Supporting Information

Enantioselective C2-Allylation of Benzimidazoles Using 1,3-Diene Pronucleophiles

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1. General Experimental Details

General Experimental Procedures: All reactions were performed in flame-dried or oven-dried glassware fitted with rubber or PTFE/silicone septa under a positive pressure of nitrogen, unless otherwise noted. Standard reactions were performed in glass culture tubes with threaded ends (Fisherbrand, 13x100 mm, 1495935C) that were sealed with screw-thread caps (Kimble Chase Open Top S/T Closure, catalog no. 73804-15425) fitted with PTFE/SIL septa (Thermo Scientific, catalog no. B7995-15). Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula. Solids were added under inert gas counter flow or were dissolved in the appropriate solvent. Reactions carried out at temperatures above room temperature (rt) were conducted in a pre-heated oil bath. All reactions were magnetically stirred and monitored by ^{1}H NMR spectroscopy or analytical thin-layer chromatography (TLC), using glass-backed plates pre-coated with silica gel (250 μm, 60-Å pore size, Extra Hard Layer, *SiliaPlate*) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV), or were stained by submersion in iodine dispersed in sand (I_2), an acidic solution of cerium ammonium molybdate (CAM) or in aqueous potassium permanganate solution ($KMnO_4$) and were developed by heating with a heat gun. Flash column chromatography was performed using SiliCycle SiliaFlash® F60 silica gel (40-63 μm, 230-400 mesh, 60 Å pore diameter) or with the aid of a Biotage Isolera or a Teledyne ISCO CombiFlash Automated Flash Chromatography System using prepacked SNAP silica cartridges (10-100 g).

Materials: Unless noted otherwise, all reagents and starting materials were purchased from commercial sources and used as received (Millipore-Sigma, Alfa Aesar, Strem, TCI-America, Combi-Blocks, or Matrix Scientific). $CDCl_3$ was purchased from Cambridge Isotope Laboratories. Tetrahydrofuran (THF), diethyl ether (Et_2O), toluene (PhMe) and dichloromethane (CH_2Cl_2) were obtained from J.T. Baker in CYCLE-TAINER® delivery kegs and purified by successive filtrations though packed columns of neutral alumina and CuO under argon pressure. Dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were purchased from Millipore-Sigma in SureSeal™ bottles and were purged with nitrogen before use. Solvents for extraction, crystallization and flash column chromatography were purchased in A.C.S. reagent grade from Millipore-Sigma, with the exception of hexane and ethyl acetate, which were purchased in HPLC grade. The yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C NMR) pure material.

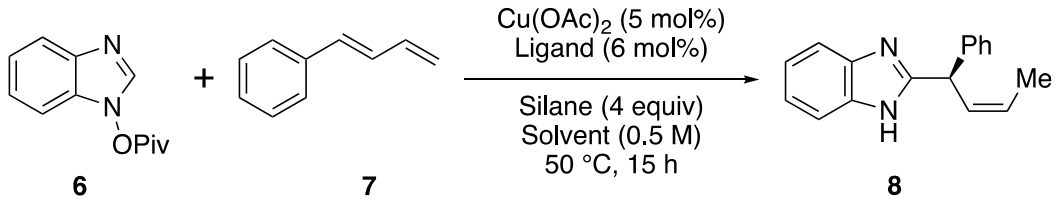
Caution: Dimethoxy(methyl)silane (DMMS, CAS #16881-77-9) is listed by several vendors (TCI, Alfa Aesar) SDS or MSDS as H318, category 1 Causes Serious Eye Damage. Other vendors (Millipore-Sigma, Gelest) list DMMS as H319, category II Eye Irritant. DMMS should be handled in a well-ventilated fumehood using proper precaution as outlined for the handling of hazardous materials in: Prudent Practices in the Laboratory.[1] **At the end of the reaction, saturated ammonium fluoride (NH_4F) in methanol (MeOH) should be carefully added to the reaction mixture as described in the detailed reaction procedure.**

Instrumentation: NMR spectra were measured on Bruker Avance III HD 400 and 500 MHz spectrometers. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the residual proton in the NMR solvent ($CDCl_3$: δ 7.26). ^{1}H NMR spectroscopic data are reported as follows: Chemical shift in ppm (multiplicity, coupling constants *J* (Hz), integration intensity, assigned proton). The multiplicities are abbreviated with s (singlet), br s

(broad singlet), d (doublet), t (triplet), q (quartet), hept (heptet) m (multiplet), a (apparent). All ^{13}C spectra recorded are proton-decoupled. The carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonance of the NMR solvent ($CDCl_3$: δ 77.16). ^{13}C NMR spectroscopic data are reported as follows: Chemical shift in ppm (multiplicity, coupling constants *J* (Hz), assigned carbon). All ^{19}F and ^{31}P chemical shifts are expressed in parts per million (ppm, δ scale). All raw fid files were processed and the spectra analyzed using the program *MestReNOVA 14.2* from *Mestrelab Research S. L*. High-resolution mass spectra were recorded on a JEOL AccuTOF LC-Plus 46 DART system and on an *Agilent Technologies* 6545 Q-TOF LC/MS system or JEOL AccuTOF 4G with an ionSense DART. IR spectra were recorded on a Nicolet iS5 spectrometer equipped with an iD5 diamond laminate ATR accessory from *Thermo Scientific*. IR spectra were acquired from neat samples. If required, substances were dissolved in CH_2Cl_2 prior to direct application on the ATR unit. Data are reported as follows: frequency of absorption (cm^{-1}). Melting points were determined on an EZ-Melt capillary melting point apparatus from *SRS Stanford Research System*. The values are uncorrected. Elemental analyses were performed by *Atlantic Microlabs Inc*., Norcross, GA, USA. Specific optical rotations were recorded for chloroform solutions using a Jasco 1010 polarimeter operating at 589 nm and 23 °C. Enantiomeric ratio (er) was determined either by chiral HPLC analysis using Agilent 1200 Series chromatographs or by Chiral SFC using a Waters Acquity UPC2 instrument; specific columns and analytic methods are provided in the experimental details for individual compounds.

2. Reaction Optimization

2.1 Screening of Solvent/Ligands/Silane



6 **7** **8**

Inside a nitrogen filled glovebox, an oven-dried reaction tube, (tube **A**), (Fisherbrand, 13x100 mm, 1495935C) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (1.4 mg, 7.5 μM, 5 mol%), ligand (9.0 μmol, 6 mol%) and solvent (0.3 mL). This solution was then capped with a screw cap fitted with a PTFE septum and allowed to stir for 10 min before the silane (0.60 mmol, 4.0 equiv) was added to tube **A** via pipette. The mixture was subsequently allowed to stir for 15 min.

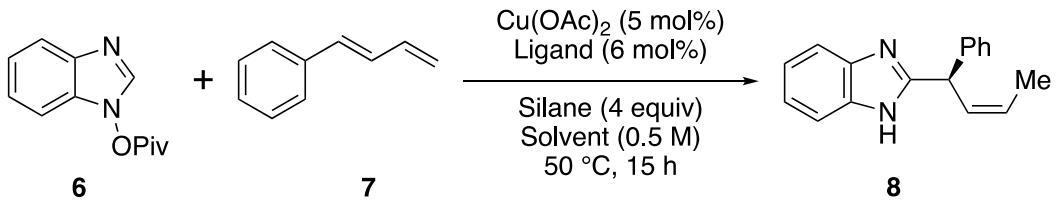
Separately, another oven-dried reaction tube, (tube **B**) (Fisherbrand, 13x100 mm, 1495935C) equipped with a magnetic stir bar, was charged with *N*-OPiv benzimidazole (**6**) (32.7 mg, 0.150 mmol, 1 equiv) and 1-phenyl-*E*-butadiene (**7**) (42.1 μL, 0.300 mmol, 2 equiv).

The copper hydride solution in tube **A** (0.375 mL) was added to reaction tube **B** with aid of a syringe**.** Reaction tube **B** was then capped with a screw cap fitted with a PTFE septum, removed from the glovebox, and placed in an oil bath preheated to 50 ºC.

After the reaction mixture was stirred for 15 h at 50 ºC, the reaction tube was removed from the oil bath and was allowed to cool to rt, at which time the cap was removed and a sat. solution of NH_4F in MeOH (1 mL) was added and allowed to stir 5 min. At this time, a sat. aq. solution of $NaHCO_3$ (2 mL) was added. The crude reaction mixture was extracted with EtOAc (3 x 3mL) and the combined organic phases were filtered through a glass pipette (Kimble, 5-3/4" Glass Monster Pipette) containing a 5 cm plug of $MgSO_4$, transferred to a 5 dram vial, then concentrated *in vacuo* with the aid of a rotary evaporator.

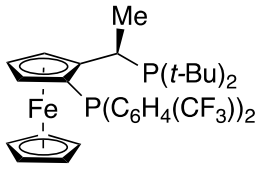
The crude oil was dissolved in $CDCl_3$ (2 mL) and an internal standard, 1,1,2,2-tetrachloroethane (10.0 μL, 15.9 mg, 0.0947 mmol) was added using a glass airtight syringe. The yield of the reaction was determined by ^1H NMR. Then, the crude material was purified using a pipette column of silica (a 5-3/4" Glass Monster Pipette was plugged with a small piece of cotton and filled with 5 cm of silica gel, then basified by rinsing with a solution of 49:50:1 EtOAc:hexane:Et_3N). The column was eluted with 49:50:1 EtOAc:hexane:Et_3N (5 mL) and the collected material was concentrated *in vacuo* with the aid of a rotary evaporator. The resultant product was evaluated by chiral SFC or chiral HPLC to determine the enantioselectivity of the reaction.

Table S1:

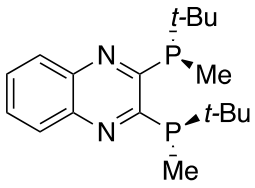


6 **7** **8**

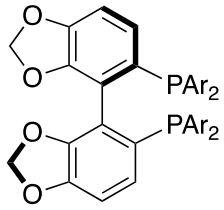
Ligand	Solvent	Silane	Yield	e.r.
JosiPhos J011	THF	DMMS	93%	69:31
QuinoxP	THF	DMMS	37%	96:4
DTBM-SEGPHOS	THF	DMMS	44%	94:6
DTBM-SEGPHOS	Toluene	DMMS	21%	94:6
DTBM-SEGPHOS	TBME	DMMS	44%	94:6
DTBM-SEGPHOS	1,4-Dioxane	DMMS	16%	88:12
DTBM-SEGPHOS	Cyclohexane	DMMS	22%	96:4
Ph-BPE	THF	DMMS	65%	95:5
Ph-BPE	Toluene	DMMS	91%	96:4
Ph-BPE	1,4-Dioxane	DMMS	30%	74:26
Ph-BPE	Cyclohexane	DMMS	52%	96:4
Ph-BPE	MTBE	DMMS	95%	97:3
Ph-BPE	MTBE	TMCTS	67%	95:5
Ph-BPE	MTBE	Me_2PhSiH	19%	97:3
Ph-BPE	MTBE	$(EtO)_2MeSiH$	50%	95:5



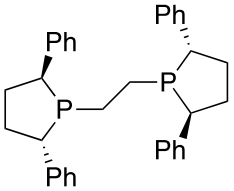
L1
JosiPhos SL-J011-1



L2
(R,R)-QuinoxP*



L3
(R)-DTBM-SEGPHOS
Ar = 3,5-(*t*-Bu)-4-$MeOC_6H_2$

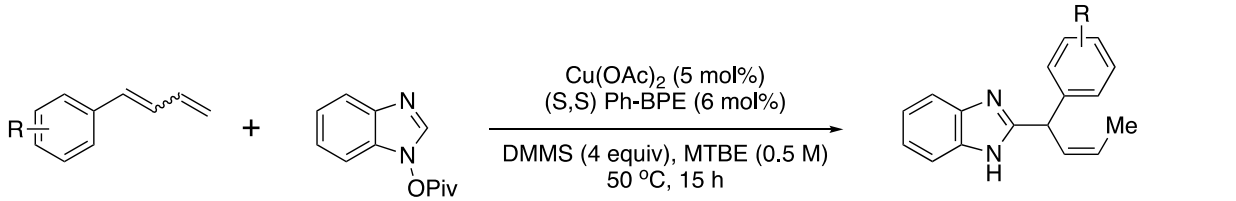


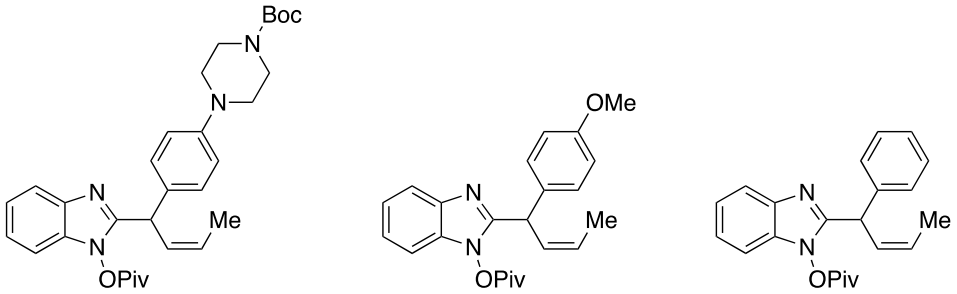
L4
(S,S)-Ph-BPE

2.2 Effect of Olefin Geometry:

Following the screening procedure described above (Section 2.1), dienes as both pure *E* isomers, and mixtures of *E/Z* isomers were subjected to the reaction conditions. It was found that the use of *E*-dienes was necessary in order to obtain the products with good e.r., as dienes used as an *E/Z* mixture gave poor e.r. Additionally, it was found that the allylation products isolated were almost exclusively the *Z*-isomer (<1:20 *E*:*Z*), regardless of the geometry of the starting diene. The results are summarized in **Scheme S1**.

Scheme S1:





E-Diene	92% 98:2 e.r.	86% 98:2 e.r.	95% 97:3 e.r.
E/Z mixture	81% 70:30 e.r.	78% 66:34 e.r.	47% 60:40 e.r.

2.3. Study on Racemization of 8.

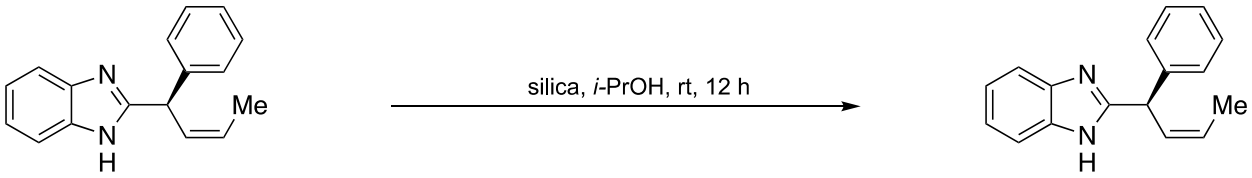
Initially, it was found that the measured enantiomeric ratio (e.r.) of the isolated product **8** was inconsistent. To ascertain the origin of this phenomenon, a series of purification conditions were evaluated, and it was found that treating the silica with Et_3N and utilizing Et_3N as a co-solvent in the eluent during chromatography resulted in reproducibly high e.r. (**Table S2**). Based on these results, we believe that silica was protonating the benzimidazole product at N3, facilitating subsequent deprotonation at the benzylic position, resulting in racemization of the product. We found more evidence for this hypothesis after stirring the isolated product (**8**) with silica in isopropyl alcohol (*i*-PrOH), observing an erosion of the e.r. There was no erosion of the e.r. observed when storing **8** in 100% isopropyl alcohol for several days.

Table S2:

crude reaction mixture: 98:2 e.r.

entry	purification conditions	er
1	silica gel chromatography	85:15
2	Et_3N Treated Silica	93:7
3	basic alumina	92:8
4	Florisil	92:8
5	Et_3N treated silica with 1% Et_3N in eluent	98:2

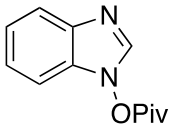
Scheme S2: Racemization studies on Pure 8



Pure **8**
90:10 e.r.

77:23 e.r.

3. Synthesis and Characterization of Starting Materials



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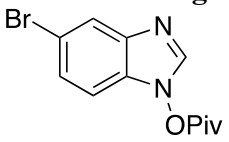
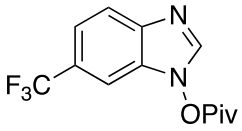


S1



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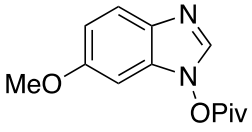
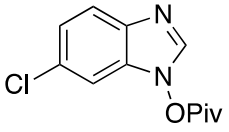


S3



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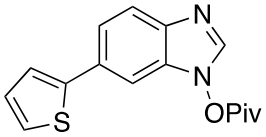
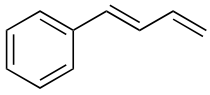


S5



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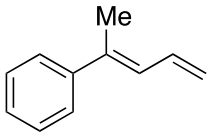
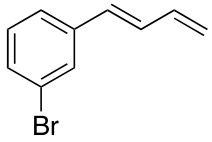


S6



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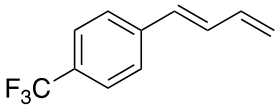
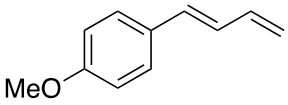
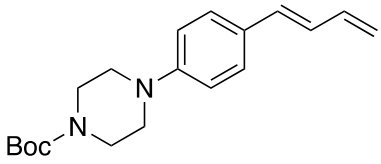


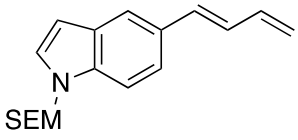
S8



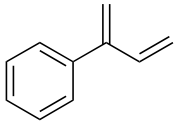
S9



S10



S11



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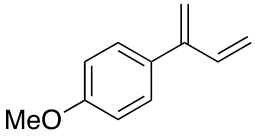

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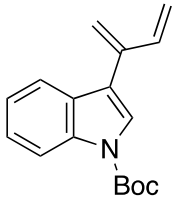
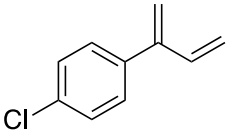
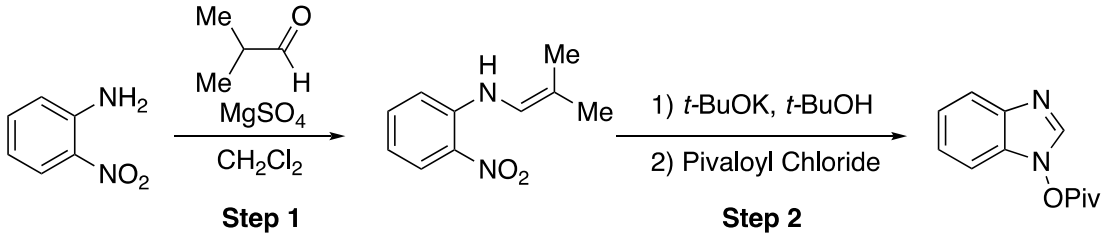


S14



S15

3.1. Synthesis and Characterization of *N*-OPiv Benzimidazoles



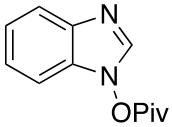
General Procedure A: for the synthesis of *N*-OPiv benzimidazoles.[2]

Step 1: An oven-dried 300 mL round-bottom flask equipped with a magnetic stir bar was charged with $MgSO_4$ (50.0 g, 0.420 mol, 5.7 equiv) and nitroaniline (72.0 mmol, 1.0 equiv). The flask was fitted with a reflux condenser, sealed with a rubber septum and attached by rubber hose via a needle to a dual manifold Schlenk line. The flask was evacuated and backfilled with nitrogen (this process was repeated a total of three times). CH_2Cl_2 (150 mL) was added, followed by isobutyraldehyde (26.0 mL, 0.290 mol, 4 equiv), then the flask was placed in an oil bath and the reaction solution was heated to reflux.

After 5 d, the reaction flask was removed from the oil bath and allowed to cool to rt. The reaction mixture was then filtered through a glass frit into a 500 mL round-bottom flask. The filter cake was washed with CH_2Cl_2 (100 mL) and the filtrate was concentrated *in vacuo* with the aid of a rotary evaporator.

Step 2: A 500 mL round-bottom flask equipped with a magnetic stir bar was charged with the enamine from step 1 (27.5 mmol, 1.0 equiv). Next, *tert*-butanol (*t*-BuOH) (200 mL) was added, followed by potassium *tert*-butoxide (*t*-BuOK) (12.4 g, 110.0 mmol, 4.0 equiv). The flask was sealed with a rubber septum and attached to a dual manifold Schlenk line by rubber hose via a needle. The rubber septum was pierced with an outlet needle, and the flask was purged with nitrogen for 10 min. The outlet needle was then removed, and the flask allowed to stir at rt.

After the reaction mixture had stirred for 15 h, the flask was placed in a rt water bath, and pivaloyl chloride (10.2 mL, 82.7 mmol, 3.0 equiv) was added dropwise via syringe (by puncturing the rubber septum). The flask was removed from the water bath and the reaction mixture was allowed to stir at rt for an additional 6 h. At this point, the reaction was quenched by the addition of sat. aq. $NaHCO_3$ solution (150 mL), and the contents of the flask were transferred to a separatory funnel and then extracted with Et_2O (3 x 150 mL). The combined organic extracts were dried over Na_2SO_4, filtered, then concentrated *in vacuo* with the aid of a rotary evaporator to obtain the crude solid. This material was purified by flash chromatography and if necessary, a subsequent recrystallization to give the *N*-OPiv benzimidazole.



1*H*-benzimidazol-1-yl pivalate (6)

Step 1: Prepared according to **General Procedure A**, with $MgSO_4$ (50.0 g, 0.420 mol, 5.7 equiv) and 2-nitroaniline (10.0 g, 72.0 mmol, 1.0 equiv), CH_2Cl_2 (150 mL) and isobutyraldehyde (26.0 mL, 0.290 mol, 4 equiv). The resultant material was dried under high vacuum for 24 h to

give a dark-purple solid (11.7 g, 84% yield). The crude product was used in the subsequent step without further purification.

N-(2-methylprop-1-en-1-yl)-2-nitroaniline
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.72–9.45 (m, 1H), 8.17 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.43 (ddd, *J* = 8.6, 6.8, 1.6 Hz, 1H), 7.04 (dd, *J* = 8.7, 1.2 Hz, 1H), 6.70 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 6.27 (dt, *J* = 9.6, 1.5 Hz, 1H), 1.81 (dd, *J* = 10.4, 1.4 Hz, 6H).

Step 2: Prepared according to **General Procedure A** with *N*-(2-methylprop-1-en-1-yl)-2-nitroaniline (5.30 g, 27.5 mmol, 1.0 equiv), *t*-BuOH (200 mL), *t*-BuOK (12.4 g, 110 mmol, 4.0 equiv), and pivaloyl chloride (10.2 mL, 82.7 mmol, 3.0 equiv). The crude material was purified by flash chromatography (50 g silica, gradient elution, hexane to 5:95 EtOAc:hexane) to obtain a light brown solid (3.16 g, 53% yield). This material was further purified through recrystallization by dissolving with 25 mL of refluxing 10:90 EtOAc:hexane, then cooling in a −5 ºC freezer to give **6** as colorless needles (2.42 g, 40% yield).

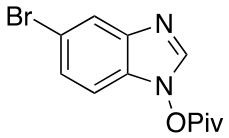
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (s, 1H), 7.81–7.79 (m, 1H), 7.31 (tt, *J* = 7.4, 5.7 Hz, 2H), 7.22 (dd, *J* = 7.7, 1.6 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 175.3, 139.3, 138.5, 130.4, 124.3, 123.0, 121.1, 108.1, 38.8, 27.2.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 3126, 2982, 1797, 1477, 1446, 1371, 1319, 1227, 1052, 1019, 851, 781, 733.

Melting Point (ºC): 85–87.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{12}H_{15}N_2O_2$: 219.1128; Found: 219.1129.



5-Bromo-1*H*-benzimidazol-1-yl pivalate (S1)

Step 1: Prepared according to **General Procedure A** with $MgSO_4$ (8.0 g, 66 mmol, 5.0 equiv), 3-bromo-6-nitroaniline (3.00 g, 13.8 mmol, 1.0 equiv), CH_2Cl_2 (100 mL), and isobutyraldehyde (5.05 mL, 55.3 mmol, 4 equiv). The resultant material was dried under high vacuum for 24 h to give an orange solid (2.48 g, 66% yield). The crude product was used in the subsequent step without further purification.

3-bromo-*N*-(2-methylprop-1-en-1-yl)-6-nitroaniline
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.56 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 9.1 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 6.81 (dd, *J* = 9.2, 2.0 Hz, 1H), 6.19 (dp, *J* = 9.3, 1.5 Hz, 1H), 1.97–1.72 (m, 6H).

Step 2: Prepared according to **General Procedure A** with 3-bromo-*N*-(2-methylprop-1-en-1-yl)-6-nitroaniline (2.40 g, 8.85 mmol, 1.0 equiv), *t*-BuOH (200 mL) *t*-BuOK (3.97 g 35.4 mmol, 4.0 equiv) and pivaloyl chloride (5.45 mL, 44.3 mmol, 5.0 equiv). The crude material was

purified by flash chromatography (50 g silica, gradient elution, hexane to 40:60 EtOAc:hexane) to obtain a light brown solid. This material was further purified through recrystallization by dissolving with 10 mL of refluxing 20:80 EtOAc:hexane, then cooling in a −5 ºC freezer to give **S1** as colorless cubic crystals (1.1 g, 42% yield).

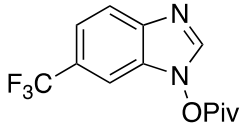
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 1.8 Hz, 1H), 7.90 (s, 1H), 7.42 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 175.1, 140.6, 139.5, 129.5, 127.5, 124.1, 116.1, 109.5, 38.9, 27.2.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 3121, 2978, 1792, 1574, 1478, 1451, 1220, 1058, 1020, 891, 849, 806, 616.

Melting Point (ºC): 109–110.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{12}H_{14}BrN_2O_2$: 297.0233; Found: 297.0232.



6-(Trifluoromethyl)-1*H*-benzimidazol-1-yl pivalate (S2)

Step 1: Prepared according to **General Procedure A** with $MgSO_4$ (16 g, 0.13 mol, 6.8 equiv), 2-nitro-4-(trifluoromethyl)aniline (4.00 g, 19.3 mmol, 1.0 equiv), CH_2Cl_2 (200 mL) and isobutyraldehyde (7.1 mL, 77.63 mmol, 4 equiv). The resultant material was dried under high vacuum for 24 h to give a dark-purple solid (3.2 g, 63% yield). The crude product was used in the subsequent step without further purification.

N-(2-methylprop-1-en-1-yl)-2-nitro-4-(trifluoromethyl)aniline
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.77 (s, 1H), 8.48 (dd, *J* = 2.3, 1.0 Hz, 1H), 7.61 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.12 (d, *J* = 9.1 Hz, 1H), 6.26 (dt, *J* = 9.3, 1.5 Hz, 1H), 1.95–1.77 (m, 6H).

Step 2: Prepared according to **General Procedure A** with *N*-(2-methylprop-1-en-1-yl)-2-nitro-4-(trifluoromethyl)aniline (3.2 g, 12.3 mmol, 1.0 equiv), *t*-BuOH (200 mL), *t*-BuOK (5.52 g, 49.19 mmol, 4.0 equiv) and pivaloyl chloride (4.54 mL, 36.9 mmol, 3.0 equiv). The crude material was purified by flash chromatography (50 g silica, gradient elution, hexane to 20:80 EtOAc:hexane) to obtain **S2** as a light brown solid (1.90 g, 54% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.57 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.48 (s, 1H), 1.51 (s, 9H).

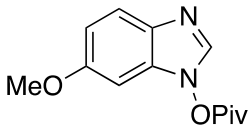
^{13}C NMR ($CDCl_3$, 126 MHz): δ 175.1, 141.4, 140.8, 129.9, 126.7 (q, *J* = 32.6 Hz), 124.5 (q, *J* = 236.9 Hz), 121.8, 120.1 (q, *J* = 3.6 Hz), 106.2 (q, *J* = 4.3 Hz), 39.0, 27.2.

^{19}F NMR ($CDCl_3$ 471 MHz): δ −61.02.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 3122, 2986, 1795, 1484, 1466, 1449, 1329, 1277, 1224, 1153, 1116, 1085, 910, 866, 746, 662.

Melting Point (ºC): 107–108.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{13}H_{14}F_3N_2O_2$: 287.1002; Found: 287.1009.



6-methoxy-1*H*-benzimidazol-1-yl pivalate (S3)

Step 1: Prepared according to **General Procedure A** with $MgSO_4$ (12.5 g, 104 mmol, 5 equiv), 4-methoxy-2-nitroaniline (3.50 g, 20.8 mmol, 1.0 equiv), CH_2Cl_2 (100 mL) and isobutyraldehyde (7.60 mL, 83.3 mmol, 4 equiv). The resultant material was dried under high vacuum for 24 h to give a dark-red, waxy, low-melting solid (4.90 g, quantitative yield). The crude product was used in the subsequent step without further purification.

6-methoxy-*N*-(2-methylprop-1-en-1-yl)-2-nitroaniline
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.58 (d, *J* = 9.7 Hz, 1H), 7.60 (d, *J* = 3.0 Hz, 1H), 7.15 (dd, *J* = 9.4, 3.1 Hz, 1H), 7.02 (d, *J* = 9.4 Hz, 1H), 6.26 (dt, *J* = 9.7, 1.5 Hz, 1H), 3.80 (s, 3H), 1.80 (dd, *J* = 7.8, 1.4 Hz, 6H).

Step 2: Prepared according to **General Procedure A** with 6-methoxy-*N*-(2-methylprop-1-en-1-yl)-2-nitroaniline (4.90 g, 22 mmol, 1.0 equiv) *t*-BuOH (150 mL), *t*-BuOK (10 g, 89 mmol, 4.0 equiv), and pivaloyl chloride (14 mL, 110 mmol, 5.0 equiv). The crude material was purified by flash chromatography (50 g silica, gradient elution, hexane to 20:80 EtOAc:hexane) to obtain **S3** as a viscous brown oil (3.1 g, 57 % yield).

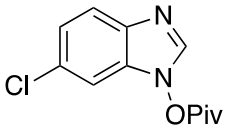
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (s, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 3H), 1.44 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 175.2, 157.7, 137.7, 133.5, 131.0, 121.5, 112.1, 91.5, 55.8, 38.7, 27.1.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2971, 1798, 1702, 1632, 1497, 1454, 1357, 1240, 1215, 1174, 1052, 1015, 936, 815.

Melting Point (ºC): 23–25.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{13}H_{17}N_2O_3$: 249.1234; Found: 249.1247.



6-chloro-1*H*-benzimidazol-1-yl pivalate (S4)

Step 1: Prepared according to **General Procedure A** with $MgSO_4$ (25 g, 208 mmol, 6 equiv), 4-chloro-2-nitroaniline (6.00 g, 34.8 mmol, 1.0 equiv), CH_2Cl_2 (100 mL), and isobutyraldehyde (12.7 mL, 139 mmol, 4 equiv). The resultant material was dried under high vacuum for 24 h to give a dark-red solid (6.40 g, 81% yield). The crude product was used in the subsequent step without further purification.

6-chloro-*N*-(2-methylprop-1-en-1-yl)-2-nitroaniline
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.56 (s, 1H), 8.18 (d, *J* = 2.5 Hz, 1H), 7.38 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.01 (d, *J* = 9.2 Hz, 1H), 6.22 (d, *J* = 9.5 Hz, 1H), 1.81 (d, *J* = 10.4 Hz, 6H).

Step 2: Prepared according to **General Procedure A** with 6-chloro-*N*-(2-methylprop-1-en-1-yl)-2-nitroaniline (6.40 g, 28.0 mmol, 1.0 equiv), *t*-BuOH (200 mL), *t*-BuOK (13 g, 110 mmol, 4.0 equiv), and pivaloyl chloride (17.2 mL, 140 mmol, 5.0 equiv). The crude material was purified by flash chromatography (50 g silica, gradient elution, hexane to 20:80 EtOAc:hexane) to obtain a brown solid. This material was further purified through recrystallization by dissolving with 10 mL of refluxing 10:90 EtOAc:hexane, then cooling in a −5 ºC freezer to obtain **S4** as colorless needles (2.00 g, 28% yield).

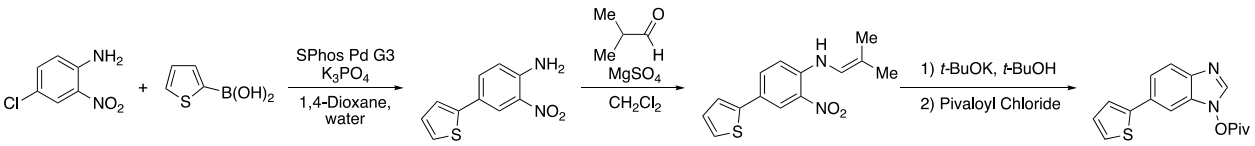
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.26 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 175.1, 139.2, 137.9, 131.0, 130.2, 123.8, 122.1, 108.4, 38.8, 27.2.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 3125, 2976, 1795, 1720, 1611, 1461, 1393, 1350, 1299, 1273, 1057, 1017, 899, 851.

Melting Point (ºC): 93–95.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{12}H_{14}ClN_2O_2$: 253.0738; Found: 253.0775.



6-(thiophen-2-yl)-1*H*-benzimidazol-1-yl pivalate (S5)

An oven-dried 300 mL round-bottom flask equipped with a magnetic stir bar was charged with SPhos Pd G3 (565 mg, 724 μM, 2.5 mol%), K_3PO_4 (12.3 g, 57.9 mmol, 2.0 equiv), 4-chloro-2-nitroaniline (5.00 g, 29.0 mmol, 1 equiv), thiophen-2-ylboronic acid (7.41 g, 57.9 mmol,

2.0 equiv), 1,4-dioxane (120 mL) and water (27 mL). The flask was sealed with a rubber septum, attached by rubber hose via a needle to a dual manifold Schlenk line, and evacuated and backfilled with nitrogen (this cycle was repeated a total of three times). The reaction flask was then placed in an oil bath preheated to 50 ºC.

After heating the reaction mixture for 20 h, the flask was removed from the oil bath and allowed to cool to rt. The crude reaction mixture was filtered through a short pad (2 cm) of silica using a fritted funnel. The reaction flask was rinsed with 30 mL of additional EtOAc, and the rinsate was passed through the filter cake. The solvent was removed *in vacuo* with the aid of a rotary evaporator and the resultant crude oil was purified by column chromatography (100 g silica, gradient elution, hexane to 40:60 EtOAc:hexane) to give a dark-red solid (6.42 g, quantitative yield).

2-nitro-4-(thiophen-2-yl)aniline
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.36 (d, *J* = 2.2 Hz, 1H), 7.62 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.25–7.23 (m, 2H), 7.07 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.12 (s, 2H).

Step 1: Prepared according to **General Procedure A** with $MgSO_4$ (35 g, 290 mmol, 10 equiv), 2-nitro-4-(thiophen-2-yl)aniline (6.42 g, 29.0 mmol, 1.0 equiv), CH_2Cl_2 (100 mL) and isobutyraldehyde (18.0 mL, 197 mmol, 6.8 equiv). The resultant material was then dried under high vacuum for 12 h to give a dark-red solid containing some unreacted starting material (7.36 g, 92% yield). This crude material was used in the subsequent step without further purification.

6-(thiophen-2-yl)-*N*-(2-methylprop-1-en-1-yl)-2-nitroaniline
^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.67 (d, *J* = 9.5 Hz, 1H), 8.42 (d, *J* = 2.3 Hz, 1H), 7.69 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.25–7.23 (m, 2H), 7.10–7.03 (m, 2H), 6.30 (dt, *J* = 9.5, 1.5 Hz, 1H), 1.89–1.72 (m, 6H).

Step 2: Prepared according to **General Procedure A** with *N*-(2-methylprop-1-en-1-yl)-2-nitro-4-(thiophen-2-yl)aniline) (7.36 g, 29 mmol, 1.0 equiv), *t*-BuOH (200 mL), *t*-BuOK (13.1 g, 116 mmol, 4.0 equiv) and pivaloyl chloride (10.8 mL, 87.3 mmol, 3.0 equiv). The crude material was purified by flash chromatography to obtain a brown solid (3.2 g, 37% yield). This material was further purified through recrystallization by dissolving with 100 mL of refluxing 10:90 EtOAc:hexane, then cooling in a −5 ºC freezer to obtain **S5** as colorless needles (1.70 g, 19% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.61–7.55 (m, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.30 (dd, *J* = 7.4, 4.3 Hz, 2H), 7.12–7.06 (m, 1H), 1.51 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 175.3, 144.5, 139.2, 139.0, 131.2, 131.0, 128.2, 125.1, 123.6, 122.1, 121.5, 105.4, 38.9, 27.3.

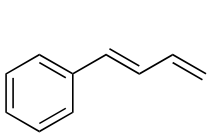
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 3118, 2960, 1791, 1482, 1449, 1348, 1285, 1243, 1228, 1183, 1056, 1018, 976, 822.

Melting Point (ºC): 135–136.

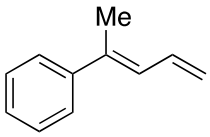
HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{16}H_{17}N_2O_2S$: 301.1005; Found: 301.1018.

3.2. Synthesis and Characterization of 1,3-Butadienes

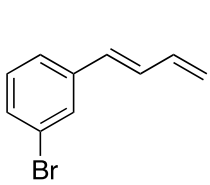
The following 1,3-butadienes were prepared according to known protocols:



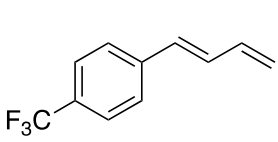
7[ref 4]



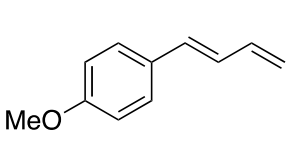
S6[ref 5]



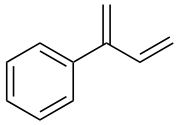
S7[ref 6]



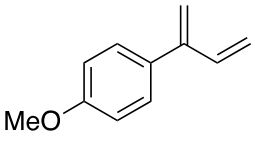
S8[ref 7]



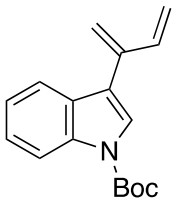
S9[ref 6]



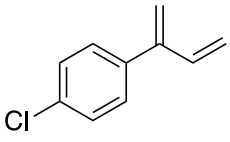
S12[ref 8]



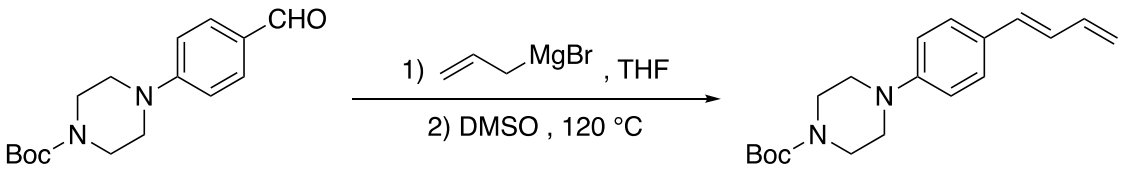
S13[ref 8]



S14[ref 8]



S15[ref 8]



***tert*-butyl (*E*)-4-(4-(buta-1,3-dien-1-yl)phenyl)piperazine-1-carboxylate (S10)**

A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with *tert*-butyl 4-(4-formylphenyl)piperazine-1-carboxylate (1.0 g, 3.44 mmol, 1.0 equiv), sealed with a rubber septum and attached by rubber hose via a needle to a dual manifold Schlenk line. The flask was evacuated and backfilled with nitrogen (this process was repeated a total of three times). THF (10 mL) was added via syringe (by puncturing the rubber septum), the flask was cooled to 0 ºC with the aid of an ice-water bath, then allyl magnesium bromide (4.12 mL, 4.12 mmol, 1.2 equiv, 1 M in THF) was added dropwise via syringe (by puncturing the rubber septum). Once the addition was complete, the reaction flask was removed from the ice bath and allowed to stir for 1 h at rt. The reaction mixture was quenched by the addition sat. aq. NH_4Cl (10 mL) then the contents of the flask were transferred to a separatory funnel and extracted with Et_2O (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* with the aid of a rotary evaporator.

The resultant crude oil was transferred to a 5 dram vial equipped with a magnetic stir bar and dissolved in DMSO (5 mL from a Millipore-Sigma Sureseal^{TM} bottle). The vial was capped and placed in an oil bath preheated to 120 ºC for 6 h. At this time, the vial was allowed to cool to rt. The crude reaction mixture was transferred to a separatory funnel, diluted with Et_2O (30 mL), and washed with water (5 x 10 mL). The ethereal layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude material was purified by column chromatography (100 g silica, hexane to 20:80 EtOAc:hexane) to give **S10** as a colorless solid (517 mg, 48% yield).

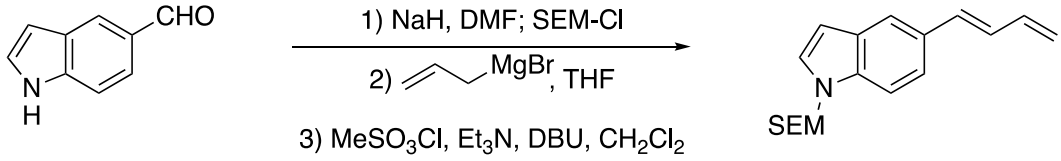
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.70–6.63 (m, 1H), 6.53–6.44 (m, 2H), 5.27 (d, J = 16.9 Hz, 1H), 5.09 (dd, J = 9.9, 1.5 Hz, 1H), 3.57 (t, J = 5.2 Hz, 4H), 3.15 (t, J = 5.2 Hz, 4H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.9, 150.8, 137.6, 132.6, 130.2, 129.2, 127.6, 127.4, 116.4, 116.3, 80.1, 49.1, 28.6.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2975, 2856, 1694, 1598, 1514, 1453, 1412, 1364, 1222, 1158, 1122, 1048, 999, 912, 862, 817.

Melting Point (ºC): 101–104.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{19}H_{27}N_2O_2$: 315.2067; Found: 315.2072.



(*E*)-5-(buta-1,3-dien-1-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole (S11)

An oven-dried 300 mL round-bottom flask equipped with a magnetic stir bar was charged with indole-5-carbaldehyde (1.65 g, 11.4 mmol, 1.0 equiv), sealed with a rubber septum. and attached by rubber hose via a needle to a dual manifold Schlenk line. The flask was evacuated and backfilled with nitrogen (this process was repeated a total of three times). DMF (40 mL from a Millipore-Sigma Sureseal^{TM} bottle) was added via syringe (by puncturing the rubber septum), and the reaction mixture was cooled to 0 °C with the aid an ice-water bath. The rubber septum was removed and NaH (333 mg, 12.5 mmol, 1.1 equiv, 90%) was added in three portions, resealing the flask with the rubber septum between additions. After the reaction mixture had stirred for 2 h, 2-(trimethylsilyl)ethoxymethyl chloride (SEM-Cl) (2.11 mL, 11.9 mmol, 1.05 equiv) was added via syringe (by puncturing the rubber septum), the reaction flask was removed from the ice-water bath, and the reaction was allowed to stir at rt for an additional 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl (50 mL), and the contents of the flask were transferred to a separatory funnel and extracted with Et_2O (3 x 100 mL). The combined organic phase was washed with water (3 x 50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* with the aid of a rotary evaporator. The crude material was purified by column chromatography

(100 g silica, gradient elution, hexane to 10:90 EtOAc:hexane) to obtain the *N*-SEM protected indole (2.45 g, 78% yield), which directly was used for the next step.

A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with *N*-SEM-indole-5-carbaldehyde (2.40 g, 8.70 mmol, 1.0 equiv), sealed with a rubber septum, and attached by rubber hose via a needle to a dual manifold Schlenk line. The flask was evacuated and backfilled with nitrogen (this process was repeated a total of three times). THF (30 mL) was added via syringe (by puncturing the rubber septum), then the reaction mixture was cooled to −78 °C with the aid of a dry ice/acetone bath. Allyl magnesium bromide (6.5 mL, 13 mmol, 1.5 equiv, 2 M in THF) was added dropwise via syringe (by puncturing the rubber septum), then the reaction flask was removed from the dry ice/acetone bath. After 1 h, the reaction mixture was quenched with sat. aq. NH_4Cl (30 mL) the contents of the flask were transferred to a separatory funnel and extracted with Et_2O (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered through a short plug of silica (3 cm) in a fritted funnel, then concentrated *in vacuo* with the aid of a rotary evaporator. The resultant crude oil was used immediately and without further purification.

A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with the allyl alcohol from the previous step (930 mg, 2.93 mmol, 1.0 equiv), sealed with a rubber septum, and attached by rubber hose via a needle to a dual manifold Schlenk line. The flask was evacuated and backfilled with nitrogen (this process was repeated a total of three times). The flask was charged with CH_2Cl_2 (15 mL), then wrapped in aluminum foil and cooled to 0 ºC with the aid of an ice-water bath. Et_3N (0.74 mL, 5.27 mmol, 1.8 equiv) was charged via syringe (by puncturing the rubber septum), followed by methanesulfonyl chloride (0.34 mL, 4.4 mmol, 1.5 equiv) via syringe (by puncturing the rubber septum), and the reaction mixture was allowed to stir at 0 ºC. After 4 h the reaction had not reached completion. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.1 mL, 7.3 mmol, 2.5 equiv) was added by syringe (by puncturing the rubber septum) and the reaction was allowed to stir for another 4 h at 0 ºC. The reaction mixture was then concentrated *in vacuo* with the aid of a rotary evaporator and the resultant oil was purified by column chromatography (100 g silica, pentane) to obtain **S11** as a colorless oil (400.0 mg, 46% yield). **S11** was used immediately in the allylation reaction below.

Note: **S11** quickly turns yellow and solidifies on exposure to light. It should be stored in a scintillation vial or appropriate flask wrapped in aluminum foil at −5 ºC.

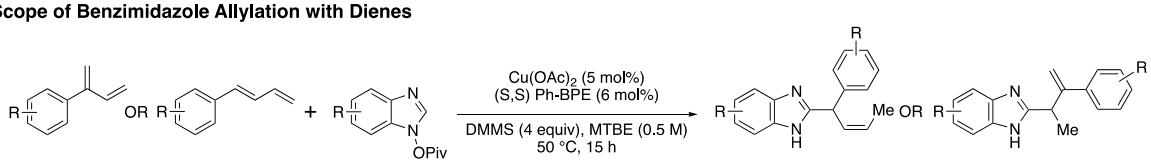
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (s, 1H), 7.44 (d, J = 8.5 Hz, 1H), 7.37 (dd, J = 8.6, 1.6 Hz, 1H), 7.15 (d, J = 3.2 Hz, 1H), 6.84–6.67 (m, 2H), 6.59–6.49 (m, 2H), 5.46 (s, 2H), 5.29 (d, J = 16.8 Hz, 1H), 5.11 (dd, J = 10.1, 1.6 Hz, 1H), 3.47 (t, J = 8.3 Hz, 2H), 0.88 (t, J = 8.3 Hz, 2H), −0.06 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 137.8, 136.3, 134.3, 129.8, 129.5, 128.7, 127.5, 120.8, 119.7, 116.0, 110.3, 102.9, 75.8, 66.0, 17.9, −1.3.

