyl glyoxylate (40.8 mg, 0.400 mmol, 2.0 equiv). Acetic acid (0.1 mL) was then added and the vial was equipped with a stir bar. The reaction vial was sealed and then outside the glove box, the vial was heated at 40 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then filtered over a plug of celite (1 cm celite in a glass pipette) eluting with CH_2Cl_2 and concentrated. Chromatography eluting with a 40/60 solution of ethyl acetate/hexanes provided the product as a mixture of diastereomers **3r** as a colorless oil. The mixture was then separated by preparatory TLC using 70/30 ethyl ether/pentane to obtain the diastereomer with higher R_f (31.7 mg) as a colorless oil and the diastereomer with lower R_f (31.5 mg) as a colorless oil (63.2 mg total, 1:1 dr, 81% yield).

Diastereomer 1 (Higher R_f): IR (film): 3527, 3064, 2983, 1741, 1678, 1208, 1024, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.3 Hz, 1H), 7.82 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 2H), 7.53-7.45 (m, 3H), 7.37-7.30 (m, 6H), 4.27 (dt, *J* = 7.7, 3.2 Hz, 1H), 4.24 (d, *J* = 3.2 Hz, 1H), 3.90 (q, *J* = 6.8 Hz, 2H), 3.26 (d, *J* = 7.6 Hz, 2H), 1.03 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 203.33, 173.23, 159.89, 148.87, 140.39, 137.28, 136.97, 136.51, 133.32, 131.43, 130.54, 128.95, 128.57, 128.56, 127.11, 124.71, 122.23, 71.03, 61.33, 50.42, 31.59, 14.02; HRMS (ESI/[M+H]+) calcd. for $C_{24}H_{23}NO_4$: 390.1700 Found 390.1701.

Diastereomer 2 (Lower R_f): IR (film): 3507, 3062, 2983, 1729, 1679, 1206, 1024, 726 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.5 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.83 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46-7.43 (m, 3H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.34-7.31 (m, 3H), 7.28-7.27 (m, 1H), 6.77 (s, 1H), 4.64 (d, *J* = 4.2 Hz, 1H), 4.49 (dt, *J* = 9.3, 4.5 Hz, 1H), 3.79 (q, *J* = 7.1 Hz, 2H), 3.42 (dd, *J* = 14.5, 9.7 Hz, 1H), 3.03 (dd, *J* = 14.5, 4.8 Hz, 1H), 1.08 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 201.10, 173.25, 159.46, 148.13, 140.01, 137.63, 136.70, 136.23, 133.18, 131.06, 130.50, 128.79, 128.73, 128.58, 126.83, 124.99, 122.25, 71.97, 61.46, 51.76, 29.87, 13.99; HRMS (ESI/[M+H]+) calcd. for $C_{24}H_{23}NO_4$: 390.1700 Found 390.1710.

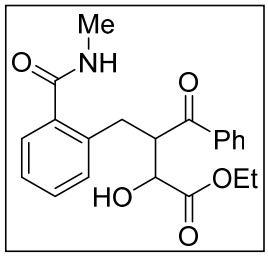


Ethyl-3-(2-(1H-pyrazol-1-yl)benzyl)-2-hydroxy-4-oxo-4-phenylbutanoate (3s):

In a N_2-filled glove box, a 2-5 mL microwave vial was charged with $AgSbF_6$ (13.8 mg, 0.0402 mmol, 0.201 equiv), $[Cp^*RhCl_2]_2$[S1] (6.2 mg, 0.010 mmol, 0.050 equiv), 1-phenylpyrazole (28.8 mg, 0.200 mmol, 1.00 equiv), phenyl vinyl ketone[S15] (29.1 mg, 0.220 mmol, 1.10 equiv), and ethyl glyoxylate (40.8 mg, 0.400 mmol, 2.00 equiv). Acetic acid (0.1 mL) was then added and the vial was equipped with a stir bar. The reaction vial was sealed and then outside the glove box, the vial was heated at 50 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then filtered over a plug of celite (1 cm celite in a glass pipette) eluting with CH_2Cl_2 and concentrated. Chromatography eluting with a 30/70 solution of ethyl acetate/hexanes provided two separate diastereomers, with the higher R_f diastereomer pure as a colorless waxy solid (26.2 mg). The lower R_f diastereomer was further purified by preparatory TLC using 4:1 dichloromethane/diethyl ether to obtain the lower R_f diastereomer (25.9 mg) as a colorless waxy solid (52.1 mg total, 1:1 dr, 69% yield).

Diastereomer 1 (Higher R_f): IR (film): 3490, 1739, 1679, 1394, 1211, 1022, 938, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77-7.76 (m, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.54-7.51 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.35-7.29 (m, 2H), 7.28-7.27 (m, 1H), 6.51 (t, *J* = 2.1 Hz, 1H), 4.18-4.15 (m, 2H), 4.12-4.11 (m, 1H), 3.94 (q, *J* = 7.1 Hz, 2H), 3.18 (dd, *J* = 13.5, 5.6 Hz, 1H), 3.07 (dd, J = 13.5, 9.7 Hz, 1H), 1.04 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 203.84, 173.13, 140.89, 140.00, 136.54, 134.20, 133.60, 132.57, 131.08, 128.94, 128.81, 128.57, 127.90, 126.74, 106.95, 71.10, 61.48, 49.07, 31.07, 14.01; HRMS (ESI/[M+H]+) calcd. for $C_{22}H_{22}N_2O_4$: 379.1652 Found 379.1641.

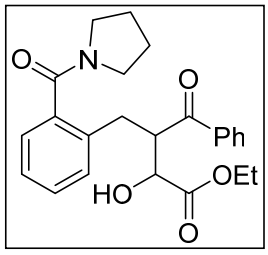
Diastereomer 2 (Lower R_f): IR (film): 3492, 1729, 1677, 1395, 1211, 1022, 938, 759 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.37-7.35 (m, 1H), 7.28-7.25 (m, 2H), 7.24-7.21 (m, 1H), 6.48 (t, *J* = 2.2 Hz, 1H), 4.45 (d, *J* = 4.5 Hz, 1H), 4.31 (s, 1H), 4.23 (dt, *J* = 7.3, 4.8 Hz, 1H), 4.01-3.89 (m, 2H), 3.18 (dd, *J* = 14.2, 7.9 Hz, 1H), 3.12 (dd, *J* = 14.2, 6.8 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 201.10, 173.11, 140.72, 139.94, 136.48, 134.65, 133.32, 132.05, 131.14, 128.72, 128.70, 128.59, 127.59, 126.55, 106.88, 71.44, 61.87, 50.74, 29.58, 14.02; HRMS (ESI/[M+H]+) calcd. for $C_{22}H_{22}N_2O_4$: 379.1652 Found 379.1639.



Ethyl-2-hydroxy-3-(2-(methylcarbamoyl)benzyl)-4-oxo-4-phenylbutanoate (3t): In a N_2-filled glove box, a 2-5 mL microwave vial was charged with $AgSbF_6$ (13.8 mg, 0.0402 mmol, 0.201 equiv), $[Cp^*RhCl_2]_2$[S1] (6.2 mg, 0.010 mmol, 0.050 equiv), N-methylbenzamide (27.1 mg, 0.200 mmol, 1.00 equiv), phenyl vinyl ketone[S15] (29.1 mg, 0.220 mmol, 1.10 equiv), and ethyl glyoxylate (40.8 mg, 0.400 mmol, 2.00 equiv). Acetic acid (0.1 mL) was then added and the vial was equipped with a stir bar. The reaction vial was sealed and then outside the glove box, the vial was heated at 50 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then filtered over a plug of celite (1 cm celite in a glass pipette) eluting with CH_2Cl_2 and concentrated. Chromatography eluting with a 95:5 solution of methyl *tert*-butyl ether/hexanes provided the product as a mixture of diastereomers **3t** as a colorless waxy solid. The mixture was then separated by preparatory TLC using 2:1 dichloromethane/ethyl acetate to obtain the diastereomer with higher R_f (20.1 mg) as a colorless waxy solid and the diastereomer with lower R_f (19.9 mg) as a colorless waxy solid (40.0 mg total, 1:1 dr, 54% yield).

Diastereomer 1 (Higher R_f): IR (film): 3348, 1737, 1632, 1597, 1447, 1210, 1093, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.21 (s, 1H), 4.53 (t, *J* = 6.3 Hz, 1H), 4.21 (s, 1H), 4.15 (s, 1H), 4.02-3.93 (m, 2H), 3.28 (dd, *J* = 13.5, 6.4 Hz, 1H), 3.16 (dd, J = 13.5, 9.3 Hz, 1H), 3.01 (d, *J* = 4.8 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 203.98, 173.11, 170.77, 137.15, 136.79, 136.33, 133.65, 131.57, 130.22, 128.89, 128.72, 127.39, 127.06, 71.29, 61.53, 50.11, 32.58, 26.89, 14.06; HRMS (ESI/[M+H]+) calcd. for $C_{21}H_{23}NO_5$: 370.1649 Found 370.1643.

Diastereomer 2 (Lower R_f): IR (film): 3371, 1737, 1631, 1597, 1447, 1210, 1096, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.3 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 3.9 Hz, 2H), 7.17-7.13 (m, 1H), 6.31 (s, 1H), 4.55-4.50 (m, 2H), 4.19 (s, 1H), 3.98-3.87 (m, 2H), 3.26 (dd, *J* = 14.0, 7.0 Hz, 1H), 3.20 (dd, *J* = 14.0, 7.0 Hz, 1H), 3.00 (d, *J* = 4.9 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 201.47, 173.00, 170.93, 137.19, 136.65, 133.38, 131.17, 129.87, 128.76, 128.72, 127.31, 126.81, 71.57, 61.90, 51.40, 30.94, 26.88, 14.02; HRMS (ESI/[M+H]+) calcd. for $C_{21}H_{23}NO_5$: 370.1649 Found 370.1648.

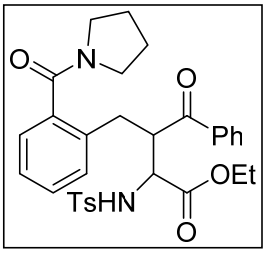


Ethyl-2-hydroxy-4-oxo-4-phenyl-3-(2-(pyrrolidine-1-carbonyl)benzyl)butanoate (3u): In a N_2-filled glove box, a 2-5 mL microwave vial was charged with $AgSbF_6$ (13.8 mg, 0.0402 mmol, 0.200 equiv), $[Cp^*RhCl_2]_2$[S1] (6.2 mg, 0.010 mmol, 0.050 equiv), phenyl(pyrrolidin-1-yl)methanone[S16] (35.1 mg, 0.200 mmol, 1.00 equiv), phenyl vinyl ketone[S15] (29.1 mg, 0.220 mmol, 1.10 equiv), and ethyl glyoxylate (40.8 mg, 0.400 mmol, 2.00 equiv). Acetic acid (0.1 mL) was then added and the vial was equipped with a stir bar. The reaction vial was sealed and then outside the glove box, the vial was heated at 60 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then filtered over a plug of celite (1 cm celite in a glass pipette) eluting with CH_2Cl_2 and concentrated. Chromatography eluting with a 1:1 solution of ethyl acetate/hexanes provided the product as a mixture of diastereomers **3u** as a colorless waxy solid. The mixture was then separated by preparatory TLC using 4:1 dichloromethane/ethyl acetate to obtain the diastereomer with higher R_f (32.9 mg) as a colorless

waxy solid and the diastereomer with lower R_f (27.4 mg) as a colorless waxy solid (60.3 mg total, 1.2:1 dr, 74% yield).

Diastereomer 1 (Higher R_f): IR (film): 3400, 1742, 1681, 1615, 1595, 1448, 1210, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46-7.42 (m, 3H), 7.29-7.24 (m, 3H), 4.44-4.40 (m, 1H), 4.18 (s, 1H), 4.02-3.93 (m, 2H), 3.72 (dt, *J* = 13.3, 6.9 Hz, 1H), 3.64 (dt, *J* = 12.5, 6.8 Hz, 1H), 3.16-3.04 (m, 4H), 1.99-1.81 (m, 4H), 1.03 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 203.91, 173.17, 169.80, 138.06, 136.63, 134.69, 133.64, 131.55, 129.23, 128.98, 128.73, 127.09, 126.39, 70.91, 61.44, 49.87, 48.93, 45.76, 32.60, 26.17, 24.69, 14.05; HRMS (ESI/[M+H]+) calcd. for $C_{24}H_{27}NO_5$: 410.1962 Found 410.1967.

Diastereomer 2 (Lower R_f): IR (film): 3326, 1732, 1677, 1610, 1595, 1447, 1209, 727 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.20-7.15 (m, 4H), 4.49 (t, *J* = 5.9 Hz, 1H), 4.46-4.42 (m, 1H), 4.18 (d, *J* = 6.6 Hz, 1H), 4.03-3.92 (m, 2H), 3.74-3.68 (m, 1H), 3.66-3.61 (m, 1H), 3.20-3.07 (m, 4H), 2.04-1.91 (m, 2H), 1.89-1.83 (m, 2H), 1.11 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 201.30, 173.12, 169.96, 137.76, 136.67, 135.27, 133.28, 131.07, 129.00, 128.79, 128.72, 126.74, 126.29, 71.70, 61.86, 51.47, 48.97, 45.78, 31.52, 26.18, 24.69, 13.99; HRMS (ESI/[M+H]+) calcd. for $C_{24}H_{27}NO_5$: 410.1962 Found 410.1958

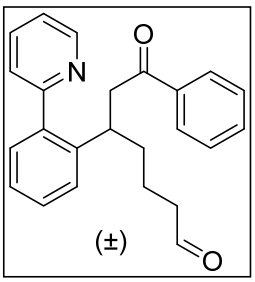


Ethyl-2-((4-methylphenyl)sulfonamido)-4-oxo-4-phenyl-3-(2-(pyrrolidine-1-carbonyl)benzyl)butanoate (3v): In a N_2-filled glove box, a 2-5 mL microwave vial was charged with crushed 3Å molecular sieves (50.0 mg), $AgSbF_6$ (13.8 mg, 0.0402 mmol, 0.201 equiv), $[Cp^*RhCl_2]_2$[S1] (6.2 mg, 0.010 mmol, 0.050 equiv), phenyl(pyrrolidin-1-yl)methanone[S16] (35.1 mg, 0.200 mmol, 1.00 equiv), phenyl vinyl ketone[S15] (29.1 mg, 0.220 mmol, 1.10 equiv), and (*E*)-ethyl-2-(tosylimino)acetate[S17] (102.1 mg, 0.4003 mmol, 2.002 equiv). 1,2-dichloroethane (0.4 mL) was then added, and the vial was equipped with a stir bar. The reaction vial was sealed and then outside the glove box, the vial was heated at 60 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then filtered over a plug of celite (1 cm celite in a glass pipette) eluting with CH_2Cl_2 and concentrated. Chromatography eluting with a 95:5 solution of methyl *tert*-butyl ether/hexanes provided the product as a mixture of diastereomers **3v** as a colorless waxy solid. The mixture was then separated by preparatory TLC using 2:1

dichloromethane/ethyl acetate to obtain the diastereomer with higher R_f (53.5 mg) as a white solid (mp: 165-167 °C), and the diastereomer with lower R_f (26.8 mg) as a colorless waxy solid (80.3 mg total, 2:1 dr, 71% yield).

Diastereomer 1 (Higher R_f): IR (film): 2979, 2891, 1750, 1671, 1609, 1164, 1092, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.75-7.71 (m, 4H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.28-7.25 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.16-7.13 (m, 1H), 7.09-7.06 (m, 2H), 6.34 (d, *J* = 9.5 Hz, 1H), 4.56 (dt, *J* = 8.8, 5.0 Hz, 1H), 4.26 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.78-3.72 (m, 1H), 3.67-3.65 (m, 3H), 3.23-3.10 (m, 3H), 3.00 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.39 (s, 3H), 2.06-1.99 (m, 1H), 1.97-1.86 (m, 3H), 0.80 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 202.57, 169.80, 169.78, 143.35, 137.77, 137.66, 136.81, 134.71, 133.46, 131.43, 129.55, 129.02, 128.73, 128.52, 127.40, 126.94, 126.27, 61.66, 57.46, 49.03, 48.29, 45.83, 33.37, 26.17, 24.68, 21.65, 13.67; HRMS (ESI/[M+H]+) calcd. for $C_{31}H_{34}N_2O_6S$: 563.2210 Found 563.2189.

Diastereomer 2 (Lower R_f): IR (film): 2973, 2873, 1735, 1671, 1597, 1155, 1092, 664 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71-7.67 (m, 4H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.28-7.25 (m, 2H), 7.23-7.18 (m, 3H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.04-6.98 (m, 2H), 6.01 (d, *J* = 9.1 Hz, 1H), 4.45 (dt, *J* = 9.0, 4.5 Hz, 1H), 4.26 (t, *J* = 8.6 Hz, 1H), 3.91-3.87 (m, 1H), 3.69-3.65 (m, 1H), 3.57 (q, *J* = 7.1 Hz, 2H), 3.28 (dd, *J* = 13.7, 4.2 Hz, 1H), 3.22-3.18 (m, 1H), 3.16-3.12 (m, 1H), 3.06 (dd, *J* = 13.7, 9.6 Hz, 1H), 2.38 (s, 3H), 2.13-2.07 (m, 1H), 1.98-1.88 (m, 3H), 0.79 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 200.83, 170.06, 169.93, 143.43, 137.99, 137.50, 137.09, 134.89, 133.22, 131.09, 129.57, 128.84, 128.70, 128.48, 127.47, 126.85, 126.30, 61.77, 57.84, 50.38, 49.06, 45.85, 33.74, 26.23, 24.73, 21.60, 13.58; HRMS (ESI/[M+H]+) calcd. for $C_{31}H_{34}N_2O_6S$: 563.2210 Found 563.2216.



(±)-7-oxo-7-phenyl-5-(2-(pyridin-2-yl)phenyl)heptanal (9a): In a N_2-filled glove box, a 2-5 mL microwave vial was charged with $AgSbF_6$ (27.5 mg, 0.0800 mmol, 0.10 equiv), $[Cp^*RhCl_2]_2$[S1] (12.4 mg, 0.0201 mmol, 0.025 equiv), (*E*)-7-oxo-7-phenylhept-5-enal[S4] (161.8 mg, 0.8000 mmol, 1.0 quiv), and 2-phenylpyridine (248.3 mg, 1.600 mmol, 2.0 equiv). A 3:2 mixture of dioxane/water (4.0 mL) was then added and the vial was equipped with a stir bar. The reaction vial was sealed and then outside the glove box, the vial was heated at 25 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then filtered

over a plug of celite (3 cm celite in a glass pipette) with CH_2Cl_2 and concentrated. Chromatography eluting with a 1:1 solution of ethyl acetate/hexanes provided the product **9a** (25.8 mg, 9% yield) as a colorless oil. IR (film): 2931, 1720, 1679, 1584, 1425, 988, 751, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.63 (d, *J* = 4.9 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.73 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.41-7.38 (m, 5H), 7.33-7.28 (m, 2H), 7.25-7.23 (m, 1H), 3.65 (tt, *J* = 9.3, 5.1 Hz, 1H), 3.43 (dd, *J* = 16.1, 5.2 Hz, 1H), 3.15 (dd, *J* = 16.0, 8.7 Hz, 1H), 2.21 (t, *J* = 7.0 Hz, 2H), 1.73-1.61 (m, 2H), 1.49-1.32 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 202.69, 199.14, 160.18, 149.15, 142.27, 141.13, 137.04, 136.44, 133.04, 130.06, 128.94, 128.62, 128.30, 126.41, 126.35, 124.62, 121.95, 46.27, 43.69, 36.09, 35.37, 20.00; HRMS (ESI/[M+H]+) calcd. for $C_{24}H_{23}NO_2$: 358.1802 Found 358.1799.

IV. Control Experiments with Intermediate 9a

Table 4, entry 1:

In a N_2-filled glove box, a 2-5 mL microwave vial was charged with $AgSbF_6$ (1.7 mg, 0.0049 mmol, 0.10 equiv), $[Cp^*RhCl_2]_2$[S1] (0.8 mg, 0.001 mmol, 0.025 equiv), and **9a** (17.9 mg, 0.0501 mmol, 1.0 equiv). A 3:2 mixture of dioxane/H_2O (0.025 mL) was then added, and the vial was equipped with a stir bar. The reaction vial was sealed, and then outside the glove box, the vial was heated at 50 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then concentrated, and 13.2 mg (0.0785 mmol) of an external standard (1,3,5-trimethoxybenzene) was added to the reaction mixture. $CDCl_3$ was added to the reaction mixture, and the crude NMR was taken to determine that 11% of compound **3a** was formed along with 1% of recovered **9a**.

Table 4, entry 2:

In a N_2-filled glove box, a 2-5 mL microwave vial was charged with **9a** (36.0 mg, 0.101 mmol, 1.0 equiv). A 3:2 mixture of dioxane/H_2O (0.05 mL) was then added, and the vial was equipped with a stir bar. The reaction vial was sealed, and then outside the glove box, the vial was heated at 50 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then concentrated, and 10.0 mg (0.0595 mmol) of an external standard (1,3,5-trimethoxybenzene) was added to the reaction mixture. $CDCl_3$ was added to the reaction mixture, and the crude NMR was taken to determine that 12% of compound **3a** was formed along with 1% of recovered **9a**.

Table 4, entry 3:

In a N_2-filled glove box, a 2-5 mL microwave vial was charged with $AgSbF_6$ (1.7 mg, 0.0049 mmol, 0.10 equiv), $[Cp^*RhCl_2]_2$[S1] (0.8 mg, 0.001 mmol, 0.025 equiv), and **9a** (17.1 mg, 0.0478 mmol, 1.0 equiv). Acetic acid (0.025 mL) was then added, and the vial was equipped with a stir bar. The reaction vial was sealed, and then outside the glove box, the vial was heated at 50 °C in a preset oil bath for 20 h with stirring. The reaction mixture was then concentrated, and 10.4 mg (0.0618 mmol) of an external standard (1,3,5-trimethoxybenzene) was added to the reaction mixture. $CDCl_3$ was added to the reaction mixture, and the crude NMR was taken to determine that 44% of compound **3a** was formed along with 1% of recovered **9a**.

Table 4, entry 4:

In a N_2-filled glove box, a 2-5 mL microwave vial was charged with **9a** (17.2 mg, 0.0481 mmol, 1.0 equiv). Acetic acid (0.025 mL) was then added, and the vial was equipped with a stir bar. The reaction vial was sealed, and then outside the glove box, the vial was heated at 50 $^{\circ}$C in a preset oil bath for 20 h with stirring. The reaction mixture was then concentrated, and 14.1 mg (0.0838 mmol) of an external standard (1,3,5-trimethoxybenzene) was added to the reaction mixture. $CDCl_3$ was added to the reaction mixture, and the crude NMR was taken to determine that 45% of compound **3a** was formed with no observed amount of recovered **9a**.

Table 4, entry 1

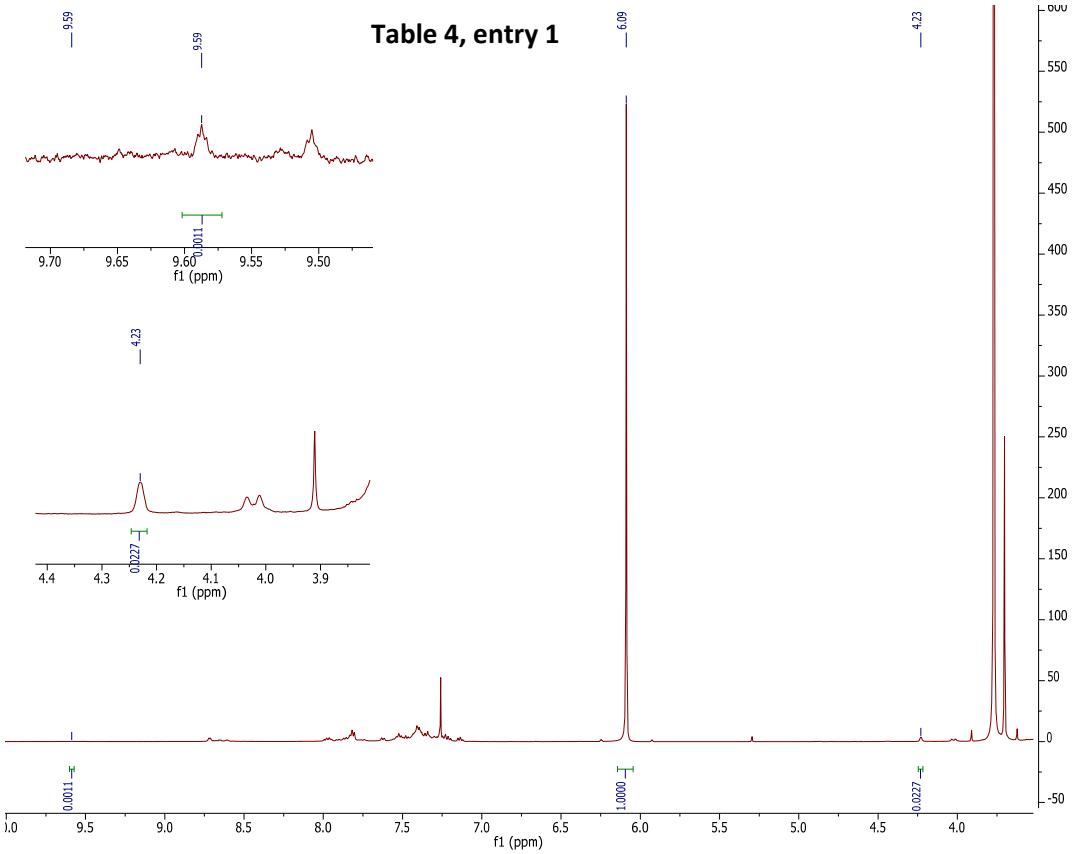


Table 4, entry 2

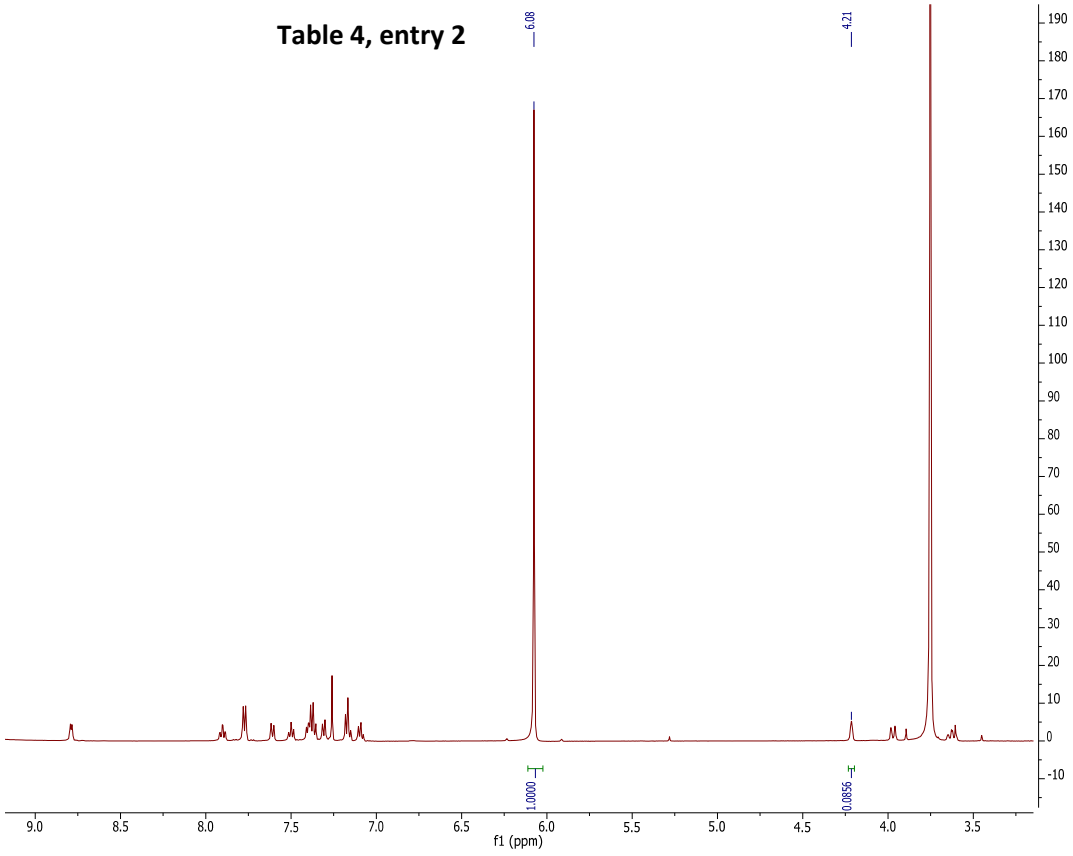


Table 4, entry 3

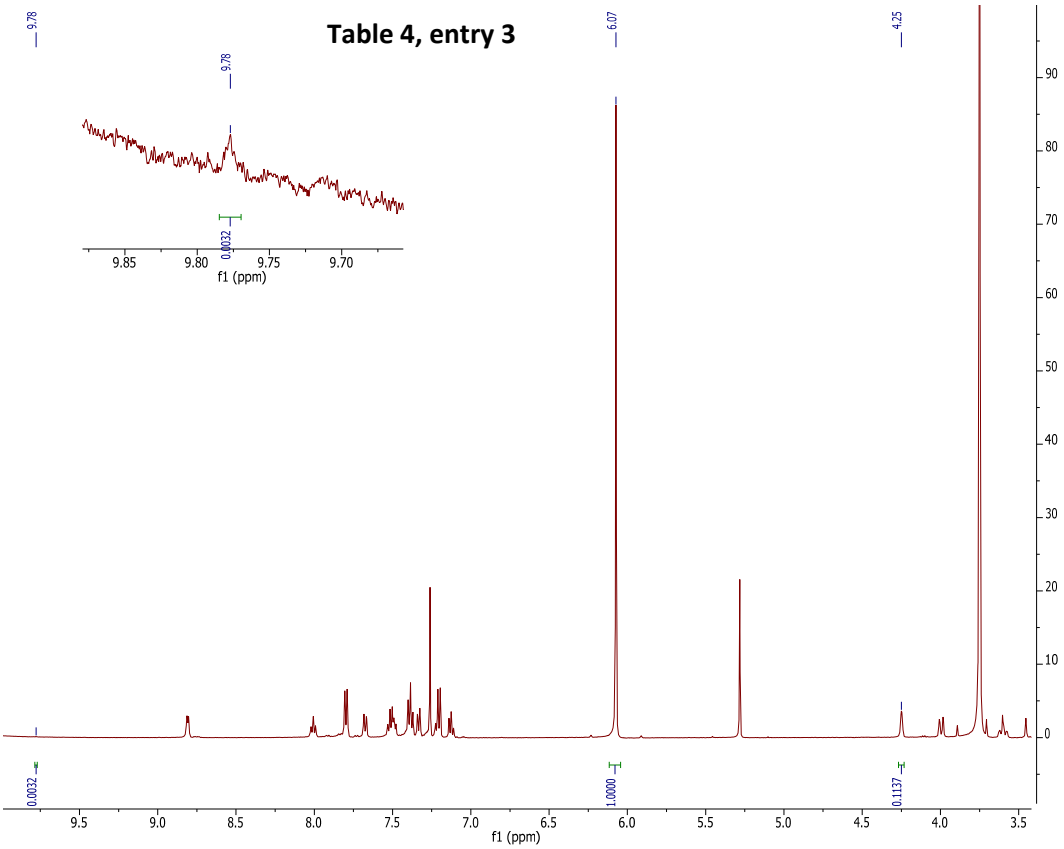
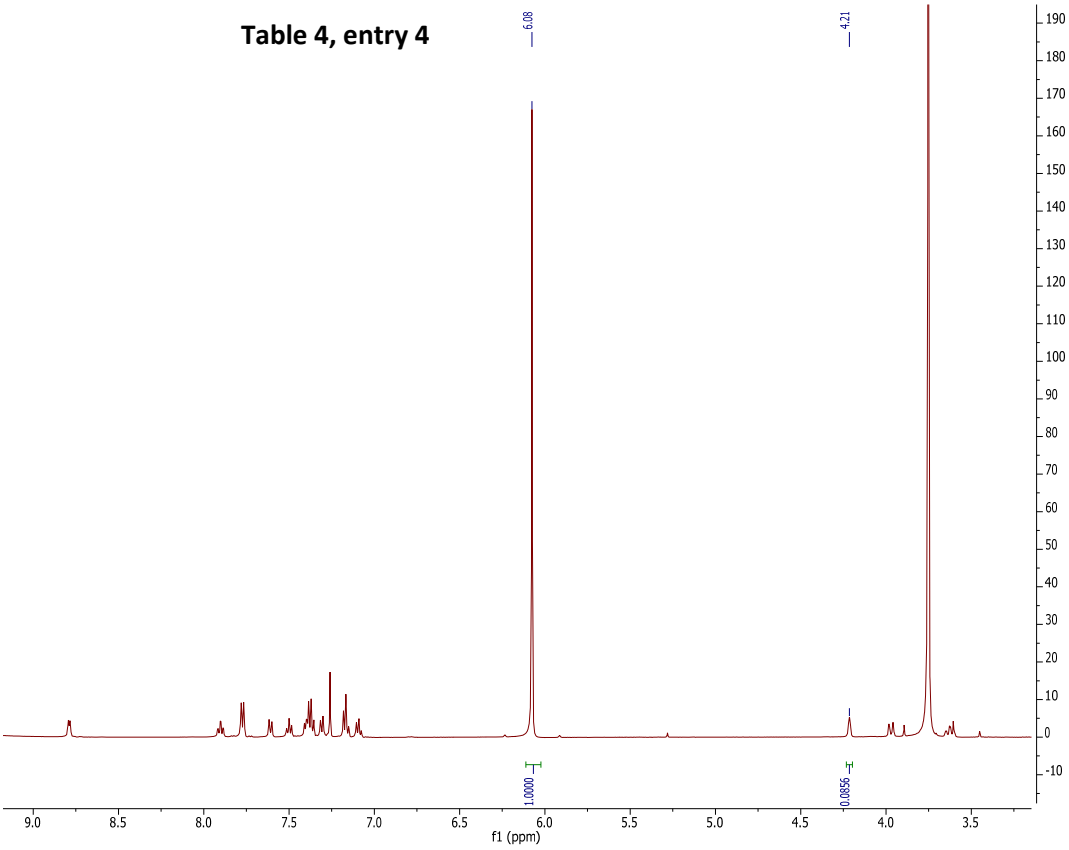
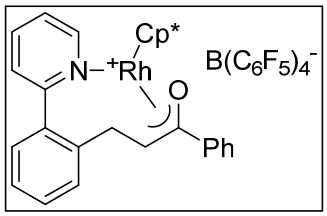


