Electronic Supporting Information(ESI) for:

Synthesis of Axially Chiral Dibenzazepines by CuH-Catalyzed Diastereo- and Enantioselective Reductive Cyclization

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Experimental Procedures

1. General information

^{1}H-NMR spectra were recorded at 400 MHz; ^{13}C-NMR spectra were recorded at 100 MHz; with the solvent peak used as the internal reference (7.26 and 77.0 ppm for ^{1}H and ^{13}C respectively for $CDCl_3$); column chromatography was performed on silica gel (Merck Kieselgel 60). Analytical TLC was performed on aluminium backed plates (1.5 × 5 cm) pre-coated (0.25 mm) with silica gel (Merck, Silica Gel 60 F254). Compounds were visualized by exposure to UV light or by dipping the plates in a solution of 5% $(NH_4)_2Mo_7O_{24}\cdot 4\ H_2O$ in 95% EtOH (w/v) and heating.

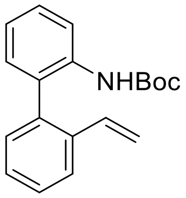
All reactions were carried out under a nitrogen atmosphere ("U" quality) using oven dried glassware and standard Schlenk techniques. Evaporations of solvents have been performed in a rotary evaporator at temperatures below 40 ^{0}C. Anhydrous THF were obtained by distillation from sodium using benzophenone as indicator. Et_2O, TBME, CH_2Cl_2 and toluene were dried by passage through solvent-purification columns containing activated alumina under a positive pressure of argon prior to use. Anhydrous t-BuOH were purchased from Sigma-Aldrich in a Sure-Seal® bottle and used as received. Diethoxymethylsilane (DEMS) was purchased from Sigma-Aldrich (stored at 4°C) and used as received. Copper(II) acetate, (-)-1,2-Bis((2*R*,5*R*)-2,5-diphenylphospholano)ethane ((*R*,*R*)-Ph-BPE) and (+)-1,2-Bis((2*S*,5*S*)-2,5-diphenylphospholano)ethane ((*S*,*S*)-Ph-BPE) were purchased from Sigma-Aldrich and stored in a nitrogen-filled glovebox. All other commercial reagents and ligands were purchased from Sigma-Aldrich or TCI Chemicals and used as received. All the compounds were purified by flash column chromatography using silica gel. Purification of imine substrates were performed on silica gel eluting with hexanes/triethylamine mixtures (20:1 v/v). The deactivated silica gel was prepared by washing the silica gel with hexanes/triethylamine (20:1 v/v) prior to purification.

Reactions were monitored by TLC, and/or NMR analysis. Final products and all new intermediate compounds were characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectrometry. The yields reported for the CuH-catalyzed synthesis are of isolated compounds on a 0.2 mmol scale. Racemic samples were prepared following general procedure for the CuH catalyzed synthesis of dibenzo[b,d]azepine 2 using a equimolar mixture of ((*R*,*R*)-Ph-BPE) and ((*S*,*S*)-Ph-BPE) as ligand.

2. Synthesis of starting materials

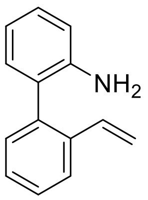
2.1. Synthesis of precursors

***Tert*-butyl (2'-vinyl-[1,1'-biphenyl]-2-yl)carbamate (9A)**. Following a described procedure.[1] An



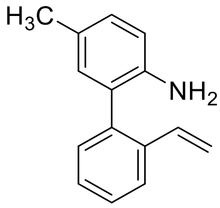
oven-dried 150 mL round-bottom flask equipped with a magnetic stir bar was charged with $Pd(dba)_2$ (110 mg, 0.19 mmol, 5 mol%), SPhos (110 mg, 0.23 mmol, 6 mol%) and the reaction vessel was capped then evacuated and backfilled with N_2 using the Schlenk line (this process was repeated a total of three times). Thoroughly degassed THF (56 mL) was then added via syringe and the resulting mixture was stirred for 5 min at room temperature. Then, 1-bromo-2-vinylbenzene (701 mg, 3.83 mmol), (2-((*tert*-butoxycarbonyl)amino)phenyl)boronic acid (1.14 g, 4.79 mmol), K_2CO_3 (1.6 g, 11.5 mmol) and H_2O (19 mL for a THF/H_2O = 3:1) were added, and the resulting mixture was placed in a preheated oil bath and stirred at 60 °C for 18 h. The reaction crude was allowed to reach room temperature, water (30 mL) was added and the resulting mixture was extracted with AcOEt (3 × 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo.* The crude mixture was purified by flash column chromatography (20:1 hexane/EtOAc) to afford the title compound as a yellow oil (941 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.48-7.37 (m, 3H), 7.27-7.24 (m, 1H), 7.17-7.10 (m, 2H), 6.49 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.14 (s, 1H), 5.75 (dd, *J* = 17.5, 1.2 Hz, 1H), 5.21 (dd, *J* = 11.0, 1.2 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 136.6, 136.4, 136.0, 134.6, 134.5, 130.7, 130.4, 129.8, 128.5, 128.5, 128.3, 125.5, 122.8, 119.6, 115.6, 115.5, 80.4, 28.3.

2'-Vinyl-[1,1'-biphenyl]-2-amine (10A). Following a described procedure.[2] Compound **9A** (1403



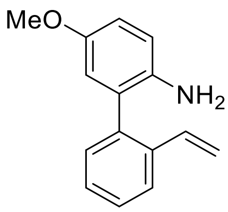
mg, 4.75 mmol) was treated with TFA (3 ml) in CH_2Cl_2 (12 ml) at rt. After 30 min, the solvent was blown off with N_2, the residue was diluted with CH_2Cl_2, basified with sat. $NaHCO_3$, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by eluting 15:1 hexane/EtOAc to give **10A** (862 mg, 93%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.0 Hz, 1H), 7.40 (m, 2H), 7.30 (m, 1H), 7.24 (td, *J* = 7.7, 1.7 Hz, 1H), 7.09 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.63 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 11.0 Hz, 1H), 3.62 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.8, 136.3, 135.0, 130.8, 130.7, 128.7, 128.2, 128.0, 126.6, 125.2, 118.6, 115.5, 114.9.

5-Methyl-2'-vinyl-[1,1'-biphenyl]-2-amine (10B). An oven-dried 150 mL round-bottom flask



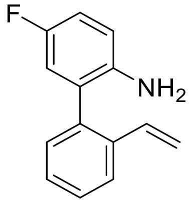
equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (20 mg, 0.022 mmol, 3 mol%), SPhos (18 mg, 0.044 mmol, 6 mol%) and the reaction vessel was capped then evacuated and backfilled with N_2 using the Schlenk line (this process was repeated a total of three times). Thoroughly degassed THF (3.6 mL) was then added via syringe and the resulting mixture was stirred for 5 min at room temperature. Then, 1-bromo-2-vinylbenzene (94 μL, 0.73 mmol), (2-((*tert*-butoxycarbonyl)amino)-5-methylphenyl)boronic acid[3] (233 mg, 0.91 mmol), K_2CO_3 (303 mg, 2.19 mmol) and H_2O (1.2 mL for a THF/H_2O = 3:1) were added, and the resulting mixture was placed in a preheated oil bath and stirred at 60 °C for 18 h. The reaction crude was allowed to reach room temperature, water (30 mL) was added and the resulting mixture was extracted with AcOEt (3 × 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo.* The residue was then treated with TFA (0.46 ml) in CH_2Cl_2 (1.8 ml) at rt. After 30 min, the solvent was blown off with N_2, the residue was diluted with CH_2Cl_2, basified with sat. $NaHCO_3$, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by eluting 15:1 hexane/EtOAc to give **10B** as a colorless oil (151 mg, 99% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 1H), 7.42-7.33 (m, 2H), 7.29-7.26 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.89 (s, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.68-6.58 (m, 1H) 5.77 (dt, *J* = 17.6, 1.6 Hz, 1H), 5.20 (dt, *J* = 11.0, 1.5 Hz, 1H), 3.41 (br s, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 138.2, 136.2, 135.1, 131.2, 130.7, 129.2, 128.2, 127.9, 127.5, 126.6, 125.1, 115.5, 114.7, 20.5..

5-Methoxy-2'-vinyl-[1,1'-biphenyl]-2-amine (10C). Following the same procedure as for



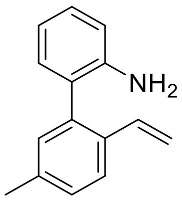
compound **10B**, using $Pd_2(dba)_3$ (19 mg, 0.021 mmol, 3 mol%), SPhos (17 mg, 0.044 mmol, 6 mol%), degassed THF (3.5 mL), 1-bromo-2-vinylbenzene (90 μL, 0.69 mmol), (2-((*tert*-butoxycarbonyl)amino)-5-methoxyphenyl)boronic acid (230 g, 0.86 mmol), K_2CO_3 (286 mg, 2.19 mmol) and H_2O (1.1 mL for a THF/H_2O = 3:1). Then TFA (0.44 ml) in CH_2Cl_2 (1.7 ml) to give **10C** as a colorless oil (110 mg, 71% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.2 Hz, 1H), 7.54-7.32 (m, 2H), 7.30-7.16 (m, 1H), 6.81 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 6.66 (d, *J* = 2.9 Hz, 1H), 6.61 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.75 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.20 (dd, *J* = 11.0, 1.2 Hz, 1H), 3.76 (s, 3H), 3.16 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 137.9, 137.6, 136.2, 134.9, 130.5, 128.2, 128.0, 127.6, 125.2, 116.6, 115.8, 115.0, 114.7, 55.8.

5-Fluoro-2'-vinyl-[1,1'-biphenyl]-2-amine (10D). Following the same procedure as for



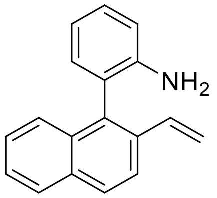
compound **10B**, using $Pd_2(dba)_3$ (23 mg, 0.025 mmol, 3 mol%), SPhos (20 mg, 0.05 mmol, 6 mol%), degassed THF (4.1 mL), 1-bromo-2-vinylbenzene (106 µL, 0.82 mmol), (2-((*tert*-butoxycarbonyl)amino)-5-fluorophenyl)boronic acid (260 mg, 1.02 mmol), K_2CO_3 (340 mg, 2.46 mmol) and H_2O (1.4 mL for a THF/H_2O = 3:1). Then TFA (0.53 ml) in CH_2Cl_2 (2 ml) to give **10D** as a colorless oil (131 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.44-7.35 (m, 2H), 7.25 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.93 (td, *J* = 8.5, 3.0 Hz, 1H), 6.81 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.71 (dd, *J* = 8.8, 4.8 Hz, 1H), 6.59 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.76 (dd, *J* = 17.6, 1.1 Hz, 1H), 5.22 (dd, *J* = 11.0, 1.1 Hz, 1H), 3.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0 (d, *J* = 236.5 Hz), 140.1 (d, *J* = 2.2 Hz), 136.8 (d, *J* = 1.5 Hz), 136.2, 134.6, 130.4, 128.3, 125.3, 117.1, 116.9, 116.1, 116.0, 115.3, 115.2, 115.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -126.9.

5'-Methyl-2'-vinyl-[1,1'-biphenyl]-2-amine (10E). An oven-dried 150 mL round-bottom flask



equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (43 mg, 0.047 mmol, 3 mol%), SPhos (45 mg, 0.094 mmol, 6 mol%) and the reaction vessel was capped then evacuated and backfilled with N_2 using the Schlenk line (this process was repeated a total of three times). Thoroughly degassed THF (5.2 mL) was then added via syringe and the resulting mixture was stirred for 5 min at room temperature. Then, 2-bromo-4-methyl-1-vinylbenzene (307 mg, 1.56 mmol), (2(2-((*tert*-butoxycarbonyl)amino)phenyl)boronic acid (460 mg, 1.94 mmol), K_2CO_3 (650 mg, 4.68 mmol) and H_2O (2.6 mL for a THF/H_2O = 3:1) were added, and the resulting mixture was placed in a preheated oil bath and stirred at 60 °C for 18 h. The reaction crude was allowed to reach room temperature, water (30 mL) was added and the resulting mixture was extracted with AcOEt (3 × 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo.* The residue was then solved in CH_2Cl_2 (3.5 ml) and HCl (4M in dioxane, 3.9 ml, 15.6 mmol) was added at 0 °C. The reaction was then allowed to reach rt and after 2 h, the solvent was removed under vacuum. The resulting mixture was dissolved with CH_2Cl_2, basified with sat. $NaHCO_3$, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by eluting 15:1 hexane/EtOAc to give **10E** as a yellow oil (135 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.26-7.22 (m, 2H), 7.15 (s, 1H) 7.10 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.63 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.18 (dd, *J* = 11.0, 1.3 Hz, 1H), 3.56 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 138.1, 137.9, 134.9, 133.5, 131.3, 130.7, 128.8, 128.6, 126.6, 125.1, 118.3, 115.2, 113.9, 21.2.

2-(2-Vinylnaphthalen-1-yl)aniline (10F). An oven-dried 150 mL round-bottom flask equipped

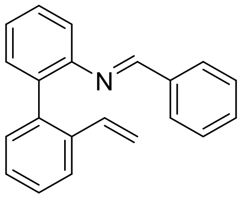


with a magnetic stir bar was charged with $Pd_2(dba)_3$ (24 mg, 0.026 mmol, 3 mol%), SPhos (24 mg, 0.05 mmol, 6 mol%) and the reaction vessel was capped then evacuated and backfilled with N_2 using the Schlenk line (this process was repeated a total of three times). Thoroughly degassed THF (3.2 mL) was then added via syringe and the resulting mixture was stirred for 5 min at room temperature. Then, 1-bromo-2-vinylnaphthalene [4] (197 mg, 0.85 mmol), (2-((*tert*-butoxycarbonyl)amino)-5-methylphenyl)boronic acid (252 mg, 1.1 mmol), K_2CO_3 (352 mg, 2.55 mmol) and H_2O (1.1 mL for a THF/H_2O = 3:1) were added, and the resulting mixture was placed in a preheated oil bath and stirred at 60 °C for 18 h. The reaction crude was allowed to reach room temperature, water (30 mL) was added and the resulting mixture was extracted with AcOEt (3 × 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo.* The residue was then solved in CH_2Cl_2 (1.5 ml) and HCl (4M in dioxane, 1.5 ml, 6.1 mmol) was added at 0 °C. The reaction was then allowed to reach rt and after 2 h, the solvent was removed under vacuum. The resulting mixture was dissolved with CH_2Cl_2, basified with sat. $NaHCO_3$, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by eluting 1:4 hexane/toluene to give **10F** as a colorless oil (144 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.87 (m, 3H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.49 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.44-7.37 (m, 1H), 7.32 (td, *J* = 7.7, 1.6 Hz, 1H), 7.09 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.94 (td, *J* = 7.4, 1.1 Hz, 1H), 6.87 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.72 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.87 (dd, *J* = 17.6, 1.1 Hz, 1H), 5.28 (dd, *J* = 11.1, 1.0 Hz, 1H), 3.36 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 135.2, 134.5, 133.6, 133.5, 132.6, 131.6, 128.9, 128.2, 128.0, 126.6, 126.6, 126.1, 123.5, 122.7, 118.5, 115.4, 115.2.

2.2. General procedure for the synthesis of aldimines substrates [1]

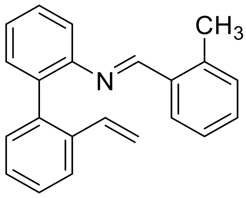
Aldimines **1** were made from corresponding aniline using a literature protocol.[5] A mixture of aniline derivative (1 equiv) and $MgSO_4$ (360 mg/mmol aniline) was evacuated/refilled with N_2 three times. To this mixture, anhydrous toluene was added, followed by the addition of aldehyde derivative (1.1 equiv) and glacial acetic acid (286 μL/mmol aniline). Then, the reaction mixture was stirred overnight at 80 °C and cooled to room temperature. The mixture was filtered through celite, and the filtrate was concentrated *in vacuo*. The residue was purified via flash column chromatography with silica gel (eluting with 20:1 Hexane/Et_3N) to yield the corresponding imine.

(*E*)-1-Phenyl-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Aa). Prepared following general



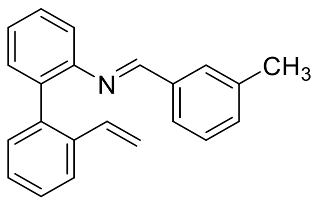
procedure, using **10A** (59 mg, 0.3 mmol), benzaldehyde (34 µL, 35 mg, 0.33 mmol) and toluene (0.7 mL) to obtain **1Aa** (81 mg, 95% yield) as yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.68-7.65 (m, 2H), 7.62 (m, 1H), 7.46-7.36 (m, 4H), 7.35-7.26 (m, 5H), 7.12 (ddd, *J* = 7.8, 1.2, 0.6 Hz, 1H), 6.60 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.60 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.10 (dd, *J* = 11.0, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 150.6, 138.7, 136.4, 136.3, 136.07, 136.05, 134.4, 131.2, 131.1, 130.9, 128.7, 128.5, 127.3, 127.1, 125.3, 124.8, 118.8, 114.0. HRMS (ESI) calcd. for $C_{21}H_{18}N$ (M + H^+) 284.1439. Found 284.1431.

(*E*)-1-o-Tolyl-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ab). Prepared following general



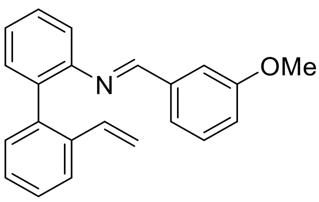
procedure, using **10A** (59 mg, 0.3 mmol), 2-methylbenzaldehyde (38 µL, 40 mg, 0.33 mmol) and toluene (0.7 mL) to obtain **1Ab** (80 mg, 90% yield) as yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.45 (m, 1H), 7.36-7.25 (m, 6H), 7.21 (m, 1H), 7.13 (m, 2H), 6.61 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.61 (d, *J* = 17.5 Hz, 1H), 5.11 (d, *J* = 11.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 151.3, 138.9, 138.5, 136.3, 135.9, 134.2, 134.1, 131.1, 130.84, 130.83, 130.6, 128.6, 128.5, 127.3, 127.2, 126.1, 125.2, 124.8, 119.1, 114.1, 19.5. HRMS (ESI) calcd. for $C_{22}H_{20}N$ (M + H^+) 298.1596. Found 298.1587.

(*E*)-1-*m*-Tolyl-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ac). Prepared following



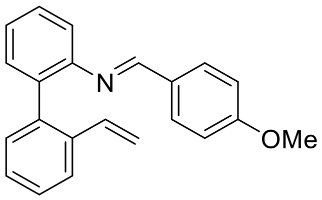
general procedure, using **10A** (59 mg, 0.3 mmol), 3-methylbenzaldehyde (39 µL, 40 mg, 0.33 mmol) and toluene (0.7 mL) to obtain **1Ac** (80 mg, 90% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.63 (m, 1H), 7.50-7.41 (m, 3H), 7.34-7.23 (m, 7H), 7.11 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.60 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.61 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.11 (dd, *J* = 11.0, 1.4 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 150.8, 138.7, 138.2, 136.4, 136.3, 136.1, 134.2, 131.9, 131.2, 130.9, 129.1, 128.5, 128.4, 127.3, 127.1, 126.0, 125.2, 124.8, 118.9, 114.0, 21.3. HRMS (ESI) calcd. for $C_{22}H_{20}N$ (M + H^+) 298.1596. Found 298.1593.

(*E*)-1-(3-Methoxyphenyl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ad). Prepared

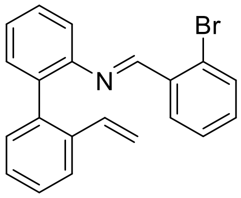


following general procedure, using **10A** (98 mg, 0.5 mmol), 3-methoxybenzaldehyde (67 µL, 75 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Ad** (126 mg, 80% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.74-7.59 (m, 1H), 7.45 (ddd, *J* = 7.9, 6.8, 2.1 Hz, 1H), 7.35-7.28 (m, 6H), 7.26 (m, 1H), 7.21 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.14 (ddd, *J* = 7.9, 1.3, 0.6 Hz, 1H), 6.99 (ddd, *J* = 8.2, 2.7, 1.1 Hz, 1H), 6.62 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.62 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.12 (dd, *J* = 11.0, 1.3 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 159.8, 150.3, 138.8, 137.9, 136.3, 136.1, 134.5, 131.1, 130.9, 129.5, 128.6, 127.3, 127.1, 125.5, 124.7, 122.1, 118.6, 118.0, 113.9, 111.8, 55.3. HRMS (ESI) calcd. for $C_{22}H_{20}NO$ (M + H$^+$) 314.1545. Found 314.1537.

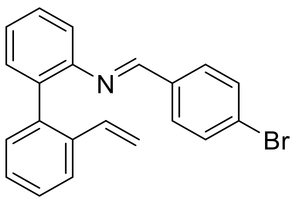
(*E*)-1-(4-Methoxyphenyl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ae). Prepared following general procedure, using **10A** (98 mg, 0.5 mmol), 4-methoxybenzaldehyde (67 μL, 75 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Ae** (145 mg, 93% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.69-7.62 (m, 3H), 7.45 (m, 1H), 7.38-7.30 (m, 5H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.92 (m, 2H), 6.65 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.64 (d, *J* = 17.5 Hz, 1H), 5.13 (d, *J* = 11.0 Hz, 1H), 3.85 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 159.8, 150.9, 139.0, 136.4, 136.2, 134.4, 131.2, 131.0, 130.4, 129.6, 128.6, 127.3, 127.1, 125.0, 124.8, 118.9, 114.0, 113.9, 55.4. HRMS (ESI) calcd. for $C_{22}H_{20}NO$ (M + H$^+$) 314.1545. Found 314.1541.



(*E*)-1-(2-Bromophenyl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Af). Prepared following general procedure, using **10A** (59 mg, 0.3 mmol), 2-bromobenzaldehyde (39 μL, 61 mg, 0.33 mmol) and toluene (0.7 mL) to obtain **1Af** (104 mg, 95% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.82-7.79 (m, 1H), 7.64-7.62 (m, 1H), 7.57-7.55 (m, 1H), 7.48-7.44 (m, 1H), 7.37-7.25 (m, 7H), 7.17-7.15 (m, 1H), 6.57 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.60 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.11 (dd, *J* = 11.0, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 150.3, 138.6, 136.3, 135.9, 134.8, 134.5, 132.9, 132.1, 131.2, 130.8, 129.2, 128.6, 127.6, 127.4, 127.1, 125.8, 125.6, 124.8, 118.9, 114.1. HRMS (ESI) calcd. for $C_{21}H_{17}BrN$ (M + H$^+$) 362.0544. Found 362.0540.

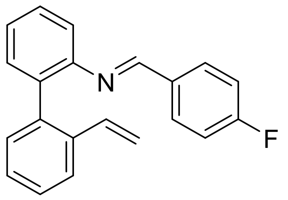


(*E*)-1-(4-Bromophenyl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ag). Prepared following general procedure, using **10A** (98 mg, 0.5 mmol), 4-bromobenzaldehyde (102 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Ag** (155 mg, 85% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.49 (s, 4H), 7.41 (ddd, *J* = 7.9, 6.1, 2.9 Hz, 1H), 7.32-7.26 (m, 4H), 7.25-7.21 (m, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.52 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.55 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.05 (dd, *J* = 11.0, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 159.1, 150.2,

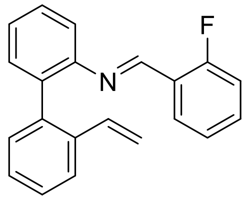


138.7, 136.3, 136.0, 135.3, 134.5, 131.9, 131.2, 130.9, 130.1, 128.6, 127.5, 127.2, 125.7, 124.8, 118.6, 114.1. HRMS (ESI) calcd. for $C_{21}H_{16}BrN$ (M + H^+) 362.0544. Found 362.0538.

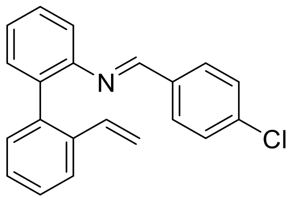
(*E*)-1-(4-Fluorophenyl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ah). Prepared following general procedure, using **10A** (98 mg, 0.5 mmol), 4-fluorobenzaldehyde (68 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Ah** (137 mg, 91% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.61 (m, 3H), 7.41 (m, 1H), 7.29 (m, 5H), 7.04 (m, 3H), 6.55 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.57 (d, *J* = 17.5 Hz, 1H), 5.06 (d, J = 11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6 (d, *J* = 251.6 Hz), 159.0, 150.3, 138.7, 136.3, 136.0, 134.5, 132.8, 131.2, 130.8, 130.7, 130.6, 128.6, 127.4, 127.1, 125.4, 124.7, 118.7, 115.8, 115.6, 114.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.6. HRMS (ESI) calcd. for $C_{21}H_{17}FN$ (M + H^+) 302.1435. Found 302.1337.



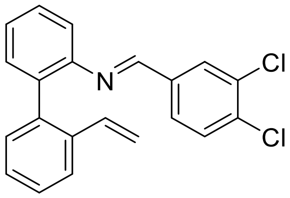
(*E*)-1-(2-Fluorophenyl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ai). Prepared following general procedure, using **10A** (59 mg, 0.3 mmol), 2-fluorobenzaldehyde (35 μL, 41 mg, 0.33 mmol) and toluene (0.7 mL) to obtain **1Ai** (76 mg, 85% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.78 (t, *J* = 6.9 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.46-7.26 (m, 7H), 7.14-7.05 (m, 3H), 6.57 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.60 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.10 (dd, *J* = 10.9, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 253.1 Hz), 153.7 (d, *J* = 5.1 Hz), 150.6, 138.7, 136.4, 136.0, 134.7, 132.7 (d, *J* = 8.8 Hz), 131.1, 130.8, 128.6, 128.1, 127.4, 127.1, 125.7, 124.7, 124.4 (d, *J* = 3.6 Hz), 124.1 (d, *J* = 9.2 Hz), 118.6, 115.6 (d, *J* = 21.0 Hz), 114.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -121.7. HRMS (ESI) calcd. for $C_{21}H_{17}FN$ (M + H^+) 302.1435. Found 302.1337.



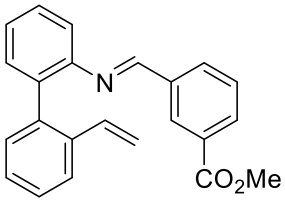
(*E*)-1-(4-Chlorophenyl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Aj). Prepared following general procedure, using **10A** (98 mg, 0.5 mmol), 4-chlorobenzaldehyde (77 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Aj** (111 mg, 70% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.56 (m, 3H), 7.42 (m, 1H), 7.31 (m, 7H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.54 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.57 (d, *J* = 17.5 Hz, 1H), 5.07 (d, *J* = 11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 150.2, 138.6, 137.1, 136.3, 136.0, 134.9, 134.5, 131.2, 130.8, 129.8, 128.9, 128.6, 127.4, 127.1, 125.6, 124.8, 118.6, 114.0. HRMS (ESI) calcd. for $C_{21}H_{17}ClN$ (M + H^+) 318.1050. Found 318.1042



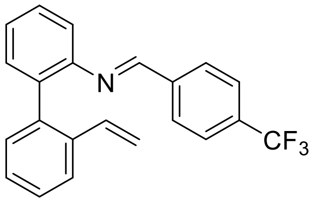
(*E*)-1-(3,4-Dichlorophenyl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ak). Prepared following general procedure, using **10A** (59 mg, 0.3 mmol), 3,4-dichlorobenzaldehyde (58 mg, 0.33 mmol) and toluene (0.7 mL) to obtain **1Ak** (75 mg, 71% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.74 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.45 (m, 3H), 7.39-7.23 (m, 5H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.55 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.60 (d, *J* = 17.5 Hz, 1H), 5.10 (d, *J* = 11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 149.8, 138.5, 136.32, 136.27, 135.9, 135.1, 134.5, 133.0, 131.2, 130.8, 130.7, 130.2, 128.6, 127.5 (2C), 127.2, 125.9, 124.8, 118.5, 114.1. HRMS (ESI) calcd. for $C_{21}H_{16}Cl_2N$ (M + H$^+$) 352.0660. Found 352.0654.



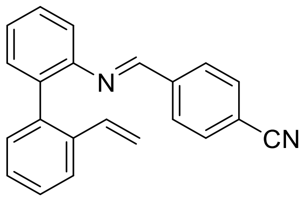
Methyl (*E*)-3-(((2'-vinyl-[1,1'-biphenyl]-2-yl)imino)methyl)benzoate (1Al). Prepared following general procedure, using **10A** (98 mg, 0.5 mmol), methyl 3-formylbenzoate (92 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Al** (145 mg, 85% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.26 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 6.7 Hz, 1H), 7.42 (m, 2H), 7.33-7.25 (m, 5H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.56 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.57 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.08 (dd, *J* = 11.0, 1.3 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 159.4, 150.2, 138.6, 136.8, 136.3, 136.0, 134.5, 132.2, 132.0, 131.2, 130.8, 130.6, 131.4, 128.8, 128.6, 127.4, 127.2, 125.7, 124.8, 118.7, 114.0, 52.3. HRMS (ESI) calcd. for $C_{23}H_{20}NO_2$ (M + H$^+$) 342.1494. Found 342.1486.



(*E*)-1-(4-(Trifluoromethyl)phenyl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Am). Prepared following general procedure, using **10A** (98 mg, 0.5 mmol), 4-(trifluoromethyl)benzaldehyde (70 µL, 96 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Am** (126 mg, 72% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.82-7.69 (m, 2H), 7.68-7.57 (m, 3H), 7.44 (ddd, *J* = 7.8, 6.2, 2.7 Hz, 1H), 7.36-7.26 (m, 5H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.57 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.59 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.09 (dd, *J* = 11.0, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, 158.8, 149.9, 139.4 (q, J = 1.4 Hz), 138.5, 136.3, 136.0, 134.7, 132.5 (q, *J* = 32.5 Hz), 131.2, 130.8, 128.8, 128.6, 127.5, 127.2, 126.0, 125.5 (q, *J* = 3.9 Hz), 124.8, 123.9 (d, *J* = 272.5 Hz), 118.5, 114.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.8. HRMS (ESI) calcd. for $C_{22}H_{17}F_3N$ (M + H$^+$) 352.1313. Found 352.1307.

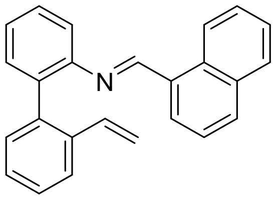


(*E*)-4-(((2'-Vinyl-[1,1'-biphenyl]-2-yl)imino)methyl)benzonitrile (1An). Prepared following



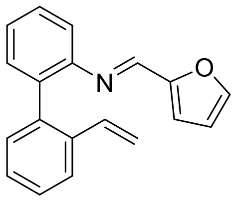
general procedure, using **10A** (98 mg, 0.5 mmol), 4-formylbenzonitrile (72 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1An** (145 mg, 94% yield) as orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.73-7.69 (m, 2H), 7.66-7.58 (m, 3H), 7.52-7.37 (m, 1H), 7.35-7.22 (m, 5H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.52 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.56 (dd, *J* = 17.6, 1.3 Hz, 1H), 5.06 (dd, *J* = 11.0, 1.3 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 149.6, 140.1, 138.4, 136.3, 135.9, 134.9, 132.4, 131.3, 130.8, 128.9, 128.7, 127.6, 127.2, 126.3, 124.8, 118.5, 118.3, 114.2, 114.1. HRMS (ESI) calcd. for $C_{22}H_{17}N_2$ (M + H$^+$) 309.1392. Found 309.1386.

(*E*)-1-(Naphthalen-1-yl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ao). Prepared



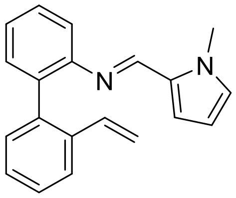
following general procedure, using **10A** (98 mg, 0.5 mmol), 1-naphthaldehyde (75 μL, 86 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Ao** (141 mg, 85% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.67 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.78 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.68 (d, *J* = 6.8 Hz, 1H), 7.53-7.46 (m, 3H), 7.43-7.29 (m, 6H), 7.23 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.67 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.63 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.11 (dd, *J* = 11.0, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 151.1, 139.2, 136.4, 135.9, 135.0, 133.8, 131.8, 131.7, 131.2, 130.9, 130.8 (x2), 128.8, 128.4, 127.4, 127.3, 127.3, 126.1, 125.6, 125.2, 125.0, 124.8, 118.3, 114.3. HRMS (ESI) calcd. for $C_{25}H_{20}N$ (M + H$^+$) 334.1596. Found 334.1587.

(*E*)-1-(Furan-2-yl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ap). Prepared following



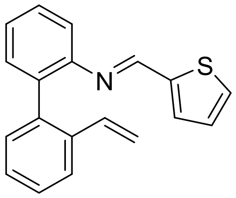
general procedure, using **10A** (98 mg, 0.5 mmol), furan-2-carbaldehyde (46 μL, 53 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Ap** (55 mg, 40% yield) as orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.61 (dd, *J* = 7.0, 1.7 Hz, 1H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.44-7.39 (m, 1H), 7.34-7.26 (m, 5H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 3.4 Hz, 1H), 6.55 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.48-6.45 (d, *J* = 1.7 Hz, 1H), 5.59 (dd, *J* = 17.6, 1.3 Hz, 1H), 5.11 (dd, *J* = 11.0, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 150.6, 149.2, 145.4, 138.5, 136.4, 136.0, 133.9, 131.4, 131.0, 128.5, 127.4, 127.2, 125.3, 124.9, 119.5, 115.2, 114.2, 111.9. HRMS (ESI) calcd. for $C_{19}H_{16}NO$ (M + H$^+$) 274.1232. Found 274.1229.

(*E*)-1-(1-Methyl-1*H*-pyrrol-2-yl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Aq).



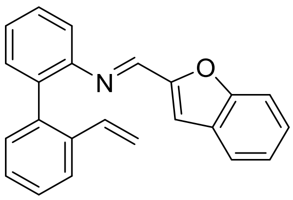
Prepared following general procedure, using **10A** (98 mg, 0.5 mmol), 1-methyl-1*H*-pyrrole-2-carbaldehyde (60 µL, 60 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Aq** (108 mg, 75% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.44 (s, 1H), 7.36-7.25 (m, 5H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.85-6.47 (m, 3H), 6.16 (s, 1H), 5.64 (d, *J* = 17.5 Hz, 1H), 5.11 (d, *J* = 11.0 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.2, 139.8, 136.2, 136.1, 135.6, 130.7, 130.7, 130.5, 129.1, 128.7, 127.1, 127.1, 124.9, 124.3, 118.7, 117.5, 113.8, 108.3, 36.9. HRMS (ESI) calcd. for $C_{20}H_{19}N_2$ (M + H$^+$) 287.1548. Found 287.1540.

(*E*)-1-(Thiophen-2-yl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Ar). Prepared



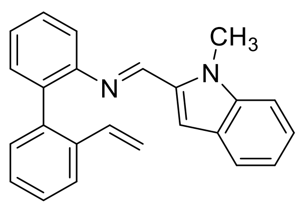
following general procedure, using **10A** (98 mg, 0.5 mmol), thiophene-2-carbaldehyde (52 µL, 62 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Ar** (75 mg, 52% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 5.9 Hz, 2H), 7.37-7.25 (m, 6H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 4.4 Hz, 1H), 6.58 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.61 (d, *J* = 17.5 Hz, 1H), 5.11 (d, *J* = 11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 150.0, 143.2, 138.6, 136.4, 136.1, 134.4, 131.4, 131.2, 130.9, 130.3, 128.5, 127.5, 127.3, 127.1, 125.4, 124.8, 119.0, 114.1. HRMS (ESI) calcd. for $C_{19}H_{16}NS$ (M + H$^+$) 290.1003. Found 290.1000.

(*E*)-1-(Benzofuran-2-yl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1As). Prepared



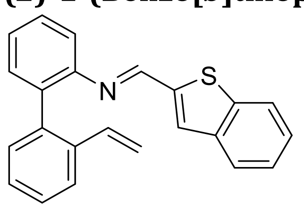
following general procedure, using **10A** (98 mg, 0.5 mmol), benzofuran-2-carbaldehyde (67 µL, 80 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1As** (124 mg, 77% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.67-7.57 (m, 2H), 7.53 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.43 (ddd, *J* = 7.9, 6.4, 2.5 Hz, 1H), 7.36 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.33-7.23 (m, 6H), 7.18-7.12 (m, 1H), 7.06 (d, *J* = 0.9 Hz, 1H), 6.56 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.59 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.12 (dd, *J* = 11.0, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 153.2, 150.4, 150.2, 138.3, 136.4, 135.9, 133.7, 131.5, 131.0, 128.5, 127.8, 127.5, 127.3, 126.8, 125.7, 125.1, 123.4, 122.2, 119.8, 114.4, 112.1, 112.0. HRMS (ESI) calcd. for $C_{23}H_{18}NO$ (M + H$^+$) 324.1388. Found 324.1380.

(*E*)-1-(1-Methyl-1*H*-indol-2-yl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1At).



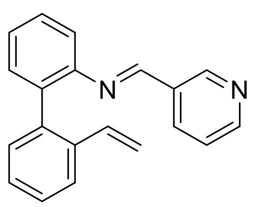
Prepared following general procedure, using **10A** (98 mg, 0.5 mmol), 1-methyl-1*H*-indole-2-carbaldehyde (90 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1At** (132 mg, 79% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.74-7.60 (m, 2H), 7.48 (ddd, *J* = 7.9, 6.8, 2.2 Hz, 1H), 7.41-7.28 (m, 7H), 7.23-7.19 (m, 1H), 7.14 (ddd, *J* = 7.9, 6.1, 1.9 Hz, 1H), 6.90 (d, *J* = 0.7 Hz, 1H), 6.62 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.64 (dd, *J* = 17.6, 1.3 Hz, 1H), 5.11 (dd, *J* = 11.0, 1.3 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 150.4, 140.4, 139.5, 136.3, 135.9, 135.7, 130.8, 130.7, 128.8, 127.3, 127.2, 126.9, 125.6, 124.5, 124.5, 121.8, 120.1, 117.4, 114.1, 111.7, 31.7. HRMS (ESI) calcd. for $C_{24}H_{21}N_2$ (M + H$^+$) 337.1705. Found 337.1699.

(*E*)-1-(Benzo[*b*]thiophen-2-yl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1u). Prepared



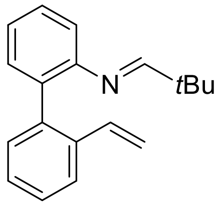
following general procedure, using **10A** (98 mg, 0.5 mmol), benzo[*b*]thiophene-2-carbaldehyde (92 mg, 0.55 mmol) and toluene (1.2 mL) to obtain **1Au** (157 mg, 93% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.77 (d, *J* = 7.3 Hz, 2H), 7.59 (s, 1H), 7.54 (s, 1H), 7.47-7.38 (m, 1H), 7.36-7.27 (m, 7H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.55 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.59 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.09 (dd, *J* = 11.0, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 149.7, 143.5, 141.3, 139.3, 138.5, 136.5, 136.0, 134.6, 131.3, 130.9, 128.8, 128.5, 127.4, 127.1, 126.3, 125.8, 124.9, 124.7, 124.5, 122.8, 118.9, 114.2. HRMS (ESI) calcd. for $C_{23}H_{18}NS$ (M + H$^+$) 340.1160. Found 340.1152.

(*E*)-1-(Pyridin-3-yl)-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)methanimine (1Av). Prepared following

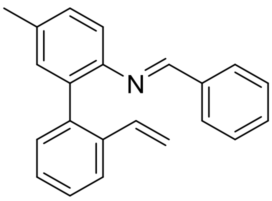


general procedure, using **10A** (59 mg, 0.3 mmol), nicotinaldehyde (31 μL, 35 mg, 0.33 mmol) and toluene (0.7 mL) to obtain **1Av** (77 mg, 90% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.64 (d, *J* = 4.8 Hz, 1H), 8.36 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.45 (m, 1H), 7.38-7.24 (m, 6H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.56 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.59 (d, *J* = 17.5 Hz, 1H), 5.09 (d, *J* = 11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 151.8, 150.7, 145.0, 138.5, 136.3, 136.0, 134.9, 134.7, 132.0, 131.2, 130.8, 128.6, 127.5, 127.2, 126.0, 124.8, 123.7, 118.4, 114.1. HRMS (ESI) calcd. for $C_{20}H_{17}N_2$ (M + H$^+$) 285.1392. Found 285.1389.

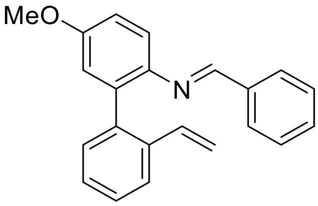
(*E*)-2,2-dimethyl-*N*-(2'-vinyl-[1,1'-biphenyl]-2-yl)propan-1-imine (1Aw). Prepared following general procedure, using **10A** (130 mg, 0.67 mmol), Pivaldehyde (220 µL, 172 mg, 2.0 mmol) and toluene (1.7 mL) to obtain **1Aw** (71 mg, 40% yield) as a yellow oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.60 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.42 (s, 1H), 7.36–7.24 (m, 3H), 7.21–7.13 (m, 3H), 6.87 (dt, *J* = 7.8, 0.9 Hz, 1H), 6.44 (dd, J = 17.6, 11.0 Hz, 1H), 5.62 (dd, *J* = 17.6, 1.3 Hz, 1H), 5.10 (dd, *J* = 11.0, 1.3 Hz, 1H), 0.89 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 173.8, 151.3, 138.7, 136.1, 135.7, 132.7, 130.9, 130.6, 128.3, 127.2, 127.0, 124.4, 124.2, 119.4, 113.8, 36.5, 26.0. HRMS (ESI) calcd. for $C_{19}H_{22}N$ (M + H$^+$) 264.1752. Found 264.1747.



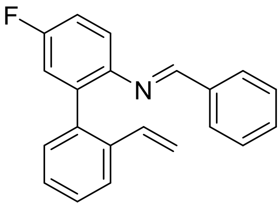
(*E*)-*N*-(5-Methyl-2'-vinyl-[1,1'-biphenyl]-2-yl)-1-phenylmethanimine (1Ba). Prepared following general procedure, using **10B** (155 mg, 0.73 mmol), benzaldehyde (81 µL, 0.8 mmol) and toluene (1.8 mL) to obtain **1Ba** (195 mg, 90% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.71-7.56 (m, 3H), 7.43-7.22 (m, 7H), 7.14 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.60 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.09 (dd, *J* = 11.0, 1.3 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 148.1, 139.0, 136.6, 136.3, 136.2, 135.1, 134.5, 131.8, 130.9, 130.9, 129.1, 128.6, 128.5, 127.3, 127.1, 124.7, 118.5, 113.9, 21.0. HRMS (ESI) calcd. for $C_{22}H_{20}N$ (M + H$^+$) 298.1596. Found 298.1587.



(*E*)-*N*-(5-Methoxy-2'-vinyl-[1,1'-biphenyl]-2-yl)-1-phenylmethanimine (1Ca). Prepared following general procedure, using **10C** (110 mg, 0.49 mmol), benzaldehyde (55 µL, 0.54 mmol) and toluene (1.3 mL) to obtain **1Ca** (123 mg, 80% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.65-7.63 (m, 3H), 7.39-7.29 (m, 6H), 7.13 (d, *J* = 8.7 Hz, 1H), 6.98 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.89 (d, *J* = 2.9 Hz, 1H), 6.62 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.61 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.09 (dd, *J* = 11.0, 1.3 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 157.5, 143.6, 138.8, 136.7, 136.4, 136.3, 136.1, 130.8, 128.6, 128.5, 127.4, 127.1, 124.8, 119.4, 116.3, 114.1, 114.0, 55.6. HRMS (ESI) calcd. for $C_{22}H_{20}NO$ (M + H$^+$) 314.1545. Found 314.1536.

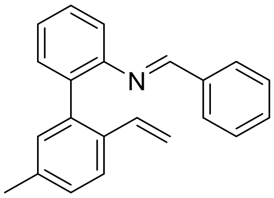


(*E*)-*N*-(5-Fluoro-2'-vinyl-[1,1'-biphenyl]-2-yl)-1-phenylmethanimine (1Da). Prepared following general procedure, using **10D** (133 mg, 0.62 mmol), benzaldehyde (69 µL, 0.68 mmol) and toluene (1.6 mL) to obtain **1Da** (70 mg, 37% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.65-7.60 (m, 3H), 7.44-7.24 (m, 6H), 7.15-7.08 (m, 2H), 7.05 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.58 (dd,

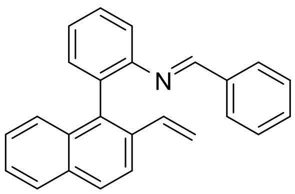


J = 17.5, 11.0 Hz, 1H), 5.60 (dd, J = 17.5, 1.2 Hz, 1H), 5.12 (dd, J = 11.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 160.48 (d, J = 1.5 Hz), 159.3, 146.7 (d, J = 2.9 Hz), 137.7 (d, J = 1.5 Hz), 136.4 (d, J = 7.8 Hz), 136.33, 136.31, 135.7, 131.2, 130.6, 128.7, 128.6, 127.7, 127.2, 125.0, 119.8 (d, J = 8.4 Hz), 117.8 (d, J = 22.5 Hz), 115.1 (d, J = 22.2 Hz), 114.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -118.3. HRMS (ESI) calcd. for $C_{21}H_{17}FN$ (M + H$^+$) 302.1345. Found 302.1337.

(*E*)-*N*-(5'-Methyl-2'-vinyl-[1,1'-biphenyl]-2-yl)-1-phenylmethanimine (1Ea). Prepared following general procedure, using **10E** (135 mg, 0.65 mmol), benzaldehyde (73 µL, 0.71 mmol) and toluene (1.6 mL) to obtain **1Ea** (140 mg, 72% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.66-7.4 (m, 2H), 7.50 (d, J = 7.9 Hz, 1H), 7.43-7.35 (m, 4H), 7.33-7.28 (m, 2H), 7.13-7.08 (m, 3H), 6.53 (dd, J = 17.5, 11.0 Hz, 1H), 5.52 (dd, J = 17.5, 1.4 Hz, 1H), 5.02 (dd, J = 11.0, 1.4 Hz, 1H), 2.36 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 150.6, 138.7, 136.8, 136.5, 135.9, 134.6, 133.7, 131.4, 131.1, 131.0, 128.7, 128.5, 128.5, 128.2, 125.4, 124.6, 118.7, 113.0, 21.2. HRMS (ESI) calcd. for $C_{22}H_{20}N$ (M + H$^+$) 298.1596. Found 298.1594.



(*E*)-1-Phenyl-*N*-(2-(2-vinylnaphthalen-1-yl)phenyl)methanimine (1Fa). Prepared following general procedure, using **10F** (144 mg, 0.59 mmol), benzaldehyde (66 µL, 69 mg, 0.65 mmol) and toluene (1.5 mL) to obtain **1Fa** (147 mg, 80% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.92-7.67 (m, 3H), 7.64-7.46 (m, 2H), 7.41 (ddd, J = 8.1, 4.0, 2.4 Hz, 3H), 7.35 (ddt, J = 8.2, 3.9, 2.2 Hz, 2H), 7.32-7.27 (m, 2H), 7.27-7.16 (m, 3H), 6.64 (dd, J = 17.6, 11.0 Hz, 1H), 5.73 (dd, J = 17.5, 1.2 Hz, 1H), 5.19 (dd, J = 11.0, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 151.7, 136.2, 136.0, 135.7, 133.1, 132.9, 131.8, 131.6, 131.0, 128.8, 128.5, 128.4, 127.8, 127.6, 126.9, 126.0, 125.5, 125.3, 122.4, 119.1, 114.5. HRMS (ESI) calcd. for $C_{25}H_{20}N$ (M + H$^+$) 334.1596. Found 334.1592.

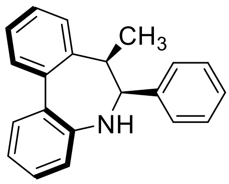


3. General procedure for the synthesis of dibenzazepines by CuH-catalyzed intramolecular cyclization.

A flamed-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (1.45 mg, 4 mol%) and (*R*,*R*)-Ph-BPE (4.45 mg, 4.4 mol%). Anhydrous THF (300 µL) was added via syringe and the reaction mixture was stirred for 15 min, until a blue homogeneous solution was obtained. Diethoxymethylsilane (64 µL, DEMS, 2.0 equiv) was added via syringe and stirring was continued for 10 min at room temperature. Into a separate flamed-dried Schlenk tube aldimine **1** (0.2 mmol, 1 equiv) was dissolved in anhydrous MTBE (1 mL) and transferred via syringe to the reaction tube containing the catalyst. Anhydrous *t*BuOH (21 μL, 1.1 equiv) was added via microsyringe and the reaction mixture was stirred at room temperature under N_2 for 48 h. The reaction mixture was then quenched with saturated aqueous Na_2CO_3 solution, extracted with EtOAc and the combined organic layers were concentrated *in vacuo*. The resulting crude product was purified by flash column chromatography (30:1 hexane/EtOAc) on silica gel to obtain dibenzo[*b*,*d*]azepine derivatives **2.**

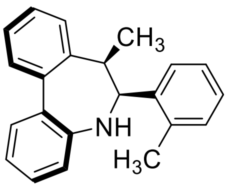
*Note. The reaction of **1Aa** at 2 mmol scale was performed following the general procedure using Cu(OAc)$_2$ (14.5 mg, 4 mol%) and (R,R)-Ph-BPE (45 mg, 4.4 mol%). Anhydrous THF (3 mL), diethoxymethylsilane (640 μL, DEMS, 2.0 equiv), aldimine **1Aa** (570 mg, 2mmol) in anhydrous MTBE (10 mL) and anhydrous tBuOH (210 μL, 1.1 equiv), affording **2Aa** (524 mg, 92 %, 98% ee) after column chromatography purification.*

(S_a,6*S*,7*R*)-7-Methyl-6-phenyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Aa). Prepared following



general procedure, using **1Aa** (57 mg, 0.2 mmol), Cu(OAc)$_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Aa** (56 mg, 99% yield) as colorless oil. $[\alpha]_D^{20}$ +52.3 (c 0.51, $CHCl_3$) for 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.29 (m, 5H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.98 (d, *J* = 5.1 Hz, 1H), 3.59 (s, 1H), 1.11 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.00, 140.4, 139.7, 133.7, 129.4, 128.9 (2C), 128.8, 128.3, 127.6, 127.4 (2C), 126.7, 126.6, 126.1, 122.5, 120.7, 58.2, 37.9, 15.0. HRMS (ESI) calcd. for $C_{21}H_{20}N$ (M + H$^+$) 286.1517. Found 286.1588. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 4.90 min (major) and 6.84 min (minor).

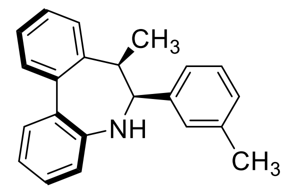
(S_a,6S,7R)-7-Methyl-6-(*o*-tolyl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ab). Prepared



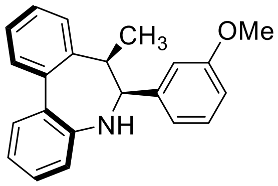
following general procedure, using **1Ab** (50 mg, 0.17 mmol), Cu(OAc)$_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ab** (48 mg, 95% yield) as colorless oil. $[\alpha]_D^{20}$ +4.0 (c 0.48, $CHCl_3$) for 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.29 (m, 2H), 7.18 (m, 3H), 7.02 (m, 2H), 6.94 (m, 2H), 5.39 (d, *J* = 5.1 Hz, 1H), 3.59 (m, 1H), 2.45 (s, 3H), 1.11 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 140.7, 140.2, 139.5, 135.9, 133.2, 130.0, 129.5, 129.0, 128.7, 128.5, 127.1, 126.8, 126.7 (2C), 125.3, 122.4, 120.7, 68.6, 39.3, 20.1, 14.0. HRMS (ESI) calcd. for $C_{22}H_{22}N$ (M + H$^+$)

300.1752. Found 300.1743. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 5.02 min (major) and 7.36 min (minor).

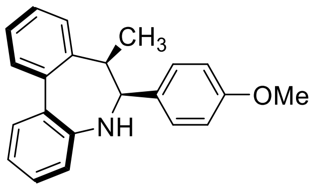
(S_a,6*S*,7*R*)-7-Methyl-6-(*m*-tolyl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ac). Prepared following general procedure, using **1Ac** (50 mg, 0.17 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ac** (44 mg, 87% yield) as colorless oil. $[\alpha]_D^{20}$ +24.7 (c 0.25, $CHCl_3$) for 98% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.42 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33-7.26 (m, 2H), 7.19-7.10 (m, 3H), 6.92-6.84 (m, 4H), 4.94 (d, *J* = 5.1 Hz, 1H), 3.57 (dd, *J* = 7.2, 5.1 Hz, 1H), 2.29 (s, 3H), 1.10 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 140.9, 140.3, 139.9, 136.9, 133.6, 129.7, 129.4, 128.7, 128.3, 128.3, 127.3, 126.6 (2C), 126.2, 126.0, 122.5, 120.7, 75.4, 37.9, 21.4, 15.0. HRMS (ESI) calcd. for $C_{22}H_{22}N$ $(M + H^+)$ 300.1752. Found 300.1745. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.12 min (major) and 10.70 min (minor).



(S_a,6*S*,7*R*)-6-(3-Methoxyphenyl)-7-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ad). Prepared following general procedure, using **1Ad** (62 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ad** (34 mg, 55% yield) as yellow oil. $[\alpha]_D^{20}$ +92.5 (c 0.54, $CHCl_3$) for 98% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 7.6, 3.7, 1.5 Hz, 2H), 7.37 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31-7.20 (m, 2H), 7.18-7.10 (m, 2H), 6.88 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.85-6.78 (m, 2H), 6.68 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.55 (dd, *J* = 2.7, 1.5 Hz, 1H), 4.93 (d, *J* = 5.0 Hz, 1H), 3.57 (s, 3H), 3.57-3.51 (m, 1H), 1.08 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 144.8, 142.7, 140.4, 139.8, 133.6, 129.4, 128.8, 128.3, 128.2, 126.6, 126.2, 122.4, 121.4, 120.7, 114.1, 113.4, 75.4, 55.0, 37.8, 15.0. HRMS (ESI) calcd. for $C_{22}H_{22}NO$ $(M + H^+)$ 316.1701. Found 316.1691. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 5.93 min (major) and 13.15 min (minor).

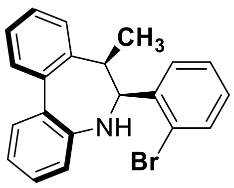


(S_a,6*S*,7*R*)-6-(4-Methoxyphenyl)-7-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ae). Prepared following general procedure, using **1Ae** (62 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ae** (38 mg, 60% yield) as yellow oil. $[\alpha]_D^{20}$ +7.1 (c 0.57, $CHCl_3$) for 99% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dt, *J* = 7.7, 2.0 Hz, 2H), 7.38 (td, *J* = 7.5, 1.2 Hz,



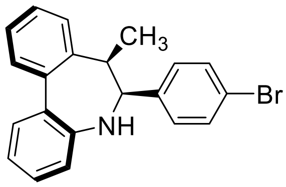
1H), 7.32-7.20 (m, 3H), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.87 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.90 (d, *J* = 5.1 Hz, 1H), 3.79 (s, 3H), 3.65 (brad s, 1H), 3.51 (dt, *J* = 12.0, 6.1 Hz, 1H), 1.05 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 144.9, 140.5, 133.7, 133.1, 129.9, 129.3, 128.7, 128.2, 126.7, 126.6, 127.1, 122.5, 120.7, 112.7, 74.9, 55.2, 37.9, 15.0. HRMS (ESI) calcd. for $C_{22}H_{22}NO$ (M + H^+) 316.1701. Found 316.1689. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 8.58 min (major) and 10.91 min (minor).

(*Sa*,6*S*,7*R*)-6-(2-Bromophenyl)-7-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Af).**



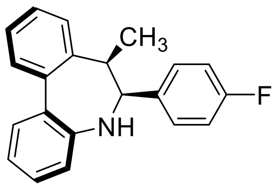
Prepared following general procedure, using **1Af** (70 mg, 0.19 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 µL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 µL, 16 mg, 0.22 mmol) to obtain **2Af** (47 mg, 66% yield) as colorless oil. $[\alpha]_D^{20}$ +35.0 (c 0.26, $CHCl_3$) for 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.49 (m, 2H), 7.43 (td, *J* = 7.5, 1.3 Hz, 1H), 7.30 (m, 2H), 7.18 (td, *J* = 7.5, 1.3 Hz, 1H), 7.15-7.05 (m, 2H), 6.97 (m, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 5.64 (d, *J* = 5.3 Hz, 1H), 3.87-3.34 (m, 2H), 1.19 (d, *J* = 7.2 Hz, 3H).). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 140.4, 140.2, 139.8, 133.6, 132.3, 131.3, 129.4, 128.9, 128.8, 128.4, 126.84, 126.82, 126.6, 126.5, 124.7, 122.7, 120.9, 72.0, 38.6, 14.1. HRMS (ESI) calcd. for $C_{21}H_{19}BrN$ (M + H^+) 364.0701. Found 364.0509. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 4.78 min (major) and 6.55 min (minor).

(S_a,6*S*,7*R*)-6-(4-Bromophenyl)-7-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ag).



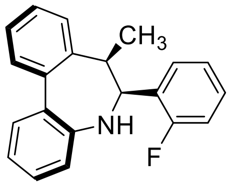
Prepared following general procedure, using **1Ag** (72 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 µL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 µL, 16 mg, 0.22 mmol) to obtain **2Ag** (58 mg, 80% yield) as colorless oil. $[\alpha]_D^{20}$ –8.1 (c 0.26, $CHCl_3$) for 91% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 3.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (q, *J* = 7.2 Hz, 2H), 7.17 (q, *J* = 8.6, 7.5 Hz, 1H), 6.90 (t, *J* = 8.1 Hz, 3H), 6.77 (d, *J* = 7.7 Hz, 1H), 4.91 (d, *J* = 5.0 Hz, 1H), 3.69 (s, 1H), 3.58-3.47 (m, 1H), 1.05 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 144.3, 140.3, 139.7, 139.0, 133.7, 130.6, 130.5, 129.4, 129.1, 128.8, 128.3, 126.9, 126.0, 122.9, 121.5, 120.8, 74.9, 37.4, 15.0. HRMS (ESI) calcd. for $C_{21}H_{19}BrN$ (M + H^+) 364.0701. Found 364.0692. HPLC (IB column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 7.38 min (minor) and 10.27 min (major).

(S_a,6S,7R)-6-(4-Fluorophenyl)-7-methyl-6,7-dihydro-5H-dibenzo[b,d]azepine (2Ah).



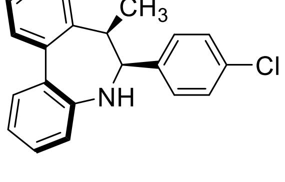
Prepared following general procedure, using **1Ah** (60 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (R,R)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ah** (58 mg, 96% yield) as colorless oil. $[\alpha]_D^{20}$ +26.2 (c 0.50, $CHCl_3$) for 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.41 (td, J = 7.5, 1.3 Hz, 1H), 7.31-7.24 (m, 2H), 7.17 (td, J = 7.5, 1.2 Hz, 1H), 7.04-7.00 (m, 2H), 6.96-6.85 (m, 3H), 6.79 (d, J = 7.7 Hz, 1H), 4.94 (d, J = 5.0 Hz, 1H), 3.54 (dt, J = 12.3, 6.1 Hz, 1H), 1.07 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 245.2 Hz), 144.5, 140.4, 139.2, 136.5, 133.7, 130.3 (d, J = 7.9 Hz), 129.4, 128.8, 128.3, 126.7, 126.8, 126.0, 122.8, 120.8, 114.2 (d, J = 21.1 Hz), 74.8, 37.6, 15.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.2. HRMS (ESI) calcd. for $C_{21}H_{19}FN$ (M + H^+) 304.1502. Found 304.1492. HPLC (IB column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 10.81 min (minor) and 12.27 min (major).

(S_a,6S,7R)-6-(2-Fluorophenyl)-7-methyl-6,7-dihydro-5H-dibenzo[b,d]azepine (2Ai).



Prepared following general procedure, using **1Ai** (60 mg, 0.19 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (R,R)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ai** (42 mg, 70% yield) as colorless oil. $[\alpha]_D^{20}$ +44.0 (c 0.48, $CHCl_3$) for 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.42 (td, J = 7.5, 1.3 Hz, 1H), 7.32-7.17 (m, 4H), 7.05 (m, 1H), 6.97-6.88 (m, 3H), 6.84 (dd, J = 8.0, 1.0 Hz, 1H), 5.50 (d, J = 5.2 Hz, 1H), 3.62 (m, 1H), 1.16 (dd, J = 7.2, 2.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7 (d, J = 245.2 Hz), 144.5, 140.3, 139.3, 133.7, 130.6 (d, J = 4.1 Hz), 129.4, 128.8, 128.7, 128.6, 128.3, 126.81, 126.77, 126.0, 123.3 (d, J = 3.6 Hz), 122.8, 120.9, 114.4 (d, J = 22.8 Hz), 66.0, 37.8, 14.1 (d, J = 1.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -118.5. HRMS (ESI) calcd. for $C_{21}H_{19}FN$ (M + H^+) 304.1502. Found 304.1494. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.36 min (major) and 8.39 min (minor).

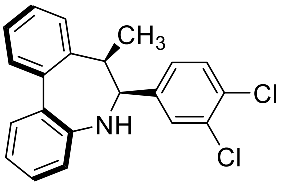
(S_a,6S,7R)-6-(4-Chlorophenyl)-7-methyl-6,7-dihydro-5H-dibenzo[b,d]azepine (2Aj).



Prepared following general procedure, using **1Aj** (63 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (R,R)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Aj** (51 mg, 80% yield) as colorless oil. $[\alpha]_D^{20}$ +3.7 (c 0.49, $CHCl_3$) for 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (ddd, J = 7.6, 3.7, 1.5 Hz, 2H), 7.39 (td, J = 7.5, 1.2 Hz, 1H), 7.33-7.22 (m, 3H), 7.21-7.11 (m, 3H), 6.98 (d, J = 8.4 Hz, 2H), 6.94-6.86 (m, 1H), 6.77 (d, J = 7.7 Hz, 1H), 4.92 (d, J = 5.0 Hz, 1H), 3.66 (br s, 1H), 3.58-3.51 (m, 1H), 1.06 (d, J = 7.2 Hz, 3H). ^{13}C NMR

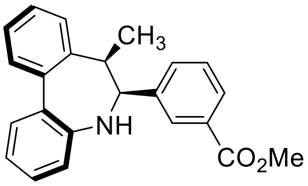
(100 MHz, $CDCl_3$) 144.5, 140.4, 139.4, 139.1, 133.7, 133.3, 130.2, 129.4, 128.8, 128.3, 127.6, 126.8, 126.8, 126.0, 122.8, 120.8, 74.9, 37.5, 15.0. HRMS (ESI) calcd. for $C_{21}H_{19}ClN$ (M + H^+) 320.1206. Found 320.1195. HPLC (IB column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 7.08 min (minor) and 9.24 min (major).

(*S*$_a$,6*S*,7*R*)-6-(3,4-Dichlorophenyl)-7-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ak).



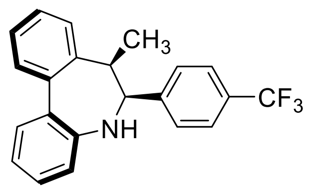
Prepared following general procedure, using **1Ak** (70 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ak** (68 mg, 99% yield) as colorless oil. $[\alpha]_D^{20}$ –5.3 (c 0.45, $CHCl_3$) for 33% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.43 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 (m, 3H), 7.19 (td, *J* = 7.5, 1.2 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 6.92-6.87 (m, 2H), 6.79 (d, *J* = 7.7 Hz, 1H), 4.92 (d, *J* = 4.9 Hz, 1H), 3.58 (dd, *J* = 7.2, 5.0 Hz, 1H), 1.11 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 141.3, 140.2, 138.6, 133.6, 131.4, 131.3, 130.8, 129.5, 129.3, 128.8, 128.4, 128.2, 127.0, 126.9, 125.9, 122.9, 120.7, 74.4, 37.4, 15.0. HRMS (ESI) calcd. for $C_{21}H_{18}Cl_2N$ (M + H^+) 354.0816. Found 354.0792. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.05 min (major) and 6.65 min (minor).

Methyl 3-((*S*$_a$,6*S*,7*R*)-7-Methyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepin-6-yl)benzoate (2Al).



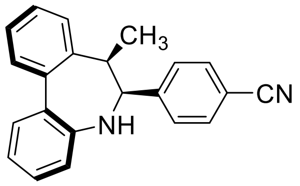
Prepared following general procedure, using **1Al** (63 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Al** (18 mg, 25% yield) as a white solid. $[\alpha]_D^{20}$ +31.4 (c 0.64, $CHCl_3$) for 86% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.74 (s, 1H), 7.46 (td, *J* = 7.4, 1.5 Hz, 2H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29-7.17 (m, 4H), 7.14 (td, *J* = 7.5, 1.2 Hz, 1H), 6.88 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 5.01 (d, *J* = 5.0 Hz, 1H), 3.88 (s, 3H), 3.70 (br s, 1H), 3.63-3.54 (m, 1H), 1.07 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 144.6, 141.5, 140.4, 139.1, 133.5, 133.4, 130.1, 129.4, 129.3, 128.9, 128.8, 128.4, 127.5, 126.8, 125.9, 122.6, 120.7, 75.1, 52.0, 37.6, 15.0. HRMS (ESI) calcd. for $C_{23}H_{22}NO_2$ (M + H^+) 344.1651. Found 344.1643. HPLC (IB column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 15.32 min (minor) and 18.26 min (major).

(S_a,6S,7R)-7-Methyl-6-(4-(trifluoromethyl)phenyl)-6,7-dihydro-5H-dibenzo[b,d]azepine



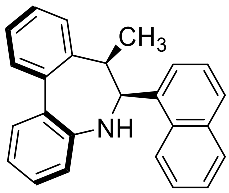
(2Am). Prepared following general procedure, using **1Am** (70 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (R,R)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Am** (24 mg, 33% yield) as white solid. $[\alpha]_D^{20}$ +21.9 (c 0.50, $CHCl_3$) for 63% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 4H), 7.42 (td, J = 7.5, 1.2 Hz, 1H), 7.33-7.28 (m, 1H), 7.25 (td, J = 7.6, 1.5 Hz, 1H), 7.20-7.16 (m, 3H), 6.91 (dd, J = 7.8, 1.2 Hz, 1H), 6.76 (d, J = 7.7 Hz, 1H), 5.03 (d, J = 5.1 Hz, 1H), 3.70 (br s, 1H), 3.61 (qd, J = 7.1, 4.9 Hz, 1H), 1.10 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.4, 140.4, 138.9, 133.6, 129.7 (q, J = 32.3 Hz), 129.5, 129.2, 128.8, 128.3, 126.9, 125.9, 124.3, 124.2, 124.27 (d, J = 272.1 Hz), 122.8, 120.8, 75.1, 37.5, 14.9. HRMS (ESI) calcd. for $C_{22}H_{19}F_3N$ (M + H^+) 354.1470. Found 354.1458. HPLC (IB column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.11 min (minor) and 7.60 min (major). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.3.

4-((S_a,6S,7R)-7-Methyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)benzonitrile (2An).



Prepared following general procedure, using **1An** (62 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (R,R)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2An** (31 mg, 50% yield) as yellow oil. $[\alpha]_D^{20}$ −10.5 (c 0.28, $CHCl_3$) for 36% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.43 (m, 4H), 7.39 (td, J = 7.5, 1.2 Hz, 1H), 7.33-7.25 (m, 1H), 7.21 (td, J = 7.5, 1.4 Hz, 1H), 7.18-7.10 (m, 3H), 6.88 (dd, J = 7.8, 1.2 Hz, 1H), 6.68 (d, J = 7.7 Hz, 1H), 5.00 (d, J = 4.9 Hz, 1H), 3.63-3.56 (m, 1H), 1.07 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.1, 140.2, 138.4, 133.5, 131.2, 129.6, 129.6, 128.9, 128.4, 127.1, 126.9, 125.8, 123.0, 120.8, 119.0, 111.4, 75.1, 37.3, 14.9. HRMS (ESI) calcd. for $C_{22}H_{19}N_2$ (M + H^+) 311.1548. Found 311.1540. HPLC (IB column, 98:2 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 33.61 min (minor) and 36.80 min (major).

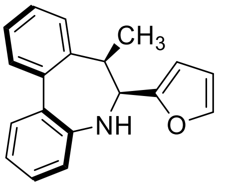
(S_a,6S,7R)-7-Methyl-6-(naphthalen-1-yl)-6,7-dihydro-5H-dibenzo[b,d]azepine (2Ao).



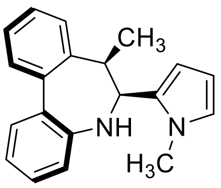
Prepared following general procedure, using **1Ao** (67 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (R,R)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ao** (33 mg, 50% yield) as colorless oil. $[\alpha]_D^{20}$ +6.8 (c 0.53, $CHCl_3$) for 97% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 9.4 Hz, 1H), 7.77 (dd, J = 5.8, 3.7 Hz, 1H), 7.53-7.49 (m, 4H), 7.41 (td, J = 7.5, 1.3 Hz, 1H), 7.35-7.23 (m, 4H), 7.18-7.10 (m, 1H), 6.92 (dd, J = 7.8, 1.2 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 6.03 (br s, 1H), 4.22-3.43 (m, 2H), 1.02 (d, J = 7.2 Hz, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 145.1, 140.6, 140.3, 137.3, 133.5, 133.1, 132.2, 129.6, 129.0, 128.8, 128.6, 127.8, 126.8, 126.8, 126.7, 125.8, 125.2, 125.0, 122.8, 122.3, 120.6, 67.0, 39.9, 14.9. HRMS (ESI) calcd. for $C_{25}H_{22}N$ (M + H^+) 336.1752. Found 336.1741. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.55 min (major) and 11.42 min (minor).

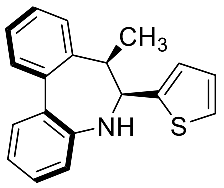
(S_a,6*S*,7*R*)-6-(Furan-2-yl)-7-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ap). Prepared following general procedure, using **1Ap** (45 mg, 0.16 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol)to obtain **2Ap** (31 mg, 56% yield) as colorless oil. $[\alpha]_D^{20}$ +31.8 (c 0.50, $CHCl_3$) for 99% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.35-7.26 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.97 (d, *J* = 3.2 Hz, 1H), 5.06 (d, *J* = 5.0 Hz, 1H), 3.73 (s, 1H), 3.51-3.40 (m, 1H), 1.18 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 144.1, 141.4, 140.0, 139.9, 133.6, 129.4, 128.6, 128.3, 126.8, 126.7, 125.7, 122.8, 120.9, 110.1, 107.5, 68.8, 38.0, 14.4. HRMS (ESI) calcd. for $C_{19}H_{18}NO$ (M + H^+) 276.1388. Found 276.1380. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.76 min (major) and 8.19 min (minor).



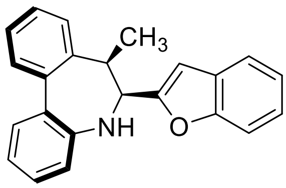
(S_a,6*S*,7*R*)-7-Methyl-6-(1-methyl-1*H*-pyrrol-2-yl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Aq). Prepared following general procedure, using **1Aq** (57 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Aq** (29 mg, 51% yield) as colorless oil. $[\alpha]_D^{20}$ –14.4 (c 0.16, $CHCl_3$) for 99% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35-7.22 (m, 2H), 7.12 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.12-7.03 (m, 1H), 6.86 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.54 (t, *J* = 2.3 Hz, 1H), 6.08 (dd, *J* = 3.5, 2.7 Hz, 1H), 5.89 (s, 1H), 5.12 (d, *J* = 4.8 Hz, 1H), 3,72 (br s, 1H), 3.46 (qd, *J* = 7.1, 4.7 Hz, 1H), 3.35 (s, 3H), 1.15 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.2, 140.3, 131.8, 129.8, 129.08, 128.7, 128.3, 127.0, 126.8, 126.3, 123.0, 122.1, 120.6, 109.0, 106.5, 67.3, 39.6, 34.6, 14.5. HRMS (ESI) calcd. for $C_{20}H_{21}N_2$ (M + H^+) 289.1705. Found 289.1703. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.78 min (major) and 9.60 min (minor).



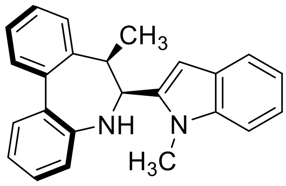
(S_a,6S,7R)-7-Methyl-6-(thiophen-2-yl)-6,7-dihydro-5H-dibenzo[b,d]azepine (2Ar). Prepared following general procedure, using **1Ar** (58 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (R,R)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 µL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 µL, 16 mg, 0.22 mmol) to obtain **2Ar** (47 mg, 80% yield) as colorless oil. $[\alpha]_D^{20}$ +44.5 (c 0.51, $CHCl_3$) for 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.40 (t, J = 7.5 Hz, 1H), 7.30-7.25 (m, 2H), 7.19-7.15 (m, 2H), 6.99-6.94 (m, 2H), 6.91-6.88 (m, 2H), 5.26 (d, J = 5.0 Hz, 1H), 3.93 (br s, 1H), 3.48 (dt, J = 12.2, 6.1 Hz, 1H), 1.18 (d, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 144.0, 140.4, 139.1, 134.2, 129.4, 128.7, 128.3, 126.8, 126.7, 126.4, 125.6, 125.3, 124.8, 123.1, 120.9, 71.4, 37.7, 14.9. HRMS (ESI) calcd. for $C_{19}H_{18}NS$ (M + H$^+$) 292.1160. Found 292.1154. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.64 min (major) and 11.95 min (minor).



(S_a,6S,7R)-6-(Benzofuran-2-yl)-7-methyl-6,7-dihydro-5H-dibenzo[b,d]azepine (2As). Prepared following general procedure, using **1As** (65 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (R,R)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 µL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 µL, 16 mg, 0.22 mmol) to obtain **2As** (36 mg, 55% yield) as colorless oil. $[\alpha]_D^{20}$ –36.3 (c 0.51, $CHCl_3$) for 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 4H), 7.40 (td, J = 7.5, 1.3 Hz, 1H), 7.32-7.25 (m, 3H), 7.25-7.15 (m, 2H), 7.04 (d, J = 7.7 Hz, 1H), 6.94 (dd, J = 7.7, 1.2 Hz, 1H), 6.36 (s, 1H), 5.17 (d, J = 5.0 Hz, 1H), 3.78 (br s, 1H), 3.55 (td, J = 7.2, 5.2 Hz, 1H), 1.27 (d, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 154.6, 144.0, 140.0, 139.7, 133.7, 129.5, 128.7, 128.4, 128.3, 126.9, 126.9, 125.9, 123.8, 123.0, 122.6, 121.0, 120.9, 111.2, 104.6, 69.1, 38.0, 14.6. HRMS (ESI) calcd. for $C_{23}H_{20}NO$ (M + H$^+$) 326.1445. Found 326.1539. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 8.92 min (major) and 10.34 min (minor).

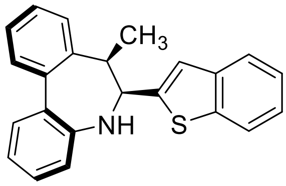


(S_a,6S,7R)-7-Methyl-6-(1-methyl-1H-indol-2-yl)-6,7-dihydro-5H-dibenzo[b,d]azepine (2At). Prepared following general procedure, using **1At** (67 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (R,R)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 µL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 µL, 16 mg, 0.22 mmol) to obtain **2At** (60 mg, 90% yield) as yellow oil. $[\alpha]_D^{20}$ –18.6 (c 0.51, $CHCl_3$) for 97% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 1H), 7.57-7.48 (m, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.33-7.28 (m, 3H), 7.23 (t, J = 7.5 Hz, 1H), 7.19-7.12 (m, 2H), 7.04 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.28 (s, 1H), 5.34 (d, J = 5.0 Hz, 1H), 3.79 (br s, 1H), 3.64-3.54 (m, 1H), 3.49 (s, 3H), 1.19 (d, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 140.8, 140.3, 139.3, 138.2, 132.9, 129.8, 128.8,



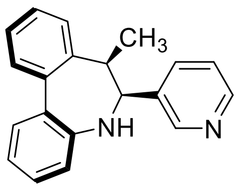
127.2, 127.2, 127.0, 126.4, 122.5, 121.3, 120.8, 120.4, 119.5, 109.2, 102.5, 68.1, 39.2, 30.7, 14.6. HRMS (ESI) calcd. for $C_{24}H_{23}N_2$ (M + H⁺) 339.1861. Found 339.1849. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 8.36 min (major) and 10.84 min (minor).

(S_a,6*S*,7*R*)-6-(Benzo[*b*]thiophen-2-yl)-7-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Au).



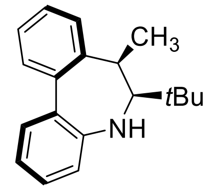
Prepared following general procedure, using **1Au** (68 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Au** (51 mg, 75% yield) as colorless oil. $[\alpha]_D^{20}$ –41.1 (c 0.50, $CHCl_3$) for 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.53-7.50 (m, 2H), 7.46 (ddt, *J* = 7.5, 6.5, 1.4 Hz, 1H), 7.40-7.28 (m, 4H), 7.25-7.18 (m, 1H), 7.17 (s, 1H), 7.09-7.03 (m, 1H), 6.92 (dd, *J* = 7.7, 1.2 Hz, 1H), 5.32 (d, *J* = 5.1 Hz, 1H), 3.95 (br s, 1H), 3.60-3.53 (m, 1H), 1.28 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 144.0, 140.4, 139.9, 139.1, 139.0, 134.2, 129.5, 128.8, 128.3, 126.9, 126.9, 126.6, 123.9, 123.8, 123.2, 122.4, 121.9, 121.0, 72.1, 37.6, 15.0. HRMS (ESI) calcd. for $C_{23}H_{20}NS$ (M + H⁺) 342.1316. Found 342.1305. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 12.07 min (major) and 16.44 min (minor).

(S_a,6*S*,7*R*)-7-Methyl-6-(pyridin-3-yl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Av). Prepared



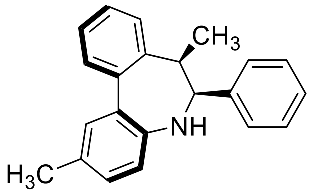
following general procedure, using **1Av** (57 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Av** (42 mg, 73% yield) as white solid. $[\alpha]_D^{20}$ +31.3 (c 0.53, $CHCl_3$) for 96% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 3.9 Hz, 1H), 8.33 (s, 1H), 7.47-7.43 (m, 2H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31-7.19 (m, 3H), 7.15 (td, *J* = 7.5, 1.2 Hz, 1H), 7.09 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.89 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 4.97 (d, *J* = 4.9 Hz, 1H), 3.65 (s, 1H), 3.64-3.56 (m, 1H), 1.08 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.1, 144.4, 140.4, 138.7, 136.4, 133.6, 129.5, 128.9, 128.4, 127.0, 125.7, 122.8, 122.6, 120.8, 72.9, 37.4, 14.9. HRMS (ESI) calcd. for $C_{20}H_{19}N_2$ (M + H⁺) 287.1548. Found 287.1543. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 14.97 min (major) and 23.91 min (minor).

(R_a,6*S*,7*R*)-6-(*tert*-butyl)-7-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Aw). Prepared



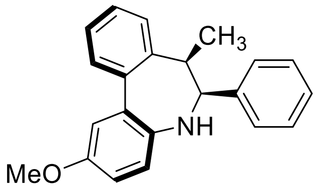
following general procedure, using **1Aw** (53 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Aw** (45 mg, 85% yield) as colorless oil. $[\alpha]_D^{20}$ -165.1 (c 0.41, $CHCl_3$) for 97% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 6.6 Hz, 1H), 6.74 (t, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.22 (s, 1H), 3.43 (d, *J* = 7.1 Hz, 1H), 3.33 (s, 1H), 1.14 (d, *J* = 7.0 Hz, 3H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 145.7, 138.4, 132.2, 130.7, 128.2, 127.6, 126.4, 126.1, 123.5, 117.2, 117.0, 69.2, 43.1, 35.3, 27.5, 14.1. HRMS (ESI) calcd. for $C_{19}H_{24}FN$ (M + H^+) 266,1909. Found 266.1904. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 5.54 min (minor) and 6.23 min (major).

(S_a,6*S*,7*R*)-2,7-Dimethyl-6-phenyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ba). Prepared



following general procedure, using **1Ba** (60 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ba** (42 mg, 70% yield) as yellow oil. $[\alpha]_D^{20}$ +25.1 (c 0.38, $CHCl_3$) for 98% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29-7.21 (m, 5H), 7.11-7.06 (m, 3H), 6.82-6.80 (m, 2H), 4.91 (d, *J* = 5.3 Hz, 1H), 3.56-3.49 (m, 1H), 2.42 (s, 3H), 1.06 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 141.0, 140.5, 139.8, 133.9, 132.0, 129.9, 129.3, 129.0, 128.1, 127.6, 127.4, 126.7, 126.6, 126.1, 120.8, 75.6, 37.8, 20.9, 15.0. HRMS (ESI) calcd. for $C_{22}H_{22}N$ (M + H^+) 300.1752. Found 300.1744. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 5.50 min (major) and 7.04 min (minor).

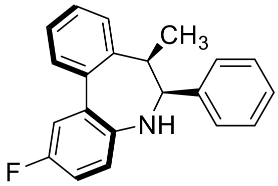
(S_a,6*S*,7*R*)-2-Methoxy-7-methyl-6-phenyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ca).



Prepared following general procedure, using **1Ca** (63 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 μL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 μL, 16 mg, 0.22 mmol) to obtain **2Ca** (33 mg, 50% yield) as yellow oil. $[\alpha]_D^{20}$ –31.2 (c 0.25, $CHCl_3$) for 99% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.28-7.20 (m, 5H), 7.08-7.03 (m, 3H), 6.88-6.82 (m, 3H), 4.86 (d, *J* = 5.5 Hz, 1H), 3.86 (s, 3H), 3.48 (m, 1H), 1.03 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 140.8, 140.4, 139.9, 138.1, 135.8, 128.9, 127.9, 127.6, 127.5, 126.9, 126.6, 126.2, 122.0, 114.7, 113.9, 75.7, 55.7, 37.7, 15.0. HRMS (ESI) calcd.

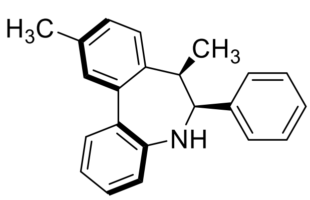
for $C_{22}H_{22}NO$ (M + H⁺) 316.1701. Found 316.1690. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.18 min (major) and 9.58 min (minor).

(*S*a,6*S*,7*R*)-2-Fluoro-7-methyl-6-phenyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Da).



Prepared following general procedure, using **1Da** (60 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 µL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 µL, 16 mg, 0.22 mmol) to obtain **2Da** (57 mg, 95% yield) as yellow oil. $[\alpha]_D^{20}$ –2.5 (c 0.58, $CHCl_3$) for 99% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.39 (m, 2H), 7.31-7.18 (m, 5H), 7.08-7.04 (m, 2H), 6.99 (td, *J* = 8.4, 3.0 Hz, 1H), 6.85-6.82 (m, 2H), 4.90 (d, *J* = 5.4 Hz, 1H), 3.58 (s, 1H), 3.51 (dd, *J* = 7.4, 5.6 Hz, 1H), 1.07 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, *J* = 239.9 Hz), 140.9, 140.7, 139.7 (d, *J* = 27.9 Hz), 135.9 (d, *J* = 7.8 Hz), 128.9, 128.0, 127.7, 127.5, 127.3, 126.7, 126.3, 121.89 (d, *J* = 8.0 Hz), 115.63 (d, *J* = 22.7 Hz), 114.95 (d, *J* = 22.1 Hz), 75.6, 37.7, 29.8, 15.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -121.8. HRMS (ESI) calcd. for $C_{21}H_{19}FN$ (M + H⁺) 304.1502. Found 304.1492. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 5.43 min (major) and 7.85 min (minor).

(*S*a,6*S*,7*R*)-7,10-Dimethyl-6-phenyl-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (2Ea). Prepared

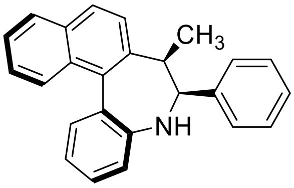


following general procedure, using **1Ea** (59 mg, 0.2 mmol), $Cu(OAc)_2$ (1.5 mg, 0.008 mmol), (*R*,*R*)-Ph-BPE (4.5 mg, 0.0088 mmol), DEMS (64 µL, 54 mg, 0.4 mmol) and anhydrous *t*BuOH (22 µL, 16 mg, 0.22 mmol) to obtain **2Ea** (24 mg, 40% yield) as colorless oil. $[\alpha]_D^{20}$ +6.3 (c 0.43, $CHCl_3$) for 96% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.29-7.19 (m, 5H), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H), 7.07-7.03 (m, 3H), 6.87 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 4.91 (d, *J* = 5.1 Hz, 1H), 3.67 (s, 1H), 3.49 (dt, *J* = 12.4, 6.1 Hz, 1H), 2.43 (s, 3H), 1.03 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 141.1, 140.2, 136.7, 136.0, 133.9, 129.3, 129.0, 128.9, 128.6, 127.5, 127.4, 126.0, 122.5, 120.8, 75.4, 37.5, 21.2, 15.0. HRMS (ESI) calcd. for $C_{22}H_{22}N$ (M + H⁺) 300.1752. Found 300.1748. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 4.99 min (major) and 6.77 min (minor).

4. Kinetic resolution of 1Ga followed by reduction of the remaining enantioenriched imine.

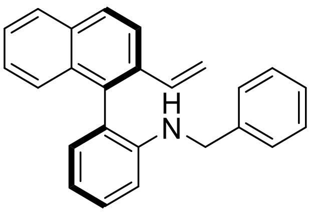
A flamed-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (1.45 mg, 4 mol%) and (*R*,*R*)-Ph-BPE (4.45 mg, 4.4 mol%). Anhydrous THF (300 µL) was added via syringe and the reaction mixture was stirred for 15 min, until a blue homogeneous solution was obtained. Diethoxymethylsilane (64 μL, DEMS, 2.0 equiv) was added via syringe and stirring was continued for 10 min at room temperature. Into a separate flamed-dried Schlenk tube aldimine **1Fa** (77 mg, 0.2 mmol, 1 equiv) was dissolved in anhydrous MTBE (1 mL) and transferred via syringe to the reaction tube containing the catalyst. Anhydrous *t*BuOH (21 μL, 1.1 equiv) was added via microsyringe and the reaction mixture was stirred at room temperature under N_2 for 48 h. The reaction mixture was then quenched with saturated aqueous Na_2CO_3 solution, extracted with EtOAc and the combined organic layers were concentrated *in vacuo*. The residue was dissolved in Et_2O (1.25 mL) and slowly added over a suspension of $LiAlH_4$ (15 mg) in Et_2O (0.4 mL) at 0ºC. The mixture was then allowed to reach room temperature and stirred for 2h. Saturated aqueous NH_4Cl solution was then added, and the mixture was extracted with AcOEt (3 × 3 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo.* The crude mixture was purified by flash column chromatography (4:1 hexane/toluene) on silica gel to obtain **2Fa** (21 mg, 39% yield) and **3Fa** (17 mg, 32% yield) as light-yellow oils.

(*S*a,6*S*,7*R*)-7-Methyl-6-phenyl-6,7-dihydro-5*H*-benzo[*b*]naphtho[1,2-*d*]azepine (2Fa). $[\alpha]_D^{20}$ +18.3 (c 0.43, $CHCl_3$) for 90% *ee*.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.0 Hz, 1H), 7.95-7.88 (m, 2H), 7.64-7.59 (m, 2H), 7.47 – 7.42 (m, 2H), 7.39-7.32 (m, 4H), 7.27-7.22 (m, 3H), 6.80 (d, *J* = 7.7 Hz, 1H), 4.34 (d, *J* = 11.2 Hz, 1H), 3.49-3.41 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.9, 139.1, 135.6, 133.2, 132.0, 131.1, 130.4, 128.9, 128.5, 128.2, 128.0, 127.7, 126.7, 126.3, 126.0, 125.1, 123.0, 122.0, 121.5, 77.0, 38.5, 16.2. HRMS (ESI) calcd. for $C_{25}H_{22}N$ (M + H$^+$) 336.1752. Found 336.1745. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 6.29 min (major) and 9.85 min (minor).

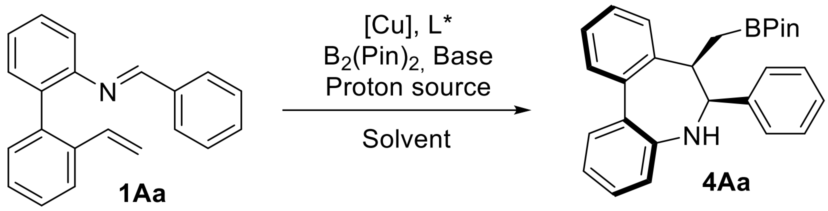
(*R*)-*N*-(2-(2-Vinylnaphthalen-1-yl)benzyl)aniline (3Fa). $[\alpha]_D^{20}$ –6.0 (c 0.43, $CHCl_3$) for >99% *ee.*

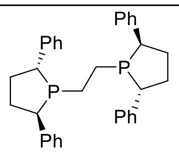
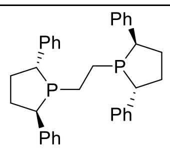
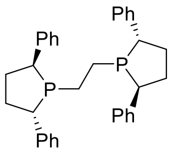
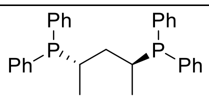
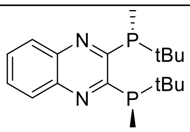
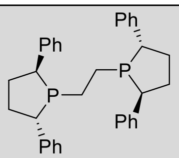


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (m, 3H), 7.51-7.46 (m, 2H), 7.41-7.37 (m, 1H), 7.30 (ddd, *J* = 8.7, 7.5, 1.7 Hz, 1H), 7.23-7.18 (m, 3H), 7.15-7.13 (m, 2H), 7.05 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.87 (td, *J* = 7.4, 1.1 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.69 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.85 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.28 (dd, *J* = 11.0, 1.0 Hz, 1H), 4.25 (d, *J* = 4.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 139.2, 135.2, 134.1, 133.9, 133.5, 132.9, 131.3, 129.0, 128.4, 128.4, 128.0, 127.0, 127.0, 126.6, 126.6, 126.1, 123.6, 122.7, 117.6, 115.3, 111.3, 48.0. HRMS (ESI) calcd. for $C_{25}H_{22}N$ (M + H$^+$) 336.1752. Found 336.1745. HPLC (OJ-H column, 98:2 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 12.70 min (major) and 25.47 min (minor).

5. Optimization studies for the Cu-catalyzed intramolecular borylative cyclization of 1Aa.

Table S1. Screening of reaction conditions and ligands[a]

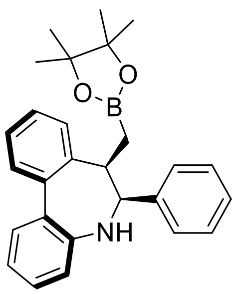


Entry[a]	[Cu] (10 mol%)	L*(12 mol%)	Base	Proton source	Solvent	Comment[b]
1	CuCl	 (R,R)-Ph-BPE	NaO*t*Bu	*t*BuOH	TBME	40% conv.
2	CuCl	 (R,R)-Ph-BPE	LiO*t*Bu	*t*BuOH	TBME	Full conv. 40% yield. 80% ee, >20:1 dr
3	$[Cu(MeCN)_4]PF_6$	 (S,S)-Ph-BPE	KO*t*Bu	*i*PrOH	THF	Full conv. 93% ee, >20:1 dr
4	$[Cu(MeCN)_4]PF_6$	 (S,S)-BDPP	KO*t*Bu	*i*PrOH	THF	Full conv. 20% ee
5	$[Cu(MeCN)_4]PF_6$	 (R)-QuinoxP	KO*t*Bu	*i*PrOH	THF	Full conv. Racemic.
6	$[Cu(MeCN)_4]PF_6$[c]	 (S,S)-Ph-BPE	KO*t*Bu	*i*PrOH	THF	Full conv. 85% yield 98% ee, >20:1 dr

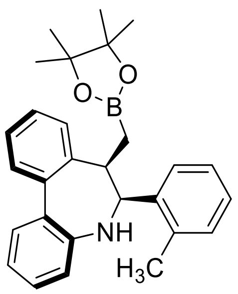
[a]0.2 mmol **1Aa** (1.2 mL THF). [b]Conversions and d.r. were estimated by ^{1}H-NMR spectroscopy. Ee's were determined by chiral HPLC analysis. [c] [Cu] (5 mol %)/L* (6 mol%).

6. General procedure for the synthesis of borylated dibenzazepines 4 by Cu-catalyzed intramolecular borylative cyclization.

To a 10 mL reaction vial was added Cu(MeCN)$_4$PF$_6$ (0.01 mmol, 3.7 mg, 5 mol %), (-)-1,2-Bis((2*R*,5*R*)-2,5-diphenylphospholano)ethane (0.012 mmol, 6.1 mg), KO*t*Bu (0.3 mmol, 34 mg) and THF (1.0 mL). The mixture was stirred at room temperature for 10-15 min before the addition of B$_2$pin$_2$ (0.3 mmol, 78.0 mg). After brief stirring (10 min), a solution of **1** (0.2 mmol) in anhydrous THF (0.7 mL) was then added at room temperature under nitrogen atmosphere. Degassed and dry isopropanol (0.4 mmol, 30 μL) was added under nitrogen atmosphere and the reaction mixture was then stirred at r.t. for 12 h. After reaction completion, the resulting solution was filtered through a silica plug, and the crude material was concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain borylated dibenzo[*b*,*d*]azepine derivatives **4.**



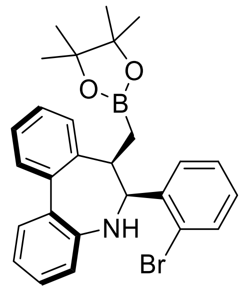
(*S*a,6*S*,7*R*)-6-Phenyl-7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (4Aa). Prepared following general procedure 5, using **1Aa** (56 mg, 0.2 mmol) to obtain **4Aa** (72 mg, 85% yield) as colorless oil. $[\alpha]_D^{20}$ +46 (c 0.55, CHCl$_3$) for 98% *ee*. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50–7.43 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.29-7.18 (m, 5H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.06 (m, 2H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.80 (br s, 1H), 5.02 (d, *J* = 4.9 Hz, 1H), 3.76-3.62 (m, 2H), 1.14 (s, 6H), 1.06 (s, 6H), 0.94 (d, *J* = 8.2 Hz, 2H).^{13}C NMR (100 MHz, CDCl$_3$). δ 145.0, 141.0, 140.5, 139.9, 134.0, 129.3, 129.0, 128.6, 128.1, 127.4, 127.4, 126.4, 122.4, 120.8, 83.1, 75.9, 39.3, 24.7, 24.5, 12.7. ^{11}B NMR (160 MHz, CDCl$_3$): δ 33.9 ppm. HRMS (ESI) calcd. for C$_{27}$H$_{31}$BNO$_2$ (M + H$^+$) 412,2448. Found 412.2438. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t$_R$ 5.04 min (major) and 6.46 min (minor).



(*S*a,6*S*,7*R*)-7-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-6-(*o*-tolyl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (4Ab). Prepared following general procedure 5, using **1Ab** (60 mg, 0.2 mmol) to obtain **4Ab** (70 mg, 82% yield) as colorless oil. $[\alpha]_D^{20}$ +19 (c 0.52, CHCl$_3$) for 97% *ee*. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50-7.45 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.25-7.21 (m, 3H), 7.15-7.10 (m, 3H), 7-01-6.87 (m, 4H), 5.37 (d, *J* = 5.1 Hz, 1H), 3.72 (br s, 1H), 2.43 (s, 3H), 1.05 (s, 6H), 0.95 (m, 8H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.4, 140.0, 136.0, 130.0, 129.4, 128.6, 127.3, 127.1, 126.7, 126.5, 125.3, 123.1, 121.1, 83.0, 70.3, 40.0, 24.7, 24.4, 20.2, 11.2. ^{11}B NMR (160 MHz, CDCl$_3$): δ 33.4 ppm. HRMS (ESI) calcd. for C$_{28}$H$_{33}$BNO$_2$ (M + H$^+$) 426,2604. Found

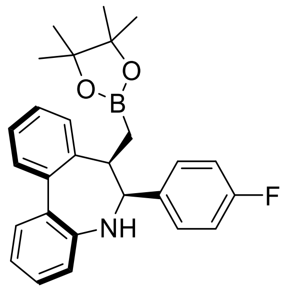
426.2598. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 4.68 min (major) and 6.49 min (minor).

(*S*a,6*S*,7*R*)-6-(2-Bromophenyl)-7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (4Af). Prepared following general procedure 5, using **1Af** (72 mg, 0.2 mmol) to obtain **4Af** (29 mg, 40% yield) as colorless oil. $[\alpha]_D^{20}$ +57 (c 1.33, $CHCl_3$) for 92% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.50–7.44 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30–7.21 (m, 2H), 7.19-7.13 (m, 1H), 7.10-7.03 (m, 3H), 6.99-6.80 (m, 2H), 5.63 (d, *J* = 5.2 Hz, 1H), 3.81 (br s, 1H), 3.63 (br s, 1H), 1.07 (s, 6H), 0.96 (s, 8H).

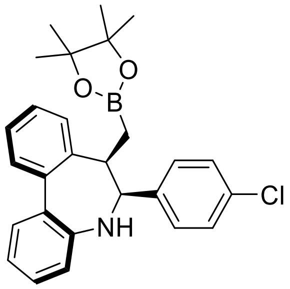


. ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 140.5, 140.2, 139.6, 134.1, 132.3, 131.3, 129.3, 128.8, 128.7, 128.3, 127.0, 126.6, 126.5, 126.4, 124.8, 122.7, 121.0, 83.0, 73.1, 40.1, 24.7, 24.4, 11.4. ^{11}B NMR (160 MHz, $CDCl_3$): δ 32.7 ppm. HRMS (ESI) calcd. for $C_{27}H_{30}BBrNO_2$ (M + H^+) 490,1553. Found 490.1545. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 4.44 min (major) and 5.76 min (minor).

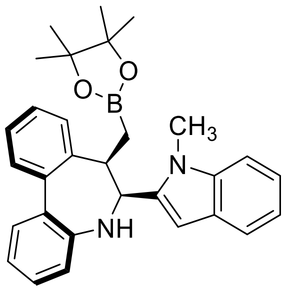
(*S*a,6*S*,7*R*)-6-(4-Fluorophenyl)-7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (4Ah). Prepared following general procedure 5, using **1Ah** (60 mg, 0.2 mmol) to obtain **4Ab** (72 mg, 84% yield) as colorless oil. $[\alpha]_D^{20}$ –59 (c 0.70, $CHCl_3$) for 97% *ee*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.29-7.12 (m, 4H), 7.05-6.96 (m, 2H), 6.93-6.83 (m, 3H), 6.77 (d, *J* = 7.0 Hz, 1H), 4.99 (d, *J* = 5.1 Hz, 1H), 3.68 (br s, 1H), 1.13 (s, 6H), 1.05 (s, 6H), 0.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245.2 Hz), 144.1, 140.2, 139.3, 136.2, 134.1, 130.5, 130.5, 129.3, 128.7, 128.3, 126.6, 126.6, 126.4, 123.0, 121.0, 114.1 (d, *J* = 21.1 Hz), 83.2, 75.1, 39.0, 24.7, 24.5, 12.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.4. ^{11}B NMR (160 MHz, $CDCl_3$): δ 33.9 ppm. HRMS (ESI) calcd. for $C_{27}H_{30}BFNO_2$ (M + H^+) 430,2354. Found 430.2345. HPLC (IB column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 5.95 min (minor) and 6.30 min (major).



(*S*a,6*S*,7*R*)-6-(4-Chlorophenyl)-7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (4Aj). Prepared following general procedure 5, using **1Aj** (64 mg, 0.2 mmol) to obtain **4Aj** (65 mg, 73% yield) as colorless oil. $[\alpha]_D^{20}$ +19 (c 0.51, $CHCl_3$) for 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.27-7.12 (m, 6H), 6.98-6.96 (m, 2H), 6.91 (d, *J* = 7.1 Hz, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 4.98 (d, *J* = 5.2 Hz, 1H), 3.66 (br s, 1H), 1.13 (s, 6H), 1.04 (s, 6H), 0.90-0.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.0, 134.2, 133.3, 130.4, 129.3, 128.7, 128.3, 127.5, 126.8, 126.4, 123.3, 121.1, 83.2, 75.1, 38.8, 24.7, 24.5, 12.4. ^{11}B NMR (160 MHz, $CDCl_3$): δ 33.7 ppm. HRMS (ESI) calcd. for $C_{27}H_{30}BClNO_2$ (M + H$^+$) 446,2058. Found 446.2049. HPLC (IB column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 5.87 min (minor) and 7.01 min (major).

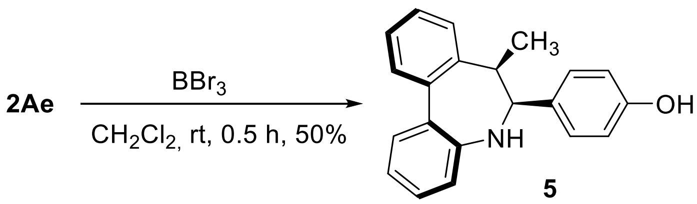


(*S*a,6*S*,7*R*)-6-(1-Methyl-1*H*-indol-2-yl)-7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-6,7-dihydro-5*H*-dibenzo[*b*,*d*]azepine (4At). Prepared following general procedure 5, using **1At** (67 mg, 0.2 mmol) to obtain **4At** (67 mg, 72% yield) as colorless oil. $[\alpha]_D^{20}$ +1.0 (c 0.53, $CHCl_3$) for 96% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.52-7.50 (m, 2H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29-7.24 (m, 4H), 7.23-7.19 (m, 1H), 7.17-7.04 (m, 3H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.31 (br s, 1H), 5.39 (d, *J* = 4.8 Hz, 1H), 3.73 (br s, 1H), 3.50 (br s, 3H), 1.09 (s, 6H), 1.03 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 140.2, 138.2, 129.9, 129.0, 128.7, 127.2, 126.9, 126.8, 121.2, 120.4, 119.4, 109.2, 102.6, 83.1, 30.6, 27.0, 24.8, 24.5, 11.8. ^{11}B NMR (160 MHz, $CDCl_3$): δ 34.3 ppm. HRMS (ESI) calcd. for $C_{30}H_{34}BN_2O_2$ (M + H$^+$) 465,2713. Found 465.2706. HPLC (IA column, 95:5 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 9.32 min (major) and 10.60 min (minor).



7. Derivatization reactions

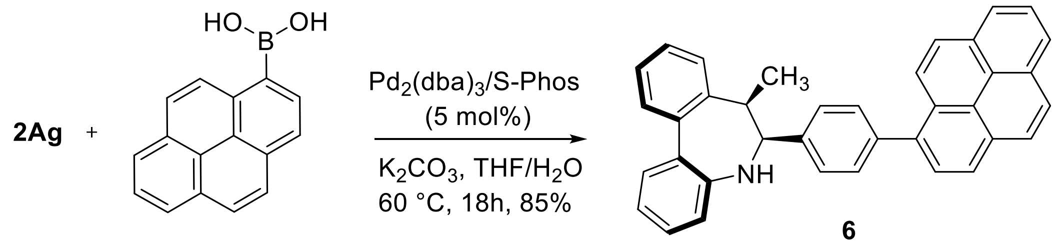
7.1. Synthesis of 5 by demethylation of 2Ae



5

Following a described procedure.[6] Boron tribromide (18 µL, 0.19 mmol) was added to a solution of **2Ae** (21 mg, 0.07 mol) in CH_2Cl_2 (1 mL) at – 40 °C, then stirred for 30 min at rt. Saturated $NaHCO_3$ solution (2 mL) was added, the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 3). The organic layers were combined and concentrated to give an orange oil. This was purified by flash column chromatography (9:1 toluene/Et_3N) to afford the title compound as a white foam (14 mg, 70% yield). $[\alpha]_D^{20}$ –17.1 (c 0.6, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 1.7 Hz, 1H), 7.43 (t, *J* = 1.7 Hz, 1H), 7.36 (td, *J* = 7.3, 1.3 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.12 (td, *J* = 7.5, 1.3 Hz, 1H), 6.90–6.85 (m, 3H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.67 (m, 2H), 4.87 (d, *J* = 5.1 Hz, 1H), 3.52-3.45 (m, 1H), 1.04 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 144.9, 140.4, 139.8, 133.7, 132.9, 130.0, 129.3, 128.7, 128.2, 126.7, 126.5, 126.1, 122.5, 120.7, 114.3, 74.9, 37.8, 15.0. HRMS (ESI) calcd. for $C_{21}H_{20}NO$ (M + H^+) 302.1545. Found 302.1539.

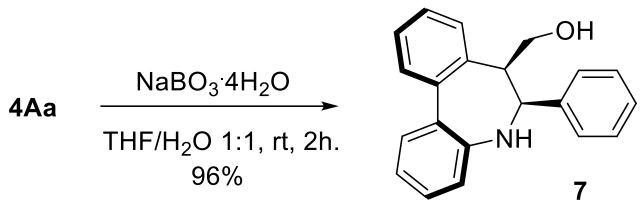
7.2. Synthesis of 6 by Suzuki-Miyaura reaction



6

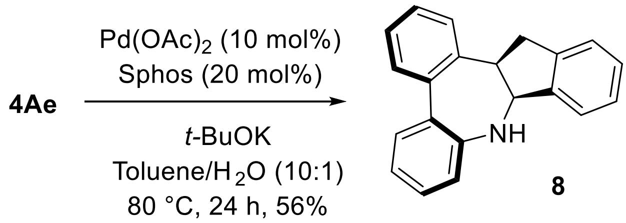
Following a described procedure.[1] An oven-dried 5 mL schlenk tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (3.2 mg, 3 mol%), SPhos (2.8 mg, 6 mol%) and the reaction vessel was capped then evacuated and backfilled with N_2 using the Schlenk line (this process was repeated a total of three times). Thoroughly degassed THF (0.6 mL) was then added via syringe and the resulting mixture was stirred for 5 min at room temperature. Then, **2Ag** (42 mg, 0.12 mmol), pyren-1-ylboronic acid (35 mg, 0.14 mmol), K_2CO_3 (48 mg, 0.35 mmol) and H_2O (0.2 mL for a THF/H_2O = 3:1) were added, and the resulting mixture was placed in a preheated oil bath and stirred at 60 °C for 18 h. The reaction crude was allowed to reach room temperature, water (3 mL) was added and the resulting mixture was extracted with AcOEt (3 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo.* The crude mixture was purified by flash column chromatography (4:1 cyclohexane/toluene) to afford the title compound as a yellow oil (48 mg, 85% yield). $[\alpha]_D^{20}$ –123.4 (c 0.51, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.27–8.19 (m, 4H), 8.13 (m, 2H), 8.08–8.02 (m, 3H), 7.58-7.52 (m, 4H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38–7.32 (m, 2H), 7.30–7.27 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.03-6.99 (m, 2H), 5.12 (d, *J* = 5.1 Hz, 1H), 3.71–3.65 (m, 1H), 1.25 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.2, 139.4, 137.5, 134.0, 131.5, 131.0, 130.5, 129.8, 129.5, 129.0, 128.8, 128.5, 128.4, 127.7, 127.4, 127.4, 127.1, 127.0, 126.3, 126.0, 125.31, 125.1, 125.0, 124.9, 124.8, 124.7, 121.1, 75.4, 37.7, 15.1. HRMS (ESI) calcd. for $C_{37}H_{28}N$ (M + H^+) 486.2222. Found 486.2210

7.3. Oxidation of organoboronate 4Aa for the synthesis of 7



Sodium perborate tetrahydrate (38 mg, 0.24 mmol) was added in one portion to a solution of boryl dibenzoacepine **4Aa** (20 mg, 0.048 mmol) in aqueous THF (560 μL, THF/H_2O = 1/1), and the mixture was stirred for 2 h. After diluting the reaction mixture with water (3 mL), the aqueous solution was extracted with EtOAc (3 × 5 mL). The combined organic layer was dried over Na_2SO_4 and the solvent evaporated. The residue was purified by flash column chromatography (SiO_2, *n*-pentane/AcOEt 1:1), affording product **3** (14 mg, 96% yield) as a yellow solid. $[\alpha]_D^{20}$ +42 (c 0.78, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.29-7.20 (m, 6H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.12-7.07 (m, 2H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 7.2 Hz, 1H), 5.23 (d, *J* = 5.0 Hz, 1H), 3.79–3.70 (m, 2H), 3.58 (q, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 140.9, 140.6, 136.2, 133.1, 129.4, 128.9, 128.7, 128.5, 127.8, 127.7, 127.0, 126.8, 125.6, 122.6, 120.9, 71.2, 61.7, 46.1, 26.9. HRMS (ESI) calcd. for $C_{21}H_{20}NO$ (M + H^+) 302,1545. Found 302.1537.

