Rhodium Catalyzed Enantioselective Cylization of Substituted Imidazoles via C–H Bond Activation

Andy S. Tsai, Rebecca M. Wilson, Hitoshi Harada, Robert G. Bergman*[a], and Jonathan A. Ellman*[b]

[a] *Division of Chemical Sciences, Lawrence Berkeley National Laboratory, and Department of Chemistry, University of California, Berkeley, California, 94720-1460, USA. E-mail: bergman@berkeley.edu*

[b] *Department of Chemistry, University of California, Berkeley, California, 94720-1460, USA. E-mail: jellman@berkeley.edu*

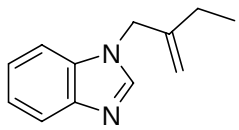
Supporting Information

Experimental:

General Procedures. All organic reactions were performed under an atmosphere of N_2 in flame- or oven-dried glassware unless otherwise stated. All preparations for all C–H activation experiments were carried out in a N_2-filled Vacuum Atmospheres inert atmosphere box (glovebox). Thin-layer chromatography was performed on Merck 60 F_{254} 250-μm silica gel plates. Visualization of the developed chromatograms was performed by fluorescence quenching. Flash chromatography was carried out using Merck 60 230-240 mesh silica gel or a Biotage SP Flash Purification System (Biotage No. SP1-B1A). IR spectra were recorded on a Thermo Nicolet Avatar 370 fitted with a single bounce ZnSe ATR plate; stretching frequencies are reported in cm^{-1} and the data shown include only major absorptions. ^{1}H, and ^{13}C NMR measurements were conducted using a Bruker AV-300, AVB-400, or DRX-500 spectrometer as noted at room temperature. NMR chemical shifts are reported in ppm and referenced to residual protonated solvent or added internal standard, and coupling constants are reported in Hz. High resolution mass spectra (HRMS) and elemental analyses were performed by the University of California, Berkeley Micro-Mass Facility using ProSpec equipped with an EI source (EI), ZAB equipped with a FAB (FAB), or LTQ Orbitrap (ESI). X-ray crystal structures were obtained by the University of California, Berkeley X-ray Crystallography Facility. Chiral HPLC analyses were performed on a Shimadzu VP Series with a Chiralcel AD-H column (250 mm x 4.6 mm) or Chiralcel AS-H (250 mm x 4.6 mm) using a flow rate of 1 mL/min. A Perkin-Elmer 241 polarimeter with a sodium lamp was used to determine specific rotations and concentrations are reported in g/dL. Melting points of the

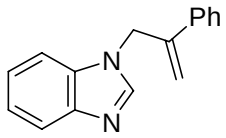
compounds obtained as solids were measured with a Laboratory Devices Inc. MEL-TEMP 3.0.

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was obtained from a Seca Solvent System by Glass Contour (solvents were passed through activated alumina columns under nitrogen pressure). (1*S*,1*S*',2*R*,2*R*')-1,1'-di-*tert*-butyl-(2,2')-diphospholane ((*S*,*S'*,*R*,*R'*)-Tangphos) was purchased from Sigma-Aldrich. $[RhCl(coe)_2]_2$ (also available from Strem Chemical) was prepared according to referenced literature procedure.[1] Tetrahydrofuran-d_8, dioxane-d_8, toluene-d_8 were dried over sodium/benzophenone ketyl and distilled using vacuum transfer procedures. All liquid reagents and deuterated solvents were thoroughly degassed using three freeze-pump-thaw cycles prior to transfer into the glovebox. Racemic samples of the cyclized products for chiral HPLC analysis were prepared by using PCy_3 as a ligand instead of (*S*,*S'*,*R*,*R'*)-Tangphos.[2]

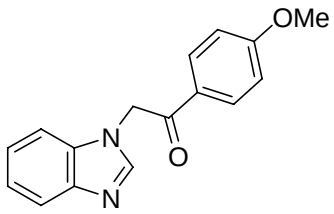


1-(2-methylenebutyl)-1H-benzo[d]imidazole. To an ice-water cooled solution of 1*H*-benzimidazole (132 mg, 1.13 mmol) in THF (5 mL) was added NaH (60%/mineral oil) (81 mg, 2.0 mmol). The mixture was stirred under the same conditions for 15 minutes. 3-bromo-2-ethyl-propene (200 mg, 1.35 mmol) was added as a solution in THF (2mL) and the mixture was stirred at rt for 18 h. The reaction was quenched with sat. $NaHCO_3$ (aq), and the resulting mixture was extracted three times with ethyl acetate. The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated.

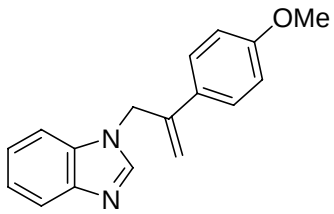
The residue was purified by silica gel column chromatography (200:10:1 CH_2Cl_2: MeOH: NH_4OH) to give the title compound as a clear oil (126 mg, 60% yield). ; υ_{max}(film)/cm^{-1}1493, 1457; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.86-7.81 (m, 1H), 7.39-7.32 (m, 1H), 7.31-7.23 (m, 2H), 4.99 (s, 1H), 4.81 (s, 1H), 4.71 (s, 2H), 1.99 (q, 2H, J = 7.4 Hz), 1.06 (t, 3H, J = 7.4 Hz); ^{13}C{1H} NMR (100 MHz, CDCl3): δ 145.3, 144.1, 143.7, 134.3, 123.2, 122.4, 120.6, 112.0, 110.3, 50.3, 26.4, 12.1; HRMS (FAB+) Calcd for $C_{12}H_{15}N_2$ $[MH]^+$ 187.1235; Found 187.1233.



1-(2-Phenylallyl)-1*H*-benzoimidazole. To a ice-water cooled solution of 1*H*-benzimidazole (249 mg, 2.11 mmol) in THF (10 mL) was added NaH (60%/mineral oil) (128 mg, 3.20 mmol). The mixture was stirred under the same conditions for 15 minutes. (1-bromomethylvinyl)benzene (389 mg, 1.98 mmol) was added as a solution in THF (3 mL), and the mixture was stirred at rt for 18 h. The reaction was quenched with sat. $NaHCO_3$ (aq), and the resulting mixture was extracted three times with ethyl acetate. The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (0-70% gradient of ethyl acetate in hexanes) followed by washing with diethyl ether to give the title compound as a white solid (326 mg, 66% yield). mp 126-127 °C; υ_{max}(film)/cm^{-1} 1490; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.84-7.77 (m, 1H), 7.45-7.26 (m, 8H), 5.55 (s, 1H), 5.18 (s, 2H), 4.98 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.8, 143.3, 142.2, 137.9, 133.9, 128.7, 128.5, 125.9, 123.0, 122.2, 120.4, 115.3, 110.0, 48.7; HRMS (EI): Calcd for $C_{16}H_{14}N_2$ $[M]^+$ 234.1157; Found 234.1162.

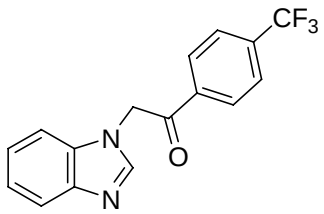


2-(1H-benzo[d]imidazol-1-yl)-1-(4-methoxyphenyl)ethanone. To a 25 mL round bottom flask was added benzimidazole (890 mg, 7.54 mmol), 2-bromo-1-(4-methoxyphenyl)ethanone (695 mg, 3.05 mmol), and DMF (4 mL). The solution was stirred at rt for 16 h during which time the solution became cloudy. DMF was removed via high-vac at 0.05 mmHg, and the resulting crude solid was suspended in CH_2Cl_2 and washed with sat. $NaHCO_3$ (aq). The layers were separated and the aqueous layer was washed three times with CH_2Cl_2. The organic layers were combined, dried over anhydrous $MgSO_4$, concentrated, and purified by silica column chromatography (200:10:1 CH_2Cl_2: MeOH: NH_4OH) to yield a white solid (350 mg, 43% yield). Physical data were consistent with the previously reported characterization.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, 2H, J = 8.8 Hz) 7.97 (s, 1H), 7.92-7.83 (m, 1H), 7.37-7.24 (m, 3H), 7.05 (d, 2H, J = 8.8 Hz), 5.55 (d, 2H), 3.95 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 189.9, 164.6, 144.0, 143.5, 134.5, 130.5, 127.3, 123.3, 122.4, 120.4, 114.4, 109.5, 55.7, 50.1;



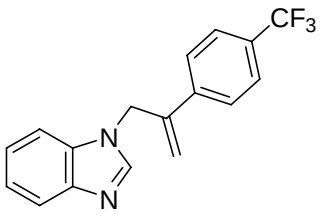
1-(2-(4-methoxyphenyl)allyl)-1H-benzo[d]imidazole. In a 25 mL Schlenk flask equipped with a stir bar was combined 2-(1H-benzo[d]imidazol-1-yl)-1-(4-methoxyphenyl)ethanone (280 mg, 1.05 mmol), methyl triphenylphosphonium bromide

(756 mg, 2.12 mmol), and K_2CO_3 (336 mg, 2.43 mmol), and THF (10 mL). The suspension was heated at 135 °C for 24 h. The reaction vessel was cooled to rt, filtered through celite, and the celite was washed with THF. The filtrate was concentrated and purified by silica column chromatography (95:5 methyl *tert*-butyl ether: triethylamine) to yield a white solid (159 mg, 57%). mp 121-123 °C; υ_{max}(film)/cm^{-1} 1605, 1513; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.84-7.76 (m, 1H), 7.45-7.38 (m, 1H), 7.37-7.22 (m, 4H), 6.86 (d, 2H, J = 8.9 Hz), 5.47 (s, 1H), 5.13 (s, 2H), 4.91 (s, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.8, 143.9, 143.4, 141.5, 134.0, 130.3, 127.1, 123.0, 122.2, 120.4, 114.1, 113.4, 110.0, 55.3, 48.8; HRMS (FAB+) Calcd for $C_{17}H_{17}N_2O$ [MH]$^+$ 265.1341; Found 265.1339.

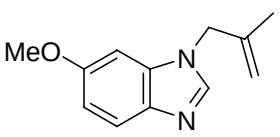


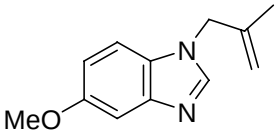
2-(1H-benzo[d]imidazol-1-yl)-1-(4-(trifluoromethyl)phenyl)ethanone. To a 25 mL round bottom flask was combined benzimidazole (231 mg, 1.96 mmol), 2-bromo-1-(4-(trifluoromethyl)phenyl)ethanone (200 mg, 0.75 mmol), and DMF (1 mL). The solution was stirred at rt for 16 h during which time it became cloudy. DMF was removed via high-vac at 0.05 mmHg, and the resulting crude solid was suspended in CH_2Cl_2 and washed with sat. $NaHCO_3$ (aq). The layers were separated and the aqueous layer was washed three times with CH_2Cl_2. The organic layers were combined, dried over anhydrous $MgSO_4$, concentrated, and purified by silica column chromatography (200:10:1 CH_2Cl_2: MeOH: NH_4OH) to yield a white solid (200 mg, 87% yield). mp 169-172 °C; υ_{max}(film)/cm^{-1} 1706, 1323; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, 2H, J = 8.1

Hz), 7.98 (s, 1H), 7.93-7.82 (m, 3H) 7.40-7.22 (m, 3H), 5.64 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 190.6, 143.6, 143.5, 135.9 (q, $J_{C\text{-}F}$ = 31.5 Hz), 136.8, 134.1, 128.5, 126.3 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.5, 123.4 (q, $J_{C\text{-}F}$ = 271.5 Hz) 122.6, 120.7, 109.2, 50.7; ^{19}F NMR (375 Mhz, $CDCl_3$): δ −62.5; HRMS (FAB+) Calcd for $C_{16}H_{12}F_3N_2O$ $[MH]^+$ 305.0896; Found 305.0899.



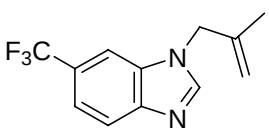
1-(2-(4-(trifluoromethyl)phenyl)allyl)-1H-benzo[d]imidazole. To a 25 mL Schlenk flask equipped with a stir bar was combined 2-(1H-benzo[d]imidazol-1-yl)-1-(4-trifluoromethyl)ethanone (450 mg, 1.47 mmol), methyl triphenylphosphonium bromide (1.06 g, 2.96 mmol), K_2CO_3 (470 mg, 3.40 mmol), and THF (15 mL). The suspension was heated at 135 °C for 24 h. The reaction vessel was cooled to rt, the reaction mixture was filtered through celite, and the celite pad was washed with THF. The filtrate was concentrated, and the crude product purified by activity III neutral alumina chromatography (2:1 hex: EtOAc) to yield a white solid (190 mg, 42%). mp 119-121 °C; υ_{max}(film)/cm^{-1} 1498, 1325; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.88-7.81 (m, 1H), 7.63 (d, 2H, J = 8.1 Hz), 7.52 (d, 2H, J = 8.1 Hz), 7.45-7.49 (m, 1H), 7.38-7.29 (m, 2H), 5.64 (s, 1H), 5.19 (s, 2H), 5.14 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 143.9, 143.2, 141.5, 141.4, 133.8, 130.5 (q, $J_{C\text{-}F}$ = 32.9 Hz), 126.3, 125.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.9 (q, $J_{C\text{-}F}$ = 271.5 Hz), 123.3, 122.4, 120.6, 117.4, 109.8, 48.6; ^{19}F NMR (375 Mhz, $CDCl_3$): δ −61.5; HRMS (FAB+) Calcd for $C_{17}H_{14}F_3N_2$ $[MH]^+$ 303.1109; Found 303.1111.

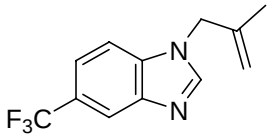




6-methoxy-1-(2-methylallyl)-1H-benzo[d]imidazole and **5-methoxy-1-(2-methylallyl)-1H-benzo[d]imidazole.** To an ice-water cooled solution of 6-methoxy-1H-benzo[d]imidazole (300 mg, 2.0 mmol) in THF (5 mL) was added NaH (60%/mineral oil) (136 mg, 3.40 mmol). The mixture was stirred under the same conditions for 15 minutes. 3-Bromo-2-methylprop-1-ene (300 mg, 2.24 mmol) was added, and the mixture was stirred at rt for 18 h. The reaction was quenched with sat. $NaHCO_3$ (aq), and the resulting mixture was extracted three times with ethyl acetate. The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (10:1 *t*-butyl methyl ether: triethylamine) to obtain two clear oils. **Less polar product (6-methoxy-1-(2-methylallyl)-1H-benzo[d]imidazole):** 100 mg (24% yield); υ_{max}(film)/cm^{-1} 1491, 1438, 1224; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.66 (d, 1H, J = 8.6 Hz), 6.90 (dd, 1H, J = 8.6, 2.0 Hz), 6.78 (d, 1H, J = 2.0 Hz), 4.97 (s, 1H), 4.79 (s, 1H), 3.83 (s, 2H), 3.83 (s, 3H), 1.69 (s, 3H); ^{13}C{1H} NMR (75 MHz, $CDCl_3$): δ 157.0, 142.9, 139.7, 138.6, 134.9, 121.0, 114.1, 111.6, 93.9, 56.1, 51.3, 20.1; HRMS (FAB+) Calcd for $C_{12}H_{15}N_2O$ $[MH]^+$ 203.1184; Found 203.1185. **More polar product (5-methoxy-1-(2-methylallyl)-1H-benzo[d]imidazole):** 60 mg (14%); υ_{max}(film)/cm^{-1} 1492, 1430, 1224; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.26 (d, 1H, J = 2.3 Hz), 7.22 (d, 1H, J = 8.9 Hz), 6.91 (dd, 1H, J = 8.9, 2.3 Hz), 4.97 (s, 1H), 4.81 (s, 1H), 4.53 (s, 2H), 3.84 (s, 3H), 1.67 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz,

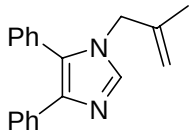
$CDCl_3$): δ 156.4, 145.0, 143.8, 139.9, 128.9, 114.2, 113.5, 110.7, 102.6, 56.0, 51.53, 20.0; HRMS (FAB+) Calcd for $C_{12}H_{15}N_2O$ $[MH]^+$ 203.1184; Found 203.1187.





1-(2-methylallyl)-6-(trifluoromethyl)-1H-benzo[d]imidazole and **1-(2-methylallyl)-5-(trifluoromethyl)-1H-benzo[d]imidazole.** To an ice-water cooled solution of 6-(trifluoromethyl)-1H-benzo[d]imidazole[4] (250 mg, 1.34 mmol) in THF (5 mL) was added NaH (60%/mineral oil) (91 mg, 2.28 mmol). The mixture was stirred under the same conditions for 15 minutes. 3-Bromo-2-methylprop-1-ene (216 mg, 1.61 mmol) was added, and the mixture was stirred at rt for 18 h. The reaction was quenched with sat. $NaHCO_3$ (aq), and the resulting mixture was extracted three times with ethyl acetate. The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (200:10:1 CH_2Cl_2: MeOH: NH_4OH) to obtain two white solids. **Less polar product (1-(2-methylallyl)-5-(trifluoromethyl)-1H-benzo[d]imidazole):** 50 mg (16%); mp 42-43 °C; υ_{max}(film)/cm^{-1} 1503, 1326; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.97 (s, 1H), 7.50 (d, 1H, J = 8.4 Hz), 7.42 (d, 1H, J = 8.4 Hz), 5.00 (s, 1H), 4.77 (s, 1H), 4.69 (s, 2H), 1.67 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.2, 143.2, 139.0, 135.9, 124.7 (q, $J_{C\text{-}F}$ = 31.5 Hz), 124.0 (q, $J_{C\text{-}F}$ = 271.4 Hz), 119.9 (q, $J_{C\text{-}F}$ = 2.9 Hz), 118.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 114.3, 110.6, 51.2, 19.7; ^{19}F NMR (375 MHz, $CDCl_3$): δ −59.8; HRMS (FAB+) Calcd for $C_{12}H_{12}F_3N_2$ $[MH]^+$ 241.0953; Found 241.0954. **More polar product (1-(2-methylallyl)-6-(trifluoromethyl)-1H-benzo[d]imidazole):** 50 mg (16%); mp 35-37 °C; υ_{max}(film)/cm^{-1} 1486, 1325; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.88 (d, 1H, J =

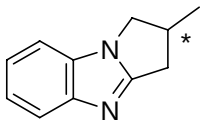
8.4 Hz), 7.64 (s, 1H), 7.52 (d, 1H, J = 8.4 Hz), 5.02 (s, 1H), 4.80 (s, 1H), 4.73 (s, 2H), 1.71 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.9, 145.6, 138.9, 133.4, 125.2 (q, $J_{C\text{-}F}$ = 32.3 Hz), 124.8 (q, $J_{C\text{-}F}$ = 270.2 Hz), 120.8, 119.2 (q, $J_{C\text{-}F}$ = 3.7 Hz), 114.4, 107.9 (q, $J_{C\text{-}F}$ = 4.1 Hz), 51.2, 19.7; ^{19}F NMR (375 MHz, $CDCl_3$): δ –59.9; HRMS (FAB+) Calcd for $C_{12}H_{12}F_3N_2$ $[MH]^+$ 241.0953; Found 241.0952.



1-(2-Methylallyl)-4,5-diphenyl-1*H*-imidazole. To an ice-water cooled solution of 4,5-diphenyl-1*H*-imidazole (1.00 g, 4.54 mmol) in THF (20 mL) was added NaH (60%/mineral oil) (284 mg, 7.10 mmol). The mixture was stirred under the same conditions for 15 minutes. 3-Bromo-2-methylpropene (0.49 mL, 4.9 mmol) was added, and the mixture was stirred at rt for 18 h. The reaction was quenched with sat. $NaHCO_3$ (aq), and the resulting mixture was extracted three times with ethyl acetate. The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (0-50% gradient of ethyl acetate in hexanes) followed by washing with diethyl ether to give the title compound as a white solid (671 mg, 54% yield). mp 94-95 °C; υ_{max}(film)/cm^{-1} 1600, 1503; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.52-7.46 (m, 2H), 7.45-7.39 (m, 3H), 7.35-7.29 (m, 2H), 7.24-7.17 (m, 2H), 7.17-7.10 (m, 1H), 4.90 (s, 1H), 4.60 (s, 1H), 4.28 (s, 2H), 1.64 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.9, 137.9, 137.2, 134.6, 130.8, 130.6, 128.9, 128.7, 128.6, 128.1, 126.5, 126.2, 113.0, 50.5, 19.9; HRMS (EI): Calcd for $C_{19}H_{18}N_2$ $[M]^+$ 274.1470; Found 274.1471.

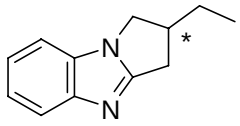
General Procedure for ligand screen and reaction optimization. In a nitrogen-filled inert atmosphere box, $[RhCl(coe)_2]_2$ (2.9 mg, 0.0040 mmol), ligand, substrate (0.05 mmol), and solvent (0.4 mL) were combined in a medium-walled NMR tube. The tube was fitted with a Cajon adapter, frozen with liquid nitrogen, and flame-sealed under vacuum. The tube was then placed in an oil bath set to the desired temperature. Periodically, the tube was removed from the bath, cooled to room temperature, and analyzed by ^{1}H-NMR spectroscopy. All optimization reactions were carried out via this procedure by varying temperature, solvent, ligand, ligand loading, and additives.

General procedure for asymmetric alkylation. To a scintillation vial in a glovebox, was added (*S*,*S'*,*R*,*R'*)-Tangphos (8.1 mg, 0.028 mmol), $[RhCl(coe)_2]_2$ (10.8 mg, 0.0150 mmol), substrate (0.15 mmol) and THF (1.5 mL). The solution was then transferred to a 15 mL Schlenk tube, heated for the specified time, cooled to rt, and concentrated. The residue was purified by silica gel column chromatography (200:10:1 CH_2Cl_2: MeOH: NH_4OH) to yield the desired product.

