Electronic Supplementary Material (ESI) for ChemComm.

— Supporting Information —

Regiocontrolled Synthesis of Enantioenriched 2-Substituted Dehydropiperidines by Stereospecific Allyl-Allyl Cross-Coupling of Chiral Allylic Boronate

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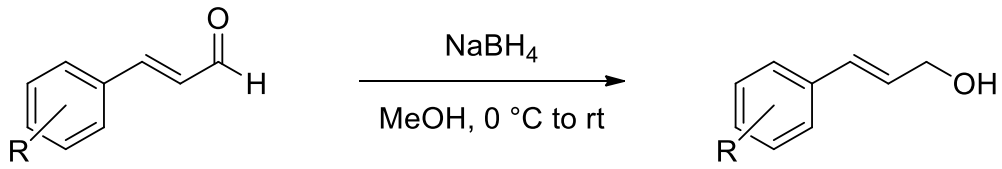
1. General Information

All reactions were performed under nitrogen atmosphere in flame dried glassware, unless otherwise stated. Tetrahydrofuran (THF), dichloromethane (DCM) and toluene were purified using a cartridge solvent purification system. Diethyl ether (Et_2O) was distilled over CaH_2. Cyclopentyl methyl ether (CPME) was purchased from Sigma-Aldrich and used as received. *N*,*N*-Diisopropylethylamine (DIPEA) was purchased from Sigma-Aldrich and distilled over CaH_2 under nitrogen prior to use. *N*,*N*-dimethylaniline (DMA) and 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU) were purchased from Sigma Aldrich and Combi-Blocks Inc., respectively, and distilled over CaH_2 under vacuum prior to use. Pinacolborane was purchased from Oakwood Chemicals and used without further purification. 1-*tert*-Butoxycarbonyl-4-piperidone, 1-carbobenzoxy-4-piperidone, perfluorobutanesulfonyl fluoride (NfF) and tris(dibenzylideneacetone)dipalladium(0) were purchased from Combi-Blocks Inc. and used as purchased without further purification. Palladium(II) acetate, Taniaphos, and DPEphos were purchased from STREM Chemicals. Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F254 plates and visualized using UV light, phosphomolybdic acid (PMA) stain, and $KMnO_4$ stain. Flash chromatography was performed on ultra-pure silica gel 230-400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded on Agilent/Varian INOVA-400, INOVA-500, INOVA-600 or INOVA-700 MHz instruments. The residual solvent proton (^1H) and carbon (^{13}C) signals were used as internal references. ^1H NMR data are represented as follows: Chemical Shift in ppm (δ) downfield from trimehtylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; t, triplet; app t, apparent triplet; dd, doublet of doublets; dt, doublet of triplets; m, multiplet. The error of coupling constants from ^1H NMR spectra is estimated to be ± 0.3 Hz. High-resolution mass spectra were recorded by the University of Alberta Mass Spectrometry Services Laboratory using electrospray ionization (ESI) method. Infrared spectra were obtained from a Nicolet Magna-IR machine with frequencies expressed in cm^{-1}. The enantiomeric excess ratios for optically enriched compounds were determined using a HPLC Agilent instrument with a Chiralcel-OD or Chiralpak IA or IB or IC column as specified in the following individual procedures.

2. Experimental Procedures for the Synthesis of Starting Materials

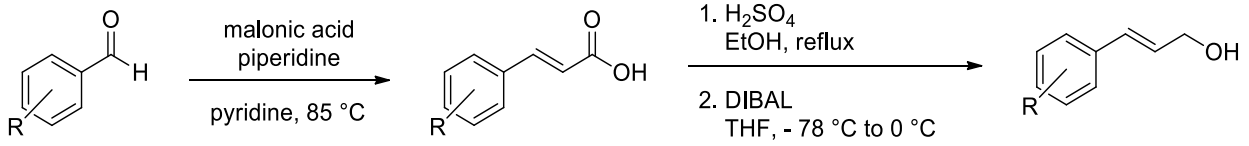
2.1 Preparation of Cinnamyl Alcohol Derivatives

Representative Procedure A



In a round bottom flask equipped with a stir bar, 4-methoxycinnamaldehyde (405 mg, 2.50 mmol) was mixed with methanol (10 mL) and cooled down to 0 °C and kept stirring for 5 min. $NaBH_4$ (94.6 mg, 2.50 mmol) was then added to the solution in three portions. The ice bath was removed, and the reaction mixture was allowed to stir at room temperature for 1 h. The reaction was quenched with H_2O and extracted with Et_2O (40 mL × 3). The organic layers were washed with brine, dried over Na_2SO_4, filtered, and then concentrated *in vacuo* to afford 4-methoxycinnamal alcohol as a yellow oil which was used in the next step without further purification.

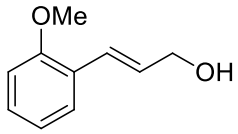
Representative Procedure B



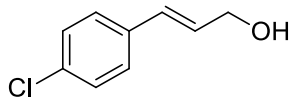
To a stirred solution of malonic acid (1.62 g, 15.6 mmol) in pyridine and piperidine (102 µL, 1.20 mmol) in a round bottom flask, 3, 5-dimethylbenzaldehyde was added slowly under 85 °C. The resulting reaction mixture was allowed to stir for 6 h then cooled down to room temperature before it was neutralized with 10% hydrochloric acid aqueous mixture under ice bath where a white solid was precipitated. The solid was filtered and washed with cooled water and dried under vacuum at 60 °C overnight to afford the corresponding (2*E*)-3-(3,5-dimethylphenyl)-2-propenoic acid in 78% yield.

The acid (666 mg, 3.78 mmol) was mixed with ethanol (50.0 mL) in a round bottom flask and a few drops of H_2SO_4 were added. The reaction mixture was allowed to stir at reflux overnight. The mixture was diluted with H_2O and extracted with EtOAc (50 mL × 3). The organic layer was

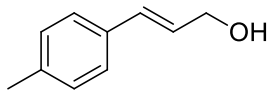
washed with $NaHCO_3$, water, brine, then dried over Na_2SO_4, filtered and the solvent was removed. The crude was then transferred into a flame dried round bottom flask equipped with a stir bar and mixed with THF (30.0 mL) under N_2 atmosphere. The reaction flask was cooled down to –78 °C then DIBAL (9.50 mL, 9.50 mmol, 1.00 M in THF) was added slowly to the reaction mixture. Upon complete addition of DIBAL, the solution was warmed up to 0 °C and kept stirring for 1 h. The reaction mixture was quenched with 15% aqueous NaOH and $MgSO_4$ was added and kept stirring for 5 min. The solids were filtered out and the organic layer was concentrated *in vacuo*. The corresponding crude alcohol was used in the next step without further purification.



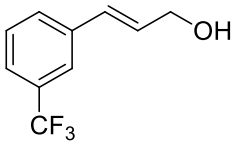
(*E*)-3-(2-Methoxyphenyl)prop-2-en-1-ol (S1). Prepared according to representative procedure A from commercial 4-methoxycinnamaldehyde (1.00 g, 6.20 mmol), $NaBH_4$ (234 mg, 6.20 mmol): yellow oil (955 mg, 97% crude yield). Spectral data are in accordance with the literature.[1]



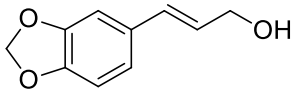
(*E*)-3-(4-Chlorophenyl)prop-2-en-1-ol (S2). Prepared according to representative procedure A from commercial 4-chlorocinnamaldehyde (415 mg, 2.50 mmol), $NaBH_4$ (94.5 mg, 2.50 mmol): yellow oil (371 mg, 88% crude yield). Spectral data are in accordance with the literature.[1]



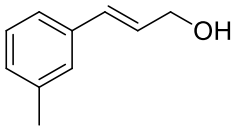
(*E*)-3-(*p*-Tolyl)prop-2-en-1-ol (S3). Prepared according to representative procedure A from commercial (*E*)-3-(*p*-tolyl)acrylaldehyde (500 mg, 3.40 mmol), $NaBH_4$ (129 mg, 3.40 mmol): yellow oil (468 mg, 93% crude yield). Spectral data are in accordance with the literature.[1]



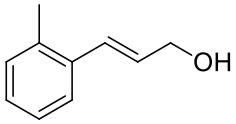
(*E*)-3-(3-(Trifluoromethyl)phenyl)prop-2-en-1-ol (S4). Prepared according to representative procedure B from commercial 3-(trifluoromethyl)benzaldehyde. Spectral data are in accordance with the literature.[2]



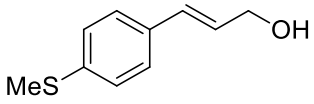
(*E*)-3-(Benzo[*d*][1,3]dioxol-5-yl)prop-2-en-1-ol (S5). Prepared according to representative procedure B from commercial piperonal. Spectral data are in accordance with the literature.[2]



(*E*)-3-(*m*-Tolyl)prop-2-en-1-ol (S6). Prepared according to representative procedure B from commercial *m*-tolualdehyde. Spectral data are in accordance with the literature.[1]

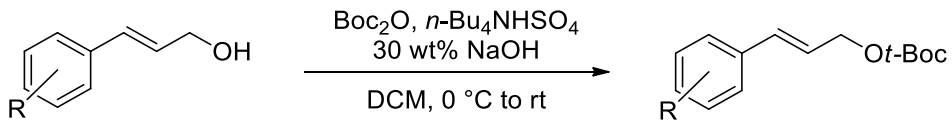


(*E*)-3-(*o*-Tolyl)prop-2-en-1-ol (S7). Prepared according to representative procedure B from commercial *o*-tolualdehyde. Spectral data are in accordance with the literature.[3]

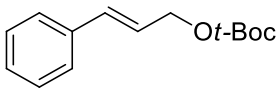


(*E*)-3-(4-(Methylthio)phenyl)prop-2-en-1-ol (S8). Prepared according to representative procedure B from commercial 4-(Methylthio)benzaldehyde. Spectral data are in accordance with the literature.[4]

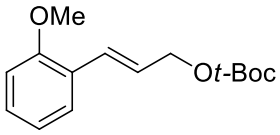
2.2 General Procedure for the Synthesis of Cinnamyl Carbonate Derivatives



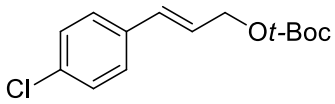
In a round bottom flask equipped with a stir bar, cinnamyl alcohol (500 mg, 3.73 mmol) and DCM (5.00 ml) were added. To the resulting solution, *n*-Bu_4NHSO_4 (25.0 mg, 0.0730 mmol) and Boc_2O (888 mg, 4.07 mmol) at room temperature. The solution was cooled to 0 °C and aqueous solution of NaOH (2.5 mL, 30 wt% solution) was added slowly. The ice-water bath was removed after 10 min and the reaction flask was allowed to stir at room temperature overnight. The reaction mixture was diluted with Et_2O and 1M HCl aqueous solution and was extracted with Et_2O (50 mL × 3). The combined organic layers were washed with water followed by a brine wash and then dried over Na_2SO_4, filtered and then concentrated *in vacuo*. The crude was purified on silica gel (5% Et2O/ pentane) to afford 646 mg (74%) of a clear oil.



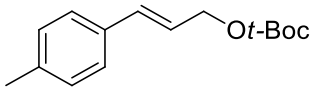
***tert*-Butyl cinnamyl carbonate (S9). The** reaction was performed according to the general procedure using commercial cinnamyl alcohol (500 mg, 3.73 mmol), Bu_4NHSO_4 (25.0 mg, 0.0730 mmol), Boc_2O (888 mg, 4.07 mmol) and NaOH (2.50 mL, 30 wt% solution). The crude reaction mixture was purified on silica gel (5% Et_2O/pentane) to afford the product as colorless oil (646 mg, 74% yield). Spectral data are in accordance with the literature.[5]



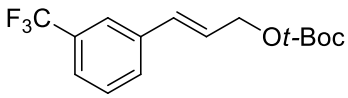
(*E*)-*tert*-Butyl (3-(2-methoxyphenyl)allyl) carbonate (S10). The reaction was performed according to the general procedure using (*E*)-3-(2-methoxyphenyl)prop-2-en-1-ol (985 mg, 6.01 mmol), Bu_4NHSO_4 (42.0 mg, 0.124 mmol), Boc_2O (1.46 g, 6.70 mmol) and NaOH (4.00 mL, 30 wt% solution). The crude reaction mixture was purified on a silica plug (4% Et_2O/pentane) to afford the product as yellow oil (1.51 g, 95% yield). Spectral data are in accordance with the literature.[6]



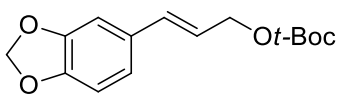
(*E*)-*tert*-Butyl (3-(4-chlorophenyl)allyl) carbonate (S11). The reaction was performed according to the general procedure using (*E*)-3-(4-chlorophenyl)prop-2-en-1-ol (371 mg, 2.20 mmol), Bu_4NHSO_4 (14.0 mg, 0.0410 mmol), Boc_2O (528 mg, 2.42 mmol) and NaOH (2.50 mL, 30 wt% solution). The crude reaction mixture was purified on a silica plug (5% Et_2O/pentane) to afford the product as yellow solid (357 mg, 60% yield). Spectral data are in accordance with the literature.[7]



(*E*)-*tert*-Butyl (3-(*p*-tolyl)allyl) carbonate (S12). The reaction was performed according to the general procedure using (*E*)-3-(*p*-tolyl)prop-2-en-1-ol (468 mg, 3.16 mmol), Bu_4NHSO_4 (21.0 mg, 0.0630 mmol), Boc_2O (758 mg, 3.48 mmol) and NaOH (2.50 mL, 30 wt% solution). The crude reaction mixture was purified on a silica gel (10% Et_2O/pentane) to afford the product as a white solid (514 mg, 66% yield). Spectral data are in accordance with the literature.[8]

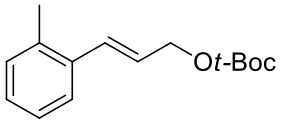


(*E*)-*tert*-Butyl (3-(3-(trifluoromethyl)phenyl)allyl) carbonate (S13). The reaction was performed according to the general procedure using (*E*)-3-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol. (485 mg, 2.40 mmol), Bu_4NHSO_4 (16.0 mg, 0.0480 mmol), Boc_2O (575 mg, 2.64 mmol) and NaOH (2.00 mL, 30 wt% solution). The crude reaction mixture was purified on a silica plug (5% Et_2O/pentane) to afford the product as a yellow oil (482 mg, 67% yield). Spectral data are in accordance with the literature.[8]

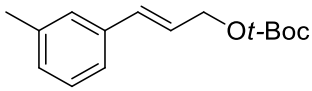


(*E*)-3-(Benzo[*d*][1,3]dioxol-5-yl)allyl *tert*-butyl carbonate (S14). The reaction was performed according to the general procedure using (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)prop-2-en-1-ol (567 mg, 3.18 mmol), Bu_4NHSO_4 (22.0 mg, 0.0630 mmol), Boc_2O (763 mg, 3.50 mmol) and NaOH (2.50

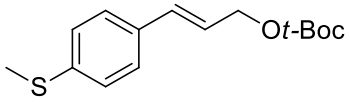
mL, 30 wt% solution). The crude reaction mixture was purified on a silica plug (10% Et_2O/pentane) to afford the product as a colorless oil (533 mg, 64% yield). Spectral data are in accordance with the literature.[7]



(*E*)-*tert*-Butyl (3-(*o*-tolyl)allyl) carbonate (S15). The reaction was performed according to the general procedure using (*E*)-3-(*o*-tolyl)prop-2-en-1-ol (1.48 g, 10.0 mmol), Bu_4NHSO_4 (67.8 mg, 0.200 mmol), Boc_2O (2.62 g, 12.0 mmol) and NaOH (5.00 mL, 30 wt% solution). The crude reaction mixture was purified on a silica plug (5% Et_2O/pentane) to afford the product as a colorless oil (1.69 g, 68% yield). Spectral data are in accordance with the literature.[9]

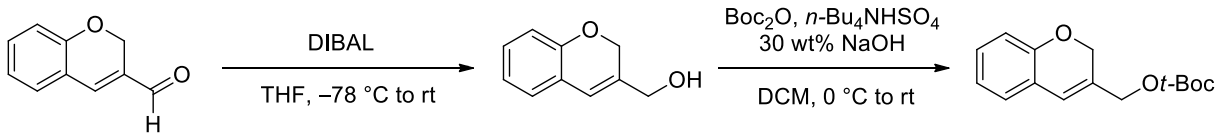


(*E*)-*tert*-Butyl (3-(*m*-tolyl)allyl) carbonate (S16). The reaction was performed according to the general procedure using (*E*)-3-(*m*-tolyl)prop-2-en-1-ol (1.63 g, 11.0 mmol), Bu_4NHSO_4 (74.7 mg, 0.220 mmol), Boc_2O (2.64 g, 12.1 mmol) and NaOH (5.00 mL, 30 wt% solution). The crude reaction mixture was purified on a silica plug (5% Et_2O/pentane) to afford the product as a colorless oil (1.94 g, 71% yield). Spectral data are in accordance with the literature.[9]



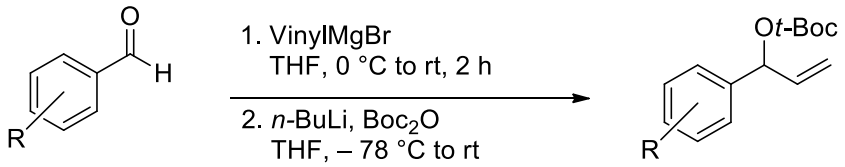
(*E*)-*tert*-Butyl (3-(4-(methylthio)phenyl)allyl) carbonate (S17). The reaction was performed according to the general procedure using (*E*)-3-(4-(methylthio)phenyl)prop-2-en-1-ol (900 mg, 5.00 mmol), Bu_4NHSO_4 (33.9 mg, 0.100 mmol), Boc_2O (1.20 g, 5.50 mmol) and NaOH (4.00 mL, 30 wt% solution). The crude reaction mixture was purified on a silica gel (10% Et_2O/pentane) to afford the product as a white solid (1.17 g, 82% yield): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.25 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.71 (dd, *J* = 6.5, 1.3 Hz, 2H), 2.48 (s, 3H), 1.50 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.9, 138.1, 133.5, 132.7, 126.6, 126.1, 121.9, 81.8, 67.1, 27.4, 15.3; **m.p.** = 56.5–58.3 °C; **IR**

(microscope, cm^{-1}) 3074, 2980, 2923, 1739, 1477, 1274, 1254, 1161; **HRMS** (ESI-TOF): For $C_{15}H_{20}NaO_3S$ $(M + Na)^+$: calcd. 303.1025; found 303.1025.

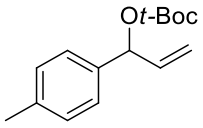


(2*H*-Chromen-3-yl)methyl *tert*-butyl carbonate (S18). To a stirred solution of 2*H*-chromene-3-carbaldehyde (400 mg, 2.50 mmol) in THF (8.00 mL), DIBAL (7 mL of 1.10 M solution in hexane, 7.70 mmol, 3.10 equiv) was added dropwise at –78 °C and kept stirring for 1 h. The reaction was quenched with MeOH and kept stirring for another hour and filtered through a pad of celite. The filtrate was concentrated *in vacuo* to give the allylic alcohol which was used with no further purification in the next step. In a round bottom flask equipped with a stir bar, the alcohol intermediate (2.50 mmol) and DCM (5 ml) were added. To the resulting solution, *n*-Bu_4NHSO_4 (17.0 mg, 0.0500 mmol) and Boc_2O (655 mg, 3.00 mmol) at room temperature. The solution was cooled to 0 °C and aqueous solution of NaOH (1.40 mL, 30 wt% solution) was added slowly. The ice-water bath was removed after 10 min and the reaction flask was allowed to stir at room temperature overnight. The reaction mixture was diluted with Et_2O and 1M HCl aqueous solution and was extracted with Et_2O (50 mL × 3). The combined organic layers were washed with water followed by a brine wash and then dried over Na_2SO_4, filtered and then concentrated *in vacuo*. The crude was purified on silica gel (5% Et_2O/pentane) to afford 472 mg (72%) of a yellow oil: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.12 (td, *J* = 7.9, 1.6 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.87 (td, *J* = 7.4, 1.1 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.46 (s, 1H), 4.80 (s, 22H), 4.63 (s, 2H), 1.50 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 153.5, 153.4, 129.6, 128.2, 127.0, 123.5, 121.8, 121.5, 115.7, 82.7, 67.1, 66.3, 27.8; **IR** (microscope, cm^{-1}) 2980, 2935, 1742, 1487, 1369, 1282 1254 1161; **HRMS** (ESI-TOF): For $C_{15}H_{18}NaO_4$ $(M + Na)^+$: calcd. 285.1097; found 285.1094.

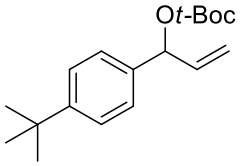
2.3 General Procedure for the Synthesis of Benzylic Allylic Secondary Carbonates



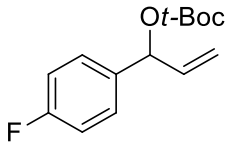
Representative Procedure: In a flamed dried round bottom flask equipped with a stir bar under nitrogen atmosphere, *p*-tolyl aldehyde (601 mg, 5.00 mmol) was dissolved in 20 mL of THF, and the solution was kept stirring at 0 °C for 10 minutes. Vinylmagnesium bromide solution in THF (6.5 mL, 1.0 M, 1.3 equiv) was added to the solution dropwise over 10 min then the reaction was warmed to room temperature and kept stirring for 2 h. The reaction mixture was quenched with 20 mL of NH_4Cl and extracted with EtOAc (50 mL × 3). The organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The concentrated crude was then transferred into a round bottom flask charged with a stir bar and mixed with THF (20 mL). The solution was cooled down to –78 °C and nBuLi in THF (2.2 mL, 2.5 M, 1.1 equiv) was added dropwise. The solution stirred for 30 minutes, then Boc_2O (1.6 g, 7.5 mmol, 1.5 equiv) was added. The reaction mixture was warmed to room temperature and kept stirred for 16 h. The reaction was quenched with water (20 mL) and extracted with Et_2O (50 mL × 3). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The crude was purified on silica gel (5% Et_2O/ pentane) to afford 820 mg (66%) of a clear oil.