7.4. Intramolecular Suzuki Coupling for the synthesis of 8



Following a described procedure.[7] $Pd(OAc)_2$ (3.6 mg, 0.016 mmol), KO*t*Bu (54 mg, 0.48 mmol),and Sphos (13 mg, 0.032 mmol) were added to a dry Schlenk tube equipped with a stir bar. The tube was evacuated and refilled with N_2. A solution of boryl dibenzoacepine **4Ae** (78 mg, 0.16 mmol) in toluene (1.6 mL) and H_2O (0.2 mL) was introduced to the Schlenk tube by syringe, respectively. The resulting reaction mixture was stirred vigorously at 80 °C for 24 h. The reaction mixture was concentrated in vacuum and the residue was purified by flash column chromatography (SiO_2, *n*-pentane/AcOEt 20:1) to afford **8** (25 mg, 56% yield) as a solid. $[\alpha]_D^{20}$ +167 (c 0.48, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.31 (m, 6H), 7.29-7.25 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 8.1 Hz, 1H), 6.46 (d, *J* = 7.6 Hz, 1H), 5.27 (d, *J* = 8.5 Hz, 1H), 3.84 (q, *J* = 9.0 Hz, 1H), 2.93 (dd, *J* = 16.3, 9.0 Hz, 1H), 2.77 (dd, *J* = 16.2, 9.3 Hz, 1H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 144.5, 143.7, 143.1, 140.3, 139.3, 136.4, 130.0, 129.8, 129.1, 128.9, 128.3, 127.9, 127.8, 127.6, 127.4, 126.0, 124.4, 124.2, 124.1, 75.1, 48.5, 39.1. HRMS (ESI) calcd. for $C_{21}H_{18}N$ (M + H^+) 284,1439. Found 284.1436.

8. Computational Details

8.1. Computational Methods

All of the calculations were performed using the Gaussian09 program.[8] Computations were done using wb97xd functional[9] in conjunction with def2SVP and def2TZVP basis sets.[10] Geometry full optimizations were made at wb97xd/def2SVP level and then single point calculations at wb97xd/def2TZVP level were carried out in order to obtain more accurate values of the energies. For the purpose of comparison and benchmarking with the experimental observations, the energy values were also calculated using m062x functional[11] in conjunction with cc-pvtz basis set[12]. Solvent effects (diisopropylether, taken as the closer to the experimentally used mixture) were considered using the CPCM model.[13] The nature of stationary points was defined on the basis of calculations of normal vibrational frequencies. The optimizations were carried out using the Berny analytical gradient optimization method.[14] Analytical second derivatives of the energy were calculated to classify the nature of stationery points and to provide zero-point vibrational energy corrections, and thermal and entropic contributions to the free energies, using the unscaled frequencies. NCI (non-covalent interactions) were computed as described.[15] Quantitative data were obtained with the NCIPLOT4 program.[16] A density cutoff of ρ=0.5 a.u. was applied and isosurfaces of s(r) =0.5 were colored by $sign(\lambda_2)\rho$ in the [-0.03,0.03] a.u. range using VMD software.[17] s(**r**) against $sign(\lambda_2)\rho(\mathbf{r})$ plots were generated with gnuplot software. Structural representations were generated using CYLView.[18]

8.2. Conformational Study

To check the possibility of a thermodynamic equilibrium between the observed S_a,6*S*,7*R*-stereoisomer and its axial epimer with R_a,6*S*,7*R* configuration we calculated the rotation about the axis of the biphenyl moiety for compound **2Aa**. The most stable conformation was found to be **C1a**, the same that had been obtained by X-ray crystallography. Actually, the cycloheptadiene ring can adopt two conformations a and b depending on the pseudoaxial/pseudoequatorial orientation of the substituents at the stereogenic centers. The interconversion of the S_a,6*S*,7*R*-**C1a**/S_a,6*S*,7*R*-**C1b** and R_a,6*S*,7*R*-**C2a**/R_a,6*S*,7*R*-**C2b** conformers have free energy barriers of 15.1 and 13.5 kcal/mol, respectively and the difference between free energy of conformers accounts for the preferred **C1a** and **C2b** conformations in each case (Figure S1). The interconversion between S_a,6*S*,7*R*-**C1b**/R_a,6*S*,7*R*-**C2b** conformations involving epimerization of the axial chirality by biphenyl bond rotation has free energy barriers of 2.3 and 7.8 kcal/mol for the direct and inverse transformation, respectively (see Figure S2 with the energy profiles). Consequently, the limiting state is the first transformation with a barrier of 15.1 kcal/mol.

Those values of energy barriers clearly showed that an equilibrium is established at 25°C (a barrier of 15.1 kcal/mol corresponds, approximately, to a kinetic constant of 52.11 s-1 with T1/2 of 0.0133 s) and, consequently, the observed population of conformers depends on their stability. In this respect, the calculated free energies for the S_a,6*S*,7*R*-**C1a**/S_a,6*S*,7*R*-**C1b** and R_a,6*S*,7*R*-**C2a**/R_a,6*S*,7*R*-**C2b** conformers correspond to a predicted 99:1 S_a,6*S*,7*R*-**C1a**/R_a,6*S*,7*R*-**C2b** ratio. Considering these values and the assumed DFT experimental error it is possible to conclude that, essentially, only S_a,6*S*,7*R*-C1a will be observed in agreement with the experimental results. Similar values were obtained by using the alternative level m062x/cc-pvtz (see below).

In order to evaluate the influence of electronic factors the conformational study was also carried out with the 4-cyanophenyl derivative **2An** (R^1 = Me, R^2 = 4-CNC_6H_4). Essentially, very similar values were obtained to those of compound **2Aa** (R^1 = Me, R^2 = Ph) demonstrating that the observed differences between stereoisomers are mostly due to steric factors (Figure S1).

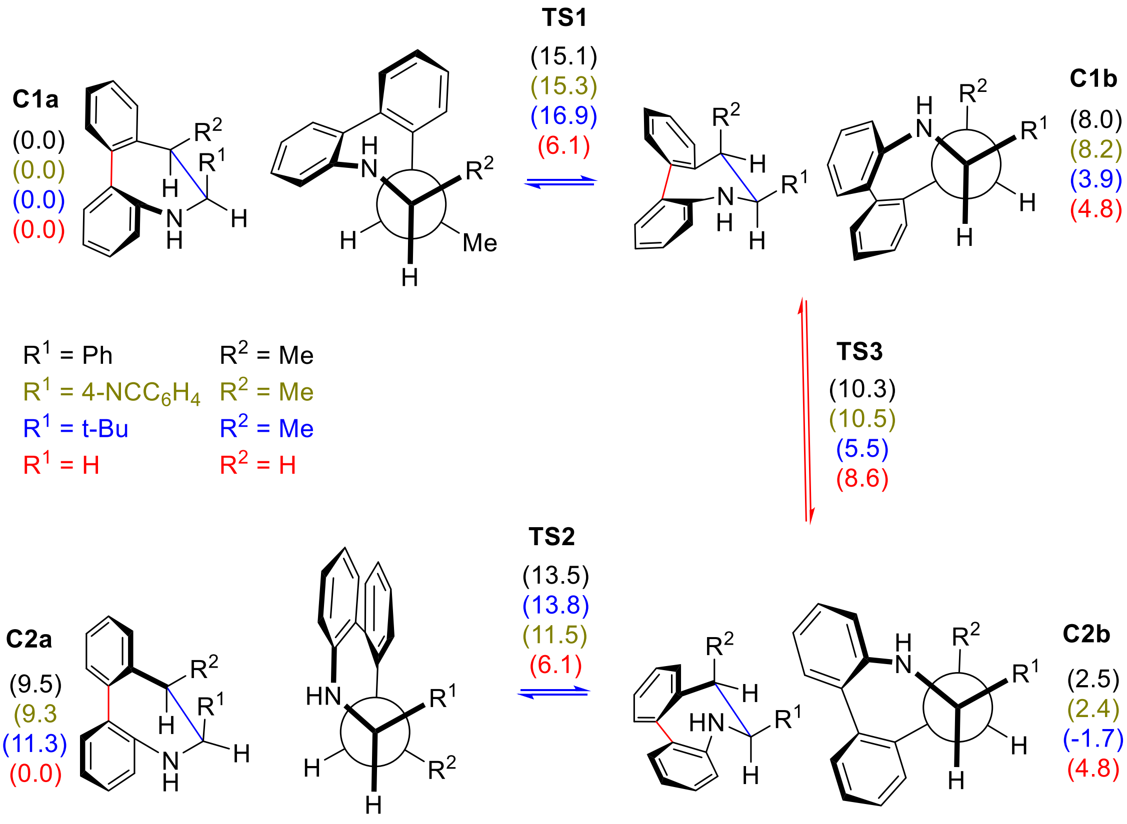


Figure S1. Conformational study of compounds **2Aa**, **2An**. Geometries have been optimized at wb97xd/def2svp/cpcm=diisopropylether level of theory and free energies have been calculated at wb97xd/def2tzp/ cpcm=diisopropylether level of theory. Relative free energies are given in kcal/mol.

On the other hand, when the aryl group is exchanged by a tert-butyl group (R^1 = Me, R^2 = *tert*-Bu, compound **2Aw**) a slight reversal in the thermodynamic stability of the conformers is observed and conformer R_a,6*S*,7*R*-**C2b** is found to be the most sable by 1.7 kcal/mol predicting that mixtures of diastereomers might be observed (a difference of 1.7 kcal/mol accounts for a 95:5 ratio at 25ºC). The rate-limiting state is also the interconversion of S_a,6*S*,7*R*-**C1a**/S_a,6*S*,7*R*-**C1b** conformers with a barrier of 16.9 kcal/mol. The interconversion between *S*a,6*S*,7*R*-**C1b**/*R*a,6*S*,7*R*-**C2b** conformations involving epimerization of the axial chirality has barriers of 1.6 and 7.2 kcal/mol for the direct and inverse transformation, respectively (see Figure S2).

With no substituents (R^1 = H, R^2 = H, compound **2Ax**) the barrier between enantiomeric conformers is 4.3 kcal/mol and the rate limiting state, corresponding to the conformational **C1a/C1b** interconversion, has a barrier of 6.1 kcal/mol.

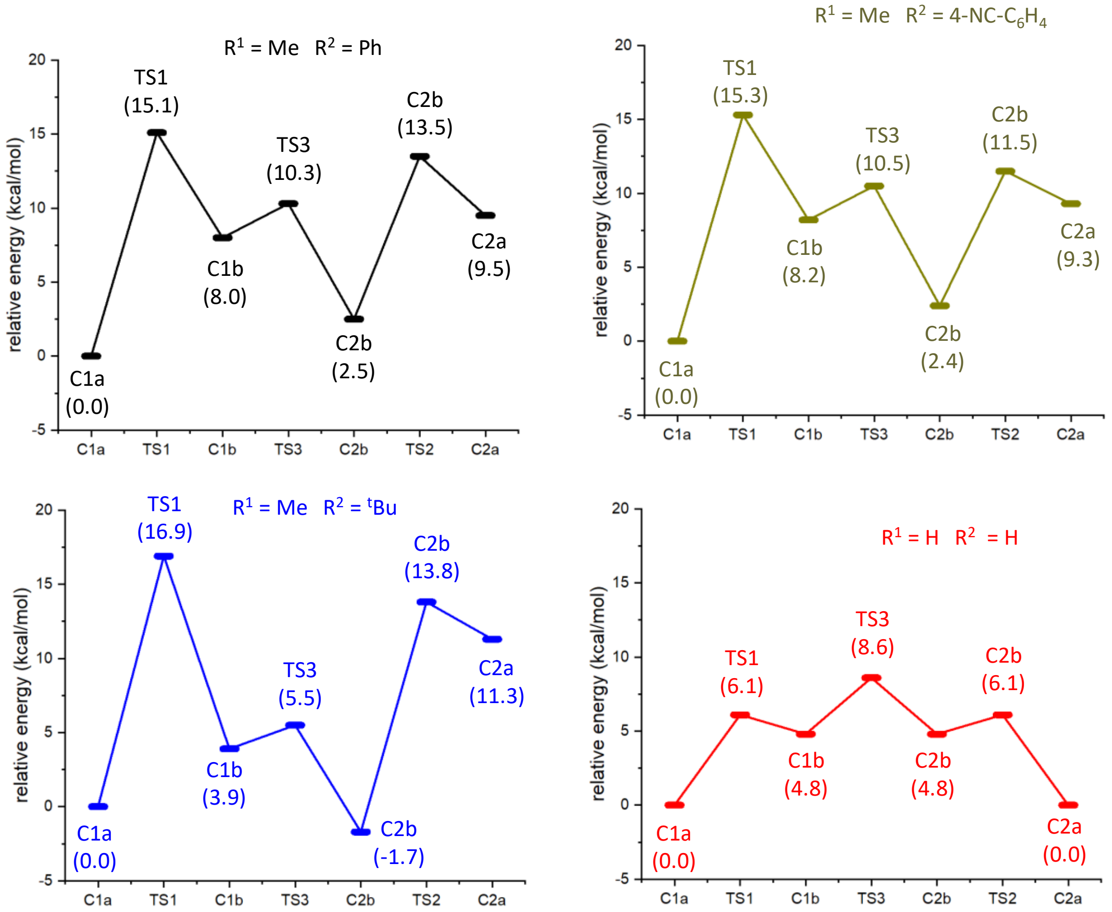


Figure S2. Energy profiles for the conformational studies illustrated in Figure S1. **TS3** corresponds to the barrier of the biphenyl bond rotation. Free energies have been calculated at wb97xd/def2tzp/cpcm=diisopropylether level of theory. Relative free energies are given in kcal/mol.

Energies

Table S2. Absolute (hartree) and relative (kcal/mol) energies for the conformational study corresponding to **2Aa** (R^1 = Me, R^2 = Ph) calculated at wb97xd/def2tzvp/cpcm=diisopropylether level from geometries optimized at wb97xd/def2svp/ cpcm=diisopropylether level.

	E_0	ΔE_0	G	ΔG	im. freq
C1a	-866.113330529	0.0	-866.157874529	0.0	
TS1	-866.091021097	14.0	-866.133746097	15.1	-46.4
C1b	-866.100397725	8.1	-866.145159725	8.0	
TS3	-866.098362862	9.4	-866.142813862	9.5	
C2b	-866.093897858	12.2	-866.136303858	13.5	-31.3
TS2	-866.108999946	2.7	-866.153892946	2.5	
C2a	-866.097882234	9.7	-866.141464234	10.3	-60.5

Table S3. Absolute (hartree) and relative (kcal/mol) energies for the conformational study corresponding to **2Aa** (R^1 = Me, R^2 = Ph) calculated at m062x/cc-pvtz/cpcm=diisopropylether level from geometries optimized at wb97xd/def2svp/ cpcm=diisopropylether level.

	E_0	ΔE_0	G	ΔG	im. freq
C1a	-866.035176280	0.0	-866.079720280	0.0	
TS1	-866.013261049	13.8	-866.055986049	14.9	-46.4
C1b	-866.023215559	7.5	-866.067977559	7.4	
TS3	-866.020182199	9.4	-866.064633199	9.5	
C2b	-866.015837444	12.1	-866.058243444	13.5	-31.3
TS2	-866.030332032	3.0	-866.075225032	2.8	
C2a	-866.020091443	9.5	-866.063673443	10.1	-60.5

Table S4. Absolute (hartree) and relative (kcal/mol) energies for the conformational study corresponding to **2An** (R^1 = Me, R^2 = 4-NC-C_6H_4) calculated at wb97xd/def2tzvp/cpcm=diisopropylether level from geometries optimized at wb97xd/def2svp/ cpcm=diisopropylether level.

	E_0	ΔE_0	G	ΔG	im. freq
C1a	-958.359339820	0.0	-958.406258820	0.0	23.8
TS1	-958.336534081	14.3	-958.381897081	15.3	-45.2
C1b	-958.345741511	8.5	-958.393134511	8.2	
TS3	-958.343253743	10.1	-958.389484743	10.5	-60.2
C2b	-958.354900958	2.8	-958.402369958	2.4	
TS2	-958.341233175	11.4	-958.387870175	11.5	-211.3
C2a	-958.344406608	9.4	-958.391454608	9.3	

Table S5. Absolute (hartree) and relative (kcal/mol) energies for the conformational study corresponding to **2Aw** derivative (R^1 = Me, R^2 = *tert*-Bu) calculated at wb97xd/def2tzvp/cpcm=diisopropylether level from geometries optimized at wb97xd/def2svp/ cpcm=diisopropylether level.

	E_0	ΔE_0	G	ΔG	im. freq
C1a	-792.289103462	0.0	-792.331998462	0.0	
TS1	-792.263296602	16.2	-792.305096602	16.9	-51.8
C1b	-792.281829039	4.6	-792.325726039	3.9	
TS3	-792.280200445	5.6	-792.323261445	5.5	-40.0
C2b	-792.290299066	-0.8	-792.334665066	-1.7	
TS2	-792.268213699	13.1	-792.310026699	13.8	-52.6
C2a	-792.270640316	11.6	-792.314035316	11.3	

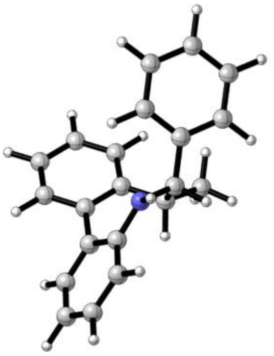
Table S6. Absolute (hartree) and relative (kcal/mol) energies for the conformational study corresponding to **2Ax** derivative (R^1 = H, R^2 = H) calculated at wb97xd/def2tzvp/cpcm=diisopropylether level from geometries optimized at wb97xd/def2svp/ cpcm=diisopropylether level.

	E_0	ΔE_0	G	ΔG	im. freq
C1a	-595.851056697	0.0	-595.887723697	0.0	
TS1	-595.842150167	5.6	-595.877962167	6.1	-124.2
C1b	-595.843370704	4.8	-595.880090704	4.8	
TS3	-595.838145029	8.1	-595.874039029	8.6	-93.0
C2b	-595.843371704	4.8	-595.880091704	4.8	
TS2	-595.842150167	5.6	-595.877962167	6.1	-124.2
C2a	-595.851056697	0.0	-595.887723697	0.0	

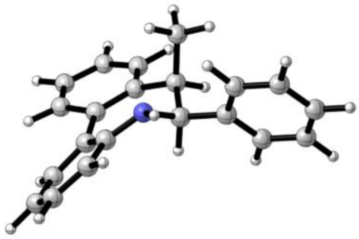
Table S7. Absolute (hartree) and relative (kcal/mol) energies for the conformational study corresponding to **2Ax** derivative (R^1 = H, R^2 = H) calculated at m062x/cc-pvtz/cpcm=diisopropylether level from geometries optimized at wb97xd/def2svp/ cpcm=diisopropylether level.

	E_0	ΔE_0	G	ΔG	im. freq
C1a	-595.797570324	0.0	-595.834237324	0.0	
TS1	-595.788767609	5.5	-595.824579609	6.1	-124.2
C1b	-595.790404771	4.5	-595.827124771	4.5	
TS3	-595.784817838	8.0	-595.820711838	8.5	-93.0
C2b	-595.790405771	4.5	-595.827125771	4.5	
TS2	-595.788767609	5.5	-595.824579609	6.1	-124.2
C2a	-595.797570324	0.0	-595.834237324	0.0	

Geometries

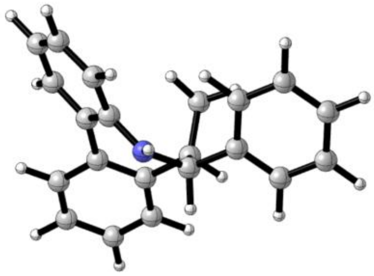


2-Aa-C1a (R^1 = Me; R^2 = Ph)



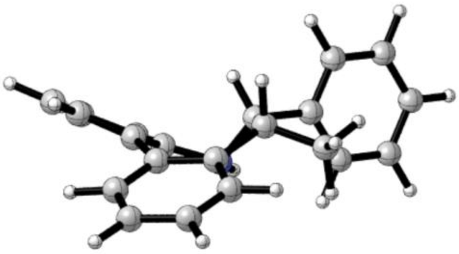
2-Aa-C1b (R^1 = Me; R^2 = Ph)

2-Aa-C2a (R^1 = Me; R^2 = Ph)

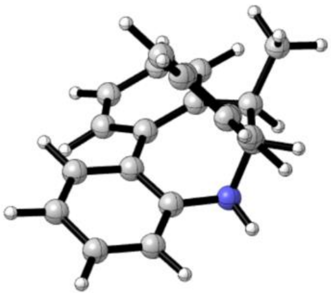


2-Aa-C2b (R^1 = Me; R^2 = Ph)

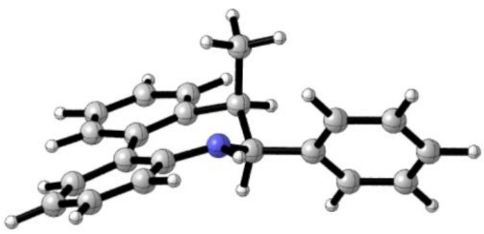
Figure S3. Optimized (wb97xd/def2svp/ cpcm=diisopropylether level) geometries of the conformers of compound **2Aa** (R^1 = Me, R^2 = Ph).



2-Aa-TS1 (R^1 = Me; R^2 = Ph)

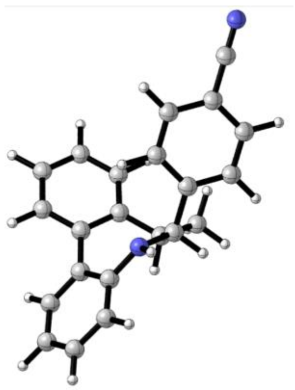


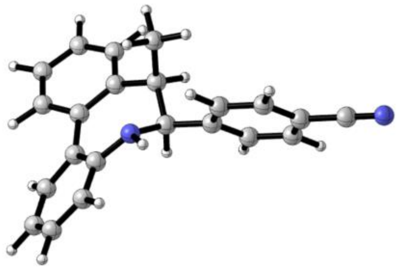
2-Aa-TS2 (R^1 = Me; R^2 = Ph)



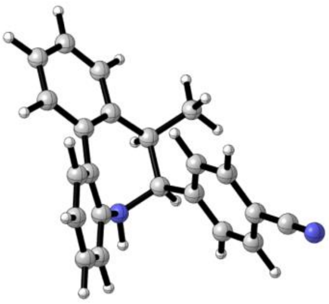
2-Aa-TS3 (R^1 = Me; R^2 = Ph)

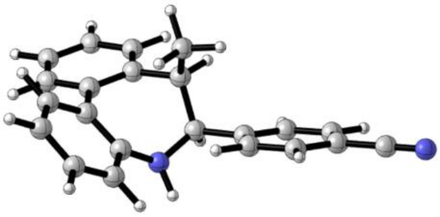
Figure S4. Optimized (wb97xd/def2svp/ cpcm=diisopropylether level) geometries of the transition structures corresponding to the conformational analysis of compound **2Aa** (R^1 = Me, R^2 = Ph).





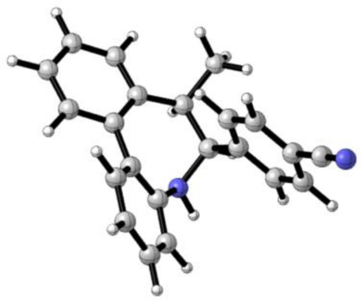
2An-C1a (R^1 = Me; R^2 = 4-NC-C_6H_4) **2An-C1b** (R^1 = Me; R^2 = 4-NC-C_6H_4)



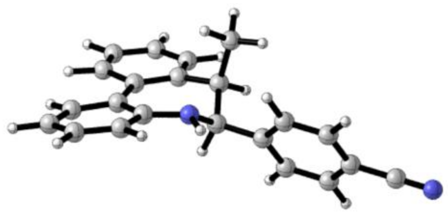


2An-C2a (R^1 = Me; R^2 = 4-NC-C_6H_4) **2An-C2b** (R^1 = Me; R^2 = 4-NC-C_6H_4)

Figure S5. Optimized (wb97xd/def2svp/ cpcm=diisopropylether level) geometries of the conformers of compound **2An** (R^1 = Me, R^2 = 4-NC-C_6H_4).

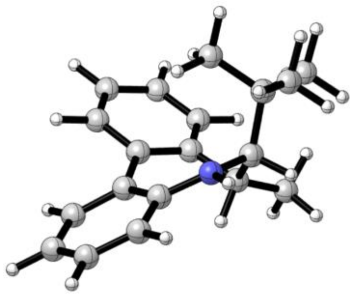


2An-TS1 (R^1 = Me; R^2 = 4-NC-C_6H_4) **2An-TS2** (R^1 = Me; R^2 = 4-NC-C_6H_4)

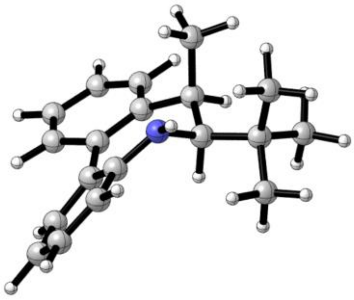


2An-TS3 (R^1 = Me; R^2 = 4-NC-C_6H_4)

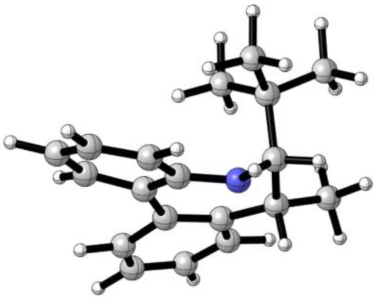
Figure S6. Optimized (wb97xd/def2svp/ cpcm=diisopropylether level) geometries of the transition structures corresponding to the conformational analysis of compound **2An** (R^1 = Me, R^2 = 4-NC-C_6H_4).



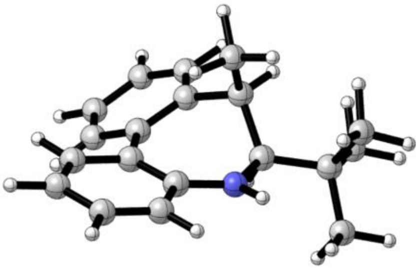
2Aw-C1a (R¹ = Me; R² = *tert*-Bu)



2Aw-C1b (R¹ = Me; R² = *tert*-Bu)

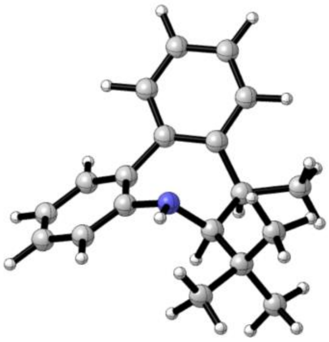


2Aw-C2a (R¹ = Me; R² = *tert*-Bu)

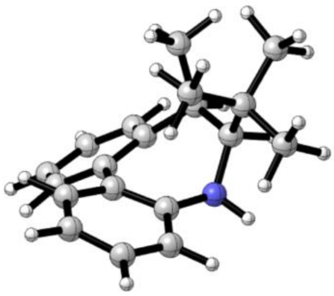


2Aw-C2b (R¹ = Me; R² = *tert*-Bu)

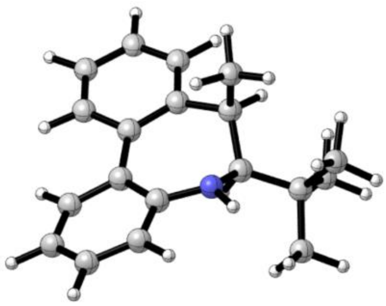
Figure S7. Optimized (wb97xd/def2svp/ cpcm=diisopropylether level) geometries of the conformers of compound **2Aw** (R¹ = Me, R² = *tert*-Bu).



2Aw-TS1 (R¹ = Me; R² = *tert*-Bu)

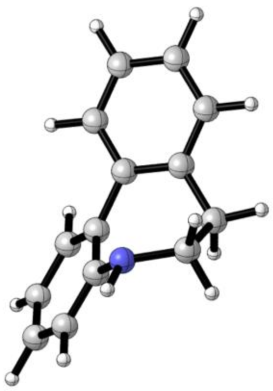


2Aw-TS2 (R¹ = Me; R² = *tert*-Bu)

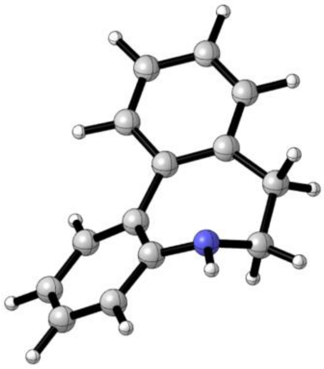


2Aw-TS3 (R¹ = Me; R² = *tert*-Bu)

Figure S8. Optimized (wb97xd/def2svp/ cpcm=diisopropylether level) geometries of the transition structures corresponding to the conformational analysis of compound **2Aw** (R¹ = Me, R² = *tert*-Bu).

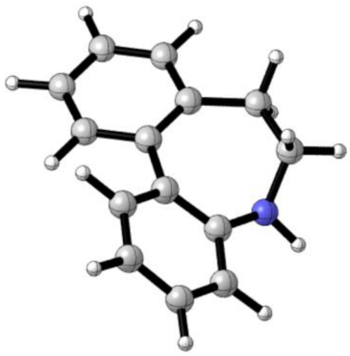


2Ax-C1a (R^1 = H; R^2 = H)

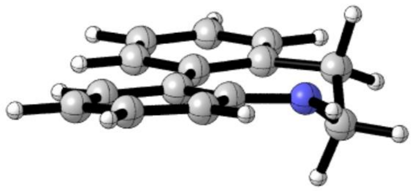


2Ax-C1b (R^1 = H; R^2 = H)

Figure S9. Optimized (wb97xd/def2svp/ cpcm=diisopropylether level) geometries of the conformers of compound **2Ax** (R^1 = H, R^2 = H).



2Ax-TS1 (R^1 = H; R^2 = H)

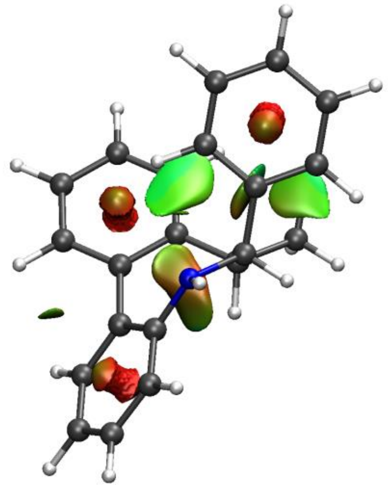


2Ax-TS3 (R^1 = H; R^2 = H)

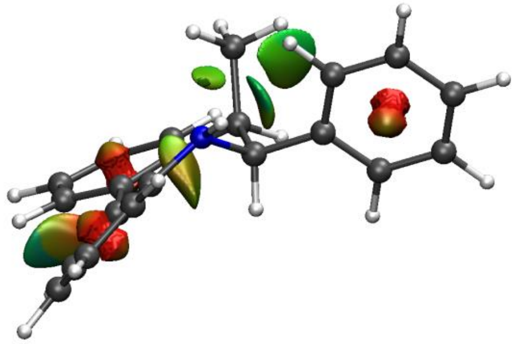
Figure S10. Optimized (wb97xd/def2svp/ cpcm=diisopropylether level) geometries of the transition structures corresponding to the conformational analysis of compound **2Ax** (R^1 = H, R^2 = H).

NCI calculations

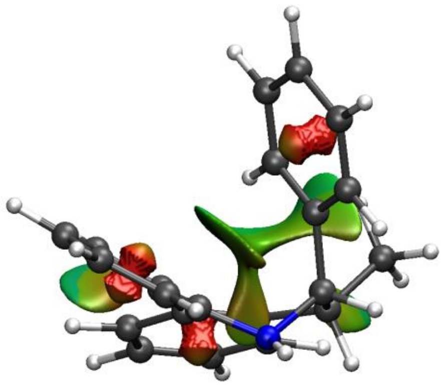
Quantitative NCI calculations were carried out for the conformers derived from **2Aa** (R^1 = Me, R^2 = Ph) and **2Aw** (R^1 = Me, R^2 = *tert*-Bu). These calculations give an idea of non-covalent interactions. From the inspection of the surfaces it can be suggested that for compound **2Aa** the conformer with less repulsive interactions is **2Aa-C1a**. On the other hand, for compound **2Aw**, the conformer with less repulsive interactions is **2Aa-C2b**. For this compound, conformer **2Aw-C1a** presents more gauche interactions. Nevertheless, the quantitative analyses are too close in their values to be conclusive, even though the above mentioned trend can be appreciated.



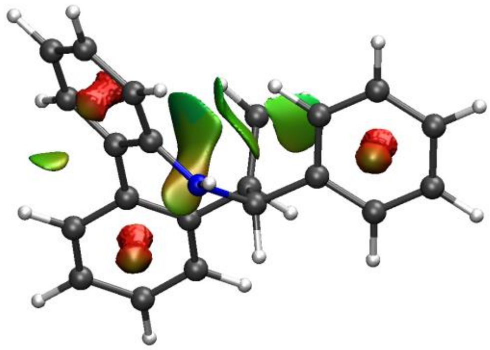
2Aa-C1a (R^1 = Me; R^2 = Ph)



2Aa-C1b (R^1 = Me; R^2 = Ph)

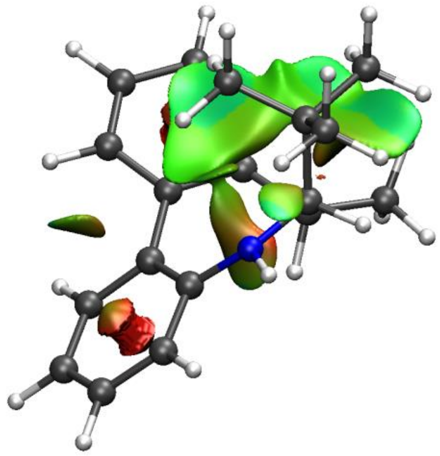


2Aa-C2a (R^1 = Me; R^2 = Ph)

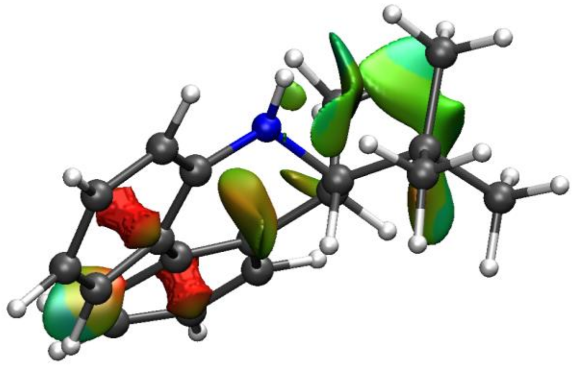


2Aa-C2b (R^1 = Me; R^2 = Ph)

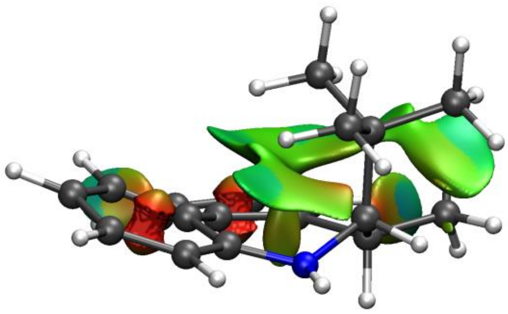
Figure S11. NCI analysis of conformers for compound **2Aa** (R^1 = Me, R^2 = Ph). Thin, delocalized green surface indicates van der Waals interactions. Small, lenticular, bluish surfaces indicate strong interactions such as hydrogen bonding. Steric clashes are shown as red isosurfaces.



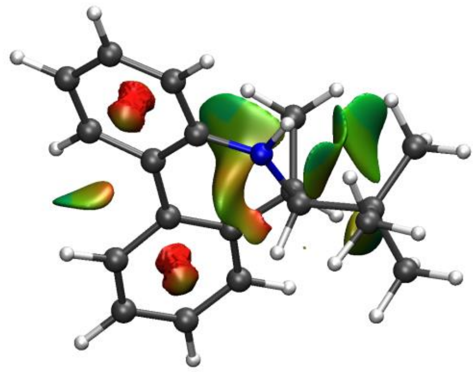
2Aw-C1a (R^1 = Me; R^2 = *tert*-Bu)



2Aw-C1b (R^1 = Me; R^2 = *tert*-Bu)

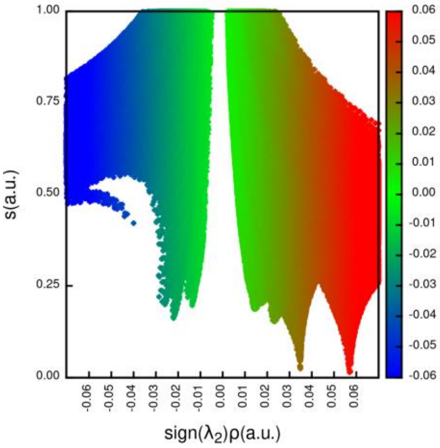


2Aw-C2a (R^1 = Me; R^2 = *tert*-Bu)

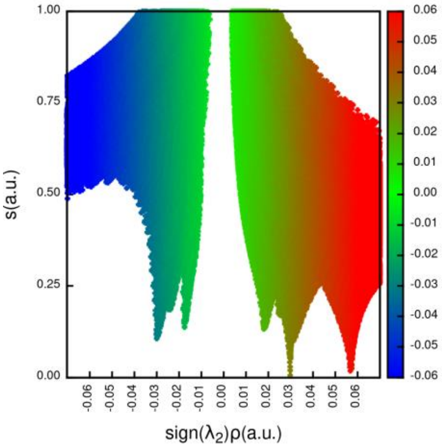


2Aw-C2b (R^1 = Me; R^2 = *tert*-Bu)

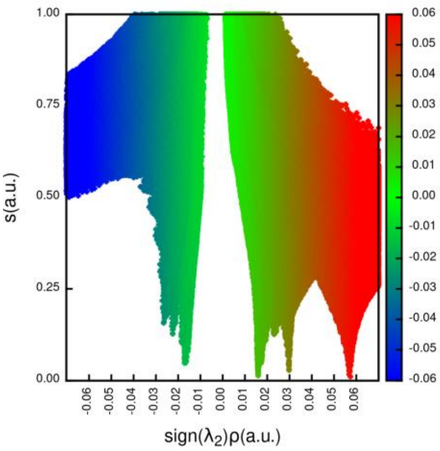
Figure S12. NCI analysis of conformers for compound **2Aw** (R^1 = Me, R^2 = *tert*-Bu). Thin, delocalized green surface indicates van der Waals interactions. Small, lenticular, bluish surfaces indicate strong interactions such as hydrogen bonding. Steric clashes are shown as red isosurfaces.



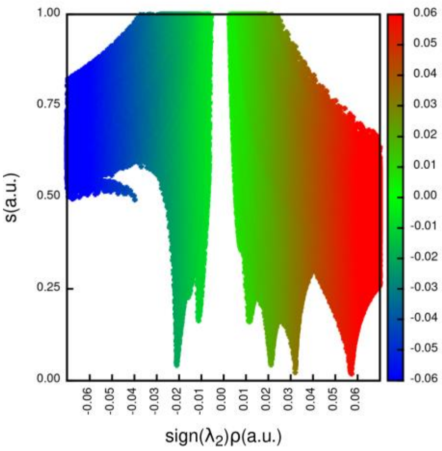
2Aa-C1a (R^1 = Me; R^2 = Ph)



2Aa-C1b (R^1 = Me; R^2 = Ph)

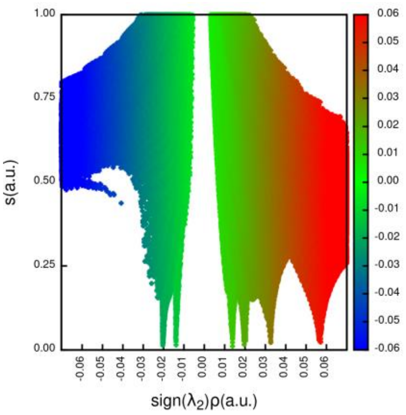


2Aa-C2a (R^1 = Me; R^2 = Ph)

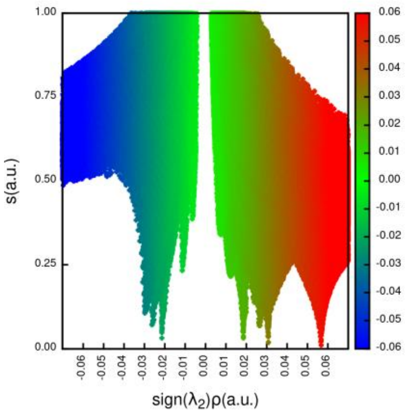


2Aa-C2b (R^1 = Me; R^2 = Ph)

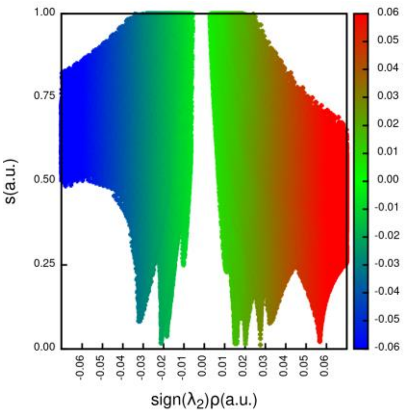
Figure S13. s(**r**) against *sign*(λ_2)ρ(**r**) plots for conformers of compound **2Aa** (R^1 = Me, R^2 = Ph). Blue area corresponds to strong NCI (H-bond, halogen, etc.); green area corresponds to van der Waals interactions and red area corresponds to repulsive interactions (steric clashes, etc.)



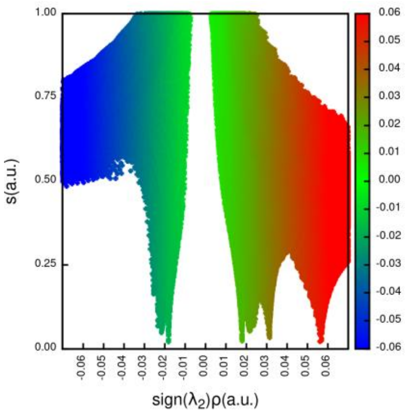
2Aw-C1a (R^1 = Me; R^2 = *tert*-Bu)



2Aw-C1b (R^1 = Me; R^2 = *tert*-Bu)



2Aw-C2a (R^1 = Me; R^2 = *tert*-Bu)



2Aw-C2b (R^1 = Me; R^2 = *tert*-Bu)

Figure S14. s(**r**) against *sign*(λ_2)ρ(**r**) plots for conformers of compound **2Aw** (R^1 = Me, R^2 = *tert*-Bu). Blue area corresponds to strong NCI (H-bond, halogen, etc.); green area corresponds to van der Waals interactions and red area corresponds to repulsive interactions (steric clashes, etc.)

Table S8. Integration over the volumes of *sign*(λ_2)ρ(**n**) according to ref. 7 for the NCI anaysis of conformers of compound **2Aa** (R^1 = Me, R^2 = Ph). A value of n=2.5 has been selected.[a]

interval	2-Aa-C1a	2-Aa-C1b	2-Aa-C2a	2-Aa-C2b
all	-1.91340375	-1.91845067	-1.91539783	-1.91831888
-1.0 to -0.02	**-0.13427248**	-0.13818054	-0.13530882	-0.13749164
-0.02 to 0.02	0.00247284	0.00247533	0.00237806	0.00251146
0.02 to 1.0	0.26053374	0.26245422	0.25972112	0.26238465

[a] The interval [-0.1, -0.02] gives information about strong NCI (H-bond, halogen, etc.). The interval [-0.02, 0.02] gives information about van der Waals interactions. The interval [0.02, 1.00] gives information about repulsive interactions (steric clashes, etc.).

Table S9. Integration over the volumes of *sign*(λ_2)ρ(**n**) according to ref. 7 for the NCI anaysis of conformers of compound **2Aw** (R^1 = Me, R^2 = *tert*-Bu). A value of n=2.5 has been selected.[a]

interval	2-Aw-C1a	2-Aw-C1b	2-Aw-C2a	2-Aw-C2b
all	-1.86361908	-1.86371795	-1.86462397	-1.86167954
-1.0 to -0.02	-0.13205122	-0.13513051	-0.13196776	-0.13407211
-0.02 to 0.02	0.00224793	0.00246851	0.00239254	0.00237936
0.02 to 1.0	0.25564306	0.26061294	0.25861175	0.26074991

[a] The interval [-0.1, -0.02] gives information about strong NCI (H-bond, halogen, etc.). The interval [-0.02, 0.02] gives information about van der Waals interactions. The interval [0.02, 1.00] gives information about repulsive interactions (steric clashes, etc.).

Cartesian Coordinates

2Aa-C1a

0 1

C	-0.1214307897	-1.1455448481	0.7549147934
C	-1.3051676785	-1.2496548360	-0.0032175099
C	-1.5763672670	-2.4376516974	-0.6943793078
C	-0.6917386299	-3.5126224158	-0.6505961273
C	0.4812444447	-3.4073573805	0.0930635756
C	0.7568381709	-2.2319458949	0.7902217420
H	-2.4883021380	-2.5099747443	-1.2918717615
H	-0.9166484224	-4.4275360132	-1.2029804475
H	1.1864869669	-4.2404523848	0.1318033495
H	1.6787754425	-2.1647599071	1.3698096735
C	-2.2588928954	-0.1131537520	-0.0864294725
C	-1.7943600350	1.1973610517	-0.3507706891
C	-3.6367882260	-0.3314906446	0.0284758891
C	-2.7317331604	2.2276888341	-0.5217364127
C	-4.5588201601	0.6992300243	-0.1402753613
H	-3.9900478971	-1.3417001527	0.2500964862
C	-4.0989355966	1.9827869291	-0.4298808085
H	-2.3708459723	3.2380099801	-0.7324140144
H	-5.6281305473	0.4995276130	-0.0483336441
H	-4.8054382578	2.8040084891	-0.5703014977
C	0.1538668021	0.1445941930	1.4999713271
H	-0.8051339152	0.4665767632	1.9399678853
C	0.5587614308	1.2806485491	0.5254954734
H	0.6088370224	2.1970134136	1.1472903815
N	-0.4299903407	1.4519113873	-0.5373804986
C	1.9350588757	1.0692387795	-0.0805369649
C	3.0591060297	1.6746594734	0.4902316294
C	2.1107237305	0.2375865067	-1.1927683072
C	4.3348876069	1.4444605784	-0.0251536187
H	2.9341268640	2.3370428654	1.3514391932
C	3.3837923004	0.0050105764	-1.7099372418
H	1.2331498497	-0.2195289045	-1.6532756481
C	4.5006675009	0.6051125307	-1.1262635167
H	5.2013430545	1.9274258661	0.4323136427
H	3.5050351797	-0.6484326596	-2.5770233598
H	5.4978022354	0.4245595341	-1.5341611865
C	1.1436436578	0.0181111785	2.6540828231
H	1.2205607200	0.9724911745	3.1961812007
H	2.1549496136	-0.2485682253	2.3147974538
H	0.8076791717	-0.7497940477	3.3656723175
H	-0.2777537413	2.3332632173	-1.0157274401

2Aa-C1b

0 1

C	1.1888815749	-1.5147865379	-0.1503249824
C	2.1304849782	-0.4571908372	-0.0919828075
C	3.4980463907	-0.8238841230	-0.0797058114
C	3.9410208889	-2.1295419514	-0.2185590246
C	3.0076662356	-3.1514351813	-0.3772735329
C	1.6611795547	-2.8286526781	-0.3277914981
H	4.2491092042	-0.0482369640	0.0665169712
H	5.0114216651	-2.3448233747	-0.2002135702
H	3.3233250326	-4.1878066860	-0.5138214899
H	0.9238188035	-3.6313803218	-0.4166889965
C	1.8602573240	1.0226004795	-0.0475993249
C	0.7133513262	1.6348728585	0.5129753206
C	2.8568655048	1.8920888175	-0.5392943794
C	0.6875385928	3.0283985567	0.7081108640
C	2.8111170587	3.2703966317	-0.3787497973
H	3.7071379684	1.4699345212	-1.0753575823
C	1.7292560160	3.8417559139	0.2913938092
H	-0.1978829385	3.4711685165	1.1724291740
H	3.6160121677	3.8924007886	-0.7744954763
H	1.6757605414	4.9209205901	0.4506062980
C	-0.3208247379	-1.4293332299	0.0330917882
H	-0.7690172533	-2.0689460051	-0.7461050036
C	-0.9075018920	-0.0254992530	-0.1755864076
H	-0.5663656580	0.3222441462	-1.1684347125
N	-0.4201008217	0.9005337837	0.8416627173
C	-2.4242358592	-0.0550731086	-0.2240371193
C	-3.0607126491	-0.2898410699	-1.4484795548
C	-3.2172415211	0.1101106782	0.9181280260
C	-4.4500272993	-0.3572404800	-1.5332617267
H	-2.4567615074	-0.4172626732	-2.3510893735
C	-4.6085943988	0.0502779843	0.8355145186
H	-2.7507550981	0.2756452735	1.8923552632
C	-5.2301736250	-0.1849267658	-0.3896945520
H	-4.9258358844	-0.5377752303	-2.4996899349
H	-5.2088747873	0.1834516070	1.7382196723
H	-6.3193293084	-0.2322993140	-0.4540936087
C	-0.7110980842	-2.0064058138	1.4000461556
H	-1.8022152412	-2.1016791665	1.4944964704
H	-0.3464677450	-1.3489584421	2.2027259485
H	-0.2735143407	-3.0031187626	1.5468912056
H	-1.1555371779	1.5028168230	1.1921670646

2Aa-C2a

0 1

C	1.8702436488	-0.9380093369	-0.3039613784
C	1.8109595801	0.4293582824	0.0621181583
C	2.9913353524	1.0300514720	0.5567624557
C	4.1795738823	0.3389996667	0.7297458304
C	4.2310938358	-1.0093968138	0.3845970572

C	3.0942193512	-1.6128449726	-0.1302266231
H	2.9773875462	2.0961009803	0.7862306885
H	5.0623680455	0.8558591673	1.1116309947
H	5.1543724896	-1.5823127967	0.4938179321
H	3.1598712469	-2.6598796246	-0.4324652144
C	0.6314310327	1.3442716373	-0.0437748536
C	-0.3080424622	1.2842217909	-1.0941081111
C	0.4801200003	2.3756331341	0.9003816770
C	-1.2651918816	2.3004782884	-1.2326840553
C	-0.4881713653	3.3650540572	0.7761447385
H	1.1430745139	2.4008728800	1.7669979164
C	-1.3478849861	3.3450933489	-0.3215801463
H	-1.9767000719	2.2393816658	-2.0605383127
H	-0.5685888767	4.1480638770	1.5325031924
H	-2.1071468837	4.1198954266	-0.4483398469
C	0.7788060297	-1.7907316715	-0.9568932777
H	1.2088349063	-2.0415101767	-1.9415097354
C	-0.5535970979	-1.1194083551	-1.3223723703
H	-0.9757498534	-1.7567963011	-2.1139452367
N	-0.3280139715	0.1868137219	-1.9610769459
C	-1.6223024202	-1.0545336439	-0.2352272914
C	-2.9662428325	-1.1340318457	-0.6192174640
C	-1.3331083001	-0.8370698033	1.1172177503
C	-3.9939361338	-0.9940536133	0.3121924741
H	-3.2140428726	-1.3060269290	-1.6710527063
C	-2.3565145563	-0.6970887322	2.0538441402
H	-0.2959847548	-0.7743858801	1.4505466720
C	-3.6905077724	-0.7720972854	1.6551071448
H	-5.0349408434	-1.0611495321	-0.0119361499
H	-2.1071323080	-0.5259500663	3.1034093541
H	-4.4913662932	-0.6614032784	2.3895341539
C	0.5286182388	-3.1244166953	-0.2351606393
H	1.4086808414	-3.7797207005	-0.2671596131
H	0.2566074353	-2.9767452238	0.8189241724
H	-0.2978052185	-3.6661295371	-0.7203794120
H	-0.9958712212	0.3343594187	-2.7098591193

2Aa-C2b

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C	-1.2914956657	-1.4854743769	-0.2343437349
C	-2.2070914591	-0.4484521376	0.0287412965
C	-3.5400099742	-0.7806321729	0.3180926431
C	-3.9707999273	-2.1036637218	0.3452395020
C	-3.0631682228	-3.1284543817	0.0857330360
C	-1.7371646045	-2.8115255474	-0.1985097531
H	-4.2482526858	0.0185932527	0.5480770775
H	-5.0127047860	-2.3326787155	0.5791750251
H	-3.3841992020	-4.1721289754	0.1071132813
H	-1.0240290720	-3.6142670542	-0.4055982457

C	-1.8067877870	0.9826131206	0.0165364101
C	-0.6077245668	1.4261478815	0.6244975336
C	-2.6598682803	1.9341182660	-0.5601202874
C	-0.3536893142	2.8094758731	0.6793508655
C	-2.3891257027	3.2982087125	-0.5153330647
H	-3.5671129504	1.5849209848	-1.0590303784
C	-1.2319195797	3.7348376246	0.1286648821
H	0.5630889944	3.1547141565	1.1654417340
H	-3.0759254888	4.0113275839	-0.9747816513
H	-0.9989347944	4.8004672045	0.1875609425
C	0.1589510506	-1.2017037885	-0.5674338169
H	0.6354960807	-2.1802865247	-0.7336122382
C	0.8997723925	-0.6364216258	0.6688344635
H	0.8391921355	-1.4355886128	1.4280760222
N	0.2876084250	0.5575843373	1.2407874373
C	2.3783596045	-0.4311774087	0.3669388184
C	3.2677768214	-1.5017732445	0.5073578506
C	2.8718376206	0.7960198199	-0.0896091297
C	4.6180006969	-1.3551927411	0.1928462399
H	2.8968312258	-2.4639590413	0.8726635402
C	4.2224757161	0.9472493253	-0.4024256914
H	2.1910529132	1.6416825458	-0.2123570961
C	5.0999732330	-0.1279756343	-0.2632510756
H	5.2985785210	-2.2013274932	0.3114821161
H	4.5907050053	1.9116135950	-0.7595990459
H	6.1581251472	-0.0090157757	-0.5061925461
C	0.3441134836	-0.4134771792	-1.8714865235
H	1.4036133849	-0.3946450366	-2.1632451873
H	-0.0056915845	0.6250979692	-1.8028505279
H	-0.2199162822	-0.9051946843	-2.6774577497
H	0.9361394783	1.0462086207	1.8462450261

2Aa-TS1

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C	-1.1670020299	-1.5238136780	0.2420519951
C	-2.1603126877	-0.5194343973	0.1010598615
C	-3.4796723478	-0.9063496439	-0.2060237077
C	-3.8570019548	-2.2316499555	-0.3688106190
C	-2.8871153906	-3.2184238459	-0.2426792901
C	-1.5774934158	-2.8556752408	0.0515244268
H	-4.2283868511	-0.1269215758	-0.3572394891
H	-4.8911796230	-2.4834259956	-0.6124409910
H	-3.1391274290	-4.2724298750	-0.3785909249
H	-0.8503980940	-3.6592127530	0.1427158051
C	-1.9411180744	0.9555672296	0.1494265002
C	-0.8361361698	1.5395196631	-0.4988037093
C	-2.9213187374	1.8083365411	0.6802831768
C	-0.7898771759	2.9264018235	-0.6921948765
C	-2.8592596338	3.1888669015	0.5137342737

H	-3.7612022961	1.3749129705	1.2278858797
C	-1.8028224712	3.7468919215	-0.2063299758
H	0.0691608818	3.3608223644	-1.2105193971
H	-3.6385747700	3.8255661281	0.9369995685
H	-1.7489404157	4.8265343068	-0.3628171775
C	0.2840221830	-1.2869063084	0.6950564843
H	0.2433977039	-1.2733833938	1.7992863017
C	0.8777553686	0.1129603502	0.3084593932
H	0.6793967178	0.7717628560	1.1716460397
N	0.2358999724	0.7160219763	-0.8699396118
C	2.3838024018	0.1115370430	0.1309777443
C	3.2135652026	0.4114260547	1.2155795194
C	2.9751365865	-0.2008763146	-1.1000250284
C	4.6017664452	0.3923420817	1.0802364190
H	2.7664701705	0.6625801602	2.1811879880
C	4.3614007587	-0.2132124246	-1.2402626475
H	2.3447039648	-0.4505044545	-1.9572292600
C	5.1803339717	0.0802924879	-0.1493099585
H	5.2336195141	0.6298349258	1.9389741077
H	4.8052874424	-0.4591851022	-2.2075284395
H	6.2669140886	0.0688138111	-0.2587607026
C	1.2158881905	-2.4503811800	0.3301112196
H	2.2352534665	-2.2519719660	0.6819703340
H	1.2575619752	-2.6182120907	-0.7573657095
H	0.9033948892	-3.3851949756	0.8114106770
H	0.9173206723	1.2468925745	-1.4030171998

2Aa-TS2

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C	1.9016649797	-0.8412885386	-0.1786630885
C	1.7391494905	0.5370227357	0.1033127618
C	2.8537026217	1.2362558790	0.6214455456
C	4.0709666794	0.6323248705	0.8916044018
C	4.2232507212	-0.7267447694	0.6263925894
C	3.1534634157	-1.4274152037	0.0918628039
H	2.7634168507	2.3098075121	0.7901951359
H	4.8989881057	1.2241280148	1.2871373119
H	5.1729370771	-1.2327327013	0.8126065037
H	3.2948745541	-2.4839782033	-0.1473798881
C	0.5135941619	1.3692736894	-0.1134621000
C	-0.3671418660	1.1945826484	-1.2022037194
C	0.2579090783	2.4450223138	0.7560561265
C	-1.3648901048	2.1486910349	-1.4523750843
C	-0.7513096967	3.3717143601	0.5221143955
H	0.8715011340	2.5579787661	1.6515375478
C	-1.5479552797	3.2409086707	-0.6148623173
H	-2.0279452582	1.9994004242	-2.3087847188
H	-0.9119218876	4.1924725168	1.2236895961
H	-2.3368899967	3.9653284119	-0.8285989015

C	0.9112378072	-1.7906290938	-0.8602373417
H	1.4014681933	-1.9819722401	-1.8283864646
C	-0.4537811382	-1.2290079787	-1.2787285127
H	-0.8344396941	-1.9404740750	-2.0280299997
N	-0.2919790946	0.0455341400	-1.9950892278
C	-1.5310441173	-1.1449923812	-0.1995444511
C	-2.8727649776	-1.1763344298	-0.5976325599
C	-1.2469313572	-0.9625826975	1.1581786186
C	-3.9035901961	-1.0192803212	0.3268873135
H	-3.1157497698	-1.3214137210	-1.6546255222
C	-2.2740906033	-0.8070804616	2.0885434982
H	-0.2104214708	-0.9426394076	1.5004399167
C	-3.6057038452	-0.8310365027	1.6765814253
H	-4.9432253805	-1.0470806769	-0.0072122948
H	-2.0294017366	-0.6636749651	3.1433599795
H	-4.4095756235	-0.7075003511	2.4056121464
C	0.7486016213	-3.1624052961	-0.1600422997
H	0.9411197967	-3.9879345273	-0.8596692302
H	1.4309897736	-3.2825786389	0.6912759932
H	-0.2698193788	-3.2968156083	0.2293116787
H	-0.9330935888	0.1036198019	-2.7783105677

2Aa-TS3

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C	-0.9956239805	-1.5835977469	-0.1233506900
C	-2.0719646154	-0.6808119662	0.0834964614
C	-3.3453055351	-1.2824410366	0.2387368187
C	-3.5613785778	-2.6520087704	0.2535970501
C	-2.4860869383	-3.5215855191	0.1041125473
C	-1.2306083298	-2.9695676148	-0.0878629187
H	-4.2339555563	-0.6667922617	0.3376816138
H	-4.5770747217	-3.0327724303	0.3801415869
H	-2.6232110895	-4.6045594798	0.1222664279
H	-0.3754253323	-3.6352646829	-0.2329149136
C	-2.0052333992	0.8341477475	0.1361102071
C	-0.8782690353	1.6640586776	-0.1345822179
C	-3.1941571269	1.5343637246	0.4614664865
C	-1.0409748356	3.0695510385	-0.1961455543
C	-3.3355460075	2.9109862394	0.4309510863
H	-4.0756263057	0.9791479921	0.7677312368
C	-2.2415878721	3.6955445500	0.0644325251
H	-0.1612080425	3.6709717949	-0.4411031445
H	-4.2934520716	3.3643787605	0.6913806505
H	-2.3163896398	4.7836787413	0.0107075182
C	0.4337899586	-1.2215825826	-0.4704338944
H	1.0566099620	-2.0523575016	-0.1039680277
C	0.9457497255	0.0333600504	0.2568479527
H	0.6086522374	-0.0417640884	1.3089878934
N	0.4157766335	1.2295777981	-0.3506520954

C	2.4630561724	0.0718388834	0.2778484623
C	3.1454854366	-0.5563384538	1.3265670739
C	3.2119080664	0.6774902161	-0.7382670273
C	4.5380206343	-0.5815643166	1.3611776012
H	2.5750847758	-1.0303535926	2.1300921371
C	4.6068561747	0.6585907791	-0.7030949899
H	2.7052236841	1.1664436568	-1.5736206846
C	5.2747599383	0.0280992088	0.3449878229
H	5.0507752326	-1.0741916947	2.1902648521
H	5.1732533592	1.1380258419	-1.5045577346
H	6.3664246545	0.0133384726	0.3721499806
C	0.6124384778	-1.1426417020	-1.9894873342
H	1.6638569129	-0.9635934369	-2.2585342108
H	0.0037144248	-0.3308829495	-2.4123548873
H	0.2990261211	-2.0874328299	-2.4563316041
H	1.0746284304	1.9975424841	-0.3552410634

2An-C1a

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C	0.1426781854	1.1306922151	0.7444237756
C	1.3198950966	1.1915316185	-0.0283527329
C	1.6135954408	2.3612017639	-0.7411453934
C	0.7578055661	3.4595166411	-0.7040794806
C	-0.4080602744	3.3973785928	0.0553331542
C	-0.7062339540	2.2404259434	0.7737078563
H	2.5200109220	2.4007519723	-1.3498973171
H	0.9999461566	4.3594785631	-1.2733676136
H	-1.0902220280	4.2495519222	0.0899092648
H	-1.6220611247	2.2076807547	1.3659012516
C	2.2441057943	0.0302948577	-0.1013559066
C	1.7465981271	-1.2727079408	-0.3380384624
C	3.6277724087	0.2164547802	0.0018328277
C	2.6561650160	-2.3295715651	-0.4935830677
C	4.5225685103	-0.8399499122	-0.1522427233
H	4.0073625724	1.2213081266	0.2029963257
C	4.0294453856	-2.1171083279	-0.4139216993
H	2.2693834851	-3.3345741415	-0.6823186589
H	5.5969843970	-0.6652415383	-0.0700642734
H	4.7144142895	-2.9582465052	-0.5420004912
C	-0.1622072573	-0.1426856729	1.5071981552
H	0.7896484568	-0.4912485548	1.9416731353
C	-0.6061079604	-1.2754818784	0.5446996743
H	-0.7011524450	-2.1814796229	1.1753425182
N	0.3743361911	-1.4992045892	-0.5136190379
C	-1.9689582810	-1.0043993531	-0.0671249820
C	-3.1247021817	-1.5253707077	0.5239866505
C	-2.0944699493	-0.1982701117	-1.2047568382
C	-4.3842250116	-1.2387444404	0.0092851768
H	-3.0392630326	-2.1681379440	1.4033675921

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H -1.1924201574 0.1895228808 -1.6796291196
C -4.4980846902 -0.4192892562 -1.1218210273
H -5.2795320354 -1.6509060497 0.4772138568
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H -1.2385418599 -0.9222401254 3.2209804829
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2An-C1b

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C -3.4609699796 -0.9507584321 0.0264904361
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H -3.1604941548 -4.3233906845 0.2909146497
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C -1.8933193031 0.9543806494 0.0974057546
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H -3.7519403123 3.7142137064 0.9765143707
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C 0.3776766628 -1.4076555548 -0.1029586398
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C 0.9099698145 0.0070862868 0.1745006033
H 0.5621313579 0.2923889197 1.1846502984
N 0.3900221013 0.9633239190 -0.7958004440
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H 2.4763616094 -0.4671706893 2.3216353527
C 4.5961445964 0.2592475663 -0.8440367106
H 2.7341677709 0.4887160253 -1.8753135925
C 5.2280200053 -0.0313377142 0.3718117689
H 4.9464700491 -0.5204397090 2.4615939571

H	5.1933748953	0.4624475839	-1.7341034338
C	0.7913334688	-1.9010754263	-1.4956356274
H	1.8851969198	-1.9585180154	-1.5911146663
H	0.4073325981	-1.2165563466	-2.2658781342
H	0.3868532571	-2.9026027745	-1.6938468758
H	1.0994415507	1.6143781207	-1.1109999874
C	6.6642816575	-0.0548966040	0.4502740995
N	7.8200655303	-0.0741427446	0.5131405199

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C	1.9201382664	-0.8547572521	-0.2155494039
C	1.7816127676	0.5251846609	0.0725605096
C	2.9194869708	1.2160709801	0.5481805327
C	4.1403438552	0.6011997150	0.7733610141
C	4.2700485554	-0.7591645409	0.5037479750
C	3.1755822721	-1.4516832241	0.0096742699
H	2.8442109334	2.2906245545	0.7183587174
H	4.9880885878	1.1854003476	1.1369592777
H	5.2213185061	-1.2735042491	0.6554349766
H	3.3021890278	-2.5085311775	-0.2334718839
C	0.5557226524	1.3660501302	-0.0989128812
C	-0.3595082008	1.1991796435	-1.1585162050
C	0.3290167536	2.4331106545	0.7890325730
C	-1.3726974167	2.1472707133	-1.3629011474
C	-0.6936821071	3.3551834609	0.6001921385
H	0.9752081104	2.5415233611	1.6619342939
C	-1.5321834972	3.2290931242	-0.5069028930
H	-2.0646866117	2.0034663897	-2.1970155280
H	-0.8331074103	4.1691697840	1.3139880066
H	-2.3333942521	3.9499329567	-0.6832909823
C	0.8857947082	-1.8015799884	-0.8303125112
H	1.3456779176	-2.0919390126	-1.7899696568
C	-0.4689961956	-1.2219927750	-1.2623084537
H	-0.8448193988	-1.9256289525	-2.0200629667
N	-0.3014044431	0.0566794319	-1.9661339574
C	-1.5624331566	-1.1432139134	-0.2003768370
C	-2.8928842701	-1.3004422369	-0.6072860051
C	-1.3092943116	-0.8315484640	1.1410512999
C	-3.9465694116	-1.1445065241	0.2848615642
H	-3.1114534107	-1.5459910186	-1.6498024947
C	-2.3500687359	-0.6712885252	2.0482899571
H	-0.2842887278	-0.7075927445	1.4915859280
C	-3.6760243641	-0.8241339158	1.6221155929
H	-4.9776149027	-1.2706065700	-0.0488848712
H	-2.1369961811	-0.4239733588	3.0892500864
C	0.6870935982	-3.0984138875	-0.0295137531
H	1.6006583156	-3.7061536154	-0.0031121255
H	0.3868579061	-2.9014380153	1.0088889154

H	-0.0985469942	-3.7136510008	-0.4945282857
H	-0.9527392970	0.1274847062	-2.7402505973
C	-4.7574048099	-0.6564147566	2.5557125942
N	-5.6283255179	-0.5212058755	3.3065231969

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C	1.2908384015	-1.4983482308	0.2185320191
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C	3.5400214404	-0.7667596034	-0.2943514573
C	3.9828758068	-2.0857194778	-0.3294184814
C	3.0809674870	-3.1213570103	-0.0946477809
C	1.7482089391	-2.8199285279	0.1749567652
H	4.2440318132	0.0414167051	-0.5051636221
H	5.0300885111	-2.3029951273	-0.5502266392
H	3.4118446608	-4.1617285120	-0.1229026012
H	1.0401915123	-3.6314174894	0.3645684692
C	1.7846186583	0.9760897528	-0.0063028278
C	0.5944961030	1.4066516030	-0.6385414974
C	2.6132753300	1.9356189877	0.5912593455
C	0.3235312761	2.7851645185	-0.6996457313
C	2.3249621421	3.2962602843	0.5422581127
H	3.5145153049	1.5970024019	1.1079483758
C	1.1781910513	3.7205188594	-0.1274581544
H	-0.5841850787	3.1203493557	-1.2092260052
H	2.9923173763	4.0173069948	1.0176963012
H	0.9349563581	4.7834680465	-0.1911257423
C	-0.1639051398	-1.2292868245	0.5461238789
H	-0.6332660899	-2.2126983322	0.7034250240
C	-0.9026907086	-0.6565166266	-0.6893897764
H	-0.8653916081	-1.4595580516	-1.4454504230
N	-0.2722629968	0.5184927938	-1.2747153137
C	-2.3736895344	-0.4278685885	-0.3700942155
C	-3.2776355975	-1.4903015811	-0.4810976548
C	-2.8430734850	0.8146023304	0.0709861543
C	-4.6184552290	-1.3270820425	-0.1548926436
H	-2.9262279143	-2.4634008167	-0.8337316593
C	-4.1815183965	0.9951870988	0.3996015235
H	-2.1510470476	1.6528531050	0.1703322827
C	-5.0763571762	-0.0780896394	0.2881247948
H	-5.3153591224	-2.1614254724	-0.2477665353
H	-4.5370641790	1.9666210633	0.7464963982
C	-0.3589760134	-0.4526535413	1.8562807119
H	-1.4165368986	-0.4563761975	2.1560746645
H	-0.0287712307	0.5927000365	1.7937162259
H	0.2180983932	-0.9394932203	2.6556821662
H	-0.8937799645	0.9875049570	-1.9229105790
C	-6.4634295204	0.1028146209	0.6233930847
N	-7.5797278469	0.2483271377	0.8938099967

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C	-1.1616612111	-1.5219945470	0.2420099783
C	-2.1534679134	-0.5168509144	0.0978537523
C	-3.4729501536	-0.9031437903	-0.2092914328
C	-3.8518392866	-2.2284774319	-0.3671987291
C	-2.8837981148	-3.2161875071	-0.2350728487
C	-1.5738514449	-2.8541884988	0.0581779904
H	-4.2205313115	-0.1233413069	-0.3637941741
H	-4.8860495148	-2.4797747126	-0.6109213914
H	-3.1373053956	-4.2704114290	-0.3658144650
H	-0.8488287598	-3.6589738149	0.1538877174
C	-1.9340834931	0.9581280977	0.1456415395
C	-0.8288934984	1.5429824419	-0.4999480081
C	-2.9142589464	1.8108837410	0.6768238644
C	-0.7792660327	2.9298473565	-0.6896392910
C	-2.8503476485	3.1915267004	0.5128830589
H	-3.7551179272	1.3774964240	1.2227963354
C	-1.7921625535	3.7504060508	-0.2037956461
H	0.0810444509	3.3645789463	-1.2055834051
H	-3.6298074698	3.8280524180	0.9360293690
H	-1.7369677018	4.8302608544	-0.3577807165
C	0.2911266315	-1.2872597182	0.6914400870
H	0.2566300543	-1.2783632472	1.7957005305
C	0.8813107126	0.1149629520	0.3068756585
H	0.6845686736	0.7728668846	1.1709360922
N	0.2444712371	0.7186090517	-0.8722137553
C	2.3865594752	0.1082241258	0.1315246325
C	3.2153138719	0.3971504659	1.2203238565
C	2.9755444807	-0.1959150743	-1.1029933886
C	4.5996228554	0.3775428748	1.0918479380
H	2.7704901899	0.6413464869	2.1876349908
C	4.3566297943	-0.2129867746	-1.2491448176
H	2.3460156534	-0.4364082604	-1.9623536475
C	5.1765712966	0.0716713464	-0.1478530393
H	5.2360220768	0.6050872840	1.9483158372
H	4.8049582205	-0.4525232717	-2.2145295593
C	1.2220691705	-2.4479833676	0.3143812049
H	2.2428929664	-2.2566540028	0.6665656789
H	1.2597924275	-2.6083380033	-0.7743251633
H	0.9107726378	-3.3860068922	0.7892958430
H	0.9237716716	1.2528162999	-1.4047810201
C	6.6078251417	0.0538334524	-0.2918449157
N	7.7595759974	0.0389375897	-0.4079101310

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C	1.9315692813	-0.7719922942	-0.2239975311
C	1.7192156414	0.5941137412	0.0818252012
C	2.8143741528	1.3307308772	0.5890737525
C	4.0599791882	0.7722884277	0.8257398864
C	4.2614230702	-0.5756715005	0.5374587434
C	3.2103890486	-1.3117673780	0.0136081956
H	2.6848831523	2.3971752124	0.7762442659
H	4.8715174180	1.3911962354	1.2137228034
H	5.2342073805	-1.0452347680	0.6976713975
H	3.3890762876	-2.3583641205	-0.2438977586
C	0.4559254272	1.3774068747	-0.0973498851
C	-0.4358005306	1.1862462370	-1.1738461499
C	0.1684110476	2.4221403122	0.7997970965
C	-1.4810801653	2.0972047419	-1.3860450867
C	-0.8866784366	3.3053677318	0.6036927011
H	0.7931279922	2.5451343616	1.6861657326
C	-1.6980424575	3.1617931669	-0.5212233612
H	-2.1523980903	1.9361351759	-2.2338229571
H	-1.0717827344	4.1030486123	1.3254436243
H	-2.5232139623	3.8532664227	-0.7046015701
C	0.9667353674	-1.7515641840	-0.8993275762
H	1.4471400636	-1.9162346683	-1.8770390432
C	-0.4227212966	-1.2359002238	-1.2930961105
H	-0.7920683782	-1.9529953241	-2.0423905879
N	-0.3250014818	0.0537966571	-1.9891091210
C	-1.4853243498	-1.1993217253	-0.1964794561
C	-2.8309538293	-1.2565029305	-0.5789154919
C	-1.1837904347	-1.0273363074	1.1590124517
C	-3.8531971909	-1.1339751160	0.3532731474
H	-3.0860176137	-1.3927039042	-1.6331339181
C	-2.1931420337	-0.9035589631	2.1068468418
H	-0.1443850574	-0.9882908022	1.4880926694
C	-3.5346626575	-0.9525758376	1.7063130061
H	-4.8970986380	-1.1795209625	0.0394206521
H	-1.9431414276	-0.7650988073	3.1596984223
C	0.8657054204	-3.1346742856	-0.2094806824
H	1.0805829392	-3.9460309217	-0.9188265686
H	1.5647642994	-3.2342825521	0.6308679289
H	-0.1407196875	-3.3157337983	0.1926220633
H	-0.9725171886	0.0989924053	-2.7679260701
C	-4.5839639582	-0.8217415637	2.6820752318
N	-5.4288913477	-0.7164502844	3.4666476106

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C	0.9889803919	-1.5798263049	0.1068216247
C	2.0659254847	-0.6747267888	-0.0832898598
C	3.3409282292	-1.2740118608	-0.2322248608

C	3.5574236006	-2.6433241786	-0.2583427084
C	2.4811425360	-3.5146591545	-0.1278076038
C	1.2237745352	-2.9653198906	0.0592885387
H	4.2300829846	-0.6568964970	-0.3162711251
H	4.5743220381	-3.0226573657	-0.3788133062
H	2.6188644036	-4.5972864640	-0.1557600434
H	0.3680159986	-3.6329386734	0.1913204551
C	1.9978185640	0.8403178196	-0.1263894135
C	0.8702591463	1.6682923804	0.1434125581
C	3.1874900618	1.5427875169	-0.4443103427
C	1.0300958254	3.0731224062	0.2098756335
C	3.3270926209	2.9193328024	-0.4077084219
H	4.0702418250	0.9894938168	-0.7501370646
C	2.2311510801	3.7016309996	-0.0432749214
H	0.1489265845	3.6729933115	0.4535829024
H	4.2855343929	3.3746073447	-0.6626048275
H	2.3045333972	4.7895614017	0.0145518929
C	-0.4413869567	-1.2214413153	0.4528062341
H	-1.0624176875	-2.0496612758	0.0776315128
C	-0.9502809123	0.0412142558	-0.2652012799
H	-0.6150788243	-0.0251900566	-1.3184043375
N	-0.4274590256	1.2328760472	0.3550687469
C	-2.4663464837	0.0702399586	-0.2830344040
C	-3.1462260880	-0.5667224152	-1.3286000792
C	-3.2137902664	0.6744040619	0.7351560346
C	-4.5339776398	-0.6045411565	-1.3640686197
H	-2.5772155776	-1.0396491476	-2.1324687117
C	-4.6043857159	0.6492194133	0.7112036413
H	-2.7078112236	1.1688017942	1.5665711212
C	-5.2710580255	0.0072867752	-0.3398503830
H	-5.0510226741	-1.1012128796	-2.1864073304
H	-5.1757189460	1.1240803653	1.5101825657
C	-0.6241516056	-1.1545722826	1.9719990391
H	-1.6763065562	-0.9818153583	2.2426719203
H	-0.0181082629	-0.3452451989	2.4028685957
H	-0.3092489266	-2.1027003988	2.4305081129
H	-1.0816325392	2.0050035532	0.3436764052
C	-6.7090378621	-0.0217262361	-0.3703316610
N	-7.8661955112	-0.0452082448	-0.3946639300

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C	0.1636317180	1.1764445460	0.9317604374
C	1.2061954355	1.1216134493	-0.0152951683
C	1.4239295186	2.2379441670	-0.8382118781
C	0.6632925493	3.3965756046	-0.7122713713
C	-0.3291658129	3.4649931752	0.2625532414
C	-0.5700263315	2.3581476502	1.0730369620
H	2.1968468579	2.1900530406	-1.6081925513

H	0.8503340798	4.2453635830	-1.3736004866
H	-0.9231766324	4.3730164202	0.3867662732
H	-1.3583807232	2.4171906680	1.8251646229
C	2.1058947689	-0.0589777811	-0.1471110008
C	1.6789465797	-1.4142204633	-0.0993489275
C	3.4746635321	0.1953346951	-0.3575901494
C	2.6492057096	-2.4239379467	-0.3085137421
C	4.4136242020	-0.8065283738	-0.5568737890
H	3.8077869101	1.2355967465	-0.3513432863
C	3.9822012294	-2.1346870485	-0.5429366000
H	2.3221066752	-3.4672067413	-0.2799002707
H	5.4645701012	-0.5571645677	-0.7125224385
H	4.6908436435	-2.9517714993	-0.6971448916
C	-0.1631541280	-0.0694920491	1.7206795296
H	0.7991239104	-0.4719456536	2.0801803768
C	-0.7141851964	-1.1984115193	0.8035620607
H	-1.0997173374	-1.9594316071	1.5063242773
N	0.3820070371	-1.8422535122	0.0862772566
C	-0.9907624424	0.1595375882	2.9861768626
H	-1.1070255603	-0.7867659226	3.5348344635
H	-1.9962485672	0.5529223842	2.7954888256
H	-0.4745822819	0.8692792859	3.6497201030
H	0.2968632636	-2.8482546582	0.0491256951
C	-1.9118577593	-0.9219991924	-0.1736687810
C	-1.5178329722	-0.0847502633	-1.3993433381
C	-2.3906308703	-2.2962795495	-0.6787470591
C	-3.0862721369	-0.2506243196	0.5467697617
H	-1.3367003161	0.9687719751	-1.1509262535
H	-0.6107518737	-0.4873275655	-1.8740774770
H	-2.3311325563	-0.1164547333	-2.1418653357
H	-2.6777730277	-2.9552079164	0.1572056520
H	-3.2702611744	-2.1794984854	-1.3303264062
H	-1.6106042764	-2.8029844295	-1.2664903047
H	-3.9584215783	-0.2076077600	-0.1241998759
H	-3.3867493845	-0.8103976648	1.4468348451
H	-2.8500341914	0.7815402045	0.8396198859

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C	-1.1921296647	-1.5956463160	0.1284195563
C	-2.1352721472	-0.5352466606	0.1043868406
C	-3.5035740880	-0.8974501018	0.1594294913
C	-3.9465484221	-2.1996237143	0.3238362552
C	-3.0104067042	-3.2247661448	0.4395554309
C	-1.6668708377	-2.9063270373	0.3295332601
H	-4.2568001864	-0.1186108256	0.0443249111
H	-5.0176233932	-2.4098191045	0.3572286007
H	-3.3225451946	-4.2598600261	0.5932632095
H	-0.9313590253	-3.7132249271	0.3924500436

C	-1.8740766554	0.9441806748	0.0158112337
C	-0.7569948058	1.5264856256	-0.6289456377
C	-2.8402956709	1.8346361815	0.5264346640
C	-0.7355038712	2.9082737513	-0.8898139465
C	-2.7958232042	3.2056884029	0.3054885965
H	-3.6641773138	1.4389771765	1.1214112817
C	-1.7520292981	3.7423503399	-0.4492025607
H	0.1244833699	3.3252175548	-1.4212968663
H	-3.5749448098	3.8495437928	0.7176937168
H	-1.7066282910	4.8137813469	-0.6566052740
C	0.3233705812	-1.5276293642	-0.0754085521
H	0.7500329606	-2.1429007079	0.7316623288
C	0.8795552887	-0.1098088979	0.0829500024
H	0.4812741222	0.2506108295	1.0498502858
N	0.3395096914	0.7504289900	-0.9658117132
C	0.7011936002	-2.1754682644	-1.4146391720
H	1.7648946835	-2.4480693967	-1.4423007588
H	0.4931446951	-1.4781321305	-2.2396895058
H	0.1256888536	-3.0941865041	-1.5914226518
H	1.0440228185	1.2695913367	-1.4728343985
C	2.4258676278	0.0694543465	0.2240893356
C	2.9874408372	-0.9868872148	1.1842510306
C	3.2007970287	-0.0043396899	-1.1031688210
C	2.6656644382	1.4612812082	0.8387588328
H	2.4234751303	-1.0082044506	2.1303696440
H	2.9623715279	-1.9962654711	0.7469527232
H	4.0368639613	-0.7576011970	1.4250994576
H	2.8949427273	0.7723707983	-1.8215732243
H	4.2713899758	0.1600092415	-0.9060272805
H	3.1017983370	-0.9767091560	-1.5999629539
H	3.7436139658	1.6616113423	0.9370964984
H	2.2335472126	2.2617403840	0.2184227014
H	2.2133416887	1.5350680894	1.8398066546

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C	1.8157291126	-0.7804729036	-0.0983651590
C	1.7504306500	0.6393509660	0.0031702230
C	2.8837187823	1.2965238923	0.5330773827
C	3.9797278968	0.6356585818	1.0676132343
C	3.9779516604	-0.7524445520	1.0854472117
C	2.9168985269	-1.4258499334	0.4936827250
H	2.9187382323	2.3844964059	0.5118042286
H	4.8217766251	1.2068738107	1.4638010703
H	4.8065245810	-1.3142785888	1.5218620768
H	2.9678314554	-2.5123053489	0.4765284616
C	0.6094729455	1.5446757827	-0.3678659080
C	-0.4003028691	1.2707254770	-1.3223333268
C	0.5325896787	2.8013127844	0.2736384811

C	-1.2676358600	2.3074256753	-1.7289355430
C	-0.3593807690	3.7991193550	-0.0920243892
H	1.2007125077	3.0074527131	1.1091789001
C	-1.2428156034	3.5618375498	-1.1451857820
H	-2.0069230229	2.0845760700	-2.5034966884
H	-0.3612042047	4.7520998956	0.4399378419
H	-1.9394814329	4.3336283501	-1.4796788414
C	0.8890146623	-1.6650774331	-0.9396343480
H	1.2927619062	-1.5446983110	-1.9595530244
C	-0.5763730872	-1.2231506872	-1.1378221104
H	-0.9714116219	-1.9504416715	-1.8647207941
N	-0.5949064522	0.0254977097	-1.8920511432
C	1.0064811561	-3.1650007503	-0.6384460249
H	1.9834615907	-3.5597268365	-0.9481416955
H	0.8740851786	-3.3997291520	0.4276679645
H	0.2478592772	-3.7217484265	-1.2056614596
H	-1.3430872922	0.0417894312	-2.5725357078
C	-1.5812292744	-1.3124340394	0.0756841896
C	-2.8518653324	-0.5188671818	-0.2711586612
C	-2.0169681016	-2.7765590104	0.2823845083
C	-1.0111089678	-0.7971367072	1.4046510443
H	-2.6671426998	0.5622904877	-0.3301841688
H	-3.2808038980	-0.8490349199	-1.2318444002
H	-3.6165133863	-0.6814179159	0.5039479072
H	-1.2106098560	-3.4098065677	0.6710713292
H	-2.8396253579	-2.8165955980	1.0132305390
H	-2.3830875990	-3.2254984503	-0.6549438675
H	-1.7562921029	-0.9385012049	2.2039806764
H	-0.1035317417	-1.3454977307	1.6977166291
H	-0.7647604223	0.2719901529	1.3642425889

2Aw-C2b

0 1

C	0.3967331378	-1.5432630004	0.4507467745
C	1.4786088806	-0.8447165428	-0.1317665027
C	2.5037610519	-1.6070632699	-0.7225940478
C	2.5026788152	-2.9980972776	-0.7000315369
C	1.4538749573	-3.6767816548	-0.0852555457
C	0.4088431188	-2.9421373825	0.4675847644
H	3.3203548330	-1.0949787685	-1.2346058978
H	3.3185675070	-3.5483488321	-1.1737782240
H	1.4368609582	-4.7683365833	-0.0544627930
H	-0.4366502464	-3.4660401272	0.9222237504
C	1.6253812446	0.6472980564	-0.1232152023
C	0.5722202080	1.6003188224	-0.2236373316
C	2.9355361727	1.1499953913	0.0247664228
C	0.9060833017	2.9772480261	-0.2216752680
C	3.2461908002	2.5010106294	0.0392997002
H	3.7464263055	0.4332946482	0.1654990882

C	2.2075328178	3.4251806371	-0.0968944580
H	0.0930881921	3.7021885518	-0.3191631139
H	4.2792331937	2.8282215414	0.1679443436
H	2.4109266914	4.4985440327	-0.0944996171
C	-0.8328731356	-0.8180982559	0.9500307942
H	-1.5760422322	-1.5921615267	1.1865523804
C	-1.3882941665	0.0095569166	-0.2492403871
H	-1.1091355003	-0.5538095780	-1.1583320154
N	-0.7658542512	1.3091149154	-0.3159195639
C	-0.5754791909	-0.0286306919	2.2390759193
H	-1.4573490810	0.5475846677	2.5477062336
H	0.2648895561	0.6710356840	2.1399393623
H	-0.3283582186	-0.7282359397	3.0511972580
H	-1.3752975357	2.1080866494	-0.2198418750
C	-2.9389431033	0.1327839523	-0.3454393914
C	-3.2972541526	0.9668979328	-1.5890586522
C	-3.5367444521	-1.2689942321	-0.5422312840
C	-3.5701154263	0.7759935747	0.8967961176
H	-3.0160318172	2.0257669847	-1.4904226192
H	-2.8001235555	0.5697491506	-2.4878723183
H	-4.3840508322	0.9371032434	-1.7610940715
H	-3.3715661512	-1.9219025602	0.3268868764
H	-4.6246236658	-1.1963594683	-0.6924043155
H	-3.1060597069	-1.7644438765	-1.4265206691
H	-4.6466277565	0.9362786754	0.7307593606
H	-3.4657670536	0.1330761904	1.7830433902
H	-3.1253925119	1.7555946943	1.1335821646

2Aw-TS1

0 1

C	-0.7753942912	-1.4921442228	0.2158393717
C	-1.7781907081	-0.4956933798	0.1082302181
C	-3.0828064046	-0.8601904124	-0.2620389530
C	-3.4297038133	-2.1737746076	-0.5551743117
C	-2.4425490165	-3.1495341003	-0.5015767513
C	-1.1480239039	-2.8035311689	-0.1199354951
H	-3.8362657405	-0.0759800089	-0.3619035700
H	-4.4522977886	-2.4220350327	-0.8468969004
H	-2.6711749172	-4.1878746506	-0.7521177174
H	-0.4139414216	-3.6052079284	-0.0790965455
C	-1.5195510210	0.9625771789	0.2246071379
C	-0.4032994407	1.5025452784	-0.4416811584
C	-2.4498266404	1.8394541708	0.7987618784
C	-0.2873442384	2.8903416965	-0.5916613578
C	-2.3154253508	3.2199671331	0.6739128799
H	-3.3049362308	1.4275487774	1.3402487963
C	-1.2440678045	3.7447005621	-0.0499028747
H	0.5751101556	3.2983712983	-1.1253050719
H	-3.0520978919	3.8844281671	1.1298924322

H	-1.1381248130	4.8249626492	-0.1724976324
C	0.6183714382	-1.2246426303	0.8191435620
H	0.4005248571	-0.9551536896	1.8671686789
C	1.3543591560	0.0568795037	0.2410368021
H	1.2999445101	0.7954926623	1.0623766223
N	0.5953149496	0.6205606820	-0.8877827138
C	1.4257489245	-2.5251065716	0.9088344334
H	2.3999112883	-2.3738843622	1.3795248999
H	1.5961926692	-2.9869390301	-0.0726892939
H	0.8909441767	-3.2536940133	1.5338083163
H	1.2105253570	1.0913171906	-1.5379803246
C	2.8873518095	0.0398285304	-0.0879242434
C	3.7060614389	-0.1112683994	1.2071868669
C	3.2895071053	-1.0099127779	-1.1359510141
C	3.2806726034	1.4287760625	-0.6462008596
H	3.5392345909	0.7531330051	1.8690923486
H	3.4713242430	-1.0129953128	1.7827357755
H	4.7802499116	-0.1453279821	0.9678827687
H	2.5777467207	-1.0209207427	-1.9762401198
H	4.2843322632	-0.7708723283	-1.5434703345
H	3.3439312068	-2.0238112346	-0.7235061234
H	4.3756082075	1.5340553214	-0.6217631360
H	2.9857413633	1.5784025019	-1.6966356138
H	2.8520724905	2.2455662157	-0.0435746724

2Aw-TS2

0 1

C	-1.5691325840	0.9944827627	-0.2279326680
C	-1.6714697284	-0.3760583320	0.0816786947
C	-2.9559509299	-0.9501605609	0.1838286732
C	-4.1167470447	-0.2171002330	-0.0145934270
C	-4.0163435726	1.1311133060	-0.3549300307
C	-2.7588516221	1.7091707782	-0.4575472463
H	-3.0375465431	-2.0198846810	0.3855668683
H	-5.0915422603	-0.7026393429	0.0665306503
H	-4.9112890336	1.7275029203	-0.5453295897
H	-2.6862657907	2.7701824817	-0.7141928453
C	-0.5228032115	-1.3138052066	0.1596974574
C	0.5374169702	-1.2091735086	-0.7659396881
C	-0.5643538444	-2.4355880654	1.0005876325
C	1.3863759733	-2.3110812280	-0.9569000324
C	0.3425900713	-3.4830401346	0.8716006588
H	-1.3444241088	-2.4960873765	1.7630436063
C	1.2903010532	-3.4401359700	-0.1519276880
H	2.1572553853	-2.2595707671	-1.7301626970
H	0.2880128663	-4.3421343205	1.5429413584
H	1.9774641053	-4.2751178471	-0.3057875564
C	-0.3052334723	1.8509605467	-0.1959807041
H	-0.5200337825	2.6459060908	-0.9254222910

C	1.0231742011	1.2109624624	-0.7471176014
H	1.3359735291	1.9051135976	-1.5422331084
N	0.7203894837	-0.0249067472	-1.4849304702
C	-0.2758638410	2.5752205118	1.1626096917
H	-1.2766422199	2.9776132906	1.3717568320
H	-0.0162802647	1.9072117020	1.9943884588
H	0.4157742576	3.4248450046	1.1623231736
H	1.3770227253	-0.1554133803	-2.2453876516
C	2.3242461054	1.1222791330	0.1453306170
C	3.4514570336	0.5588348487	-0.7429242869
C	2.7858011302	2.5316685923	0.5718837510
C	2.2189459080	0.2359344738	1.3991249166
H	3.2719475416	-0.4815328532	-1.0419936660
H	3.5869017395	1.1655088996	-1.6537138610
H	4.4035540682	0.5727474888	-0.1910789091
H	2.2631306662	2.9006847253	1.4610794378
H	3.8569955588	2.5065004265	0.8240687627
H	2.6548590503	3.2690090289	-0.2367299599
H	3.1262134124	0.3665491530	2.0113480051
H	1.3565816217	0.4956036480	2.0264406651
H	2.1406963970	-0.8306103184	1.1533070671

2Aw-TS3

0 1

C	-0.6322901896	-1.5938140014	-0.1038054901
C	-1.6313516649	-0.5999835737	0.0931100615
C	-2.9443359723	-1.0921780021	0.2897286686
C	-3.2635733055	-2.4400142203	0.3740513543
C	-2.2606090251	-3.3953843559	0.2506630949
C	-0.9704811748	-2.9526341464	0.0025222318
H	-3.7798741687	-0.4012939390	0.3604565416
H	-4.3031289979	-2.7357562006	0.5310643436
H	-2.4799342678	-4.4624531272	0.3244833552
H	-0.1729349896	-3.6883692559	-0.1333022736
C	-1.4555711846	0.9084006392	0.0847759609
C	-0.3029630011	1.6455797752	-0.3240319945
C	-2.5617767074	1.7030114799	0.4743913198
C	-0.3920188313	3.0469584668	-0.5031883606
C	-2.6243702160	3.0807529008	0.3452808279
H	-3.4339531532	1.2245875934	0.9125587318
C	-1.5315070081	3.7614156998	-0.1950132807
H	0.4973124594	3.5712033845	-0.8638433311
H	-3.5210530675	3.6163256665	0.6617661960
H	-1.5544288492	4.8441434186	-0.3367727883
C	0.8007346105	-1.3319322807	-0.5250778345
H	1.3844964830	-2.2040849825	-0.1987693483
C	1.3675250849	-0.0849485578	0.1750429578
H	0.9068136534	-0.0568014715	1.1818624633
N	0.9333004843	1.0890680912	-0.5410557656

C	0.8577671707	-1.2748625282	-2.0583419328
H	1.8703564693	-1.0713389823	-2.4301792436
H	0.1927748673	-0.4891069713	-2.4428774830
H	0.5258466146	-2.2355829636	-2.4792505018
H	1.6499991667	1.7492778402	-0.8050417865
C	2.8988332258	-0.0609738278	0.4595194108
C	3.2514000965	-1.2287306513	1.3935484540
C	3.7582728068	-0.1580091320	-0.8084322369
C	3.2368078580	1.2462462005	1.1999145938
H	2.6502834786	-1.1971419279	2.3158656777
H	3.0930852577	-2.2071384930	0.9174881263
H	4.3125742964	-1.1739886330	1.6805611341
H	3.4895233119	0.6053704228	-1.5555785849
H	4.8191660237	-0.0101290036	-0.5534602564
H	3.6692864738	-1.1453298144	-1.2841921404
H	4.2816135938	1.2255145827	1.5452256706
H	3.1272996715	2.1382986951	0.5648013502
H	2.5903526159	1.3808161861	2.0813691073

2Ax-C1a

0 1

C	1.5054611561	0.5564648483	0.4336011132
C	0.7497632777	-0.5527045607	0.0072814451
C	1.4180004784	-1.6851165718	-0.4786171791
C	2.8085017596	-1.7244902667	-0.5504275698
C	3.5541830215	-0.6225493128	-0.1348918531
C	2.8998783624	0.5072404754	0.3533360674
H	0.8345057681	-2.5419748666	-0.8238649556
H	3.3086242130	-2.6143447822	-0.9388967072
H	4.6448481030	-0.6416121234	-0.1902522531
H	3.4830208596	1.3695501639	0.6881428595
C	-0.7351658208	-0.5319102921	0.0713200250
C	-1.4724070136	0.5899594416	-0.3844327211
C	-1.4331467251	-1.6579635845	0.5263906663
C	-2.8751227041	0.5145685583	-0.3976476804
C	-2.8244136015	-1.7181898556	0.5122525721
H	-0.8609687197	-2.5126359867	0.8959855393
C	-3.5457143535	-0.6261160780	0.0325057104
H	-3.4433498120	1.3771559632	-0.7564127732
H	-3.3392884697	-2.6115680939	0.8707305753
H	-4.6375309681	-0.6526374356	0.0072512741
C	0.7964674821	1.7682088768	0.9773416119
H	0.0829108862	1.4531496876	1.7569270476
C	0.0501279844	2.5539054794	-0.0951996494
H	-0.5170104577	3.3643401743	0.4024915822
N	-0.8303177279	1.7179352259	-0.9082494235
H	-1.4754009744	2.2923780327	-1.4391573705
H	0.7806947024	3.0365489396	-0.7647903818
H	1.5139732936	2.4460789437	1.4615934281

2Ax-C1b

0 1

C	1.2319658512	-1.5323524811	-0.1718395563
C	2.1586064105	-0.4644955299	-0.1274938922
C	3.5297019724	-0.8031451201	-0.0469781361
C	3.9901729145	-2.1105346429	-0.0668080721
C	3.0719580748	-3.1553796214	-0.1584375073
C	1.7202854536	-2.8513095799	-0.1987785782
H	4.2627841223	-0.0035267304	0.0635428168
H	5.0613375831	-2.3112849221	0.0024589763
H	3.4049715153	-4.1952569500	-0.1785872181
H	0.9925235273	-3.6665577862	-0.2449623707
C	1.8537605710	1.0056442918	-0.1260999437
C	0.7256258199	1.5848985934	0.5031686523
C	2.7977887636	1.8889553742	-0.6836892060
C	0.6617912676	2.9777709376	0.6753243017
C	2.7127927412	3.2690988341	-0.5408165058
H	3.6355423513	1.4773923876	-1.2490611089
C	1.6519030759	3.8157201868	0.1806070517
H	-0.2074450695	3.4008271514	1.1863912483
H	3.4741019488	3.9118181603	-0.9868324440
H	1.5733107097	4.8956122826	0.3244532446
C	-0.2807361077	-1.4358038423	-0.1582296995
H	-0.6808339428	-1.9934602896	-1.0215918781
C	-0.9036544282	-0.0563281553	-0.1396286414
H	-0.7905856666	0.4292145724	-1.1272586428
N	-0.3456381660	0.7902782404	0.9086626124
H	-1.0599582554	1.3396368796	1.3719600384
H	-1.9836575287	-0.1639966787	0.0359574330
H	-0.6266124090	-1.9777653122	0.7374265056

2Ax-TS1

0 1

C	1.5826827781	0.6404298921	0.2580422274
C	0.7563178668	-0.4863556386	0.0551500045
C	1.3652125873	-1.7077474588	-0.2945964950
C	2.7411170666	-1.8427412979	-0.4253811253
C	3.5557933881	-0.7315754787	-0.2191269978
C	2.9705997444	0.4848595751	0.1099111384
H	0.7297749367	-2.5722542793	-0.4966007955
H	3.1715185796	-2.8068776570	-0.7042048814
H	4.6401338488	-0.8071768315	-0.3256666682
H	3.6114500518	1.3573206892	0.2642663489
C	-0.7332935259	-0.4798243062	0.1283886534
C	-1.4978334219	0.5681492250	-0.4288694189
C	-1.4149950509	-1.5996677195	0.6303861876

C	-2.8878441892	0.4253296527	-0.5459001659
C	-2.7975756656	-1.7260070677	0.5323831996
H	-0.8403389688	-2.3993099080	1.1031928667
C	-3.5348544113	-0.7170772766	-0.0863854932
H	-3.4651972423	1.2393289417	-0.9927448298
H	-3.2950465621	-2.6122456542	0.9311214333
H	-4.6189308271	-0.8050555481	-0.1870588358
C	1.1170899054	2.0115553544	0.7065841514
H	1.1855876679	2.0526397101	1.8071021791
C	-0.2798809176	2.4961845491	0.2881857746
H	-0.9609957137	2.4696919839	1.1595424725
N	-0.8624261945	1.7541211397	-0.8266384967
H	-1.5026971623	2.3457644053	-1.3456342712
H	-0.2077731408	3.5505779616	-0.0137648289
H	1.8646825725	2.7313380422	0.3432156666

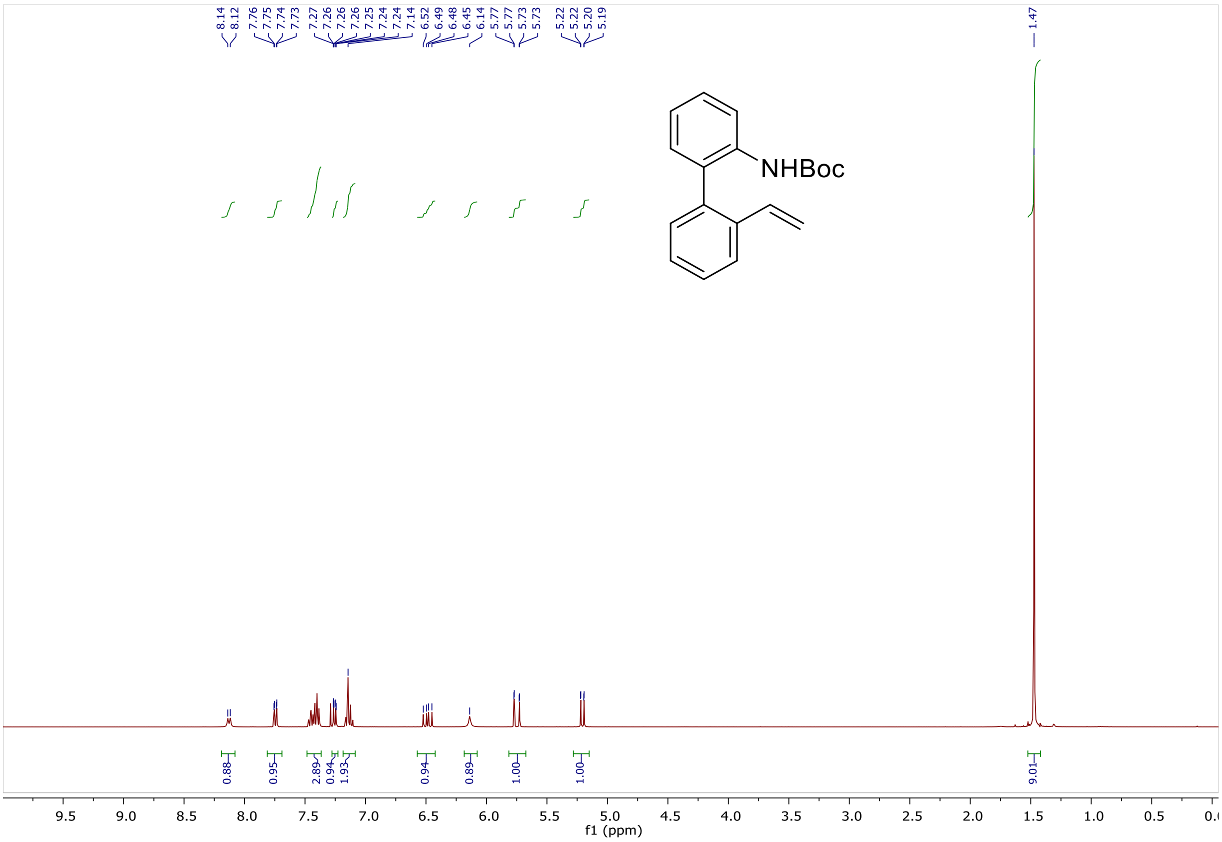
2Ax-TS3

0 1

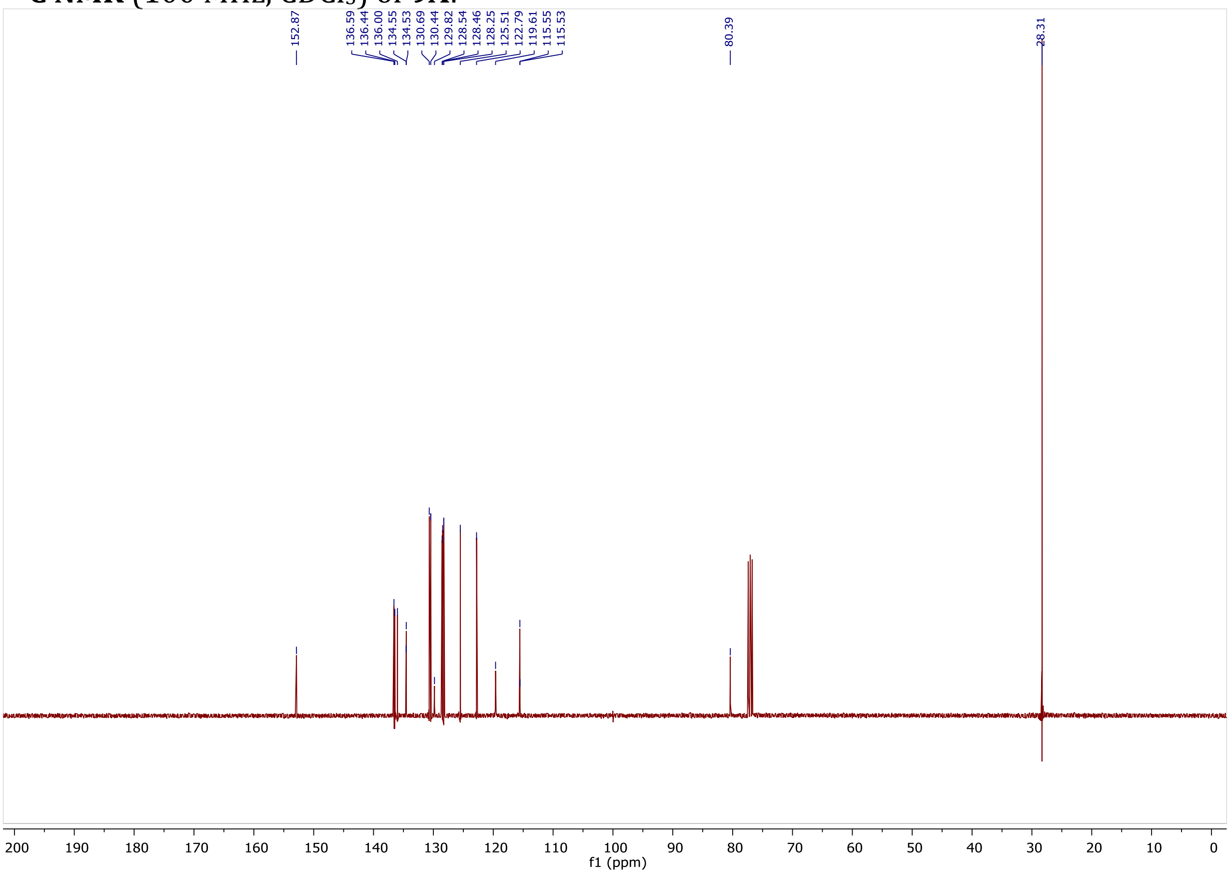
C	1.6250515187	0.6668179536	-0.0798381080
C	0.7684724132	-0.4644280353	0.0161788832
C	1.4287810974	-1.7171403658	0.0622283606
C	2.8060214918	-1.8753425200	0.0289040700
C	3.6270742924	-0.7562851505	-0.0562703830
C	3.0197518578	0.4873749789	-0.1056020959
H	0.8578500696	-2.6382437132	0.1175360815
H	3.2303190550	-2.8808531246	0.0685601225
H	4.7146661143	-0.8484481424	-0.0823318913
H	3.6469447016	1.3803151902	-0.1703928092
C	-0.7521199351	-0.4734487060	0.0387095389
C	-1.6284581309	0.6477873893	-0.0813829858
C	-1.4050392864	-1.7271468635	0.1374566170
C	-3.0251689412	0.4390899885	-0.1908609280
C	-2.7740302582	-1.9186244816	0.0529063670
H	-0.8195717842	-2.6290397567	0.2852848615
C	-3.6016585923	-0.8126040338	-0.1391768997
H	-3.6613046433	1.3215149166	-0.3026506893
H	-3.1866451180	-2.9258310864	0.1320116217
H	-4.6848534584	-0.9224992825	-0.2247785243
C	1.1944000846	2.1113345787	-0.1721213417
H	2.0162528300	2.7364731479	0.2070943421
C	-0.0750300467	2.4619360839	0.5737630299
H	-0.0218005725	2.0835696949	1.6135917574
N	-1.2387190840	1.9698002521	-0.1138042173
H	-2.0200026525	2.6110846799	-0.1184576073
H	-0.1676755774	3.5549230242	0.6334497488
H	1.0522965548	2.3924393832	-1.2289389212

9. NMR spectra of new compounds

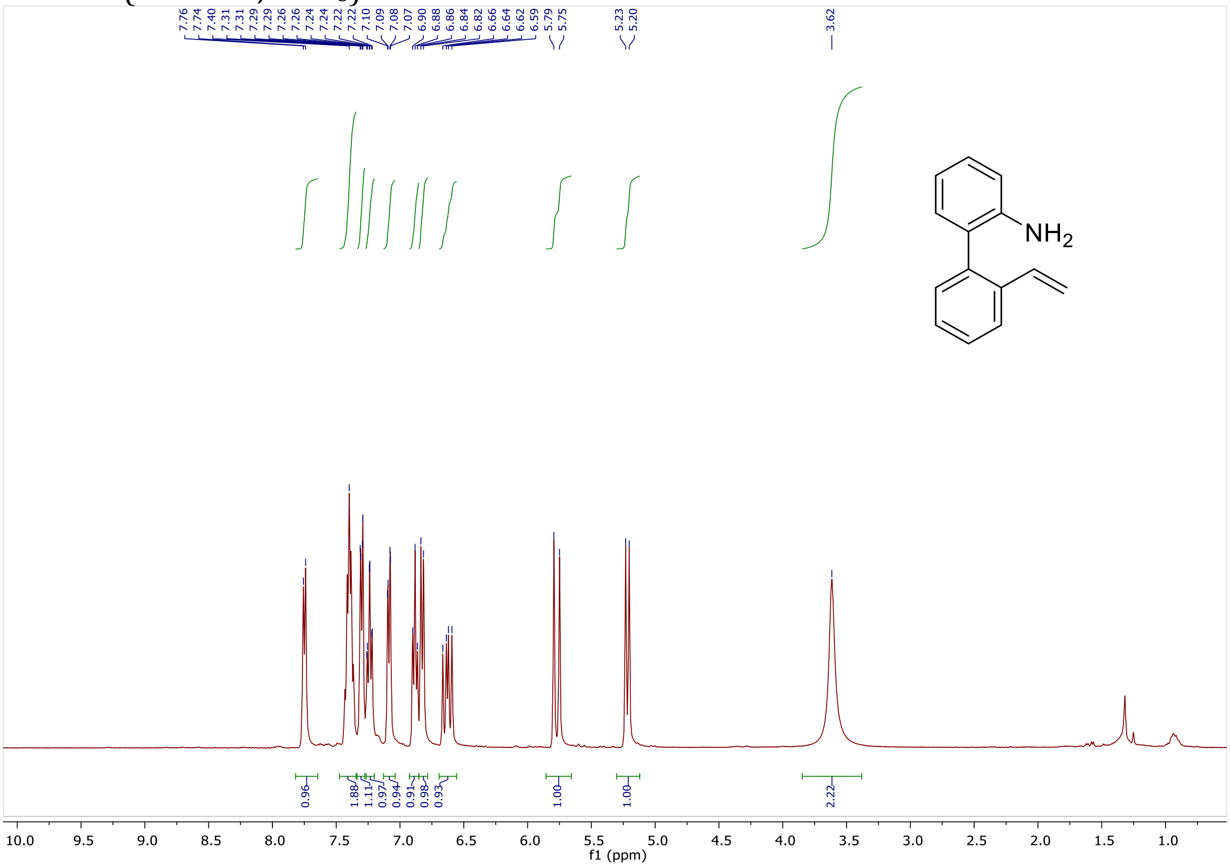
[1]H NMR (400 MHz, $CDCl_3$) of **9A**:



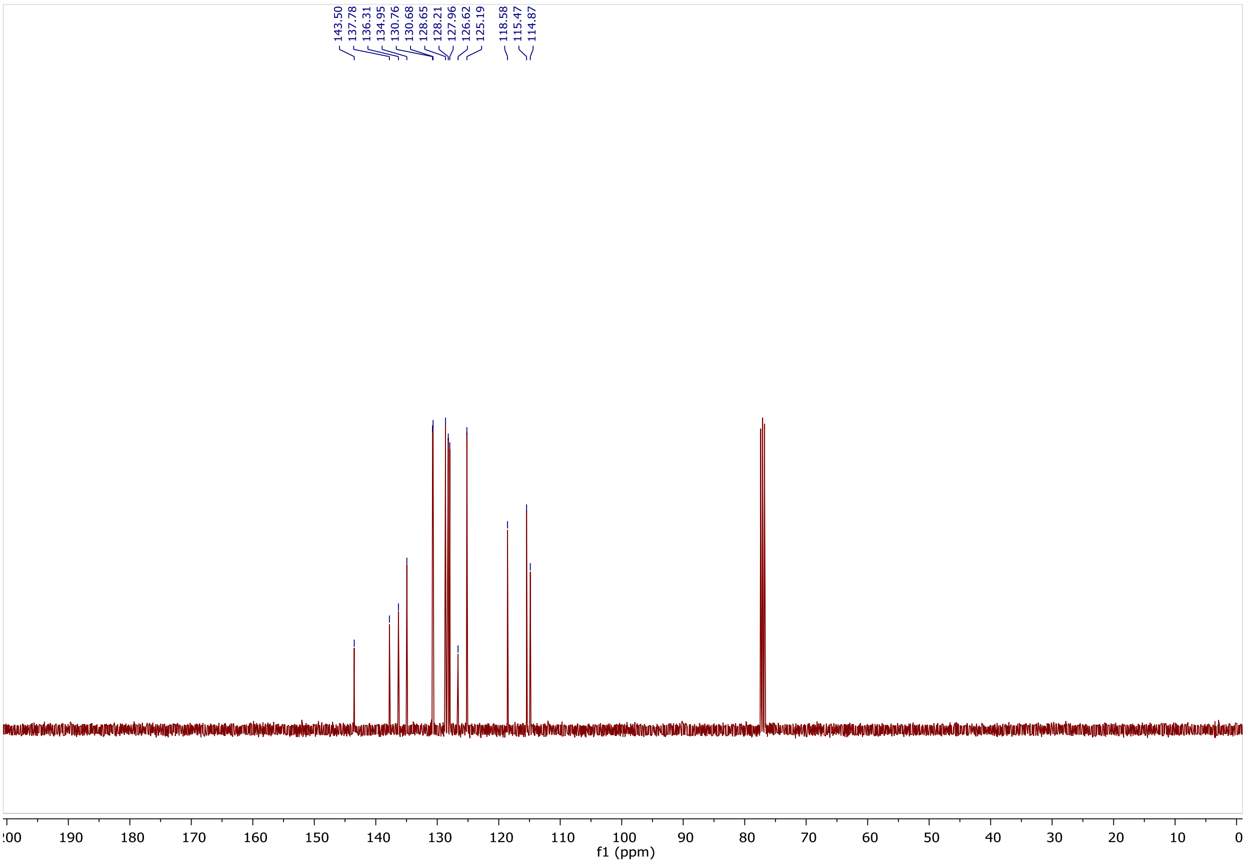
[13]C NMR (100 MHz, $CDCl_3$) of **9A**:



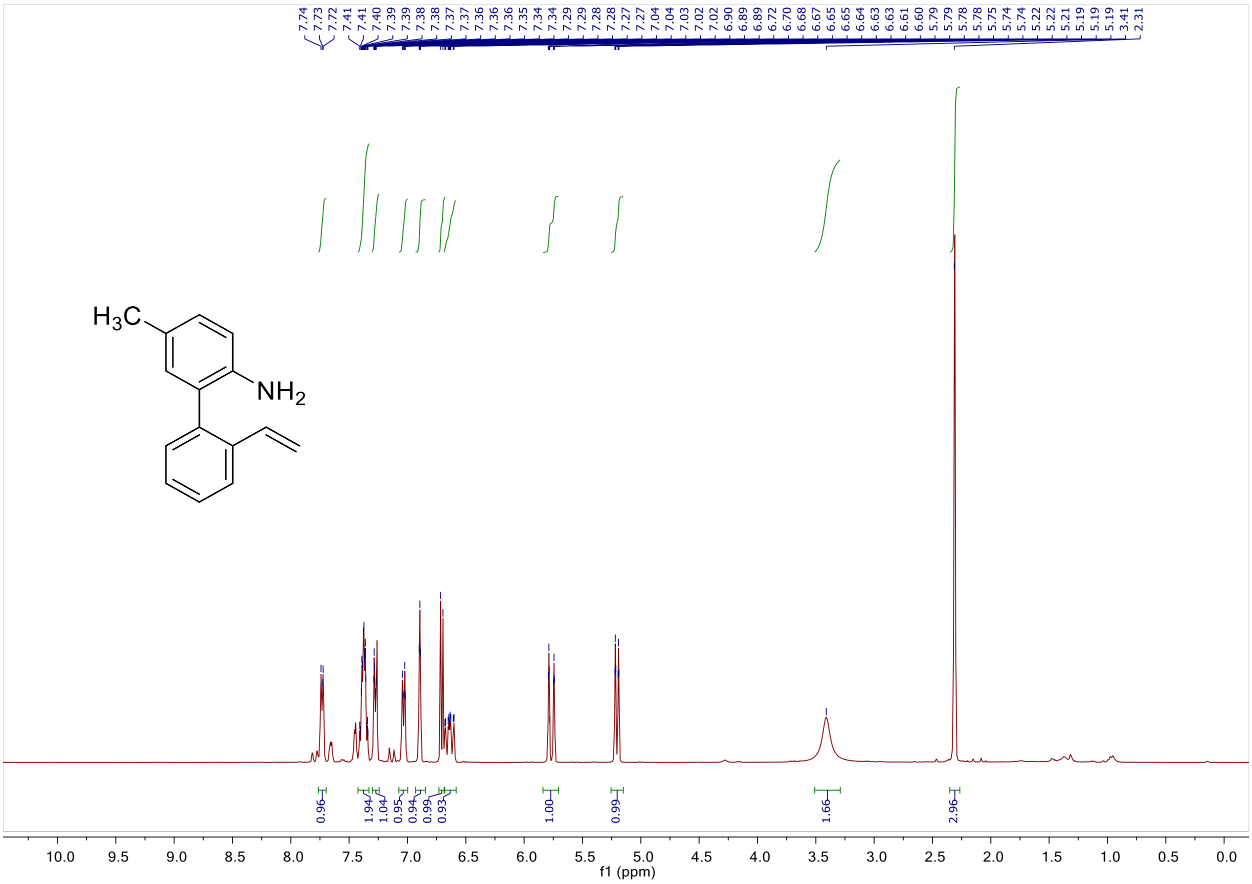
¹H NMR (400 MHz, $CDCl_3$) of **10A**:



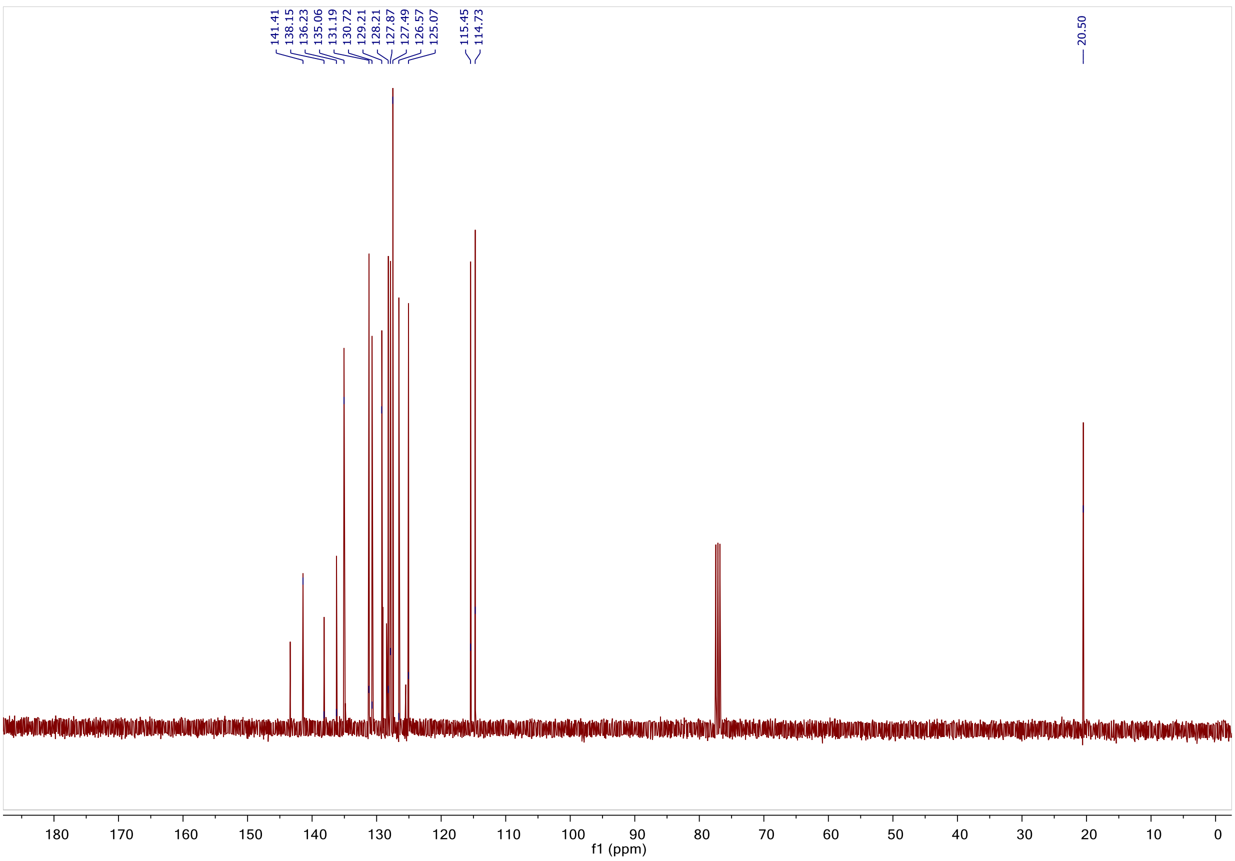
¹³C NMR (100 MHz, $CDCl_3$) of **10A**



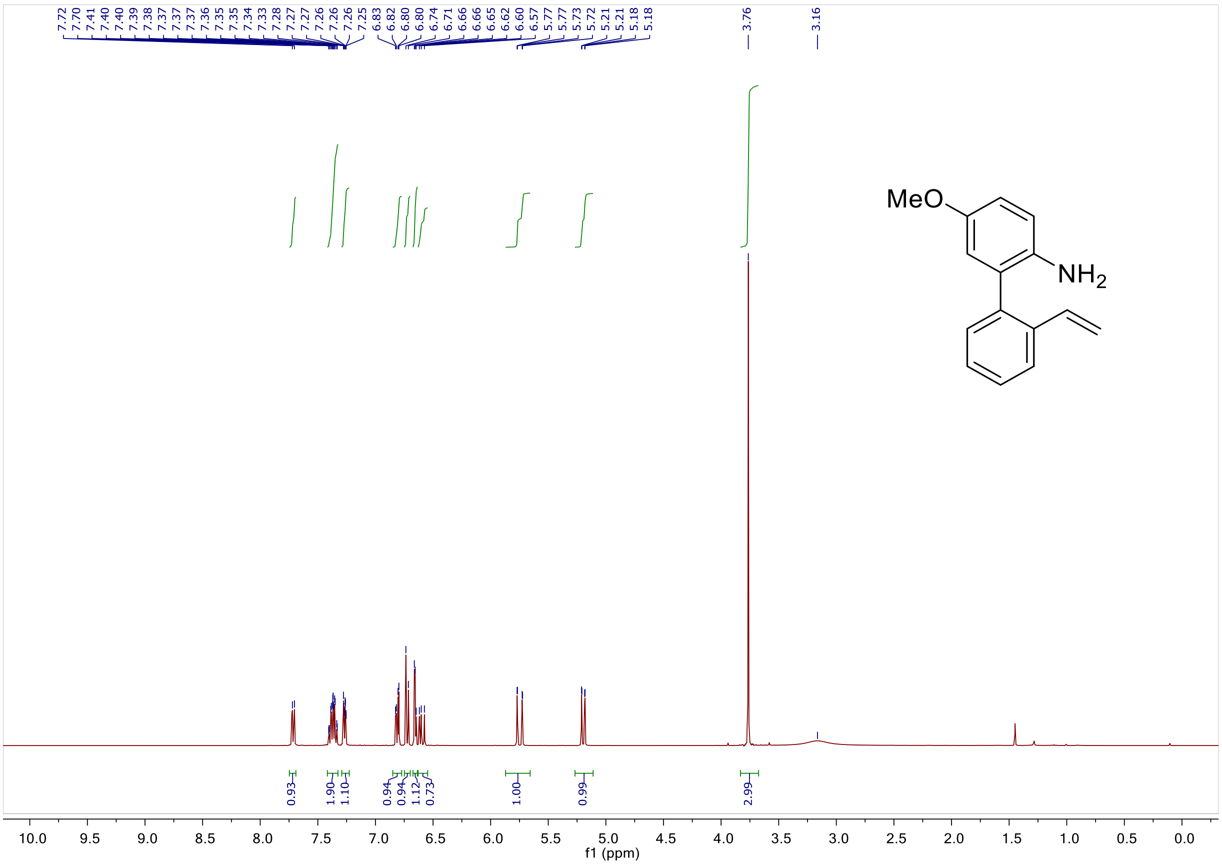
[1]H NMR (400 MHz, $CDCl_3$) of **10B**:



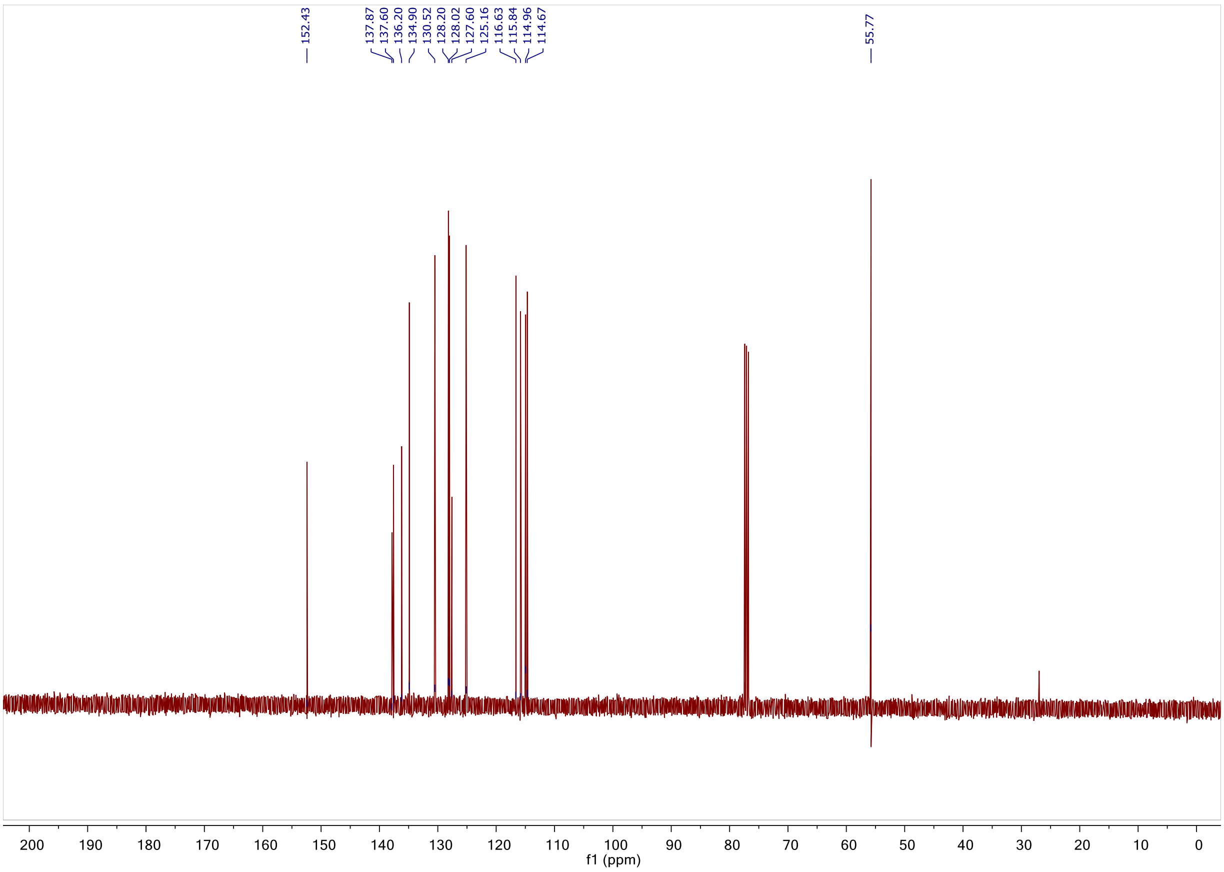
[13]C NMR (100 MHz, $CDCl_3$) of **10B**



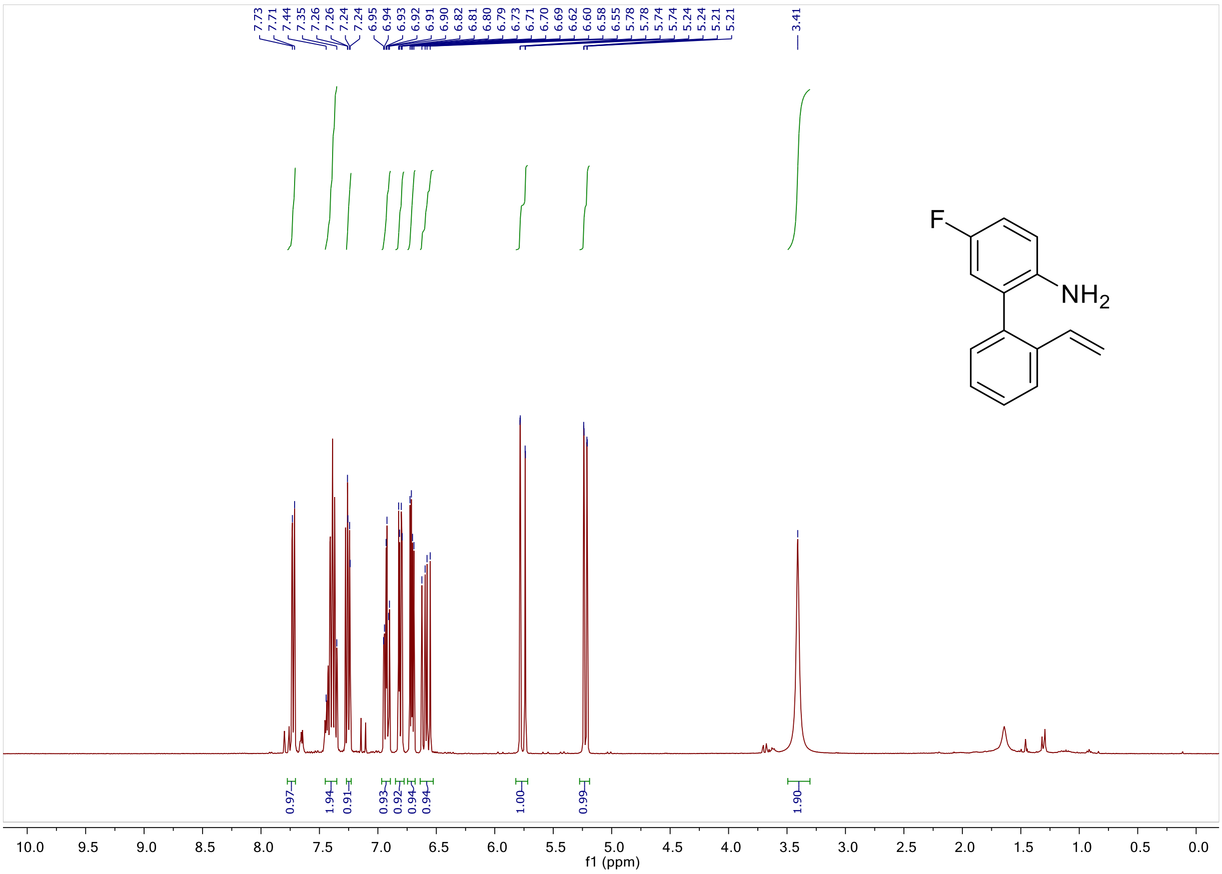
^{1}H NMR (400 MHz, $CDCl_3$) of **10C**:



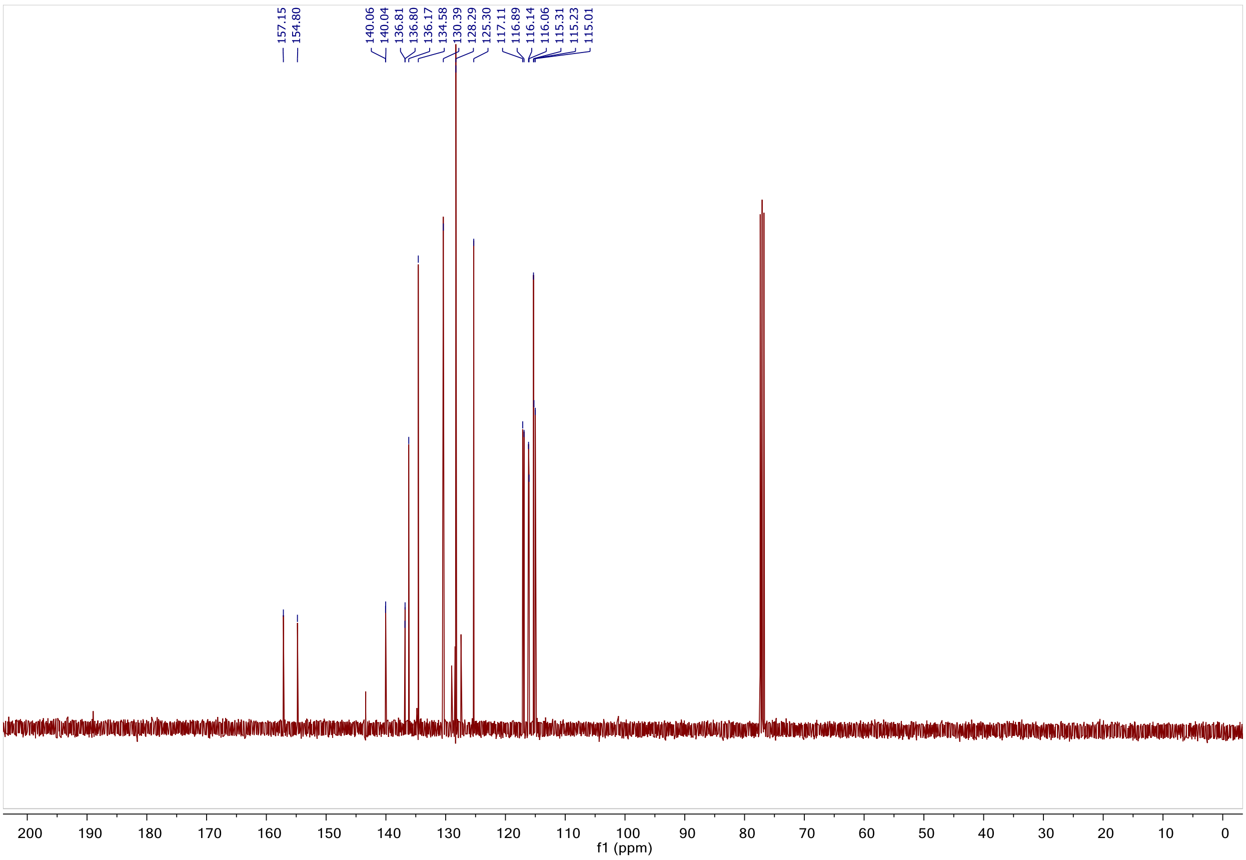
^{13}C NMR (100 MHz, $CDCl_3$) of **10C**



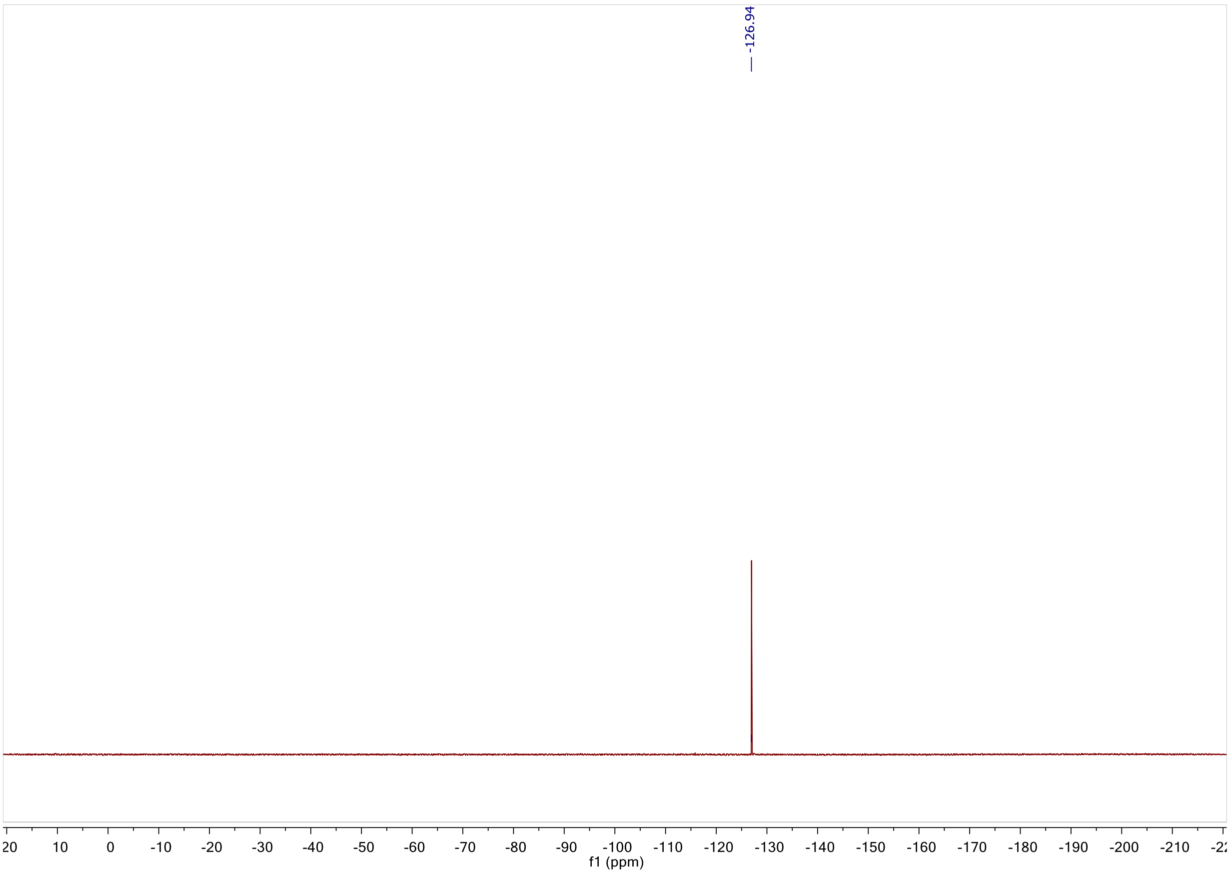
^{1}H NMR (400 MHz, $CDCl_3$) of **10D**:



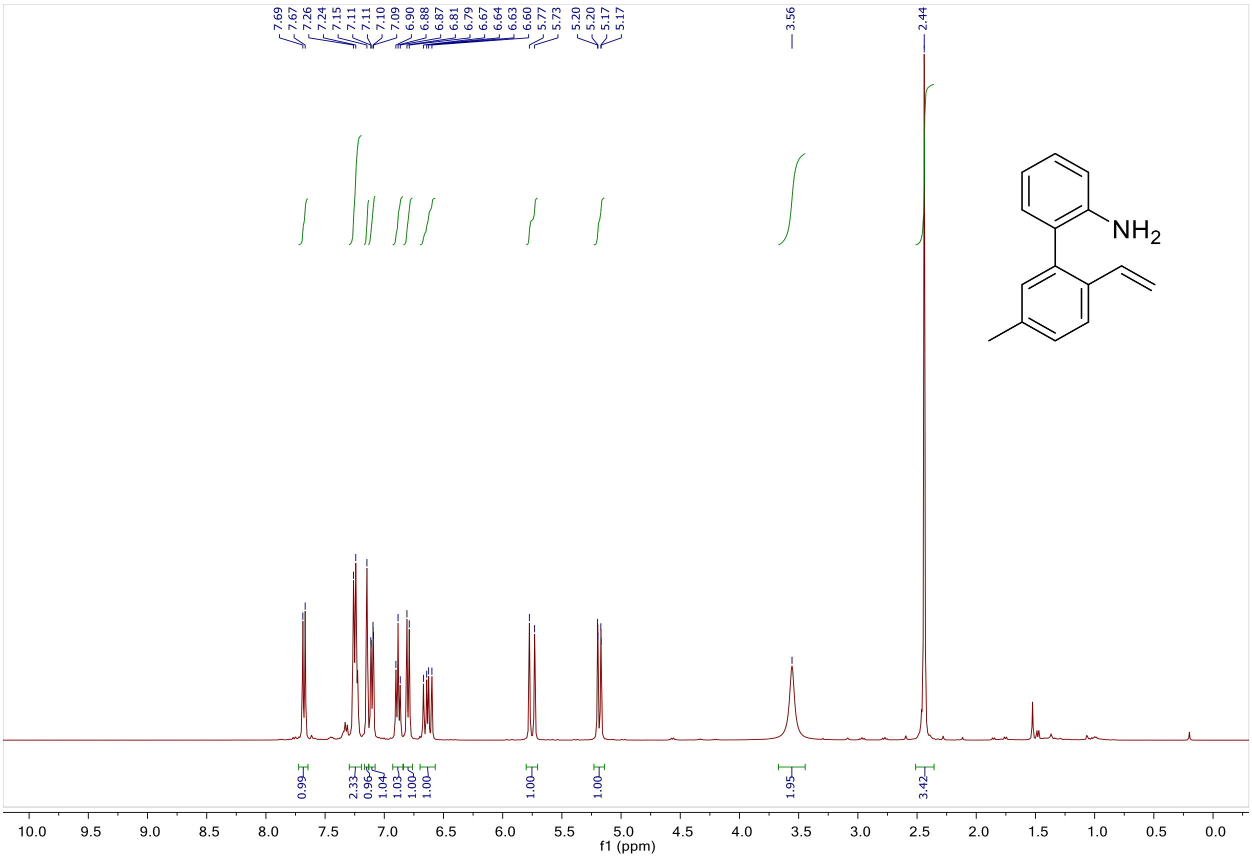
^{13}C NMR (100 MHz, $CDCl_3$) of **10D**



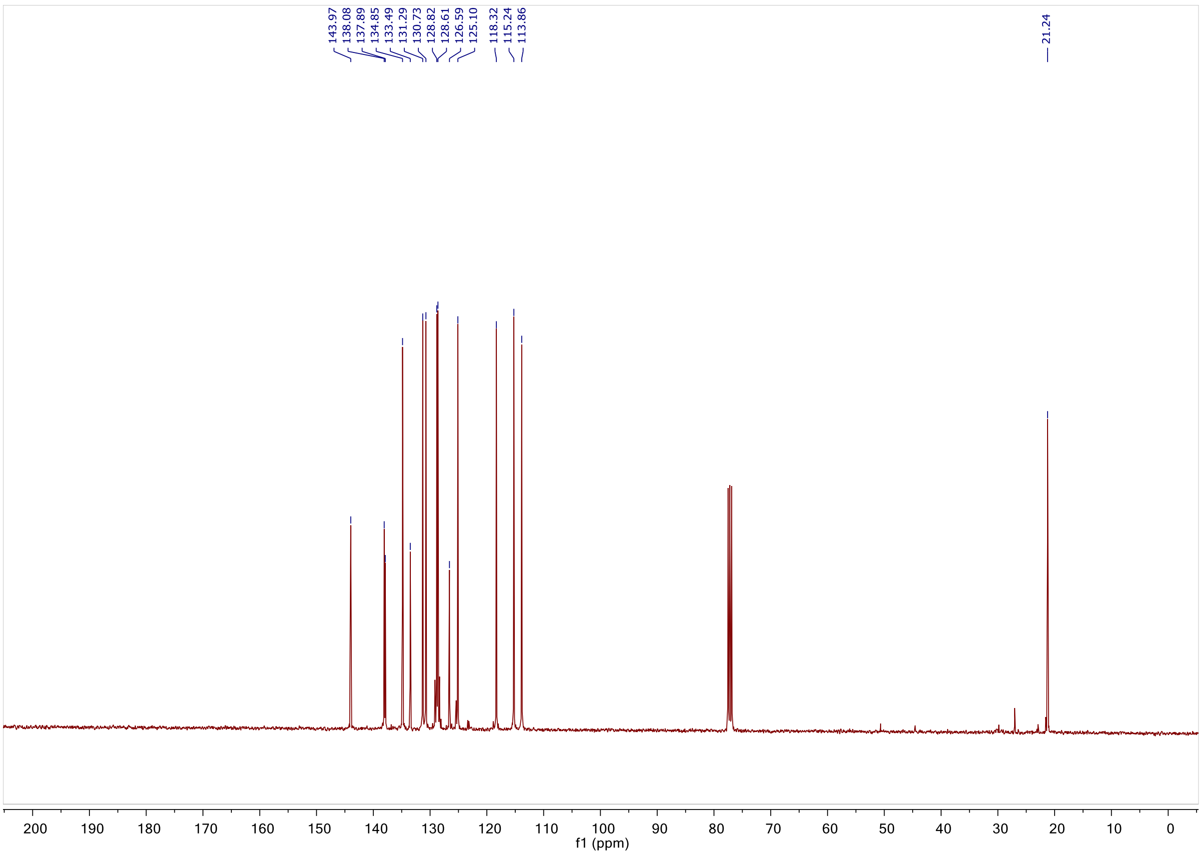
^{19}F NMR (377 MHz, $CDCl_3$) of **10D**:



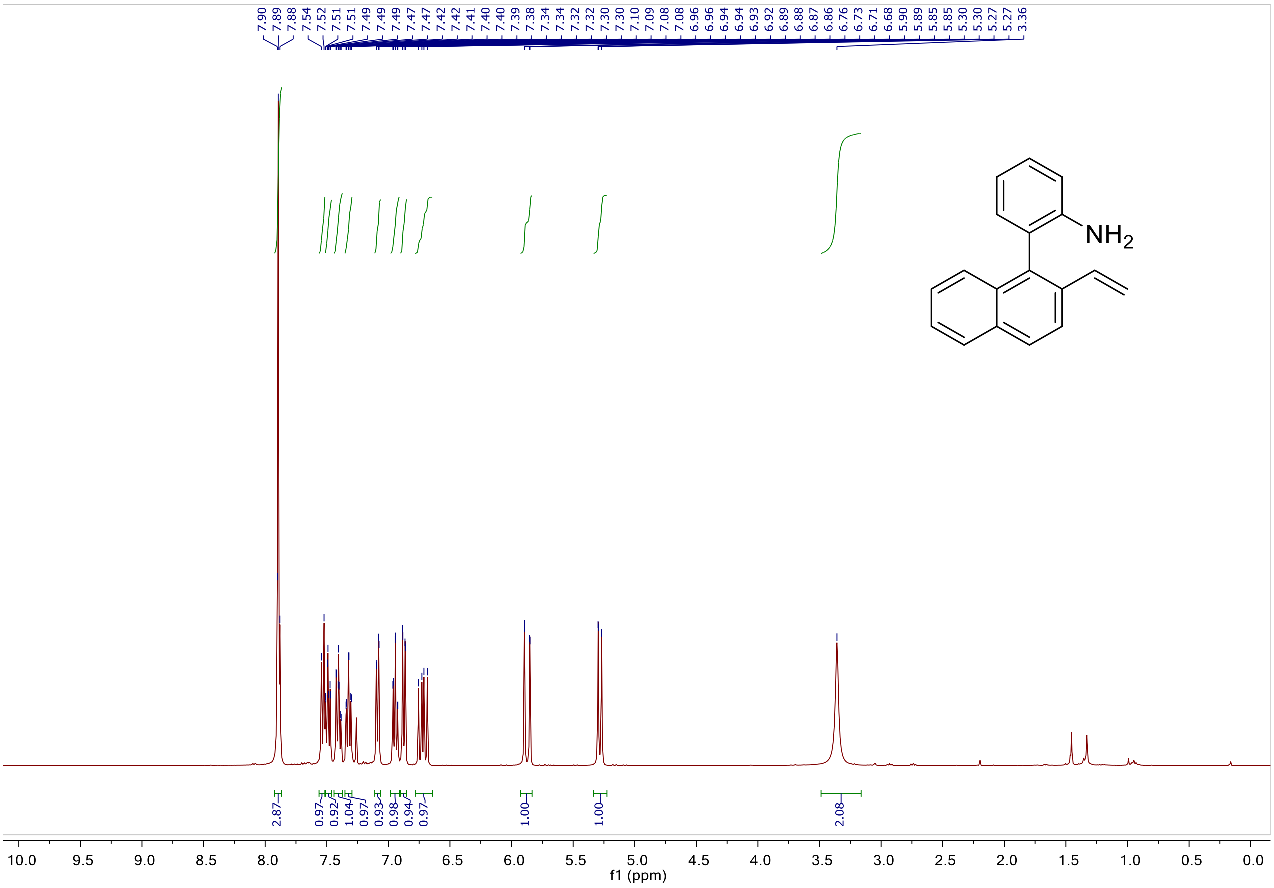
[1]H NMR (400 MHz, $CDCl_3$) of **10E**:



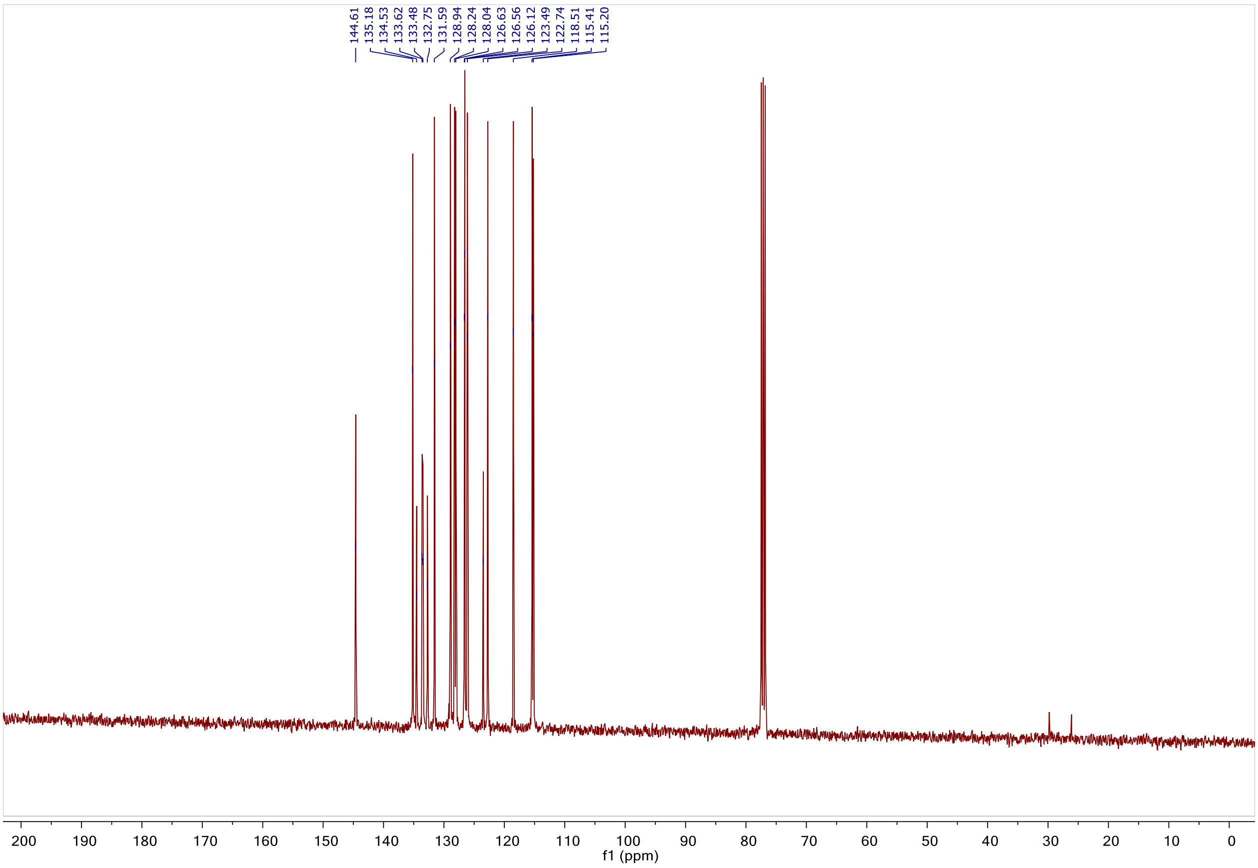
[13]C NMR (100 MHz, $CDCl_3$) of **10E**



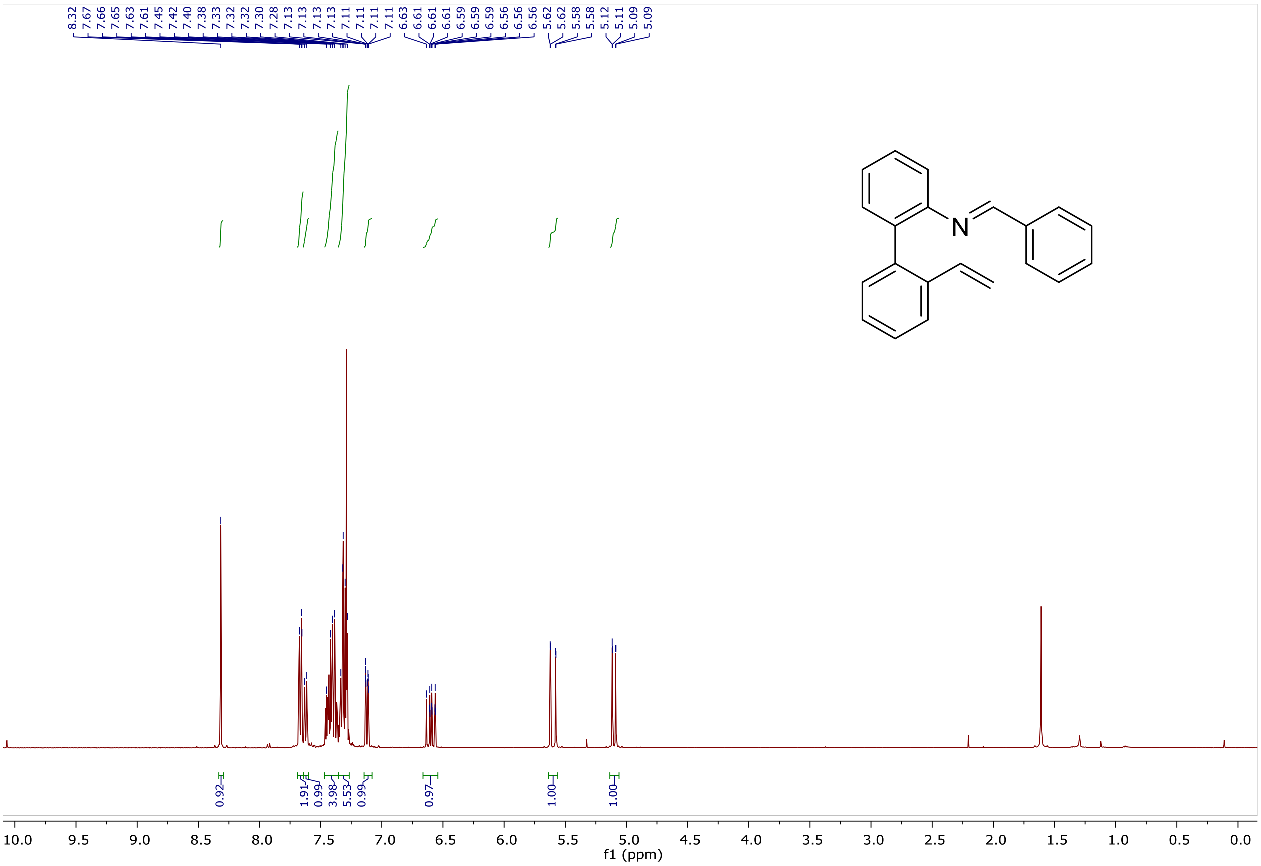
[1]H NMR (400 MHz, $CDCl_3$) of **10F**:



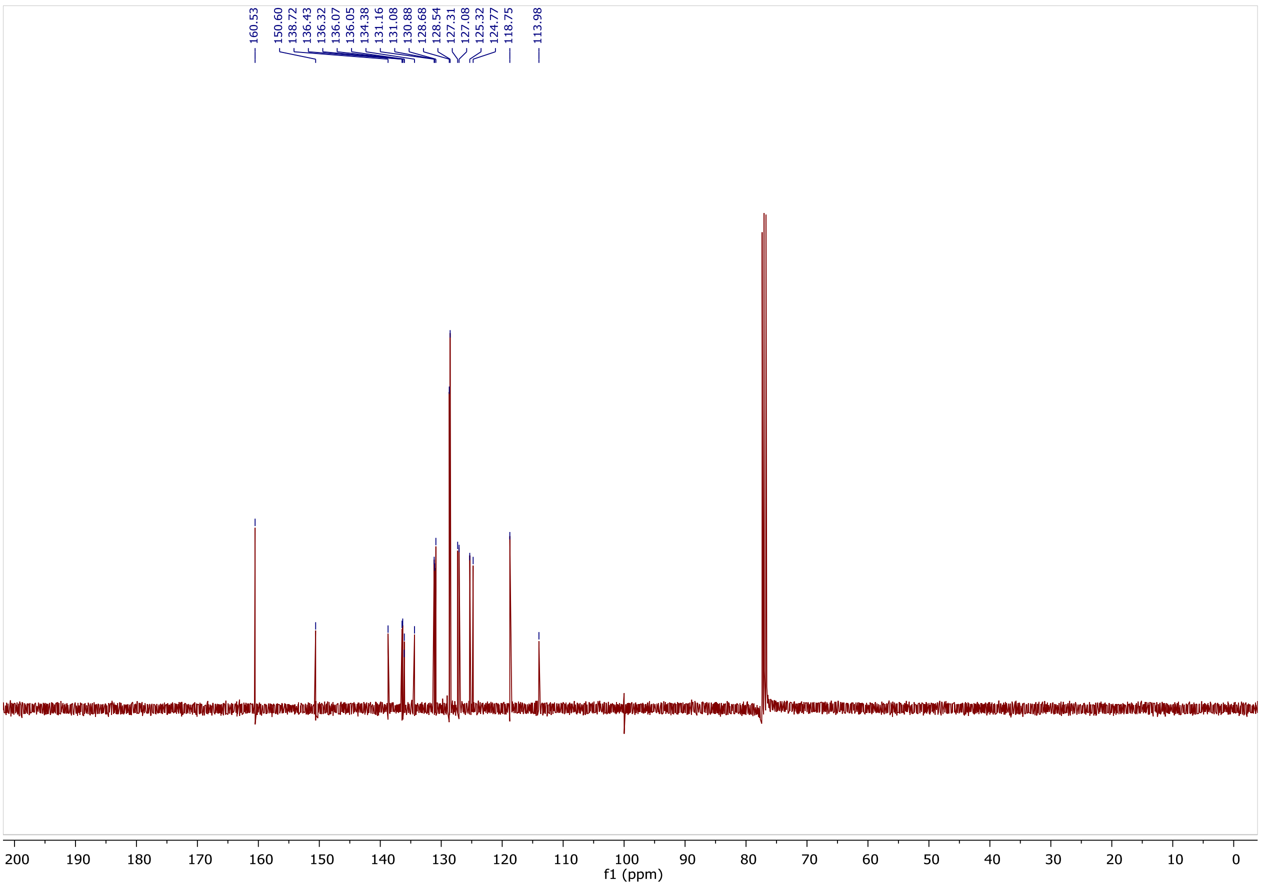
[13]C NMR (100 MHz, $CDCl_3$) of **10F**



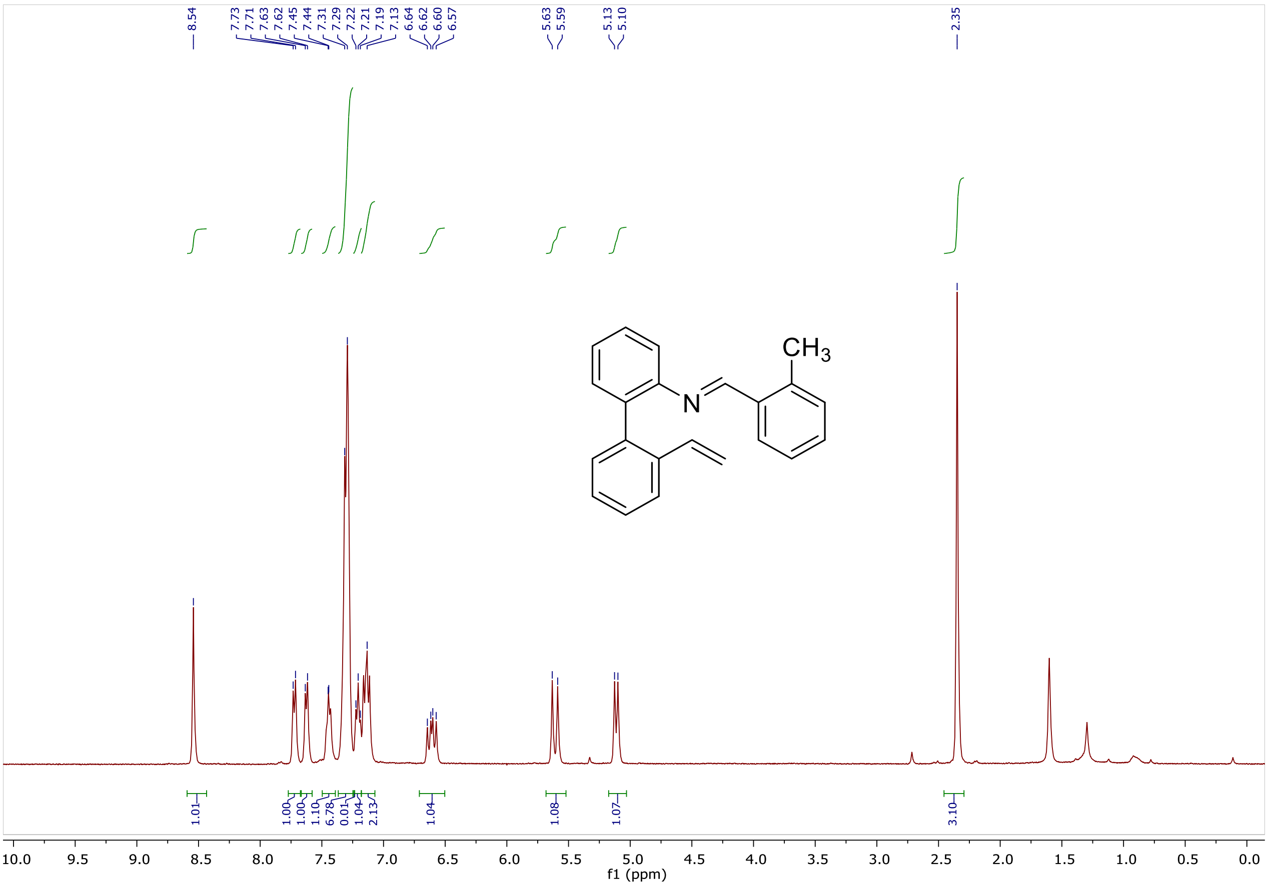
^{1}H NMR (400 MHz, $CDCl_3$) of **1Aa**:



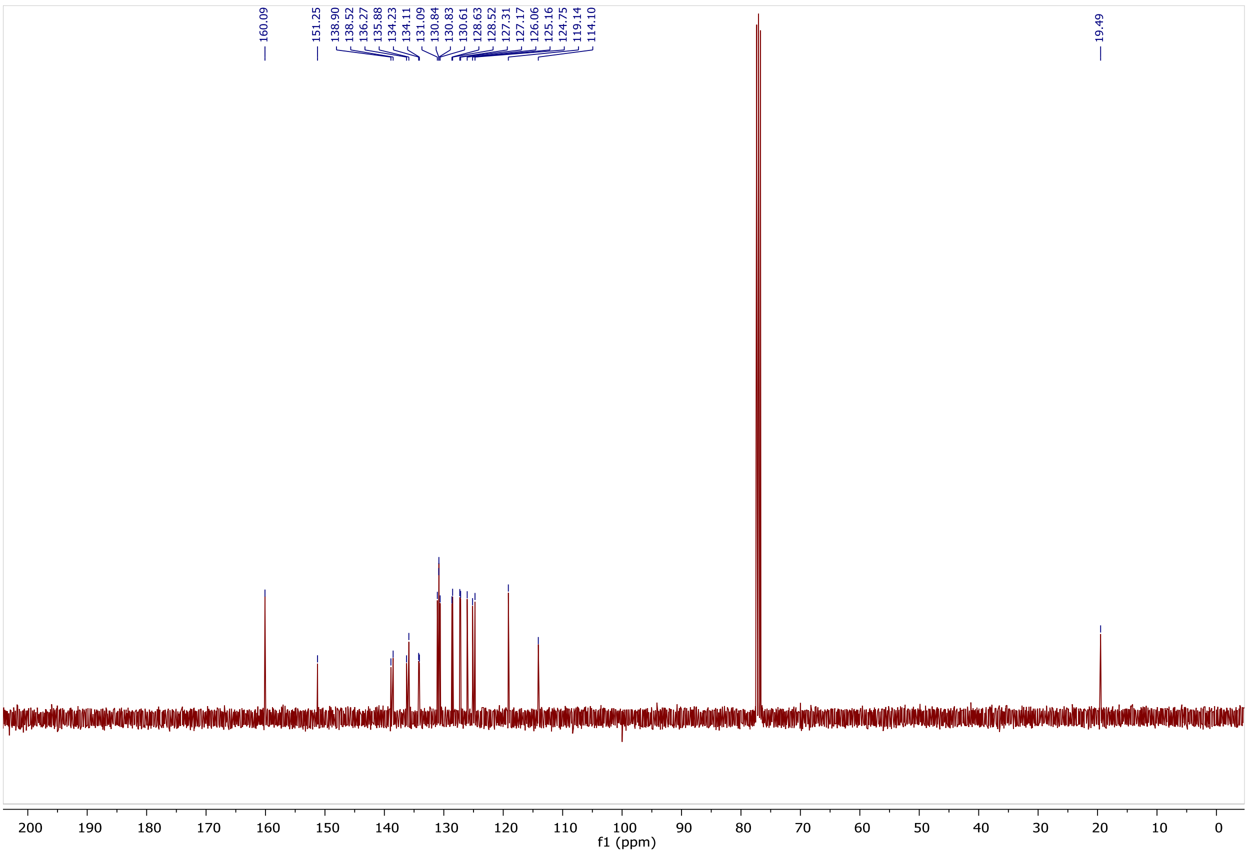
^{13}C NMR (100 MHz, $CDCl_3$) of **1Aa**



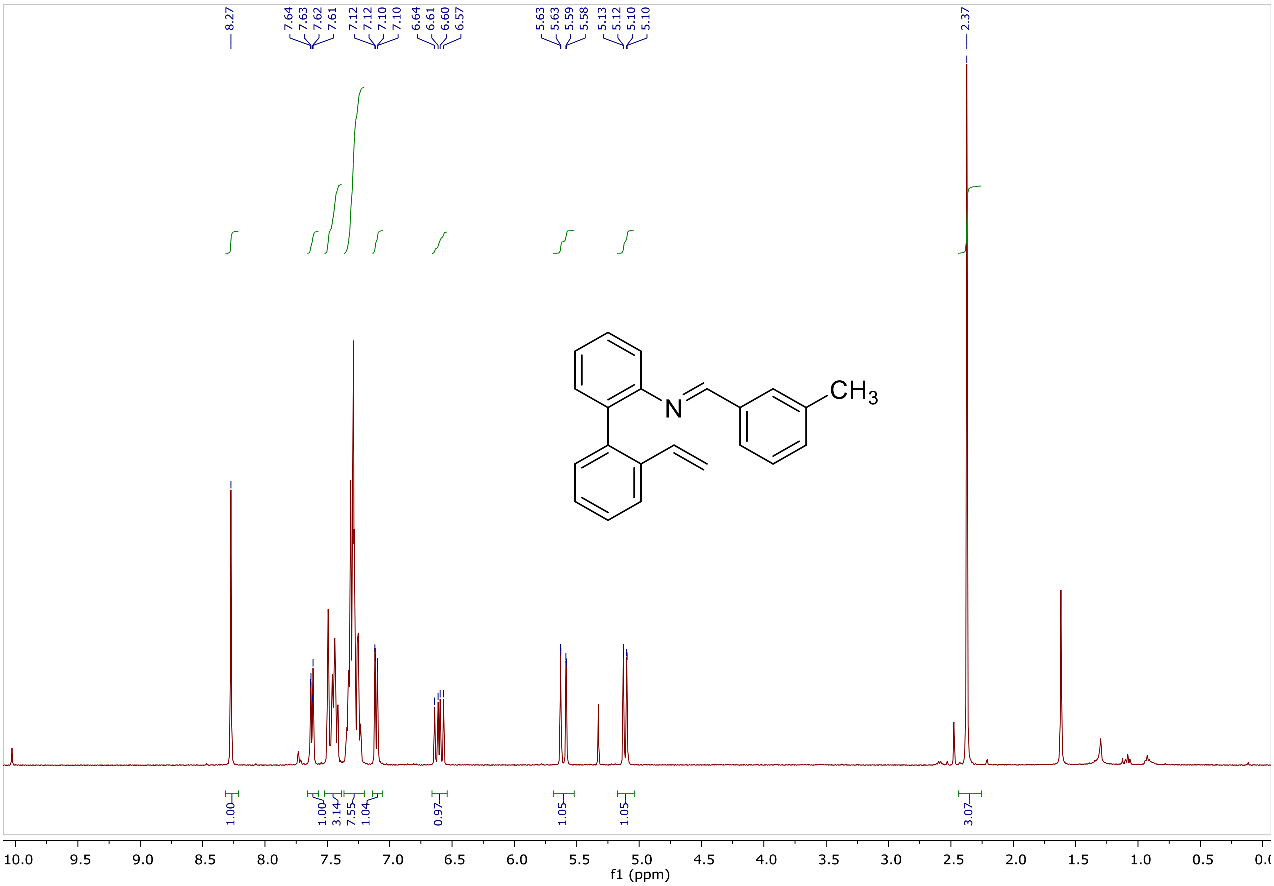
^{1}**H NMR** (400 MHz, $CDCl_3$) of **1Ab**



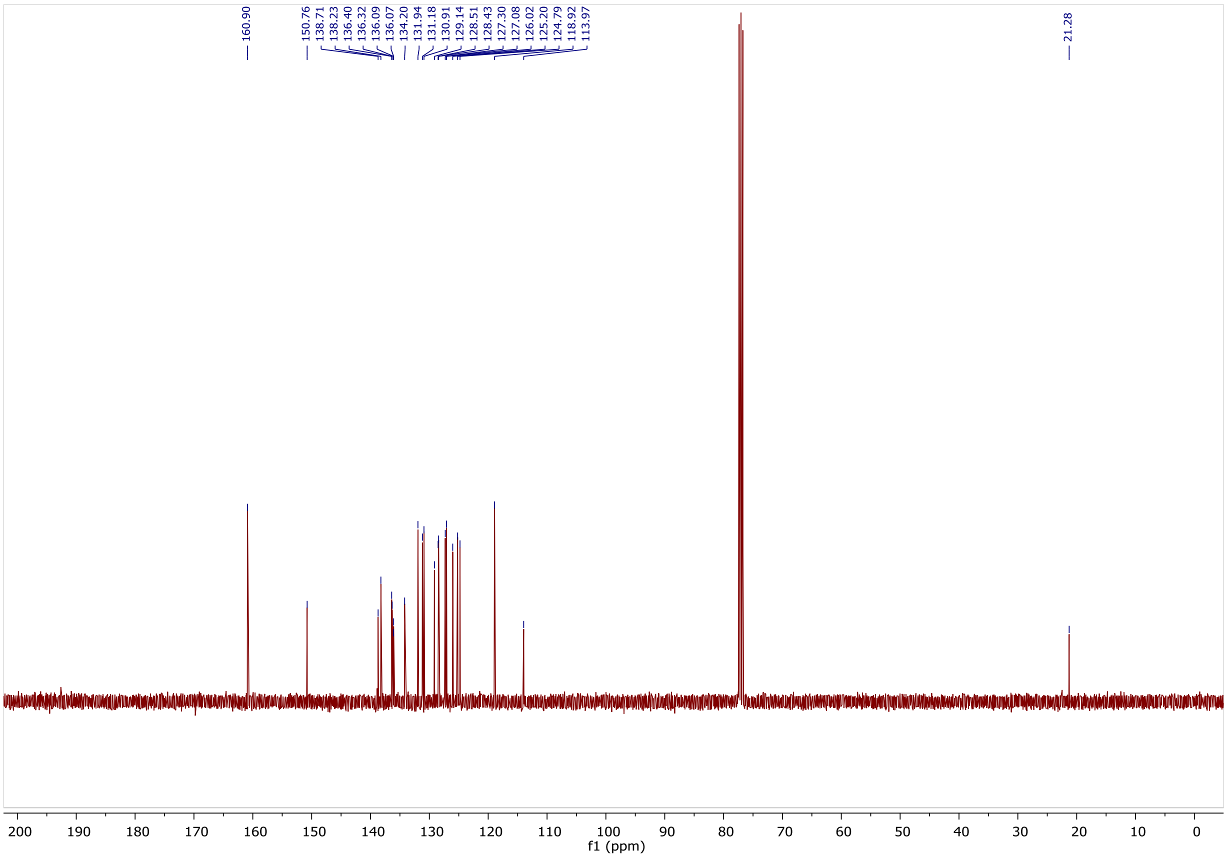
^{13}**C NMR** (100 MHz, $CDCl_3$) of **1Ab**



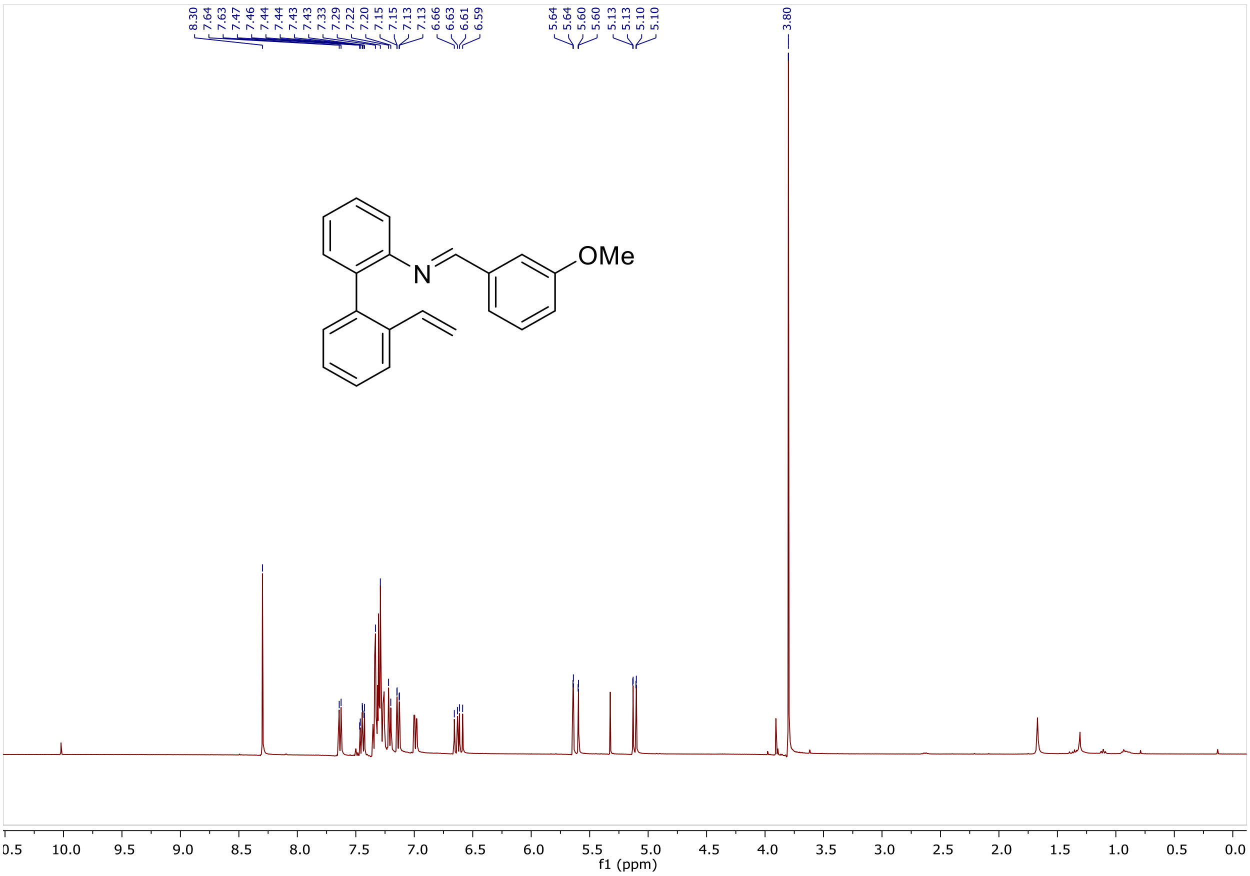
1H NMR (400 MHz, CDCl3) of **1Ac**:



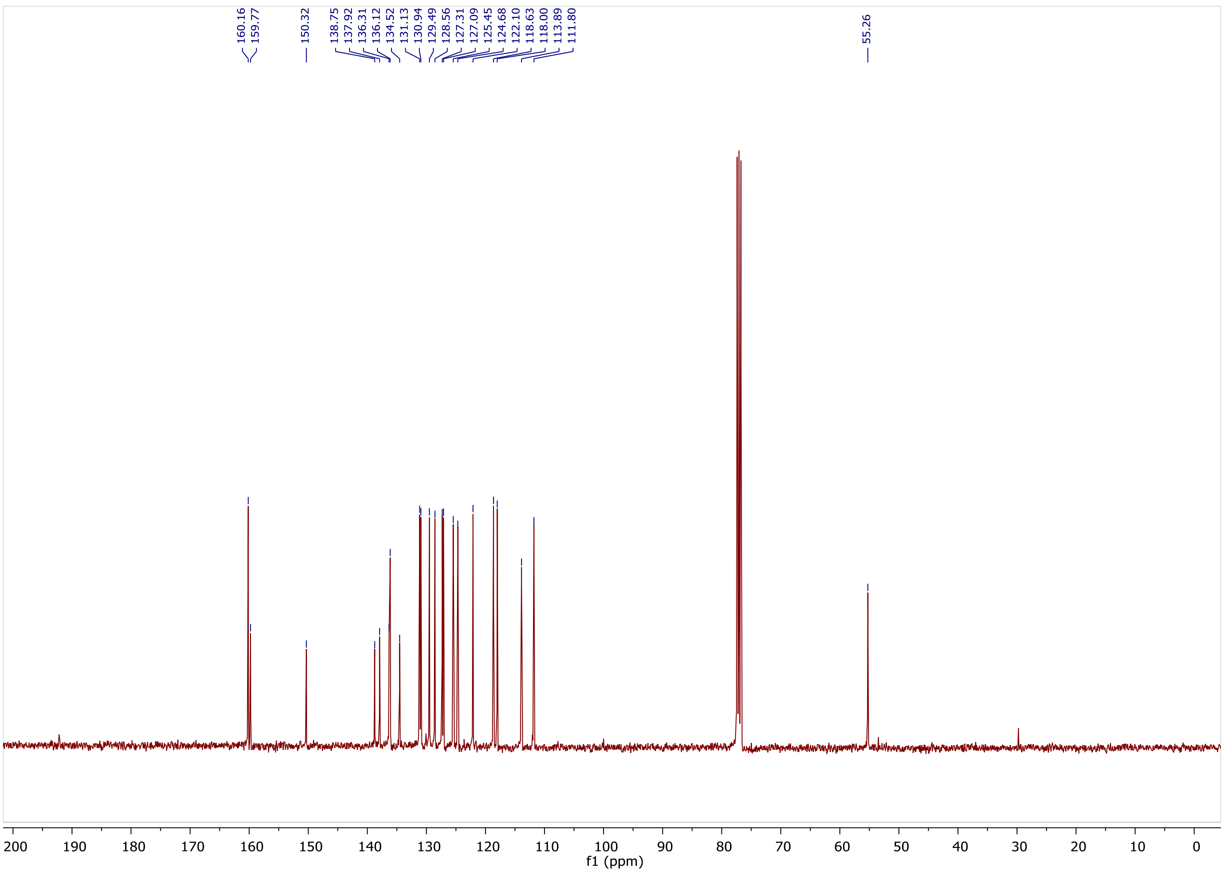
13C NMR (100 MHz, CDCl3) of **1Ac:**



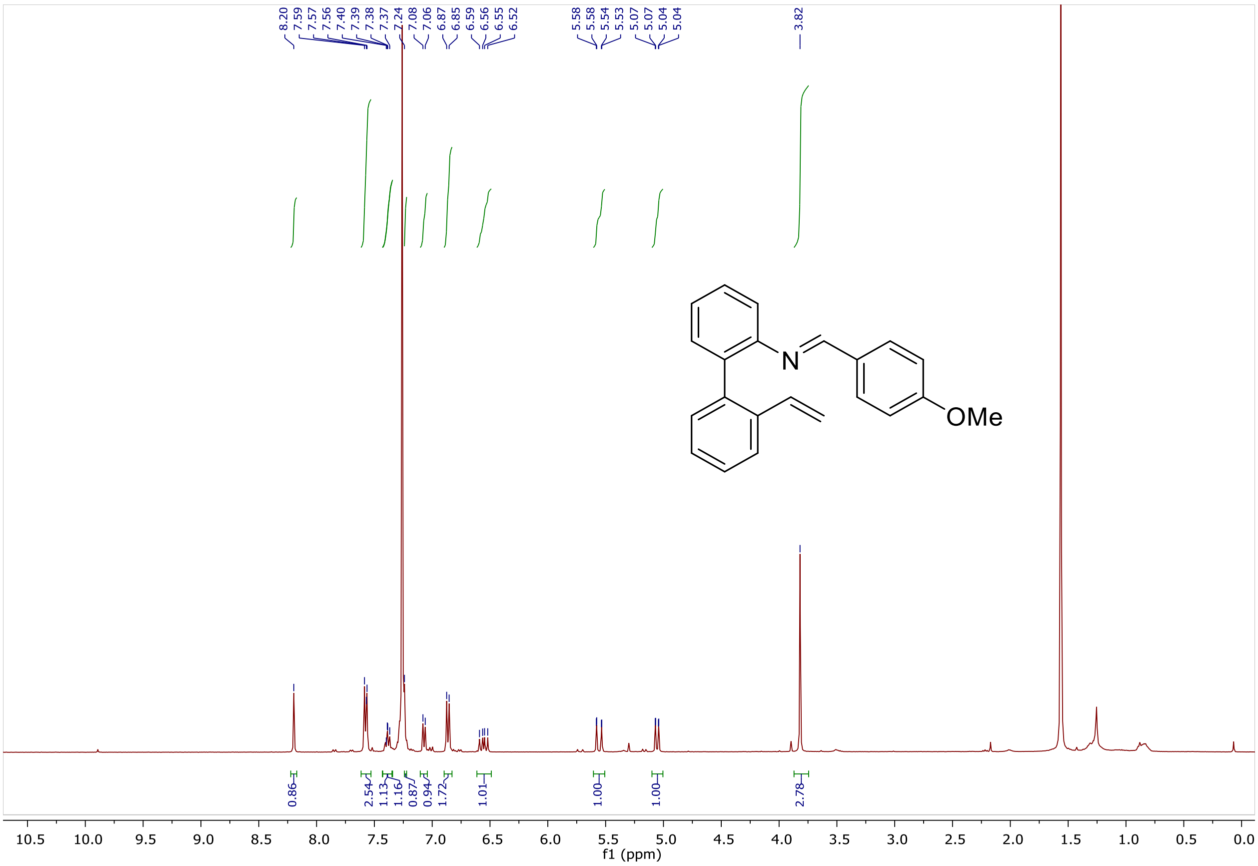
^{1}H NMR (400 MHz, $CDCl_3$) of **1Ad**



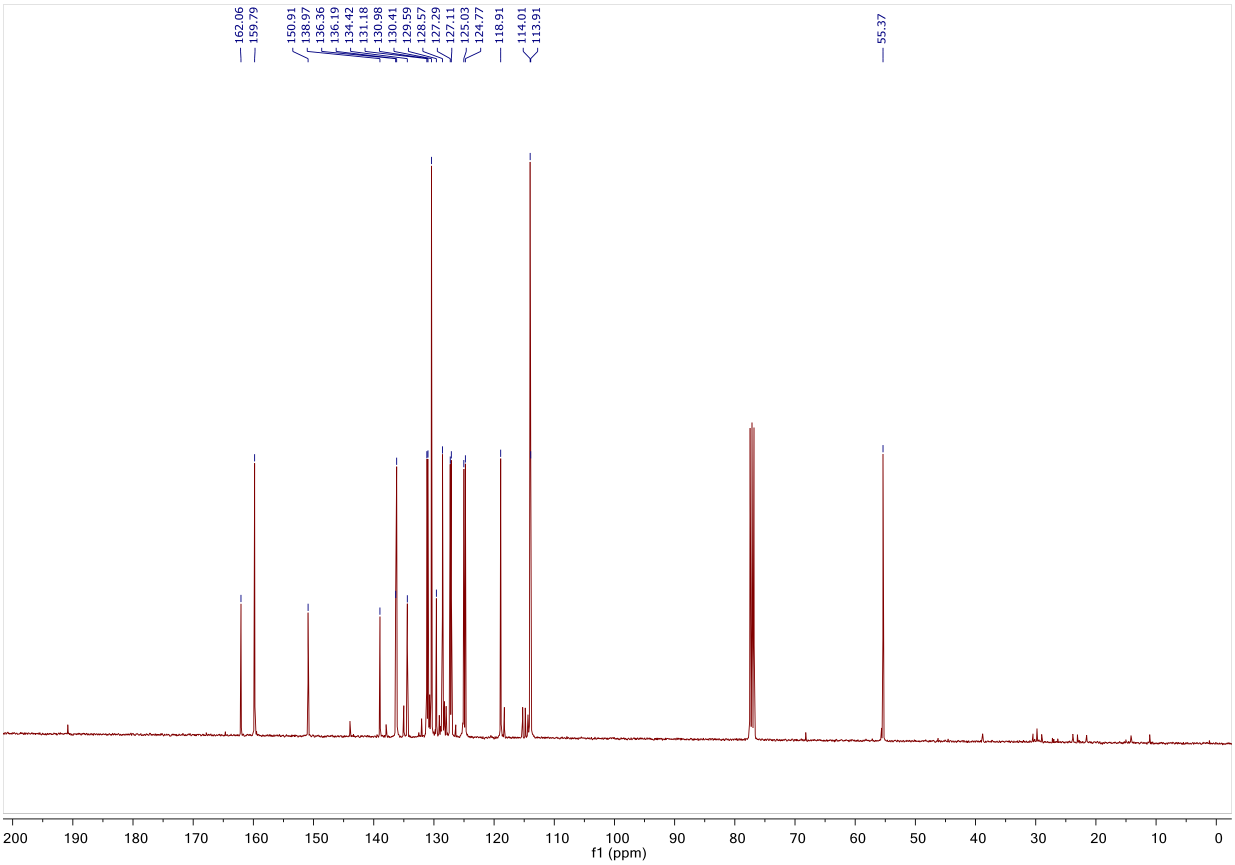
^{13}C NMR (100 MHz, $CDCl_3$) of **1Ad**



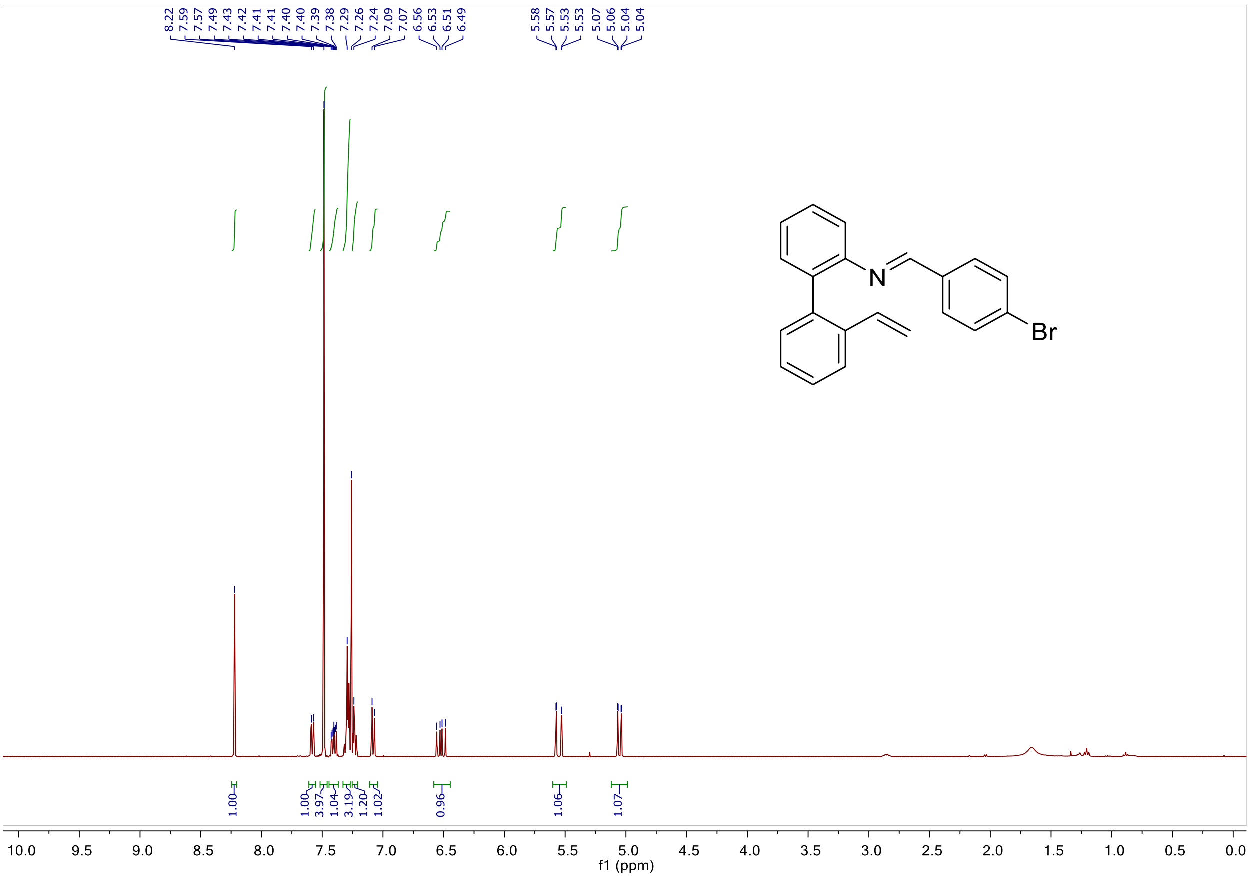
[1]H NMR (400 MHz, $CDCl_3$) of **1Ae**:



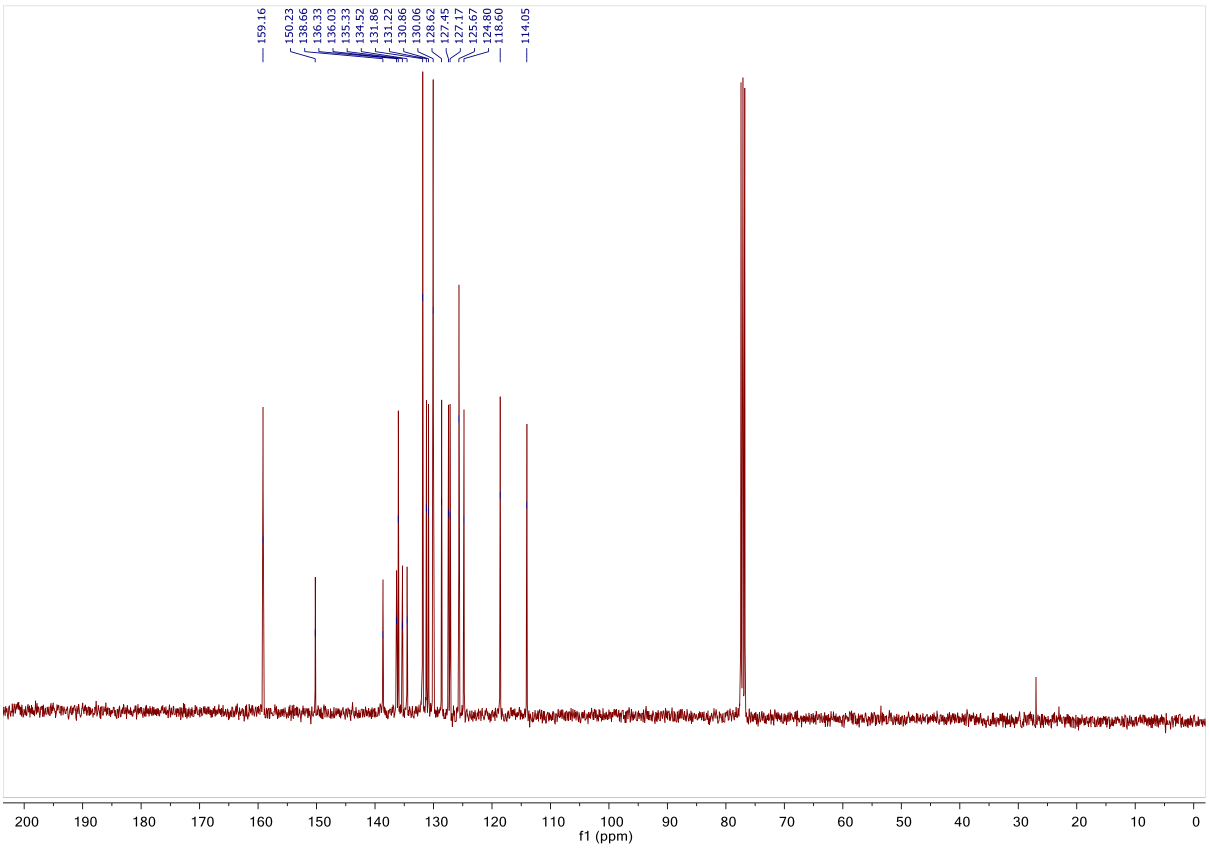
[13]C NMR (100 MHz, $CDCl_3$) of **1Ae**



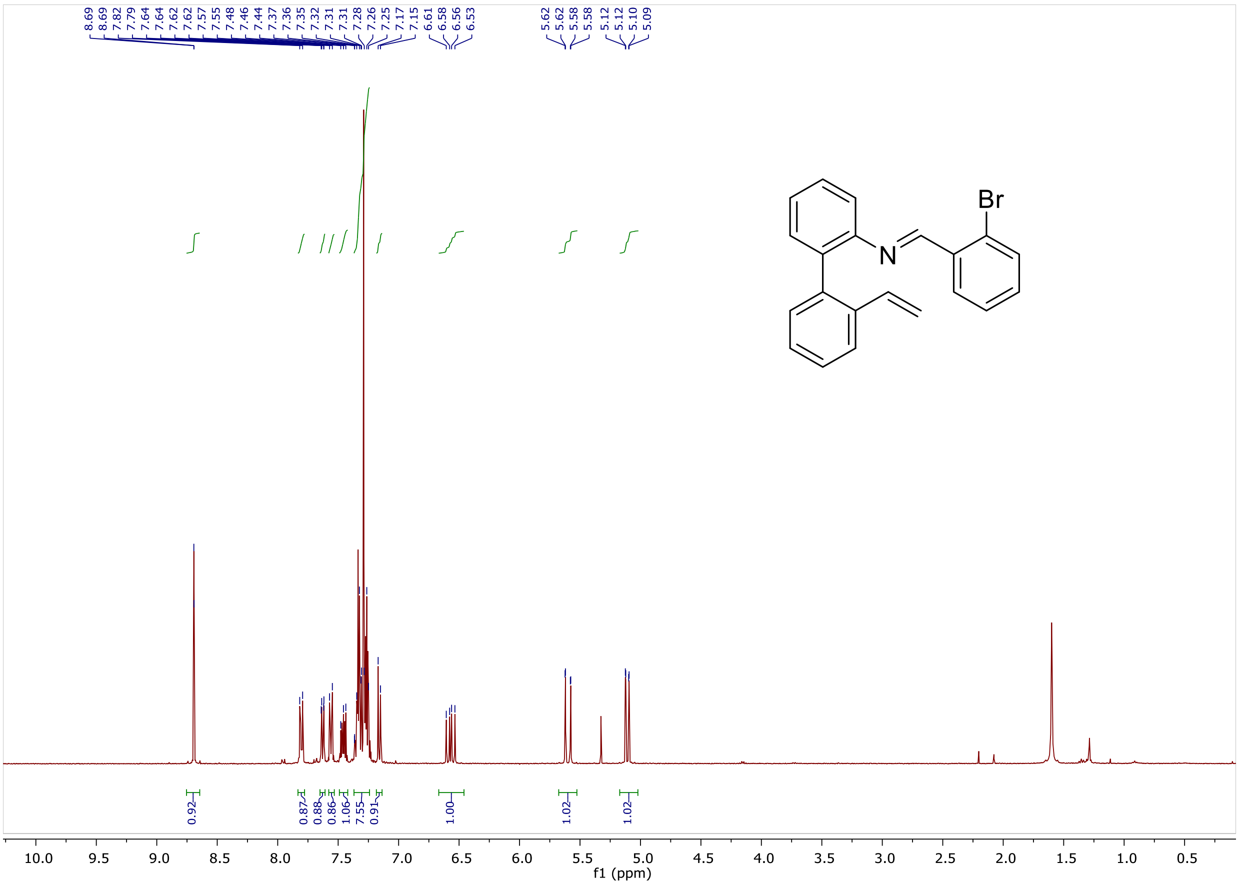
^{1}H NMR (400 MHz, $CDCl_3$) of **1Af**:



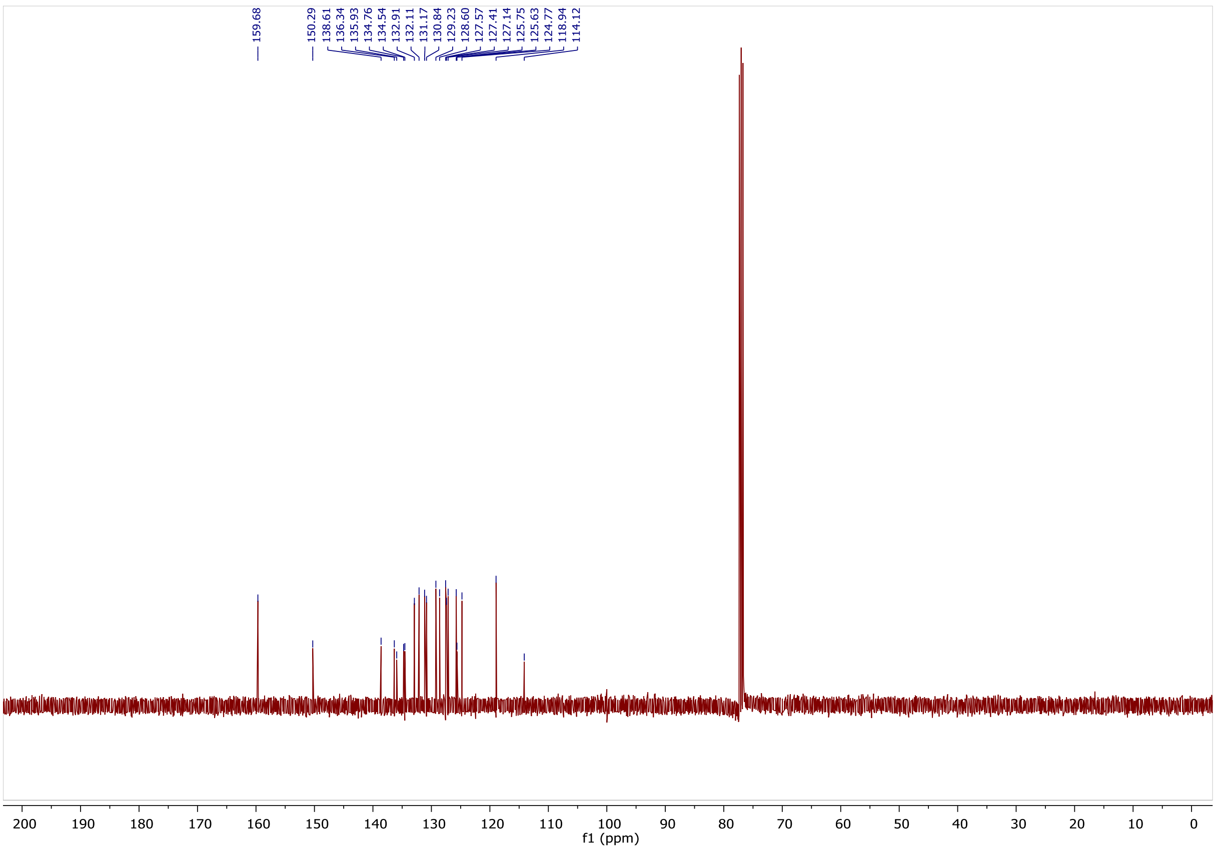
^{13}C NMR (100 MHz, $CDCl_3$) of **1Af**



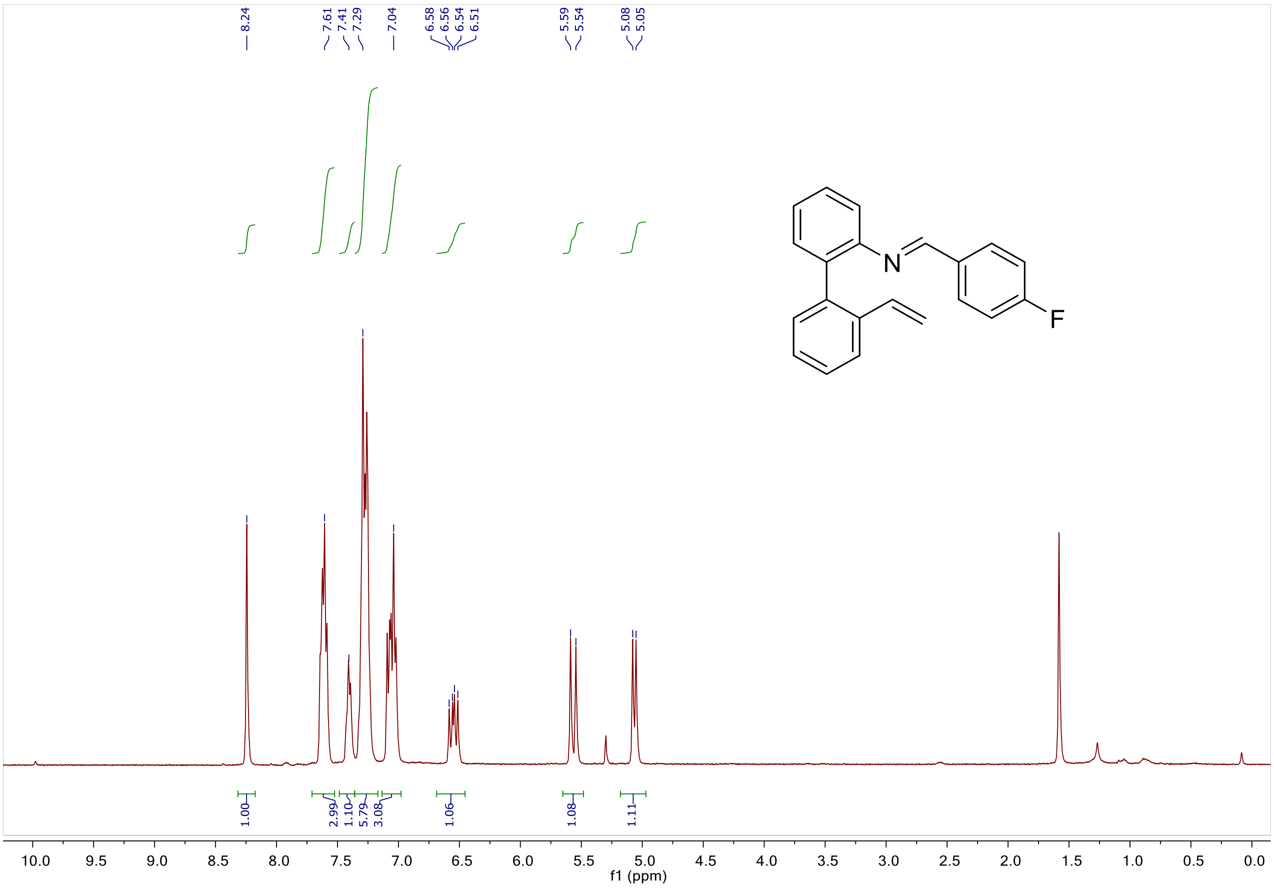
^{1}H NMR (400 MHz, $CDCl_3$) of **1Ag**



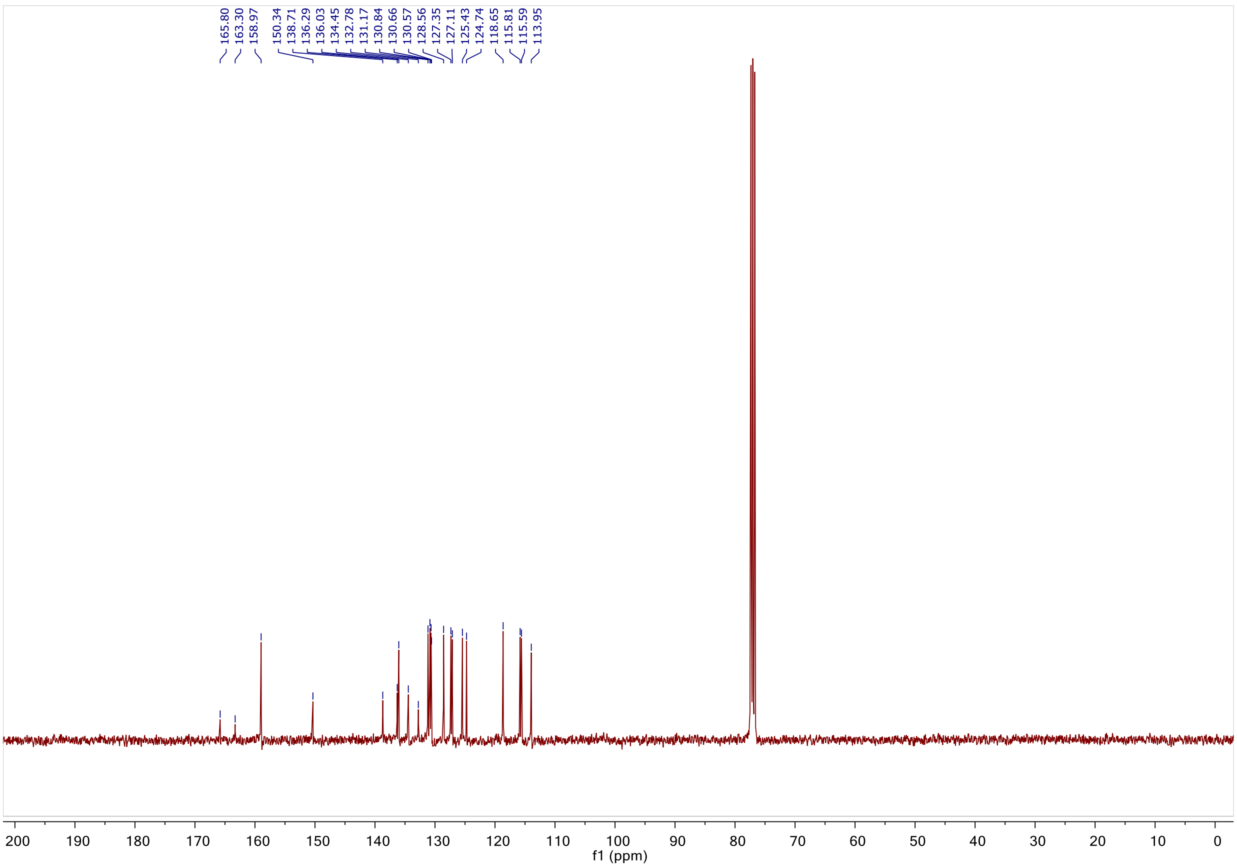
^{13}C NMR (100 MHz, $CDCl_3$) of **1Ag**



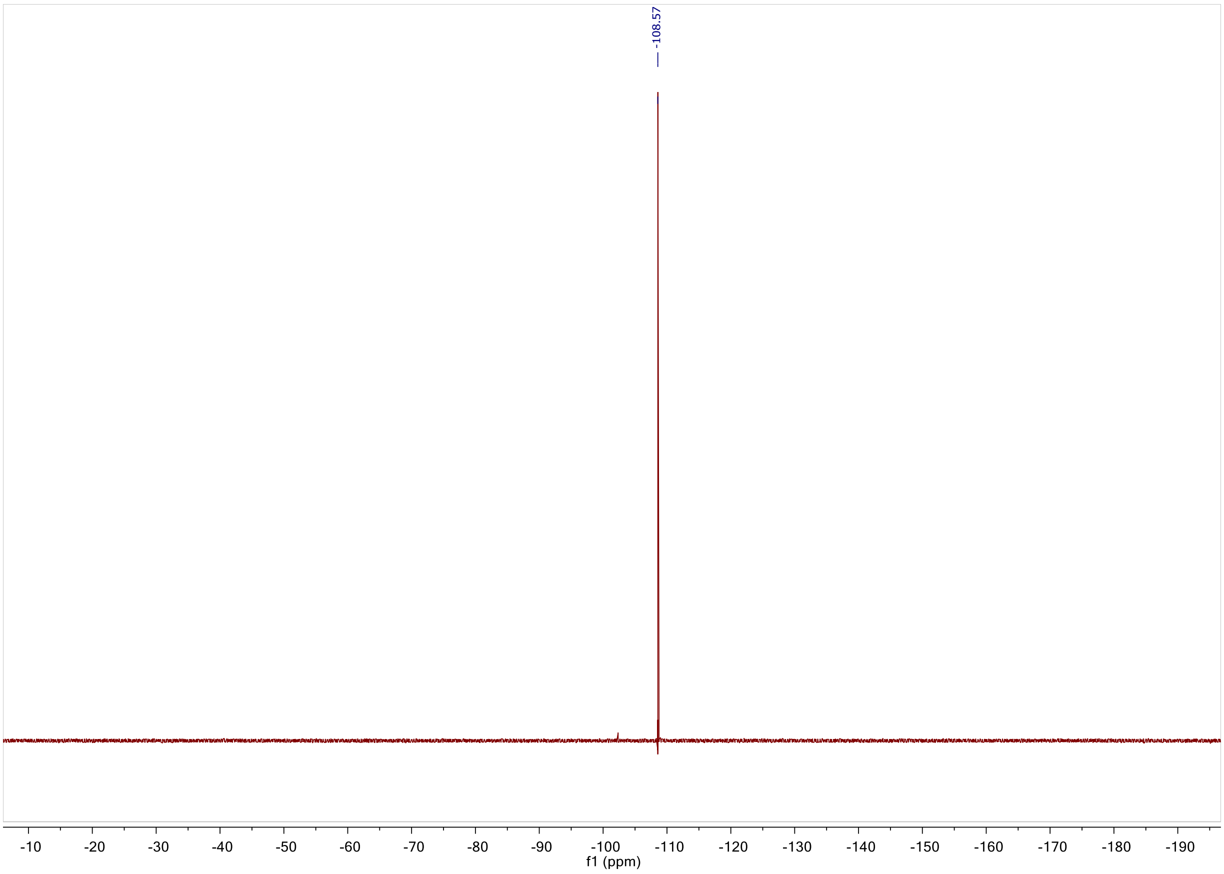
^{1}H NMR (400 MHz, $CDCl_3$) of **1Ah**



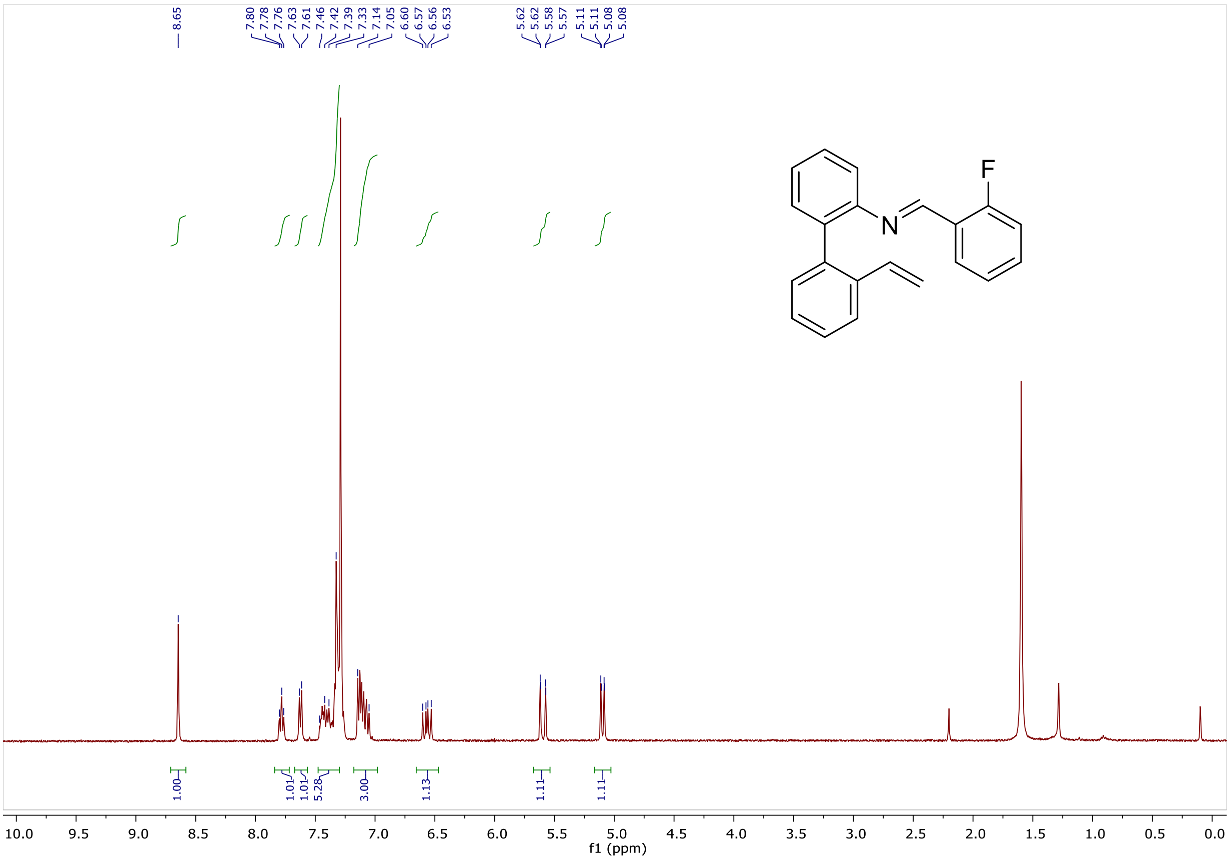
^{13}C NMR (100 MHz, $CDCl_3$) of **1Ah**



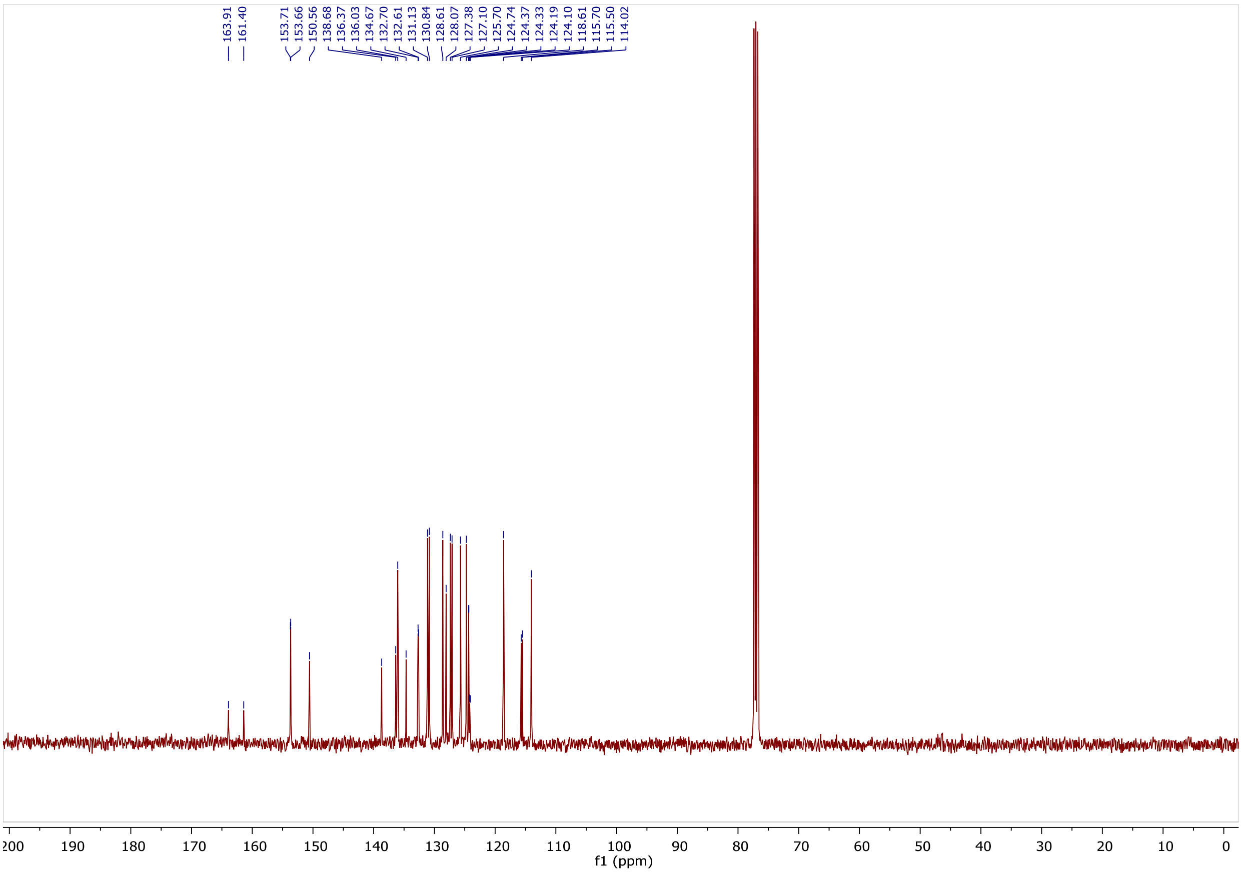
^{19}F NMR (377 MHz, $CDCl_3$) of **1Ah**