Table 4, entry 4



V. Procedure for Rhodacycle Synthesis:



Synthesis of Rh(III)-Enolate 10:

In a N_2-filled glove box, a 2-5 mL microwave vial was charged with $AgB(C_6F_5)_4(Et_2O)_2$[S2] (187.0 mg, 0.2000 mmol, 4.000 equiv), $[Cp^*RhCl_2]_2$[S1] (30.9 mg, 0.0500 mmol, 1.00 equiv), 2-phenylpyridine (17.1 mg, 0.110 mmol, 2.20 equiv), and phenyl vinyl ketone[S15] (14.5 mg, 0.110 mmol, 2.20 equiv). 1,2-dichloroethane (0.5 mL) was then added, and the vial was equipped with a stir bar. The reaction vial was sealed and then outside the glove box, the vial was stirred at room temperature for 30 min. The reaction mixture was then filtered over a plug of celite (1 cm celite in a glass pipette) eluting with CH_2Cl_2 and concentrated. Chromatography eluting with a 4:1 solution of dichloromethane/hexanes provided the product **10** (58.0 mg, 96% yield) as a reddish-orange solid (mp: 104-106 °C). IR (film): 1644, 1513, 1459, 1083, 977, 756, 683, 655 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.23 (d, *J* = 5.2 Hz, 1H), 8.06 (dt, *J* = 7.7, 1.4 Hz, 1H), 8.02 (d, *J* = 7.4 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.60-7.47 (m, 7H), 4.89 (dd, *J* = 11.8, 5.3 Hz, 1H), 3.07 (dd, *J* = 13.5, 5.3 Hz, 1H), 2.22-2.17 (m, 1H), 0.99 (s, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), 126 MHz): δ 161.22, 153.80, 153.79, 149.42-149.18 (m), 147.49-147.27 (m), 139.90, 139.06, 137.51-137.21 (m), 135.99, 135.57-135.24 (m), 134.69, 132.78, 131.16, 130.14, 130.11, 129.20, 128.82, 128.60, 127.75, 124.16, 98.95, 65.51, 34.54, 8.36.; HRMS (ESI) calcd. for $C_{30}H_{31}NORh^+$: 524.1455 Found 524.1457.

VI. X-Ray Crystallographic Data:

Single crystals of **3b** were obtained by slow diffusion of hexanes into a concentrated solution of product **3b** in toluene.

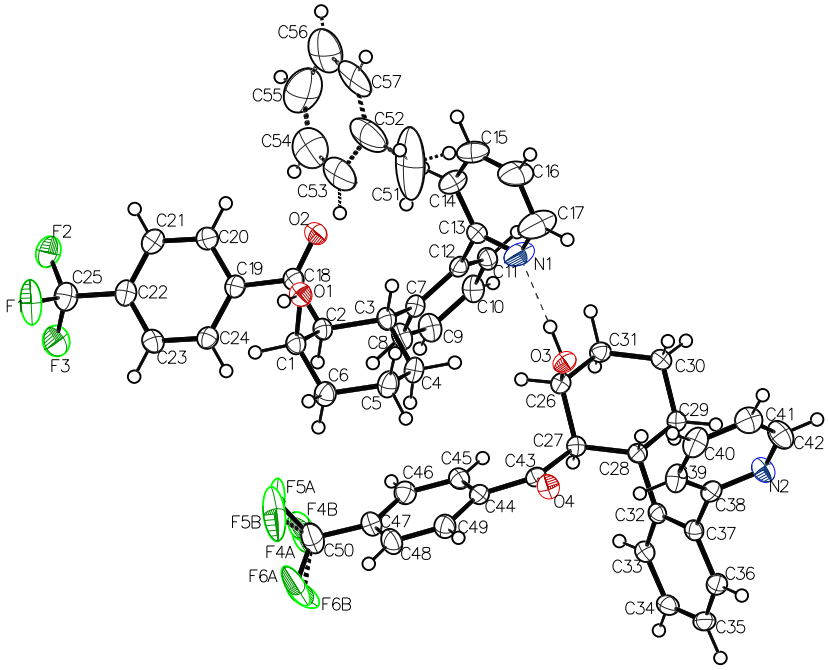


Figure S1. A thermal ellipsoid plot of **3b** at a 50% probability level. The full numbering scheme is shown. All hydrogen atoms are depicted as spheres. Carbon atoms C1 has R chirality; C2 has S; C3 has R; C26 has S; C27 has R; C28 has S.

Table S1. Crystal data and structure refinement for **3b**.

Identification code	007-15013	
Empirical formula	$C_{53.50}H_{48}F_6N_2O_4$	
Formula weight	896.94	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.6325(2) Å	α = 96.651(7)°.
	b = 13.4130(3) Å	β = 91.573(7)°.
	c = 18.8693(13) Å	γ = 109.521(8)°.
Volume	2276.6(2) $Å^3$	
Z	2	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	0.825 mm^{-1}	
F(000)	938	
Crystal size	0.200 x 0.200 x 0.040 mm^3	
Crystal color and habit	Colorless Prism	
Diffractometer	Rigaku Saturn 944+ CCD	
Θ range for data collection	2.363 to 66.591°.	
Index ranges	$-11 \le h \le 11$, $-15 \le k \le 15$, $-22 \le l \le 22$	
Reflections collected	59268	
Independent reflections	7910 [R(int) = 0.0480]	
Observed reflections (I > 2σ(I))	7081	
Completeness to θ = 66.591°	98.3 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.968 and 0.802
Solution method	SHELXS-2013 (Sheldrick, 2013)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	7910 / 51 / 659
Goodness-of-fit on F^2	1.072
Final R indices [$I>2\sigma(I)$]	R1 = 0.0394, wR2 = 0.1018
R indices (all data)	R1 = 0.0428, wR2 = 0.1039
Largest diff. peak and hole	0.529 and -0.338 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 007-15013. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	3262(2)	10021(1)	9526(1)	63(1)
F(2)	1167(1)	9285(1)	9938(1)	51(1)
F(3)	3126(1)	9208(1)	10442(1)	57(1)
O(1)	3633(1)	5870(1)	6631(1)	31(1)
O(2)	736(1)	4918(1)	7512(1)	33(1)
N(1)	908(2)	1503(2)	6125(1)	54(1)
C(1)	4388(2)	5836(1)	7280(1)	26(1)
C(2)	3257(2)	5038(1)	7691(1)	24(1)
C(3)	2784(2)	3894(1)	7290(1)	24(1)
C(4)	4155(2)	3576(1)	7162(1)	29(1)
C(5)	5273(2)	4354(1)	6753(1)	32(1)
C(6)	5723(2)	5487(1)	7147(1)	31(1)
C(7)	1704(2)	3070(1)	7679(1)	24(1)
C(8)	1893(2)	3097(1)	8418(1)	31(1)
C(9)	976(2)	2317(1)	8776(1)	34(1)
C(10)	-154(2)	1476(1)	8402(1)	32(1)
C(11)	-363(2)	1428(1)	7668(1)	27(1)
C(12)	551(2)	2215(1)	7303(1)	23(1)
C(13)	276(2)	2105(1)	6510(1)	25(1)
C(14)	-626(2)	2562(1)	6194(1)	37(1)

C(15)	-889(2)	2394(2)	5459(1)	44(1)
C(16)	-231(2)	1792(2)	5064(1)	57(1)
C(17)	652(3)	1365(2)	5414(1)	80(1)
C(18)	1932(2)	5388(1)	7833(1)	25(1)
C(19)	2096(2)	6343(1)	8379(1)	24(1)
C(20)	899(2)	6708(1)	8439(1)	27(1)
C(21)	988(2)	7597(1)	8914(1)	30(1)
C(22)	2290(2)	8145(1)	9329(1)	29(1)
C(23)	3485(2)	7786(1)	9285(1)	29(1)
C(24)	3382(2)	6885(1)	8816(1)	26(1)
C(25)	2449(2)	9154(1)	9807(1)	36(1)
F(4A)	6589(12)	4971(8)	10219(5)	55(2)
F(4B)	6474(10)	5019(9)	10180(6)	52(2)
F(5A)	6900(20)	5826(10)	9325(5)	67(2)
F(5B)	7300(30)	5917(13)	9337(8)	99(5)
F(6A)	8710(13)	5529(10)	9766(9)	80(3)
F(6B)	8672(13)	5322(18)	9965(13)	87(4)
O(3)	3063(1)	730(1)	6629(1)	27(1)
O(4)	6408(1)	1326(1)	7031(1)	29(1)
N(2)	5224(1)	-2531(1)	5777(1)	32(1)
C(26)	2909(2)	535(1)	7352(1)	23(1)
C(27)	4315(1)	325(1)	7604(1)	21(1)
C(28)	4412(1)	-690(1)	7168(1)	21(1)
C(29)	3019(2)	-1641(1)	7244(1)	23(1)
C(30)	1618(2)	-1444(1)	7014(1)	26(1)

C(31)	1538(2)	-419(1)	7425(1)	25(1)
C(32)	5746(1)	-975(1)	7376(1)	21(1)
C(33)	6195(2)	-920(1)	8094(1)	24(1)
C(34)	7304(2)	-1297(1)	8292(1)	28(1)
C(35)	8000(2)	-1732(1)	7775(1)	28(1)
C(36)	7586(2)	-1783(1)	7059(1)	26(1)
C(37)	6465(2)	-1414(1)	6854(1)	22(1)
C(38)	6016(2)	-1537(1)	6076(1)	24(1)
C(39)	6406(2)	-680(1)	5686(1)	33(1)
C(40)	5977(2)	-854(1)	4963(1)	38(1)
C(41)	5159(2)	-1872(1)	4652(1)	37(1)
C(42)	4808(2)	-2677(1)	5076(1)	39(1)
C(43)	5668(2)	1291(1)	7545(1)	23(1)
C(44)	6082(2)	2235(1)	8124(1)	24(1)
C(45)	5197(2)	2319(1)	8684(1)	25(1)
C(46)	5590(2)	3237(1)	9175(1)	29(1)
C(47)	6887(2)	4067(1)	9118(1)	32(1)
C(48)	7803(2)	3980(1)	8575(1)	36(1)
C(49)	7394(2)	3073(1)	8080(1)	31(1)
C(50)	7304(2)	5078(1)	9627(1)	45(1)
C(51)	1421(12)	4315(9)	4219(6)	154(5)
C(52)	422(5)	4809(4)	4737(3)	85(2)
C(53)	1078(8)	5216(7)	5421(3)	68(2)
C(54)	117(5)	5508(4)	5869(3)	78(1)
C(55)	-1234(8)	5564(9)	5630(4)	100(3)

C(56)	-1820(6)	5304(4)	4921(3)	84(2)
C(57)	-822(7)	5009(7)	4498(4)	67(2)

Single crystals of **10** were obtained by slow evaporation of a concentrated solution of product **10** in ethyl ether.

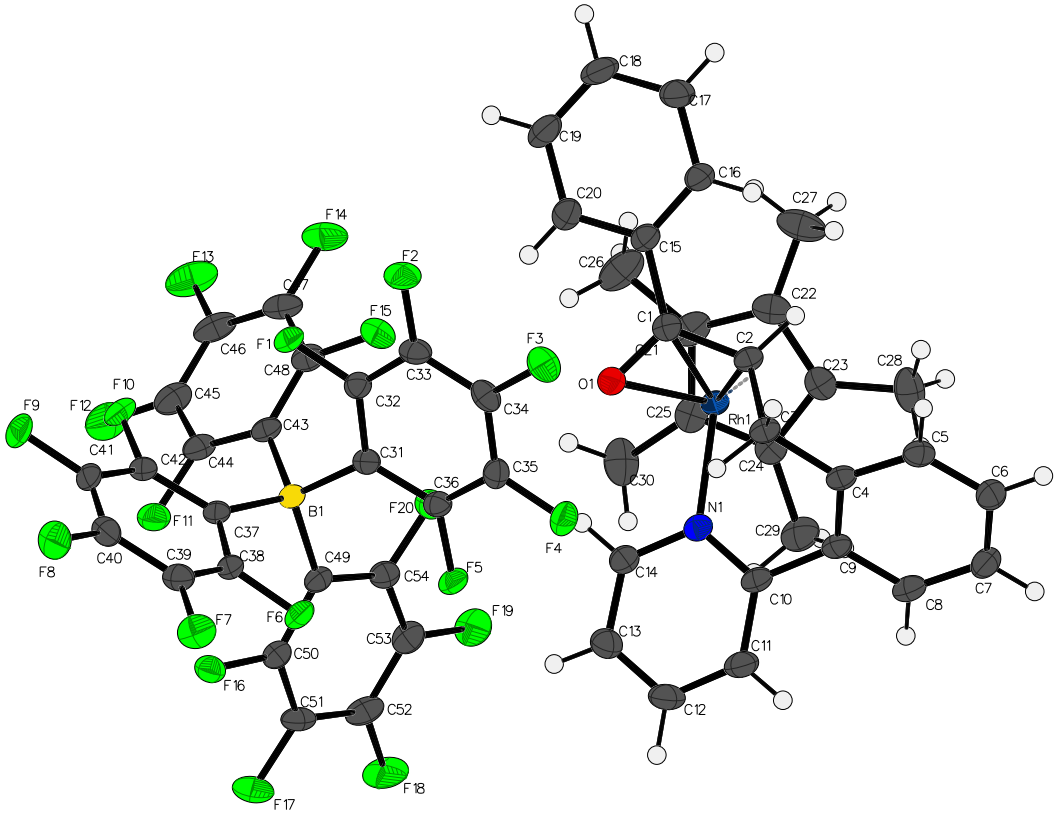


Figure S2. The full numbering scheme of **10** with 50% thermal ellipsoids. The hydrogen atoms are show as arbitrary circles for clarity.

Table S3. Crystal data and structure refinement for **10**.

Identification code	007-15127	
Empirical formula	$C_{54}H_{31}BF_{20}NORh$	
Formula weight	1203.52	
Temperature	93(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8540(8) Å	α = 79.702(2)°.
	b = 13.0781(9) Å	β = 80.128(2)°.
	c = 16.1540(11) Å	γ = 73.163(2)°.
Volume	2339.2(3) $Å^3$	
Z	2	
Density (calculated)	1.709 Mg/m^3	
Absorption coefficient	4.074 mm^{-1}	
F(000)	1200	
Crystal size	0.080 x 0.080 x 0.040 mm^3	
Theta range for data collection	2.803 to 68.095°.	
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 15$, $-19 \le l \le 19$	
Reflections collected	75602	
Independent reflections	8279 [R(int) = 0.0573]	
Completeness to theta = 67.679°	97.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.788	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	8279 / 0 / 712
Goodness-of-fit on F^2	1.126
Final R indices [I>2sigma(I)]	R1 = 0.0250, wR2 = 0.0727
R indices (all data)	R1 = 0.0260, wR2 = 0.0731
Largest diff. peak and hole	0.401 and -0.735 e.$Å^{-3}$

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 007-15127. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	573(1)	8052(1)	2161(1)	18(1)
O(1)	998(1)	6541(1)	2990(1)	22(1)
N(1)	2173(2)	8191(1)	2511(1)	20(1)
C(1)	-95(2)	7006(2)	3263(1)	20(1)
C(2)	-337(2)	8096(2)	3439(1)	19(1)
C(3)	350(2)	8431(2)	4006(1)	20(1)
C(4)	380(2)	9591(2)	3726(1)	20(1)
C(5)	-526(2)	10422(2)	4048(1)	24(1)
C(6)	-543(2)	11500(2)	3790(1)	27(1)
C(7)	375(2)	11765(2)	3220(1)	28(1)
C(8)	1293(2)	10954(2)	2900(1)	27(1)
C(9)	1299(2)	9869(2)	3137(1)	21(1)
C(10)	2336(2)	9038(2)	2809(1)	21(1)
C(11)	3475(2)	9125(2)	2822(1)	28(1)
C(12)	4455(2)	8353(2)	2532(2)	32(1)
C(13)	4286(2)	7478(2)	2250(1)	29(1)
C(14)	3138(2)	7419(2)	2260(1)	24(1)
C(15)	-1021(2)	6439(2)	3283(1)	22(1)
C(16)	-2194(2)	6851(2)	3627(1)	26(1)
C(17)	-3038(2)	6292(2)	3648(2)	33(1)

C(18)	-2704(2)	5306(2)	3342(2)	36(1)
C(19)	-1533(2)	4877(2)	3025(2)	33(1)
C(20)	-689(2)	5433(2)	2989(1)	26(1)
C(21)	-43(2)	7720(2)	1052(1)	30(1)
C(22)	-918(2)	8583(2)	1430(1)	28(1)
C(23)	-381(2)	9444(2)	1392(1)	25(1)
C(24)	810(2)	9111(2)	977(1)	24(1)
C(25)	1027(2)	8047(2)	772(1)	27(1)
C(26)	-211(3)	6669(2)	929(2)	44(1)
C(27)	-2186(2)	8620(2)	1753(2)	41(1)
C(28)	-989(2)	10521(2)	1669(2)	38(1)
C(29)	1662(2)	9796(2)	771(1)	34(1)
C(30)	2167(2)	7408(2)	326(2)	40(1)
F(1)	2851(1)	2278(1)	3557(1)	24(1)
F(2)	1125(1)	3289(1)	4648(1)	31(1)
F(3)	1106(1)	5281(1)	4987(1)	33(1)
F(4)	2896(1)	6175(1)	4241(1)	29(1)
F(5)	4591(1)	5203(1)	3128(1)	24(1)
F(6)	6071(1)	3257(1)	3903(1)	24(1)
F(7)	6920(1)	1799(1)	5177(1)	32(1)
F(8)	6864(1)	-290(1)	5282(1)	37(1)
F(9)	5924(1)	-874(1)	4062(1)	34(1)
F(10)	5067(1)	548(1)	2804(1)	28(1)
F(11)	6221(1)	1566(1)	1432(1)	29(1)
F(12)	5538(1)	887(1)	189(1)	44(1)

F(13)	3205(1)	1523(1)	-84(1)	47(1)
F(14)	1595(1)	2863(1)	925(1)	37(1)
F(15)	2254(1)	3630(1)	2106(1)	29(1)
F(16)	7547(1)	2593(1)	2396(1)	25(1)
F(17)	8793(1)	3726(1)	1290(1)	34(1)
F(18)	7701(1)	5503(1)	274(1)	42(1)
F(19)	5276(1)	6098(1)	376(1)	38(1)
F(20)	3996(1)	4962(1)	1473(1)	28(1)
C(31)	3779(2)	3707(2)	3249(1)	19(1)
C(32)	2878(2)	3266(2)	3692(1)	20(1)
C(33)	1980(2)	3767(2)	4267(1)	24(1)
C(34)	1973(2)	4761(2)	4446(1)	24(1)
C(35)	2874(2)	5215(2)	4057(1)	22(1)
C(36)	3741(2)	4692(2)	3474(1)	20(1)
C(37)	5512(2)	2003(2)	3271(1)	19(1)
C(38)	6012(2)	2236(2)	3915(1)	20(1)
C(39)	6456(2)	1504(2)	4580(1)	24(1)
C(40)	6434(2)	442(2)	4636(1)	27(1)
C(41)	5966(2)	157(2)	4022(1)	25(1)
C(42)	5526(2)	926(2)	3362(1)	21(1)
C(43)	4278(2)	2598(2)	1874(1)	20(1)
C(44)	5047(2)	1917(2)	1330(1)	25(1)
C(45)	4721(2)	1548(2)	685(1)	31(1)
C(46)	3555(2)	1863(2)	545(1)	33(1)
C(47)	2746(2)	2545(2)	1049(1)	28(1)

C(48)	3118(2)	2914(2)	1681(1)	24(1)
C(49)	5691(2)	3717(2)	2009(1)	19(1)
C(50)	6920(2)	3464(2)	1924(1)	21(1)
C(51)	7597(2)	4045(2)	1354(1)	25(1)
C(52)	7052(2)	4940(2)	834(1)	29(1)
C(53)	5830(2)	5231(2)	887(1)	26(1)
C(54)	5194(2)	4624(2)	1459(1)	22(1)
B(1)	4822(2)	3007(2)	2599(1)	19(1)

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S15. S. Chanthamath, S. Takaki, K. Shibatomi and S. Iwasa, *Angew. Chem. Int. Ed.,* 2013, **52**, 5818.