***tert*-Butyl (1-(*p*-tolyl)allyl) carbonate (S19). The** reaction was performed according to the general procedure using *p*-tolyl aldehyde (600 mg, 5.0 mmol), Vinylmagnesium bromide solution in THF (6.5 mL, 1.0 M, 1.3 equiv), nBuLi in THF (2.2 mL, 2.5 M, 1.1 equiv), and Boc_2O (1.6 g, 7.5 mmol, 1.5 equiv) The crude was purified on silica gel (5% Et_2O/ pentane) to afford 820 mg (66%) of a clear oil. Spectral data are in accordance with the literature.[10]

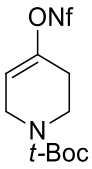


***tert*-Butyl (1-(4-(*tert*-butyl)phenyl)allyl) carbonate (S20). The** reaction was performed according to the general procedure using 4-(*tert*-butyl)benzaldehyde (810 mg, 5.0 mmol), Vinylmagnesium bromide solution in THF (6.5 mL, 1.0 M, 1.3 equiv), nBuLi in THF (2.2 mL, 2.5 M, 1.1 equiv), and Boc_2O (1.6 g, 7.5 mmol, 1.5 equiv) The crude was purified on silica gel (5% Et_2O/ pentane) to afford 790 mg (54%) of a white solid. Spectral data are in accordance with the literature.[11]



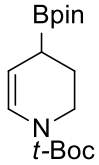
***tert*-Butyl (1-(4-fluorophenyl)allyl) carbonate (S21). The** reaction was performed according to the general procedure using 4-fluorobenzaldehyde (620 mg, 5.0 mmol), Vinylmagnesium bromide solution in THF (6.5 mL, 1.0 M, 1.3 equiv), nBuLi in THF (2.2 mL, 2.5 M, 1.1 equiv), and Boc_2O (1.6 g, 7.5 mmol, 1.5 equiv) The crude was purified on silica gel (5% Et_2O/ pentane) to afford 770 mg (61%) of a clear oil. Spectral data are in accordance with the literature.[12]

2.4 Synthesis of Allyl Piperidinyl Boronate

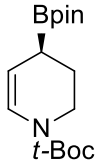


***tert*-Butyl 4-(((perfluorobutyl)sulfonyl)oxy)-5,6-dihydropyridine-1(2*H*)-carboxylate (S22).** In a flame dried round bottom flask equipped with a stir bar, 1-Boc-4-piperidone (5.0 g, 25 mmol) was dissolved in THF (130 mL) under a nitrogen atmosphere. The solution was cooled down to 0 °C using an ice-bath and stirred for 5 min. DBU (4.5 mL, 30 mmol) and perfluorobutanesulfonyl fluoride (5.4 mL, 30 mmol) were added respectively. The ice-bath was removed, and the solution was allowed to stir at room temperature overnight. The reaction mixture was quenched by slow addition of water and extracted with Et_2O (100 mL × 3). The organic layers were washed with

brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The brown crude oil was then purified by silica gel (15% Et_2O/pentane). Spectral data are in accordance with the literature.[13]



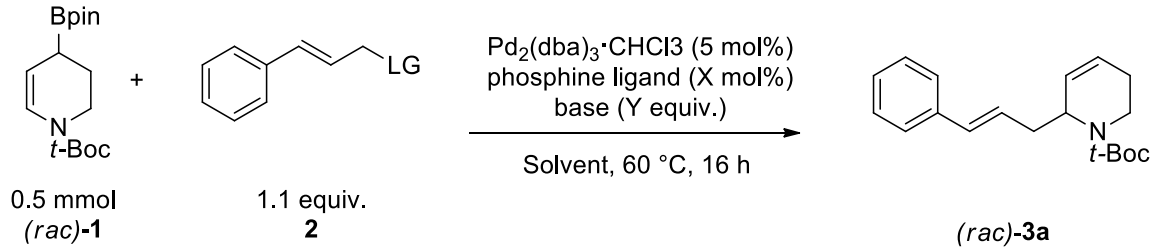
***tert*-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydropyridine-1(*2H*)-carboxylate (*rac*)-1**. In a flame dried round bottom flask equipped with a stir bar, palladium acetate (54 mg, 0.24 mmol) and DPEphos (140 mg, 0.26 mmol) were mixed with freshly distilled Et_2O (24 mL) and kept stirring at room temperature for 10 min. DIPEA (1.5 mL, 8.8 mmol), pinacolborane (1.3 mL, 8.8 mmol) and *tert*-butyl-4-(nonafluorobutylsulfonyloxy)-5,6-dihydropyridine-1(*2H*)-carboxylate (3.9 g, 8.0 mmol) were added respectively, and the mixture was stirred at room temperature for 16 h. The mixture was filtered through a short silica plug (100% Et_2O) and concentrated *in vacuo*, the crude was purified by silica gel (15% Et_2O/pentane) which provided the allylic boronate as a colorless oil (1.66 g, 67% yield). Spectral data are in accordance with the literature.[13]



(*4S*)-*tert*-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydropyridine-1(*2H*)-carboxylate (*S*)-1. In a flame dried round bottom flask equipped with a stir bar, palladium acetate (25 mg, 0.11 mmol) and (+)-Taniaphos (110 mg, 0.17 mmol) were mixed with CPME (12 mL) and kept stirring at room temperature for 10 min. DMA (510 µL, 4.1 mmol), pinacolborane (590 µL, 4.1 mmol) and *tert*-butyl-4-(nonafluorobutylsulfonyloxy)-5,6-dihydropyridine-1(*2H*)-carboxylate (1.8 g, 3.7 mmol) were added respectively, and the mixture was stirred at room temperature for 16 h. The mixture was filtered through a short silica plug (100% Et_2O) and concentrated *in vacuo*, the crude was purified by silica gel (15% Et_2O/pentane) which provided the allylic boronate as a colorless oil (910 mg, 79% yield). Spectral data are in accordance with the literature.[13]

3. Experimental Procedures for Allyl-Allyl Cross-Coupling Reaction

3.1 Additional Optimization of the Reaction on Racemic Allylic Boronate



0.5 mmol *(rac)*-**1**

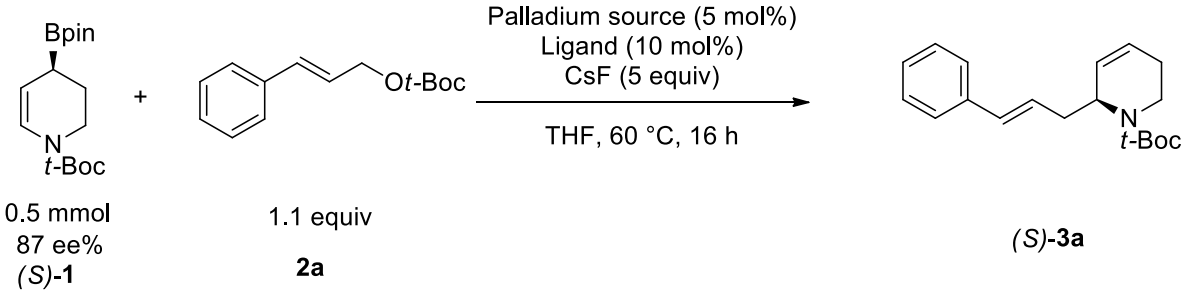
1.1 equiv. **2**

(rac)-**3a**

Entry	LG	Solvent	Ligand	Additive	X	Y	Yield (%)
1	O*t*-Boc	THF	PPh_3	—	10	—	31
2	O*t*-Boc	THF	dppp	—	5	—	20
3	O*t*-Boc	THF	Xantphos	—	5	—	20
4	O*t*-Boc	THF	MeO-furyl-biphep	Ag_2CO_3	5	—	n.d.[a]
5	O*t*-Boc	THF	PPh_3	Ag_2CO_3	10	2.5	64
6	O*t*-Boc	THF	PPh_3	CsF	10	5	75
7[b]	O*t*-Boc	THF	—	—	—	—	n.d.[a]
8[b, *]	O*t*-Boc	THF	—	Cs_2CO_3	—	2.5	n.d.[a]
9	Br	THF	PPh_3	—	10	—	n.d.[a]
10	Br	THF	PPh_3	Ag_2CO_3	10	2.5	59
11	Cl	THF	PPh_3	Ag_2CO_3	10	2.5	37
12	Cl	THF	PPh_3	CsF	10	5	62
13	O*t*-Boc	DCE	PPh_3	CsF	10	5	48
14	O*t*-Boc	MeCN	PPh_3	CsF	10	5	50
15	O*t*-Boc	EtOH	PPh_3	CsF	10	5	n.d.[a]
16*	O*t*-Boc	THF	PPh_3	CsF	5	5	< 5%

[a] n.d.: not detected. [b] catalyst used: PEPPSI-*i*Pr. * Additional entries not shown in the manuscript.

3.2 Optimization of the Reaction on Chiral Allylic Boronate



0.5 mmol
87 ee%
(S)-**1**

1.1 equiv

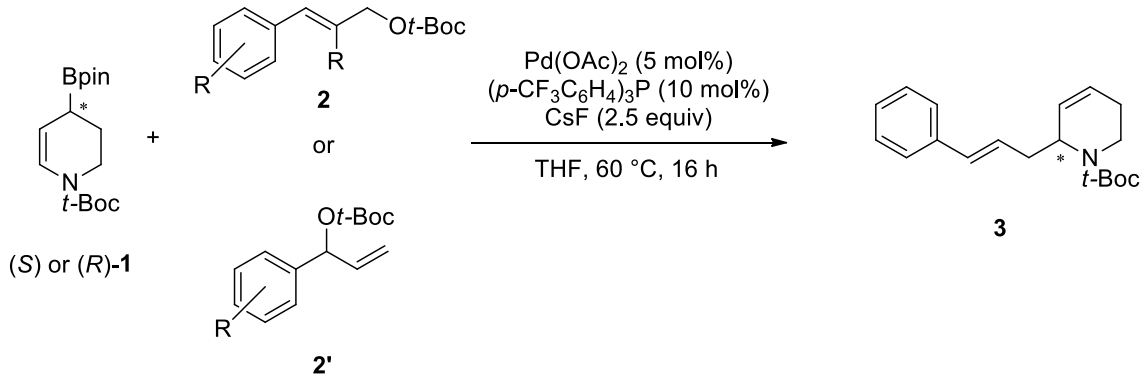
2a

(S)-**3a**

Entry	Palladium Source	Concentration	Ligand	Yield %	es%
1	$Pd_2(dba)_3 \cdot CHCl_3$	0.1	PPh_3	72	57
2	$Pd_2(dba)_3 \cdot CHCl_3$	0.1	PPh_3	40	63[a]
3	$Pd_2(dba)_3 \cdot CHCl_3$	0.1	$(p\text{-}CF_3C_6H_4)_3P$	25	94
4	$Pd_2(dba)_3 \cdot CHCl_3$	0.1	$(p\text{-}MeOC_6H_4)_3P$	60	40
5	$Pd_2(dba)_3 \cdot CHCl_3$	0.1	$(C_6F_5)_3P$	NR	NR
6	$Pd(OAc)_2$	0.1	$(p\text{-}CF_3C_6H_4)_3P$	68	97[b]
7*	$Pd(OAc)_2$	0.05	$(p\text{-}CF_3C_6H_4)_3P$	68	96[b]
8*	$Pd(OAc)_2$	0.025	$(p\text{-}CF_3C_6H_4)_3P$	68	97[b]
9*	$Pd(OAc)_2$	0.1	$(p\text{-}CF_3C_6H_4)_3P$	NR	NR[b, c]

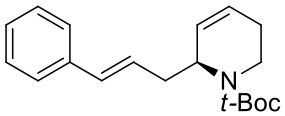
[a] Reaction was performed at rt. [b] Reaction was performed using 0.5 mmol of cinnamyl carbonate and 0.6 mmol of allyl boronate and 1.25 mmol of CsF. [c] Reaction was performed using 5 mol% of ligand and 5 mol% of catalyst. * Additional entries not shown in the manuscript.

3.3 Substrate Scope of the Allyl-Allyl Cross-Coupling Reaction

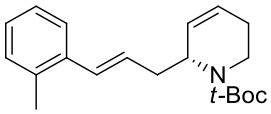


Example procedure A In a flame dried sealed tube equipped with a stir bar, palladium acetate (2.2 mg, 0.010 mmol), tris(4-trifluoromethylphenyl)phosphine (9.3 mg, 0.020 mmol) and cesium fluoride (76 mg, 0.50 mmol) were mixed with THF under an argon atmosphere and kept stirring for 5 min. Then, (*E*)-*tert*-butyl (3-(2-methoxyphenyl)allyl) carbonate (53 mg, 0.20 mmol) and (*S*) or (*R*) allylic boronate **1** (74 mg, 0.24 mmol) were added respectively. The reaction tube was sealed and heated to 60 °C and kept stirring for 16 h. The reaction mixture was filtered through a silica plug (100% Et_2O) and concentrated *in vacuo*. The crude was purified by silica gel (0-5% Et_2O/pentane) to afford the product as a colorless oil (16 mg, 25%).

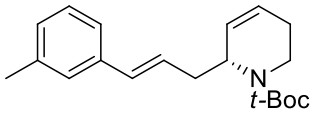
Example procedure B. In a glovebox, palladium acetate (2.2 mg, 0.010 mmol), tris(4-trifluoromethylphenyl)phosphine (9.3 mg, 0.020 mmol) and cesium fluoride (76 mg, 0.50 mmol) were mixed with THF under an argon atmosphere in an oven dried sealed reaction tube and kept stirring for 5 min. Then, (*E*)-*tert*-butyl (3-(4-(methylthio)phenyl)allyl) carbonate (56 mg, 0.20 mmol) and (*S*) or (*R*) allylic boronate **1** (74 mg, 0.24 mmol) were added respectively. The reaction tube was sealed, taken out of the glovebox and heated to 60 °C and kept stirring for 16 h. The reaction mixture was filtered through a silica plug (100% Et_2O) and concentrated *in vacuo*. The crude was purified by silica gel (0-5% Et_2O/pentane) to afford the product as a colorless oil (41 mg, 59%)



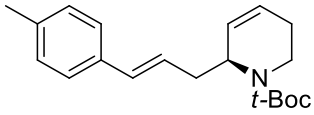
***(S)-tert*-Butyl 2-cinnamyl-5,6-dihydropyridine-1(2*H*)-carboxylate (3a).** Prepared by procedure A using *tert*-butyl cinnamyl carbonate **S9** (47 mg, 0.20 mmol) and *(S)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a clear oil (41 mg, 68%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.24 (br s, 1H), 5.86 (br s, 1H), 5.71 (br s, 1H), 4.70–4.34 (m, 1H), 4.30–3.92 (m, 1H), 2.88 (br s, 1H), 2.48 (t, *J* = 6.0 Hz, 2H), 2.20 (br s, 1H), 1.96 (d, *J* = 16.2 Hz, 1H), 1.43 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.6, 137.5, 132.2, 128.5, 128.0, 127.1, 126.6, 126.1, 125.8, 79.5, 52.7, 38.0, 36.4, 28.7, 24.9; **IR** (microscope, cm^{-1}) 3027, 3006, 2974, 2928, 1693, 1416, 1364, 1171, 1109; **HRMS** (ESI-TOF): for $C_{19}H_{25}NNaO_2$ $(M + Na)^+$: calcd. 322.1778; found 322.1777; **$[\alpha]_D^{20}$**: 123 (*c* = 1.04, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 280 nm, T_{minor} = 9.7 min, T_{major} = 11.4 min, er = 93.0:7.0.



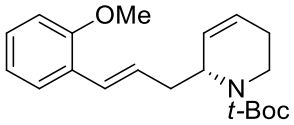
***(R,E)-tert*-Butyl 2-(3-(*o*-tolyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3b).** Prepared by procedure A using (*E*)-*tert*-butyl (3-(*o*-tolyl)allyl) carbonate **S15** (50 mg, 0.20 mmol) and *(R)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a yellow oil (40 mg, 65%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.40 (dd, *J* = 6.0, 1.5 Hz, 1H), 7.20–7.09 (m, 3H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.16–6.00 (m, 1H), 6.87 (br s, 1H), 5.73 (br s, 1H), 4.66–4.35 (m, 1H), 4.30–3.95 (m, 1H), 2.87 (br s, 1H), 2.50 (t, *J* = 5.0 Hz, 2H), 2.30 (s, 3H), 2.20 (br s, 1H), 1.96 (d, *J* = 17.3 Hz, 1H), 1.44 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.6, 136.6, 135.0, 130.1, 127.9, 127.1, 126.0, 125.7, 79.5, 52.8, 51.5, 38.5, 36.4, 28.6, 25.0, 19.8.; **IR** (microscope, cm^{-1}) 3064, 3017, 2974, 2926, 2869, 2838, 1694, 1416, 1364, 1172, 1110, 761; **HRMS** (ESI-TOF): For $C_{20}H_{27}NNaO_2$ $(M + Na)^+$: calcd. 336.1934; found 336.1935; **$[\alpha]_D^{20}$**: –95.7 (*c* = 1.53, CH_2Cl_2); **HPLC** (Chiralpak IA): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 254 nm, T_{major} = 11.0 min, T_{minor} = 11.8 min, er = 94.3:5.7.



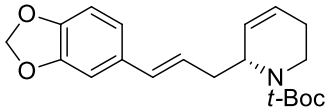
***(R,E)-tert*-Butyl 2-(3-(*m*-tolyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3c).** Prepared by procedure A using (*E*)-*tert*-butyl (3-(*m*-tolyl)allyl) carbonate **S16** (50 mg, 0.20 mmol) and *(R)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a yellow oil (47.6 mg, 76%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.21–7.11 (m, 3H), 7.02 (d, *J* = 7.0 Hz, 1H), 6.38 (d, *J* = 15.0 Hz, 1H), 6.28–6.11 (m, 1H), 5.86 (br s, 1H), 5.70 (br s, 1H), 4.65–4.35 (m, 1H), 4.28–3.90 (m, 1H), 2.88 (br s, 1H), 2.46 (t, *J* = 6.5, 2H), 2.33 (s, 3H), 2.20 (br s, 1H), 1.96 (d, *J* = 15.9 Hz, 1H), 1.45 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.6, 138.0, 137.5, 132.3, 128.4, 128.1, 127.9, 126.8, 126.4, 125.8, 123.3, 79.6, 52.6, 38.1, 36.2, 28.5, 24.9, 21.4; **IR** (microscope, cm^{-1}) 3030, 2974, 2926, 2870, 1693, 1416, 1364, 1171, 1110, 771; **HRMS** (ESI-TOF): For $C_{20}H_{27}NNaO_2$ $(M + Na)^+$: calcd. 336.1934; found 336.1934; **[α]$_D^{20}$**: –9.3 (*c* = 1.8, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 280 nm, T_{major} = 11.8 min, T_{minor} = 11.7 min, er = 94.8:5.2.



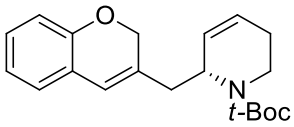
(*S,E*)-*tert*-Butyl 2-(3-(*p*-tolyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3d). Prepared by procedure A using (*E*)-*tert*-butyl (3-(*p*-tolyl)allyl) carbonate **S12** (50 mg, 0.20 mmol) and *(S)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a yellow oil (39.5 mg, 63%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.23 (d, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 6.38 (d, *J* = 15.5 Hz, 1H), 6.16 (br s, 1H), 5.86 (br s, 1H), 5.70 (br s, 1H), 4.68–4.34 (m, 1H), 4.29–3.94 (m, 1H), 2.87 (br s, 1H), 2.47 (t, *J* = 7.3, 2H), 2.32 (s, 3H), 2.20 (br s, 1H), 1.96 (d, *J* = 17.4 Hz, 1H), 1.44 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.5, 138.8, 134.7, 132.0, 129.1, 128.1, 125.9, 125.7, 125.5, 79.5, 52.7, 38.0, 36.3, 28.7, 25.1, 21.2; **IR** (microscope, cm^{-1}) 3022, 3006, 2974, 2924, 1693, 1417, 1171, 967; **HRMS** (ESI-TOF): For $C_{20}H_{27}NNaO_2$ $(M + Na)^+$: calcd. 336.1934; found 336.1932; **[α]$_D^{20}$**: 129 (*c* = 0.540, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 280 nm, T_{minor} = 10.3 min, T_{major} = 12.4 min, er = 93.0:7.0.



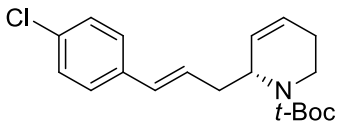
***(R,E)-tert*-Butyl 2-(3-(2-methoxyphenyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3e).** Prepared by procedure A using (*E*)-*tert*-butyl (3-(2-methoxyphenyl)allyl) carbonate **S10** (53 mg, 0.20 mmol) and *(R)*-**1** (74 mg, 0.24 mmol) Flash chromatography afforded the product as a clear oil (16.5 mg, 25%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.41 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.18 (td, *J* = 7.8, 1.5 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 15.0 Hz, 1H), 6.22 (dt, *J* = 16.0, 7.0 Hz), 6.85 (br s, 1H), 5.72 (br s, 1H), 4.65–4.33 (m, 1H), 4.30–3.94 (m, 1H), 3.83 (s, 3H), 2.90 (br s, 1H), 2.50 (t, 6.5 Hz, 2H), 2.20 (br s, 1H), 1.96 (d, *J* = 15.6 Hz, 1H), 1.45 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 156.4, 154.6, 128.1, 127.2, 126.8, 126.6, 125.6, 120.6, 110.9, 79.4, 55.5, 52.7, 38.4, 36.4, 28.6, 25.1; **IR** (microscope, cm^{-1}) 3012, 2975, 2930, 1692, 1491, 1367, 756; **HRMS** (ESI-TOF): For $C_{20}H_{27}NNaO_3$ $(M + Na)^+$: calcd. 352.1883; found 352.1880; **$[\alpha]_D^{20}$**: 11.3 (*c* = 0.710, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 254 nm, T_{major} = 16.9 min, T_{minor} = 20.7 min, er = 92.7:7.3.



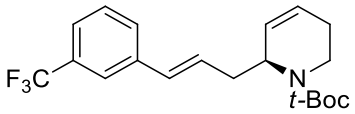
(*R,E*)-*tert*-Butyl 2-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3f). Prepared by procedure A using (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)allyl *tert*-butyl carbonate **S14** (56 mg, 0.20 mmol) and *(R)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a pale-yellow oil (43.3 mg, 43.3%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 6.88 (d, *J* = 1.4 Hz, 1H), 6.78–6.69 (m, 2H), 6.31 (d, *J* = 15.7 Hz, 1H), 6.04 (br s, 1H), 5.93 (s, 2H), 5.85 (br s, 1H), 5.69 (br s, 1H), 4.62–4.31 (m, 1H), 4.27–3.90 (m, 1H), 2.85 (br s, 1H), 2.44 (t, *J* = 6.7 Hz, 2H), 2.19 (br s, 1H), 1.95 (d, *J* = 16.5 Hz, 1H), 1.44 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.6, 147.9, 146.8, 132.2, 131.7, 128.6, 128.2, 125.7, 124.9, 120.5, 108.2, 105.6, 100.9, 79.5, 52.6, 51.5, 37.9, 36.4, 28.6, 28.5, 25.0; **IR** (microscope, cm^{-1}) 3031, 2975, 2926, 2838, 1689, 1490 1416, 1248, 1170, 1039, 813, 768; **HRMS** (ESI-TOF): For $C_{20}H_{25}NNaO_4$ $(M + Na)^+$: calcd. 366.1676; found 366.1676; **$[\alpha]_D^{20}$**: –4.0 (*c* = 1.2, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 254 nm, T_{major} = 17.2 min, T_{minor} = 18.3 min, er = 95.4:4.6.



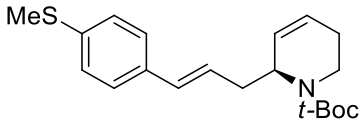
***(R)-tert*-Butyl 2-((2*H*-chromen-3-yl)methyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3g).** Prepared by procedure A using (2*H*-chromen-3-yl)methyl *tert*-butyl carbonate **S18** (52 mg, 0.20 mmol) and *(R)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a clear oil (49.1 mg, 75%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.05 (t, *J* = 8.0 Hz, 1H), 6.91 (dd, *J* = 7.0, 1.0 Hz, 1H), 6.83 (t, *J* = 7.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.19 (s, 1H), 5.87 (br s, 1H), 5.70 (br s, 1H), 4.76 (s, 2H), 4.65–4.35 (m, 1H), 4.30–3.90 (m, 1H), 2.87 (br s, 1H), 2.46–2.12 (m, 3H), 1.97 (d, *J* = 15.7 Hz, 1H), 1.43 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.4, 152.9, 131.1, 128.5, 127.6, 126.1, 122.7, 121.8, 121.3, 115.3, 79.9, 68.3, 50.9, 38.3, 35.9, 28.4, 25.0; **IR** (microscope, cm^{-1}) 3031, 2974, 2928, 2870, 1691, 1417, 1365, 1240, 1170, 902; **HRMS** (ESI-TOF): For $C_{20}H_{25}NNaO_3$ $(M + Na)^+$: calcd. 350.1727; found 350.1721; **$[\alpha]_D^{20}$**: –8.5 (*c* = 0.47, CH_2Cl_2); **HPLC** (Chiralpak IC): 5:95 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 280 nm, T_{major} = 13.9 min, T_{minor} = 14.9 min, er = 92.5:7.5.



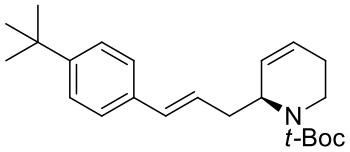
(*R*,*E*)-*tert*-Butyl 2-(3-(4-chlorophenyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3h). Prepared by procedure A using (*E*)-*tert*-butyl (3-(4-chlorophenyl)allyl) carbonate (54 mg, 0.20 mmol) and *(R)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a pale-yellow oil (44.1 mg, 66%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.24 (s, 4H), 6.34 (d, *J* = 15.5 Hz, 1H), 6.20 (br s, 1H), 5.85 (br s, 1H), 5.68 (br s, 1H), 4.66–4.32 (m, 1H), 4.29–3.90 (m, 1H), 2.85 (br s, 1H), 2.45 (t, *J* = 6.5 Hz, 2H), 2.19 (br s, 1H), 1.95 (d, *J* = 16.0 Hz, 1H), 1.42 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.6, 135.9, 132.6, 130.9, 128.6, 127.9, 127.5, 127.3, 126.0, 79.6, 52.7, 38.1, 36.3, 28.5, 24.9; **IR** (microscope, cm^{-1}) 3004, 2974, 2927, 1694, 1417, 1365, 1171, 816; **HRMS** (ESI-TOF): For $C_{19}H_{24}ClNNaO_2$ $(M + Na)^+$: calcd. 356.1388; found 356.1390; **$[\alpha]_D^{20}$**: –4.5 (*c* = 0.63, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 254 nm, T_{major} = 9.7 min, T_{minor} = 10.4 min, er = 94.9:5.1.