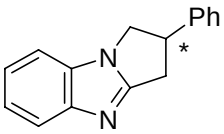


2-Methyl-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole (2). The general procedure was applied using 1-(2-methylallyl)-1H-benzo[d]imidazole as the substrate. The reaction vial was heated at 135 °C for 20 h, and after purification the product was obtained as a white solid (23 mg, 89%). mp 85-87 °C; $[\alpha]_D^{25}$ +21.43 (c 0.19, $CHCl_3$); υ_{max}(film)/cm^{-1} 1615, 1521, 1453; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.66 (m, 1H), 7.32-7.17 (m, 3H), 4.26 (dd, 1H, *J* = 7.6, 10.0 Hz), 3.66 (dd, 1H, *J* = 6.0, 10.0 Hz), 3.29-3.12 (m, 2H), 2.69 (dd, 1H, *J* = 6.0, 15.6 Hz), 1.35 (d, 3H, *J* = 6.8 Hz); ^{13}C{^{1}H} NMR

(100 MHz, $CDCl_3$): δ 160.6, 148.5, 132.4, 121.8, 121.6, 119.6, 109.4, 50.1, 35.7, 32.2, 20.0; HRMS (EI): *m*/*z* calcd. for $C_{11}H_{12}N_2$ (M^+): 172.1000; found: 172.1006; HPLC (Chiralcel AD-H column, 5% *i*PrOH/hexanes, 1mL/min): major, 18.45 min; minor, 21.50 min; 98% ee. X-ray quality crystals of the HCl salt of **2** (CCDC 727522) were obtained by dissolving the compound in a minimal amount of Et_2O, precipitation with 1M HCl in Et_2O, and recrystallation from CH_2Cl_2/hexanes.

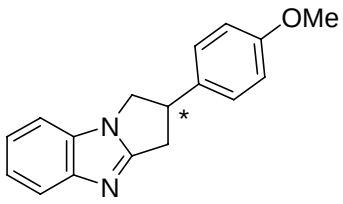


2-Ethyl-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole. The general procedure was applied using 1-(2-methylenebutyl)-1H-benzo[d]imidazole as the substrate. The reaction vial was heated at 135 °C for 60 h, and after purification the product was obtained as a yellowish oil (20 mg, 71%). $[\alpha]_D^{25}$ +7.28 (c 0.38, $CHCl_3$); υ_{max}(film)/cm^{-1} 1525, 1451; ^1H NMR (400 MHz, $CDCl_3$): δ 7.77-7.69 (m, 1H), 7.35-7.29 (m, 1H), 7.29-7.20 (m, 2H), 4.29 (dd, 1H, *J* = 10.1, 8.1 Hz), 3.75 (dd, 1H, *J* = 10.1, 6.8 Hz), 3.26 (dd, 1H, *J* = 16.6, 8.6 Hz), 3.06 (apparent septet, 1H), 2.77 (dd, 1H, *J* = 16.6, 7.1 Hz), 1.75 (m, 2H), 1.09 (t, 3H, *J* = 7.3 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.6, 148.5, 132.4, 121.8, 121.6, 119.6, 109.4, 48.4, 42.8, 30.1, 27.8, 12.1; HRMS (EI): *m*/*z* calcd. for $C_{12}H_{15}N_2$ $[MH]^+$ 187.1232; Found 187.1230; HPLC (Chiralcel AD-H column, 5% EtOH/hexanes, 1mL/min): major, 30.85 min; minor, 28.20 min; 90% ee.



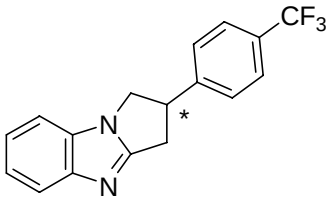
2-Phenyl-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole. The general procedure was applied using 1-(2-Phenylallyl)-1H-benzoimidazole as the substrate. The

reaction vial was heated at 135 °C for 46 h, and after purification the product was obtained as a white solid (32 mg, 91%). mp 144-146 °C; $[\alpha]_D^{25}$ +64.55 (c 0.44, $CHCl_3$); υ_{max}(film)/cm^{-1} 1618, 1516; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.70 (m, 1H), 7.46-7.19 (m, 8H), 4.54 (dd, 1H, *J* = 8.4, 10.0 Hz), 4.28 (m, 1H), 4.10 (dd, 1H, *J* = 7.2, 10.0 Hz), 3.53 (dd, 1H, *J* = 8.4, 16.8 Hz), 3.21 (dd, 1H, *J* = 7.2, 16.8 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 148.6, 141.8, 132.3, 129.1, 127.6, 126.9, 122.1, 121.9, 119.8, 109.6, 50.4, 46.2, 32.4; HRMS (EI): *m*/*z* calcd. for $C_{16}H_{14}N_2$ (M^+): 234.1157; found: 234.1160; HPLC (Chiralcel AD-H column, 10% *i*PrOH/hexanes, 1mL/min): major, 41.78 min; minor, 35.43 min; 97% ee.

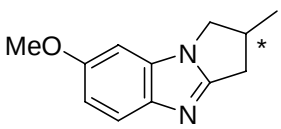


2-(4-methoxy-phenyl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole. The general procedure was applied using 1-(2-(4-methoxyphenyl)allyl)-1H-benzo[d]imidazole as the substrate. The reaction vial was heated at 175 °C for 24 h, and after purification the product was obtained as a yellowish solid (33 mg, 83%). mp 115-117 °C; $[\alpha]_D^{25}$ +48.11 (c 0.9, $CHCl_3$); υ_{max}(film)/cm^{-1} 1513; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.69 (m, 1H), 7.35-7.15 (m, 5H), 6.88 (d, 2H, *J* = 8.6 Hz), 4.47 (dd, 1H, *J* = 10.1, 8.1 Hz), 4.21 (m, 1H), 4.02 (dd, 1H, *J* = 10.1, 8.1 Hz), 3.80 (s, 3H), 3.48 (dd, 1H, *J* = 16.9, 8.8 Hz), 3.14 (dd, 1H, *J* = 16.9, 8.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 158.8, 148.5, 133.6, 132.2, 127.9, 121.9, 121.7, 119.6, 114.3, 109.5, 55.3, 50.4, 45.4, 32.5; HRMS (FAB+): *m*/*z* calcd. for $C_{17}H_{17}N_2O$ (MH^+): 265.1335; found:

265.1333; HPLC (Chiralcel AD-H column, 10% EtOH/hexanes, 1mL/min): major, 47.10 min; minor, 32.32 min; 87% ee.

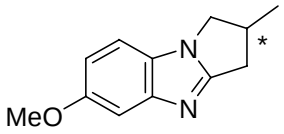


2-(4-trifluoromethyl-phenyl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole. The general procedure was applied using 1-(2-(4-(trifluoromethyl)phenyl)allyl)-1H-benzo[d]imidazole as the substrate. The reaction mixture was heated at 175 °C for 24 h, and after purification the product was obtained as a yellowish solid (39 mg, 87%). mp 162-165 °C; $[\alpha]_D^{25}$ +36.63 (c 0.8, $CHCl_3$); υ_{max}(film)/cm^{-1} 1538, 1412, 1324; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.71 (m, 1H), 7.62 (d, 2H, J = 8.2 Hz), 7.39 (d, 2H, J = 8.2 Hz), 7.34-7.21 (m, 3H), 4.56 (dd, 1H, J = 10.4, 8.1 Hz), 4.33 (m, 1H), 4.10 (dd, 1H, J = 10.4, 7.9 Hz), 3.56 (dd, 1H, J = 16.9, 8.8 Hz), 3.19 (dd, 1H, J = 16.9, 7.3 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.4, 148.7, 145.9, 132.2, 130.0 (q, $J_{C\text{-}F}$ = 33.0 Hz), 127.4, 126.3 (q, $J_{C\text{-}F}$ = 3.9 Hz), 124.0 (q, $J_{C\text{-}F}$ = 272.3 Hz), 122.3, 122.1, 119.9, 109.6, 50.1, 45.8, 32.2; ^{19}F NMR (375 MHz, $CDCl_3$): δ −61.7; HRMS (FAB+) Calcd for $C_{17}H_{14}F_3N_2$ $[MH]^+$ 303.1109; Found 303.1106; HPLC (Chiralcel AD-H column, 10% EtOH/hexanes, 1mL/min): major, 26.66 min; minor, 22.43 min; 79% ee.



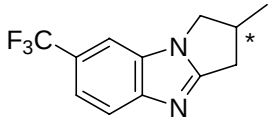
2-Methyl-2,3-dihydro-1H-7-methoxy-benzo[d]pyrrolo[1,2-a]imidazole. The general procedure was applied using (6-methoxy-1-(2-methylallyl)-1H-

benzo[d]imidazole) as the substrate. The reaction vial was heated at 175 °C for 36 h, and after purification the product was obtained as a yellowish solid (27 mg, 89%). mp 100-103 °C; $[\alpha]_D^{25}$ +22.95 (c 0.9, $CHCl_3$); υ_{max}(film)/cm^{-1} 1626, 1457, 1408; ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, 1H, *J* = 8.1 Hz), 6.83 (dd, 1H, *J* = 8.1, 2.3 Hz), 6.74 (d, 1H, *J* = 2.3 Hz), 4.17 (dd, 1H, 1H, *J* = 9.9, 7.6 Hz), 3.83 (s, 3H), 3.58 (dd, 1H, *J* = 9.9, 6.9 Hz), 3.22-3.07 (m, 2H), 2.68-2.56 (m, 1H), 1.31 (d, 3H, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 159.7, 155.8, 142.8, 132.8, 119.8, 110.2, 93.5, 55.8, 49.9, 35.6, 32.0, 19.9; HRMS (FAB+): *m*/*z* calcd. for $C_{12}H_{15}N_2O$ (MH^+): 203.1179; found: 203.1175; HPLC (Chiralcel AS-H column, 2% EtOH/hexanes w/ 0.1% diethylamine, 1mL/min): major, 33.96 min; minor, 40.53 min; 71% ee.



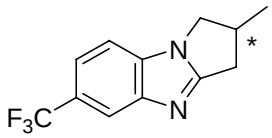
2-Methyl-2,3-dihydro-1H-6-methoxy-benzo[d]pyrrolo[1,2-a]imidazole. The general procedure was applied using (5-methoxy-1-(2-methylallyl)-1H-benzo[d]imidazole) as the substrate. The reaction vial was heated at 175 °C for 24 h, and after purification the product was obtained as a yellowish solid (28 mg, 92%). mp 119-122 °C; $[\alpha]_D^{25}$ +12.56 (c 0.7, $CHCl_3$); υ_{max}(film)/cm^{-1} 1522, 1282, 1442; ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, 1H, *J* = 2.3 Hz), 7.14 (d, 1H, *J* = 8.8 Hz), 6.84 (dd, 1H, *J* = 8.8, 2.3 Hz), 4.21 (dd, 1H, *J* = 10.0, 7.7 Hz), 3.85 (s, 3H), 3.62 (dd, 1H, *J* = 10.0, 6.0 Hz), 3.26-3.09 (m, 2H), 2.72-2.59 (m, 1H), 1.33 (d, 3H, *J* = 6.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl3): δ 162.4, 155.7, 149.2, 127.0, 111.2, 109.6, 102.3, 55.8, 50.2, 35.6, 32.3, 20.0; HRMS (FAB+): *m*/*z* calcd. for $C_{12}H_{15}N_2O$ (MH^+): 203.1184; found: 203.1177; HPLC

(Chiralcel AS-H column, 2% EtOH/hexanes w/ 0.1% diethylamine, 1mL/min): major, 33.67 min; minor, 38.65 min; 81% ee.



2-Methyl-2,3-dihydro-1H-7-trifluoromethyl-benzo[d]pyrrolo[1,2-a]imidazole.

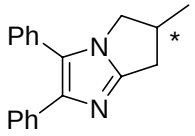
The general procedure was applied using (1-(2-methylallyl)-6-(trifluoromethyl)-1H-benzo[d]imidazole) as the substrate. The reaction vial was heated at 175 °C for 24 h, and after purification the product was obtained as a yellowish solid (30 mg, 83%). mp 80-83 °C; $[\alpha]_D^{25}$ +10.89 (c 0.9, $CHCl_3$); υ_{max}(film)/cm^{-1} 1523, 1454, 1309; ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, 1H, J = 8.6 Hz), 7.58 (s, 1H), 7.48 (d, 1H, J = 8.6 Hz), 4.32 (dd, 1H, J = 10.2, 7.8 Hz), 3.73 (dd, 1H, J = 10.2, 6.3 Hz), 3.36-3.17 (m, 2H), 2.72 (dd, 1H, J = 15.1, 5.6 Hz), 1.37 (d, 3H, J = 6.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.3, 150.6, 131.8, 124.9 (q, $J_{C\text{-}F}$ = 271.5 Hz), 124.0 (q, $J_{C\text{-}F}$ = 32.2 Hz), 119.8, 118.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 107.2 (q, $J_{C\text{-}F}$ = 4.4 Hz), 50.3, 35.7, 32.2, 19.9; HRMS (FAB+): *m*/*z* calcd. for $C_{12}H_{12}F_3N_2$ (MH^+): 241.0953; found: 241.0944; HPLC (Chiralcel AS-H column, 2% EtOH/hexanes, 1mL/min): major, 22.75 min; minor, 17.55 min; 53% ee.



2-Methyl-2,3-dihydro-1H-6-trifluoromethyl-benzo[d]pyrrolo[1,2-a]imidazole.

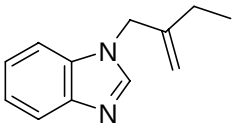
The general procedure was applied using (1-(2-methylallyl)-5-(trifluoromethyl)-1H-benzo[d]imidazole) as the substrate. The reaction vial was heated at 175 °C for 24 h, and after purification the product was obtained as a yellowish solid (29 mg, 81%). mp 107-110 °C; $[\alpha]_D^{25}$ +4.02 (c 1.0, $CHCl_3$); υ_{max}(film)/cm^{-1} 1531, 1322; ^1H NMR (400 MHz,

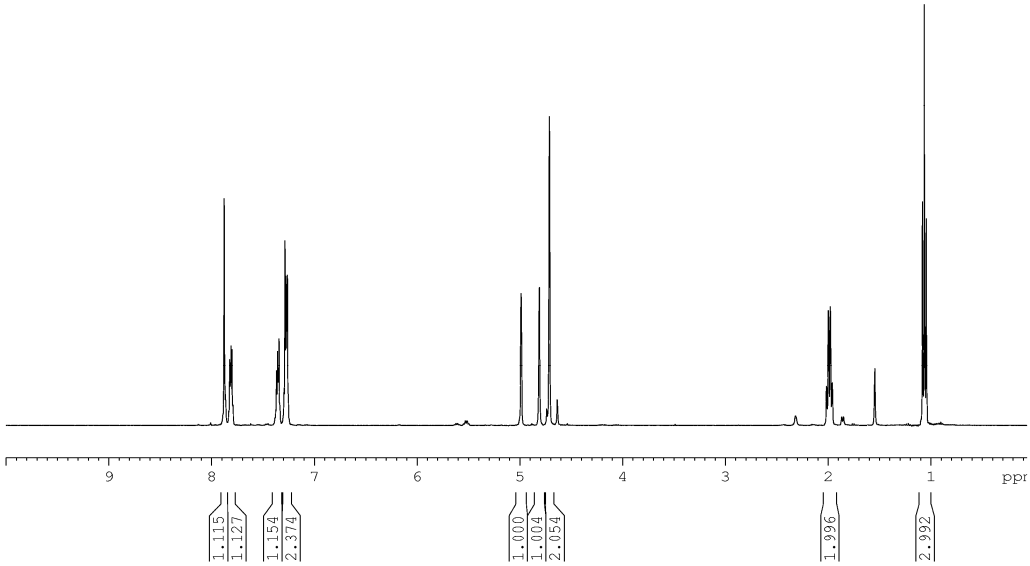
$CDCl_3$): δ 7.95 (s, 1H), 7.46 (d, 1H, J = 8.3 Hz), 7.3 (d, 1H, J = 8.3 Hz), 4.29 (dd, 1H, J = 10.1, 7.6 Hz), 3.69 (dd, 1H, J = 10.1, 6.3 Hz), 3.32-3.15 (m, 2H), 2.72 (dd, 1H, J = 15.7, 5.8 Hz), 1.36 (d, 3H, J = 6.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.7, 147.9, 134.4, 125.0 (q, $J_{C\text{-}F}$ = 271.5 Hz), 124.1 (q, $J_{C\text{-}F}$ = 3.1 Hz), 118.9 (q, $J_{C\text{-}F}$ = 3.6 Hz), 117.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 109.7, 50.2, 35.8, 32.2, 19.9; HRMS (FAB+): m/z calcd. for $C_{12}H_{12}F_3N_2$ (MH^+): 241.0953; found: 241.0947; HPLC (Chiralcel AS-H column, 2% EtOH/hexanes, 1mL/min): major, 13.44 min; minor, 14.75 min; 71% ee.



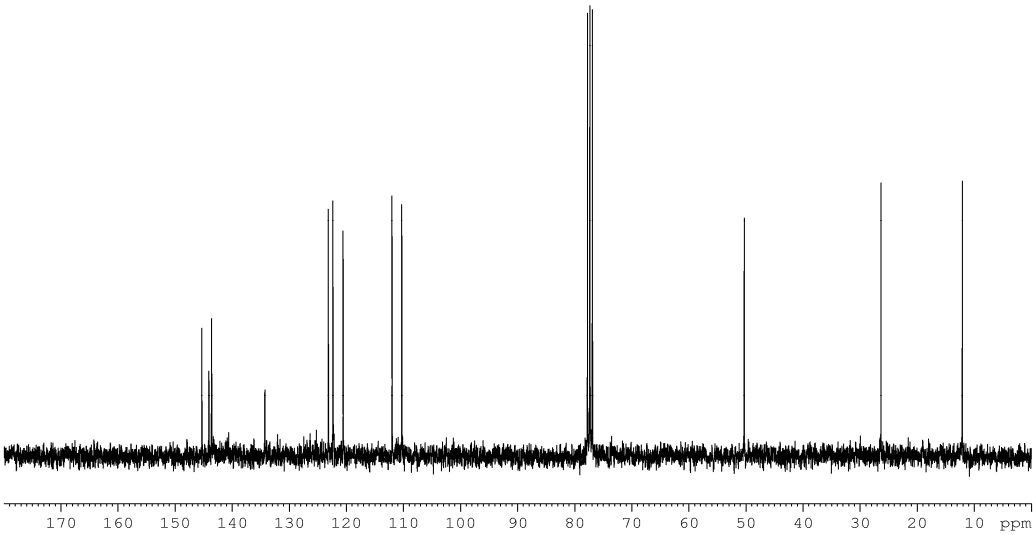
6-Methyl-2,3-diphenyl-6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole. The general procedure was applied using 1-(2-Methylallyl)-4,5-diphenyl-1H-imidazole as the substrate. The reaction vial was heated at 135 °C for 98 h, and after purification the product was obtained as a white solid (37 mg, 90%). mp 139-141 °C; $[\alpha]_D^{25}$ +4.09 (c 0.29, $CHCl_3$); υ_{max}(film)/cm^{-1} 1599; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, 2H, J = 7.2 Hz), 7.42-7.12 (m, 8H), 4.08 (dd, 1H, J = 7.6, 10.4 Hz), 3.53 (dd, 1H, J = 6.4, 10.4 Hz), 3.23-3.04 (m, 2H), 2.63 (dd, 1H, J = 6.4, 15.6 Hz), 1.30 (d, 3H, J = 6.8 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.1, 141.2, 135.2, 131.3, 128.9, 128.8, 128.2, 127.7, 127.1, 126.4, 125.2, 51.8, 35.6, 32.3, 19.8; HRMS (EI): m/z calcd. for $C_{19}H_{18}N_2$ (M^+): 274.1470; found: 274.1474; HPLC (Chiralcel AD-H column, 3% EtOH/hexanes, 1mL/min): major, 18.40 min; minor, 16.20 min; 95% ee.