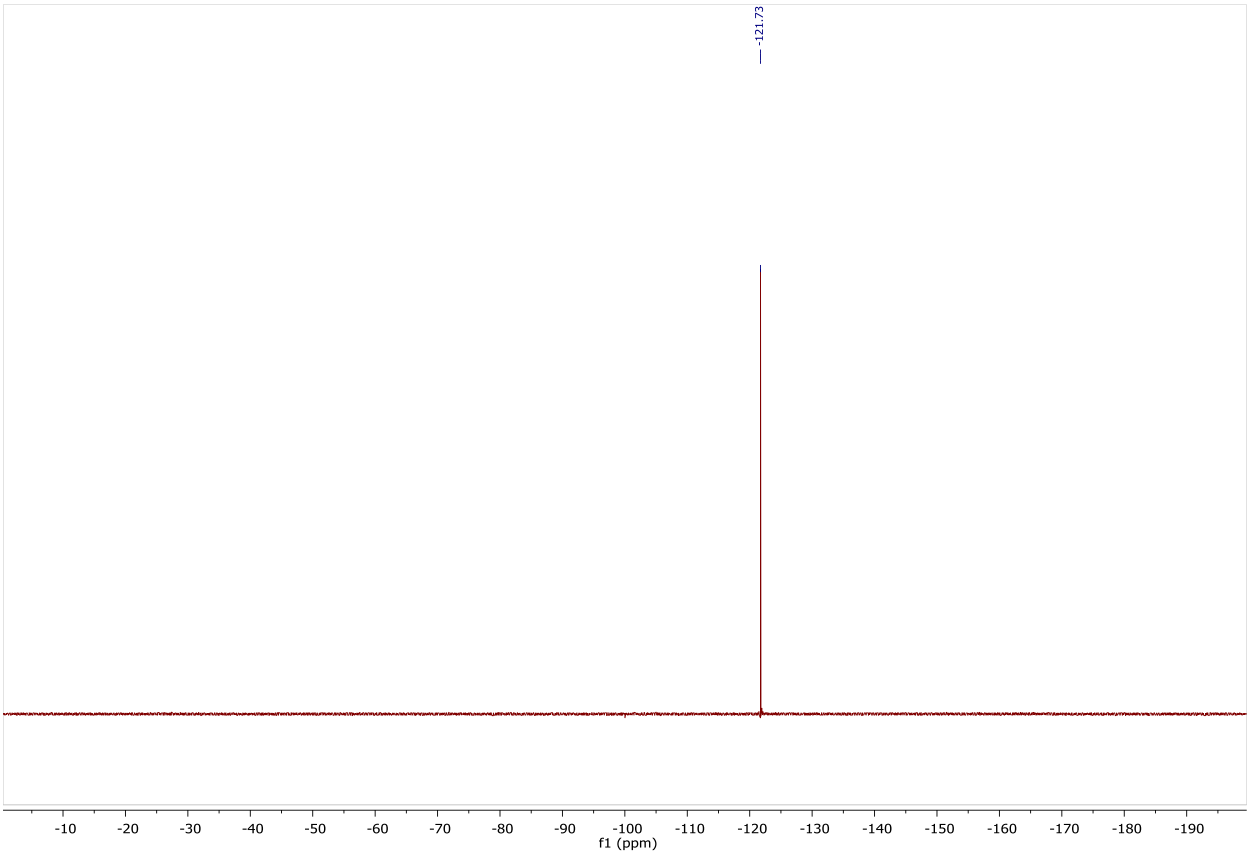
^{1}H NMR (400 MHz, $CDCl_3$) of **1Ai**:



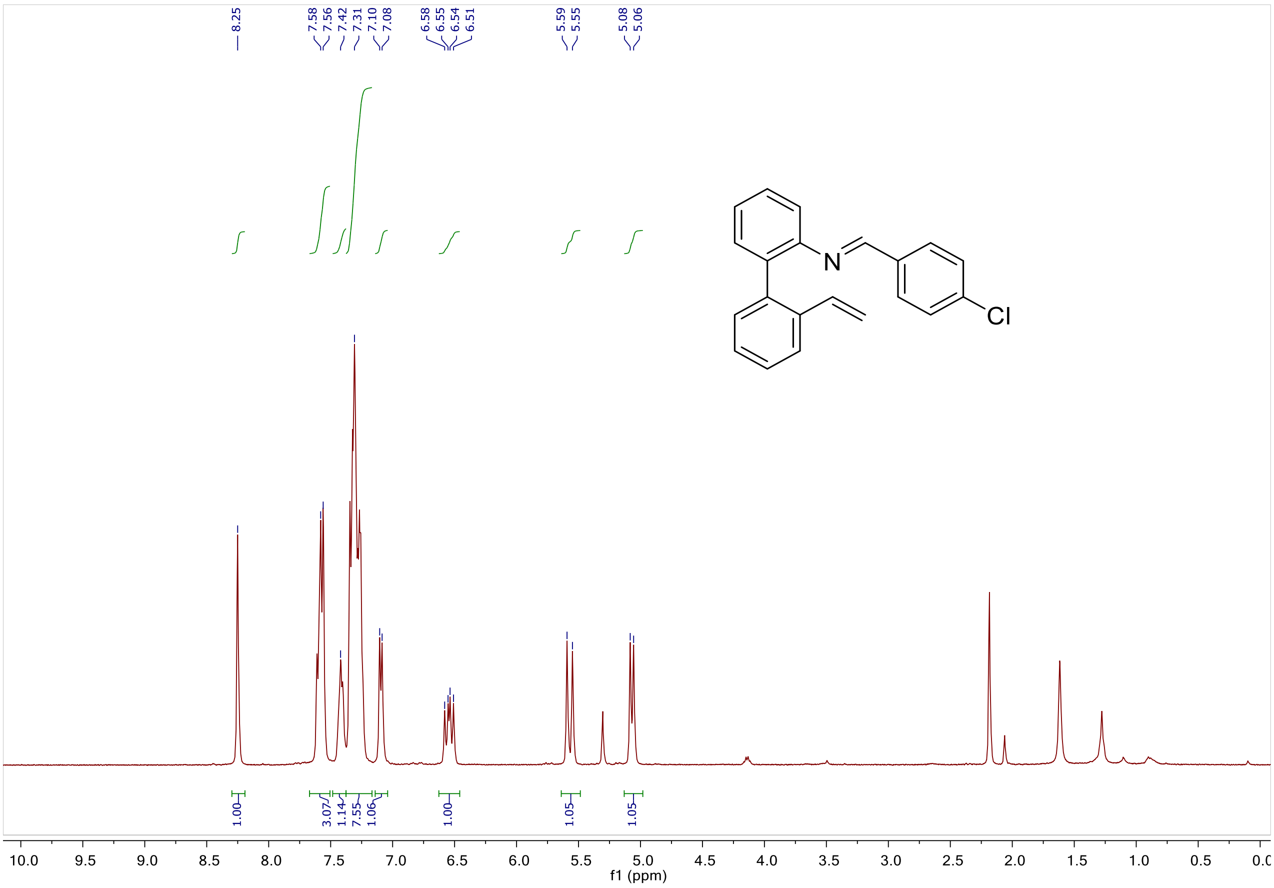
^{13}C NMR (100 MHz, $CDCl_3$) of **1Ai**



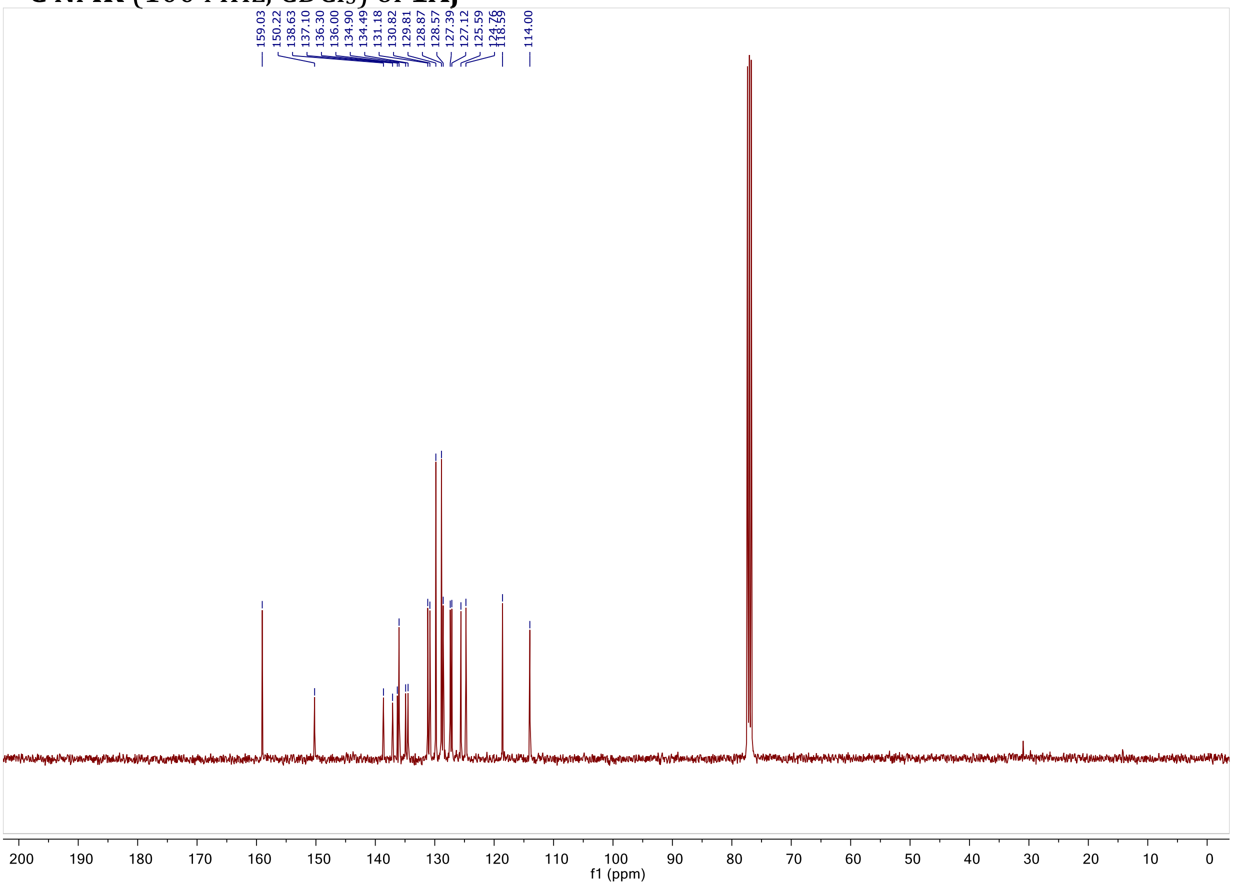
^{19}F NMR (377 MHz, $CDCl_3$) of **1Ai**:



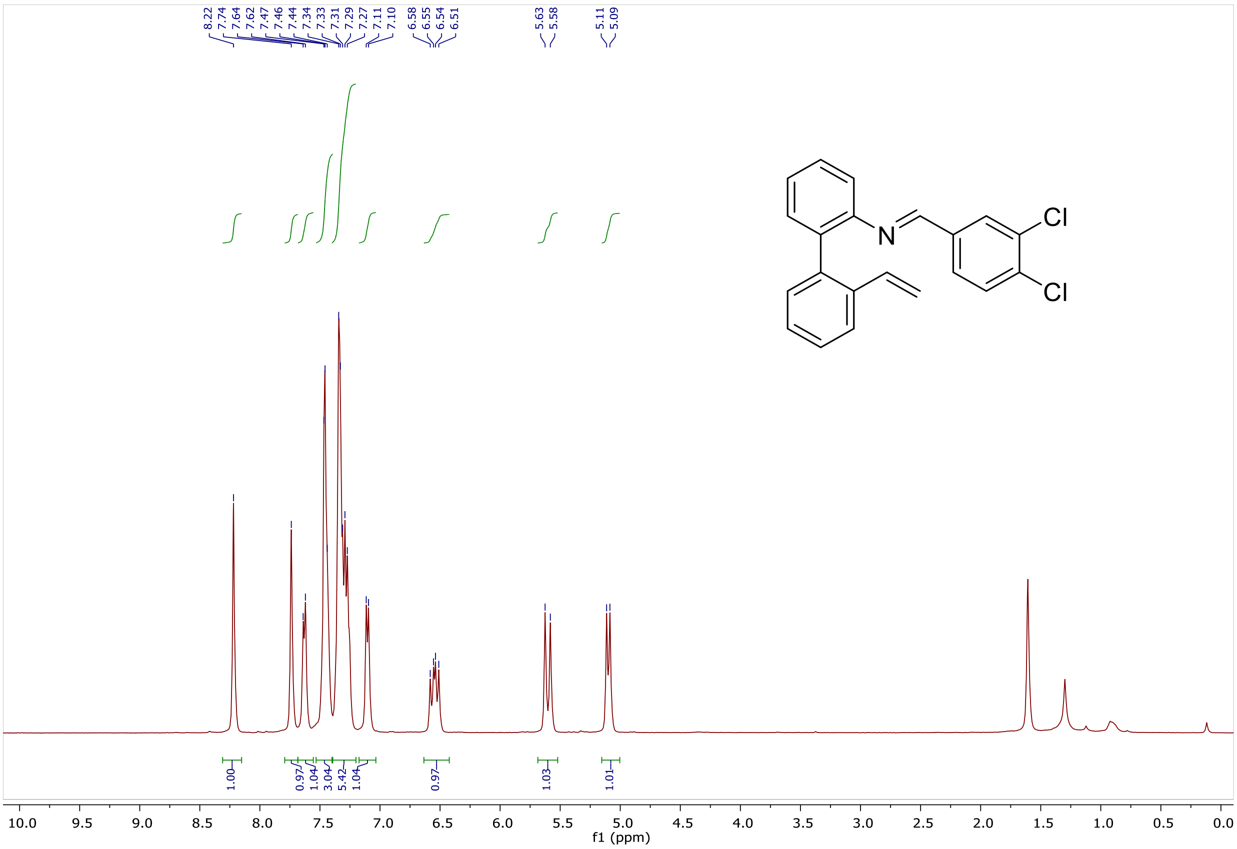
^{1}H NMR (400 MHz, $CDCl_3$) of **1Aj**:



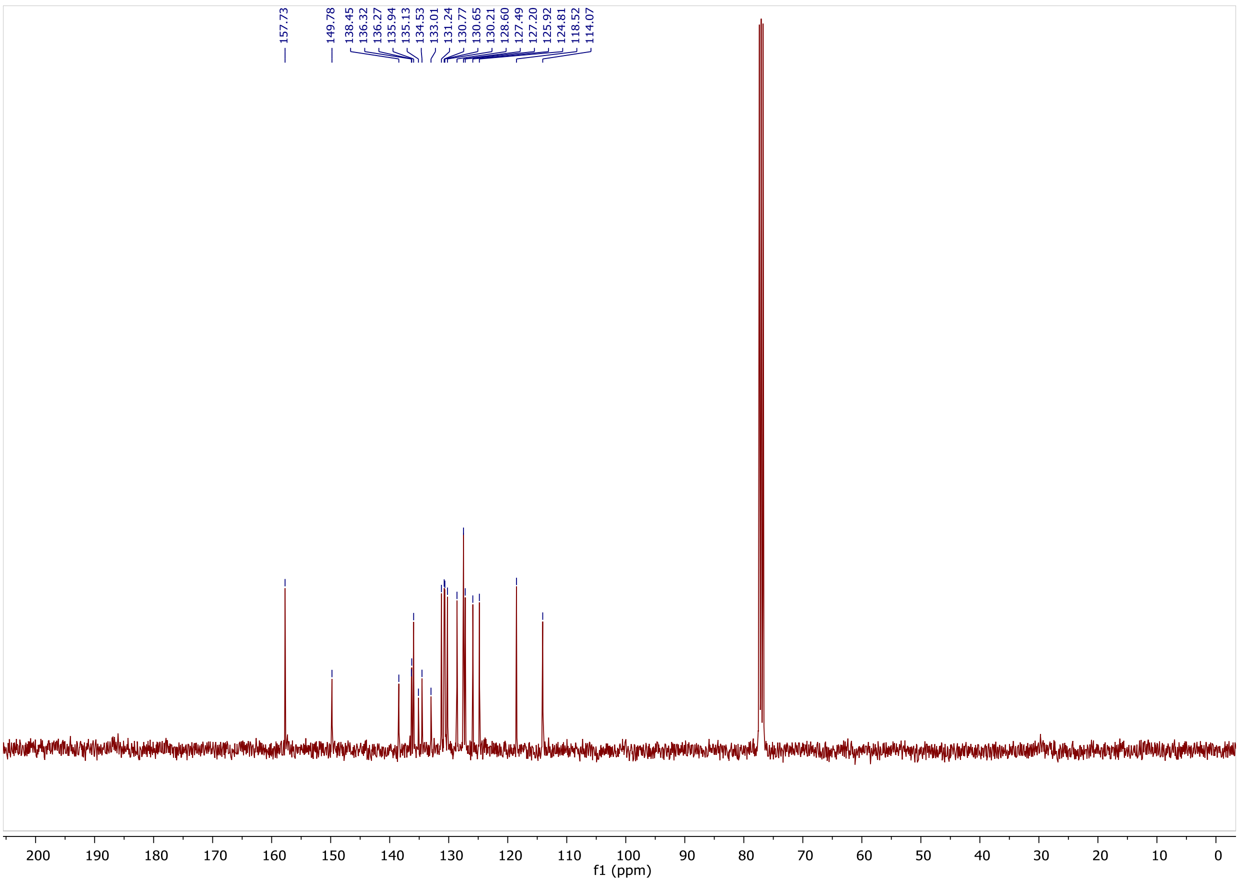
^{13}C NMR (100 MHz, $CDCl_3$) of **1Aj**



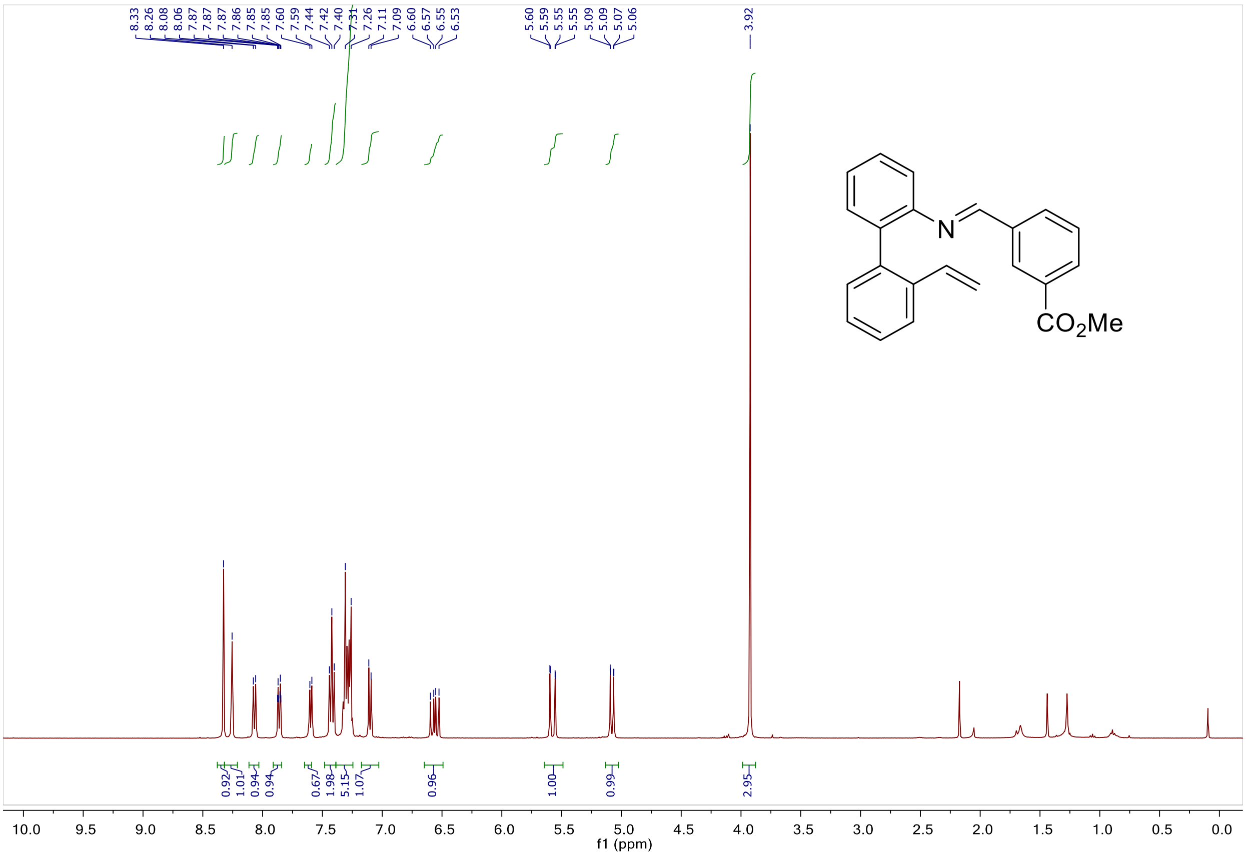
^{1}H NMR (400 MHz, $CDCl_3$) of **1Ak**:



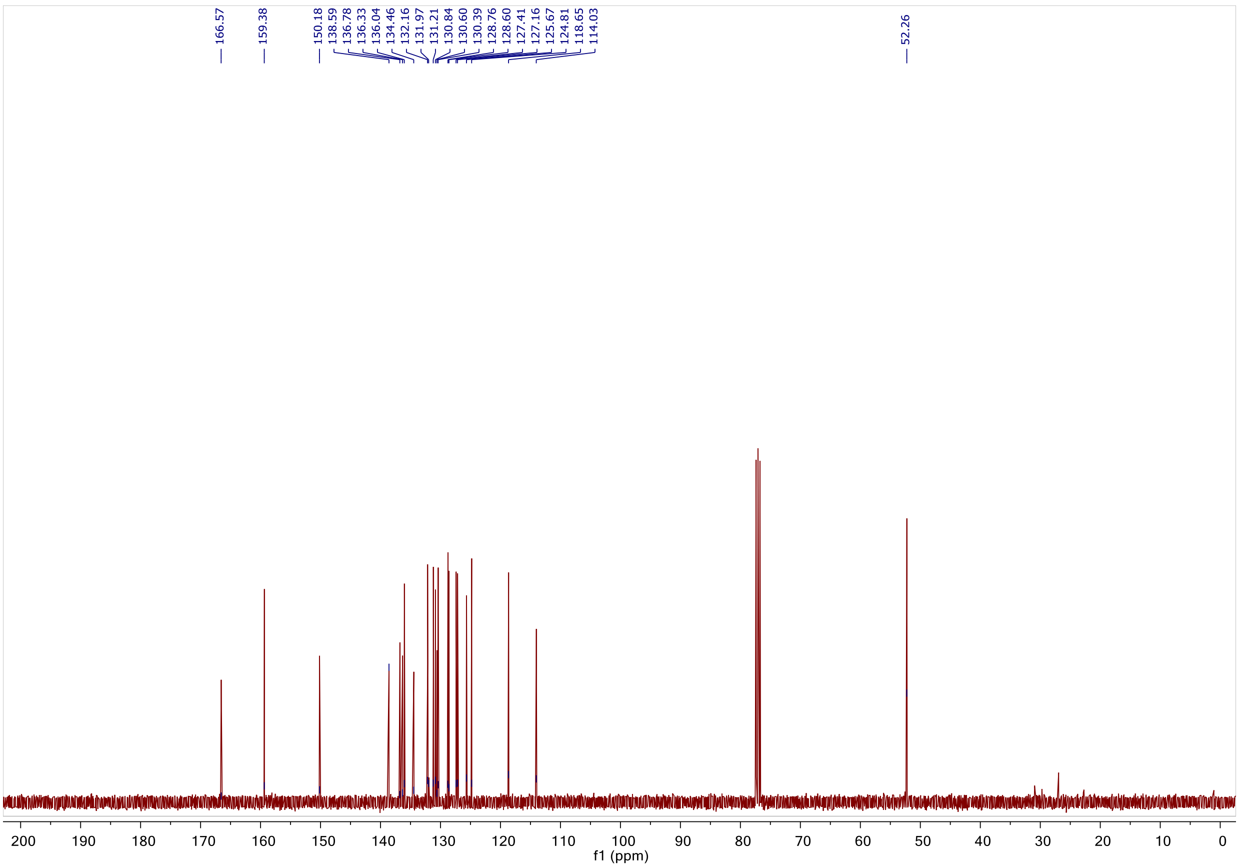
^{13}C NMR (100 MHz, $CDCl_3$) of **1Ak**



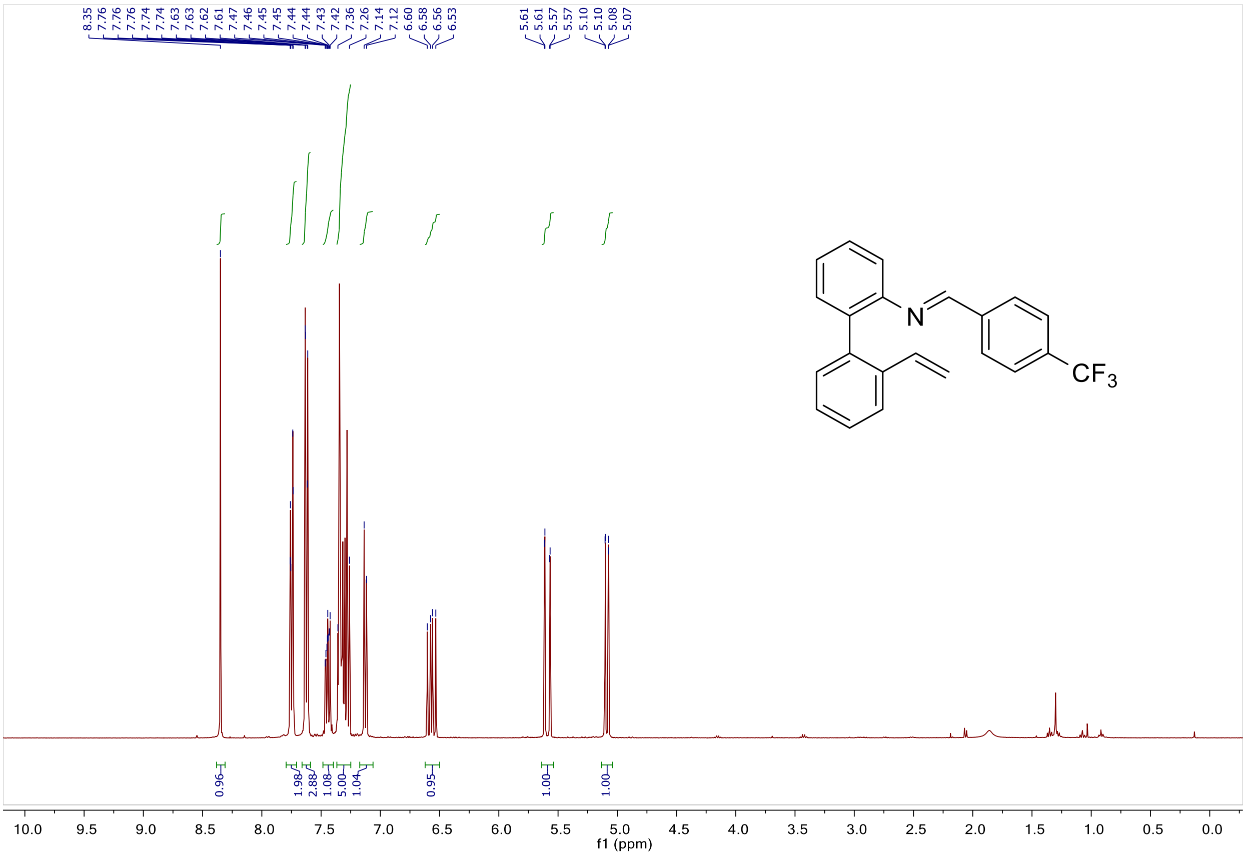
[1]H NMR (400 MHz, $CDCl_3$) of **1Al**



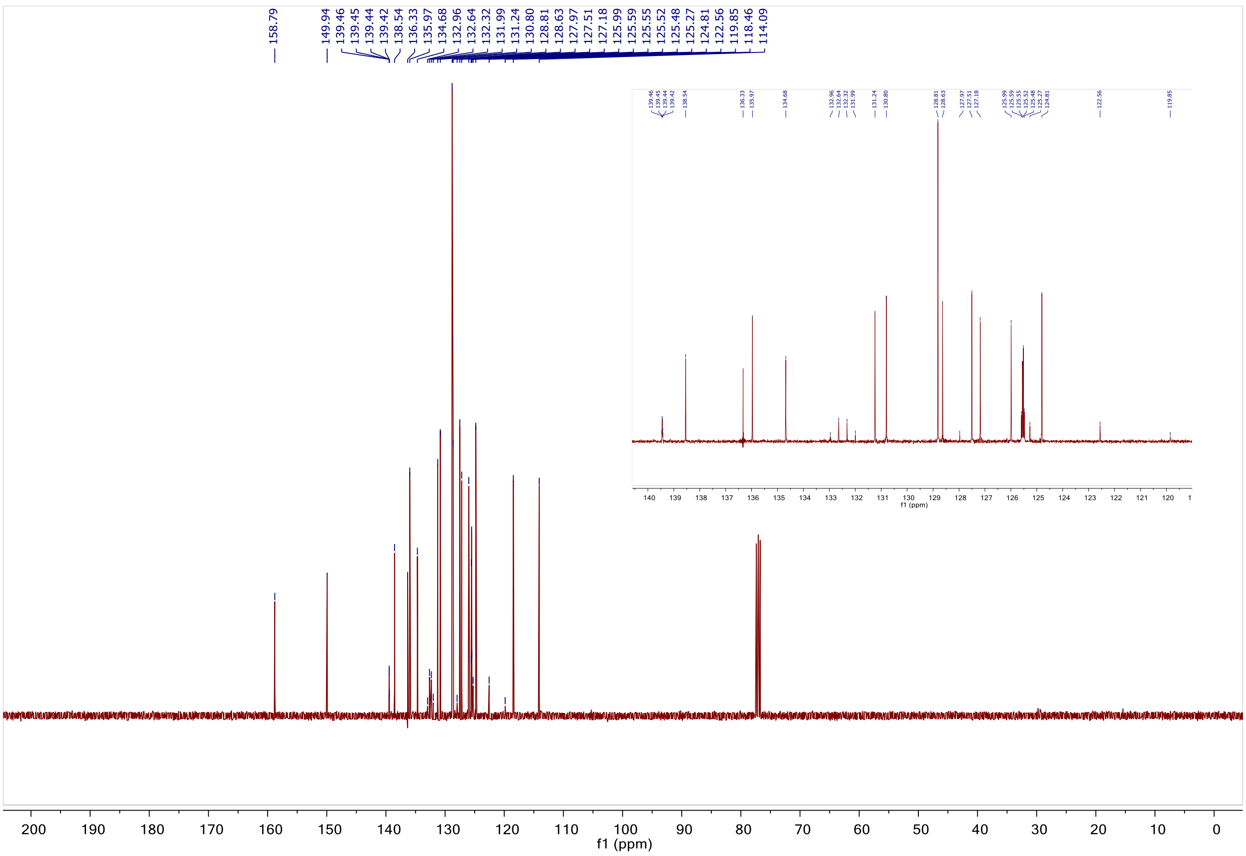
[13]C NMR (100 MHz, $CDCl_3$) of **1Al**



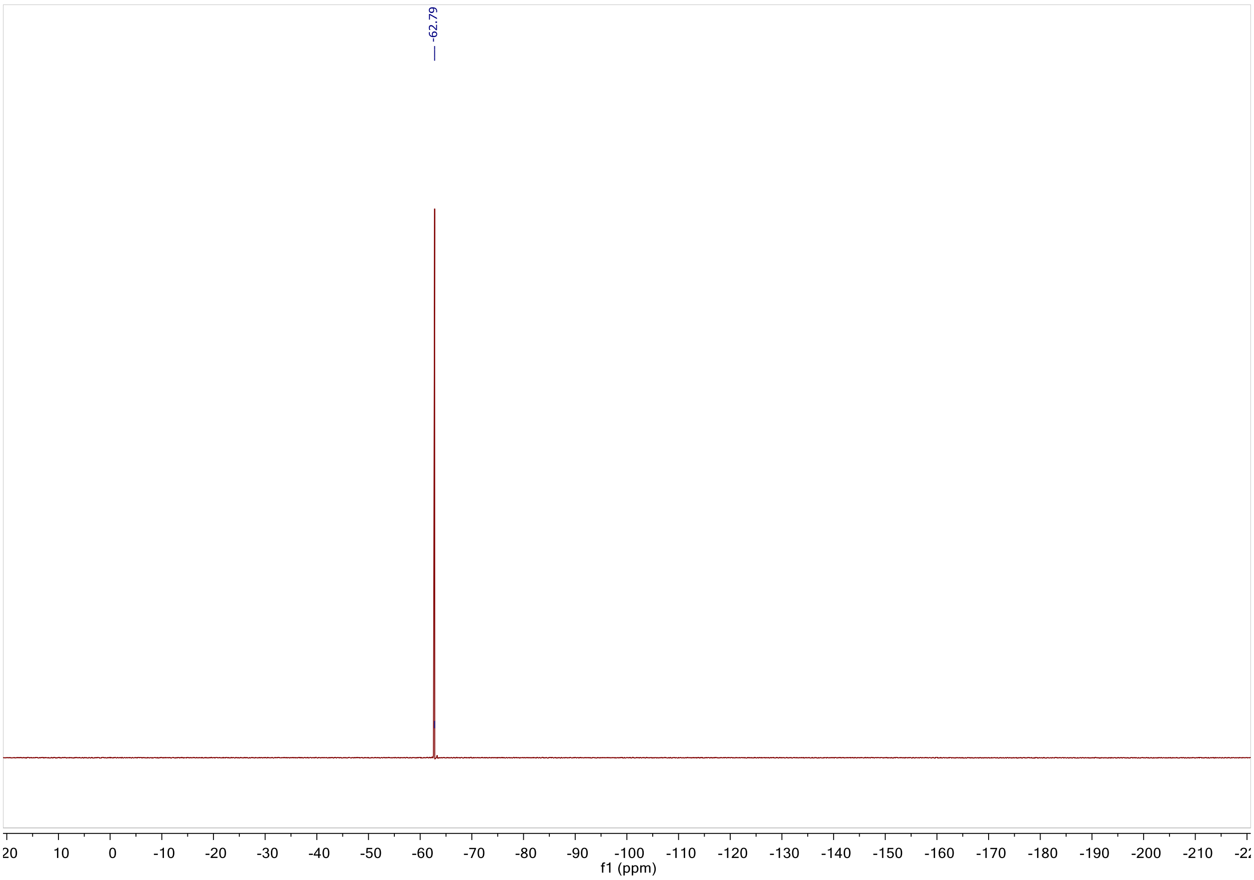
¹H NMR (400 MHz, $CDCl_3$) of **1Am**:



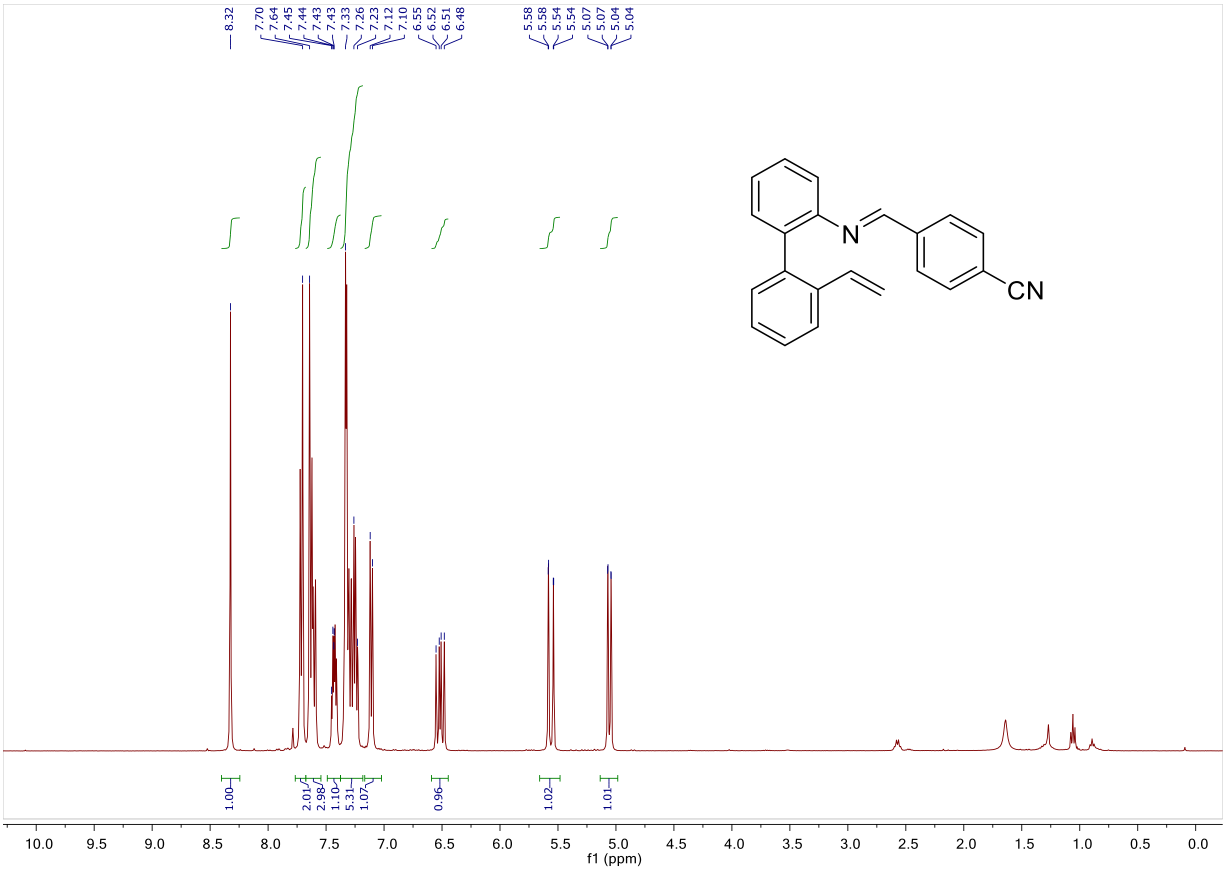
¹³C NMR (100 MHz, $CDCl_3$) of **1Am**



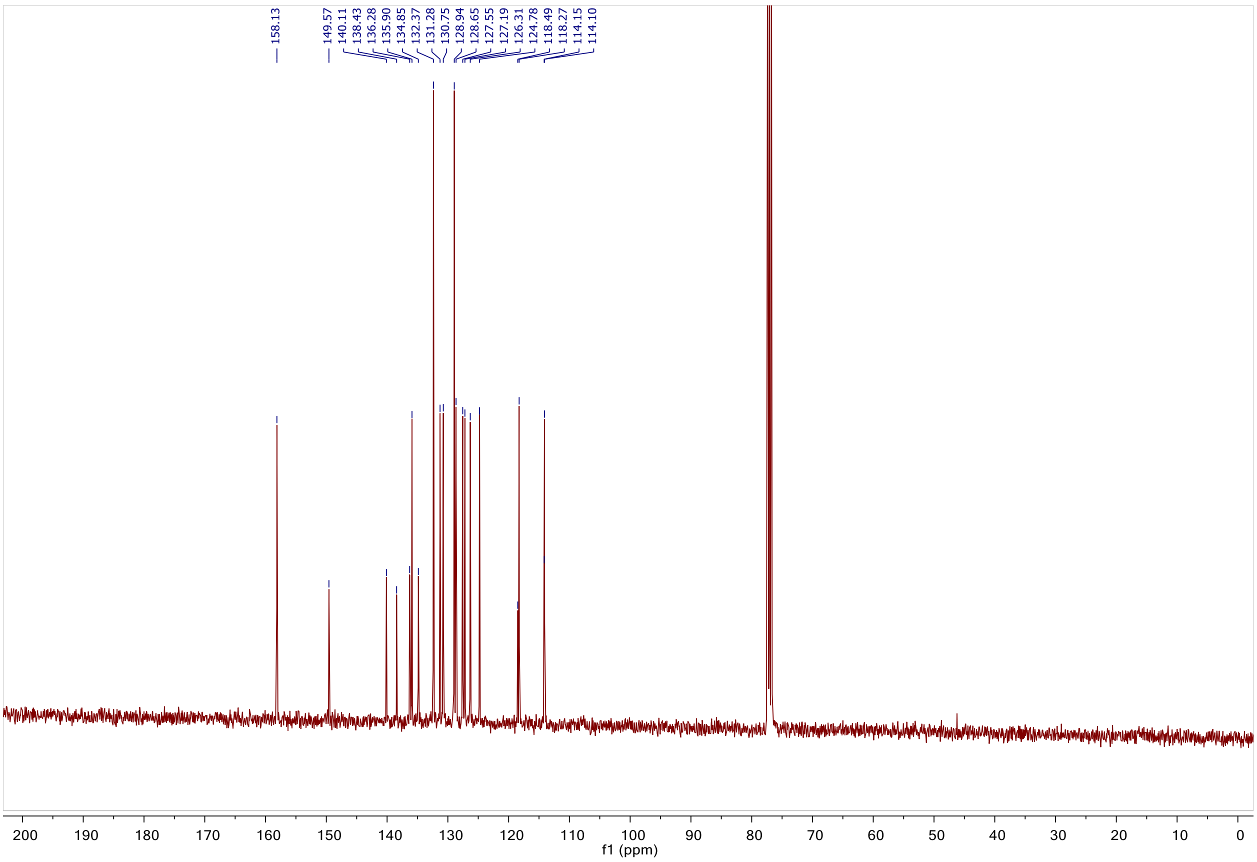
^{19}F NMR (400 MHz, $CDCl_3$) of **1Am**:



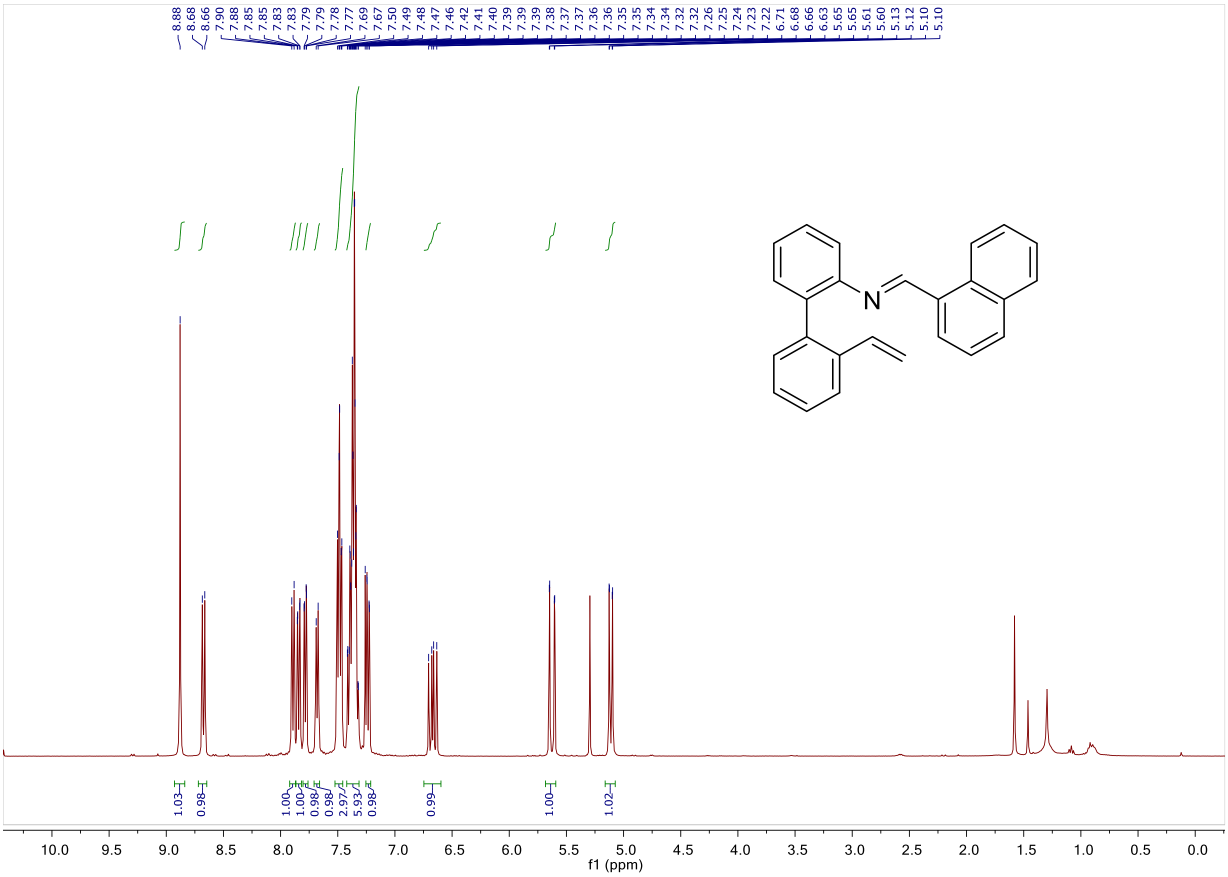
[1]H NMR (400 MHz, $CDCl_3$) of **1An**:



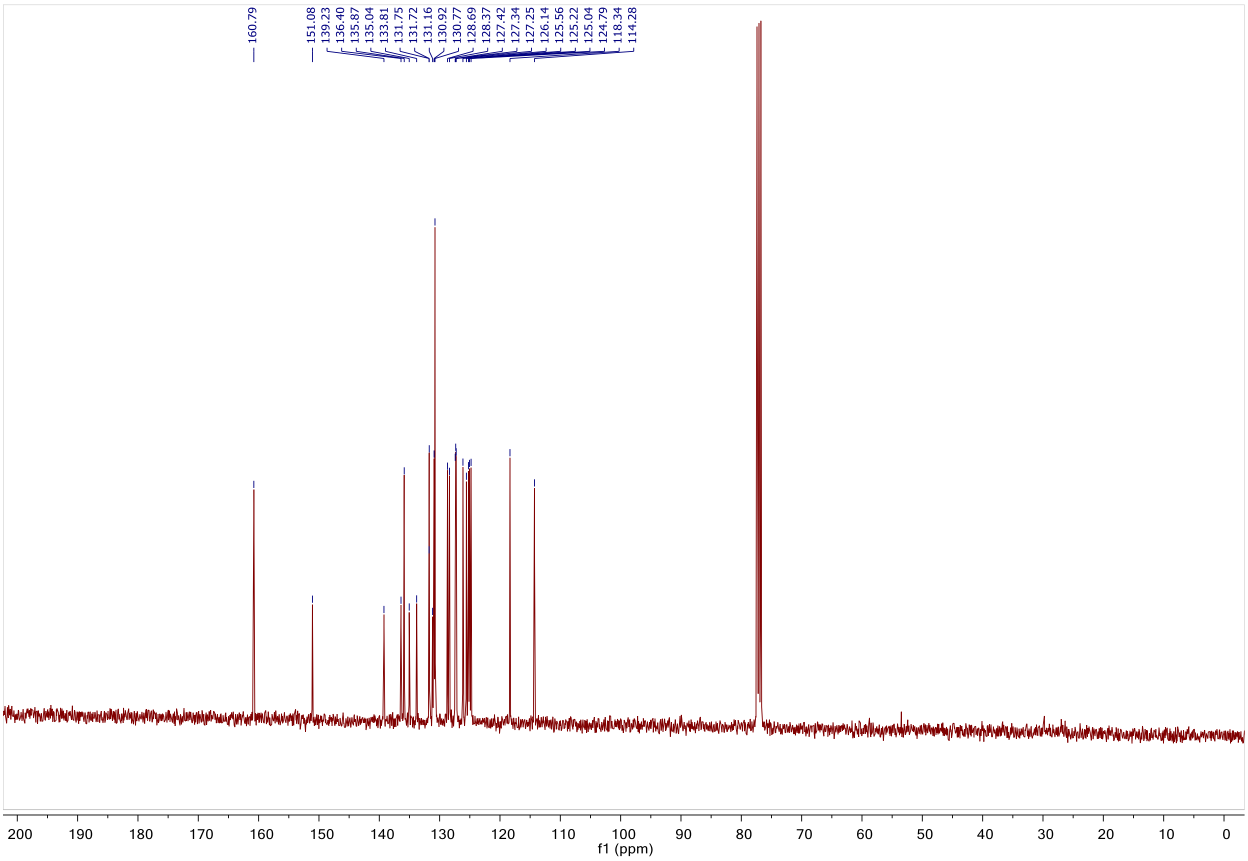
[13]C NMR (100 MHz, $CDCl_3$) of **1An**



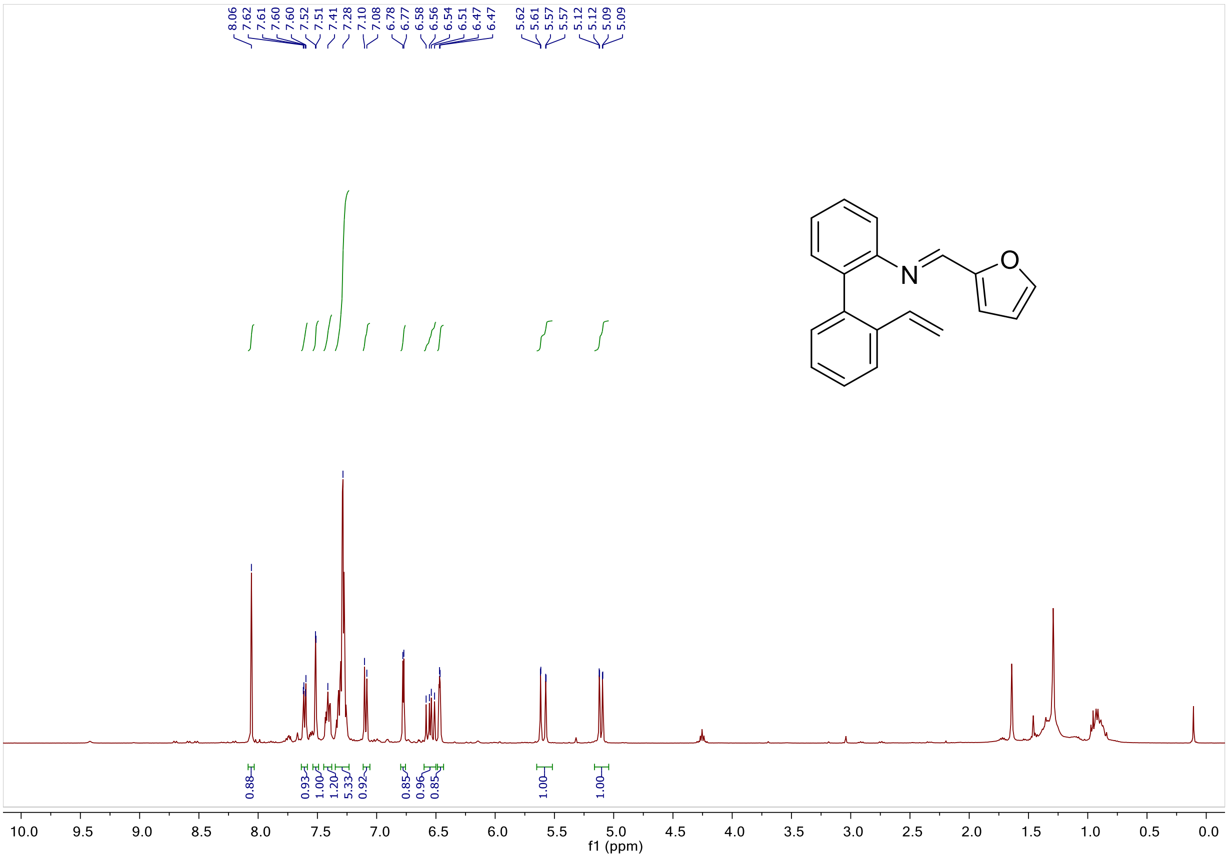
[1]H NMR (400 MHz, $CDCl_3$) of **1Ao**



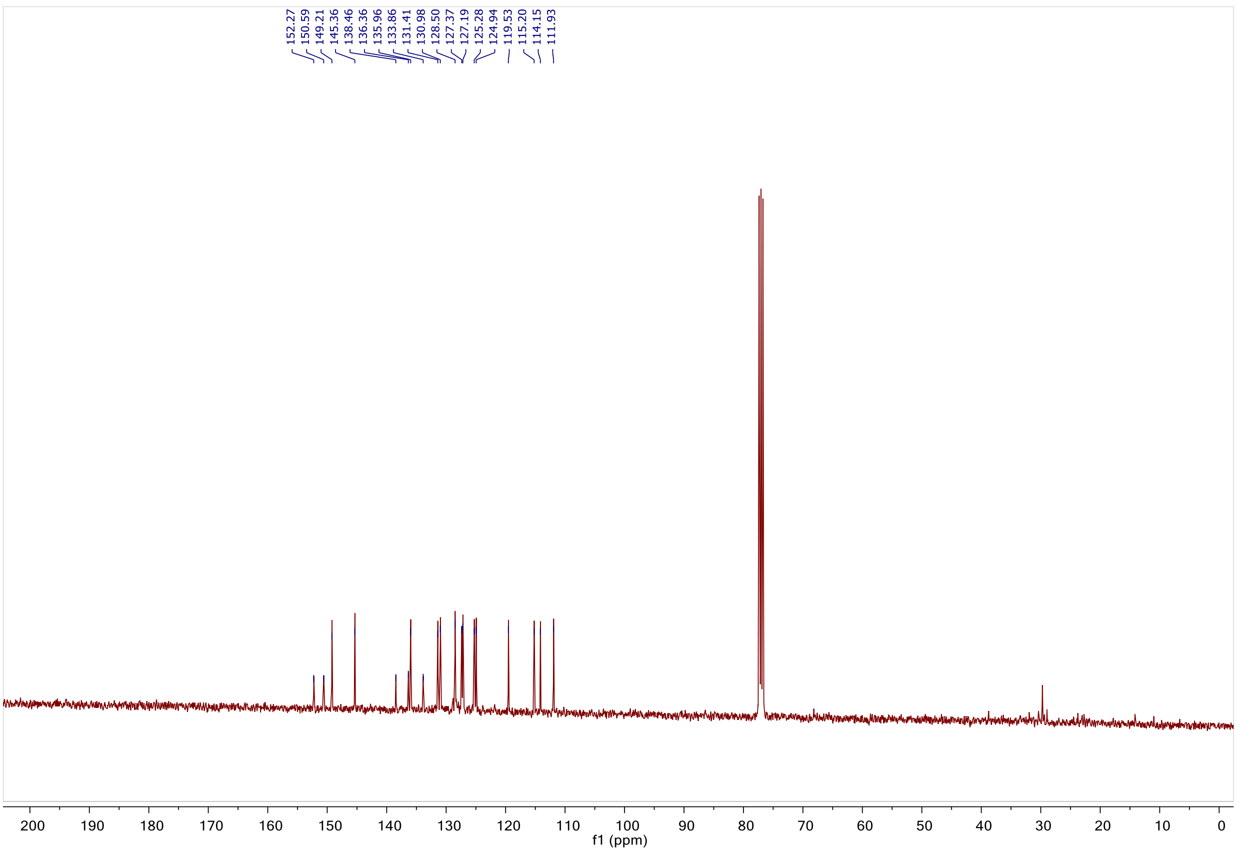
[13]C NMR (100 MHz, $CDCl_3$) of **1Ao**



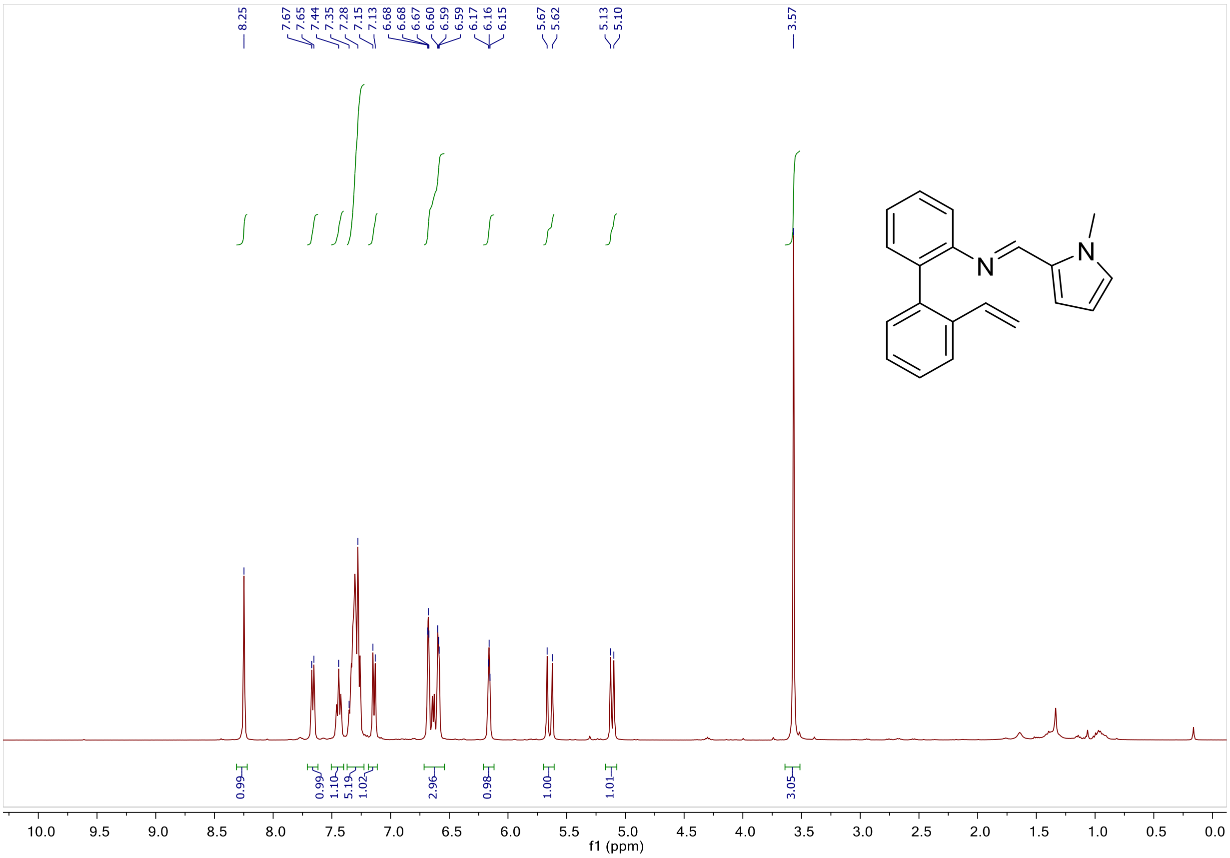
^{1}H NMR (400 MHz, $CDCl_3$) of **1Ap**:



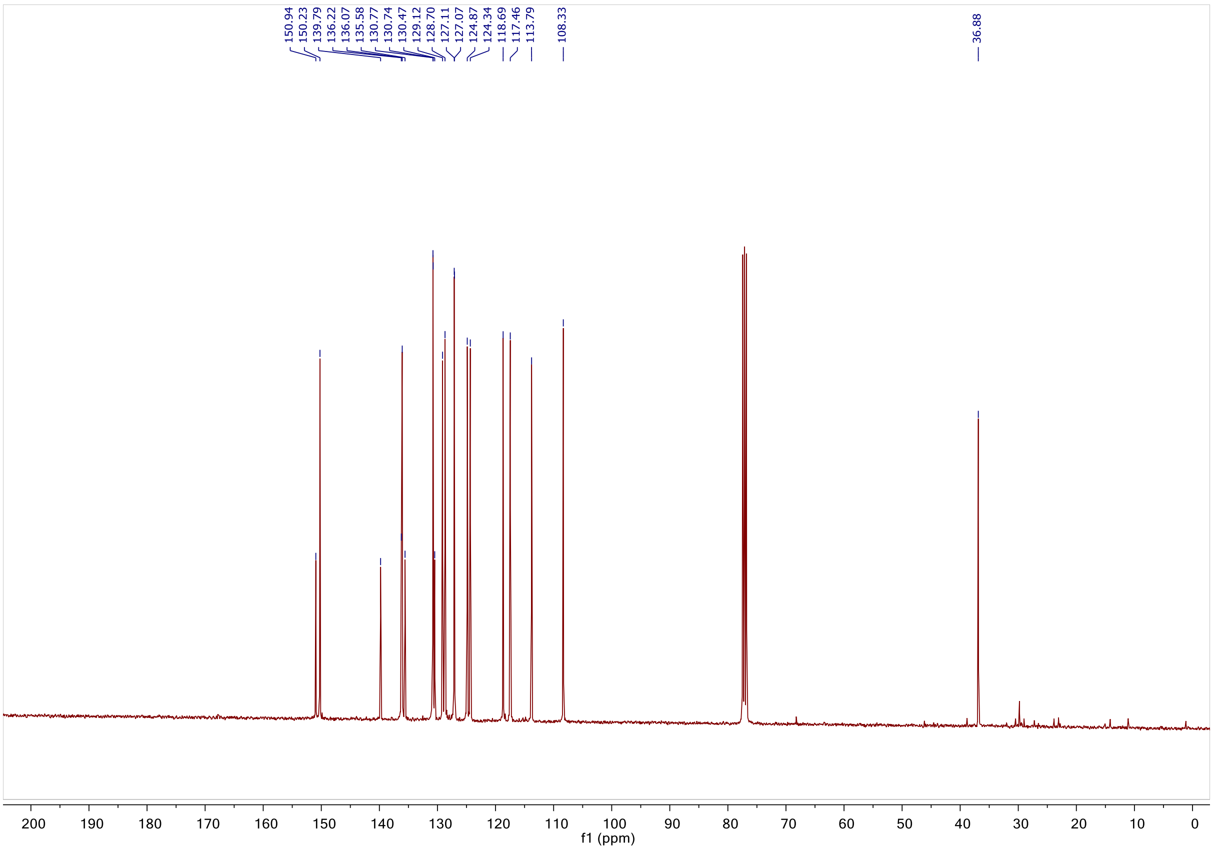
^{13}C NMR (100 MHz, $CDCl_3$) of **1Ap**



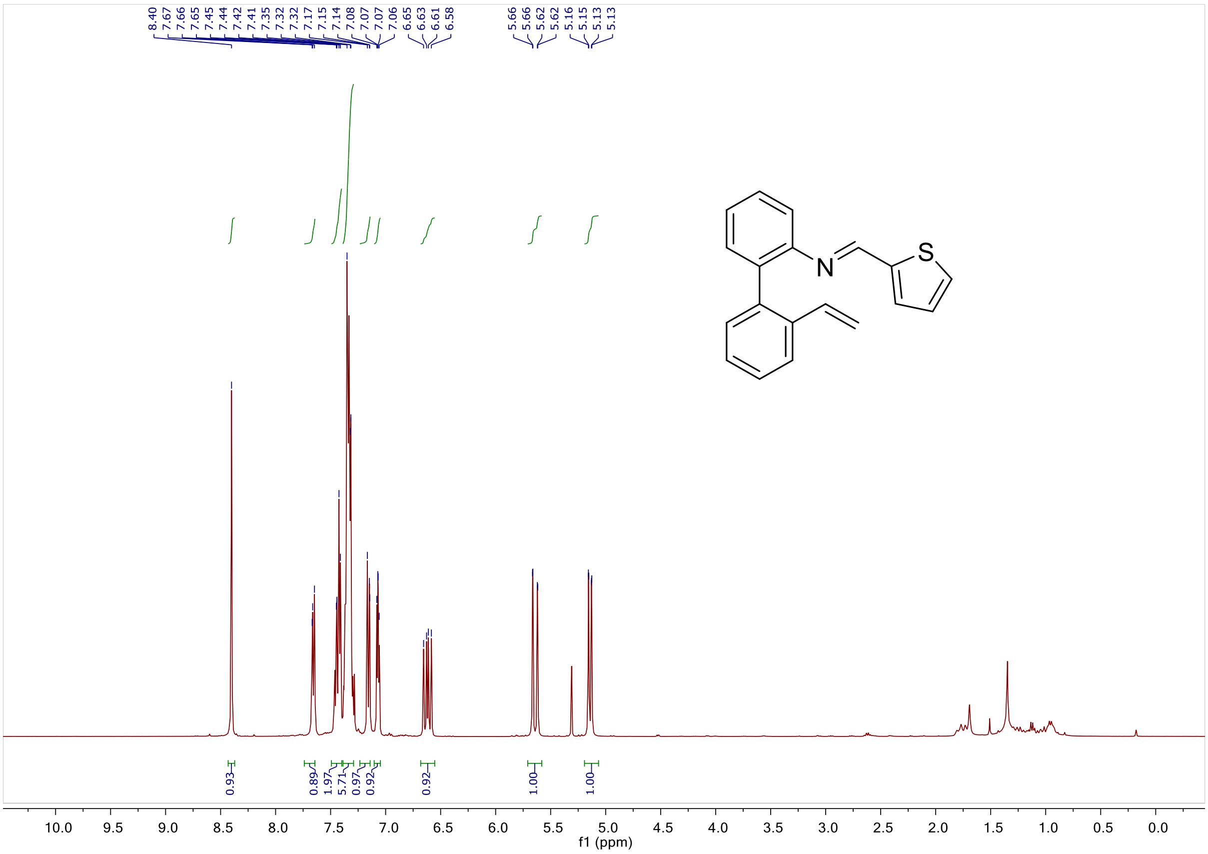
^{1}**H NMR** (400 MHz, $CDCl_3$) of **1Aq**:



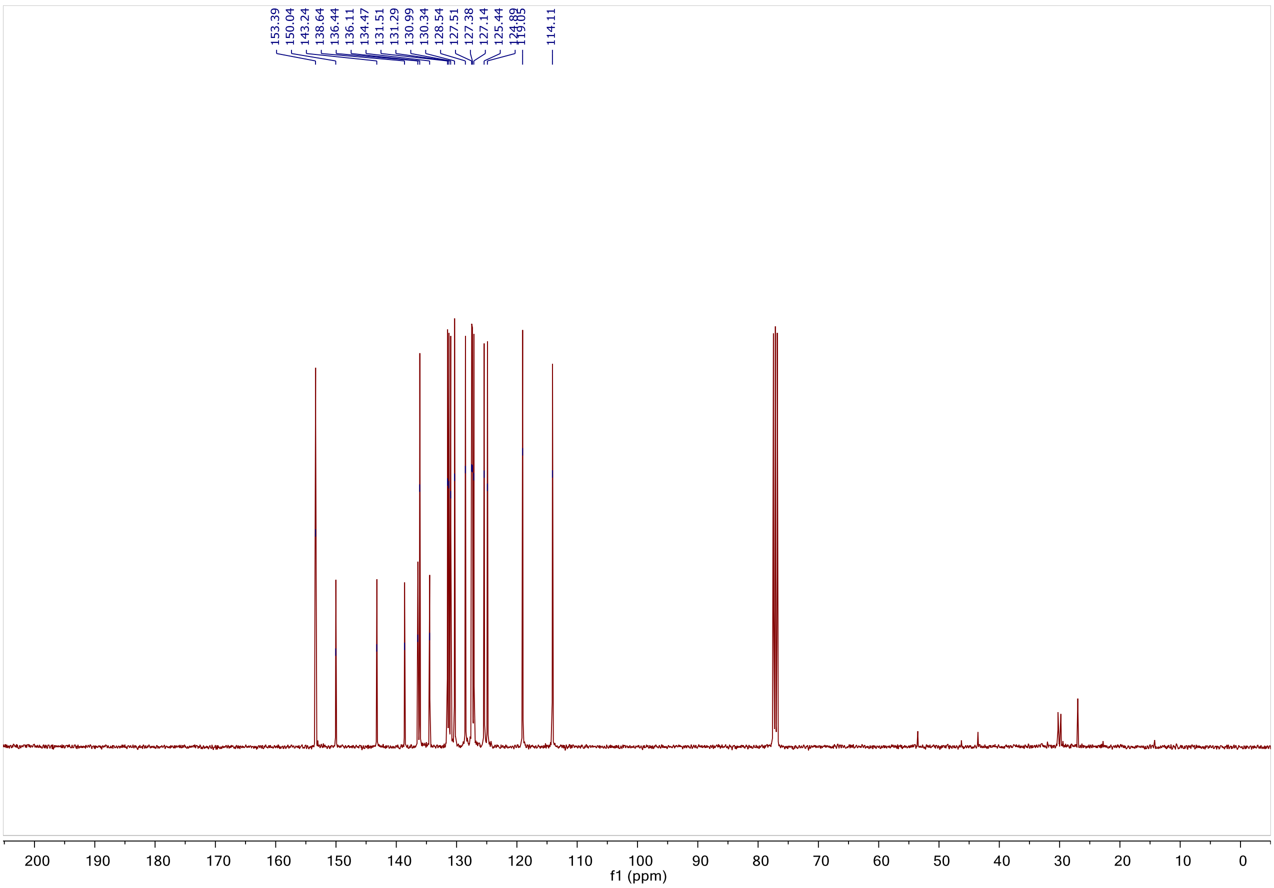
^{13}**C NMR** (100 MHz, $CDCl_3$) of **1Aq**



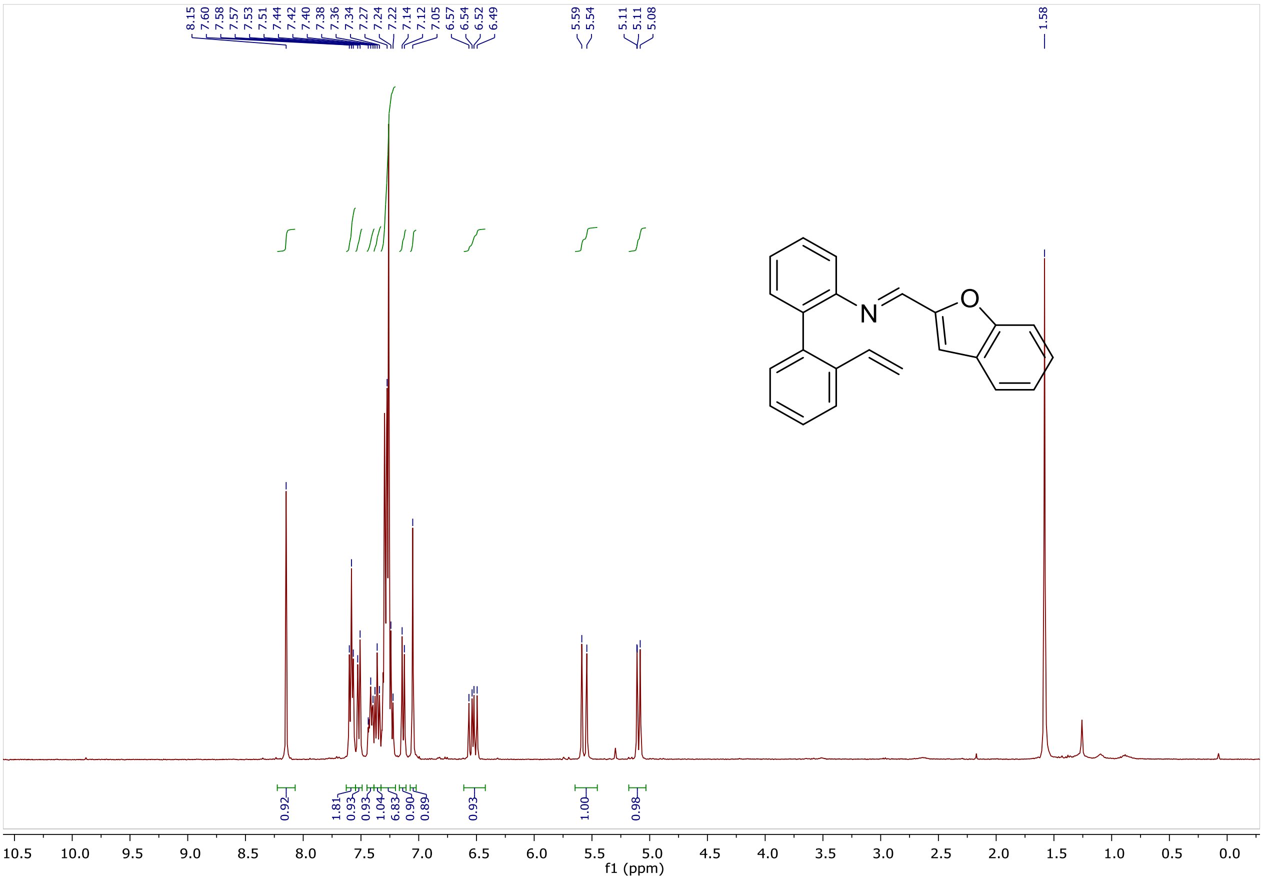
[1]H NMR (400 MHz, $CDCl_3$) of **1Ar**



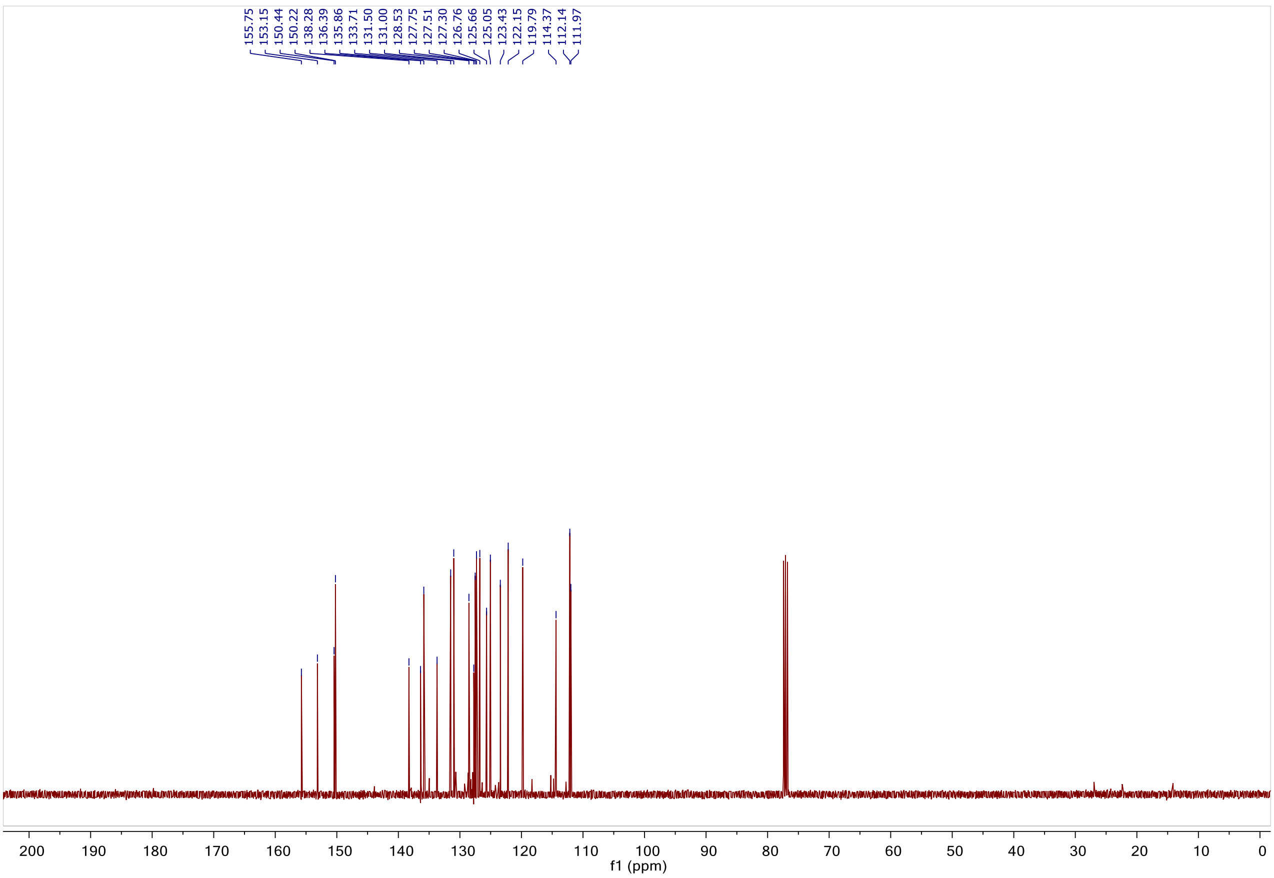
[13]C NMR (100 MHz, $CDCl_3$) of **1Ar**



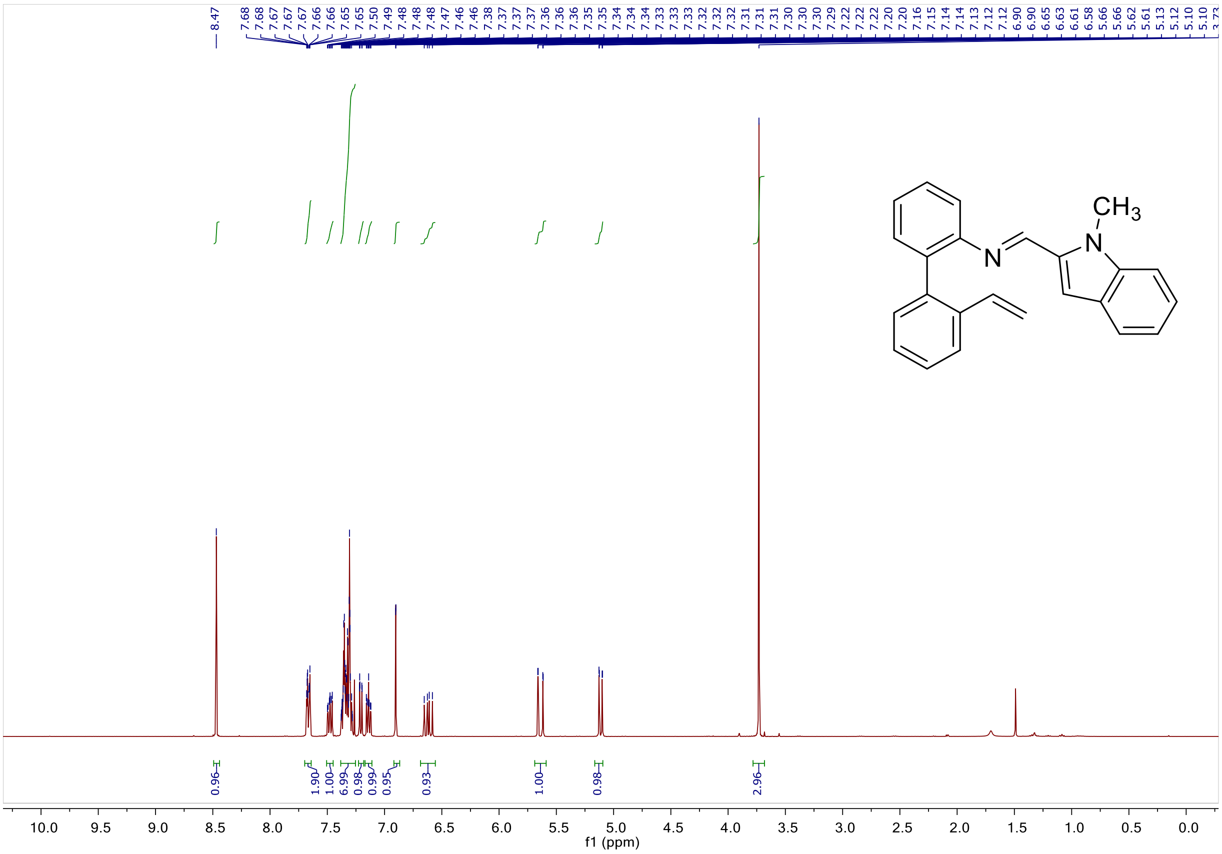
^{1}**H NMR** (400 MHz, $CDCl_3$) of **1As**:



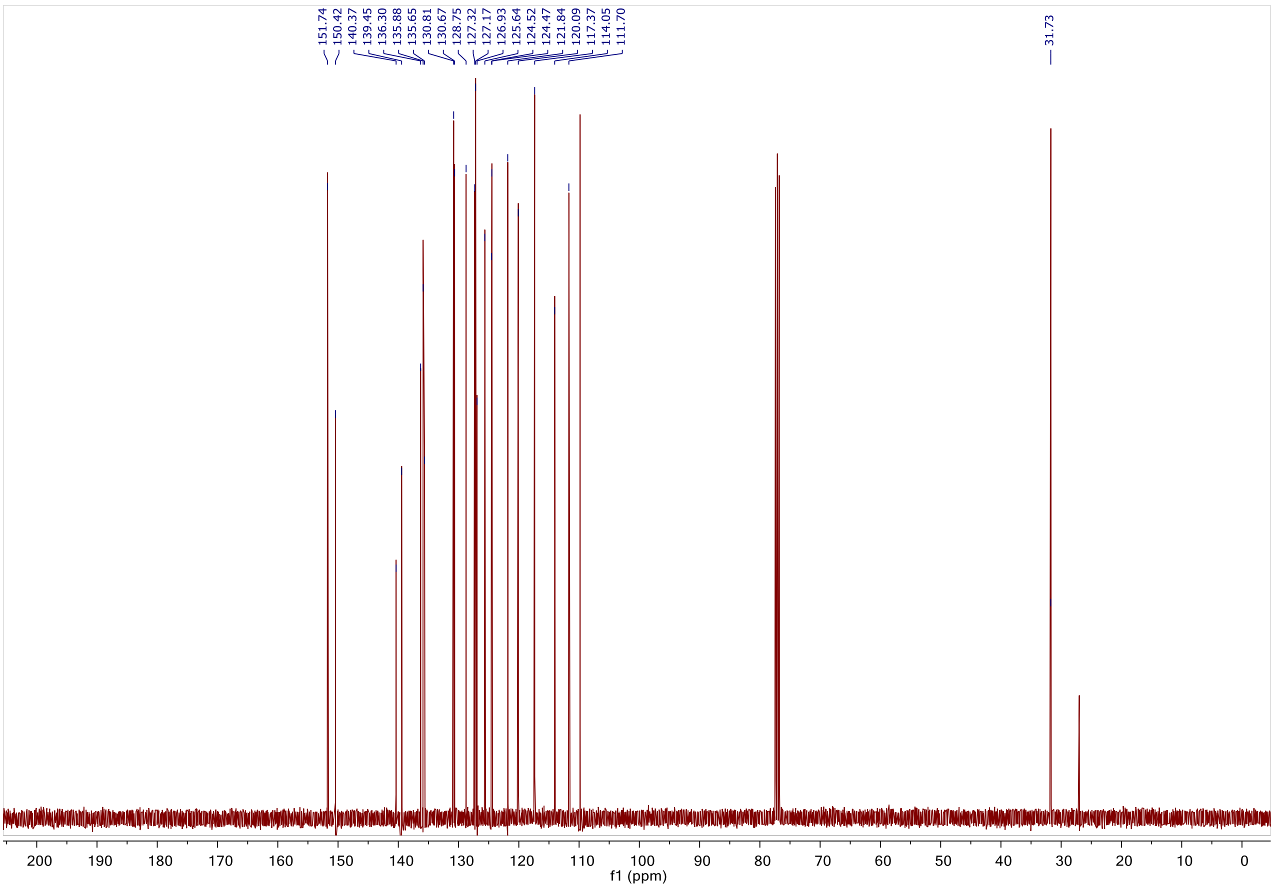
^{13}**C NMR** (100 MHz, $CDCl_3$) of **1As**



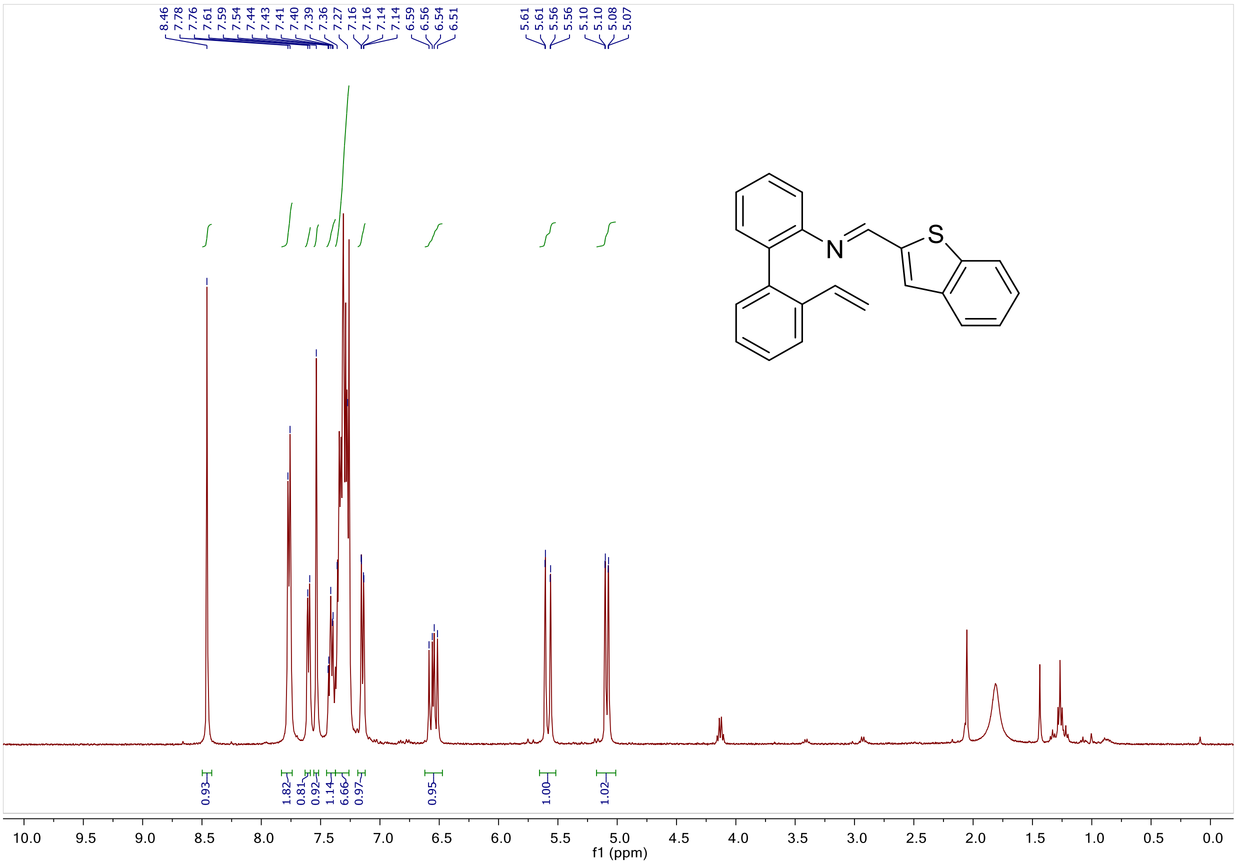
^{1}H NMR (400 MHz, $CDCl_3$) of **1At**:



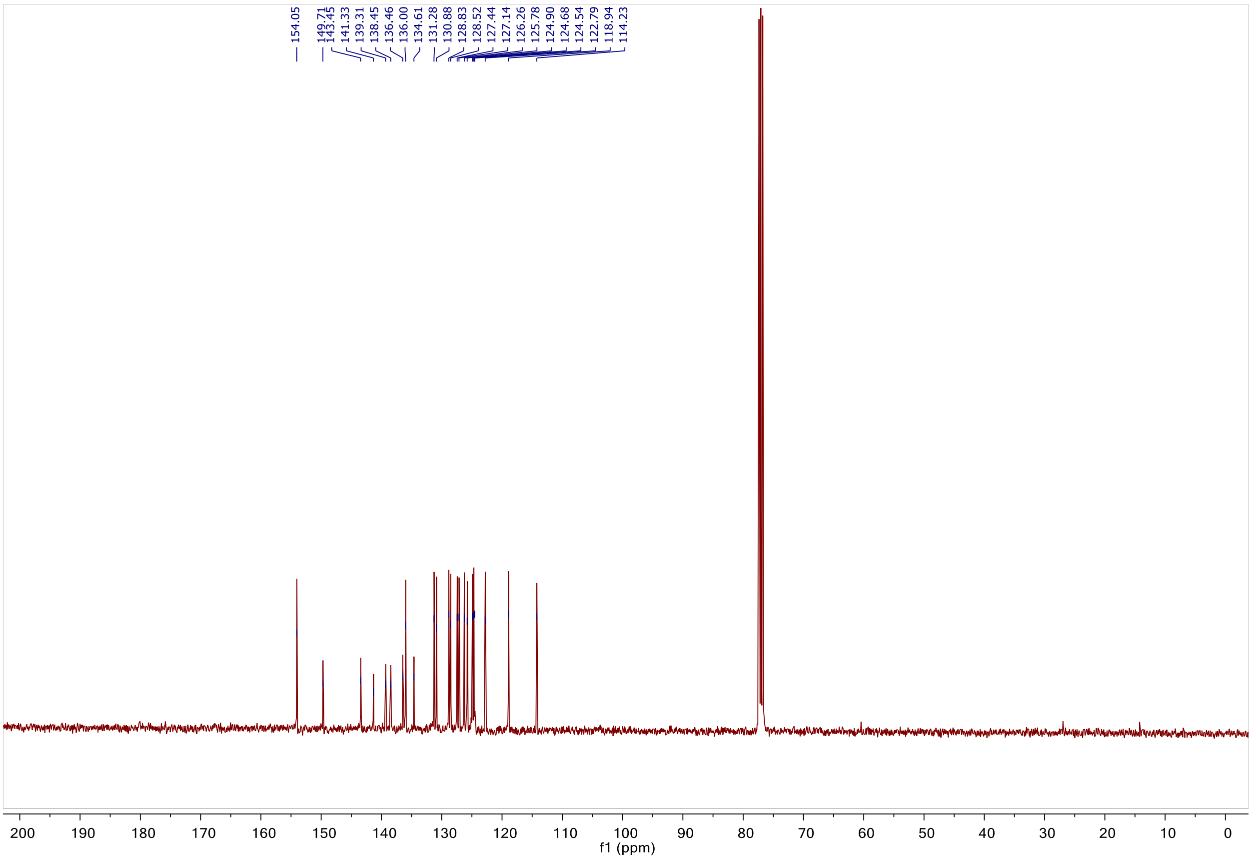
^{13}C NMR (100 MHz, $CDCl_3$) of **1At**



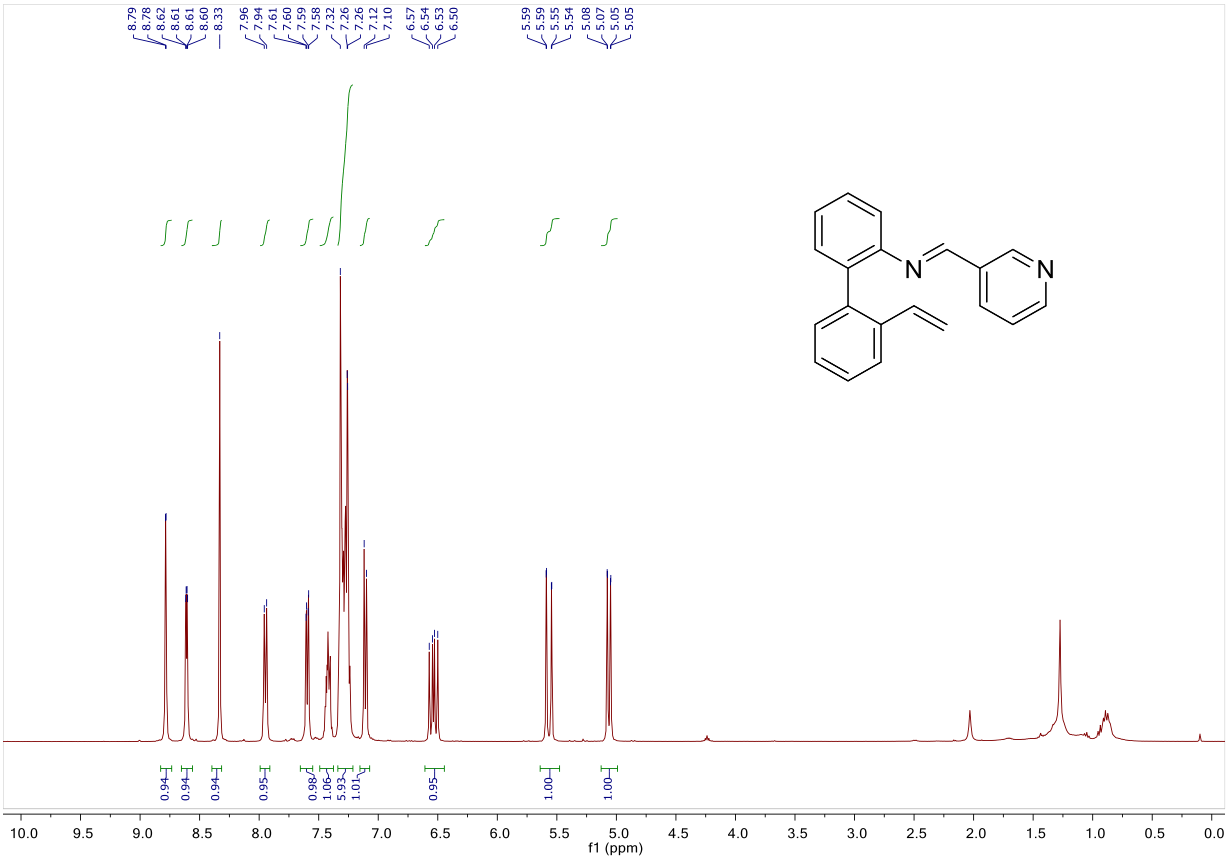
^{1}H NMR (400 MHz, $CDCl_3$) of **1Au**:



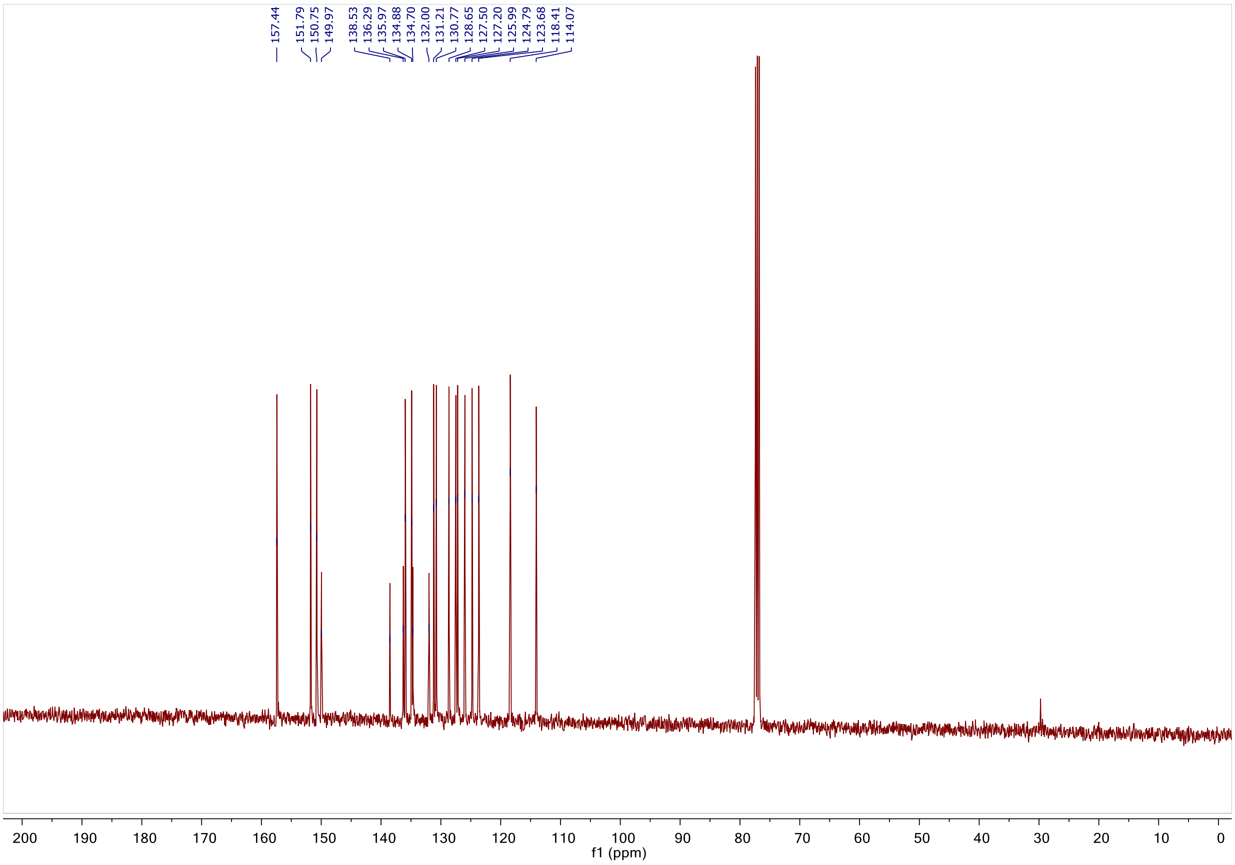
^{13}C NMR (100 MHz, $CDCl_3$) of **1Au**



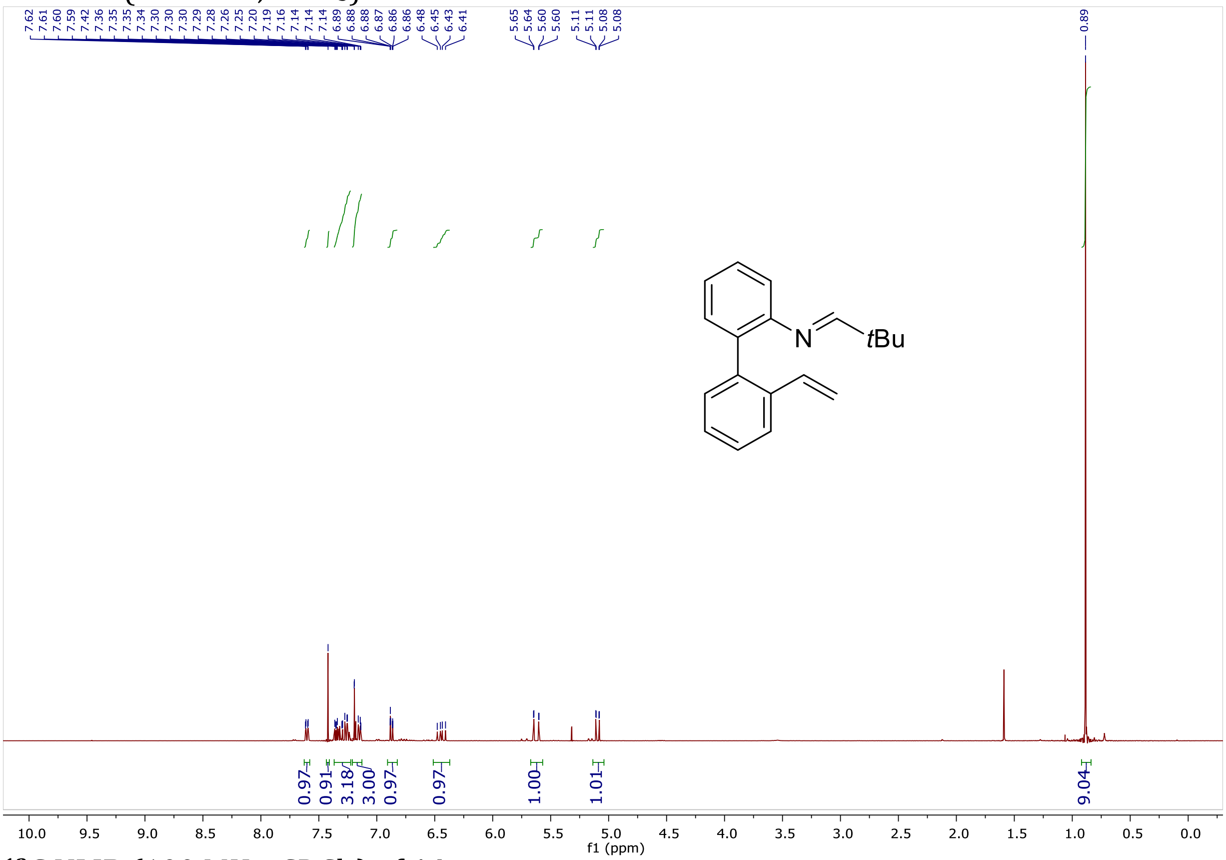
^{1}H NMR (400 MHz, $CDCl_3$) of **1Av**



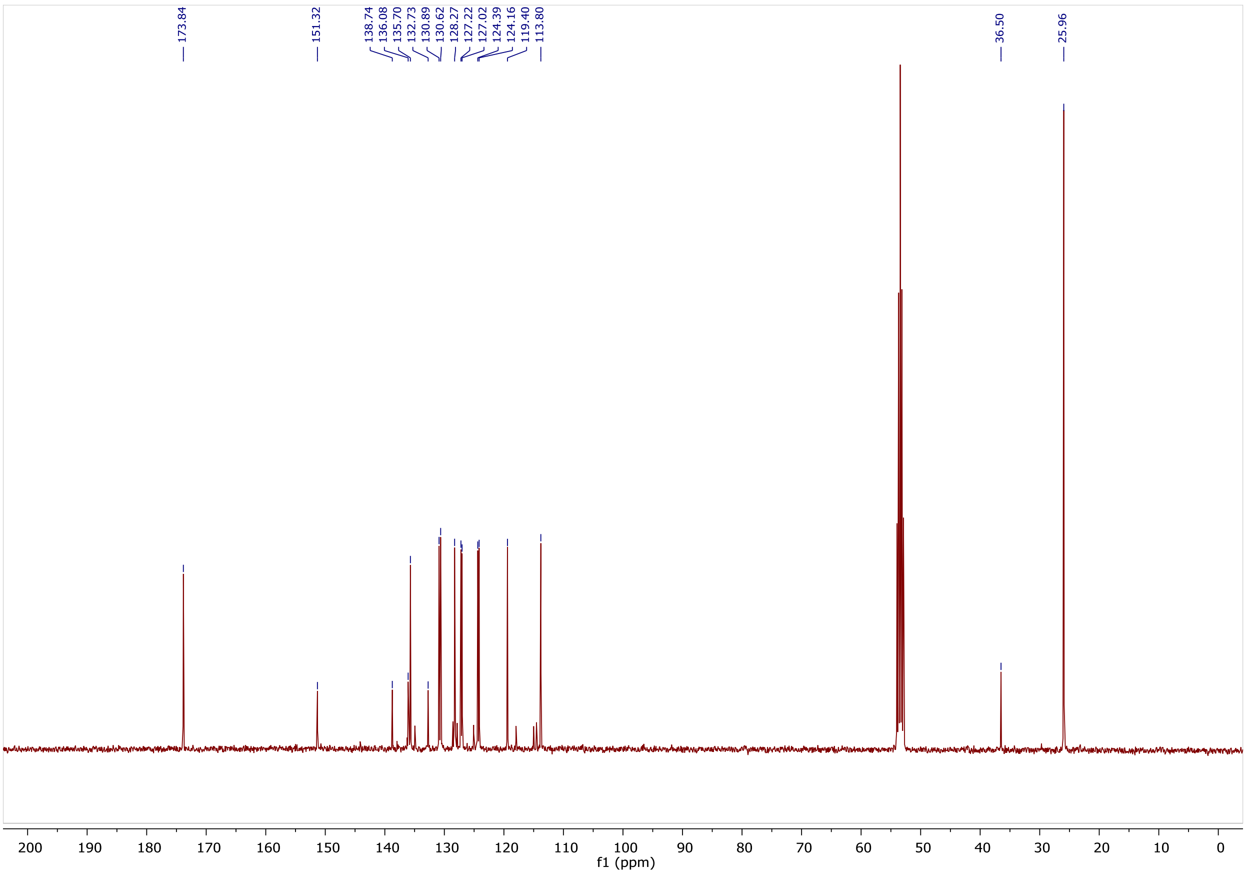
^{13}C NMR (100 MHz, $CDCl_3$) of **1Av**



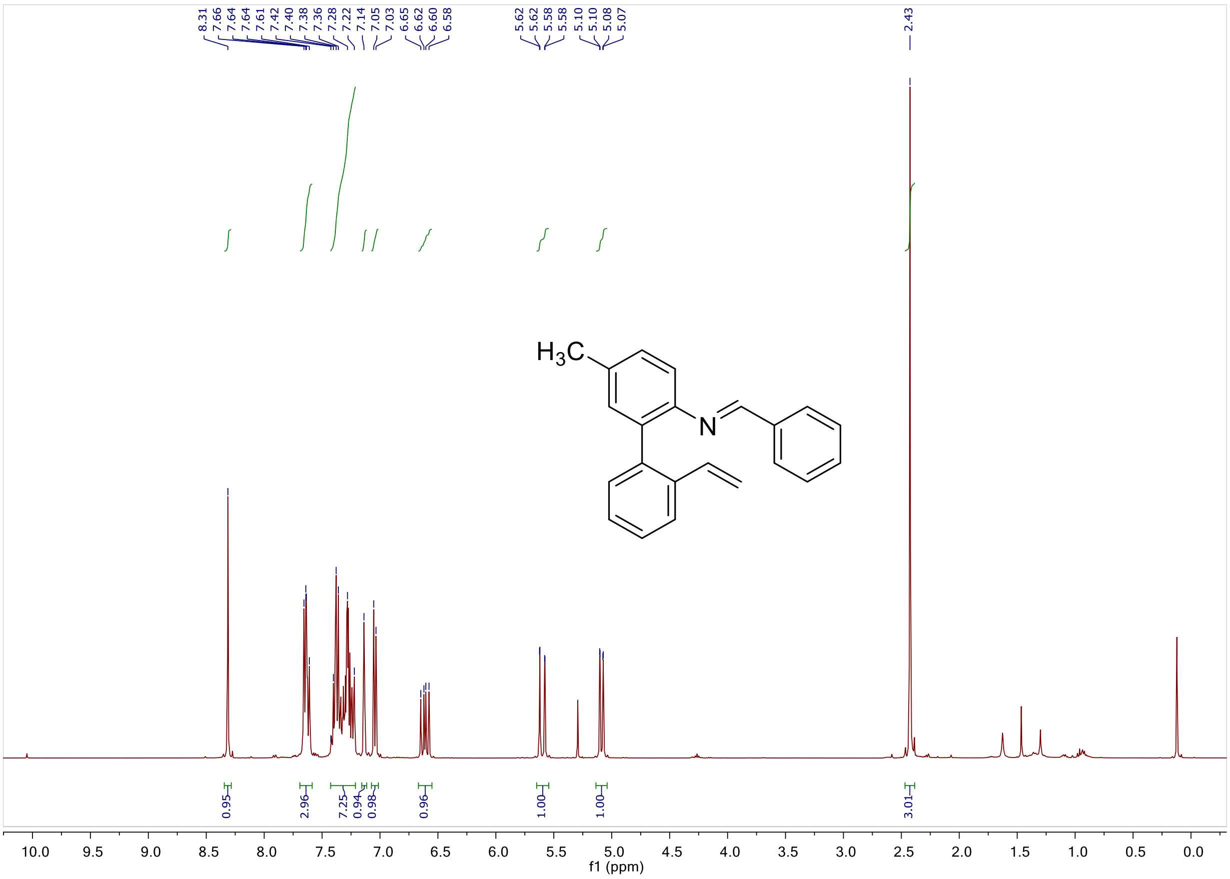
¹H NMR (400 MHz, $CDCl_3$) of **1Aw**



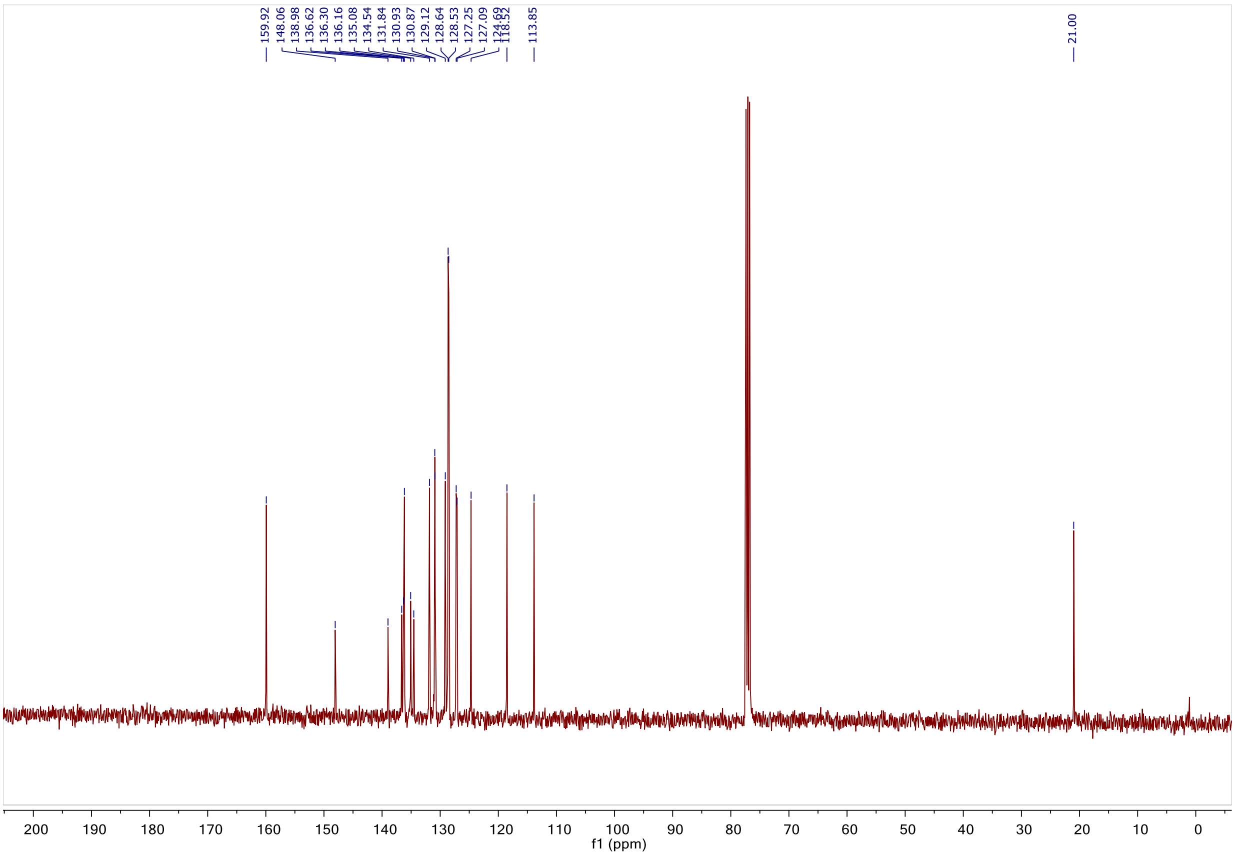
¹³C NMR (100 MHz, $CDCl_3$) of **1Aw**



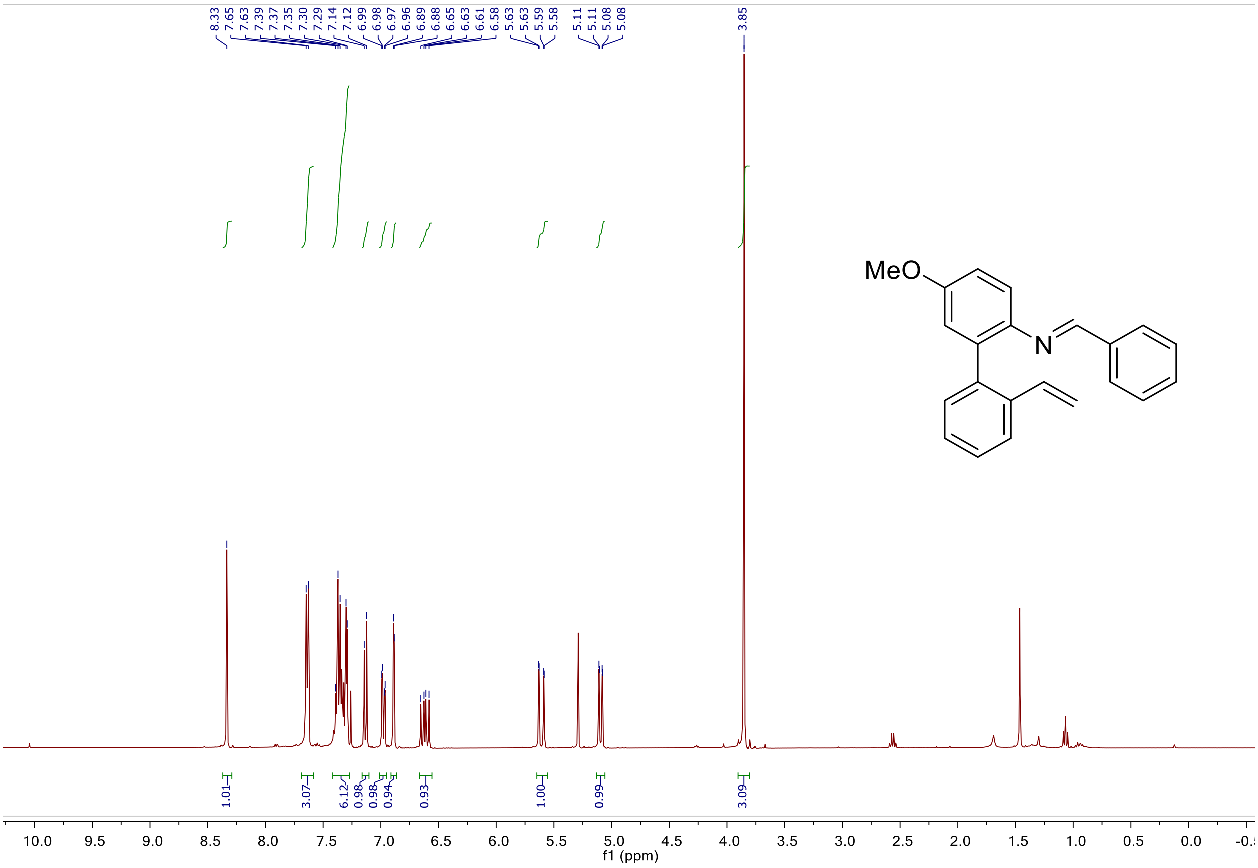
^{1}**H NMR** (400 MHz, $CDCl_3$) of **1Ba**:



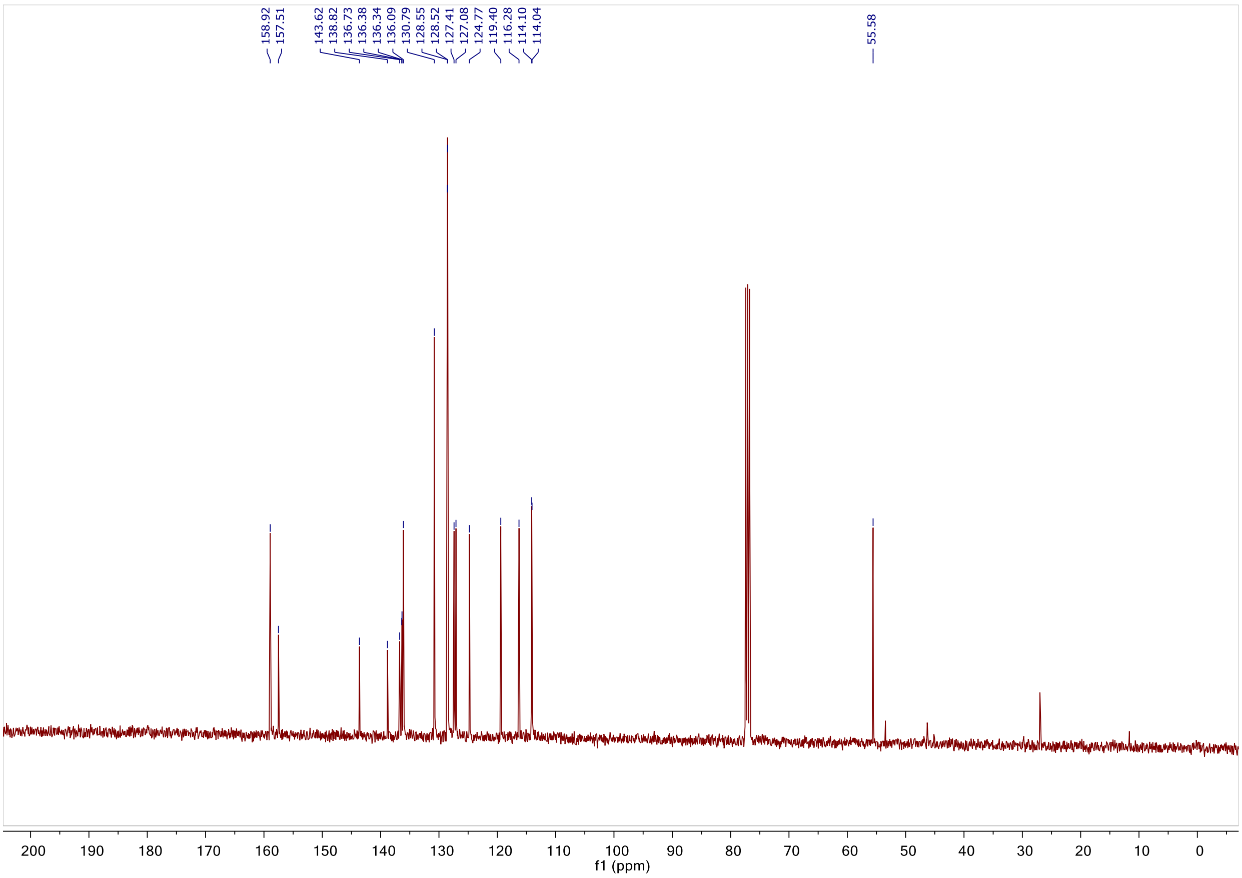
^{13}**C NMR** (100 MHz, $CDCl_3$) of **1Ba**



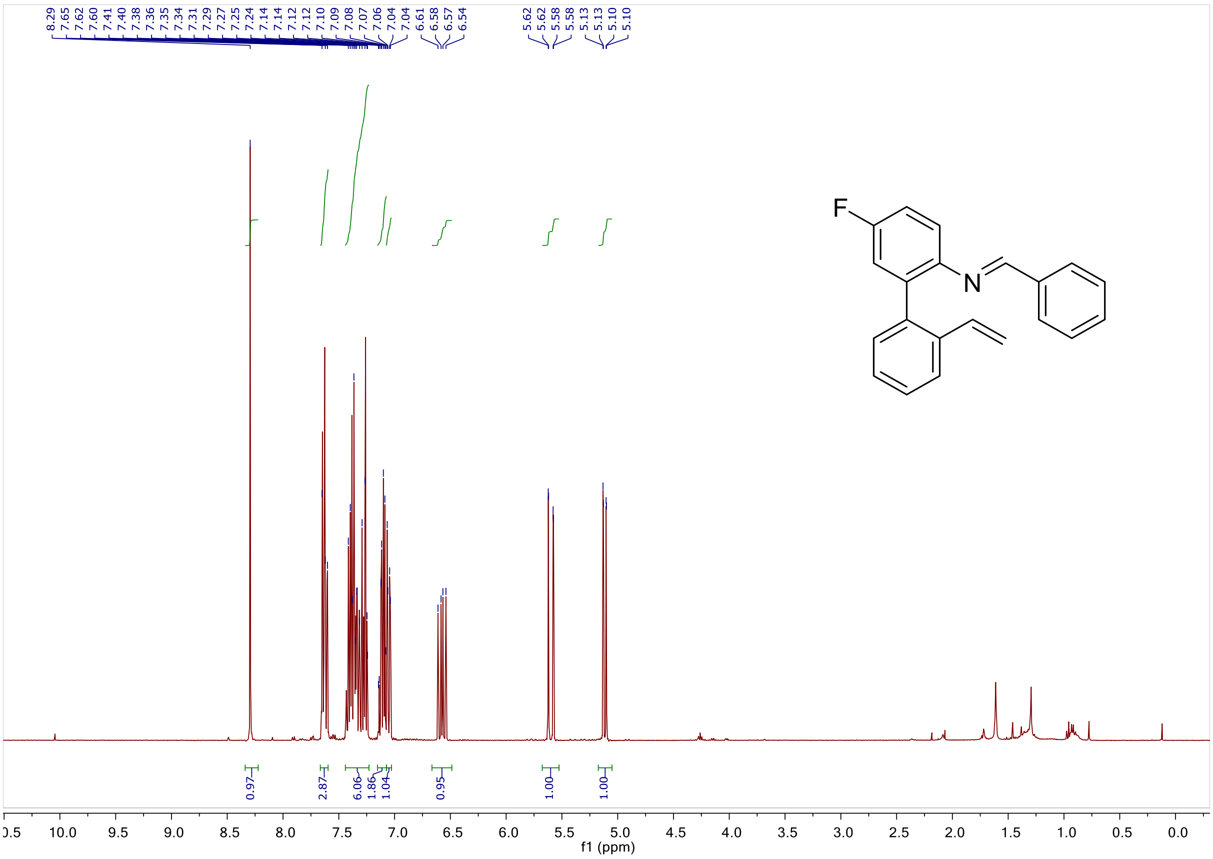
^{1}H NMR (400 MHz, $CDCl_3$) of **1Ca**:



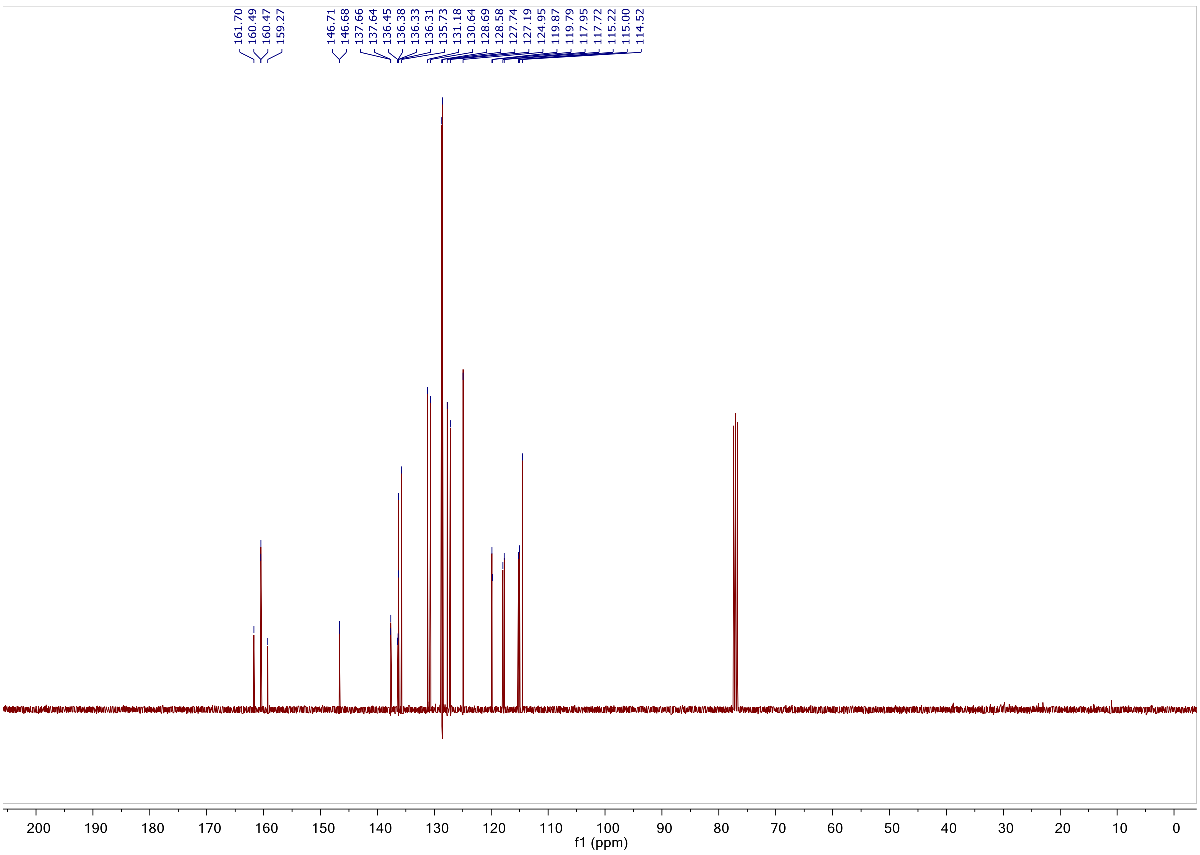
^{13}C NMR (100 MHz, $CDCl_3$) of **1Ca**



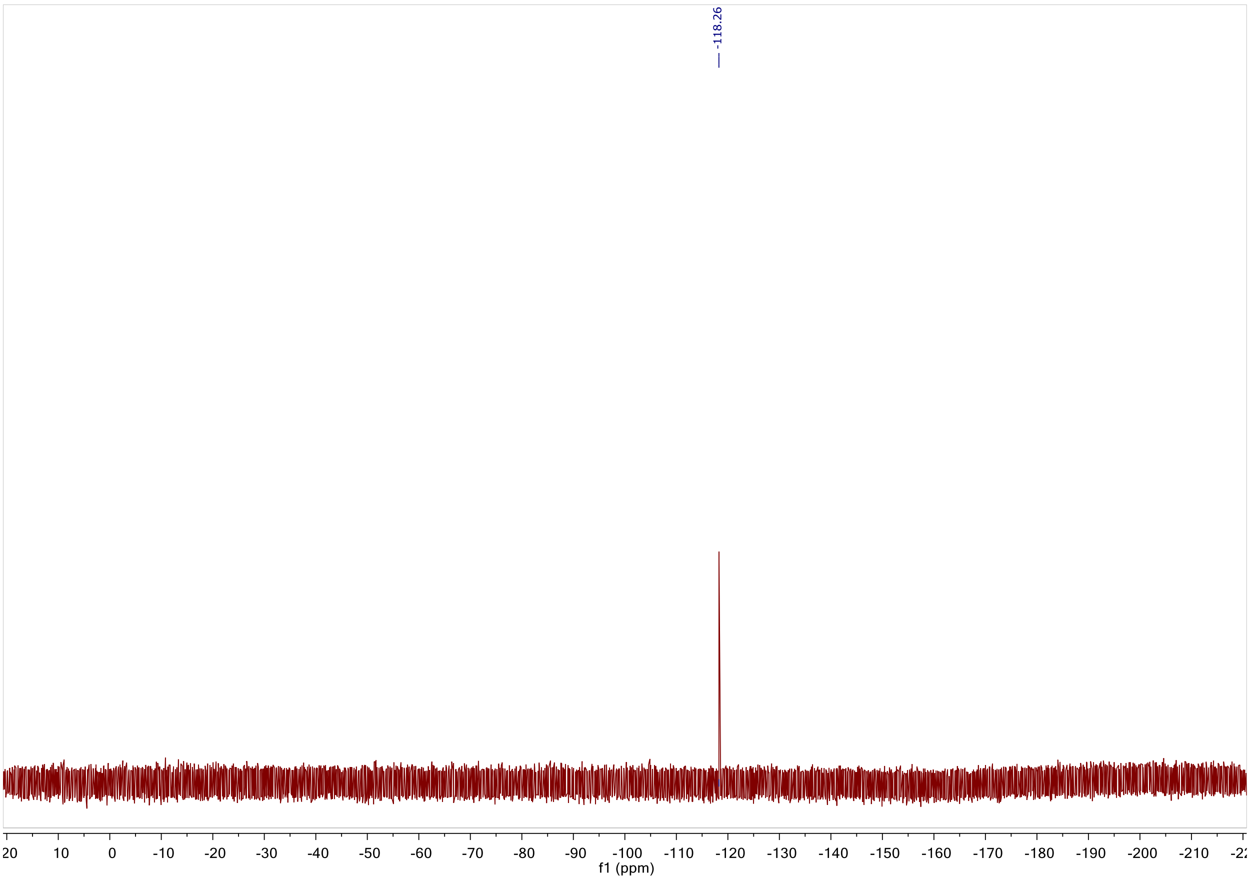
[1]H NMR (400 MHz, $CDCl_3$) of **1Da**:



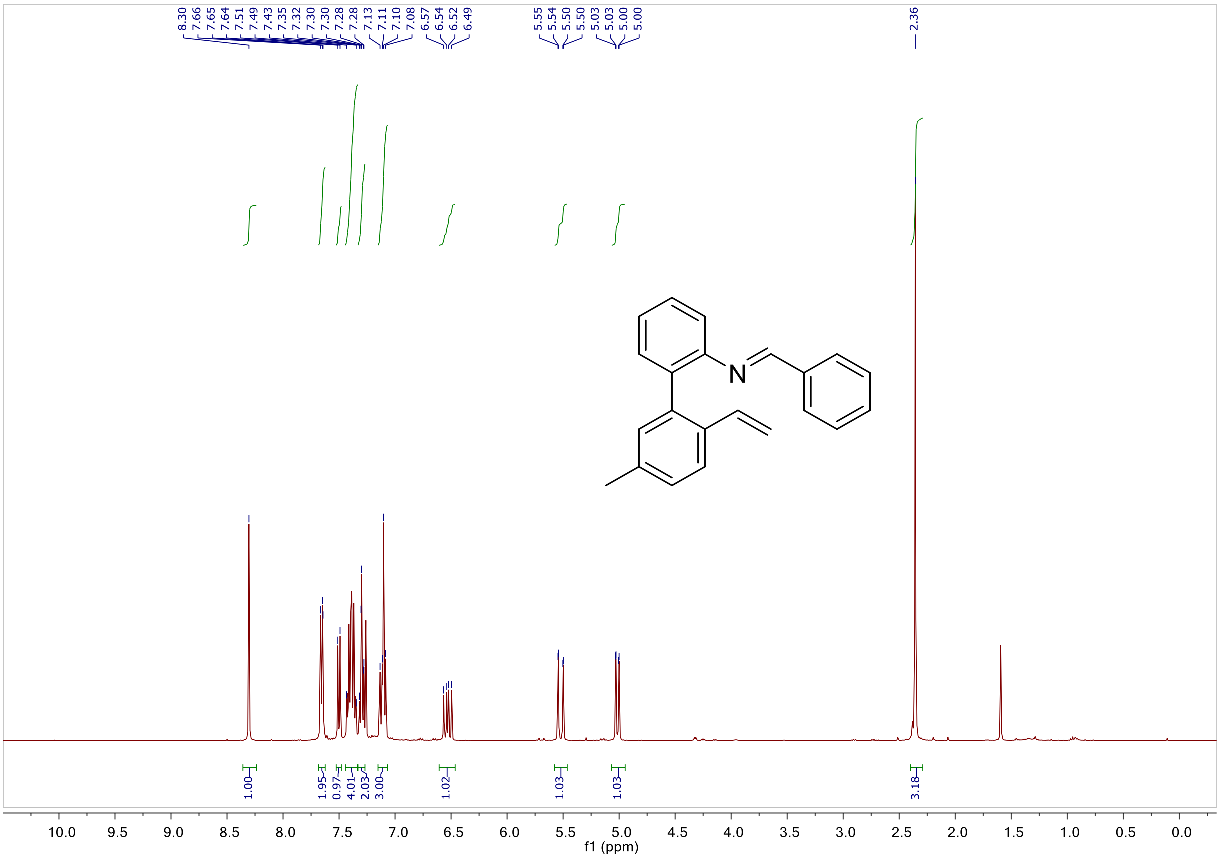
[13]C NMR (100 MHz, $CDCl_3$) of **1Da**



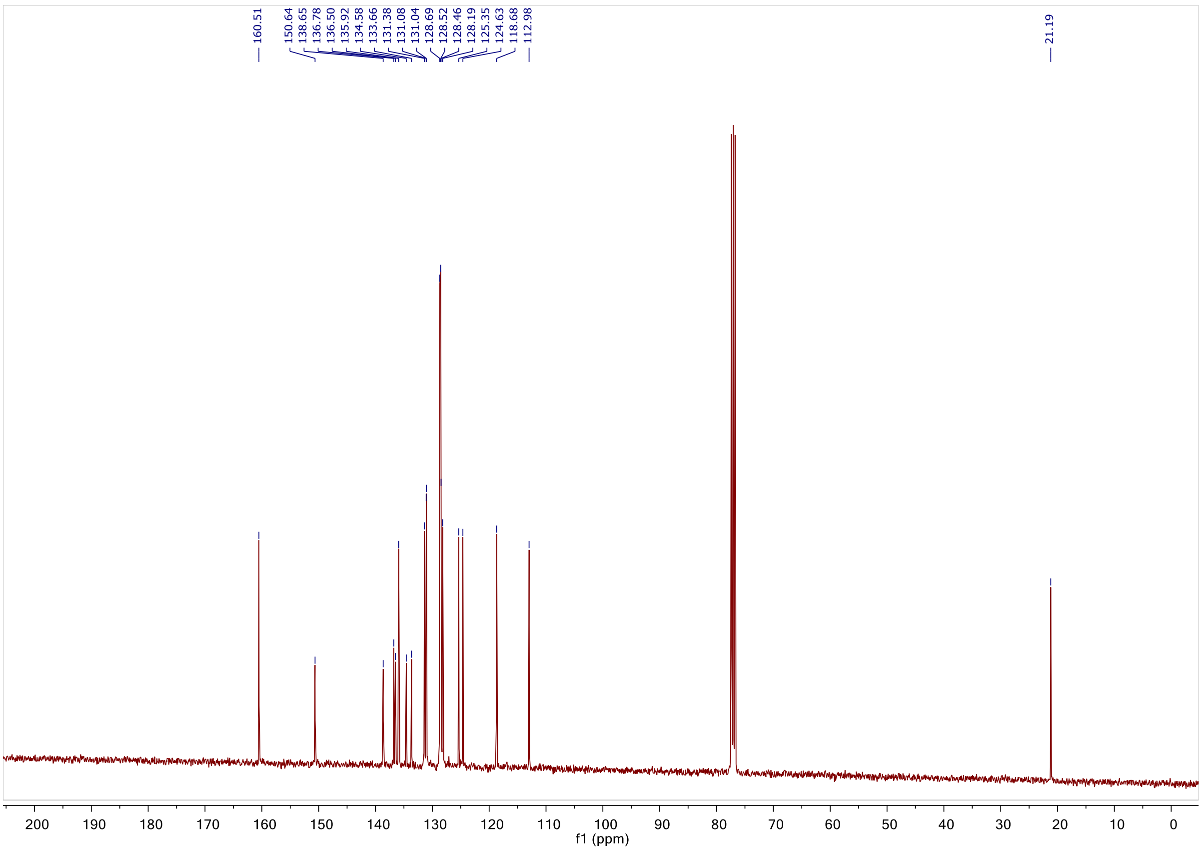
^{19}F NMR (400 MHz, $CDCl_3$) of **1Da**



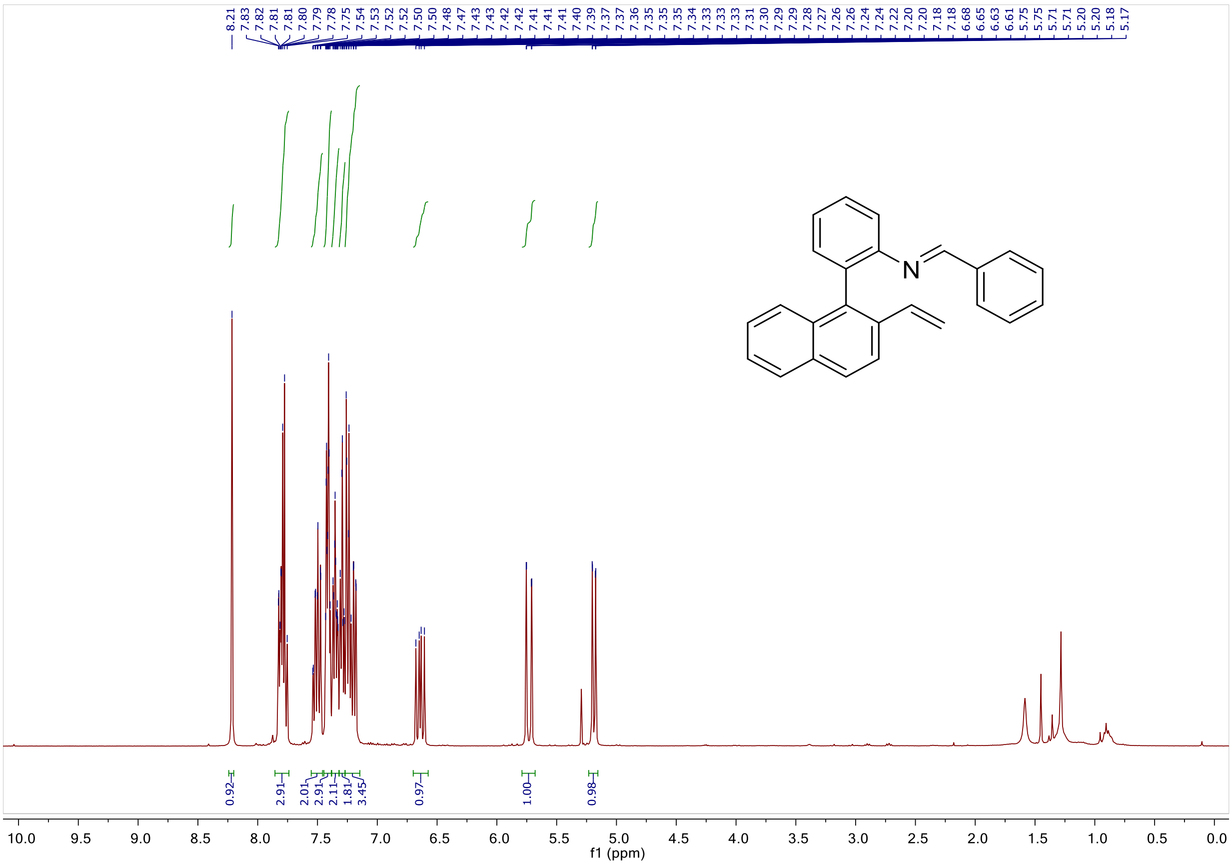
[1]H NMR (400 MHz, $CDCl_3$) of **1Ea**:



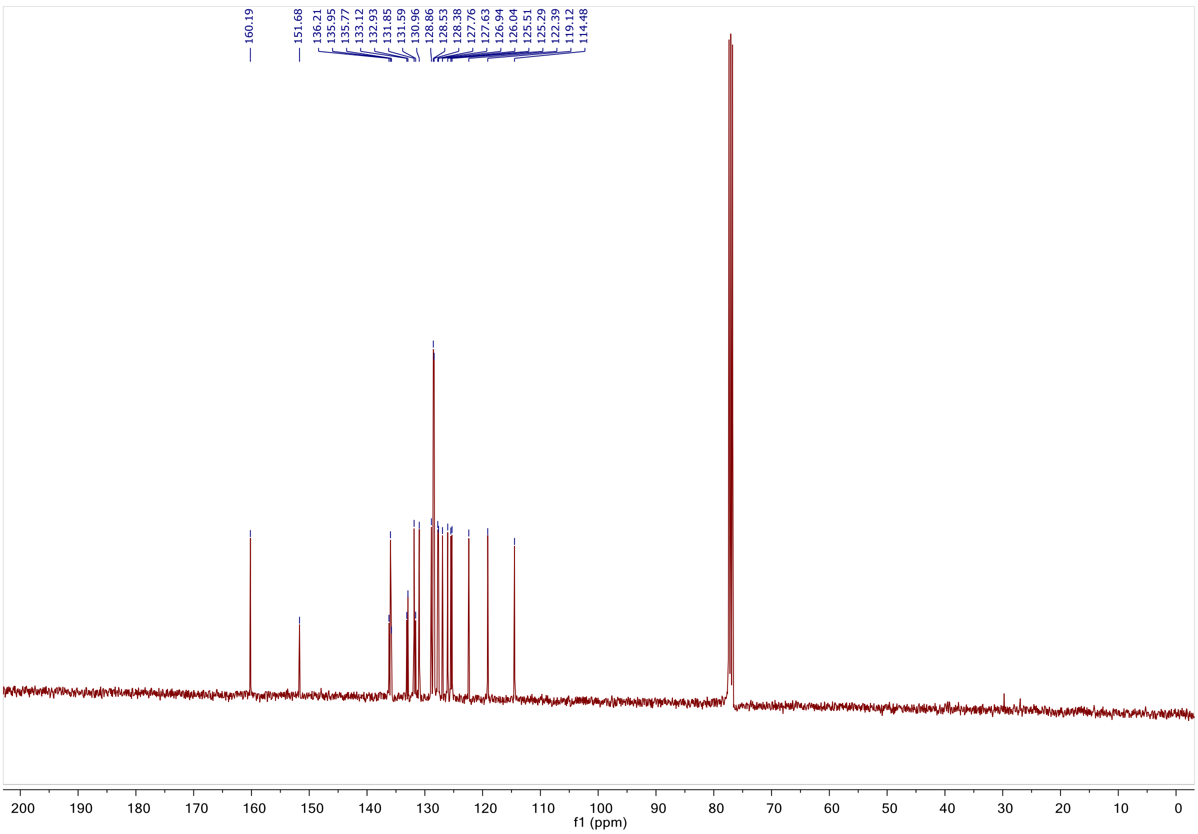
[13]C NMR (100 MHz, $CDCl_3$) of **1Ea**



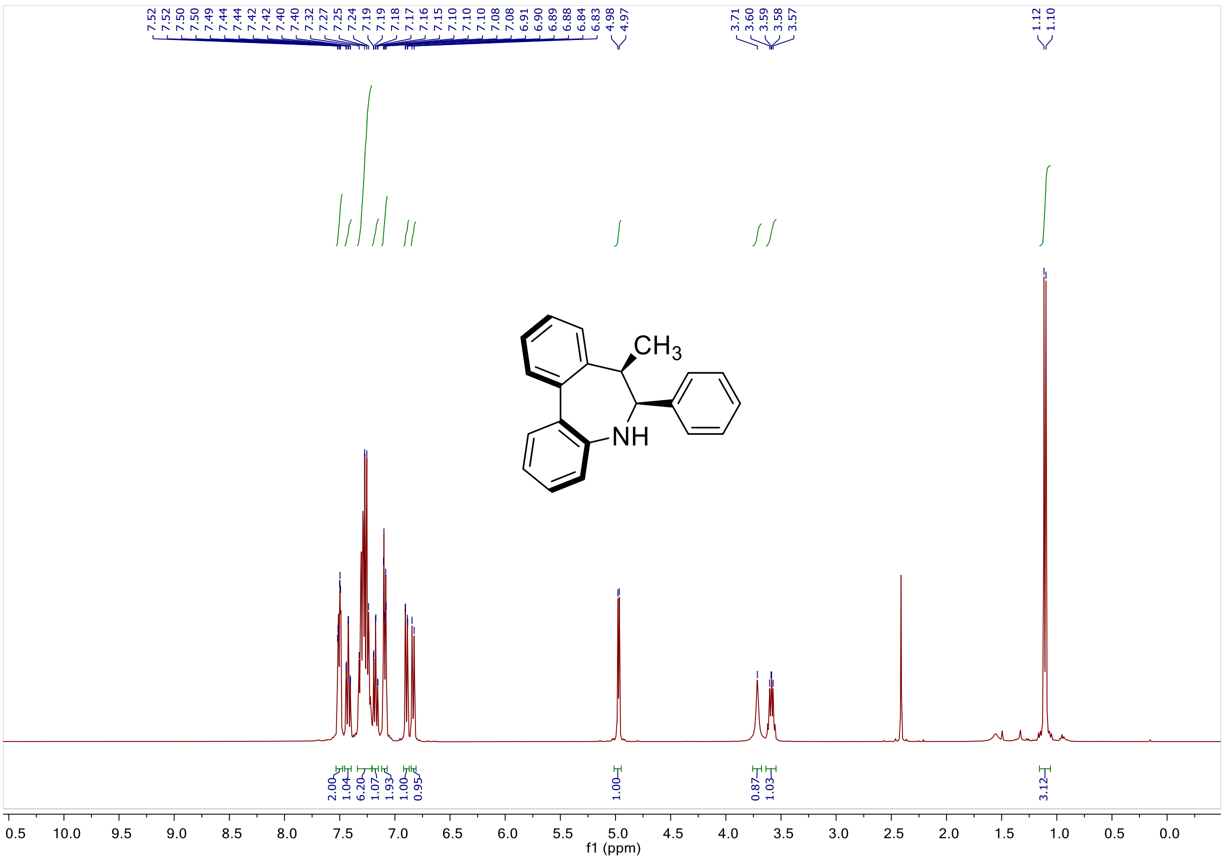
^{1}**H NMR** (400 MHz, CDCl$_3$) of **1Fa**:



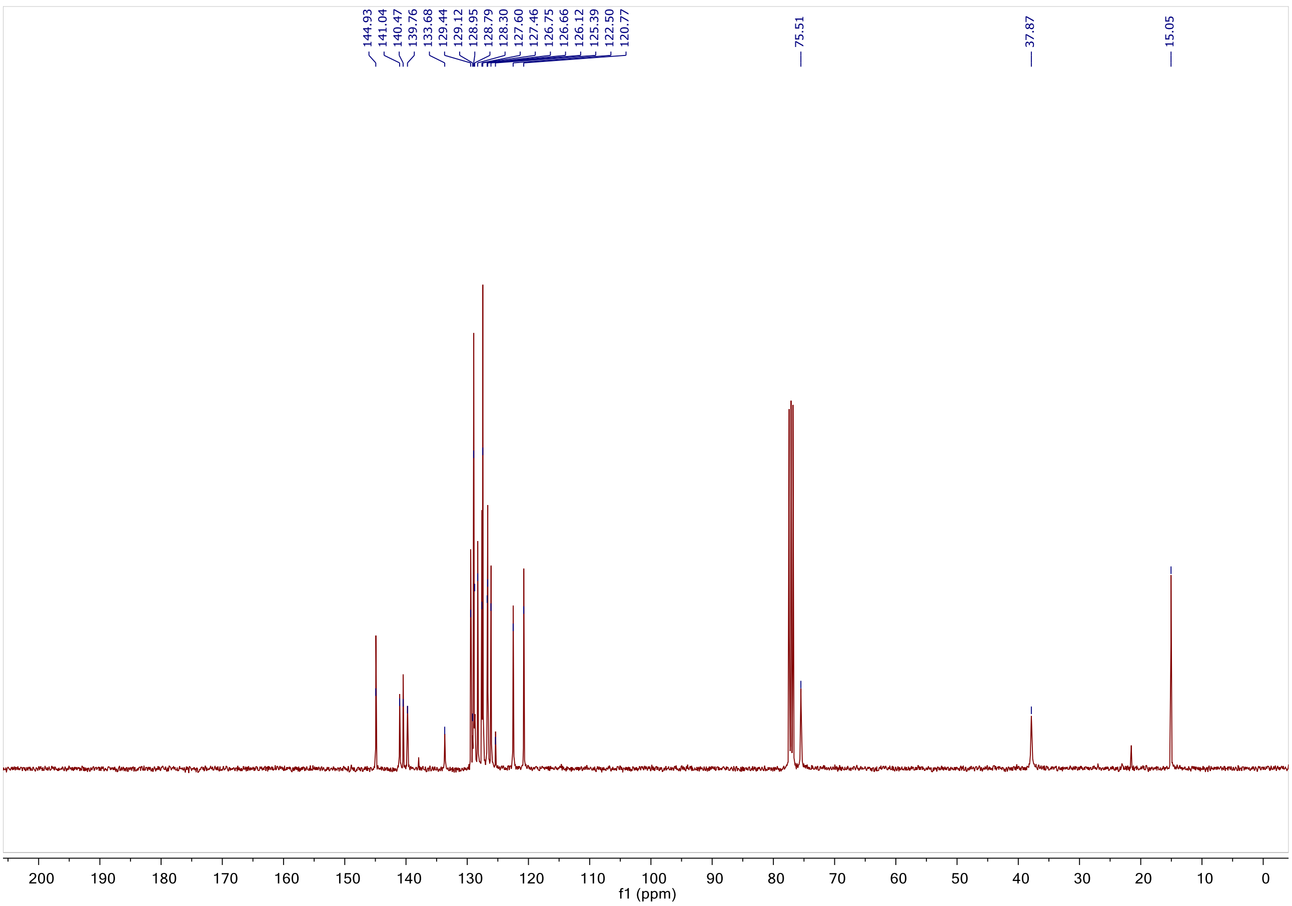
^{13}**C NMR** (100 MHz, CDCl$_3$) of **1Fa**



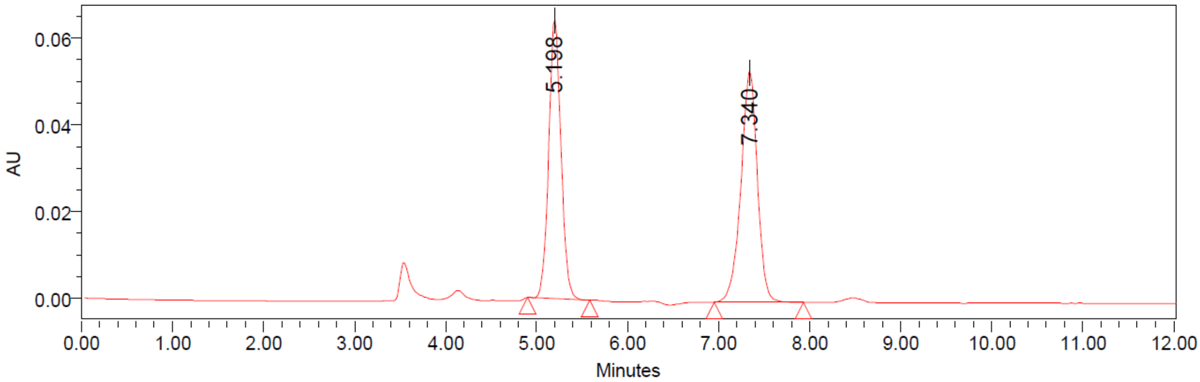
^{1}H NMR (400 MHz, $CDCl_3$) of **2Aa**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Aa:**



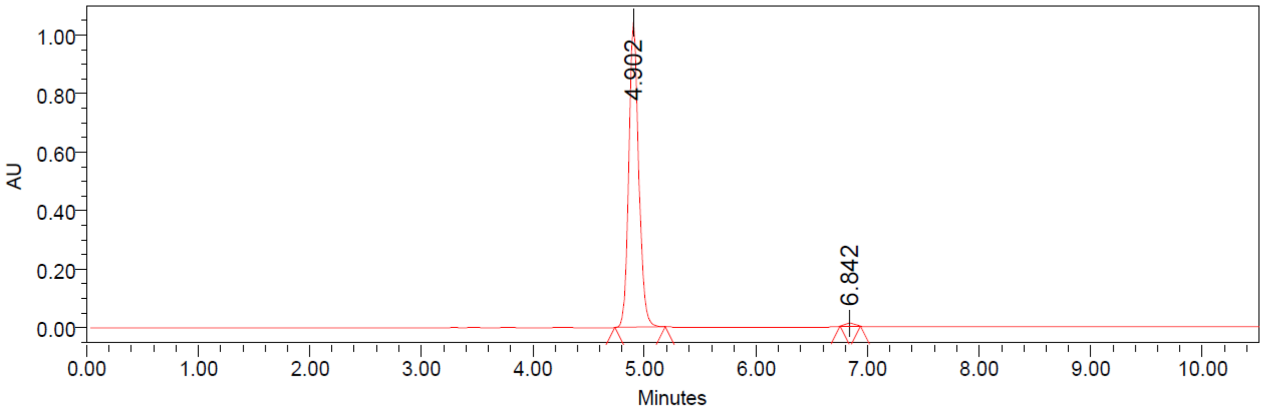
Racemic sample of 2Aa: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	5.198	603226	47.26	64337
2	PDA 234.0 nm	7.340	673267	52.74	53216

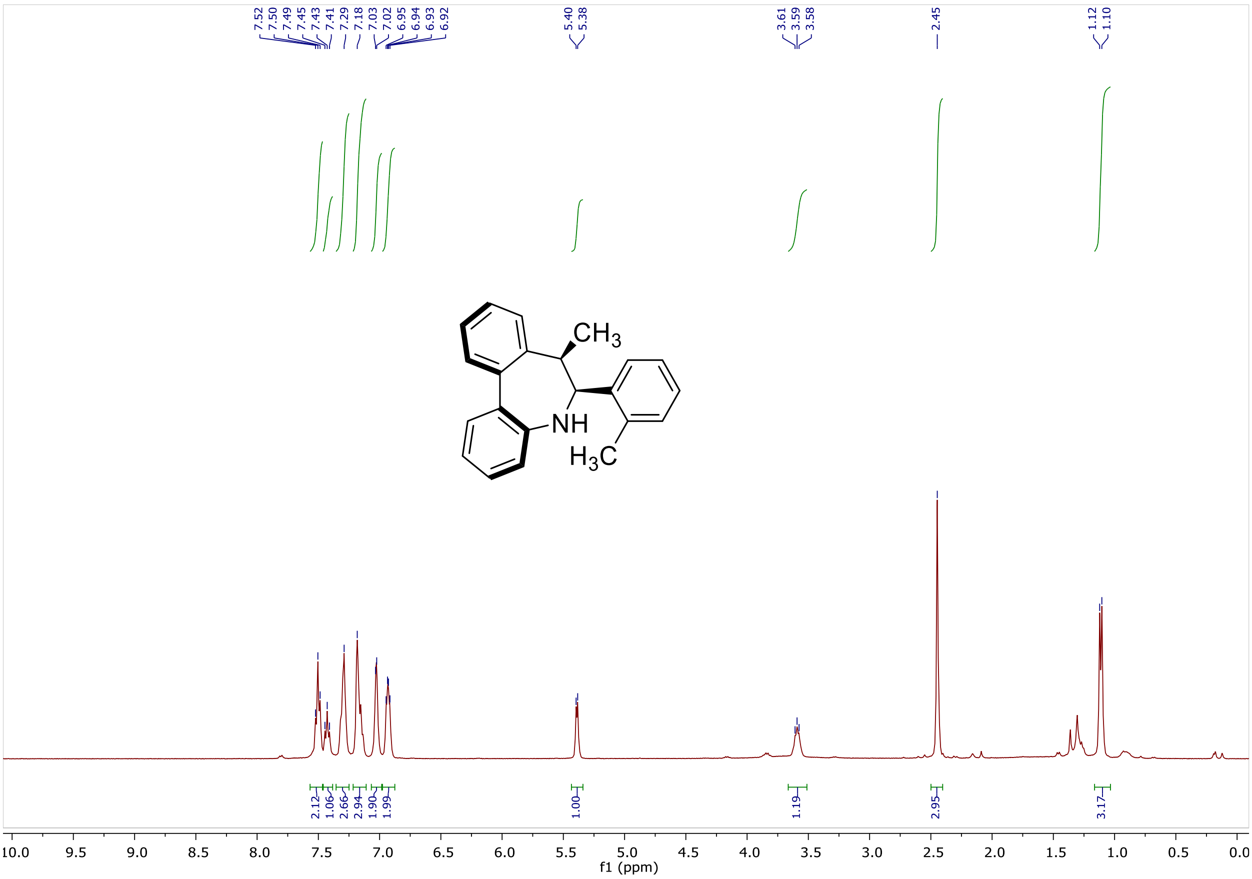
Enantioenriched sample of (*Sa*,6*S*,7*R*)-2Aa:



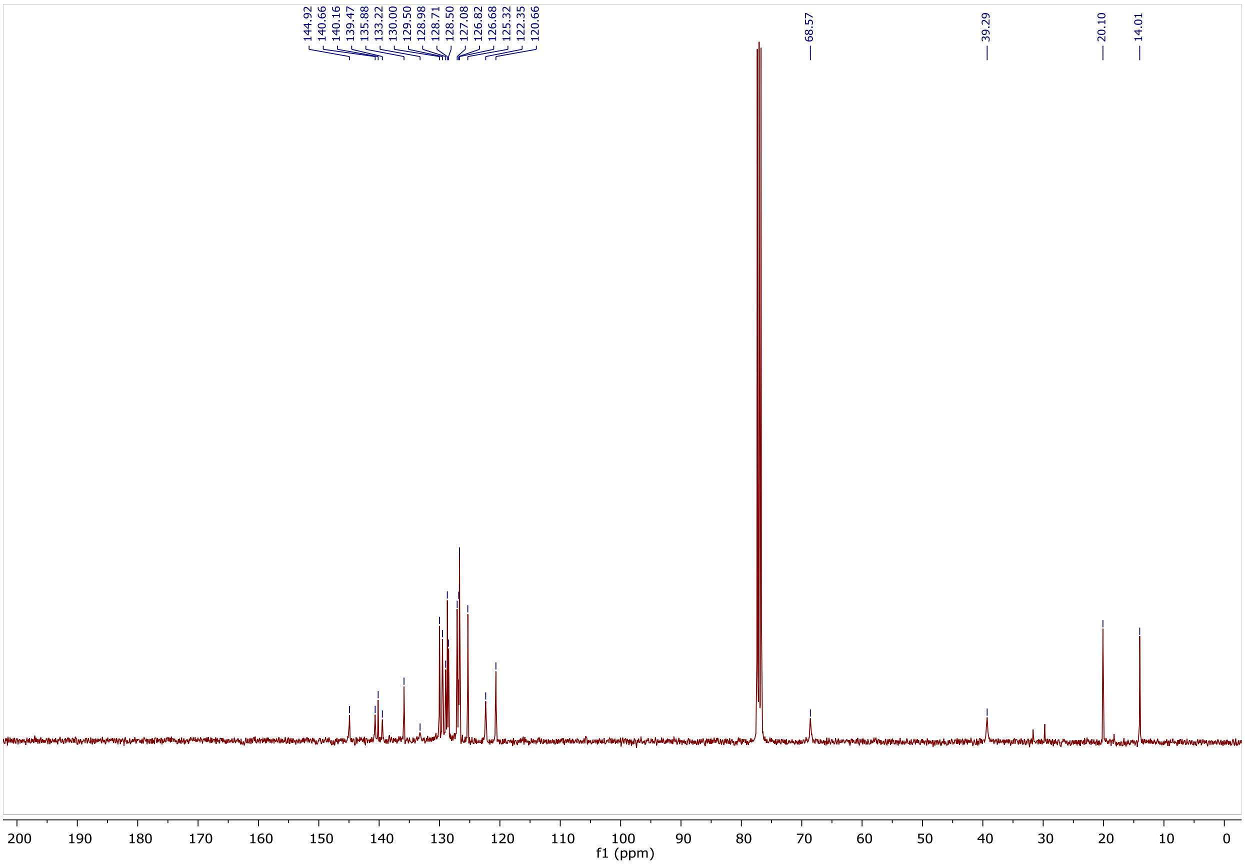
Processed Channel: PDA 245.1 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 245.1 nm	4.902	6476546	99.10	1036772
2	PDA 245.1 nm	6.842	59117	0.90	9630

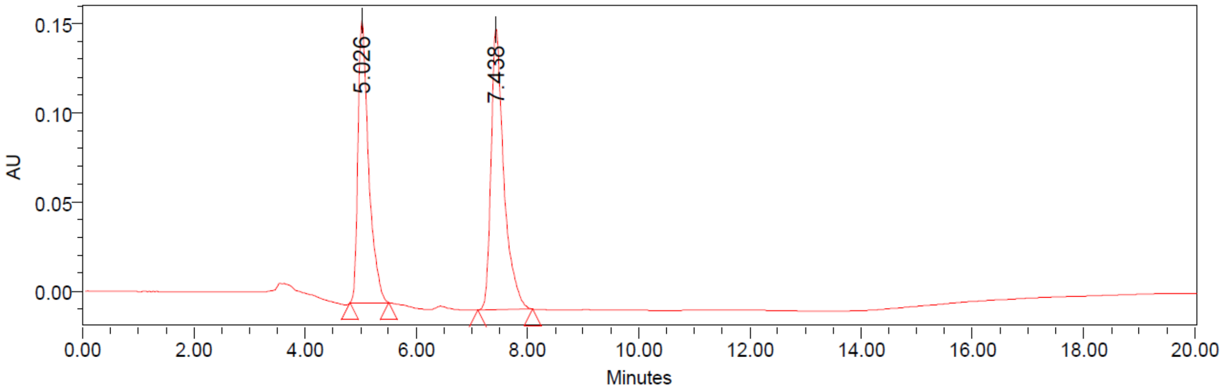
¹H NMR (400 MHz, CDCl₃) of **2Ab**:



¹³C NMR (100 MHz, CDCl₃) of **2Ab:**



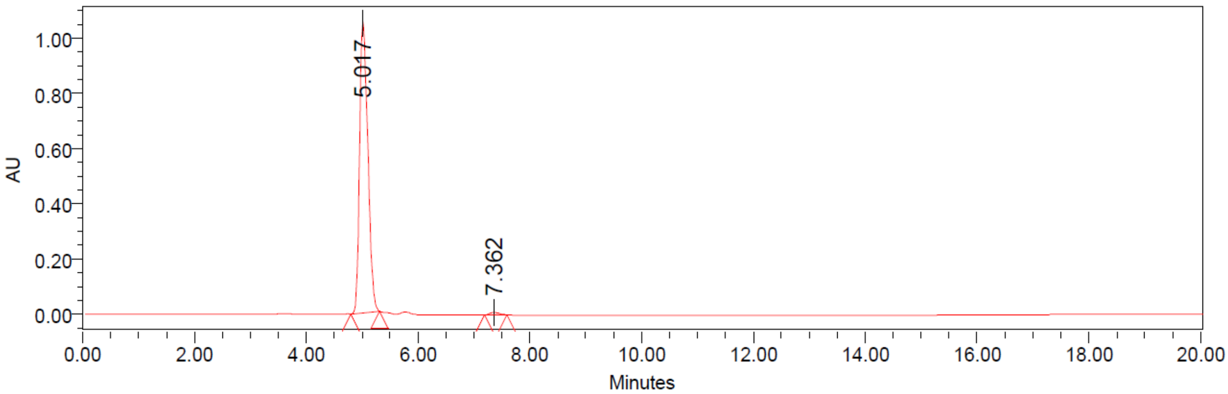
Racemic sample of 2Ab: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 235.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.0 nm	5.026	2103494	45.47	158412
2	PDA 235.0 nm	7.438	2522207	54.53	157652

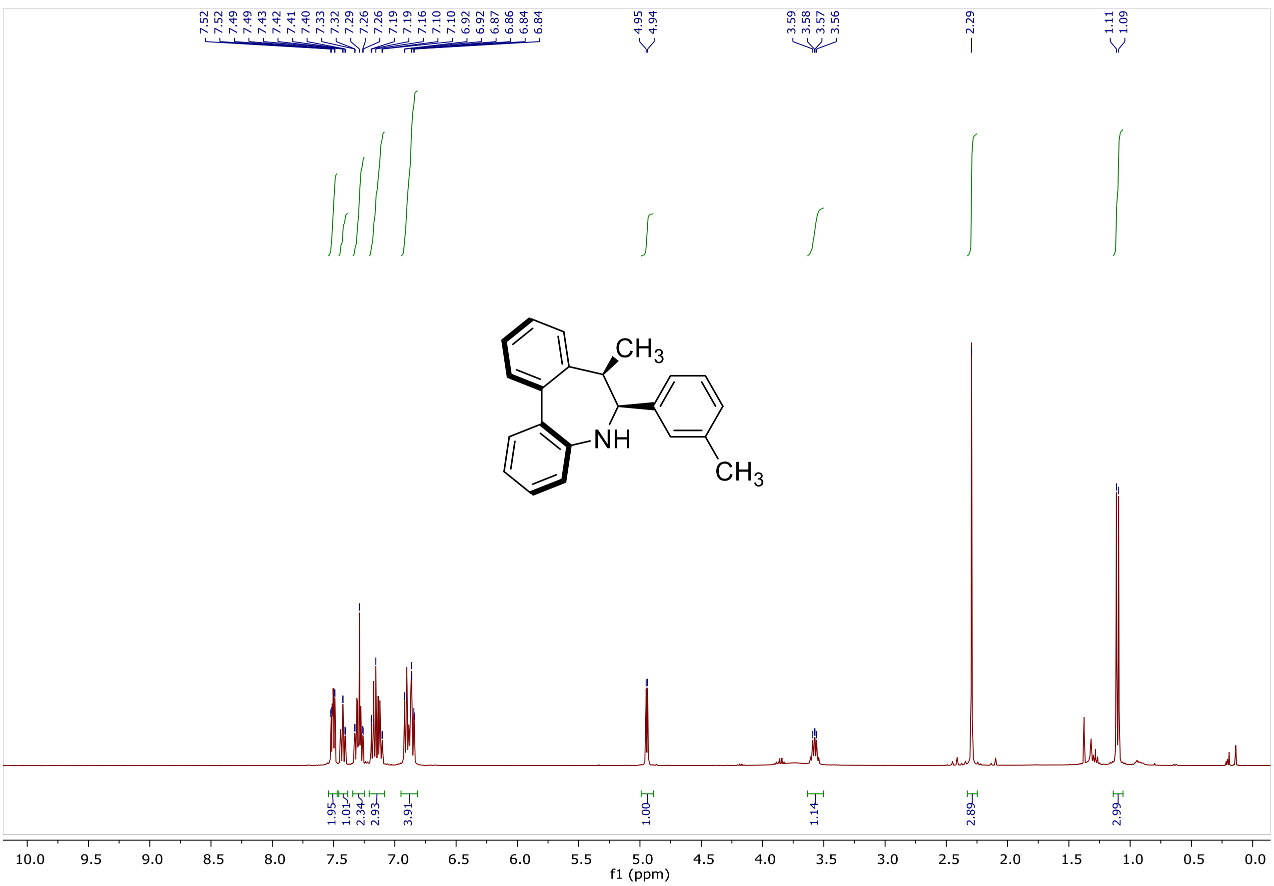
Enantioenriched sample of (S_a,6S,7R)-2Ab:



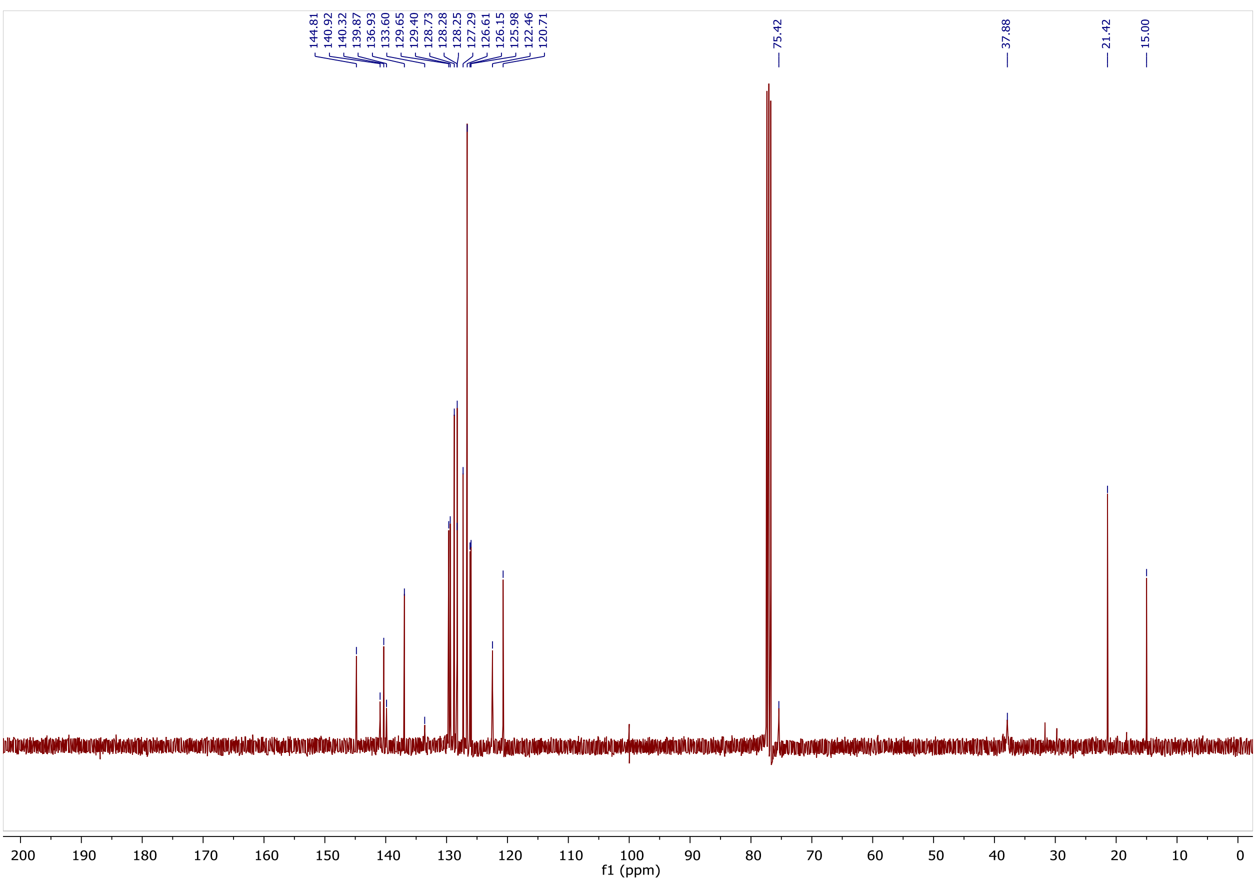
Processed Channel: PDA 245.8 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 245.8 nm	5.017	10849002	99.06	1060209
2	PDA 245.8 nm	7.362	103489	0.94	8646

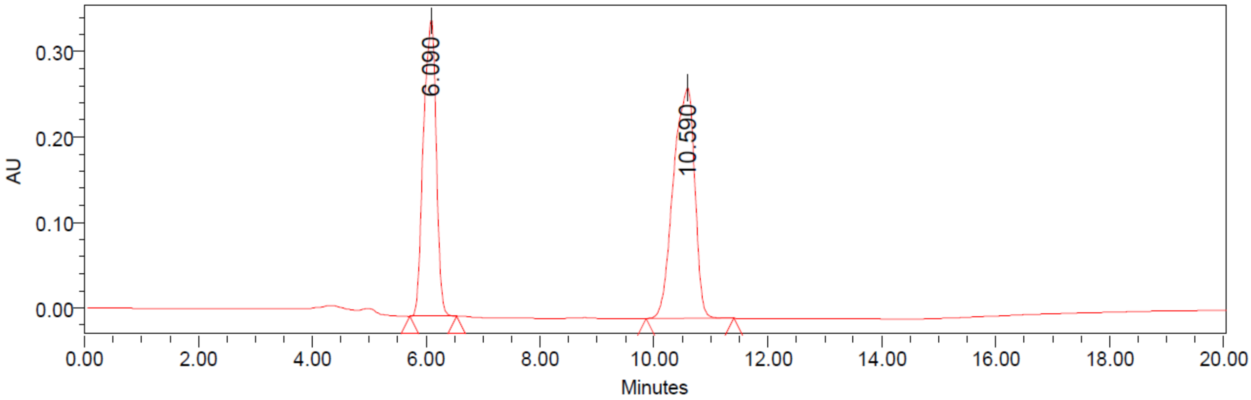
[1]H NMR (400 MHz, $CDCl_3$) of **2Ac**:



[13]C NMR (100 MHz, $CDCl_3$) of **2Ac:**



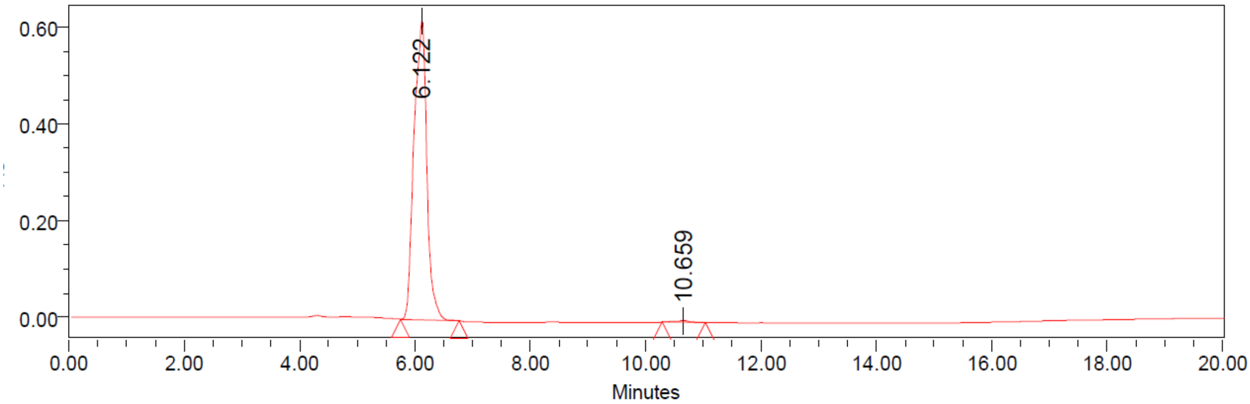
Racemic sample of 2Ac: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	6.090	5373781	43.34	348407
2	PDA 234.0 nm	10.590	7026617	56.66	270283

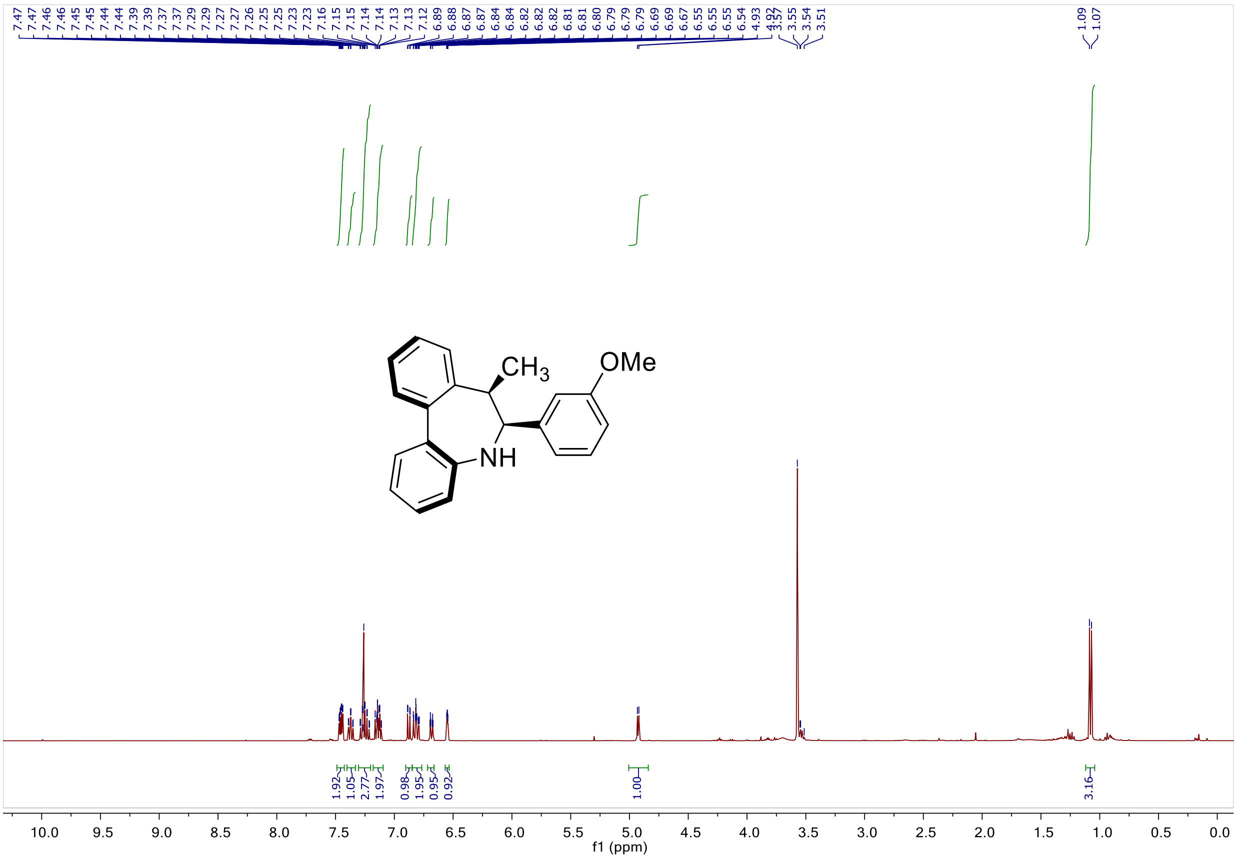
Enantioenriched sample of (S_a,6S,7R)-2Ac:



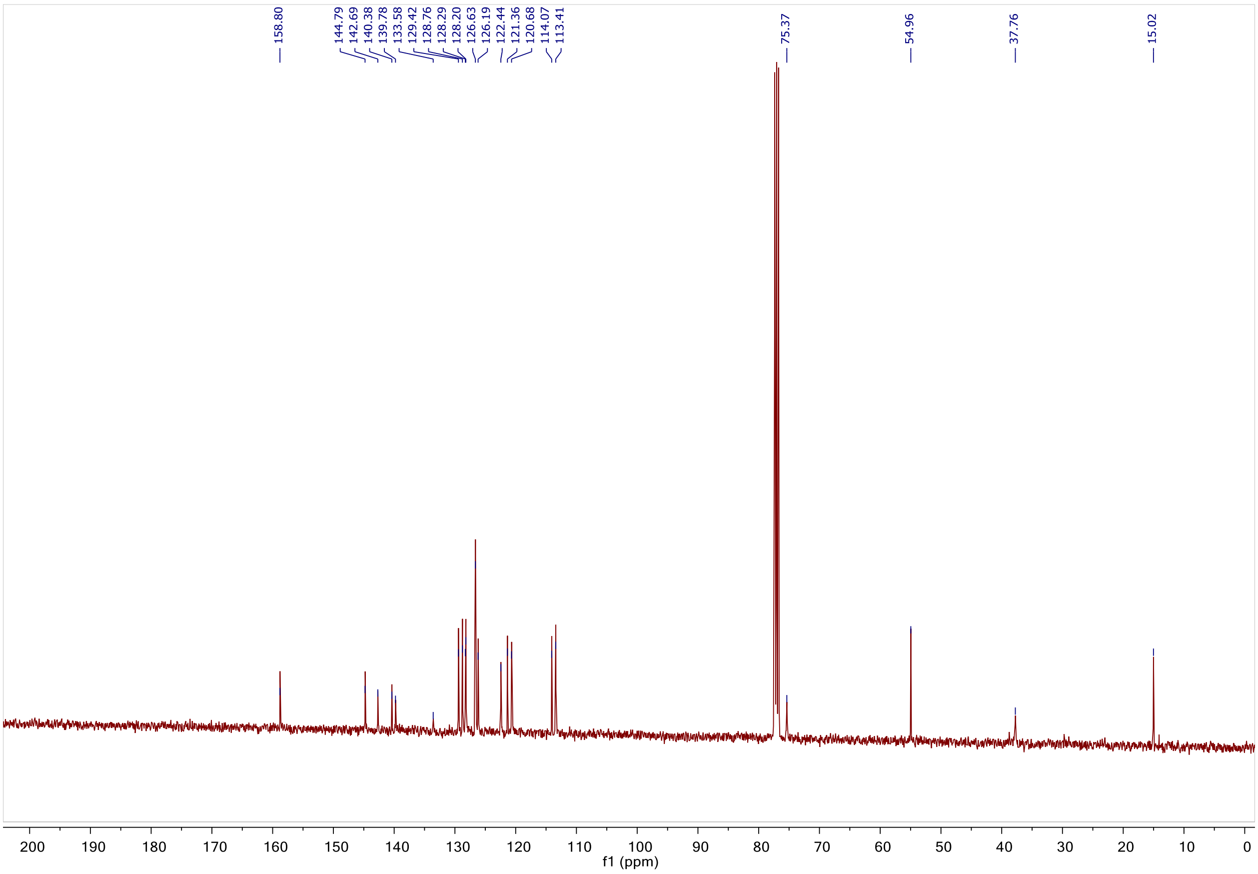
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	6.122	9452680	99.29	618385
2	PDA 234.0 nm	10.659	67829	0.71	3173

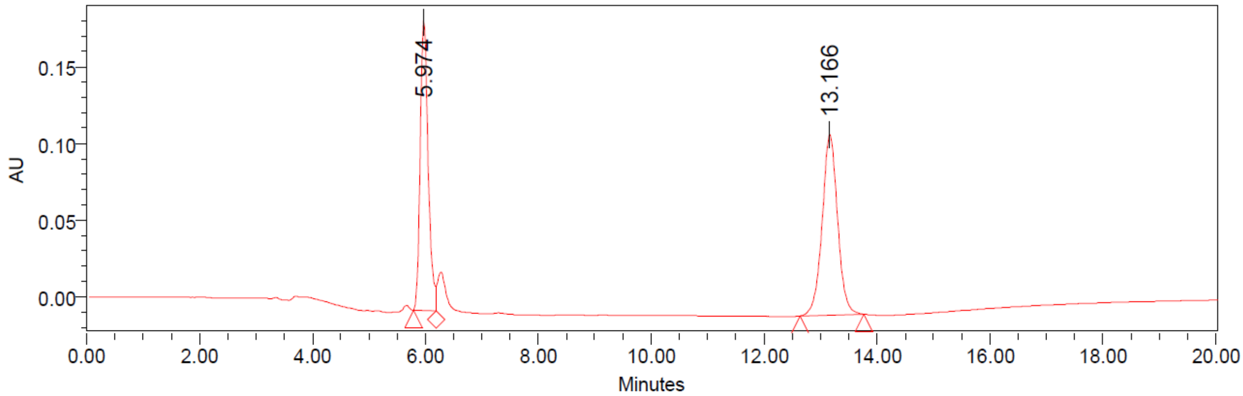
^{1}H NMR (400 MHz, $CDCl_3$) of **2Ad**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Ad**:



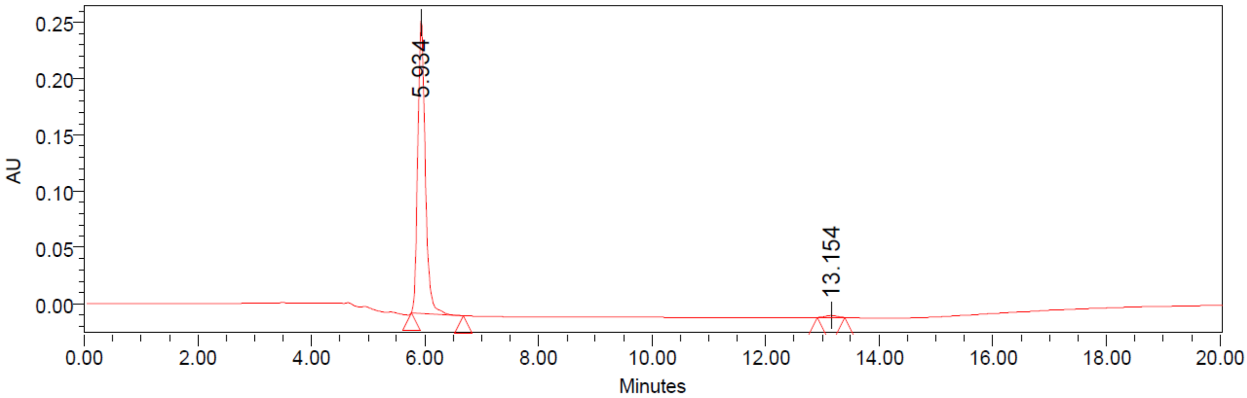
Racemic sample of 2Ad: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 233.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.7 nm	5.974	1848821	45.22	189036
2	PDA 233.7 nm	13.166	2239602	54.78	117882

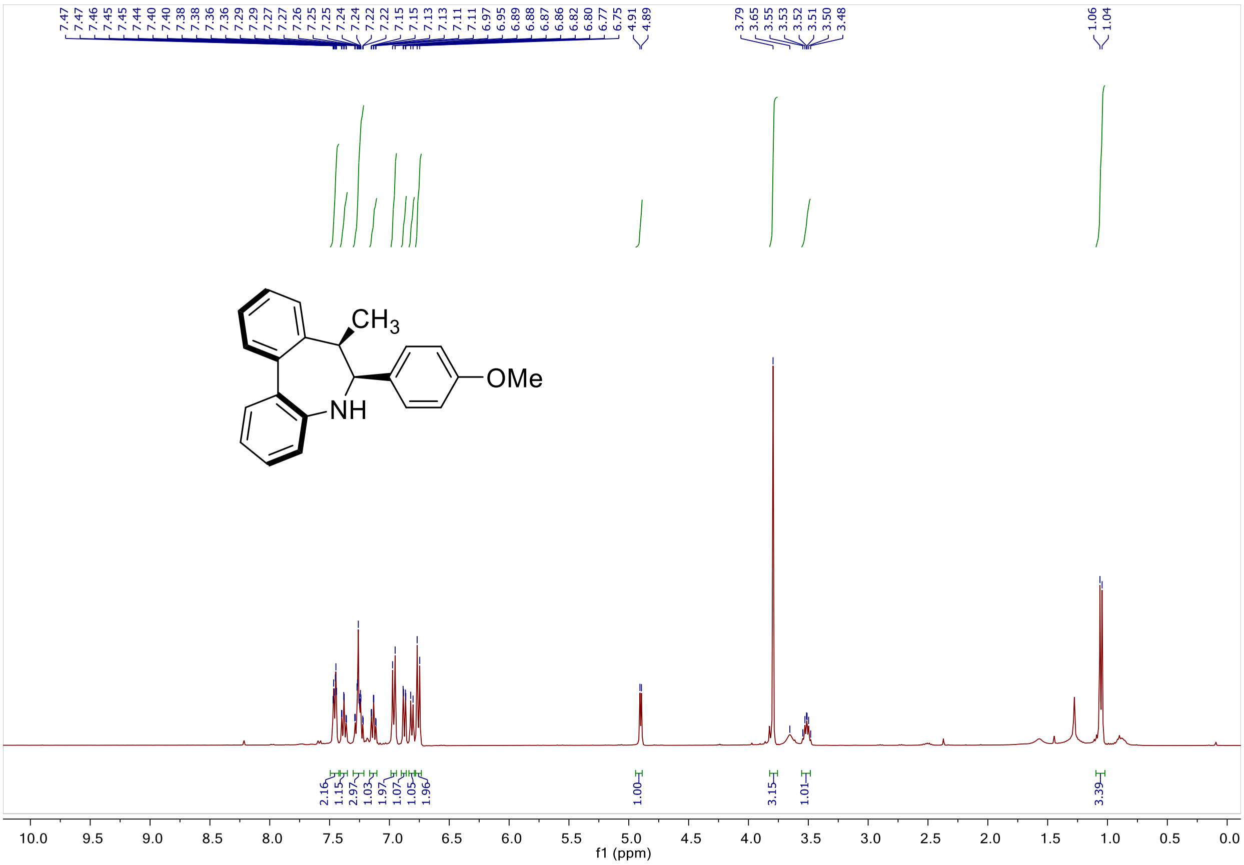
Enantioenriched sample of (S_a,6*S*,7*R*)-2Ac:



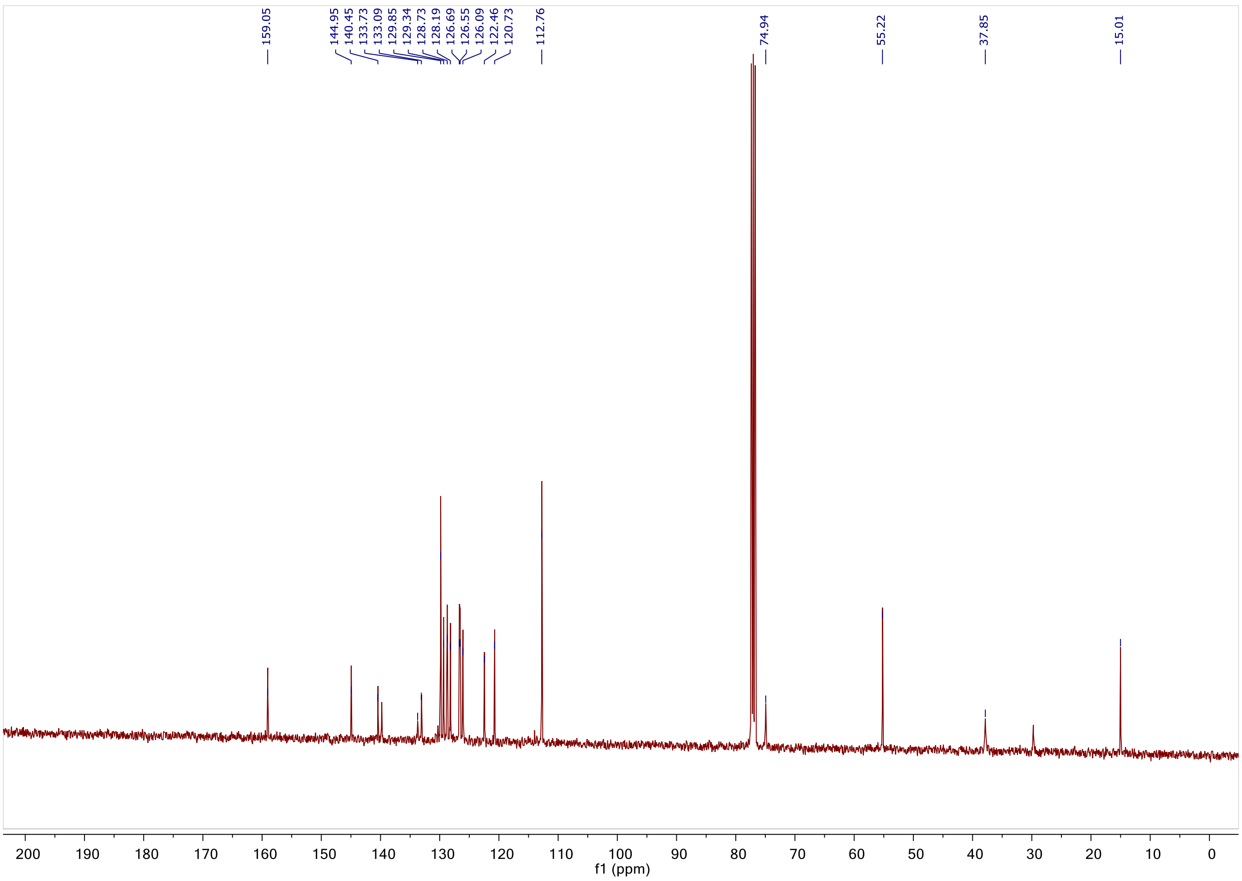
Processed Channel: PDA 233.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.0 nm	5.934	2372681	98.94	260684
2	PDA 233.0 nm	13.154	25424	1.06	1695

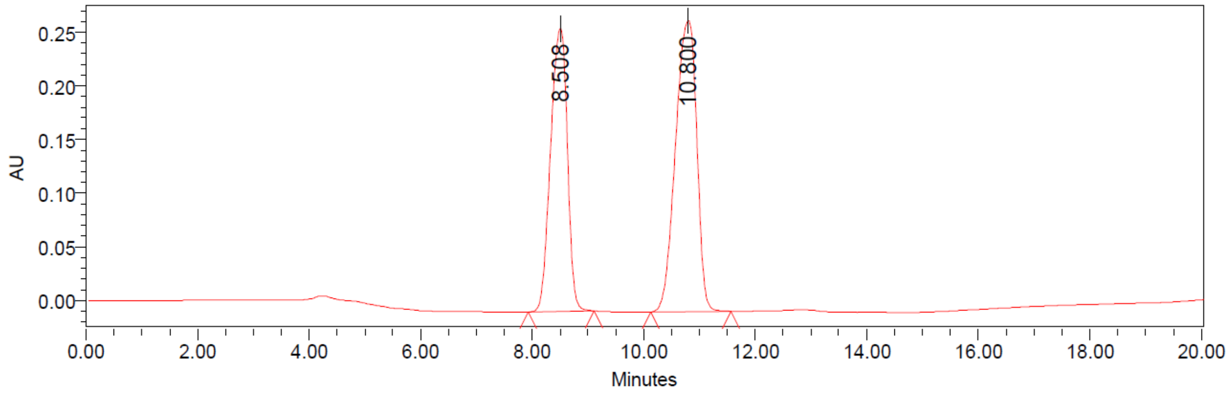
^{1}H NMR (400 MHz, $CDCl_3$) of **2Ae**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Ae**:



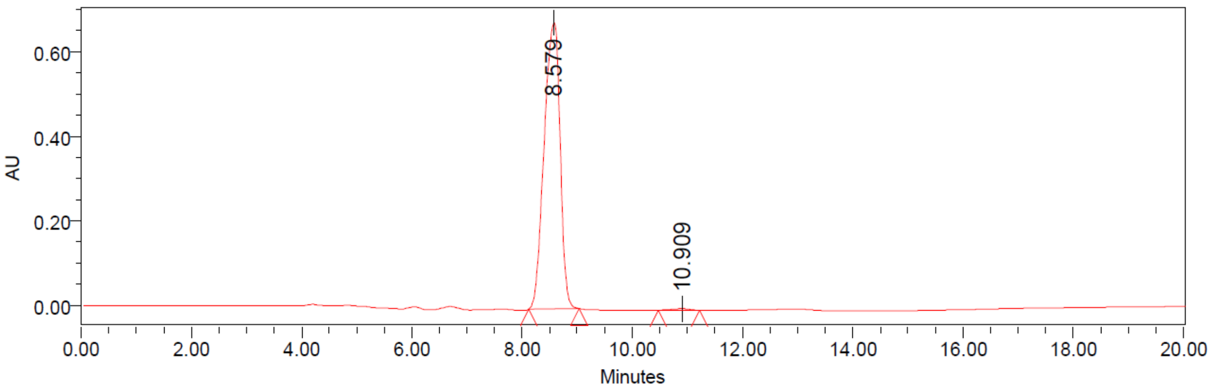
Racemic sample of 2Ae: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	8.508	5508492	43.40	264045
2	PDA 234.0 nm	10.800	7182522	56.60	271380

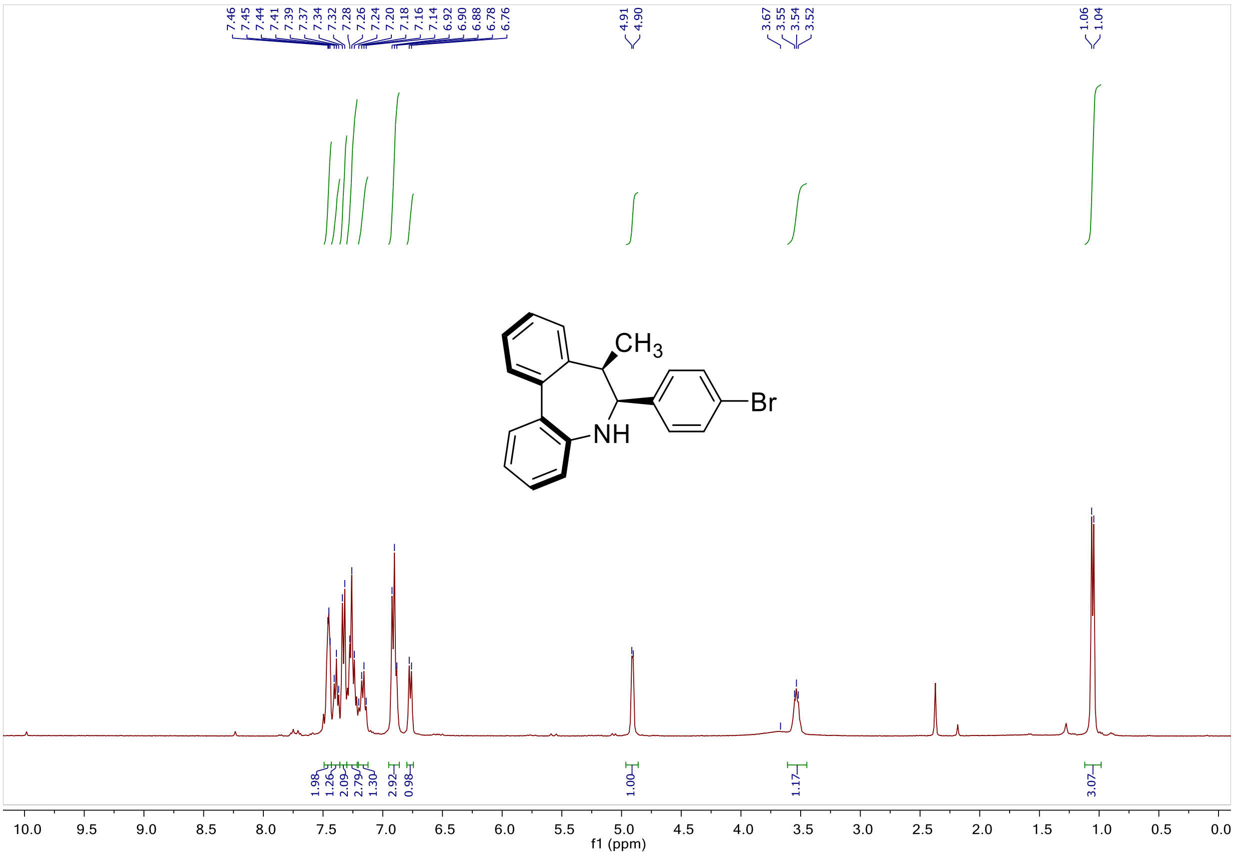
Enantioenriched sample of (*S*



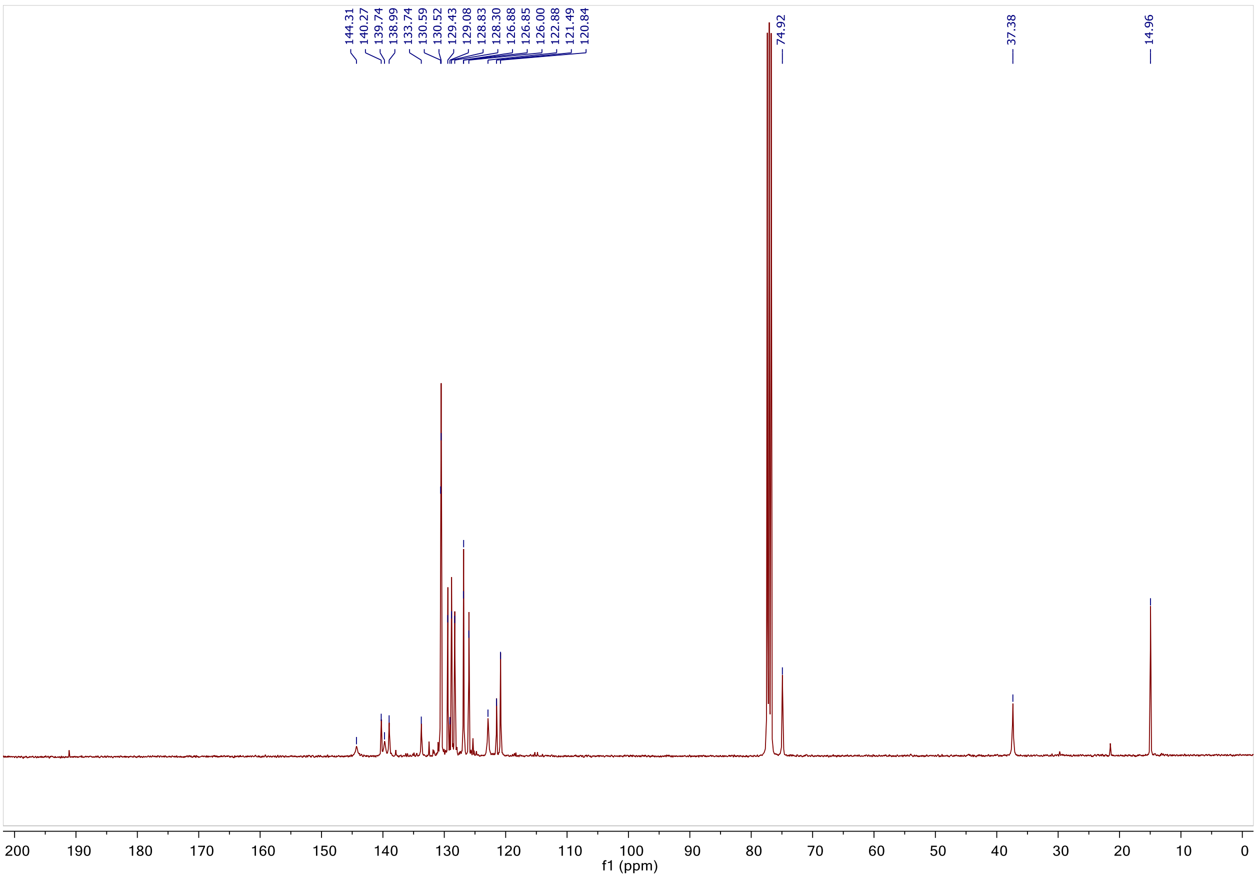
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	8.579	13613167	99.36	678233
2	PDA 234.0 nm	10.909	88198	0.64	3629

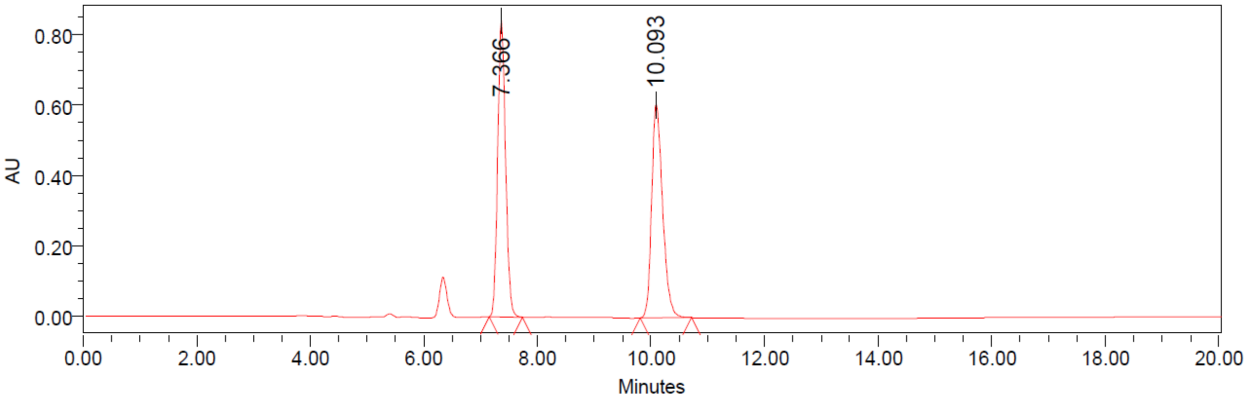
[1]H NMR (400 MHz, $CDCl_3$) of **2Af**:



[13]C NMR (100 MHz, $CDCl_3$) of **2Af**:



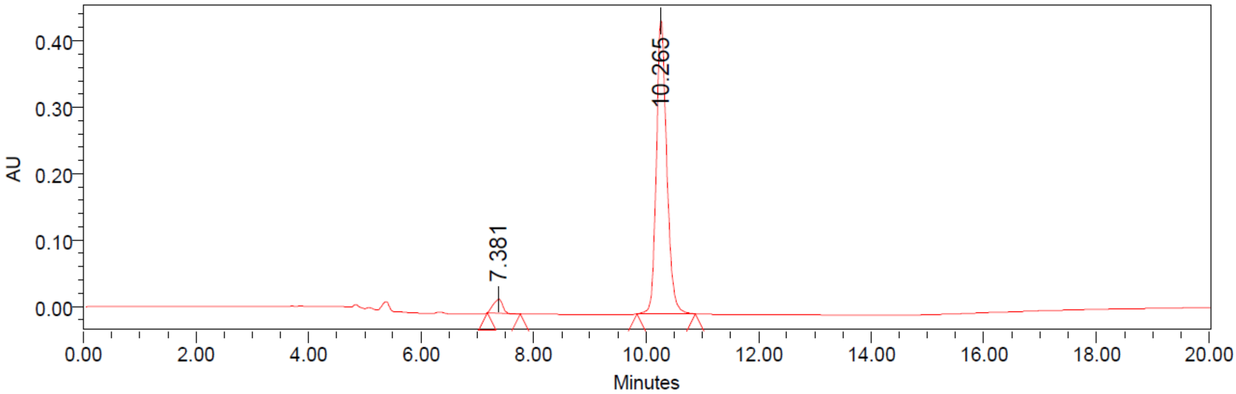
Racemic sample of 2Af: IB column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 243.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 243.0 nm	7.366	8055364	49.70	840406
2	PDA 243.0 nm	10.093	8153199	50.30	605033

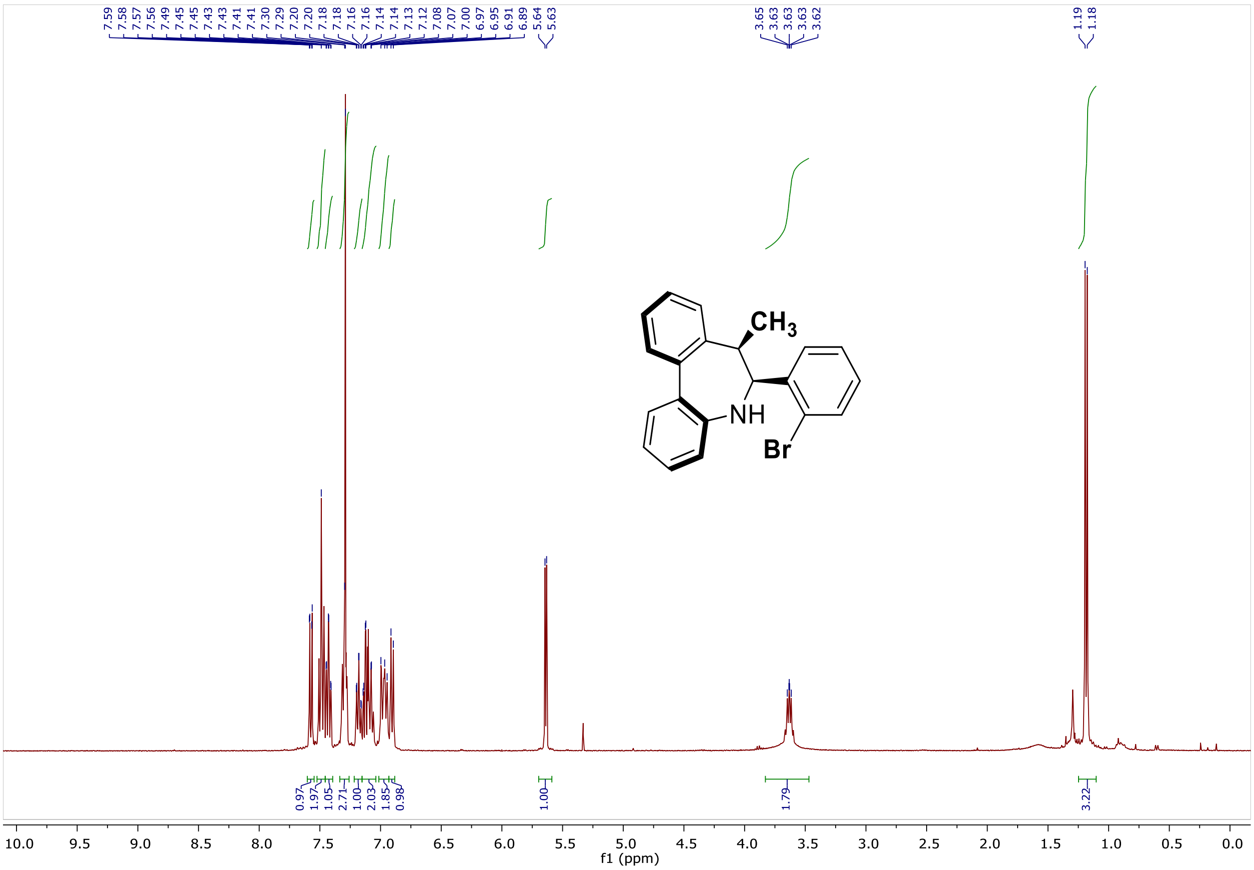
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-2Af:



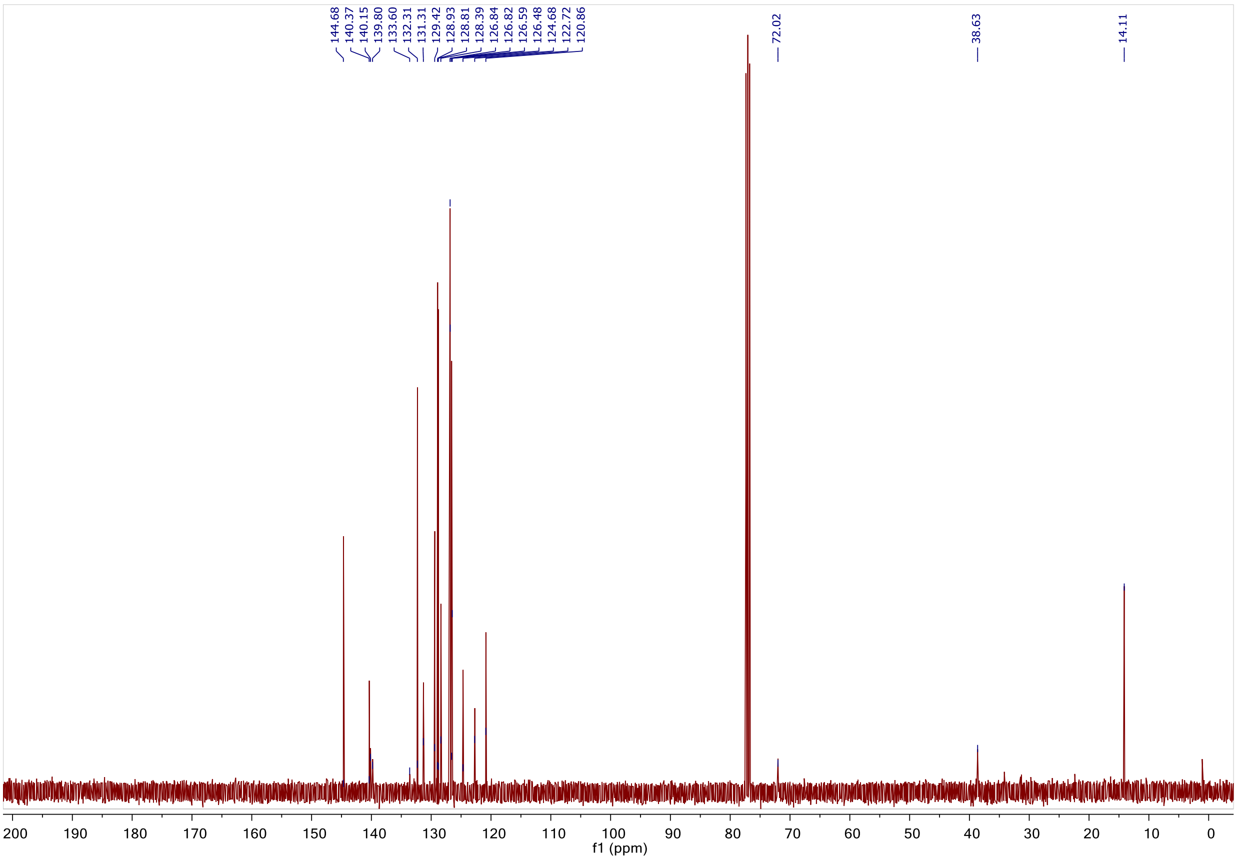
Processed Channel: PDA 233.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.0 nm	7.381	250337	4.24	21879
2	PDA 233.0 nm	10.265	5660245	95.76	442671

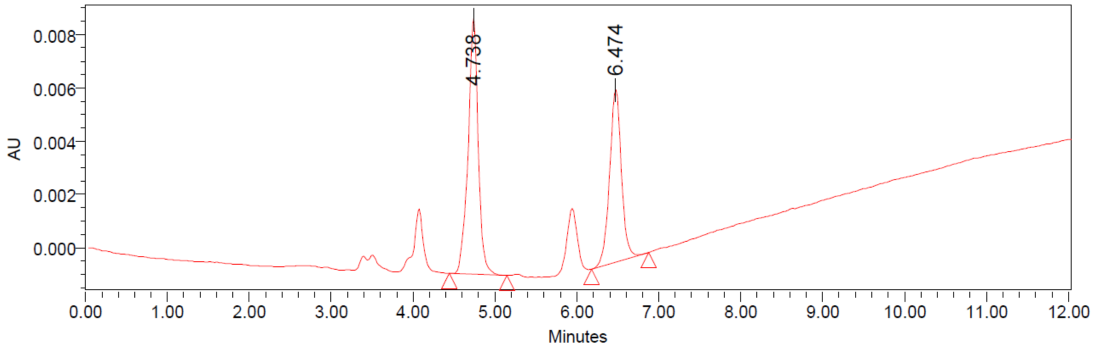
¹H NMR (400 MHz, CDCl₃) of **2Ag**:



¹³C NMR (100 MHz, CDCl₃) of **2Ag**:



Racemic sample of 2Ag: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min

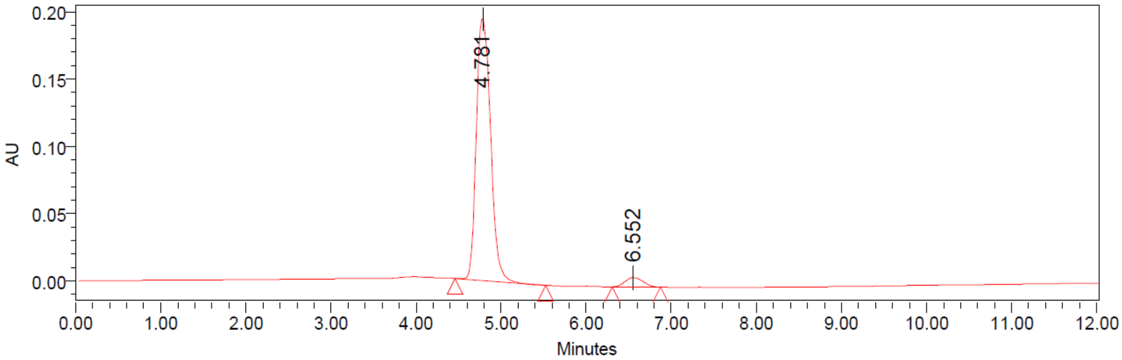


Processed Channel: PDA 235.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.0 nm	4.738	82866	56.20	9609
2	PDA 235.0 nm	6.474	64578	43.80	6461

Spectrum Index Plot

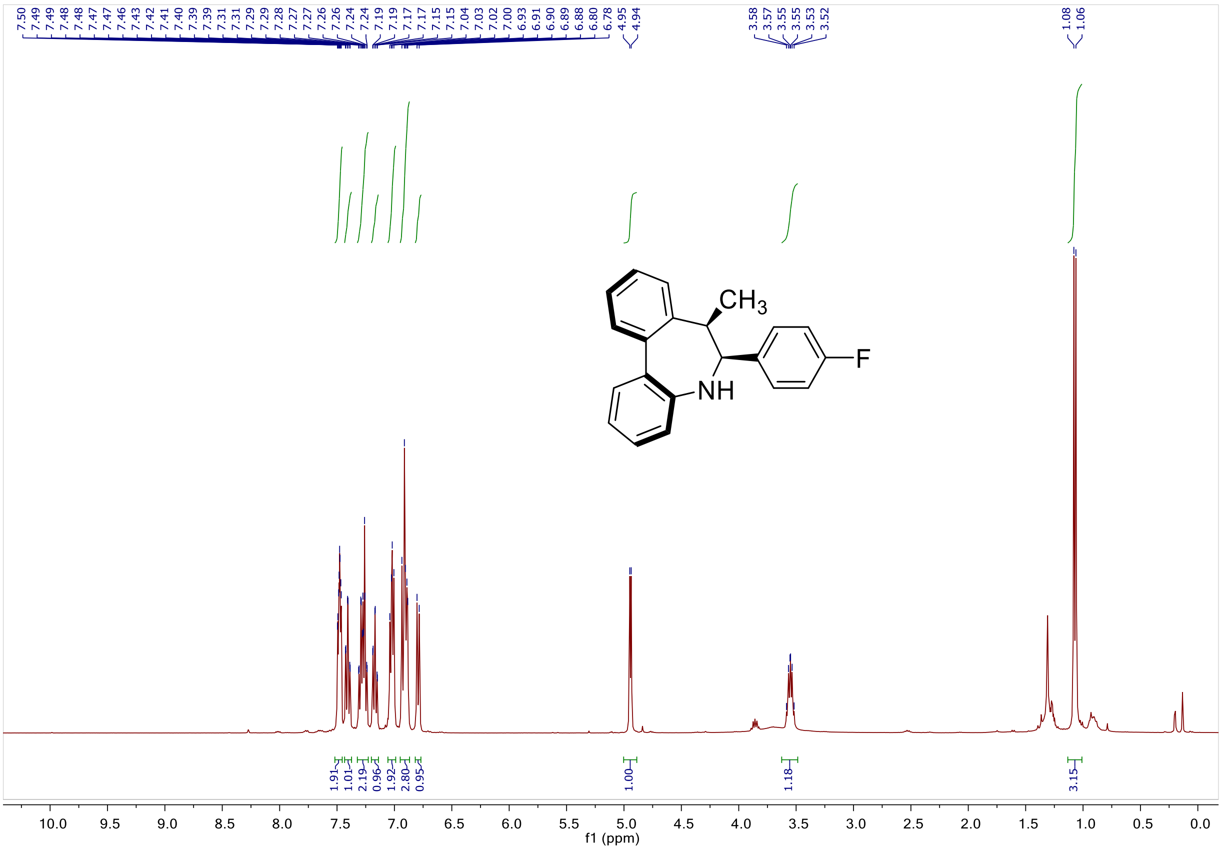
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-2Ag:



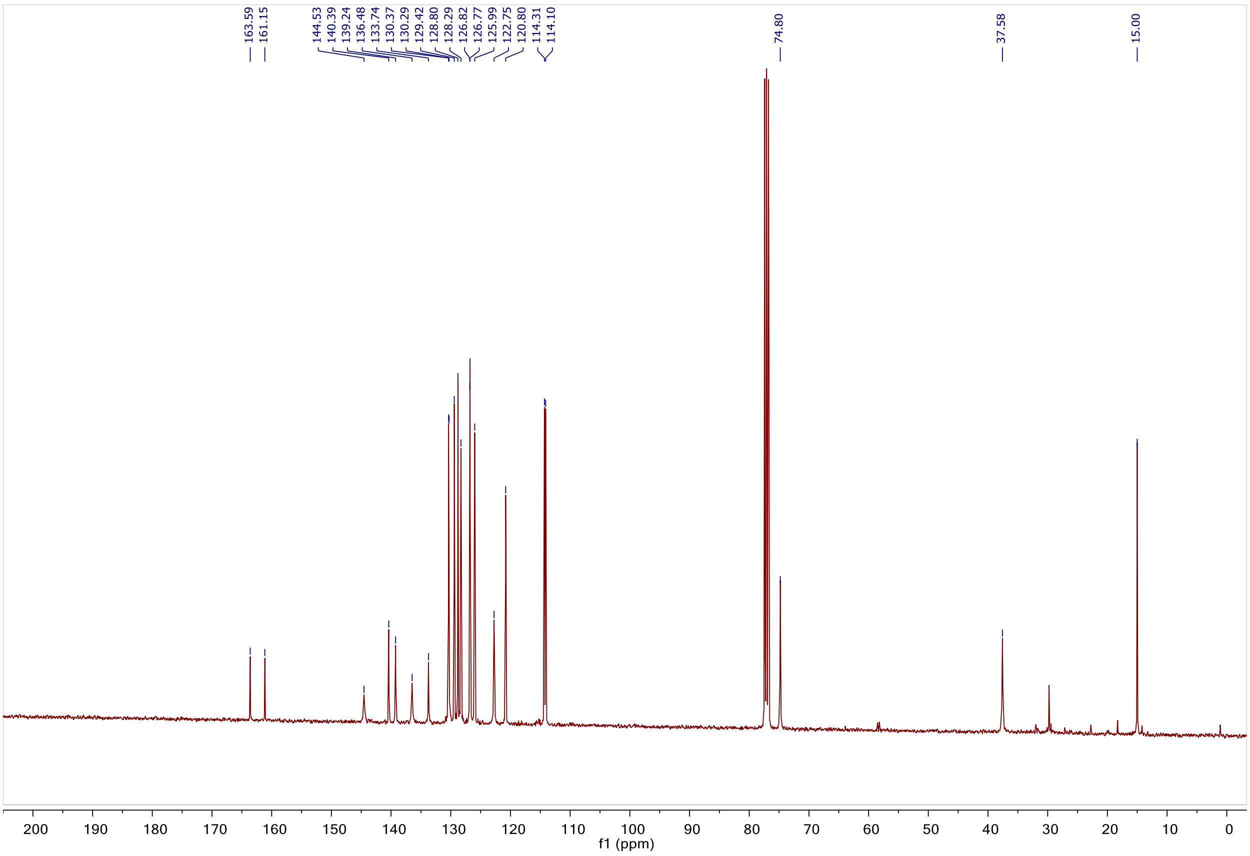
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	4.781	2275768	95.73	195997
2	PDA 234.0 nm	6.552	101409	4.27	6842

