Supporting Information

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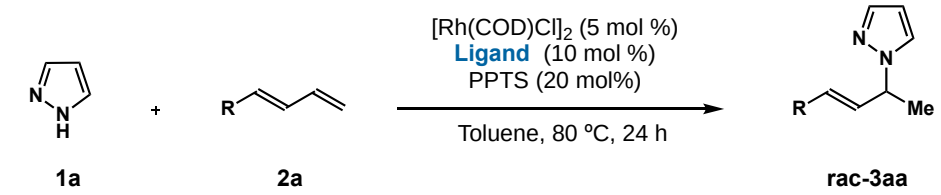
1. General

Commercial reagents were purchased from Sigma Aldrich, Strem, Alfa Aesar, Acros Organics, and Combi-blocks. Anhydrous cyclopentylmethyl ether (CPME) was purchased from Sigma Aldrich, degassed by three freeze-pump-thaw cycles, and stored within a N_2-filled glove box. All experiments were performed in oven-dried or flame-dried glassware. Reactions were monitored using either thin-layer chromatography (TLC) or gas chromatography using an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Purification and isolation of products were performed via silica gel chromatography (both column and preparative thin-layer chromatography). Column chromatography was performed with Silicycle Silia-P Flash Silica Gel using glass columns. Reversed-phase high-performance liquid chromatography was carried out using an Agilent 1100 HPLC-MSD system consisting of a 6130B single quadrupole mass-selective detector (MSD), G1315B diode array detector, G2258A autosampler, two G1361A preparative pumps, one G1379A quaternary pump with degasser, one G1312A binary pump, and three G1364B fraction collectors from Agilent Technologies. System control and data analysis was performed using Agilent's ChemStation software, revision B.03.01-SR.1. A Waters XBridge C18 OBD Prep Column, 100 Å, 5 µm, 19 mm × 150 mm column was used as the stationary phase (Waters Corporation). Gradient elution was carried out using water and acetonitrile as the mobile phase. An aqueous 10% trifluoroacetic acid or 10% ammonium hydroxide solution was teed into the mobile phase as a modifier using a static mixer prior to the column, pumped at 1% of the total mobile phase flow rate. ESI mass-triggered fraction collected was employed using positive ion polarity scanning to monitor for the target mass. Aqueous fractions were concentrated using a SP Industries, Inc. Genevac HT-12 Series 3i instrument. Solvents were purchased from Fisher. ^1H, ^2H, and ^{13}C NMR spectra were recorded on Bruker CRYO500 or DRX400 spectrometer. ^1H NMR spectra were internally referenced to the residual solvent signal or TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constant (Hz), integration. Data for ^2H and ^{13}C NMR are reported in terms of chemical shift (δ ppm). Infrared (IR) spectra were obtained on a Nicolet iS5 FT-IR spectrometer with an iD5 ATR and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI), an ABI/Sciex QStar Mass Spectrometer (ESI), or Waters LCT (TOF). Enantiomeric ratio for enantioselective reactions was determined by chiral SFC analysis using an Agilent Technologies HPLC (1200 series) system and Aurora A5 Fusion. 1,3-Dienes **2a-2l** were known compounds and synthesized according to reported methods.[1,2]

2. Optimization of the hydroamination of 1,3-diene (2a) with pyrazole (1a)

(1) Rhodium precatalyst evaluation

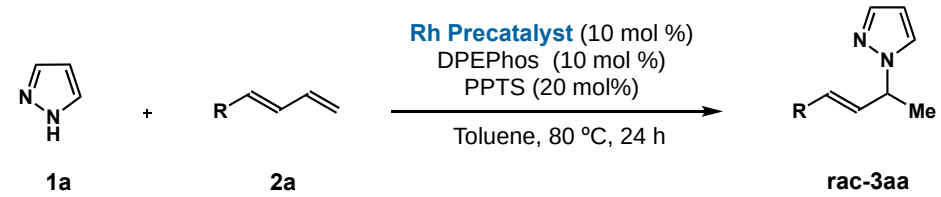
In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with Rh pre-catalyst (10 mol%), ligand (10 mol%), PPTS (20 mol%) and toluene (0.45 mL). The resulting mixture was stirred for 10 mins and then 1,3-diene (0.2 mmol) followed by a solution of freshly recrystallized pyrazole (0.1 mmol) were added. The mixture was stirred at 80 ºC and monitored by TLC or GCMS. Yields were obtained using ^{1}H NMR using trimethoxybenzene as an internal standard.



dppm	dppe	dppp	dppb	dppf
0% yield	0% yield	0% yield	0% yield	0% yield

Xantphos	DPEPhos	BINAP	PPh_3	PCy_3
0% yield	5% yield	0% yield	0% yield	0% yield

Figure S1. Achiral ligand evaluation with $[Rh(COD)Cl]_2$.



$[Rh(C_2H_4)_2Cl]_2$	$[Rh(COD)OMe]_2$	$[Rh(COE)Cl]_2$
0% yield	0% yield	0% yield

$Rh(COD)_2BF_4$	$Rh(NBD)_2BF_4$	$[Rh(COD)_2SbF_6$
0% yield	0% yield	0% yield

Figure S2. Rhodium pre-catalyst evaluation.

(2) Palladium precatalyst evaluation

In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with Pd precatalyst (10 mol%), ligand (10-15 mol%) and CPME (0.45 mL). The resulting mixture was stirred for 10 mins and then 1,3-diene (0.2 mmol) followed by a solution of freshly recrystallized pyrazole (0.1 mmol) were added. The mixture was stirred at 23 ºC and monitored by TLC or GCMS. Yields were obtained using ^{1}H NMR using trimethoxybenzene as an internal standard.

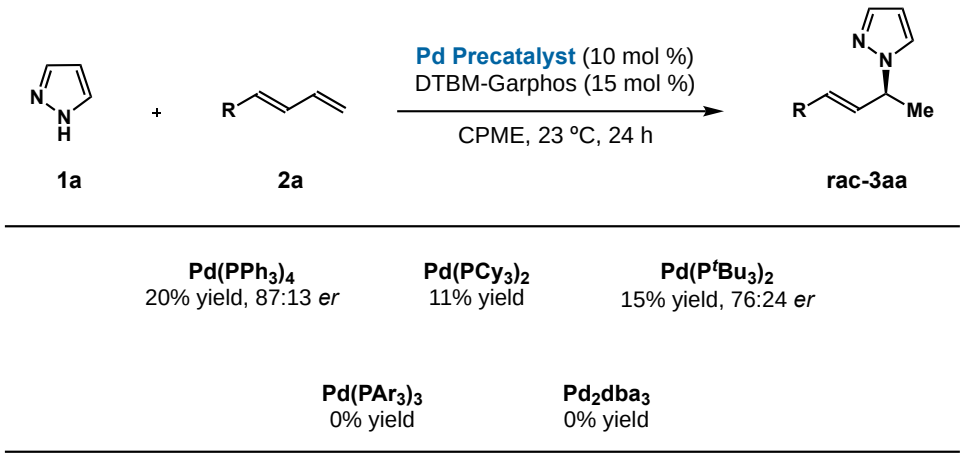


Figure S3. Pd(0) sources. Ar = 3,5-CF_3-Ph.

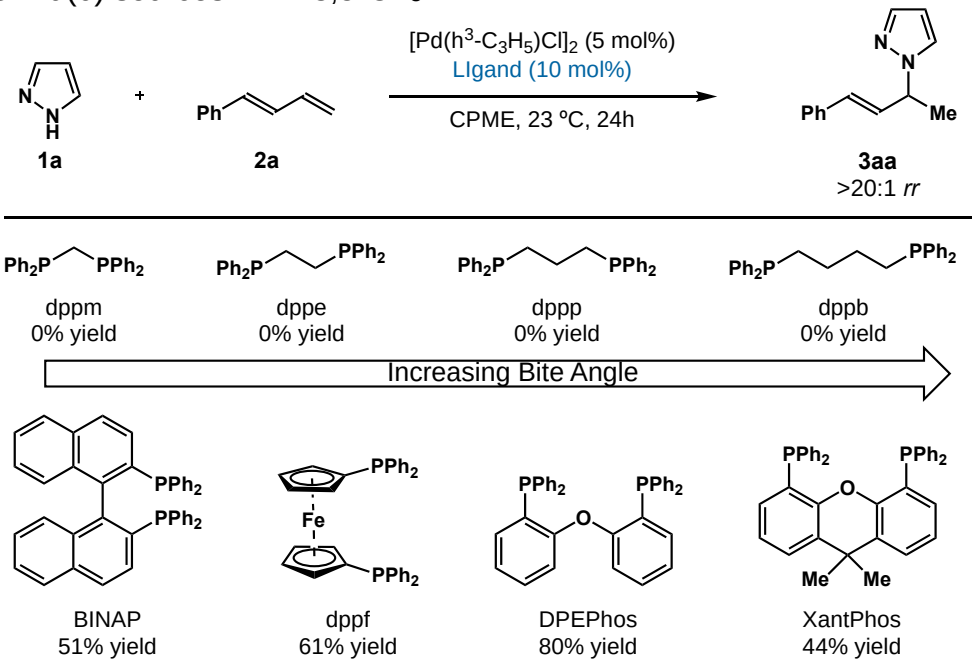
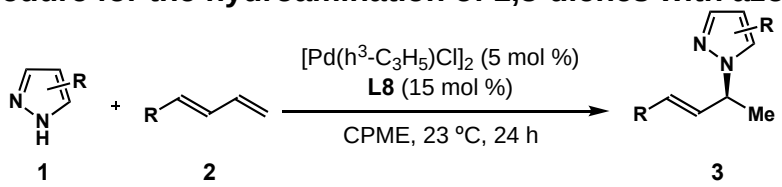


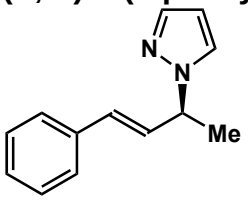
Figure S4. Achiral ligand screen with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$.

3. General procedure for the hydroamination of 1,3-dienes with azoles



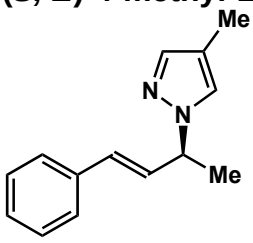
In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.8 mg, 5.0 µmol), MeO-BIPHEP **L8** (16.4 mg, 15.0 µmol) and CPME (0.3 mL). The resulting mixture was stirred for 10 mins and then 1,3-diene (500.0 µmol) followed by a solution of freshly recrystallized pyrazole (100.0 µmol) in CPME (0.1 mL) were added dropwise. The mixture was removed from the glovebox and stirred at 23 ºC until no starting material was observed by TLC or GCMS. Regioselectivity was determined by ^{1}H NMR analysis of the reaction prior to purification. Isolated yields (obtained by column chromatography or preparative thin-layer chromatography on silica gel using 10% EtOAc in Hexanes) of the title compounds are reported.

(*S*, *E*)-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3aa)



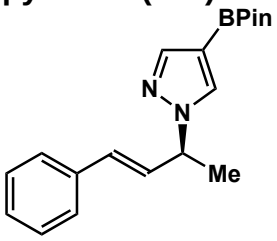
Colorless oil, 91% yield, 96:4 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -8.8 (*c* 0.62, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.4 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.40 (dd, *J* = 16.0, 6.4 Hz, 1H), 6.29 (t, *J* = 2.1 Hz, 1H), 5.12 (apparent p, *J* = 6.4 Hz, 1H), 1.73 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.15, 136.35, 131.53, 129.80, 128.72, 128.10, 127.31, 125.55, 105.55, 59.49, 20.93. **IR** (ATR) 3026, 2977, 2925, 1735, 1599, 1509 cm^{-1}. **HRMS** calculated for $C_{13}H_{14}N_2$ $[M]^+$ 198.1157, found 198.1158. **Chiral SFC:** 100 mm CHIRALCEL IC, 3.0% *i*PrOH, 3.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 6.9 min, t_{R2} (major) = 8.0 min.

(*S, E*)-4-methyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ab)



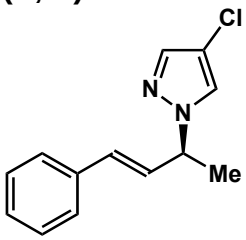
Colorless oil, 78% yield, 93:7 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -6.3 (*c* 1.5, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.7 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 8.1 Hz, 2H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.38 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.05 (apparent p, *J* = 6.7 Hz, 1H), 2.08 (s, 3H), 1.70 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.19, 136.30, 131.34, 129.81, 128.62, 127.97, 126.64, 126.21, 116.06, 59.25, 20.75, 8.99. **IR** (ATR): 3026, 2978, 2932, 965, 752, 692, 624. **HRMS** calculated for $C_{14}H_{16}N_2Na$ $[M+Na]^+$ 235.1209, found 235.1211. **Chiral SFC:** 150 mm CHIRALCEL AD-H, 10.0% *i*PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 3.3 min, t_{R2} (major) = 3.7 min.

(*S*, *E*)-1-(4-phenylbut-3-en-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (3ac)



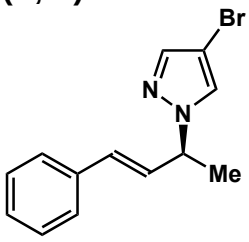
Separated using previously reported technique for boron-containing compounds.[3] Due to the nuclear quadrupole of the boron, the carbon directly bonded is not visible via ^{13}C NMR. Colorless oil, 92% NMR yield, 36% isolated yield due to purification difficulties, 95:5 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -6.3 (*c* 0.83, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.80 (s, 1H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.38 (dd, *J* = 15.9, 6.7 Hz, 1H), 5.11 (apparent p, *J* = 6.8 Hz, 1H), 1.72 (d, *J* = 6.9 Hz, 3H), 1.31 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.34, 136.16, 134.20, 131.79, 129.24, 128.62, 128.05, 126.66, 83.33, 59.37, 24.83, 20.83. **IR** (ATR): 2977, 1553, 1246, 1142, 985, 856, 752, 691. **HRMS** calculated for $C_{19}H_{25}BN_2O_2$ $[M]^+$ 324.2013, found 324.1994. **Chiral SFC:** 150 mm CHIRALCEL OJ-H, 2.0 % ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 3.1 min, t_{R2} (major) = 3.4 min.

(*S*, *E*)-4-chloro-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ad)



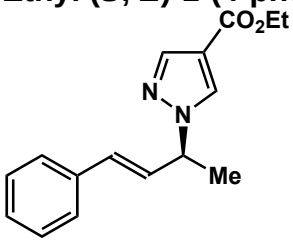
Colorless oil, 86% yield, 94:6 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -3.8 (*c* 0.94, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 5.1 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.34 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.02 (apparent p, *J* = 6.7 Hz, 1H), 1.70 (d, *J* = 6.9 Hz, 3H)**. ^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.50, 135.97, 132.07, 128.83, 128.70, 128.23, 126.69, 125.48, 109.88, 60.24, 20.56. **IR** (ATR): 3130, 2985, 1303, 965, 839, 752, 692, 612. **HRMS** calculated for $C_{13}H_{13}ClN_2$ $[M]^+$ 232.0767, found 232.0775. **Chiral SFC:** 150 mm CHIRALCEL OJ-H, 4.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 3.1 min, t_{R2} (major) = 3.4 min.

(*S*, *E*)-4-bromo-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ae)



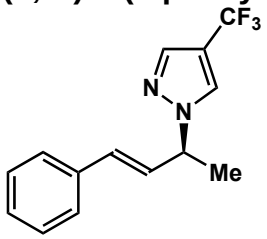
Colorless oil, 76% yield, 94:6 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -2.5 (*c* 1.9, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.8 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.34 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.05 (apparent p, *J* = 6.8 Hz, 1H), 1.71 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.65, 135.98, 132.12, 128.83, 128.70, 128.24, 127.62, 126.69, 93.00, 60.22, 20.61. **IR** (ATR): 3026, 2979, 1303, 969, 951, 840, 750, 691, 612. **HRMS** calculated for $C_{13}H_{13}BrN_2$ $[M]^+$ 276.0262, found 276.0250**. Chiral SFC:** 150 mm CHIRALCEL OJ-H, 2.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 6.0 min, t_{R2} (major) = 6.4 min.

Ethyl (*S*, *E*)-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole-4-carboxylate (3af)



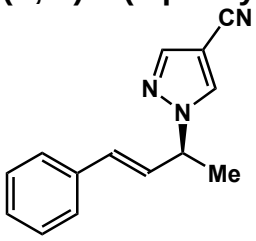
Colorless oil, 70% yield, 95:5 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -0.322 (*c* 1.9, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 14.1 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.36 (dd, *J* = 15.9, 6.8 Hz, 1H), 5.10 (dd, *J* = 13.5, 6.8 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.74 (d, *J* = 6.9 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.16, 140.94, 135.87, 132.43, 130.78, 128.71, 128.40, 128.30, 126.71, 115.05, 60.21, 60.07, 20.72, 14.45. **IR** (ATR): 2980, 1711, 1551, 1227, 1205, 1174, 1025, 970, 767, 751, 692. **HRMS** calculated for $C_{16}H_{18}N_2O_2$ $[M]^+$ 270.1368, found 270.1380. **Chiral SFC:** 150 mm CHIRALCEL AD-H, 5.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 7.2 min, t_{R2} (major) = 8.7 min.

(*S, E*)-1-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)-1*H*-pyrazole (3ag)



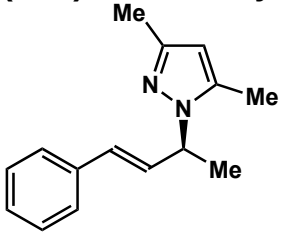
Colorless oil, 73% yield, 92:8 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -6.3 (*c* 1.6, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.37 (dd, *J* = 16.0, 6.9 Hz, 1H), 5.10 (apparent p, *J* = 6.8 Hz, 1H), 1.75 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.87 (q, *J* = 2.6 Hz), 135.75, 132.62, 128.77, 128.42, 128.22, 126.78, 126.74, 122.74 (q, *J* = 265.9 Hz), 113.46 (q, *J* = 38.2 Hz), 60.22, 20.76. **IR** (ATR): 2984, 1574, 1184, 1112, 966, 752, 692, 682**. HRMS** calculated for $C_{14}H_{13}F_3N_2$ $[M]^+$ 266.1031, found 266.1040. **Chiral SFC:** 150 mm CHIRALCEL OD-H, 1.0% ^{i}PrOH, 1.5 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 3.9 min, t_{R2} (minor) = 4.4 min.

(*S*, *E*)-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole-4-carbonitrile (3ah)



Colorless oil, 64% yield, 88:12 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -8.9 (*c* 0.99, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.84 (s, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.1 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.34 (dd, *J* = 16.0, 6.9 Hz, 1H), 5.11 (apparent p, *J* = 6.9 Hz, 1H), 1.75 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.28, 135.51, 133.15, 132.62, 128.82, 128.59, 127.52, 126.76, 113.65, 92.17, 60.66, 20.73. **IR** (ATR): 3136, 2924, 2236, 1541, 1354, 1149, 968, 876, 754, 693, 632. **HRMS** calculated for $C_{14}H_{13}N_3$ $[M]^+$ 223.1109, found 223.1117. **Chiral SFC:** 150 mm CHIRALCEL OD-H, 1.0% ^{i}PrOH, 1.5 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 26.0 min, t_{R2} (minor) = 28.9 min.

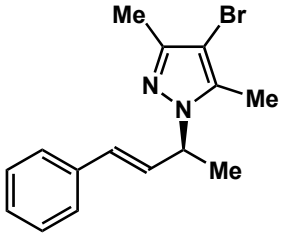
(*S*, *E*)-3,5-dimethyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ai)



Colorless oil, 69% yield, 89:11 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = +26.1 (*c* 0.15, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.42 (dd, *J* = 16.0, 6.5 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 5.82 (s, 1H), 4.94 (apparent p, *J* = 6.7 Hz, 1H), 2.27 (d, *J* = 4.5 Hz, 6H), 1.72 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.29, 138.65, 136.47, 130.41, 130.29,

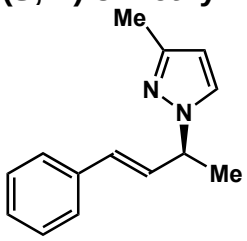
128.55, 127.75, 126.59, 105.34, 55.93, 20.62, 13.62, 11.24. **IR** (ATR): 3026, 2979, 2931, 1552, 1448, 1419, 965, 777, 748, 693. **HRMS** calculated for $C_{15}H_{18}N_2Na$ $[M+Na]^+$ 249.1368, found 249.1367. **Chiral SFC:** 150 mm CHIRALCEL AD-H, 5.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 2.9 min, t_{R2} (major) = 4.5 min.

(*S*, *Z*)-4-bromo-3,5-dimethyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3aj)



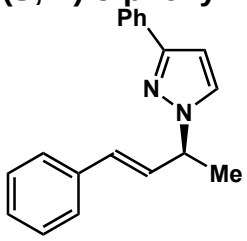
Colorless oil, 29% yield, 97:3 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -42.4 (*c* 0.755, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.42 – 6.28 (m, 2H), 4.95 (dq, *J* = 6.9, 4.5 Hz, 1H), 2.26 (d, *J* = 10.6 Hz, 6H), 1.70 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.91, 136.66, 136.22, 130.61, 129.82, 128.63, 127.94, 126.60, 94.38, 57.12, 20.38, 12.54, 10.49. **IR** (ATR): 3029, 2983, 2919, 1057, 966, 756, 695. **HRMS** calculated for $C_{15}H_{17}BrN_2$ $[M]^+$ 304.0575, found 304.0574. **Chiral SFC:** 150 mm CHIRALCEL AD-H, 10.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 1.9 min, t_{R2} (major) = 2.1 min.

(*S*, *E*)-3-methyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ak)



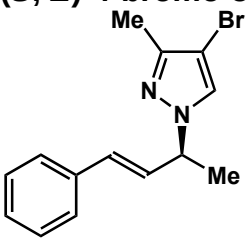
Colorless oil, 89% yield, 93:7 *er*, >20:1 *rr,* 11:1 *N*^{1}:*N*^{2}, $[\alpha]^{24}_D$ = -17.2 (*c* 0.12, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 3H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.38 (dd, *J* = 16.0, 6.5 Hz, 1H), 6.05 (d, *J* = 2.1 Hz, 1H), 5.05 (apparent p, *J* = 6.8 Hz, 1H), 2.32 (s, 3H), 1.70 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.19, 136.33, 131.35, 129.79, 128.62, 127.96, 127.92, 126.64, 105.08, 59.13, 20.84, 13.61. **IR** (ATR): 2979, 2929, 1520, 1447, 1199, 1051, 983, 964, 749, 692. **HRMS** calculated for $C_{14}H_{16}N_2$ $[M]^+$ 121.1313, found 212.1319. **Chiral SFC:** 150 mm CHIRALCEL AD-H, 10.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 1.7 min, t_{R2} (major) = 2.1 min.

(*S*, *E*)-3-phenyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3al)



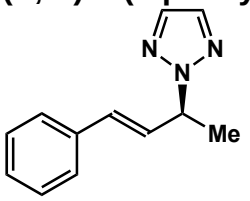
Colorless oil, 83% yield, 94:6 *er*, >20:1 *rr*, >20:1 *N*^{1}:*N*^{2}, $[\alpha]^{24}_D$ = -15.5 (*c* 2.0, CH_2Cl_2). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.50 (s, 1H), 7.40 (t, *J* = 8.1 Hz, 4H), 7.31 (m, 3H), 7.26 (t, *J* = 7.1 Hz, 1H), 6.59 (s, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.46 (dd, *J* = 16.0, 6.2 Hz, 1H), 5.17 (apparent p, *J* = 6.7 Hz, 1H), 1.78 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** δ 151.14, 136.33, 133.81, 131.42, 129.77, 128.66, 128.62, 128.44, 128.01, 127.52, 126.66, 125.71, 102.83, 59.57, 20.93. **IR** (ATR): 3027, 2978, 2932, 1496, 1457, 964, 747, 691. **HRMS** calculated for $C_{19}H_{18}N_2Na$ $[M+Na]^+$ 297.1368, found 297.1368. **Chiral SFC:** 150 mm CHIRALCEL OJ-H, 10.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 11.729 min, t_{R2} (minor) = 14.144 min.

(*S*, *E*)-4-bromo-5-methyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3am)



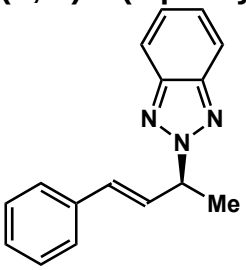
Colorless oil, 82% yield, 93:7 *er*, >20:1 *rr*, >20:1 N^1:N^2, $[\alpha]^{24}_D$ = -3.6 (*c* 2.1, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.33 (dd, *J* = 16.0, 6.6 Hz, 1H), 4.97 (apparent p, *J* = 6.8 Hz, 1H), 2.26 (s, 3H), 1.68 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.07, 136.09, 131.86, 129.11, 128.67, 128.14, 127.86, 126.67, 93.56, 59.91, 20.64, 12.02. **IR** (ATR): 3026, 2979, 2928, 1151, 1056, 963, 752, 692. **HRMS** calculated for $C_{14}H_{15}BrN_2$ $[M]^+$ 290.0419, found 290.0421. **Chiral SFC:** 150 mm CHIRALCEL AD-H, 5.0 % ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 3.792 min, t_{R2} (major) = 4.311 min.

(*S*, *E*)-2-(4-phenylbut-3-en-2-yl)-2*H*-1,2,3-triazole (3an)



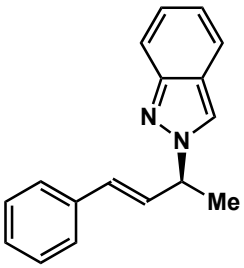
White crystalline solid, 70% yield, 91:9 *er*, >20:1 *rr,* >20:1 N^2:N^1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (s, 2H), 7.37 (m, 2H), 7.30 (m, 2H), 7.24 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.46 (dd, *J* = 16.0, 7.1 Hz, 1H), 5.44 (dp, *J* = 6.9, 0.6 Hz, 1H), 1.80 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.11, 133.96, 132.01, 128.61, 128.59, 128.08, 126.71, 62.89, 20.72. **IR** (ATR): 3026, 2984, 2935, 1332, 961, 815, 751, 691. **HRMS** calculated for $C_{12}H_{14}N_3H$ $[M+H]^+$ 200.1188, found 200.1190. **Chiral SFC:** 150 mm CHIRALCEL AD-H, 5.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 2.118 min, t_{R2} (major) = 2.654 min.

(*S*, *E*)-2-(4-phenylbut-3-en-2-yl)-2*H*-benzo[*d*][1,2,3]triazole (3ao)



White crystalline solid, 85% yield, 52:48 *er*, >20:1 *rr,* 1.2:1 N^2:N^1. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.60 (dd, *J* = 16.0, 7.1 Hz, 1H), 5.72 (apparent p, *J* = 6.9 Hz, 1H), 1.95 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.20, 135.95, 132.74, 128.63, 128.23, 128.19, 126.80, 126.29, 118.16, 64.83, 21.20. **IR** (ATR): 2985, 2933, 1269, 1038, 975, 748, 692. **HRMS** calculated for $C_{16}H_{15}N_3$ $[M]^+$ 249.1266, found 249.1277. **Chiral SFC:** 150 mm CHIRALCEL AD-H, 10.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 3.216 min, t_{R2} (major) = 4.245 min.

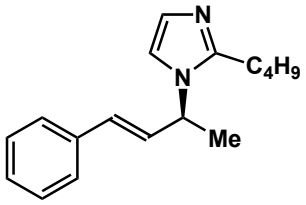
(*S*,*E*)-2-(4-phenylbut-3-en-2-yl)-2*H*-indazole (3ap)



White crystalline solid, 69% yield, 65:35 *er*, >20:1 *rr*, 1.2:1 N^1:N^2. $[\alpha]^{24}_D$ = -3.5 (*c* 0.75, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.22 (m, 4H), 7.09 (dd, *J* = 7.9, 7.2 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.53 (dd, *J* = 15.9, 6.4 Hz, 1H), 5.39 (apparent p, *J* = 6.7 Hz, 1H), 1.88 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.66, 136.06, 132.15, 129.07, 128.68, 128.20, 126.73, 125.89, 121.75, 121.68, 120.85, 120.24, 117.64, 61.10, 21.29. **IR** (ATR): 3117, 2924, 1154, 1126, 963, 788, 753, 739, 698. **HRMS** calculated for $C_{17}H_{16}N_2$ $[M]^+$ 248.1313, found

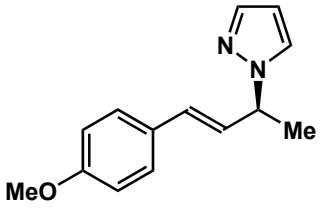
248.1306. **Chiral SFC:** 150 mm CHIRALCEL AD-H, 15.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 5.2 min, t_{R2} (major) = 6.9 min.

(S, E)-2-butyl-1-(4-phenylbut-3-en-2-yl)-1H-imidazole (3aq)



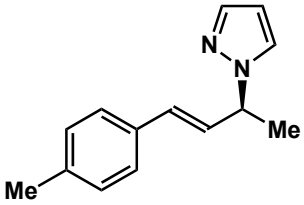
Off-white crystalline solid (isolated as trifluoroacetic acid salt) obtained by preparative HPLC (reverse phase C18, acetonitrile/water with 0.1% trifluoroacetic acid modifier), 76% yield, 70:30 *er*, >20:1 *rr*. **^{1}H NMR** (600 MHz, CD3CN) δ 7.43 (s, 1H), 7.42 (s, 1H), 7.38 – 7.37 (m, 1H), 7.36 – 7.35 (m, 1H), 7.35 (s, 1H), 7.34 (s, 1H), 7.31 – 7.28 (m, 1H), 6.56 (d, *J* = 16.1 Hz, 1H), 6.41 (dd, *J* = 16.0, 6.1 Hz, 1H), 5.21 (p, *J* = 6.1 Hz, 1H), 3.03 (td, *J* = 7.4, 1.8 Hz, 2H), 1.73 (p, *J* = 7.7 Hz, 2H), 1.68 (d, *J* = 6.9 Hz, 3H), 1.38 (h, *J* = 7.2 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, CD_3CN) δ 161.36 (q, J = 34.1 Hz), 148.14, 136.77, 133.27, 129.71, 129.34, 128.43, 127.59, 119.97, 119.43, 117.94 (q, J = 293.7 Hz), 55.70, 29.93, 25.18, 22.76, 20.85, 13.74. **LRMS** calculated for C17H23N2 $[M+H]^+$ 255, found 255. **Chiral SFC**: 100 mm Lux-2, 30% MeOH with 0.1% NH4OH, 3.5 mL/min, outlet pressure = 138 bar, tR1 (minor) = 0.69 min, tR2 (major) = 0.78 min.

(*S*, *E*)-1-(4-(4-methoxyphenyl)but-3-en-2-yl)-1*H*-pyrazole (3ba)



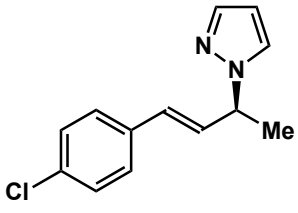
White solid, 82% yield, 96:4 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -53.7 (*c* 0.19, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.8 Hz, 1H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.33 – 7.28 (m, 2H), 6.87 – 6.82 (m, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.30 – 6.23 (m, 2H), 5.08 (apparent p, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 1.71 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.60, 139.12, 130.96, 129.11, 127.92, 127.62, 127.20, 114.12, 105.42, 59.55, 55.42, 21.03. **IR** (ATR) 2982, 2933, 2836, 1734, 1672, 1610, 1510 cm^{-1}. **HRMS** calculated for $C_{14}H_{16}N_2ONa$ $[M+Na]^+$ 251.1160, found 251.1170. **Chiral SFC:** 100 mm CHIRALCEL AD-H, 8.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 3.4 min, t_{R2} (major) = 4.2 min.

(*S*, *E*)-1-(4-(*p*-tolyl)but-3-en-2-yl)-1*H*-pyrazole (3ca)



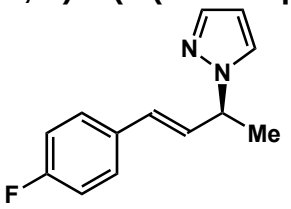
Colorless oil, 92% yield, 93:7 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -16.8 (*c* 0.60, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.4 Hz, 1H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.35 (dd, *J* = 16.0, 6.6 Hz, 1H), 6.28 (t, *J* = 2.0 Hz, 1H), 5.10 (apparent p, *J* = 6.7 Hz, 1H), 2.33 (s, 3H), 1.72 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.13, 137.96, 133.56, 131.39, 129.41, 128.77, 127.24, 126.62, 105.46, 59.52, 21.34, 20.98. **IR** (ATR) 3027, 2978, 2923, 2864, 1512, 1396, 801, 751 cm^{-1}. **HRMS** calculated for $C_{14}H_{16}N_2Na$ $[M+Na]^+$ 235.1211, found 235.1218. **Chiral SFC:** 100 mm CHIRALCEL AD-H, 8.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 3.3 min, t_{R2} (major) = 4.0 min.

(*S*, *E*)-1-(4-(4-chlorophenyl)but-3-en-2-yl)-1*H*-pyrazole (3da)



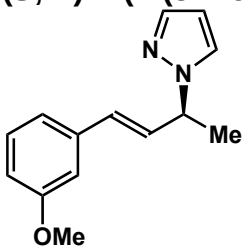
Colorless oil, 31% yield, 89:11 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -25.5 (*c* 0.06, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.7 Hz, 1H), 7.45 (d, *J* = 2.3 Hz, 1H), 7.28 – 7.23 (m, 4H), 6.43 – 6.32 (m, 2H), 6.31 – 6.26 (m, 1H), 5.09 (apparent p, *J* = 6.9 Hz, 1H), 1.71 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.23, 134.85, 133.73, 130.55, 130.20, 128.87, 127.93, 127.33, 105.61, 59.35, 20.83. **IR** (ATR) 2980, 2933, 1683, 1593, 808, 748 cm^{-1}. **HRMS** calculated for $C_{13}H_{14}N_2Cl$ $[M+H]^+$ 233.0845, found 233.0836. **Chiral SFC:** 100 mm CHIRALCEL AD-H, 4.0% ^{i}PrOH, 3.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 7.4 min, t_{R2} (major) = 9.8 min.

(*S*, *E*)-1-(4-(4-fluorophenyl)but-3-en-2-yl)-1*H*-pyrazole (3ea)



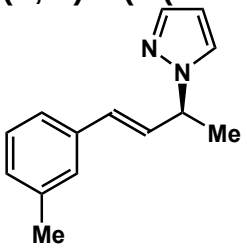
Colorless oil, 93% yield, 94:6 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -5.4 (*c* 0.64, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.8 Hz, 1H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.02 – 6.96 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.34 – 6.27 (m, 2H), 5.14 – 5.07 (m, 1H), 1.72 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.63 (d, *J* = 247.4 Hz), 139.19, 132.51 (d, *J* = 3.4 Hz), 130.29, 129.62 (d, *J* = 2.3 Hz), 128.27 (d, *J* = 8.0 Hz), 127.30, 115.64 (d, *J* = 21.7 Hz), 105.57, 59.40, 20.90. **IR** (ATR) 2981, 2933, 1682, 1601, 1512, 1230 cm^{-1}. **HRMS** calculated for $C_{13}H_{14}N_2F$ $[M+H]^+$ 217.1141, found 217.1135. **Chiral SFC:** 100 mm CHIRALCEL IC, 3.0% ^{i}PrOH, 3.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 5.1 min, t_{R2} (major) = 6.0 min.

(*S*, *E*)-1-(4-(3-methoxyphenyl)but-3-en-2-yl)-1*H*-pyrazole (3fa)



Colorless oil, 79% yield, 91:9 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -5.0 (*c* 0.60, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.3 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.91 – 6.89 (m, 1H), 6.80 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.39 (dd, *J* = 16.0, 6.2 Hz, 1H), 6.29 (t, *J* = 2.1 Hz, 1H), 5.12 (apparent p, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 1.73 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.96, 139.13, 137.79, 131.45, 130.08, 129.71, 127.35, 119.43, 113.89, 111.92, 105.57, 59.46, 55.39, 20.92. **IR** (ATR) 2982, 2935, 2835, 1600, 1579, 1288 cm^{-1}. **HRMS** calculated for $C_{14}H_{16}N_2ONa$ $[M+Na]^+$ 251.1160, found 251.1167. **Chiral SFC:** 100 mm CHIRALCEL AD-H, 8.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 3.4 min, t_{R2} (major) = 4.0 min.

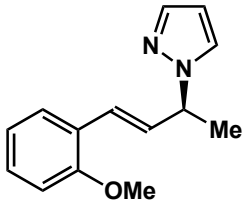
(*S*, *E*)-1-(4-(*m*-tolyl)but-3-en-2-yl)-1*H*-pyrazole (3ga)



Colorless oil, 87% yield, 95:5 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -11.1 (*c* 0.69, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, J = 1.2 Hz, 1H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.18 (dd, *J* = 13.0, 7.2 Hz, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.38 (dd, *J* = 16.0, 6.3 Hz, 1H), 6.28 (t, *J* = 2.0 Hz, 1H), 5.11 (apparent p, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 1.73 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.11, 138.29, 136.28, 131.61, 129.57, 128.88, 128.61, 127.38, 127.28, 123.93, 105.51, 59.50, 21.48, 20.96. **IR** (ATR) 3027, 2979, 2931, 1736, 1604, 1396 cm^{-1}. **HRMS**

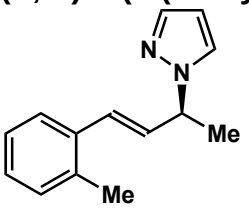
calculated for $C_{14}H_{16}N_2Na$ $[M+Na]^+$ 235.1211, found 235.1208. **Chiral SFC:** 100 mm CHIRALCEL IC, 8.0% *i*PrOH, 2.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 2.8 min, t_{R2} (major) = 3.1 min.

(*S*, *E*)-1-(4-(2-methoxyphenyl)but-3-en-2-yl)-1*H*-pyrazole (3ha)



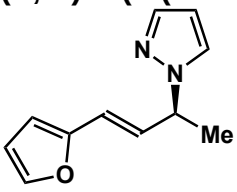
Colorless oil, 40% yield, 92:8 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = +5.3 (*c* 0.3, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.5 Hz, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.93 – 6.85 (m, 3H), 6.43 (dd, *J* = 16.0, 6.9 Hz, 1H), 6.27 (t, *J* = 2.0 Hz, 1H), 5.10 (apparent p, *J* = 6.8 Hz, 1H), 3.84 (s, 3H), 1.73 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.0, 139.1, 130.2, 129.2, 127.3, 127.2, 126.6, 125.3, 120.8, 111.0, 105.4, 60.0, 55.6, 21.1. **IR** (ATR) 2978, 2934, 2837, 1684, 1598, 1242 cm^{-1}. **HRMS** calculated for $C_{14}H_{16}N_2ONa$ $[M+Na]^+$ 251.1160, found 251.1167. **Chiral SFC:** 100 mm CHIRALCEL IC, 8.0% *i*PrOH, 2.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 3.3 min, t_{R2} (major) = 4.0 min.

(*S*, *E*)-1-(4-(*o*-tolyl)but-3-en-2-yl)-1*H*-pyrazole (3ia)



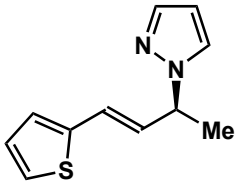
Colorless oil, 62% yield, 90:10 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = +5.5 (*c* 0.44, $CHCl_3$). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 1.8 Hz, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.43 – 7.41 (m, 1H), 7.18 – 7.12 (m, 3H), 6.68 (dd, *J* = 15.8, 1.3 Hz, 1H), 6.32 – 6.25 (m, 2H), 5.13 (apparent pd, *J* = 6.9, 1.3 Hz, 1H), 2.32 (s, 3H), 1.74 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.1, 135.8, 135.5, 131.2, 130.5, 129.4, 128.0, 127.3, 126.3, 126.0, 105.6, 59.8, 21.1, 19.9. **HRMS** calculated for $C_{14}H_{16}N_2Na$ $[M+Na]^+$ 235.1211, found 235.1210. **IR** (ATR) 3019, 2977, 2933, 1680, 1396 cm^{-1}. **Chiral SFC:** 100 mm CHIRALCEL AD-H, 4.0% *i*PrOH, 3.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 4.6 min, t_{R2} (minor) = 5.5 min.

(*S*, *E*)-1-(4-(furan-2-yl)but-3-en-2-yl)-1*H*-pyrazole (3ja)



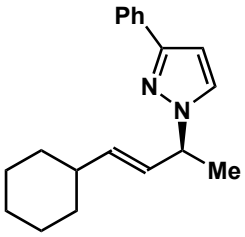
Colorless oil, 34% yield, 90:10 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -7.6 (*c* 0.21, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.8 Hz, 1H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 6.35 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.34 – 6.21 (m, 4H), 5.10 (apparent p, *J* = 6.4 Hz, 1H), 1.70 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.95, 142.36, 139.12, 128.31, 127.31, 119.83, 111.48, 108.90, 105.58, 59.09, 20.80. **IR** (ATR) 3118, 2981, 2933, 1668, 1508, 1397 cm^{-1}. **HRMS** calculated for $C_{11}H_{12}N_2O$ $[M]^+$ 188.0950, found 188.0943. **Chiral SFC:** 100 mm CHIRALCEL AD-H, 3.0% *i*PrOH, 3.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 4.1 min, t_{R2} (minor) = 8.0 min.

(*S*, *E*)-1-(4-(thiophen-2-yl)but-3-en-2-yl)-1*H*-pyrazole (3ka)



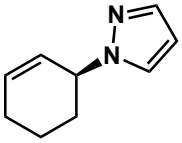
Colorless oil, 95% yield, 93:7 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = -34.8 (*c* 0.43, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.8 Hz, 1H), 7.47 (d, *J* = 2.7 Hz, 1H), 7.17 – 7.14 (m, 1H), 6.97 – 6.93 (m, 2H), 6.58 (dd, *J* = 15.7, 1.3 Hz, 1H), 6.29 – 6.27 (m, 1H), 6.22 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.08 (apparent p, J = 6.4 Hz, 1H), 1.71 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.3, 139.2, 129.2, 127.5, 127.3, 126.5, 124.8, 124.7, 105.6, 59.2, 20.8. **IR** (ATR) 3104, 2979, 2932, 1648, 1509, 1396 cm^{-1}. **HRMS** calculated for $C_{11}H_{12}N_2S$ $[M]^+$ 204.0721, found 204.0711. **Chiral SFC:** 100 mm CHIRALCEL AD-H, 3.0% ^{i}PrOH, 3.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 8.2 min, t_{R2} (minor) = 12.6 min.

(*S*, *E*)-1-(4-cyclohexylbut-3-en-2-yl)-3-phenyl-1*H*-pyrazole (3la)



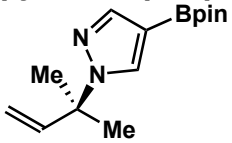
Colorless oil, 45% yield, 95:5 *er*, 2.2:1 *rr*, >20:1 N^1:N^2, $[\alpha]^{24}_D$ = +11.26 (*c* 0.23, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.26 (m, 1H), 6.54 (d, *J* = 2.3 Hz, 1H), 5.70 – 5.59 (m, 2H), 4.93 (apparent p, *J* = 6.6 Hz, 1H), 2.03 – 1.95 (m, 1H), 1.77 – 1.65 (m, 5H), 1.62 (d, *J* = 6.9 Hz, 3H), 1.31 – 1.03 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.91, 139.06, 133.98, 128.67, 128.21, 127.74, 127.51, 125.77, 102.60, 77.16, 59.65, 40.47, 32.87, 26.26, 26.11, 21.32. **IR** (ATR) 2978, 2922, 2850, 1497, 1458, 1215, 746 cm^{-1}. **HRMS** calculated for $C_{19}H_{24}N_2$ $[M]^+$ 280.1939, found 280.1935. **Chiral SFC:** 100 mm CHIRALCEL AD-H, 4.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 4.7 min, t_{R2} (major) = 5.5 min.

(*S*)-1-(cyclohex-2-en-1-yl)-1*H*-pyrazole (3ma)



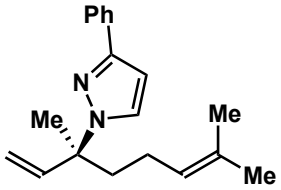
Colorless oil, 73% yield, 81:19 *er*, >20:1 *rr*, $[\alpha]^{24}_D$ = +38.95 (*c* 0.19, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 6.26 – 6.22 (m, 1H), 6.10 – 6.06 (m, 1H), 5.83 – 5.80 (m, 1H), 4.98 – 4.91 (m, 1H), 2.21 – 2.05 (m, 3H), 2.00 – 1.94 (m, 1H), 1.72 – 1.65 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.18, 132.76, 127.74, 125.62, 105.00, 57.16, 30.68, 24.94, 19.45. **IR** (ATR) 3029, 2929, 2865, 1668, 1508, 1395, 1293 cm^{-1}. **HRMS** calculated for $C_9H_{13}N_2$ $[M+H]^+$ 149.1079, found 149.1078. **Chiral SFC:** 100 mm CHIRALCEL AD-H, 4.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 ºC, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 4.7 min, t_{R2} (major) = 5.5 min.

1-(2-methylbut-3-en-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (3na)



Colorless oil, 52% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.82 (s, 1H), 6.09 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.15 (d, *J* = 10.7 Hz, 1H), 5.08 (d, *J* = 17.4 Hz, 1H), 1.68 (s, 6H), 1.31 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.09, 142.86, 133.72, 113.69, 83.22, 61.82, 27.42, 24.76. **IR** (ATR): 2979, 1553, 1404, 1370, 1299, 1247, 1141, 986, 857 cm^{-1}. **HRMS** calculated for $C_{14}H_{24}BN_2O_2Na$ $[M+Na]^+$ 285.1573, found 285.1572.

(*S*)-1-(3,7-dimethylocta-1,6-dien-3-yl)-3-phenyl-1*H*-pyrazole (3oa)

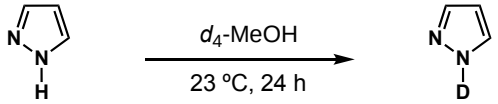


Colorless oil, 42% yield, 78:22 *er*, >20:1 *rr*, >20:1 N^1:N^2. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.4, 0.9 Hz, 2H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 10.5, 5.0 Hz, 2H), 7.30 – 7.25 (m, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.21 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.22 (d, *J* = 10.8 Hz, 1H), 5.13 (d, *J* = 17.5 Hz, 1H), 5.11 – 5.07 (m, 1H), 2.24 – 2.12 (m, 1H), 2.05 – 1.98 (m, 1H), 1.94 – 1.82 (m, 2H), 1.71 (s, 3H), 1.66 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.78, 142.59, 134.31, 132.11, 128.61, 127.38, 125.78, 123.77, 114.38, 102.16, 77.16, 64.72, 40.63, 25.80, 24.52, 22.75, 17.72. **IR** (ATR): 2969, 2925, 1496, 1457, 1374, 1210, 1073, 1048, 922, 745 cm^{-1}. **HRMS** calculated for $C_{14}H_{23}BN_2O_2Na$ $[M+Na]^+$ 303.1837, found 303.1841. **Chiral SFC**: 250 mm CHIRALCEL OJ-H, 4.0% ^{i}PrOH, 2.0 mL/min, 240 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 2.6 min, t_{R2} (minor) = 2.8 min.

4. Mechanism studies

4A. Deuterium-labeling study

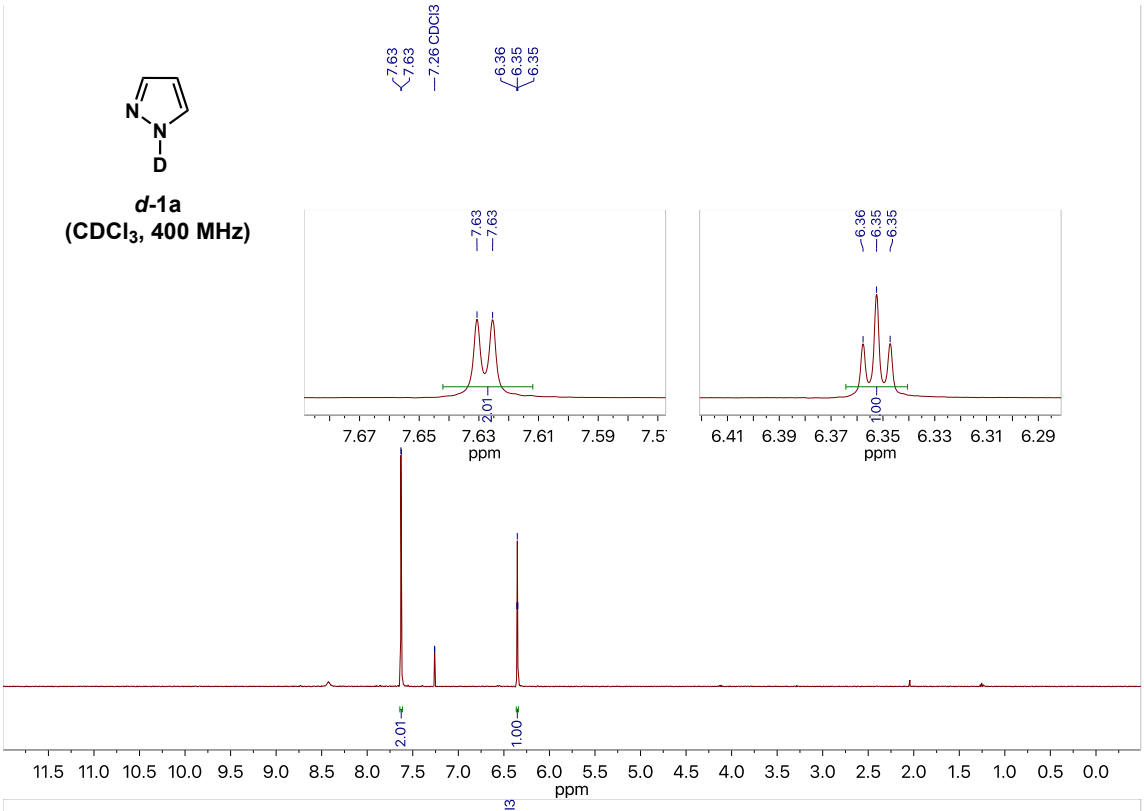
(1) Synthesis of *d*-1a:

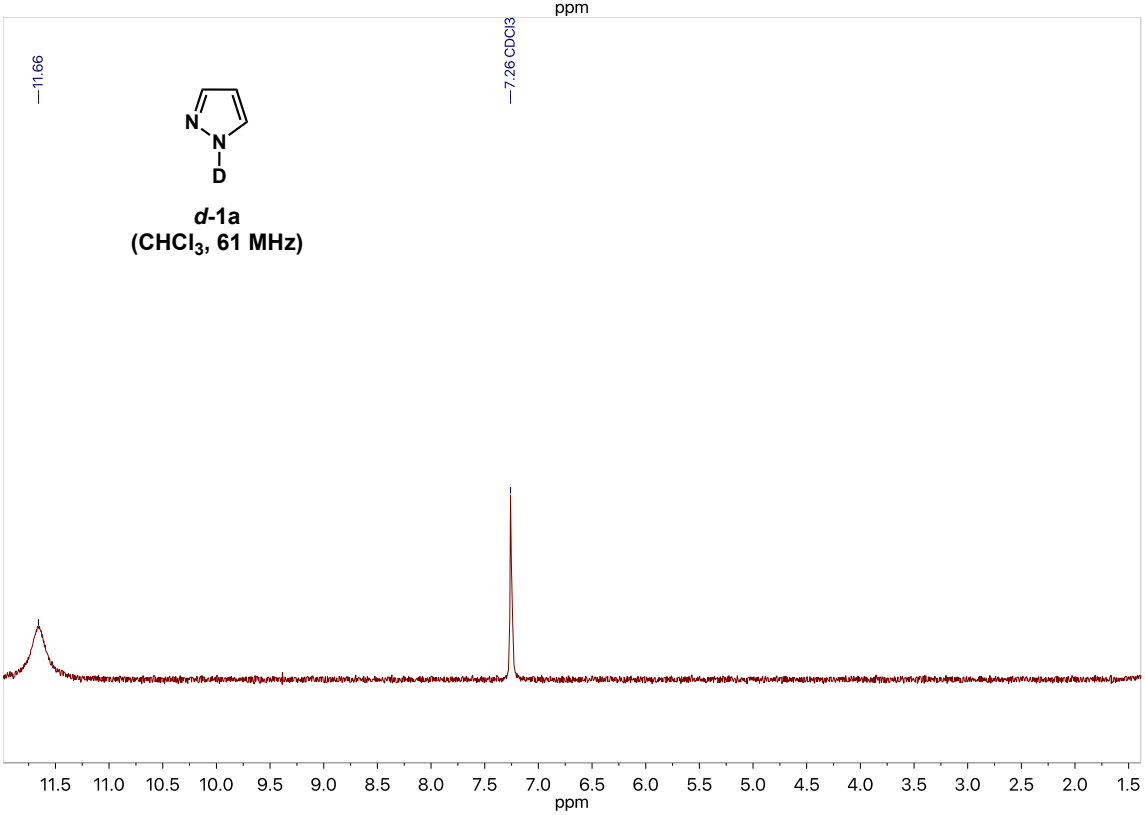


1a **_d_-1a**

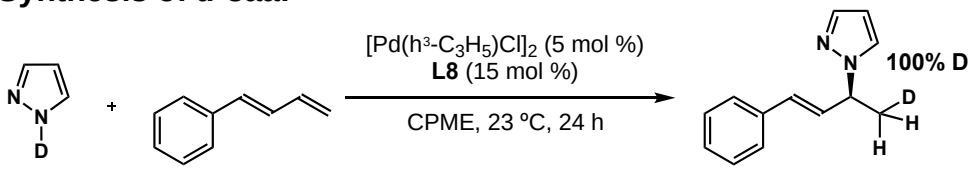
>95% D-incorporation

An oven dried vial equipped with a magnetic stir bar was charged with pyrazole (**1a**, 1.47 mmol). The solid was then dissolved in d_4-MeOH (2.94 mL) to obtain a 0.5 M solution. The reaction was then stirred at 23 ºC for 24 hours. The solution was then concentrated *in vacuo* affording the title compound ***d*-1a** as a white solid quantitatively (>99%). ^{1}H NMR shows >95% D incorporation. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 2.1 Hz, 2H), 6.35 (t, *J* = 2.1 Hz, 1H). **^{2}H NMR** (61 MHz, $CHCl_3$) δ 11.66 (s, 1H).


