Stereodivergent, Kinetically Controlled Isomerization of Terminal Alkenes via Nickel Catalysis

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General Information

All materials received new from commercial sources were used without further purification, and all materials previously opened or used were filtered through a silica plug and sparged with nitrogen prior to use. The following compounds were purchased from MilliporeSigma: 2-allylphenol, 11-bromo-1-undecene, allyltriphenylsilane, 1,2-epoxy-oct-7-ene, hydrocinnemaldehyde (purified by column before use), nonanal (distilled before use), 4-pentenoic acid, and 1-allylfluorobenzene. The following compound was purchased from Alfa-Aesar: 2-methyl-4-pentenoic acid. The following compounds were purchased from Combi-Blocks: 4-iodobenzotrifluoride, 1-phenyl-4-penten-1-yne, 1-allyl-2-bromobenzene, and 1-phenyl-4-penten-1-yne. The following compounds were purchased from Oakwood: 4-phenyl-1-butene and 3-(3-chlorophenyl)-1-propene. The following compound was purchased from Thermo Fisher Scientific: 11-chloro-1-undecene. The following compounds were purchased from TCI: 8-nonen-1-ol (purified by silica plug before use), 2-allylaniline hydrochloride, 1,4-dihydronaphthalene, and KO*t*Bu (opened and used in an argon-filled glovebox). The following compound was purchased from Indofine Chemical Company: 7-allyloxycoumarine. The following compound was purchased from VWR: PCy_3•HBF_4. The following compounds were purchased from Cambridge Isotopes Laboratory: D_2O, DMF-d_7, and $CDCl_3$. The following compounds were purchased from Strem: Ni($^{4\text{-}t\text{Bu}}$stb)$_3$ and Ni(COD)$_2$. The following compound was purchased from ChemScene: Methyltriphenylphosphonium bromide and was heated to 120 °C under vacuum overnight before use. The free aniline, 2-allylaniline, was prepared by washing 2-allylaniline hydrochloride with a saturated solution of $NaHCO_3$ in using ether as the organic phase. The following compounds were prepared according to literature procedure: 11-fluoroundec-1-ene,[1] 1-allyl-1*H*-indole,[2] (*E*)-hexa-1,5-dien-1-ylbenzene,[3] (*E*)-hepta-1,6-dien-1-ylbenzene,[4] 2-(but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,[5] *N*-phenylpent-4-enamide,[6] 2-(but-3-en-1-yl)pyridine,[7] pent-4-en-1-yl(p-tolyl)sulfane,[8] 1-hexene-6-triphenylphosphonium bromide (dried under high vacuum at 110 °C overnight before use),[9] and [Ni(μ-I)(dppf)]$_2$.[10] Ni(COD)(DQ), Ni(COD)(BQ$^{t\text{Bu}}$), Ni(COD)(BQ$^{\text{Cy}}$), Ni(COD)(TO$^{\text{H}}$), Ni(COD)(TO$^{\text{CF3}}$), Ni(COD)(CPD$^{\text{H}}$), Ni(COD)(CPD$^{\text{OMe}}$), Ni(COD)(CPD$^{\text{CF3}}$), and Ni(COD)(TO$^{\text{A}}$) nickel(0) pre-catalysts were prepared according to literature protocols.[11] Anhydrous solvents were purchased from Fischer Scientific or VWR in extra dry form over molecular sieves. The ^{1}H, ^{13}C, ^{19}F, and ^{31}P spectroscopic data were recorded with Bruker AVIII 400 MHz, Bruker AV NEO 500 MHz, Bruker AV NEO 600, Bruker AV NEO 399 MHz, and JEOL JNM-ECZ400R 400 MHz NMR instruments. Spectra were internally referenced to $SiMe_4$ or residual deuterated solvent signals. The following abbreviations, or combinations thereof, were used to describe multiplicities: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. GC-MS spectra were acquired on an Agilent Technologies 7820A GC System. GCMS data are reported as integer values, as recorded by MS on this instrument. The data for relevant compounds are attached in the spectra section. Preparative Thin-Layer Chromatography (PTLC) plates were acquired from MilliporeSigma as 1,000 micron or 500 micron size particles. Flash column chromatography was performed using silica gel from SILICYCLE in 40–63 micron size particles, or $AgNO_3$ impregnated silica, prepared using 1 g $AgNO_3$ dissolved in CH_3CN (10 mL per 10 g silica) and dried in the oven overnight.

General Procedures

General Procedure 1A: *Z*-selective reaction conditions

In a nitrogen- or argon-filled glovebox, to a 8-mL screw-cap reaction vial equipped with a stir bar, were added $Ni(COD)_2$ (7 mg, 10 mol%), dppf (10 mg, 7.5 mol%), alkene (0.25 mmol, 1 equiv), and 4-iodobenzotrifluoride (34 mg, 0.125 mmol, 0.5 equiv), and DMA (2.5 mL). The reaction vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The reaction was stirred at room temperature overnight. After this time, the mixture was quenched with 1 M HCl (aq.) solution, unless otherwise stated. The reaction mixture was extracted with diethyl ether (2 × 5 mL), and the combined organic layers were washed with brine (3 × 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was analyzed by ^1H NMR using CH_2Br_2 as internal standard. The product was purified by either preparative thin-layer chromatography (PTLC) or by flash column chromatography (silica 2 cm^3, or $AgNO_3$-impregnated silica, 4 cm^3).

General Procedure 1B: *Z*-selective reaction conditions at 55 °C

In a nitrogen- or argon-filled glovebox, to a 8-mL screw-cap reaction vial equipped with a stir bar were added $Ni(COD)_2$ (7 mg, 10 mol%), dppf (10 mg, 7.5 mol%), alkene (0.25 mmol, 1 equiv), 4-iodobenzotrifluoride (34 mg, 0.125 mmol, 0.5 equiv), and DMA (2.5 mL). The reaction vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The reaction was stirred at 55 °C overnight. After this time, the mixture was quenched with 1 M HCl (aq.) solution, unless otherwise stated. The reaction mixture was extracted with diethyl ether (2 × 5 mL) and the combined organic layers were washed with brine (3 × 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was analyzed by ^1H NMR using CH_2Br_2 as internal standard. The product was purified by either preparative thin-layer chromatography (PTLC) or by flash column chromatography (silica 2 mL, or $AgNO_3$ impregnated silica, 4 mL).

General Procedure 2A: *E*-selective reaction conditions

In a nitrogen- or argon-filled glovebox, to a 8-mL screw-cap reaction vial equipped with a stir bar were added $Ni(COD)_2$ (7 mg, 10 mol%), PCy_3•HBF_4 (10 mg, 11 mol%), alkene (0.25 mmol, 1 equiv), and DMF (5 mL). The reaction vial was sealed with a Teflon-lined screw cap and removed from the glovebox. Nitrogen-sparged water (2.2 μL, 0.5 equiv) was added to the reaction mixture via a microsyringe. The reaction was stirred at room temperature overnight. The reaction mixture was extracted with diethyl ether (2 × 5 mL) and the combined organic layers were washed with brine (3 × 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was analyzed by ^1H NMR using CH_2Br_2 as internal standard. The product was purified by either preparative thin-layer chromatography (PTLC) or by flash column chromatography (silica 2 mL, or $AgNO_3$ impregnated silica, 4 mL).

General Procedure 2B: *E*-selective reaction conditions for isomerization to a conjugated position

In a nitrogen- or argon-filled glovebox, to a 8 mL screw-cap reaction vial equipped with a stir bar were added $Ni(COD)_2$ (7 mg, 10 mol%), PCy_3•HBF_4 (10 mg, 11 mol%), TBABr (40 mg, 0.5 equiv), alkene (0.25 mmol, 1 equiv) and DMF (5 mL). The reaction vial was sealed with a Teflon-lined screw cap and removed from the glovebox. Nitrogen-sparged water (2.2 μL, 0.5 equiv) was added to the reaction mixture via a microsyringe. The reaction was stirred at room temperature overnight. After this time, the mixture was quenched with 1 M HCl (aq.) solution, unless otherwise stated. The reaction mixture was extracted with

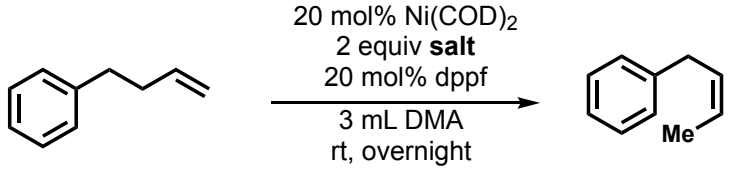
diethyl ether (2 × 5 mL) and the combined organic layers were washed with brine (3 × 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was analyzed by ^1H NMR using CH_2Br_2 as internal standard. The product was purified by either preparative thin-layer chromatography (PTLC) or by flash column chromatography (silica 2 mL, or $AgNO_3$ impregnated silica, 4 mL).

Reaction Optimization

All optimization experiments were run on a 0.15 mmol scale of the alkene according to General Procedures 1A or 2A for *Z*-selective or *E*-selective alkene products, respectively, unless otherwise stated. Deviations from the standard protocols are stated in the schemes and tables below (Tables S1–S15).

Optimization of *Z*-selective conditions

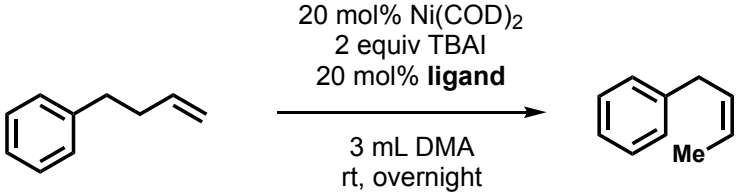
Table S1: Salt screen for *Z*-selective conditions[a]



Entry	Salt	Yield (%)[b]	*Z*:*E* ratio
1	TBACl	74	75:25
2	TBABr	68	83:17
3	TBAI	62	91:9
4	$ZnBr_2$	49	83:17
5	LiCl	36	70:30
6	MgI_2	83	88:12
7	KI	20	88:12
8	NaI	33	87:13
9	I_2	0	-
10	$MgCl_2$	80	50:50

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^1H NMR analysis using CH_2Br_2 as internal standard.

Table S2: Ligand screen for *Z*-selective conditions[a]

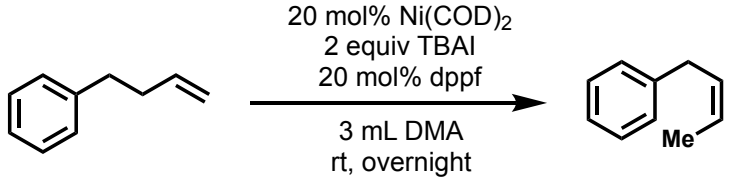


Entry	Ligand	Yield (%)[b]	*Z*:*E* ratio
1	$PCy_3 \bullet HBF_4$	0	-
2	$P(tBu)_3 \bullet HBF_4$	90	83:17
3	PPh_3	12	66:44
4	DPPB	71	88:12
5	BINAP	0	-
6	CPhos	0	-
7	DCYPE	45	91:9
8	DPPF	20	89:11

9	Xantphos	45	35:65
10	None	0	-
11	1,1-bis(dicyclohexylphosphino)ferrocene	0	-
12	1,1-bis(diisopropylphosphino)ferrocene	0	-

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

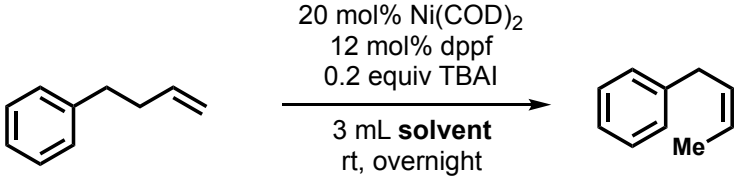
Table S3: Screen of relative equivalence of catalyst, additive, *etc.* for *Z*-selective conditions[a]



Entry	Deviation from above	Yield (%)[b]	*Z*:*E* ratio
1	10 mol% Ni, 10 mol% dppf	30	21:79
2	1.5 mL DMA	15	64:44
3	10 mol% dppf	-	-
4	1 equiv TBAI	74	88:12
5	0.75 equiv TBAI	83	79:21
6	0.2 equiv TBAI	68	86:14
7	0.1 equiv TBAI	60	70:30
8	10 mol% dppf, 10 mol% $Ni(COD)_2$, 10 mol% TBAI	20	60:40
9	5 mol% dppf, 5 mol% $Ni(COD)_2$, 5 mol% TBAI	-	-
10	50 °C	13	-

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

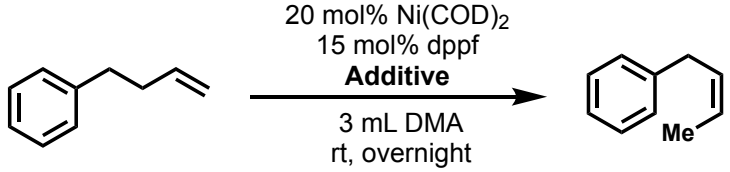
Table S4: Solvent screen for *Z*-selective conditions[a]



Entry	Solvent	Yield (%)[b]	*Z*:*E* ratio
1	THF	30	21:79
2	Toluene	15	64:44
3	DMA with molecular sieves	53	85:15
4	NMP	60	70:30
5	MeCN	20	60:40

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

Table S5: Screening of aryl iodide additives in *Z*-selective conditions[a]

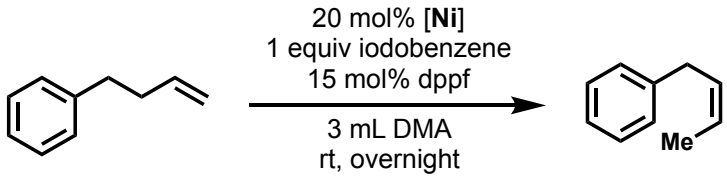


Entry	Additive	Yield (%)[b]	*Z*:*E* ratio
1	0.2 equiv TBAI + 0.2 equiv iodobenzene	68	73:27
2	1 equiv iodobenzene	80	83:17

2	1 equiv 4-methoxyiodobenzene	68	73:27
3	1 equiv 4-cyanoiodobenzene	18	100:0
4	1 equiv 4-nitroiodobenzene	12	100:0
5	1 equiv 4-methylester iodobenzene	55	95:5
6	1 equiv 2-methyliodobenzene	74	76:24
7	1 equiv 4-iodobenzotrifluoride	74	92:8

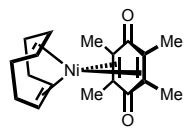
[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

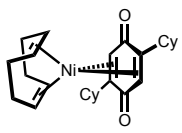
Table S6: Screening of Ni(0) precatalysts for *Z*-selective conditions[a]
For Ni(0) precatalyst synthesis see General Information.[11]

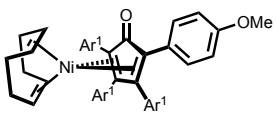


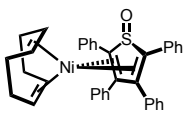
Entry	[Ni]	Yield (%)[b]	*Z*:*E* ratio
1	Ni(COD)(DQ)	-	-
2	Ni(COD)(BQ^{tBu})	30	100:0
3	Ni(COD)(BQ^{Cy})	-	-
4	Ni(COD)(TO^{H})	-	-
5	Ni(COD)(TO^{CF3})	77	90:10
6	Ni(COD)(TO^{CF3}) with 1 equiv *p*-$F_3CC_6H_4I$ instead of iodobenzene	72	96:4
7	Ni(COD)(CPD^{H})	-	-
8	Ni(COD)(CPD^{OMe})	-	-
9	Ni(COD)(CPD^{CF3})	-	-
10	Ni(COD)(TO^{A})	-	-
11	Ni($^{4\text{-}tBu}$stb)$_3$	13	17:83

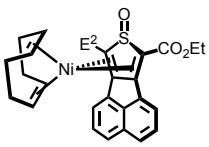
[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

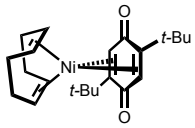

Ni(COD)(DQ)

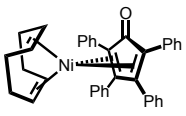

Ni(COD)(BQ^{Cy})

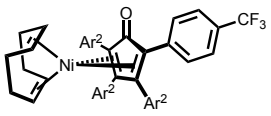

Ni(COD)(CPD^{OMe})

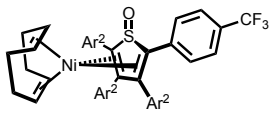

Ni(COD)(TO^{H})


Ni(COD)(TO^{A})


Ni(COD)(BQ^{tBu})


Ni(COD)(CPD^{H})


Ni(COD)(CPD^{CF3})


Ni(COD)(TO^{CF3})

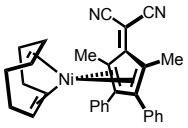
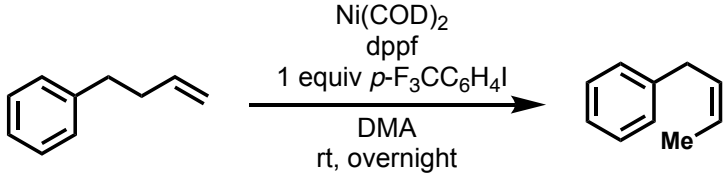

Ni(COD)(FV^{CN})

Table S7: Catalyst loading and concentration screen for *Z*-selective conditions[a]

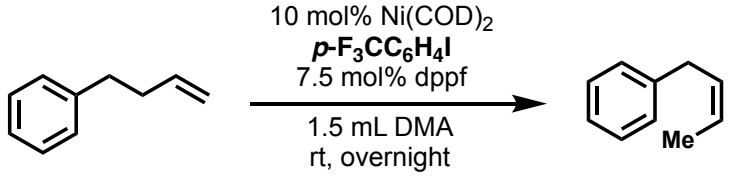


Entry	Ni(COD)$_2$ (mol%)	dppf (mol%)	DMA (mL)	Yield (%)[a]	*Z*:*E* ratio

1	20	15	3	76	93:7
2	10	7.5	1.5	79	94:6
3	5	3.75	0.75	74	93:7

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

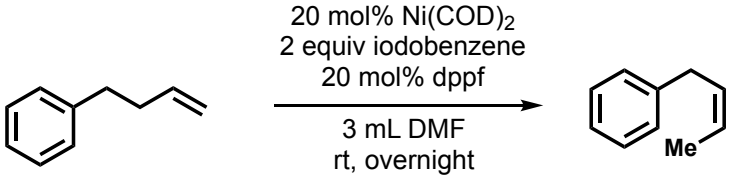
Table S8: Screening of *p*-$F_3CC_6H_4I$ equivalents for *Z*-selective conditions[a]



Entry	*p*-$F_3CC_6H_4I$ (equiv)	Yield (%)[b]	*Z*:*E* ratio
1	0.5	83	93:7
2	0.25	79	93:7
3	0.1	75	88:12

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

Table S9: Control experiments for *Z*-selective conditions[a]

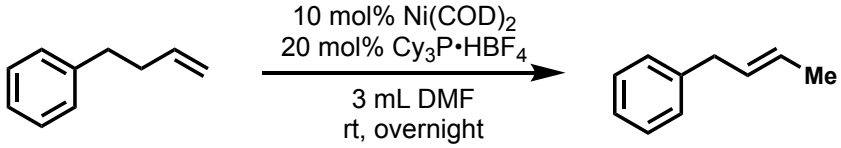


Entry	Deviation from above	Yield (%)[b]	*Z*:*E* ratio
1	1 equiv water	30	-
2	Without Ni	0	-
3	In the dark	64	90:10

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

Optimization of *E*-selective conditions

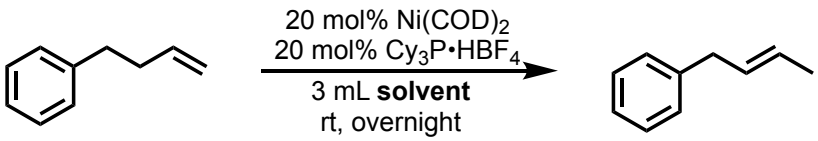
Table S10: General screening for *E*-selective conditions[a]



Entry	Deviation from above	Yield (%)[b]	*Z*:*E* ratio
1	none	96	18:82
2	50 °C	68	19:81
3	10 mol% [P] + 5 mol% [Ni]	53	16:84
4	1.5 mL DMF	56	16:84
5	10 mol% [P] + 10 mol% [Ni]	17	21:79

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

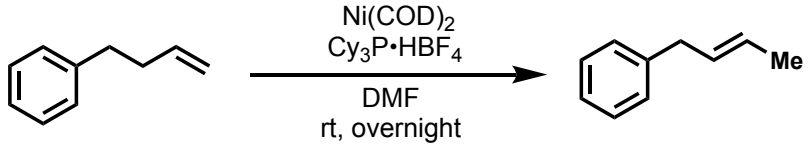
Table S11: Solvent screen for *E*-selective conditions[a]



Entry	Solvent	Yield (%)[b]	*Z*:*E* ratio
1	DMF	100	18:82
2	DMSO	33	30:70
3	MeCN	70	29:71
4	NMP	100	25:75
5	toluene	68	40:60
6	THF	17	25:75

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

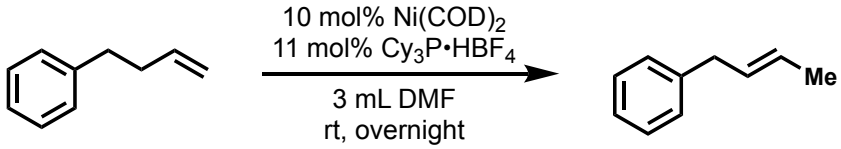
Table S12: Screening of catalyst loading and concentration for *E*-selective conditions[a]



Entry	$Ni(COD)_2$ (mol%)	Cy_3PHBF_4 (mol%)	DMF (mL)	Yield (%)[b]	*Z*:*E* ratio
1	10	10	3	96	18:82
2	5	5	1.5	48	19:81
3	2.5	2.5	0.75	17	20:80

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

Table S13: Screening of ligand component for *E*-selective conditions[a]

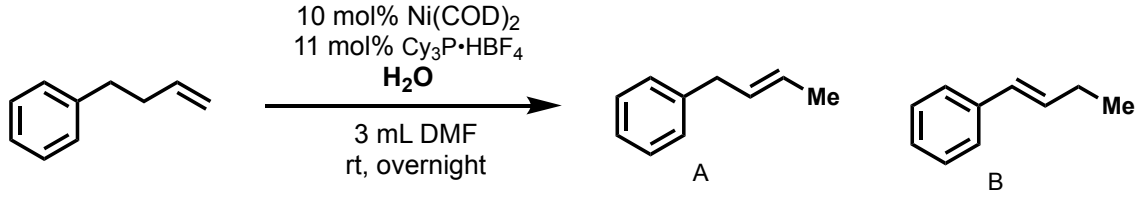


Entry	Deviations from above	Yield (%)[b]	*Z*:*E* ratio
1	Stir 10 min before alkene addition	71	17:83
2	10 mol% PCy_3 instead of PCy_3•HBF_4	-	-
3	10 mol% NH_4BH_4 instead of PCy_3•HBF_4	-	-
4	10 mol% $TBABF_4$ instead of PCy_3•HBF_4	-	-
5	10 mol% PCy_3 + 10 mol% $TBABF_4$ instead of PCy_3•HBF_4	-	-
6	Addition of 11 equiv Et_3N	58	17:83

[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

Table S14: Screening of water addition to *E*-selective conditions[a]

During our optimization experiments, we changed bottles of PCy_3•HBF_4. The original bottle was used outside the glovebox, and the new bottle was opened and used inside the glovebox. After switching to a new bottle, we observed significantly more of the chain walking isomerization product. This prompted us to evaluate whether water that was trapped by the hygroscopic salt was increasing the regioselectivity of the reaction. The following equivalents of degassed water were added to the reaction mixture using the new dry PCy_3•HBF_4.

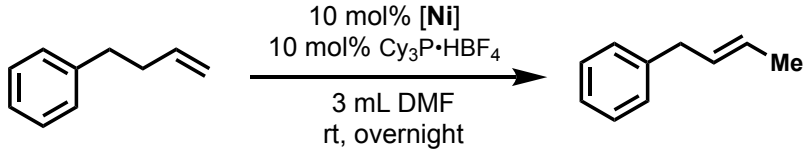


Entry	Equiv H_2O	Yield A (%)[b]	Yield B (%)[b]	*Z*:*E* ratio

1	None	83	17	17:83
2	0.5	88	6	17:83
3	1.0	83	<5	19:81
5	1.5	29	5	21:79

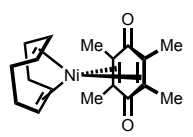
[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

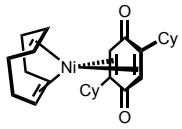
Table S15: Screening of Ni(0) precatalysts for *E*-selective conditions[a]
For Ni(0) precatalyst synthesis see General Information.[11]

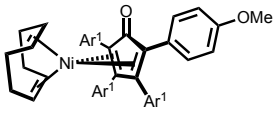


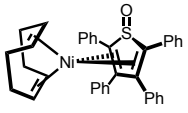
Entry	[Ni]	Yield (%)[b]	*Z*:*E* ratio
1	Ni(COD)(DQ)	-	-
2	Ni(COD)(BQ$^{t\text{Bu}}$)	-	-
3	Ni(COD)(BQ$^{\text{Cy}}$)	-	-
4	Ni(COD)(TO$^{\text{H}}$)	-	-
5	Ni(COD)(TO$^{\text{CF3}}$)	-	-
6	Ni(COD)(CPD$^{\text{H}}$)	-	-
7	Ni(COD)(CPD$^{\text{OMe}}$)	-	-
8	Ni(COD)(CPD$^{\text{CF3}}$)	-	-
9	Ni(COD)(TO$^{\text{A}}$)	-	-
10	Ni($^{4\text{-}t\text{Bu}}$stb)$_3$	69	20:80

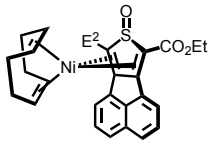
[a] Reactions performed on 0.15 mmol scale of alkene. [b] Yields determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

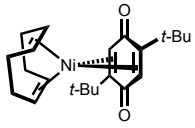

Ni(COD)(DQ)

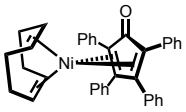

Ni(COD)(BQ$^{\text{Cy}}$)

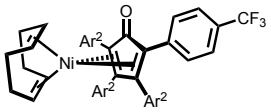

Ni(COD)(CPD$^{\text{OMe}}$)

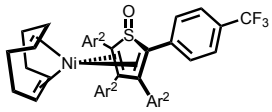

Ni(COD)(TO$^{\text{H}}$)

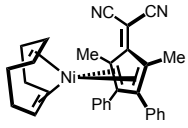

Ni(COD)(TO$^{\text{A}}$)


Ni(COD)(BQ$^{t\text{Bu}}$)


Ni(COD)(CPD$^{\text{H}}$)

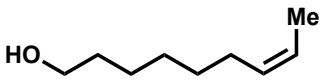

Ni(COD)(CPD$^{\text{CF3}}$)


Ni(COD)(TO$^{\text{CF3}}$)


Ni(COD)(FV$^{\text{CN}}$)

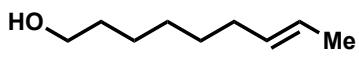
Characterization of Products

(*Z*)-Non-7-en-1-ol **2*Z***



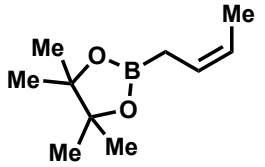
The title compound was prepared according to General Procedure 1A, employing non-8-en-1-ol (36 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 93% yield with unclear *Z*:*E* ratio. Column chromatography (silica, hexane to 20% diethyl ether in hexane) afforded the title compound as a colorless oil, containing 7% starting material that could not be separated (34 mg, 87% corrected yield, 94:6 *Z*:*E*). The spectroscopic data correspond to reported data from the literature.[12]

(*E*)-Non-7-en-1-ol **2*E***



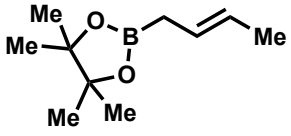
The title compound was prepared according to General Procedure 2A, employing non-8-en-1-ol (36 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 91% yield, 21:79 *Z*:*E* ratio. Column chromatography (silica, hexane to 20% diethyl ether in hexane) afforded the title compound as a colorless oil (31 mg, 84% yield, 20:80 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[12]

(*Z*)-2-(But-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3*Z***



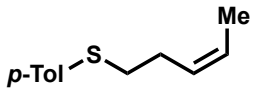
The title compound was prepared according to General Procedure 1A, employing 2-(but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (46 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 82% yield, 11:89 *Z*:*E* ratio. Column chromatography ($AgNO_3$ impregnated silica, hexane to 20% diethyl ether in hexane) afforded the title compound as a colorless oil containing 23% starting material that could not be separated (42 mg, 70% corrected yield, 13:87 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[13]

(*E*)-2-(But-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3*E***



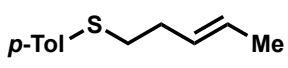
The title compound was prepared according to General Procedure 2A, employing 2-(but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (46 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 49% yield, 19:89 *Z*:*E* ratio. Column chromatography (silica, pentane to 20% diethyl ether in pentane) afforded the title compound as a colorless oil containing 19% starting material and 4% overisomerized alkene that could not be separated (29 mg, 48% corrected yield, 15:85 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[13]

(*Z*)-Pent-3-en-1-yl(*p*-tolyl)sulfane **4*Z***



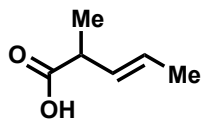
The title compound was prepared according to General Procedure 1A, employing pent-4-en-1-yl(*p*-tolyl)sulfane (48 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 95% yield, 82:18 *Z*:*E* ratio. PTLC (silica, hexane) afforded the title product as a colorless oil containing 20% starting material that could not be separated (46 mg, 76% corrected yield, 86:14 *Z*:*E*). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.23 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.59–5.51 (m, 1H), 5.46–5.39 (m, 1H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.39–2.33 (m, 2H), 2.32 (d, *J* = 1.8 Hz, 3H), 1.59 (ddt, *J* = 6.7, 1.8, 0.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 130.0, 130.00, 129.6, 129.6, 128.1, 125.8, 34.2, 26.8, 21.0, 12.9. HRMS calculated for $[C_{12}H_{17}S]^+$ 193.1051, found 193.1051.

(*E*)-Pent-3-en-1-yl(*p*-tolyl)sulfane **4*E***



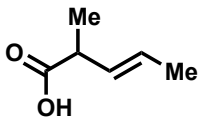
The title compound was prepared according to General Procedure 2A, employing pent-4-en-1-yl(*p*-tolyl)sulfane (48 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 100% yield, 21:79, *Z*:*E* ratio. PTLC (silica, hexane) afforded the title product as a colorless oil (43 mg, 90%, yield 21:79 *Z*:*E*). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2 Hz, 2H), 7.10–7.07 (m, 2H), 5.59–5.33 (m, 2H), 2.88 (td, *J* = 7.6, 4.7 Hz, 2H), 2.30 (d, *J* = 2.2 Hz, 3H), 2.29–2.22 (m, 2H), 1.68–1.61 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.0, 132.9, 130.0, 129.6, 129.1, 126.8, 34.4, 32.5, 21.0, 17.9. HRMS calculated for $[C_{12}H_{17}S]^+$ 193.1051, found 193.1049.

(*E*)-2-Methylpent-3-enoic acid **5*E***



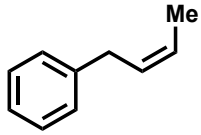
The title compound was prepared according to General Procedure 1A, employing 2-methylpent-4-enoic acid (29 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 64% yield, 18:82 *Z*:*E* ratio. Column chromatography (silica, 10% diethyl ether in hexane to 40% diethyl ether in hexane) afforded the title compound as a pale-yellow oil containing 9% starting material and 7% overisomerized alkene that could not be separated (20 mg, 59% corrected yield, 17:83 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[14]

(*E*)-2-Methylpent-3-enoic acid **5*E***



The title compound was prepared according to General Procedure 2A, employing 2-methylpent-4-enoic acid (29 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 69% yield, 18:82 *Z*:*E* ratio. Column chromatography (silica, 10% diethyl ether in hexane to 40% diethyl ether in hexane) afforded the title compound as a colorless oil containing 4% starting material that could not be separated (26 mg, 75% corrected yield, 14:86 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[14]

(*Z*)-But-2-en-1-ylbenzene **1Z**

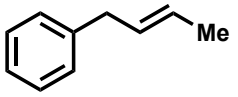


The title compound was prepared according to General Procedure 1A, employing but-3-en-1-ylbenzene (33 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 91% yield, 93:7 *Z*:*E* ratio. Column chromatography ($AgNO_3$ impregnated silica, pentane) afforded the title product as a colorless oil containing 11% of starting material that could not be separated (27 mg, 73% corrected yield, >95:5 *Z*:*E*).