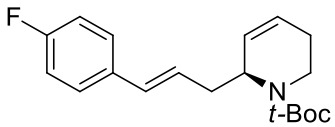
(*S*,*E*)-*tert*-Butyl 2-(3-(3-(trifluoromethyl)phenyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3i). Prepared by procedure B using (*E*)-*tert*-butyl (3-(3-(trifluoromethyl)phenyl)allyl) carbonate **S13** (61 mg, 0.20 mmol) and *(S)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a pale-yellow oil (29 mg, 40%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.58 (s, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.37–6.25 (m, 1H), 5.87 (br s, 1H), 5.69 (br s, 1H), 4.68–4.37 (m, 1H), 4.32–3.94 (m, 1H), 2.87 (br s, 1H), 2.49 (t, *J* = 6.8 Hz, 2H), 2.21 (br s, 1H), 1.96 (d, *J* = 16.6 Hz, 1H), 1.42 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.6, 138.4, 130.7, 129.3, 128.9, 128.5, 127.9, 126.2, 125.8, 125.3, 123.6, 123.1, 122.7, 79.6, 52.4, 51.3, 38.1, 36.3, 28.5, 25.2; **^{19}F NMR** (469 MHz, $CDCl_3$): δ –62.7; **IR** (microscope, cm^{-1}) 3012, 2974, 2922, 1693, 1477, 1454, 1365, 1170, 814; **HRMS** (ESI-TOF): For $C_{20}H_{24}F_3NNaO_2$ $(M + Na)^+$: calcd. 390.1651; found 390.1652; **$[\alpha]_D^{20}$**: –4.0 (*c* = 0.42, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 280 nm, T_{minor} = 7.3 min, T_{major} = 7.6 min, er = 94.4:5.6.



(*S*,*E*)-*tert*-Butyl 2-(3-(4-(methylthio)phenyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3j). Prepared by procedure B using (*E*)-*tert*-butyl (3-(4-(methylthio)phenyl)allyl) carbonate **S17** (56 mg, 0.20 mmol) and *(S)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a pale-yellow oil (41.5 mg, 60%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.22 (br s, 1H), 5.88 (br s, 1H), 5.72 (br s, 1H), 4.68–4.34 (m, 1H), 4.32–3.96 (m, 1H), 2.89 (br s, 1H), 2.55–2.44 (m, 5H), 2.22 (br s, 1H), 1.98 (d, *J* = 16.3 Hz, 1H), 1.46 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.6, 136.9, 134.5, 131.5, 128.6, 127.9, 126.8, 126.5, 126.2, 79.5, 52.7, 51.4, 37.9, 36.5, 28.5, 25.0, 16.1; **IR** (microscope, cm^{-1}) 3029, 2975, 2922, 2837, 1690, 1454, 1416, 1171, 815; **HRMS** (ESI-TOF): For $C_{20}H_{27}NNaO_2S$ $(M + Na)^+$: calcd. 368.1655; found 368.1653; **$[\alpha]_D^{20}$**: 0.68 (*c* = 0.46, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 280 nm, T_{minor} = 7.3 min, T_{major} = 7.6 min, er = 94.4:5.6.



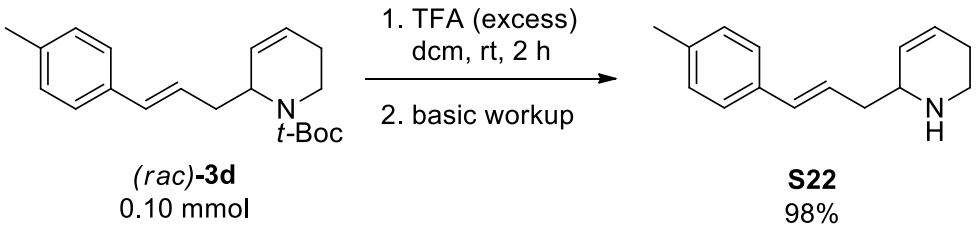
(*S*,*E*)-*tert*-Butyl 2-(3-(4-(tert-butyl)phenyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3k). Prepared by procedure B using *tert*-butyl (1-(4-(*tert*-butyl)phenyl)allyl) carbonate **S20** (58, 0.20 mmol) and *(S)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a clear oil (46.9 mg, 66%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.18 (br s, 1H), 5.85 (br s, 1H), 5.70 (br s, 1H), 4.62–4.32 (m, 1H), 4.82–3.93 (m, 1H), 2.88 (br s, 1H), 2.47 (t, *J* = 6.4 Hz, 2H), 2.19 (br s, 1H), 1.95 (d, *J* = 16.3 Hz, 1H), 1.45 (s, 9H), 1.31 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 154.6, 150.2, 134.4, 132.0, 128.5, 128.1, 125.8, 125.4, 79.5, 52.5, 51.4, 37.8, 36.4, 34.6, 31.4, 28.6, 24.9; **IR** (microscope, cm^{-1}) 3030, 2964, 2929, 2869, 1694, 1415, 1364, 1171, 1109, 825; **HRMS** (ESI-TOF): For $C_{23}H_{33}NNaO_2$ $(M + Na)^+$: calcd. 378.2404; found 378.2409; **$[\alpha]_D^{20}$**: 11.3 (*c* = 0.710, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 254 nm, T_{minor} = 8.1 min, T_{major} = 8.9 min, er = 92.7:7.3.



(*S*,*E*)-*tert*-Butyl 2-(3-(4-fluorophenyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (3l). Prepared by procedure B using *tert*-butyl (1-(4-fluorophenyl)allyl) carbonate **S21** (51 mg, 0.2 mmol) and *(S)*-**1** (74 mg, 0.24 mmol). Flash chromatography afforded the product as a pale-yellow oil (35.5 mg, 56%): **^{1}H NMR** (500 MHz, $CDCl_3$), rotamers are present: δ 7.32–7.27 (m, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.35 (d, *J* = 15.5 Hz, 1H), 6.14 (br s, 1H), 5.85 (br s, 1H), 5.69 (br s, 1H), 4.63–4.34 (m, 1H), 4.30–3.91 (m, 1H), 2.86 (br s, 1H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.20 (br s, 1H), 1.95 (d, *J* = 17.2 Hz, 1H), 1.42 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$), rotamers are present: δ 163.0, 161.1, 154.6, 133.7, 130.9, 128.6, 128.2, 127.5, 126.6, 125.8, 125.5, 115.4, 115.2, 79.5, 52.7, 51.3, 37.7, 36.3, 28.5, 24.9; **^{19}F NMR** (469 MHz, $CDCl_3$): δ –115.4; **IR** (microscope, cm^{-1}): 3034, 2973, 2928, 2832, 1726, 1692, 1508, 1417, 1364, 1228, 1172, 821; **HRMS** (ESI-TOF): For $C_{19}H_{24}FNNaO_2$ $(M + Na)^+$: calcd. 340.1683; found 340.1688; **$[\alpha]_D^{20}$**: 119 (*c* = 0.550, CH_2Cl_2); **HPLC** (Chiralpak IC): 2:98 iso-propanol:hexanes, 0.5 mL/min, 20 °C, λ = 254 nm, T_{minor} = 7.1 min, T_{major} = 7.6 min, er = 93.5:6.5.

Amine Deprotection Example

To further assess the product structure of the allyl-allyl cross-coupling reaction and confirm its identity, the piperidinyl product was deprotected under acidic conditions to eliminate the rotamers and obtain a clear ^{1}H and ^{13}C NMR spectra as shown below.



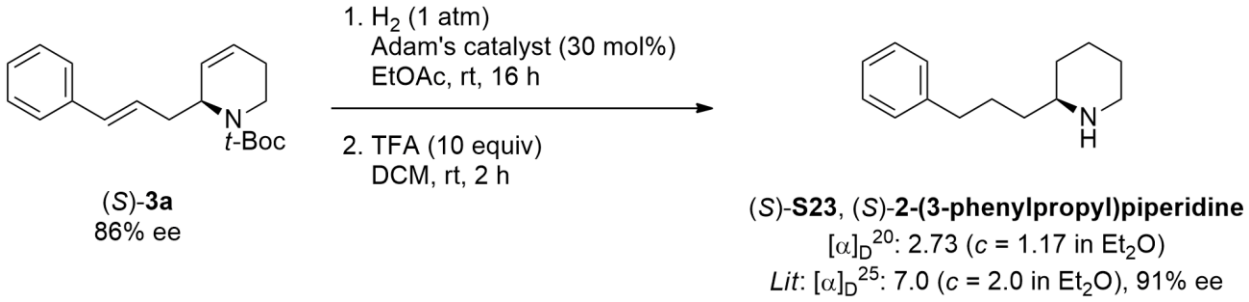
(rac)-**3d**
0.10 mmol

S22
98%

(*rac*)-(*E*)-6-(3-(*p*-Tolyl)allyl)-1,2,3,6-tetrahydropyridine (S23). In a 1-dram vial equipped with a stir bar, compound (*rac*)-**3d** (31 mg, 0.10 mmol) was dissolved in dichloromethane (2.0 mL), then trifluoracetic acid (0.20 mL, 2.6 mmol, 26 equiv) was added dropwise. The reaction mixture was allowed to stir for 2 hours. The reaction mixture was then concentrated *in vacuo* to remove the excess acid. The crude was then redissolved in dichloromethane (10 mL) and washed with NaOH (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford free amine **S22** as a yellow oil (20.9 mg, 98%): **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.18 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.8, 7.0, 1H), 5.74 (ddt, *J* = 9.7, 4.7, 2.3 Hz, 1H), 5.59 (dq, *J* = 10.2, 2.0 Hz, 1H), 3.36 (dq, *J* = 5.3, 2.7 Hz, 1H), 3.02 (ddd, *J* = 12.0, 5.7, 2.8 Hz, 1H), 2.79 (ddd, *J* = 12.1, 9.6, 4.6 Hz, 1H), 2.35–2.19 (m, 5H), 2.09 (dddq, *J* = 18.0, 9.0, 5.9, 2.8 Hz, 1H), 1.94–1.83 (m, 1H), 1.67 (br s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 136.9, 134.6, 132.6, 130.6, 129.2, 126.2, 126.0, 125.9, 53.7, 42.3, 39.9, 25.9, 21.2; **IR** (microscope, cm^{-1}): 3330, 3022, 2943, 2915, 2832, 1512, 1429, 1114; **HRMS** (ESI-TOF): For $C_{15}H_{20}N$ $(M + H)^+$: calcd. 214.1590; found 214.1586.

4. Proof of Absolute Stereochemistry

To confirm the absolute configuration of the cross-coupled products, compound (*S*)-**3a** was derivatized to the previously reported compound (*S*)-**S23**, (*S*)-2-(3-phenylpropyl)piperidine,[14] and their optical rotation values were compared.



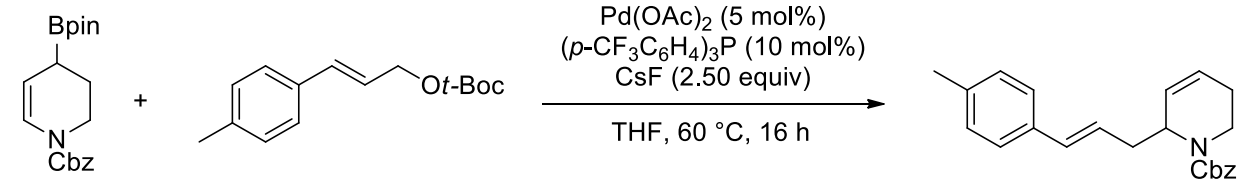
(*S*)-**3a**
86% ee

(*S*)-**S23**, (*S*)-**2-(3-phenylpropyl)piperidine**
$[\alpha]_D^{20}$: 2.73 (*c* = 1.17 in Et_2O)
Lit: $[\alpha]_D^{25}$: 7.0 (*c* = 2.0 in Et_2O), 91% ee

(*S*)-2-(3-phenylpropyl)piperidine ((*S*)-S23). In a flame dried 10 mL pear-shaped flask charged with a stir bar was added Adam's catalyst (4.9 mg, 20 µmol, 0.30 equiv), and compound (*S*)-**3a** (20 mg, 67 µmol) and evacuated and backfilled with nitrogen for three cycles. Ethyl acetate (5.0 mL) was added to the flask via syringe and mixture was stirred for 5 min. The solution was purged with a hydrogen balloon for 10 min. The balloon was then moved into the flask's headspace, and the reaction then stirred for 16 h. The mixture was then filtered through a silica plug with (100% EtOAc), then concentrated *in vacuo* and used in the next deprotection step without further purification. The deprotection step was carried out using the same procedure as mentioned for the preparation of compound **S22**, delivering compound (*S*)-**S23** (11.7 mg, 86% overall yield). Spectral data matches those previously reported.[14]

$[\alpha]_D^{20}$: 2.73 (*c* = 1.17 in Et_2O), (*Lit*[14]: 7.0, *c* = 2.0 in Et_2O, 91% ee).

5. Example of Cross-Coupling Reaction with Cbz Protected Piperidine

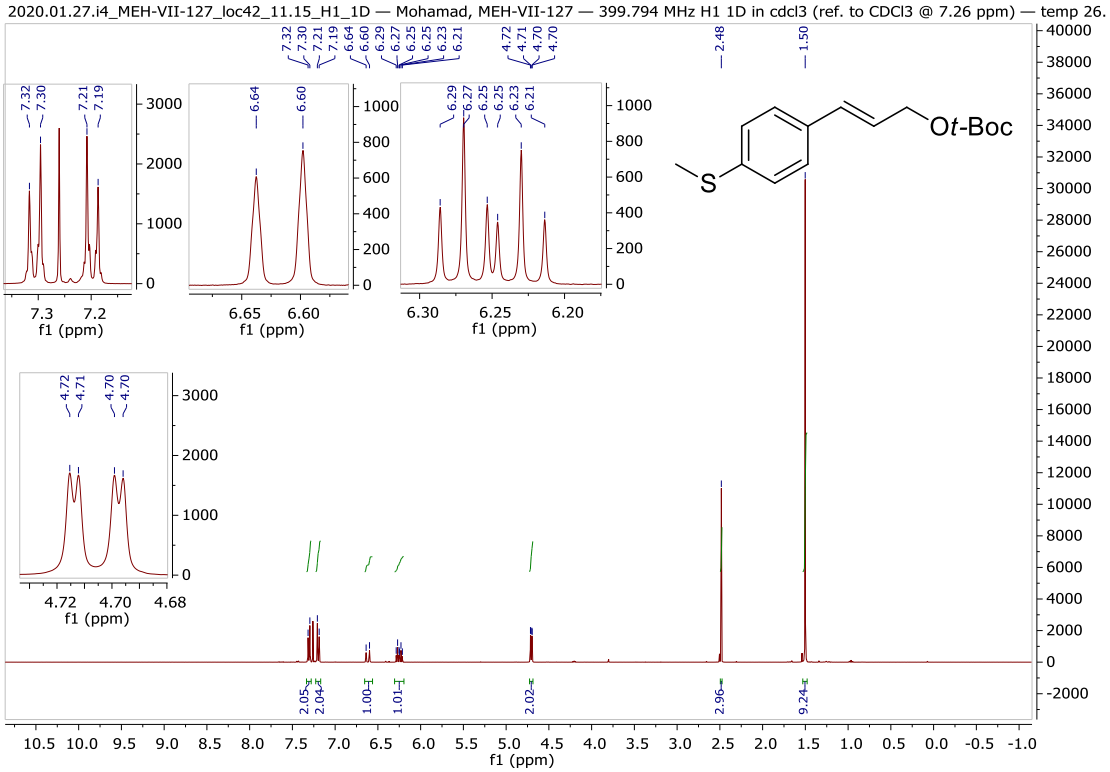


(*rac*)-**1'** 1.20 equiv | **2** 1.00 mmol | (*rac*)-**3d'** 72%

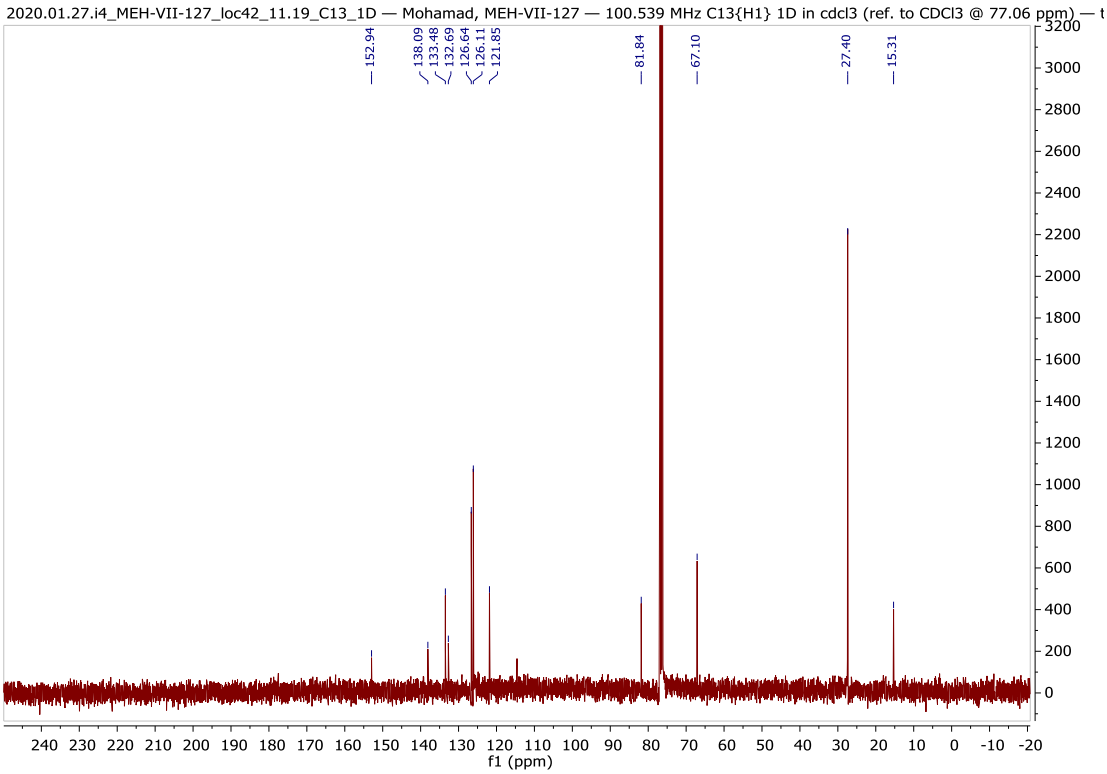
(*E*)-benzyl 2-(3-(*p*-tolyl)allyl)-5,6-dihydropyridine-1(2*H*)-carboxylate ((*rac*)-3d′). Prepared by example procedure A under Section 3.3 using (*E*)-*tert*-butyl (3-(*p*-tolyl)allyl) carbonate (246 mg, 1.00 mmol) and (*rac*)-**1′** (412 mg, 1.20 mmol). Flash chromatography afforded the product as a yellow oil (250 mg, 72%): **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.40–7.28 (m Hz, 5H), 7.27–7.16 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.47–6.28 (m, 1H), 6.26–6.4.05 (s, 1H), 5.87 (br s, 1H), 5.80–5.64 (m, 1H), 5.14 (s, 2H), 4.69–4.46 (m, 1H), 4.33–4.05 (m, 1H), 2.97 (br s, 1H), 2.59–2.41 (m, 2H), 2.34 (s, 3H), 2.30–2.13 (m, 1H), 2.08–1.89 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 155.4, 137.0, 134.8, 132.3, 129.2, 128.5, 128.2, 127.9, 126.0, 125.8, 125.4, 125.1, 125.1, 67.2, 52.5, 38.1, 37.8, 37.2, 25.1, 24.8, 21.2; **IR** (microscope, cm^{-1}): 3031, 2921, 2837, 1699, 1424, 1391, 1248, 1105, 697; **HRMS** (ESI-TOF): For $C_{23}H_{25}NNaO_2$ $(M + Na)^+$: calcd. 370.1778; found 370.1772.

6. Copies of NMR Spectra of Novel Compounds

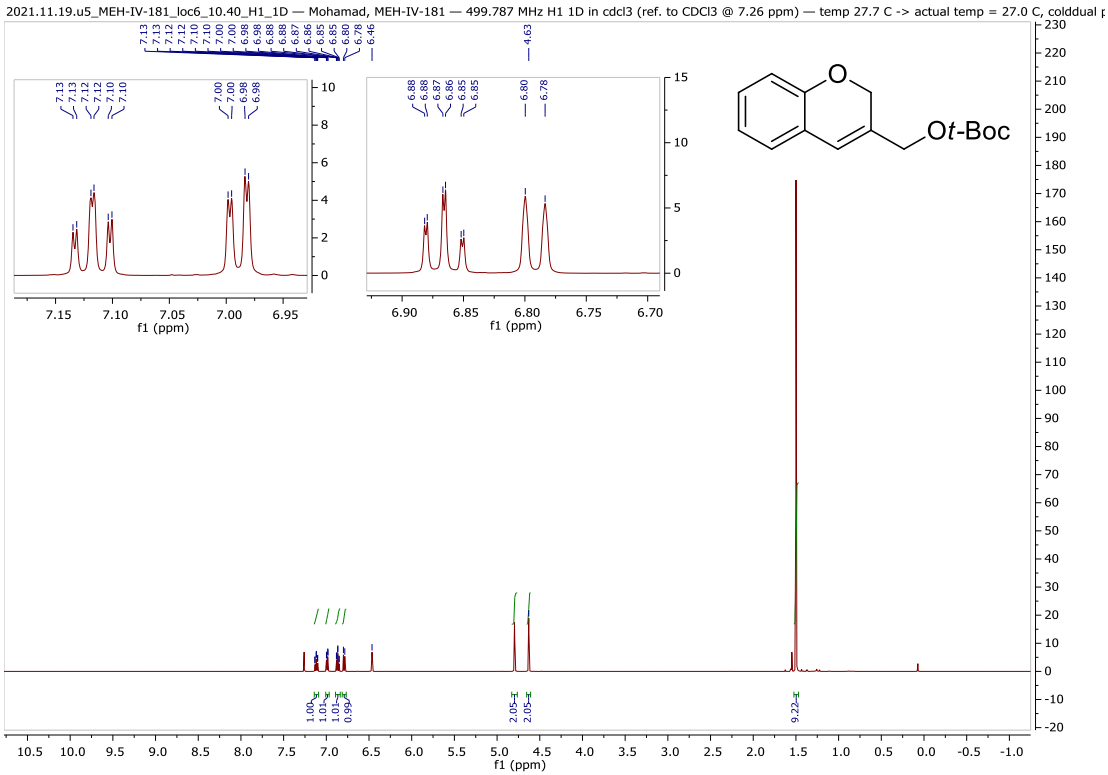
^{1}H NMR for compound **S17** (400 MHz, $CDCl_3$)



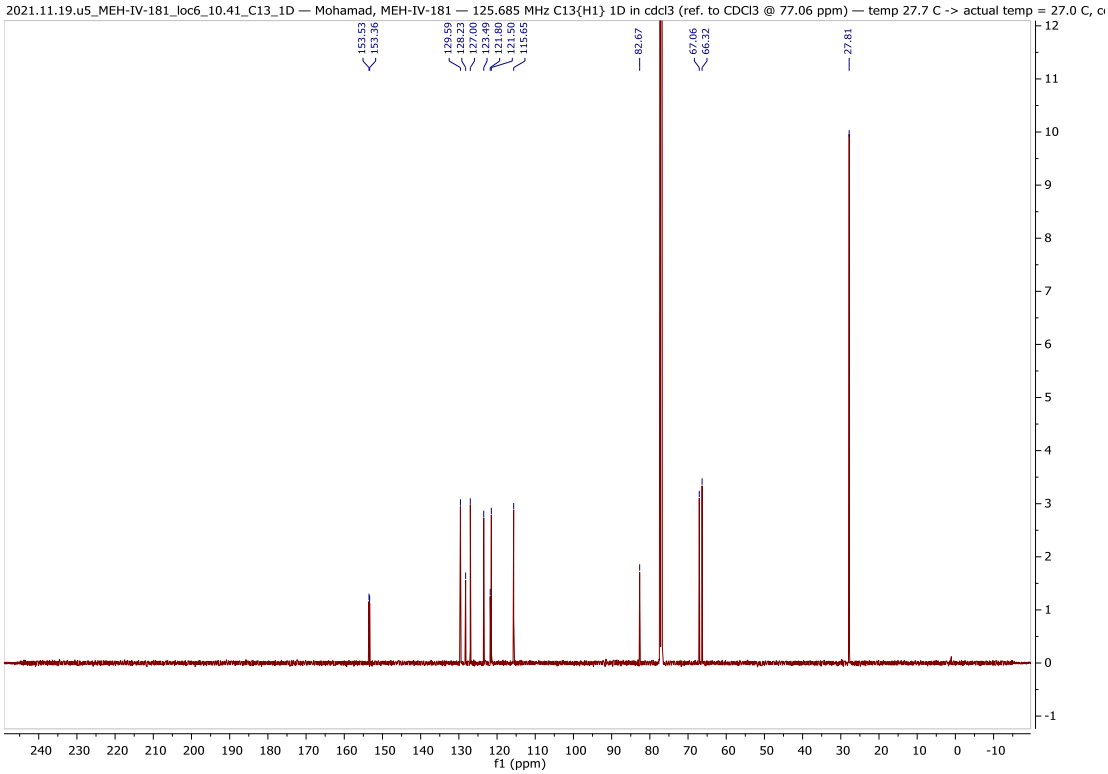
^{13}C NMR for compound **S17** (101 MHz, $CDCl_3$)