7.63
7.63
7.26 CDCl3
6.36
6.35
6.35
N
N
D
d-1a
(CDCl3, 400 MHz)
2.01
1.00
ppm
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
7.67 7.65 7.63 7.61 7.59
6.41 6.39 6.37 6.35 6.33 6.31 6.29

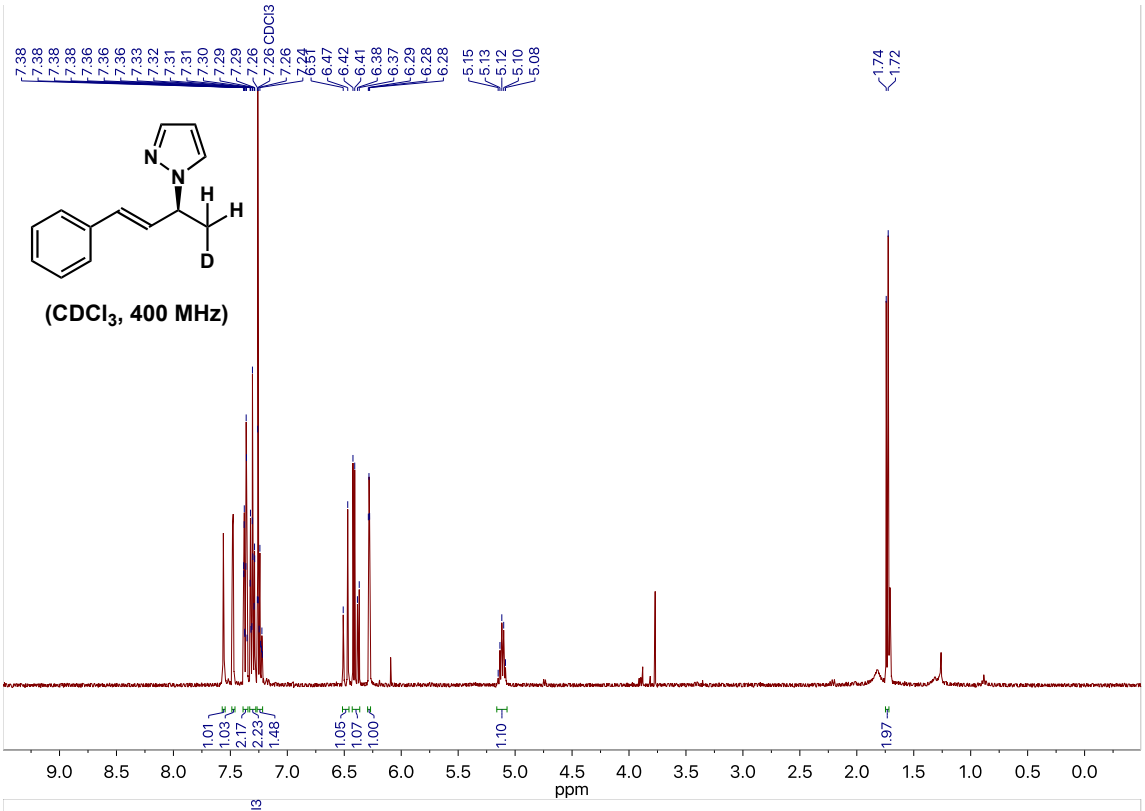

11.66
7.26 CDCl3
N
N
D
d-1a
(CHCl3, 61 MHz)
ppm
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5

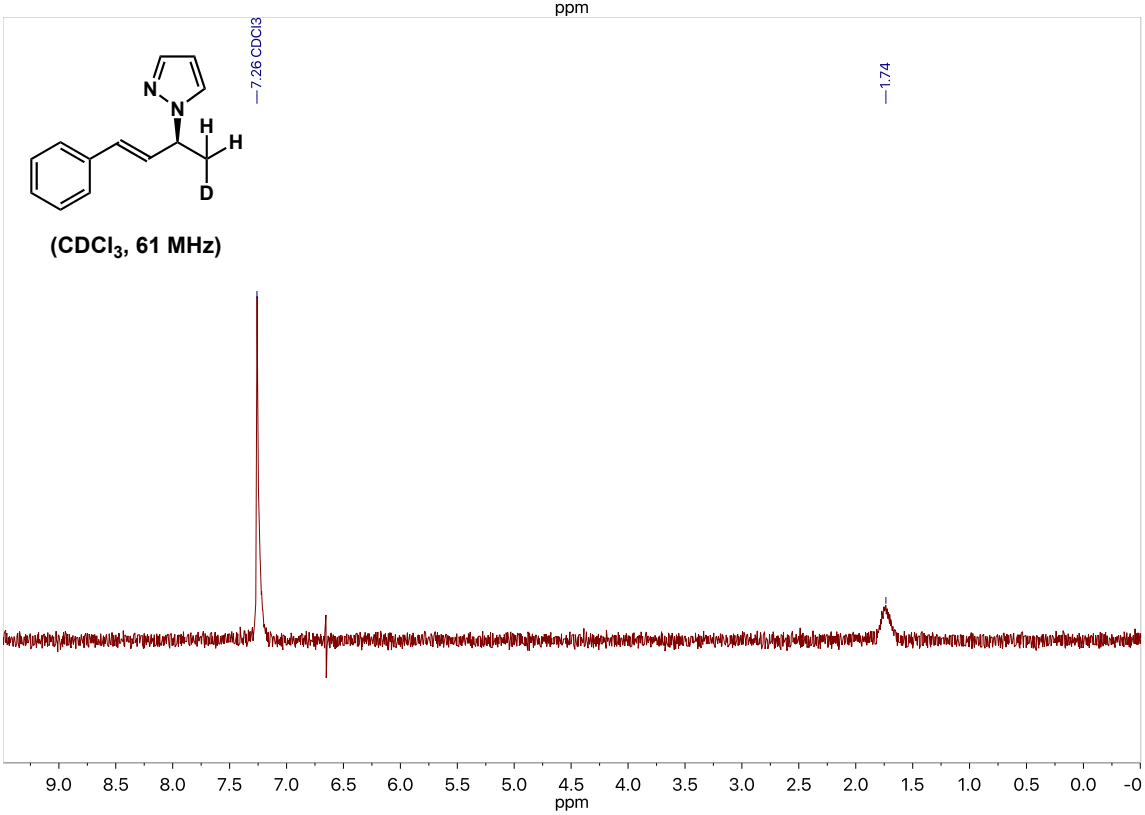
(2) Synthesis of *d*-3aa:



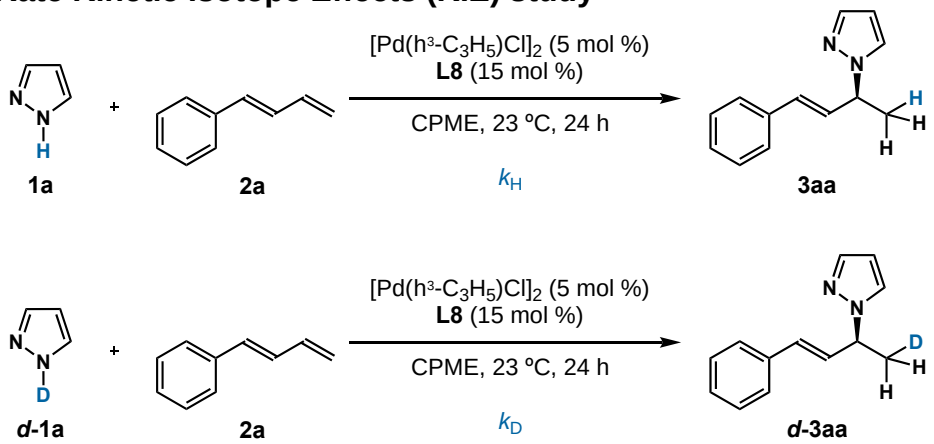
***d*-1a** **2a** ***d*-3aa**

Following the "General procedure for the hydroamination of 1,3-dienes with azoles" on page **S5**, ***d*-1a** was used as the pyrazole coupling partner. The target compound ***d*-3aa** was obtained in 41% yield. Colorless oil, >20:1 *rr.* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.3 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.31 (ddd, *J* = 7.5, 6.7, 1.2 Hz, 2H), 7.27 – 7.22 (m, 1H), 6.52 – 6.36 (m, 2H), 6.29 – 6.27 (m, 1H), 5.12 (p, *J* = 6.3 Hz, 1H), 1.73 (d, *J* = 6.9 Hz, 2H). **^{2}H NMR** (61 MHz, $CHCl_3$) δ 1.74 (s, 1H). Deuterium incorporation was determined by ^{1}H NMR. Percent deuterium (% D) incorporation is depicted as the amount of deuterium in place of a single hydrogen atom at that site.


(CDCl3, 400 MHz)
ppm


(CDCl3, 61 MHz)
ppm

4B. Initial Rate Kinetic Isotope Effects (KIE) study



In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with [Pd(η^3-C_3H_5)Cl]$_2$ (1.8 mg, 5.0 µmol), MeO-BIPHEP **L8** (16.4 mg, 15.0 µmol) and CPME (0.2 mL). The resulting mixture was stirred for 10 mins and then diene **2a** (500.0 µmol) followed by a solution of freshly recrystallized pyrazole **1a** or ***d*-1a** (100.0 µmol) in CPME (0.1 mL) and 1,3,5-trimethoxybenzene (8.4 mg, 50.0 µmol) in CPME (0.1 mL) were added dropwise. The mixtures were capped with Teflon caps, removed from the glovebox and stirred at 23 ºC. Aliquots (10 µL) were taken every 30 mins and quenched in 100 µL of methanol. The concentration of **3aa** and ***d*-3aa** was monitored by GC-FID analysis using 1,3,5-trimethoxybenzene as an internal standard. The KIE was calculated to be 1.4 using the following equation:

$$KIE = \frac{k_H}{k_D}$$

Trial	A	B	A	B	H average k_{obs}	D average k_{obs}
Pyrazole	H	H	D	D		
k_{obs} (µmol/min)	0.0143	0.0138	0.0098	0.0109	0.0141	0.0104
R^2	0.95	0.95	0.98	0.99	–	–

Table S1. KIE data for the reaction. Each H and D experiment was repeated in duplicate, and the KIE was calculated from the averages of the H and D k_{obs}.

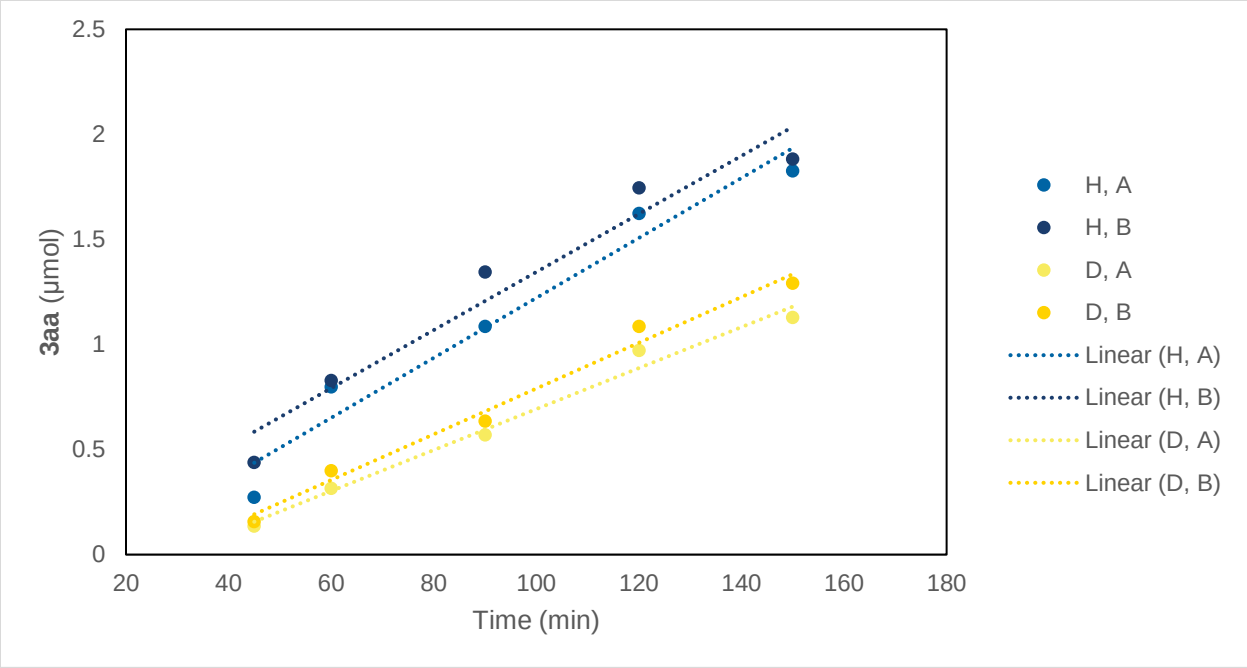
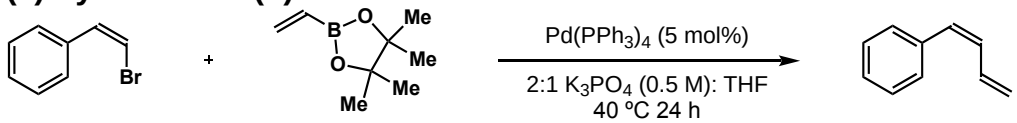


Figure S5. Graph illustrating the KIE data. Slopes were fit using a least-square linear regression model.

4C. Diene Geometry Study

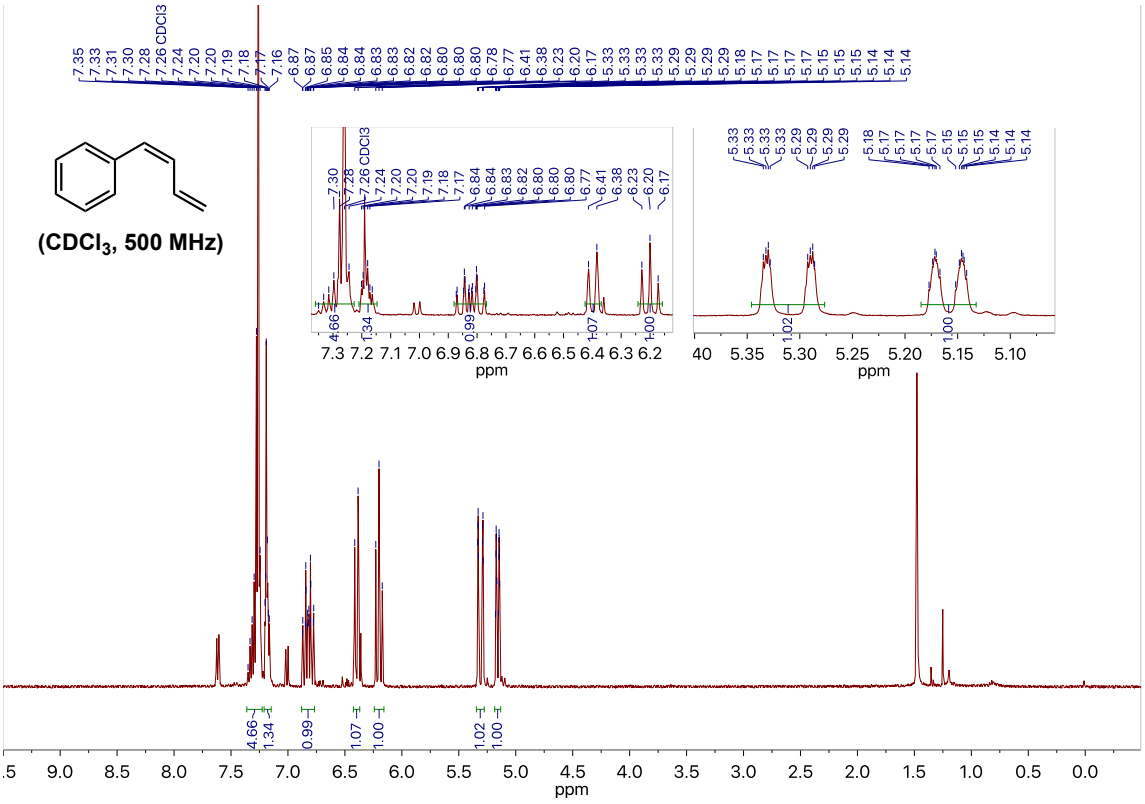
(1) Synthesis of (*Z*)-2a:



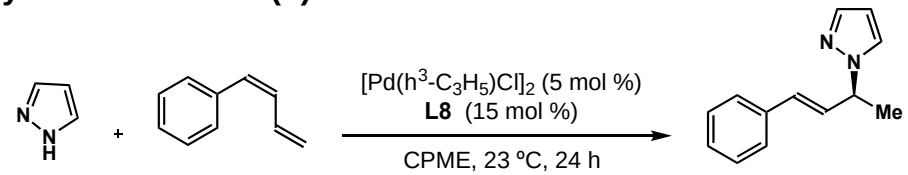
S1 **S2** **Z-2a**

35%, >10:1 Z:E content

In a N_2-filled glovebox, an oven dried 50 mL flask equipped with a magnetic stir bar was charged with **S1** (1.0 g, 5.5 mmol, 1 equiv), **S2** (1.0 g, 6.6 mmol, 1.2 equiv), and $Pd(PPh_3)_4$ (0.63 g, 0.55 mmol, 0.1 equiv).[4] The flask was capped with a rubber septum and removed from the glovebox. THF (11 mL) and 0.5 M aq. K_3PO_4 (22 mL, degassed by sparging with N_2 for 30 mins) were added sequentially via syringe. The reaction mixture was vigorously stirred at 40 ºC for 18 hours. The reaction was cooled to rt and then diluted with 20 mL of H_2O and 20 mL Et_2O. The mixture was then extracted with Et_2O (3 x 15 mL) and combined. The organic phase was then washed with 40mL of sat. aq. brine, dried over $MgSO_4$ and concentrated in vacuo. The target compound was then purified via flash silica gel chromatography (100% hexanes) to yield **(*Z*)-2a** as a clear oil (250 mg, 1.92 mmol, 35% yield) as a >10:1 mixture of *Z:E* isomers. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 4H), 7.20 – 7.16 (m, 1H), 6.82 (dddd, *J* = 16.9, 11.2, 10.2, 1.0 Hz, 1H), 6.40 (d, *J* = 11.7 Hz, 1H), 6.20 (t, *J* = 11.3 Hz, 1H), 5.33 – 5.29 (m, 1H), 5.18 – 5.13 (m, 1H). The spectral data match those previously reported.[5]



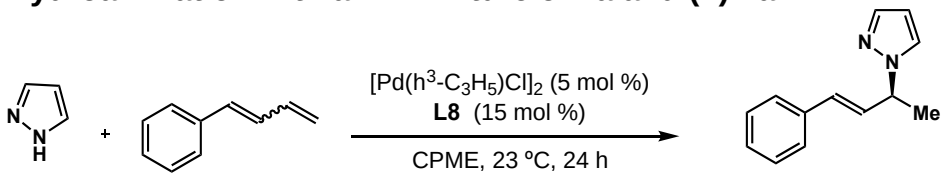
(2) Hydroamination of (*Z*)-2a:



1a + **Z-2a** → **3aa**
0% yield

In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.8 mg, 5.0 µmol), MeO-BIPHEP **L8** (16.4 mg, 15.0 µmol) and CPME (0.3 mL). The resulting mixture was stirred for 10 mins and then **(*Z*)-2a** (500.0 µmol) followed by a solution of freshly recrystallized pyrazole (100.0 µmol) in CPME (0.1 mL) were added dropwise. The mixture was removed from the glovebox and stirred at 23 ºC for 24 hours. No desired product observed by LCMS or TLC after 24 hours.

(3) Hydroamination with a 1:1 mixture of 2a and (*Z*)-2a:

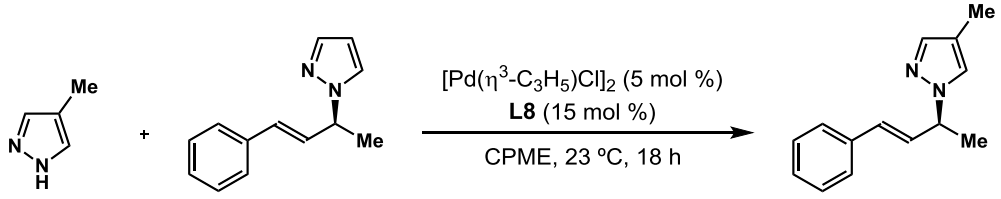


1a + **2a** (E:Z = 1:1) → **3aa**
50% yield (brsm)
100% *Z*-Olefin Recovered

In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.8 mg, 5.0 µmol), MeO-BIPHEP **L8** (16.4 mg, 15.0 µmol) and CPME (0.3 mL). The resulting mixture was stirred for 10 mins. Then a 1:1 mixture of **(*E*)-2a** (50.0 µmol) and **(*Z*)-2a** (50.0 µmol) were added, followed by a solution of freshly recrystallized pyrazole (100.0 µmol) in CPME (0.1 mL) were added dropwise. The mixture was removed from the glovebox and stirred at 23 ºC for 24 hours. The target compound was isolated via preparatory thin-layer chromatography on silica gel using 10% EtOAc in Hexanes. Colorless oil, 25% yield, 94:6 *er*, >20:1 *rr*.

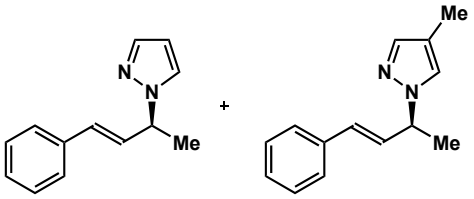
4D. Crossover Studies

(1) Crossover study with 3aa

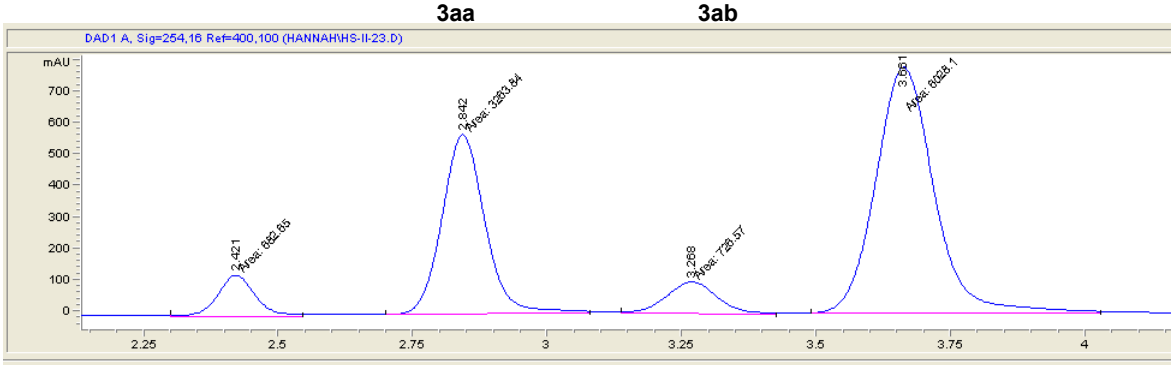


1b | **3aa** 90:10 *er* | **3ab** 40%, 89:11 *er*

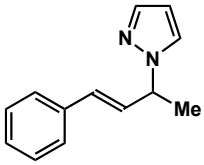
In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.9 mg, 2.0 µmol), MeO-BIPHEP **L8** (8.4 mg, 7.7 µmol) and CPME (0.4 mL). The resulting mixture was stirred for 10 mins. Then **3aa** (10.2 mg, 51.4 µmol, 90:10 *er*) was added followed by a solution of **2b** (4.6 mg, 56 µmol) in CPME (0.1 mL). The reaction was removed from the glovebox and stirred at rt for 18 hours. Resulting yields were determined by NMR of the crude mixture (13.2 µmol **3aa** at 83:7 *er*, 21.3 µmol **3ab** at 89:11 *er*). The products were isolated as a mixture using preparatory thin-layer chromatography (6 mg). Enantioselectivity was determined by chiral SFC characterization. **SFC**: 150 mm CHIRALCEL AD-H, 10.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2; **3aa:** t_{R1} (minor) = 2.4 min, t_{R2} (major) = 2.8min. **3ab**: t_{R1} (minor) = 3.3 min, t_{R2} (major) = 3.7 min.



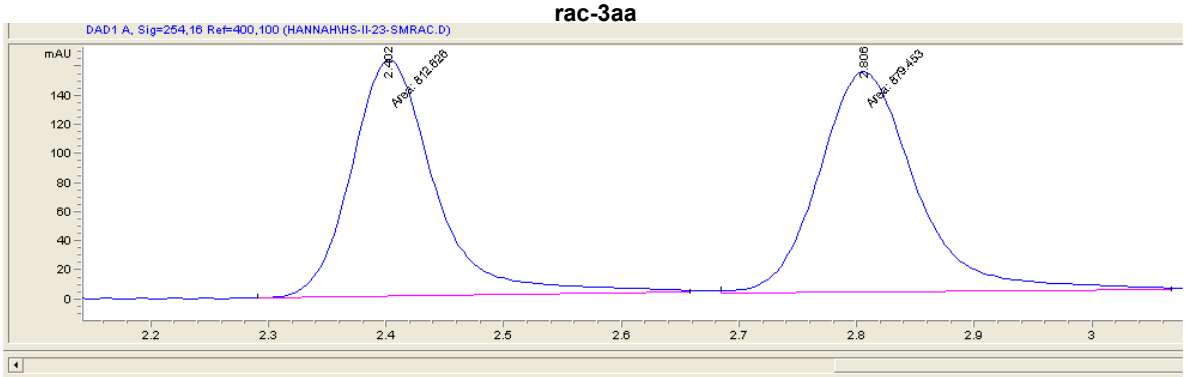
3aa **3ab**



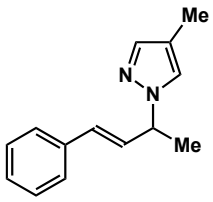
#	Time	Area	Height	Width	Area%	Symmetry
1	2.421	682.7	133	0.0855	6.379	0.971
2	2.842	3263.8	574.4	0.0947	30.500	0.878
3	3.268	726.6	104.6	0.1158	6.790	0.938
4	3.661	6028.1	785.4	0.1279	56.331	0.854



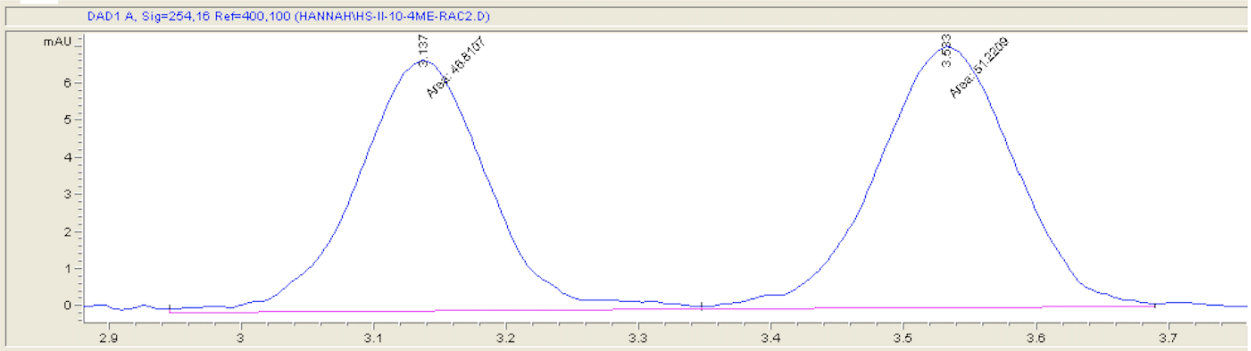
rac-3aa



#	Time	Area	Height	Width	Area%	Symmetry
1	2.402	812.6	163.1	0.083	48.025	0.788
2	2.806	879.5	151.9	0.0965	51.975	0.812

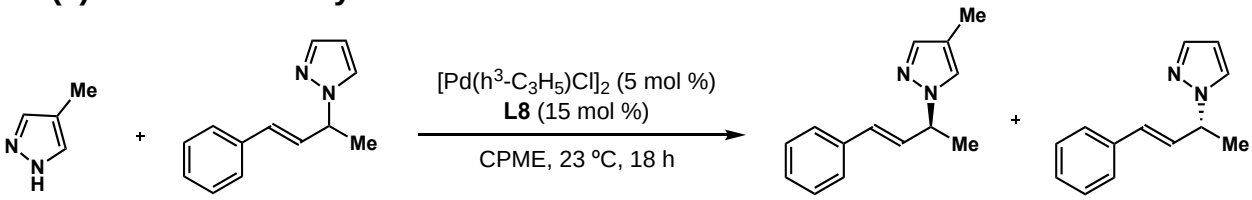


rac-3ab



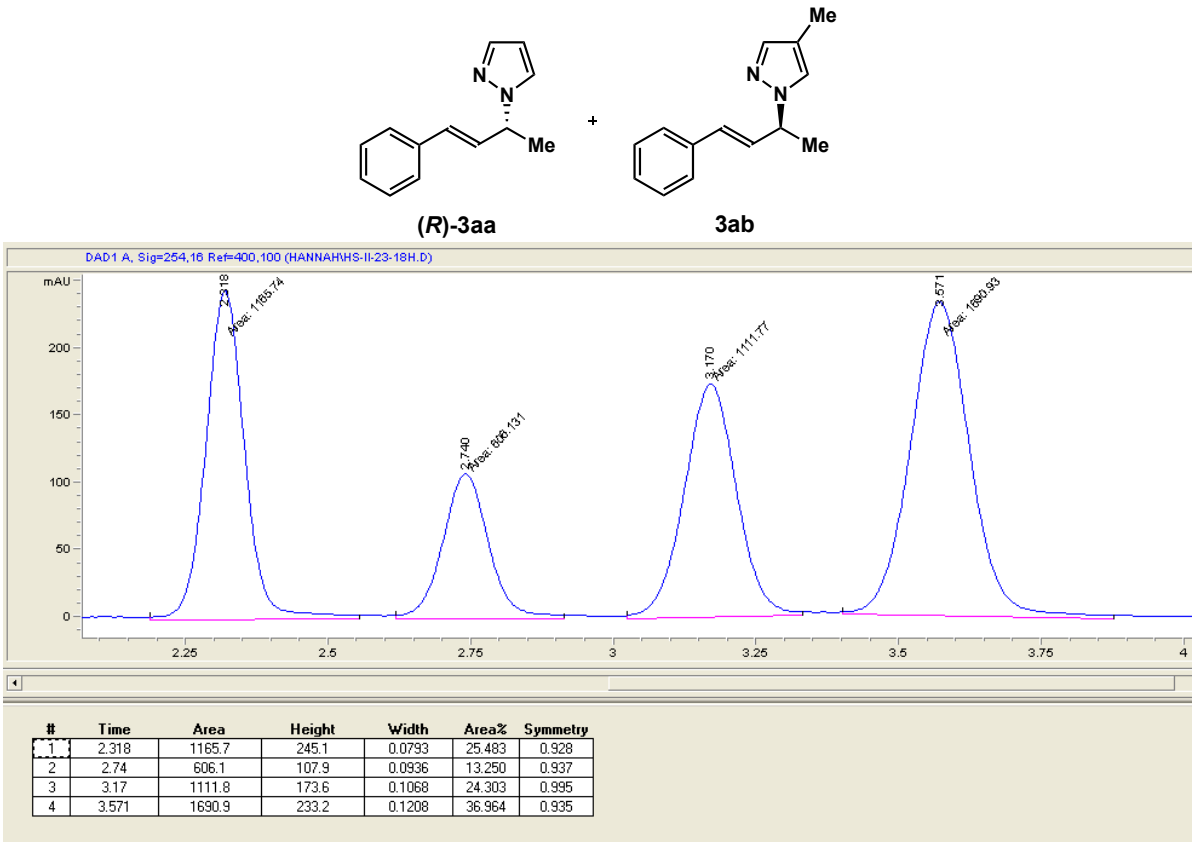
#	Time	Area	Height	Width	Area%	Symmetry
1	3.137	46.8	6.8	0.1151	47.751	1.046
2	3.533	51.2	7.1	0.1209	52.249	1.043

(2) Crossover study with *rac*-3aa



1b | **rac-3aa** | **(*S*)-3ab** 28%, 60:40 *er* | **(*R*)-3aa** 66:34 *er*

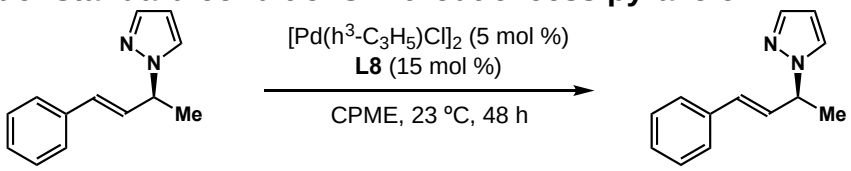
In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.0 mg, 5.5 µmol), MeO-BIPHEP **L8** (18.5 mg, 16.9 µmol) and CPME (0.4 mL). The resulting mixture was stirred for 10 mins. Then *rac*-**3aa** (22.4 mg, 113 µmol) was added, followed by a solution of **2b** (9.4 mg, 110 µmol) in CPME (0.1 mL). The reaction was removed from the glovebox and stirred at rt for 18 hours. Resulting yields were determined by NMR of the crude mixture (18.7 µmol **3aa**, 31.4 µmol **3ab**). The products were isolated as a mixture using preparatory thin-layer chromatography (10.3 mg). Enantioselectivity was determined by chiral SFC characterization. **SFC**: 150 mm CHIRALCEL AD-H, 10.0% ^{i}PrOH, 2.0 mL/min, 254 nm, 44 °C, nozzle pressure = 200 bar CO_2; **3aa:** t_{R1} (major) = 2.3 min, t_{R2} (minor) = 2.7 min. **3ab**: t_{R1} (minor) = 3.2 min, t_{R2} (major) = 3.6 min.



#	Time	Area	Height	Width	Area%	Symmetry
1	2.318	1165.7	245.1	0.0793	25.483	0.928
2	2.74	606.1	107.9	0.0936	13.250	0.937
3	3.17	1111.8	173.6	0.1068	24.303	0.995
4	3.571	1690.9	233.2	0.1208	36.964	0.935

4E. Stability of Product 3aa

(1) 3aa under standard conditions without excess pyrazole

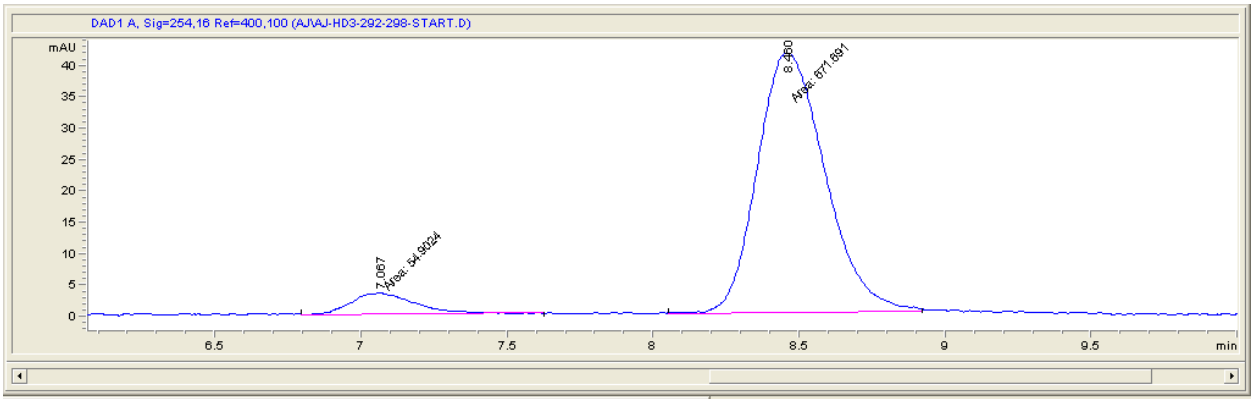


3aa
92.5:7.5 *er*

3aa
92.5:7.5 *er*

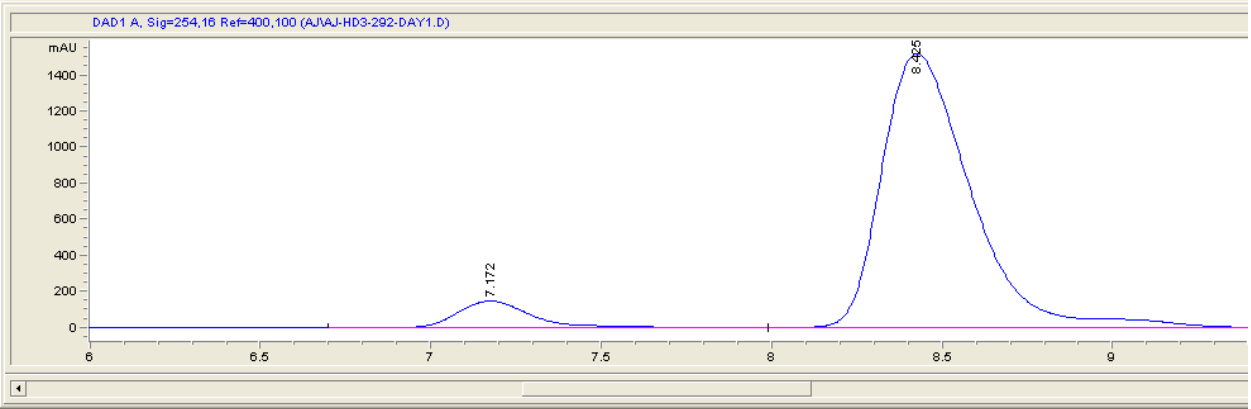
In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.8 mg, 4.92 µmol), MeO-BIPHEP **L8** (16.4 mg, 14.8 µmol) and CPME (0.3 mL). The resulting mixture was stirred for 10 mins. Then a solution of **3aa** (19.5 mg, 98.4 µmol) in CPME (0.1 mL) was added dropwise. The mixture was removed from the glovebox and stirred at 23 ºC for 48 hours. Aliquots were taken every 24 hours and the target compound was isolated via preparatory thin-layer chromatography on silica gel using 10% EtOAc in Hexanes. No change in *er* for **3aa** was observed after 48 hours.

-Start



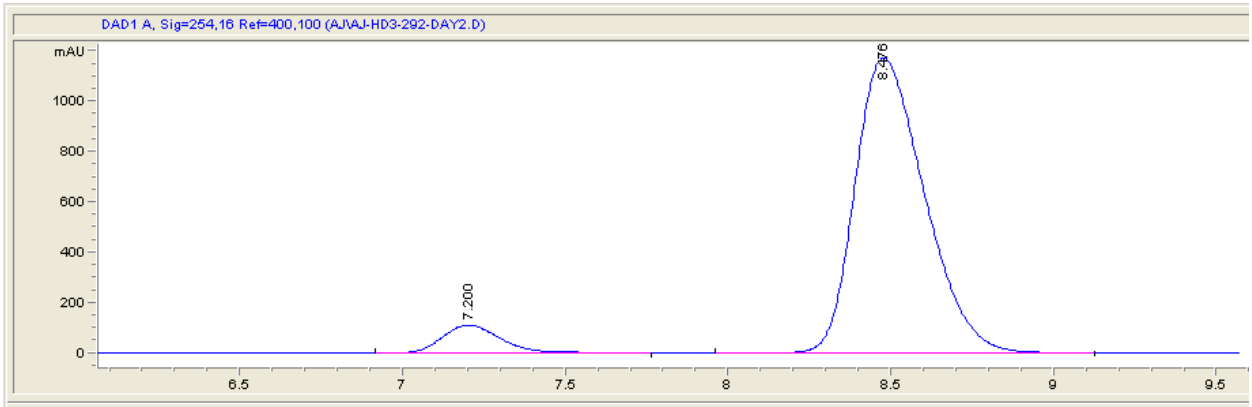
#	Time	Area	Height	Width	Area%	Symmetry
1	7.067	54.9	3.4	0.2681	7.556	0.835
2	8.46	671.7	41.4	0.2704	92.444	0.802

-24 hours



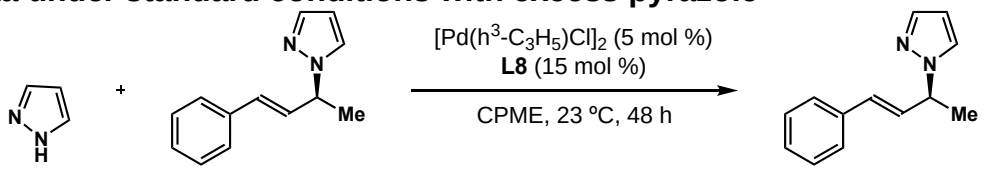
#	Time	Area	Height	Width	Area%	Symmetry
1	7.172	2260.7	148	0.2322	7.572	0.714
2	8.425	27596.3	1520.4	0.2808	92.428	0.607

-48 hours



#	Time	Area	Height	Width	Area%	Symmetry
1	7.2	1406.5	111	0.1959	7.491	0.748
2	8.476	17368.9	1172.7	0.2308	92.509	0.664

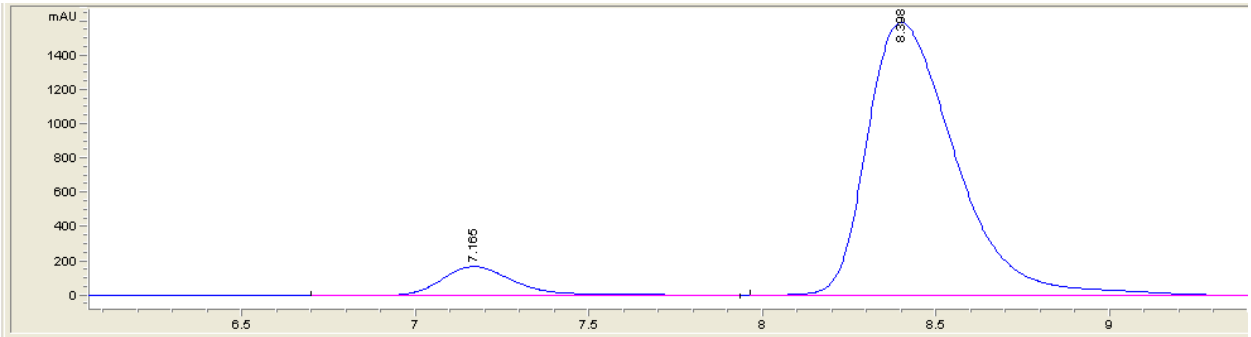
(2) 3aa under standard conditions with excess pyrazole



1a **3aa** 92.5:7.5 *er* **3aa** 91:9 *er*

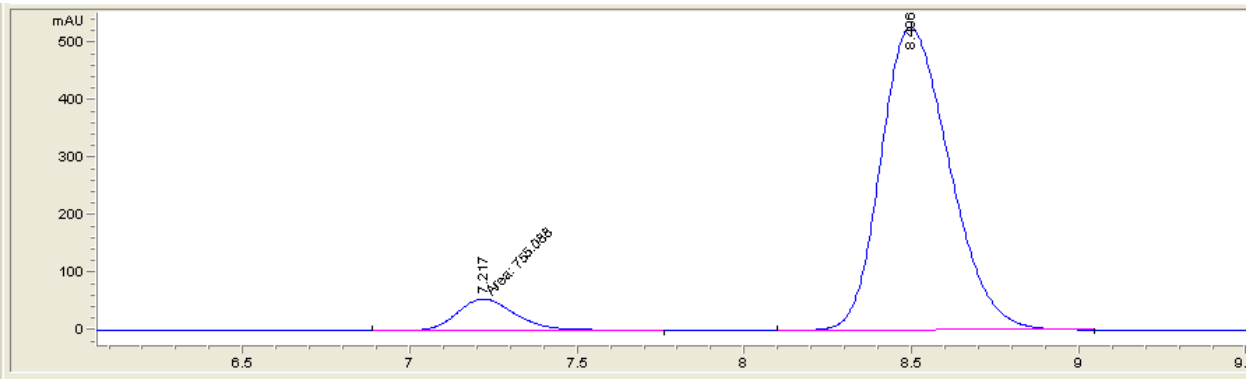
In a N_2-filled glovebox, an oven dried 1-dram vial equipped with a magnetic stir bar was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.1 mg, 2.90 µmol), MeO-BIPHEP (9.5 mg, 8.70 µmol) and CPME (0.1 mL). The resulting mixture was stirred for 10 mins. Then a solution of **3aa** (11.5 mg, 58.0 µmol) and pyrazole **1a** (3.95 mg, 58.0 µmol) in CPME (0.1 mL) was added dropwise. The mixture was removed from the glovebox and stirred at 23 ºC for 48 hours. Aliquots were taken every 24 hours and the target compound was isolated via preparatory thin-layer chromatography on silica gel using 10% EtOAc in Hexanes. (24 h, 92:8 *er* and 48 h, 91:9 *er*).

-24 hours



#	Time	Area	Height	Width	Area%	Symmetry
1	7.165	2534.6	169.2	0.2258	8.237	0.698
2	8.398	28237.5	1594.3	0.2766	91.763	0.583

-48 hours



#	Time	Area	Height	Width	Area%	Symmetry
1	7.217	755.1	56.3	0.2235	9.122	0.741
2	8.496	7522.7	526.9	0.2226	90.878	0.732

4F. Rate studies

The kinetic profile of the reaction was determined using the variable time normalization analysis (VTNA) method described by Burés.[6] Rates were monitored using GCFID analysis with 1,3,5-trimethoxybenzene as a standard. DTBM-SEGPHOS was utilized to ensure full dissolution. 1,3,5-trimethoxybenzene was determined to have no effect on the reaction. Catalyst concentration was assumed to remain constant over the duration of the reaction. Integrals were calculated using the trapezoid rule approximation:

$$f(t_n) = \int_0^{t_n} [X]^x dt \approx \sum_{i=1}^{n} \left(\frac{[X]_i + [X]_{i-1}}{2} \right)^2 (t_i - t_{i-1})$$

Determination of the reaction order of pyrazole (1):

Representative procedure: In an N_2-filled glovebox, solutions of **1a** (117.3 mg, 1.723 mmol) in CPME (0.300 mL), **2a** (120.6 mg, 926.3 µmol) in CPME (0.900 mL), $[Pd(C_3H_5)Cl]_2$ (5.5 mg, 15 µmol) and DTBM-SEGPHOS (35.7 mg, 30.3 µmol) in CPME (0.300 mL), and 1,3,5-trimethoxybenzene (51.3 mg, 305 µmol) in CPME (0.300 mL) were prepared. The catalyst solution was stirred for 30 minutes to establish complexation. An oven-dried 1-dram vial was charged with a stir bar, the catalyst solution (50.00 µL), **2a** solution (150.0 µL), 1,3,5-trimethoxybenzene solution (50.00 µL), **1a** solution (50.00 µL), and additional solvent (100.0 µL). The vial was sealed with a septa cap and removed from the glovebox. Using an N_2-filled balloon, the vial was put under positive pressure and aliquots (approximately 25 µL) were taken every 30 minutes, quenched with methanol (approximately 0.5 mL), and diluted with ethyl acetate. The reaction is quenched in methanol. The amount of **3aa** was monitored using GCFID analysis. By visual analysis, it is concluded that the reaction rate is zero order with respect to pyrazole (**1**).

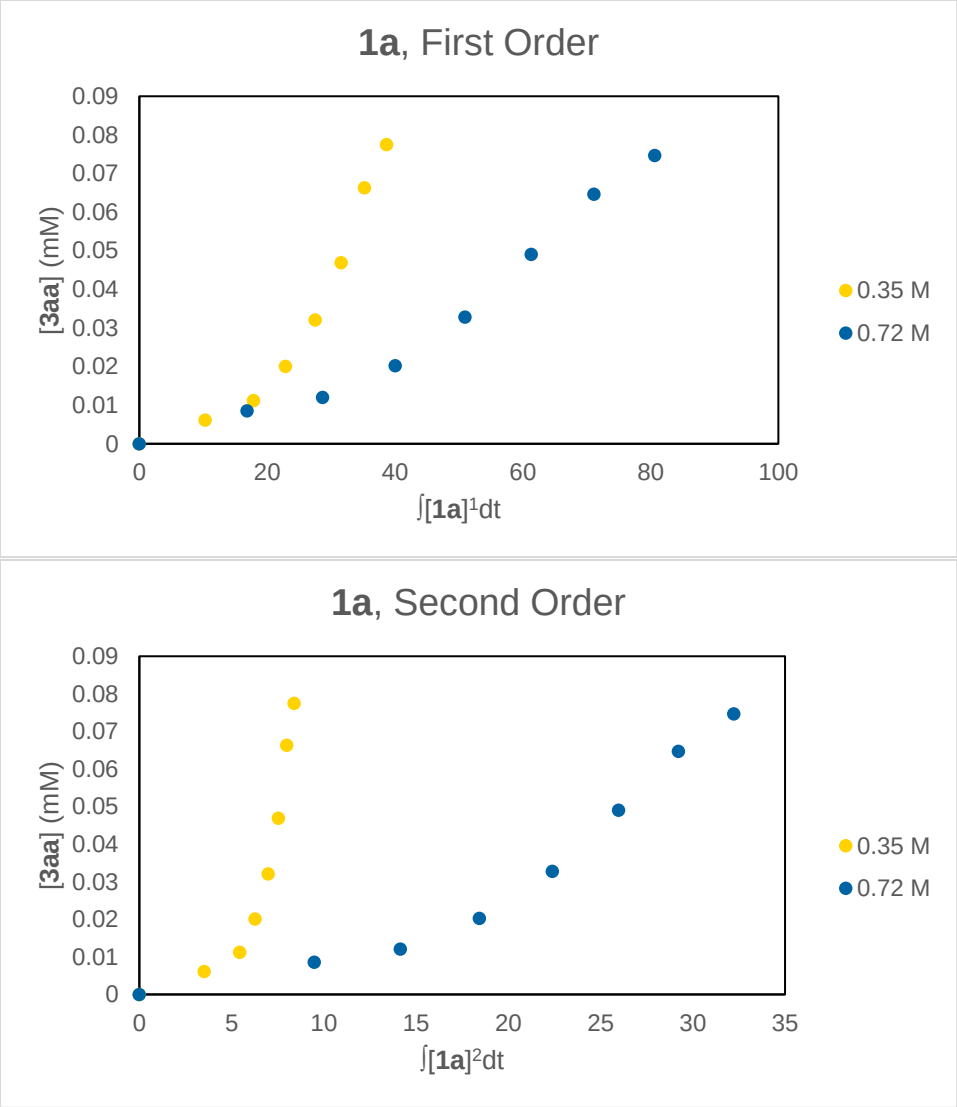
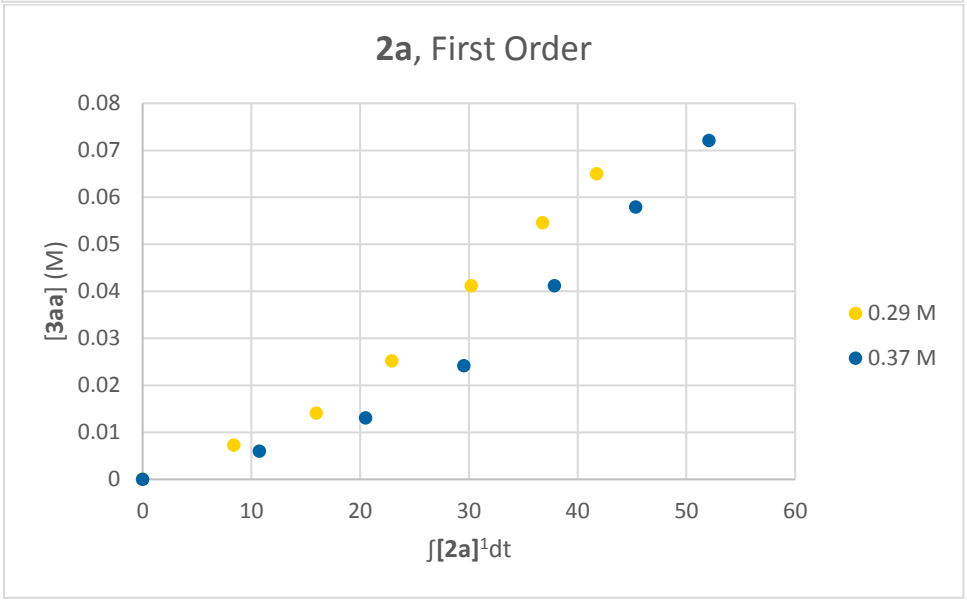


Figure S6. VTNA graphs for **1a** in zero, first, and second order. Overlay of the reaction profiles when using zero order analysis indicates that the reaction is zero order with respect to pyrazole (**1**).