4. Benzimidazole Allylation with Dienes and Characterization of Products

Table S3: Scope of Benzimidazole Allylation with Dienes

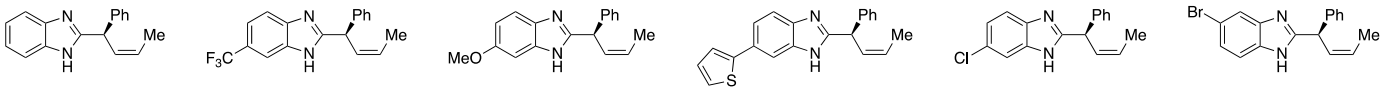
Scope of Benzimidazole Allylation with Dienes



Bold yields denote reactions at 0.50 mmol scale
Run 1:
Run 2:
e.r.

Italic yields denote reactions at 0.15 mmol scale
Isolated yield (NMR yield) e.r.

Benzimidazole Scope



8
Run 1: 89%
Run 2: 93%
95:5 e.r

9
Run 1: 62%
Run 2: 62%
95:5 e.r.

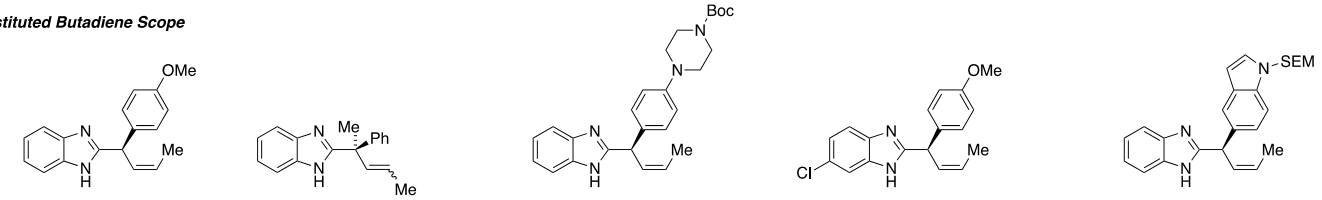
10
Run 1: 71%
Run 2: 78%
97:3 e.r.

11
Run 1: 84%
Run 2: 88%
96:4 e.r.

12
Run 1: 71%
Run 2: 77%
94:6 e.r.

13
Run 1: 50%
Run 2: 70%
Run 3 : 59%
96:4 e.r.

1-Substituted Butadiene Scope



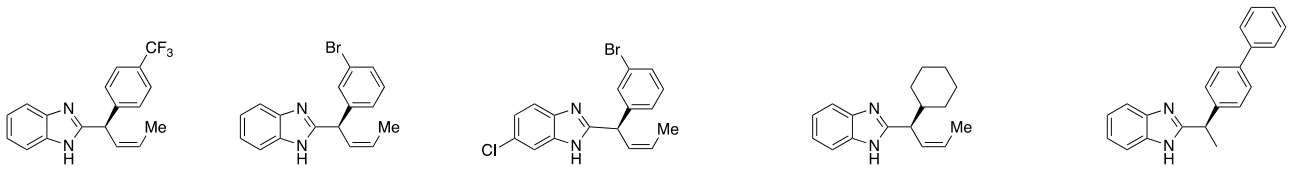
14
Run 1: 52%
Run 2: 59%
98:2 e.r.

15
Run 1: 29%
Run 2: 28%
96:4 e.r.

16
Run 1: 78%
Run 2: 79%
96:4 e.r.

17
Run 1: 68%
Run 2: 67%
90:10 e.r

18
Run 1: 59%
Run 2: 55%
96:4 e.r.



19
Run 1: 78%
Run 2: 72%
63:47 e.r.

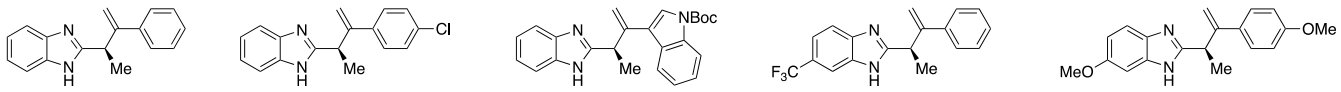
70% (90%) 83:17 e.r.

20
Run 1: 61%
Run 2: 71%
88:12 e.r.

0%

18% (23%) 80:20 e.r.

2-Substituted Butadiene Scope



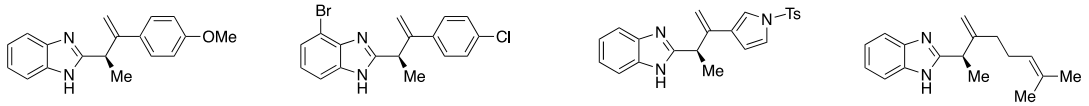
21
Run 1: 77%
Run 2: 72%
95:25 e.r.

22
Run 1: 11%
Run 2: 21%
Run 3: 23%
96:4 e.r.

23
Run 1: 77%
Run 2: 73%
96:4 e.r.

24
Run 1: 45%
Run 2: 47%
99:1 e.r.

25
Run 1: 52%
Run 2: 42%
92:8 e.r.



67% (98%) 94:6 e.r.

Run 1: 20%
89:11 e.r.

Run 1: 40%*
***formed precipitate**
***Several side products**

(30%) 80:20 e.r.

4.1. General Procedure D for the Allylation of *N*-OPiv Benzimidazoles

Procedure:

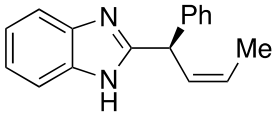
Inside a nitrogen filled glovebox, an oven-dried reaction tube (Fisherbrand, 13x100 mm, 1495935C) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (4.5 mg, 25.0 μmol, 5 mol%), (*S,S*)-Ph-BPE (15 mg, 30.0 μmol, 6 mol%) and methyl *tert*-butyl ether (1 mL). This solution was capped with a screw cap containing a PTFE septum and allowed to stir for 10 min. The cap was removed and dimethoxy(methyl)silane (247 μL, 2.00 mmol, 4.0 equiv) was added by pipette.

After stirring for 15 min, the cap was removed and the diene (1.00 mmol, 2.0 equiv) was added to the reaction tube as a powder, or if liquid via pipette. The reaction tube was capped and the reaction mixture was allowed to stir for 10 min, then the cap was removed and the appropriate *N*-OPiv benzimidazole (0.500 mmol, 1.0 equiv) was added. The reaction tube was once again capped, removed from the glovebox and placed in an oil bath preheated to 50 ºC.

After the reaction mixture had stirred for 15 h at 50 ºC, the reaction tube was removed from the oil bath and allowed to cool to rt. Once at rt, the cap was removed from the reaction tube and the reaction mixture was quenched by the addition of sat. NH_4F in MeOH (5 mL) and allowed to stir 5 min. The reaction mixture was then transferred into a separatory funnel containing sat. aq. $NaHCO_3$ (8 mL), and the tube was rinsed with EtOAc (8 mL). The phases were separated, and the aq. phase was extracted with EtOAc (2 x 15 mL). The combined organic layers were dried over Na_2SO_4, filtered through a fritted glass funnel, and concentrated *in vacuo* with the aid of a rotary evaporator.

The resultant crude material was dissolved in CH_2Cl_2 (1 mL) and purified by column chromatography on silica gel that had been basified with eluent containing 1% Et_3N. The purified product was dried under high vacuum overnight, and the enantiomeric ratio was determined by chiral SFC.

4.2. Characterization of Allylation Products



(*R,Z*)-2-(1-phenylbut-2-en-1-yl)-1*H*-benzimidazole (8)

Prepared according to **General Procedure D** using 1-phenyl-*E*-butadiene (**7**) (140 μL, 1.00 mmol, 2.0 equiv) and 1*H*-benzimidazol-1-yl pivalate (**6)** (109 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 250 mL of 10:89:1, 250 mL of 20:79:1, 250 mL of 30:69:1, and 250 mL of 35:64:1 of EtOAc:hexane:Et_3N) to afford **8** as a colorless solid (1st run: 111 mg, 89% yield, 96:4 e.r., 2nd run: 115 mg, 93% yield, 94:6 e.r.).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.27 (s, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.35–7.30 (m, 3H), 7.29–7.25 (m, 3H), 7.21 (q, *J* = 4.0 Hz, 2H), 6.10–6.03 (m, 1H), 5.80 (dqd, *J* = 10.7, 6.9, 1.2 Hz, 1H), 5.33–5.28 (m, 1H), 1.72 (dd, *J* = 6.9, 1.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.8, 143.5, 141.1, 133.7, 129.2, 129.1, 128.1, 127.5, 127.4, 122.8, 122.2, 119.7, 110.6, 43.8, 13.3.

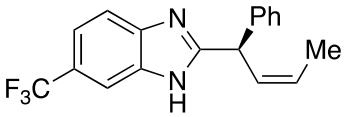
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2359, 2343, 2324, 1532, 1454, 1428, 1279, 932, 607, 600.

Melting Point (ºC): 186–188.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{17}H_{17}N_2$: 249.1386; Found: 249.1395.

Specific Rotation $[\alpha]^{23}_D$: +2.7 (c = 0.23, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 9.94 min (major), 9.07 min (minor). The absolute configuration was assigned by analogy to compound **13.**



(*R,Z*)-2-(1-phenylbut-2-en-1-yl)-6-(trifluoromethyl)-1*H*-benzimidazole (9)

Prepared according to **General Procedure D** using 1-phenyl-*E*-butadiene (**7**) (140 μL, 1.00 mmol, 2.0 equiv) and 6-trifluoromethyl-1*H*-benzimidazol-1-yl pivalate (**S2)** (143 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 350 mL of 10:89:1, 500 mL of 15:84:1, 500 mL of 20:79:1, and 250 mL of 25:74:1, EtOAc:hexane:Et_3N) to afford **9** as a colorless solid (1st run: 98 mg, 62% yield, 97:3 e.r., 2nd run: 98 mg, 62% yield, 94:6 e.r.).

^{1}H NMR ($CDCl_3$, 500 MHz):
Major tautomer: δ 9.67 (s, 1H), 7.98 (s, 1 H), 7.47 (d, *J* = 9.4 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.35–7.29 (m, 2H) 7.29–7.23 (m, 3H), 6.05 (t, *J* = 10.5 Hz, 1H), 5.82 (dq, *J* = 13.8, 6.9 Hz, 1H), 5.31 (dd, *J* = 9.2, 3.2 Hz, 1H), 1.71 (d, *J* = 6.7, 3H).

Minor tautomer: δ 9.88 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.47 (d, *J* = 9.4 Hz, 1H), 7.35–7.29 (m, 2H) 7.29–7.23 (m, 3H), 6.05 (t, *J* = 10.5 Hz, 1H), 5.82 (dq, *J* = 13.8, 6.9 Hz, 1H), 5.31 (dd, *J* = 9.2, 3.2 Hz, 1H), 1.71 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.8, 158.1, 145.5, 142.8, 140.5, 135.8, 135.8, 133.3, 129.3, 128.7, 128.6, 128.0, 128.0, 127.6, 126.0, 123.8, 121.7, 119.9, 119.7, 119.3, 117.2, 111.2, 108.6, 43.9, 13.3.

^{19}F NMR ($CDCl_3$, 471 MHz): δ −60.71.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2722, 1630, 1600, 1420, 1326, 1241, 1155, 1123, 1006, 890, 696.

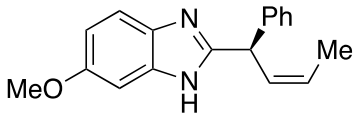
Melting Point (ºC): 167–168.

HRMS (DART) m/z $[M+H]^+$ calcd. for: $C_{18}H_{16}F_3N_2$: 317.1260; Found: 317.1268.

Specific Rotation $[\alpha]^{23}_D$: −1.4 (c = 0.9,$CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 7.12 min (major), 5.89 min (minor). The absolute configuration was assigned by analogy to compound **13.**

Notes: Compound **9** exhibits tautomerization on the NMR timescale, with the compound in equilibrium with the trifluoromethyl in the 5 and 6 position.



(*R,Z*)-6-methoxy-2-(1-phenylbut-2-en-1-yl)-1*H*-benzimidazole (10)

Prepared according to **General Procedure D** using 1-phenyl-*E*-butadiene (**7**) (140 μL, 1.00 mmol, 2.0 equiv) and 6-methoxy-1*H*-benzimidazol-1-yl pivalate (**S3)** (124 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 350 mL of 10:89:1, 350 mL of 15:84:1, 350 mL of 20:79:1, 250 mL of 25:74:1, 250 mL of 30:69:1, and 250 mL of 35:64:1, EtOAc:hexane:Et_3N) to afford **10** as a colorless solid (1st run: 100 mg, 71% yield, 97:3 e.r., 2nd run: 109 mg, 78% yield, 94:6 e.r.). A 55:45 ratio of tautomers was observed by ^1H NMR in $CDCl_3$.

^1H NMR ($CDCl_3$, 500 MHz):
Major tautomer: δ 9.22 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.34–7.29 (m, 2H), 7.28–7.24 (m, 3H), 7.23 (s, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.05 (t, *J* = 9.9 Hz, 1H), 5.78 (dq, *J* = 13.8, 6.8 Hz, 1H), 5.26 (d, *J* = 8.9 Hz, 1H), 3.79 (d, *J* = 6.2 Hz, 3H), 1.71 (d, *J* = 6.4 Hz, 3H).

Minor tautomer: δ 9.26 (s, 1H), 7.34–7.29 (m, 2H), 7.28–7.24 (m, 3H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.80 (s, 1H), 6.05 (t, *J* = 9.9 Hz, 1H), 5.78 (dq, *J* = 13.8, 6.8 Hz, 1H), 5.26 (d, *J* = 8.9 Hz, 1H), 3.79 (d, *J* = 6.2 Hz, 3H), 1.71 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 156.4, 155.5, 141.1, 129.2, 129.1 128.7, 128.1, 127.4, 127.4, 111.9, 56.0, 43.8, 34.3, 22.5, 14.2, 13.3.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2931, 1631, 1595, 1492, 1429, 1269, 1199, 1160, 1029, 805, 692.

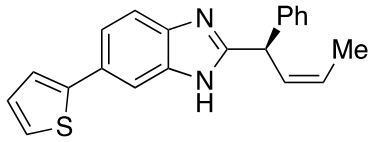
Melting Point (ºC): decomp. 126–133.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{18}H_{19}N_2O$: 279.1492; Found: 279.1493.

Specific Rotation $[\alpha]^{23}_D$: −1.7 (c = 0.30, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 13.13 min (major), 10.95 min (minor). The absolute configuration was assigned by analogy to compound **13**.

Notes: Compound **10** exhibits tautomerization on the NMR timescale, with the compound in equilibrium with the methoxy group in the 5 and 6 position.



(*R,Z)*-2-(1-phenylbut-2-en-1-yl)-6-(thiophen-2-yl)-1*H*-benzimidazole (11)

Prepared according to **General Procedure D** using 1-phenyl-*E*-butadiene (**7**) (140 μL, 1.00 mmol, 2.0 equiv) and 6-(thiophen-2-yl)-1*H*-benzimidazol-1-yl pivalate (**S5)** (150 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 250 mL of 10:89:1, 250 mL of 20:79:1, 500 mL of 25:74:1, 500 mL of 30:69:1, and 500 mL of 35:64:1, EtOAc:hexane:Et_3N) to afford **11** as a colorless solid (1st run: 138 mg, 84% yield 96:4 e.r., 2nd run: 146 mg, 88% yield, 96:4 e.r.). A 55:45 mixture of tautomers was observed by ^{1}H NMR in $CDCl_3$.

^{1}H NMR ($CDCl_3$, 500 MHz):
Major tautomer: δ 9.63 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.54 (s, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.36–7.18 (m, 7H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.07 (tq, *J* = 9.3, 1.8 Hz, 1H), 5.85–5.73 (m, 1H), 5.29 (d, *J* = 9.4 Hz, 1H), 1.70 (dd, *J* = 6.9, 1.8 Hz, 3H).

Minor tautomer: δ 9.63 (s, 1H) 7.97 (s, 1H), 7.57–7.42 (m, 1H), 7.36–7.18 (m, 8H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.07 (tq, *J* = 9.3, 1.8 Hz, 1H), 5.85–5.73 (m, 1H), 5.29 (d, *J* = 9.4 Hz, 1H), 1.70 (dd, *J* = 6.9, 1.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 156.9, 156.7, 145.4, 145.3, 144.0, 143.1, 140.9, 134.3, 133.5, 129.6, 129.2, 128.9, 128.7, 128.1, 128.1, 127.6, 127.4, 124.4, 124.3, 122.9, 122.7, 121.7, 121.2, 119.8, 116.9, 111.0, 108.2, 43.9, 13.3.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 3025, 1451, 1414, 1285, 1225, 1031,1005, 846, 807, 738, 691.

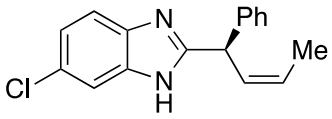
Melting Point (ºC): 98–102.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{21}H_{19}N_2S$: 331.1263; Found: 331.1263.

Specific Rotation $[\alpha]^{23}_D$: +24.7 (c = 1.27, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 19.46 min (major), 17.84 min (minor). The absolute configuration was assigned by analogy to compound **13**.

Notes: Compound **11** exhibits tautomerization on the NMR timescale, with the compound in equilibrium with the thiophene in the 5 and 6 position.



(*R,Z*)-6-chloro-2-(1-phenylbut-2-en-1-yl)-1*H*-benzimidazole (12)

Prepared according to **General Procedure D** using 1-phenyl-*E*-butadiene (**7**) (140 μL, 1.00 mmol, 2.0 equiv) and 6-chloro-1*H*-benzimidazol-1-yl pivalate (**S4)** (126 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 350 mL of 10:89:1, 350 mL of 15:84:1, 350 mL of 20:79:1, 250 mL of 25:74:1, 250 mL of 30:69:1 and 250 mL of 35:64:1, EtOAc:hexane:Et_3N) to afford **12** as a colorless solid (1st run: 100 mg, 71% yield, 93:7 e.r., 2nd run: 109 mg, 77% yield, 96:4 e.r.). A 50:50 mixture of tautomers was observed by ^{1}H NMR in $CDCl_3$.

^{1}H NMR ($CDCl_3$, 500 MHz):
Major tautomer: δ 9.73 (s, 1H), 7.64 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.28–7.21 (m, 3H), 7.18–7.14 (m, 1H) 6.03 (t, *J* = 10.1 Hz, 1H), 5.79 (dq, *J* = 13.7, 6.8 Hz, 1H), 5.26 (d, *J* = 9.1 Hz, 1H), 1.70 (d, *J* = 6.9 Hz, 3H).

Minor tautomer: δ 9.63 (s, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.28–7.21 (m, 4H), 7.20 (s, 1H), 7.18–7.14 (m, 1H), 6.03 (t, *J* = 10.1 Hz, 1H), 5.79 (dq, *J* = 13.7, 6.8 Hz, 1H), 5.26 (d, *J* = 9.1 Hz, 1H), 1.70 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 157.4, 156.8, 144.3, 142.0, 140.7, 134.4, 132.3, 129.2, 128.8, 128.7, 128.4, 128.0, 127.8, 127.7, 127.5, 123.3, 122.9, 120.3, 119.4, 111.5, 110.9, 43.8, 13.3.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2639, 2359, 1622, 1586, 1446, 1422, 1278, 1223, 1059, 921, 803, 737, 598.

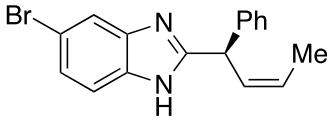
Melting Point (ºC): 168–170.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{17}H_{16}ClN_2$: 283.0997; Found: 283.0995.

Specific Rotation $[\alpha]^{23}_D$: +5.7 (c = 0.37, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 12.00 min (major), 10.25 min (minor). The absolute configuration was assigned by analogy to compound **13**.

Notes: Compound **12** exhibits tautomerization on the NMR timescale, with the compound in equilibrium with the chlorine in the 5 and 6 position.



(*R,Z*)-5-Bromo-2-(1-phenylbut-2-en-1-yl)-1*H*-benzimidazole (13)

Prepared according to **General Procedure D** using 1-phenyl-*E*-butadiene (**7**) (140 μL, 1.00 mmol, 2.0 equiv) and 5-bromo-1*H*-benzimidazol-1-yl pivalate (**S1)** (149 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 350 mL of 10:89:1, 350 mL of 15:84:1, 350 mL of 20:79:1, 250 mL of 25:74:1, and 250 mL of 30:69:1, EtOAc:hexane:Et_3N) to afford **13** as a colorless solid (1st run: 82 mg, 50% yield, 94:6 e.r., 2nd run: 115 mg, 70% yield, 96:4 e.r., 3rd run: 96 mg, 59% 96:4 e.r.). A 51:49 mixture of tautomers was observed by ^{1}H NMR in $CDCl_3$.

^{1}H NMR ($CDCl_3$, 500 MHz)
Major tautomer: δ 9.88 (s, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.42 (s, 1H), 7.33–7.27 (m, 3H), 7.25–7.21 (m, 2H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.02 (t, *J* = 10.3 Hz, 1H), 5.78 (dq, *J* = 10.6, 6.9 Hz, 1H), 5.26 (d, *J* = 9.4 Hz, 1H), 1.69 (d, *J* = 6.9 Hz, 3H).

Minor tautomer: δ 9.75 (s, 1H), 7.79 (s, 1H), 7.33–7.27 (m, 4H), 7.25–7.21 (m, 3H) 6.02 (t, *J* = 10.3 Hz, 1H), 5.78 (dq, *J* = 10.6, 6.9 Hz, 1H), 5.26 (d, *J* = 9.4 Hz, 1H), 1.69 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 157.2, 156.8, 144.7, 142.3, 140.7, 134.9, 132.7, 129.2, 128.7, 128.7, 128.0, 127.8, 127.7, 127.5, 125.9, 125.5, 122.4, 120.7, 115.9, 115.2, 113.9, 112.0, 43.8, 13.3.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2359, 2340, 2324, 1621, 1494, 1443, 1419, 1277, 909. 801, 730, 698.

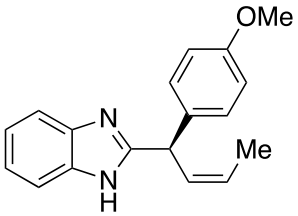
Melting Point (ºC): decomp. 172–175.

Elemental Analysis calcd. for $C_{17}H_{15}BrN_2$: C, 62.40% H, 4.62%; Found: C, 62.14% H. 4.59%.

Specific Rotation $[\alpha]^{23}_D$: +6.2 (c = 0.11, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 13.24 min (major), 11.44 min (minor). The absolute configuration was determined by single crystal x-ray diffraction.

Notes: Compound 13 exhibits tautomerization on the NMR timescale, with the compound in equilibrium with the bromine in the 5 position and the 6 position. This was corroborated by the single crystal x-ray diffraction data (see section **5.1** and **5.2**).



***(R,Z)*-2-(1-(4-methoxyphenyl)but-2-en-1-yl)-1*H*-benzimidazole (14)**

Prepared according to **General Procedure D** using 1-(*p*-methoxyphenyl)-*E*-butadiene (**S9**) (160 mg, 1.00 mmol, 2.0 equiv) and 1*H*-benzimidazol-1-yl pivalate (**6)** (109 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 500 mL of 10:89:1, 350 mL of 15:84:1, 350 mL of 20:79:1, 250 mL of 25:74:1, 250 mL of 30:69:1, 250 mL of 35:64:1, 500 mL of 40:59:1, 250 mL of 45:54:1, and 250 mL of 50:49:1, EtOAc:hexane:Et_3N) to obtain **14** as a solid (1st run: 82% yield, 2nd run: 92% yield). The solid was then triturated with 1.5 mL of MeCN, filtered, and dried under high vacuum to obtain analytically pure **14** as a colorless solid (1st run: 72 mg, 52% yield, 98:2 e.r., 2nd run: 82 mg, 59%, 97:3 e.r.).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.79 (s, 1H), 7.76 (d, J = 7.4 Hz, 1H), 7.33 (dd, J = 7.0, 1.9 Hz, 1H), 7.21 (dq, J = 7.5, 5.7 Hz, 4H), 6.90–6.86 (m, 2H), 6.04 (tq, J = 9.2, 1.8 Hz, 1H), 5.86–5.78 (m, 1H), 5.27 (d, J = 9.3 Hz, 1H), 3.79 (s, 3H), 1.75 (dd, J = 6.9, 1.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.0, 156.2, 143.6, 133.6, 133.0, 129.3, 129.2, 127.3, 122.8, 122.2, 119.8, 114.6, 110.5, 55.5, 43.0, 13.4.

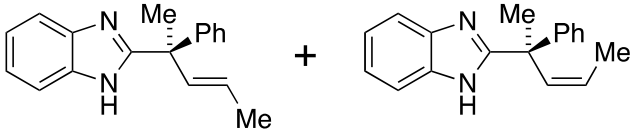
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2840, 1614, 1513, 1453, 1429, 1307, 1271, 1178, 1031, 1008, 934, 813, 740, 696.

Melting Point (ºC): 209–216.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{18}H_{19}N_2O$: 279.1492; Found: 279.1499.

Specific Rotation $[\alpha]^{23}_D$: −7.4 (c = 0.52, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 11.53 min (major), 10.89 min (minor). The absolute configuration was assigned by analogy to compound **13**.



(*R*)-2-(2-phenylpent-3-en-2-yl)-1*H*-benzimidazole (15)

Prepared according to **General Procedure D** using 2-phenylpenta-2,4-diene (**S6**) (162 μL, 1.00 mmol, 2.0 equiv) and 1*H*-benzimidazol-1-yl pivalate (**6)** (109 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 500 mL of 10:89:1, 500 mL of 15:84:1, 500 mL of 20:79:1, and 500 mL of 25:74:1, EtOAc:hexane:Et_3N) to afford **15** as a colorless solid (1st run: 38 mg, 29% yield, 82:18 *E:Z*, 96:4

e.r. (*E* isomer), 99:1 e.r. (*Z* isomer). 2nd run: 37 mg, 28% yield, 81:19 *E:Z*, 96:4 e.r. (*E* isomer), 99:1 e.r. (*Z* isomer)).

^{1}H NMR: *Z*-Isomer: ($CDCl_3$, 500 MHz) δ 8.70 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.37–7.32 (m, 4H), 7.31–7.27 (m, 2H), 7.25 (qd, *J* = 7.5, 1.5 Hz, 2H), 6.27 (dq, *J* = 11.5, 1.8 Hz, 1H), 5.79 (dq, *J* = 11.5, 7.3 Hz, 1H), 2.08 (s, 3H), 1.24 (dd, *J* = 7.3, 1.8 Hz, 3H).

E-Isomer: ($CDCl_3$, 500 MHz) δ 8.70 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.37–7.32 (m, 4H), 7.31–7.27 (m, 2H), 7.25 (qd, *J* = 7.5, 1.5 Hz, 2H), 6.13 (dq, *J* = 15.5, 1.7 Hz, 1H), 5.43 (dq, *J* = 15.5, 6.5 Hz, 1H), 2.01 (s, 3H), 1.79 (dd, *J* = 6.5, 1.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.0, 145.5, 143.1, 136.2, 136.1, 133.5, 128.7, 128.7, 128.6, 128.0, 127.3, 127.1, 127.0, 126.9, 126.3, 122.7, 122.0, 122.0, 119.8, 119.8, 110.4, 110.4, 47.8, 46.6, 28.5, 27.0, 18.1, 14.0.

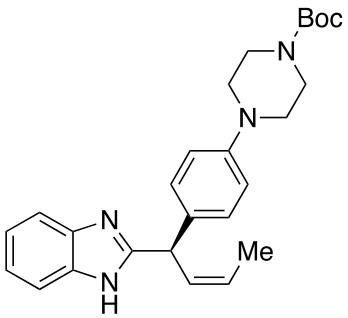
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 3059, 2980, 2359, 1620, 1591, 1490, 1406, 1369, 1274, 1226, 977, 744, 702.

Melting Point (ºC): 215–219.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{18}H_{19}N_2$: 263.1543; Found: 263.1546.

Specific Rotation $[\alpha]^{23}_D$: −34.1 (c = 0.20, $CHCl_3$).

Chiral HPLC: Chiralcel OJ-H (85:15 hexane:IPA, isocratic, 0.8 mL/min), *Z:* 5.67 min (minor), 6.42 min (major). *E:* 7.15 min (major), 10.14 min (minor). The absolute configuration was assigned by analogy to compound **13**.



***tert*-butyl (*R*,*Z*)-4-(4-(1-(1*H*-benzimidazol-2-yl)but-2-en-1-yl)phenyl)piperazine-1-carboxylate (16)**

Prepared according to **General Procedure D** using *tert*-butyl (*E*)-4-(4-(buta-1,3-dien-1-yl)phenyl)piperazine-1-carboxylate (**S10**) (314 mg, 1.00 mmol, 2.0 equiv) and 1*H*-benzimidazol-1-yl pivalate (**6)** (109 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 250 mL of 12:87:1, 250 mL of 20:79:1, 250 mL of 30:69:1, 250 mL of 40:59:1, and 250 mL of 45:54:1, EtOAc:hexane:Et_3N) to afford **16** as a colorless solid (1st run: 169 mg, 78% yield, 96:4 e.r., 2nd run: 171 mg, 79% yield 96:4 e.r.).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.67 (s, 1H), 7.70 (s, 1H), 7.29 (s, 1H), 7.17 (dd, *J* = 9.7, 6.7 Hz, 4H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.05 (tq, *J* = 9.4, 1.8 Hz, 1H), 5.79–5.71 (m, 1H), 5.23 (d, *J* = 9.4 Hz, 1H), 3.53 (t, *J* = 5.0 Hz, 4H), 3.06 (t, *J* = 5.2 Hz, 4H), 1.70 (dd, *J* = 6.9, 1.8 Hz, 3H), 1.48 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 156.4, 154.9, 150.4, 143.5, 133.9, 132.6, 129.3, 128.8, 126.9, 122.6, 122.0, 119.6, 117.1, 116.1, 110.7, 80.1, 49.4, 42.9, 28.6, 13.3.

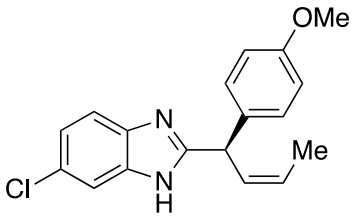
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2978, 2839, 1695, 1613, 1515, 1454, 1268, 1226, 999, 926, 736, 668.

Melting Point (ºC): decomp. 203–204.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{26}H_{33}N_4O_2$: 433.2598; Found: 433.2605.

Specific Rotation $[\alpha]^{23}_D$: −37.1 (c = 1.23, $CHCl_3$).

Chiral SFC: Chiralcel OD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min) 16.64 min (major), 15.84 min (minor). The absolute configuration was assigned by analogy to compound **13**.



(*R*,*Z*)-6-chloro-2-(1-(4-methoxyphenyl)but-2-en-1-yl)-1*H*-benzimidazole (17)

Prepared according to **General Procedure D** using 1-(*p*-methoxyphenyl)-*E*-butadiene (**S9**) (160 mg, 1.00 mmol, 2.0 equiv) and 6-chloro-1*H*-benzimidazol-1-yl pivalate (**S4)** (126 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 250 mL of 10:89:1, 250 mL of 20:79:1, 250 mL of 30:69:1 and 250 mL of 40:59:1, EtOAc:hexane:Et_3N) to afford **17** as a colorless solid (1st run: 106 mg, 68% yield, 89:11 e.r. 2nd run: 104 mg, 67% yield, 91:9 e.r.). A 50:50 mixture of tautomers was observed by ^{1}H NMR in $CDCl_3$.

^{1}H NMR: ($CDCl_3$, 500 MHz):
Major tautomer: δ 9.87 (s, 1H), 7.55 (s, 1H), 7.37–7.10 (bs, 1H), 7.18–7.10 (m, 3H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.00 (tq, *J* = 9.4, 1.8 Hz, 1H), 5.76 (dqd, *J* = 10.6, 6.9, 1.1 Hz, 1H), 5.21 (d, *J* = 9.3 Hz, 1H), 3.75 (s, 3H), 1.68 (dd, *J* = 6.9, 1.8 Hz, 3H).

Minor tautomer: δ 9.75 (s, 1H), 7.62 (s, 1H), 7.37–7.10 (bs, 1H), 7.18–7.10 (m, 3H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.00 (tq, *J* = 9.4, 1.8 Hz, 1H), 5.76 (dqd, *J* = 10.6, 6.9, 1.1 Hz, 1H), 5.21 (d, *J* = 9.3 Hz, 1H), 3.75 (s, 3H), 1.68 (dd, *J* = 6.9, 1.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.0, 157.5, 132.7, 131.0, 130.5, 130.0, 129.1, 129.0, 128.1, 127.5, 123.0, 114.6, 114.1, 55.4, 43.0, 13.3.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2912, 2834, 2703, 2358, 1608, 1582, 1511, 1441, 1423, 1277, 1181, 1029, 809, 685.

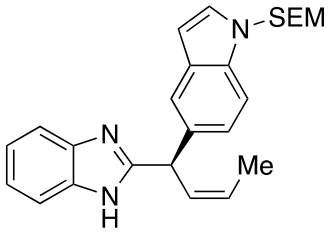
Melting Point (ºC): 169–171.

Elemental Analysis calcd. for $C_{18}H_{17}ClN_2O$: C, 69.12% H, 5.48%; Found: C, 69.00% H, 5.67%.

Specific Rotation $[\alpha]^{23}_D$: −13.5 (c = 0.63, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 14.27 min (major), 12.68 min (minor). The absolute configuration was assigned by analogy to compound **13**.

Notes: Compound **17** exhibits tautomerization on the NMR timescale, with the compound in equilibrium with the chlorine in the 5 and 6 position.



***(R,Z)*-2-(1-(1-((2-(trimethylsilyl)ethoxy)methyl)-1H-indol-5-yl)but-2-en-1-yl)-1*H*-benzimidazole (18)**

Prepared according to a modified **General Procedure D** using (*E*)-5-(buta-1,3-dien-1-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole (**S11**) (250 mg, .840 mmol, 1.66 equiv) and 1*H*-benzimidazol-1-yl pivalate (**6)** (109 mg, 0.500 mmol, 1.0 equiv). *To protect the photosensitive diene, the reaction tube was wrapped in aluminum foil.* The crude material was purified by column chromatography (40 g silica, gradient: 250 mL of 10:89:1, 500 mL of 15:84:1, and 1000 mL of 20:79:1, EtOAc:hexane:Et_3N) to afford **18** as a colorless solid. (1st run: 124 mg, 59% yield, 96:4 e.r., 2nd run: 114 mg, 55% yield, 96:4 e.r.).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.26 (s, 1H), 7.53 (s, 1H), 7.84–7.28 (bs, 2H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, *J* = 7.1, 3.3 Hz, 3H), 7.13 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.47 (d, *J* = 3.2 Hz, 1H), 6.17 (tq, *J* = 9.4 1.8 Hz, 1H), 5.78 (dqd, *J* = 10.6, 6.8, 1.1 Hz, 1H), 5.44 (s, 2H), 5.37 (d, *J* = 9.3 Hz, 1H), 3.47 (t, *J* = 8.1 Hz, 2H), 1.72 (dd, *J* = 6.9, 1.8 Hz, 3H), 0.89 (dd, *J* = 8.8, 7.6 Hz, 2H), −0.05 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 157.0, 135.7, 132.8, 132.0, 130.8, 129.8, 129.6, 128.8, 126.7, 126.7, 123.2, 122.5, 122.3, 121.0, 120.3, 110.8, 102.6, 75.8, 66.0, 43.8, 17.8, 13.3, −1.3.

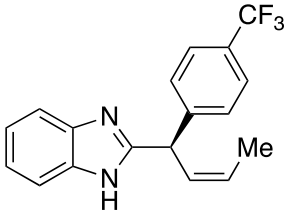
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2951, 2891, 1532, 1454, 1426, 1351, 1351, 1299, 1248, 1215, 1070, 834, 736, 714.

Melting Point (ºC): 175–176.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{25}H_{32}N_3OSi$: 418.2309; Found: 418.2300.

Specific Rotation $[\alpha]^{23}_D$: −44.8 (c = 1.24, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 12.28 min (major), 11.19 min (minor). The absolute configuration was assigned by analogy to compound **13**.



(*R*,*Z*)-2-(1-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)-1*H*-benzimidazole (19)

Prepared according to **General Procedure D** using 1-(*p*-trifluoromethylphenyl)-*E*-butadiene (**S8**) (198 mg, 1.00 mmol, 2.0 equiv) and 1*H*-benzimidazol-1-yl pivalate (**6)** (109 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 350 mL of 5:94:1, 250 mL of 15:84:1, 250 mL of 20:79:1, 500 mL of 25:74:1, and 250 mL of 30:69:1, EtOAc:hexane:Et_3N) to afford **19** as a colorless solid (1st run: 123 mg, 78% yield, 63:37 e.r., 2nd run: 114 mg, 72% yield, 63:37 e.r.).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 7.7 Hz, 4H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 9.1 Hz, 2H), 6.05 (t, *J* = 10.1 Hz, 1H), 5.93–5.81 (m, 1H), 5.43 (d, *J* = 9.3 Hz, 1H), 1.76 (dd, *J* = 6.9, 1.8 Hz, 3H).

^{19}F NMR ($CDCl_3$, 471 MHz): δ −62.58.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.5, 144.8, 129.9, 129.7, 128.9, 128.5, 128.0, 126.1, 126.1, 125.3, 123.1, 43.5, 13.4.

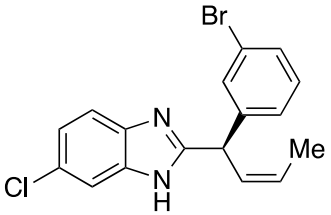
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 3057, 2632, 1619, 1429, 1326, 1269, 1133, 1068, 1018, 818, 739, 599.

Melting Point (ºC): decomp. 161–162.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{18}H_{16}F_3N_2$: 317.1260; Found: 317.1266.

Specific Rotation $[\alpha]^{23}_D$: −4.6 (c = 1.11, $CHCl_3$).

Chiral SFC: Chiralcel OD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 8.01 min (major), 7.24 min (minor). The absolute configuration was assigned by analogy to compound **13**.



(*R*,*Z*)-2-(1-(3-bromophenyl)but-2-en-1-yl)-6-chloro-1*H*-benzimidazole (20)

Prepared according to **General Procedure D** using 1-(*m*-bromophenyl)-*E*-butadiene (**S7**) (158 μL, 1.00 mmol, 2.0 equiv) and 6-chloro-1*H*-benzimidazol-1-yl pivalate (**S4)** (126 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 350 mL of 10:89:1, 350 mL of 15:84:1, 500 mL of 20:79:1, 250 mL of 25:74:1, 250 mL of 30:69:1, and 350 mL of 35:64:1, EtOAc:hexane:Et_3N) to afford **20** as a colorless solid (1st run: 111 mg, 61% yield, 51:49 e.r., 2nd run: 128 mg, 71% yield, 87:13 e.r.). A 50:50 mixture of tautomers was observed by ^{1}H NMR in $CDCl_3$.

^{1}H NMR ($CDCl_3$, 500 MHz):
Major tautomer: δ 10.07 (s, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.39–7.32 (m, 2H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.18 (dt, *J* = 8.8, 1.7 Hz, 1H), 7.16–7.11 (m, 2H), 5.96 (dddd, *J* = 11.1, 9.0, 3.9, 1.9 Hz, 1H), 5.80 (dq, *J* = 13.5, 7.1 Hz, 1H), 5.21 (d, *J* = 9.3 Hz, 1H), 1.68 (dt, *J* = 7.1, 1.7 Hz, 3H).

Minor tautomer: δ 9.95 (s, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.39–7.32 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.18 (dt, *J* = 8.8, 1.7 Hz, 1H), 7.16–7.11 (m, 2H), 5.96 (dddd, *J* = 11.1, 9.0, 3.9, 1.9 Hz, 1H), 5.80 (dq, *J* = 13.5, 7.1 Hz, 1H), 5.21 (d, *J* = 9.3 Hz, 1H), 1.68 (dt, *J* = 7.1, 1.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 156.5, 156.0, 144.1, 142.9, 141.8, 134.4, 132.4, 131.0, 130.7, 130.7, 128.5, 128.1, 126.7, 123.5, 123.2, 123.1, 120.3, 119.3, 111.7, 111.0, 43.4, 13.4.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2706, 2359, 1586, 1470, 1410, 1268, 1058, 996, 927, 851, 682.

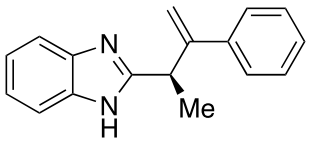
Melting Point (ºC): 81–83.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{17}H_{15}BrClN_2$: 361.0102; Found: 361.0104.

Specific Rotation $[\alpha]^{23}_D$: −7.5 (c = 1.09, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 13.86 min (major), 11.86 min (minor). The absolute configuration was assigned by analogy to compound **13**.

Notes: Compound **20** exhibits tautomerization on the NMR timescale, with the compound in equilibrium with the chlorine in the 5 and 6 position.



(*R*)-2-(3-phenylbut-3-en-2-yl)-1*H*-benzimidazole (21)

Prepared according to **General Procedure D** using 2-phenylbutadiene (**S12**) (141 μL, 1.00 mmol, 2.0 equiv) and 1*H*-benzimidazol-1-yl pivalate (**6)** (109 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 500 mL of 10:89:1, 350 mL of 15:84:1, 350 mL of 20:79:1, 250 mL of 25:74:1, 250 mL of 30:69:1, and 250 mL of 35:64:1, EtOAc:hexane:Et_3N) to afford **21** as a colorless solid (1st run: 95 mg, 77% yield, 95:5 e.r., 2nd run: 90 mg, 72% yield, 95:5 e.r.).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.85 (s, 1H), 7.73 (s, 1H), 7.35–7.28 (m, 3H), 7.26–7.22 (m, 3H), 7.20 (d, *J* = 5.5 Hz, 2H), 5.56 (s, 1H), 5.31 (s, 1H), 4.39 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 156.9, 149.7, 143.5, 140.2, 133.8, 128.7, 128.1, 126.5, 122.7, 122.1, 119.4, 114.8, 110.8, 39.7, 19.1.

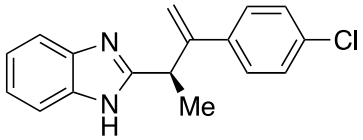
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2984, 2742, 2359, 1623, 1599, 1493, 1427, 1327, 1271, 1239, 1108 1083, 978, 908, 737.

Melting Point (ºC): 181–182.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{17}H_{17}N_2$: 249.1386; Found: 249.1387.

Specific Rotation $[\alpha]^{23}_D$: +18.1 (c = 0.80, $CHCl_3$).

Chiral SFC: Chiralcel OD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 11.15 min (major), 10.87 min (minor). The absolute configuration was assigned by analogy to Li et al.[9]



(*R*)-2-(3-(4-chlorophenyl)but-3-en-2-yl)-1*H*-benzimidazole (22)

Prepared according to **General Procedure D** using 2-(*p*-chlorophenyl)-butadiene (**S15**) (159 μL, 1.00 mmol, 2.0 equiv) and 1*H*-benzimidazol-1-yl pivalate (**6)** (109 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 350 mL of 10:89:1, 350 mL of 15:84:1, 500 mL of 20:79:1, 500 mL of 25:74:1, 250 mL of 27:72:1, and 250 mL of 30:69:1, EtOAc:hexane:Et_3N) to obtain **22** as a solid (1st run: 35% yield, 2nd run: 45% yield, 3rd run: 35% yield). The solid was then triturated with 1.5 mL of MeCN, filtered, and dried under high vacuum to obtain analytically pure **22** as a colorless solid (1st run: 15 mg, 11% yield, 93:7 e.r., 2nd run: 30 mg, 21% yield, 94:6 e.r., 3rd run 32 mg, 23%, 94:6 e.r.).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.84 (s, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.29–7.19 (m, 6H), 5.60 (s, 1H), 5.39 (d, *J* = 1.2 Hz, 1H), 4.36 (q, *J* = 7.0 Hz, 1H), 1.68 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 156.1, 148.2, 138.3, 134.2, 128.9, 128.8, 127.9, 127.9, 123.1, 115.4, 39.3, 18.9.

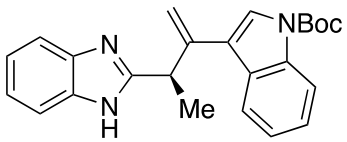
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2962, 1490, 1429, 1259, 1092, 1009, 834, 788, 749.

Melting Point (ºC): decomp. 210–214.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{17}H_{16}ClN_2$: 283.0997; Found: 283.1001.

Specific Rotation $[\alpha]^{23}_D$: −8.2 (c = 0.10, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 10.67 min (major), 11.78 min (minor). The absolute configuration was assigned by analogy to Li et al.[9]



***tert*-butyl (*R*)-3-(3-(1*H*-benzimidazol-2-yl)but-1-en-2-yl)-1*H*-indole-1-carboxylate (23)**

Prepared according to **General Procedure D** using *tert*-butyl-3-(buta-1,3-dien-2-yl)-1*H*-indole-1-carboxylate (**S14**) (269 mg, 1.00 mmol, 2.0 equiv) and 1*H*-benzimidazol-1-yl pivalate (**6)** (109 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 250 mL of 10:89:1, 500 mL of 15:84:1, 500 mL of 20:79:1, and 500 mL of 25:74:1, EtOAc:hexane:Et_3N) to afford **23** as a colorless solid (1st run: 149 mg, 77% yield, 96:4 e.r., 2nd run: 142 mg, 73% yield, 96:4 e.r.).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.23 (s, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.37–7.30 (m, 2H), 7.29–7.23 (m, 2H), 7.20 (dd, *J* = 6.1, 3.1 Hz, 2H), 5.76 (s, 1H), 5.54 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 1H), 1.73 (d, *J* = 7.1 Hz, 3H), 1.54 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 156.6, 149.5, 143.5, 142.2, 135.9, 133.5, 129.0, 124.8, 123.7, 123.1, 122.5, 120.3, 120.1, 119.6, 115.5, 115.1, 110.7, 84.1, 41.1, 28.4, 28.2, 18.7.

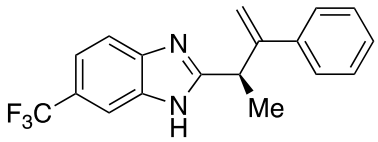
IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2978, 1732, 1450, 1366, 1271, 1240, 1151, 1060, 902, 852, 739,

Melting Point (ºC): 143–148.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{24}H_{26}N_3O_2$: 388.2020; Found: 388.2015.