^{1}HNMR

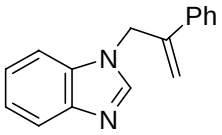


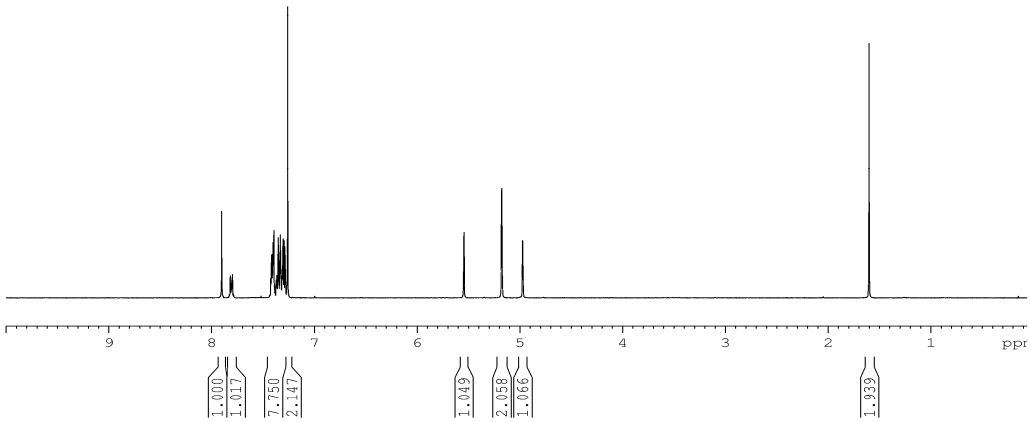


^{13}C NMR

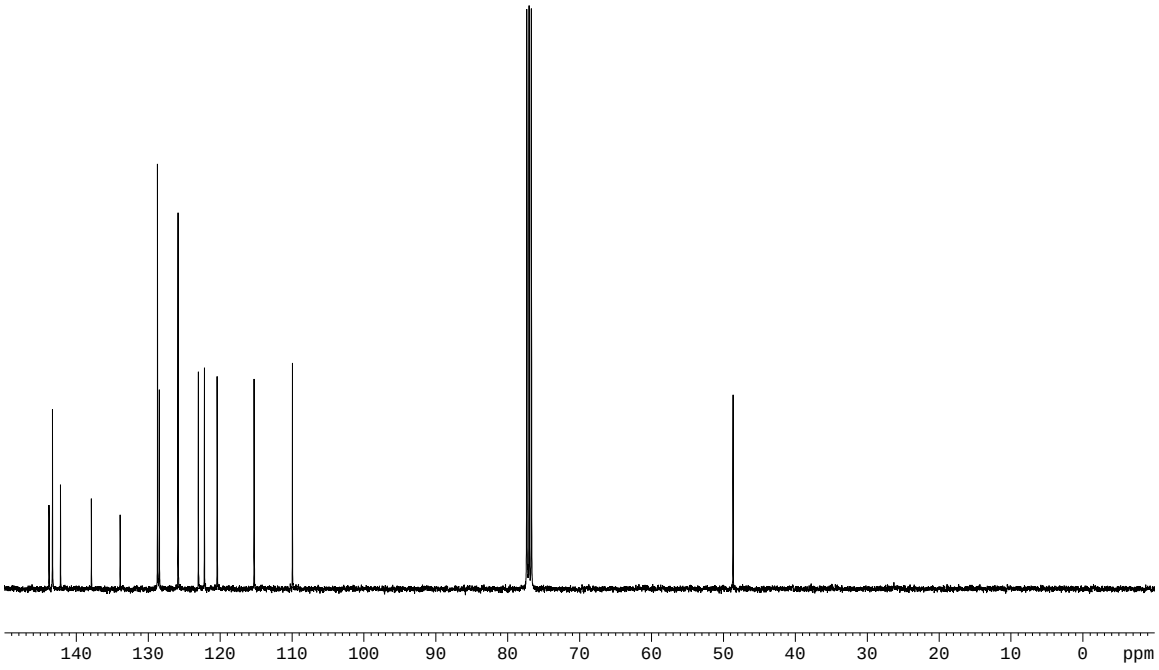


^{1}H NMR

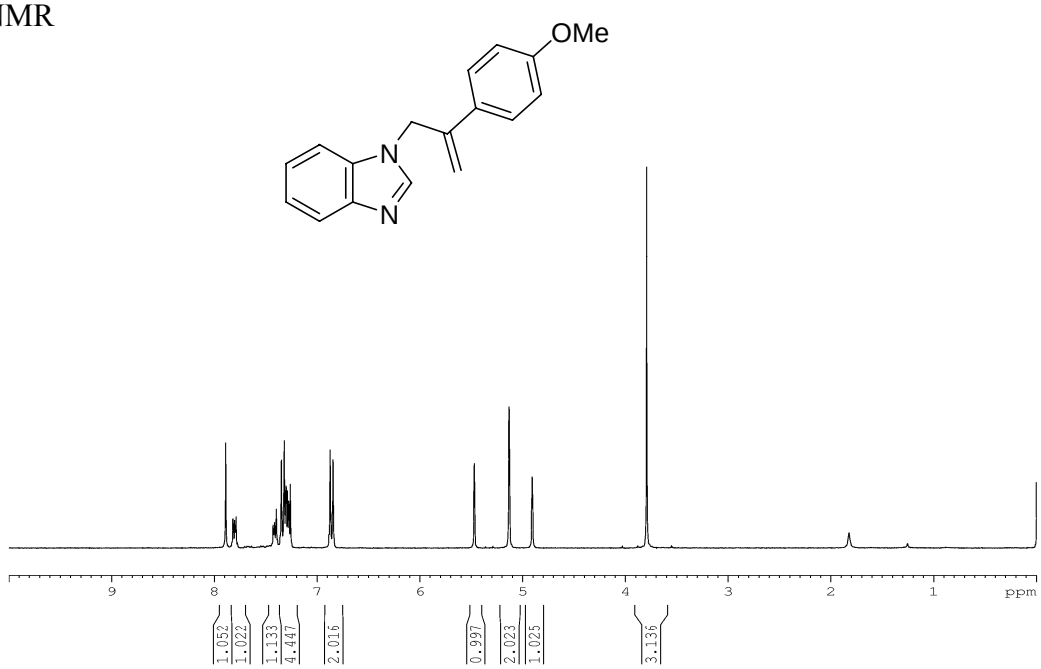




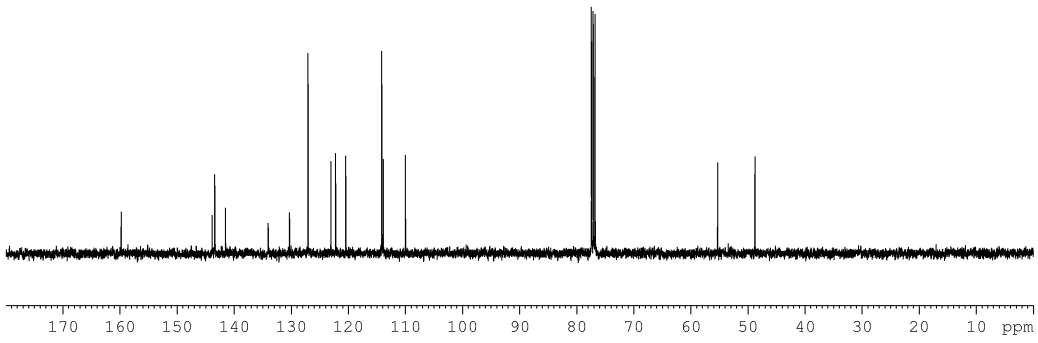
^{13}C NMR



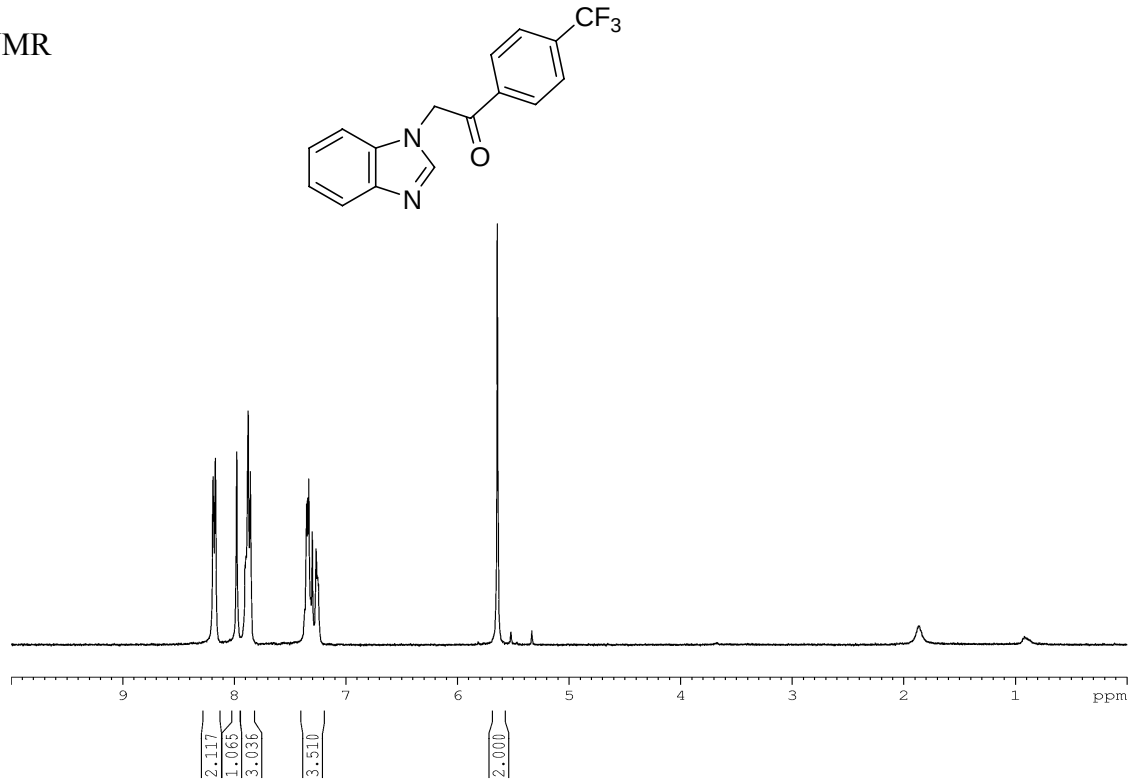
^{1}HNMR



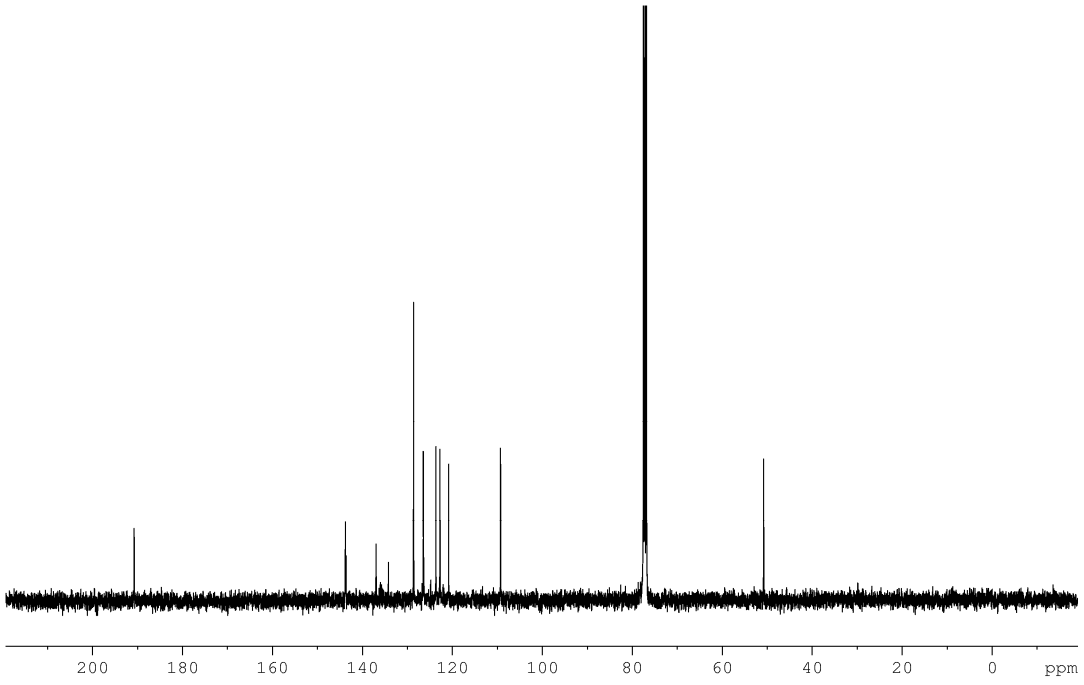
^{13}C NMR



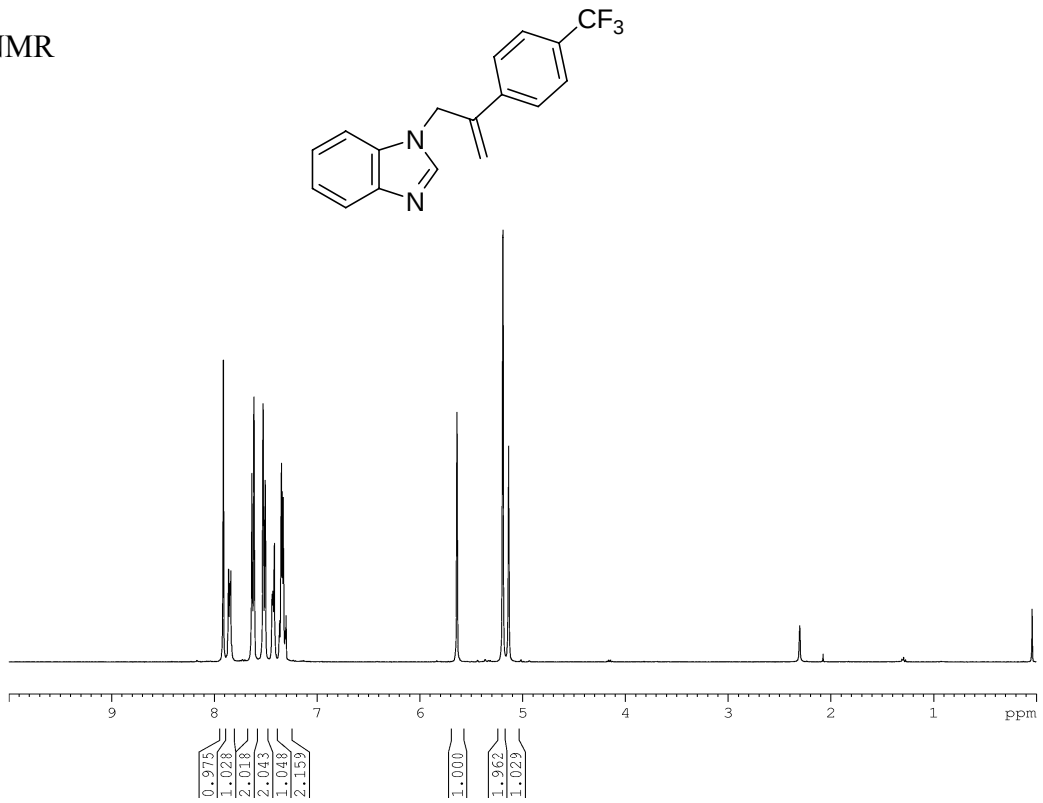
^{1}HNMR



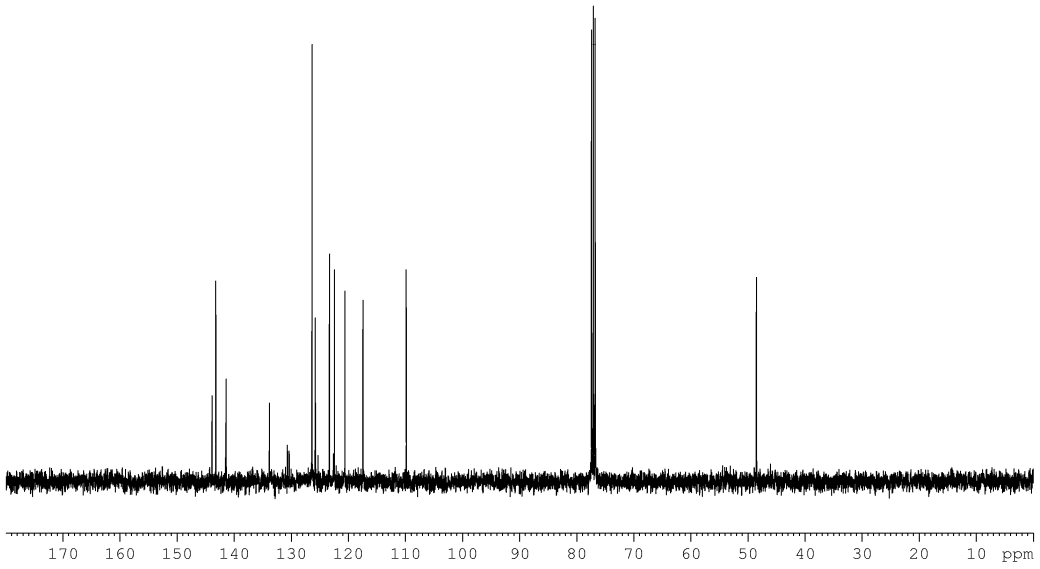
^{13}C NMR



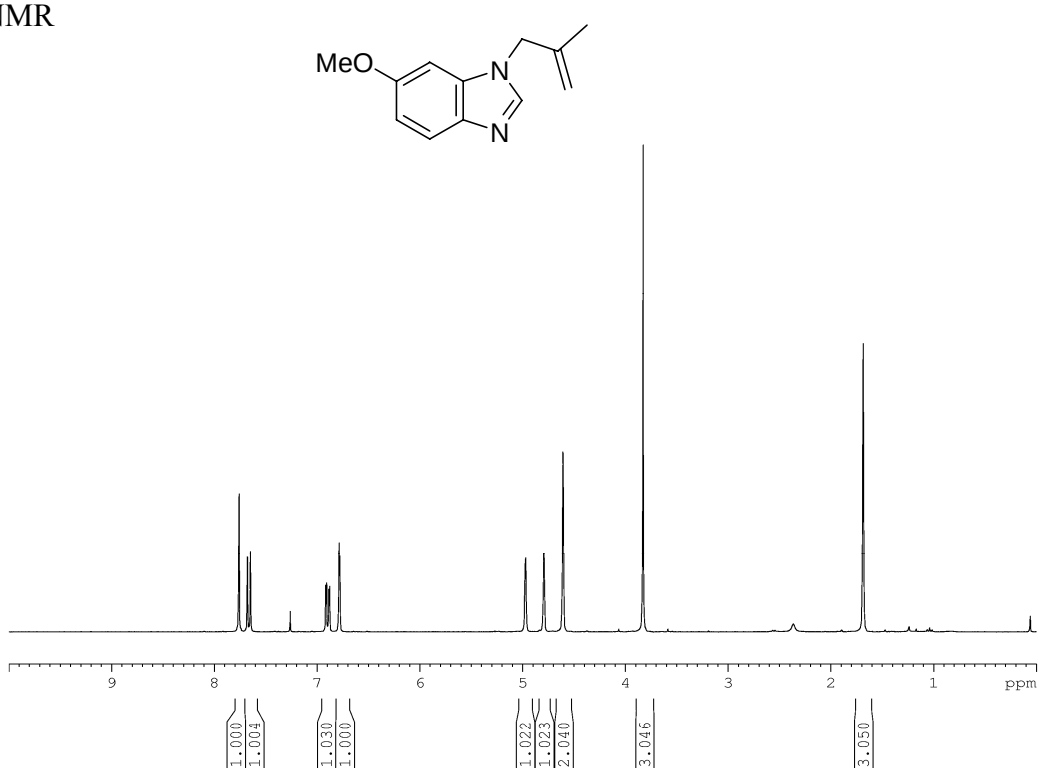
^{1}HNMR



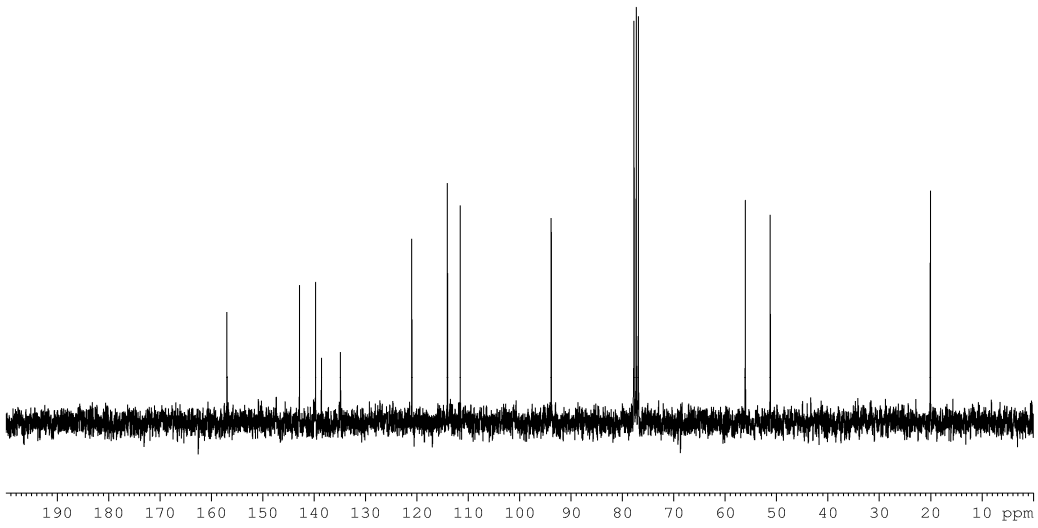
^{13}C NMR



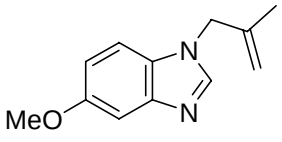
^{1}HNMR

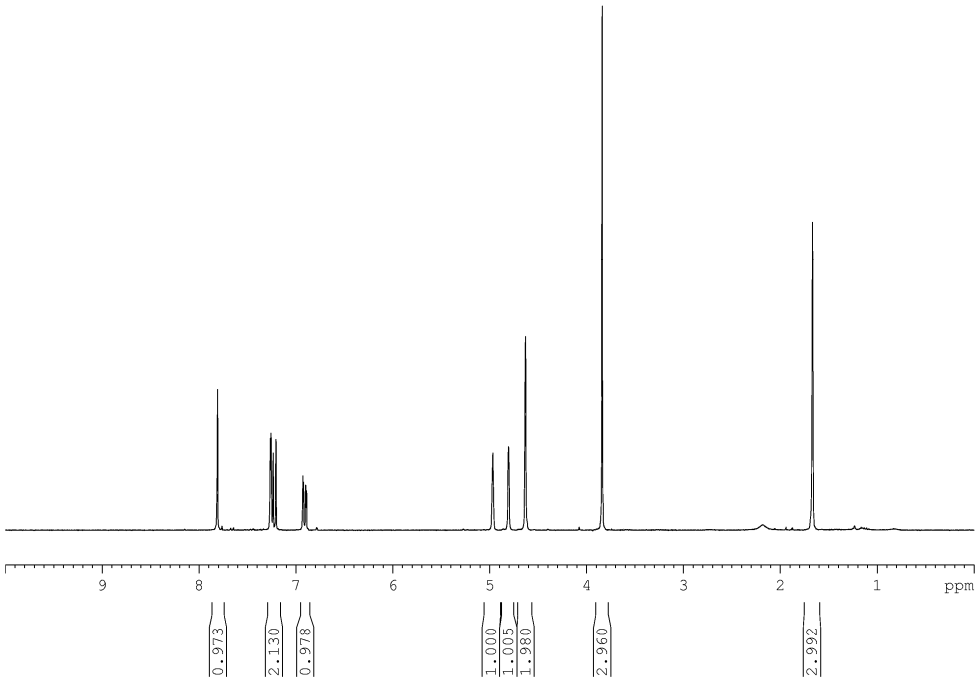


^{13}C NMR

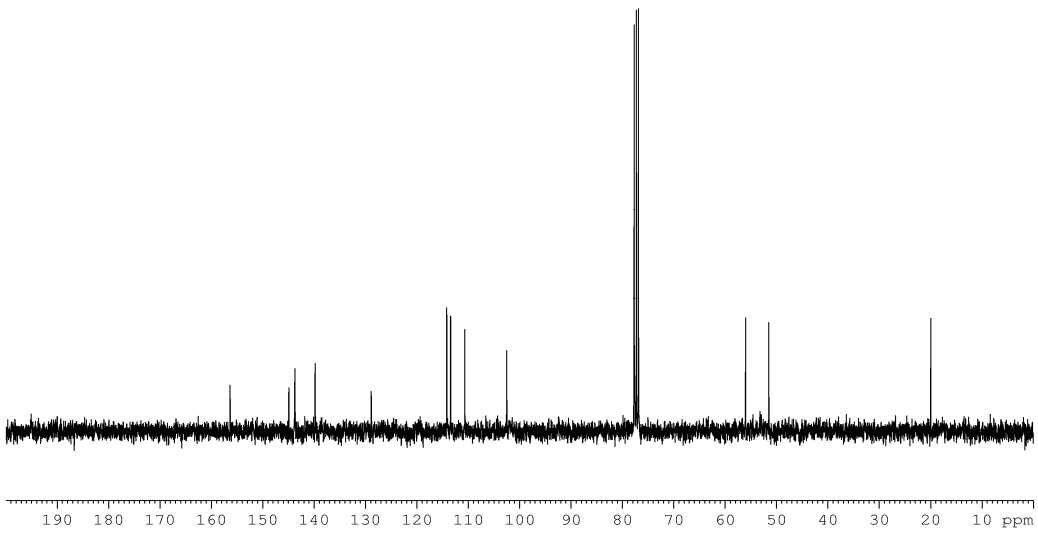


^{1}HNMR

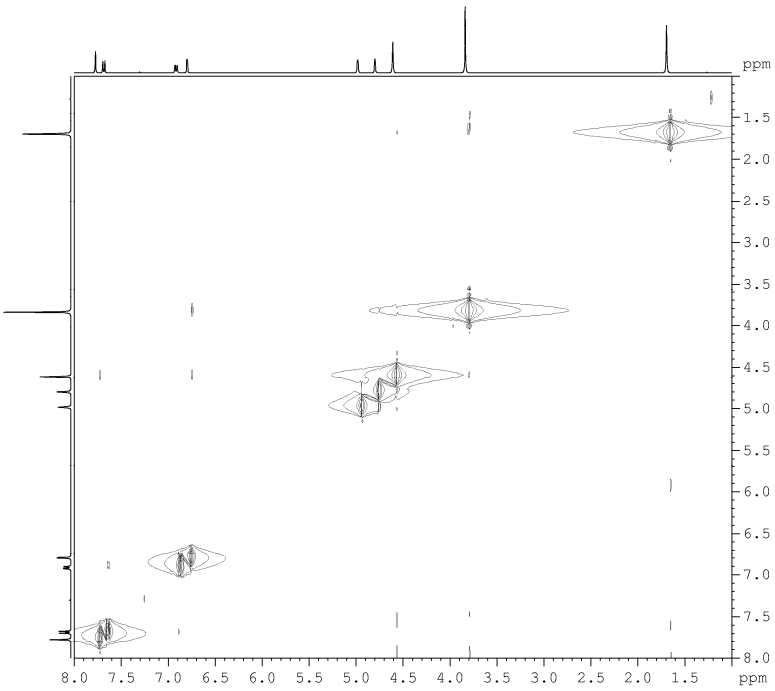


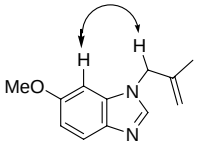