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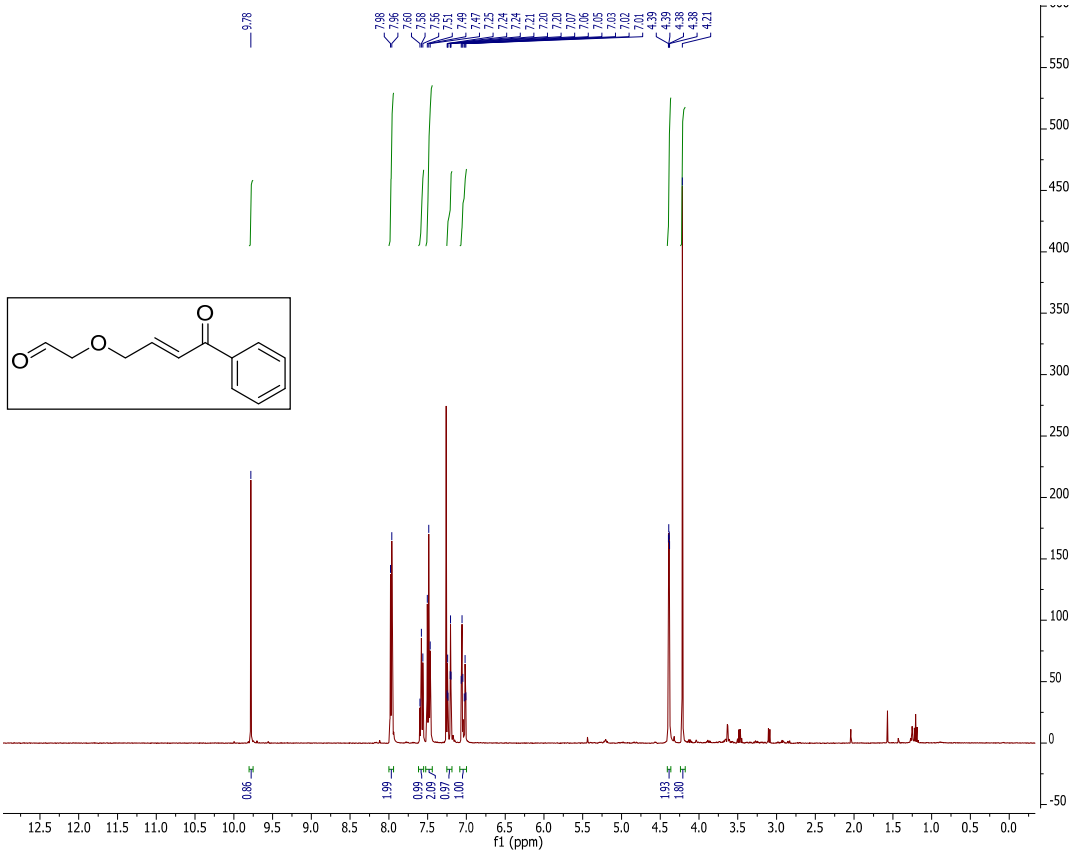
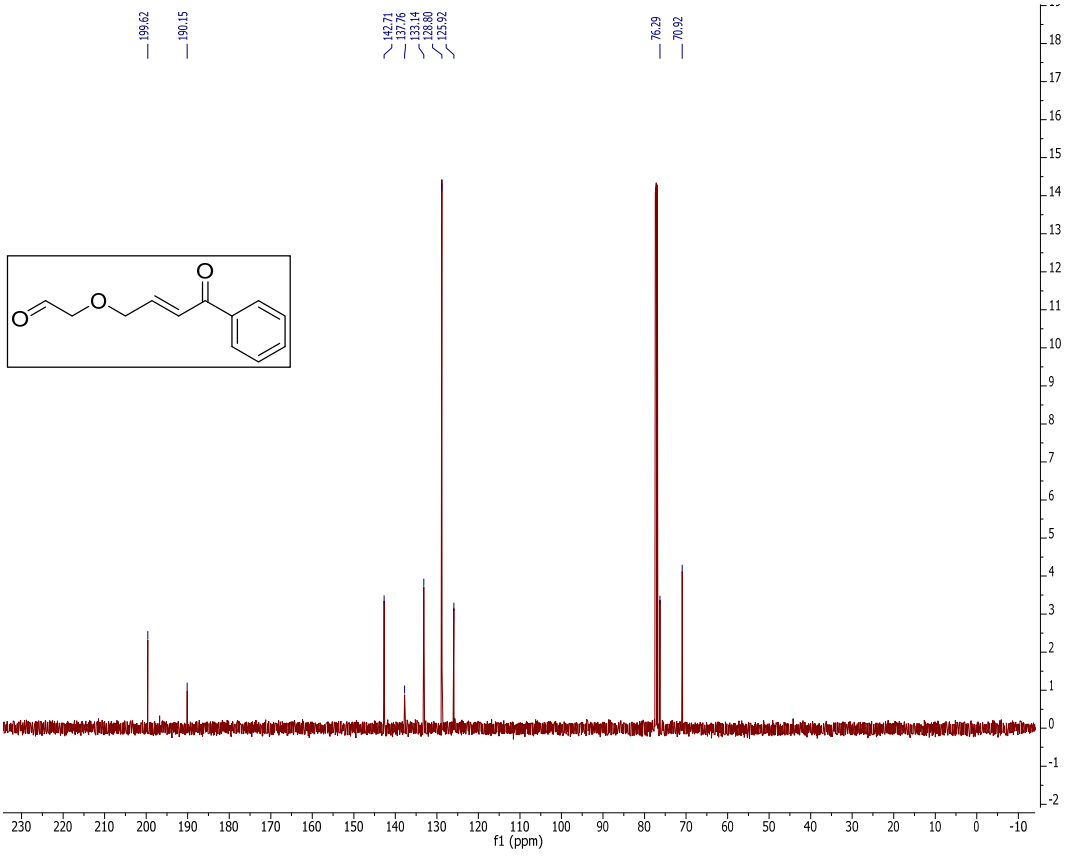
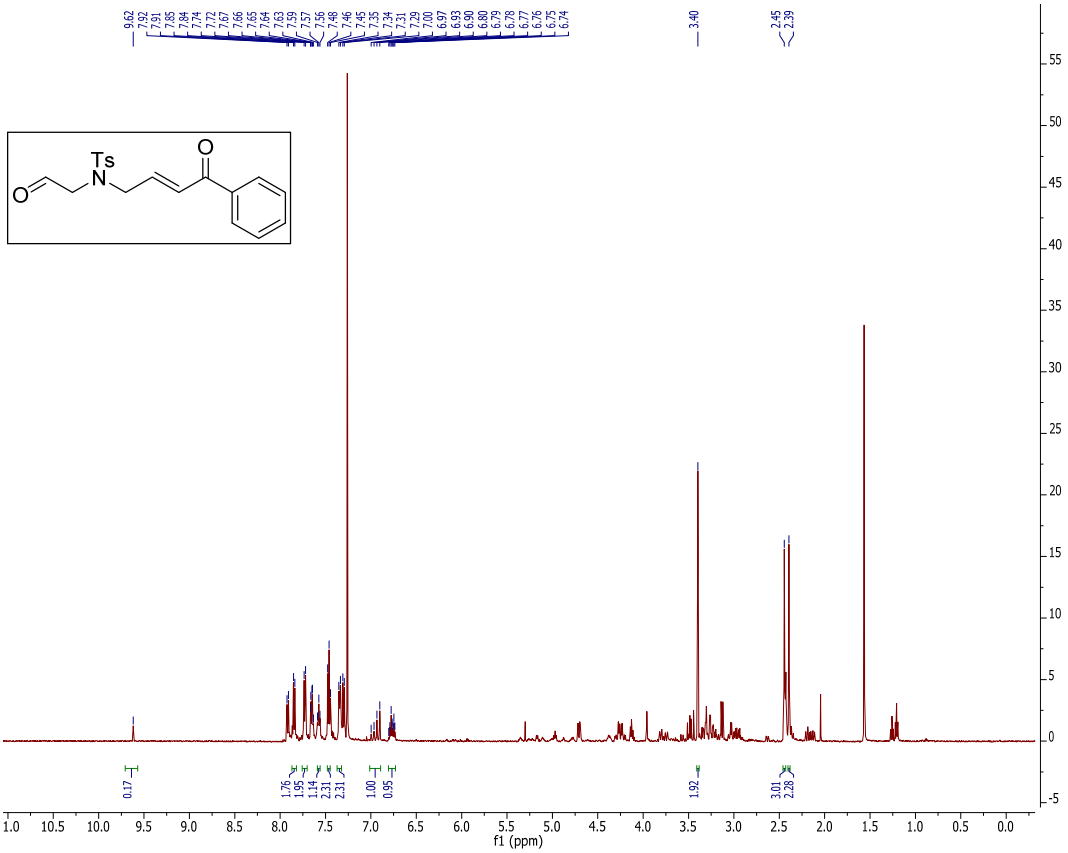
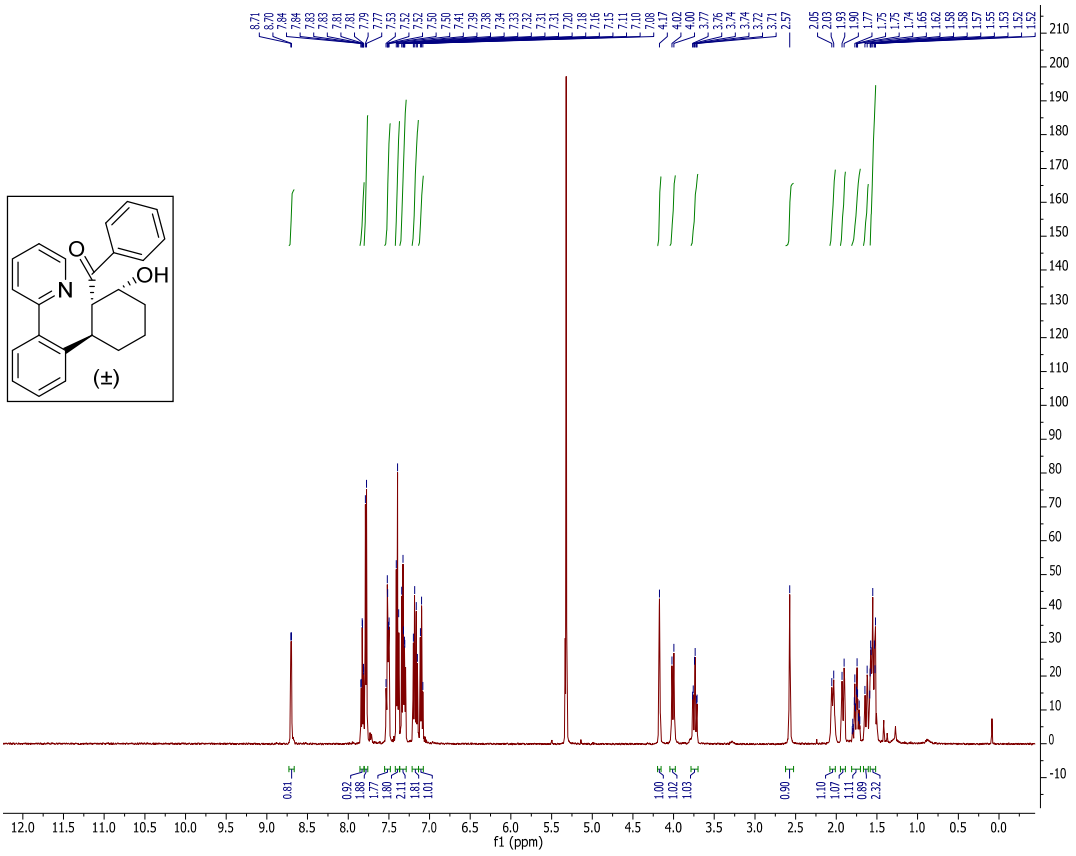
VIII: NMR Data





Crude ^{1}H NMR of **2g** (500 MHz, $CDCl_3$):