Specific Rotation $[\alpha]^{23}_D$: −4.1 (c = 1.02, $CHCl_3$)

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 11.61 min (major), 10.39 min (minor). The absolute configuration was assigned by analogy to Li et al.[9]



(*R*)-2-(3-phenylbut-3-en-2-yl)-6-(trifluoromethyl)-1*H*-benzimidazole (24)

Prepared according to **General Procedure D** using 2-phenylbutadiene (**S12**) (141 μL, 1.00 mmol, 2.0 equiv) and 6-trifluoromethyl-1*H*-benzimidazol-1-yl pivalate (**S2)** (109 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 250 mL of 10:89:1, 500 mL of 15:84:1, 500 mL of 20:79:1, and 500 mL of 25:74:1, EtOAc:hexane:Et_3N), and dried under high vacuum at 45 °C with sonication to obtain **24** as a colorless foam (1st run: 71 mg, 45% yield, 99:1 e.r., 2nd run: 74 mg, 47% yield, 99:1 e.r.). A 55:45 mixture of tautomers was observed by ^{1}H NMR in $CDCl_3$.

^{1}H NMR ($CDCl_3$, 500 MHz):
Major tautomer: δ 9.59 (s, 1H), 8.01 (s, 1H), 7.46 (s, 1H), 7.43–7.37 (m, 1H), 7.35–7.29 (m, 2H), 7.28 (dd, *J* = 4.9, 2.2 Hz, 3H), 5.61 (s, 1H), 5.34 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 1H), 1.70 (d, *J* = 7.1 Hz, 3H).

Minor tautomer: 9.65 (s, 1H), 7.78 (s, 1H), 7.61 (s, 1H), 7.47 (s, 1H), 7.35–7.29 (m, 2H), 7.28 (dd, *J* = 4.9, 2.2 Hz, 3H), 5.61 (s, 1H), 5.34 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 1H), 1.70 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.6, 158.9, 149.2, 145.7, 143.0, 139.9, 135.7, 133.1, 128.8, 128.3, 126.4, 123.8, 119.8, 119.3, 117.1, 115.1, 111.0, 108.4, 39.7, 18.9.

^{19}F NMR $CDCl_3$, 471 MHz): δ −60.84.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2979, 2360, 1629, 1533, 1419, 1326, 1158, 1243, 1111, 1051, 932.

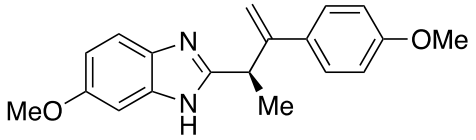
Melting Point (ºC): 93–95.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{18}H_{16}F_3N_2$: 317.1260; Found 317.1263.

Specific Rotation $[\alpha]^{23}_D$: +10.4 (c = 0.25, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 6.67 min (major), 4.54 min (minor). The absolute configuration was assigned by analogy to Li et al.[9]

Notes: Compound **24** exhibits tautomerization on the NMR timescale, with the compound in equilibrium with the trifluoromethyl group in the 5 and 6 position.



(*R*)-6-methoxy-2-(3-(4-methoxyphenyl)but-3-en-2-yl)-1*H*-benzimidazole (25)

Prepared according to **General Procedure D** using 2-(*p*-methoxyphenyl)-butadiene (**S13**) (172 μL, 1.00 mmol, 2.0 equiv) and 6-methoxy-1*H*-benzimidazol-1-yl pivalate (**S3)** (124 mg, 0.500 mmol, 1.0 equiv). The crude material was purified by column chromatography (40 g silica, gradient: 350 mL of 10:89:1, 350 mL of 15:84:1, 350 mL of 20:79:1, 350 mL of 25:74:1, 600 mL of 30:29:1, 250 mL of 32:27:1, and 250 mL of 33:26:1, EtOAc:hexane:Et_3N) to afford **25** as a colorless solid (1st run: 80 mg, 52% yield, 94:6 e.r., 2nd run: 65 mg, 42% yield, 89:11 e.r.). A 50:50 mixture of tautomers was observed by ^{1}H NMR in $CDCl_3$.

^{1}H NMR ($CDCl_3$, 500 MHz):
Major tautomer: δ 9.52 (s, 1H), 7.70–7.50 (bs, 1H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.30–7.23 (bs, 1H), 6.83 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.80–6.76 (m, 2H), 5.52 (s, 1H), 5.26 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 1.68 (d, *J* = 7.1 Hz, 3H).

Minor tautomer: δ 9.52 (s, 1H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.24–7.14 (bs, 1H), 6.83 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.86–6.76 (bs, 1H), 6.80–6.76 (m, 2H), 5.52 (s, 1H), 5.26 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 1.68 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.5, 156.4, 155.9, 148.9, 134.3, 132.4, 127.7, 119.9, 114.0, 113.1, 111.0, 102.0, 94.6, 55.9, 55.4, 39.7, 19.0.

IR (Diamond-ATR, neat, cm^{-1}) $\tilde{\upsilon}_{max}$: 2934, 2833, 2360, 2343, 1627, 1606, 1510, 1451, 1414, 1243, 1153, 1028, 832, 803, 750.

HRMS (DART) m/z $[M+H]^+$ calcd. for $C_{19}H_{21}N_2O_2$: 309.1598, Found: 309.1592.

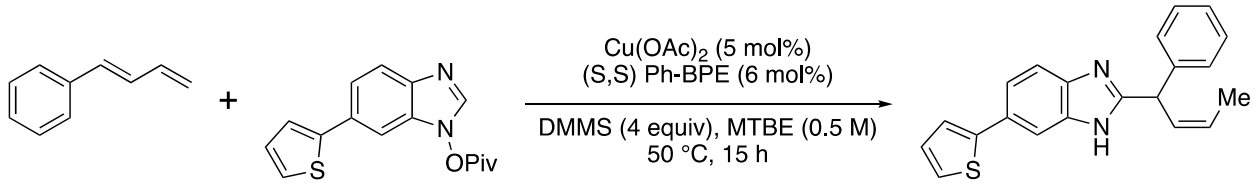
Melting Point (ºC): decomp. 205–210.

Specific Rotation $[\alpha]^{23}_D$: +26.8 (c = 0.25, $CHCl_3$).

Chiral SFC: Chiralcel AD-H (5:95 MeOH (0.1% Et_2NH):scCO2 to 20:80 MeOH (0.1% Et_2NH):scCO2 linear gradient over 20 min, 2.50 mL/min), 12.81 min (major), 15.08 min (minor). The absolute configuration was assigned by analogy to Li et al.[9]

Notes: Compound **25** exhibits tautomerization on the NMR timescale, with the compound in equilibrium with the methoxy group in the 5 and 6 position.

4.3. Synthesis of 11 on a 1.0 mmol Scale



11
Run 1: 76%
Run 2: 74%
96:4 e.r.

Procedure:

Inside a nitrogen filled glovebox, an oven-dried reaction tube (Fisherbrand, 20x125 mm, 1495937A) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (9.0 mg, 50.0 μmol, 5 mol%), (*S,S*)-Ph-BPE (30.4 mg, 60.0 μmol, 6 mol%) and methyl *tert*-butyl ether (2 mL). This solution was capped with a screw cap containing a PTFE septum and allowed to stir for 10 min. The cap was removed and dimethoxy(methyl)silane (490 μL, 2.00 mmol, 4.0 equiv) was added by pipette.

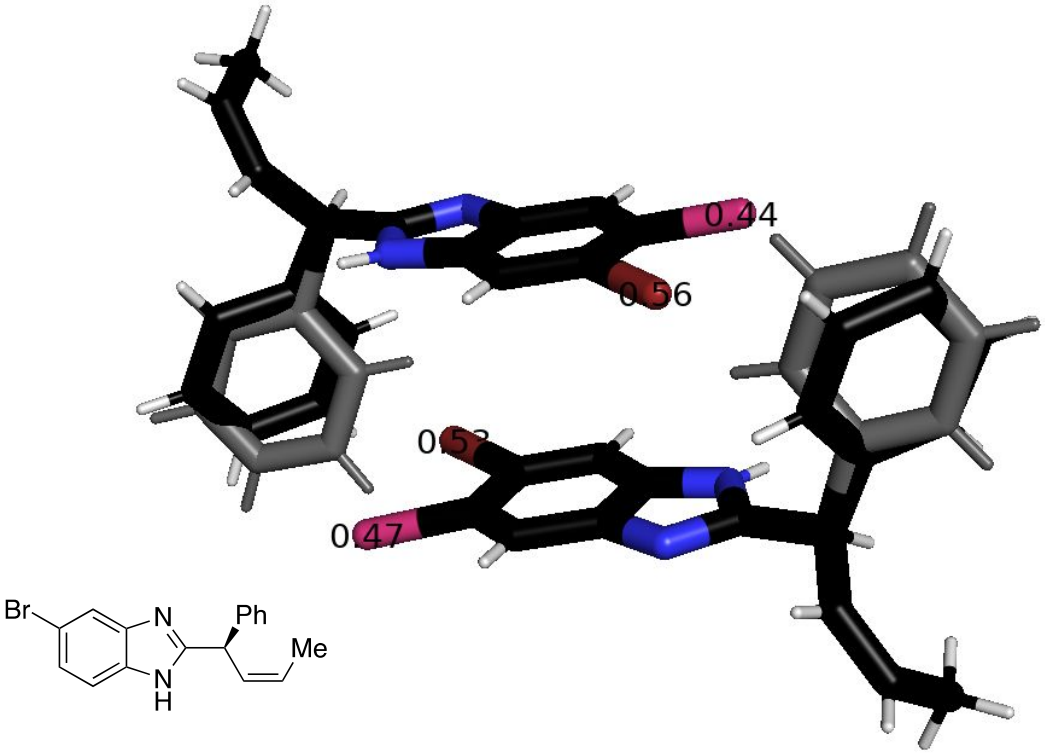
After stirring for 15 min, the cap was removed and 1-phenyl-*E*-butadiene (**7**) (280 μL, 2.00 mmol, 2.0 equiv) was added to the reaction tube via pipette. The reaction tube was capped and the reaction mixture was allowed to stir for 10 min, then the cap was removed and 6-(thiophen-2-yl)-1*H*-benzimidazol-1-yl pivalate (**S5)** was added (300 mg, 1.00 mmol, 1.0 equiv). The reaction tube was once again capped, removed from the glovebox and placed in an oil bath preheated to 50 ºC.

After the reaction mixture had stirred for 15 h at 50 ºC, the reaction tube was removed from the oil bath and allowed to cool to rt. Once at rt, the cap was removed from the reaction tube and the reaction mixture was quenched by the addition of sat. NH_4F in MeOH (10 mL) and allowed to stir 5 min. The reaction mixture was then transferred into a separatory funnel containing sat. aq. $NaHCO_3$ (20 mL), and the tube was rinsed with EtOAc (20 mL). The phases were separated, and the aq. phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered through a fritted glass funnel, and concentrated *in vacuo* with the aid of a rotary evaporator.

The resultant crude material was dissolved in CH_2Cl_2 (2 mL) and purified by column chromatography (70 g silica, gradient: 500 mL of 10:89:1, 500 mL of 20:79:1, 500 mL of 30:69:1, and 500 mL of 35:64:1, EtOAc:hexane:Et_3N) to afford **11** as a colorless solid (1st run: 250 mg, 76% yield, 96:4 e.r., 2nd run: 245 mg, 74% yield, 95:5 e.r.).

5. Single Crystal X-Ray Diffraction Data

5.1 Crystal Growth and Refinement Procedure:



10 mg of (*R,Z*)-5-bromo-2-(1-phenylbut-2-en-1-yl)-1*H*-benzimidazole (**13**) was dissolved in 0.5 mL of THF in a 1 dram vial. The vial was capped and sonicated for 5 min at rt. The resulting solution was taken up in a syringe, and filtered through a 0.4 micron PTFE syringe filter into a new clean 1 dram vial without a cap. Using forceps, this vial was placed in a 4 dram vial containing hexane, and the 4 dram vial was capped. The entire setup was then placed in a freezer at −5 ºC. The crystals were allowed to grow by vapor diffusion over one week.

Low-temperature diffraction data (φ-and ω-scans) were collected on a Bruker D8 Venture diffractometer equipped with an Incoatec microfocus 3.0 (Cu) source (λ = 1.54178 Å). Data reduction was performed with the program SAINT.[11] Absorption correction and scaling were performed with the program SADABS.[12] The structure was solved by direct methods using SHELXT[13] and refined against F2 on all data by full-matrix least squares with SHELXL,[14] following established refinement strategies.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atom attached to N1 was found in the difference Fourier map and refined semi-freely. All other hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to 1.2 times the Ueq value of the atoms they are bonded to (1.5 times for methyl groups). Disordered solvent molecules were accounted for utilizing SQUEEZE.[16]

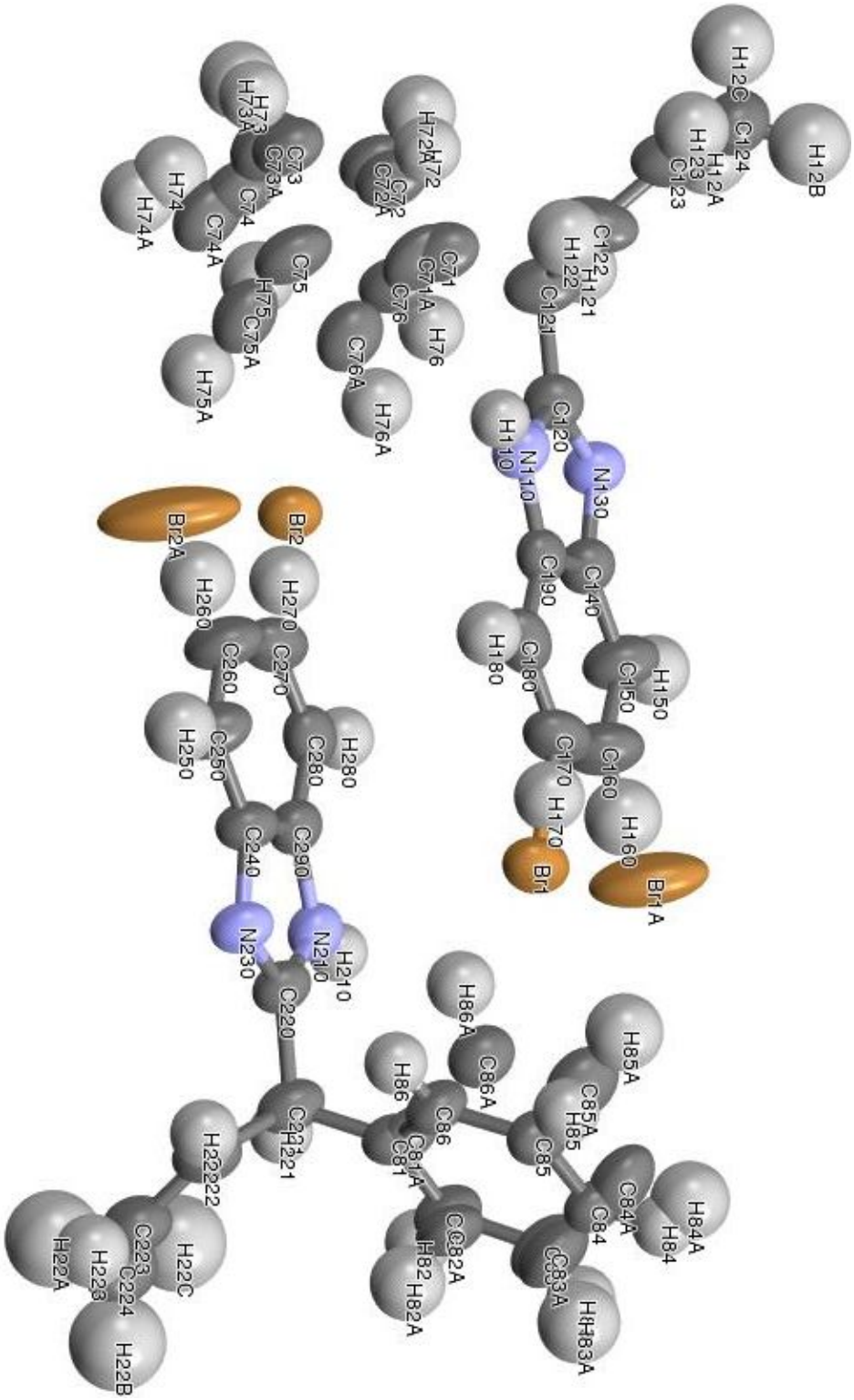
The compound crystallized in the R3 space group, with two molecules in the asymmetric unit, which were found to be disordered in the positional placement of the bromine atoms (at the C5 and C6 positions). Additionally, the phenyl substituents were found to be rotationally disordered, with two distinct conformations visible in the difference Fourier map. There is a pi-

stacking interaction between the bromine atom of molecule 1 and the phenyl ring of molecule 2. This interaction appears coupled to the positional disorder of the bromine, and so these were refined together, having the same part numbers in shellxl, and refined such that the sum of both components was 1.00. The bromine in molecule one was found to have positional disorder between C5:C6 in a 56:44 ratio, in molecule two it was found to be 53:47. Rigid bond restraints, as well as similarity restraints on displacement parameters were applied. The benzimidazole rings were restrained to be flat, as were the phenyl rings.

5.2 Crystal Data and Structure Refinement Details

Empirical formula	$C_{17}\ H_{15}\ Br\ N_2$	
Identification code	P8_20013	
Formula weight	327.22	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Trigonal	
Space group	R3	
Unit cell dimensions:	a = 24.4004(3) Å	α= 90°
	b = 24.4004(3) Å	β= 90°
	c = 14.6467(3) Å	γ = 120°
Volume	7552(02) $Å^3$	
Z	2	
Absorption coefficient:	4.349 mm^{-1}	
F(000):	3984	
Theta range for data collection:	3.623 to 70.183°	
Index ranges:	-29 =< h =< 29, -29 =< k =< 29, -17 =< l =< 17	
Reflections collected:	29577	
Independent reflections:	6361 [Rint = 0.0448]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction:	Spherical	
Max. and min. transmission:	0.22438 and 0.1109	
Refinement method:	Full-matrix least-squares on F2	
Data / restraints / parameters:	6361 / 1067 / 497	
Goodness-of-fit on F2:	1.082	
Final R indices [I>2σ(I)]:	R1 = 0.0480, wR2 = 0.1354	
R indices (all data):	R1 = 0.0510 wR2 = 0.1378	
Largest diff. peak and hole:	0.599 and -0.627 $e.Å^{-3}$	

5.3 Thermal Ellipsoid Plot



Thermal ellipsoid plot of asymmetric unit at 50% probability and 100 K.

6. References and Notes

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4. Lebel, H.; Paquet, V. Catalytic Activity of a New Ruthenium−(Trimethylsilyl)Diazomethane Complex. *Organometallics* **2004**, *23*, 1187–1190.
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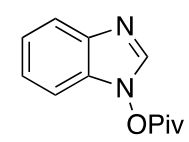
16. Spek, A. L. *PLATON* SQUEEZE: A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. *Acta Cryst. C* **2015**, *71*, 9–18.

7: Associated Analytical Data

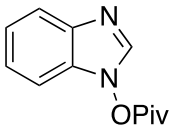
7.1: NMR Spectra of Products and Starting Materials



6

^{1}H NMR

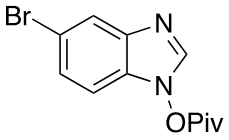
$CDCl_3$, 400 MHz



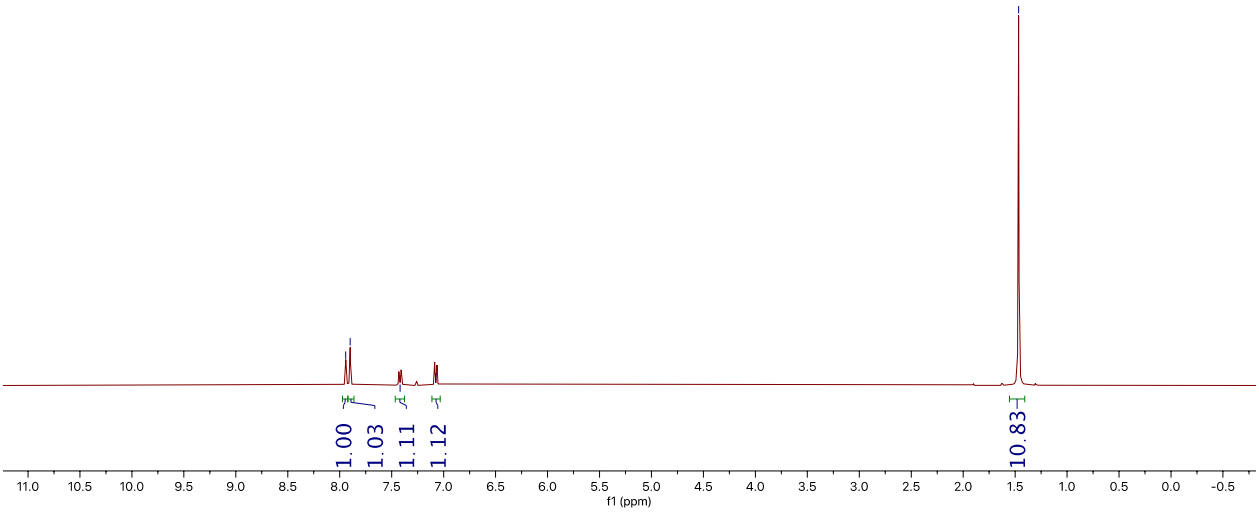
6

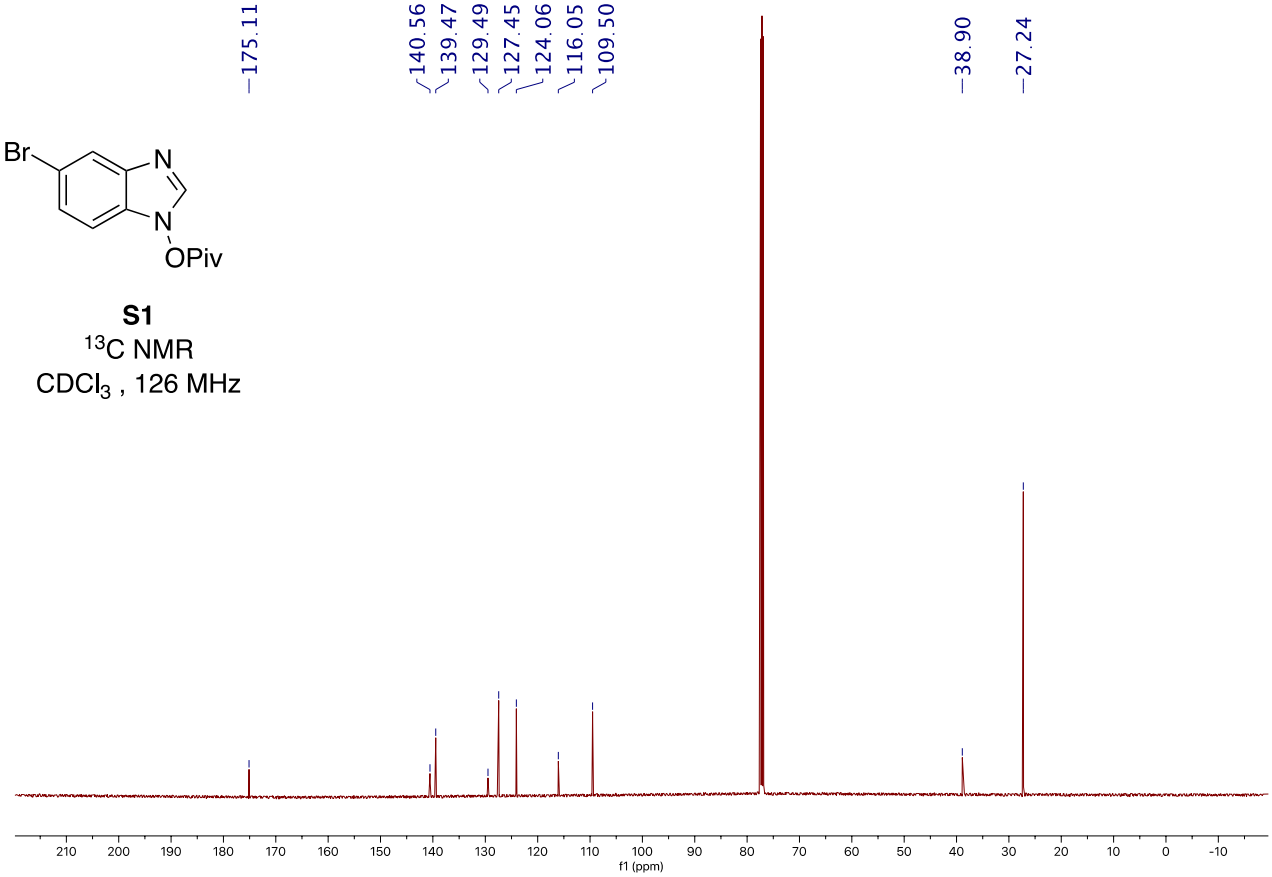
^{13}C NMR

$CDCl_3$, 126 MHz

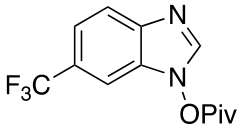


S1
^{1}H NMR
$CDCl_3$, 400 MHz





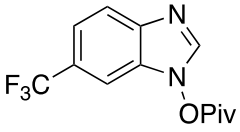
S1
^{13}C NMR
$CDCl_3$, 126 MHz



S2

^{1}H NMR

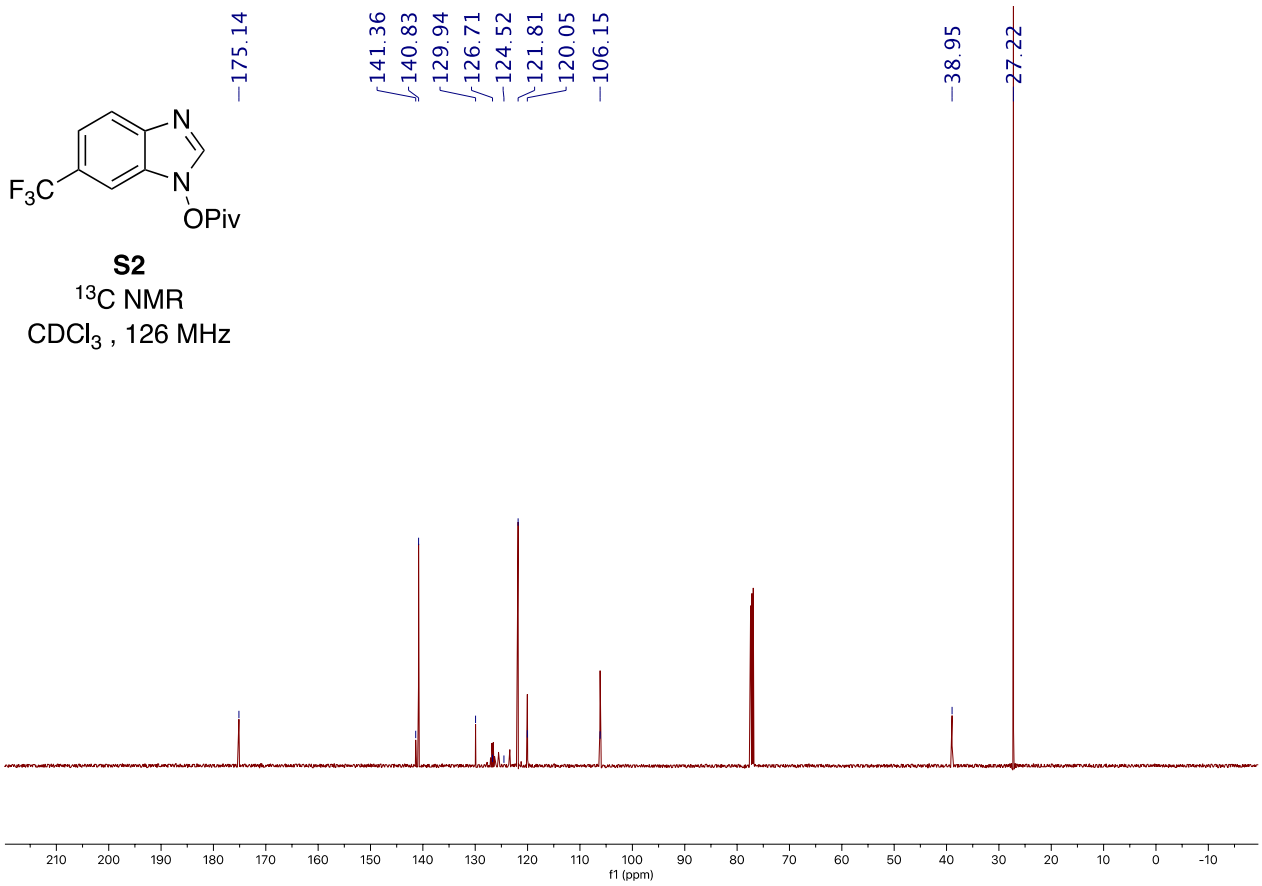
$CDCl_3$, 500 MHz

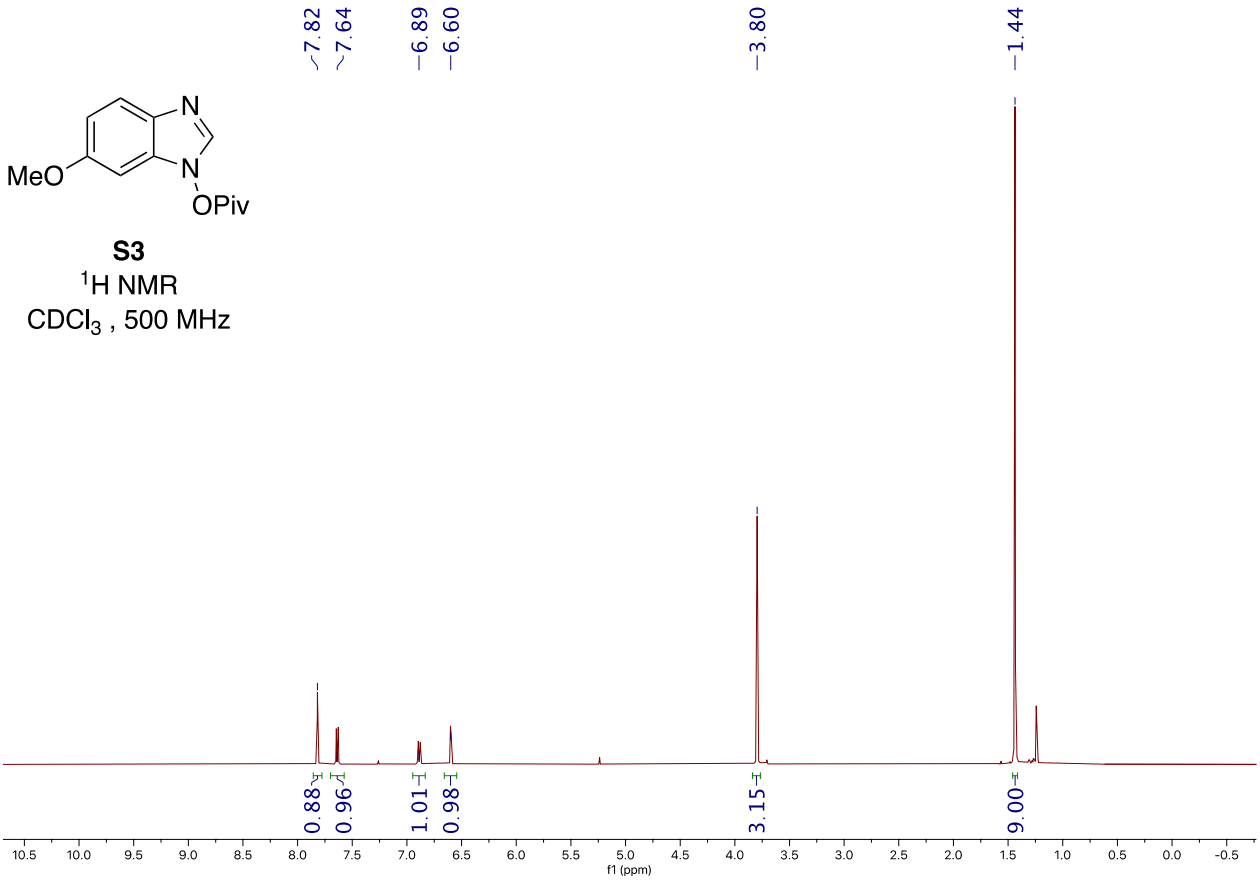


S2

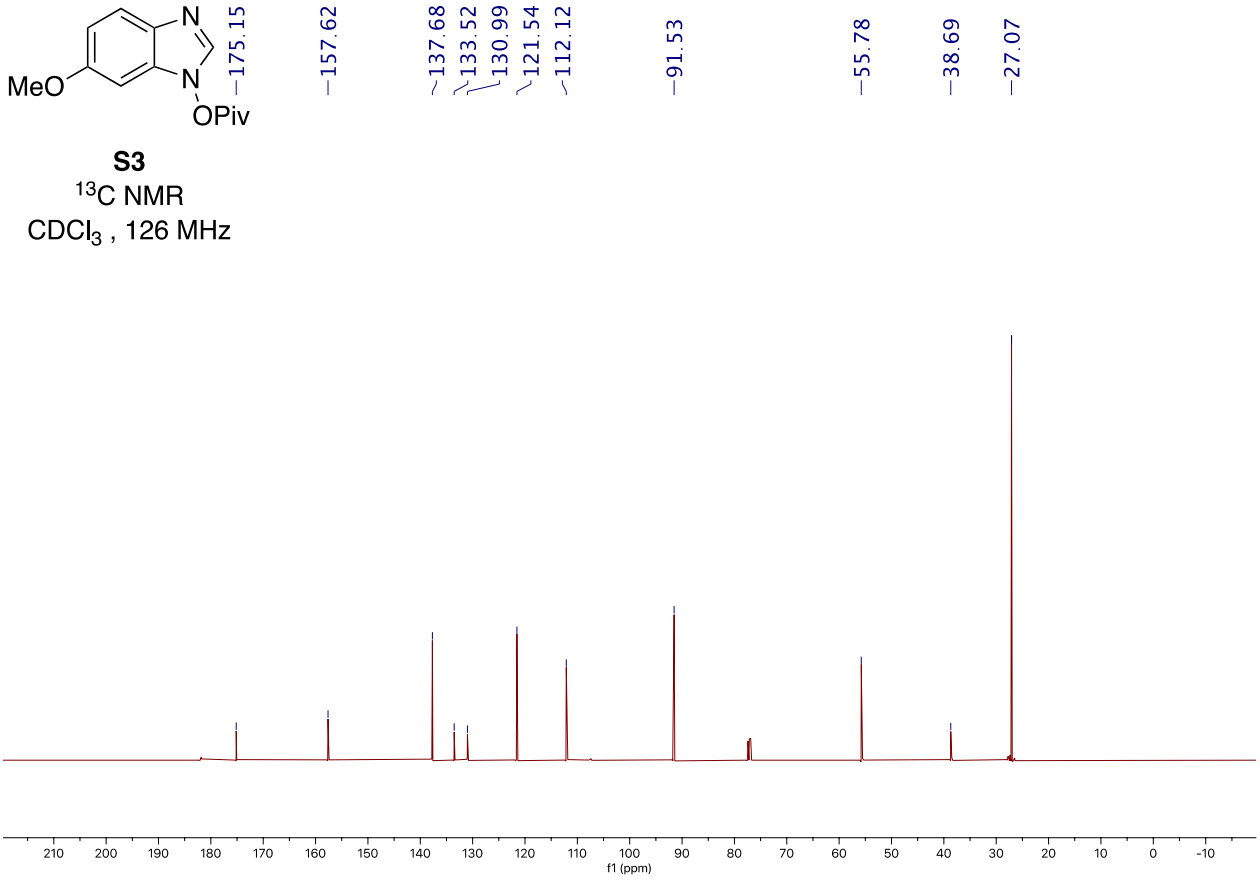
^{19}F NMR

$CDCl_3$, 471 MHz

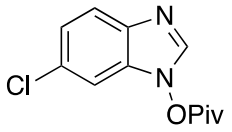

175.14
141.36
140.83
129.94
126.71
124.52
121.81
120.05
106.15
38.95
27.22
N
N
F3C
OPiv
S2
13C NMR
CDCl3 , 126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