0.250 mmol scale: In a nitrogen- or argon-filled glovebox to a 40-mL screw-cap reaction vial equipped with a stir bar were added $Ni(COD)_2$ (69 mg, 10 mol%), dppf (104 mg, 7.5 mol%), but-3-en-1-ylbenzene (330 mg, 2.5 mmol, 1 equiv), 4-iodobenzotrifluoride (340 mg, 1.25 mmol), and DMA (25 mL). The reaction vial was sealed with a screw cap and stirred at room temperature in the glovebox overnight. The reaction was removed from the glovebox, and the mixture was diluted with diethyl ether and quenched with 1 M HCl (aq.) solution. The organic layer was separated, and the aqueous phase extracted with diethyl ether (2 × 10 mL). The organic phases were combined and washed with brine (3 × 20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Column chromatography ($AgNO_3$ impregnated silica, pentane)

afforded the title compound as a colorless oil (245 mg, 74% yield, 93:7 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[15]

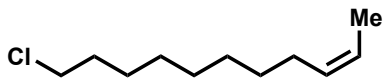
(*E*)-But-2-en-1-ylbenzene **1*E***



The title compound was prepared according to General Procedure 2A, employing but-3-en-1-ylbenzene (33 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 86% yield, 17:83 *Z*:*E* ratio. Column chromatography (silica, pentane) afforded the title product as a colorless oil containing 7% of overisomerized alkene that could not be separated (28 mg, 79% corrected yield, 15:85 *Z*:*E*).

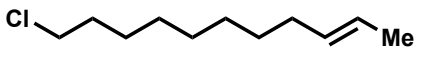
0.25 mmol Scale: In nitrogen-filled glovebox, to a 50-mL round-bottomed flask equipped with a stir bar were added $Ni(COD)_2$ (69 mg, 10 mol%), PCy_3•HBF_4 (101 mg, 11 mol%), but-3-en-1-ylbenzene (330 mg, 2.5 mmol, 1 equiv), and DMF (20 mL). The flask was sealed with a septum and parafilm. The reaction was removed from the glovebox, and nitrogen sparged water (22 μL, 0.5 equiv) was added under a nitrogen atmosphere. The reaction mixture was transferred back into the nitrogen-filled glovebox and stirred overnight at room temperature. After this time, the reaction was removed from the glovebox, and the mixture was diluted with diethyl ether and quenched with 1 M HCl (aq.) solution. The organic layer was separated, and the aqueous phase extracted with diethyl ether (2 × 10 mL). The organic phases were combined and washed with brine (3 × 20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Column chromatography (silica, pentane) afforded the product as a colorless oil (311 mg, 94% yield, 15:85 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[15]

(*Z*)-11-Chloroundec-2-ene **6*Z***



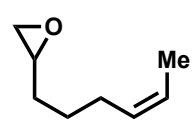
The title compound was prepared according to General Procedure 1A, employing 11-chloroundec-1-ene (47 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 94% yield, 94:6 *Z*:*E* ratio. Column chromatography ($AgNO_3$ impregnated silica, pentane) afforded the title compound as a colorless oil (42 mg, 89% yield, >95:5 *Z*:*E*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48–5.33 (m, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 2.05–2.00 (m, 2H), 1.81–1.73 (m, 2H), 1.60 (d, J = 6.3 Hz, 3H), 1.47–1.28 (m, 10H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 130.9, 123.8, 45.3, 32.8, 29.6, 29.5, 29.3, 29.0, 27.0, 26.9, 12.9. GCMS calculated for [$C_{11}H_{21}Cl$] 188, found 188.

(*E*)-11-Chloroundec-2-ene **6*E***



The title compound was prepared according to General Procedure 2A, employing 11-chloroundec-1-ene (47 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 98% yield, 20:80 *Z*:*E* ratio. PTLC (hexane) afforded the title compound as a colorless oil (40 mg, 85% yield, 21:79 *Z*:*E*). The spectroscopic data correspond to reported data from literature. [16]

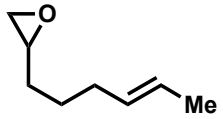
(*Z*)-2-(Hex-4-en-1-yl)oxirane **7*Z***



The title compound was prepared according to General Procedure 1A, employing 2-(hex-5-en-1-yl)oxirane (32 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 81% yield, with unclear *Z*:*E* ratio. Column chromatography ($AgNO_3$ impregnated silica, pentane to 20% E_2O in pentane) afforded the product as a colorless oil containing 12% starting material that could not be separated (22 mg, 60% corrected yield, 91:9 *Z*:*E*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50–5.34 (m, 2H), 2.93–2.90 (m, 1H), 2.76–2.74 (m,

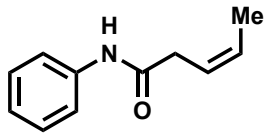
1H), 2.47 (dd, 1H), 2.13–2.05 (m, 2H), 1.62–1.58 (m, 3H), 1.58–1.48 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 130.1, 124.5, 52.4, 47.3, 32.2, 26.8, 26.0, 12.9. GCMS calculated for [$C_8H_{14}O$] 126, found 126.

(*E*)-2-(Hex-4-en-1-yl)oxirane **7*E***



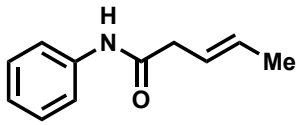
The title compound was prepared according to General Procedure 2A, employing 2-(hex-5-en-1-yl)oxirane (32 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 44% yield with unclear *Z*:*E* ratio. Column chromatography (silica, pentane to 20% E_2O in pentane) afforded the product as a colorless oil containing 38% starting material that could not be separated (25 mg, 48% corrected yield, 23:77 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[16]

(*Z*)-*N*-Phenylpent-3-enamide **8*Z***



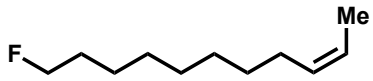
The title compound was prepared according to General Procedure 1A, employing *N*-phenylpent-4-enamide (44 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 92% yield, 78:22 *Z*:*E* ratio. Column chromatography (silica, hexane to 50% diethyl ether in hexane) afforded the title compound as a colorless solid (42 mg, 94% yield, 78:22 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[17]

(*E*)-*N*-Phenylpent-3-enamide **8*E***



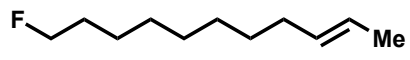
The title compound was prepared according to General Procedure 2A, employing *N*-phenylpent-4-enamide (44 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 93% yield, 21:79 *Z*:*E* ratio. Column chromatography (silica, hexane to 50% diethyl ether in hexane) afforded the title compound as a colorless solid (34 mg, 77% yield, 22:78 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[17]

(*Z*)-11-Fluoroundec-2-ene **9*Z***



The title compound was prepared according to General Procedure 1A, employing 11-fluoroundec-1-ene (47 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 89% yield, 94:6 *Z*:*E* ratio. Column chromatography ($AgNO_3$ impregnated silica, pentane) afforded the title compound as a colorless oil containing 14% starting material that could not be separated (24 mg, 56% corrected yield, >95:5 *Z*:*E*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47–5.33 (m, 2H), 4.44 (dt, *J* = 47.4, 6.2 Hz, 2H), 2.03 (q, *J* = 6.9 Hz, 2H), 1.74–1.64 (m, 2H), 1.60 (d, *J* = 6.34 Hz, 3H), 1.41–1.26 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) 131.0, 125.1, 84.4 (d, *J* = 163.9 Hz), 30. 6 (d, *J* = 19.2 Hz), 29.7, 29.6, 29.4, 29.3, 27.0, 25.3 (d, *J* = 5.4 Hz), 12.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -220.66. GCMS calculated for [$C_{11}H_{21}F$] 172, found 172.

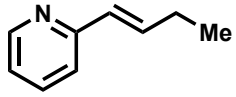
(*E*)-11-Fluoroundec-2-ene **9*E***



The title compound was prepared according to General Procedure 2A employing 11-fluorundec-1-ene (43 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 92% yield, 22:78 *Z*:*E* ratio. Column chromatography (silica, pentane) afforded the title compound as a colorless oil (29 mg, 67% yield, 19:81 *Z*:*E*).^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46–5.37 (m, 2H), 4.43 (dt, *J* = 47.4, 6.2 Hz, 2H). 2.00 (m, 2H), 1.74–1.66 (m, 2H), 1.66–1.63 (m, 3H), 1.42–1.26 (m, 10H). ^{13}C NMR (126 MHz,

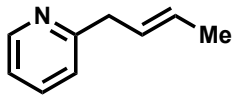
$CDCl_3$) δ 131.7, 125.3, 84.4 (d, *J* = 164.0 Hz), 32.7, 30.6 (d, *J* = 19.2 Hz), 29.7, 29.5, 29.4, 29.2, 25.3 (d, *J* = 5.7 Hz), 18.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -220.7. GCMS calculated for [$C_{11}H_{21}F$] 172, found 172.

(*E*)-2-(But-3-en-1-yl)pyridine **10*Z***



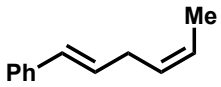
The title compound was prepared according to General Procedure 1A, employing 2-(but-3-en-1-yl)pyridine (33 mg, 1 equiv). Column chromatography (silica, hexane to 20% diethyl ether in hexane) afforded the title product as a colorless oil (20 mg, 60% yield, <5:95 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[18]

(*E*)-2-(But-2-en-1-yl)pyridine **10*E***



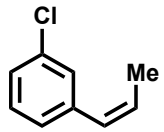
The title compound was prepared according to General Procedure 2A, employing 2-(but-3-en-1-yl)pyridine (33 mg, 1 equiv). Column chromatography (silica, hexane to 20% diethyl ether in hexane) afforded the title product as a colorless oil containing 32% starting material that could not be separated (18 mg, 36% corrected yield, 21:79 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[19]

((*1E,4Z*)-Hexa-1,4-dien-1-yl)benzene **11Z**



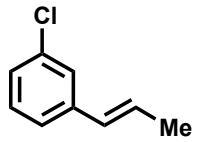
The title compound was prepared according to General Procedure 1A, employing (*E*)-hexa-1,5-dien-1-ylbenzene (40 mg, 1 equiv). The crude reaction mixture was analyzed by ^1H NMR and contained the desired product in 47% yield with unclear *Z*:*E* ratio. PTLC (silica, hexane) afforded the title product as a colorless oil containing 16% starting material that could not be separated (25 mg, 46% corrected yield, 89:11 *Z*:*E*) The spectroscopic data correspond to reported data from literature.[20]

(*Z*)-1-Chloro-3-(prop-1-en-1-yl)benzene **12*Z***



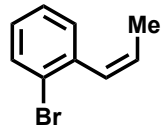
The title compound was prepared according to General Procedure 1A, employing 1-allyl-3-chlorobenzene (38 mg, 1 equiv). The crude reaction mixture was analyzed by ^1H NMR and contained the desired product in 85% yield, 93:7 *Z*:*E* ratio. The spectroscopic data correspond to reported data from literature.[21]

(*E*)-1-Chloro-3-(prop-1-en-1-yl)benzene **12*E***



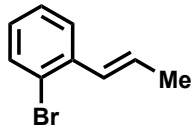
The title compound was prepared according to General Procedure 2B, employing 1-allyl-3-chlorobenzene (38 mg, 1 equiv). The crude reaction mixture was analyzed by ^1H NMR and contained the desired product in 47% yield, <5:95 *Z*:*E* ratio. PTLC ($AgNO_3$ impregnated silica, hexane) afforded the title product as a colorless oil (29 mg, 59% yield, <5:95 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[22]

(*Z*)-1-Bromo-2-(prop-1-en-1-yl)benzene **13*Z***



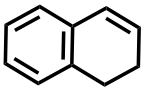
The title compound was prepared according to General Procedure 1A, employing 1-allyl-2-bromobenzene (49 mg, 1 equiv). The crude reaction mixture was analyzed by ^1H NMR and contained the desired product in 64% yield, 78:22 *Z*:*E* ratio. Column chromatography ($AgNO_3$ impregnated silica, pentane) afforded the title product as a clear oil (12 mg, 25% yield, 82:18 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[23]

(*E*)-1-Bromo-2-(prop-1-en-1-yl)benzene **13*E***



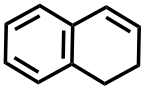
The title compound was prepared according to General Procedure 2B, employing 1-allyl-2-bromobenzene (49 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 42% yield, 8:92 *Z*:*E* ratio. Column chromatography (silica, pentane) afforded the title product as a clear oil containing 84% of starting material that could not be separated (38 mg, 12% corrected yield, 13:87 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[23]

1,2-Dihydronaphthalene **14*Z***



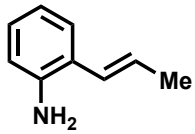
The title compound was prepared according to General Procedure 1A, employing 1,4-dihydronaphthalene (33 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 80% yield. PTLC (silica, hexane) afforded the title product as a colorless oil (13 mg, 39% yield). The spectroscopic data correspond to reported data from literature.[24]

1,2-Dihydronaphthalene **14*Z***



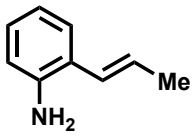
The title compound was prepared according to General Procedure 2A, employing 1,4-dihydronaphthalene (33 mg, 1 equiv). Column chromatography (silica, hexane) afforded the title product as a colorless oil containing 50% yield of starting material that could not be separated (16 mg, 24% corrected yield). The spectroscopic data correspond to reported data from literature.[24]

(*E*)-2-(Prop-1-en-1-yl)aniline **15*E***



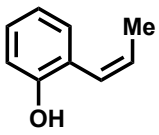
The title compound was prepared according to General Procedure 1A, employing 2-allylaniline (33 mg, 1 equiv). After end reaction, the mixture was quenched with 1 M HCl and the aqueous layer was washed three times with 5 mL diethyl ether. Then, $NaCO_3$ was slowly added to the aqueous layer until bubbles stopped forming. At this point, the desired product was extracted from the slightly basic aqueous layer three times with 7 mL diethyl ether. The combined organic phases were dried and to afford the title product as a light brown oil (27.8 mg, 84% yield, 5<:95 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[25]

(*E*)-2-(Prop-1-en-1-yl)aniline **15*E***



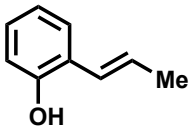
The title compound was prepared according to General Procedure 2B, employing 2-allylaniline (33 mg, 1 equiv). After end reaction, the mixture was quenched with 1 M HCl and the aqueous layer was washed three times with 5 mL diethyl ether. Then, $NaCO_3$ was slowly added to the aqueous layer until bubbles stopped forming. At this point, the desired product was extracted from the slightly basic aqueous layer three times with 7 mL diethyl ether. The combined organic phases were dried and to afford the title product as a light brown oil (29 mg, 89% yield, <5:95 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[25]

(*Z*)-2-(Prop-1-en-1-yl)phenol **16*Z***



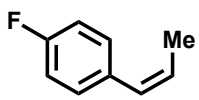
The title compound was prepared according to General Procedure 1A, employing 2-allylphenol (34 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 81% yield, 76:24 *Z*:*E* ratio. PTLC (silica, hexane) afforded the title compound as a clear oil containing 18% starting material that could not be separated (23 mg, 52% corrected yield, 73:27 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[15]

(*E*)-2-(Prop-1-en-1-yl)phenol **16*E***



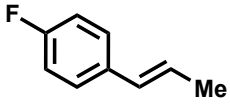
The title compound was prepared according to General Procedure 2B, employing 2-allylphenol (34 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 84% yield, 5:95 *Z*:*E* ratio with 10% starting material. Column chromatography (silica, pentane to 20% diethyl ether in pentane) afforded the title compound as a colorless oil containing 10% starting material that could not be separated (31 mg, 82% corrected yield, 6:94 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[15]

(*Z*)-1-Fluoro-4-(prop-1-en-1-yl)benzene **17*Z***



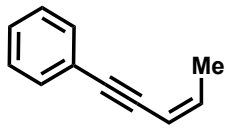
The title compound was prepared according to General Procedure 1A, employing 1-allyl-4-fluorobenzene (34 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 74% yield, 92:8 *Z*:*E* ratio. Column chromatography ($AgNO_3$ impregnated silica, pentane) afforded the title product as a colorless oil (16 mg, 48% yield, >95:5 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[26]

(*E*)-1-Fluoro-4-(prop-1-en-1-yl)benzene **17*E***



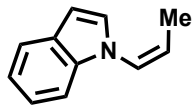
The title compound was prepared according to General Procedure 2B, employing 1-allyl-4-fluorobenzene (34 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 64% yield, <5:95 *Z*:*E* ratio. Column chromatography (silica, hexane) afforded the title product as a colorless oil (17 mg, 50% yield, <5:95 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[26]

(*Z*)-Pent-3-en-1-yn-1-ylbenzene **18*Z***



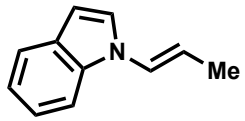
The title compound was prepared according to General Procedure 1A, employing pent-4-en-1-yn-1-ylbenzene (36 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 37% yield, 87:13 *Z*:*E* ratio. PTLC (silica, hexane) afforded the title product as a clear oil (15 mg, 45% yield, 94:6 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[27]

(*Z*)-1-(Prop-1-en-1-yl)-1*H*-indole **19*Z***



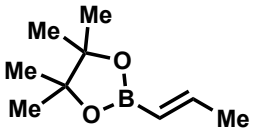
The title compound was prepared according to General Procedure 1B, employing 1-allyl-1*H*-indole (39 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 72% yield, 59:41 *Z*:*E* ratio. PTLC (silica, 15% EtOAc in hexanes) afforded the title product as a colorless oil (29 mg, 75% yield, 60:40 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[28]

(*E*)-1-(Prop-1-en-1-yl)-1*H*-indole **19*E***



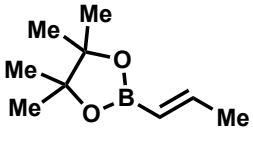
The title compound was prepared according to General Procedure 2A, employing 1-allyl-1*H*-indole (39 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 72% yield, 20:80 *Z*:*E* ratio. PTLC (silica, 15% EtOAc in hexanes) afforded the title product as a colorless oil (20 mg, 59% yield, 21:79 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[28]

(*E*)-4,4,5,5-tetramethyl-2-(prop-1-en-1-yl)-1,3,2-dioxaborolane **20*E***



The title compound was prepared according to General Procedure 1B, employing 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 50% yield, 40:60 *Z*:*E* ratio. Column chromatography (silica, hexane to 5% diethyl ether in hexane) afforded the title product as a colorless oil containing 22% of starting material that could not be separated (11 mg, 20% corrected yield, 40:60 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[13]

(*E*)-4,4,5,5-Tetramethyl-2-(prop-1-en-1-yl)-1,3,2-dioxaborolane **20*E***



The title compound was prepared according to General Procedure 2A, employing 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 72% yield, 8:92 *Z*:*E* ratio. Column chromatography (silica, hexane to 5% diethyl ether in hexane) afforded the title product as a colorless oil (27 mg, 65% yield, 8:92 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[13]

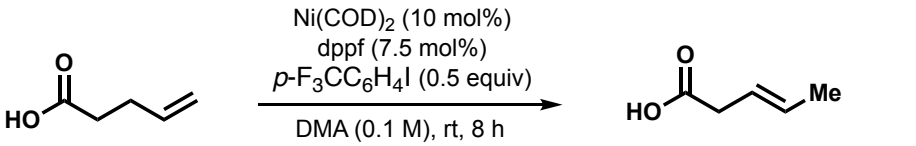
(*E*)-Triphenyl(prop-1-en-1-yl)silane **21*E***

The title compound was prepared according to General Procedure 2A, employing allyltriphenylsilane (75 mg, 1 equiv). The crude reaction mixture was analyzed by ^{1}H NMR and contained the desired product in 100% yield, >5:95 *Z*:*E* ratio. PTLC (silica, hexane) afforded the title product as a white solid (56 mg, 75% yield, <5:95 *Z*:*E*). The spectroscopic data correspond to reported data from literature.[15]

Reaction with 4-pentenoic acid

The reaction was performed according to General Procedure 1A employing 0.25 mmol of 4-pentenoic acid. The reaction was stirred at room temperature for 8 h. After this time, the reaction was quenched with 1M NaOH (aq.), and the aqueous layer washed with diethyl ether (3 × 5 mL). At this point, the water phase was acidified using 1M HCl (aq.) and the title compound was extracted using diethyl ether (3 × 7 mL). The organic layers were dried over Na_2SO_4 and concentrated. The reaction mixture was analyzed by ^{1}H NMR using 2 µL CH_2Br_2 as internal standard to determine yield and selectivity. The spectroscopic data correspond to the reported data from literature.[29]

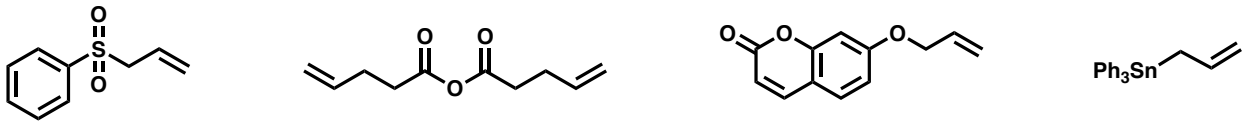
Scheme S1: Reaction of 4-pentenoic acid.



>99% yield by NMR, 23:77 *Z*:*E*

Unsuccessful Substrates

No reaction took place with the substrates below and no conversion was observed by ^{1}H NMR analysis.



Mechanistic Experiments

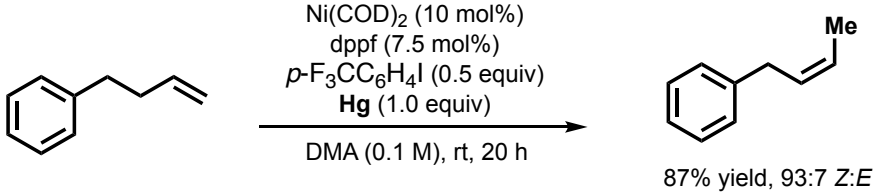
Synthesis of PCy_3•HCl

Into a mixture of PCy_3 (285 mg) and diethyl ether (5 mL) was added HCl (1 mL, 2 M solution in diethyl ether, 2 equiv). A white suspension was immediately observed. The mixture was stirred for 20 min and then concentrated to dryness, resulting in a white powder in quantitative yield. The white powder was used without further purification. Note: PCy_3•HCl is highly hygroscopic and was only handled inside the glovebox. Spectroscopic characterization was in accordance with the literature.[30]

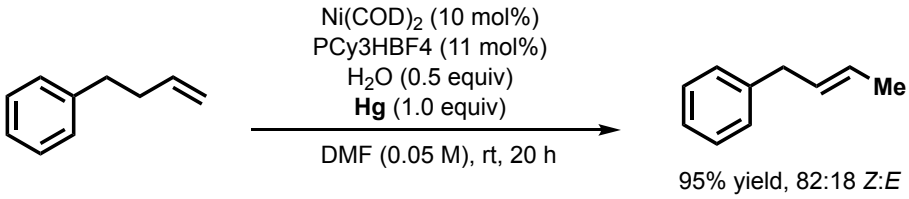
Mercury Drop Test

Mercury drop experiments were performed according to General Procedure 1A or 2A on 0.15 mmol scale of alkene. After the reaction setup was complete, one drop of elemental mercury was added via syringe to the sealed reaction mixture. The reaction was allowed to stir overnight. After reaction completion, the cap was unscrewed, and a pipette was used to carefully remove and discard the drop of mercury from the bottom of the vial. The reaction mixture was quenched with 1 M HCl (aq.) solution, and the organic phase was extracted with diethyl ether. The organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was analyzed by ^1H NMR ($CDCl_3$) using CH_2Br_2 (1 µL) added as internal standard.

Scheme S2: Mercury drop test experiments for *Z*-selective reaction conditions.



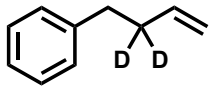
Scheme S3: Mercury drop test experiments for *E*-selective reaction conditions.



Deuterium Labeling Experiments

Synthesis of deuterated starting materials

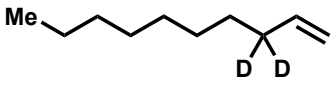
Synthesis of 4-phenyl-1-butene-3-d_2 **1D**



To a flamed-dried 25-mL flask under N_2 was added a stir bar, hydrocinnemaldehyde (1.10 g, 8.20 mmol, 1.0 equiv), 4-dimethylaminopyridine (100 mg, 0.820 mmol, 0.1 equiv), D_2O (2.0 mL, 4.0 M), and was heated to 100 °C for 2 h. The reaction was cooled to room temperature and diluted with diethyl ether (25 mL). The layers were separated, and the organic layer was washed with 1 N HCl (10 mL x 2) and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure at room temperature. The yellow oil was then resubjected to the same reaction condition to form cinnemaldehyde-d_2, which was carried through to the next step without further purification. To a flamed–dried 100 mL flask under N_2 was added methyltriphenylphosphonium bromide (3.17 g, 8.87 mmol, 1.7 equiv) and diethyl ether (20 mL). Then, KO*t*Bu (878 mg, 7.83 mmol, 1.5 equiv) was

added resulting in an yellow solution. After stirring for 30 minutes, cinnemaldehyde-d_2 (700 mg, 5.2 mmol, 1.0 equiv), was added as a single portion at 0 °C. The reaction was allowed to warm up to room temperature and stirred for additional 3 h. Upon completion, the reaction was quenched with sat. aq. NH_4Cl. Layers were separated, and the aqueous layer was extracted with diethyl ether (25 mL x 2). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure at room temperature. The resulting mixture was purified by flash column chromatography (hexane) to afford the 4-phenyl-1-butene-3-d_2 in a 70% yield as a colorless oil (490 mg, 5.22 mmol) with >99% D incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 2H), 7.25–7.19 (m, 3H), 5.89 (dd, *J* = 17.1, 10.2 Hz, 1H), 5.16–4.97 (m, 1H), 2.73 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.9, 138.1, 125.8, 115.0, 35.4. GCMS calculated for [$C_{10}D_2H_{10}$] 134, found 134.

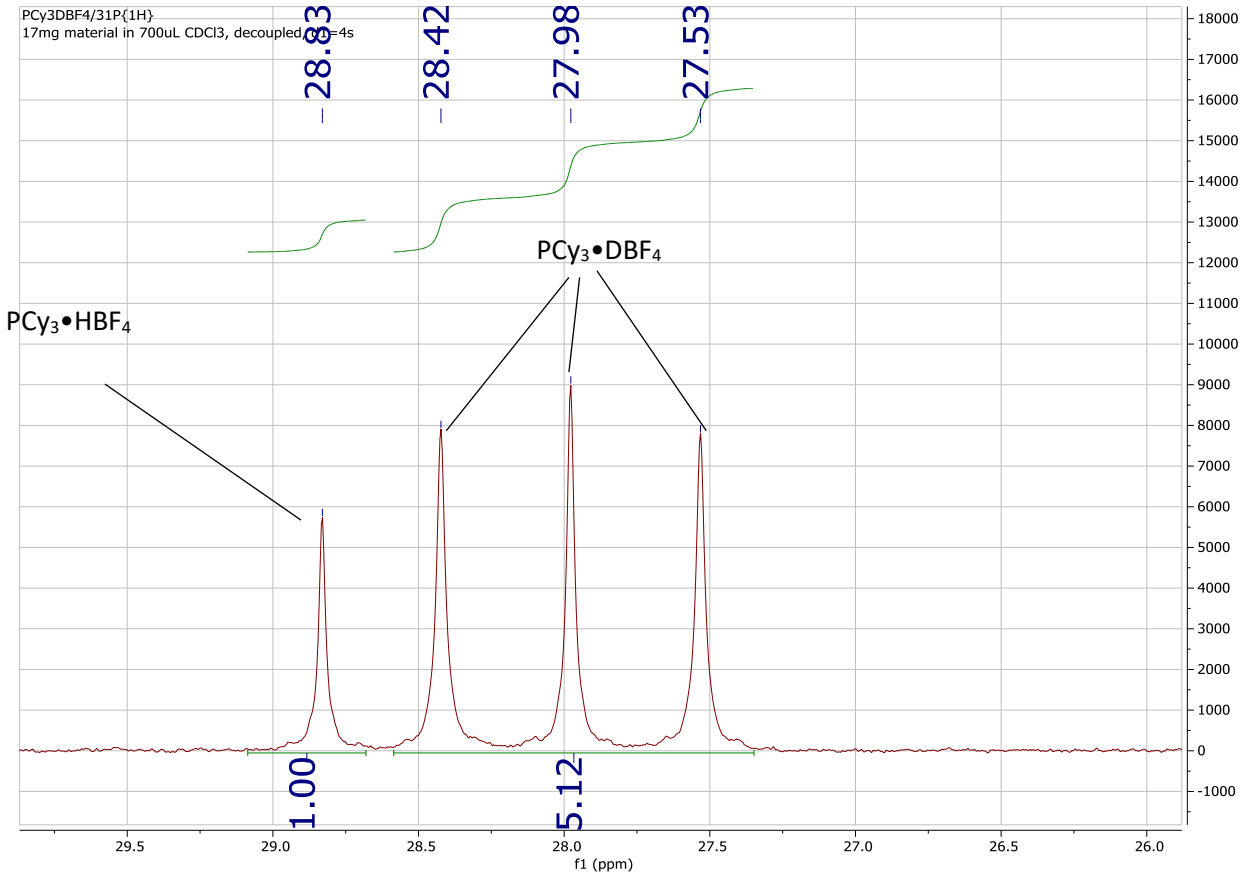
Synthesis of 1-decene-d_2 **22D**



To a flamed-dried 25 mL flask under N_2 was added a stir bar, nonanal (1.42 g, 10 mmol, 1.0 equiv), 4-dimethylaminopyridine (122.2 mg, 1 mmol, 0.1 equiv), D_2O (2.5 mL, 4.0 M), and was heated to 100 °C for 2 h. The reaction was cooled to room temperature and diluted with CH_2Cl_2 (25 mL). The layers were separated, and the organic layer was washed with 1 N HCl (10 mL x 2) and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure at room temperature. The yellow oil was then resubjected to the same reaction conditions to achieve nonanal-d_2 with >95% D incorporation. The nonanal-d_2 was carried through to the next step without further purification. To a flamed–dried 100 mL flask under N_2 was added methyltriphenylphosphonium bromide (3.25 g, 8.8 mmol, 1.7 equiv) and diethyl ether (20 mL). Then, KO*t*Bu (953 mg, 7.8 mmol, 1.5 equiv) was added. The reaction was stirred for 30 minutes, and nonanal-d_2 (750 mg, 5.2 mmol, 1.0 equiv) was added in a single portion at 0 °C. The reaction was allowed to warm up to room temperature and stirred for additional 3 h. Upon completion, the reaction was quenched with sat. aq. NH_4Cl. Layers were separated, and the aqueous layer was extracted with diethyl ether (25 mL x 3). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure at room temperature. The resulting mixture was purified via flash column chromatography (hexane) to afford 1-decene-d_2 in 80% yield as a colorless oil (591 mg, 4.16 mmol) with >99% D incorporation. The spectroscopic data correspond to reported literature.[31]

Synthesis of PCy_3•DBF_4

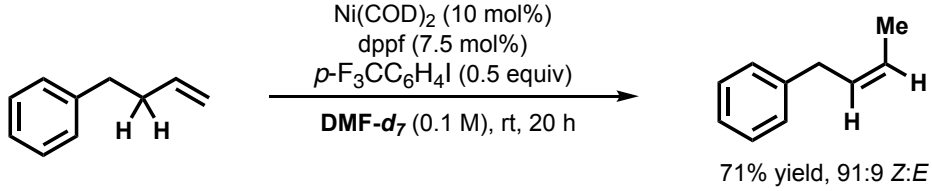
To a Schlenk tube was added PCy_3•HBF_4 (330 mg, 0.90 mmol), 4 mL THF, and 1 mL D_2O. The tube was sealed and refluxed at 100 °C overnight. Solids dissolved upon heating. After this time, the mixture was then concentrated to dryness, and the resulting white powder was used without further purification. ^{31}P NMR analysis revealed that the solid comprised of a mixture of 5:1 of D to H salts. Note: PCy_3•DBF_4 is hygroscopic and was only handled inside the glovebox. ^{31}P NMR (162 MHz, $CDCl_3$): 28.0 ppm (t, $J_{P\text{-}D}$ = 72 Hz).