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7.52
7.50
7.50
7.41
7.39
7.38
7.34
7.33
7.32
7.31
7.31
7.20
7.18
7.16
7.15
7.11
7.10
7.08
4.17
4.02
4.00
3.77
3.76
3.74
3.74
3.72
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2.05
2.03
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1.75
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1.65
1.62
1.58
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1.57
1.55
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1.52
1.52
O
N
OH
(±)
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0.92
1.88
1.77
1.80
2.11
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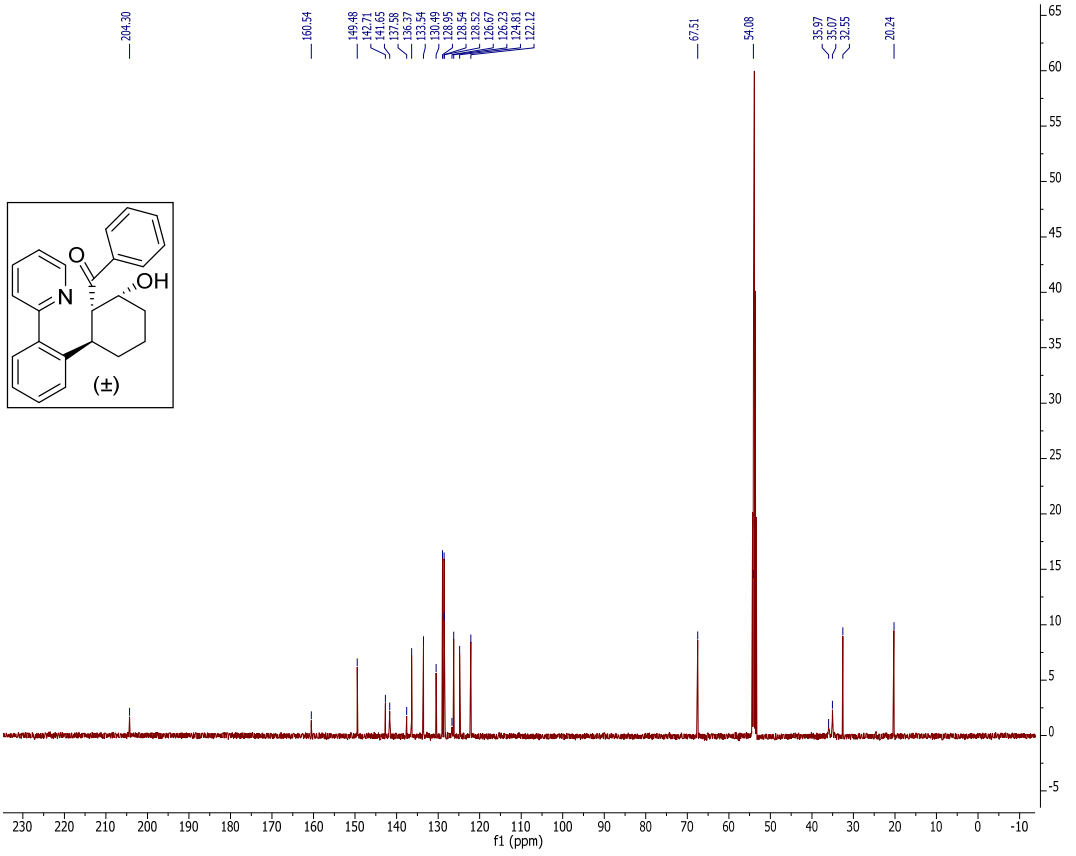
f1 (ppm)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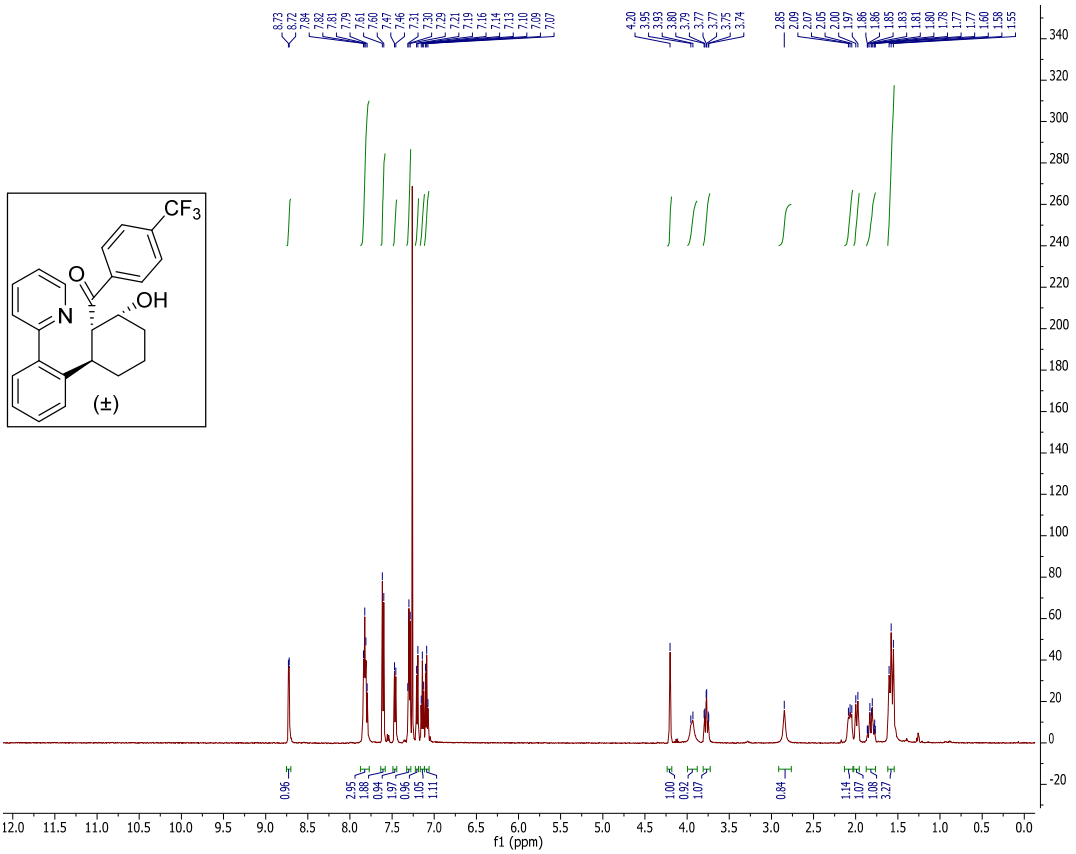
(±)
f1 (ppm)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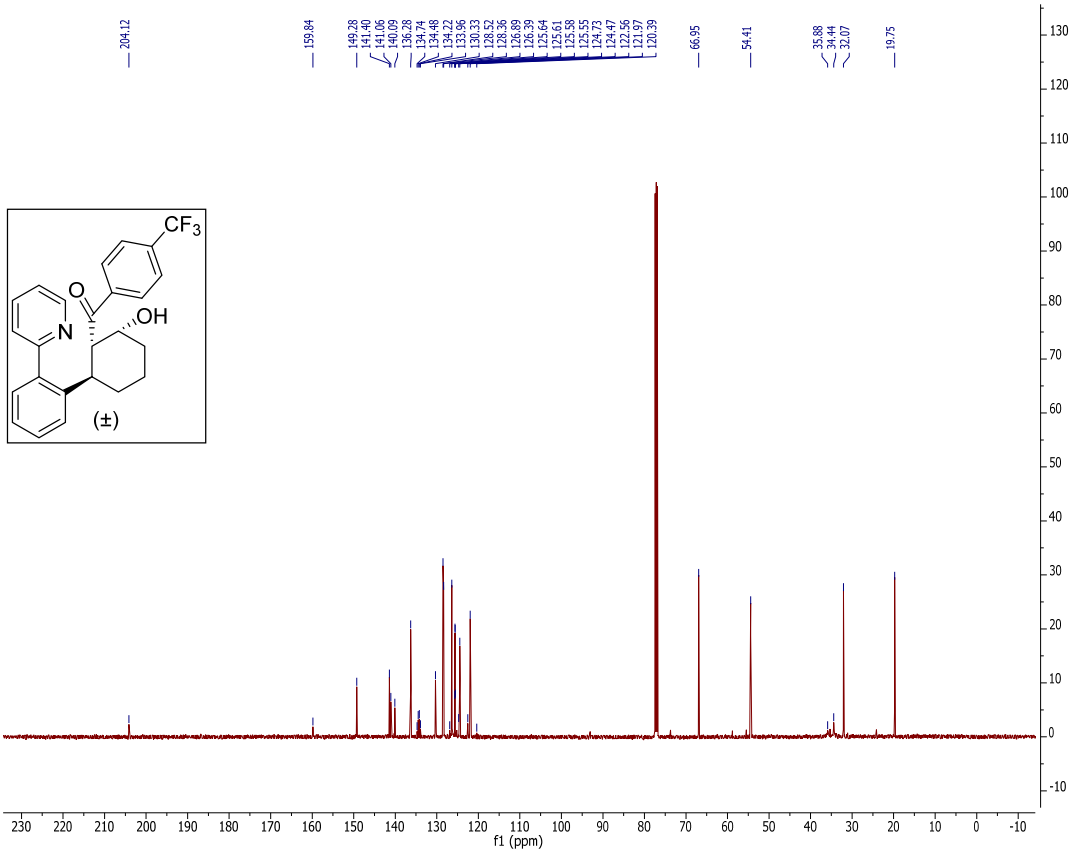
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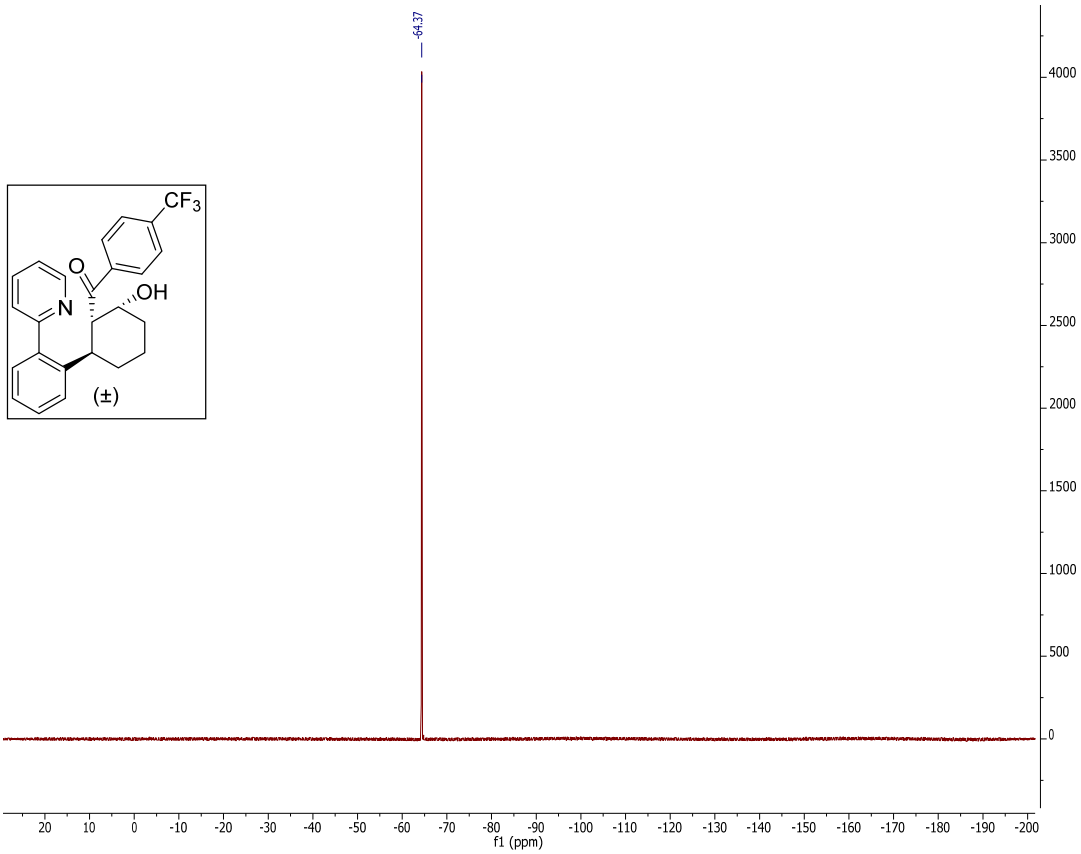
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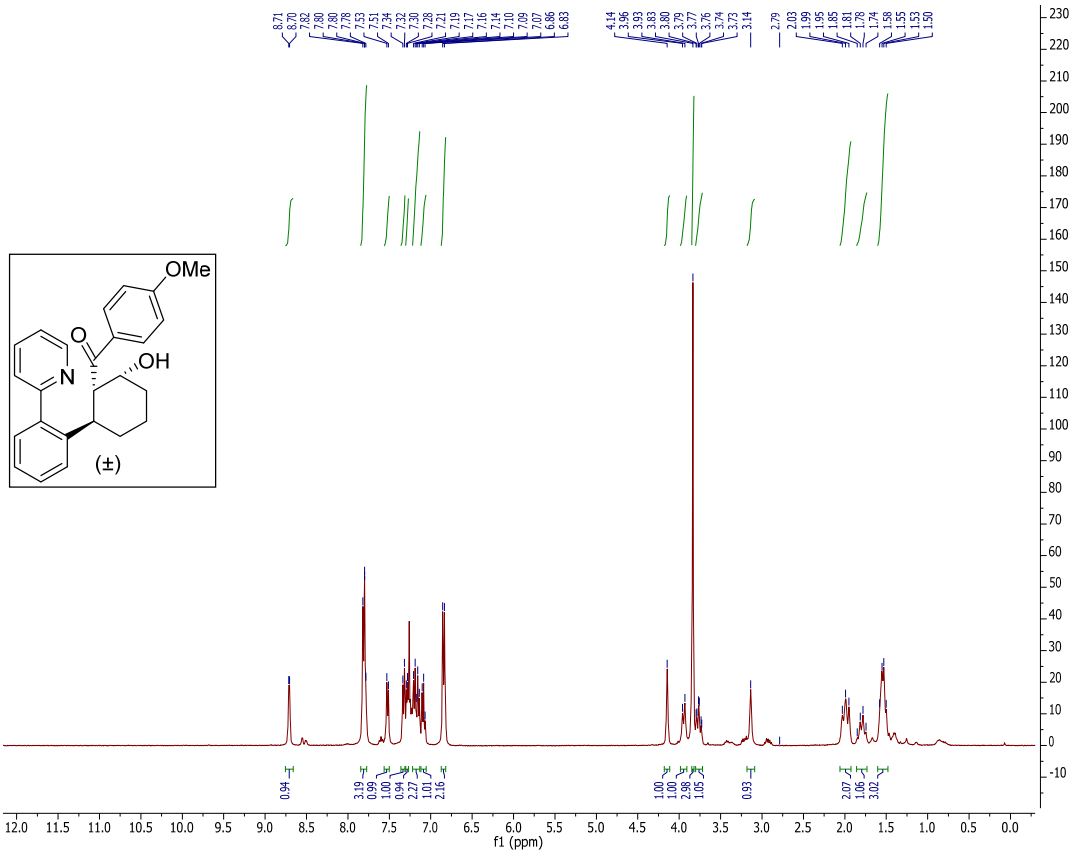
f1 (ppm)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OH
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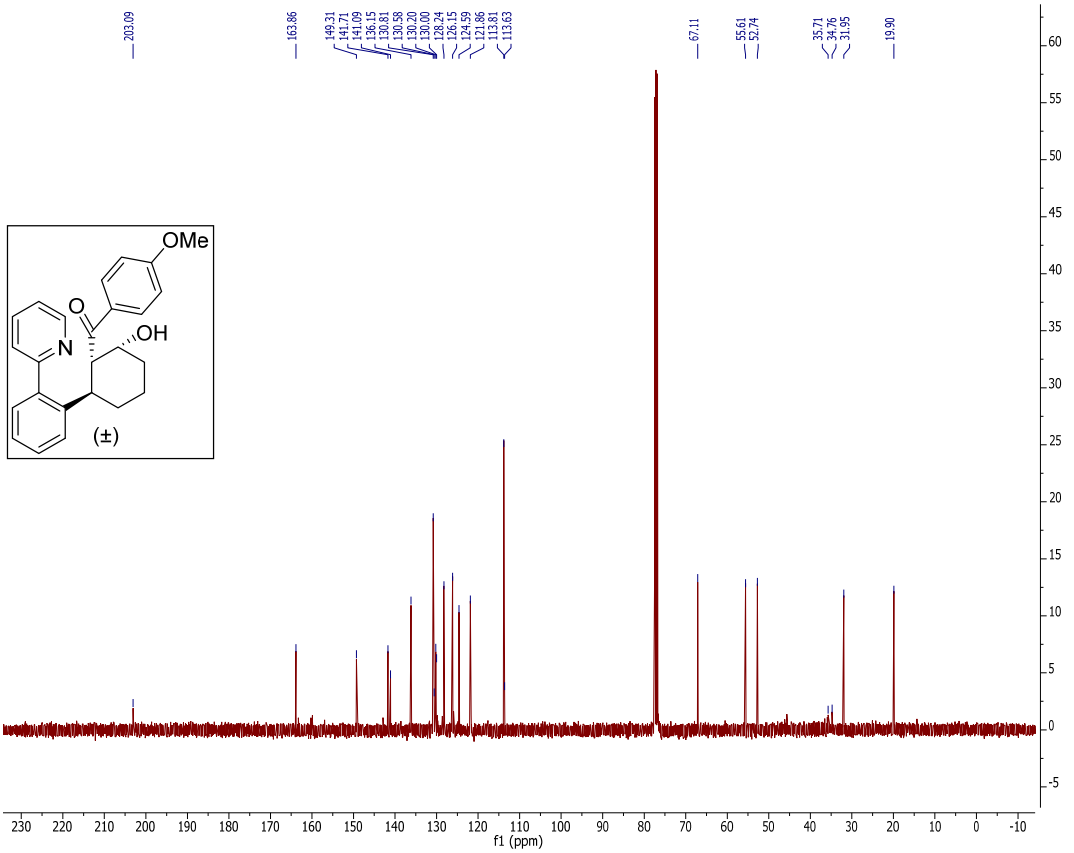
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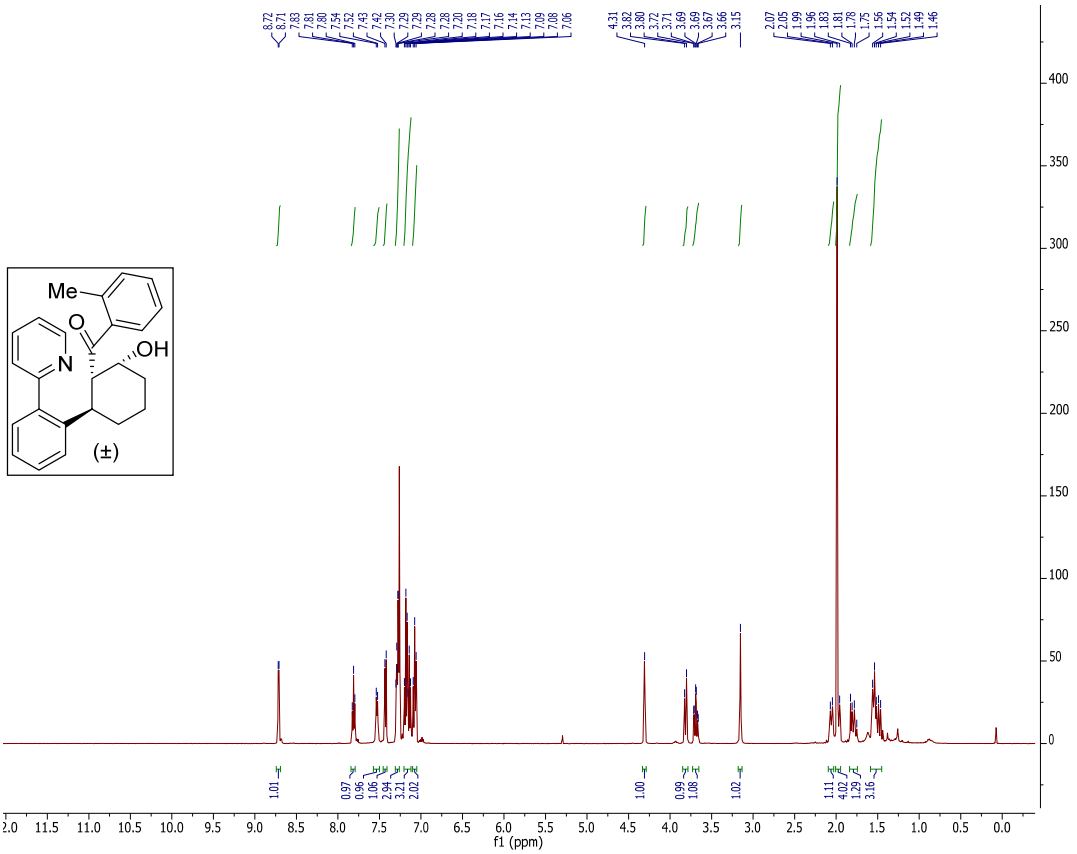
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7.08
7.06
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3.69
3.67
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3.15
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2.05
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1.96
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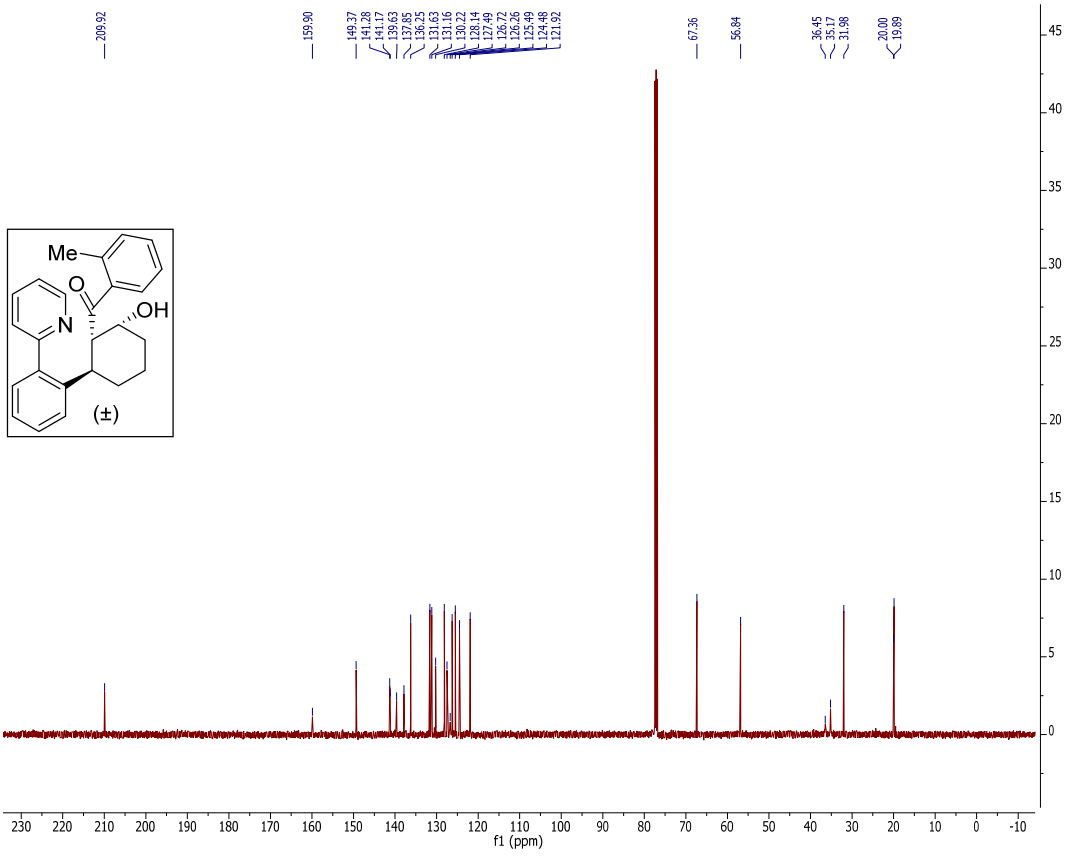
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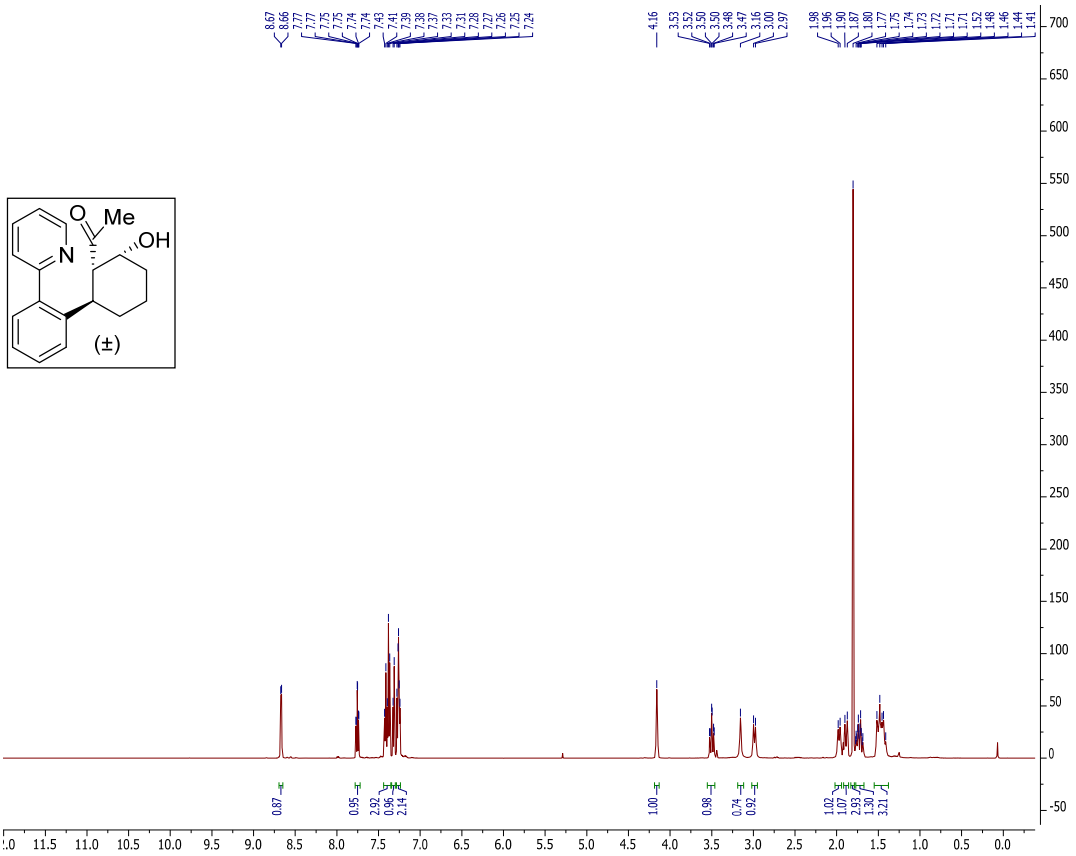
(±)
f1 (ppm)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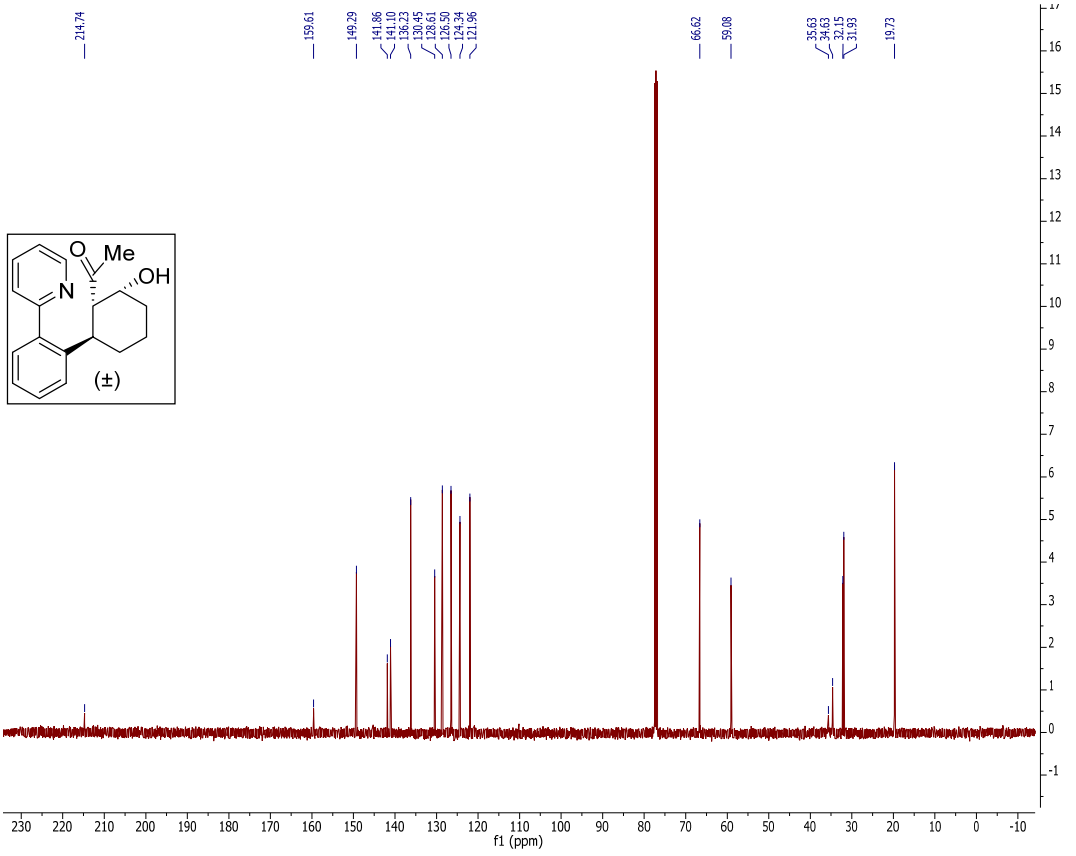
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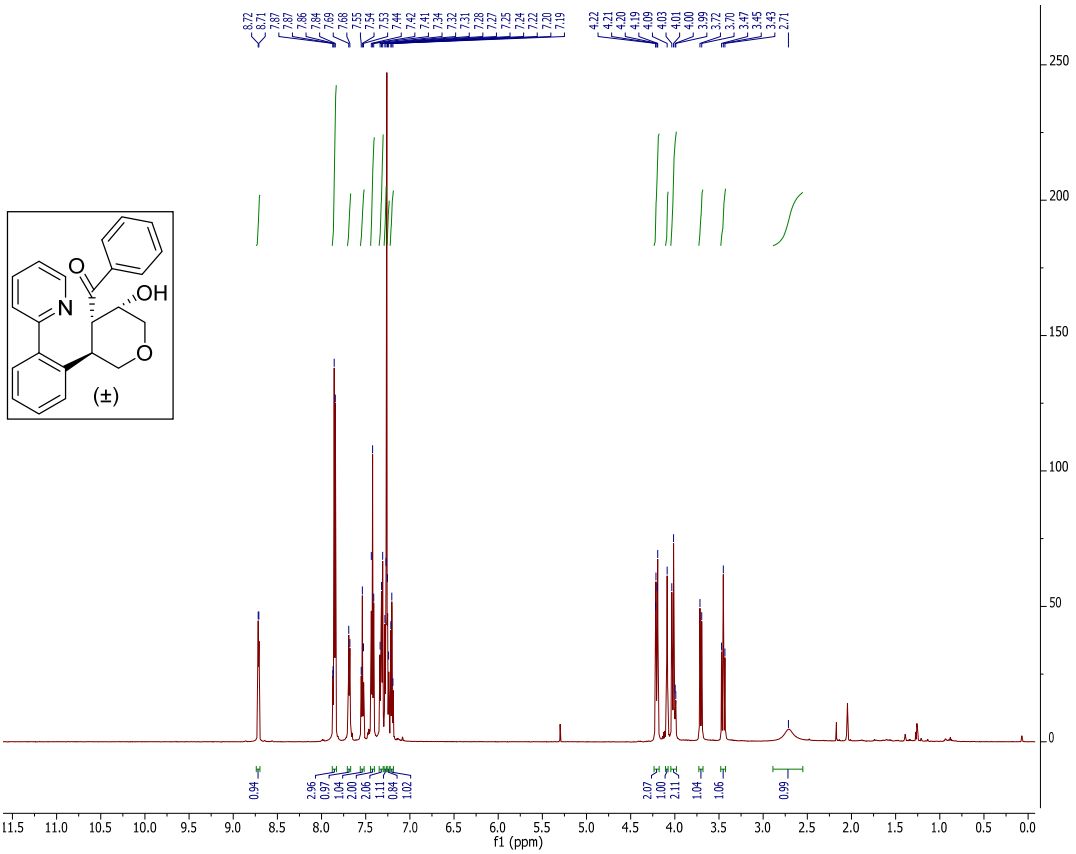
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7.20
7.19
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4.21
4.20
4.19
4.09
4.03
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4.00
3.99
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(±)
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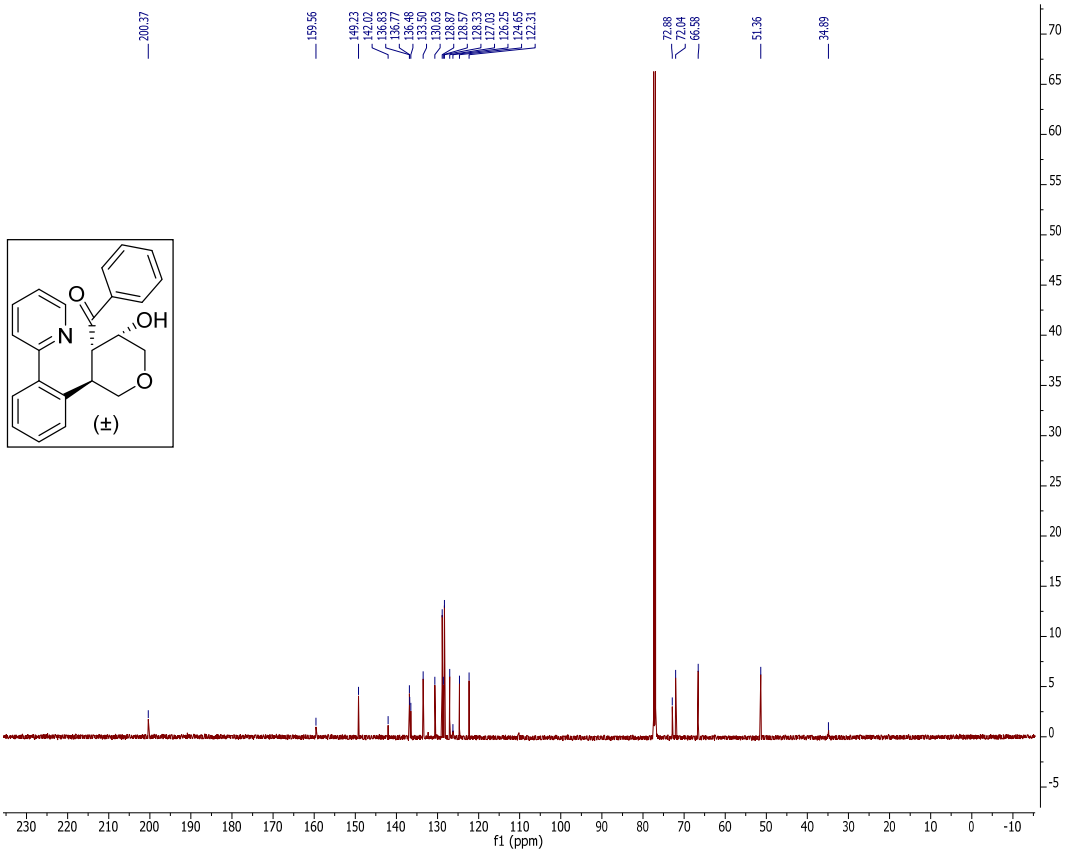
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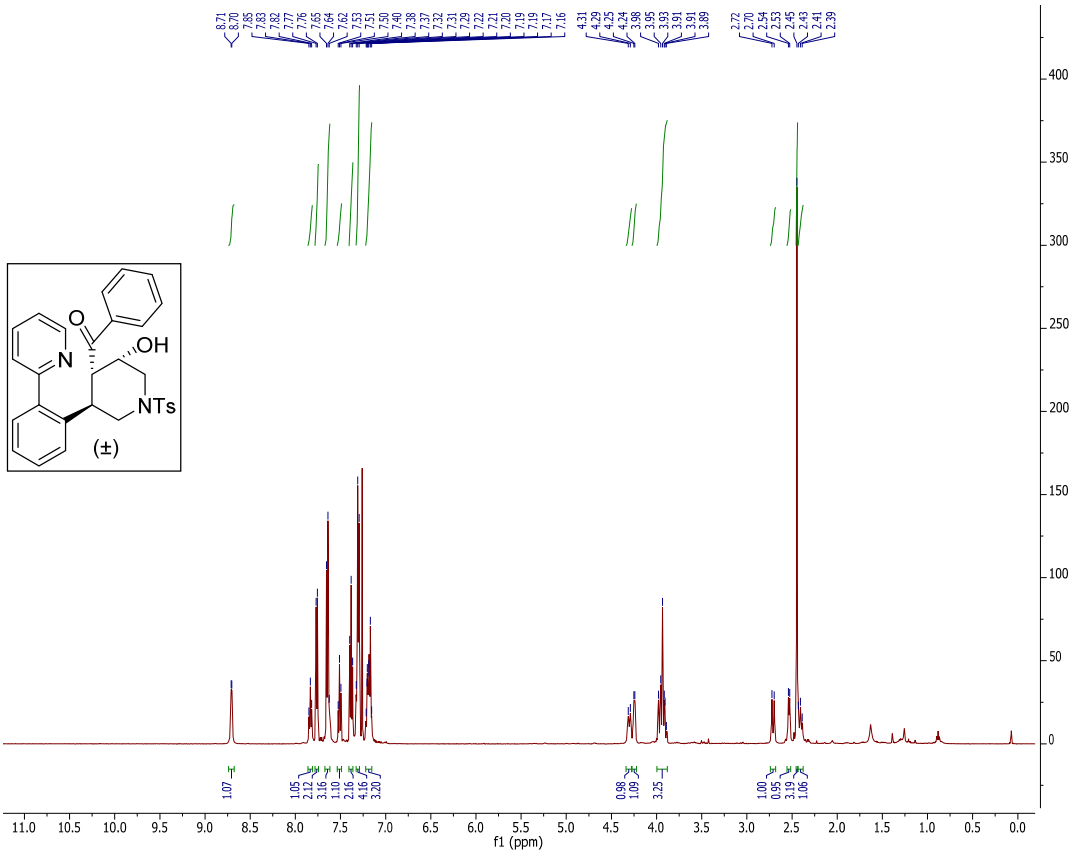
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(±)
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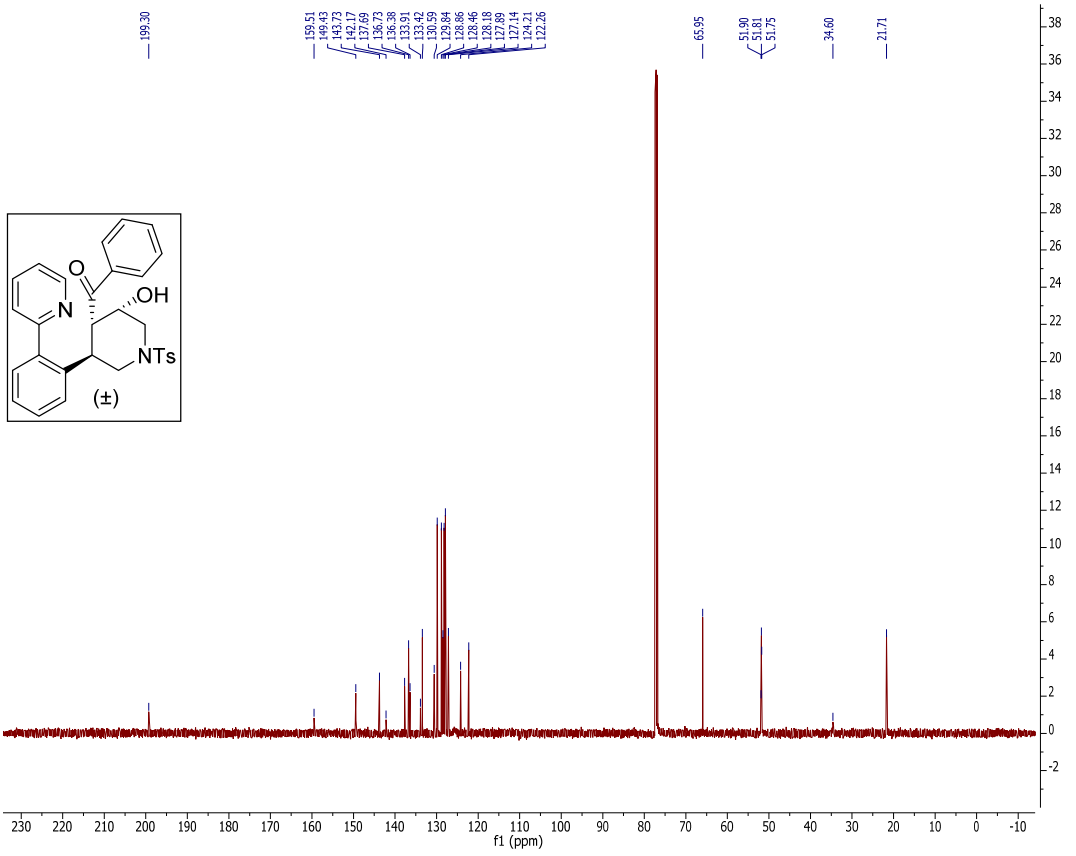
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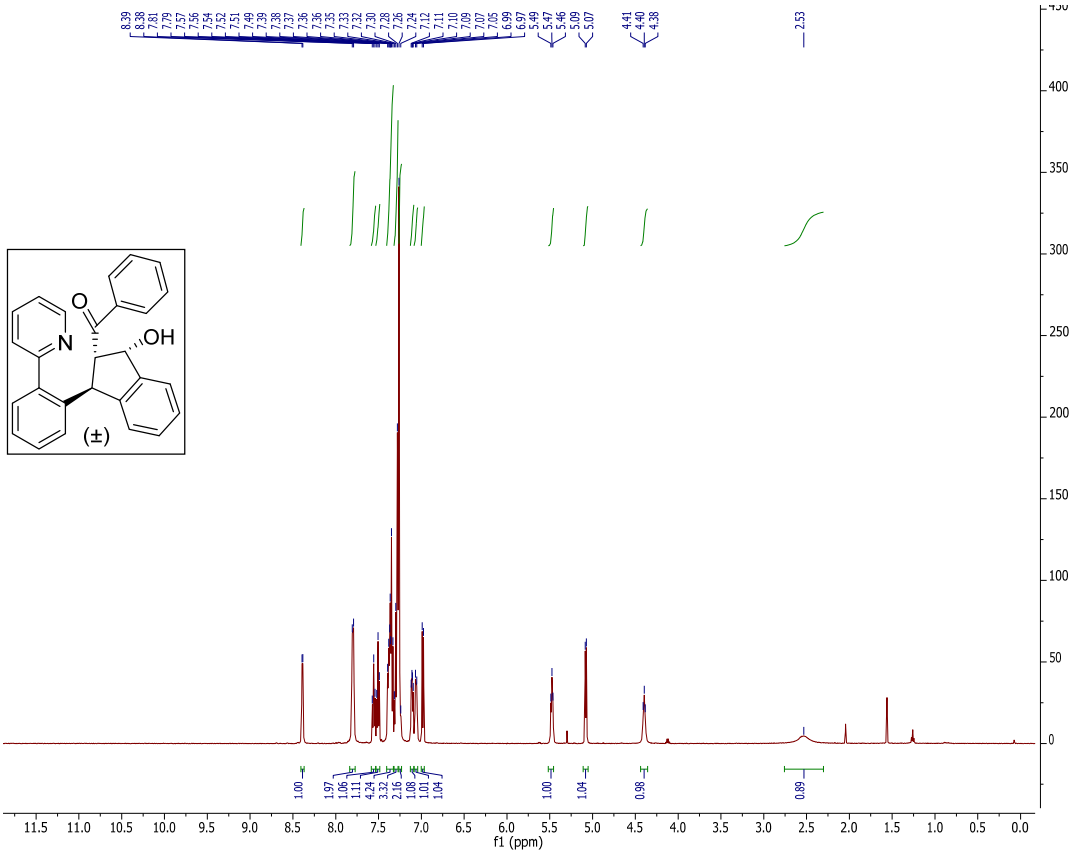
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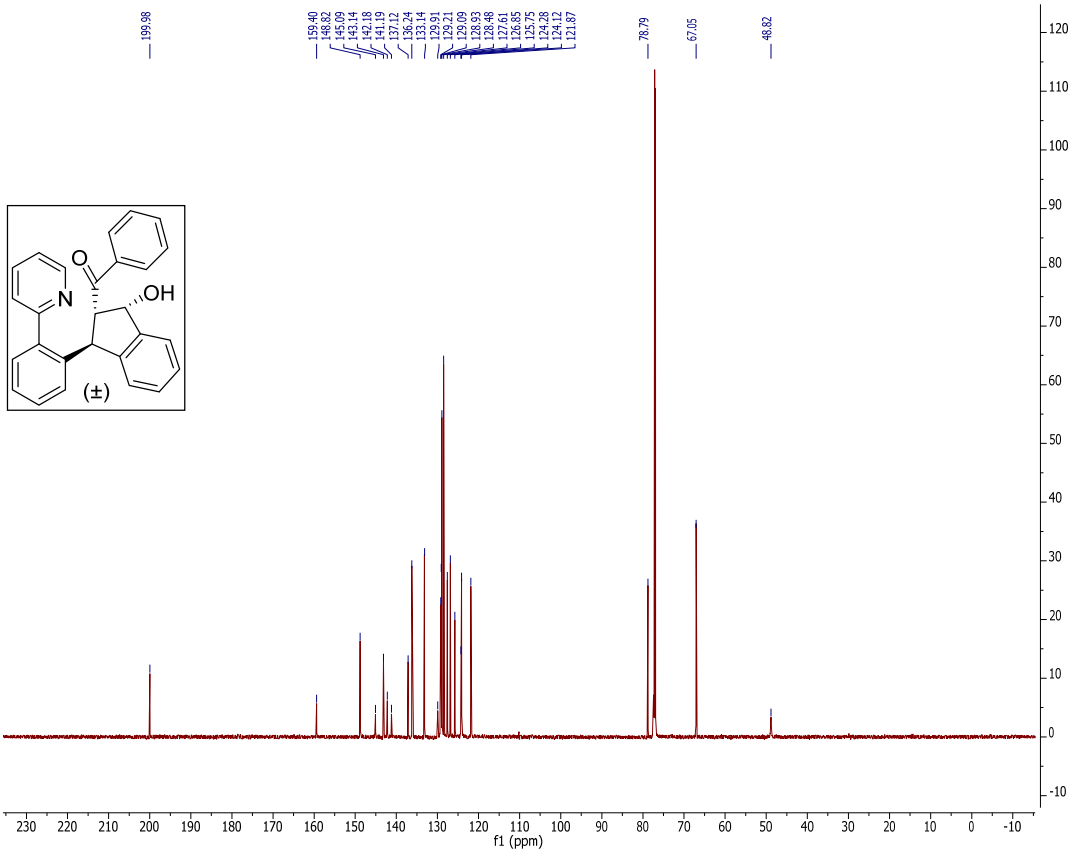
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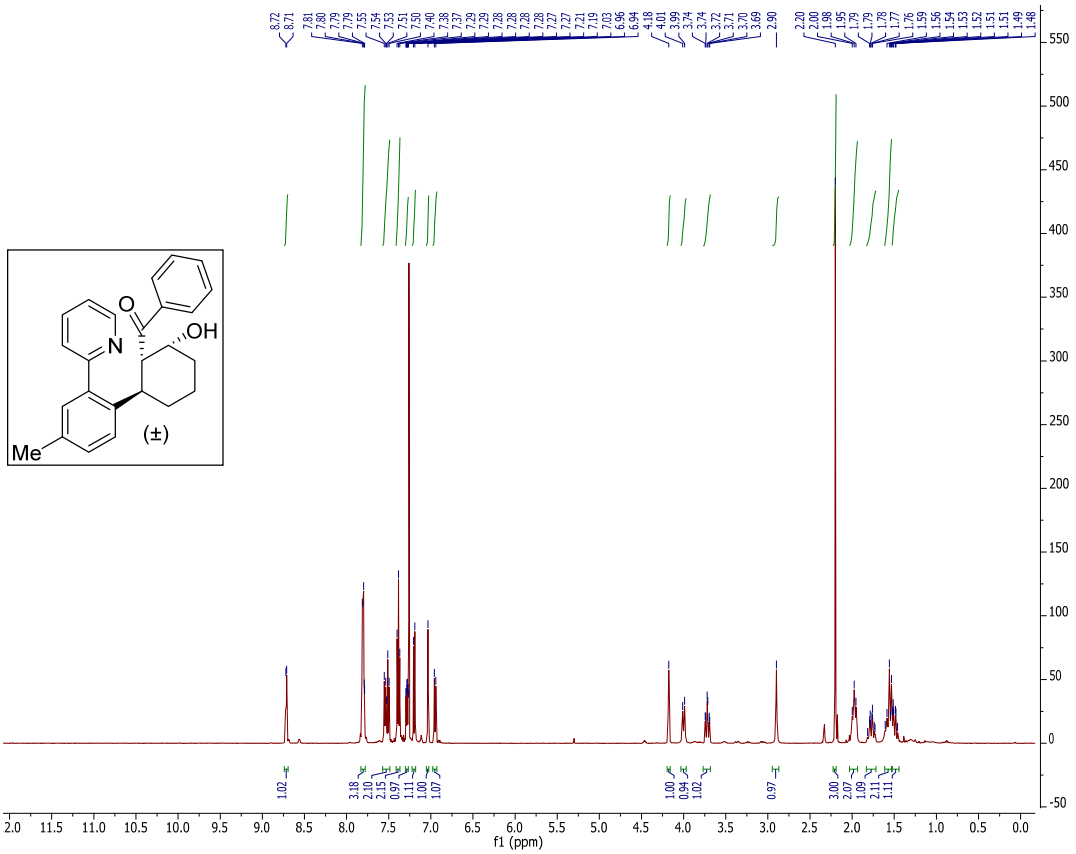
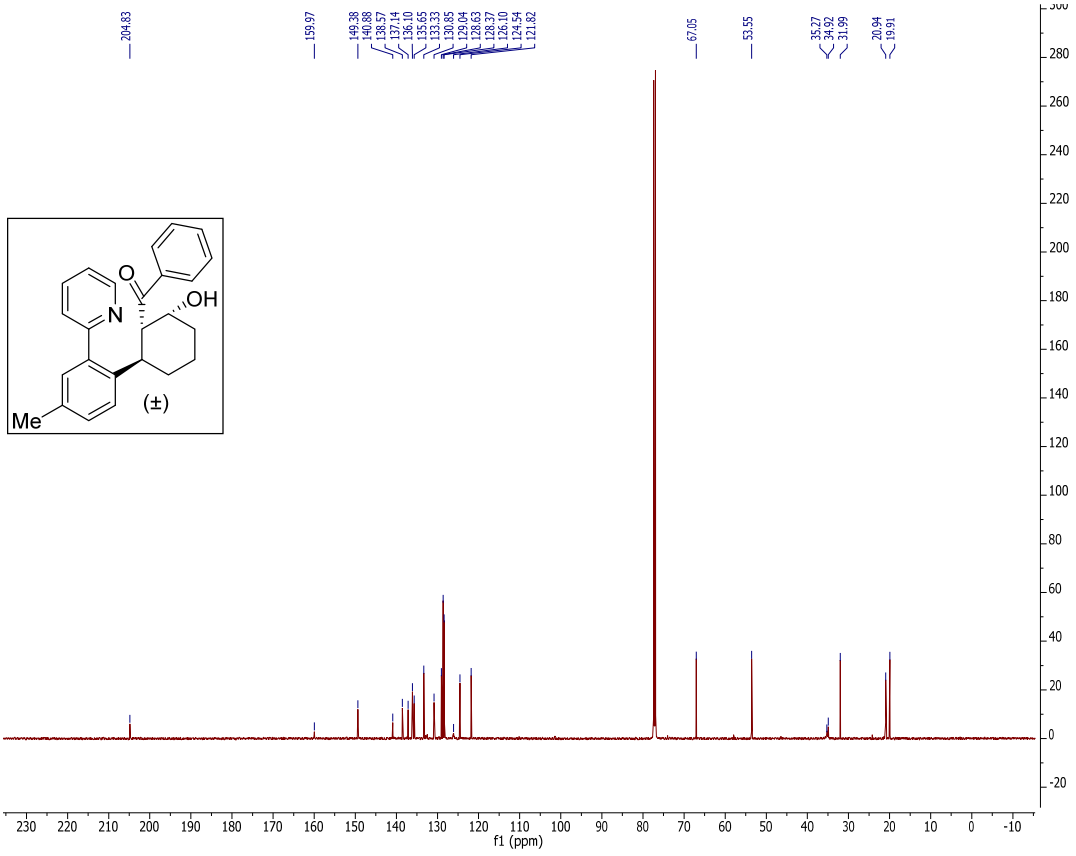
124.28
124.12
121.87
78.79
67.05
48.82
O
N
OH
(±)
f1 (ppm)