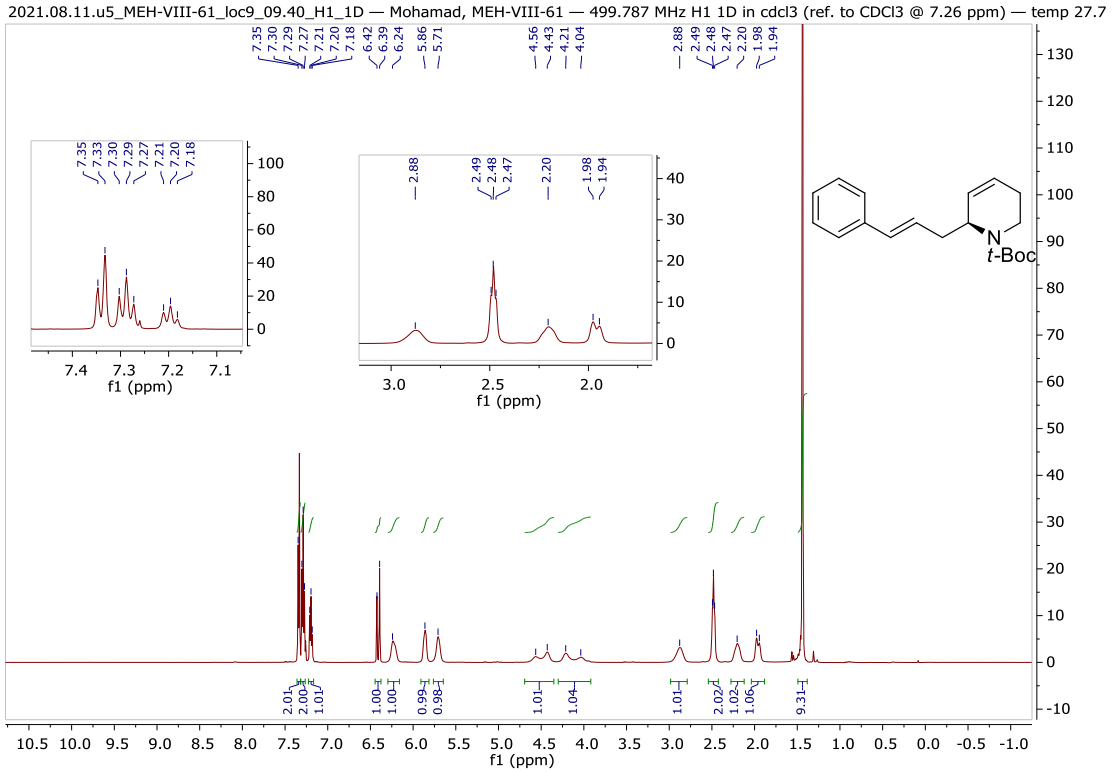
^{1}H NMR for compound **S18** (500 MHz, $CDCl_3$)



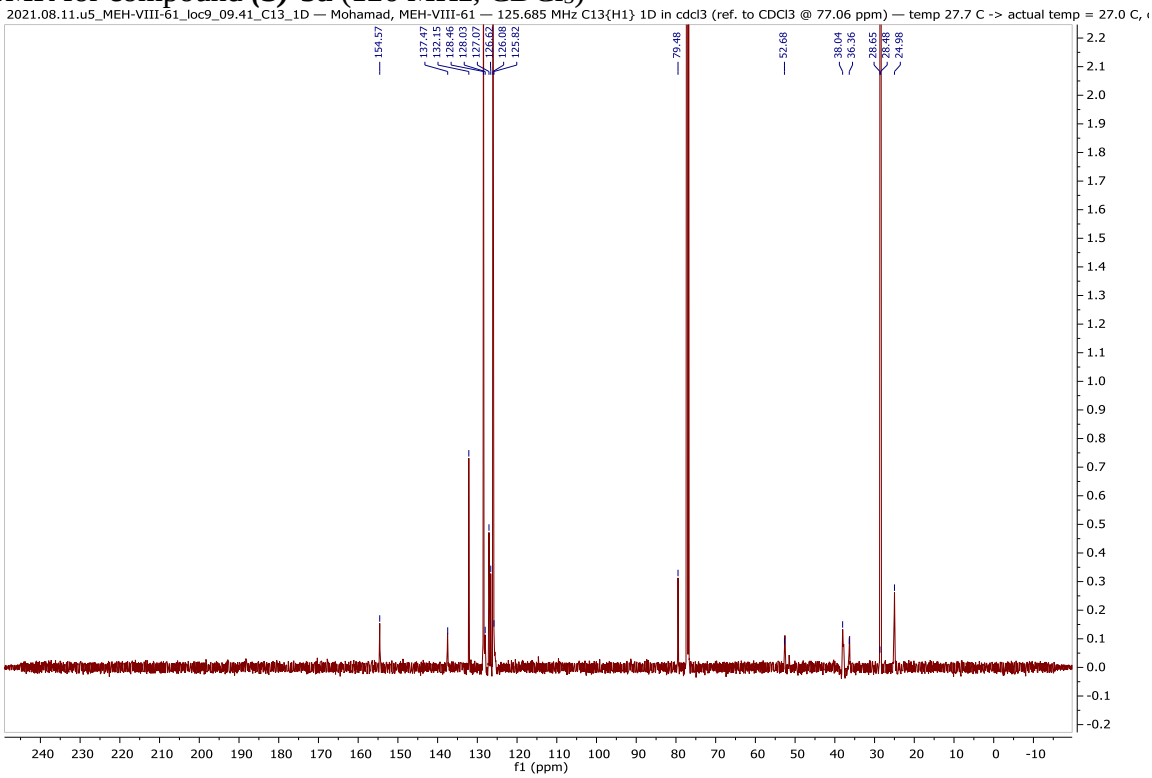
^{13}C NMR for compound **S18** (126 MHz, $CDCl_3$)



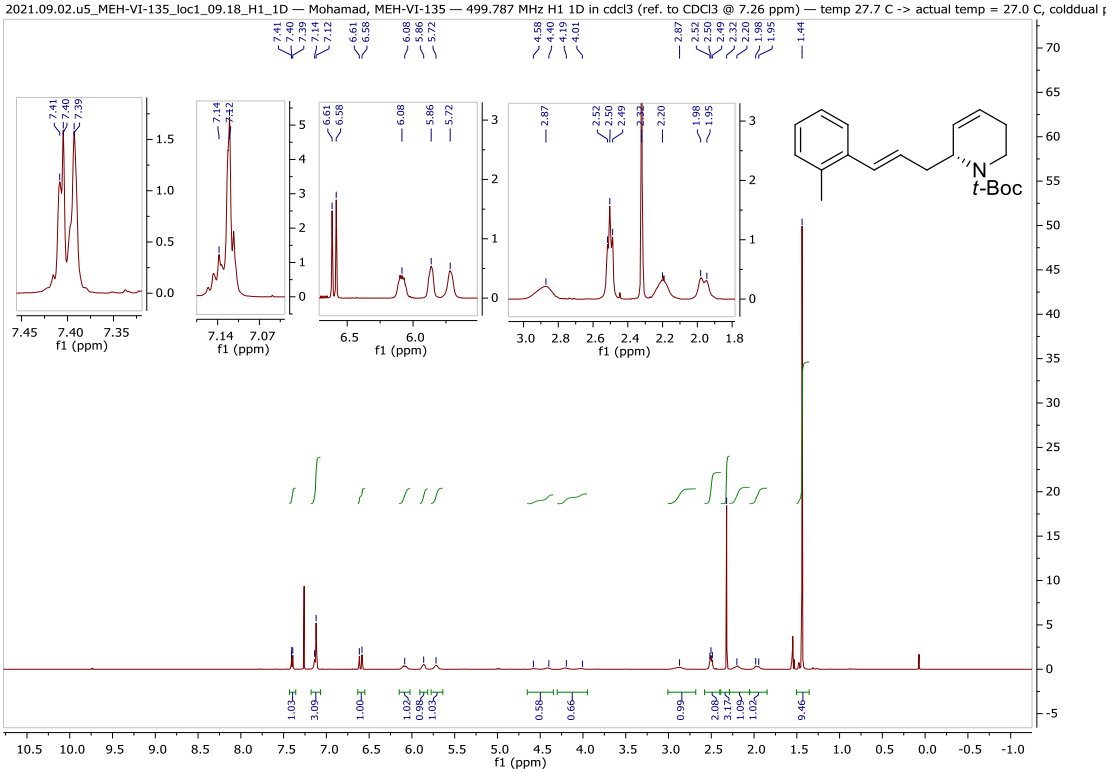
^{1}H NMR for compound ***(S)*-3a** (500 MHz, $CDCl_3$)



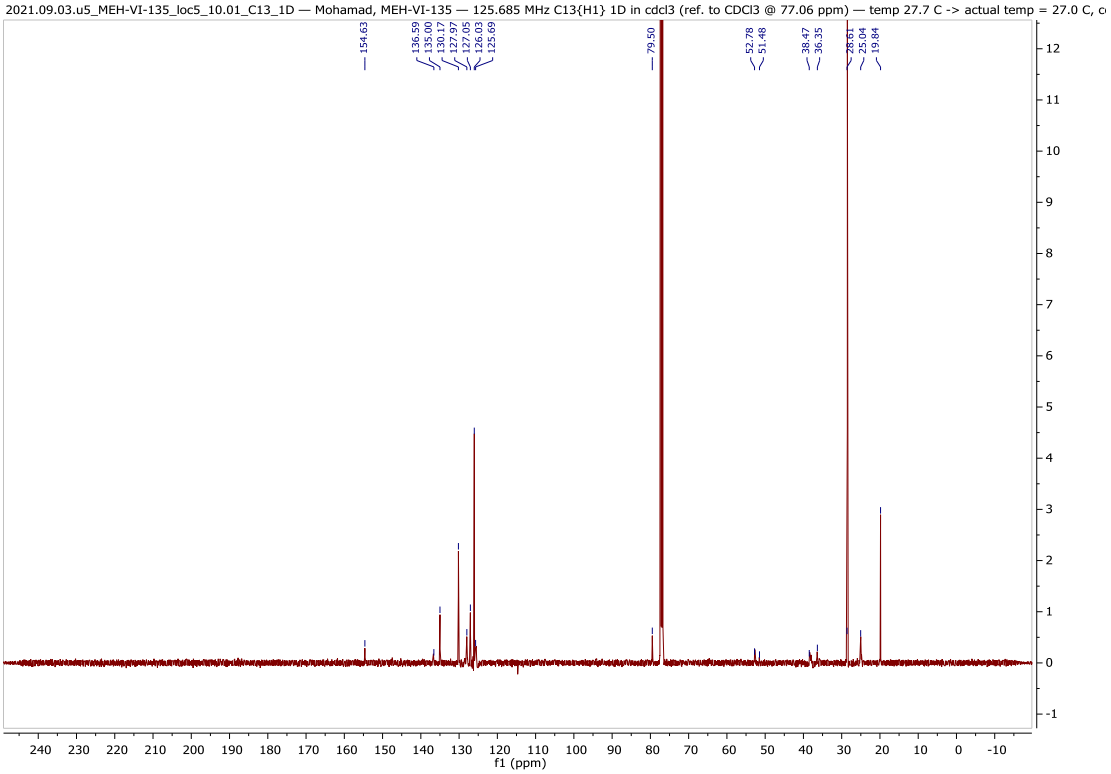
^{13}C NMR for compound ***(S)*-3a** (126 MHz, $CDCl_3$)



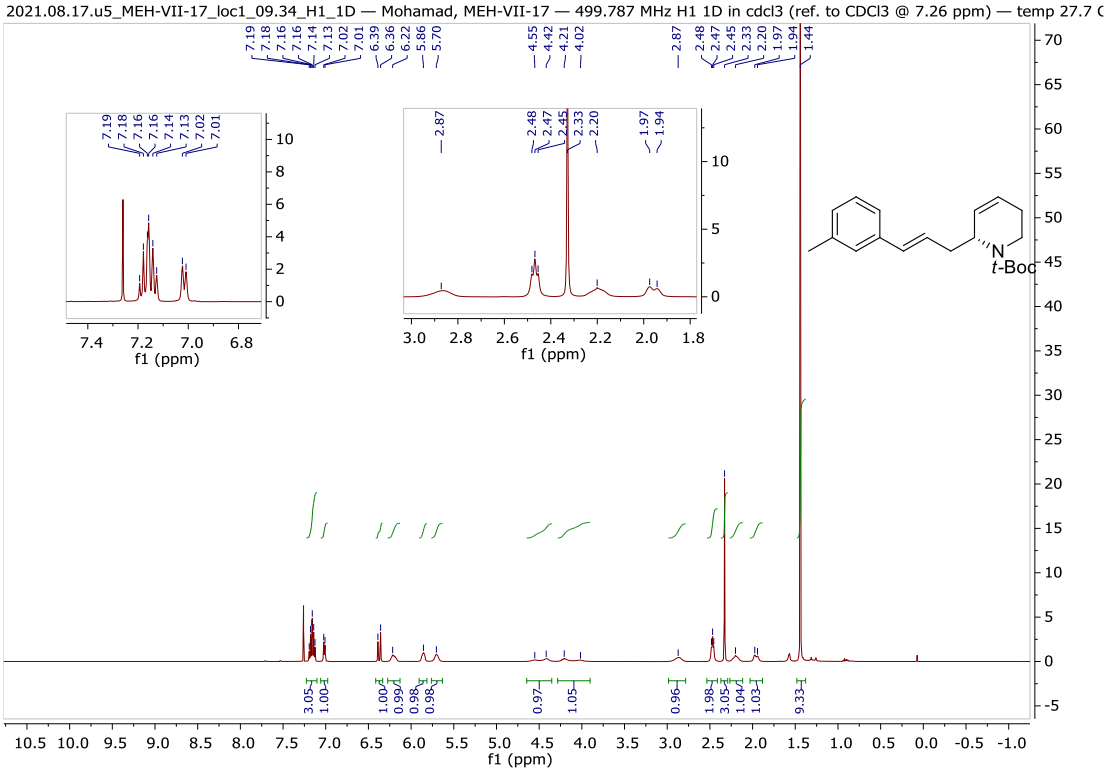
^{1}H NMR for compound **3b** (500 MHz, $CDCl_3$)



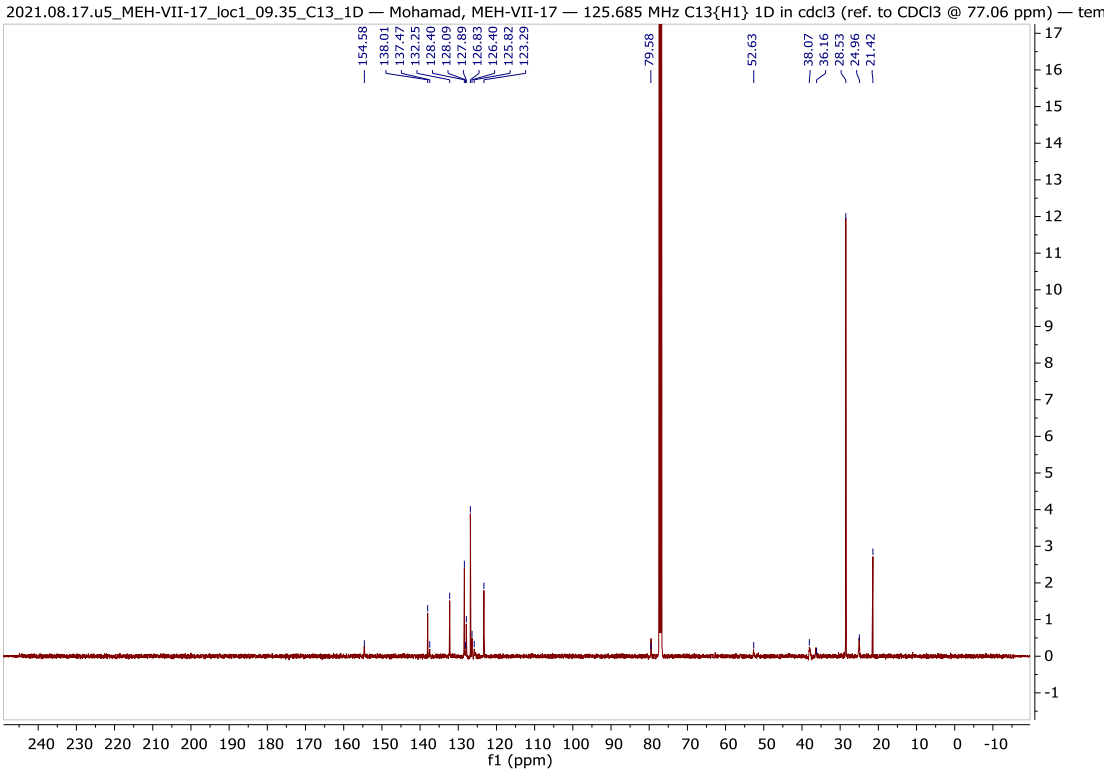
^{13}C NMR for compound **3c** (126 MHz, $CDCl_3$)



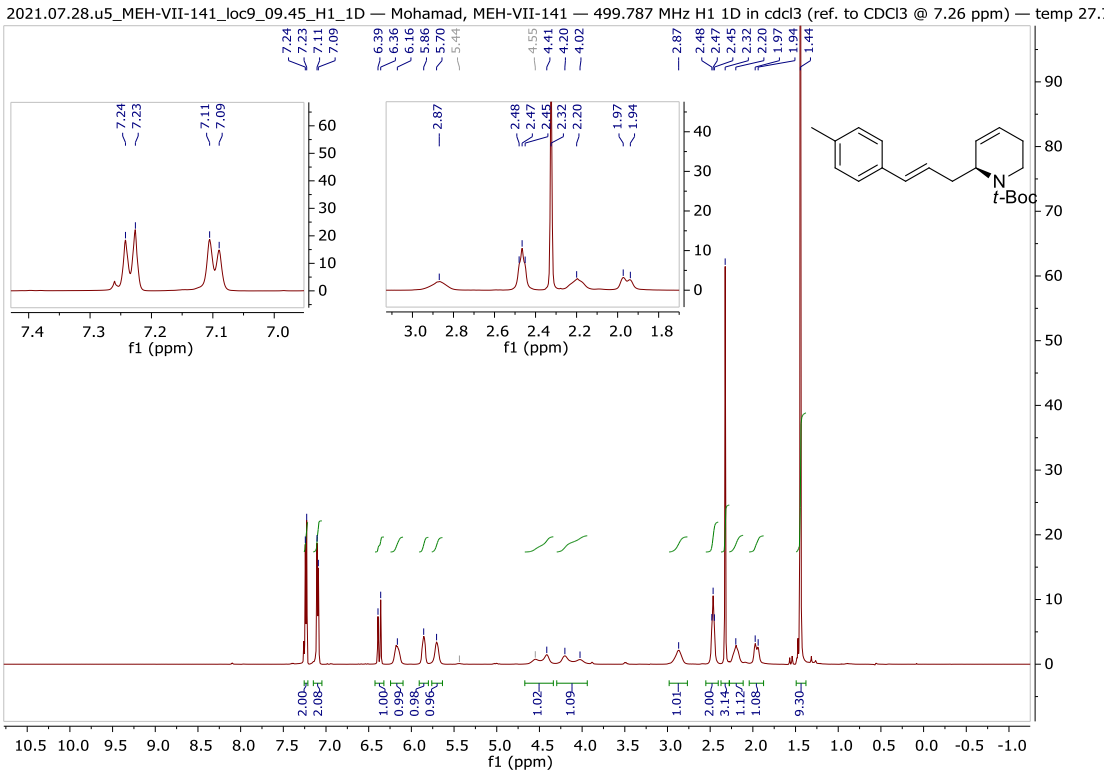
^{1}H NMR for compound **3c** (500 MHz, $CDCl_3$)



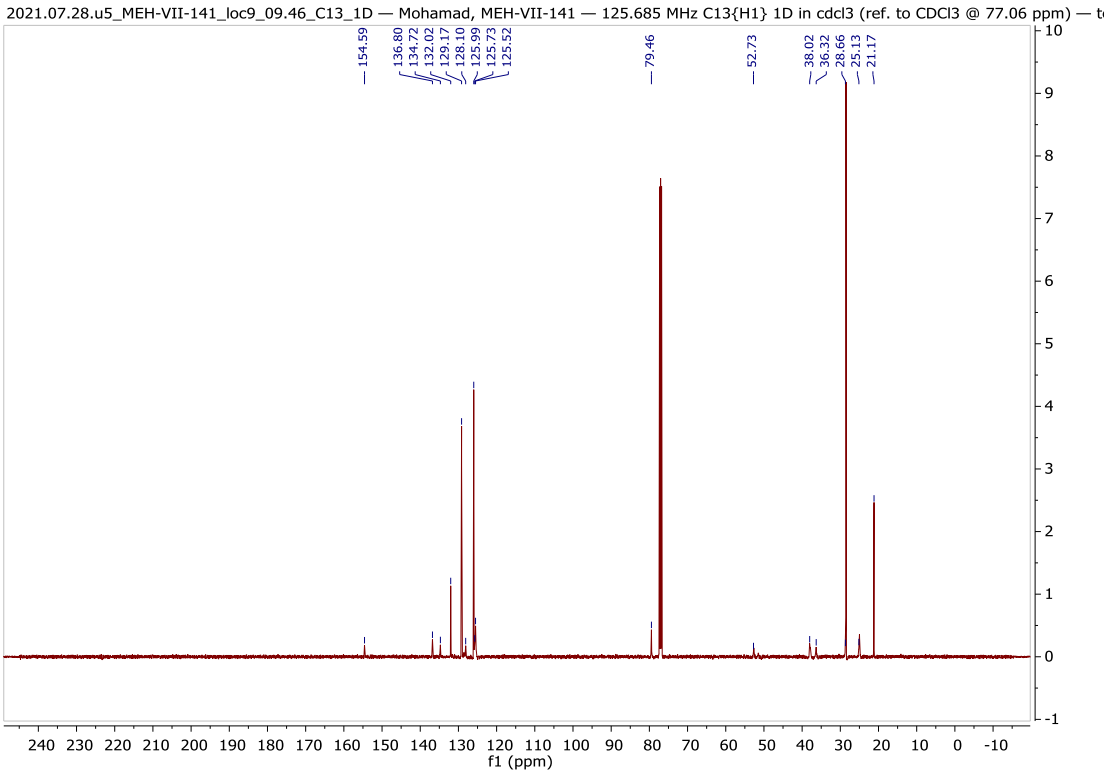
^{13}C NMR for compound **3c** (126 MHz, $CDCl_3$)