Determination of the reaction order of diene (2):

Representative procedure: In an N_2-filled glovebox, solutions of **1a** (119.9 mg, 1.761 mmol) in CPME (1.750 mL), **2a** (231.7 mg, 1.780 mmol) in CPME (1.750 mL), $[Pd(C_3H_5)Cl]_2$ (18.3 mg, 50.0 μmol) and DTBM-SEGPHOS (119.4 mg, 101.2 μmol) in CPME (1.000 mL), and 1,3,5-trimethoxybenzene (142.0 mg, 844.3 μmol) in CPME (0.800 mL) were prepared. The catalyst solution was stirred for 30 minutes to establish complexation. An oven-dried 1-dram vial was charged with a stir bar, the catalyst solution (100.0 μL), **2a** solution (200.0 μL), 1,3,5-trimethoxybenzene solution (100.0 μL), **1a** solution (200.0 μL), and additional CPME (200.0 μL). The vial was sealed with a septa cap and removed from the glovebox. Using an N_2-filled balloon, the vial was put under positive pressure and aliquots (approximately 50 μL) were taken every 30 minutes, quenched with methanol (approximately 0.5 mL), and diluted with ethyl acetate. The

reaction is quenched in methanol. The amount of **3aa** was monitored using GCFID analysis. By visual analysis, it is concluded that the reaction rate is zero order with respect to diene (**2**).



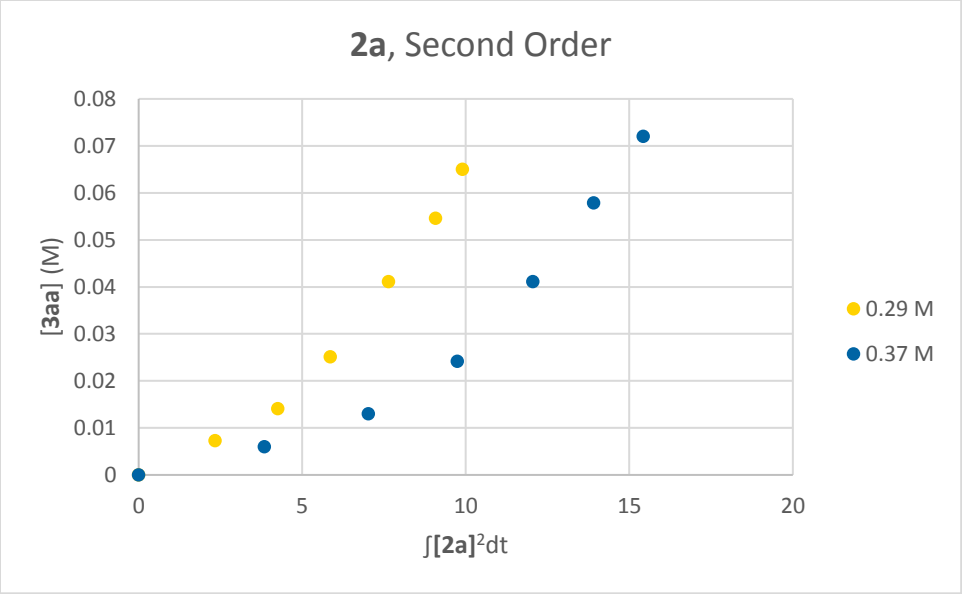
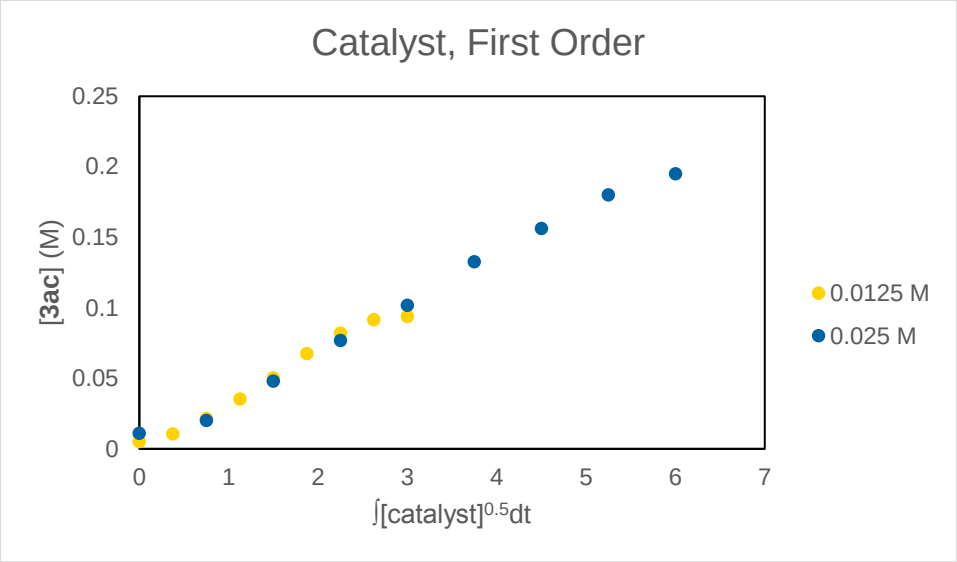
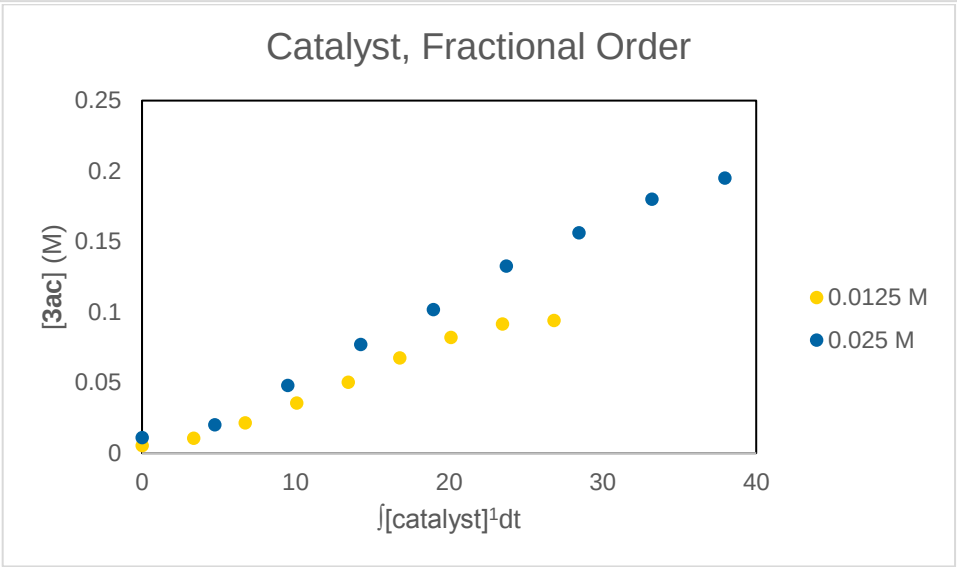


Figure S7. VTNA graphs for **2a** in zero, first, and second order. Overlay of the reaction profiles when using zero order analysis indicates that the reaction is zero order with respect to diene (**2**).

Determination of the reaction order of catalyst:

Representative procedure: In an N_2-filled glovebox, solutions of **1c** (194.1 mg, 1.000 mmol) in CPME (1.000 mL), **2a** (132.4 mg, 1.017 mmol) in CPME (1.000 mL), $[Pd(C_3H_5)Cl]_2$ (11.0 mg, 30.1 µmol) and DTBM-SEGPHOS (72.0 mg, 61.0 µmol) in CPME (0.600 mL), and 1,3,5-trimethoxybenzene (68.0 mg, 404 µmol) in CPME (0.400 mL) were prepared. The catalyst solution was stirred for 30 minutes to establish complexation. An oven-dried 1- dram vial was charged with a stir bar, the catalyst solution (50.00 µL), **2a** solution (100.0 µL), 1,3,5-trimethoxybenzene solution (50.00 µL), **1a** solution (100.0 µL), and additional CPME (100.0 µL). The vial was sealed with a septa cap and removed from the glovebox. Using an N_2-filled balloon, the vial was put under positive pressure and aliquots (approximately 25 µL) were taken every 30 minutes, quenched with methanol (approximately 0.5 mL), and diluted with ethyl acetate. The reaction is quenched in methanol. The amount of **3ac** was monitored using GCFID analysis. By visual analysis, it is concluded that the reaction rate is first order with respect to catalyst.


Catalyst, First Order
[3ac] (M)
0.25
0.2
0.15
0.1
0.05
0
0
1
2
3
4
5
6
7
∫[catalyst]^0.5dt
0.0125 M
0.025 M


Catalyst, Fractional Order
[3ac] (M)
0.25
0.2
0.15
0.1
0.05
0
0
10
20
30
40
∫[catalyst]^1dt
0.0125 M
0.025 M

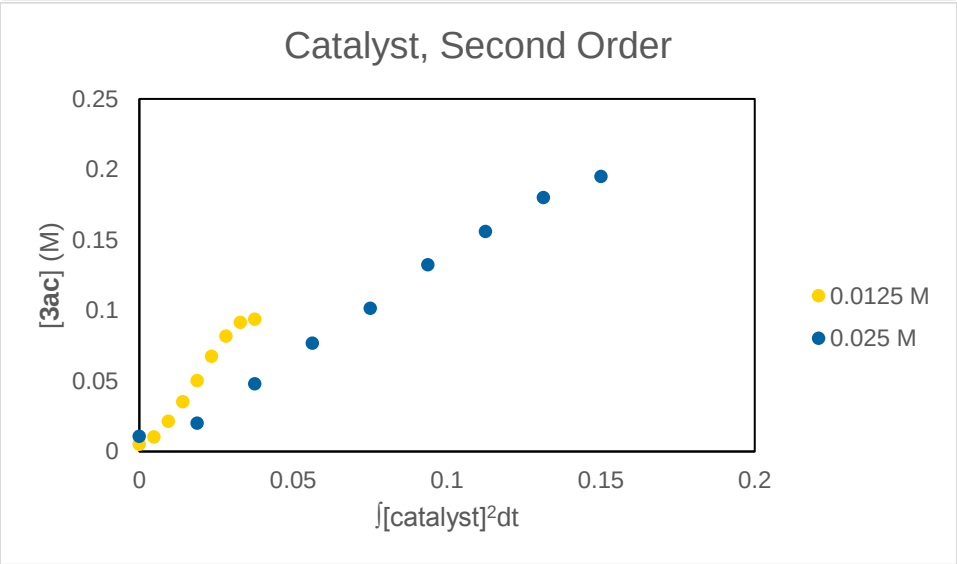

Catalyst, Second Order
[3ac] (M)
0.25
0.2
0.15
0.1
0.05
0
0
0.05
0.1
0.15
0.2
∫[catalyst]^2dt
0.0125 M
0.025 M

Figure S8. VTNA graphs for catalyst in first, fractional, and second order. Overlay of the reaction profiles when using first order analysis indicates that the reaction is first order with respect to catalyst.

5. ECD Studies

Experimental ECD data was obtained using a Jasco J-810 spectropolarimeter. Solutions of pure **3aa** (0.86 mM) and **3ab** (0.38 mM) in acetonitrile were made. Spectra were obtained using a 1.00 mm quartz cuvette. Data was smoothed using a Savitsky-Golay filter with a convolution width of 9. Ground state and time-dependent density functional theory (TDDFT) results were obtained using Turbomole V7.5.[7] Ground state geometry structure optimizations were performed using the B3-LYP hybrid density functional[8] and the conductor-like screening model (COSMO) with the dielectric constant of acetonitrile (ε = 37.5).[9] The split valence polarization basis set def2-SVP,[10] the Resolution-of-the-identity approximation (RI),[11] and a DFT quadrature grid of size m3[12] were used. ECD spectra were acquired using TDDFT[13] using the same parameters, and the RPA singlet approximation.[14] CD spectra were simulated using the TmoleX built-in Gaussian line broadening.

(1) 3aa:

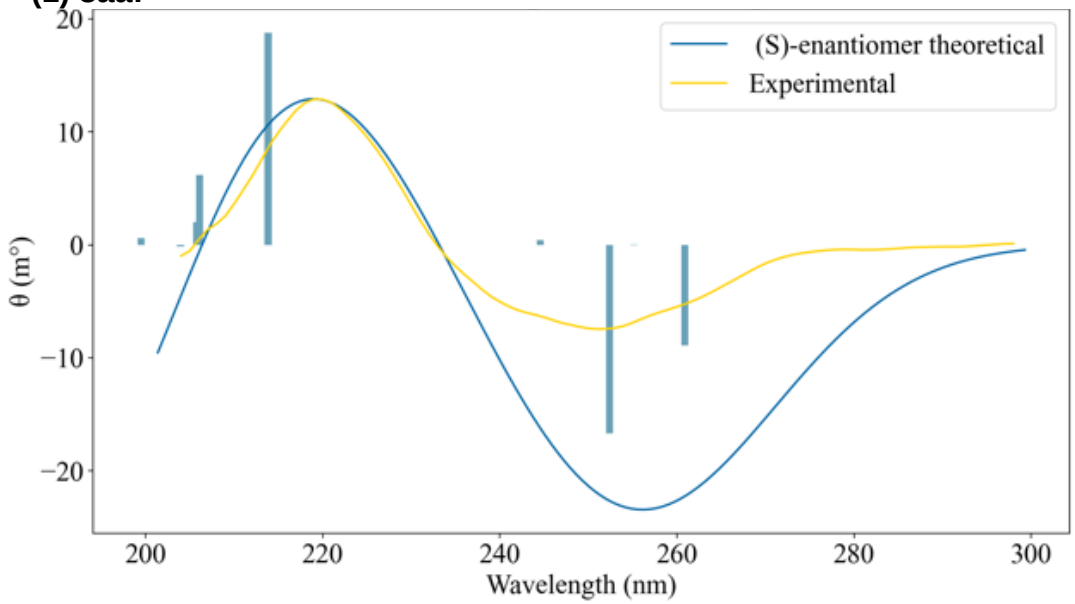


Figure S9. Computational results for the (*S*)-enantiomer and the experimental spectrum of **3aa**. Theoretical data was scaled to match the maximum of the experimental data, and fitting functions were performed using Gaussian statistics in TmoleX. Experimental data was smoothed using a Savitzky-Golay filter.

Experimental Data

Raw data		Smoothed data	
Wavelength	mDeg	Wavelength	mDeg
300	0.118266	300	0.103899
299	0.0595256	299	0.108234
298	0.094574	298	0.10815
297	0.122371	297	0.086314

296	0.0839991	296	0.0332798
295	-0.0125534	295	-0.0184225
294	-0.12836	294	-0.0726643
293	-0.184223	293	-0.132071
292	-0.111836	292	-0.162778
291	-0.132594	291	-0.167789
290	-0.220407	290	-0.165686
289	-0.165311	289	-0.18362
288	-0.188607	288	-0.199179
287	-0.229075	287	-0.213897
286	-0.267876	286	-0.253965
285	-0.236964	285	-0.322966
284	-0.394409	284	-0.377357
283	-0.488905	283	-0.41627
282	-0.455862	282	-0.436875
281	-0.41388	281	-0.447855
280	-0.407814	280	-0.422846
279	-0.411125	279	-0.411312
278	-0.450605	278	-0.425625
277	-0.455146	277	-0.470919
276	-0.534294	276	-0.549352
275	-0.623099	275	-0.643884
274	-0.796748	274	-0.744416
273	-0.941092	273	-0.897491
272	-1.04105	272	-1.09668
271	-1.26689	271	-1.34299
270	-1.69516	270	-1.64289
269	-2.03852	269	-2.0192
268	-2.40704	268	-2.44419
267	-2.86878	267	-2.86895
266	-3.33725	266	-3.30413
265	-3.72291	265	-3.72512
264	-4.12674	264	-4.15557
263	-4.58666	263	-4.54439
262	-4.83647	262	-4.9031
261	-5.31273	261	-5.21036
260	-5.47747	260	-5.48588
259	-5.73449	259	-5.73592
258	-5.91373	258	-5.97953

257	-6.27245	257	-6.2459
256	-6.52884	256	-6.56445
255	-6.81323	255	-6.89077
254	-7.25983	254	-7.17926
253	-7.39457	253	-7.35118
252	-7.52326	252	-7.43241
251	-7.4051	251	-7.45159
250	-7.26053	250	-7.3897
249	-7.25183	249	-7.25427
248	-7.25083	248	-7.0788
247	-6.91377	247	-6.91122
246	-6.51791	246	-6.67112
245	-6.45059	245	-6.40513
244	-6.23275	244	-6.19167
243	-5.84404	243	-5.9988
242	-5.80637	242	-5.77114
241	-5.60015	241	-5.4349
240	-4.99719	240	-5.0344
239	-4.53283	239	-4.56441
238	-3.91849	238	-3.95407
237	-3.31868	237	-3.29352
236	-2.65372	236	-2.62159
235	-1.81215	235	-1.89876
234	-1.0479	234	-1.09911
233	-0.208641	233	-0.12422
232	0.801196	232	0.972108
231	2.18052	231	2.17615
230	3.66916	230	3.51776
229	4.82562	229	4.87199
228	6.15909	228	6.16808
227	7.47779	227	7.40626
226	8.44928	226	8.52717
225	9.55094	225	9.55862
224	10.618	224	10.4541
223	11.1482	223	11.2504
222	11.8653	222	11.9914
221	12.5007	221	12.5786
220	12.9499	220	12.8516
219	13.122	219	12.886

218	12.677	218	12.5641
217	11.6193	217	11.8931
216	11.0413	216	10.9588
215	9.93503	215	9.94056
214	8.67889	214	8.80083
213	7.54987	213	7.38001
212	6.39214	212	6.02996
211	4.46635	211	4.81436
210	2.95882	210	3.61688
209	3.24508	209	2.53754
208	1.88644	208	1.84964
207	0.791935	207	1.34491
206	0.613372	206	0.473079

Theoretical data

Wavelength	Rotatory strength
173.507426	0.548119
174.263315	-4.5555945
174.370493	0.61602423
175.618448	1.12900225
180.044076	10.9937404
180.220756	-10.292896
183.722704	-0.1195331
185.119829	-10.294263
188.665581	28.3519989
190.802257	-56.224584
194.572165	-8.0373511
208.203526	12.2305626
213.213617	8.49286052
216.077808	0.41977558
220.112104	1.73034454
250.894691	-17.055073
256.797743	-0.1901558
263.539188	-9.2875019
268.3673	5.44434419

(1) 3ab

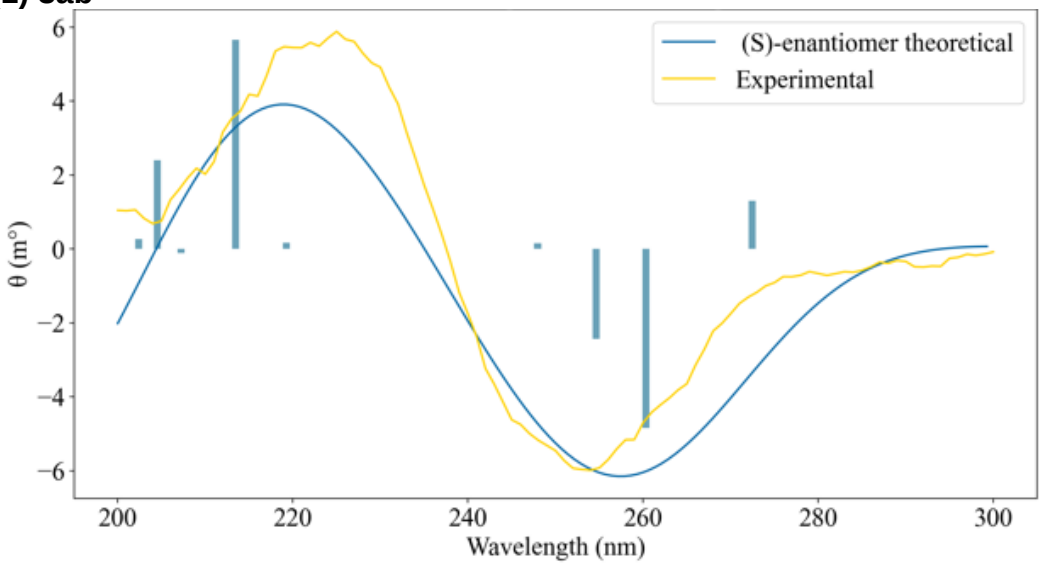


Figure S10. Computational results for the (*S*)-enantiomer and the experimental spectrum of **3ab**. Theoretical data was scaled to match the maximum of the experimental data, and fitting functions were performed using Gaussian statistics in TmoleX. Experimental data was smoothed using a Savitzky-Golay filter.

Experimental Data

raw		smooth	
wavelength	mDeg	wavelength	mDeg
300	-0.0990612	300	-0.0794332
299	-0.119451	299	-0.136095
298	-0.131108	298	-0.173826
297	-0.179289	297	-0.141294
296	-0.242963	296	-0.225768
295	-0.31314	295	-0.253591
294	-0.399159	294	-0.468848
293	-0.459209	293	-0.462111
292	-0.460231	292	-0.490033
291	-0.443227	291	-0.481172
290	-0.382671	290	-0.337368
289	-0.355291	289	-0.3114
288	-0.356764	288	-0.387955
287	-0.404821	287	-0.358103
286	-0.479597	286	-0.485019
285	-0.543523	285	-0.578378
284	-0.603879	284	-0.630772
283	-0.659853	283	-0.61456

282	-0.662794	282	-0.667067
281	-0.660851	281	-0.713714
280	-0.669435	280	-0.663237
279	-0.672248	279	-0.612545
278	-0.686135	278	-0.711057
277	-0.720005	277	-0.751699
276	-0.797887	276	-0.749413
275	-0.898285	275	-0.911375
274	-0.99976	274	-0.998123
273	-1.14083	273	-1.17135
272	-1.32414	272	-1.30542
271	-1.49549	271	-1.4762
270	-1.71886	270	-1.75279
269	-1.9823	269	-2.01565
268	-2.34358	268	-2.22081
267	-2.73865	267	-2.71431
266	-3.13142	266	-3.13706
265	-3.50138	265	-3.64818
264	-3.81402	264	-3.81474
263	-4.02816	263	-4.0322
262	-4.26899	262	-4.21668
261	-4.48538	261	-4.4158
260	-4.72992	260	-4.70245
259	-4.97872	259	-5.15903
258	-5.24509	258	-5.16349
257	-5.49707	257	-5.4088
256	-5.69582	256	-5.70305
255	-5.84904	255	-5.9247
254	-5.98265	254	-5.98681
253	-5.97909	253	-5.96538
252	-5.87391	252	-5.9336
251	-5.71448	251	-5.72825
250	-5.5384	250	-5.45753
249	-5.33613	249	-5.31509
248	-5.16374	248	-5.17086
247	-4.99889	247	-4.98904
246	-4.78532	246	-4.74646
245	-4.52836	245	-4.62376
244	-4.15799	244	-4.14079

243	-3.6746	243	-3.65924
242	-3.12257	242	-3.23388
241	-2.47959	241	-2.38066
240	-1.8047	240	-1.75779
239	-1.08203	239	-1.1789
238	-0.353087	238	-0.345066
237	0.338383	237	0.399333
236	1.05125	236	1.08091
235	1.79263	235	1.72716
234	2.48607	234	2.45103
233	3.19631	233	3.15292
232	3.8378	232	3.92606
231	4.37056	231	4.37892
230	4.80623	230	4.91751
229	5.12092	229	5.03657
228	5.37692	228	5.2948
227	5.58881	227	5.61287
226	5.67743	226	5.67587
225	5.74393	225	5.88504
224	5.71013	224	5.70396
223	5.62048	223	5.48788
222	5.55165	222	5.58586
221	5.53083	221	5.44627
220	5.51393	220	5.45129
219	5.34499	219	5.4731
218	5.09902	218	5.35495
217	4.78765	217	4.68716
216	4.42612	216	4.13866
215	4.09682	215	4.18374
214	3.74224	214	3.72608
213	3.36442	213	3.52278
212	2.98971	212	3.16205
211	2.59616	211	2.36486
210	2.29176	210	2.02546
209	2.03527	209	2.18497
208	1.78379	208	1.92524
207	1.54158	207	1.60958
206	1.23491	206	1.32408
205	0.963603	205	0.758729

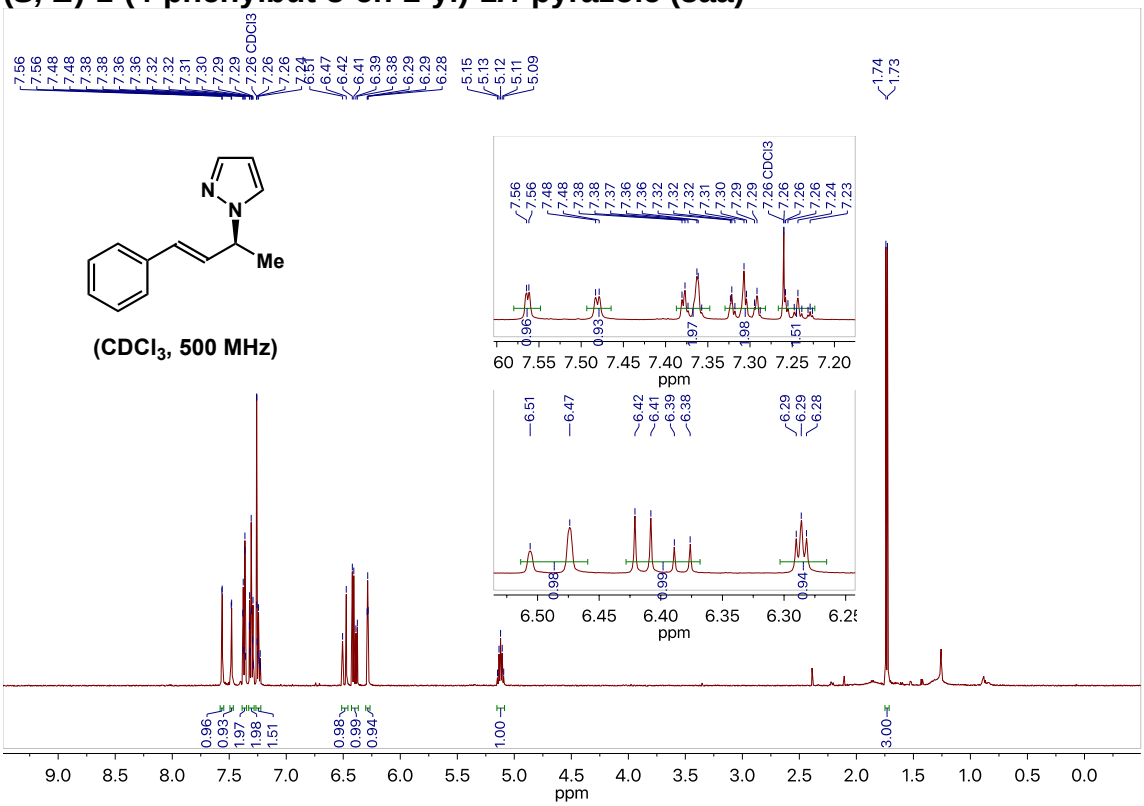
204	0.838812	204	0.685622
203	0.824622	203	0.82957
202	0.892495	202	1.05897
201	1.01393	201	1.0342
200	1.06538	200	1.04648

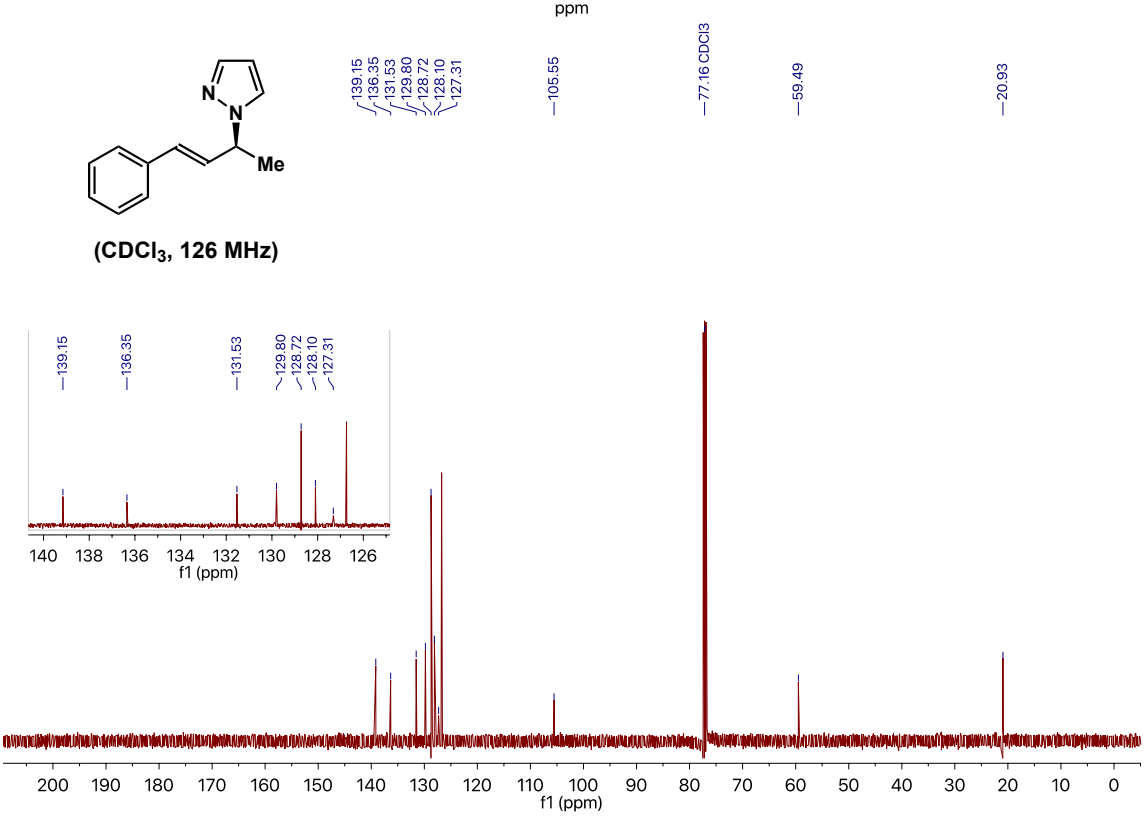
Theoretical data

wavelength	rotatory strength
172.843139	-0.3568048
175.708929	-0.9051742
175.87822	2.19564809
175.963168	-11.610989
177.583501	0.94857959
179.676693	0.39707566
182.410037	-6.1617676
182.801104	-1.876557
190.677006	-4.84516
194.953025	1.70702447
198.934191	-34.72199
202.418195	1.42821712
204.536209	12.5613761
207.236496	-0.5691502
213.477117	29.5821057
219.238049	0.84861878
247.960614	0.80822344
254.651128	-12.747652
260.320093	-25.332058
272.483443	6.82050656

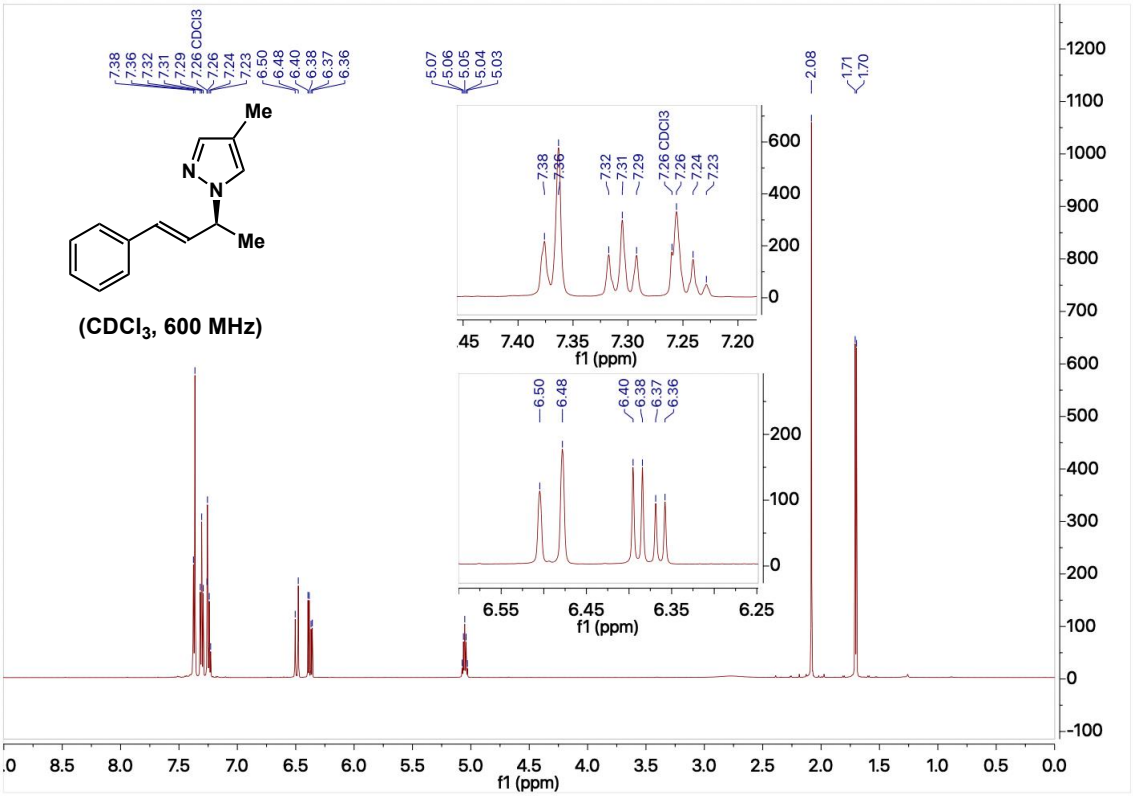
6. NMR spectra of unknown compounds

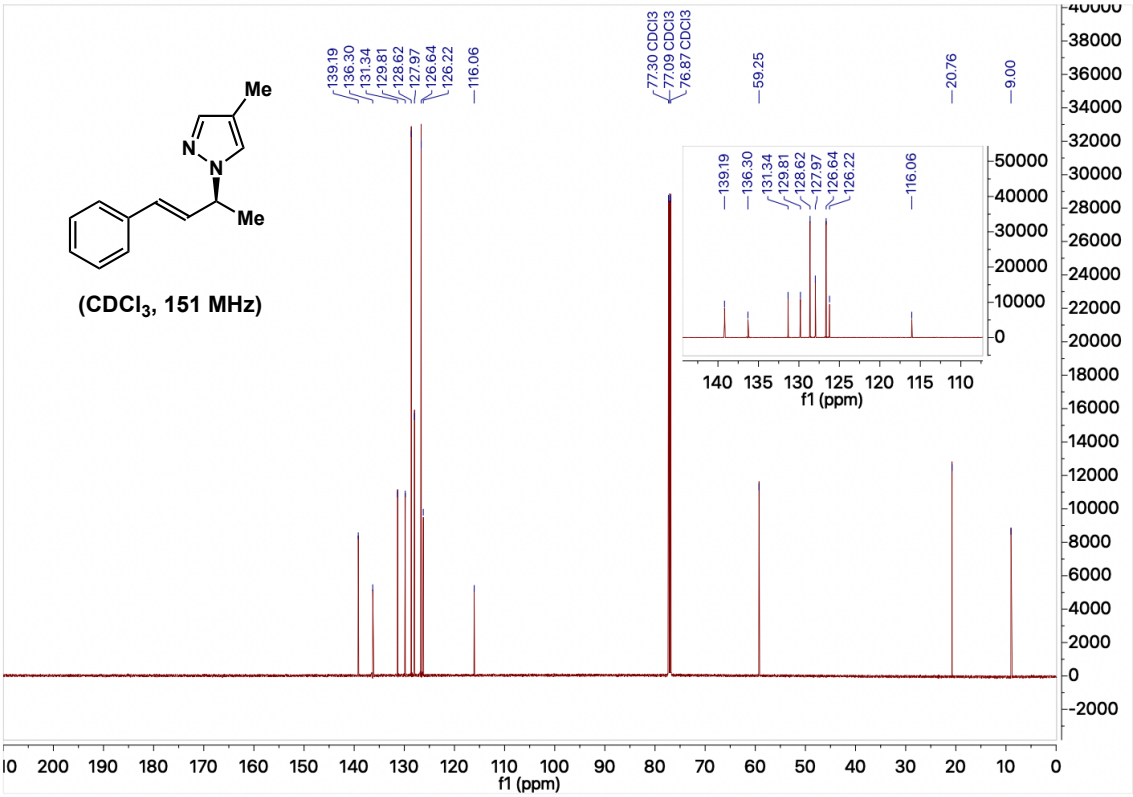
(*S*, *E*)-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3aa)



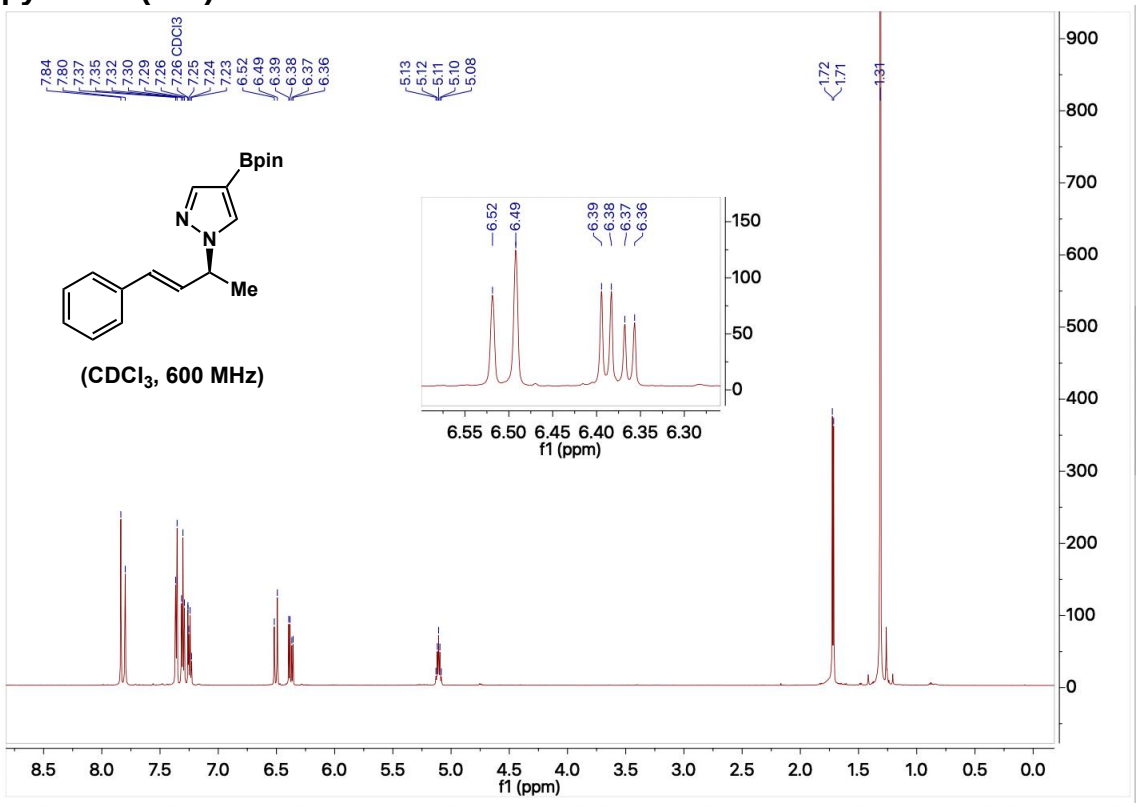


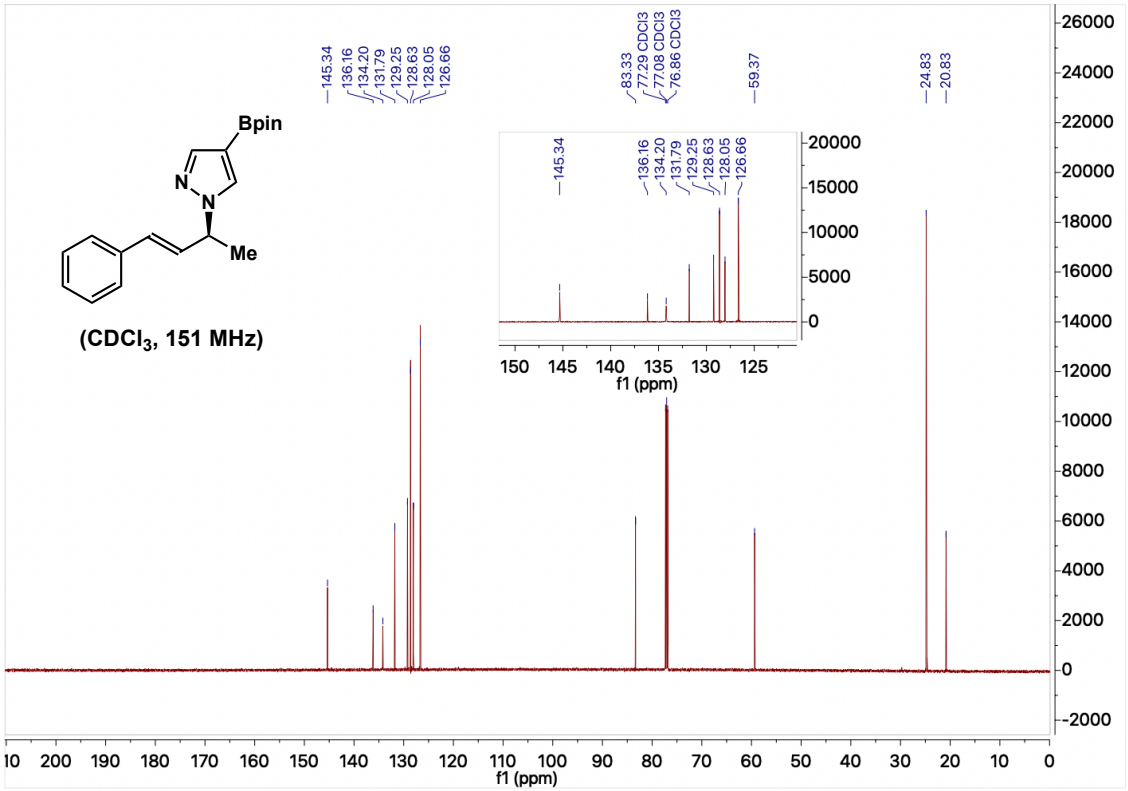
(S, E)-4-methyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ab)



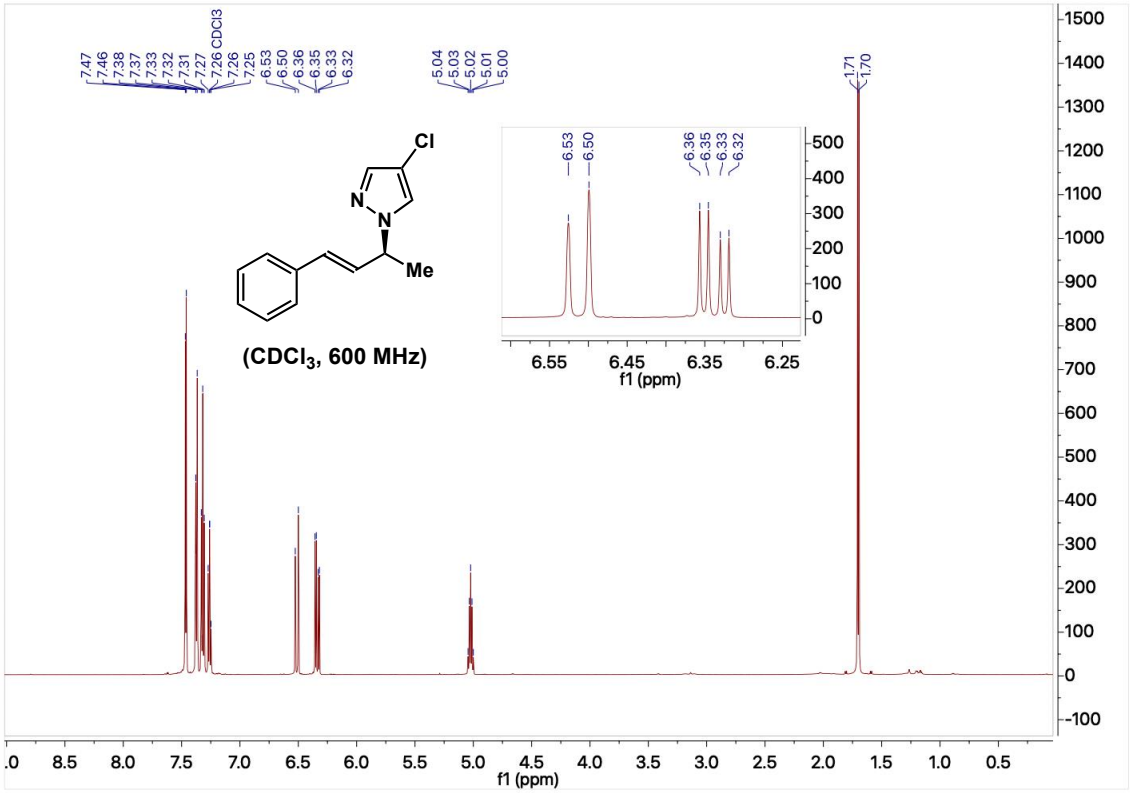


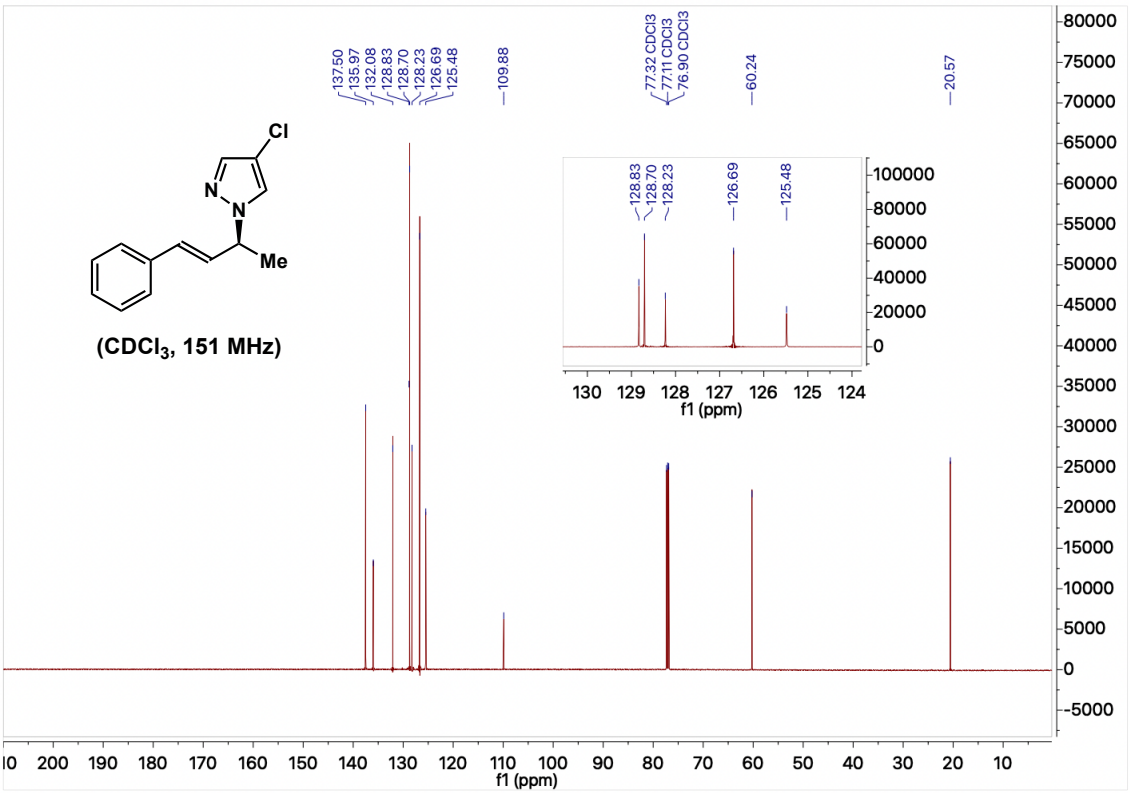
(*S, E*)-1-(4-phenylbut-3-en-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (3ac)