S3
^{1}H NMR
$CDCl_3$, 500 MHz



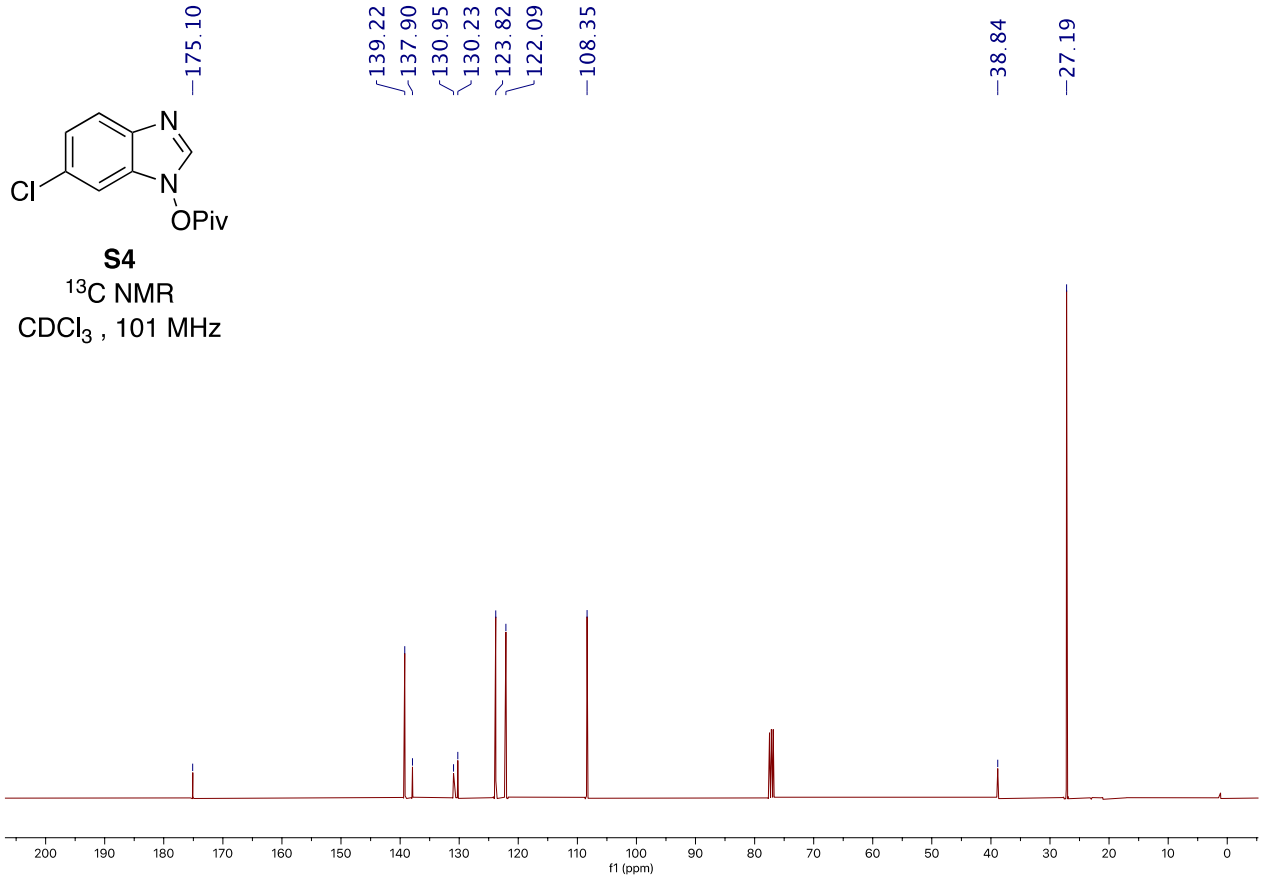
S3
^{13}C NMR
$CDCl_3$, 126 MHz



S4

^{1}H NMR

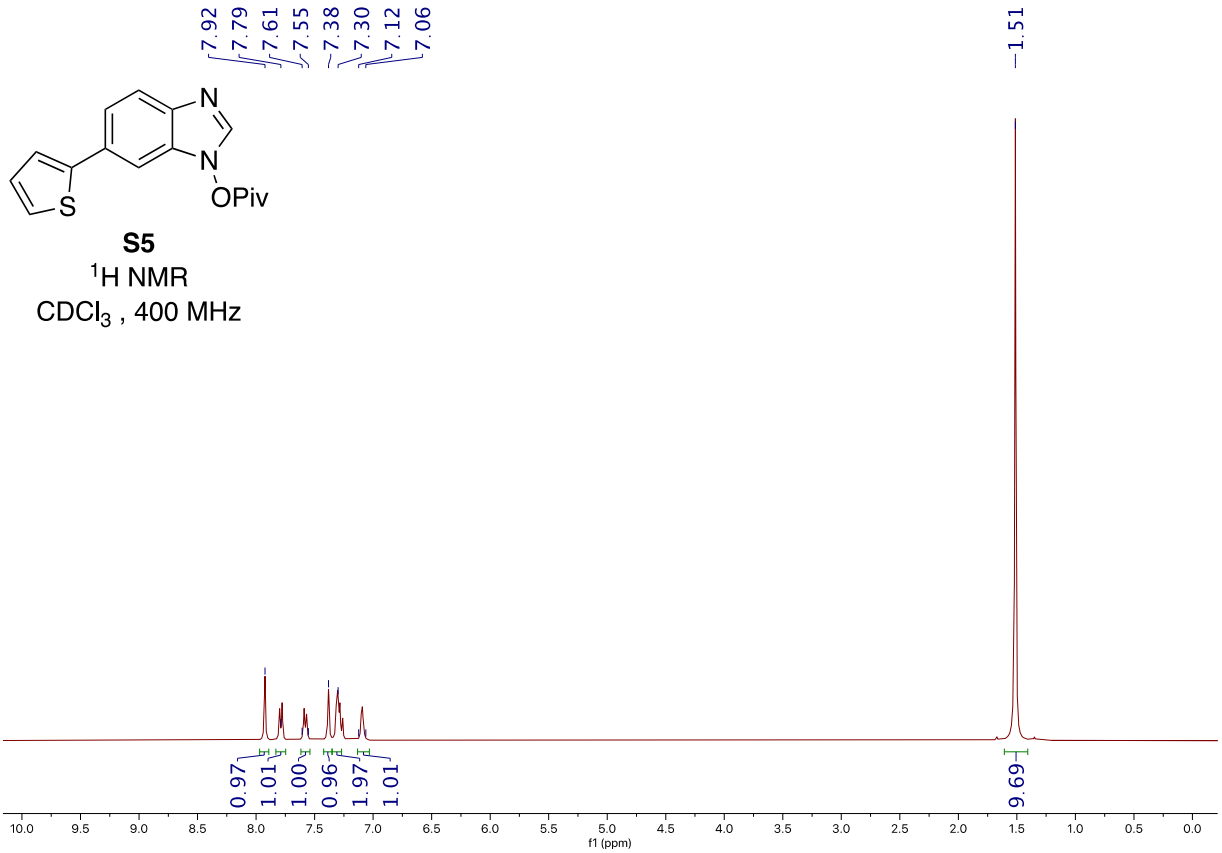
$CDCl_3$, 400 MHz



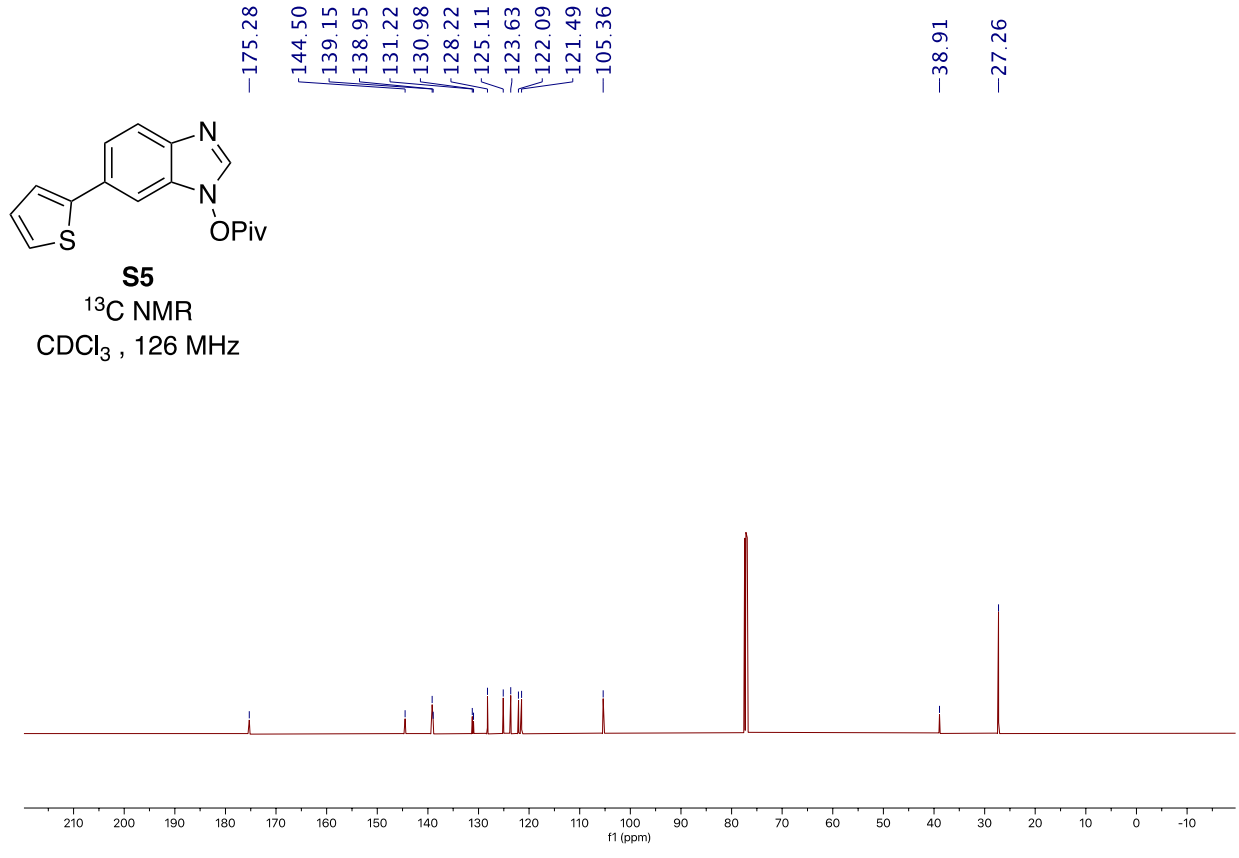
S4

^{13}C NMR

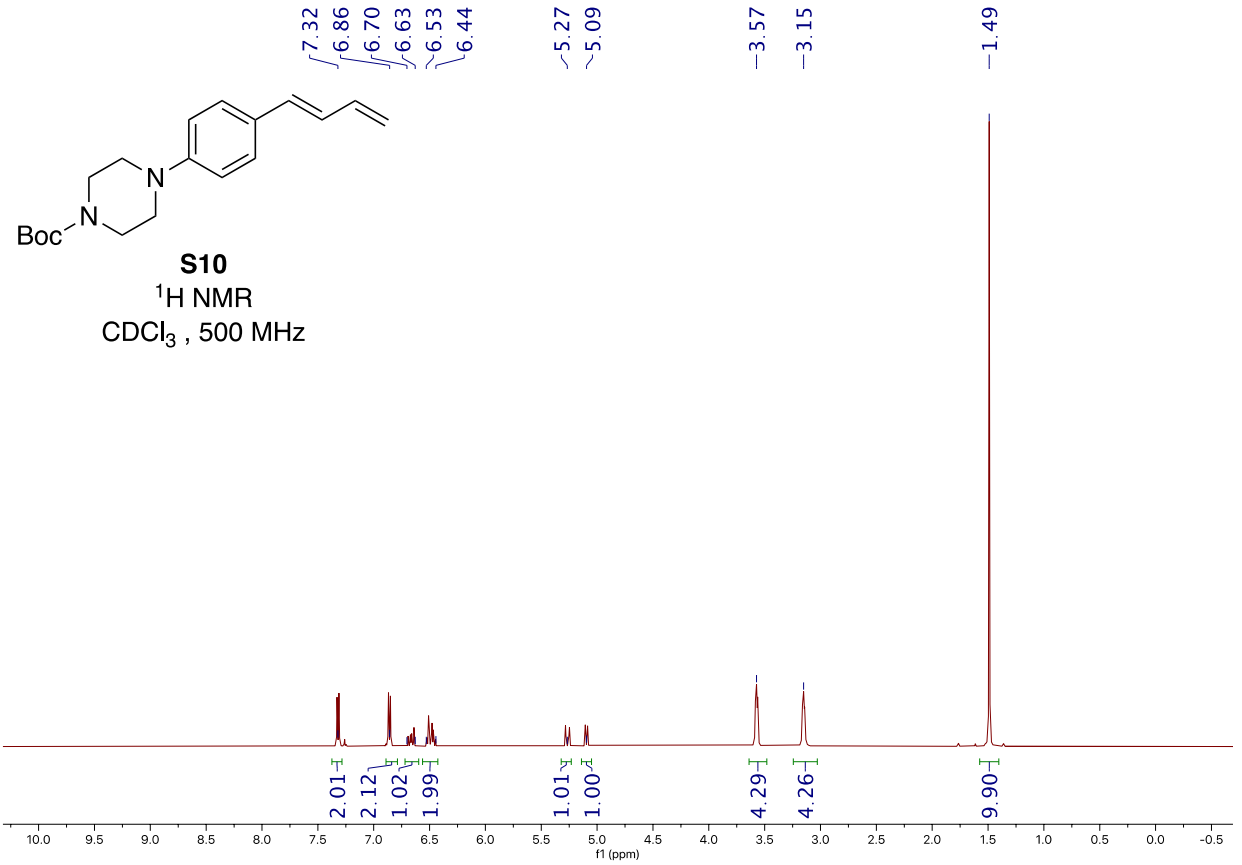
$CDCl_3$, 101 MHz



S5
^{1}H NMR
$CDCl_3$, 400 MHz



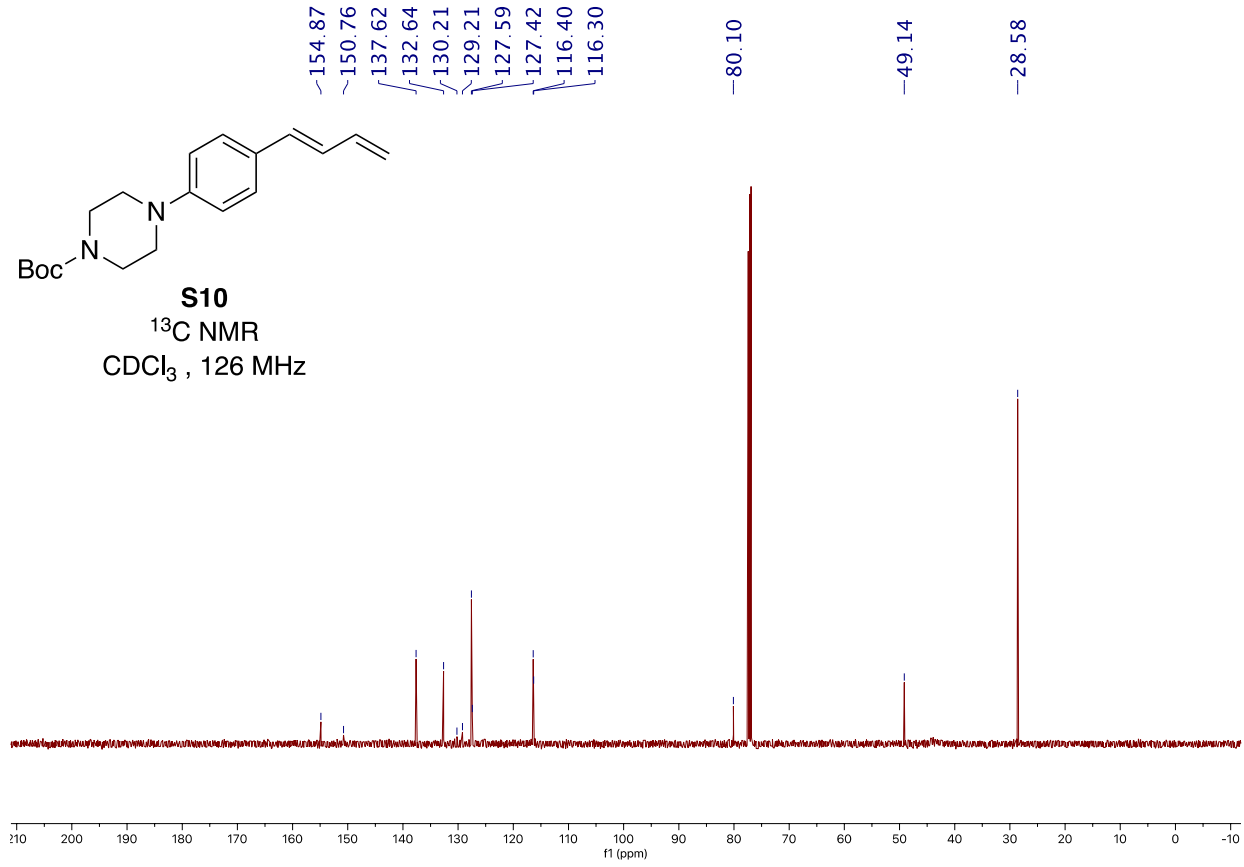
S5
^{13}C NMR
$CDCl_3$, 126 MHz



S10

^{1}H NMR

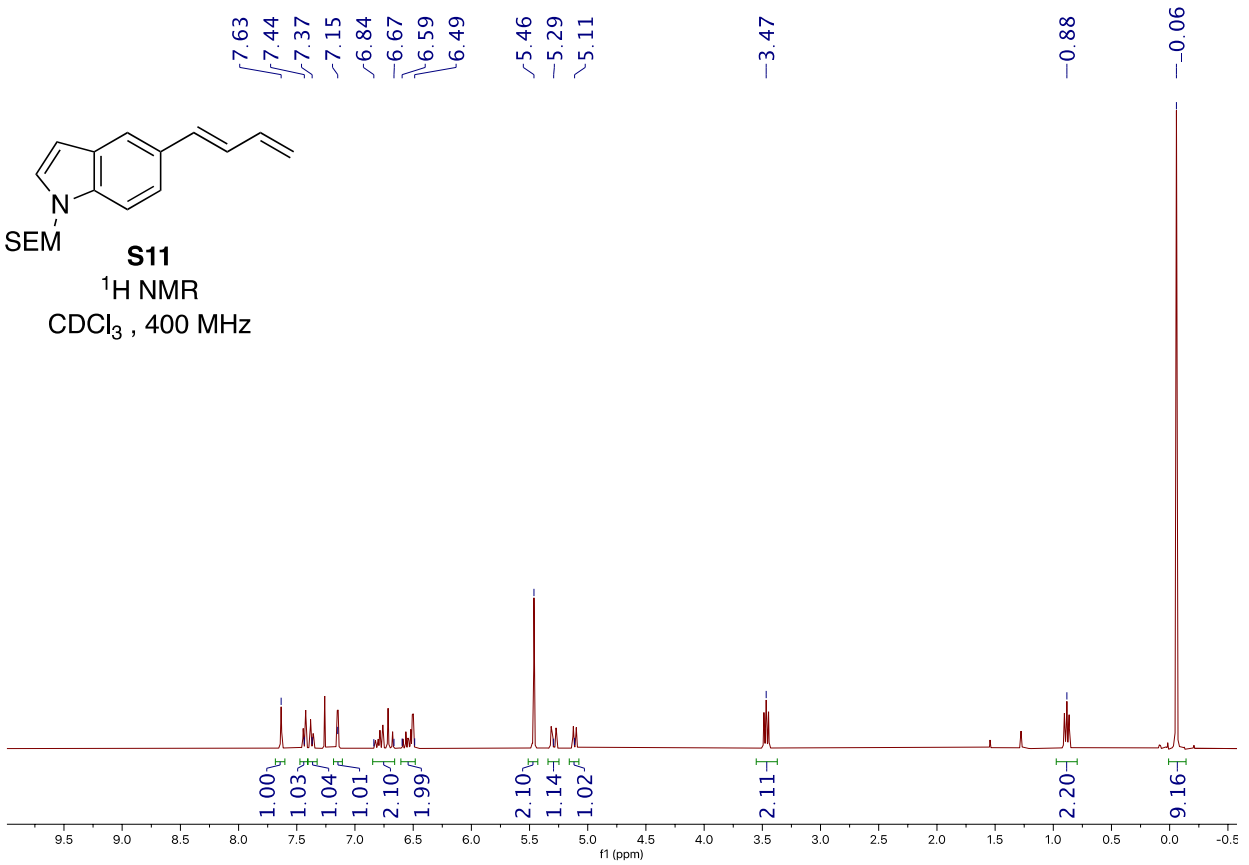
$CDCl_3$, 500 MHz

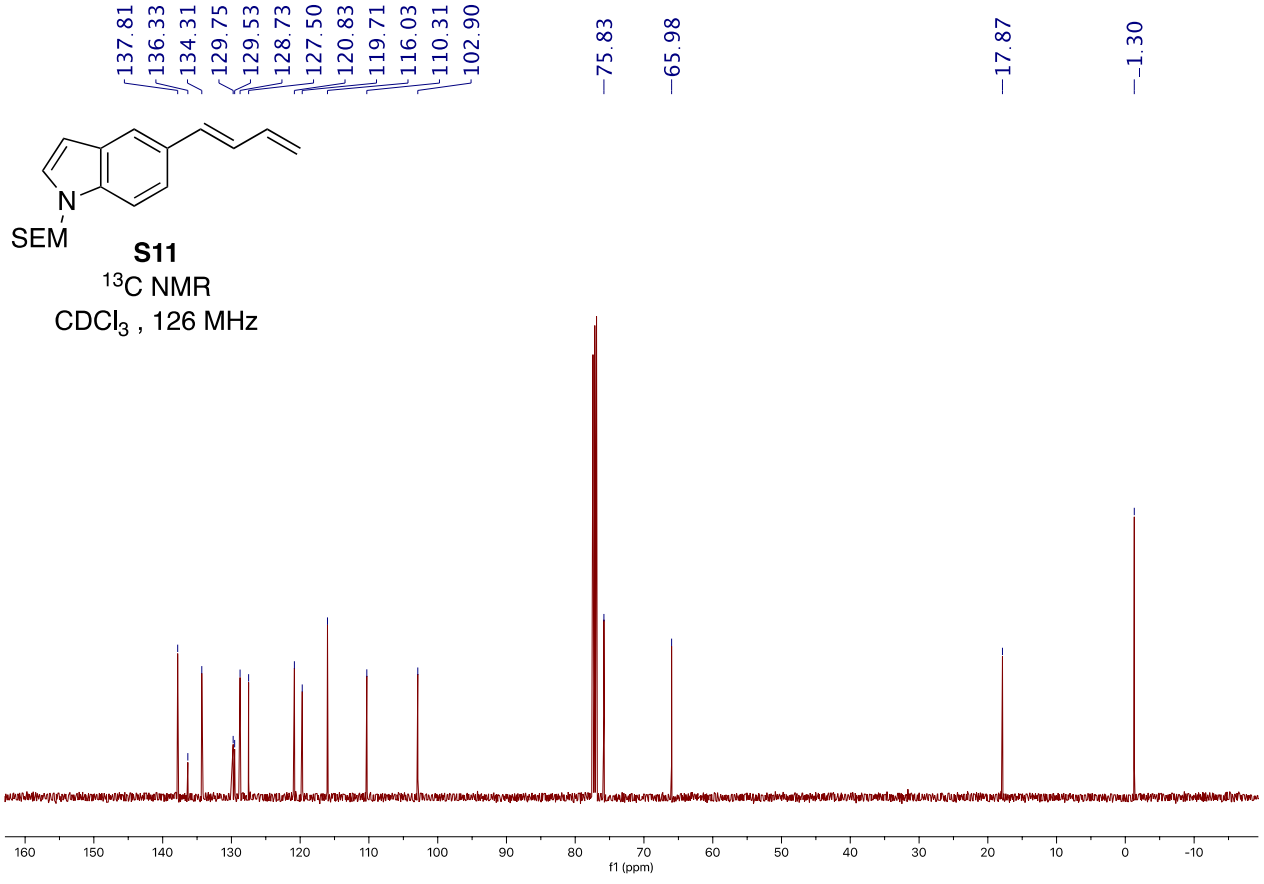


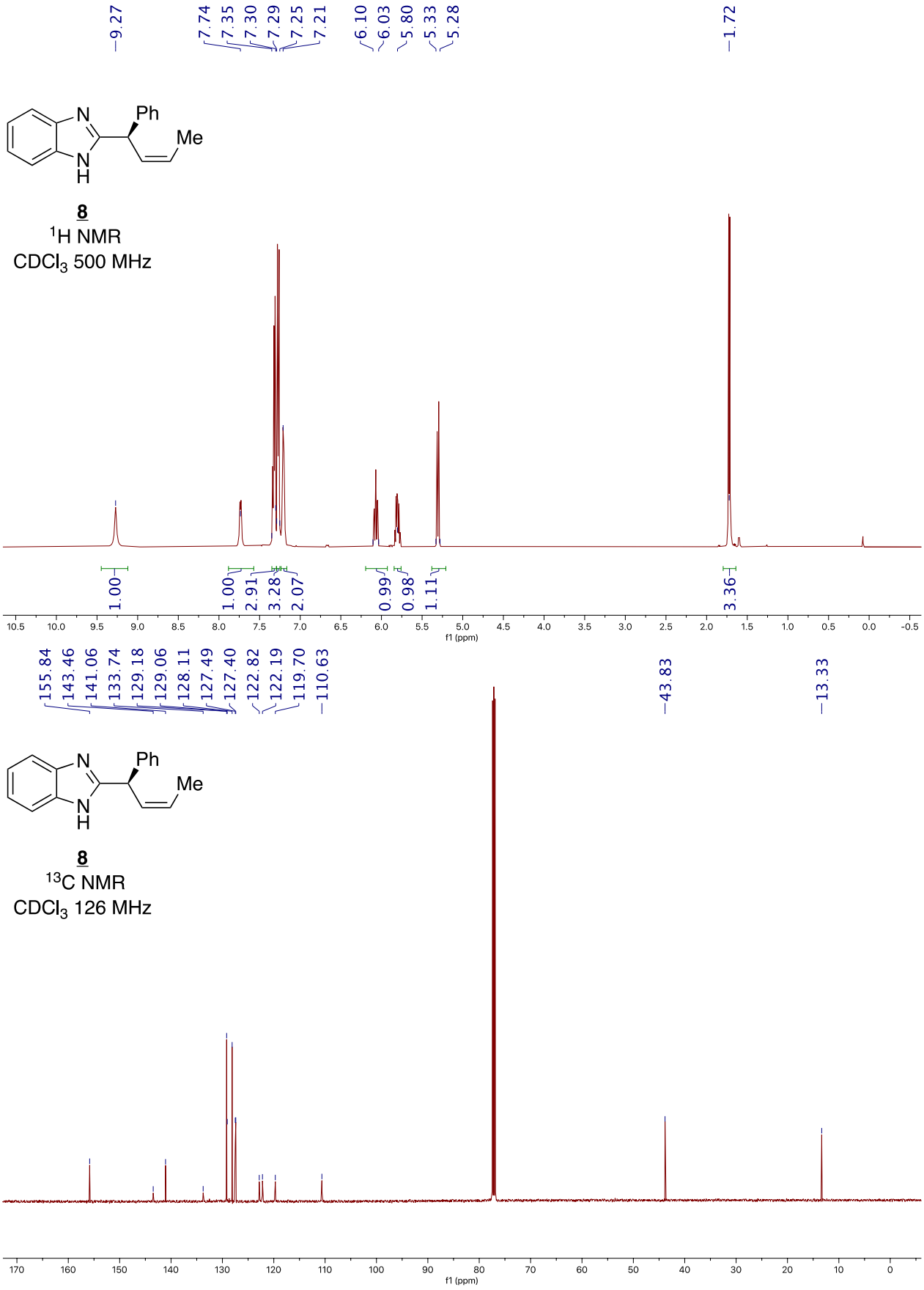
S10

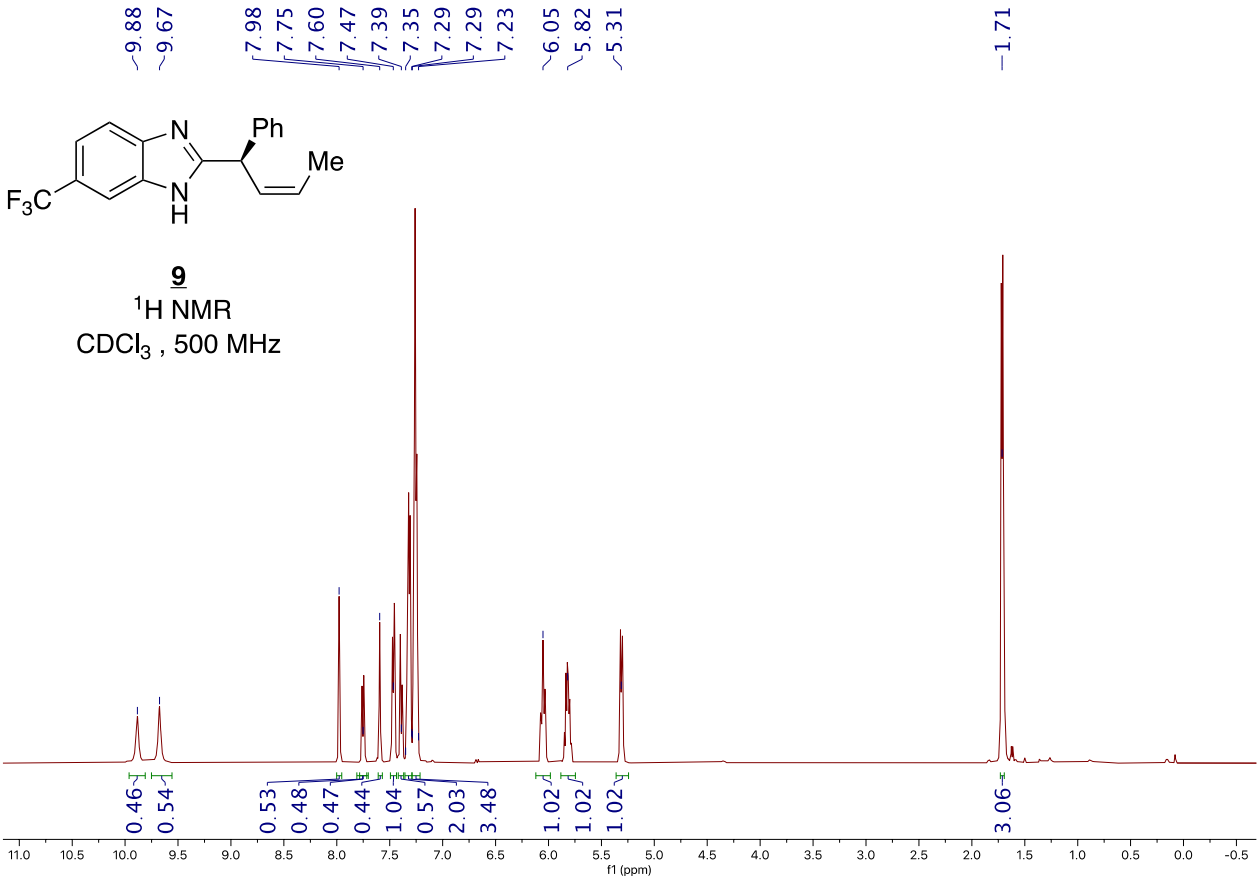
^{13}C NMR

$CDCl_3$, 126 MHz


7.63
7.44
7.37
7.15
6.84
6.67
6.59
6.49
5.46
5.29
5.11
3.47
0.88
0.06
N
SEM
S11
1H NMR
CDCl3 , 400 MHz
1.00
1.03
1.04
1.01
2.10
1.99
2.10
1.14
1.02
2.11
2.20
9.16
f1 (ppm)


137.81
136.33
134.31
129.75
129.53
128.73
127.50
120.83
119.71
116.03
110.31
102.90
75.83
65.98
17.87
1.30
N
SEM
S11
13C NMR
CDCl3 , 126 MHz
f1 (ppm)

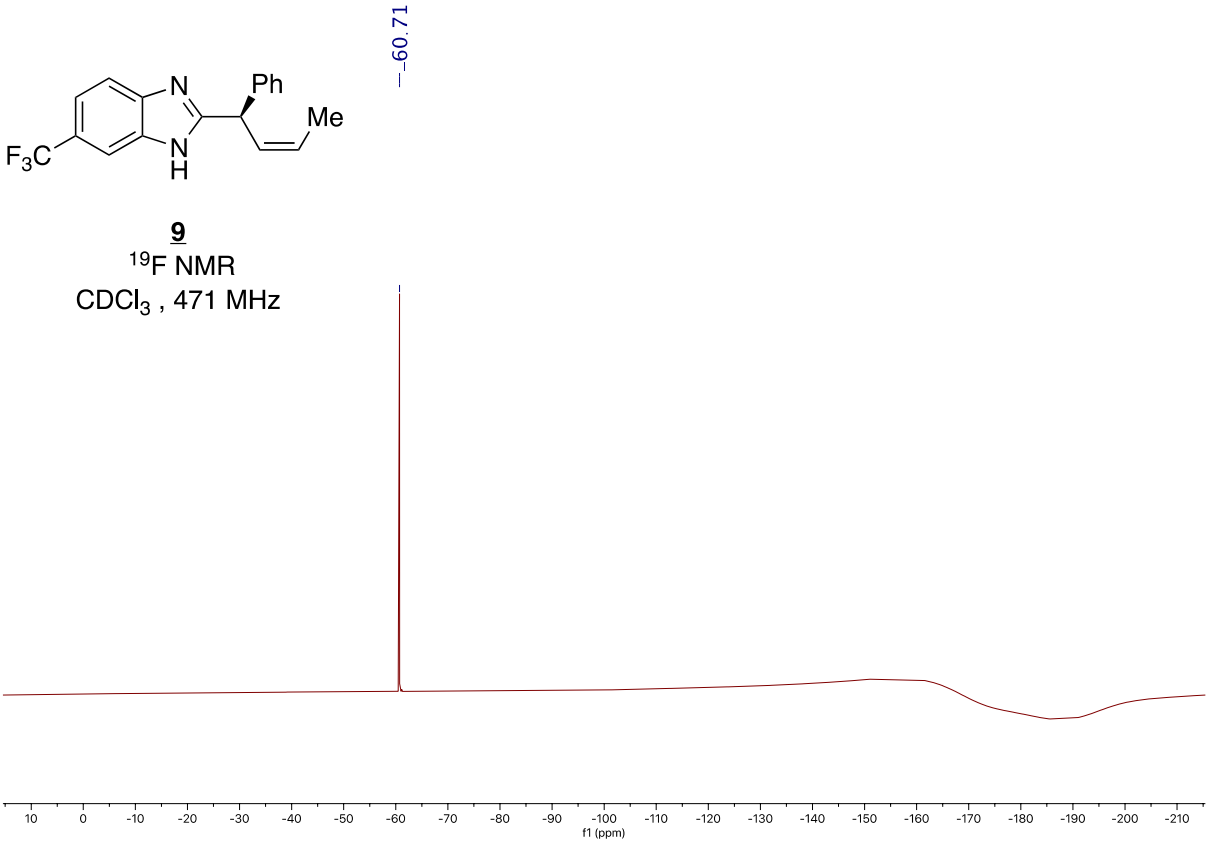

9.27
7.74
7.35
7.30
7.29
7.25
7.21
6.10
6.03
5.80
5.33
5.28
1.72
Ph
Me
N
N
H
8
1H NMR
CDCl3 500 MHz
1.00
1.00
2.91
3.28
2.07
0.99
0.98
1.11
3.36
f1 (ppm)
155.84
143.46
141.06
133.74
129.18
129.06
128.11
127.49
127.40
122.82
122.19
119.70
110.63
43.83
13.33
8
13C NMR
CDCl3 126 MHz
f1 (ppm)



9

^{1}H NMR

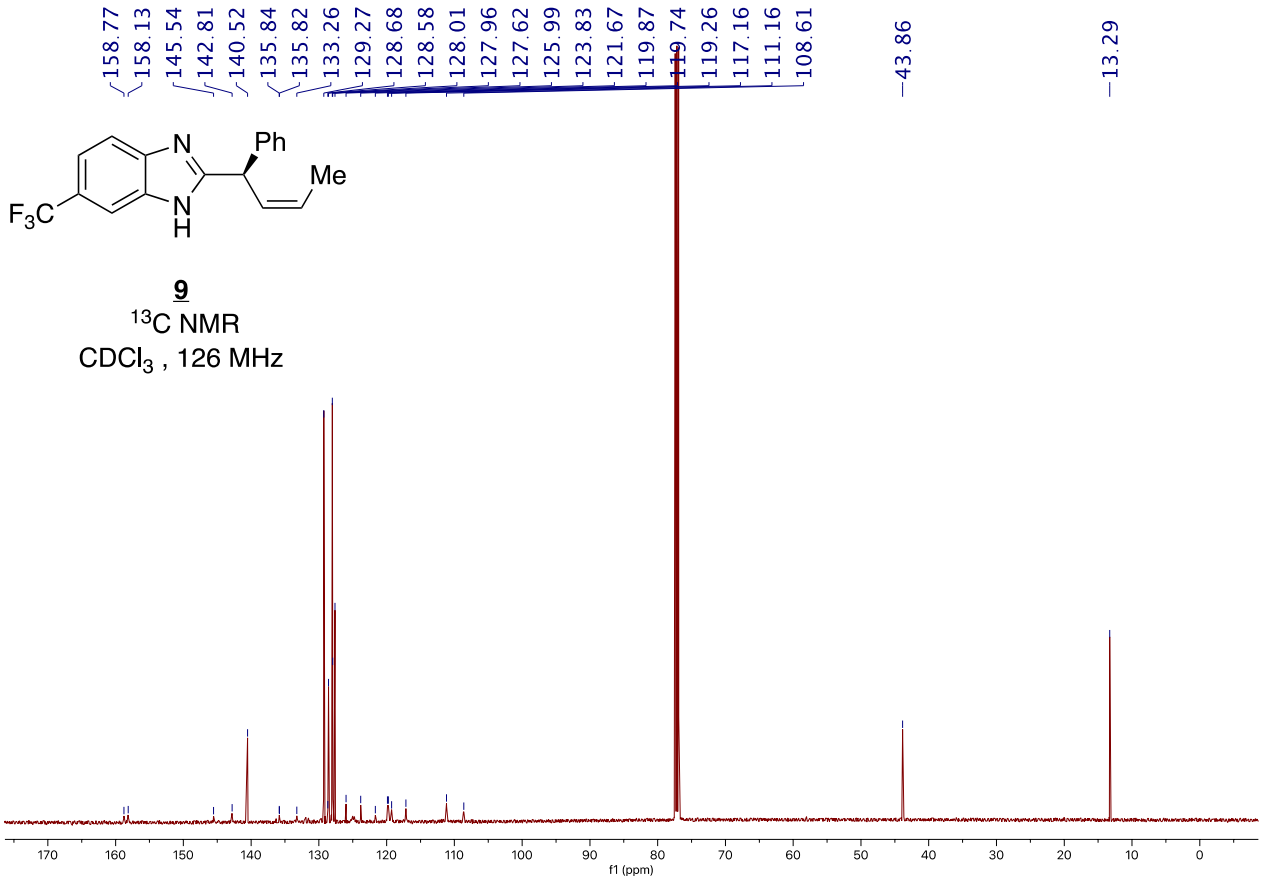
$CDCl_3$, 500 MHz

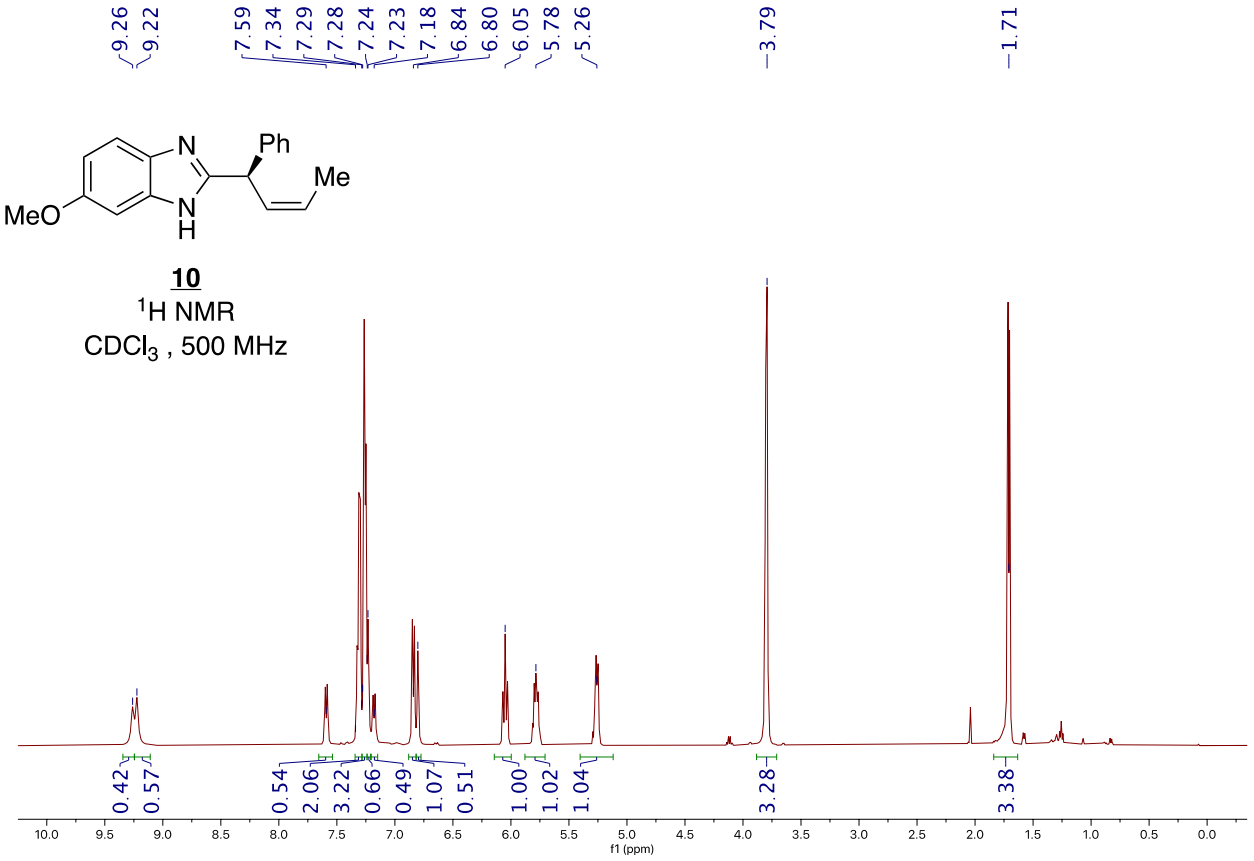


9

^{19}F NMR

$CDCl_3$, 471 MHz

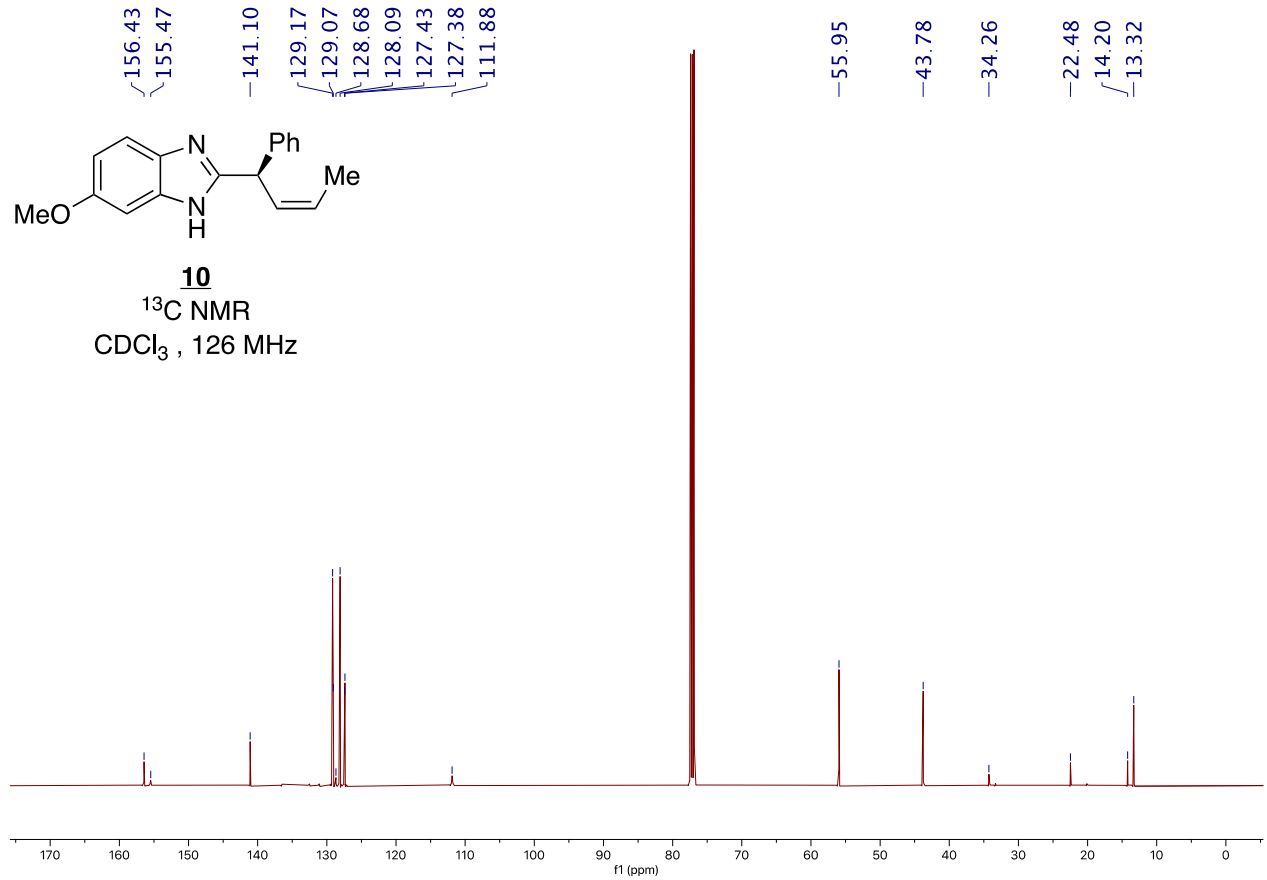

158.77
158.13
145.54
142.81
140.52
135.84
135.82
133.26
129.27
128.68
128.58
128.01
127.96
127.62
125.99
123.83
121.67
119.87
119.74
119.26
117.16
111.16
108.61
43.86
13.29
N
Ph
Me
F3C
N
H
9
13C NMR
CDCl3 , 126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



10

^{1}H NMR

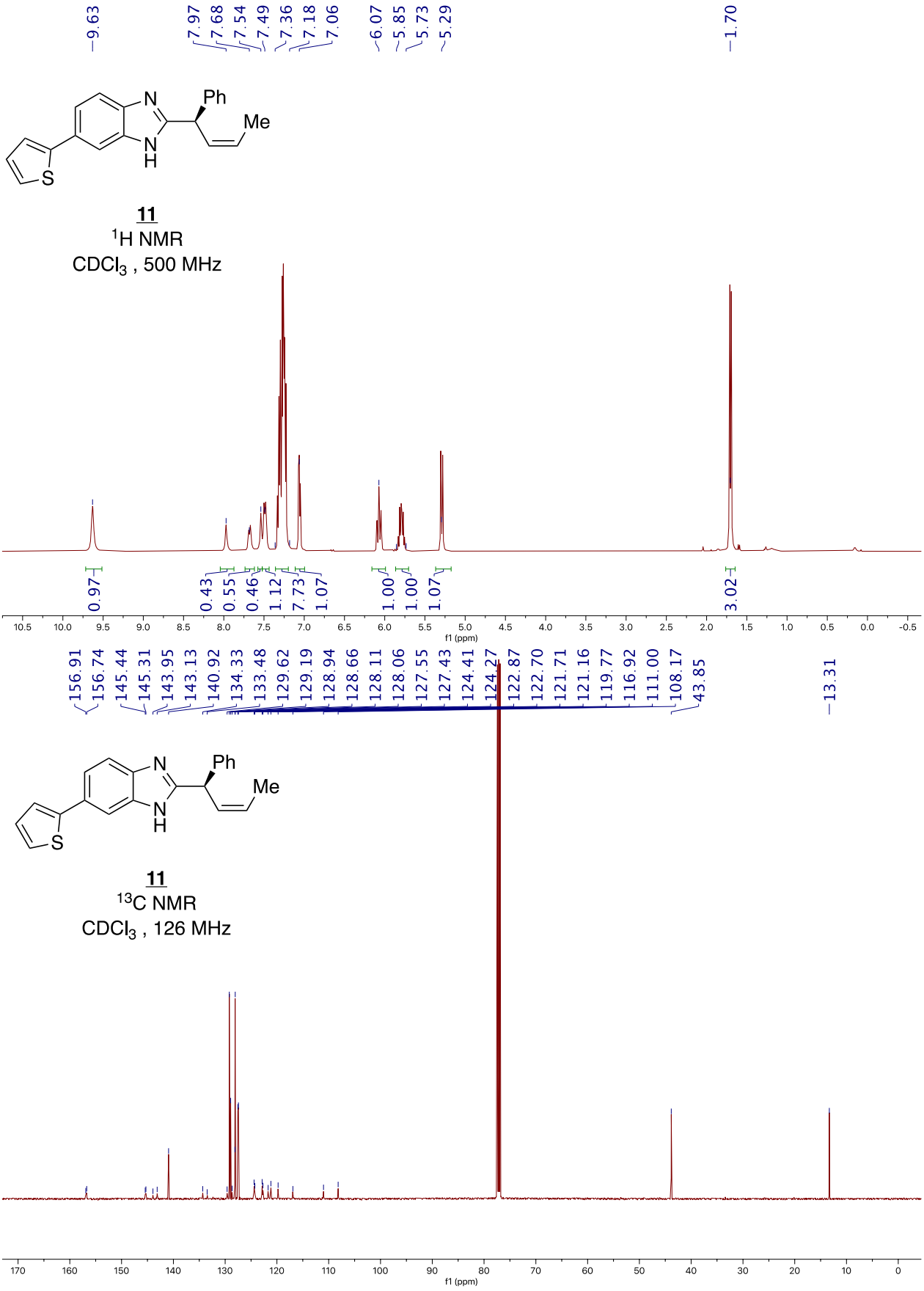
$CDCl_3$, 500 MHz

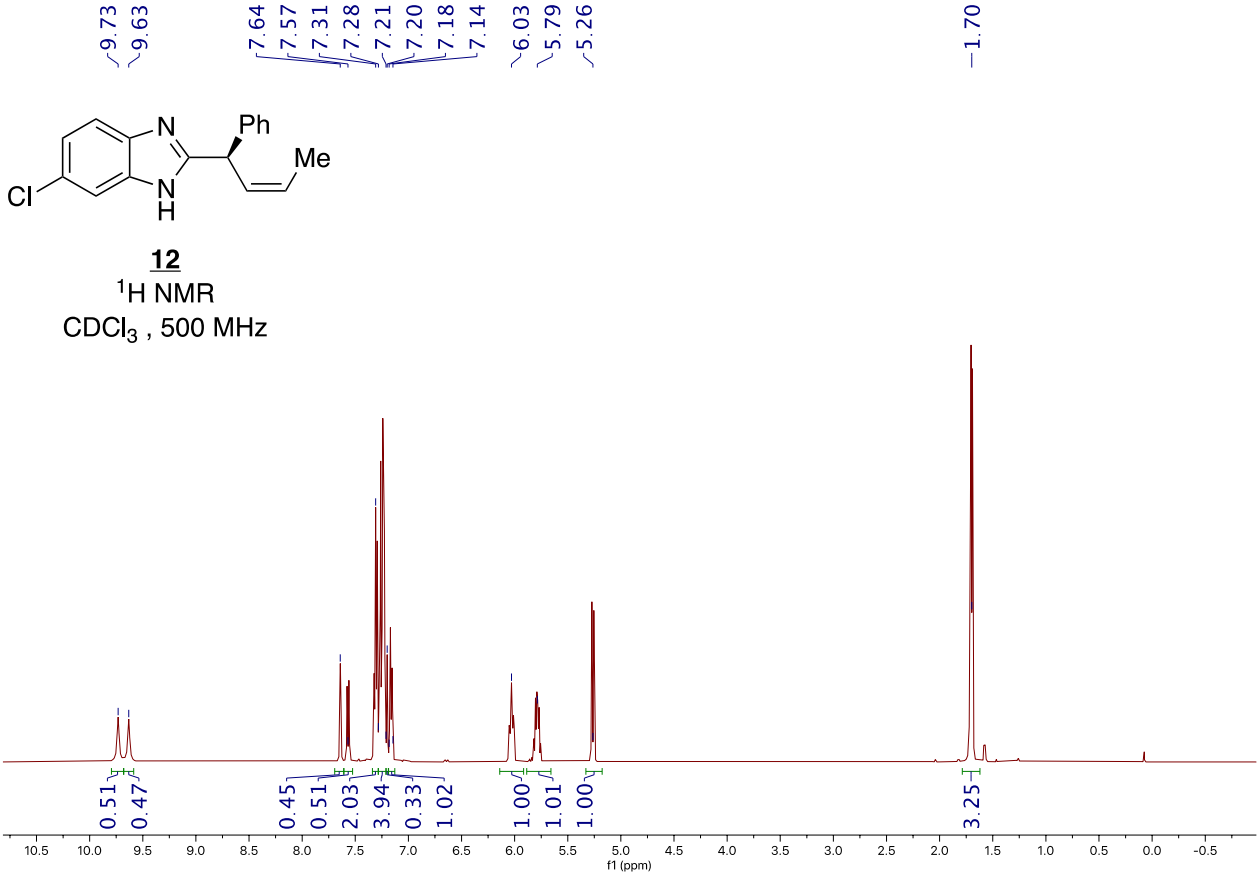


10

^{13}C NMR

$CDCl_3$, 126 MHz

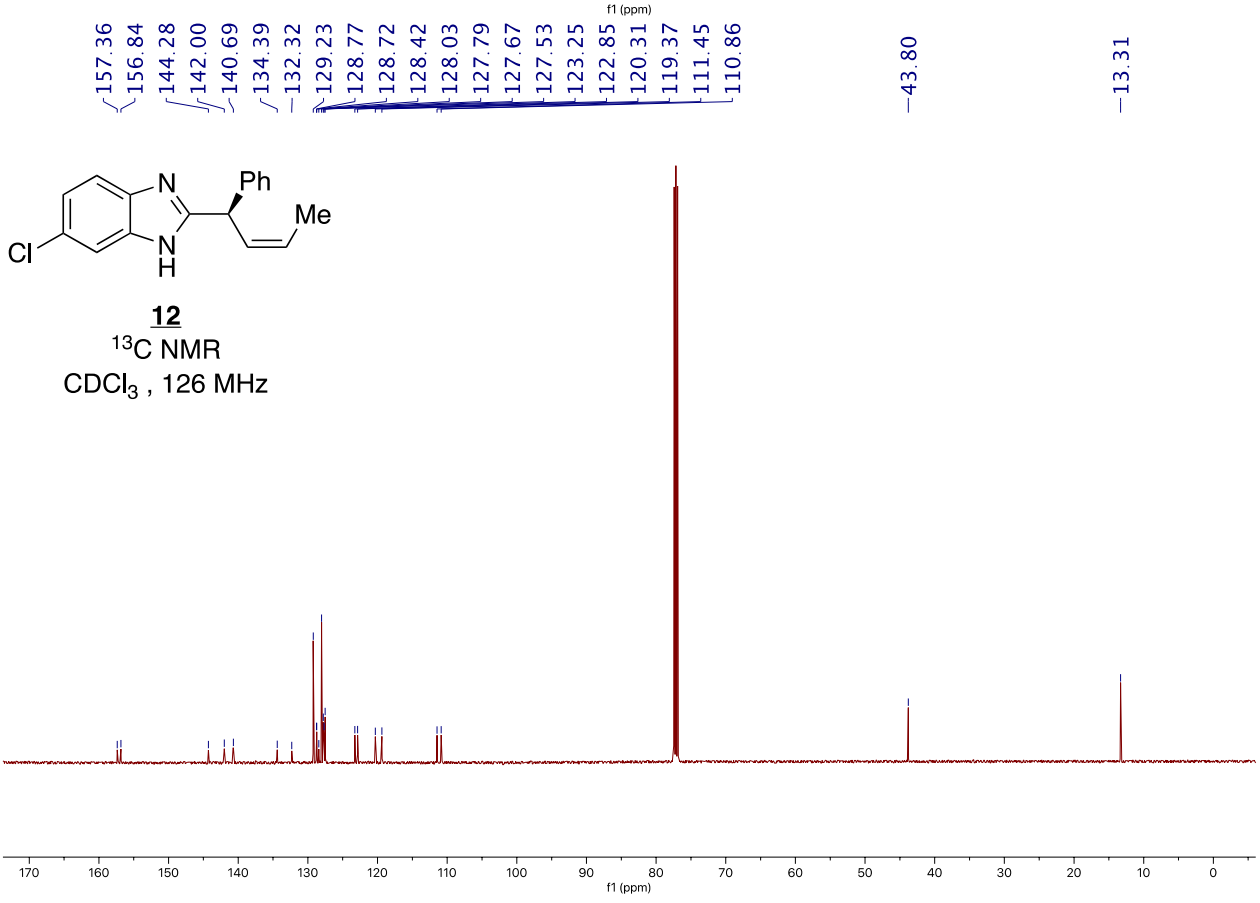

9.63
7.97
7.68
7.54
7.49
7.36
7.18
7.06
6.07
5.85
5.73
5.29
1.70
Ph
Me
N
N
H
S
11
1H NMR
CDCl3 , 500 MHz
0.97
0.43
0.55
0.46
1.12
7.73
1.07
1.00
1.00
1.07
3.02
f1 (ppm)
156.91
156.74
145.44
145.31
143.95
143.13
140.92
134.33
133.48
129.62
129.19
128.94
128.66
128.11
128.06
127.55
127.43
124.41
124.27
122.87
122.70
121.71
121.16
119.77
116.92
111.00
108.17
43.85
13.31
11
13C NMR
CDCl3 , 126 MHz
f1 (ppm)