^{13}C NMR

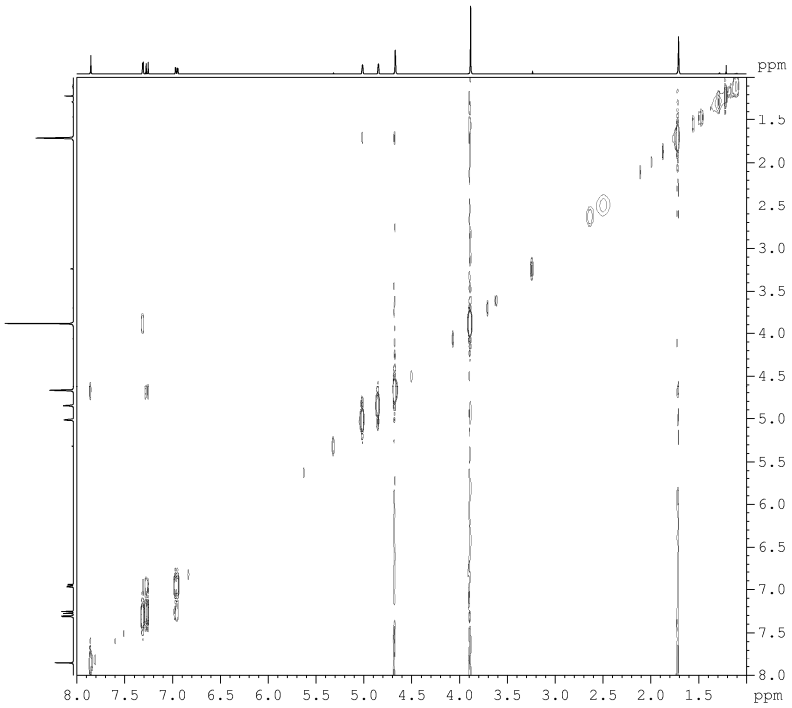


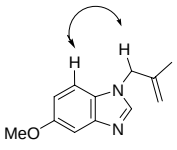
NOESY:


ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

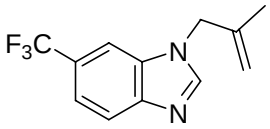

H
H
MeO
N
N

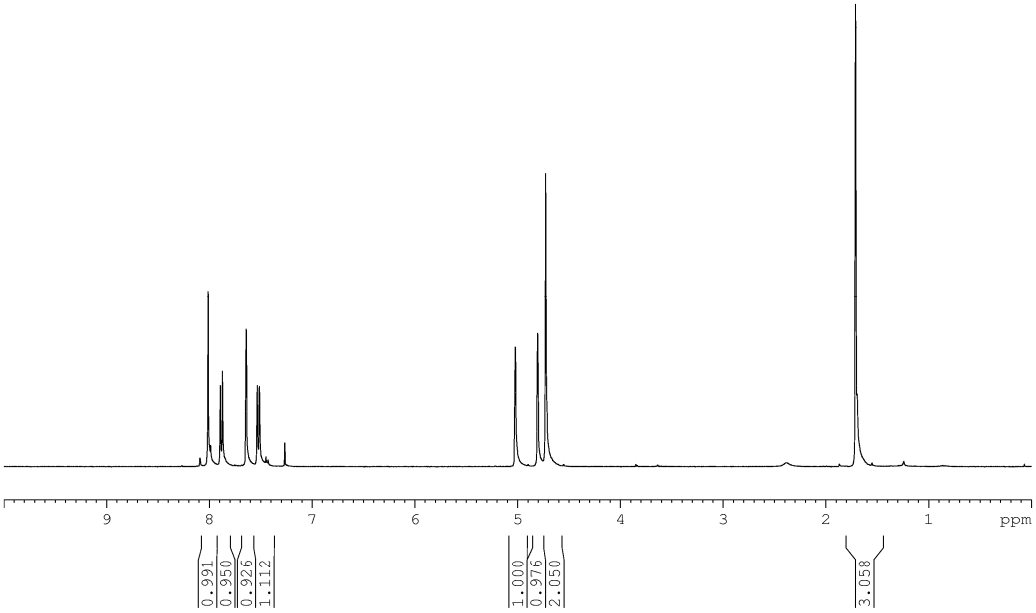
NOESY


ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

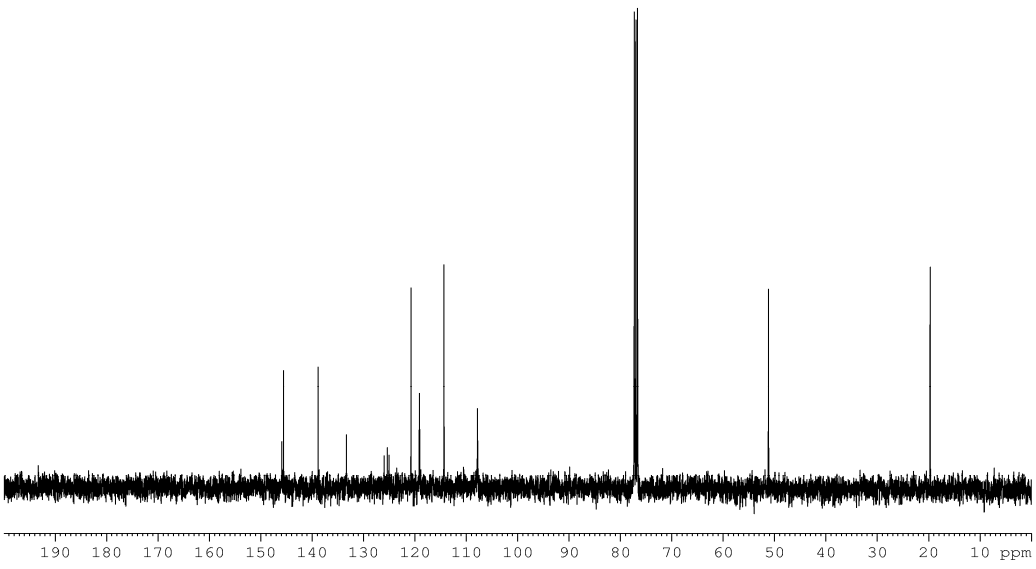

H
H
N
N
MeO

^{1}HNMR

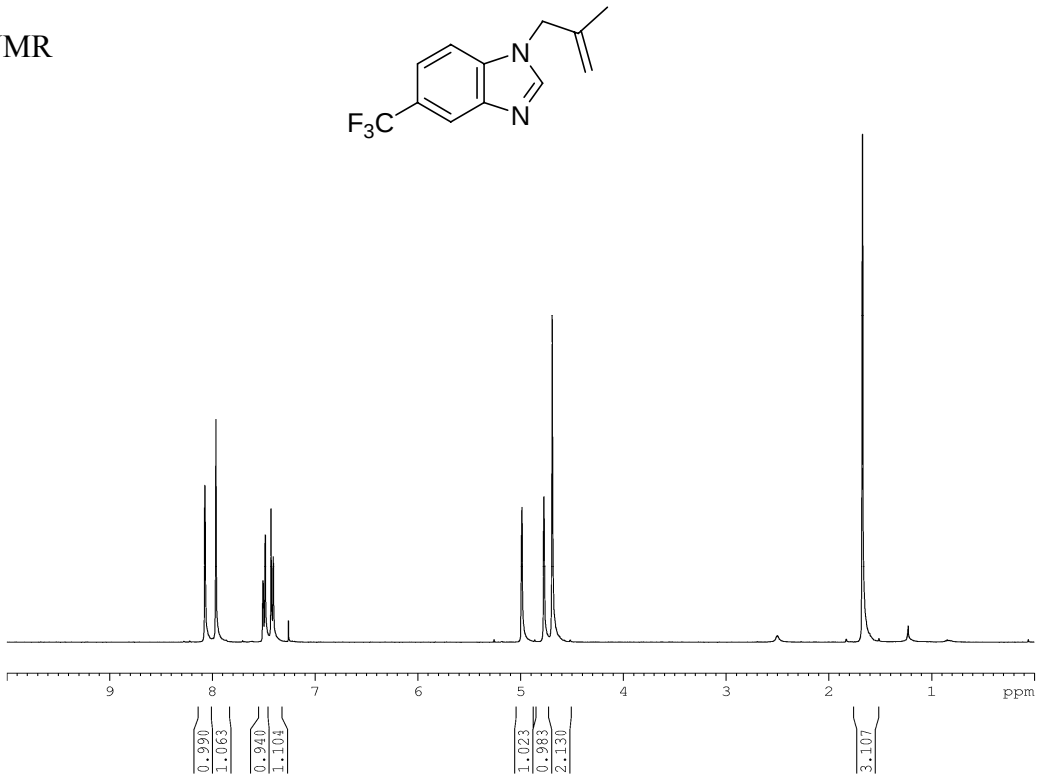




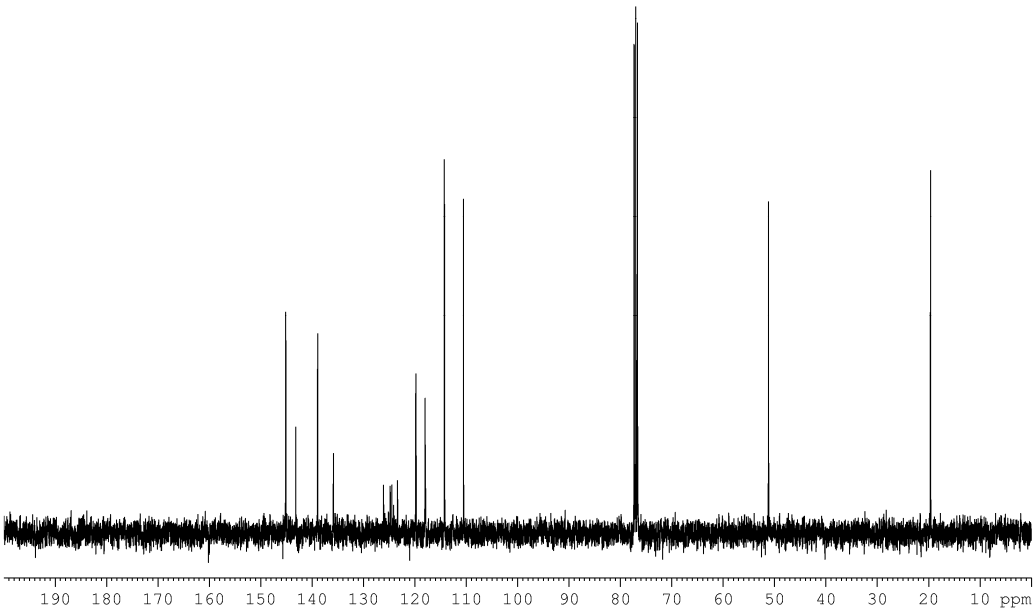
^{13}C NMR



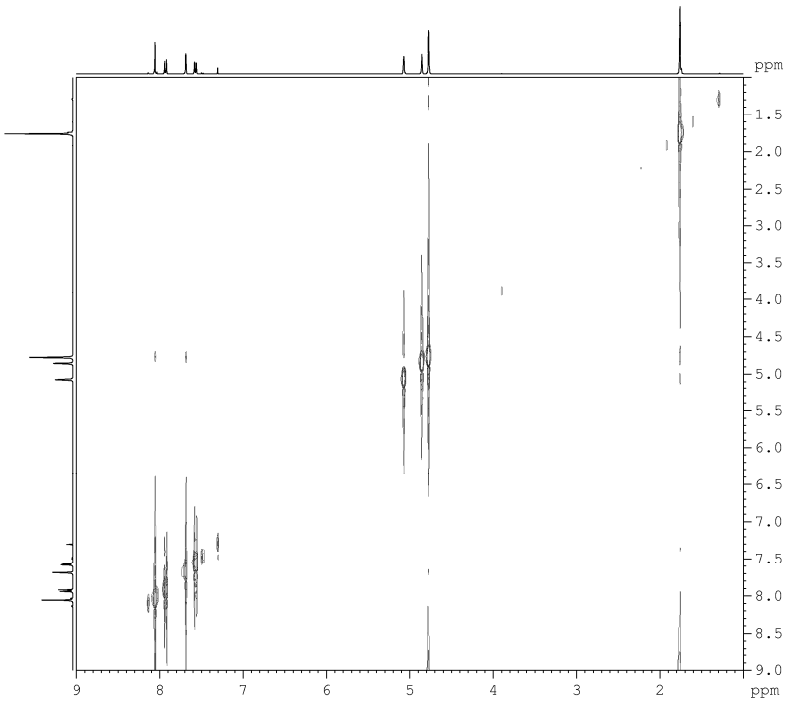
^{1}HNMR

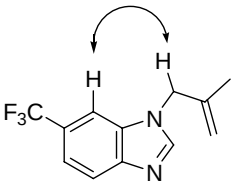


^{13}C NMR

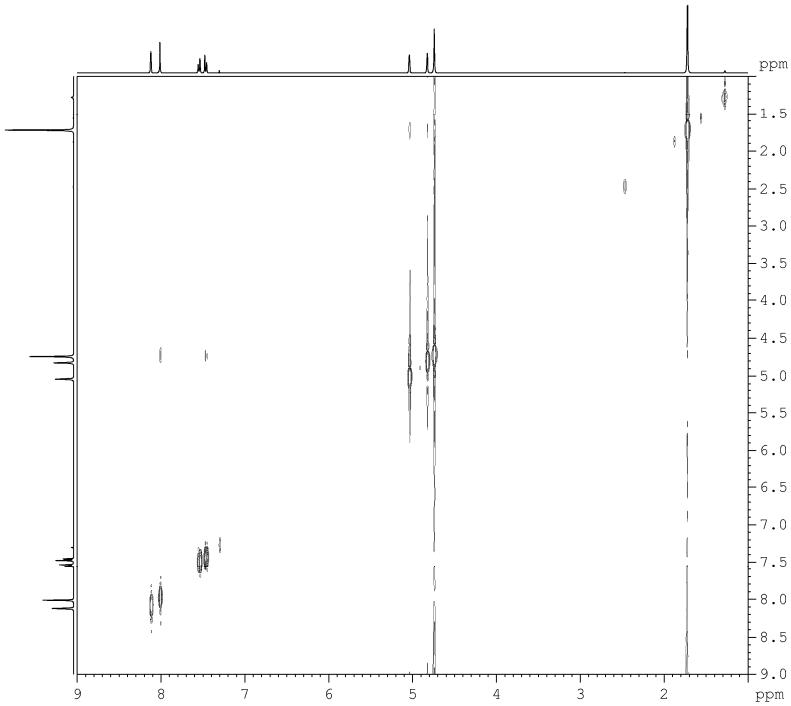


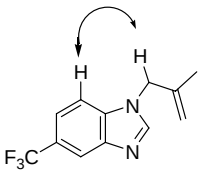
NOESY:


ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9
8
7
6
5
4
3
2
ppm

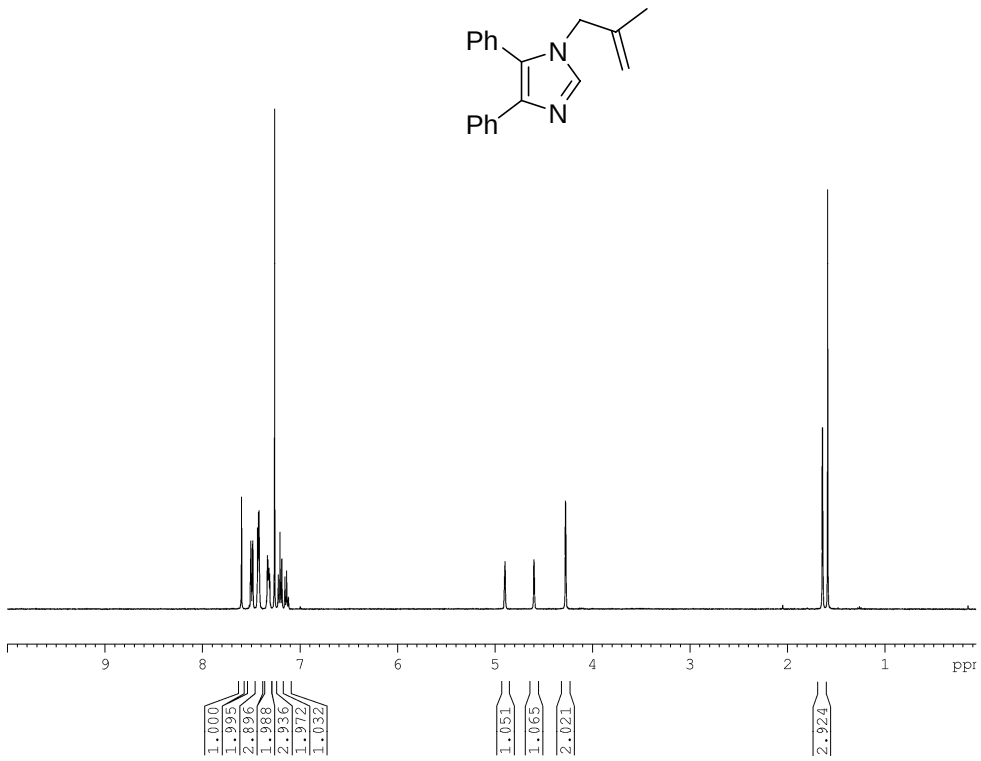

H
H
F3C
N
N

NOESY:

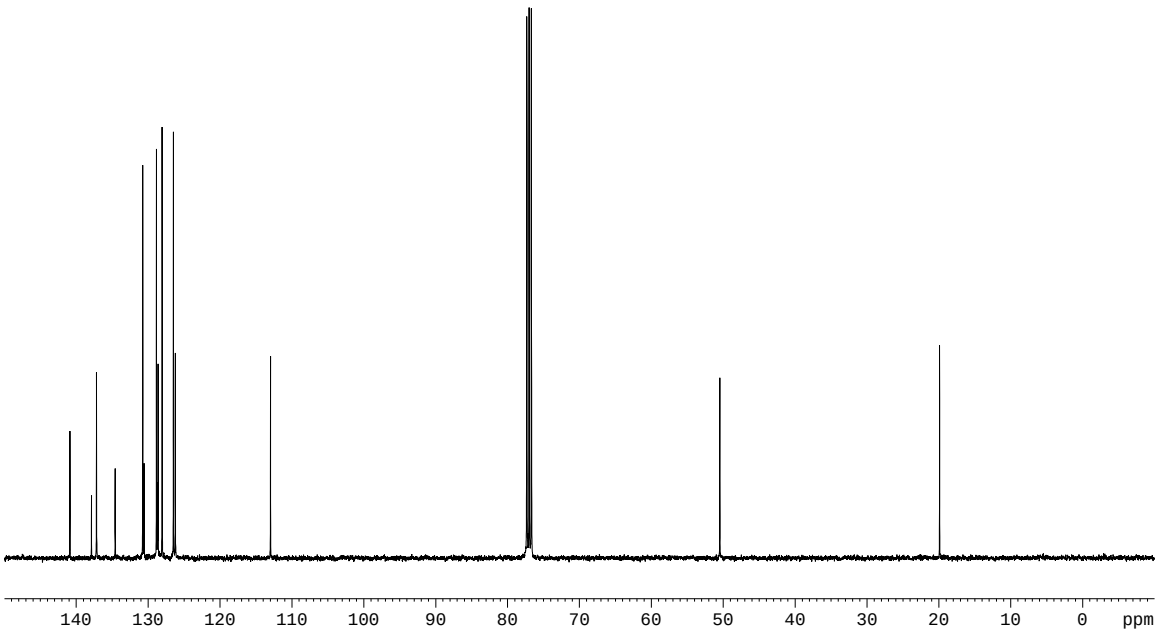

ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9
8
7
6
5
4
3
2
ppm


H
H
F3C
N
N

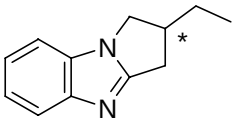
^{1}H NMR

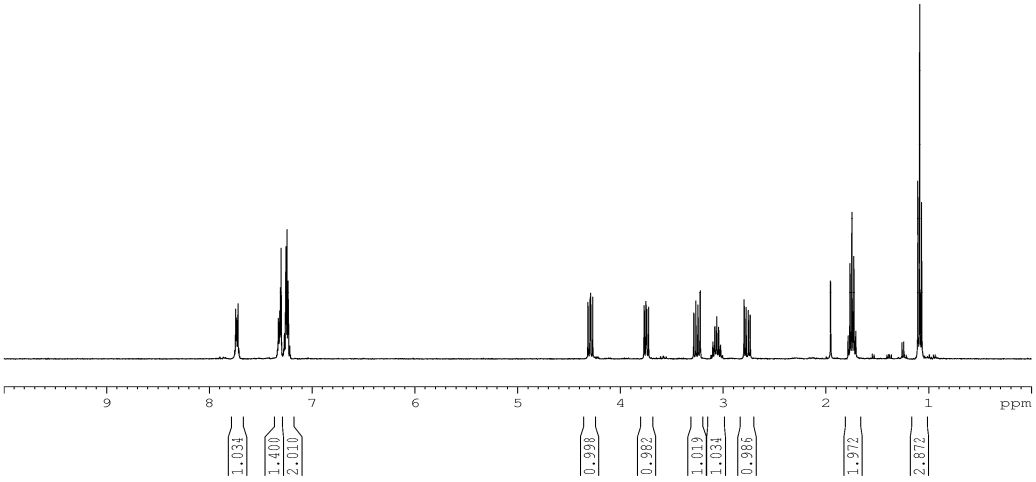


^{13}C NMR

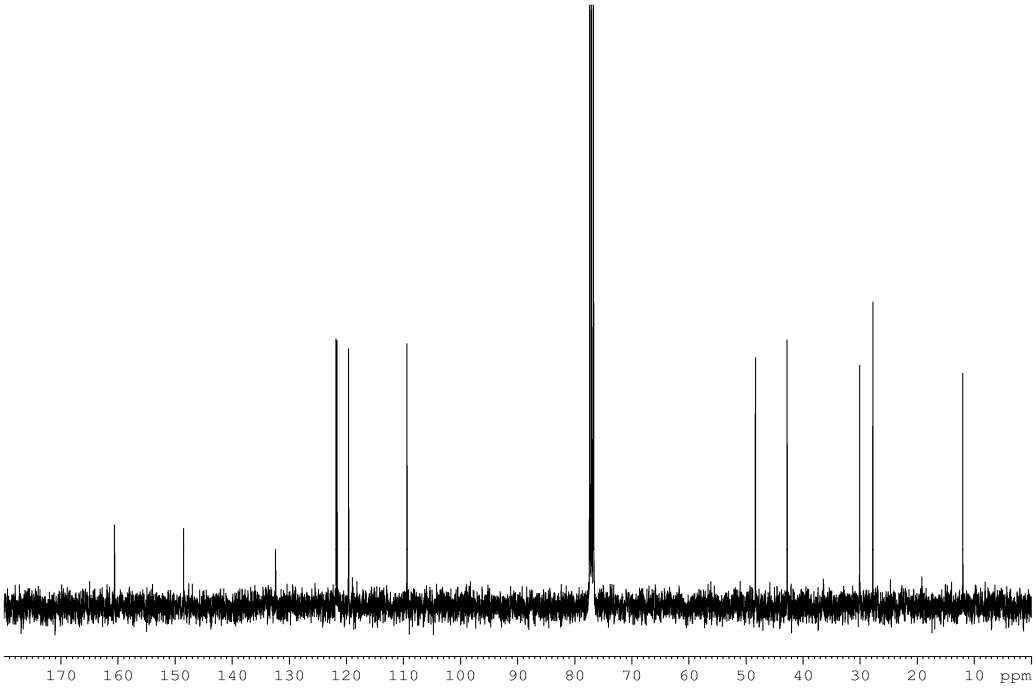


^{1}HNMR

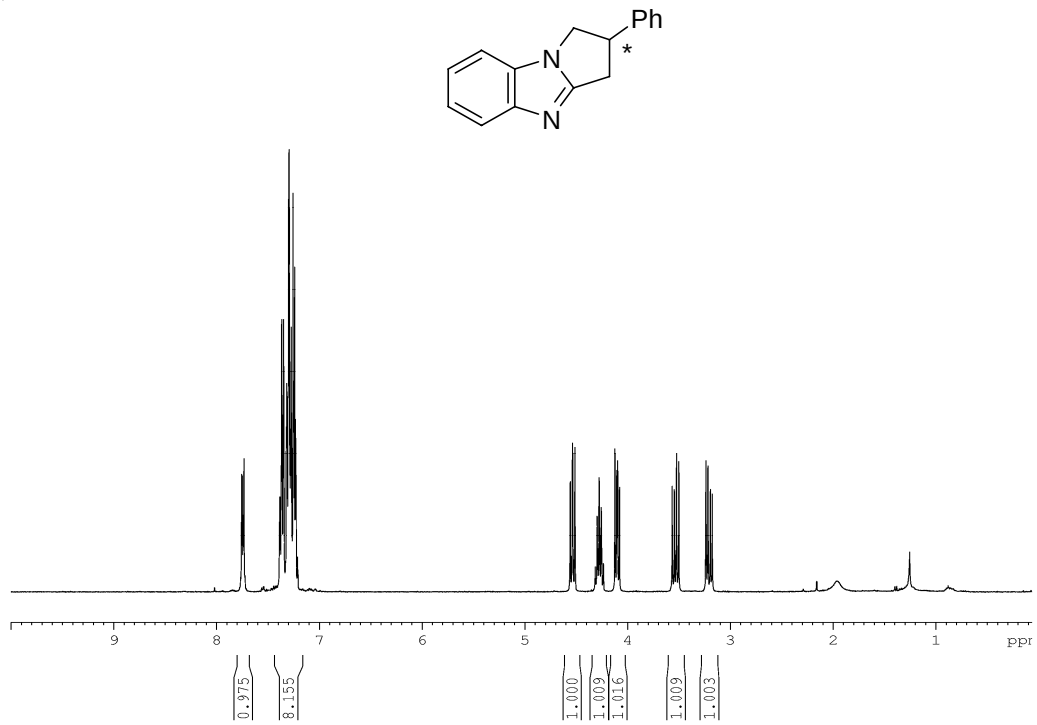




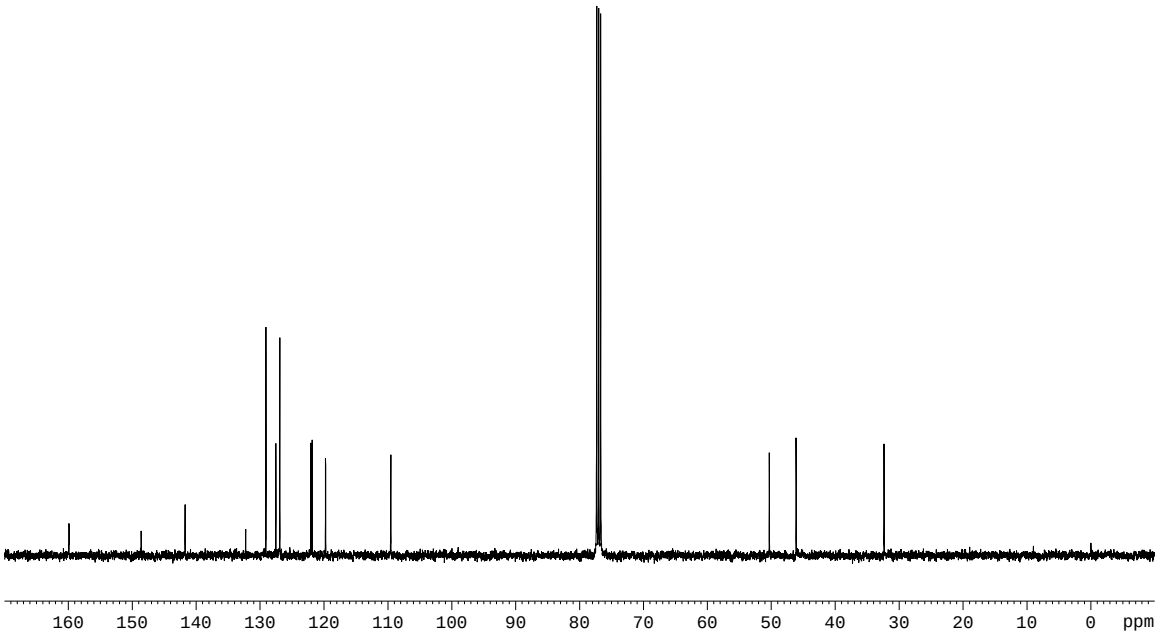
^{13}C NMR



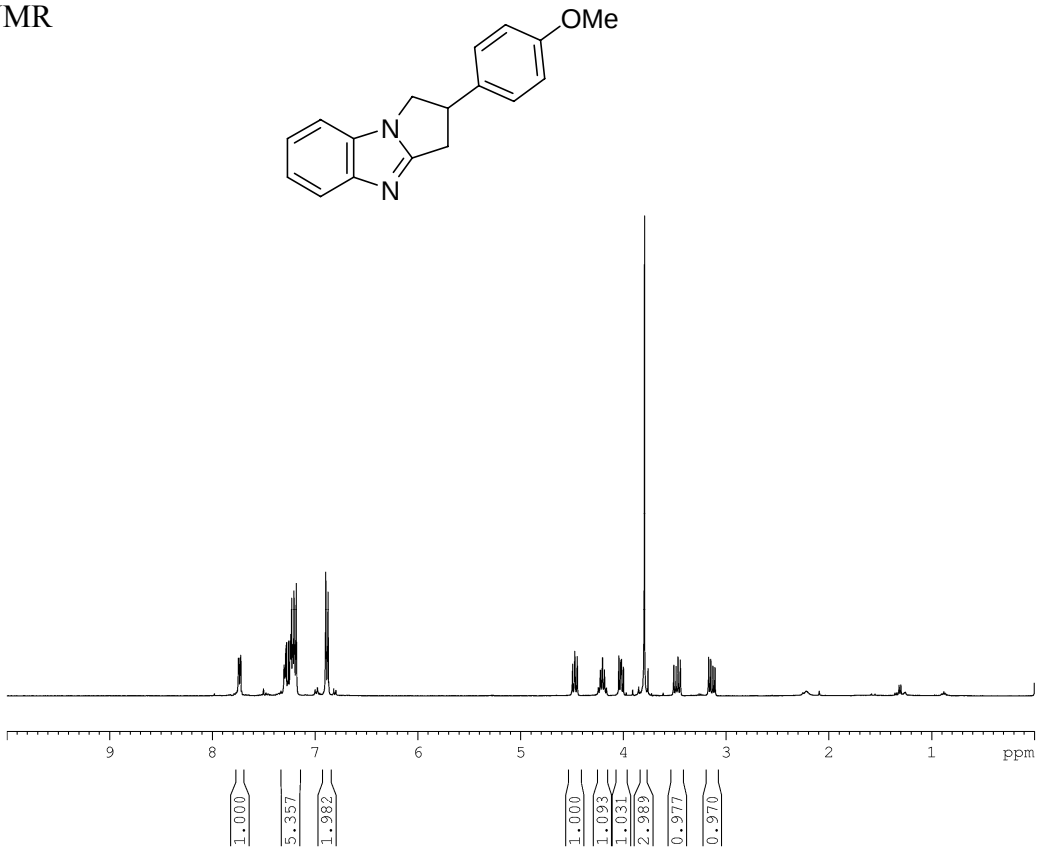
^{1}H NMR



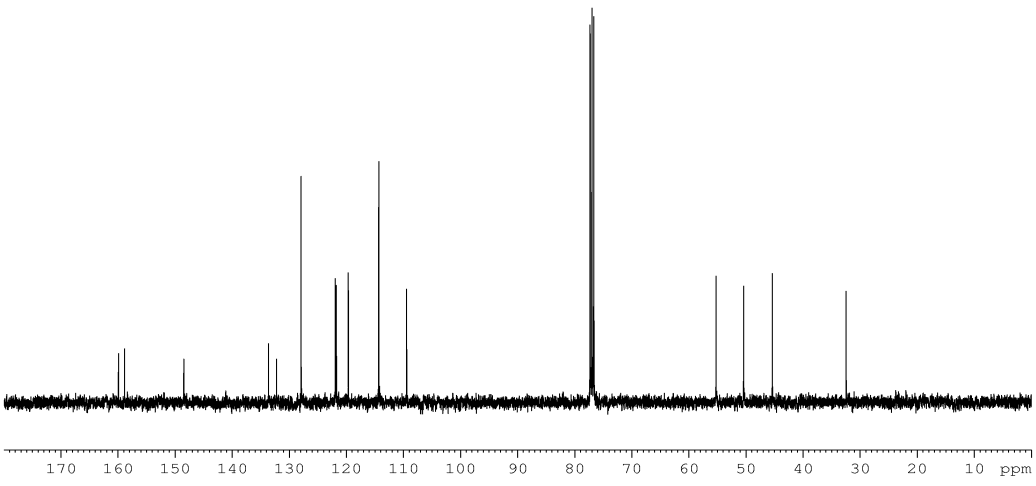
^{13}C NMR



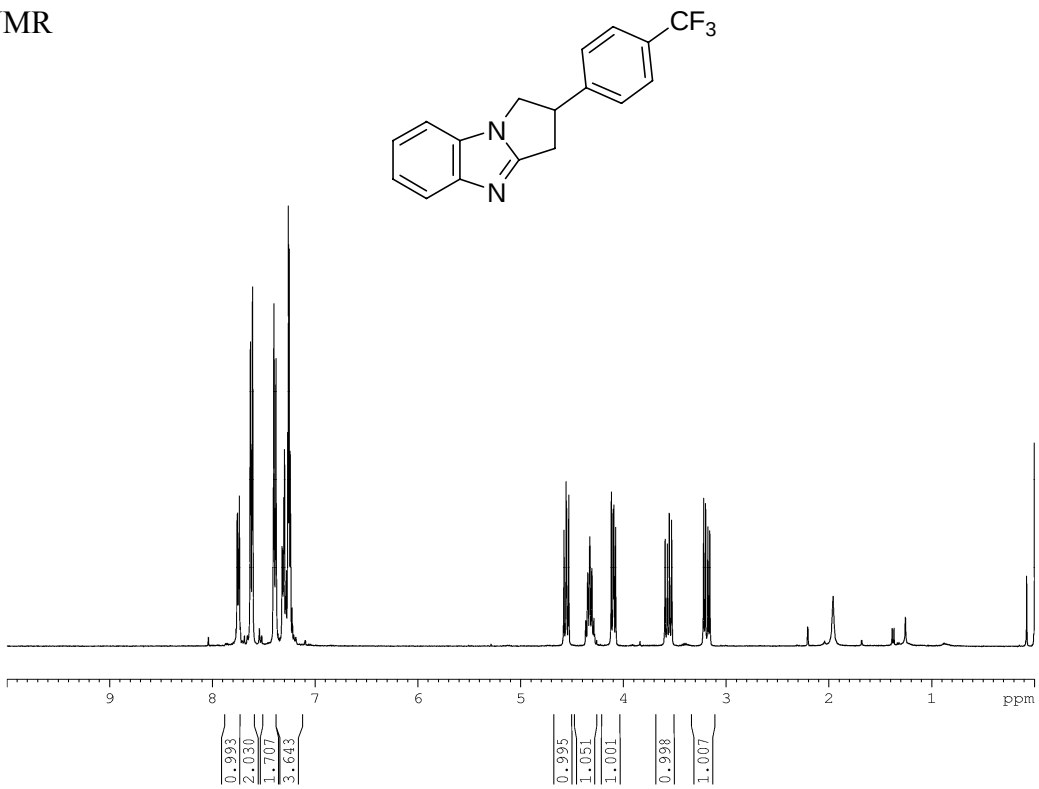
^{1}HNMR



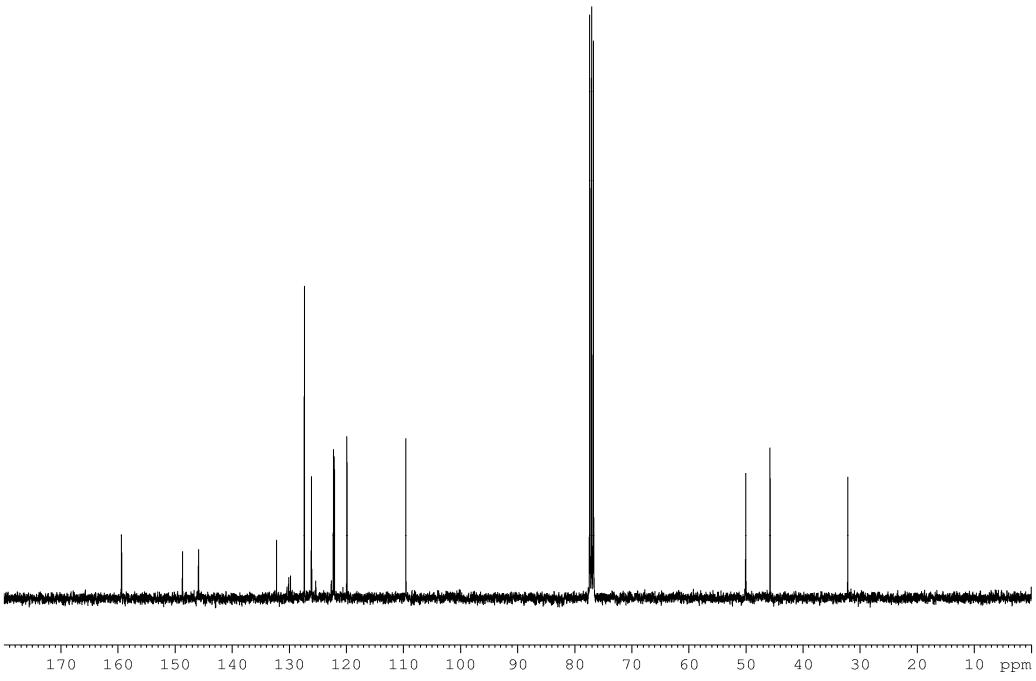
^{13}C NMR



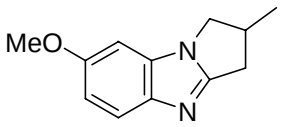
^{1}HNMR

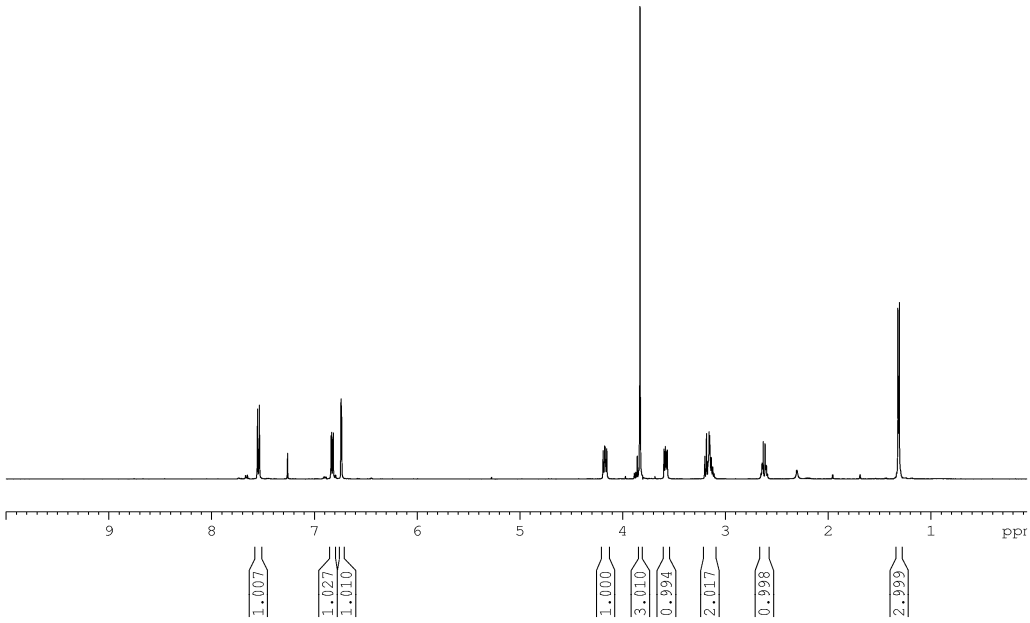


^{13}C NMR

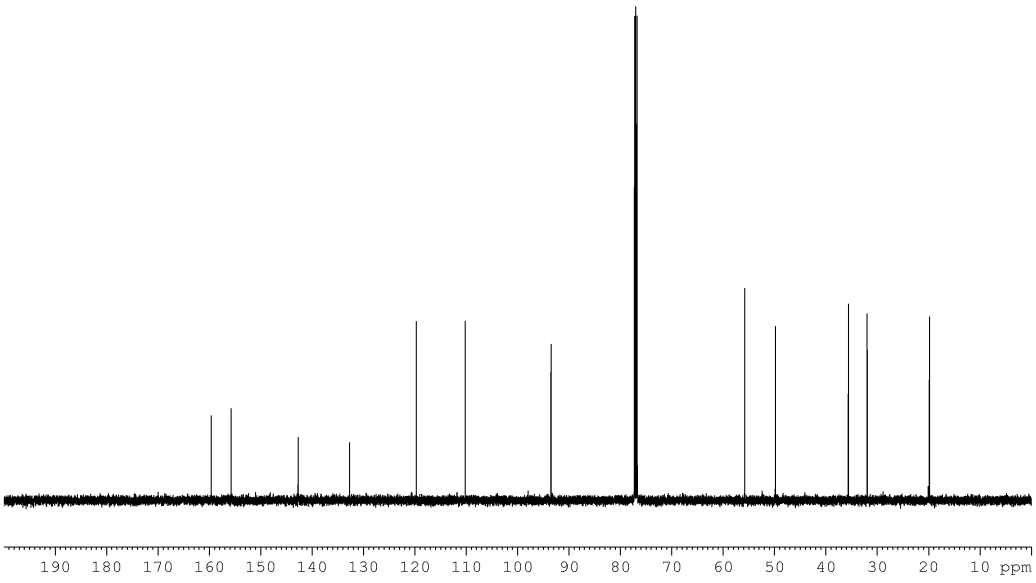


^{1}HNMR