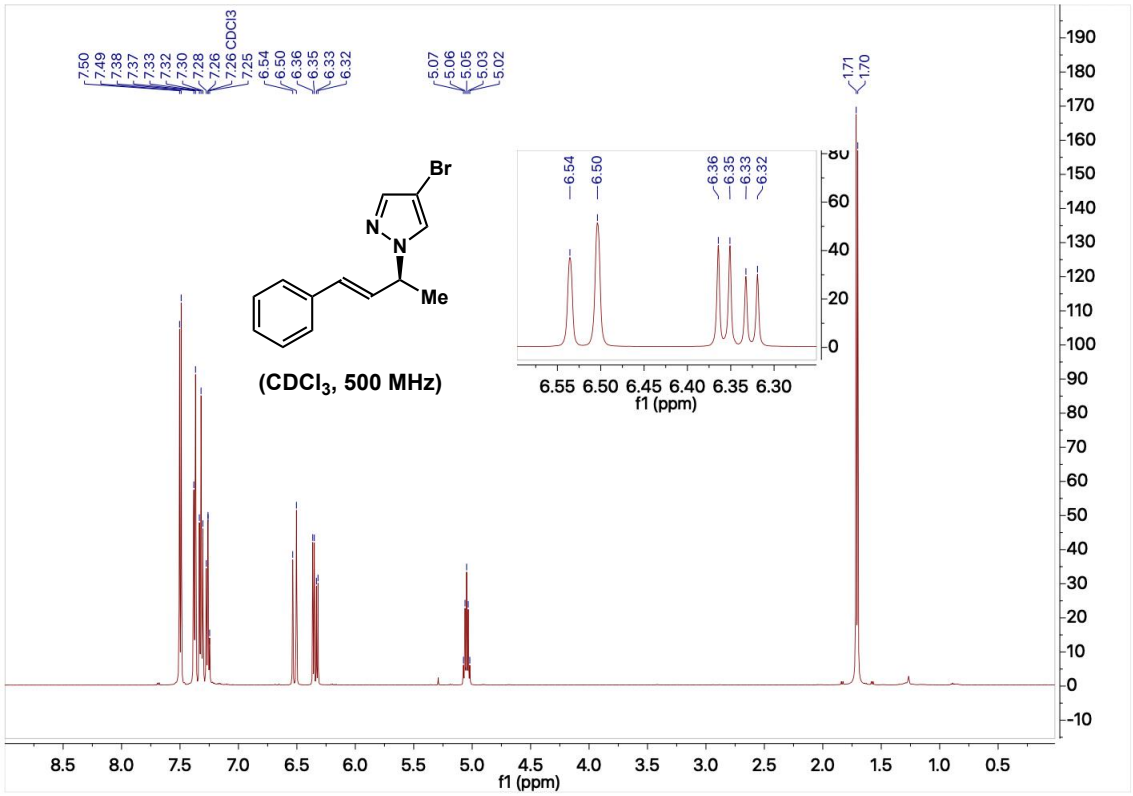


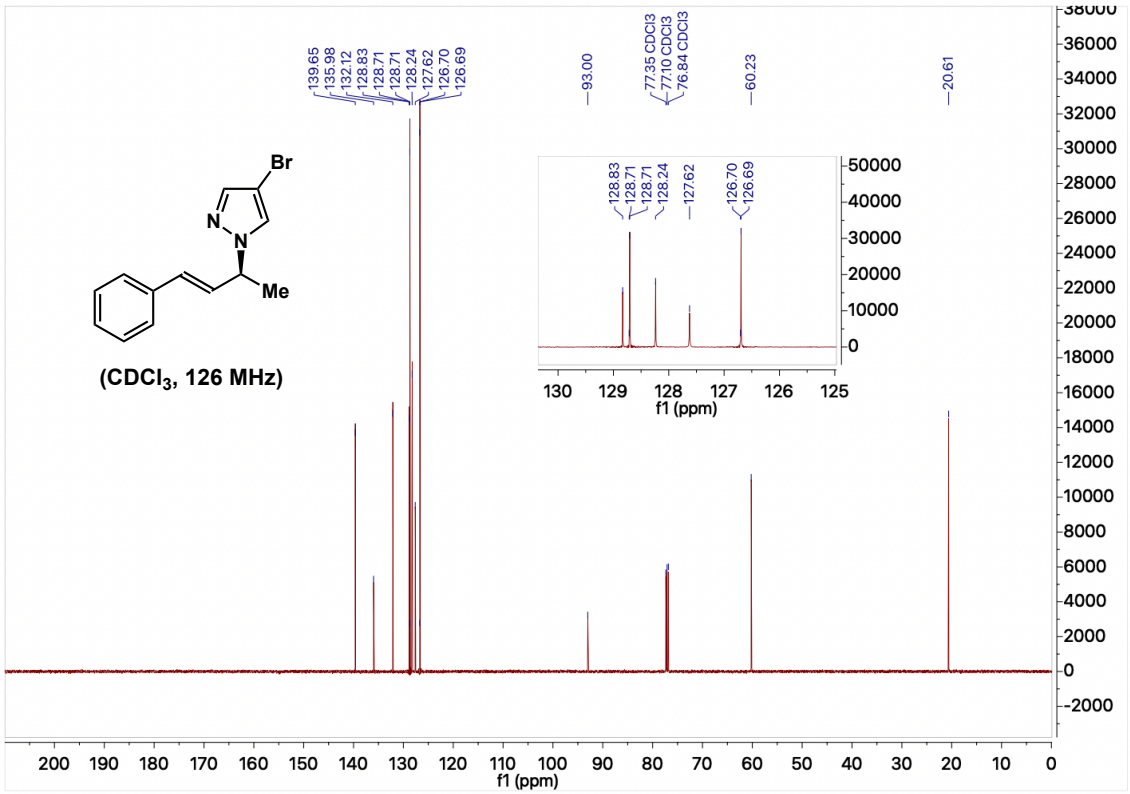
(S, E)-4-chloro-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ad)



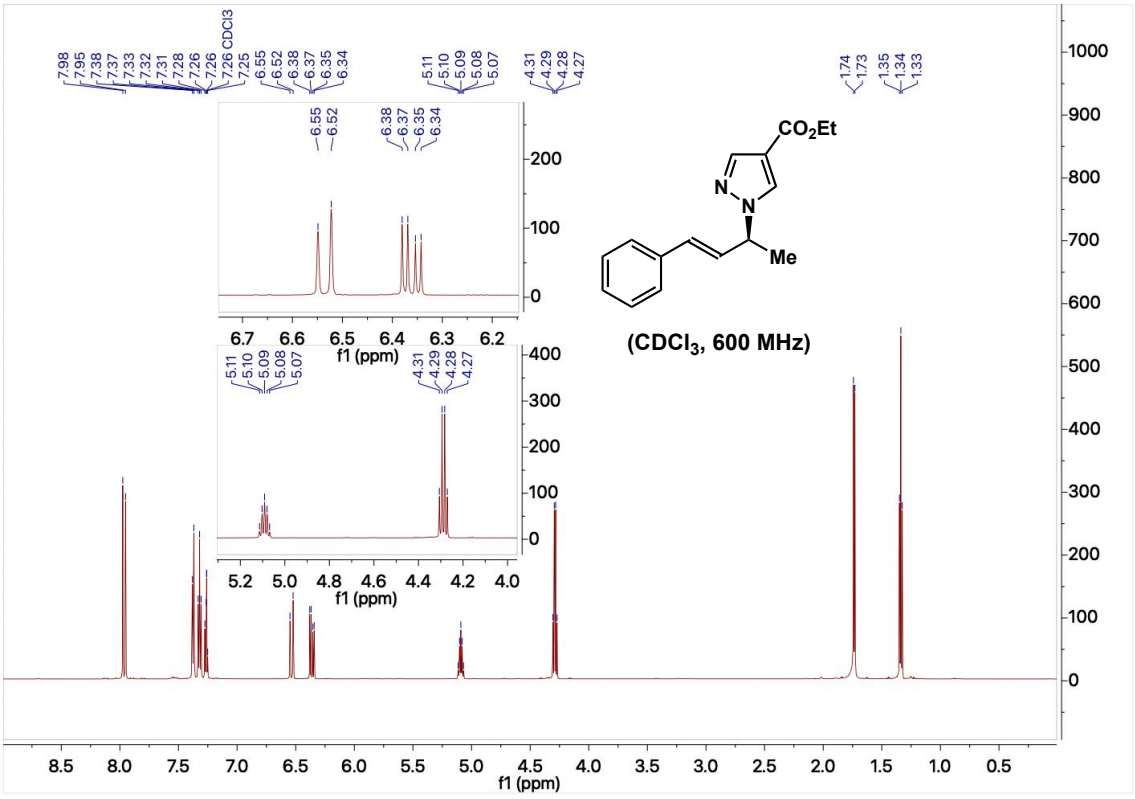


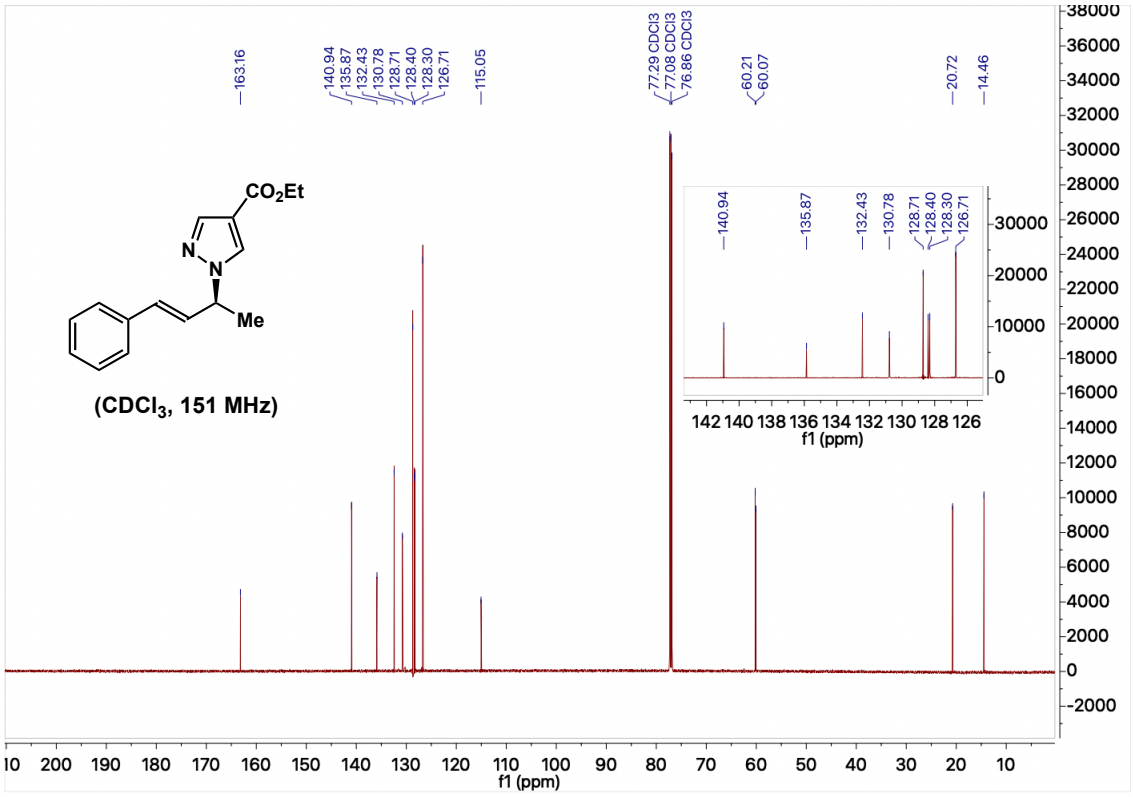
(S, E)-4-bromo-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ae)



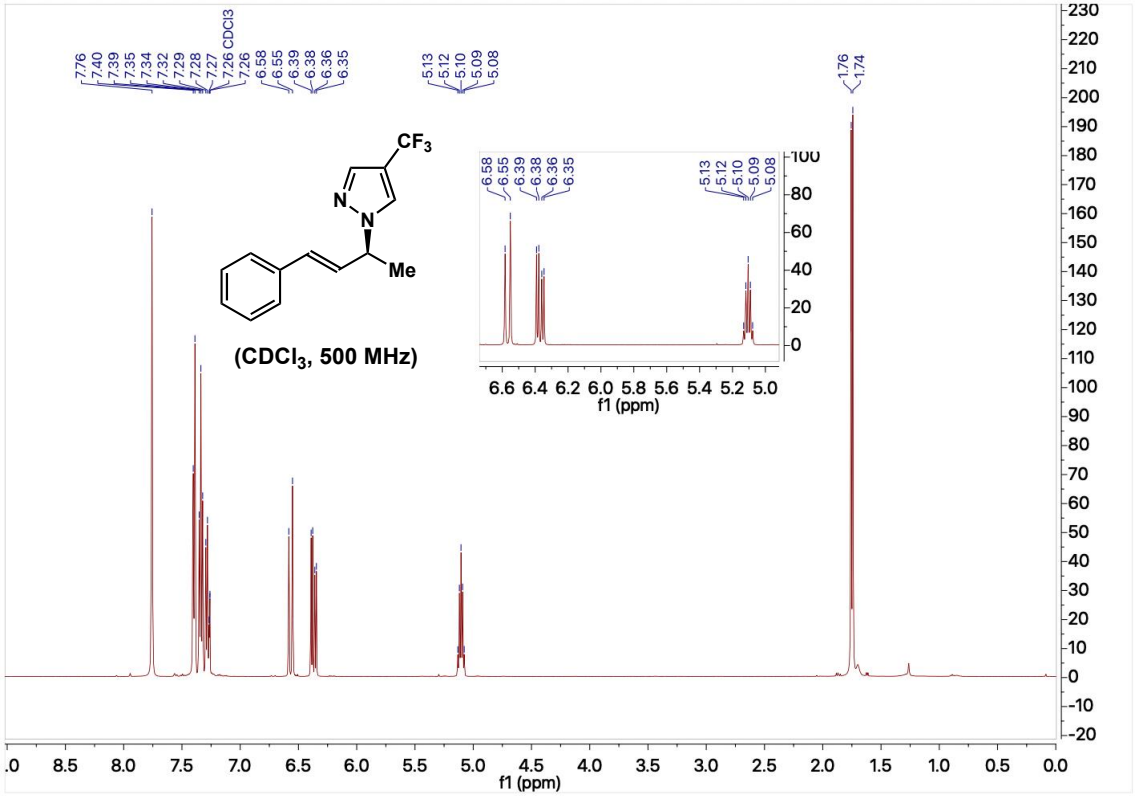


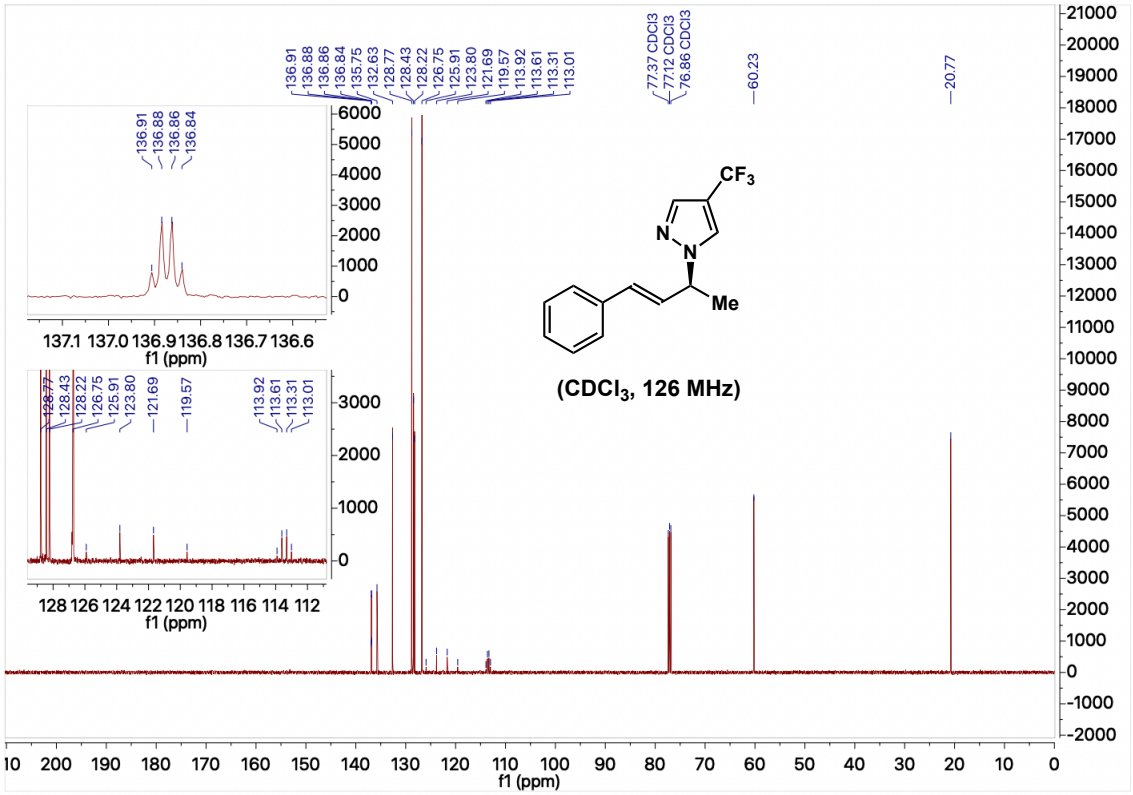
Ethyl (*S*, *E*)-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole-4-carboxylate (3af)



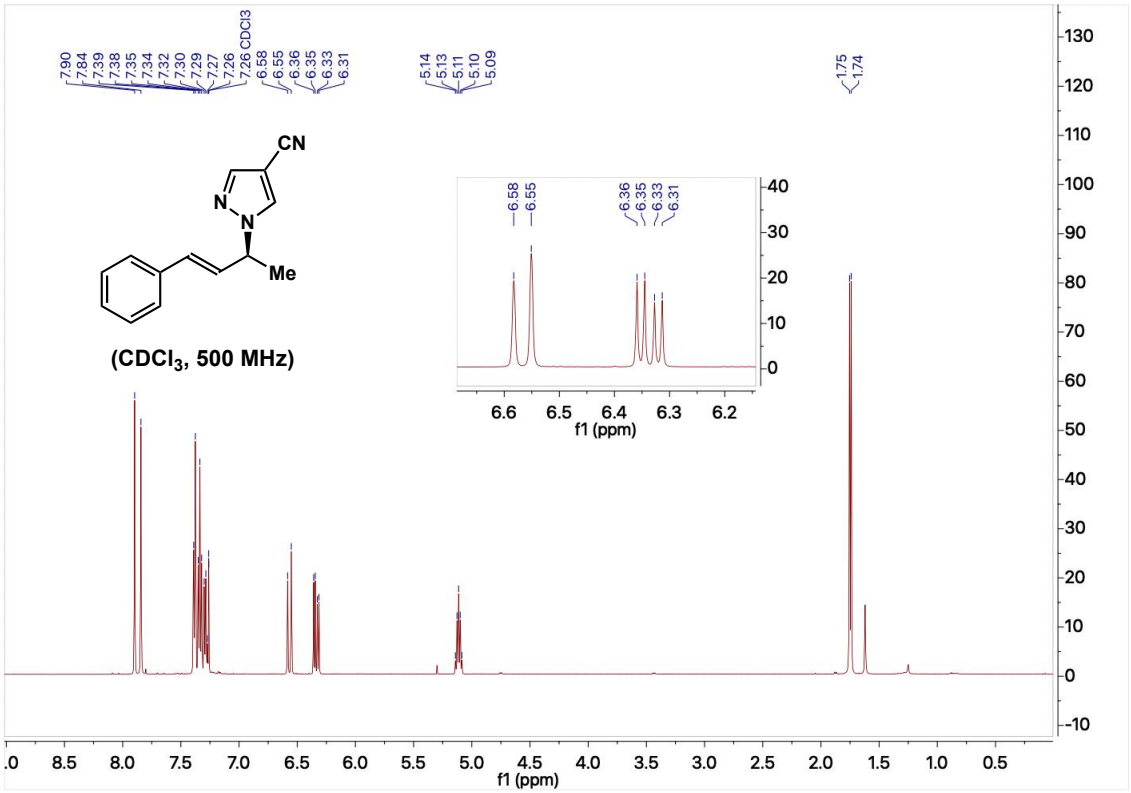


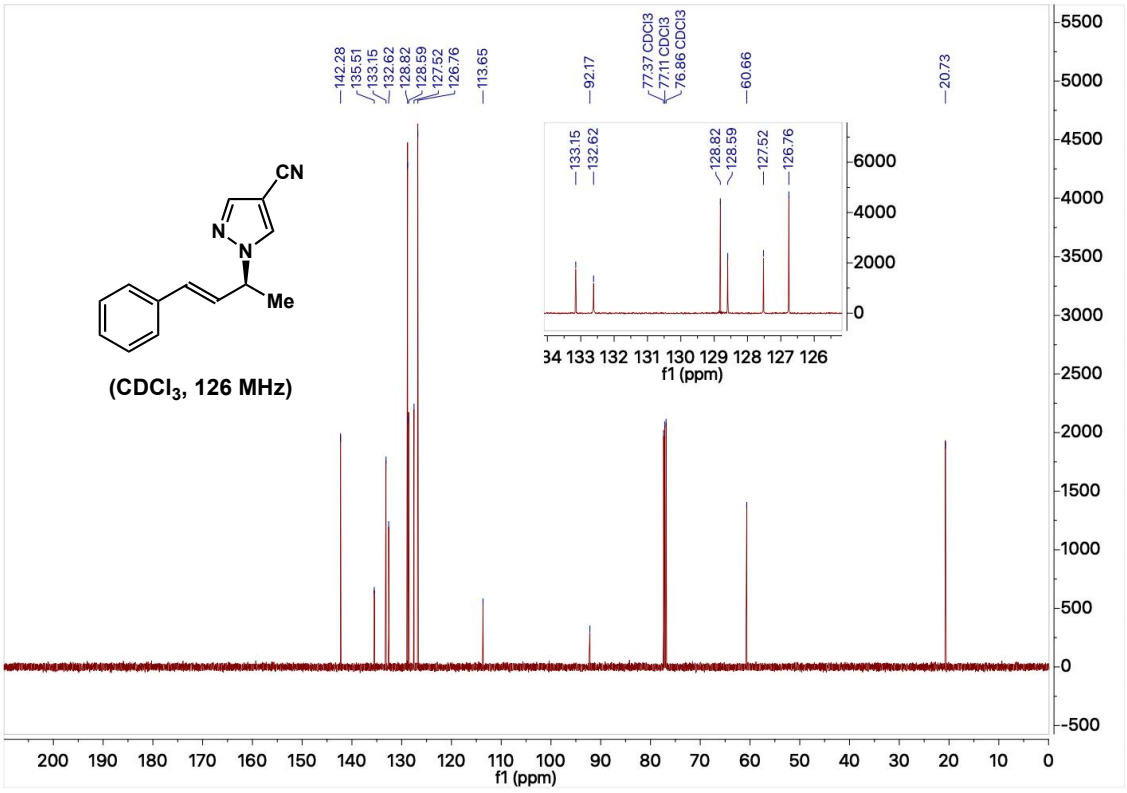
(S, E)-1-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)-1*H*-pyrazole (3ag)



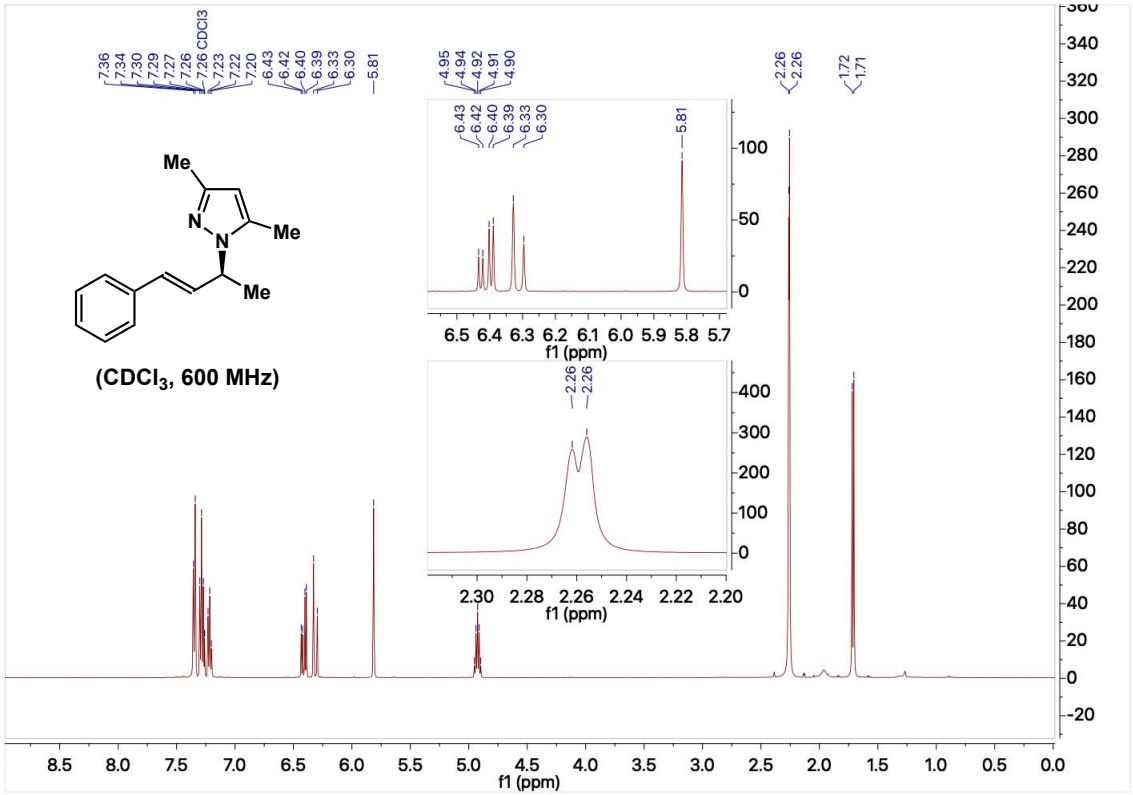


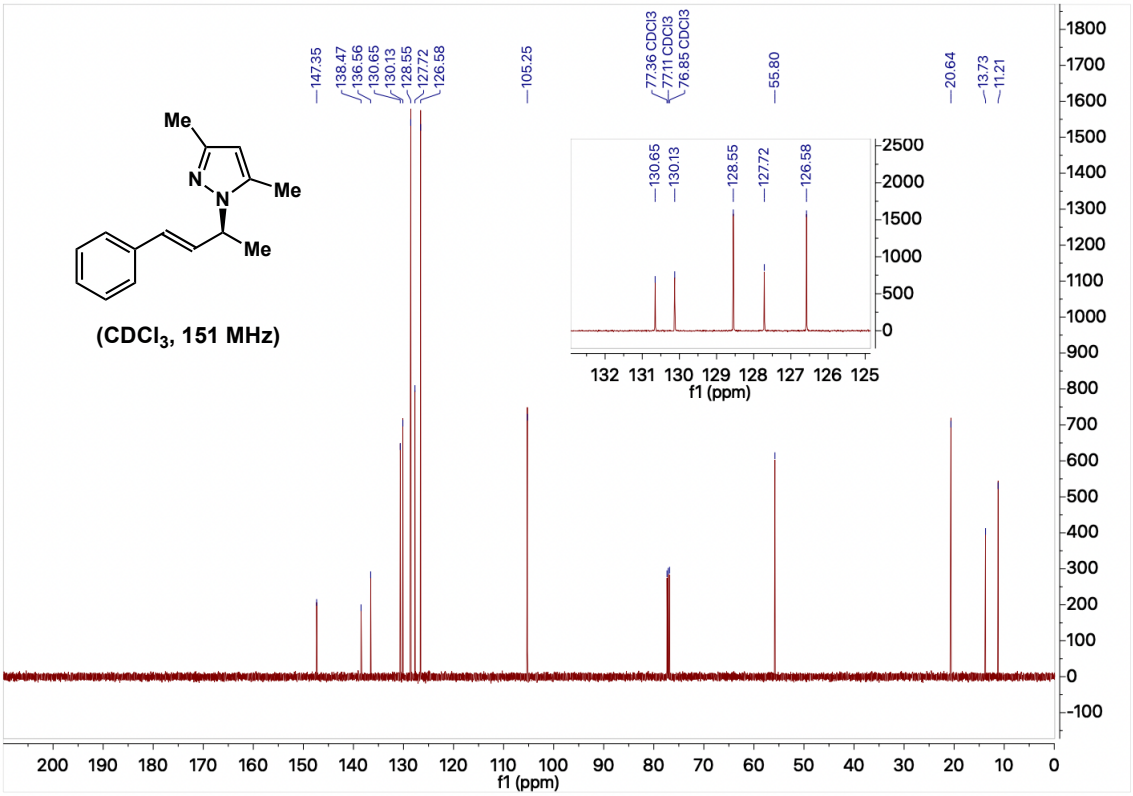
(S, E)-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole-4-carbonitrile (3ah)



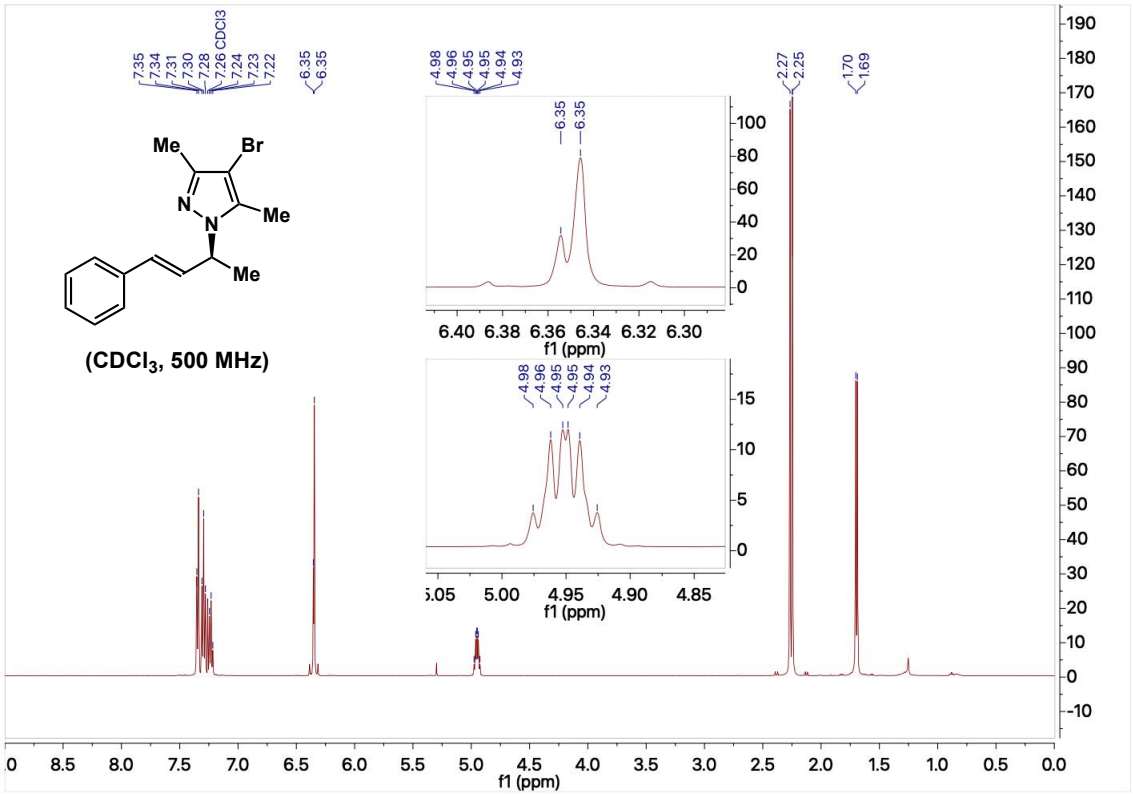


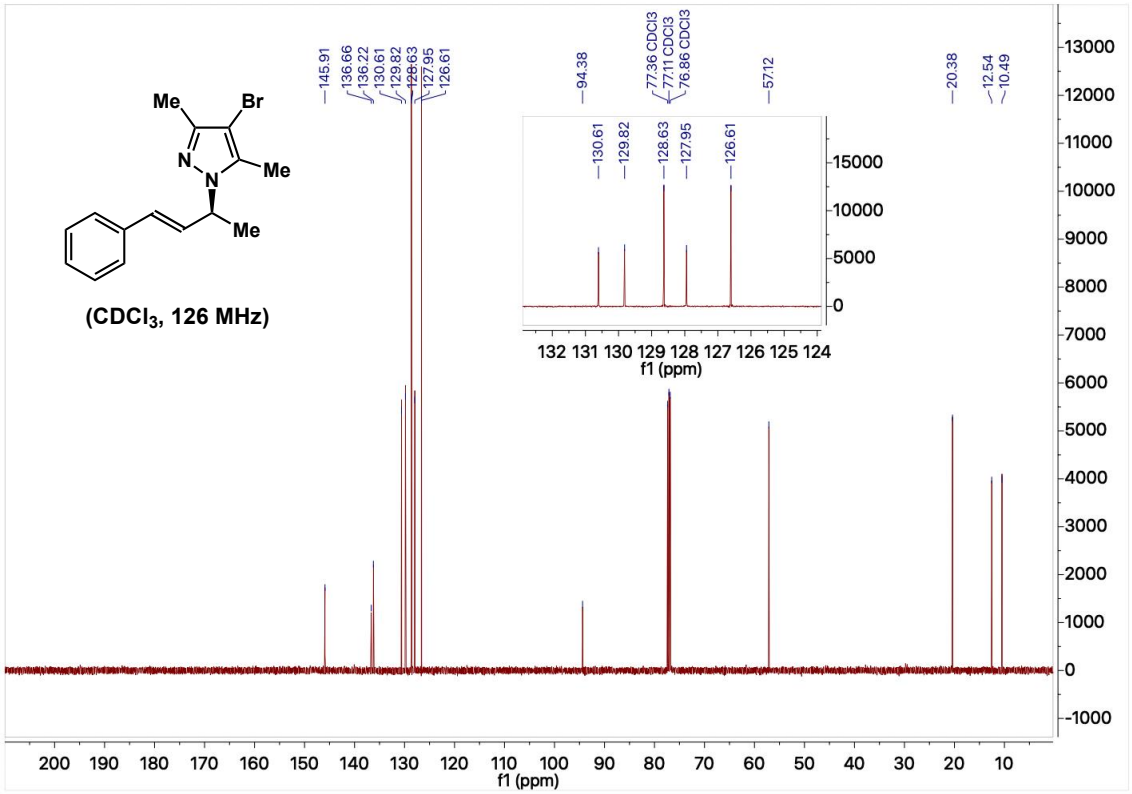
(S, E)-3,5-dimethyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ai)



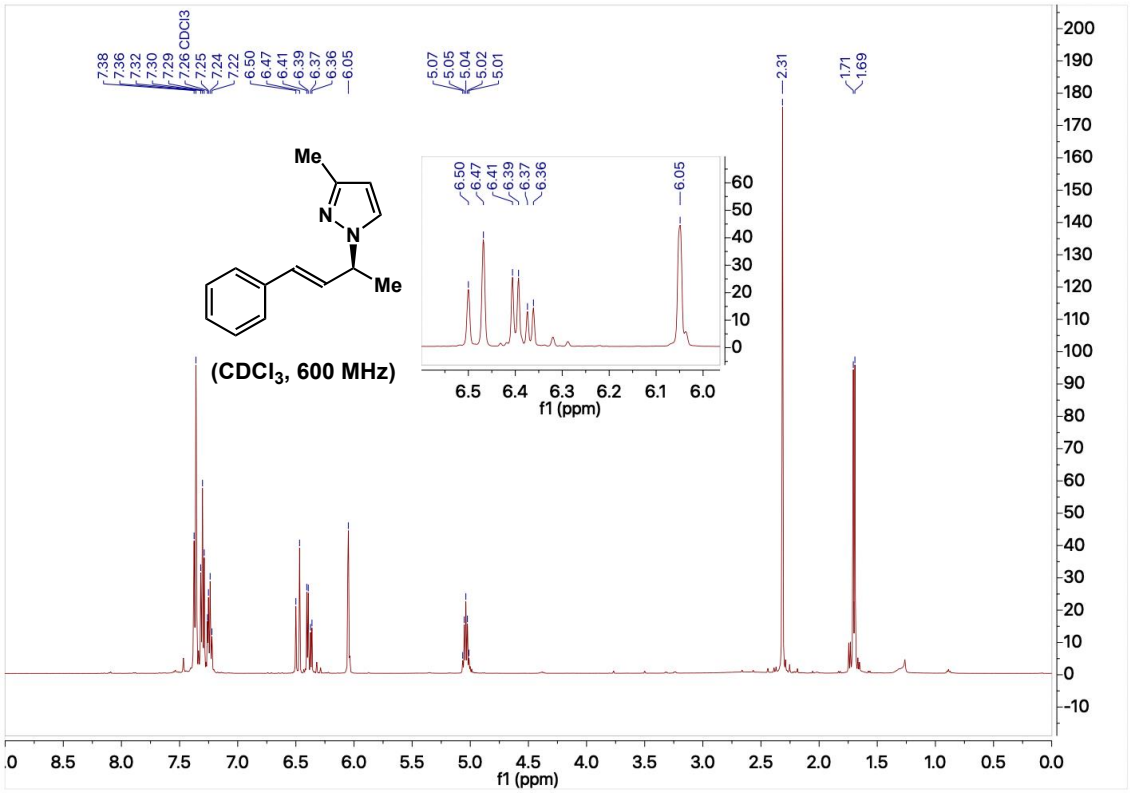


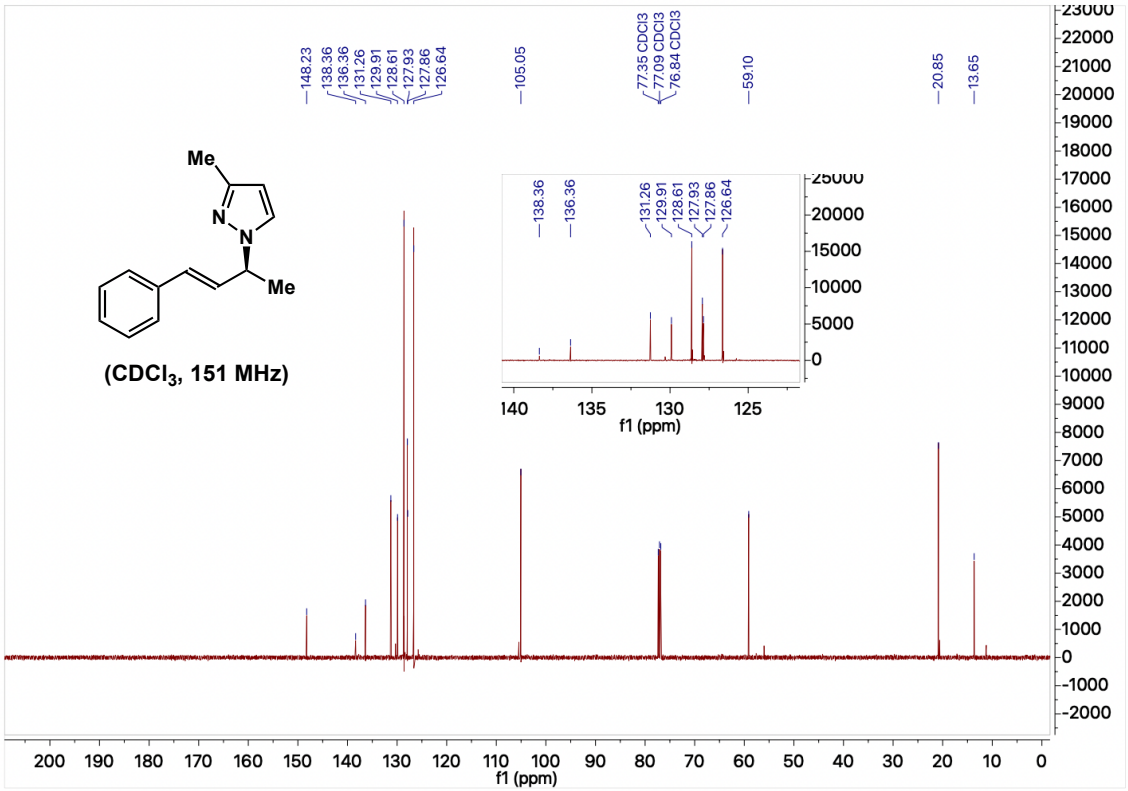
(S, E)-4-bromo-3,5-dimethyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3aj)



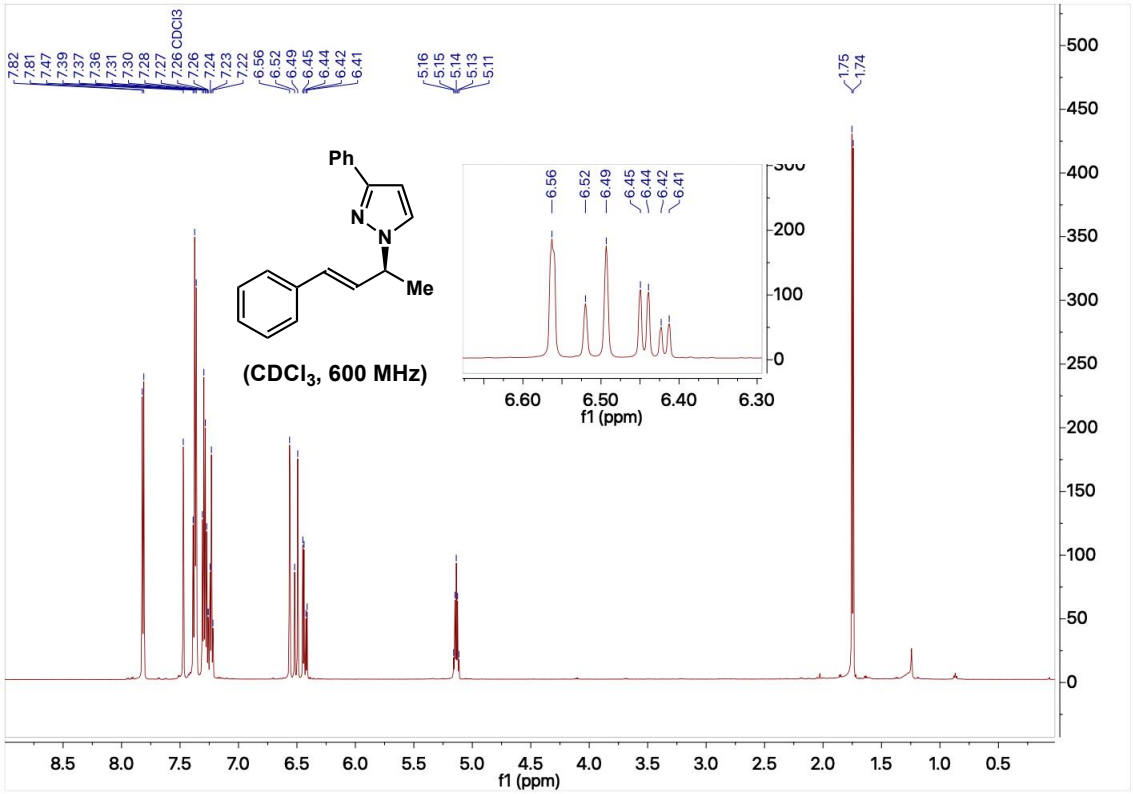


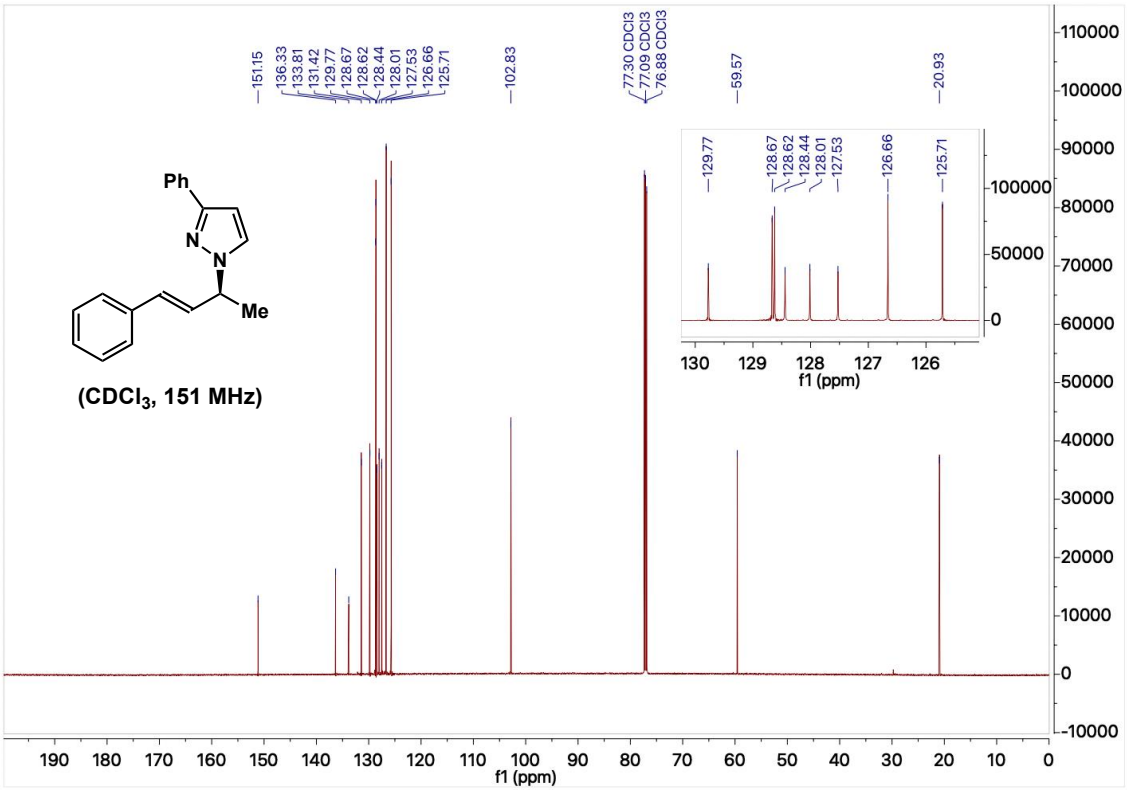
(S, E)-3-methyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3ak)



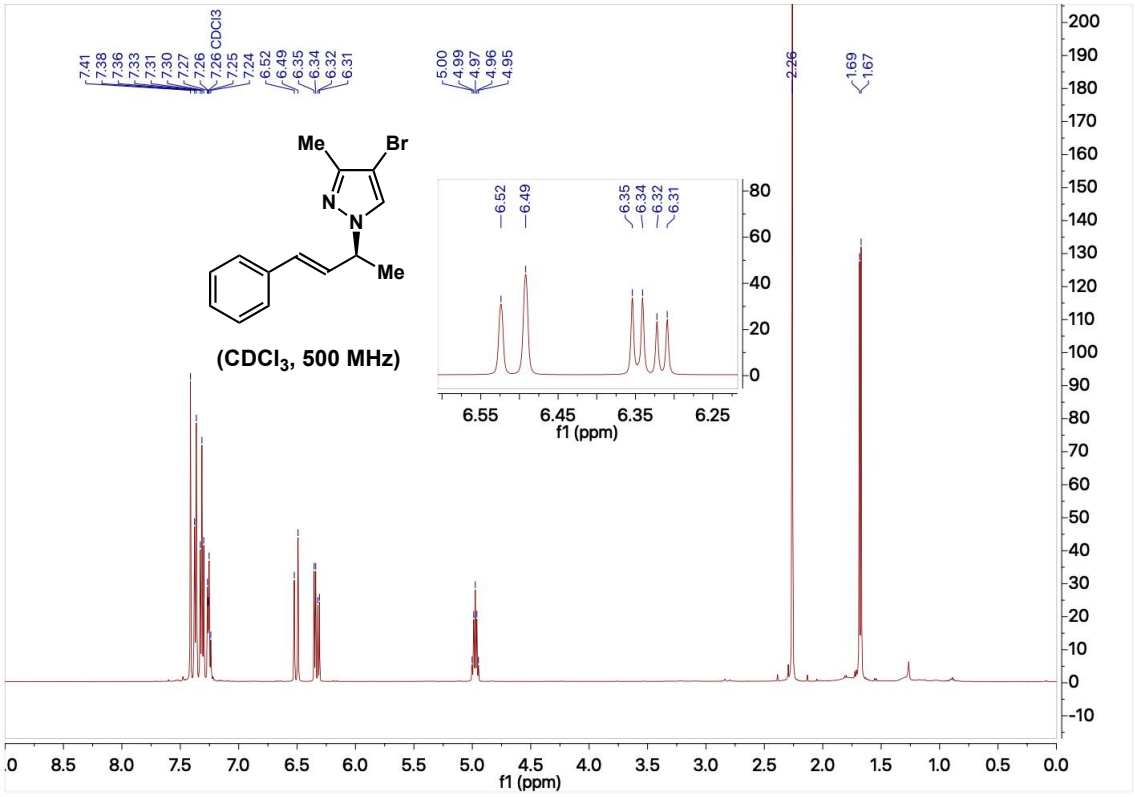


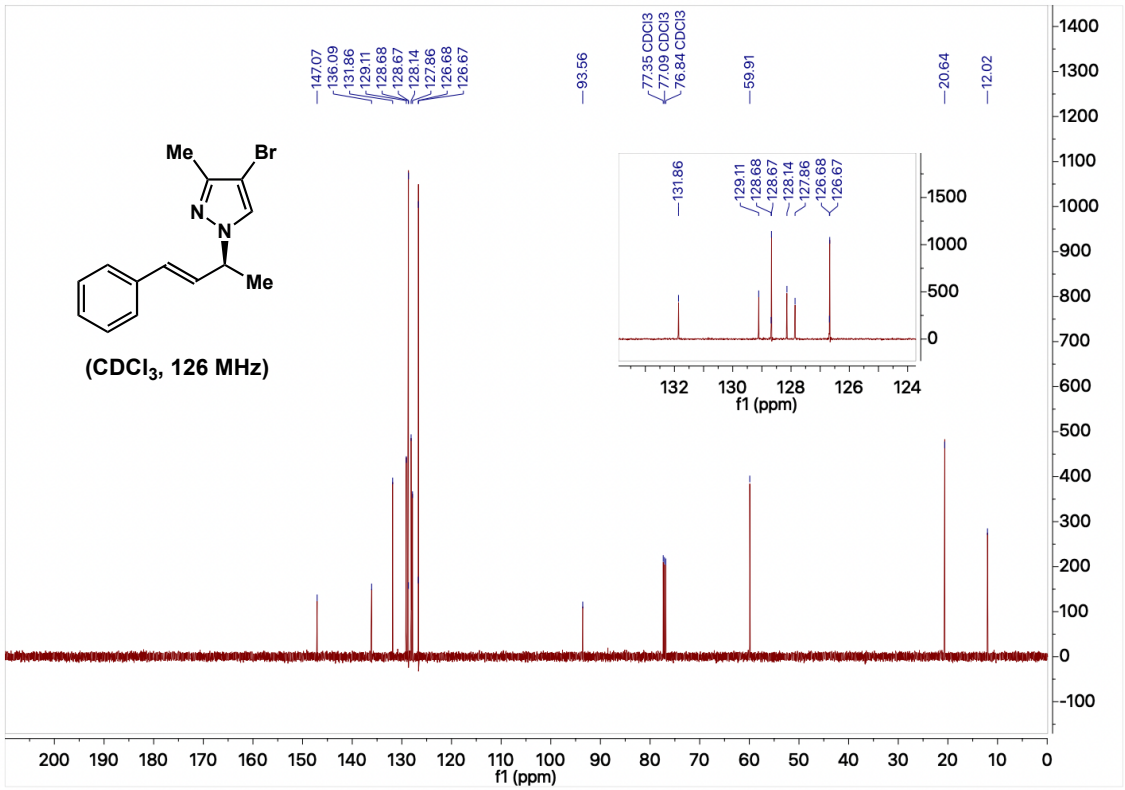
(S, E)-3-phenyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3al)



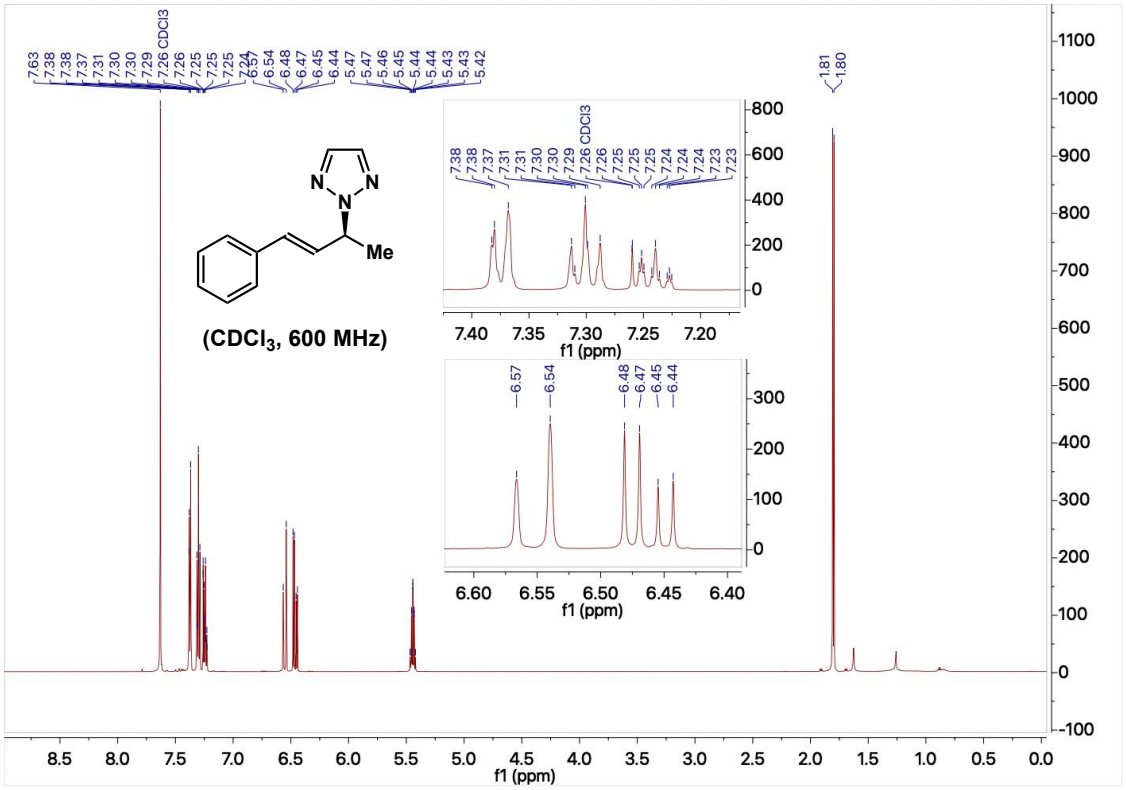


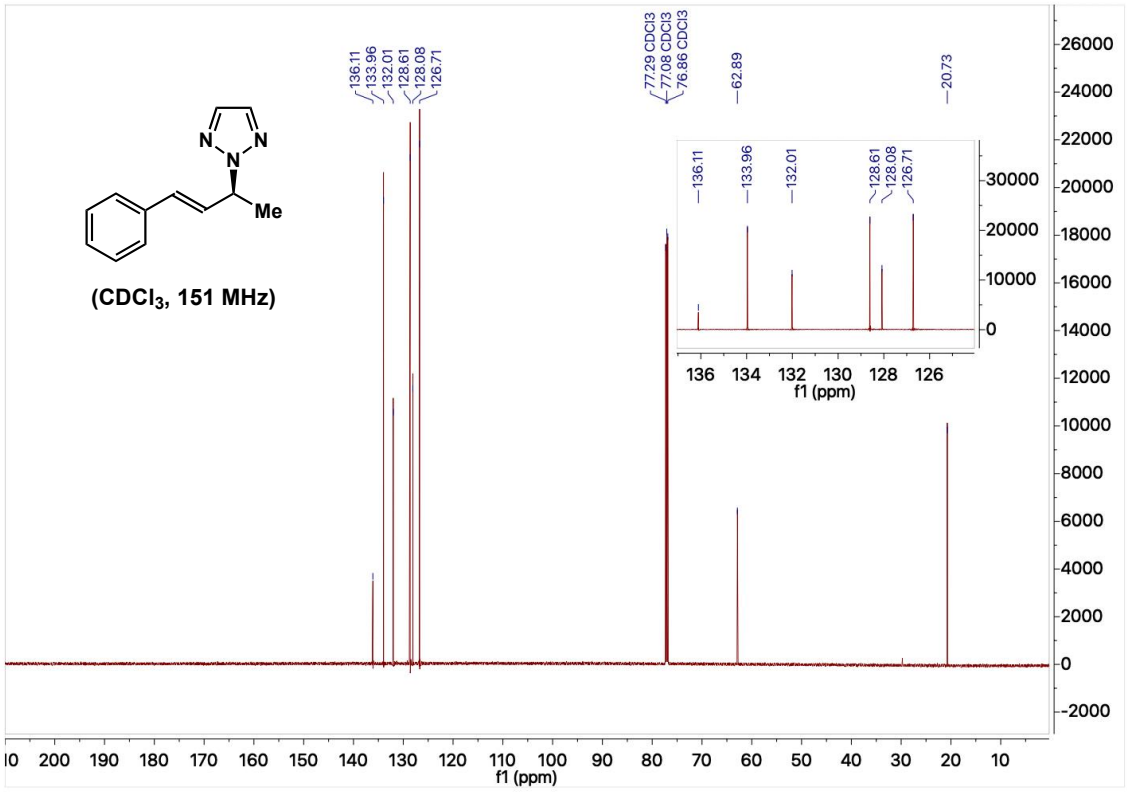
(S, E)-4-bromo-5-methyl-1-(4-phenylbut-3-en-2-yl)-1*H*-pyrazole (3am)