Deuterium Labeling Experiments using DMF-d_7

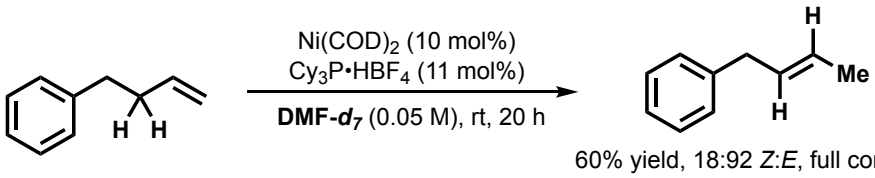
Experiments were performed according to General Procedure 1A or 2A, on a 0.05 mmol scale of alkene using DMF-d_7 as solvent. The crude reaction mixtures were analyzed by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

Scheme S4: Experiment performed in deuterated solvent for *Z*-selective reaction conditions.



71% yield, 91:9 *Z*:*E*

Scheme S5: Experiment performed in deuterated solvent for *E*-selective reaction conditions.

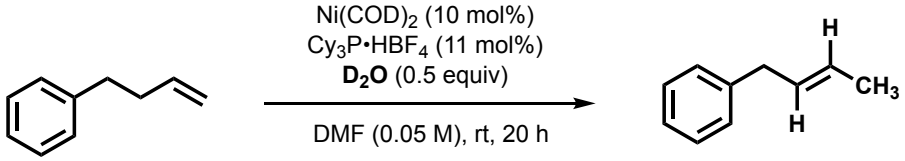


60% yield, 18:92 *Z*:*E*, full conversion

Deuterium Labeling Experiments for the *E*-selective Reaction

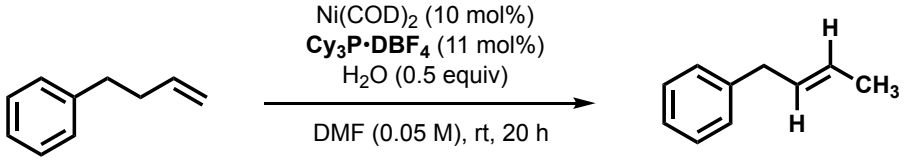
The experiments were performed according to General Procedure 2A, on a 0.25 mmol scale of alkene **1** using either D_2O or $Cy_3P{\bullet}DBF_4$ instead of H_2O or $Cy_3P{\bullet}HBF_4$, respectively. The crude reaction mixtures were analyzed by quantitative ^1H NMR analysis using CH_2Br_2 as internal standard.

Scheme S6: Experiment performed using D_2O instead of H_2O in *E*-selective reaction conditions.



87% yield, 17:83 *Z*:*E*

Scheme S7: Experiment performed using $Cy_3P{\bullet}DBF_4$ instead of $Cy_3P{\bullet}HBF_4$in *E*-selective reaction conditions.

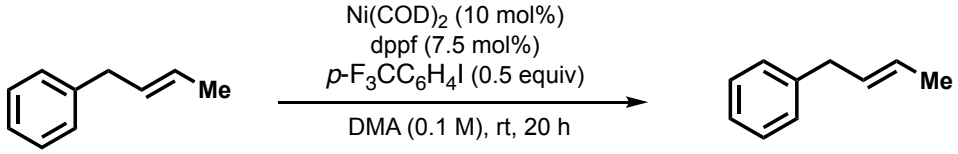


95% yield, 17:83 Z:E

Regioconvergent Experiments

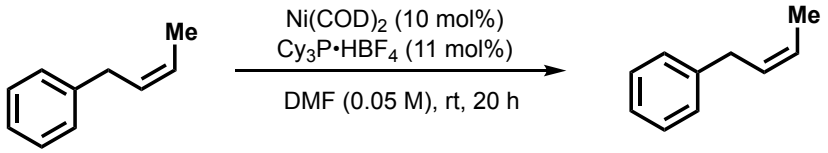
The experiments were performed following General Procedure 1A or 2A, on a 0.25 mmol scale of either alkene **1*E*** or **1*Z***. The crude reaction mixtures were analyzed by ^1H NMR analysis using CH_2Br_2 as internal standard. No reaction was observed, and the starting material was fully recovered with retained *Z*:*E* ratios under both *Z*- and *E*- selective reaction conditions.

Scheme S8: Internal alkene **1*E*** subjected to *Z*-selective reaction conditions.



92% yield, 25:75 *Z*:*E* (which is ratio of SM).

Scheme S9: Internal alkene **1*Z*** subjected to *E*-selective reaction conditions.



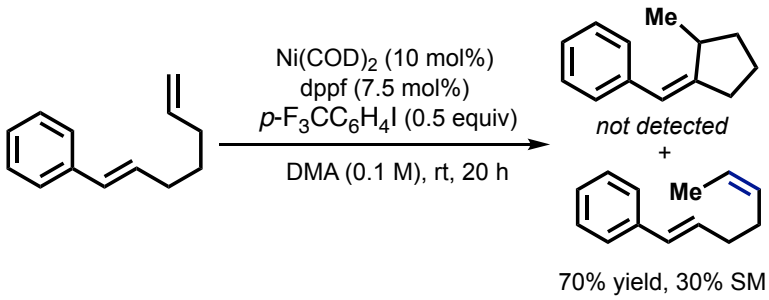
66% yield, 93:8 *Z*:*E* (which is ratio of SM)

Radical Clock Experiment

The experiments were performed following General Procedure 1A, on a 0.25 mmol scale employing (*E*)-hepta-1,6-dien-1-ylbenzene. The crude reaction mixtures were analyzed by ^1H NMR analysis using CH_2Br_2

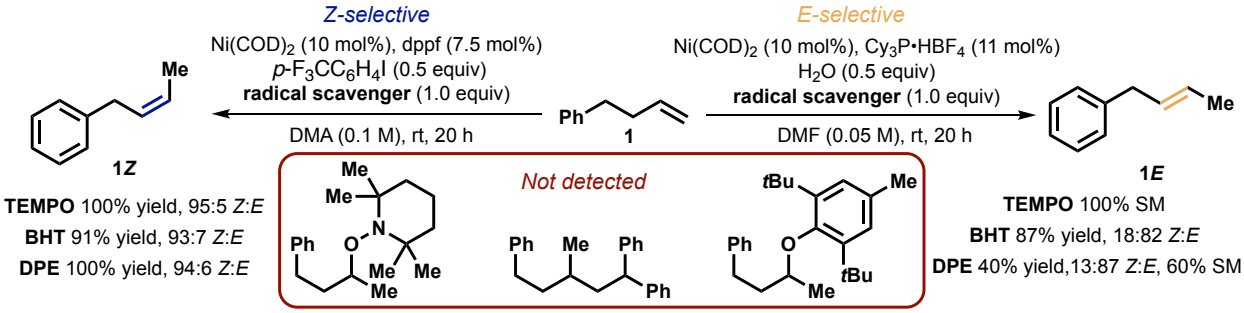
as internal standard. Ring closure products were not detected by ^{1}H NMR analysis, and 70% yield of the isomerization product was observed.

Scheme S10: Radical clock experiment using (*E*)-hepta-1,6-dien-1-ylbenzene as substrate.



Radical Scavenger Experiments

The experiments were performed according to General Procedure 1A or 2A, on a 0.25 mmol scale of alkene **1**. After reaction setup was complete, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), 2,6-Di-*tert*-butyl-4-methylphenol (BHT), or 1,1-diphenylethylene (DPE) (0.25 mmol, 1.0 equiv) was added to the reaction and stirred at room temperature overnight. After this time, the mixture was quenched with 1 M HCl (aq.) solution. The reaction mixture was extracted with diethyl ether (2 × 5 mL), and the combined organic layers were washed with brine (3 × 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixtures were analyzed by ^{1}H NMR analysis using CH_2Br_2 as internal standard and by GCMS. No derivatives of the radical scavengers were observed.

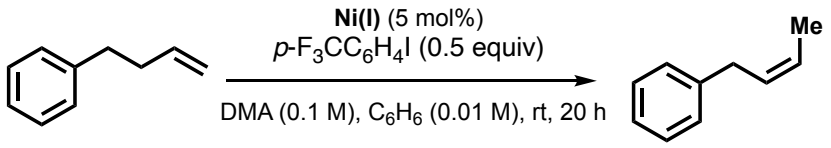


Active Catalyst Experiments for *Z*-Selective Reaction Conditions

Modified reaction using [Ni(μ-I)(dppf)]$_2$ precatalyst

In a nitrogen- or argon-filled glovebox to a 4 mL reaction vial equipped with a stir bar and screw cap was added [Ni(μ-I)(dppf)]$_2$ (19 mg, 5 mol%), **1** (33 mg, 0.25 mmol, 1 equiv), 4-iodobenzotrifluoride (34 mg, 0.125 mmol, 0.5 equiv), benzene (250 μL), and DMA (2.5 mL). The reaction vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The reaction was stirred vigorously at room temperature overnight. After this time, the mixture was quenched with 1 M HCl (aq.). The reaction mixture was extracted with diethyl ether (2 x 5 mL) and the combined organic layers were washed with brine (3 x 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The reaction mixture was analyzed by ^{1}H NMR using 1 μL CH_2Br_2 as internal standard to determine yield and selectivity.

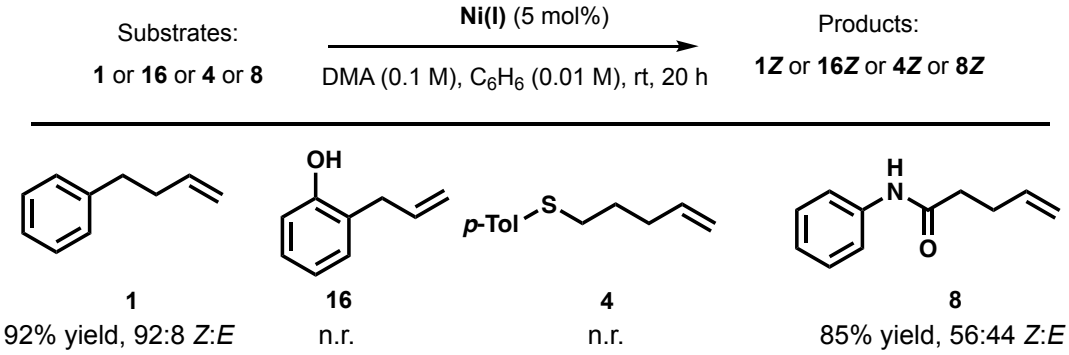
Scheme S11: Modified conditions using Ni(I) precatalyst, [Ni(μ-I)(dppf)]$_2$, for Z-selective conditions.



Reactions using $[Ni(\mu\text{-}I)(dppf)]_2$ precatalyst to evaluate different substrate classes

In a nitrogen- or argon-filled glovebox to a 4 mL reaction vial equipped with a stir bar and screw cap was added $[Ni(\mu\text{-}I)(dppf)]_2$ (19 mg, 5 mol%), alkene **1**, **16**, **4**, or **8** (0.25 mmol, 1 equiv), benzene (250 µL), and DMA (2.5 mL). The reaction vial was sealed with a Teflon-lined screw cap, removed from the glovebox, and stirred vigorously at room temperature overnight. After this time, the reaction the mixture was quenched with 1 M HCl (aq.). The reaction mixture was extracted with diethyl ether (2 x 5 mL) and the combined organic layers were washed with brine (3 x 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The reaction mixture was analyzed by ^1H NMR using 1 µL CH_2Br_2 as internal standard to determine yield and selectivity.

Scheme S12: Evaluation of Ni(I) precatalyst for different alkene substrates under *Z*-selective reaction conditions.



Active Catalyst Experiments for *E*-Selective Reaction Conditions

Synthesis of Nickel Complexes

Synthesis of $Ni(PCy_3)_2Br_2$

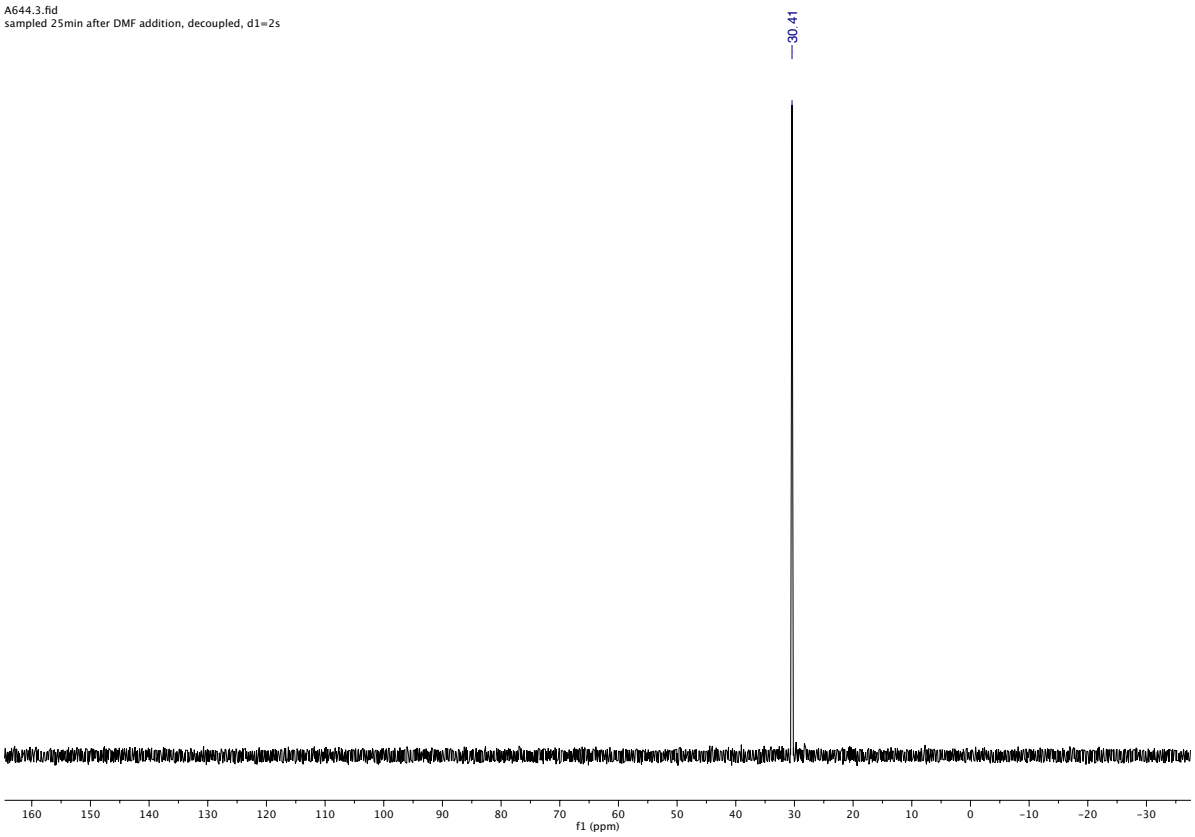
To a solution of $NiBr_2$ (440 mg, 2.01 mmol, 1 equiv) in 20 mL EtOH was added PCy_3 (1.18 g, 4.21 mmol, 2.1 equiv) under a nitrogen atmosphere. The resulting brown suspension was refluxed at 80 °C for 4 hours. The mixture was then cooled to room temperature and filtered. The title compound was obtained as a brown solid (1.43 g, 92%) and used without further purification.

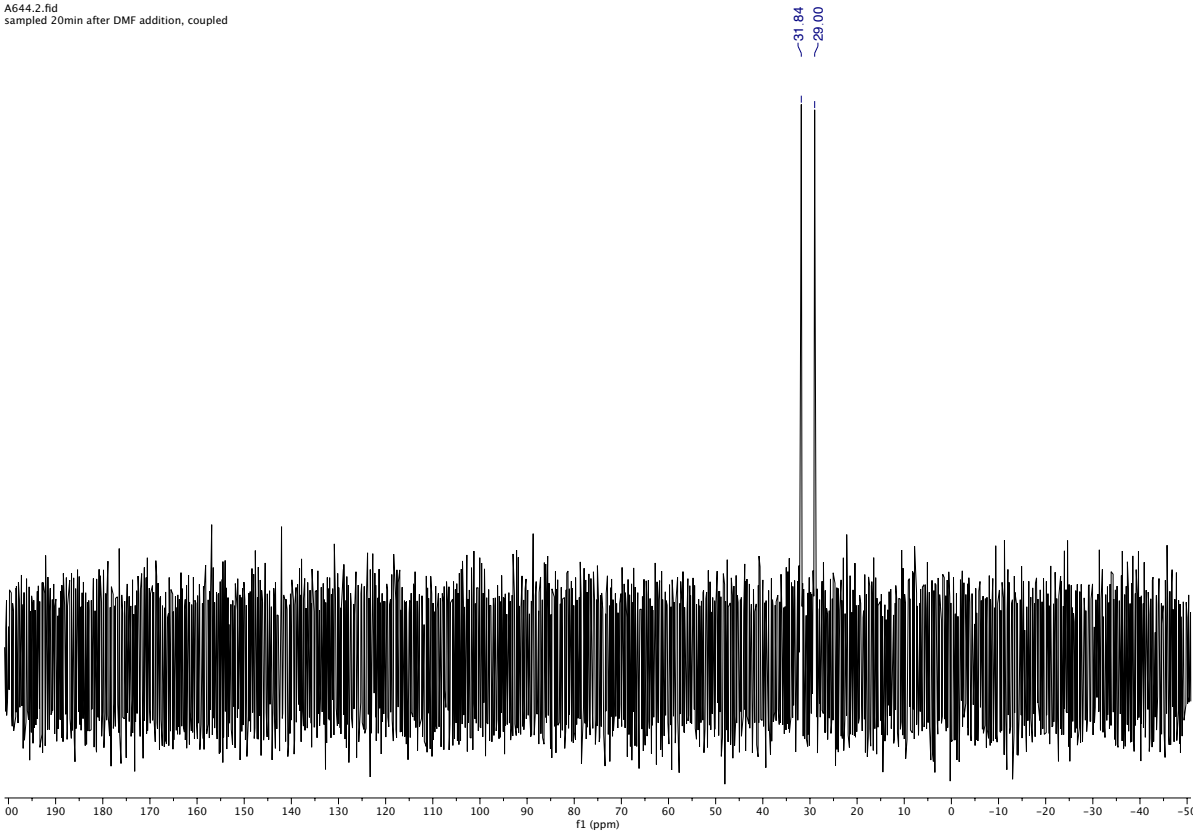
Synthesis of $Ni(PCy_3)_2(H)(Br)$

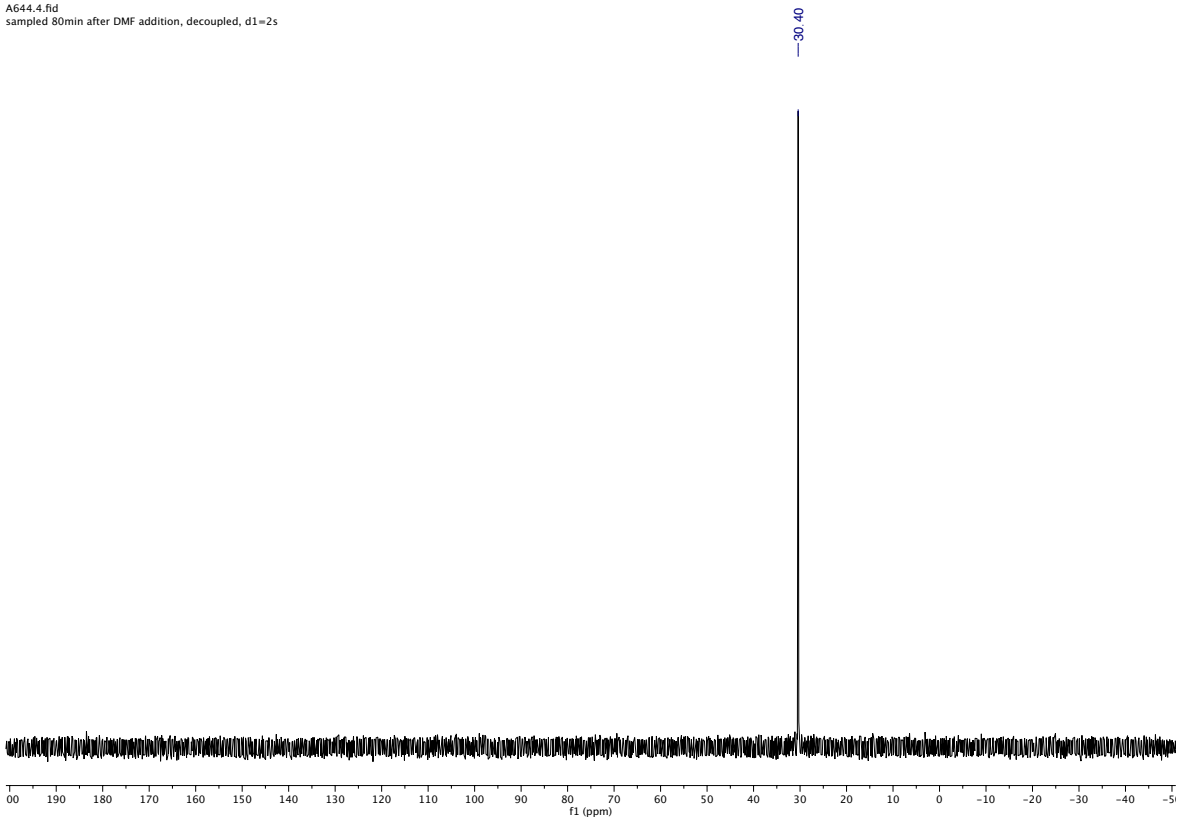
$Ni(PCy_3)_2Br_2$ (156 mg, 0.20 mmol) was suspended in 5 mL THF inside a nitrogen- or argon-filled glovebox. DIBAL (1 M in THF, 0.22 mL, 1.1 equiv) was added to the mixture in one portion and the reaction was stirred at room temperature overnight. The mixture was then concentrated to dryness under high vacuum. The solid residue was suspended in pentane and filtered through celite. The pentane filtrate was concentrated to dryness, resulting in a yellow solid (42 mg, 30%). Spectroscopic characterization was in accordance with literature.[32]

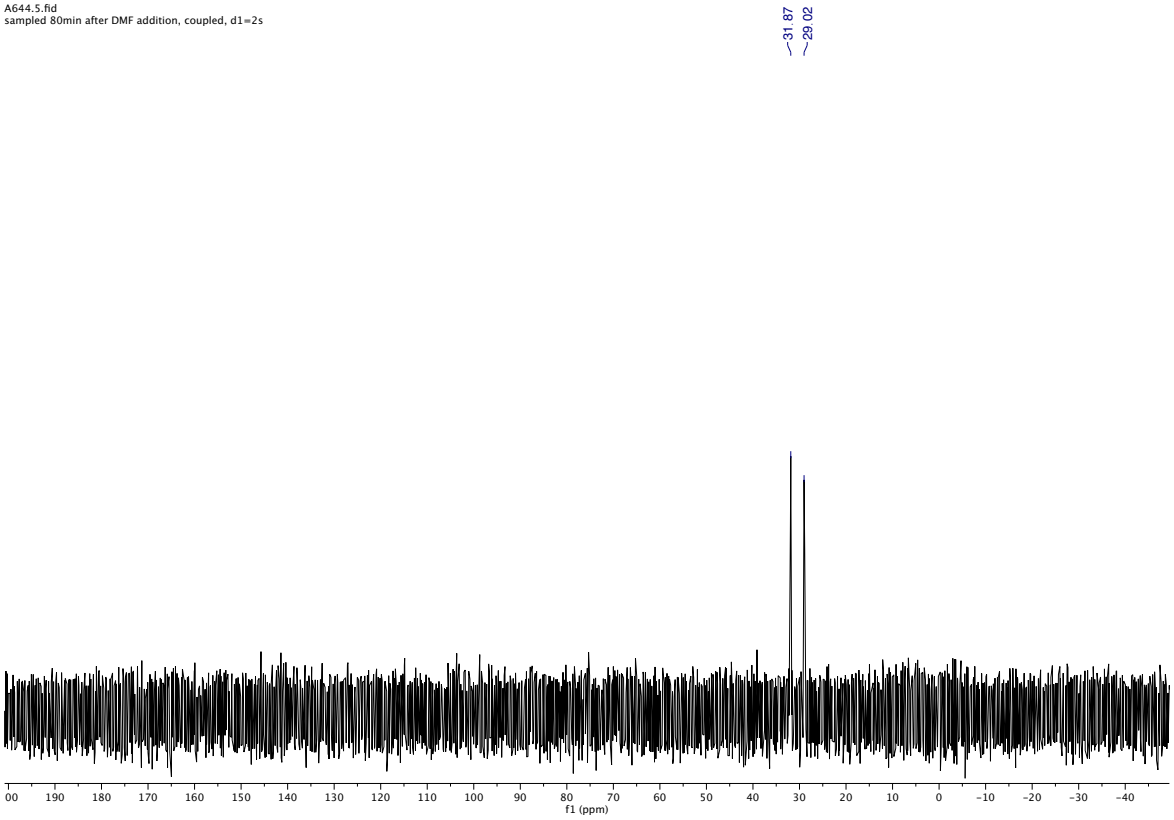
General Procedure 2A followed by ^{31}P NMR analysis

Into a 2-dram (8 mL) vial containing $Ni(COD)_2$ (28 mg, 0.1 mmol) and $PCy_3 \bullet HBF_4$ (76 mg, 0.2 mmol) was added 5 mL DMF. The reaction mixture was stirred at room temperature. Aliquots from the reaction mixture were collected after 25 and 80 minutes of stirring, and the homogenous yellow solution was analyzed by ^{31}P NMR. During these times, there was no evidence of substitution. The only species observed by ^{31}P NMR was $PCy_3 \bullet HBF_4$. $^{31}P\{^1H\}$ NMR (162 MHz, DMF) δ 30.40. Coupled and proton-decoupled spectra are shown below.




A644.2.fid
sampled 20min after DMF addition, coupled
31.84
29.00
f1 (ppm)

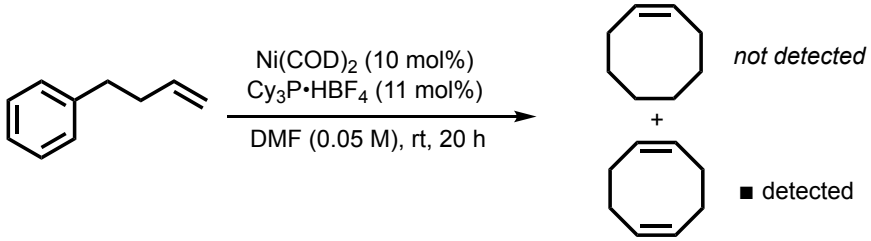

A644.4.fid
sampled 80min after DMF addition, decoupled, d1=2s
30.40
f1 (ppm)



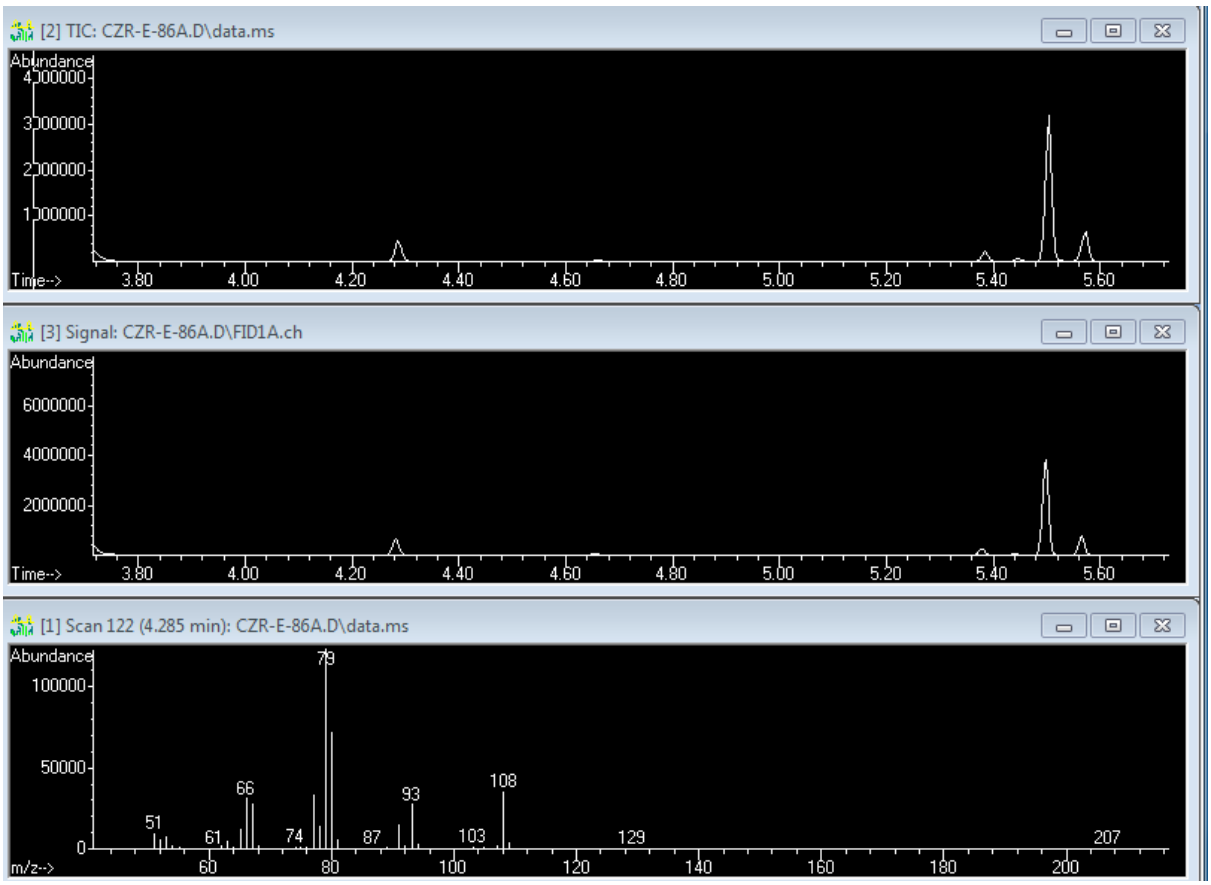
Investigation of the fate of COD

The experiment was performed in accordance with General procedure 2A, except the aqueous workup was omitted. Instead, 20 µL of the reaction mixture were filtered through a silica plug and washed with hexanes. The filtrate was collected into a vial suitable for GCMS. The GCMS analysis revealed a peak with a mass and splitting pattern consistent with 1,5-cyclooctadiene. Cyclooctene was not detected under these conditions.