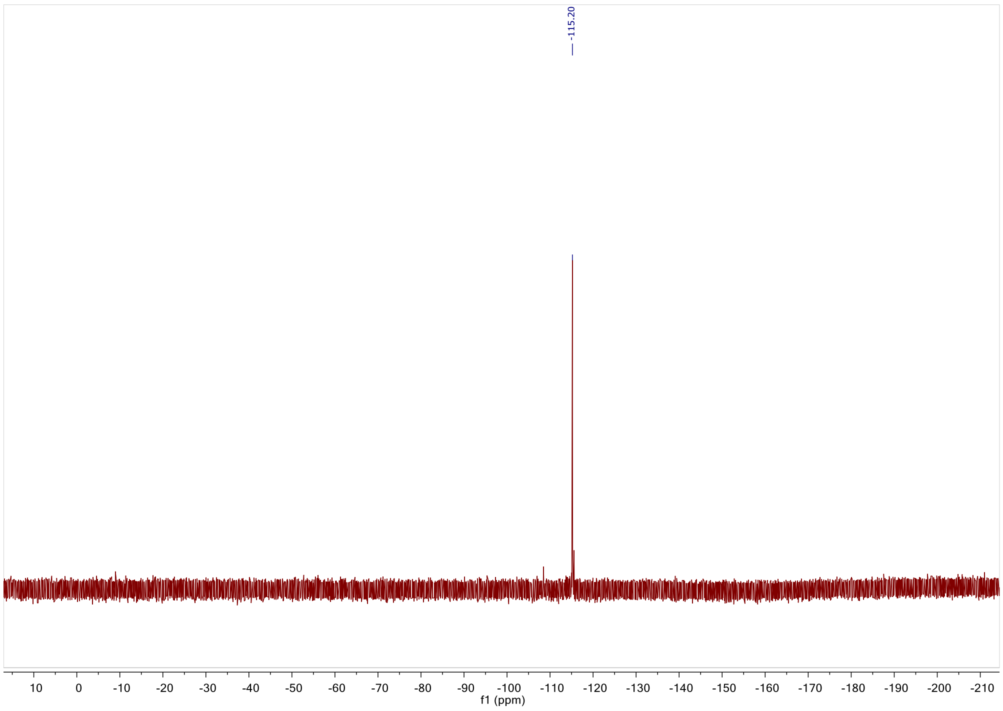
^{1}H NMR (400 MHz, $CDCl_3$) of **2Ah**:



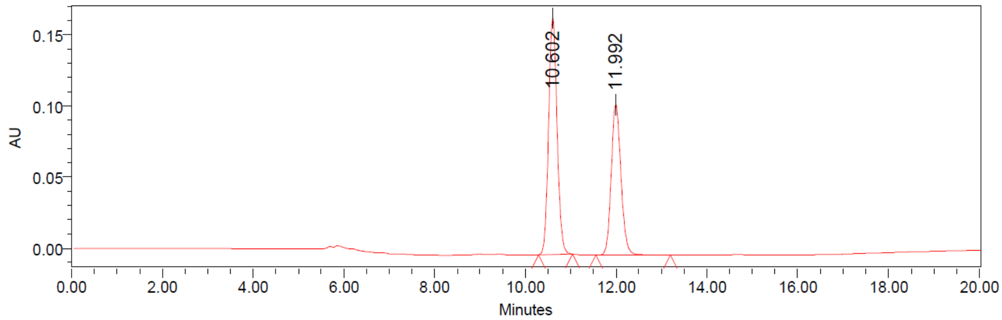
^{13}C NMR (100 MHz, $CDCl_3$) of **2Ah**:



^{19}F NMR (377 MHz, $CDCl_3$) of **2Ah**:



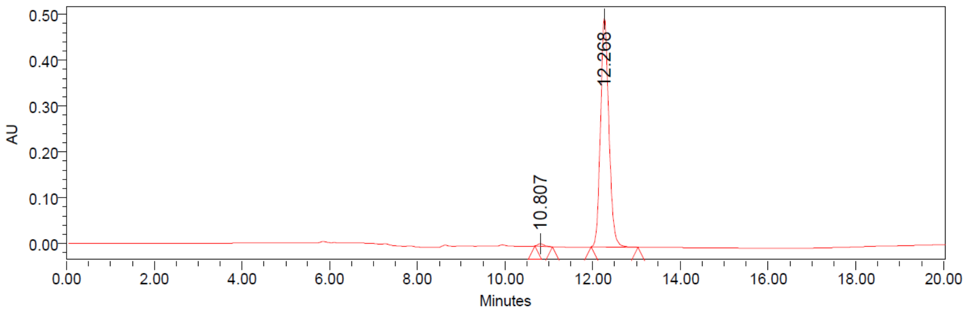
Racemic sample of 2Ah: IB column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 244.4 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 244.4 nm	10.602	2143330	57.76	166660
2	PDA 244.4 nm	11.992	1567404	42.24	105863

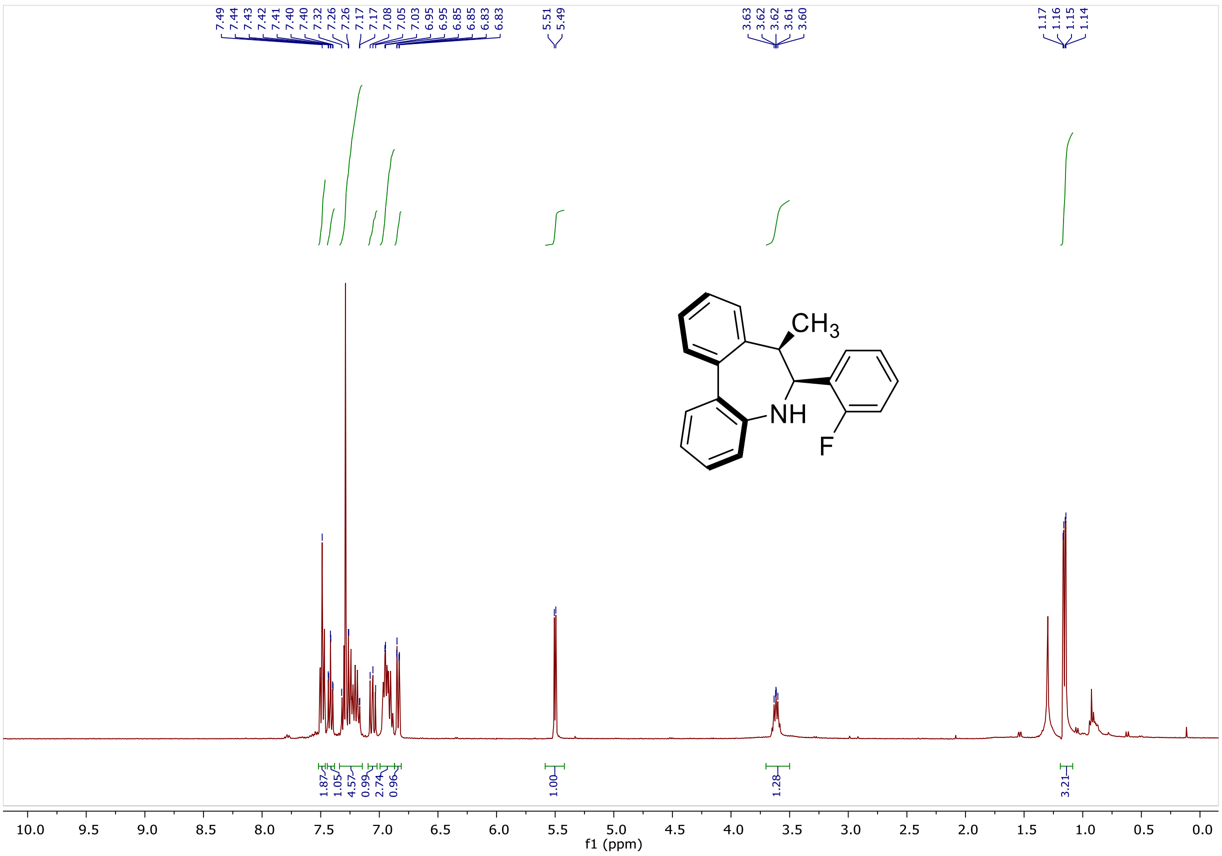
Enantioenriched sample of (*S*a,6*S*,7*R*)-2Ah:



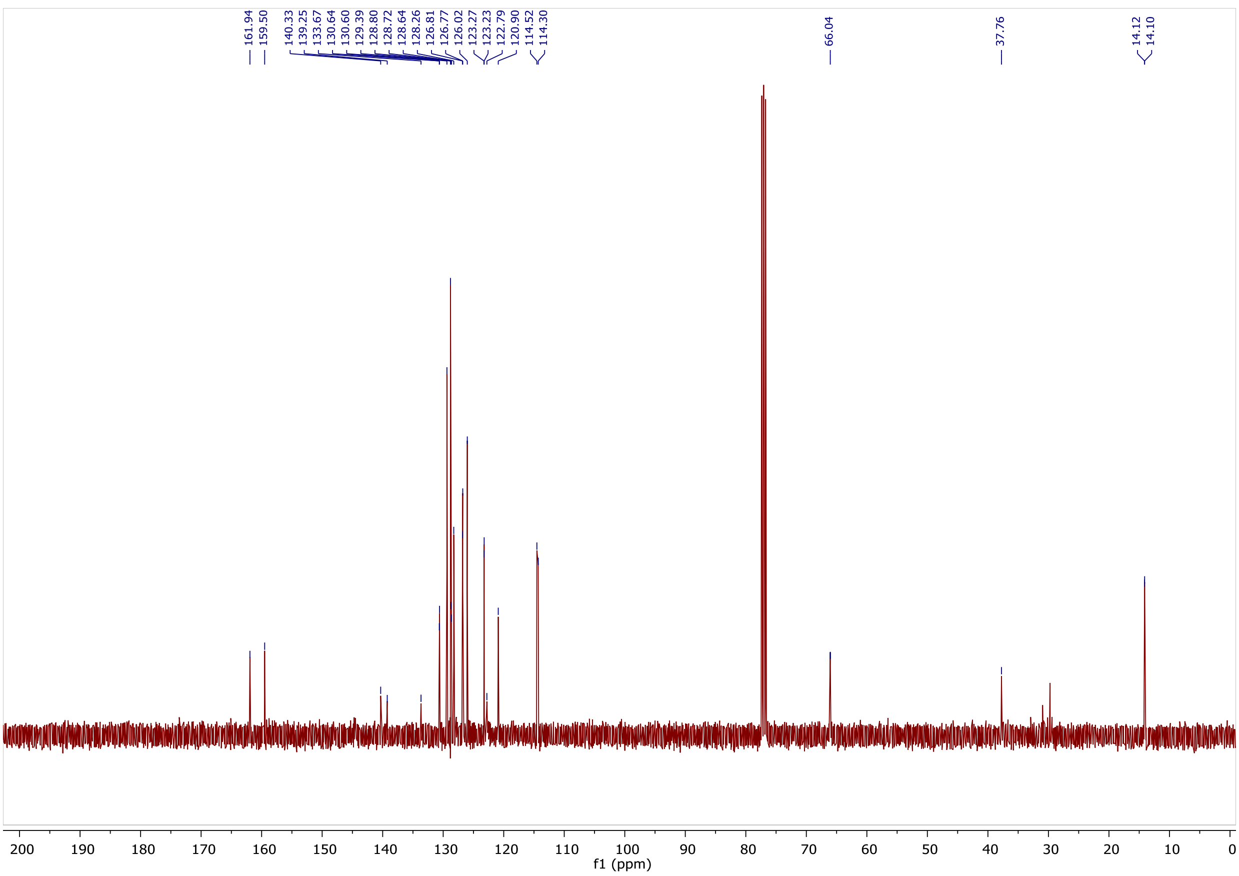
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	10.807	56114	0.84	5543
2	PDA 234.0 nm	12.268	6636890	99.16	499097

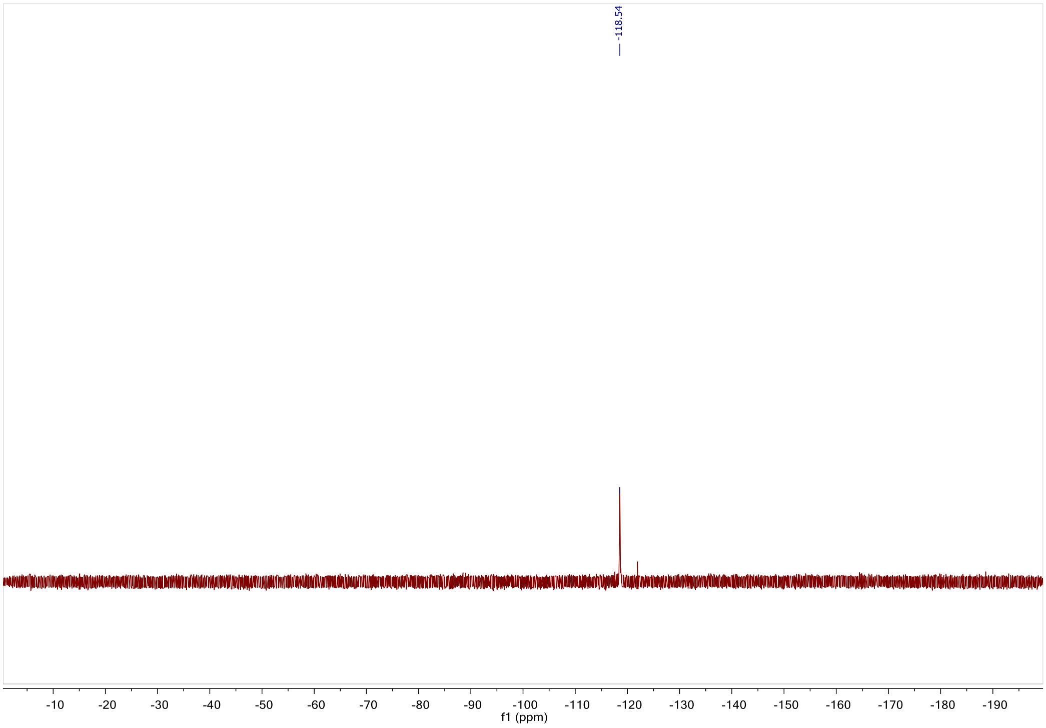
^{1}H NMR (400 MHz, $CDCl_3$) of **2Ai**:



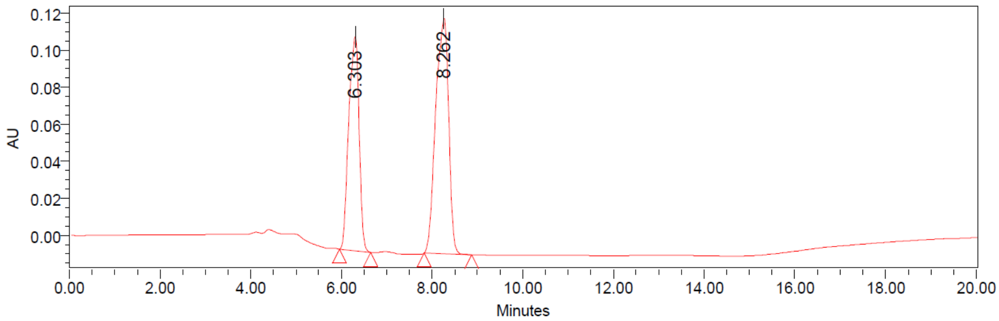
^{13}C NMR (100 MHz, $CDCl_3$) of **2Ai**:



^{19}F NMR (377 MHz, $CDCl_3$) of **2Ai**:



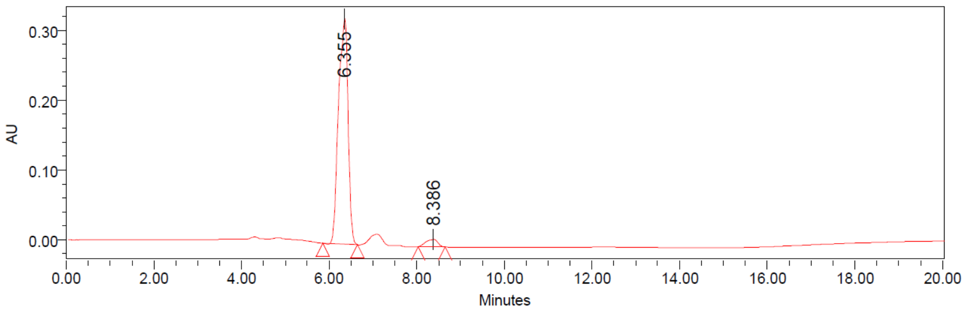
Racemic sample of 2Ai: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	6.303	1818150	41.92	115776
2	PDA 234.0 nm	8.262	2519022	58.08	127235

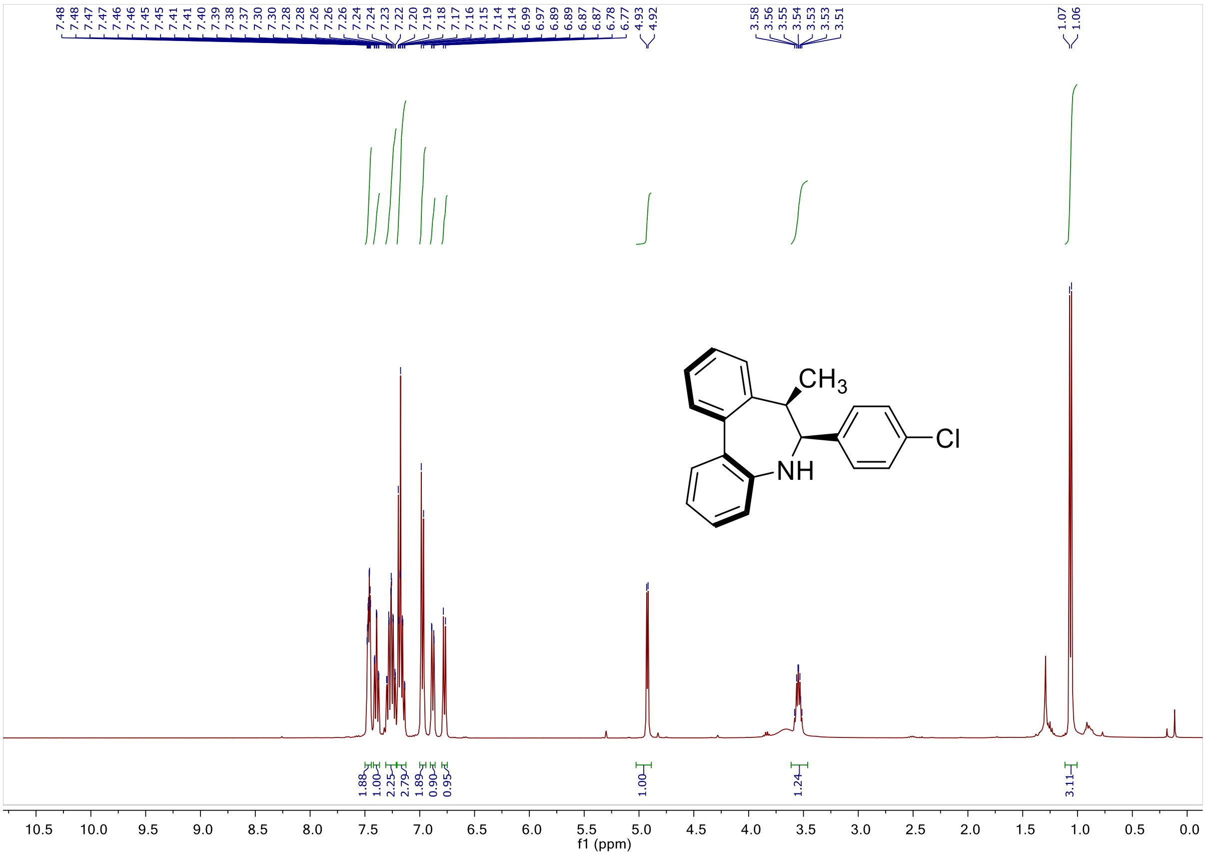
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-2Ai:



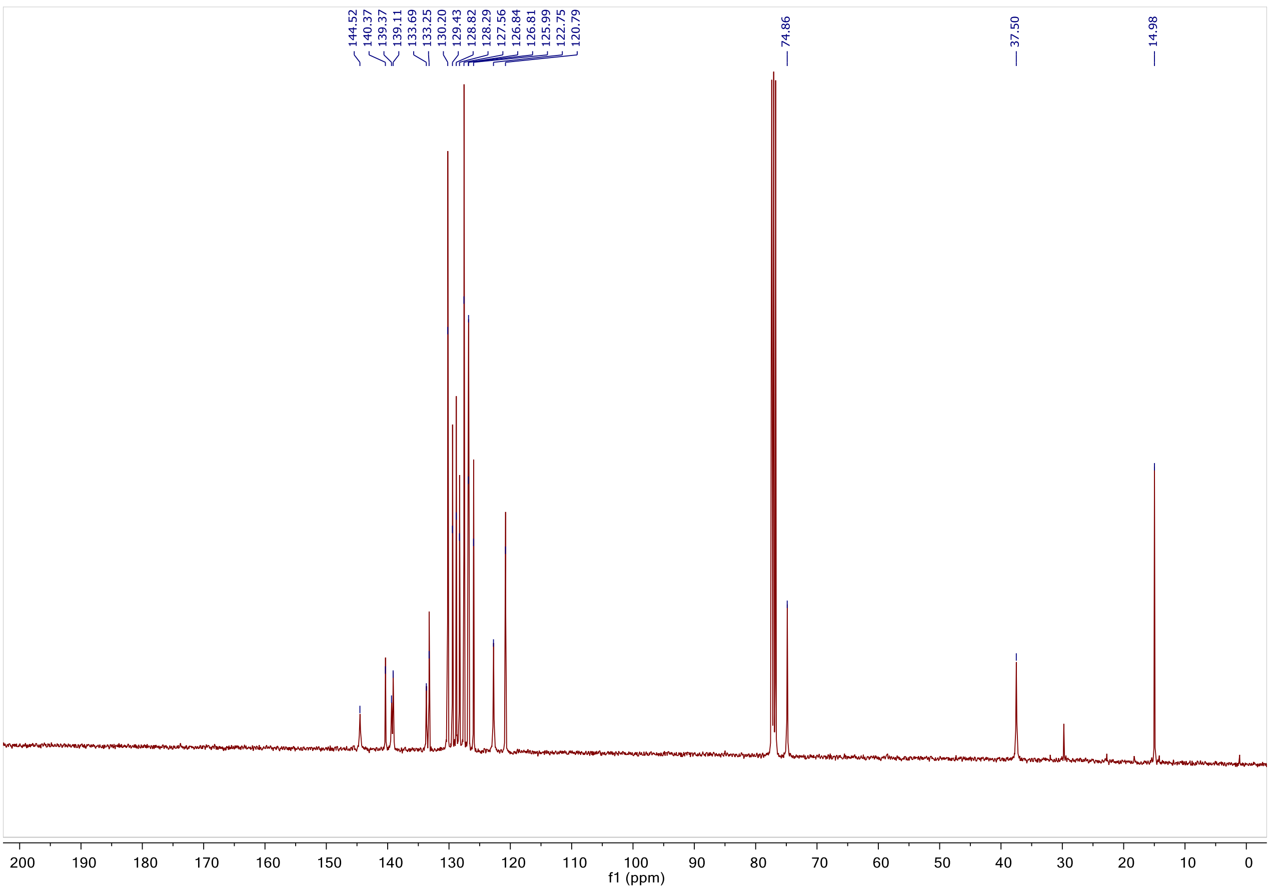
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	6.355	4881350	96.01	324575
2	PDA 234.0 nm	8.386	203095	3.99	10900

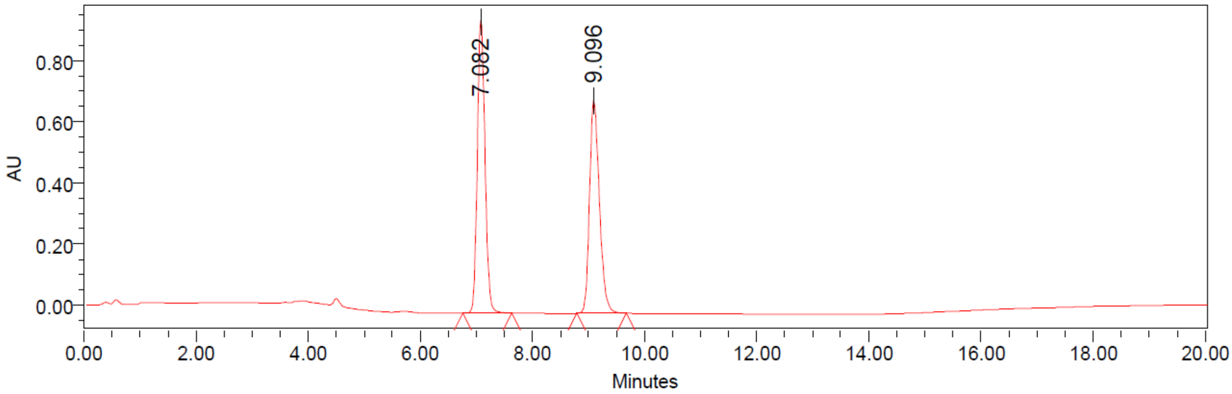
^{1}H NMR (400 MHz, $CDCl_3$) of **2Aj**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Aj**:



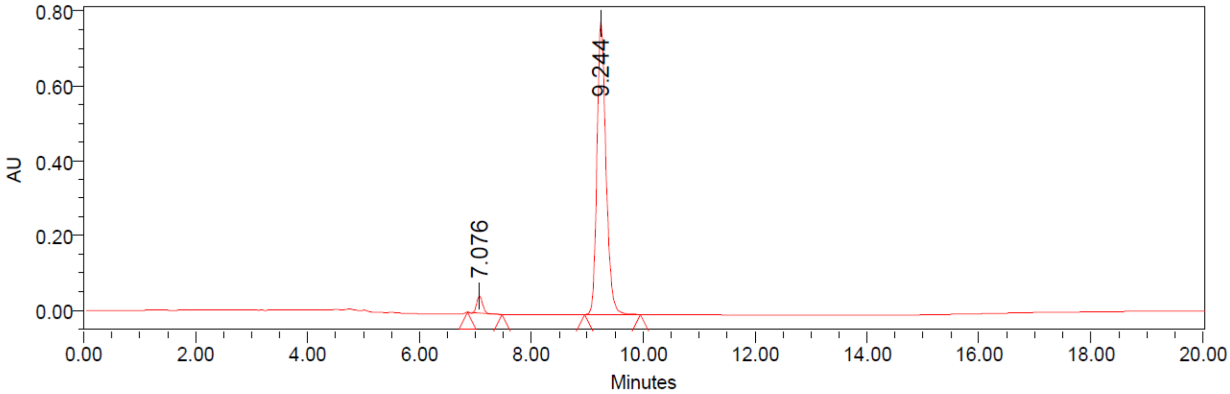
Racemic sample of 2Aj: IB column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 221.3 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 221.3 nm	7.082	9103454	51.52	958646
2	PDA 221.3 nm	9.096	8565291	48.48	696010

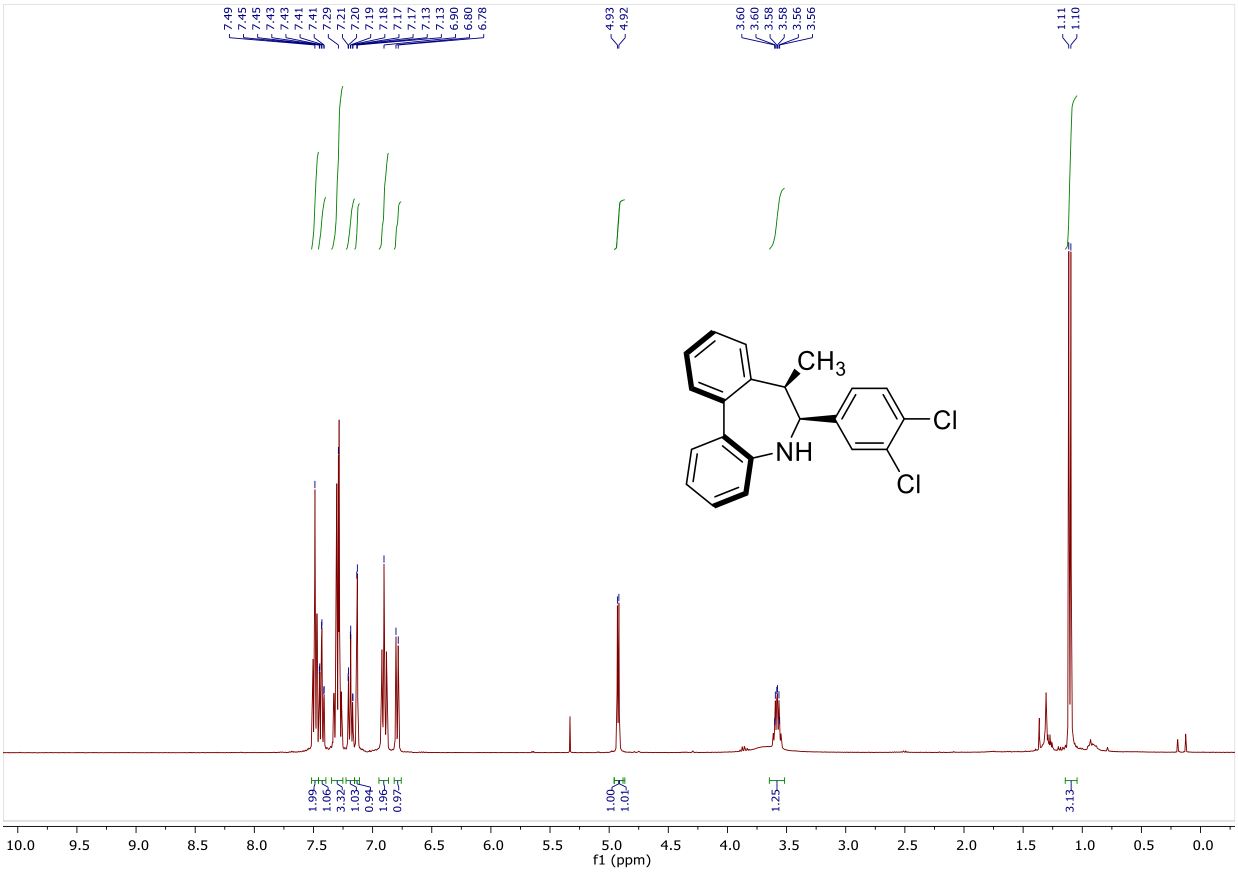
Enantioenriched sample of (*S*a,6*S*,7*R*)-2Aj:



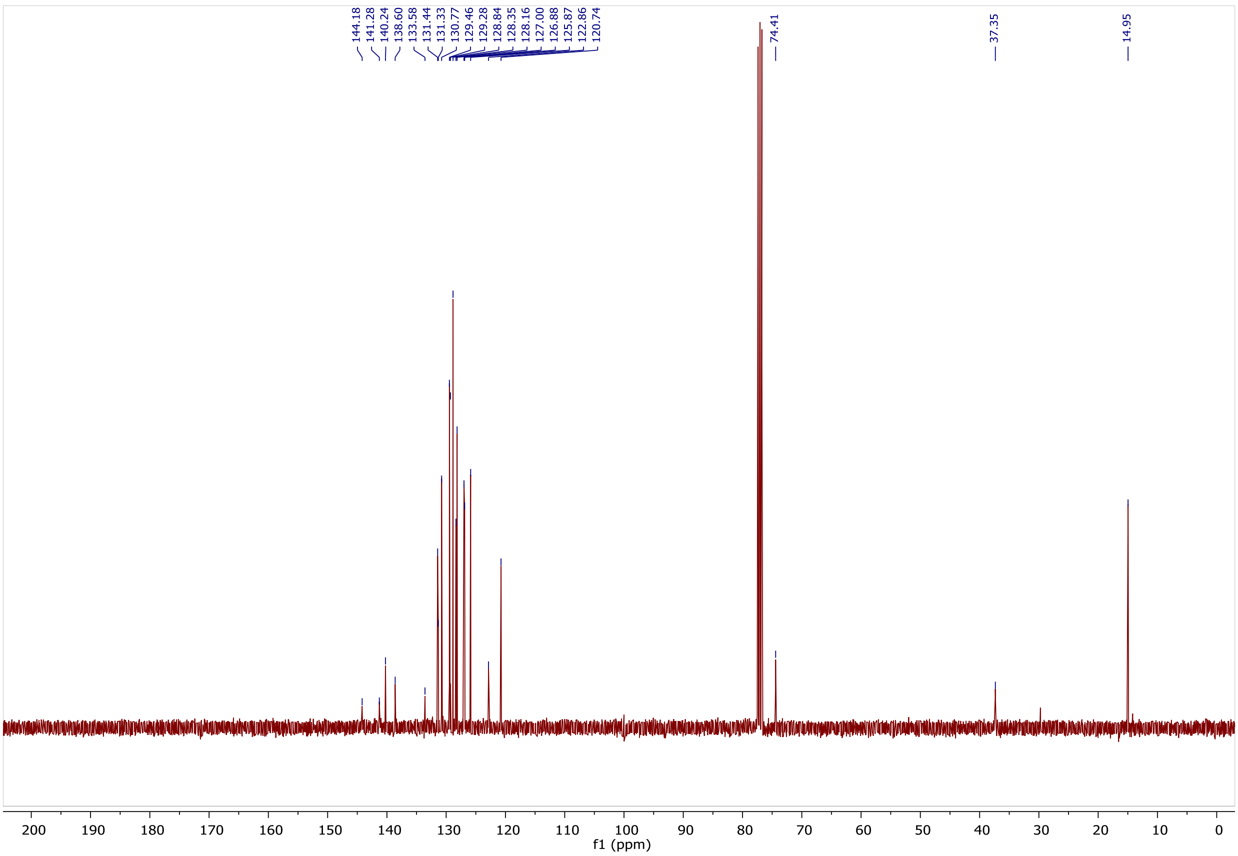
Processed Channel: PDA 233.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.0 nm	7.076	349455	3.81	45880
2	PDA 233.0 nm	9.244	8814796	96.19	784408

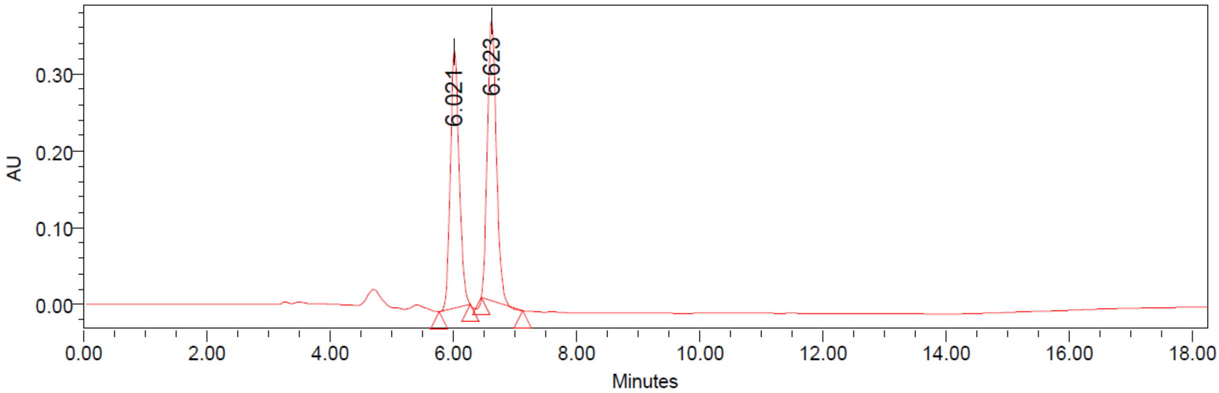
[1]H NMR (400 MHz, $CDCl_3$) of **2Ak**:



[13]C NMR (100 MHz, $CDCl_3$) of **2Ak**:



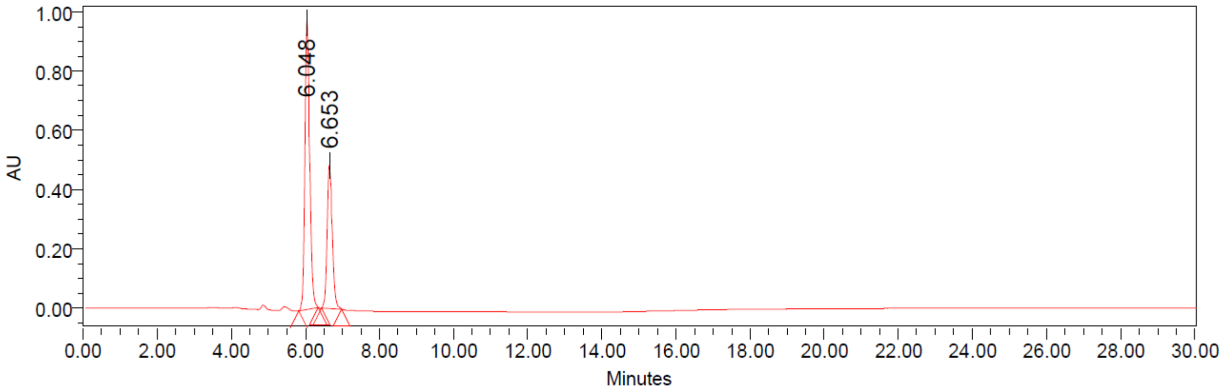
Racemic sample of 2Ak: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 233.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.7 nm	6.021	3307003	47.05	334899
2	PDA 233.7 nm	6.623	3722402	52.95	365119

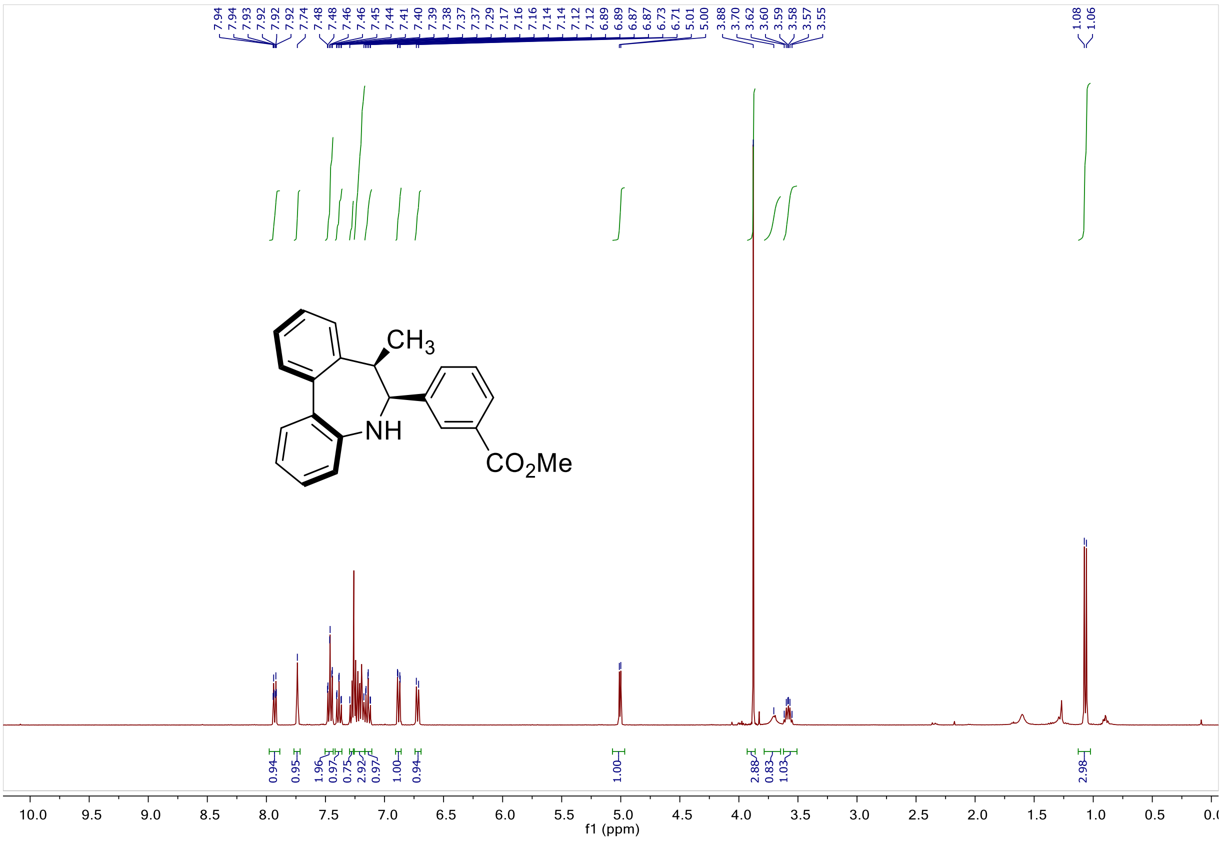
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-2Ak:



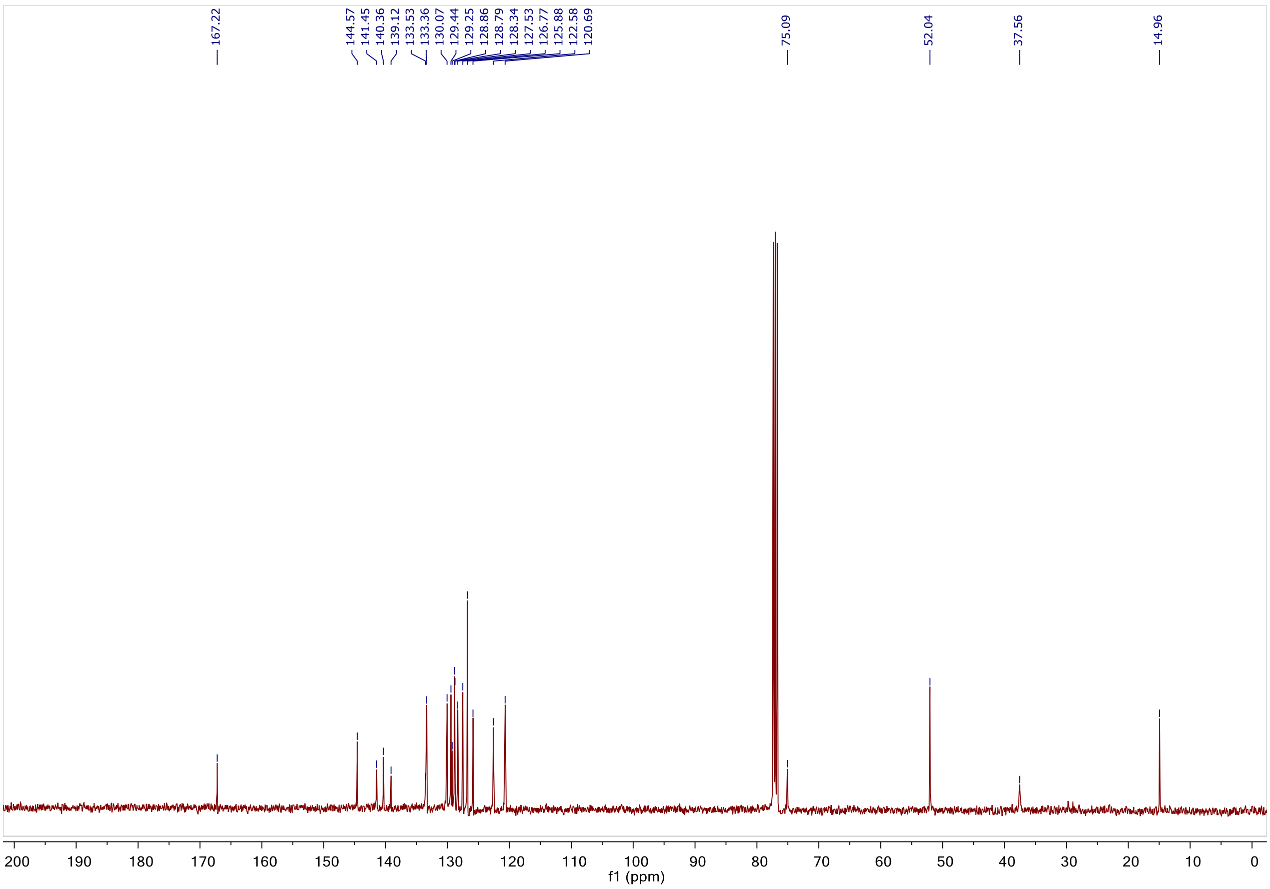
Processed Channel: PDA 233.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.0 nm	6.048	8778234	65.17	976061
2	PDA 233.0 nm	6.653	4691599	34.83	486397

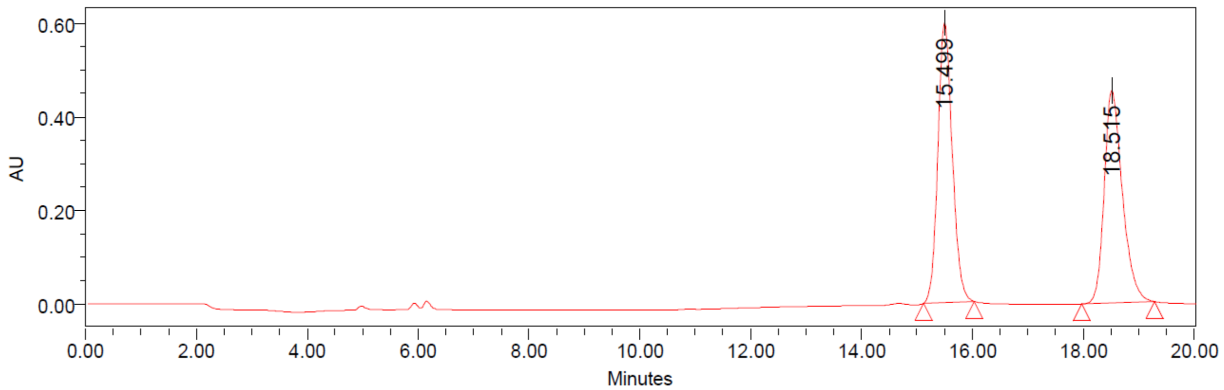
[1]H NMR (400 MHz, $CDCl_3$) of **2Al**:



[13]C NMR (100 MHz, $CDCl_3$) of **2Al**:



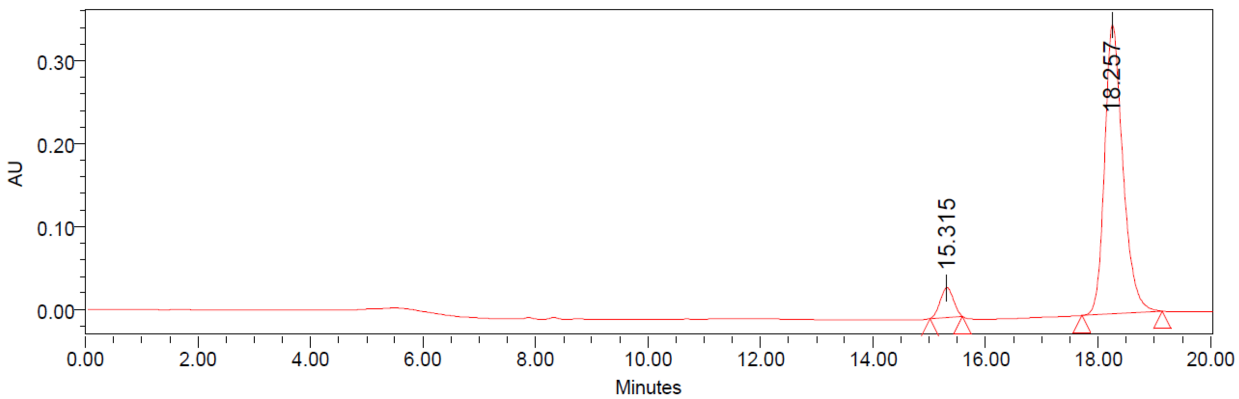
Racemic sample of 2Al: IB column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 231.3 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 231.3 nm	15.499	10808313	50.97	599725
2	PDA 231.3 nm	18.515	10398567	49.03	455290

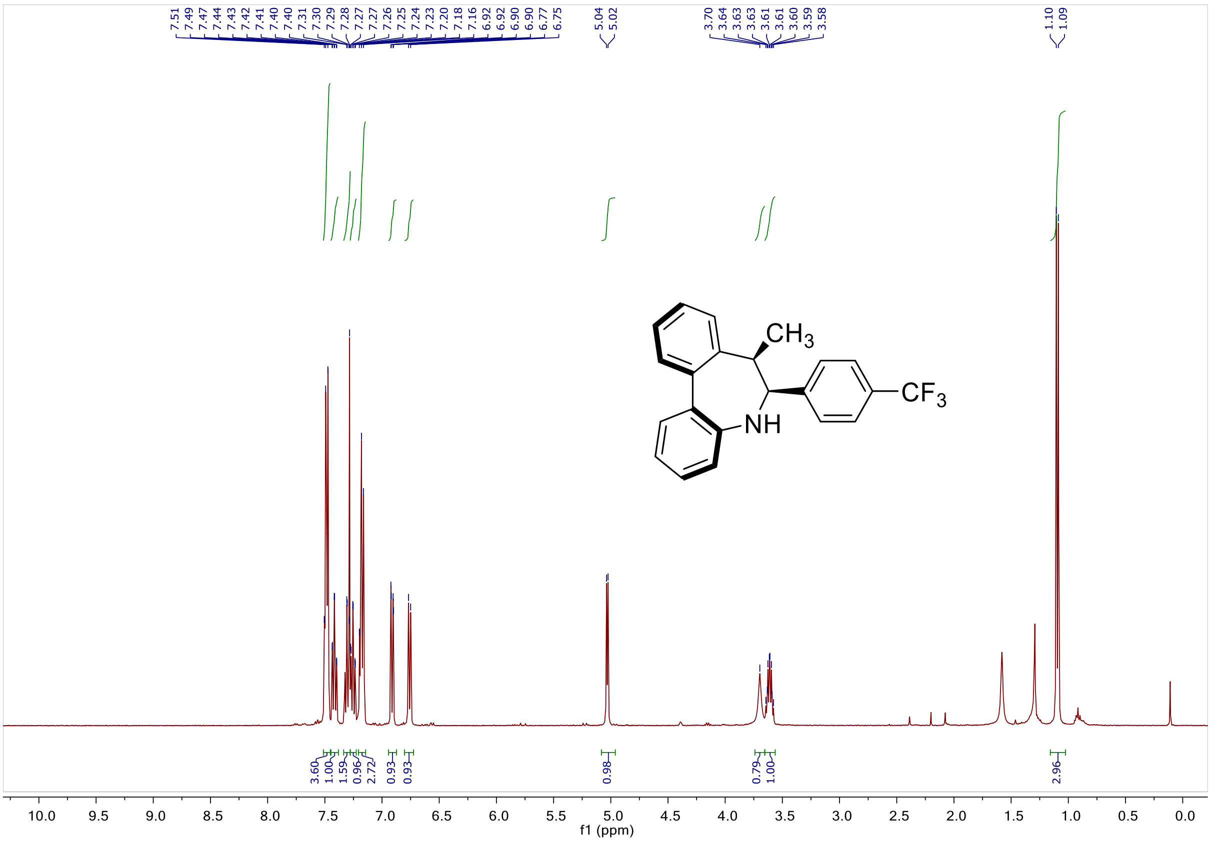
Enantioenriched sample of (*S*a,6*S*,7*R*)-2Al:



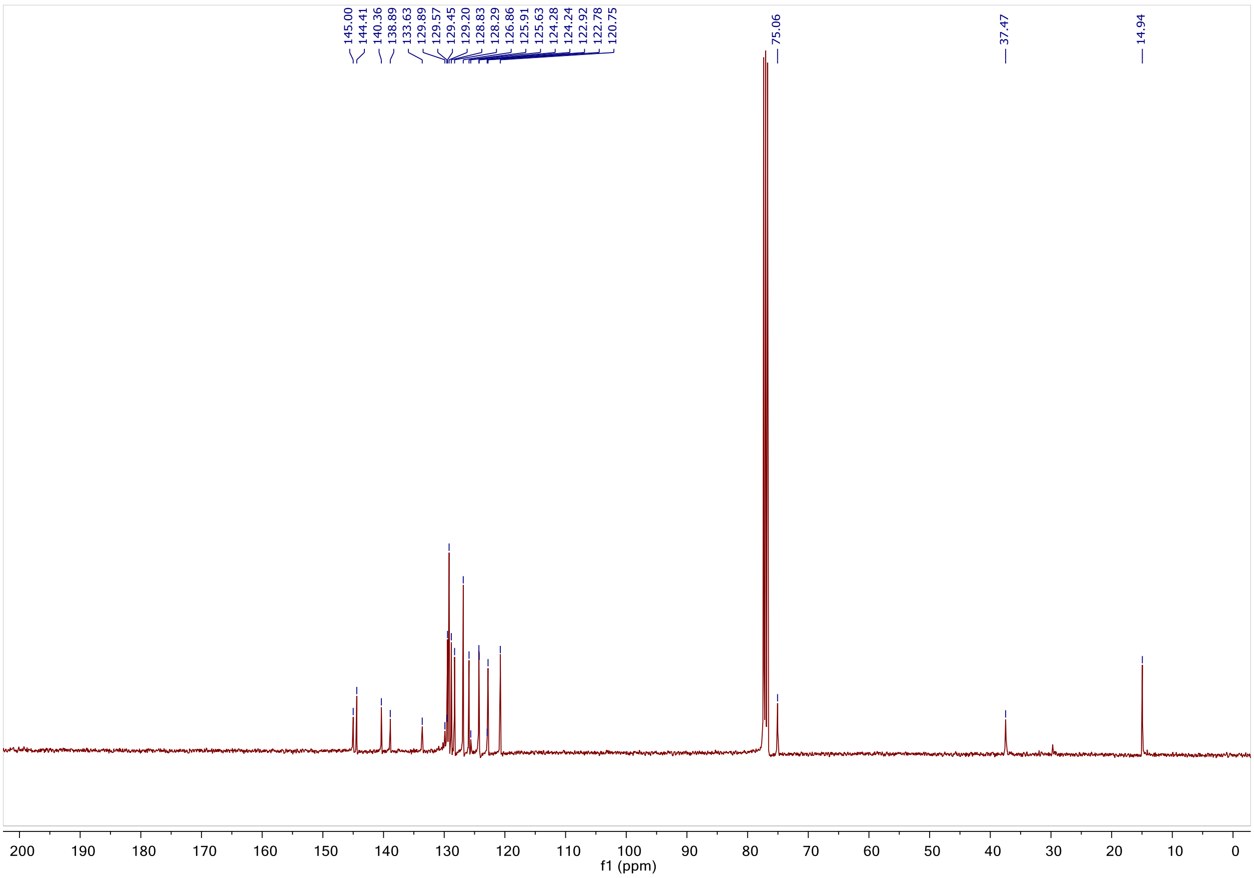
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	15.315	583088	6.89	36025
2	PDA 234.0 nm	18.257	7874959	93.11	349064

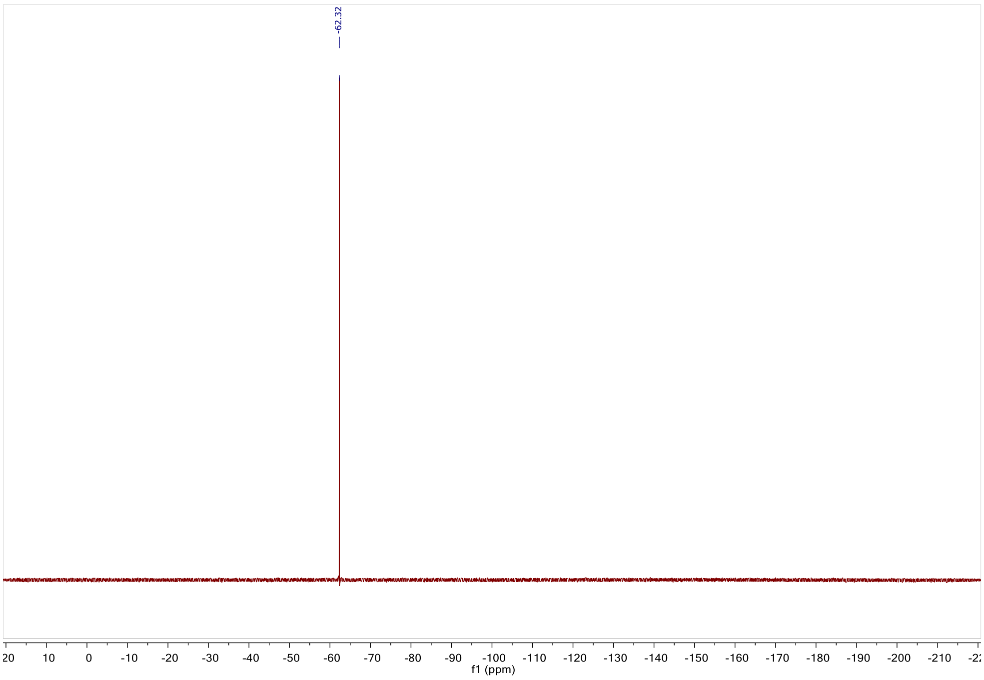
[1]H NMR (400 MHz, $CDCl_3$) of **2Am**:



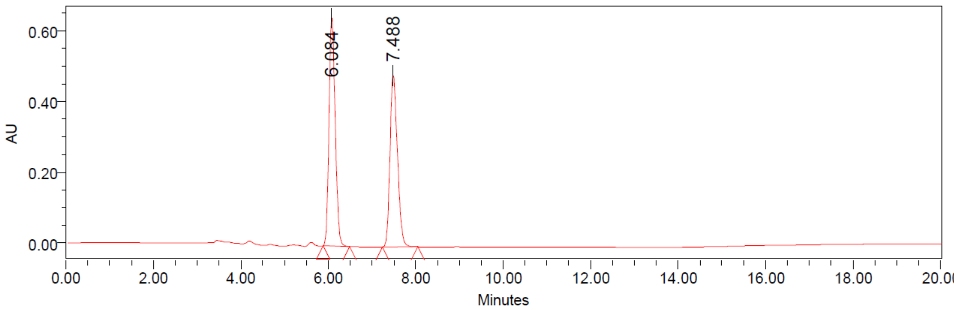
[13]C NMR (100 MHz, $CDCl_3$) of **2Am**:



^{19}F NMR (377 MHz, $CDCl_3$) of **2Am**:



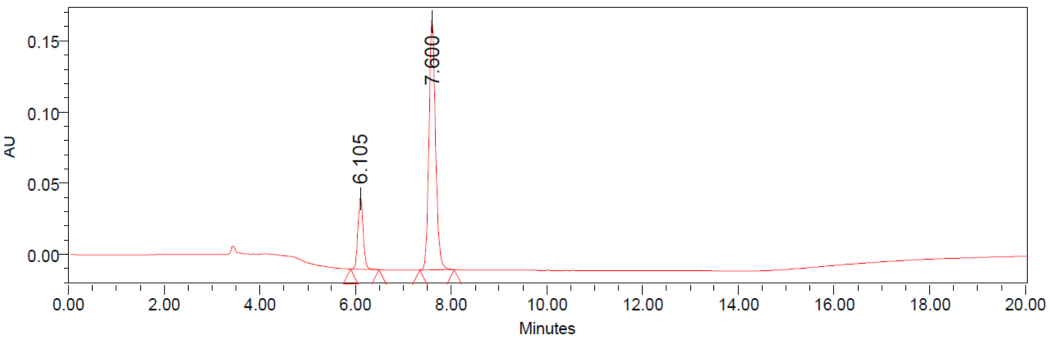
Racemic sample of 2Am: IB column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	6.084	6417989	52.77	644239
2	PDA 234.0 nm	7.488	5744530	47.23	485139

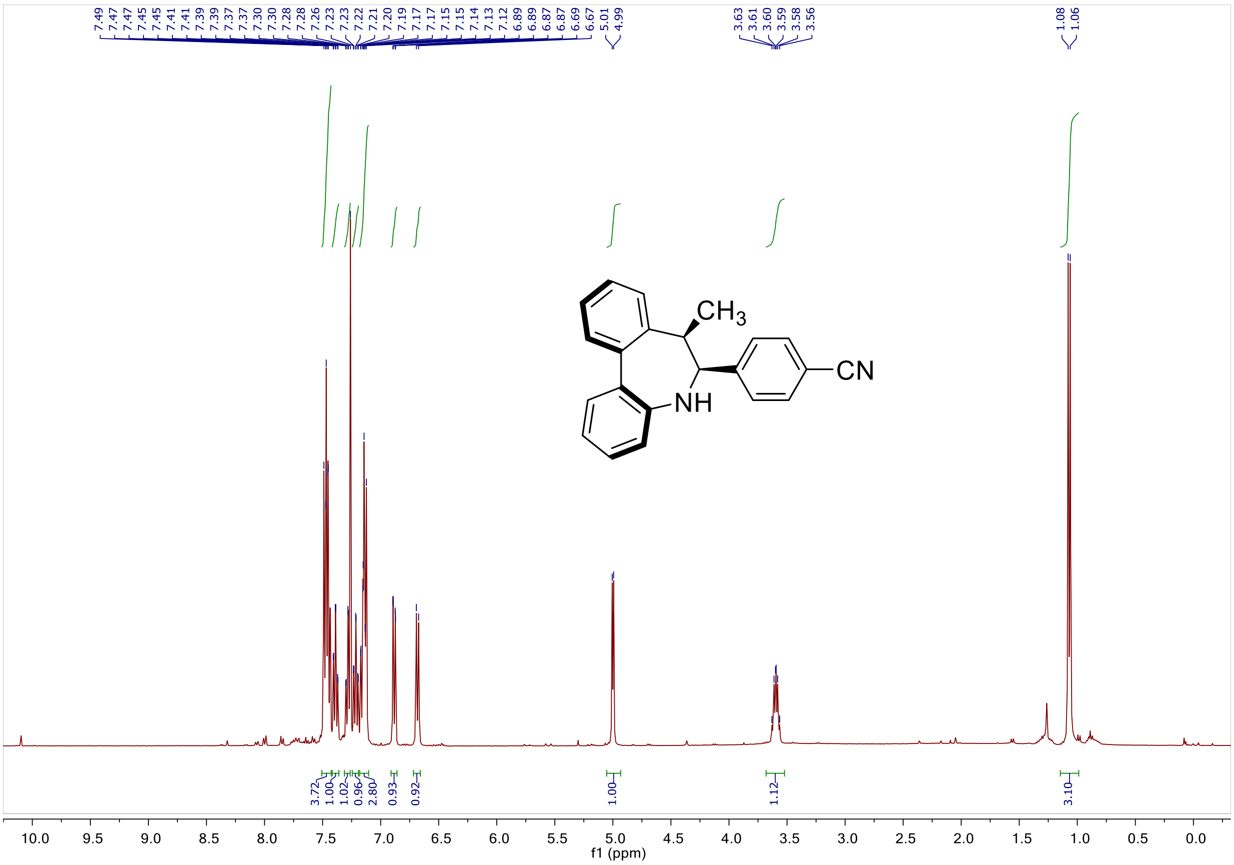
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-2Am:



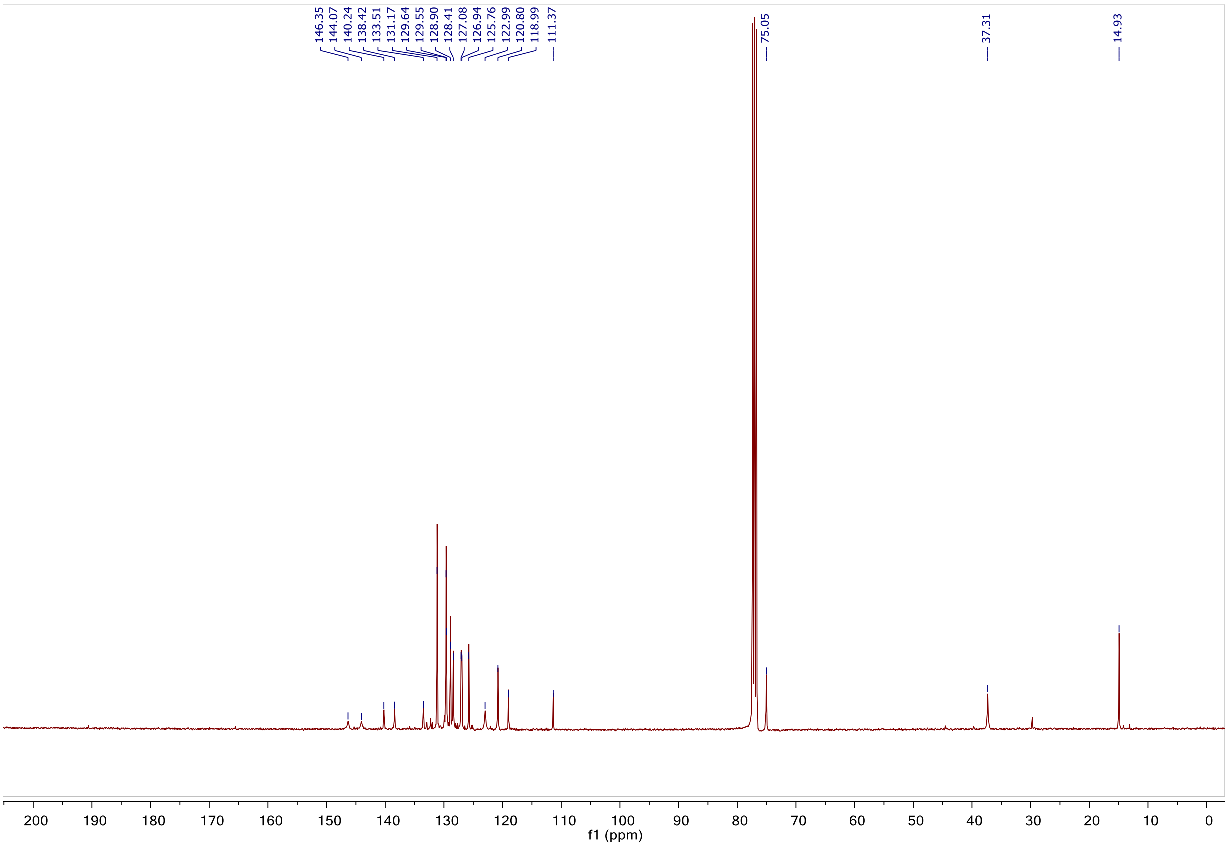
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	6.105	381337	18.40	50043
2	PDA 234.0 nm	7.600	1691505	81.60	175532

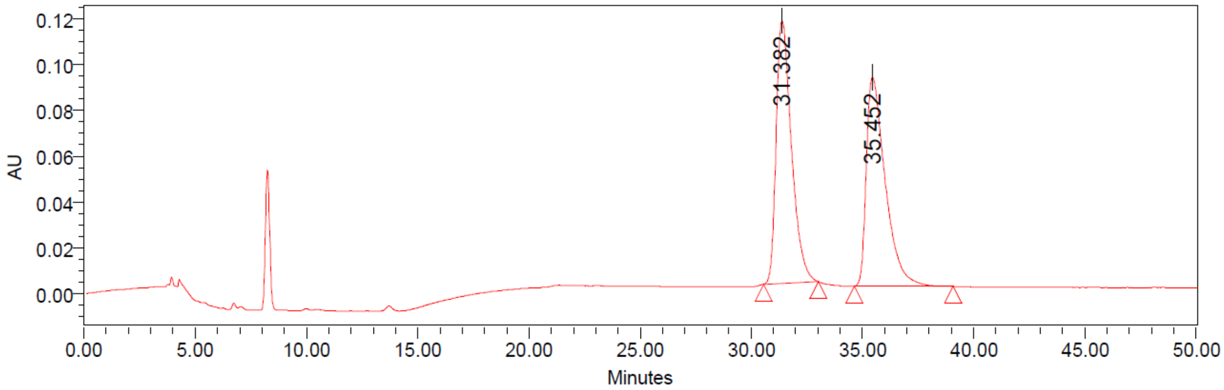
^{1}H NMR (400 MHz, $CDCl_3$) of **2An**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2An**:



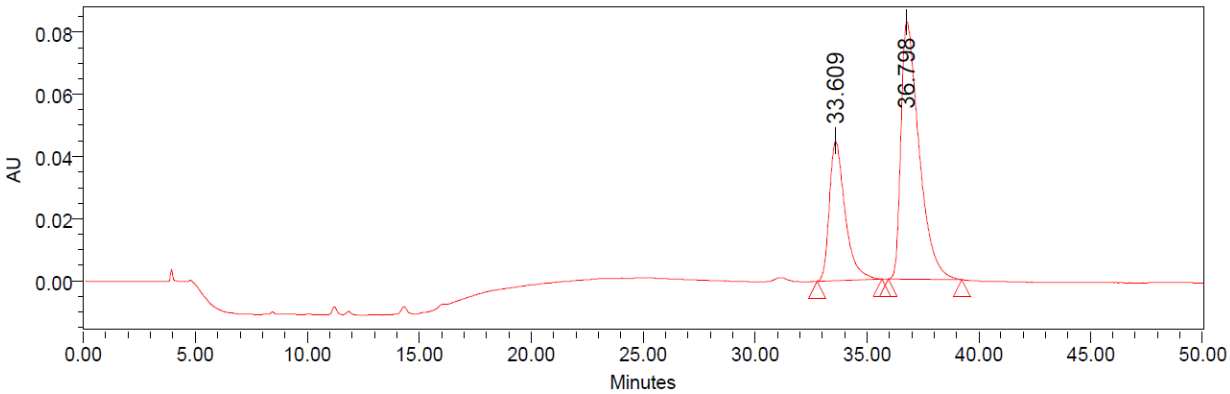
Racemic sample of 2An: IB column, *n*-Hex/*i*-PrOH 98:2, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	31.382	5486584	50.45	114833
2	PDA 234.0 nm	35.452	5387654	49.55	91089

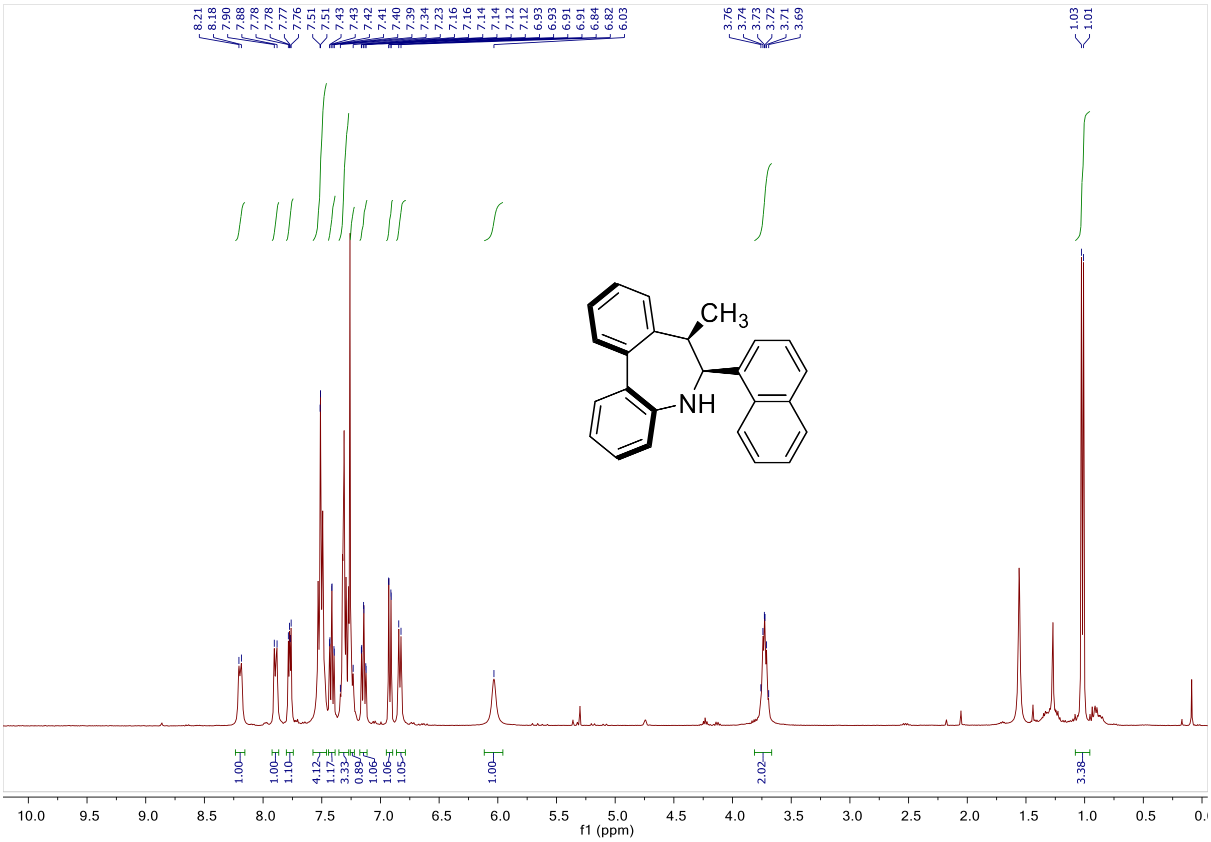
Enantioenriched sample of (S_a,6*S*,7*R*)-2An:



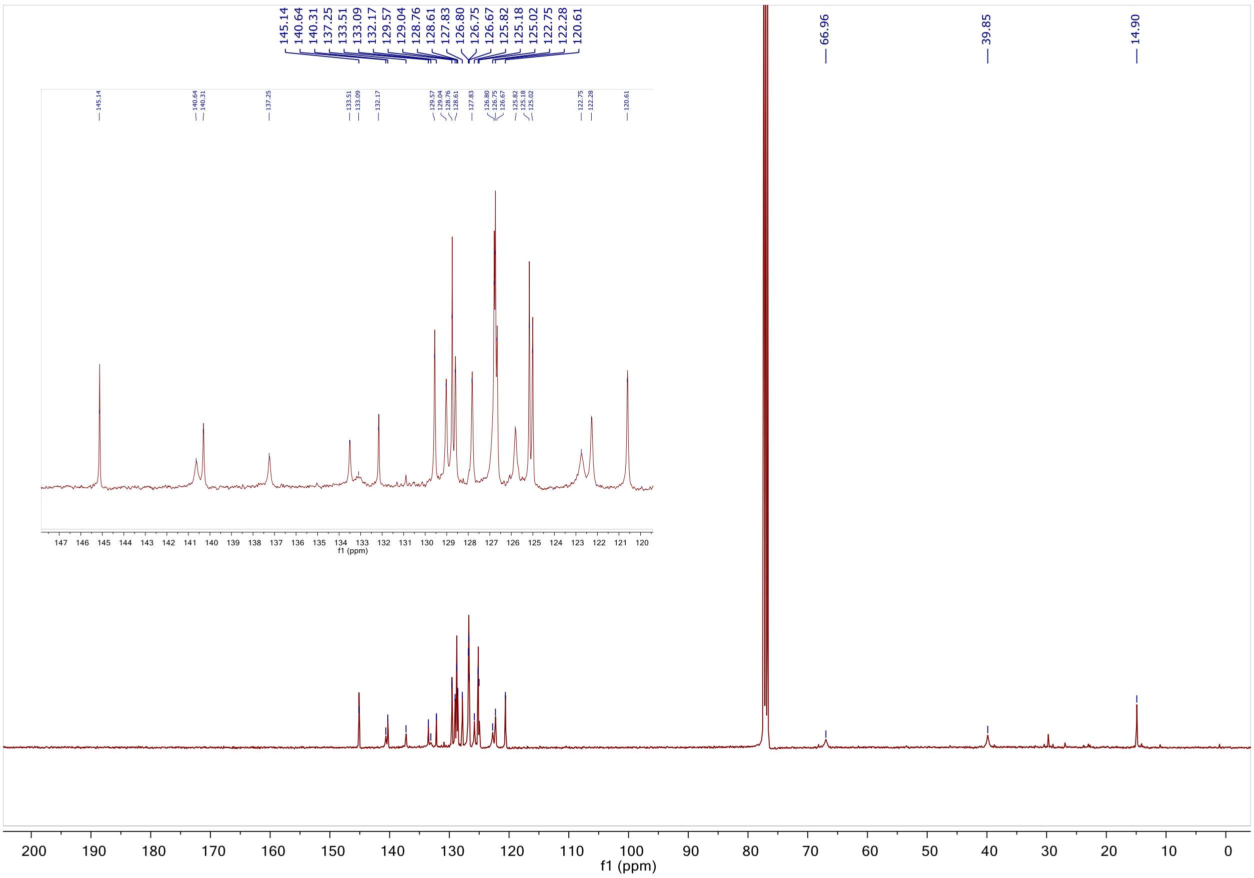
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	33.609	2183704	31.88	44811
2	PDA 234.0 nm	36.798	4666538	68.12	82829

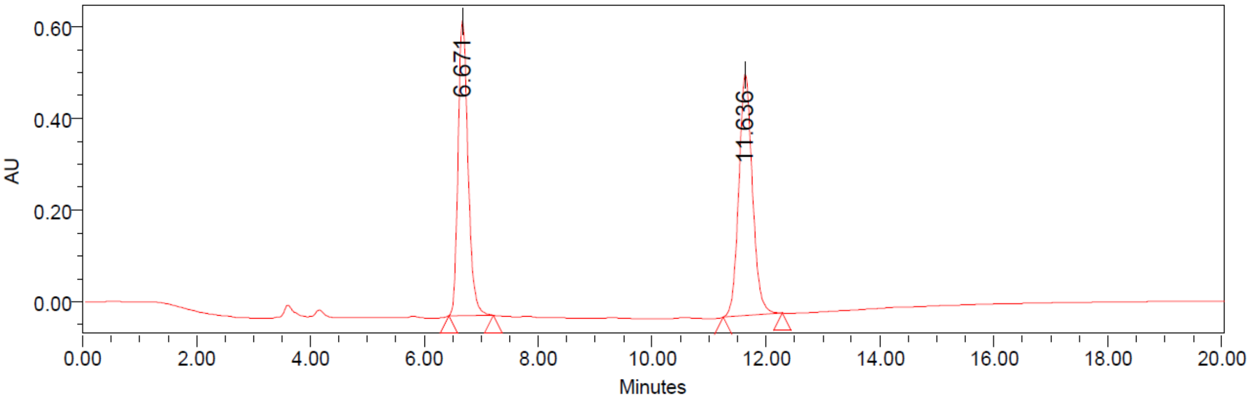
^{1}H NMR (400 MHz, $CDCl_3$) of **2Ao**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Ao**:



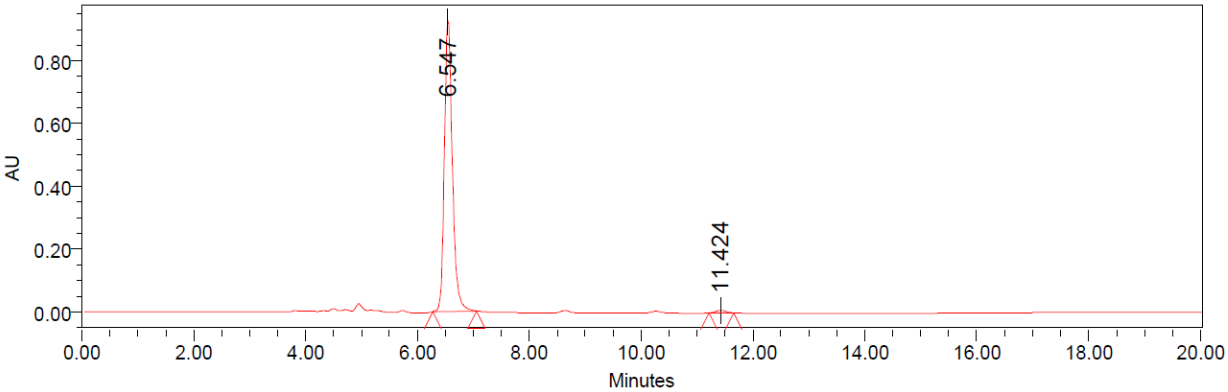
Racemic sample of 2Ao: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 219.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 219.7 nm	6.671	7795156	47.06	644867
2	PDA 219.7 nm	11.636	8767993	52.94	525993

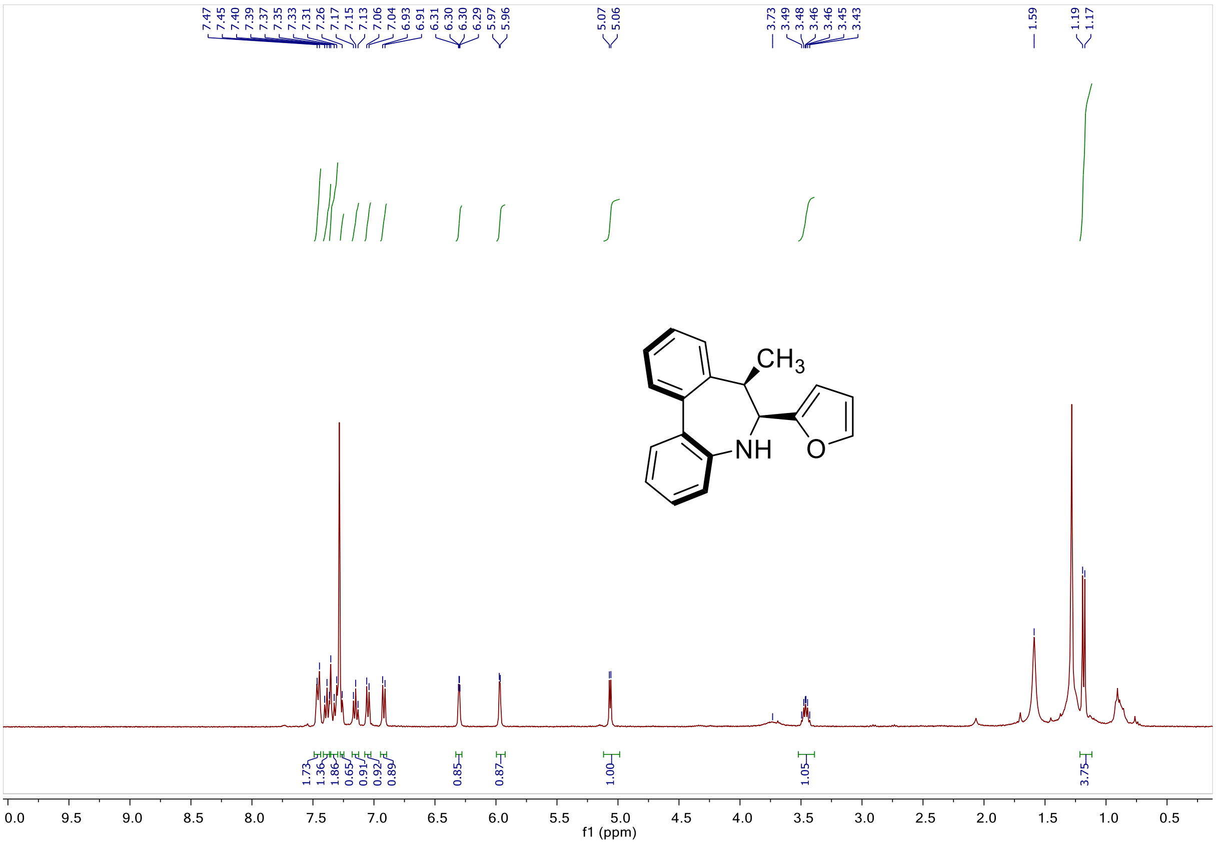
Enantioenriched sample of (S_a,6S,7R)-2Ao:



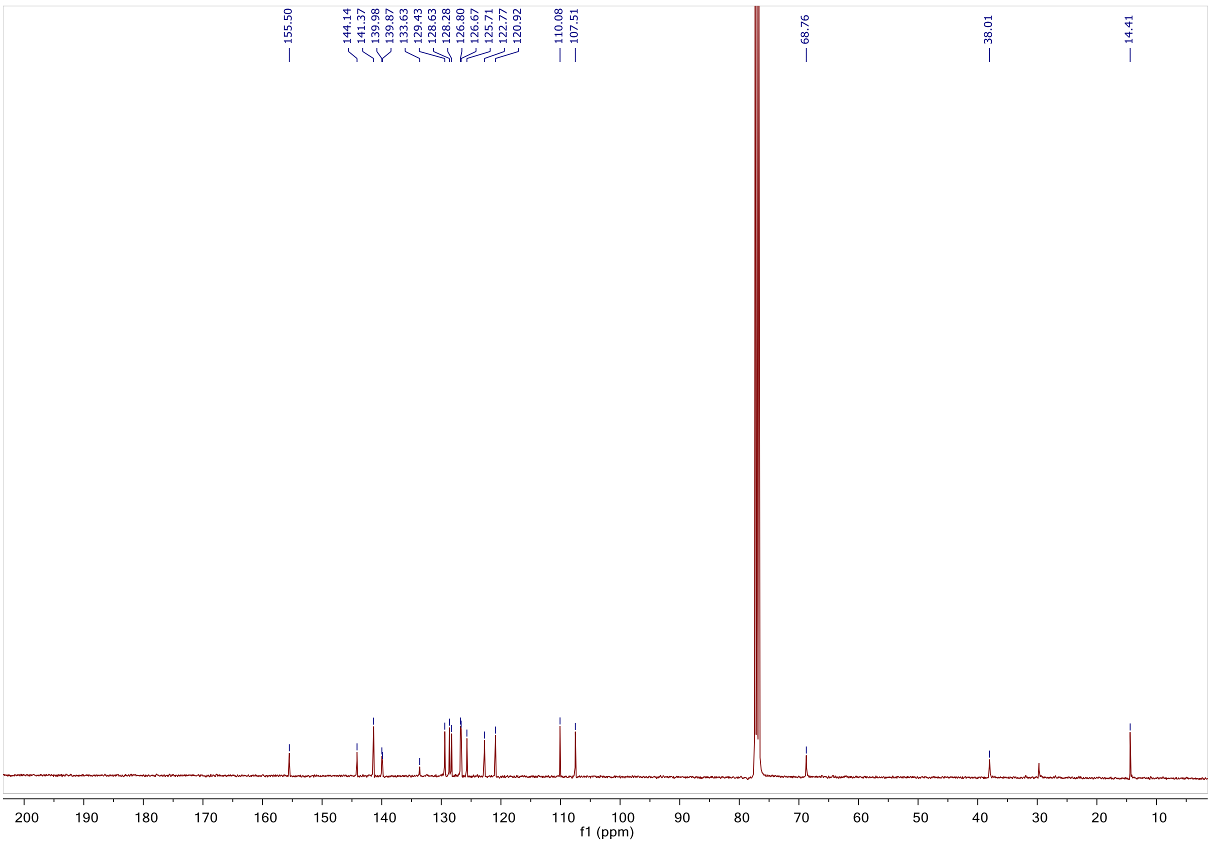
Processed Channel: PDA 245.8 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 245.8 nm	6.547	9173026	98.88	931507
2	PDA 245.8 nm	11.424	104343	1.12	7919

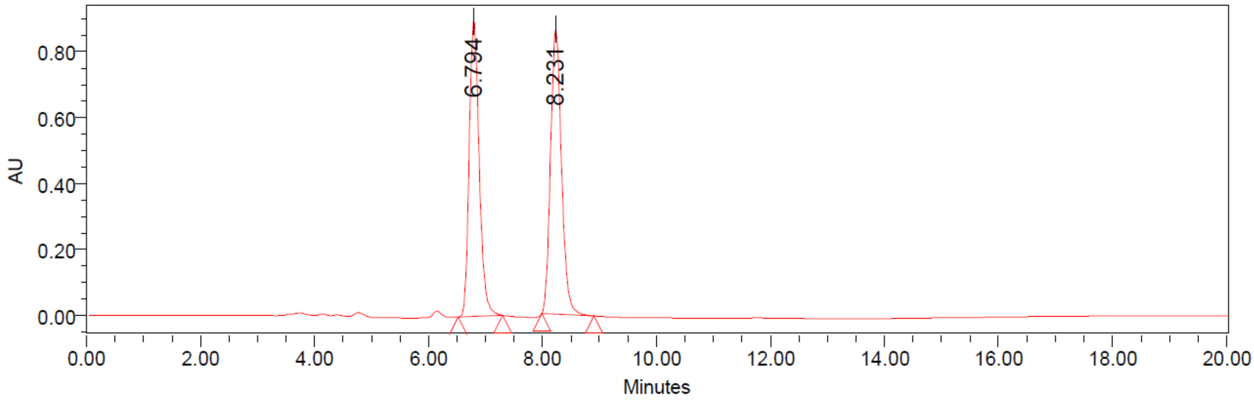
^{1}H NMR (400 MHz, $CDCl_3$) of **2Ap**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Ap**:



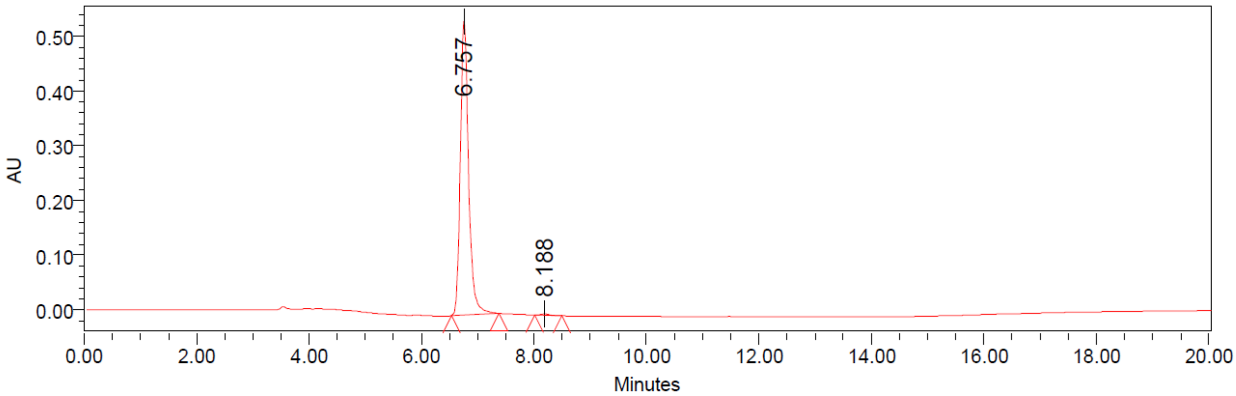
Racemic sample of 2Ap: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 235.3 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.3 nm	6.794	10916973	48.66	900090
2	PDA 235.3 nm	8.231	11517262	51.34	866490

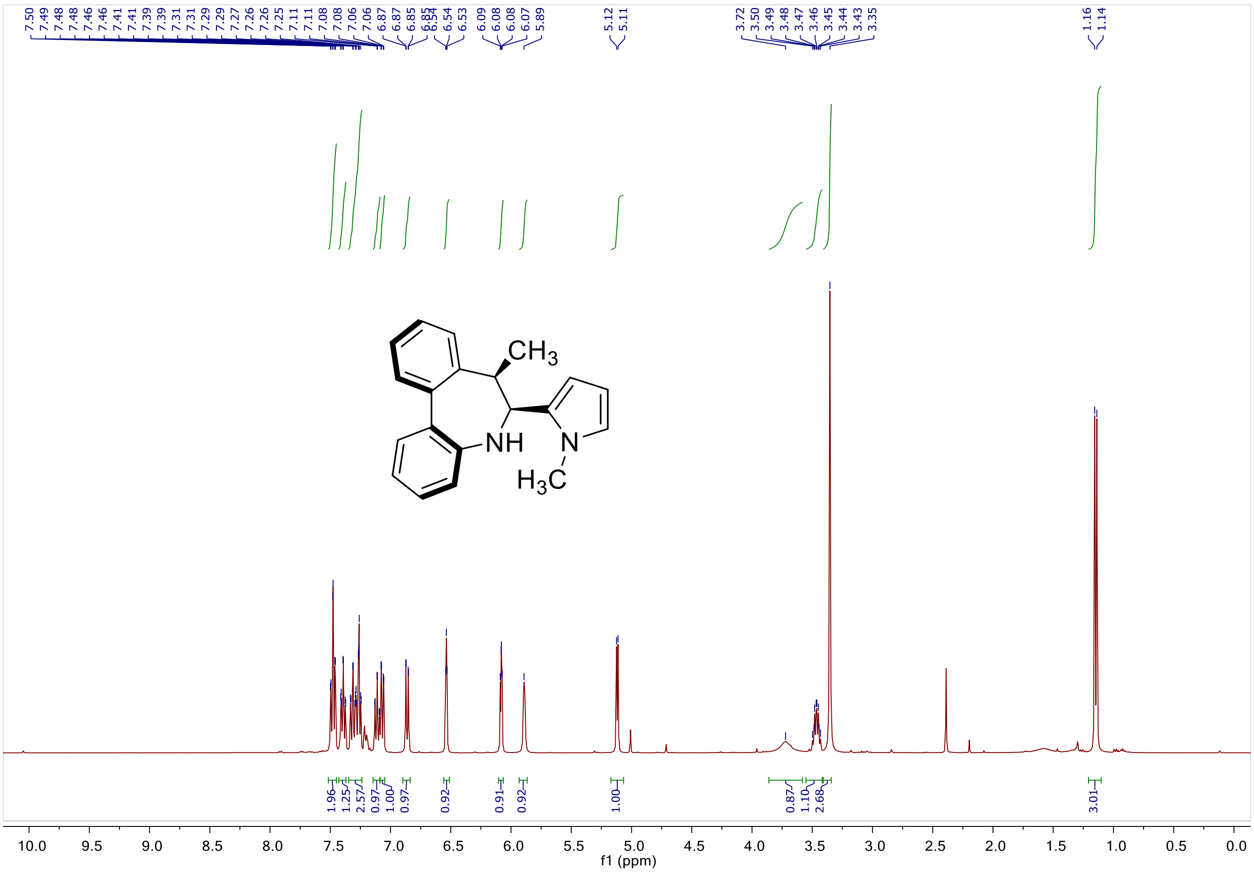
Enantioenriched sample of (S_a,6*S*,7*R*)-2Ap:



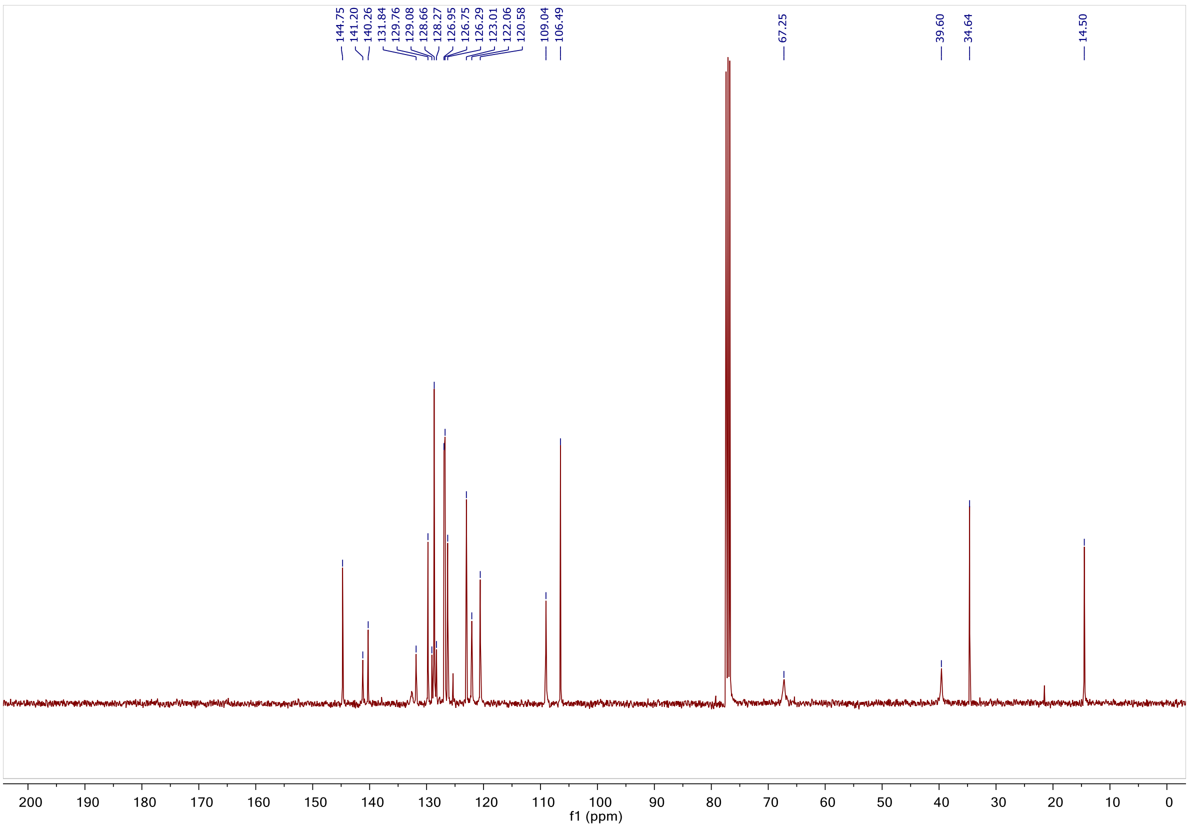
Processed Channel: PDA 233.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.0 nm	6.757	5485491	99.53	541464
2	PDA 233.0 nm	8.188	25786	0.47	2458

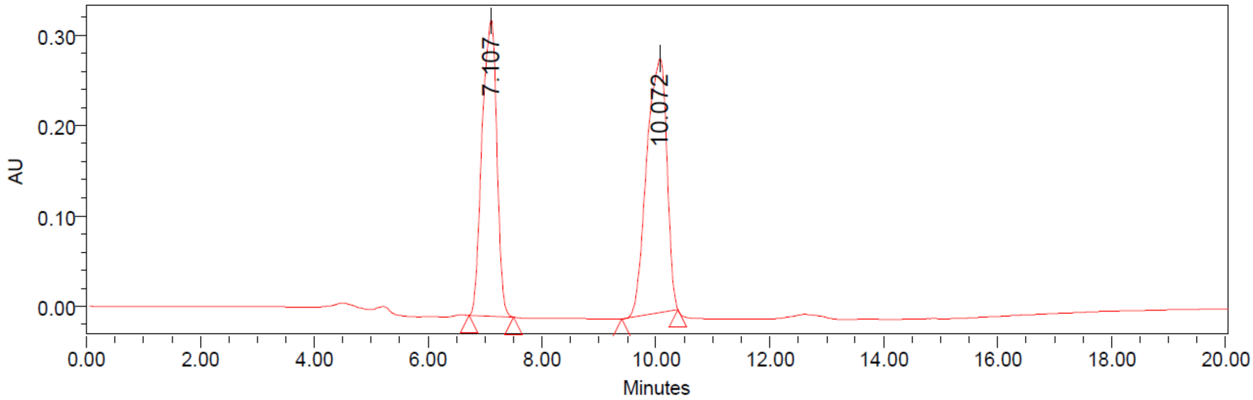
^{1}H NMR (400 MHz, $CDCl_3$) of **2Aq**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Aq**:



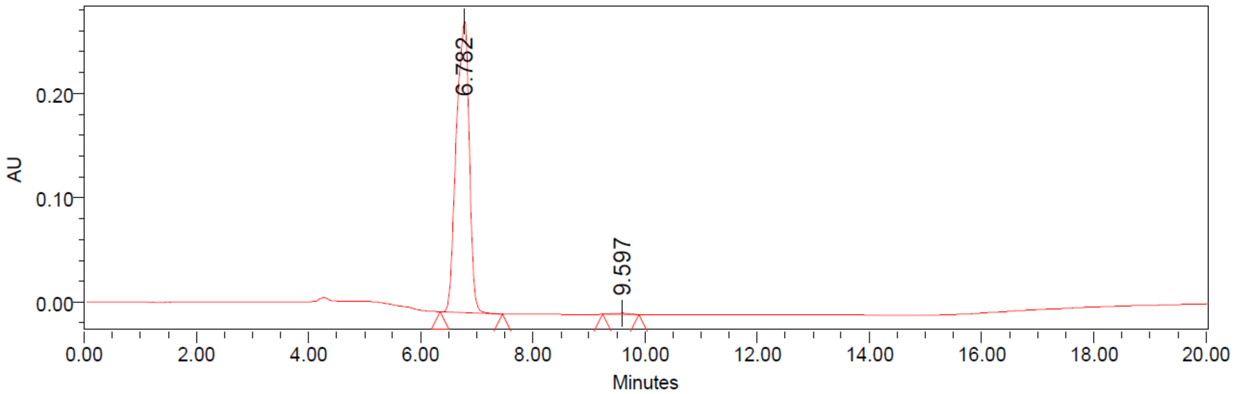
Racemic sample of 2Aq: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 232.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 232.0 nm	7.107	5866723	45.95	328398
2	PDA 232.0 nm	10.072	6901892	54.05	281246

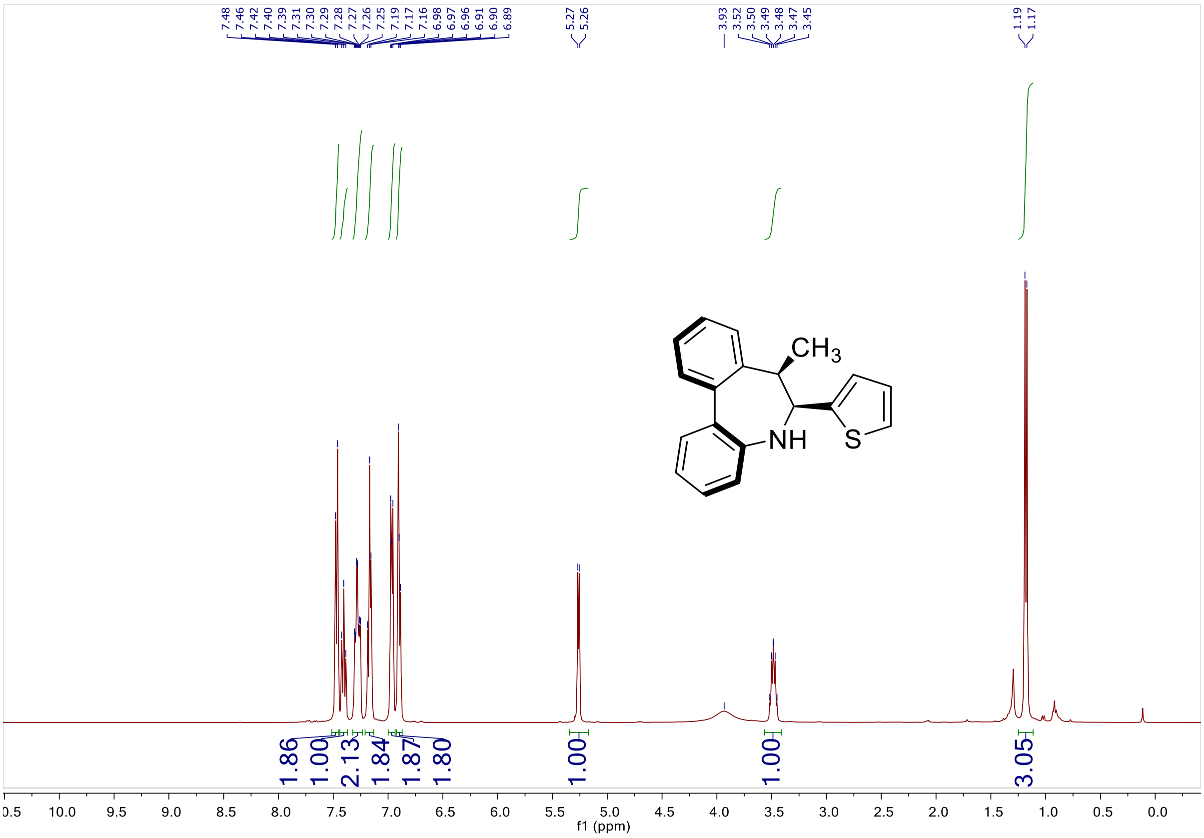
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-2Aq:



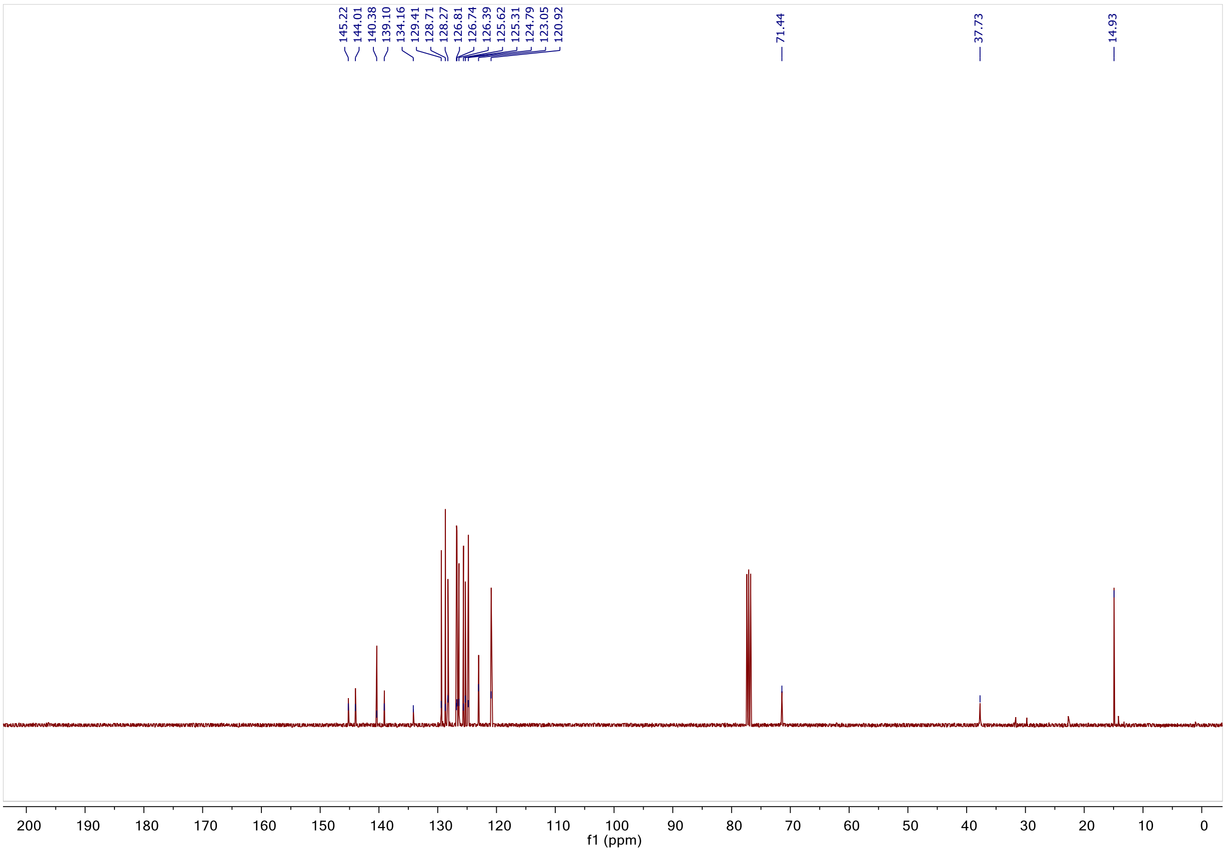
Processed Channel: PDA 233.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.0 nm	6.782	4471491	99.48	279358
2	PDA 233.0 nm	9.597	23260	0.52	1153

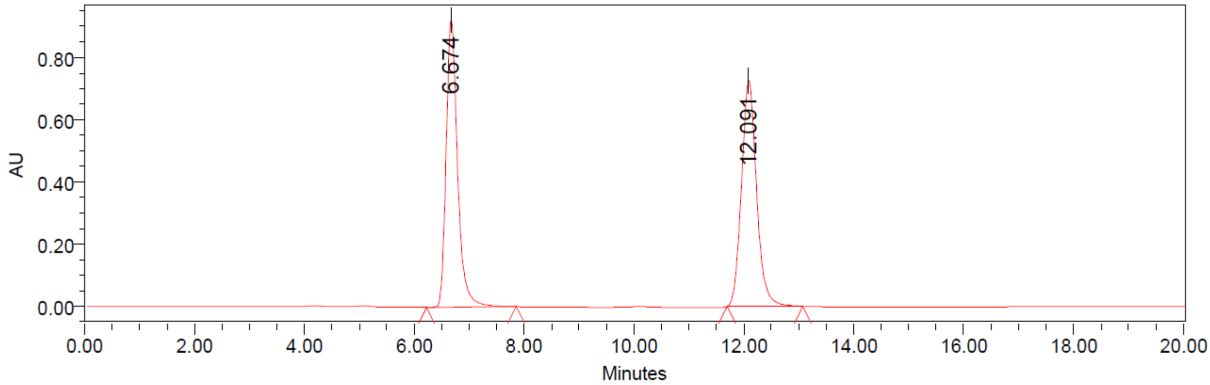
^{1}**H NMR** (400 MHz, $CDCl_3$) of **2Ar**:



^{13}**C NMR** (100 MHz, $CDCl_3$) of **2Ar**:



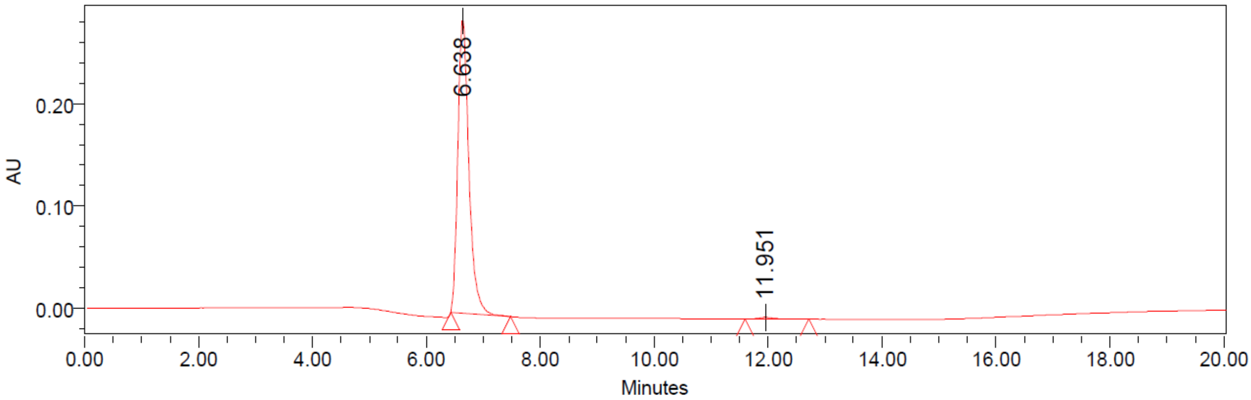
Racemic sample of 2Ar: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 246.8 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.8 nm	6.674	13325882	49.02	924101
2	PDA 246.8 nm	12.091	13859483	50.98	725947