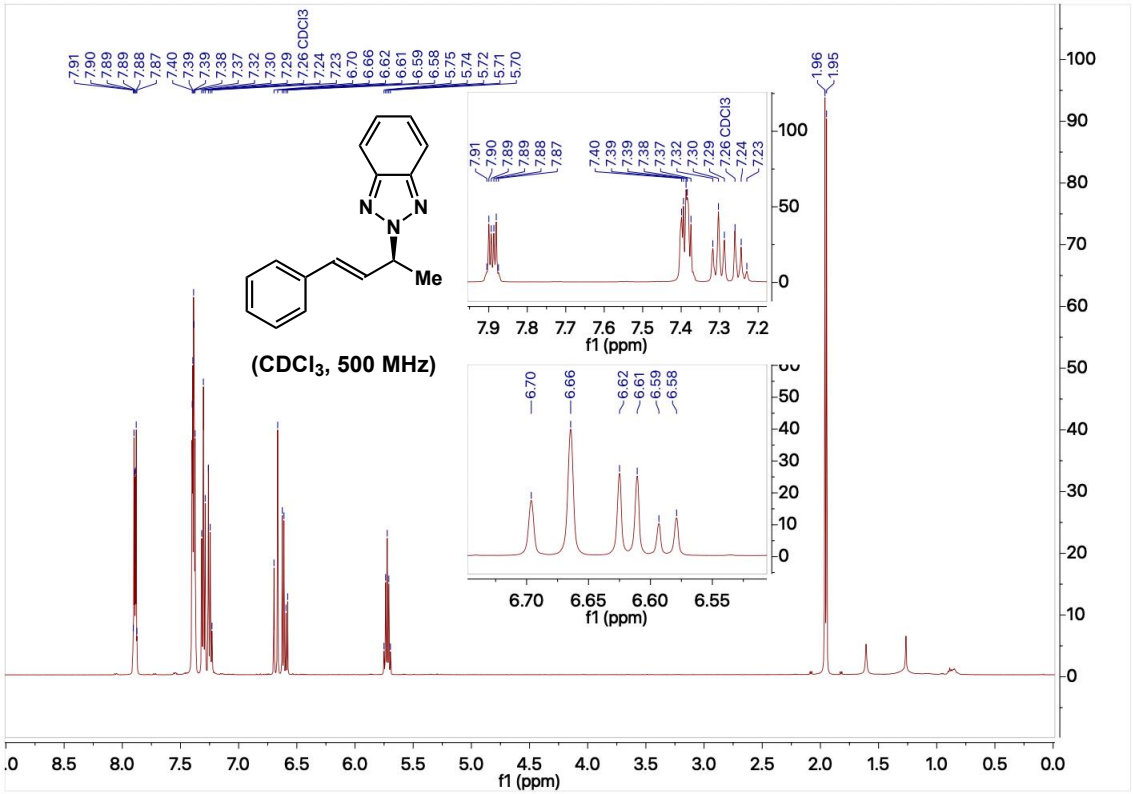


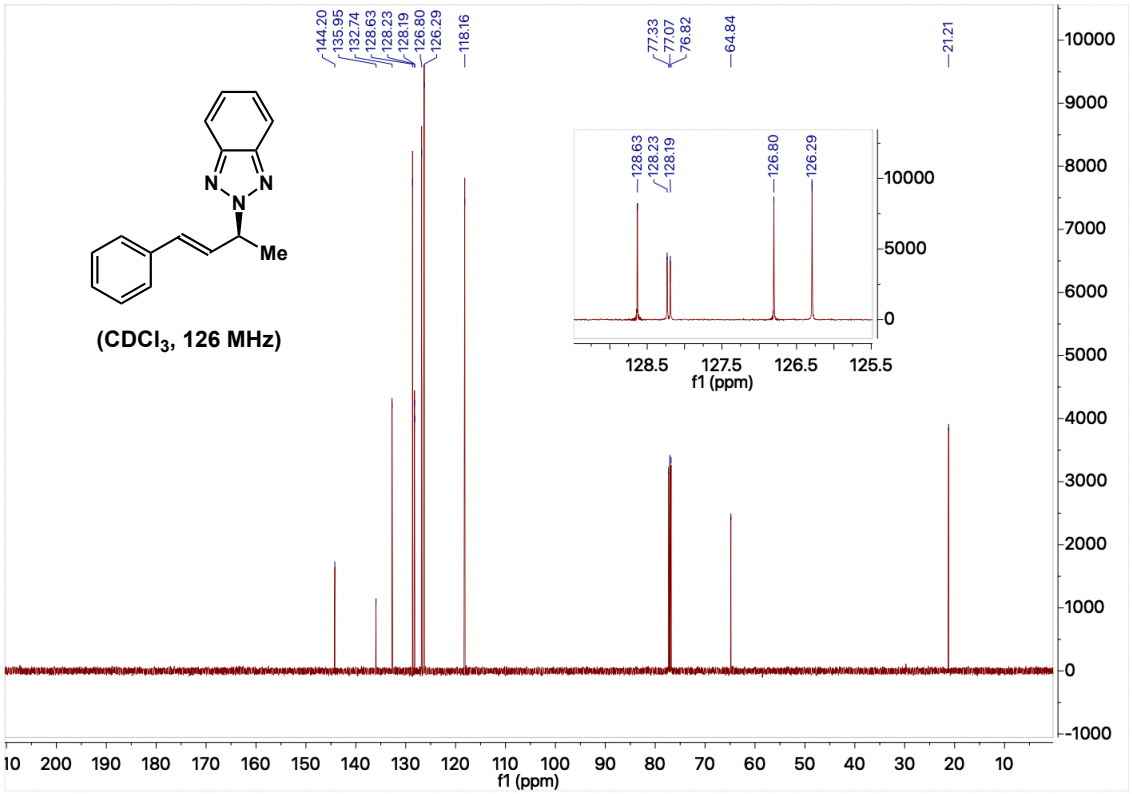
(S, E)-2-(4-phenylbut-3-en-2-yl)-2*H*-1,2,3-triazole (3an)



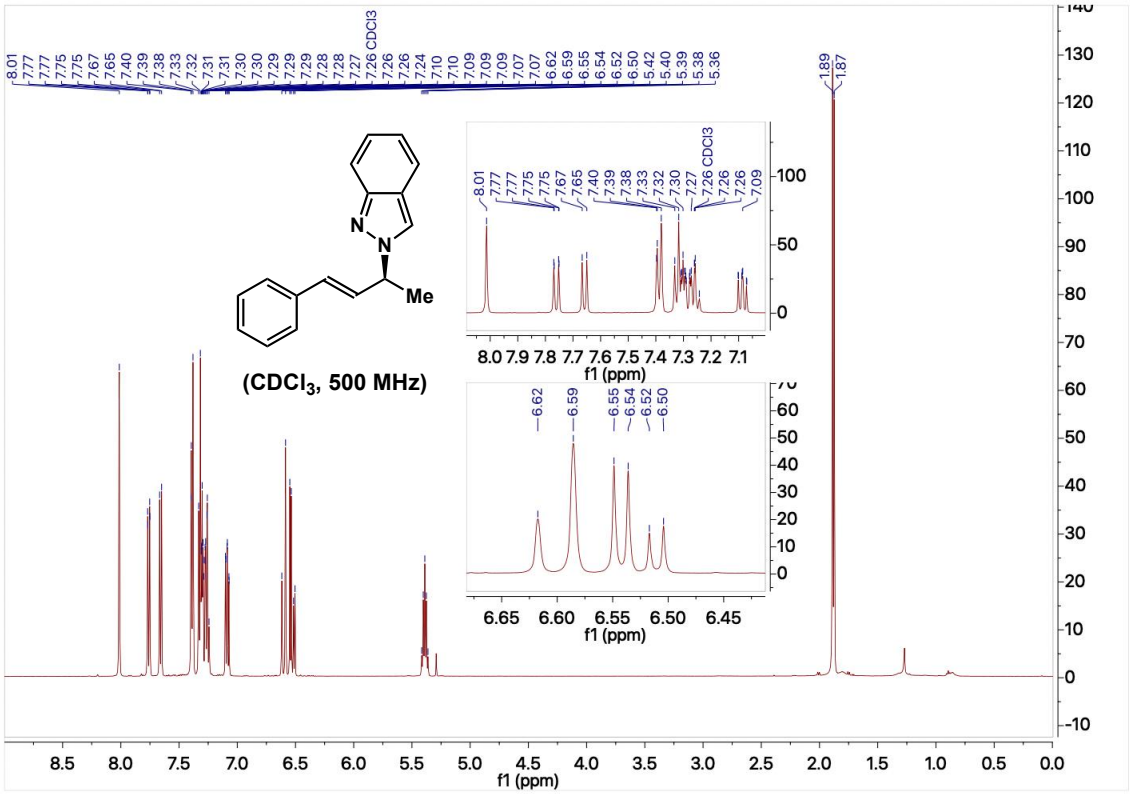


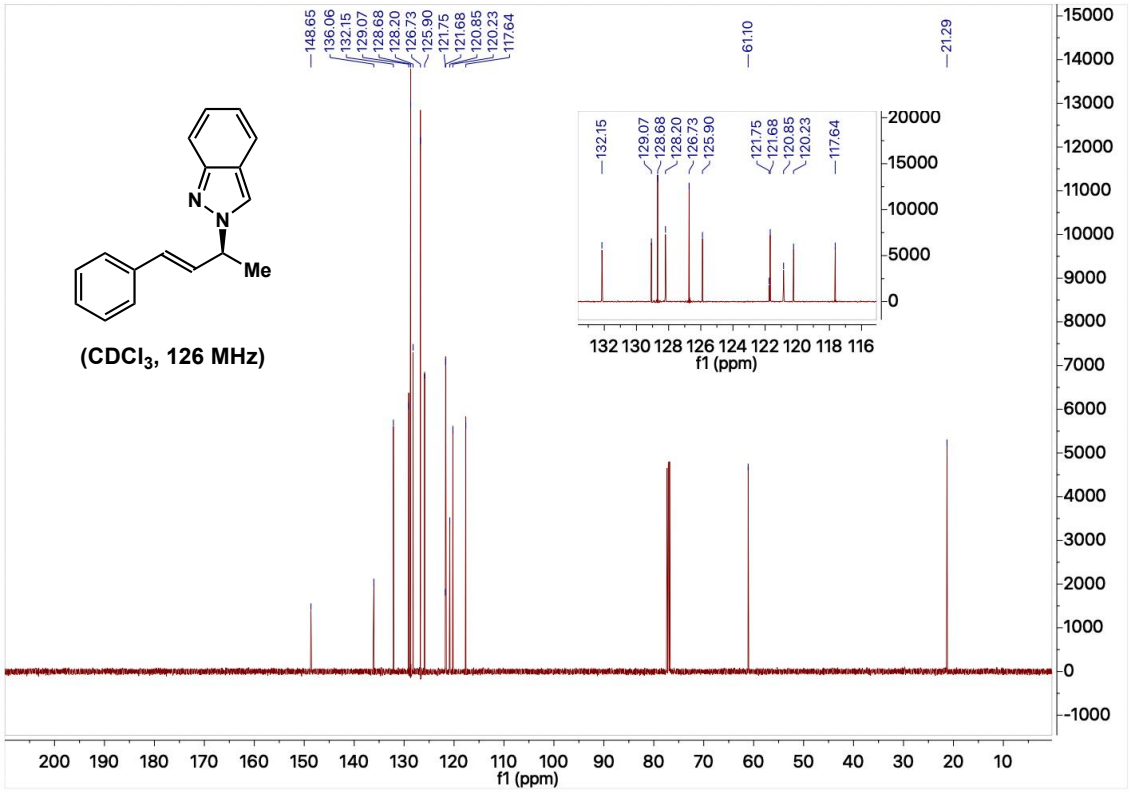
(S, E)-2-(4-phenylbut-3-en-2-yl)-2*H*-benzo[*d*][1,2,3]triazole (3ao)



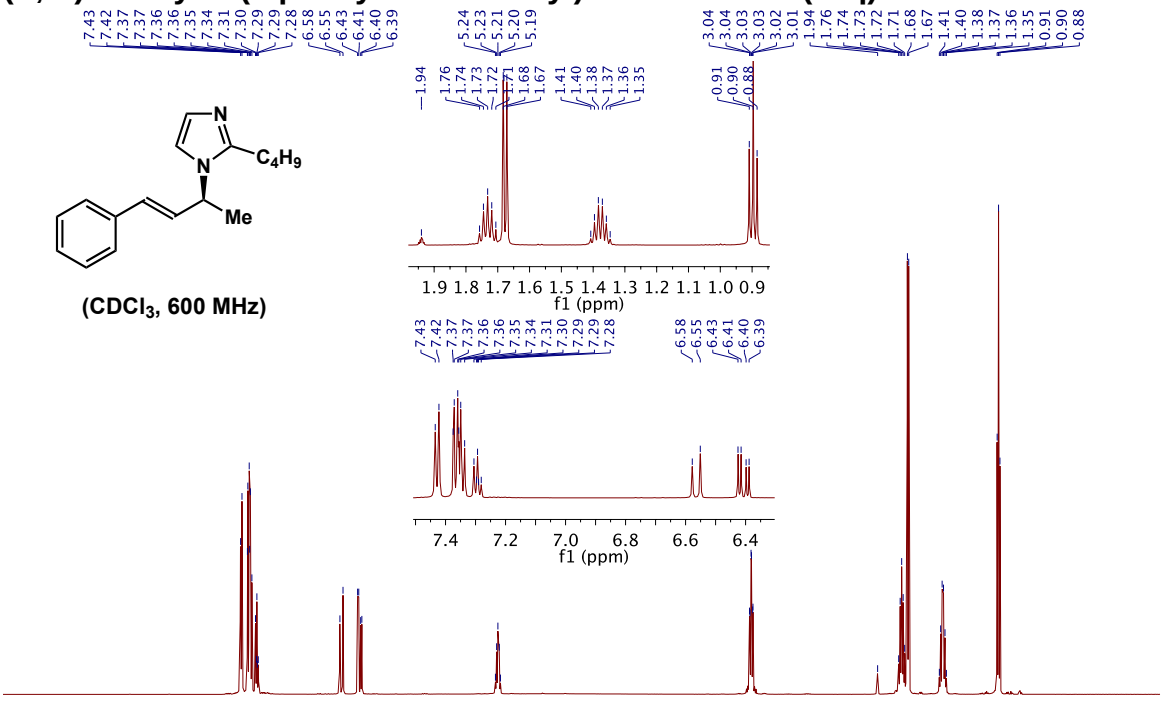


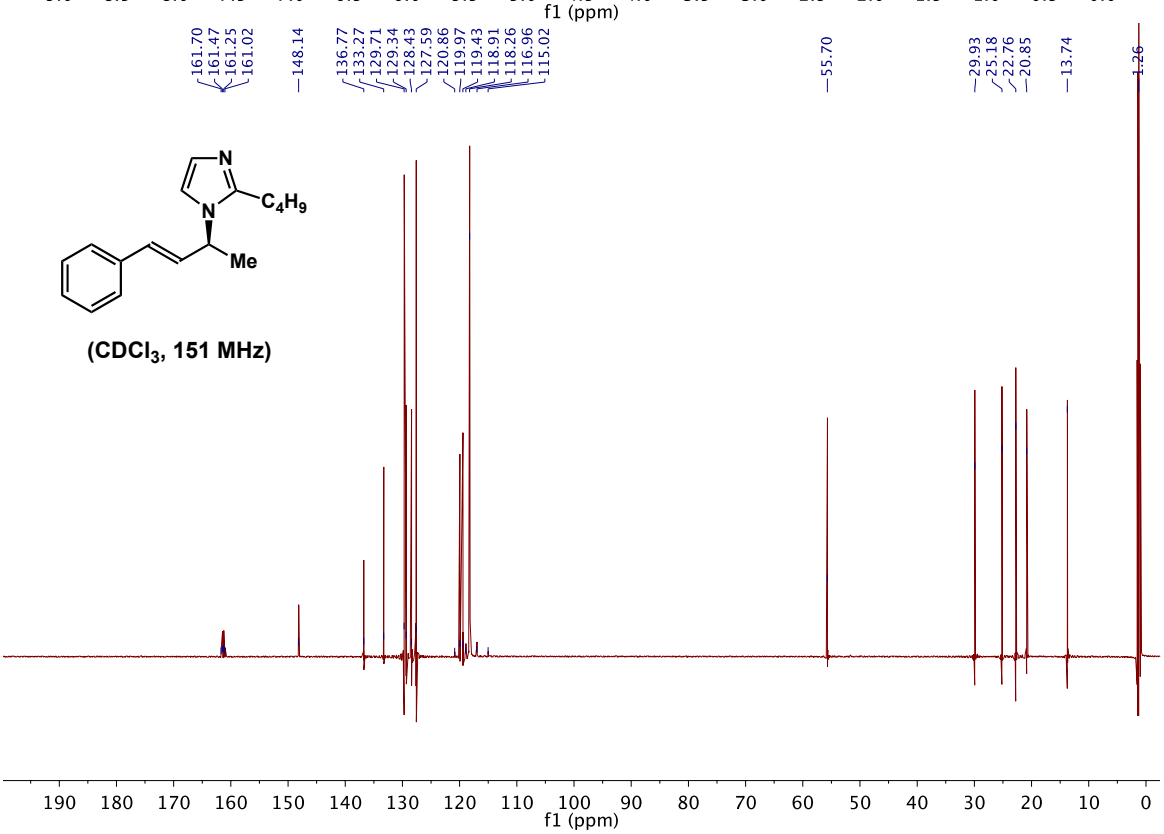
(*S*, *E*)-2-(4-phenylbut-3-en-2-yl)-2*H*-indazole (3ap)



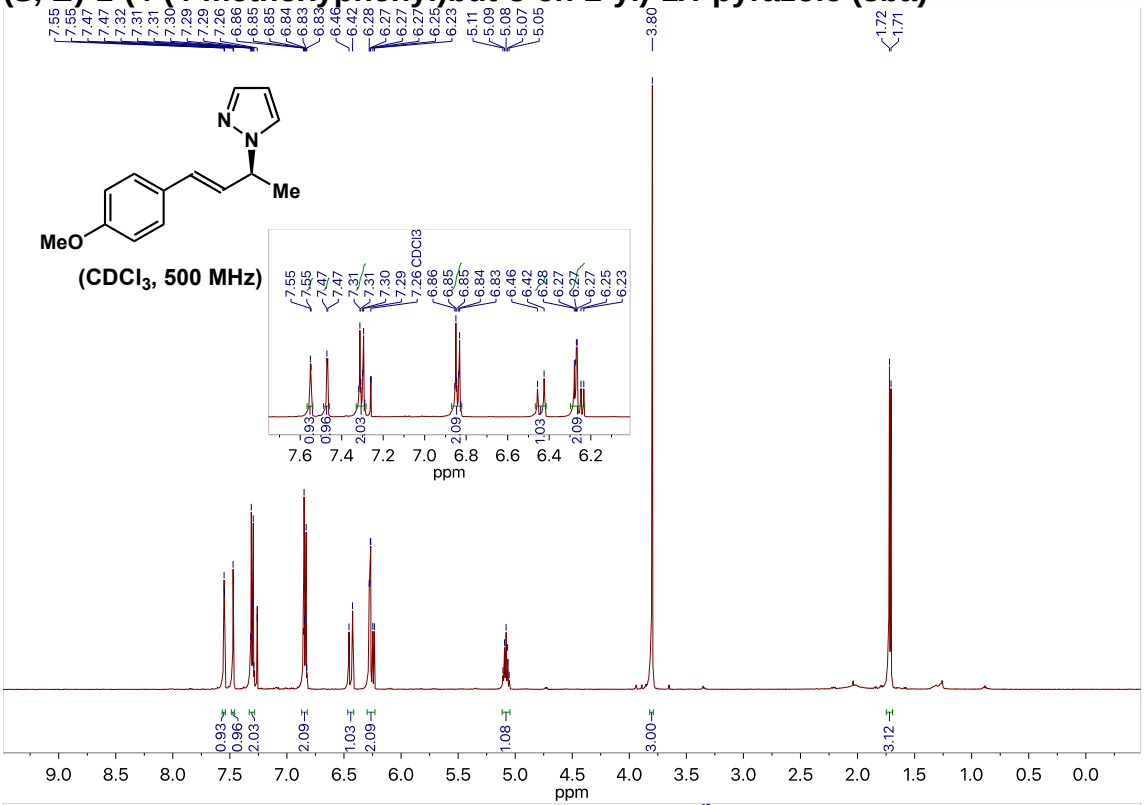


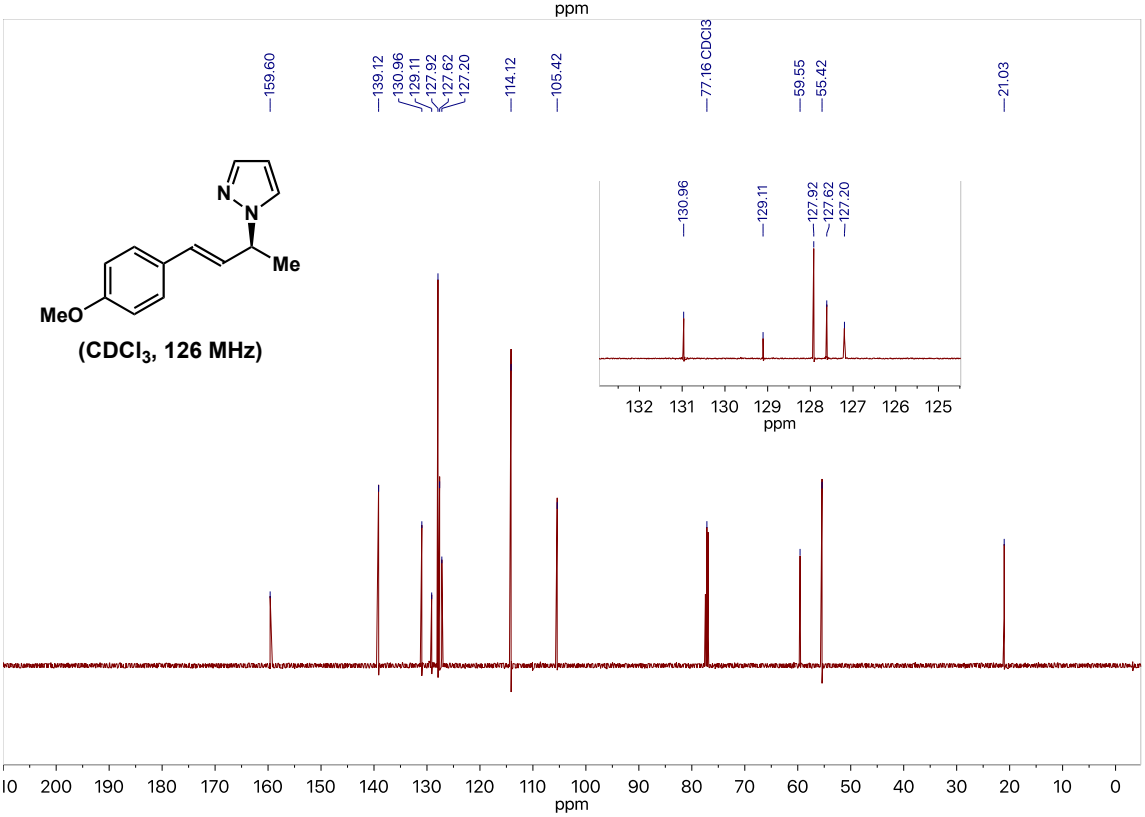
(S, E)-2-butyl-1-(4-phenylbut-3-en-2-yl)-1H-imidazole (3aq)



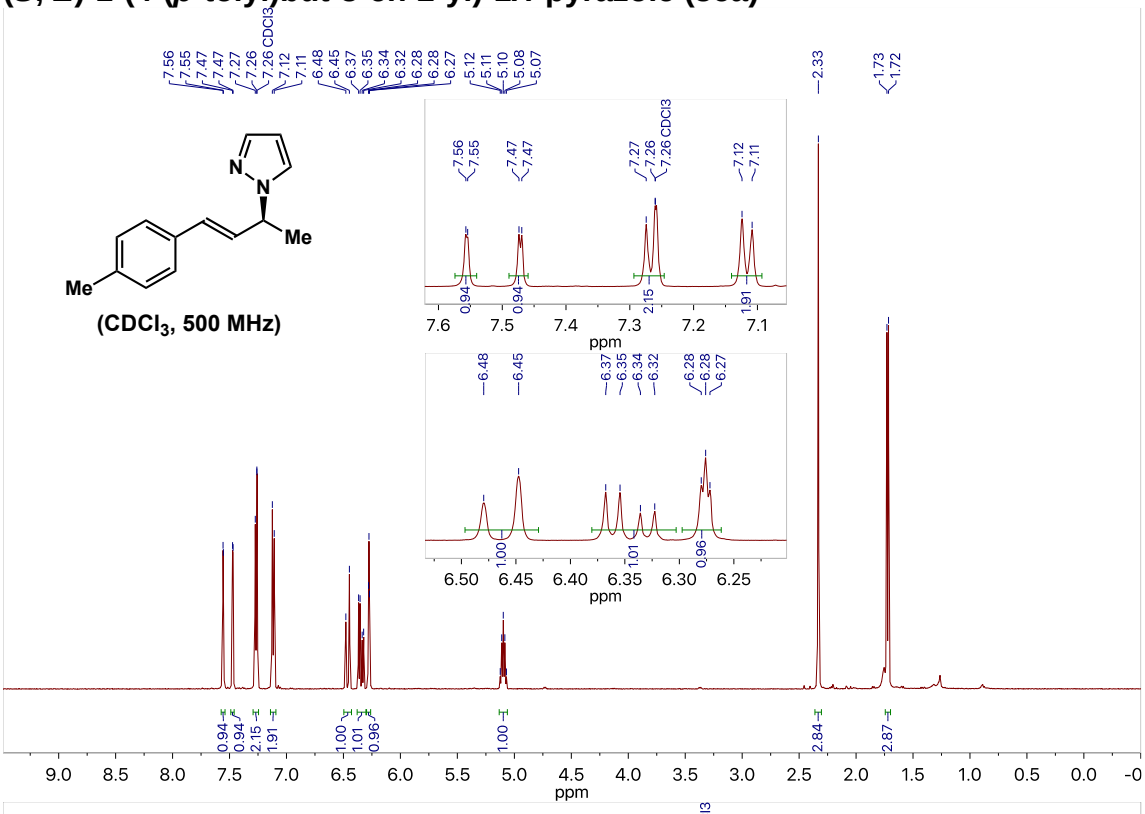


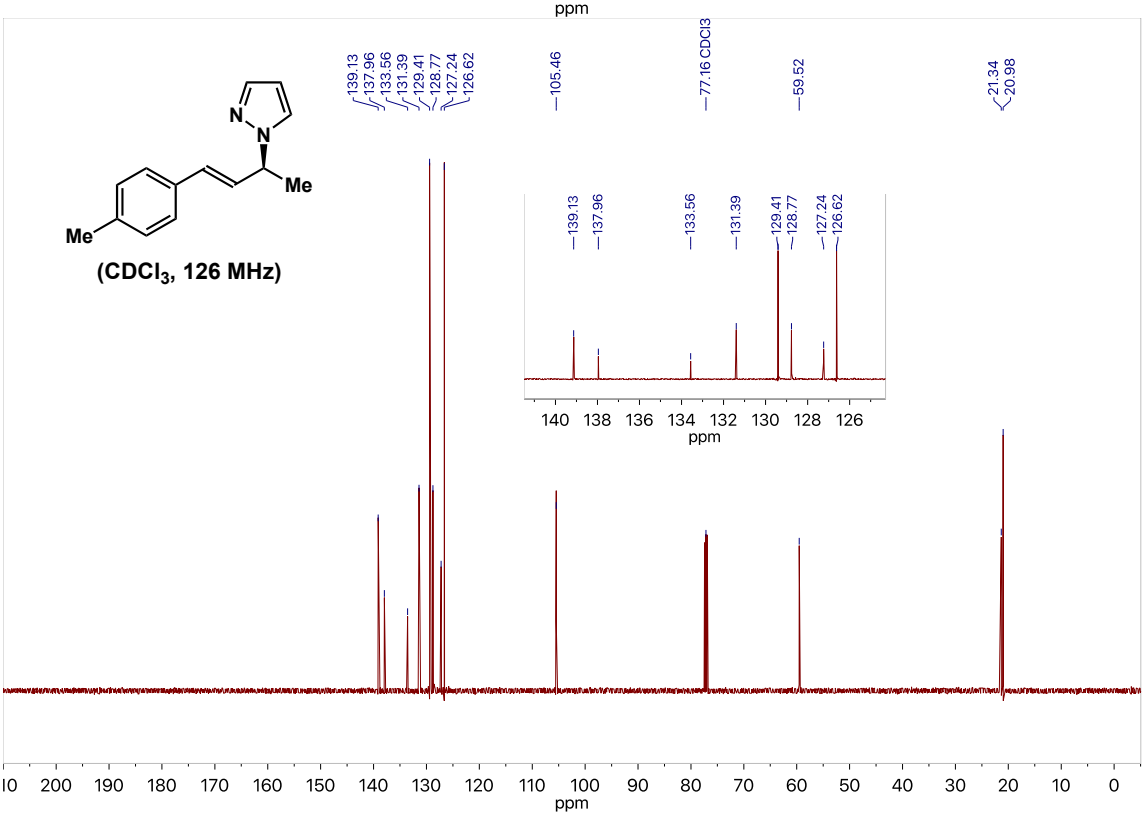
(*S*, *E*)-1-(4-(4-methoxyphenyl)but-3-en-2-yl)-1*H*-pyrazole (3ba)



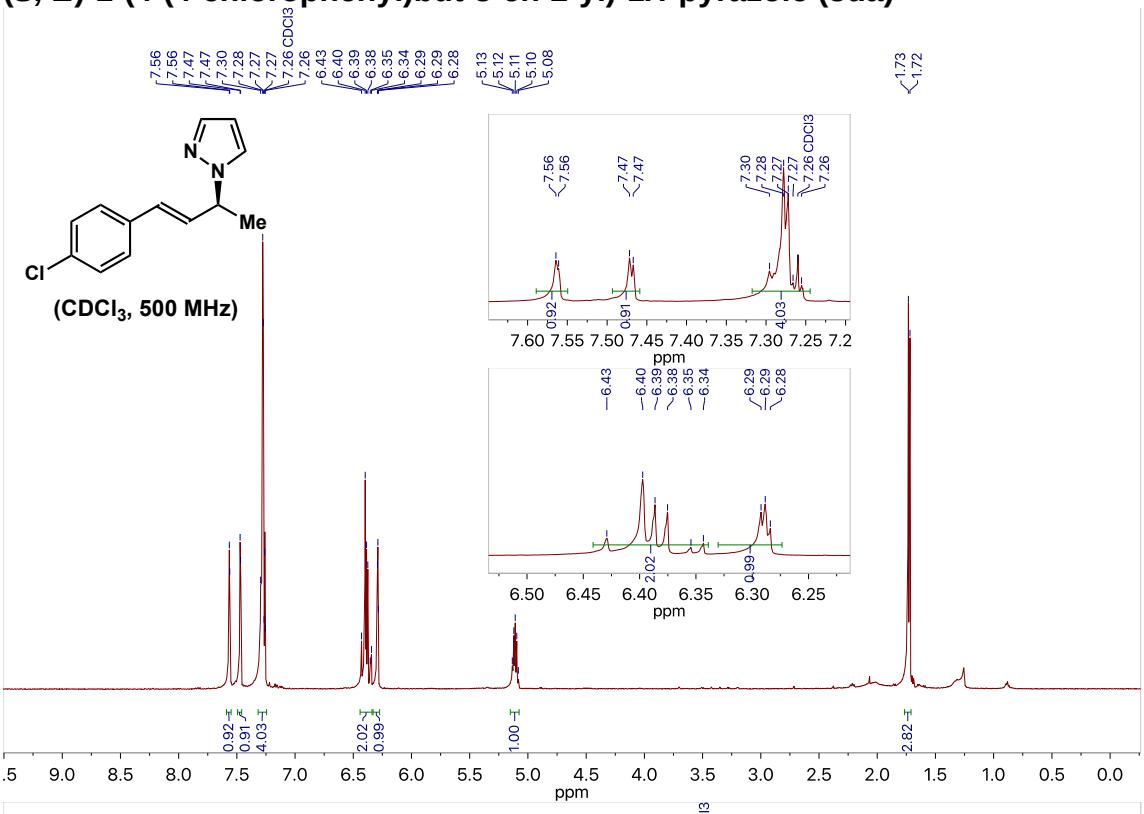


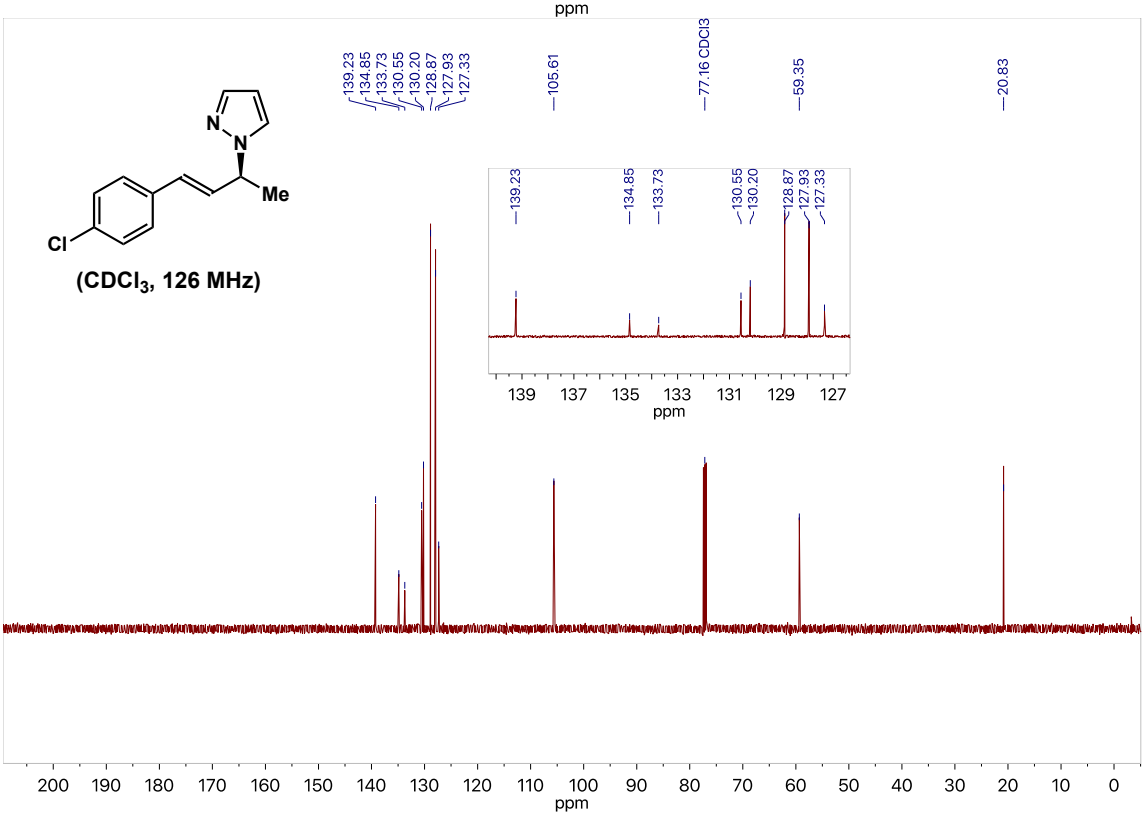
(*S*, *E*)-1-(4-(*p*-tolyl)but-3-en-2-yl)-1*H*-pyrazole (3ca)



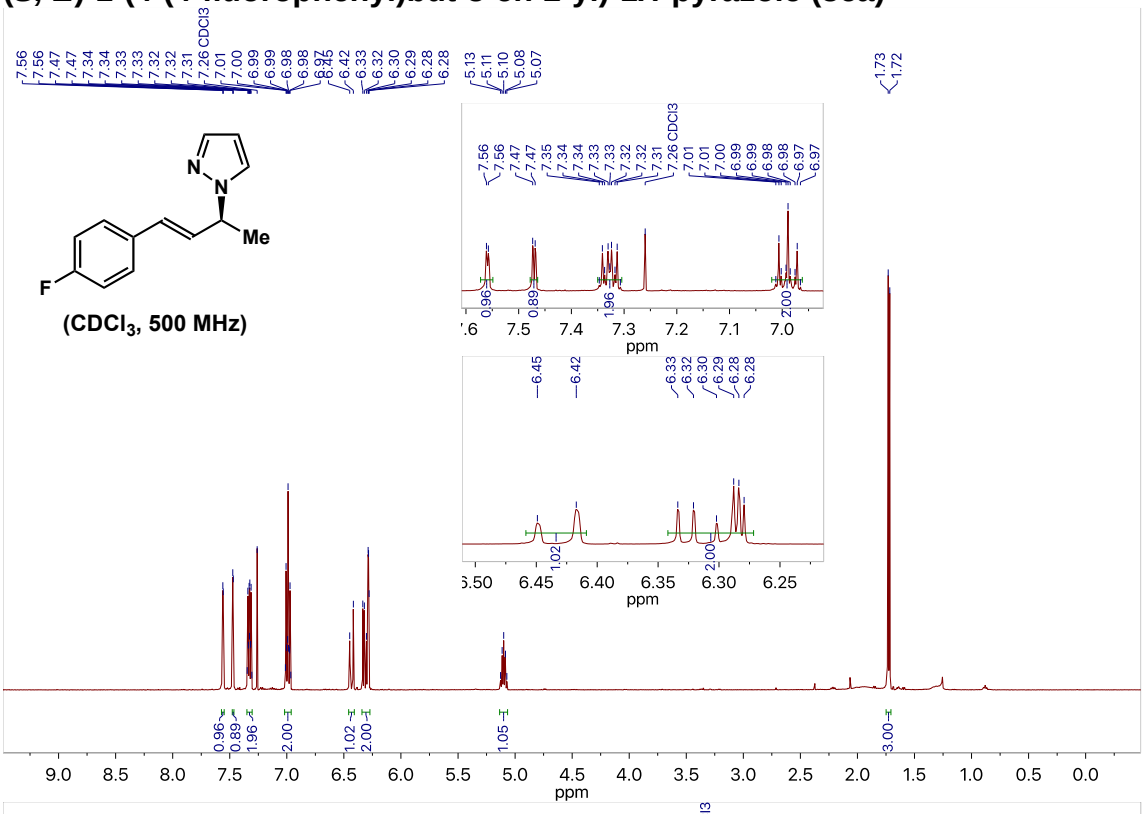


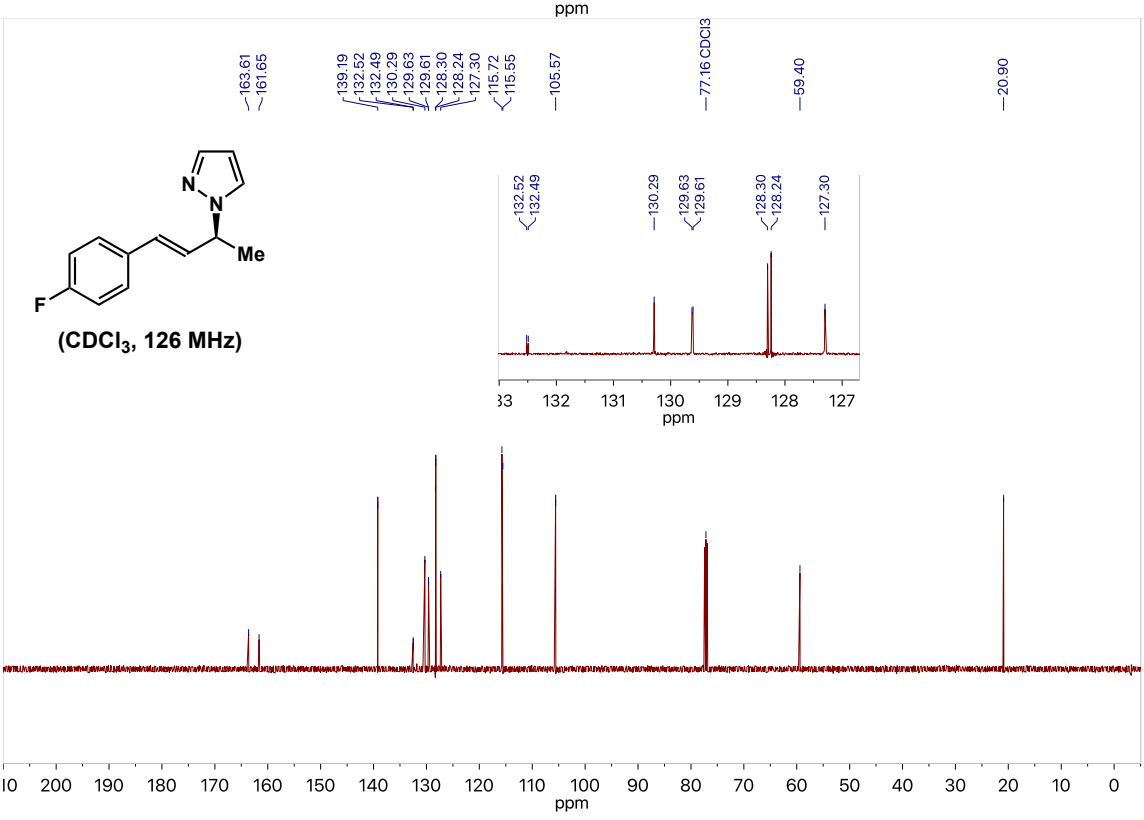
(*S*, *E*)-1-(4-(4-chlorophenyl)but-3-en-2-yl)-1*H*-pyrazole (3da)



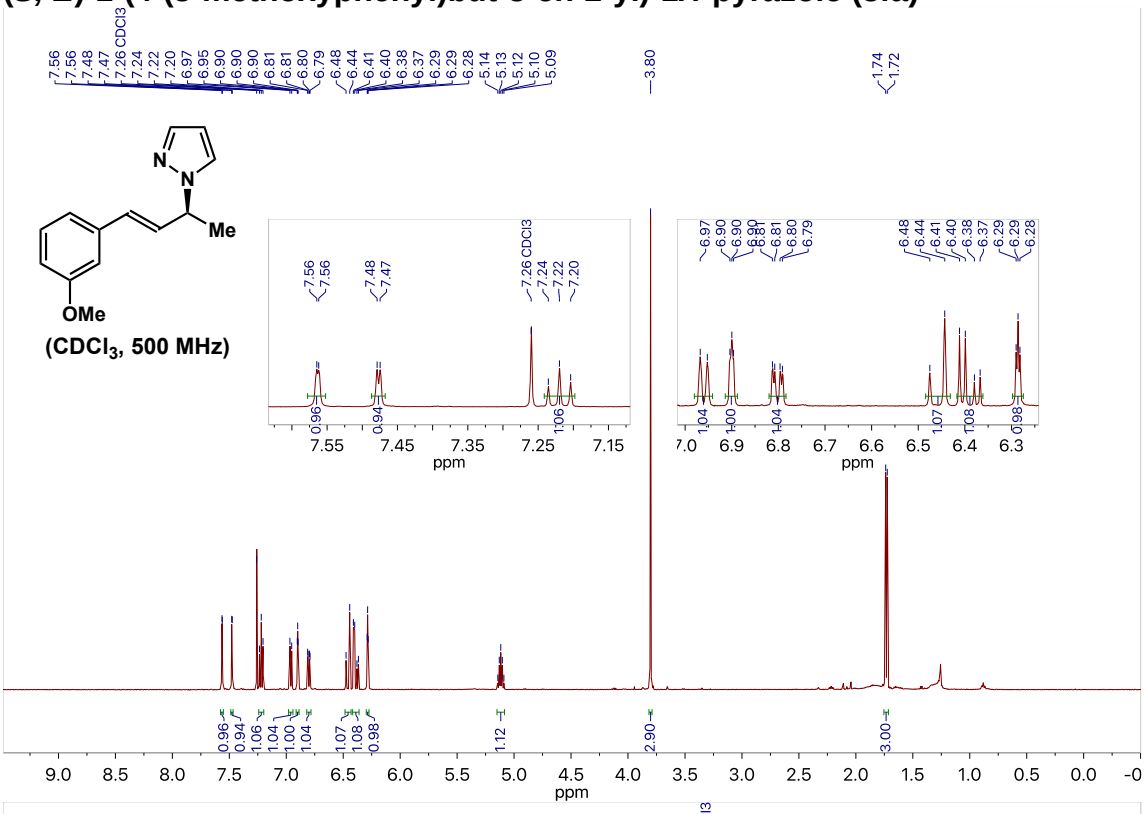


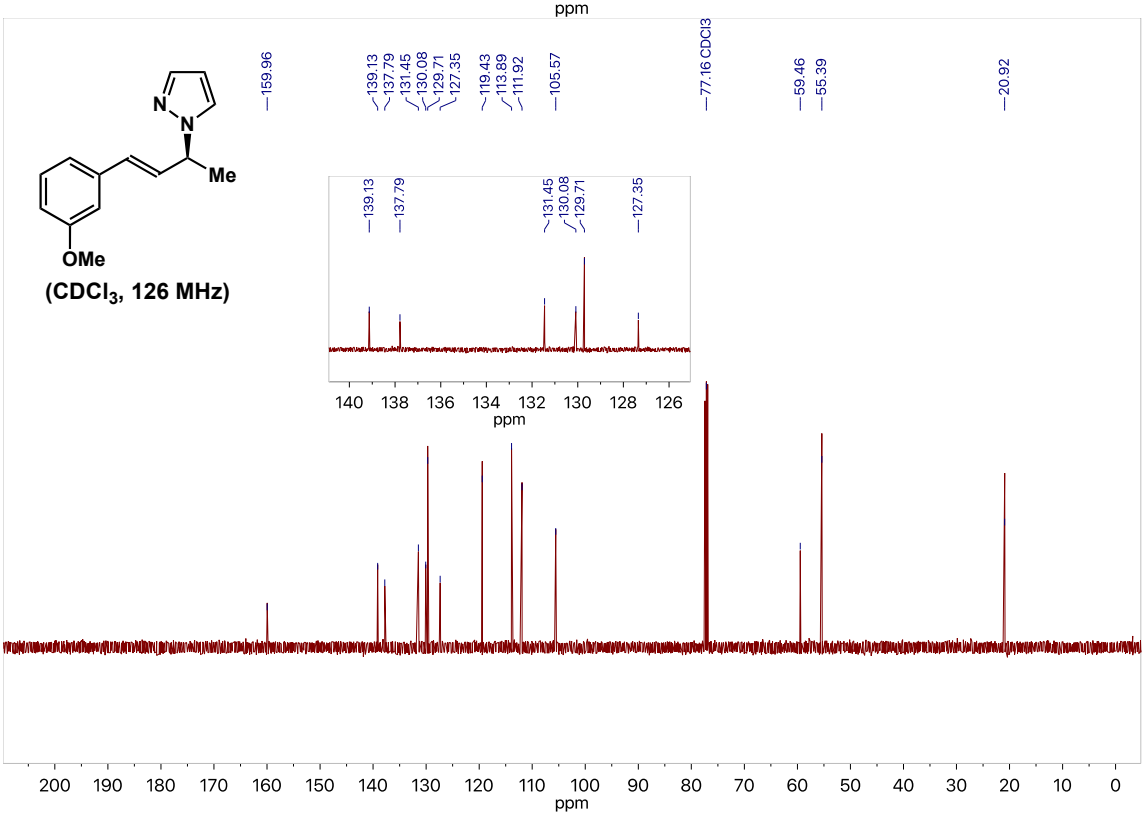
(*S*, *E*)-1-(4-(4-fluorophenyl)but-3-en-2-yl)-1*H*-pyrazole (3ea)