Scheme S13: Experiments to investigate the fate of COD under *E*-selective reaction conditions



GCMS data for Scheme S12 that shows detection of 1,5-cyclooctadiene under General Procedure 2A and no detection of cyclooctene:


[2] TIC: CZR-E-86A.D\data.ms
Abundance
4000000
3000000
2000000
1000000
Time-->
3.80
4.00
4.20
4.40
4.60
4.80
5.00
5.20
5.40
5.60
[3] Signal: CZR-E-86A.D\FID1A.ch
Abundance
6000000
4000000
2000000
Time-->
3.80
4.00
4.20
4.40
4.60
4.80
5.00
5.20
5.40
5.60
[1] Scan 122 (4.285 min): CZR-E-86A.D\data.ms
Abundance
100000
50000
0
m/z-->
79
66
93
108
51
61
74
87
103
129
207
60
80
100
120
140
160
180
200

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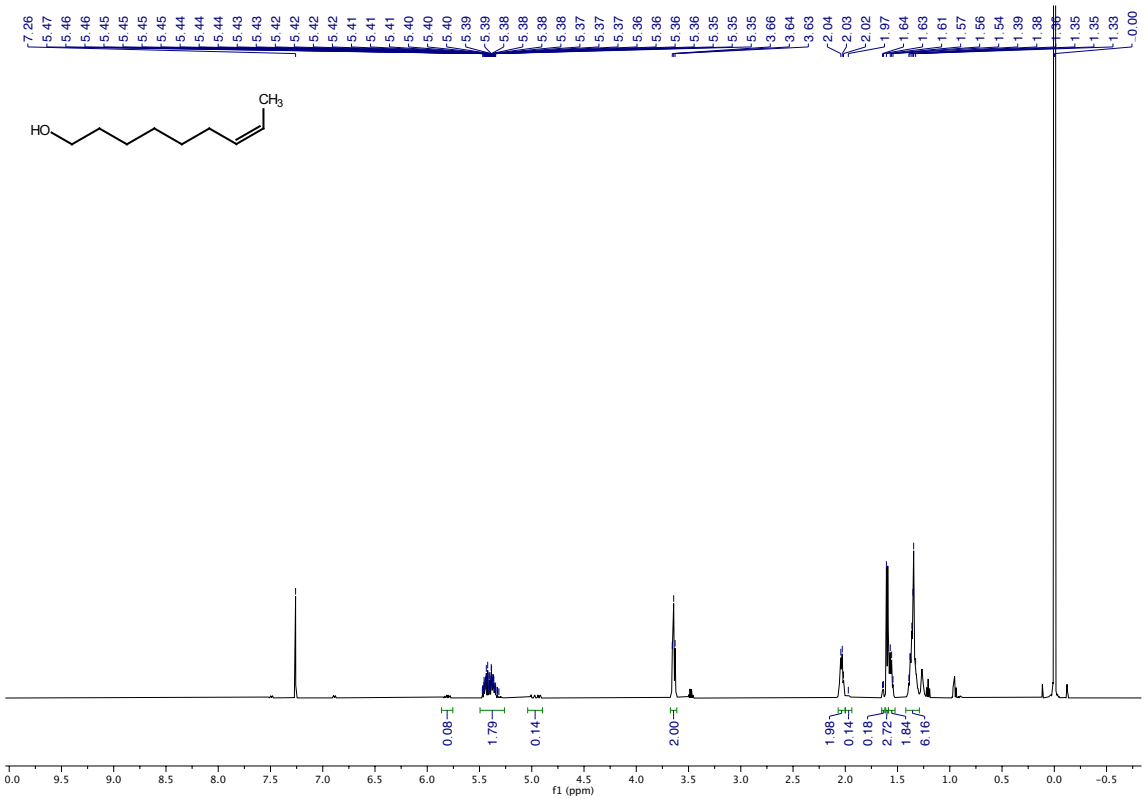
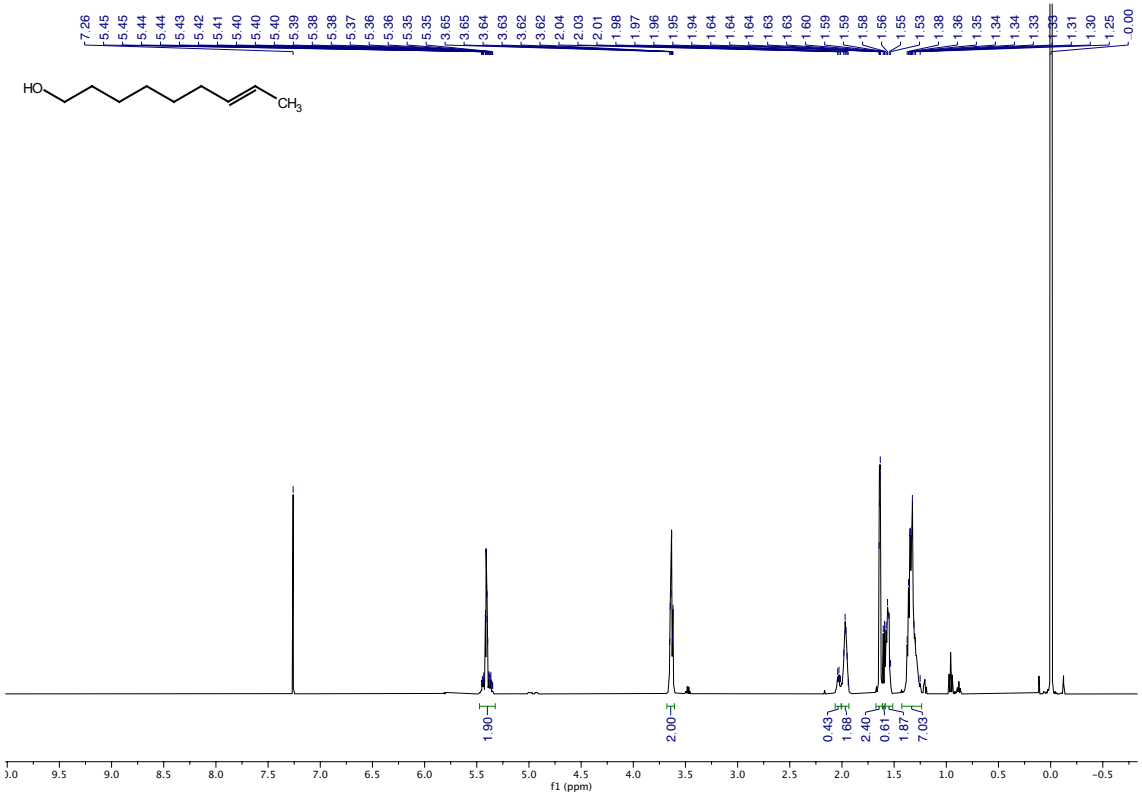
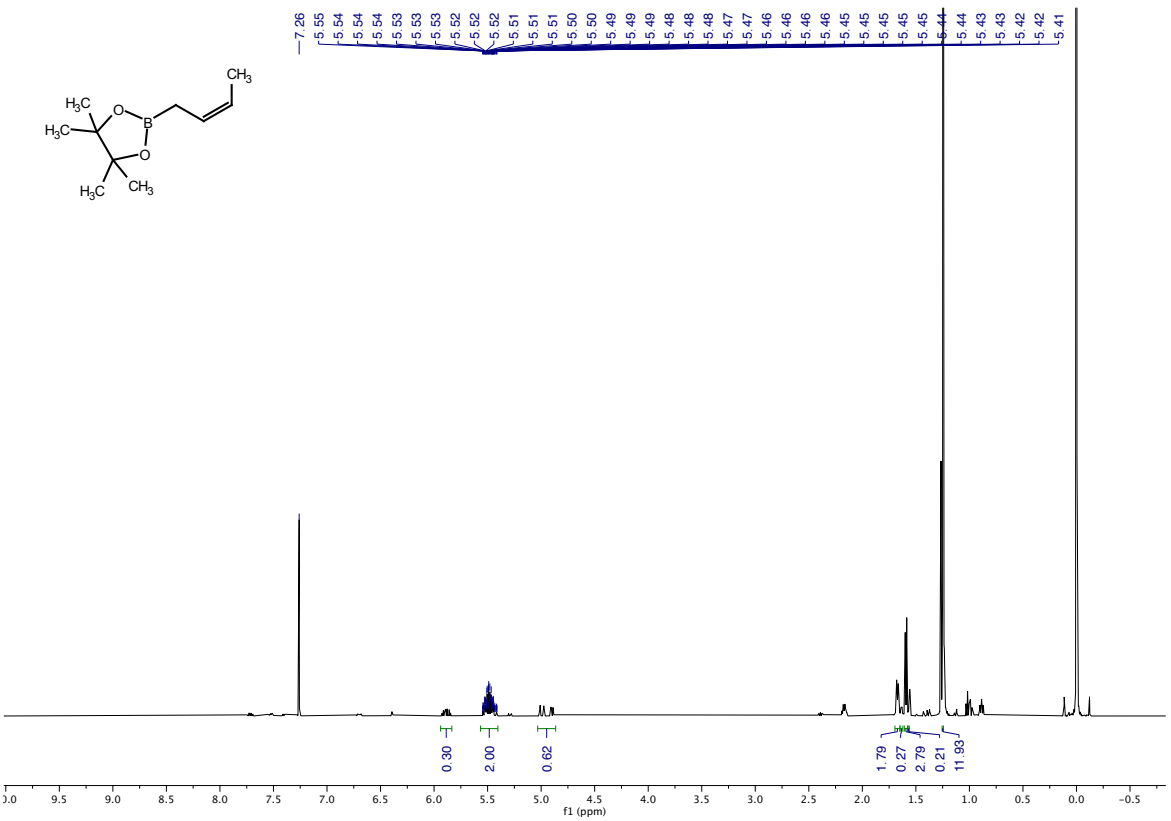
Spectra