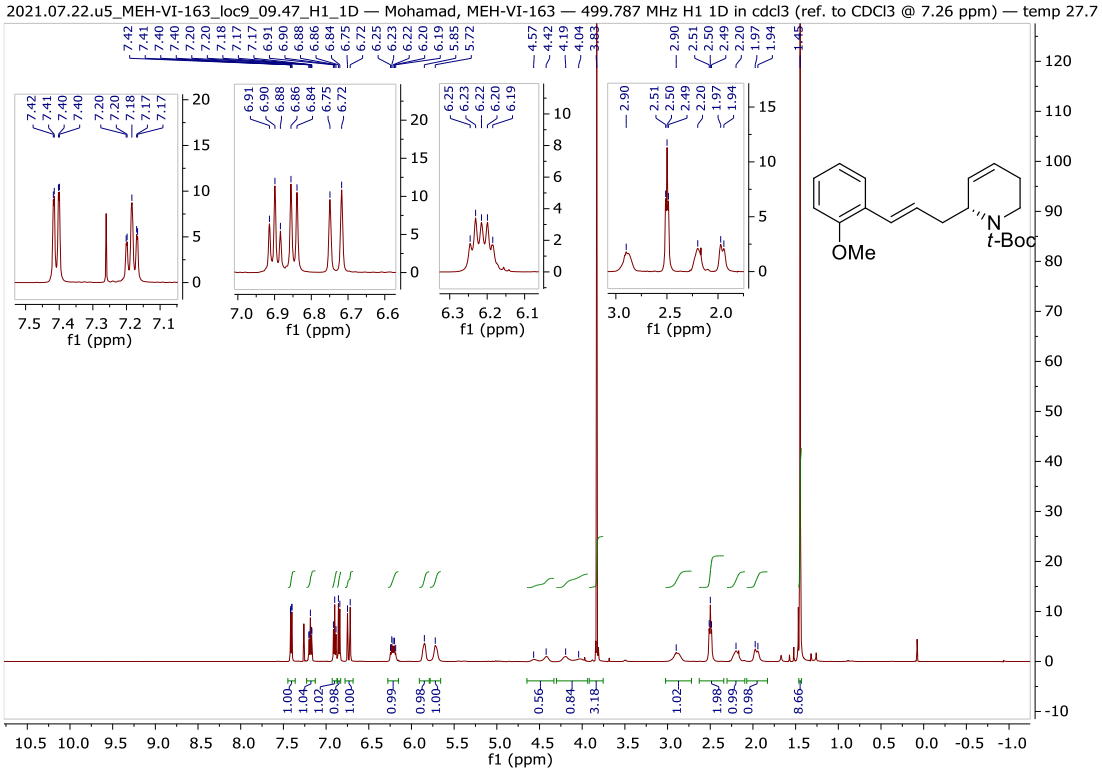
^{1}H NMR for compound **3d** (500 MHz, $CDCl_3$)



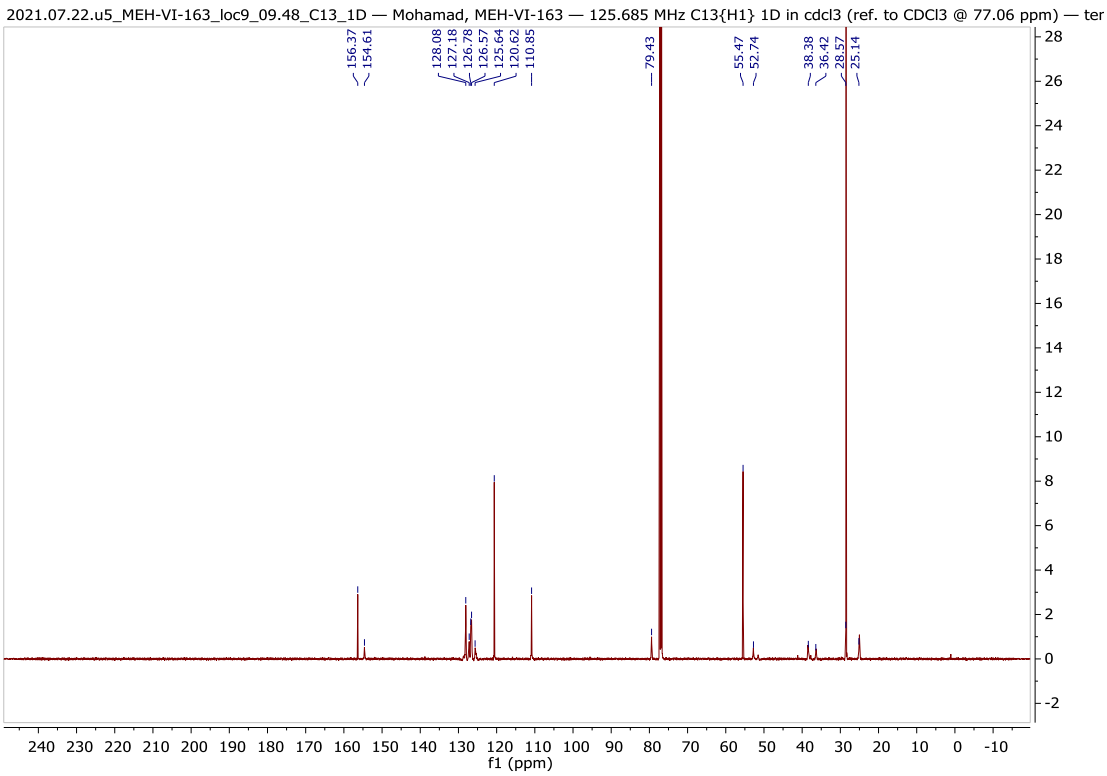
^{13}C NMR for compound **3d** (126 MHz, $CDCl_3$)



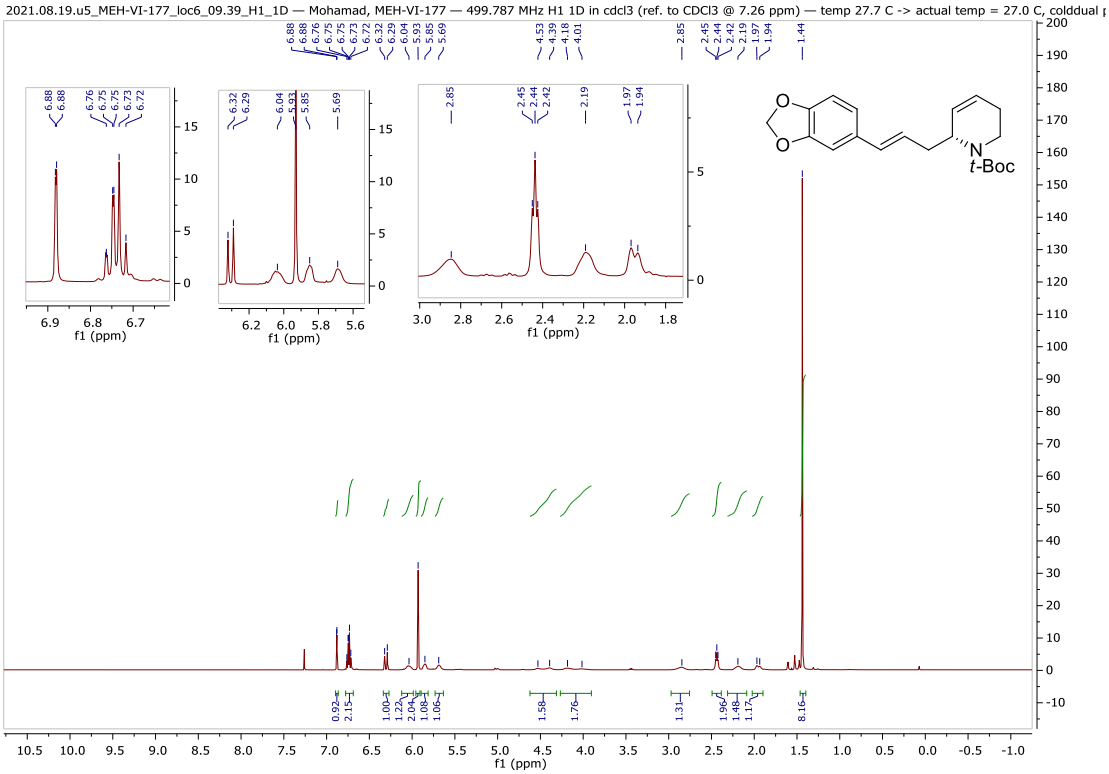
^{1}H NMR for compound **3e** (500 MHz, $CDCl_3$)



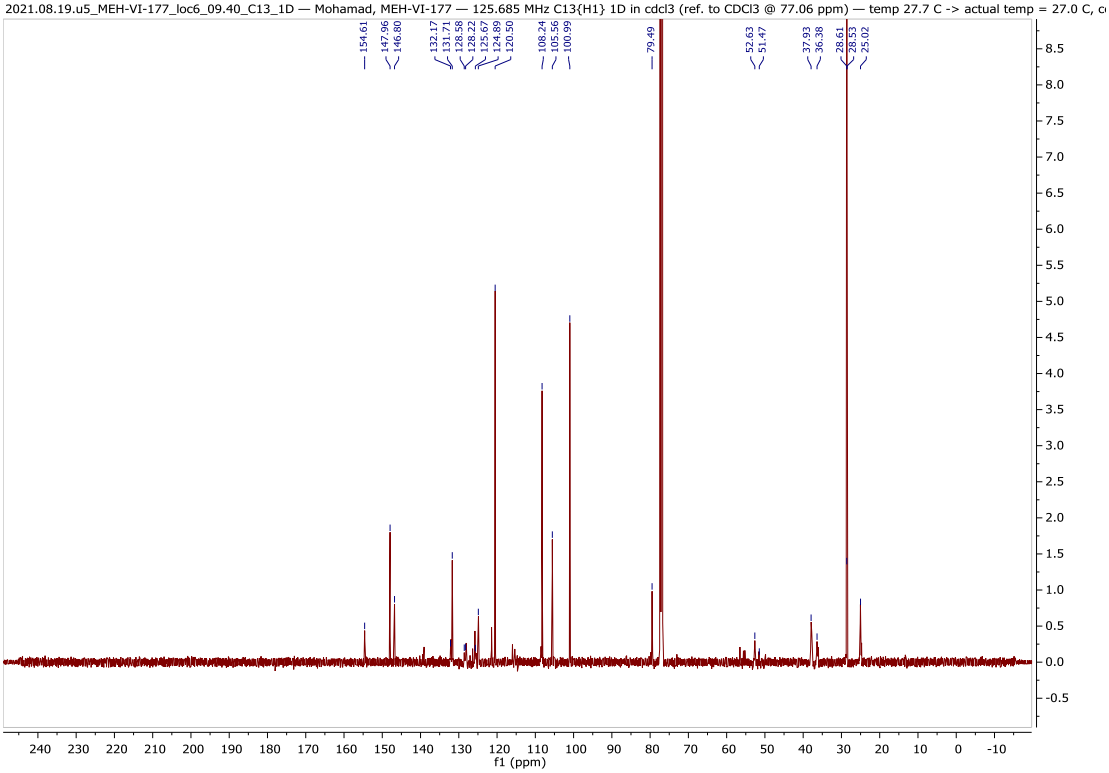
^{13}C NMR for compound **3e** (126 MHz, $CDCl_3$)



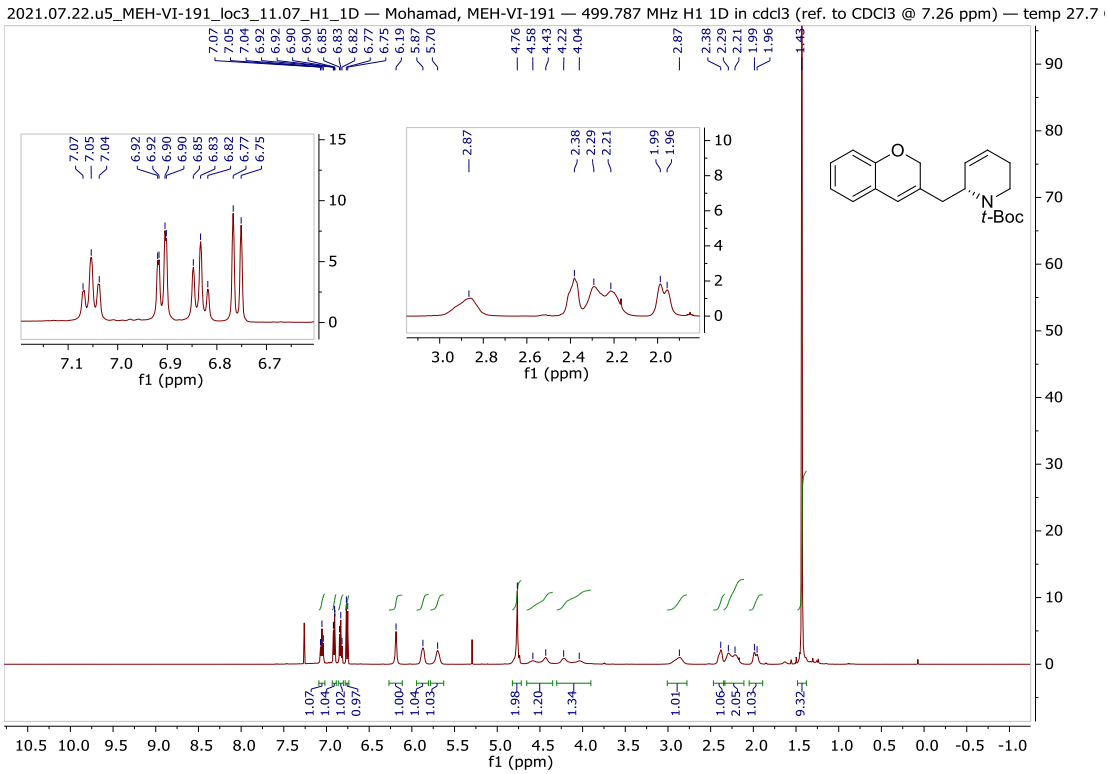
^{1}H NMR for compound **3f** (500 MHz, $CDCl_3$)



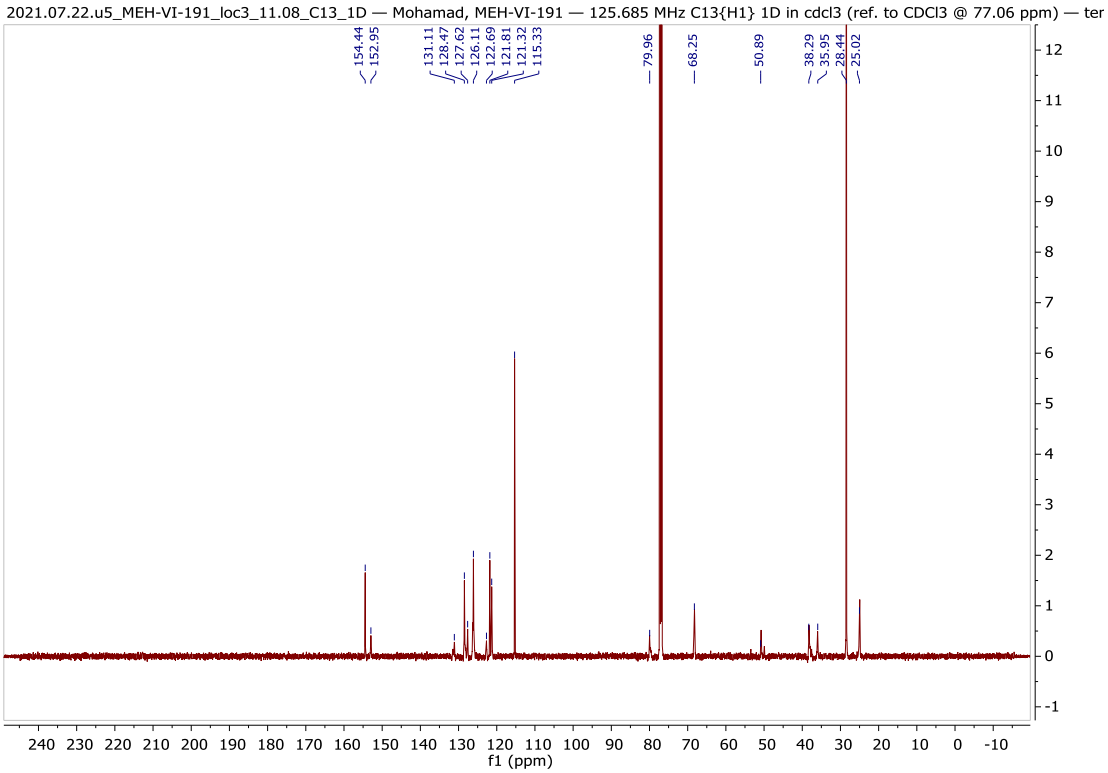
^{13}C NMR for compound **3f** (126 MHz, $CDCl_3$)



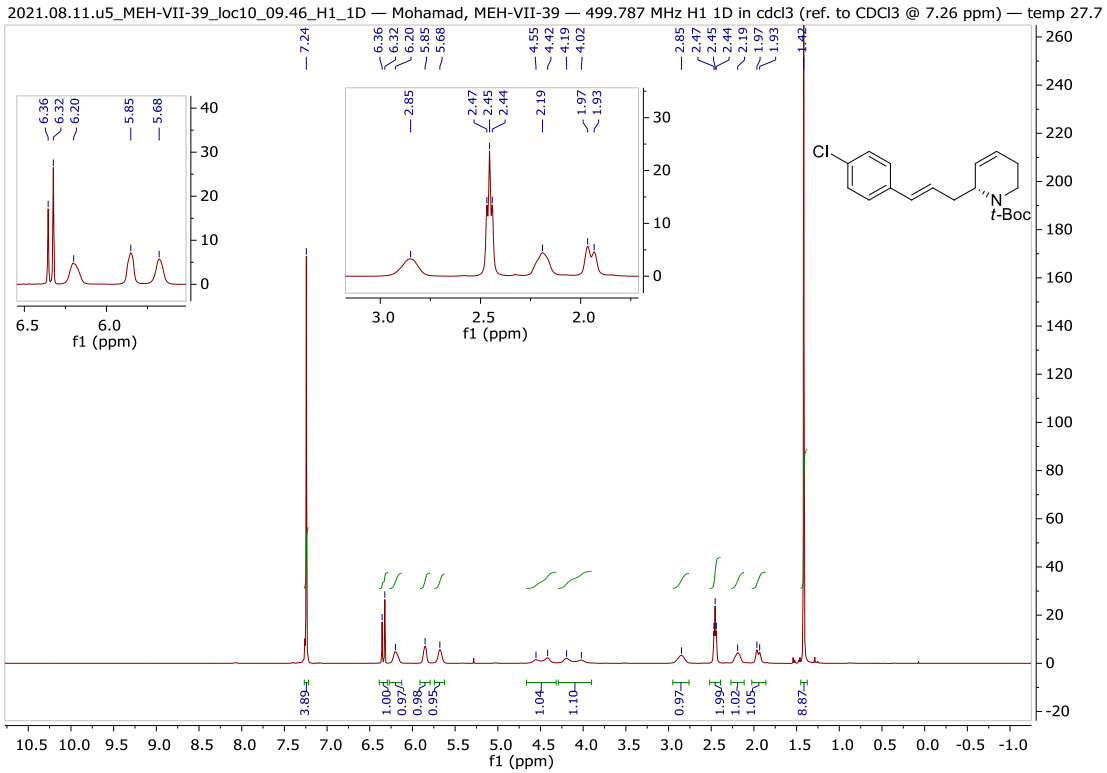
^{1}H NMR for compound **3g** (500 MHz, $CDCl_3$)



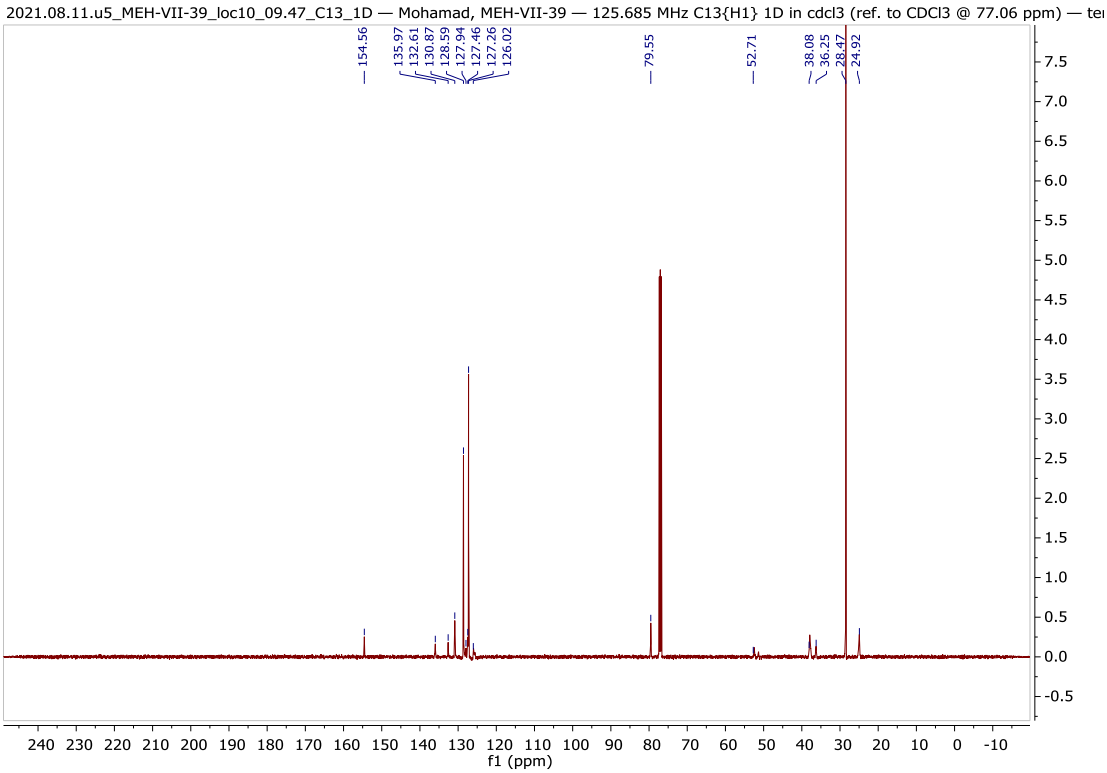
^{13}C NMR for compound **3g** (126 MHz, $CDCl_3$)



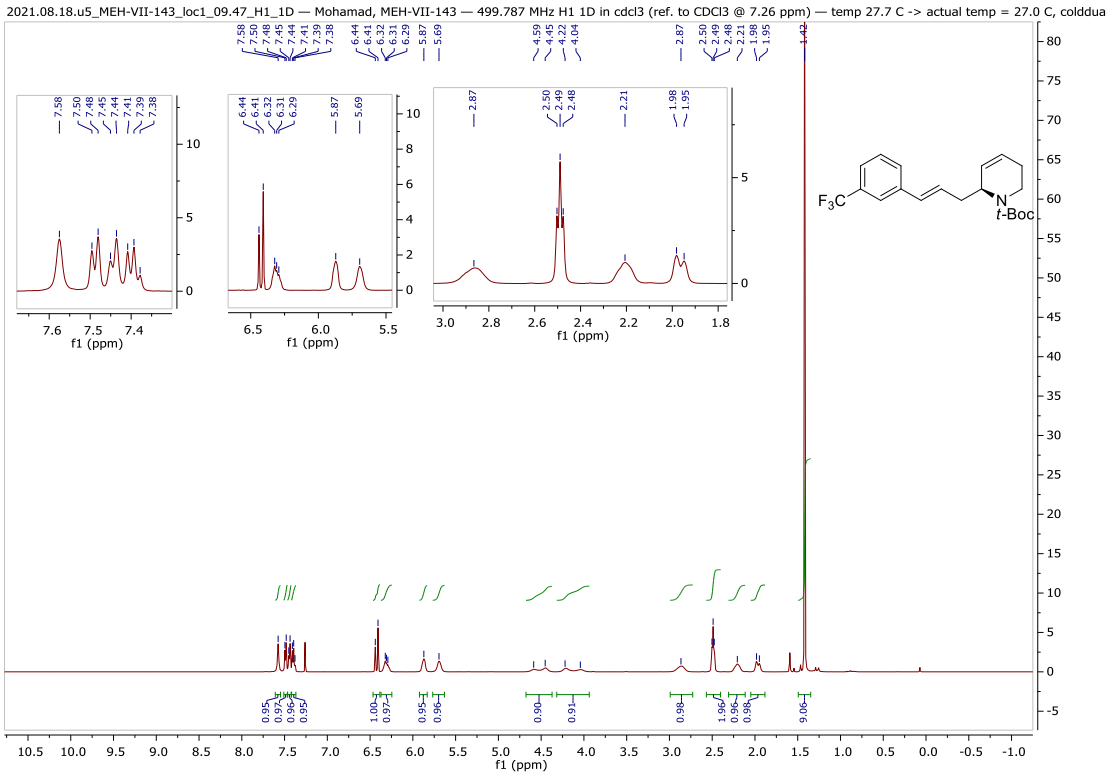
^{1}H NMR for compound **3h** (500 MHz, $CDCl_3$)