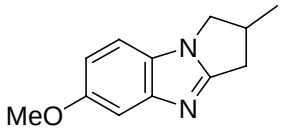


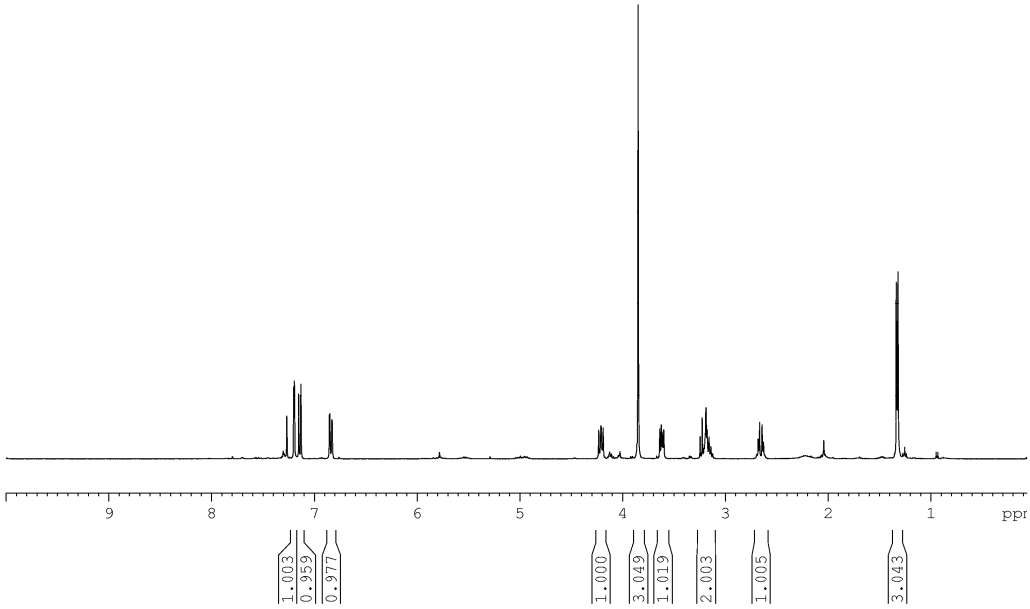


^{13}C NMR

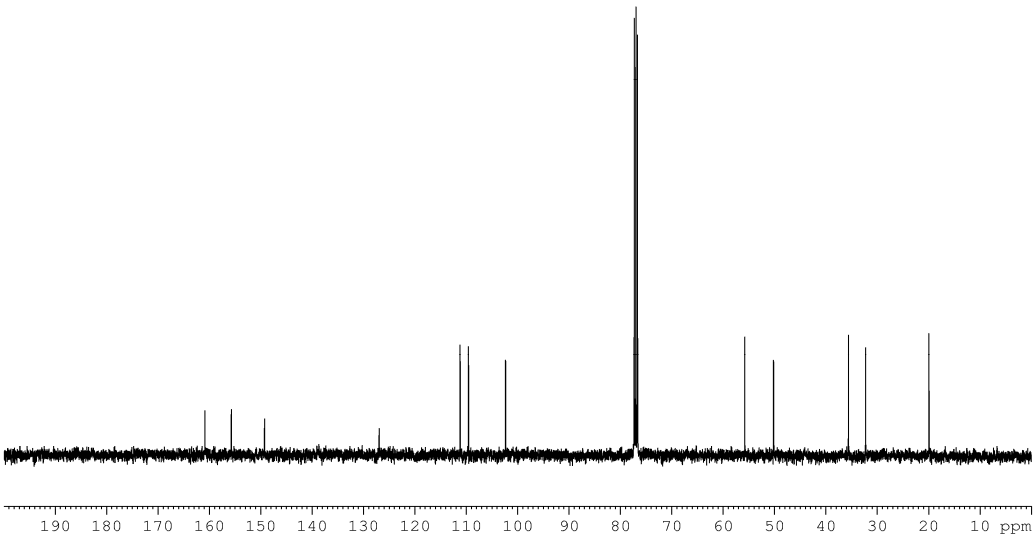


^{1}HNMR

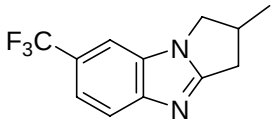


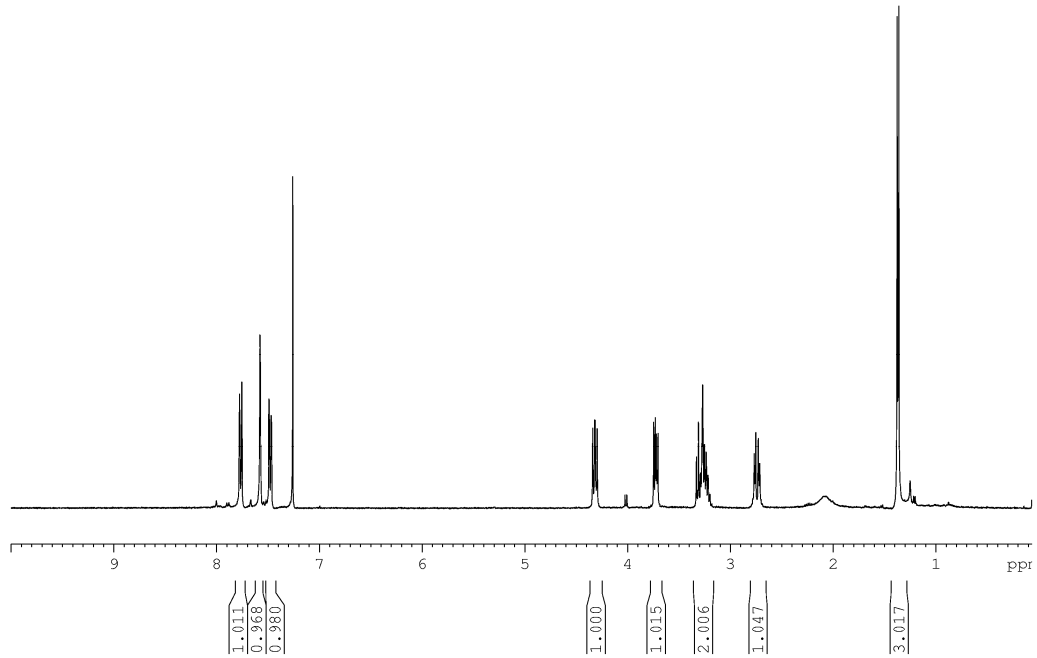


^{13}C NMR

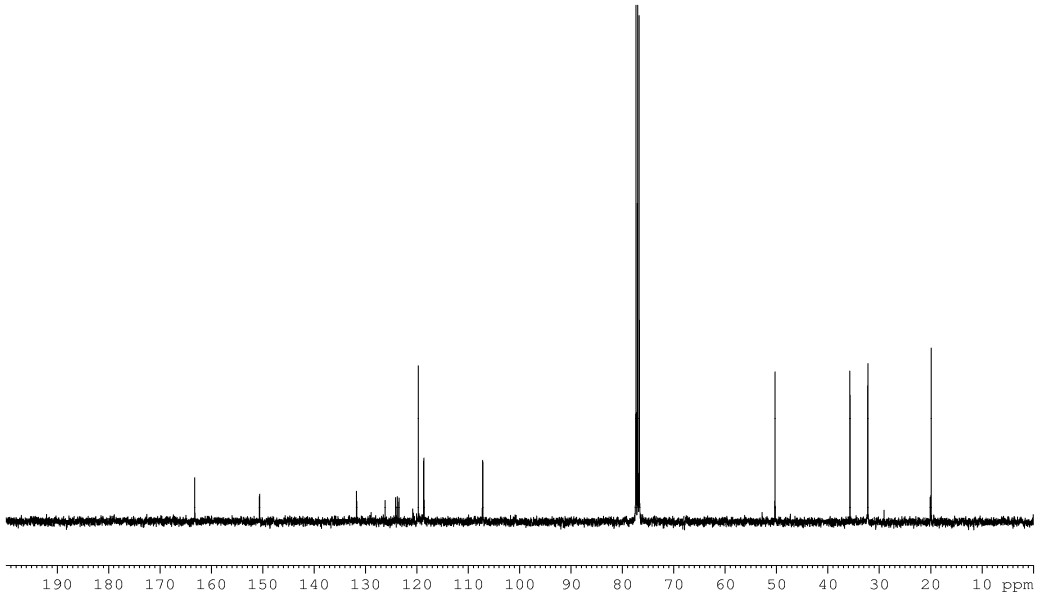


^{1}HNMR

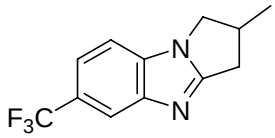


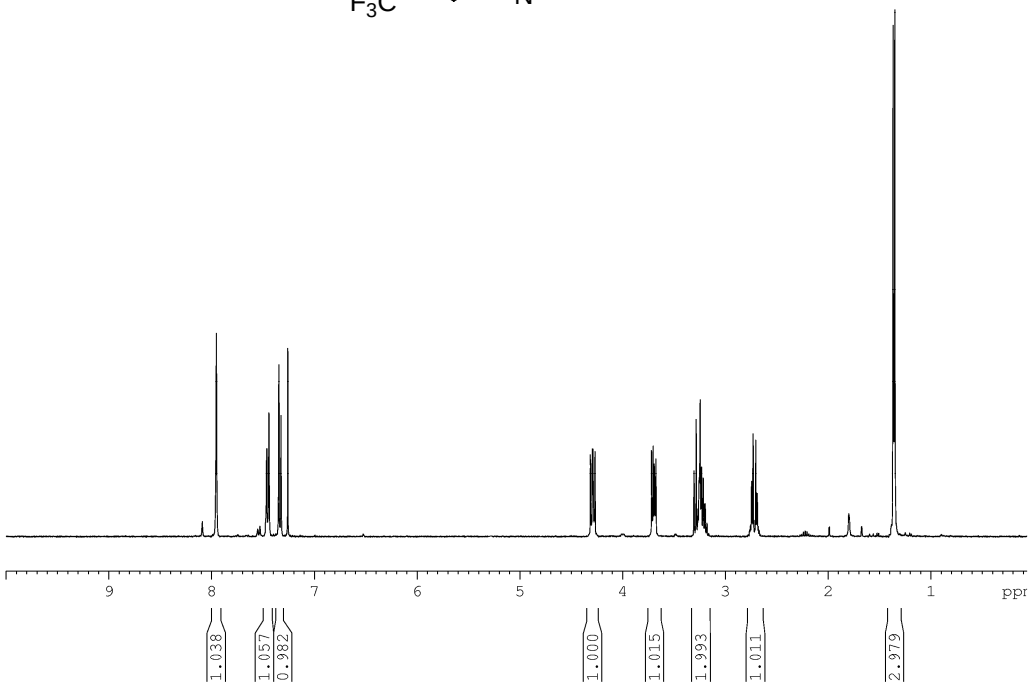


^{13}C NMR

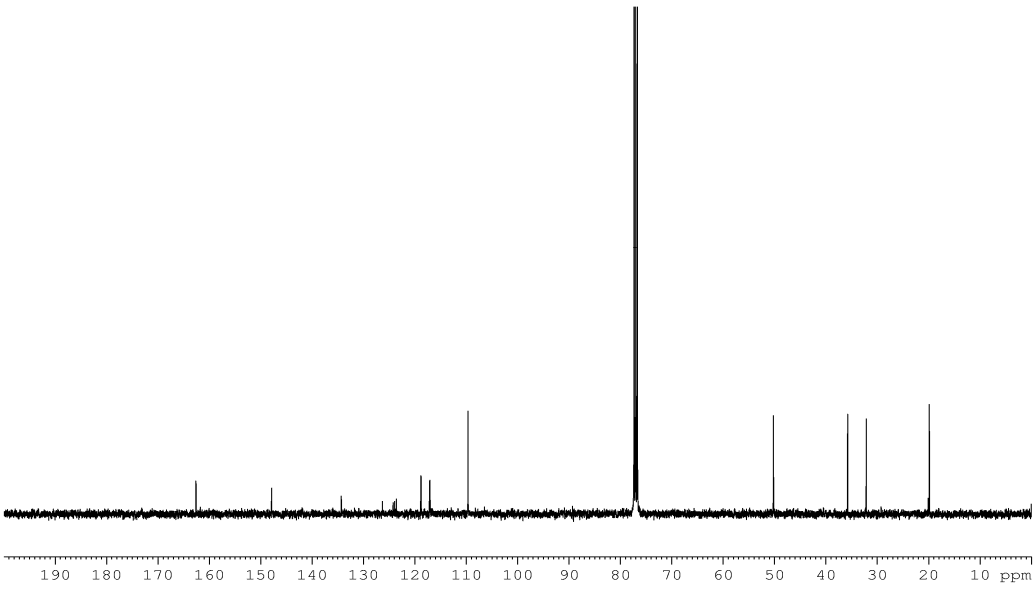


^{1}HNMR

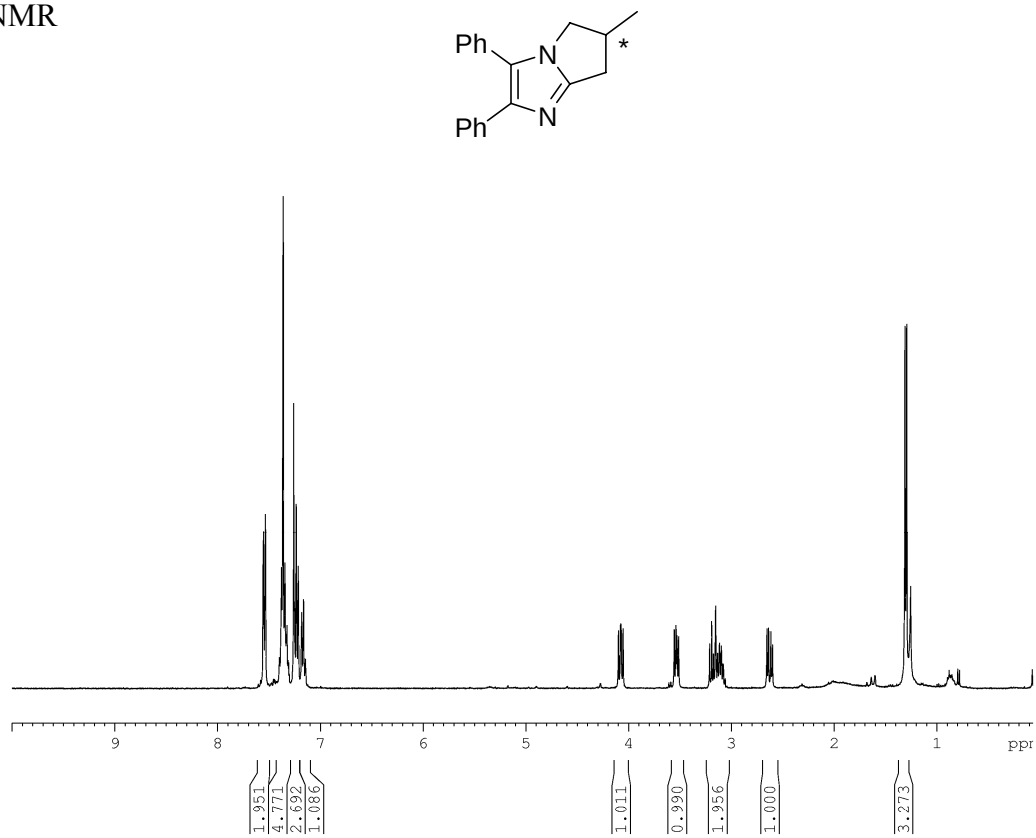




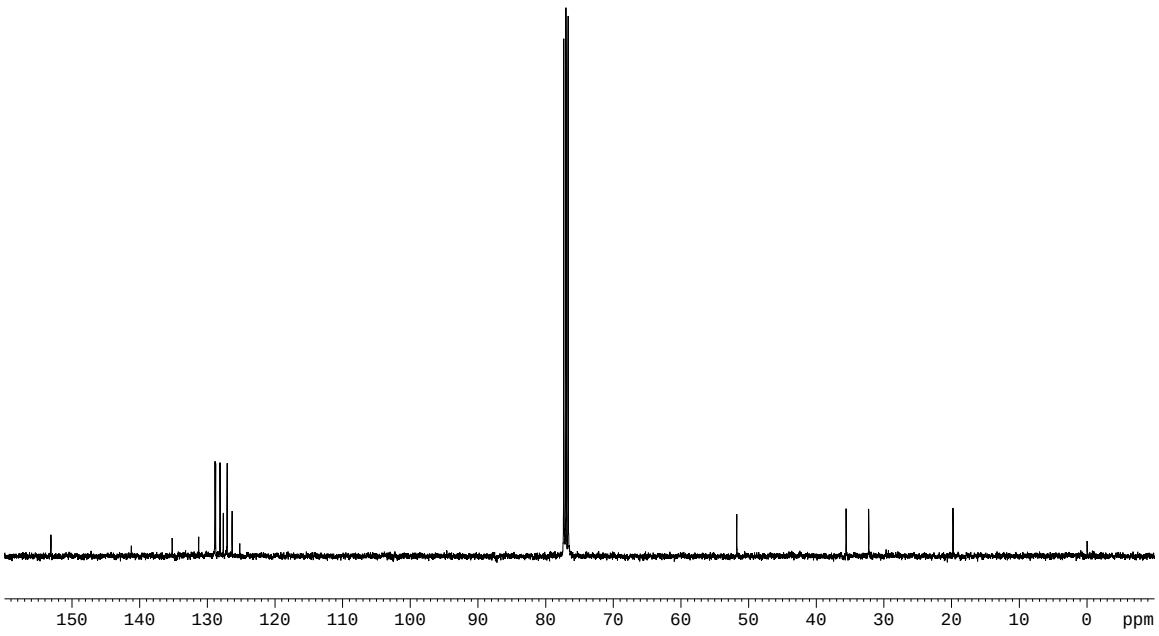
^{13}C NMR



^{1}H NMR

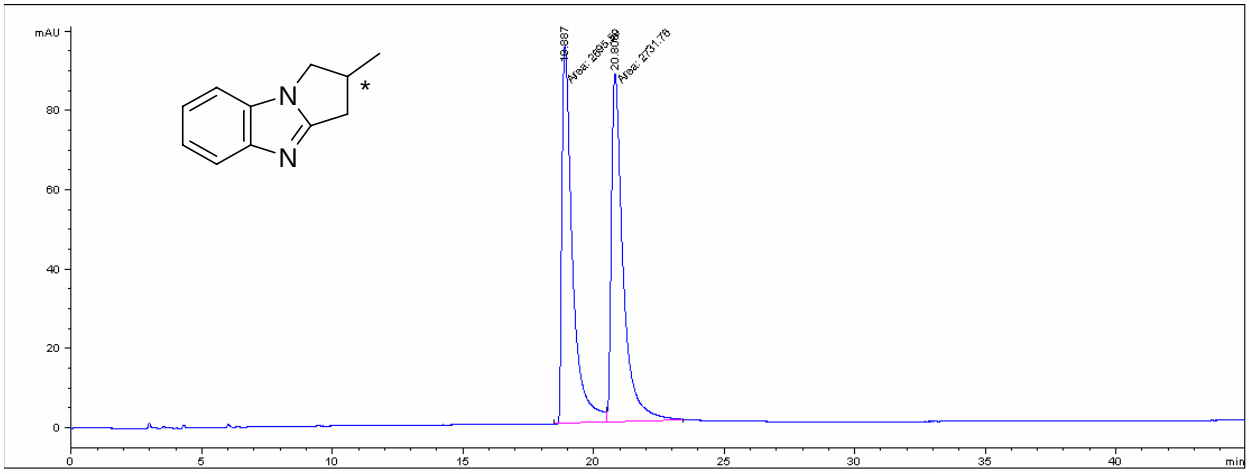


^{13}C NMR



2-Methyl-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole

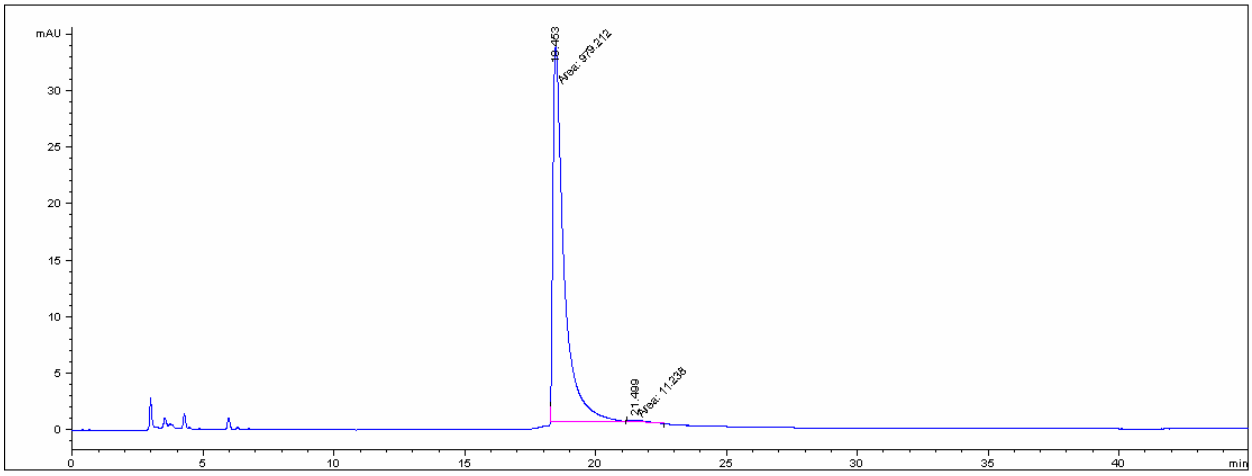
Racemic (Chiralcel AD-H column, 5% *i*PrOH/hexanes, 1mL/min, λ = 254 nm)