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5.42
5.41
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O
B
H3C
O
H3C
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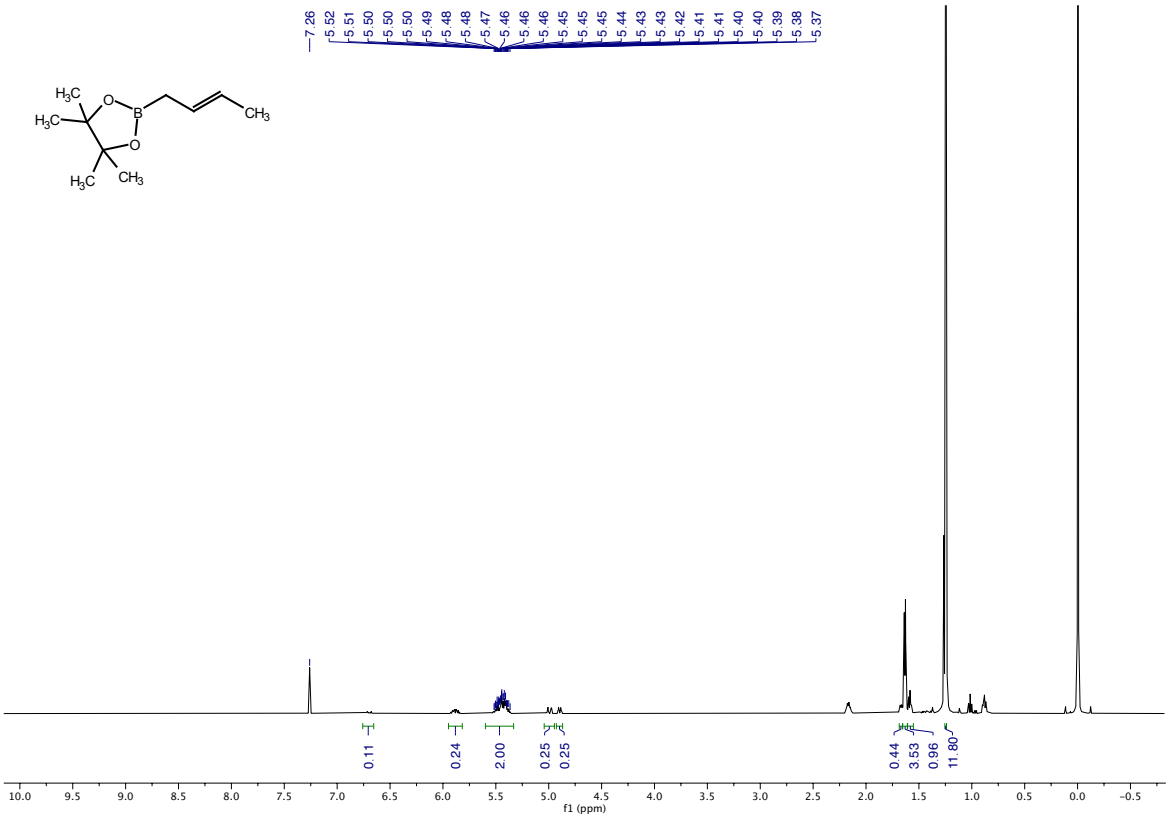
f1 (ppm)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5.38
5.37
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B
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H3C
O
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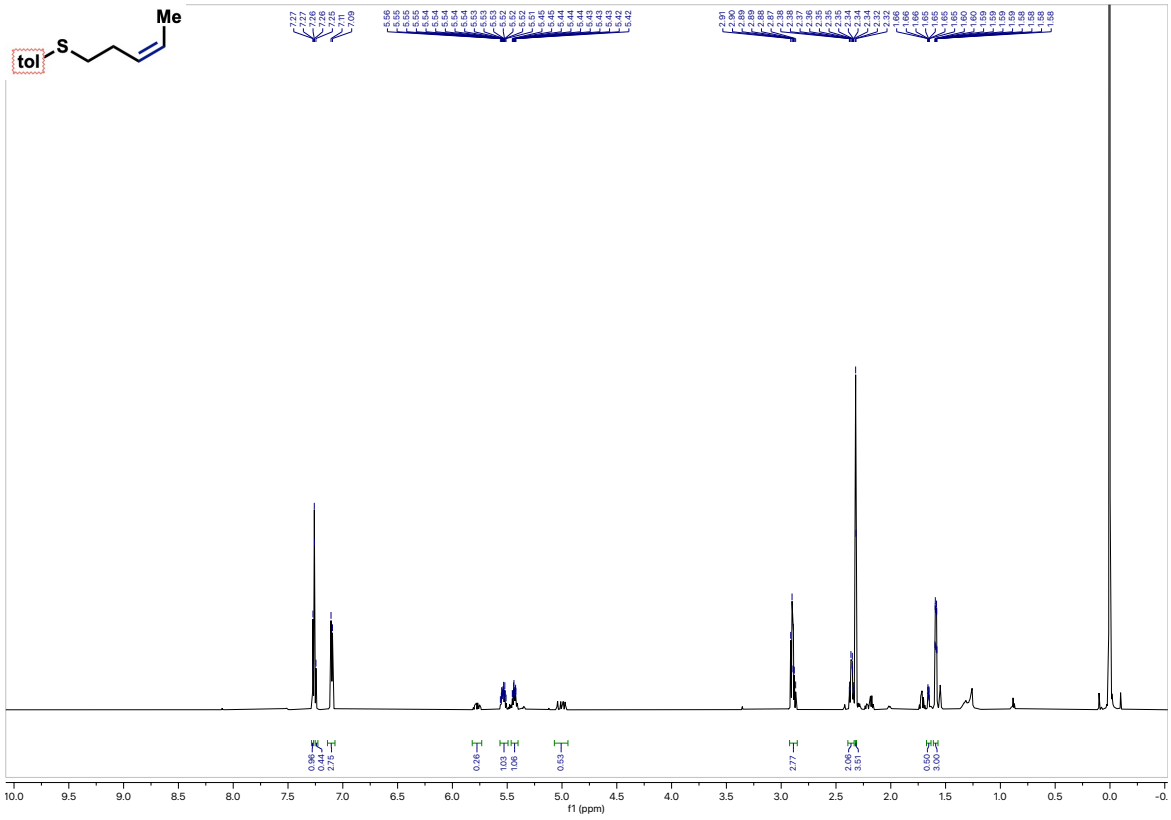
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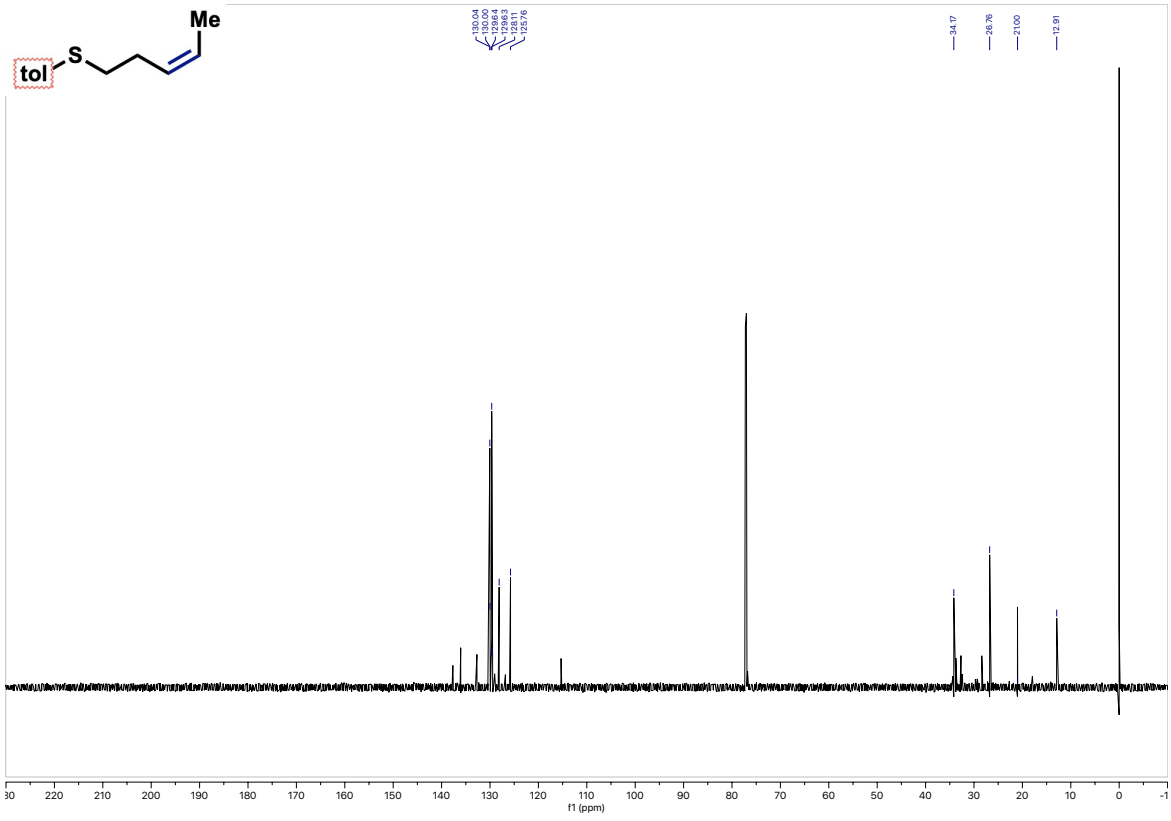
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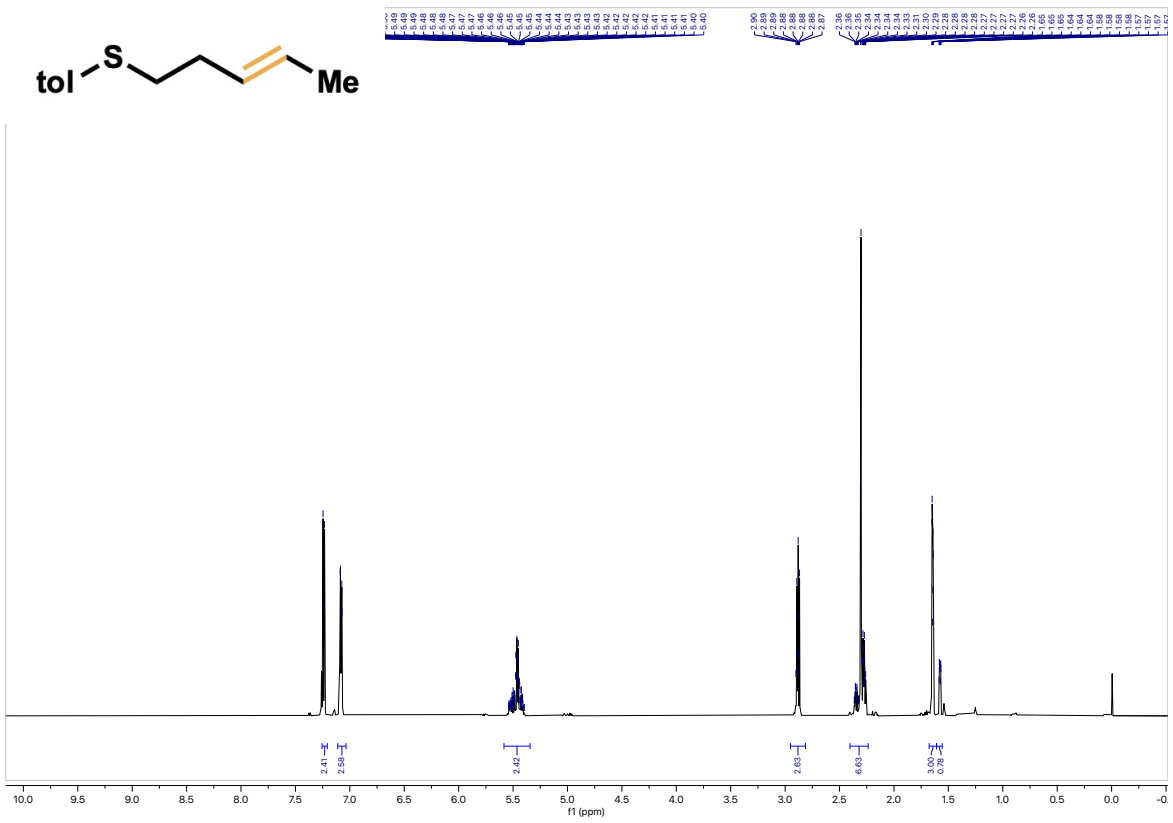
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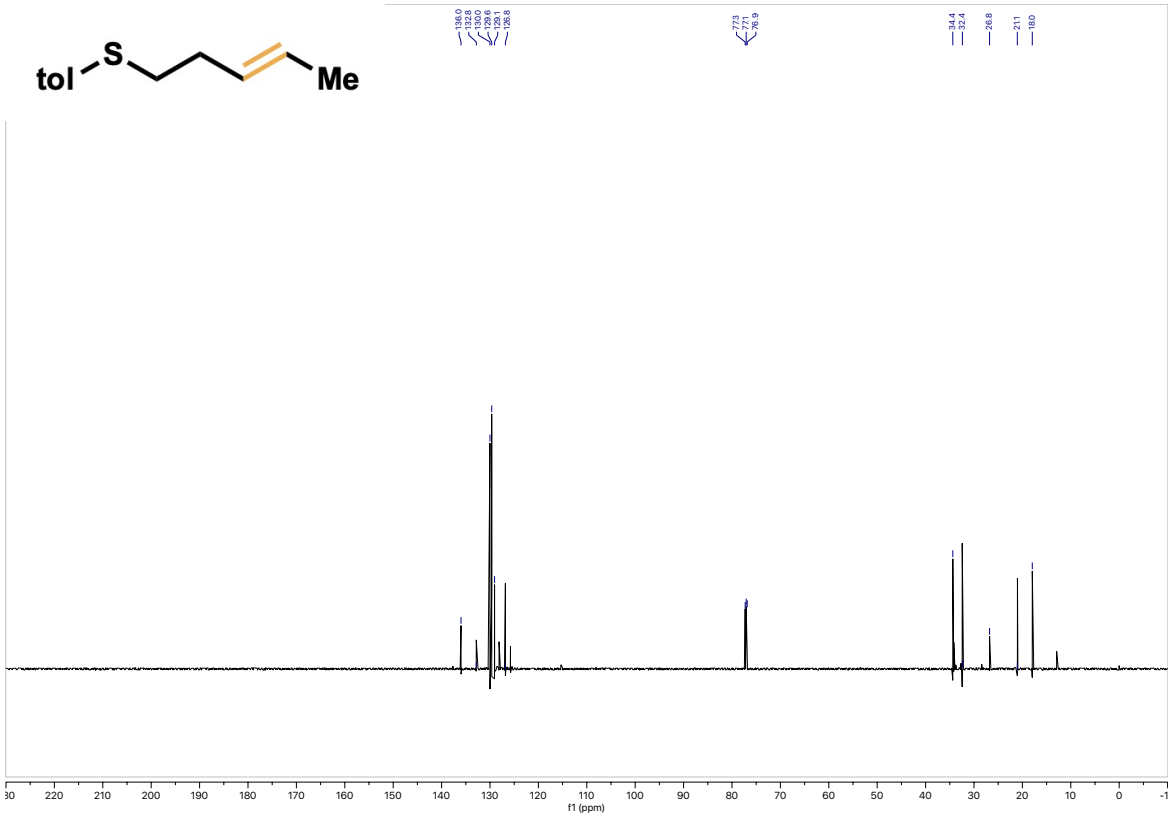
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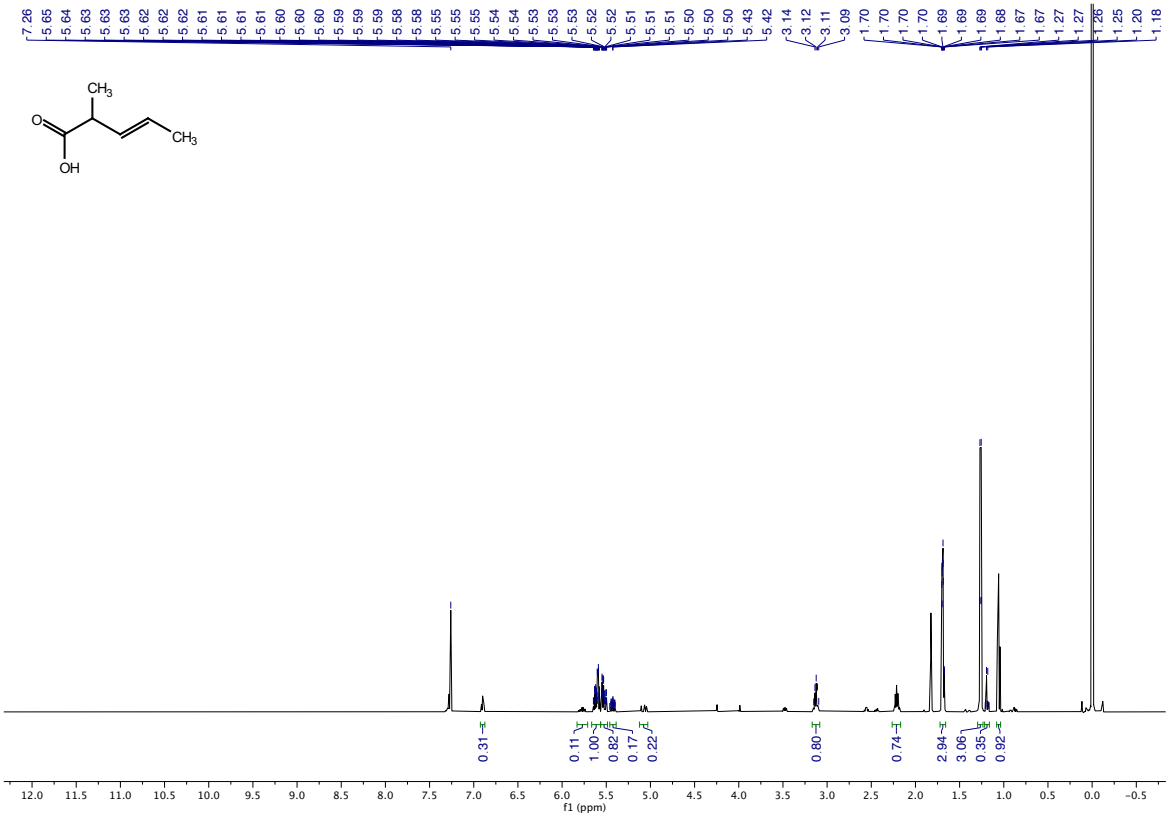
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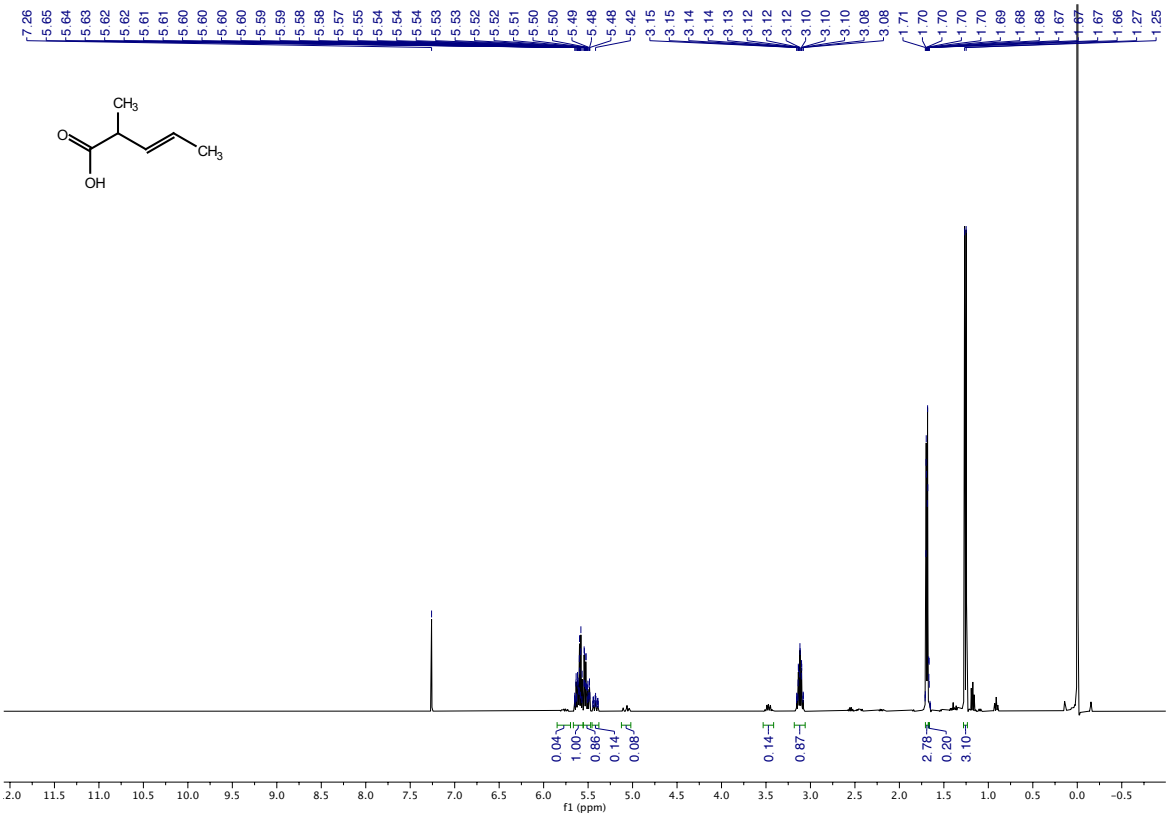
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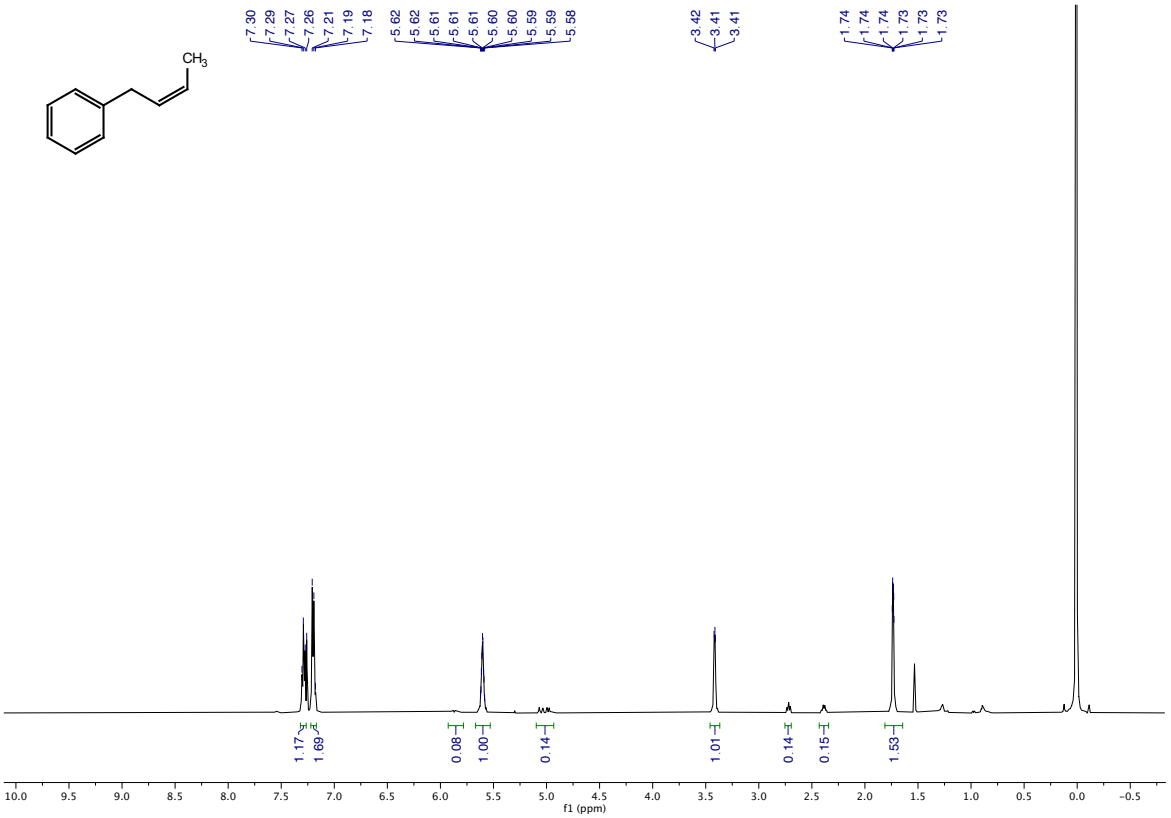
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1.74
1.74
1.73
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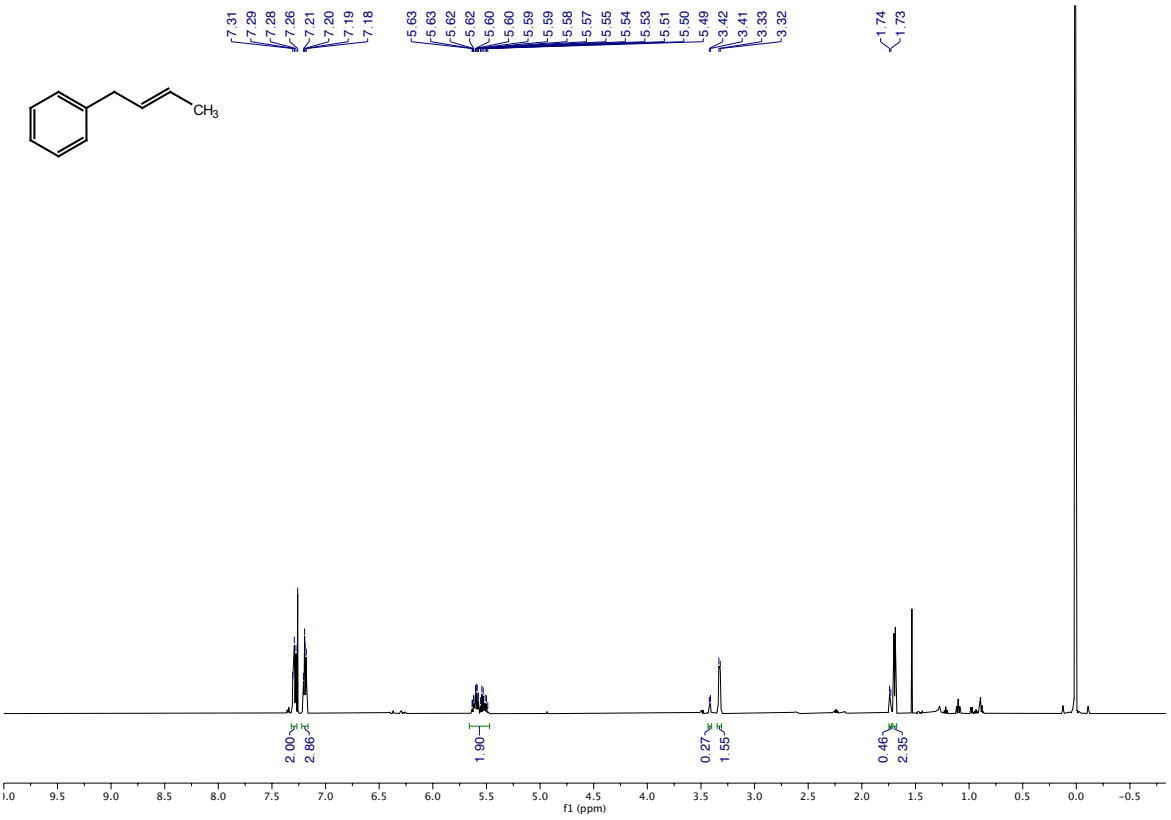
f1 (ppm)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5.51
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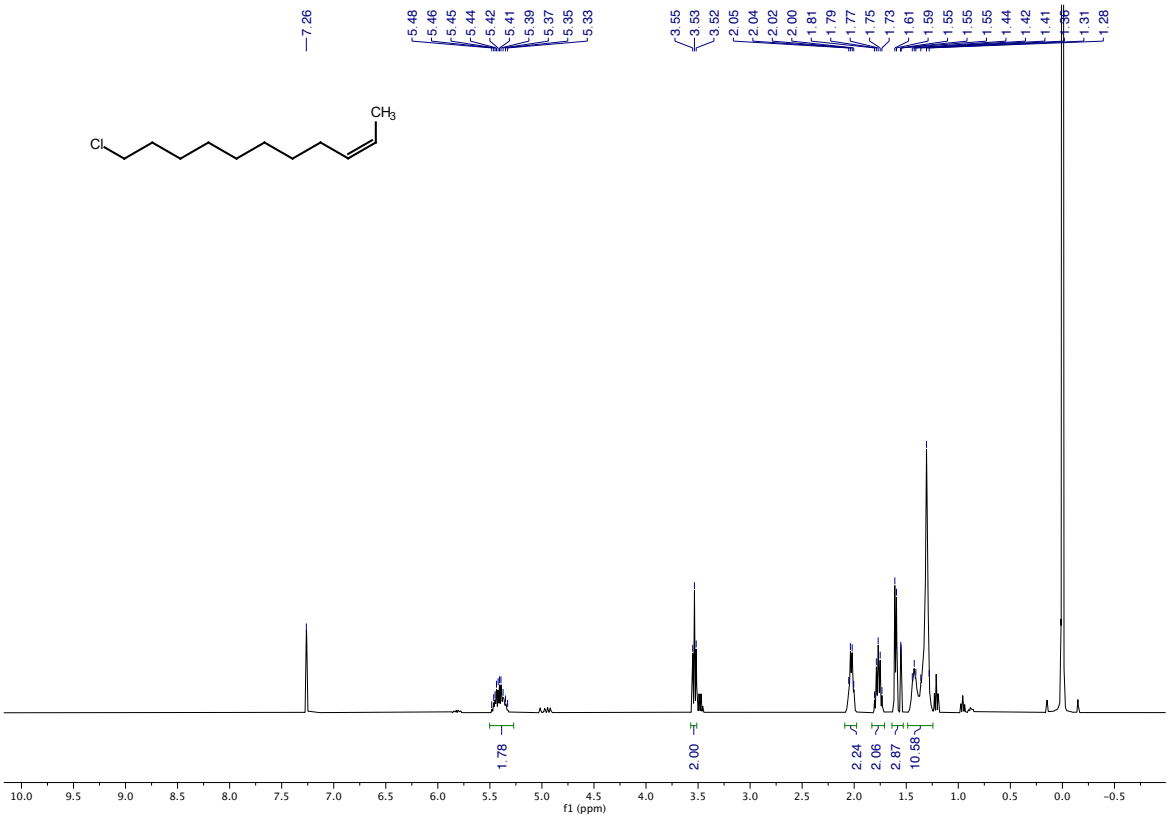
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1.55
1.55
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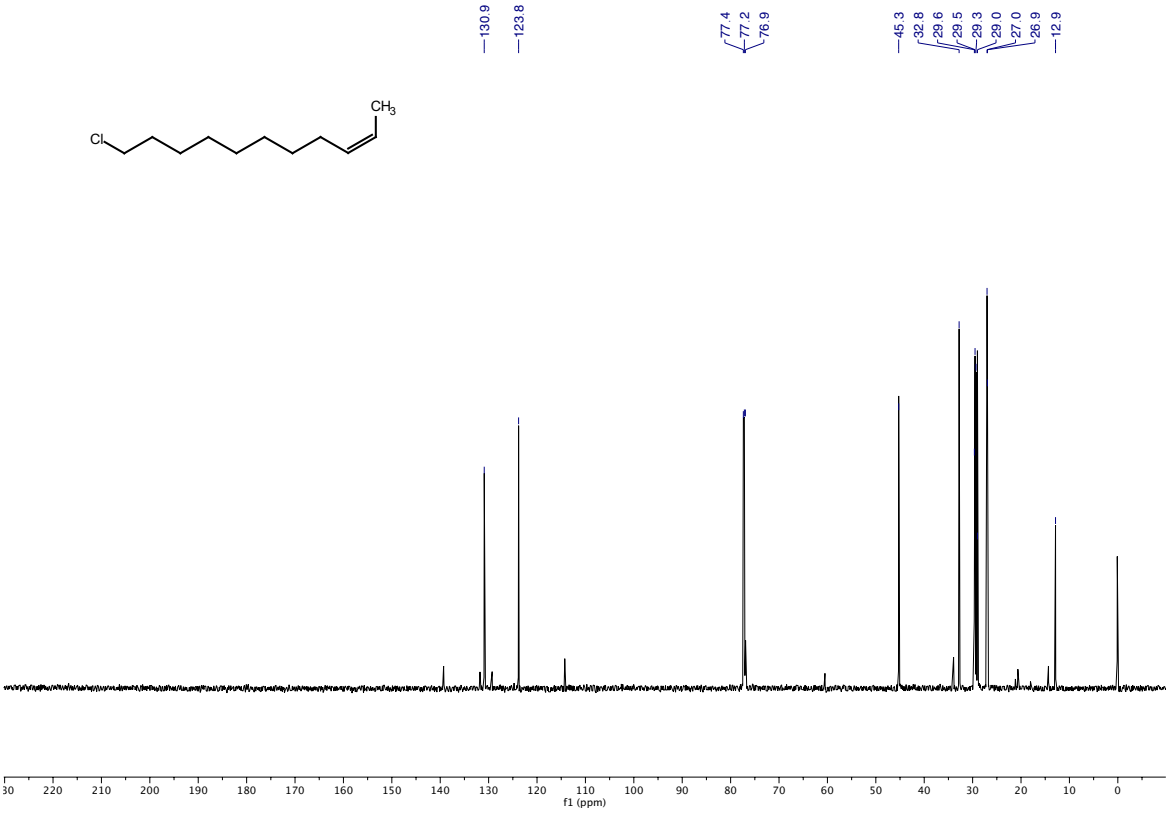
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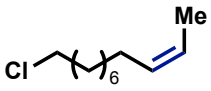
Cl
CH3
f1 (ppm)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Cl
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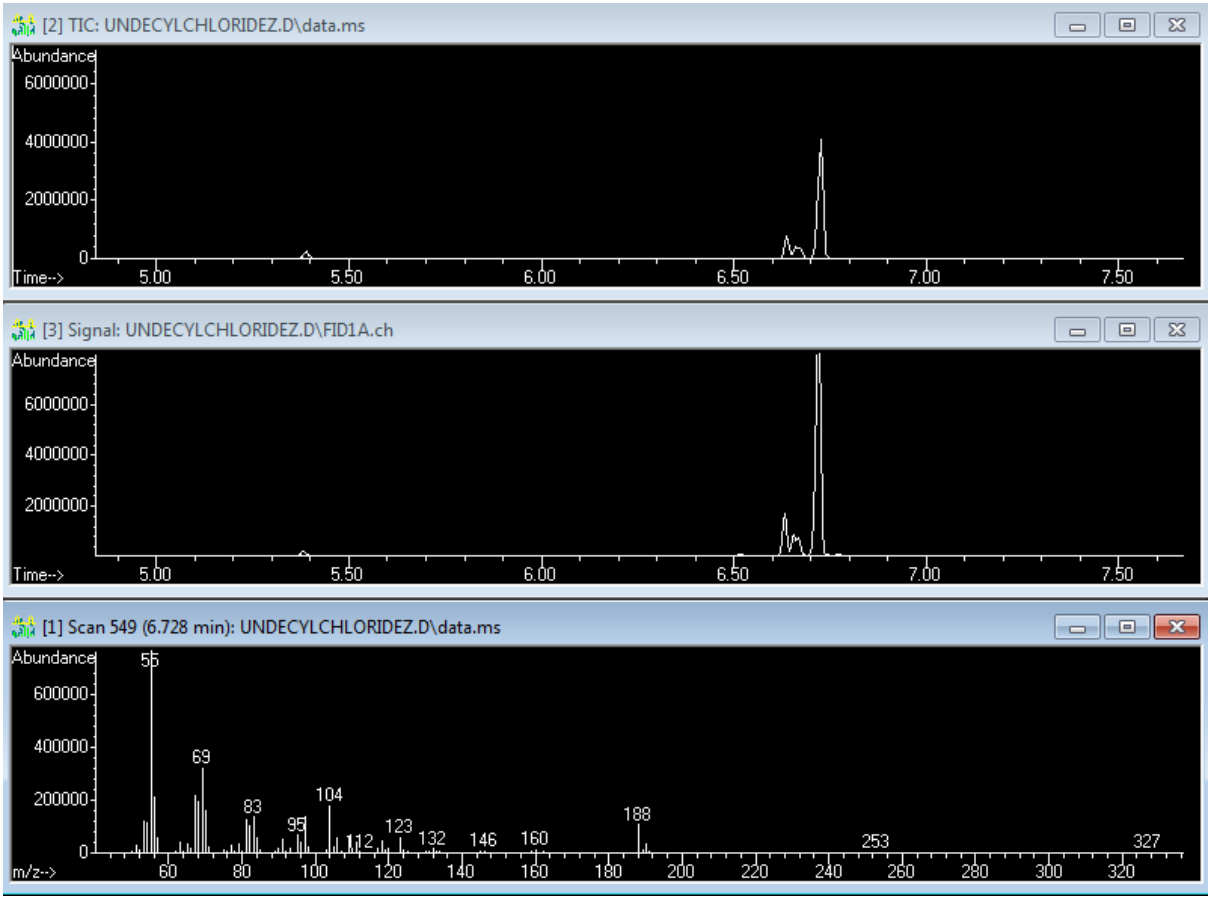
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6.50
7.00
7.50
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4000000
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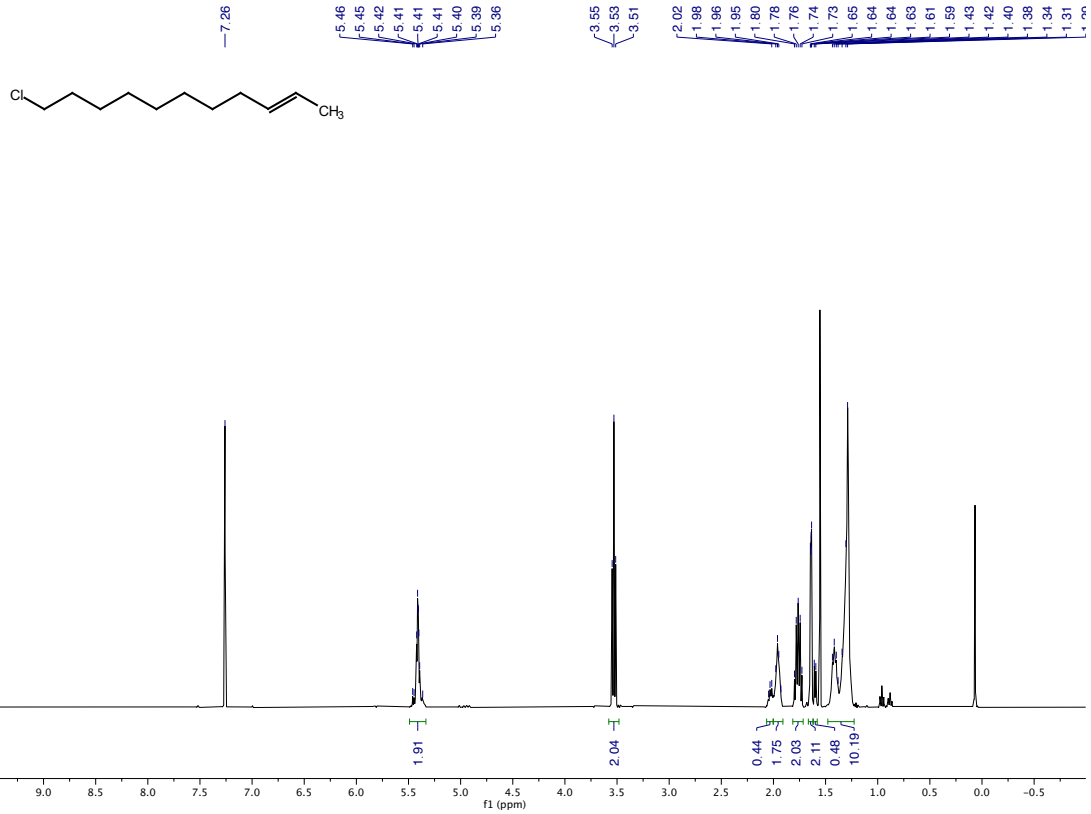
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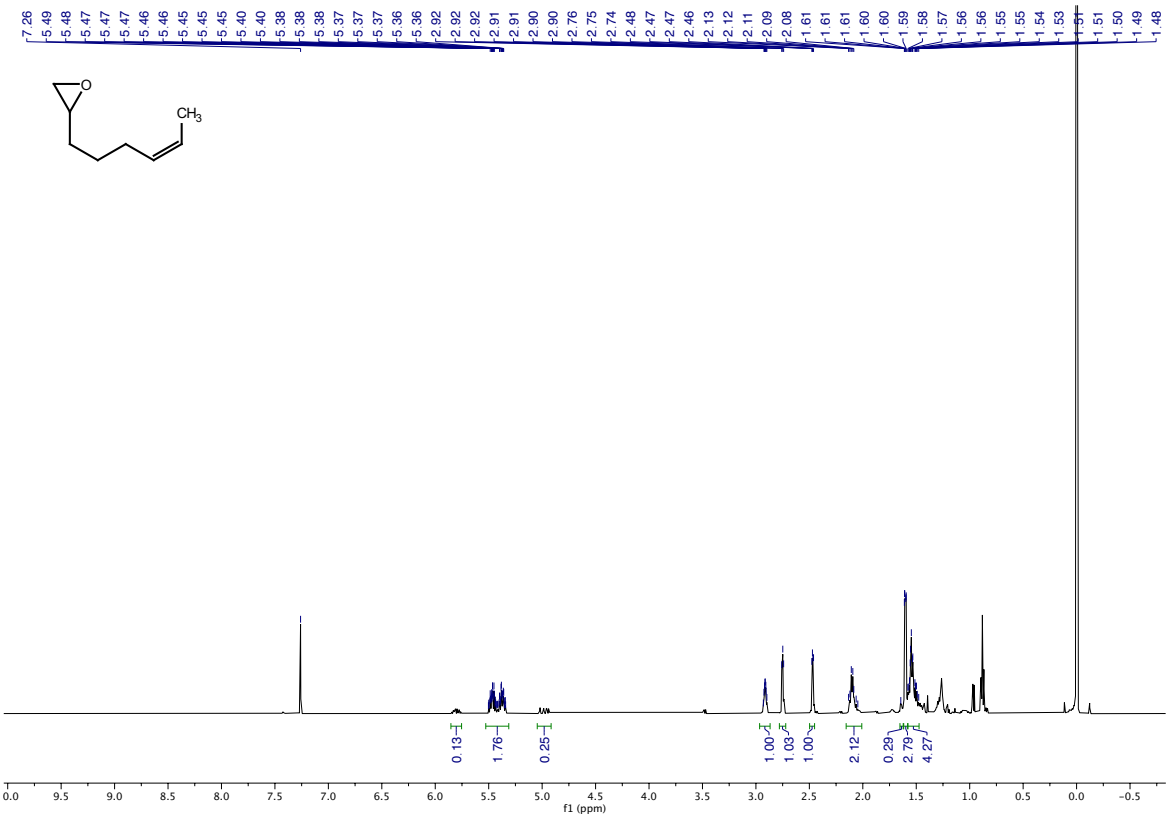
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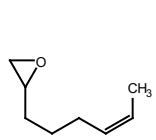
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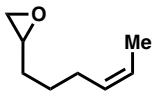
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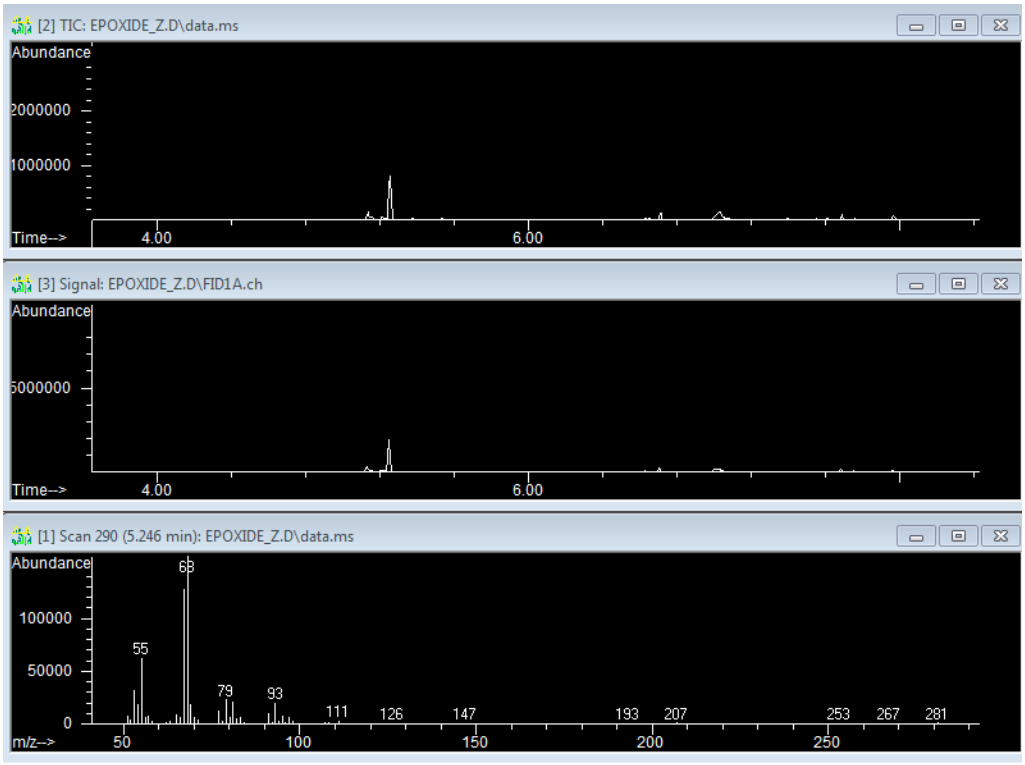
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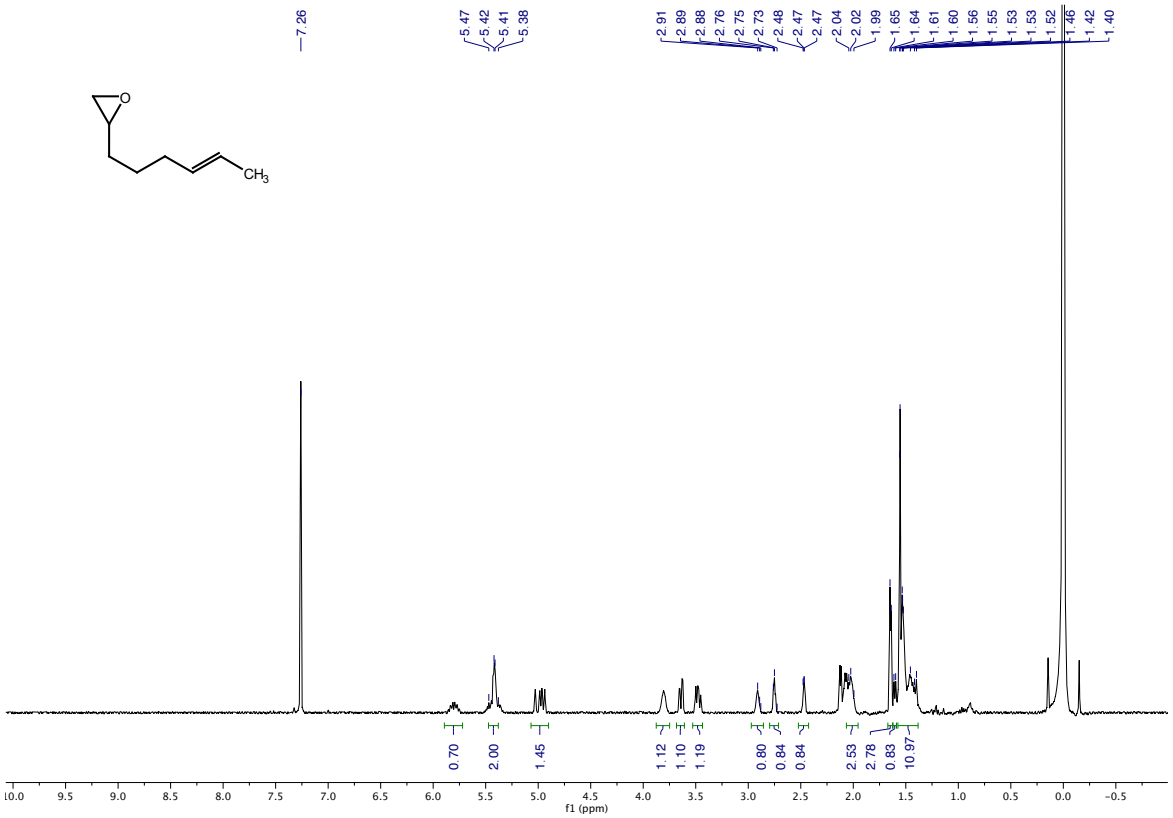
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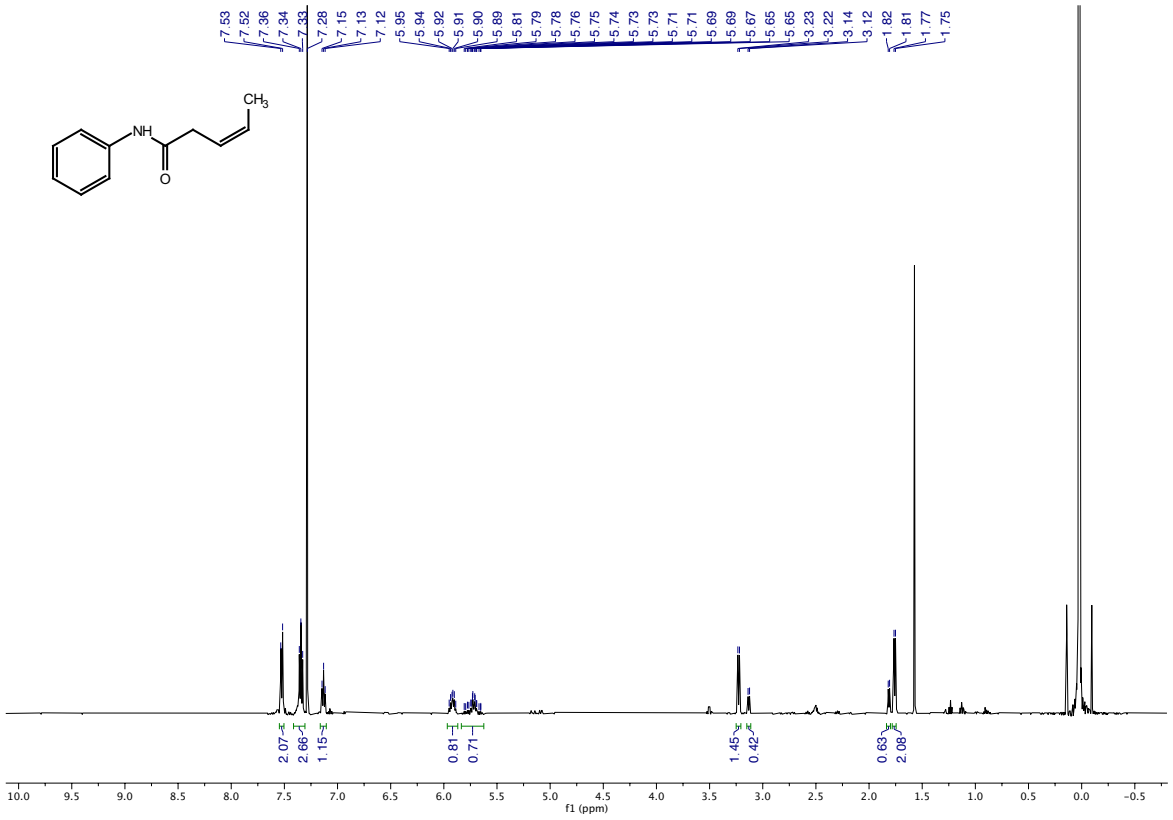
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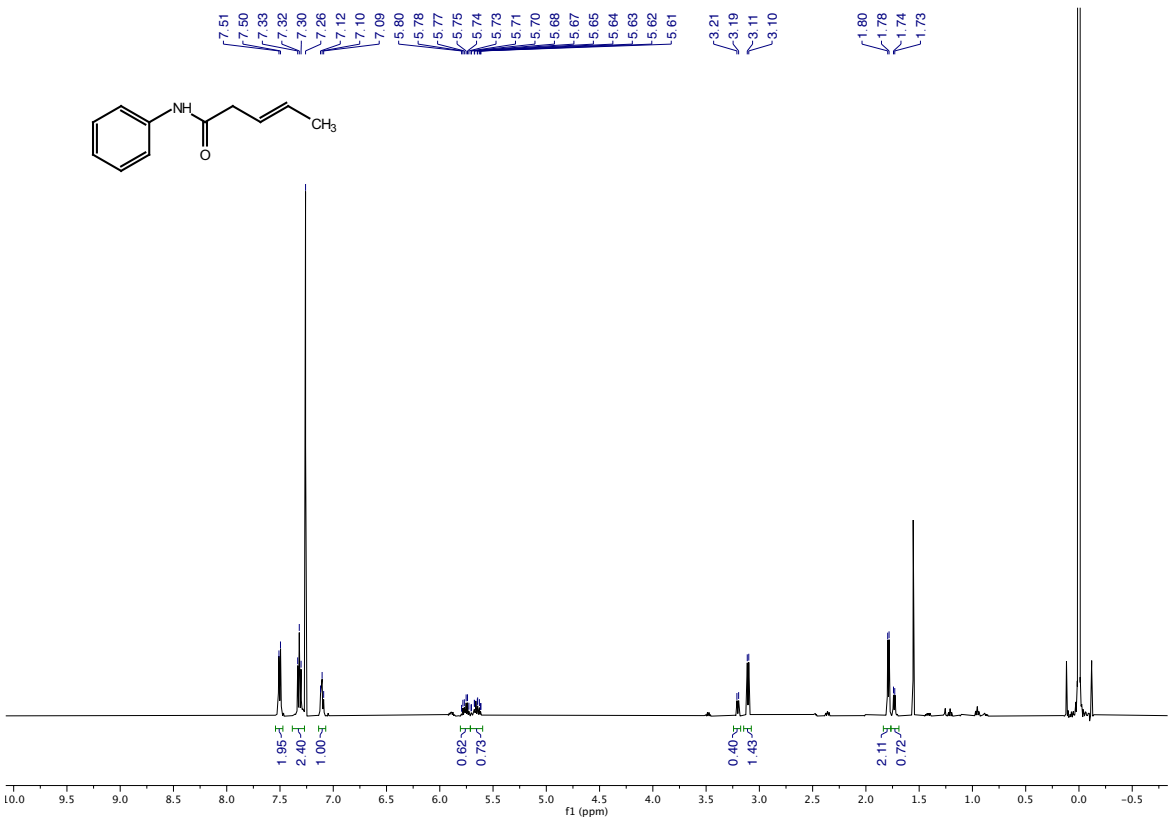
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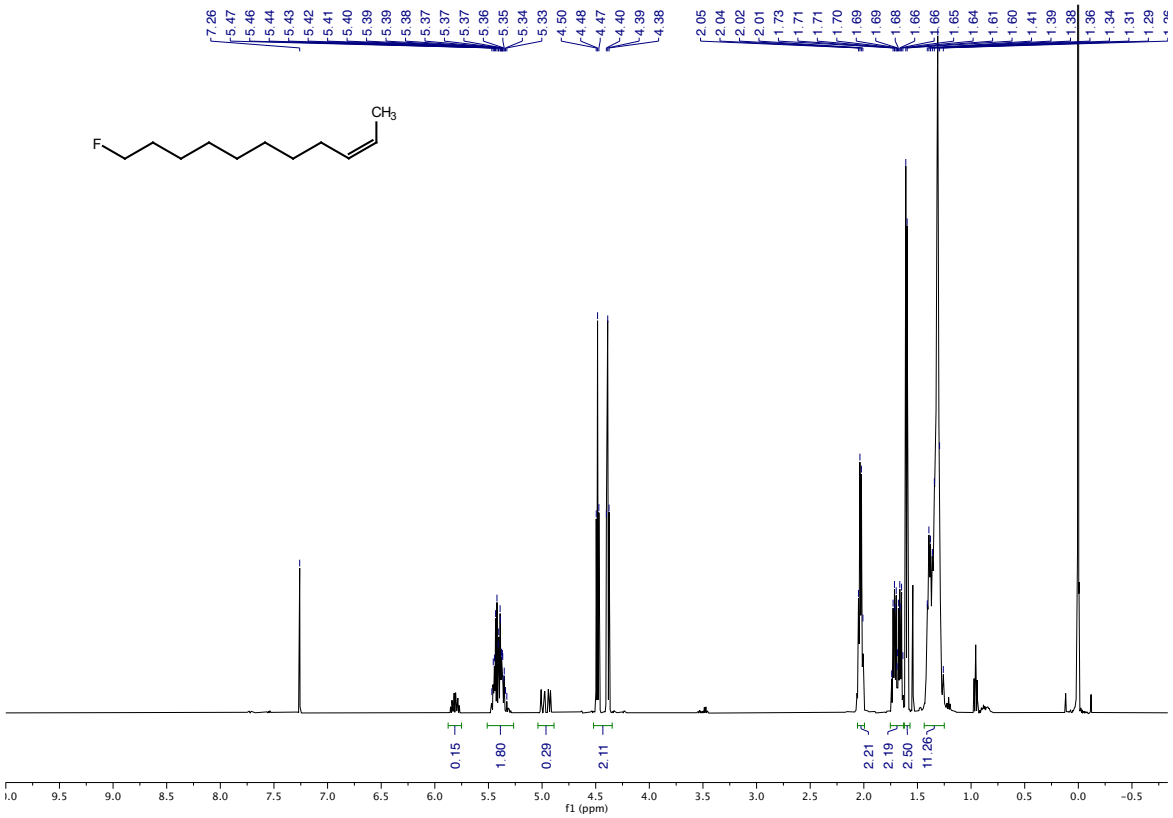
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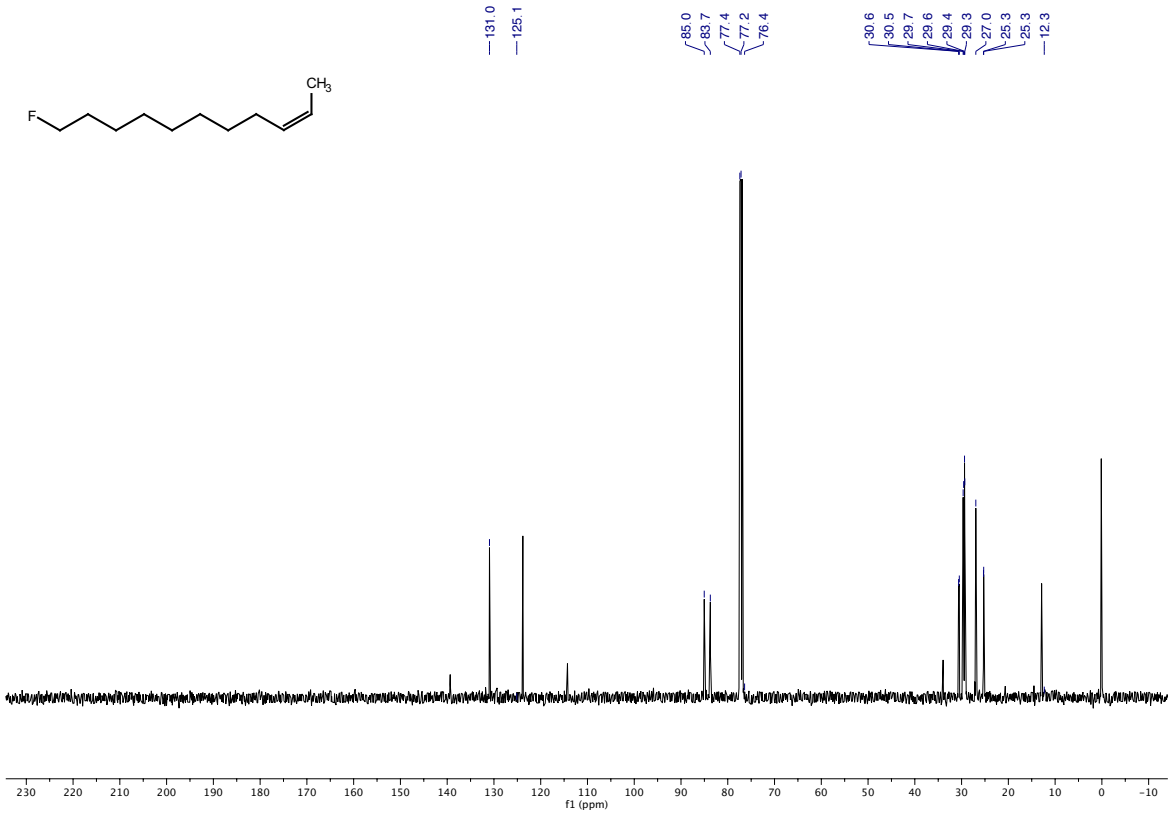
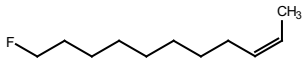
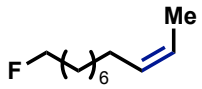
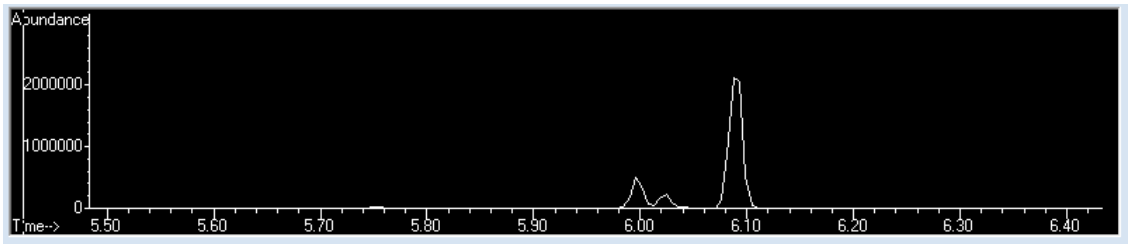
CH3
F
0.15
1.80
0.29
2.11
2.21
2.19
2.50
11.26
f1 (ppm)