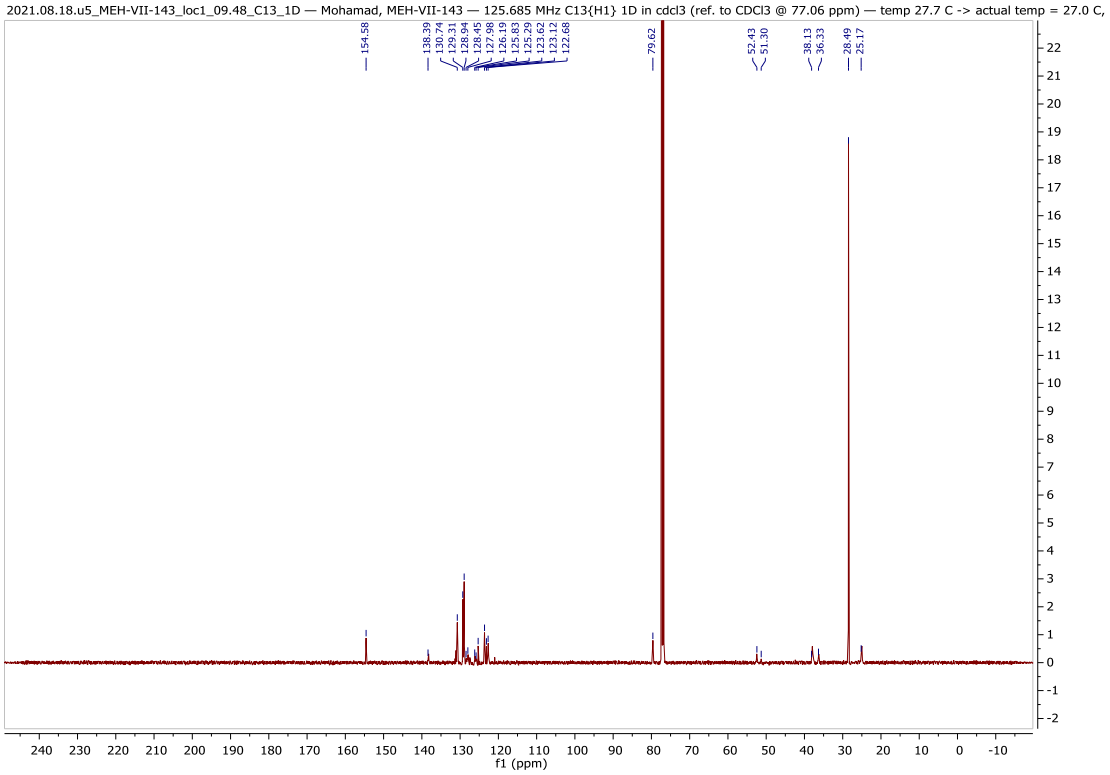
^{13}C NMR for compound **3h** (126 MHz, $CDCl_3$)



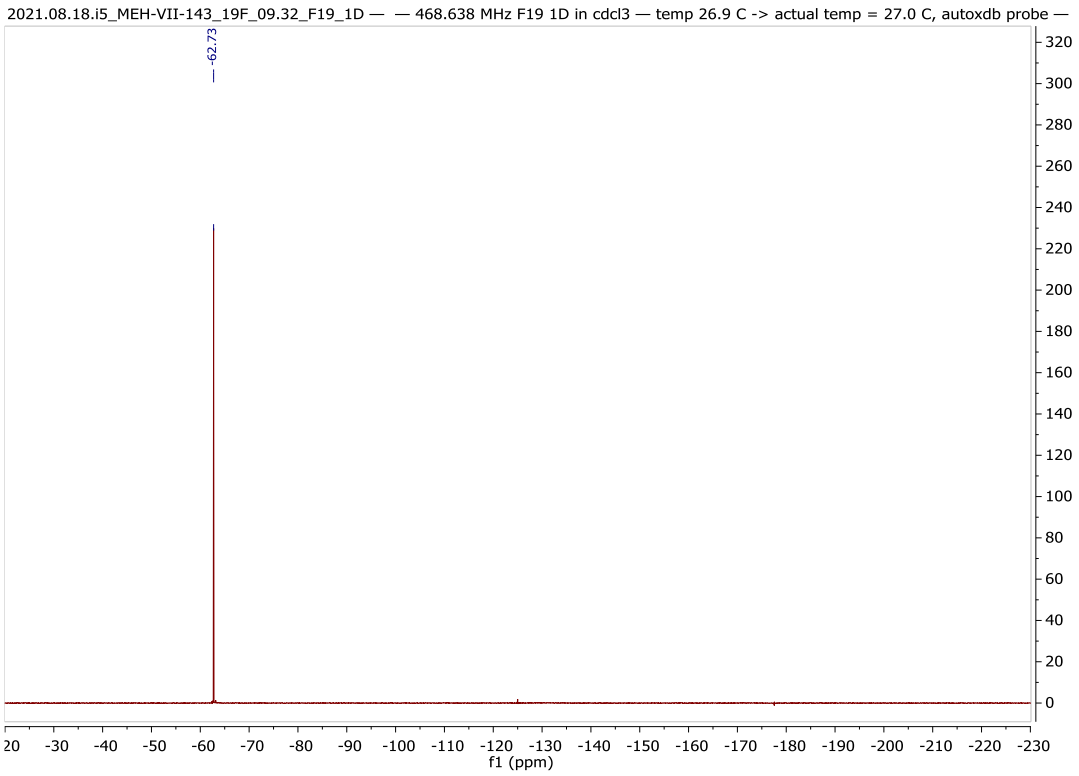
^{1}H NMR for compound **3i** (500 MHz, $CDCl_3$)



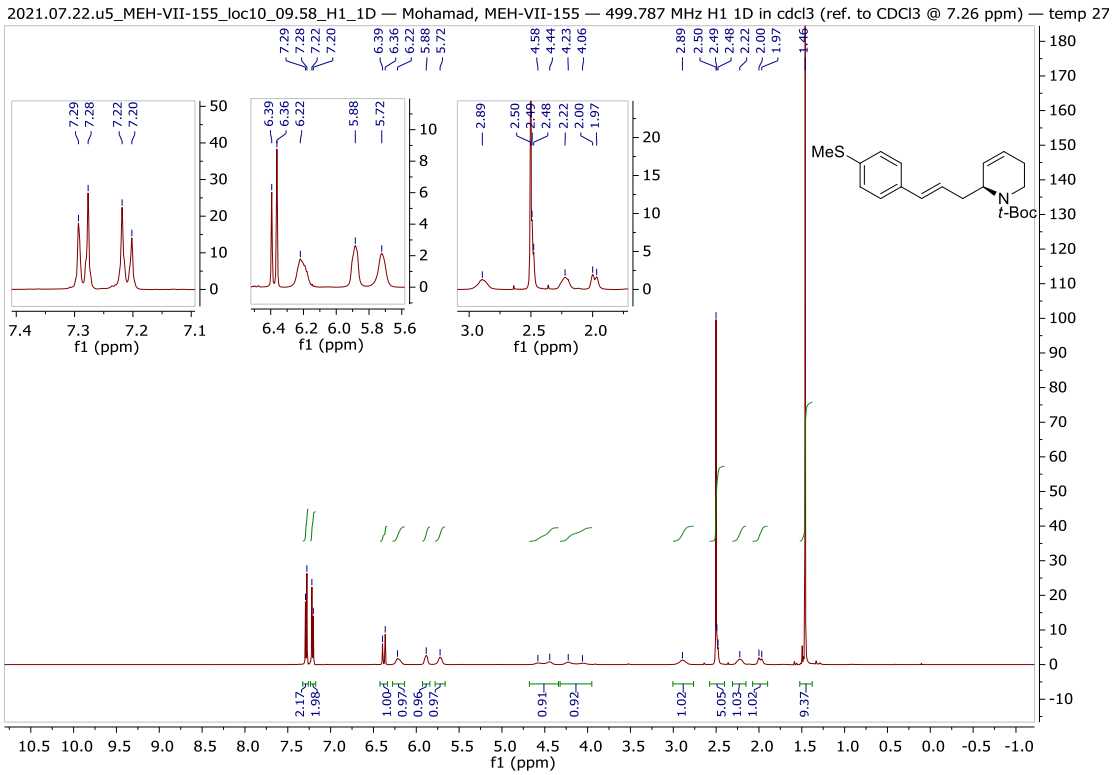
^{13}C NMR for compound **3i** (126 MHz, $CDCl_3$)



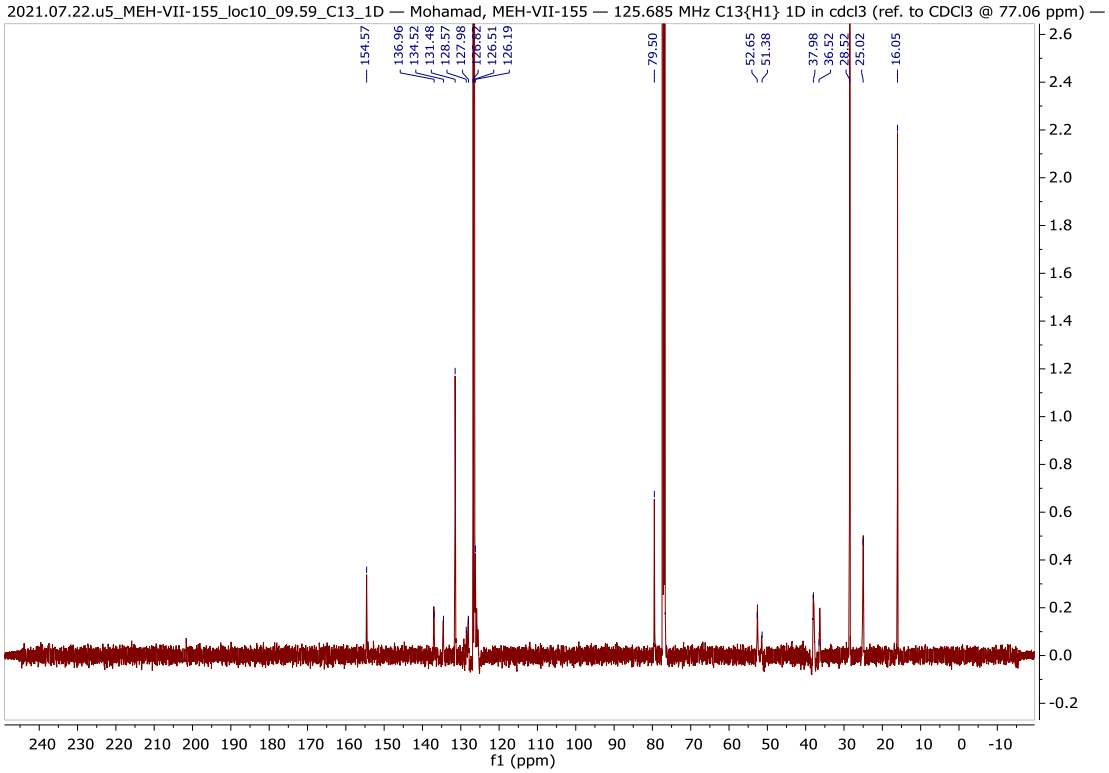
^{19}F NMR for compound **3i** (469 MHz, $CDCl_3$)



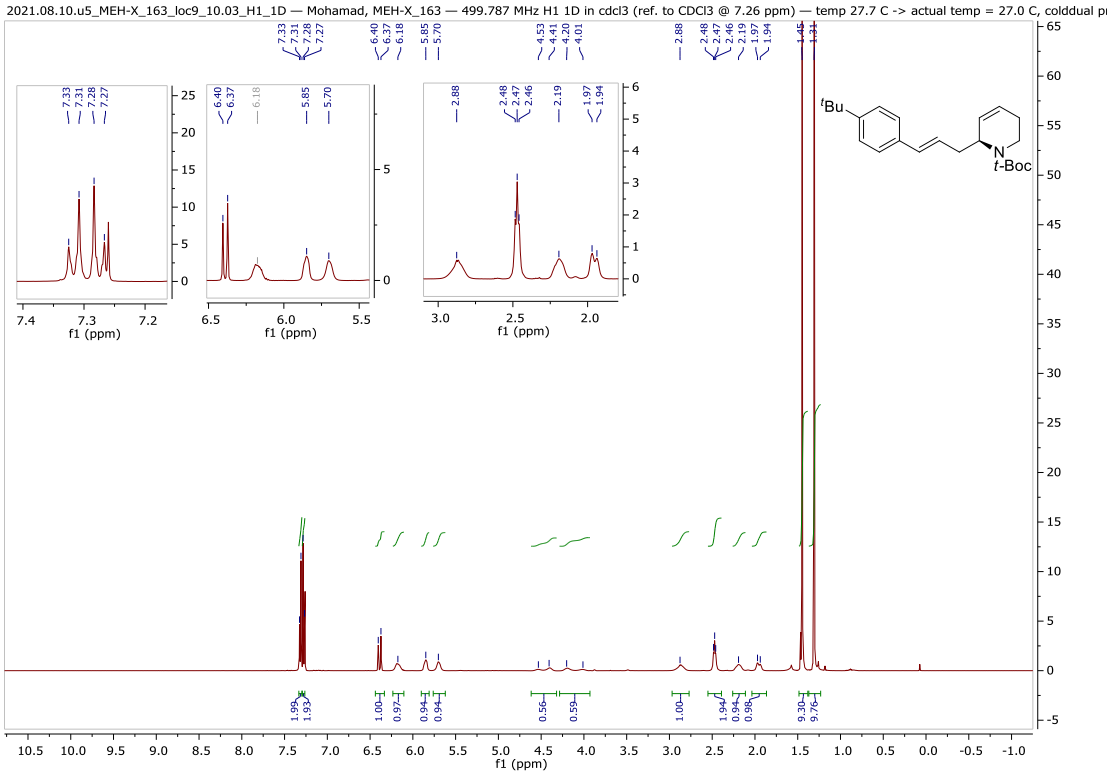
^{1}H NMR for compound **3j** (500 MHz, $CDCl_3$)



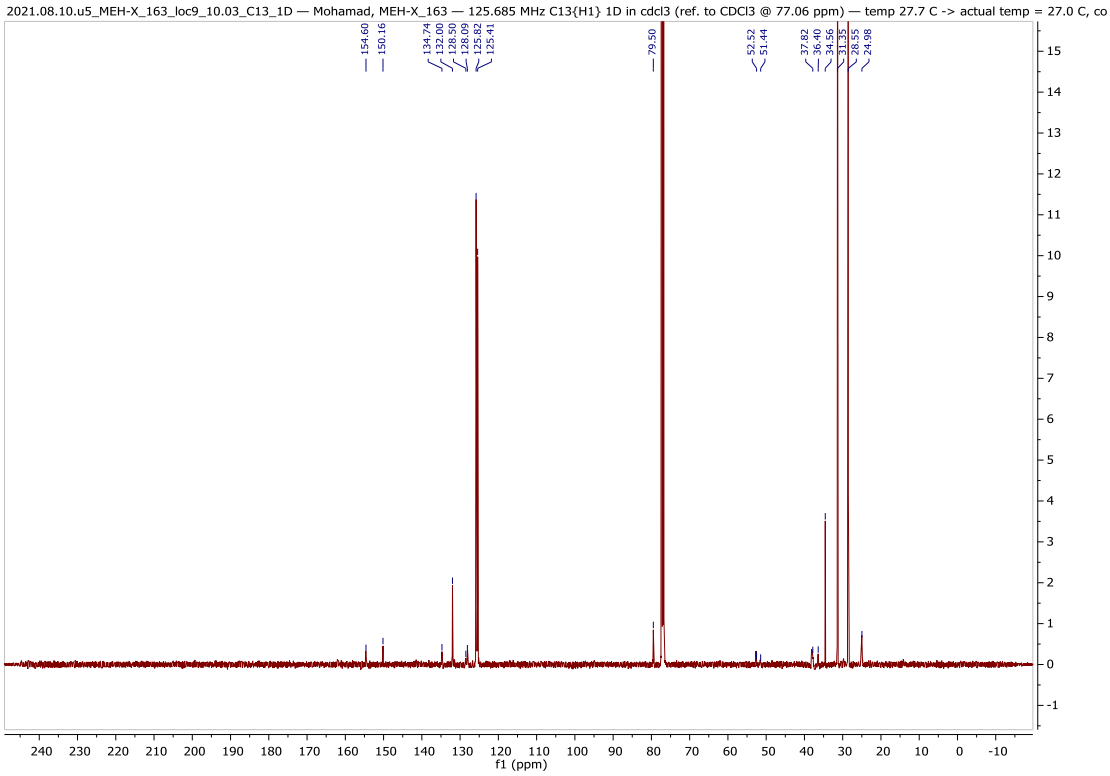
^{13}C NMR for compound **3j** (126 MHz, $CDCl_3$)



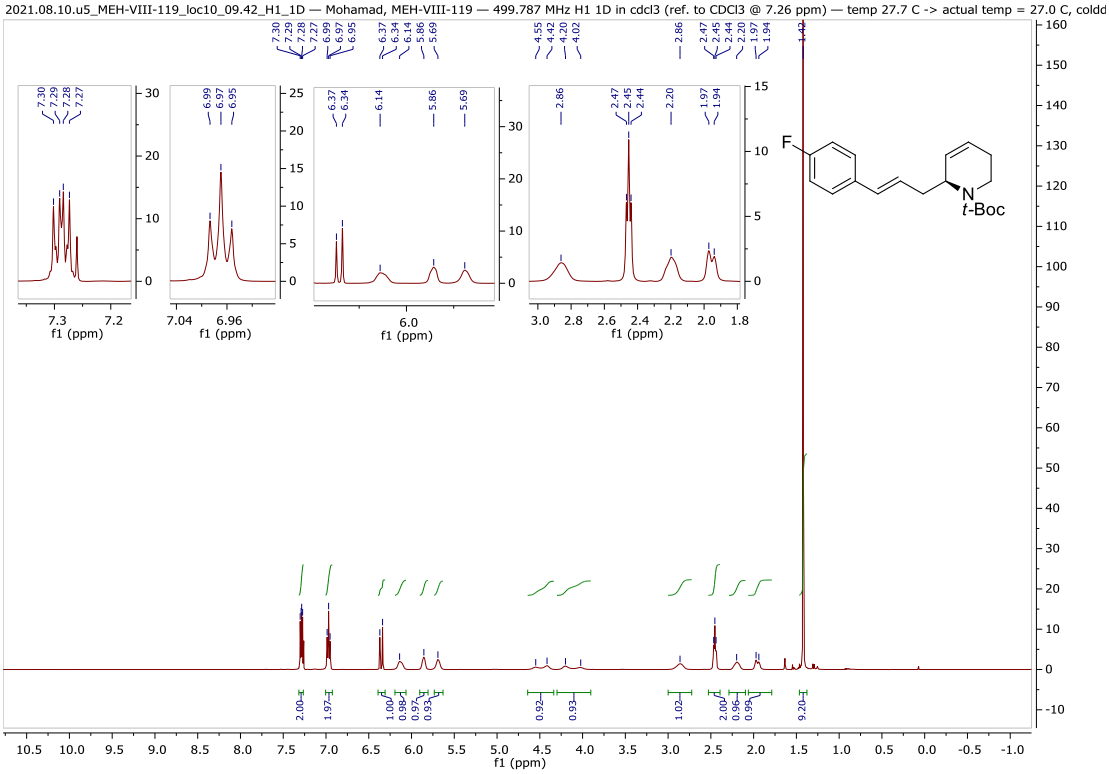
^{1}H NMR for compound **3k** (500 MHz, $CDCl_3$)



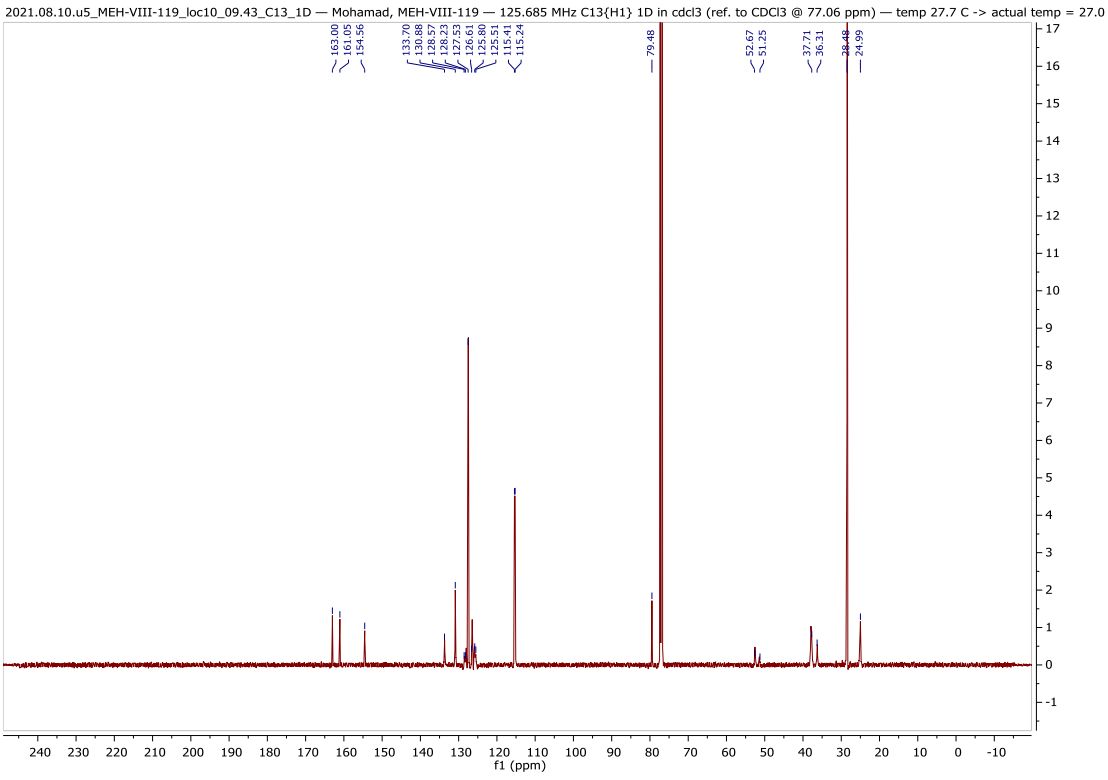
^{13}C NMR for compound **3k** (126 MHz, $CDCl_3$)



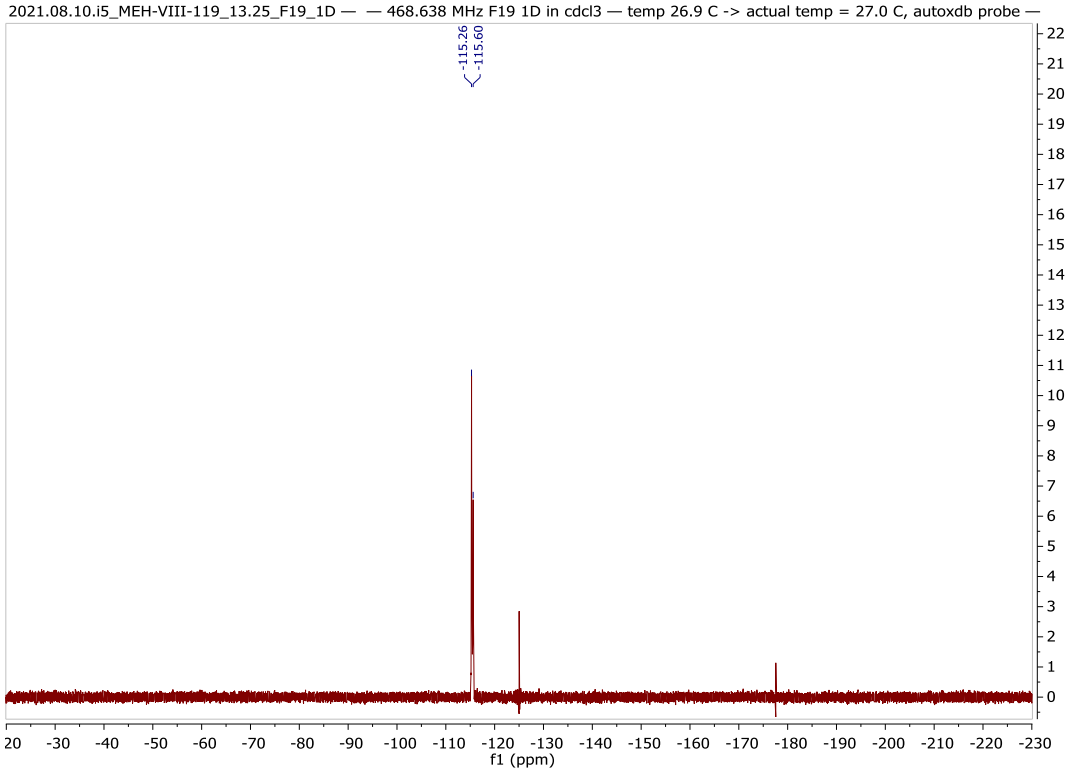
^{1}H NMR for compound **3l** (500 MHz, $CDCl_3$)