O
N
OH
Me
(±)
f1 (ppm)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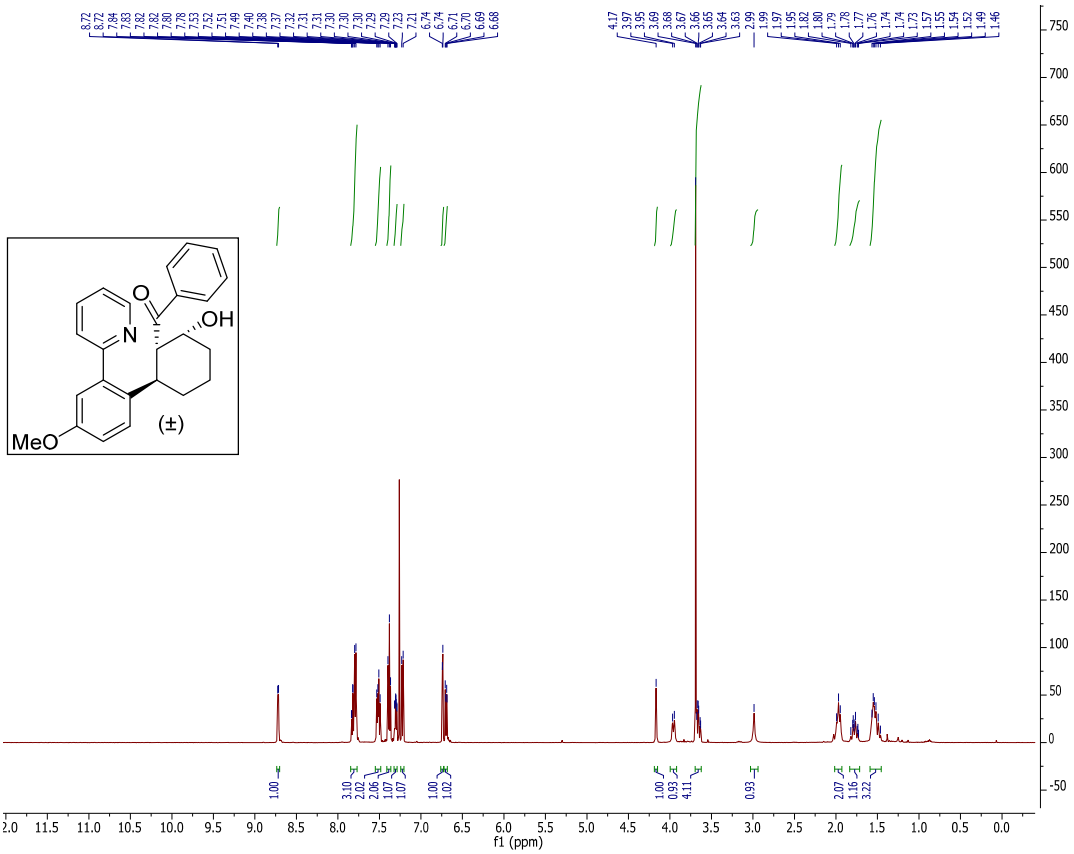
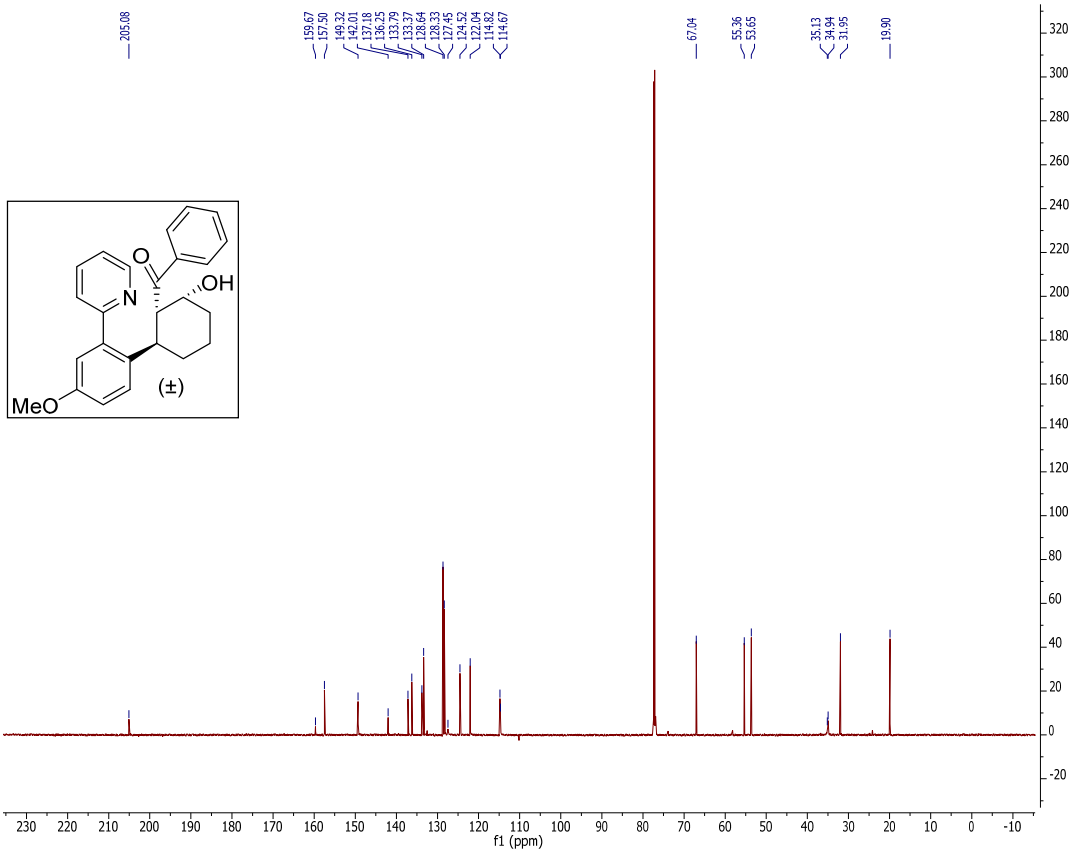
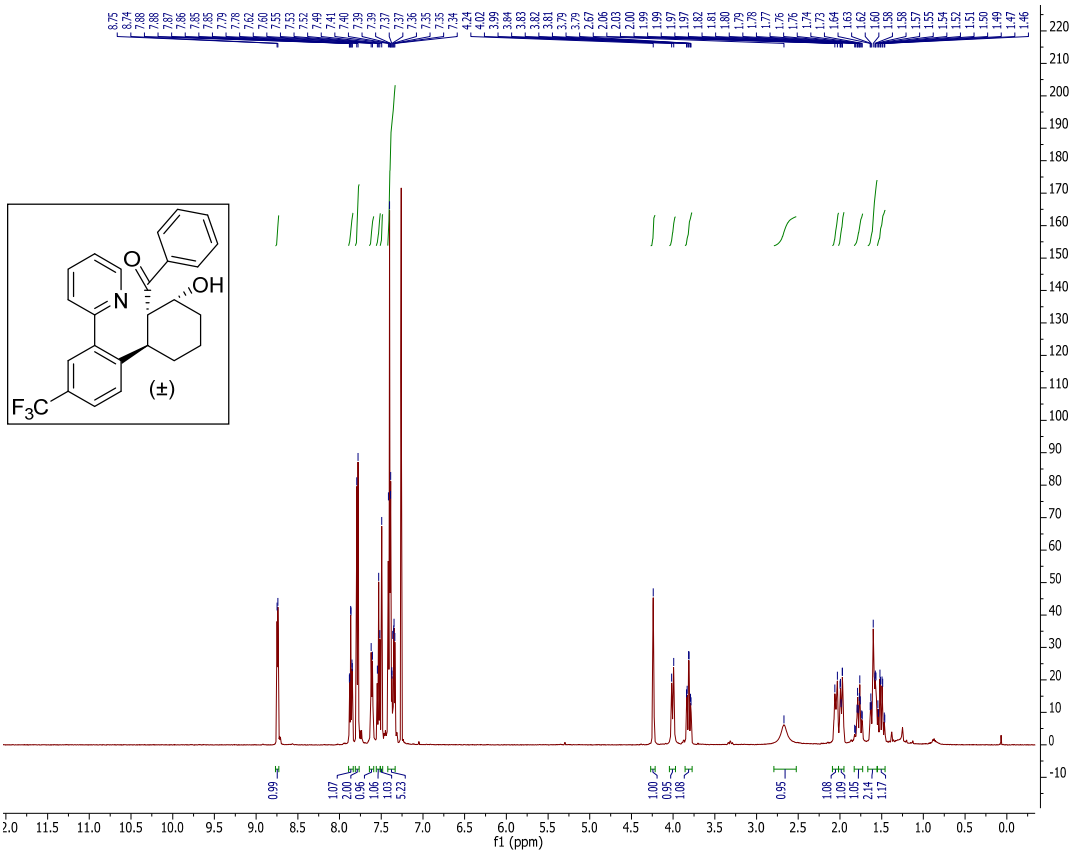
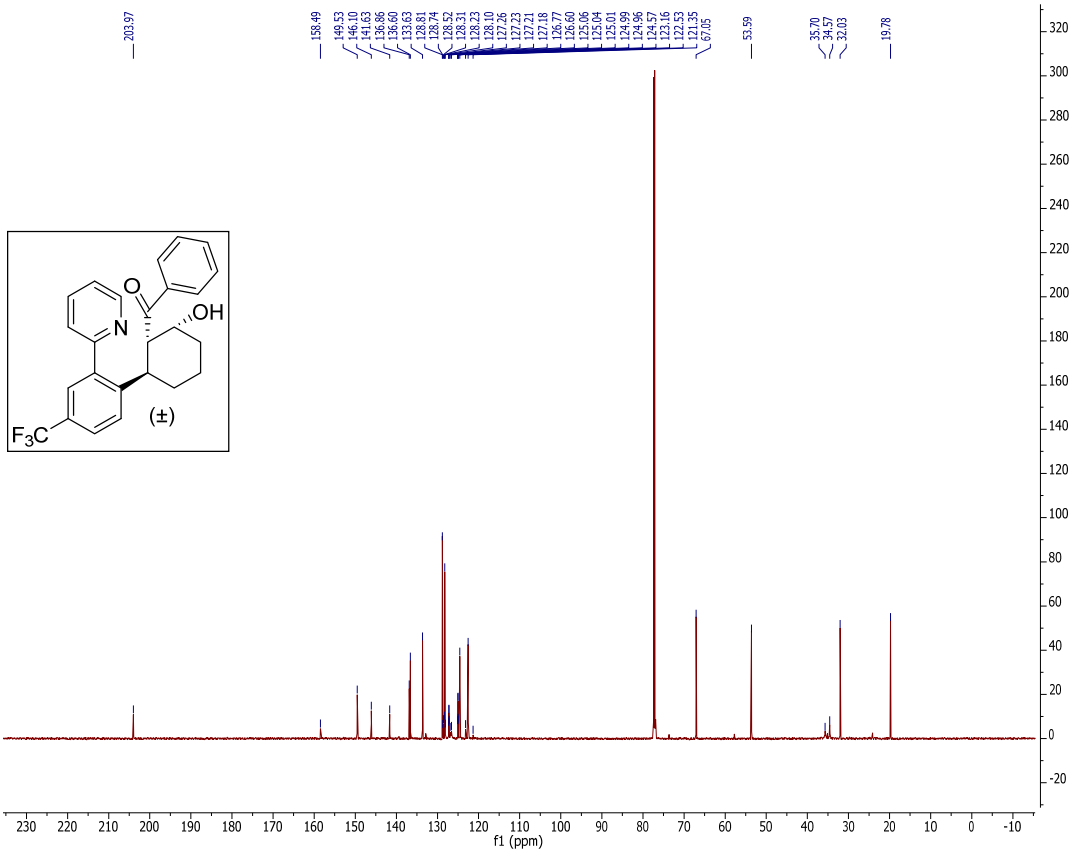
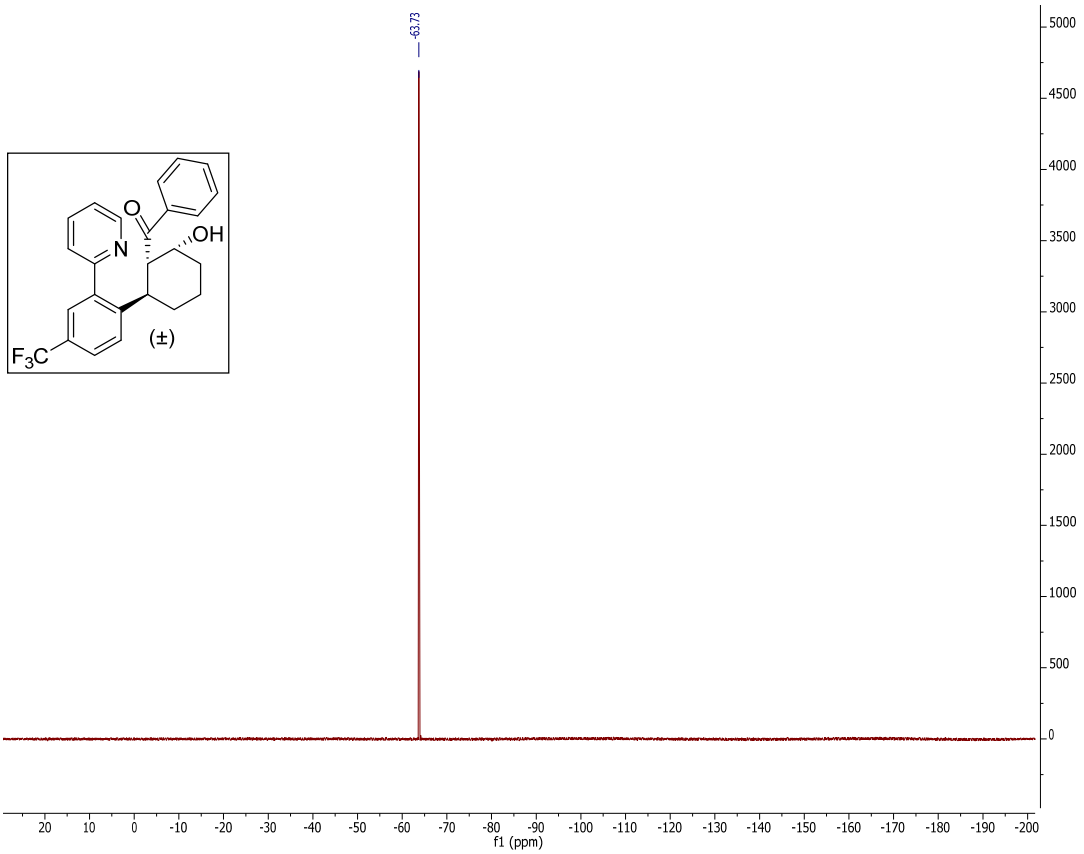
N
OH
Me
(±)
f1 (ppm)

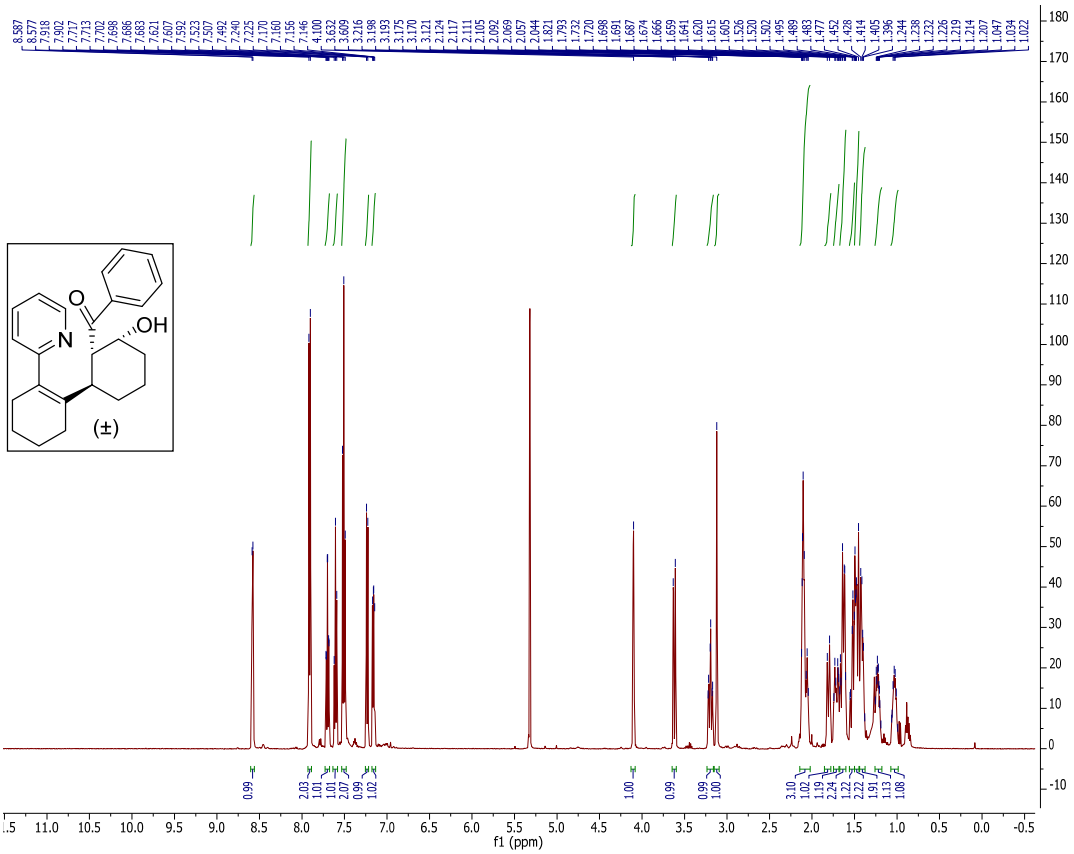

O
N
OH
MeO
(±)
f1 (ppm)

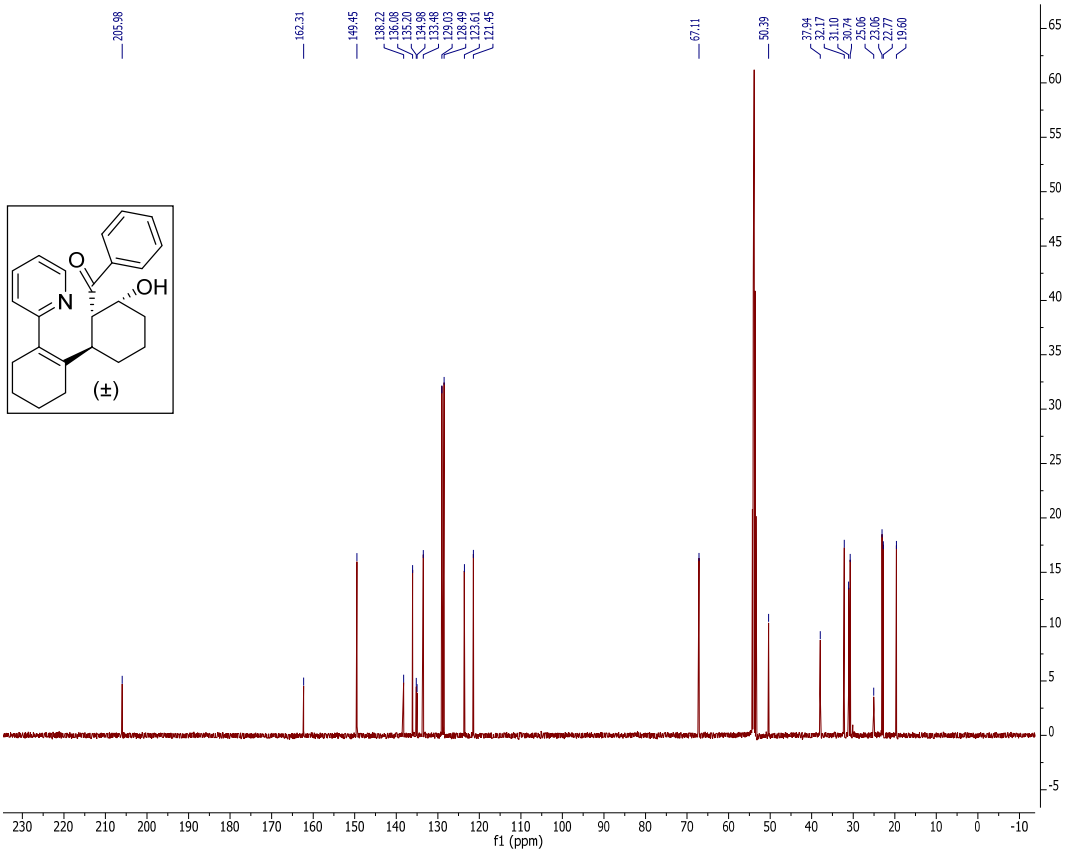

O
N
OH
MeO
(±)
f1 (ppm)

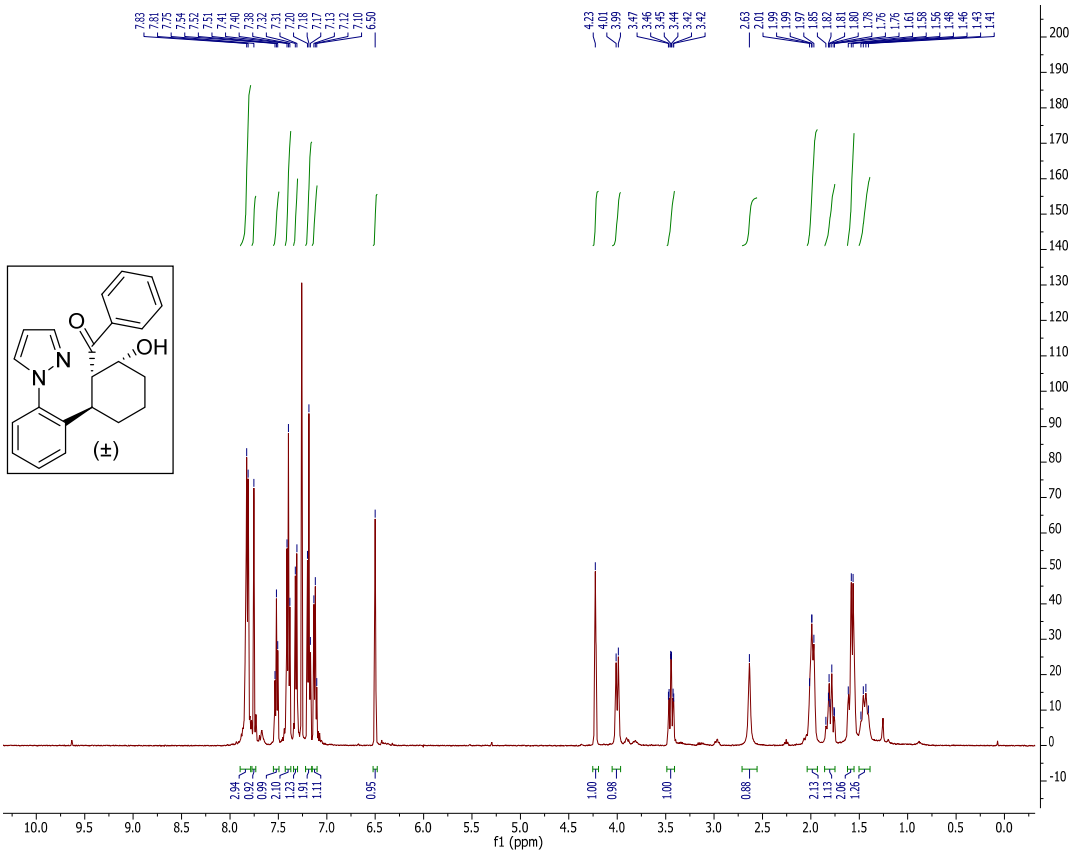

O
N
OH
F3C
(±)
f1 (ppm)

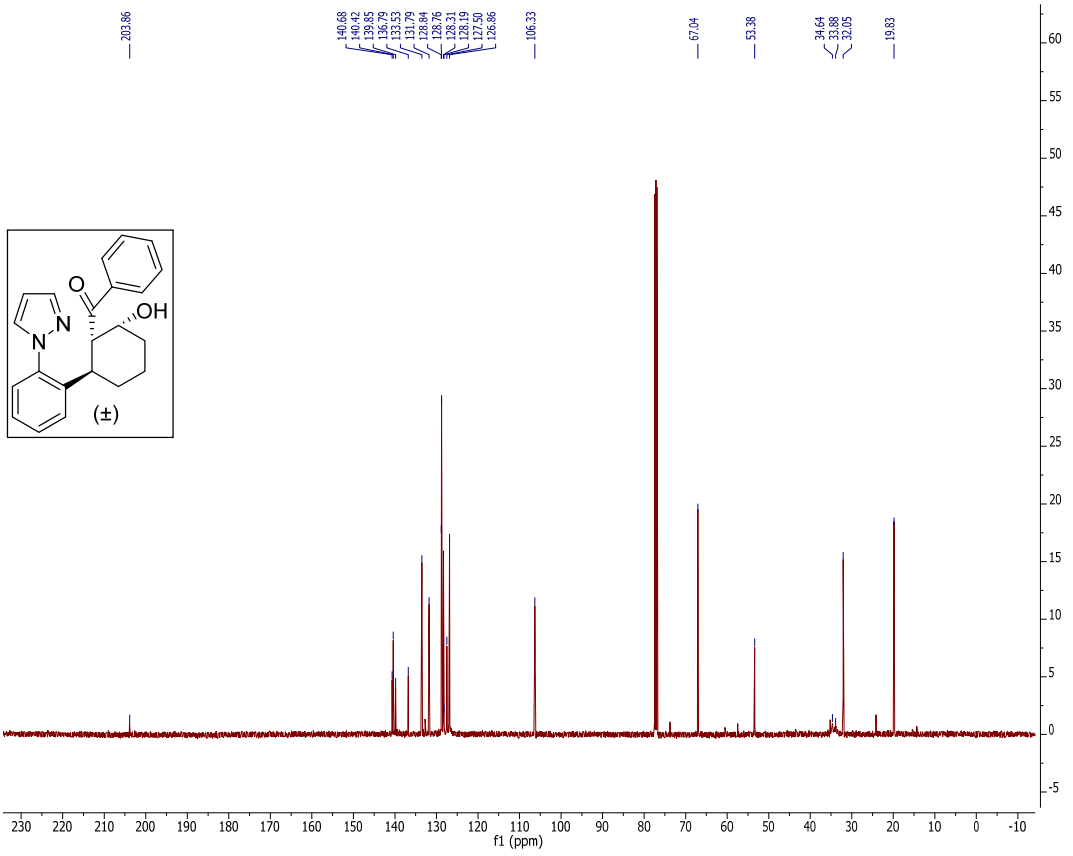

O
N
OH
F3C
(±)
f1 (ppm)

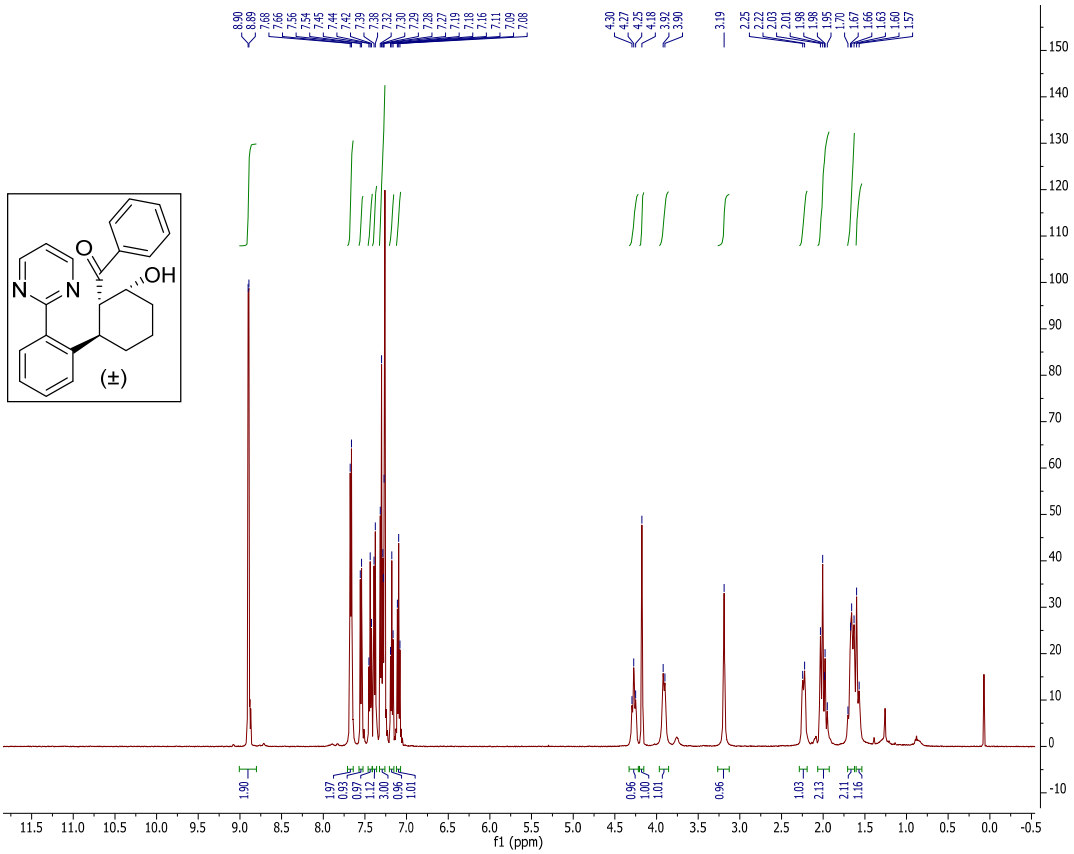

63.73
O
N
OH
(±)
F3C
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

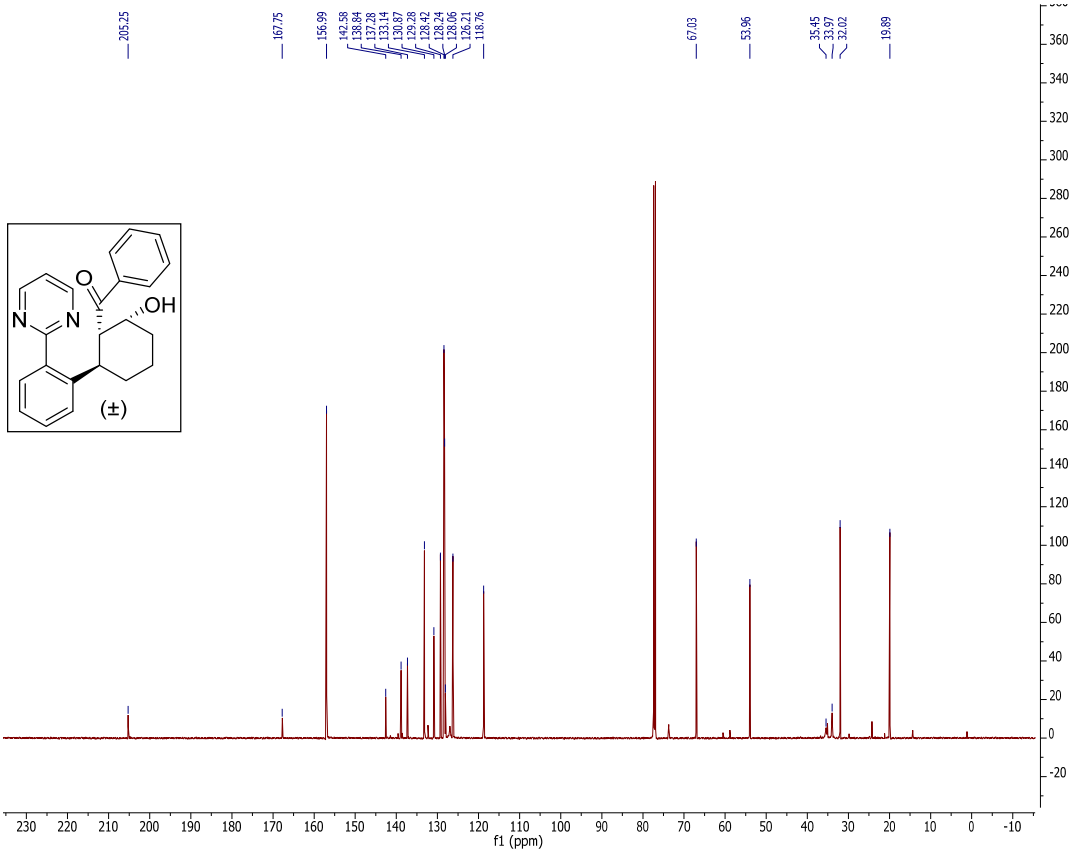

O
N
OH
(±)
f1 (ppm)