12

^{1}H NMR

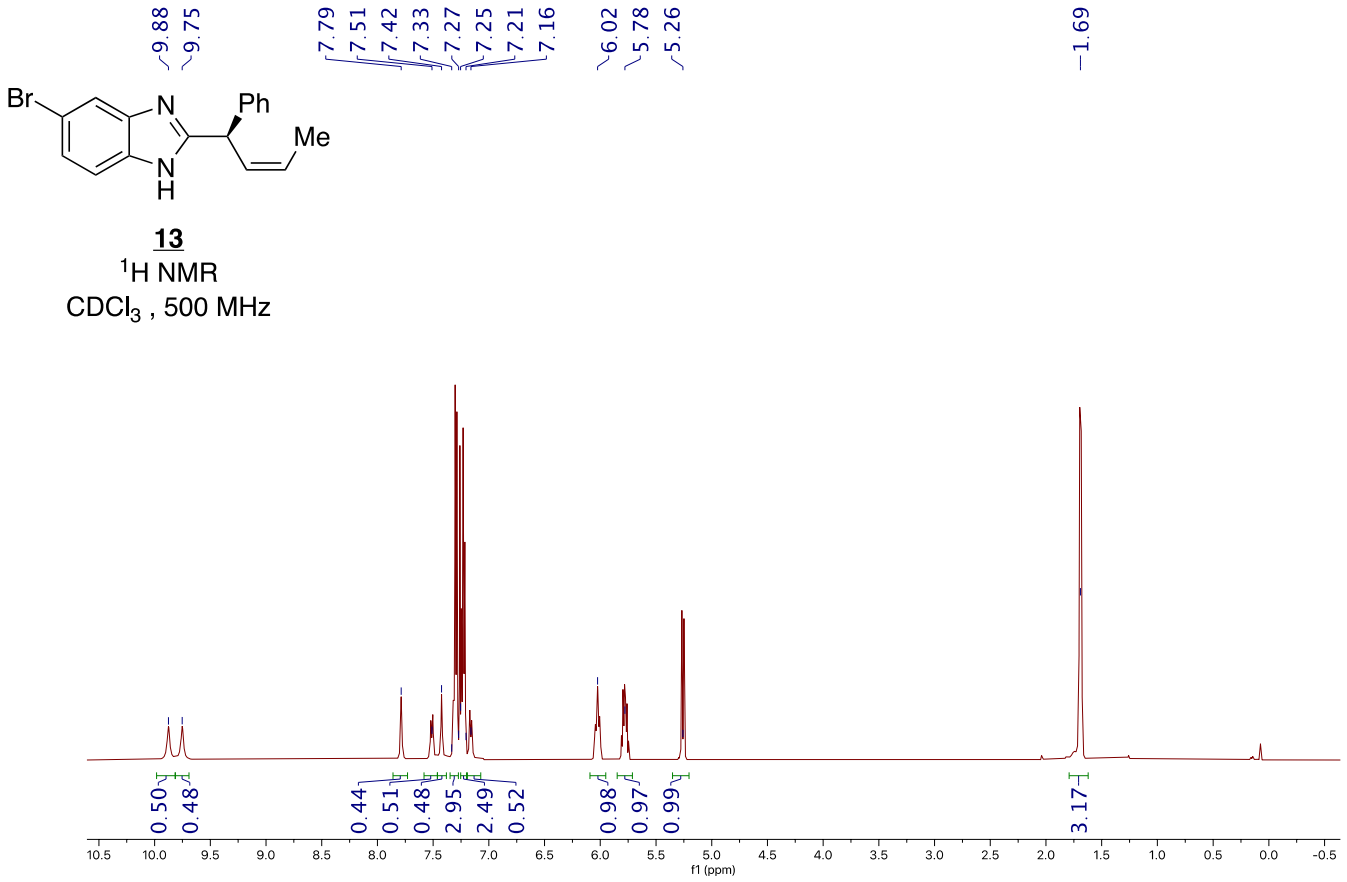
$CDCl_3$, 500 MHz



12

^{13}C NMR

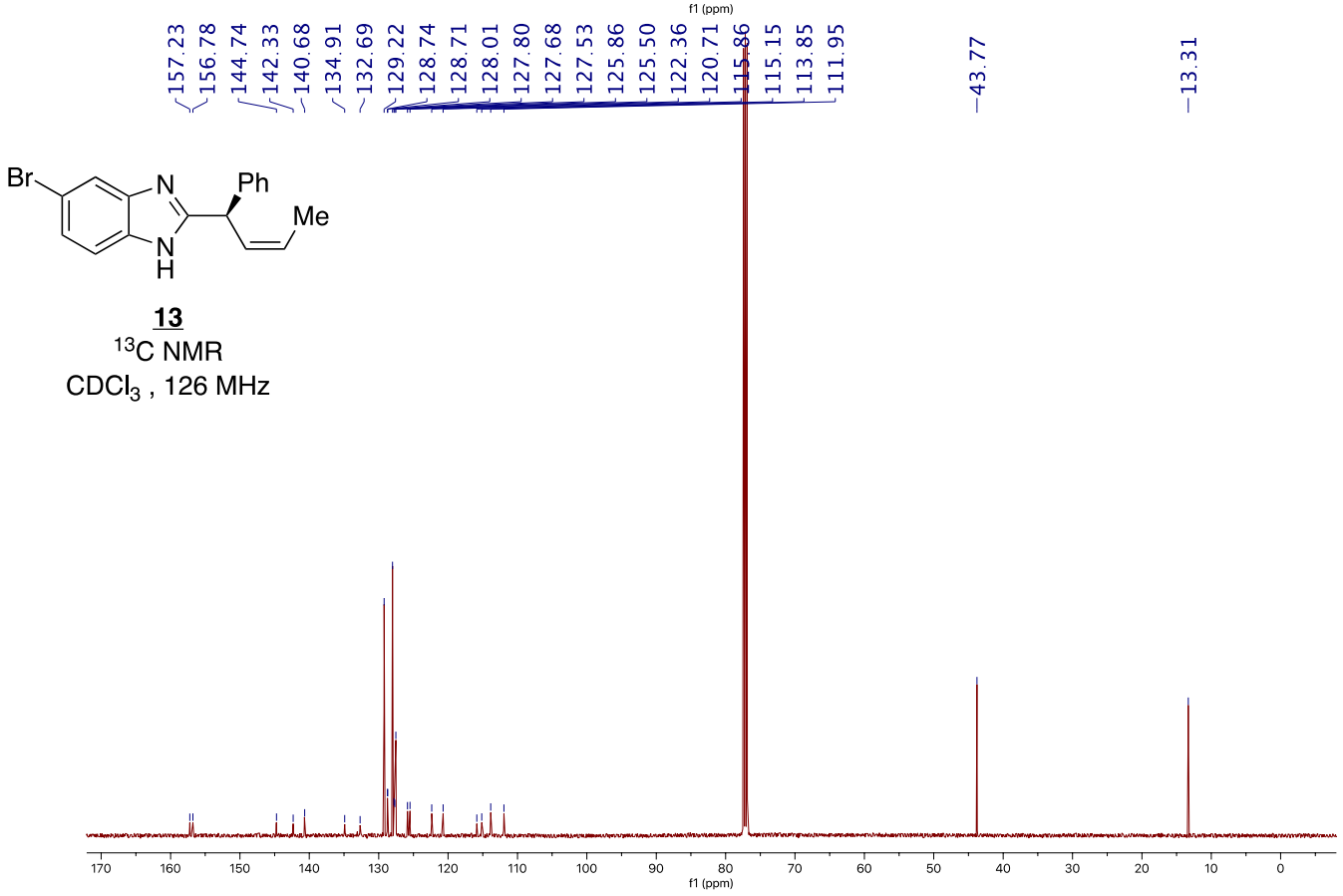
$CDCl_3$, 126 MHz



13

^{1}H NMR

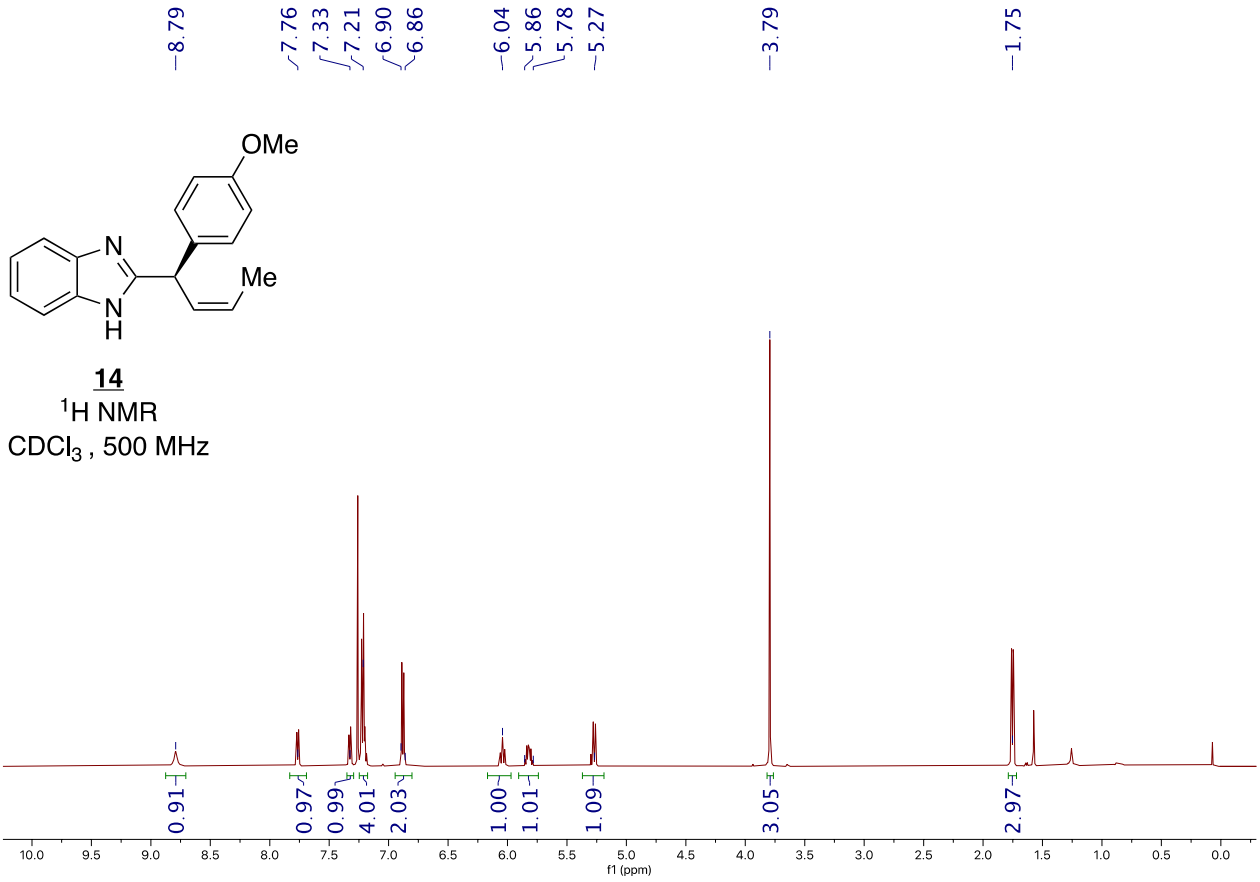
$CDCl_3$, 500 MHz



13

^{13}C NMR

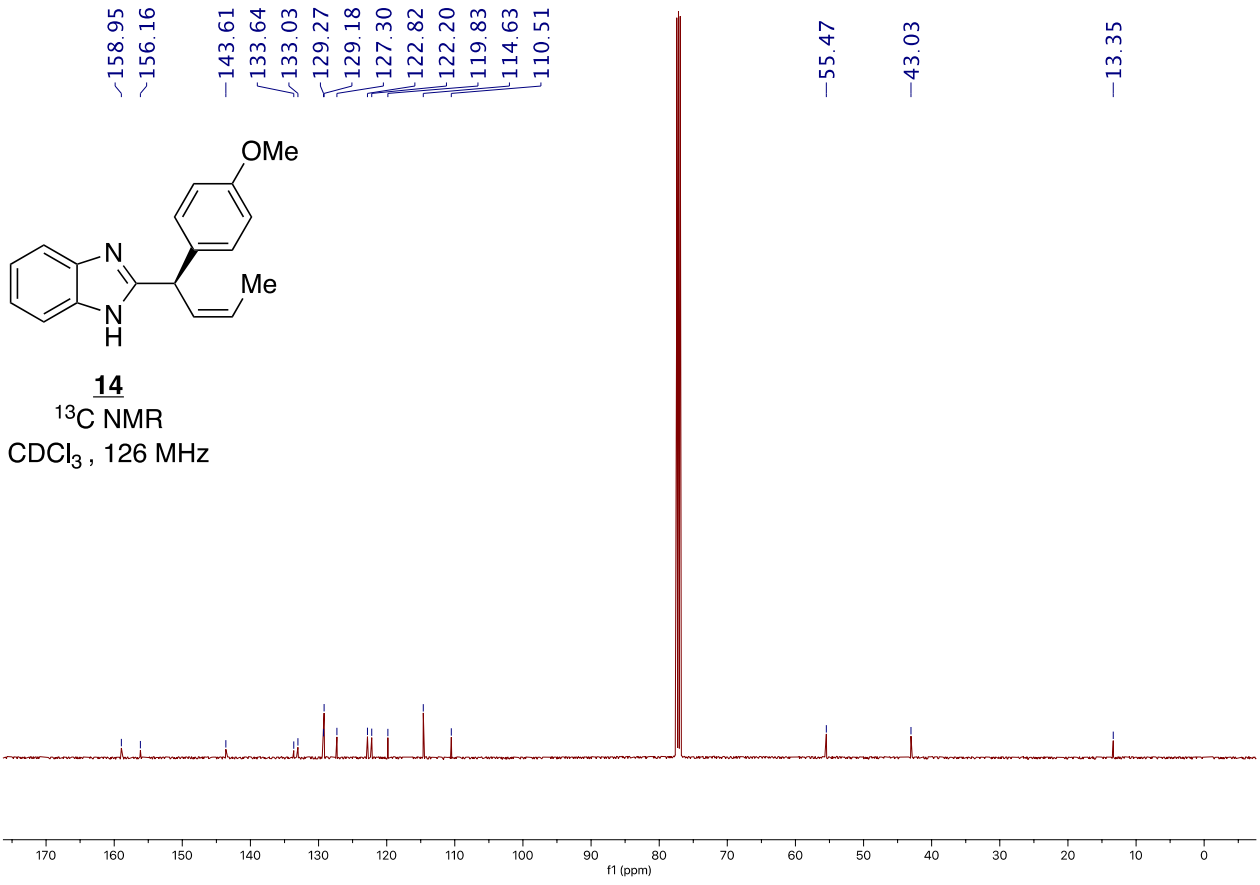
$CDCl_3$, 126 MHz



14

^{1}H NMR

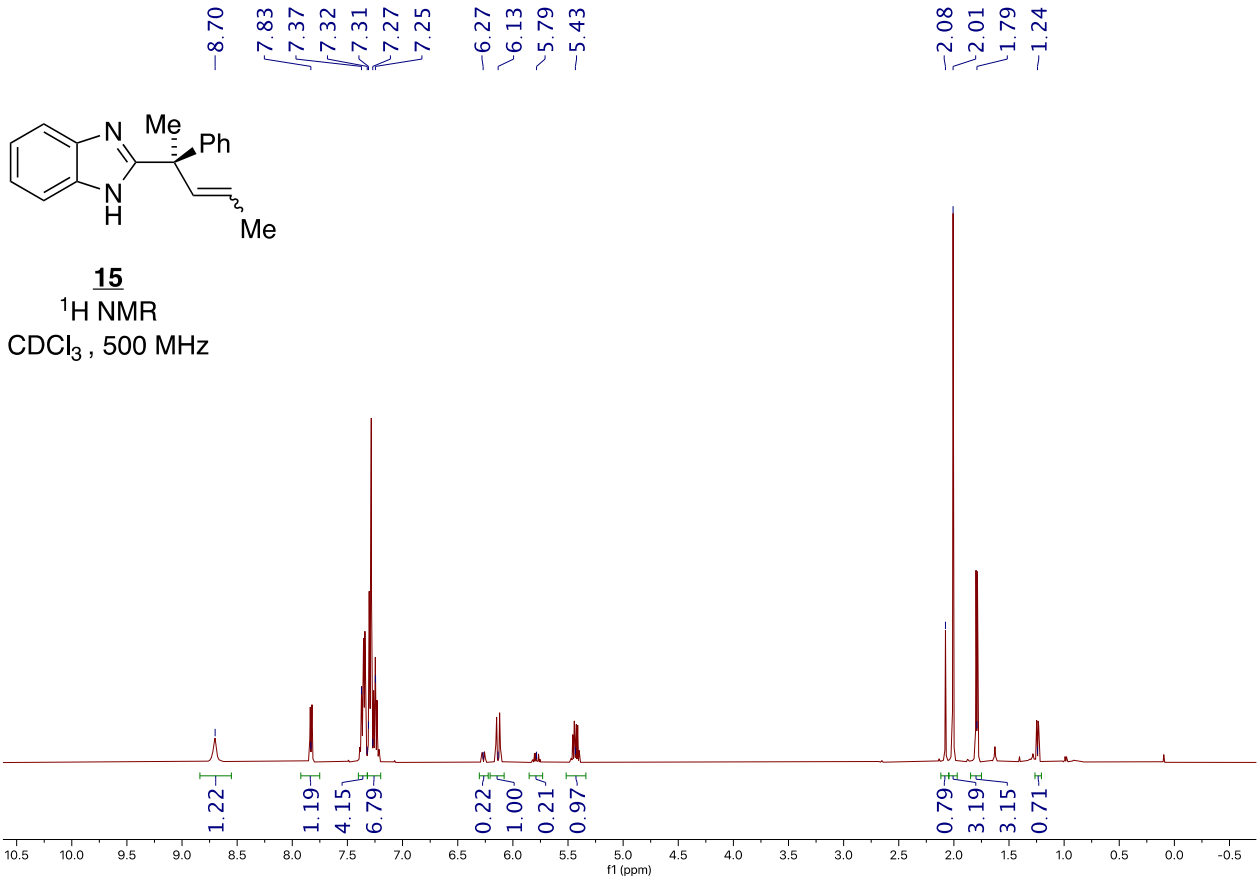
$CDCl_3$, 500 MHz



14

^{13}C NMR

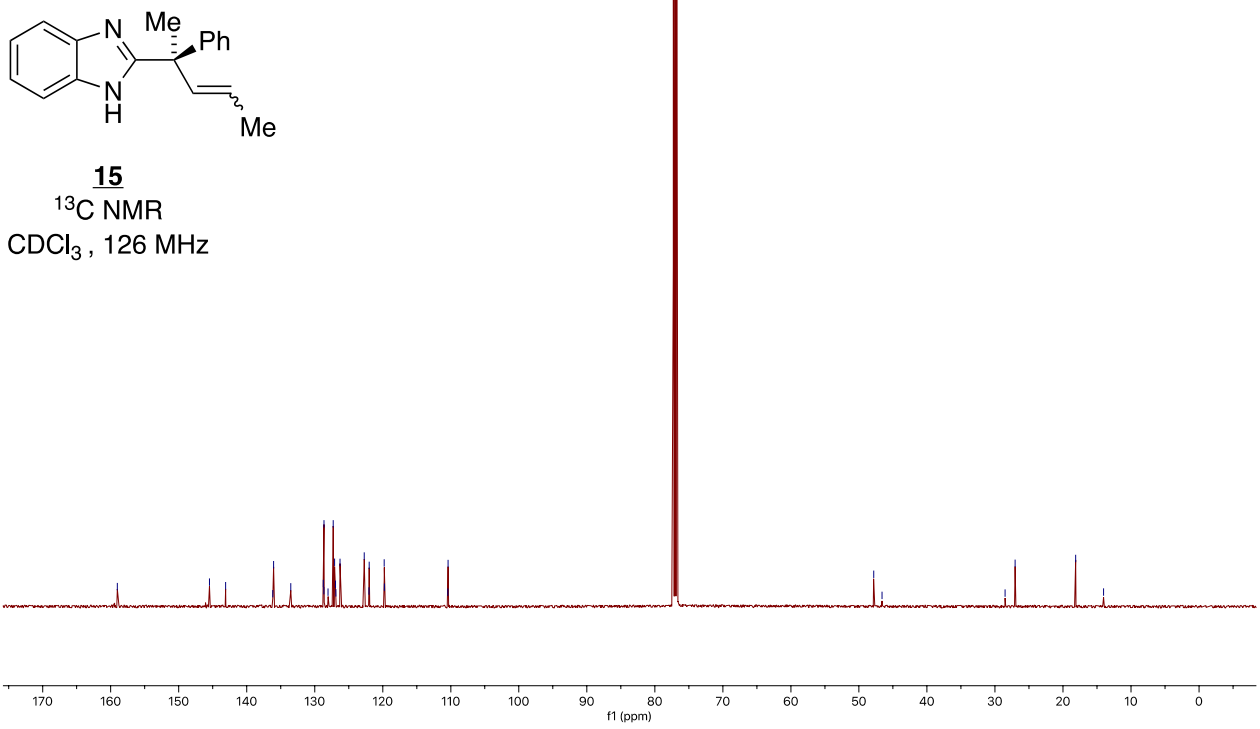
$CDCl_3$, 126 MHz



15

^{1}H NMR

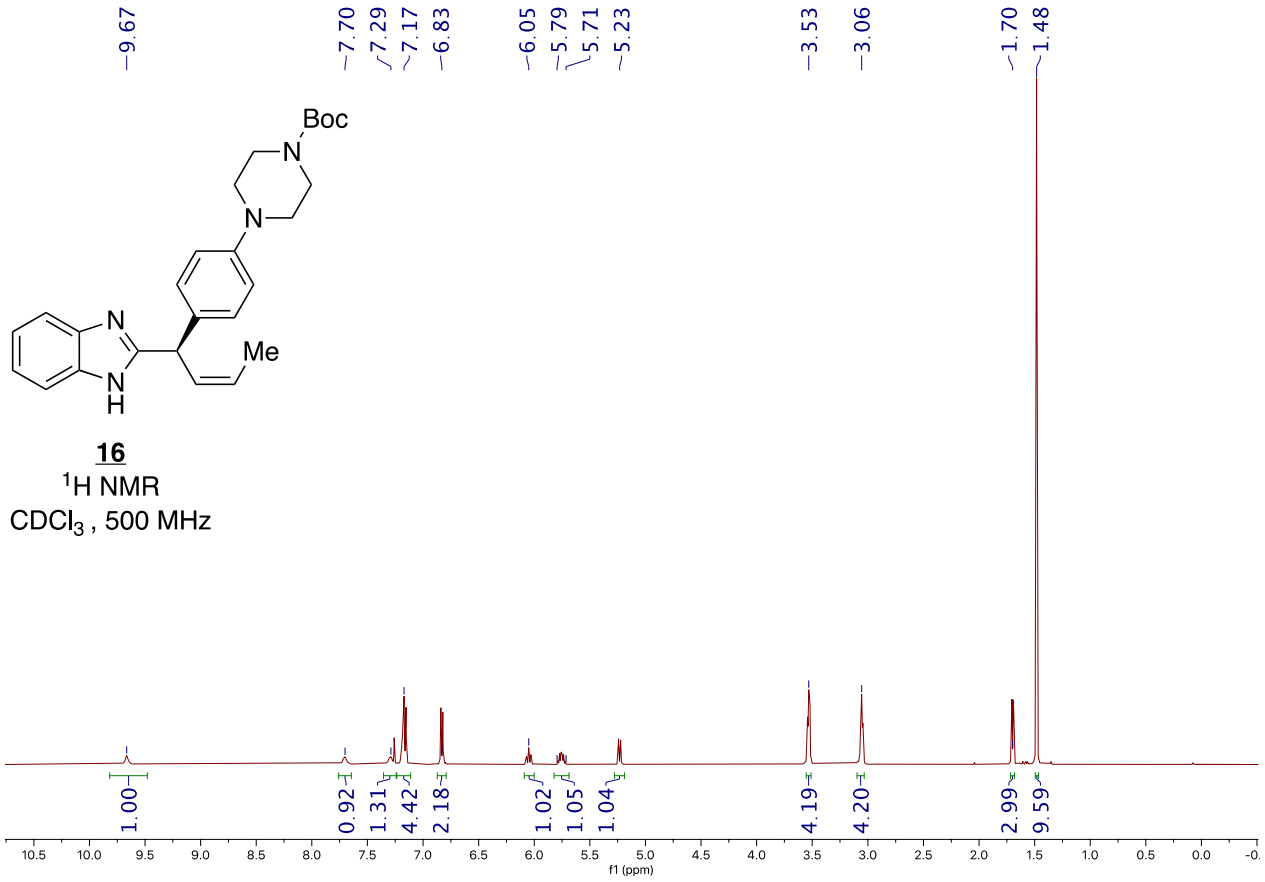
$CDCl_3$, 500 MHz



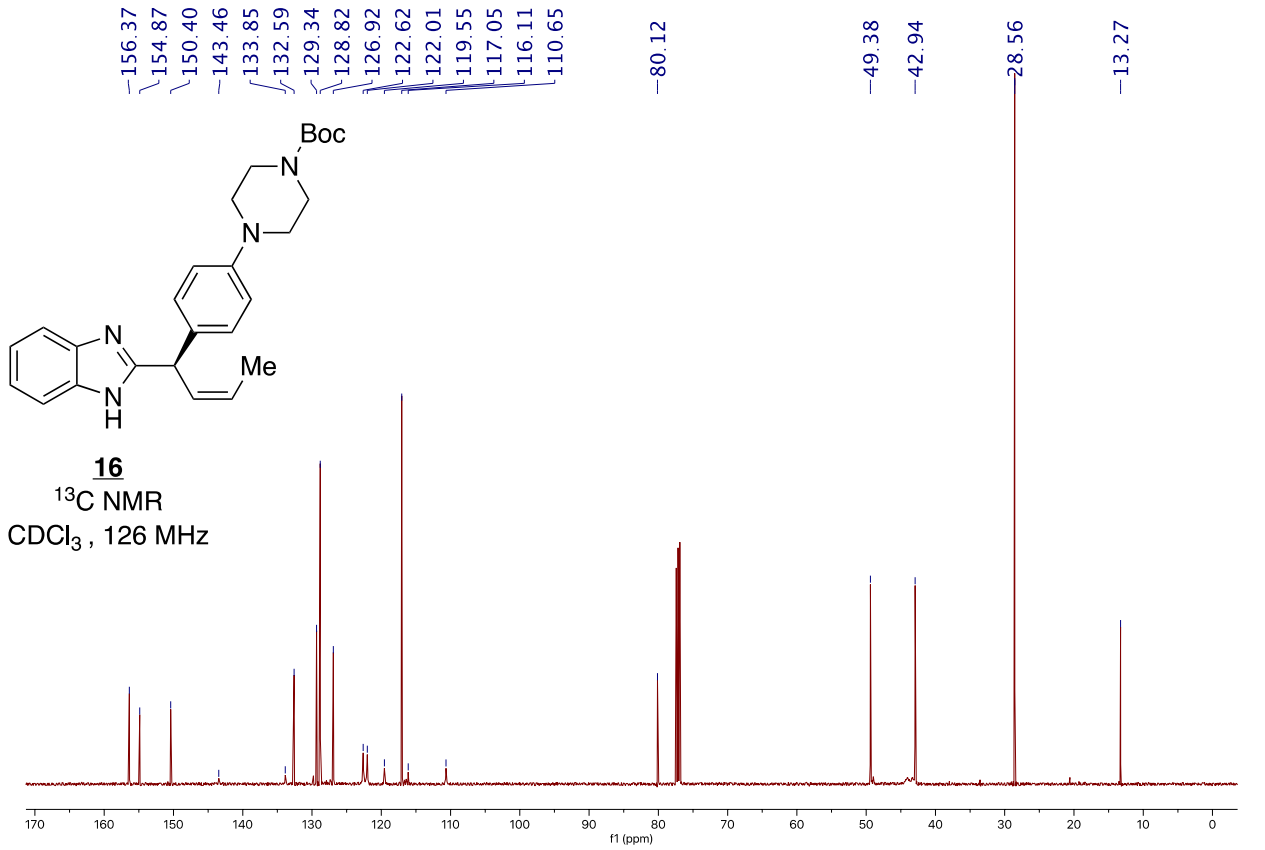
15

^{13}C NMR

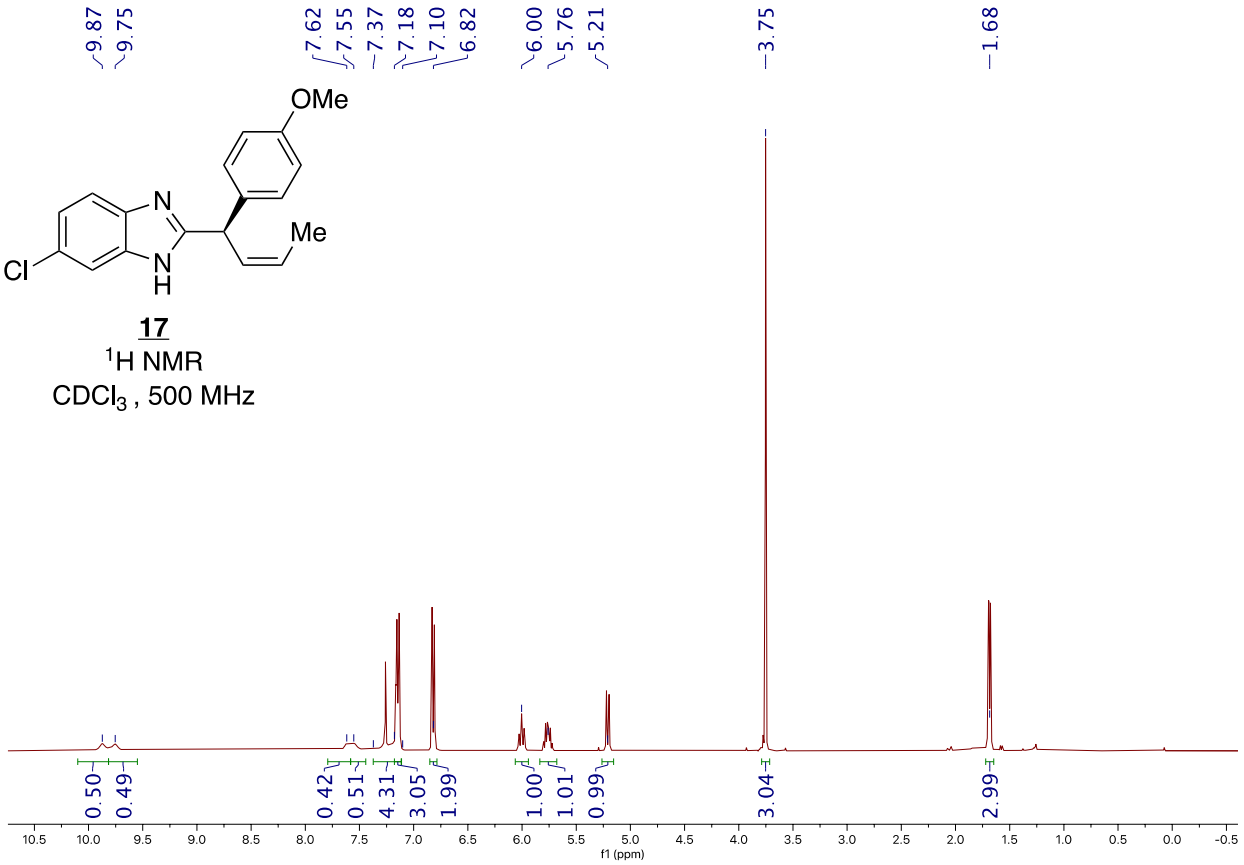
$CDCl_3$, 126 MHz



16
^{1}H NMR
$CDCl_3$, 500 MHz



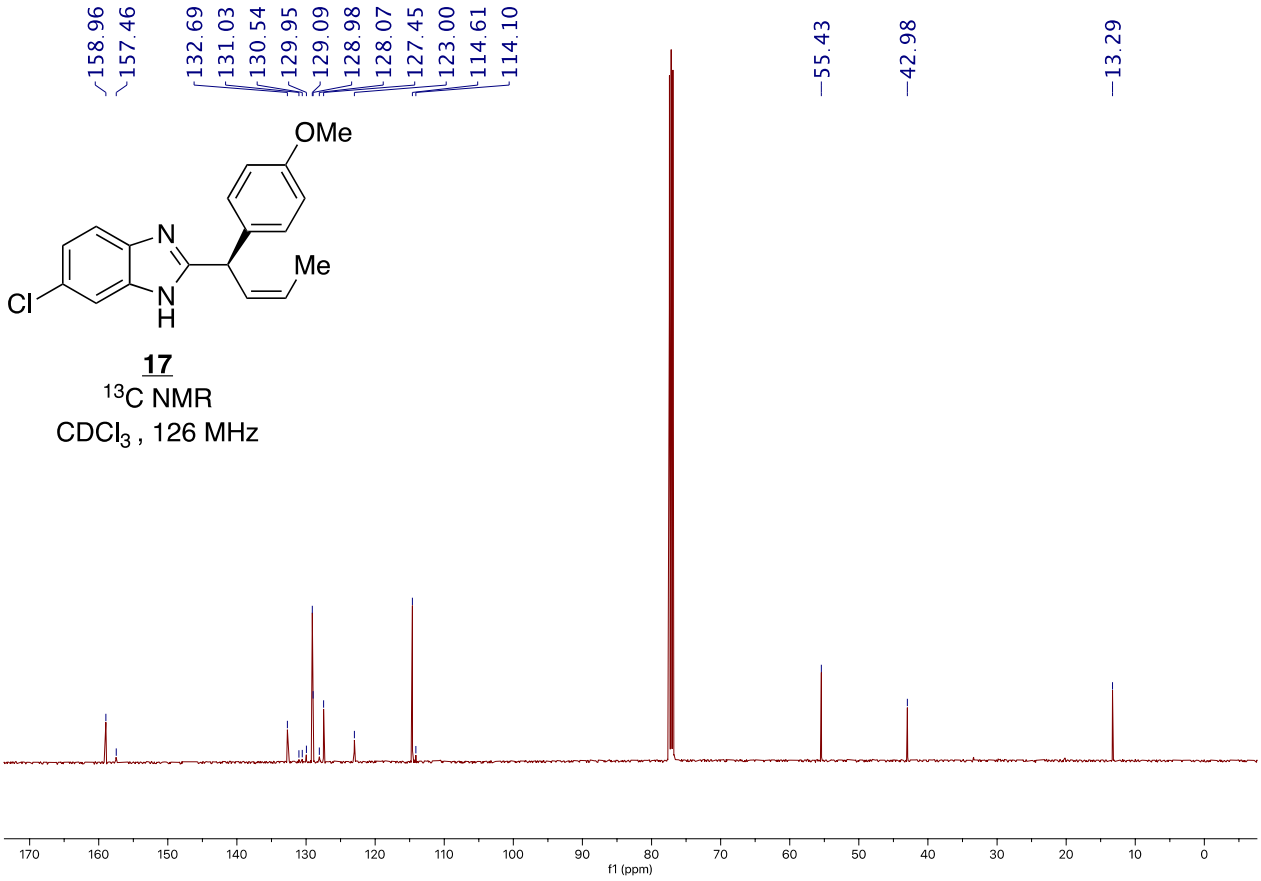
16
^{13}C NMR
$CDCl_3$, 126 MHz



17

^{1}H NMR

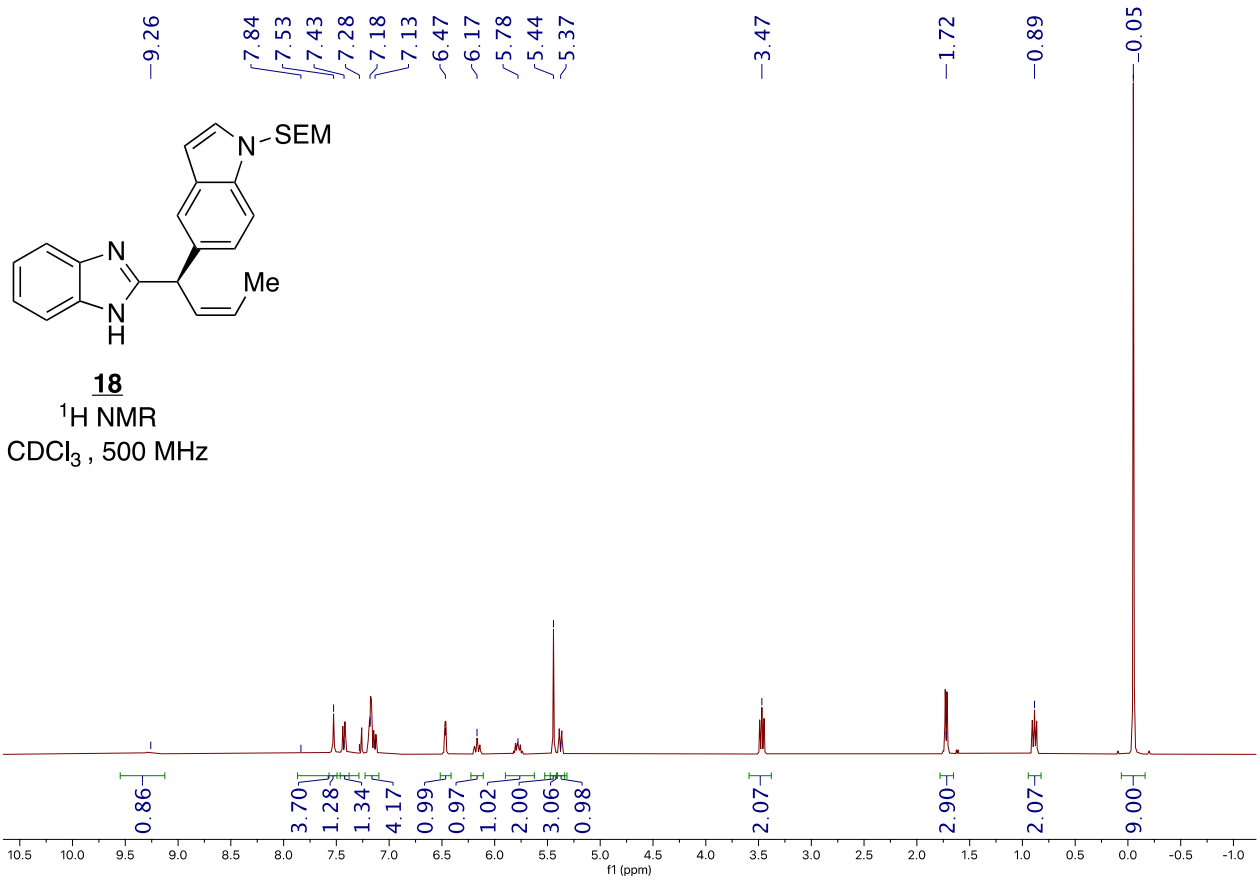
$CDCl_3$, 500 MHz



17

^{13}C NMR

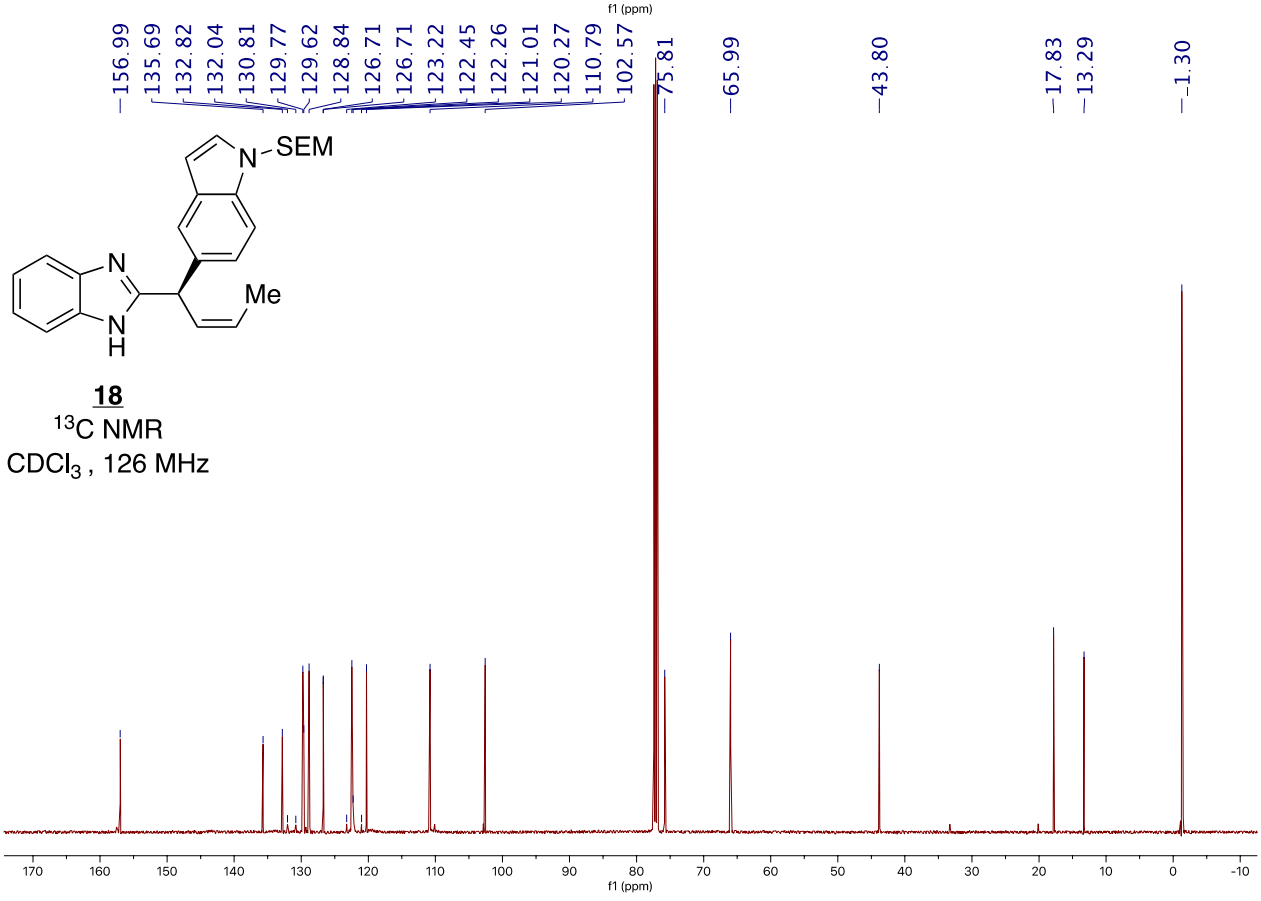
$CDCl_3$, 126 MHz



18

^{1}H NMR

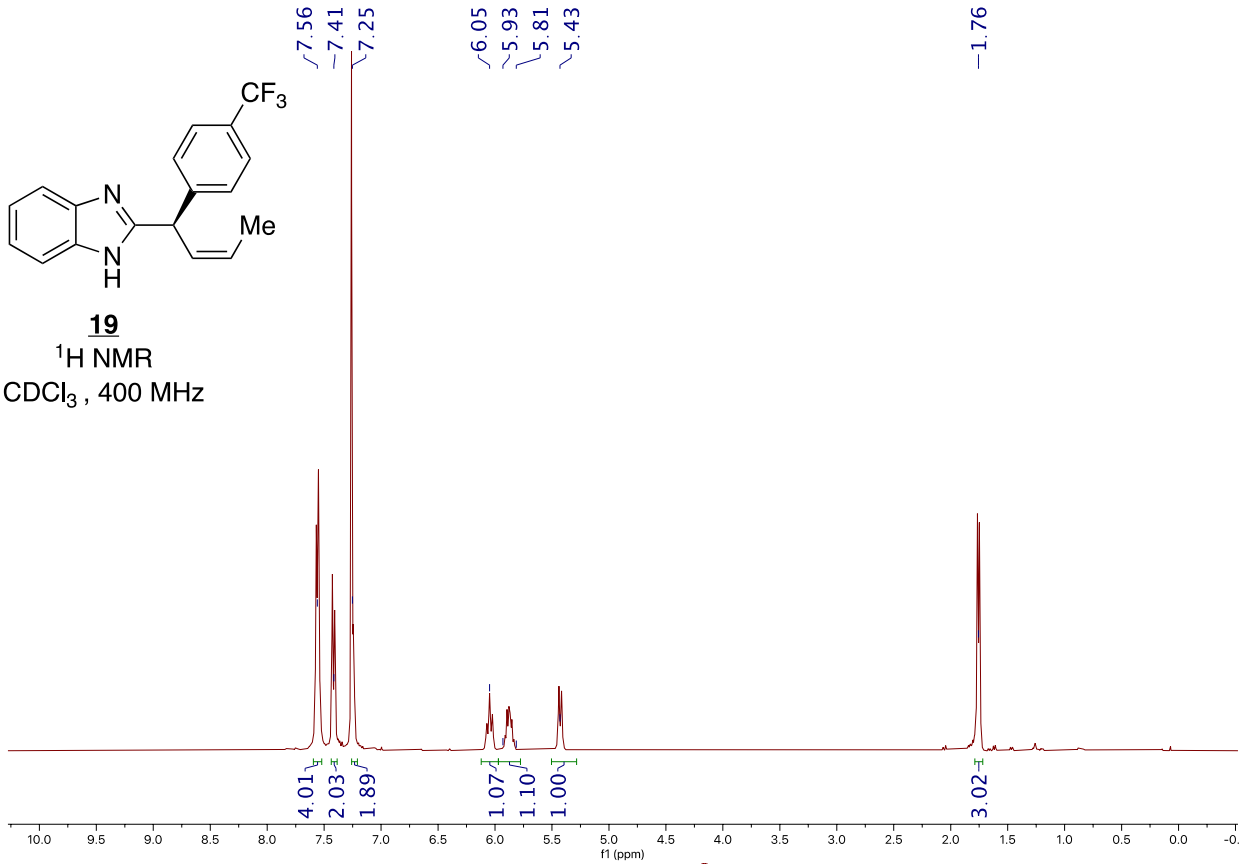
$CDCl_3$, 500 MHz



18

^{13}C NMR

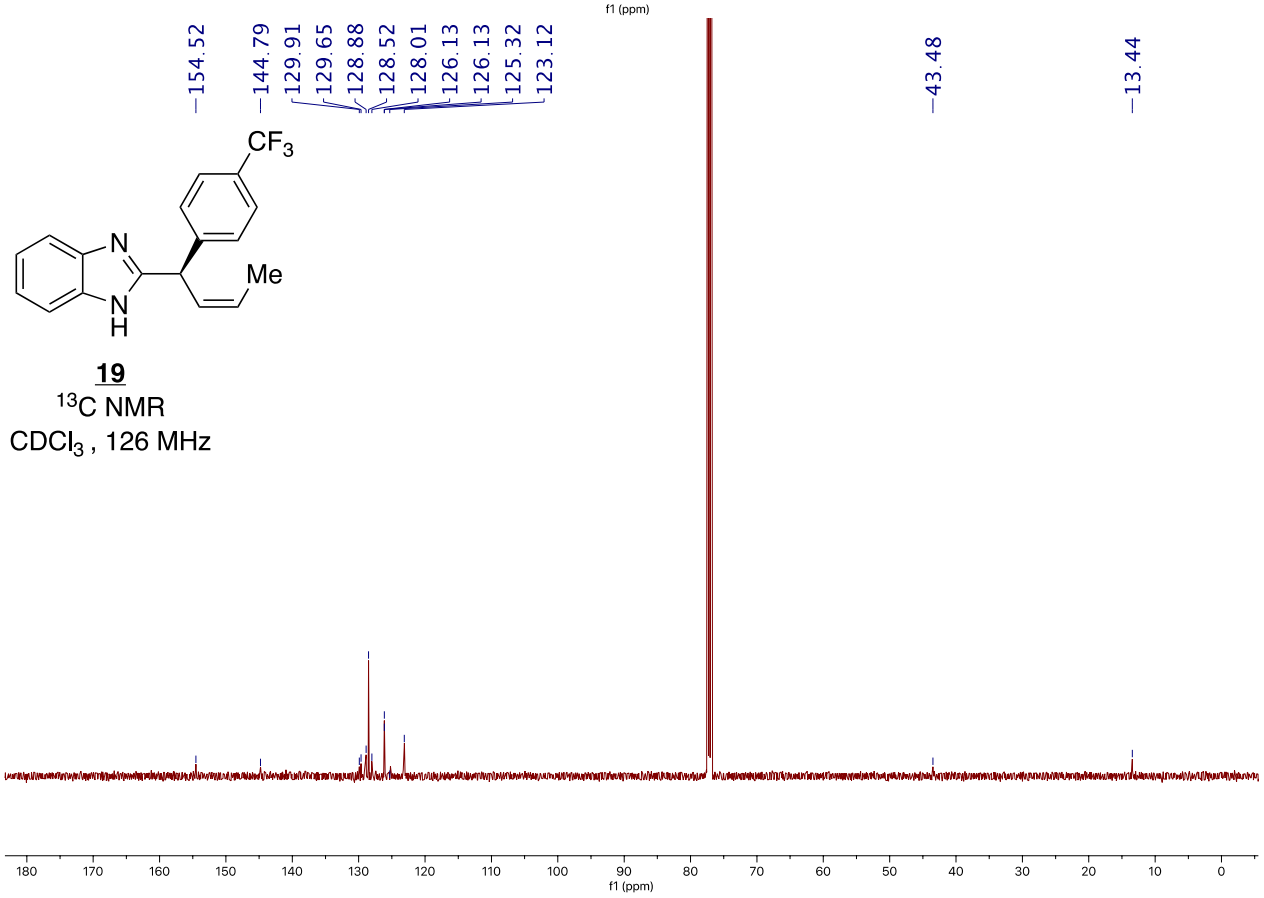
$CDCl_3$, 126 MHz



19

^{1}H NMR

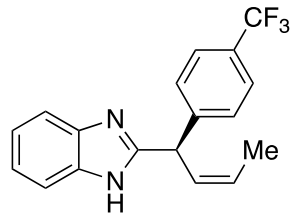
$CDCl_3$, 400 MHz



19

^{13}C NMR

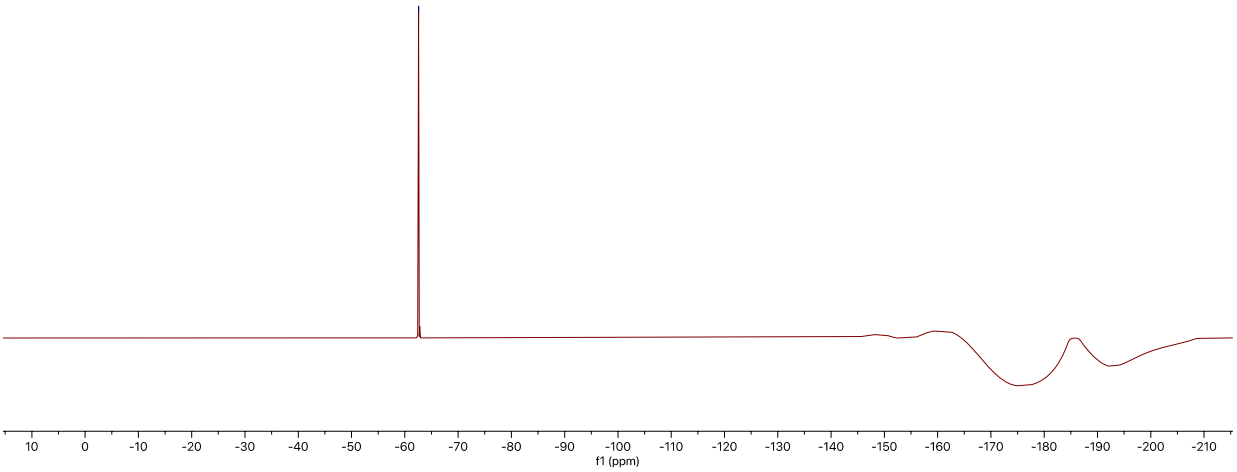
$CDCl_3$, 126 MHz