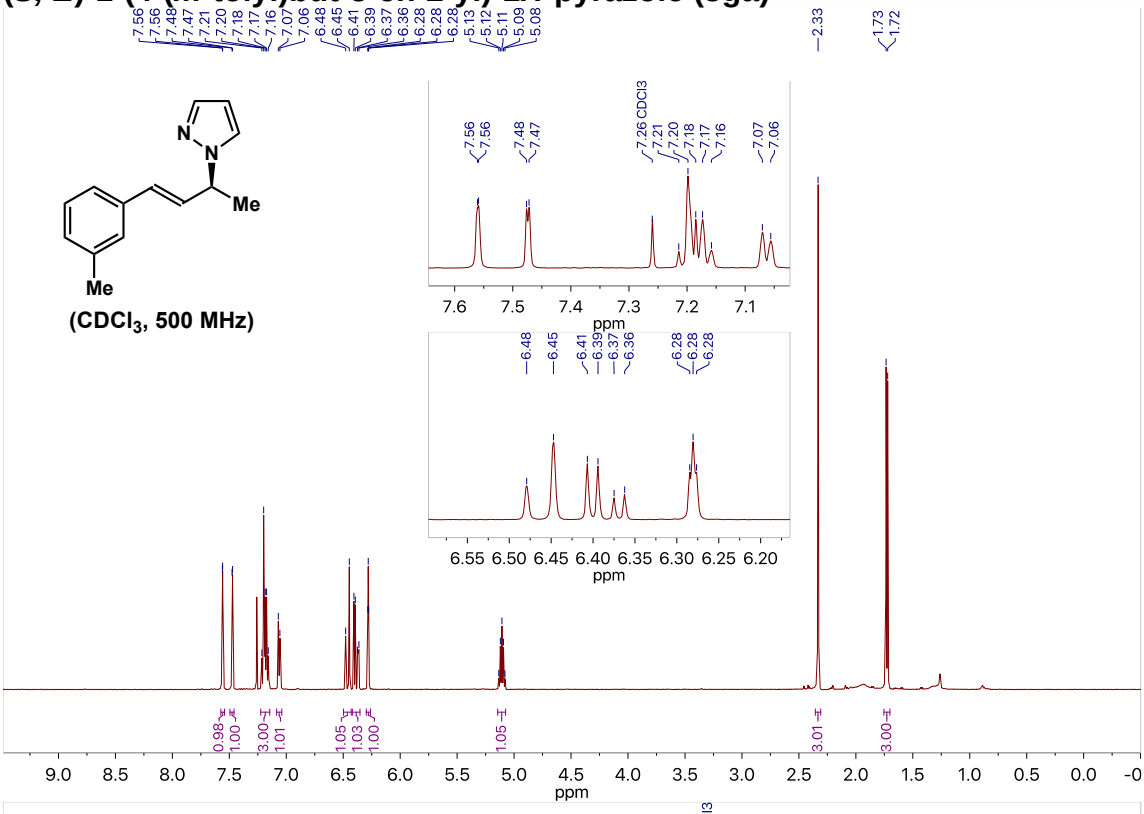


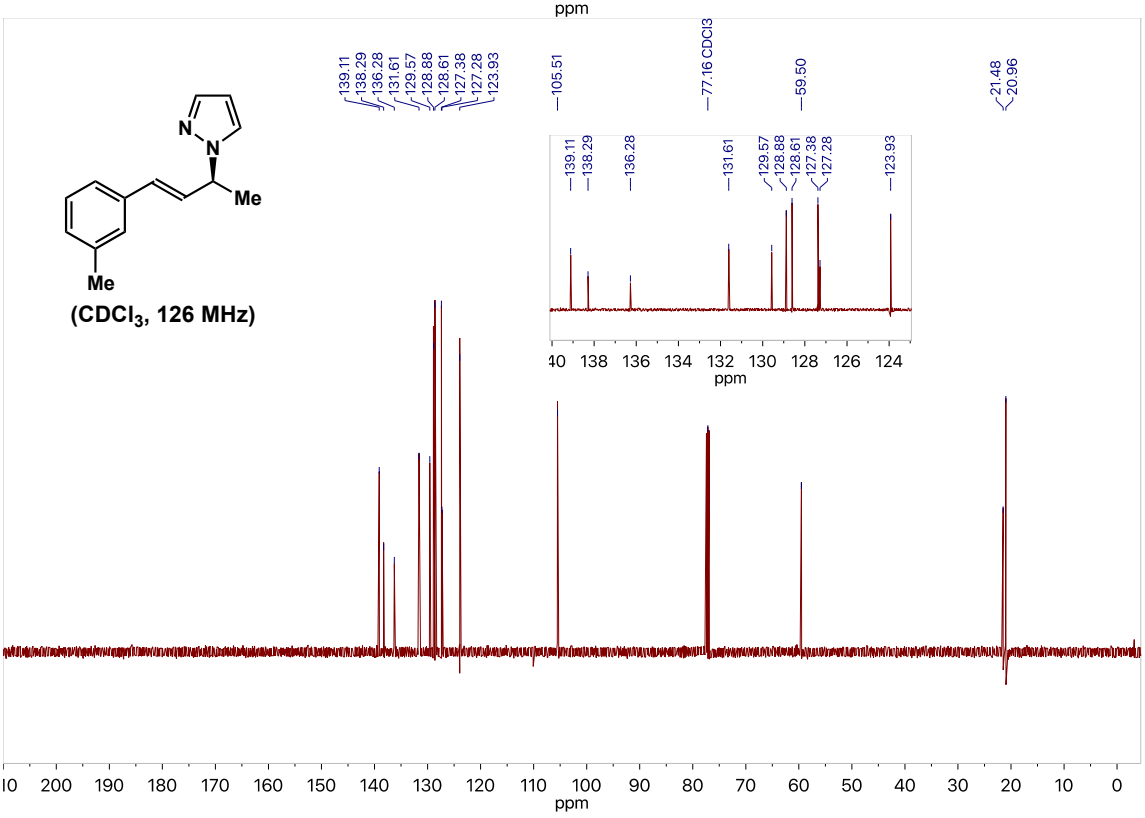
(*S*, *E*)-1-(4-(3-methoxyphenyl)but-3-en-2-yl)-1*H*-pyrazole (3fa)



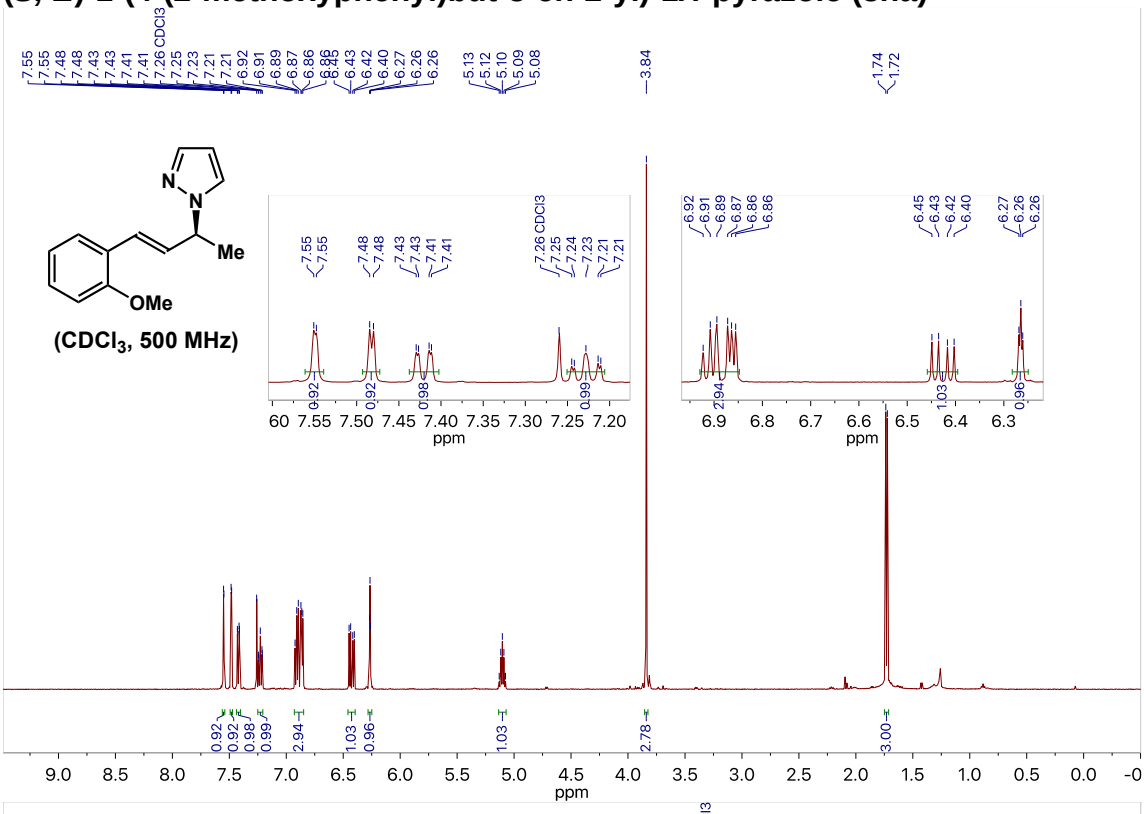


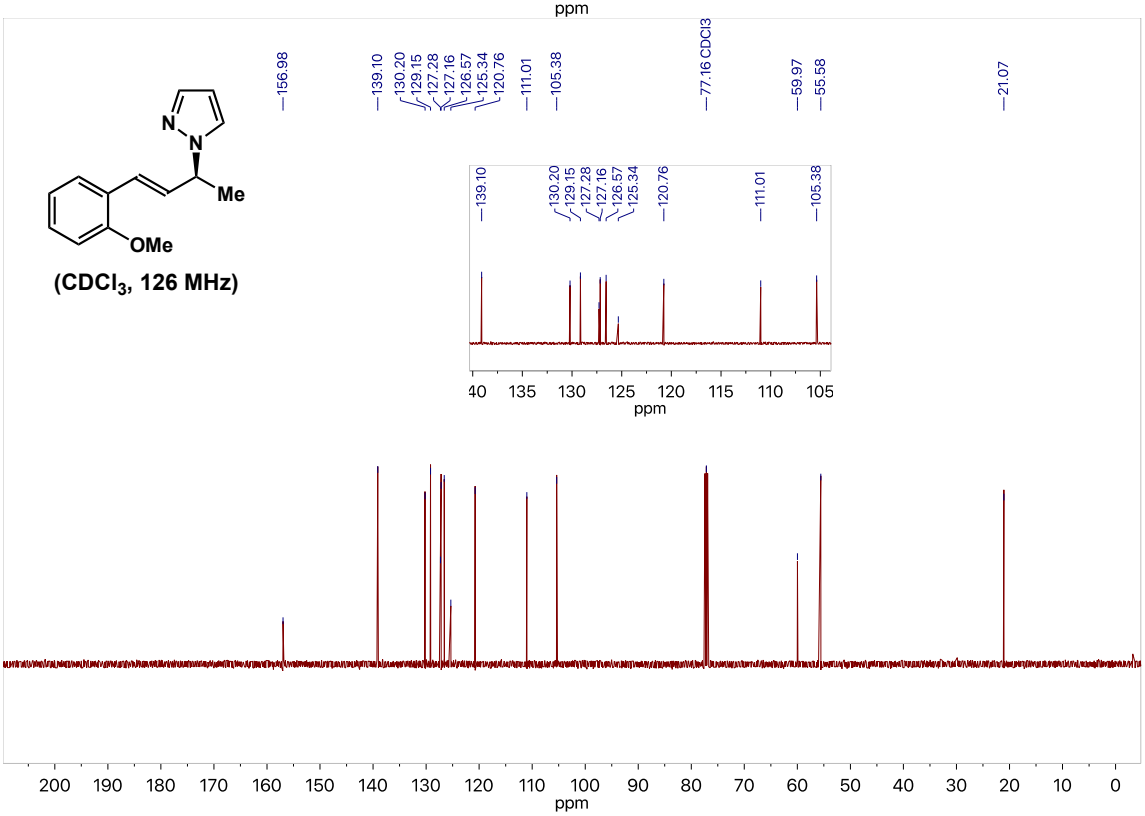
(*S*, *E*)-1-(4-(*m*-tolyl)but-3-en-2-yl)-1*H*-pyrazole (3ga)



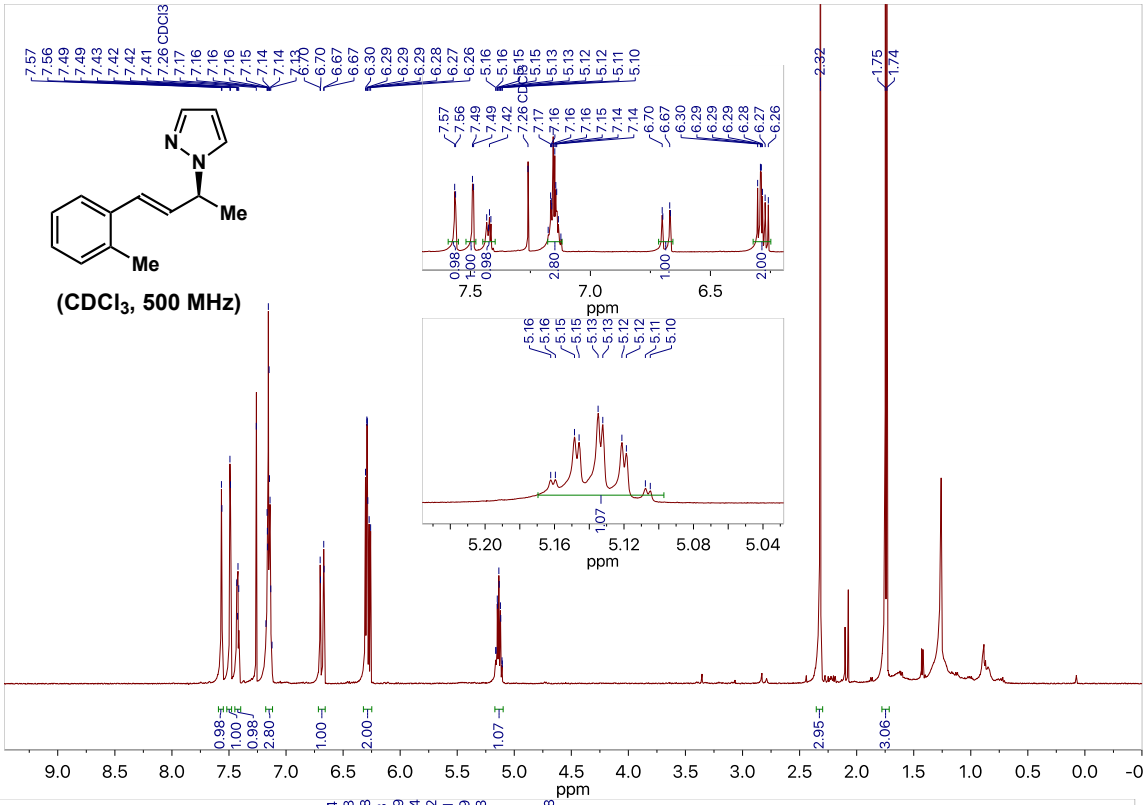


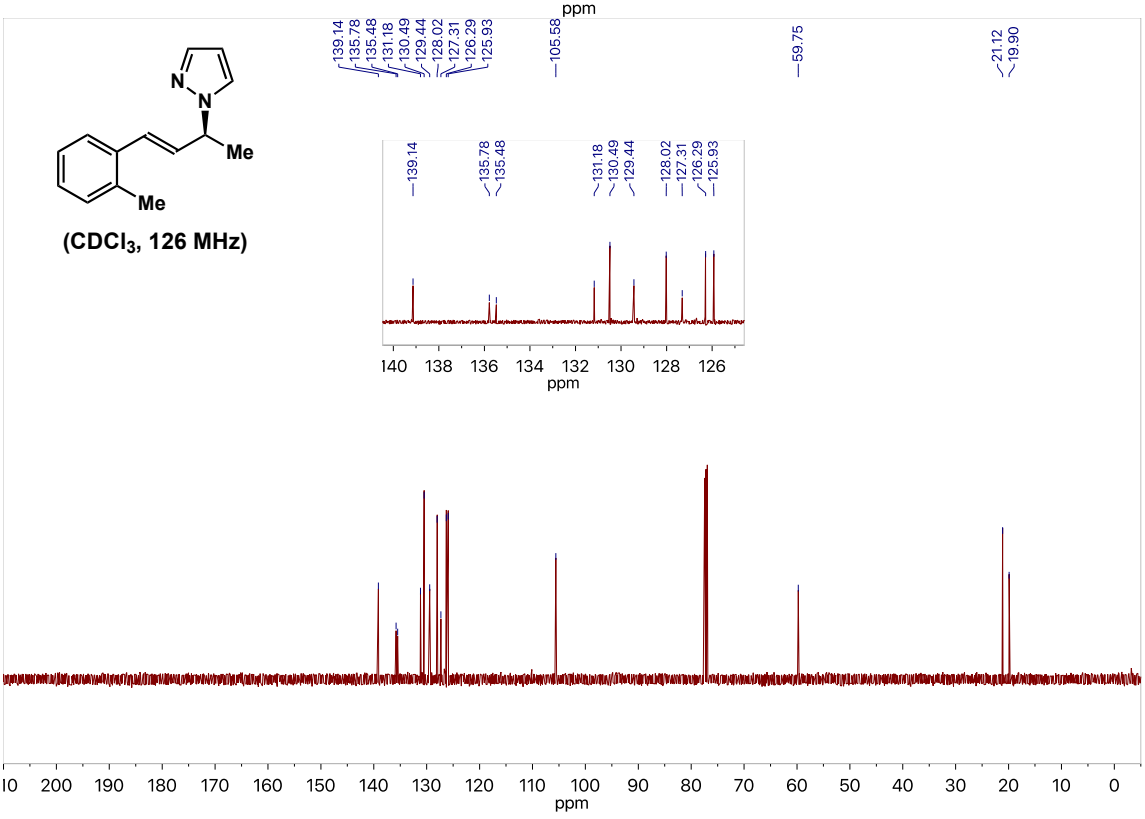
(*S*, *E*)-1-(4-(2-methoxyphenyl)but-3-en-2-yl)-1*H*-pyrazole (3ha)



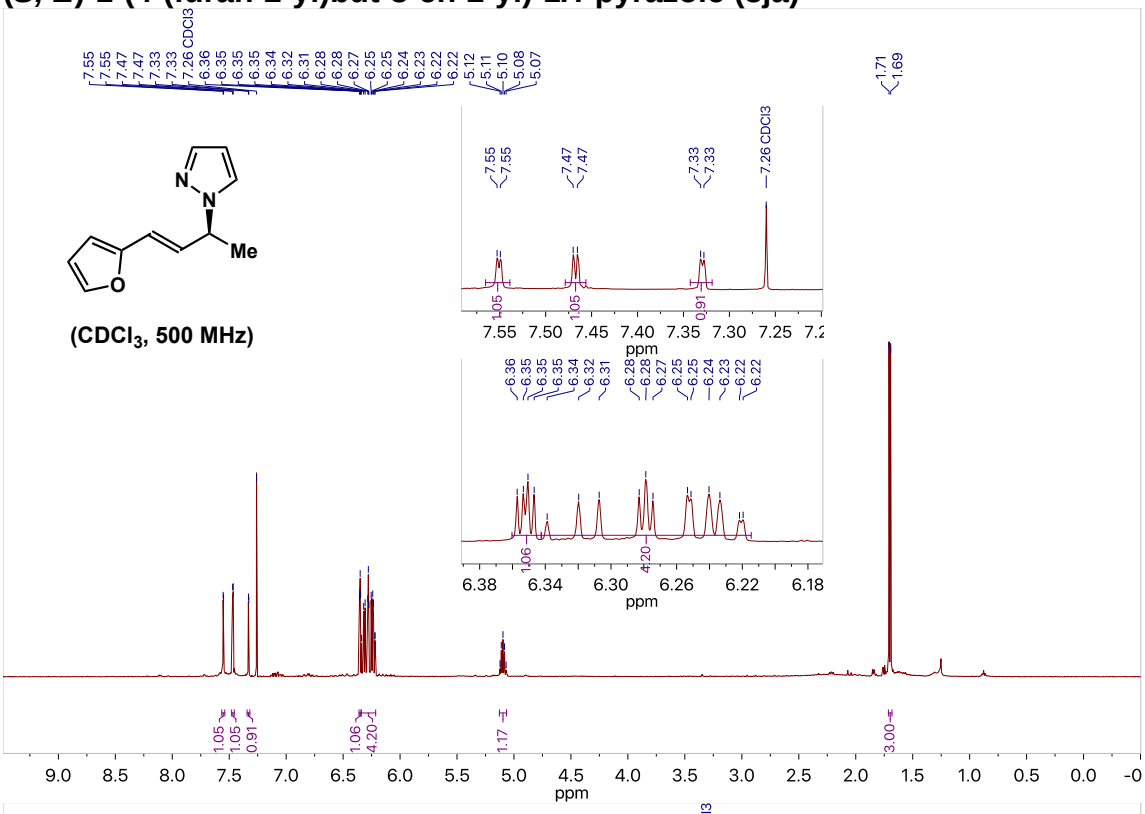


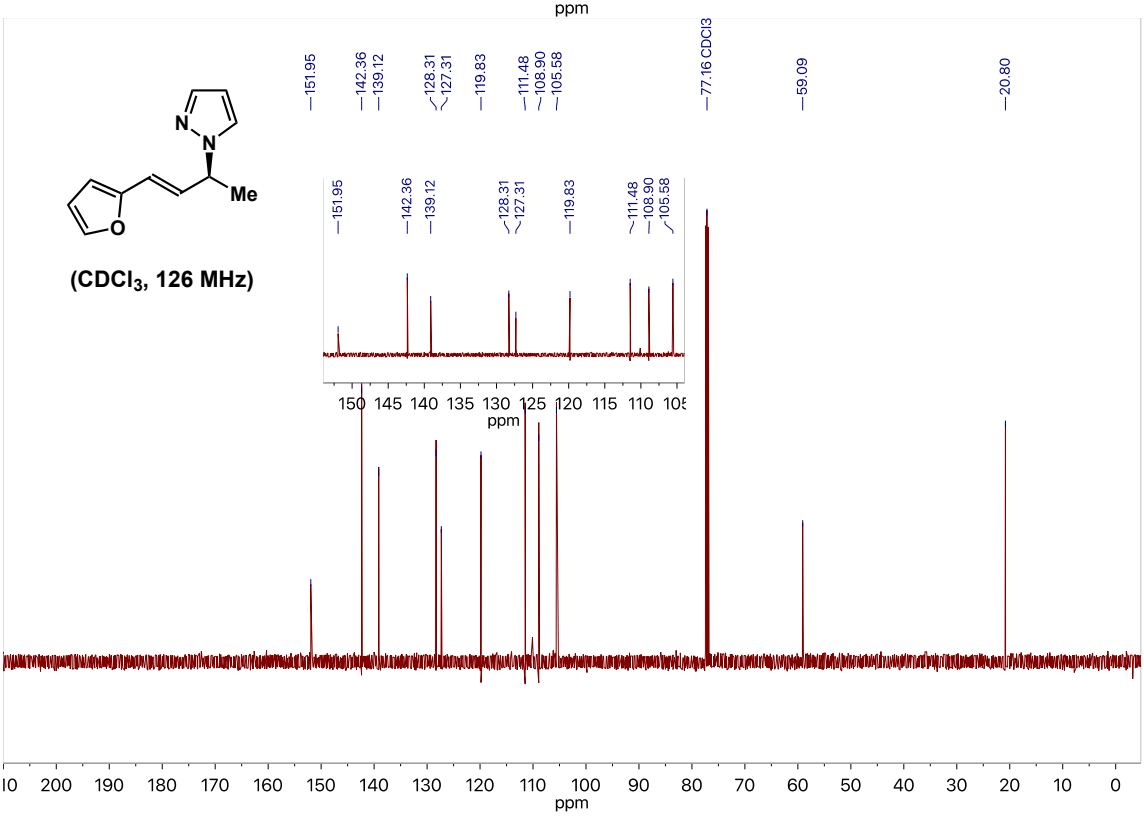
(*S*, *E*)-1-(4-(*o*-tolyl)but-3-en-2-yl)-1*H*-pyrazole (3ia)



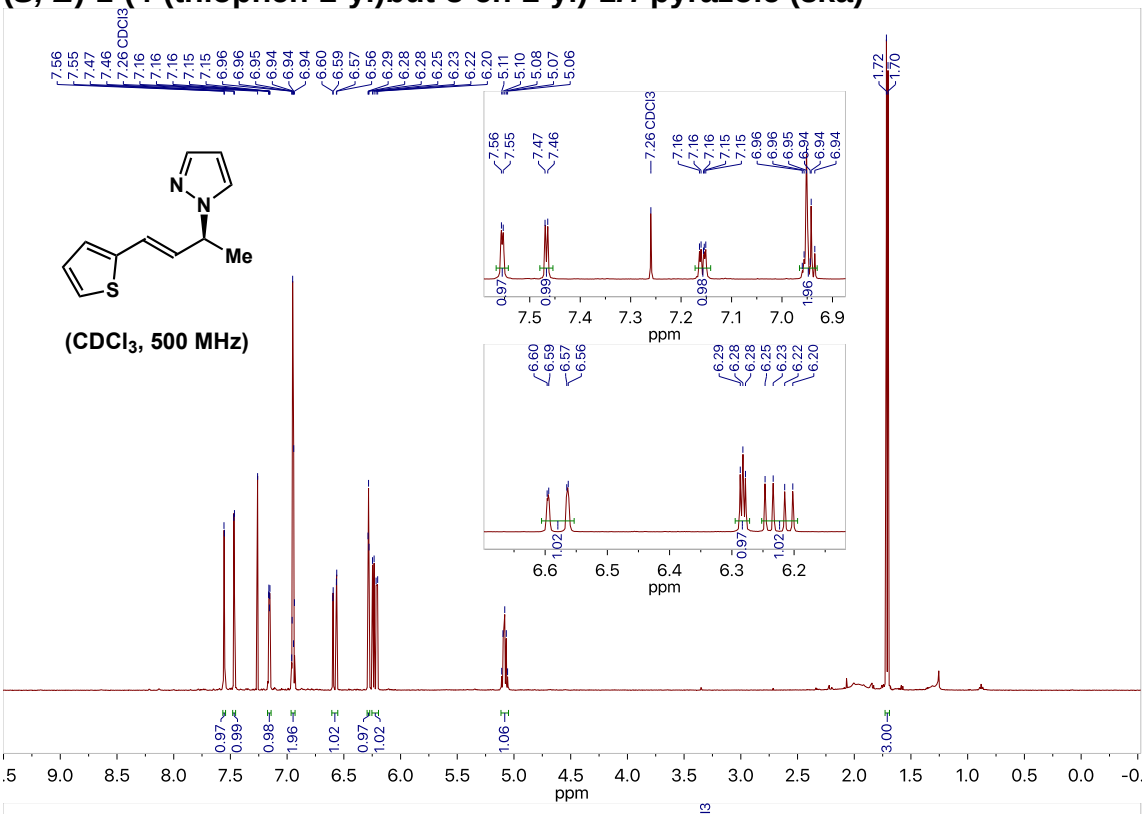


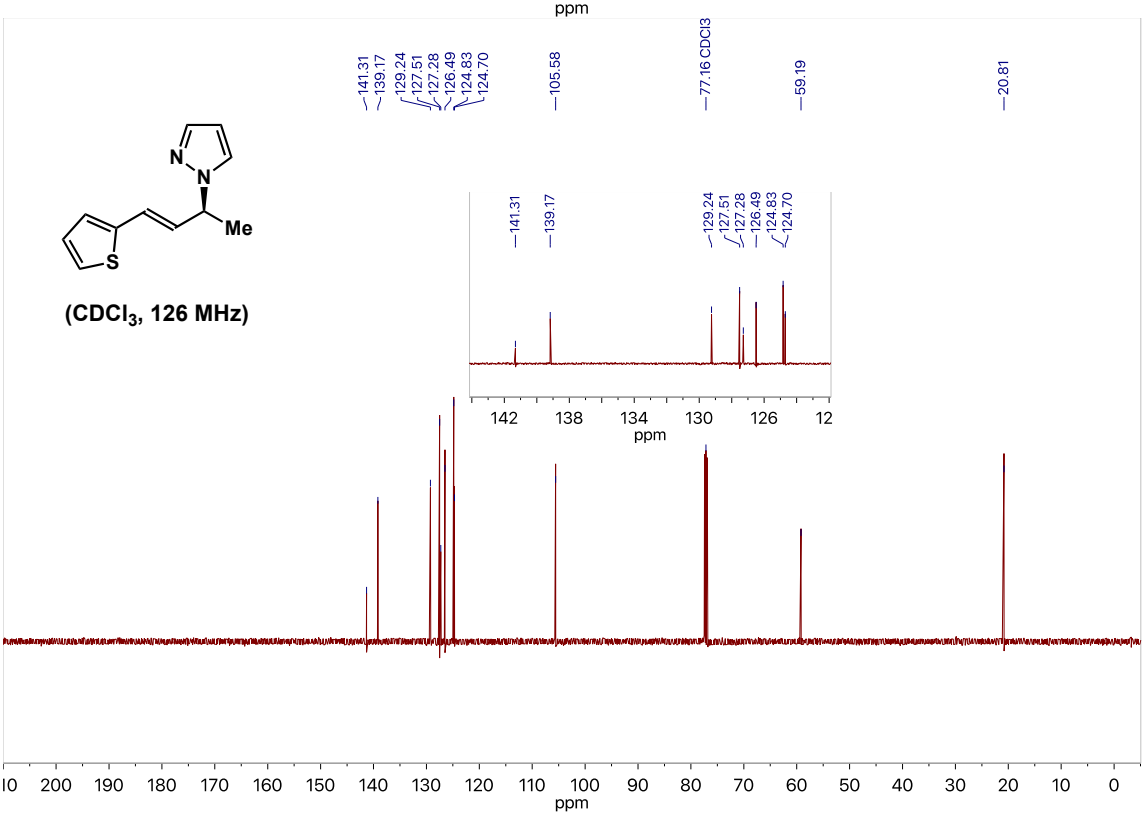
(*S*, *E*)-1-(4-(furan-2-yl)but-3-en-2-yl)-1*H*-pyrazole (3ja)



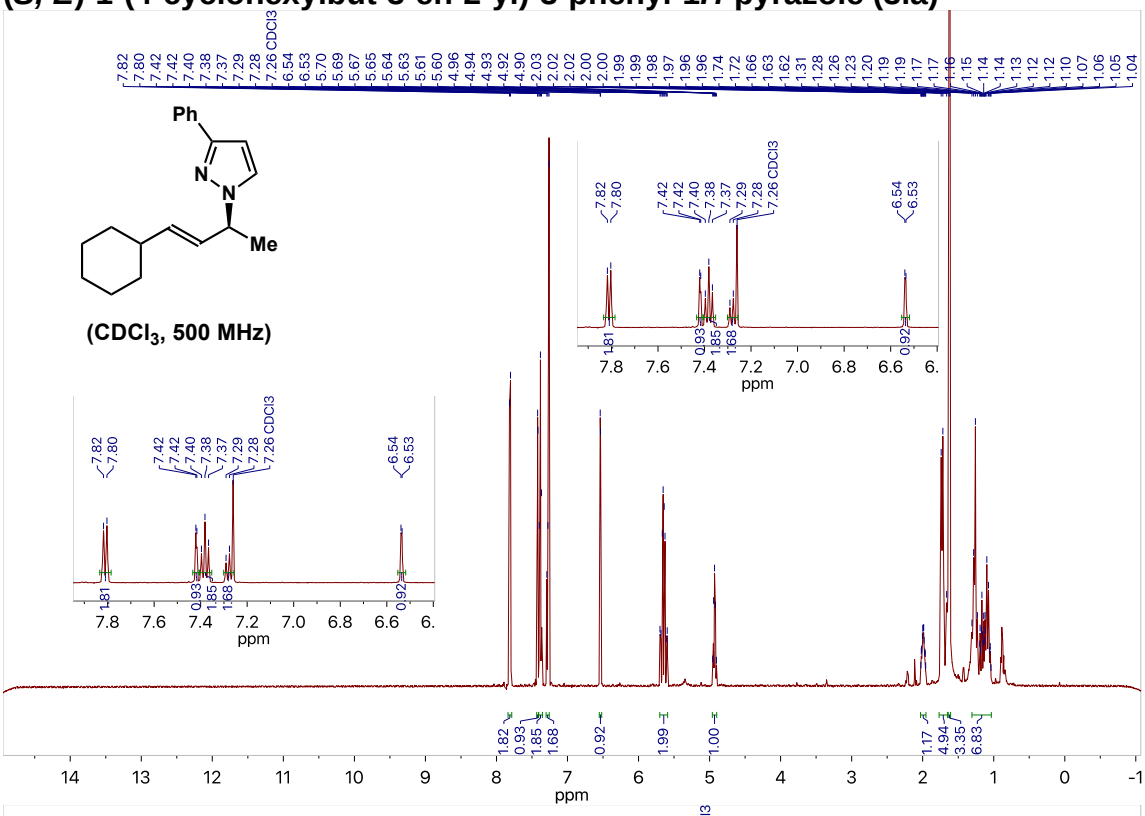


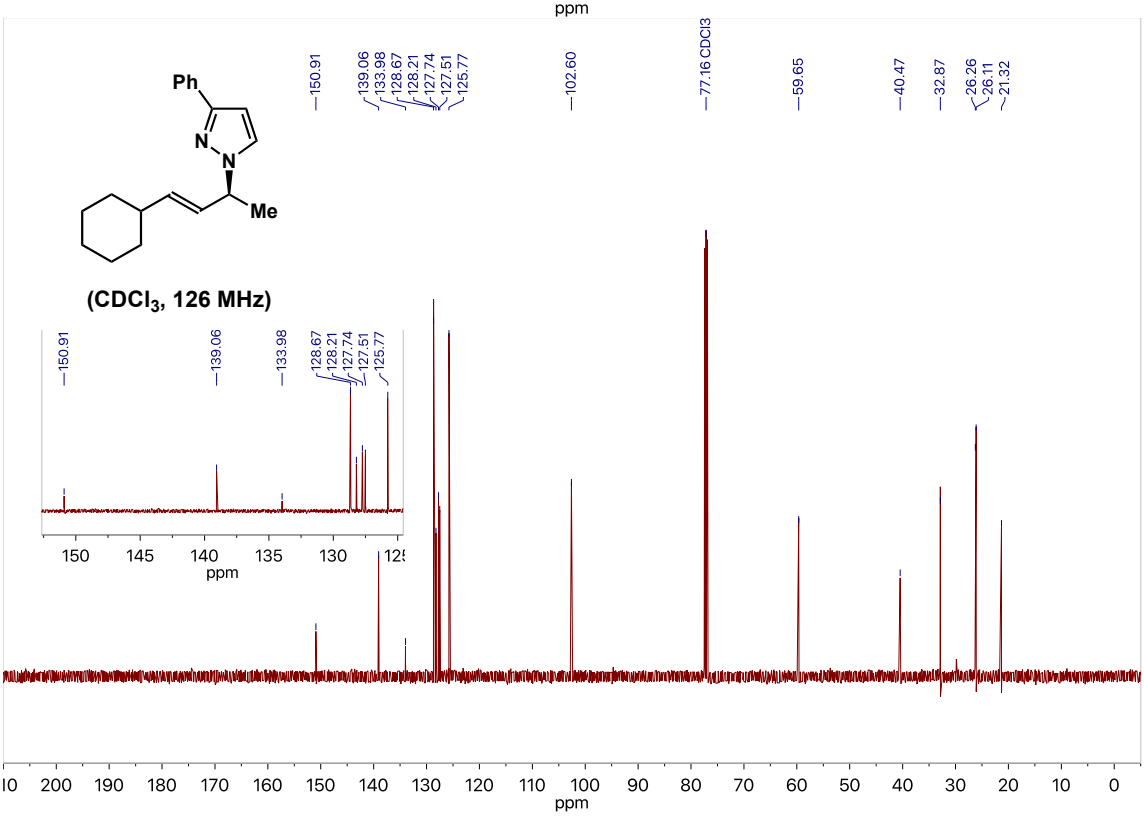
(*S*, *E*)-1-(4-(thiophen-2-yl)but-3-en-2-yl)-1*H*-pyrazole (3ka)



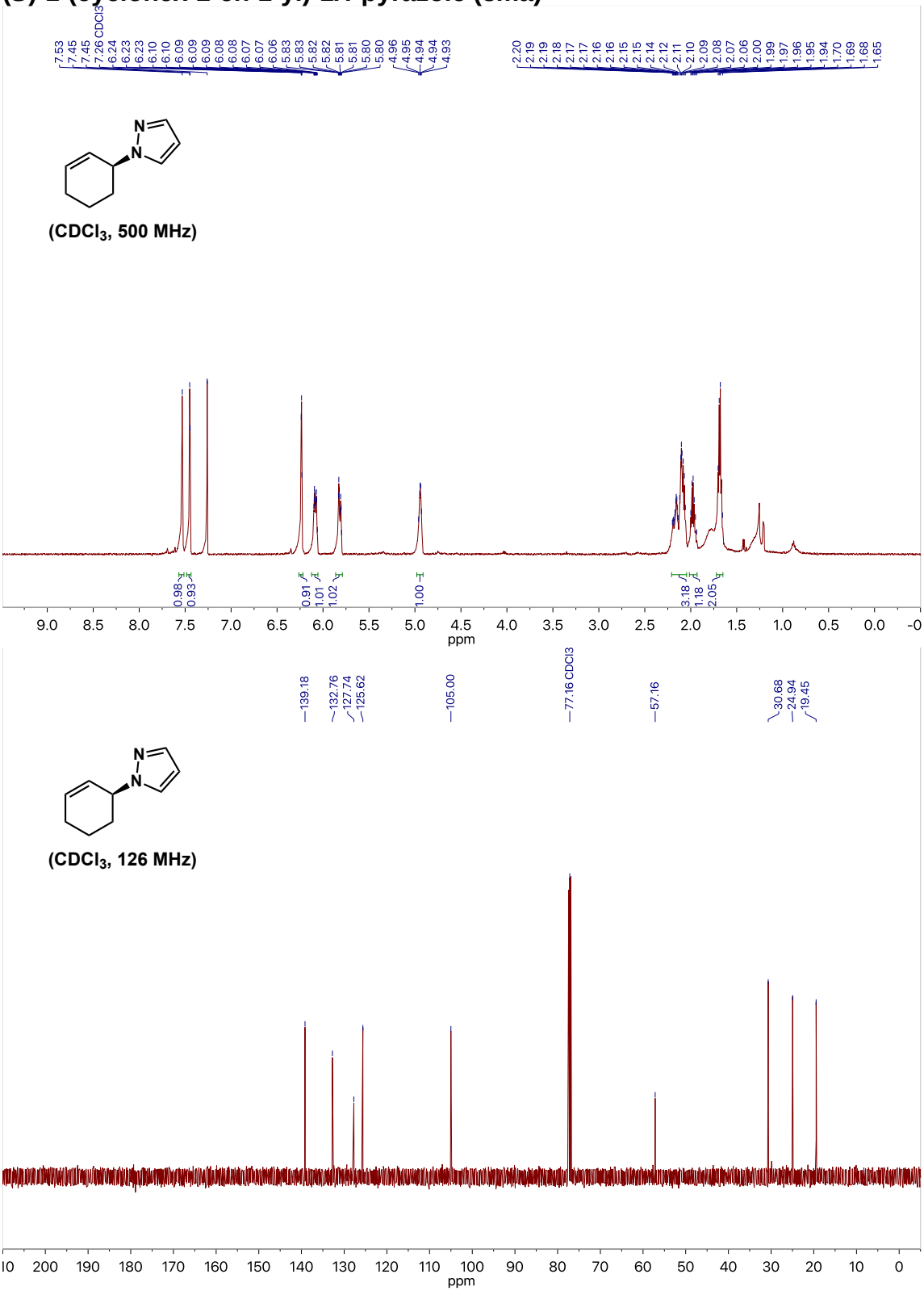


(*S*, *E*)-1-(4-cyclohexylbut-3-en-2-yl)-3-phenyl-1*H*-pyrazole (3la)

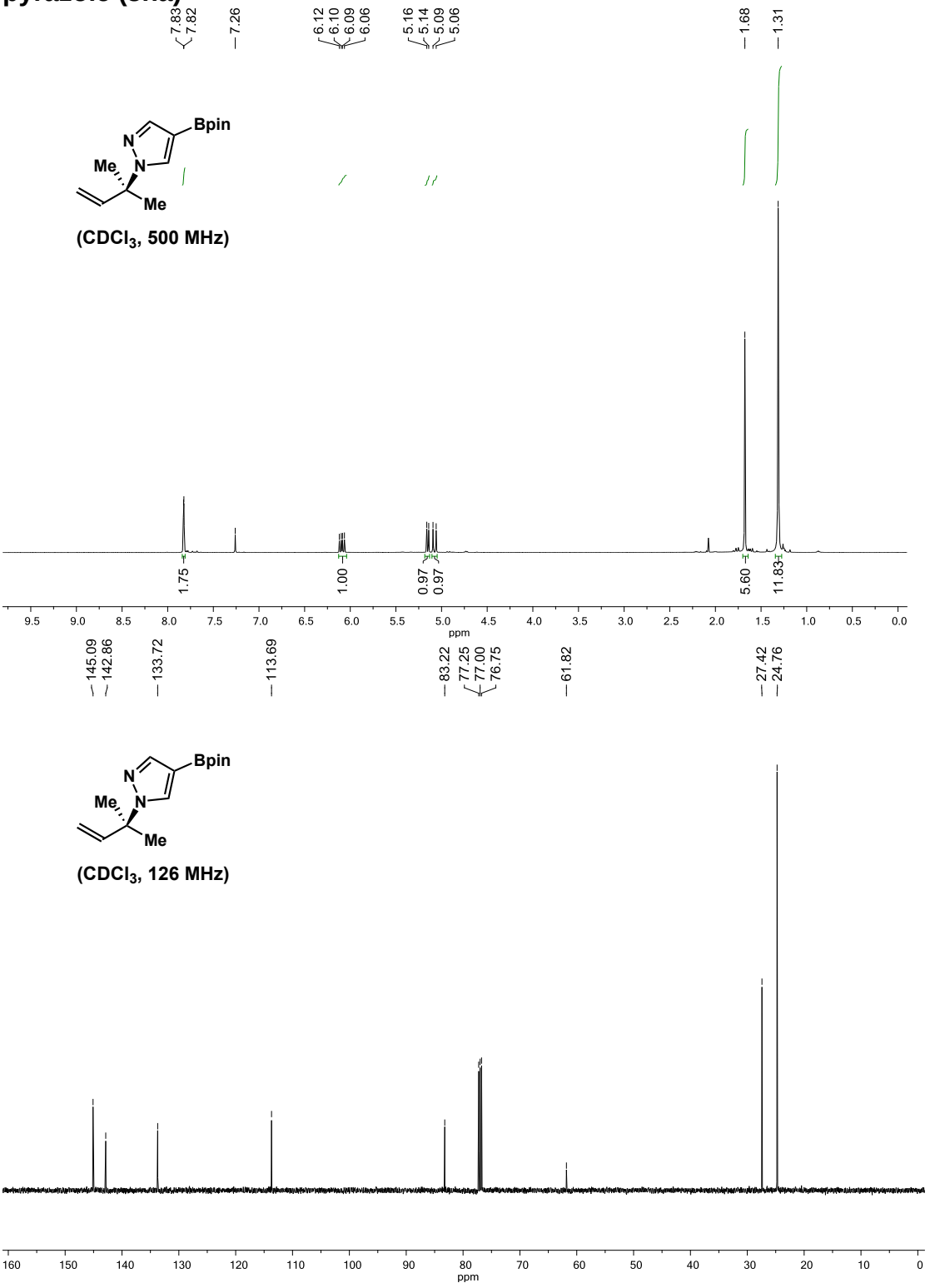




(*S*)-1-(cyclohex-2-en-1-yl)-1*H*-pyrazole (3ma)



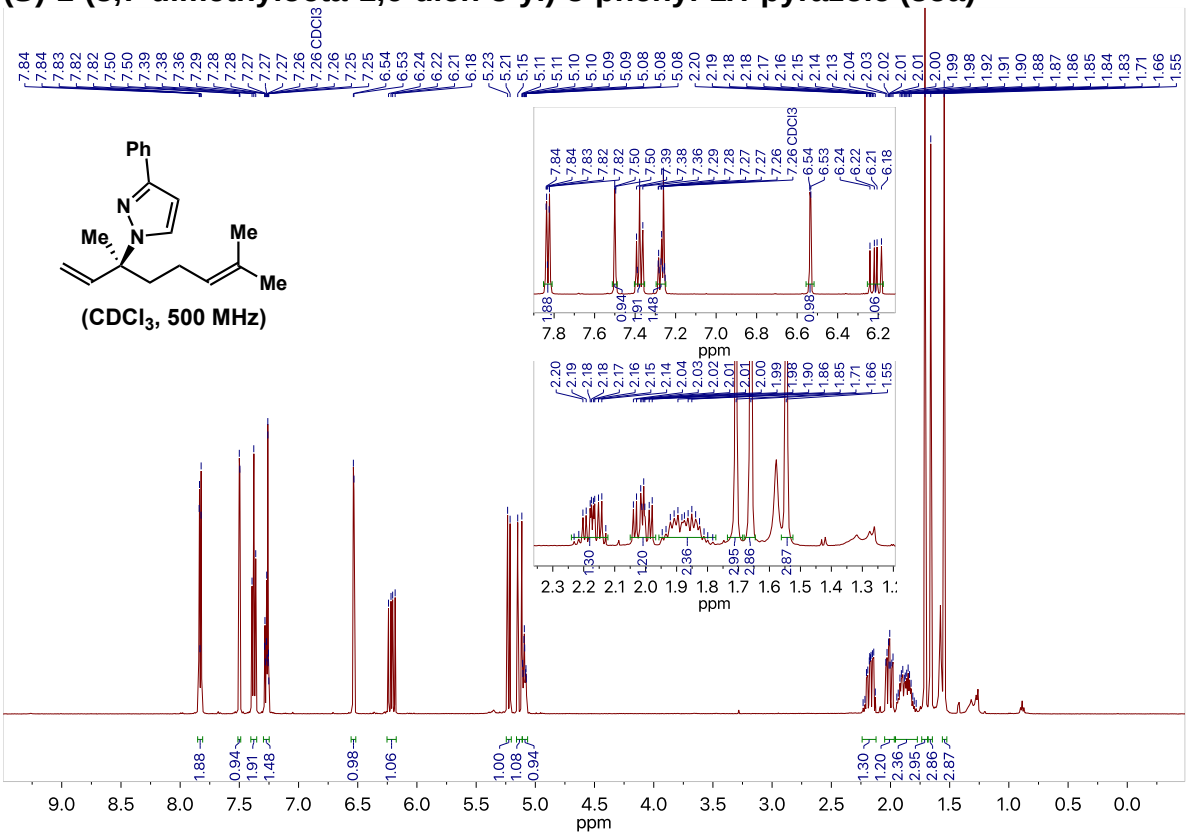
1-(2-methylbut-3-en-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (3na)

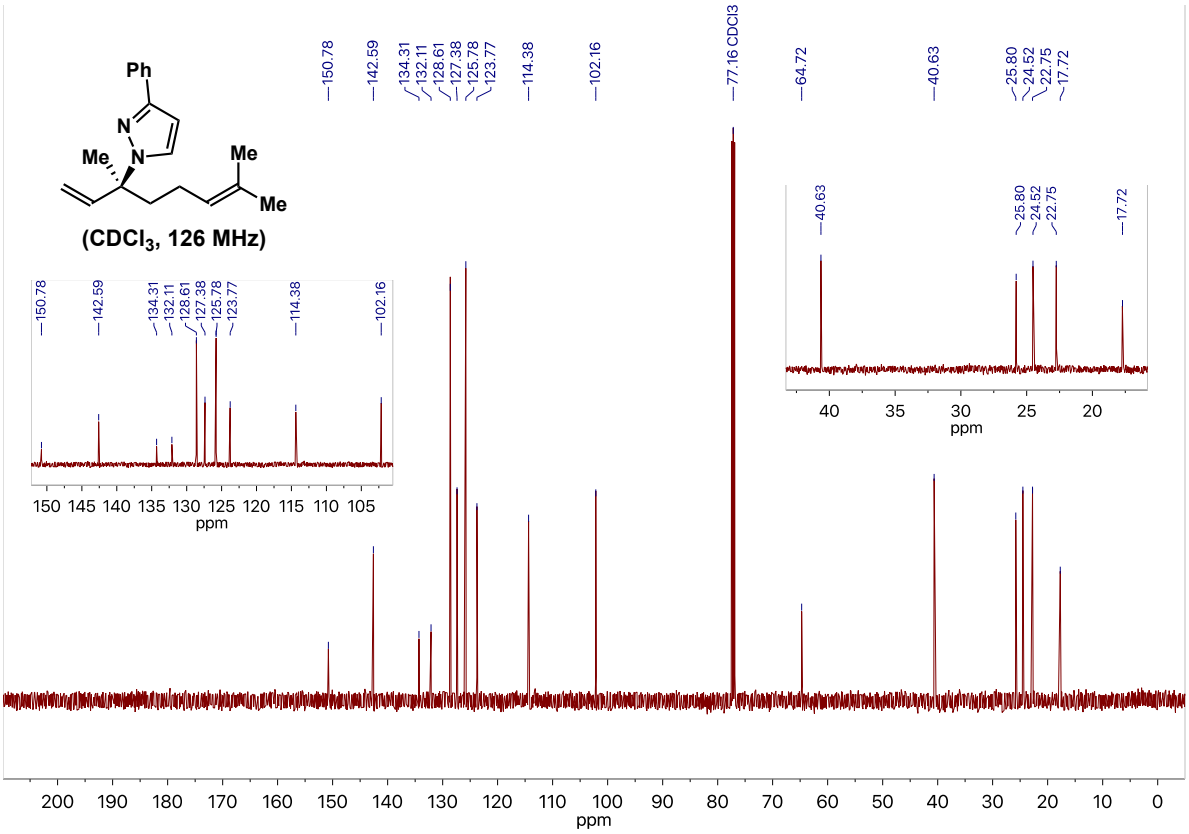


($CDCl_3$, 500 MHz)

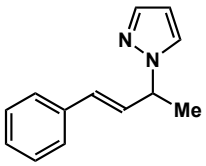
($CDCl_3$, 126 MHz)

(*S*)-1-(3,7-dimethylocta-1,6-dien-3-yl)-3-phenyl-1*H*-pyrazole (3oa)

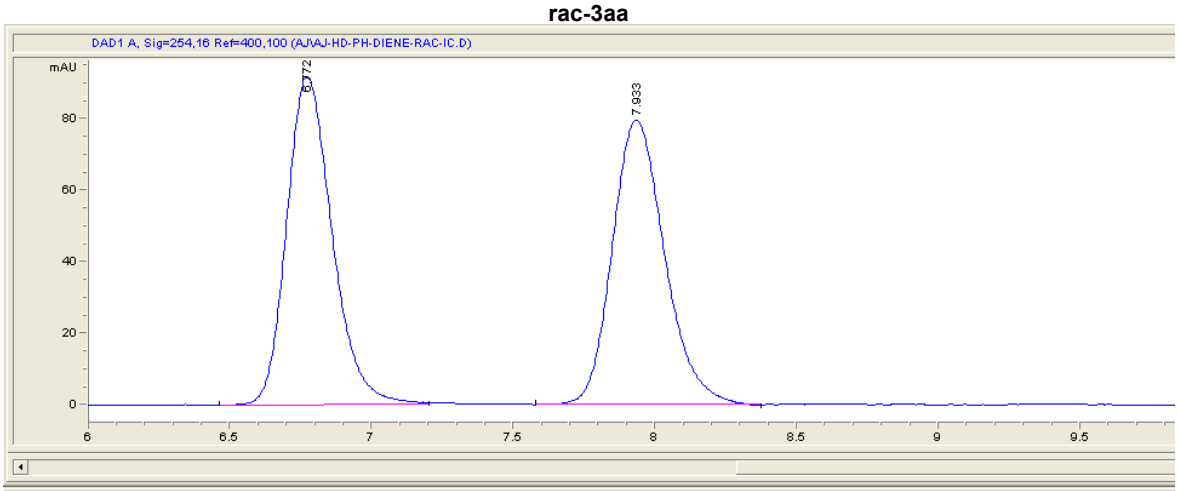




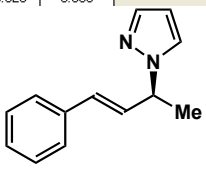
7. SFC spectra



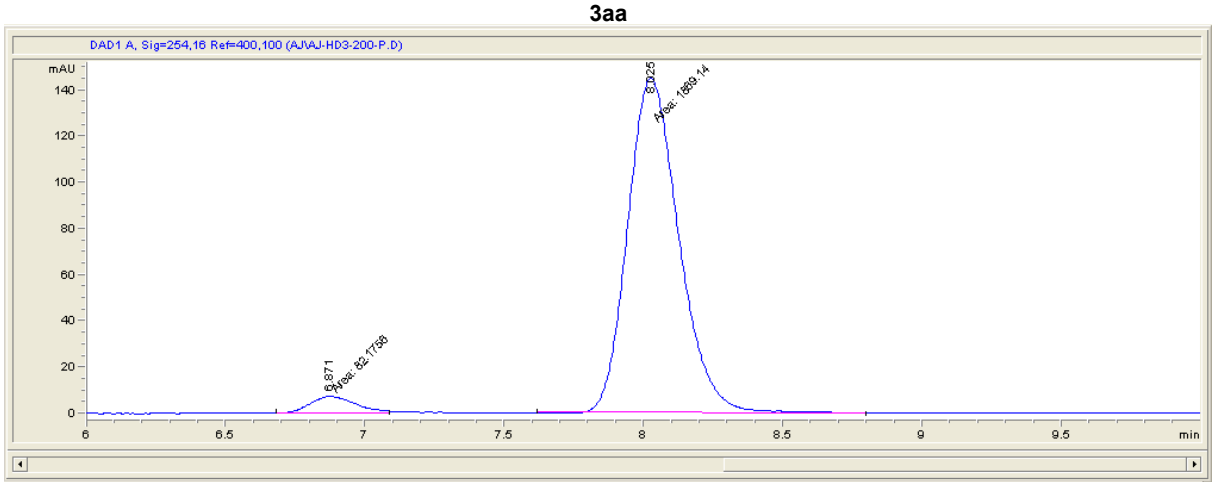
rac-3aa



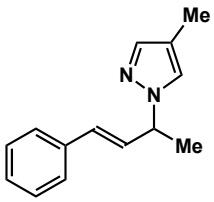
#	Time	Area	Height	Width	Area%	Symmetry
1	6.772	1027.3	92	0.1723	50.075	0.777
2	7.933	1024.2	79.6	0.2001	49.925	0.803