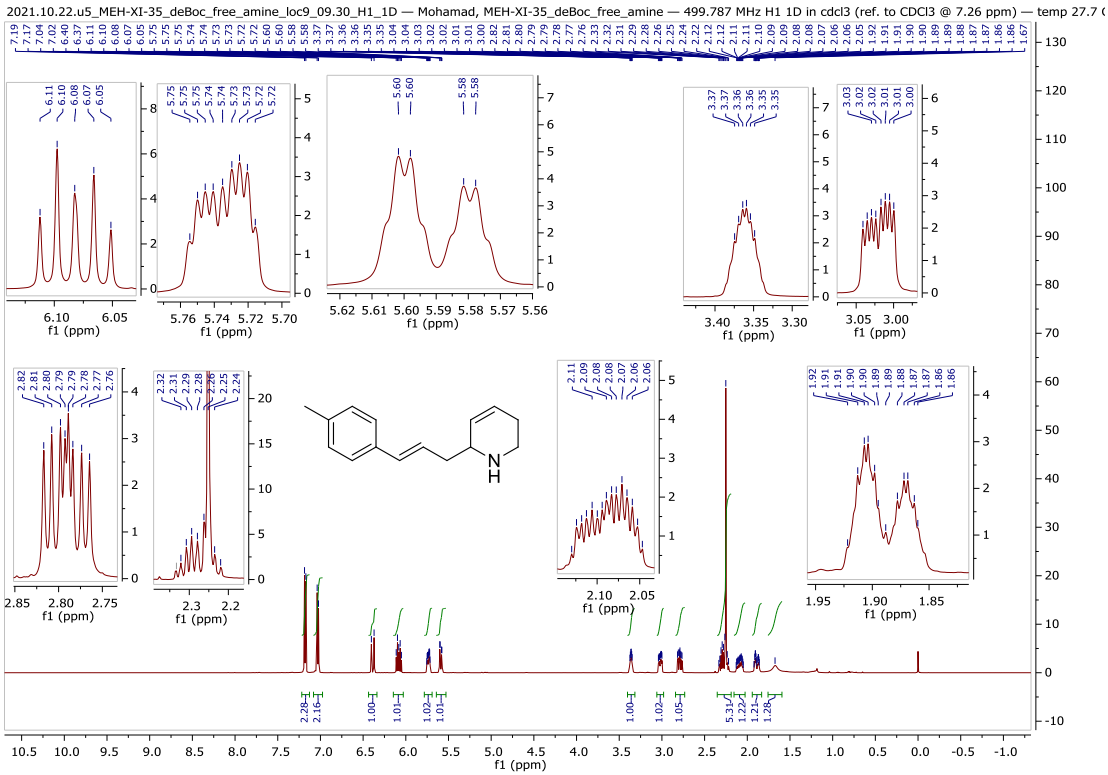
^{13}C NMR for compound **3l** (126 MHz, $CDCl_3$)



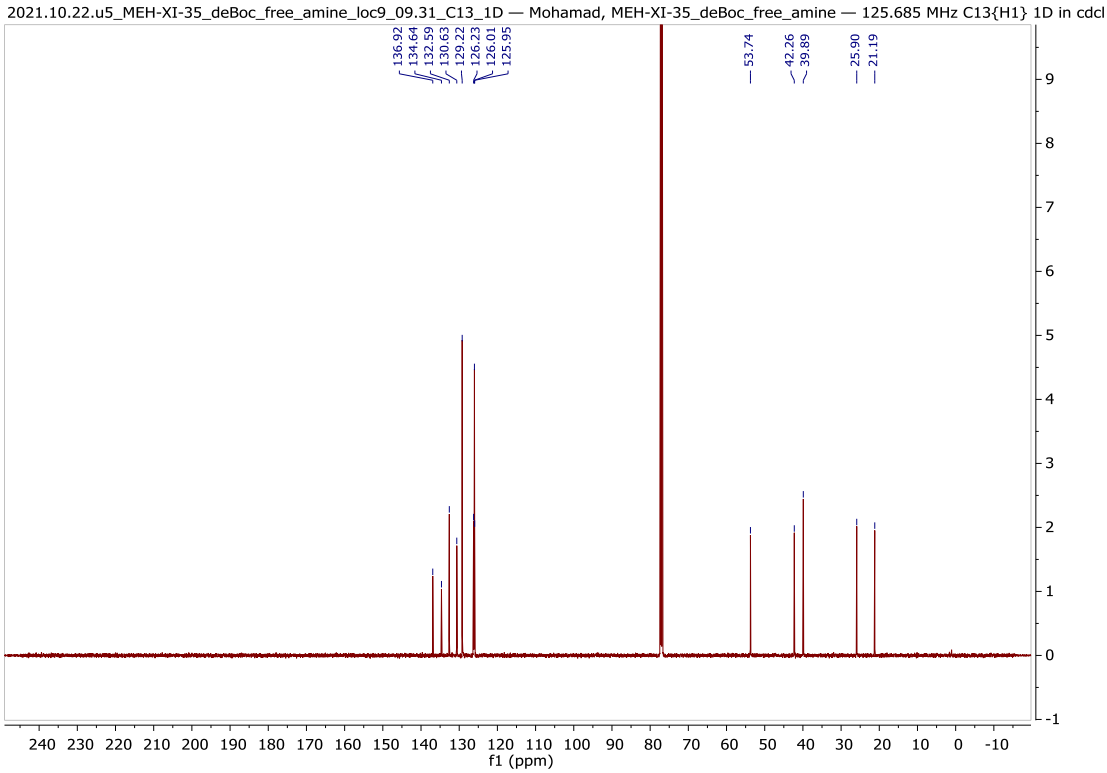
^{19}F NMR for compound **3l** (469 MHz, $CDCl_3$)



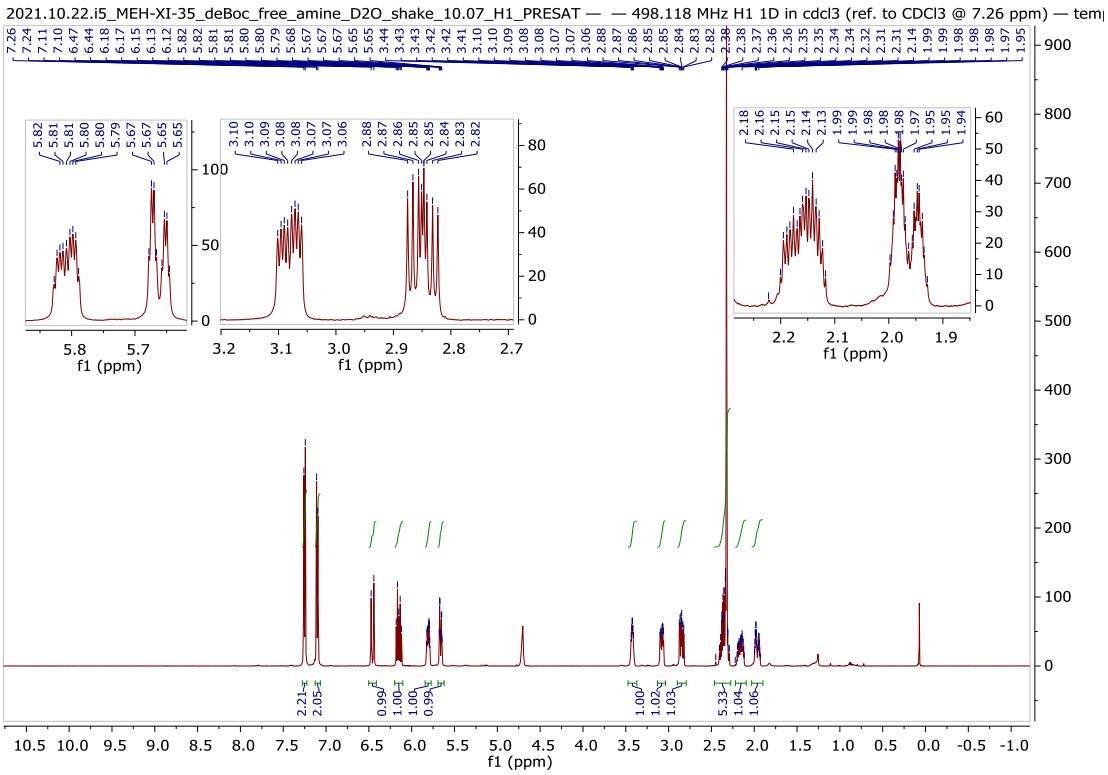
^{1}H NMR for compound **S23** (500 MHz, $CDCl_3$)



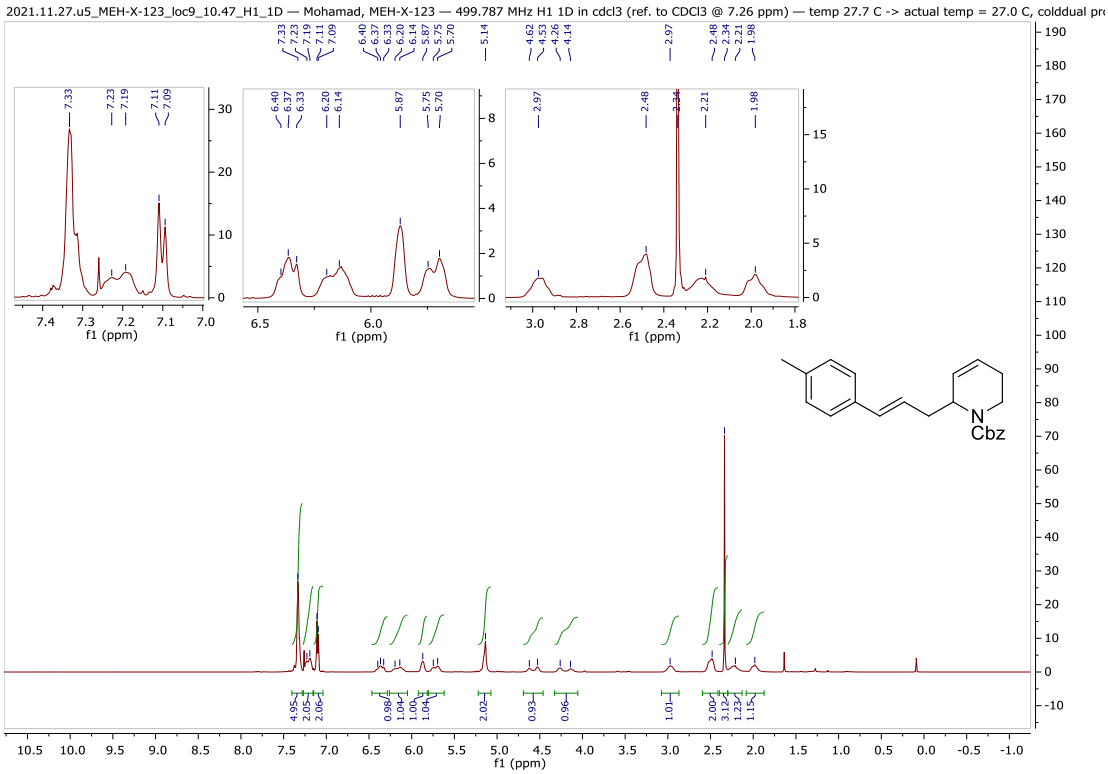
^{13}C NMR for compound **S23** (126 MHz, $CDCl_3$)



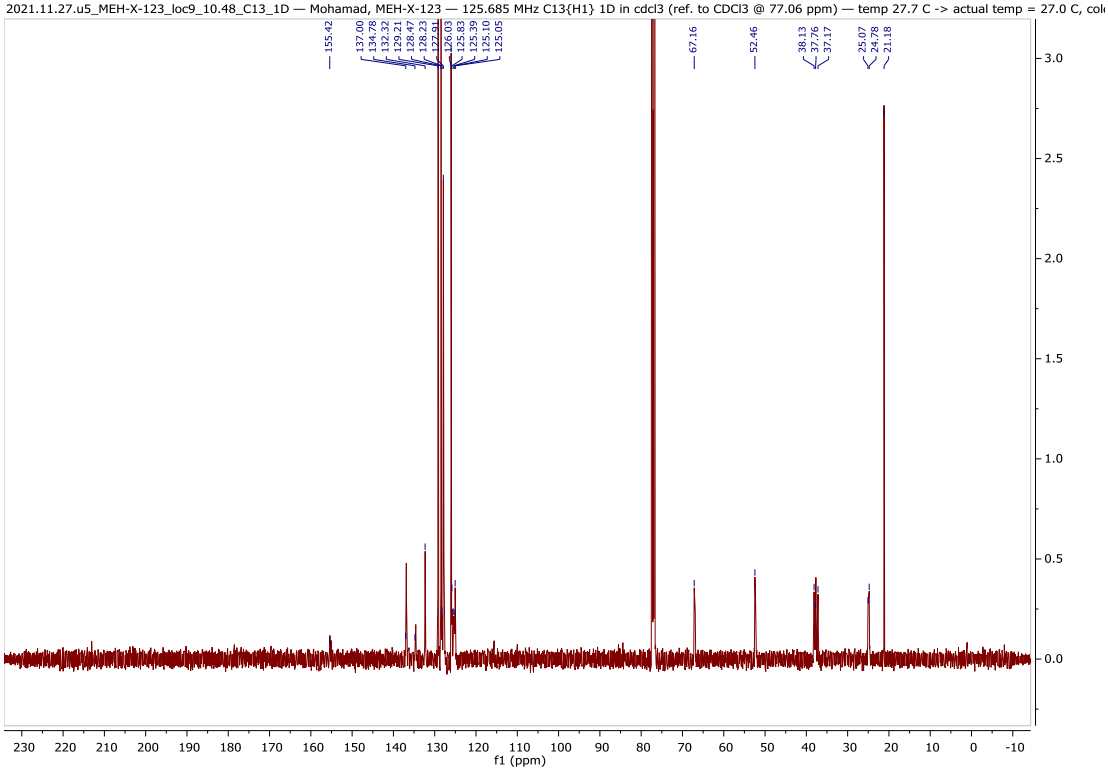
^{1}H NMR for compound **S23** (500 MHz, $CDCl_3$ + 1 drop D_2O)



^{1}H NMR for compound (*rac*)-**3d′** (500 MHz, $CDCl_3$)

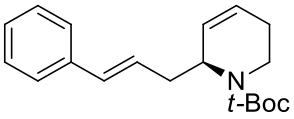


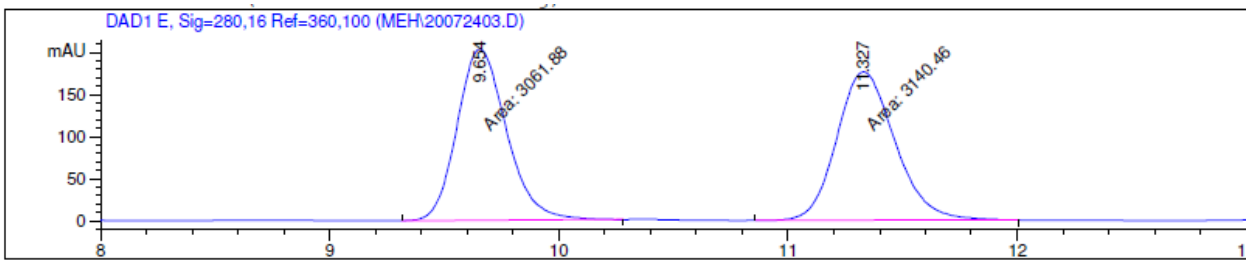
^{13}C NMR for compound (*rac*)-**3d′** (126 MHz, $CDCl_3$)



7. HPLC Chromatograms for Enantioenriched Compounds

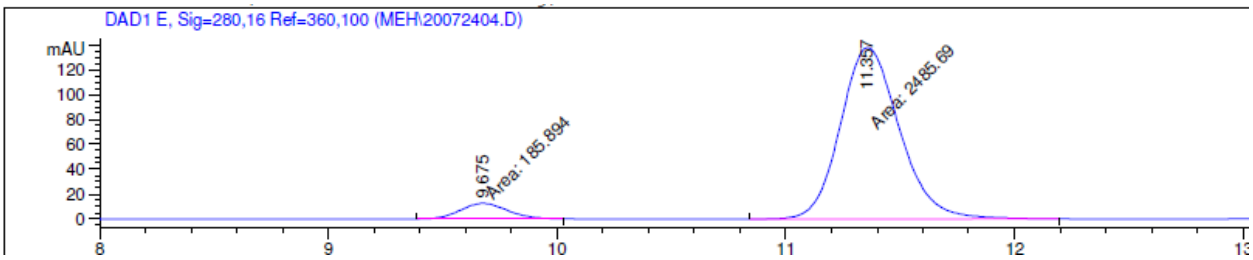
HPLC trace for (±)-**3a** (top) and enantioenriched **3a** (bottom)





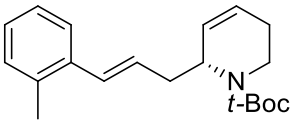
Signal 1: DAD1 E, Sig=280,16 Ref=360,100

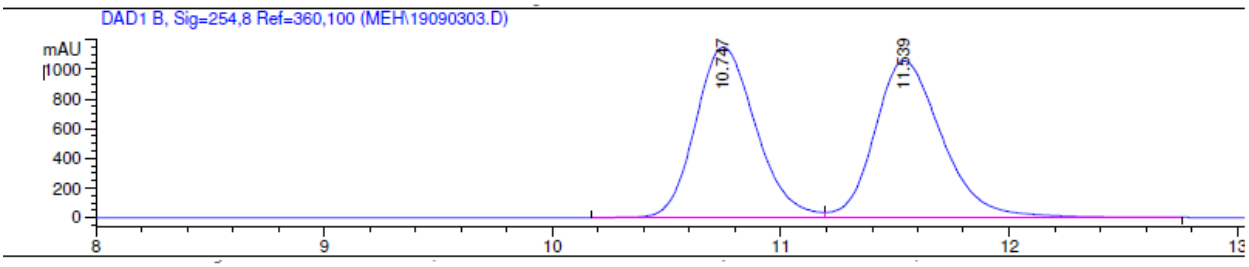
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.654	MM	0.2499	3061.88403	204.22751	49.3666
2	11.327	MM	0.2959	3140.45874	176.89635	50.6334
Totals :				6202.34277	381.12386	



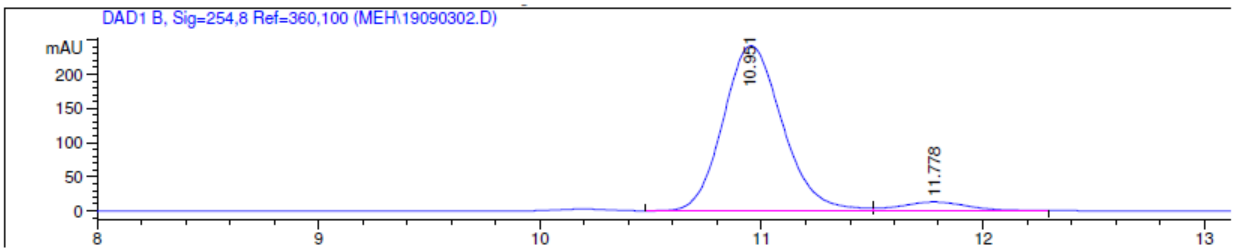
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.675	MM	0.2447	185.89436	12.66230	6.9582
2	11.357	MM	0.3004	2485.68579	137.90472	93.0418
Totals :				2671.58015	150.56702	

HPLC trace for (±)-**3b** (top) and enantioenriched **3b** (bottom)



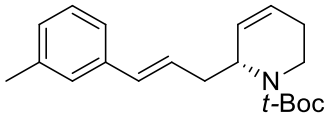


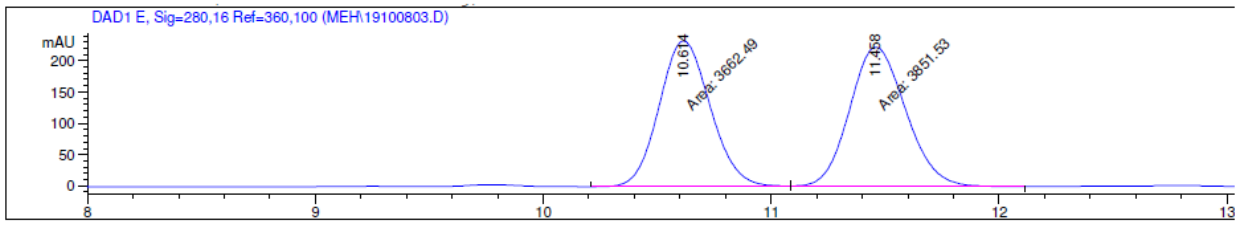
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.747	BV	0.2841	2.11436e4	1152.28040	49.3382
2	11.539	VB	0.3150	2.17108e4	1059.69092	50.6618
Totals :				4.28544e4	2211.97131	



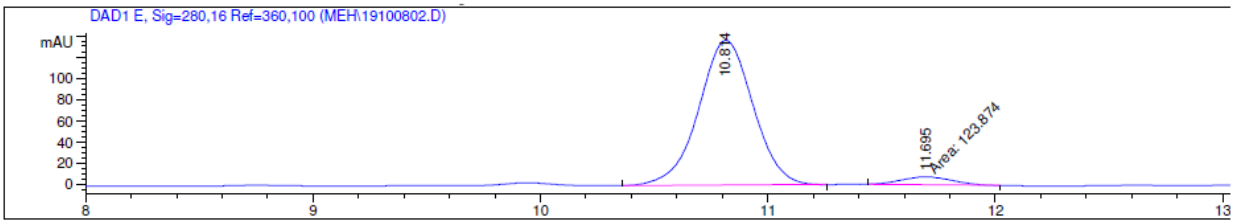
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.951	VV	0.2871	4503.35840	242.01489	94.2949
2	11.778	VB	0.3201	272.46707	12.91806	5.7051
Totals :				4775.82547	254.93295	

HPLC trace for (±)-**3c** (top) and enantioenriched **3c** (bottom)



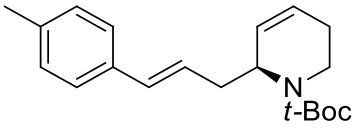


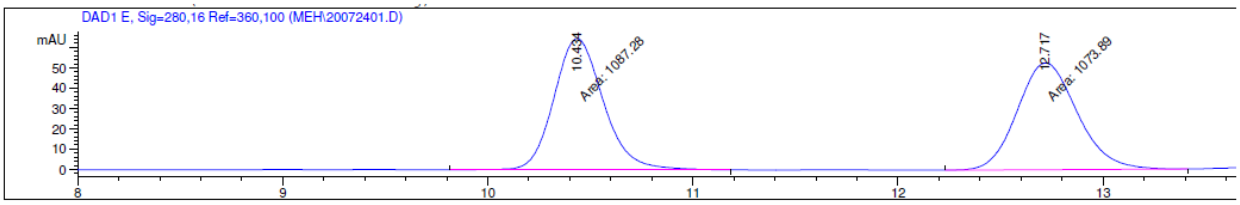
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.614	MF	0.2610	3662.48975	233.86827	48.7421
2	11.458	FM	0.2866	3851.53369	223.95952	51.2579
Totals :				7514.02344	457.82779	



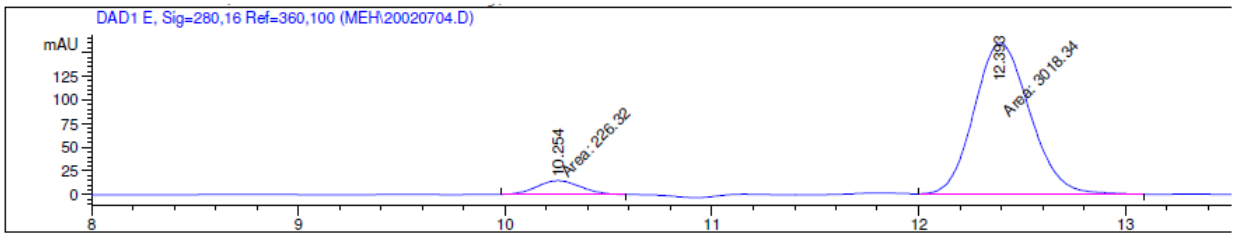
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.814	BP	0.2561	2267.71826	136.28812	94.8205
2	11.695	MM	0.2706	123.87367	7.62920	5.1795
Totals :				2391.59193	143.91731	