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.887	MF	0.4711	2695.59155	95.35656	49.6668
2	20.806	FM	0.5199	2731.75952	87.57645	50.3332

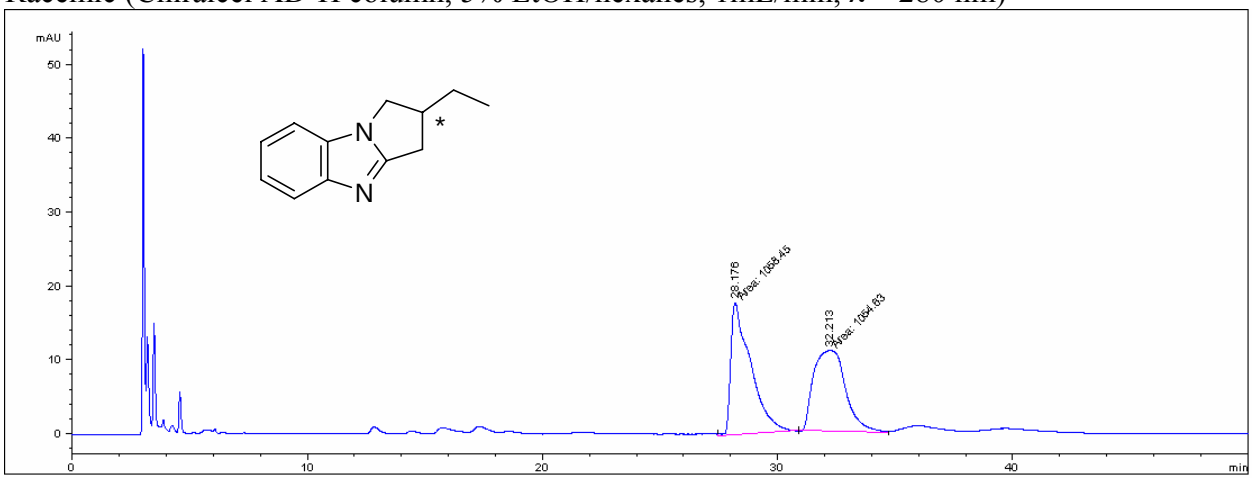
Enantiomerically enriched (98% ee)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.453	MM	0.4899	979.21173	33.31308	98.8654
2	21.499	MM	0.7845	11.23800	2.38741e-1	1.1346

2-Ethyl-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole

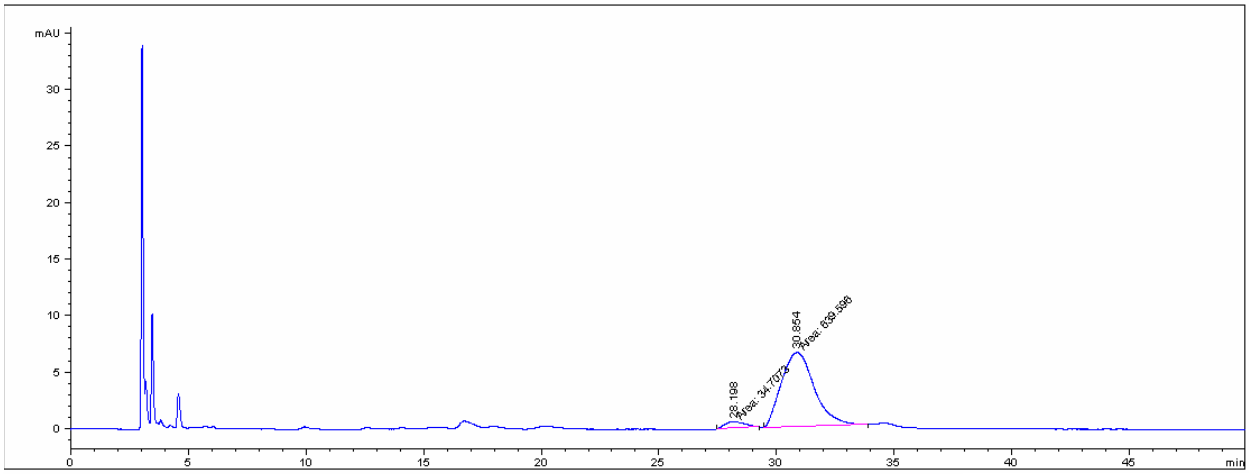
Racemic (Chiralcel AD-H column, 5% EtOH/hexanes, 1mL/min, λ = 280 nm)



Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.176	MM	0.9860	1058.45264	17.89218	50.0903
2	32.213	MM	1.5966	1054.63464	11.00931	49.9097

Enantiomerically enriched (90% ee)

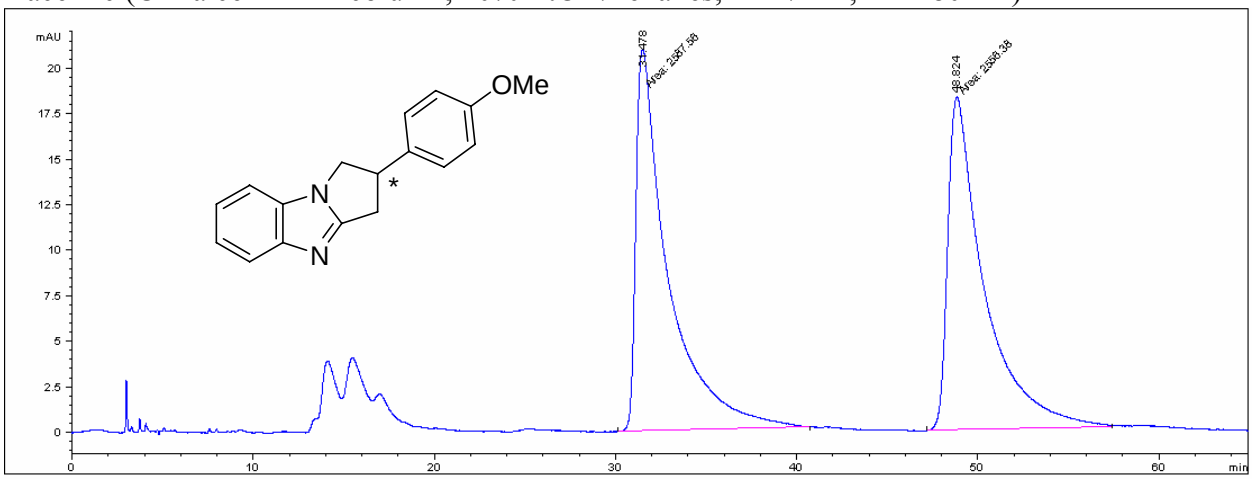


Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.198	MM	1.0463	34.70732	5.52842e-1	5.1471
2	30.854	MM	1.6288	639.59619	6.54467	94.8529

2-(4-methoxy-phenyl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole.

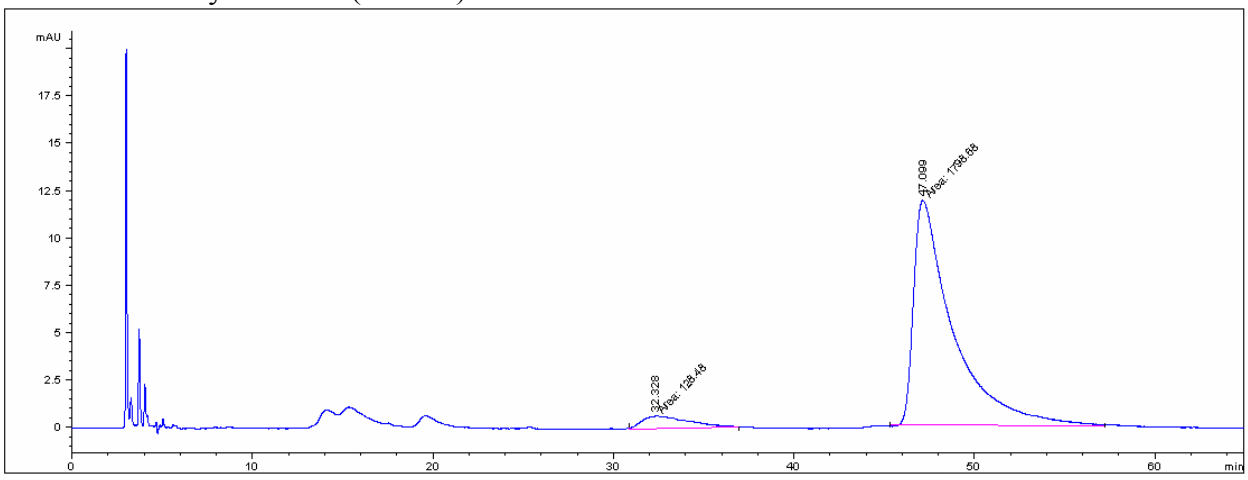
Racemic (Chiralcel AD-H column, 10% EtOH/hexanes, 1mL/min, λ = 280 nm)



Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.478	MM	2.0557	2587.55688	20.97914	50.3030
2	48.824	MM	2.3286	2556.38159	18.29736	49.6970

Enantiomerically enriched (87% ee)

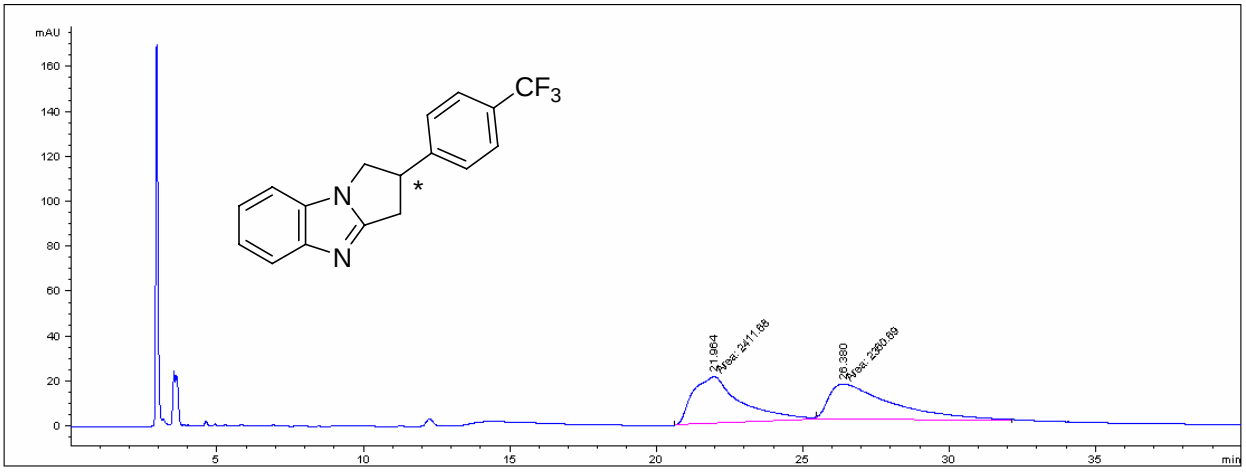


Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.328	MM	3.0648	128.47971	6.98679e-1	6.6668
2	47.099	MM	2.5286	1798.67822	11.85556	93.3332

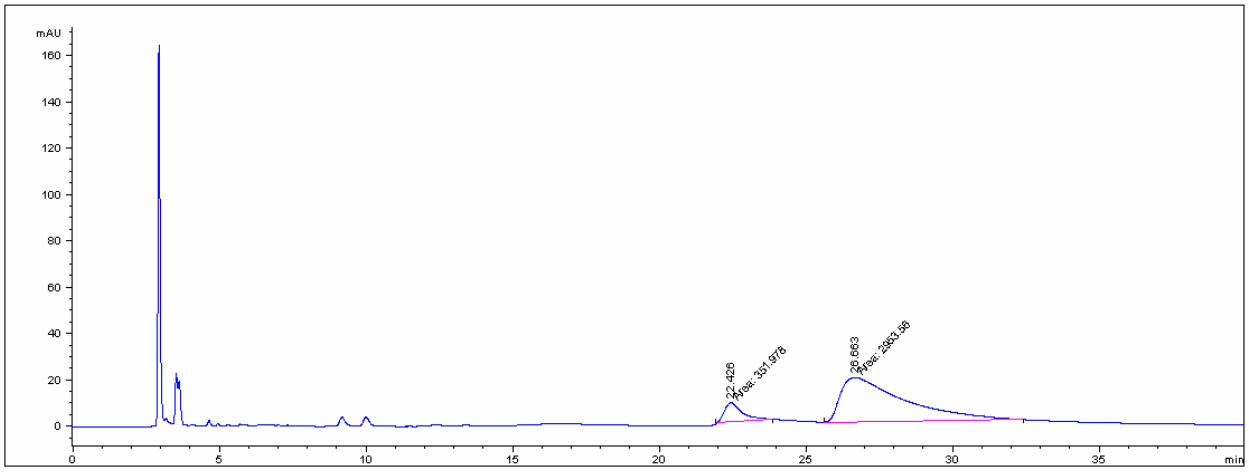
2-(4-trifluoromethyl-phenyl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole

Racemic ((Chiralcel AD-H column, 10% EtOH/hexanes, 1mL/min, λ = 230 nm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.964	MM	1.9093	2411.67847	21.05252	50.5342
2	26.380	MM	2.5031	2360.69092	15.71821	49.4658

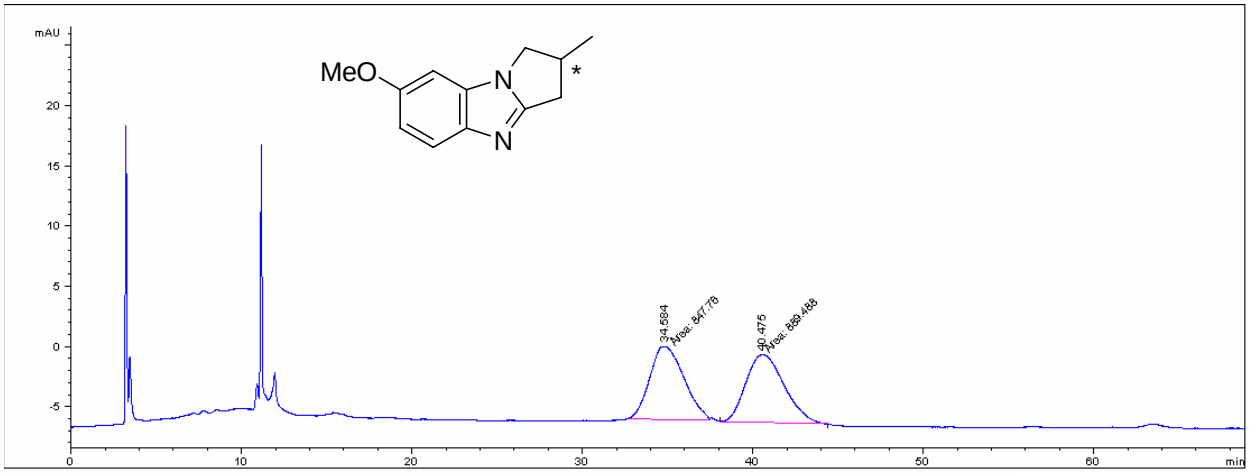
Enantiomerically enriched (79% ee)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.426	MM	0.7140	351.97824	8.21624	10.6481
2	26.663	MM	2.5632	2953.56177	19.20501	89.3519

2-Methyl-2,3-dihydro-1H-7-methoxy-benzo[d]pyrrolo[1,2-a]imidazole

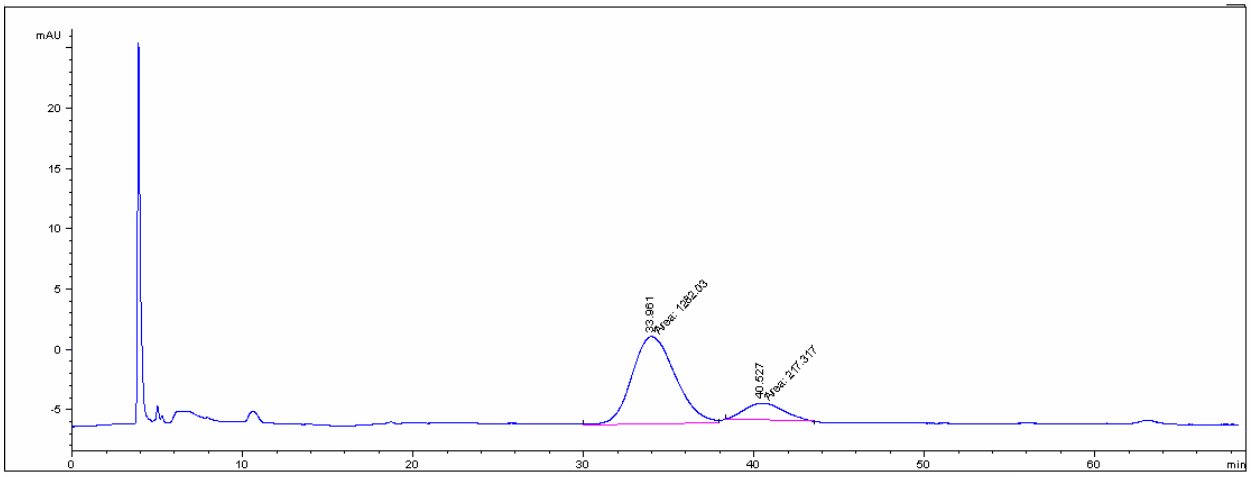
Racemic (Chiralcel AS-H column, 2% EtOH/hexanes w/ 0.1% diethylamine, 1mL/min, λ = 280 nm)



Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.584	MM	2.5242	847.75989	5.95445	48.7990
2	40.475	MM	2.5611	889.48822	5.65677	51.2009

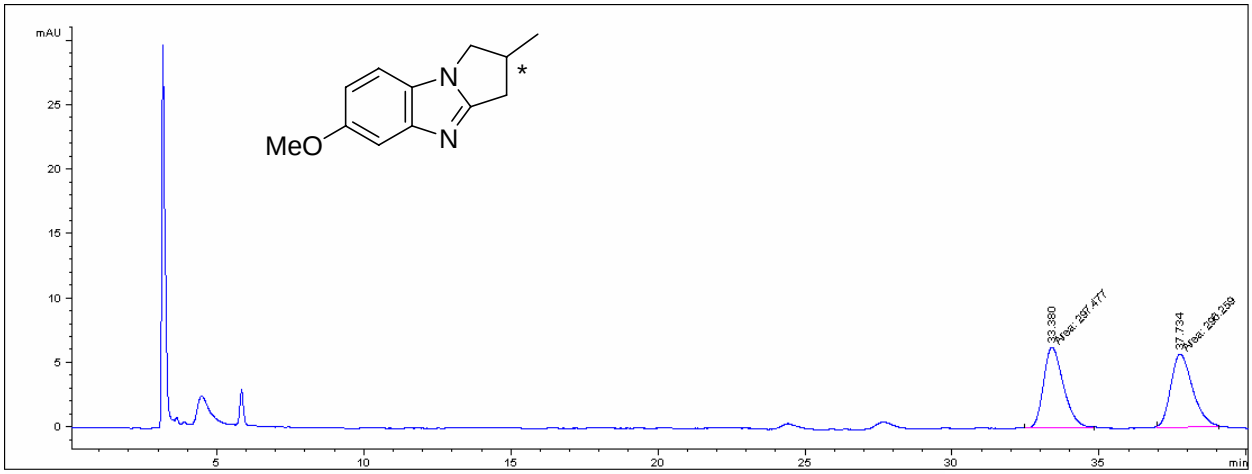
Enantiomerically enriched (71% ee)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.961	MM	1.8336	1282.03345	11.65306	85.5059
2	40.527	MM	1.6160	217.31677	2.24133	14.4941