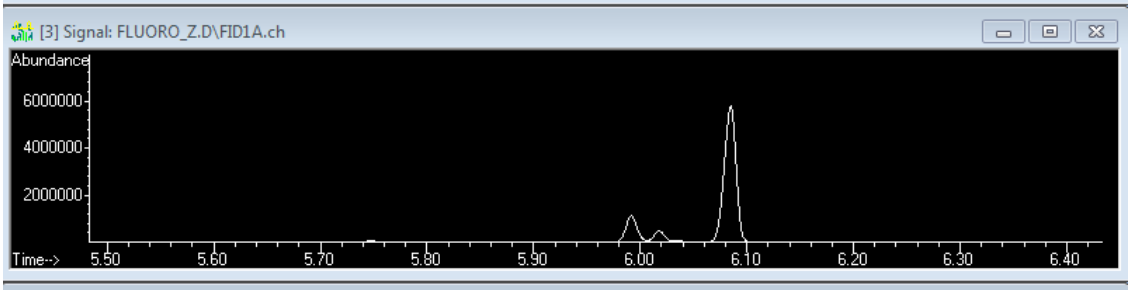

131.0
125.1
85.0
83.7
77.4
77.2
76.4
30.6
30.5
29.7
29.6
29.4
29.3
27.0
25.3
25.3
12.3
CH3
F
f1 (ppm)

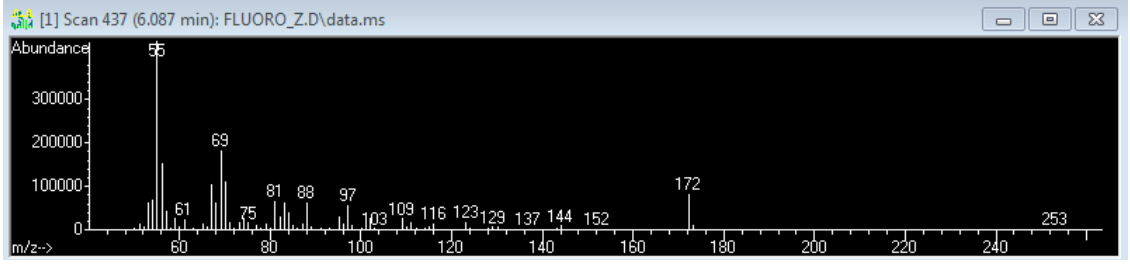

CH3
F

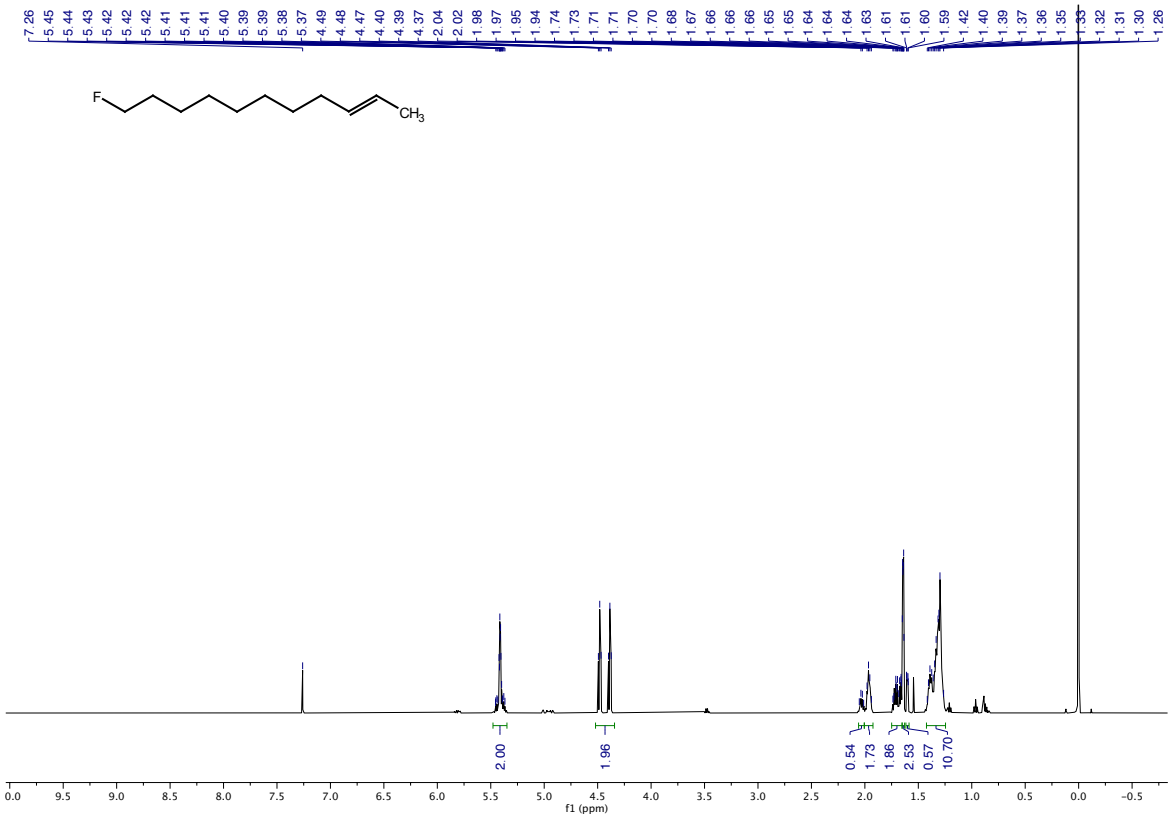
220.66
f1 (ppm)

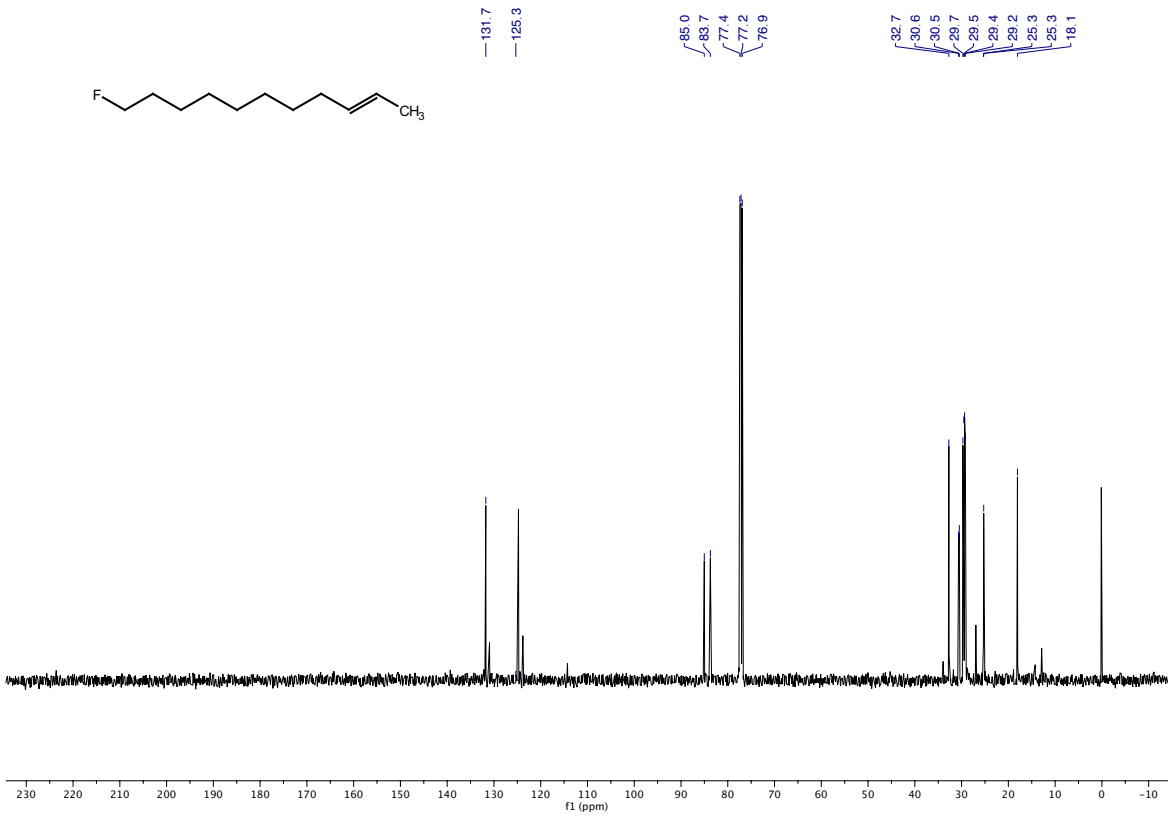

Me
F
6

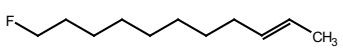

Abundance
2000000
1000000
0
Time-->
5.50
5.60
5.70
5.80
5.90
6.00
6.10
6.20
6.30
6.40


[3] Signal: FLUORO_Z.D\FID1A.ch
Abundance
6000000
4000000
2000000
Time-->
5.50
5.60
5.70
5.80
5.90
6.00
6.10
6.20
6.30
6.40

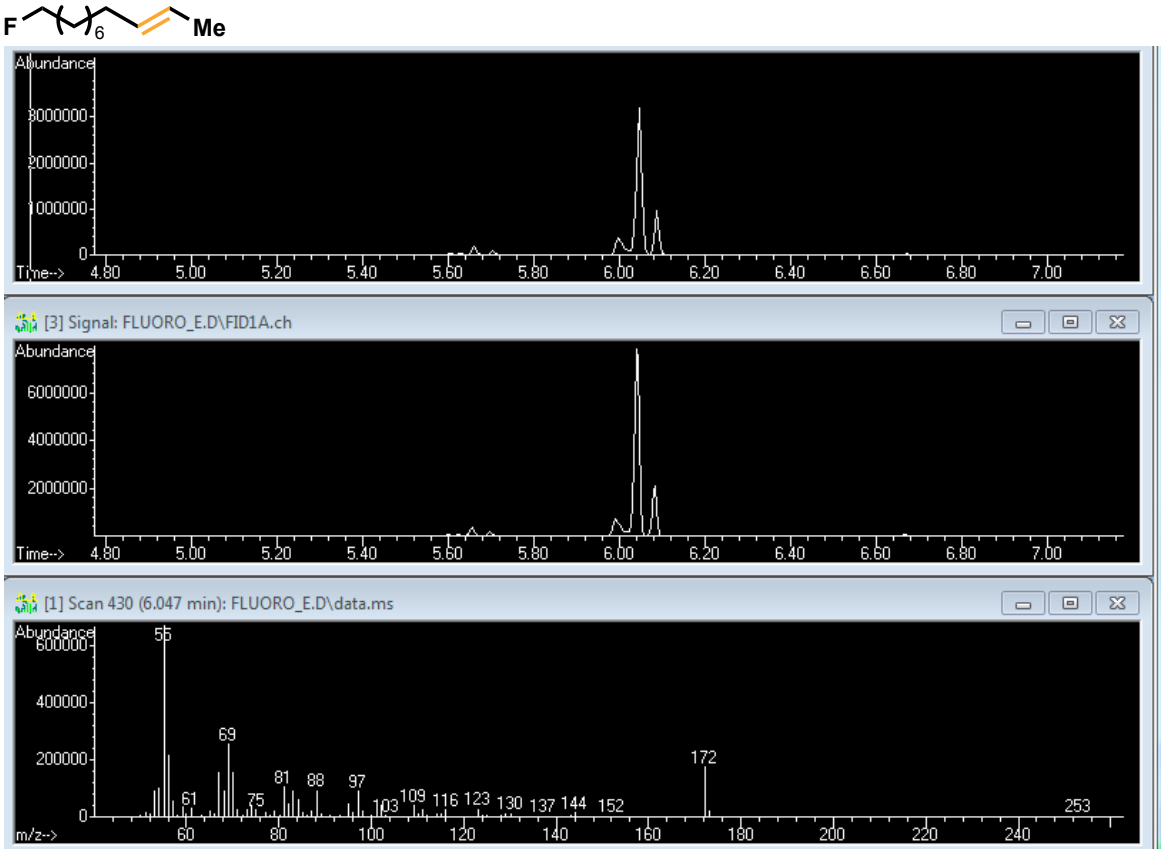

[1] Scan 437 (6.087 min): FLUORO_Z.D\data.ms
Abundance
300000
200000
100000
0
m/z-->
55
69
61
75
81
88
97
103
109
116
123
129
137
144
152
172
253
60
80
100
120
140
160
180
200
220
240

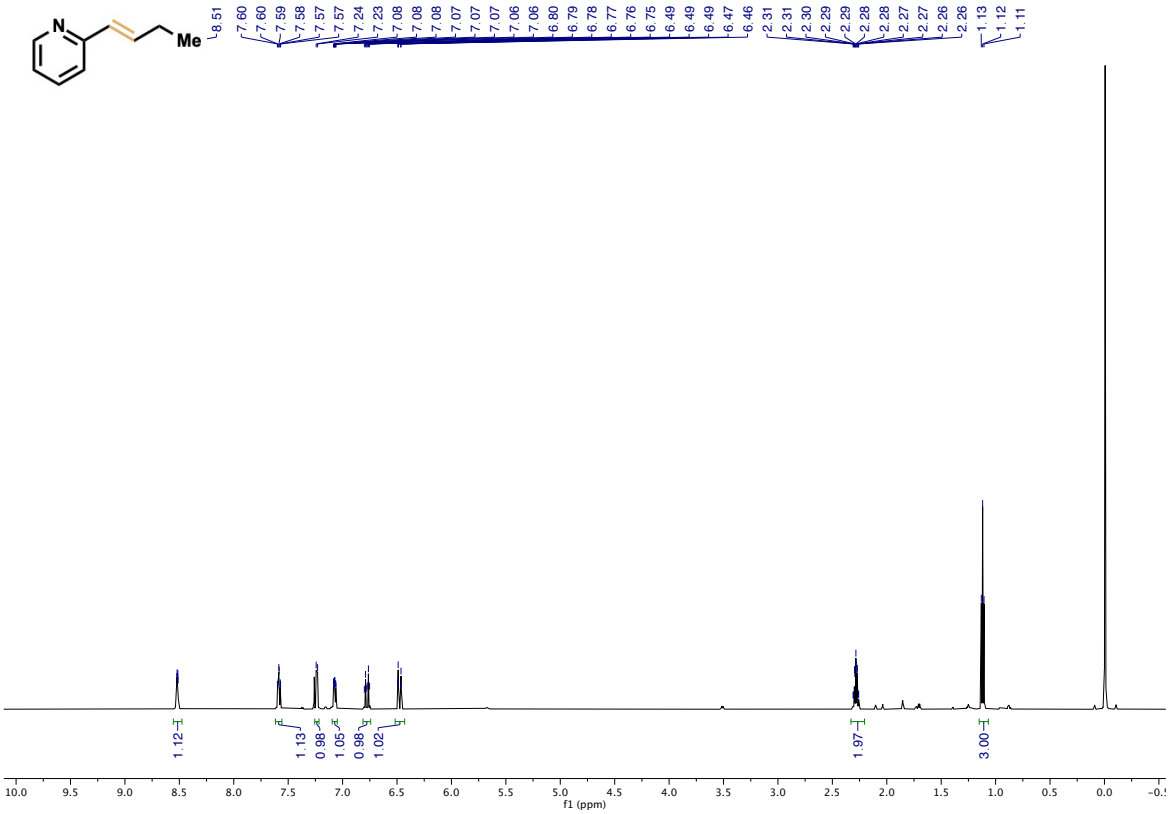

7.26
5.45
5.44
5.43
5.42
5.42
5.42
5.41
5.41
5.41
5.40
5.39
5.39
5.38
5.37
4.49
4.48
4.47
4.40
4.39
4.37
2.04
2.02
1.98
1.97
1.95
1.94
1.74
1.73
1.71
1.71
1.70
1.70
1.68
1.67
1.66
1.66
1.66
1.65
1.65
1.64
1.64
1.64
1.63
1.61
1.61
1.60
1.59
1.42
1.40
1.39
1.37
1.36
1.35
1.33
1.32
1.31
1.30
1.26
F
CH3
2.00
1.96
0.54
1.73
1.86
2.53
0.57
10.70
f1 (ppm)

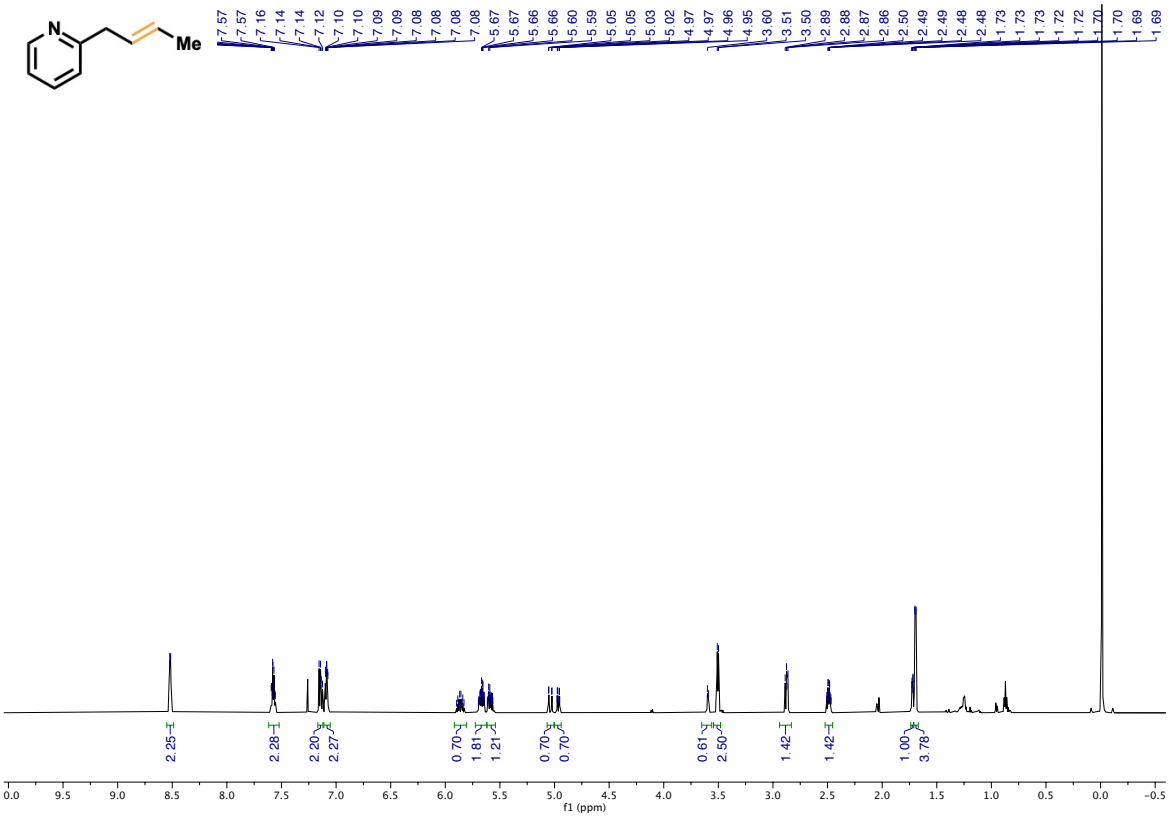

131.7
125.3
85.0
83.7
77.4
77.2
76.9
32.7
30.6
30.5
29.7
29.5
29.4
29.2
25.3
25.3
18.1
F
CH3
f1 (ppm)

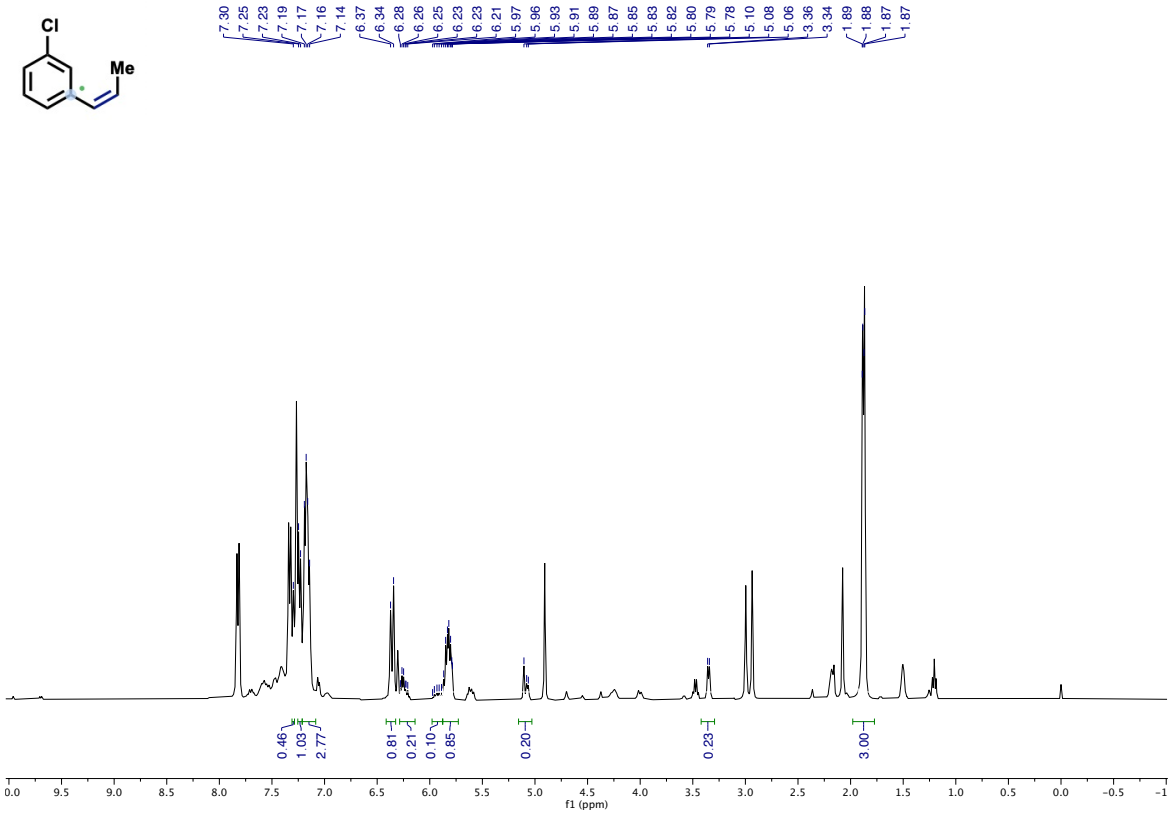

F
CH3

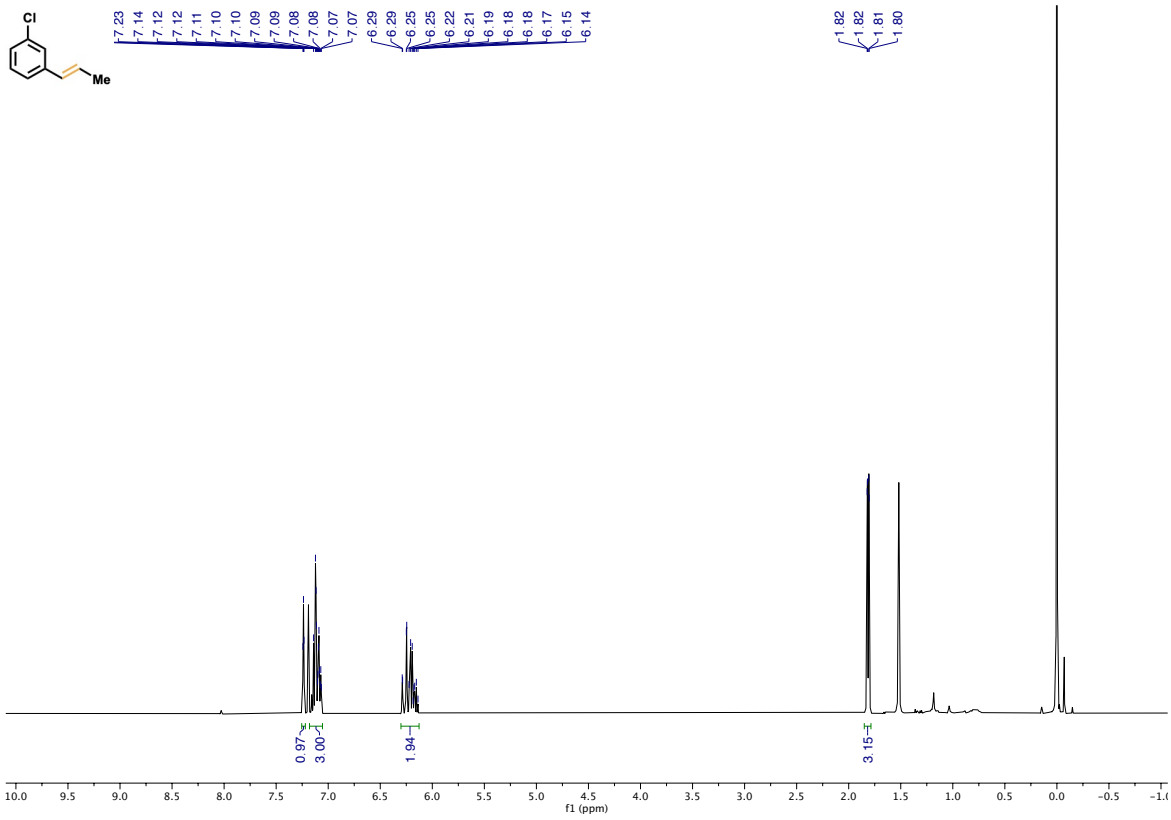
220.66
f1 (ppm)

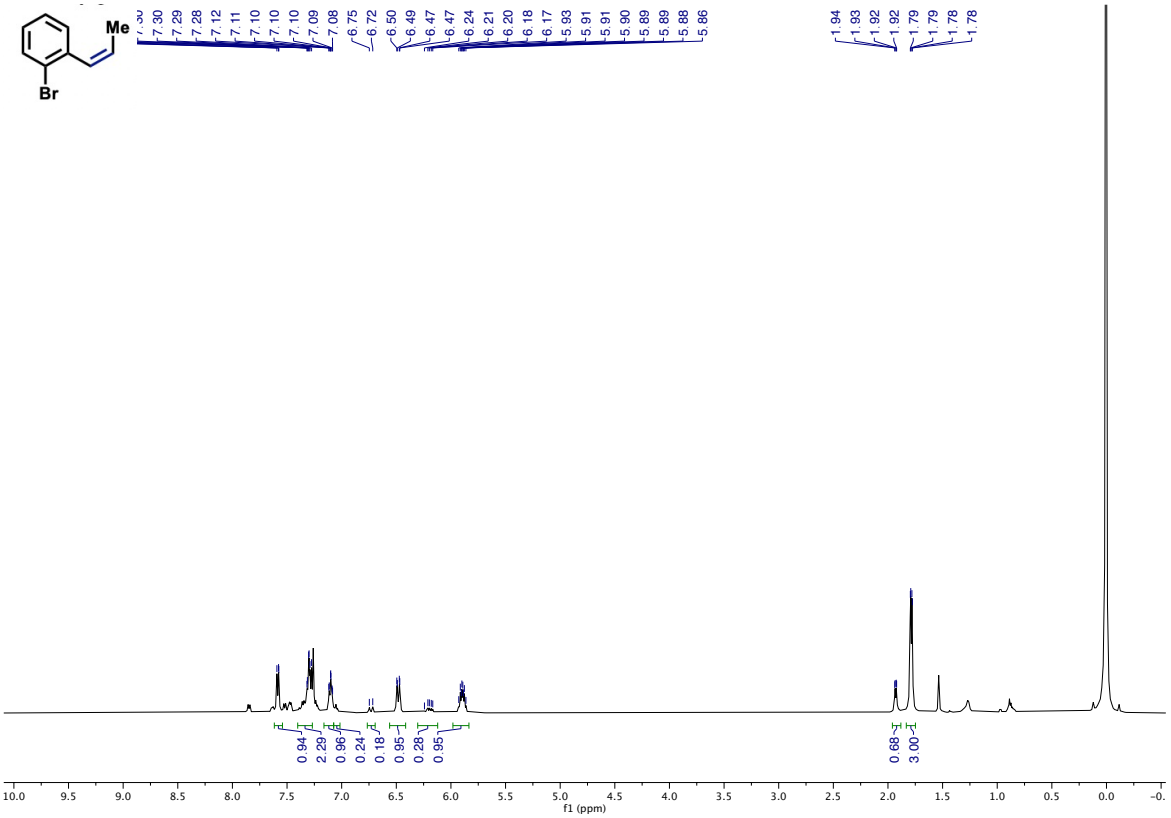

F
6
Me
Abundance
Time-->
[3] Signal: FLUORO_E.D\FID1A.ch
[1] Scan 430 (6.047 min): FLUORO_E.D\data.ms
m/z-->