HPLC trace for (±)-**3d** (top) and enantioenriched **3d** from **2** (middle) and **2′** (bottom)

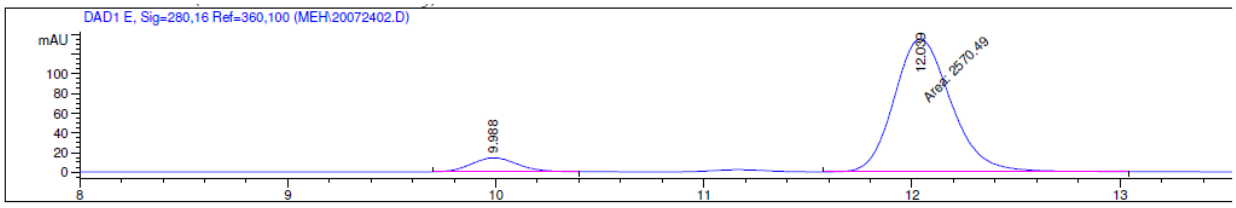




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.434	MM	0.2801	1087.28333	64.70607	50.3098
2	12.717	MM	0.3399	1073.89258	52.66484	49.6902
Totals :				2161.17590	117.37091	

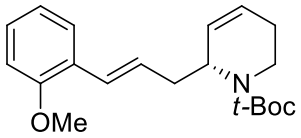


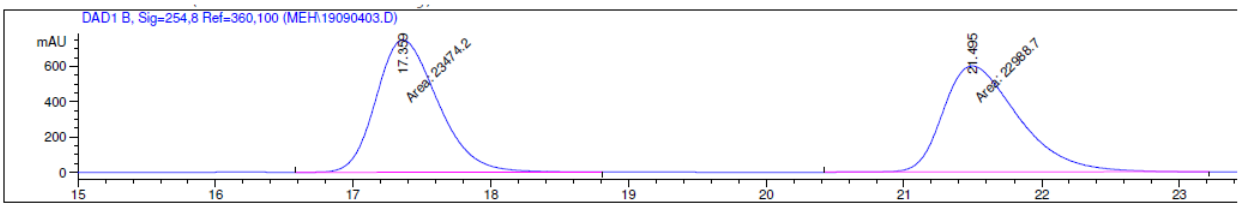
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.254	MM	0.2531	226.31989	14.90441	6.9752
2	12.393	MM	0.3145	3018.33789	159.94223	93.0248
Totals :				3244.65778	174.84664	



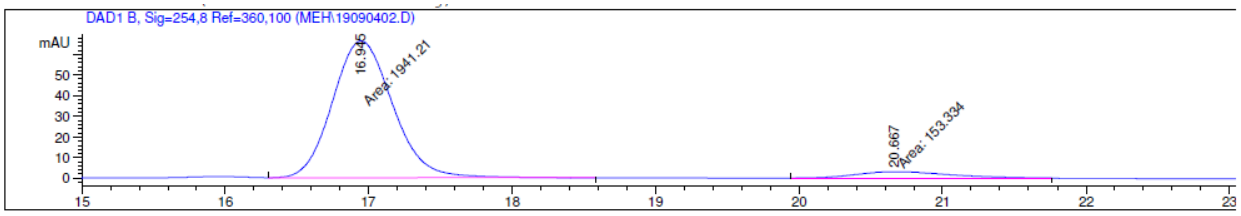
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.988	BB	0.2416	223.07236	14.33113	7.9852
2	12.039	MM	0.3166	2570.49121	135.30162	92.0148
Totals :				2793.56357	149.63275	

HPLC trace for (±)-**3e** (top) and enantioenriched **3e** (bottom)



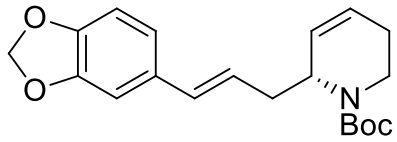


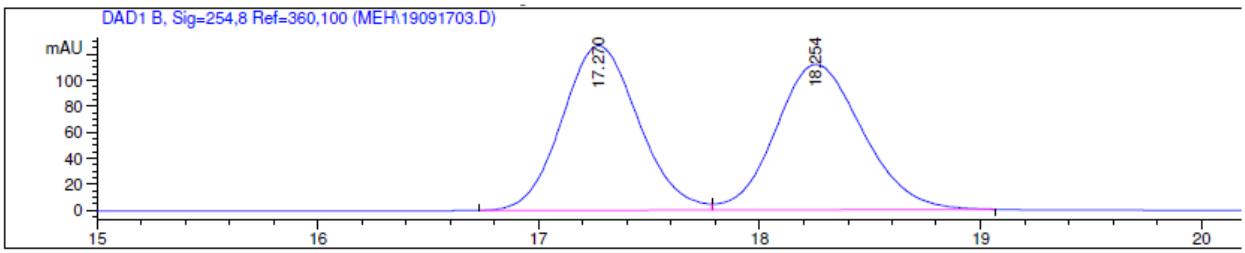
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.359	MM	0.5217	2.34742e4	749.90808	50.5225
2	21.495	MM	0.6371	2.29887e4	601.42139	49.4775
Totals :				4.64629e4	1351.32947	



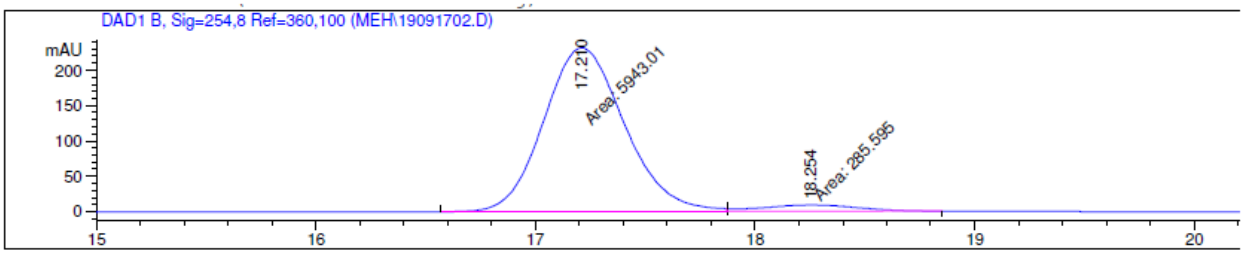
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.945	MM	0.4882	1941.21240	66.26708	92.6794
2	20.667	MM	0.7942	153.33423	3.21763	7.3206
Totals :				2094.54663	69.48471	

HPLC trace for (±)-**3f** (top) and enantioenriched **3f** (bottom)



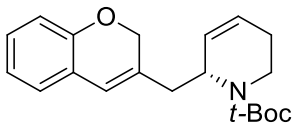


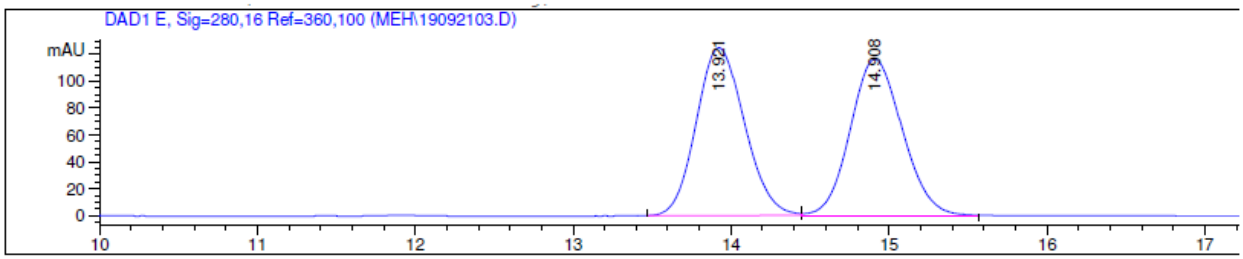
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.270	BV	0.3733	3056.04419	126.72529	49.8166
2	18.254	VB	0.4245	3078.54004	112.07335	50.1834
Totals :				6134.58423	238.79864	



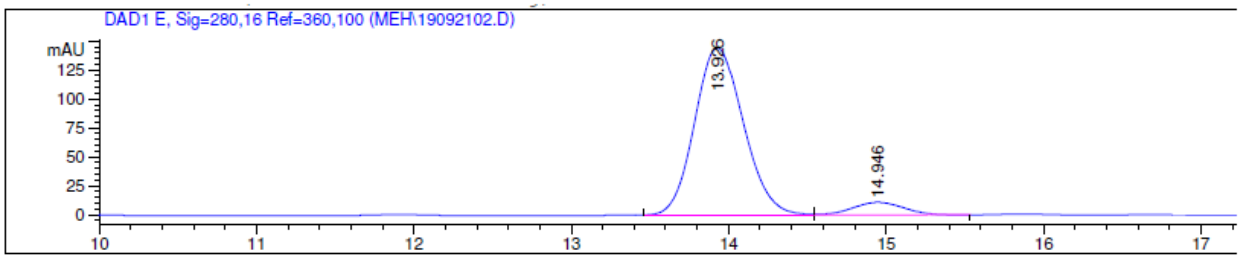
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.210	MF	0.4271	5943.01074	231.91661	95.4148
2	18.254	FM	0.5141	285.59528	9.25942	4.5852
Totals :				6228.60602	241.17603	

HPLC trace for (±)-**3g** (top) and enantioenriched **3g** (bottom)



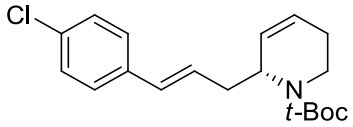


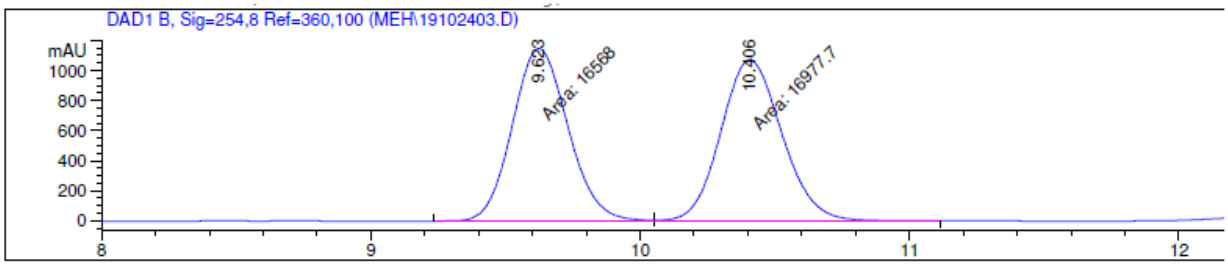
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.921	BV	0.3306	2676.27441	125.59457	49.9374
2	14.908	VB	0.3579	2682.98486	116.85542	50.0626
Totals :				5359.25928	242.45000	



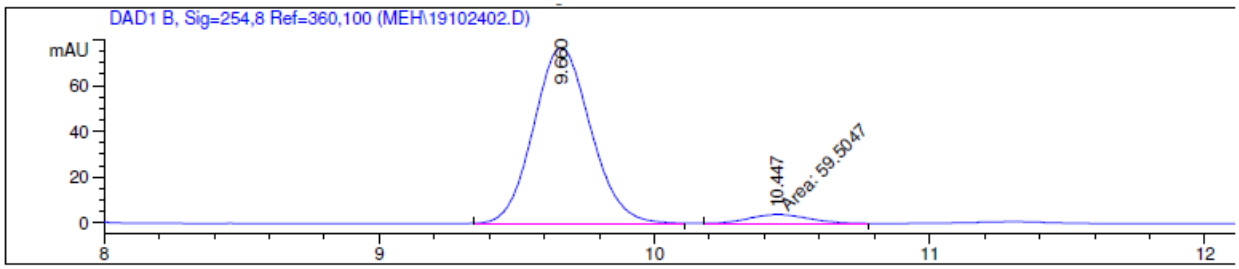
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.926	BB	0.3357	3128.53467	145.01659	92.4596
2	14.946	BP	0.3553	255.14180	11.13578	7.5404
Totals :				3383.67647	156.15237	

HPLC trace for (±)-**3h** (top) and enantioenriched **3h** (bottom)



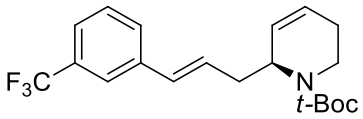


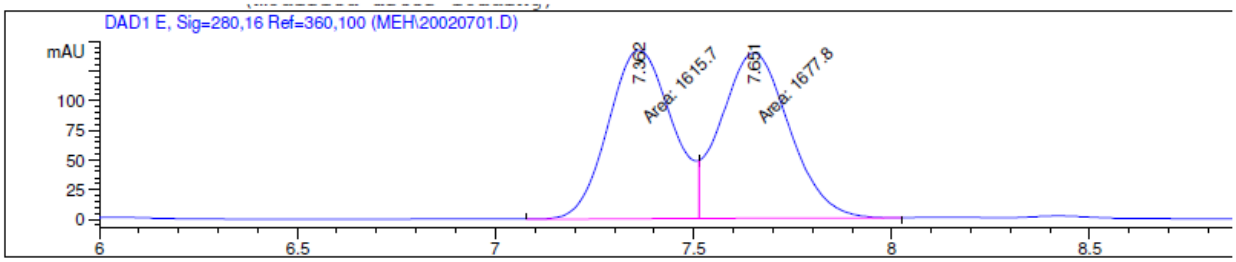
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.623	MF	0.2403	1.65680e4	1149.24426	49.3893
2	10.406	FM	0.2638	1.69777e4	1072.75830	50.6107
Totals :				3.35456e4	2222.00256	



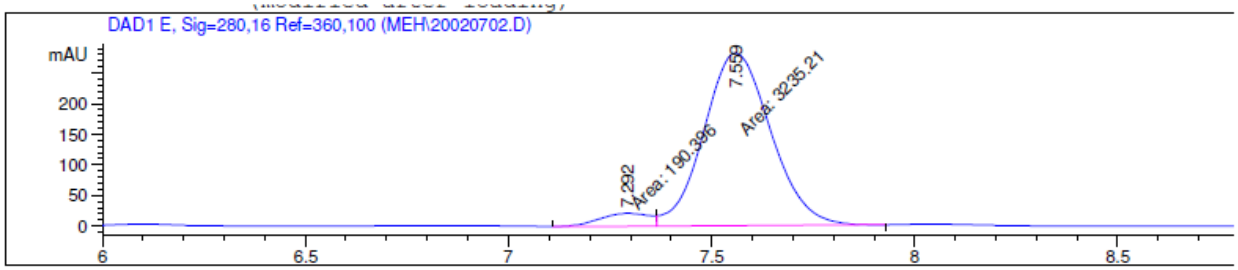
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.660	BB	0.2245	1111.93347	76.97248	94.9204
2	10.447	MM	0.2530	59.50470	3.91940	5.0796
Totals :				1171.43817	80.89188	

HPLC trace for (±)-**3i** (top) and enantioenriched **3i** (bottom)



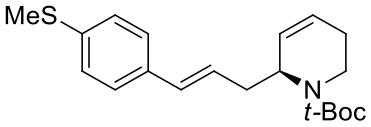


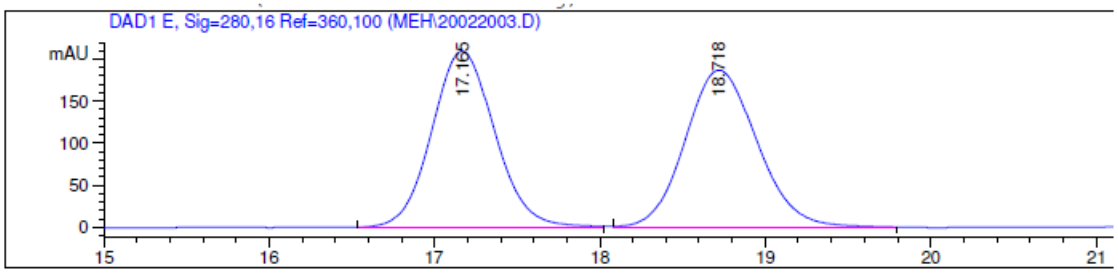
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.362	MF	0.1888	1615.70166	142.61624	49.0573
2	7.651	FM	0.1998	1677.79590	139.95151	50.9427
Totals :				3293.49756	282.56775	



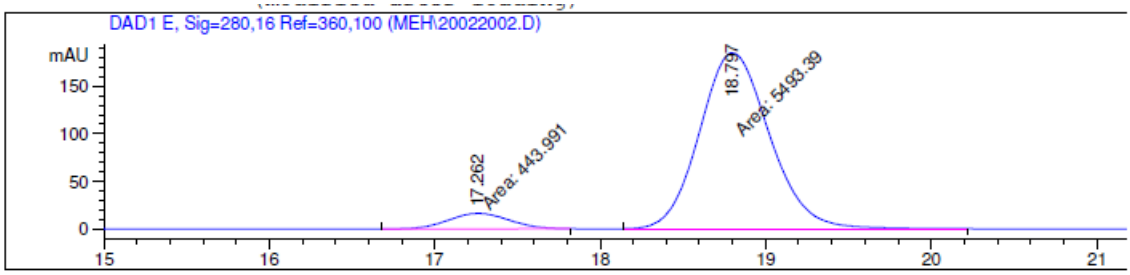
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.292	MF	0.1484	190.39609	21.38748	5.5580
2	7.559	FM	0.1909	3235.20874	282.40302	94.4420
Totals :				3425.60483	303.79049	

HPLC trace for (±)-**3j** (top) and enantioenriched **3j** (bottom)



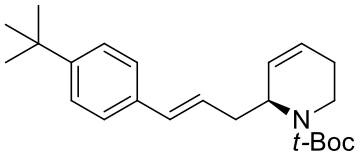


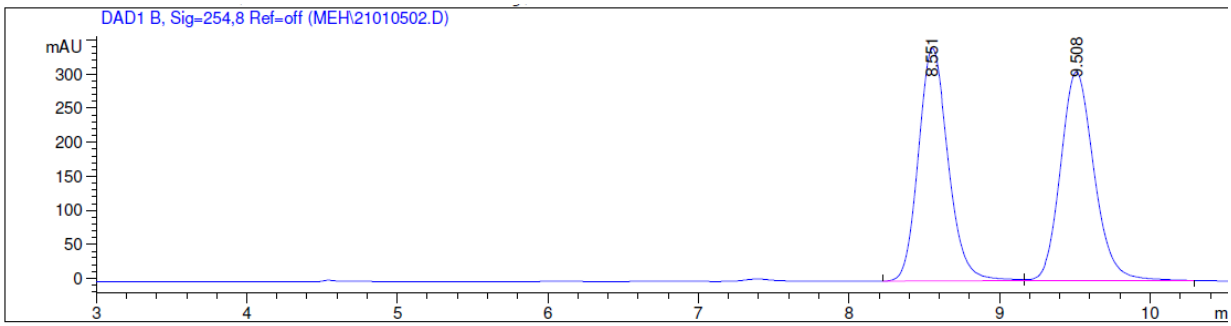
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.165	BB	0.4128	5576.94580	209.37207	49.4702
2	18.718	BB	0.4757	5696.39941	186.82304	50.5298
Totals :				1.12733e4	396.19511	



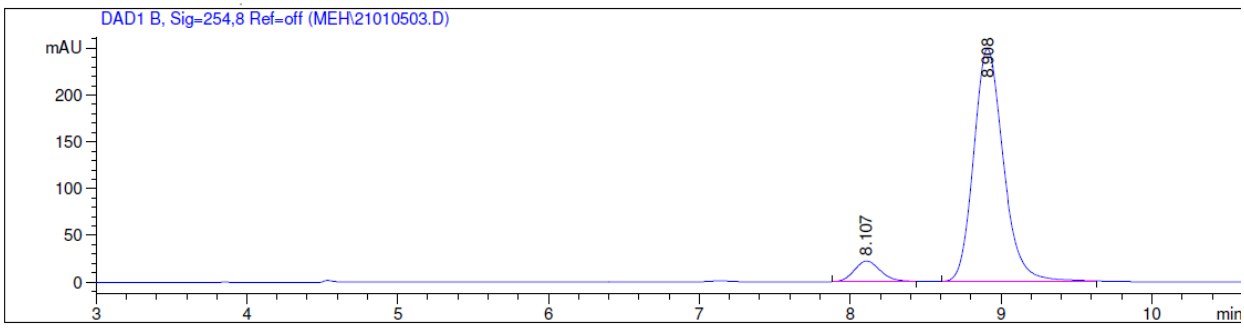
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.262	MM	0.4441	443.99146	16.66128	7.4779
2	18.797	MM	0.4943	5493.39355	185.22372	92.5221
Totals :				5937.38501	201.88501	

HPLC trace for (±)-**3k** (top) and enantioenriched **3k** (bottom)



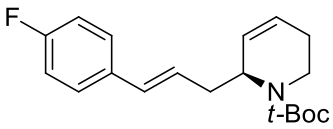


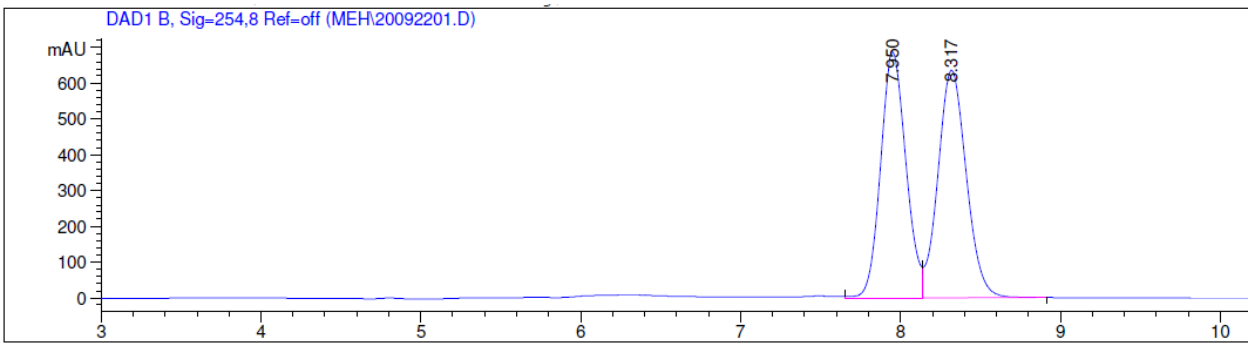
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.551	BV	0.2135	4733.62500	342.04077	49.9077
2	9.508	VB	0.2386	4751.13867	306.95721	50.0923
Totals :				9484.76367	648.99799	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.107	BB	0.1874	267.60303	22.08076	7.2773
2	8.908	BB	0.2100	3409.60352	248.60757	92.7227
Totals :				3677.20654	270.68833	

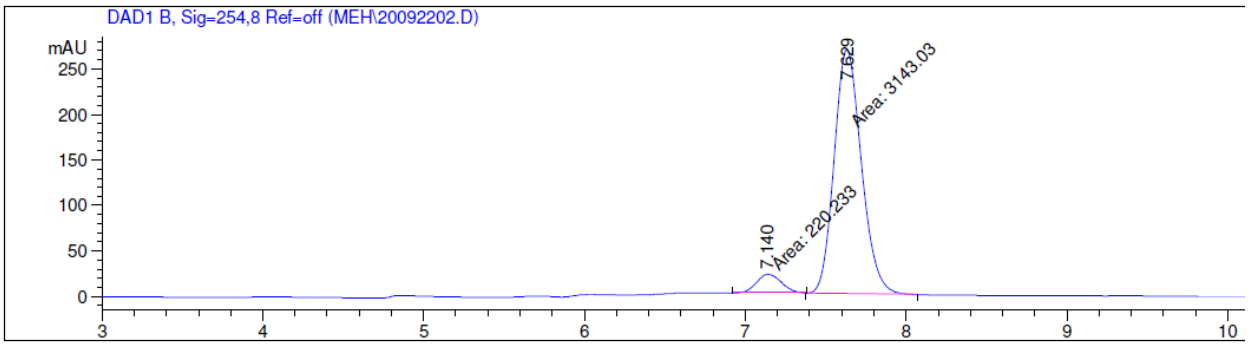
HPLC trace for (±)-**3l** (top) and enantioenriched **3l** (bottom)





Signal 1: DAD1 B, Sig=254,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.950	VV	0.1718	7658.71240	688.23566	49.5030
2	8.317	VB	0.1892	7812.48877	636.35492	50.4970
Totals :				1.54712e4	1324.59058	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.140	MM	0.1793	220.23280	20.47015	6.5482
2	7.629	MM	0.1952	3143.03320	268.30289	93.4518
Totals :				3363.26601	288.77304	

8. References

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