2-Methyl-2,3-dihydro-1H-6-methoxy-benzo[d]pyrrolo[1,2-a]imidazole

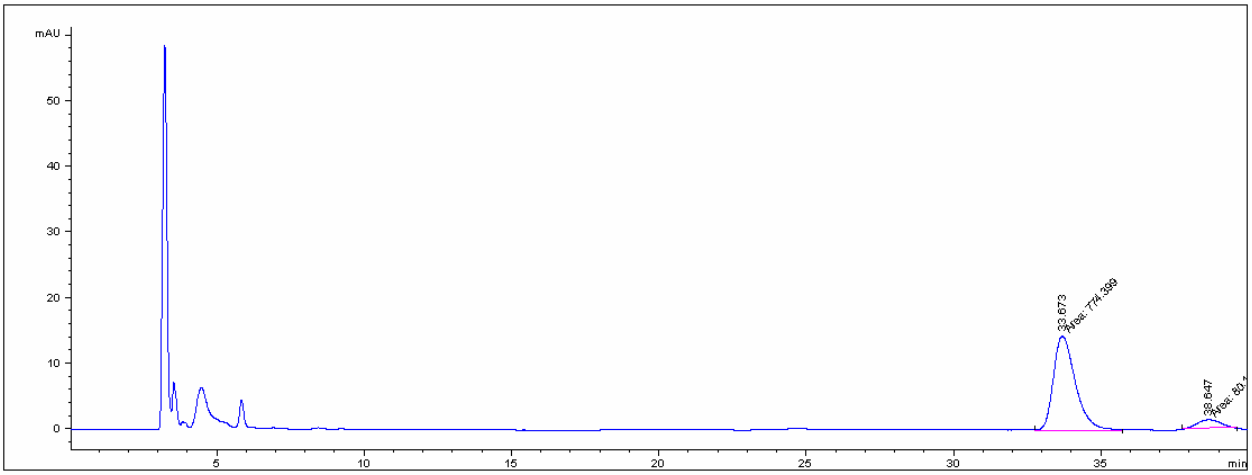
Racemic (Chiralcel AS-H column, 2% EtOH/hexanes w/ 0.1% diethylamine, 1mL/min, λ = 280 nm)



Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.380	MM	0.7905	297.47684	6.27186	50.1026
2	37.734	MM	0.8652	296.25900	5.70670	49.8974

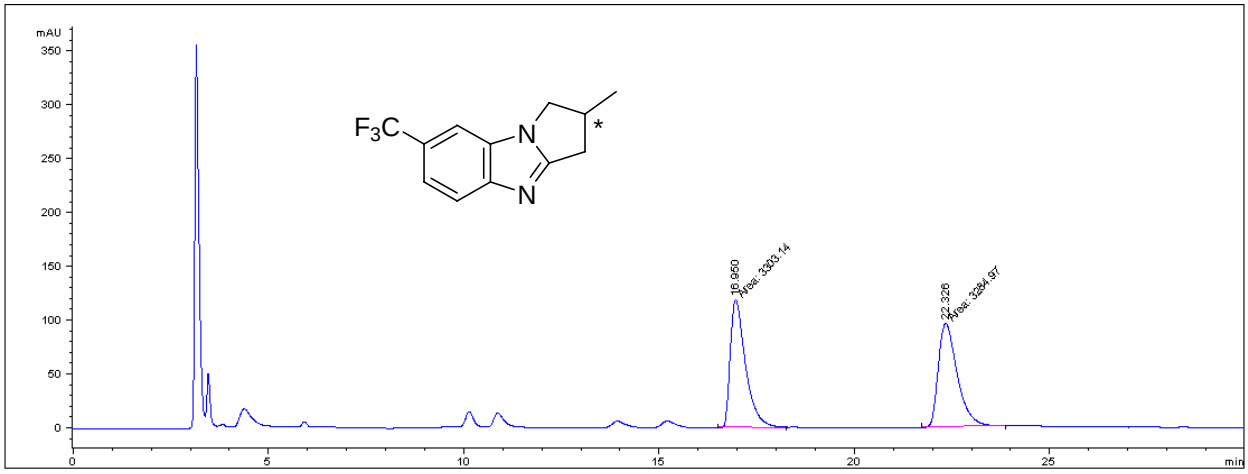
Enantiomerically enriched (81% ee)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.673	MM	0.8873	774.39880	14.54603	90.6260
2	38.647	MM	0.9637	80.10098	1.38529	9.3740

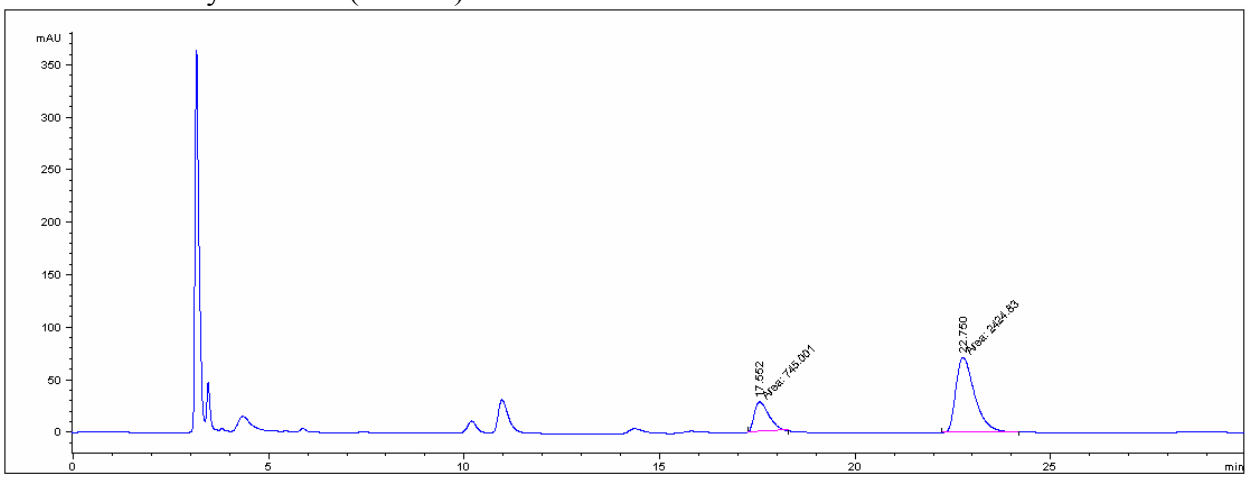
2-Methyl-2,3-dihydro-1H-7-trifluoromethyl-benzo[d]pyrrolo[1,2-a]imidazole

Racemic (Chiralcel AS-H column, 2% EtOH/hexanes, 1mL/min, λ = 250 nm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Heiqht [mAU]	Area %
1	16.950	MM	0.4631	3303.14136	118.86766	50.1379
2	22.326	MM	0.5677	3284.96997	96.43585	49.8621

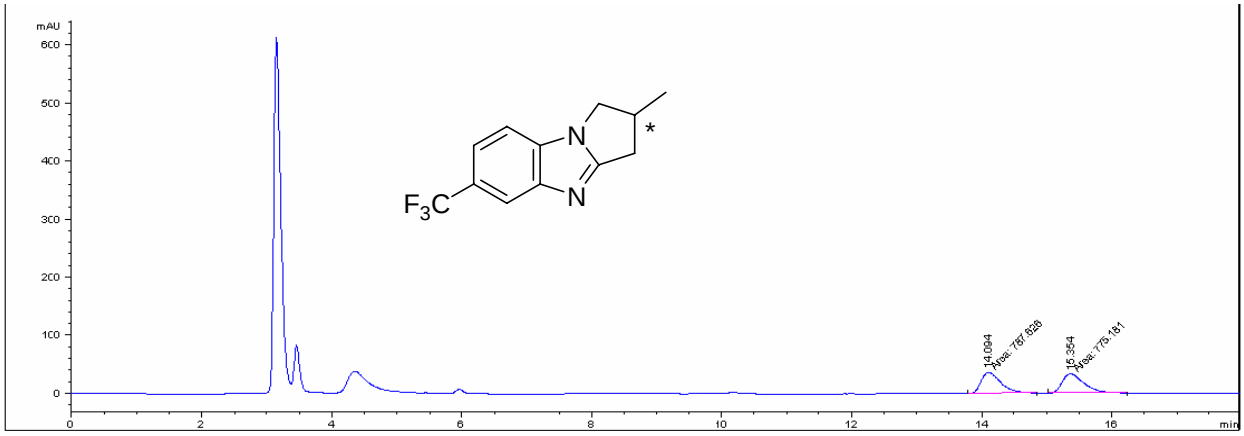
Enantiomerically enriched (53% ee)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Heiqht [mAU]	Area %
1	17.552	MM	0.4337	745.00134	28.63176	23.5029
2	22.750	MM	0.5627	2424.82715	71.82219	76.4971

2-Methyl-2,3-dihydro-1H-6-trifluoromethyl-benzo[d]pyrrolo[1,2-a]imidazole

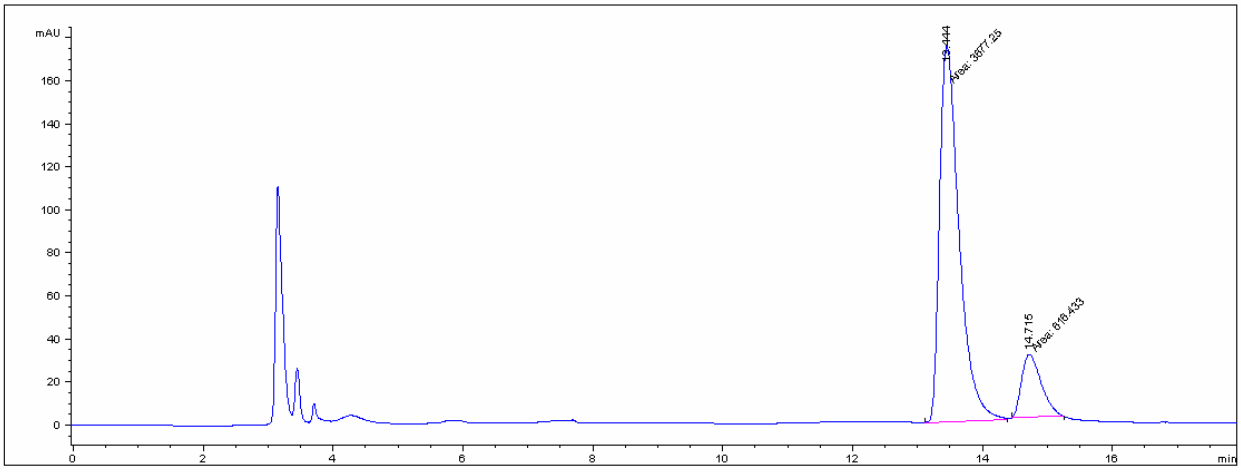
Racemic (Chiralcel AS-H column, 2% EtOH/hexanes, 1mL/min,, λ = 250 nm)



Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.094	MM	0.3633	787.62561	36.13475	50.3982
2	15.354	MM	0.3899	775.18097	33.13570	49.6018

Enantiomerically enriched (71% ee)

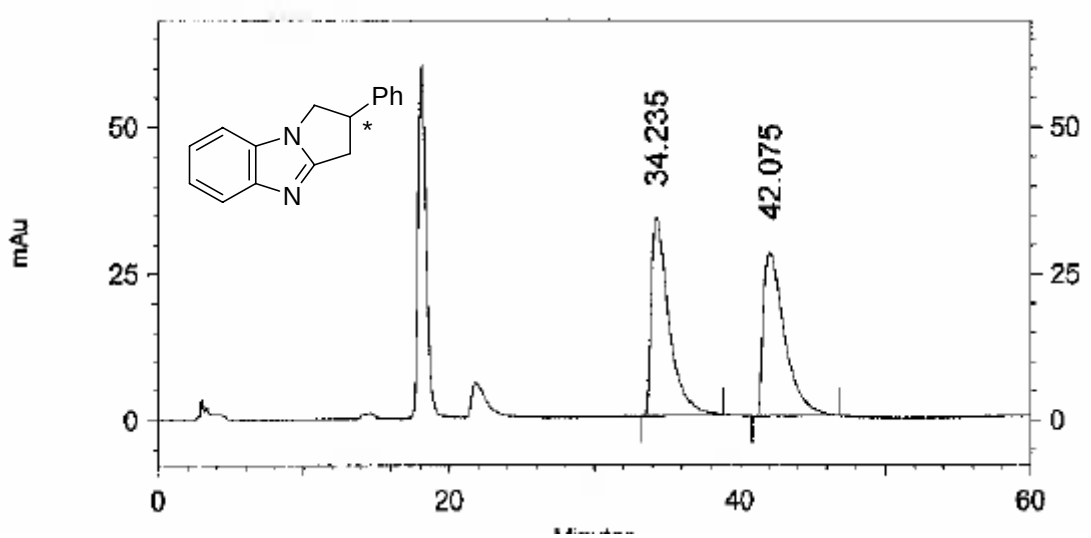


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.444	MM	0.3495	3677.24707	175.35199	85.6433
2	14.715	MM	0.3523	616.43256	29.16059	14.3567

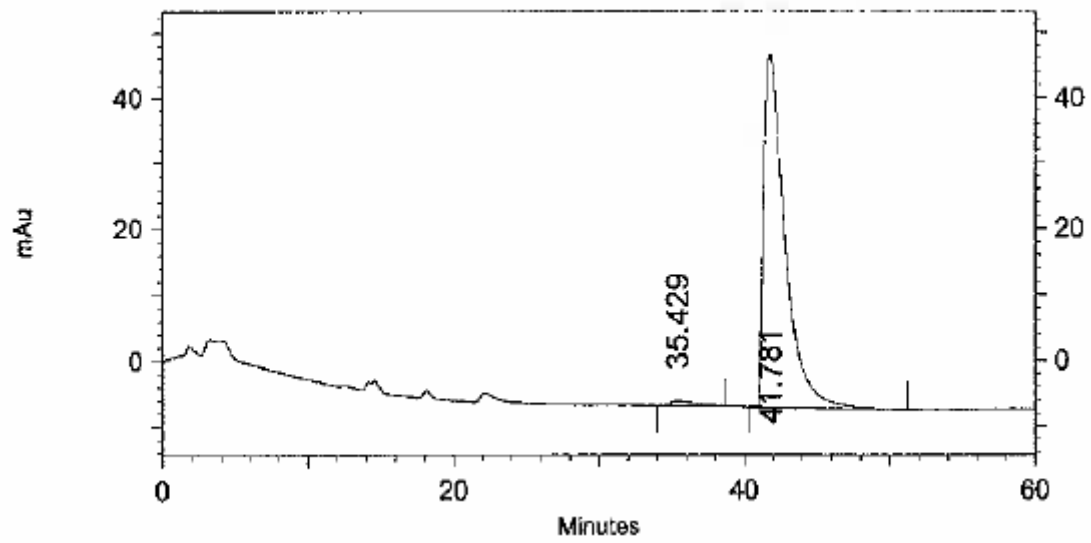
2-Phenyl-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole

Racemic (Chiralcel AD-H column, 10% *i*PrOH/hexanes, 1mL/min, λ = 280 nm)



Retention Time	Area	Area Percent
34.235	2914998	50.674
42.075	2837497	49.326

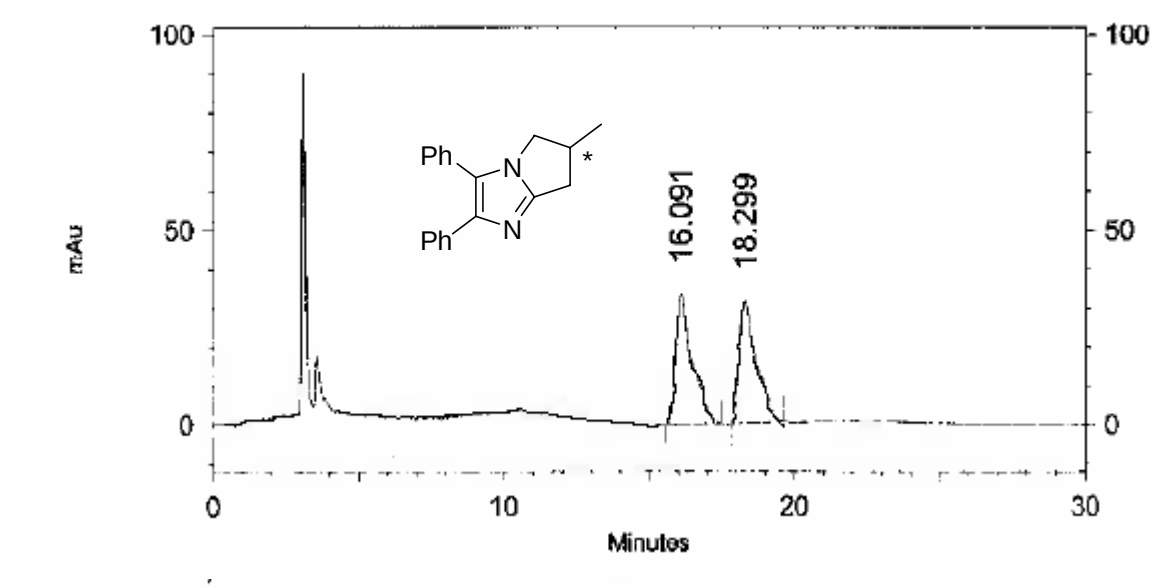
Enantiomerically enriched (97% ee)



Retention Time	Area	Area Percent
35.429	95501	1.725
41.781	5441061	98.275

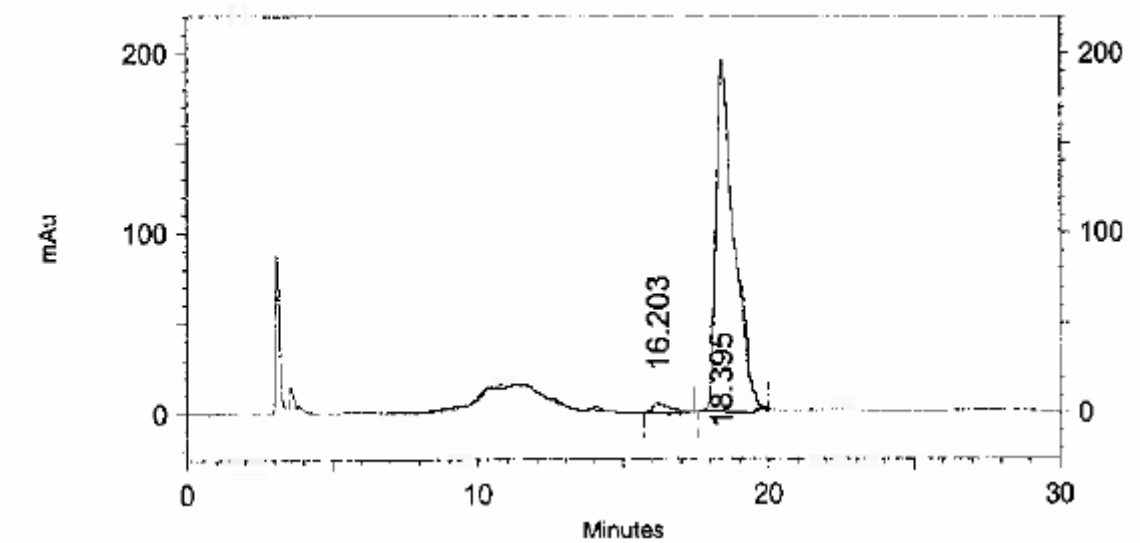
6-Methyl-2,3-diphenyl-6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole

Racemic (Chiralcel AD-H column, 3% EtOH/hexanes, 1mL/min, λ = 230 nm)



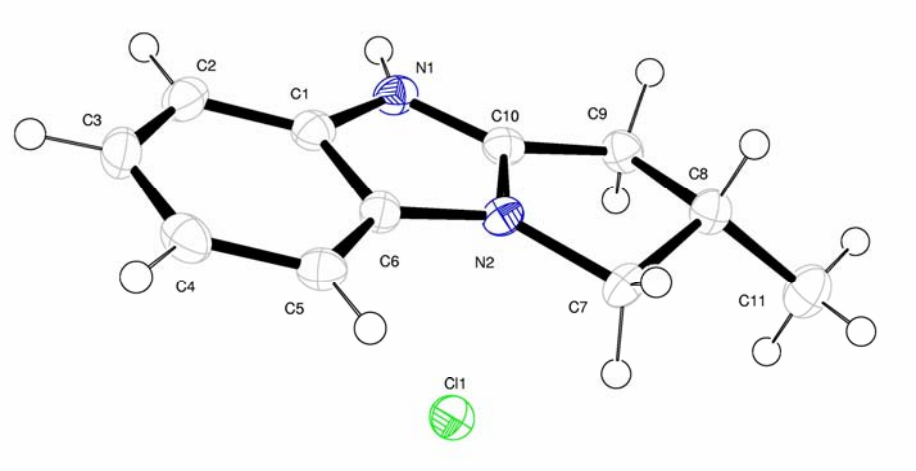
Retention Time	Area	Area Percent
16.091	1327012	50.463
18.299	1302667	49.537

Enantiomerically enriched (95% ee)



Retention Time	Area	Area Percent
16.203	210908	2.513
18.395	8181906	97.487

ORTEP diagram of the HCl salt of 2-Methyl-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole (2•HCl) (CCDC 727522)



Empirical formula	$C_{11}H_{13}ClN_2$	
Formula weight	208.68	
Crystal system	Orthorhombic	
Unit cell dimensions	a = 14.8792(16) Å	α= 90°.
	b = 7.4397(8) Å	β= 90°.
	c = 10.0119(11) Å	γ = 90°.
Volume	1108.3(2) $Å^3$	
Temperature	100(2) K	
Space group	P2(1)2(1)2	
Z	4	
Reflections collected	9520	
Independent reflections	1990 [R(int) = 0.0186]	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0933	
R indices (all data)	R1 = 0.0357, wR2 = 0.0936	
Absolute structure parameter (Flack parameter and esd)	0.03(2)	

References

1. A. Van der Ent and A. L. Onderdelinden, *Inorg. Synth.,* 1973, **14**, 92–93.
2. K. L. Tan, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc*., 2002, **124**, 13964-13965.
3. E. C. Yanez, J. M. Serrano, G. Huert,, J. M. Muchowski and R. C. Almanza, *Tetrahedron,* 2004, **60**, 9391-9396.
4. C. L. Moore, A. Zivkovic, J. W. Engels and R. D. Kuchta, *Biochemistry,* 2004, **43**, 12367-12374.