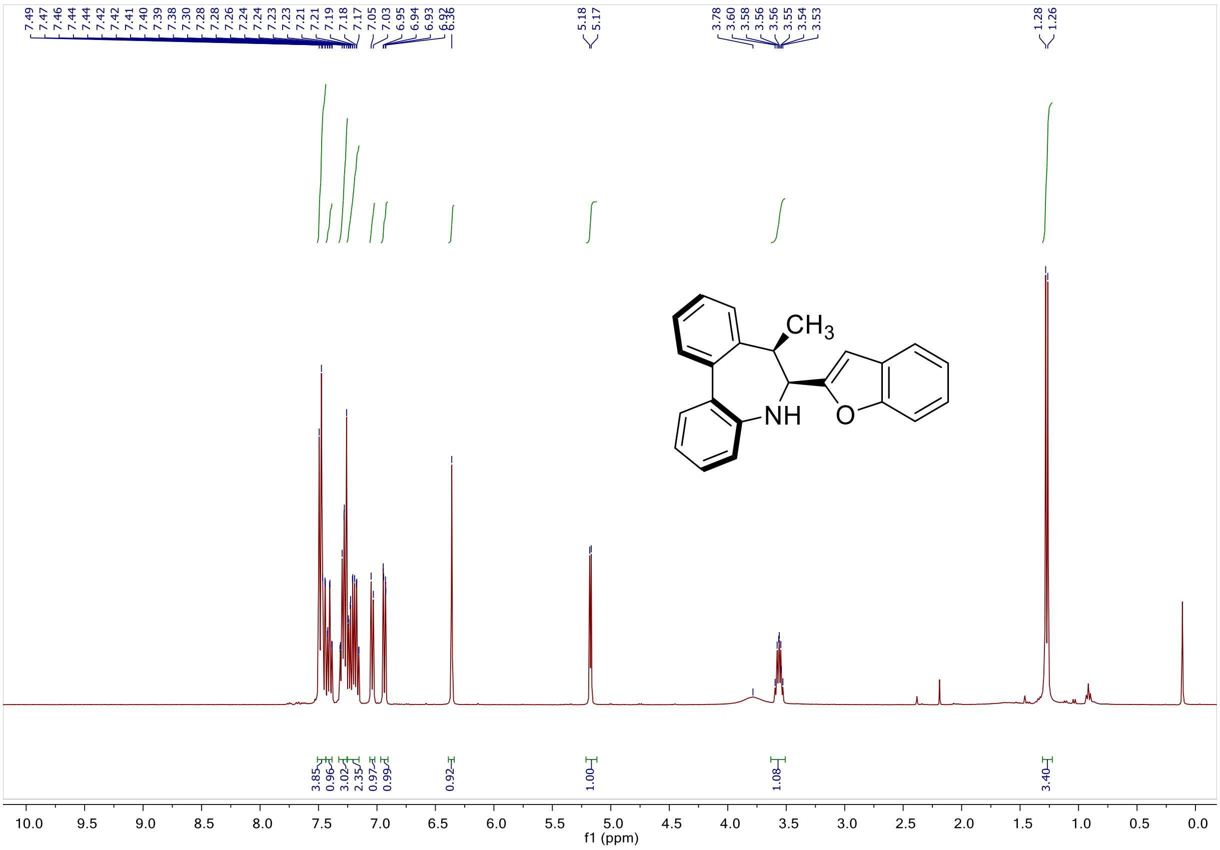
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-2Ar:



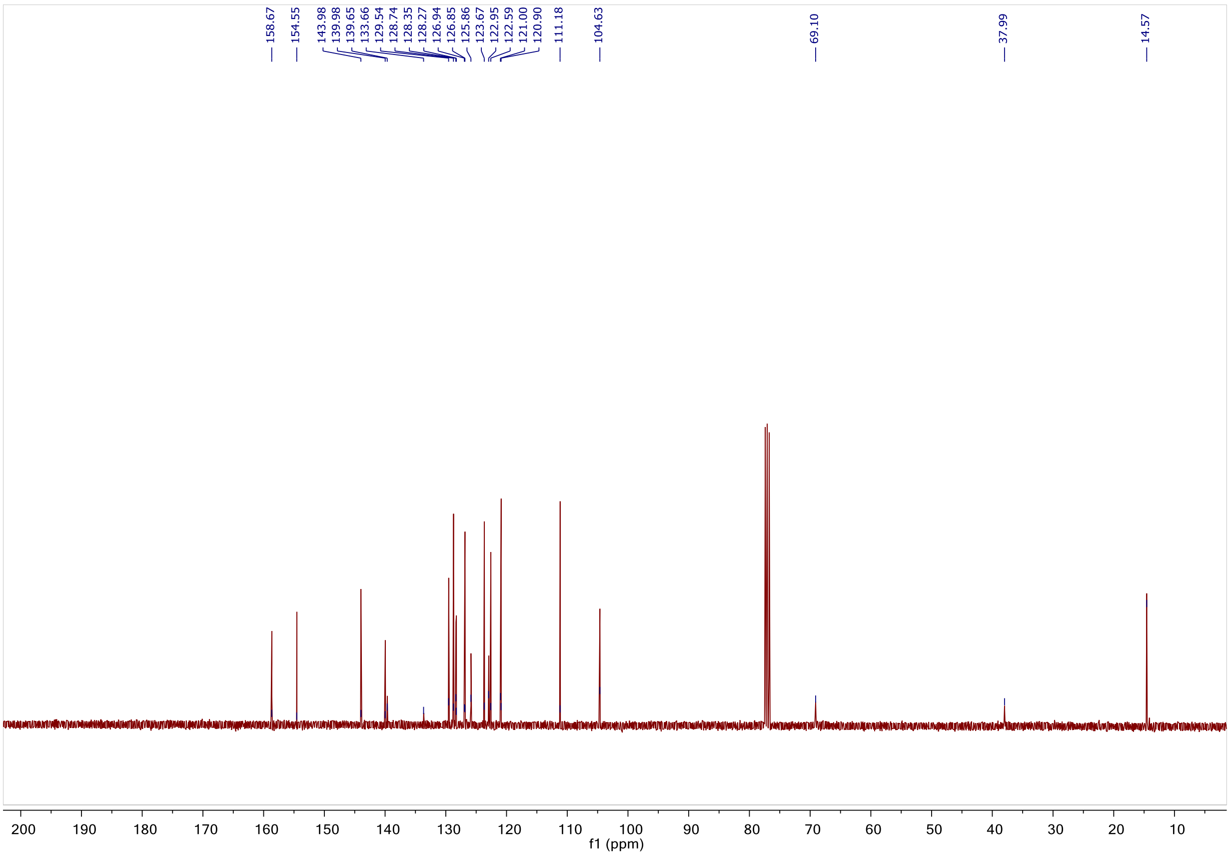
Processed Channel: PDA 235.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.0 nm	6.638	3843886	99.19	287177
2	PDA 235.0 nm	11.951	31545	0.81	1674

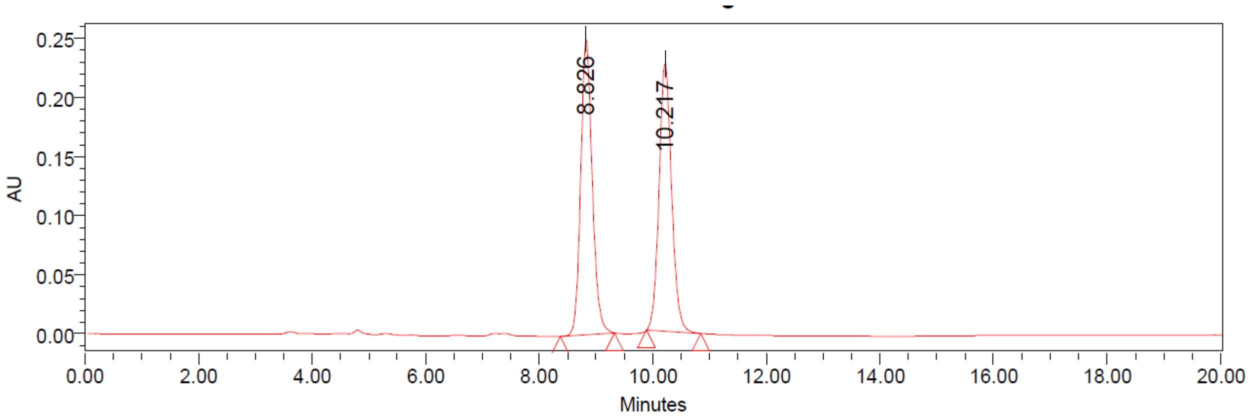
^{1}H NMR (400 MHz, $CDCl_3$) of **2As**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2As**:



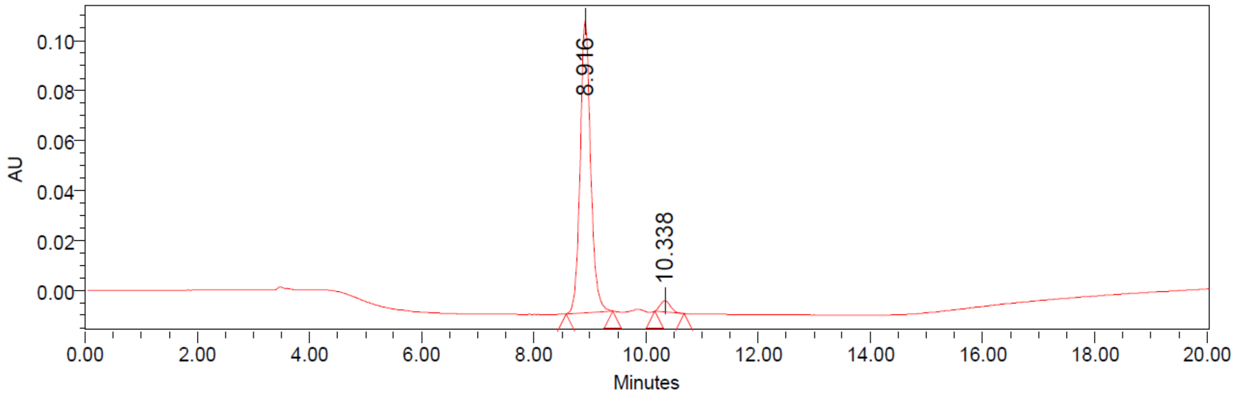
Racemic sample of 2As: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 255.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 255.7 nm	8.826	3505343	50.14	250219
2	PDA 255.7 nm	10.217	3486338	49.86	226975

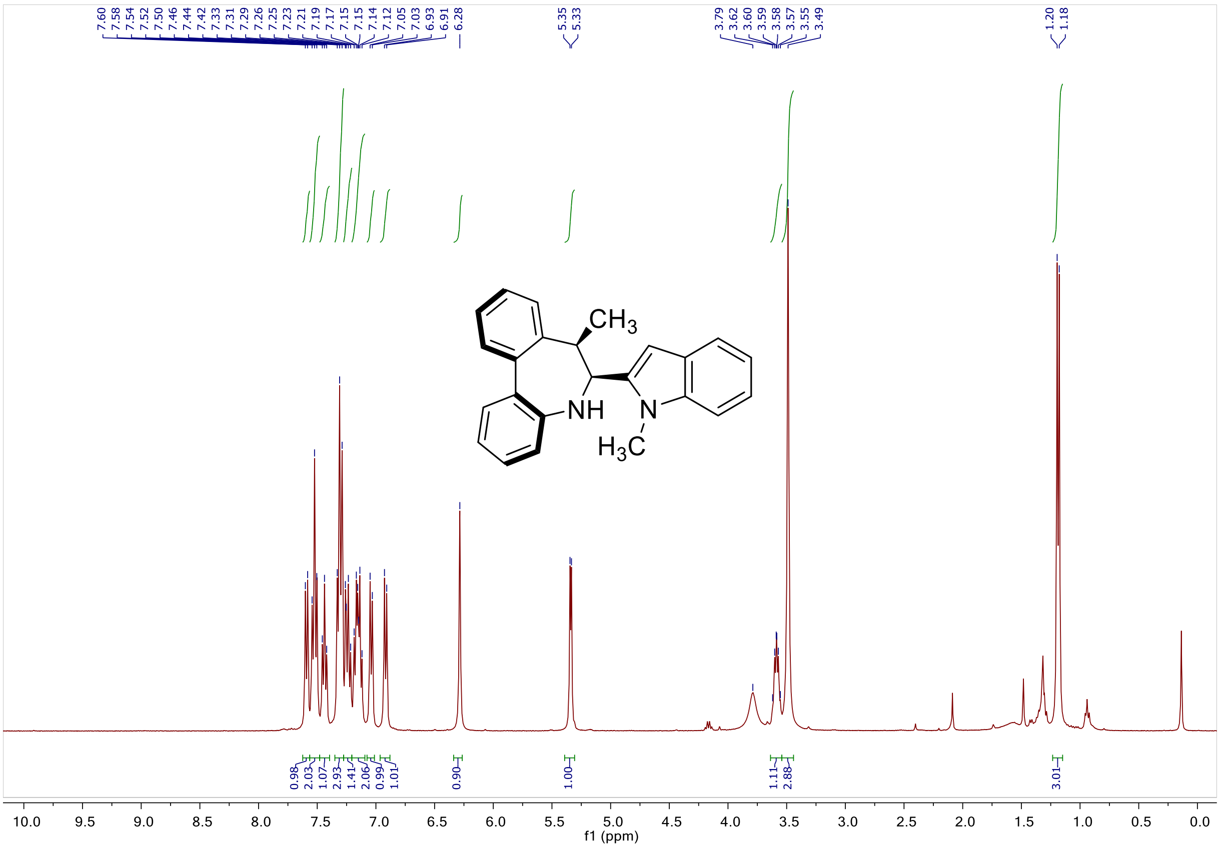
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-2As:



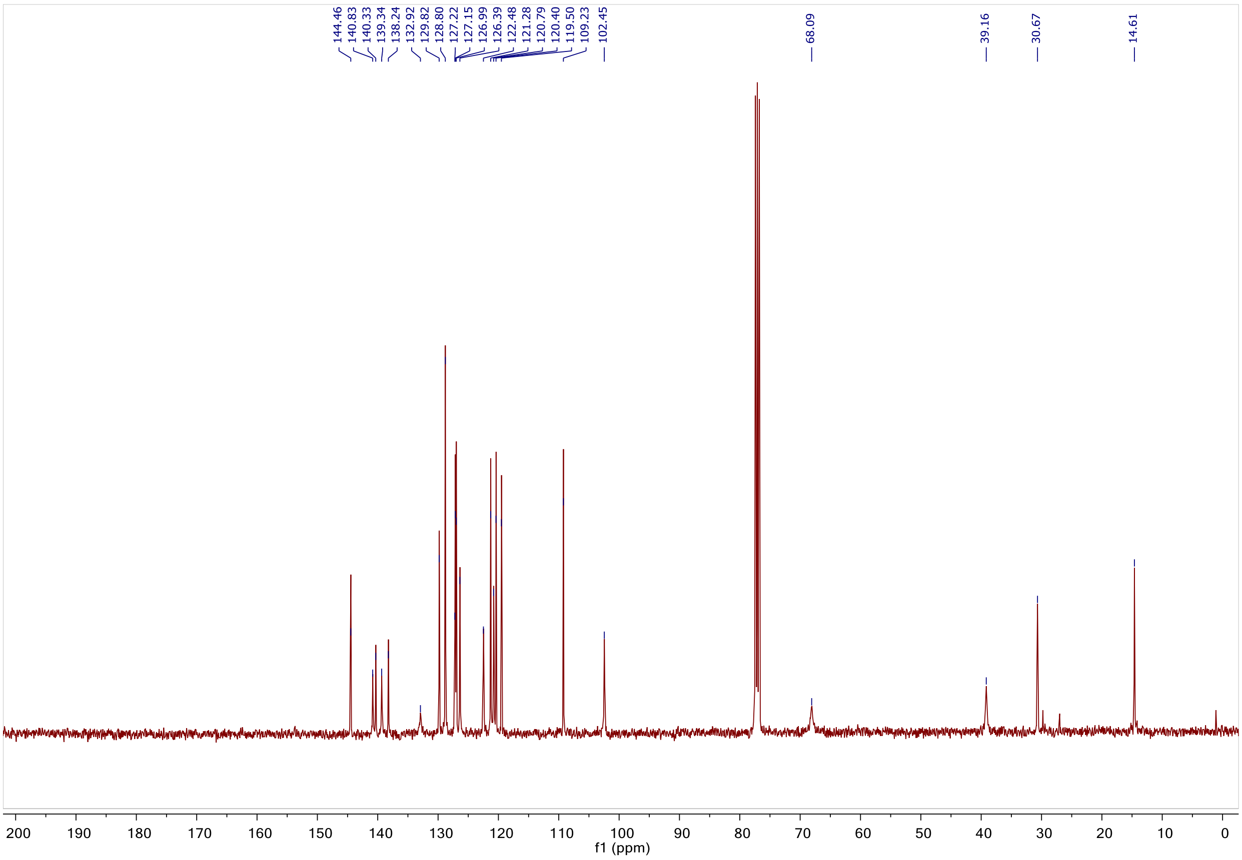
Processed Channel: PDA 236.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 236.0 nm	8.916	1518131	96.53	117018
2	PDA 236.0 nm	10.338	54605	3.47	4371

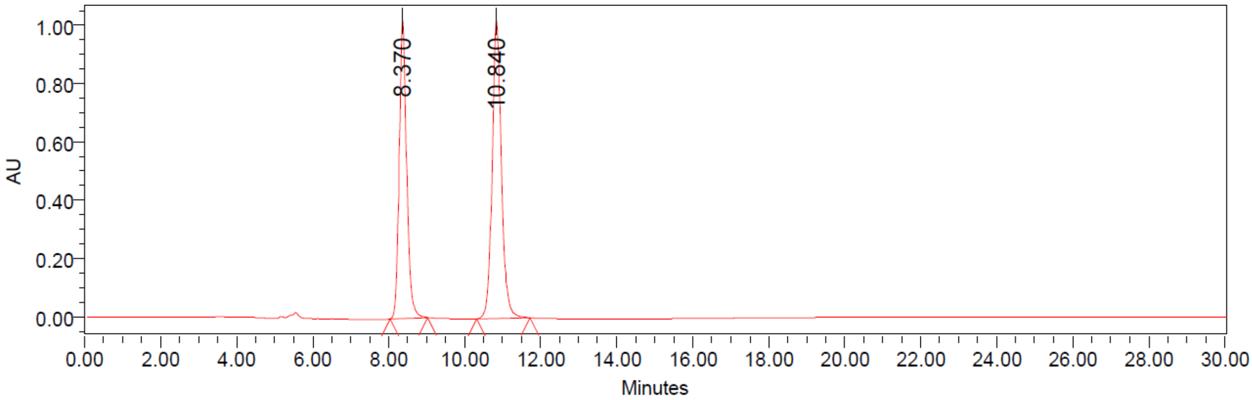
^{1}H NMR (400 MHz, $CDCl_3$) of **2At**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2At**:



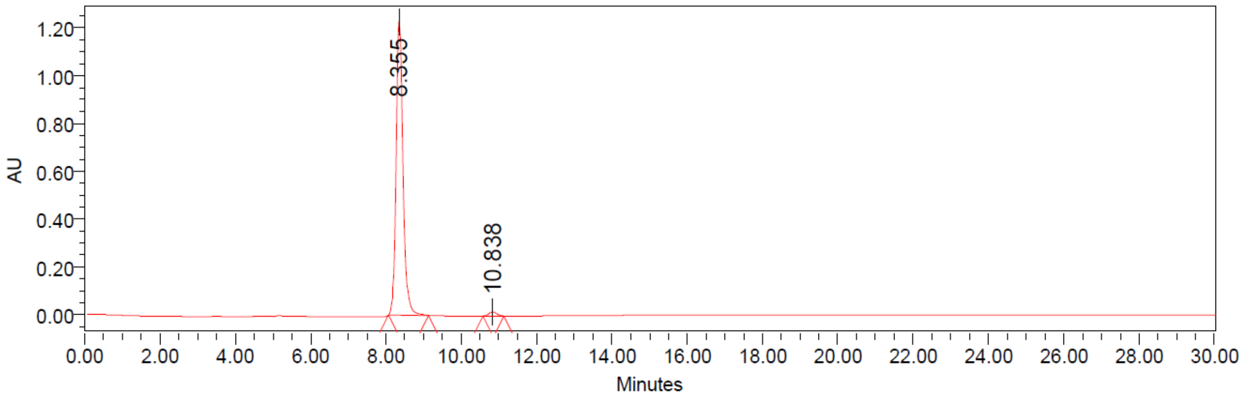
Racemic sample of 2At: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 238.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 238.7 nm	8.370	13887583	44.51	1022750
2	PDA 238.7 nm	10.840	17310472	55.49	1020348

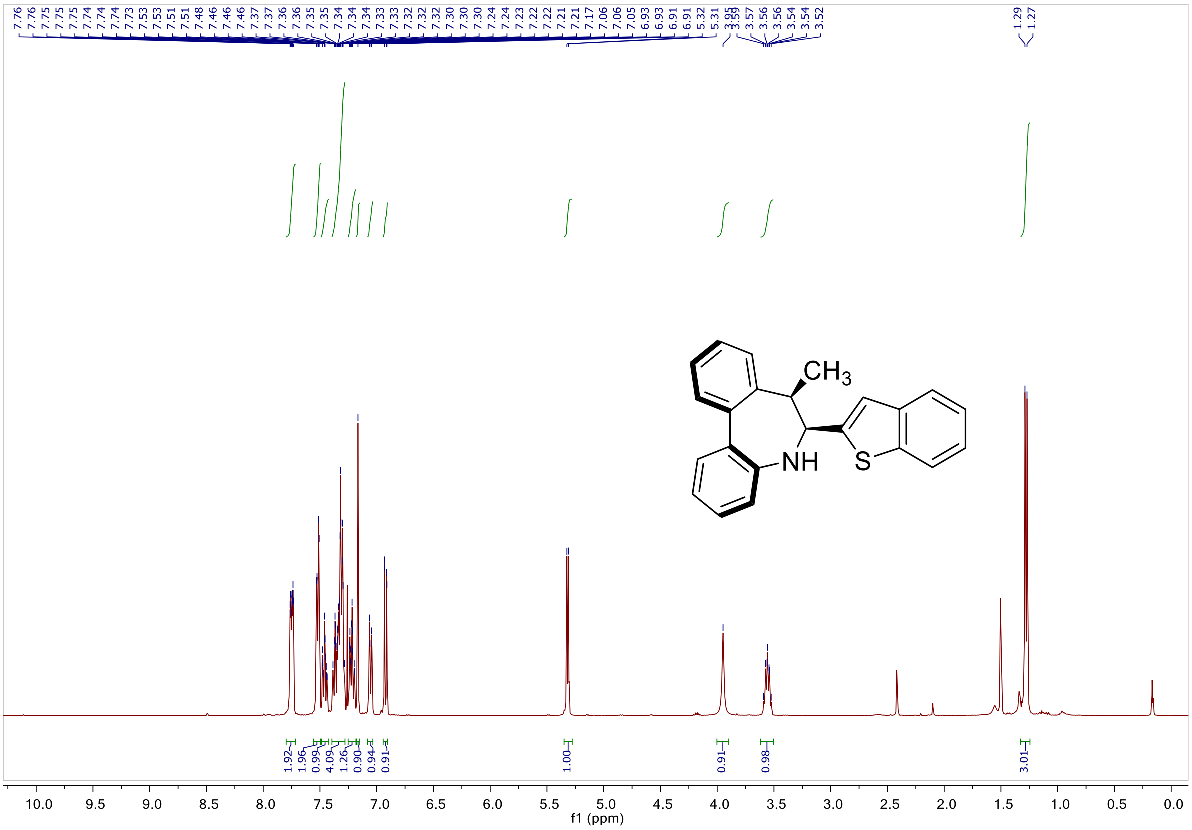
Enantioenriched sample of (*S*a,6*S*,7*R*)-2At:



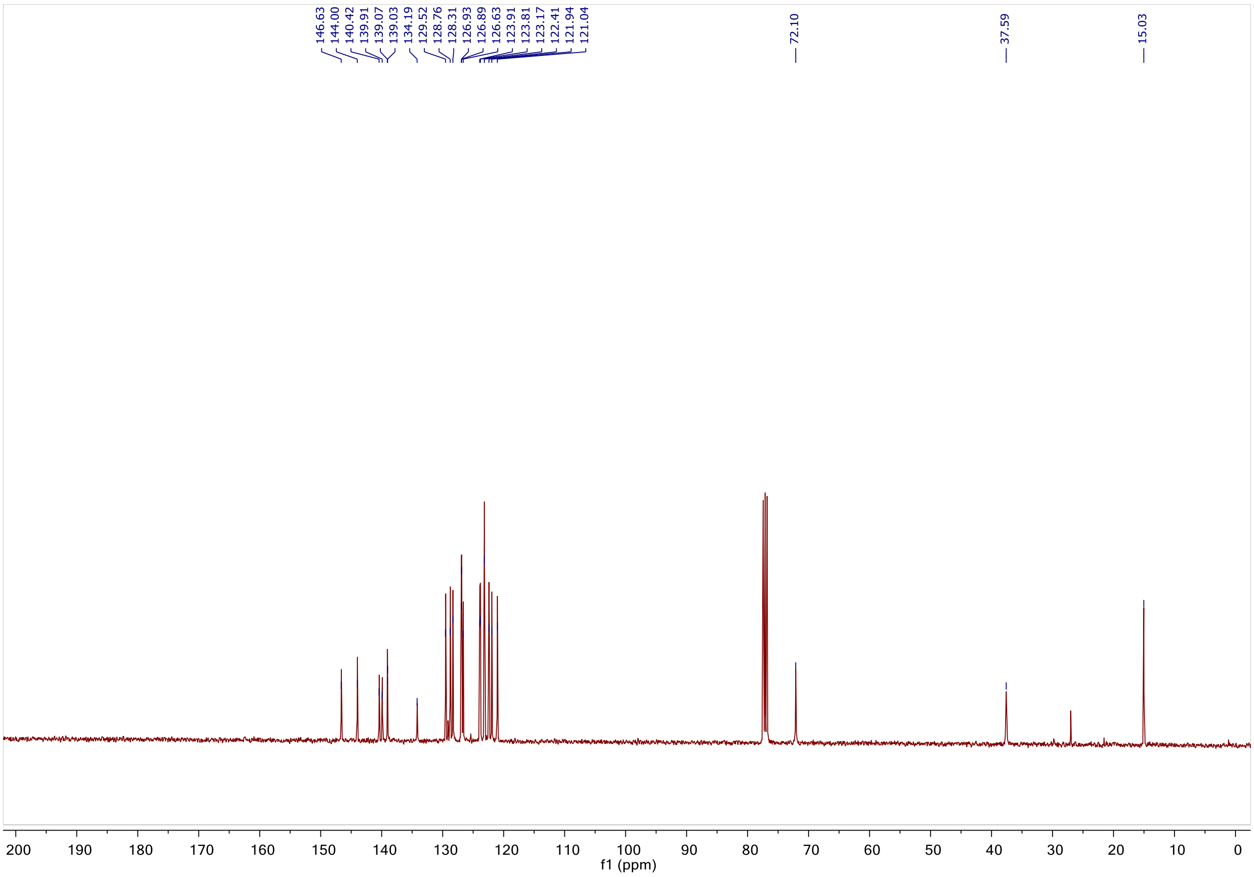
Processed Channel: PDA 238.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 238.7 nm	8.355	15584108	98.47	1230793
2	PDA 238.7 nm	10.838	242523	1.53	17085

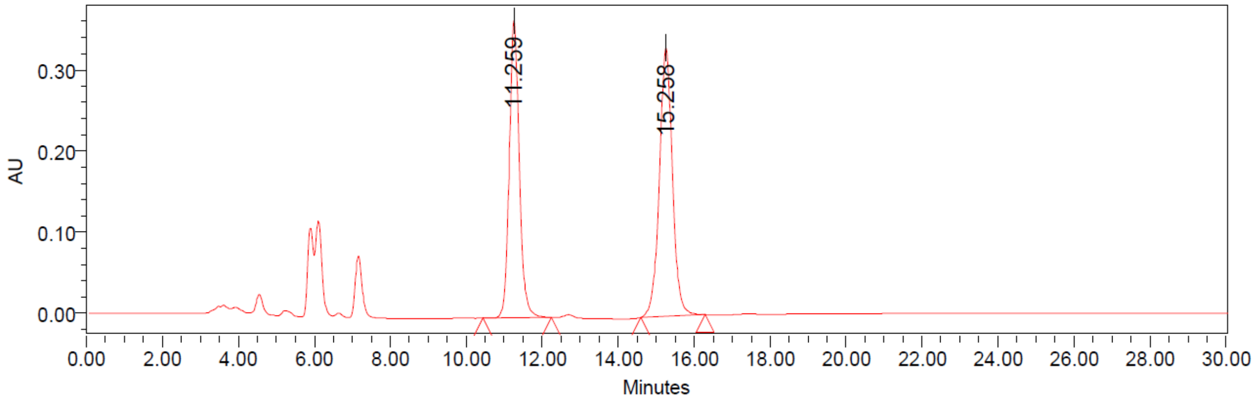
^{1}H NMR (400 MHz, $CDCl_3$) of **2Au**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Au**:



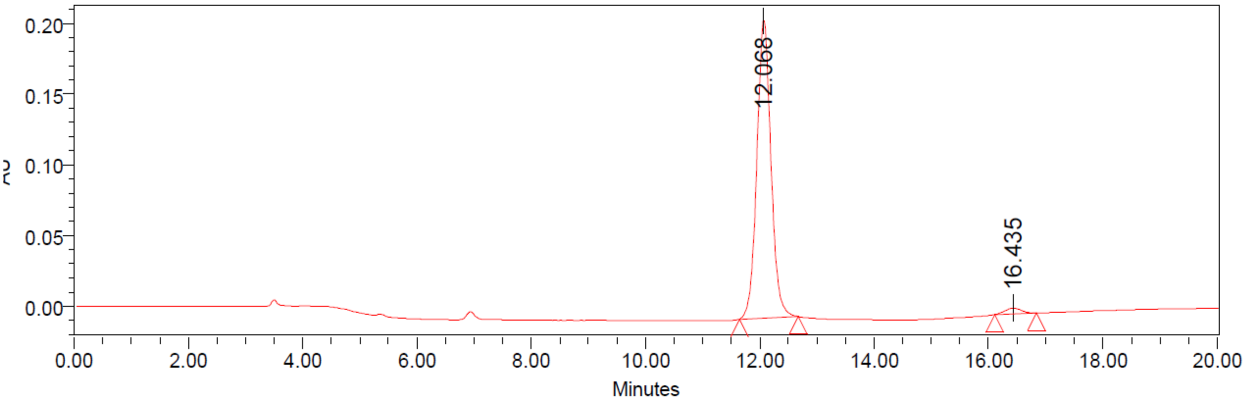
Racemic sample of 2Au: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 239.5 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 239.5 nm	11.259	6717687	45.93	366738
2	PDA 239.5 nm	15.258	7907553	54.07	331495

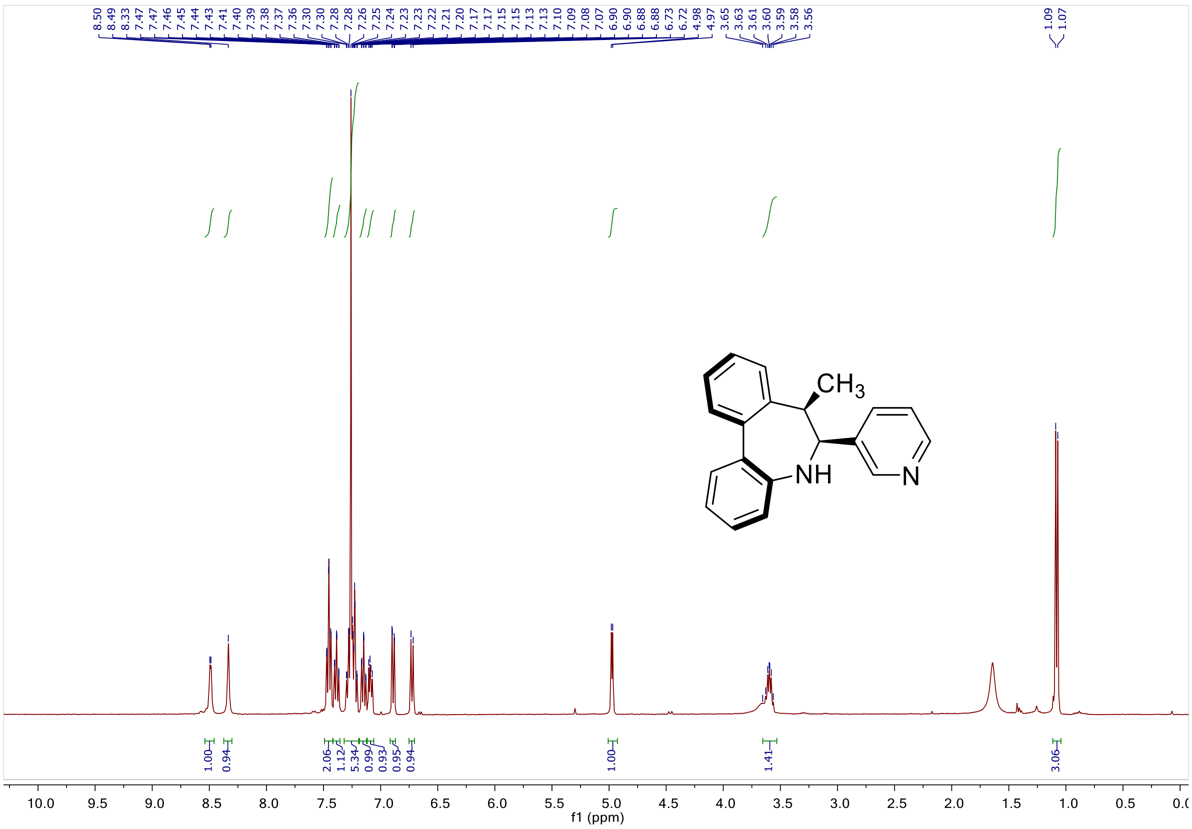
Enantioenriched sample of (S_a,6*S*,7*R*)-2Au:



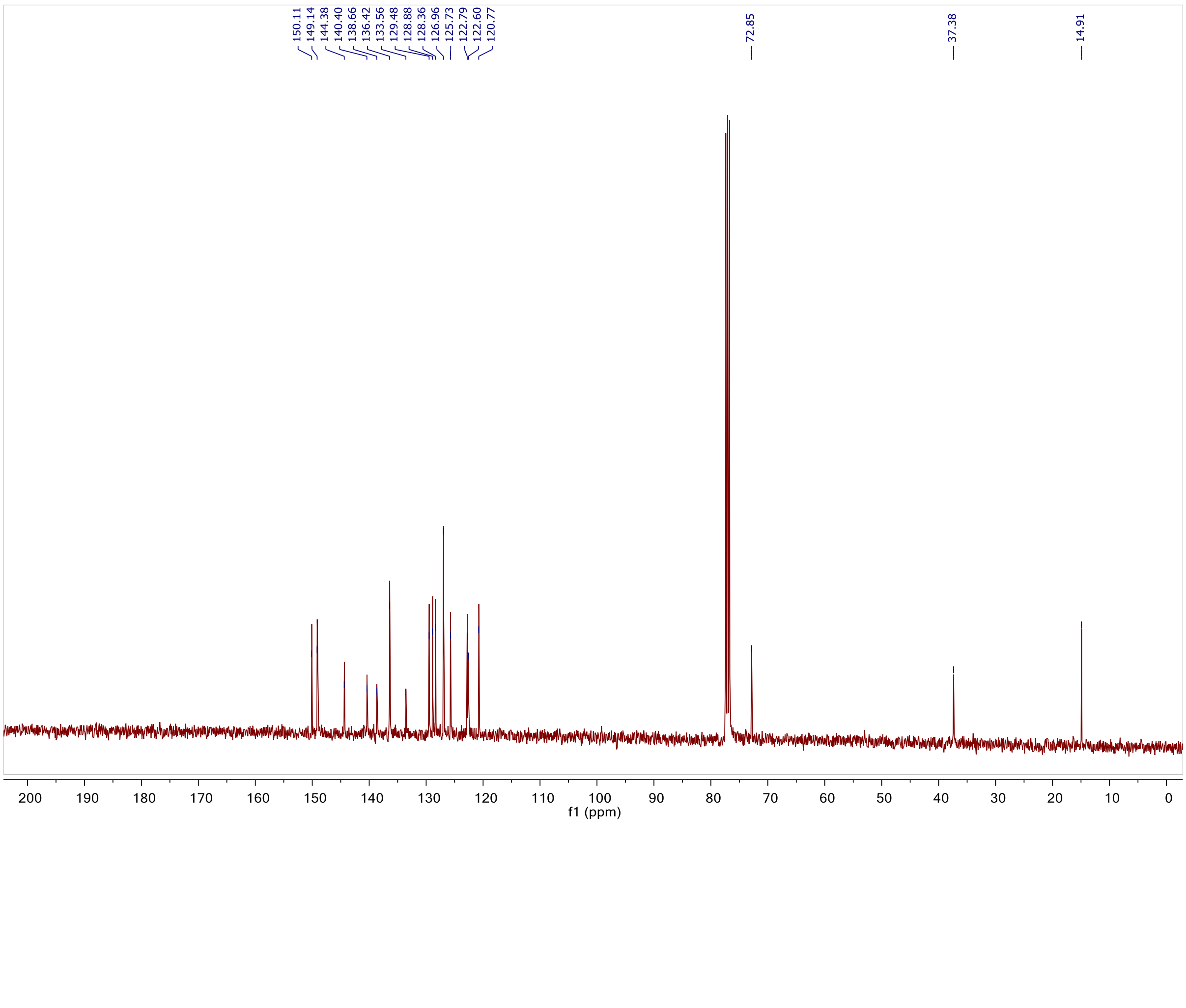
Processed Channel: PDA 236.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 236.0 nm	12.068	3600296	97.80	210776
2	PDA 236.0 nm	16.435	80871	2.20	4008

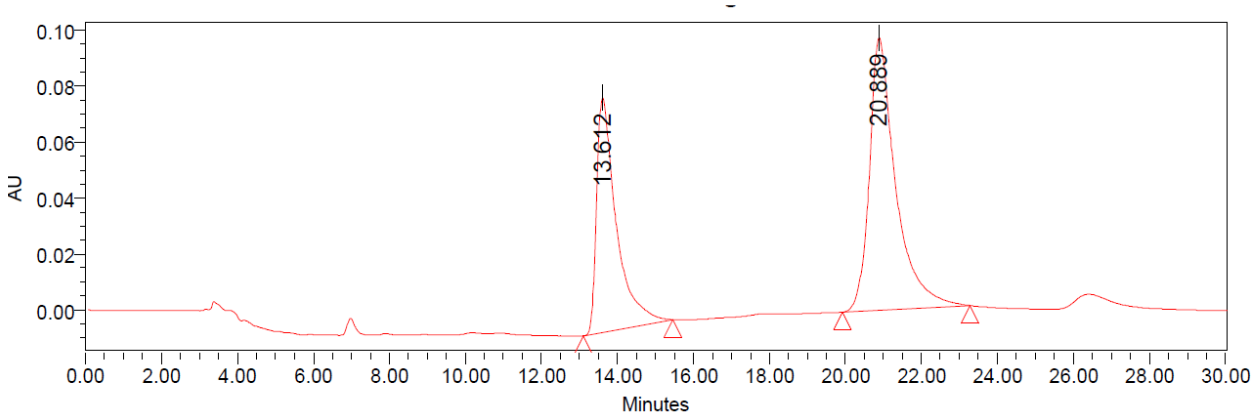
^{1}H NMR (400 MHz, $CDCl_3$) of **2Av**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Av**:



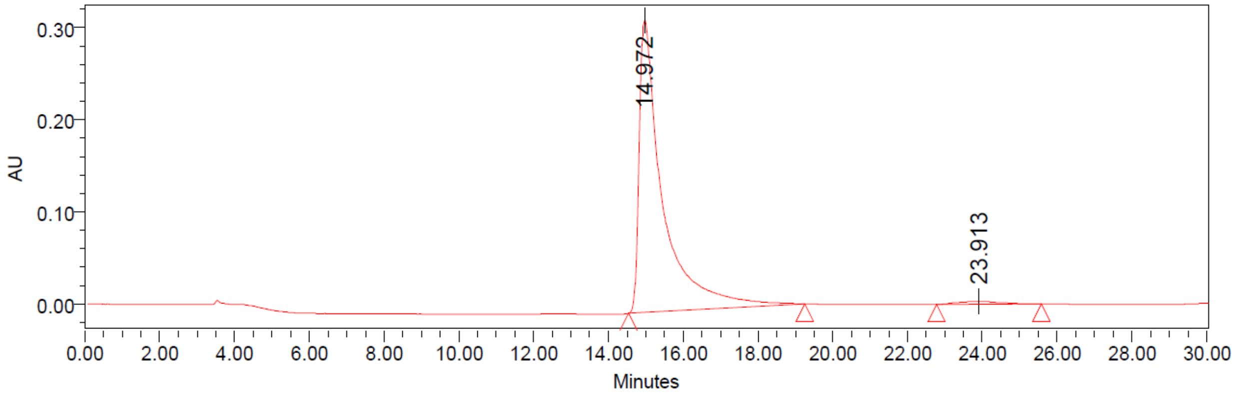
Racemic sample of 2Av: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 237.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 237.0 nm	13.612	3025129	39.23	83853
2	PDA 237.0 nm	20.889	4685645	60.77	97368

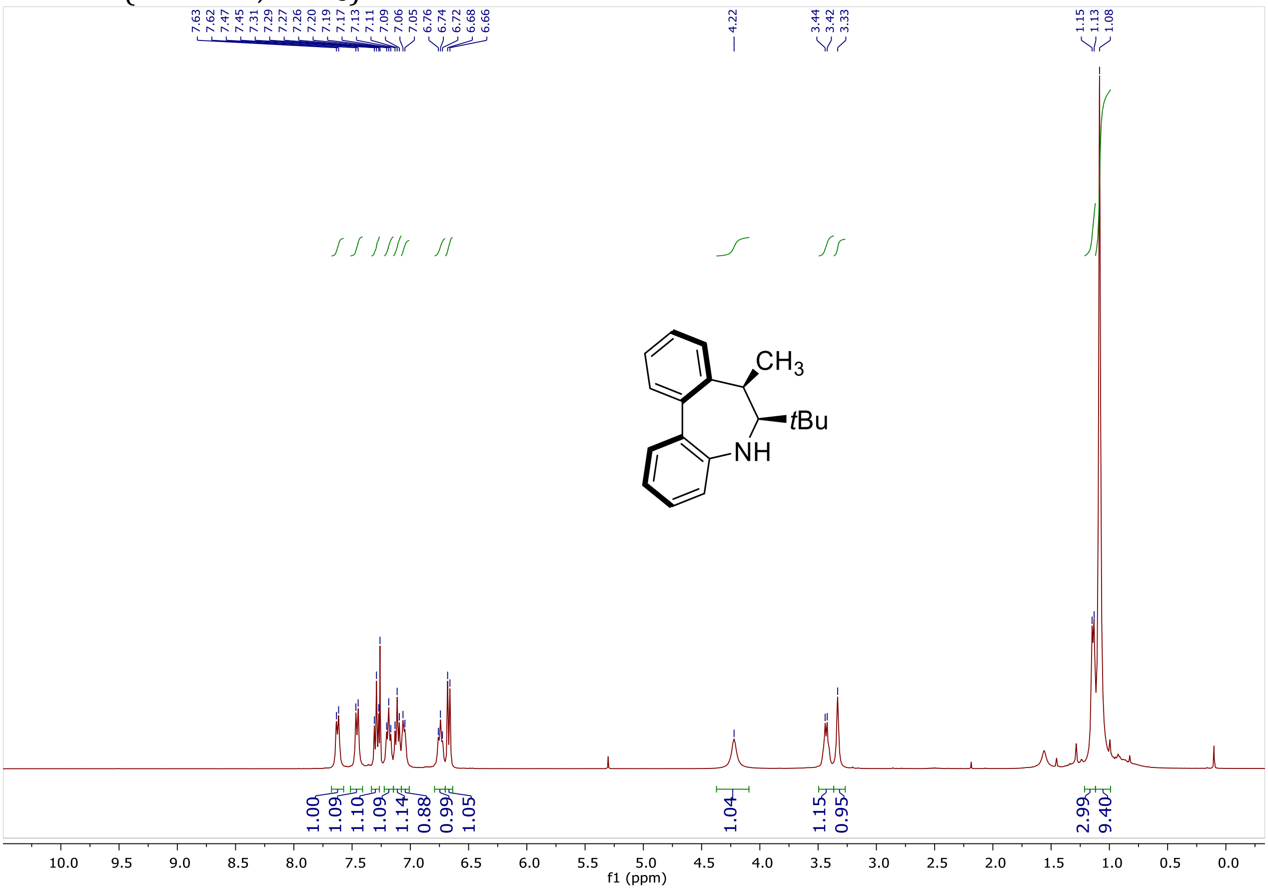
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-2Av:



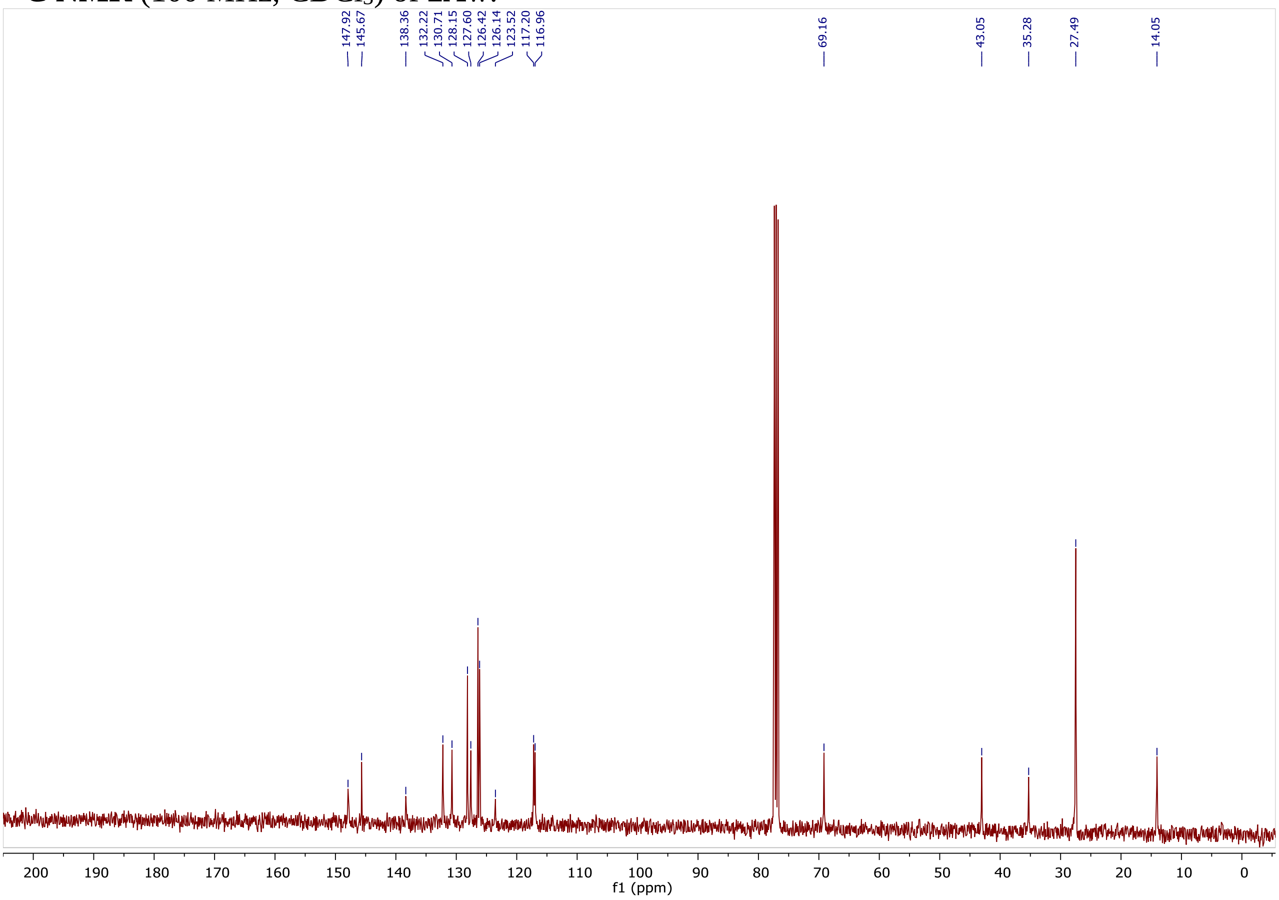
Processed Channel: PDA 235.3 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.3 nm	14.972	13963259	98.30	318008
2	PDA 235.3 nm	23.913	241184	1.70	3112

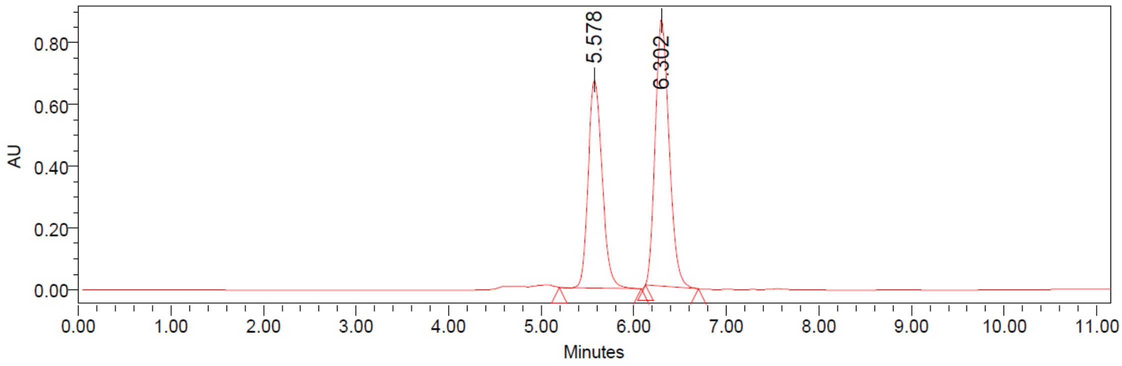
^{1}H NMR (400 MHz, $CDCl_3$) of **2Aw**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Aw**:



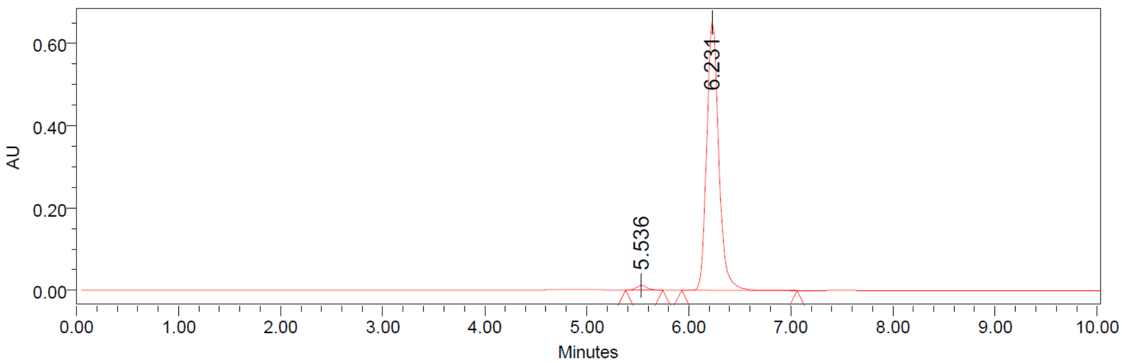
Racemic sample of 2Aw: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 233.9 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.9 nm	5.578	7102788	44.01	675739
2	PDA 233.9 nm	6.302	9036592	55.99	865397

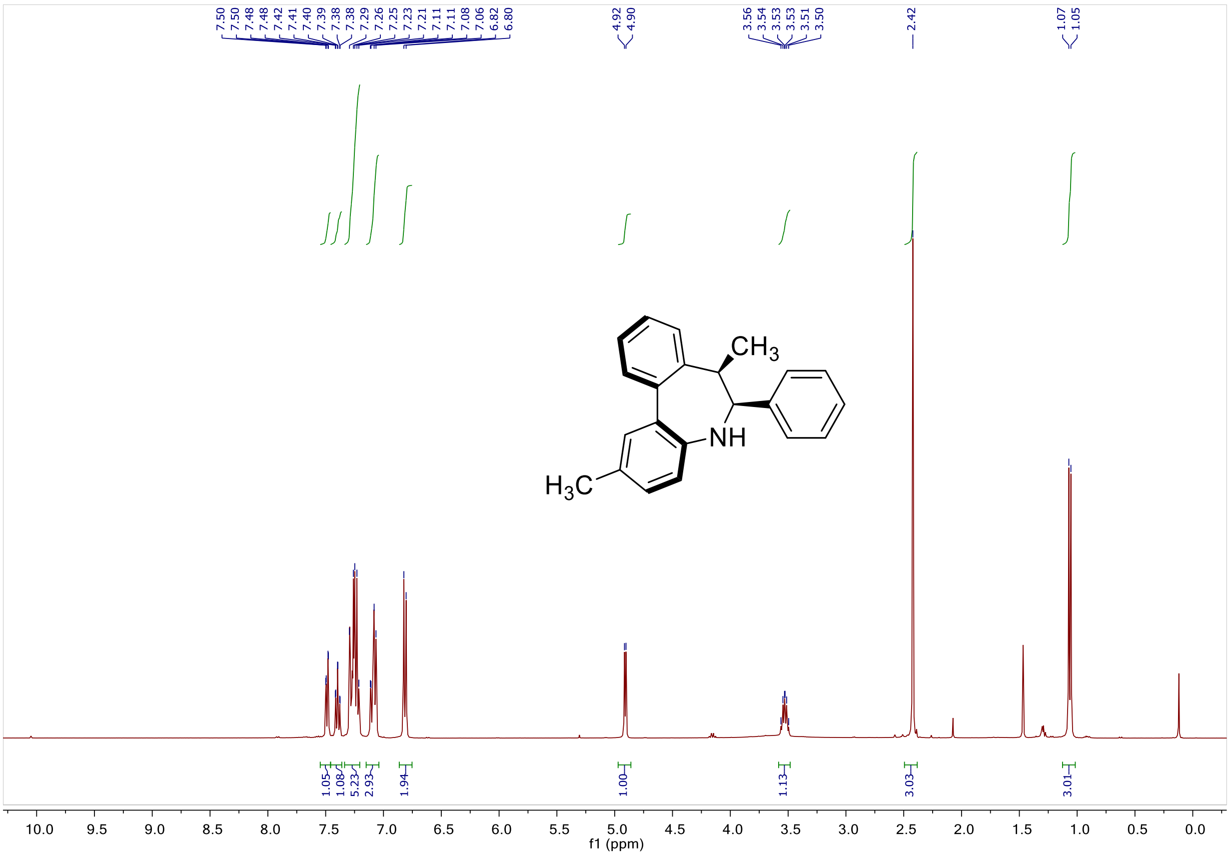
Enantioenriched sample of (*R*$_a$,6*S*,7*R*)-2Aw:



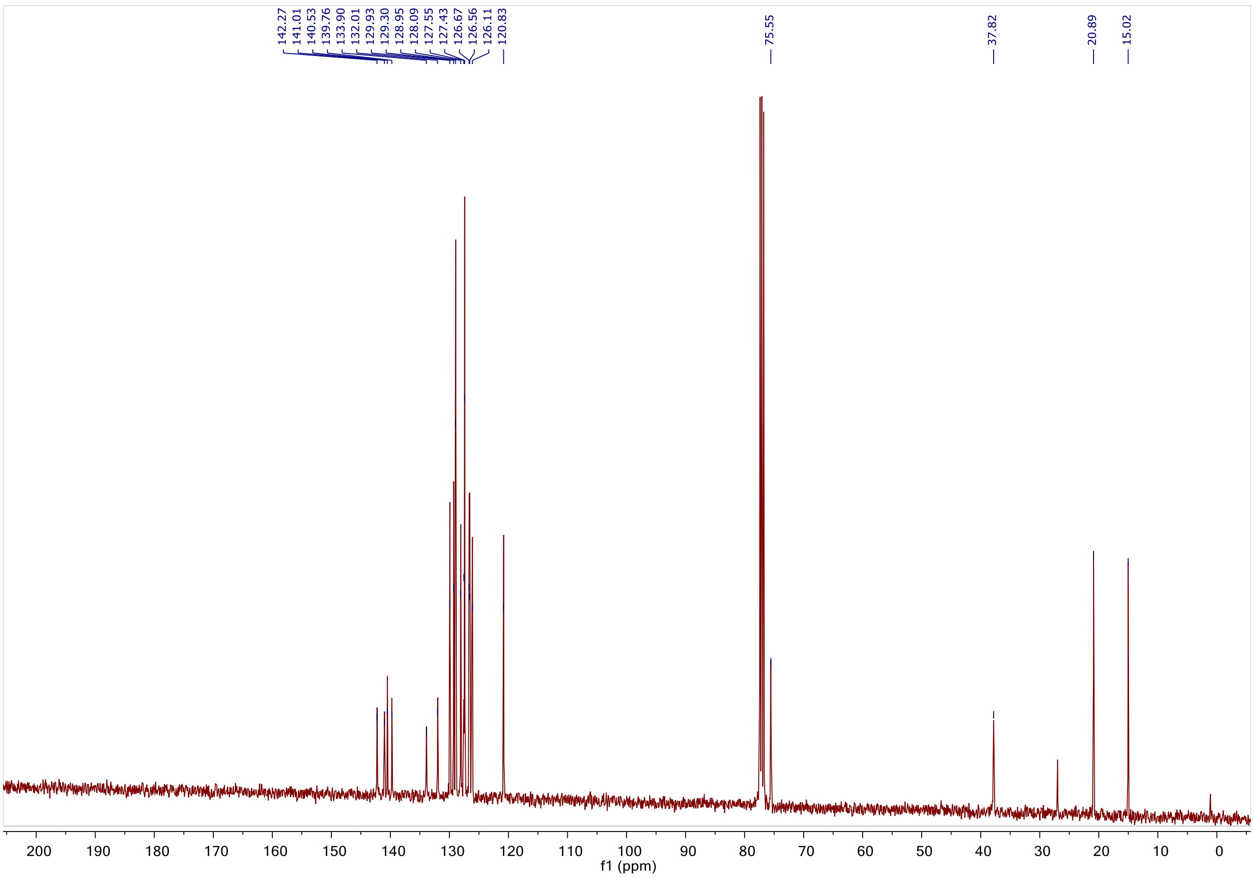
Processed Channel: PDA 267.2 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 267.2 nm	5.536	84037	1.54	11390
2	PDA 267.2 nm	6.231	5366566	98.46	651136

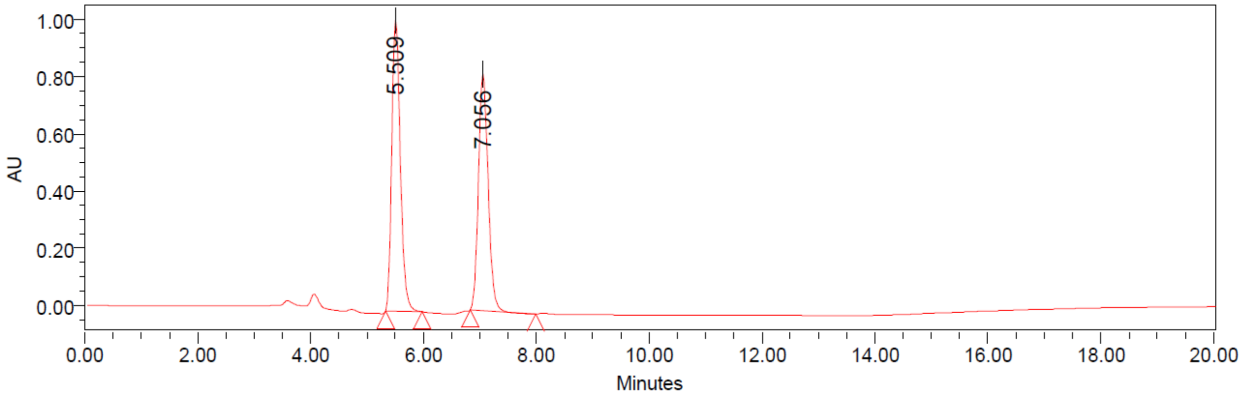
[1]H NMR (400 MHz, $CDCl_3$) of **2Ba**:



[13]C NMR (100 MHz, $CDCl_3$) of **2Ba**:



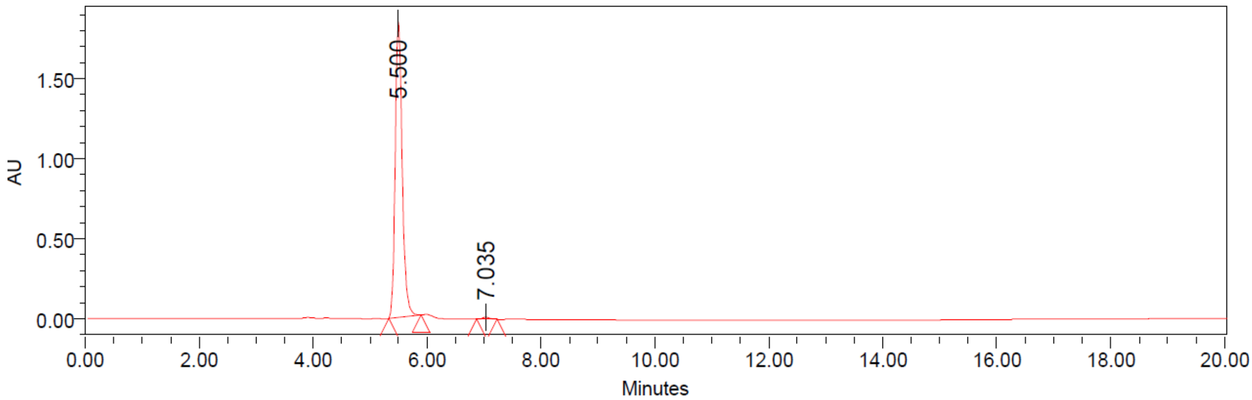
Racemic sample of 2Ba: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 221.3 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 221.3 nm	5.509	10732290	52.01	1017607
2	PDA 221.3 nm	7.056	9901192	47.99	829385

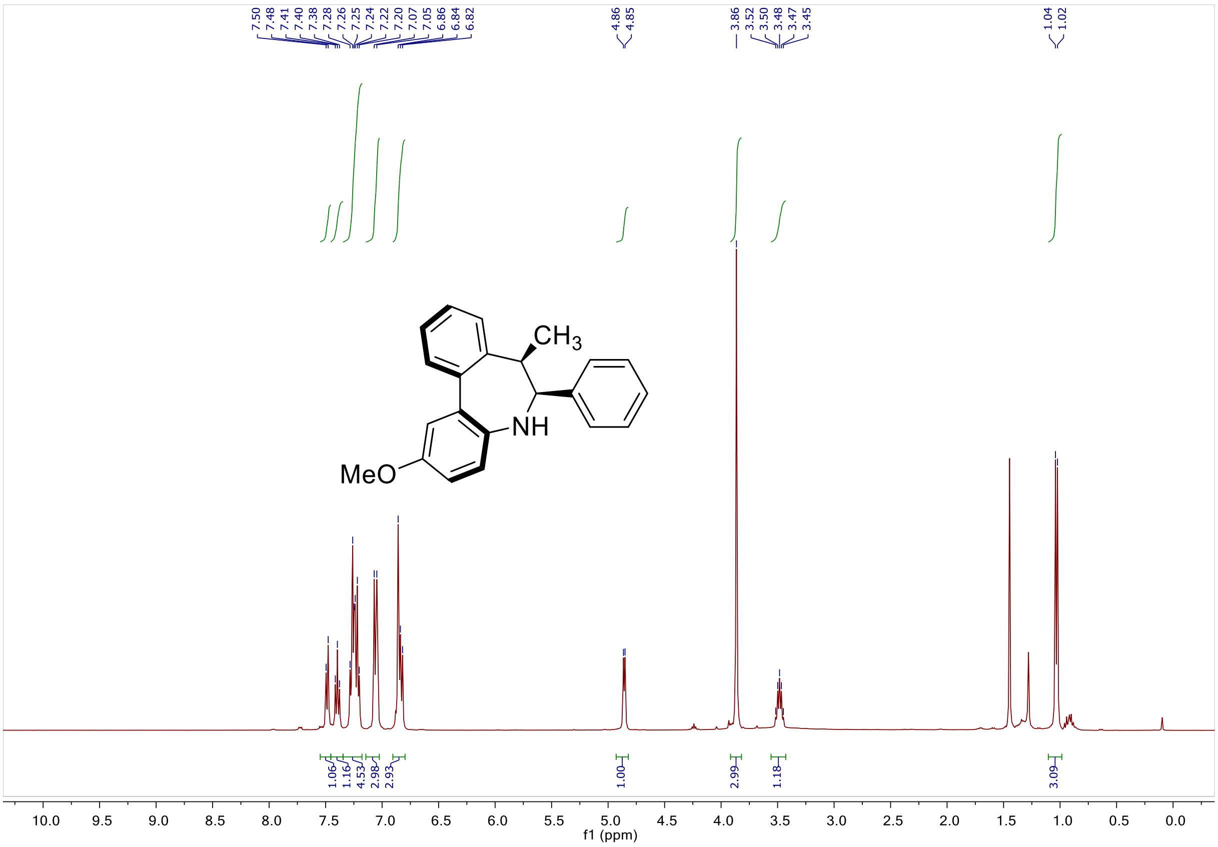
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)- 2Ba:



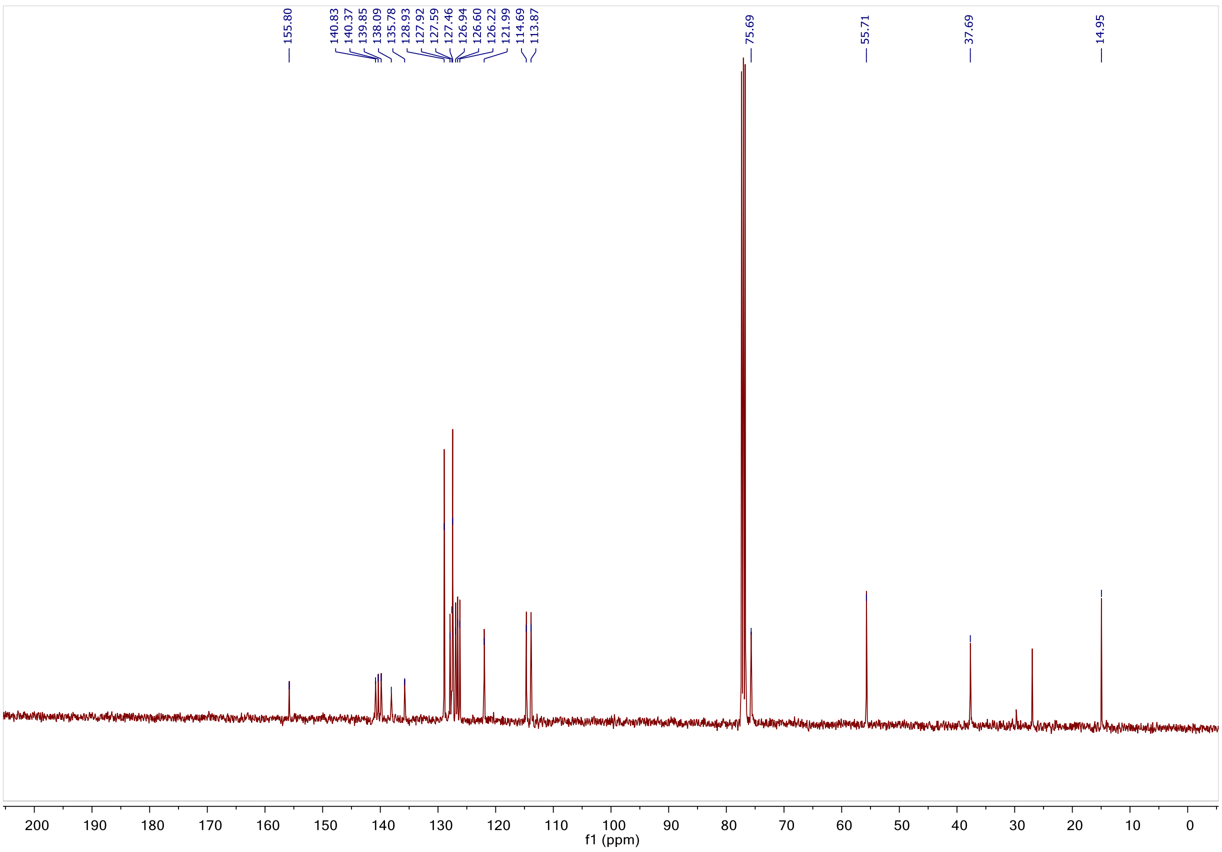
Processed Channel: PDA 235.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.0 nm	5.500	15640488	99.28	1859247
2	PDA 235.0 nm	7.035	113880	0.72	12397

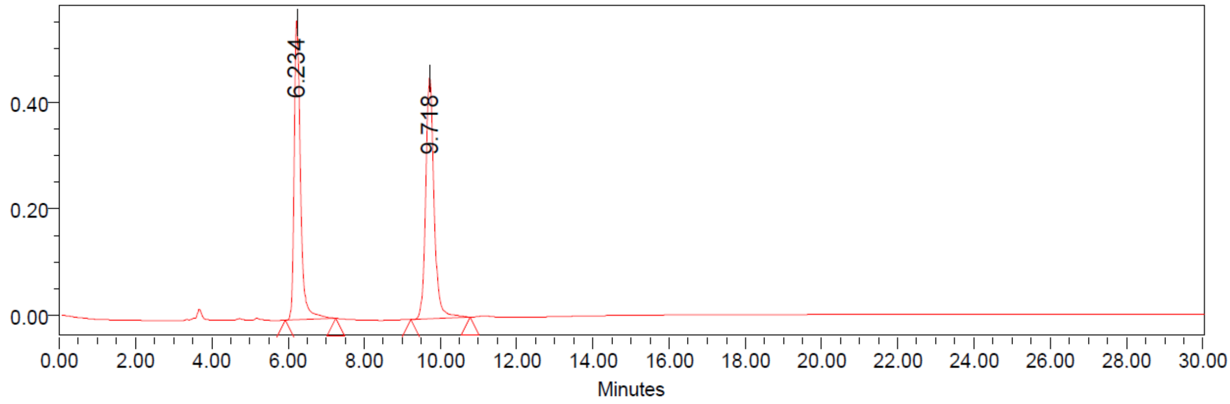
¹H NMR (400 MHz, $CDCl_3$) of **2Ca**:



¹³C NMR (100 MHz, $CDCl_3$) of **2Ca**:



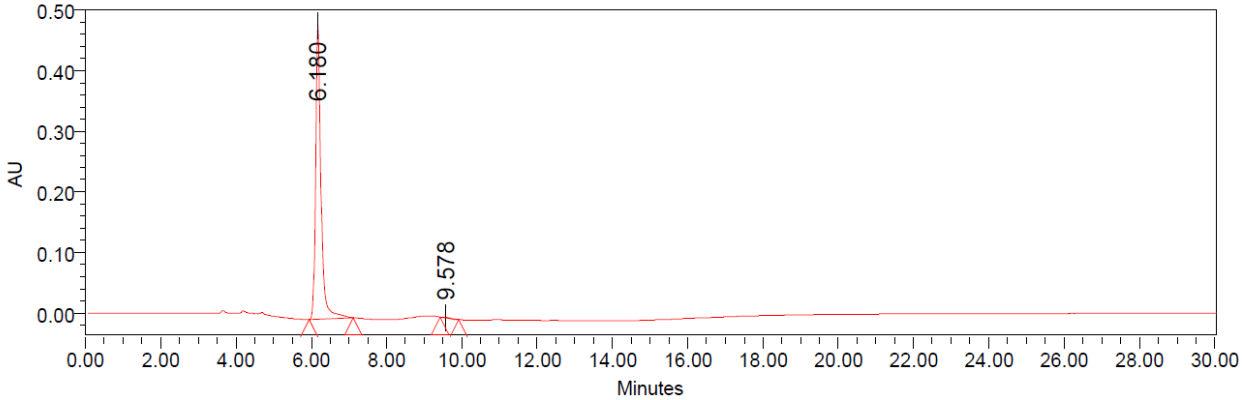
Racemic sample of 2Ca: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 233.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 233.7 nm	6.234	6452477	48.32	563794
2	PDA 233.7 nm	9.718	6902172	51.68	452973

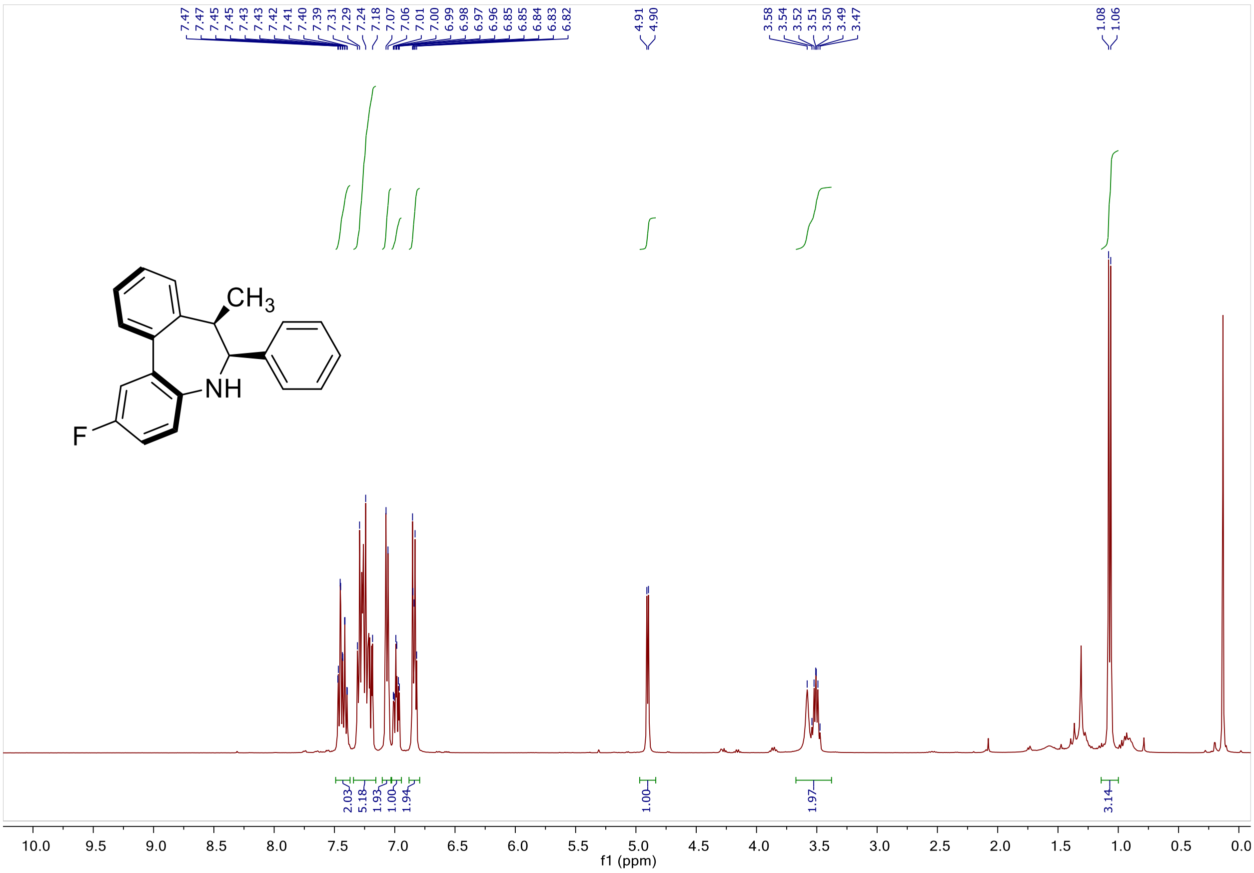
Enantioenriched sample of (*S*a,6*S*,7*R*)- 2Ca:



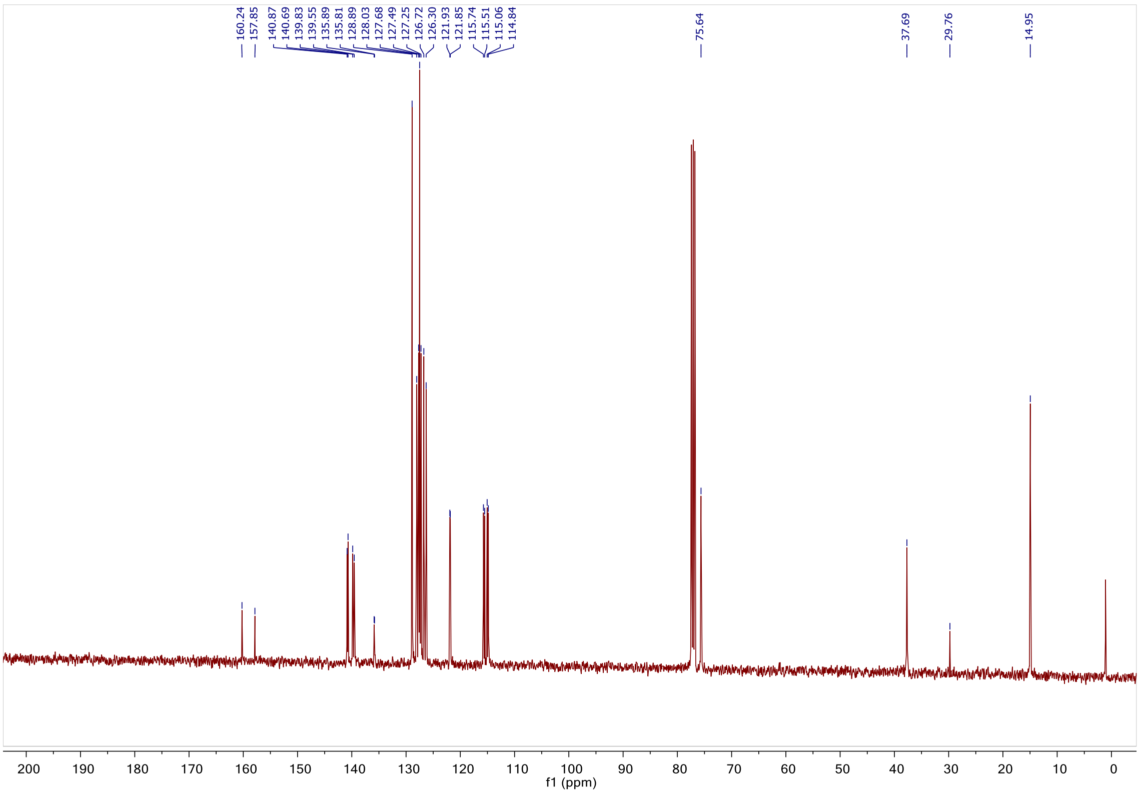
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	6.180	4872724	99.74	484271
2	PDA 234.0 nm	9.578	12611	0.26	850

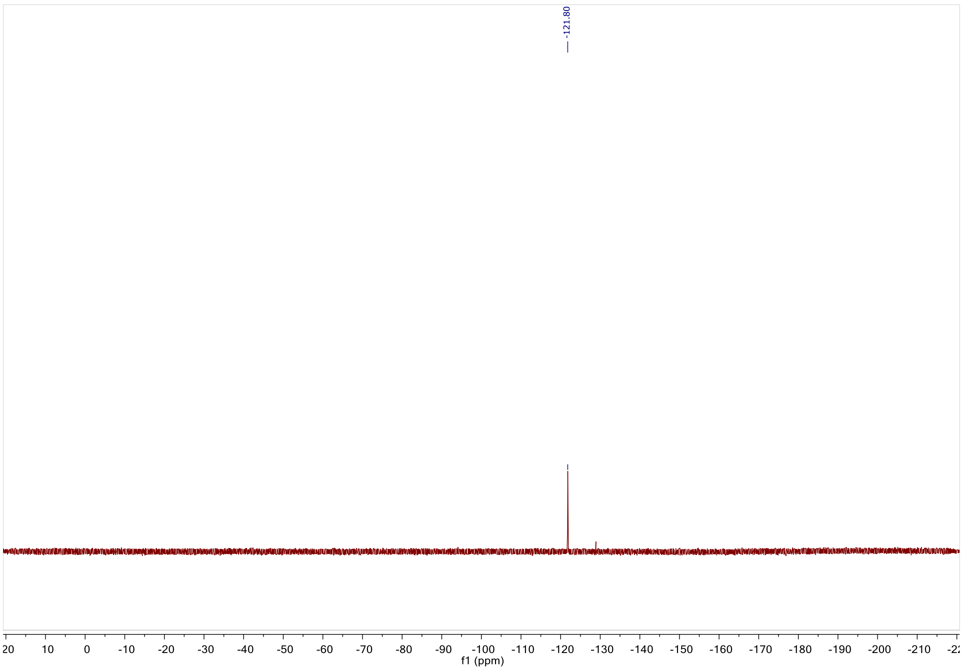
^{1}H NMR (400 MHz, $CDCl_3$) of **2Da**:



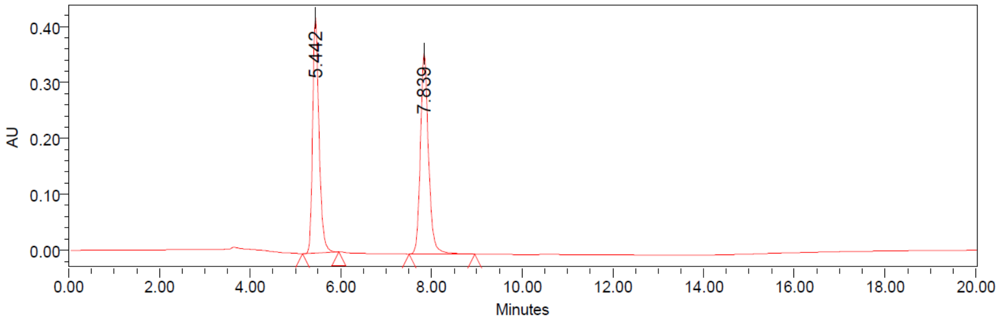
^{13}C NMR (100 MHz, $CDCl_3$) of **2Da**:



[19]F NMR (377 MHz, $CDCl_3$) of **2Da**:



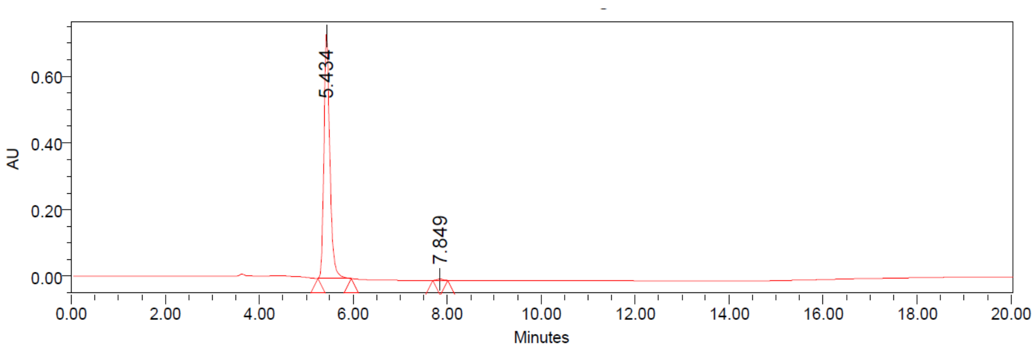
Racemic sample of 2Da: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 236.1 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 236.1 nm	5.442	4155746	48.21	421188
2	PDA 236.1 nm	7.839	4465047	51.79	358417

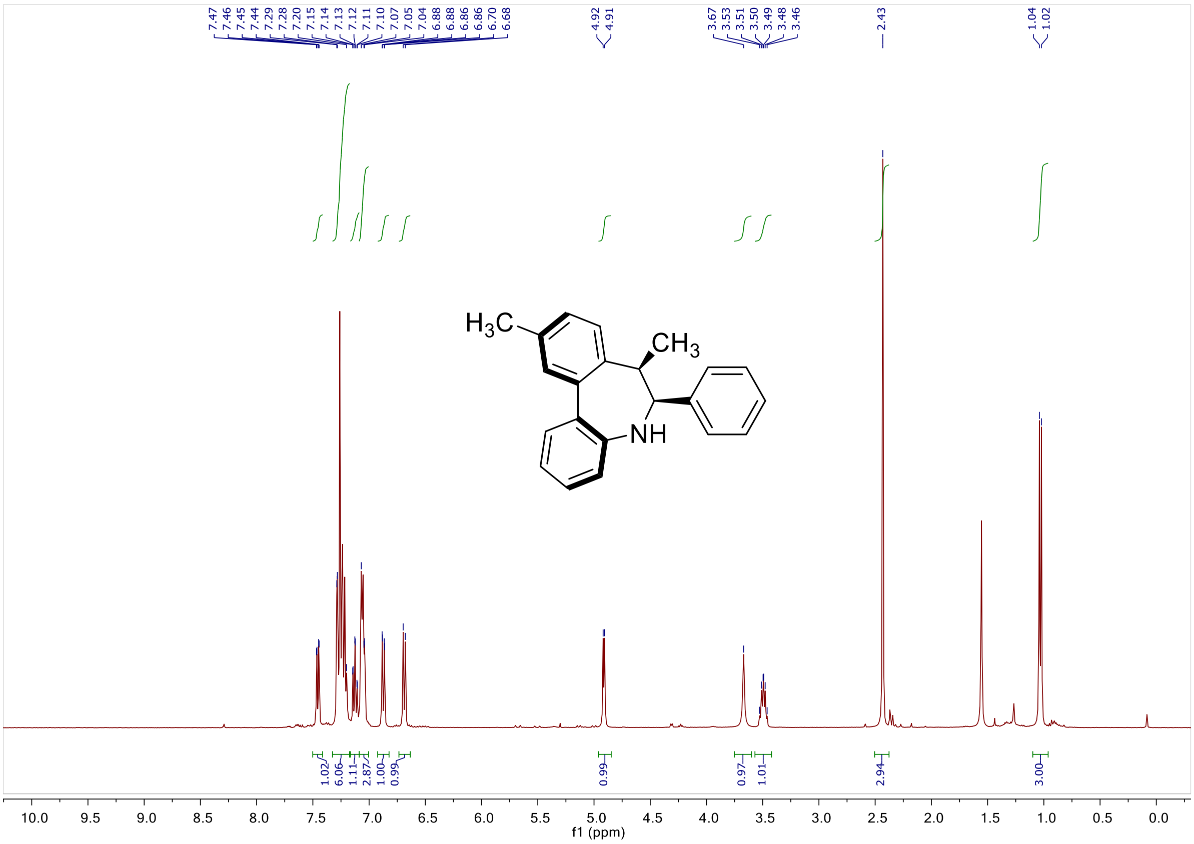
Enantioenriched sample of (*S*



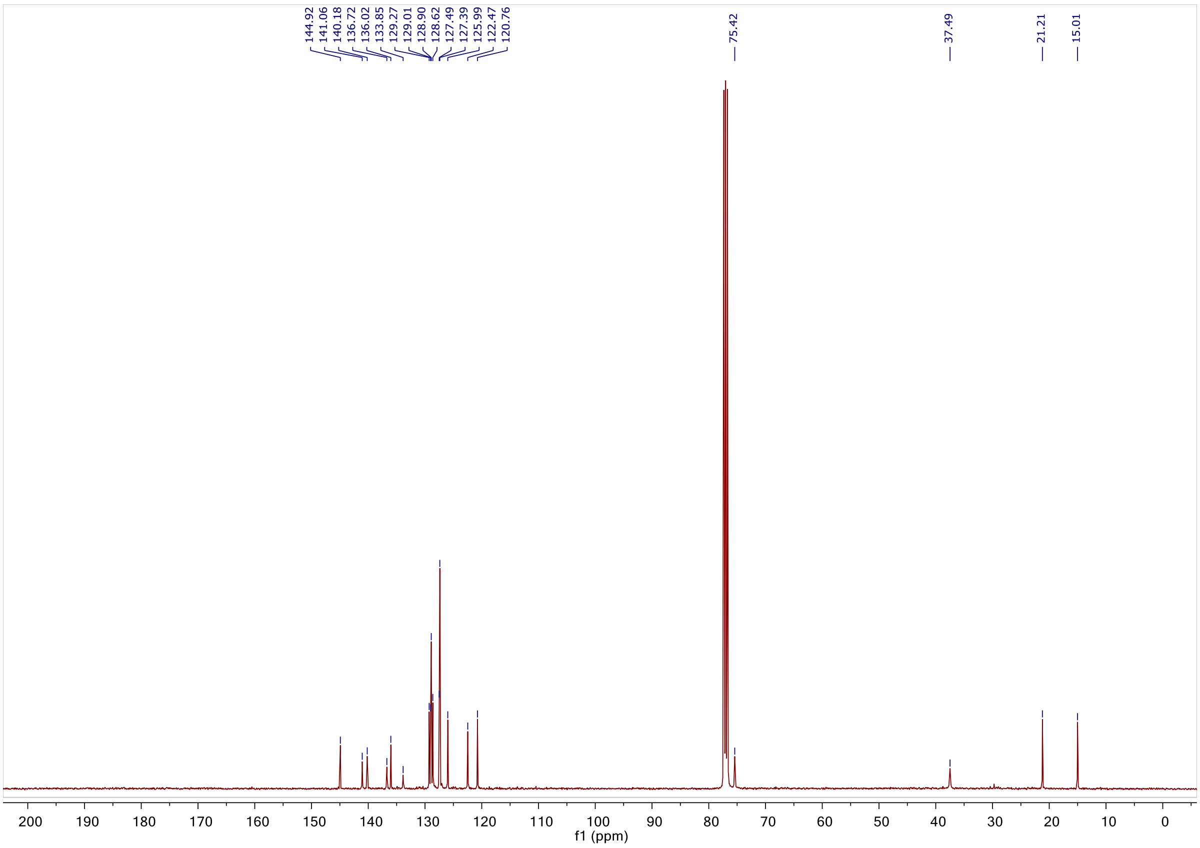
Processed Channel: PDA 232.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 232.0 nm	5.434	6378329	99.42	731838
2	PDA 232.0 nm	7.849	36925	0.58	3910

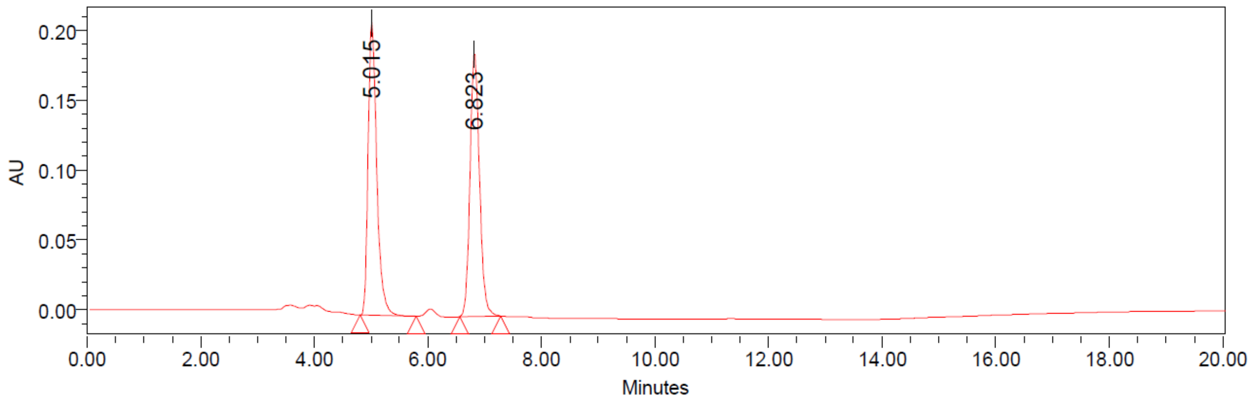
¹H NMR (400 MHz, $CDCl_3$) of **2Ea**:



¹³C NMR (100 MHz, $CDCl_3$) of **2Ea**:



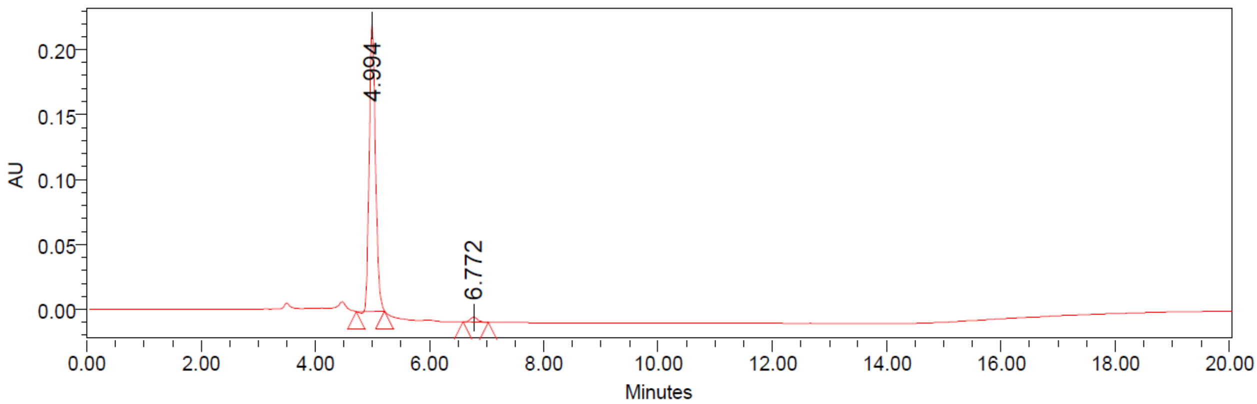
Racemic sample of 2Ea: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 240.6 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 240.6 nm	5.015	2208534	50.28	209806
2	PDA 240.6 nm	6.823	2184220	49.72	188305

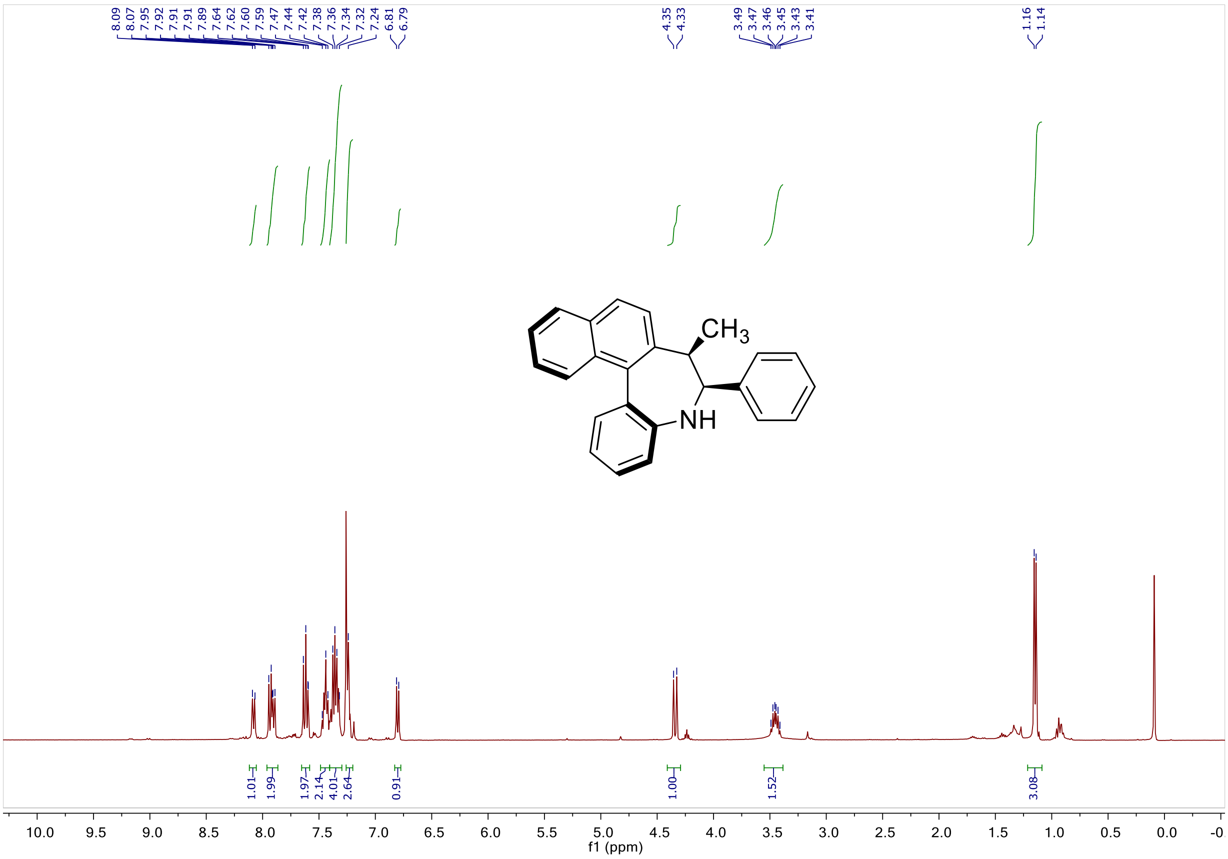
Enantioenriched sample of (S_a,6*S*,7*R*)- 2Ea:



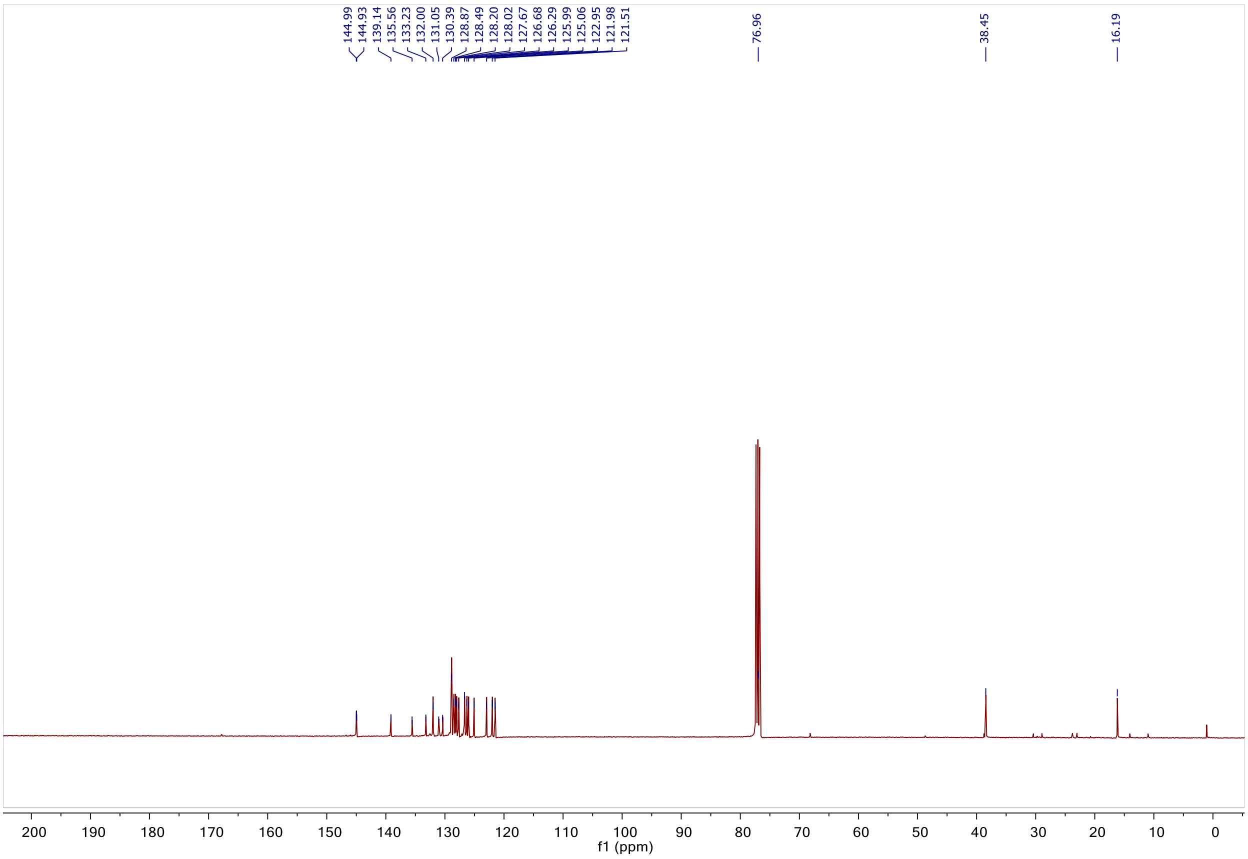
Processed Channel: PDA 235.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.0 nm	4.994	1698548	98.07	221557
2	PDA 235.0 nm	6.772	33448	1.93	3628

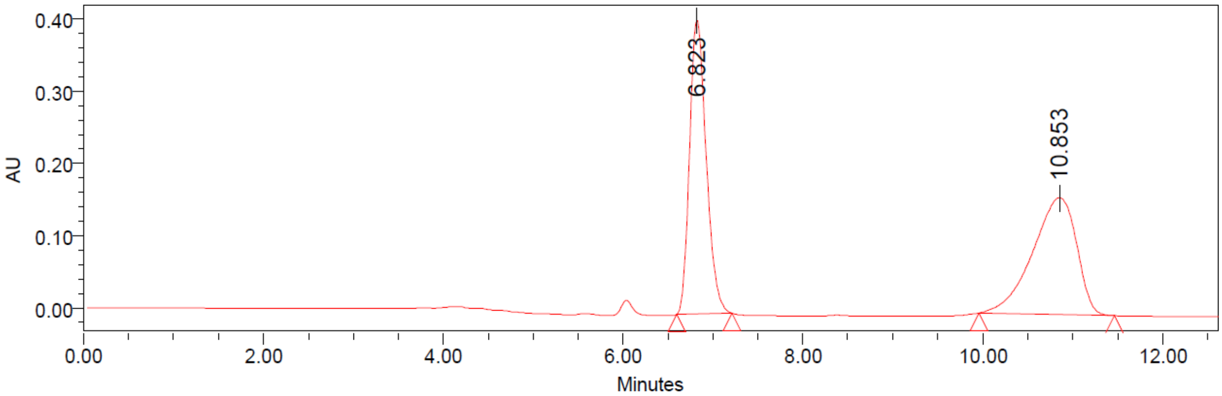
^{1}H NMR (400 MHz, $CDCl_3$) of **2Fa**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2Fa**:



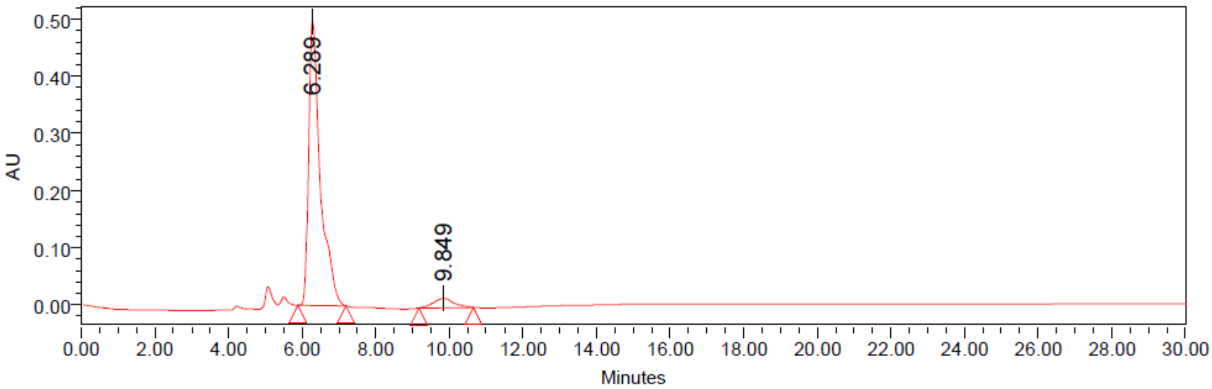
Racemic sample of 2Fa: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	6.823	5242128	48.81	406603
2	PDA 234.0 nm	10.853	5496826	51.19	161681

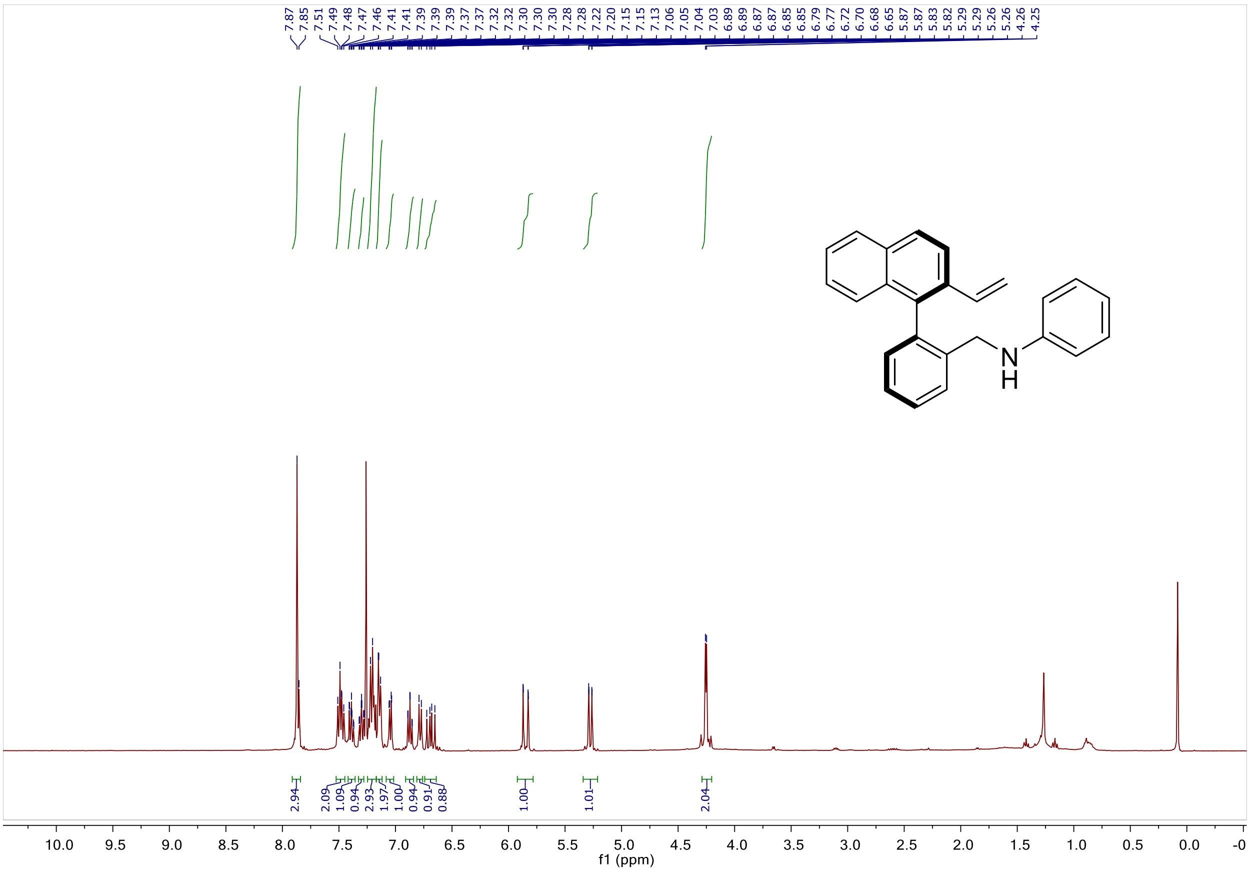
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)- 2Fa:



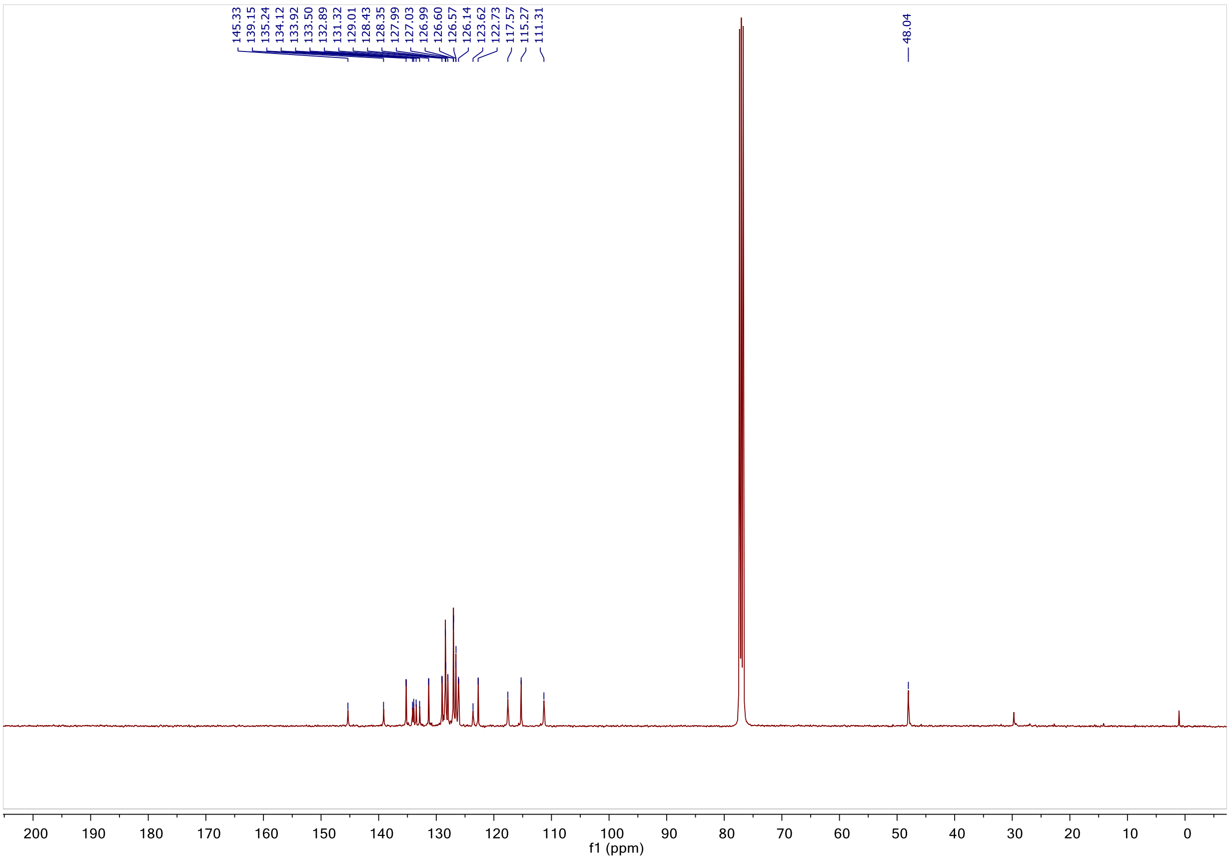
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	6.289	10955575	94.56	497113
2	PDA 234.0 nm	9.849	629680	5.44	16355