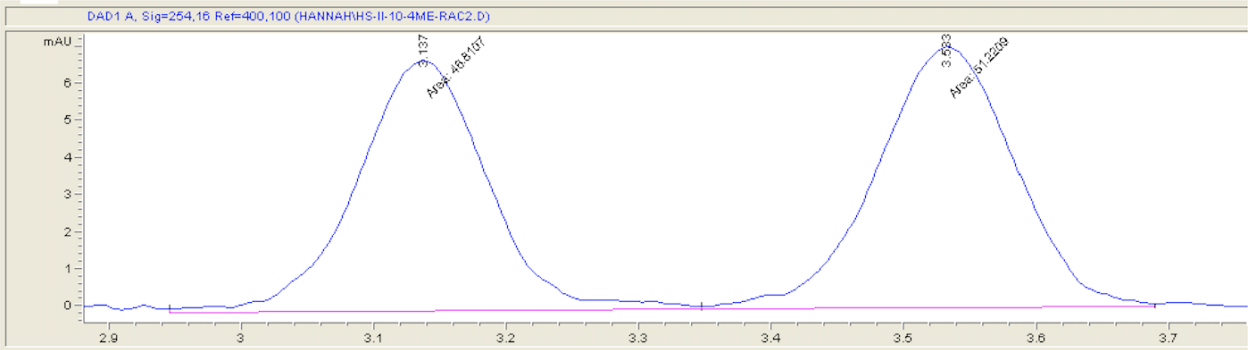
3aa



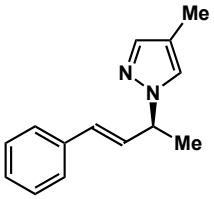
#	Time	Area	Height	Width	Area%	Symmetry
1	6.871	82.2	7.3	0.188	4.211	0.713
2	8.025	1869.1	145	0.2148	95.789	0.794



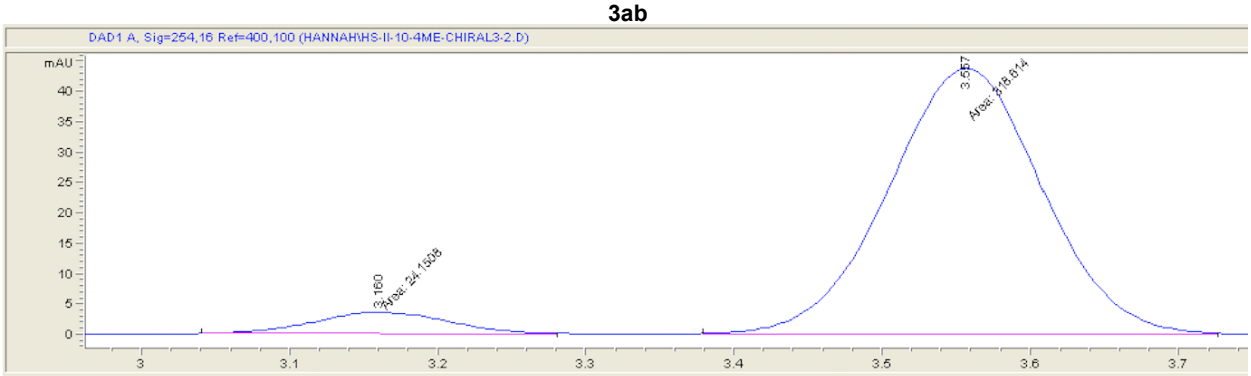
rac-3ab



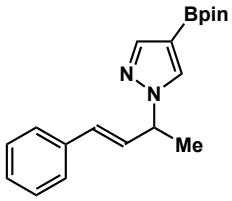
#	Time	Area	Height	Width	Area%	Symmetry
1	3.137	46.8	6.8	0.1151	47.751	1.046
2	3.533	51.2	7.1	0.1209	52.249	1.043



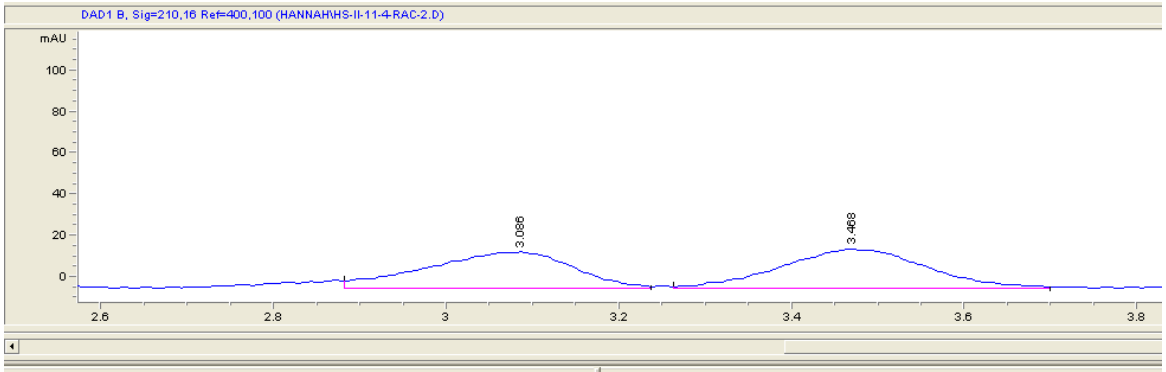
3ab



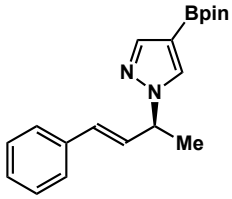
#	Time	Area	Height	Width	Area%	Symmetry
1	3.16	24.2	3.6	0.1107	7.046	0.847
2	3.557	318.6	43.9	0.121	92.954	1.016



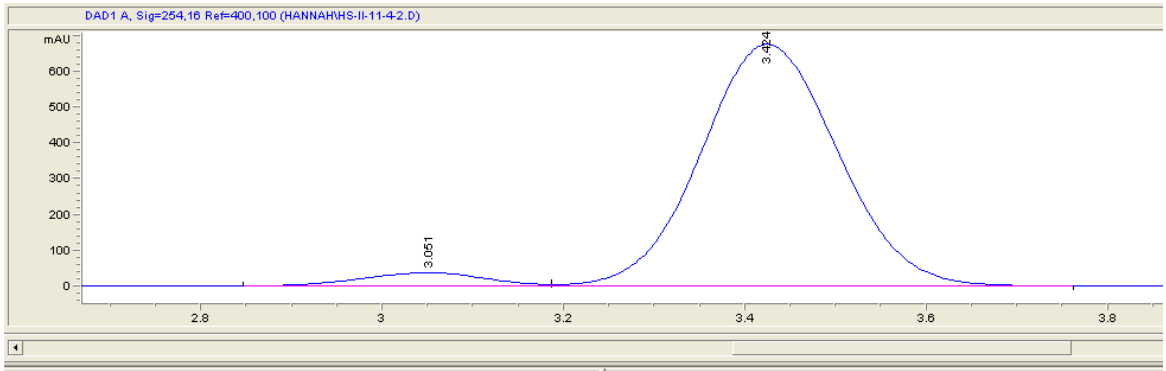
rac-3ac



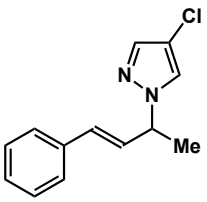
#	Time	Area	Height	Width	Area%	Symmetry
1	3.086	217.8	18.1	0.1467	48.324	1.705
2	3.468	232.9	19.4	0.1451	51.676	0.936



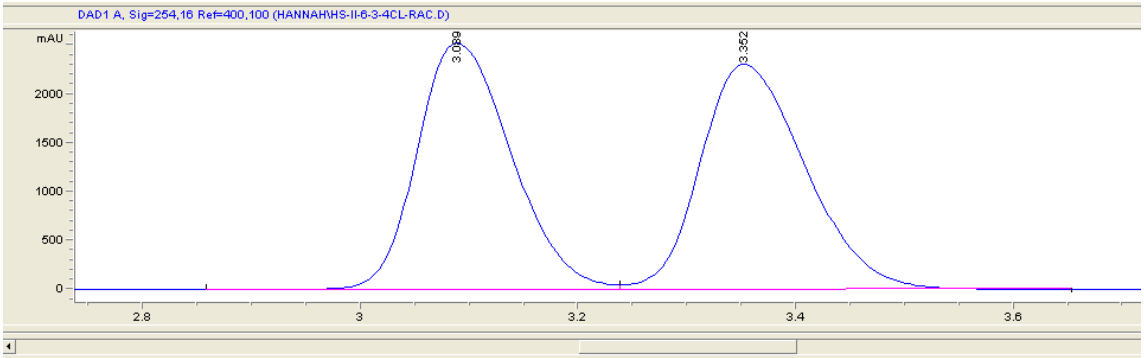
3ac



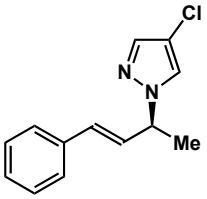
#	Time	Area	Height	Width	Area%	Symmetry
1	3.051	362.2	37.5	0.1438	4.847	1.165
2	3.424	7110.5	675.5	0.1648	95.153	0.924



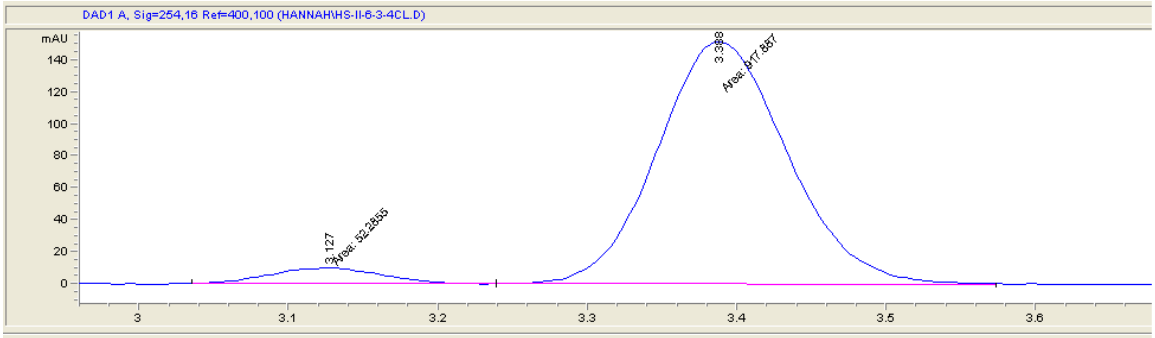
rac-3ad



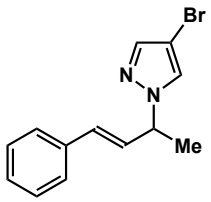
#	Time	Area	Height	Width	Area%	Symmetry
1	3.089	15183.7	2518.8	0.0953	49.608	0.722
2	3.352	15423.8	2299.9	0.1052	50.392	0.69



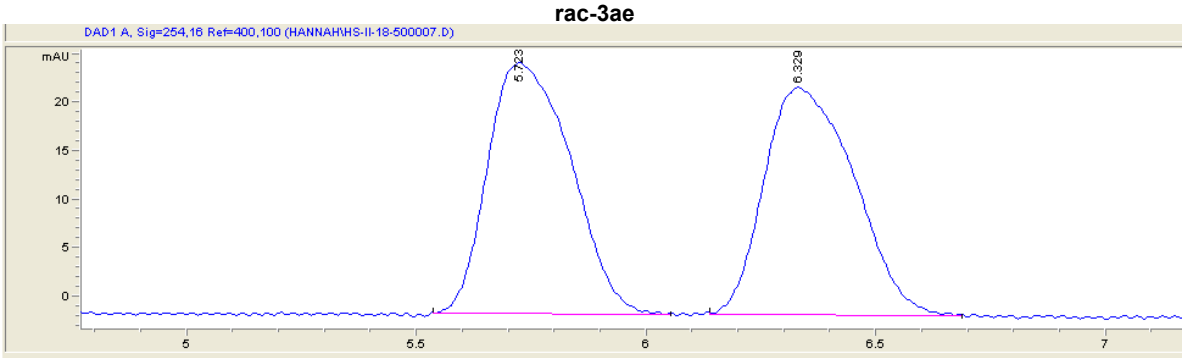
3ad



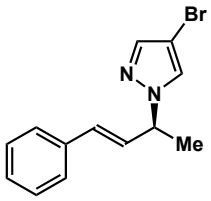
#	Time	Area	Height	Width	Area%	Symmetry
1	3.127	52.3	9.8	0.0891	5.389	7390.06
2	3.388	917.9	151.7	0.1008	94.611	0.885



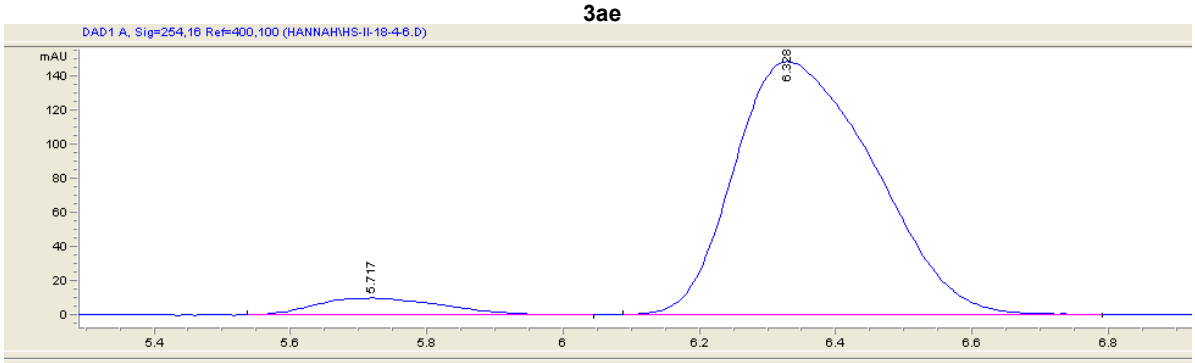
rac-3ae



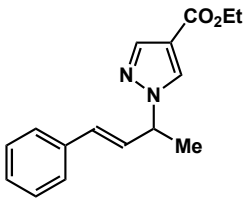
#	Time	Area	Height	Width	Area%	Symmetry
1	5.723	328.5	26.1	0.1701	50.438	0.589
2	6.329	322.8	23.6	0.1828	49.562	0.574



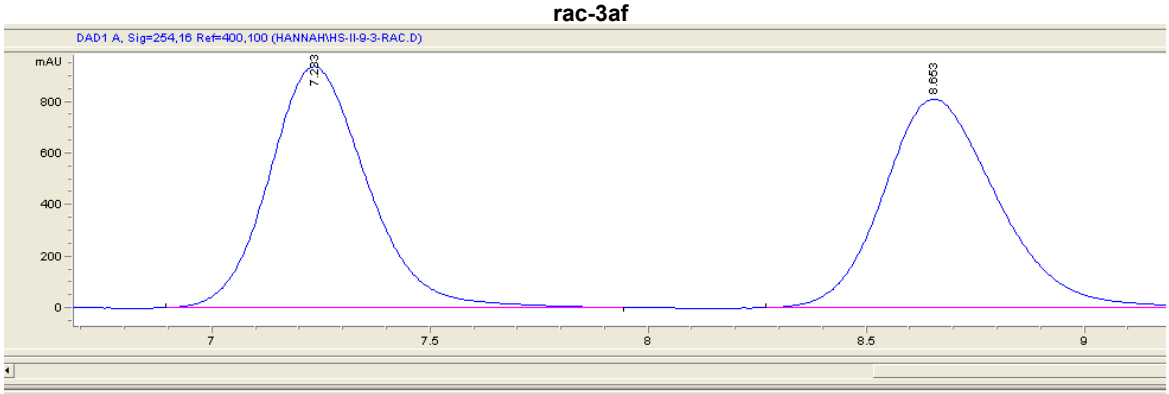
3ae



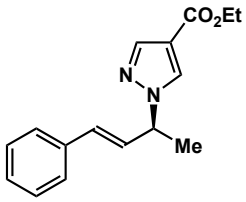
#	Time	Area	Height	Width	Area%	Symmetry
1	5.717	125.5	9.9	0.1532	5.608	0.765
2	6.328	2112.3	148.5	0.2349	94.392	0.602



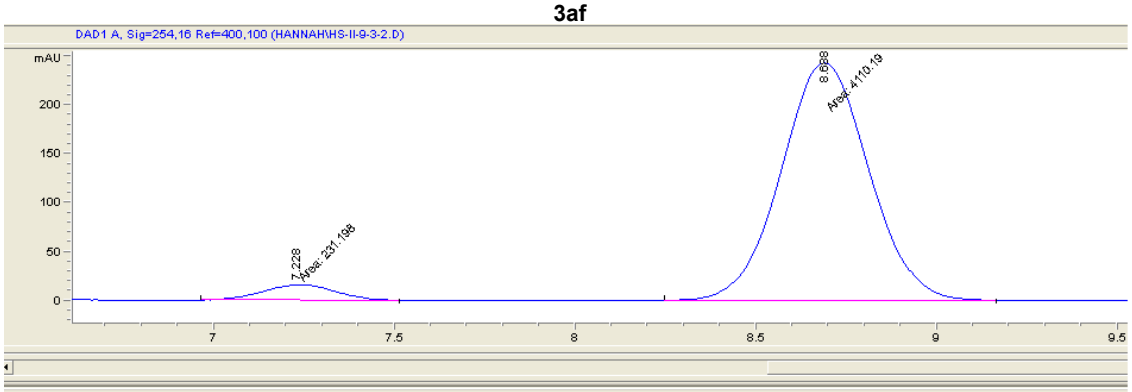
rac-3af



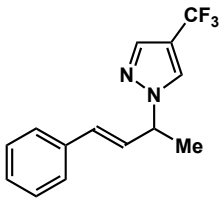
#	Time	Area	Height	Width	Area%	Symmetry
1	7.233	14682.6	935.4	0.2411	49.830	0.803
2	8.653	14782.9	810	0.2789	50.170	0.757



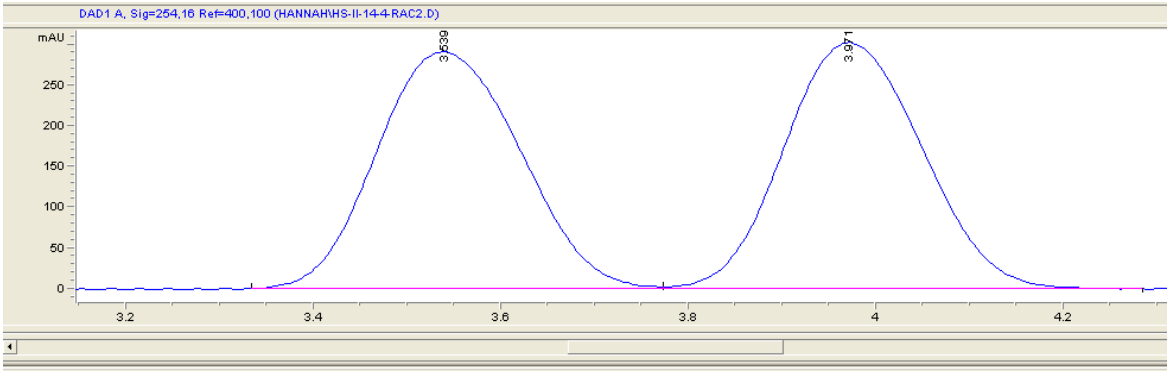
3af



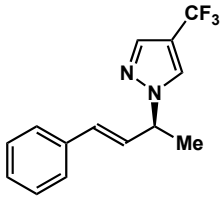
#	Time	Area	Height	Width	Area%	Symmetry
1	7.228	231.2	16.1	0.2387	5.325	0.861
2	8.688	4110.2	243	0.2819	94.675	0.94



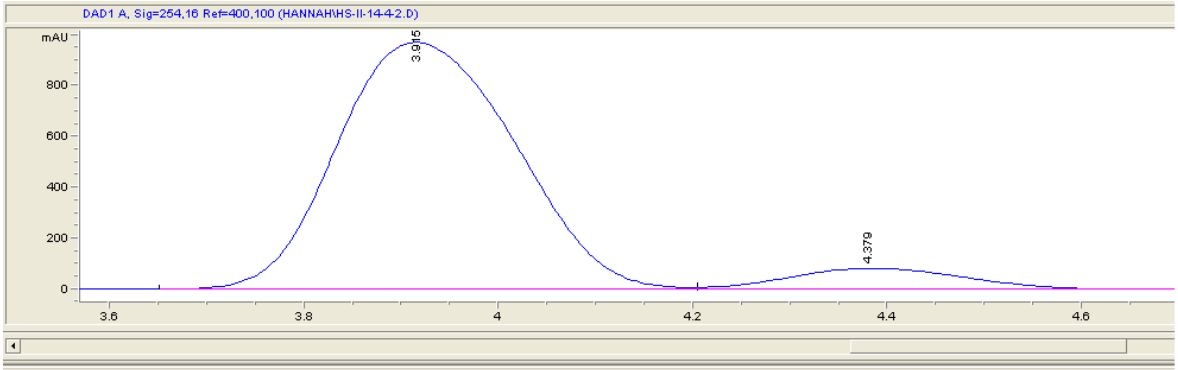
rac-3ag



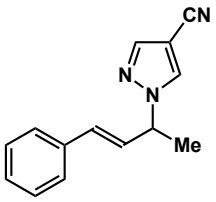
#	Time	Area	Height	Width	Area%	Symmetry
1	3.539	3110.3	291.3	0.1696	49.990	0.853
2	3.971	3111.6	302.9	0.1638	50.010	0.866



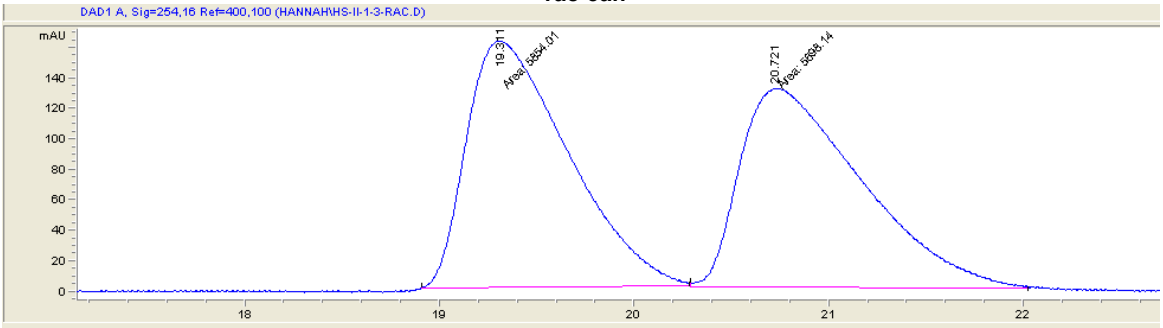
3ag



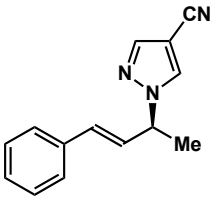
#	Time	Area	Height	Width	Area%	Symmetry
1	3.915	12300.6	970.4	0.2079	92.380	0.782
2	4.379	1014.6	82.2	0.161	7.620	0.773



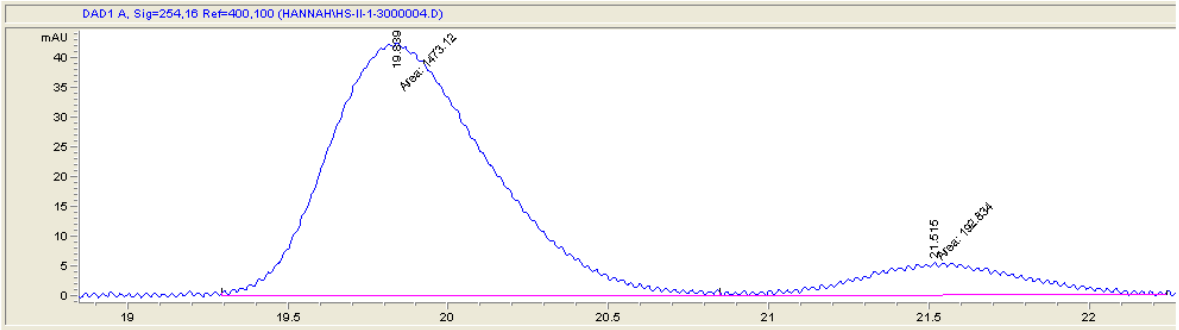
rac-3ah



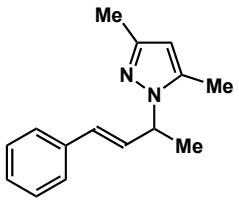
#	Time	Area	Height	Width	Area%	Symmetry
1	19.311	5854	161.7	0.6033	50.675	0.493
2	20.721	5698.1	130.6	0.7272	49.325	0.4



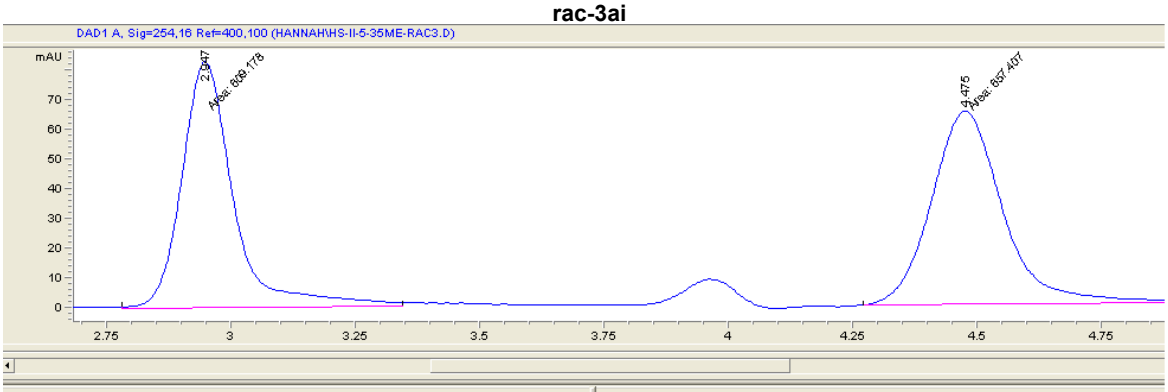
3ah



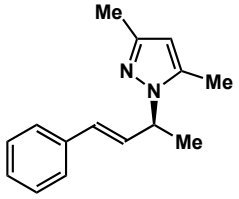
#	Time	Area	Height	Width	Area%	Symmetry
1	19.839	1473.1	42.5	0.5777	88.425	0.729
2	21.515	192.8	5.5	0.5796	11.575	0.832



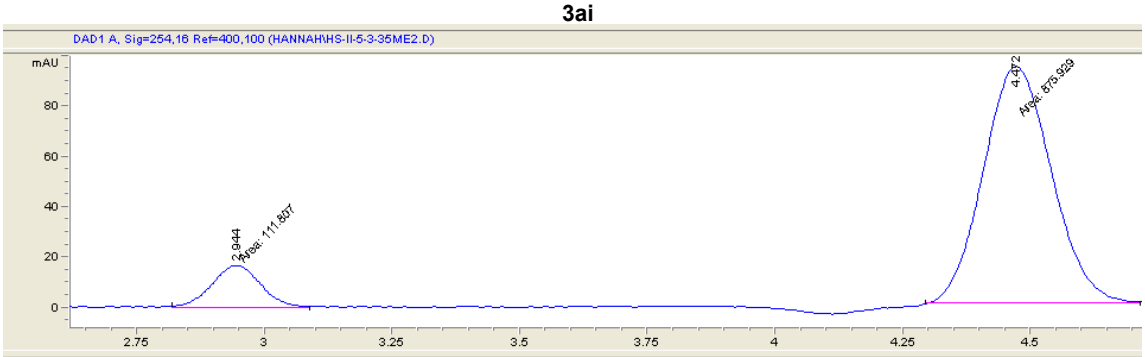
rac-3ai



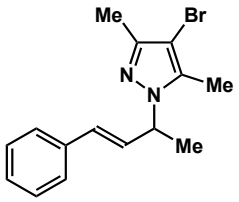
#	Time	Area	Height	Width	Area%	Symmetry
1	2.947	609.2	83.3	0.1219	48.096	0.768
2	4.475	657.4	65.1	0.1682	51.904	0.847



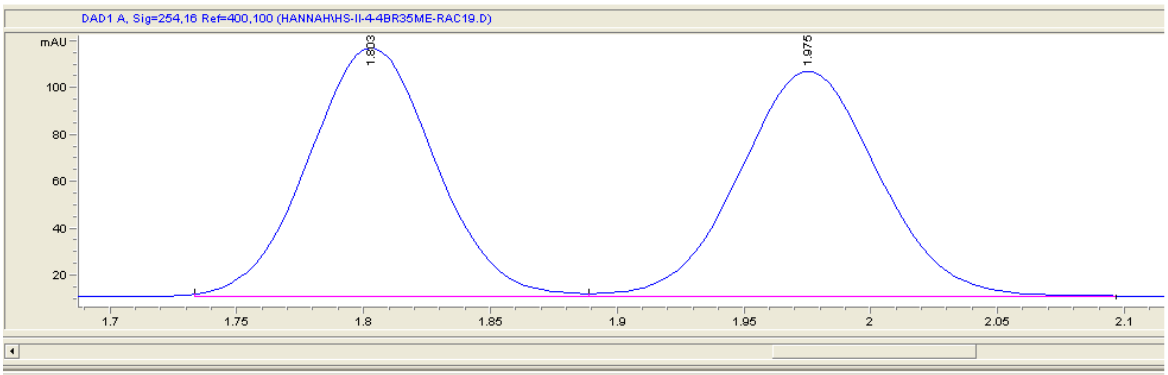
3ai



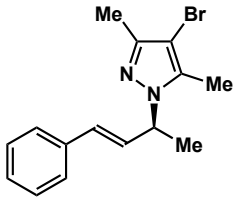
#	Time	Area	Height	Width	Area%	Symmetry
1	2.944	111.8	16.8	0.1108	11.320	0.982
2	4.472	875.9	94.1	0.1552	88.680	0.913



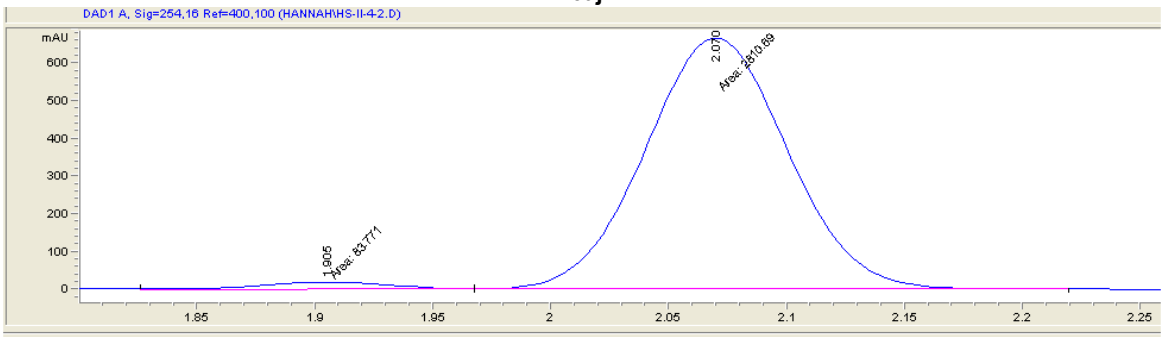
rac-3aj



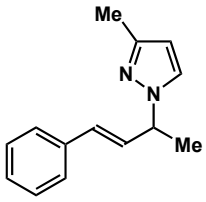
#	Time	Area	Height	Width	Area%	Symmetry
1	1.803	369.8	106.5	0.0545	50.069	0.956
2	1.975	368.8	96.3	0.0597	49.931	0.956



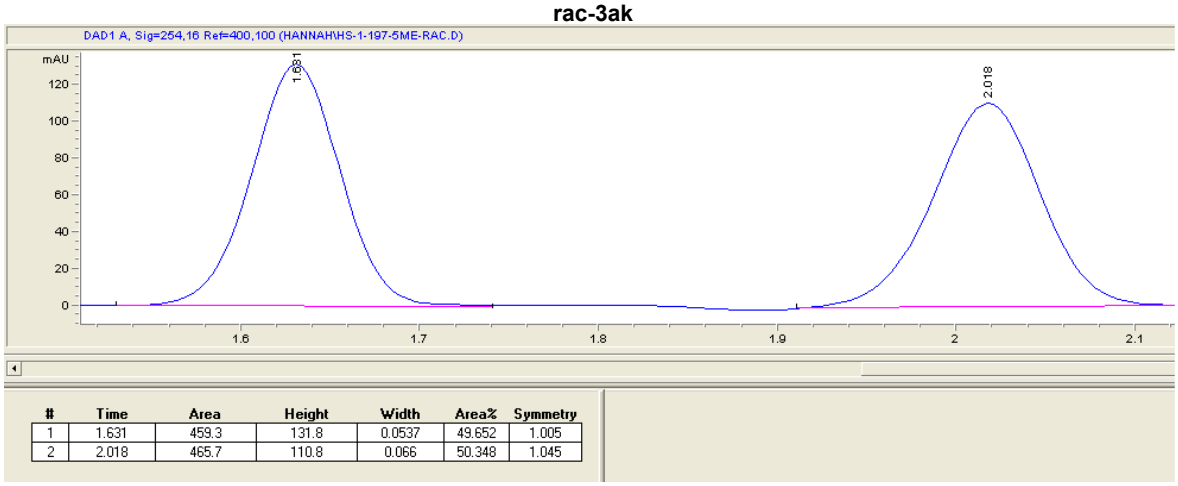
3aj



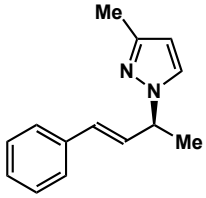
#	Time	Area	Height	Width	Area%	Symmetry
1	1.905	83.8	20.3	0.0687	2.894	1.073
2	2.07	2810.7	668.8	0.07	97.106	0.968



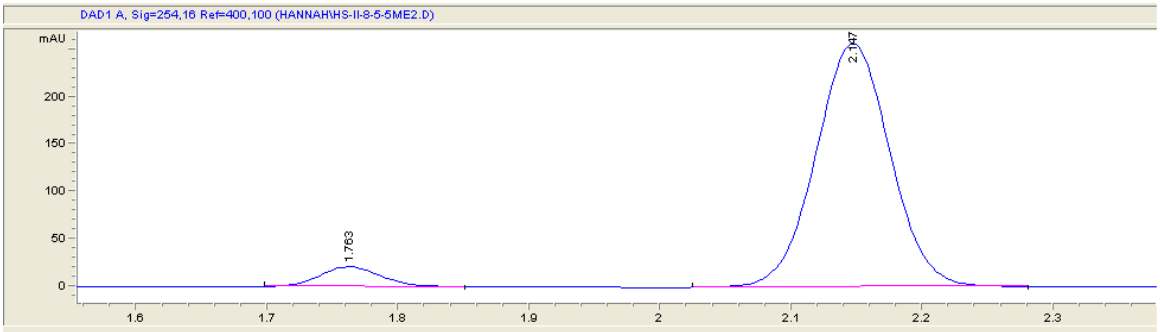
rac-3ak



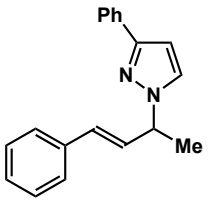
#	Time	Area	Height	Width	Area%	Symmetry
1	1.631	459.3	131.8	0.0537	49.652	1.005
2	2.018	465.7	110.8	0.066	50.348	1.045



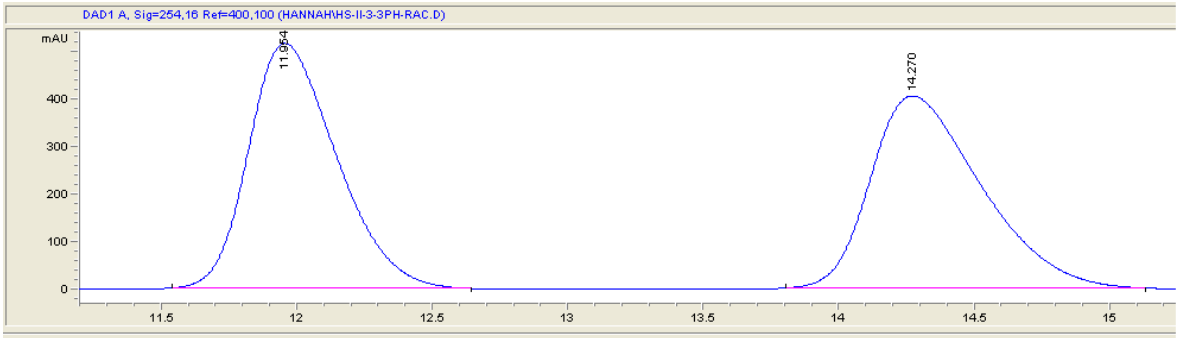
3ak



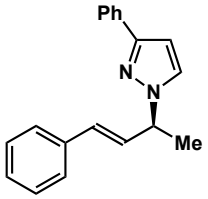
#	Time	Area	Height	Width	Area%	Symmetry
1	1.763	69.3	21.1	0.0513	6.414	0.916
2	2.147	1011.4	256.7	0.062	93.586	0.963



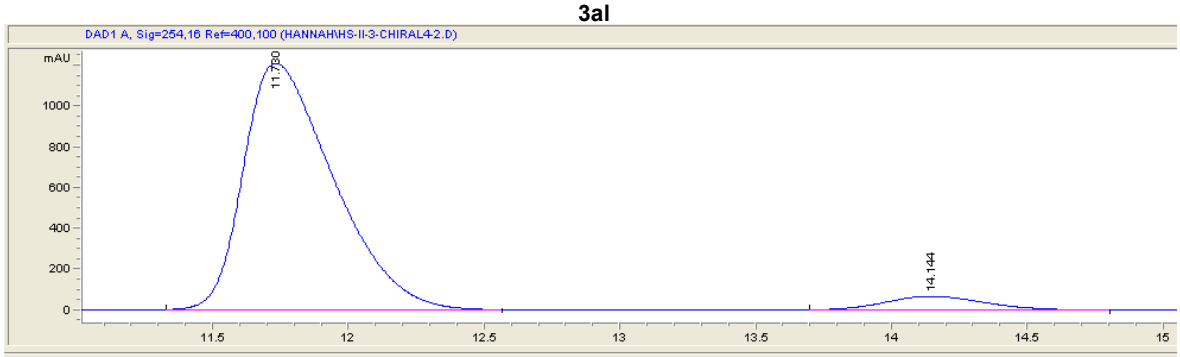
rac-3al



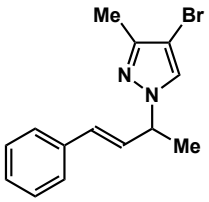
#	Time	Area	Height	Width	Area%	Symmetry
1	11.954	11723.4	516.1	0.347	50.330	0.675
2	14.27	11569.9	405.6	0.4248	49.670	0.589



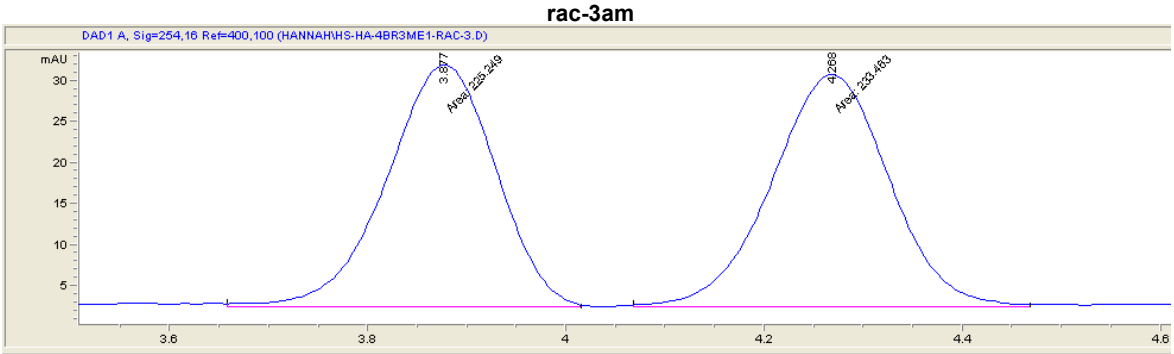
3al



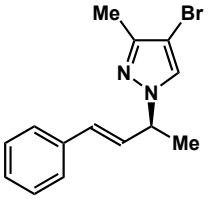
#	Time	Area	Height	Width	Area%	Symmetry
1	11.73	27967.5	1210.7	0.3405	94.190	0.535
2	14.144	1725.2	67.6	0.313	5.810	0.823



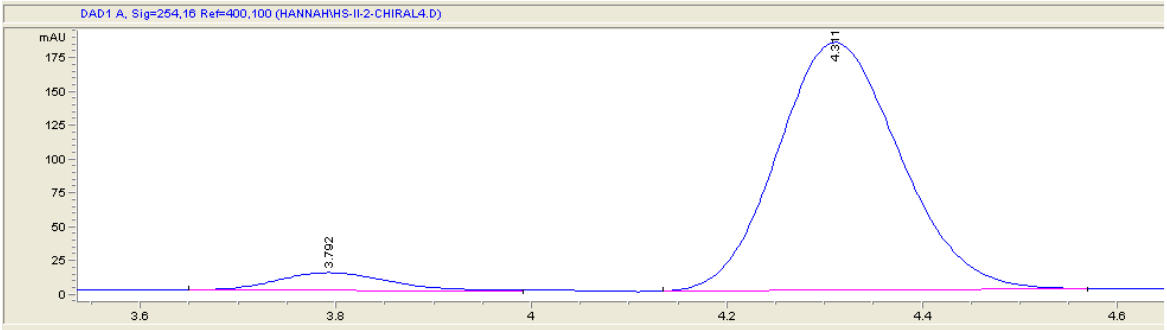
rac-3am



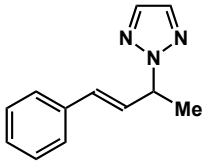
#	Time	Area	Height	Width	Area%	Symmetry
1	3.877	225.2	29.5	0.1273	49.105	1.115
2	4.268	233.5	28.3	0.1376	50.895	1.026



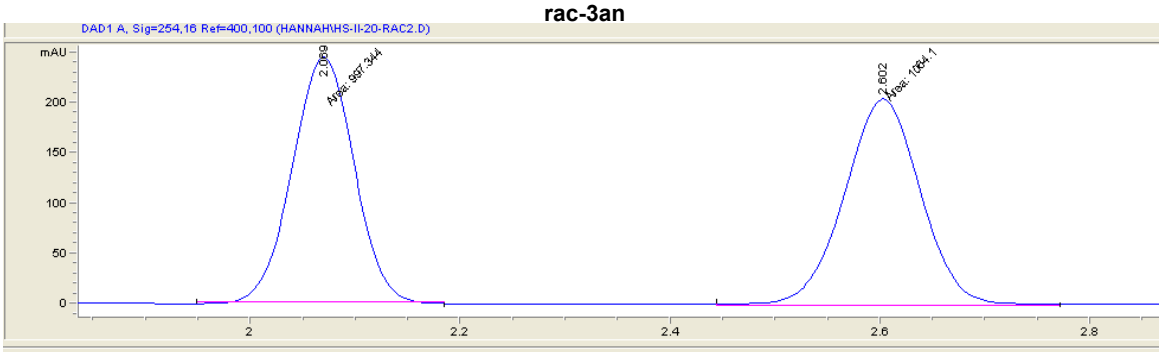
3am



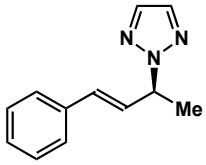
#	Time	Area	Height	Width	Area%	Symmetry
1	3.792	108	13.4	0.1163	6.326	0.813
2	4.311	1598.6	183.4	0.1377	93.674	0.862



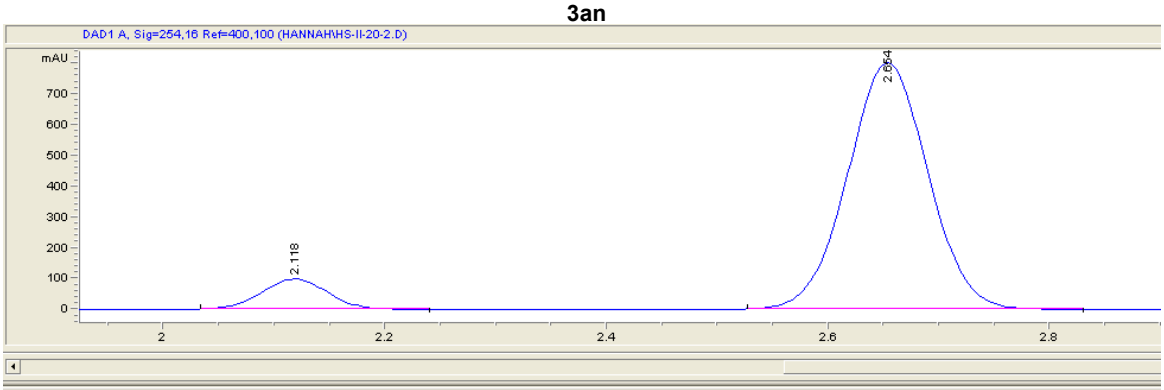
rac-3an



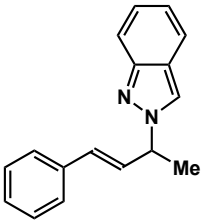
#	Time	Area	Height	Width	Area%	Symmetry
1	2.069	997.3	244.5	0.068	48.381	1.006
2	2.602	1064.1	206.5	0.0859	51.619	1.007



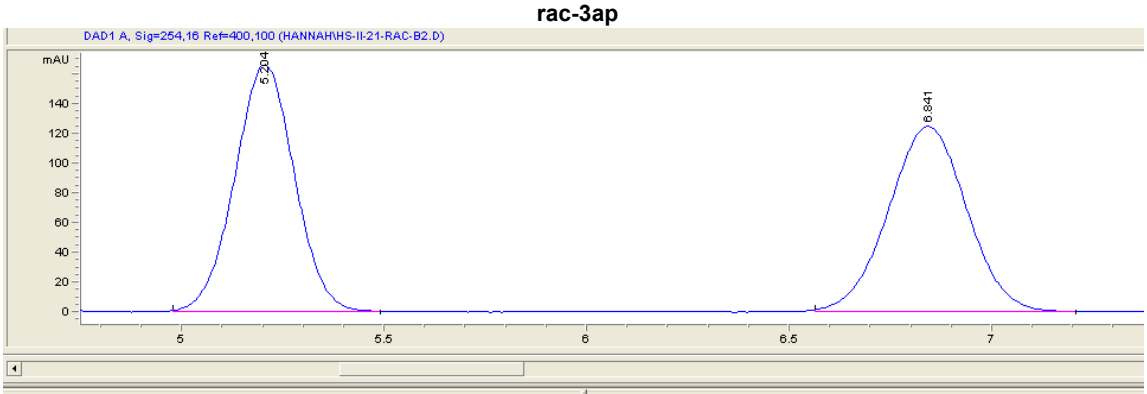
3an



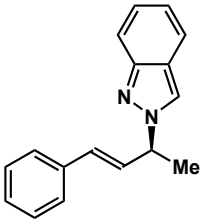
#	Time	Area	Height	Width	Area%	Symmetry
1	2.118	409.4	98.7	0.0654	9.194	1.002
2	2.654	4043.3	800.1	0.078	90.806	0.973



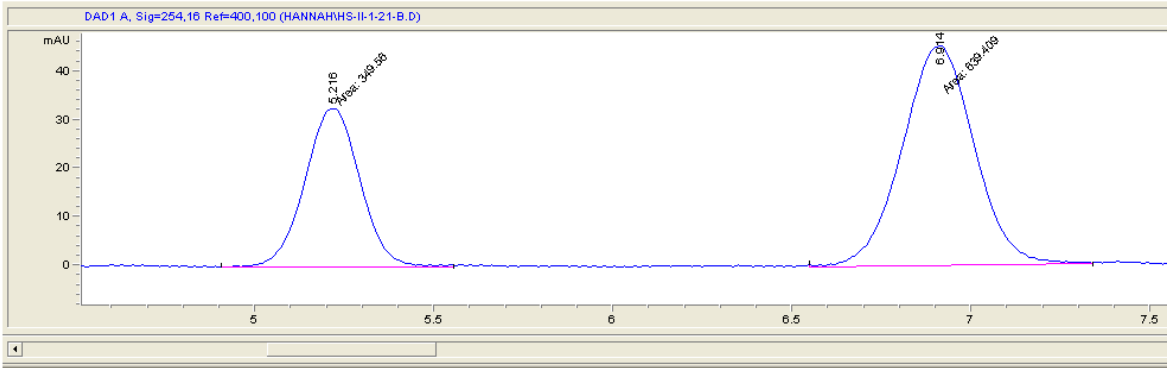
rac-3ap



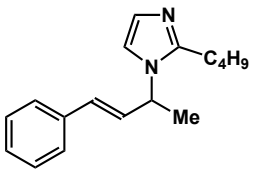
#	Time	Area	Height	Width	Area%	Symmetry
1	5.204	1705	166	0.1598	50.420	0.992
2	6.841	1676.6	124.4	0.2122	49.580	0.995



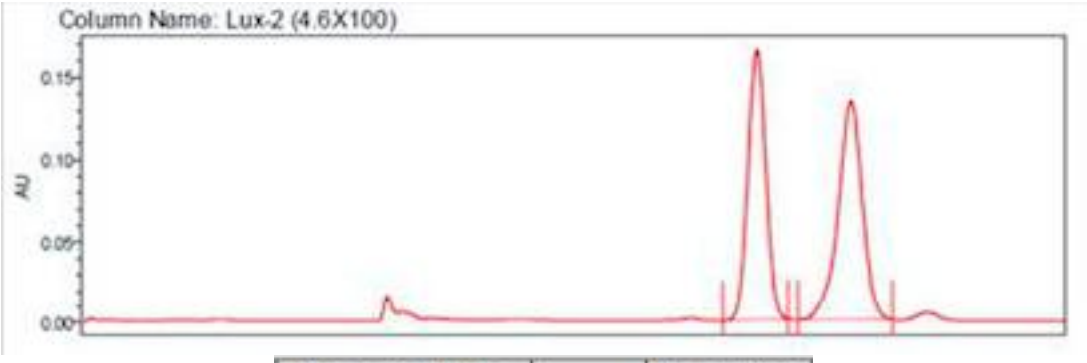
3ap



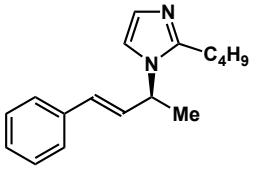
#	Time	Area	Height	Width	Area%	Symmetry
1	5.216	349.6	32.8	0.1779	35.346	0.993
2	6.914	639.4	45.2	0.2356	64.654	1.104



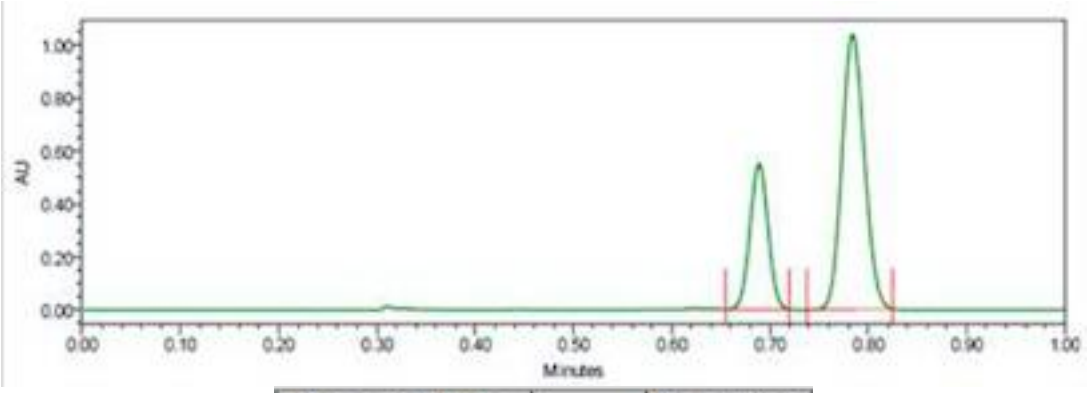
rac-3aq



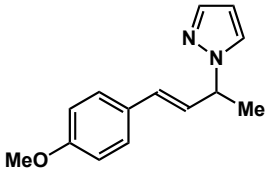
Retention Time (mins)	% Area	Base Peak (m/z)
0.687	47.59	255.36
0.783	52.41	255.37