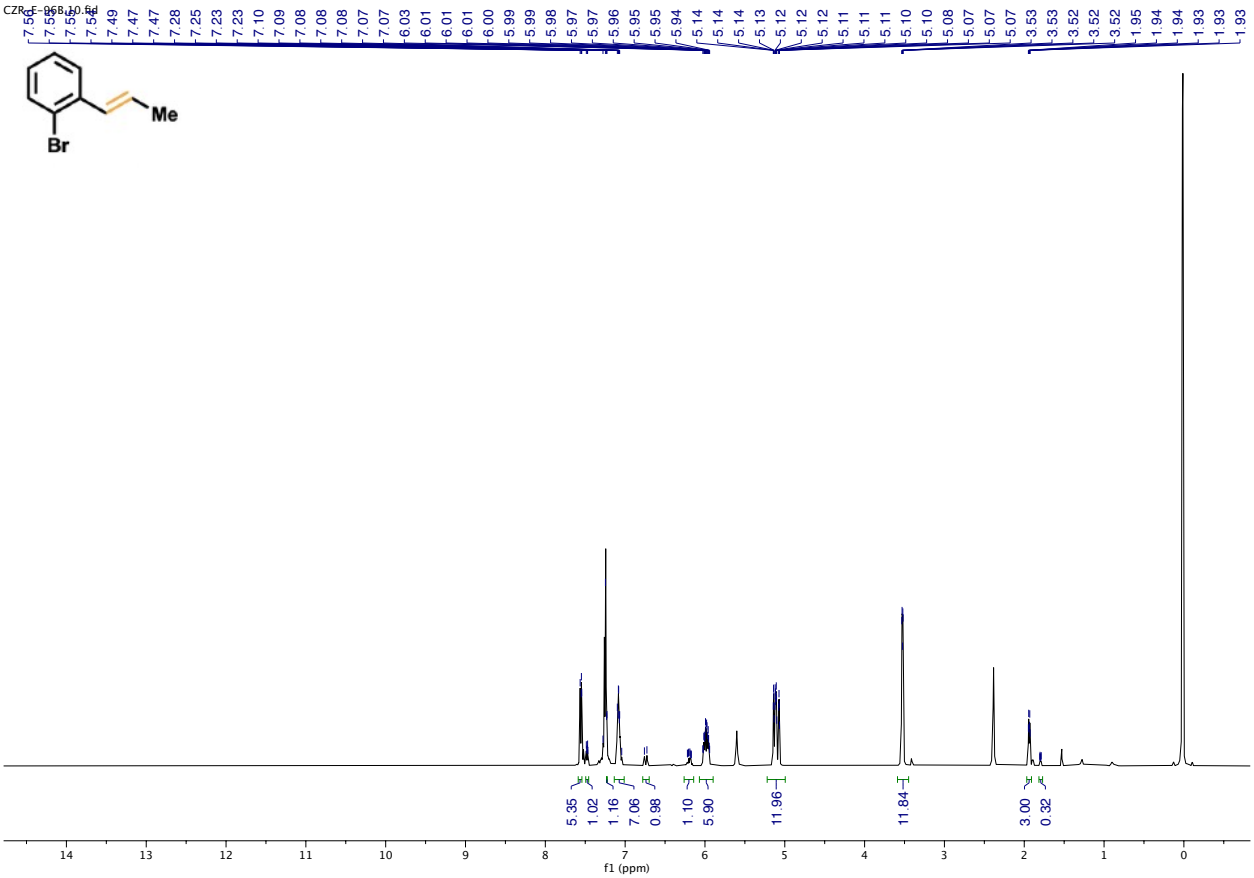

N
Me
8.51
7.60
7.59
7.58
7.57
7.24
7.23
7.08
7.07
7.06
6.80
6.79
6.78
6.77
6.76
6.75
6.49
6.47
6.46
2.31
2.30
2.29
2.28
2.27
2.26
1.13
1.12
1.11
1.12
1.13
0.98
1.05
0.98
1.02
1.97
3.00
f1 (ppm)

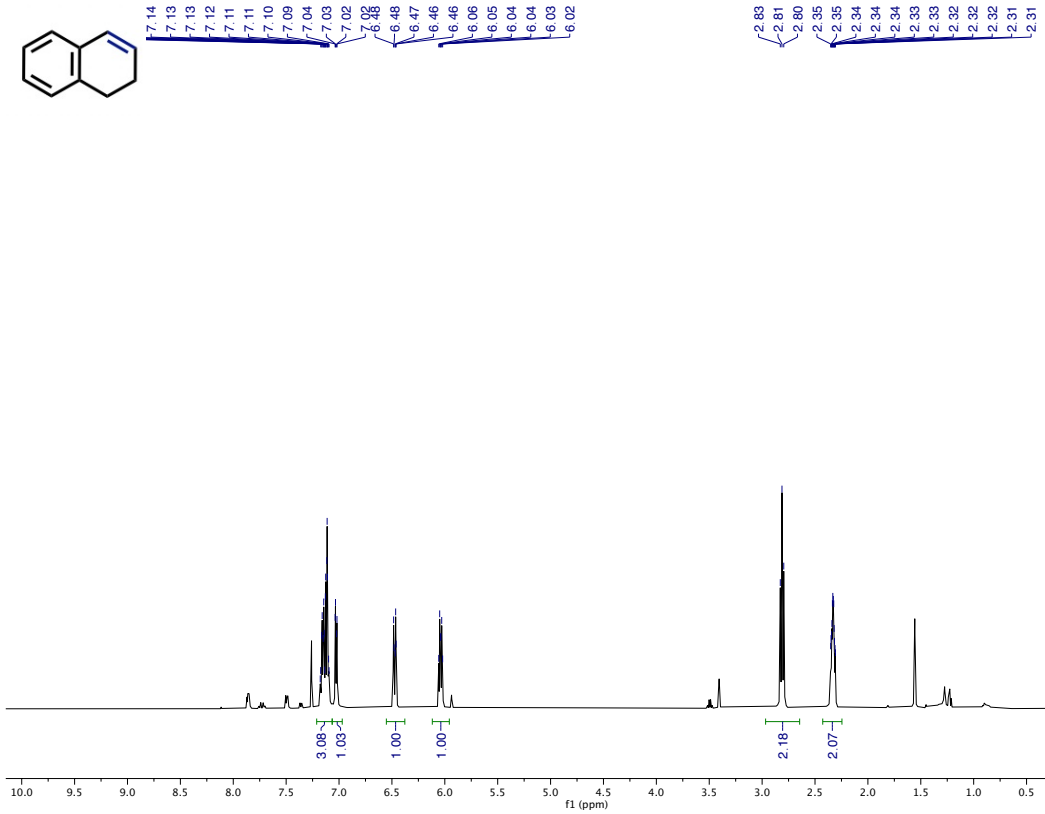

N
Me
7.57
7.16
7.14
7.12
7.10
7.09
7.08
5.67
5.66
5.60
5.59
5.05
5.03
5.02
4.97
4.96
4.95
3.60
3.51
3.50
2.89
2.88
2.87
2.86
2.50
2.49
2.48
1.73
1.72
1.70
1.69
2.25
2.28
2.20
2.27
0.70
1.81
1.21
0.70
0.70
0.61
2.50
1.42
1.42
1.00
3.78
f1 (ppm)

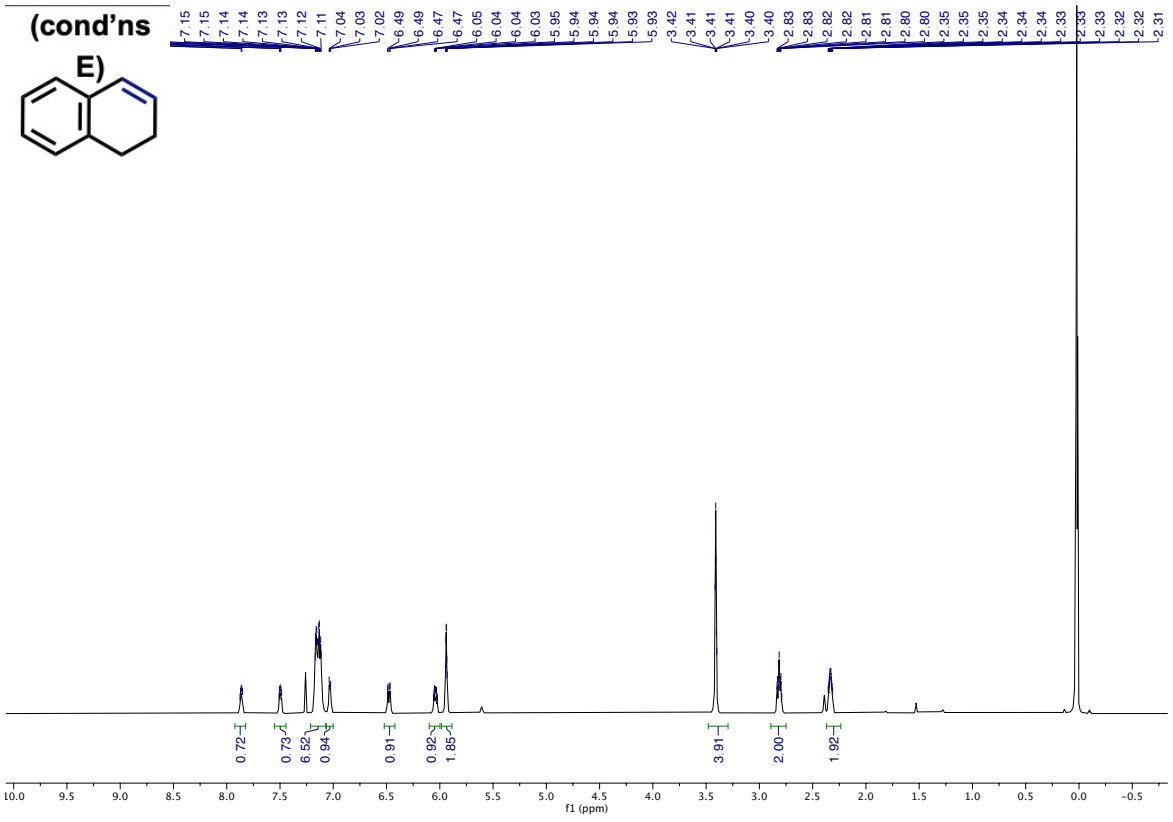

Cl
Me
7.30
7.25
7.23
7.19
7.17
7.16
7.14
6.37
6.34
6.28
6.26
6.25
6.23
6.23
6.21
5.97
5.96
5.93
5.91
5.89
5.87
5.85
5.83
5.82
5.80
5.79
5.78
5.10
5.08
5.06
3.36
3.34
1.89
1.88
1.87
1.87
0.46
1.03
2.77
0.81
0.21
0.10
0.85
0.20
0.23
3.00
f1 (ppm)

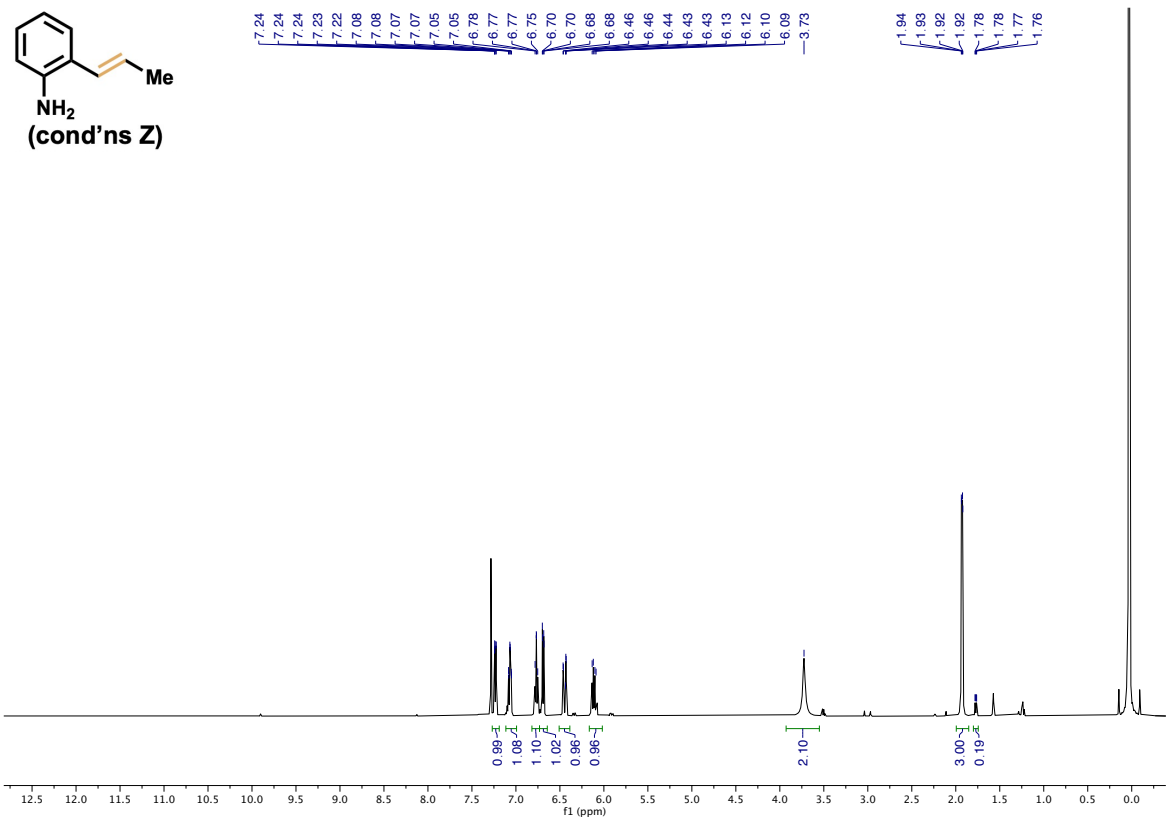

Cl
Me
7.23
7.14
7.12
7.12
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.07
6.29
6.29
6.25
6.25
6.22
6.21
6.19
6.18
6.18
6.17
6.15
6.14
1.82
1.82
1.81
1.80
0.97
3.00
1.94
3.15
f1 (ppm)

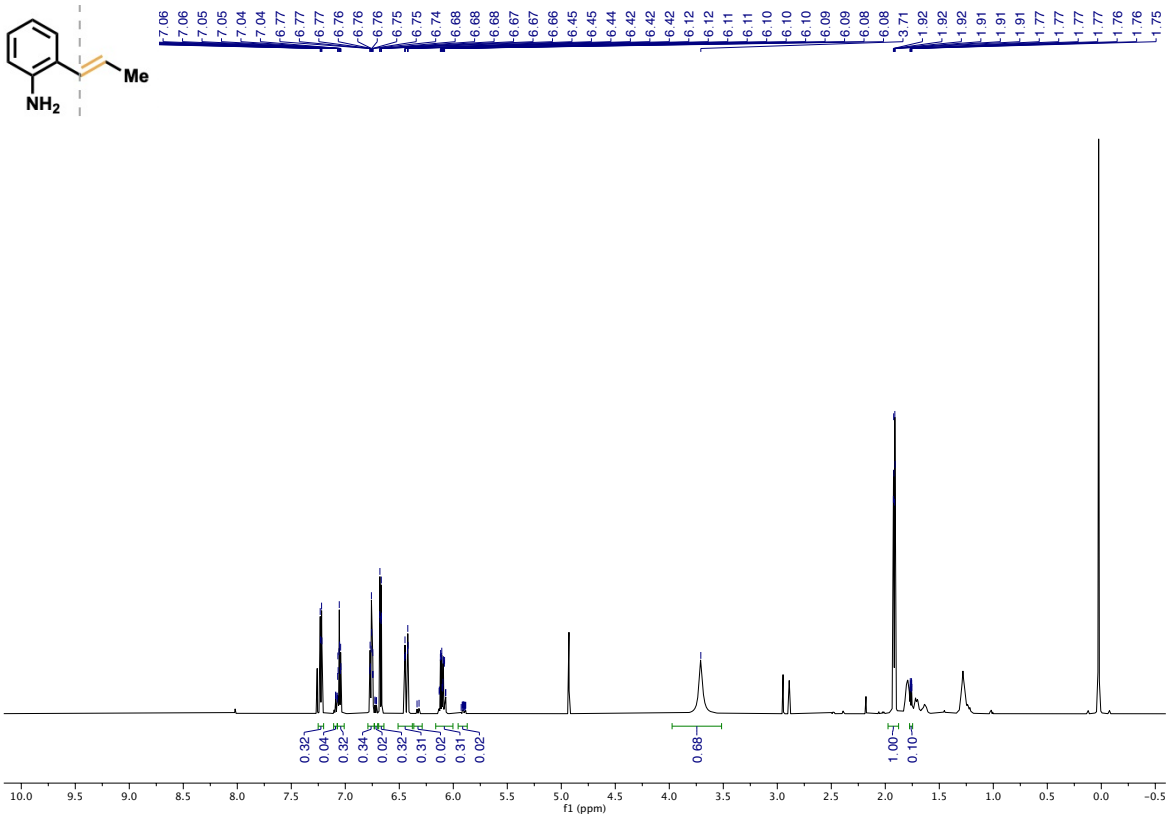

Me
Br
f1 (ppm)

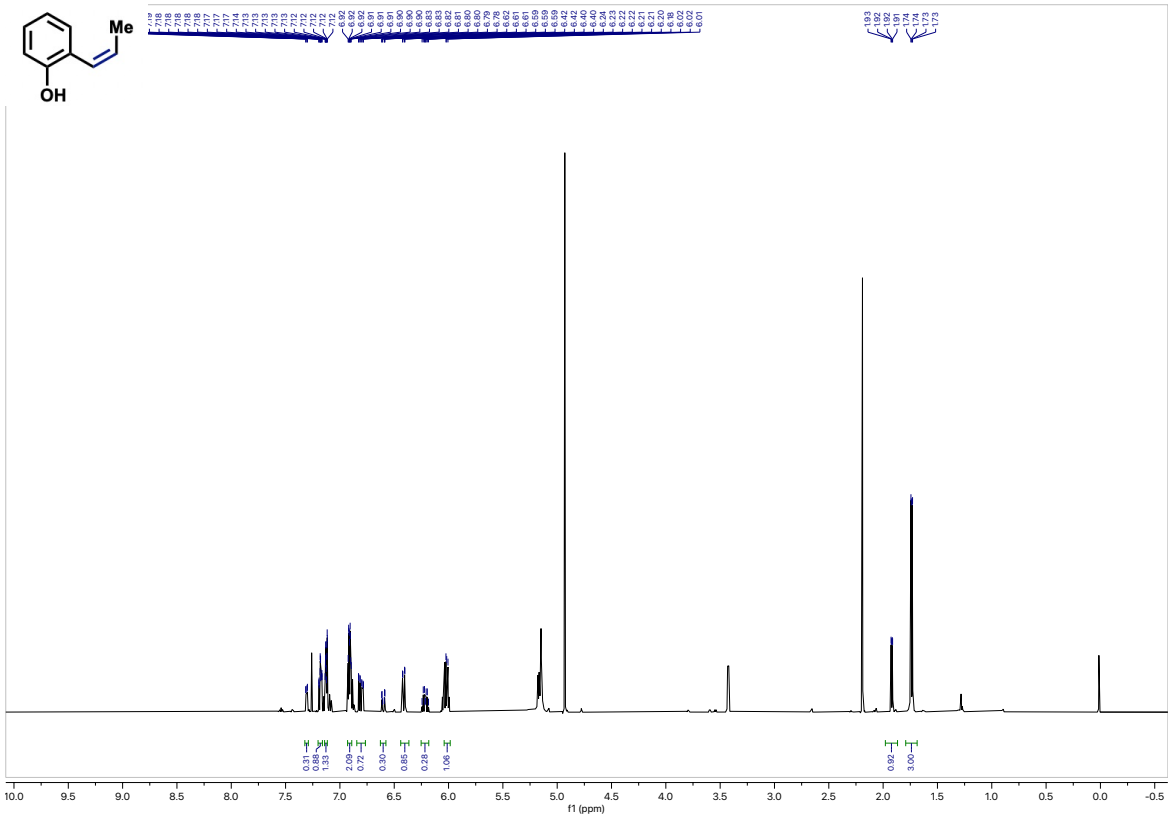

Me
Br
f1 (ppm)

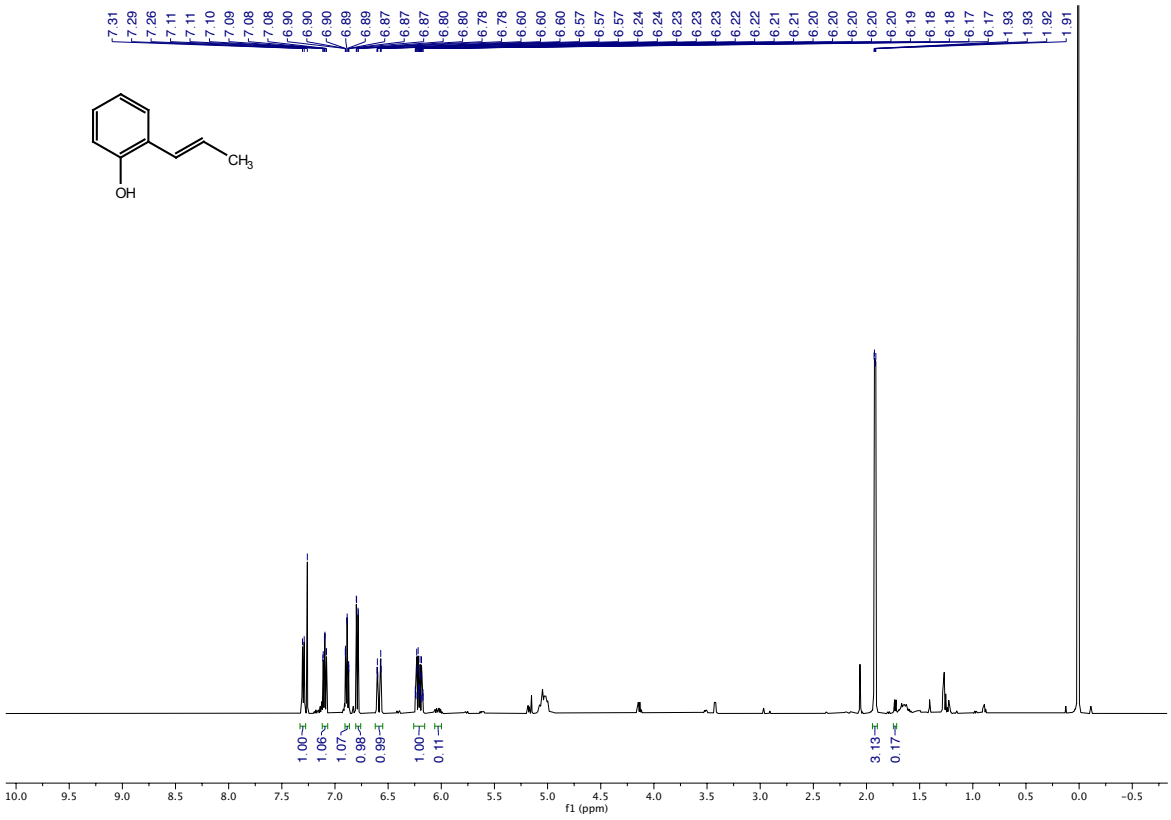

7.14
7.13
7.13
7.12
7.11
7.11
7.10
7.09
7.04
7.03
7.02
6.48
6.47
6.46
6.46
6.06
6.05
6.04
6.04
6.03
6.02
2.83
2.81
2.80
2.35
2.34
2.34
2.34
2.33
2.32
2.32
2.31
2.31
3.08
1.03
1.00
1.00
2.18
2.07
f1 (ppm)

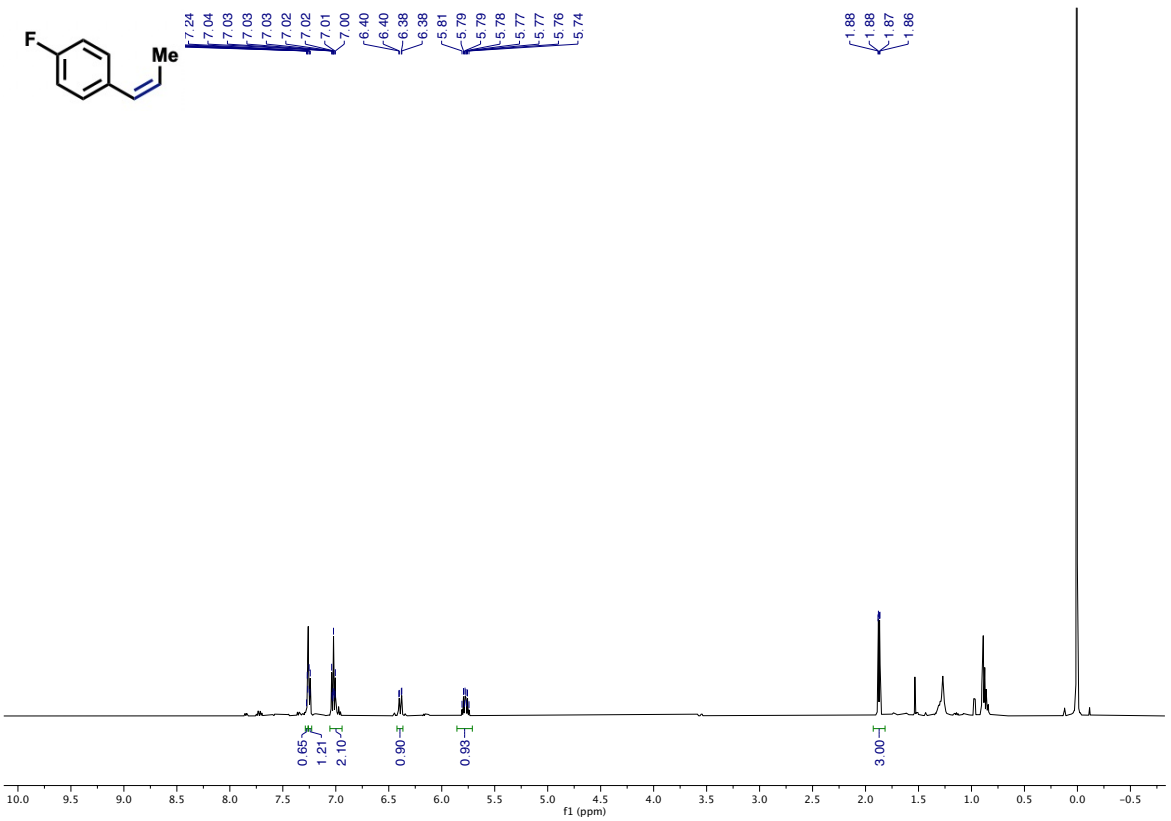

(cond'ns
E)
f1 (ppm)

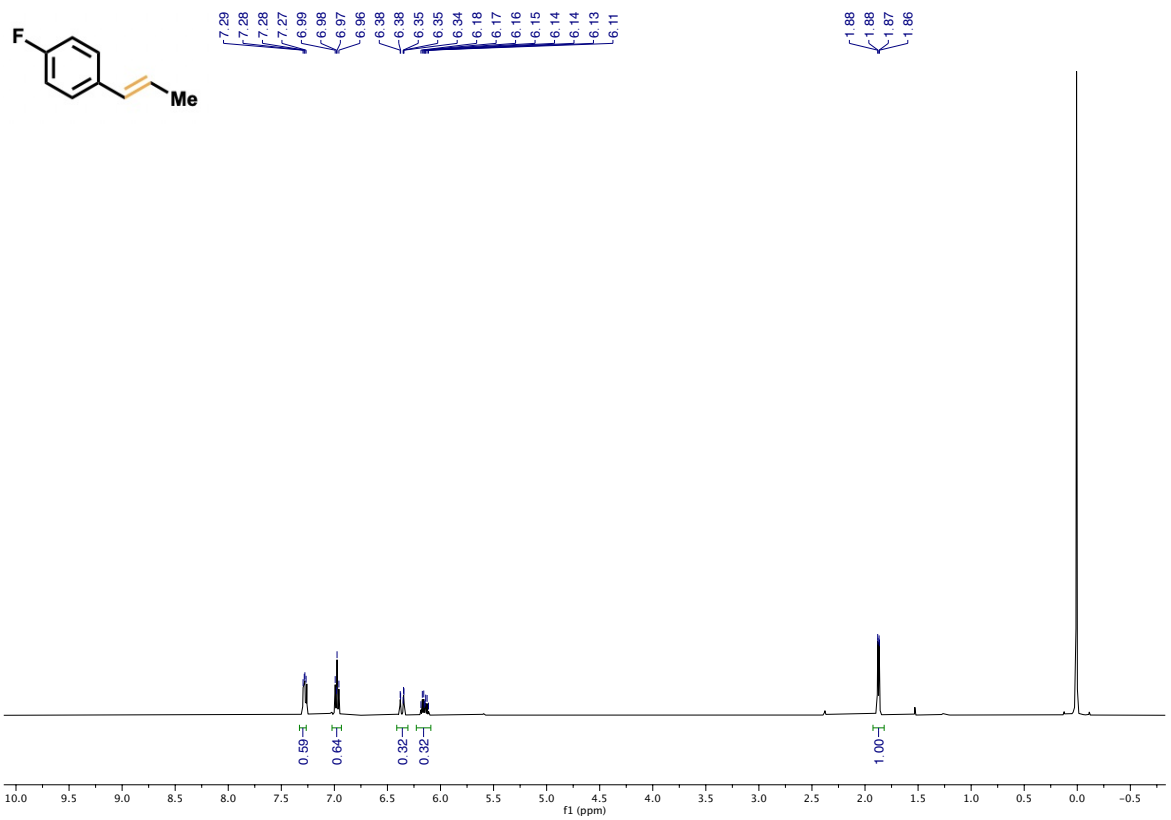

Me
NH2
(cond'ns Z)
7.24
7.24
7.24
7.23
7.22
7.08
7.08
7.07
7.07
7.05
7.05
6.78
6.77
6.77
6.75
6.70
6.70
6.68
6.68
6.46
6.46
6.44
6.43
6.43
6.13
6.12
6.10
6.09
3.73
1.94
1.93
1.92
1.92
1.78
1.78
1.77
1.76
0.99
1.08
1.10
1.02
0.96
0.96
2.10
3.00
0.19
f1 (ppm)

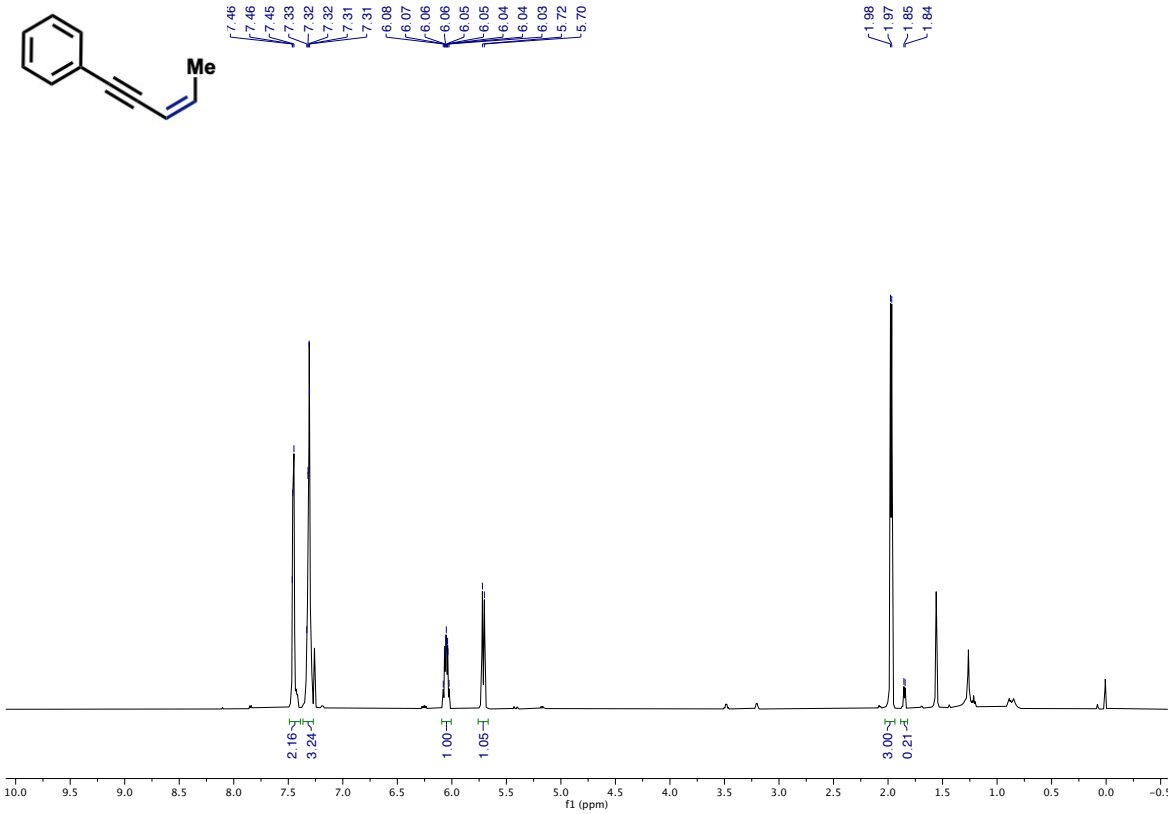

Me
NH2
7.06
7.06
7.05
7.05
7.04
7.04
6.77
6.77
6.77
6.76
6.76
6.76
6.75
6.75
6.74
6.68
6.68
6.67
6.67
6.66
6.45
6.45
6.44
6.42
6.42
6.42
6.12
6.12
6.11
6.11
6.10
6.10
6.10
6.09
6.09
6.08
6.08
3.71
1.92
1.92
1.92
1.91
1.91
1.91
1.77
1.77
1.77
1.77
1.76
1.75
0.32
0.04
0.32
0.34
0.02
0.32
0.31
0.02
0.31
0.02
0.68
1.00
0.10
f1 (ppm)