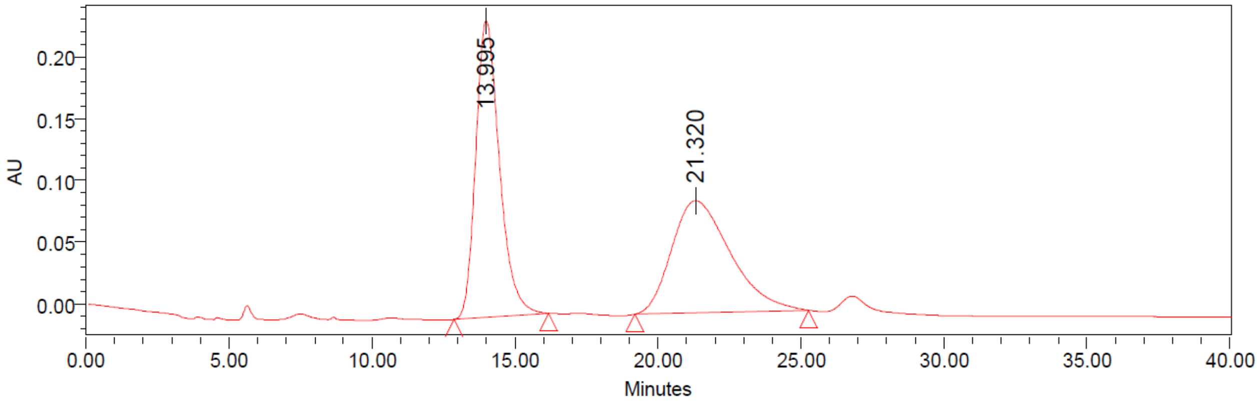
¹H NMR (400 MHz, CDCl₃) of **3Fa**:



¹³C NMR (100 MHz, CDCl₃) of **3Fa**:



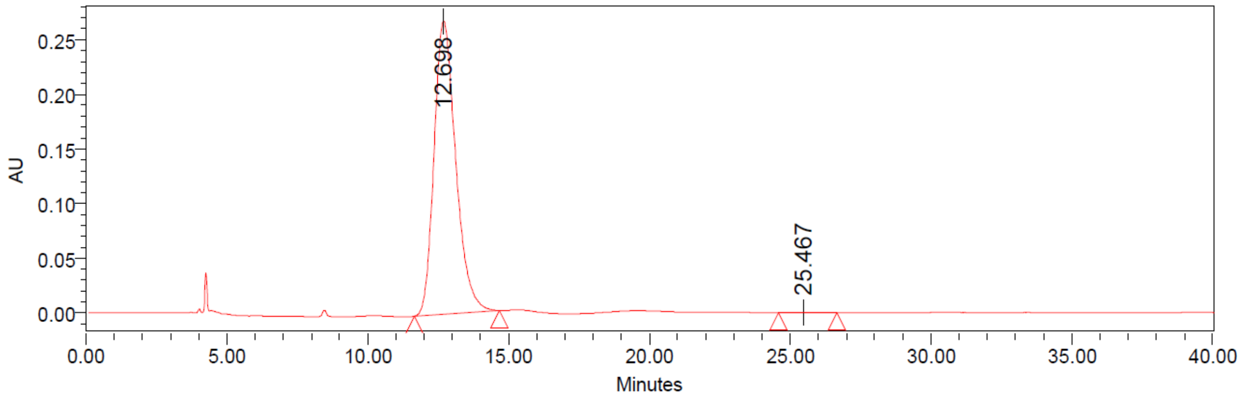
Racemic sample of 3Fa: OJ-H column, *n*-Hex/*i*-PrOH 98:2, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 246.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.0 nm	13.995	13819289	51.62	240021
2	PDA 246.0 nm	21.320	12954376	48.38	90901

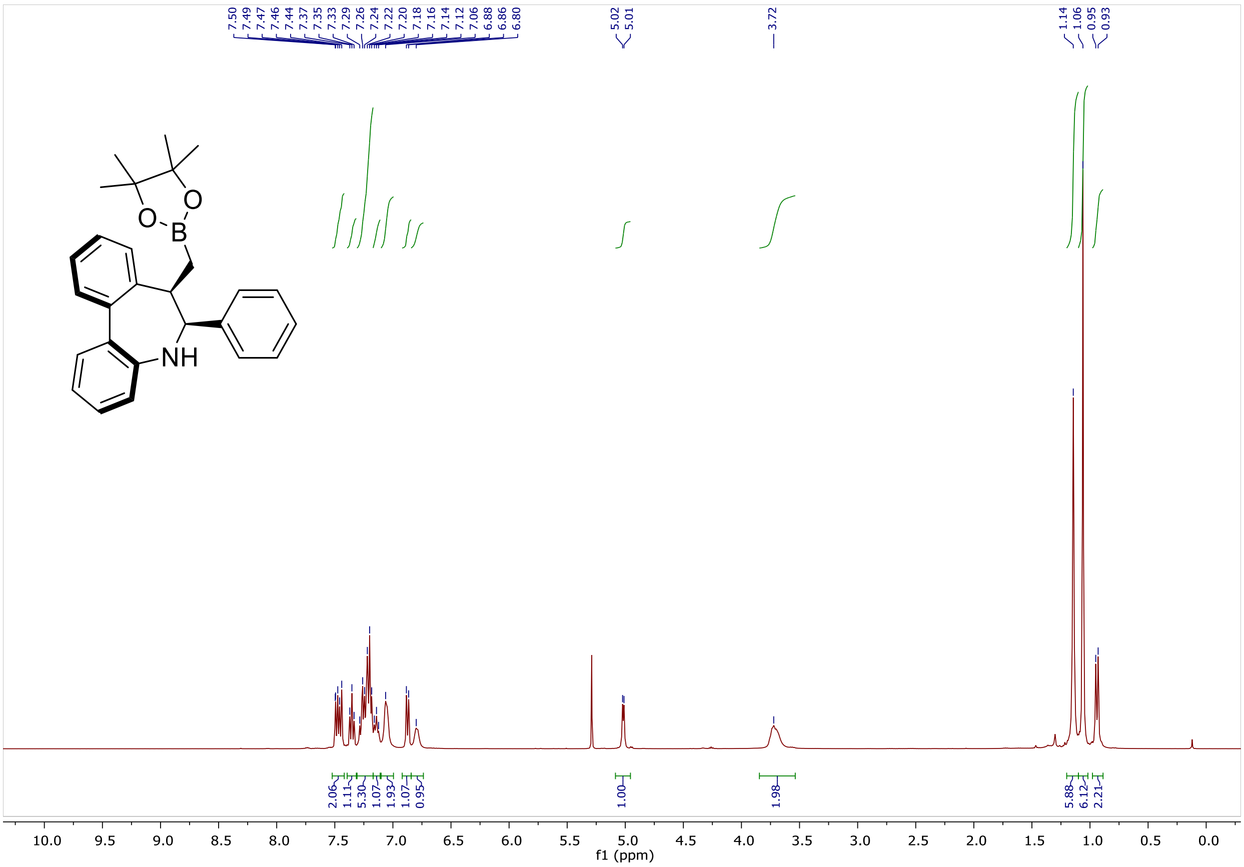
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)- 3Fa:



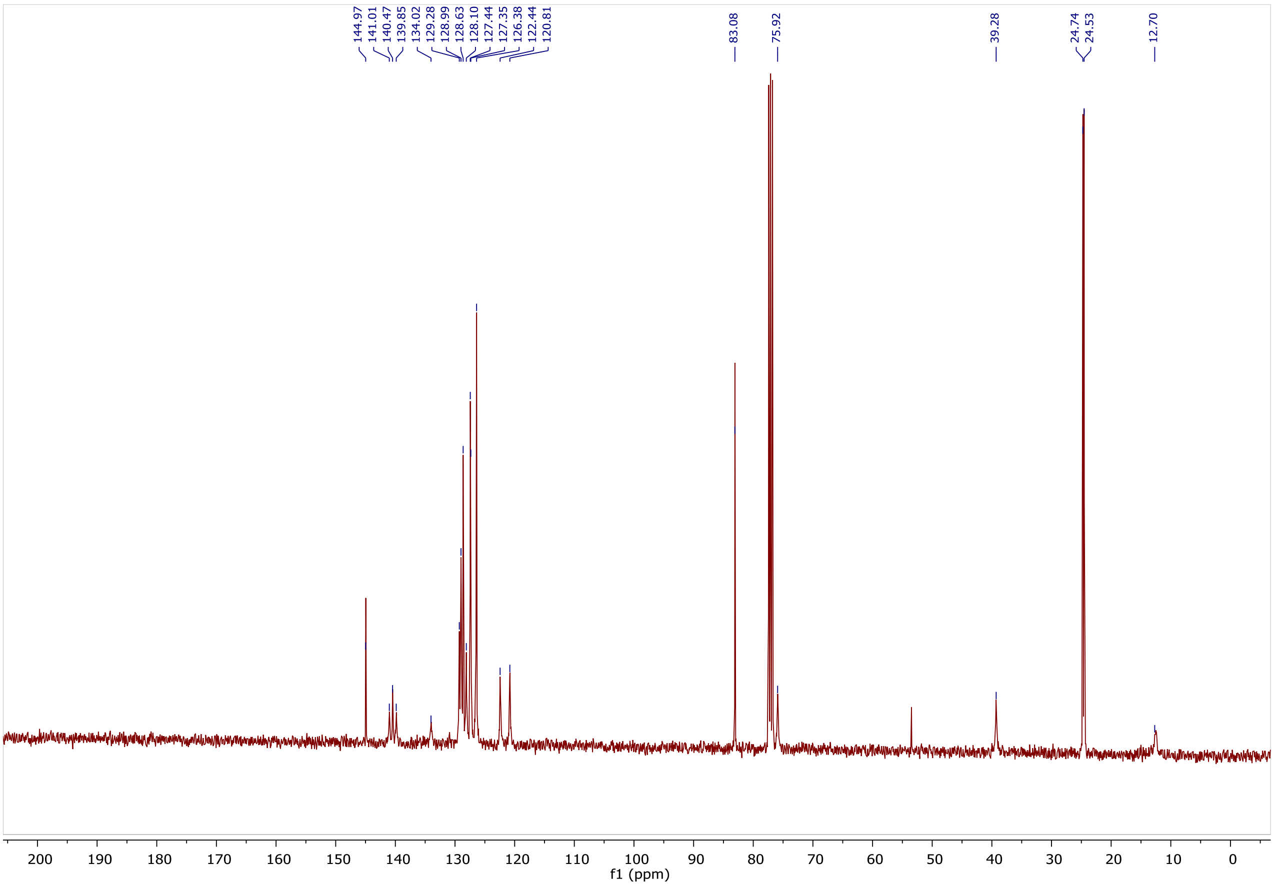
Processed Channel: PDA 246.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.0 nm	12.698	14364349	99.90	268471
2	PDA 246.0 nm	25.467	15078	0.10	281

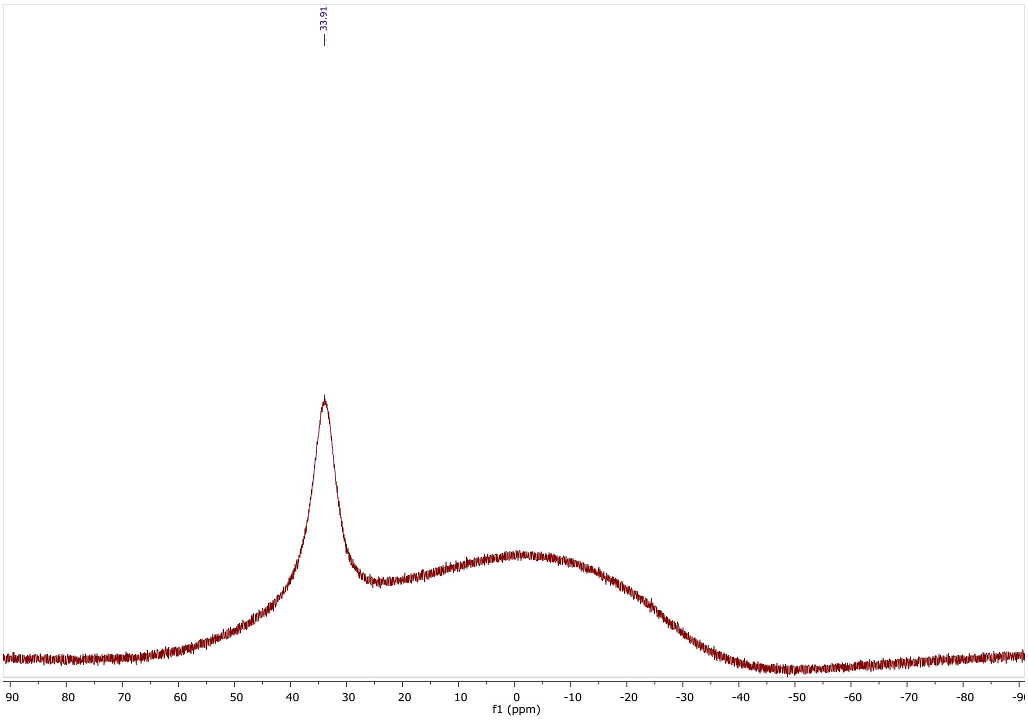
¹H NMR (400 MHz, $CDCl_3$) of **4Aa**:



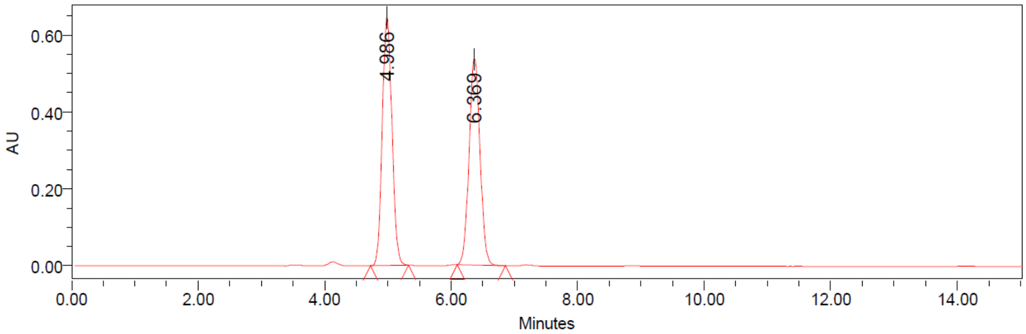
¹³C NMR (100 MHz, $CDCl_3$) of **4Aa**:



^{11}**B NMR** (160 MHz, $CDCl_3$) of **4Aa**



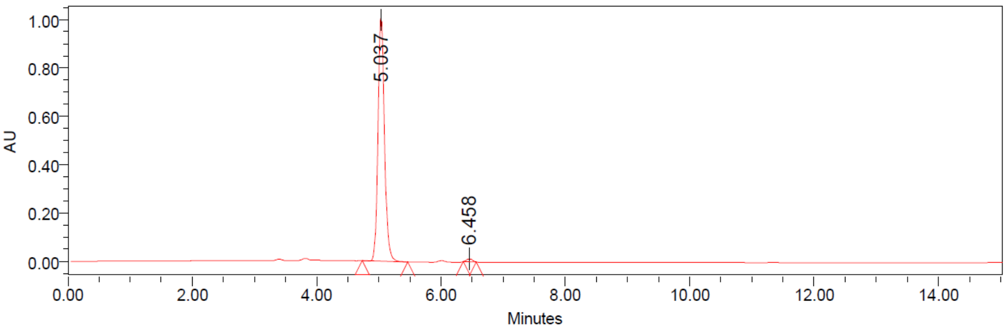
Racemic sample of 4Aa: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 254.9 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.9 nm	4.986	6920137	51.51	647504
2	PDA 254.9 nm	6.369	6513534	48.49	537394

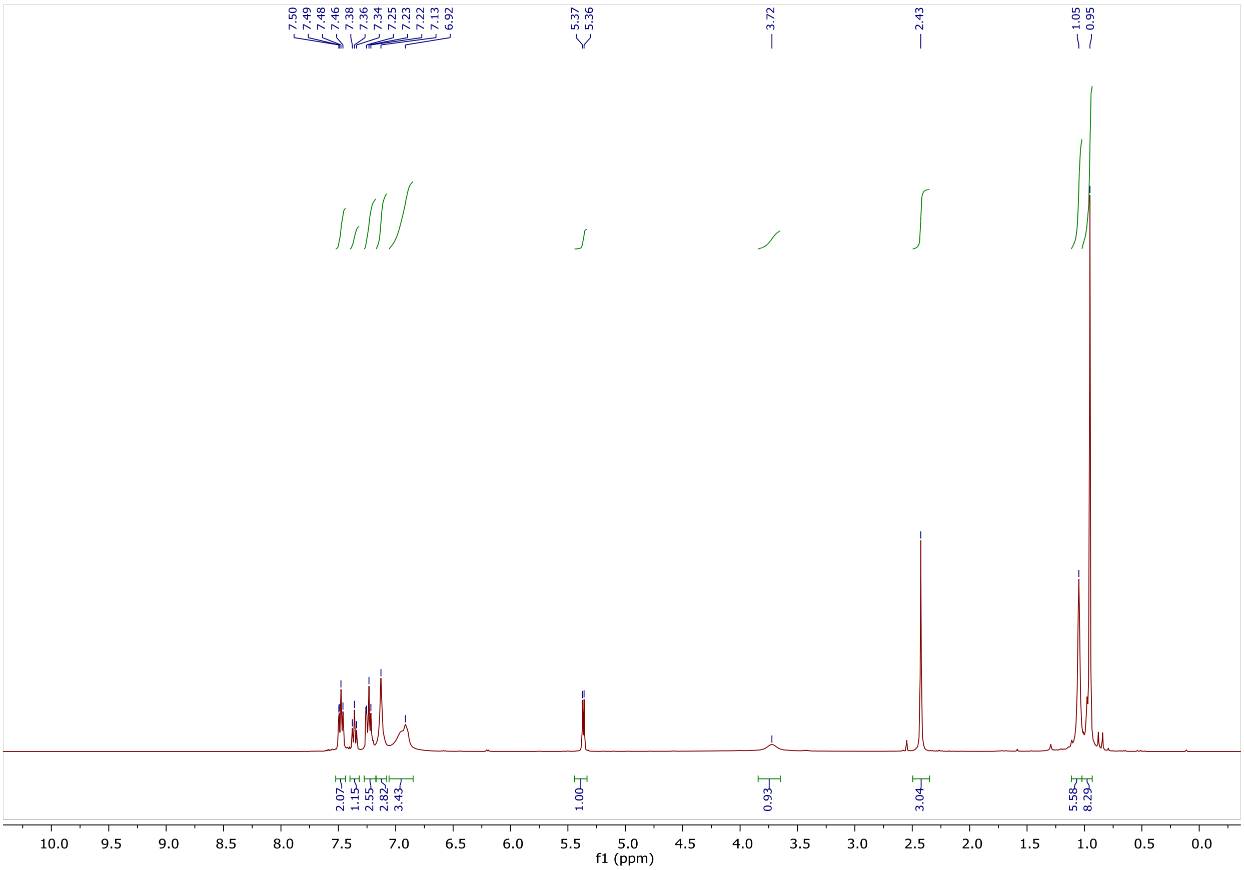
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-4Aa:



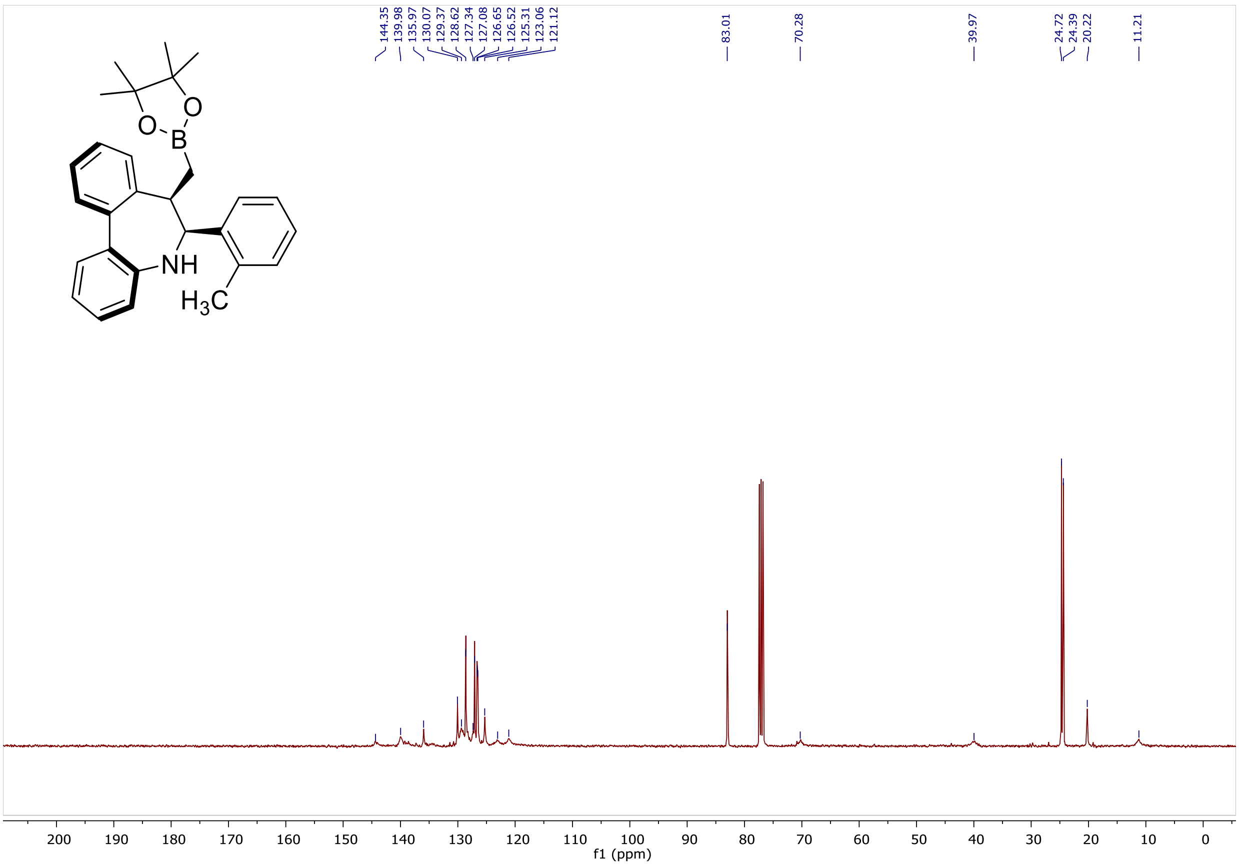
Processed Channel: PDA 235.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.0 nm	5.037	7243718	98.91	1007723
2	PDA 235.0 nm	6.458	79552	1.09	12048

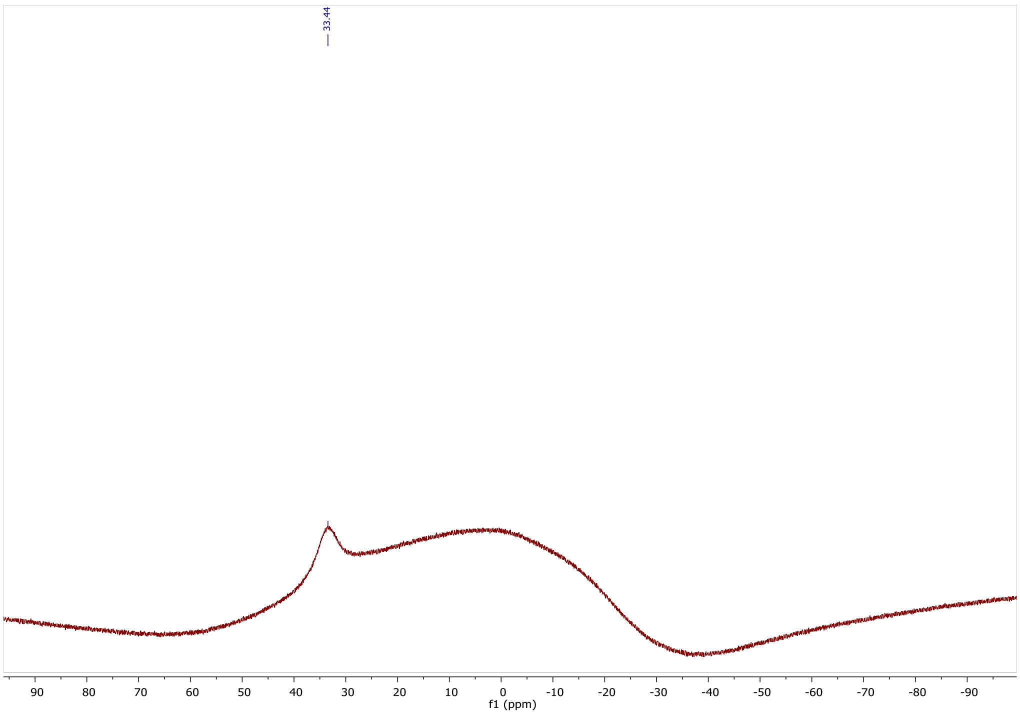
^{1}H NMR (400 MHz, $CDCl_3$) of **4Ab**:



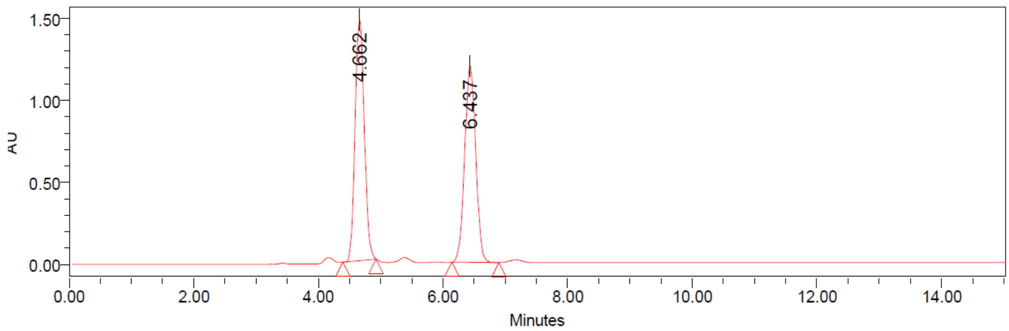
^{13}C NMR (100 MHz, $CDCl_3$) of **4Ab**:



^{11}B NMR (160 MHz, $CDCl_3$) of **4Ab**



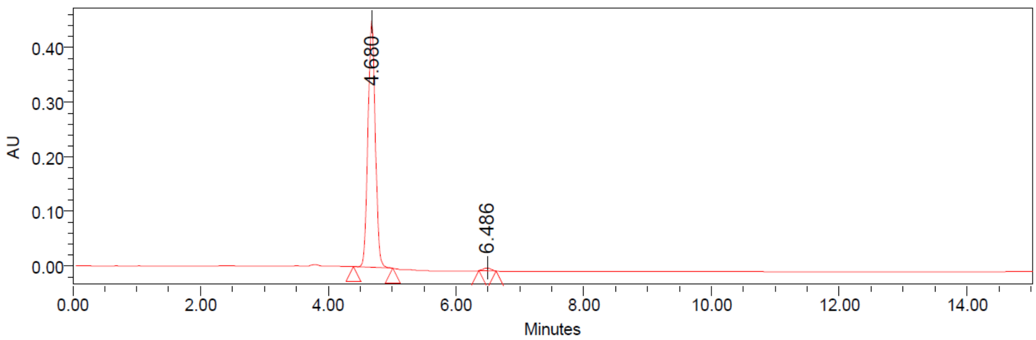
Racemic sample of 4Ab: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 236.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 236.0 nm	4.662	15244158	50.69	1468978
2	PDA 236.0 nm	6.437	14828685	49.31	1199214

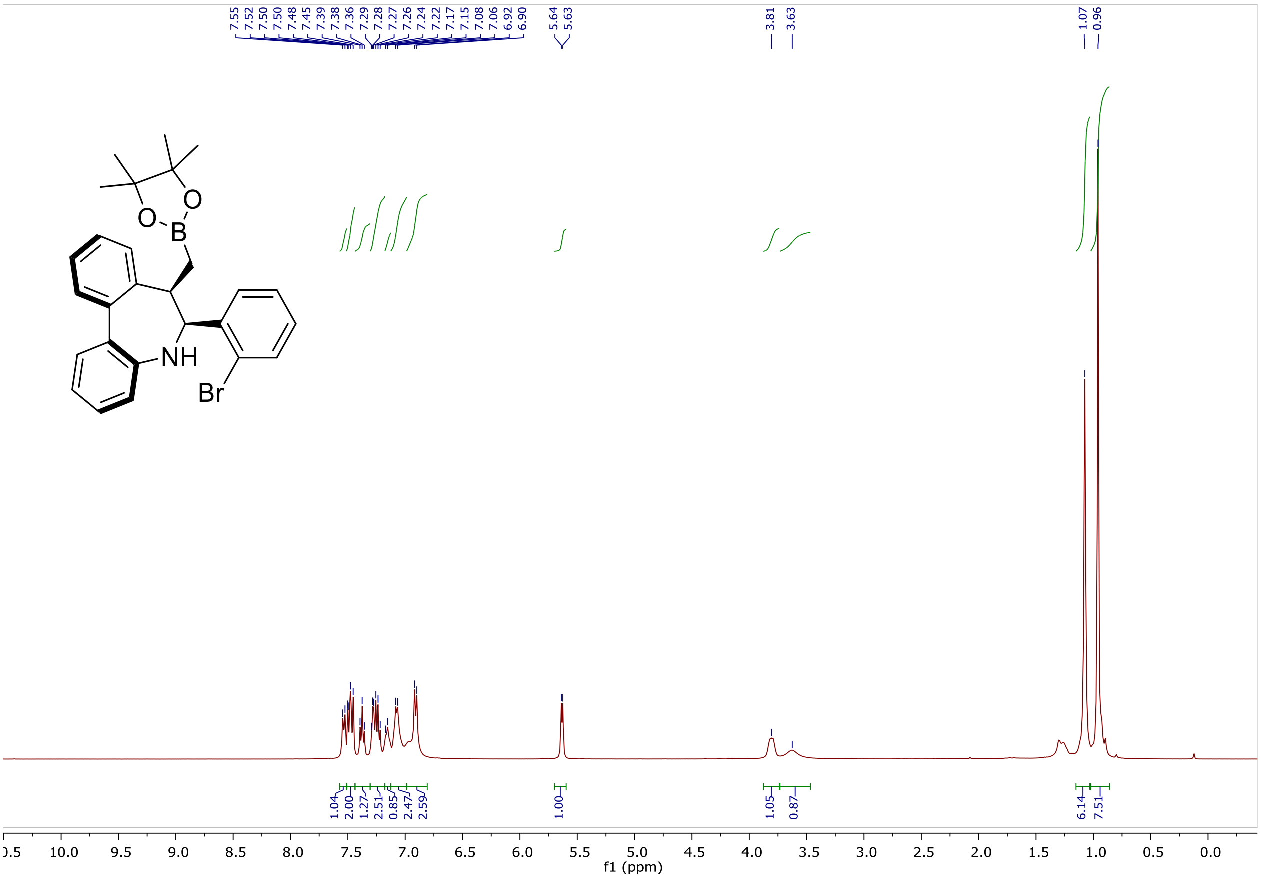
Enantioenriched sample of (S_a,6*S*,7*R*)-4Ab:



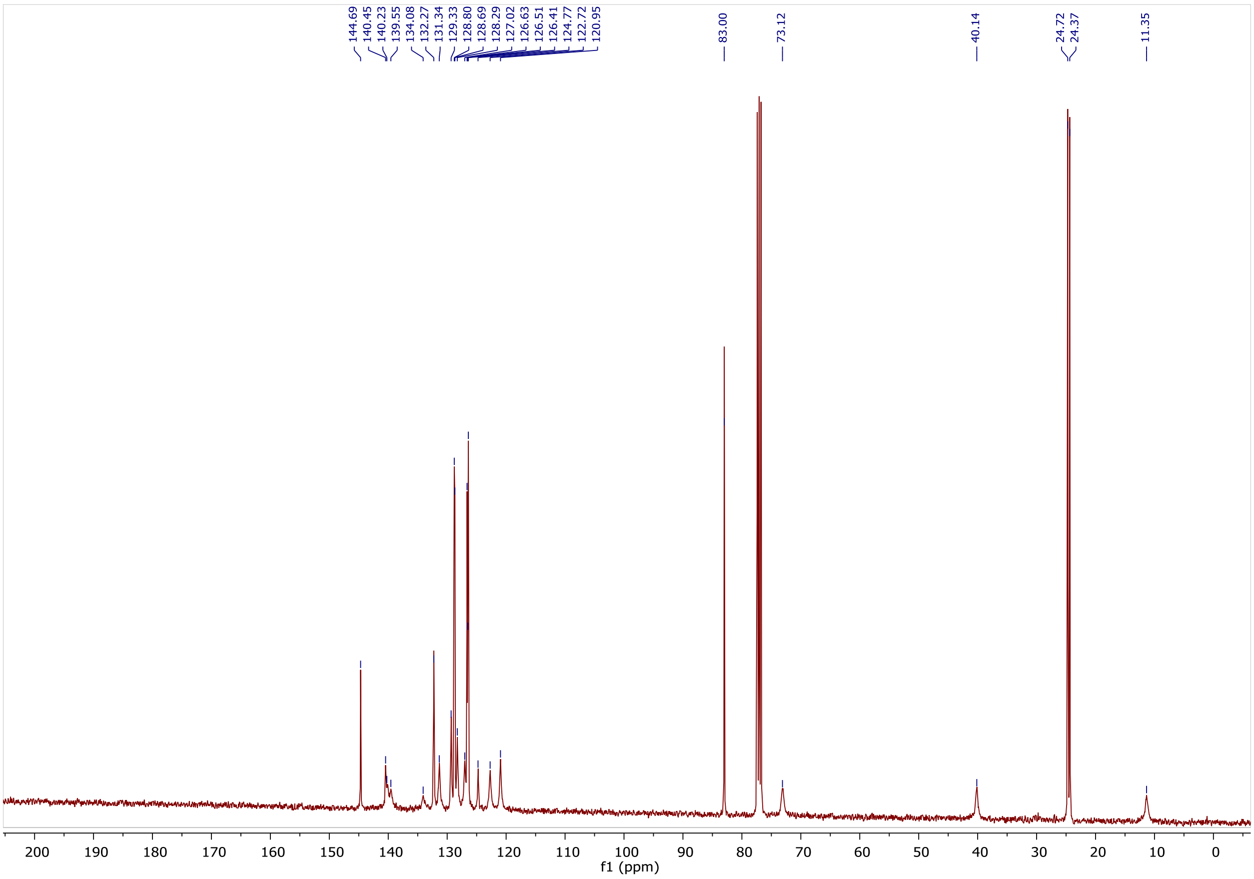
Processed Channel: PDA 236.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 236.0 nm	4.680	3638268	98.74	451100
2	PDA 236.0 nm	6.486	46605	1.26	5418

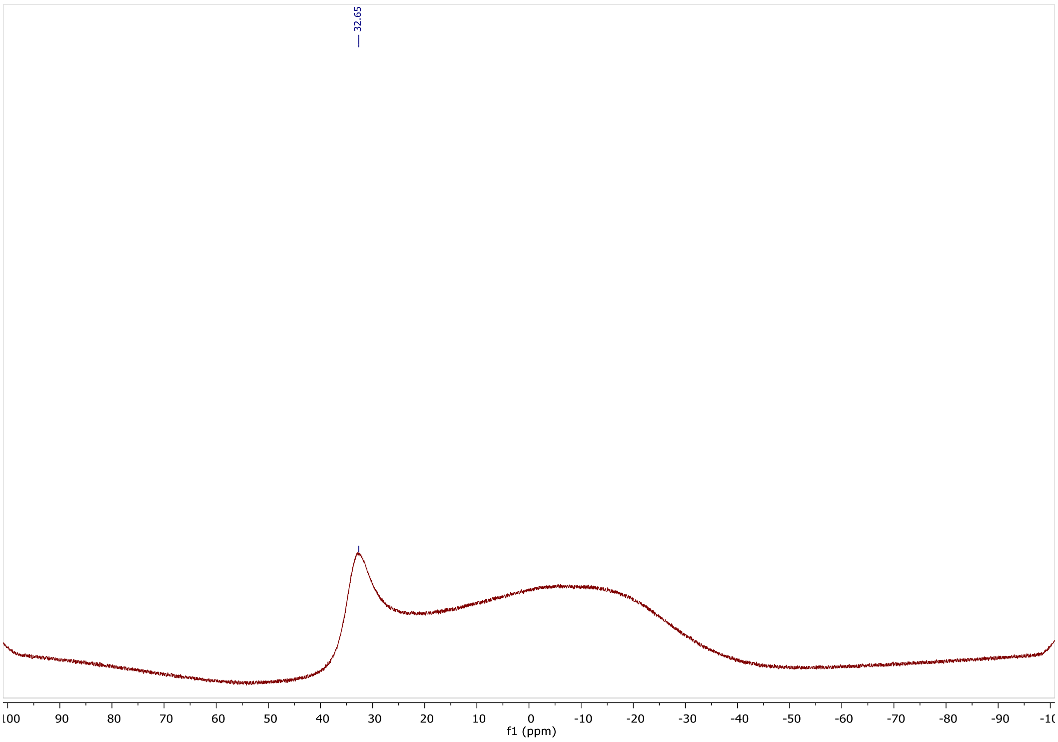
^{1}H NMR (400 MHz, $CDCl_3$) of **4Af**:



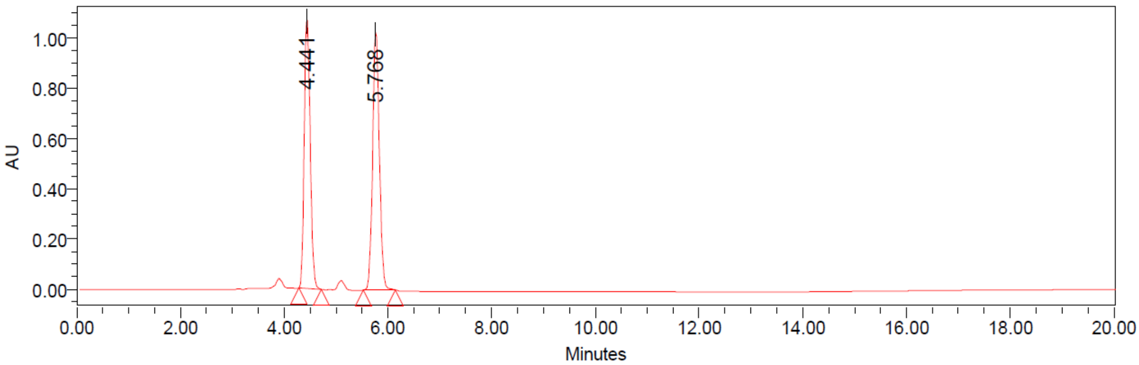
^{13}C NMR (100 MHz, $CDCl_3$) of **4Af**:



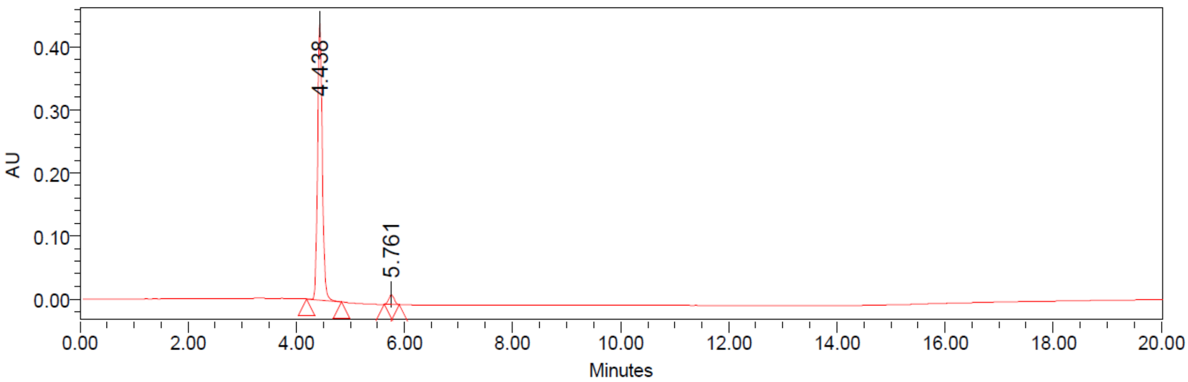
^{11}B NMR (160 MHz, $CDCl_3$) of **4Af**



Racemic sample of 4Aa: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



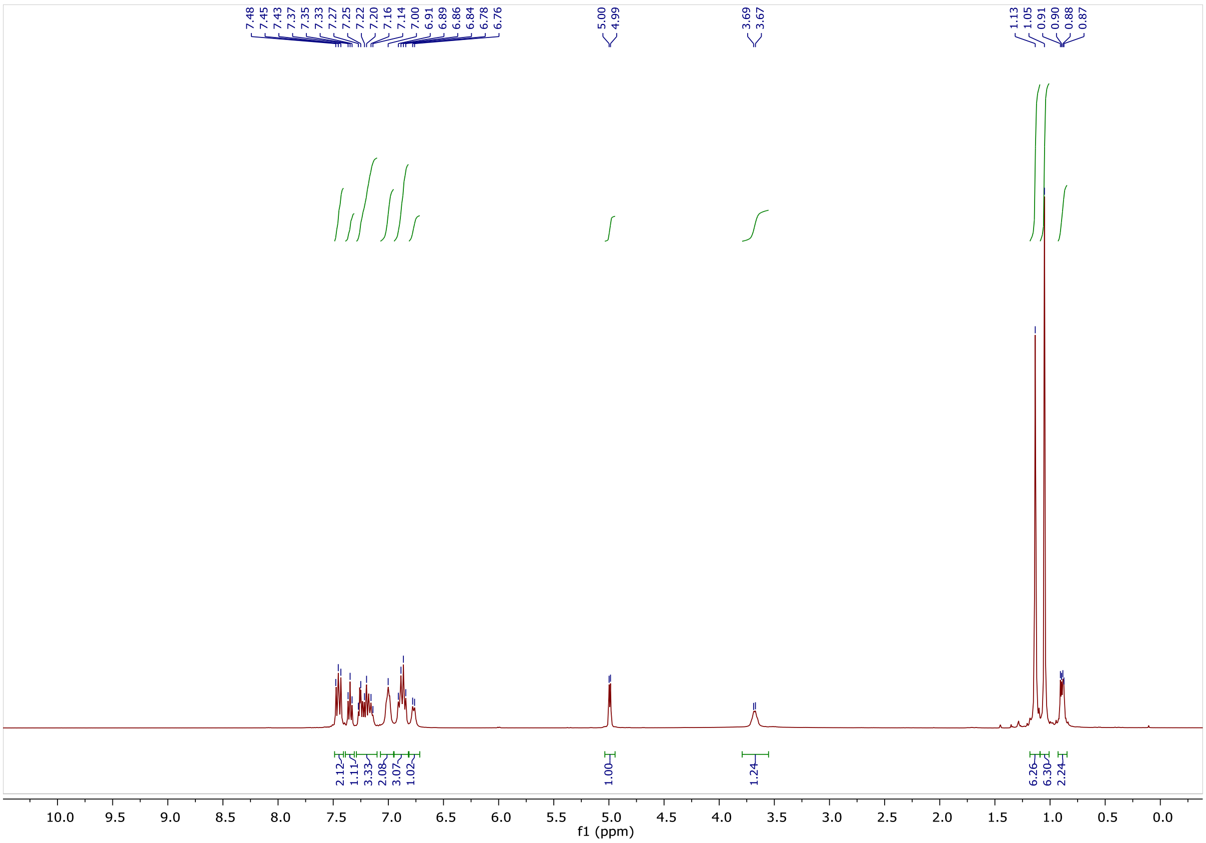
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-4Af:



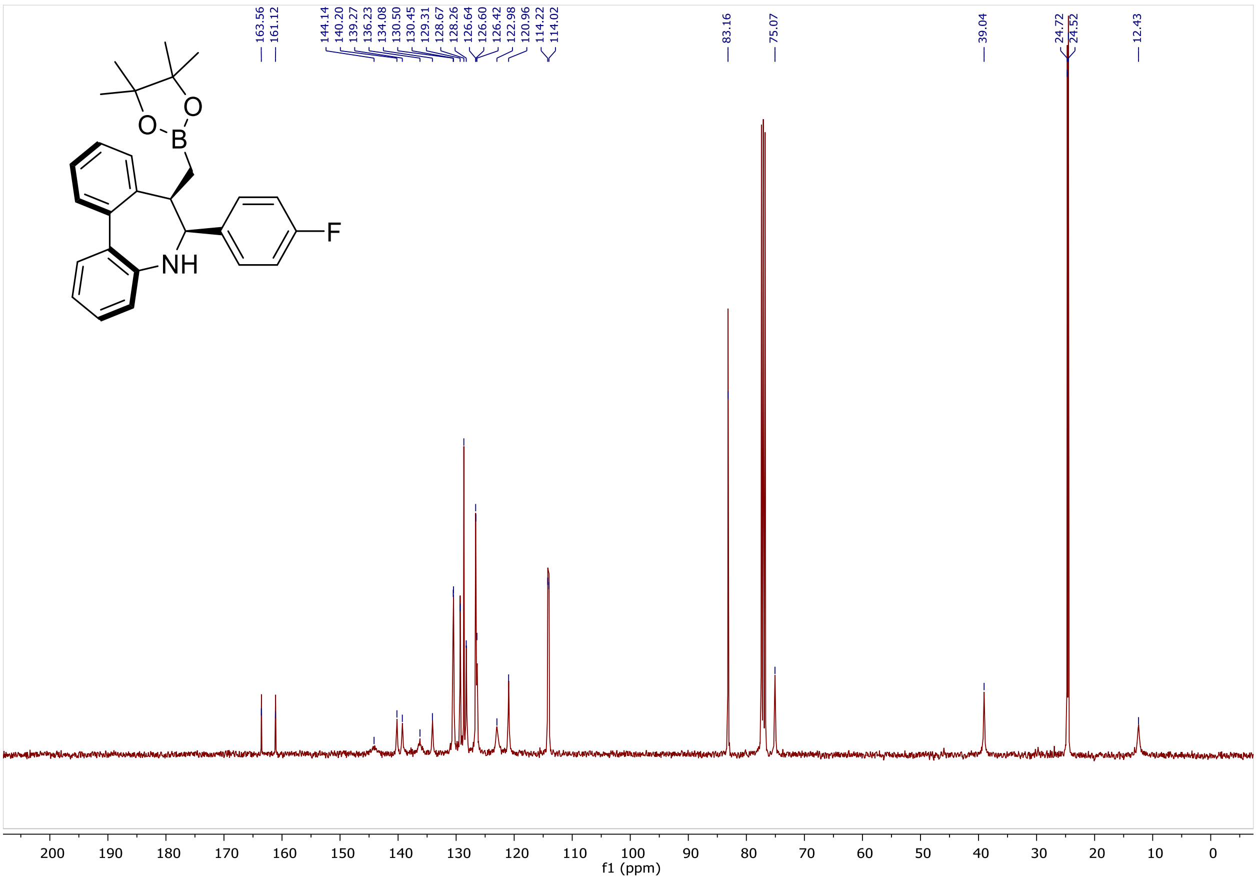
Processed Channel: PDA 235.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.0 nm	4.438	2666500	96.05	440781
2	PDA 235.0 nm	5.761	109660	3.95	15778

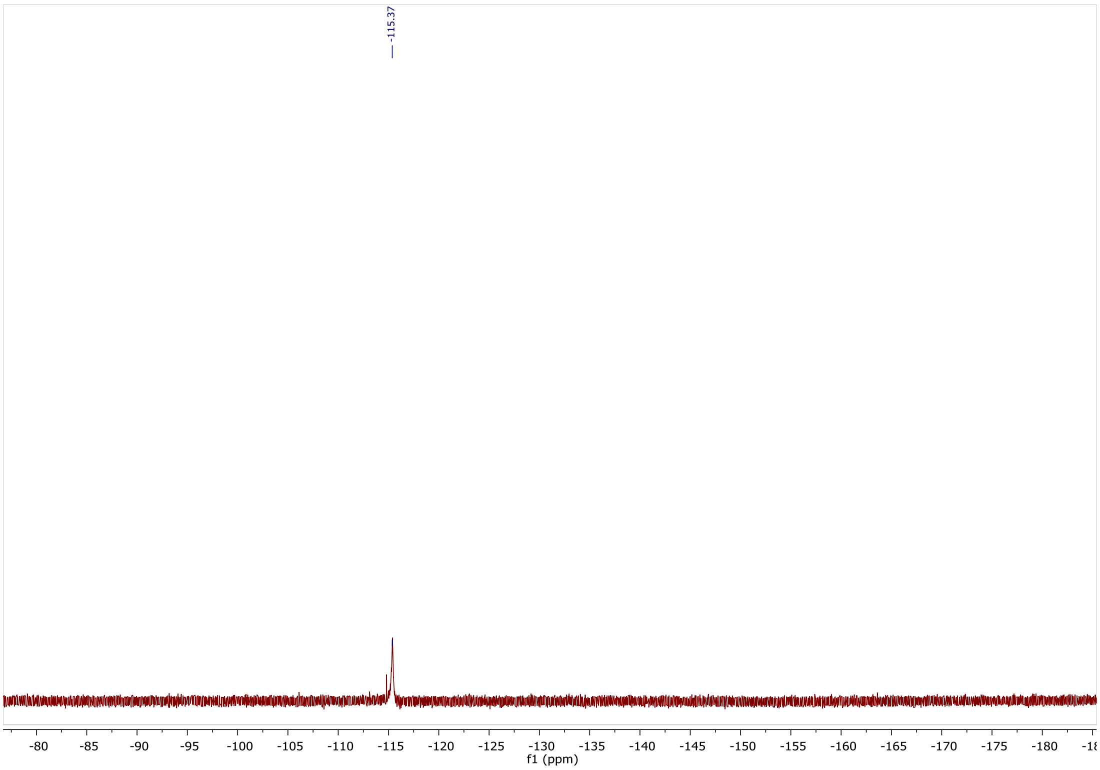
[1]H NMR (400 MHz, $CDCl_3$) of **4Ah**:



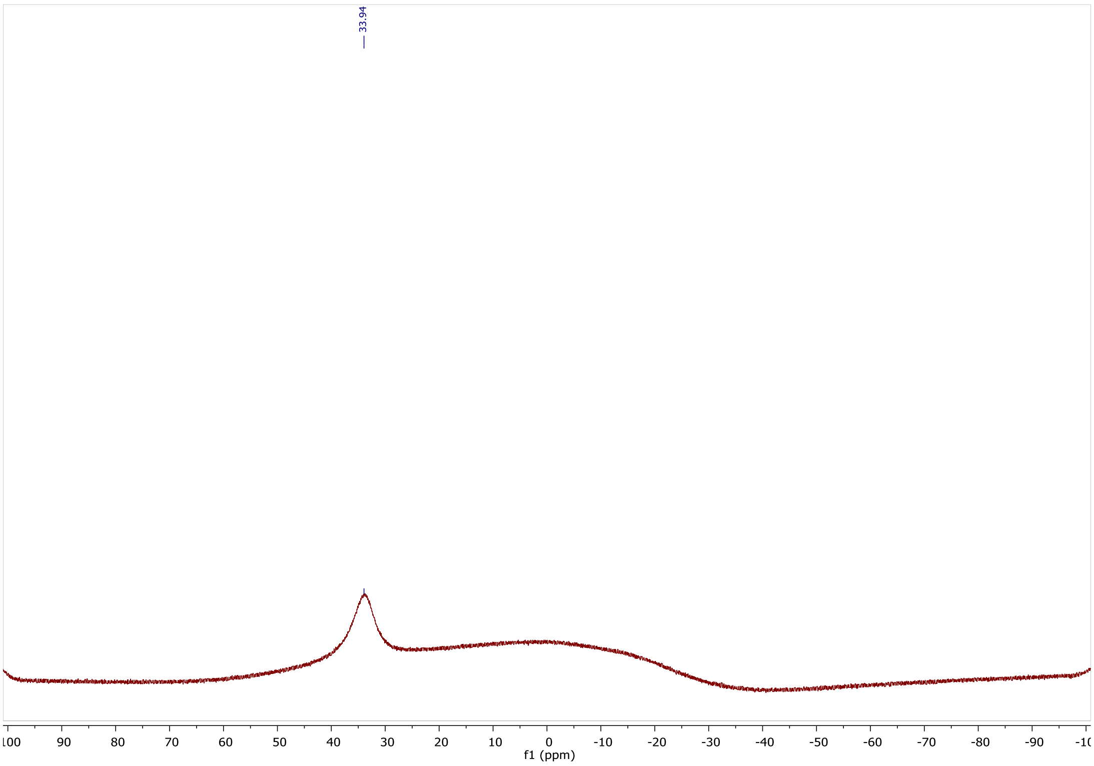
[13]C NMR (100 MHz, $CDCl_3$) of **4Ah**:



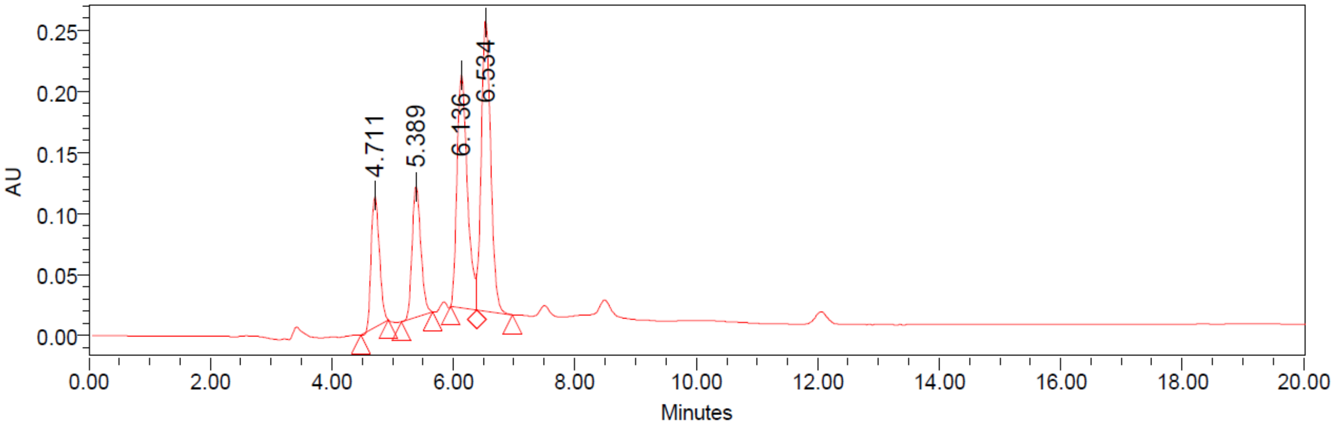
^{19}F NMR (377 MHz, $CDCl_3$) of **4Ah**:



^{11}B NMR (160 MHz, $CDCl_3$) of **4Ah**



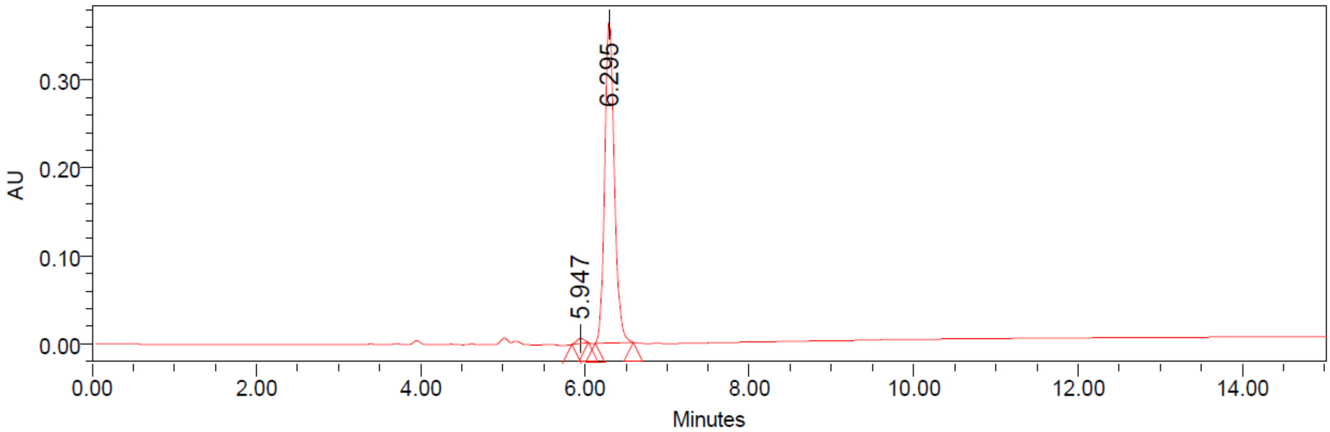
Racemic sample of 4Ah: IB column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 235.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.0 nm	4.711	997646	14.52	107398
2	PDA 235.0 nm	5.389	1071032	15.59	106697
3	PDA 235.0 nm	6.136	2279025	33.18	190892
4	PDA 235.0 nm	6.534	2521473	36.71	238130

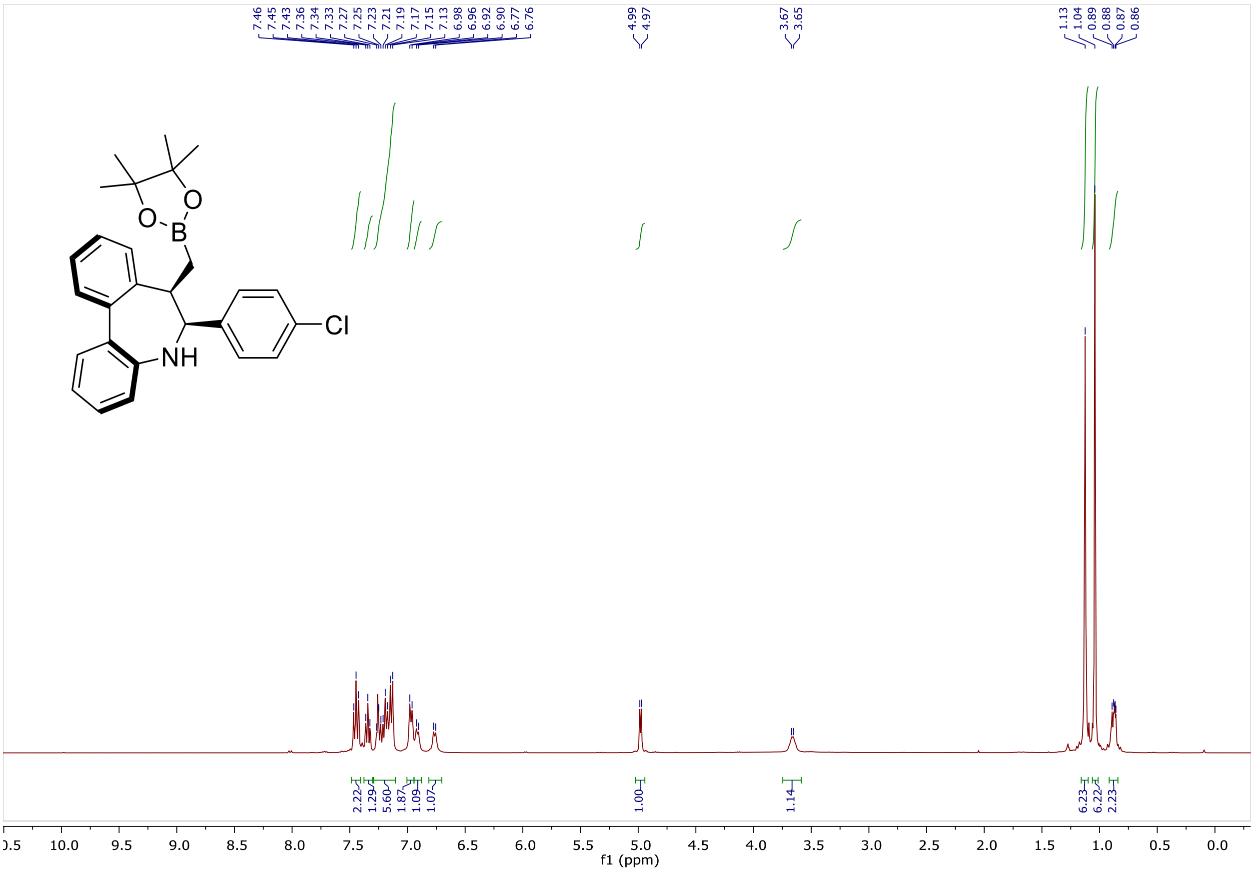
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-4Ah:



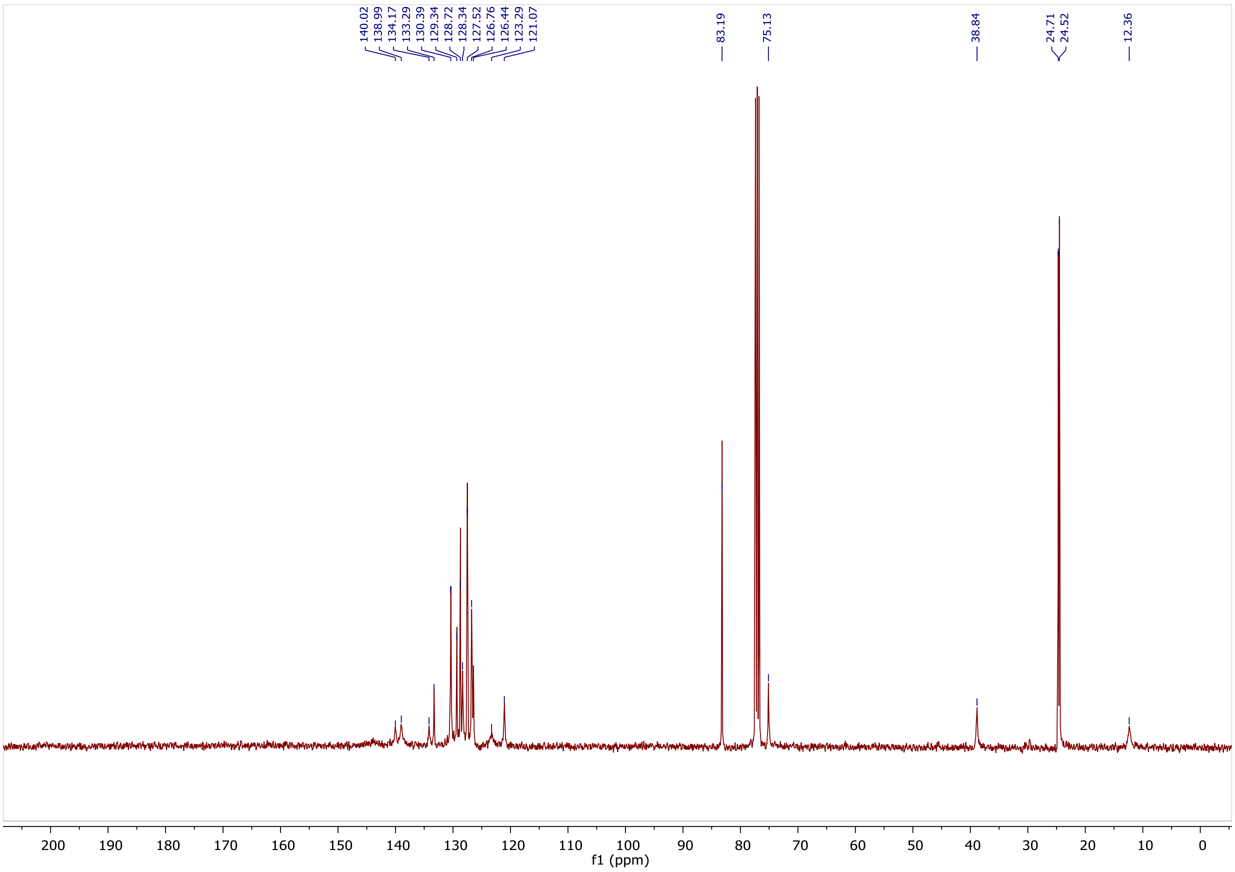
Processed Channel: PDA 235.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 235.0 nm	5.947	38481	1.27	5719
2	PDA 235.0 nm	6.295	2981086	98.73	364880

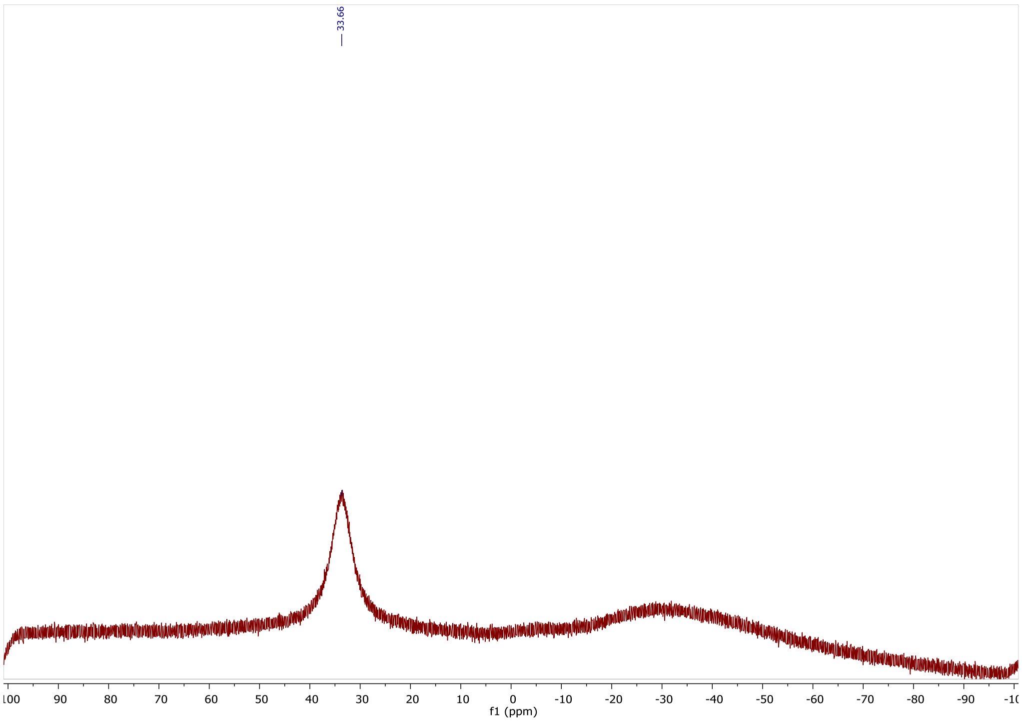
^{1}H NMR (400 MHz, $CDCl_3$) of **4Aj**:



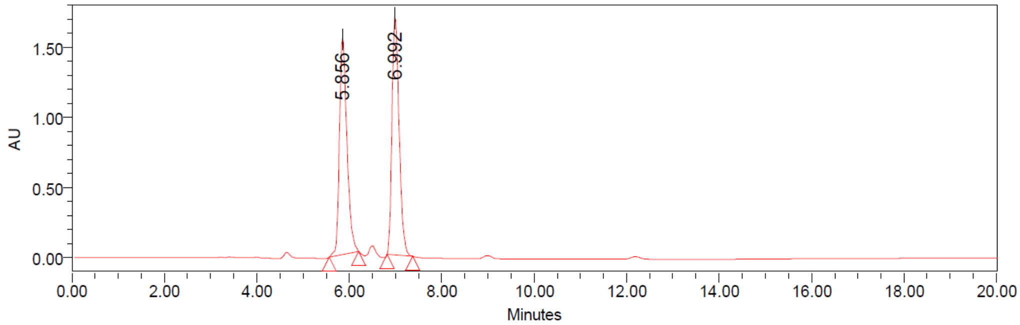
^{13}C NMR (100 MHz, $CDCl_3$) of **4Aj**:



^{11}**B NMR** (160 MHz, $CDCl_3$) of **4Aj**



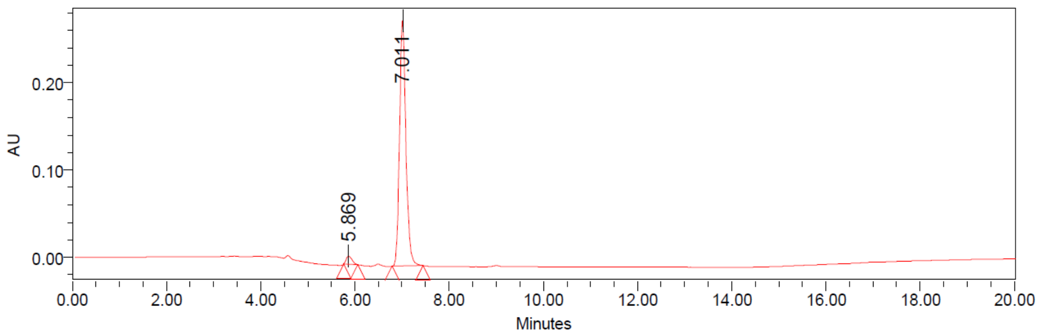
Racemic sample of 4Aj: IB column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	5.856	17287211	48.68	1541413
2	PDA 234.0 nm	6.992	18221420	51.32	1699526

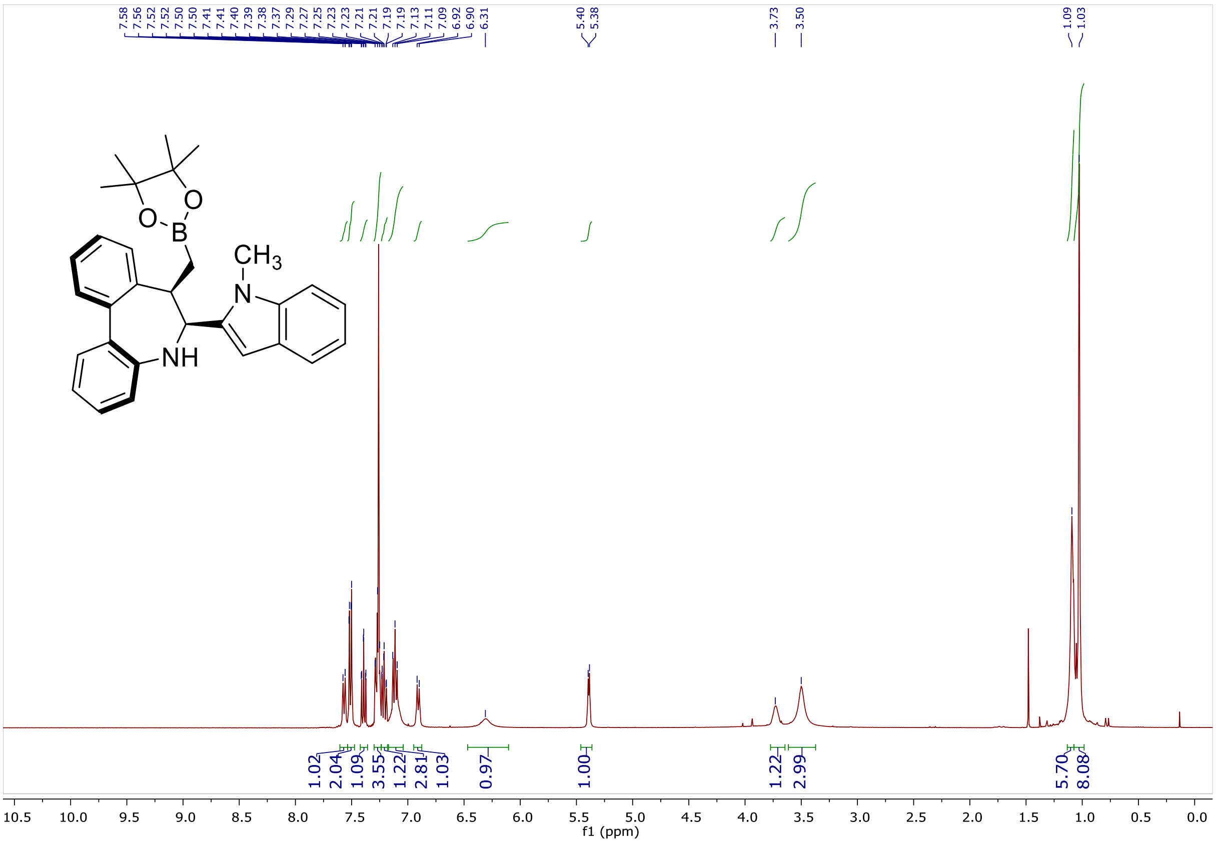
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-4Aj:



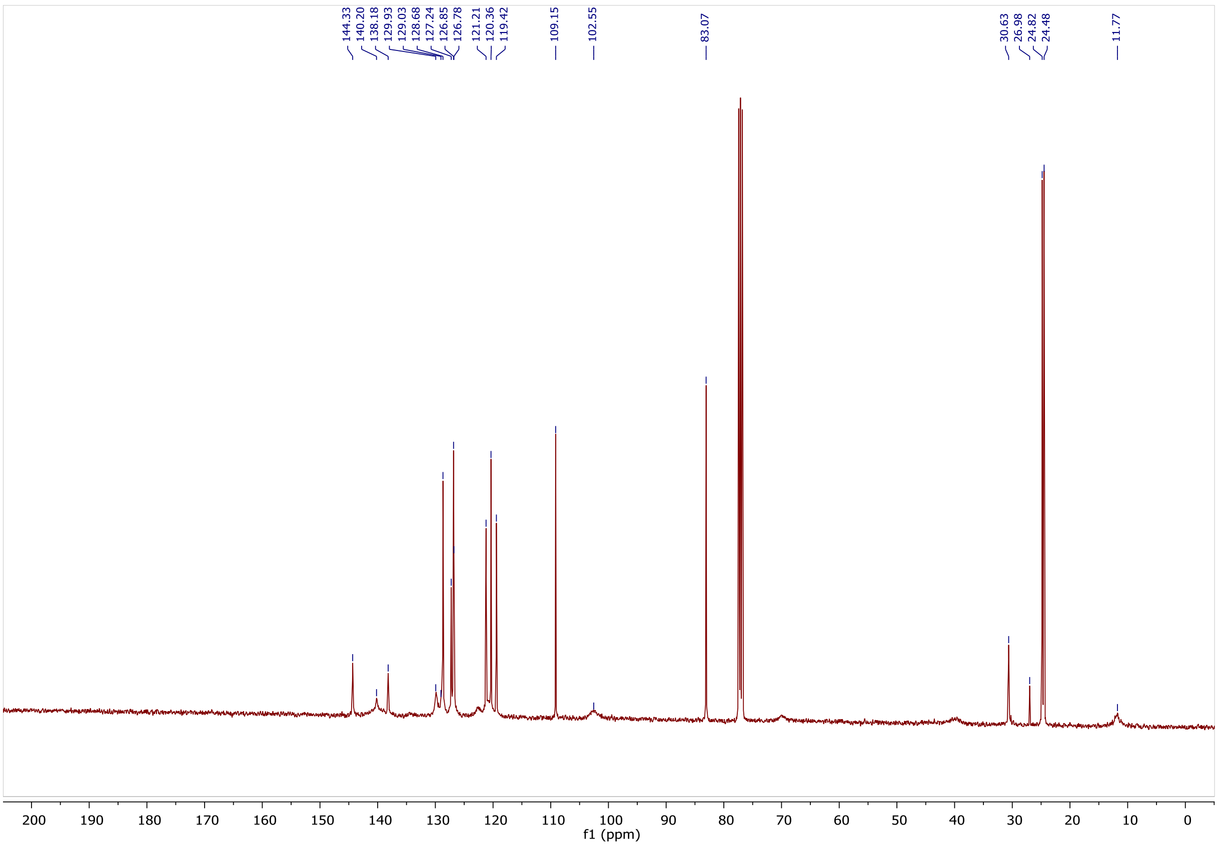
Processed Channel: PDA 234.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.0 nm	5.869	82060	3.00	9380
2	PDA 234.0 nm	7.011	2657455	97.00	280532

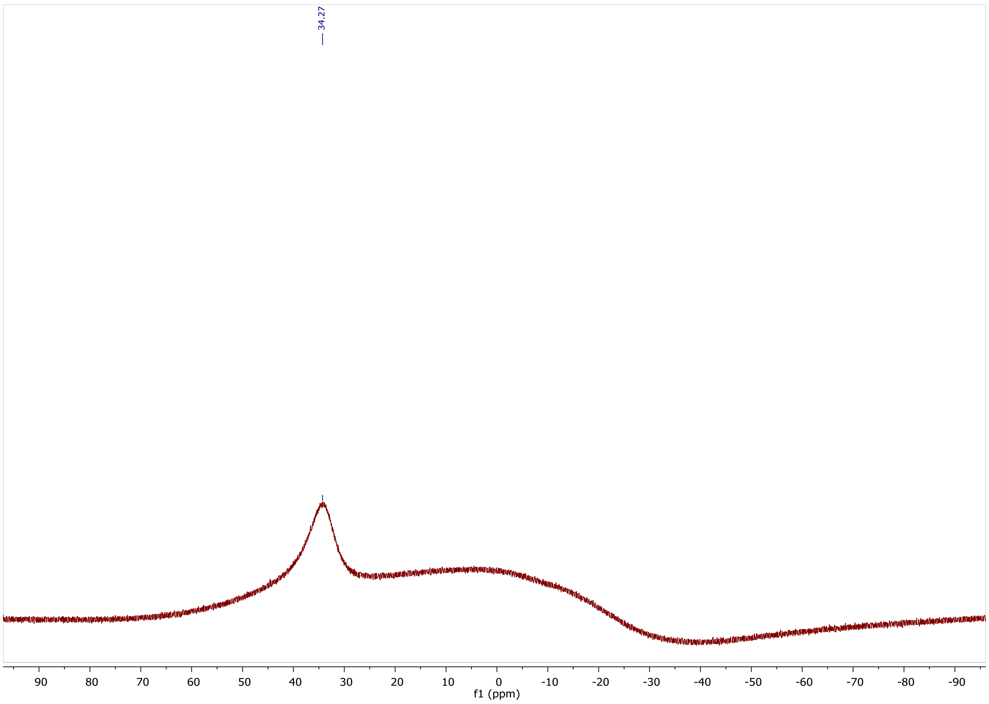
^{1}**H NMR** (400 MHz, $CDCl_3$) of **4At**:



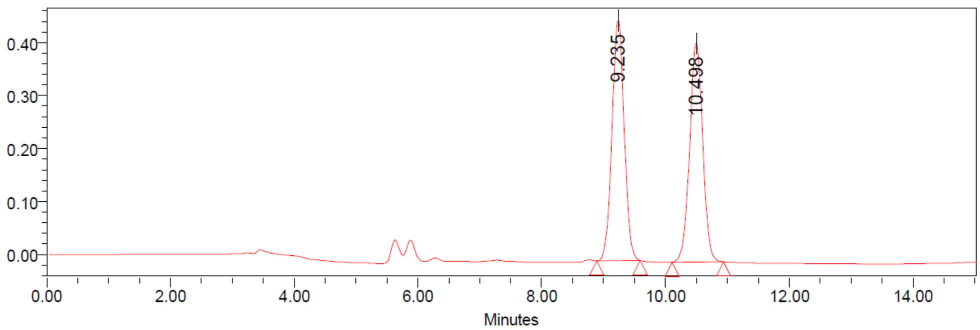
^{13}**C NMR** (100 MHz, $CDCl_3$) of **4At**:



^{11}B NMR (160 MHz, $CDCl_3$) of **4At**



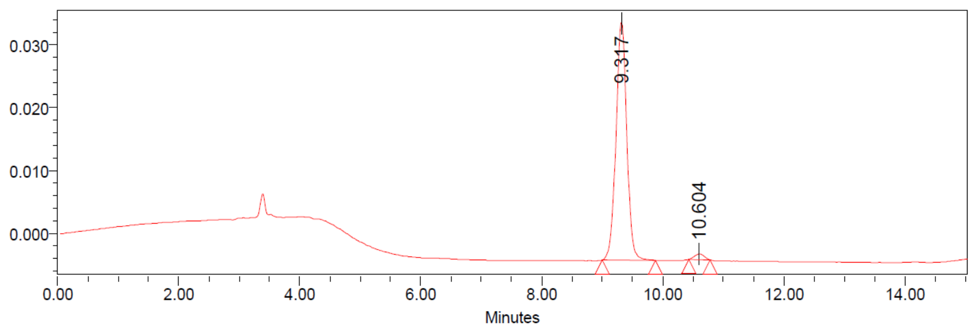
Racemic sample of 4At: IA column, *n*-Hex/*i*-PrOH 95:5, T = 30 °C, F = 1 mL/min



Processed Channel: PDA 227.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 227.0 nm	9.235	6171524	50.51	453877
2	PDA 227.0 nm	10.498	6047631	49.49	413472

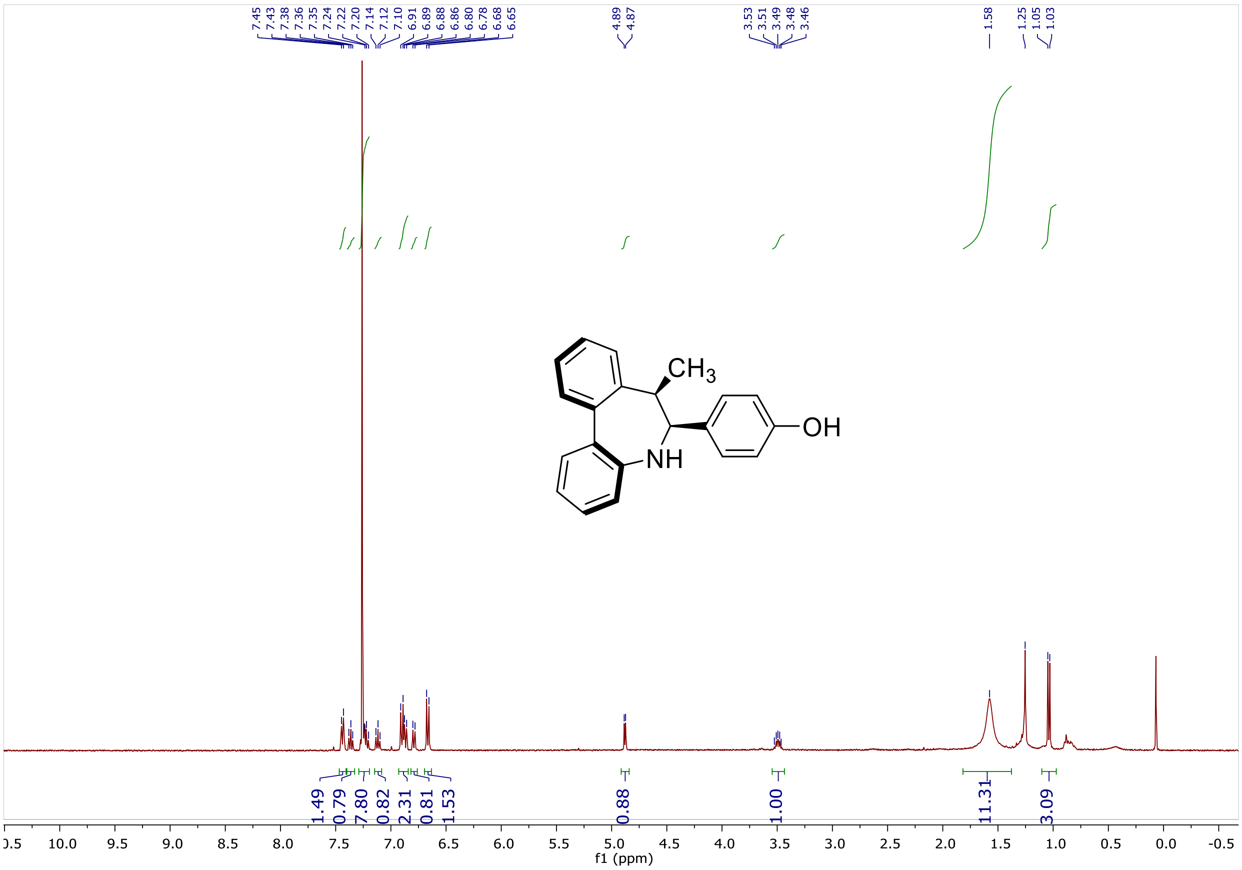
Enantioenriched sample of (*S*$_a$,6*S*,7*R*)-4At:



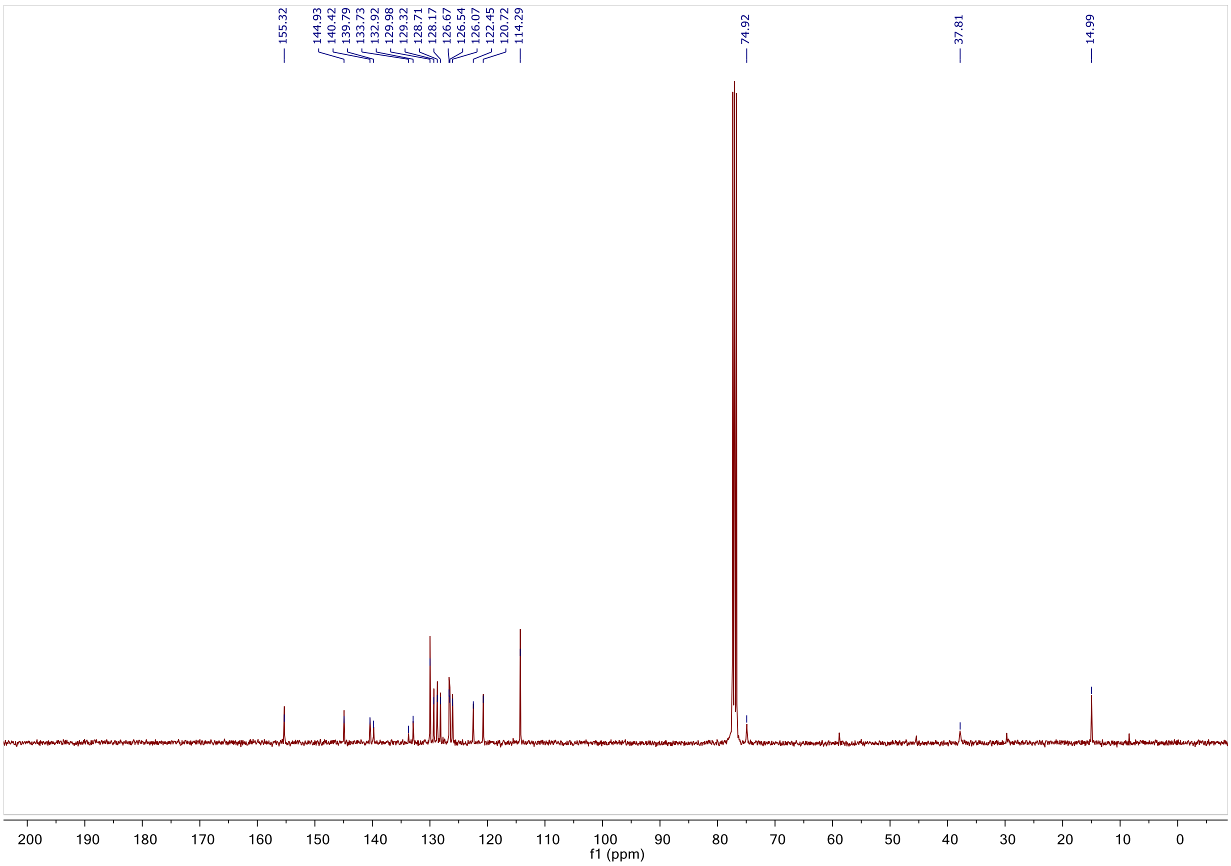
Processed Channel: PDA 238.8 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 238.8 nm	9.317	468495	97.87	37822
2	PDA 238.8 nm	10.604	10172	2.13	904

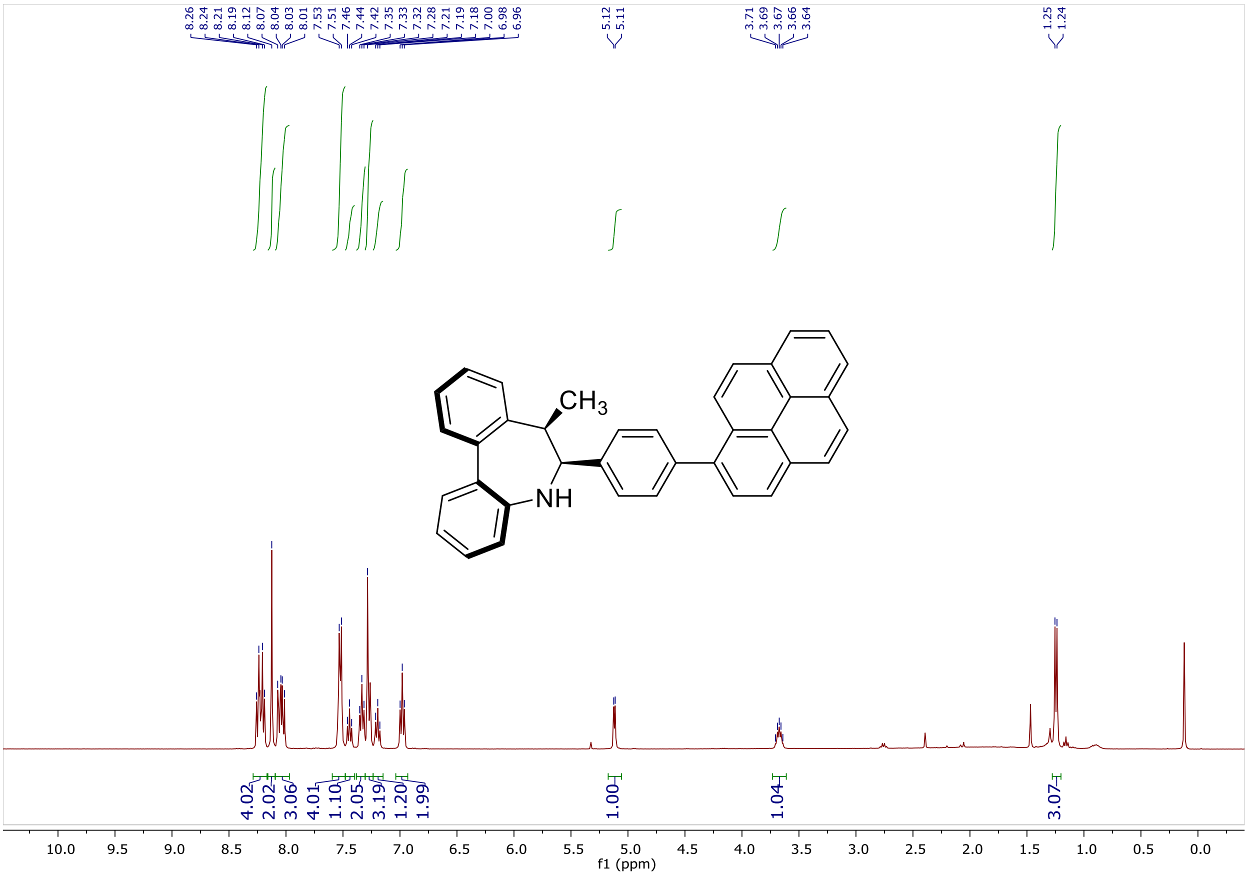
[1]H NMR (400 MHz, $CDCl_3$) of **5**:



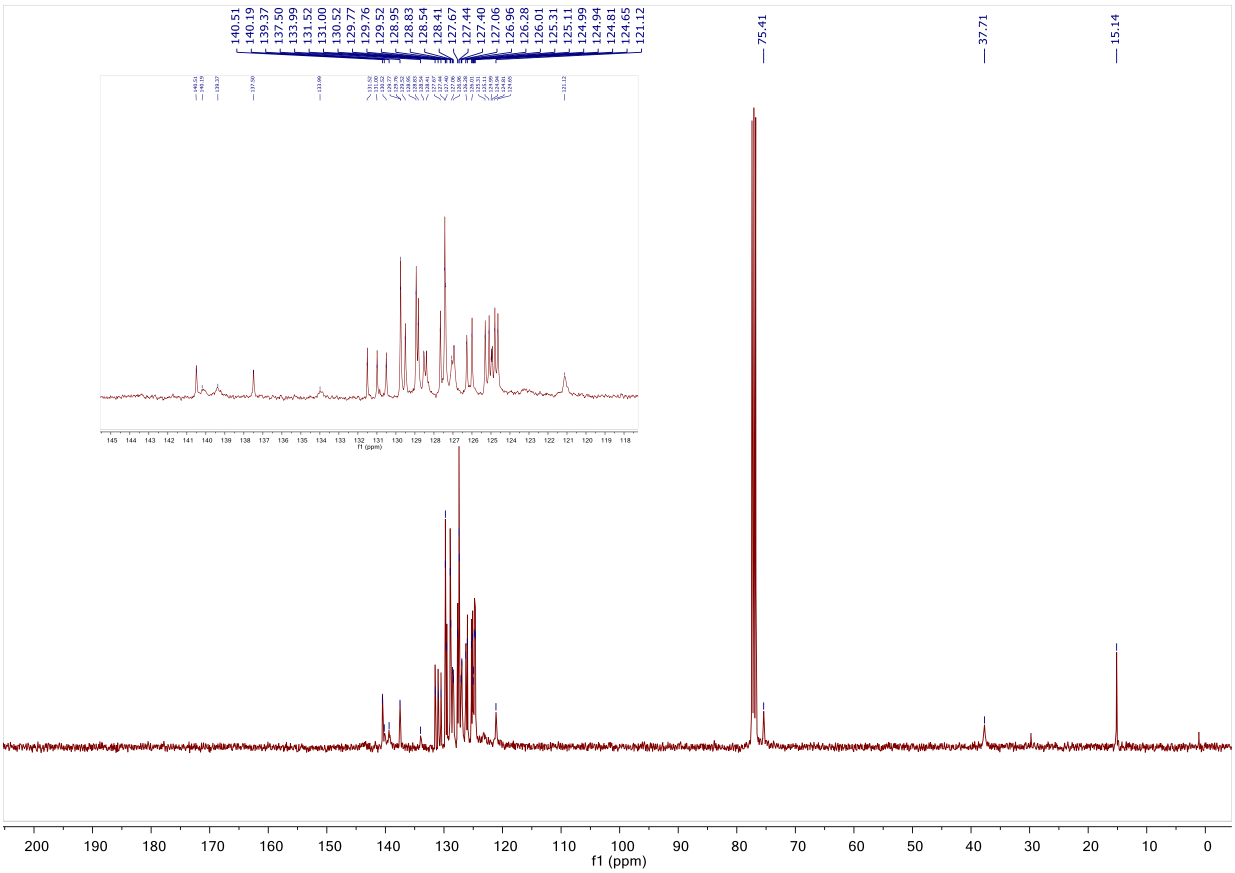
[13]C NMR (100 MHz, $CDCl_3$) of **5**:



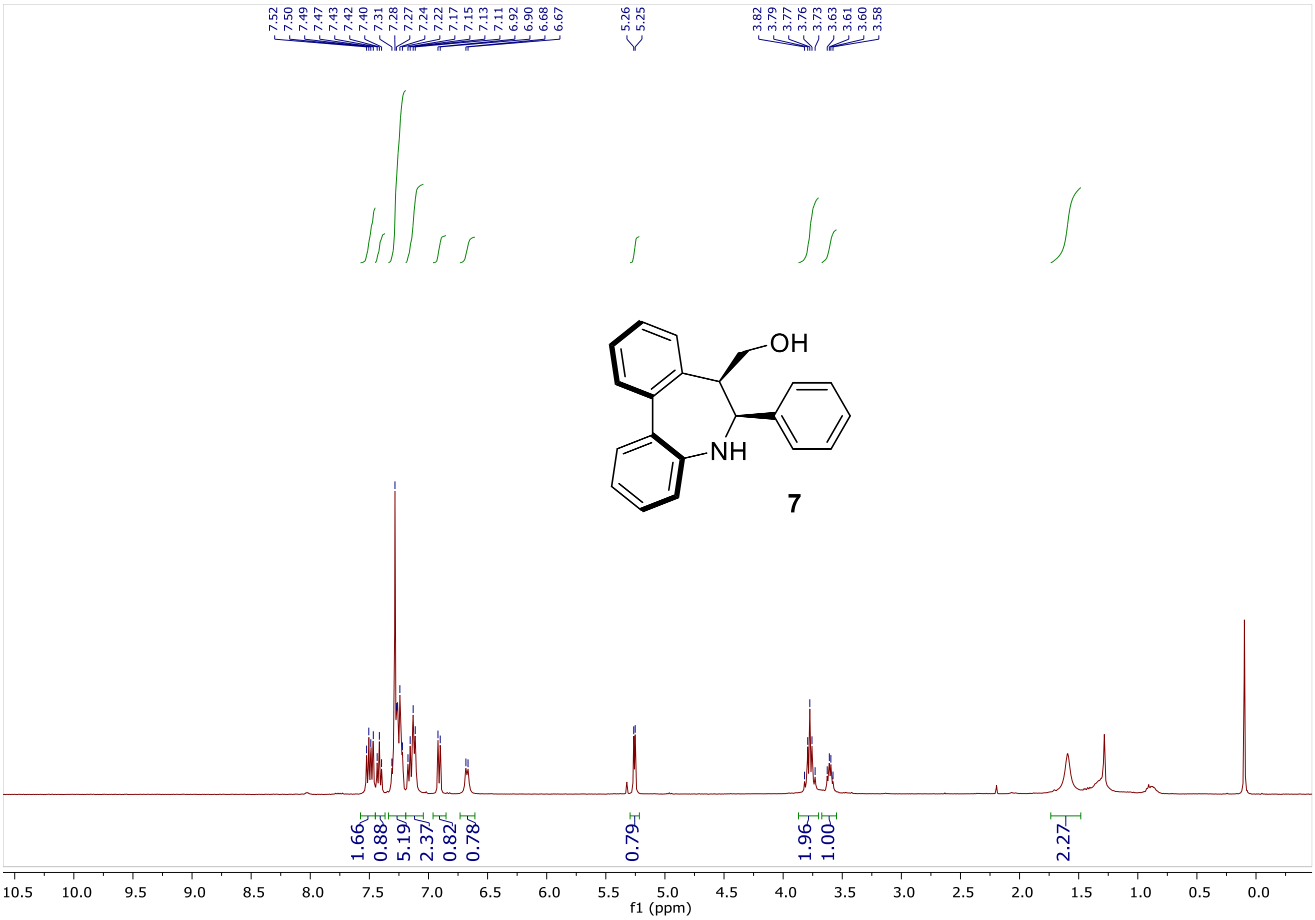
[1]H NMR (400 MHz, $CDCl_3$) of **6**:



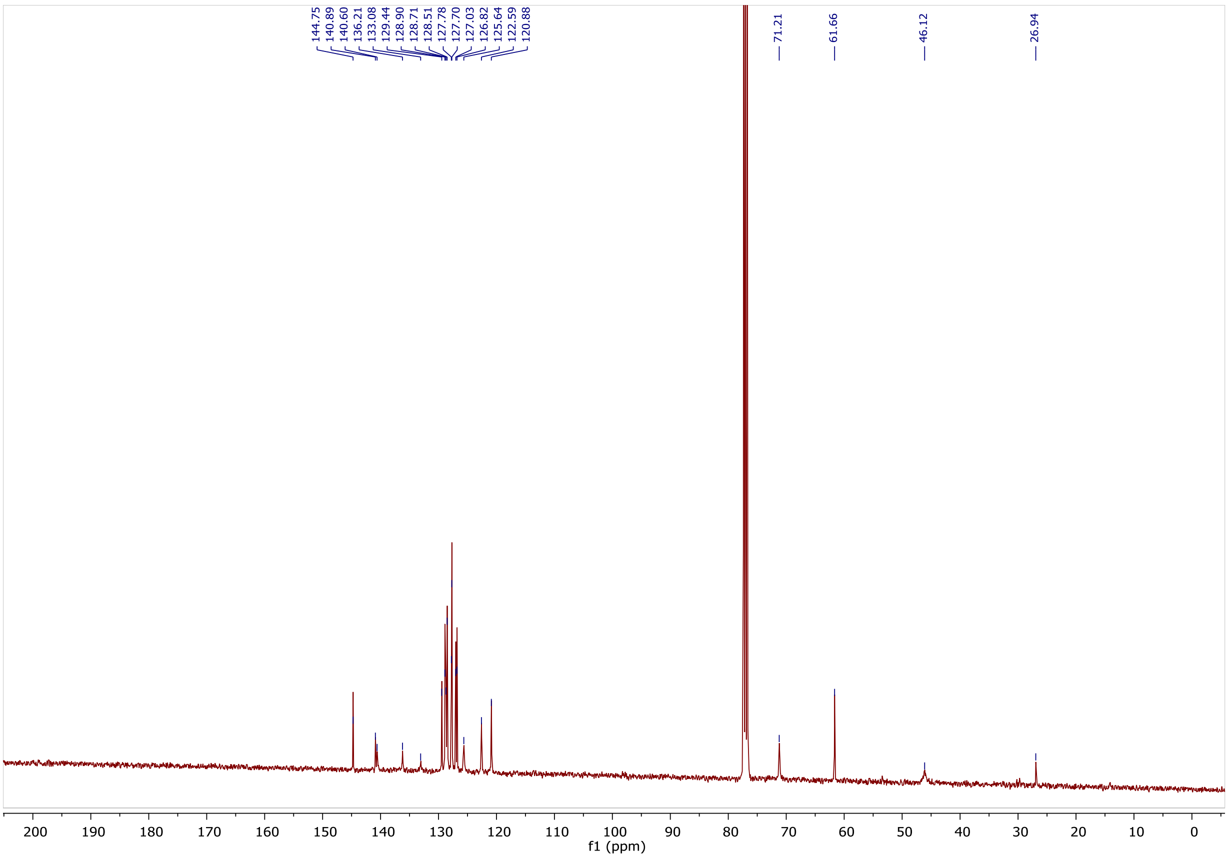
[13]C NMR (100 MHz, $CDCl_3$) of **6**:



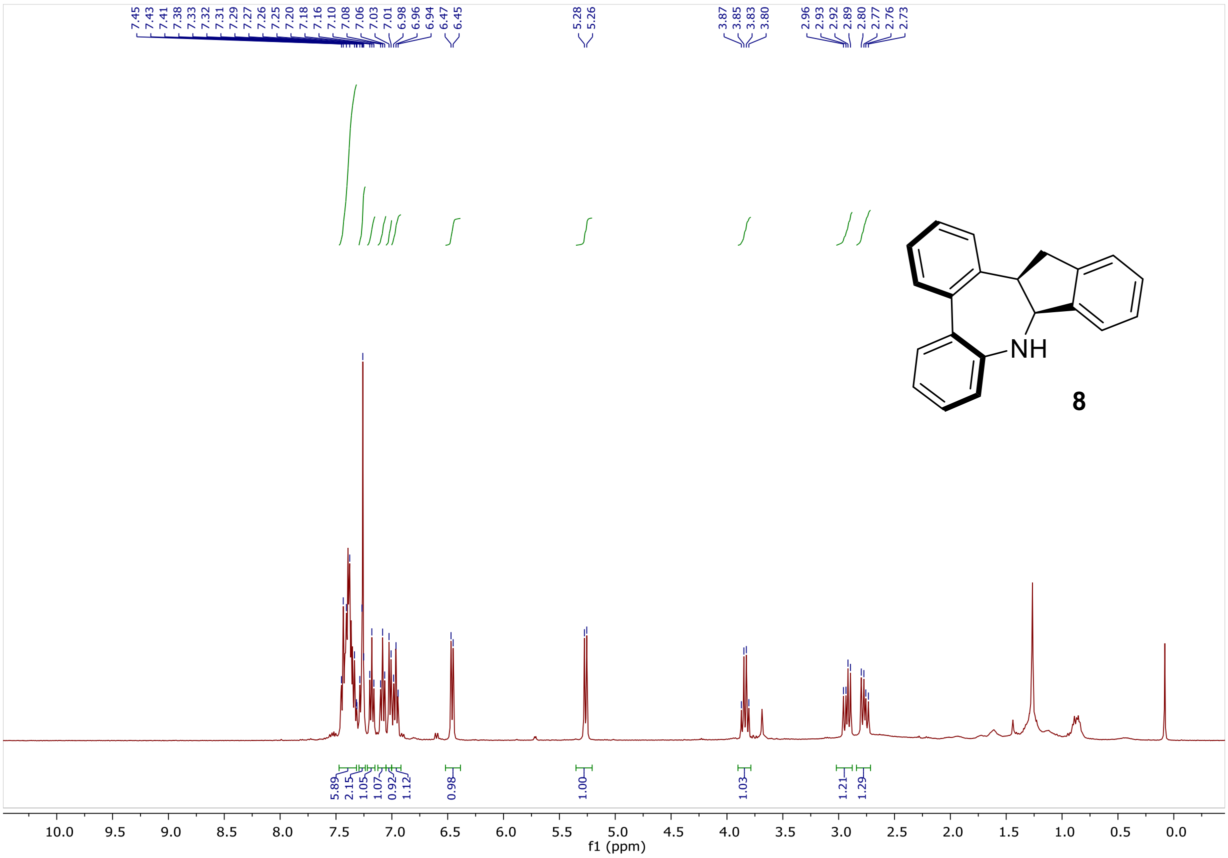
^{1}H NMR (400 MHz, $CDCl_3$) of **7**:



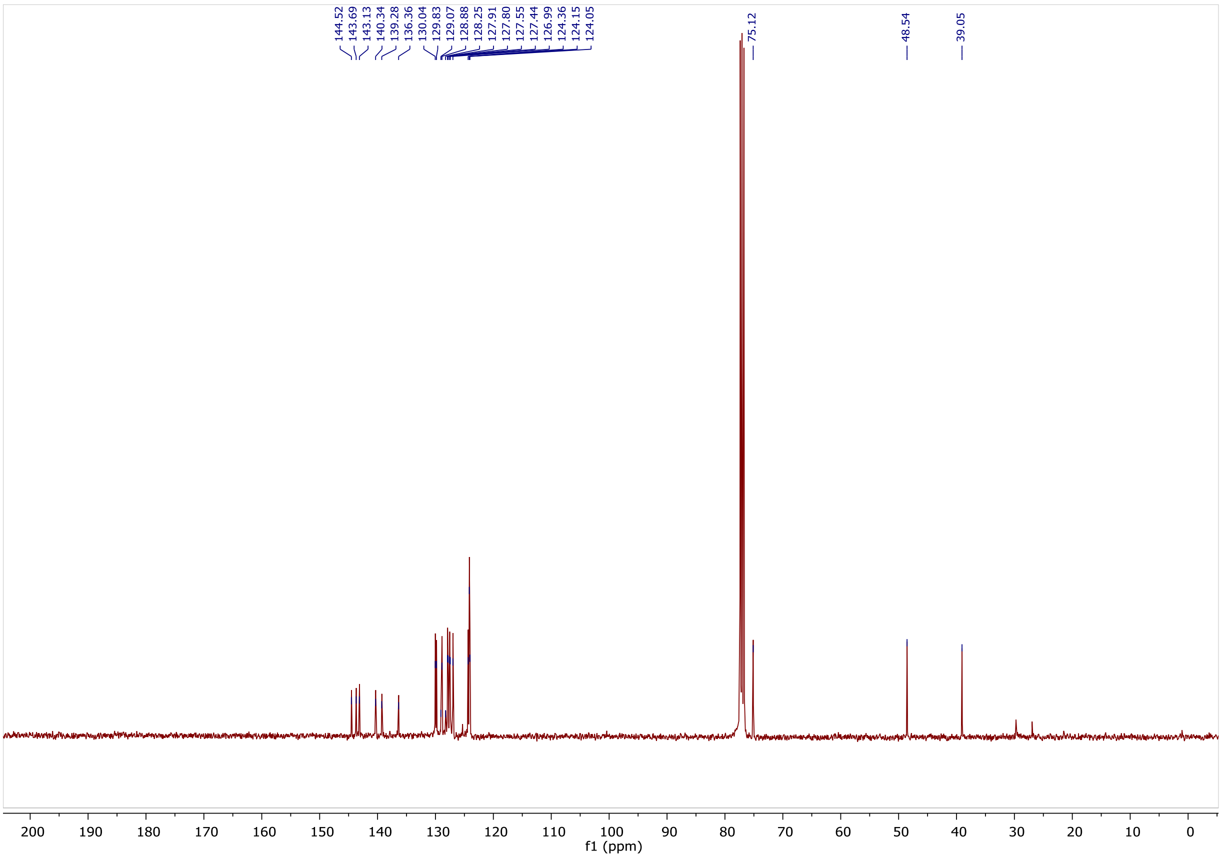
^{13}C NMR (100 MHz, $CDCl_3$) of **7**:



^{1}H NMR (400 MHz, $CDCl_3$) of **8**:



^{13}C NMR (100 MHz, $CDCl_3$) of **8**:



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