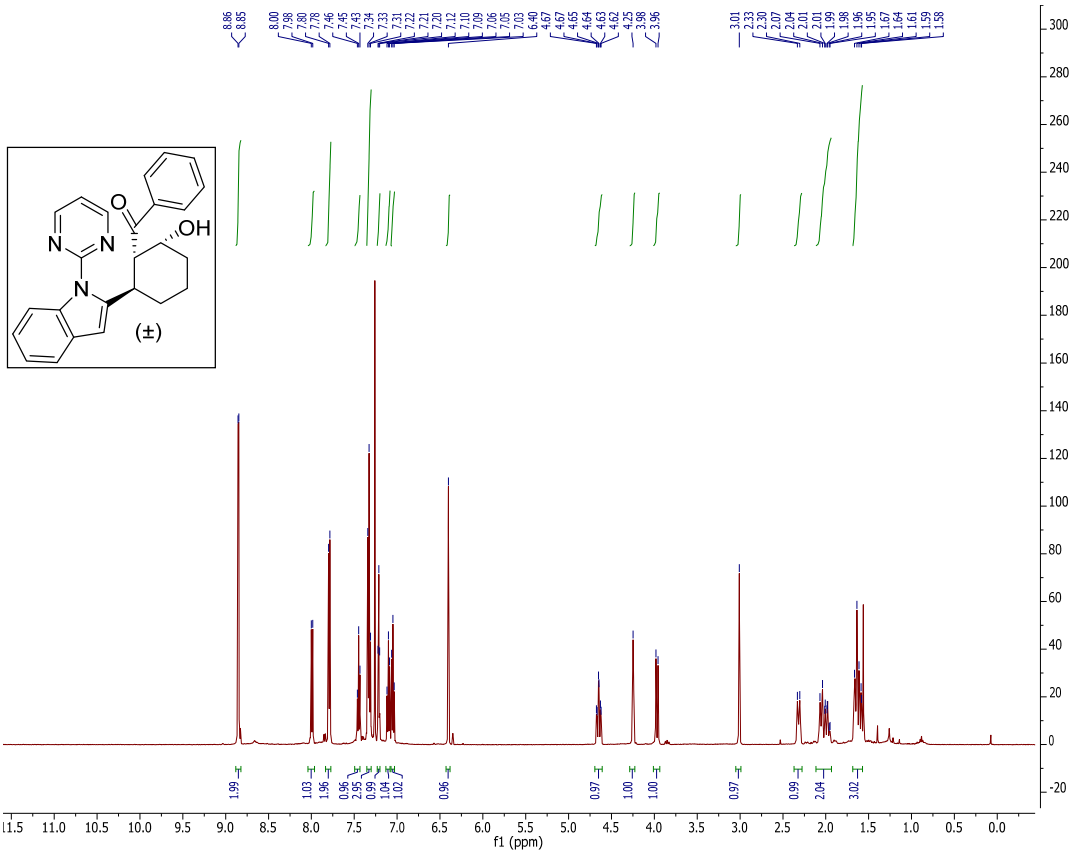

O
N
OH
(±)
f1 (ppm)

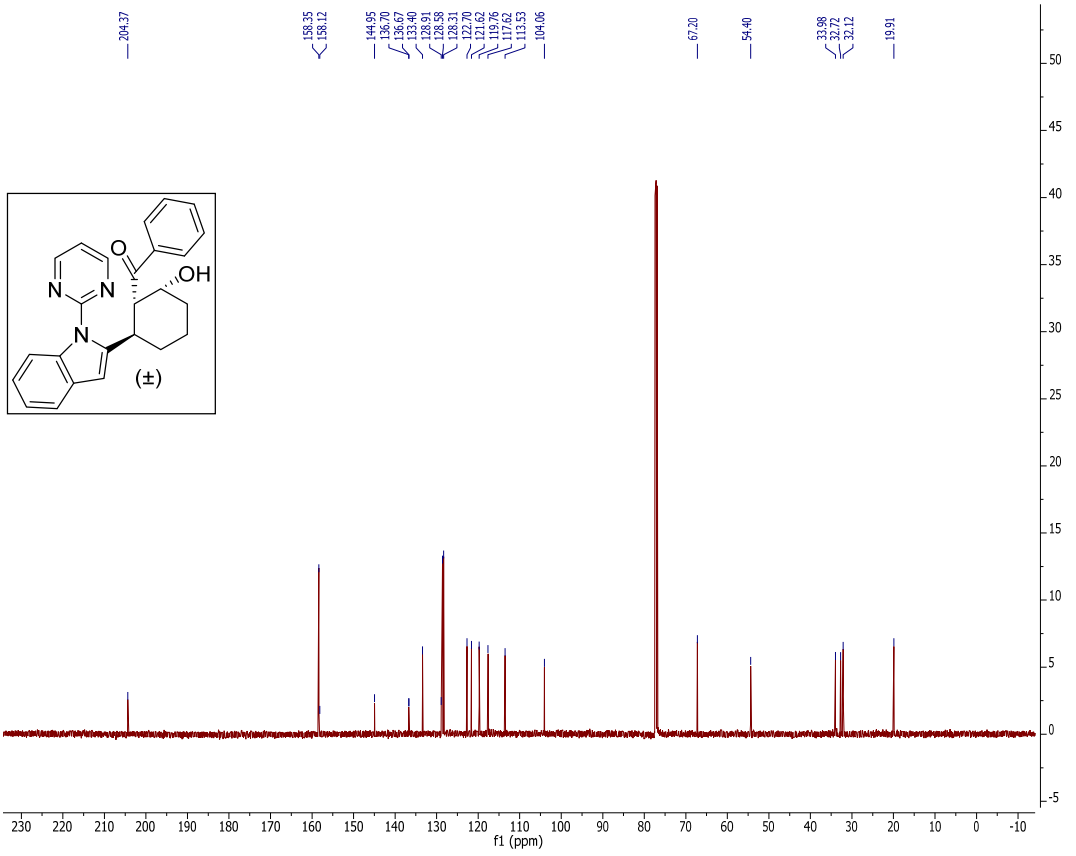

7.83
7.81
7.75
7.54
7.52
7.51
7.41
7.40
7.38
7.32
7.31
7.20
7.18
7.17
7.13
7.12
7.10
6.50
4.23
4.01
3.99
3.47
3.46
3.45
3.44
3.42
3.42
2.63
2.01
1.99
1.99
1.97
1.85
1.82
1.81
1.80
1.78
1.76
1.76
1.61
1.58
1.56
1.48
1.46
1.43
1.41
O
OH
N
N
(±)
2.94
0.92
0.99
2.10
1.23
1.91
1.11
0.95
1.00
0.98
1.00
0.88
2.13
1.13
2.06
1.26
f1 (ppm)

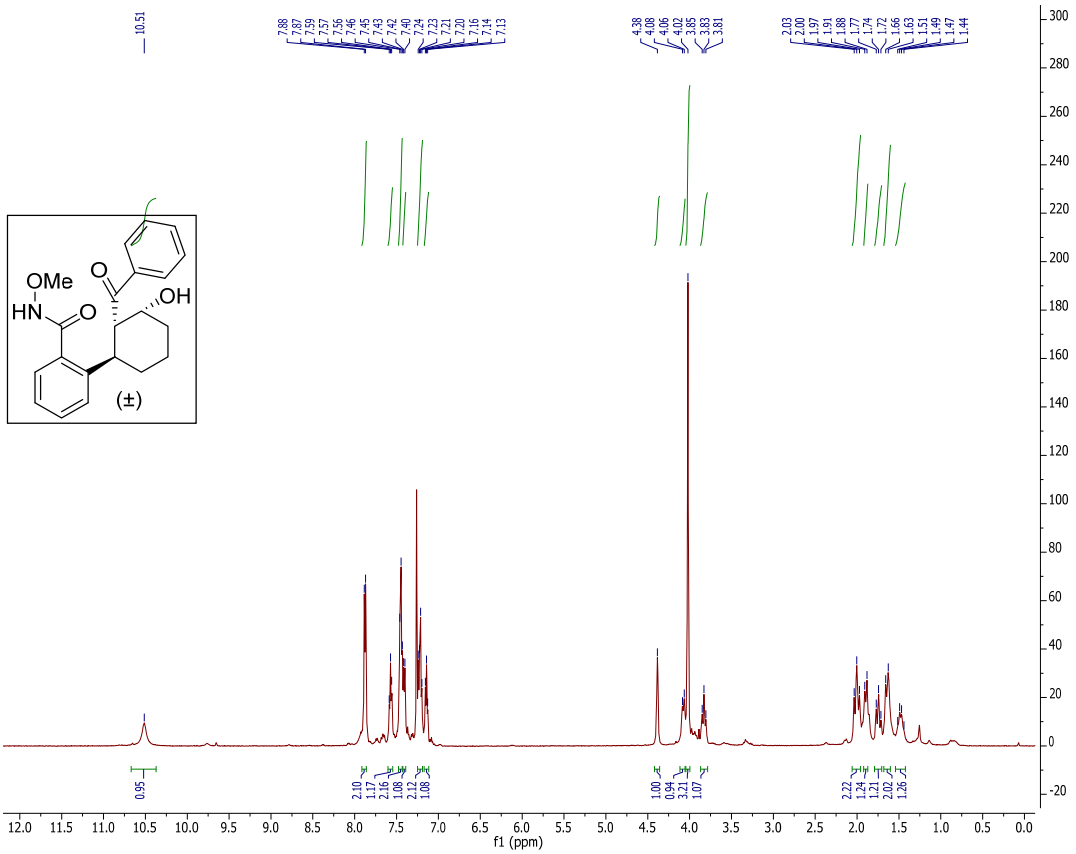

203.86
140.68
140.42
139.85
136.79
133.53
131.79
128.84
128.76
128.31
128.19
127.50
126.86
106.33
67.04
53.38
34.64
33.88
32.05
19.83
O
OH
N
N
(±)
f1 (ppm)

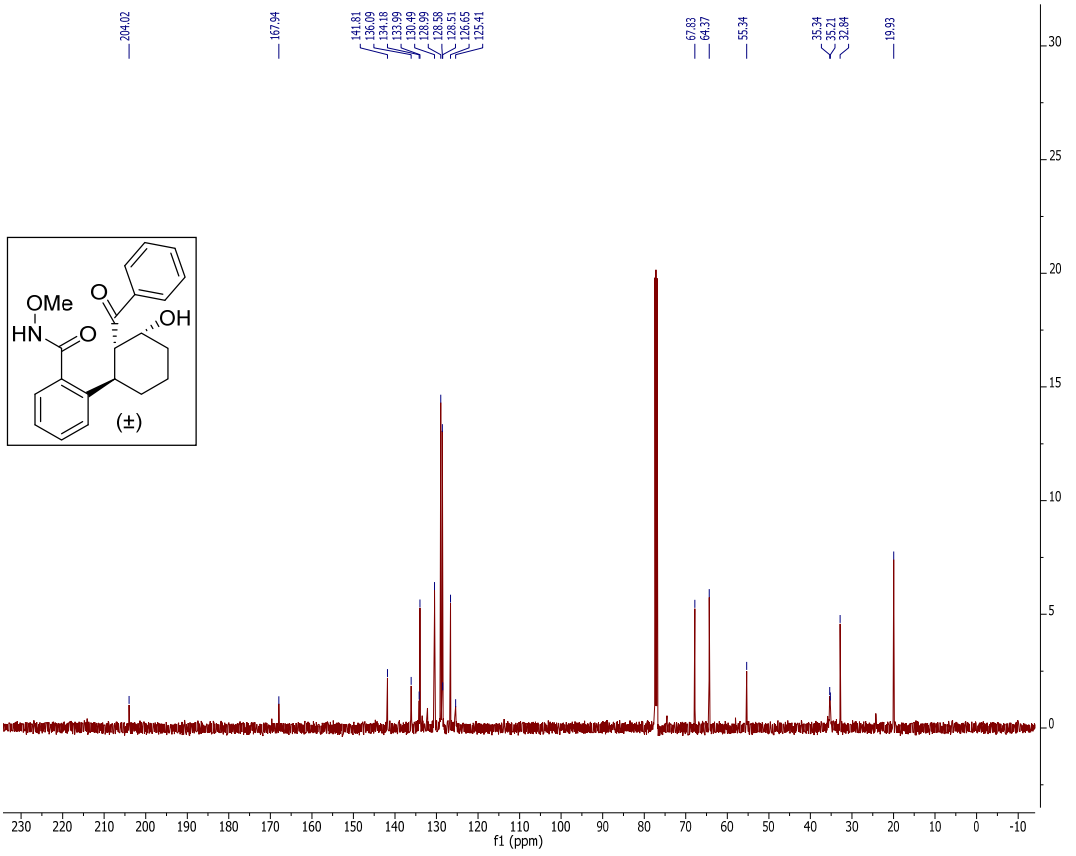

8.90
8.89
7.68
7.66
7.56
7.54
7.45
7.44
7.42
7.39
7.38
7.32
7.30
7.29
7.28
7.27
7.19
7.18
7.16
7.11
7.09
7.08
4.30
4.27
4.25
4.18
3.92
3.90
3.19
2.25
2.22
2.03
2.01
1.98
1.98
1.95
1.70
1.67
1.66
1.63
1.60
1.57
1.90
1.97
0.93
0.97
1.12
3.00
0.96
1.01
0.96
1.00
1.01
0.96
1.03
2.13
2.11
1.16
f1 (ppm)
O
N
N
OH
(±)

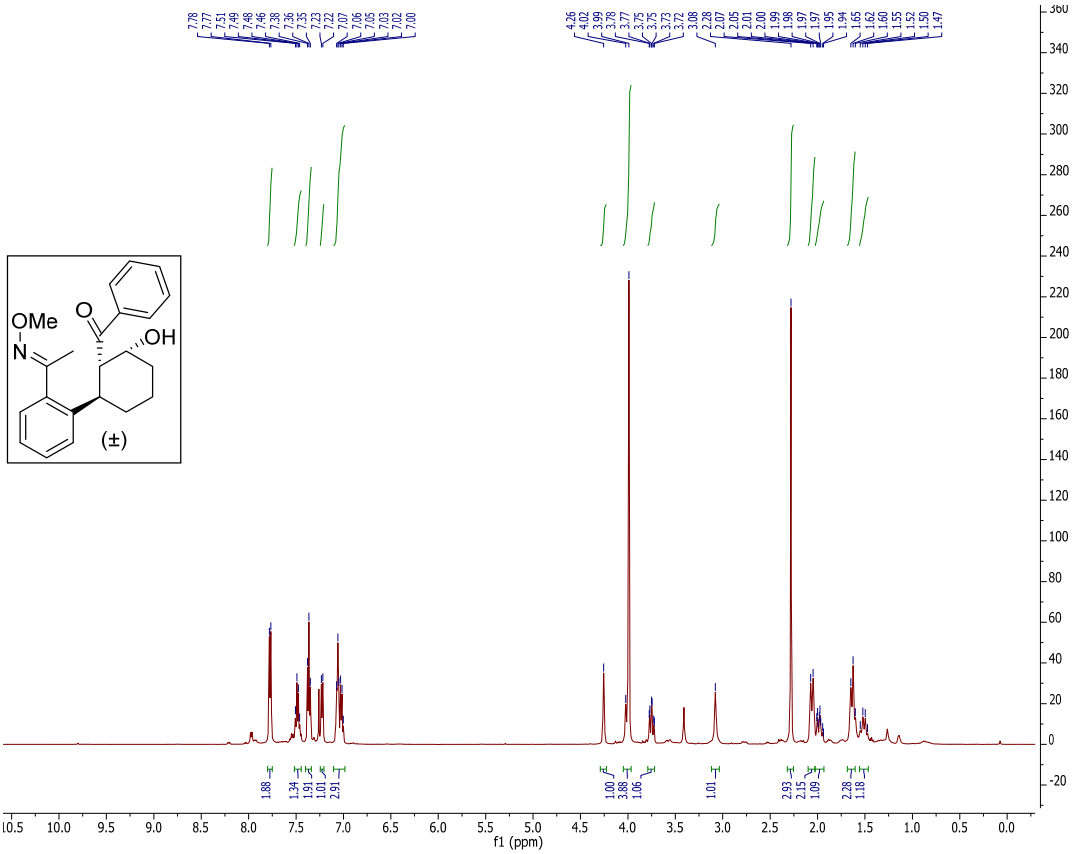

205.25
167.75
156.99
143.58
138.84
137.28
133.14
130.87
129.28
128.42
128.24
128.06
126.21
118.76
67.03
53.96
35.45
33.97
32.02
19.89
f1 (ppm)
O
N
N
OH
(±)

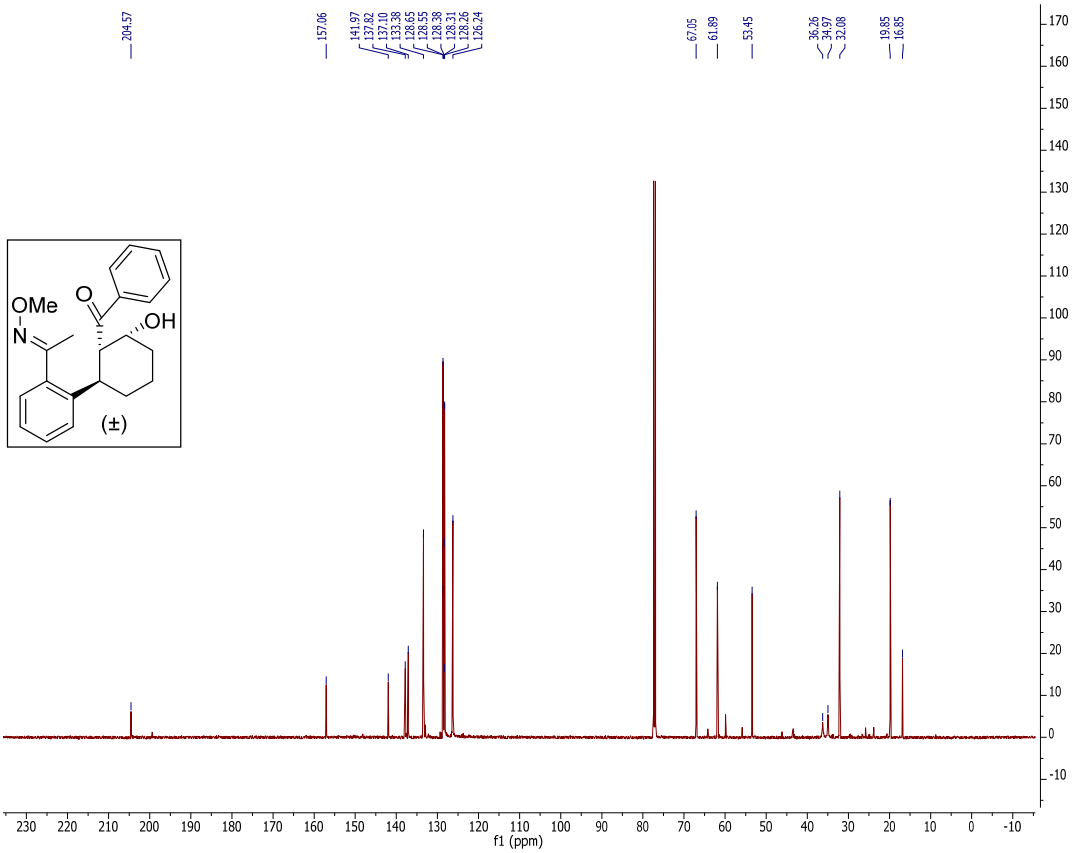

O
OH
N
N
N
(±)
f1 (ppm)

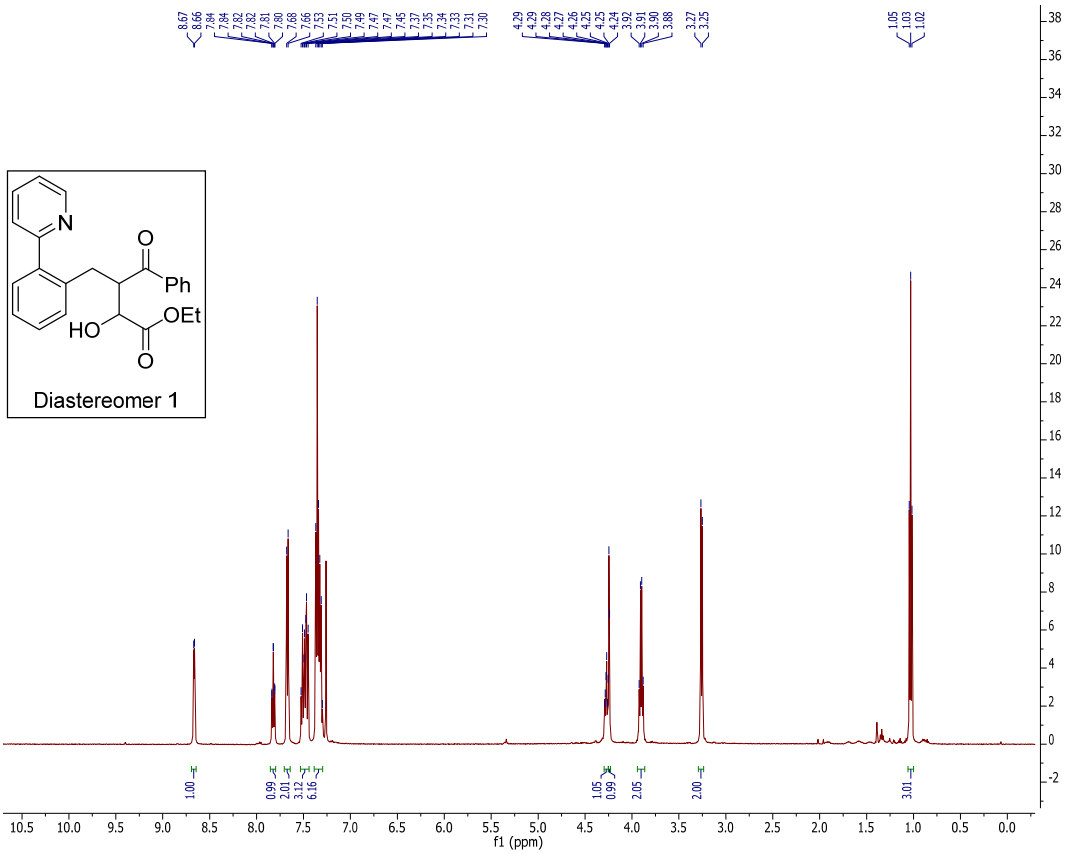

O
OH
N
N
N
(±)
f1 (ppm)

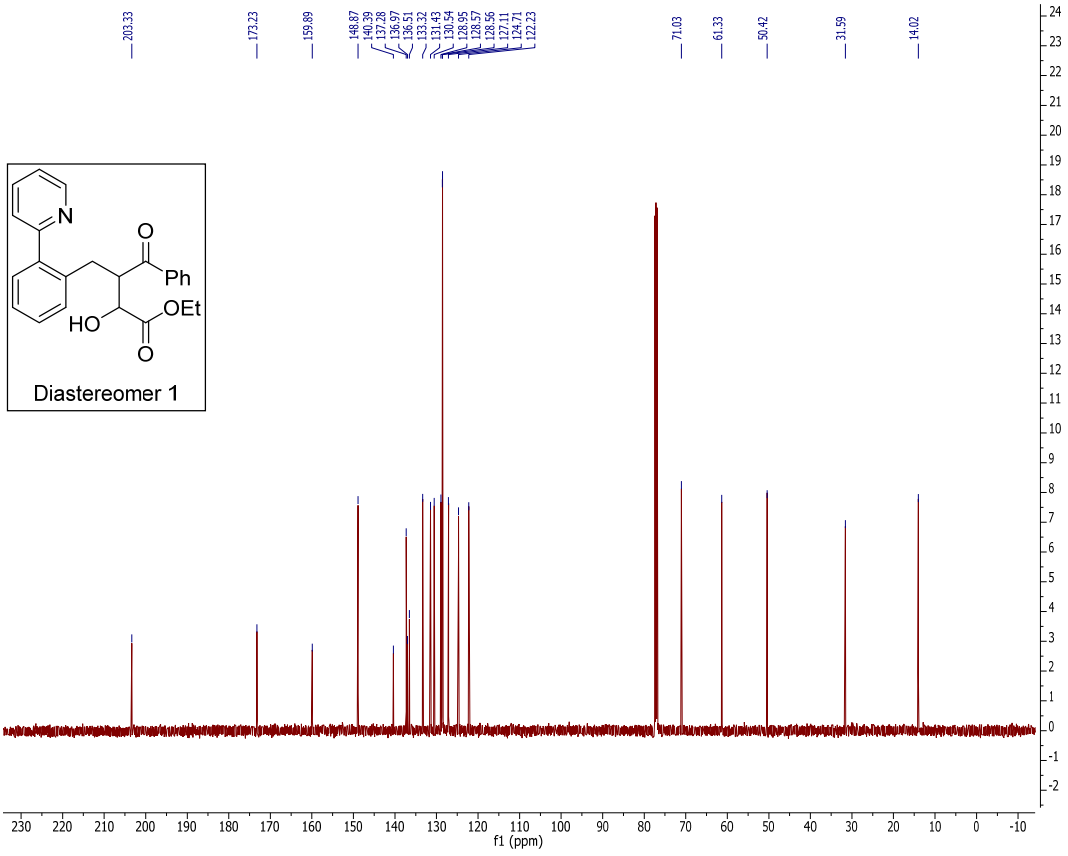

OMe
HN
O
O
OH
(±)
f1 (ppm)

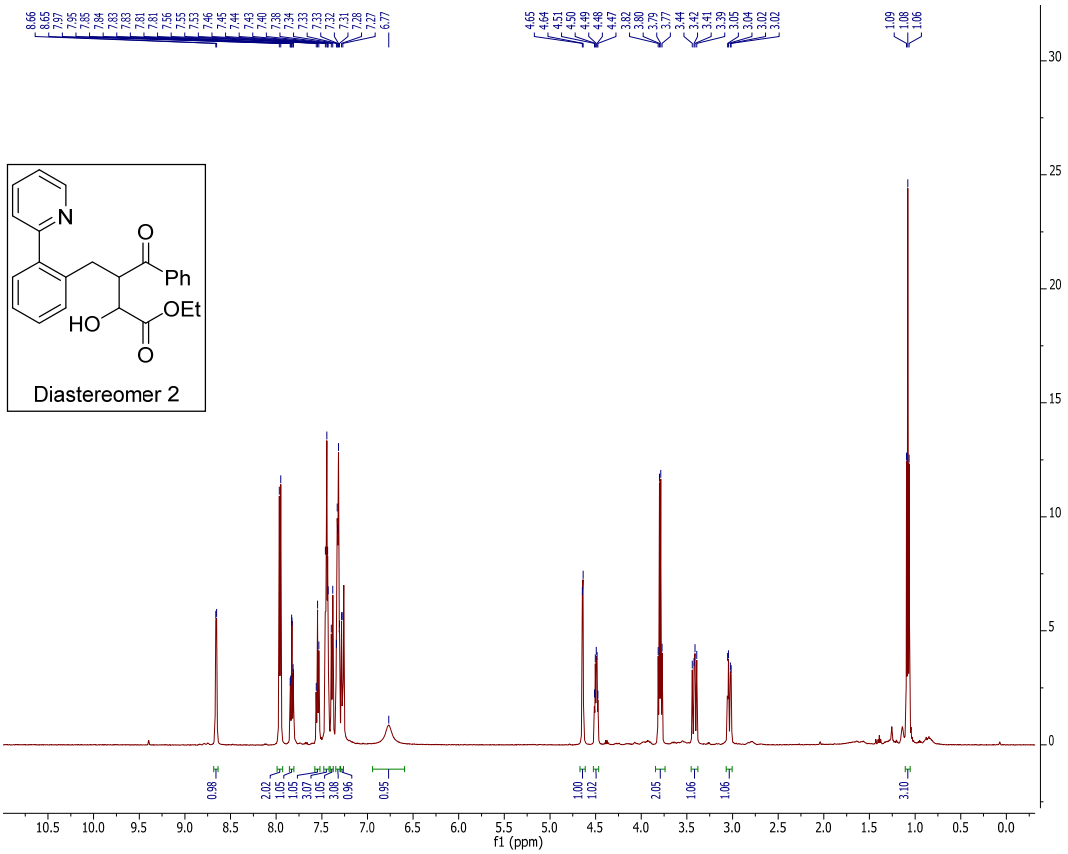

OMe
HN
O
O
OH
(±)
f1 (ppm)