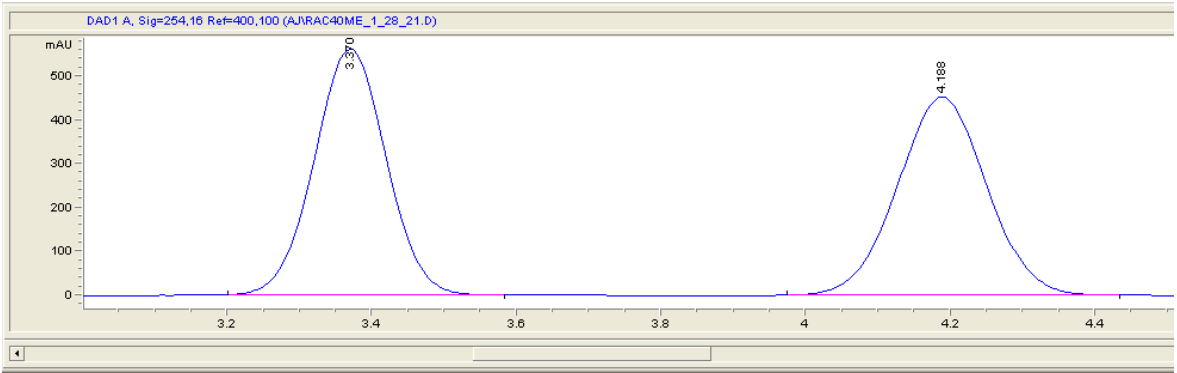
3aq



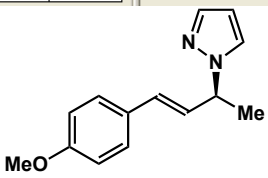
Retention Time (mins)	% Area	Base Peak (m/z)
0.689	29.89	255.36
0.784	70.11	255.37



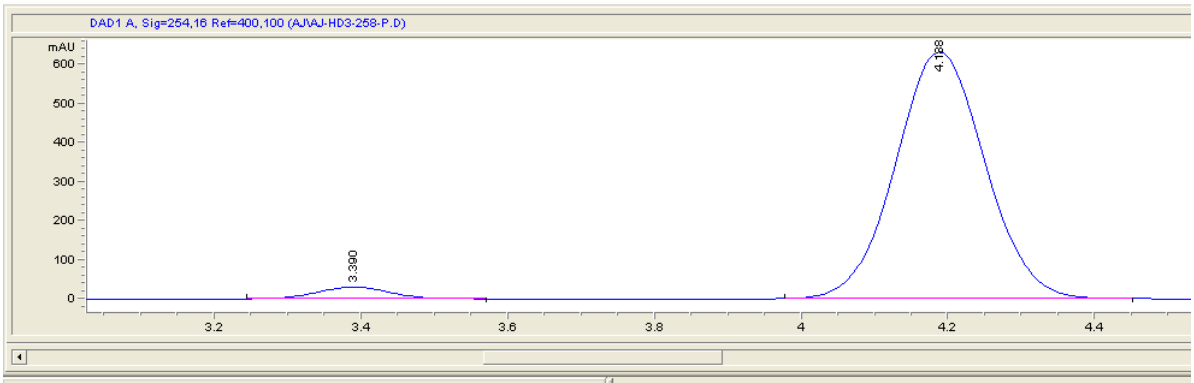
rac-3ba



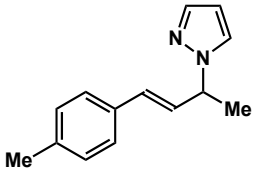
#	Time	Area	Height	Width	Area%	Symmetry
1	3.37	3895.9	561	0.107	49.949	0.978
2	4.188	3903.9	452.1	0.1347	50.051	0.969



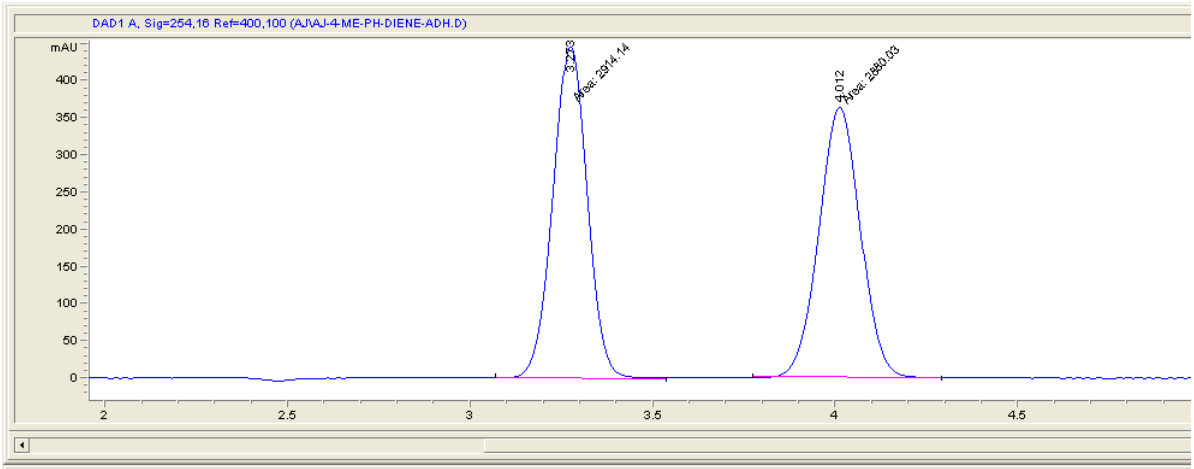
3ba



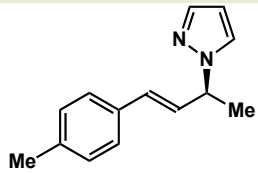
#	Time	Area	Height	Width	Area%	Symmetry
1	3.39	205.6	30.3	0.1061	3.698	0.994
2	4.188	5354.9	631.1	0.133	96.302	0.94



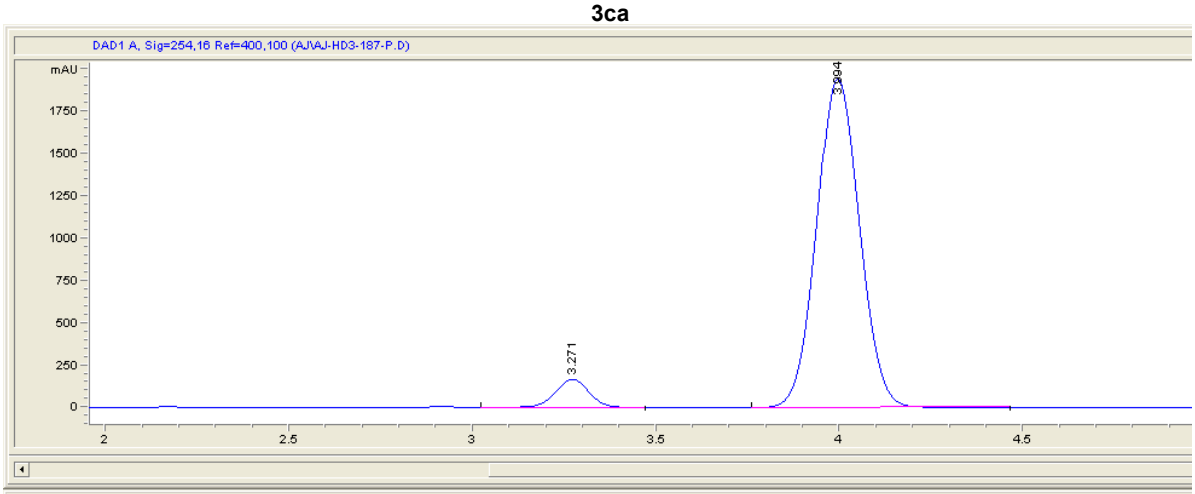
rac-3ca



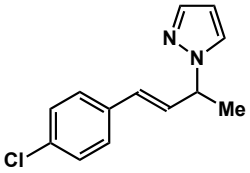
#	Time	Area	Height	Width	Area%	Symmetry
1	3.273	2914.1	446.7	0.1087	50.294	0.993
2	4.012	2880	363.9	0.1319	49.706	0.996



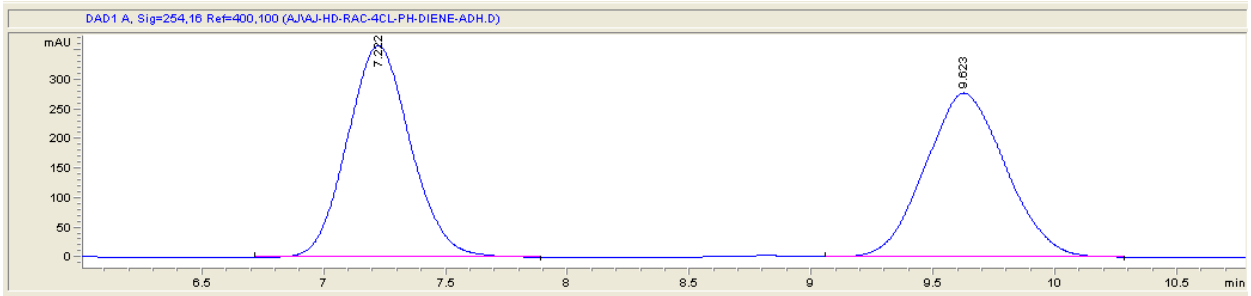
3ca



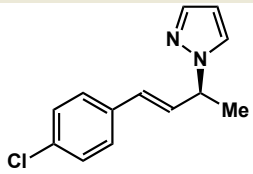
#	Time	Area	Height	Width	Area%	Symmetry
1	3.271	1148.3	169.6	0.104	6.795	1.064
2	3.994	15752.3	1947.3	0.1264	93.205	0.912



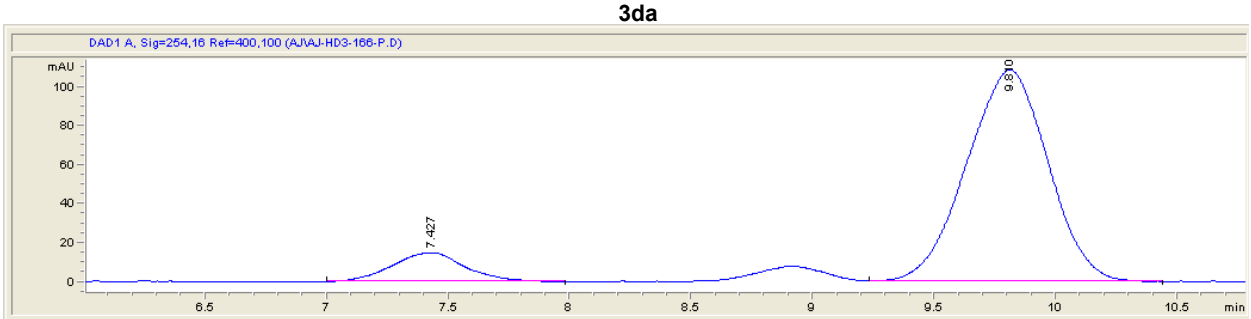
rac-3da



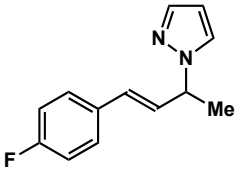
#	Time	Area	Height	Width	Area%	Symmetry
1	7.222	6461.7	357.7	0.2808	50.389	0.92
2	9.623	6362	277.6	0.3424	49.611	0.889



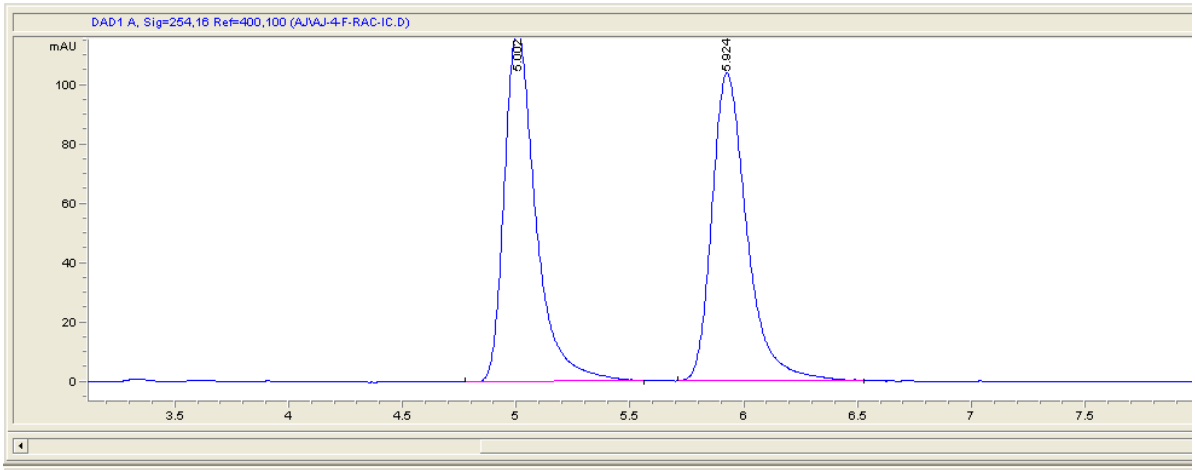
3da



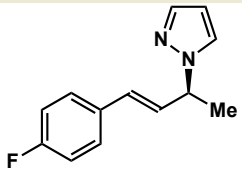
#	Time	Area	Height	Width	Area%	Symmetry
1	7.427	309.9	14.9	0.2789	10.902	1.077
2	9.81	2533	108.6	0.3642	89.098	1.093



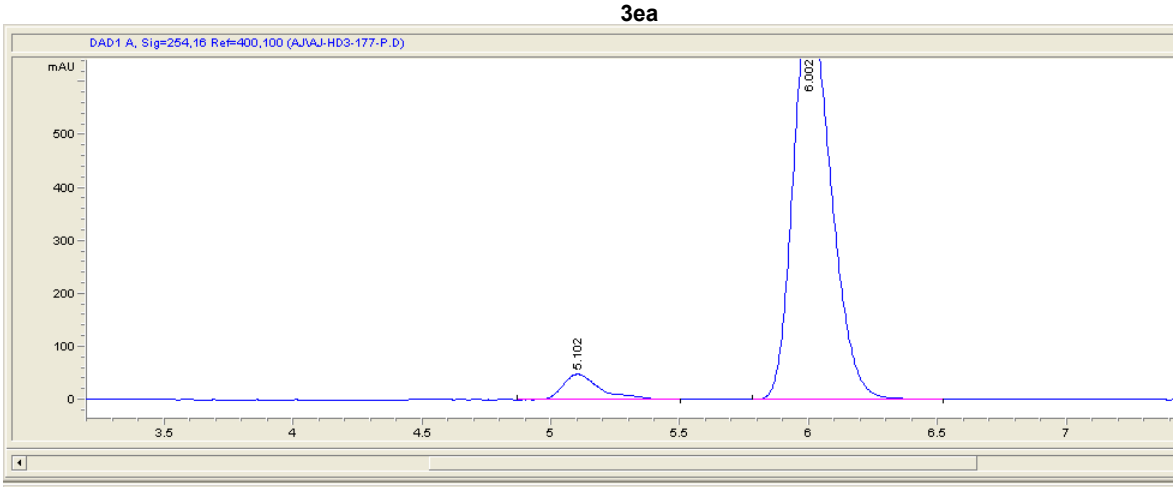
rac-3ea



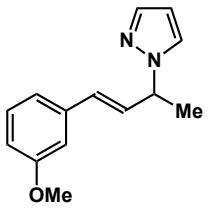
#	Time	Area	Height	Width	Area%	Symmetry
1	5.002	1143.6	119.4	0.1447	50.558	0.637
2	5.924	1118.4	104	0.1634	49.442	0.695



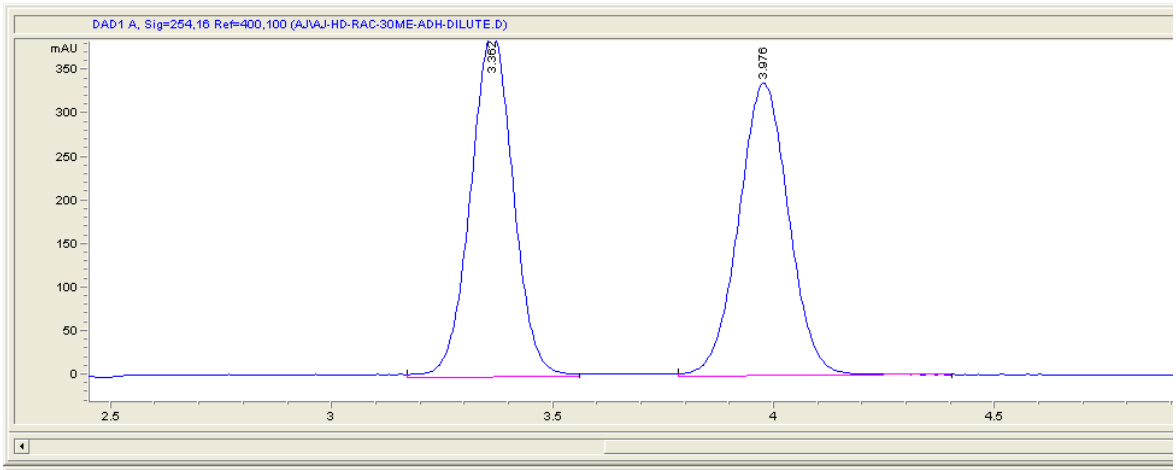
3ea



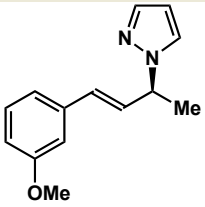
#	Time	Area	Height	Width	Area%	Symmetry
1	5.102	488.8	47.9	0.1531	6.012	0.59
2	6.002	7640.4	745.2	0.1606	93.988	0.74



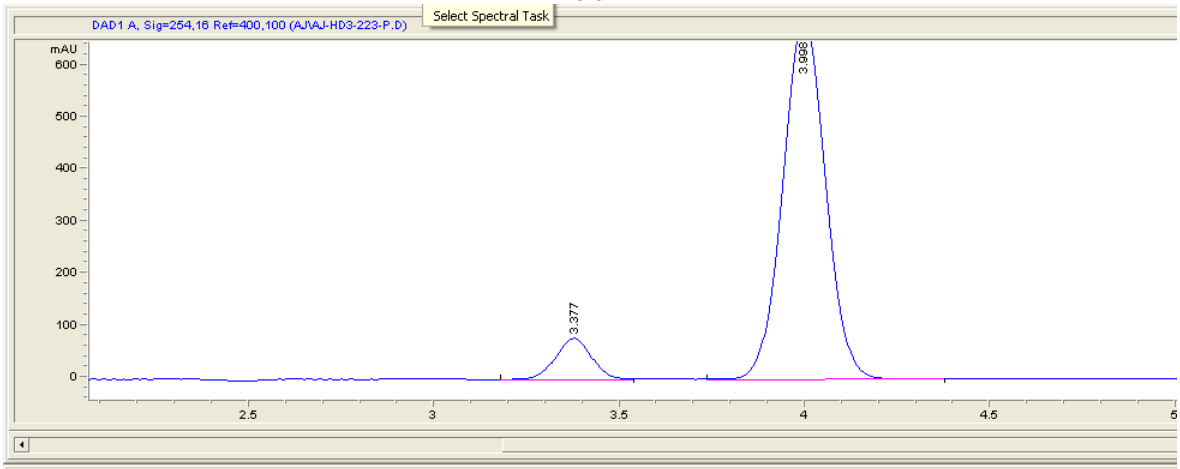
rac-3fa



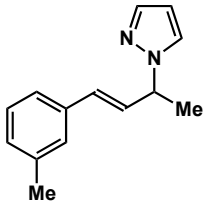
#	Time	Area	Height	Width	Area%	Symmetry
1	3.362	2684.1	397.7	0.1047	50.162	0.99
2	3.976	2666.8	336.3	0.1235	49.838	0.97



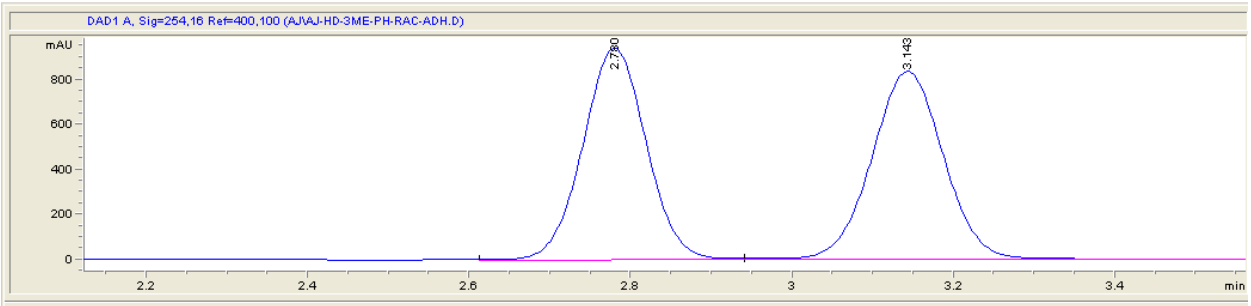
3fa



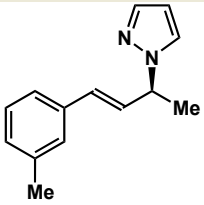
#	Time	Area	Height	Width	Area%	Symmetry
1	3.377	578	80.8	0.1104	9.416	1.052
2	3.998	5560.4	691.5	0.1238	90.584	0.956



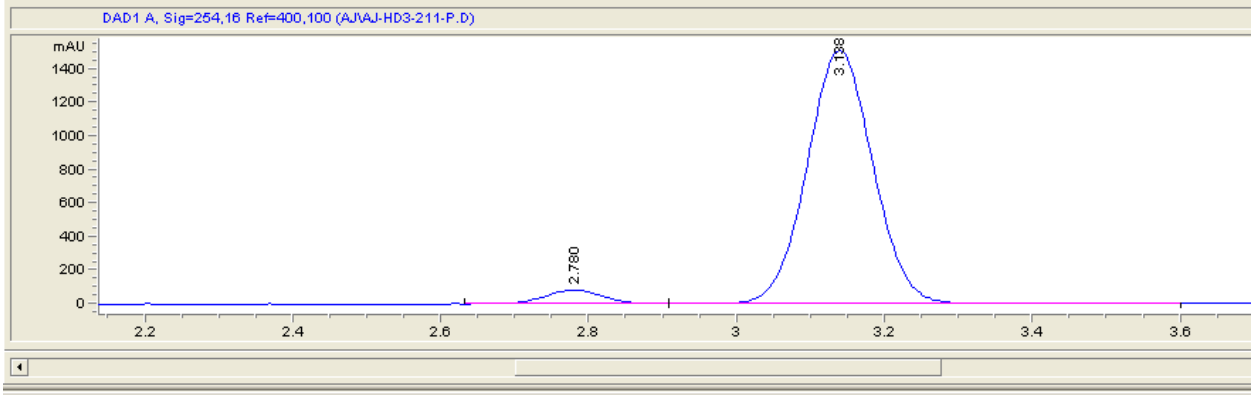
rac-3ga



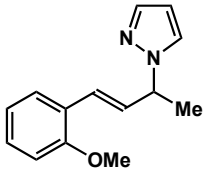
#	Time	Area	Height	Width	Area%	Symmetry
1	2.78	5175.2	944.3	0.0849	49.588	0.97
2	3.143	5261.3	839.2	0.0971	50.412	0.965



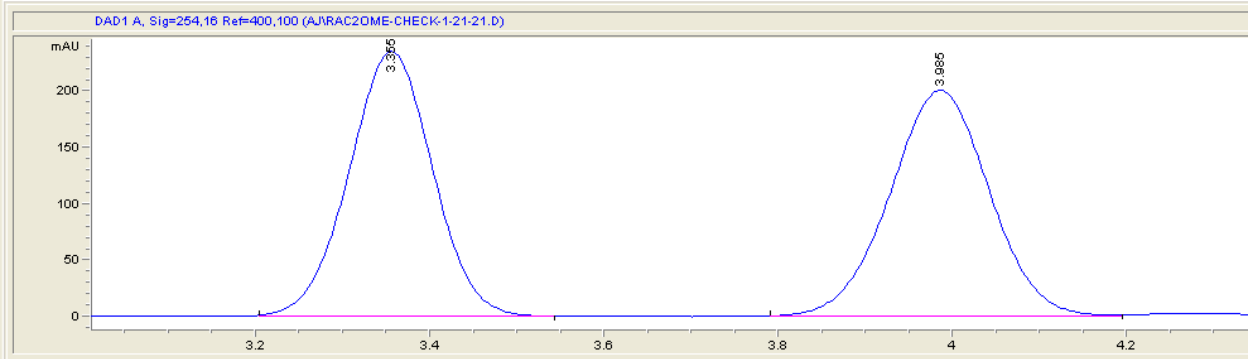
3ga



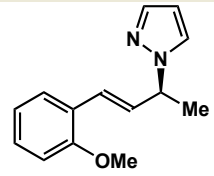
#	Time	Area	Height	Width	Area%	Symmetry
1	2.78	502.6	85.4	0.0897	5.054	1.044
2	3.138	9443.6	1513.3	0.0968	94.946	0.942



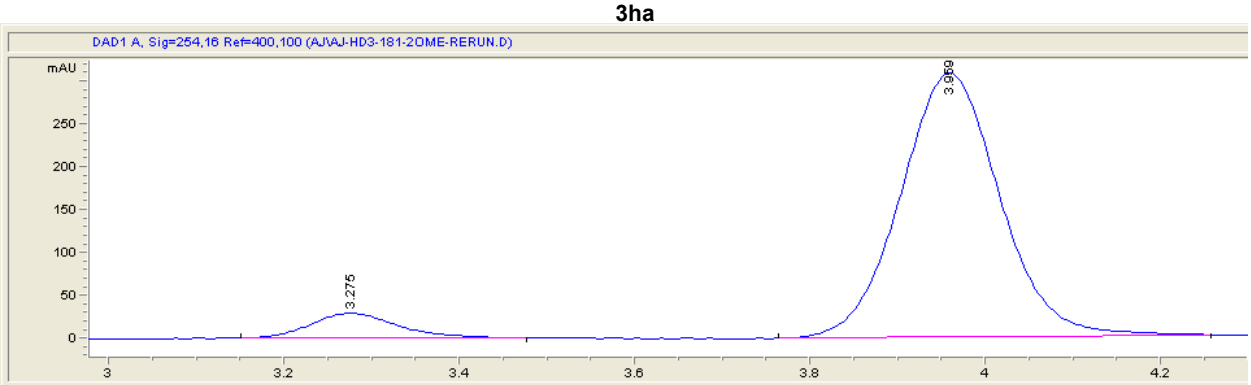
rac-3ha



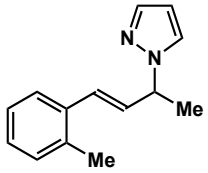
#	Time	Area	Height	Width	Area%	Symmetry
1	3.355	1572.9	235	0.1041	49.582	1.003
2	3.985	1599.4	200.5	0.1241	50.418	1.006



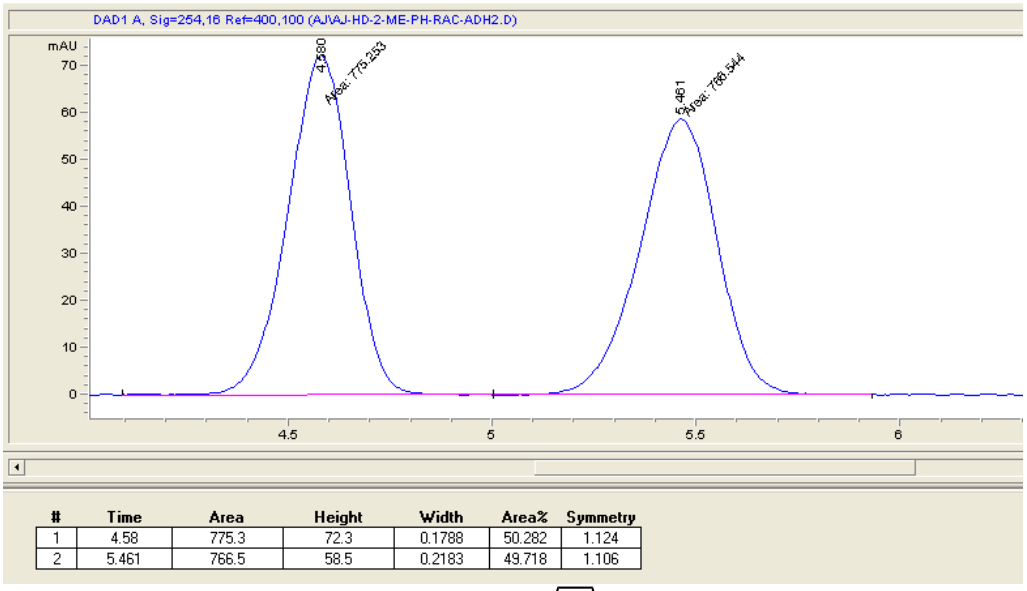
3ha



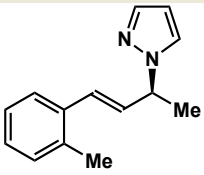
#	Time	Area	Height	Width	Area%	Symmetry
1	3.275	206.2	29.3	0.104	7.797	0.785
2	3.959	2438.2	307.9	0.1224	92.203	0.921



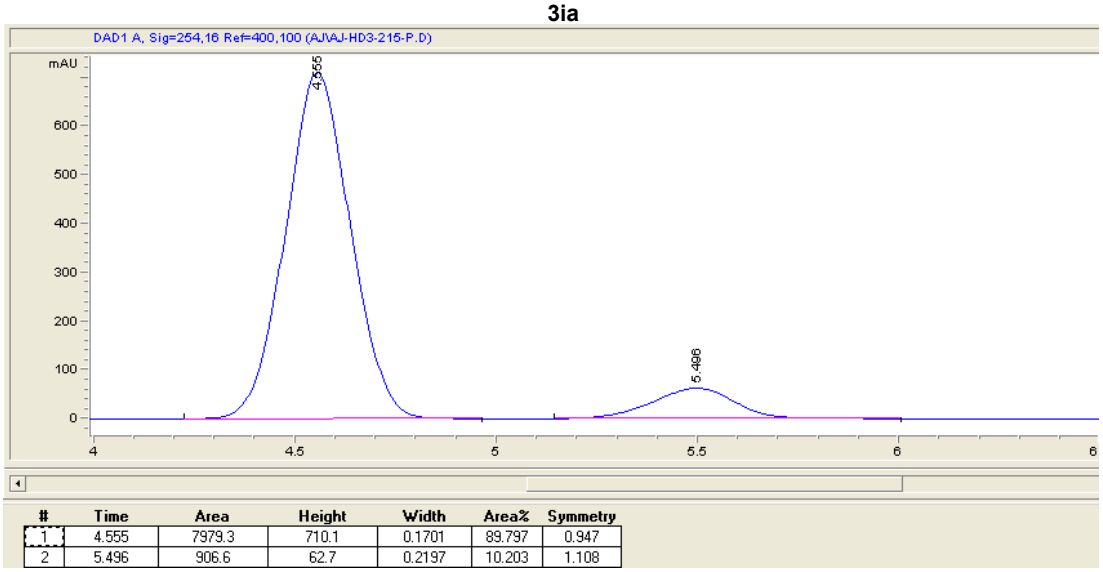
rac-3ia



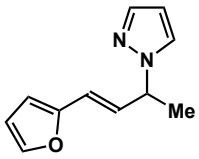
#	Time	Area	Height	Width	Area%	Symmetry
1	4.58	775.3	72.3	0.1788	50.282	1.124
2	5.461	766.5	58.5	0.2183	49.718	1.106



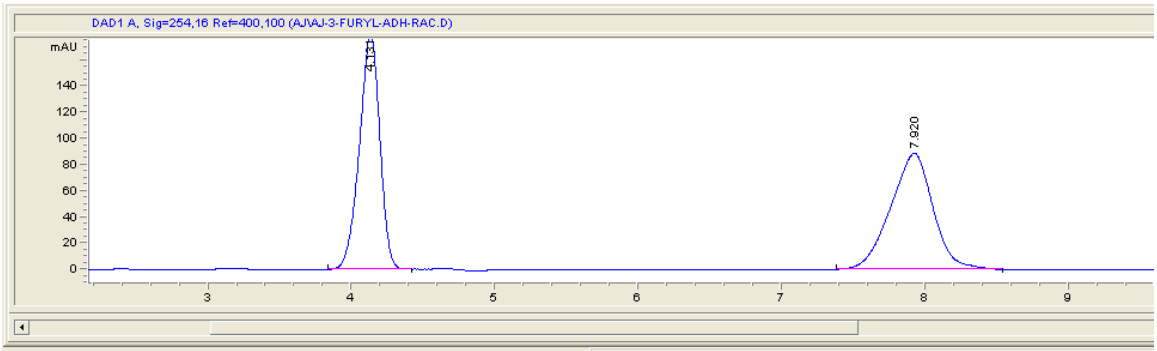
3ia



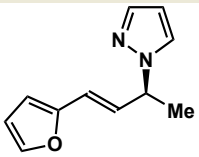
#	Time	Area	Height	Width	Area%	Symmetry
1	4.555	7979.3	710.1	0.1701	89.797	0.947
2	5.496	906.6	62.7	0.2197	10.203	1.108



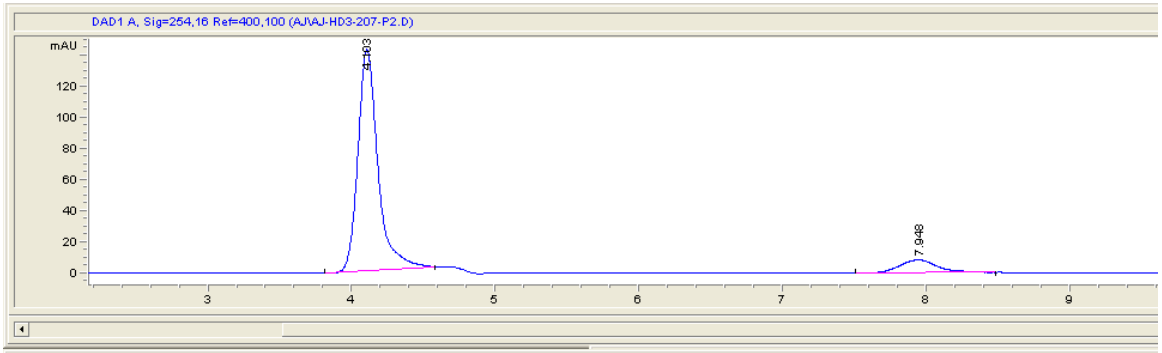
rac-3ja



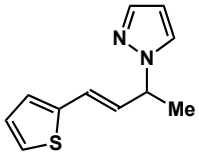
#	Time	Area	Height	Width	Area%	Symmetry
1	4.131	1774.8	179.3	0.1515	49.282	1.181
2	7.92	1826.5	88.7	0.3011	50.718	1.198



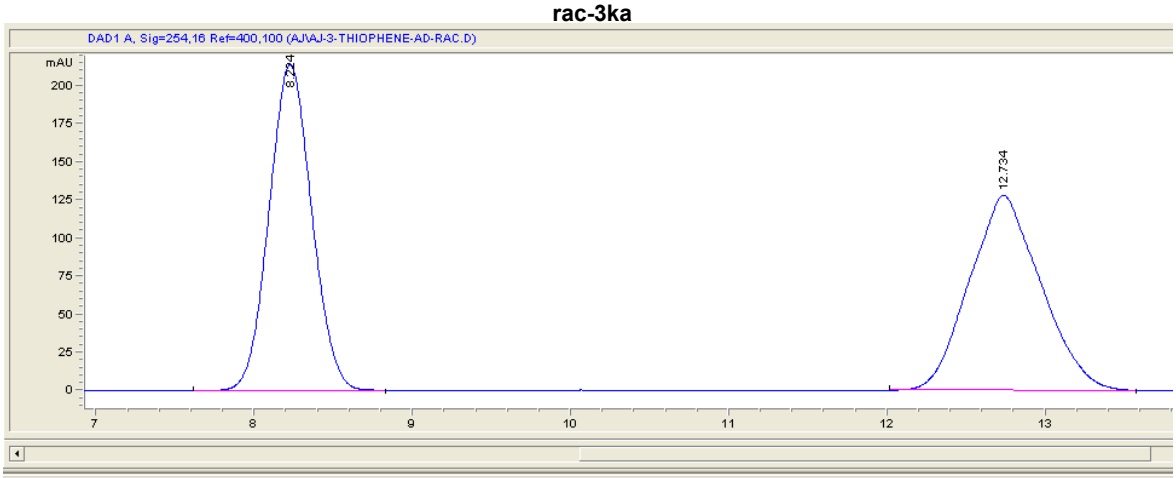
3ja



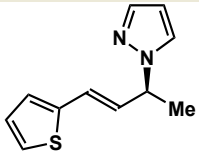
#	Time	Area	Height	Width	Area%	Symmetry
1	4.103	1382.1	142.3	0.1454	89.618	0.746
2	7.948	160.1	8.4	0.2356	10.382	0.963



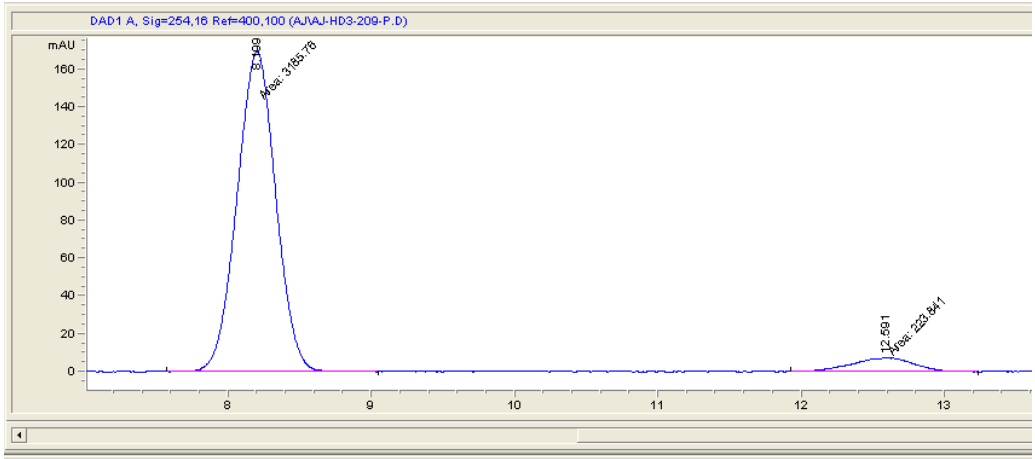
rac-3ka



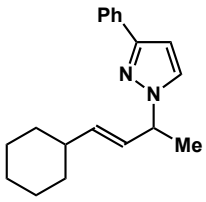
#	Time	Area	Height	Width	Area%	Symmetry
1	8.224	4058.4	214.9	0.2903	50.150	0.941
2	12.734	4034.1	128.3	0.4068	49.850	0.885



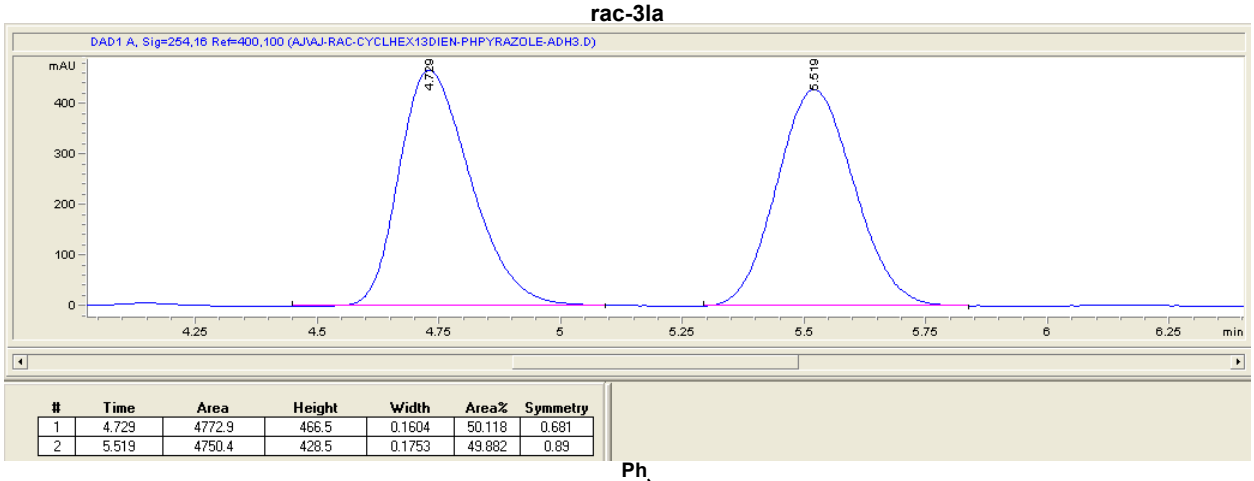
3ka



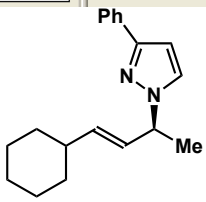
#	Time	Area	Height	Width	Area%	Symmetry
1	8.199	3185.8	169.5	0.3132	93.435	1.03
2	12.591	223.8	7.2	0.5188	6.565	1.31



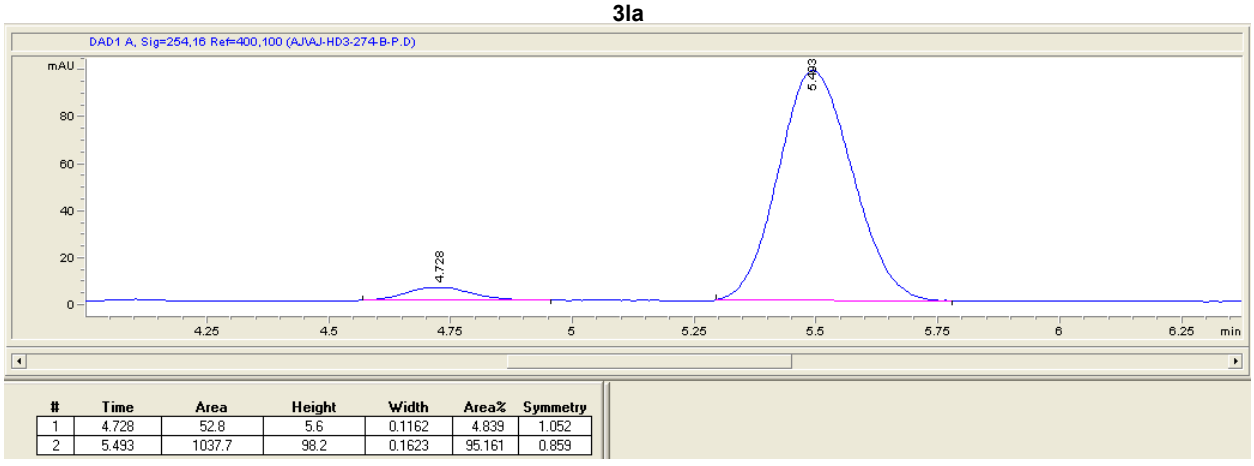
rac-3la



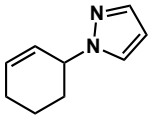
#	Time	Area	Height	Width	Area%	Symmetry
1	4.729	4772.9	466.5	0.1604	50.118	0.681
2	5.519	4750.4	428.5	0.1753	49.882	0.89



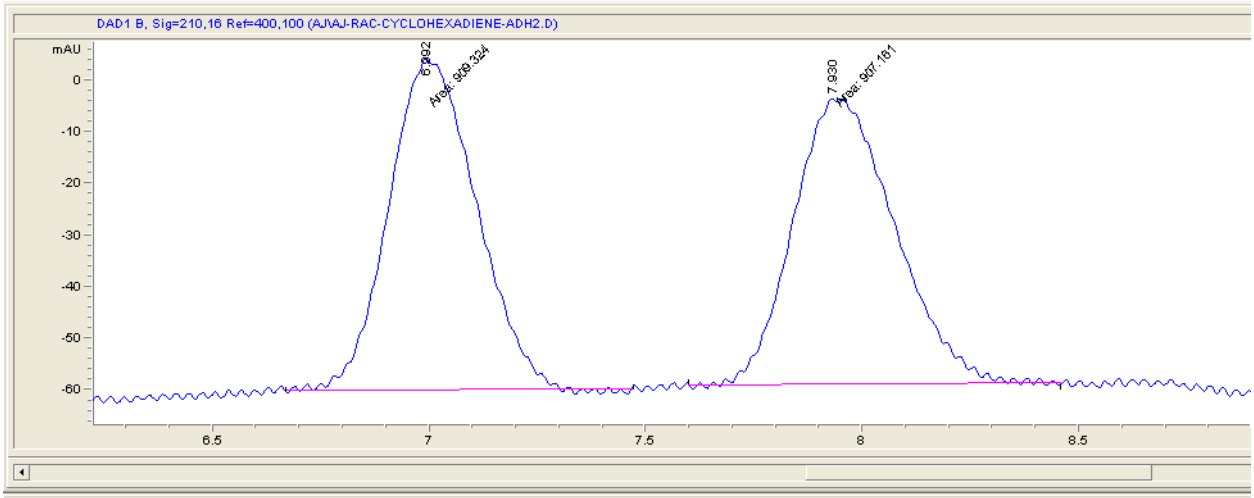
3la



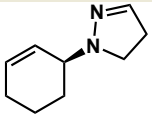
#	Time	Area	Height	Width	Area%	Symmetry
1	4.728	52.8	5.6	0.1162	4.839	1.052
2	5.493	1037.7	98.2	0.1623	95.161	0.859



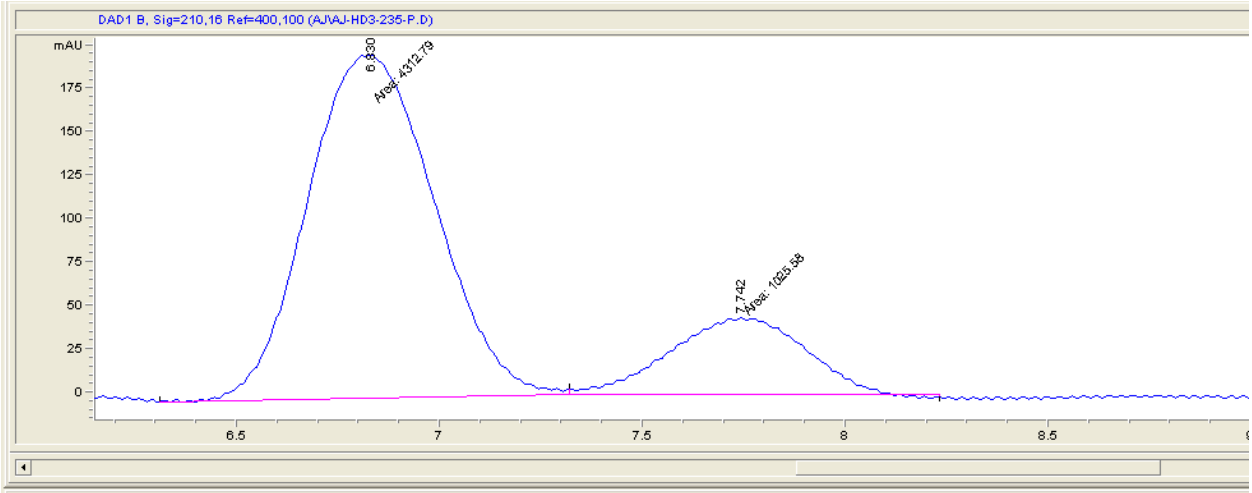
rac-3ma



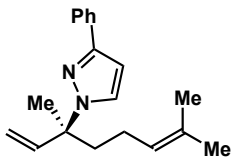
#	Time	Area	Height	Width	Area%	Symmetry
1	6.992	909.3	64.3	0.2356	50.060	0.736
2	7.93	907.2	55.3	0.2732	49.940	0.623



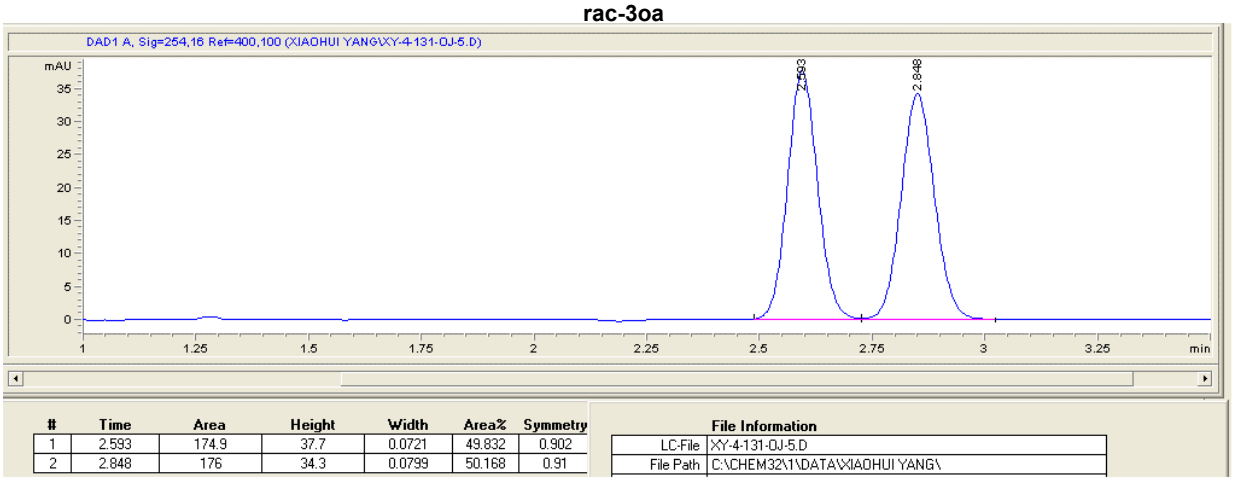
3ma



#	Time	Area	Height	Width	Area%	Symmetry
1	6.83	4312.8	197.9	0.3632	80.789	0.97
2	7.742	1025.6	44.3	0.3858	19.211	1.086



rac-3oa



#	Time	Area	Height	Width	Area%	Symmetry
1	2.593	174.9	37.7	0.0721	49.832	0.902
2	2.848	176	34.3	0.0799	50.168	0.91

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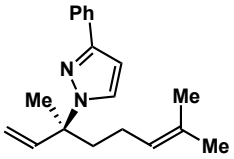
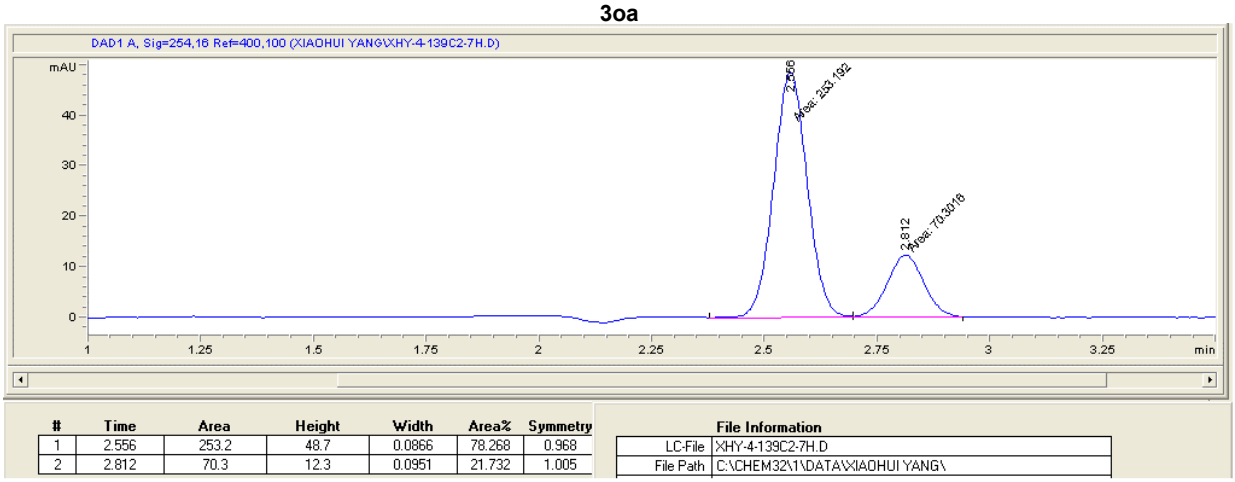


3oa



#	Time	Area	Height	Width	Area%	Symmetry
1	2.556	253.2	48.7	0.0866	78.268	0.968
2	2.812	70.3	12.3	0.0951	21.732	1.005

File Information	
LC-File	XHY-4-139C2-7H.D
File Path	C:\CHEM32\1\DATA\XIAOHUI YANG\

8. References

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