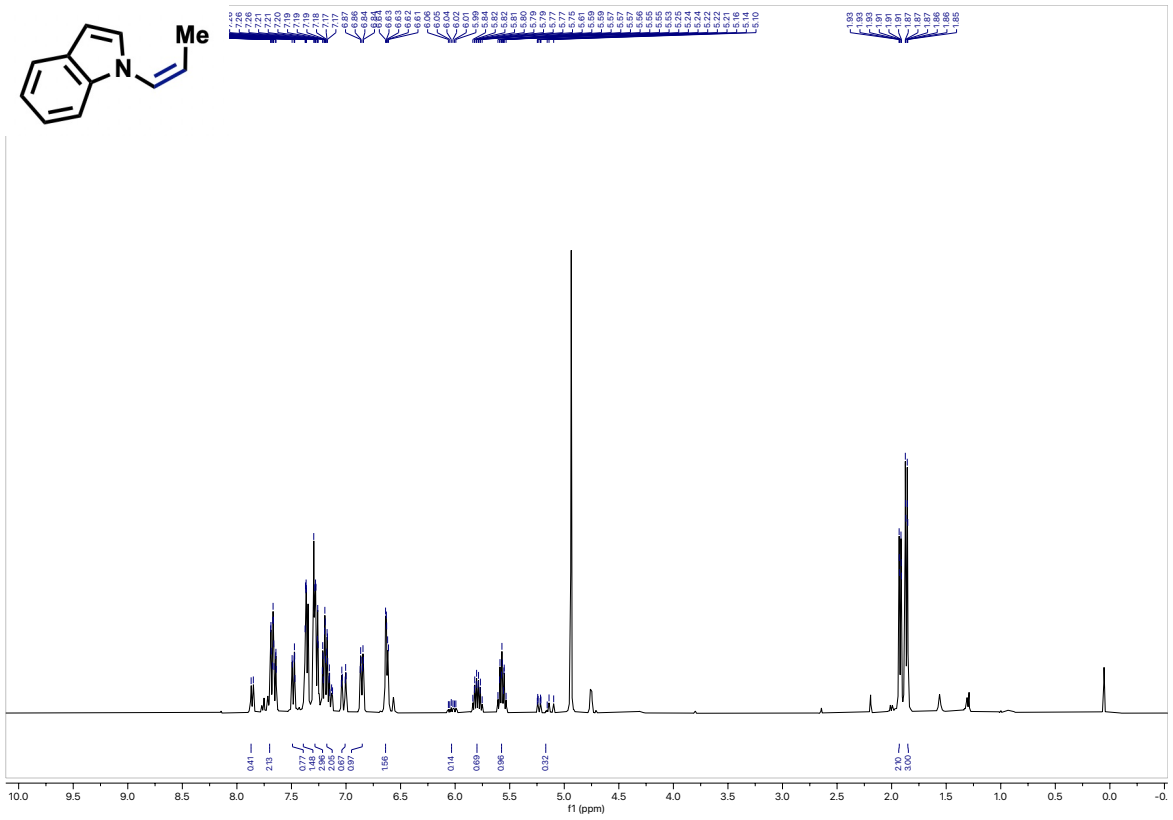

Me
OH
f1 (ppm)

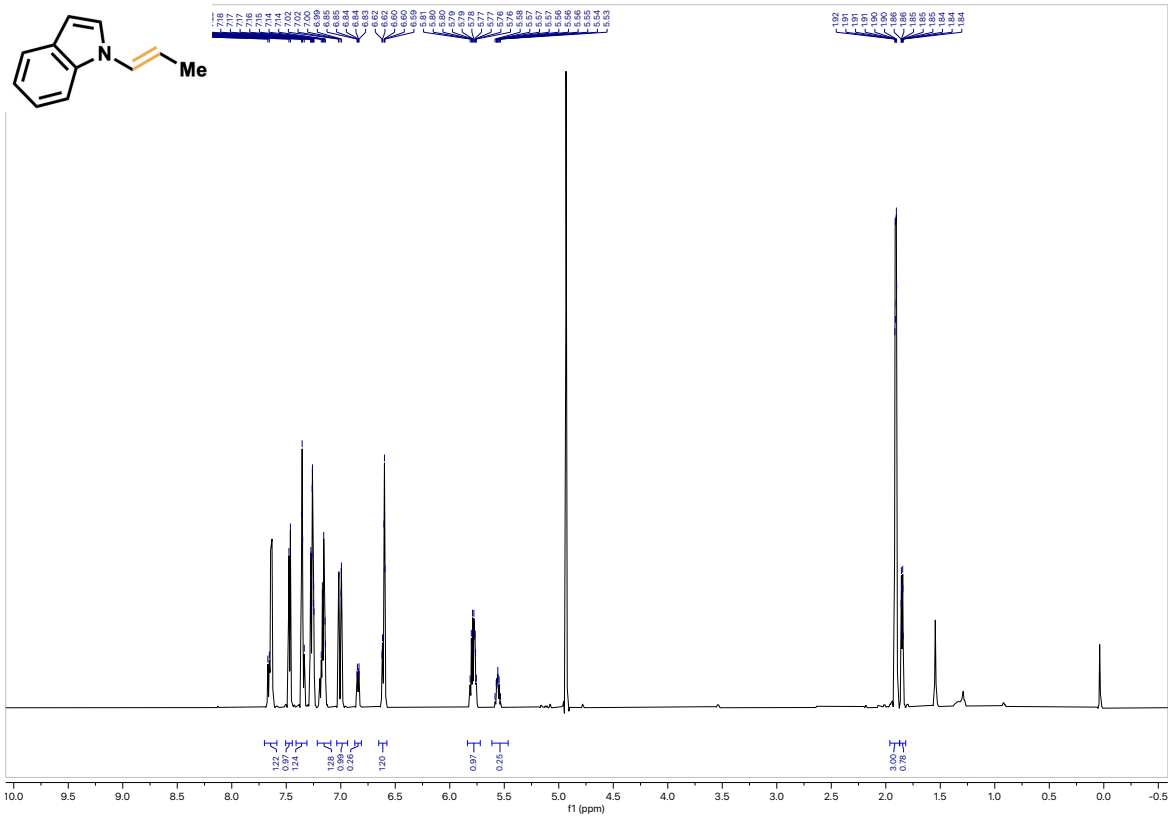

CH3
OH
f1 (ppm)

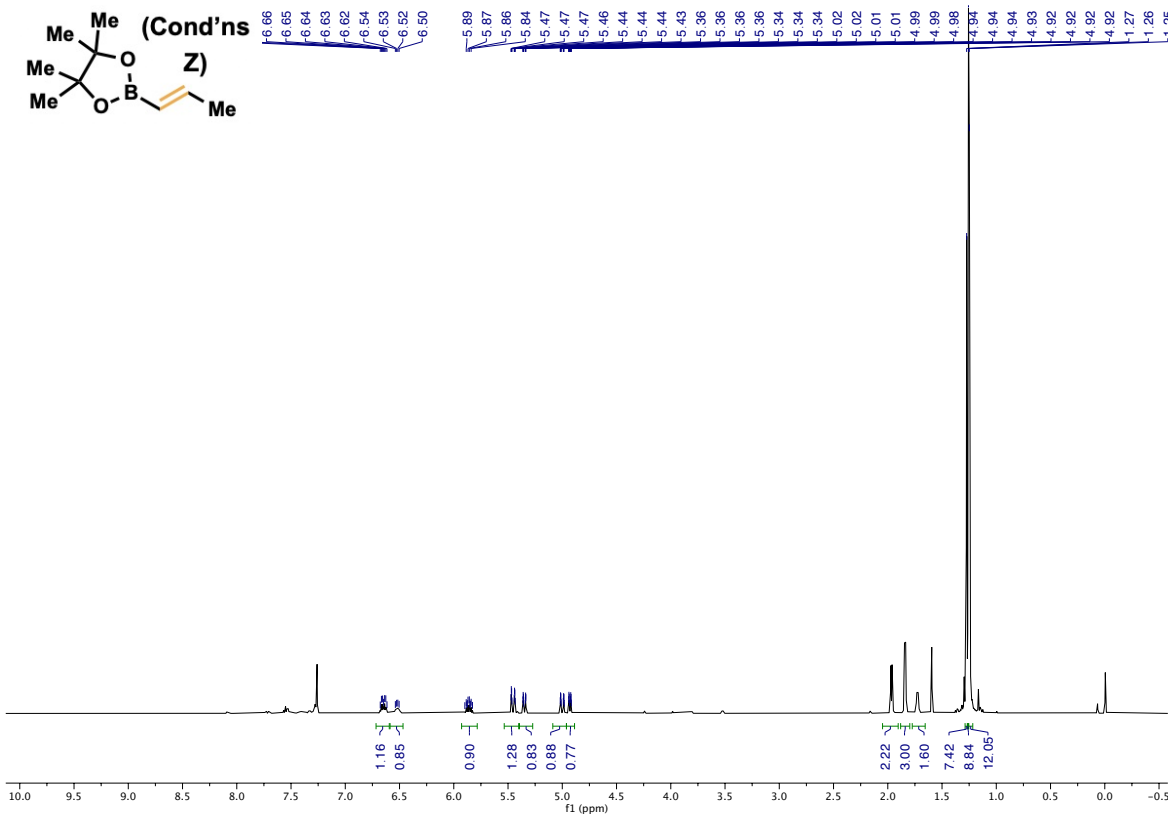

F
Me
7.24
7.04
7.03
7.03
7.03
7.02
7.02
7.01
7.00
6.40
6.40
6.38
6.38
5.81
5.79
5.79
5.78
5.77
5.77
5.76
5.74
1.88
1.88
1.87
1.86
0.65
1.21
2.10
0.90
0.93
3.00
f1 (ppm)

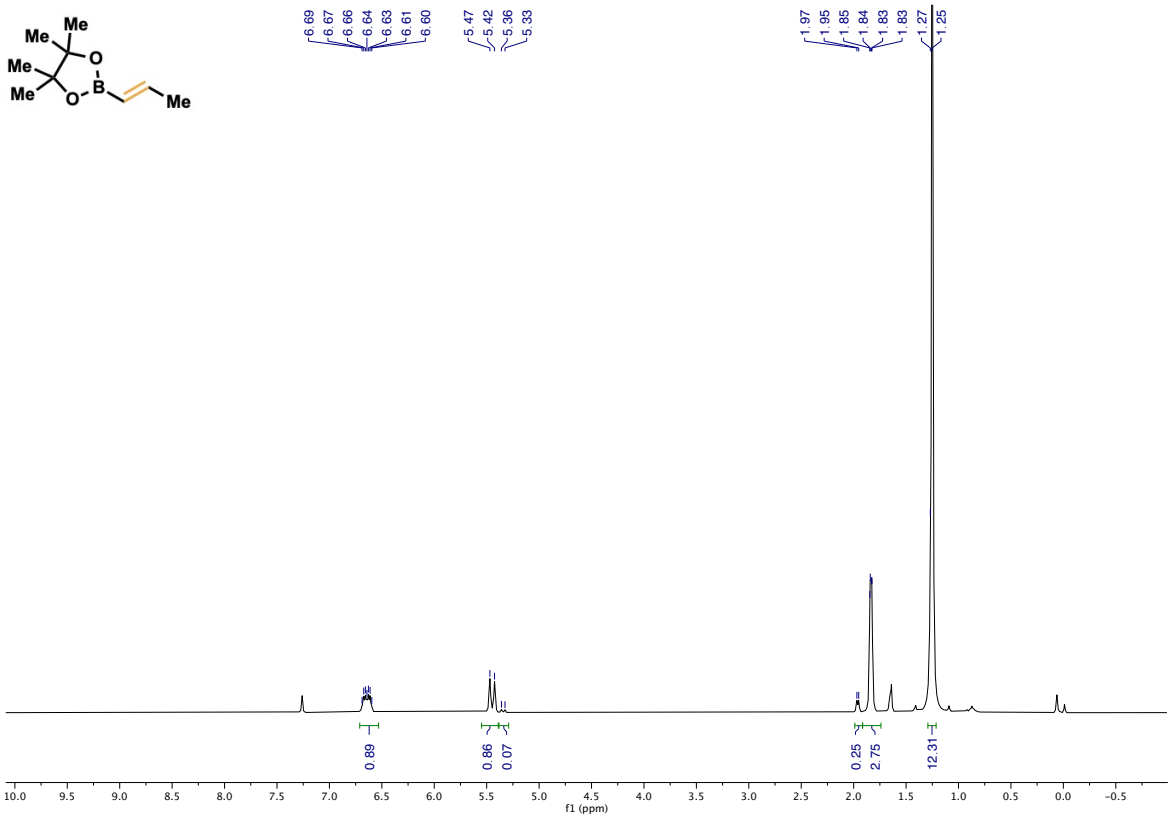

F
Me
7.29
7.28
7.28
7.27
6.99
6.98
6.97
6.96
6.38
6.38
6.35
6.35
6.34
6.18
6.17
6.16
6.15
6.14
6.14
6.13
6.11
1.88
1.88
1.87
1.86
0.59
0.64
0.32
0.32
1.00
f1 (ppm)

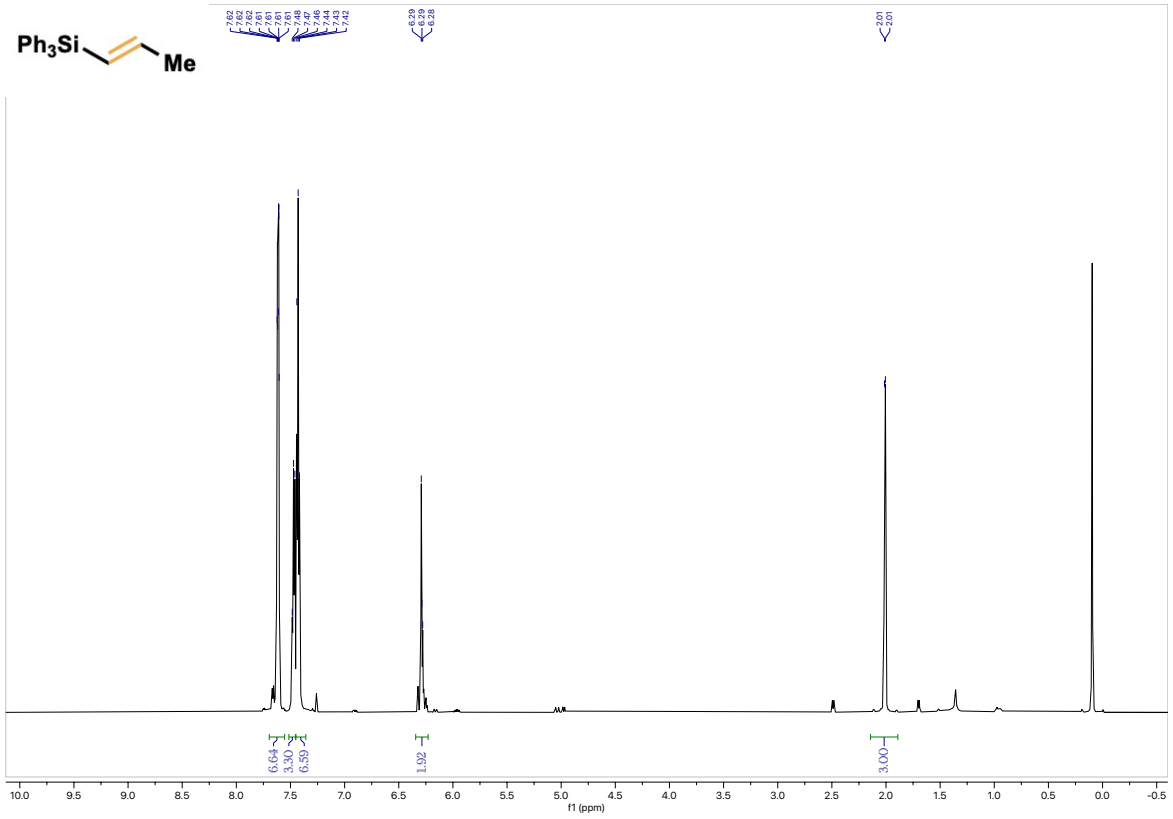

Me
7.46
7.46
7.45
7.33
7.32
7.32
7.31
7.31
6.08
6.07
6.06
6.06
6.05
6.05
6.04
6.04
6.03
5.72
5.70
1.98
1.97
1.85
1.84
2.16
3.24
1.00
1.05
3.00
0.21
f1 (ppm)

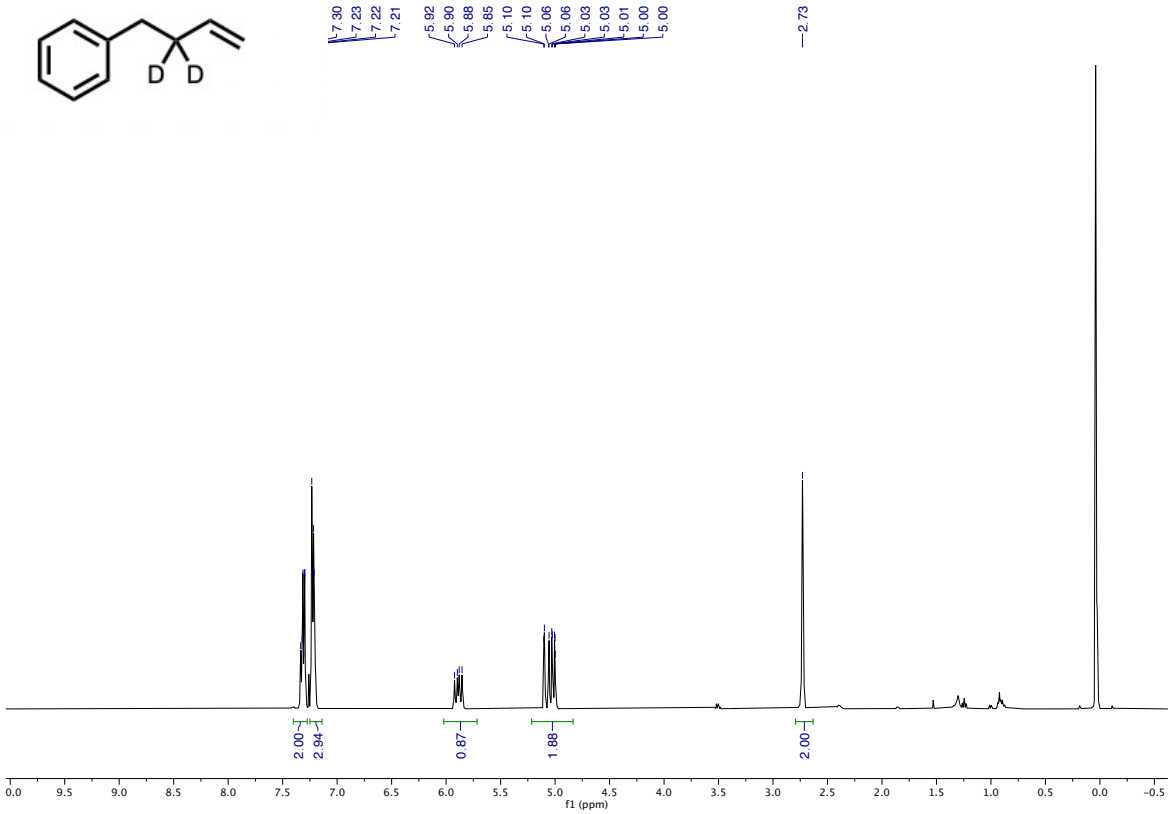

Me
N
0.41
2.13
0.77
1.48
1.98
2.05
0.67
0.97
1.56
0.14
0.69
0.96
0.32
2.10
3.00
f1 (ppm)

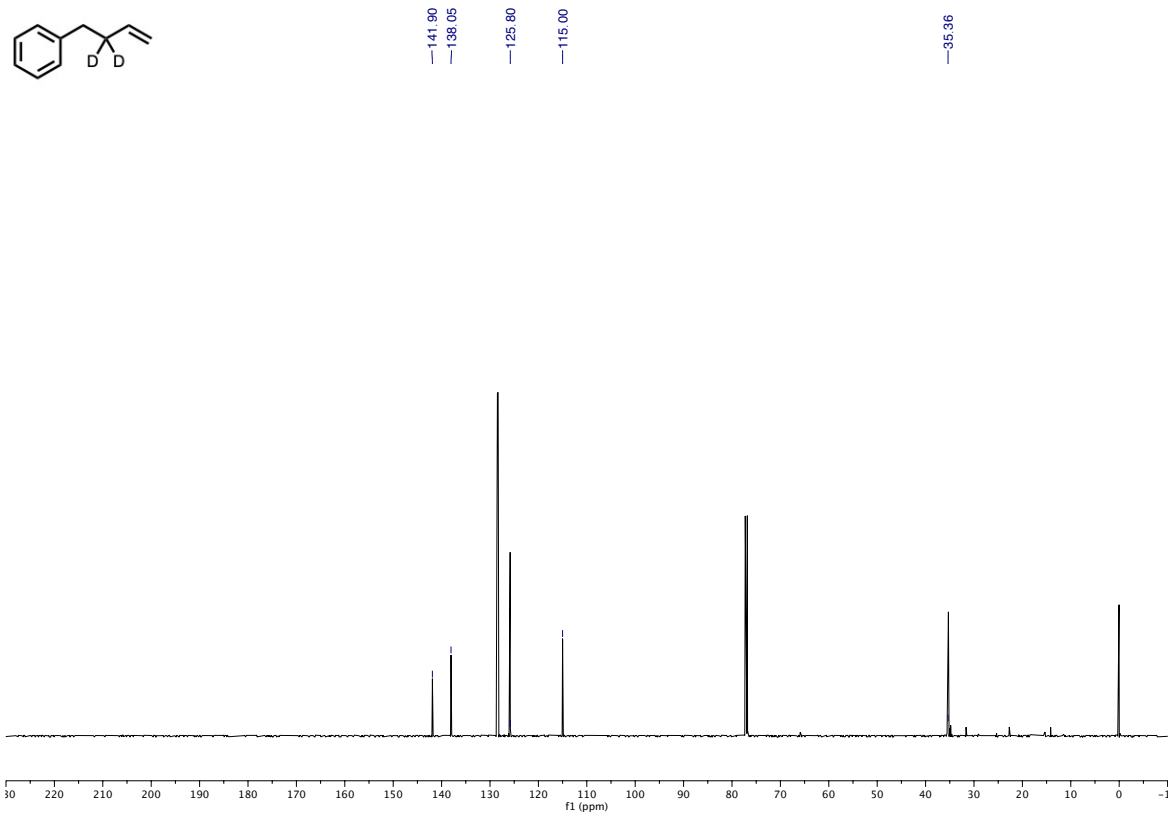

N
Me
f1 (ppm)

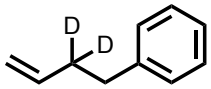

Me
Me
Me
Me
O
O
B
(Cond'ns
Z)
f1 (ppm)

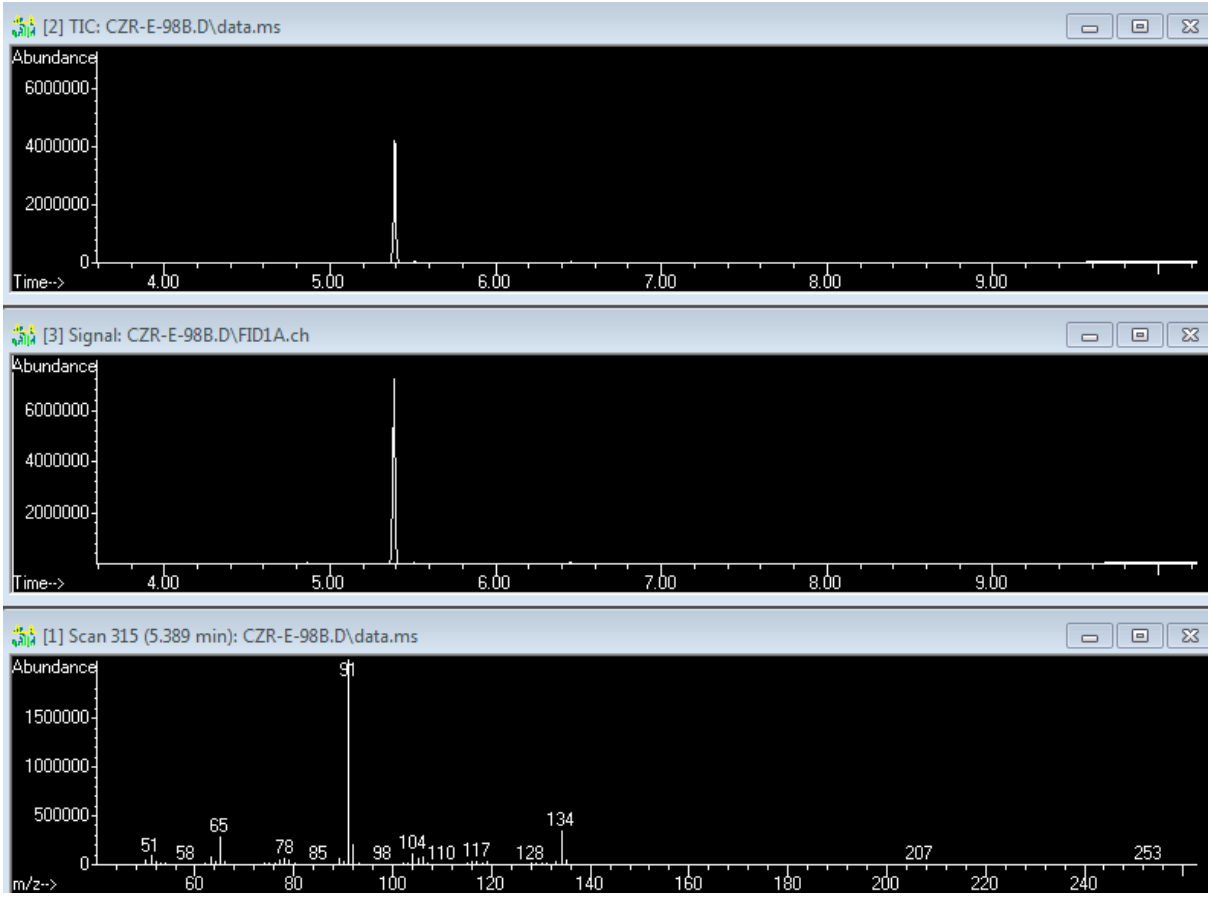

Me
Me
Me
Me
O
O
B
Me
6.69
6.67
6.66
6.64
6.63
6.61
6.60
5.47
5.42
5.36
5.33
1.97
1.95
1.85
1.84
1.83
1.83
1.27
1.25
0.89
0.86
0.07
0.25
2.75
12.31
f1 (ppm)


Ph3Si
Me
7.62
7.62
7.62
7.61
7.61
7.61
7.61
7.48
7.47
7.46
7.44
7.43
7.42
6.29
6.29
6.28
2.01
2.01
6.64
3.30
6.59
1.92
3.00
f1 (ppm)


D D
7.30
7.23
7.22
7.21
5.92
5.90
5.88
5.85
5.10
5.10
5.06
5.06
5.03
5.03
5.01
5.00
5.00
2.73
2.00
2.94
0.87
1.88
2.00
f1 (ppm)

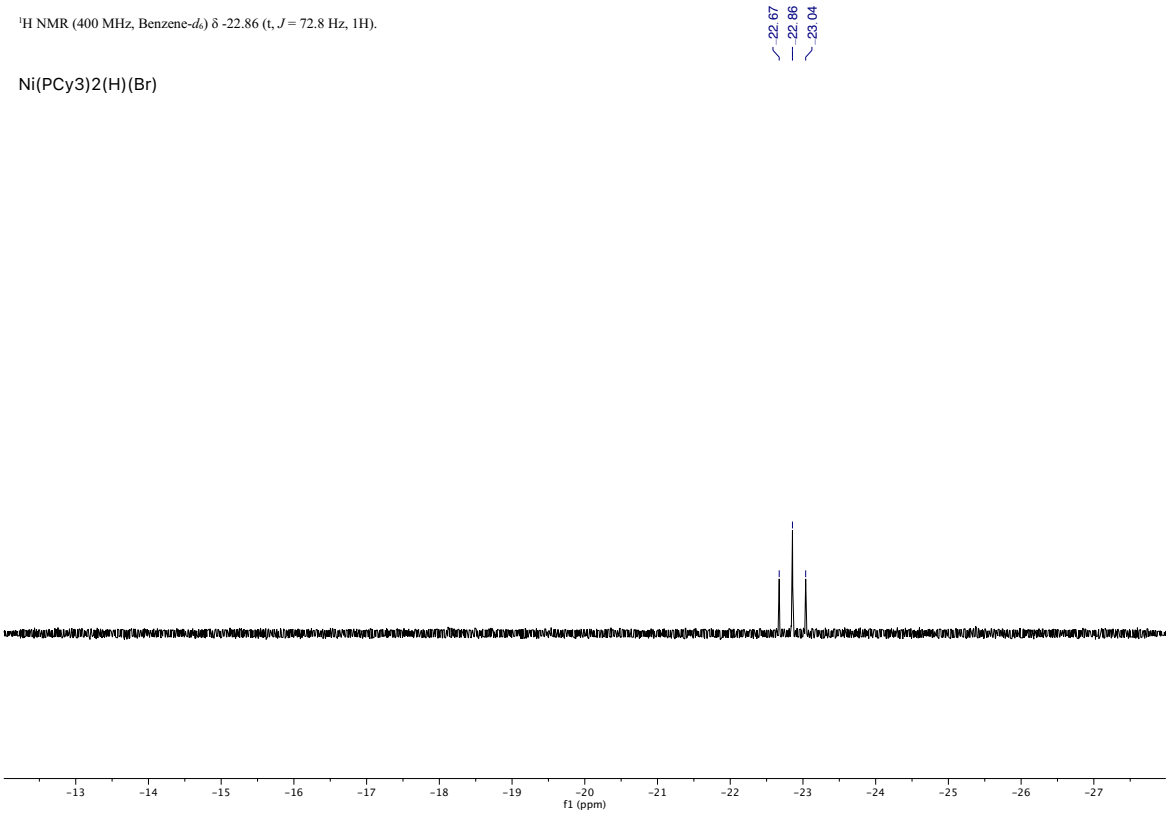

D D
141.90
138.05
125.80
115.00
35.36
f1 (ppm)


D
D


[2] TIC: CZR-E-98B.D\data.ms
Abundance
6000000
4000000
2000000
0
Time-->
4.00
5.00
6.00
7.00
8.00
9.00
[3] Signal: CZR-E-98B.D\FID1A.ch
Abundance
6000000
4000000
2000000
Time-->
4.00
5.00
6.00
7.00
8.00
9.00
[1] Scan 315 (5.389 min): CZR-E-98B.D\data.ms
Abundance
91
1500000
1000000
500000
0
65
134
51
58
78
85
98
104
110
117
128
207
253
m/z-->
60
80
100
120
140
160
180
200
220
240

^{1}H NMR (400 MHz, Benzene-d_6) δ -22.86 (t, J = 72.8 Hz, 1H).

Ni(PCy3)2(H)(Br)



^{31}P NMR (162 MHz, Benzene-d_6) δ 34.77 (d, J = 73.7 Hz).

Ni(PCy3)2(H)(Br)