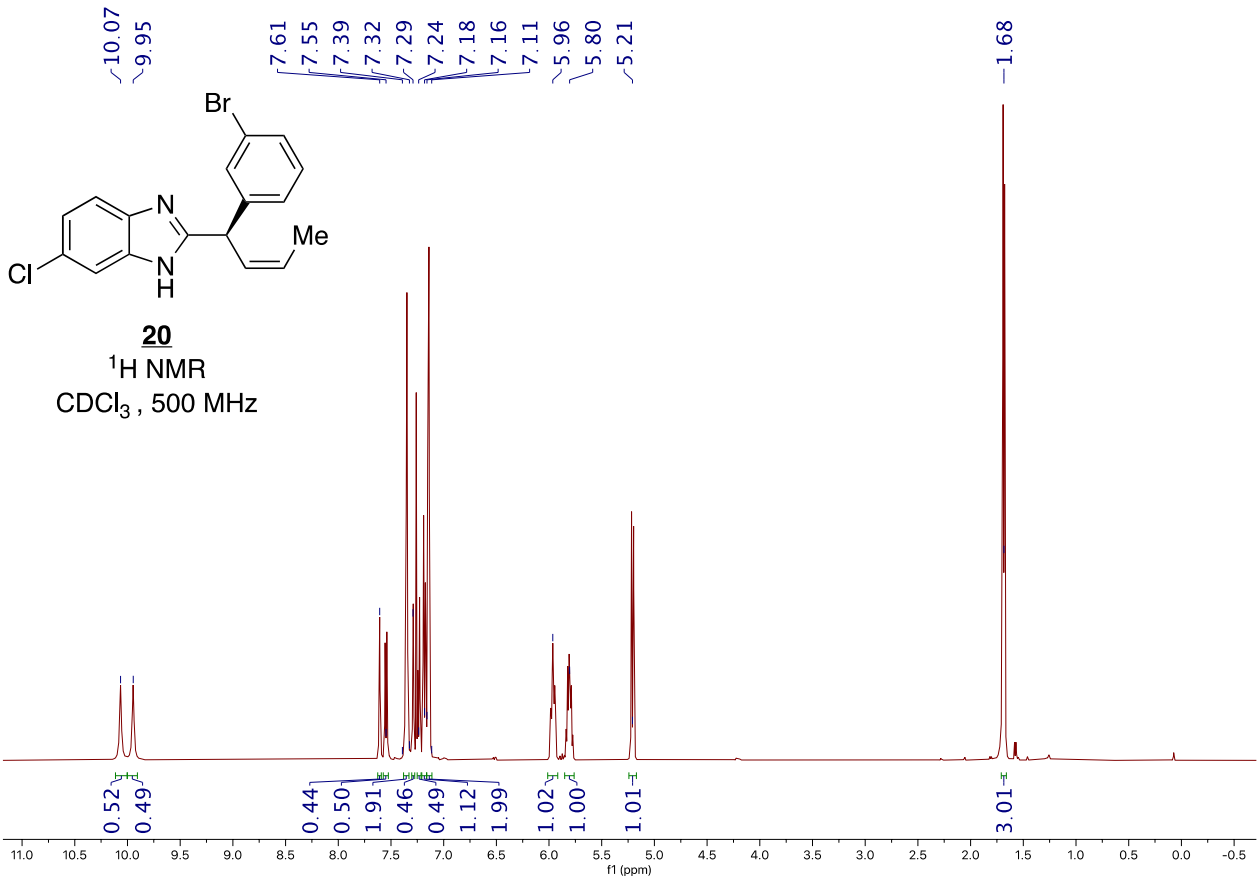


19

^{19}F NMR

$CDCl_3$, 471 MHz

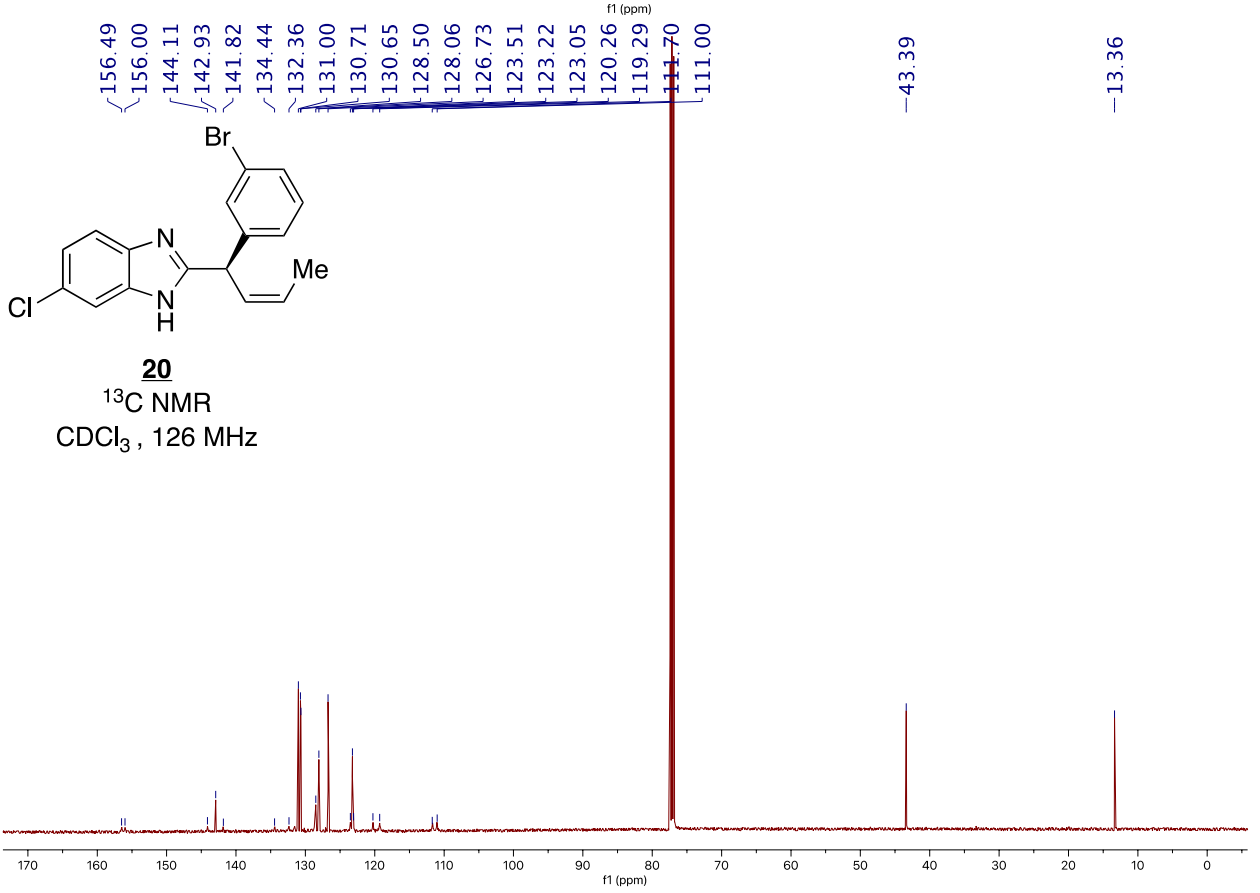




20

^{1}H NMR

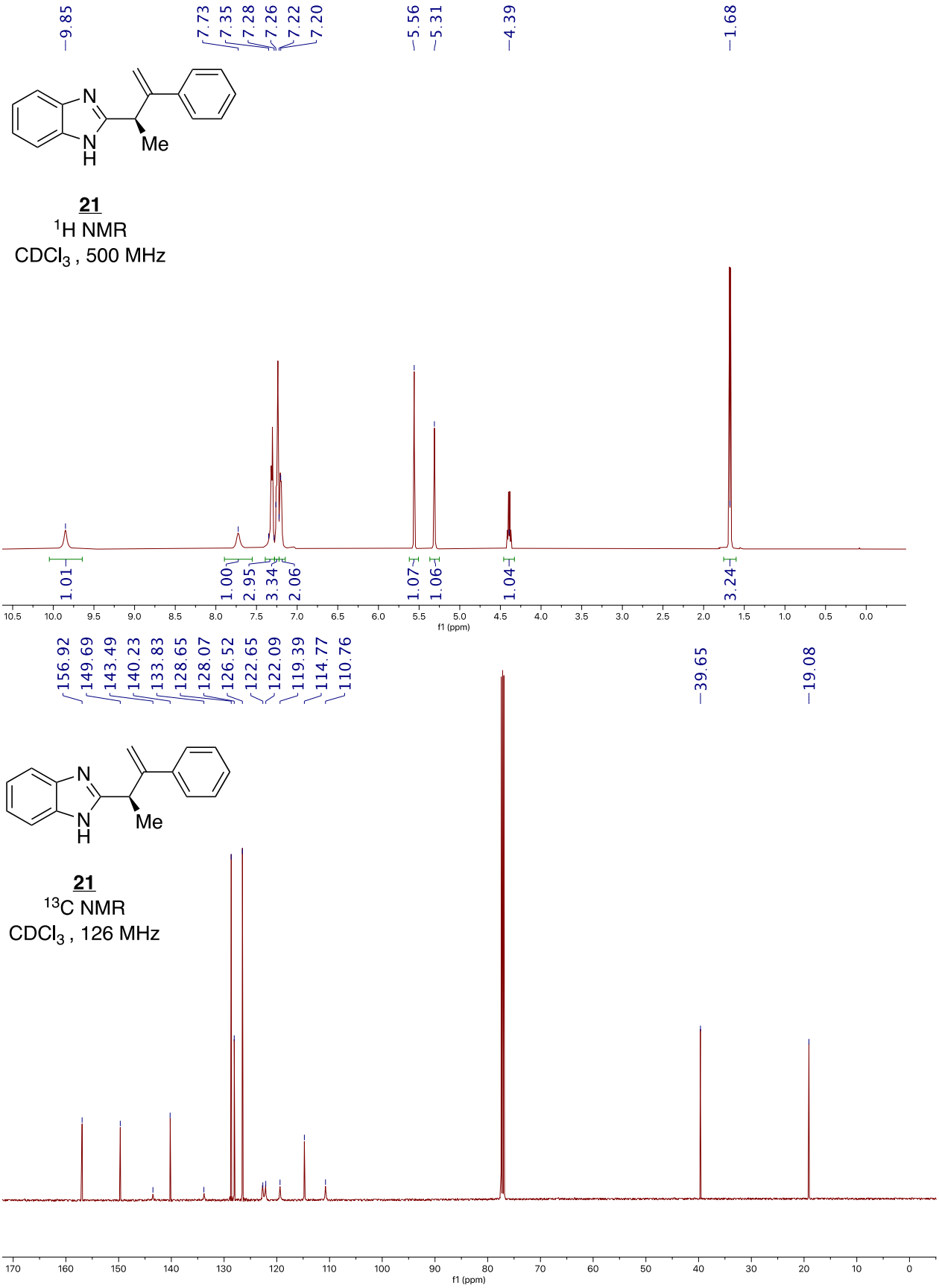
$CDCl_3$, 500 MHz

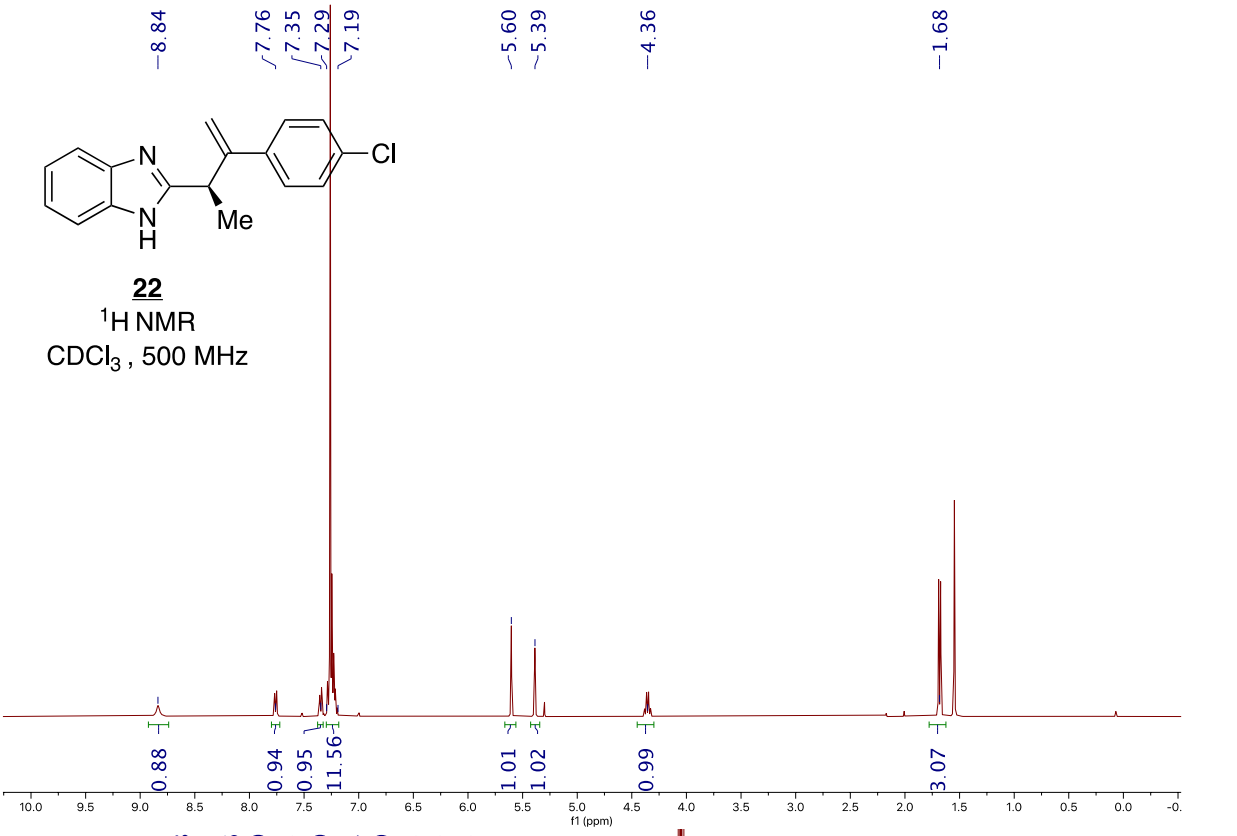


20

^{13}C NMR

$CDCl_3$, 126 MHz

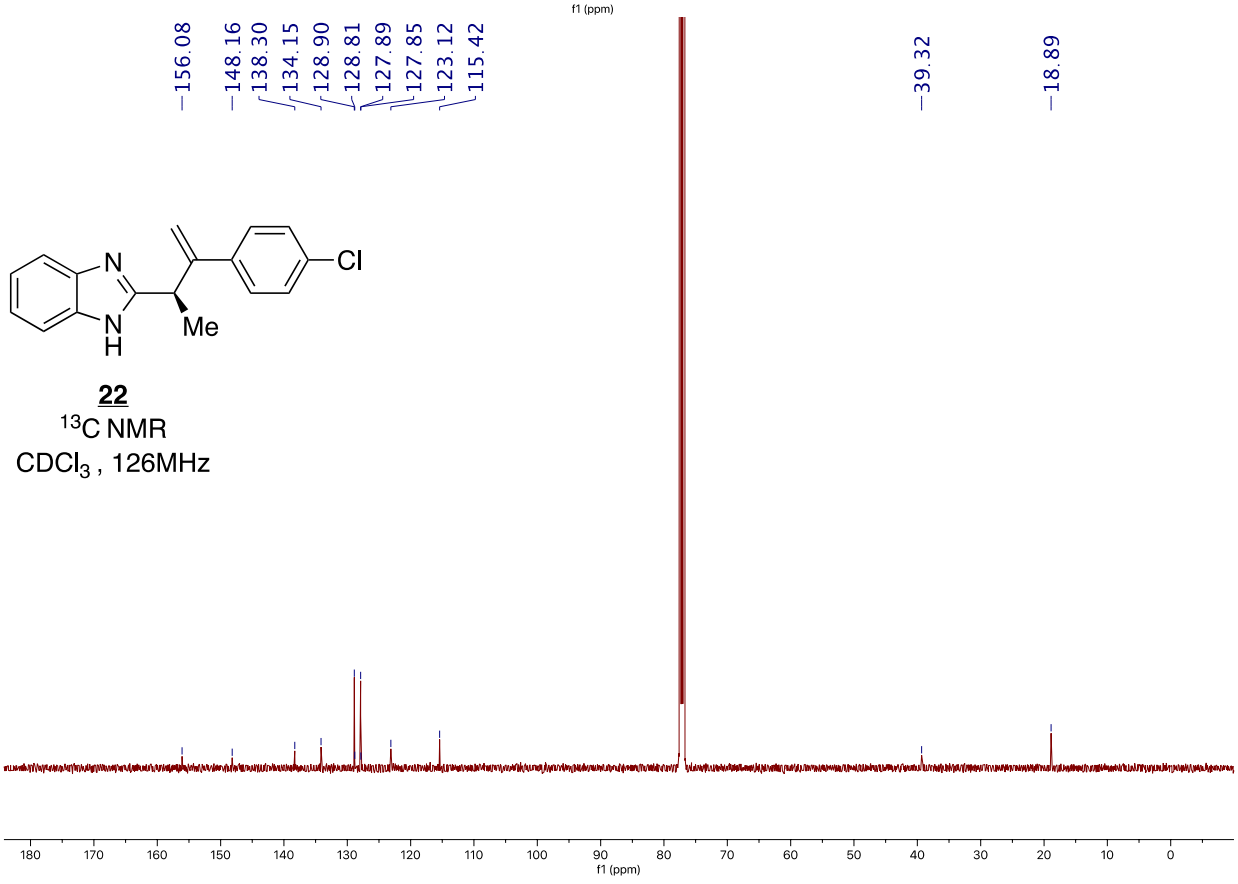

9.85
7.73
7.35
7.28
7.26
7.22
7.20
5.56
5.31
4.39
1.68
N
N
H
Me
21
1H NMR
CDCl3 , 500 MHz
1.01
1.00
2.95
3.34
2.06
1.07
1.06
1.04
3.24
f1 (ppm)
156.92
149.69
143.49
140.23
133.83
128.65
128.07
126.52
122.65
122.09
119.39
114.77
110.76
39.65
19.08
21
13C NMR
CDCl3 , 126 MHz
f1 (ppm)



22

^{1}H NMR

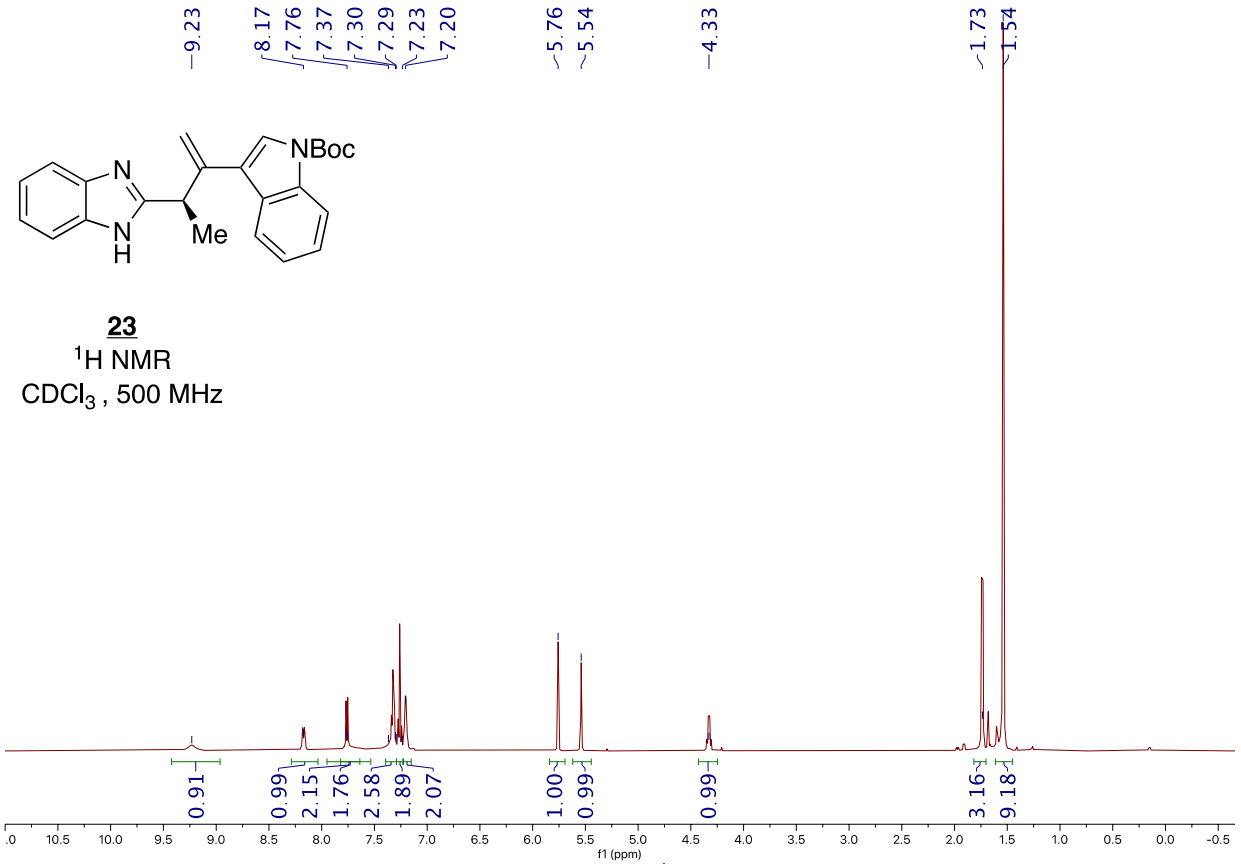
$CDCl_3$, 500 MHz



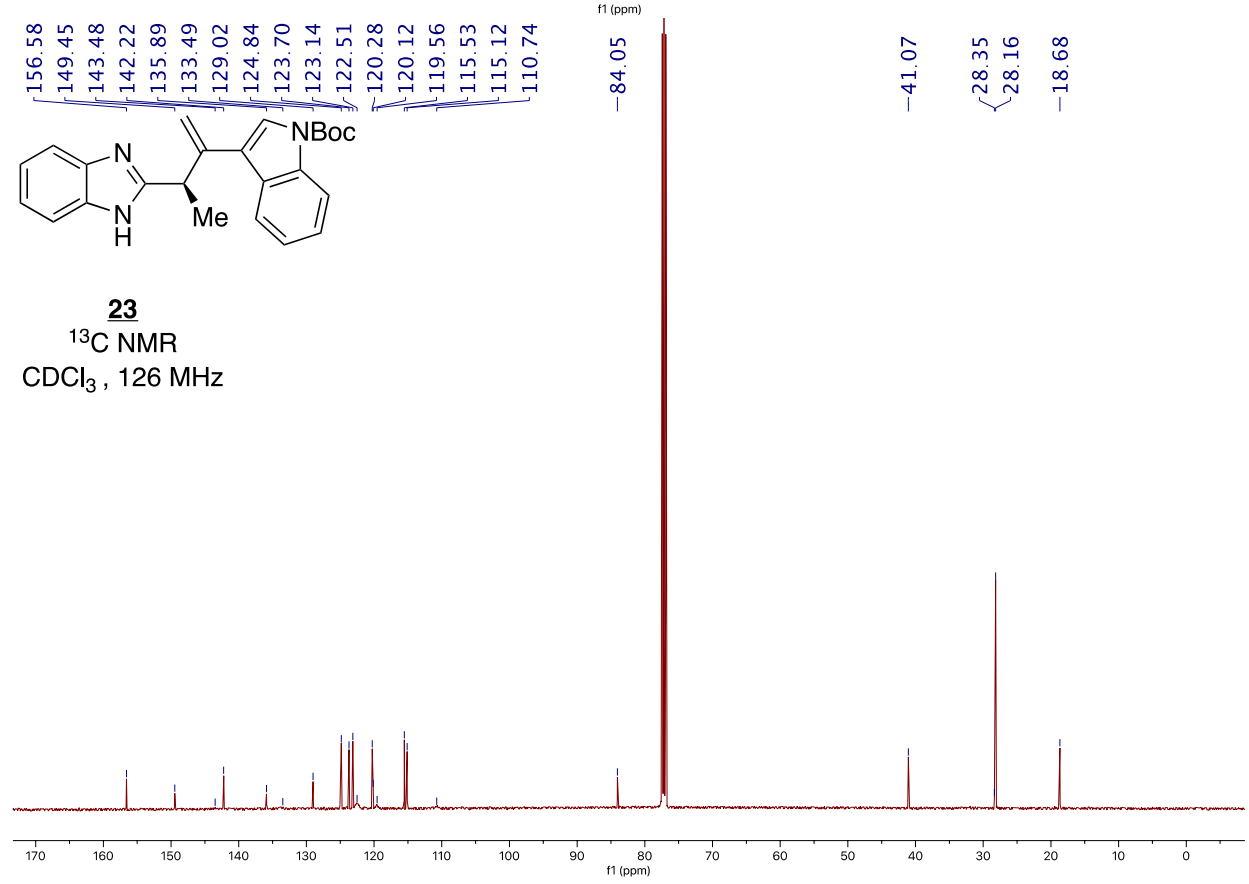
22

^{13}C NMR

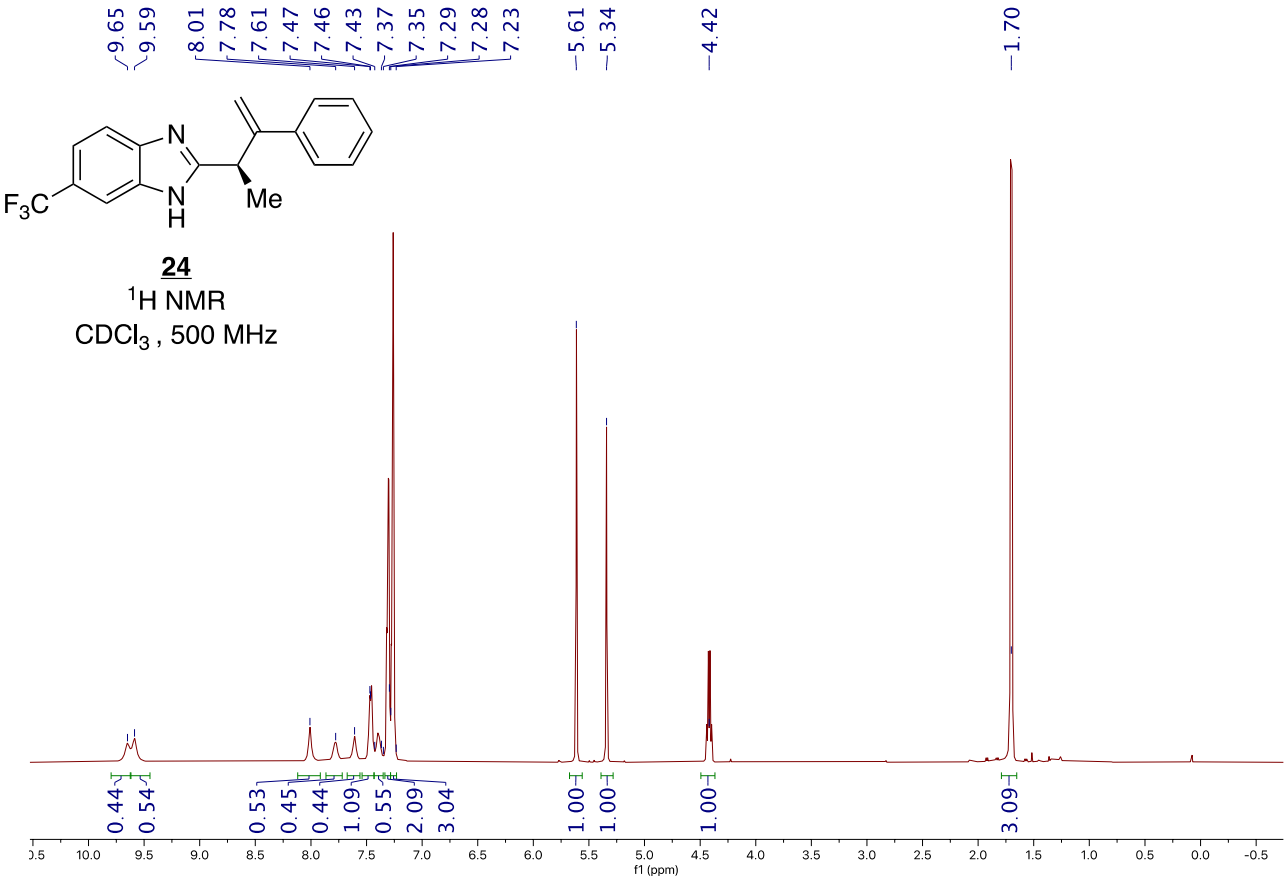
$CDCl_3$, 126MHz

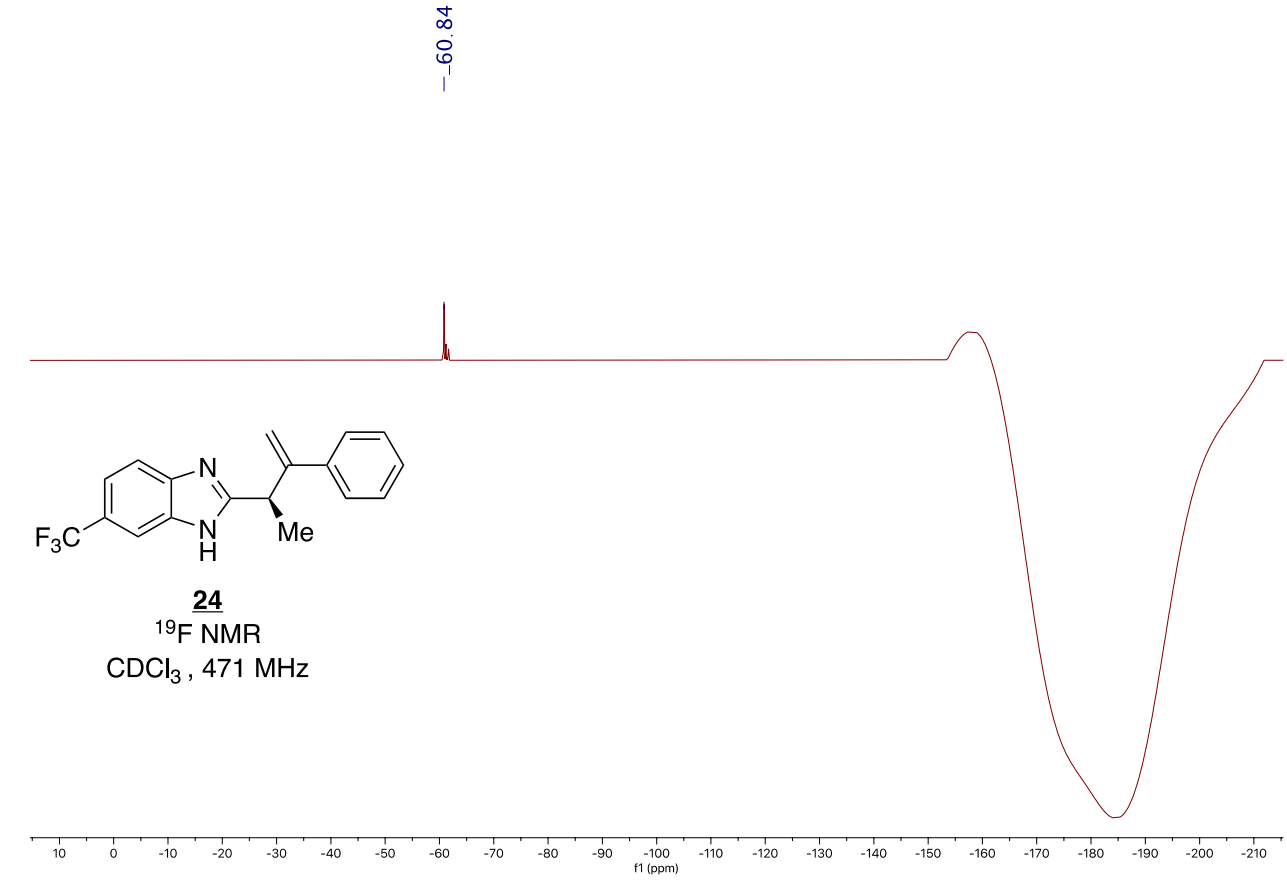


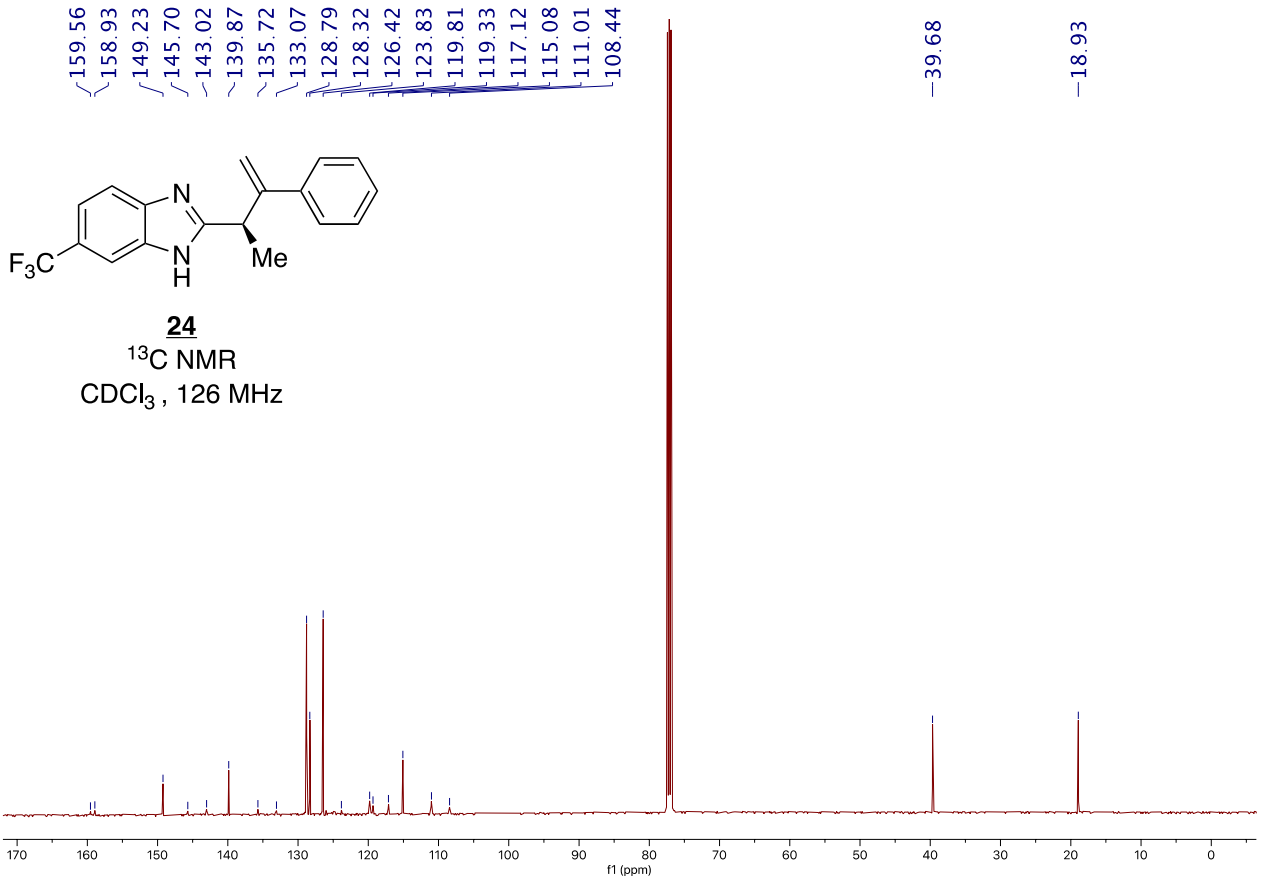
23
^{1}H NMR
$CDCl_3$, 500 MHz



23
^{13}C NMR
$CDCl_3$, 126 MHz


9.65
9.59
8.01
7.78
7.61
7.47
7.46
7.43
7.37
7.35
7.29
7.28
7.23
5.61
5.34
4.42
1.70
N
N
H
Me
F3C
24
1H NMR
CDCl3 , 500 MHz
0.44
0.54
0.53
0.45
0.44
1.09
0.55
2.09
3.04
1.00
1.00
1.00
3.09
f1 (ppm)

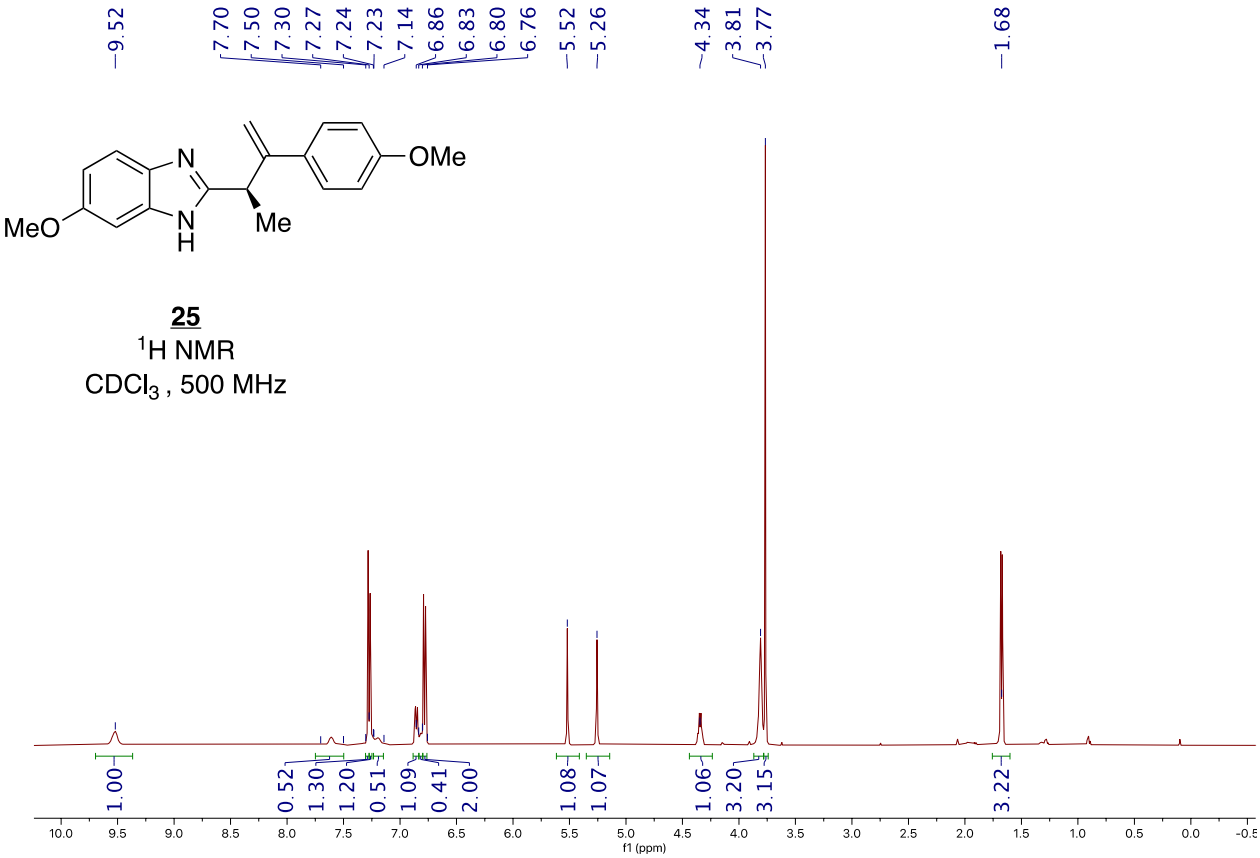

-60.84
N
N
H
Me
F3C
24
19F NMR
CDCl3 , 471 MHz
f1 (ppm)