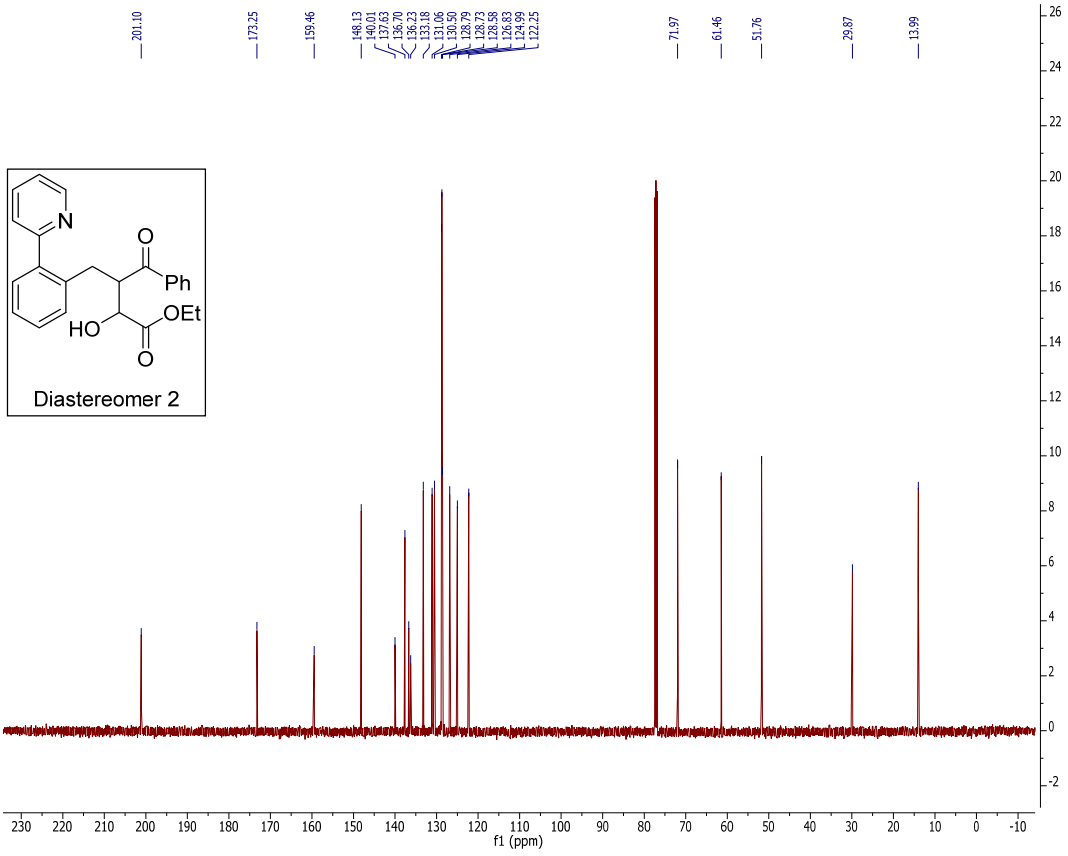

OMe
N
O
OH
(±)
f1 (ppm)

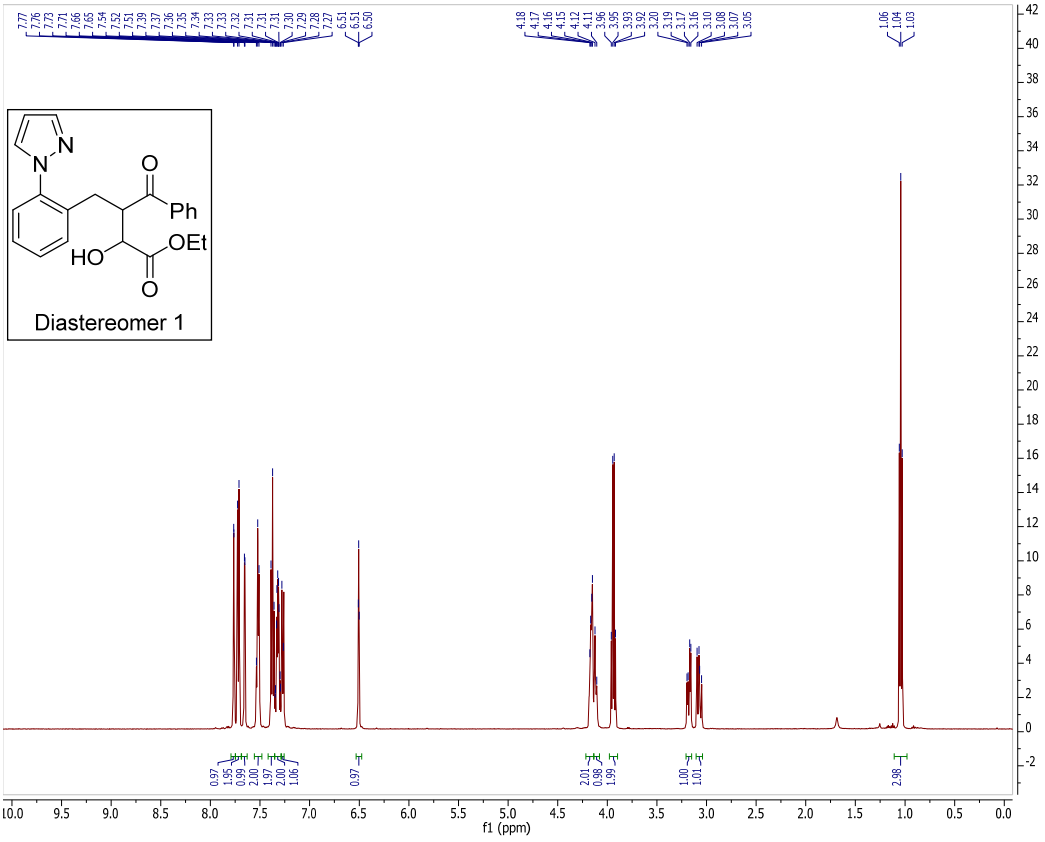

OMe
N
O
OH
(±)
f1 (ppm)

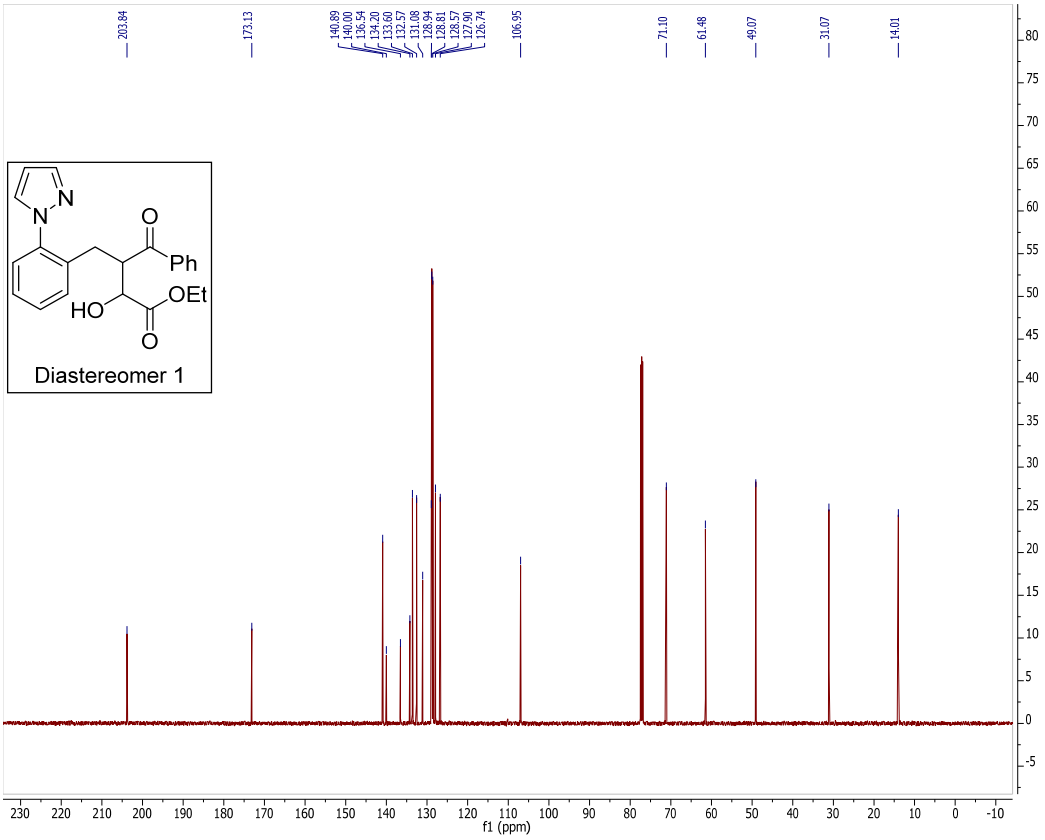

Diastereomer 1
f1 (ppm)

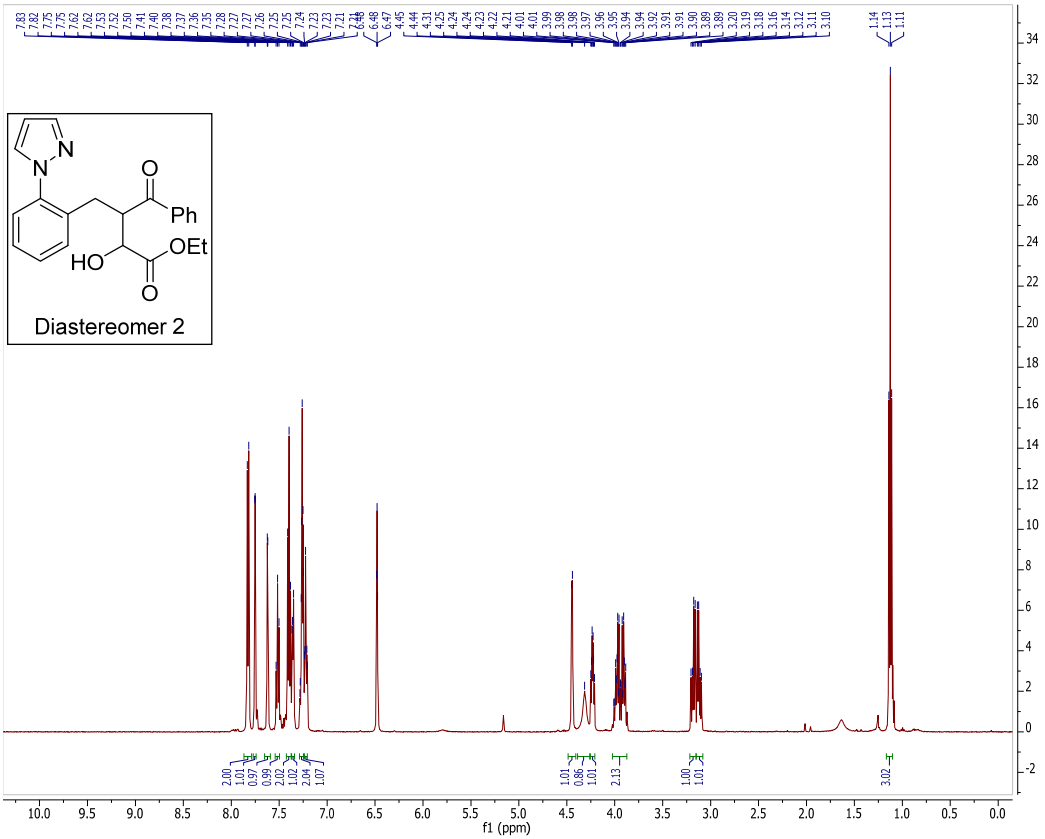

Diastereomer 1
f1 (ppm)

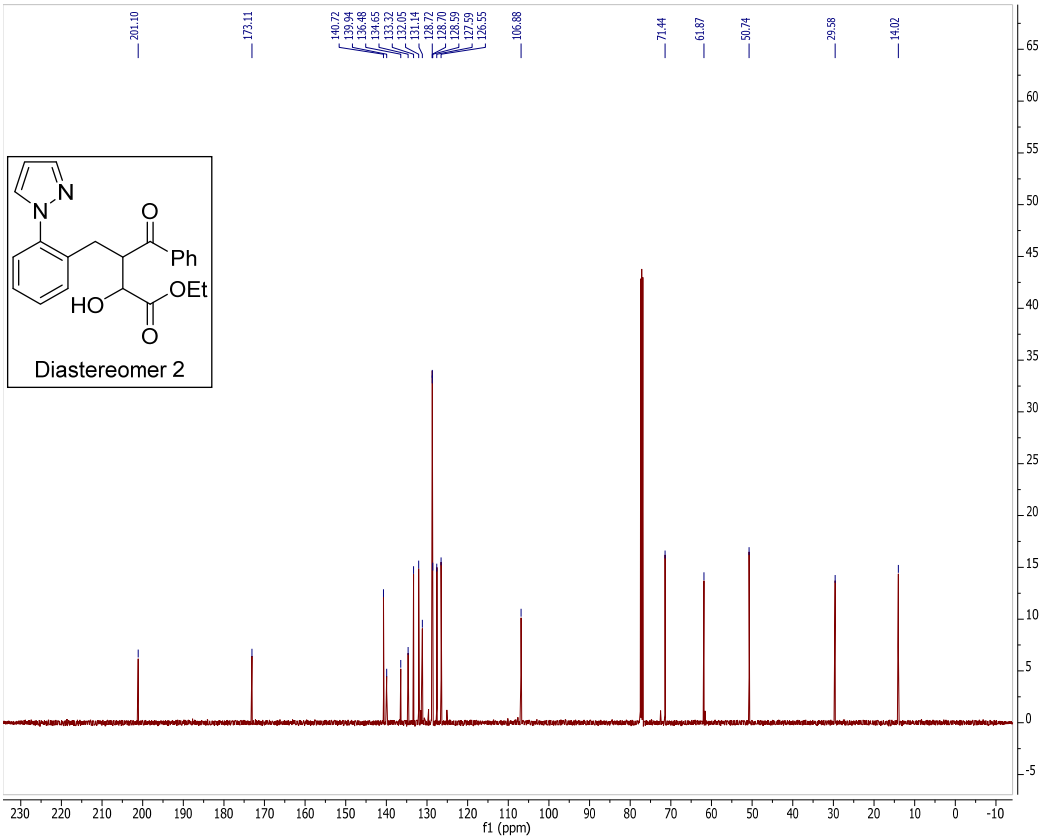

Diastereomer 2
f1 (ppm)

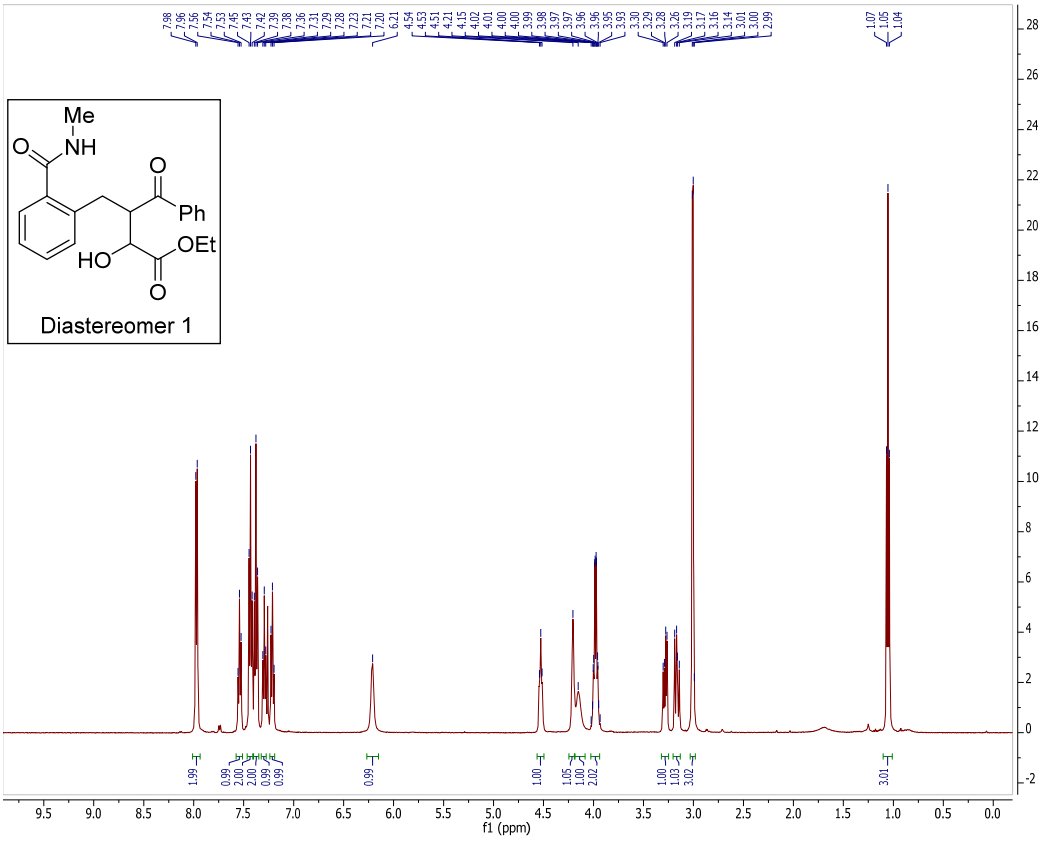

Diastereomer 2
f1 (ppm)

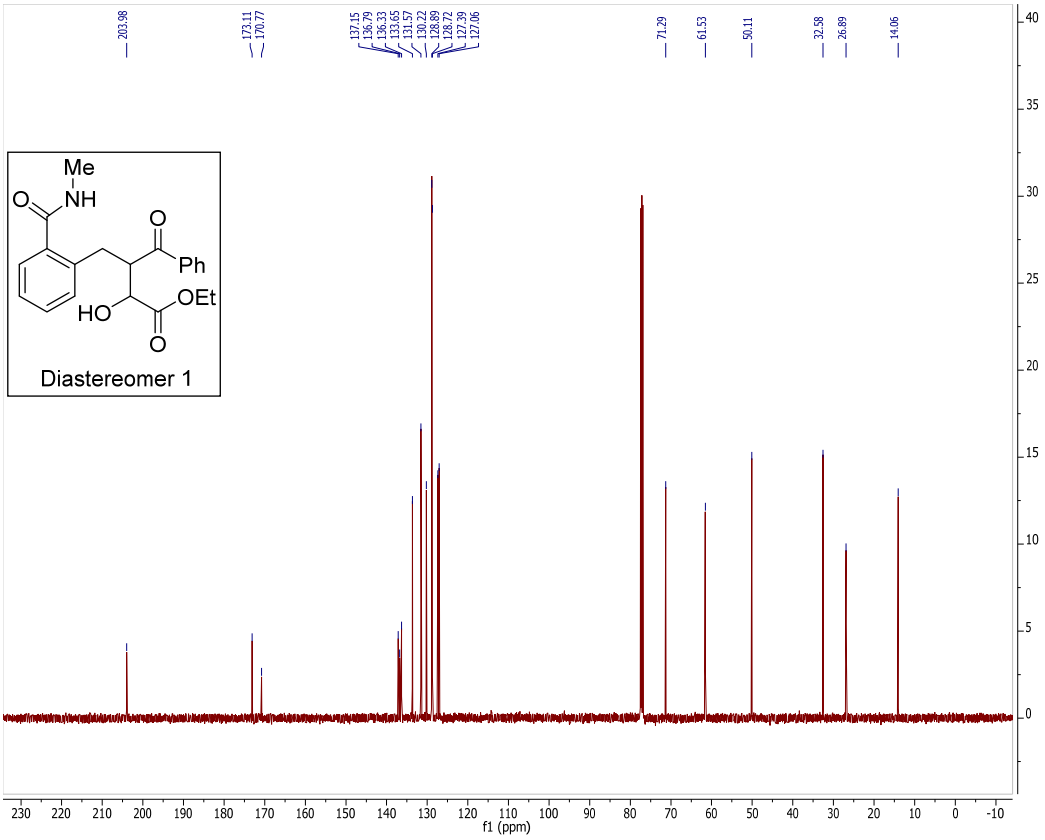

Diastereomer 1
f1 (ppm)

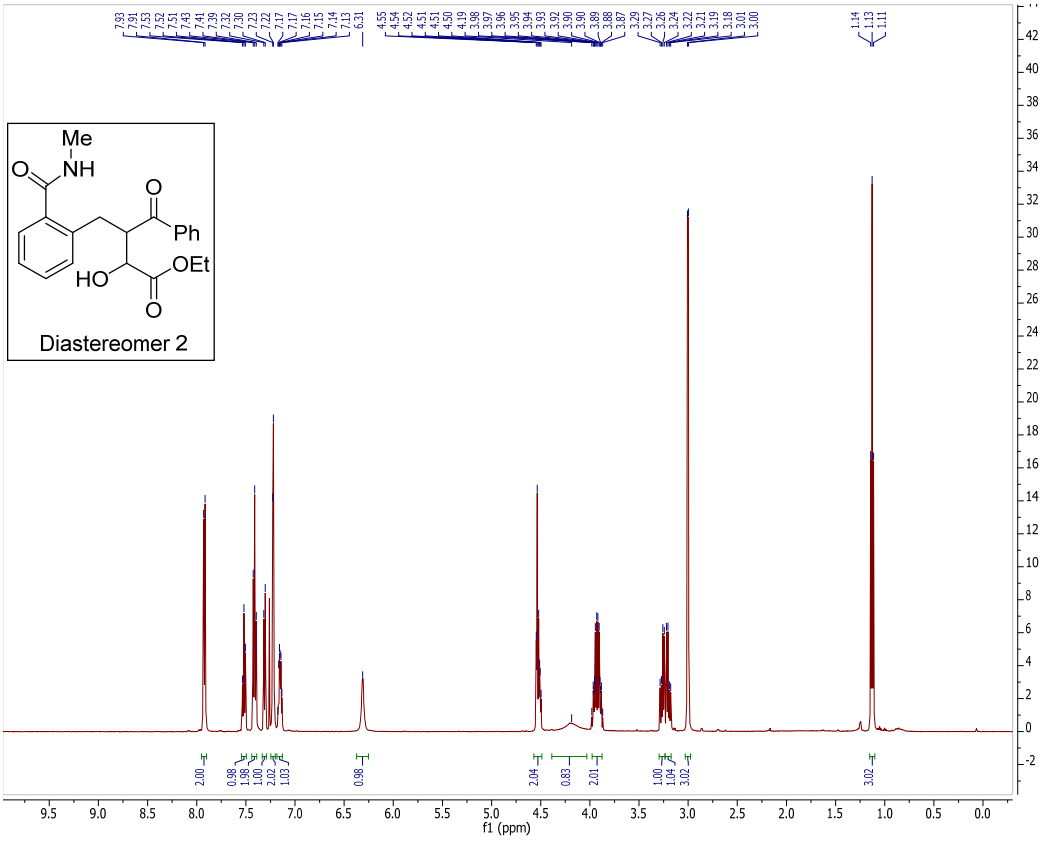

Diastereomer 1
f1 (ppm)

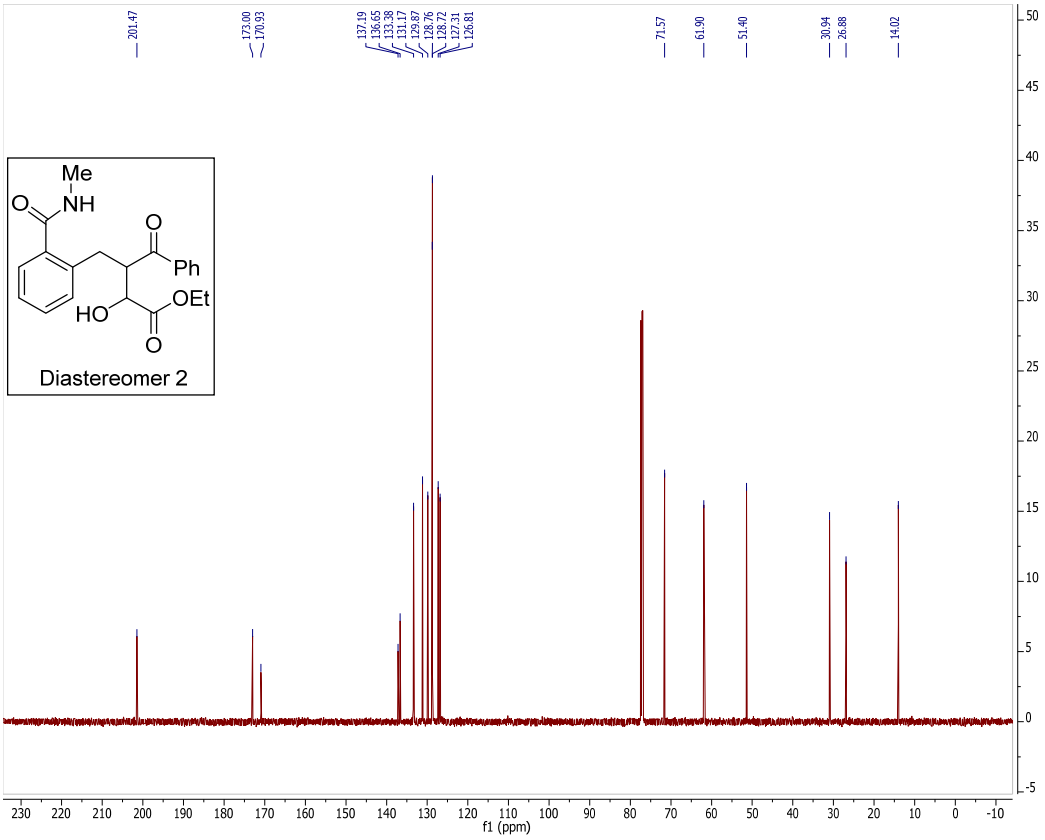

Diastereomer 2
f1 (ppm)

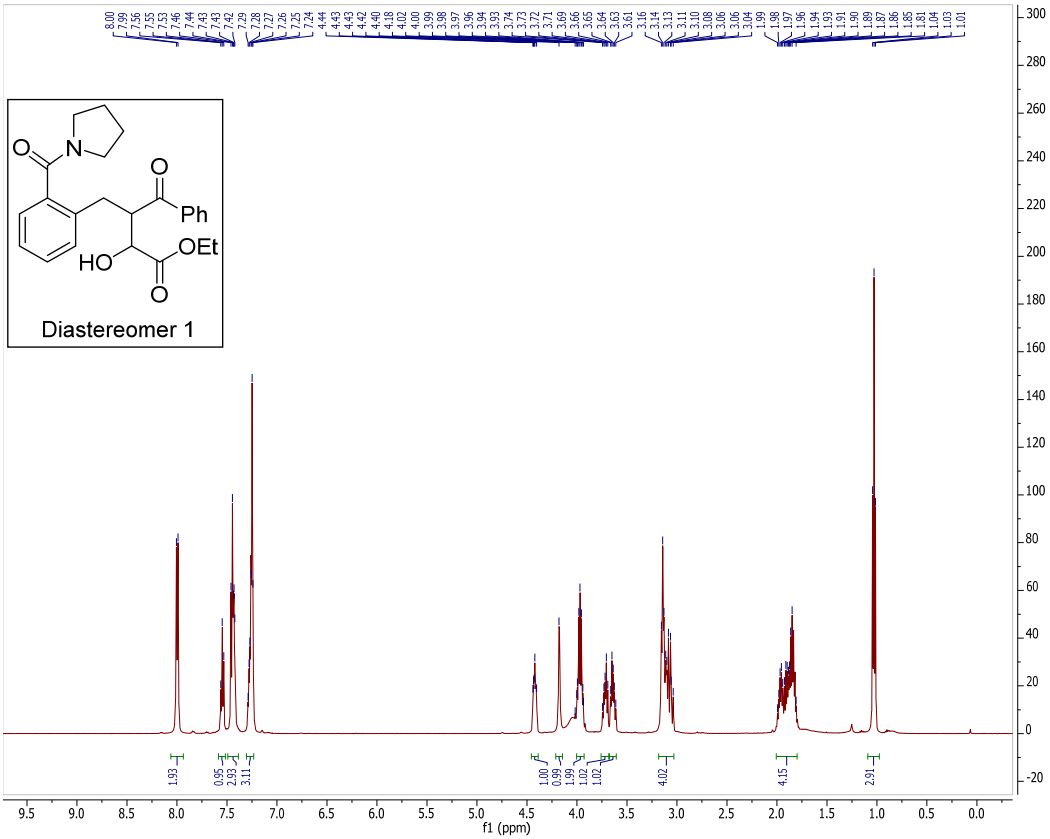

Diastereomer 2
f1 (ppm)

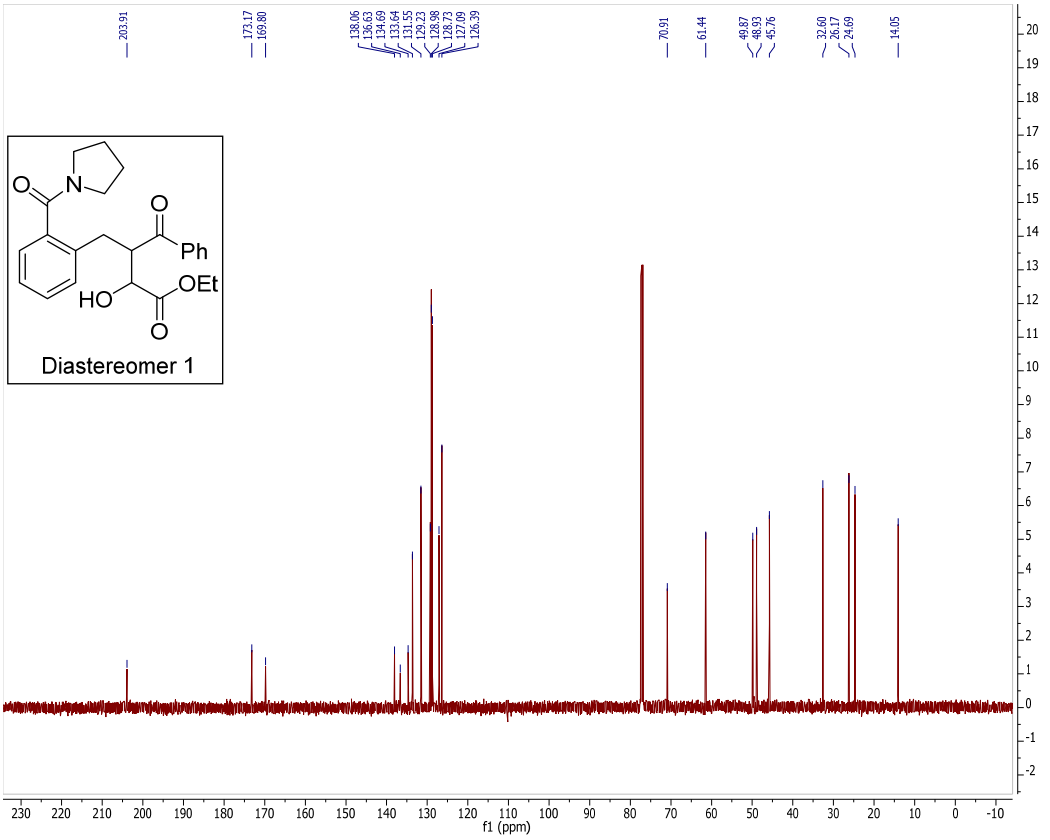

Me
NH
O
O
Ph
OEt
HO
O
Diastereomer 1
f1 (ppm)