24

^{13}C NMR

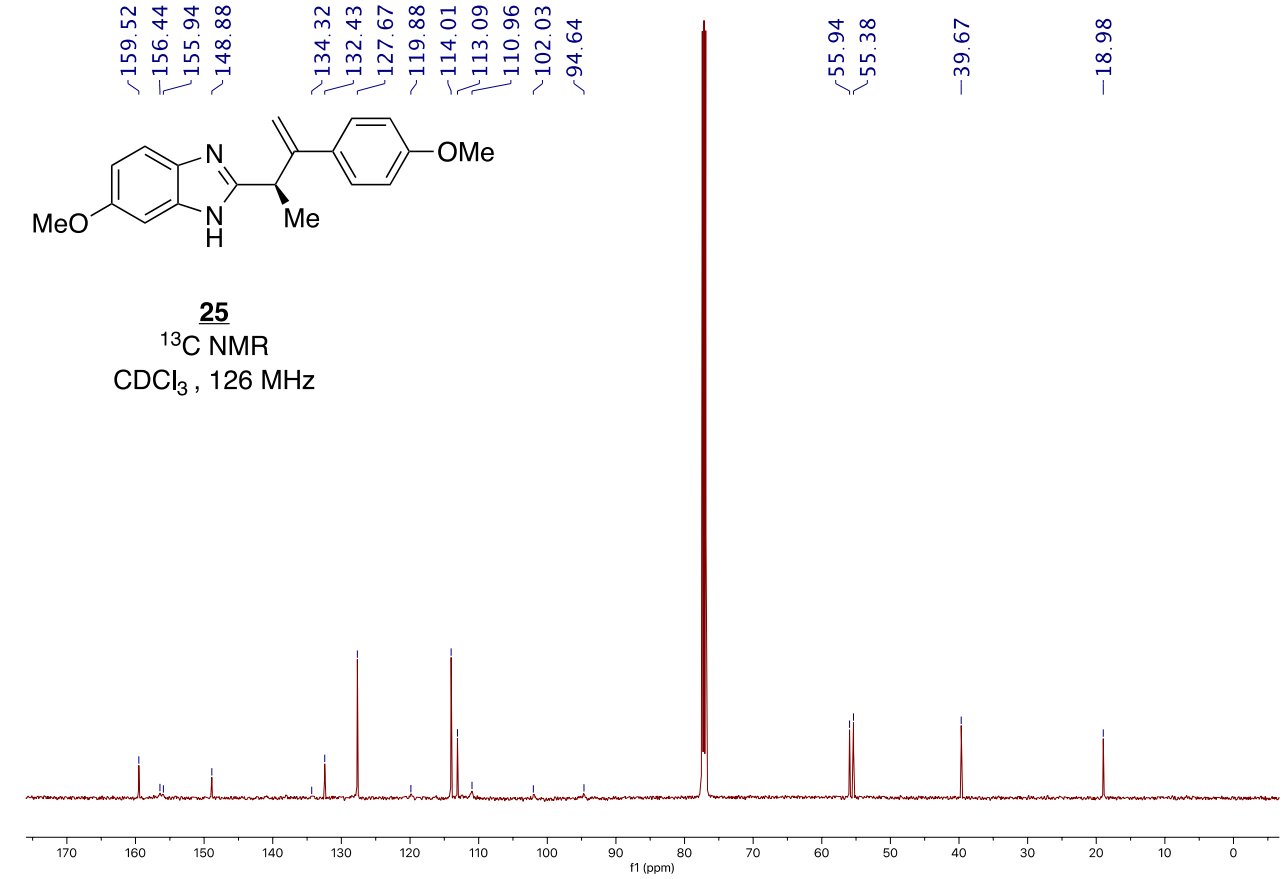
$CDCl_3$, 126 MHz



25

^{1}H NMR

$CDCl_3$, 500 MHz

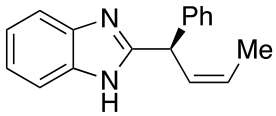


25

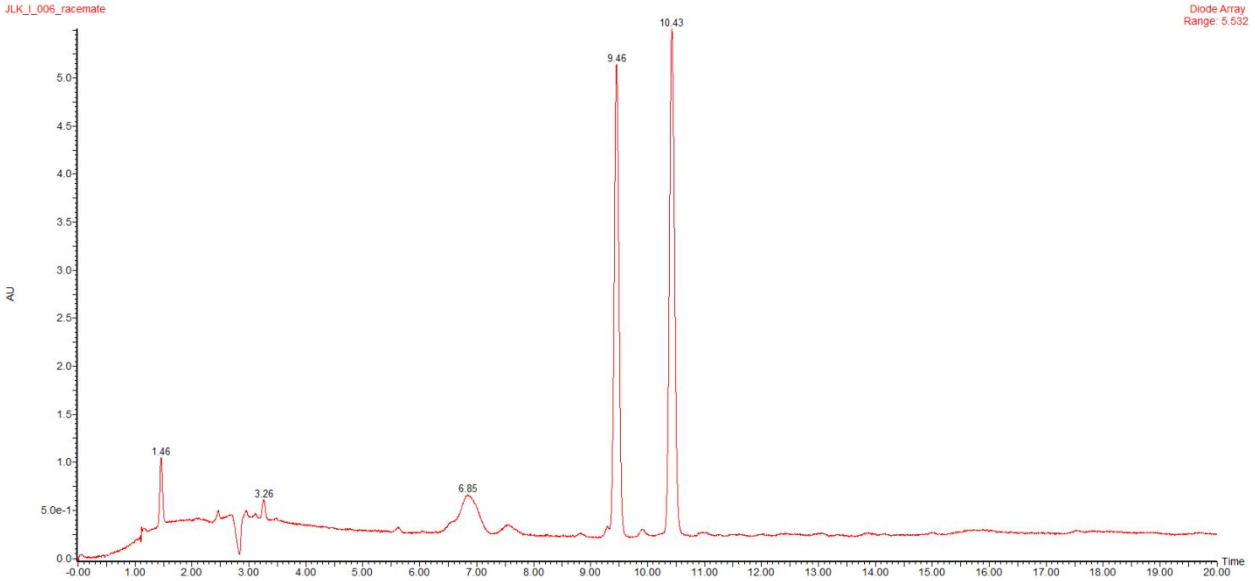
^{13}C NMR

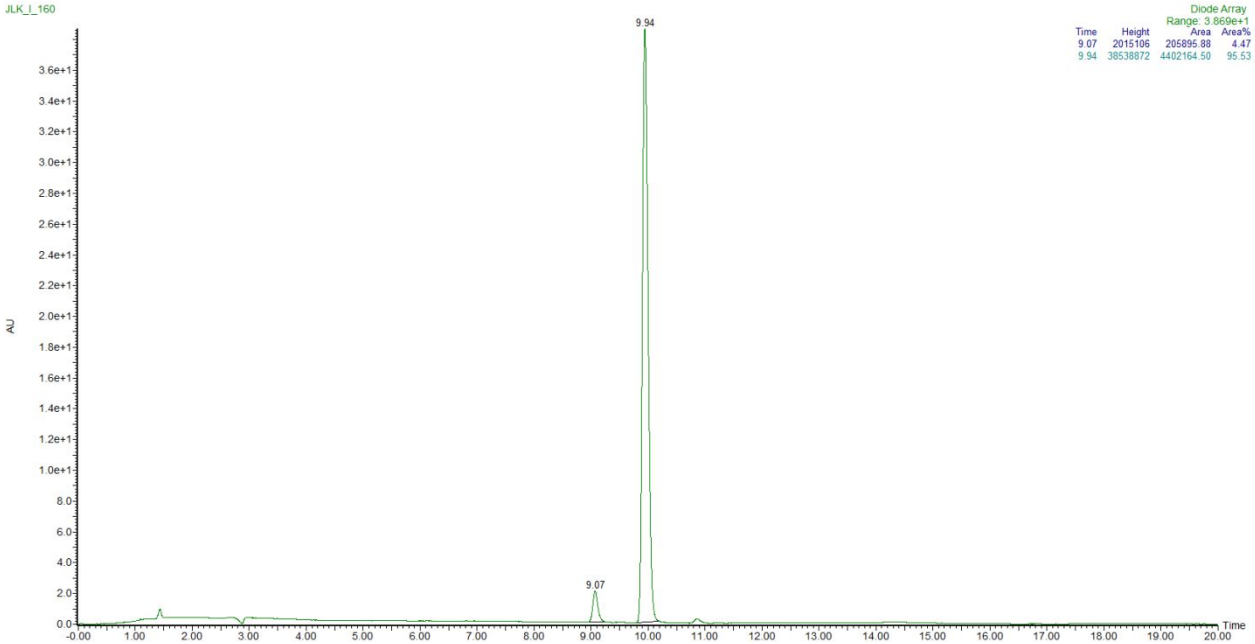
$CDCl_3$, 126 MHz

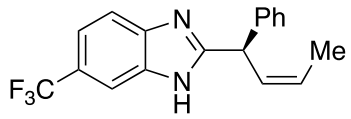
7.2 Chiral SFC and HPLC Traces of Allylation Products



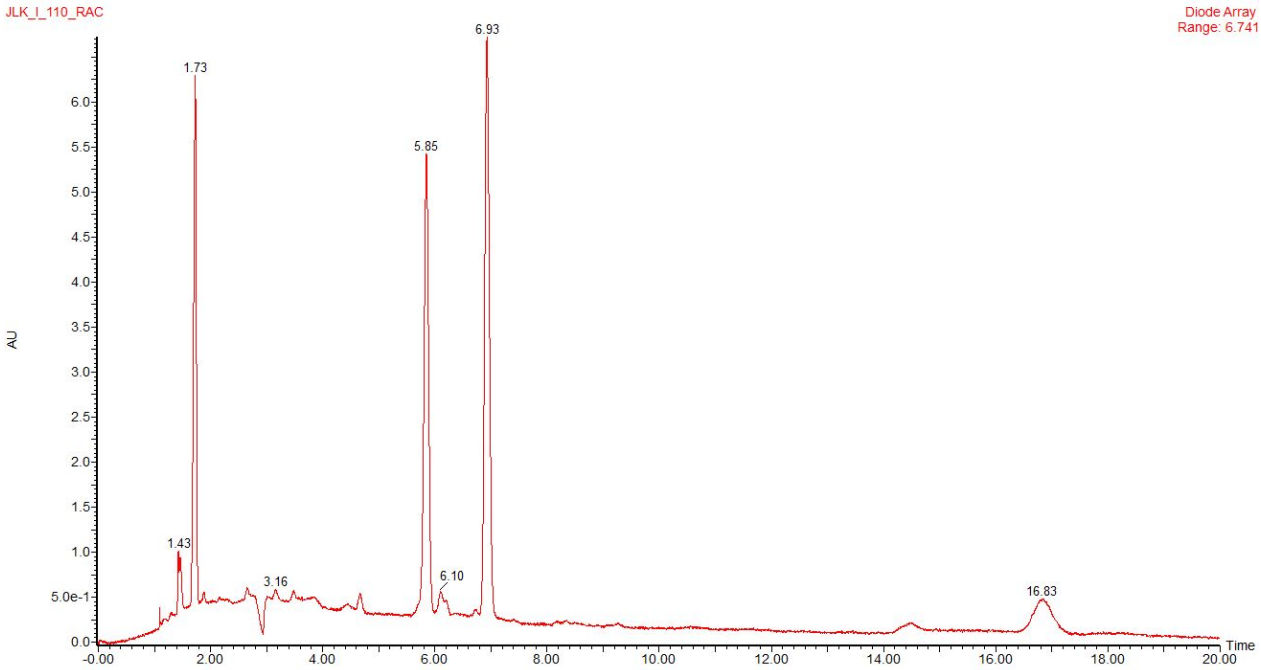
8

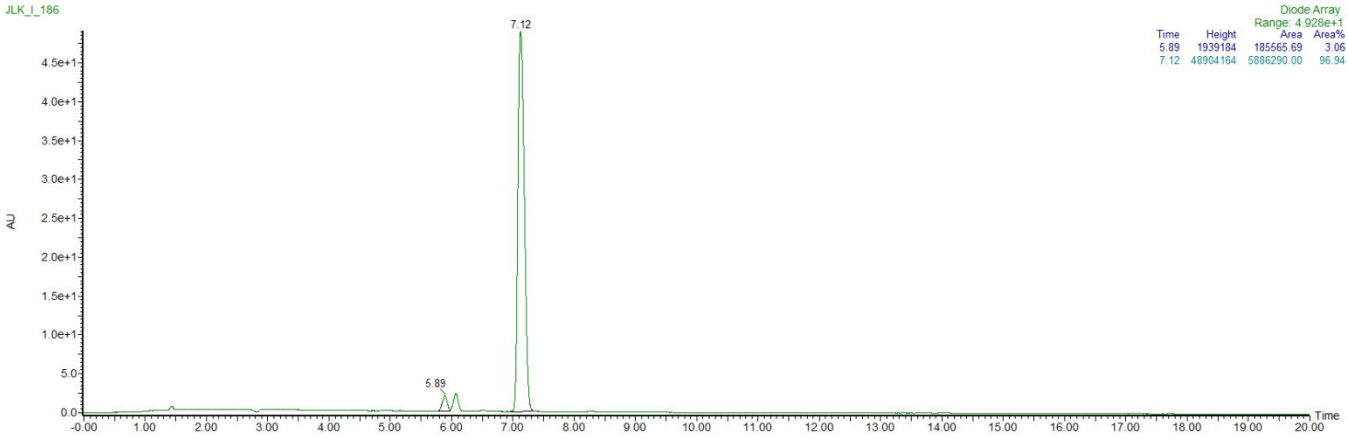


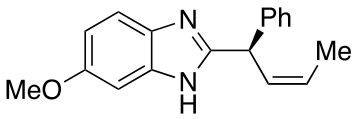



N
Ph
Me
N
H
F3C

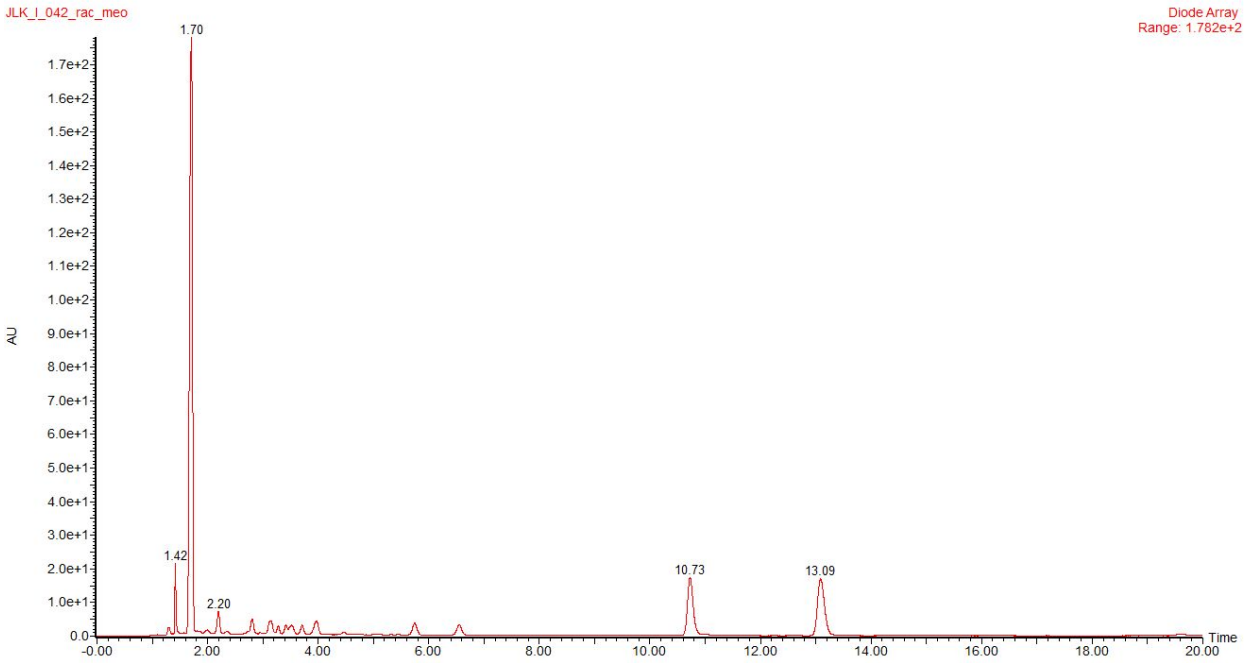
9

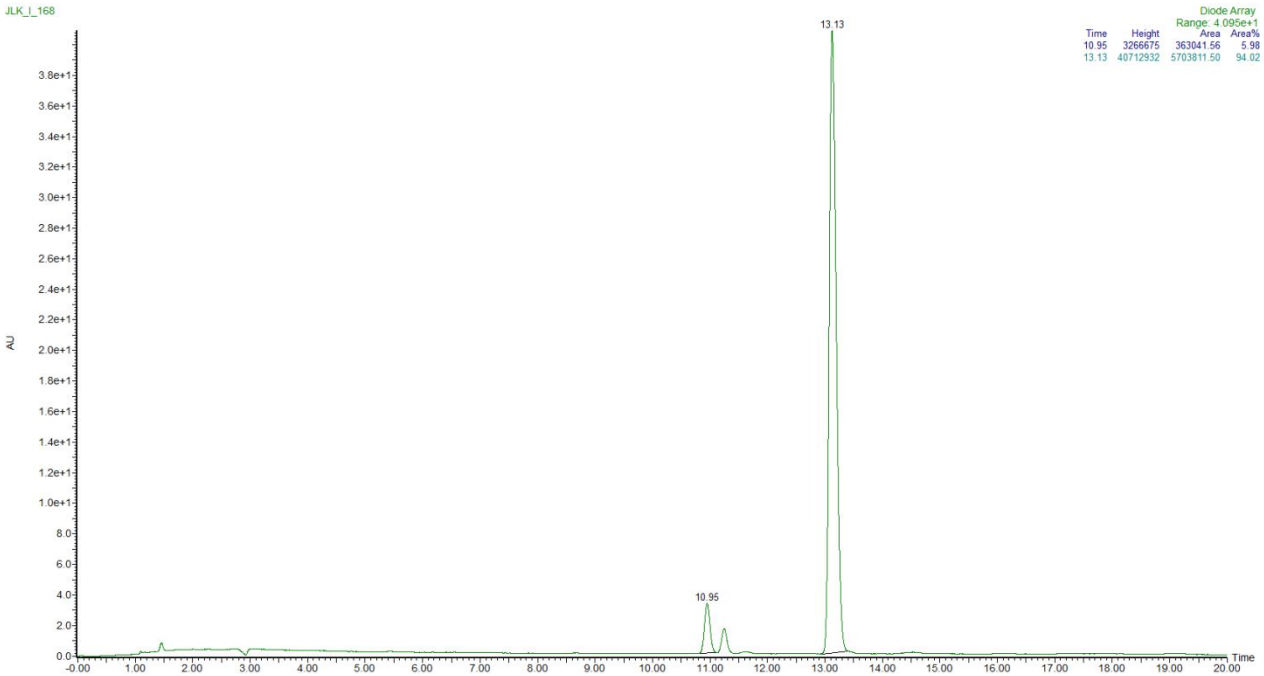

JLK_I_110_RAC
Diode Array
Range: 6.741
1.73
6.93
5.85
1.43
3.16
6.10
16.83
AU
Time

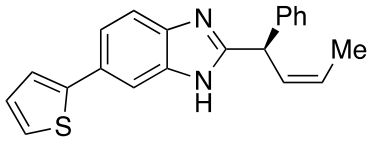

JLK_I_186
Diode Array
Range: 4.928e+1
Time Height Area Area%
5.89 1939184 185565.69 3.06
7.12 48904164 5886290.00 96.94
7.12
5.89
AU
Time


N
Ph
Me
MeO
N
H

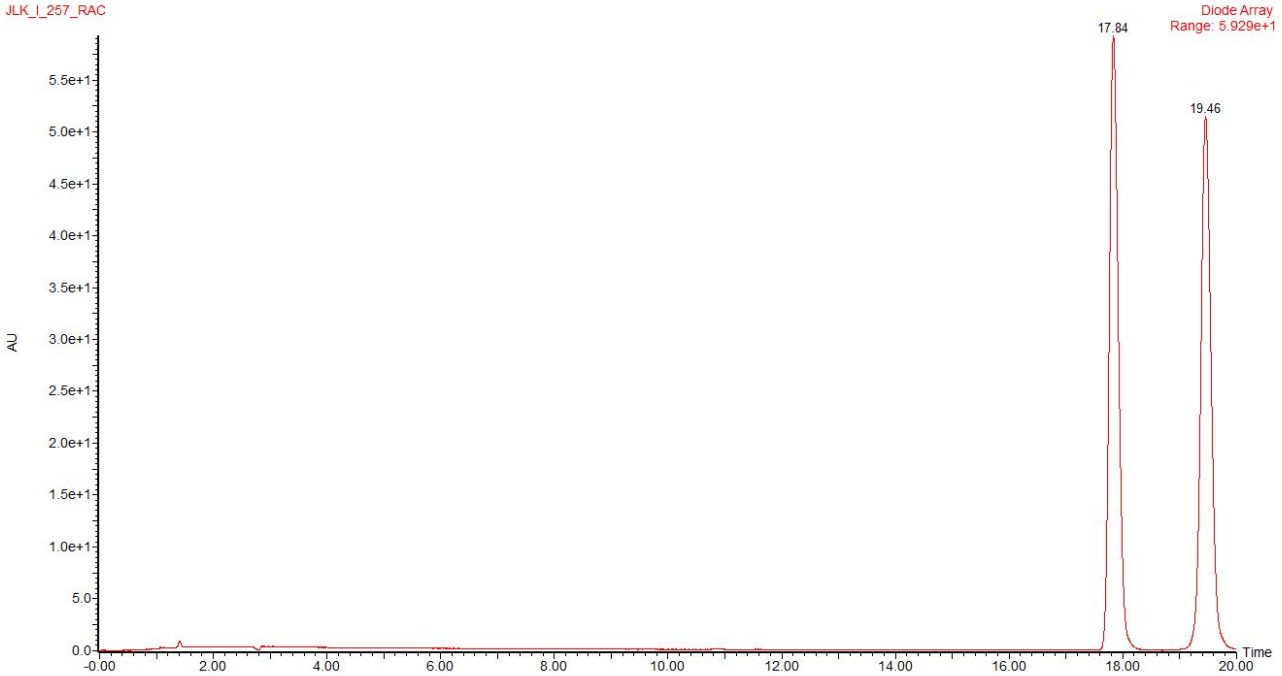
10

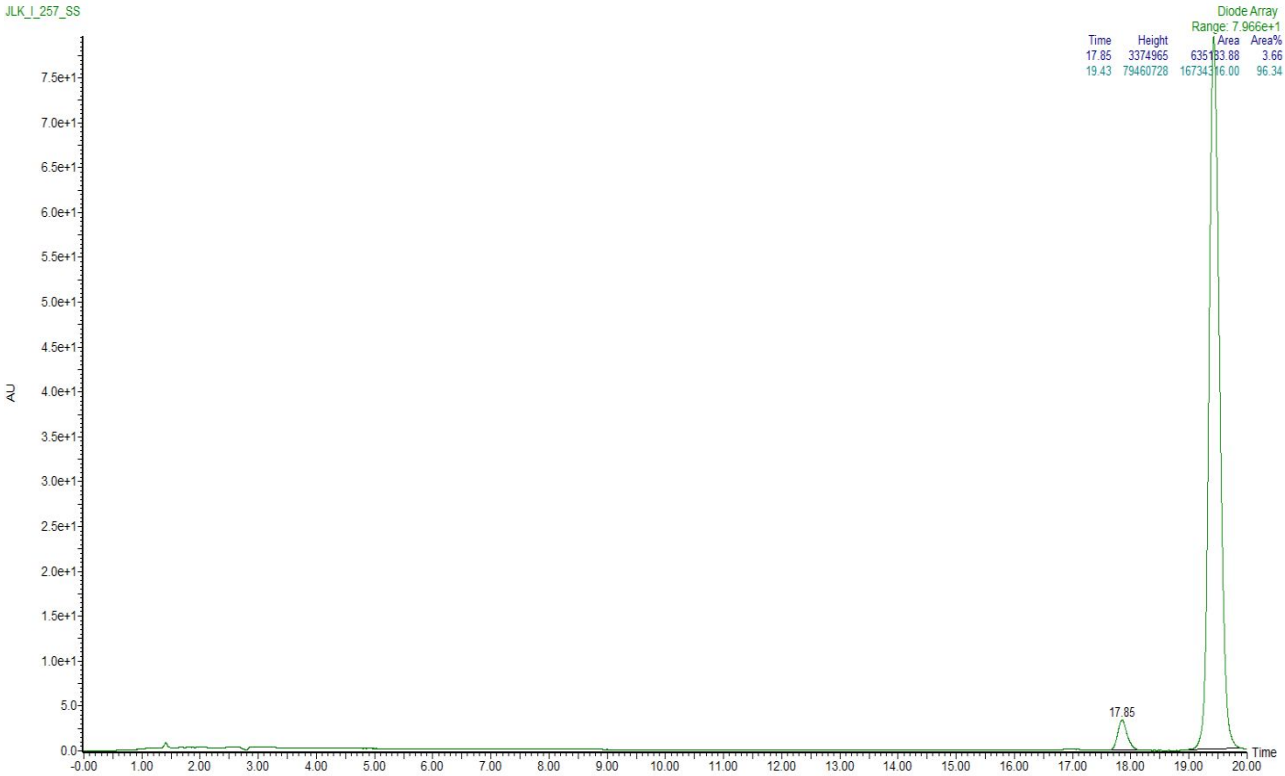

JLK_I_042_rac_meo
Diode Array
Range: 1.782e+2
1.70
1.42
2.20
10.73
13.09
AU
Time

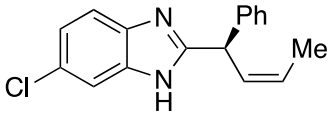

JLK_I_168
Diode Array
Range: 4.095e+1
Time Height Area Area%
10.95 3266675 363041.56 5.98
13.13 40712932 5703811.50 94.02
13.13
10.95
AU
Time


N
Ph
Me
N
H
S

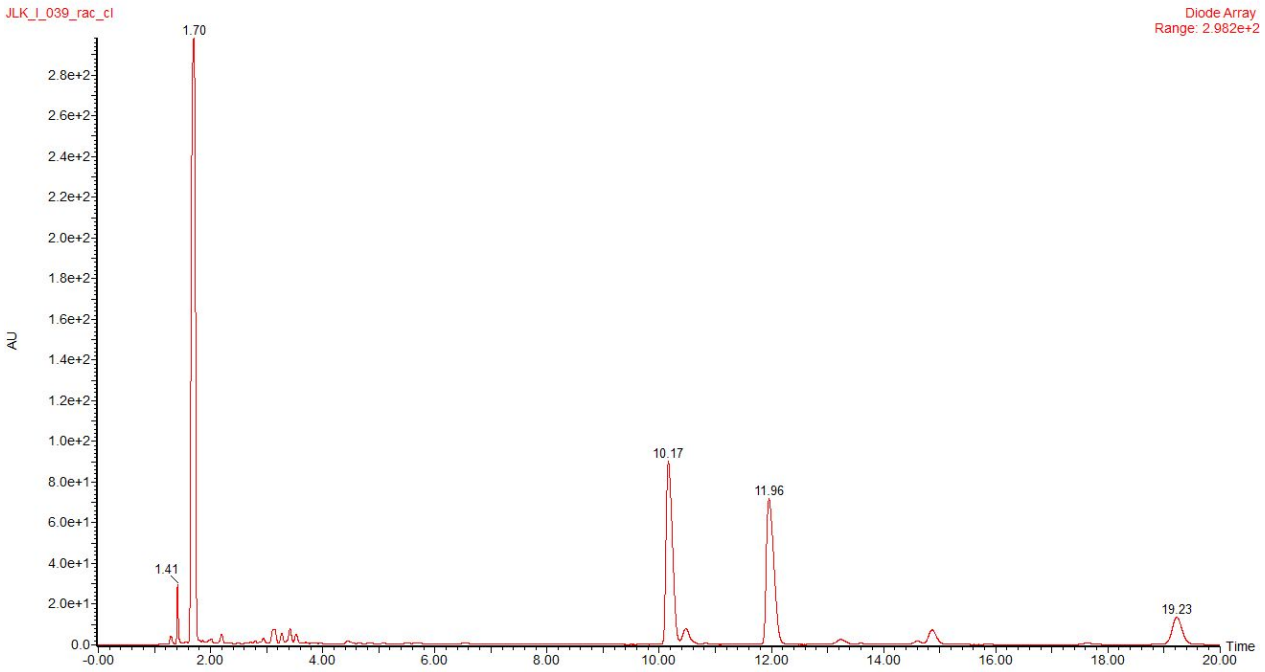
11

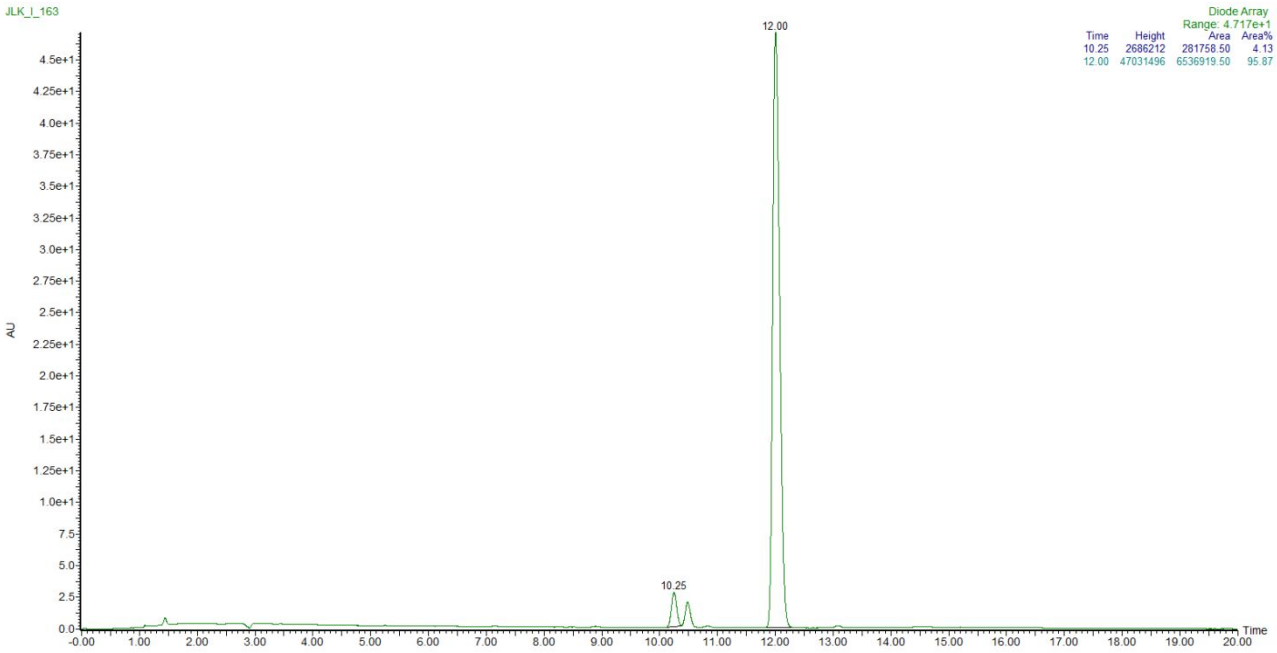

JLK_I_257_RAC
Diode Array
Range: 5.929e+1
17.84
19.46
AU
Time

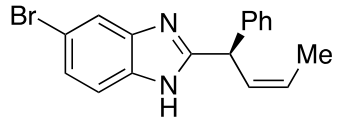

JLK_I_257_SS
Diode Array
Range: 7.966e+1
Time Height Area Area%
17.85 3374965 63583.88 3.66
19.43 79460728 1673416.00 96.34
17.85
AU
Time


N
Ph
Me
Cl
N
H

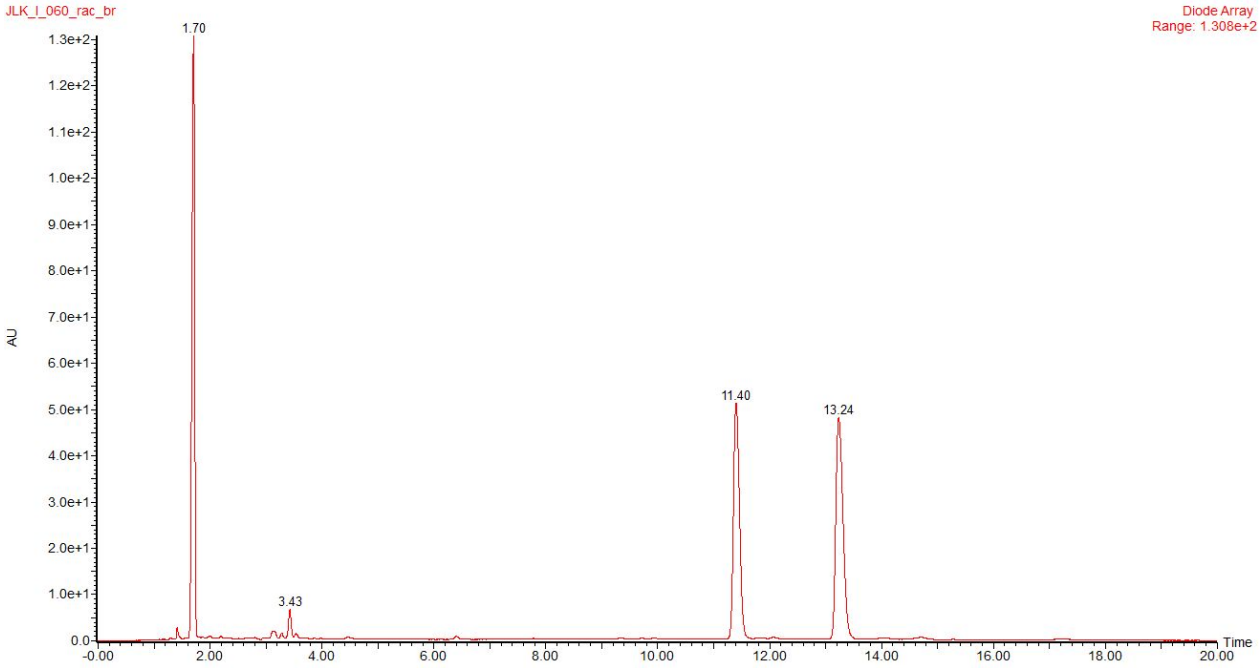
12

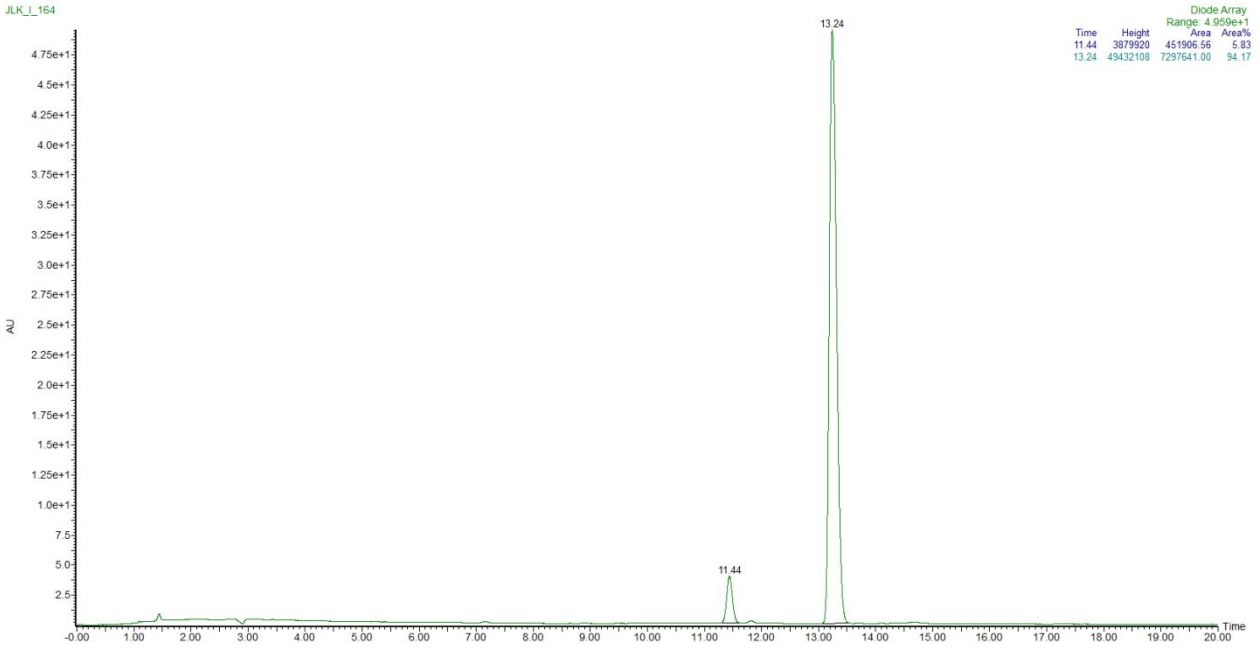

JLK_I_039_rac_cl
Diode Array
Range: 2.982e+2
1.70
10.17
11.96
1.41
19.23
AU
Time

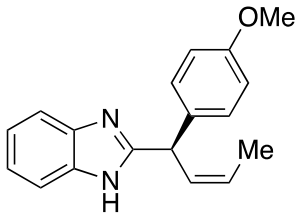

JLK_I_163
Diode Array
Range: 4.717e+1
Time Height Area Area%
10.25 2686212 281758.50 4.13
12.00 47031496 6536919.50 95.87
12.00
10.25
AU
Time


Br
N
Ph
Me
N
H

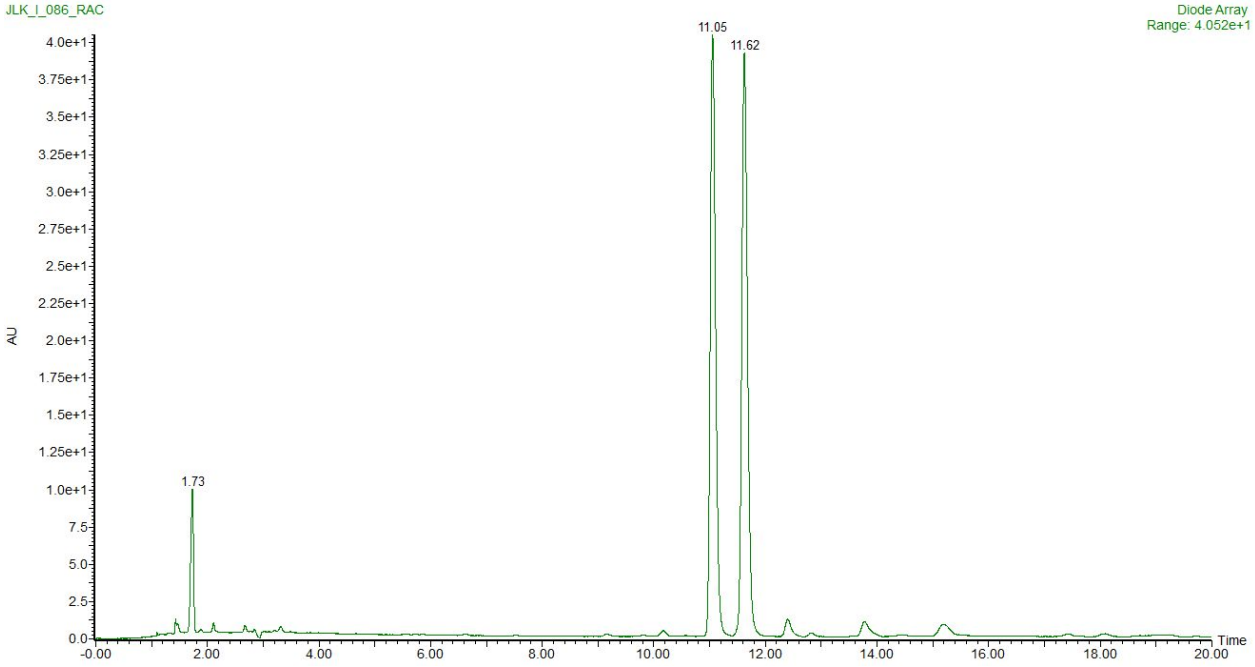
13

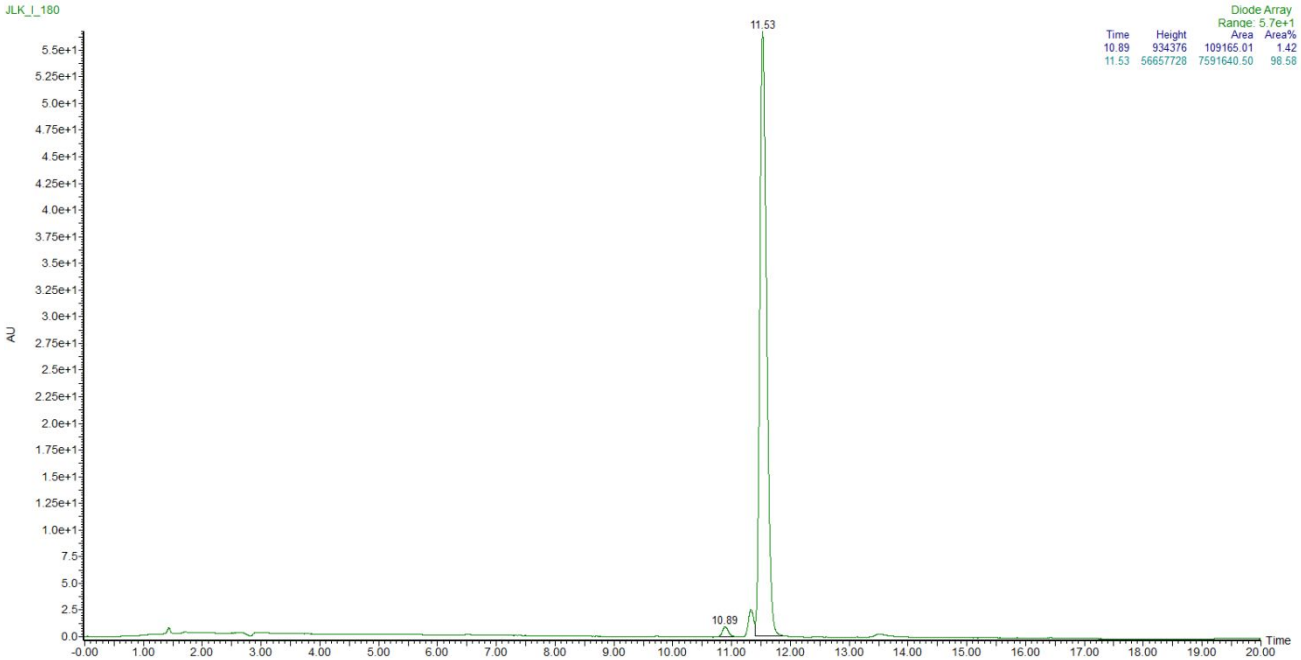

JLK_I_060_rac_br
Diode Array
Range: 1.308e+2
1.70
3.43
11.40
13.24
AU
Time

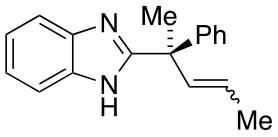

JLK_I_164
Diode Array
Range: 4.959e+1
Time Height Area Area%
11.44 3879920 451906.56 5.83
13.24 49432108 7297641.00 94.17
13.24
11.44
AU
Time


OMe
N
N
H
Me

14

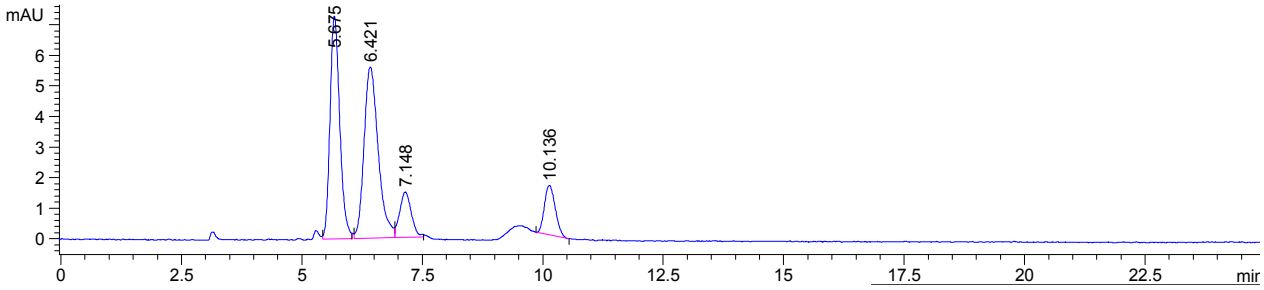

JLK_I_086_RAC
Diode Array
Range: 4.052e+1
11.05
11.62
1.73
AU
Time


JLK_I_180
Diode Array
Range: 5.7e+1
Time Height Area Area%
10.89 934376 109165.01 1.42
11.53 56657728 7591640.50 98.58
11.53
10.89
AU
Time



15

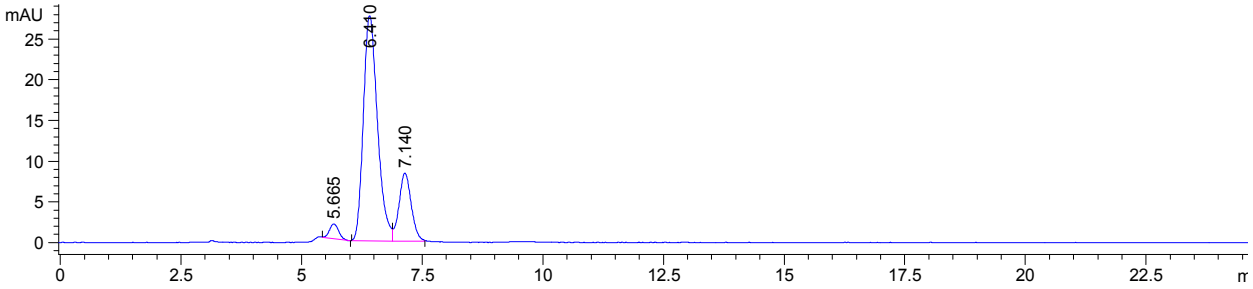
DAD1 B, Sig=254,8 Ref=360,100 (LEVI\HHD 2020-06-16 15-15-22\JLK-I-079_RAC85.D)



Signal 2: DAD1 B, Sig=254,8 Ref=360,100

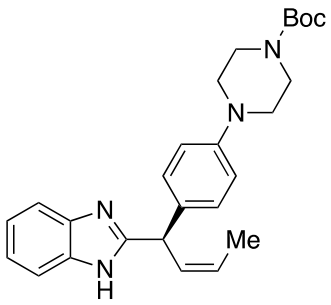
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.675	BB	0.2156	102.20571	7.28937	38.2547
2	6.421	BB	0.3087	114.56918	5.59960	42.8822
3	7.148	BB	0.2482	24.89992	1.48061	9.3198
4	10.136	BB	0.2429	25.49686	1.62604	9.5433

DAD1 B, Sig=254,8 Ref=360,100 (LEVI\HHD 2020-06-16 15-15-22\JLK-I-205.D)

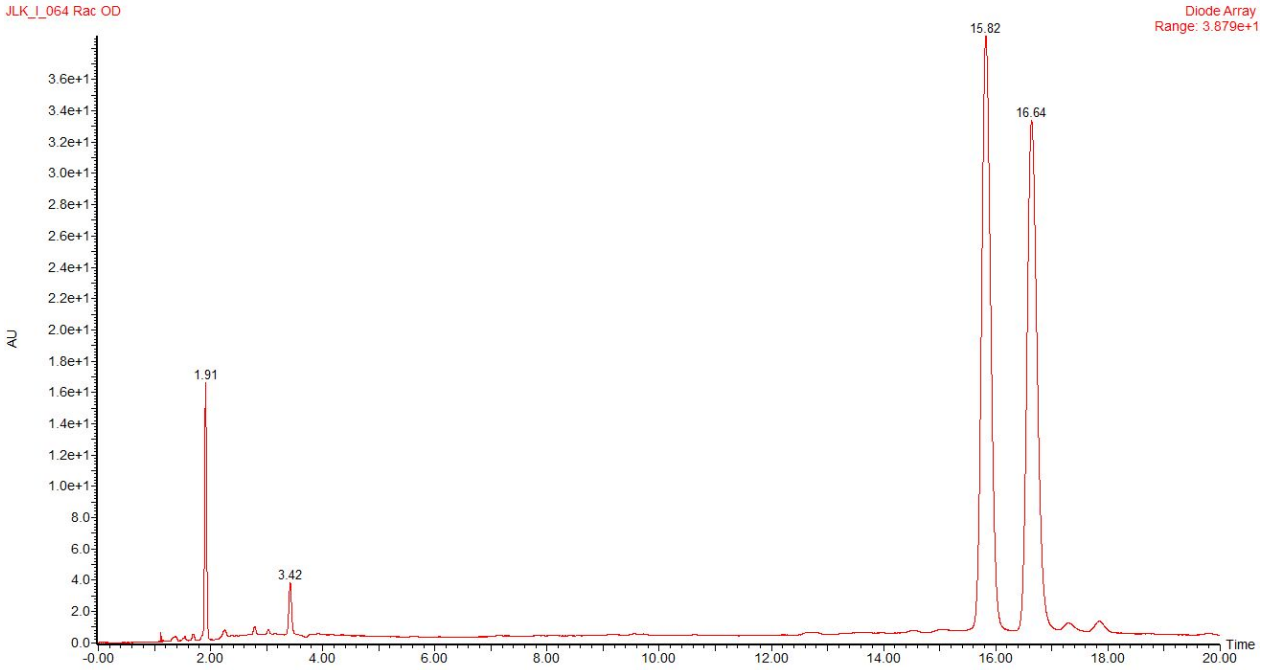


Signal 2: DAD1 B, Sig=254,8 Ref=360,100

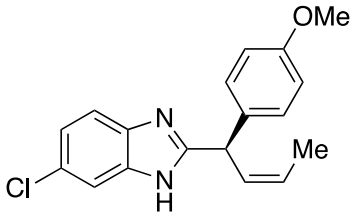
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.665	BB	0.2067	24.06004	1.81427	3.2743
2	6.410	BV	0.3137	562.95508	27.63331	76.6125
3	7.140	VB	0.2681	147.79326	8.36795	20.1132


Boc
N
N
N
N
H
Me

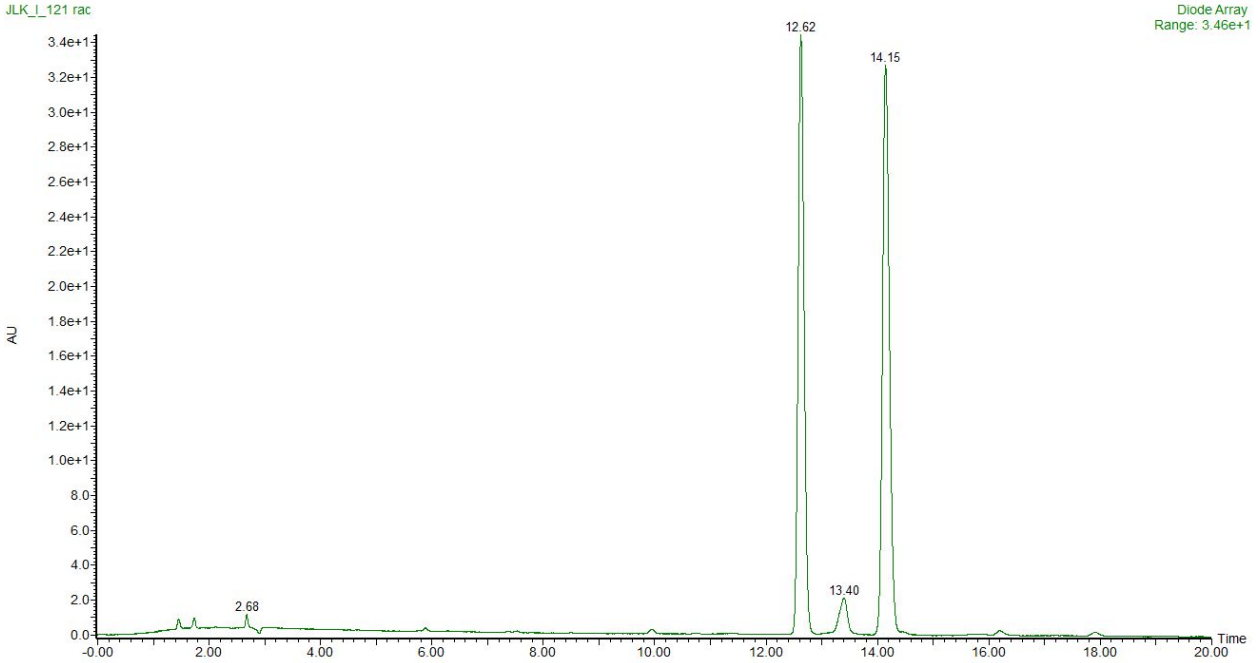
16

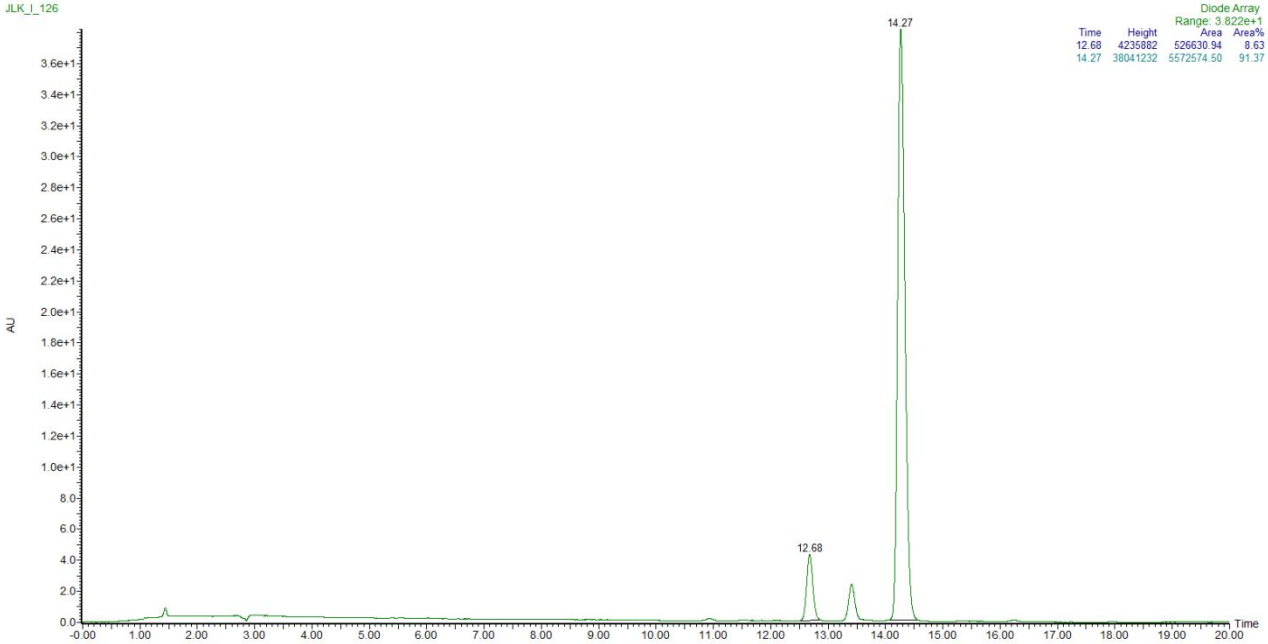

JLK_I_064 Rac OD
Diode Array
Range: 3.879e+1
15.82
16.64
1.91
3.42
AU
Time

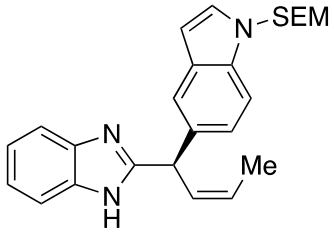

JLK_I_139 OD
Diode Array
Range: 3.068e+1
Time Height Area Area%
15.84 1455783 267880.81 4.12
16.64 30223178 6233031.00 95.88
16.64
15.84
AU
Time


OMe
N
Me
N
H
Cl

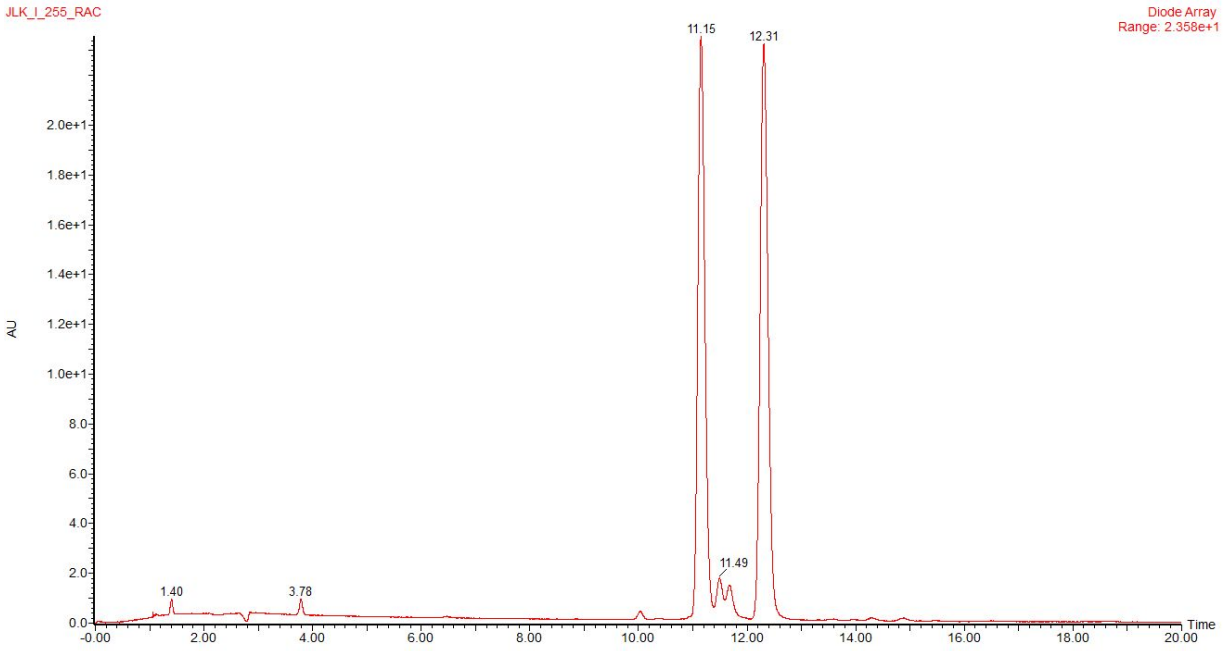
17

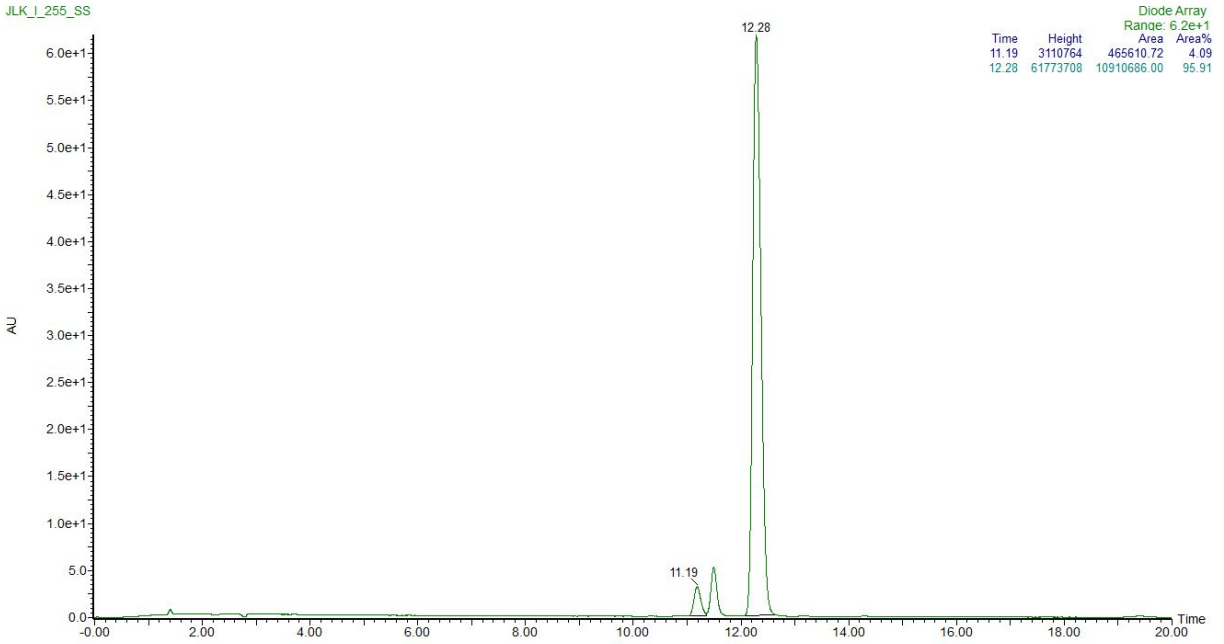

JLK_I_121 rac
Diode Array
Range: 3.46e+1
12.62
14.15
13.40
2.68
AU
Time

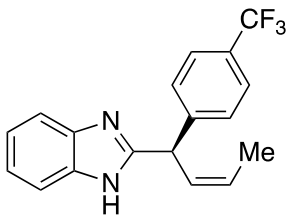

JLK_I_126
Diode Array
Range: 3.822e+1
Time Height Area Area%
12.68 4235882 526630.94 8.63
14.27 38041232 5572574.50 91.37
14.27
12.68
AU
Time


N
SEM
N
H
Me

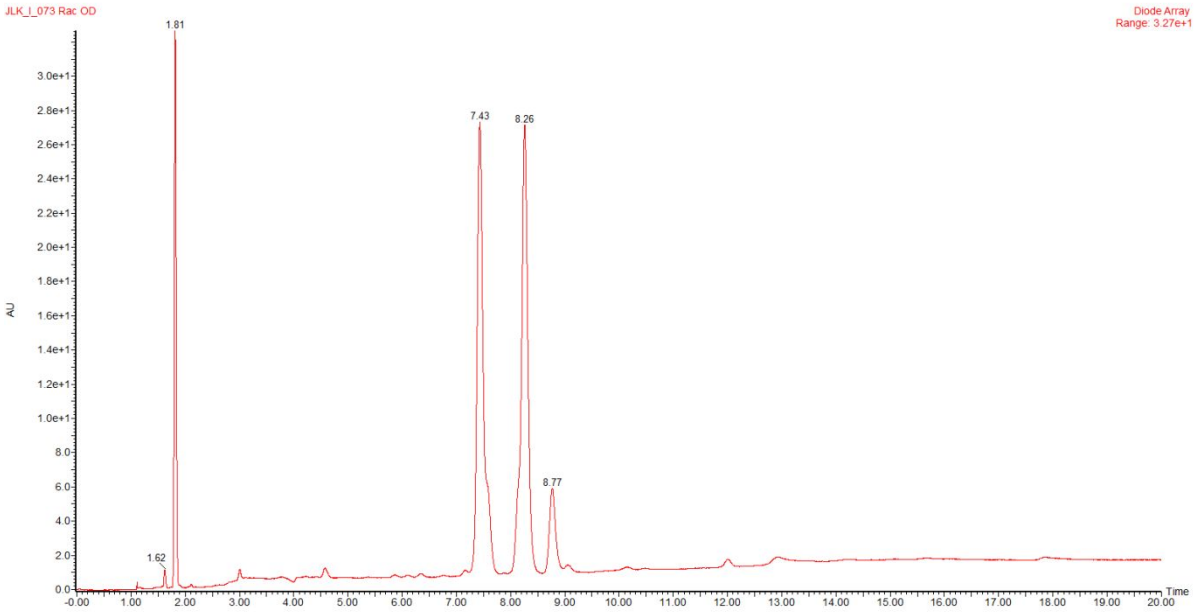
18

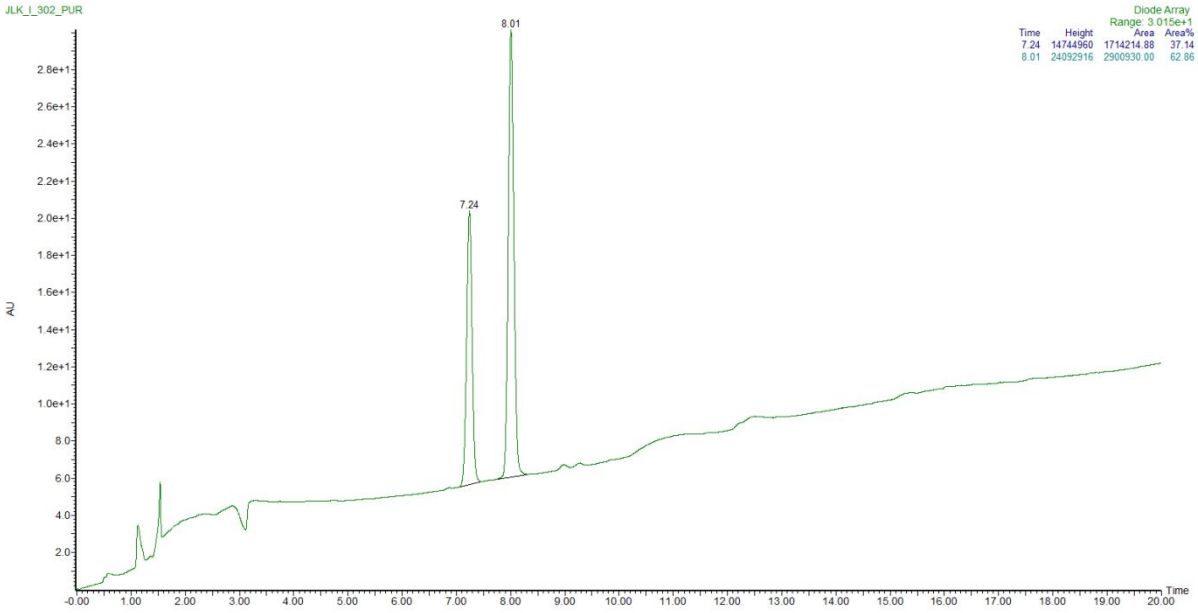

JLK_I_255_RAC
Diode Array
Range: 2.358e+1
11.15
12.31
11.49
1.40
3.78
AU
Time

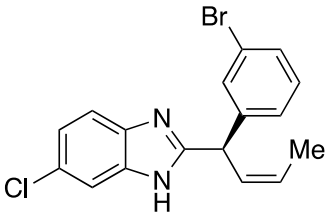

JLK_I_255_SS
Diode Array
Range: 6.2e+1
Time Height Area Area%
11.19 3110764 465610.72 4.09
12.28 61773708 10910686.00 95.91
12.28
11.19
AU
Time


CF3
N
N
H
Me

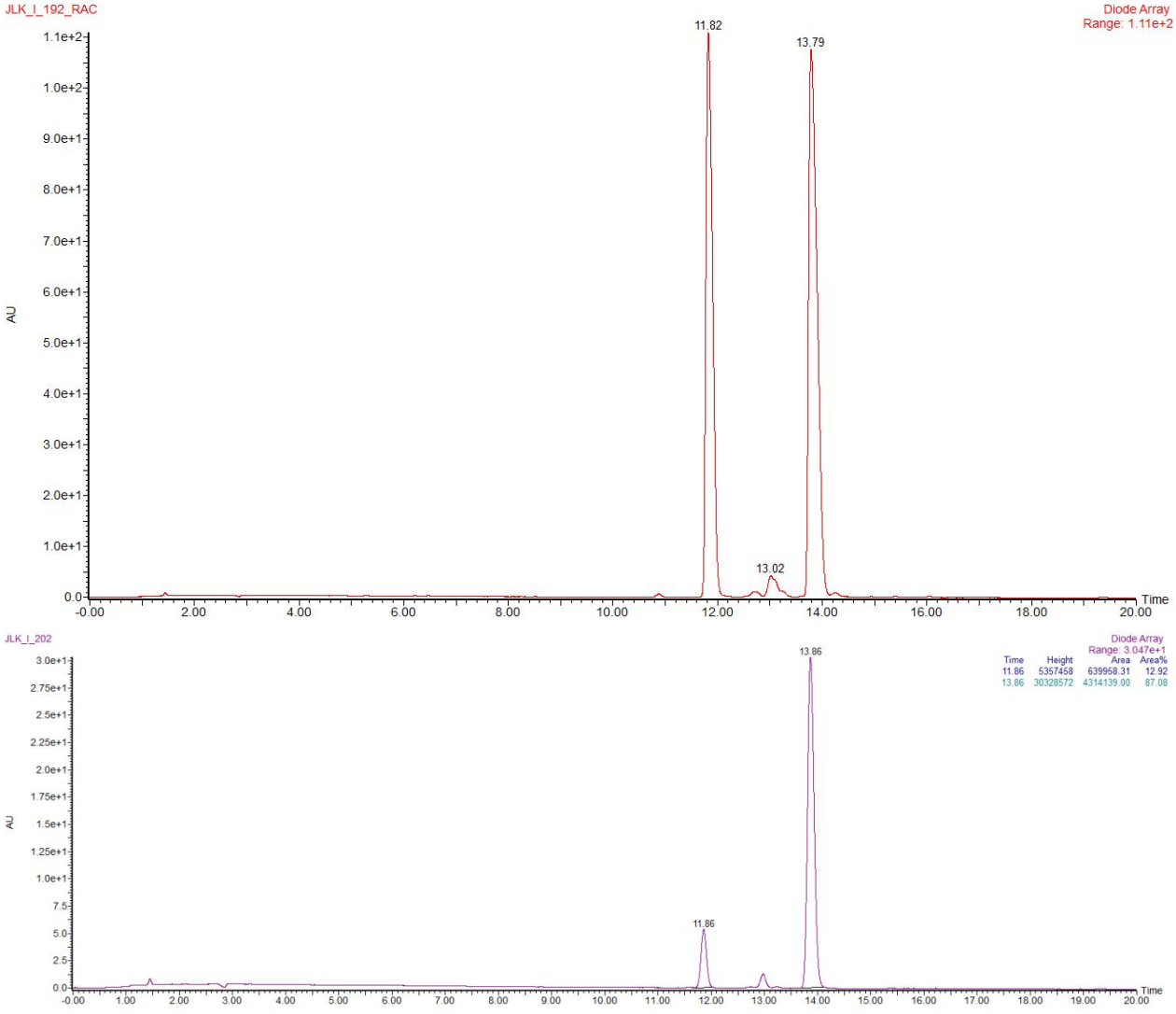
19

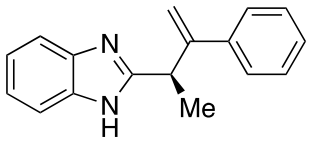

JLK_I_073 Rac OD
Diode Array
Range: 3.27e+1
1.81
7.43
8.26
8.77
1.62
AU
Time


JLK_I_302_PUR
Diode Array
Range: 3.015e+1
Time Height Area Area%
7.24 14744960 1714214.88 37.14
8.01 24092916 2900930.00 62.86
8.01
7.24
AU
Time

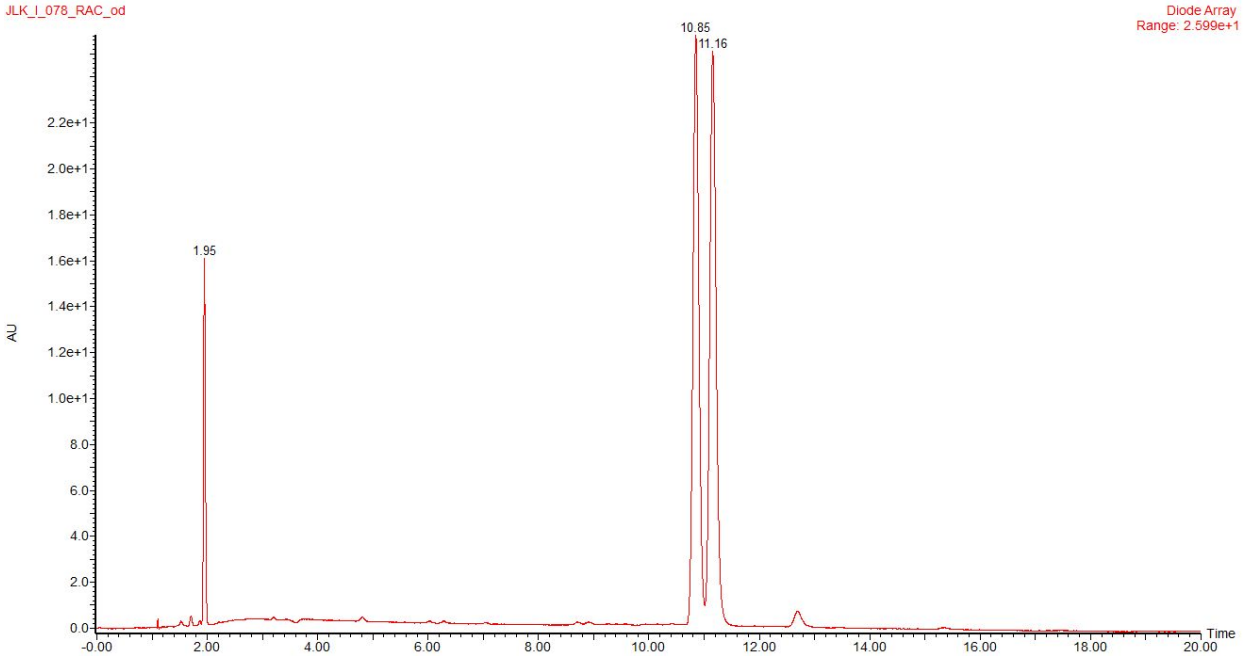

Br
N
Me
Cl
N
H

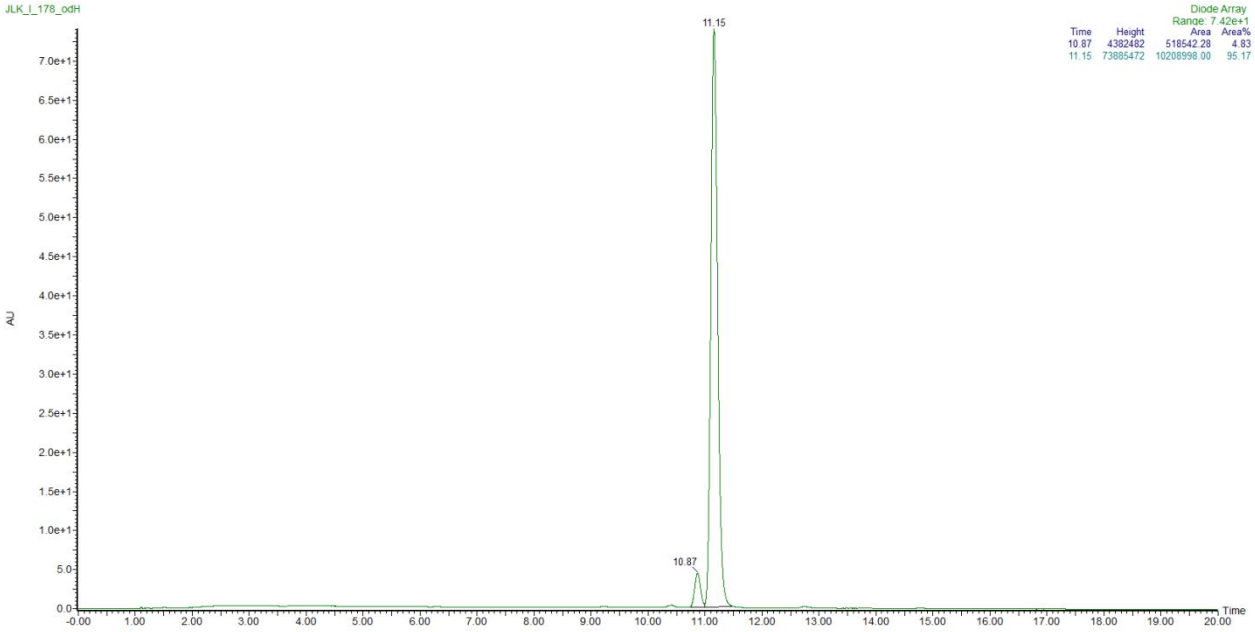
20

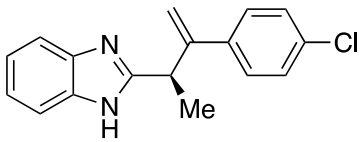

JLK_I_192_RAC
Diode Array
Range: 1.11e+2
11.82
13.79
13.02
AU
Time
JLK_I_202
Diode Array
Range: 3.047e+1
Time Height Area Area%
11.86 5357458 639958.31 12.92
13.86 30328572 4314139.00 87.08
13.86
11.86
AU
Time


N
N
H
Me

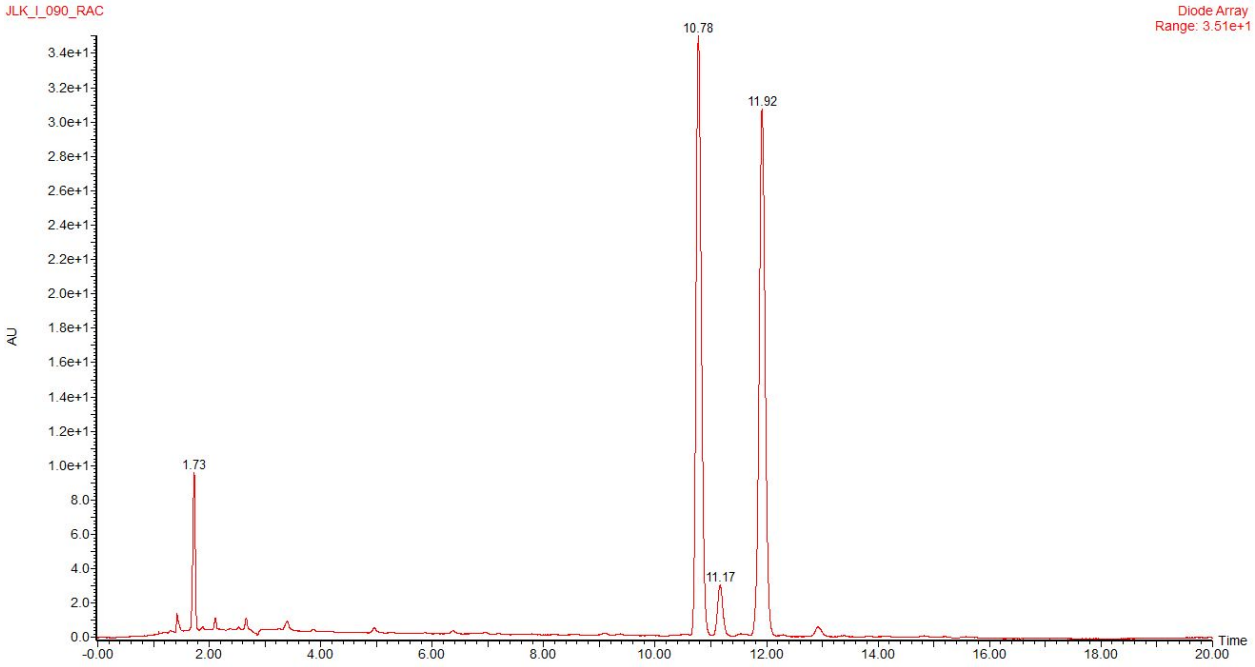
21

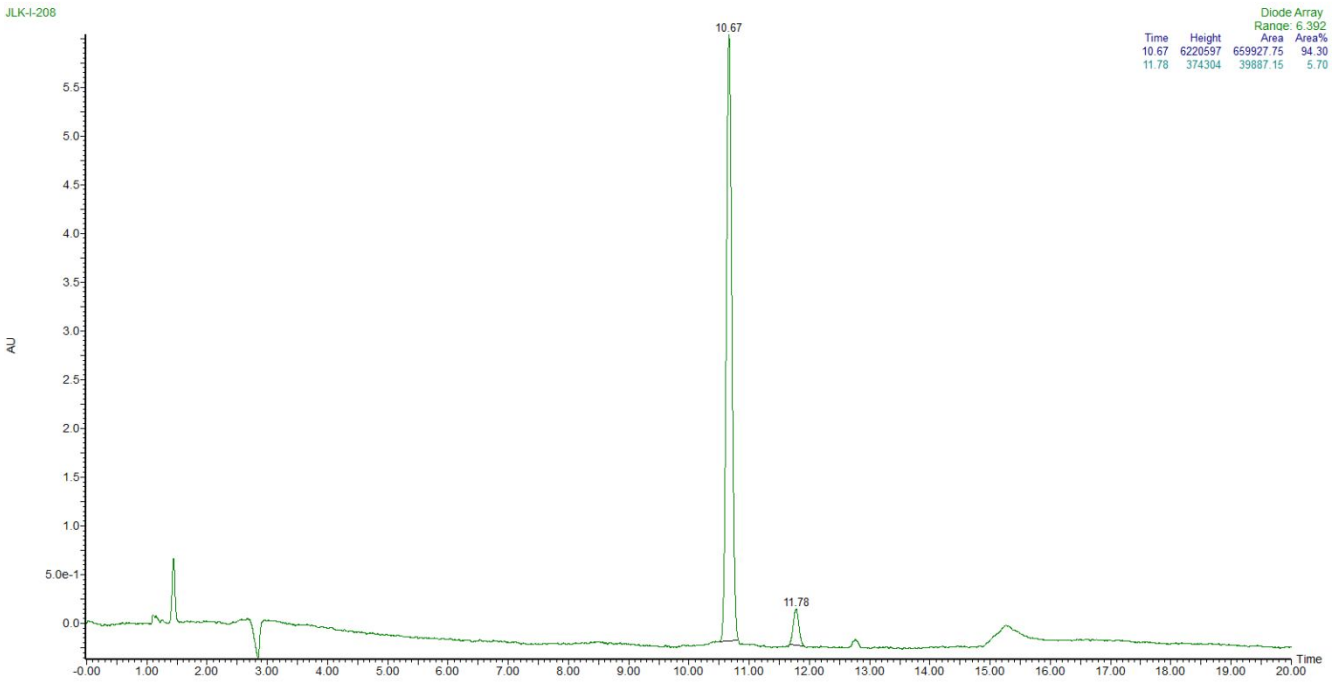

JLK_I_078_RAC_od
Diode Array
Range: 2.599e+1
10.85
11.16
1.95
AU
Time

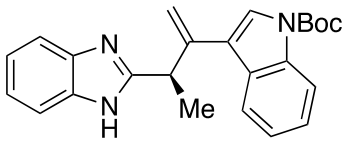

JLK_I_178_odH
Diode Array
Range: 7.42e+1
Time Height Area Area%
10.87 4382482 518542.28 4.83
11.15 73885472 10208998.00 95.17
11.15
10.87
AU
Time


N
N
H
Me
Cl

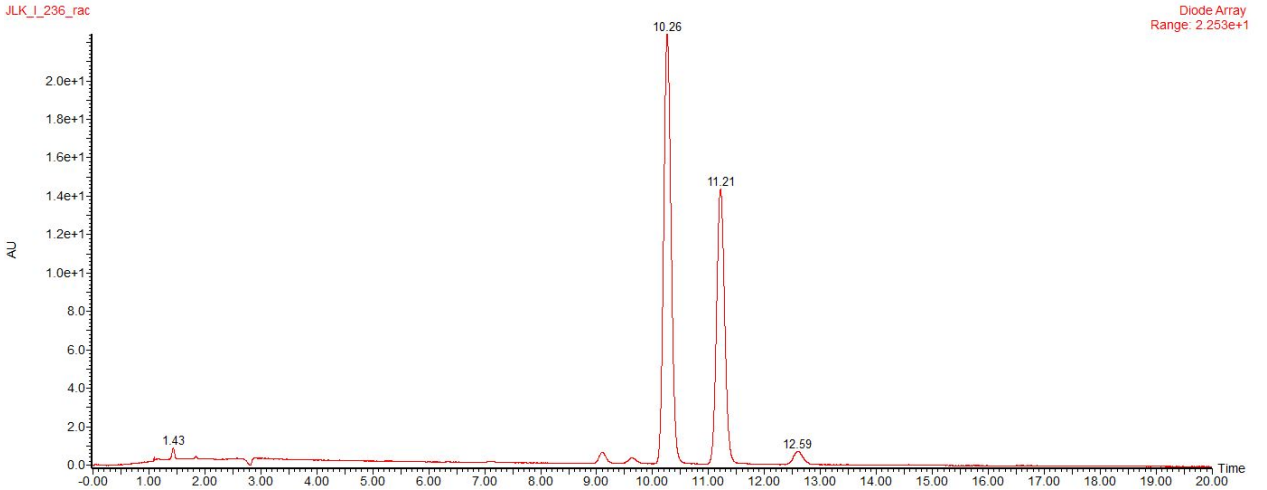
22

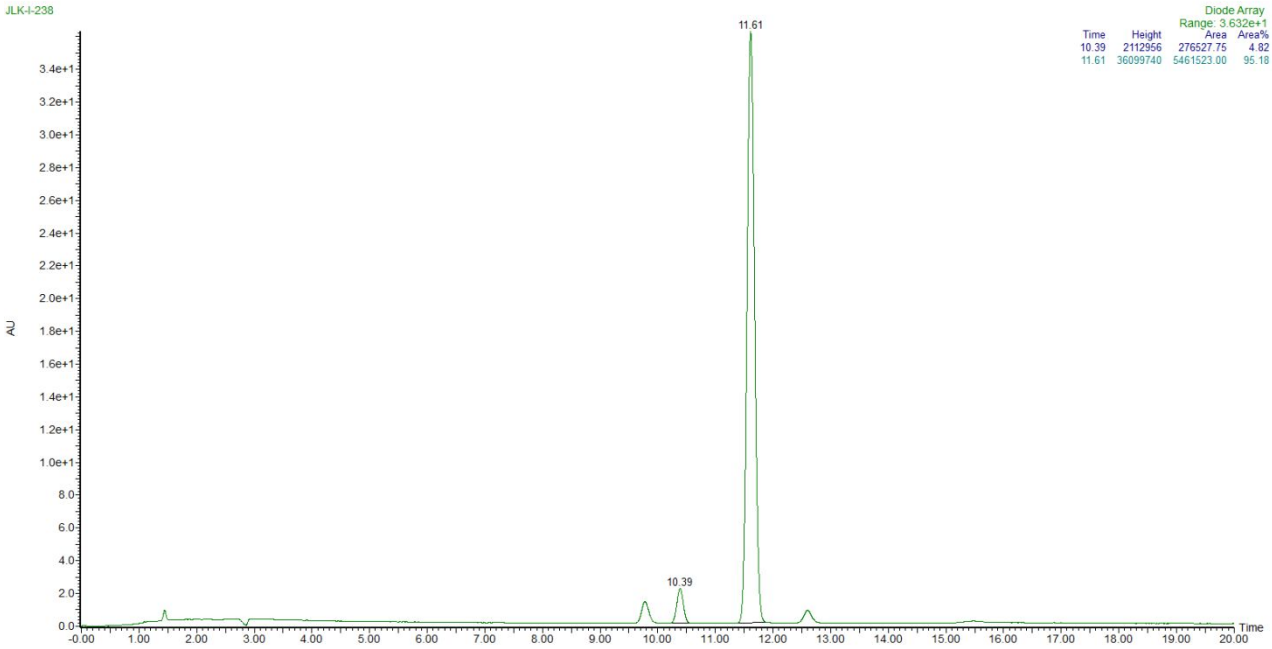

JLK_I_090_RAC
Diode Array
Range: 3.51e+1
10.78
11.92
1.73
11.17
AU
Time

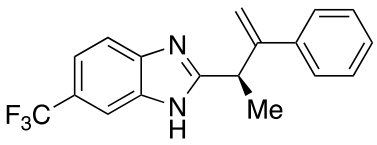

JLK-I-208
Diode Array
Range: 6.392
Time Height Area Area%
10.67 6220597 659927.75 94.30
11.78 374304 39887.15 5.70
10.67
11.78
AU
Time


N
N
H
Me
NBoc

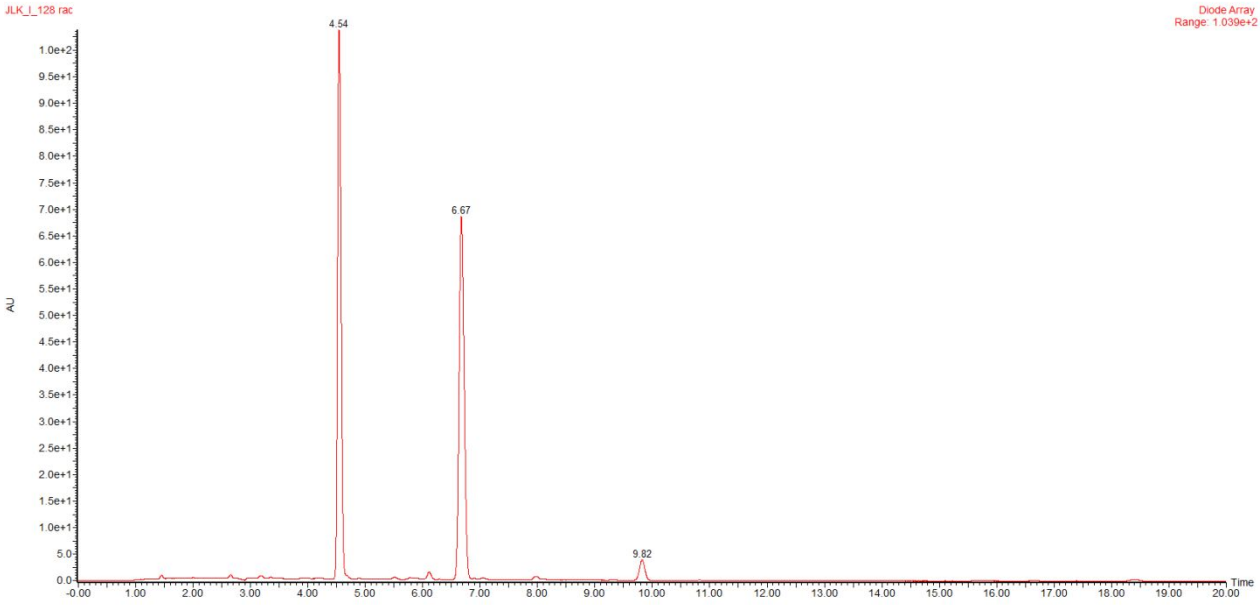
23

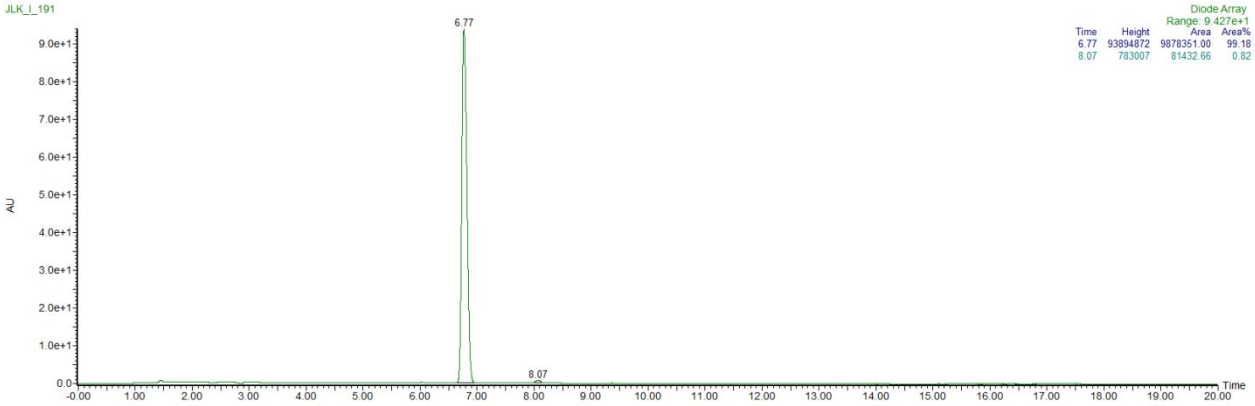

JLK_I_236_rac
Diode Array
Range: 2.253e+1
10.26
11.21
1.43
12.59
AU
Time

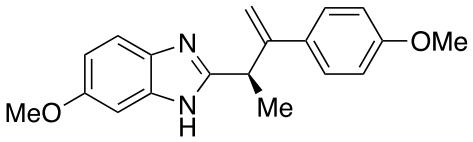

JLK-I-238
Diode Array
Range: 3.632e+1
Time Height Area Area%
10.39 2112956 276527.75 4.82
11.61 36099740 5461523.00 95.18
11.61
10.39
AU
Time


N
N
H
Me
F3C

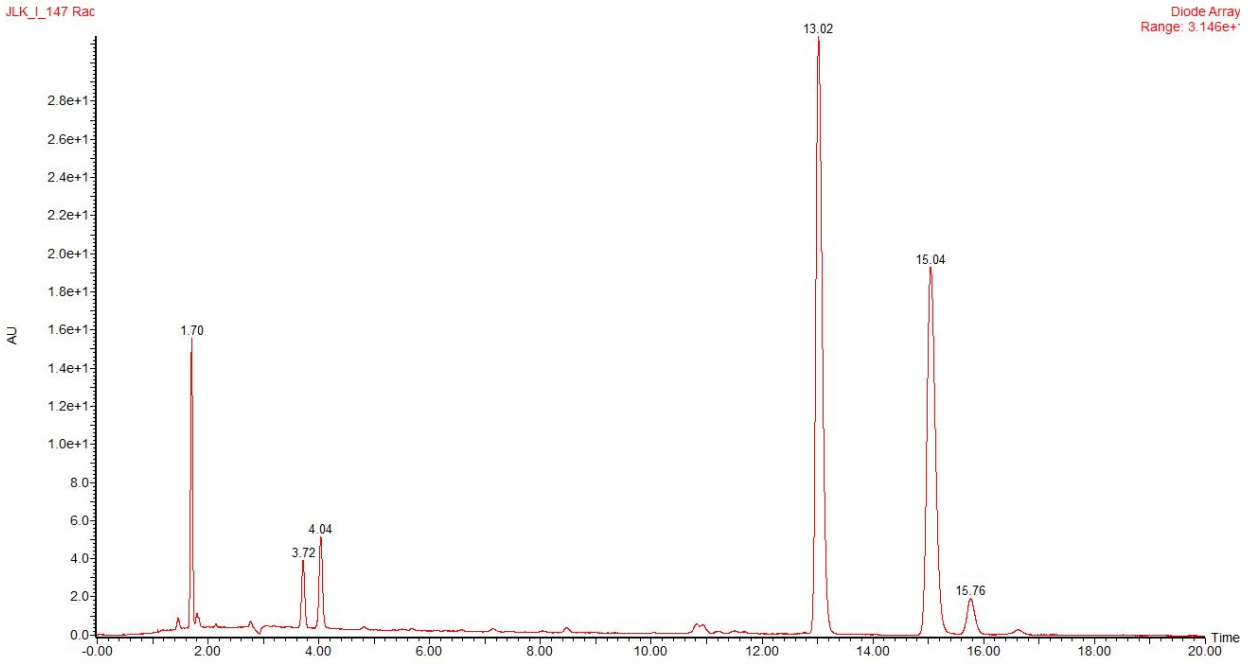
24


JLK_I_128 rac
Diode Array
Range: 1.039e+2
4.54
6.67
9.82
AU
Time


JLK_I_191
Diode Array
Range: 9.427e+1
Time Height Area Area%
6.77 93894872 9878351.00 99.18
8.07 783007 81432.66 0.82
6.77
8.07
AU
Time


N
N
H
MeO
Me
OMe

25


JLK_I_147 Rac
Diode Array
Range: 3.146e+
AU
1.70
3.72
4.04
13.02
15.04
15.76
Time


JLK_I_162
Diode Array
Range: 6.543e+1
Time Height Area Area%
12.81 65202760 9625024.00 93.65
15.08 3393615 652743.50 6.35
AU
12.81
15.08
Time