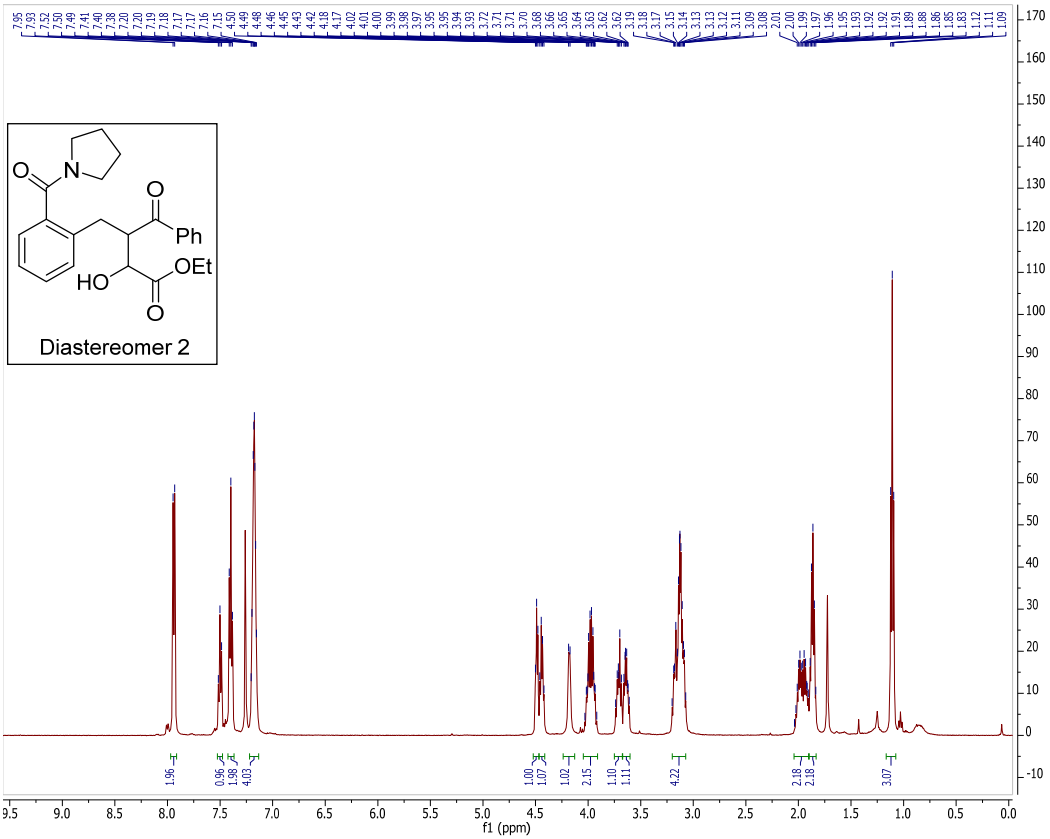

Me
NH
O
O
Ph
OEt
HO
O
Diastereomer 1
f1 (ppm)

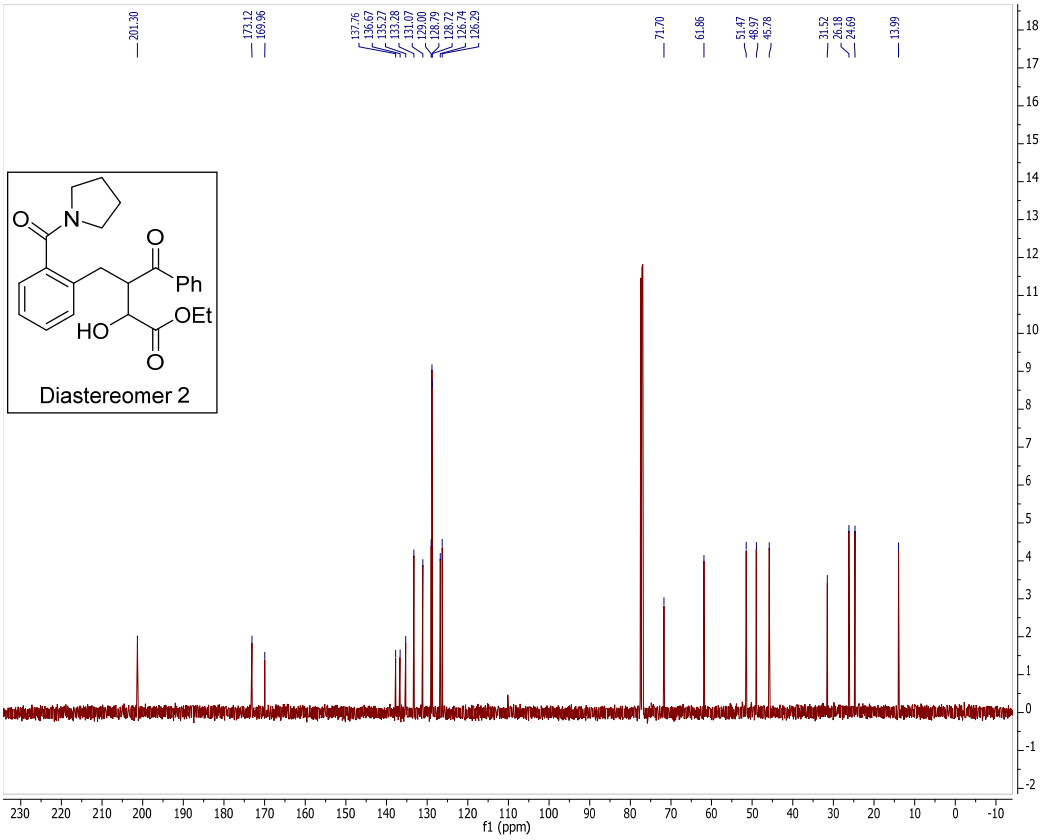

Me
NH
O
O
Ph
OEt
HO
O
Diastereomer 2
f1 (ppm)

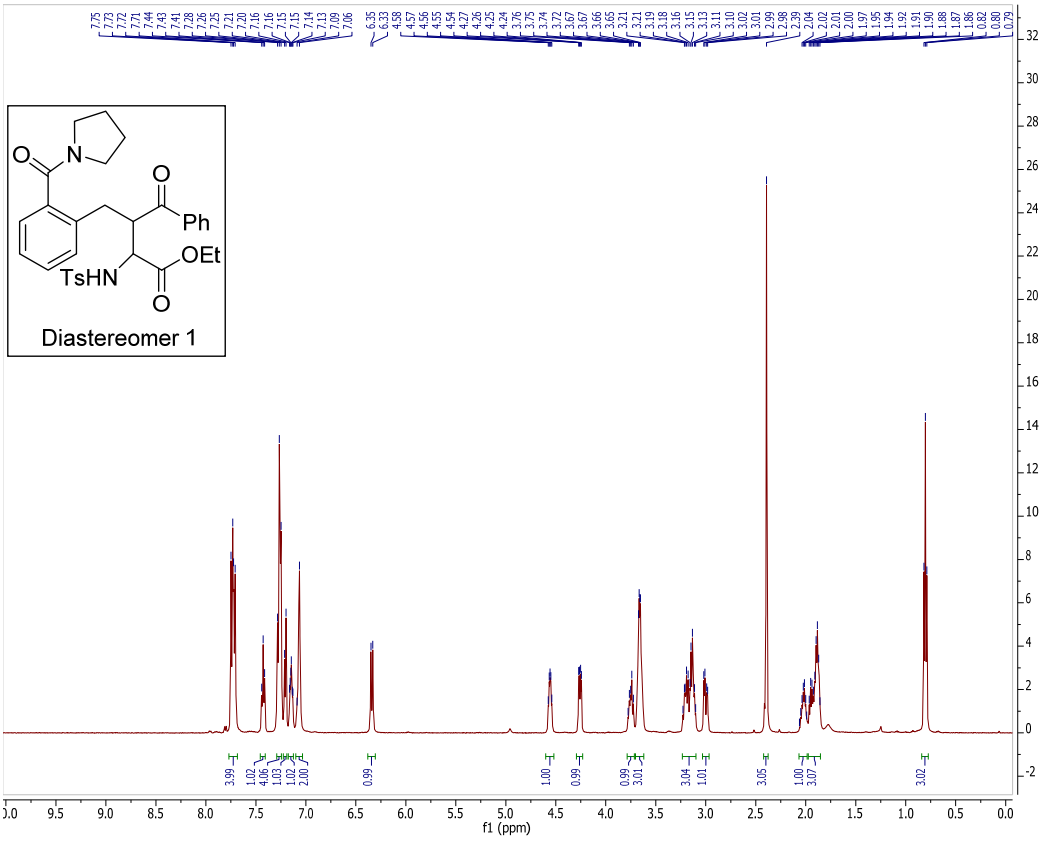

Me
NH
O
O
Ph
OEt
HO
O
Diastereomer 2
f1 (ppm)

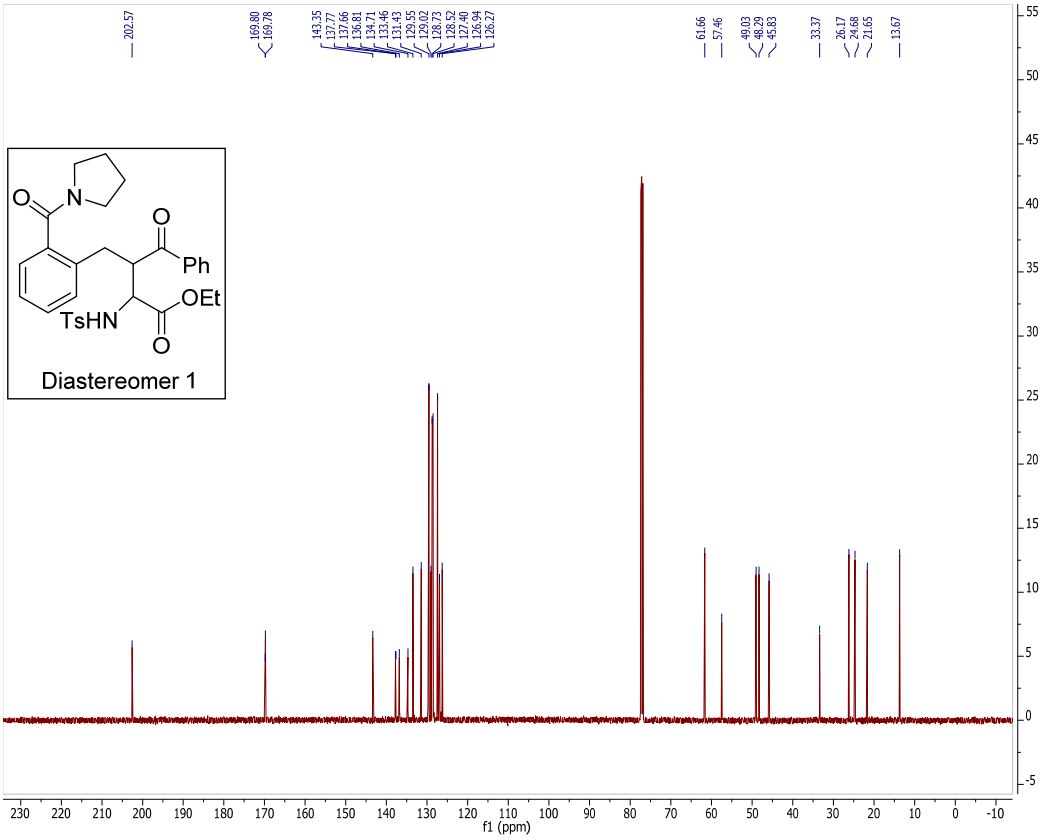

Diastereomer 1
f1 (ppm)

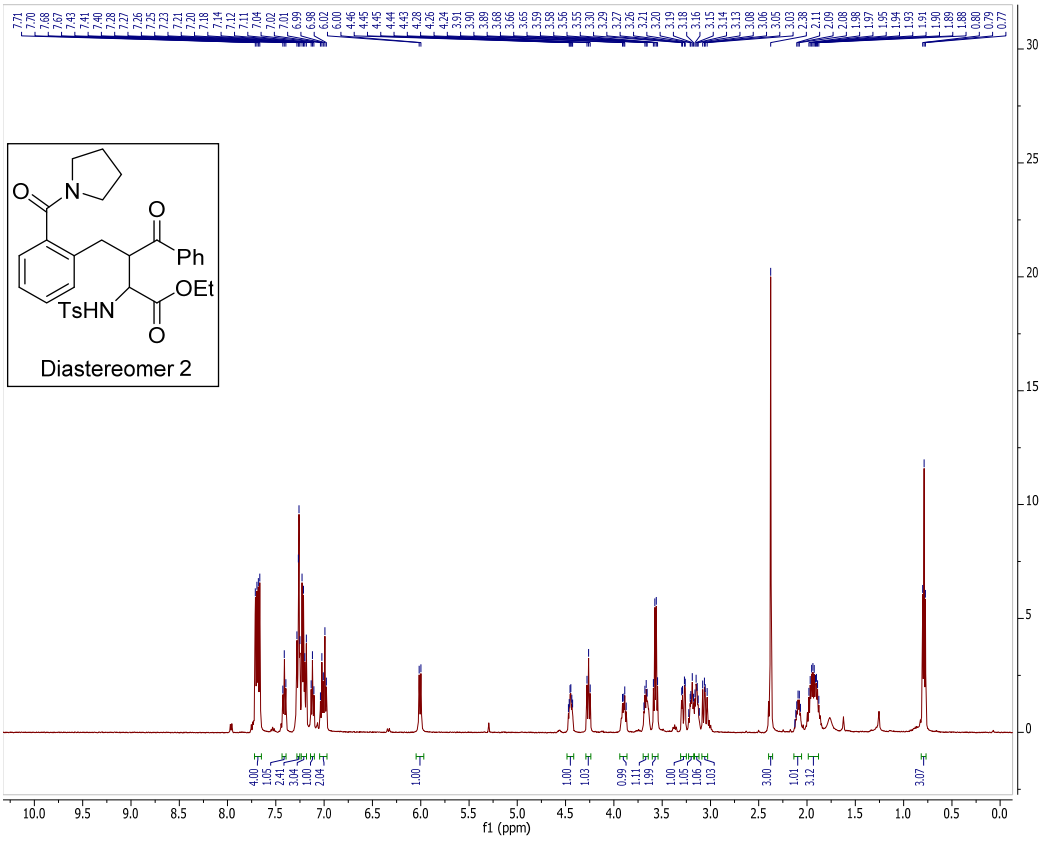

Diastereomer 1
f1 (ppm)

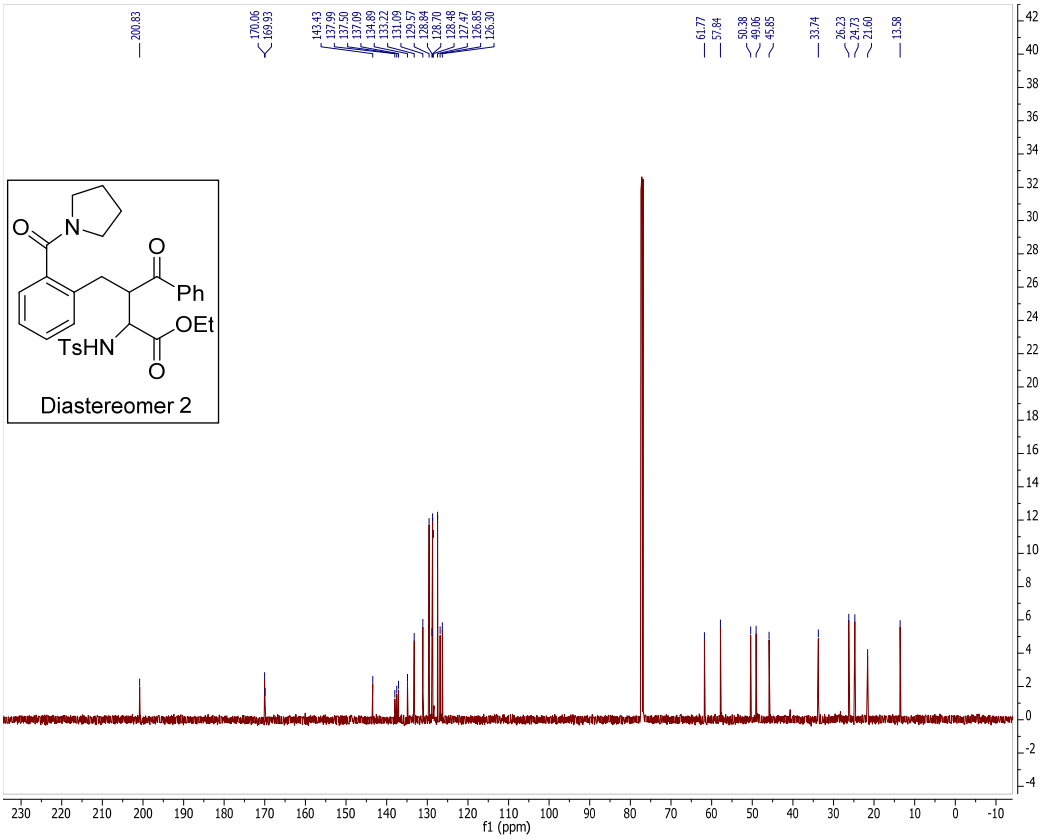

Diastereomer 2
f1 (ppm)

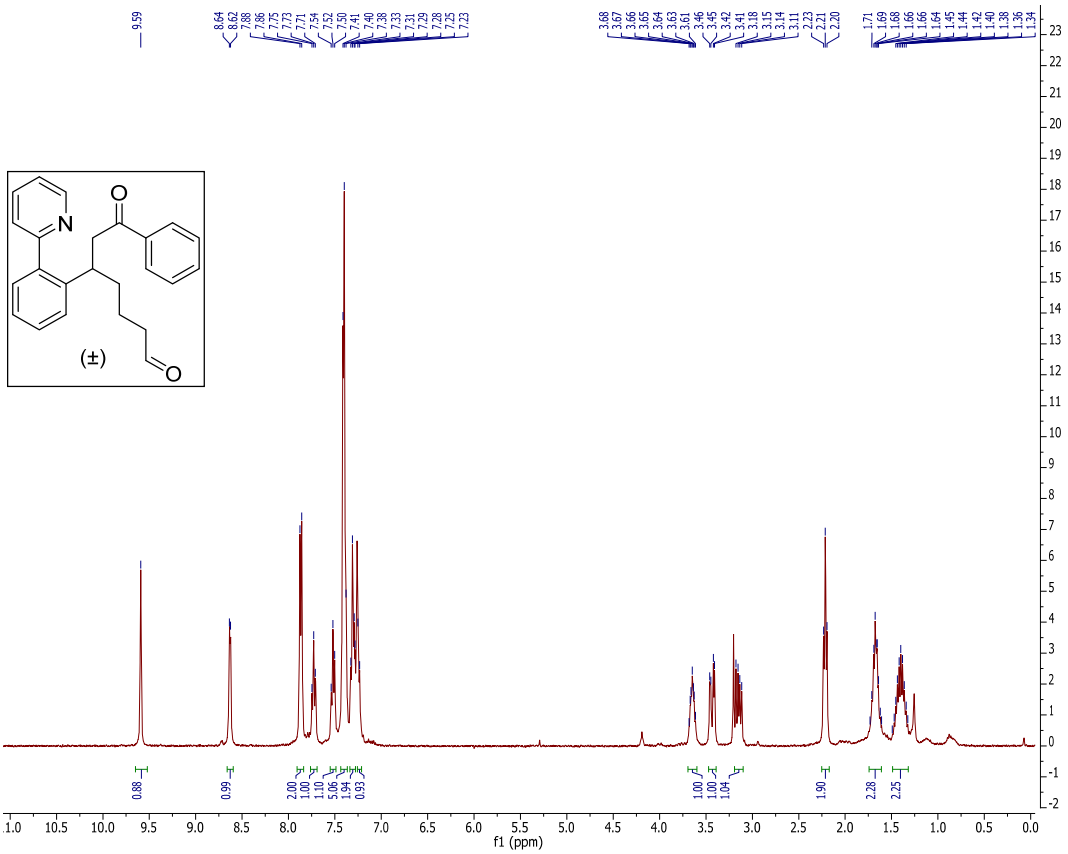

Diastereomer 2
f1 (ppm)


Diastereomer 1
f1 (ppm)


Diastereomer 1
f1 (ppm)


Ph
OEt
TsHN
Diastereomer 2
f1 (ppm)


Ph
OEt
TsHN
Diastereomer 2
f1 (ppm)


9.59
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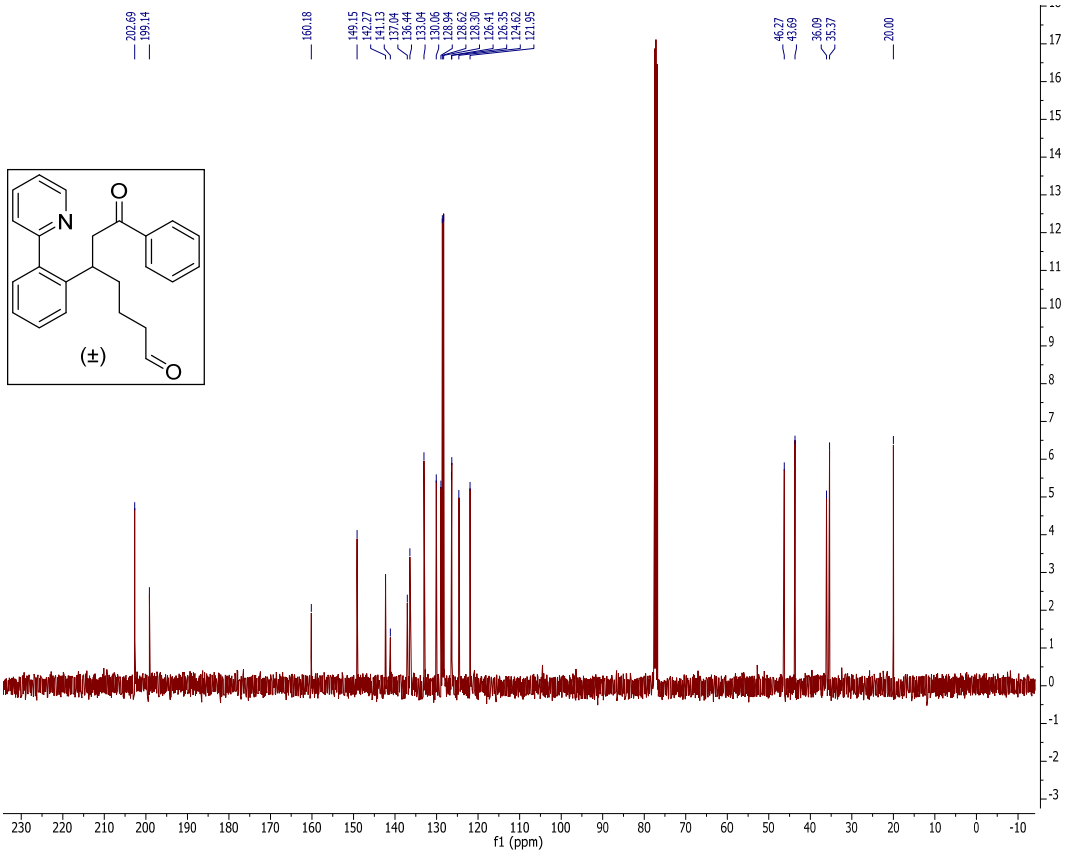
7.75
7.73
7.71
7.54
7.52
7.50
7.41
7.40
7.38
7.33
7.31
7.29
7.28
7.25
7.23
3.68
3.67
3.66
3.65
3.64
3.63
3.61
3.46
3.45
3.42
3.41
3.18
3.15
3.14
3.11
2.23
2.21
2.20
1.71
1.69
1.68
1.66
1.66
1.64
1.45
1.44
1.42
1.40
1.38
1.36
1.34
0.88
0.99
2.00
1.00
1.10
5.06
1.94
0.93
1.00
1.00
1.04
1.90
2.28
2.25
f1 (ppm)


202.69
199.14
160.18
149.15
142.27
141.13
137.04
136.44
133.04
130.06
128.94
128.62
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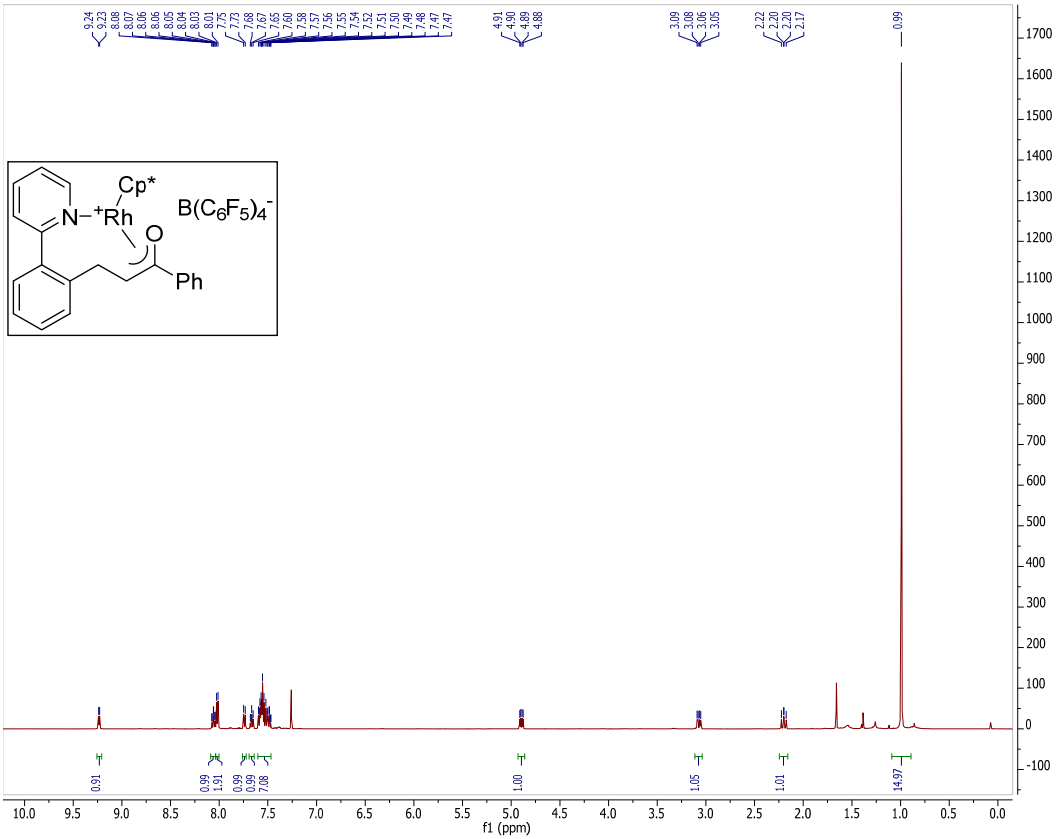
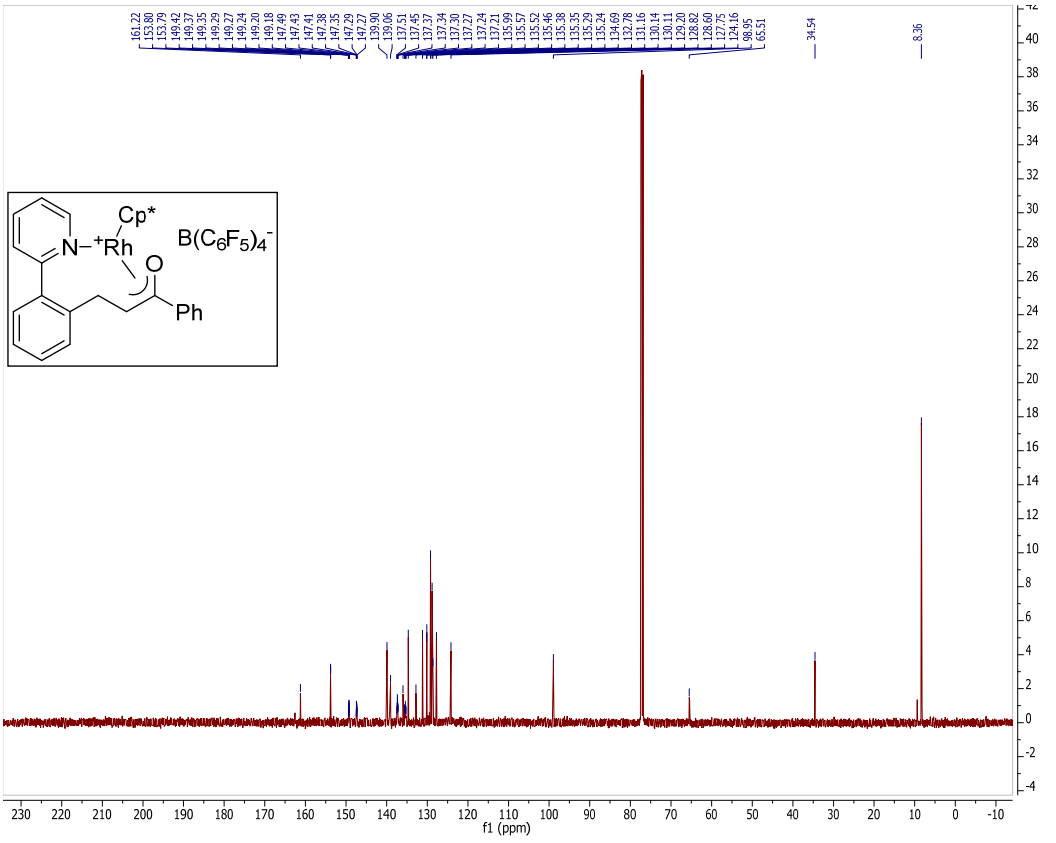
43.69
36.09
35.37
20.00
f1 (ppm)


Cp*
N
Rh
O
Ph
B(C6F5)4-
f1 (ppm)


Cp*
N
Rh
O
Ph
B(C6F5)4-
f1 (ppm)